Organic & Biomolecular Chemistry

Electronic Supplementary Information (ESI)

Synthesis and aggregation behaviour of single-chain, 1,32-alkyl-branched bis(phospho-cholines) – Part 2: lateral chain length triggers self-assembling from sheets to fibres to vesicles

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1. Synthetic aspects

Table S1. Reagents and conditions for the selective Grignard mono-coupling reactions performed in this work.[a]

Entry	Lateral alkyl chain	Educt 1 (Grignard reagent)	Yield[b] (%) of Grignard reagent	Educt 2 (coupling reagent)	Ratio Ed1 : Ed2	Cat. (1/60 mol%)[c]	Temp. of coupling reaction[d]	Product	Yield[e] (%)
1	*n*-C8	**6a** (39.48 mmol)	>98	**6** (37.60 mmol)	1.05 : 1	Li_2CuCl_4	−70 °C → r.t.	**8a**	78
2	*n*-C12	**6b** (22.50 mmol)	>98	**6** (25.17 mmol)	1 : 1.12	Li_2CuCl_4	−70 °C → r.t.	**8b**	76
3	*n*-C15	**6c** (34.33 mmol)	94	**6** (37.76 mmol)	1 : 1.10	Li_2CuCl_4	−70 °C → r.t.	**8c**	77

[a] All reactions were performed in THF.

[b] Yields determined by weighing the Mg left after Grignard formation.

[c] 1/60 mol% of Cu-catalyst with respect to the molar amount of Grignard reactions.

[d] The formation of the Grignard reagent (RMgBr) was carried out at 50 °C, whereas the subsequently performed coupling reaction was done at the temperature mentioned in the table (r.t. = room temperature).

[e] Isolated yields after chromatography.

2. DSC measurements

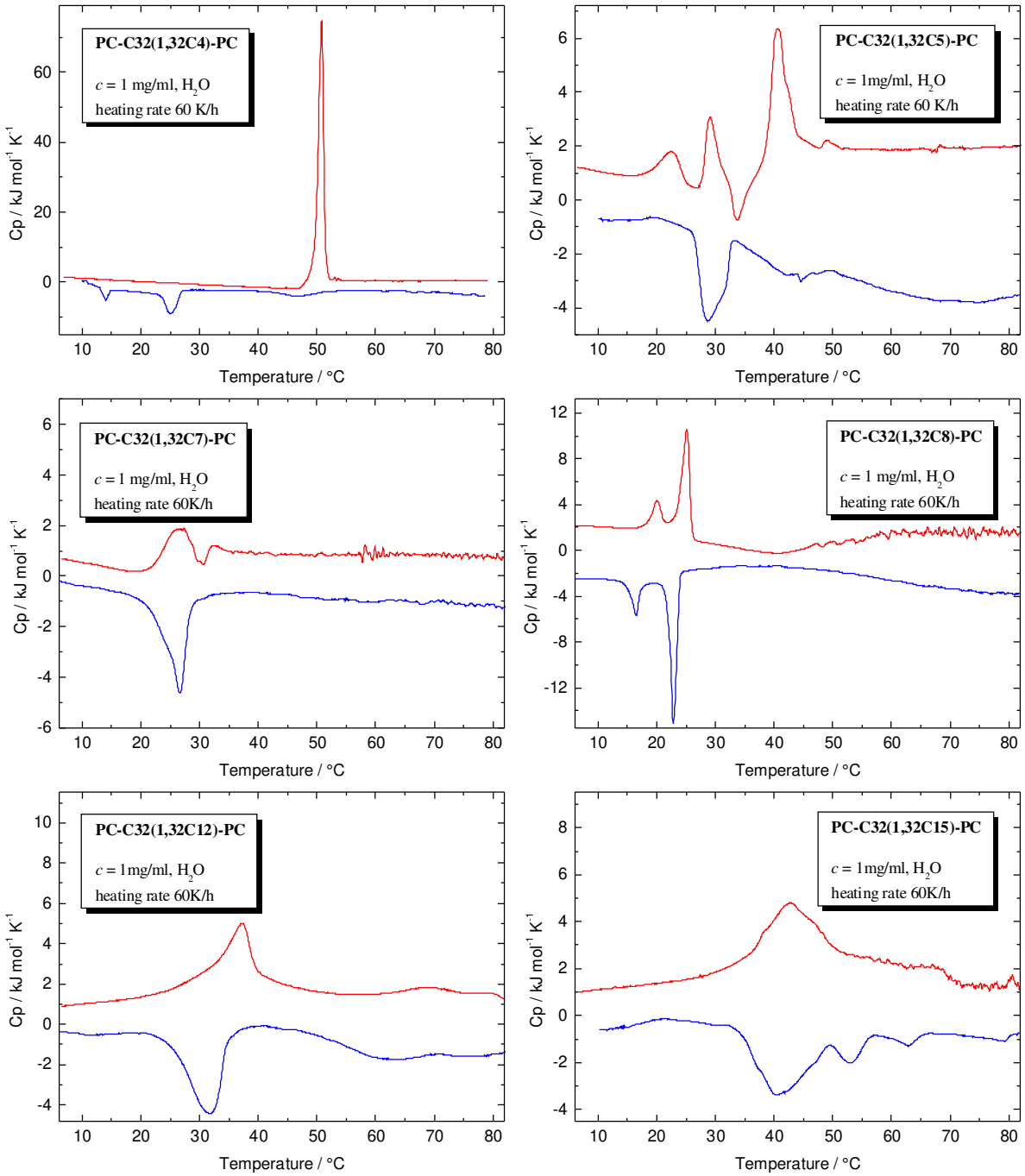


Figure S1. DSC heating (red lines) and cooling (blue lines) curves of aqueous suspensions of bolalipids **PC-C32(1,32C*m*)-PC** with *m* = 4 (top left), 5 (top right), 7 (middle left), 8 (middle right), 12 (bottom left), and 15 (bottom right).

Table S2. Data taken from DSC measurements of aqueous suspensions of **PC-C32(1,32C*m*)-PC**. Data for m = 3, 6, and 9, respectively, are shown for comparison.[1] Data analysis was performed using Origin 8.0 software.

Bolalipid	Peak	Enthalpy (ΔH / kJ mol^{-1})	Transition (°C)			FWHM (K)	Left half width (K)	Right half width (K)
			Begin	End	Maximum			
C3	1	94.6	57.4	67.2	63.8	0.6	0.4	0.2
C4	1	89.5	47.2	52.3	50.8	1.0	0.6	0.4
C5	1	5.0	14.9	25.5	22.5	4.1	2.5	1.6
	2	4.7	27.3	31.5	29.0	2.0	0.8	1.2
	3	−7.4	31.5	38.5	33.8	3.3	1.1	2.2
	4	13.7	38.5	47.3	40.6	2.8	1.1	1.7
C6	1	44.8	16.2	22.9	20.7	1.0	0.6	0.4
C7	1	7.5	20.9	30.4	27.4	5.1	3.6	1.5
	2	1.5	30.8	35.6	32.3	2.6	1.0	1.6
C8	1	7.0	15.7	21.8	20.1	2.1	1.1	1.0
	2	17.5	21.8	26.6	25.1	1.5	1.0	0.5
C9	1	27.2	16.7	23.3	20.6	2.0	0.9	1.1
C12	1	27.3	22.8	51.9	37.2	4.8	3.4	1.4
	2	1.6	63.7	73.8	68.9	5.9	3.0	2.9
C15	1	24.5	30.5	52.8	42.7	9.8	4.9	4.9
	2	2.4	62.8	71.3	67.9	3.8	2.7	1.1

FWHM = full width at half maximum

3. TEM

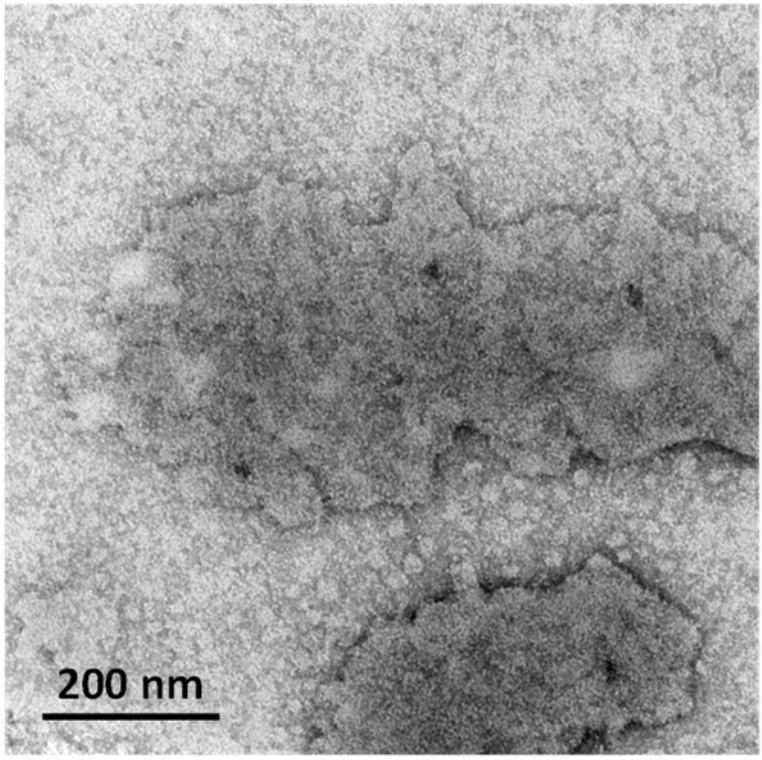


Figure S2. TEM image of an aqueous suspension of **PC-C32(1,32C7)-PC** (c = 0.05 mg mL^{-1}). Sample was prepared at T = 22 °C and stained with uranyl acetate before drying.

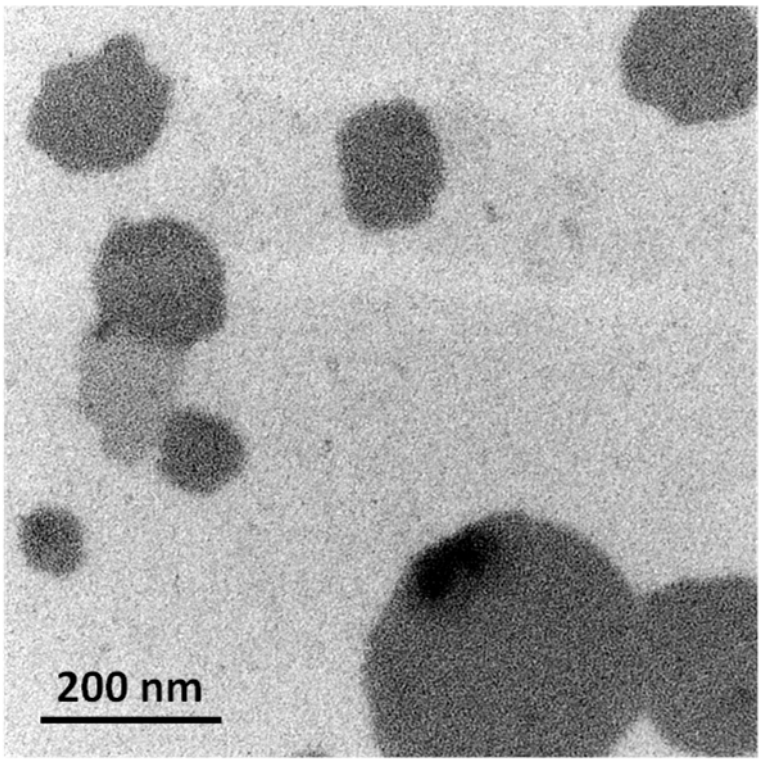


Figure S3. TEM image of an aqueous suspension of **PC-C32(1,32C8)-PC** (c = 0.05 mg mL^{-1}). Samples was prepared at about 50 °C and stained with uranyl acetate before drying.

4. Synthesis of compounds 3a-c, 4a-f, 5a-f, and 10a-f

General procedure for the synthesis of alkane-1,5-diols 3. For the reduction of the lactones, lithium aluminium hydride (1.1 equiv.) was suspended in dry diethyl ether (200 mL) in a 1 L-round-bottomed flask under argon atmosphere. The suspension was cooled to −10 °C and stirred for 1 h. The corresponding lactone **2** (1 equiv.), dissolved in dry Et_2O (50 mL), was added slowly. The ice bath was removed, and the mixture was stirred for 20 h at room temperature. Afterwards, the reaction mixture was hydrolysed with ice and acidified using sulphuric acid (30%, 40 mL). The layers were separated, and the aqueous phase was extracted three times with diethyl ether (200 mL). The combined ethereal phases were washed with brine (300 mL), dried over sodium sulphate, and evaporated. The crude product was purified by column chromatography with the use of heptane/chloroform (2/8, v/v) as eluent yielding the diol **3** as a white solid or colourless oil.

(5*RS*)-Nonane-1,5-diol (3a).[2] Following the general procedure, **2a** (12.50 g, 80.02 mmol) and lithium aluminium hydride (3.35 g, 88.02 mmol) gave **3a** (11.17 g, 87%) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.88 (t, J = 6.4 Hz, 3 H, CH_3), 1.19–1.65 (m, 12 H, CH_2), 2.33 (s, 2 H, 2× OH), 3.51–3.65 (m, 3 H, CHOH, CH_2OH); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.03 (CH_3), 21.77 ($CH_2(CH_2)_2OH$), 22.72 (CH_3CH_2), 27.83 ($CH_3CH_2CH_2$), 32.53 (CH_2CH_2OH), 36.91 ($CH_2(CH_2)_3OH$), 37.21 ($CH_3(CH_2)_2CH_2$), 62.61 (CH_2OH), 71.77 ($CHOH$); ESI-MS m/z 183.48 (M + Na). Analytical data are in accordance with data published previously.[2]

(5*RS*)-Decane-1,5-diol (3b).[2] Following the general procedure, **2b** (12.20 g, 71.66 mmol) and lithium aluminium hydride (3.12 g, 82.11 mmol) gave **3b** (11.39 g, 92%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 0.85-0.93 (m, 3 H, CH_3), 1.23–1.67 (m, 14 H, CH_2), 3.57–3.64 (m, 1 H, CHOH), 3.66 (t, J = 6.4 Hz, 2 H, CH_2OH); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 14.01 (CH_3), 21.81 ($CH_2(CH_2)_2OH$), 22.61 (CH_3CH_2), 25.31 ($CH_3(CH_2)_2CH_2$), 31.86 and 32.60 ($CH_3CH_2CH_2$ and CH_2CH_2OH), 37.00 and 37.50 ($CH_2(CHOH)CH_2$), 62.81 (CH_2OH), 71.88 ($CHOH$); APCI-MS m/z 157.1 (M − H_2O + H), 175.1 (M + H). Analytical data are in accordance with data published previously.[2]

(5*RS*)-Dodecane-1,12-diol (3c).[2] Following the general procedure, **2c** (15.70 g, 79.17 mmol) and lithium aluminium hydride (3.40 g, 89.47 mmol) gave **3c** (14.40 g, 90%) as a white solid. M.p. 36–38 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 0.85–0.91 (m, 3 H, CH_3), 1.20–1.66 (m, 18 H, CH_2), 3.58–3.63 (m, 1 H, CHOH), 3.66 (t, J = 6.4 Hz, 2 H, CH_2OH); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 14.06 (CH_3), 21.82 ($CH_2(CH_2)_2OH$), 22.63 (CH_3CH_2), 25.64 ($CH_3(CH_2)_4CH_2$), 29.26 and 29.63 ($CH_3(CH_2)_2CH_2CH_2$), 31.80 ($CH_3CH_2CH_2$), 32.65 (CH_2CH_2OH), 37.03 and 37.54 ($CH_2(CHOH)CH_2$), 62.85 (CH_2OH), 71.88 ($CHOH$); APCI-MS m/z 185.2 (M − H_2O + H), 203.2 (M + H). Analytical data are in accordance with data described previously.[2]

General procedure for the synthesis of bromoalkanols 4a-c *via* Appel-reaction. The diol **3** (1 equiv.) was placed in a 250 mL-round-bottomed flask and dry CH_2Cl_2 (150 mL) was added and cooled to 10 °C. Triphenylphosphane (1.1 equiv.) and tetrabromomethane (1.1 equiv.) were added in one portion and the colourless solution was stirred for 20 h at 10 °C. Afterwards, silica gel (amount of the total weight) was added and the solvent was evaporated. The adsorbed crude product was purified by column chromatography using heptane/diethyl ether (8/2, v/v) as eluent.

(5*RS*)-1-Bromononan-5-ol (4a). Following the general procedure, **3a** (11.17 g, 69.70 mmol), triphenylphosphane (20.11 g, 76.67 mmol) and tetrabromomethane (25.43 g, 76.67 mmol) gave **4a** as colourless oil (8.16 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.62–0.94 (m, 3 H, CH_3), 1.10–1.69 (m, 10 H, CH_2), 1.74–2.02 (m, 2 H, CH_2CH$_2$Br), 3.29–3.43 (m, 2 H, CH_2Br), 3.51–3.62 (m, 1 H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.03 (*C*H$_3$), 22.70 (*C*H$_2$CH$_3$), 24.30 (*C*H$_2$(CH$_2$)$_2$Br), 27.78 (*C*H$_2$CH$_2$CH$_3$), 32.76 (*C*H$_2$CH$_2$Br), 33.71 (*C*H$_2$Br), 36.40 and 37.17 (*C*H$_2$(CHOH)*C*H$_2$), 71.72 (*C*H); APCI-MS *m*/*z* 205.0 (M − H$_2$O + H, ^{79}Br isotope), 207.0 (M − H$_2$O + H, ^{81}Br isotope).

(5*RS*)-1-Bromodecan-5-ol (4b). Following the general procedure, **3b** (11.39 g, 65.36 mmol), triphenylphosphane (18.87 g, 71.89 mmol) and tetrabromomethane (23.87 g, 71.89 mmol) gave **4b** (9.97 g, 65%) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.82–0.93 (m, 3 H, CH_3), 1.21–1.68 (m, 12 H, CH_2), 1.80–1.97 (m, 2 H, CH_2CH$_2$Br), 3.42 (t, J = 6.8 Hz, 2 H, CH_2Br), 3.55–3.65 (m, 1 H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.01 (*C*H$_3$), 22.61 (*C*H$_2$CH$_3$), 24.31 (*C*H$_2$(CH$_2$)$_2$Br), 25.28 (*C*H$_2$(CH$_2$)$_2$CH$_3$), 31.84 (*C*H$_2$CH$_2$CH$_3$), 32.77 (*C*H$_2$CH$_2$Br), 33.71 (*C*H$_2$Br), 36.43 (*C*H$_2$(CH$_2$)$_3$CH$_3$), 37.49 (*C*H$_2$(CH$_2$)$_3$Br), 71.70 (*C*H); APCI-MS *m*/*z* 219.1 (M − H$_2$O + H, ^{79}Br isotope), 221.1 (M − H$_2$O + H, ^{81}Br isotope).

(5*RS*)-1-Bromododecan-5-ol (4c). Following the general procedure, **3c** (14.40 g, 71.17 mmol), triphenylphosphane (20.55 g, 78.29 mmol) and tetrabromomethane (26.94 g, 78.29 mmol) gave **4c** (10.87 g, 58%) as colourless oil. $C_{12}H_{25}BrO$ requires C, 54.34; H, 9.50; found: C, 53.94; H, 9.02; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.82–0.92 (m, 3 H, CH_3), 1.20–1.67 (m, 16 H, CH_2), 1.80–1.97 (m, 2 H, CH_2CH$_2$Br), 3.42 (t, J = 6.8 Hz, 2 H, CH_2Br), 3.55–3.65 (m, 1 H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.01 (*C*H$_3$), 22.62 (*C*H$_2$CH$_3$), 24.31 (*C*H$_2$(CH$_2$)$_2$Br), 25.61 (*C*H$_2$(CH$_2$)$_4$CH$_3$), 29.25 (*C*H$_2$(CH$_2$)$_2$CH$_3$), 29.61 (*C*H$_2$(CH$_2$)$_3$CH$_3$), 31.79 (*C*H$_2$CH$_2$CH$_3$), 32.77 (*C*H$_2$CH$_2$Br), 33.71 (*C*H$_2$Br), 36.41 (*C*H$_2$(CH$_2$)$_5$CH$_3$), 37.51 (*C*H$_2$(CH$_2$)$_3$Br), 71.73 (*C*H); APCI-MS *m*/*z* 247.2 (M − H$_2$O + H, ^{79}Br isotope), 249.2 (M − H$_2$O + H, ^{81}Br isotope).

General procedure for the synthesis of 1-bromoalkan-5-ols 4d-f *via* reduction. For the reduction of the bromoketones **8**, lithium aluminium hydride (0.4 equiv.) was suspended in dry diethyl ether (100 mL) in a 500 mL-round-bottomed flask under argon atmosphere. The suspension was cooled to −10 °C and stirred for 1 h. The corresponding bromoketone **8** (1 equiv.), dissolved in dry diethyl ether (150 mL), was added slowly. The mixture was stirred for 20 h at −10 °C. Afterwards, the reaction mixture was hydrolysed with ice and acidified using sulphuric acid (30%, 40 mL). The layers were separated, and the aqueous phase was extracted three times with diethyl ether (200 mL). The combined ethereal phases were washed with brine (300 ml), dried over sodium sulphate and evaporated. The crude product was purified by column chromatography with the use of heptane/diethyl ether (92/8, v/v) as eluent yielding the bromoalkanols **4d-f** as a white solid or colourless oil.

(5*RS*)-1-Bromotridecan-5-ol (4d). Following the general procedure, **8a** (8.10 g, 29.22 mmol) and lithium aluminium hydride (0.47 g, 12.37 mmol) gave **4d** (4.57 g, 57%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 0.88 (t, J = 6.9 Hz, 3 H, CH_3), 1.21–1.71 (m, 18 H, CH_2), 1.81–1.95 (m, 2 H, CH_2CH$_2$Br), 3.41 (t, J = 6.8 Hz, 2 H, CH_2Br), 3.55–3.64 (m, 1 H, CH); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 14.07 (CH$_3$), 22.64 (CH$_2$CH$_3$), 24.31 (CH$_2$(CH$_2$)$_2$Br), 25.61 (CH$_2$(CH$_2$)$_5$CH$_3$), 29.24, 29.55 and 29.65 (CH$_2$), 31.85 (CH$_2$CH$_2$CH$_3$), 32.77 (CH$_2$CH$_2$Br), 33.70 (CH$_2$Br), 36.43 (CH$_2$(CH$_2$)$_6$CH$_3$), 37.53 (CH$_2$(CH$_2$)$_3$Br), 71.69 (CH); APCI-MS m/z 261.1 (M − H$_2$O + H, ^{79}Br isotope), 263.1 (M − H$_2$O + H, ^{81}Br isotope).

(5*RS*)-1-Bromoheptadecan-5-ol (4e). Following the general procedure, **8b** (5.69 g, 17.07 mmol) and lithium aluminium hydride (0.26 g, 6.83 mmol) gave **4e** (4.59 g, 81%) as white solid. M.p. 45–46 °C; $C_{17}H_{35}BrO$ requires C, 60.88; H, 10.52; found: C, 60.95; H, 10.42; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.84–0.92 (m, 3 H, CH_3), 1.23–1.67 (m, 26 H, CH_2), 1.82–1.95 (m, 2 H, CH_2CH$_2$Br), 3.42 (t, J = 6.8 Hz, 2 H, CH_2Br), 3.56–3.65 (m, 1 H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.09 (CH$_3$), 22.67 (CH$_2$CH$_3$), 24.31 (CH$_2$(CH$_2$)$_2$Br), 25.61 (CH$_2$(CH$_2$)$_9$CH$_3$), 29.34, 29.58, 29.59, 29.62, 29.63 and 29.65 (CH$_2$), 31.90 (CH$_2$CH$_2$CH$_3$), 32.77 (CH$_2$CH$_2$Br), 33.71 (CH$_2$Br), 36.43 (CH$_2$(CH$_2$)$_{10}$CH$_3$), 37.54 (CH$_2$(CH$_2$)$_3$Br), 71.70 (CH); APCI-MS m/z 255.7 (M − HBr + H).

(5*RS*)-1-Bromoicosan-5-ol (4f). Following the general procedure, **8c** (9.9 g, 26.40 mmol) and lithium aluminium hydride (0.43 g, 11.32 mmol) gave **4f** (6.94 g, 70%) as white solid. M.p. 57–58 °C; $C_{20}H_{41}BrO$ requires C, 63.64; H, 10.95; found: C, 63.49; H, 11.03; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.88 (t, J = 6.7 Hz, 3 H, CH_3), 1.21–1.68 (m, 32 H, CH_2), 1.82–1.95 (m, 2 H, CH_2CH$_2$Br), 3.42 (t, J = 6.8 Hz, 2 H, CH_2Br), 3.57–3.64 (m, 1 H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.09 (CH$_3$), 22.67 (CH$_2$CH$_3$), 24.31 (CH$_2$(CH$_2$)$_2$Br), 25.61 (CH$_2$(CH$_2$)$_{12}$CH$_3$), 29.34, 29.58, 29.60, 29.64, 29.65 and 29.67 (CH$_2$), 31.90 (CH$_2$CH$_2$CH$_3$), 32.78 (CH$_2$CH$_2$Br), 33.70 (CH$_2$Br), 36.44 (CH$_2$(CH$_2$)$_{13}$CH$_3$), 37.54 (CH$_2$(CH$_2$)$_3$Br), 71.70 (CH); APCI-MS m/z 359.3 (M − H$_2$O + H, ^{79}Br isotope), 361.3 (M − H$_2$O + H, ^{81}Br isotope), 295.3 (M − HBr + H).

General procedure for the synthesis of THP-protected 1-bromoalkan-5-ols 5. The bromoalkanols **4a-f** (1 equiv.) were dissolved in dry di-chloromethane (150 mL) at room temperature. 3,4-Dihydro-2*H*-pyran (DHP; 1.8 equiv.) and pyridinium p-toluenesulfonate (PPTS; 10 mol%) were added and the mixture was stirred for 20 h. Afterwards, the organic solution was washed with water (150 mL), dried over sodium sulphate and concentrated to dryness under reduced pressure. The crude oil was purified by column chromatography using heptane/triethylamine/diethyl ether (98.5/0.5/1, v/v/v) as eluent yielding the THP-protected bromoalkanols **5a-f**.

2-{[(1*RS*)-5-Bromo-1-butylpentyl]oxy}tetrahydro-2*H*-pyran (5a). Following the general procedure, **4a** (8.16 g, 36.57 mmol) and 3,4-dihydro-2*H*-pyran (5.55 g, 65.98 mmol) gave **5a** (9.22 g, 82%) as a colourless oil. $C_{14}H_{27}BrO_2$ requires C, 54.72; H, 8.86; found: C, 54.25; H, 8.66; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.76–0.90 (m, 3 H, C*H*$_3$), 1.14–1.72 (m, 16 H, C*H*$_2$), 1.72–1.90 (m, 2 H, C*H*$_2$CH$_2$Br), 3.32–3.49 (m, 3 H, C*H*$_2$Br and OCHOCH*H*), 3.51–3.97 (m, 2 H, C*H*Othp and OCHOC*H*H), 4.55–4.63 (m, 1 H, OC*H*O); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.03 (*C*H$_3$), 19.91 and 20.05 (OCHO(CH$_2$)$_2$*C*H$_2$), 22.81 and 22.88 (*C*H$_2$CH$_3$), 23.57, 24.17, 25.50 and 25.51 (*C*H$_2$(CH$_2$)$_2$Br and OCHOCH$_2$*C*H$_2$), 27.24 and 27.73 (*C*H$_2$CH$_2$CH$_3$), 31.17, 31.20, 32.47, 32.93, 32.94, 33.22, 33.58, 33.59, 33.68, 33.69, 34.03 and 34.63 (*C*H$_2$), 62.61 and 62.83 (OCHO*C*H$_2$), 76.33 and 76.36 (*C*HOthp), 97.57 and 97.70 (O*C*HO); ESI-MS *m*/*z* 329.77 (M + Na, ^{79}Br isotope), 331.46 (M + Na, ^{81}Br isotope).

2-{[(1*RS*)-1-(4-Brombutyl)hexyl]oxy}tetrahydro-2*H*-pyran (5b). Following the general procedure, **4b** (9.77 g, 41.19 mmol) and 3,4-dihydro-2*H*-pyran (6.30 g, 74.89 mmol) gave **5b** (11.51 g, 87%) as a colourless oil. $C_{15}H_{29}BrO_2$ requires C, 56.07; H, 9.10; found: C, 55.57; H, 9.12; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.89 (t, J = 6.9 Hz, 3 H, C*H*$_3$), 1.20–1.95 (m, 20 H, C*H*$_2$), 3.37–3.44 (m, 2 H, C*H*$_2$Br), 3.45–3.52 (m, 1 H, C*H*Othp), 3.55–3.66 (m, 1 H, OCHOCH*H*), 3.85–3.96 (m, 1 H, OCHOC*H*H), 4.59–4.68 (m, 1 H, OC*H*O); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.01 and 14.06 (*C*H$_3$), 19.93 and 20.10 (OCHO(CH$_2$)$_2$*C*H$_2$), 22.61 (*C*H$_2$CH$_3$), 23.62 (*C*H$_2$(CH$_2$)$_2$Br), 24.23, 24.71, 25.26, 25.51 and 25.53 (*C*H$_2$(CH$_2$)$_2$CH$_3$ and OCHOCH$_2$*C*H$_2$), 31.19 and 31.23 (*C*H$_2$CH$_2$CH$_3$), 32.01, 32.05, 32.51, 32.96, 32.97, 33.51, 33.75 and 33.85 (*C*H$_2$), 34.07 and 34.94 (*C*H$_2$(CH$_2$)$_3$Br and *C*H$_2$(CH$_2$)$_3$CH$_3$), 62.69 and 62.94 (OCHO*C*H$_2$), 76.43 and 76.49 (*C*HOthp), 97.64 and 97.77 (O*C*HO); ESI-MS *m*/*z* 343.38 (M + Na, ^{79}Br isotope), 345.34 (M + Na, ^{81}Br isotope).

2-{[(1*RS*)-1-(4-Brombutyl)octyl]oxy}tetrahydro-2*H*-pyran (5c). Following the general procedure, **4c** (10.66 g, 40.19 mmol) and 3,4-dihydro-2*H*-pyran (6.10 g, 72.52 mmol) gave **5c** (12.88 g, 92%) as a colourless oil. $C_{17}H_{33}BrO_2$ requires C, 58.45; H, 9.52; found: C, 57.86; H, 9.74; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.88 (t, J = 6.7 Hz, 3 H, C*H*$_3$), 1.24–1.94 (m, 24 H, C*H*$_2$), 3.38–3.44 (m, 2 H, C*H*$_2$Br), 3.45–3.52 (m, 1 H, C*H*Othp), 3.55–3.66 (m, 1 H, OCHOCH*H*), 3.85–3.95 (m, 1 H, OCHOC*H*H), 4.59–4.67 (m, 1 H, OC*H*O); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.07 (*C*H$_3$), 19.93 and 20.09 (OCHO(CH$_2$)$_2$*C*H$_2$), 22.63 (*C*H$_2$CH$_3$), 23.62 (*C*H$_2$(CH$_2$)$_2$Br), 24.22, 25.05, 25.51 and 25.60 (*C*H$_2$(CH$_2$)$_4$CH$_3$ and OCHOCH$_2$*C*H$_2$), 31.19 and 31.23 (*C*H$_2$CH$_2$CH$_3$), 31.80, 31.85, 32.51, 32.96, 32.97, 33.56, 33.74 and 33.84 (*C*H$_2$), 34.07 and 34.98

($CH_2(CH_2)_3Br$ and $CH_2(CH_2)_5CH_3$), 62.69 and 62.93 ($OCHOCH_2$), 76.42 and 76.48 (*C*HOthp), 97.64 and 97.77 (O*C*HO); ESI-MS *m*/*z* 371.70 (M + Na, ^{79}Br isotope), 373.56 (M + Na, ^{81}Br isotope).

2-{[(1*RS*)-1-(4-Brombutyl)nonyl]oxy}tetrahydro-2*H*-pyran (5d). Following the general procedure, **4d** (4.04 g, 14.47 mmol) and 3,4-dihydro-2*H*-pyran (2.19 g, 26.04 mmol) gave **5d** (5.22 g, 99%) as a colourless oil. $C_{18}H_{35}BrO_2$ requires C, 59.50; H, 9.71; found: C, 59.29; H, 9.74; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 0.88 (t, J = 6.9 Hz, 3 H, C*H*$_3$), 1.20–1.94 (m, 26 H, C*H*$_2$), 3.37–3.43 (m, 2 H, C*H*$_2$Br), 3.45–3.52 (m, 1 H, C*H*Othp), 3.56–3.65 (m, 1 H, OCHOCH*H*), 3.85–3.97 (m, 1 H, OCHOC*H*H), 4.59–4.67 (m, 1 H, OC*H*O); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 14.08 (*C*H$_3$), 19.93 (OCHO(CH$_2$)$_2$*C*H$_2$), 22.65 (*C*H$_2$CH$_3$), 23.62 (*C*H$_2$(CH$_2$)$_2$Br), 25.53 and 25.59 (*C*H$_2$(CH$_2$)$_5$CH$_3$ and OCHOCH$_2$*C*H$_2$), 29.29, 29.55, 29.80, 31.19 and 31.87 (*C*H$_2$), 32.51 and 32.96 (*C*H$_2$CH$_2$Br and *C*H$_2$Br), 33.73 and 34.98 (*C*H$_2$(CH$_2$)$_3$Br and *C*H$_2$(CH$_2$)$_6$CH$_3$), 62.69 (OCHO*C*H$_2$), 76.47 (*C*HOthp), 97.63 (O*C*HO); ESI-MS *m*/*z* 385.63 (M + Na, ^{79}Br isotope), 387.49 (M + Na, ^{81}Br isotope).

2-{[(1*RS*)-1-(4-Brombutyl)tridecyl]oxy}tetrahydro-2*H*-pyran (5e). Following the general procedure, **4e** (4.16 g, 12.41 mmol) and 3,4-dihydro-2*H*-pyran (2.11 g, 25.08 mmol) gave **5e** (4.82 g, 93%) as a colourless oil. $C_{22}H_{43}BrO_2$ requires C, 62.99; H, 10.33; found: C, 62.36; H, 10.41; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.85–0.91 (m, 3 H, C*H*$_3$), 1.21–1.76 (m, 32 H, C*H*$_2$), 1.77–1.96 (m, 2 H, C*H*$_2$CH$_2$Br), 3.36–3.44 (m, 2 H, C*H*$_2$Br), 3.44–3.52 (m, 1 H, C*H*Othp), 3.55–3.66 (m, 1 H, OCHOCH*H*), 3.85–3.96 (m, 1 H, OCHOC*H*H), 4.59–4.67 (m, 1 H, OC*H*O); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.08 (*C*H$_3$), 19.93 and 20.10 (OCHO(CH$_2$)$_2$*C*H$_2$), 22.66 (*C*H$_2$CH$_3$), 23.62 and 24.22 (*C*H$_2$(CH$_2$)$_2$Br), 25.05, 25.52 and 25.59 (*C*H$_2$(CH$_2$)$_9$CH$_3$ and OCHOCH$_2$*C*H$_2$), 29.33, 29.58, 29.60, 29.63, 29.65, 29.66, 29.80, 29.85, 31.19 and 31.23 (*C*H$_2$), 31.90 (*C*H$_2$CH$_2$CH$_3$), 32.96 and 32.97 (*C*H$_2$CH$_2$Br), 33.56 (*C*H$_2$Br), 33.72, 33.82, 34.07 and 34.98 (*C*H$_2$(CH$_2$)$_3$Br and *C*H$_2$(CH$_2$)$_{10}$CH$_3$), 62.68 and 62.93 (OCHO*C*H$_2$), 76.43 and 76.47 (*C*HOthp), 97.62 and 97.77 (O*C*HO); ESI-MS *m*/*z* 441.80 (M + Na, ^{79}Br isotope), 443.62 (M + Na, ^{81}Br isotope).

2-{[(1*RS*)-1-(4-Brombutyl)hexadecyl]oxy}tetrahydro-2*H*-pyran (5f). Following the general procedure, **4f** (6.94 g, 18.39 mmol) and 3,4-dihydro-2*H*-pyran (2.80 g, 33.29 mmol) gave **5f** (6.96 g, 82%) as a colourless oil. $C_{25}H_{49}BrO_2$ requires C, 65.06; H, 10.70; found: C, 64.71; H, 10.57; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.84–0.92 (m, 3 H, C*H*$_3$), 1.23–1.93 (m, 40 H, C*H*$_2$), 3.36–3.44 (m, 2 H, C*H*$_2$Br), 3.44–3.52 (m, 1 H, C*H*Othp), 3.55–3.66 (m, 1 H, OCHOCH*H*), 3.85–3.95 (m, 1 H, OCHOC*H*H), 4.59–4.67 (m, 1 H, OC*H*O); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C) δ 14.08 (*C*H$_3$), 19.93 and 20.10 (OCHO(CH$_2$)$_2$*C*H$_2$), 22.67 (*C*H$_2$CH$_3$), 23.62 (*C*H$_2$(CH$_2$)$_2$Br), 24.22, 25.05, 25.52 and 25.59 (*C*H$_2$(CH$_2$)$_{12}$CH$_3$ and OCHOCH$_2$*C*H$_2$), 29.34, 29.59, 29.60, 29.64, 29.66, 29.68, 29.80, 31.19 and 31.23 (*C*H$_2$), 31.90 (*C*H$_2$CH$_2$CH$_3$), 32.51, 32.96 and 32.97 (*C*H$_2$CH$_2$Br and *C*H$_2$Br), 34.07 and 34.98 (*C*H$_2$(CH$_2$)$_3$Br and *C*H$_2$(CH$_2$)$_{13}$CH$_3$), 62.67 and 62.69 (OCHO*C*H$_2$), 76.42 (*C*HOthp), 97.61 and 97.76 (O*C*HO); ESI-MS *m*/*z* 484.83 (M + Na, ^{79}Br isotope), 486.17 (M + Na, ^{81}Br isotope).

General procedure for the synthesis of alkyl-branched diols 10. The bis-THP-ether **9a-f** and catalytic amounts of pyridinium *p*-toluenesulfonate were suspended in dry methanol (150 mL) and the mixture was heated under reflux for at least 3 h until a white precipitate appeared and no educt is detectable via TLC. The hot suspension was filtered off giving the diols **10a-f** as white solids.

(5*RS*,36*RS*)-Tetracontane-5,36-diol (10a). Following the general procedure, **9a** (1.50 g, 1.97 mmol) gave **10a** (1.14 g, 97%) as white solid. M.p. 109–110 °C; $C_{40}H_{82}O_2$ requires C, 80.73; H, 13.89; found: C, 80.05; H, 14.20; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 0.91 (t, J = 6.9 Hz, 6 H, 2× CH_3), 1.13–1.80 (m, 72 H, CH_2), 3.40–3.76 (m, 2 H, 2× C*H*OH); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ 13.90 (*C*H_3), 22.68 (*C*H_2CH$_3$), 25.58 (*C*H_2CH$_2$CHOH(CH$_2$)$_3$CH$_3$), 27.78 (*C*H_2CH$_2$CH$_3$), 29.53, 29.55, 29.57, 29.59, 29.61 and 29.64 (*C*H_2), 37.17 (*C*H_2(CH$_2$)$_2$CH$_3$), 37.50 (*C*H_2CHOH(CH$_2$)$_3$CH$_3$), 71.96 (*C*HOH); APCI-MS *m*/*z* 559.9 (M – 2× H_2O + H), 595.9 (M + H).

(6*RS*,37*RS*)-Dotetracontane-6,37-diol (10b). Following the general procedure, **9b** (2.71 g, 3.43 mmol) gave **10b** (2.08 g, 98%) as white solid. M.p. 109–111 °C; $C_{42}H_{86}O_2$ requires C, 80.95; H, 13.91; found: C, 80.60; H, 14.17; ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 0.90 (t, J = 6.9 Hz, 6 H, 2× CH_3), 1.25–1.47 (m, 76 H, CH_2), 3.48–3.64 (m, 2 H, 2× C*H*OH); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ 13.87 (*C*H_3), 22.54 (*C*H_2CH$_3$), 25.23 (*C*H_2CH$_2$CHOH(CH$_2$)$_4$CH$_3$), 25.58 (*C*H_2(CH$_2$)$_2$CH$_3$), 29.53, 29.55, 29.61 and 29.65 (*C*H_2), 31.87 (*C*H_2CH$_2$CH$_3$), 37.45 and 37.50 (*C*H_2CHOH*C*H_2), 71.99 (*C*HOH); APCI-MS *m*/*z* 588.2 (M – 2× H_2O + H).

(8*RS*,39*RS*)-Hexatetracontane-8,39-diol (10c). Following the general procedure, **9c** (4.39 g, 5.18 mmol) gave **10c** (3.38 g, 97%) as white solid. M.p. 110–112 °C; $C_{46}H_{94}O_2$ requires C, 81.34; H, 13.95; found: C, 81.08; H, 14.18; ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 0.89 (t, J = 6.8 Hz, 6 H, 2× CH_3), 1.12–1.64 (m, 84 H, CH_2), 3.54–3.62 (m, 2 H, 2× C*H*OH); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ 13.91 (*C*H_3), 22.55 (*C*H_2CH$_3$), 25.58 (*C*H_2CH$_2$CHOHCH$_2$*C*H_2), 29.20, 29.54, 29.55, 29.58, 29.59, 29.61 and 29.66 (*C*H_2), 31.76 (*C*H_2CH$_2$CH$_3$), 37.49 (*C*H_2CHOH*C*H_2), 71.99 (*C*HOH); APCI-MS *m*/*z* 644.1 (M – 2× H_2O + H).

(9*RS*,40*RS*)-Octatetracontane-9,40-diol (10d). Following the general procedure, **9d** (0.17 g, 0.19 mmol) gave **10d** (0.11 g, 82%) as white solid. M.p. 112–113 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 0.89 (t, J = 6.7 Hz, 6 H, 2× CH_3), 1.24–1.49 (m, 88 H, CH_2), 3.45–3.72 (m, 2 H, 2× C*H*OH); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 13.92 (*C*H_3), 22.56 (*C*H_2CH$_3$), 25.58 (*C*H_2CH$_2$CHOHCH$_2$*C*H_2), 29.18, 29.51, 29.53, 29.55, 29.61 and 29.65 (*C*H_2), 31.80 (*C*H_2CH$_2$CH$_3$), 37.49 (*C*H_2CHOH*C*H_2), 71.98 (*C*HOH); APCI-MS *m*/*z* 672.2 (M – 2× H_2O + H).

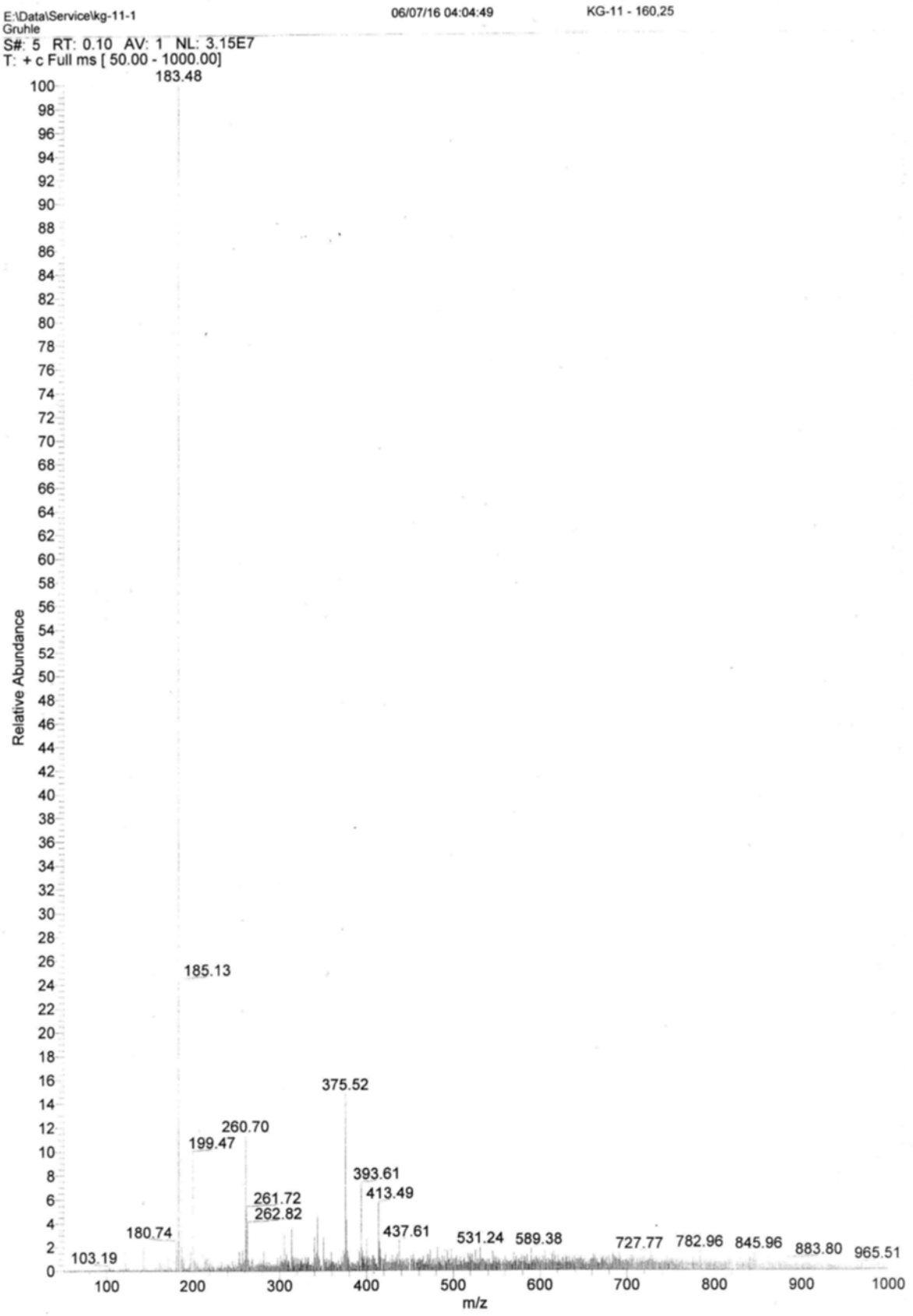
(13*RS*,44*RS*)-Hexapentacontane-13,44-diol (10e). Following the general procedure, **9e** (0.61 g, 0.62 mmol) gave **10e** (0.50 g, 99%) as white solid. M.p. 114–116 °C; $C_{56}H_{114}O_2$ requires C, 82.07; H, 14.02; found: C, 81.66; H, 13.80; ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 0.90 (t, J = 6.8 Hz, 6 H, 2× CH_3), 1.18–1.45 (m, 104 H, CH_2), 3.55–3.65 (m, 2 H, 2× C*H*OH); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ 13.94 (*C*H_3), 22.56 (*C*H_2CH$_3$), 25.59 (*C*H_2CH$_2$CHOHCH$_2$*C*H_2), 29.26, 29.56, 29.62 and 29.66 (*C*H_2), 31.85

($CH_2CH_2CH_3$), 37.51 ($CH_2CHOHCH_2$), 71.99 ($CHOH$); APCI-MS m/z 784.5 (M – 2× H_2O + H).

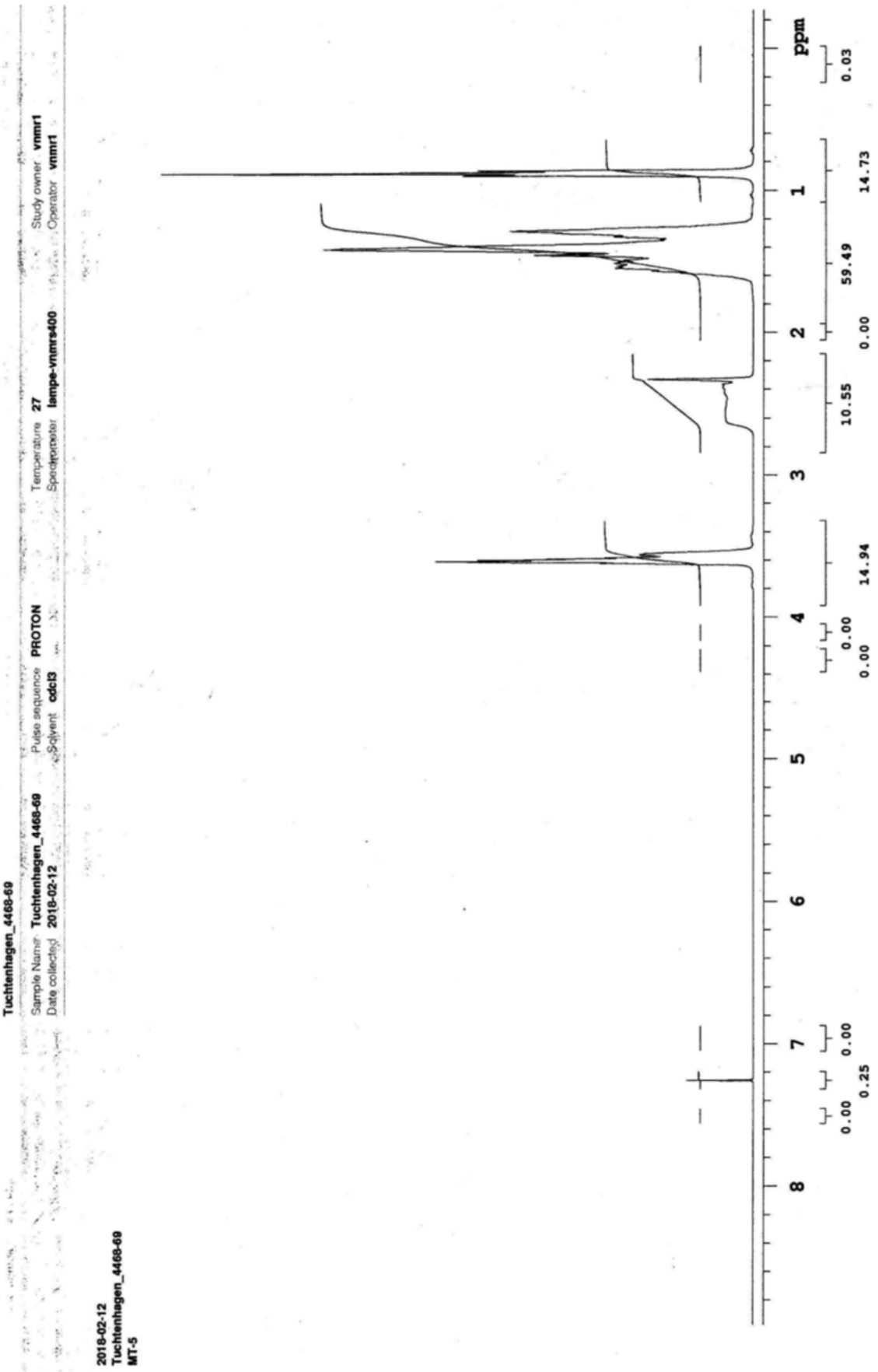
(16*RS*,47*RS*)-Dohexacontane-16,47-diol (10f). Following the general procedure, but using dry ethanol instead of methanol, **9f** (1.00 g, 0.94 mmol) gave **10f** (0.68 g, 80%) as white solid. M.p. 116–118 °C; $C_{62}H_{126}O_2$ requires C, 82.41; H, 14.05; found: C, 82.14; H, 14.37; ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 0.89 (t, J = 6.8 Hz, 6 H, 2× CH_3), 1.09–1.71 (m, 116 H, CH_2), 3.51–3.61 (m, 2 H, 2× $CHOH$); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ 13.93 (CH_3), 22.58 (CH_2CH_3), 25.58 ($CH_2CH_2CHOHCH_2CH_2$), 29.25, 29.54, 29.55, 29.61, 29.65 and 29.79 (CH_2), 31.84 ($CH_2CH_2CH_3$), 37.50 ($CH_2CHOHCH_2$), 71.98 ($CHOH$); APCI-MS m/z 884.0 (M – H_2O + H), 900.0 (M + H).

5. Characterization of products: MS, ^{1}H NMR, ^{13}C NMR spectra

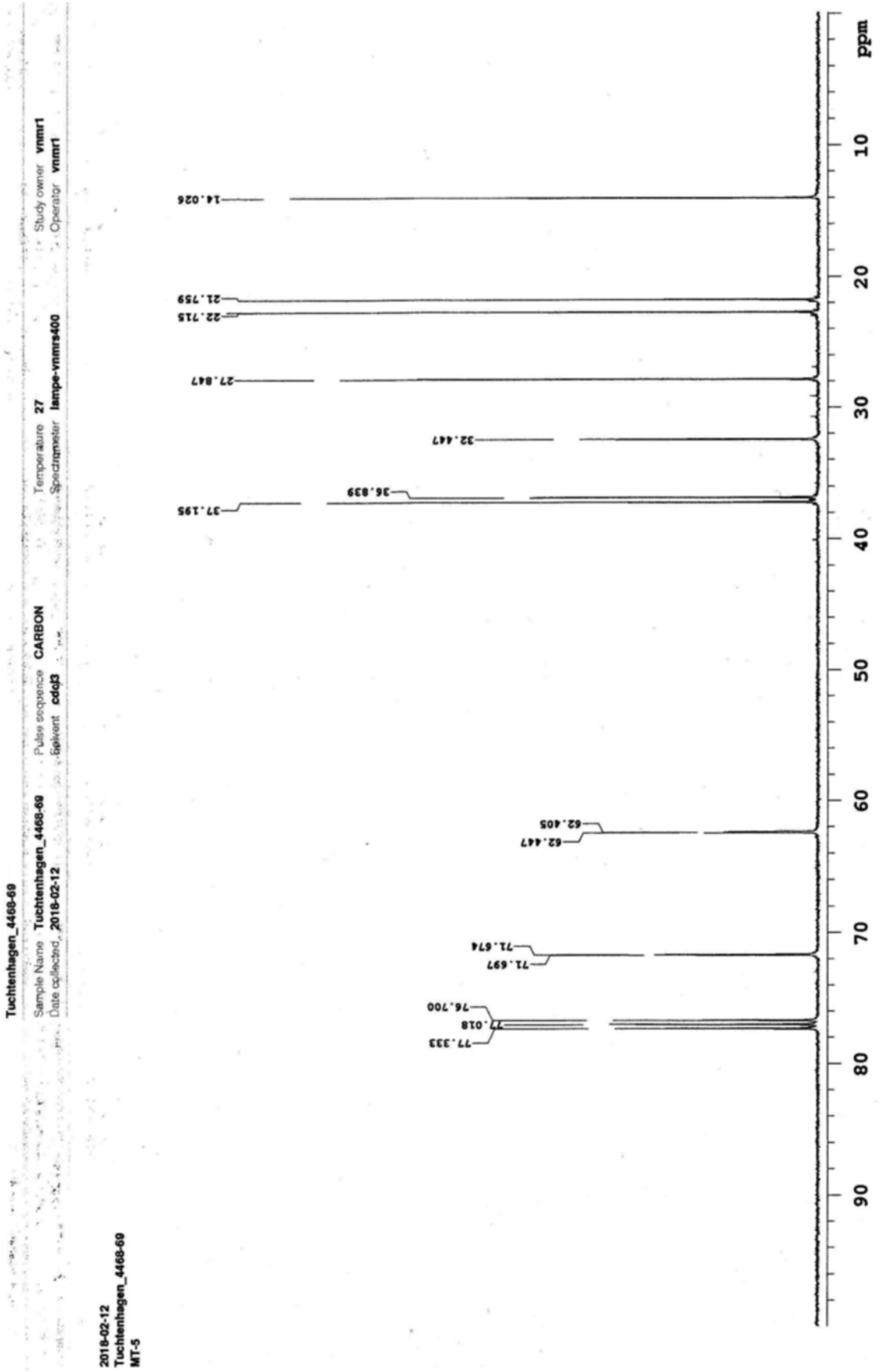
*Compound **3a** – ESI-MS (positive mode)*



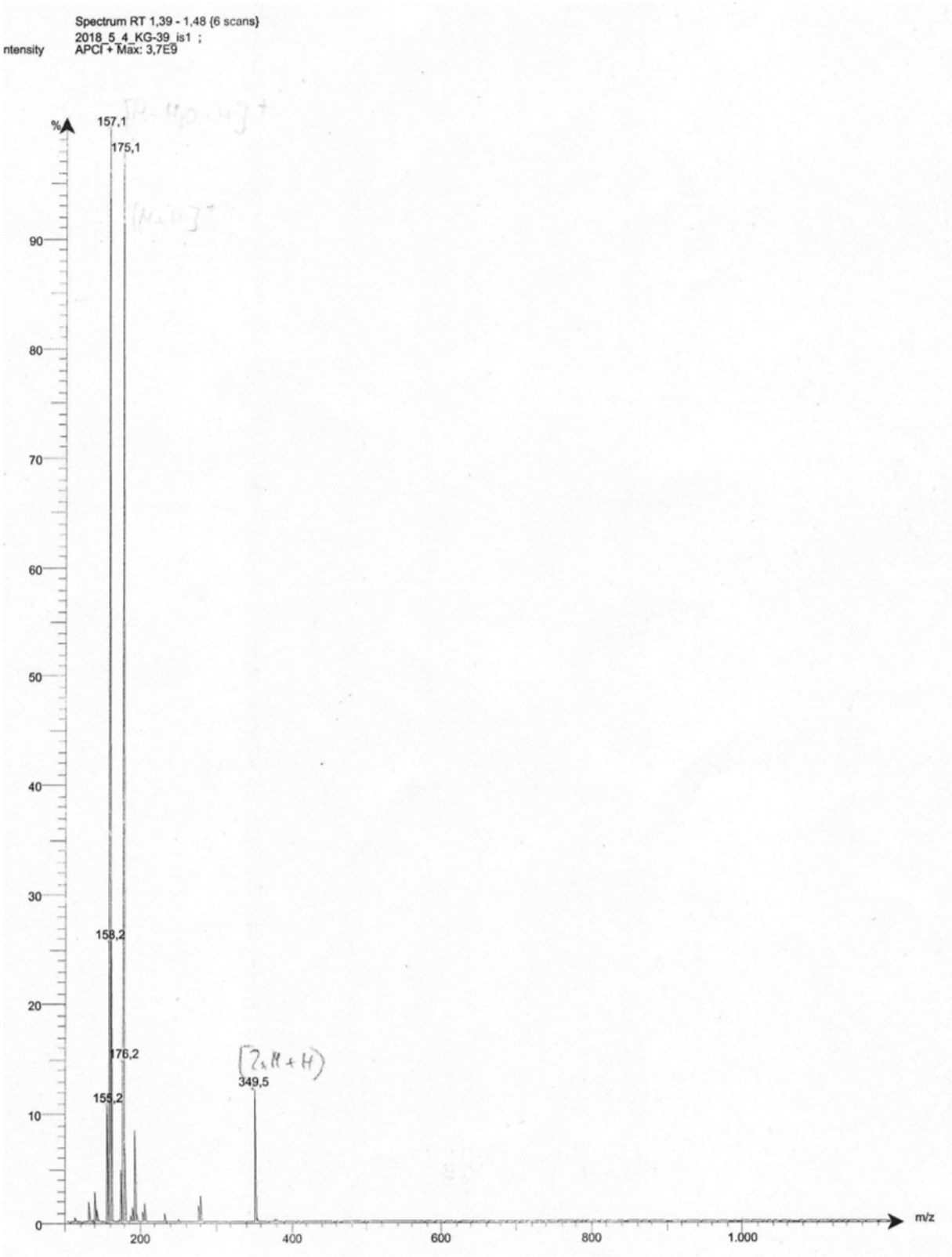
*Compound **3a** – ^{1}H NMR*



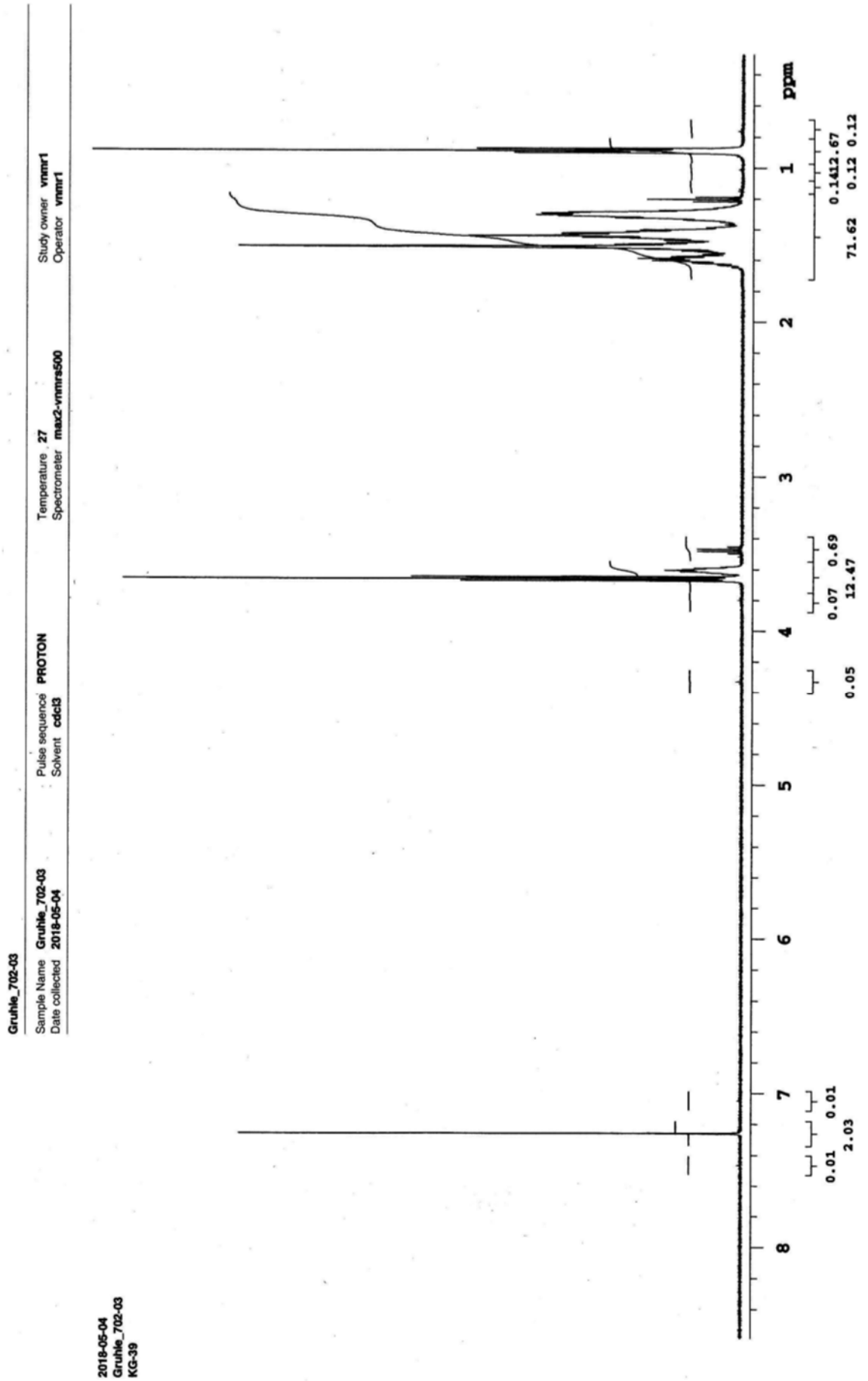
*Compound **3a** – ^{13}C NMR*



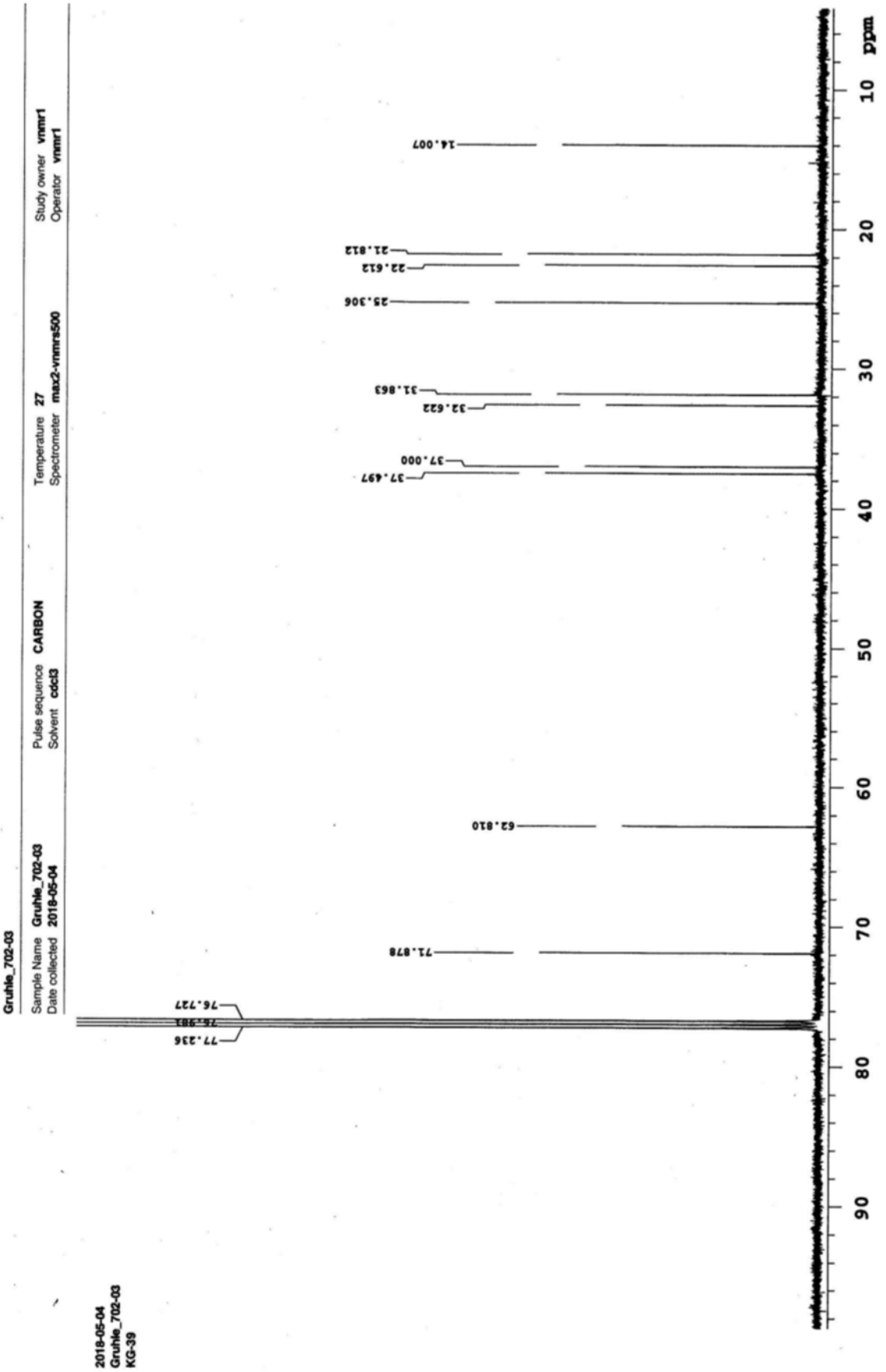
*Compound **3b** – APCI-MS (positive mode)*



*Compound **3b** – ^{1}H NMR*

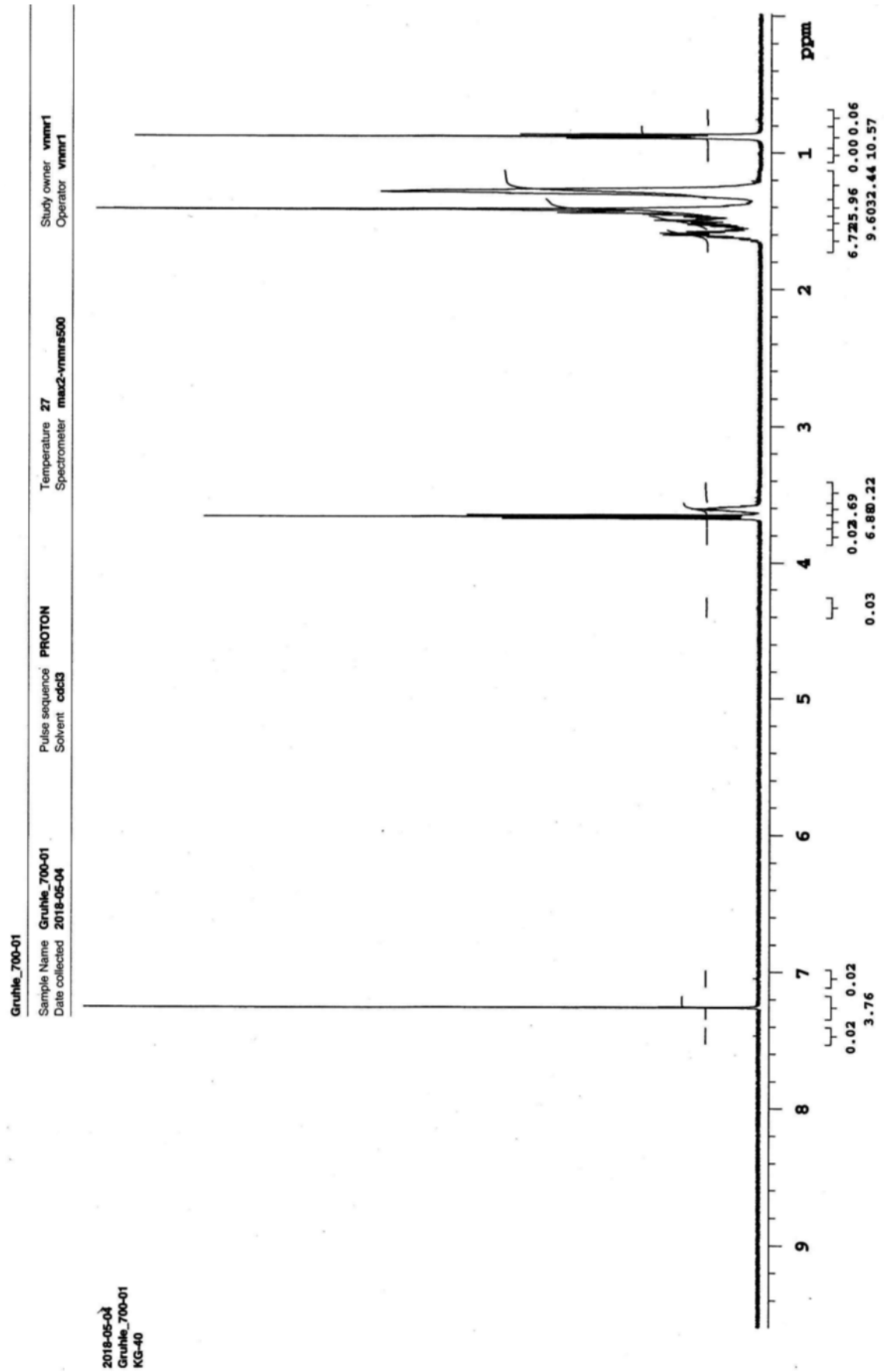


*Compound **3b** – ^{13}C NMR*

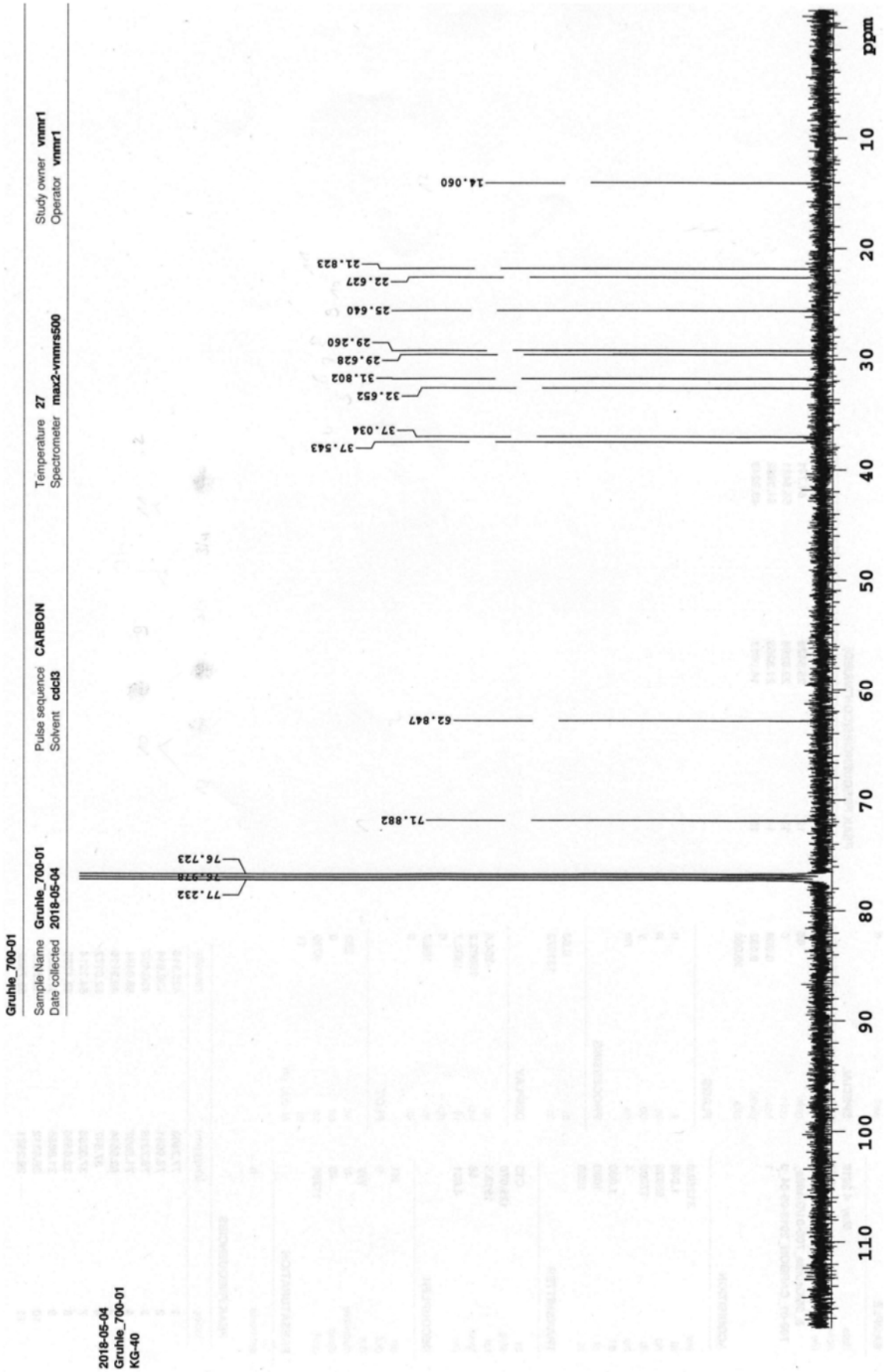


*Compound **3c** – APCI-MS (positive mode)*

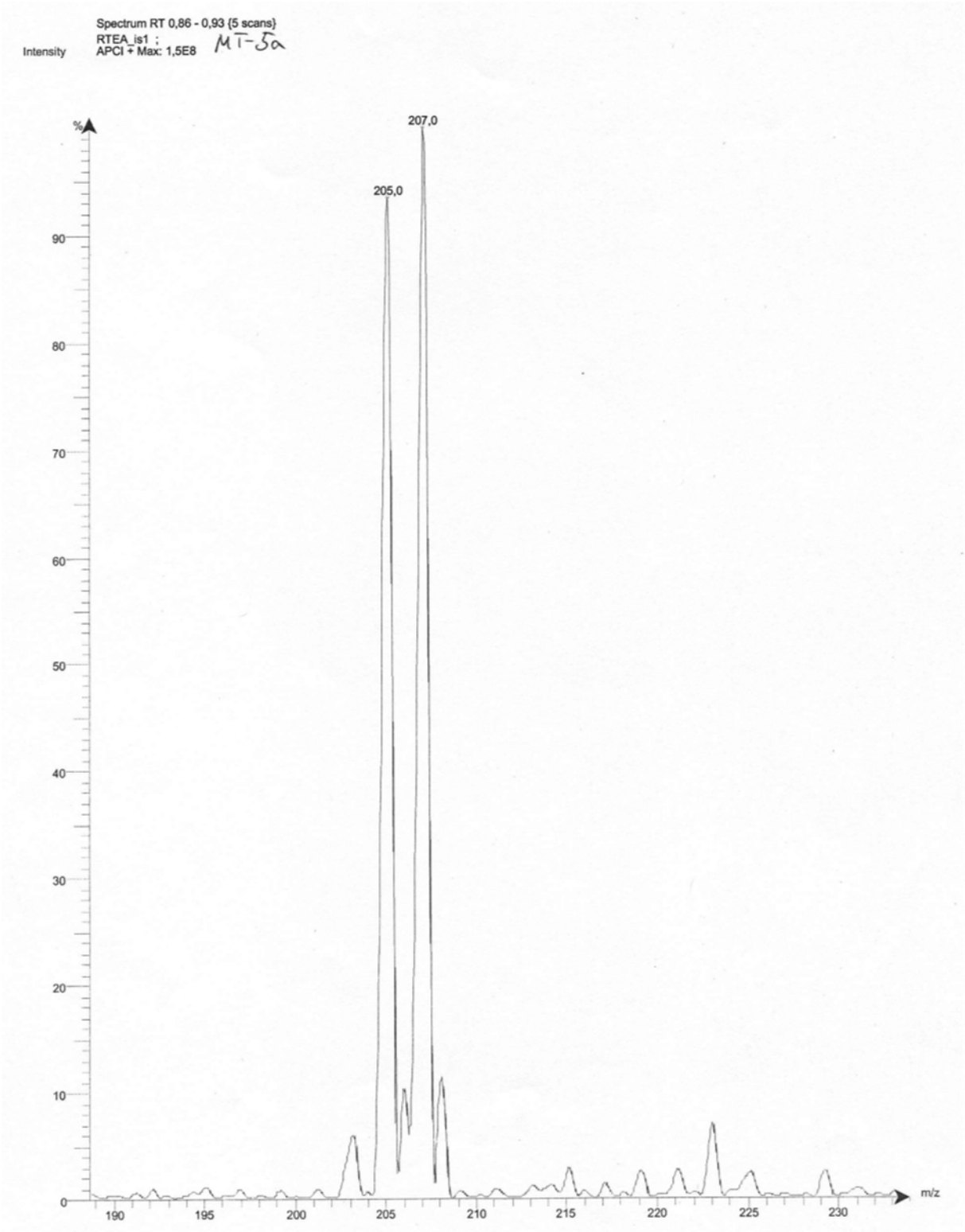
Compound ***3c*** *– ^{1}H NMR*



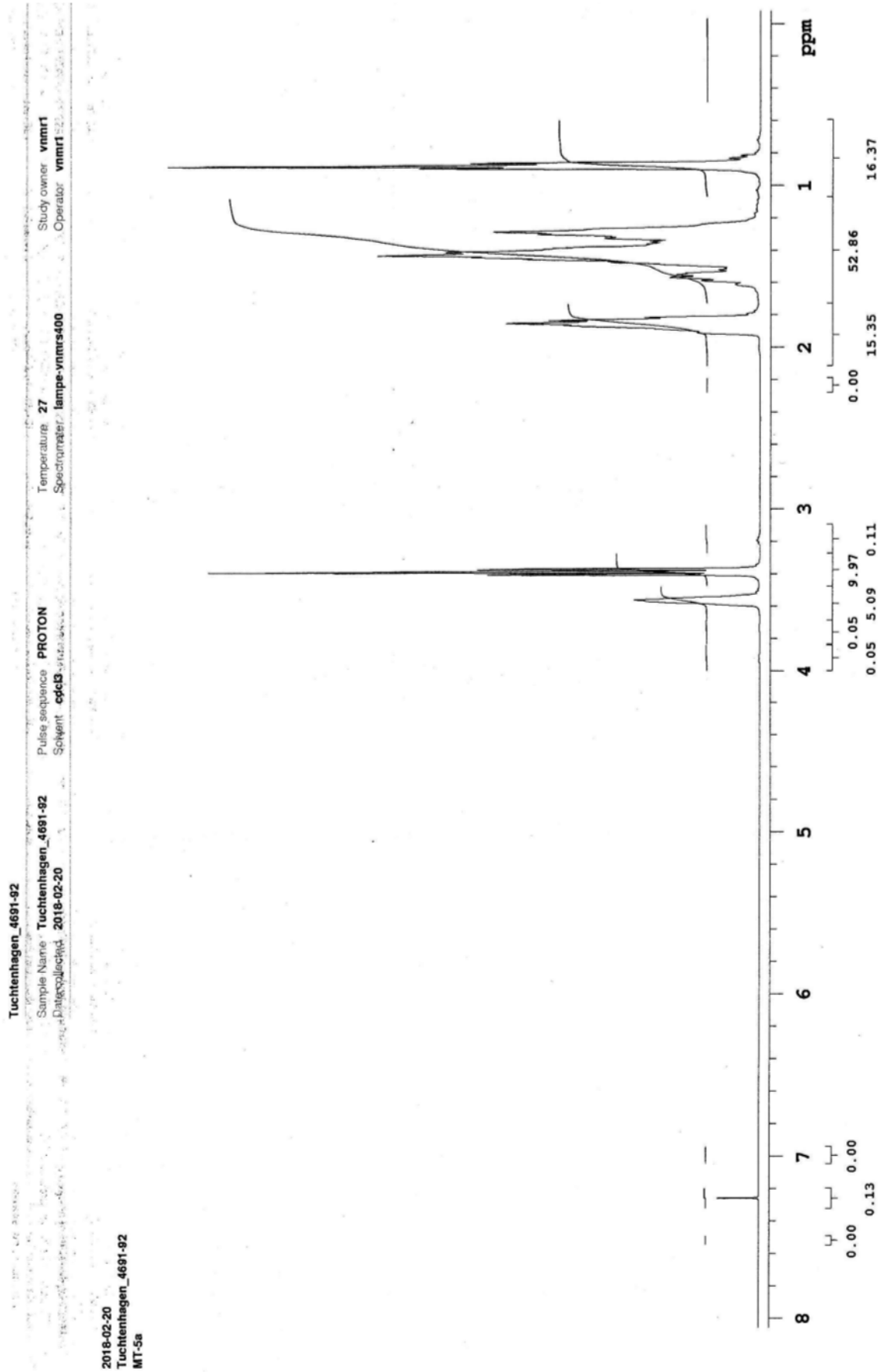
Compound ***3c*** *– ^{13}C NMR*



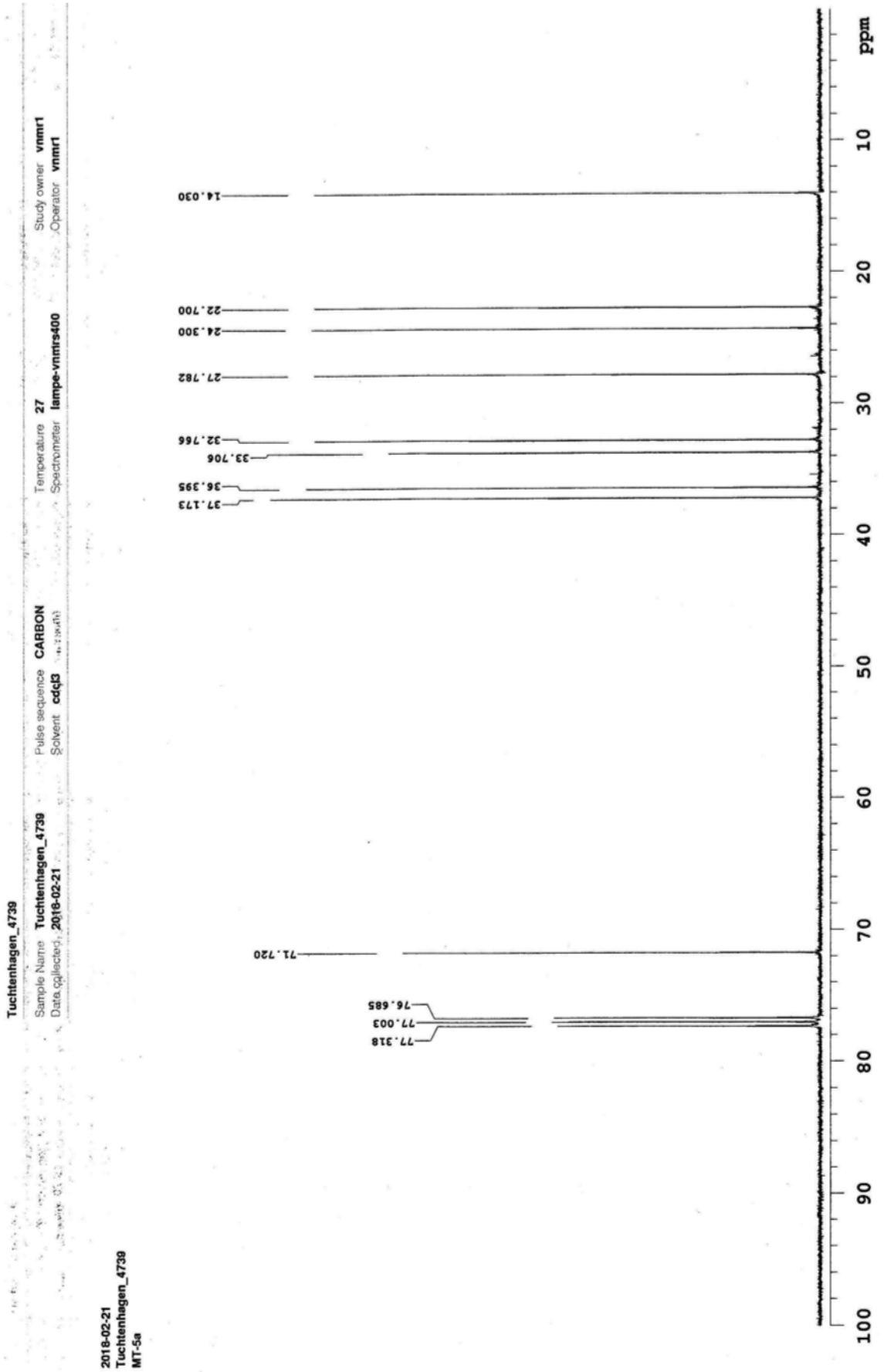
*Compound **4a** – APCI-MS (positive mode)*



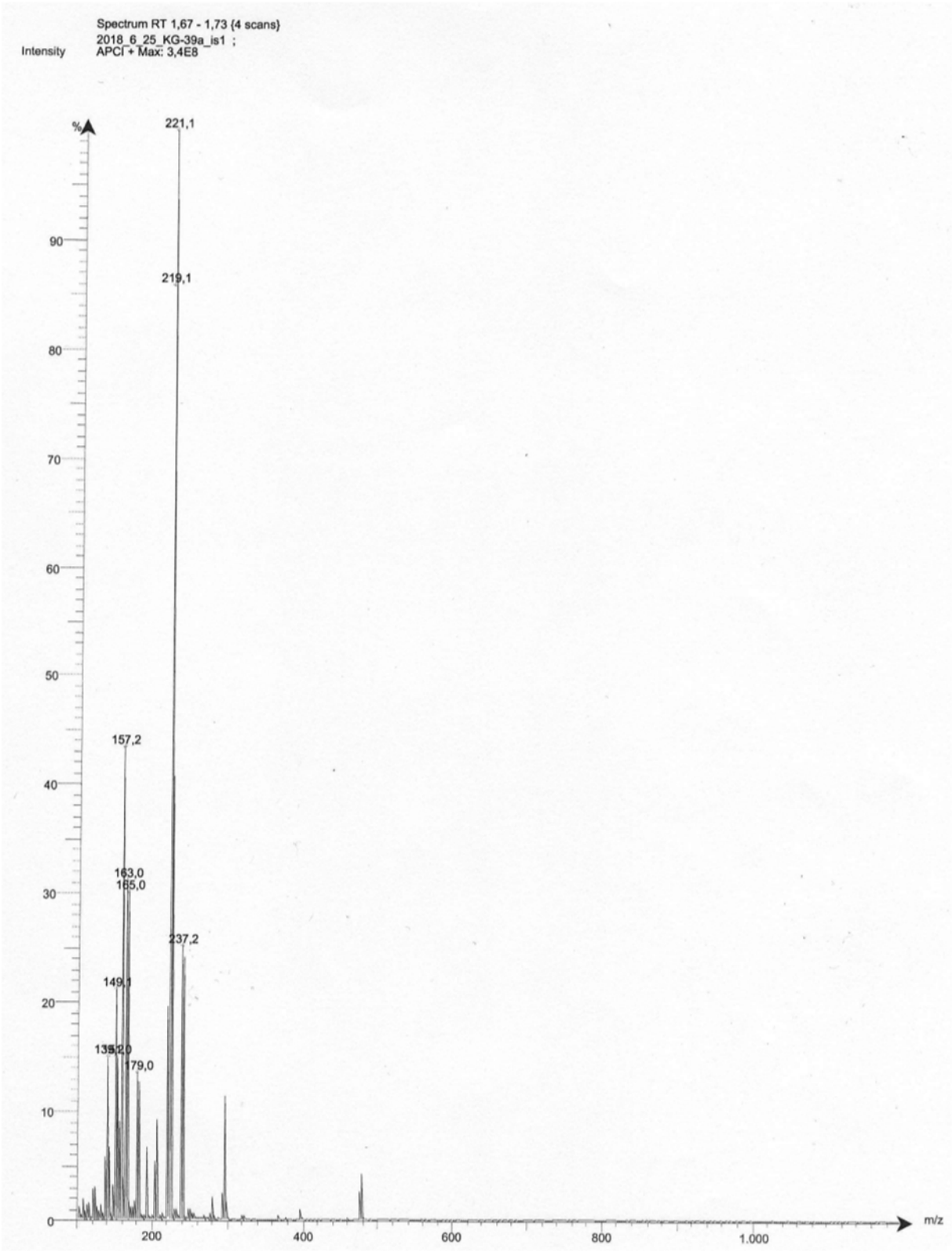
*Compound **4a** – ^{1}H NMR*



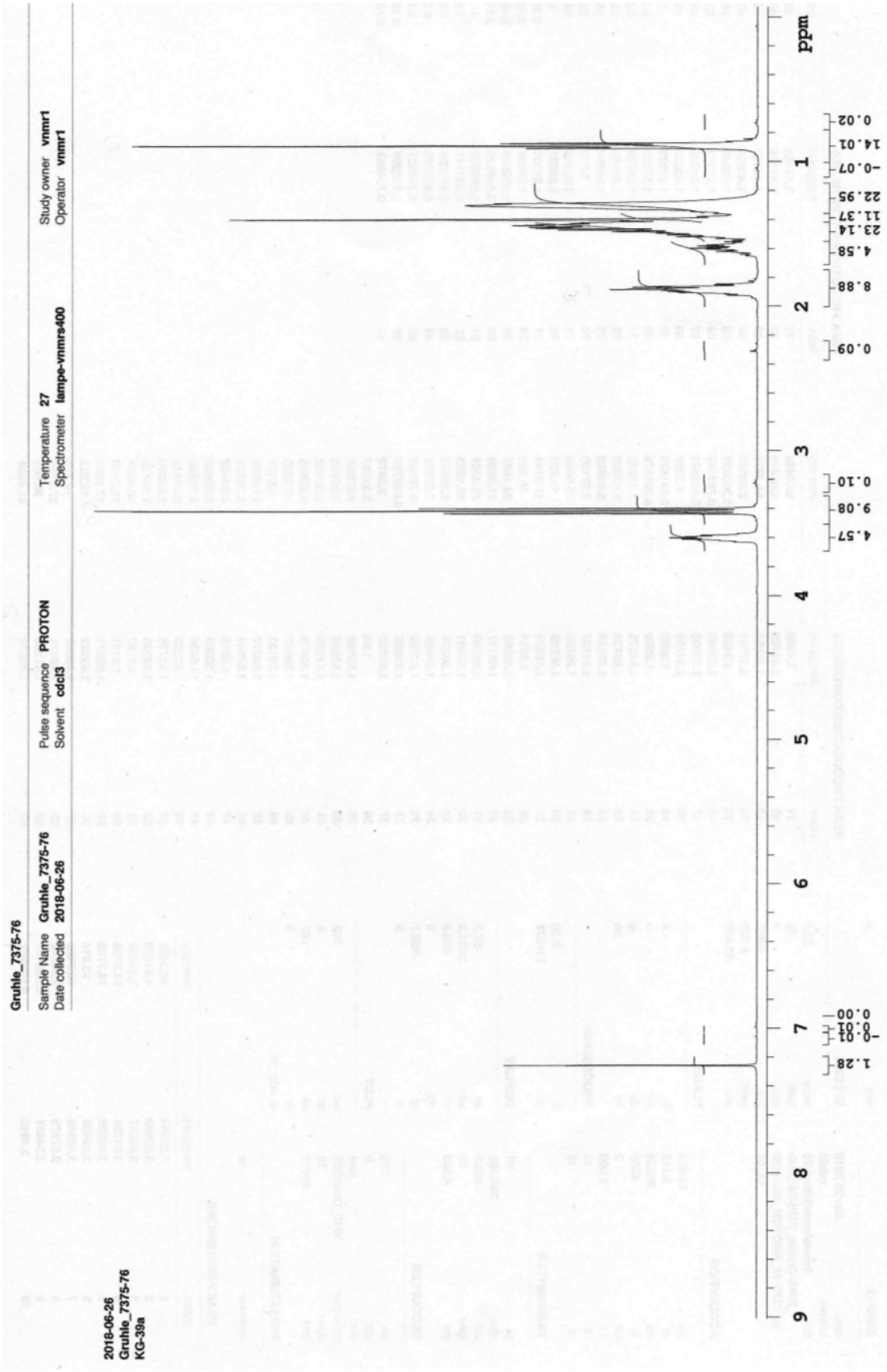
*Compound **4a** – ^{13}C NMR*



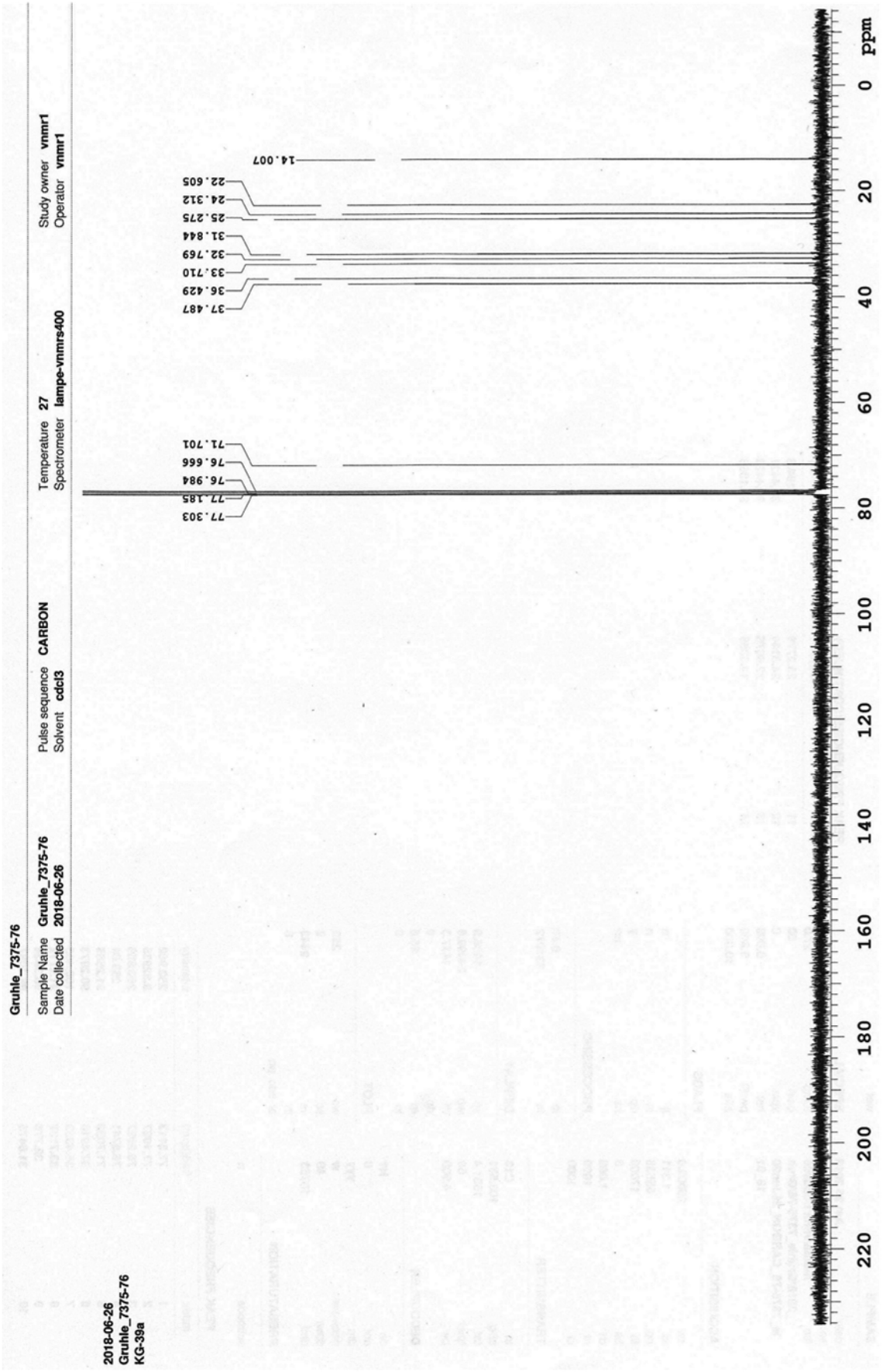
*Compound **4b** – APCI-MS (positive mode)*



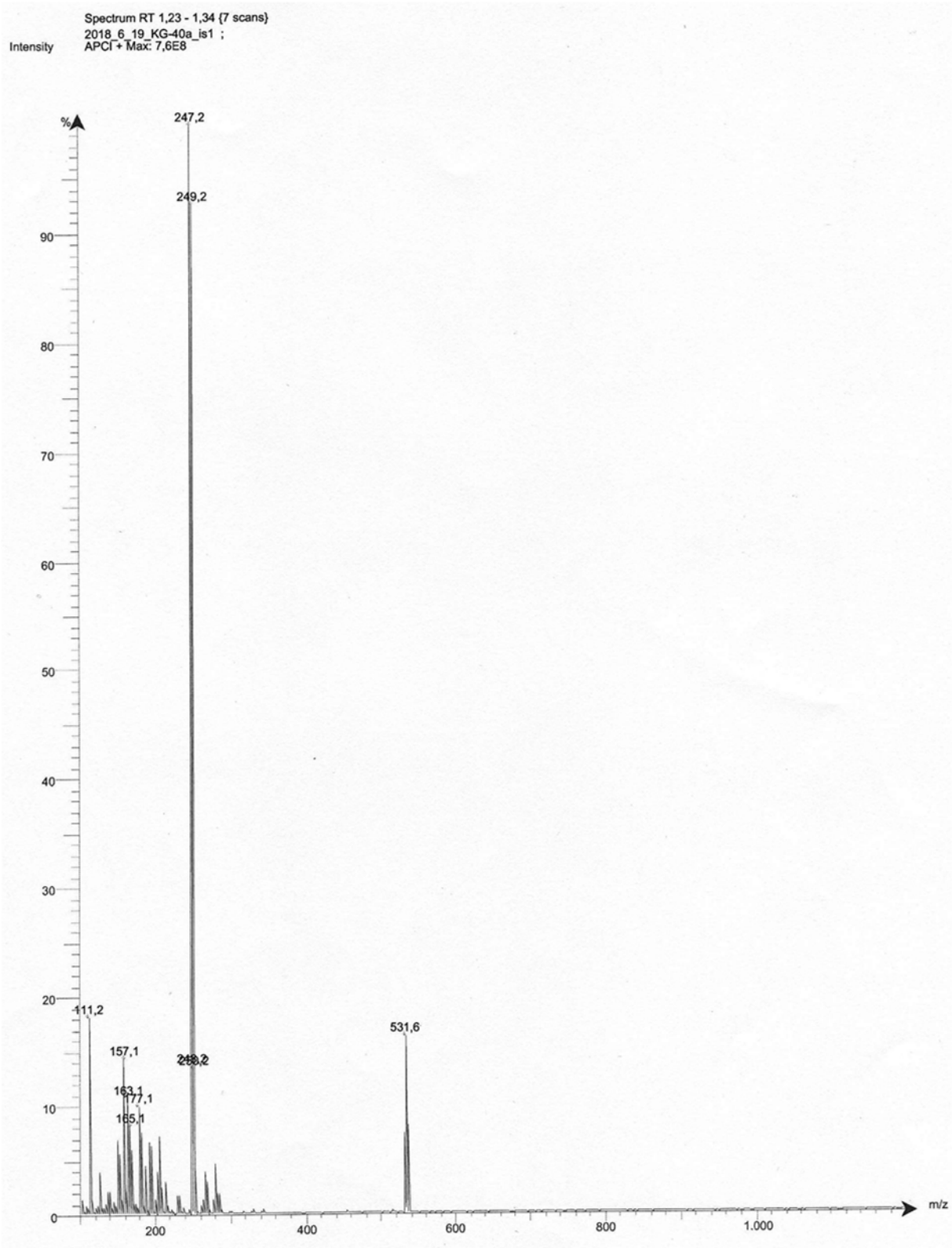
*Compound **4b** – ^{1}H NMR*



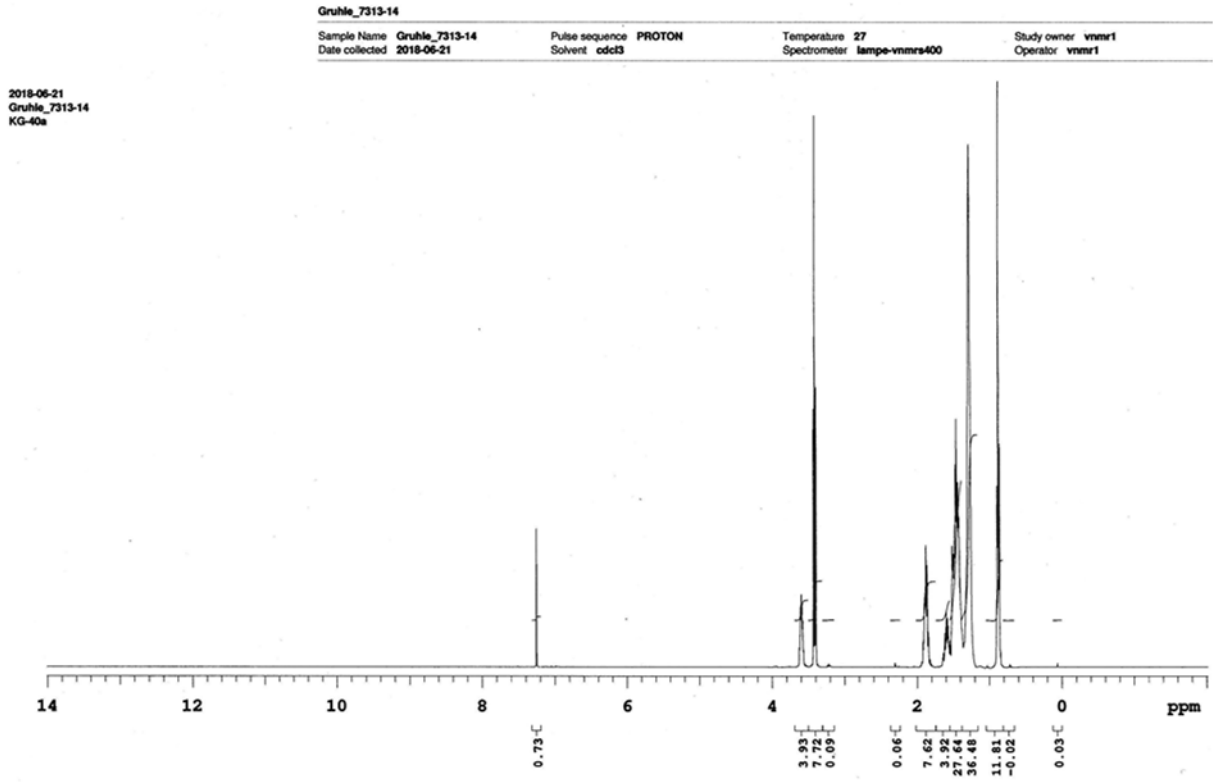
*Compound **4b** – ^{13}C NMR*



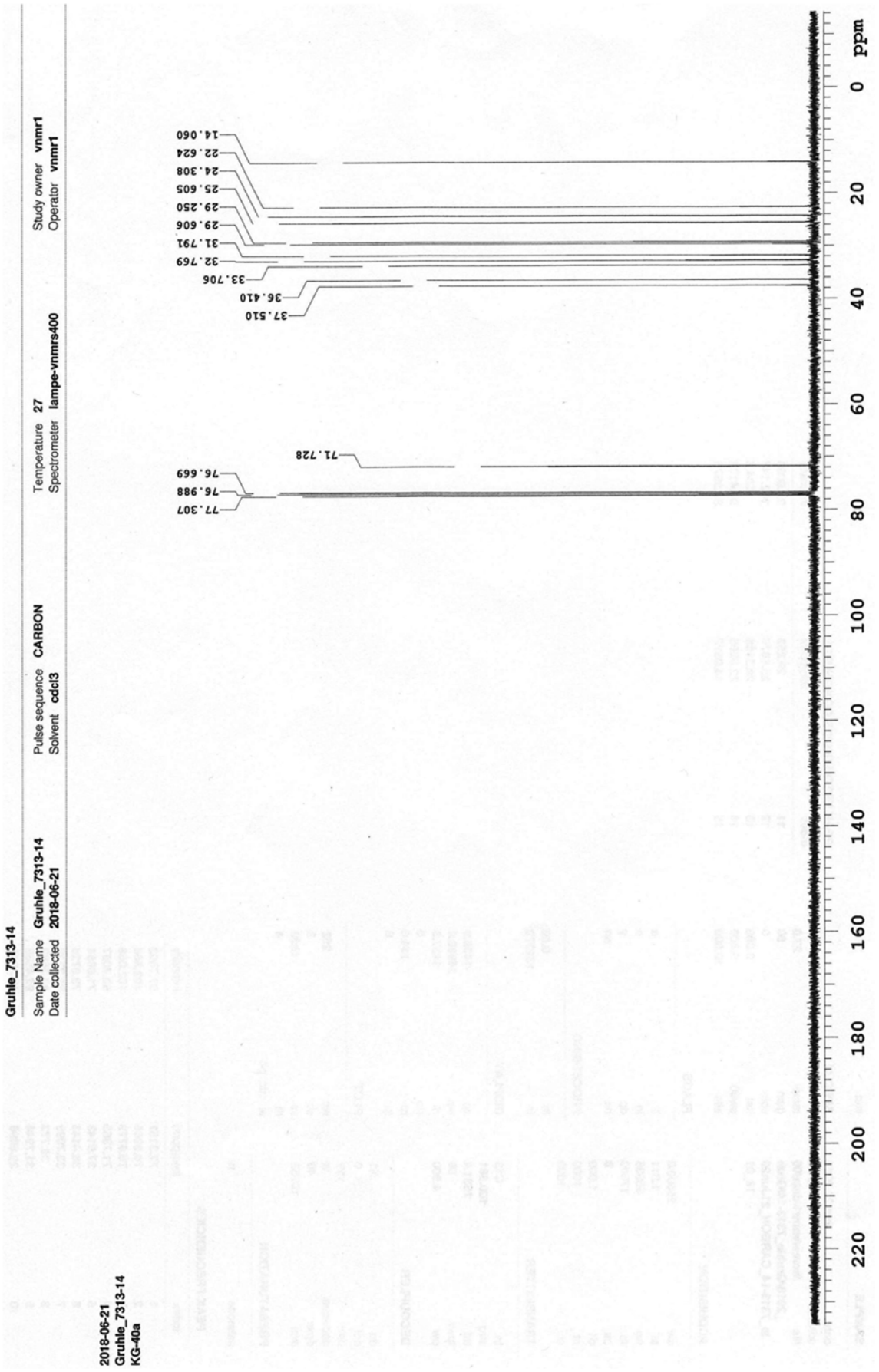
*Compound **4c** – APCI-MS (positive mode)*



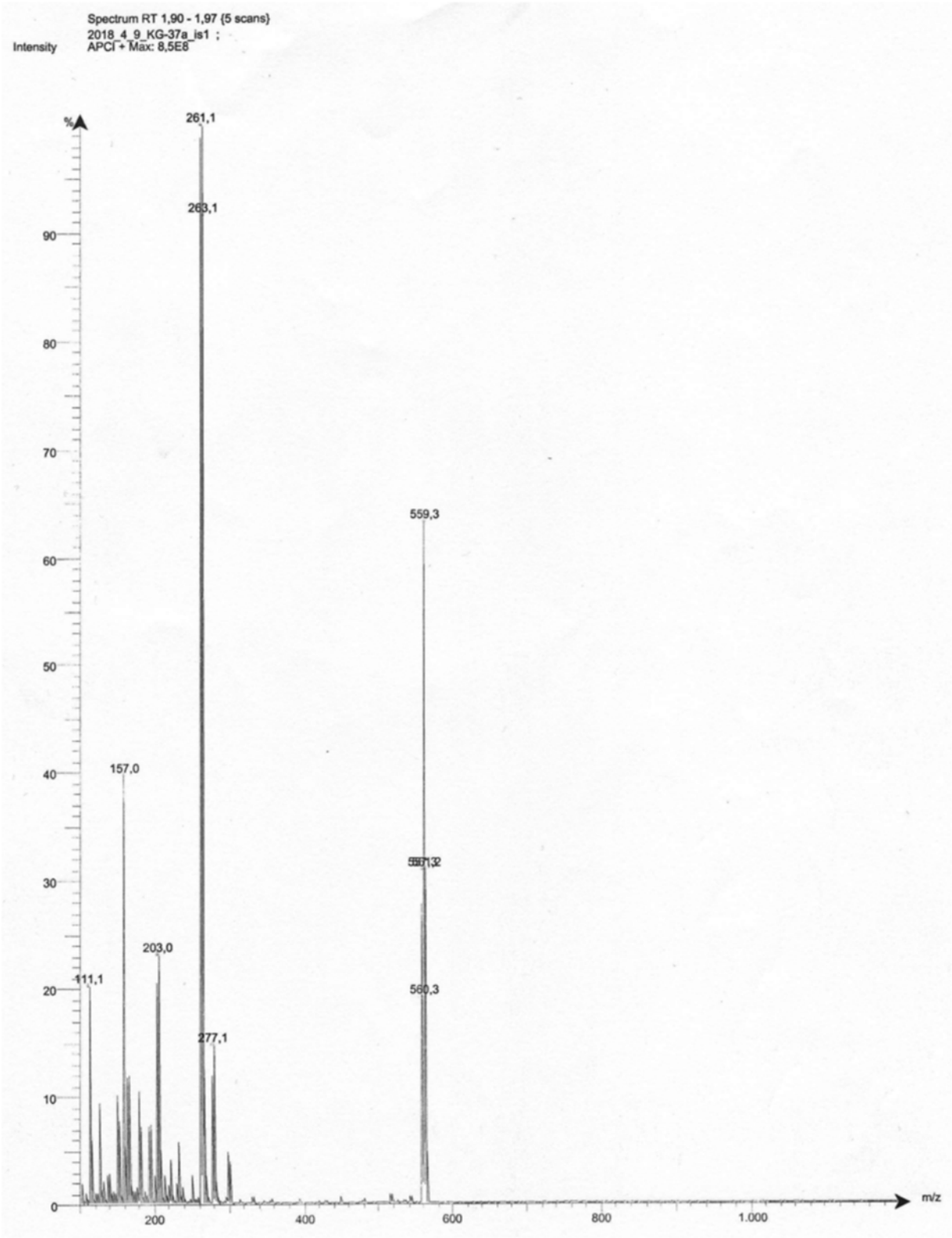
*Compound **4c** – ^{1}H NMR*



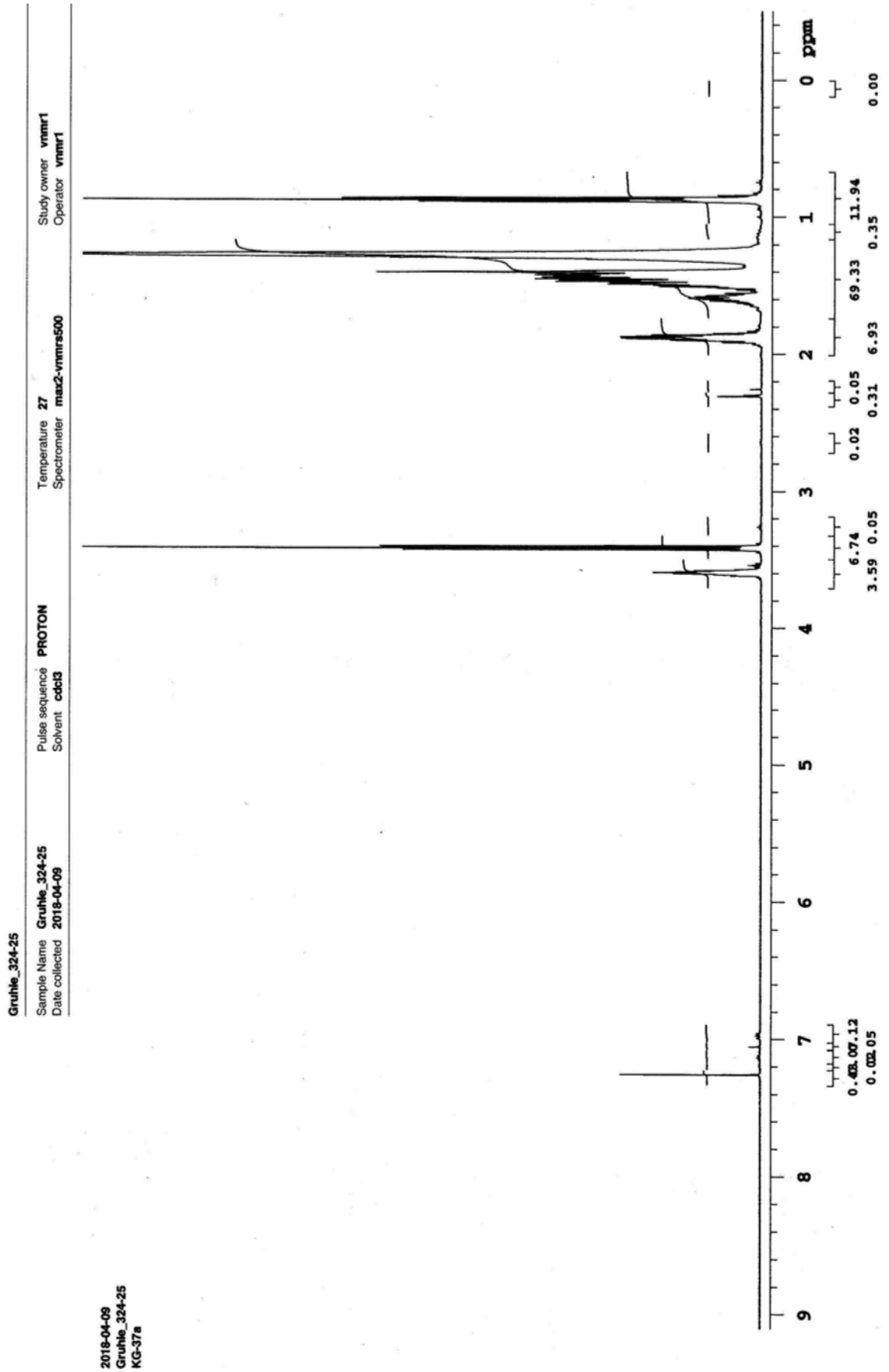
*Compound **4c** – ^{13}C NMR*



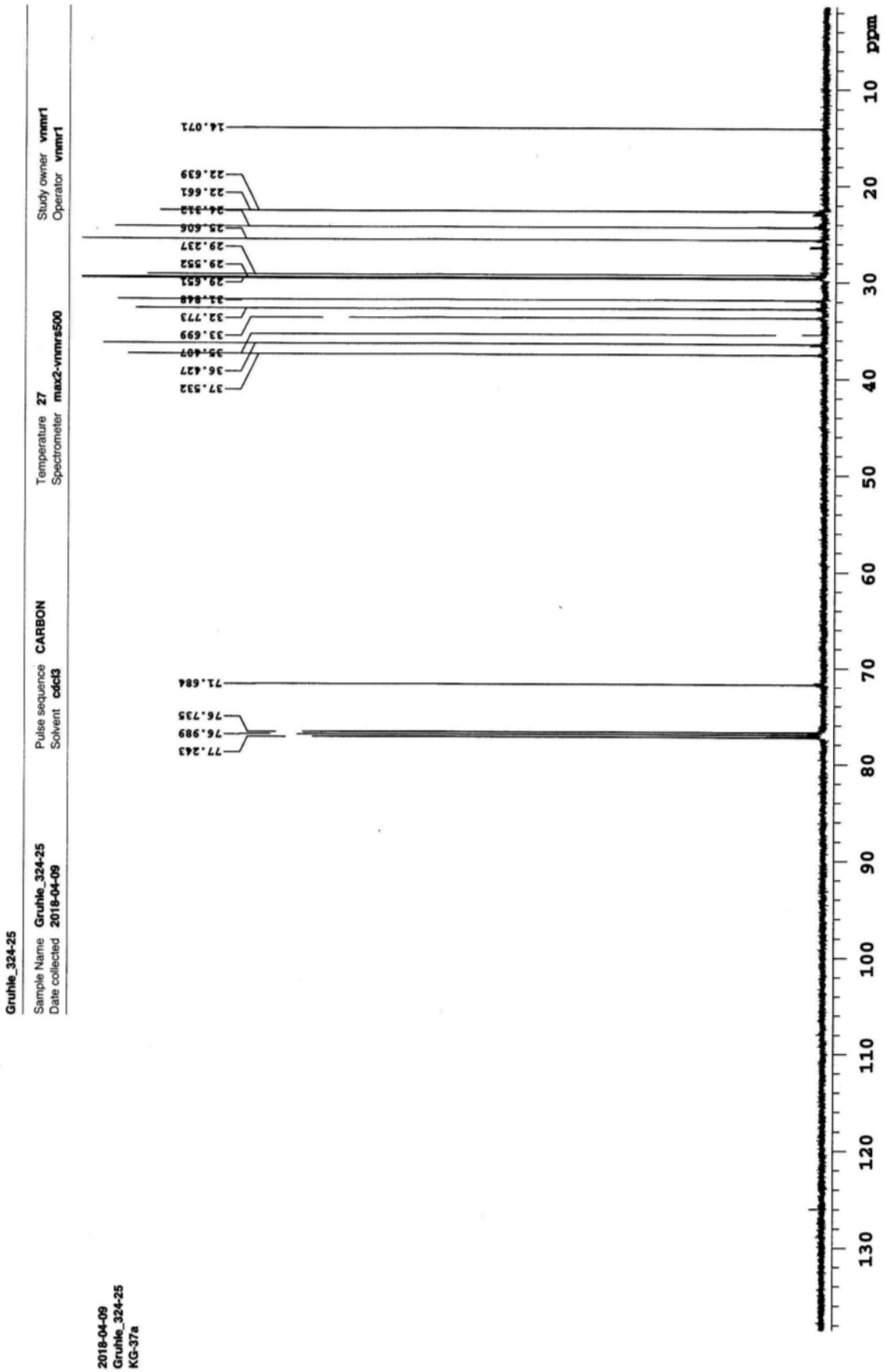
*Compound **4d** – APCI-MS (positive mode)*



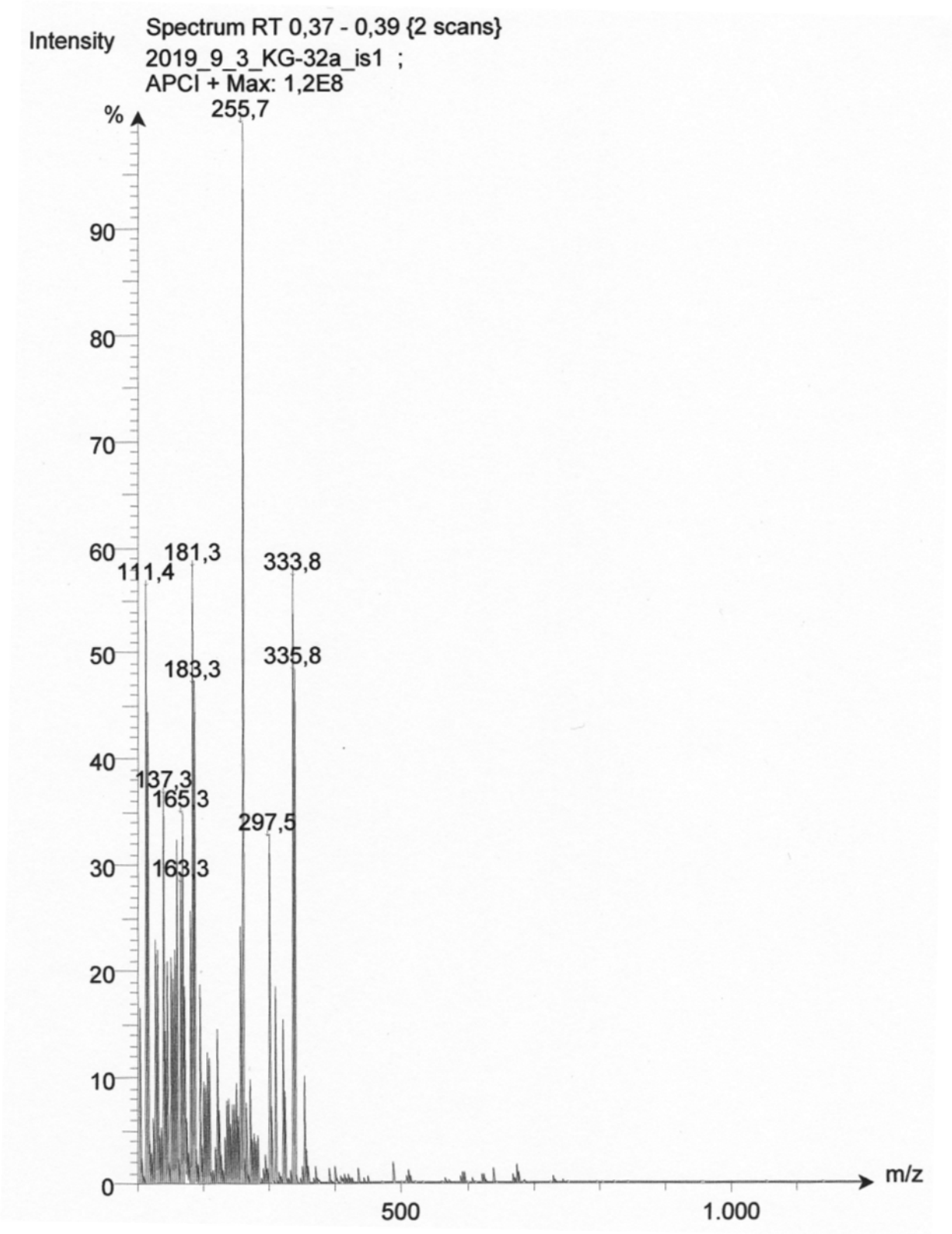
*Compound **4d** – ^{1}H NMR*



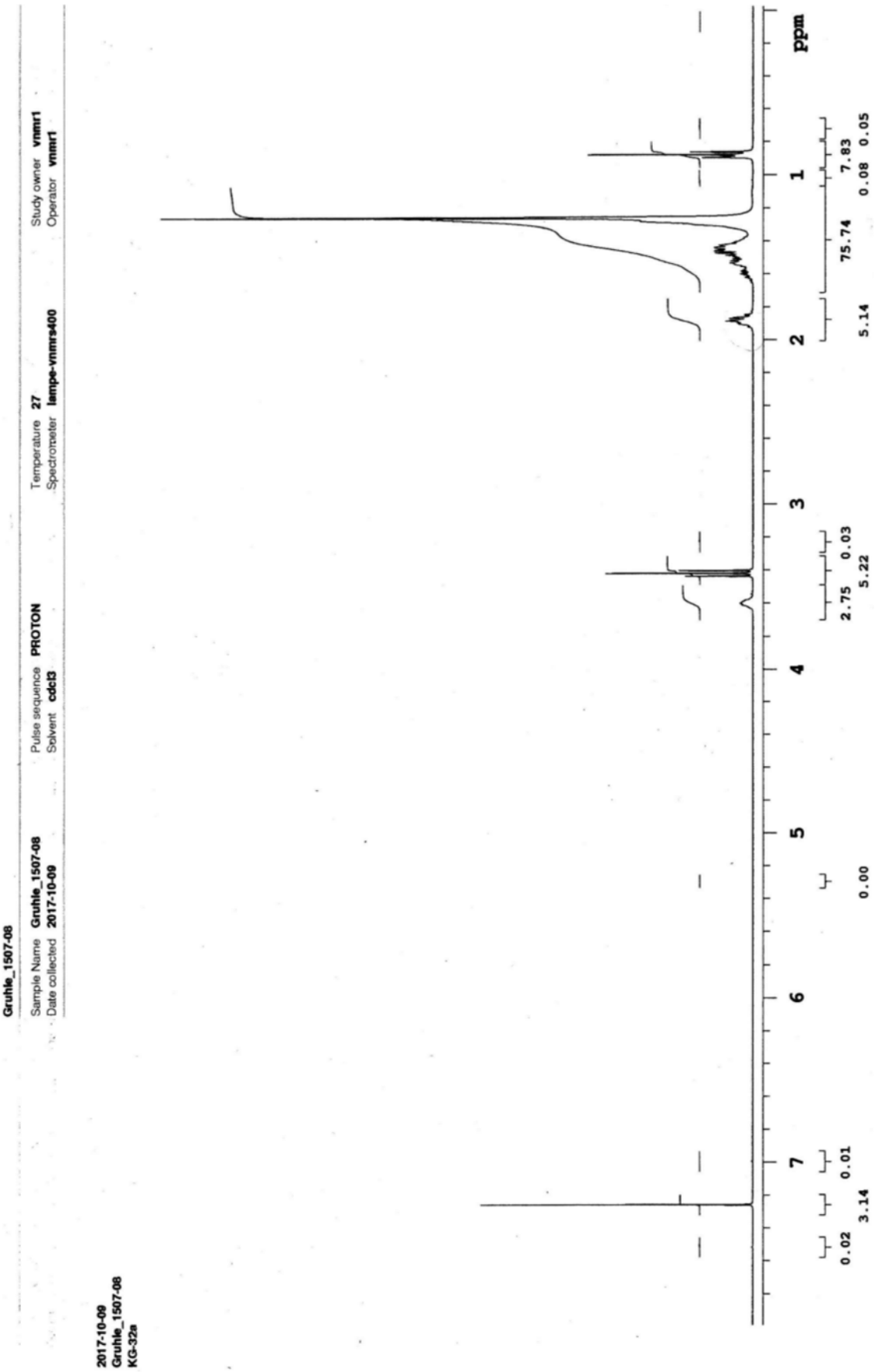
*Compound **4d** – ^{13}C NMR*



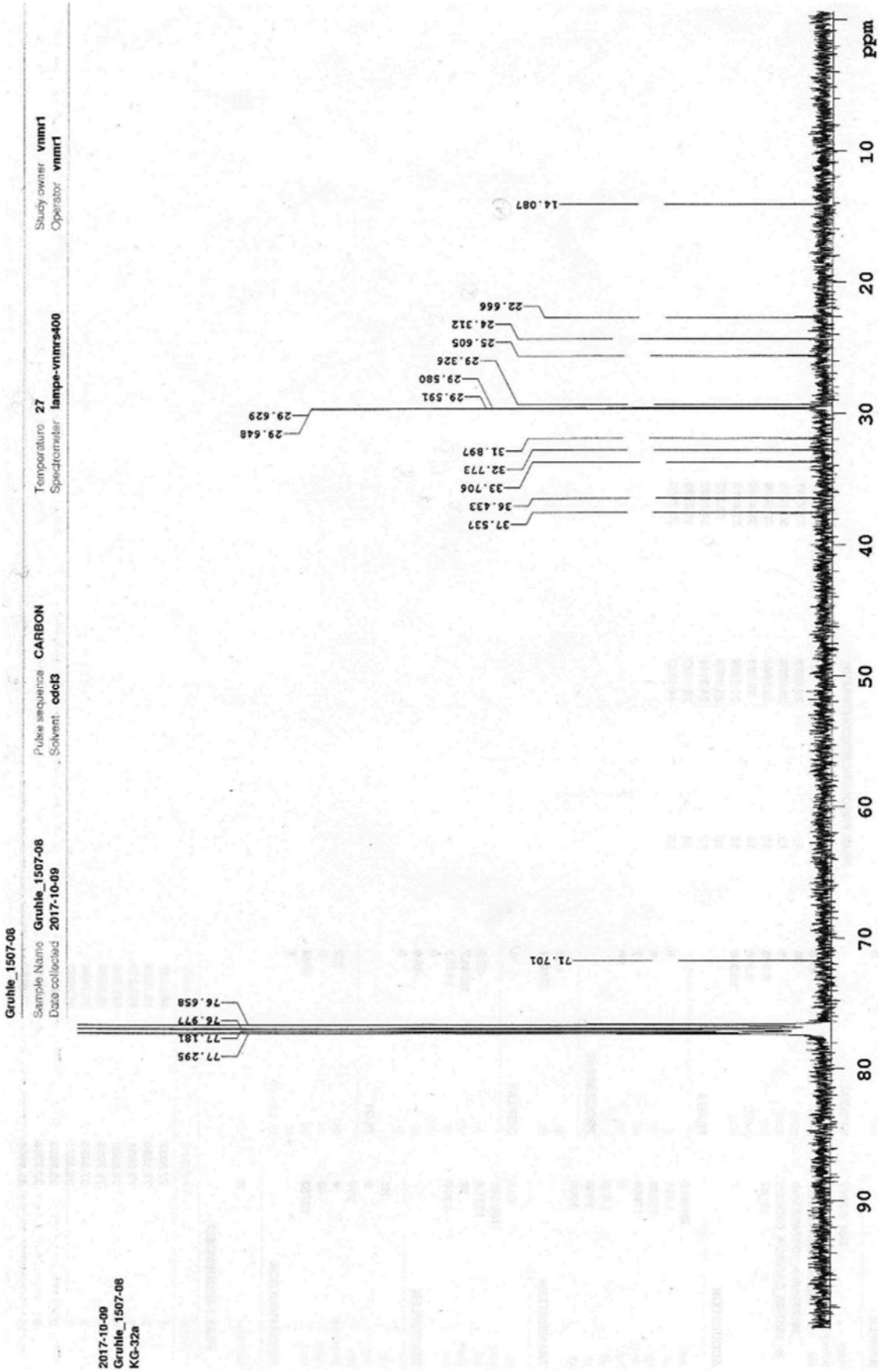
*Compound **4e** – APCI-MS (positive mode)*



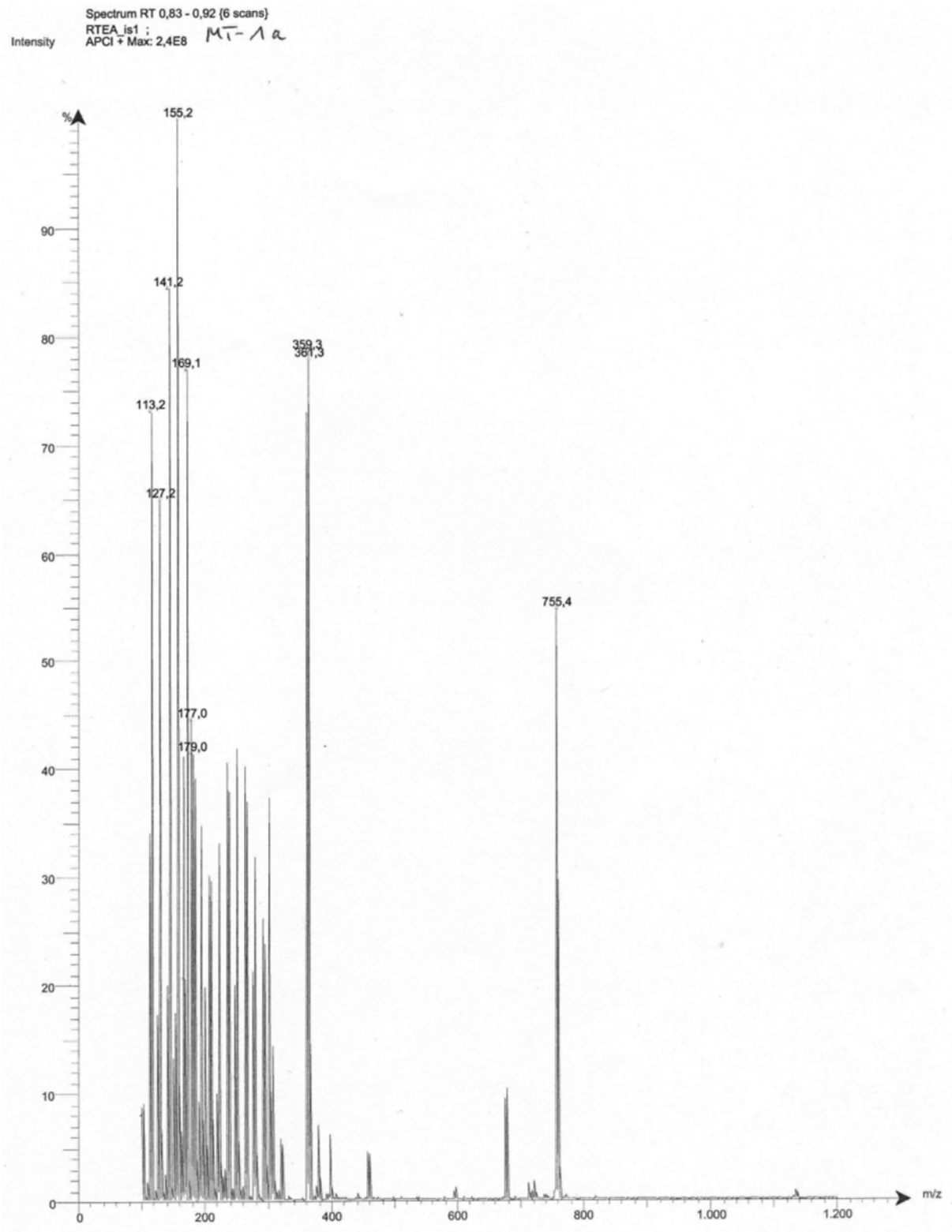
*Compound **4e** – ^{1}H NMR*



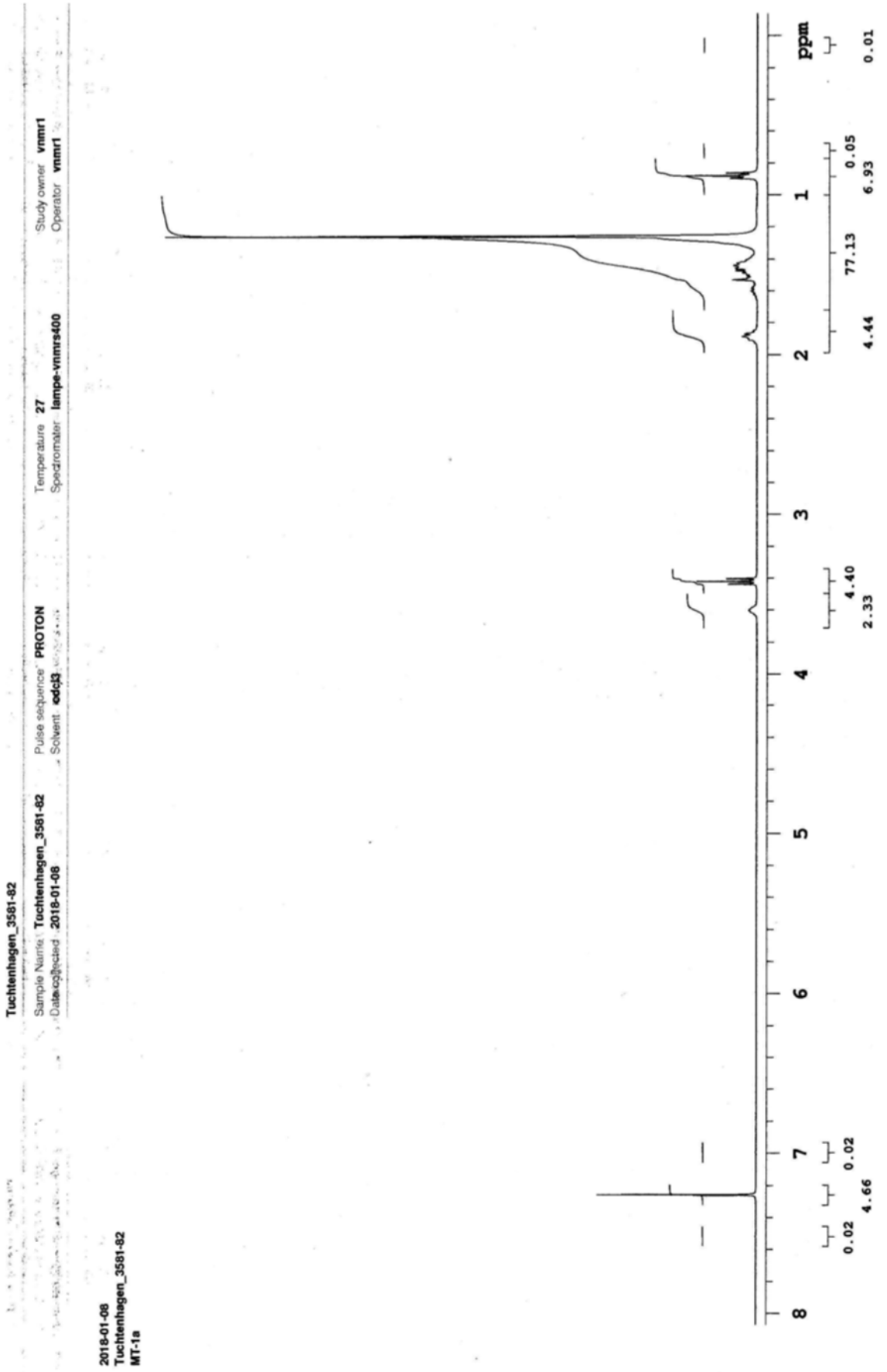
*Compound **4e** – ^{13}C NMR*



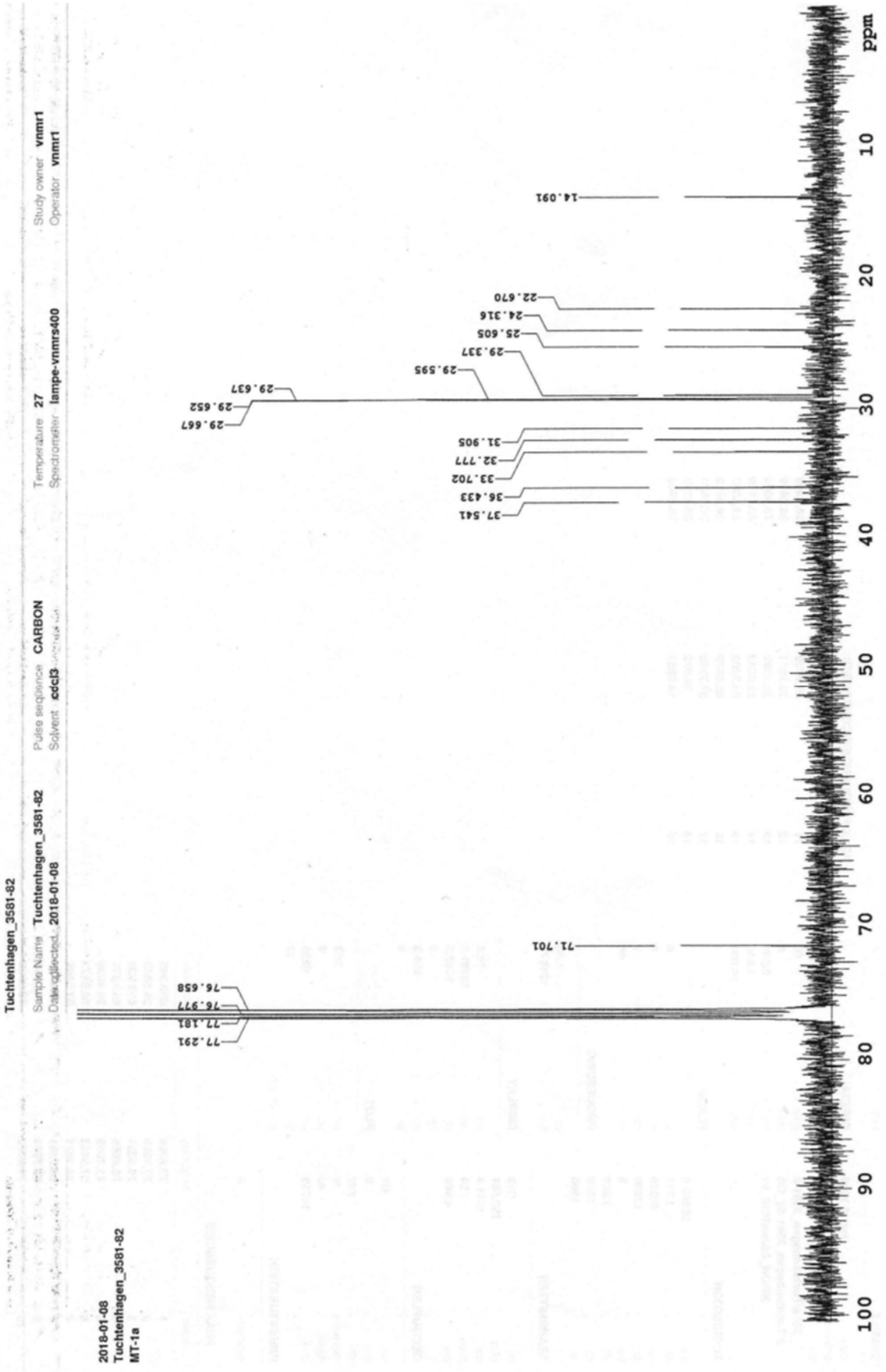
*Compound **4f** – APCI-MS (positive mode)*



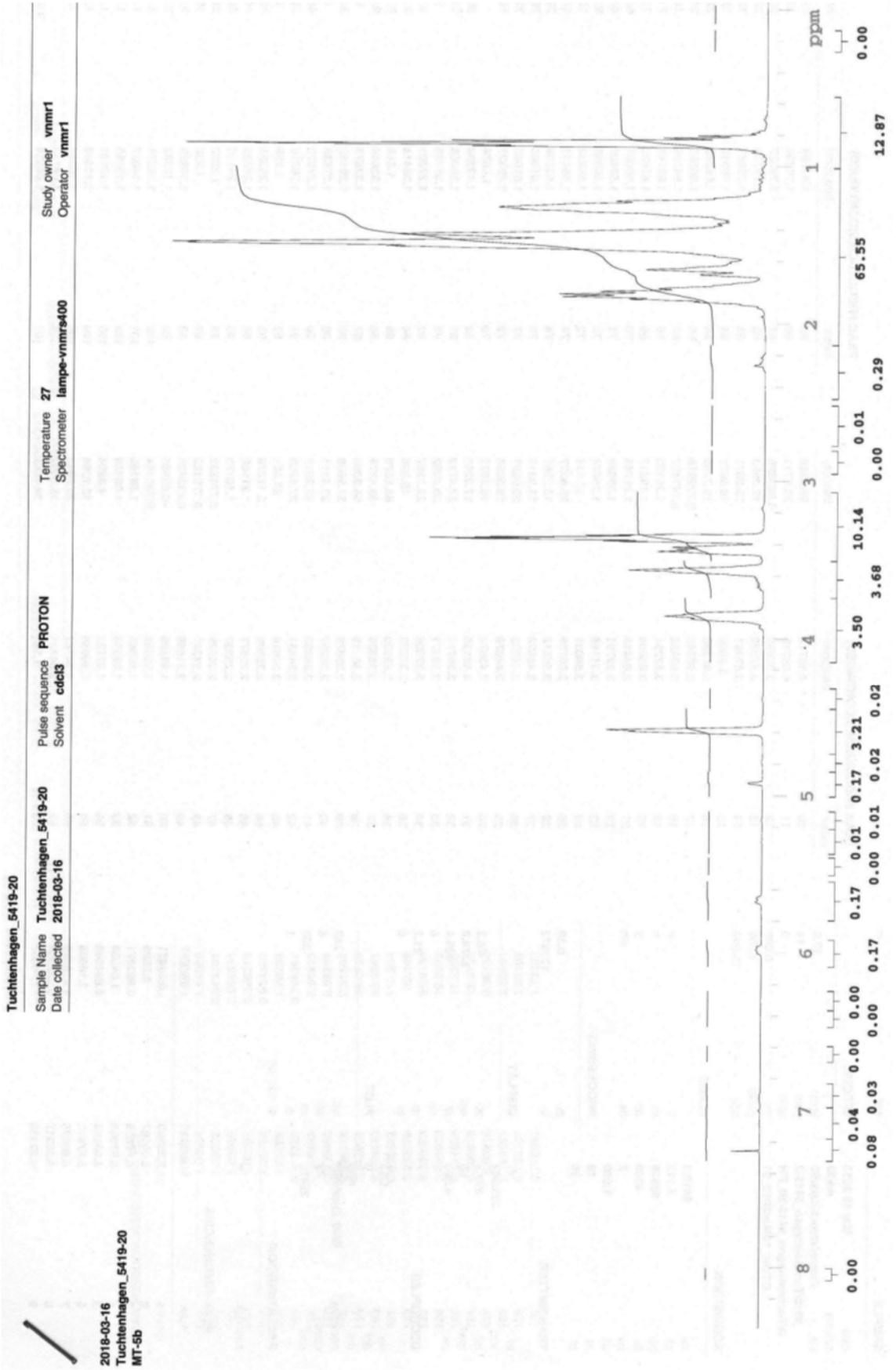
*Compound **4f** – ^{1}H NMR*



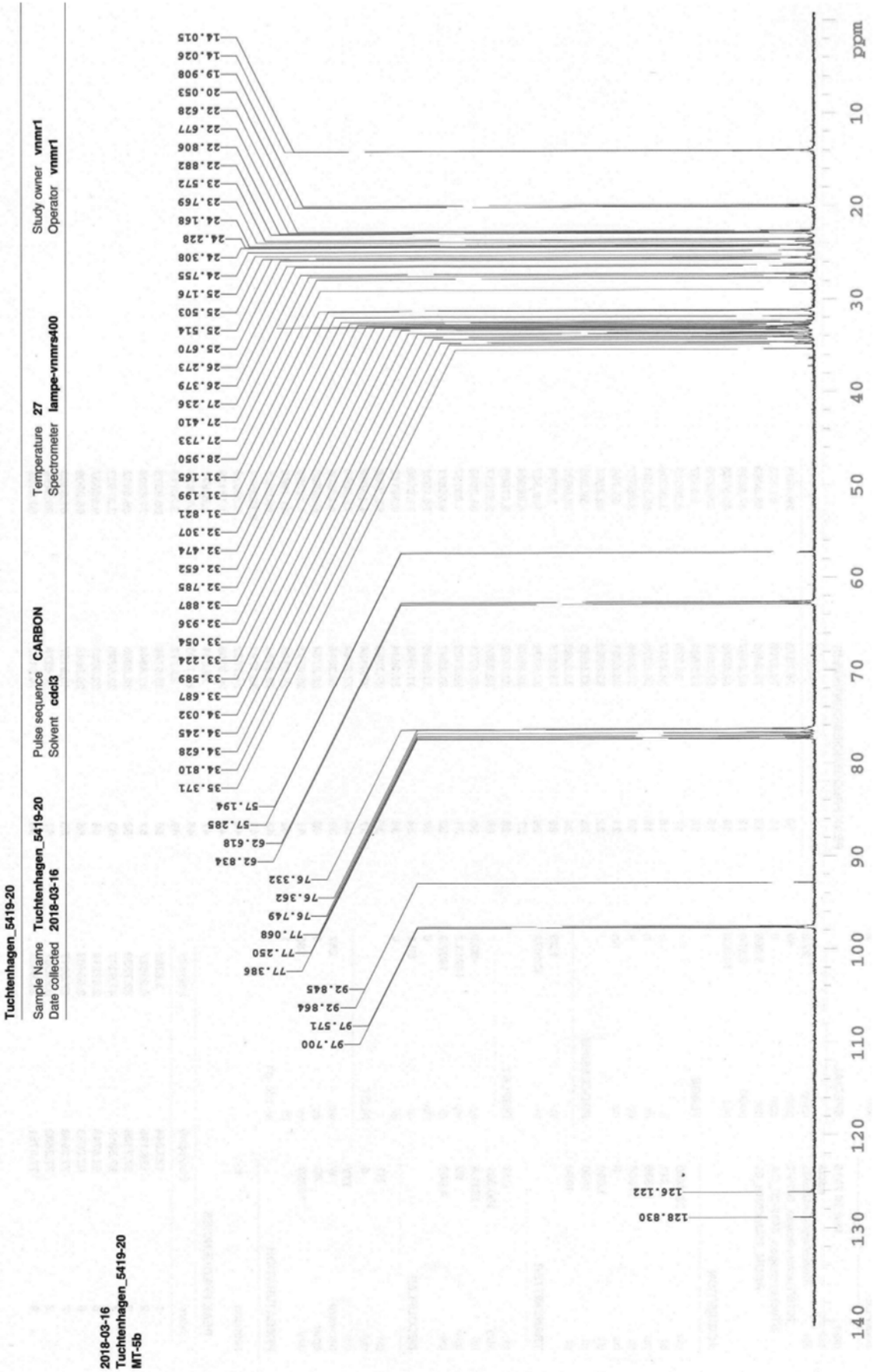
*Compound **4f** – ^{13}C NMR*



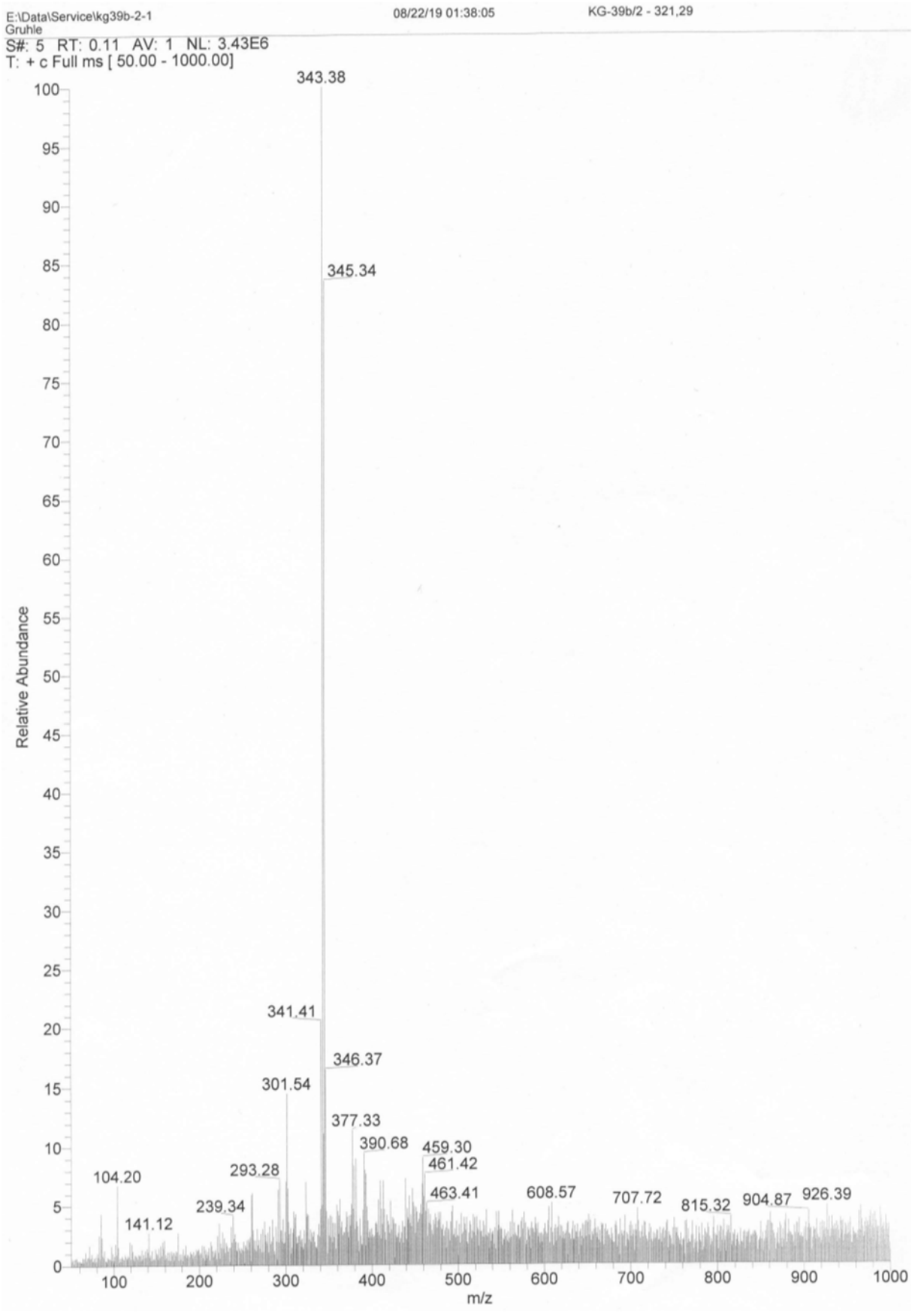
*Compound **5a** – ^{1}H NMR*



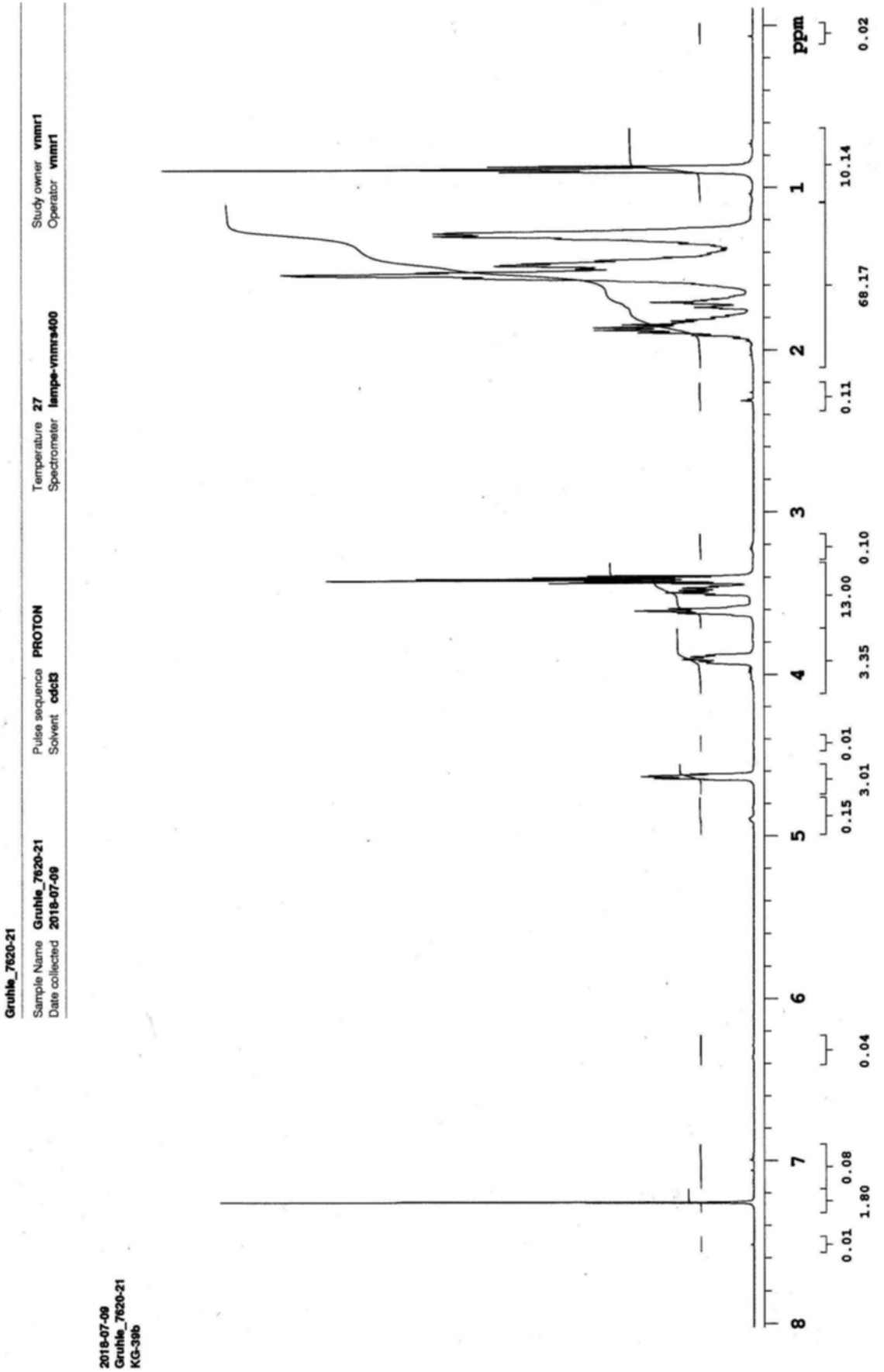
*Compound **5a** – ^{13}C NMR*



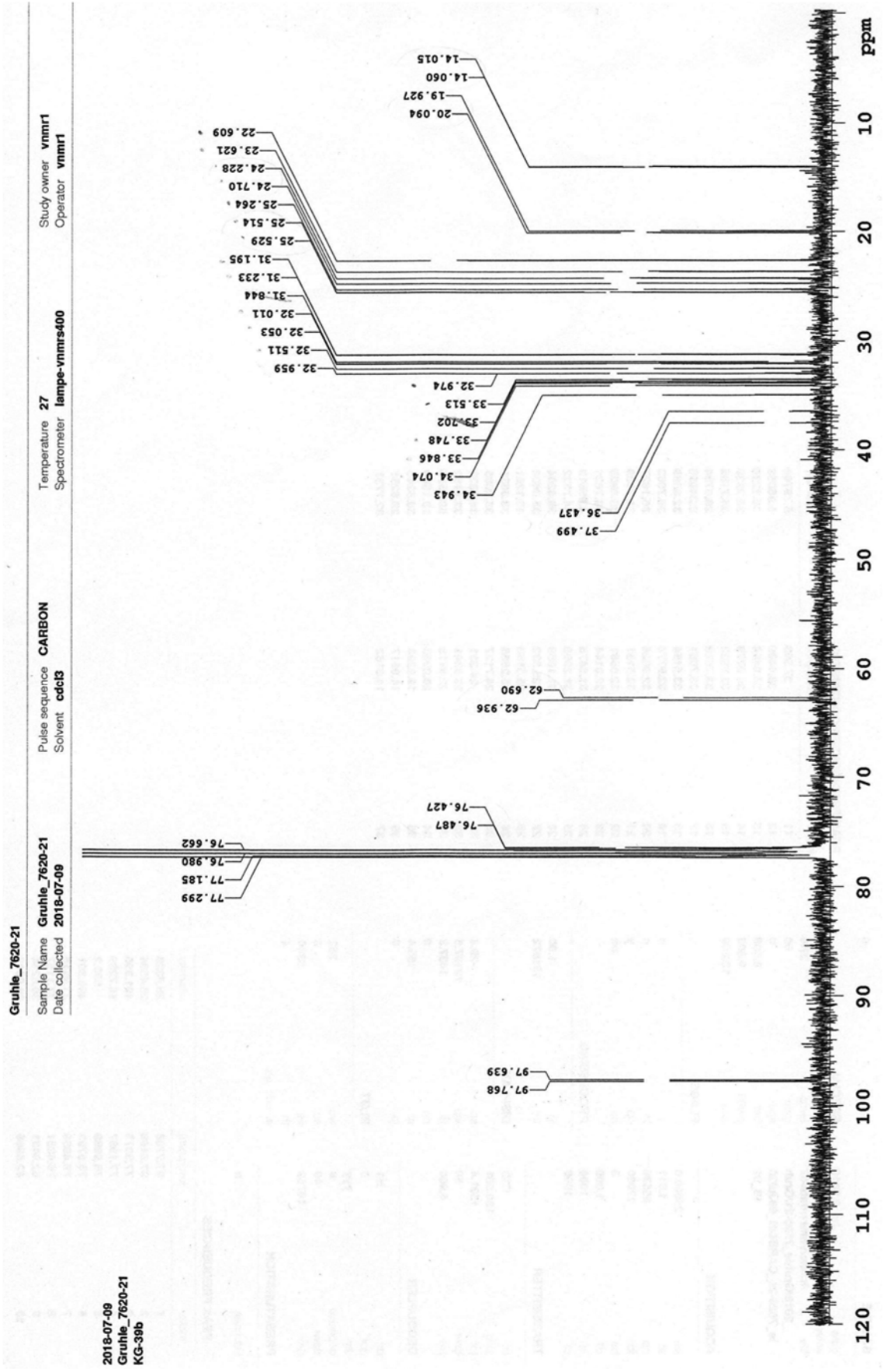
*Compound **5b** – ESI-MS (positive mode)*



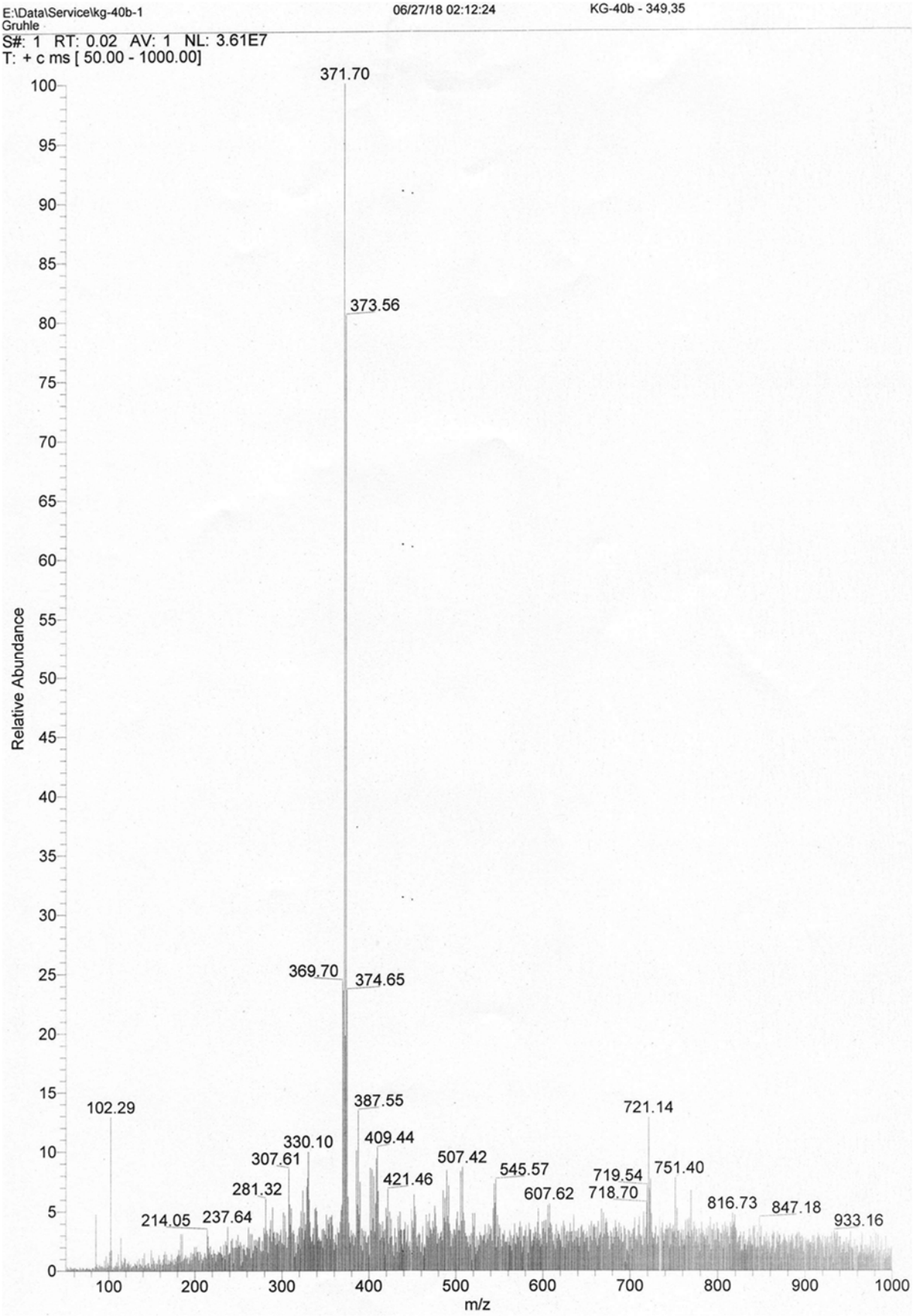
Compound ***5b*** *– ^{1}H NMR*



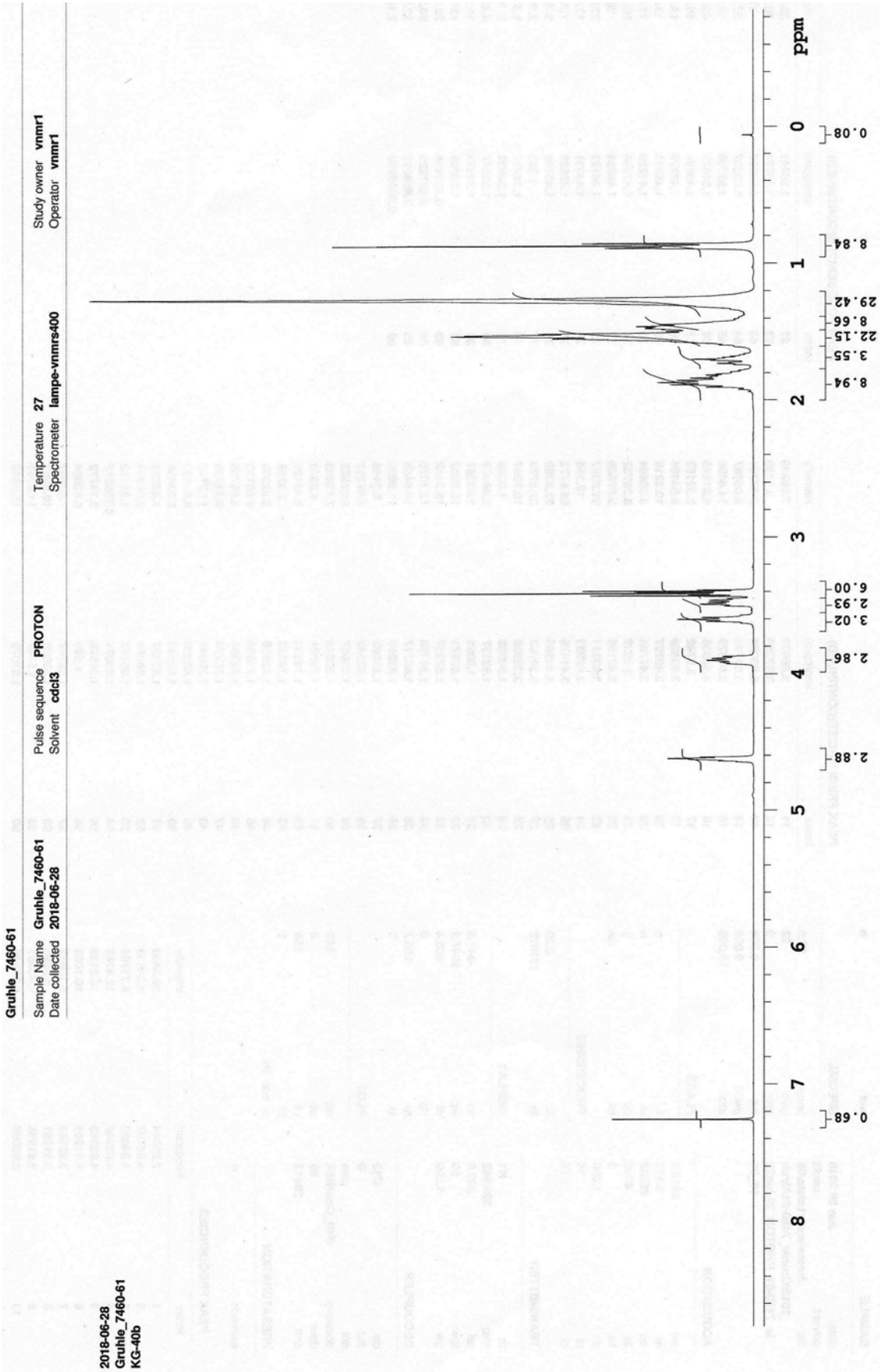
Compound ***5b*** *– ^{13}C NMR*



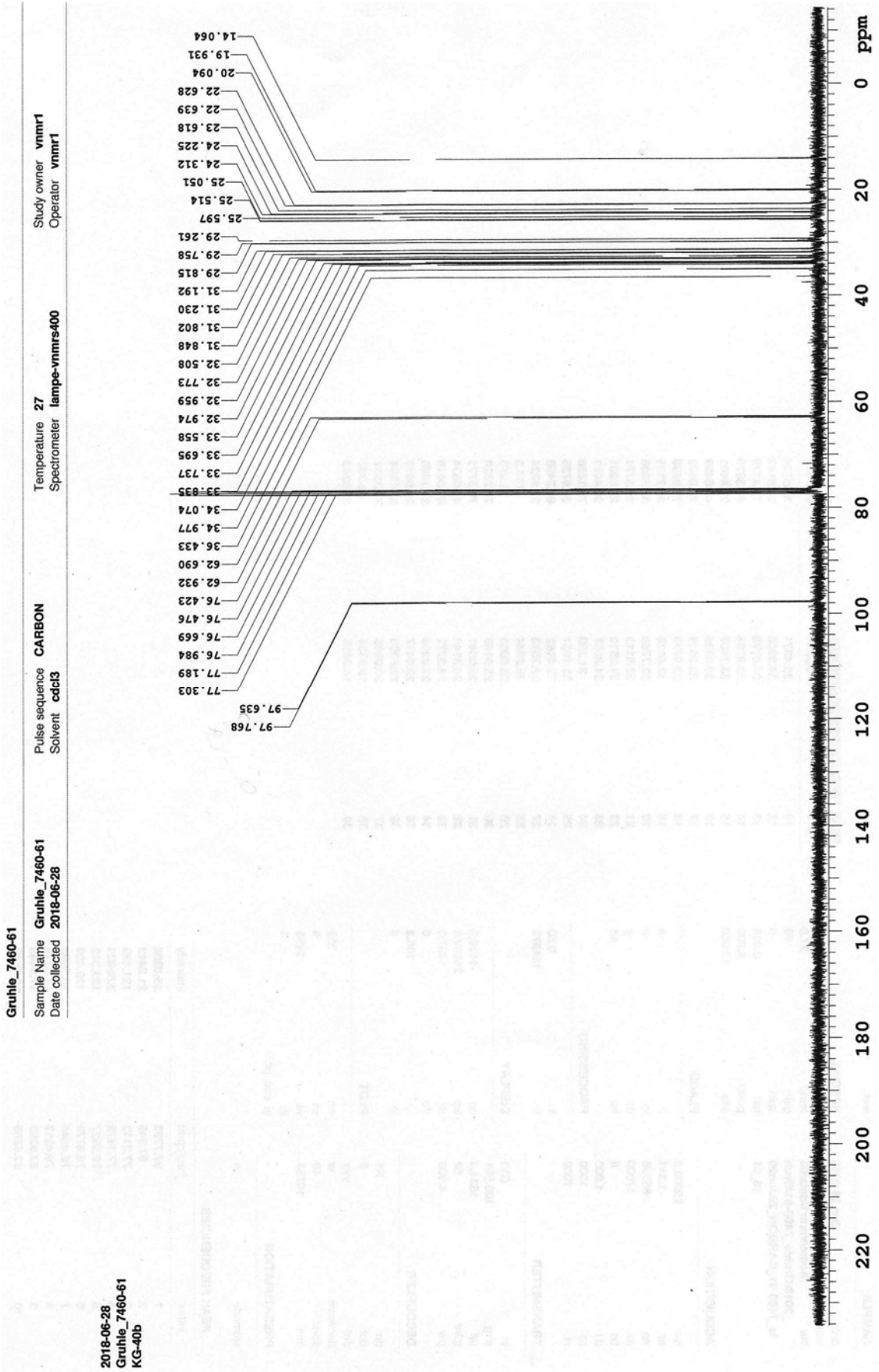
*Compound **5c** – ESI-MS (positive mode)*



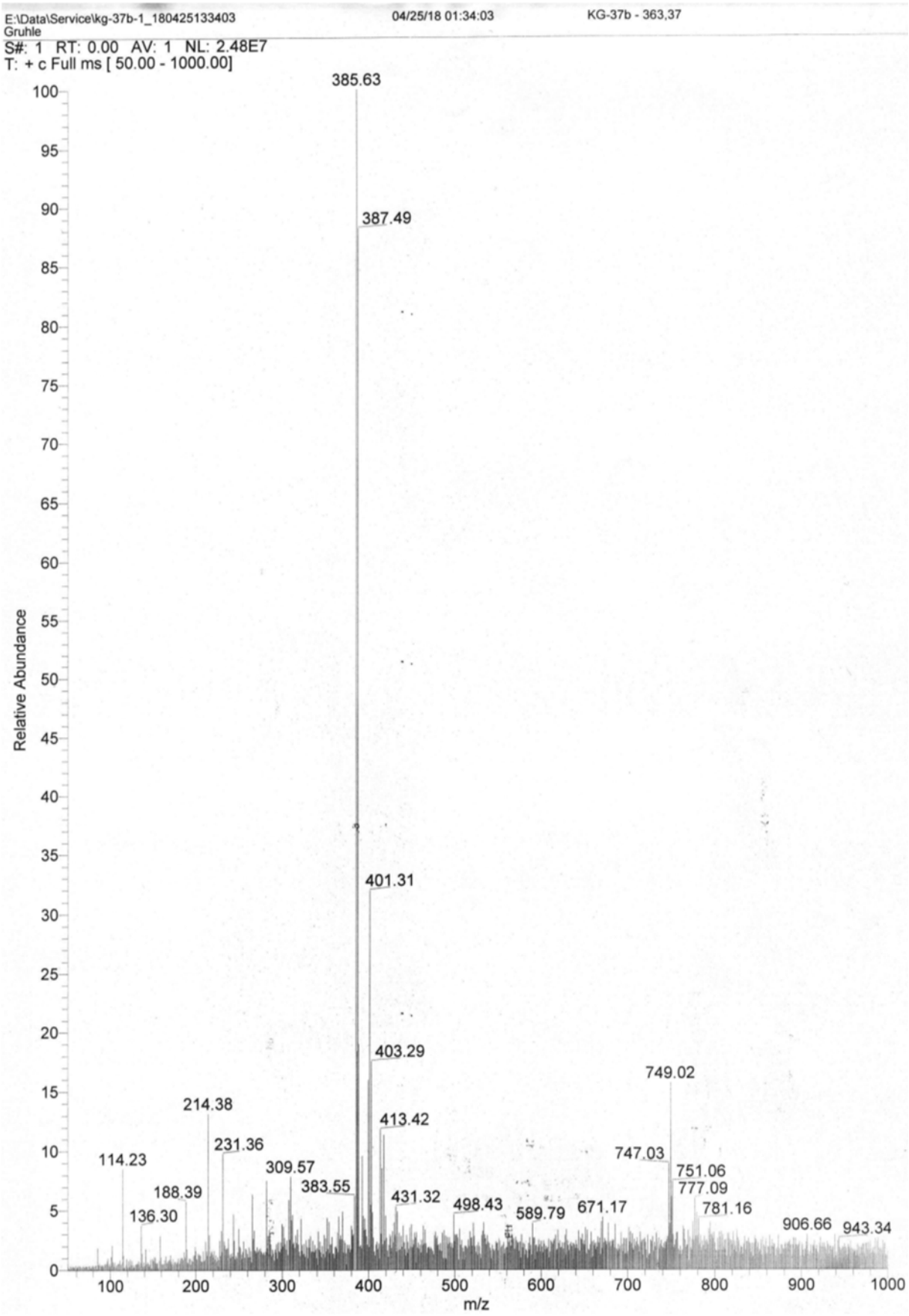
Compound **5c** *– ^{1}H NMR*



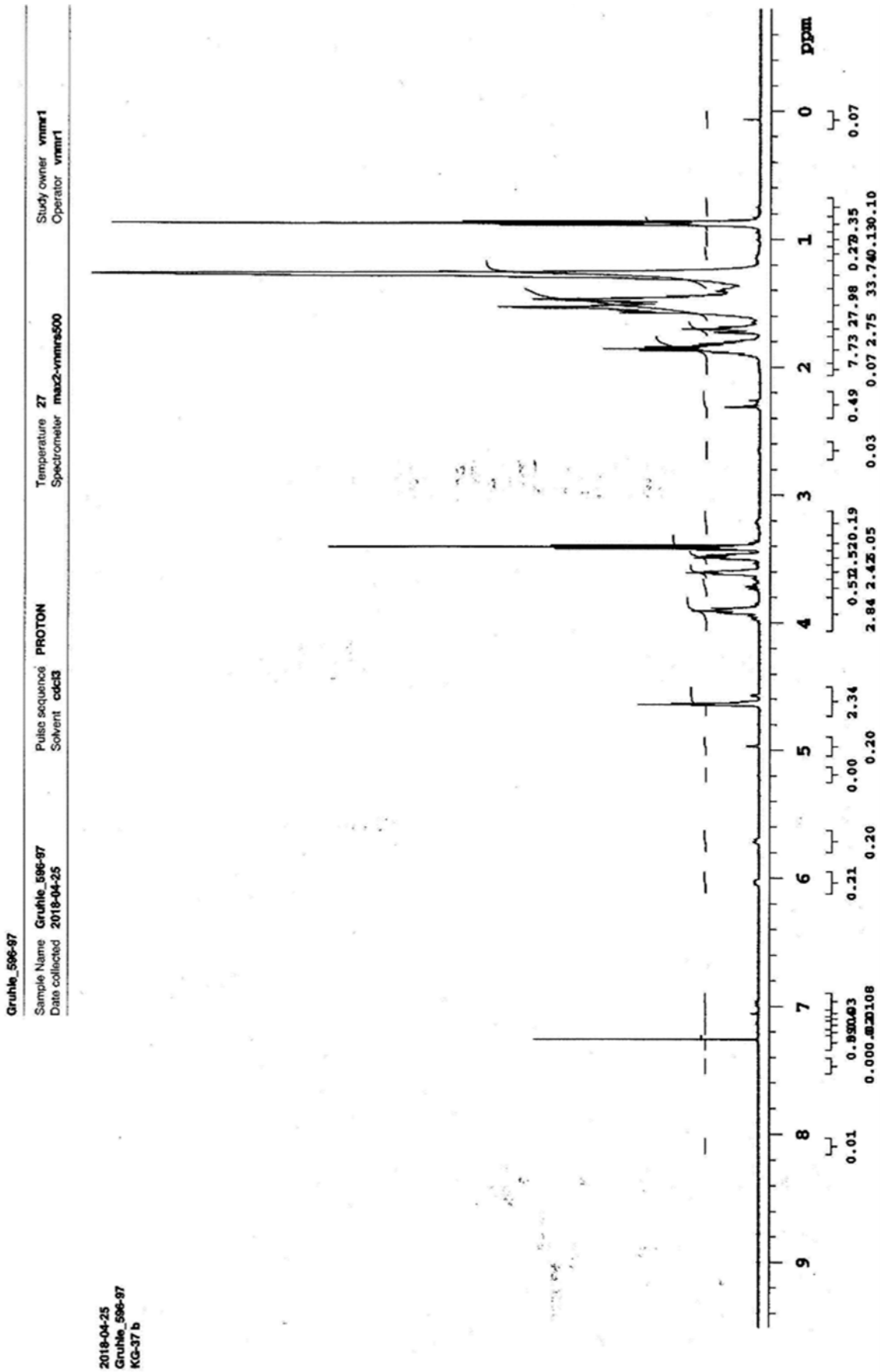
Compound ***5c*** *– ^{13}C NMR*



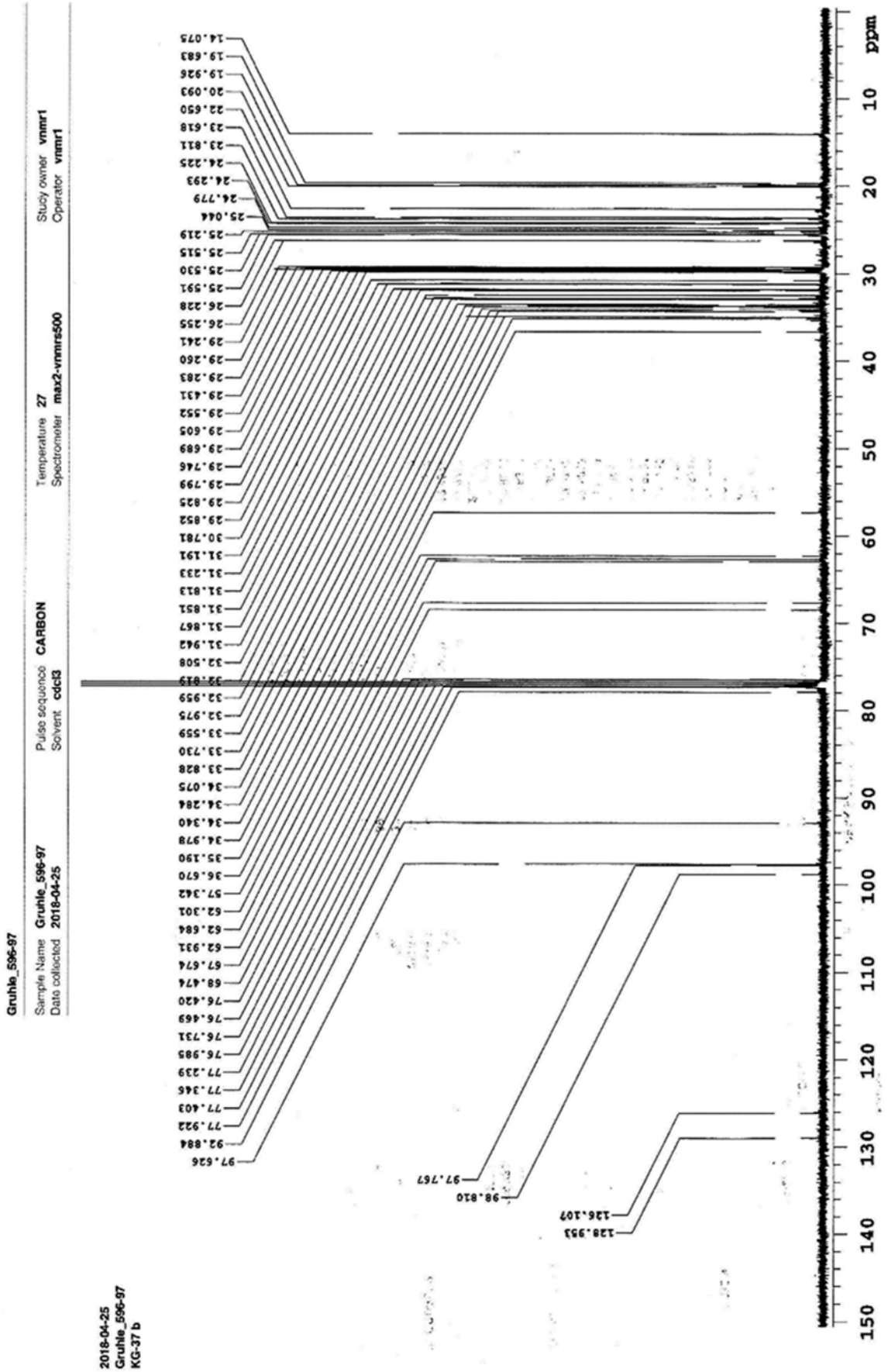
*Compound **5d** – ESI-MS (positive mode)*



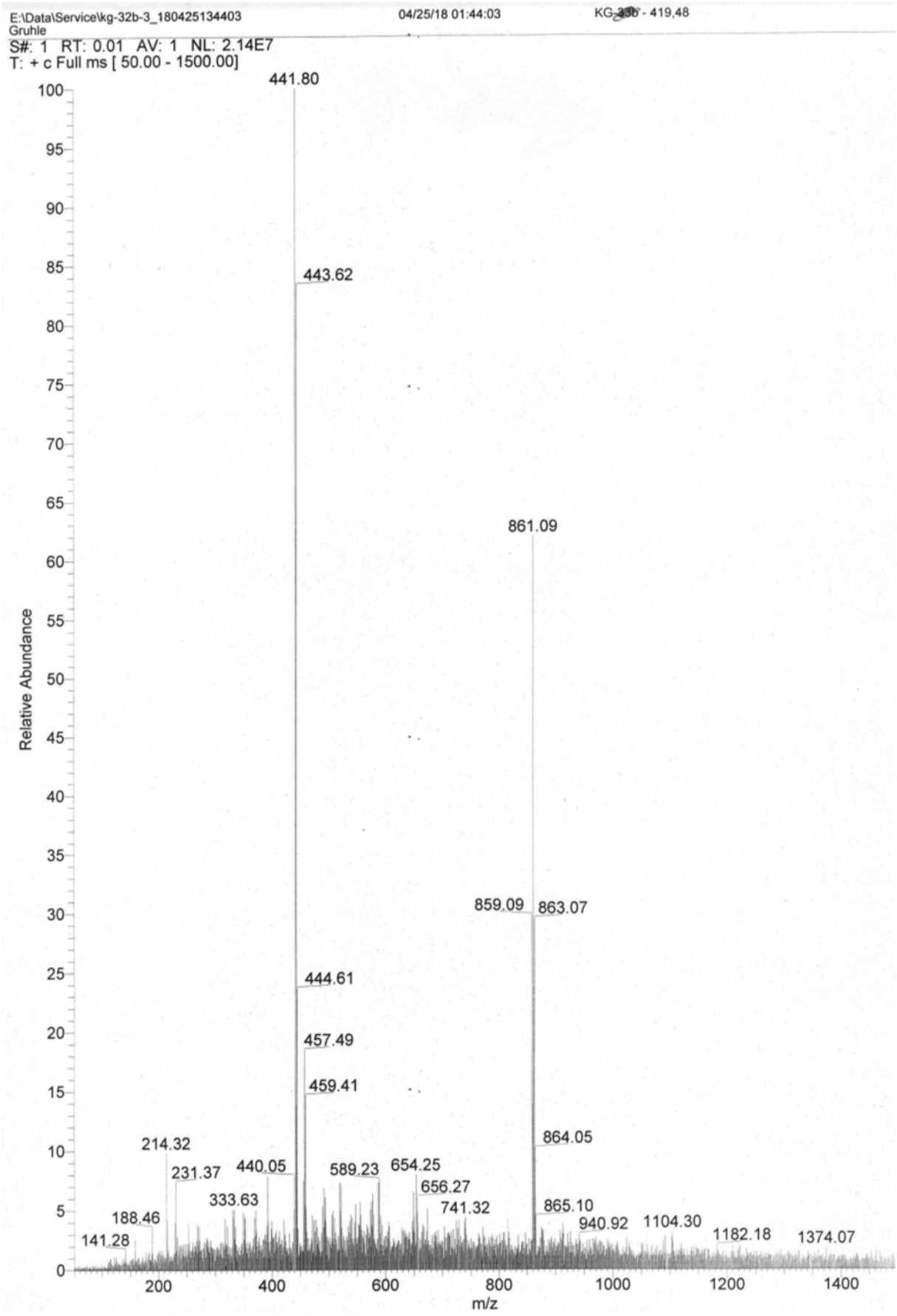
Compound ***5d*** *– ^{1}H NMR*



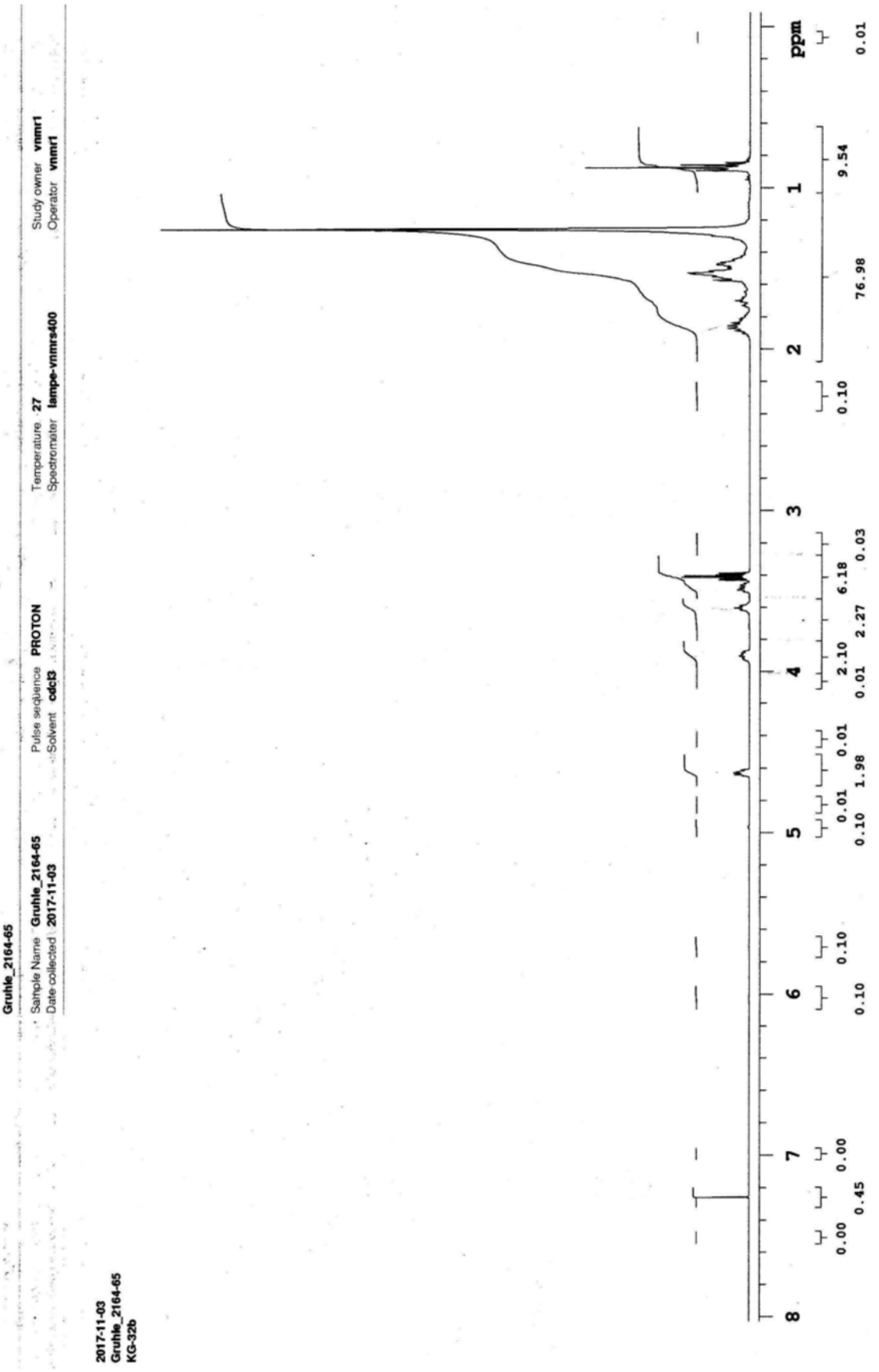
*Compound **5d** – ^{13}C NMR*



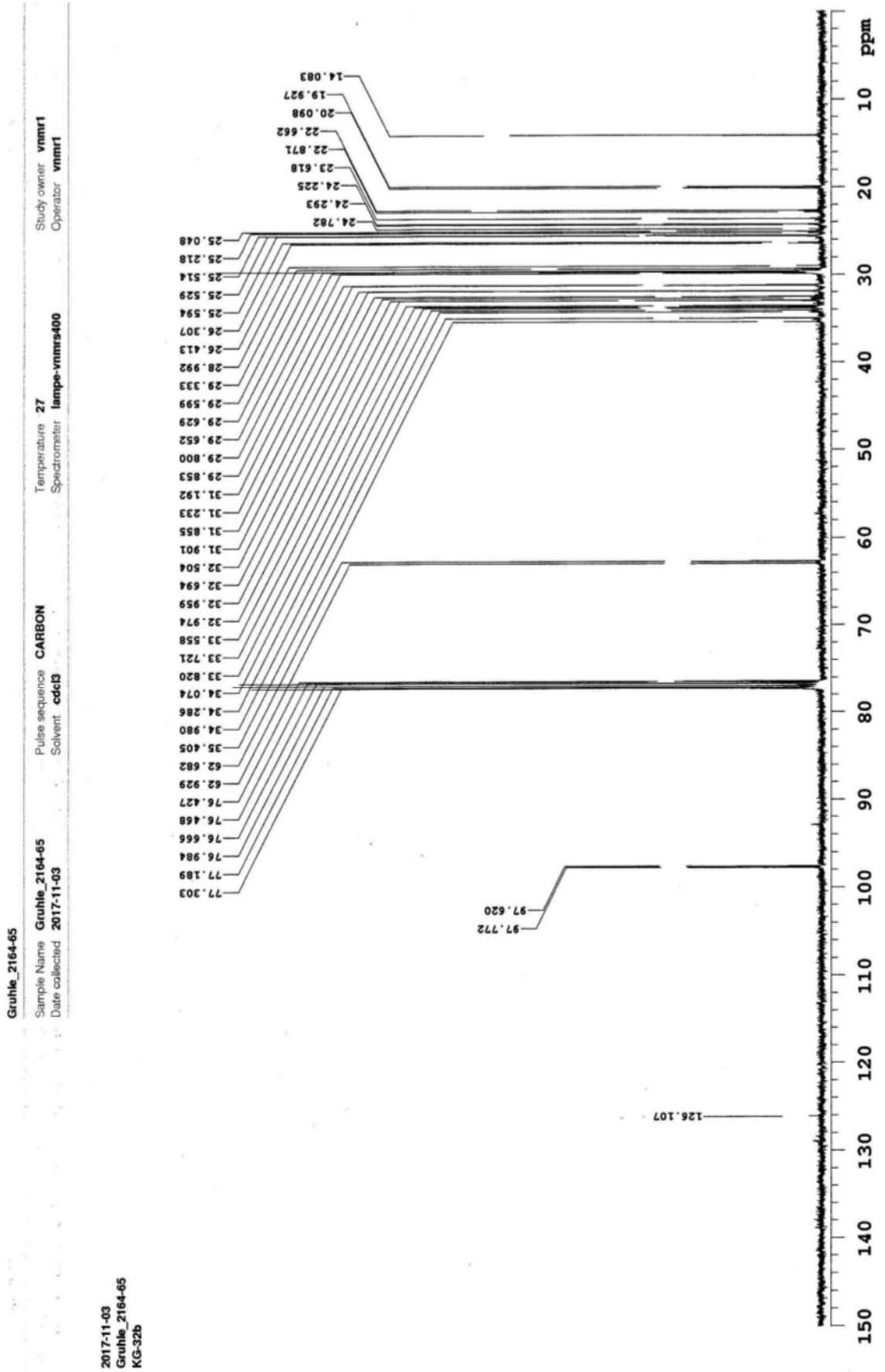
*Compound **5e** – ESI-MS (positive mode)*



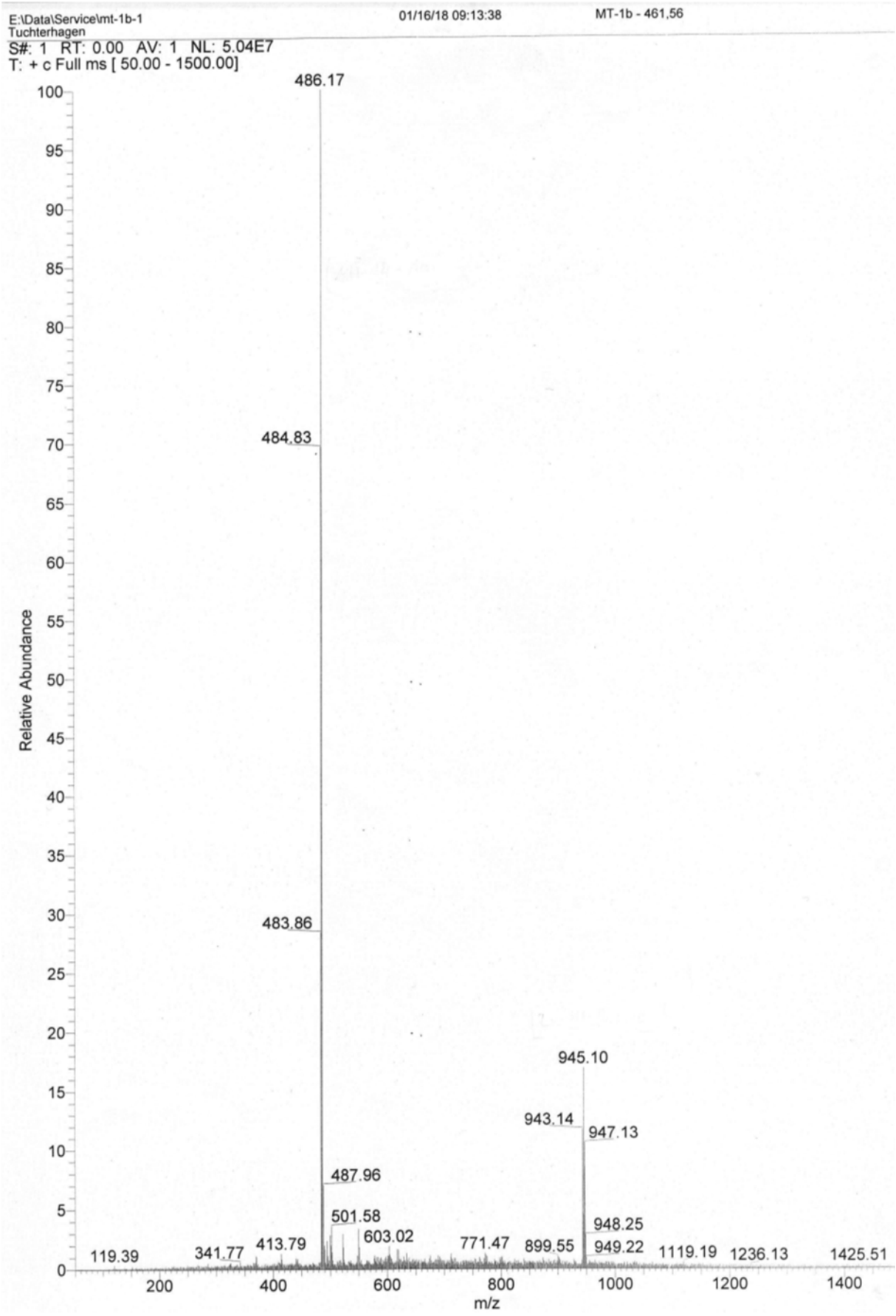
*Compound **5e** – ^{1}H NMR*



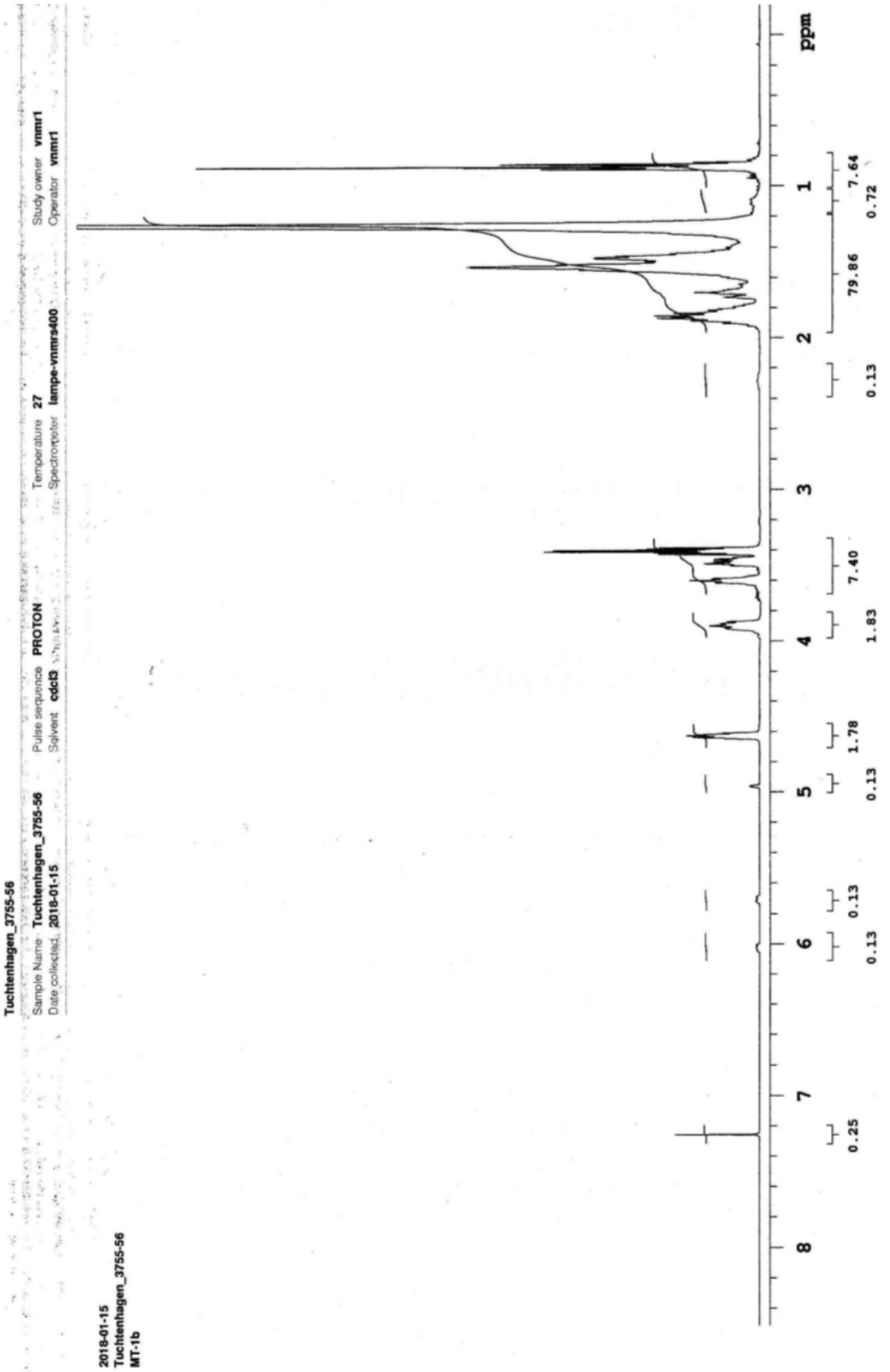
Compound ***5e*** *– ^{13}C NMR*



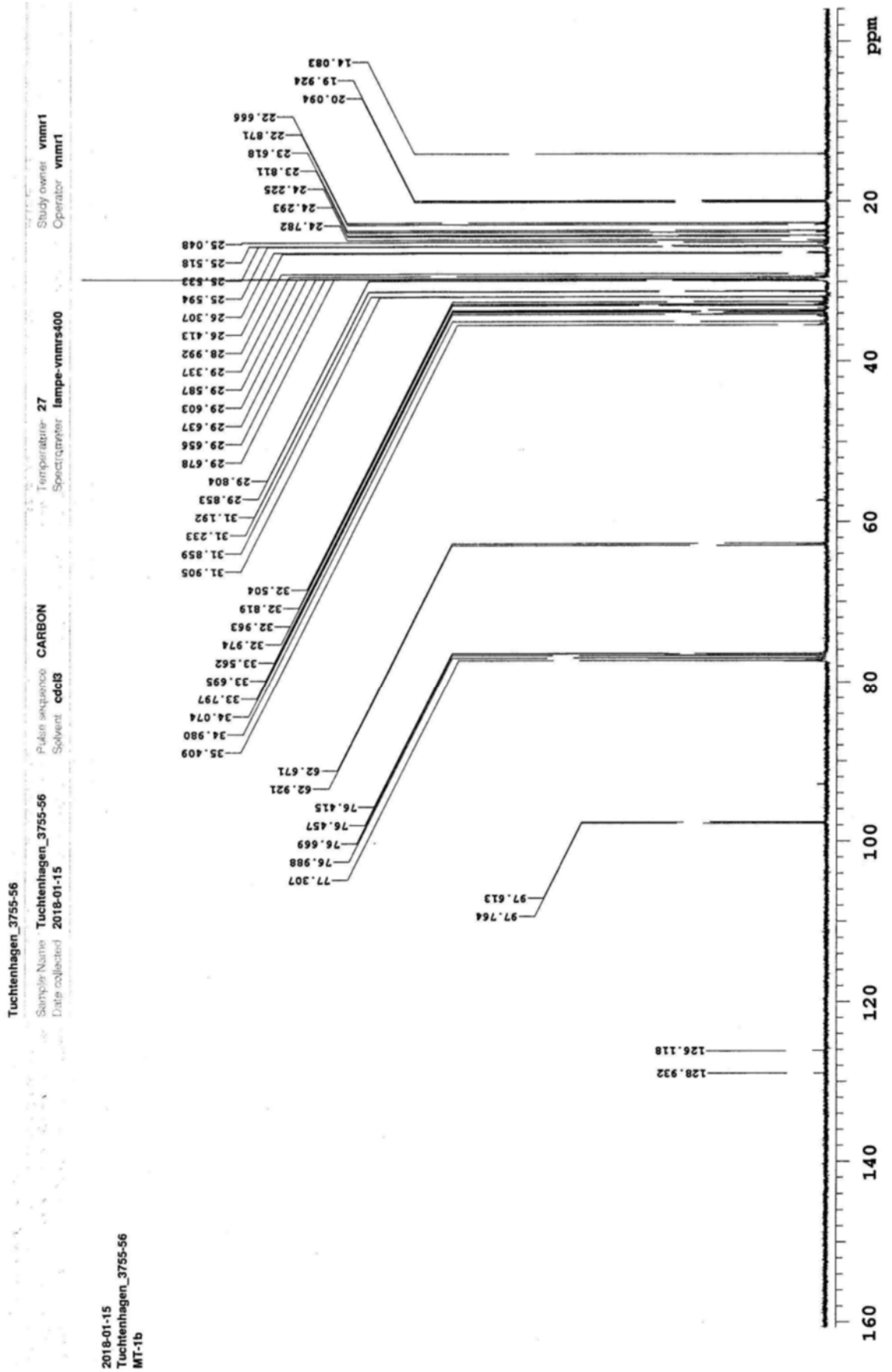
*Compound **5f** – ESI-MS (positive mode)*



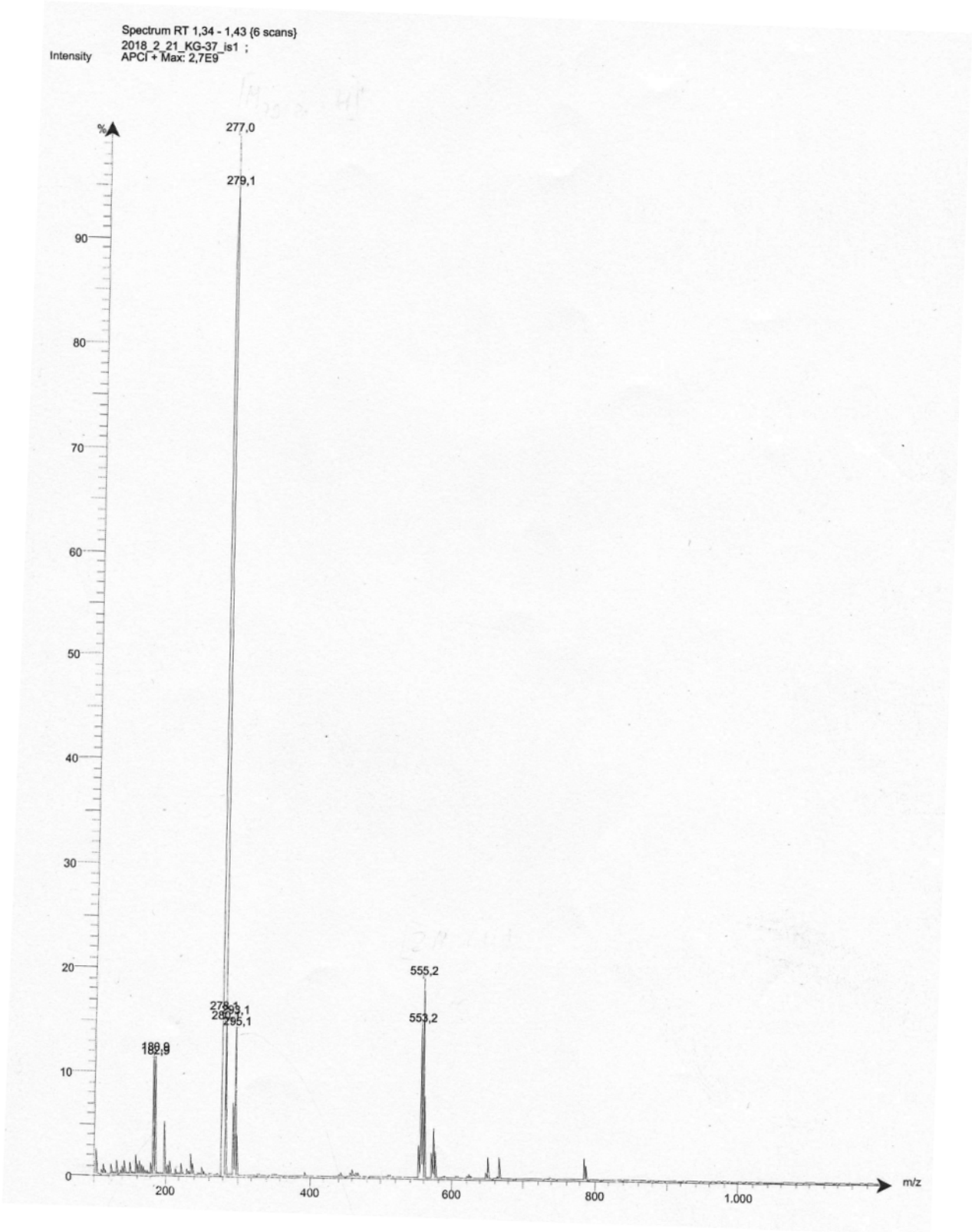
Compound ***5f*** *– ^{1}H NMR*



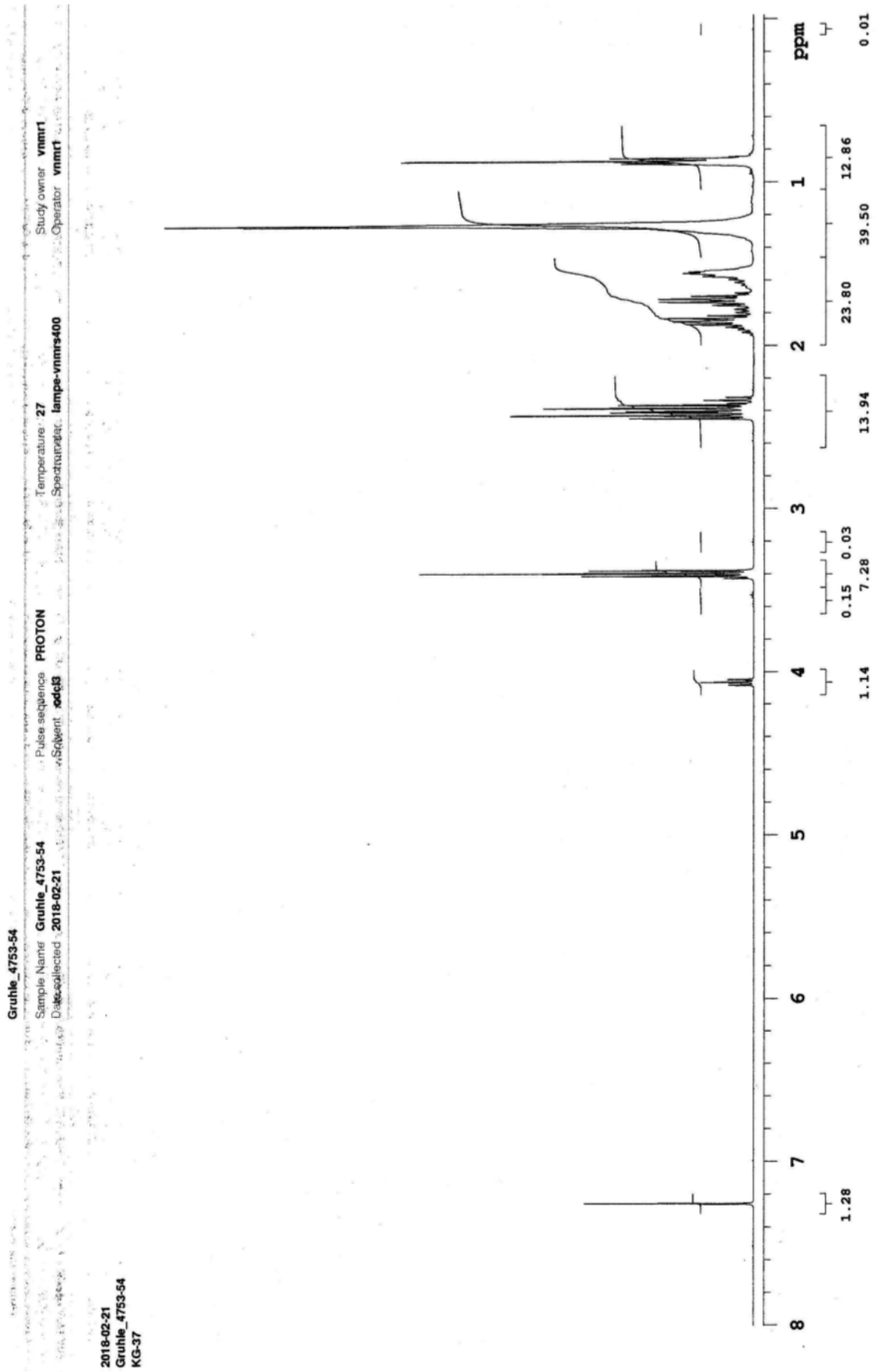
Compound ***5f*** *– ^{13}C NMR*



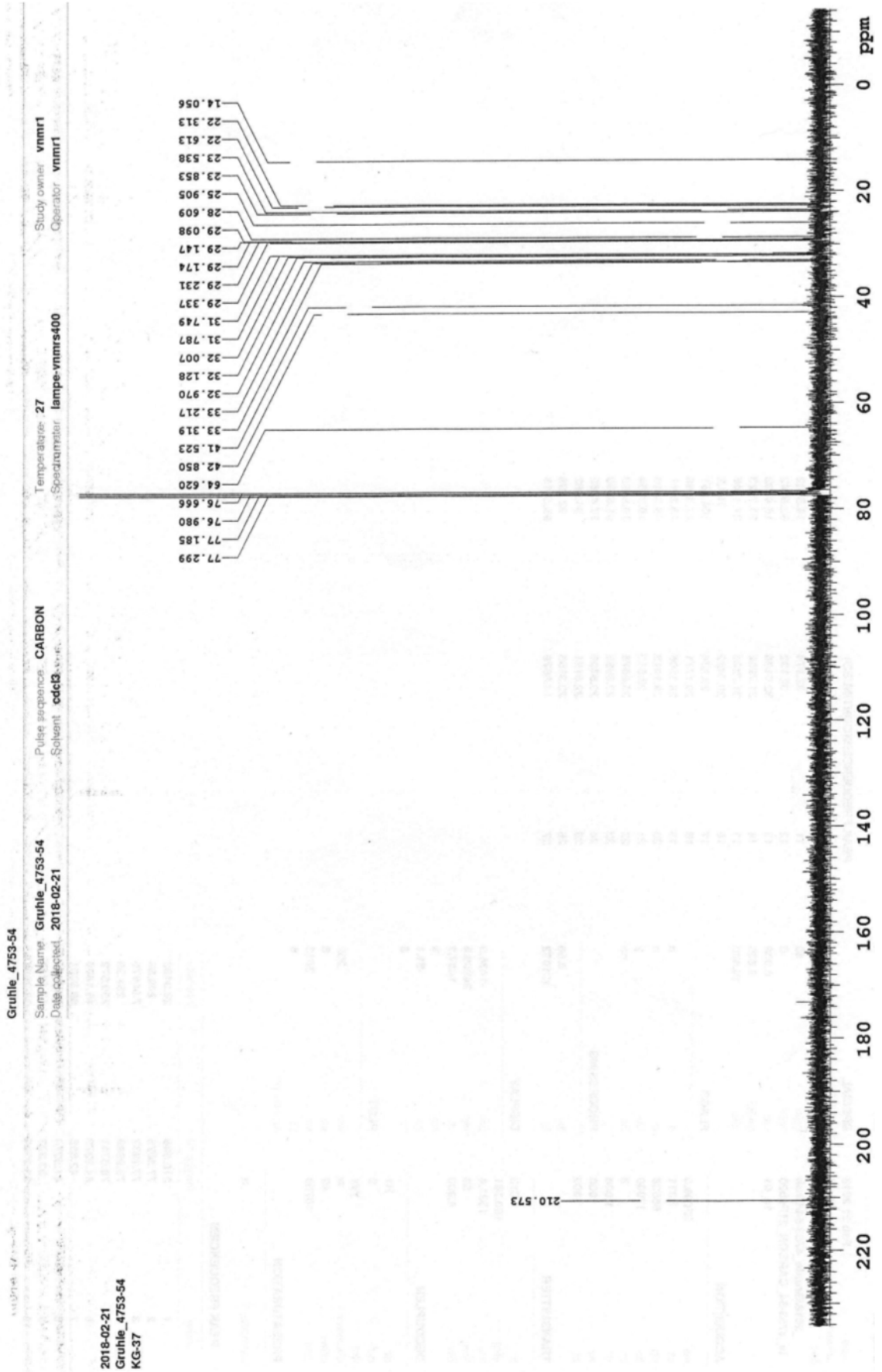
*Compound **8a** – APCI-MS (positive mode)*



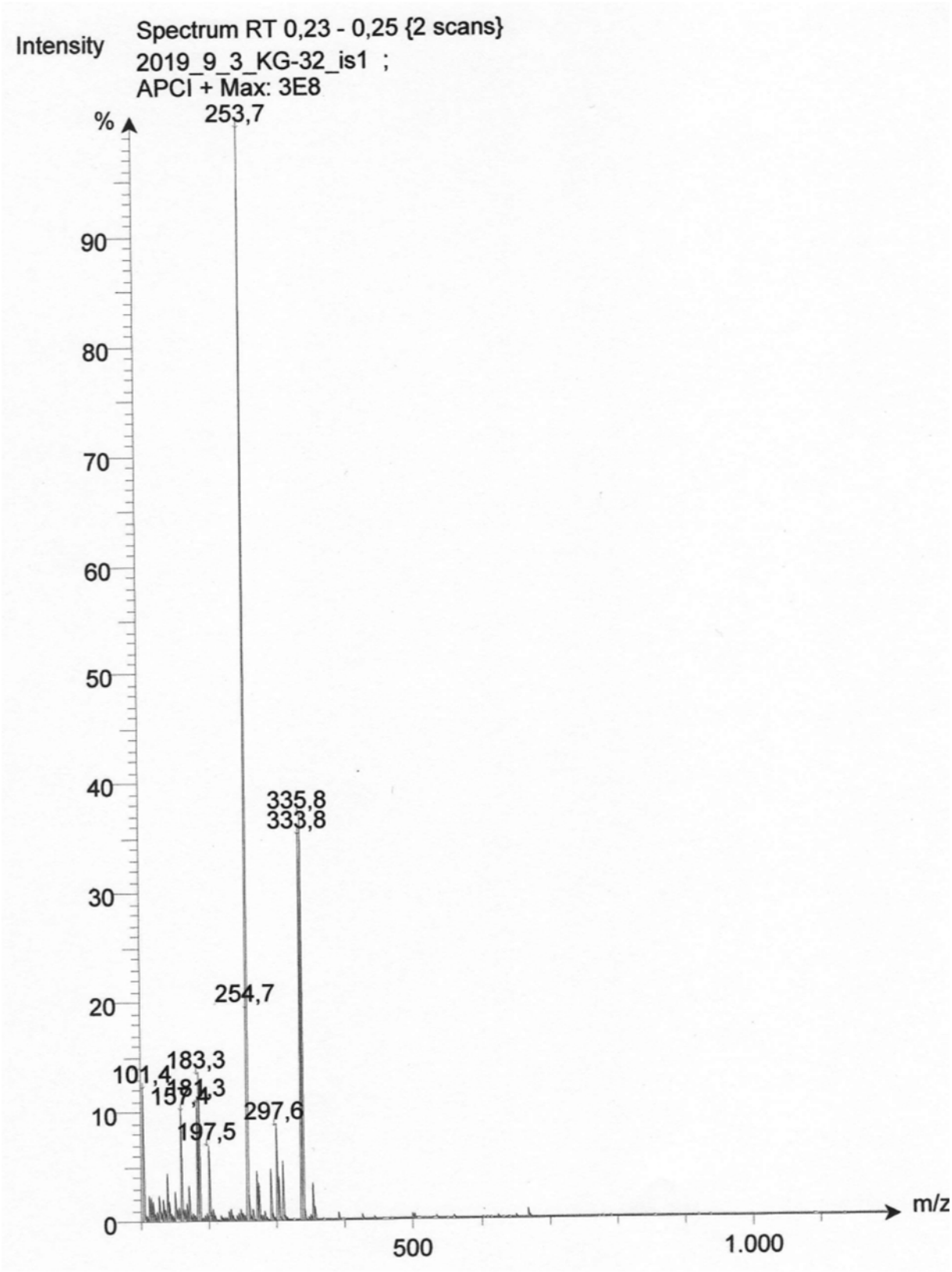
Compound ***8a*** *– ^{1}H NMR*



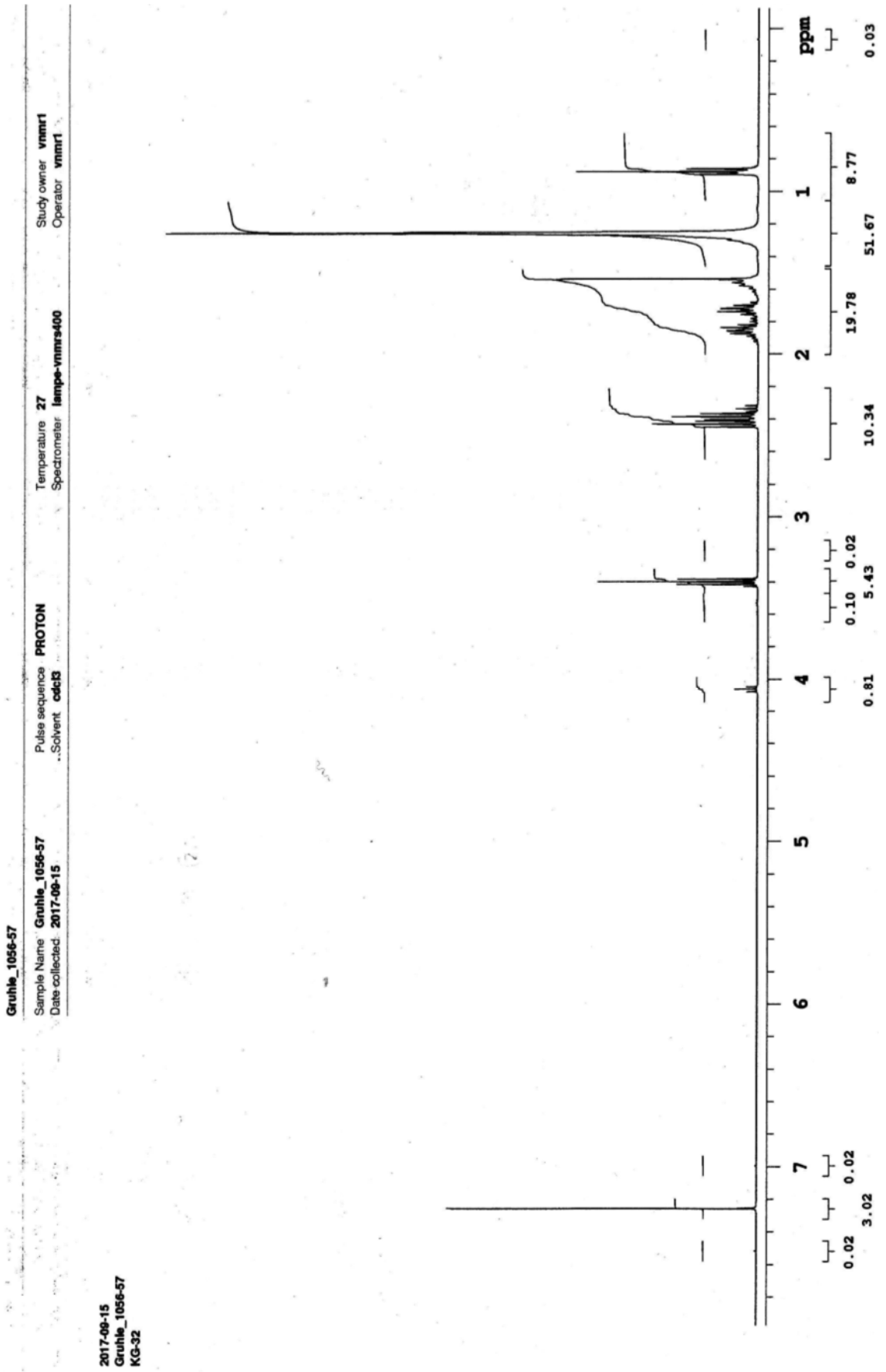
Compound ***8a*** *– ^{13}C NMR*



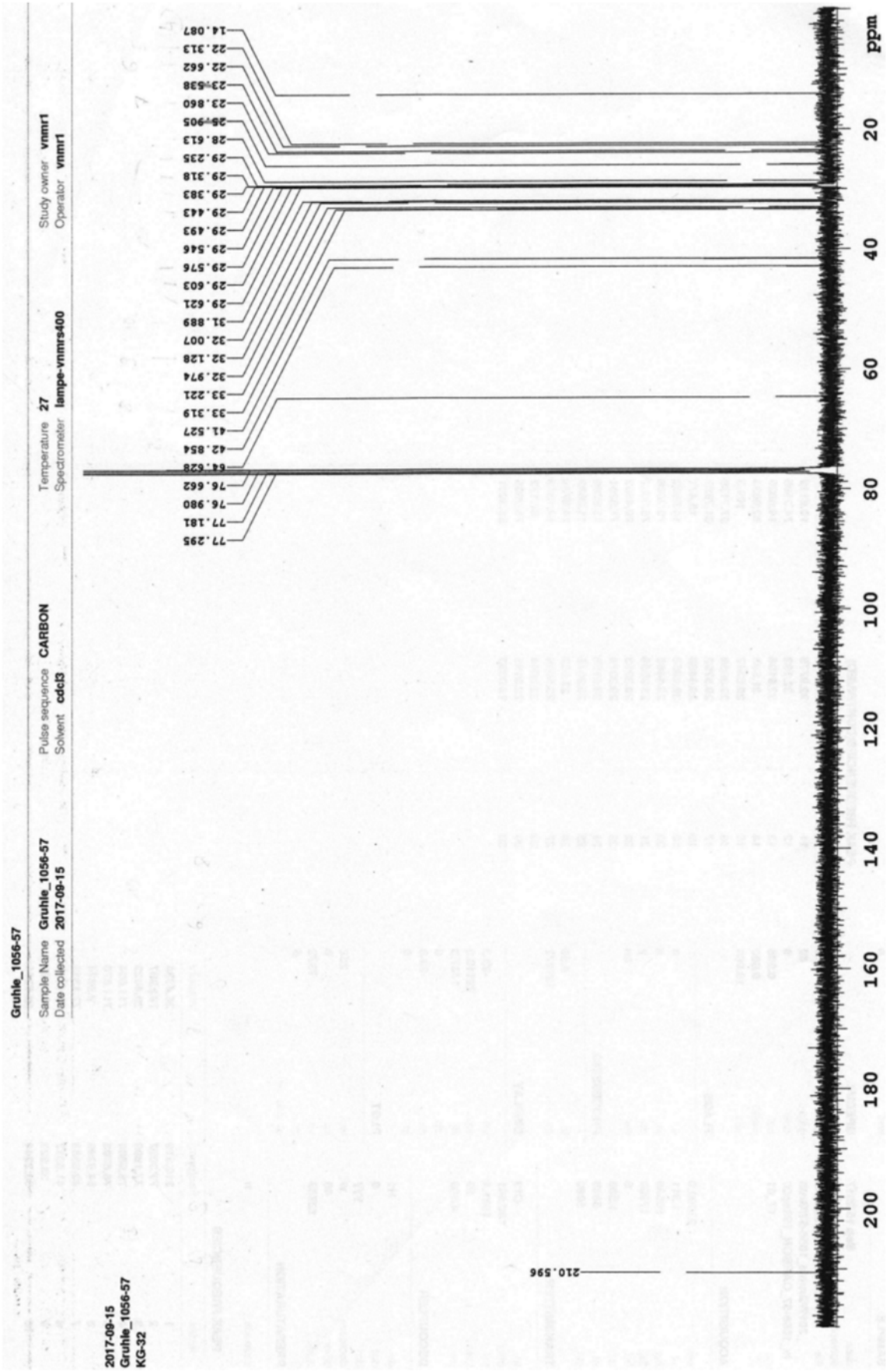
*Compound **8b** – APCI-MS (positive mode)*



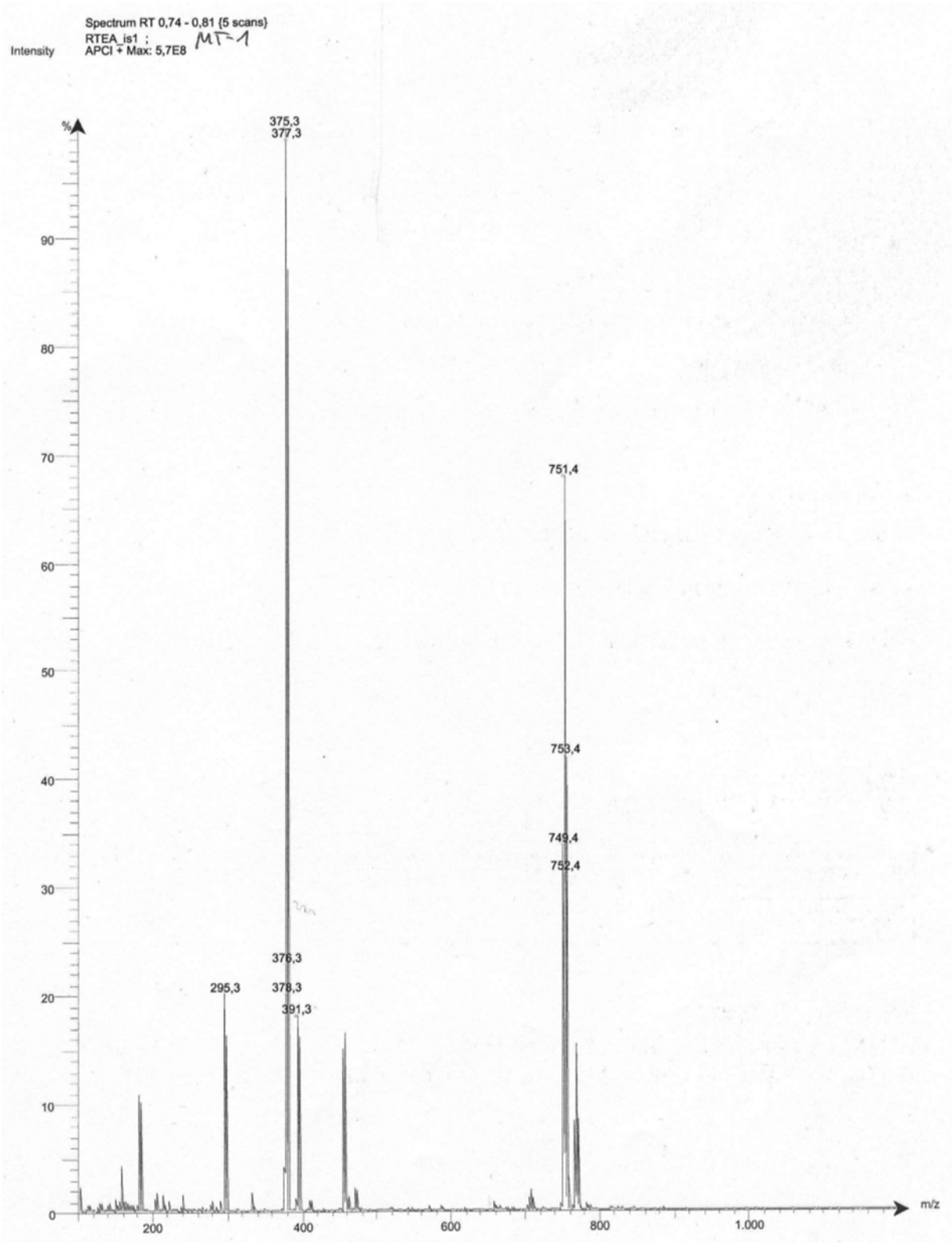
*Compound **8b** – ^{1}H NMR*



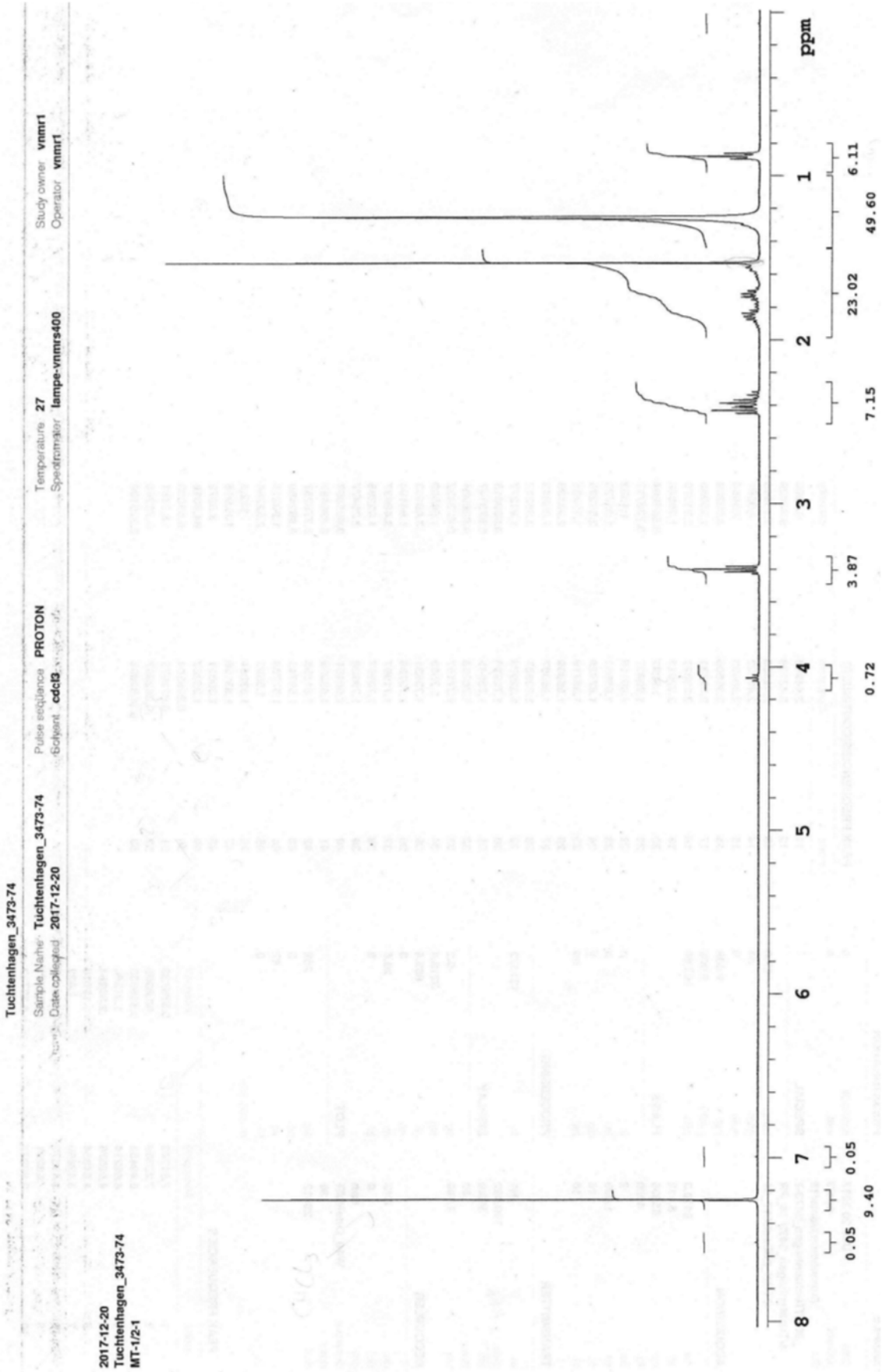
*Compound **8b** – ^{13}C NMR*



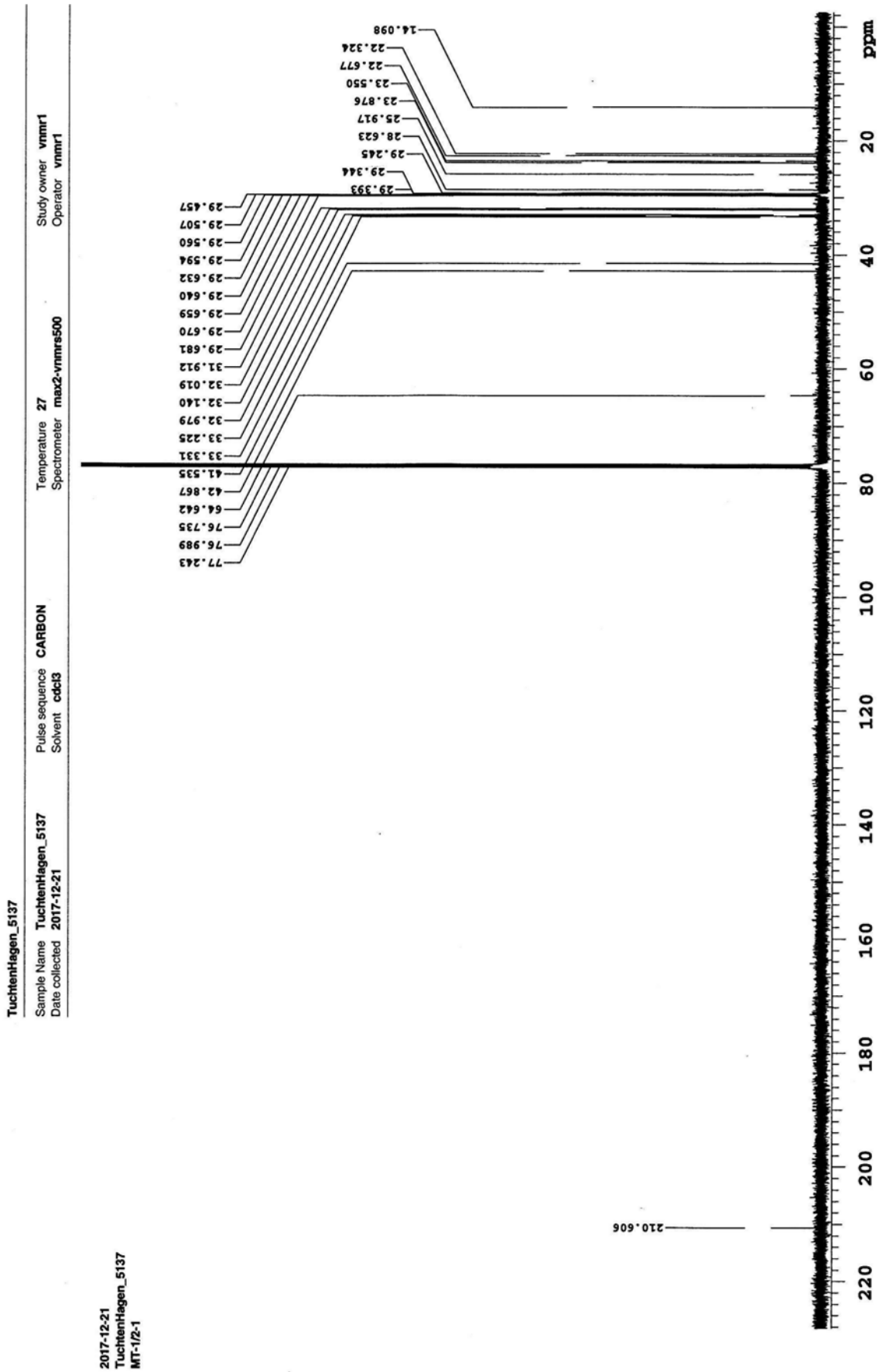
*Compound **8c** – APCI-MS (positive mode)*



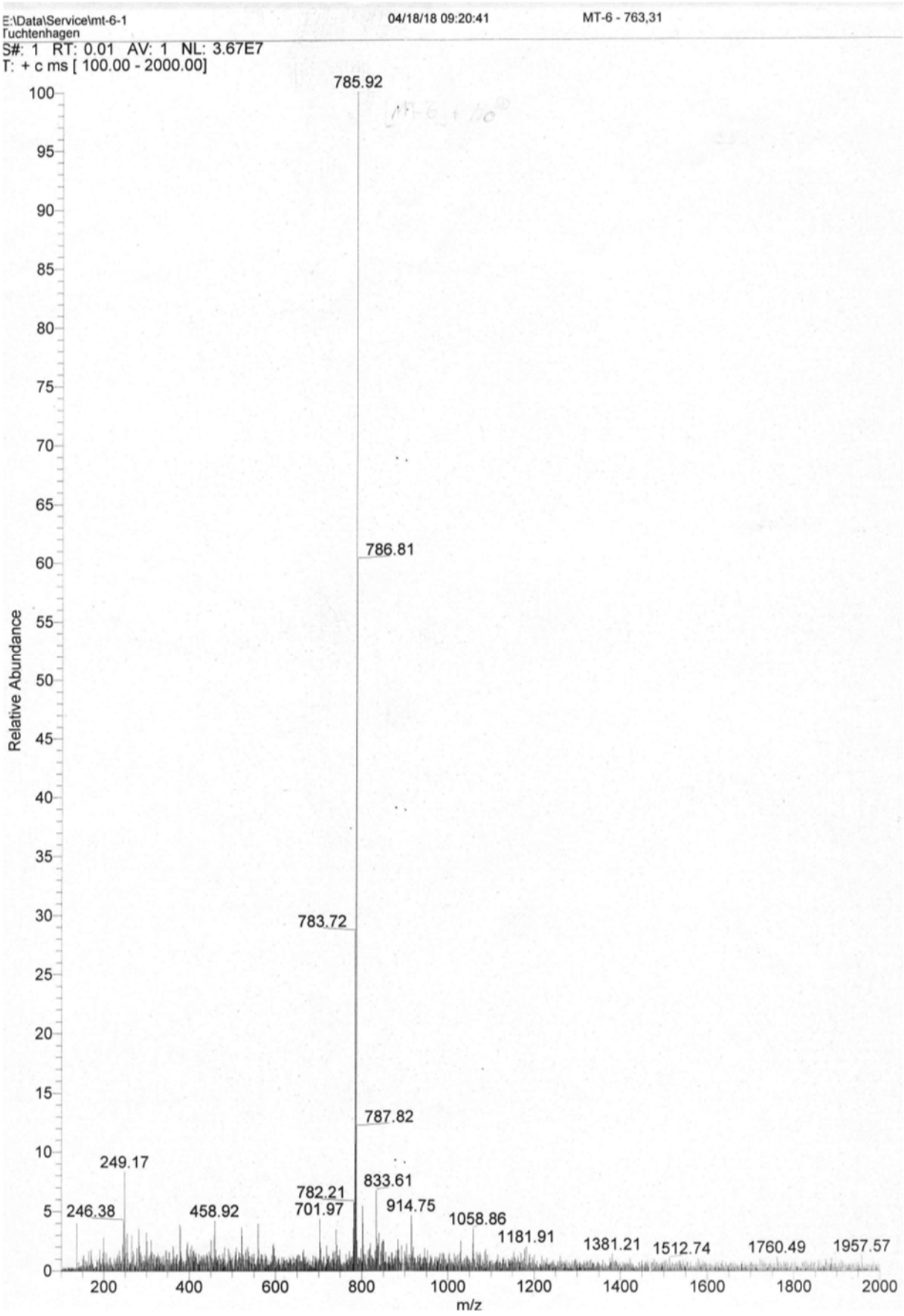
Compound ***8c*** *– ^{1}H NMR*



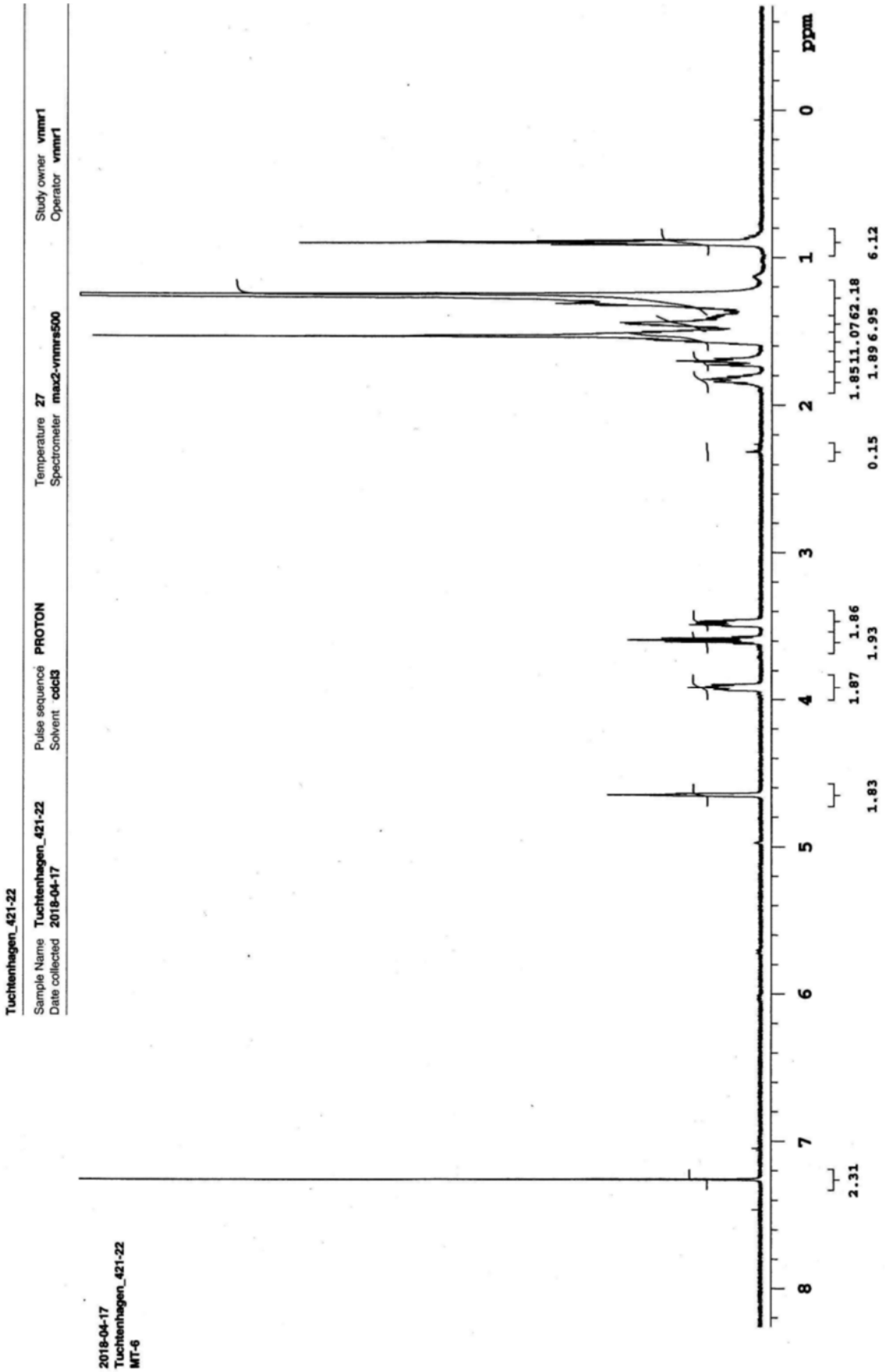
Compound ***8c*** *– ^{13}C NMR*



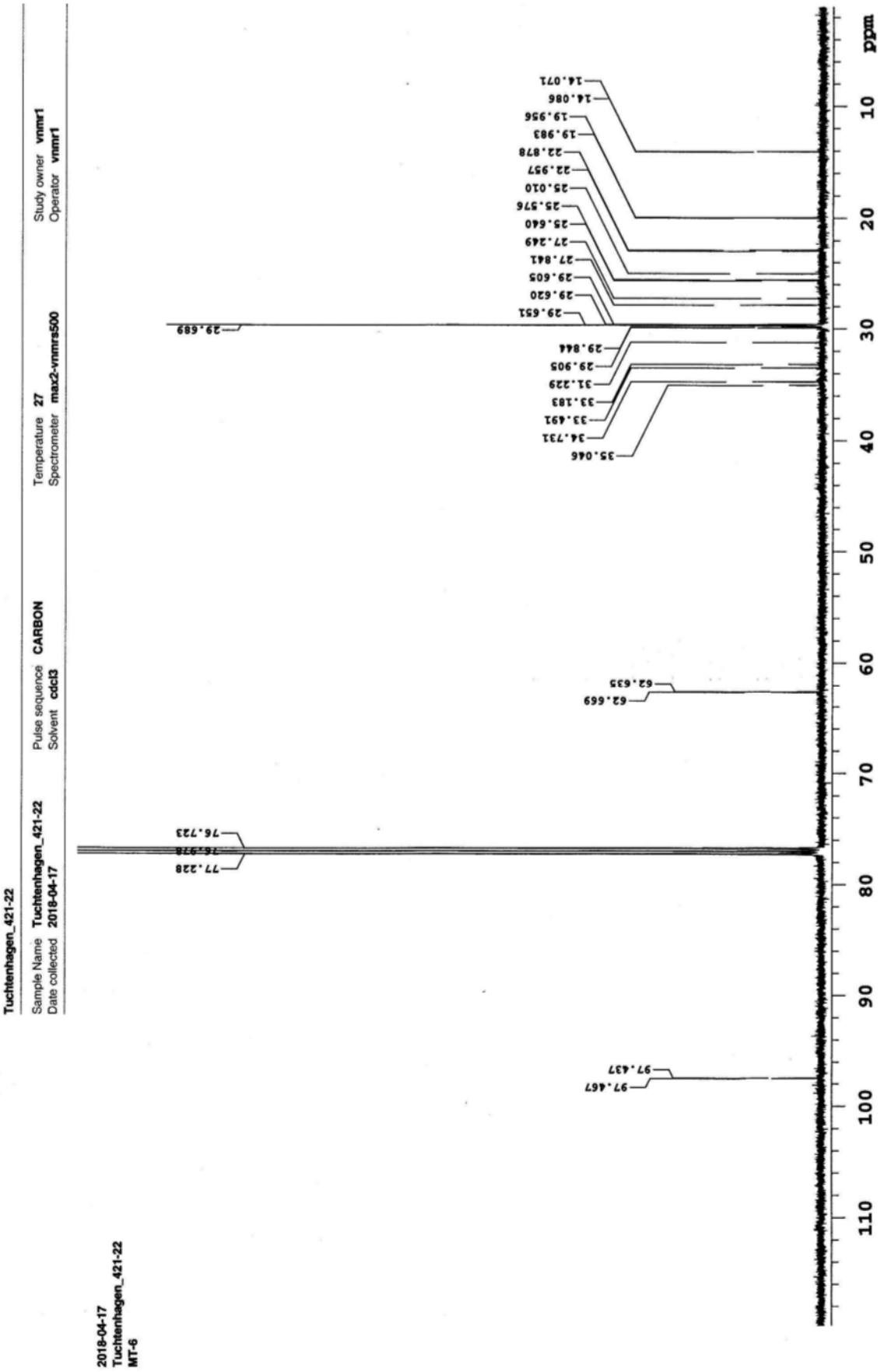
*Compound **9a** – ESI-MS (positive mode)*



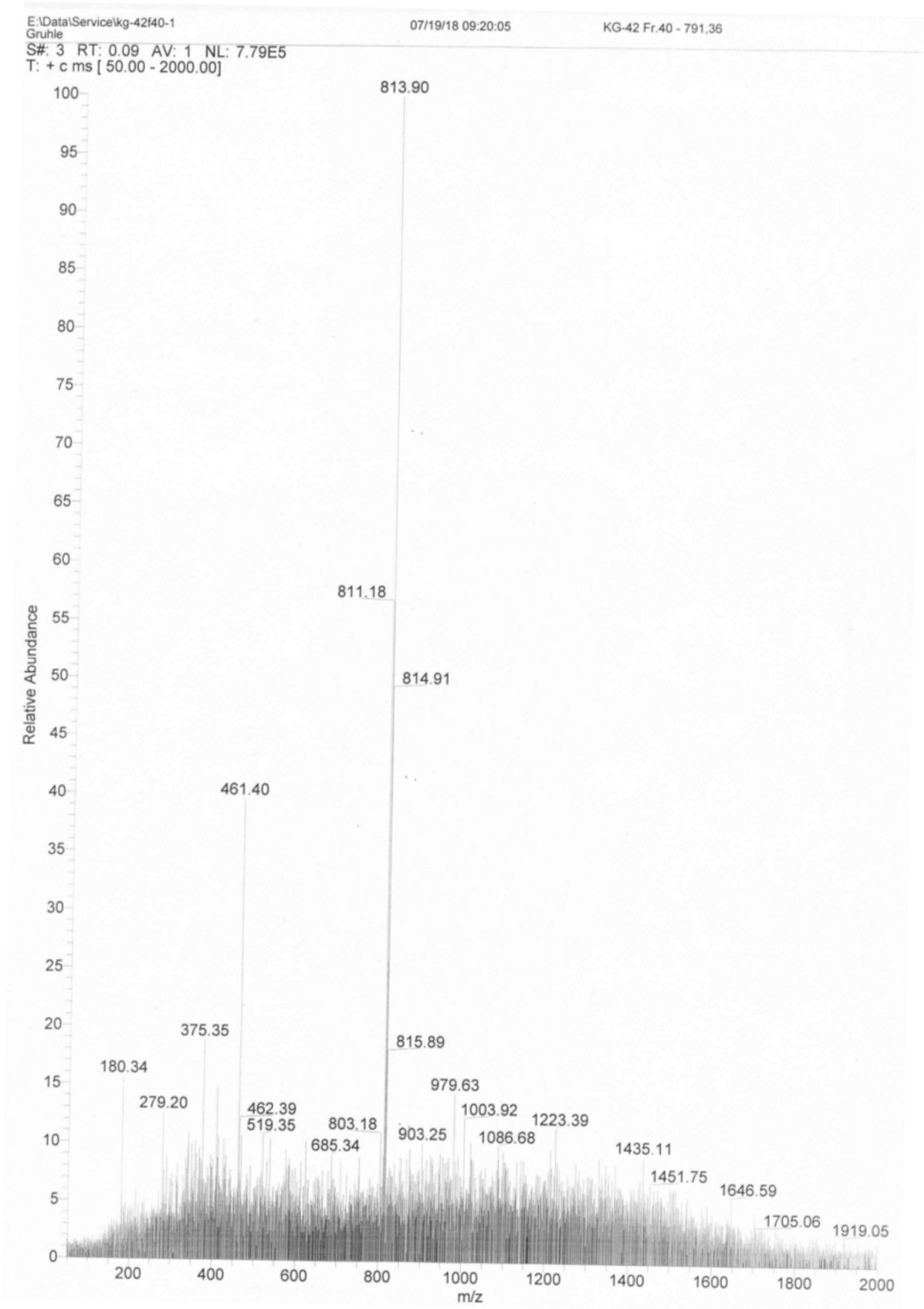
*Compound **9a** – ^{1}H NMR*



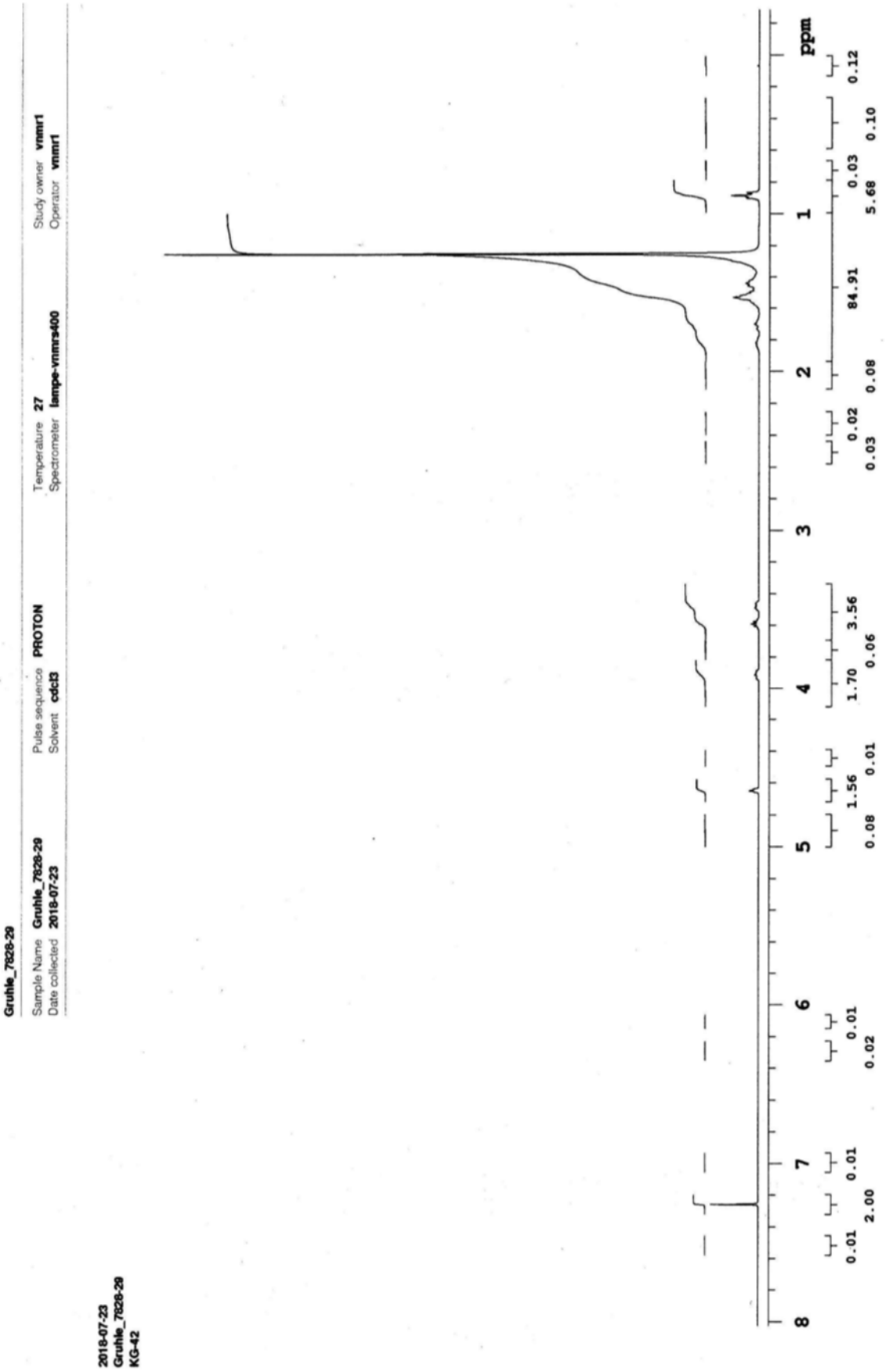
*Compound **9a** – ^{13}C NMR*



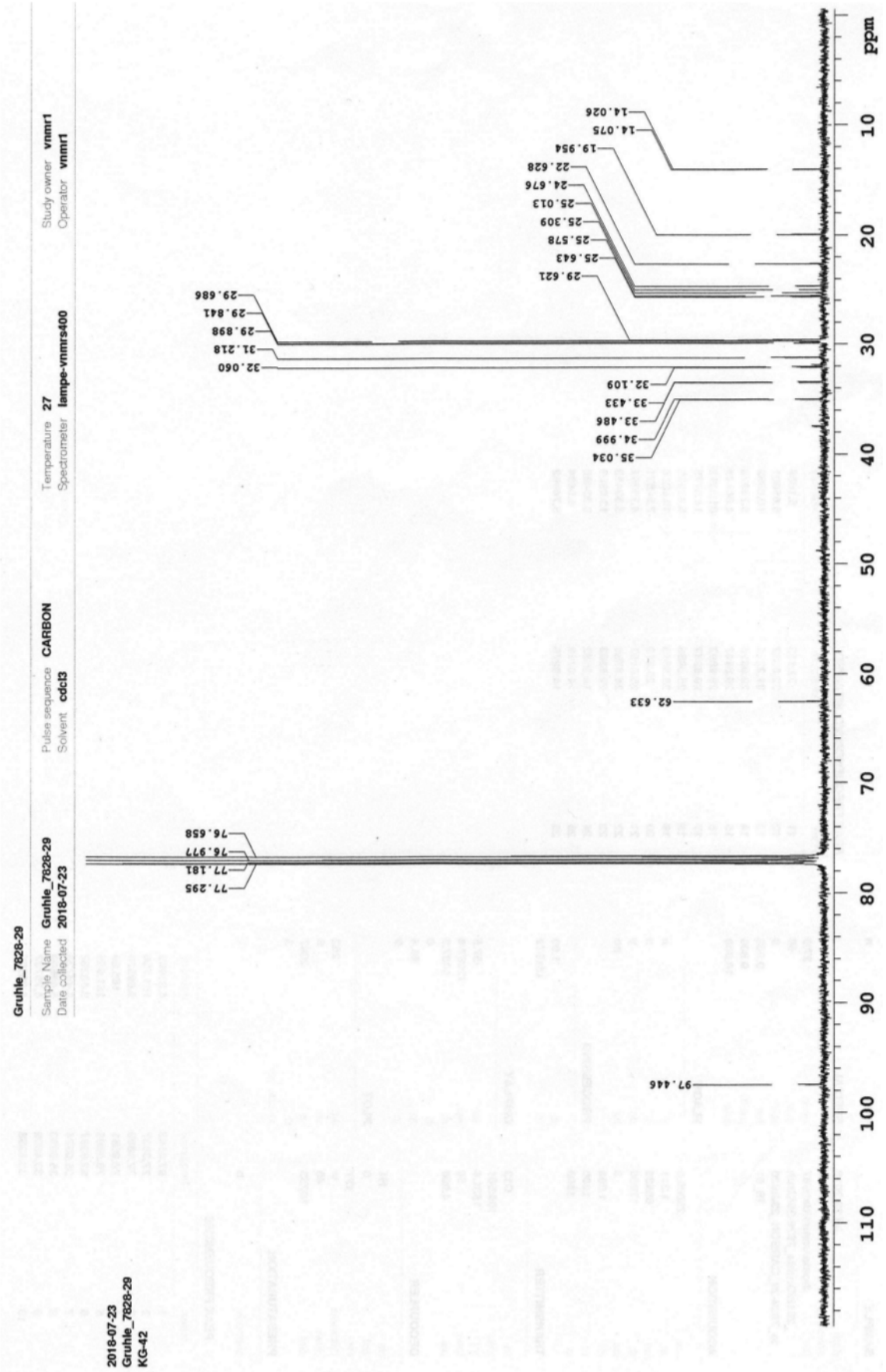
*Compound **9b** – ESI-MS (positive mode)*



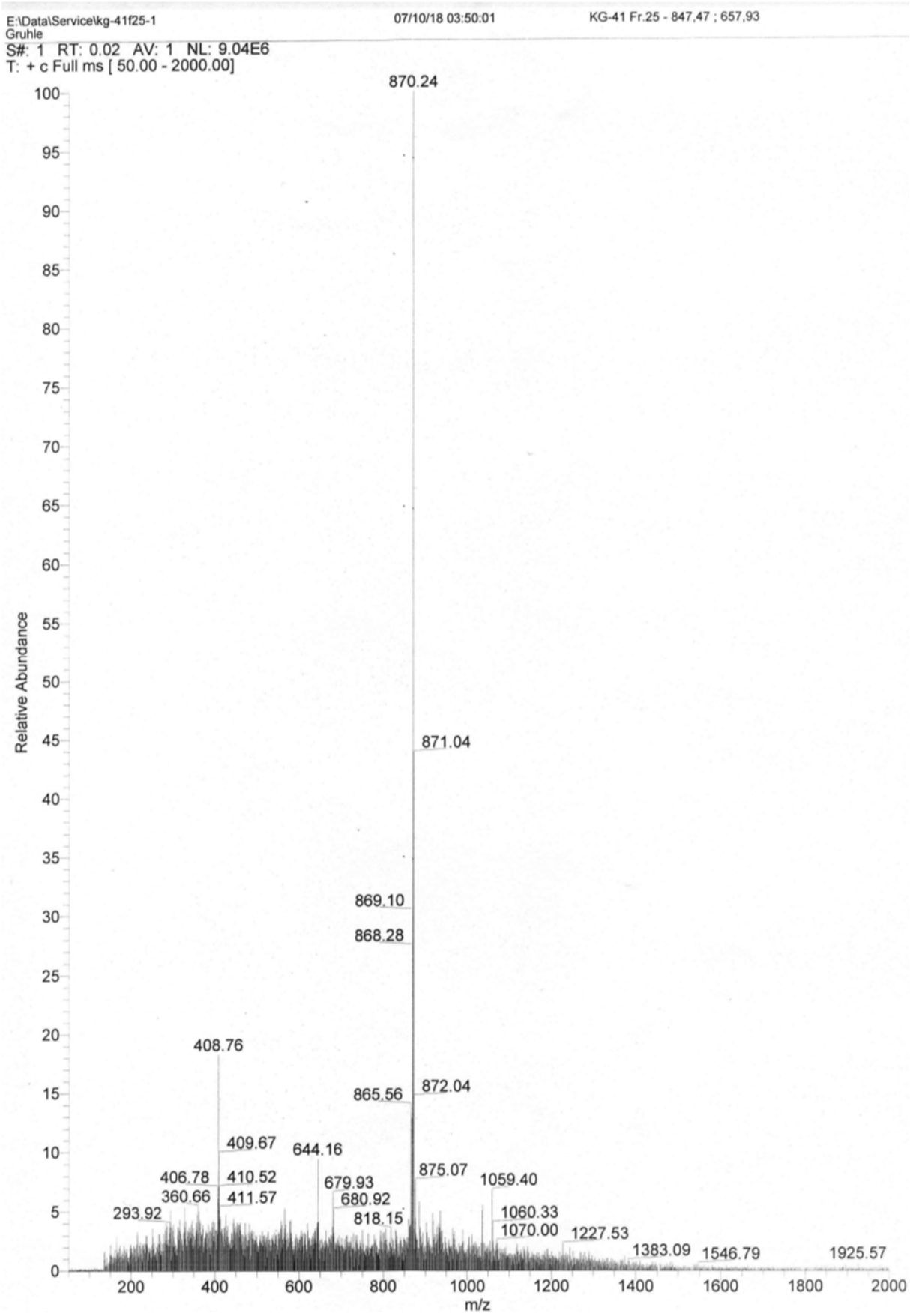
*Compound **9b** – ^{1}H NMR*



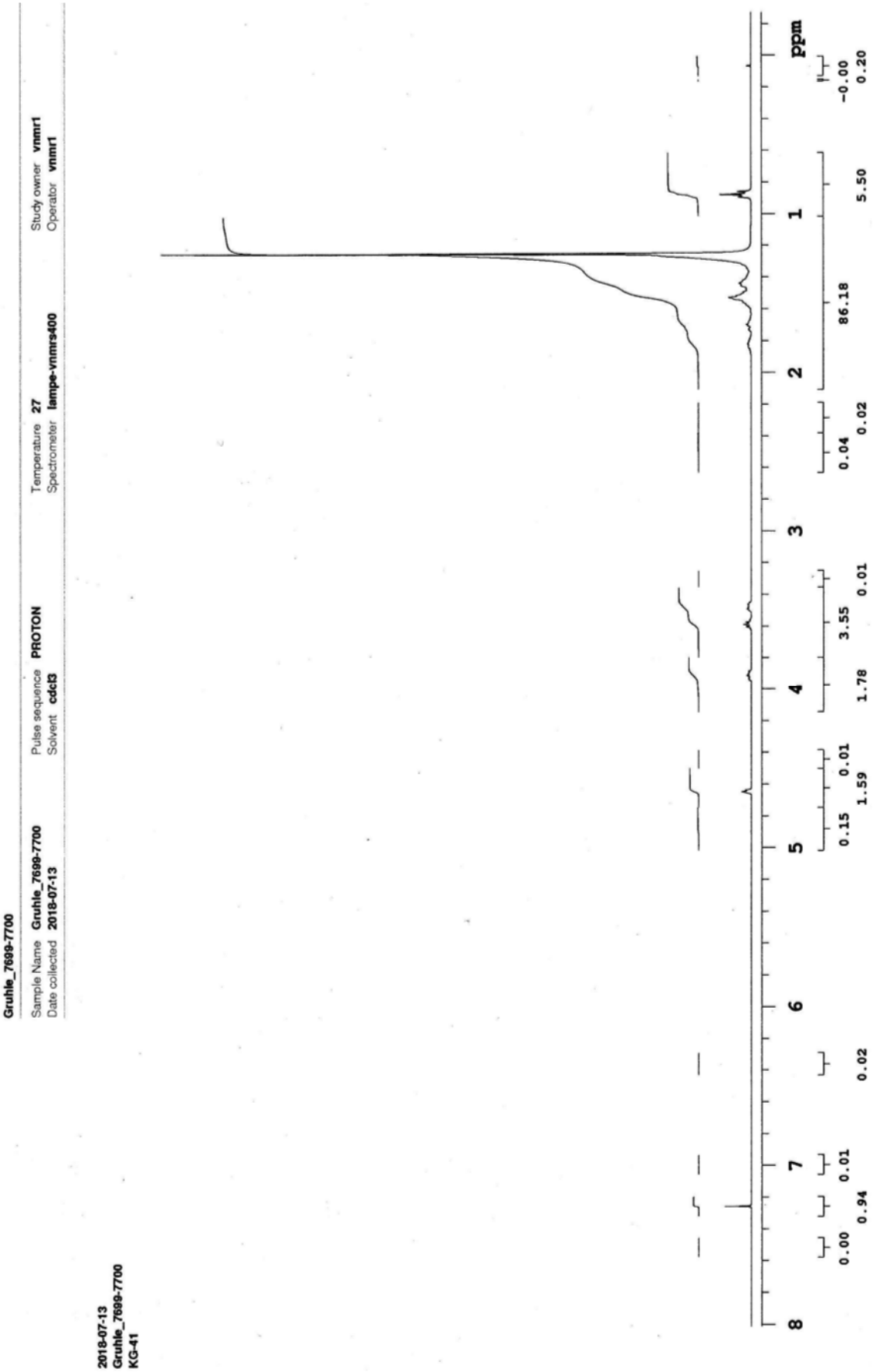
*Compound **9b** – ^{13}C NMR*



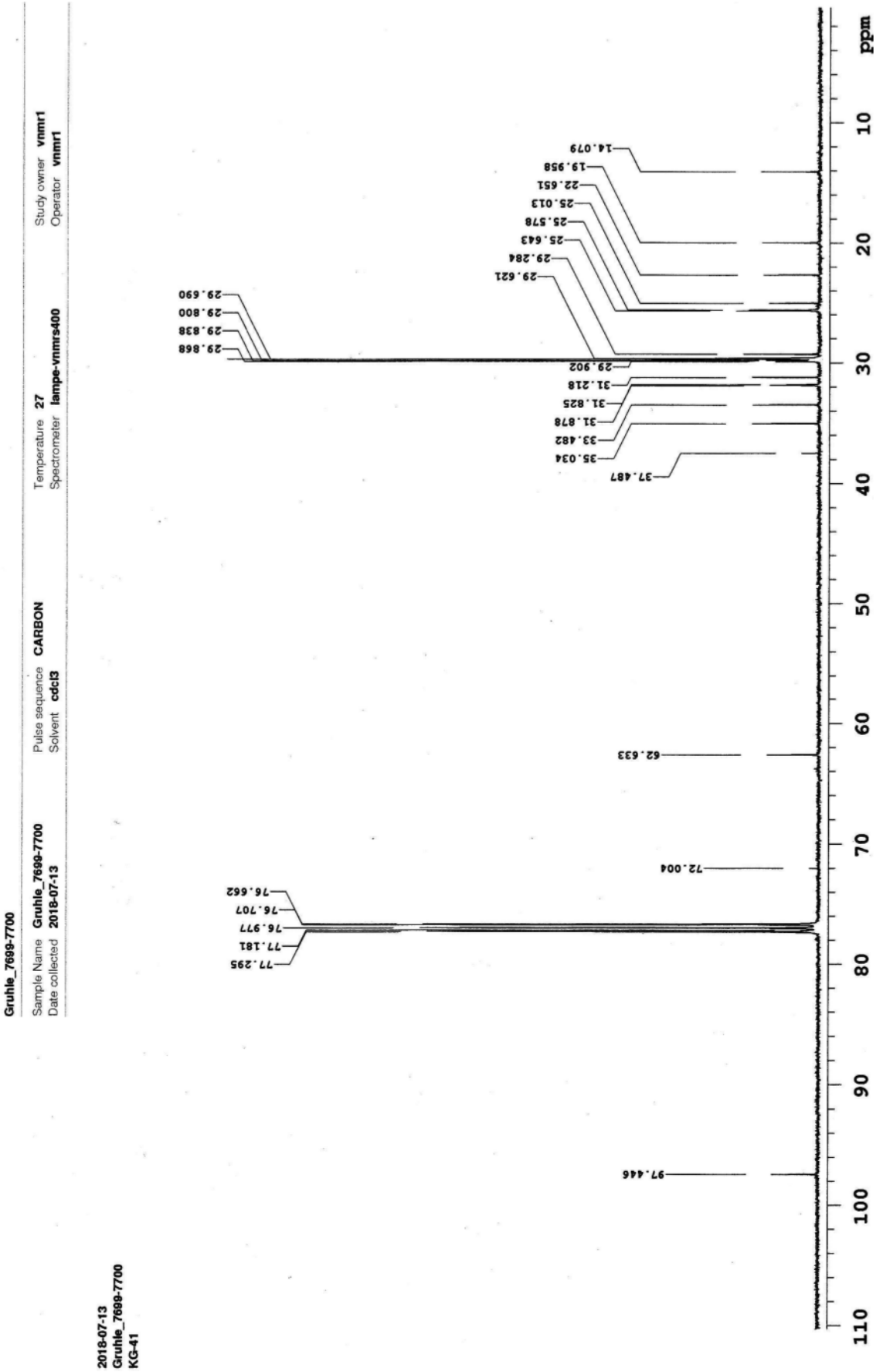
*Compound **9c** – ESI-MS (positive mode)*



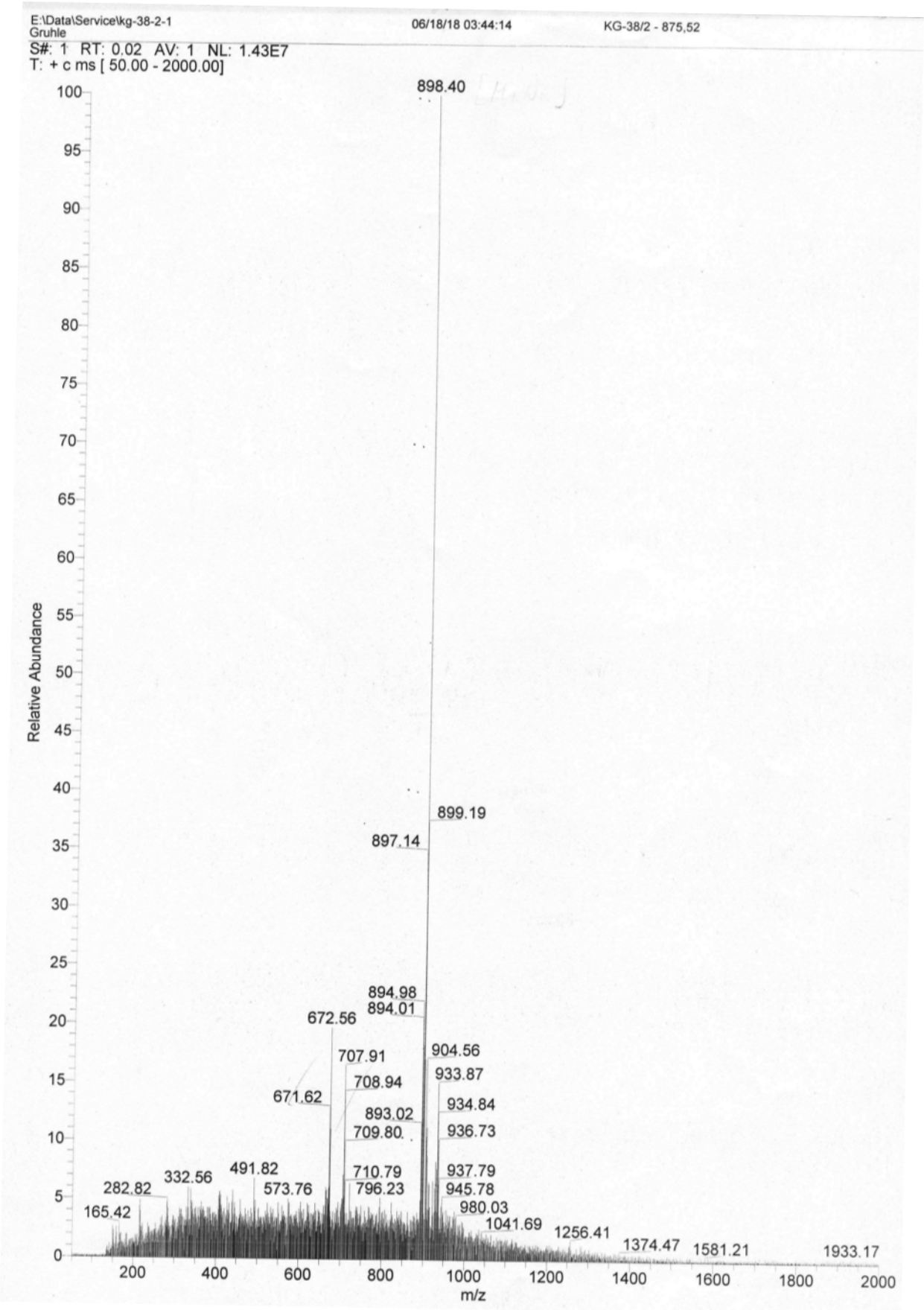
Compound ***9c*** *– ^{1}H NMR*



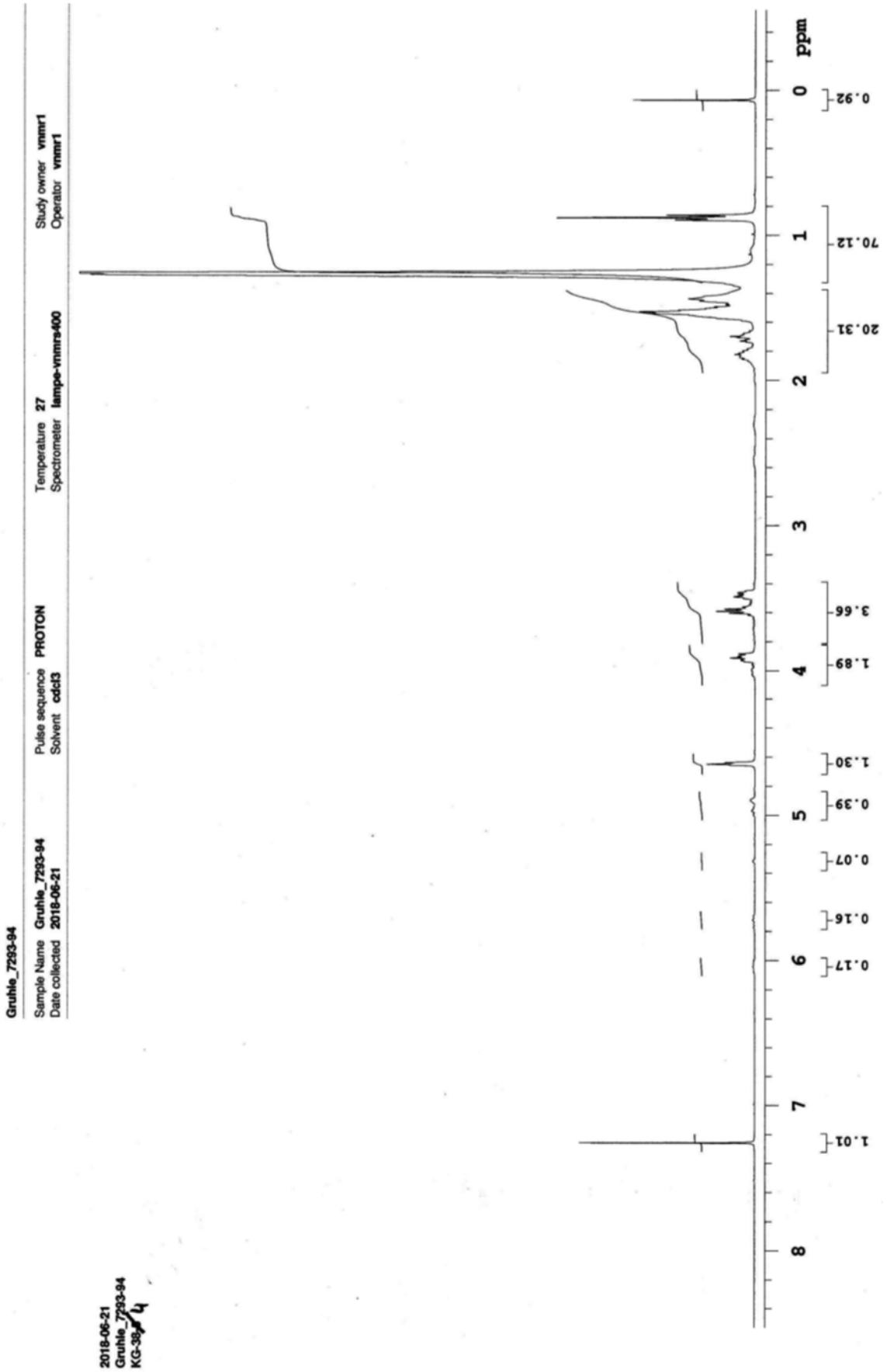
*Compound **9c** – ^{13}C NMR*



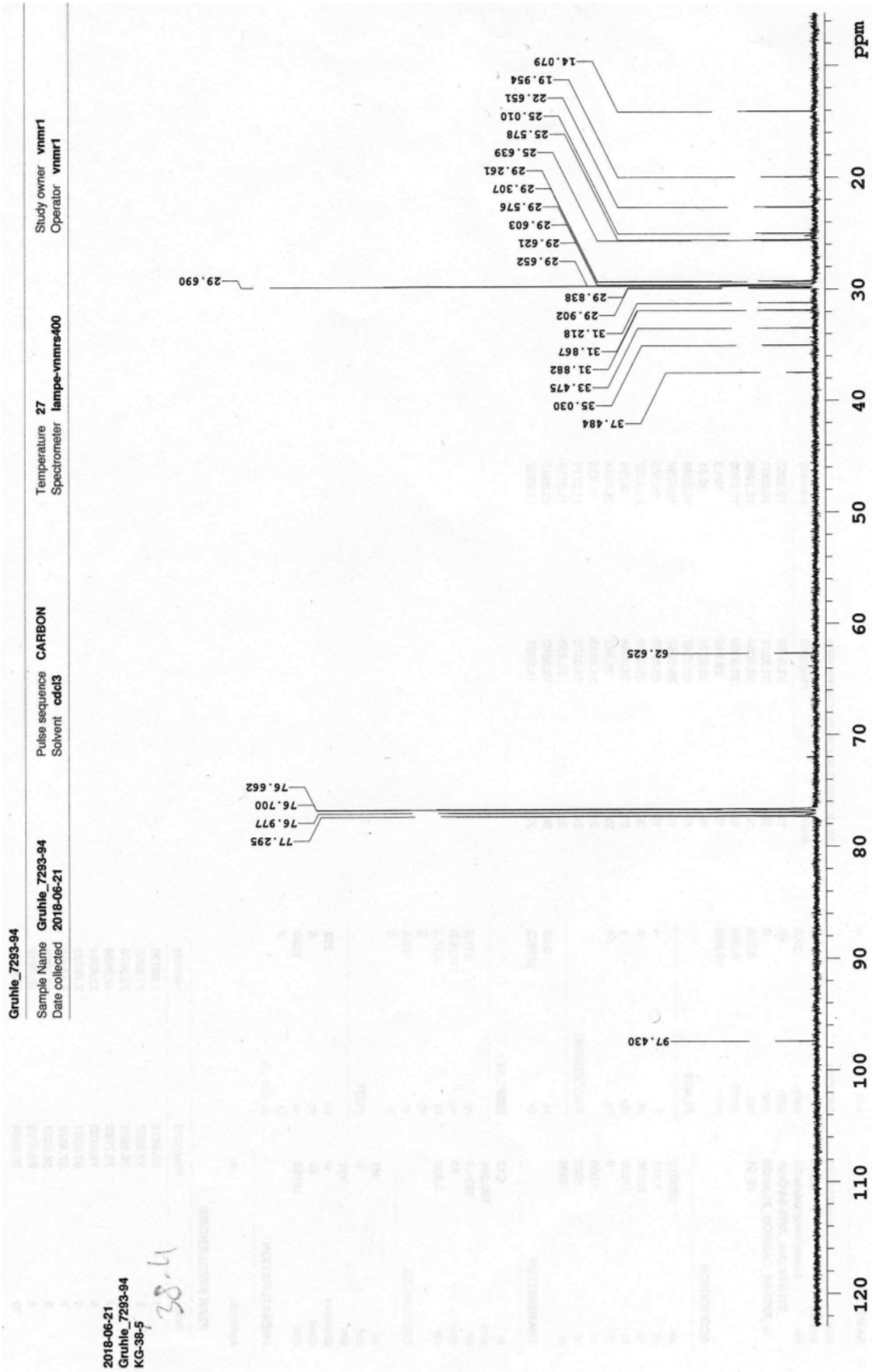
*Compound **9d** – ESI-MS (positive mode)*



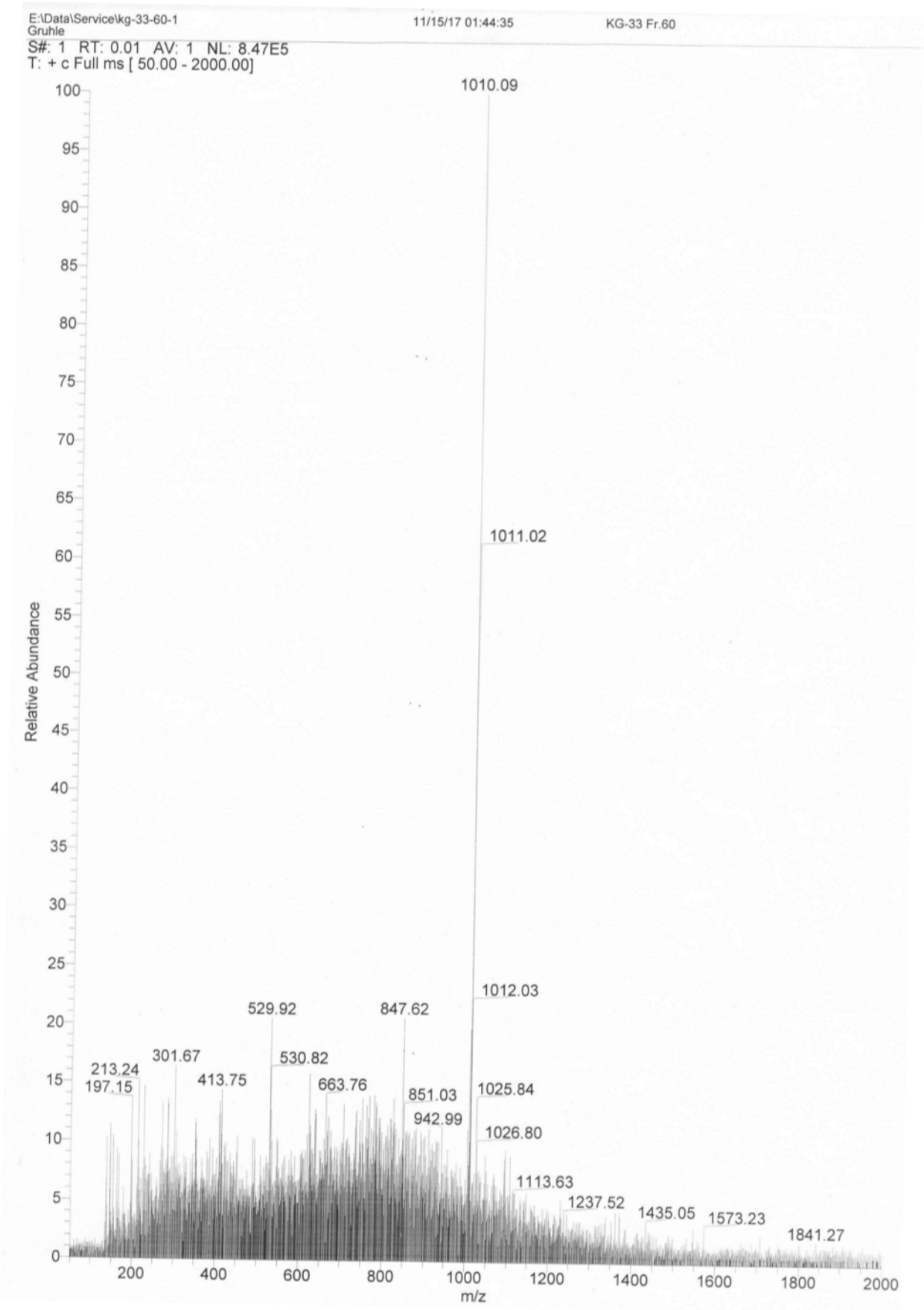
*Compound **9d** – ^{1}H NMR*



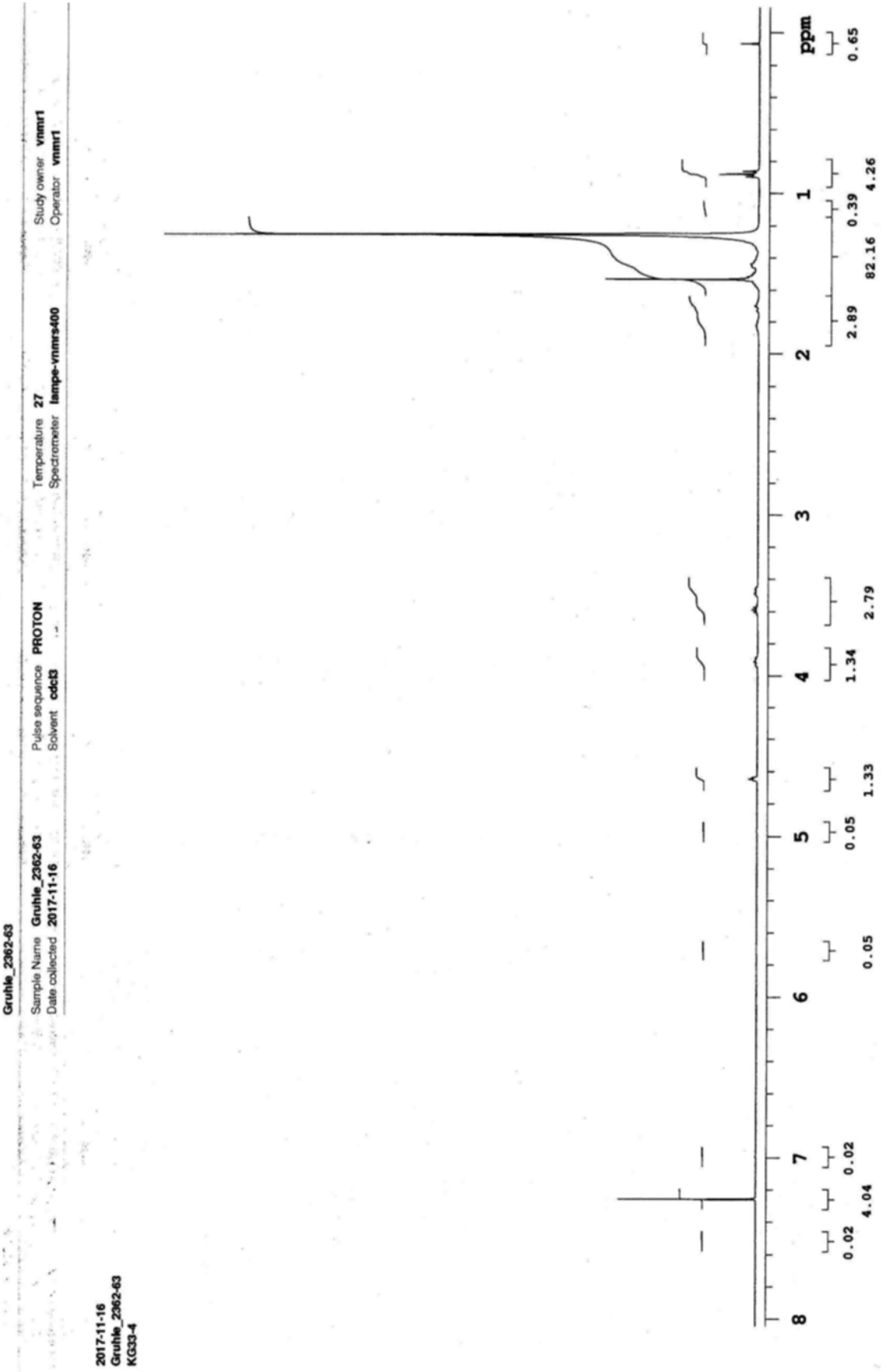
*Compound **9d** – ^{13}C NMR*



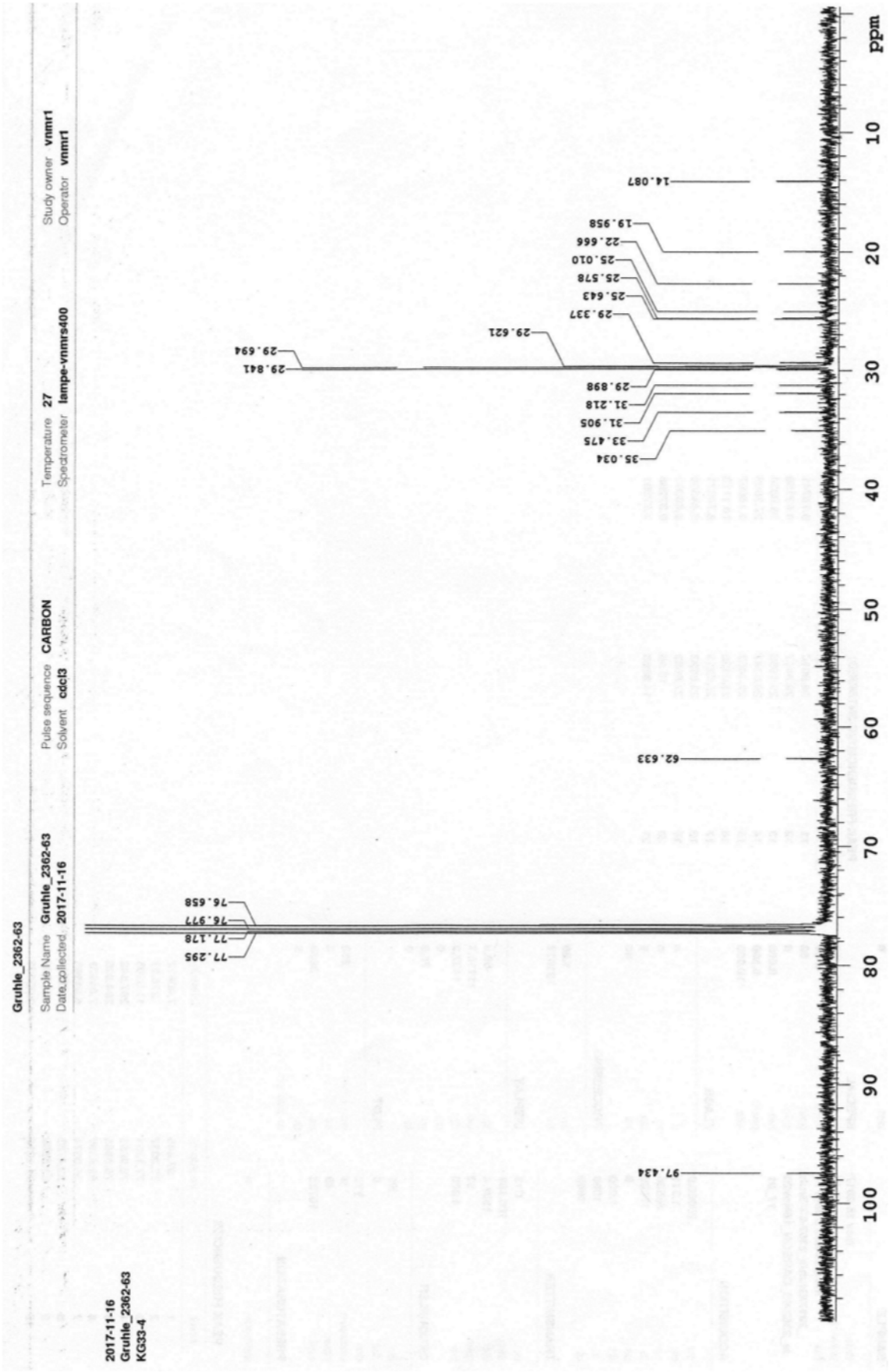
*Compound **9e** – ESI-MS (positive mode)*



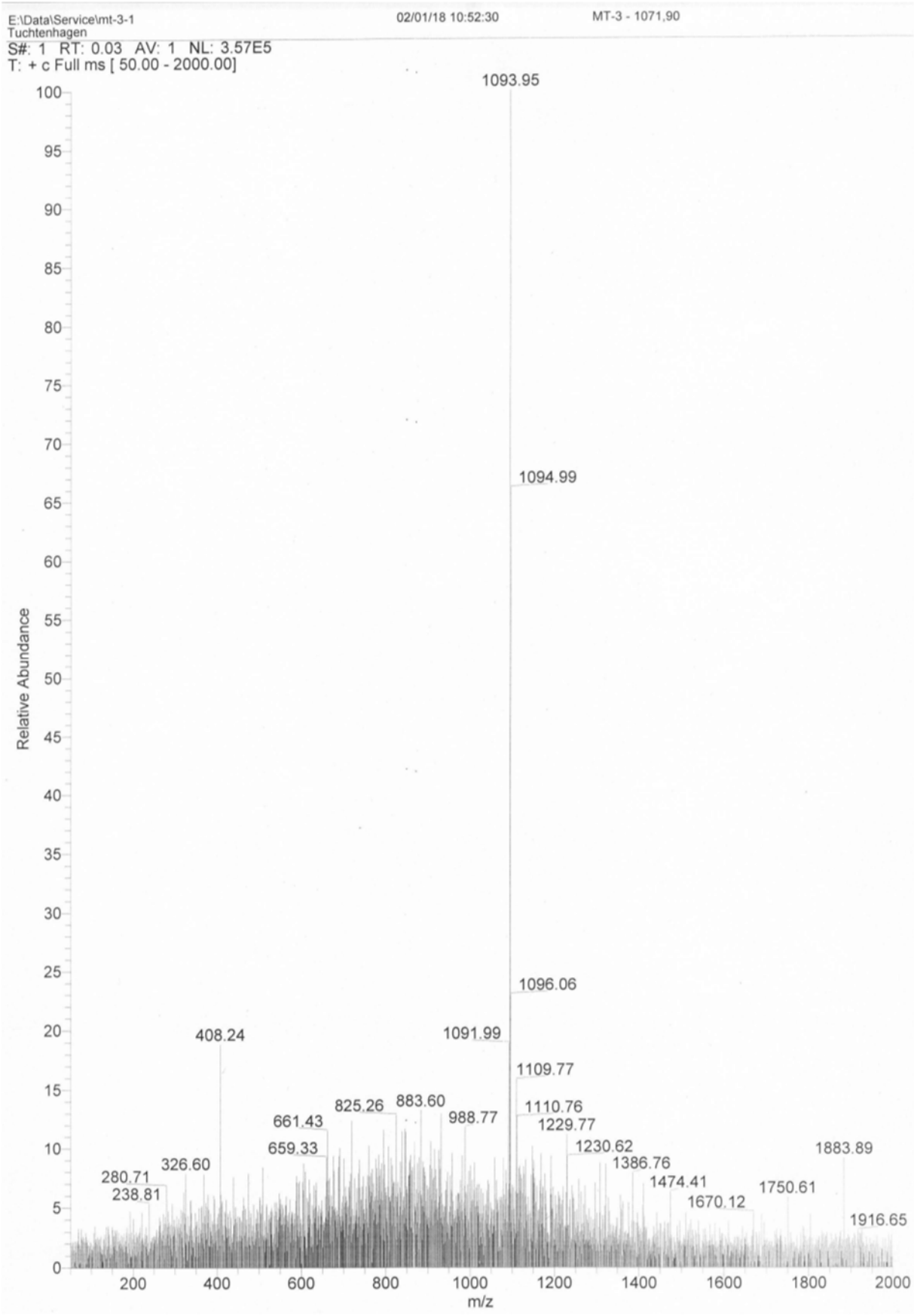
*Compound **9e** – ^{1}H NMR*



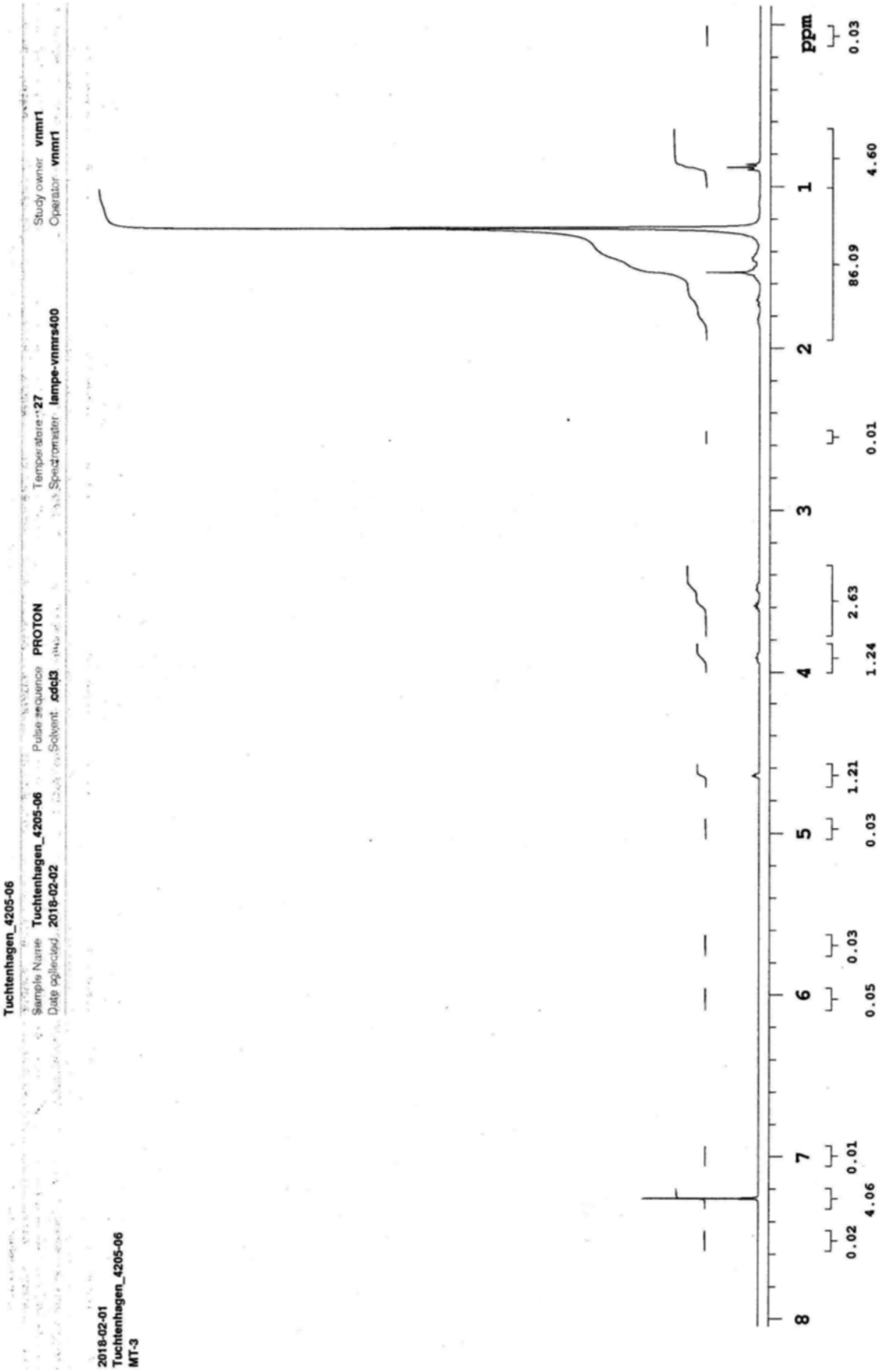
*Compound **9e** – ^{13}C NMR*



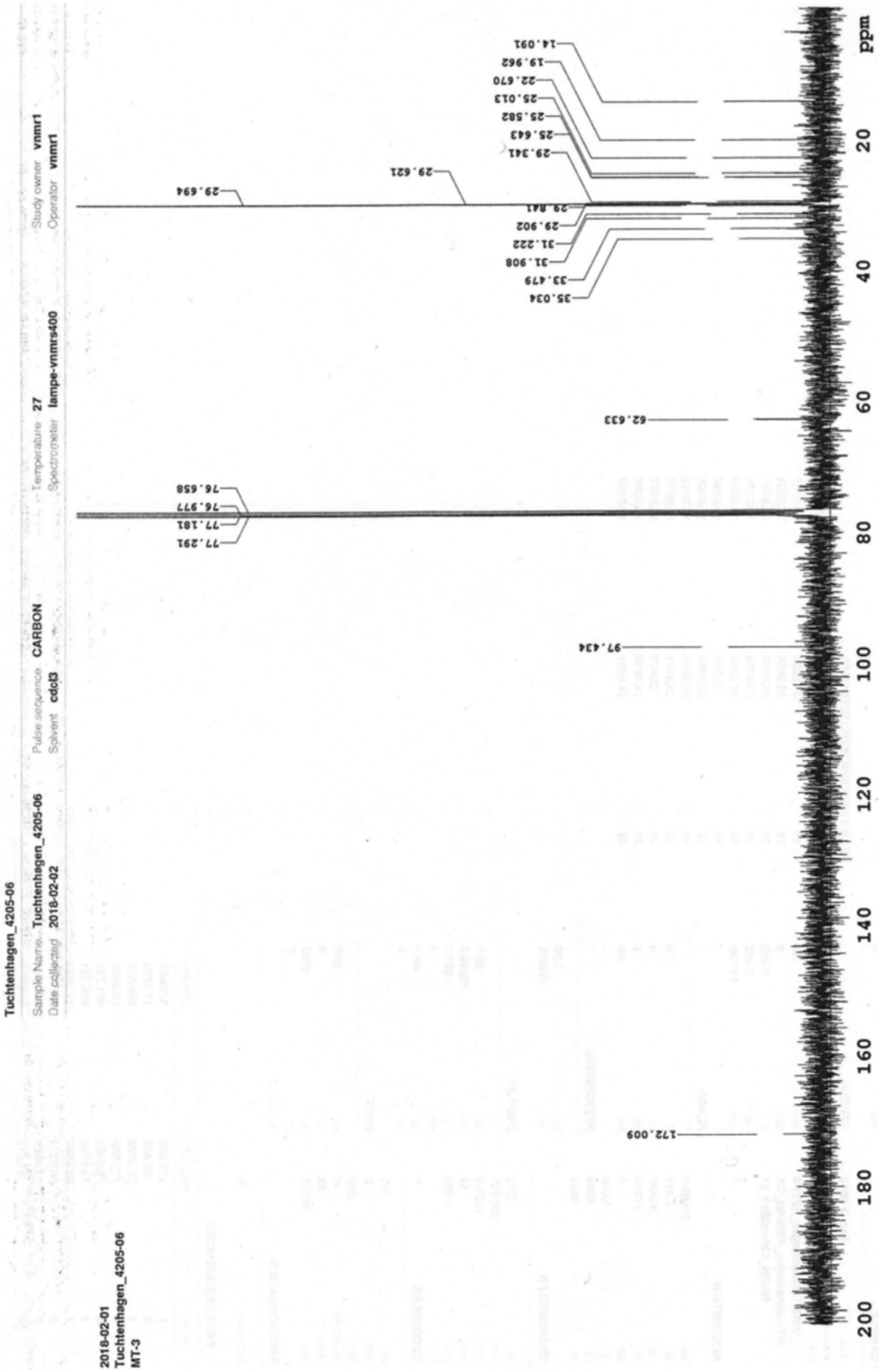
*Compound **9f** – ESI-MS (positive mode)*



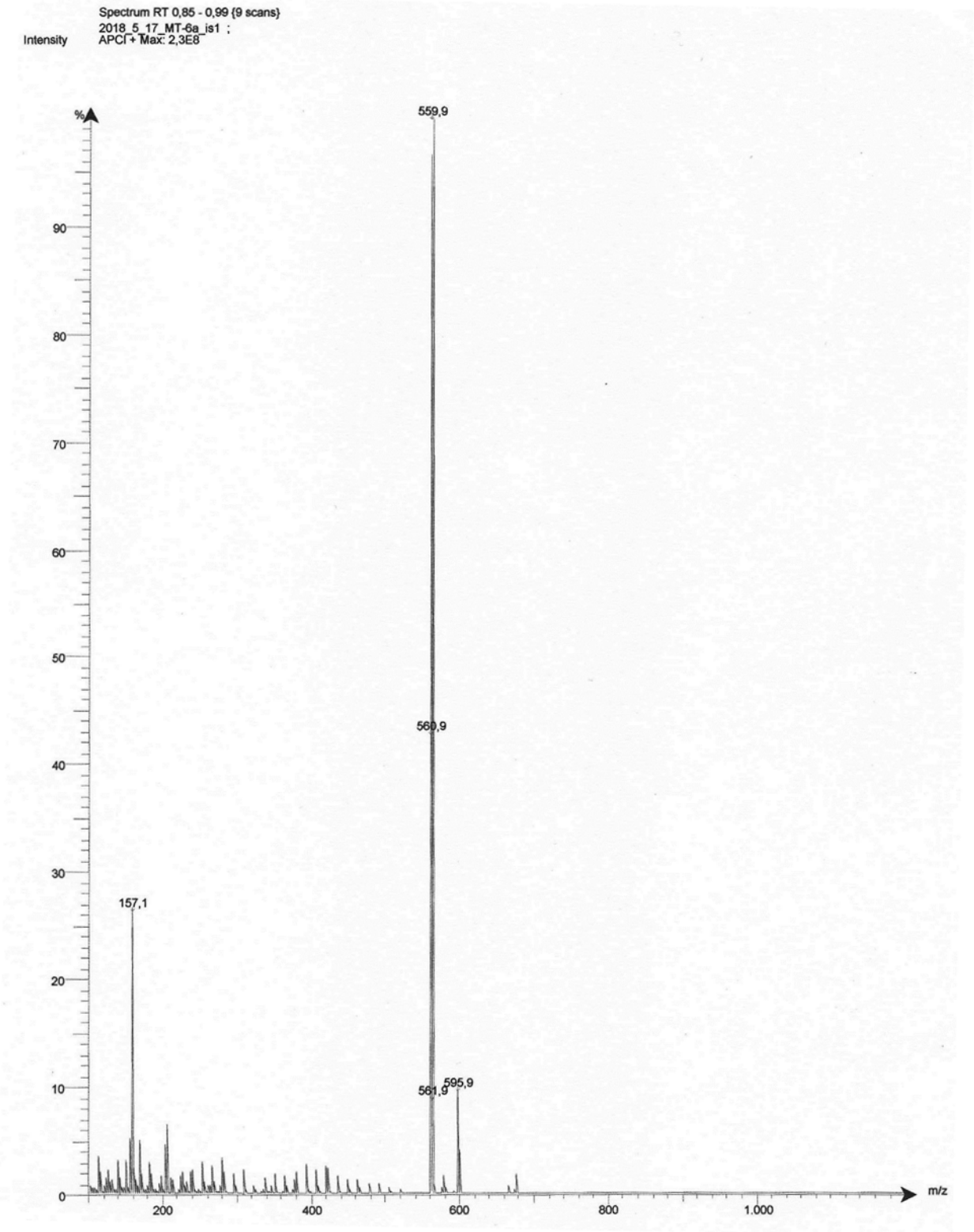
*Compound **9f** – ^{1}H NMR*



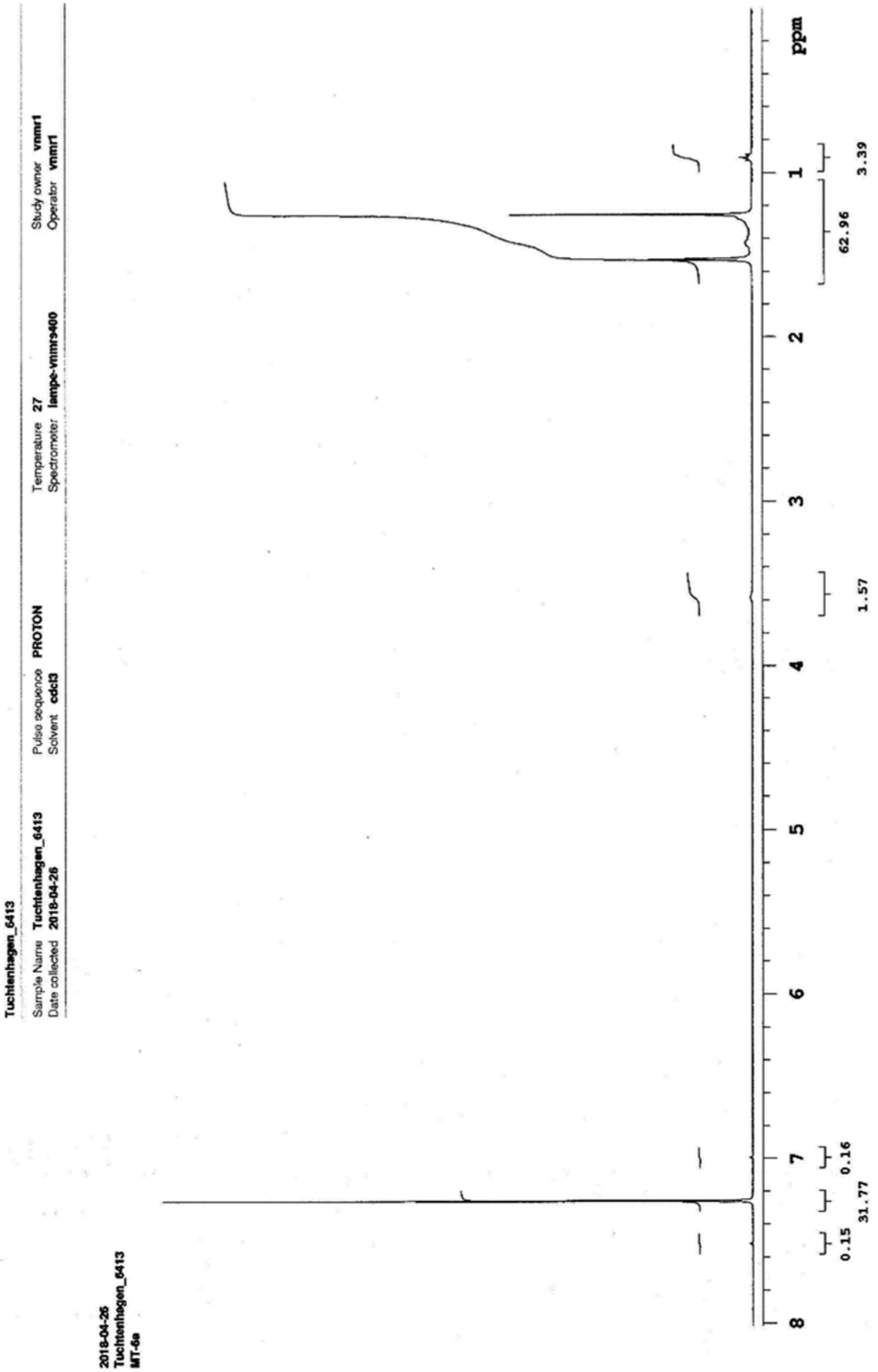
*Compound **9f** – ^{13}C NMR*



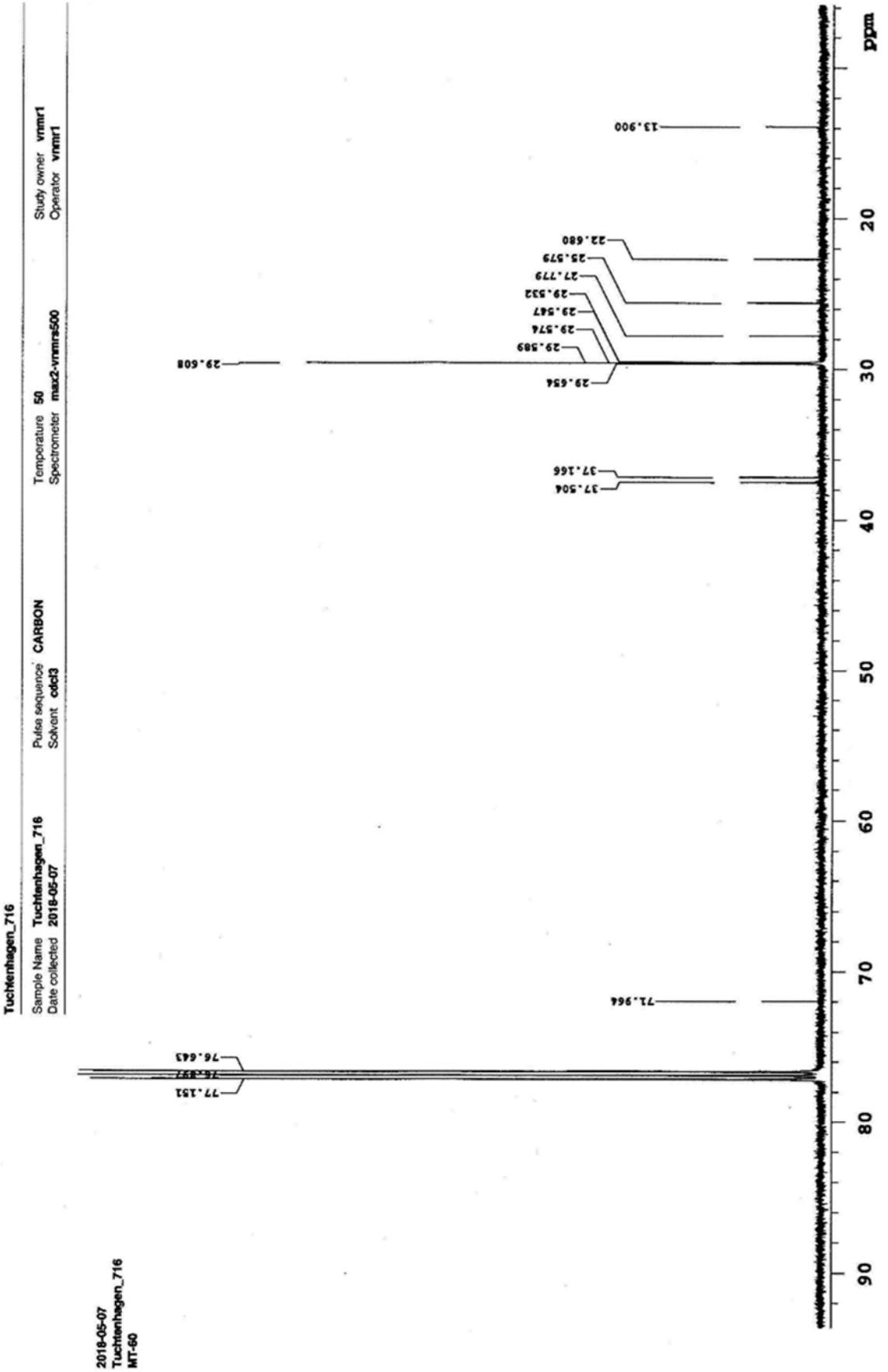
*Compound **10a** – APCI-MS (positive mode)*



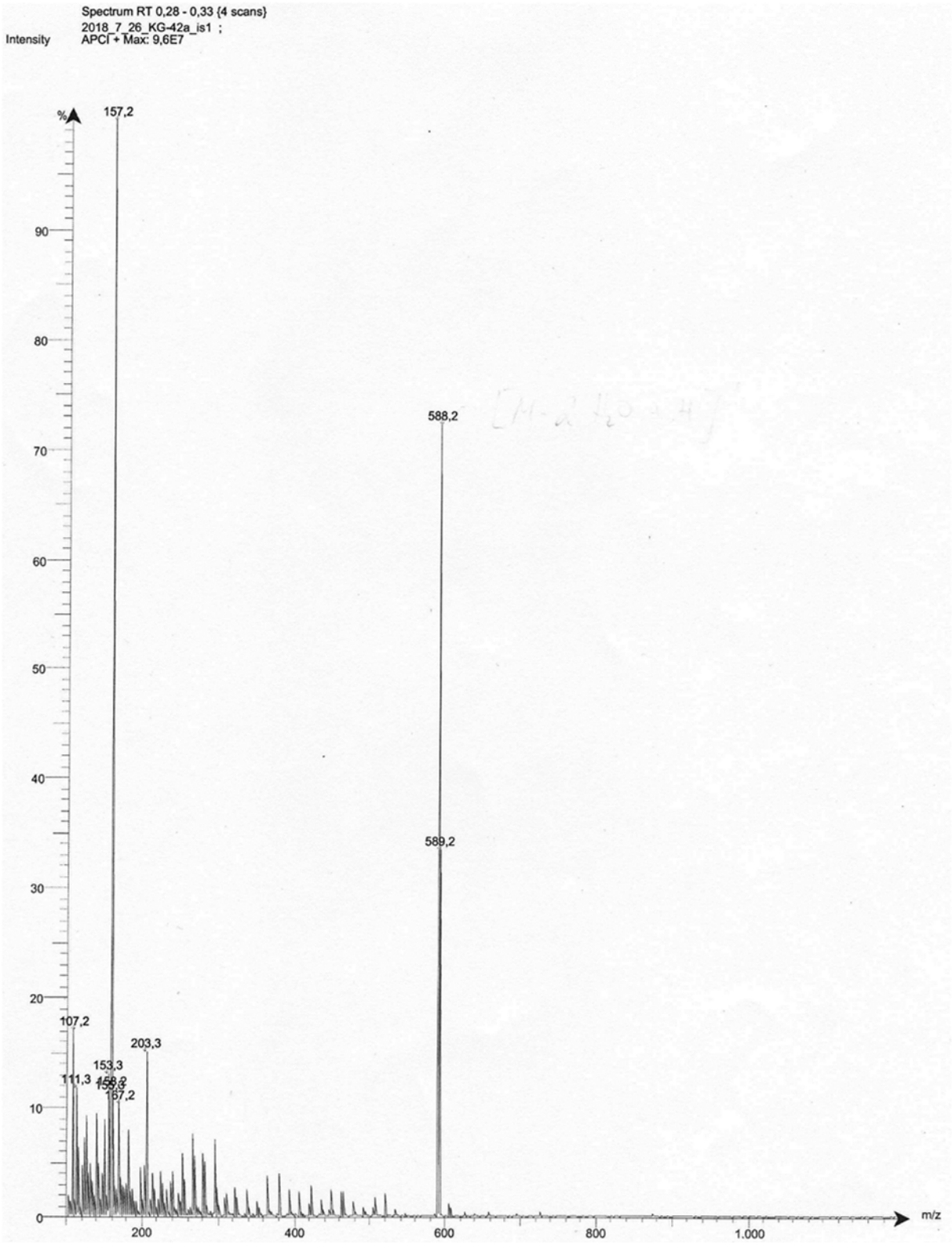
*Compound **10a** – ^{1}H NMR*



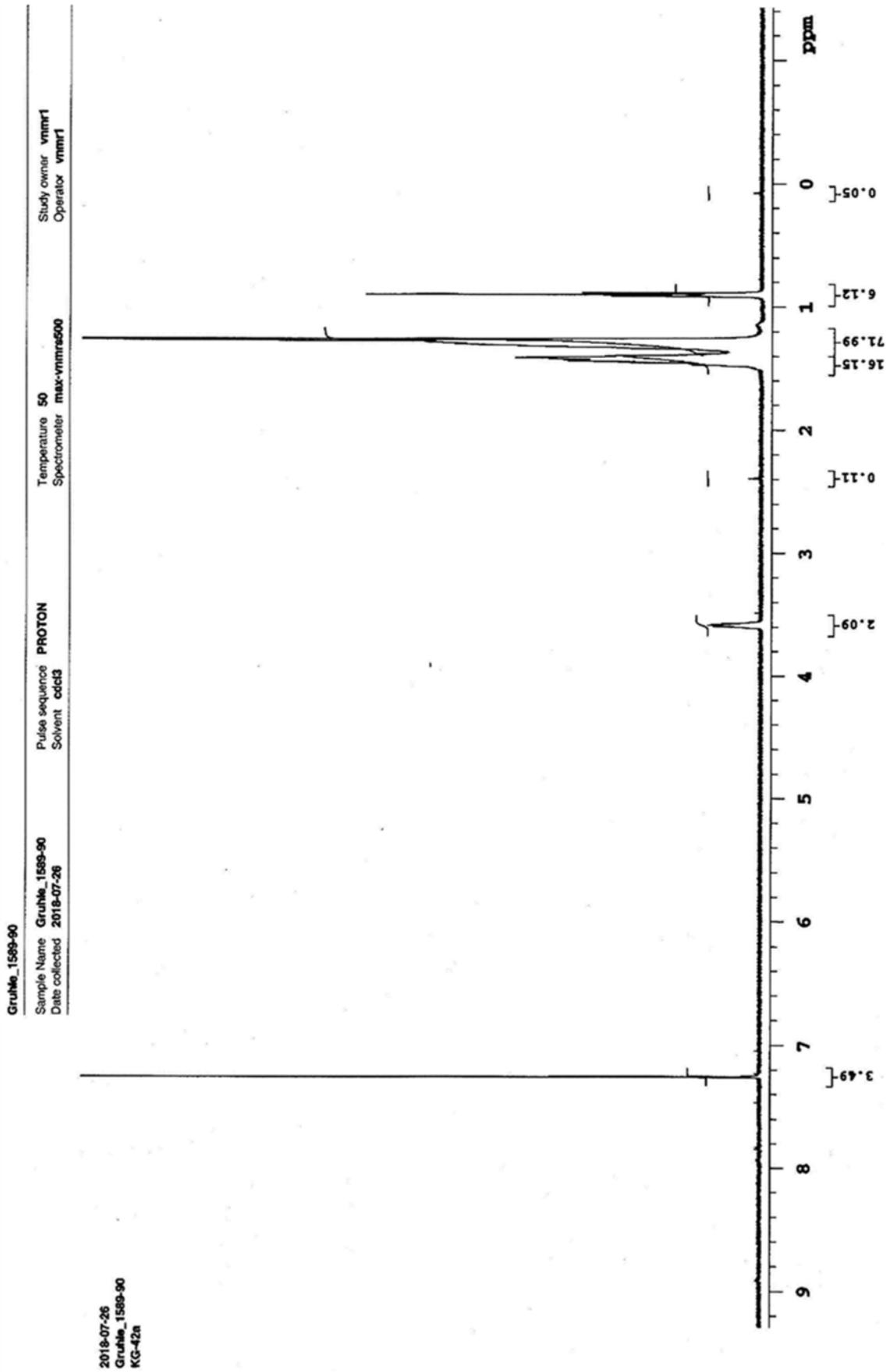
*Compound **10a** – ^{13}C NMR*



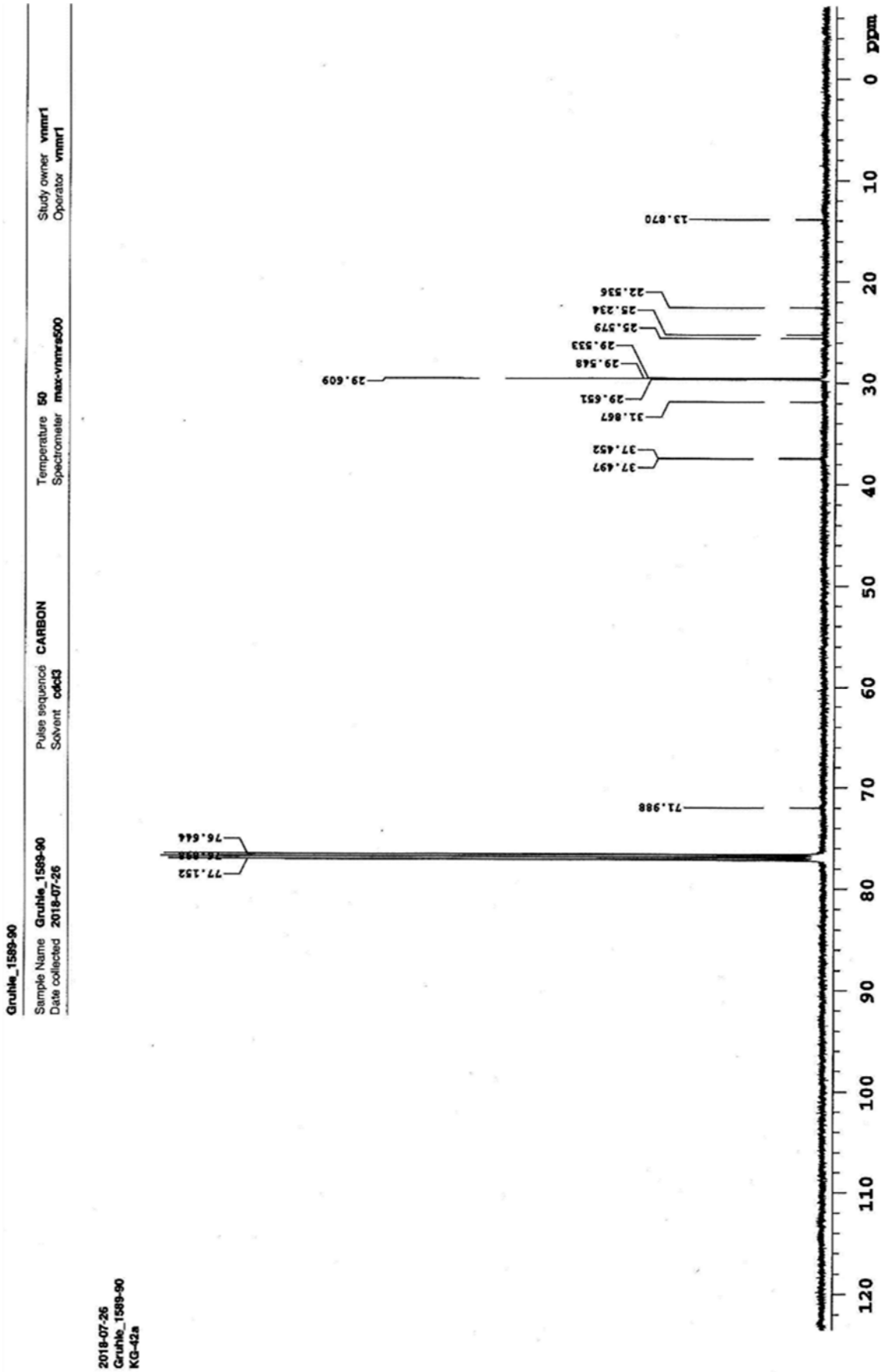
*Compound **10b** – APCI-MS (positive mode)*



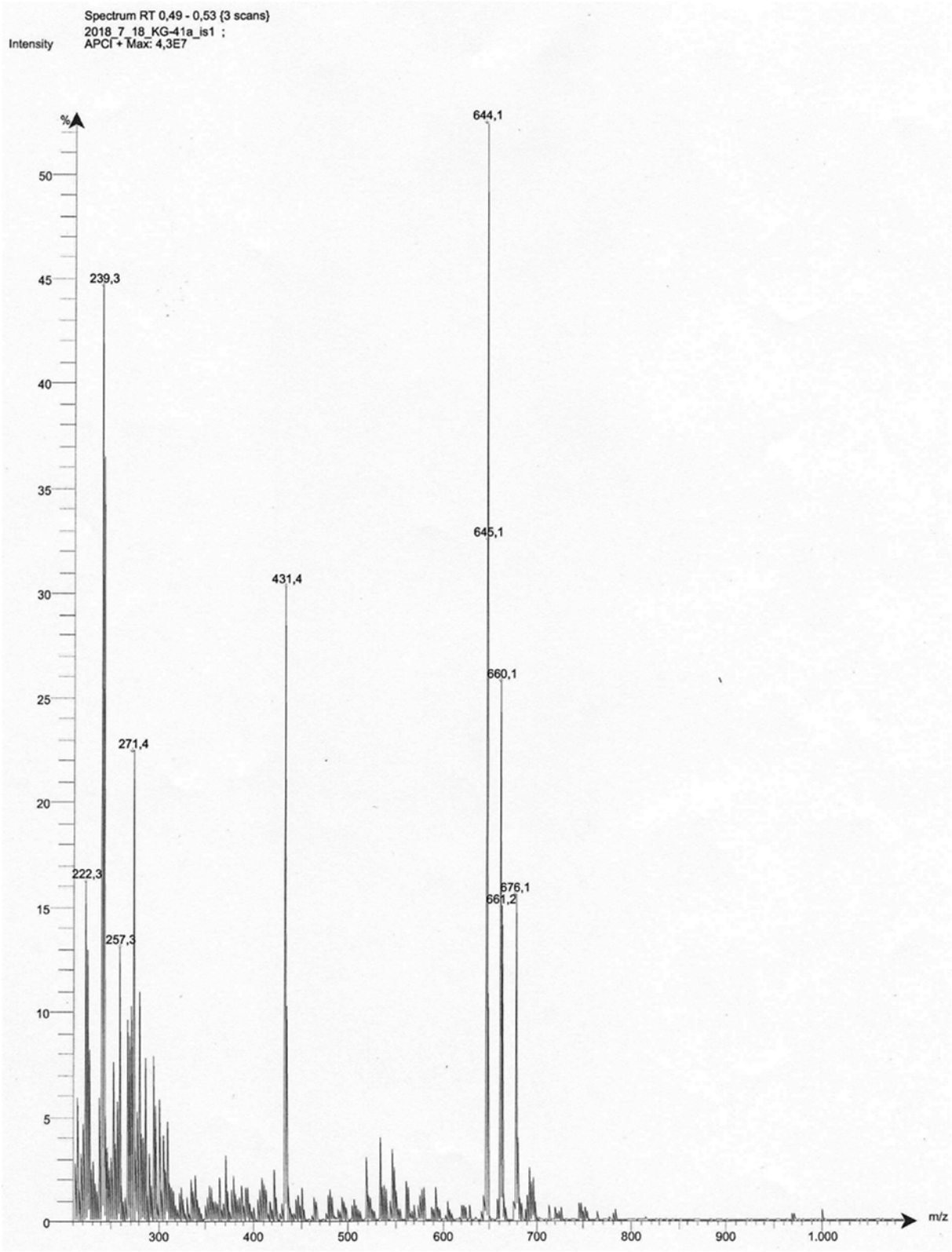
*Compound **10b** – ^{1}H NMR*



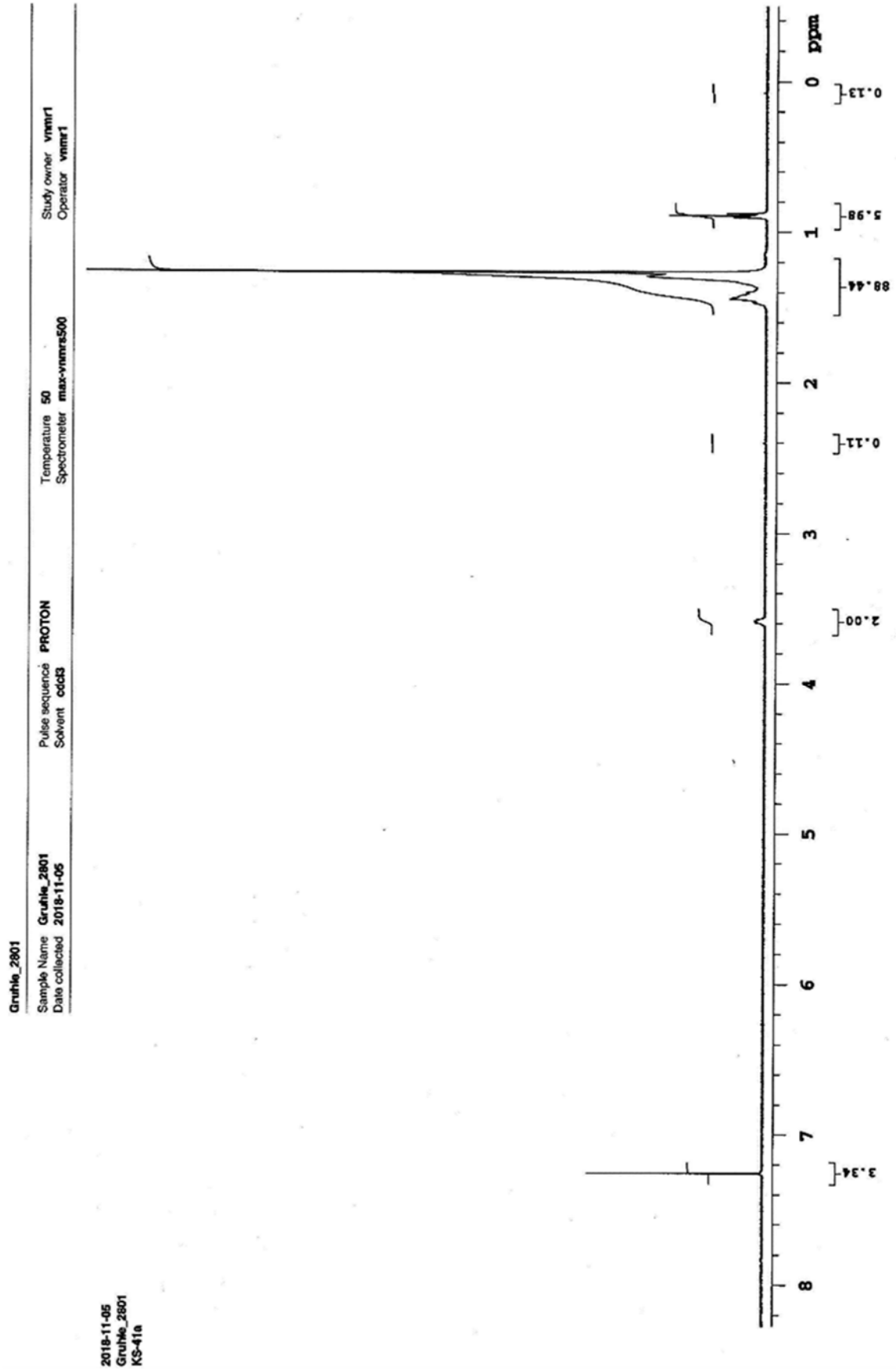
*Compound **10b** – ^{13}C NMR*



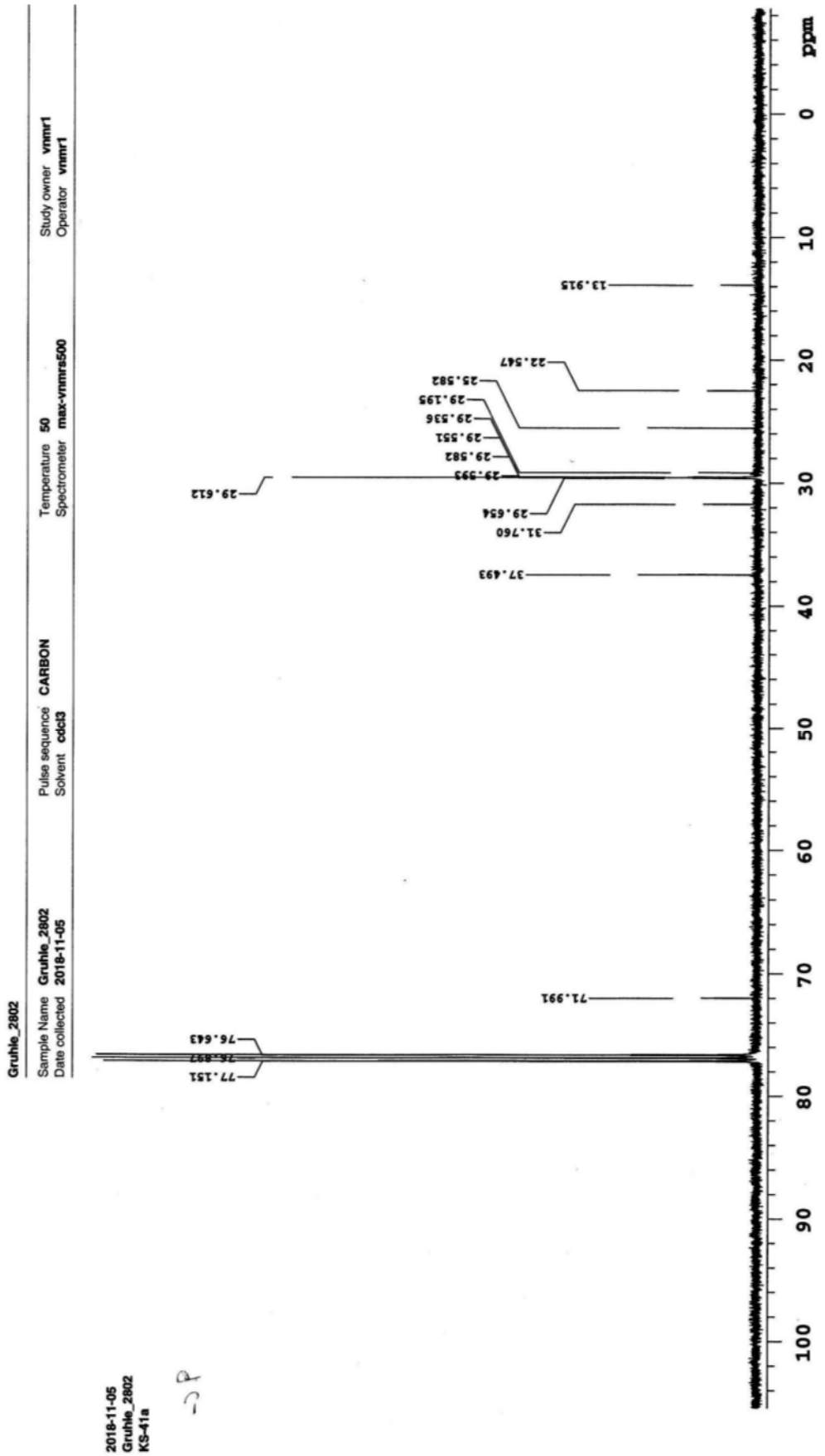
*Compound **10c** – APCI-MS (positive mode)*



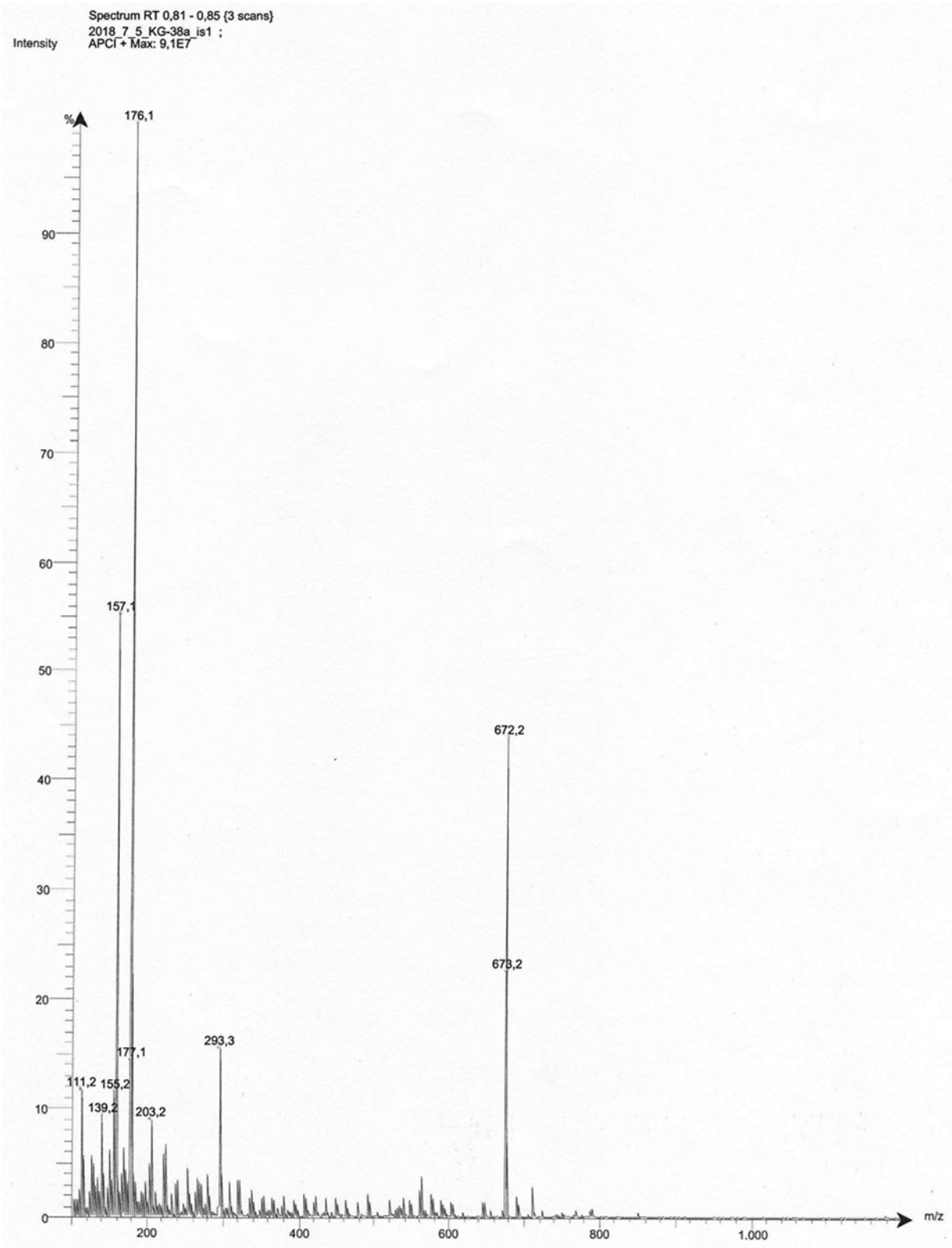
*Compound **10c** – ^{1}H NMR*



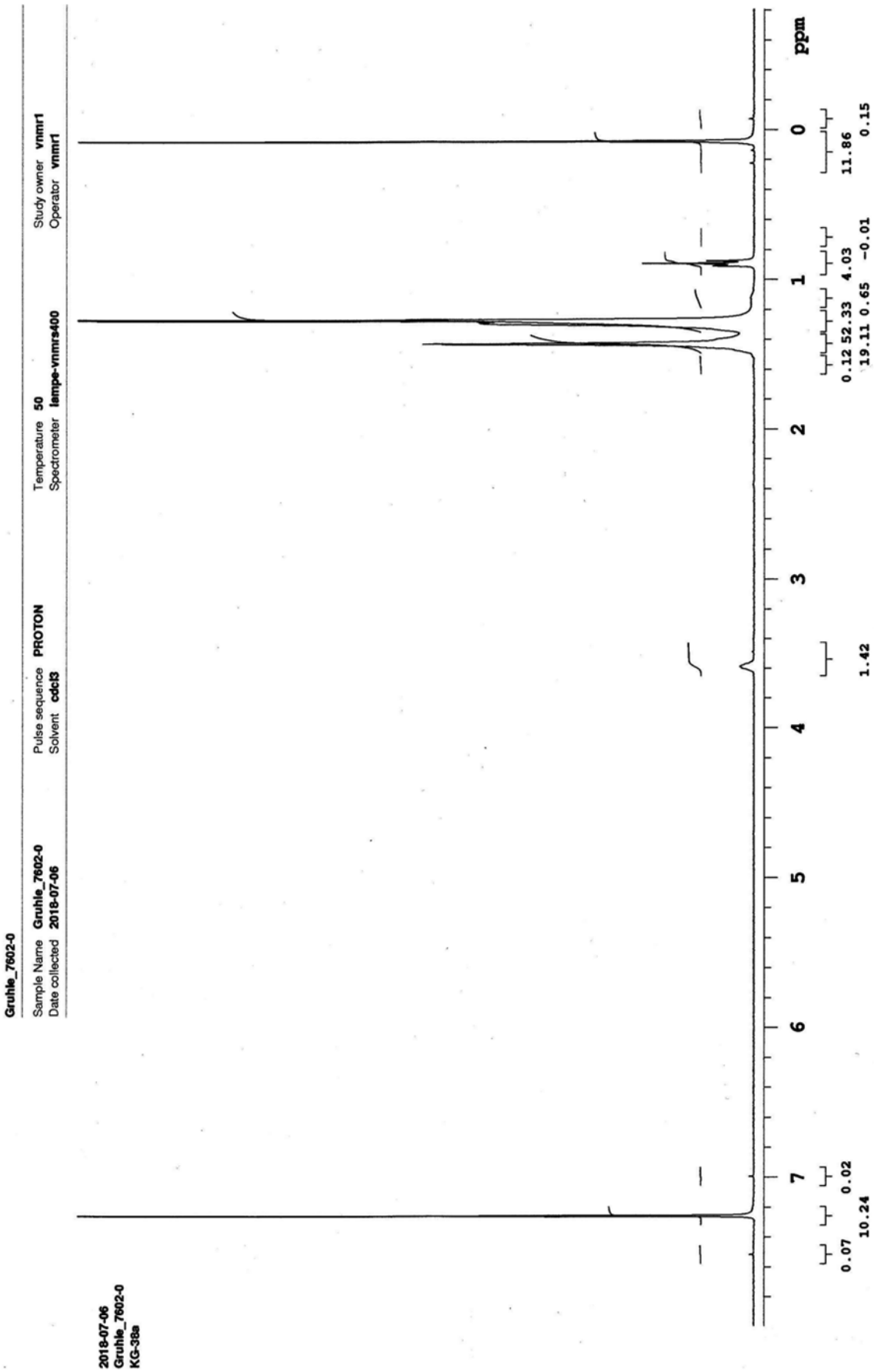
*Compound **10c** – ^{13}C NMR*



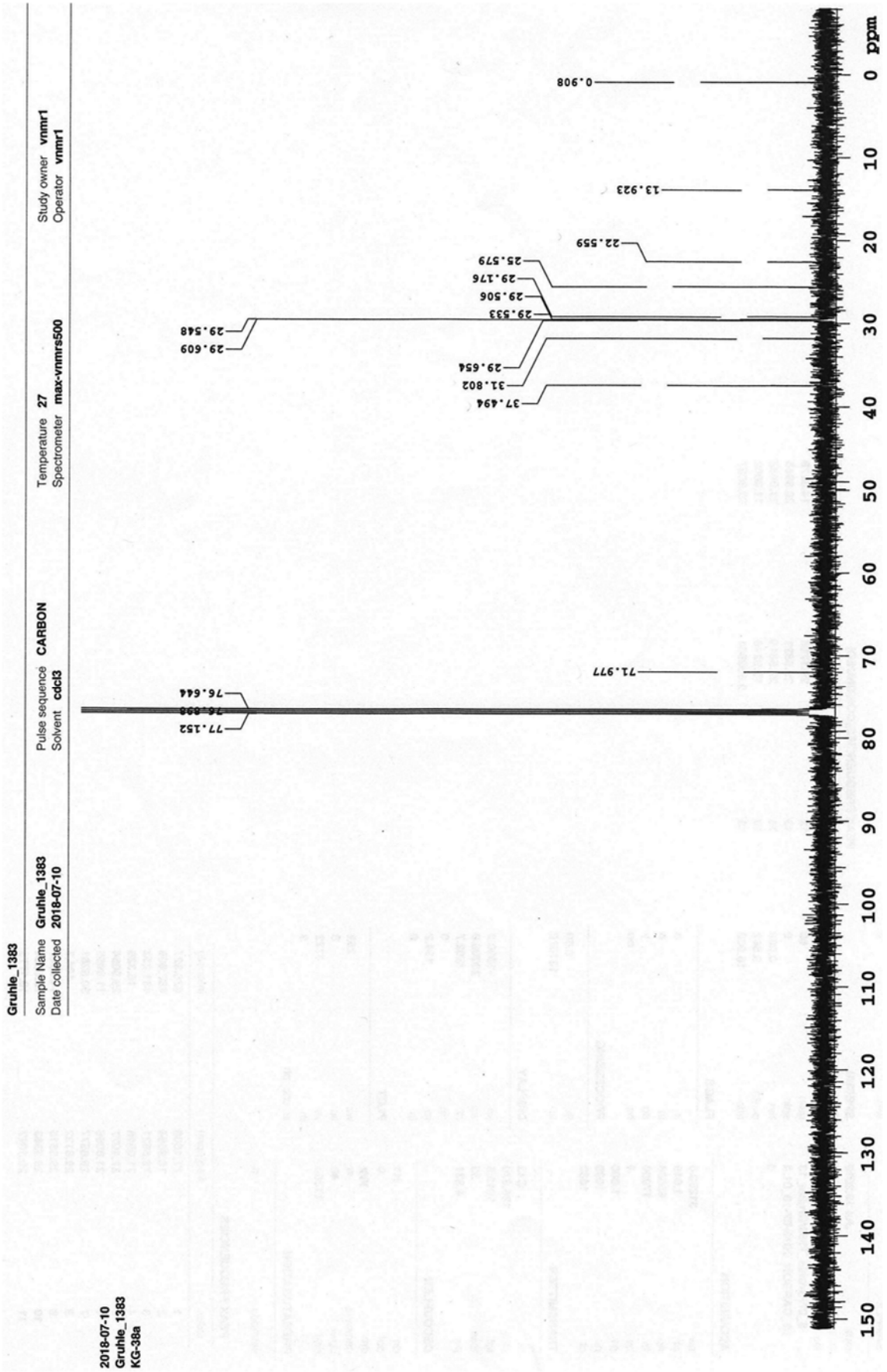
*Compound **10d** – APCI-MS (positive mode)*



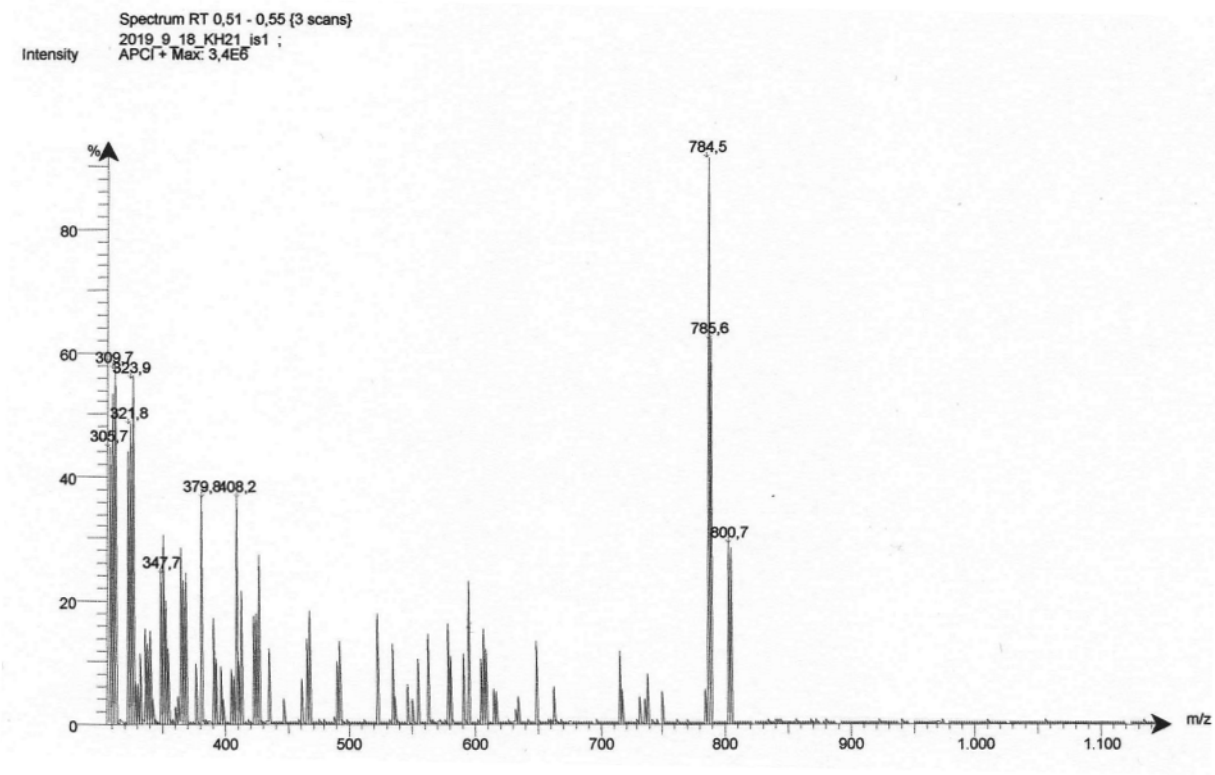
*Compound **10d** – ^{1}H NMR*



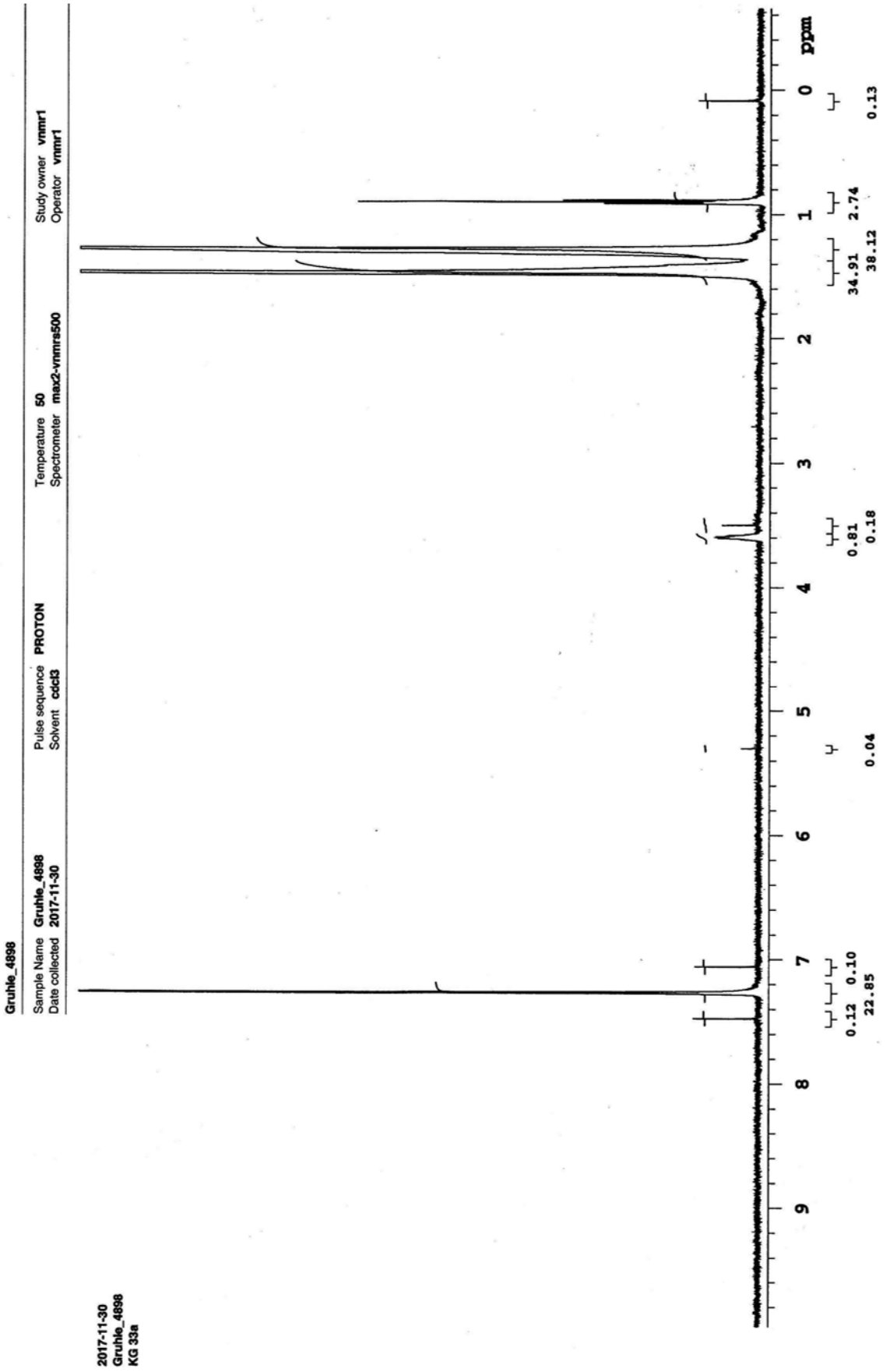
*Compound **10d** – ^{13}C NMR*



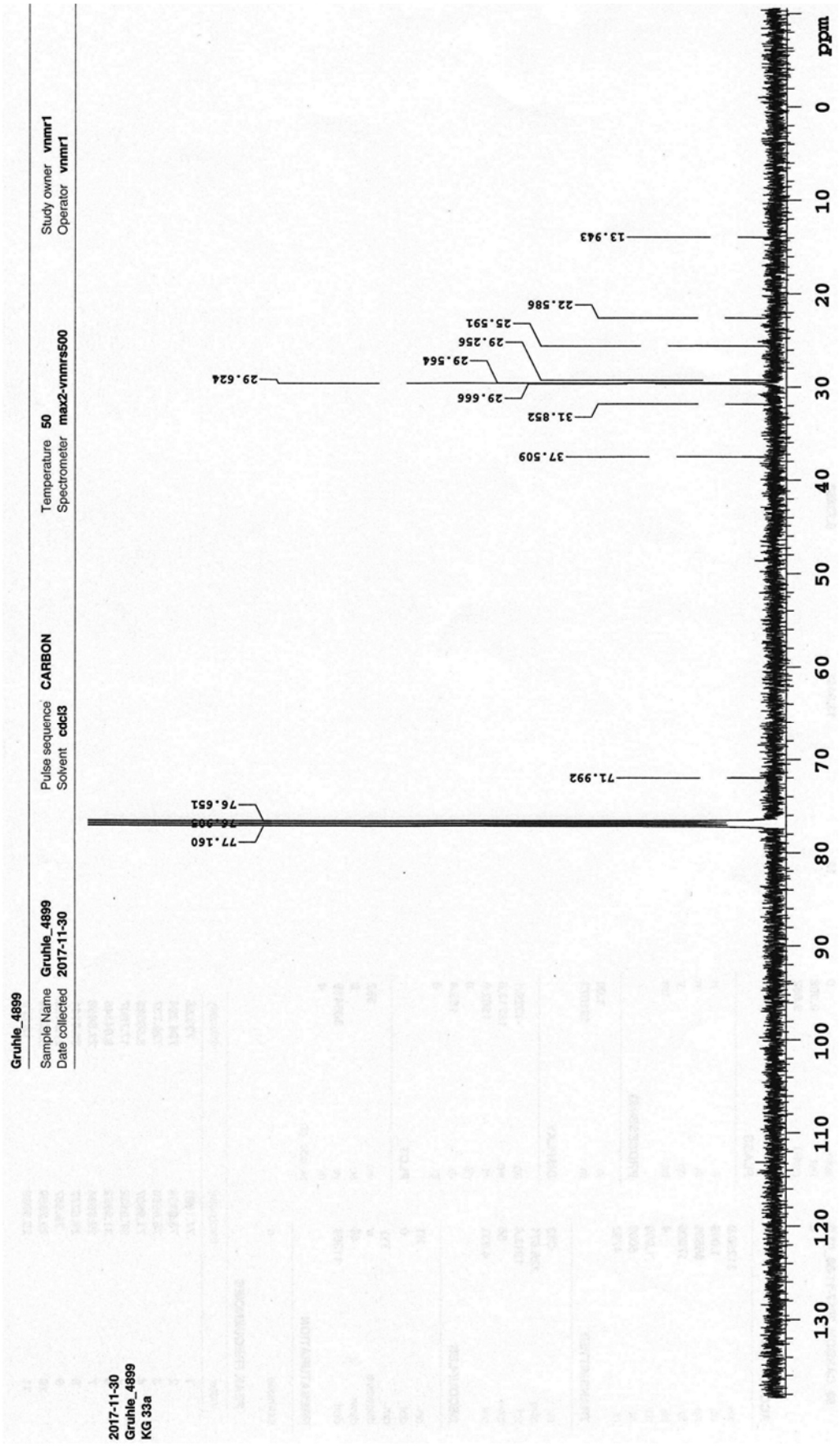
*Compound **10e** – APCI-MS (positive mode)*



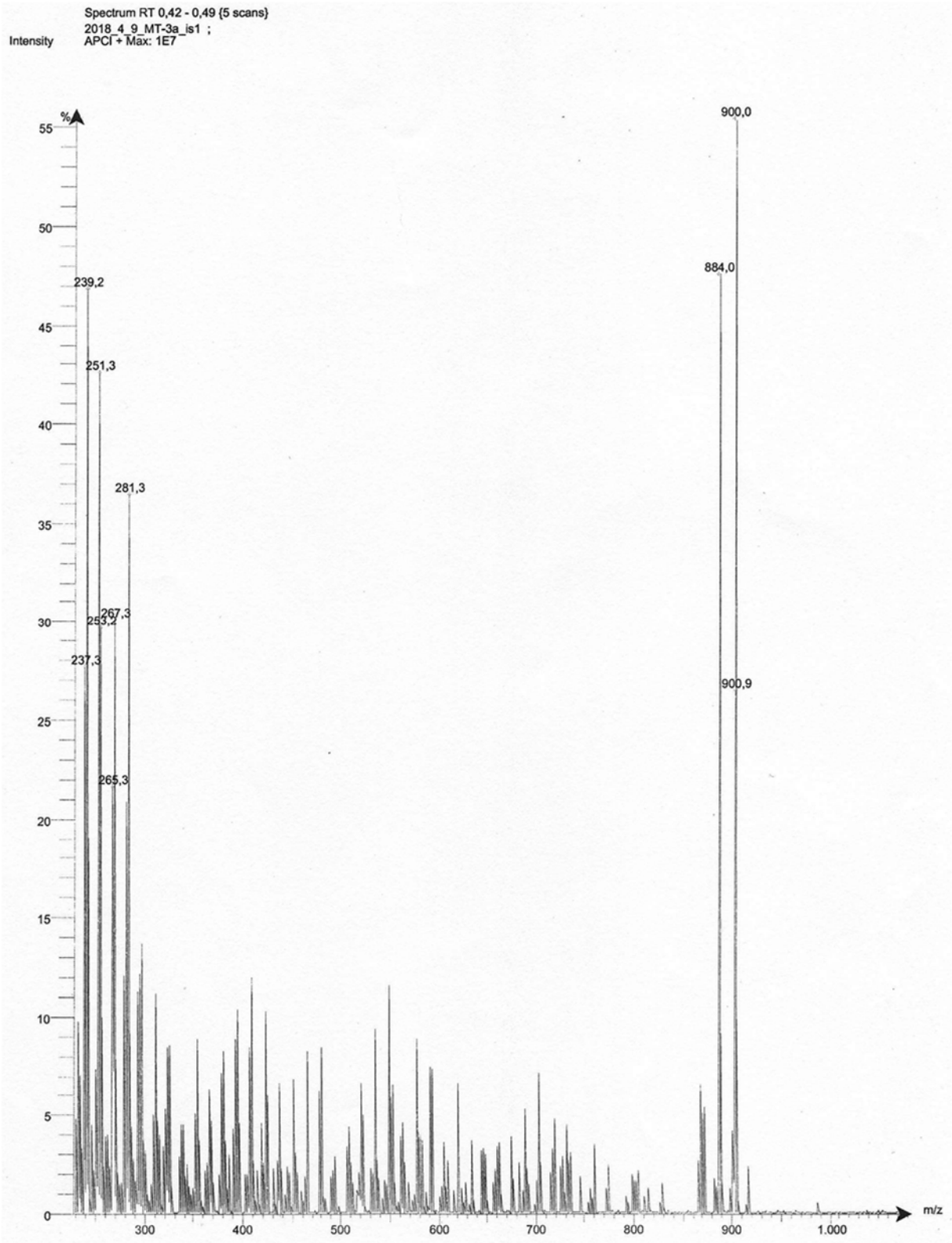
*Compound **10e** – ^{1}H NMR*



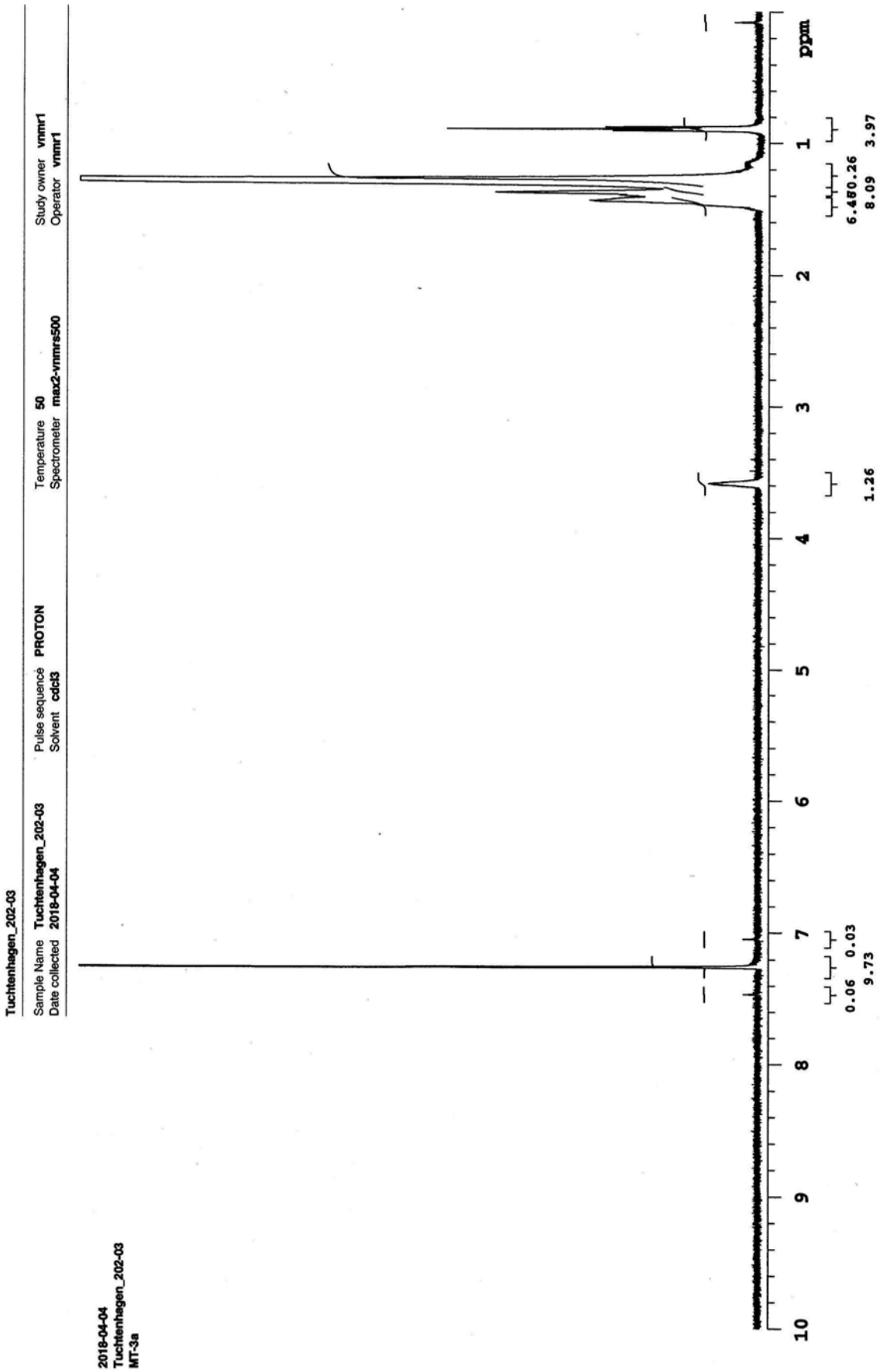
*Compound **10e** – ^{13}C NMR*



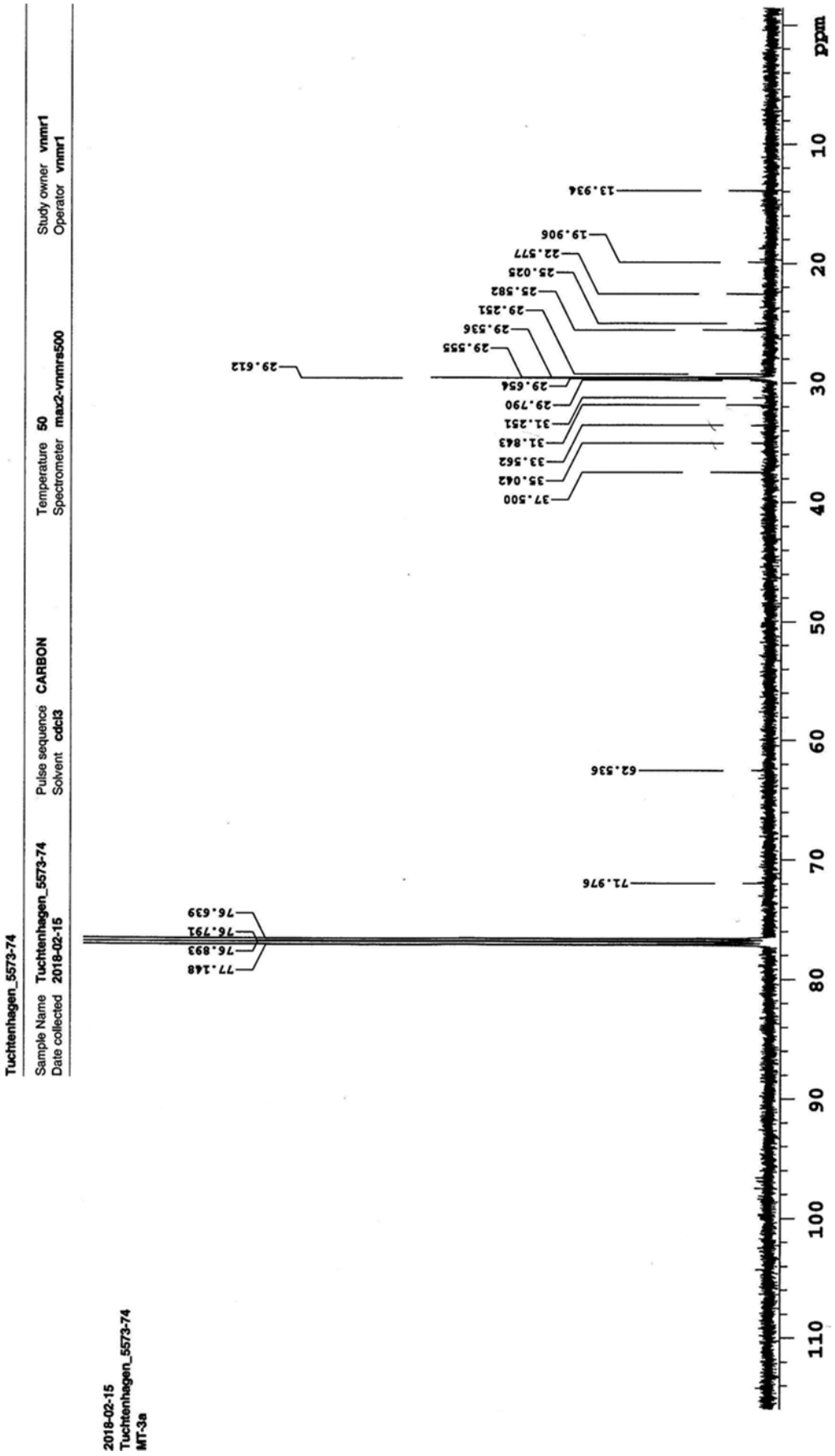
*Compound **10f** – APCI-MS (positive mode)*



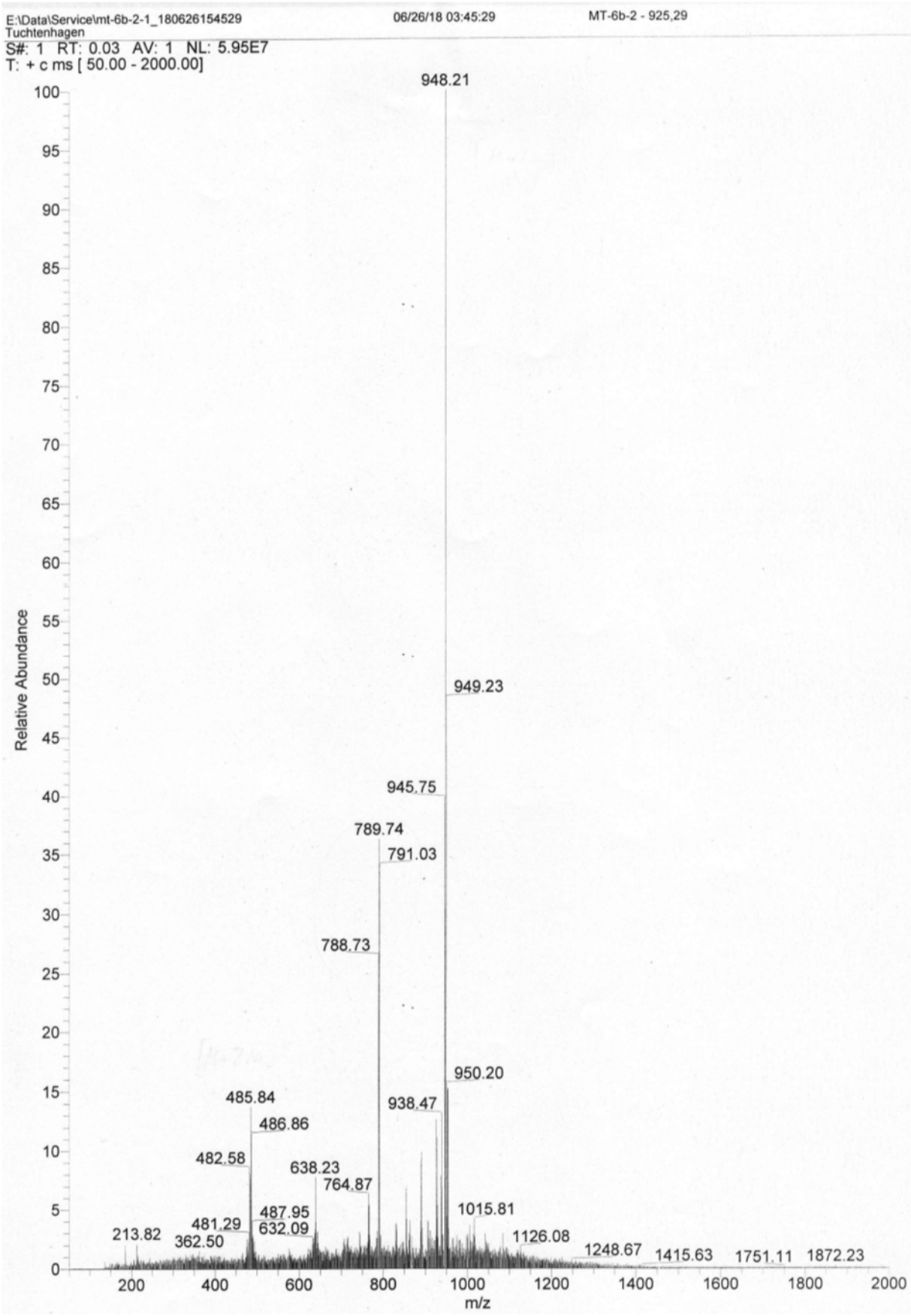
*Compound **10f** – ^{1}H NMR*



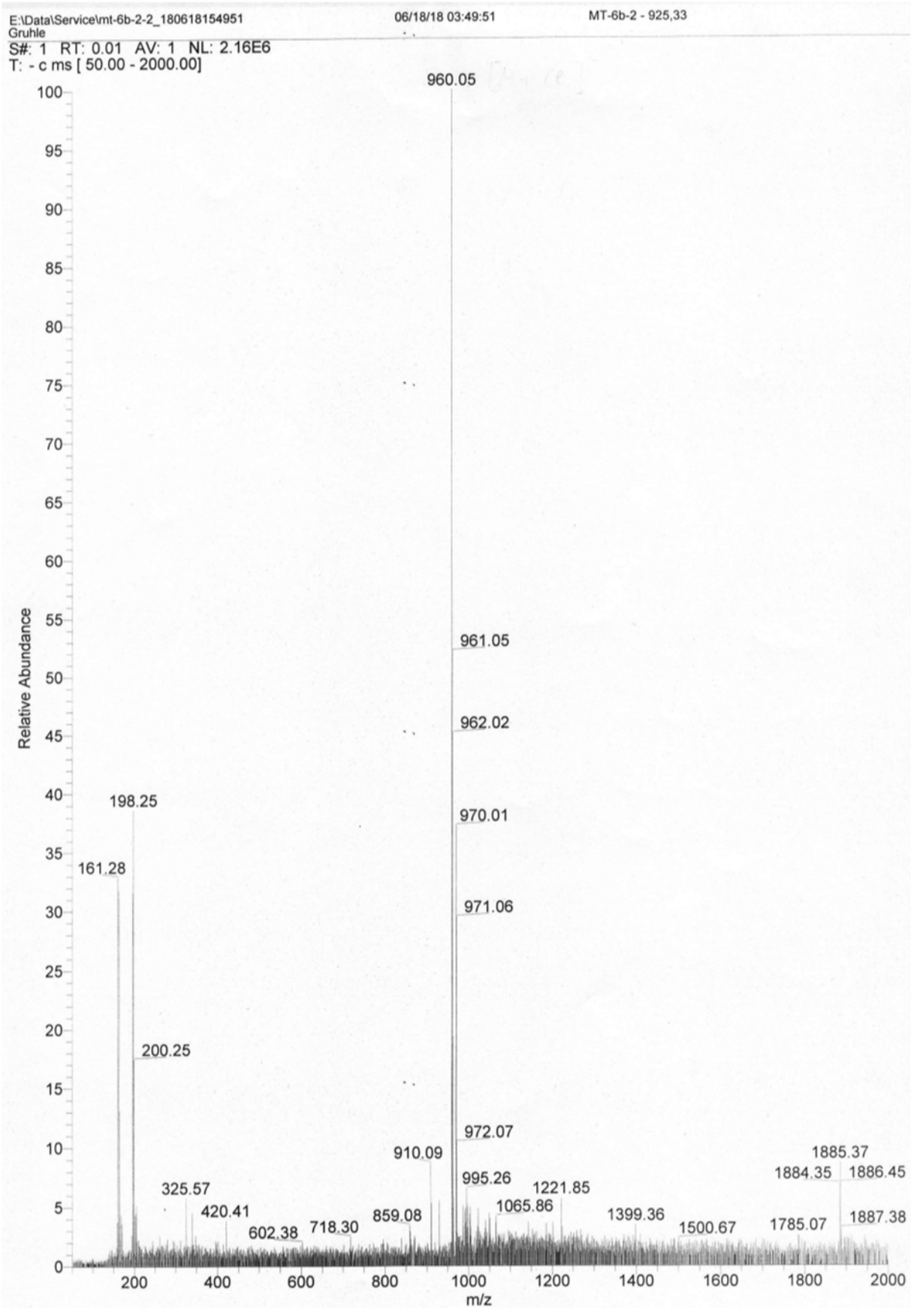
*Compound **10f** – ^{13}C NMR*



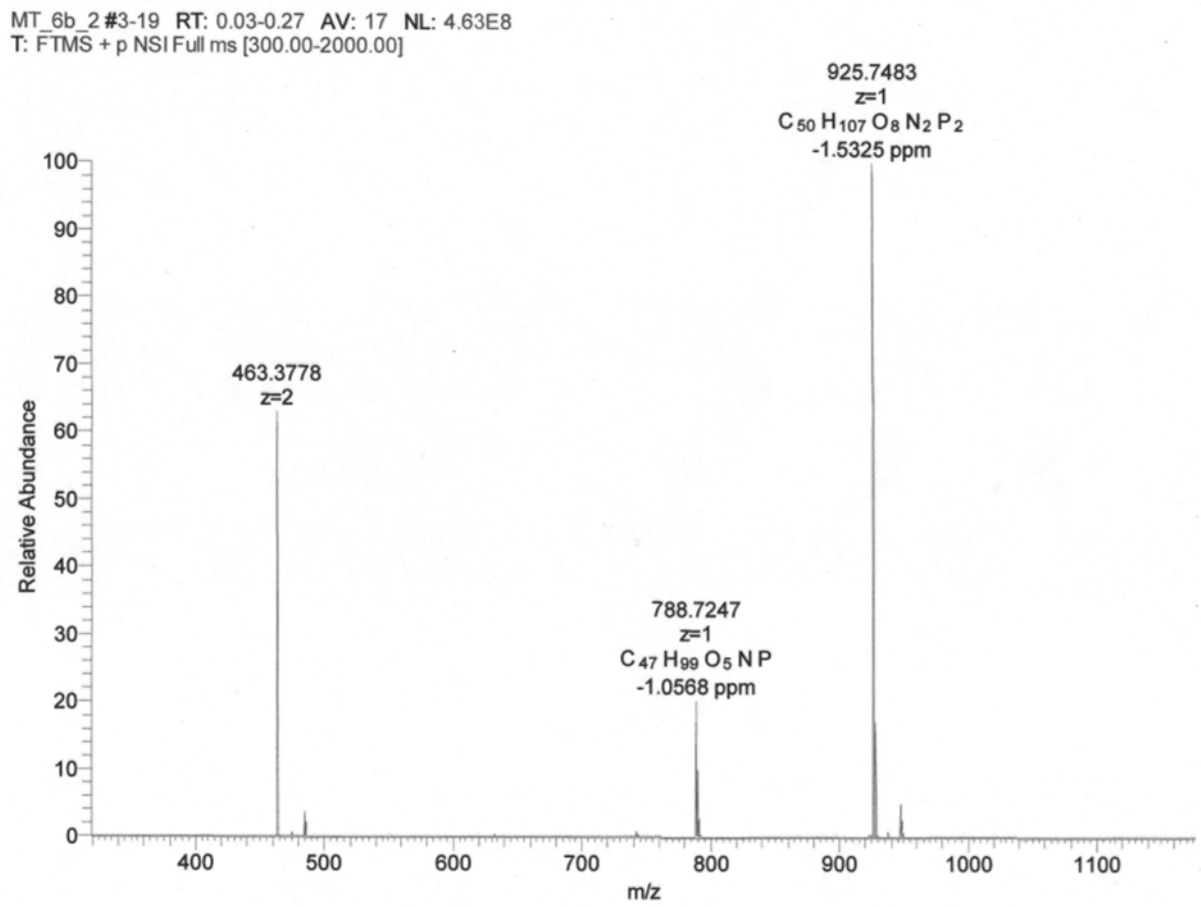
PC-C32(1,32C4)-PC *– ESI-MS (positive mode)*



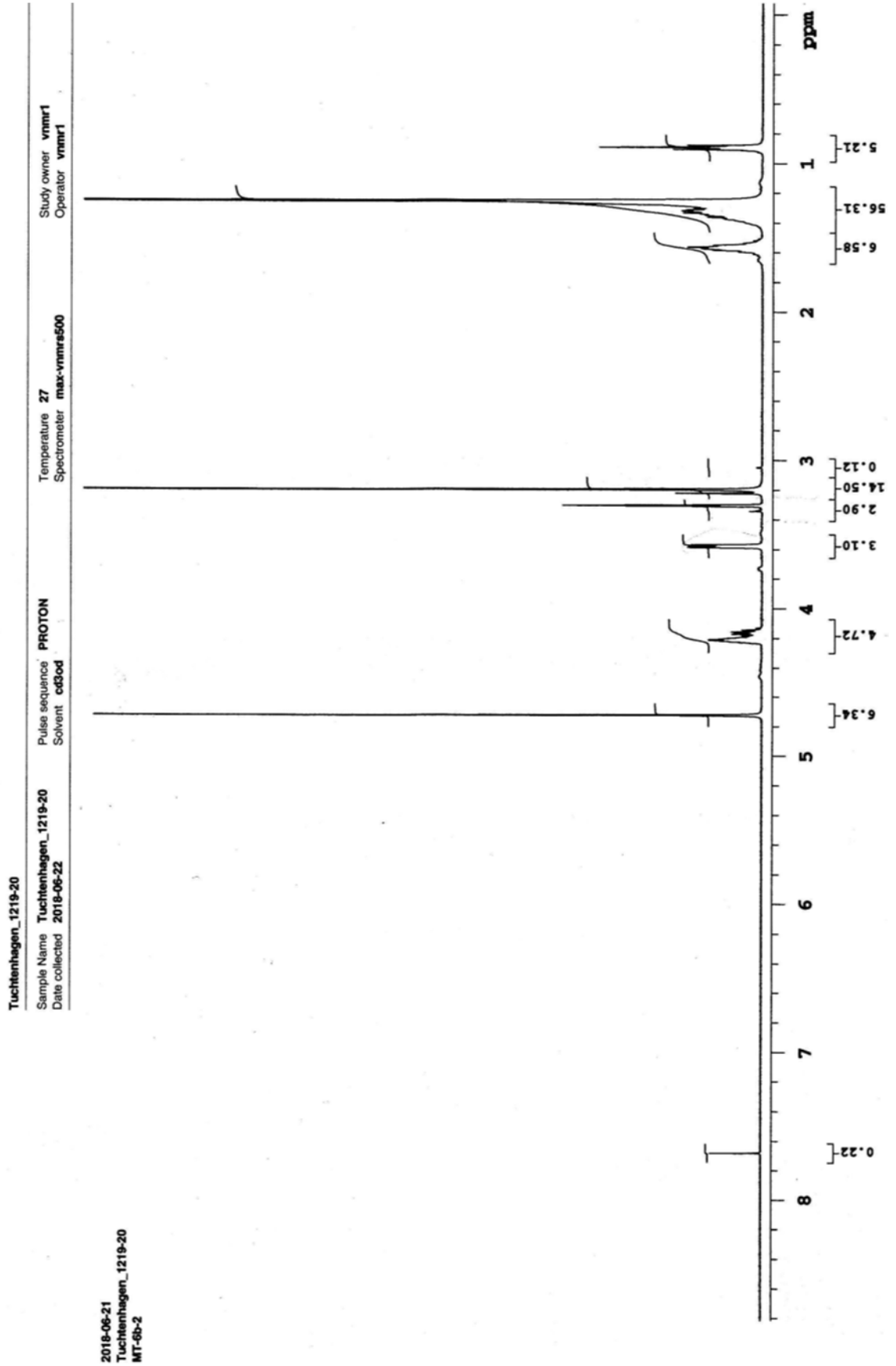
***PC-C32(1,32C4)-PC** – ESI-MS (negative mode)*



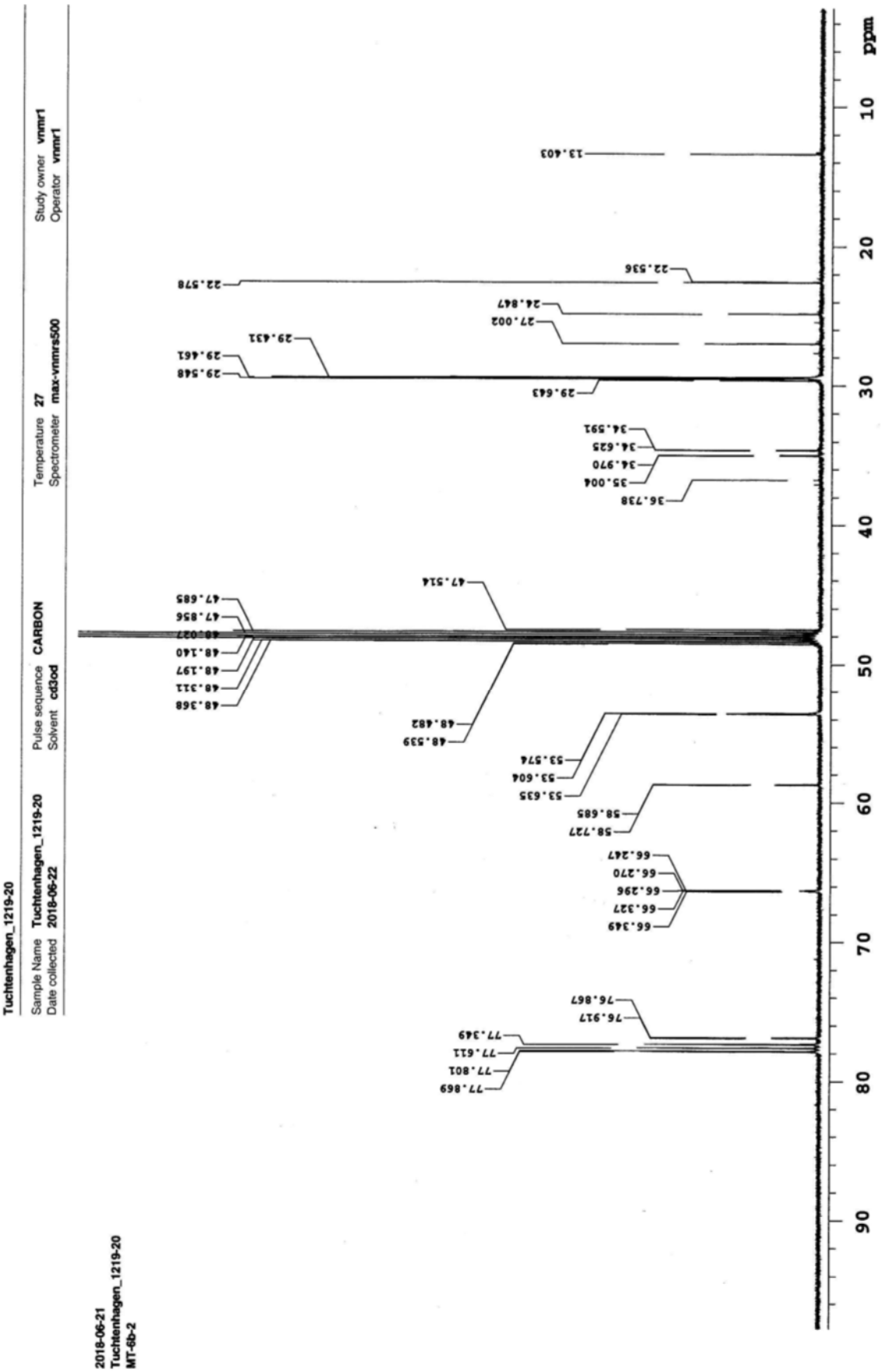
PC-C32(1,32C4)-PC *– HRMS (positive mode)*



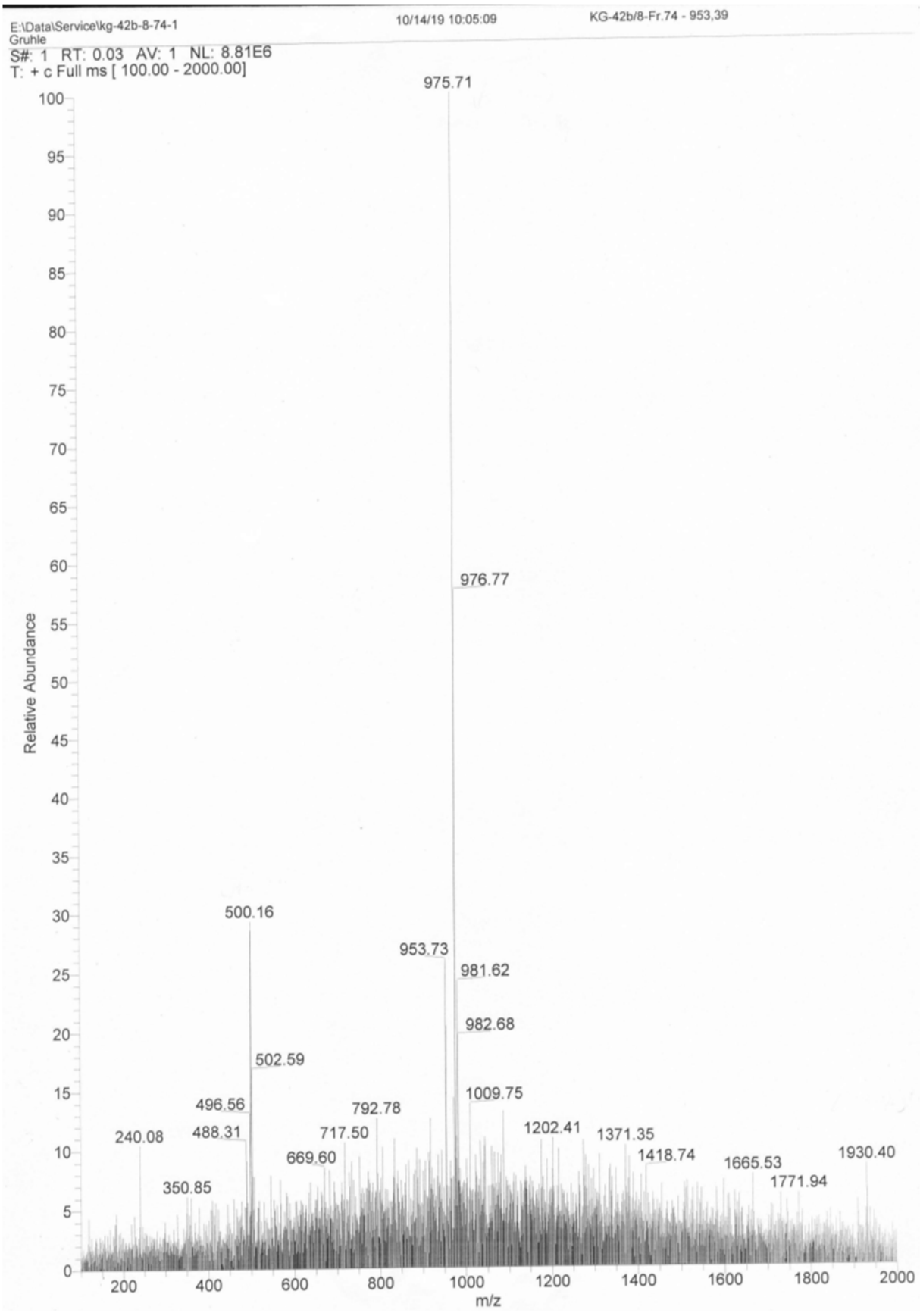
PC-C32(1,32C4)-PC *– ^{1}H NMR*



PC-C32(1,32C4)-PC *– ^{13}C NMR*

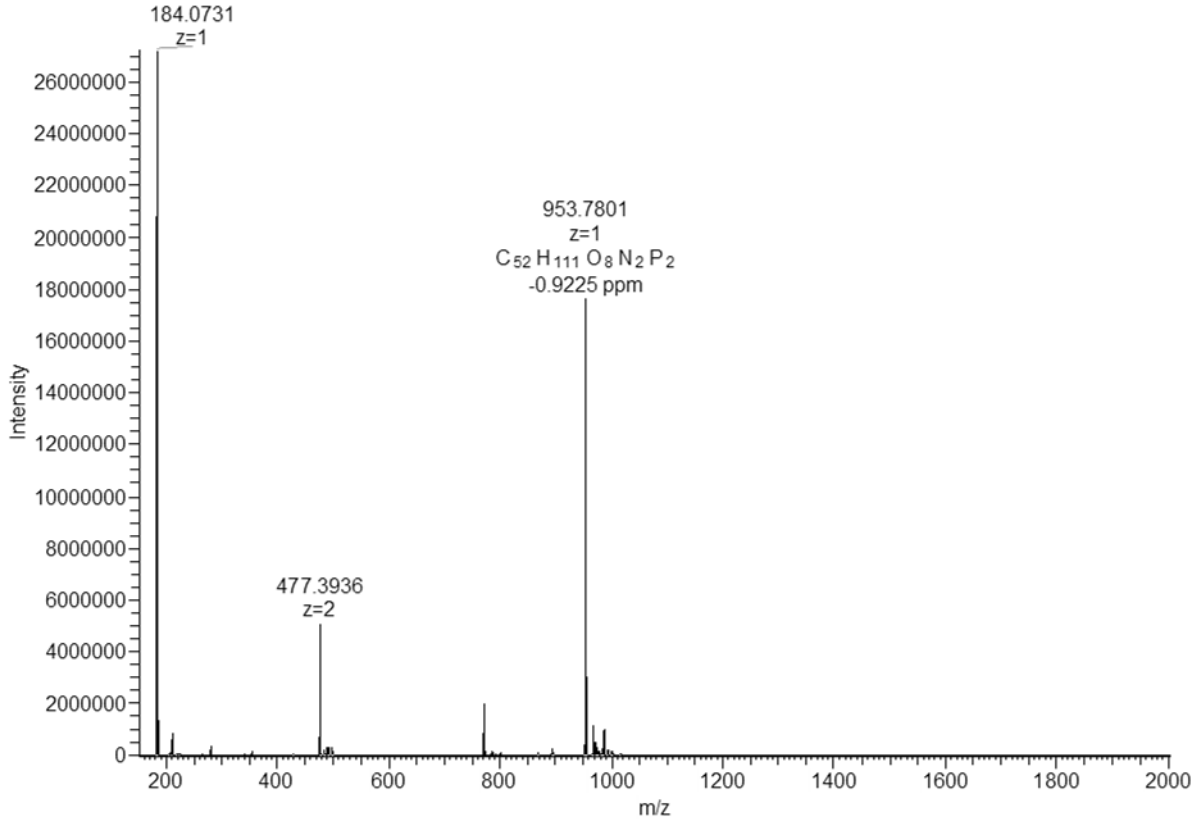


***PC-C32(1,32C5)-PC** – ESI-MS (positive mode)*

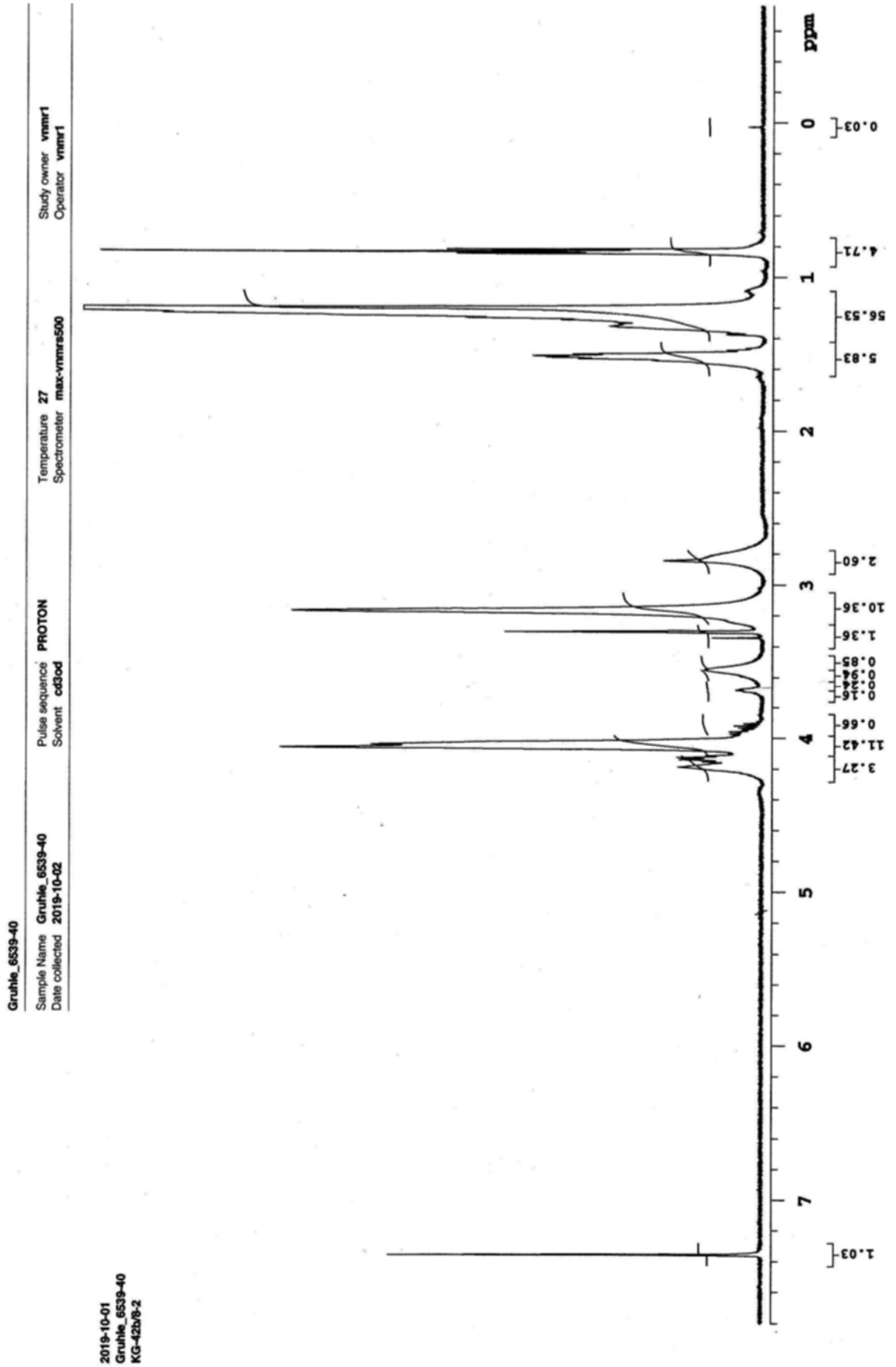


***PC-C32(1,32C5)-PC** – HRMS (positive mode)*

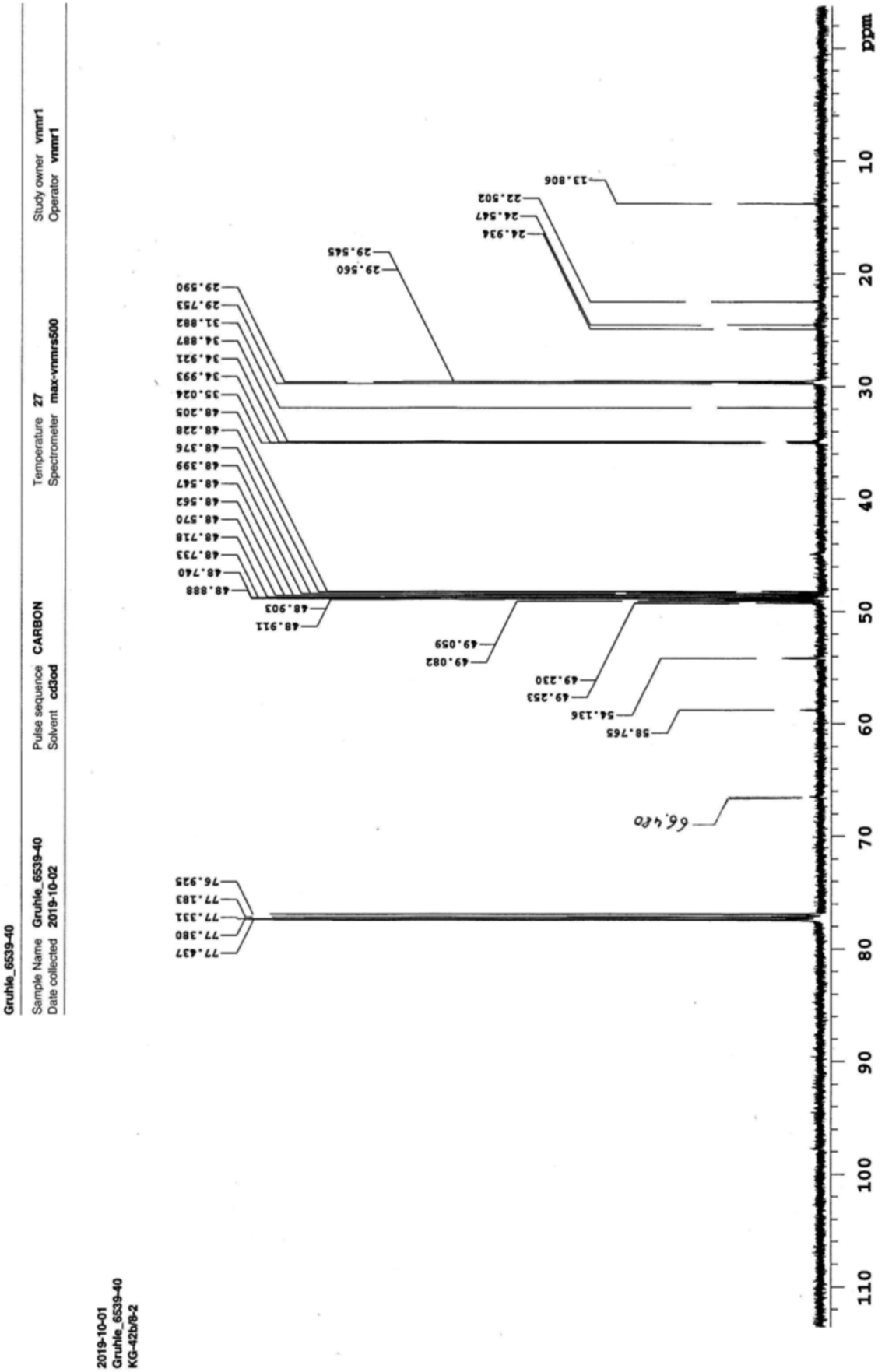
KG-42b-2 #2-15 RT: 0.03-0.40 AV: 14 NL: 2.72E7
F: FTMS + p NSI Full ms



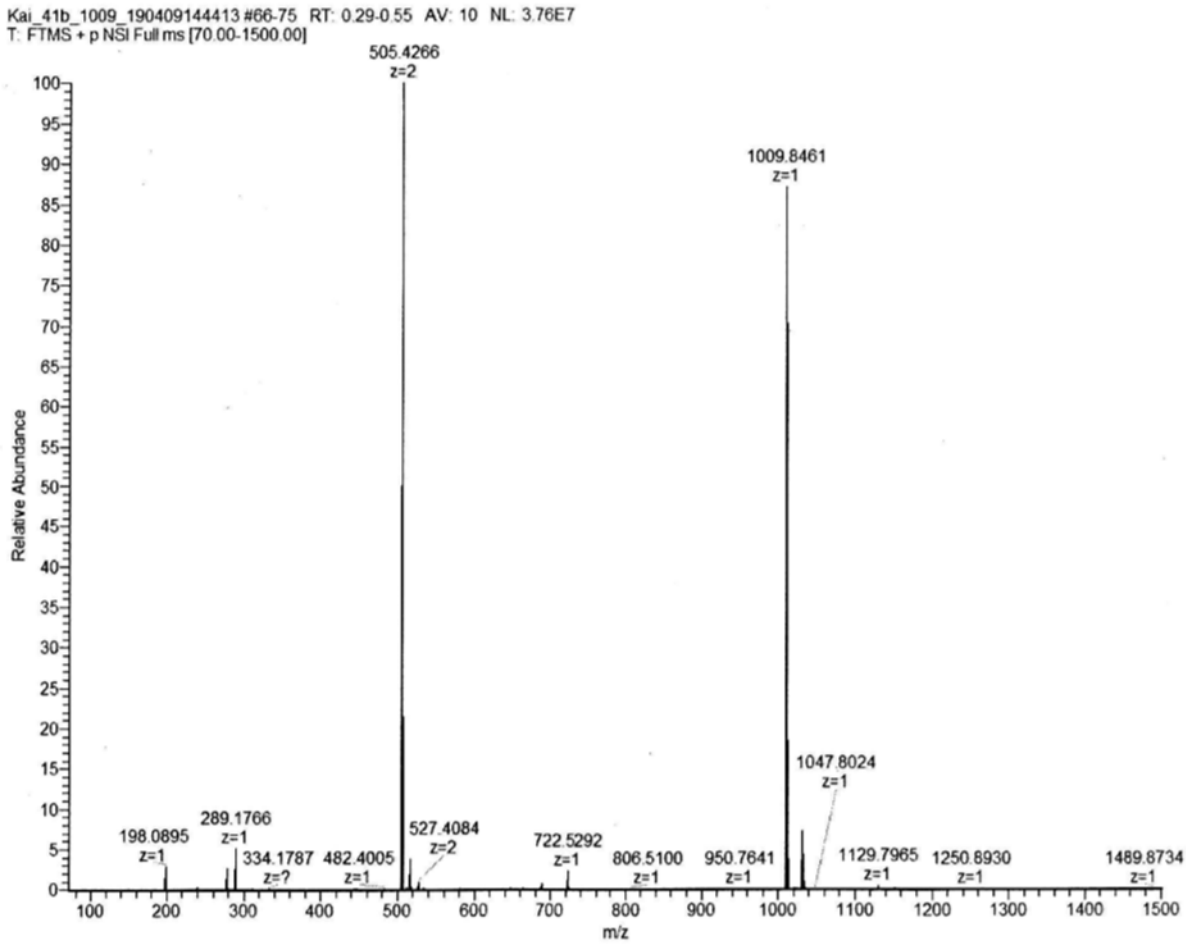
PC-C32(1,32C5)-PC *– ^{1}H NMR*



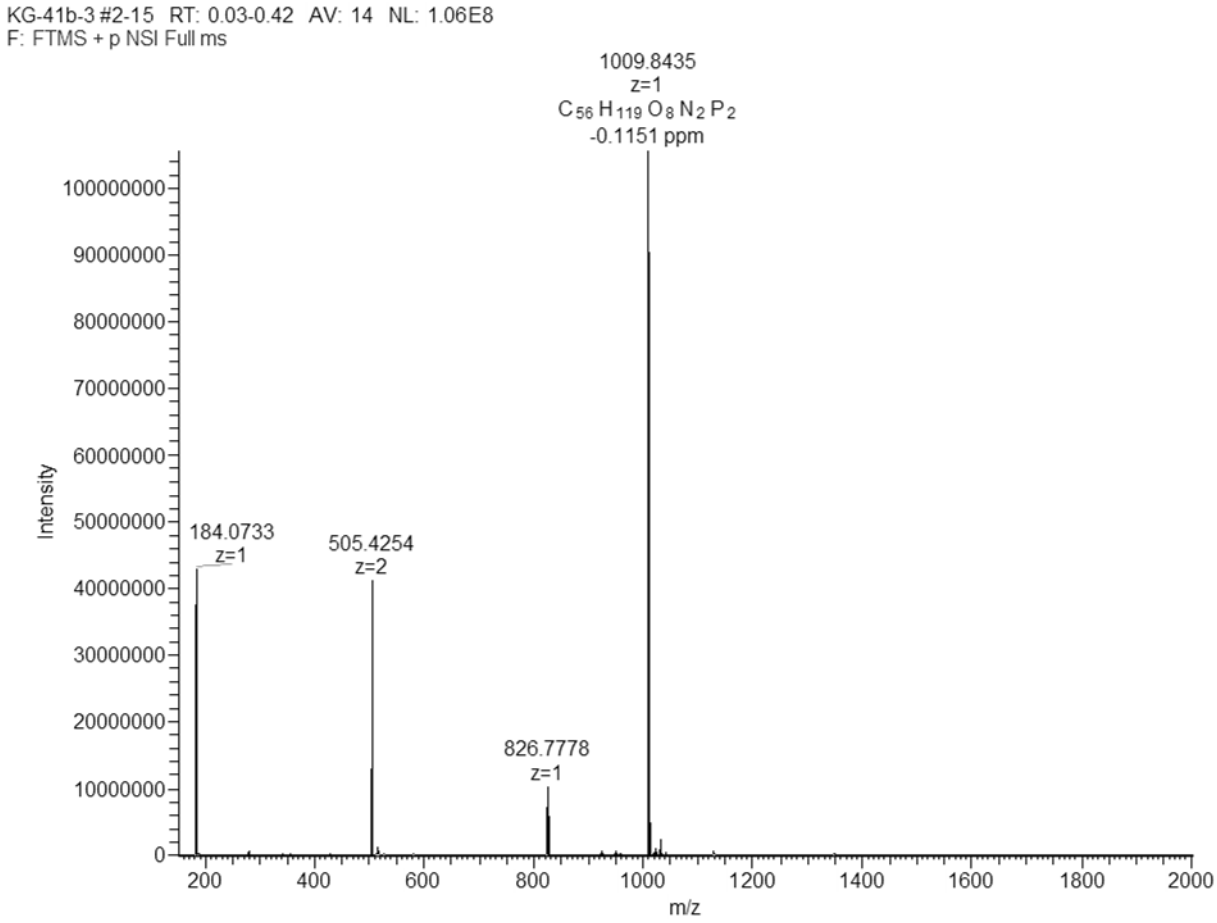
PC-C32(1,32C5)-PC *– ^{13}C NMR*



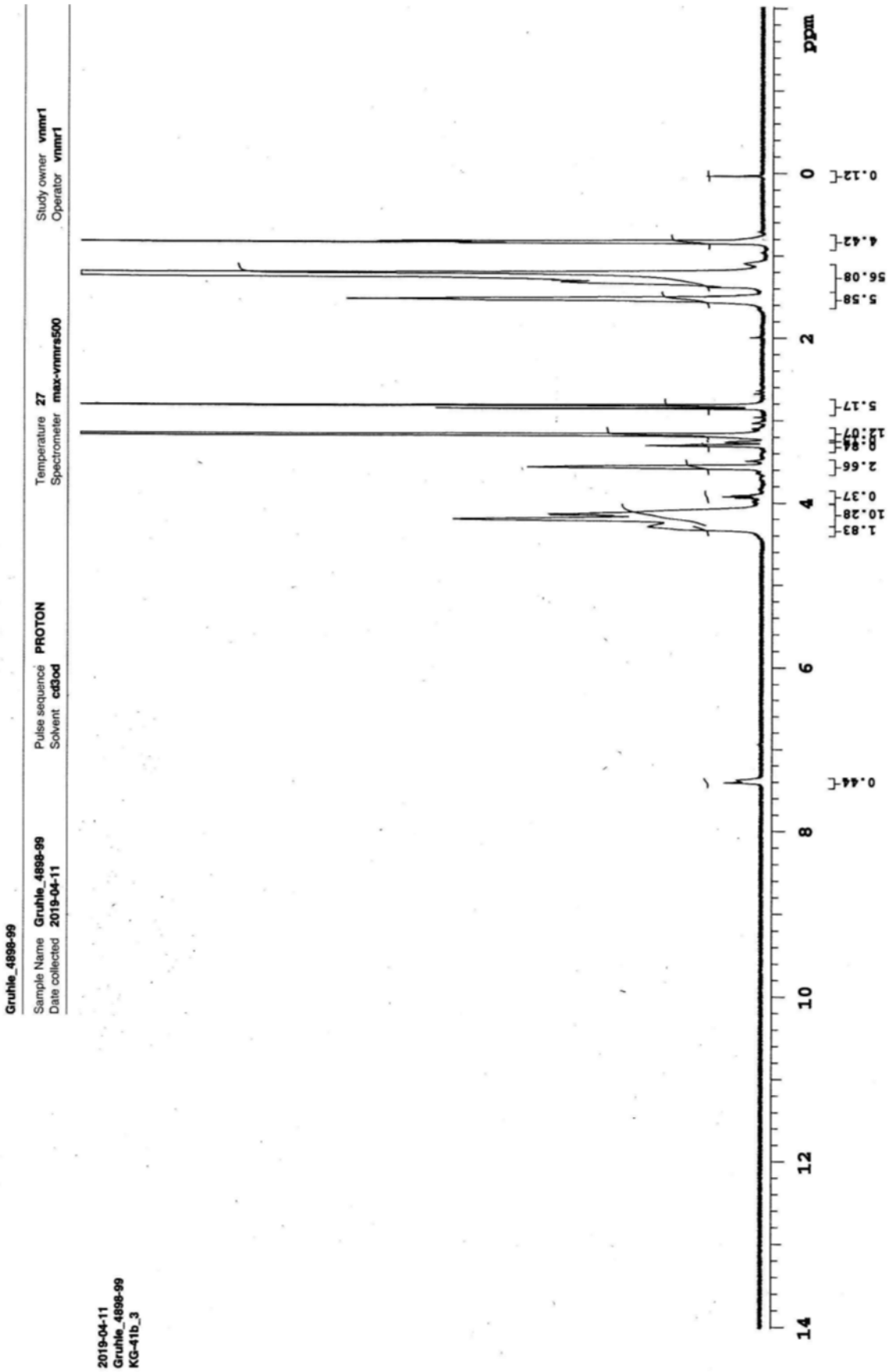
***PC-C32(1,32C7)-PC** – ESI-MS (positive mode)*



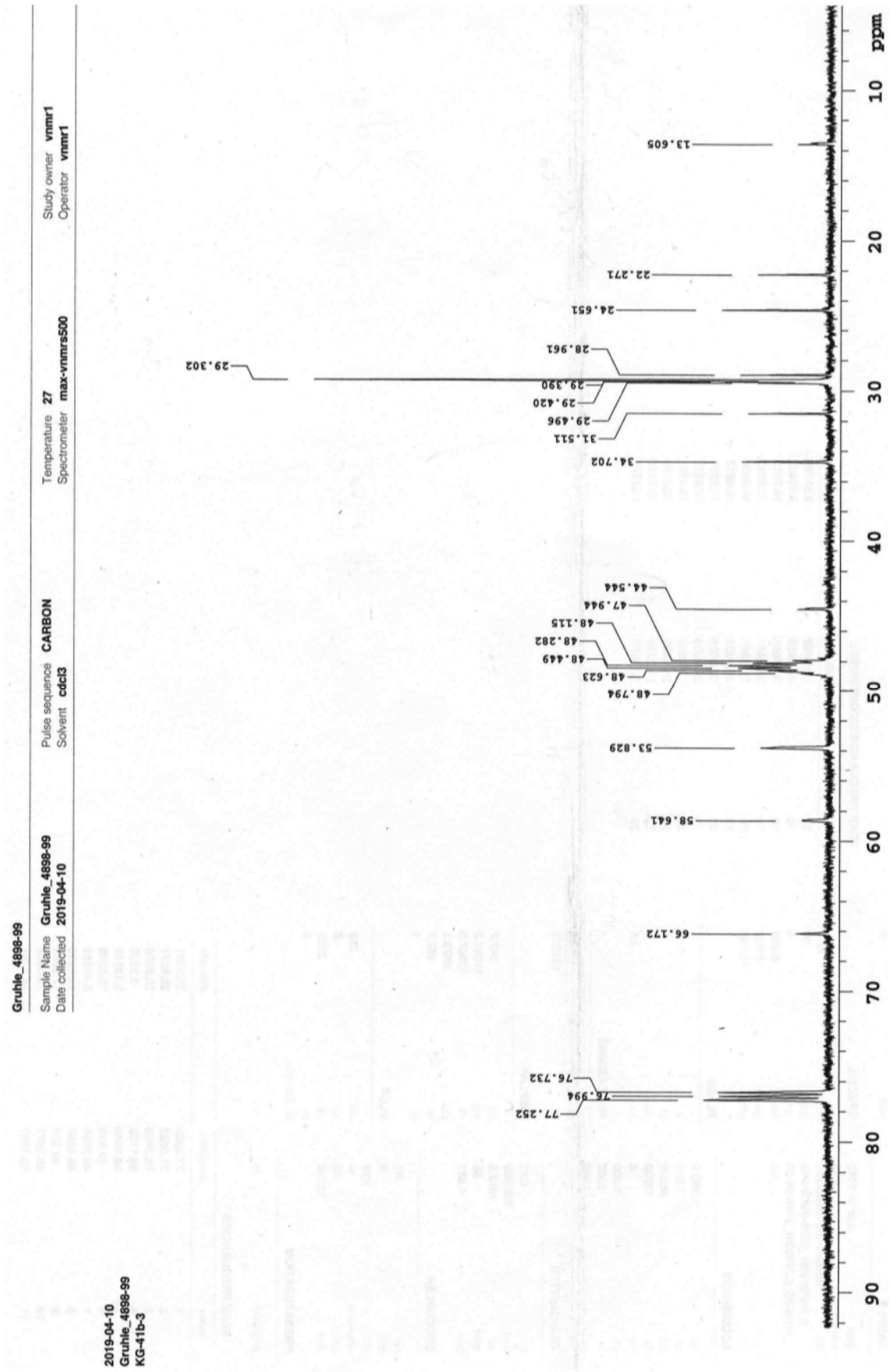
***PC-C32(1,32C7)-PC** – HRMS (positive mode)*



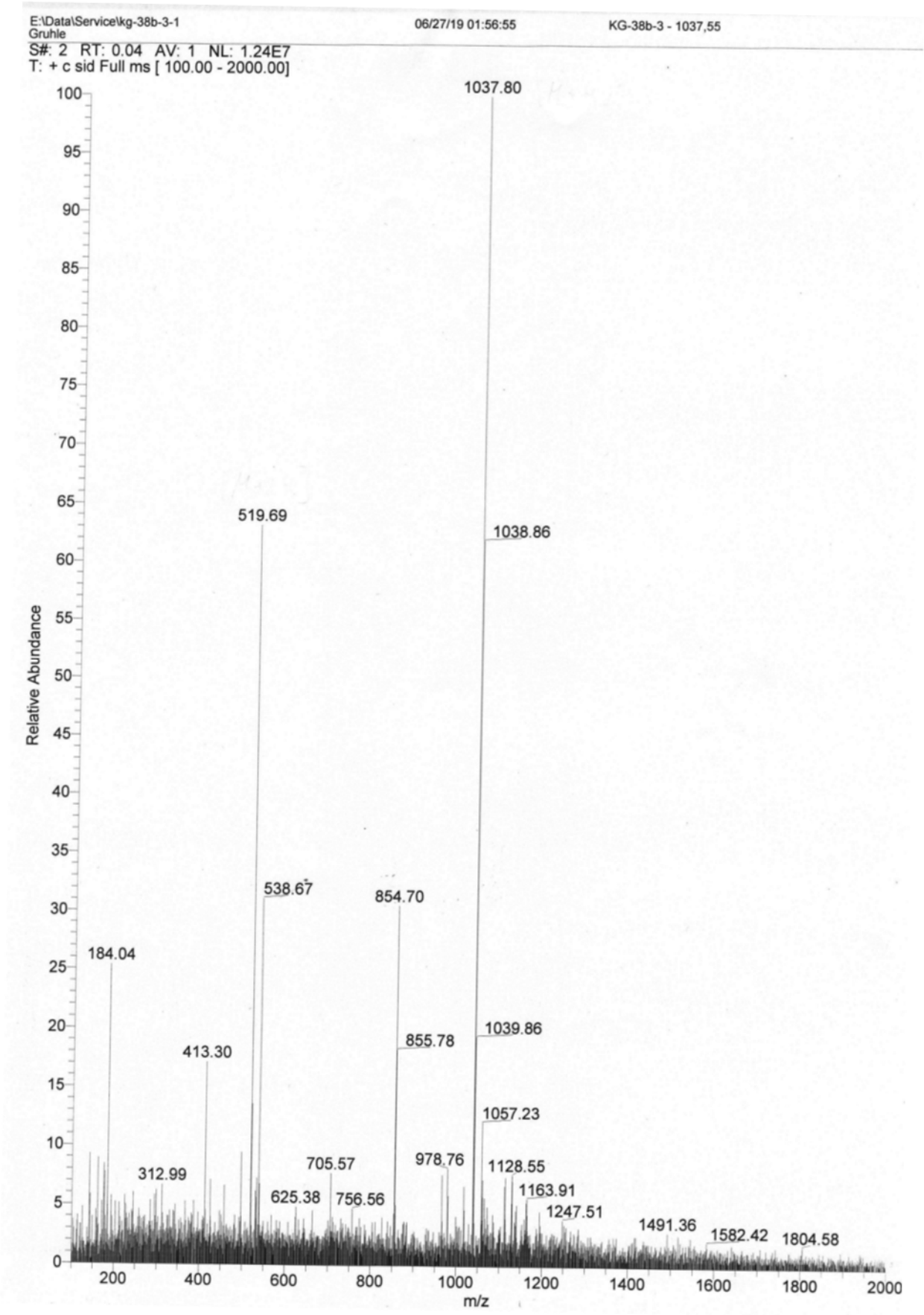
PC-C32(1,32C7)-PC *– ^{1}H NMR*



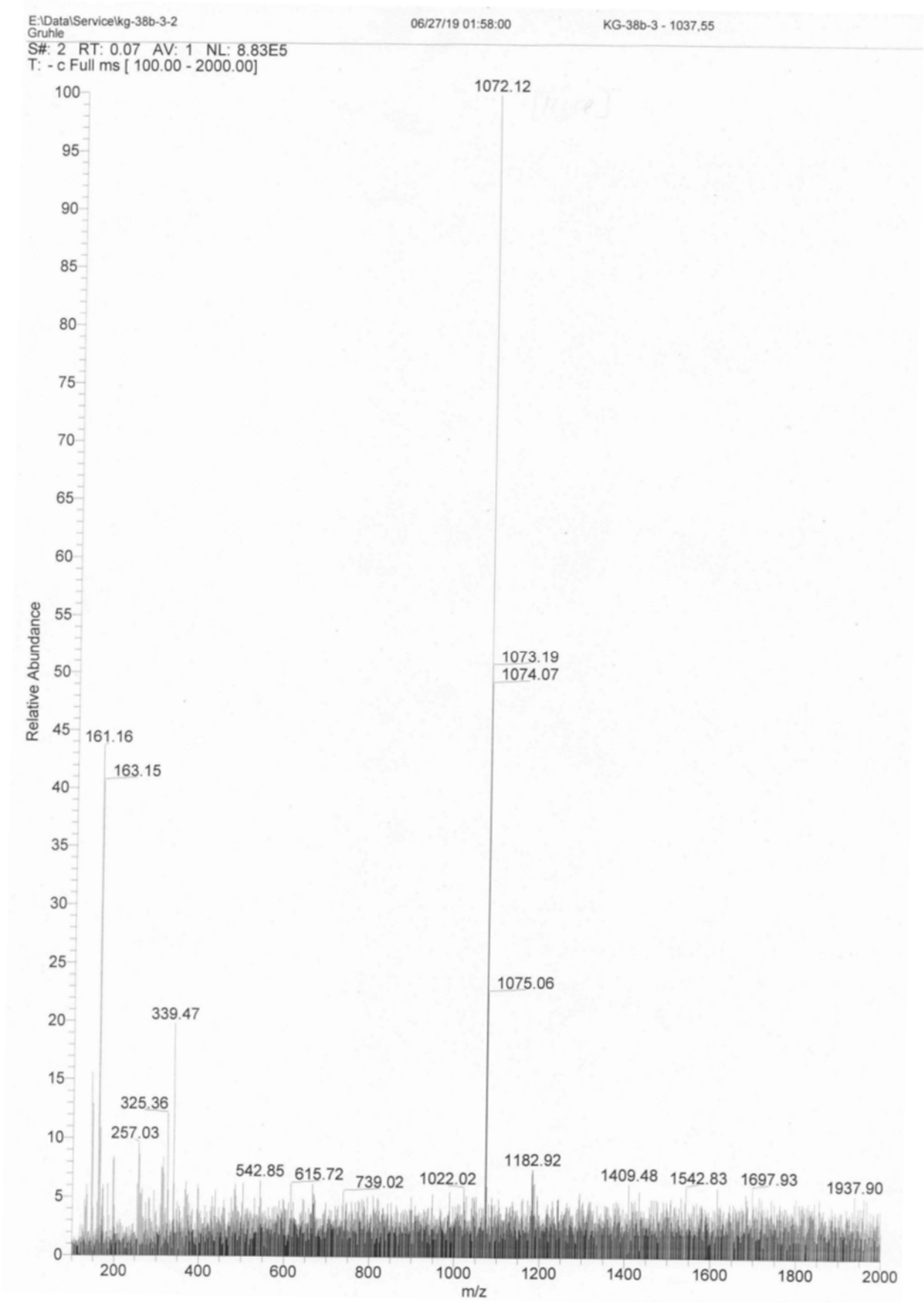
PC-C32(1,32C7)-PC *– ^{13}C NMR*



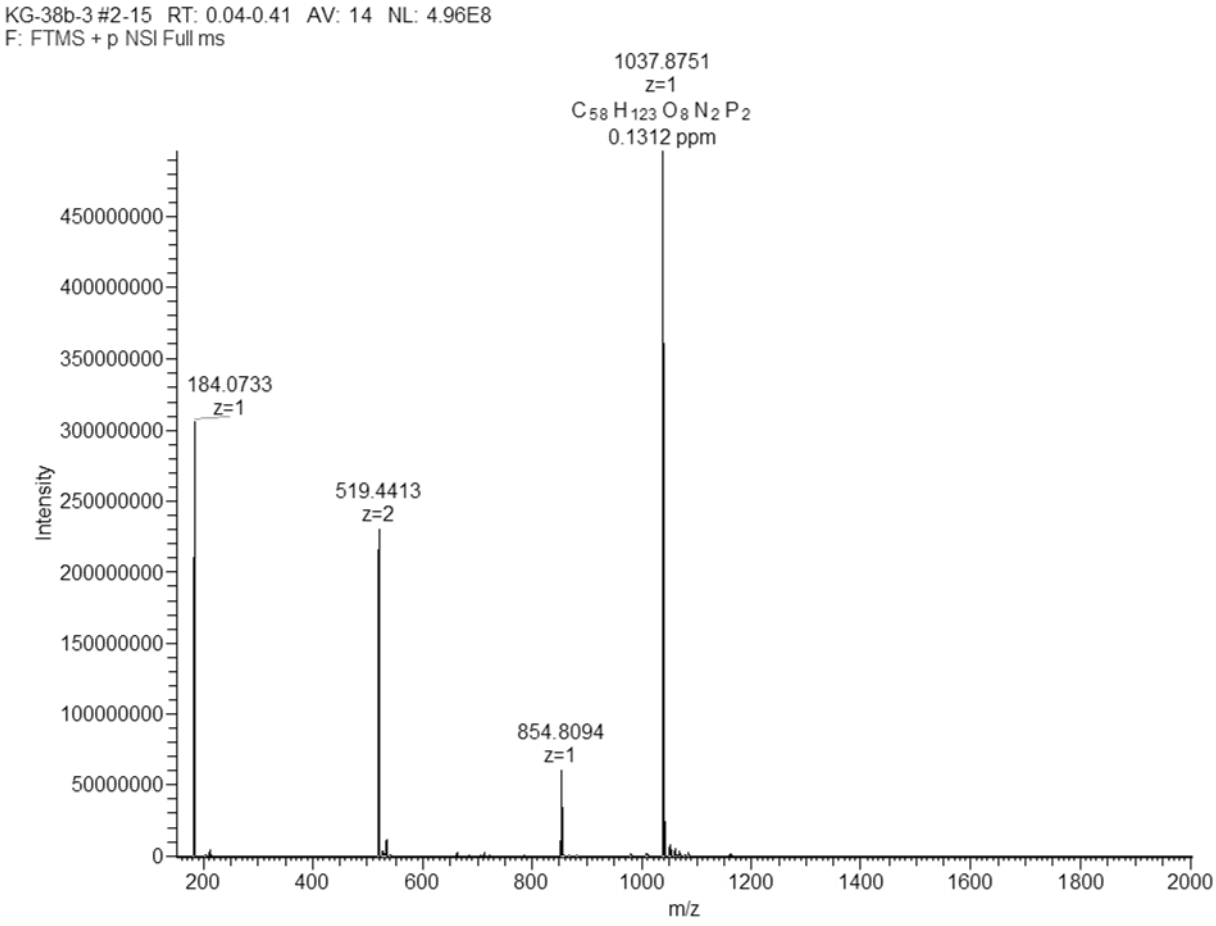
***PC-C32(1,32C8)-PC** – ESI-MS (positive mode)*



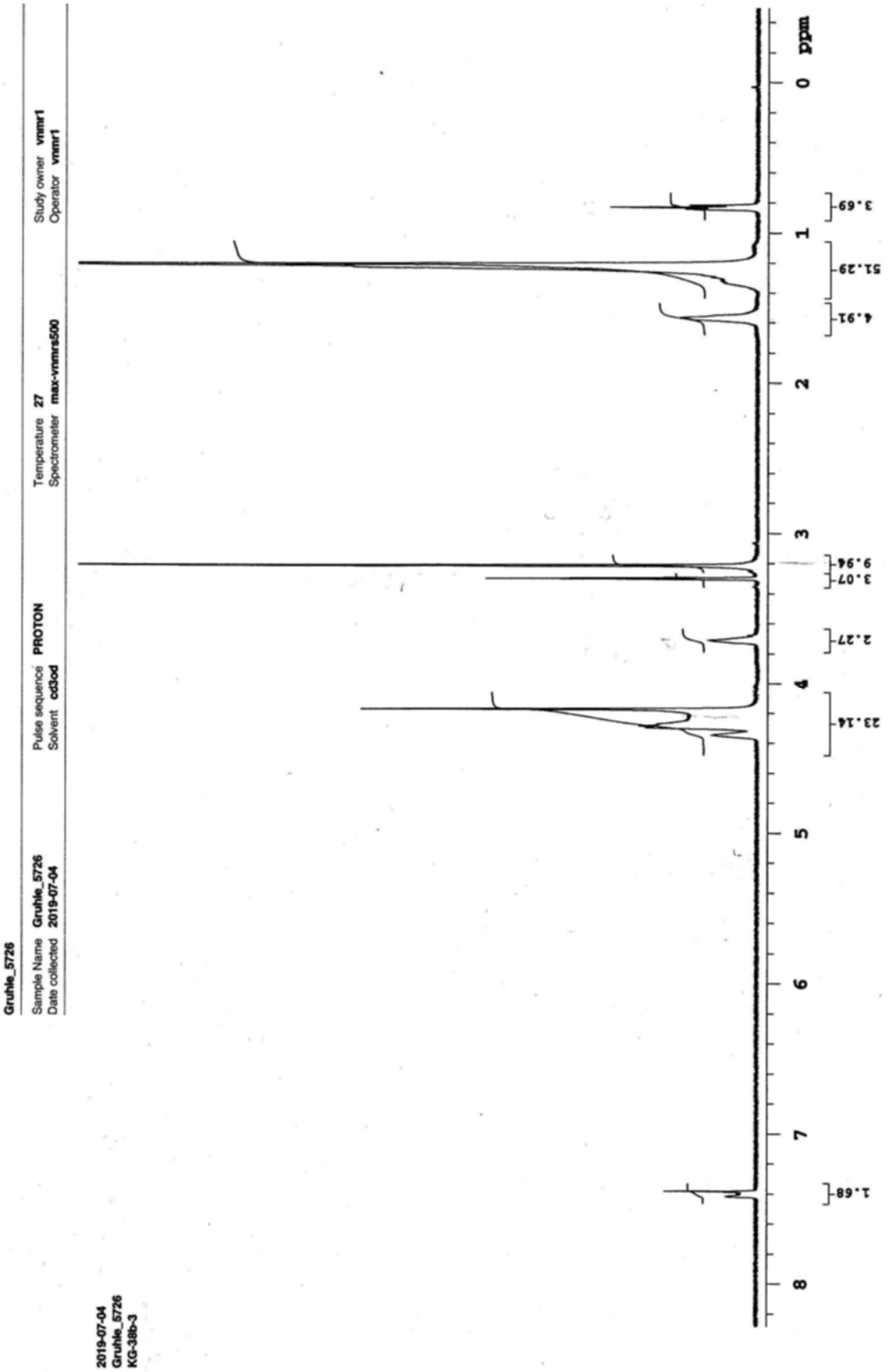
***PC-C32(1,32C8)-PC** – ESI-MS (negative mode)*



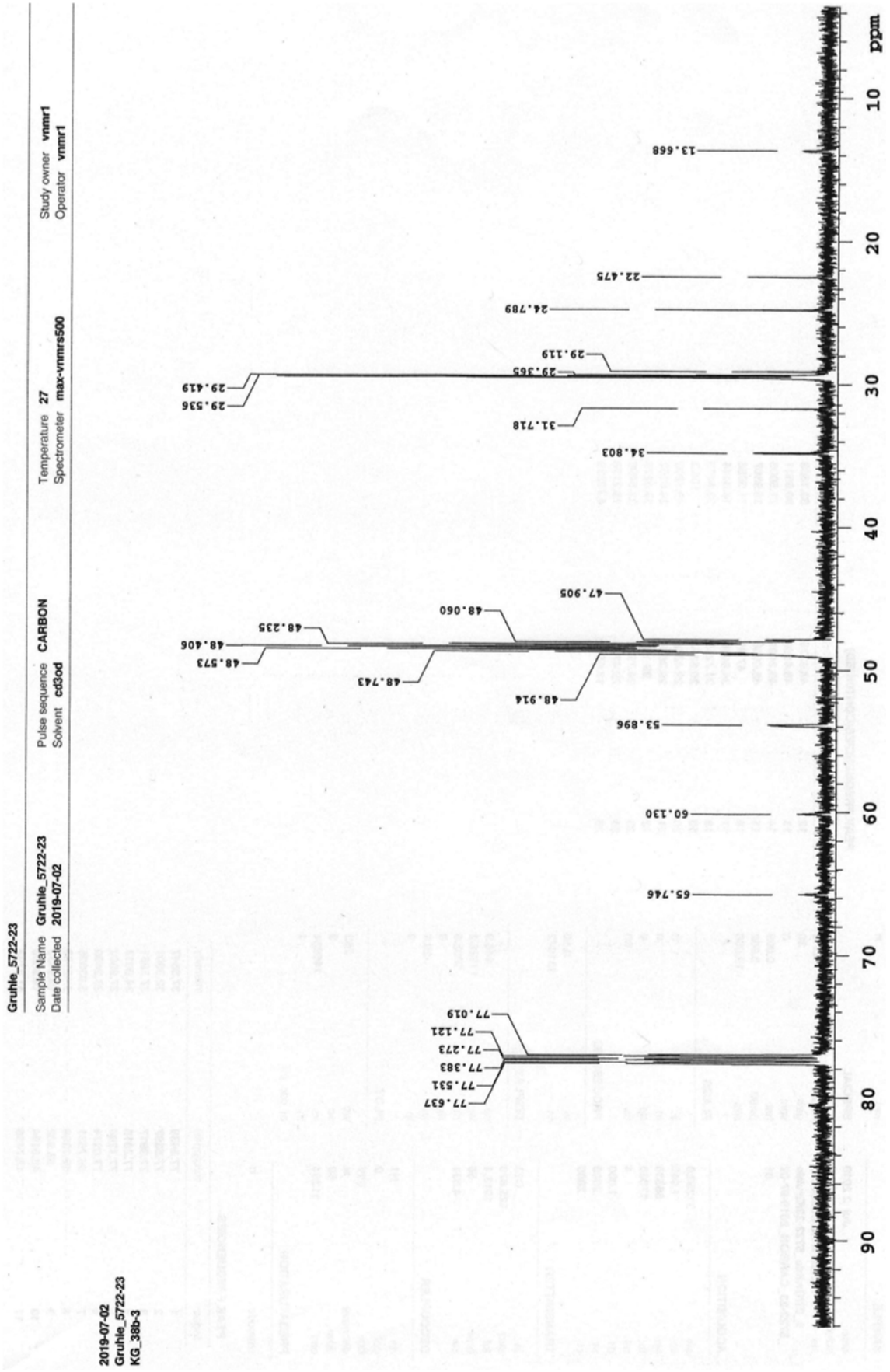
PC-C32(1,32C8)-PC *– HRMS (positive mode)*



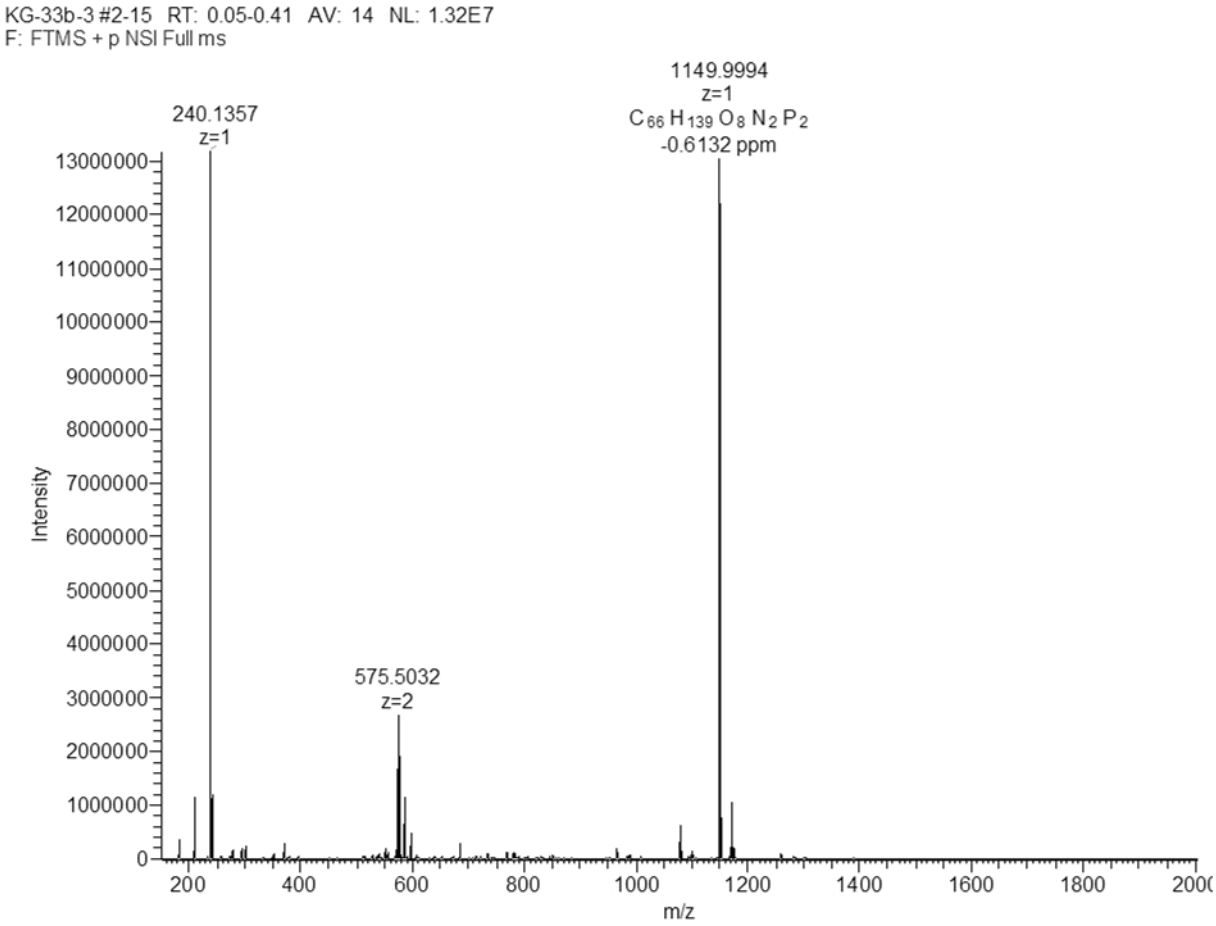
PC-C32(1,32C8)-PC *– ^{1}H NMR*



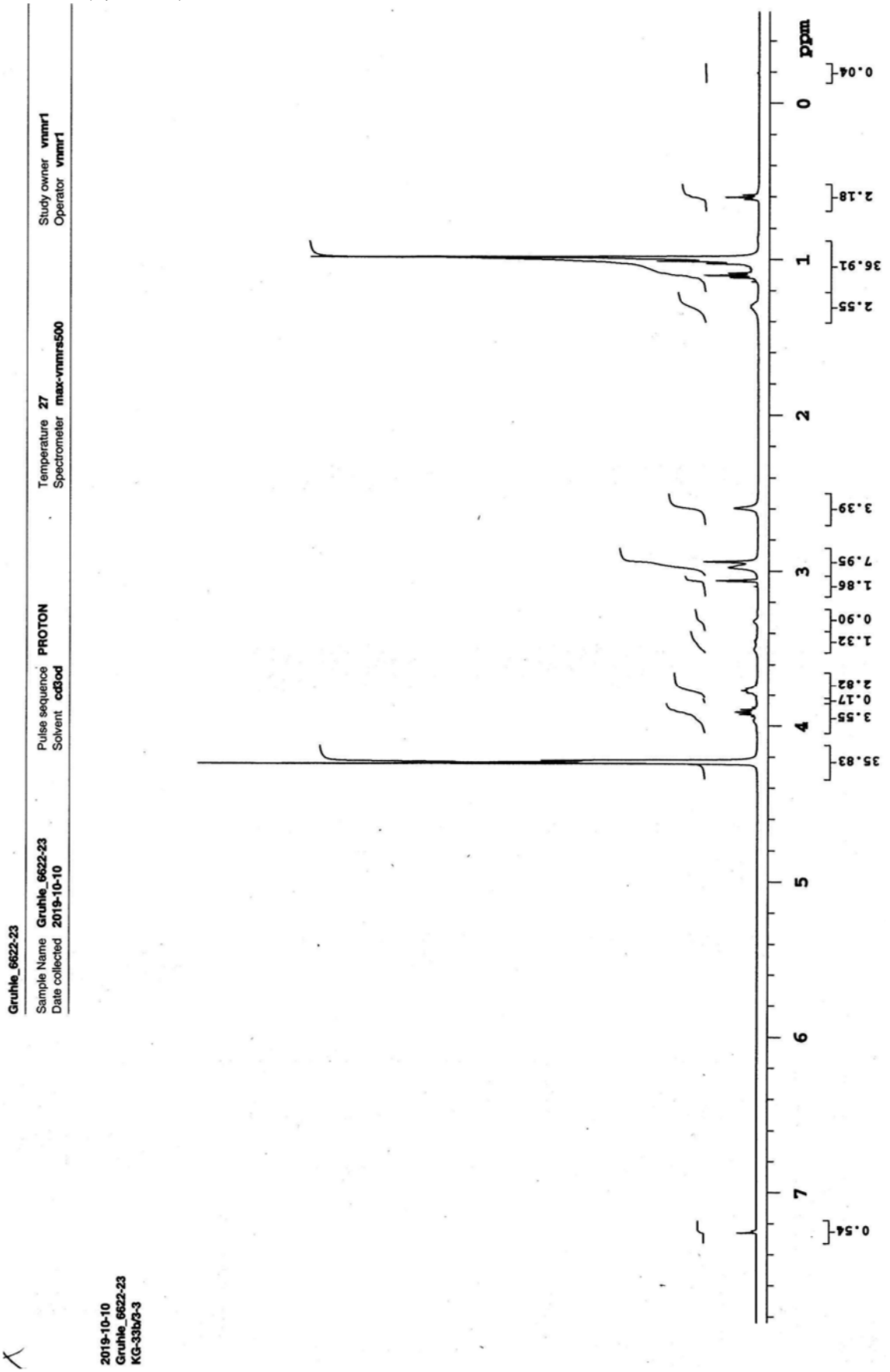
PC-C32(1,32C8)-PC *– ^{13}C NMR*



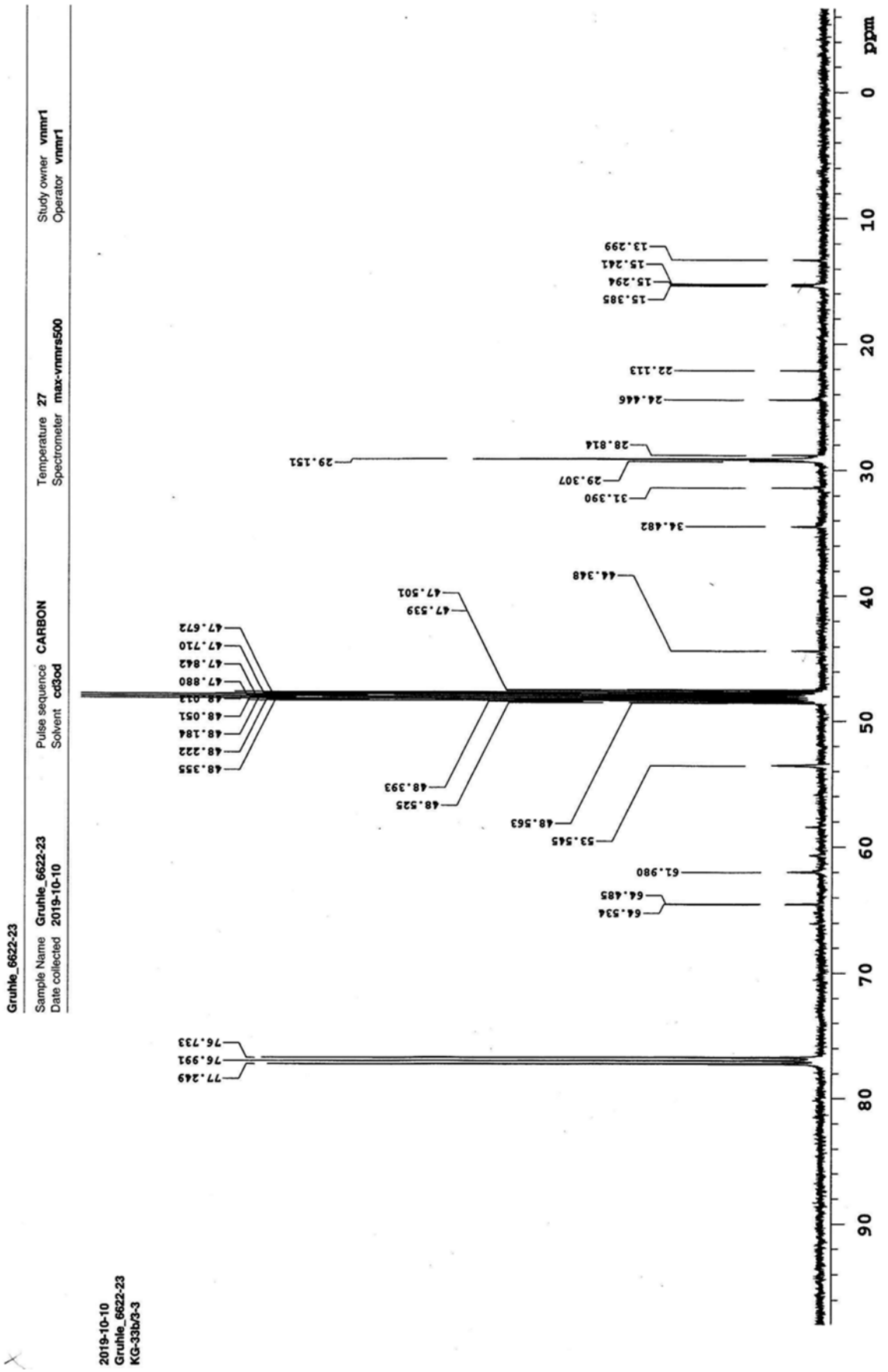
PC-C32(1,32C12)-PC *– HRMS (positive mode)*



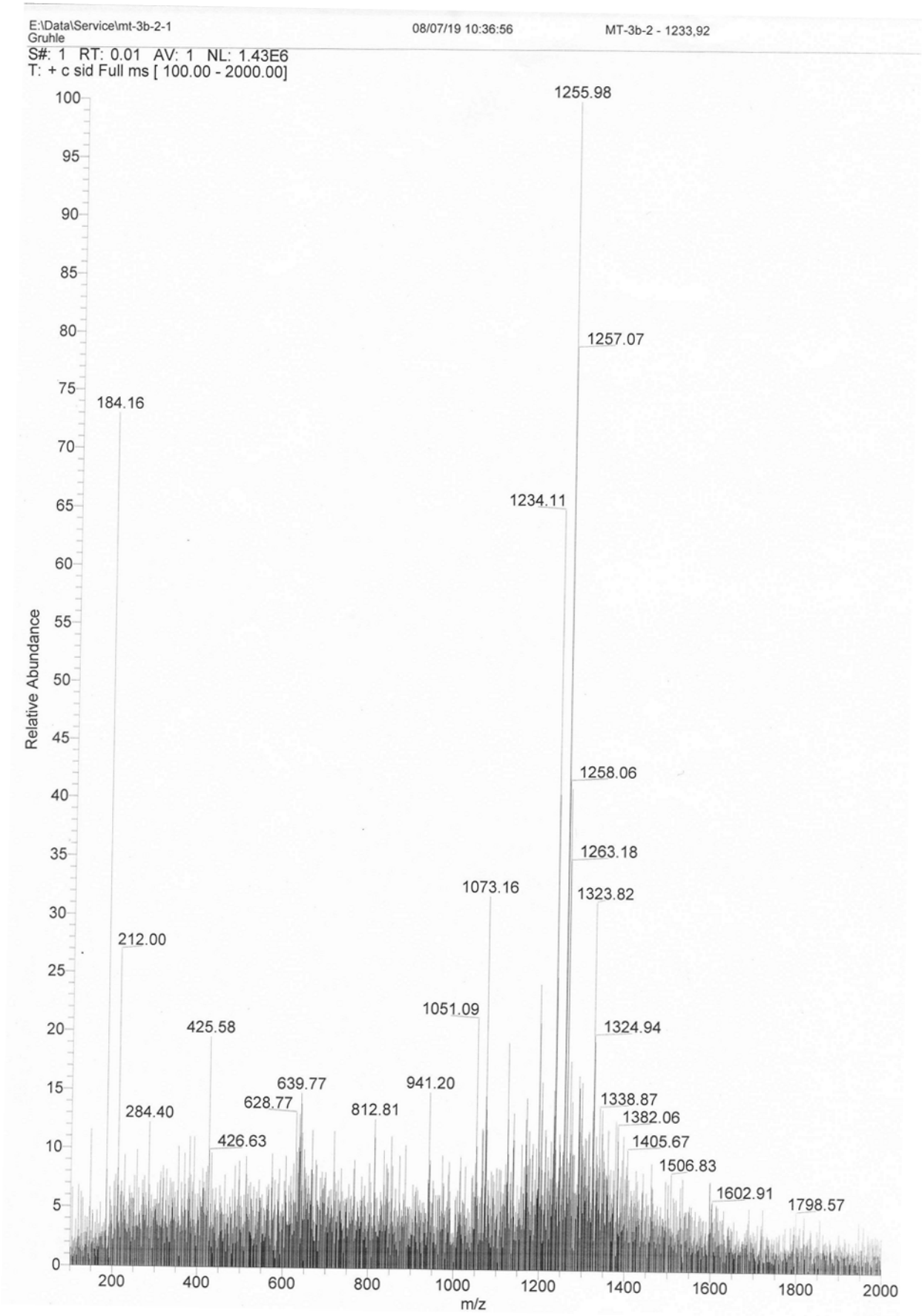
PC-C32(1,32C12)-PC *– ^{1}H NMR*



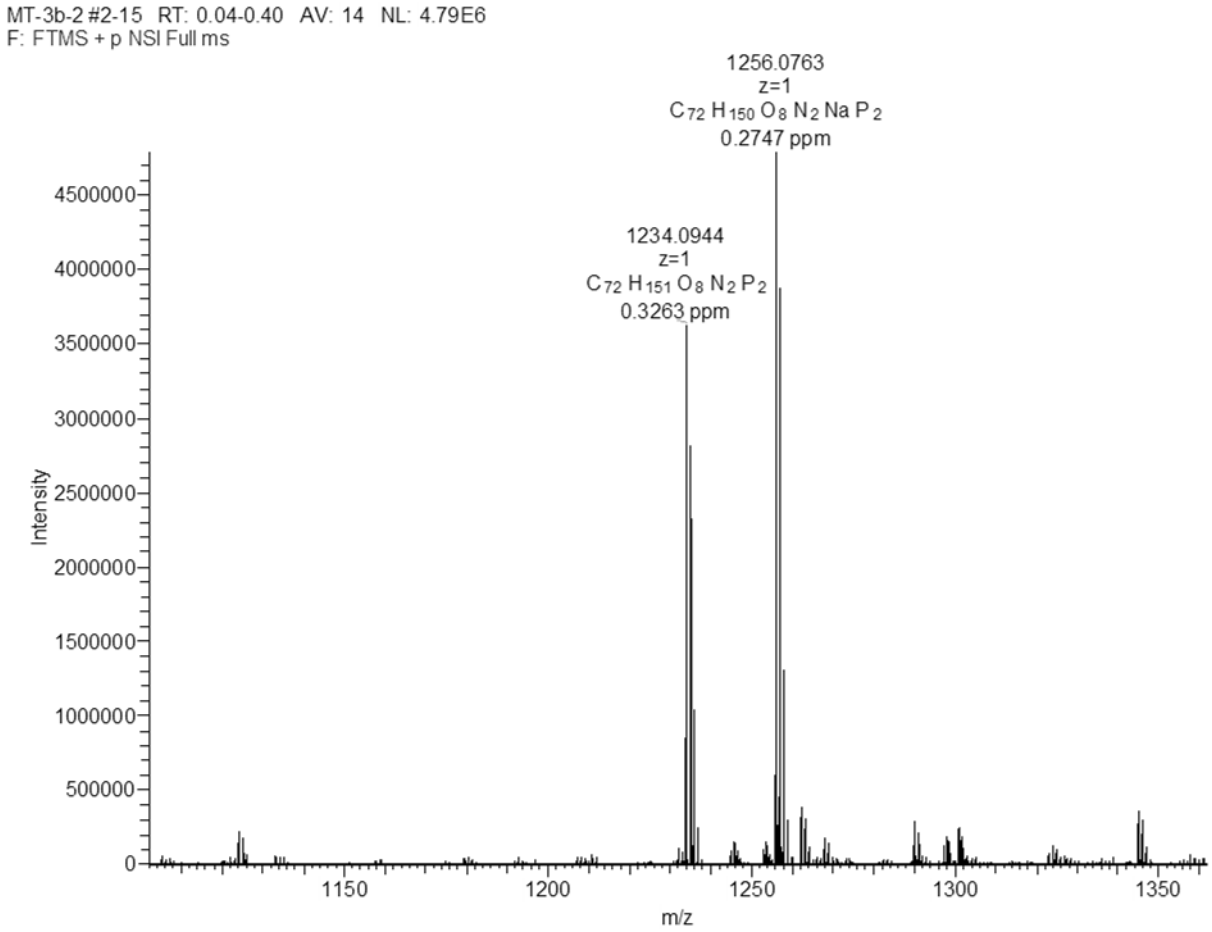
PC-C32(1,32C12)-PC *– ^{13}C NMR*



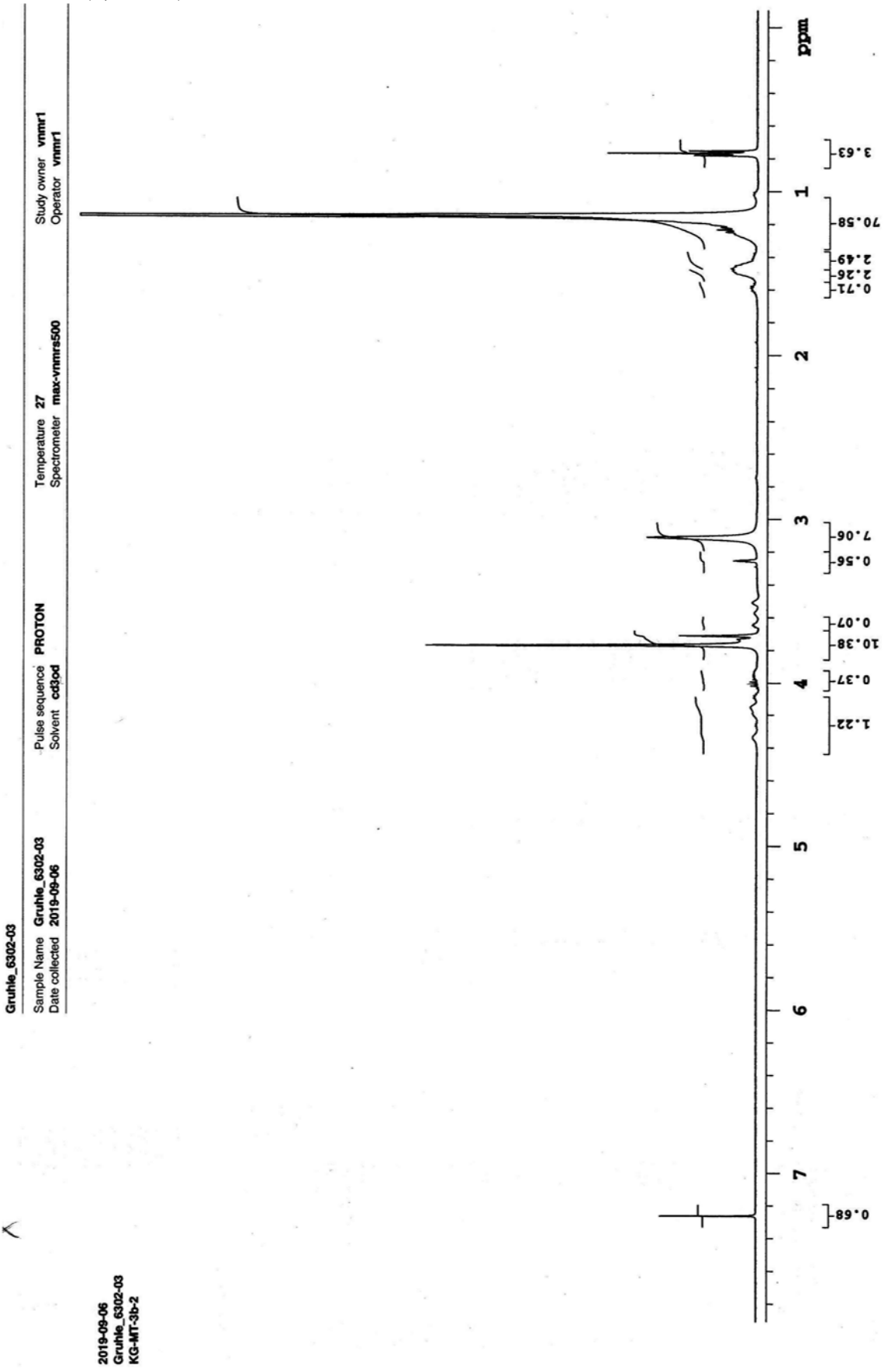
PC-C32(1,32C15)-PC *– ESI-MS (positive mode)*



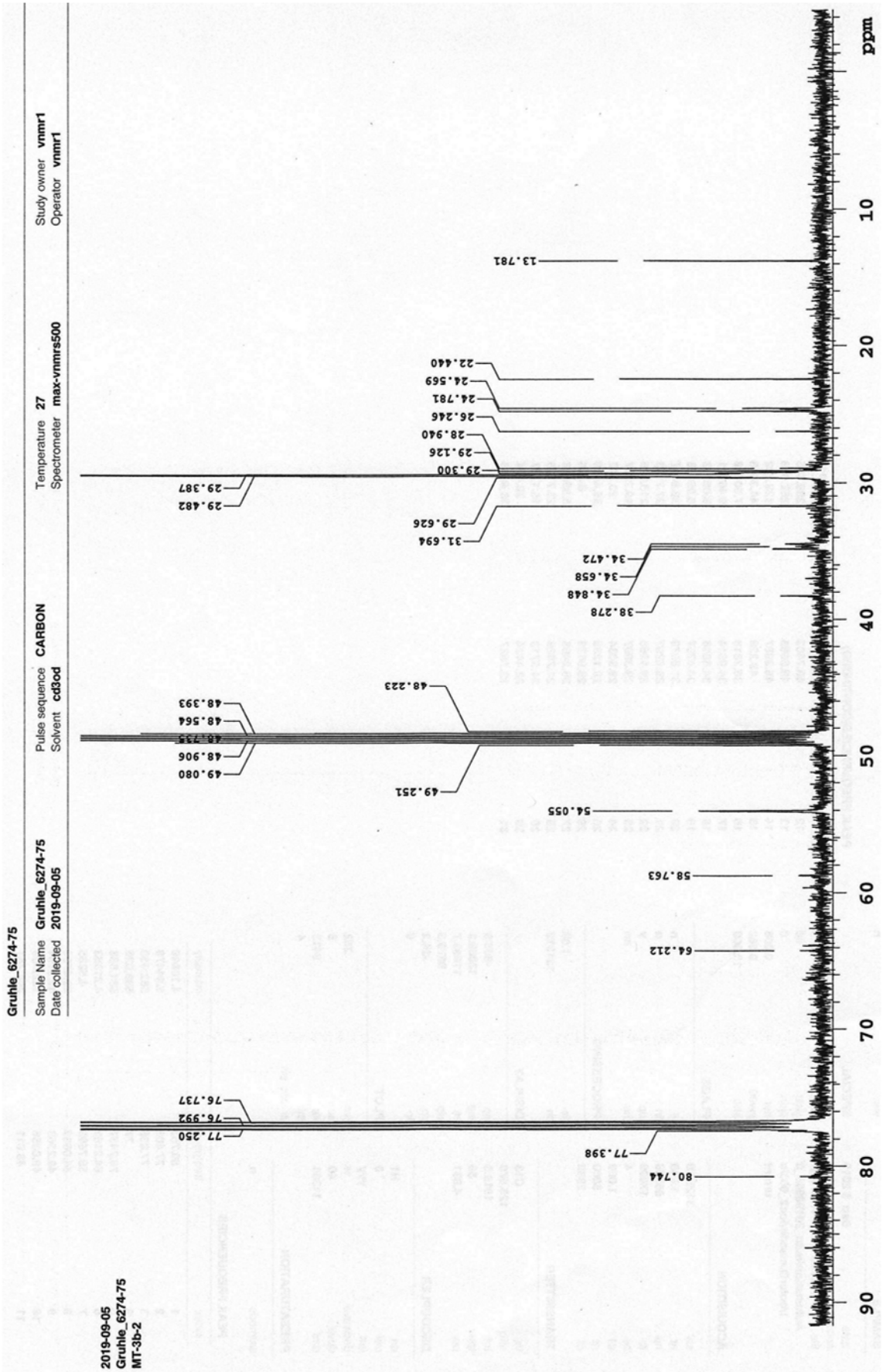
PC-C32(1,32C15)-PC *– HRMS (positive mode)*



PC-C32(1,32C15)-PC *– ^{1}H NMR*



PC-C32(1,32C15)-PC *– ^{13}C NMR*



6. References

1. K. Gruhle, S. Müller, A. Meister and S. Drescher, *Org. Biomol. Chem.*, 2018, **16**, 2711-2724.
2. I. A. Baser, *Fette, Seifen, Anstrichmittel*, 1972, **74**, 524-526.