Supporting Information

A Convergent Approach to Polycyclic Aromatic Hydrocarbons

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General Experimental Methods

Purification procedures were in accordance with the instructions in D. D. Perrin and W. L. F. Armarego, "Purification of Laboratory Chemicals", Fourth Edition, The Bath Press, Bath, 2002. All reactions were carried out under dry, oxygen free nitrogen. Flash chromatography was performed on silica gel (SDS, 60 Å C. C. 40-63 mm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on alumina plates pre-coated with silica gel (Merck silica gel, 60 F254), which were visualized by the quenching of UV fluorescence when applicable (λmax = 254 nm and/or 366 nm) and/or by staining with vanillin or anisadehyde in acidic ethanol followed by heating. Infrared spectra were recorded as solutions in CH2Cl2 using NaCl cells, on a Perkin-Elmer FT 2000. Absorption maxima (nmax) are reported in wavenumbers (cm^{-1}) and only selected peaks are reported. Magnetic resonance spectra were recorded at room temperature on a Bruker Avance DPX 400 instrument. Proton magnetic resonance spectra (1H NMR) were recorded at 400 MHz and coupling constants (*J*) are reported to ± 0.5 Hz. The following abbreviations were utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, hex = hexuplet, hept = heptuplet, oct = octuplet and m = multiplet. Carbon magnetic resonance spectra (13C NMR) were recorded in the same instrument at 100.6 MHz. Chemical shifts (δH, δC) are quoted in parts per million (ppm) and are referenced to TMS (0 ppm). Low-resolution mass spectra (*m*/*z*) were recorded by chemical ionization (CI/NH3) on a Hewlett-Packard HP 5989B and only report molecular species ([M+H]+, [M+NH4]+) and other major fragments. High-resolution mass spectra were recorded by positive electron impact ionization (EI+) at 70 e.V. on a JEOL JMS-GCmate II mass spectrometer. The quoted masses are accurate to ± 5 ppm. The names of the molecules that appear in the following pages were generated using either Beilstein AutoNom 2000 (CAS) or ChemBioDraw Ultra 10.0.

List of the Abbreviations Used

AcOEt	Ethyl acetate
DCM	Dichloromethane
DLP	Dilauroyl peroxide
EP	Petroleum ether
EtOH	Ethanol
IR	Infrared
iPrOH	Isopropanol
Mp	Melting point
P-TSA	p-Toluenesulfonic acid
RT	Room temperature

Experimental Procedures and Spectroscopic Data

General procedure A for the preparation of xanthates

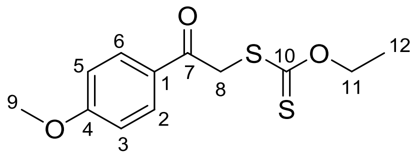
To a solution of the corresponding bromo-acetophenone (1.0 eq) in acetone (1 mL.mmol^{-1}) under a nitrogen at 0 °C was added potassium O-ethylxanthate (1.2 eq) portionwise. The mixture was stirred for 15 min and then quenched by the addition of water (1 mL.mmol^{-1}). The solvent was removed under reduced pressure and the residue was diluted with ethyl acetate (5 mL.mmol^{-1}). The organic layer was separated and the aqueous layer extracted with ethyl acetate (5 mL.mmol^{-1}). The combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified by recrystalisation in a mixture of hexane and ethyl acetate.

General procedure B for radical addition/cyclisation reactions

A stirred solution of xanthate (1.0 eq) and olefin (2.0 eq) in ethyl acetate (3 mL.mmol^{-1} with respect to the xanthate) was refluxed for 15 minutes under a nitrogen atmosphere. Dilauroyl peroxide (DLP) was then added in 20 %mol portions every 60 minutes until complete consumption of the starting material xas observed. The reaction mixture was then cooled to room temperature and evaporated to dryness under reduced pressure. The crude residue was purified by flash chromatography on silica gel to yield the desired compound.

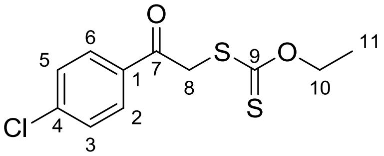
General procedure C for the addition of phenyl lithium to ketones

To a solution of iodobenzene (3.3 eq) in diethylether (1.0 ml.mmol^{-1}) at -78 °C under a nitrogen atmosphere was added *n*BuLi (3.0 eq) dropwise. The solution was stirred for 60 min at -78 °C. After this time a solution of the ketone (1.0 eq) in diethylether (0.15 mL.mmol^{-1}) was added dropwise to the mixture. After 15 min the solution was allowed to warm up to RT and the reaction was stirred for 1 h. Water (5 mL.mmol^{-1}) and NH_4Cl (sat. aq.) (5 mL.mmol^{-1}) were added to the reaction mixture. The layers were separated and the aqueous phase extracted further with DCM three times (5 mL.mmol^{-1}). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel to give the desired product.



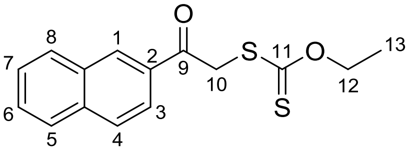
Compound **3a**: O-ethyl S-2-(4-methoxyphenyl)-2-oxoethyl carbonodithioate

Following the general procedure **A**, the reaction was carried out with 2-bromo-1-(4-methoxyphenyl)ethanone (12.0 g, 52.4 mmol). Recrystalisation afforded the desired product as a yellow solid (12.2 g, 45.0 mmol, 86 %). **^{1}H NMR** (δ, ppm) ($CDCl_3$, 400 MHz): 8.01 (m, 2H, C_2H & C_6H); 6.96 (m, 2H, C_3H & C_5H); 4.63 (q, 2H, J = 7.1 Hz, $OC_{11}H_2$); 4.62 (s, 2H, SC_8H_2); 3.88 (s, 3H, OC_9H_3); 1.39 (t, 3H, J = 7.1 Hz, $C_{12}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 213.48 ($C_{10}S$); 190.78 (C_7O); 164.00 (C_4O); 130.82 (C_2H & C_6H); 128.78 (C_1); 113.96 (C_3H & C_5H); 70.61 ($C_{11}H_2O$); 55.54 (OC_9H_3); 43.36 (C_8H_2); 13.73 ($C_{12}H_3$). **IR** (cm^{-1}) (CCl_4): 2986, 2961, 2938, 2840, 1681, 1602, 1222. **HRMS** (EI+) calcd for $C_{12}H_{14}O_3S_2$ 270.0384, found: 270.0392. **Mp**: 67 °C.



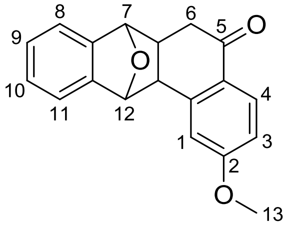
Compound **3b**: O-ethyl S-2-(4-chlorophenyl)-2-oxoethyl carbonodithioate

Following the general procedure **A**, the reaction was carried out with 2-bromo-1-(4-chlorophenyl)ethanone (9.00 g, 38.5 mmol). Recrystalisation afforded the desired product as a white solid (8.79 g, 32.0 mmol, 83 %). **^{1}H NMR** (δ, ppm) ($CDCl_3$, 400 MHz): 8.02 (d, 2H, J = 8.7 Hz, C_2H & C_6H); 7.53 (d, 2H, J = 8.7 Hz, C_3H & C_5H); 4.69 (q, 2H, J = 7.1 Hz, $OC_{10}H_2$); 4.68 (s, 2H, SC_8H_2); 1.45 (t, 3H, J = 7.1 Hz, $C_{11}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 213.18 (C_9S); 191.41 (C_7O); 140.39 (C_1); 130.17 (C_4Cl); 129.91 (C_2H & C_6H); 129.23 (C_3H & C_5H); 71.02 ($C_{10}H_2O$); 43.54 (C_8H_2); 13.73 ($C_{11}H_3$). **IR** (cm^{-1}) (CCl_4): 2987, 2902, 1690, 1590, 1221. **HRMS** (EI+) calcd for $C_{12}H_{14}O_3S_2$ 270.0384, found: 270.0373. **Mp**: 69 °C (decomp.).



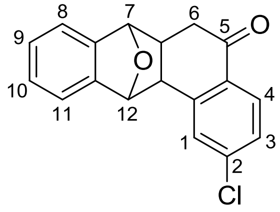
Compound **3c**: O-ethyl S-2-(naphthalen-2-yl)-2-oxoethyl carbonodithioate

Following the general procedure **A**, the reaction was carried out with 2-bromo-1-(naphtalen-2-yl)ethanone (11.1 g, 44.58 mmol). Recrystalisation afforded the desired product as a yellow solid (11.4 g, 49.3 mmol, 88 %). **^{1}H NMR** (δ, ppm) ($CDCl_3$, 400 MHz): 8.57 (s, 1H, C_1H); 8.48 (dd, 1H, J_1 = 1.2 Hz, J_2 = 8.5 Hz, C_3H); 8.00 (d, 1H, J = 8.0 Hz, C_5H); 7.93 (d, 1H, J = 8.7 Hz, C_4H); 7.90 (d, 1H, J = 8.1 Hz, C_8H); 7.63 (t, 1H, J = 7.4 Hz, C_7H); 7.58 (t, 1H, J = 7.4 Hz, C_6H); 4.80 (s, 2H, $C_{10}H_2$); 4.66 (q, 2H, J = 7.1 Hz, $O_{C12}H_2$); 1.40 (t, 3H, J = 7.1 Hz, $C_{13}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 213.34 ($C1_1S$); 192.27 ($C_{10}O$); 135.84 (C_2); 133.16 (C_{IV}); 132.43 (C_{IV}); 130.34 (C_1H); 129.68 (C_5H); 128.86 (C_7H); 128.72 (C_4H); 127.83 (C_8H); 127.00 (C_6H); 123.90 (C_3H); 70.72 ($OC_{12}H_2$); 43.61 ($C_{10}H_2$); 13.74 ($C_{13}H_3$). **IR** (cm^{-1}) (CCl_4): 3063, 2987, 2902, 1685, 1220. **HRMS** (EI+) calcd for $C_{15}H_{14}O_2S_2$ 290.0435, found: 290.0422. **Mp**: 98 °C.



Compound **4a**: 7,12-epoxy-5,6,6A,7,12,12A-hexahydro-2-methoxybenz(a)anthrac-5-one

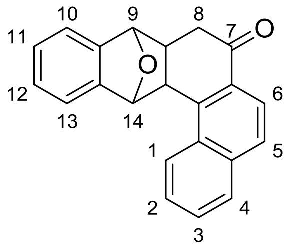
Following the general procedure **B**, the reaction was carried out with xanthate **3a** (400 mg, 1.48 mmol). Total consumption of starting material took 160 %mol of DLP. Purification by column chromatography (EP/Ether from 90/10 to 60/40) yielded the desired product as a white solid (189 mg, 0.647 mmol, 43 %).
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.86 (d, 1H, J = 8.5 Hz, C_4H); 7.39 – 7.37 (m, 1H, $C_{11}H$); 7.34 – 7.32 (m, 1H, C_8H); 7.25 – 7.23 (m, 2H, C_9H & $C_{10}H$); 6.92 (d, 1H, J = 2.4 Hz, C_1H); 6.89 (dd, 1H, $_{J1}$ = 2.5 Hz, J_2 = 8.5 Hz, C_3H); 5.18 (s, 1H, $C_{12}H$); 5.05 (s, 1H, C_7H); 3.19 (d, 1H, J = 7.9 Hz, $C_{12'}H$); 2.89 (dd, 1H, J_1 = 3.4 Hz, J_2 = 15.6 Hz, C_6H), 2.82 (dd, 1H, J_1 = 8.2 Hz, J_2 = 15.6 Hz, C_6H); 2.52 (ddd, 1H, J_1 = 3.3 Hz, J_2 = 7.9 Hz, J_3 = 8.3 Hz, $C_{6'}H$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 196.60 (C_5O); 163.74 (C_2); 145.17 (C_{IV}); 145.03 (C_{IV}); 144.49 (C_{IV}); 128.21 (C_4H); 128.05 (C_{IV}); 127.21 & 127.132 (C_8H & $C_{11}H$); 119.35 (C_8H); 119.24 ($C_{11}H$); 113.43 (C_1H); 112.67 (C_3H); 87.80 (OC_7H); 86.46 ($OC_{12}H$); 55.54 ($OC_{13}H_3$); 44.11 ($C_{12'}$); 41.81 (C_6H_2); 37.66 ($C_{6'}H$). **IR** (cm^{-1}) (CCl_4): 3002, 2942, 2839, 1692, 1602, 1271. **HRMS** (EI+) calcd for $C_{19}H_{16}O_3$ 292.1099, found: 292.1102. **Mp**: 142 °C.



Compound **4b**: 2-chloro-7,12-epoxy-5,6,6A,7,12,12A-hexahydrobenz(a)anthrac-5-one

Following the general procedure **B**, the reaction was carried out with xanthate **3b** (1.88 g, 13.1 mmol). Total consumption of starting material took 160 %mol of DLP. Purification by column chromatography (EP/Ether: 85/15) yielded the desired product as a slightly yellow solid (713 mg, 2.40 mmol, 36 %).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.80 (d, 1H, J = 8.3 Hz, C_4H); 7.48 (d, 1H, J = 1.7 Hz, C_1H); 7.40 – 7.38 (m, 1H, $C_{11}H$); 7.40 – 7.33 (m, 2H); 7.27 – 7.24 (m, 2H); 5.18 (s, 1H, $OC_{12}H$); 5.02 (s, 1H, OC_7H); 3.21 (d, 1H, J = 7.8 Hz; $C_{12'}H$); 2.93 (dd, 1H, J_1 = 2.8 Hz, J_2 = 15.4 Hz, C_6H_2); 2.81 (dd, 1H, J_1 = 8.3 Hz, J_2 = 15.4 Hz, C_6H_2); 2.55 (ddd, 1H, J_1 = 2.8 Hz, J_2 = 8.1 Hz, J_3 = 8.1 Hz, $C_{6'}H$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 196.70 (C_5O); 144.88 (C_{IV}); 144.66 (C_{IV}); 144.07 (C_{IV}); 139.50 (C_{IV})133.02 (C_{IV}); 128.83 (C_1H); 127.44 (CH); 127.39 (CH); 127.32 (2CH); 119.37 (2C, C_8H & $C_{11}H$); 87.61 (OC_7H); 86.32 ($OC_{12}H$); 43.81 ($C_{12'}H$); 41.94 (C_6H_2); 37.87 ($C_{6'}H$). **IR** (cm^{-1}) (CCl_4): 2928, 2856, 1706, 1595, 1282. **HRMS** (EI+) calcd for $C_{19}H_{16}O_3$ 292.1099, found: 296.0604. **Mp**: 195 °C.

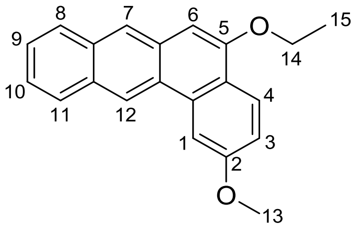


Compound **4c** : 9,14-epoxy-7,8,8A,9,14,14A-hexahydronaphth(1,2-a)anthrac-7-one

Following the general procedure **B**, the reaction was carried out with xanthate **3c** (1.74 g, 6.00 mmol). Total consumption of starting material took 160 %mol of DLP. Purification by column chromatography (EP/Ether from 95/5 to 80/20) yielded the desired product as a slightly yellow solid (424 mg, 1.36 article8 mmol, 23 %).

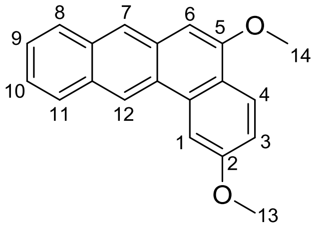
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.16 (d, 1H, J = 8.2 Hz, C_1H); 7.97 (d, 1H, J = 8.5 Hz, C_6H); 7.96 - 7.94 (m, 1H, C_4H); 7.84 (d, 1H, J = 8.5 Hz, C_5H); 7.73 – 7.65 (m, 2H, C_2H & C_3H); 7.52 – 7.50 (m, 1H, $C_{13}H$); 7.41 – 7.39 (m, 1H, $C_{10}H$); 7.34 – 7.27 (m, 2H, $C_{11}H$ & $C_{12}H$); 4.00 (s, 1H, $C_{14}H$); 3.98 (s, 1H, C_9H); 7.85 (d, 1H, J = 7.8 Hz, $C_{14'}H$); 3.07 (dd, 1H, J_1 = 1.9 Hz, J_2 = 15.6 Hz, C_8H_2); 2.93 (dd, 1H, J_1 = 8.9 Hz, J_2 = 15.6 Hz, C_8H_2); 2.71 – 2.66 (m, 1H, $C_{8'}H$). **^{13}C**

NMR (δ, ppm) ($CDCl_3$, 100.6 MHz): 197.86 (C_7O); 145.25 ($C_{9'}$); 144.38 ($C_{13'}$); 140.14 (C_{IV}); 136.23 (C_{IV}); 132.07 (C_{IV}); 131.13 (C_{IV}); 129.47 (C_4H); 127.88 (CH); 127.46 (CH); 127.39 (CH); 127.32 (2C, CH); 124.00 (C_1H); 122.24 (C_6H); 119.51 ($C_{10}H$); 119.10 ($C_{13}H$); 86.81 (${}_{C14}H$), 86.56 (C_9H); 41.45 (C_8H_2); 40.00 ($C_{14'}H$); 37.40 ($C_{8'}H$). **IR** (cm^{-1}) (CCl_4): 3067, 2953, 1696, 1282. **HRMS** (EI+) calcd for $C_{22}H_{16}O_2$ 312.1150, found: 312.1149. **Mp**: 188 °C.



Compound **5a**: 5-ethoxy-2-methoxybenz(a)anthracene

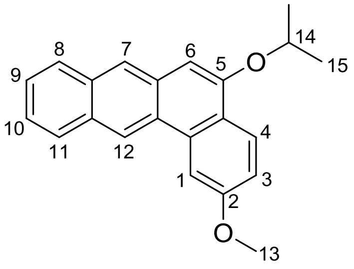
Ketone **4a** (49.0 mg, 0.168 mmol, 1.0 eq) was dissolved in EtOH (2.0 ml) containing H_2SO_4 (1.0 M). The solution was refluxed. After 36 h, the reaction mixture was cooled down at room temperature and water (3 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography (Pentane/Ether from 100/0 to 50/50). The desired compound was obtained as a brown solid and 3 mg of the starting material were recovered (35 mg, 0.168 mmol, 69 % (74 %)). **^{1}H NMR** (δ, ppm) ($CDCl_3$, 400 MHz): 8.93 (s, 1H, $C_{12}H$); 8.29 (d, 1H, J = 8.9 Hz, C_4H); 8.16 (d, 1H, J = 2.4 Hz, C_1H); 8.14 (s, 1H, C_7H); 8.06 (d, 1H, J = 7.9 Hz, $C_{11}H$); 7.95 (d, 1H, J = 7.9 Hz, C_8H); 7.53 – 7.45 (m, 2H, C_9H & $C_{10}H$); 7.25 (dd, 1H, J_1 = 2.4 Hz, J_2 = 9.0 Hz, C_3H); 6.84 (s, 1H, C_6H); 4.28 (q, 2H, J = 6.9 Hz, $OC_{14}H_2$); 4.05 (s, 3H, $OC_{13}H_3$); 1.60 (t, 3H, J = 6.9 Hz, $C_{15}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 159.06 (C_2O); 152.73 (C_5O); 132.97 ($C_{4'}$); 132.47 ($C_{12'}$); 132.17 ($C_{11'}$); 130.29 ($C_{7'}$); 128.40 ($C_{11}H$); 127.00 (C_8H); 125.82 ($C_{6'}$); 125.73 ($C_{10}H$); 124.42 (C_9H); 124.34 (C_4H); 124.23 (C_7H); 121.63 ($C_{12''}$), 124.38 ($C_{12}H$); 115.49 (C_3H); 105.30 (C_1H); 99.74 (C_6H); 63.39 ($OC_{14}H_2$); 55.49 ($OC_{13}H_3$); 14.78 ($C_{15}H_3$). **IR** (cm^{-1}) (CCl_4): 3055, 2929, 2855. **HRMS** (EI+) calcd for $C_{21}H_{18}O_2$ 302.1307, found: 302.1309. **Mp**: 102 °C.



Compound **5b**: 2,5-dimethoxybenz(a)anthracene

Ketone **4a** (51.2 mg, 0.178 mmol, 1.0 eq) was dissolved in MeOH (2.0 ml) containing H_2SO_4 (1.0 M). The solution was refluxed. After 18 h, the reaction mixture was cooled down at room temperature, water (3mL) was added and the precipitate was filtrated, dissolved in DCM and dried over $MgSO_4$. The solvent was then evaporated under reduced pressure and the crude residue dissolved in acetonitrile. This solution was washed with pentane and the solvent was evaporated under reduced pressure. We obtained a 2:1 mixture of the desired product and dimethylsulfate as a brown solid (45.5 mg, 0.158 mmol, 88 %).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.94 (s, 1H, $C_{12}H$); 8.24 (d, 1H, J = 8.9 Hz, C_4H); 8.17 (s, 2H, C_1H & C_7H); 8.06 (d, 1H, J = 7.9 Hz, $C_{11}H$); 7.95 (d, 1H, J = 8.0 Hz, C_8H); 7.52 – 7.45 (m, 2H, C_9H & $C_{10}H$); 7.24 (dd, 1H, J_1 = 2.4 Hz, J_2 = 8.9 Hz, C_3H); 6.88 (s, 1H, C_6H); 4.09 & 4.06 (s, 3H, $OC_{13}H_3$ & $OC_{14}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 159.10 (C_2O); 153.59 (C_5O); 133.06 ($C_{4'}$); 132.50 ($C_{11'}$); 132.01 ($C_{12'}$); 130.36 ($C_{7'}$); 128.41 ($C_{11}H$); 127.03 (C_8H); 125.87 ($C_{12''}$); 125.84 & 124.56 (C_9 & C_{10}); 124.40 (C_7H); 124.30 (C_4H); 121.54 ($C_{6'}$), 124.47 ($C_{12}H$); 115.52 (C_3H); 105.49 (C_1H); 99.23 (C_6H); 55.60 & 55.35 ($OC_{13}H_3$ & $OC_{14}H_3$).

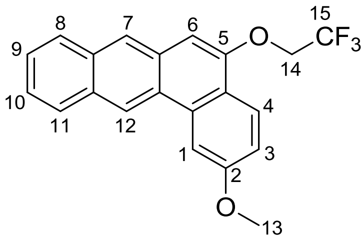


Compound **5c**: 5-isopropoxy-2-methoxybenz(a)anthracene

Ketone **4a** (100 mg, 0.342 mmol, 1.0 eq) was dissolved in iPrOH (3.4 ml) containing H_2SO_4 (1.0 M). The solution was refluxed. After 18 h, the reaction mixture was cooled down at room temperature and water (3mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography (EP/AcOEt : 95/5). The desired compound was obtained as an orange solid (43 mg, 0.136 mmol, 40 %).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.97 (s, 1H, $C_{12}H$); 8.30 (d, 1H, J = 8.9 Hz, C_4H); 8.19 (d, 1H, J = 2.5 Hz, C_1H); 8.16 (s, 1H, C_7H); 8.08 (d, 1H, J = 8.0 Hz, $C_{11}H$); 7.96 (d, 1H, J = 8.0 Hz, C_8H); 7.53 – 7.45 (m, 2H, C_9H & $C_{10}H$); 7.25 (dd, 1H, J_1 = 2.5 Hz, J_2 = 8.9 Hz, C_3H); 6.90 (s, 1H, C_6H); 4.89 (sept, 1H, J = 6.0 Hz, $OC_{14}H$); 4.07 (s, 3H, $OC_{13}H_3$); 1.53 (t, 6H, J = 6.0 Hz, $C_{15}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 159.07 (C_2O); 151.42 (C_5O); 133.15

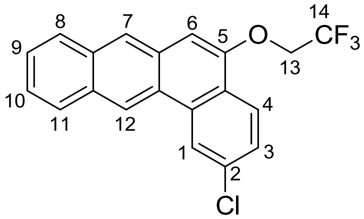
($C_{4'}$); 132.51 & 132.27 ($C_{11'}$ & $C_{12'}$); 130.29 ($C_{7'}$); 128.41 ($C_{11}H$); 127.01 (C_8H); 125.75 (2C, C_9 & $C_{12''}$); 124.64 (C_4H); 125.42 ($C_{10}H$); 124.13 (C_7H); 122.30 ($C_{6'}$); 121.39 ($C_{12}H$); 115.50 (C_3H); 105.30 (C_1H); 100.94 (C_6H); 69.75 ($OC_{14}H$); 55.55 ($OC_{13}H_3$); 22.10 (2C, $C_{15}H_3$). **IR** (cm^{-1}) (CCl_4): 3055, 2979, 2929, 2855, 1622. **HRMS** (EI+) calcd for $C_{22}H_{20}O_2$ 316,1463, found: 316.1471.



Compound **5d**: 2-methoxy-5-(2,2,2-trifluoroethoxy)benz(a)anthracene

Ketone **4a** (55.6 mg, 0.190 mmol, 1.0 eq) was dissolved in 2,2,2-trifluoroethanol (2.0 ml) containing H_2SO_4 (1.0 M). The solution was refluxed. After 3 h, the reaction mixture was cooled down at room temperature and water (3mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography (Pentane/Ether from 100/0 to 80/20). The desired compound was obtained as a brown solid (31 mg, $8.7*10^{-2}$ mmol, 46 %).

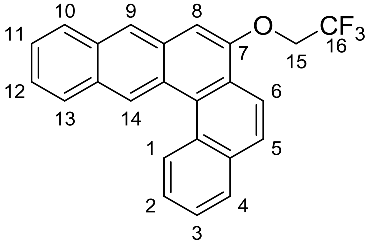
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.94 (s, 1H, $C_{12}H$); 8.24 (d, 1H, J = 8.8 Hz, C_4H); 8.17 – 8.13 (m, 2H, C_1H & C_7H); 8.07 (d, 1H, J = 8.8 Hz, $C_{11}H$); 7.96 (d, 1H, J = 7.4 Hz, C_8H); 7.55 – 7.49 (m, 2H, C_9H & $C_{10}H$); 7.29 – 7.25 (m, 1H, C_3H); 6.80 (s, 1H, C_6H); 4.59 (q, 2H, J = 7.8 Hz, $OC_{14}H_2$); 4.06 (s, 3H, $OC_{13}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 159.49 (C_2O); 151.29 (C_5O); 133.21 ($C_{4'}$); 132.44 ($C_{12'}$); 130.98 ($C_{11'}$); 130.78 ($C_{7'}$); 128.44 ($C_{11}H$); 127.13 (C_8H); 126.06 ($C_{10}H$); 125.05 & 124.98 (C_7H & C_9H); 124.23 (C_4H); 123.47 (q, J = 277.7 Hz, $C_{15}F_3$); 121.63 ($C_{12}H$); 120.52 ($C_{12''}$); 115.79 (C_3H); 105.51 (C_1H); 100.73 (C_6H); 65.53 (q, J = 35.9 Hz, $OC_{14}H_2$); 55.55 ($OC_{13}H_3$). **IR** (cm^{-1}) (CCl_4): 3057, 2938, 2839, 1629, 1615, 1285. **HRMS** (EI+) calcd for $C_{21}H_{15}F_3O_2$ 356,1024, found: 356.1027. **Mp**: 120 °C.



Compound **5e**: 2-chloro-5-(2,2,2-trifluoroethoxy)benz(a)anthracene

Ketone **4b** (90 mg, 0.296 mmol, 1.0 eq) and P-TSA (15 mg) were dissolved in 2,2,2-trifluoroethanol (3.0 ml). The solution was refluxed. After 3 h, the reaction mixture was cooled down at room temperature and water (4mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (4 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography (Pentane/Ether from 100/0 to 95/5). The desired compound was obtained as a yellow solid (69 mg, 0.192 mmol, 63 %).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.80 (s, 1H, $C_{12}H$); 8.57 (s, 1H, C_1H); 8.16 (d, 1H, J = 8.7 Hz, C_4H); 8.08 (s, 1H,C_7H); 8.02 (d, 1H, J = 7.4 Hz, $C_{11}H$); 7.94 (d, 1H, J = 8.2 Hz, C_8H); 7.57 – 7.50 (m, 3H, C_3H, C_9H & $C_{10}H$); 6.80 (s, 1H, C_6H); 4.54 (q, 2H, J = 7.9 Hz, $OC_{13}H_2$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 151.29 (C_5O); 134.15 (C_{IV}); 132.77 (C_{IV}); 132.58 (C_{IV}); 130.97 (C_{IV}); 130.40 (C_{IV}); 128.50 ($C_{11}H$); 127.41 (CH); 127.14 (C_8H); 126.40 (CH); 125.43(CH); 125.14 (C_7H & C_{IV}); 124.64 (C_{IV}); 124.10 (C_4H); 123.35 (q, J = 277.5 Hz, $C_{14}F_3$); 122.56 (C_1H); 121.82 ($C_{12}H$); 103.04 (C_6H); 65.56 (q, J = 36.0 Hz, $OC_{13}H_2$). **IR** (cm^{-1}) (CCl_4): 3058, 2942, 2856, 1629. **HRMS** (EI+) calcd for $C_{21}H_{12}F_3ClO$ 360.0529, found: 360.0535. **Mp**: 87 °C.

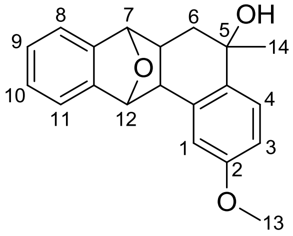


Compound **5f**: 7-(2,2,2-trifluoroethoxy)naphth(1,2-a)anthracene

Ketone **4c** (80 mg, 0.256 mmol, 1.0 eq) and P-TSA (12 mg) were dissolved in 2,2,2-trifluoroethanol (2.5 ml). The solution was refluxed. After 130 h, the reaction mixture was cooled down at room temperature and water (3 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography (Pentane/Ether from 100/0 to 90/10). The desired compound was obtained as a yellow solid (91 mg, 0.242 mmol, 94 %).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 9.48 (s, 1H, $C_{14}H$); 9.21 (d, 1H, J = 8.4 Hz, C_1H); 8.34 (d, 1H, J = 8.8 Hz, C_6H); 8.31 (s, 1H, C_9H); 8.10 (d, 1H, J = 7.9 Hz, $C_{13}H$); 8.07 (dd, 1H, J_1 = 0.9 Hz, J_2 = 7.9 Hz, C_4H); 8.03 – 8.01 (m, 1H, $C_{10}H$); 8.00 (d, 1H, J = 9.0 Hz, C_5H); 7.727 (ddd, 1H, J_1 = 1.4 Hz, J_2 = 6.9 Hz, J_3 = 8.5 Hz, C_2H); 7.69 – 7.65 (m, 1H,

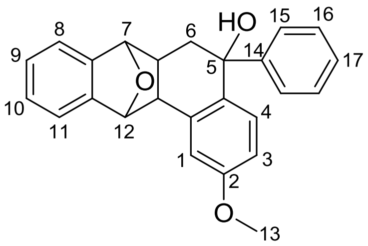
C_3H); 7.59 – 7.51 (m, 2H, $C_{11}H$ & $C_{12}H$); 7.11 (s, 1H, C_8H); 4.65 (q, 2H, $C_{15}H_2$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 151.12 (C_7); 133.88 (C_{IV}); 131.73 (C_{IV}); 131.37 (C_{IV}); 130.76 (C_{IV}); 130.10 (C_{IV}); 128.92 (C_{IV}); 128.71(CH); 128.64(CH); 127.95(CH); 127.76(CH); 127.65(CH); 127.10(CH); 126.53(CH); 126.26(CH); 126.23(CH); 126.02 (C_{IV}); 125.12(CH); 125.10 (C_{IV}); 124.62(CH); 123.47 (q, J = 277.6 Hz, $C_{15}F_3$); 119.70 (C_6H); 103.87 (C_8H); 65.98 (q, J = 35.9 Hz, $C_{15}H_2$). **IR** (cm^{-1}) (CCl_4): 3055, 2927, 2855, 1631. **HRMS** (EI+) calcd for $C_{24}H_{15}F_3O$ 376.1075, found: 376.1076. **Mp**: 140 °C.



Compound **6a**: 7,12-epoxy-5,6,6A,7,12,12A-hexahydro-2-methoxy-5-methylbenz(a)anthrac-5-ol

To a solution of Ketone **4a** (100 mg, 0.342 mmol, 1.0 eq) in diethylether (3.5 ml) at 0 °C under a nitrogen atmosphere was added MeLi (1.7 mmol, 5.0 eq) dropwise. The solution was stirred for 1 h at 0 °C and for another hour at RT. The reaction mixture was quenched by addition of NH_4Cl (sat. aq.) (5mL). The layers were separated and the aqueous phase extracted further with DCM three times (5 mL). The combined organic layers were dried over $MgSO_4$ and then evaporated. The crude residue was purified by two column chromatography (EP/AcOEt 70/30 and EP/AcOEt from 80 /20 to 75/25). The desired compound was obtained as a brown solid and 8 mg of the starting material were recovered (50 mg, 0.16 mmol, 48 % (52 %)).

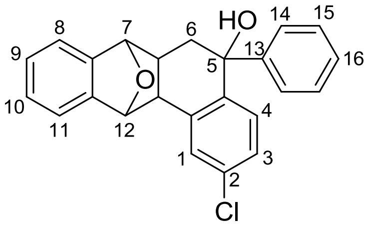
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.58 (d, 1H, J = 8.6 Hz, C_4H); 7.40 – 7.38 (m, 1H, $C_{11}H$); 7.35 – 7.33 (m, 1H, C_8H); 7.24 – 7.22 (m, 2H, C_9H & $C_{10}H$); 6.89 (d, 1H, J = 2.6 Hz, C_1H); 6.85 (dd, 1H, J_1 = 2.7 Hz, J_2 = 8.6 Hz, C_3H); 5.35 (s, 1H, $OC_{12}H$); 5.23 (s, 1H, OC_7H); 4.03 (s, 1H, OH); 3.86 (s, 3H, $OC_{13}H_3$); 3.09 (d, 1H, J = 8.5 Hz, $C_{12'}H$); 2.36 (ddd, 1H, J_1 = 4.0 Hz, J_2 = 7.4 Hz, J_3 = 8.3, $C_{6'}H$); 2.23 (dd, 1H, J_1 = 3.9 Hz, J_2 = 13.9 Hz, C_6H_2); 2.10 (dd, 1H, J_1 = 7.3 Hz, J_2 = 13.9 Hz, C_6H_2); 1.59 (s, 3H, $C_{14}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 158.94 (C_2O); 145.10 ($C_{7'}$); 144.37 ($C_{11'}$); 137.78 ($C_{12''}$); 136.05 ($C_{4'}$); 127.12 & 126.97 (C_9H & $C_{10}H$); 126.26 (C_4H); 119.28 & 119.19 (C_8H & $C_{11}H$); 114.49 (C_1H); 112.32 (C_3H); 87.25 (OC_7H); 85.70 ($OC_{12}H$); 67.92 (C_5); 55.36 ($OC_{13}H_3$); 44.45 ($C_{12'}H$); 41.39 (C_6H_2); 37.90 ($C_{6'}H$); 28.33 (C_{14}H3). **IR** (cm^{-1}) (CCl_4): 2927, 2855, 1789, 1464.



Compound **6b**: 7,12-epoxy-5,6,6A,7,12,12A-hexahydro-2-methoxy-5-phenylbenz(a)anthrac-5-ol

Following the general procedure **C**, the reaction was carried out with ketone **4a** (100 mg, 0,342 mmol). Purification by flash chromatography (EP/AcOEt: 90/10) gave the desired compound as an orange solid (60 mg, 0.162 mmol, 48 % (53 %)).

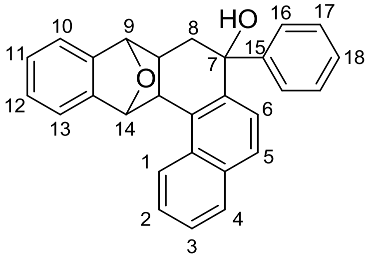
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.41 – 7.36 (m, 3H, $C_{11}H$ & $C_{16}H$); 7.33 – 7.30 (m, 3H, C_8H & $C_{15}H$); 7.27 – 7.25 (m, 1H, $C_{17}H$); 7.24 – 7.21 (m, 2H, C_9H & $C_{10}H$); 6.99 (d, 1H, J = 8.6 Hz, C_4H); 6.95 (d, 1H, J = 2.6 Hz, C_1H); 6.73 (dd, 1H, J_1 = 2.7 Hz, J_2 = 8.7 Hz, C_3H); 5.37 (s, 1H, $OC_{12}H$); 5.29 (s, 1H, OC_7H); 4.38 (s, 1H, OH); 3.86 (s, 3H, $OC_{13}H_3$); 3.14 (d, 1H, J = 8.4 Hz, $C_{12'}H$); 2.52 (dd, 1H, J_1 = 7.1 Hz, J_2 = 13.9 Hz, C_6H_2); 2.34 (dd, 1H, J_1 = 4.2 Hz, J_2 = 13.9 Hz, C_6H_2); 2.27 (ddd, 1H, J_1 = 4.3 Hz, J_2 = 7.2 Hz, J_3 = 8.2 Hz, $C_{6'}H$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 159.06 (C_2O); 146.83 (C_{14}); 145.09 ($C_{11'}$); 144.31 ($C_{7'}$); 138.52 ($C_{4'}$); 136.17 ($C_{12''}$); 129.63 (C_4H); 127.81 (2C, $C_{16}H$); 127.13 ($C_{17}H$); 126.99 & 126.65 (C_9H & $C_{10}H$); 126.49 (2C, $C_{15}H$); 119.31 & 119.24 (C_8H & $C_{11}H$); 114.00 (C_1H); 112.26 (C_3H); 87.38 (OC_7H); 85.56 ($OC_{12}H$); 73.20 (C_5); 55.35 ($OC_{13}H_3$); 44.35 ($C_{12'}H$); 43.07 (C_6H_2); 37.91 ($C_{6'}H$). Mp: 99 °C.



Compound **6c**: 2-chloro-7,12-epoxy-5,6,6A,7,12,12A-hexahydro-5-phenylbenz(a)anthrac-5-ol

Following the general procedure **C**, the reaction was carried out with ketone **4b** (55 mg, 0,185 mmol). Purification by flash chromatography (EP/AcOEt: from 90/10 to 75/25) gave the desired compound as a white solid (39.9 mg, 0.106 mmol, 57 %).

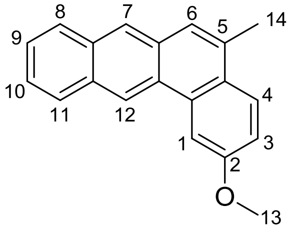
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.46 (d, 1H, J = 1.9 Hz, C_1H); 7.41 (dd, 1H, J_1 = 1.5 Hz, J_2 = 6.1 Hz, $C_{11}H$), 7.33 – 7.20 (m, 8H, C_8H, C_9H, $C_{10}H$, $C_{14}H$, $C_{15}H$ & $C_{16}H$); 7.16 (dd, 1H, J_1 = 2.1 Hz, J_2 = 8.4 Hz, C_3H); 7.07 (d, 1H, J = 8.4 Hz, C_4H); 5.34 (s, 1H, $C_{12}H$); 5.31 (s, 1H, C_7H); 4.35 (s, 1H, OH); 3.10 (d, 1H, J = 8.4 Hz, $C_{12'}H$); 2.53 (dd, 1H, J_1 = 7.0 Hz, J_2 = 13.9 Hz, C_6H), 2.32 (dd, 1H, J_1 = 5.0 Hz, J_2 = 13.9 Hz, C_6H); 2.27 – 2.21 (m, 1H, $C_{6'}H$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 145.94 (C_{IV}); 144.78 (C_{IV}); 144.11 (C_{IV}); 142.10 (C_{IV}); 139.02 (C_{IV}); 133.52 (C_{IV}); 129.67 (C_4H); 128.67 (C_1H); 127.97 (2C, $C_{14}H$); 127.23 (CH); 127.10 (CH); 126.97 (CH); 126.90 (CH); 126.38 (2C, $C_{15}H$); 87.00 (OC_7H); 85.30 ($OC_{12}H$); 73.26 (C_5); 43.93 ($C_{12'}H$); 42.69 (C_6H_2); 37.83 ($C_{6'}H$).



Compound **6d**: 9,14-epoxy-7,8,8A,9,14,14A-hexahydro-7-phenylnaphth(1,2-a)anthrac-7-ol

Following the general procedure **C**, the reaction was carried out with ketone **4c** (70 mg, 0,224 mmol). Purification by flash chromatography (EP/AcOEt: from 95/5 to 85/15) gave the desired compound as a white solid (64.2 mg, 0.164 mmol, 73 %).

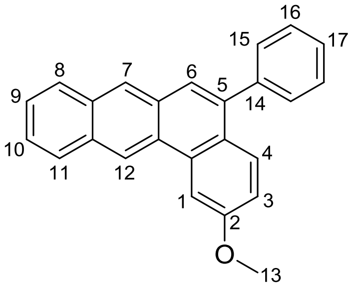
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.14 (d, 1H, J = 8.5 Hz, C_1H); 7.89 (d, 1H, J = 8.0 Hz, C_4H); 7.70 (t, 1H, J = 7.6 Hz, C_2H); 7.64 (d, 1H, J = 8.7 Hz, C_5H); 7.60 – 7.57 (m, 2H, C_3H & $C_{13}H$); 7.53 – 7.51 (m, 2H); 7.435 – 7.29 (m, 6H); 7.08 (d, 1H, J = 8.7 Hz, C_6H); 5.56 (s, 1H, $OC_{14}H$); 5.16 (s, 1H, OC_9H); 5.1 (s, 1H, OH); 4.04 (d, 1H, J = 8.1 Hz, $C_{14'}H$); 2.61 – 2.54 (m, 3H, C_8H_2 & $C_{8'}H$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 147.40 (C_{IV}); 145.29 (C_{IV}); 143.84 (C_{IV}); 140.68 (C_{IV}); 133.41 (C_{IV}); 132.07 (C_{IV}); 131.56 (C_{IV}); 129.52 (C_{IV}); 129.19 (C_4H); 127.81 (2C, $C_{16}H$); 127.35 (CH); 127.18 (CH); 127.06 (CH); 126.97 (CH); 126.78 (CH); 126.53 (CH); 126.46 (2C, $C_{17}H$); 125.81 (CH); 123.11 (C_1H); 119.36 (CH); 119.23 (CH); 115.27 (C_{IV}); 86.24 & 86.16 (OC_9H & $OC_{14}H$); 73.47 (C_7); 42.41 (C_8H_2); 40.17 ($C_{16'}H$); 37.76 ($C_{8'}H$). **HRMS** (EI+) calcd for $C_{28}H_{22}O_2$ 390.1620, found: 390.1620. Mp: 64 °C.



Compound **7a**: 2-methoxy-5-(methyl)benz(a)anthracene

Alcohol **6a** (36.0 mg, 0.117 mmol, 1.0 eq) was dissolved in EtOH (3.0 ml) containing H_2SO_4 (1.0 M). The solution was refluxed. After 12 h, the reaction mixture was cooled down at room temperature and water (3 mL) was added. The precipitate was filtrated, dissolved in DCM and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude residue was dissolved in acetonitrile. This solution was washed with pentane and the solvent was evaporated under reduced pressure. The desired product was obtained as a brown solid (24 mg, $8.8*10^{-2}$ mmol, 75 %).

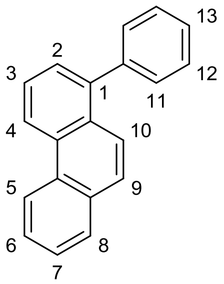
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 9.03 (s, 1H, $C_{12}H$); 8.26 (d, 1H, J = 2.5 Hz, C_1H); 8.23 (s, 1H, C_7H); 8.10 (dd, 1H, J_1 = 4.1 Hz, J_2 = 5.4 Hz, $C_{11}H$); 8.01 (dd, 1H, J_1 = 4.1 Hz, J_2 = 5.4 Hz, C_8H); 7.94 (d, 1H, J = 8.8 Hz, C_4H); 7.54 – 7.51 (m, 2H, C_9H & $C_{10}H$); 7.49 (s, 1H, C_6H); 7.28 (dd, 1H, J_1 = 2.6 Hz, J_2 = 8.9 Hz, C_3H); 4.07 (s, 3H, $OC_{13}H_3$); 2.68 (s, 3H, $C_{14}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 158.33 (C_2O); 132.27 & 132.15 & 132.06 & 131.27 & 131.10 ($C_{4'}$ & C_5 & $C_{7'}$ & $C_{11'}$ & $C_{12'}$); 128.40 ($C_{11}H$); 128.27 ($C_{12''}H$); 127.52 (C_8H); 126.63 (C6'); 126.16 & 125.67 & 125.52 & 125.14 (C_4H & C_7H & C_9H & $C_{10}H$); 124.46 ($C_{12}H$); 121.34 (C_3H); 115.54 (C_1H); 105.83 (C_6H); 55.54($OC_{13}H_3$); 20.24 ($C_{14}H_3$). **IR** (cm^{-1}) (CCl_4): 3057, 2929, 1613, 1514. **HRMS** (EI+) calcd for $C_{20}H_{16}O$ 272,1201, found: 272.1200. **Mp**: 107 °C.



Compound **7b**: 2-methoxy-5-phenylbenz(a)anthracene

Alcohol **6b** (56.0 mg, 0.151 mmol, 1.0 eq) was dissolved in EtOH (1.5 ml) containing H_2SO_4 (1.0 M). The solution was refluxed. After 6 h, the reaction mixture was cooled down at room temperature and water (2mL) was added. The precipitate was filtrated, dissolved in DCM and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude residue was dissolved in acetonitrile. This solution was washed with pentane and the solvent was evaporated under reduced pressure. The crude residue was purified by column chromatography (EP/AcOEt: 90/10). The desired product was obtained as a brown solid (29 mg, 8.7*10^{-2} mmol, 57 %).

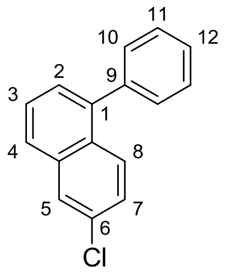
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 9.11 (s, 1H, $C_{12}H$); 8.35 (s, 1H, C_7H); 8.33 (d, 1H, J = 2.5 Hz, C_1H); 8.15 – 8.13 (m, 1H, $C_{11}H$); 8.05 – 8.02 (m, 1H, C_8H); 7.81 (d, 1H, J = 8.9 Hz, C_4H); 7.61 (s, 1H, C_6H); 7.59 – 7.51 (m, 6H, C_9H, $C_{10}H$, $C_{15}H$ & $C_{16}H$); 7.49 – 7.45 (m, 1H, $C_{17}H$), 7.18 (dd, 1H, J_1 = 2.6 Hz, J_2 = 8.9 Hz, C_3H); 4.08 (s, 3H, $OC_{13}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 158.50 (C_2O); 140.88 (C_{IV}); 138.54 ($C_{4'}$); 132.38 (C_{IV}); 132.27 (C_{IV}); 131.70 (C_{IV}); 130.62 (C_{IV}); 129.89 (2C, $C_{15}H$); 128.57 (CH); 128.46 (CH); 128.30 (2C, $C_{16}H$); 128.26 (C_{IV}); 127.63 (CH); 127.35 ($C_{17}H$); 126.74 (C_7H); 125.86 (CH); 125.6 (C_{IV}); 125.52 (CH); 125.39 (C_6H); 121.45 ($C_{12}H$); 115.53 (C_3H); 105.81 (C_1H); 55.60 ($OC_{13}H_3$).



Compound **8a**: 1-phenylphenanthrene

Alcohol **6d** (44 mg, 0.11 mmol, 1.0 eq) and P-TSA (5 mg) were refluxed in EtOH (1.2 ml). After 11h, the reaction mixture was cooled down at RT and water (2 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over $MgSO_4$ and then evaporated. The crude residue was purified by column chromatography (EP/AcOEt: from 100/0 to 95/5). The product was obtained as a white solid (23 mg, 9.1*10^{-2} mmol, 81 %).

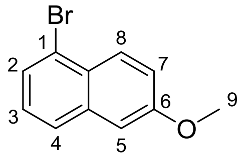
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.81 (d, 1H, J = 8.2 Hz, C_5H); 8.80 (d, 1H, J = 8.3 Hz, C_4H); 7.90 (d, 1H, J = 7.6 Hz, C_8H); 7.84 (d, 1H, J = 9.2 Hz, $C_{9/10}H$); 7.74 – 7.68 (m, 3H, C_3H, C_6H & $C_{9/10}H$); 7.69 – 7.65 (m, 1H, C_7H); 7.58 (d, 1H, J = 7.1 Hz, C_2H); 7.54 – 7.53 (m, 4H, $C_{11}H$ & $C_{12}H$); 7.50 – 7.45 (m, 1H, $C_{14}H$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 141.07 (C_{IV}); 140.97 (C_{IV}); 131.69 (C_{IV}); 130.64 (C_{IV}); 130.37 (C_{IV}); 130.19 (2C, C13H); 129.88 (C_{IV}); 128.43 (C8H); 128.24 (2C, C12H); 127.86 (C14H); 127.21 (C7H); 126.83 (CH); 126.66 (CH); 126.62 (CH); 125.92 (CH); 124.57 ($C_{9/10}H$); 122.93 (C_5H); 122.10 (C_4H). **IR** (cm^{-1}) (CCl_4): 3061, 2927, 2855, 1455. **HRMS** (EI+) calcd for $C_{20}H_{14}$ 254.1096, found: 254.1095. **Mp**: 75 °C.



Compound **8b**: 6-chloro-1-phenylnaphthalene

Alcohol **6c** (38 mg, 0.10 mmol, 1.0 eq) and P-TSA (5 mg) were refluxed in EtOH (1.2 ml). After 30 h, the reaction mixture was cooled down at RT and water (2mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over $MgSO_4$ and then evaporated. The crude residue was purified by column chromatography (EP/AcOEt: from 100/0 to 90/10). The product was obtained as a transparent oil (22 mg, 9.1*10^{-2} mmol, 90 %).

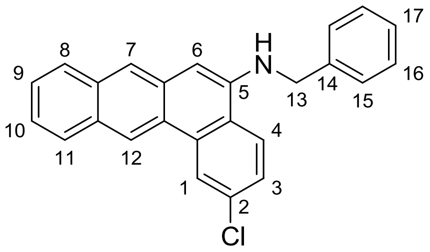
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.89 (d, 1H, J = 2.1 Hz, C_5H); 7.84 (d, 1H, J = 9.1 Hz, C_8H); 7.77 (d, 1H, J = 8.2 Hz, C_4H); 7.55 (dd, 1H, J_1 = 7.2 Hz, J_2 = 8.1 Hz, C_3H); 7.53 – 7.45 (m, 5H, $C_{10}H$, $C_{11}H$ & $C_{12}H$); 7.42 (dd, 1H, J_1 = 1.1 Hz, J_2 = 7.0 Hz, C_2H); 7.36 (dd, 1H, J_1 = 2.2 Hz, J_2 = 9.1 Hz, C_7H). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 140.41 (C_{IV}); 140.21 (C_{IV}); 134.48 (C_{IV}); 131.62 (C_{IV}); 129.94 (2C, C10H); 129.91 (C6); 128.35 (2C, C11H); 127.85 (CH); 127.47 (CH); 127.11 (CH); 126.81 (2CH); 126.73 (CH); 126.54 (CH). **IR** (cm^{-1}) (CCl_4): 3060, 2927, 2855, 1590. **HRMS** (EI+) calcd for $C_{16}H_{11}Cl$ 238.0549, found: 238.0548.



Compound **8c**: 1-bromo-6-methoxynaphthalene

To a solution of ketone **4a** (50 mg, 0.17 mmol, 1.0 eq) in toluene (1.7 ml) at 0 °C under a nitrogen atmosphere was added PBr_3 (80 µL, 0.86 mmol, 5.0 eq) dropwise. The solution was refluxed for 16 h. The reaction mixture was cooled down at RT and water (3 mL) was added. The solution was washed with $NaHCO_3$ (sat. aq.) (3 mL). The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over $MgSO_4$ and then evaporated. The crude residue was purified by column chromatography (EP/AcOEt 90/10). The product was obtained as a yellowish oil (17 mg, $7.2*10^{-2}$ mmol, 44 %).

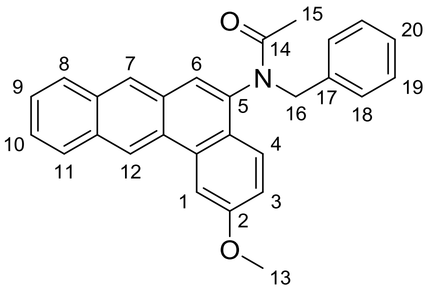
^{1}**H NMR** (δ, ppm) ($CDCl_3$, 400 MHz): 8.14 (d, 1H, J = 9.2 Hz, C_8H); 7.69 (d, 1H, J = 8.2 Hz, C_2H ou C_4H); 7.62 (dd, 1H, J_1 = 1.0 Hz, J_2 = 7.4 Hz, C_2H ou C_4H); 7.27 (dd, J_1 = 7.7 Hz, J_2 = 8.0 Hz, C_3H); 7.24 (dd, 1H, J_1 = 2.4 Hz, J_2 = 9.3 Hz, C_7H); 7.12 (d, 1H, J = 2.5 Hz, C_5H); 3.93 (s, 3H, OC_9H_3). ^{13}**C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 158.12 (C_6O); 135.84 ($C_{4'}$); 128.73 (C_8H); 127.57 (C_2H ou C_4H); 127.43 ($C_{8'}$); 126.75 (C_3H); 126.70 (C_2H ou C_4H); 122.64 (C_1Br); 119.96 (C_7H); 106.06 (C_5H); 55.40 (OC_9H_3). **IR** (cm^{-1}) (CCl_4): 3059, 3006, 2958, 2937, 2838, 1625. **HRMS** (EI+) calcd for $C_{11}H_9BrO$ 235,9837, found: 235.9835.



Compound **9b**: N-benzyl-2-chlorotetraphen-5-amine

To a solution of ketone **4b** (70 mg, 0.24 mmol, 1.0 eq) and benzylamine (29 µL, 0.26 mmol, 1.1 eq) in chlorobenzene (1.2 mL) at 0 °C under a nitrogen atmosphere was added $TiCl_4$ (16 µL, 0.14 mmol, 0.6 eq) dropwise. After 16 h at RT, H_2SO_4 (60 µL) and $TiCl_4$ (32 µL, 0.28 mmol, 1.2 eq) were added to the crude mixture at 0 °C. The solution was warmed at 80 °C for 3 h. The reaction mixture was cooled down at RT and water (2 mL) was added. The solution was filtrated and the crude residue was purified by column chromatography (EP/AcOEt: from 95/5 to 90/10). The product was obtained as a yellowish solid (11 mg, $3.0*10^{-2}$ mmol, 12 %).

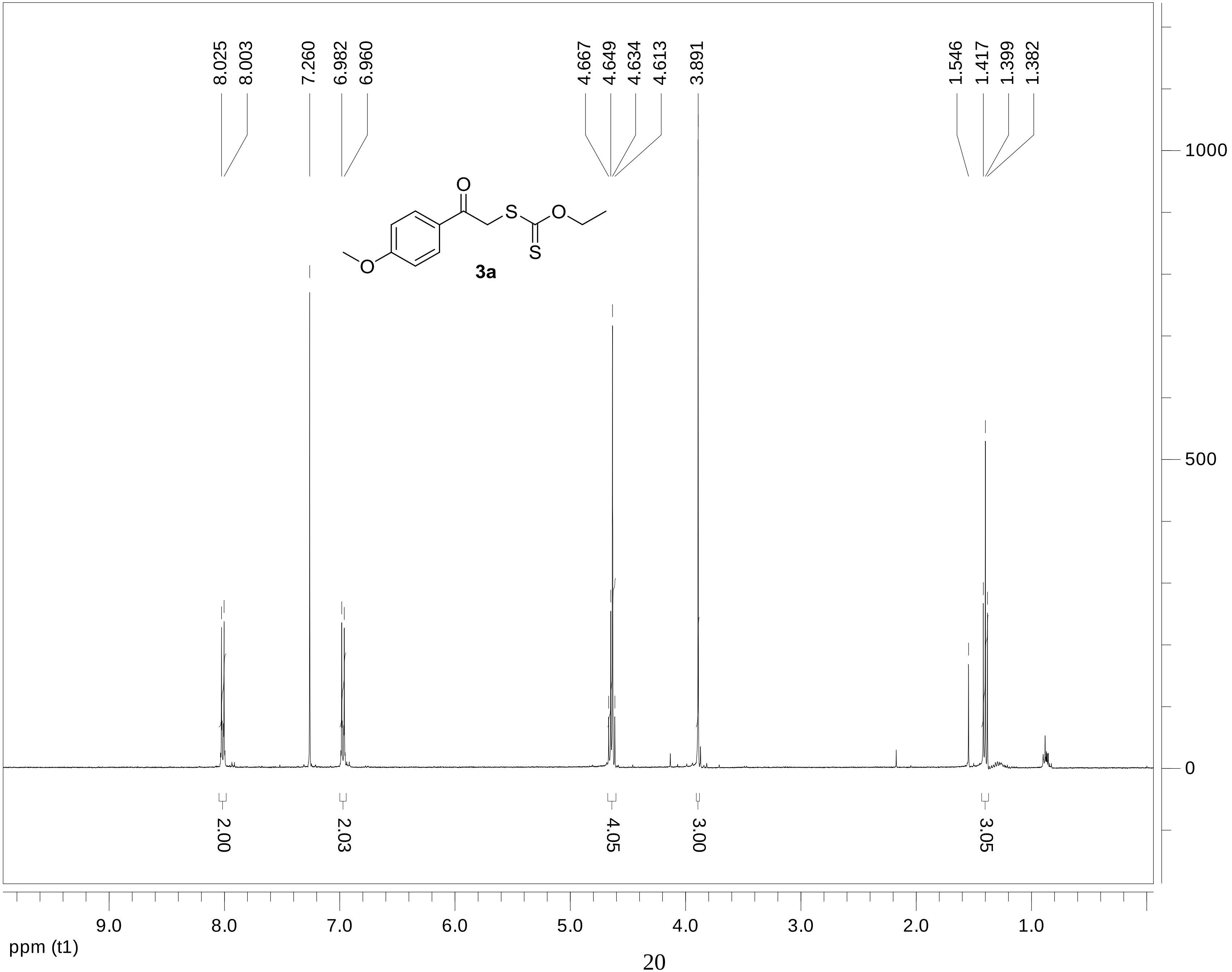
^{1}**H NMR** (δ, ppm) ($CDCl_3$, 400 MHz): 8.92 (s 1H, $C_{12}H$); 8.79 (d, 1H, J = 2.0 Hz, C_4H); 8.08 (s, 1H, C_7H); 8.03 (d, 1H, J = 8.1 Hz, $C_{11}H$); 7.91 (d, 1H, J = 7.9 Hz, C_8H); 7.81 (d, 1H, J = 8.7 Hz, C_1H); 7.57 (dd, 1H, J_1 = 1.8 Hz, J_2 = 8.6 Hz, C_3H); 7.53 – 7.40 (m, 6H, C_9H, $C_{10}H$, $C_{15}H$ & $C_{16}H$); 7.37 – 7.33 (m, 1H, C_{17}); 6.85 (s, 1H, C_6H); 4.58 (s, 3H, $NC_{13}H_2$ & NH). ^{13}**C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz):140.04 (C_{IV}); 138.65 (C_{IV}); 133.11 (C_{IV}); 132.99 (C_{IV}); 132.84 (C_{IV}); 130.07 (C_{IV}); 128.83 (2C, $C_{15}H$); 128.52 ($C_{11}H$); 127.96 (2C, $C_{16}H$); 127.63 ($C_{17}H$); 127.04 (C_3H); 126.92 (C_8H); 126.07 (C_9H); 124.90 (C_{IV}); 124.63 (C_{IV}); 124.35 ($C_{10}H$); 123.49 (C_4H); 123.42 (C_7H); 122.03 (C_1H); 121.64 ($C_{12}H$); 102.13 (C_6H); 48.70 ($NC_{13}H_2$). **IR** (cm^{-1}) (CCl_4):3059, 2928, 2856, 1623. **HRMS** (EI+) calcd for $C_{25}H_{18}NCl$ 367.1128, found: 367.1132.



Compound **10**: N-benzyl-N-(2-methoxytetraphen-5-yl)acetamide

To a solution of ketone **4a** (70 mg, 0.24 mmol, 1.0 eq) and benzylamine (29 µL, 0.26 mmol, 1.1 eq) in chlorobenzene (1.2 mL) at 0 °C under a nitrogen atmosphere was added $TiCl_4$ (16 µL, 0.14 mmol, 0.6 eq) dropwise. After 12 h at RT, H_2SO_4 (60 µL) and $TiCl_4$ (32 µL, 0.28 mmol, 1.2 eq) were added to the crude mixture at 0 °C. The solution was warmed at 80 °C for 3 h. The reaction mixture was cooled down at RT and water (2mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude was directly treated with acetic anhydride (190µL). The reaction was stirred for 2.5 h at RT then water (3 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography (EP/AcOEt: from 95/5 to 80/20). The product was obtained as a strong yellow solid (19.6 mg, $4.8{*}10^{-2}$ mmol, 20 %).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 9.07 (s 1H, $C_{12}H$); 8.29 (d, 1H, J = 2.4 Hz, C_1H); 8.16 (s, 1H, C_7H); 8.14 – 8.12 (m, 1H, $C_{11}H$); 7.99 – 7.96 (m, 1H, C_8H); 7.73 (d, 1H, J = 8.9 Hz, C_4H); 7.59 – 7.53 (m, 2H, C_9H & $C_{10}H$); 7.29 – 7.25 (m, 6H, C_3H, $C_{18}H$, $C_{19}H$ & $C_{20}H$); 7.13 (s, 1H, C_6H); 5.74 (d, 1H, J = 14.0 Hz, $NC_{16}H_2$); 4.21 (d, 1H, J = 14.0 z, $NC_{16}H_2$); 4.09 (s, 3H, $OC_{13}H_3$); 1.93 (s, 3H, $C_{15}H_3$). **^{13}C NMR** (δ, ppm) ($CDCl_3$, 100.6 MHz): 171.34 ($C_{14}O$); 159.34 (C_2); 137.73 (C_{IV}); 136.79 (C_{IV}); 133.64 (C_{IV}); 132.15 (C_{IV}); 132.08 (C_{IV}); 129.90 (C_{IV}); 129.35 (2C, $C_{18}H$); 128.41 ($C_{11}H$); 128.33 (2C, $C_{19}H$); 127.89 (C_{IV}); 127.61 (C_8H); 127.48 (C_3H); 127.37 (C_7H); 126.32 & 126.19 (C_9H & $C_{10}H$); 125.55 (C_6H); 124.87 (C_4H); 123.07 (C_{IV}); 121.70 ($C_{12}H$); 116.36 ($C_{20}H$); 106.51 (C1H); 55.67 ($O_{C13}H_3$); 51.91 ($NC_{16}H_2$); 22.24 ($C_{15}H_3$) . **IR** (cm^{-1}) (CCl_4):2927, 2855, 1686, 1622. **HRMS** (EI+) calcd for $C_{28}H_{23}NO_2$ 405.1729, found: 405.1719. **Mp**: 130°C.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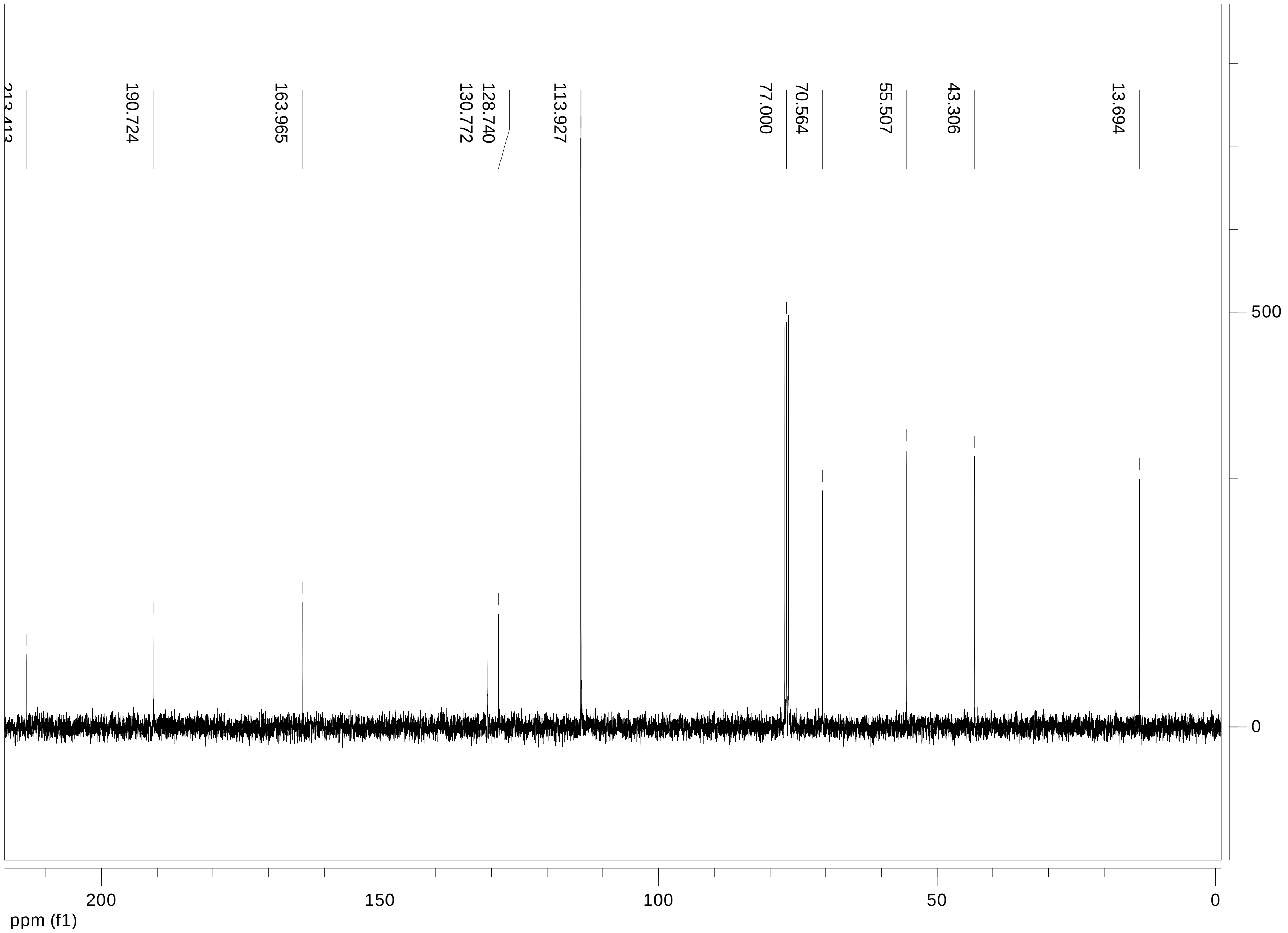
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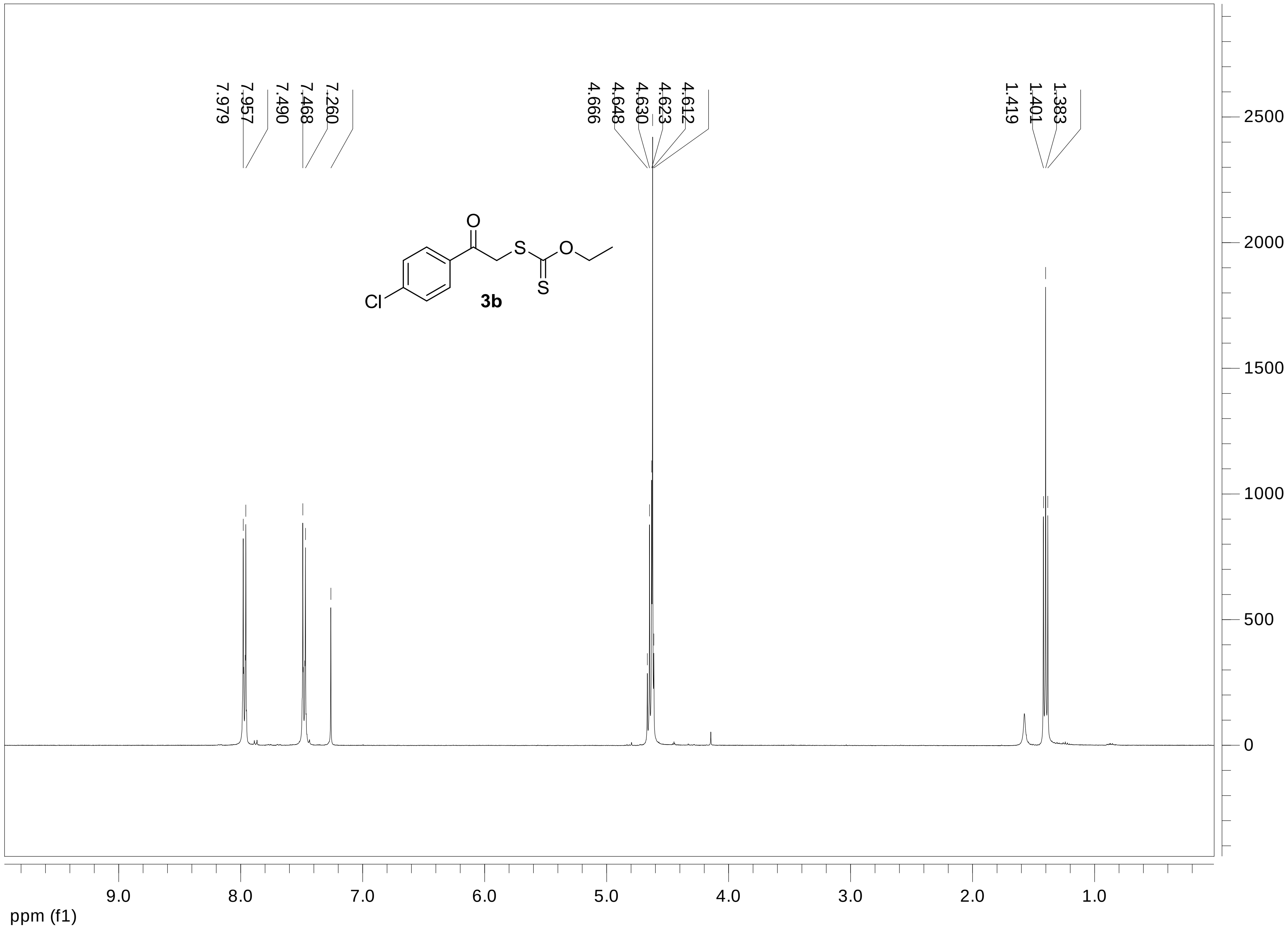
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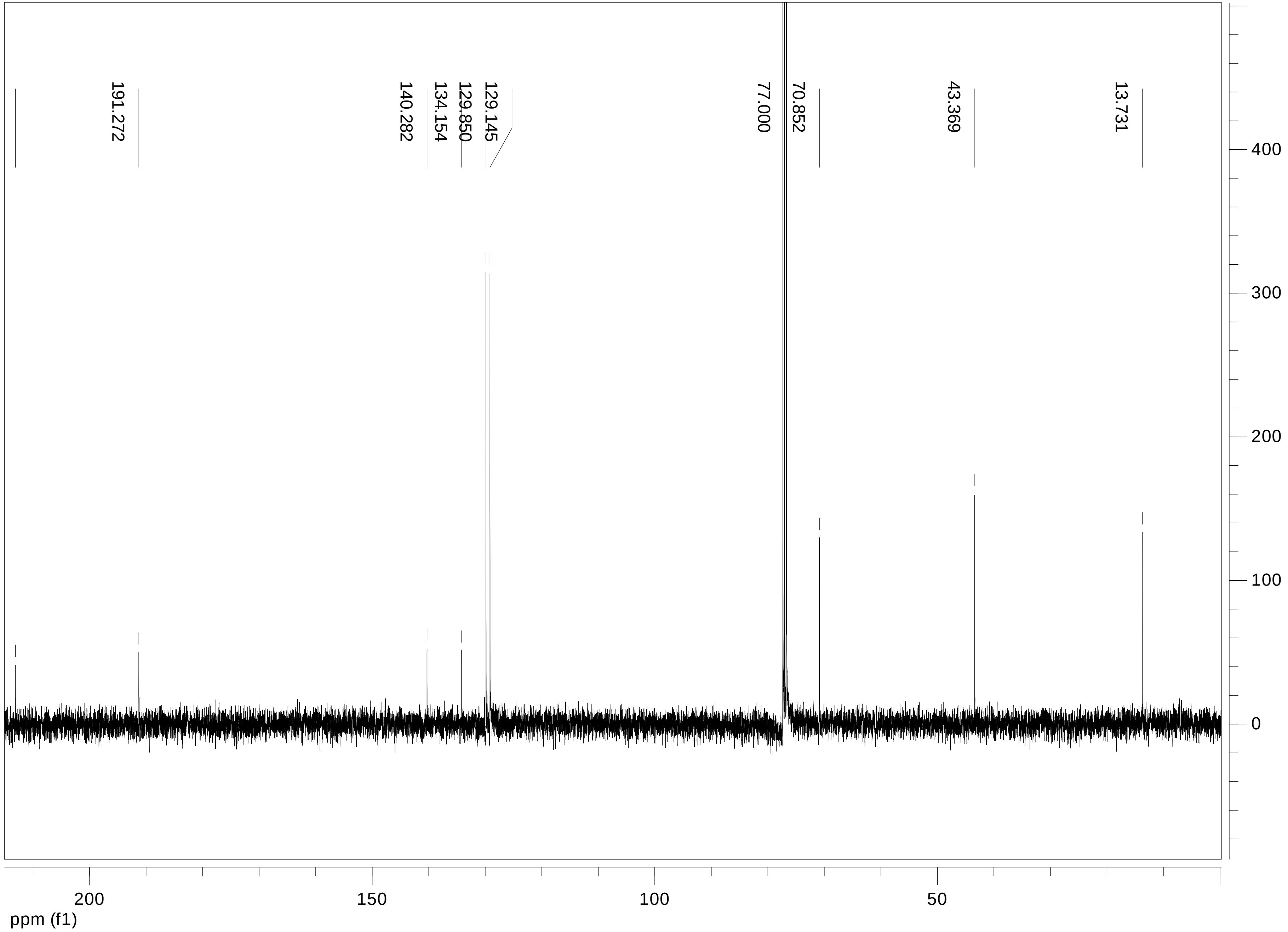
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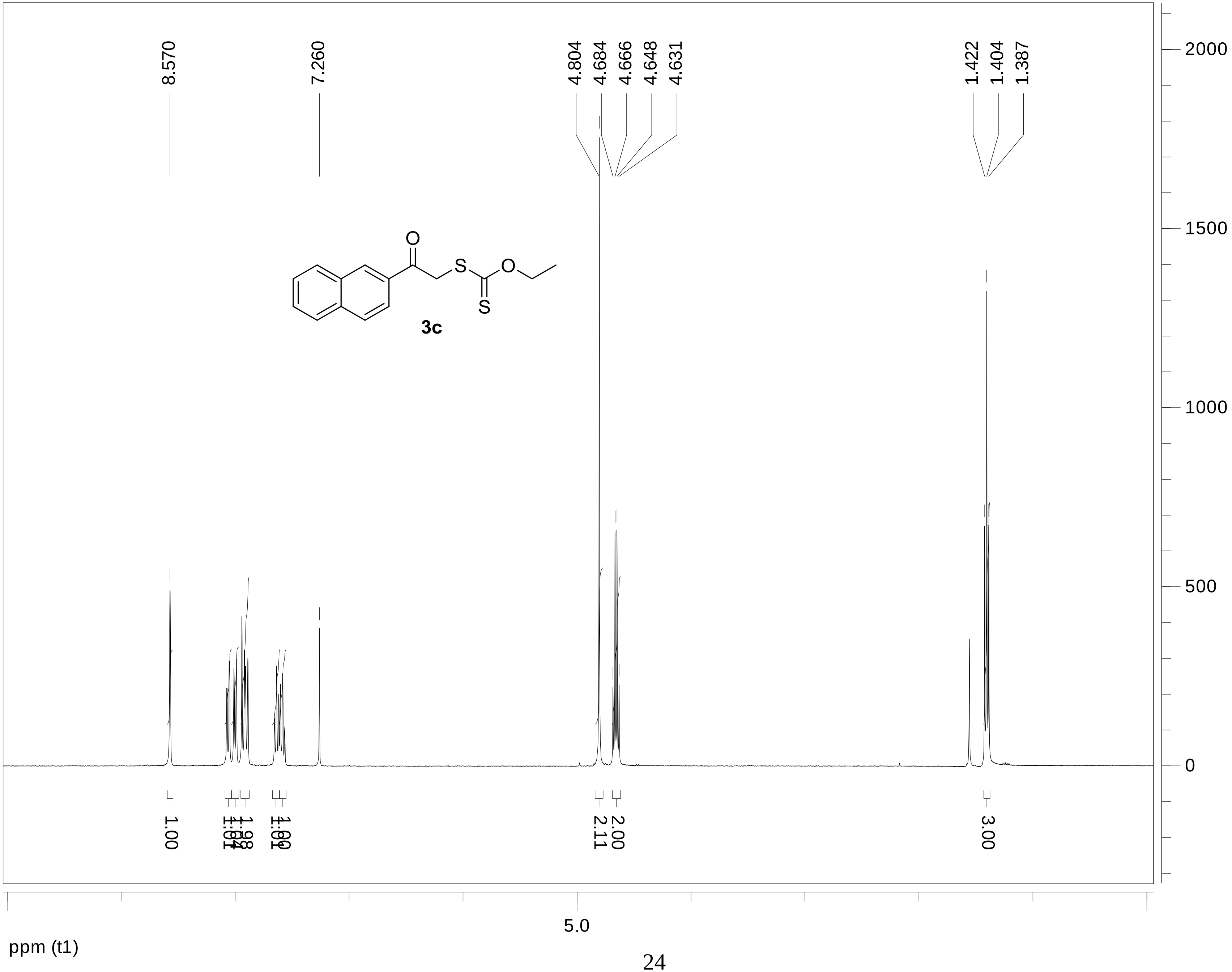
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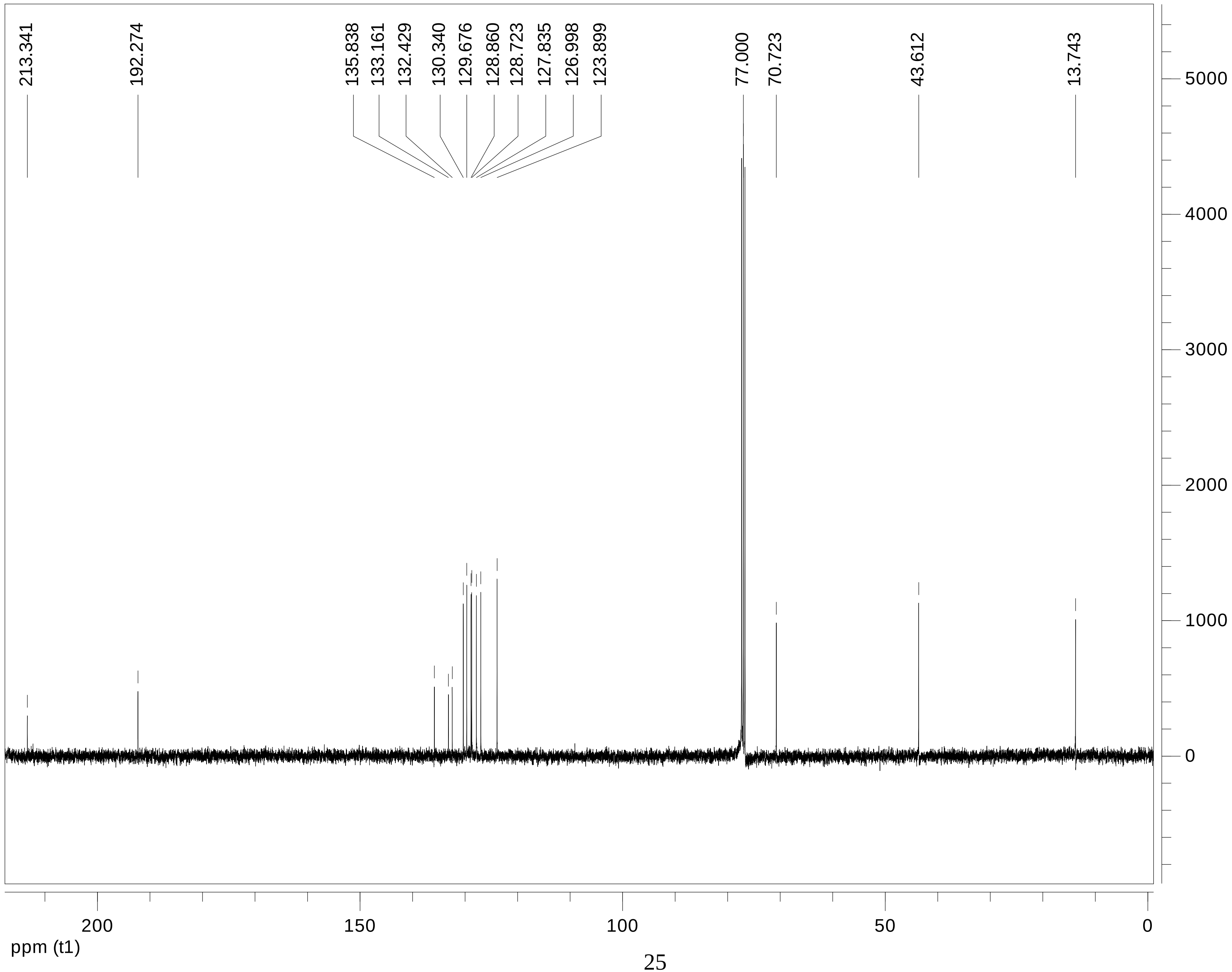
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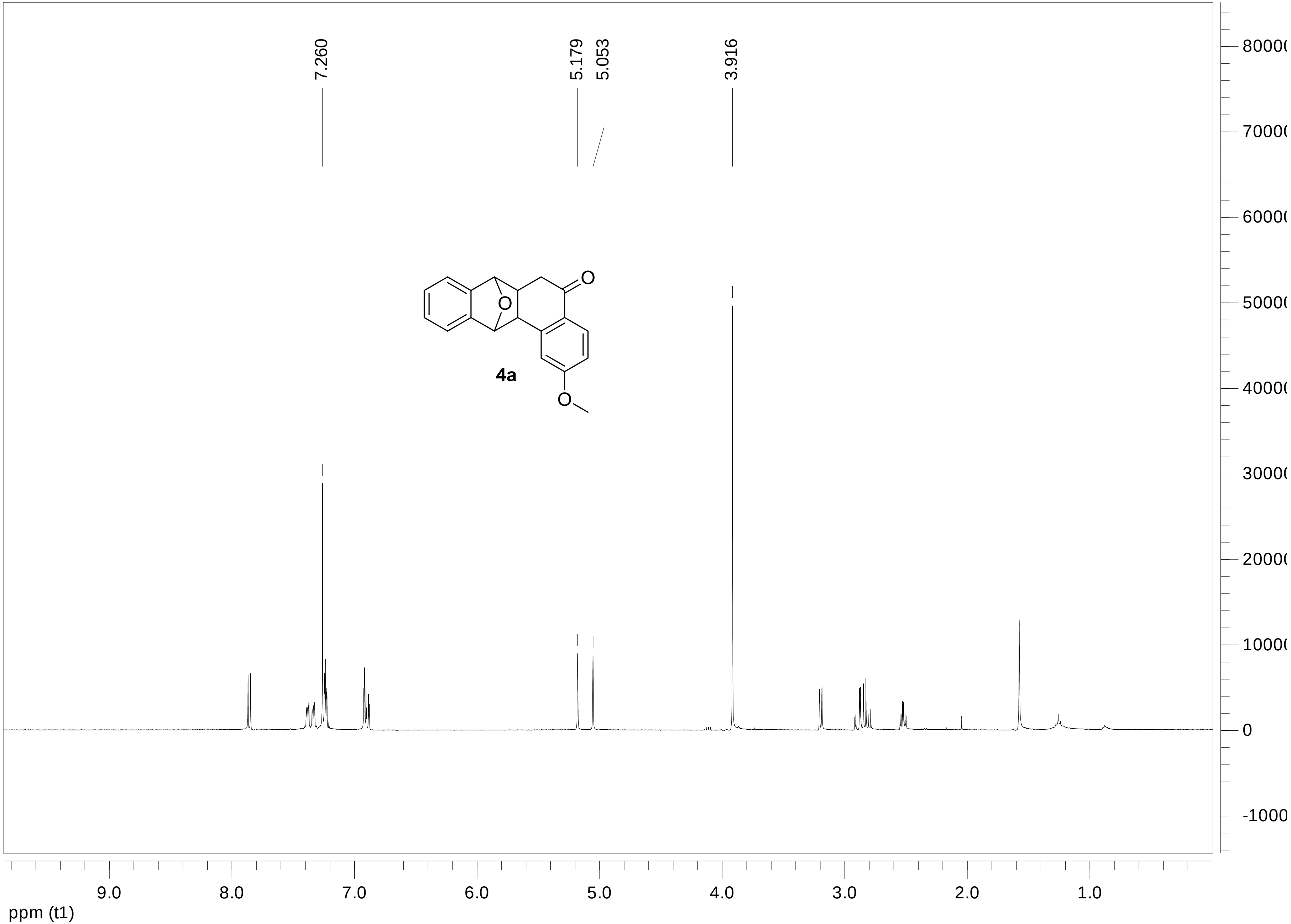
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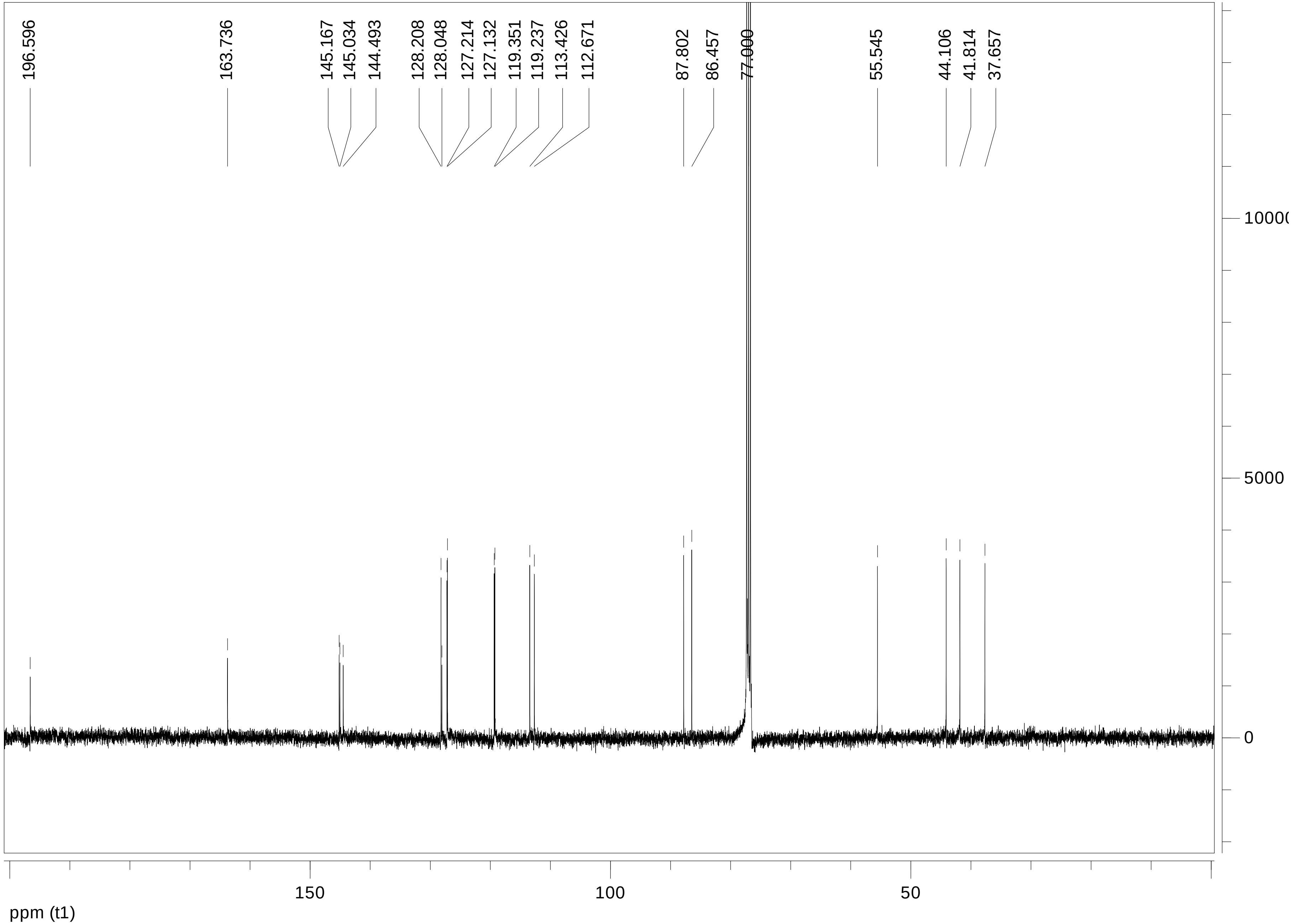
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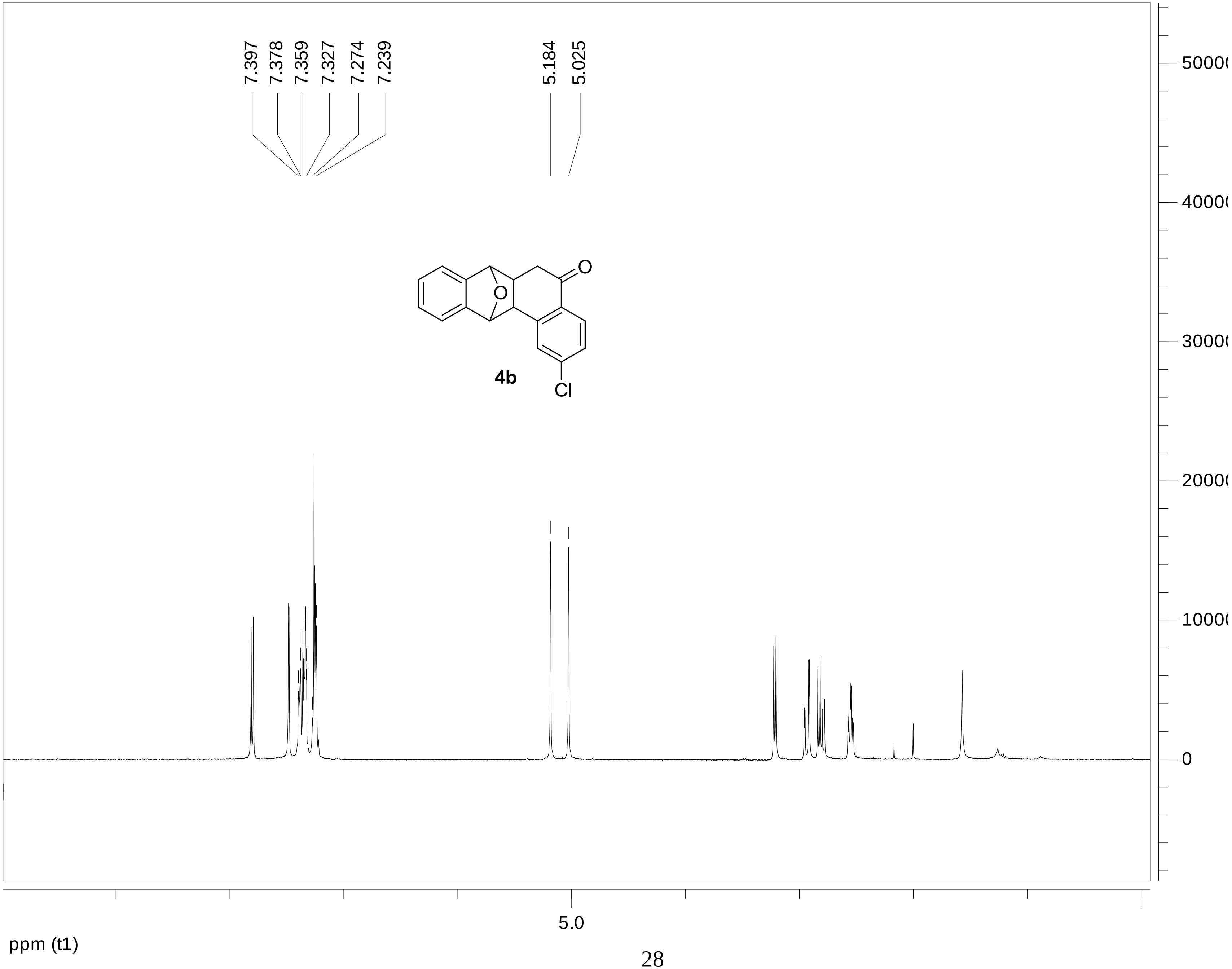
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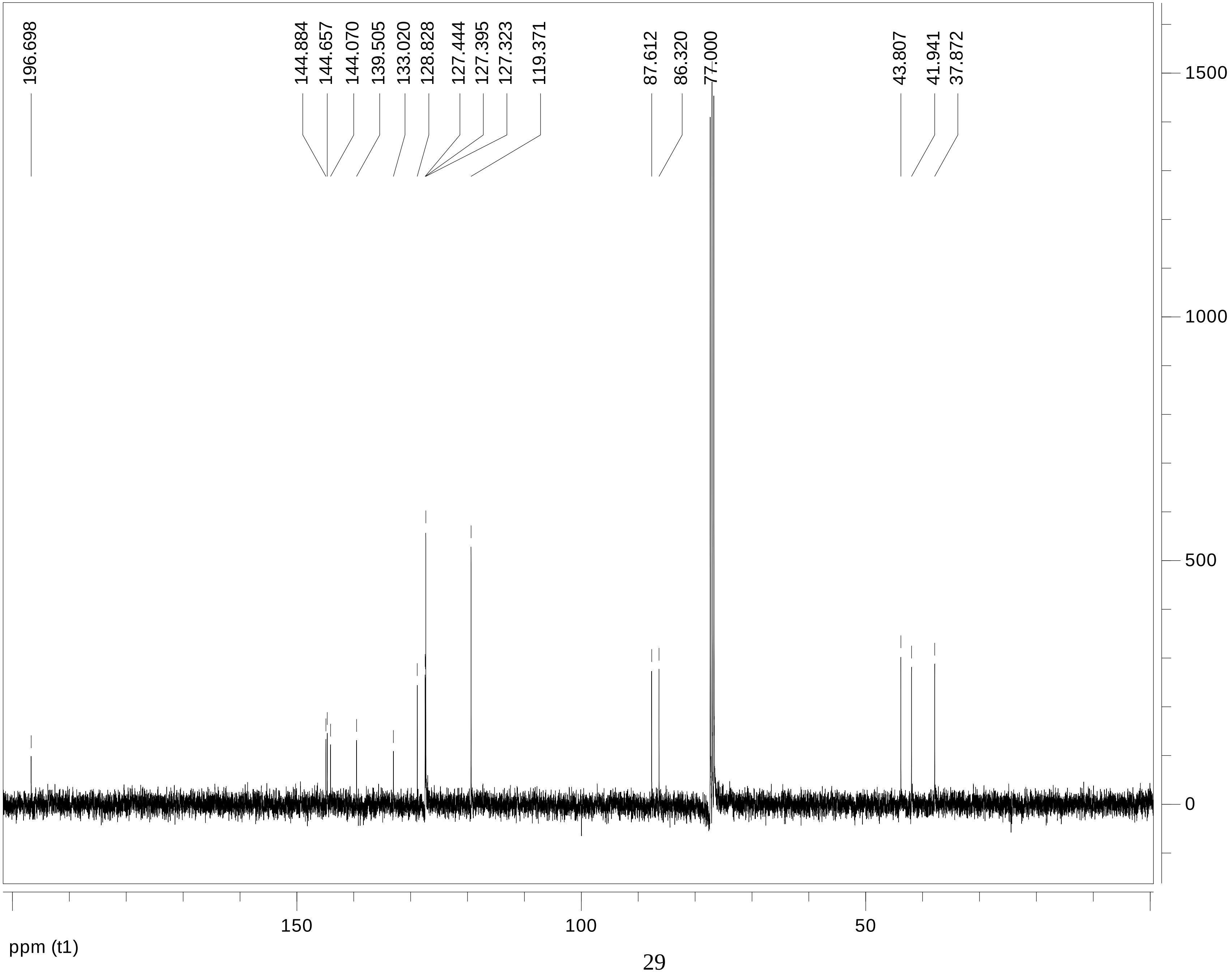
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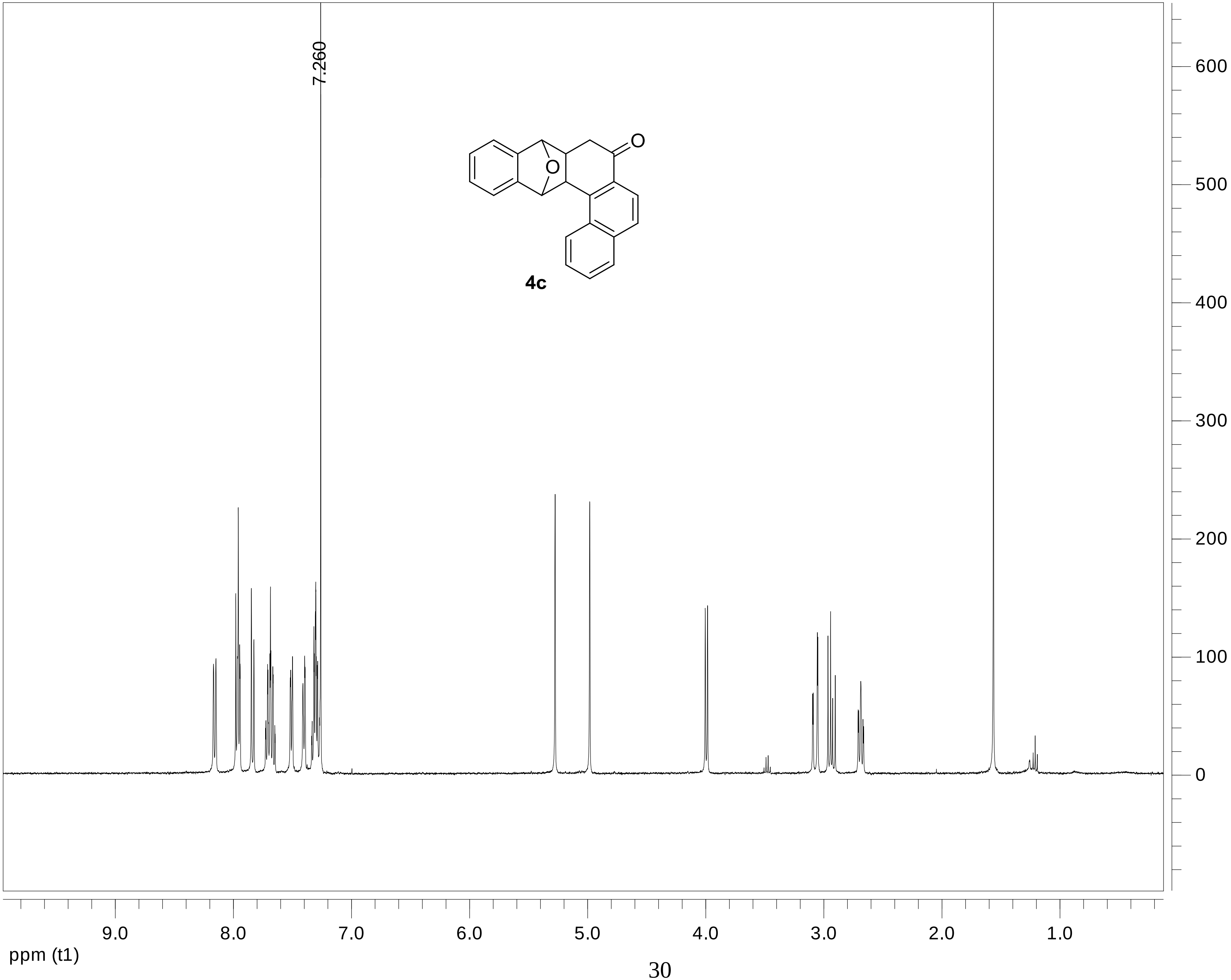
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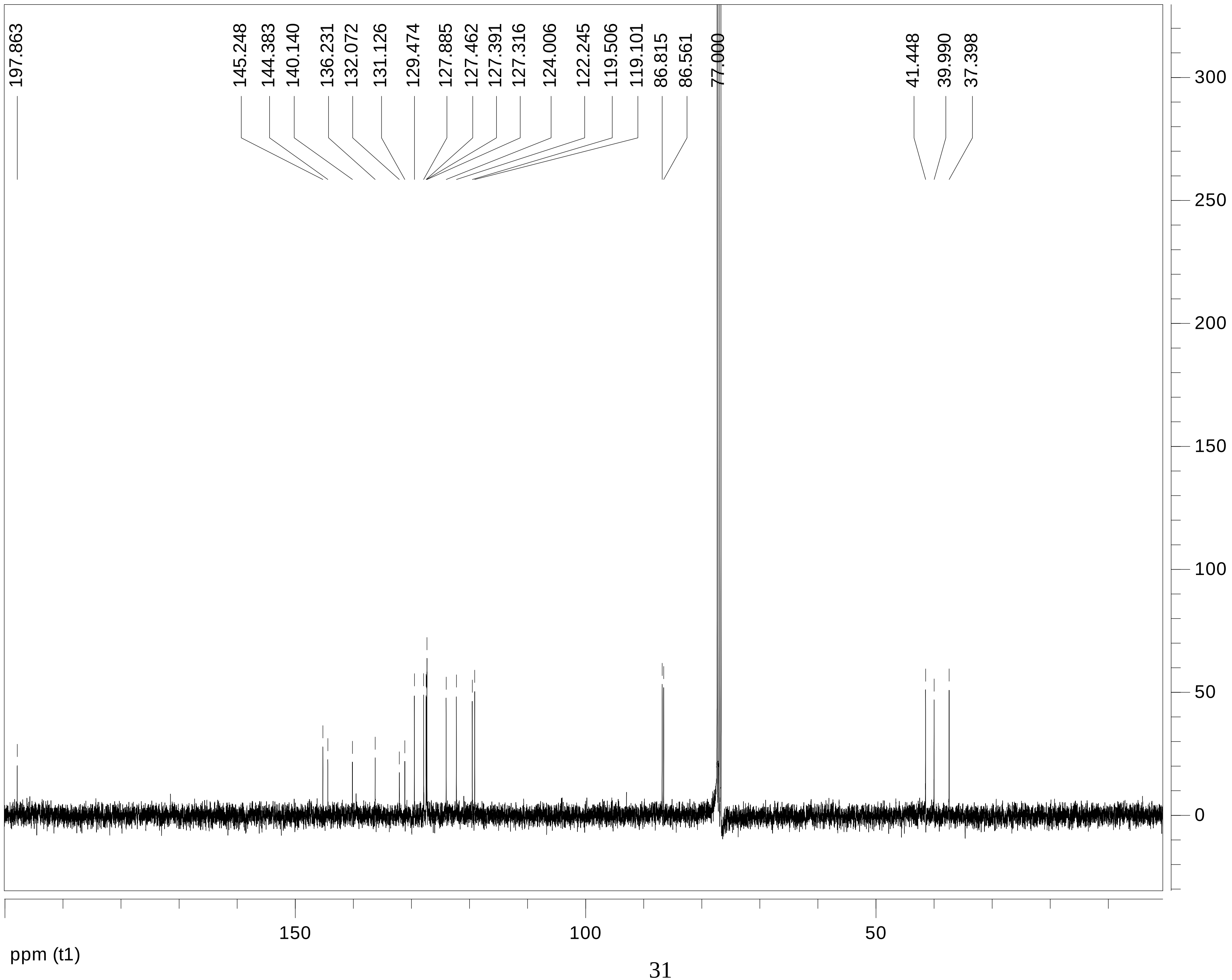
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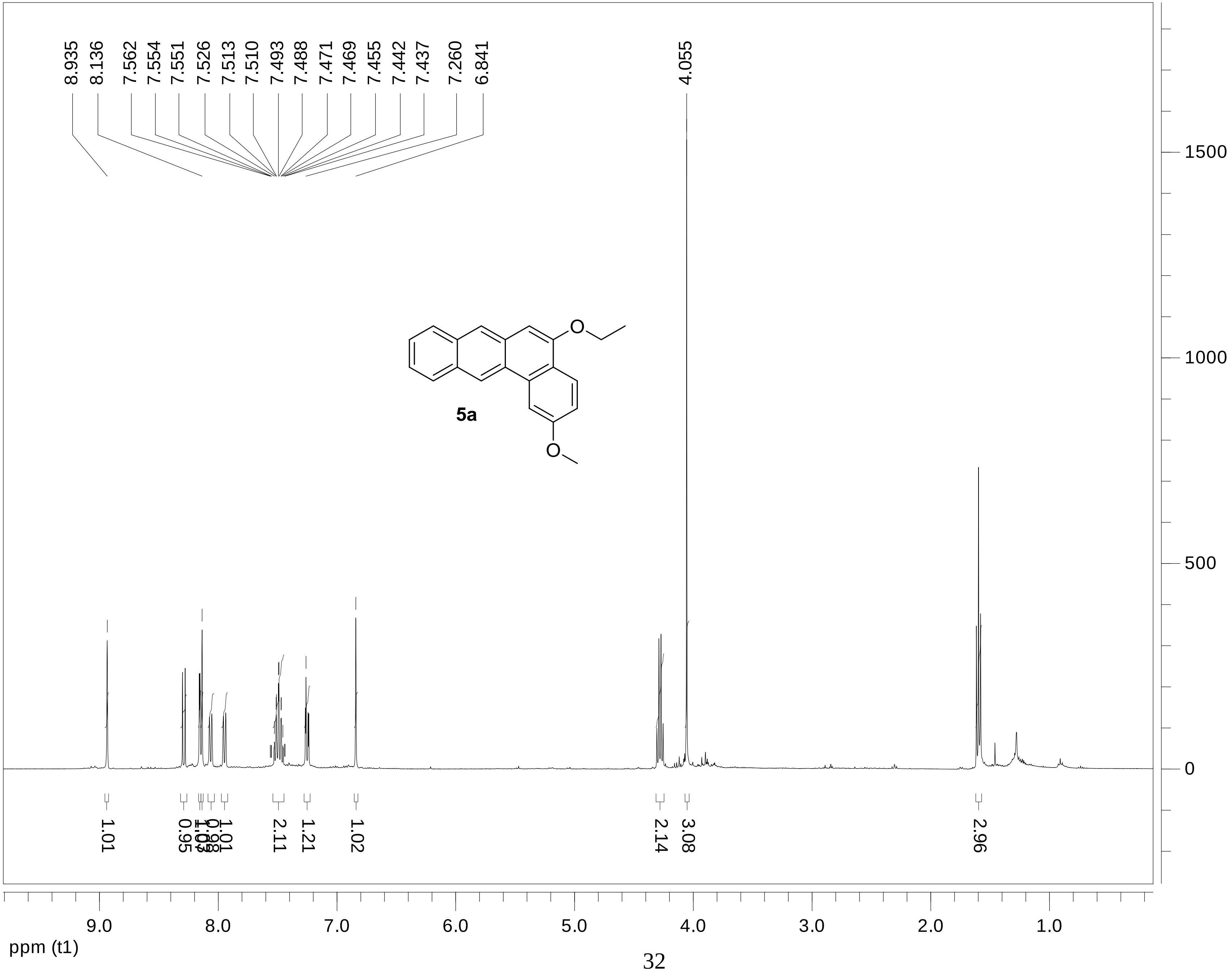
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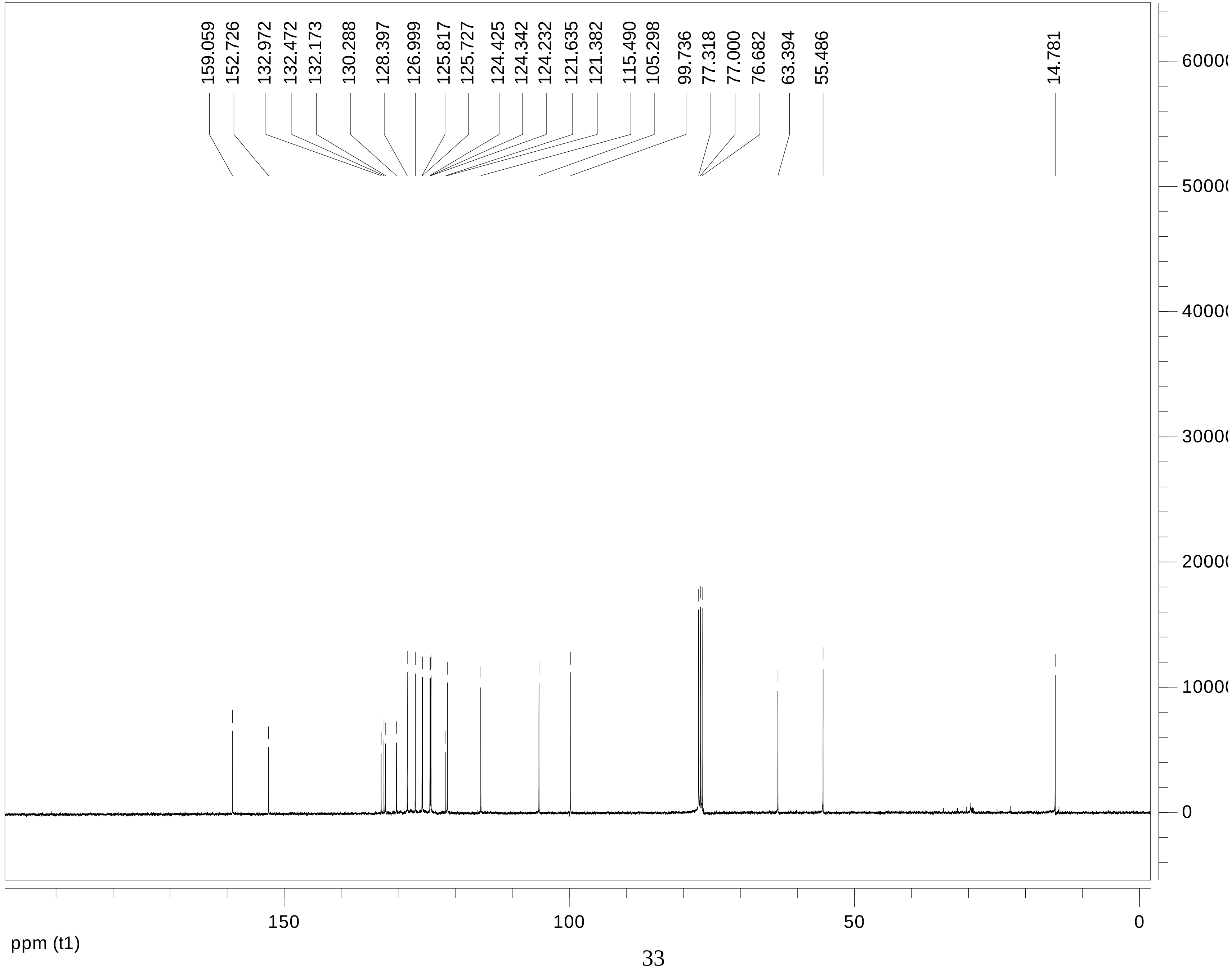
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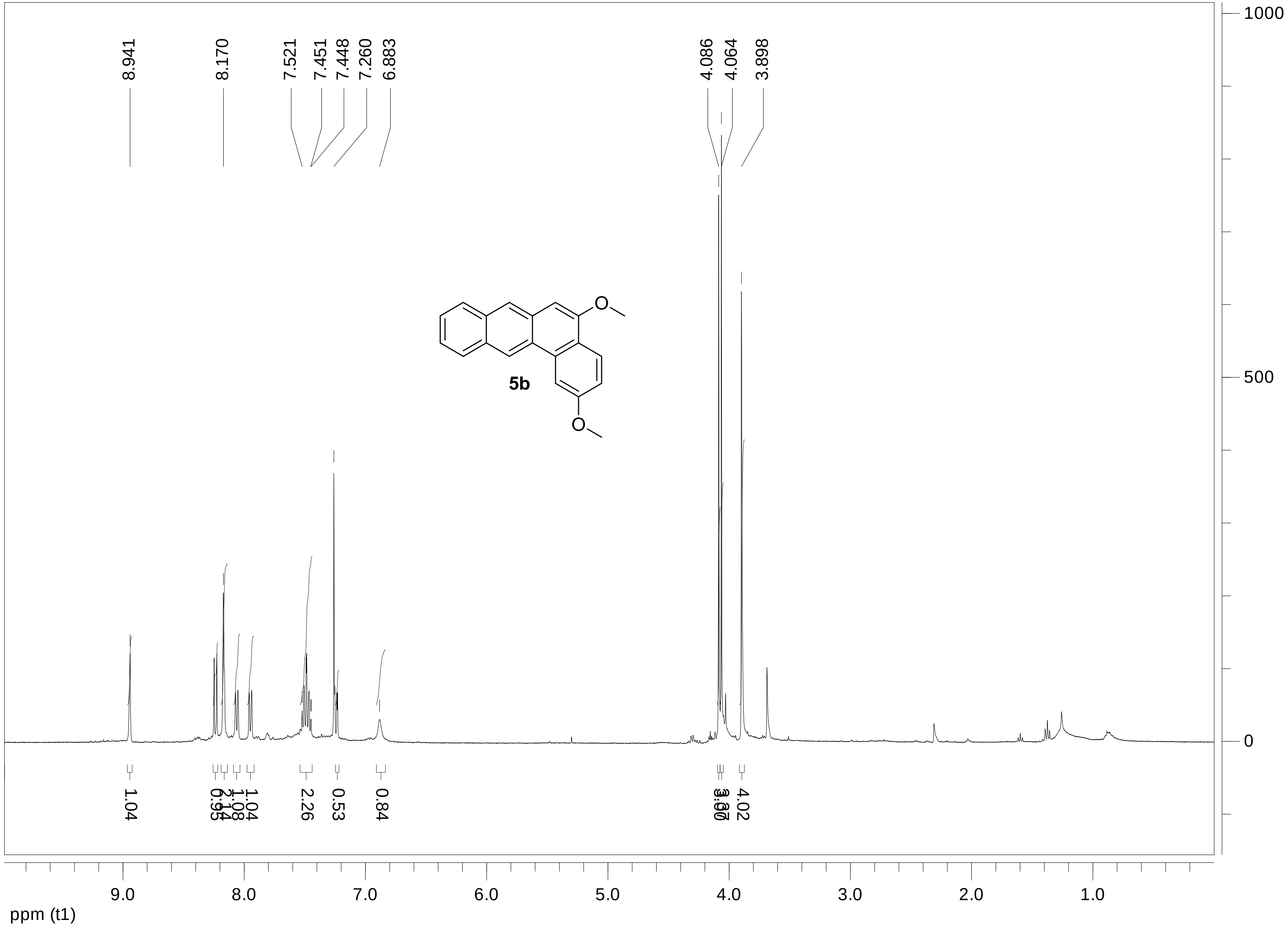
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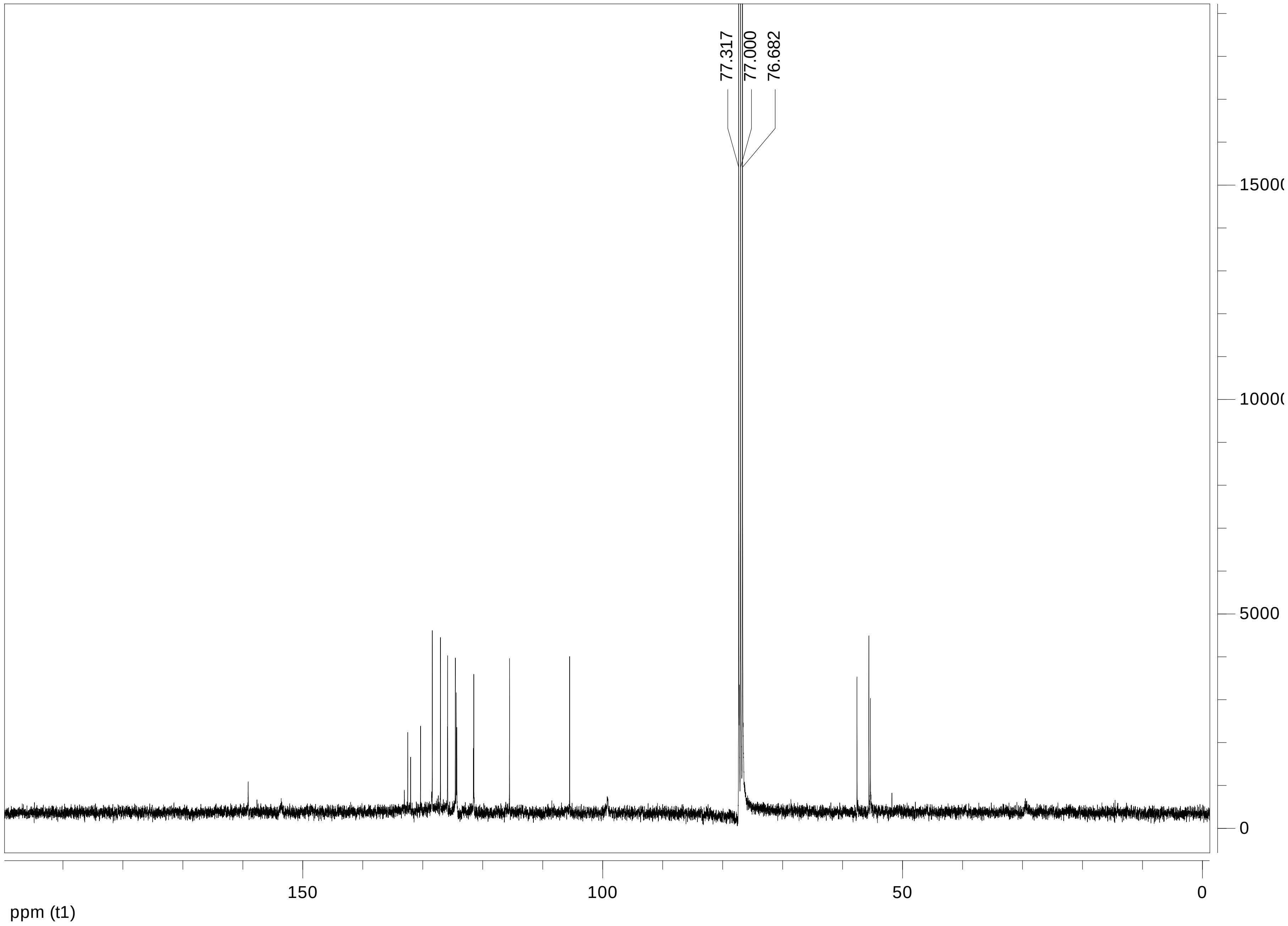
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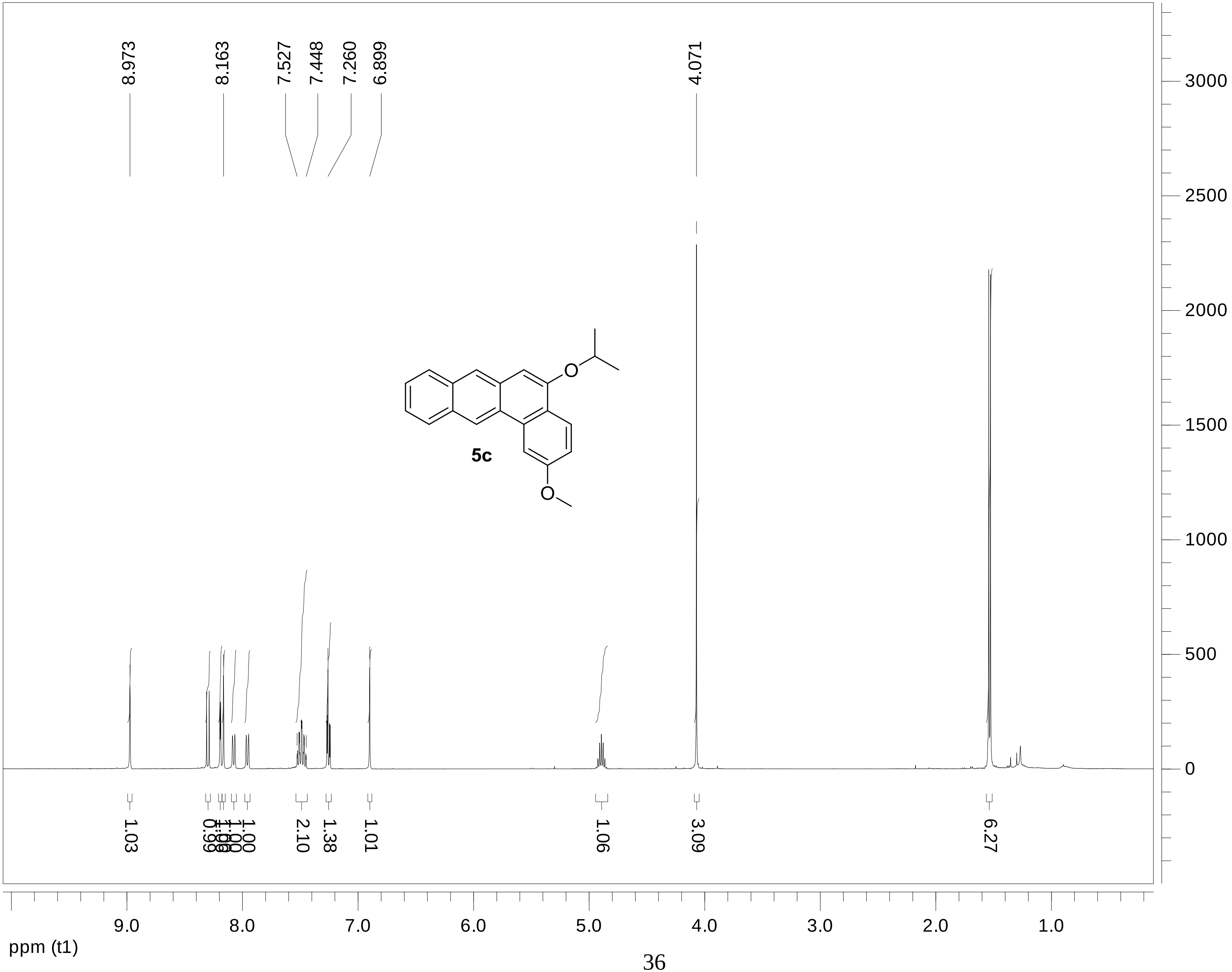
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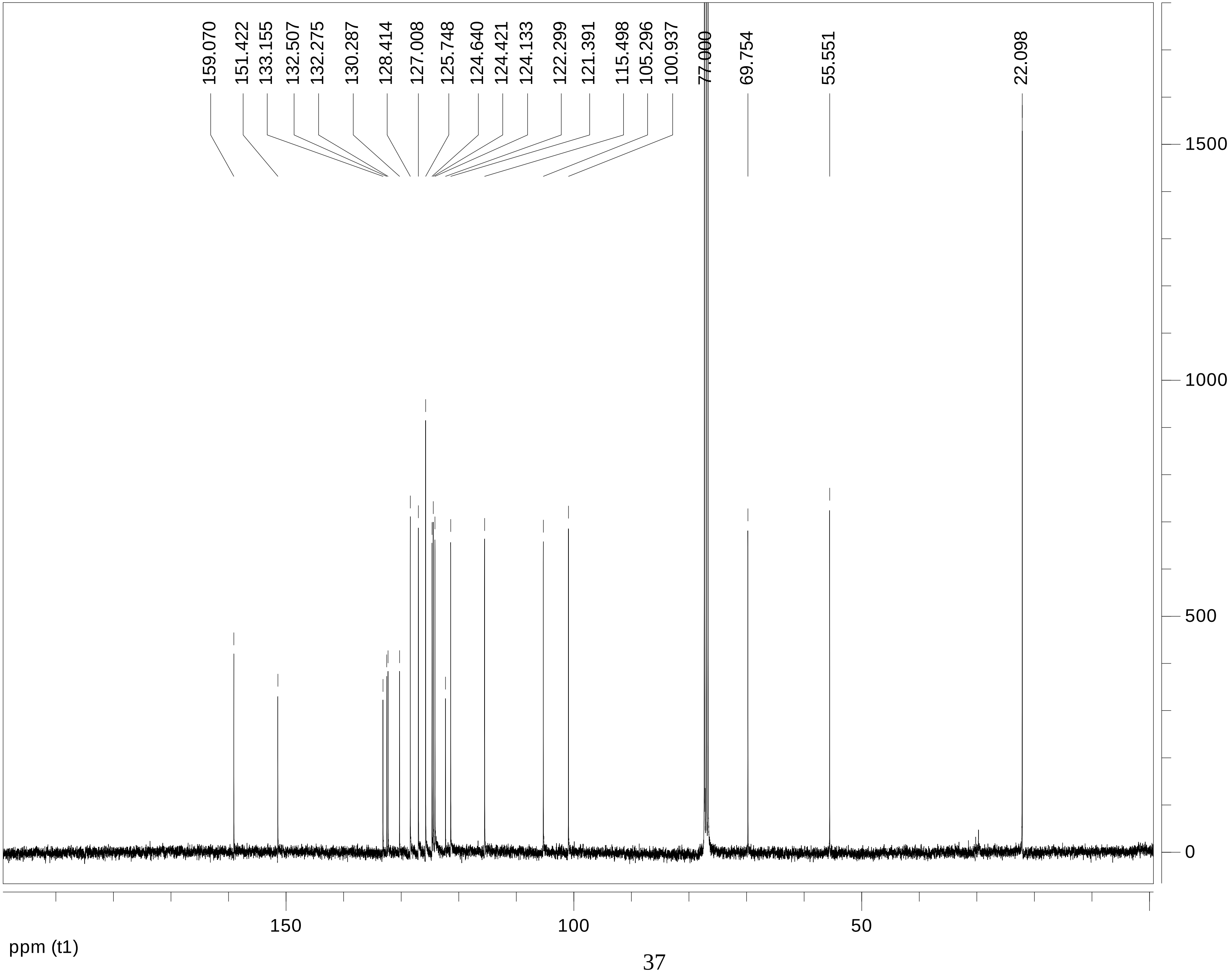
ppm (t1)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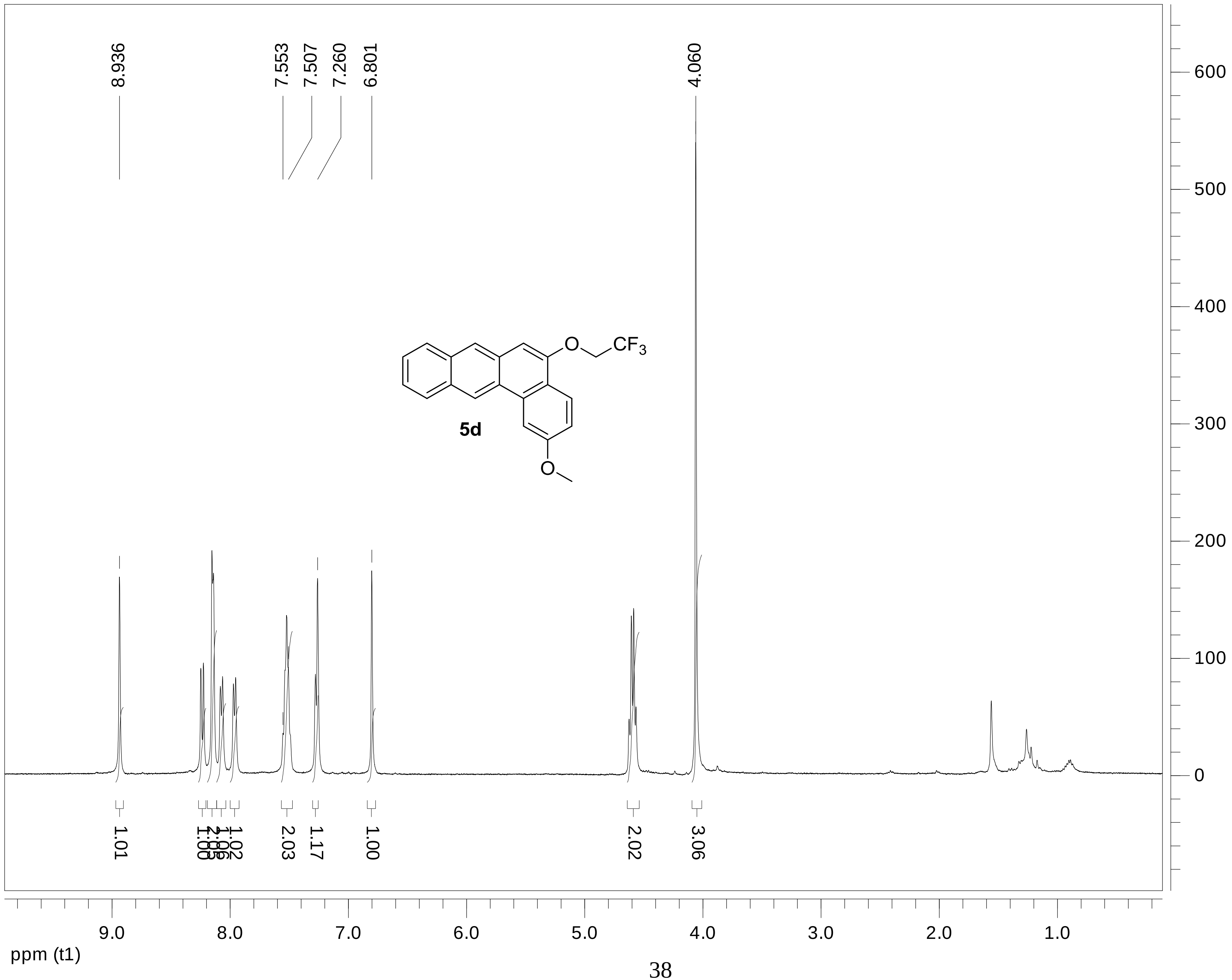
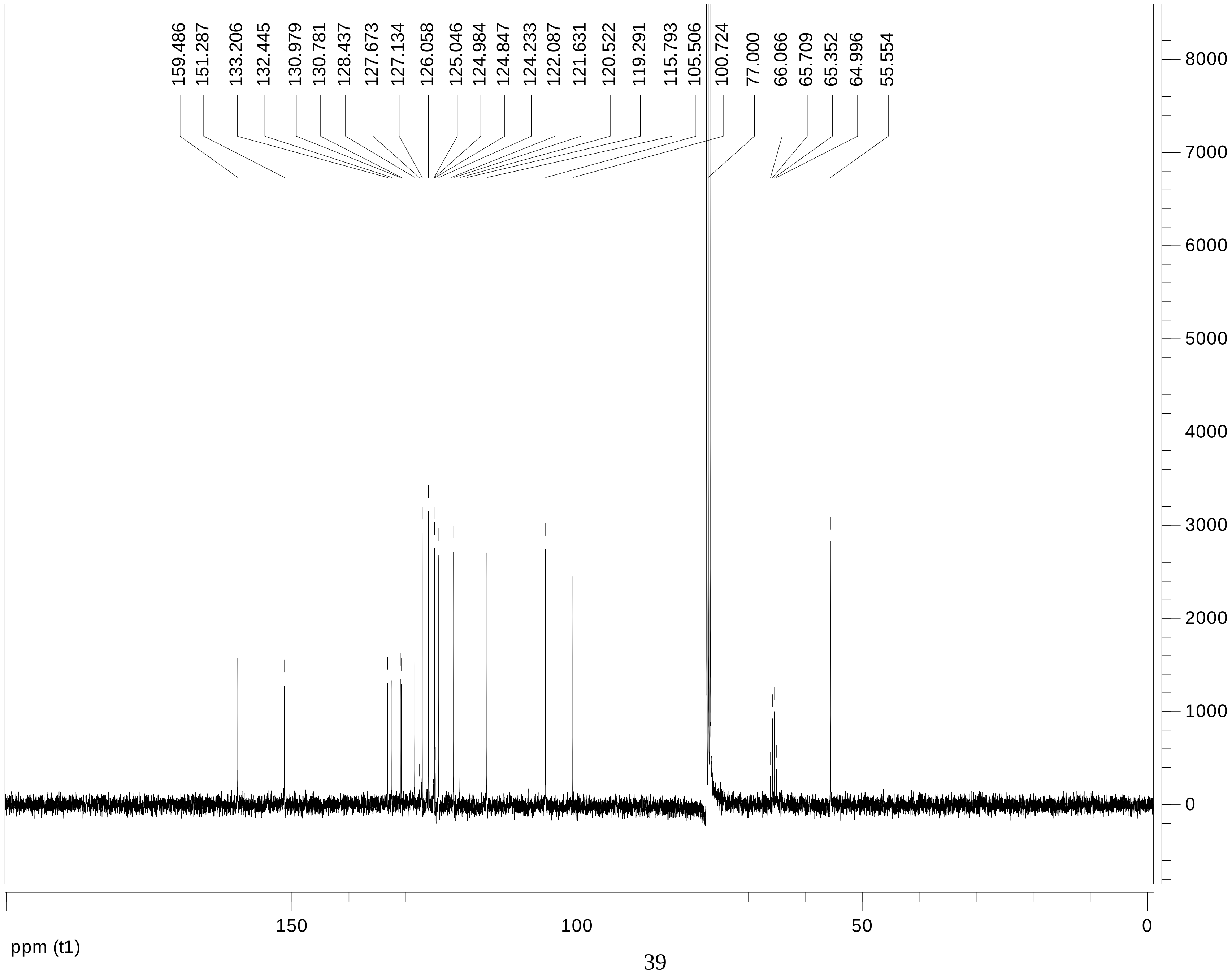
151.422
133.155
132.507
132.275
130.287
128.414
127.008
125.748
124.640
124.421
124.133
122.299
121.391
115.498
105.296
100.937
77.000
69.754
55.551
22.098
1500
1000
500
0
150
100
50
ppm (t1)


8.936
7.553
7.507
7.260
6.801
4.060
O
CF_3
O
5d
1.01
1.00
2.05
1.06
1.02
2.03
1.17
1.00
2.02
3.06
600
500
400
300
200
100
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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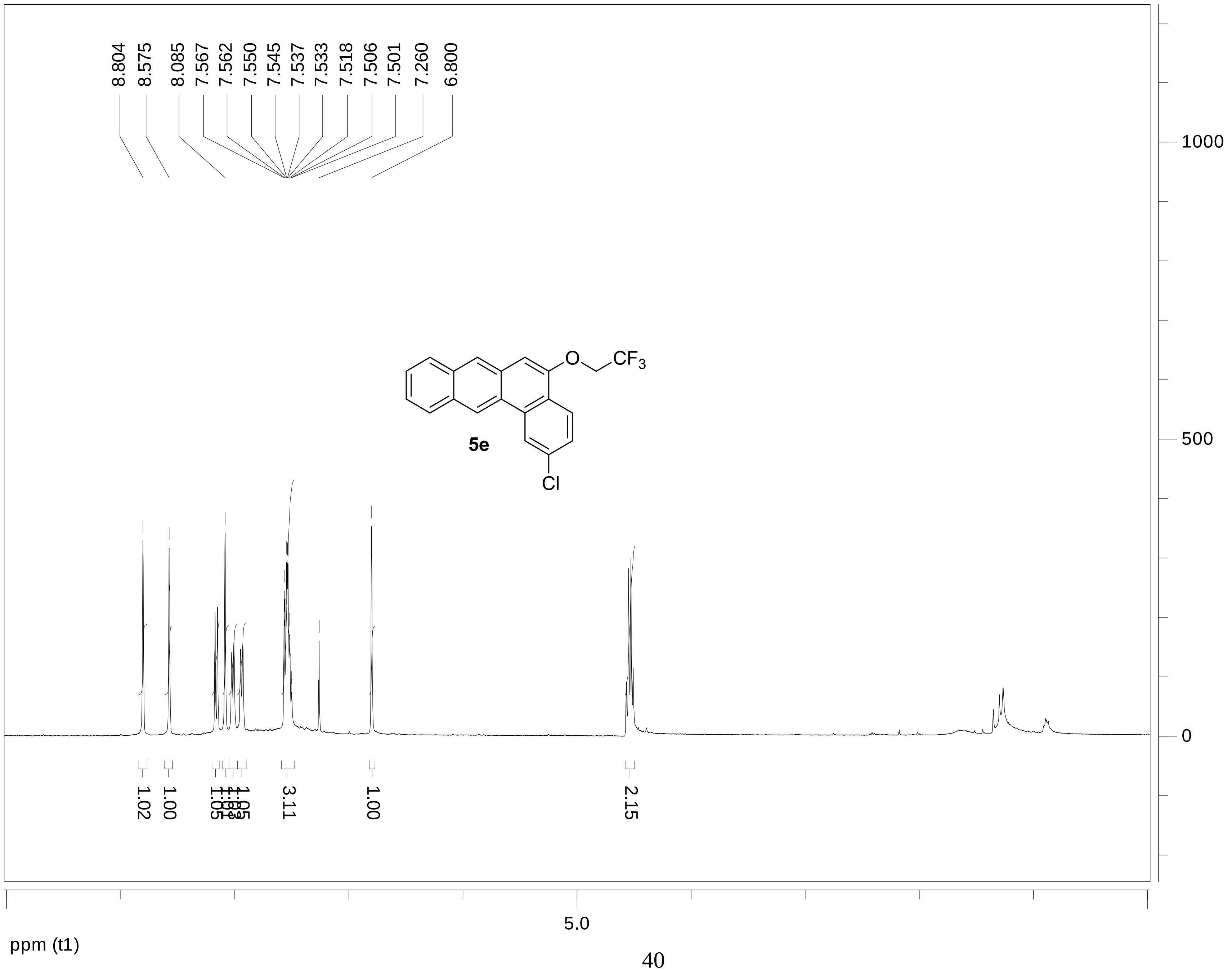
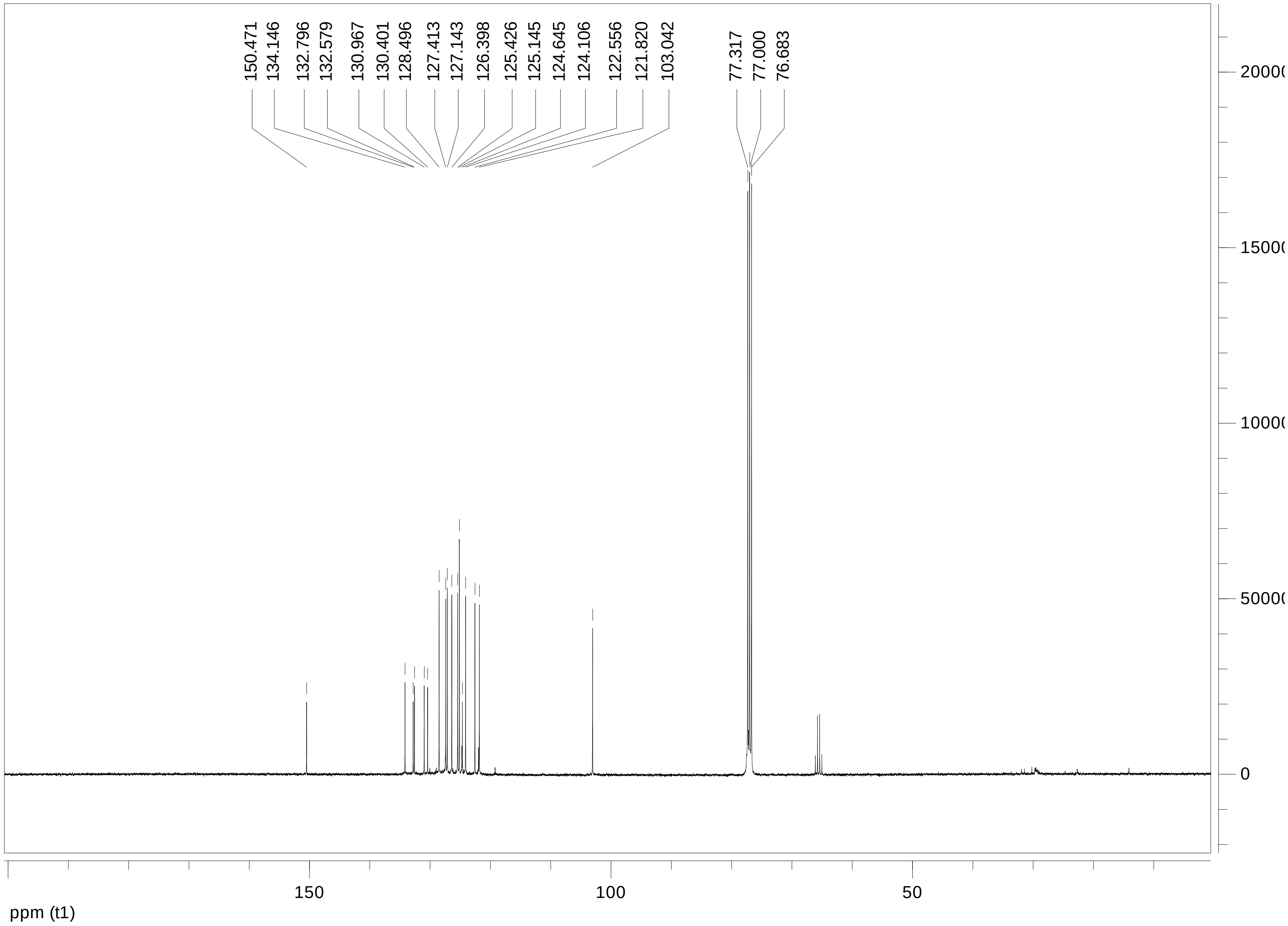
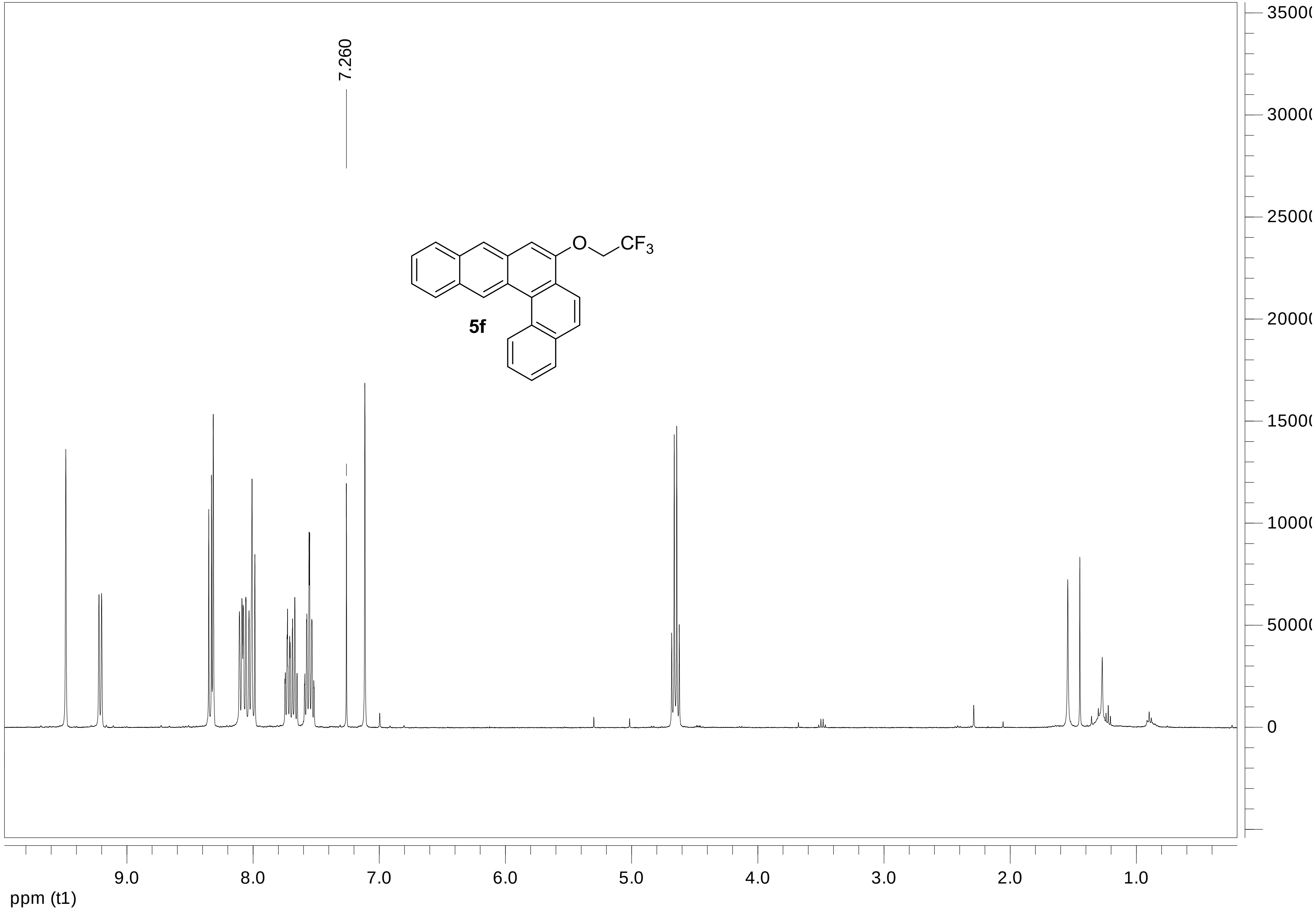
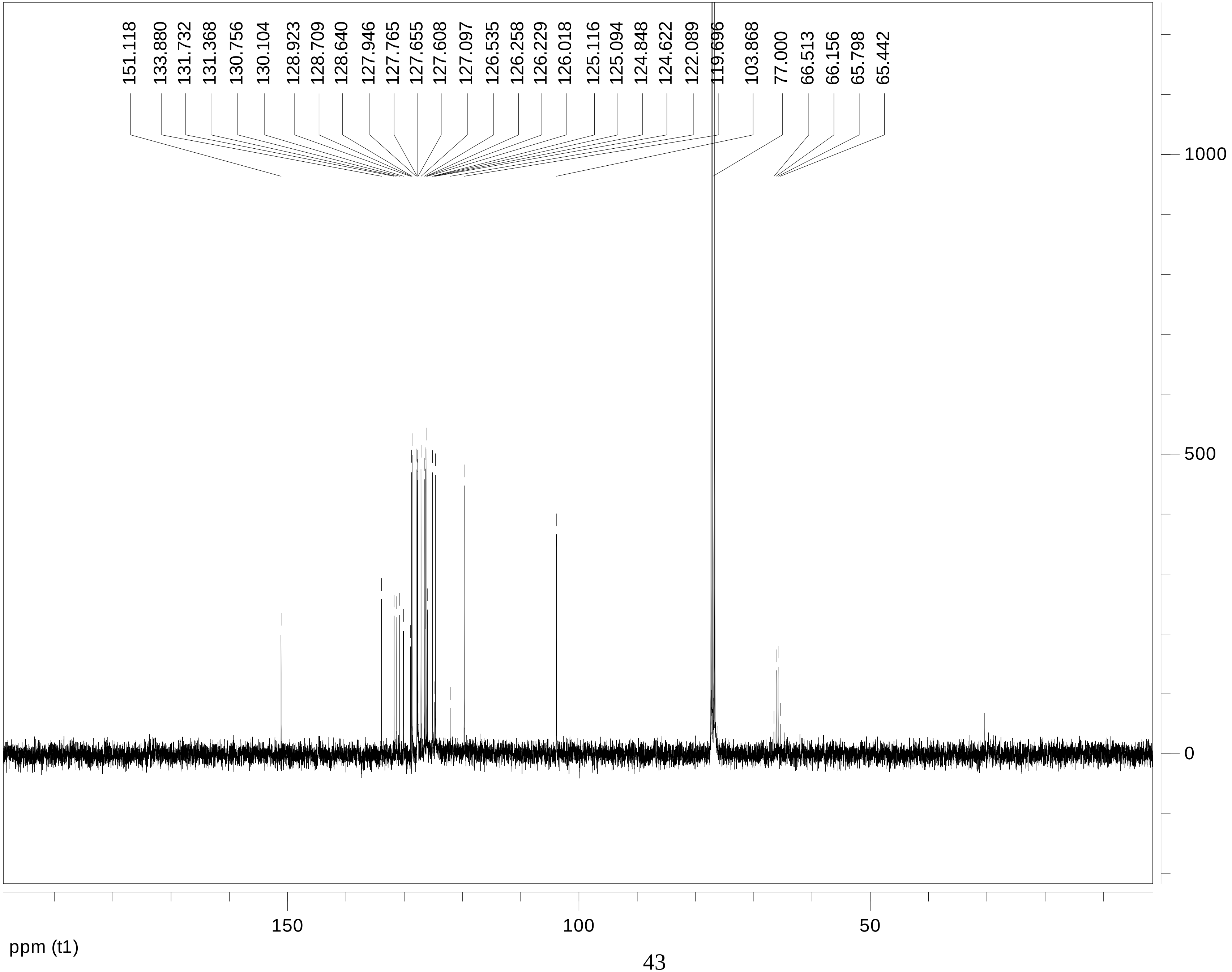
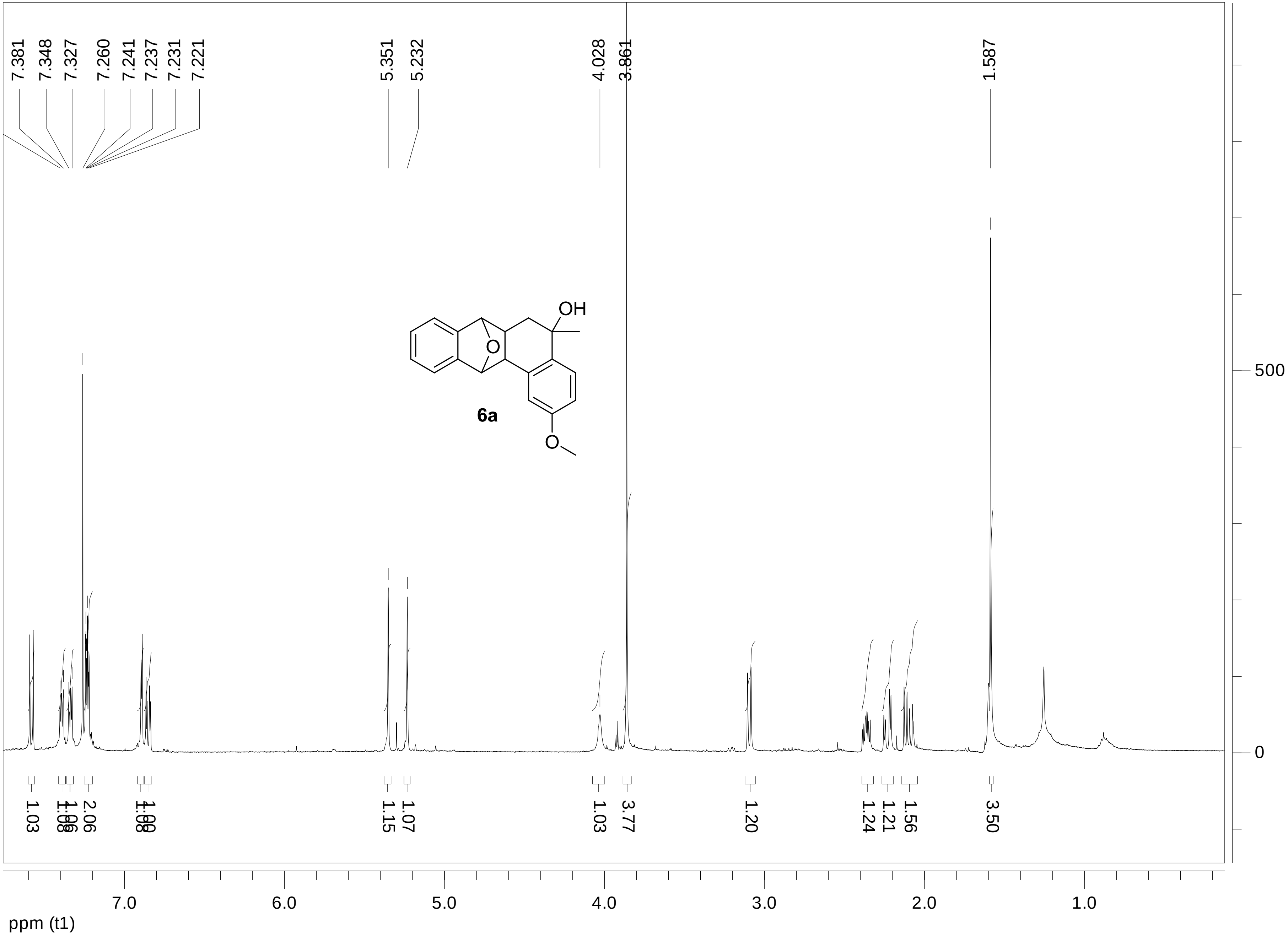
133.206
132.445
130.979
130.781
128.437
127.673
127.134
126.058
125.046
124.984
124.847
124.233
122.087
121.631
120.522
119.291
115.793
105.506
100.724
77.000
66.066
65.709
65.352
64.996
55.554
8000
7000
6000
5000
4000
3000
2000
1000
0
150
100
50
0
ppm (t1)

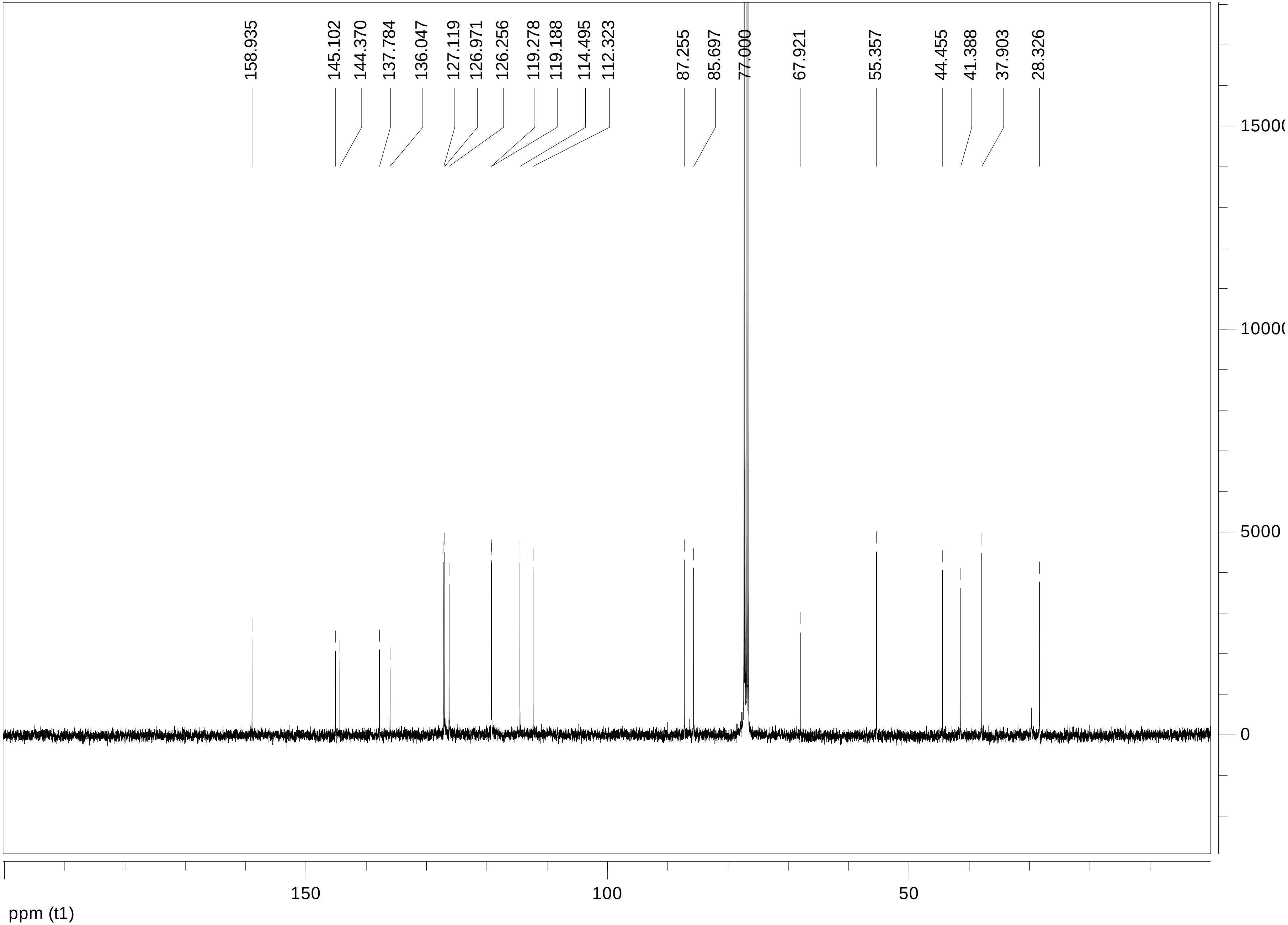

8.804
8.575
8.085
7.567
7.562
7.550
7.545
7.537
7.533
7.518
7.506
7.501
7.260
6.800
O
CF3
5e
Cl
1000
500
0
1.02
1.00
1.05
1.01
1.03
1.05
3.11
1.00
2.15
5.0
ppm (t1)

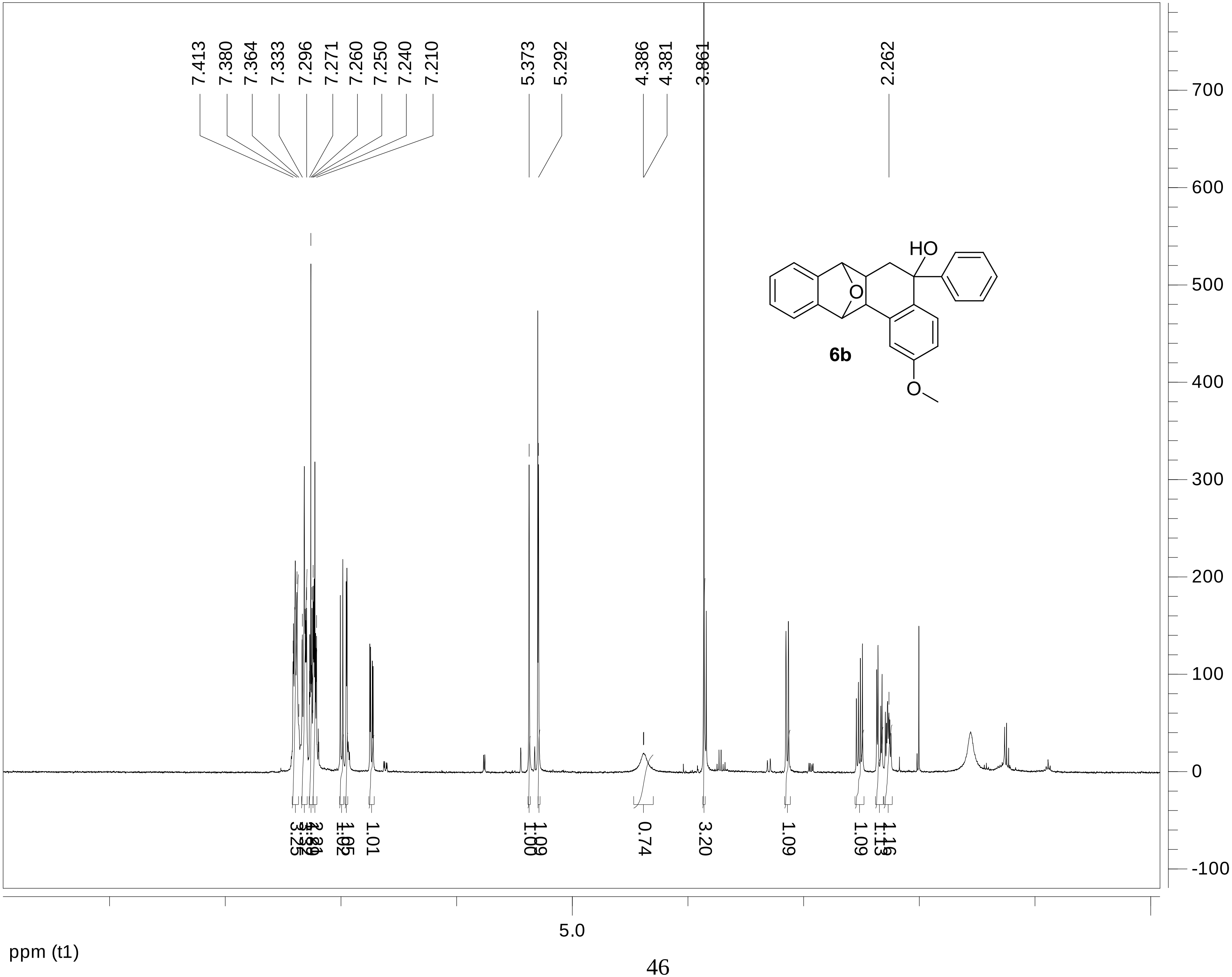

150.471
134.146
132.796
132.579
130.967
130.401
128.496
127.413
127.143
126.398
125.426
125.145
124.645
124.106
122.556
121.820
103.042
77.317
77.000
76.683
20000
15000
10000
50000
0
150
100
50
ppm (t1)


7.260
O
CF3
5f
3500
3000
2500
2000
1500
1000
5000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

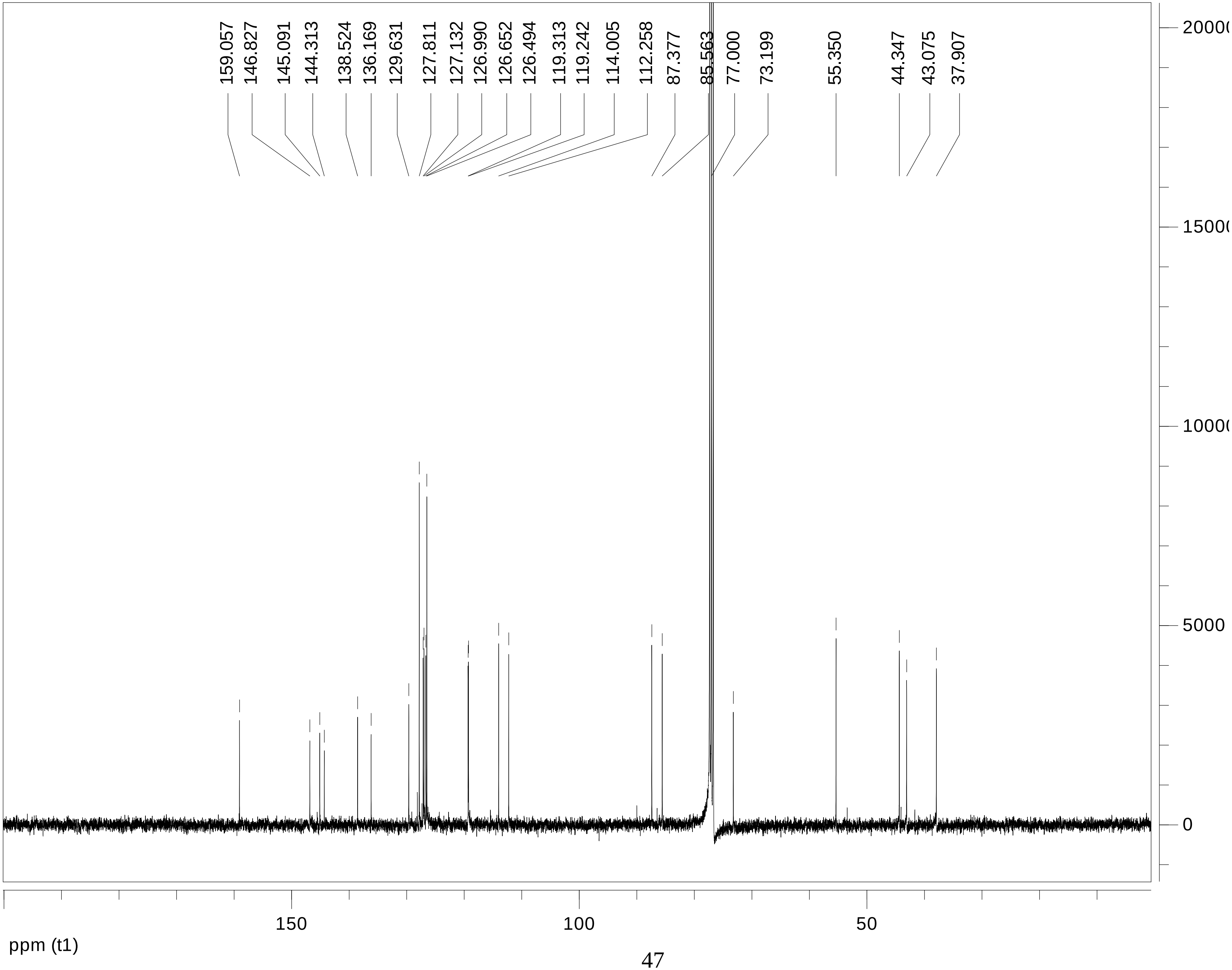

151.118
133.880
131.732
131.368
130.756
130.104
128.923
128.709
128.640
127.946
127.765
127.655
127.608
127.097
126.535
126.258
126.229
126.018
125.116
125.094
124.848
124.622
122.089
119.696
103.868
77.000
66.513
66.156
65.798
65.442
1000
500
0
150
100
50
ppm (t1)

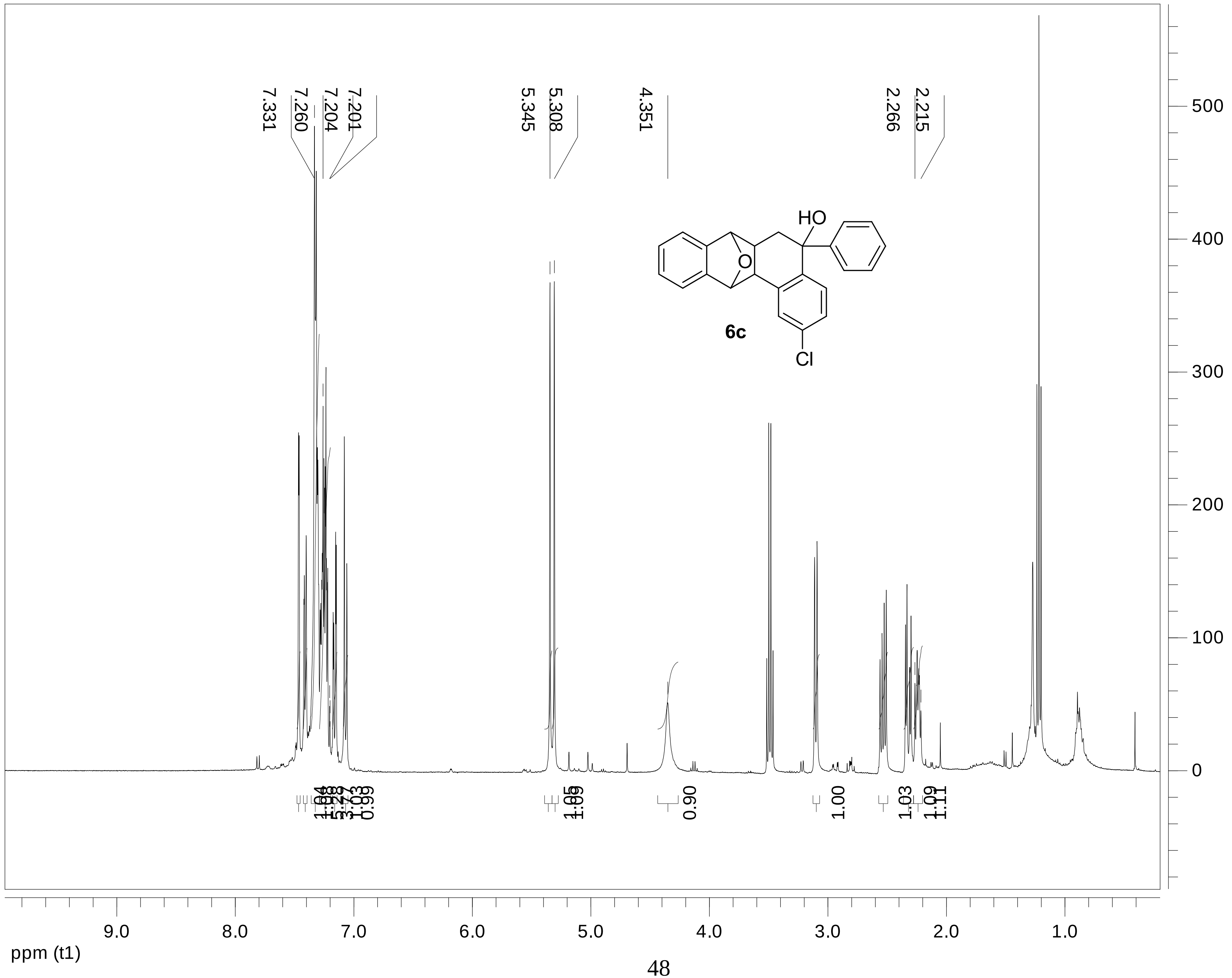

7.381
7.348
7.327
7.260
7.241
7.237
7.231
7.221
5.351
5.232
4.028
3.861
1.587
OH
O
O
6a
500
0
1.03
1.08
1.06
2.06
1.08
1.00
1.15
1.07
1.03
3.77
1.20
1.24
1.21
1.56
3.50
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

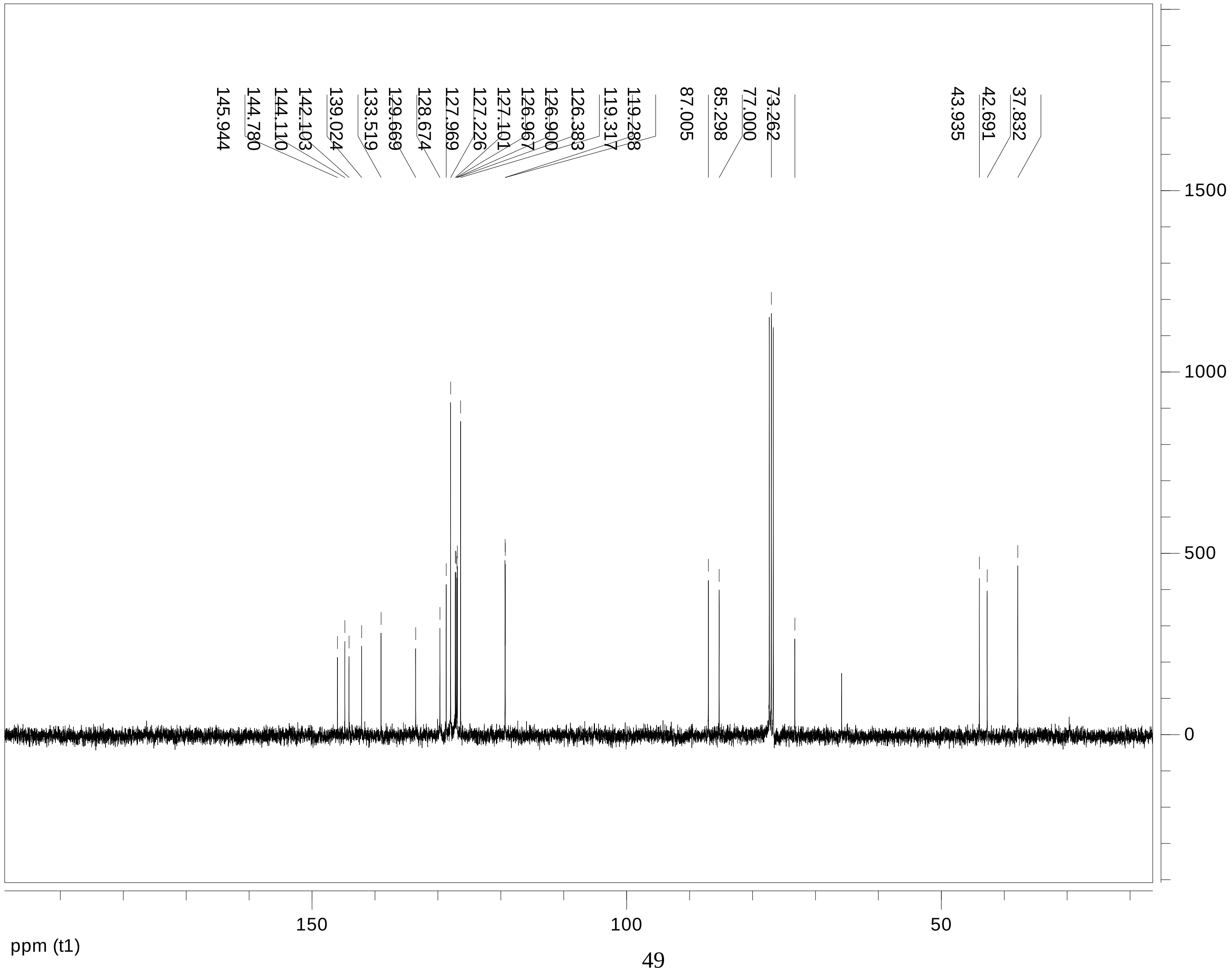

158.935
145.102
144.370
137.784
136.047
127.119
126.971
126.256
119.278
119.188
114.495
112.323
87.255
85.697
77.000
67.921
55.357
44.455
41.388
37.903
28.326
1500
1000
5000
0
150
100
50
ppm (t1)

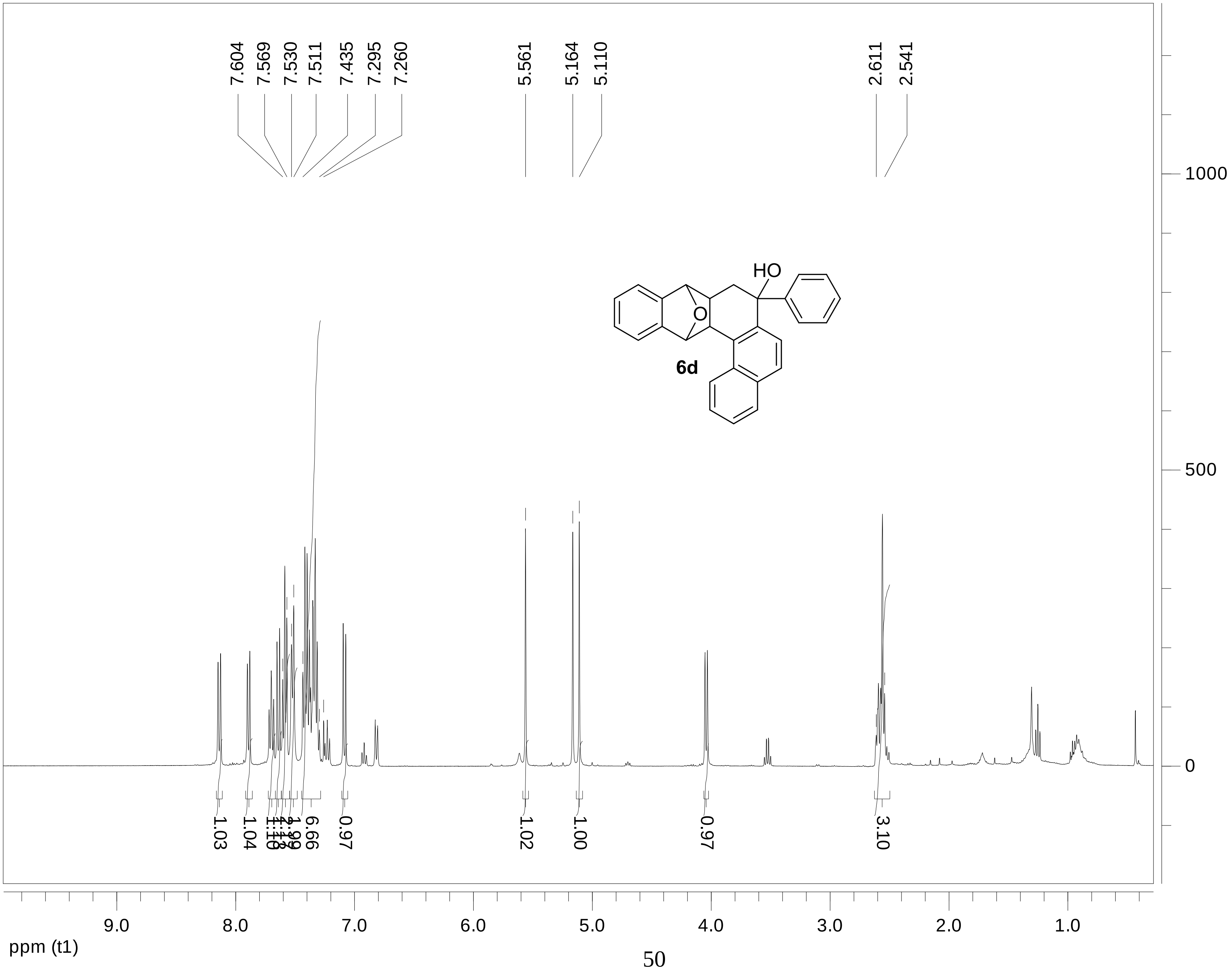

7.413
7.380
7.364
7.333
7.296
7.271
7.260
7.250
7.240
7.210
5.373
5.292
4.386
4.381
3.861
2.262
HO
O
O
700
600
500
400
300
200
100
0
-100
3.25
1.02
1.05
1.01
1.00
1.09
0.74
3.20
1.09
1.09
1.13
1.16
5.0
ppm (t1)

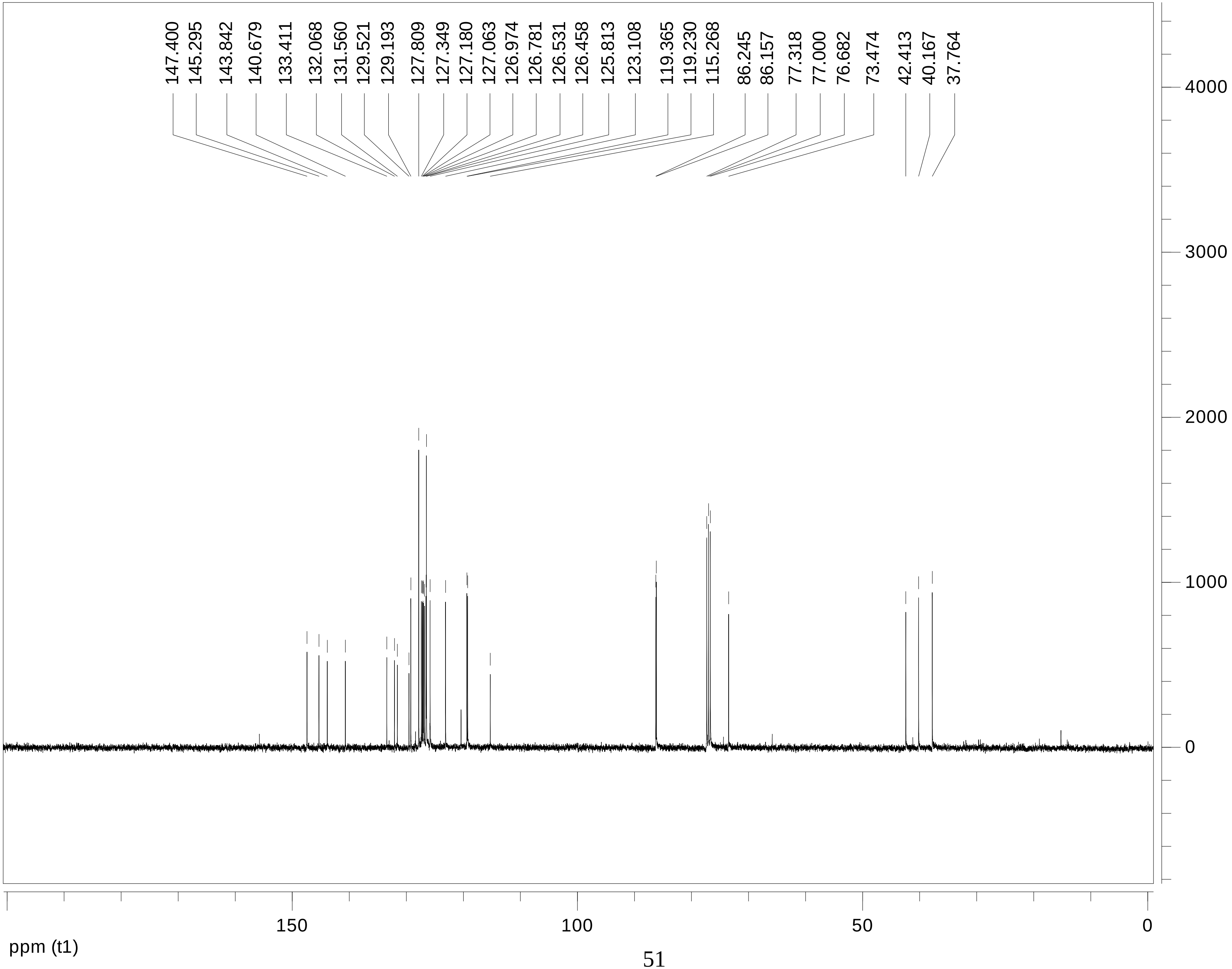
6b

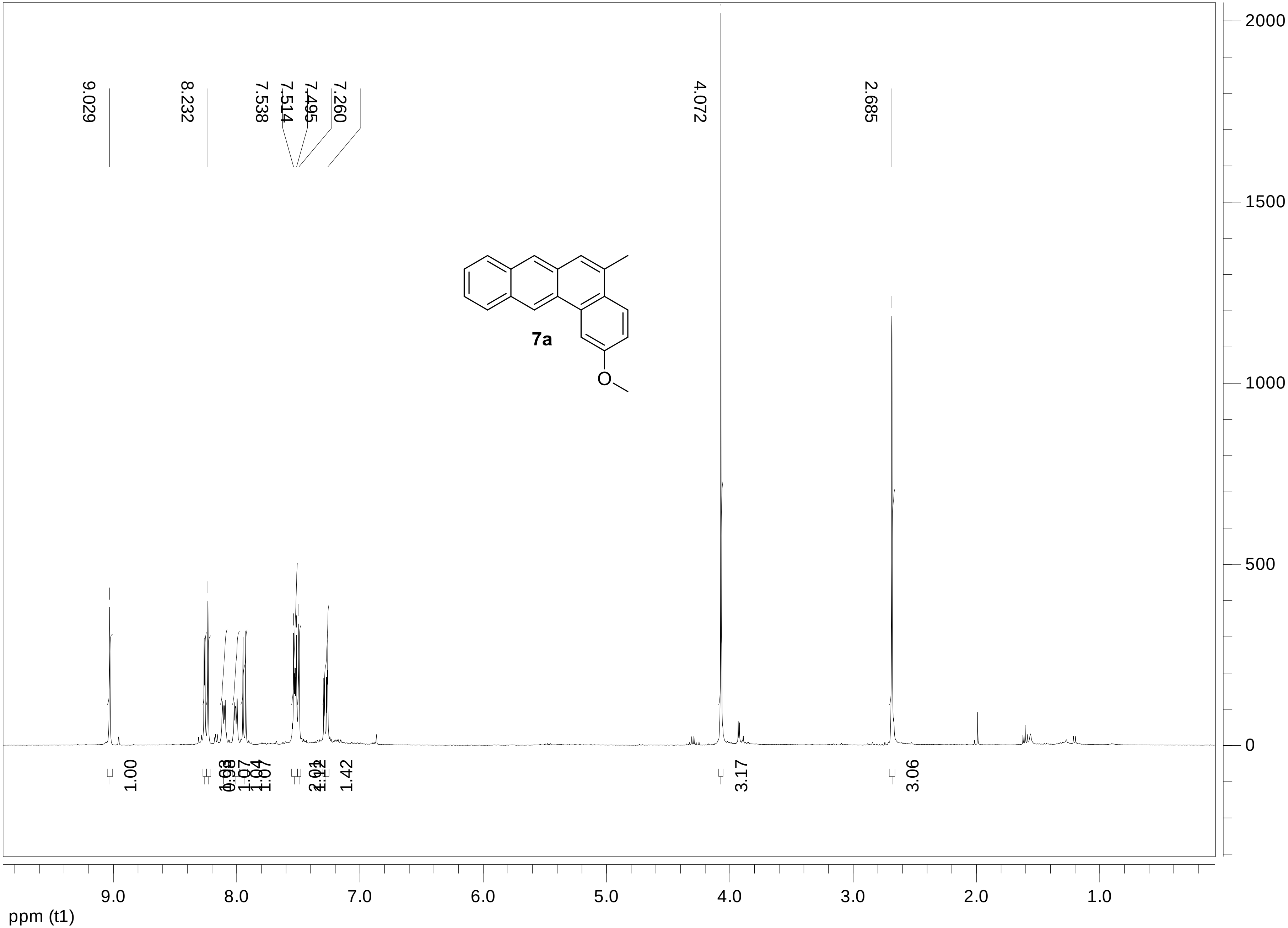

159.057
146.827
145.091
144.313
138.524
136.169
129.631
127.811
127.132
126.990
126.652
126.494
119.313
119.242
114.005
112.258
87.377
85.563
77.000
73.199
55.350
44.347
43.075
37.907
20000
15000
10000
5000
0
150
100
50
ppm (t1)

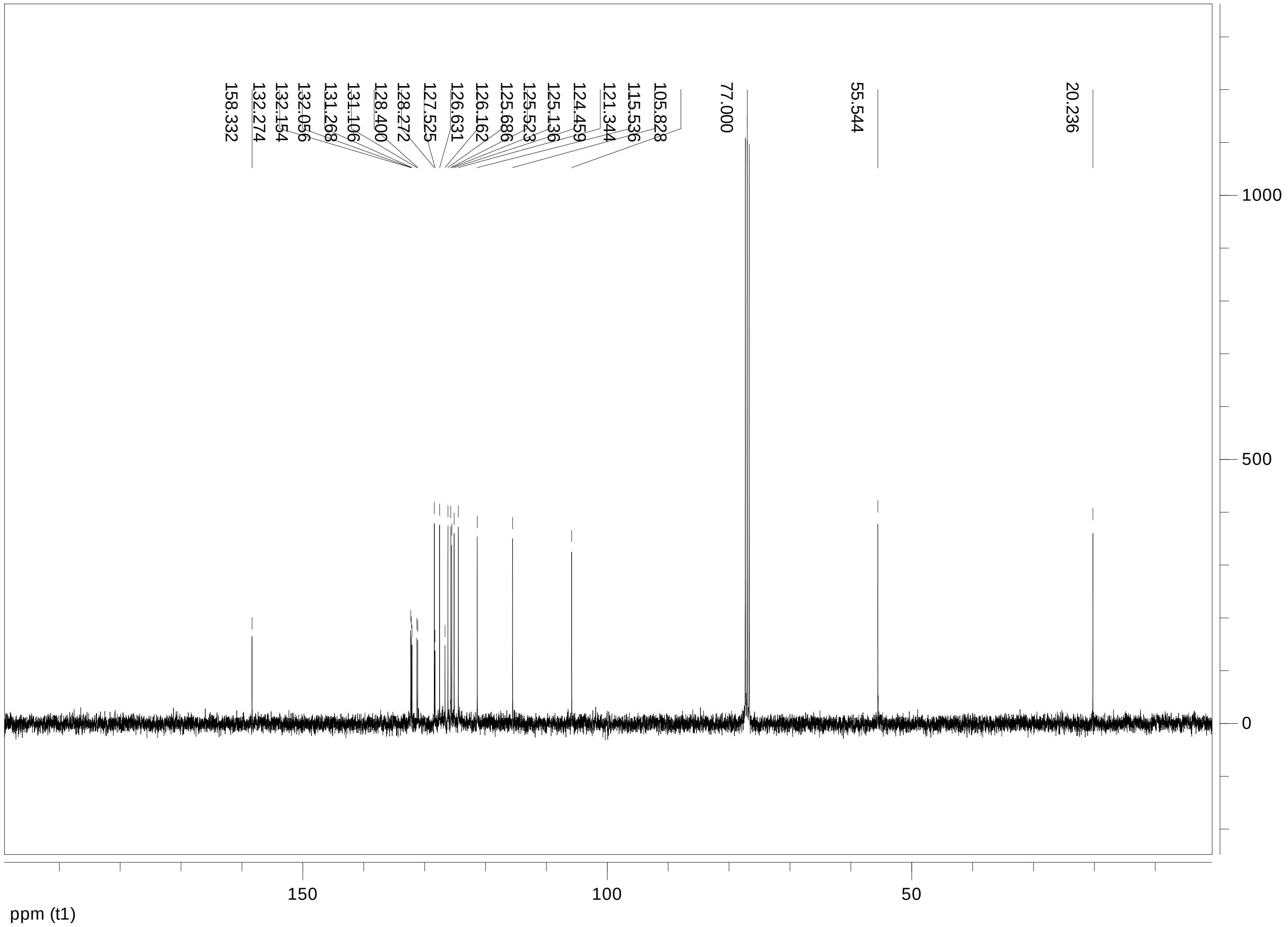

7.331
7.260
7.204
7.201
5.345
5.308
4.351
2.266
2.215
HO
O
Cl
6c
1.04
1.03
0.99
1.05
1.09
0.90
1.00
1.03
1.09
1.11
500
400
300
200
100
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


145.944
144.780
144.110
142.103
139.024
133.519
129.669
128.674
127.969
127.226
127.101
126.967
126.900
126.383
119.317
119.288
87.005
85.298
77.000
73.262
43.935
42.691
37.832
1500
1000
500
0
150
100
50
ppm (t1)


7.604
7.569
7.530
7.511
7.435
7.295
7.260
5.561
5.164
5.110
2.611
2.541
HO
O
6d
1000
500
0
1.03
1.04
1.10
1.13
2.07
1.99
6.66
0.97
1.02
1.00
0.97
3.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


147.400
145.295
143.842
140.679
133.411
132.068
131.560
129.521
129.193
127.809
127.349
127.180
127.063
126.974
126.781
126.531
126.458
125.813
123.108
119.365
119.230
115.268
86.245
86.157
77.318
77.000
76.682
73.474
42.413
40.167
37.764
4000
3000
2000
1000
0
150
100
50
0
ppm (t1)


9.029
8.232
7.538
7.514
7.495
7.260
4.072
2.685
7a
O
1.00
1.03
0.98
1.07
1.04
1.07
2.01
1.12
1.42
3.17
3.06
2000
1500
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


158.332
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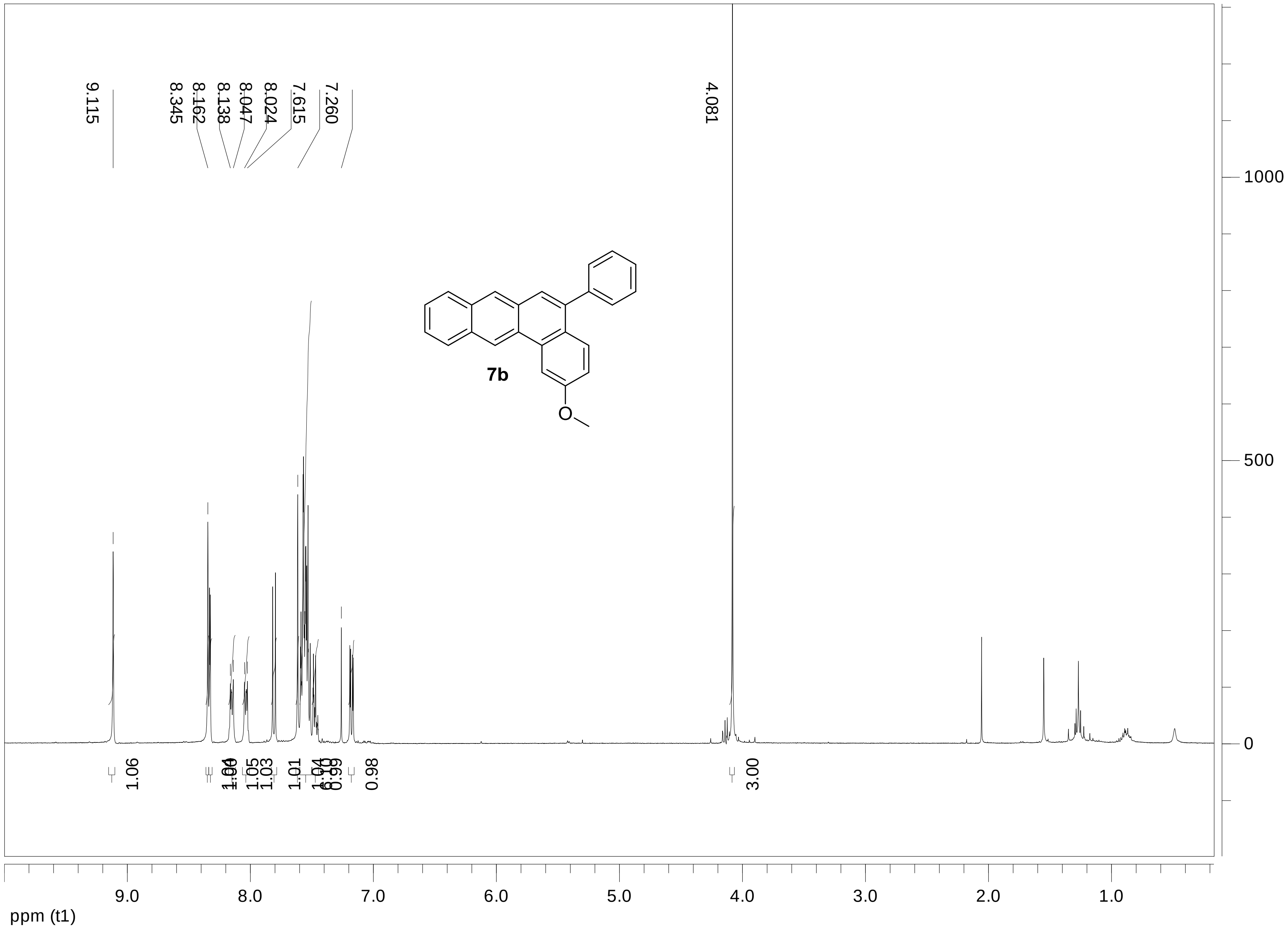
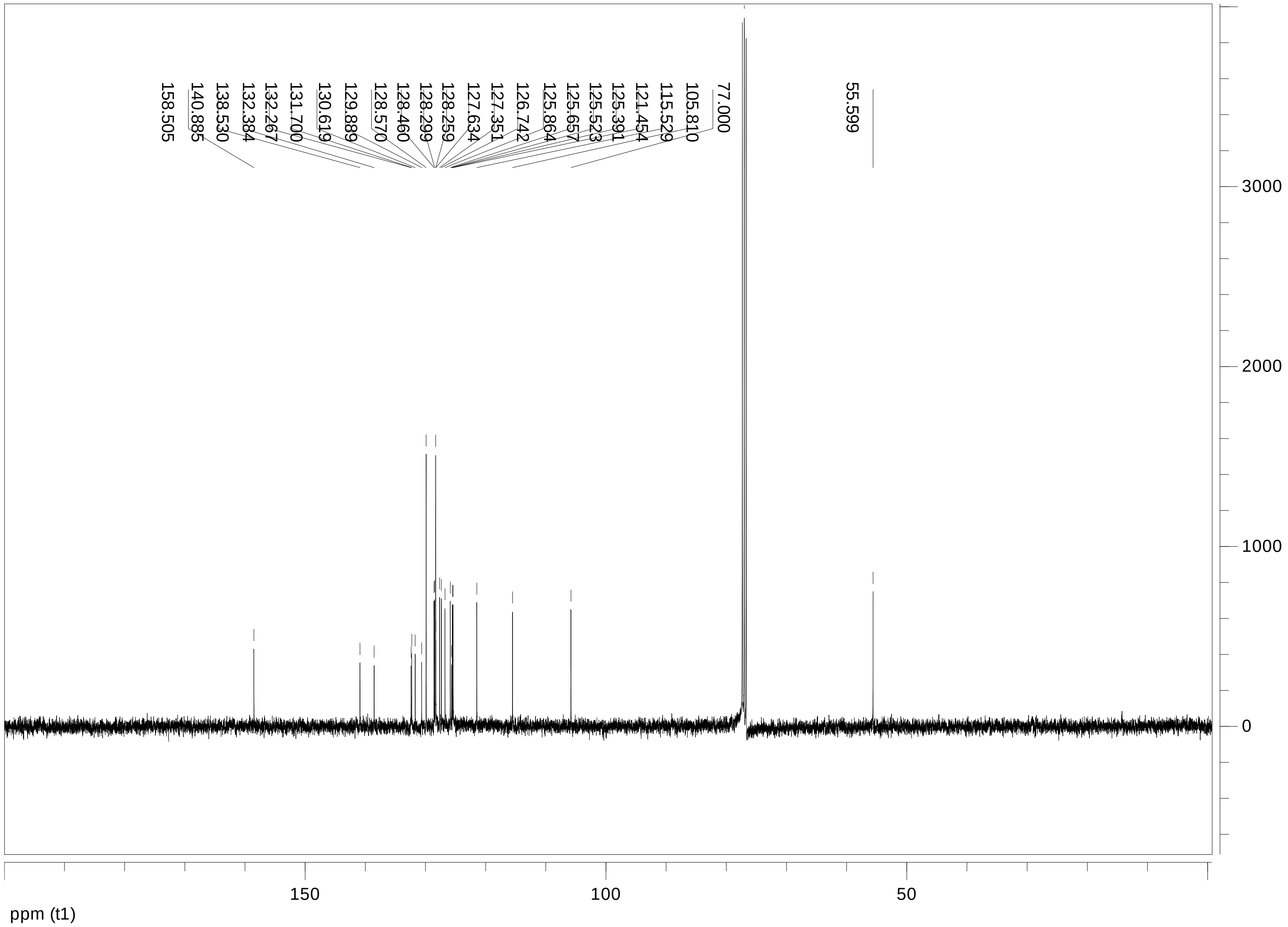
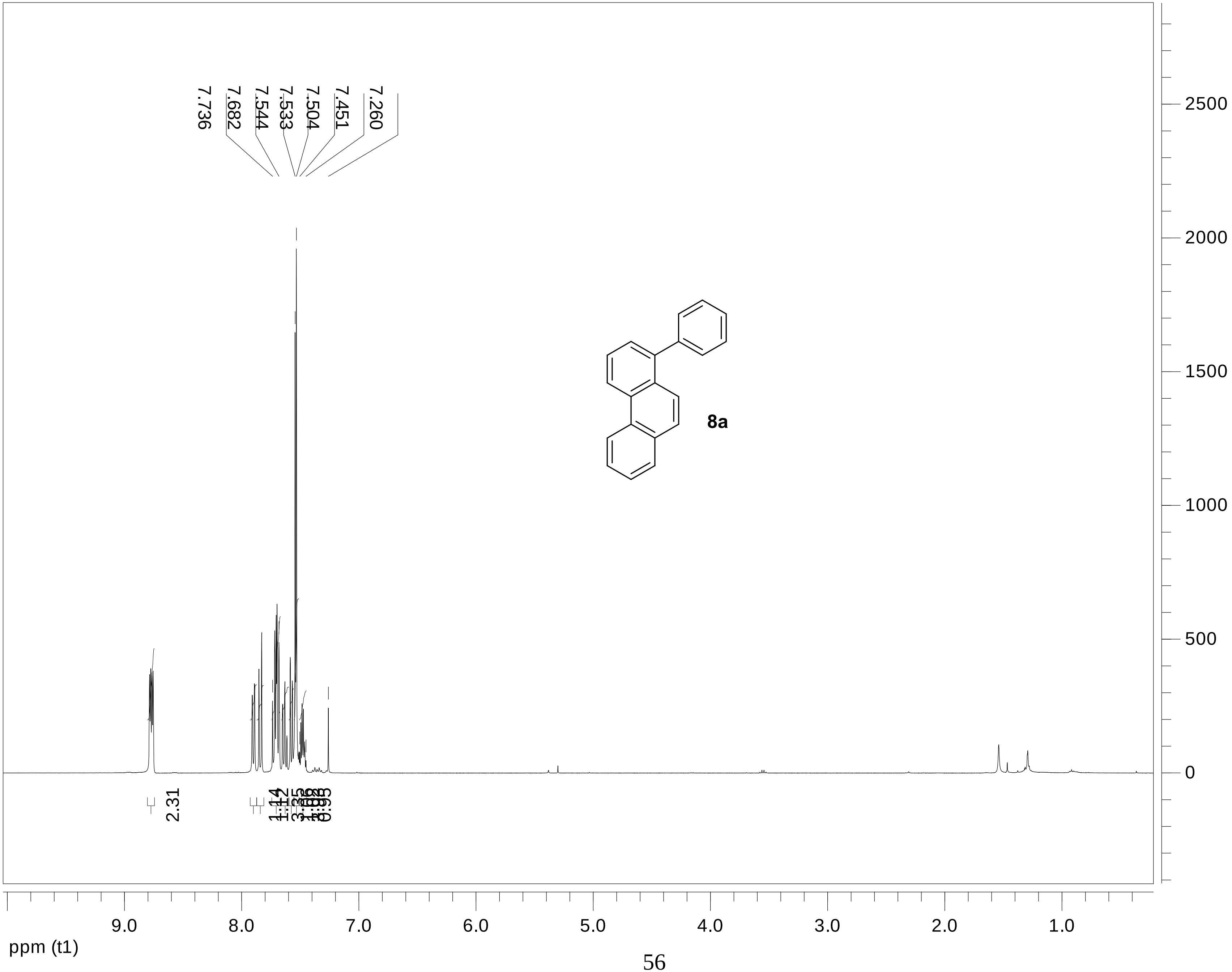
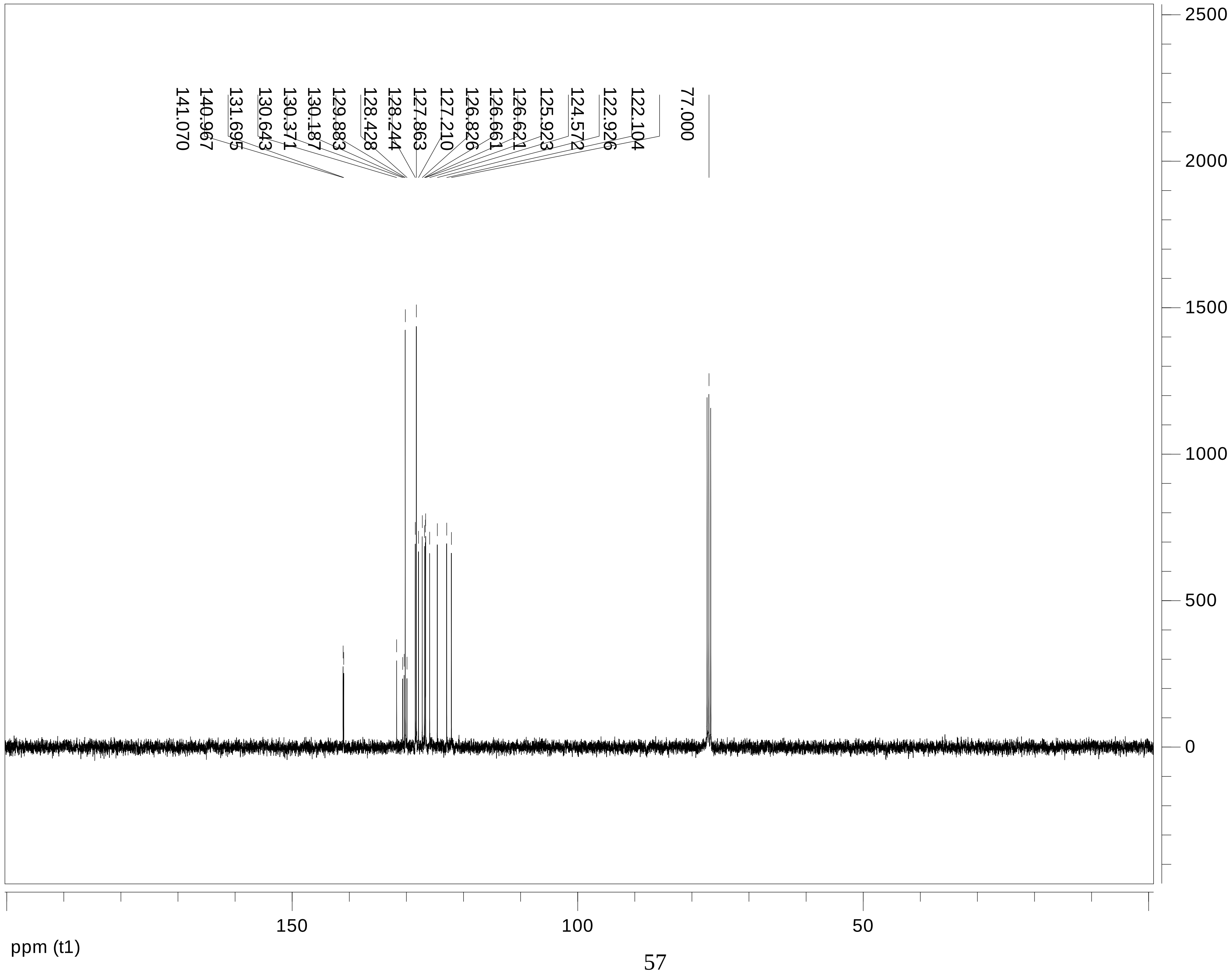
132.056
131.268
131.106
128.400
128.272
127.525
126.631
126.162
125.686
125.523
125.136
124.459
121.344
115.536
105.828
77.000
55.544
20.236
1000
500
0
150
100
50
ppm (t1)


9.115
8.345
8.162
8.138
8.047
8.024
7.615
7.260
4.081
7b
1.06
1.04
1.00
1.05
1.03
1.01
1.04
6.10
0.99
0.98
3.00
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


158.505
140.885
138.530
132.384
132.267
131.700
130.619
129.889
128.570
128.460
128.299
128.259
127.634
127.351
126.742
125.864
125.657
125.523
125.391
121.454
115.529
105.810
77.000
55.599
3000
2000
1000
0
150
100
50
ppm (t1)


7.736
7.682
7.544
7.533
7.504
7.451
7.260
2500
2000
1500
1000
500
0
2.31
1.14
1.12
3.35
0.93
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

8a


141.070
140.967
131.695
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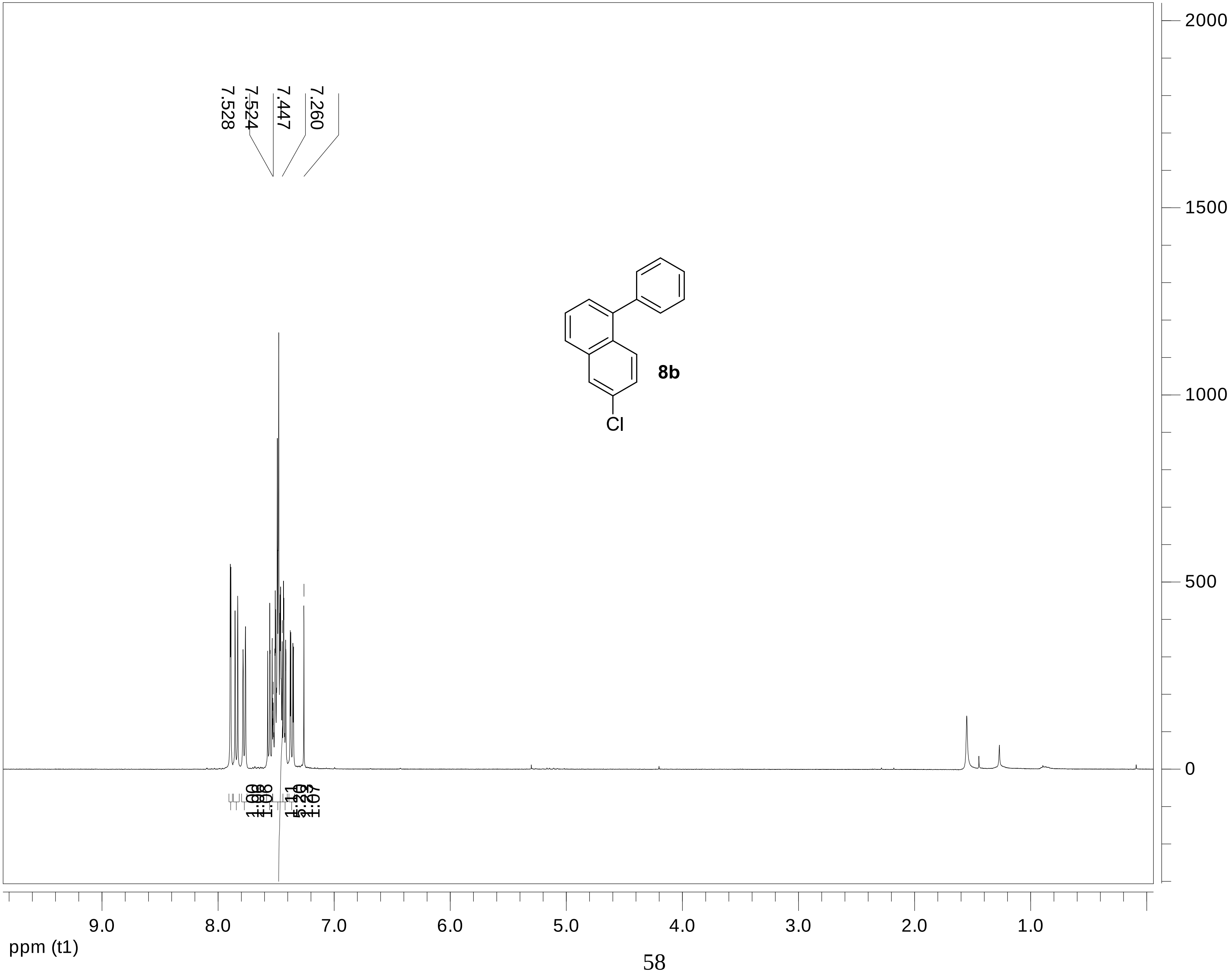
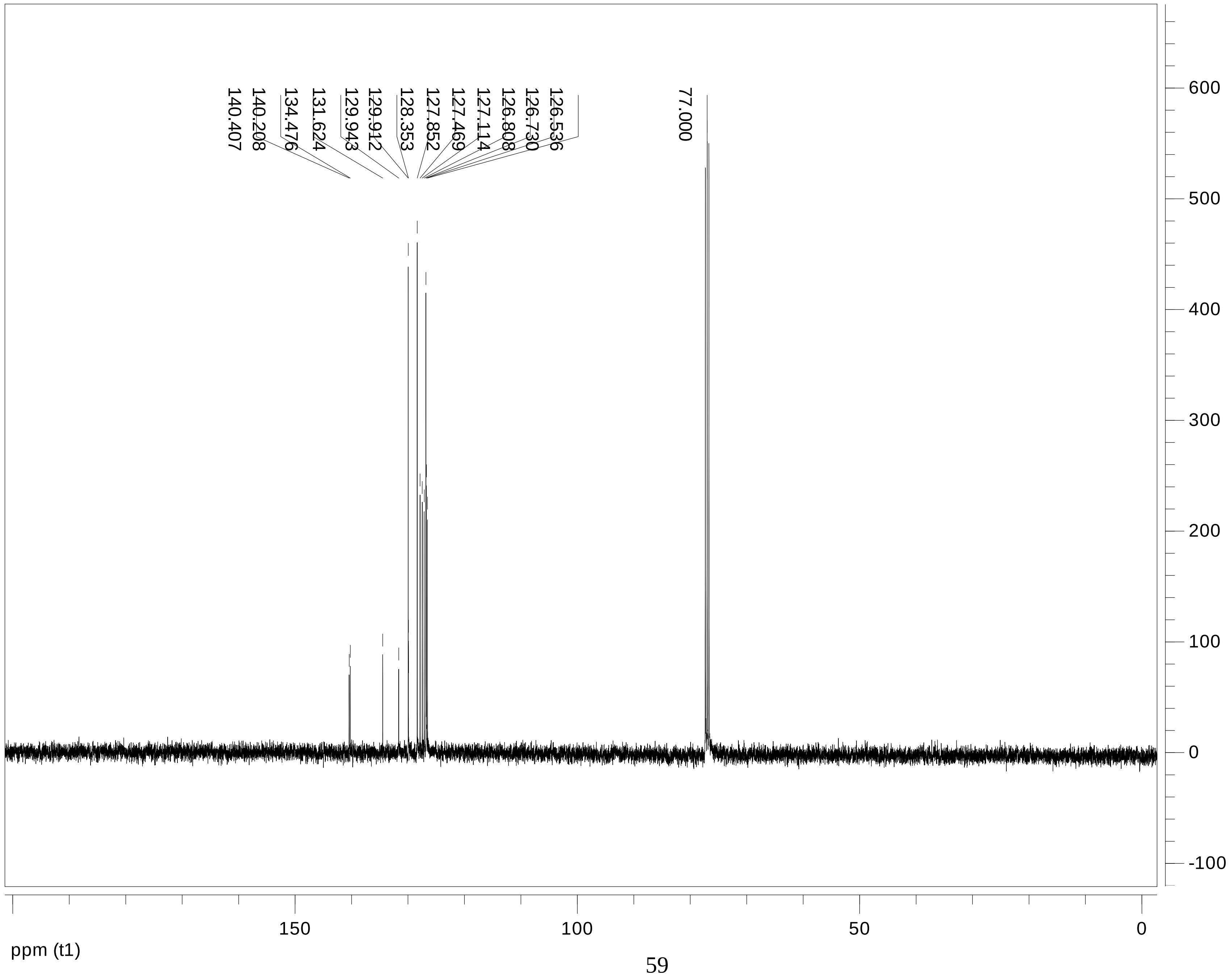
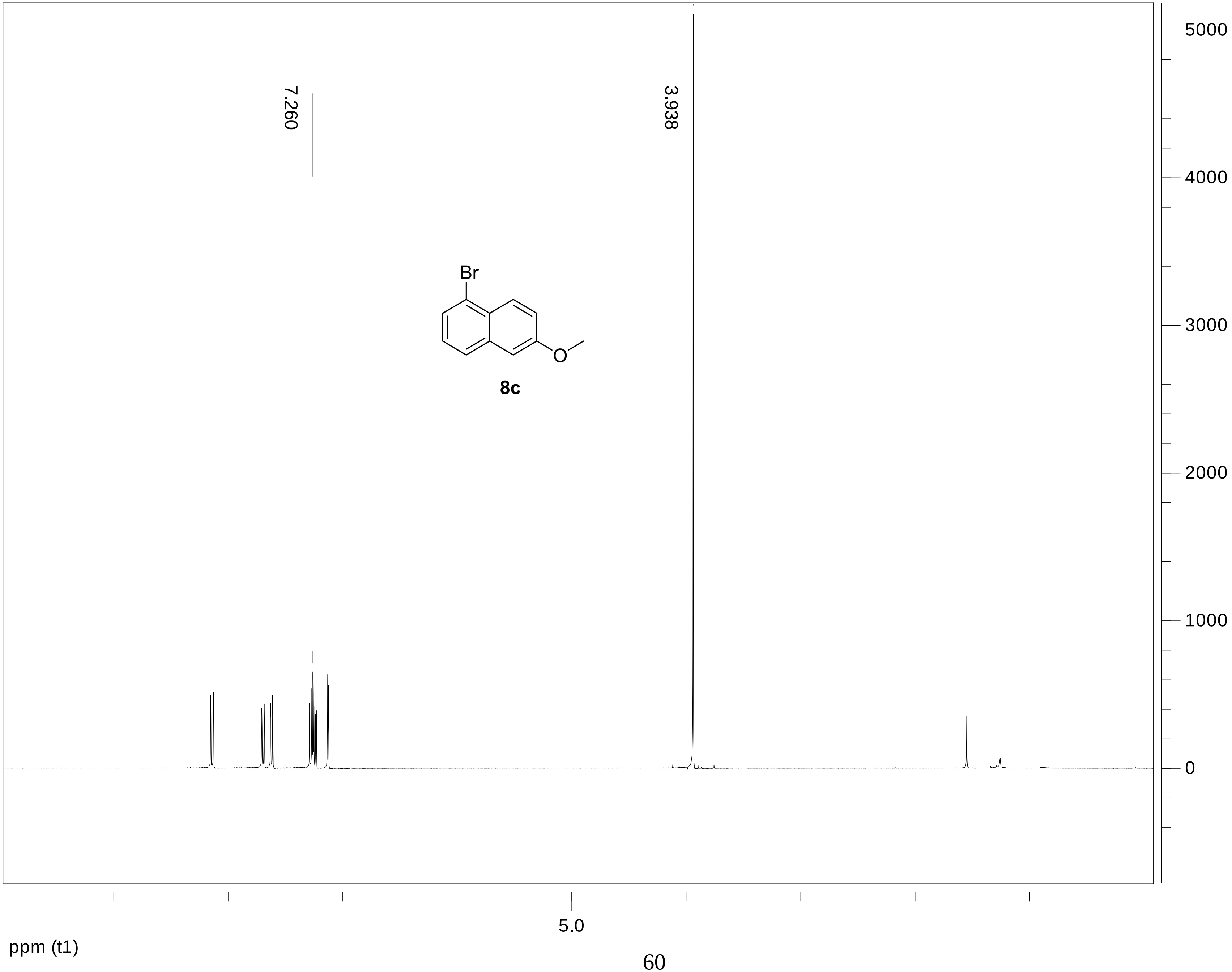
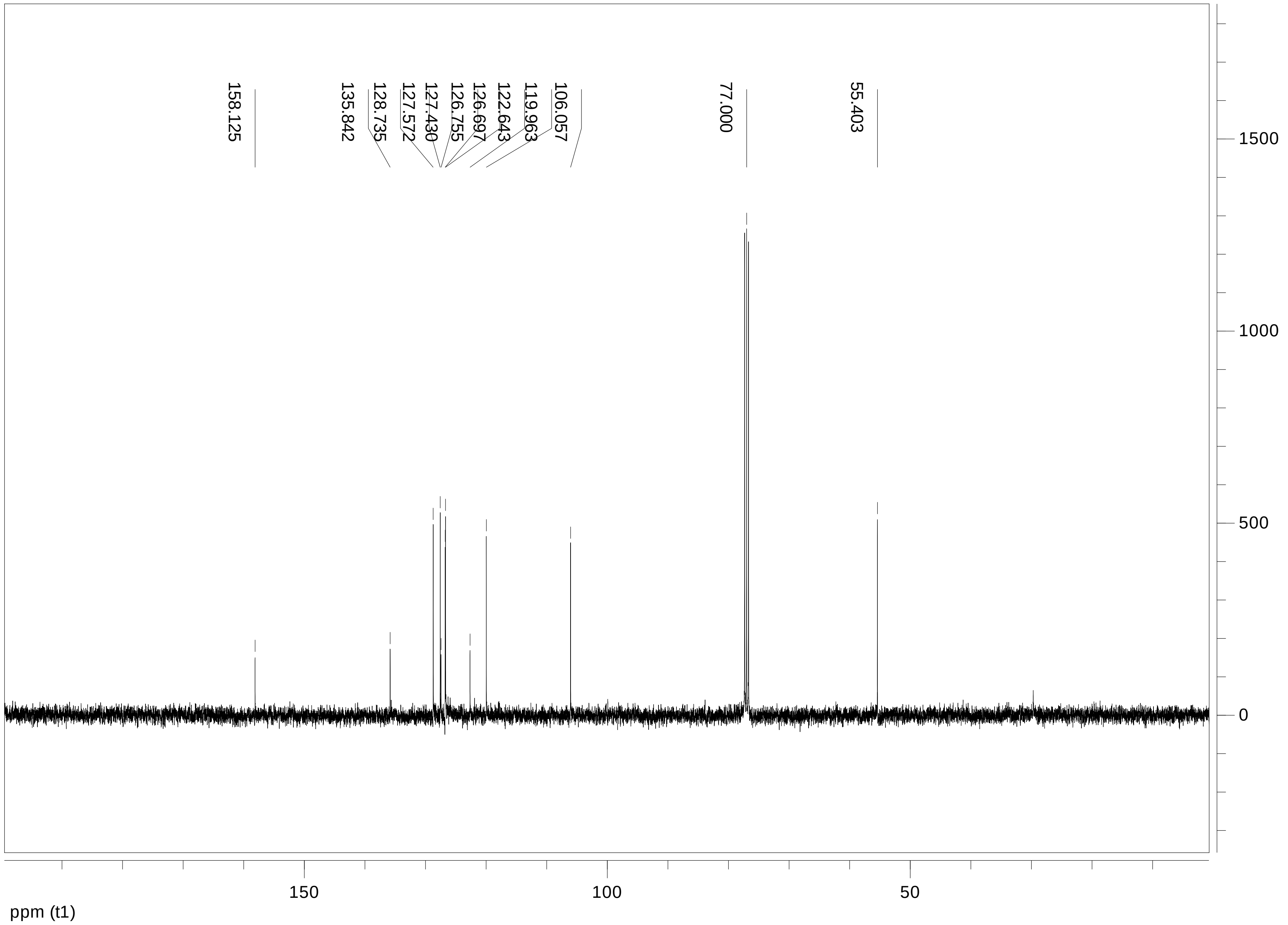
130.371
130.187
129.883
128.428
128.244
127.863
127.210
126.826
126.661
126.621
125.923
124.572
122.926
122.104
77.000
2500
2000
1500
1000
500
0
150
100
50
ppm (t1)

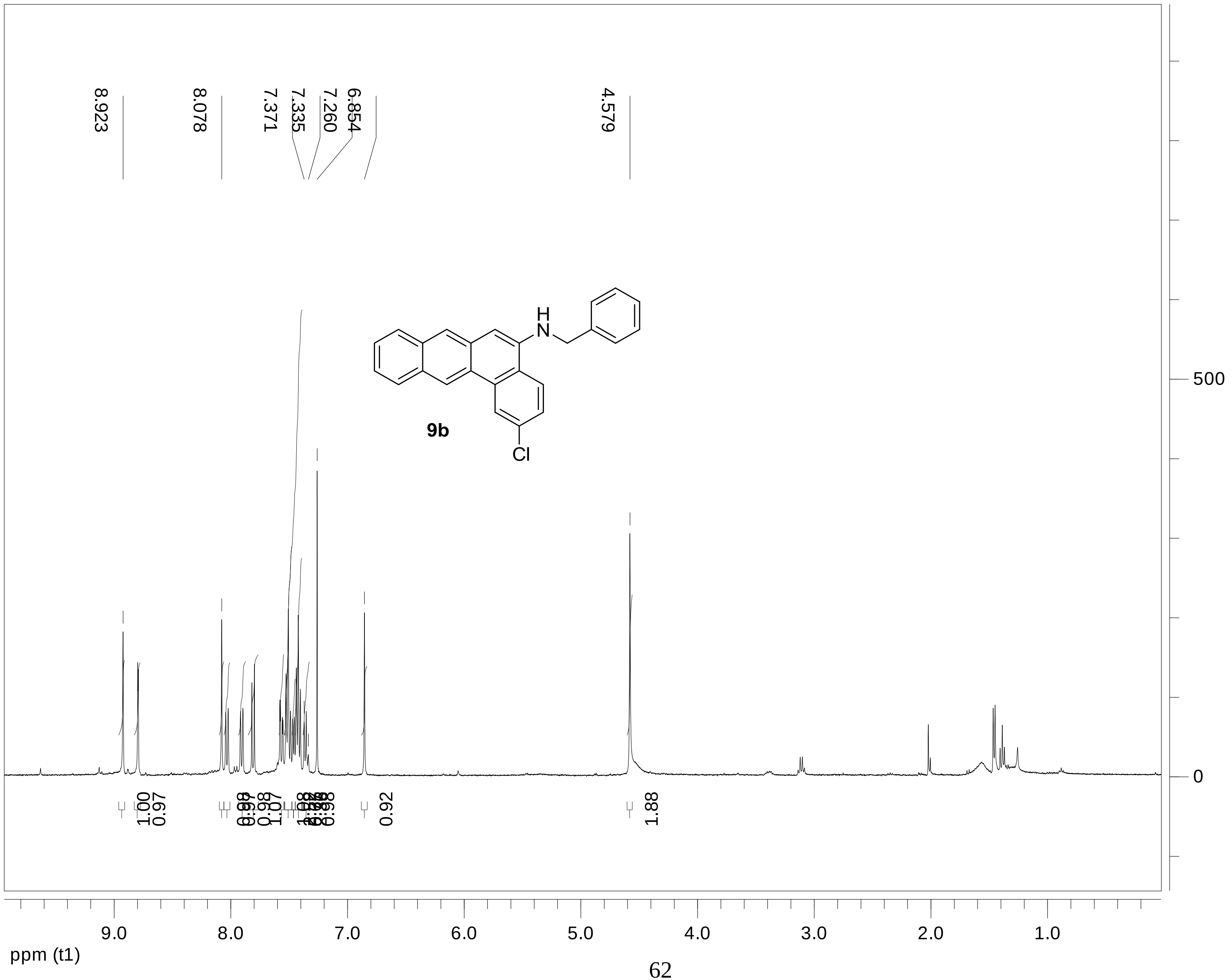

7.528
7.524
7.447
7.260
8b
Cl
2000
1500
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


140.407
140.208
134.476
131.624
129.943
129.912
128.353
127.852
127.469
127.114
126.808
126.730
126.536
77.000
600
500
400
300
200
100
0
-100
150
100
50
0
ppm (t1)



8c


158.125
135.842
128.735
127.572
127.430
126.755
126.697
122.643
119.963
106.057
77.000
55.403
1500
1000
500
0
150
100
50
ppm (t1)


8.923
8.078
7.371
7.335
7.260
6.854
4.579
H
N
Cl
9b
500
0
1.00
0.97
0.99
0.97
0.98
1.07
0.92
1.88
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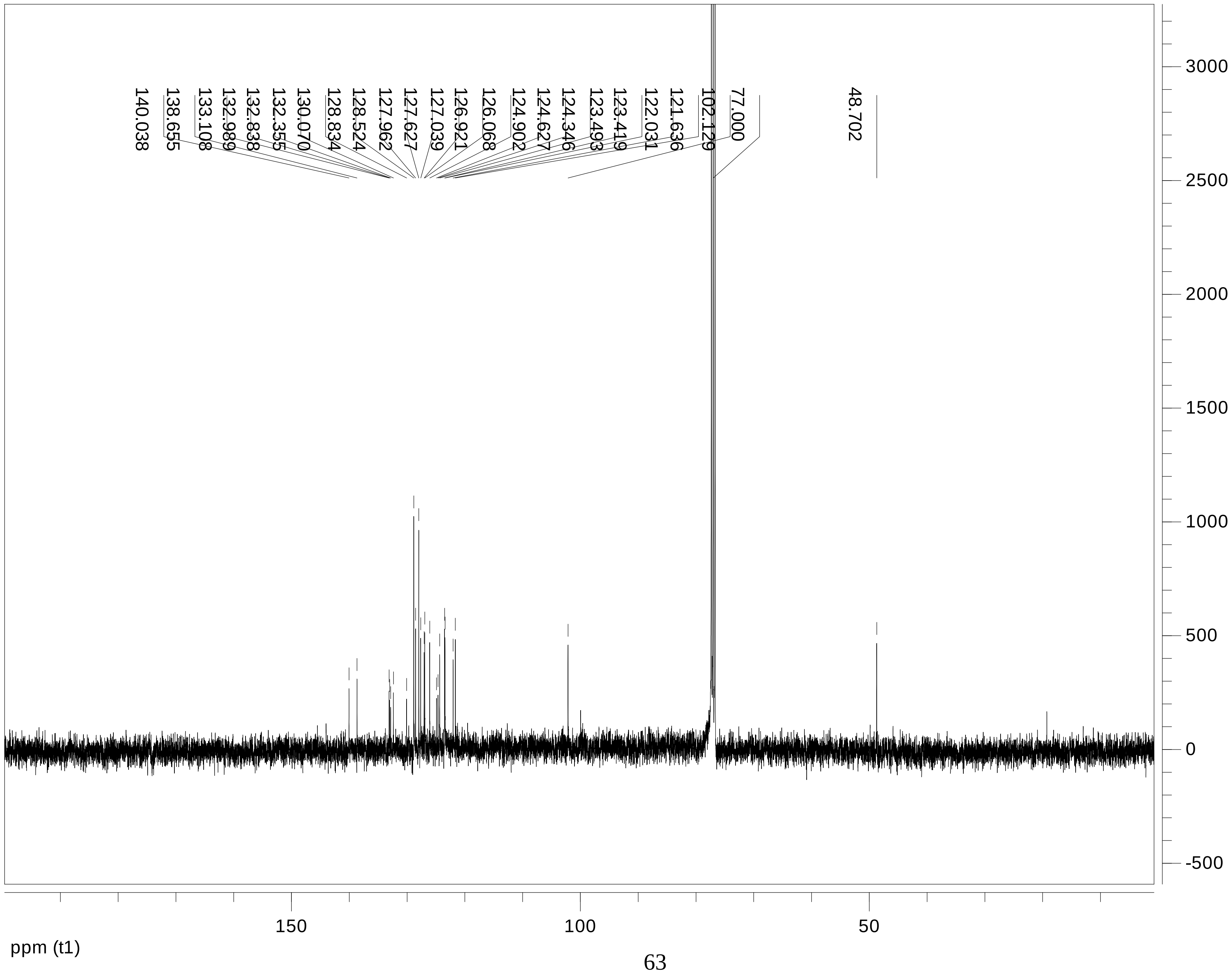
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


140.038
138.655
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132.838
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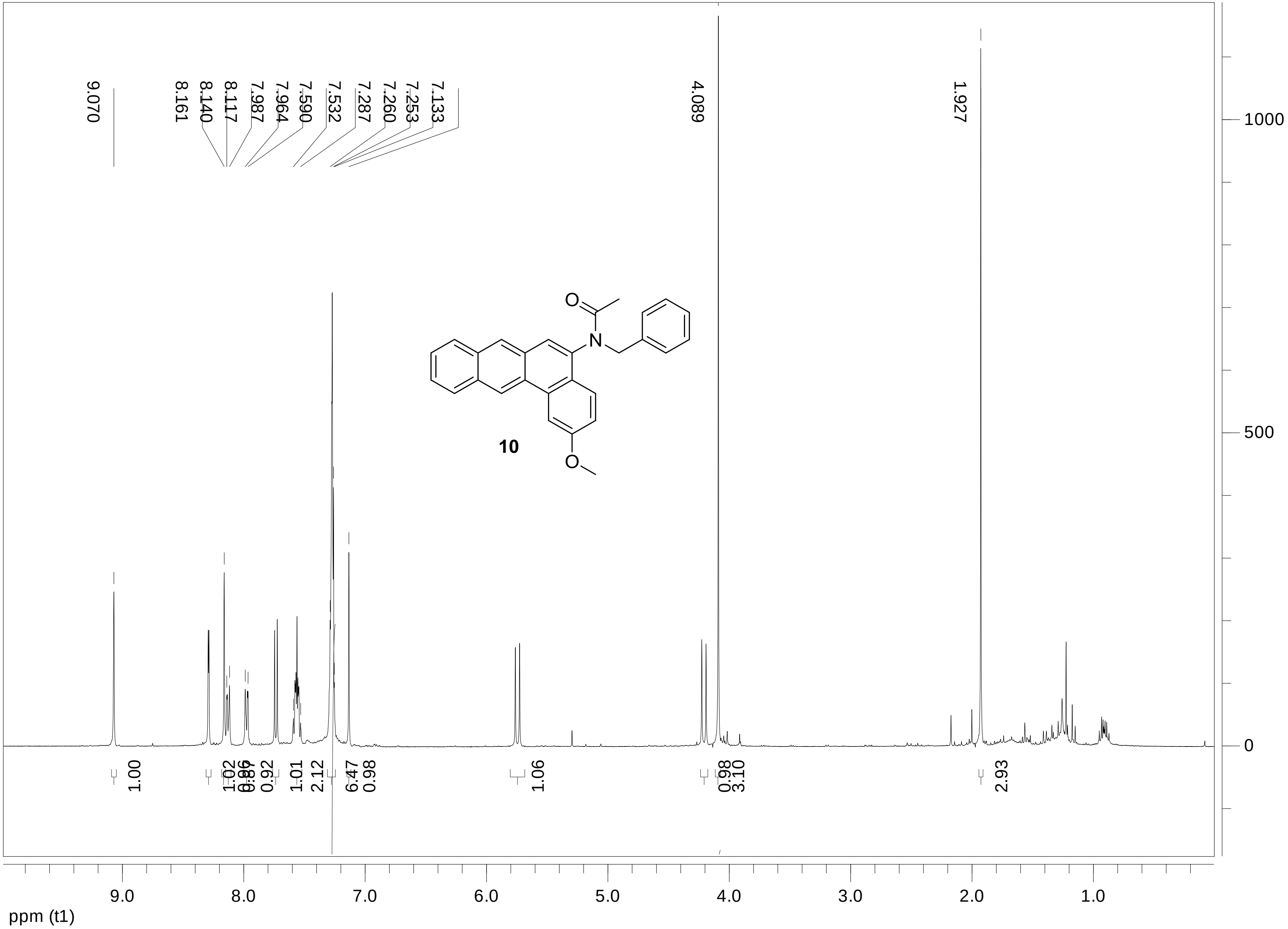
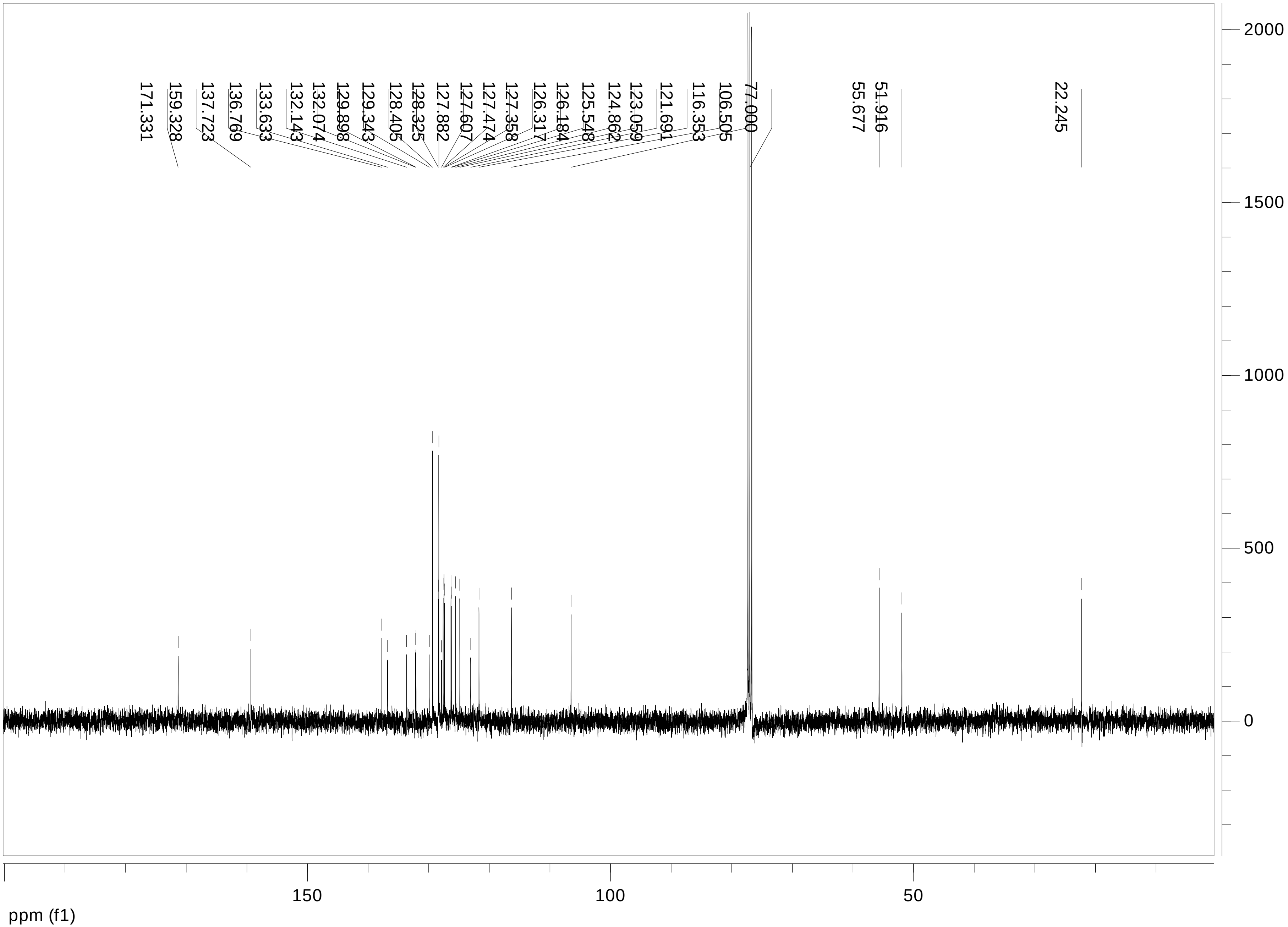
130.070
128.834
128.524
127.962
127.627
127.039
126.921
126.068
124.902
124.627
124.346
123.493
123.419
122.031
121.636
102.129
77.000
48.702
3000
2500
2000
1500
1000
500
0
-500
150
100
50
ppm (t1)


9.070
8.161
8.140
8.117
7.987
7.964
7.590
7.532
7.287
7.260
7.253
7.133
4.089
1.927
10
O
N
O
1.00
1.02
0.96
0.87
0.92
1.01
2.12
6.47
0.98
1.06
0.98
3.10
2.93
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


171.331
159.328
137.723
136.769
133.633
132.143
132.074
129.898
129.343
128.405
128.325
127.882
127.607
127.474
127.358
126.317
126.184
125.548
124.862
123.059
121.691
116.353
106.505
77.000
55.677
51.916
22.245
2000
1500
1000
500
0
150
100
50
ppm (f1)