Electronic Supplementary Information Material

Evaluation of energy transfer in perylene-cored anthracene dendrimers

Masaki Takahashi,[a] *Hironao Morimoto,*[b] *Kentaro Miyake,*[a] *Mitsuji Yamashita,*[a] *Hideki Kawai,*[c] *Yoshihisa Sei,*[d] *and Kentaro Yamaguchi*[d]

[a] Department of Materials Science and Chemical Engineering, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan

[b] Graduate School of Science and Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan

[c] Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8011, Japan

[d] Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, Shido, Sanuki, Kagawa 769-2193, Japan

General: All solvents and reagents were of reagent grade quality from Wako Pure Chemicals used without further purification. The ^{1}H- and ^{13}C- nuclear magnetic resonance (NMR) spectra operating at the frequencies of 300 and 75 MHz, respectively, were recorded on a JEOL JNM-AL300 spectrometer in chloroform-*d* ($CDCl_3$) or acetone-d_6 ($(CD_3)_2CO$). Chemical Shifts are reported in parts per million (ppm) relative to TMS and the solvent used as internal standards, and the coupling constants are reported in hertz (Hz). Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR-410 spectrometer as KBr disks. Absorption spectra were recorded on a JASCO model V-570 UV-VIS-NIR spectrophotometer. Fluorescence spectra were measured on a Hitachi F-4500 spectrofluorometer. All the absorption and fluorescence measurements were conducted in sufficiently low concentrations (10^{-8}~10^{-5} M) of the analytes to exclude the possibilities of intermolecular chromophoric interactions. Melting points were measured with a Yanaco MP-S3 melting point apparatus. Fast atom bombardment (FAB) mass spectra were determined by a JASCO JMS-HX110A using a 3-nitrobenzyl alcohol matrix. Electrospray ionization-time-of-flight (ESI-TOF) mass spectra were recorded on a Micromass LCT mass spectrometer KB 201. Cold-spray ionization mass spectrometry (CSI-MS) of **3** was performed by two-sector (BE) mass spectrometer (JMS-700, JEOL) equipped with a cold-spray ionization (CSI) source. Elemental analyses were obtained from Thermo Flash EA 1112 instrument. Gel permeation chromatography (GPC) was performed on a system consisting of a JASCO model 880-PU pump at a flow rate of 0.5 mL min^{-1} and JASCO 875-UV absorbance detector (254 nm) equipped with a Shodex K-802.5 column, where chloroform was used as mobile phase. Preparative high-performance liquid chromatography (HPLC) was performed on a Japan Analytical Industry LC-918 recycling system. Three types of anthryl chlorides **A1**-**A3** were prepared by the procedures reported in the previous publication.[1] Although tetrakis(3,5-di(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate and tetrakis(3,5-dihydroxybenzyl) 3,4,9,10-perylenetetracarboxylate **P2** were available from our preliminary study,[2] modification procedures for their preparations were carried out to increase the product yields. These compounds were further characterized by complete spectroscopic data as described below. Due to inherent poor stability of the poly(anthracenemethyl)-ether linkages under conditions of mass

spectroscopic measurements, attempts to detect molecular ion peaks of the dendrimers **5** and **6** eventually failed by means of all available mass spectral techniques such as FAB-, MALDI-TOF-, ESI-, and CSI-MS. For definitive support for complementary structural evidence of these dendrimer structures, molecular weight estimation using GPC and determination of extinction coefficients were performed. Consequently, the precise chromophore compositions of these dendrimers (anthracene/perylene stoichiometry) can be adequately rationalized on the basis of relative proportions of the extinction coefficients for each chromophoric component. Purity of all the dendrimer samples was confirmed by elemental analyses and was also elucidated using GPC for **1**-**6**. The energy transfer efficiencies of **1**-**6** were calculated according to literature.[3] For precise determination of these values, tetrabenzyl 3,4,9,10-perylenetetracarboxylate, being prepared according to the reported procedure,[2] was employed as a reference substrate.

Preparation and characterization of tetrakis(3-(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate. A solution containing 3,4,9,10-perylenetetracarboxylic acid (0.063 g, 0.15 mmol), 3-(benzyloxy)benzyl bromide (0.41 g, 1.23 mmol), potassium carbonate (0.41 g, 2.97 mmol), 18-crown-6 (0.039 g, 0.15 mmol), and 4-(dimethylamino)pyridine (0.018 g, 0.15 mmol) in DMF (5 mL) was heated at 85 °C with stirring under argon atmosphere. After 12 hours, the reaction mixture was cooled to room temperature, filtered through a pad of celite to remove insoluble materials and excess potassium carbonate. The filtrate was extracted with ethyl acetate (50 mL), and the extracts were intensively washed with water (20 mL) and brine (20 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated in a vacuum. Purification of the residue by flush column chromatography on silica gel (eluent: chloroform) gave tetrakis(3-(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate (0.13 g, 72%) as a dark orange powdery material: mp 44-45 ºC; IR (KBr) 1587 cm^{-1} (C=C), 1716 cm^{-1} (C=O); MS (FAB, positive) *m/z* 1212 (*M*+), 1213 (*MH*+); ^{1}H-NMR ($CDCl_3$) δ 5.01 (s, 8H, C*H*$_2$), 5.28 (s, 8H, C*H*$_2$), 6.89-7.11 (m, 12H, Ar*H*), 7.22-7.38 (m, 24H, Ar*H*), 7.69 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.75 (d, *J* = 8.0 Hz, 4H, Ar*H*); ^{13}C-NMR ($CDCl_3$) δ 66.8 (*C*H$_2$), 69.9 (*C*H$_2$), 114.8

(*C*H), 120.9 (*C*H), 121.3 (*C*H), 127.5 (*C*H), 128.0 (*C*H), 128.3 (*C*), 128.6 (*C*H), 128.7 (*C*H), 129.6 (*C*), 129.7 (*C*H), 130.5 (*C*H), 132.5 (*C*), 136.9 (*C*), 137.3 (*C*), 159.1 (*C*), 168.2 (*C*). Anal Calcd for $C_{80}H_{60}O_{12}$: C, 79.19; H, 4.98; N, 0.00. Found: C, 79.33; H, 4.75; N, 0.00.

Preparation and characterization of tetrakis(3-hydroxybenzyl) 3,4,9,10-perylenetetracarboxylate P1. A solution of tetrakis(3-(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate (0.16 g, 0.13 mmol) in a mixture of methanol (17 mL) and chloroform (17 mL) was hydrogenated in the presence of 10% Pd on activated carbon (0.15 g) at room temperature. After 18 hours, the catalyst was removed by filtration, intensively washed with methanol (50 mL). The solvent was evaporated under vacuum. Purification of the residue by flush column chromatography on silica gel (eluent: acetone/hexane = 50/50) gave tetrakis(3-hydroxybenzyl) 3,4,9,10-perylenetetracarboxylate **P1** (0.090 g, 80%) as a dark red solid: mp 73-74 ºC; IR (KBr) 1591 cm^{-1} (C=C), 1707 cm^{-1} (C=O), 3394 cm^{-1} (OH); MS (FAB, positive) *m/z* 852 (*M*+); ^{1}H-NMR (acetone-d_6) δ 5.34 (s, 8H, CH_2), 6.84 (ddd, J_1 = 1.0 Hz, J_2 = 2.4 Hz, J_3 = 8.1 Hz, 4H, Ar*H*), 7.03-7.10 (m, 8H, Ar*H*), 7.25 (t, *J* = 7.7 Hz, 4H, Ar*H*), 7.54 (d, *J* = 8.1 Hz, 4H, Ar*H*), 7.64 (d, *J* = 8.1 Hz, 4H, Ar*H*), 8.40 (s, 4H, O*H*); ^{13}C-NMR (acetone-d_6) δ 67.4 (CH_2), 116.1 (*C*H), 116.2 (*C*H), 120.4 (*C*H), 122.1 (*C*H), 128.7 (*C*), 129.1 (*C*), 130.5 (*C*H), 130.7 (*C*), 131.0 (*C*H), 132.8 (*C*), 138.6 (*C*), 158.4 (*C*), 168.5 (*C*). Anal Calcd for $C_{52}H_{36}O_{12}$: C, 73.23; H, 4.25; N, 0.00. Found: C, 73.31; H, 4.26; N, 0.16.

Preparation and characterization of tetrakis(3,5-di(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate. A solution containing 3,4,9,10-perylenetetracarboxylic acid (0.10 g, 0.23 mmol), 3,5-(dibenzyloxy)benzyl bromide (0.90 g, 2.35 mmol), potassium carbonate (0.55g, 4.70 mmol), 18-crown-6 (0.065 g, 0.25 mmol), and 4-(dimethylamino)pyridine (0.03, 0.25 mmol) in DMF (5 mL) was heated at 85 °C with stirring under argon atmosphere. After 12 hours, the reaction mixture was cooled to room temperature, filtered through a pad of celite to remove insoluble materials and excess potassium carbonate. The filtrate was extracted with ethyl acetate (50 mL), and the extracts were intensively washed with water (20 mL) and brine (20 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated in a vacuum. Purification of the residue by flush column

chromatography on silica gel (eluent: chloroform) gave tetrakis(3-(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate (0.18 g, 76%) as a dark orange powdery material: mp 56-57 ºC; IR (KBr) 1595 cm^{-1} (C=C), 1730 cm^{-1} (C=O); MS (FAB, positive) m/z 1636 (*M*+), 1637 (*MH*+); ^{1}H-NMR ($CDCl_3$) δ 4.95 (s, 16H, CH_2), 5.23 (s, 8H, CH_2), 6.54 (t, *J* = 2.3 Hz, 4H, Ar*H*), 6.70 (d, *J* = 2.3 Hz, 8H, Ar*H*), 7.25-7.36 (m, 40H, Ar*H*), 7.88 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.94 (d, *J* = 8.0 Hz, 4H, Ar*H*); ^{13}C-NMR ($CDCl_3$) δ 66.9 (*C*H_2), 70.0 (*C*H_2), 102.0 (*C*H), 107.2 (*C*H), 121.5 (*C*H), 127.6 (*C*H), 128.0 (*C*H), 128.6 (*C*H), 128.9 (*C*), 129.8 (*C*), 130.7 (*C*H), 132.9 (*C*), 136.8 (*C*), 138.0 (*C*), 160.2 (*C*), 168.2 (*C*). Anal Calcd for $C_{108}H_{84}O_{16}$: C, 79.20; H, 5.17; N, 0.00. Found: C, 79.12; H, 5.03; N, 0.00.

Preparation and characterization of tetrakis(3,5-dihydroxybenzyl) 3,4,9,10-perylenetetracarboxylate P2. A solution of tetrakis(3,5-di(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate (0.14 g, 0.086 mmol) in a mixture of methanol (17 mL) and chloroform (17 mL) was hydrogenated in the presence of 10% Pd on activated carbon (0.15 g) at room temperature. After 18 hours, the catalyst was removed by filtration, intensively washed with methanol (50 mL). The solvent was evaporated under vacuum. Purification of the residue by flush column chromatography on silica gel (eluent: acetone/hexane = 67/33) gave tetrakis(3,5-dihydroxybenzyl) 3,4,9,10-perylenetetracarboxylate **P2** (0.069 g, 88%) as a dark red solid: mp 139-140 ºC; IR (KBr) 1603 cm^{-1} (C=C), 1703 cm^{-1} (C=O), 3371 cm^{-1} (OH); MS (FAB, positive) *m/z* 916 (*M*+); ^{1}H-NMR (acetone-d_6) δ 5.29 (s, 8H, CH_2), 6.36 (t, *J* = 2.2 Hz, 4H, Ar*H*), 6.60 (d, *J* = 2.2 Hz, 8H, Ar*H*), 7.69 (dd, J_1 = 2.8 Hz, J_2 = 8.1 Hz, 4H, Ar*H*), 7.75 (d, *J* = 7.9 Hz, 4H, Ar*H*), 8.41 (s, 8H, O*H*); ^{13}C-NMR (acetone-d_6) δ 67.3 (*C*H_2), 103.3 (*C*H), 107.7 (*C*H), 122.3 (*C*H), 128.8 (*C*), 129.1 (*C*), 130.9 (*C*), 131.2 (*C*H), 133.0 (*C*), 139.3 (*C*), 159.6 (*C*), 168.5 (*C*). Anal Calcd for $C_{52}H_{36}O_{16}$: C, 68.12; H, 3.96; N, 0.00. Found: C, 68.17; H, 4.12; N, 0.00.

Preparation and characterization of the dendrimers 1-3. A typical procedure: a solution containing **A1** (0.16 g, 0.52 mmol), **P1** (0.072 g, 0.084 mmol), potassium carbonate (0.070 g, 0.51 mmol), and 18-crown-6 (0.090 g, 0.34 mmol) in DMF (5 mL) was heated at 55 °C with stirring under argon atmosphere. After 4 hours, the reaction mixture was cooled to room temperature, and poured into

saturated ammonium chloride solution to precipitate the product. The precipitate was collected by filtration, intensively washed with water, and dried in a vacuum. Purification of the residue by the preparative HPLC (chloroform as eluent) gave the dendrimer **1** (0.071 g, 43%) as an orange solid: mp 183-184 ºC; UV ($CHCl_3$) 359 nm (ε 22900), 378 nm (ε 35600), 399 nm (ε 37400), 446 nm (ε 34900), 475 nm (ε 42600); IR (KBr) 1589 cm^{-1} (C=C), 1742 cm^{-1} (C=O); MS (ESI, positive) *m/z* 1972.9 (*MNa*+); ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, *J* = 6.8 Hz, 12H, $(CH_2)_5CH_3$), 1.26-1.39 (m, 16H, $(CH_2)_3(CH_2)_2CH_3$), 1.47-1.60 (m, 8H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.66-1.78 (m, 8H, $CH_2CH_2(CH_2)_3CH_3$), 3.38-3.53 (t, *J* = 8.0 Hz, 8H, $CH_2(CH_2)_4CH_3$), 5.32 (s, 8H, CH_2), 5.76 (s, 8H, CH_2), 6.98-7.08 (m, 8H, Ar*H*), 7.23-7.38 (m, 24H, Ar*H*), 7.71 (d, *J* = 8.1 Hz, 4H, Ar*H*), 7.79 (d, *J* = 8.1 Hz, 4H, Ar*H*), 8.12-8.18 (m, 16H, Ar*H*); ^{13}C-NMR ($CDCl_3$) δ 14.1 (CH_3), 22.8 (CH_2), 28.4 (CH_2), 30.1 (CH_2), 31.4 (CH_2), 31.8 (CH_2), 62.9 (CH_2), 67.0 (CH_2), 114.6 (*C*H), 115.1 (*C*H), 121.1 (*C*H), 121.5 (*C*H), 124.8 (*C*H), 125.1 (*C*H), 125.2 (*C*H), 125.4 (*C*), 126.1 (*C*H), 127.4 (*C*H), 128.6 (*C*), 129.0 (*C*), 129.4 (*C*), 129.9 (*C*), 130.0 (*C*H), 130.8 (*C*), 131.0 (C), 132.9 (*C*), 137.5 (*C*), 138.1 (*C*), 159.8 (*C*), 168.4 (*C*). Anal Calcd for $C_{136}H_{124}O_{12}$: C, 83.75; H, 6.41; N, 0.00. Found: C, 83.67; H, 6.32; N, 0.00.

2: yield 41%; mp 160-161 ºC; UV ($CHCl_3$) 357 nm (ε 48100), 375 nm (ε 73000), 396 nm (ε 73400), 448 nm (ε 34400), 477 nm (ε 41400); IR (KBr) 1593 cm^{-1} (C=C), 1728 cm^{-1} (C=O); MS (ESI, positive) *m/z* 3222.7 (*MNa*+); ^{1}H-NMR ($CDCl_3$) δ 0.83-0.95 (m, 12H, $(CH_2)_5CH_3$), 1.27-1.41 (m, 16H, $(CH_2)_3(CH_2)_2CH_3$), 1.48-1.63 (m, 8H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.70-1.83 (m, 8H, $CH_2CH_2(CH_2)_3CH_3$), 3.46-3.61 (m, 8H, $CH_2(CH_2)_4CH_3$), 5.25 (s, 8H, CH_2), 5.57 (s, 8H, CH_2), 5.76 (s, 16H, CH_2), 6.70-7.11 (m, 32H, Ar*H*), 7.28-7.45 (m, 32H, Ar*H*), 7.63-7.81 (m, 8H, Ar*H*), 7.99-8.12 (m, 12H, Ar*H*), 8.17-8.34 (m, 20H, Ar*H*); ^{13}C-NMR ($CDCl_3$) δ 14.0 (CH_3), 22.6 (CH_2), 28.4 (CH_2), 30.0 (CH_2), 31.3 (CH_2), 31.7 (CH_2), 60.0 (CH_2), 62.4 (CH_2), 62.5 (CH_2), 62.8 (CH_2), 101.9 (*C*H), 107.2 (*C*H), 107.5 (*C*H), 114.6 (*C*H), 114.7 (*C*H), 121.0 (*C*H), 121.6 (*C*H), 122.0 (*C*H), 124.6 (*C*H), 124.8 (*C*H), 125.1 (*C*H), 125.2 (*C*H), 126.1 (*C*H), 129.0 (*C*), 129.4 (*C*), 129.9 (*C*), 130.3 (*C*), 130.7 (*C*), 131.0 (*C*), 137.3 (*C*), 138.1 (C), 159.5 (*C*), 160.6 (*C*), 160.7 (*C*), 168.2 (*C*). Anal Calcd for $C_{224}H_{188}O_{20}$: C, 84.08; H, 5.92; N, 0.00. Found: C, 83.80; H, 6.03; N, 0.00.

3: yield 53%; mp 154-155 ºC; UV ($CHCl_3$) 358 nm (ε 73200), 377 nm (ε 114000), 398 nm (ε 114000), 448 nm (ε 34000), 476 nm (ε 41400); IR (KBr) 1593 cm^{-1} (C=C), 1718 cm^{-1} (C=O); MS (CSI, negative) *m/z* 4393.2 (*MCl*-); ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 24H, $(CH_2)_5CH_3$), 1.24-1.37 (m, 32H, $(CH_2)_3(CH_2)_2CH_3$), 1.46-1.59 (m, 16H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.60-1.80 (m, 16H, $CH_2CH_2(CH_2)_3CH_3$), 3.46-3.60 (m, 16H, $CH_2(CH_2)_4CH_3$), 5.17 (s, 8H, CH_2), 5.52 (s, 8H, CH_2), 5.59 (s, 8H, CH_2), 5.71 (s, 16H, CH_2), 6.54-6.66 (m, 12H, Ar*H*), 6.88-7.05 (m, 16H, Ar*H*), 7.41-7.44 (m, 48H, Ar*H*), 7.90-8.31 (m, 56H, Ar*H*); ^{13}C-NMR ($CDCl_3$) δ 14.0 (CH_3), 22.6 (CH_2), 28.3 (CH_2), 29.9 (CH_2), 31.3 (CH_2), 31.7 (CH_2), 62.4 (CH_2), 62.8 (CH_2), 66.6 (CH_2), 94.7 (*C*H), 95.1 (*C*H), 114.4 (*C*H), 114.7 (*C*H), 121.1 (*C*H), 121.5 (*C*H), 122.0 (*C*H), 124.6 (*C*H), 124.7 (*C*H), 125.1 (*C*H), 125.2 (*C*), 126.0 (*C*H), 127.3 (*C*H), 128.8 (*C*), 128.9 (*C*), 129.3 (*C*), 129.8 (*C*H), 130.5 (*C*), 130.9 (*C*), 132.2 (*C*), 137.4 (*C*), 138.0 (C), 139.3 (*C*), 141.0 (*C*), 159.4 (*C*), 161.3 (*C*), 161.4 (*C*), 168.0 (*C*). Anal Calcd for $C_{308}H_{276}O_{24}$: C, 84.82; H, 6.38; N, 0.00. Found: C, 84.58; H, 6.36; N, 0.00.

Preparation and characterization of the dendrimers 4-6. A typical procedure: a solution containing **A1** (0.15 g, 0.48 mmol), **P2** (0.043 g, 0.047 mmol), potassium carbonate (0.065 g, 0.47 mmol), and 18-crown-6 (0.099 g, 0.38 mmol) in DMF (5 mL) was heated at 55 °C with stirring under argon atmosphere. After 4 hours, the reaction mixture was cooled to room temperature, and poured into saturated ammonium chloride solution to precipitate the product. The precipitate was collected by filtration, intensively washed with water, and dried in a vacuum. Purification of the residue by the preparative HPLC (chloroform as eluent) gave the dendrimer **4** (0.076 g, 52%) as an orange solid: mp 119-120 ºC; UV ($CHCl_3$) 360 nm (ε 46200), 378 nm (ε 73000), 399 nm (ε 73200), 448 nm (ε 34700), 477 nm (ε 42200); IR (KBr) 1593 cm^{-1} (C=C), 1718 cm^{-1} (C=O); MS (ESI, positive) *m/z* 3135.0 (*MNa*+); ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 24H, $(CH_2)_5CH_3$), 1.24-1.38 (m, 32H, $(CH_2)_3(CH_2)_2CH_3$), 1.46-1.57 (m, 16H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.63-1.74 (m, 16H, $CH_2CH_2(CH_2)_3CH_3$), 3.31-3.43 (m, 16H, $CH_2(CH_2)_4CH_3$), 5.32 (s, 8H, CH_2), 5.66 (s, 16H, CH_2), 6.81 (s, 4H, Ar*H*), 6.86 (s, 8H, Ar*H*), 7.23-7.33 (m, 32H, Ar*H*), 7.74 (d, *J* = 7.8 Hz, 4H, Ar*H*), 7.89 (d, *J* = 7.8 Hz, 4H, Ar*H*), 8.06-8.12 (m, 32H, Ar*H*); ^{13}C-NMR ($CDCl_3$) δ 14.0 (CH_3), 22.6 (CH_2), 28.2 (CH_2), 29.9 (CH_2), 31.2 (CH_2),

31.6 (*C*H_2), 62.8 (*C*H_2), 67.1 (*C*H_2), 101.8 (*C*H), 107.3 (*C*H), 121.5 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.1 (*C*), 126.0 (*C*H), 127.2 (*C*), 128.5 (*C*), 129.2 (*C*), 129.7 (*C*), 130.9 (*C*H), 132.8 (*C*), 137.9 (*C*), 138.1 (*C*), 139.3 (*C*), 141.0 (*C*), 160.8 (*C*), 168.2 (*C*). Anal Calcd for $C_{220}H_{212}O_{16}$: C, 84.91; H, 6.87; N, 0.00. Found: C, 85.03; H, 6.69; N, 0.00.

5: yield 40%; mp 139-140 ºC; UV ($CHCl_3$) 358 nm (ε 96400), 376 nm (ε 148000), 397 nm (ε 146000), 449 nm (ε 35700), 477 nm (ε 41900); IR (KBr) 1591 cm^{-1} (C=C), 1714 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.85-0.94 (m, 24H, $(CH_2)_5CH_3$), 1.26-1.40 (m, 32H, $(CH_2)_3(CH_2)_2CH_3$), 1.49-1.59 (m, 16H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.68-1.79 (m, 16H, $CH_2CH_2(CH_2)_3CH_3$), 3.44-3.56 (m, 16H, $CH_2(CH_2)_4CH_3$), 5.18 (s, 8H, CH_2), 5.59 (s, 16H, CH_2), 5.71 (s, 32H, CH_2), 6.54 (s, 8H, Ar*H*), 6.60 (s, 4H, Ar*H*), 6.92-7.04 (m, 32H, Ar*H*), 7.40-7.44 (m, 64H, Ar*H*), 7.88-8.29 (m, 72H, Ar*H*); ^{13}C-NMR ($CDCl_3$) δ 14.0 (*C*H_3), 22.6 (*C*H_2), 28.3 (*C*H_2), 29.9 (*C*H_2), 31.3 (*C*H_2), 31.6 (*C*H_2), 62.3 (*C*H_2), 62.8 (*C*H_2), 101.8 (*C*H), 107.3 (*C*H), 107.8 (*C*H), 112.4 (*C*H), 115.4 (*C*H), 124.5 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.3 (*C*H), 126.0 (*C*H), 128.7 (*C*), 128.9 (*C*), 130.3 (*C*), 130.4 (*C*H), 130.9 (*C*), 138.0 (C), 160.5 (*C*), 160.7 (*C*), 168.1 (*C*). Anal Calcd for $C_{396}H_{340}O_{32}$: C, 84.77; H, 6.11; N, 0.00. Found: C, 84.65; H, 5.99; N, 0.02.

6: yield 49%; mp 153-154 ºC; UV ($CHCl_3$) 358 nm (ε 141000), 378 nm (ε 224000), 399 nm (ε 223000), 449 nm (ε 36300), 478 nm (ε 43300); IR (KBr) 1591 cm^{-1} (C=C), 1718 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.80-0.96 (m, 48H, $(CH_2)_5CH_3$), 1.22-1.38 (m, 64H, $(CH_2)_3(CH_2)_2CH_3$), 1.44-1.57 (m, 32H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.63-1.80 (m, 32H, $CH_2CH_2(CH_2)_3CH_3$), 3.31-3.58 (m, 32H, $CH_2(CH_2)_4CH_3$), 5.29-5.84 (m, 72H, CH_2), 6.38-6.74 (m, 36H, Ar*H*), 7.08-7.50 (m, 96H, Ar*H*), 7.87-8.34 (m, 104H, Ar*H*); ^{13}C-NMR ($CDCl_3$) δ 14.0 (*C*H_3), 22.6 (*C*H_2), 28.2 (*C*H_2), 29.9 (*C*H_2), 31.2 (*C*H_2), 31.6 (*C*H_2), 62.4 (*C*H_2), 62.8 (*C*H_2), 94.7 (*C*H), 95.0 (*C*H), 107.5 (*C*H), 121.9 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 126.0 (*C*H), 127.2 (*C*), 128.8 (*C*), 129.3 (*C*), 130.5 (*C*), 130.9 (*C*), 138.0 (C), 160.5 (*C*), 161.3 (*C*), 161.4 (*C*), 168.0 (*C*); Anal. Calcd for $C_{564}H_{516}O_{40}$: C, 85.38; H, 6.56; N, 0.00. Found: C, 85.35; H, 6.52; N, 0.00.

Molecular weight determinations for the dendrimers 1-6 using GPC analyses. The molecular weights of these materials were determined using gel permeation chromatography (GPC) calibrated

with polystyrene standards. A series of the polystyrene standards (molecular weights = 800, 1300, 2000, 2500, 4000, and 13000) were purchased from Pressure Chemical Co. and used without further purification. All dendritic compounds exhibited sharp and symmetrical peaks at discrete retention times with low polydispersity values (M_w/M_n < 1.1) that should be in the range typically found for unified dendrimers (Table 1). Figure 1 demonstrates that a series of dendrimers **1**-**6** provided almost monomodal distributions fitted well with the linear polystyrene series in the correlation diagram, where observed retention volumes of all dendritic compounds exhibited a linear dependence on logarithmic numbers of the averaged molecular weights. As can be seen from Table 1, the estimated molecular weights (M_w) except for the case of **6** are satisfactorily close to the nominal molecular weights with small differences less than 6%, indicating this analytical experiment provides reliable information on the approximate molecular sizes. Unlike the cases of **1**-**5**, M_w value for **6** was found to be *ca.* 20% smaller than the actual molecular weight. This observation may be understood on the basis of compressed structural property of the dendrimer, which should be denser and more compact than linear polymers, giving underestimated values when determining the M_w value by calibration with the linear polystyrenes.

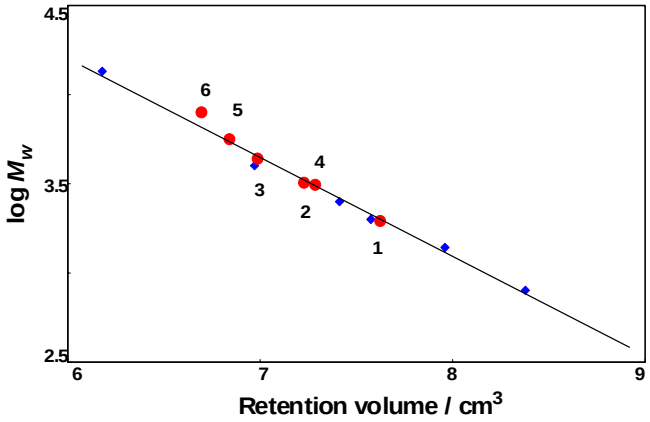

Figure 1. Semilogarithmic plot of average molecular weights (M_w) vs GPC retention volumes for polystyrene standards (♦) and dendrimers (●).

Table 1. GPC results of **1-6**.

entry	formula	M_w/M_n[a]	nominal M_w	M_w[a]
1	$C_{136}H_{124}O_{12}$	1.025	1,950	1,984
2	$C_{224}H_{188}O_{20}$	1.036	3,200	3,266
3	$C_{308}H_{276}O_{24}$	1.032	4,361	4,426
4	$C_{220}H_{212}O_{16}$	1.028	3,112	3,034
5	$C_{396}H_{340}O_{32}$	1.069	5,611	5,319
6	$C_{564}H_{516}O_{40}$	1.026	7,934	6,389

[a]Calibrated with narrow-dispersity polystyrene standards.

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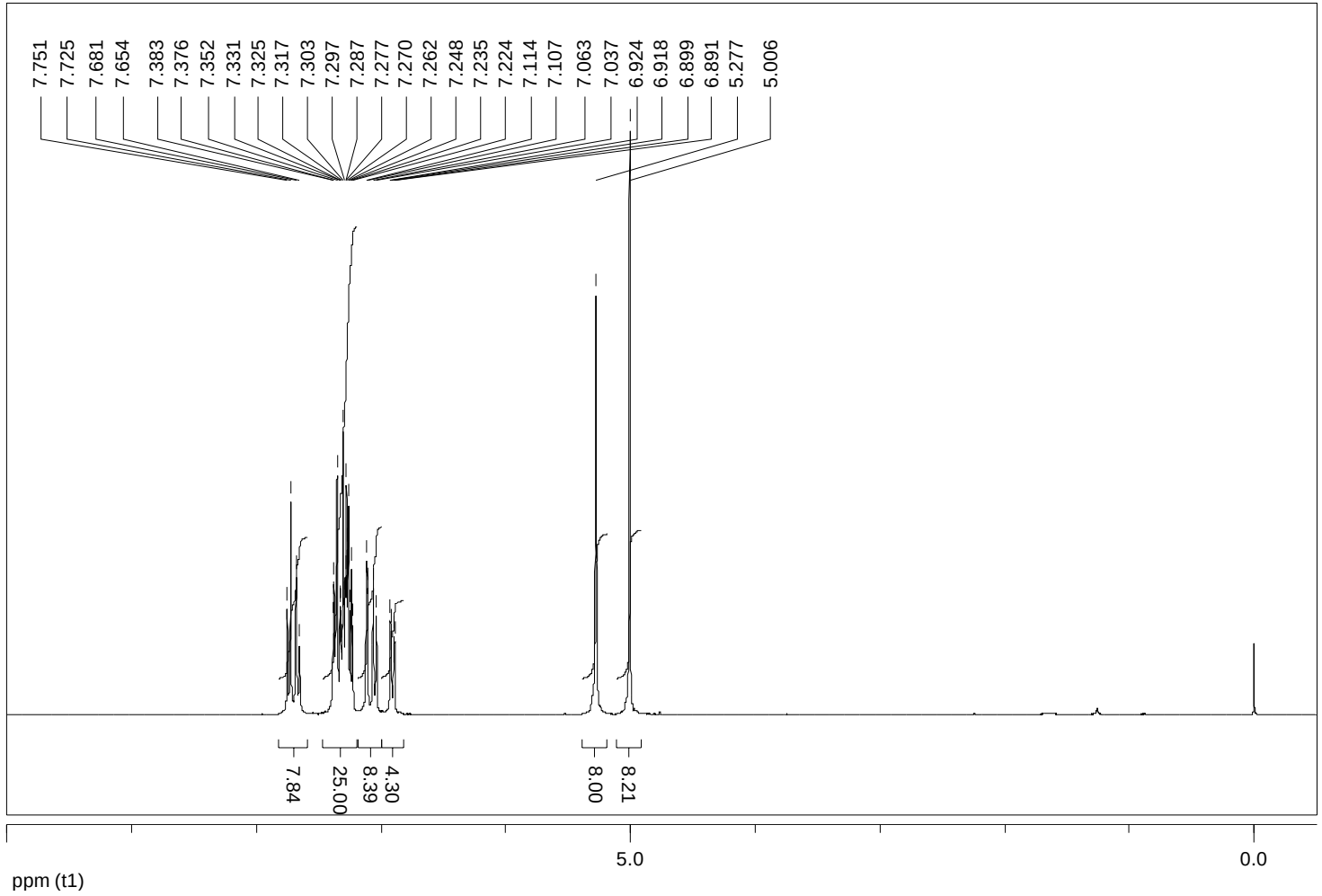
1 M. Takahashi, H. Morimoto, Y. Suzuki, M. Yamashita, H. Kawai, Y. Sei, K. Yamaguchi, *Tetrahedron*, 2006, **62**, 3065.

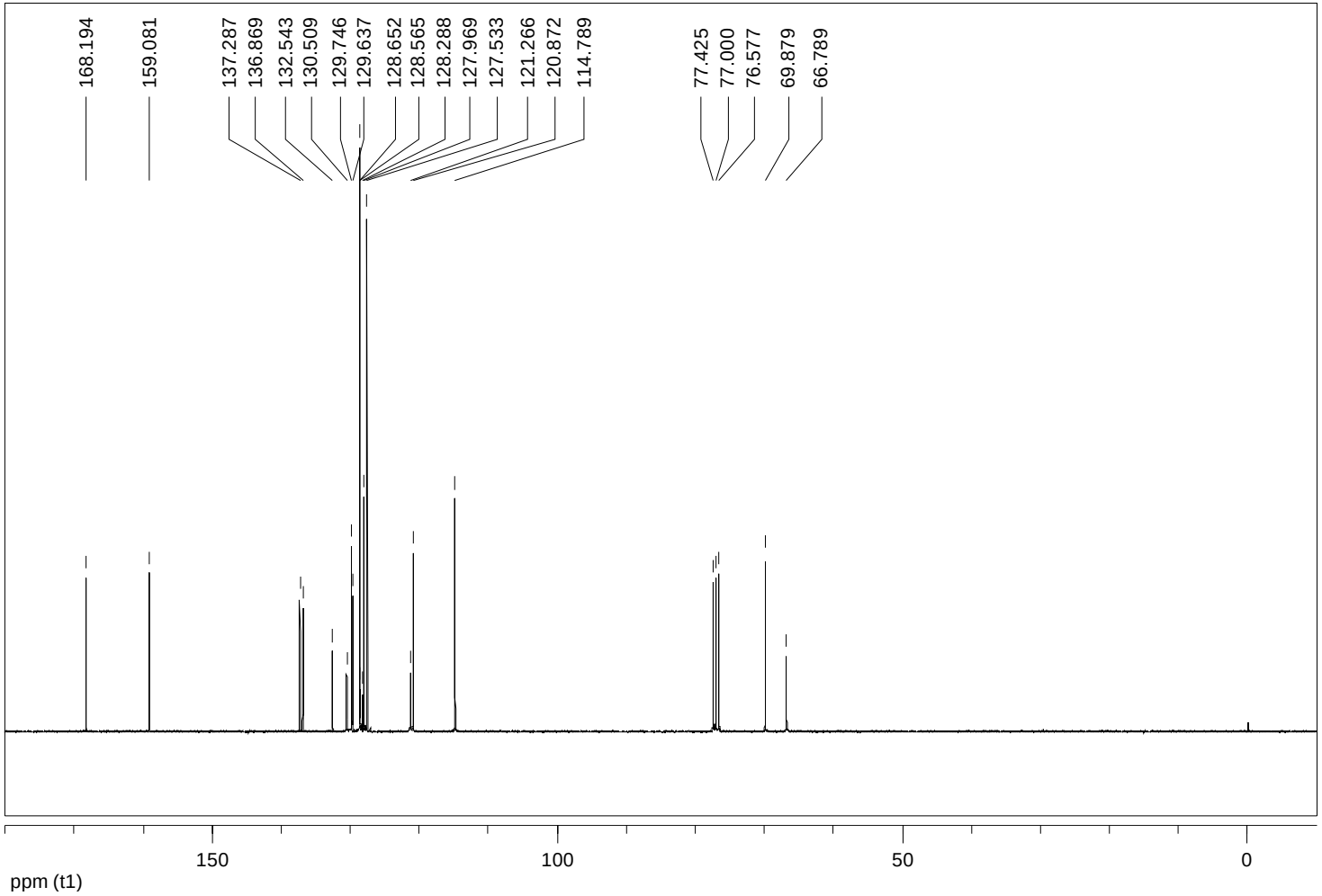
2 M. Takahashi, H. Morimoto, Y. Suzuki, M. Yamashita, H. Kawai, *Polymer Preprints*, 2004, **45**, 959.

3 B. Valeur, *Molecular Fluorescence Principles and Applications*, Wiley-VCH, Weinheim, New York, Chichester, Brisbane, Singapore, Toronto, 2002, pp. 247-272.

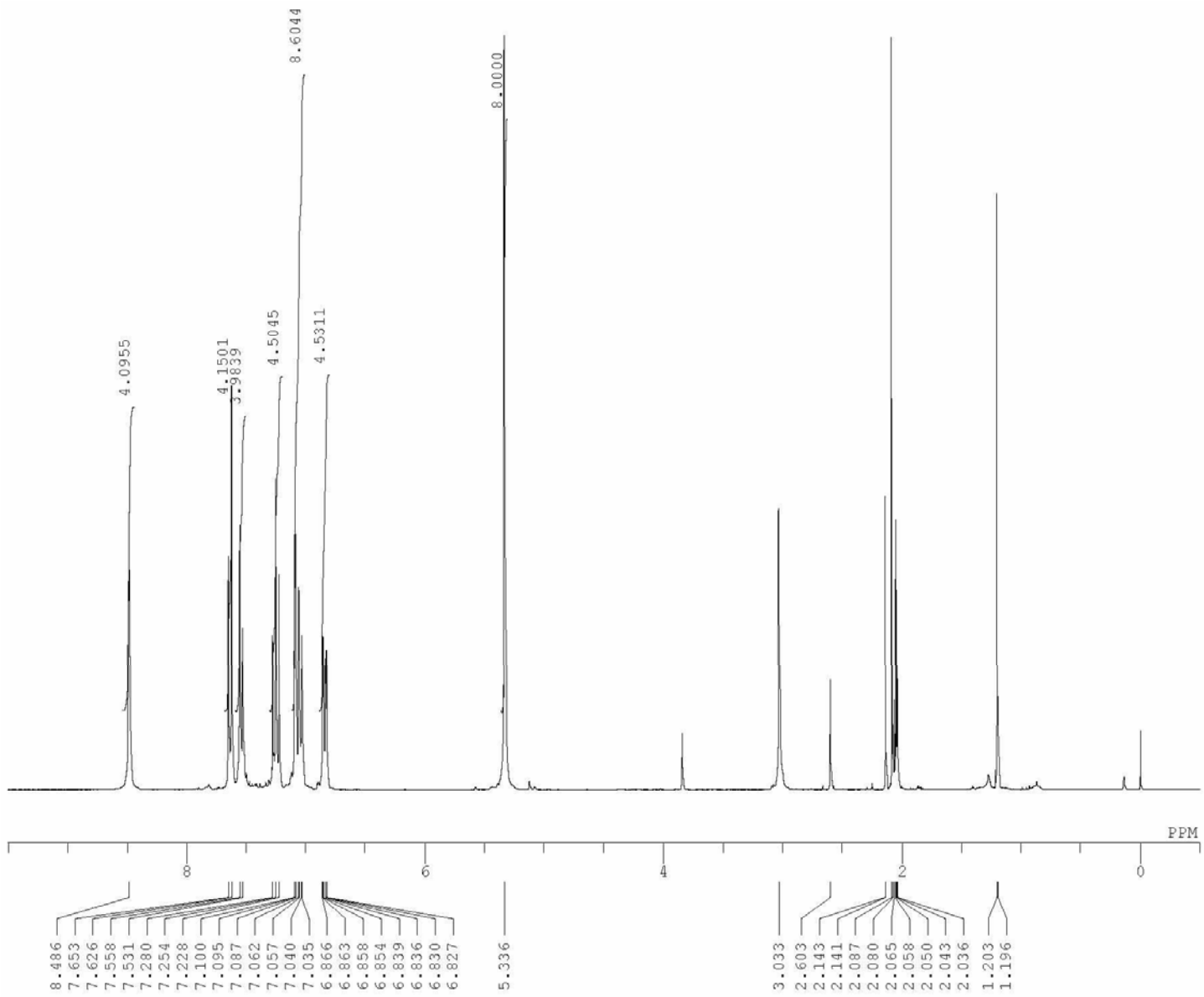
^{1}H-NMR spectrum of tetrakis(3-(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate



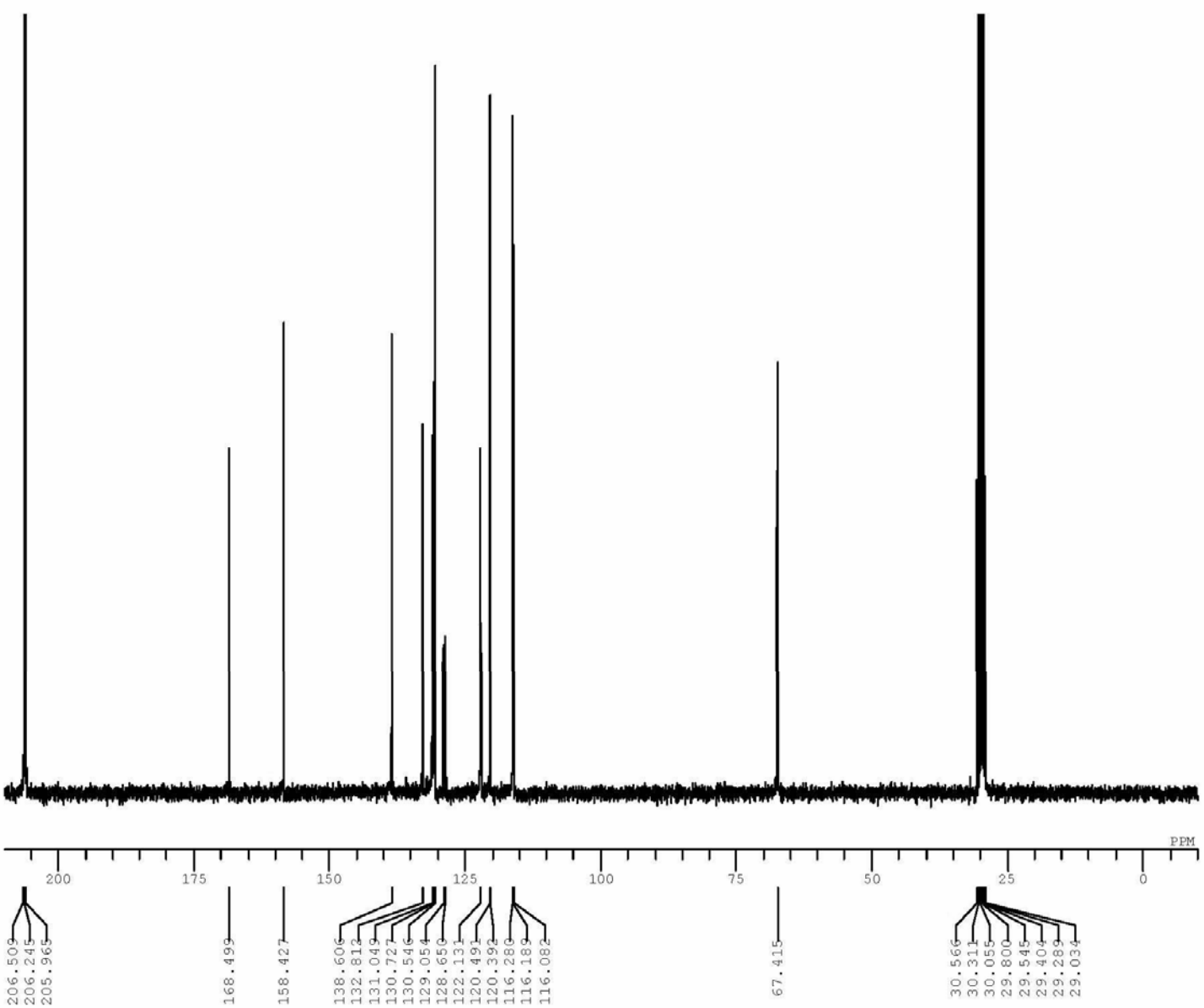
^{13}C-NMR spectrum of tetrakis(3-(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate



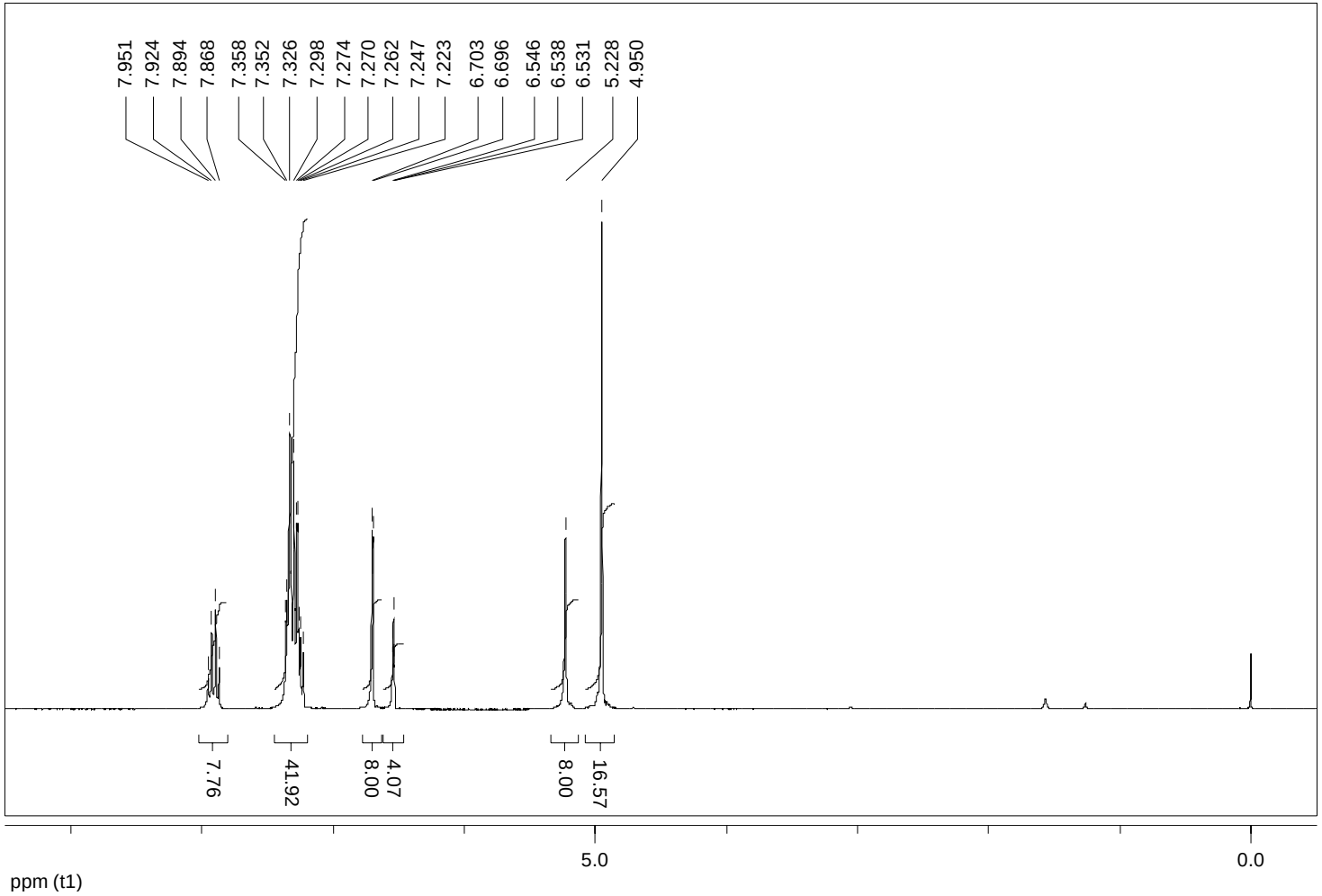
^{1}H-NMR spectrum of **P1**



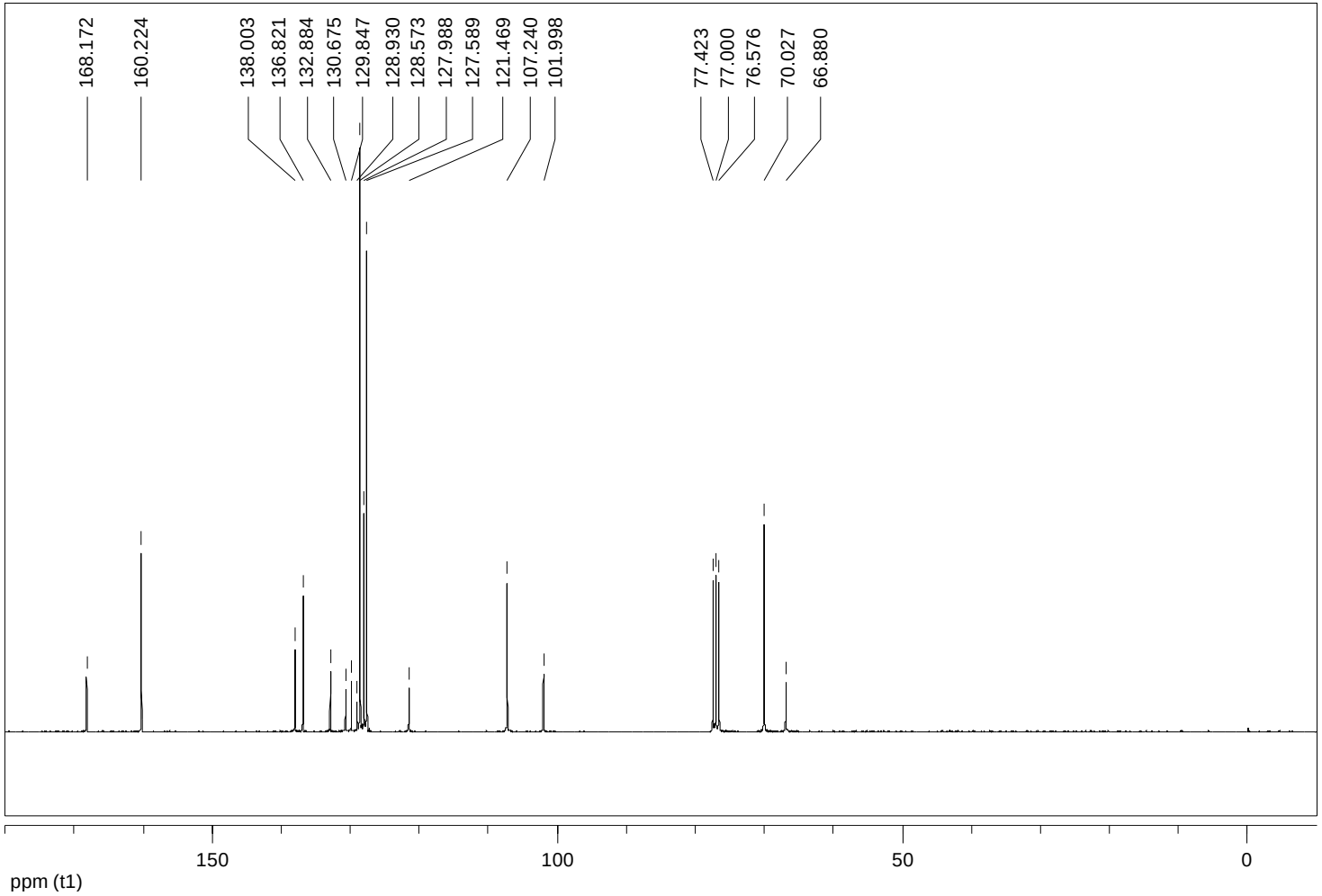
^{13}C-NMR spectrum of **P1**



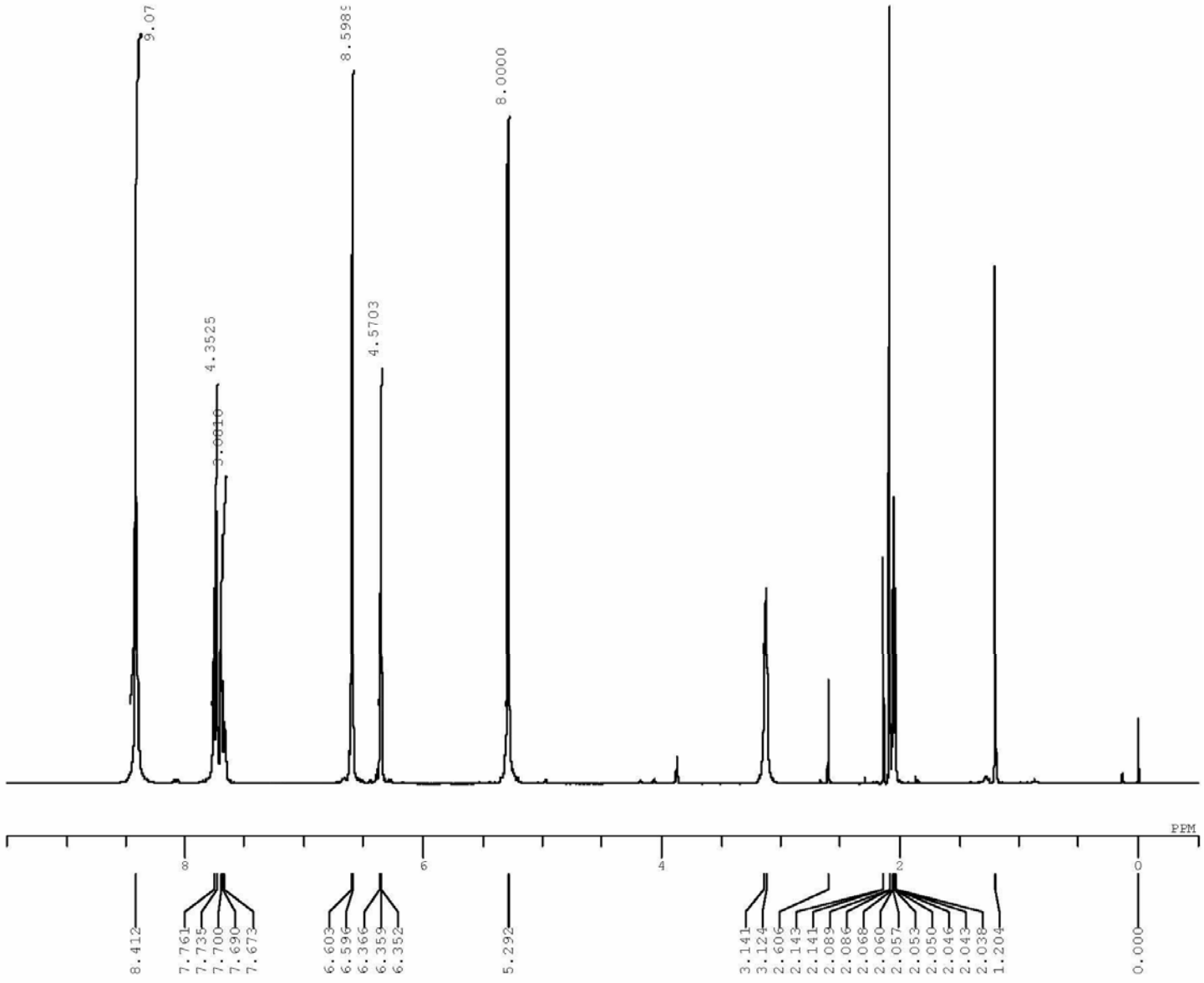
^{1}H-NMR spectrum of tetrakis(3,5-di(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate



^{13}C-NMR spectrum of tetrakis(3,5-di(benzyloxy)benzyl) 3,4,9,10-perylenetetracarboxylate



^{1}H-NMR spectrum of **P2**



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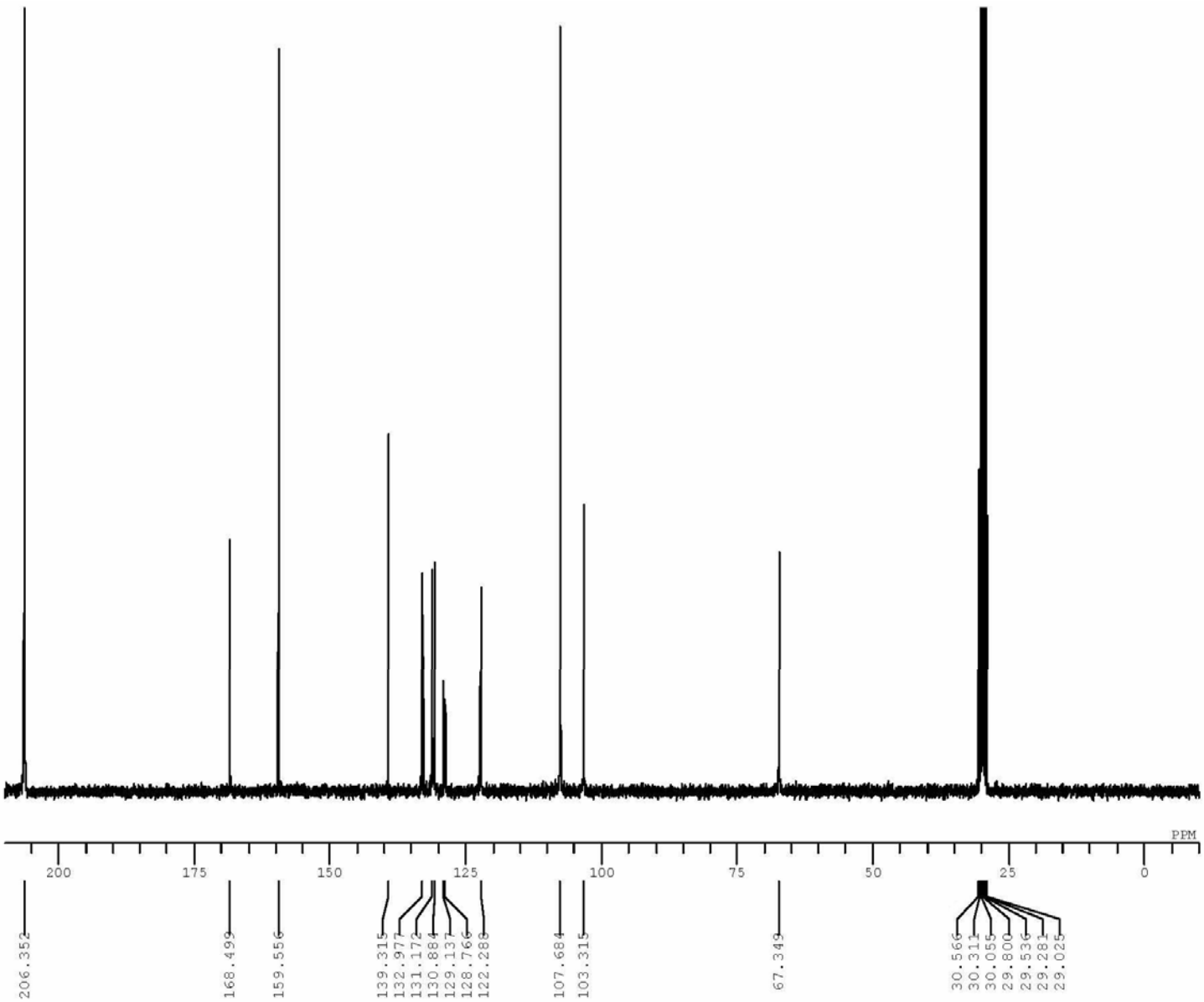
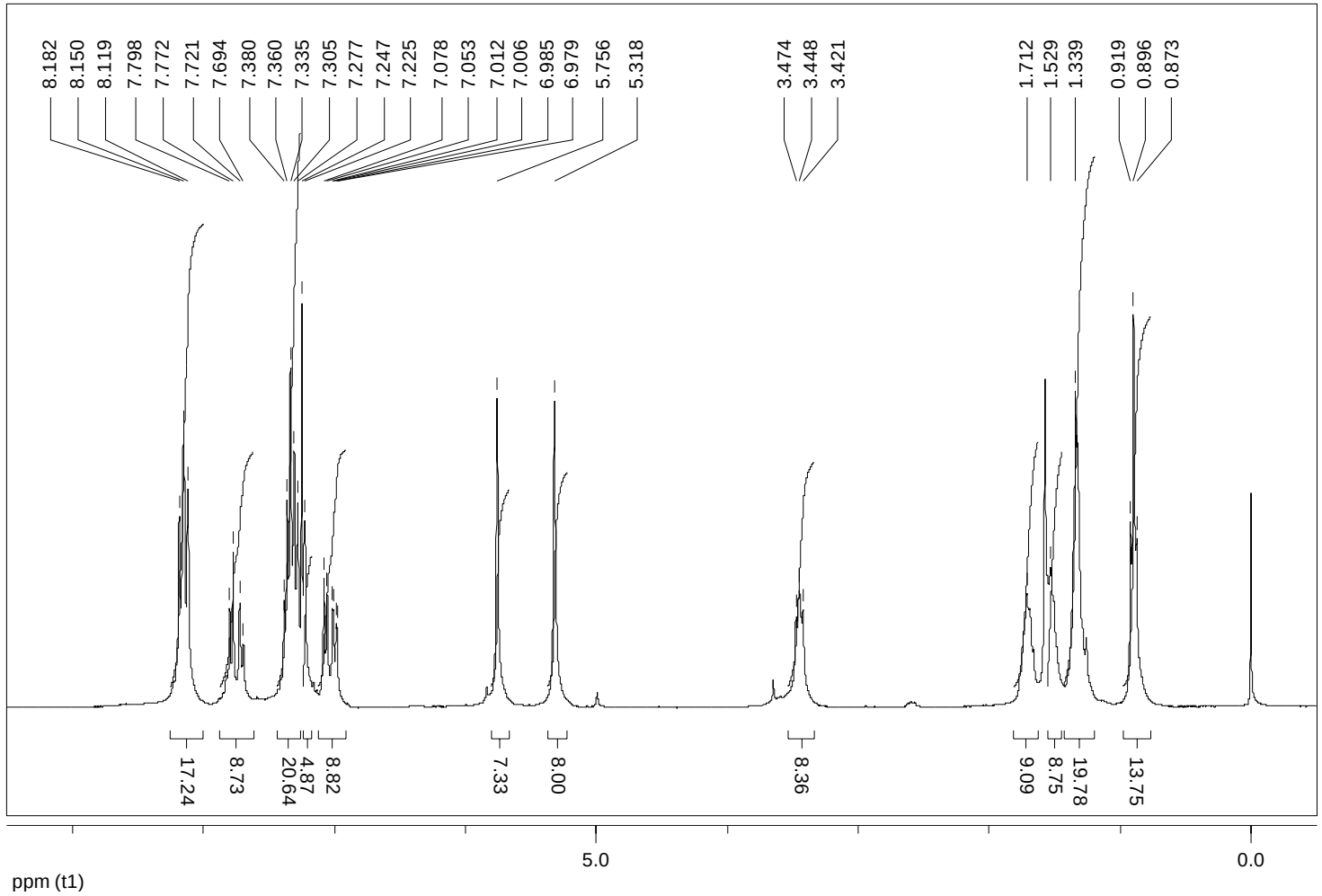


^{1}H-NMR spectrum of **1**



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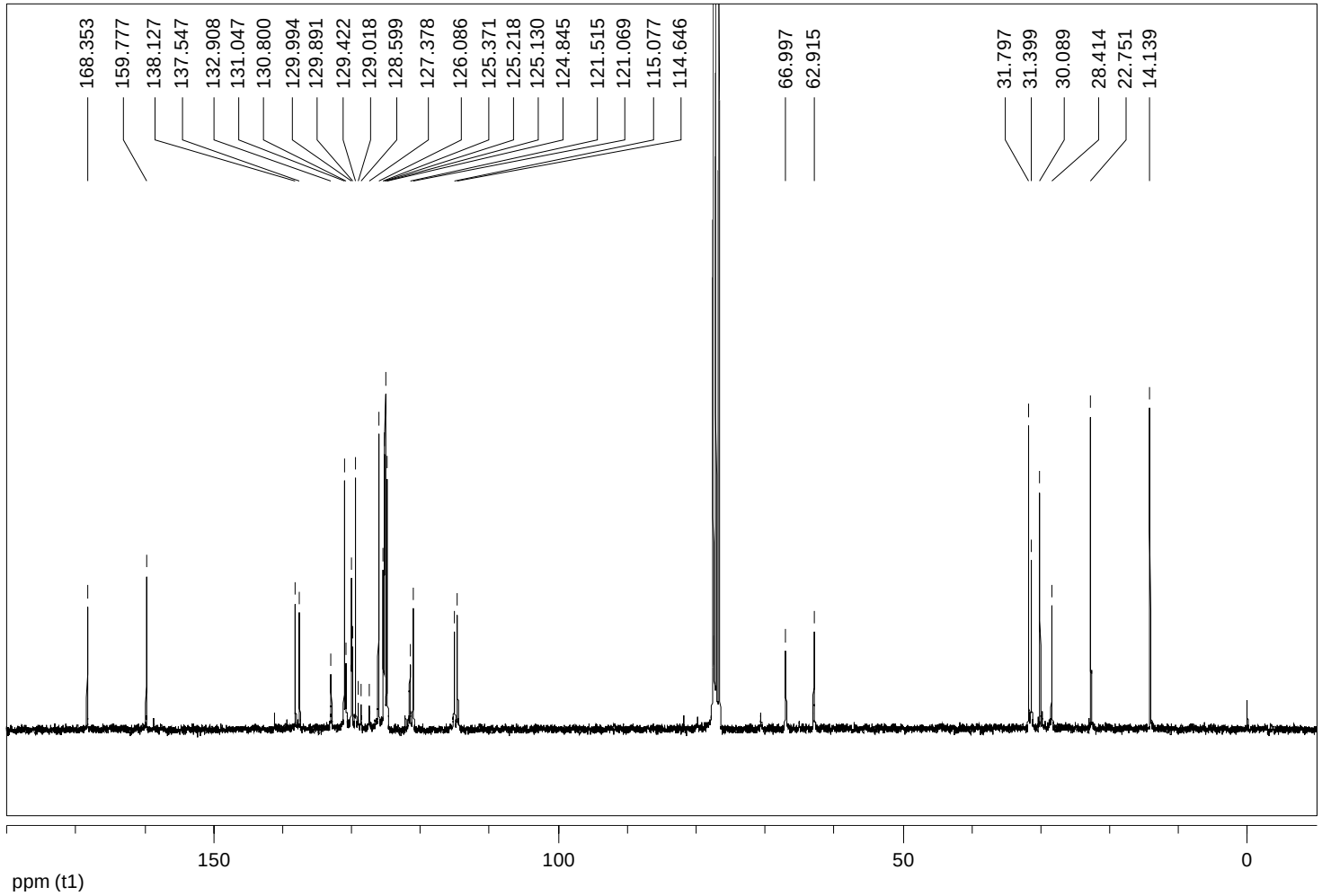
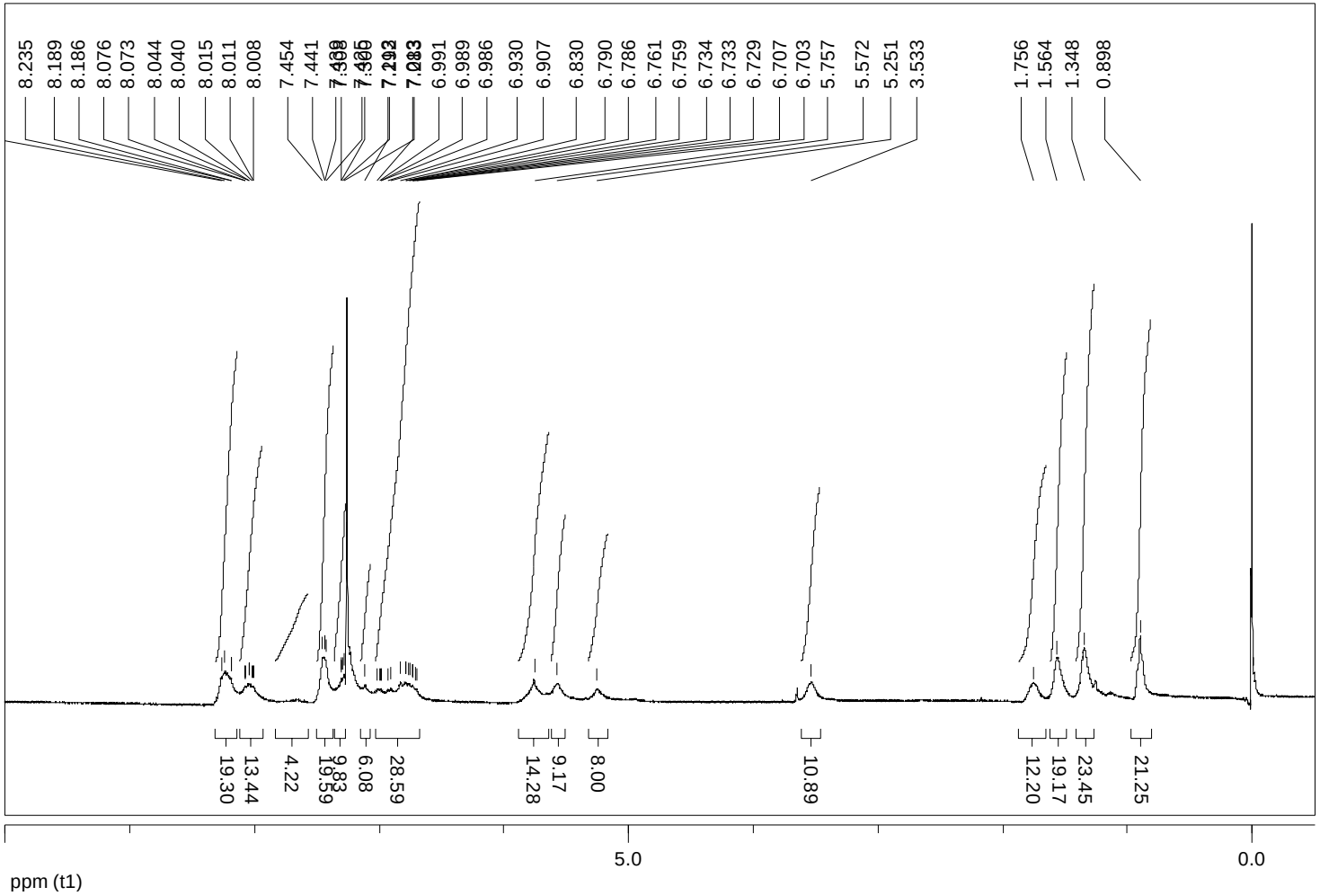


^{1}H-NMR spectrum of **2**



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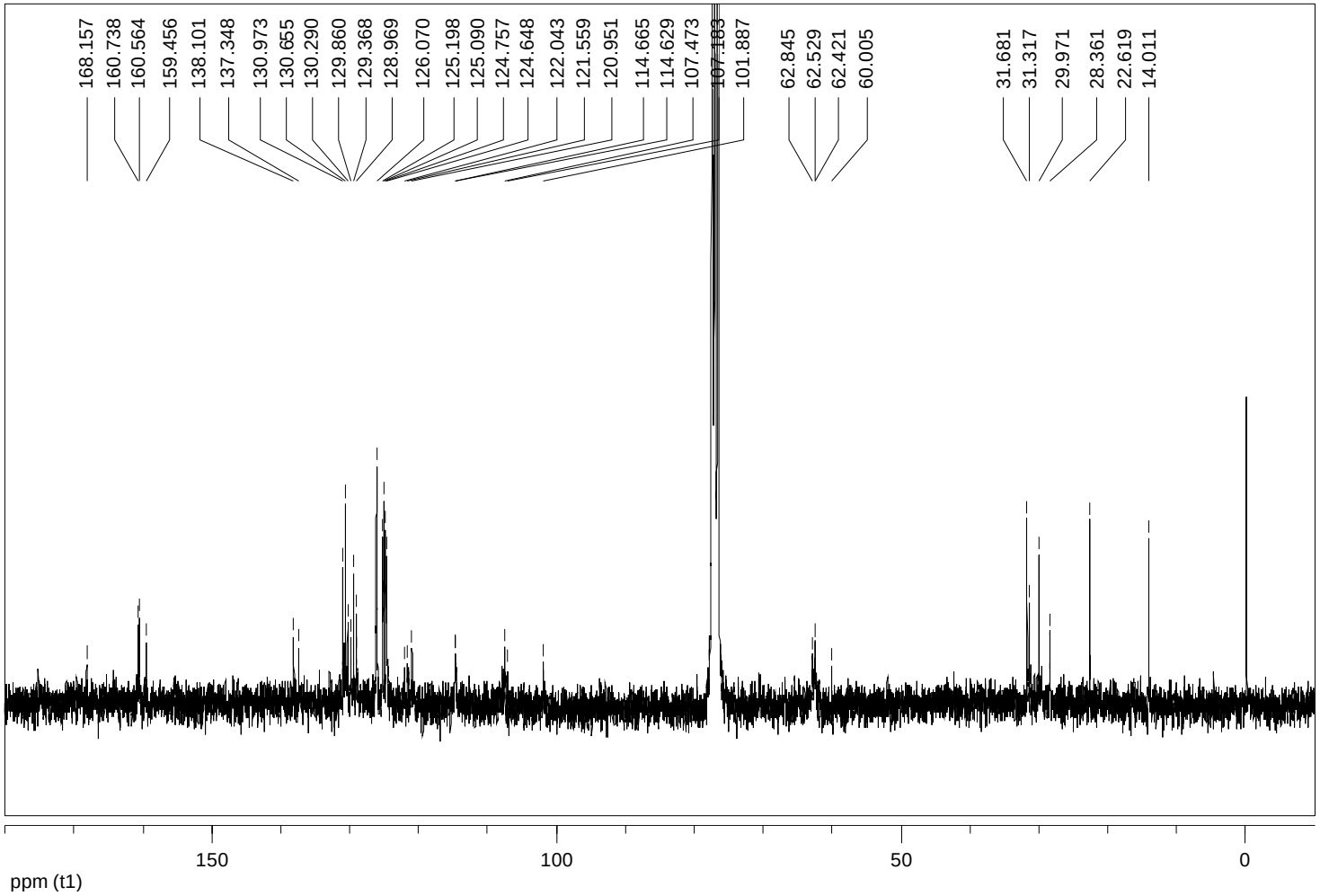
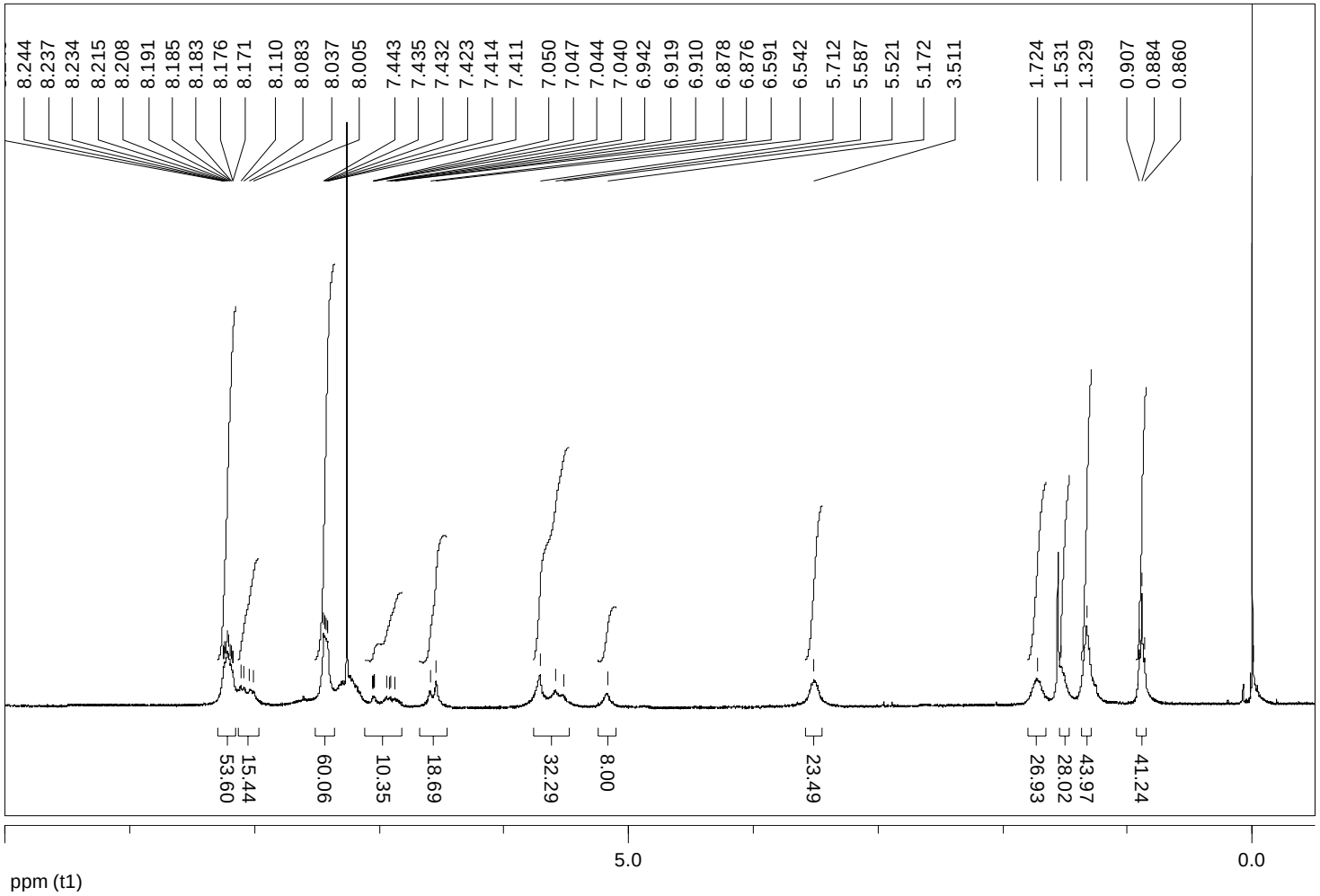
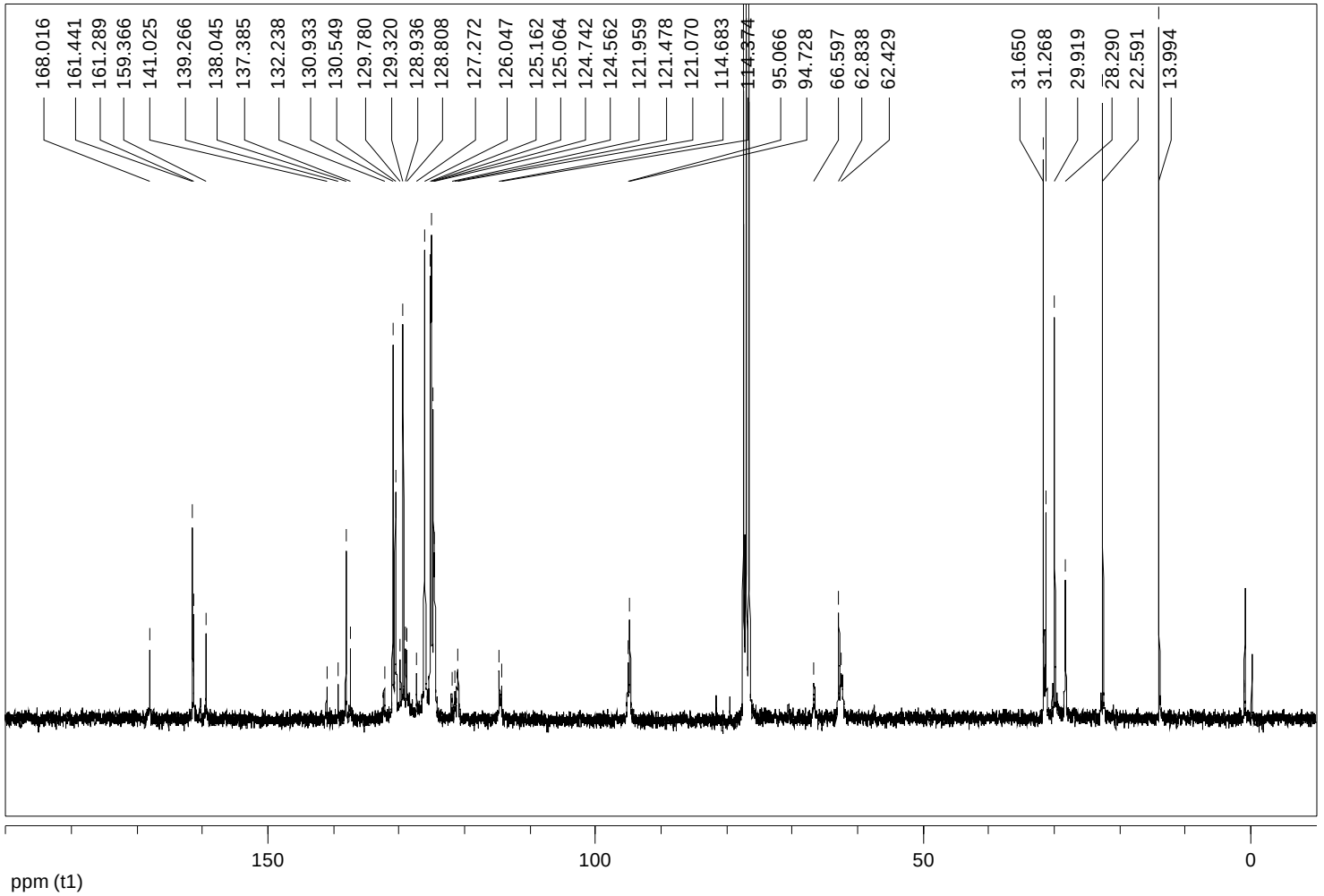


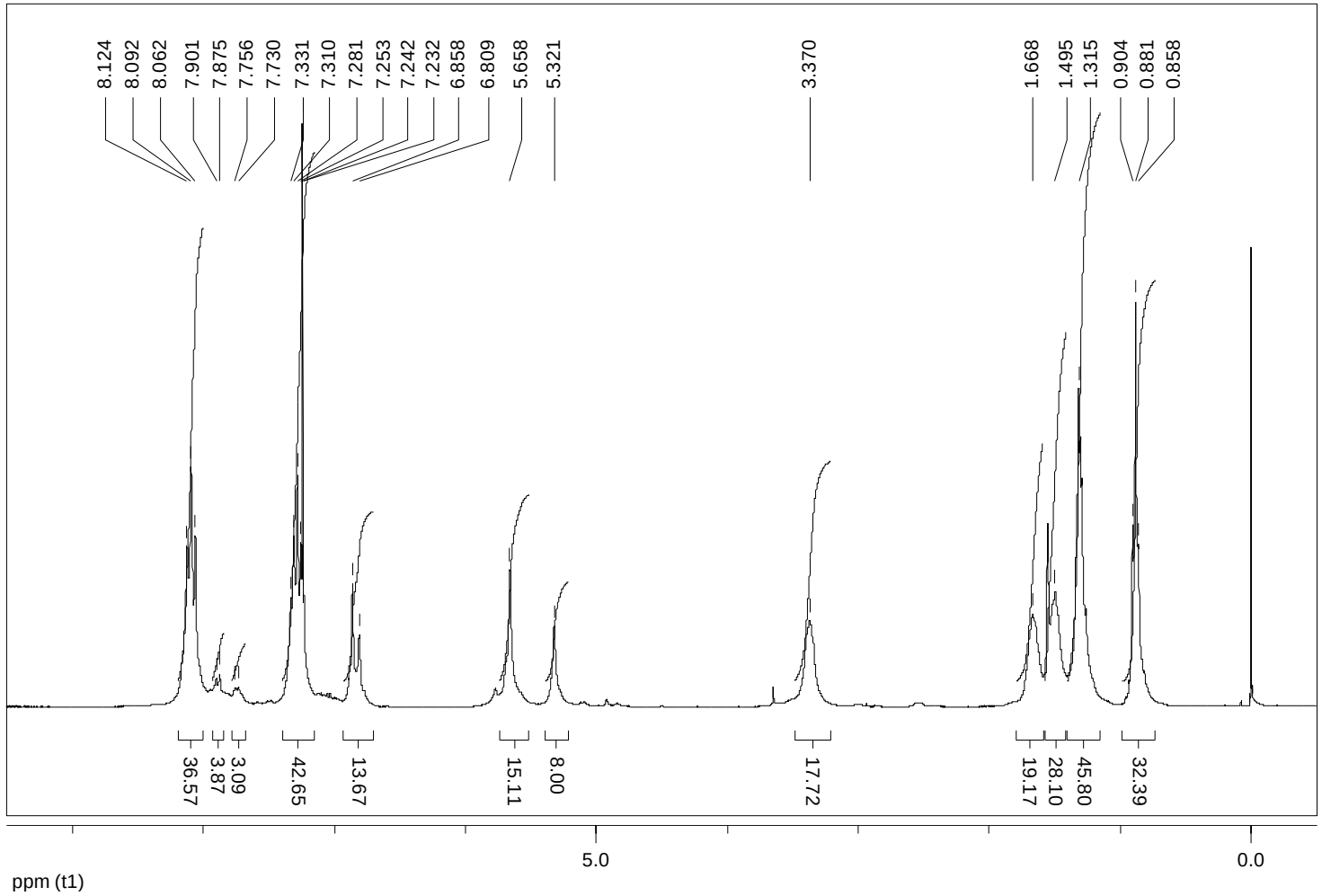
^{1}H-NMR spectrum of **3**



^{13}C-NMR spectrum of **3**



^{1}H-NMR spectrum of **4**



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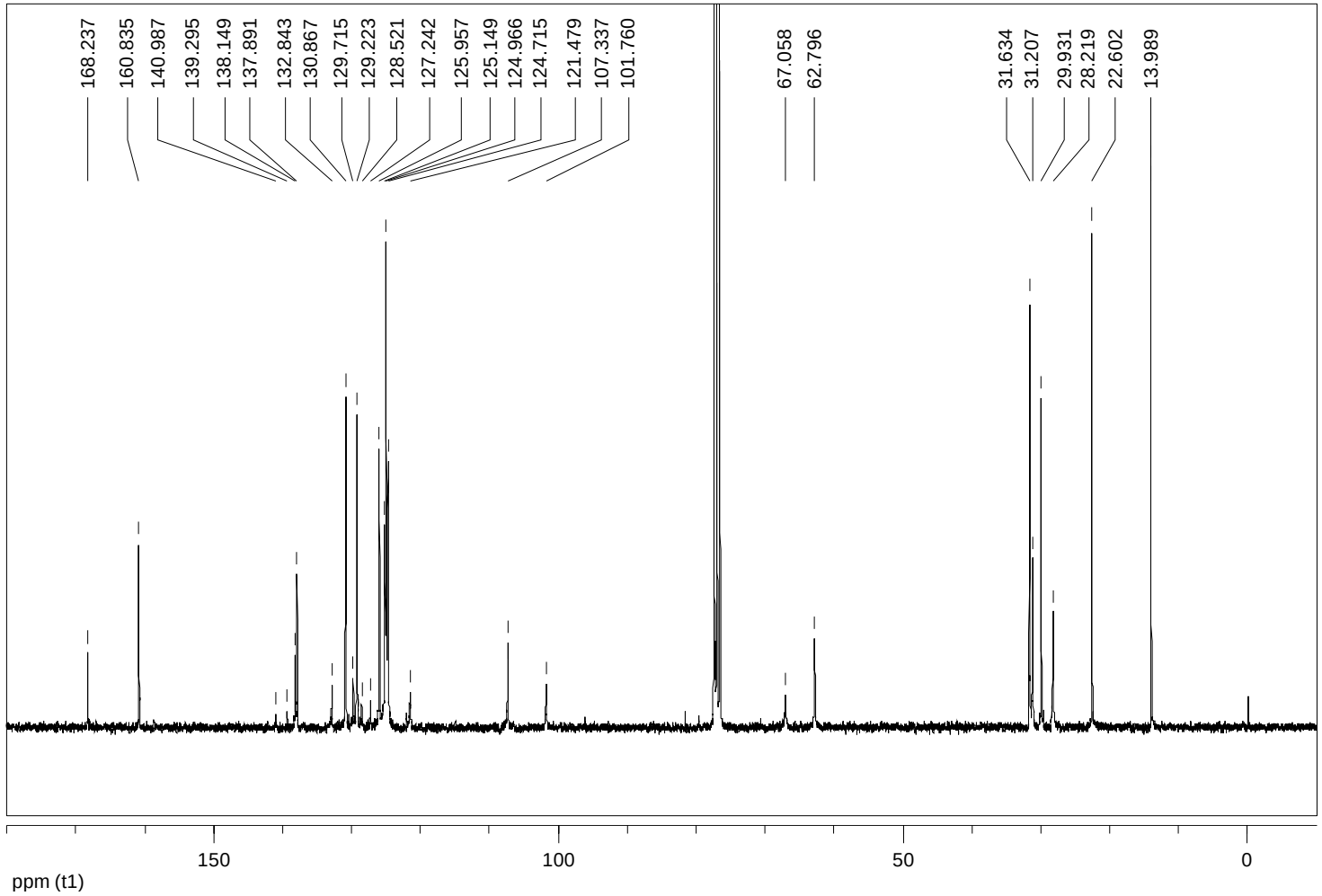
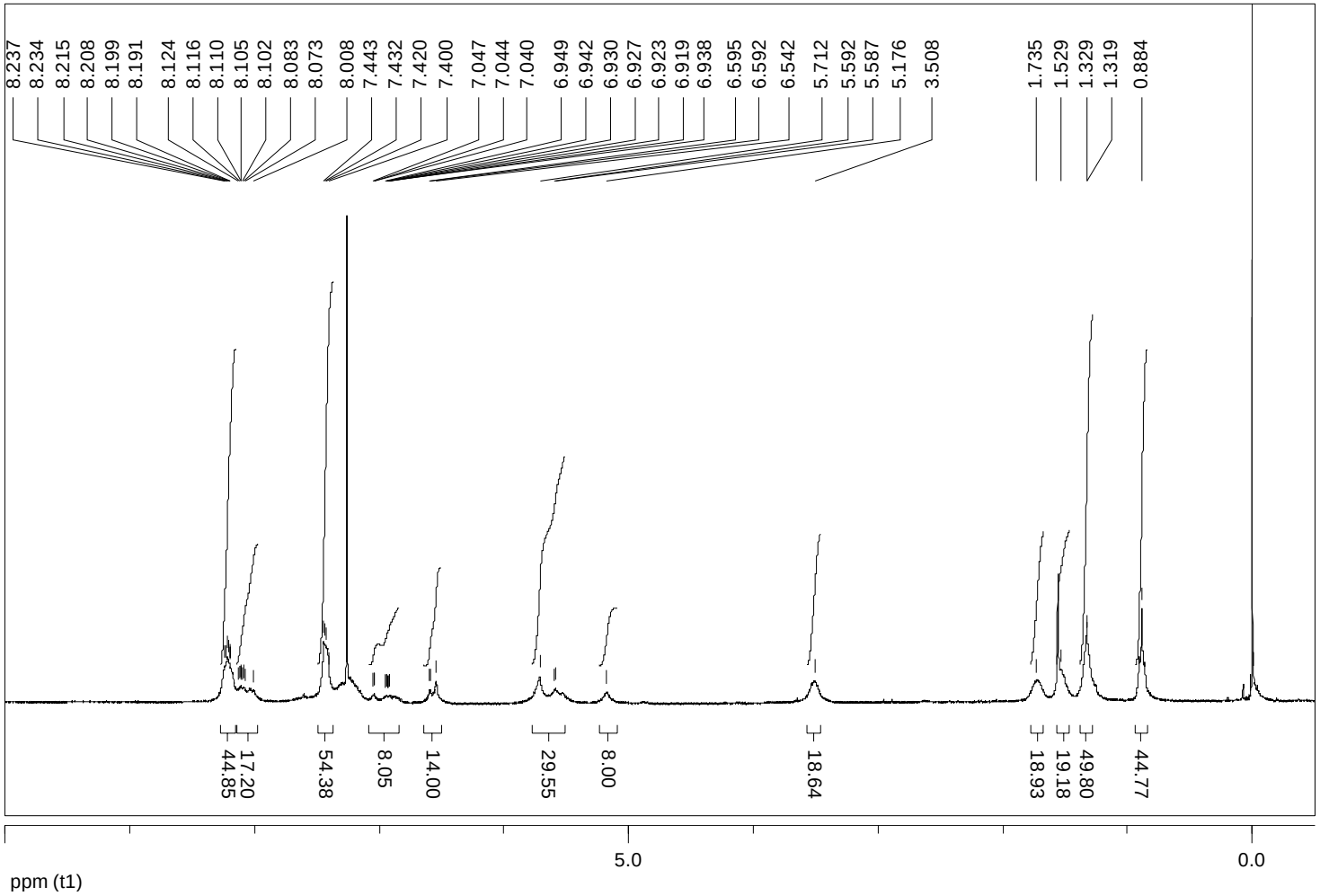


^{1}H-NMR spectrum of **5**



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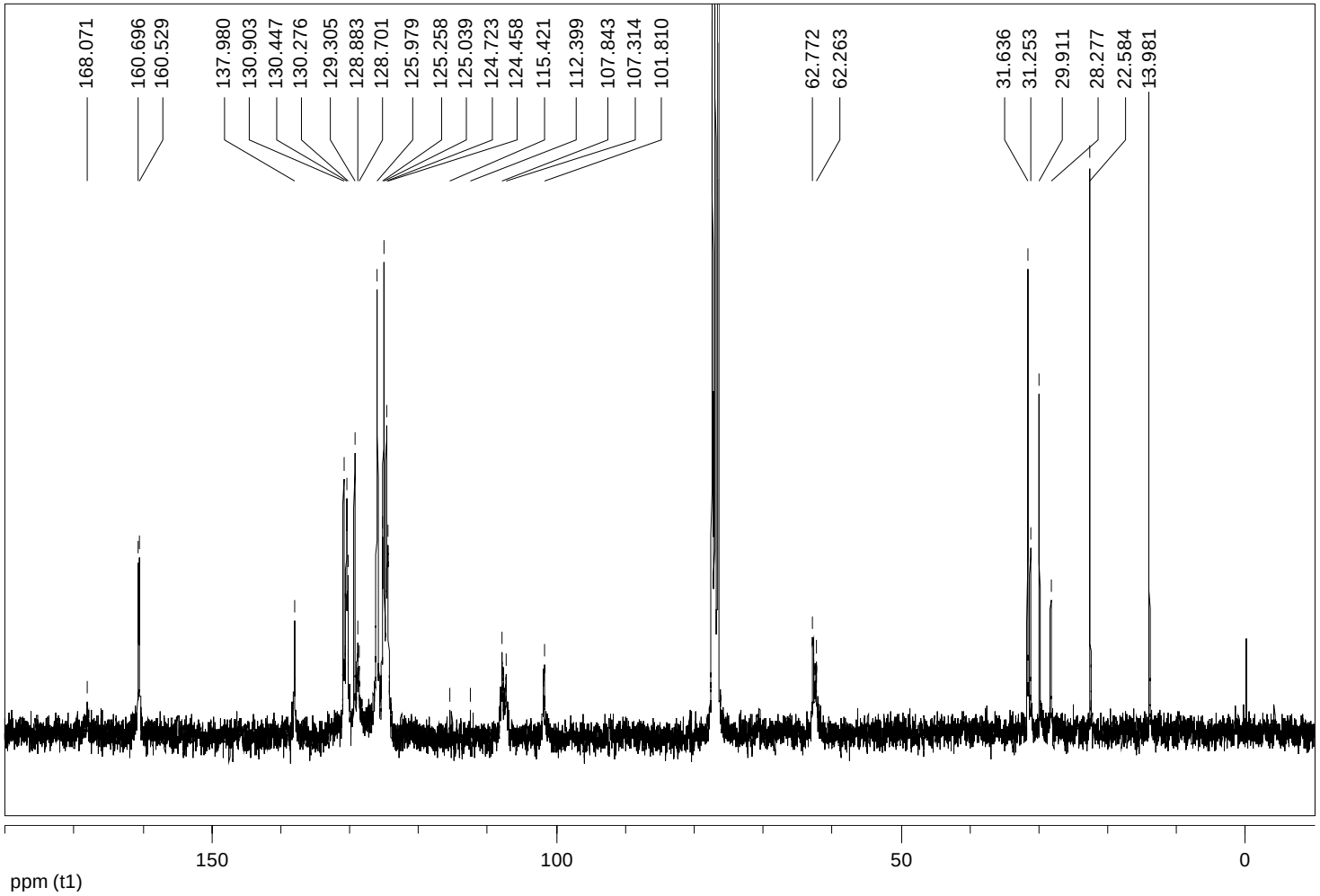
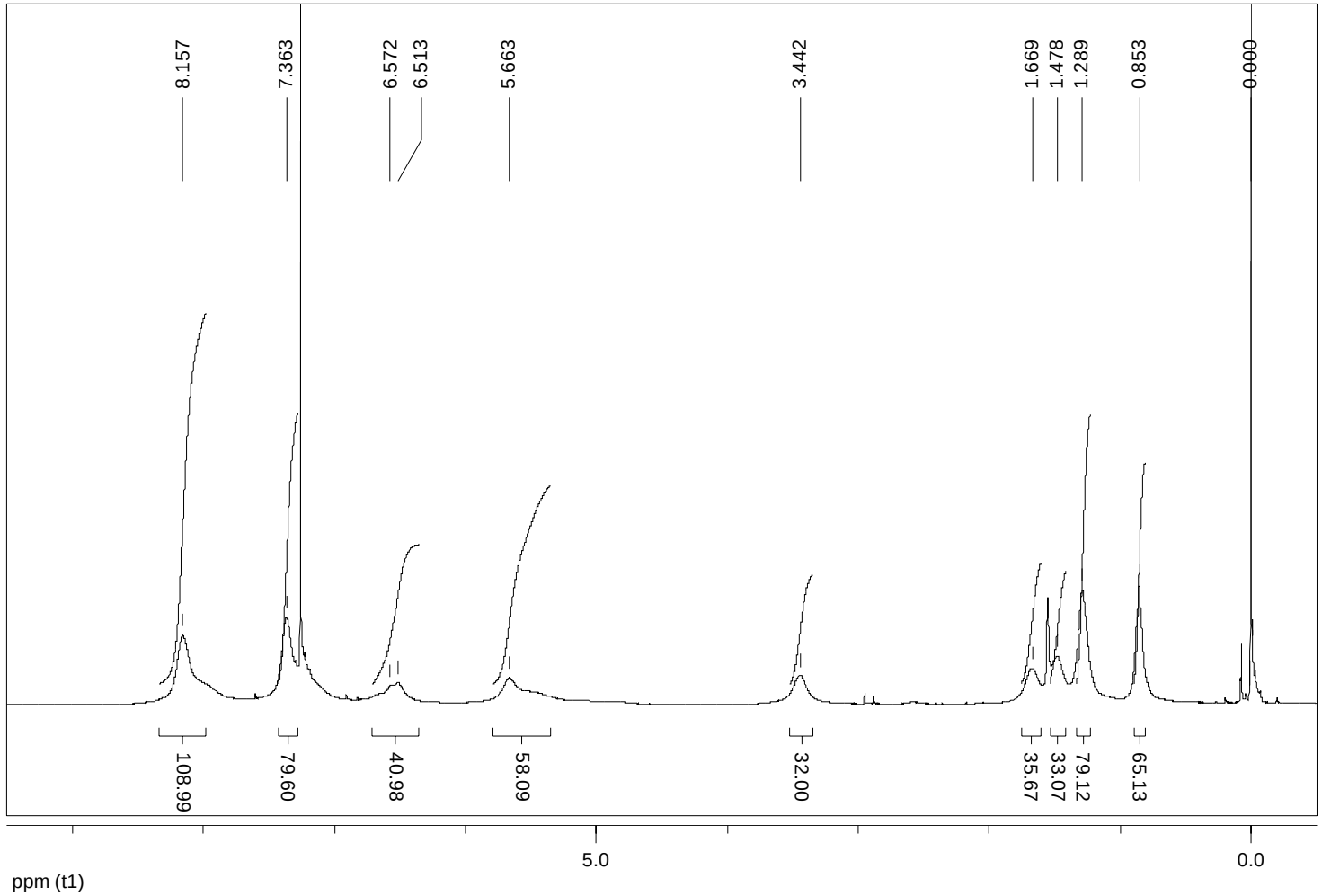


^{1}H-NMR spectrum of **6**



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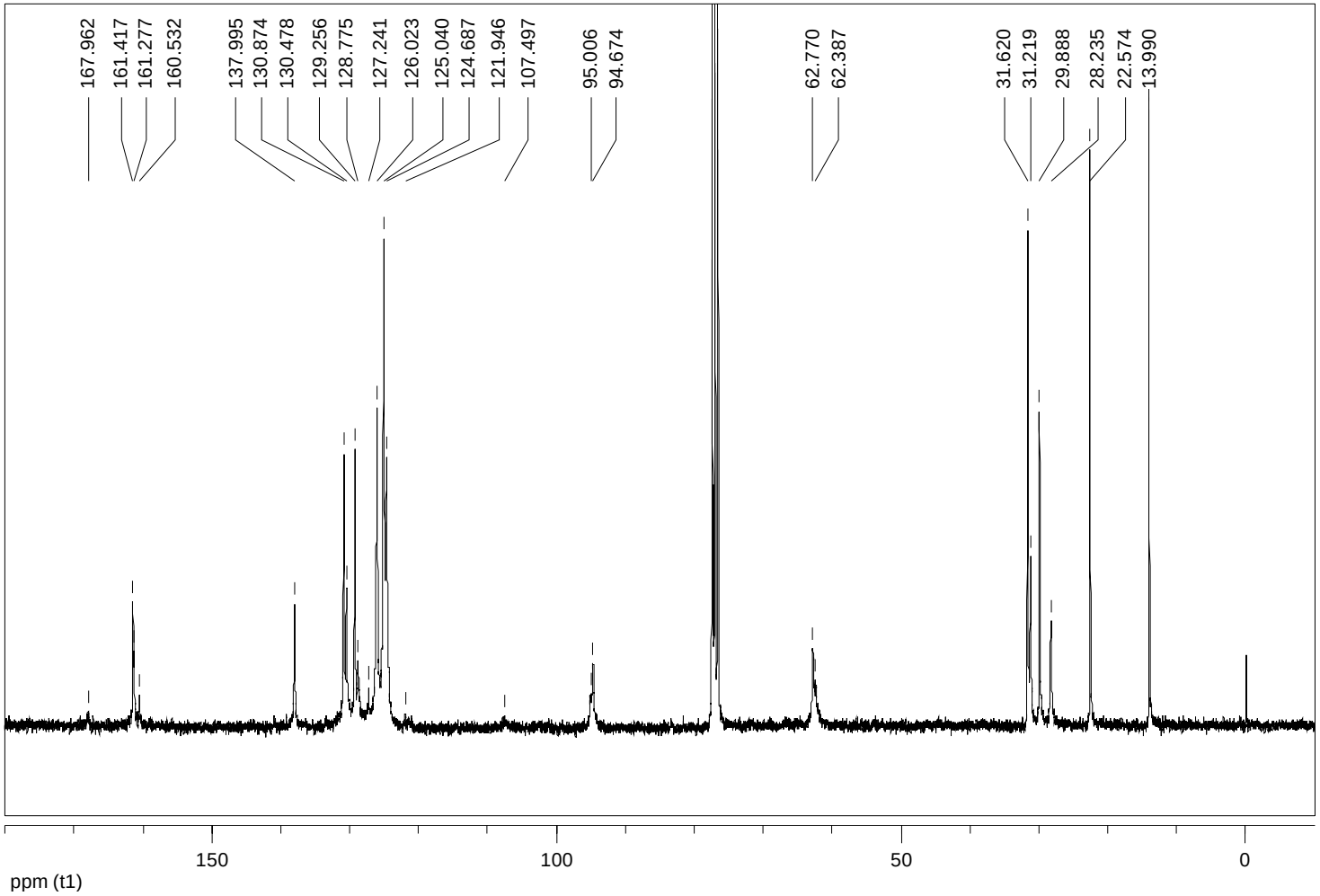
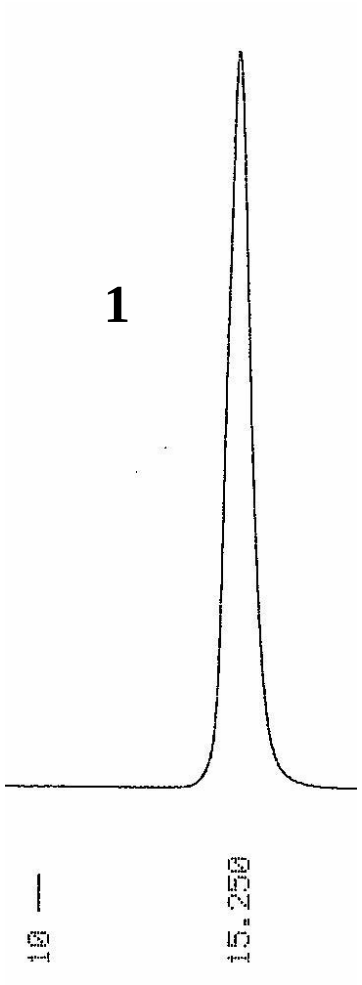
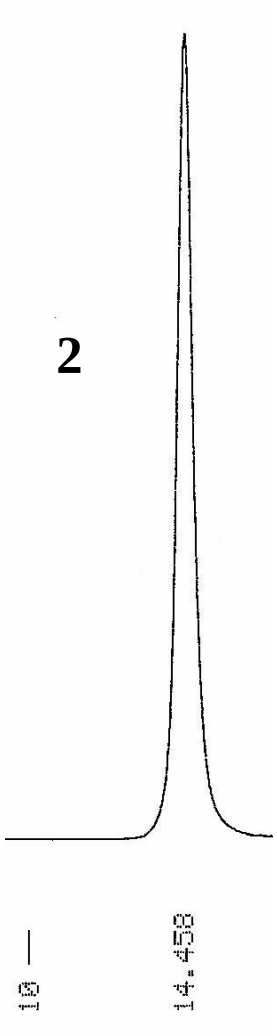
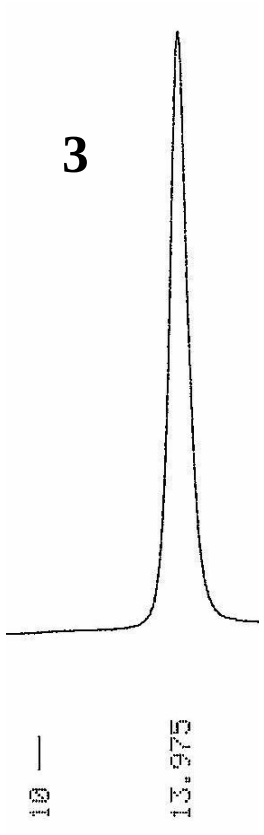


GPC results of **1-3**







GPC results of **4-6**