One-Pot Synthesis of Porphyrin-based [5]Rotaxanes

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1. General comments

Solvents and reagents were obtained from Millipore-Sigma, Tokyo Chemical Industry Co. Ltd., Lancaster Synthesis, Frontier Scientific, or Strem Chemicals. 1,2-Diamino-3,6-di(4'-*t*-butylphenyl)-benzene,[S1] diethyl-5-aminoisophtalate,[S2] 3,5-dibromoaniline,[S3] 4-(5,5-dimethyl-1,3-dioxan-2-yl) benzaldehyde,[S4] 4,7-dibromo-2,1,3-benzothiadiazole,[S5] and 4,7-bis(4-bromophenyl)-2,1,3-benzothiadiazole[S6] were synthesized according to literature methods. Solvents were dried over molecular sieves for at least 24 h. Deuterated solvents were obtained from Cambridge Isotope Laboratories and stored over molecular sieves after opening. Solution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III console equipped with an 11.7 T magnet. All chemical shifts are listed in ppm relative to TMS using the residual solvent peak as a secondary reference. Column chromatography was performed using Silicycle Ultra Pure Silica Gel (230-400 mesh) or Sigma-Aldrich Aluminum oxide (Activated, neutral, Brockmann I, ~150 mesh). IR spectra were collected on a Bruker Alpha-T ATR-FTIR spectrometer.

2. Synthesis

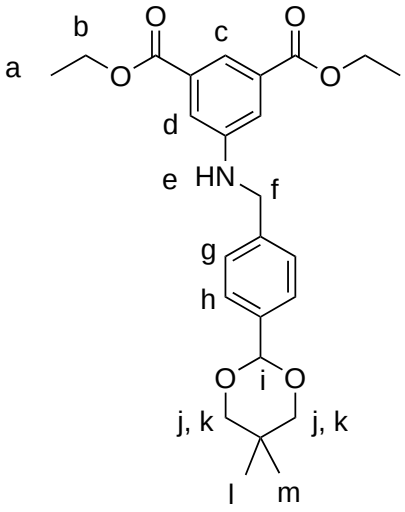

Figure S1. Diethyl 5-((4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)amino)isophthalate (**1a**).

To a solution of diethyl-5-aminoisophtalate (1.58 g, 6.7 mmol) and 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (1.47 g, 6.7 mmol) in dichloromethane (35 mL), under N_2, was added sodium triacetoxyborohydride (1.98 g, 9.3 mmol). The solution was stirred for 16 h and quenched with a saturated sodium bicarbonate solution. The organic phase was isolated and washed with

water (50 mL) and brine (10 mL), dried over anhydrous $MgSO_4$, and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, dichloromethane/ethyl acetate/triethylamine 100:2:0.5 *v/v*, R_f = 0.60). Yield: 1.8 g white solid, 62%. MP: 109-116 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.99 (1H, c), 7.48 (d, 2H, *J* = 7.9 Hz, h), 7.45 (s, 2H, d), 7.36 (d, 2H, *J* = 7.9 Hz, g), 5.38 (s, 1H, i), 4.37 (s, 2H, f), 4.35 (q, 4H, *J* = 7.1 Hz, b), 3.76 (d, 2H, *J* = 10.9 Hz, j, k), 3.64 (d, 2H, *J* = 10.9 Hz, j, k), 1.37 (t, 6H, *J* = 7.1 Hz, a), 1.28 (s, 3H, l), 0.79 (s, 3H, m). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) = 166.3, 148.1, 139.2, 138.0, 131.8, 127.6, 126.7, 119.6, 117.6, 101.6, 77.7, 61.3, 48.0, 30.3, 23.1, 22.0, 14.4. HR-MS (ESI +): Calculated for $[M\text{-}H]^+$ $[C_{25}H_{32}NO_6]^+$ *m/z* = 442.2230; found *m/z* = 442.2224.

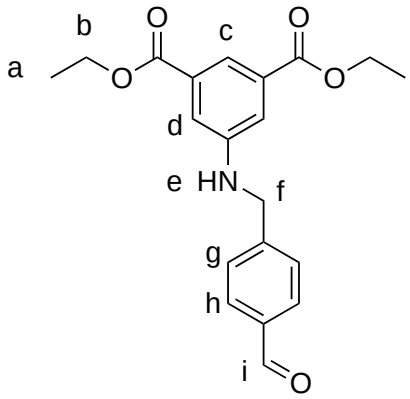

Figure S2. Diethyl-5-((4-formylbenzyl)amino)isophthalate (**Aldehyde 1**).

1a (1.8 g, 4.1 mmol) was dissolved in THF (75 mL) and HCl (5 mL conc. HCl in 25 mL water) was added. The reaction mixture was refluxed for 16 h. After cooling down to room temperature, sodium bicarbonate was added until no further CO_2 evolution was observed. The organic solvent was removed under reduced pressure and the aqueous residue extracted with ethyl acetate. After drying over anhydrous $MgSO_4$ the solvent was removed under reduced pressure and the resulting solid was washed with methanol to yield a white crystalline powder. Yield: 1.2 g, 83%. MP: 112-116 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 10.00 (s, 1H, i), 8.04 (s, 1H, c), 7.87 (d, *J* = 8.0 Hz, 2H, h), 7.53 (d, *J* = 8.0 Hz, 2H, g), 7.48 (s, 2H, d), 4.52 (s, 2H, f), 4.36 (q, 4H, *J* = 7.2 Hz, b), 1.38 (t, 6H, *J* = 7.2 Hz, a). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) = 191.9, 166.2, 147.8, 145.8, 135.8, 131.9, 130.3, 127.9, 120.0, 117.7, 61.3, 47.9, 14.4. HR-MS (ESI +): Calculated for $[M\text{-}H]^+$ $[C_{20}H_{22}NO_5]^+$ *m/z* = 356.1498; found *m/z* = 356.1500.

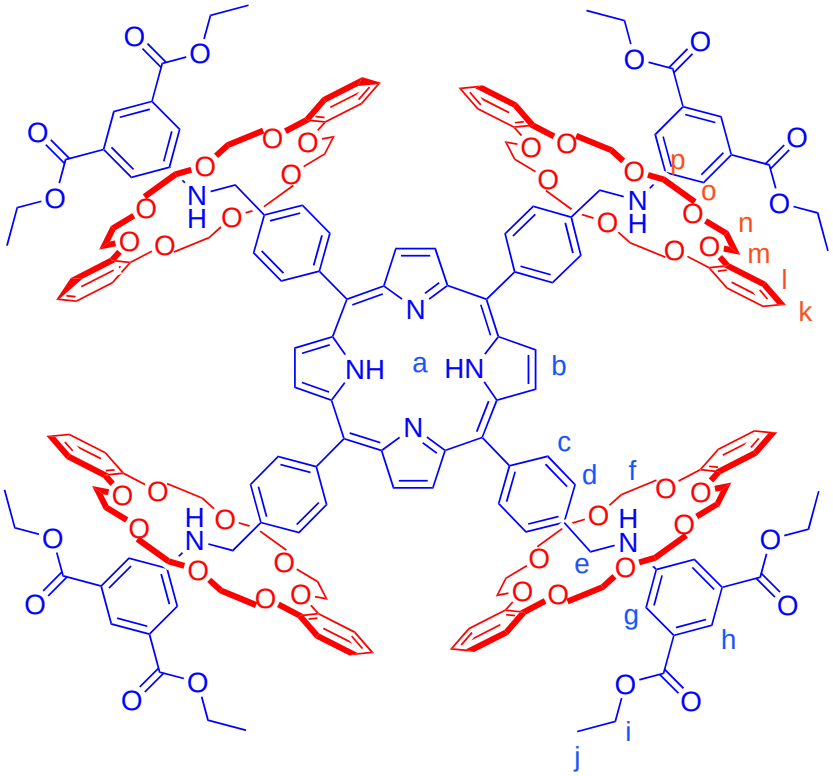

Figure S3. [5]Rotaxane **R1**.

To a solution of aldehyde **1** (200 mg, 0.56 mmol) in dry, degassed dichloromethane (50 mL) was added tetrafluoroboric acid diethyl ether complex (76.6 µL, 0.56 mmol). After stirring for 30 min at room temperature, dibenzo-24-crown-8 ether (1.01 g, 2.24 mmol) was added and the solution stirred for and additional 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (39.0 µL, 0.56 mmol) was added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (7.5 µL) was added. After 2 h of stirring at room temperature, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 96 mg, 0.42 mmol) was added. After heating at 40 °C for 2 h, the reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude product was washed with hot toluene (100 mL), dissolved in dichloromethane (50 mL), and washed with saturated sodium bicarbonate solution (50 mL). Further purification by flash column chromatography (SiO_2, dichloromethane/methanol 95:5 *v/v*, R_f = 0.45) followed by recrystallization from acetonitrile/diisopropyl ether gave pure green crystals of the desired product in the form of its tetrafluoroborate salt. Yield: 85 mg, 18%. MP: 207 °C (decomp). ^{1}H NMR for [**R1**-H_6][BF_4]$_6$ (500

MHz, CD_2Cl_2, 298 K) δ (ppm) = 9.87 (b, 8H, f), 8.80 (s, 8H, b), 8.79 (d, 8H, *J* = 7.6 Hz, c), 8.55 (s, 8H, g), 8.33 (s, 4H, h), 8.31 (d, 8H, *J* = 7.6 Hz, d), 6.73 (s, 32H, k, l), 5.95-5.92 (m, 8H, e), 4.44 (q, 16H, *J* = 7.0 Hz, i), 4.23 (b, 32H, m), 4.18 (m, 16H, n), 4.00 (m, 16H, o), 3.85-3.80 (b, 32H, p), 1.48 (t, 24H, *J* = 7.0 Hz, j), -2.80 (s, 4H, a). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ (ppm) = 164.4, 147.6, 146.2 139.9, 139.5, 136.1, 134.5, 132.6, 131.1, 130.4, 129.1, 128.0, 123.1, 121.8, 112.5, 71.4, 70.9, 68.6, 624, 54.3, 53.8, 53.6, 53.4, 14.6. HR-MS (ESI+): Calculated for $[M\text{-}H_4]^{4+}$ $[C_{192}H_{222}N_8O_{48}]^{4+}$ *m/z* = 852.3810; found *m/z* = 852.3811. IR (cm^{-1}): 3392.9, 3313.8, 3067.4, 2917.6, 2872.3, 1713.5, 1593.7, 1503.3, 1451.6, 1368.5, 1350.8, 1231.8, 1104.5, 1051.2, 1024.2, 950.0, 856.0, 801.8, 757.6, 671.4. UV-Vis (CH_2Cl_2, λ_{nm}) = 420 (Soret), 519, 556, 595, 650

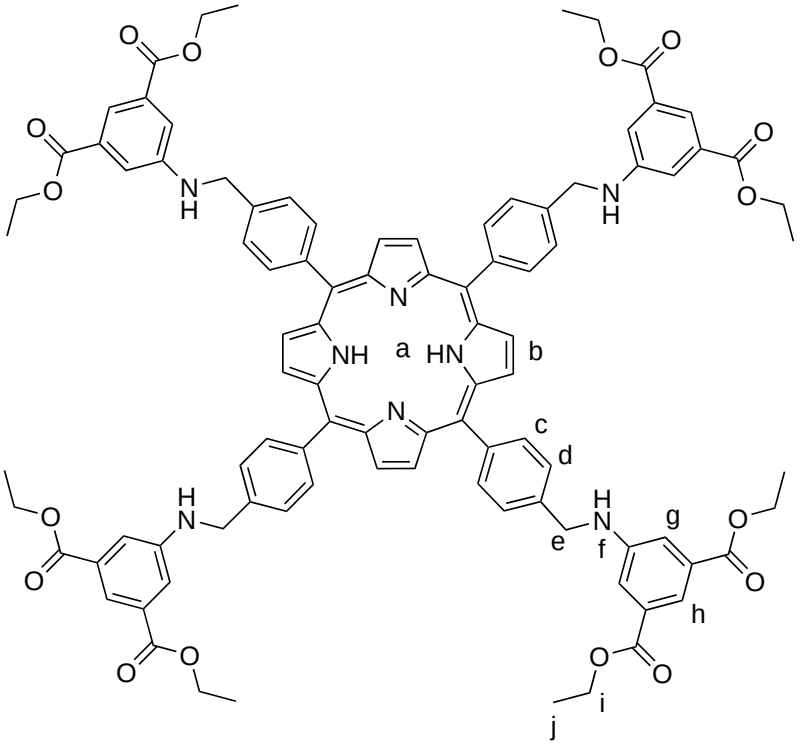

Figure S4. 5,10,15,20-Tetrakis(4-(diethyl-*N*-(3,5-aminomethylisophtalate)-phenyl)porphyrin (**P1**)

To a solution of aldehyde **1** (355 mg, 1.0 mmol) in dry, degassed dichloromethane (100 mL) and protected from light was added freshly distilled pyrrole (69.4 µL, 1.0 mmol). After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (12.6 µL) was added. After 6 h of stirring at room temperature more boron trifluoride diethyl etherate (20.0 µL) was added and left to stir at room temperature overnight. Then, DDQ (170 mg, 0.75 mmol) was added and

stirred at room temperature for 4 h followed by removal of the solvent under reduced pressure. The crude mixture was then purified via column chromatography (Al_2O_3, dichloromethane/methanol 100:1 *v/v*). The fluorescent red band was collected, and the solvent removed under reduced pressure. The crude product was purified via column chromatography (SiO_2, dichloromethane/methanol 100:1 *v/v*, R_f = 0.26) to yield a red solid (105 mg, 26%). MP: 228 °C (decomp). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ (ppm) = 8.85 (s, 8H, b), 8.15 (d, *J* = 7.7 Hz, 8H, c), 8.06 (t, *J* = 1.4 Hz, 4H, h), 7.70 (d, *J* = 7.7 Hz, 8H, d), 7.68 (d, *J* = 1.4 Hz, 8H, g), 4.77 (b, 4H, f), 4.70 (s, 8H, e), 4.41 (q, *J* = 7.1 Hz, 16H, i), 1.43 (t, *J* = 7.1 Hz, 24H, j), -2.82 (s, 2H, a). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ (ppm) = 166.5, 148.9, 141.5, 138.8, 135.2, 132.4, 126.3, 120.3, 119.6, 117.9, 61.6, 48.4, 14.6. HR-MS (ESI+): Calculated for $[M-H]^+$ $[C_{96}H_{91}N_8O_{16}]^+$ *m/z* = 1612.6586; found *m/z* = 1612.6616. IR (cm^{-1}): 3390.3, 3314.0, 2977.9, 2929.2, 2901.2, 2869.2, 2848.4, 1708.2, 1599.2, 1507.5, 1452.7, 1394.7, 1227.8, 1125.7, 1092.4, 1024.1, 966.7, 860.2, 796.1, 754.6 671.3. UV-Vis (CH_2Cl_2, λ_{nm}) = 419 (Soret), 515, 550, 590, 646.

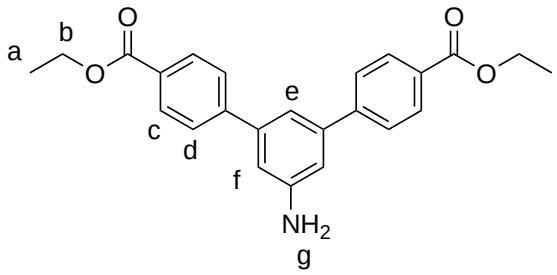

Figure S5. Diethyl-3,5-carboxyphenylaniline (**2a**).

3,5-Dibromoaniline (0.50 g, 2.0 mmol) and 4-(ethoxycarbonyl)phenylboronic acid (0.97 g. 5.0 mmol) were added to a Schlenk flask under an N_2 atmosphere. Degassed THF (100 mL) and a degassed Na_2CO_3 solution (2 M, 50 mL) were added and the reaction mixture stirred for 10 min. Tetrakis(triphenylphosphine)palladium (230 mg, 0.2 mmol) was added and the reaction mixture refluxed at 80 °C for 3 days. After cooling to room temperature, the organic fraction was isolated, and the aqueous fraction was extracted with ethyl acetate (2 x 50 mL). All the organic fractions were combined, washed with water (2 x 50 mL) and brine (50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product recrystallized from CH_3CN to yield a pale yellow solid (0.64 g, 82%). MP: 175-177 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 8.11 (d, 2H, *J* = 8.4 Hz, c), 7.67 (d, 2H, *J* = 8.4 Hz, d), 7.23 (s,

1H, e), 6.95 (s, 2H, f), 4.40 (q, 4H, *J* = 7.1 Hz, b), 3.94 (b, 2H, g), 1.42 (t, 6H, *J* = 7.1 Hz, a). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) = 166.6, 147.5, 145.6, 142.1, 130.1, 129.6, 127.2, 117.1, 113.7, 61.1, 14.5. HR-MS (ESI+): Calculated for $[M\text{-}H]^+$ $[C_{24}H_{24}NO_4]^+$ *m/z* = 390.1705; found *m/z* = 390.1711.

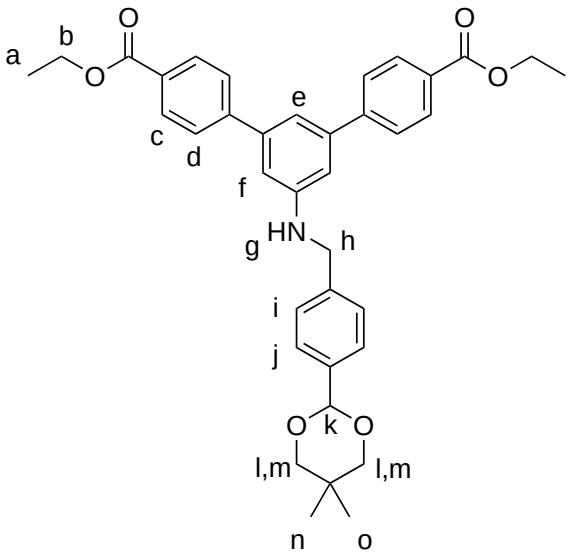

Figure S6. Diethyl 5'-((4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)amino)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (**2b**).

To a solution of **2a** (1.10 g, 2.8 mmol) and 4-(5,5-dimethyl-1,3-dioxan-2-yl)- benzaldehyde (0.62 g, 2.8 mmol) in dichloroethane (25 mL), under N_2, was added sodium triacetoxyborohydride (0.90 g, 4.2 mmol). The solution was stirred overnight and quenched with saturated sodium bicarbonate solution. The organic phase was isolated and washed with water (2 x 50 mL) and brine (10 mL), dried over anhydrous $MgSO_4$, and the solvent removed under reduced pressure. The crude product was used for the next reaction without further purification. MP: 144-148 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 8.09 (d, 4H, *J* = 8.2 Hz, c), 7.62 (d, 4H *J* = 7.7 Hz, d), 7.51 (d, 2H, *J* = 8.1 Hz, j), 7.42 (d, 2H, *J* = 8.1 Hz, i), 7.20 (s, 1H, e), 6.90 (s, 2H, f), 5.39 (s, 1H, g), 4.45 (s, 2H, h), 4.40 (q, 6H, *J* = 7.1 Hz, b), 3.77 (d, 2H, *J* = 10.9 Hz, l,m), 3.65 (d, 2H, *J* = 10.9 Hz, l,m), 1.41 (t, 6H, *J* = 7.1 Hz, a), 1.29 (s, 3H, n), 0.80 (s, 3H, o). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) = 166.6, 145.8, 142.0, 139.3, 138.1, 130.1, 129.5, 127.7, 127.2, 126.7, 116.7, 112.1, 101.6, 77.8, 61.1, 48.6, 30.3, 23.1, 22.0, 14.5. HR-MS (ESI+): Calculated for $[M\text{-}H]^+$ $[C_{37}H_{40}NO_6]^+$ *m/z* = 594.2856; found *m/z* = 594.2866.

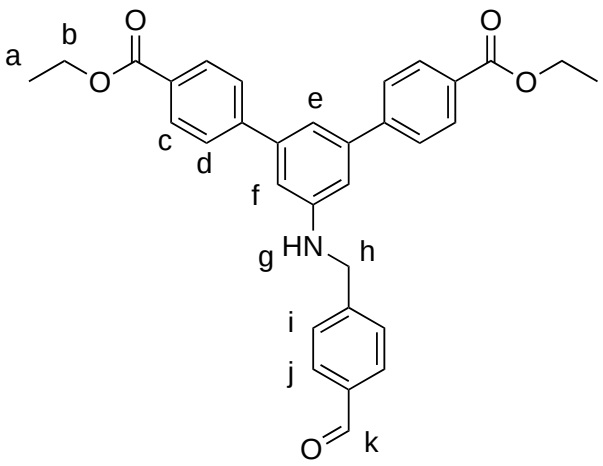

Figure S7. Diethyl 5'-((4-formylbenzyl)amino)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (**Aldehyde 2**).

2b (1.1 g, 1,8 mmol) was dissolved in THF (60 mL) and HCl (5 mL conc. HCl in 30 mL water) was added. The reaction mixture was refluxed overnight. After cooling to room temperature, sodium bicarbonate was added until no further CO_2 evolution was observed. The organic solvent was removed under reduced pressure and the aqueous residue extracted with ethyl acetate. After drying over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the resulting solid was washed with methanol to yield a pale yellow solid (770 mg, 82%). MP: 144-147 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 10.00 (s, 1H, k), 8.08 (d, 4H, *J* = 8.2 Hz, c), 7.88 (d, 2H, *J* = 8.0 Hz, j), 7.60 (m, 6H, d,i), 7.22 (s, 1H, e), 6.88 (s, 2H, f), 4.57 (s, 2H, h), 4.39 (q, 4H, *J* = 7.1 Hz, b), 1.41 (t, 6H, *J* = 7.1 Hz, a). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) = 191.9, 166.5, 148.6, 146.5, 145.7, 142.0, 135.7, 130.3, 130.1, 129.5, 127.8, 127.1, 116.4, 111.5, 61.1, 48.0, 14.4. HR-MS (ESI+): Calculated for $[M-H]^+$ $[C_{32}H_{30}NO_5]^+$ *m/z* = 508.2124; found *m/z* = 508.2131.

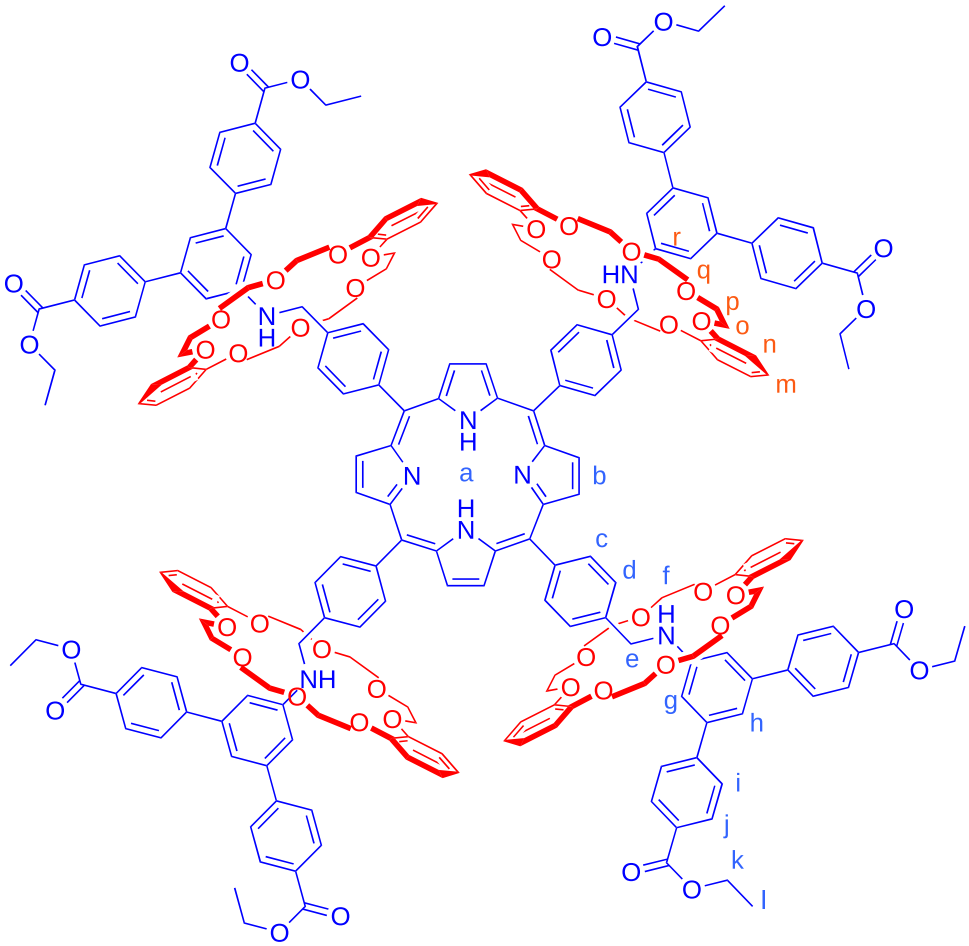

Figure S8. [5]Rotaxane **R2**.

To a solution of aldehyde **2** (250 mg, 0.5 mmol) in dry, degassed dichloromethane (50 mL) was added tetrafluoroboric acid diethyl ether complex (67 µL, 0.5 mmol). After stirring for 30 min at room temperature, dibenzo-24-crown-8 ether (442 mg, 1.0 mmol) was added and the solution stirred for additional 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (34.0 µL, 0.5 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (15 µL) was added. After 3 h of stirring at room temperature, DDQ (85 mg, 0.38 mmol) was added and the reaction mixture stirred for a further 2 h. After removal of the solvent under reduced pressure, the crude mixture was purified via column chromatography (Al_2O_3, dichloromethane/methanol 100:2.5 *v/v*). The fluorescent red band was collected and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO_2, dichloromethane/methanol 100:2.5 *v/v*, R_f = 0.32), neutralized with triethylamine, washed several times with hot acetonitrile, and recrystallized

from toluene to give bright red crystals. Yield: 150 mg, 30%. MP: 210 °C (decomp). ^{1}H NMR for (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 8.73 (s, 8H, b), 7.99-7.96 (m, 32H, c,d,j), 7.70 (d, *J* = 8.4 Hz, 16H, i), 7.48 (s, 8H, g), 7.14 (s, 4H, h), 7.70 (s, 4H), 6.90 (m, 32H, m,n), 6.17 (t, *J* = 3.8 Hz, 4H, f), 5.32 (d, *J* = 3.8 Hz, 8H, e) 4.41 (q, *J* = 7.1 Hz, 16H, k), 4.23 (m, 32H, o), 3.85 (m, 32H, p), 3.51 (m, 32H, q,r), 1.43 (t, *J* = 7.1 Hz, 24H, l), -2.83 (s, 2H, a). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ (ppm) = 166.0, 151.6, 148.9, 146.9, 141.4, 140.6, 140.0, 134.5, 130.0, 129.2, 127.5, 127.2, 121.2, 112.7, 112.3, 71.0, 70.2, 68.7, 61.2, 47.3, 14.6. HR-MS (ESI+): Calculated for $[M\text{-}H_4]^{4+}$ $[C_{240}H_{254}N_8O_{48}]^{4+}$ *m/z* = 1004.4437; found *m/z* = 1004.4454. IR (cm^{-1}): 3385.8, 3308.7, 3061.4, 2959.5, 2922.0, 2869.8, 1708.5, 1594.2, 1502.3, 1451.4, 1397.3, 1366.0, 1252.5, 1213.8, 1181.2, 1099.4, 1050.6, 1017.7, 948.8, 930.4, 851.7, 800.6, 770.6, 738.2, 702.9, 599.4, 497.7. UV-Vis (CH_2Cl_2, λ_{nm}) = 419 (Soret), 517, 552, 591, 647.

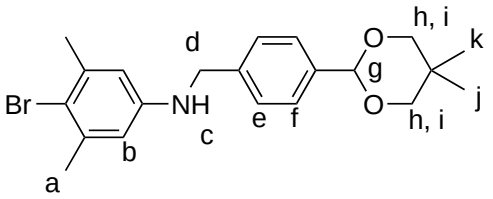

Figure S9. 4-Bromo-N-(4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)-3,5-dimethylaniline (**3a**).

4-Bromo-3,5-dimethylaniline (400 mg, 2.0 mmol) and 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (463 mg, 2.1 mmol) were dissolved in chloroform and anhydrous $MgSO_4$ was added to make a slurry. After stirring at RT for 48 h, the reaction mixture was filtered, and the solvent removed under reduced pressure. The resultant solid was then dissolved in THF:ethanol (1:1, 40 mL), sodium borohydride (227 mg, 6.0 mmol) was added portion-wise and the reaction mixture was stirred overnight at room temperature. After removal of the solvents under reduced pressure, the crude mixture was dissolved in ethyl acetate and washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure to yield a yellow oil. Yield: 710 mg, 88 %. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.55 (d, 2H, *J* = 8.0 Hz, f), 7.36 (d, 2H, *J* = 8.0 Hz, e), 6.37 (s, 2H, b), 5.43 (s, 1H, c), 4.27, (s, 2H, d), 3.82 (d, 2H, *J* = 10.9 Hz, h,i), 3.69 (d, 2H, *J* = 10.9 Hz, h,i), 2.36 (s, 6H, a), 1.36 (s, 3H, j), 0.85 (s, 3H, k). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) = 146.7, 140.0, 138.5, 137.5, 127.1,

126.5, 114.7, 112.8, 101.5, 77.6, 47.8, 30.1, 24.0, 23.0, 21.8. HR-MS (ESI+): Calculated for $[M-H]^+$ $[C_{21}H_{27}BrNO_2]^+$ *m/z* = 404.1223; found *m/z* = 404.1225.

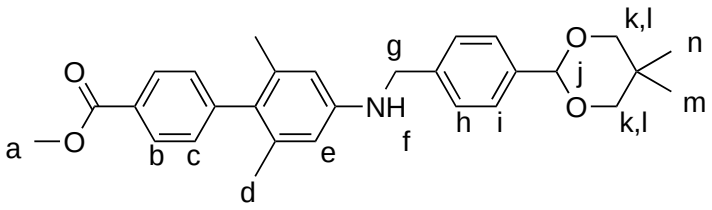

Figure S10. Methyl 4'-((4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)amino)-2',6'-dimethyl-[1,1'-biphenyl]-4-carboxylate (**3b**).

To a solution of **3a** (717 mg, 1.8 mmol) in degassed DMF (10 mL), cesium carbonate (722 mg, 2.2 mmol), 4-(methoxycarbonyl)phenylboronic acid (399 mg, 2.2 mmol), and tetrakis(triphenylphosphine) palladium (205 mg, 0.2 mmol) were added. The reaction mixture was heated at 110 °C for 48 h. After cooling the mixture, the mixture was partitioned between water (100 mL) and ethyl acetate (100 mL). The organic phase was then washed with more water and brine and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography (SiO_2, hexanes/ethyl acetate 10:1 *v/v*, R_f = 0.32) to yield a white powder (490 mg, 60 %). MP: 101-104 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 8.07 (d, 2H, *J* = 8.3 Hz, b), 7.51 (d, 2H, *J* = 8.1 Hz, i), 7.41 (d, 2H, *J* = 8.1 Hz, c), 7.23, (d, 2H, 8.3 Hz, h), 6.39 (s, 2H, e), 5.41 (s, 1H, j), 4.35 (s, 2H, g), 3.94 (s, 3H, a), 3.79 (d, 2H, *J* = 10.7 Hz, k,l), 3.67 (d, 2H, *J* = 10.7 Hz, k,l), 1.94 (s, 6H, d), 1.31 (s, 3H, m), 0.81 (s, 3H, n). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) = 167.4, 147.4, 146.8, 140.4, 137.7, 136.8, 130.7, 130.3, 129.7, 128.2, 127.5, 126.6, 111.9,101.7, 77.8, 52.2, 48.2, 30.4, 23.2, 22.0, 21.2. HR-MS (ESI+): Calculated for $[M-H]^+$ $[C_{29}H_{34}NO_4]^+$ *m/z* = 460.2483; found *m/z* = 460.2488.

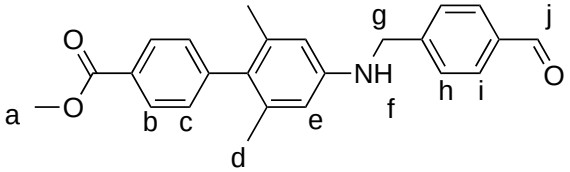

Figure S11. Methyl 4'-((4-formylbenzyl)amino)-2',6'- dimethyl-[1,1'-biphenyl]-4-carboxylate (**Aldehyde 3)**.

3b (850 mg, 1.7 mmol) was dissolved in THF and HCl (3 mL in 10 mL of water) was added. After refluxing the reaction mixture for 12 h, sodium bicarbonate was added until no CO_2 evolution was observed. The organic solvent was removed under reduced pressure and ethyl acetate was added to the aqueous phase. The organic phase was washed with water and brine, dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was washed with cold methanol to yield an off-white solid (572 mg, 57%). MP: 250 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 10.01 (s, 1H, j), 8.07 (d, *J* = 8.5 Hz, 2H, b), 7.87 (d, *J* = 8.3 Hz, 2H, i), 7.57 (d, *J* = 8.1 Hz, 2H, h), 7.21 (d, *J* = 8.5 Hz, 2H, c), 6.40 (s, 2H, e), 4.46 (s, 2H, g), 3.93 (s, 3H, a), 1.93 (s, 6H, d). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) = 192.2, 167.2, 147.2, 147.0, 146.6, 136.9, 135.6, 131.9, 130.3, 130.2, 129.7, 128.3, 127.8, 115.4, 112.0, 52.3, 48.1, 21.1. HR-MS (ESI+): Calculated for $[M-H]^+$ $[C_{24}H_{24}NO_3]^+$ *m/z* = 374.1755; found *m/z* = 374.1756.

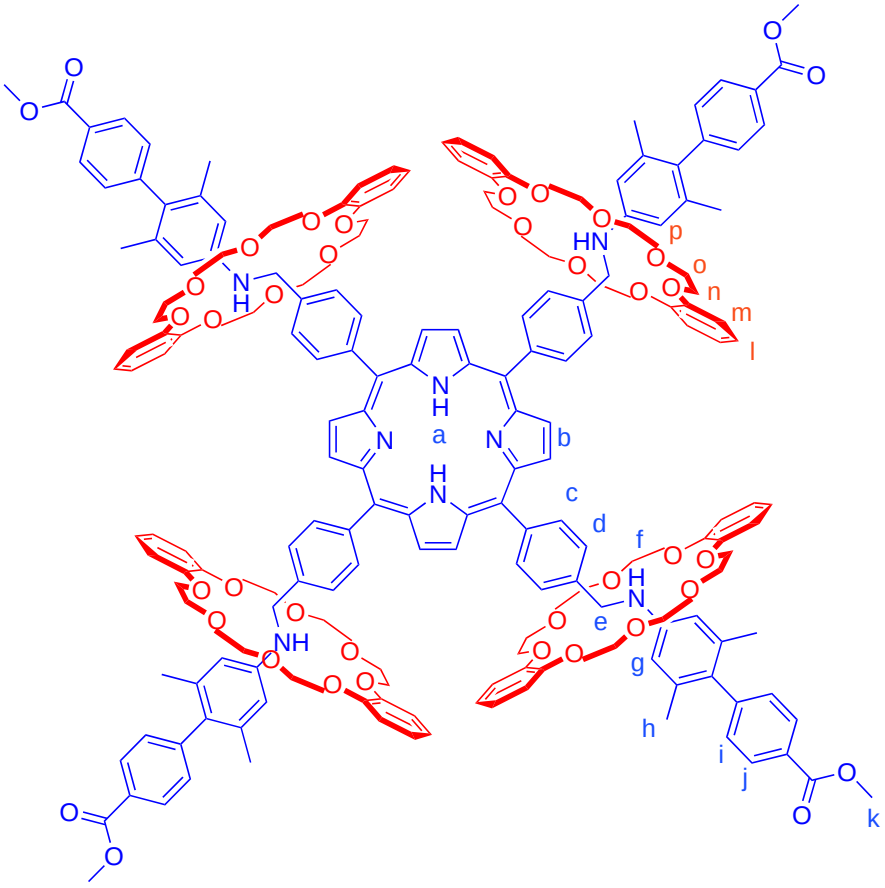

Figure S12. [5]Rotaxane **R3**.

To a solution of **3c** (230 mg, 0.6 mmol) in dry, degassed dichloromethane (65 mL) was added tetrafluoroboric acid diethyl ether complex (84 µL, 0.6 mmol). After stirring for 30 min at room temperature, dibenzo-24-crown-8 ether (1.105 g, 2.5 mmol) was added and the solution stirred for an additional 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (42.7 µL, 0.6 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (15 µL) was added. After 4 h of stirring at room temperature, DDQ (105 mg) was added and the reaction mixture stirred for a further 2 h. The solvent removed under reduced pressure and the crude mixture was then purified via column chromatography (Al_2O_3, dichloromethane/ methanol 100:2 *v/v*). The fluorescent red band was collected, and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO_2, dichloromethane/methanol 100:3 *v/v*, R_f = 0.44). After removal of the solvent under reduced pressure, the product was neutralised with triethylamine, washed several times with hot acetonitrile, and recrystallized from toluene to give bright red crystals. Yield: 180 mg, 33%. MP: 221 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 8.73 (s, 8H, b), 8.10 (d, *J* = 8.0 Hz, 8H, c), 8.07 (m, 16H, I,j), 7.97 (d, *J* = 8.0 Hz, d), 7.28 (s, 8H, g), 6.88 (m, 32H, l,m), 5.82 (t, *J* = 4.4 Hz, 4H, f), 5.19 (d, *J* = 4.4 Hz, 8H, e), 4.30 (b, 32H, n), 4.09-3.84 (m, 44H, k,o), 3.61 (b, 32H, p), 1.84 (s, 24H, h), -2.82 (s, 2H, a). ^{13}C NMR (75 MHz, CDCl3, 298 K) δ (ppm) = 167.6, 149.3, 148.5, 148.2, 141.0, 139.6, 135.1, 134.1, 130.9, 129.3, 127.9, 127.6, 127.3, 120.8, 112.9, 111/9, 70.4, 69.8, 68.3, 52.1, 47.0, 21.1. HR-MS (ESI+): Calculated for $[M\text{-}H_4]^{4+}$ $[C_{208}H_{230}N_8O_{40}]^{4+}$ *m/z* =870.4064; found *m/z* = 870.4085. IR (cm^{-1}): 3512.6, 3126.2, 3053.8, 2918.5, 2877.2, 1715.1, 1609.0, 1592.2, 1566.6, 1503.6, 1453.4, 1436.7, 1415.0, 1352.9, 1285.2, 1248.7, 1208.0, 1093.5, 1049.6, 1004.8, 985.8, 947.3, 915.1, 858.9, 822.4, 776.8, 742.0 712.1, 598.9, 580.2, 518.5. UV-Vis (CH_2Cl_2, λ_{nm}) = 423 (Soret), 518, 555, 592, 650, 734.

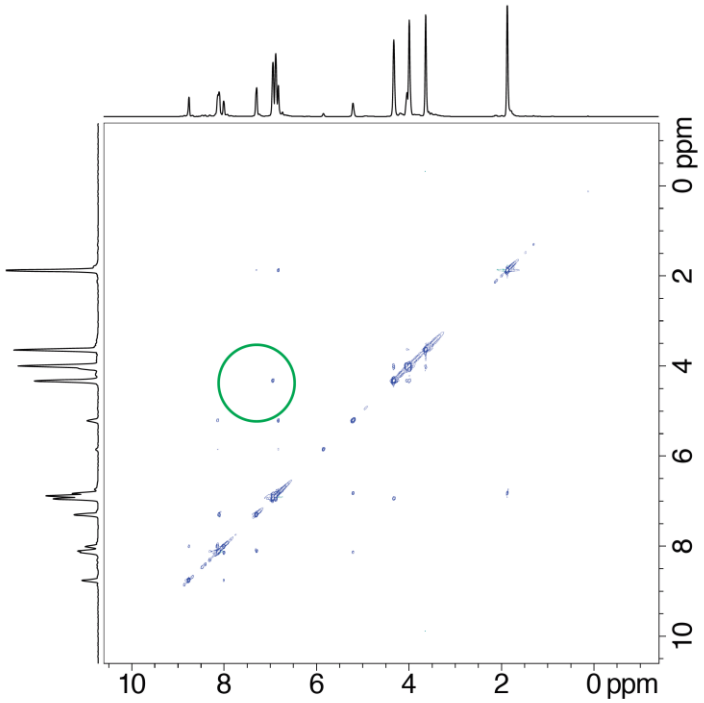

Figure S13. ^{1}H-^{1}H NOESY spectra (500 MHz, $CDCl_3$, 298 K, mixing time 400 ms) of neutral **R3**.

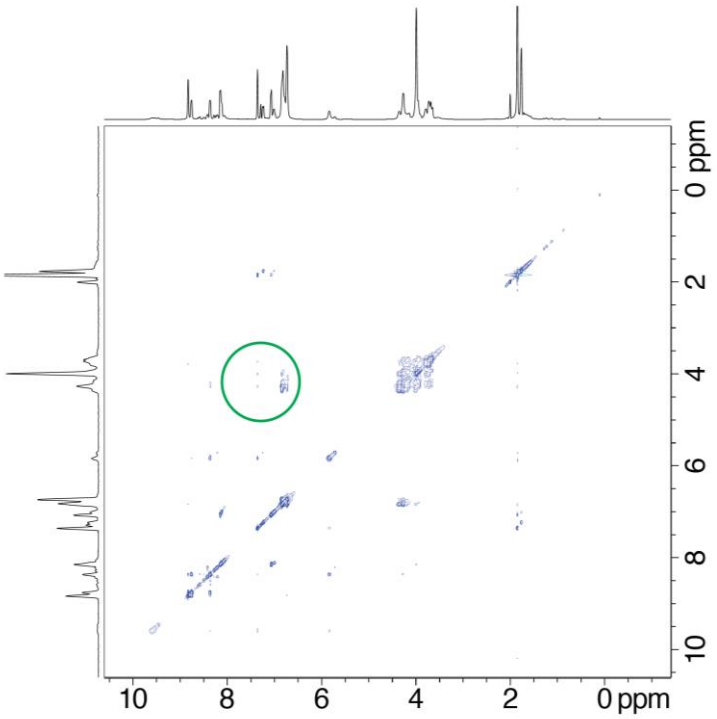

Figure S14. ^{1}H-^{1}H NOESY spectra (500 MHz, $CDCl_3$, 298 K, mixing time 400 ms) of protonated [**R3** H_6]$^{6+}$.

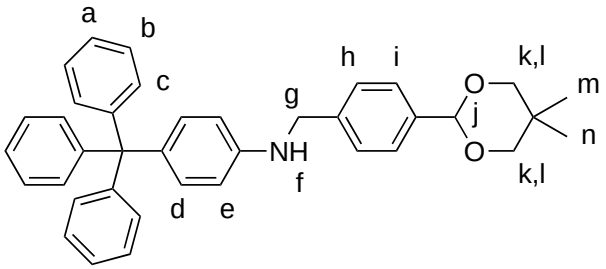

Figure S15. N-(4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)-4-tritylaniline (**4a**).

4-Tritylaniline (335 mg, 1.0 mmol) and 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (220 mg, 1.0 mmol) were dissolved in chloroform and anhydrous $MgSO_4$ was added to make a slurry. After stirring at RT for 48 h, the reaction mixture was filtered, and the solvent removed under reduced pressure. The resultant solid was then dissolved in THF:ethanol (1:1, 40 mL), sodium borohydride (114 mg, 3.0 mmol) was added portion-wise and the reaction mixture was stirred at room temperature for 48 h. After removal of the solvents under reduced pressure, the crude mixture was dissolved in ethyl acetate, washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure to yield a beige fluffy powder (400 mg, 74 %). MP: 160-164 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ (ppm) = 7.50 (d, 2H, *J* = 8.1 Hz, i), 7.40 (d, 2H, *J* = 8.1 Hz, h), 7.32-7.18 (m, 15H, a-c), 7.03 (d, 2H, *J* = 8.8 Hz, e), 6.54 (d, 2H, *J* = 8.8 Hz, d), 4.32 (s, 2H, g), 4.17 (s, 1H, f), 3.78 (d, 2H, *J* = 11.1 Hz, j,k), 3.68 (d, 2H, *J* = 10.5 Hz, j,k), 1.30 (s, 3H, m), 0.82 (s, 3H, n). ^{13}C NMR (125 MHz, CDCl3, 298 K) δ (ppm) = 147.8, 146.5, 140.7, 138.3, 136.1, 132.2, 131.3, 127.8, 127.6, 126.8, 126.0, 112.1, 101.8, 77.9, 64.6, 48.4, 30.4, 23.2, 22.0. HR-MS (ESI+): Calculated for $[M-H]^+$ $[C_{38}H_{38}NO_2]^+$ *m/z* = 540.2903; found *m/z* = 540.2905.

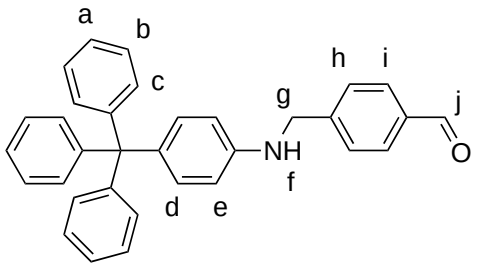

Figure S16. 4-(((4-Tritylphenyl)amino)methyl)benzaldehyde (**4b**).

4a (400 mg, 0.7 mmol) was dissolved in THF and HCl (3 mL in 10 mL of water) was added. After refluxing the reaction mixture for 12 h, $NaHCO_3$ was added until no CO_2 evolution was observed. The organic solvent was removed under reduced pressure and ethyl acetate was added to the aqueous phase. The organic phase was washed with water and brine, dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was washed with cold methanol to yield an off-white solid (310 mg, 92%). MP: 196-198 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ (ppm) = 9.99 (s, 1H, j), 7.86 (d, *J* = 8.2 Hz, 2H, i), 7.57 (d, *J* = 8.0 Hz, 2H, h), 7.25-7.17 (m, 15H, a-c), 7.00 (d, *J* = 8.8 Hz, 2H, e), 6.50 (d, *J* = 8.8 Hz, 2H, d), 4.43 (s, 2H, g), 3.44 (s, 1H, f). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ (ppm) = 192.1, 147.8, 147.5, 146.1, 136.5, 132.2, 131.3, 130.3, 128.1, 127.8, 127.3, 126.1, 112.2, 48.4. HR-MS (ESI+): Calculated for $[M-H]^+$ $[C_{33}H_{28}NO]^+$ *m/z* = 454.2171; found *m/z* = 454.2161.

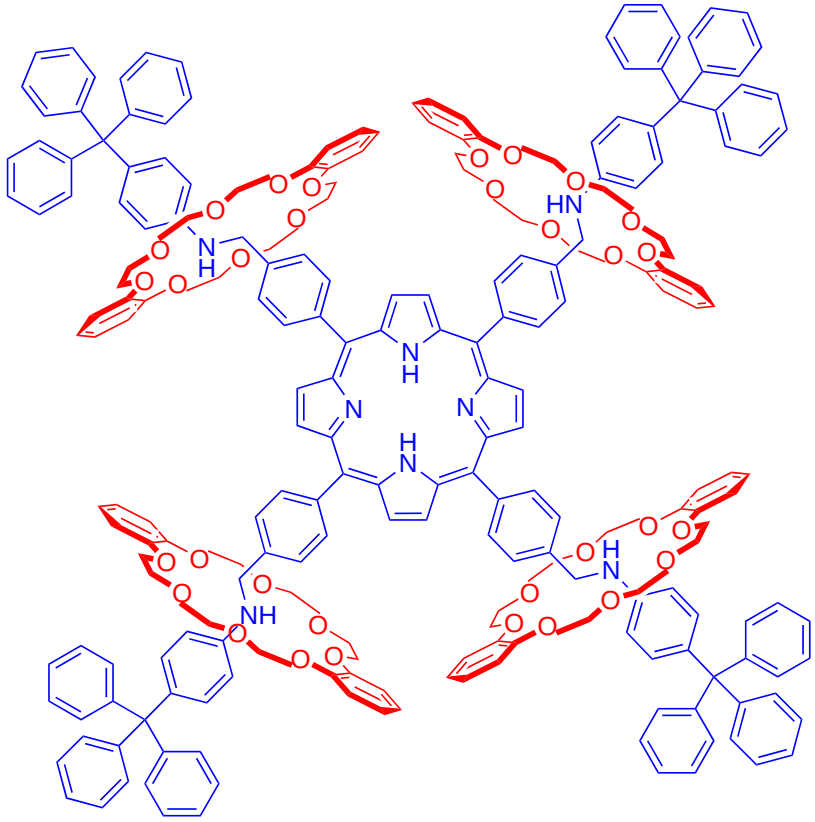

Figure S17. [5]Rotaxane **R4**.

To a solution of **4b** (453 mg, 1.0 mmol) in dry, degassed dichloromethane (100 mL) was added tetrafluoroboric acid diethyl ether complex (161.0 µL, 1.0 mmol). After stirring for 30 min at room temperature, dibenzo-24-crown-8 ether (897 mg, 2.0 mmol) was added and the solution

stirred for an additional 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (69.4 µL, 1.0 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (40 µL) was added. After 3 h of stirring at room temperature, DDQ (170 mg, 0.8 mmol) was added and the reaction mixture stirred for a further 2 h. The solvent removed under reduced pressure and the crude mixture was then purified via column chromatography (Al_2O_3, dichloromethane/methanol 100:5 *v/v*). The fluorescent red band was collected and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO_2, dichloromethane/methanol 100:5 *v/v*, R_f = 0.74). The crude product was then neutralised with triethylamine, washed several times with hot acetonitrile, and recrystallized from toluene to give bright red crystals. Yield: 155 mg, 16%. MP: 255 °C (decomp). The acquisition of ^{1}H NMR spectrum where individual peaks could be resolved was not possible due to aggregation of the sample. Spectra roughly matching the total number of protons on this molecule were collected in different solvents and at different temperatures without significant improvement of the resolution. The acquisition of a ^{13}C NMR spectrum with reasonable S/N from which individual carbon assignments could be made was not possible due to the limited solubility and aggregation phenomena of this material in common organic solvents. HR-MS (ESI+): Calculated for $[M\text{-}H_4]^{4+}$ $[C_{244}H_{246}N_8O_{32}]^{4+}$ *m/z* = 950.4484; found *m/z* = 950.4498. IR (cm^{-1}): 3636.6, 3562.6, 3058.4, 3032.9, 2924.3, 2877.6, 1593.8, 1503.6, 1450.2, 1353.9, 1323.8, 1288.4, 1249.9, 1209.0, 1051.6, 948.0, 851.6, 746.3, 702.2, 629.2, 599.7, 550.3, 520.4, 498.8. UV-Vis (CH_2Cl_2, λ_{nm}) = 423 (Soret), 443 (Soret), 519, 552, 652, 732.

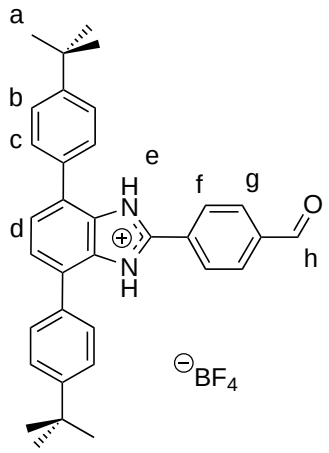

Figure S18. 4-(4,7-Bis(4-(tert-butyl)phenyl)-1H-benzo[d]imidazol-2-yl)benzaldehyde (**5a**).

1,2-Diamino-3,6-di(4'-*t*-butylphenyl)-benzene (350 mg, 0.1 mmol) and terephthalaldehyde (626 mg, 0.5 mmol) were dissolved in acetonitrile/chloroform (125 mL/25 mL) and $ZrCl_4$ (22 mg, 0.01 mmol) was added. The mixture was stirred at room temperature for 24 h and filtered. The solvents were removed under reduced pressure and the crude product was dissolved in ether. HCl⍰Et_2O (0.250 mL, 2 M) was added and the precipitate was filtered. After an anion exchange reaction with HBF_4, the product was isolated as a yellow powder. Yield: 300 mg, 62%. MP: 196-200 °C. ^{1}H NMR (500 MHz, CD_3CN, 298 K) δ (ppm) = 10.05 (s, 1H), 8.35 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 4H), 7.59 (d, *J* = 8.4 Hz, 4H), 7.45 (s, 2H), 1.40 (s, 18H) matching the reported literature values.[S1] HR-MS (ESI+): Calculated for $[M-H]^+$ $[C_{34}H_{35}N_2O]^+$ *m/z* = 487.2744; found *m/z* = 487.2745.

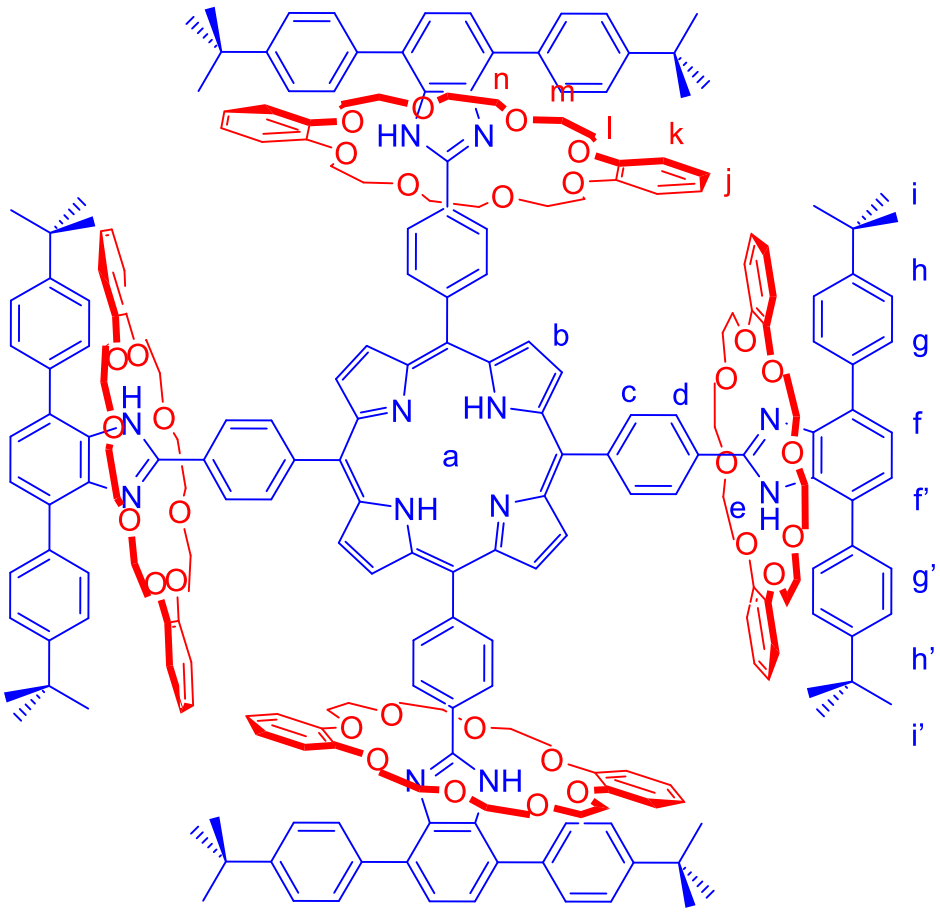

Figure S19. [5]Rotaxane **R5**.

To a solution of [**5a**][HBF_4] (150 mg, 0.3 mmol) in dry, degassed dichloromethane (30 mL) was added dibenzo-24-crown-8 ether (184 mg, 0.4 mmol) and the solution stirred for 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (19.0 µL, 0.3 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (15 µL) was added. After 4 h of stirring at room temperature, DDQ (45 mg, 0.2 mmol) was added and the reaction mixture stirred for a further 2 h. The solvent removed under reduced pressure and the crude mixture was then purified via column chromatography (Al_2O_3, dichloromethane/methanol 100:3 *v/v*). The fluorescent red band was collected, and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO_2, dichloromethane/methanol 95:3 *v/v*, R_f = 0.24). The crude product was then neutralised with triethylamine, washed several times with hot acetonitrile, and recrystallized from toluene to give bright red crystals. Yield: 45 mg, 18%. MP: 245 °C (decomp). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ (ppm) = 11.90 (s, 4H, e), 9.61 (d, *J* = 8.1 Hz, 8H, d), 9.04 (s, 8H, b), 8.48 (d, *J* = 8.5 Hz , 8H, c), 8.24 (d, *J* = 8.3 Hz , 8H), 7.62 (d, *J* = 7.9 Hz , 4H,f), 7.54 (d, *J* = 8.3 Hz , 8H, h'), 7.29-7.26 (m, 12H, f', g'), 7.19 (d, *J* = 8.4 Hz , 8H, h), 6.75 (s, 32H, j, k), 4.10-3.99 (m, 32H, l), 3.76-3.70 (m, 32H, m), 3.27-3.25 (m, 16H, n), 3.03-3.01 (m, 16H, n), 1.26-1.26 (m, 72H, i, i'), -2.88 (s, 2H, a). ^{13}C DEPTQ135 NMR (125 MHz, CD_2Cl_2, 298 K) δ (ppm) = 154.1 (n), 150.3 (n), 150.2 (n), 148.7 (n), 143.1 (n), 142.8 (n), 136.5 (n), 136.1 (n), 135.0 (p), 133.8 (n), 130.5 (n), 130.3 (p), 130.2 (n), 129.5 (p), 128.5 (p), 125.8 (p), 125.5 (n), 125.4 (p), 123.6 (p), 121.0 (p), 120.9 (p), 112.0 (p), 69.8 (n), 69.4 (n), 68.6 (n), 34.7 (n), 31.5 (p), 31.5 (p). HR-MS (ESI+): Calculated for $[M\text{-}H_4]^{4+}$ $[C_{248}H_{274}N_{12}O_{32}]^{4+}$ *m/z* = 983.5057; found *m/z* = 983.5062. IR (cm^{-1}): 3539.9, 3240.7, 3101.5, 2948.9, 2903.5, 2871.1, 1636.3, 1615.5, 1580.0, 1502.5, 1454.8, 1391.5, 1364.4, 1353.0, 1318.9, 1286.7, 1246,3, 1208.5, 1122.3, 1097.4, 1051.2, 948.9, 821.4, 776.7, 740.7, 670.2, 599.7, 562.4, 518.. UV-Vis (CH_2Cl_2, λ_{nm}) = 230-320, 436 (Soret), 518, 560, 598, 650, 695.

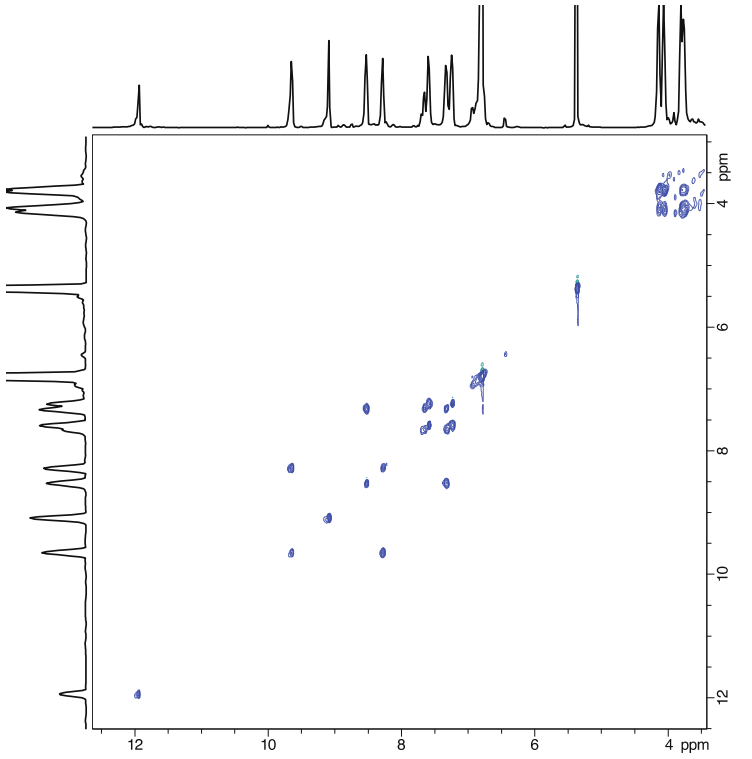

Figure S20. Partial ^{1}H-^{1}H COSY NMR spectrum of **R5**.

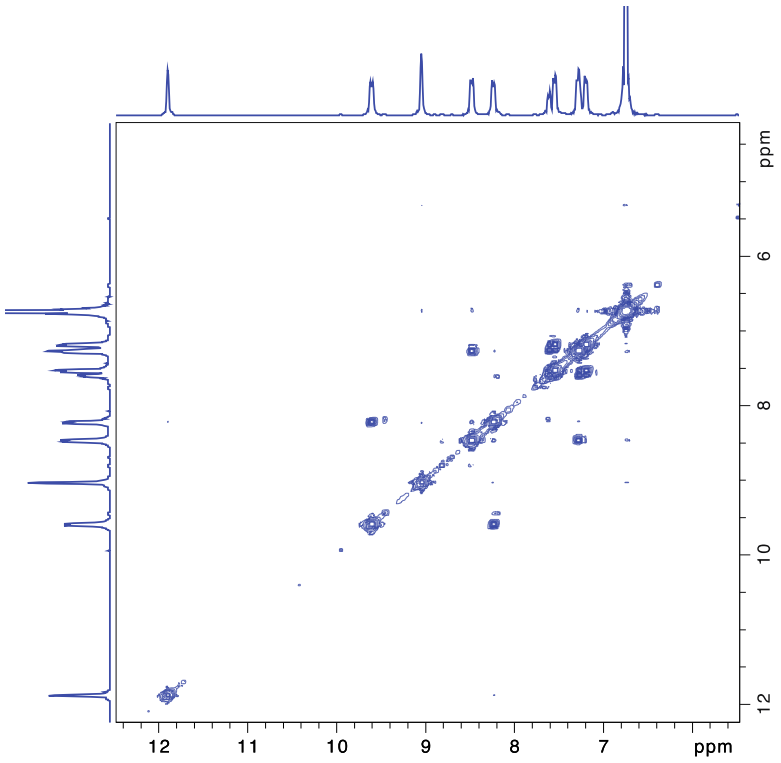

Figure S21. Partial ^{1}H-^{1}H TOCSY NMR spectrum of **R5**.

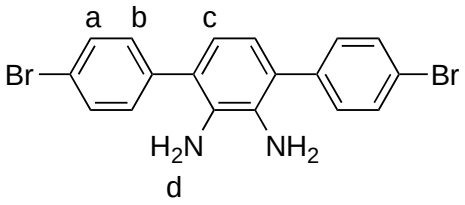

Figure S22. 1,2-Diamino-3,6-bis(4-bromophenyl)benzene (**6a**).

To a solution of 4,7-bis(4-bromophenyl)-2,1,3-benzotiadiazole (1.70 g, 3.8 mmol) in THF/Ethanol (1:3, 120 mL) was added sodium borohydride (500 mg, 13.2 mmol) and cobalt(II) chloride (50 mg, 0.2 mmol). The reaction mixture was heated to reflux for 5 h, filtered while hot, and the solvents removed under reduced pressure. The crude product was dissolved in dichloromethane (100 mL) and washed with water (2 x 100 mL) and brine (50 mL), dried over anhydrous $MgSO_4$, and the solvent removed under reduced pressure to give a white solid. Yield: 1.45 g, 95%. MP: 200 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.60 (d, *J* = 8.5 Hz, 4H, a), 7.36 (d, *J* = 8.5 Hz, 4H, b), 6.73 (s, 2H, c), 3.57 (bs, 4H, d) matching the reported literature values.[S6]

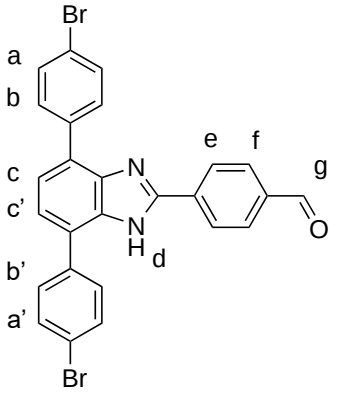

Figure S23. 4-(4,7-Bis(4-bromophenyl)-1H-benzo[d]imidazol-2-yl)benzaldehyde (**6b**).

To a solution of 1,2-diamino-3,6-bis(4-bromophenyl)benzene (1.45 g, 3.5 mmol) in chloroform (100 mL) was added terephthaldehyde (2.50 g, 18.5 mmol) and zirconium tetrachloride (90 mg, 0.4 mmol). The reaction mixture was stirred at RT for 48 h and filtered. After removal of the solvent under reduced pressure, the crude product was washed with chloroform to give a pale-yellow powder. 1.59 g, 86%. MP: 175 °C (decomp). ^{1}H NMR (500 MHz, DMSO-*d*$_6$, 298 K) δ (ppm): 12.94 (bs, 1H, d), 10.08 (s, 1H, g), 8.53 (d, *J* = 8.1 Hz, 2H, f), 8.28-7.86 (b, 4H, b,b'), 8.05

(d, *J* = 8.1 Hz, 2H, e), 7.73 (d, *J* = 8.3 Hz, 4H, a,a'), 7.43 (bs, 2H, c,c'). ^{13}C NMR (125 MHz, DMSO-d_6, 298 K) δ (ppm): 193.11, 152.1, 151.4, 141.9, 139.7, 137.0, 135.7, 135.0, 132.9, 132.3, 131.8, 131.6, 131.4, 131.3, 131.1, 131.1, 130.9, 130.8, 129.9, 129.5, 129.0, 128.6, 128.4, 127.9, 127.4, 124.8, 123.8, 121.8, 121.5, 121.1, 120.8. HR-MS (ESI+): Calculated for $[M]^+$ $[C_{26}H_{17}Br_2N_2O]^+$ *m/z* = 532.9682; found *m/z* = 532.9689.

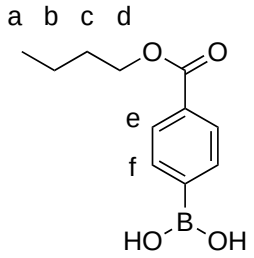

Figure S24. n-Butyl ester 4-carboxyphenyl boronic acid.

4-Carboxyphenyl boronic acid (3.0 g, 18 mmol) was suspended in n-butanol (20 mL) and concentrated hydrochloric acid (0.5 mL) added to the mixture and refluxed for 5 h. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was dissolved in ethyl acetate (100 mL) and washed with water (3 x 50 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure to give a white powder 3.98 g, Quantitative yield. MP: 86-89 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) δ (ppm): 8.01 (d, *J* = 7.9 Hz, 2H, f), 7.97 (d, *J* = 8.1 Hz, 2H, e), 7.91* (s, 4H), 4.27 (q, *J* = 6.4 Hz, 2H, d), 1.73-1.65* (m, 2H, c), 1.47-1.38* (m, 2H, b), 0.97-0.90* (m, 3H, a). *The integration was done considering the monomer and trimer species. ^{13}C DEPTQ135 NMR (125 MHz, DMSO-d_6, 298 K) δ (ppm): 166.0 (n), 165.9 (n), 134.2 (p), 133.6 (p), 131.0 (n), 130.7 (n), 128.1 (p), 127.9 (p), 64.3 (n), 64.3 (n), 30.3 (n), 18.7 (n), 13.6 (p). The carbon atom attached to the boron could not be observed due to quadrupolar relaxation effects. HR-MS (ESI−): Calculated for $[M]^-$ $[C_{11}H_{14}BO_4]^-$ *m/z* = 221.0991; found *m/z* = 221.1021.

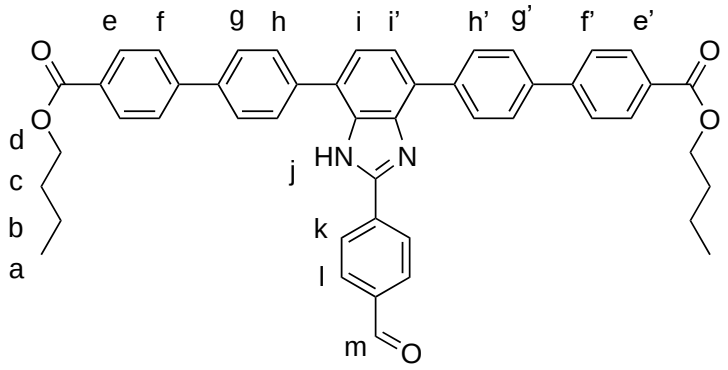

Figure S25. Dibutyl-4',4'''-(2-(4-formylphenyl)-1H-benzo[d]imidazole-4,7-diyl)bis([1,1'-biphenyl]-4-carboxylate) (**6c**)

To a solution of **6b** (1.40 g, 2.6 mmol) in degassed toluene (50 mL) was added butyl ester 4-carboxyphenyl boronic acid (1.46 g, 6.6 mmol, 2.5 eq), caesium carbonate (2.15 g, 6.6 mmol), and $Pd(PPh_3)_4$ (300 mg, 0.26 mmol) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the product was recrystallized twice from toluene to give a bright yellow powder. Yield: 800 mg, 58%. Mp: 154 °C (decomp). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) δ (ppm): 13.04 (bs, 1H, j), 10.09 (s, 1H, m), 8.58 (d, *J* = 8.3 Hz, 2H, l), 8.50-7.74 (b, 22H, e-i, e'-i', k), 4.32 (t, *J* = 6.4 Hz, 4H, d), 1.73 (q, *J* = 7.8 Hz, 4H, c), 1.47 (sextet, *J* = 7.5 Hz, 4H, b), 0.97 (t, *J* = 7.4 Hz, 6H, a). ^{13}C NMR (125 MHz, DMSO-d_6, 298 K) δ (ppm): 192.7, 165.6, 144.2, 129.9, 129.8, 129.4, 128.7, 127.9, 126.8, 126.4, 68.0, 64.4, 39.0, 30.3, 18.8, 13.6. Resonances for quaternary carbons could not be observed due to low receptivity. HR-MS (ESI+): Calculated for $[M]^+$ $[C_{11}H_{14}BO_4]^-$ *m/z* = 727.3166; found *m/z* = 727.3172.

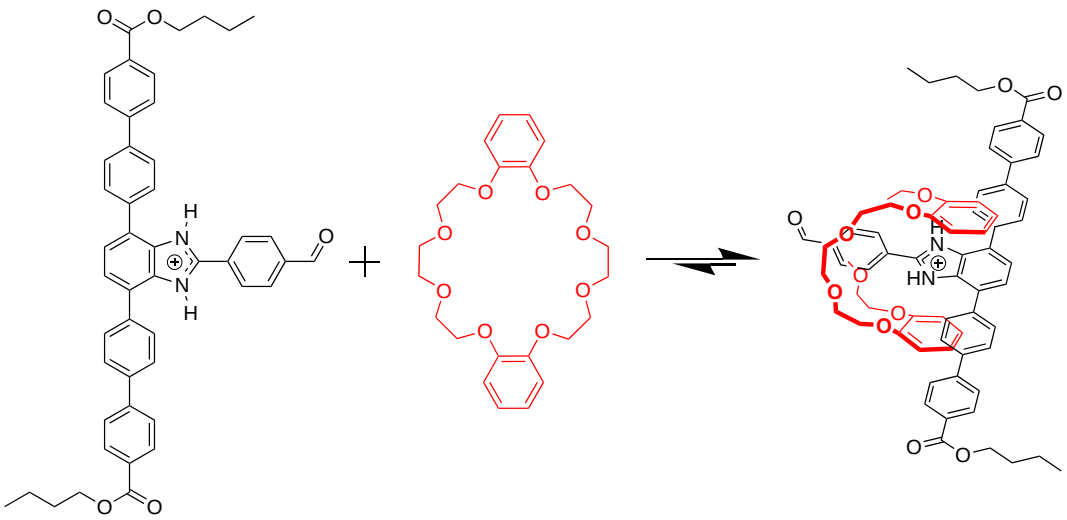

Figure S26. Pseudorotaxane equilibrium for [**6b**-H][BF_4] and **DB24C8**.

The low solubility of aldehyde 6 results in a poorly resolved ^{1}H NMR spectrum; however, when a pseudorotaxane is formed, it is possible to resolve all the proton environments. Figure S2 shows a comparison between the ^{1}H NMR spectra of the pure aldehyde and the pseudorotaxane.

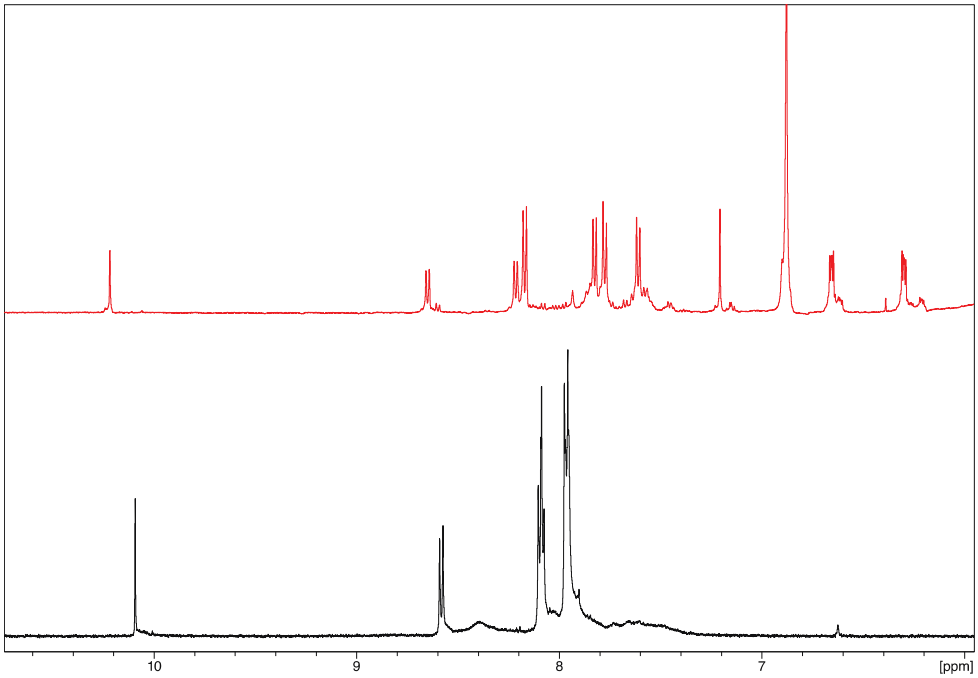

Figure S27. Partial ^{1}H NMR spectra for **6b** (bottom, DMSO-d_6) and pseudorotaxane with [**6b**-H][BF_4] and **DB24C8** (top, CD_2Cl_2).

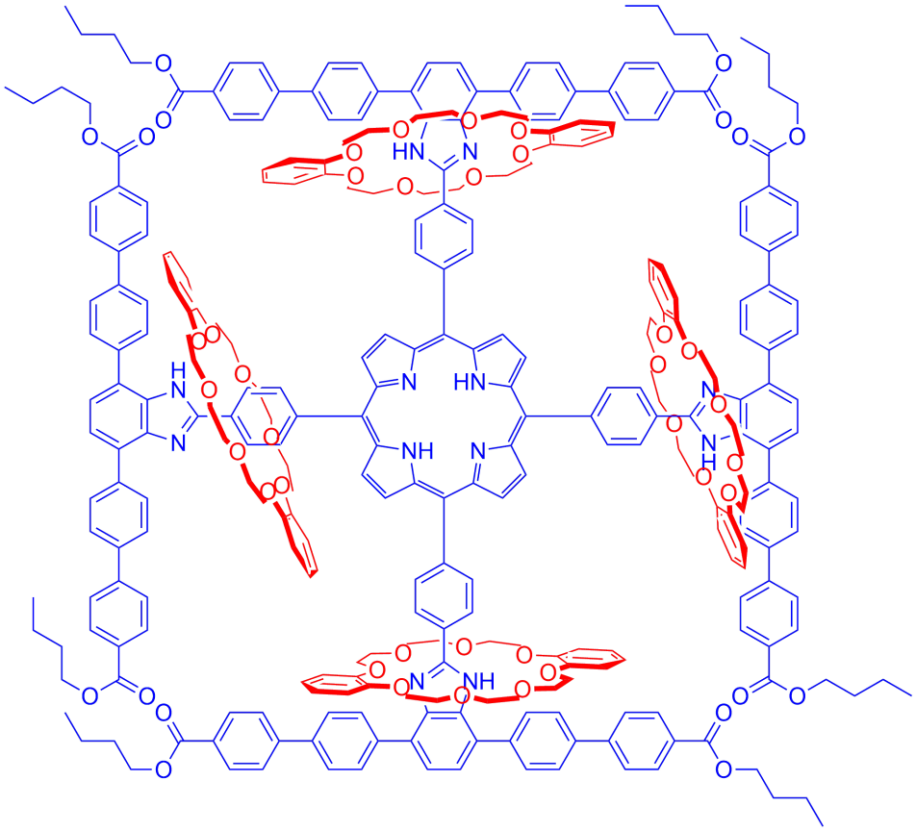

Figure S28. [5]Rotaxane **R6**.

To a solution of [**6b**-H][BF_4] (450 mg, 0.55 mmol) in dry, degassed dichloromethane (60 mL) was added dibenzo-24-crown-8 ether (279 mg, 0.60 mmol) and the solution stirred for 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (38.3 µL, 0.55 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (20 µL) was added. After 2.5 h of stirring at room temperature, DDQ (94 mg, 0.41 mmol) was added and the reaction mixture stirred for a further 2 h. The solvent removed under reduced pressure and the crude mixture was then purified via column chromatography (Al_2O_3, dichloromethane/methanol 100:2.5 *v/v*). The fluorescent red band was collected, and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO_2, dichloromethane/methanol 95:5 *v/v*, R_f = 0.63). After removal of the solvent under reduced pressure and recrystallization from acetonitrile-ethyl ether the product was isolated as a dark red solid. Yield: 295 mg, 39%. MP: 261 °C (decomp). ^{1}H NMR [**R6**-H_6][BF_4]$_6$ (500 MHz, CD_2Cl_2, 298 K) δ (ppm) =13.37 (s, 8H), 9.21 (d, *J* = 8.2 Hz, 8H), 9.17 (d, *J* = 8.2 Hz, 8H), 8.92 (s, 8H), 8.16(b, 16H), 7.88-7.70 (m, 48H), 7.30 (s, 8H), 6.66 (b, 16H), 6.42 (m,

16H), 4.33 (t, *J* = 6.6 Hz, 16H),4.05-3.07 (b, 96H), 1.77 (quintet, *J* = 6.7 Hz, 16H), 1.49 (sextet, *J* = 7.4 Hz, 16H), 1.00 (t, *J* = 7.3 Hz, 24H), -2.34 (s, 4H) . HR-MS (ESI+): Calculated for $[M - 4H]^{4+}$ $[C_{304}H_{304}N_{14}O_{48}]^{4+}$ *m/z* = 1223.7932; found *m/z* = 1223.7993. IR (cm^{-1}): 3498.2, 3199.0, 3066.5, 2926.8, 2871.3, 1708.2, 1633.5, 1553.0, 1501.9, 1468.1, 1452.2, 1383.4, 1352.4, 1273.5, 1247.5, 1205.5, 1098.2, 1047.6, 1003.8, 945.8, 820.0, 771.3, 737.1, 700.2, 598.3, 550.8, 518.0, 506.2. UV-Vis (CH_2Cl_2, λ_{nm}): 350, 432 (Soret), 521, 561, 606, 654.

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3. Single crystal X-ray diffraction

X-ray data for [**R1**-H_6][BF_4]$_6$ were collected on a Bruker D8 Venture diffractometer, equipped with a PHOTON 100 detector, kappa goniometer, and a Cu high brilliance IμS microfocus source. Crystals were mounted on MiTeGen MicroMounts™ and frozen in paratone oil under a cold stream of N_2. Reflection data were integrated using the APEX III software package. See Table S1 for a summary and CIF file deposited with the CCDC (2000087) for details.

It should be noted that all of the [5]rotaxanes tended to crystallize (see Figure S27), but it was not possible to obtain single crystals of sufficient size for SC-XRD analysis other than for [**R1**-H_6][BF_4]$_6$. Samples of some of these crystals were sent to the Canadian Light Source, but the diffraction was too poor to allow the determination of their unit cell parameters and structure.

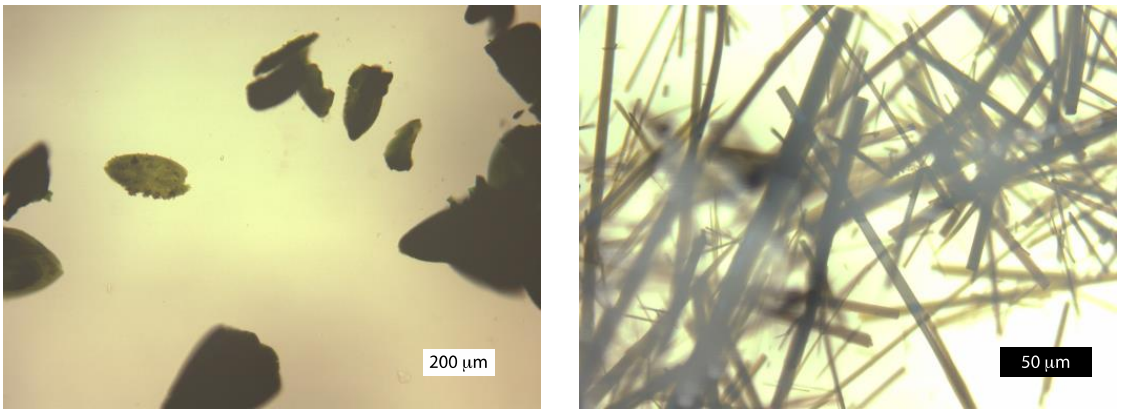

Figure S29. Optical micrographs of crystals of **R3** (left) and **R5** (right).

Table S1. Crystal data, solution, and refinement parameters for [**R1**-H_6][BF_4]$_6$

CCDC Accession Number	2000087	ρ (g·cm^{-3})	1.372
Chemical formula	$C_{192}H_{224}B_6F_{24}N_8O_{48}$	μ (mm^{-1})	0.957
Formula weight (g·mol^{-1})	3932.64	F (000)	4124
Crystal system	Tetragonal	Radiation (Å)	1.54184
Space group	$P4_2/n$ (No. 86)	2θ range (°)	4.98 to 89.04
Colour	Metallic green	Reflections collected	4886
T (K)	173(2)	Unique reflections	2121
a (Å)	25.0521(11)	Parameters	656
b (Å)	25.0521(11)	Restraints	611
c (Å)	15.1716(18)	R_{int}	7.76
α (°)	90	R_1 [I > 2σ (I)]*	18.92
β (°)	90	R_1 all	27.52
γ (°)	90	wR_2 [I > 2σ (I)]*	46.26
V (Å^3)	9521.8(14)	wR_2 all	52.16
Z	2	GoF on F^2	1.677

$$R_1 = \frac{\sum|F_{obs} - F_{calc}|}{\sum|F_{obs}|}; wR_2 = \left(\frac{\sum|w|F_{obs}^2 - F_{calc}^2|^2|}{\sum|wF_{obs}^2|}\right)^{1/2}, w = q[\sigma^2(F_{obs}^2) + (aP)^2 + bP]^{-1}$$

4. UV-Vis Spectroscopy Studies

UV-Vis-NIR spectra were recorded on a Varian Cary 50E Spectrometer using a quartz glass cuvette of 10 × 10 mm. Solutions were prepared using solvents containing oxygen and moisture from the atmosphere.

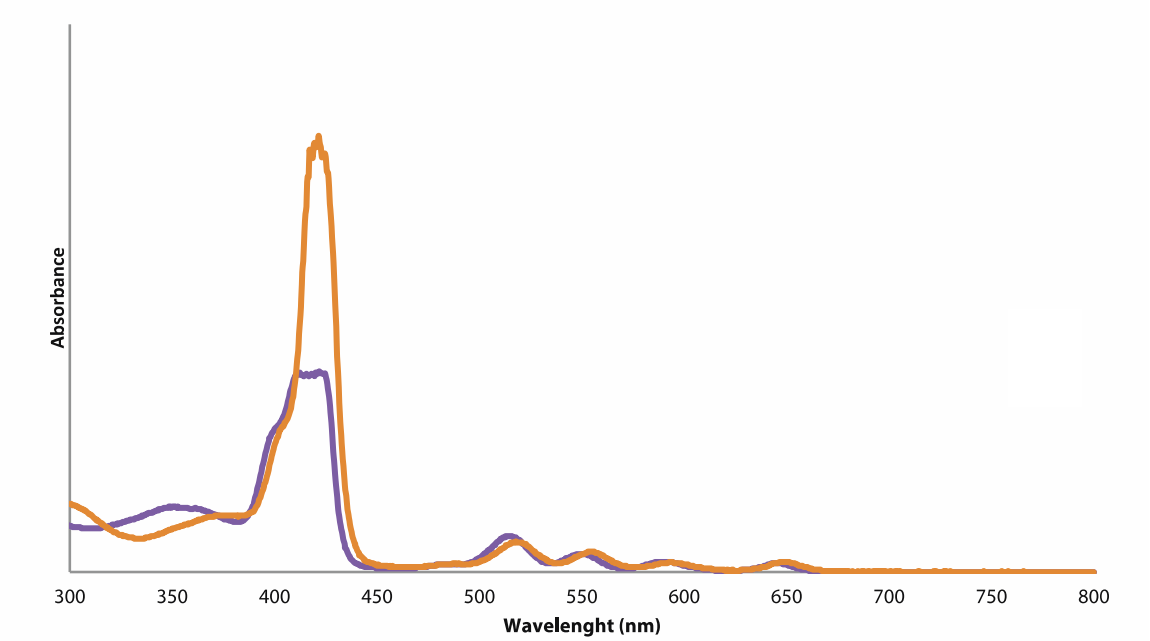

Figure S30. Comparison of UV-Vis spectra of **R1** (orange) and **P1** (purple); CH_2Cl_2 (1.0×10^{-5} M).

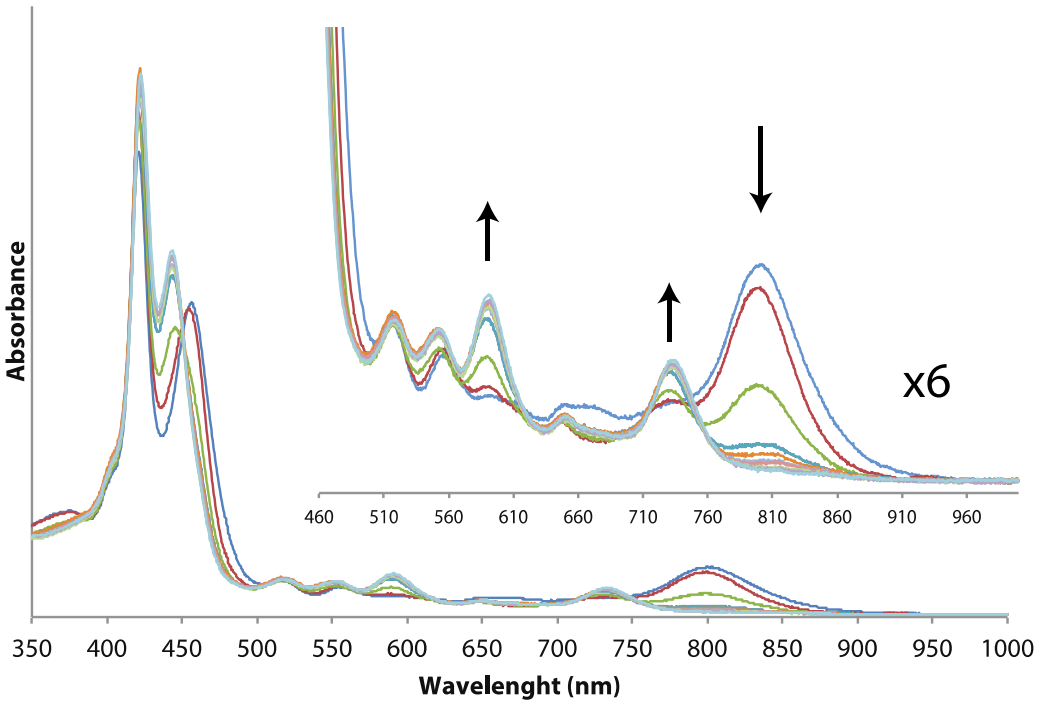

Figure S31. UV-Vis titration plot for [**R5**-H_6][BF_4]$_6$ with DBU; CH_2Cl_2 (1.7 x 10^{-5} M).

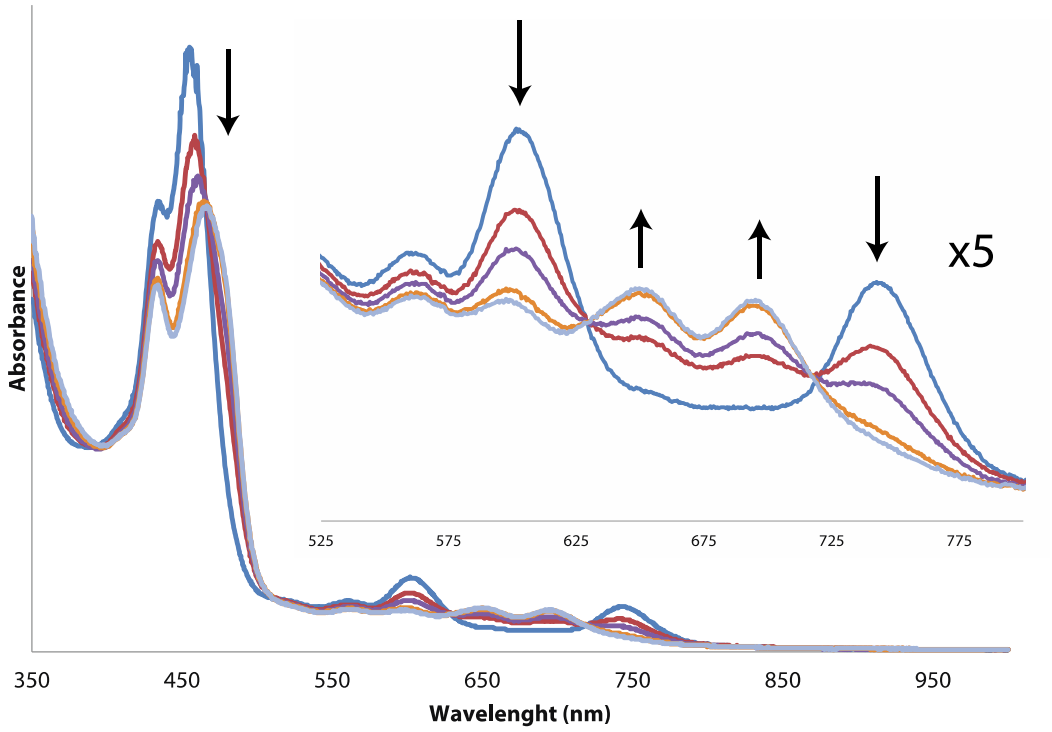

Figure S32. UV-Vis titration plot for [**R4**-H_6][BF_4]$_6$ with added DBU; CH_2Cl_2 (1.7 x 10^{-5} M).

5. Mass Spectrometry

High-resolution mass spectrometry experiments were performed on a Waters XEVO G2-XS ToF instrument in electrospray ionization (ESI) or atmospheric solids analysis probe (ASAP) mode. For **R1**, an additional spectrum was collected using a Waters SYNAPT G2-Si instrument in matrix-assisted laser desorption ionization (MALDI) mode.

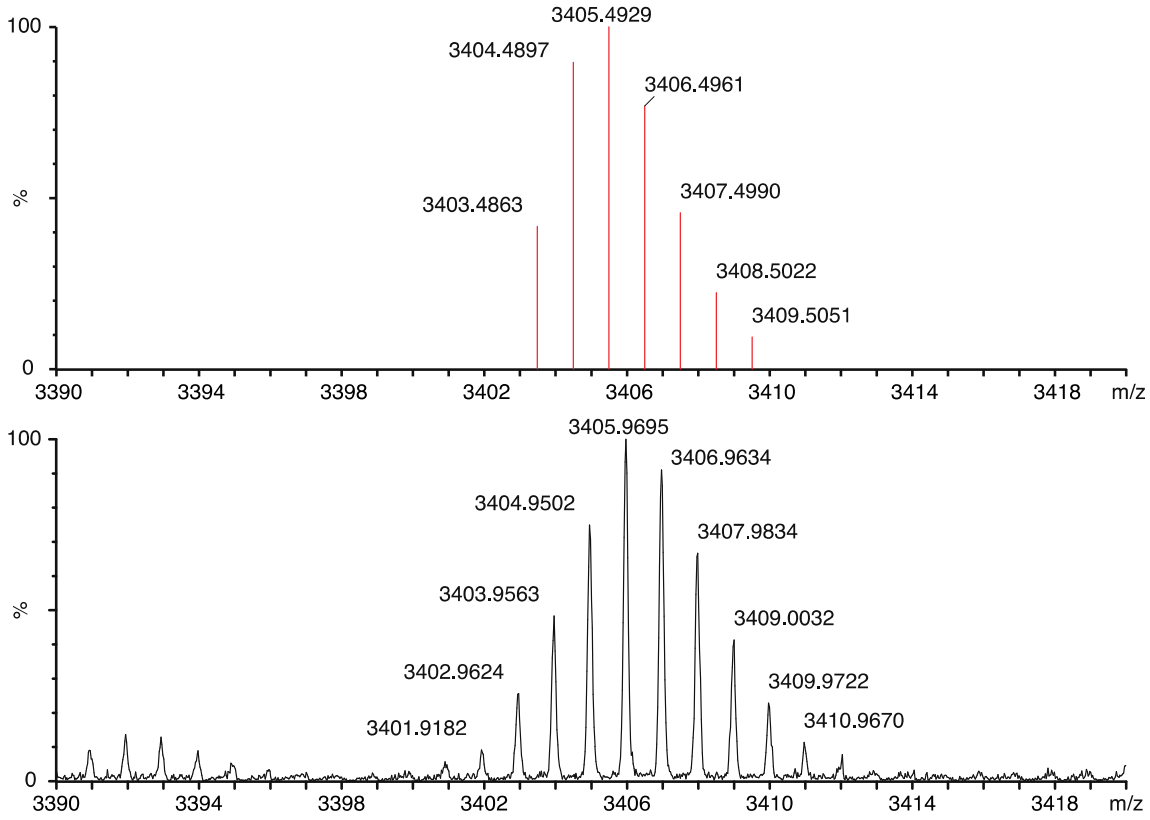

Figure S33. Experimental mass spectrum (black) and calculated isotope pattern (red) of **R1** in MALDI mode, showing the [**R1**-H]$^+$ molecular ion.

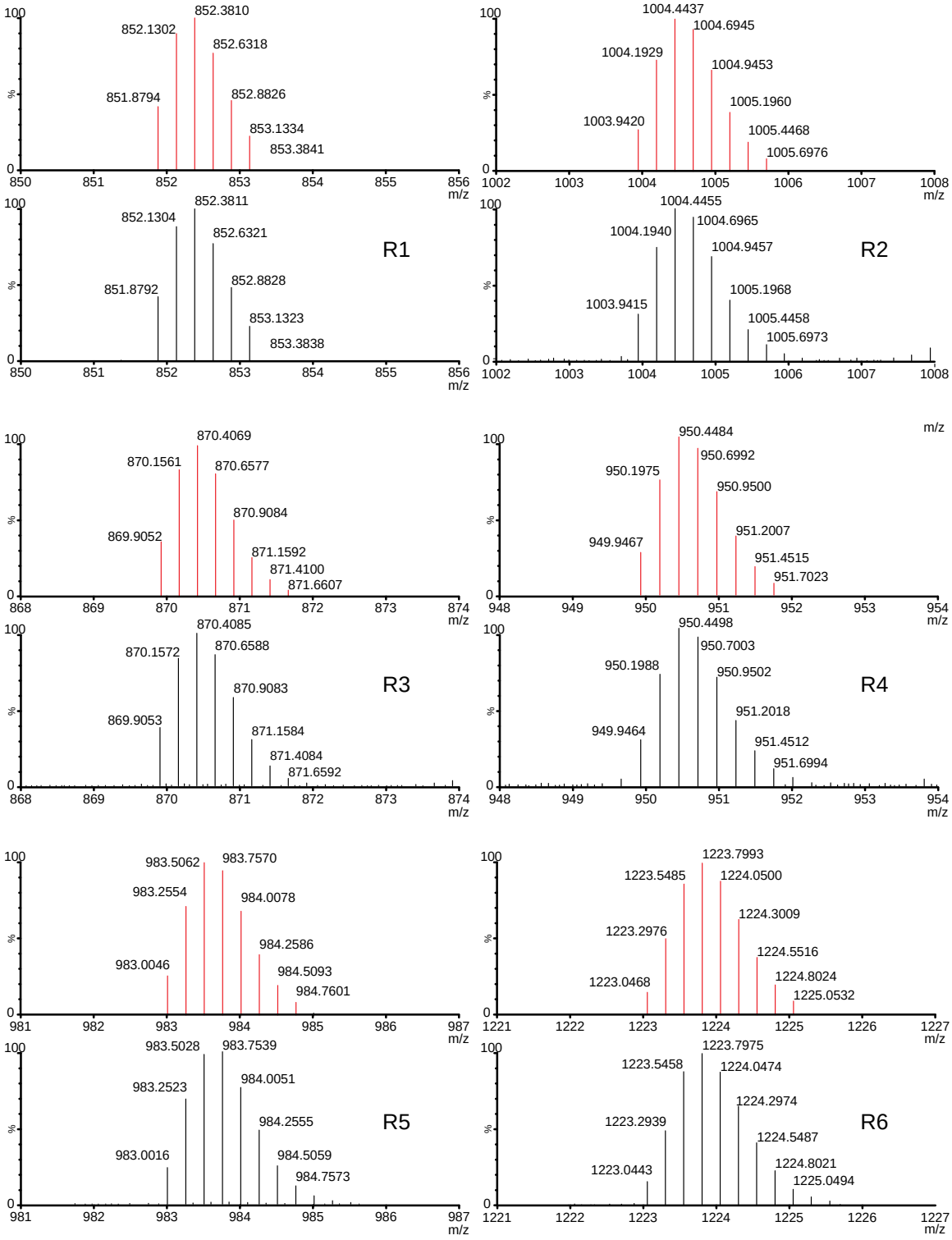

Figure S34. Experimental mass spectra (black) and calculated isotope pattern (red) of [5]rotaxanes **R1**-**R6** showing the [**R#**-H_4]$^{4+}$ molecular ion.

6. References

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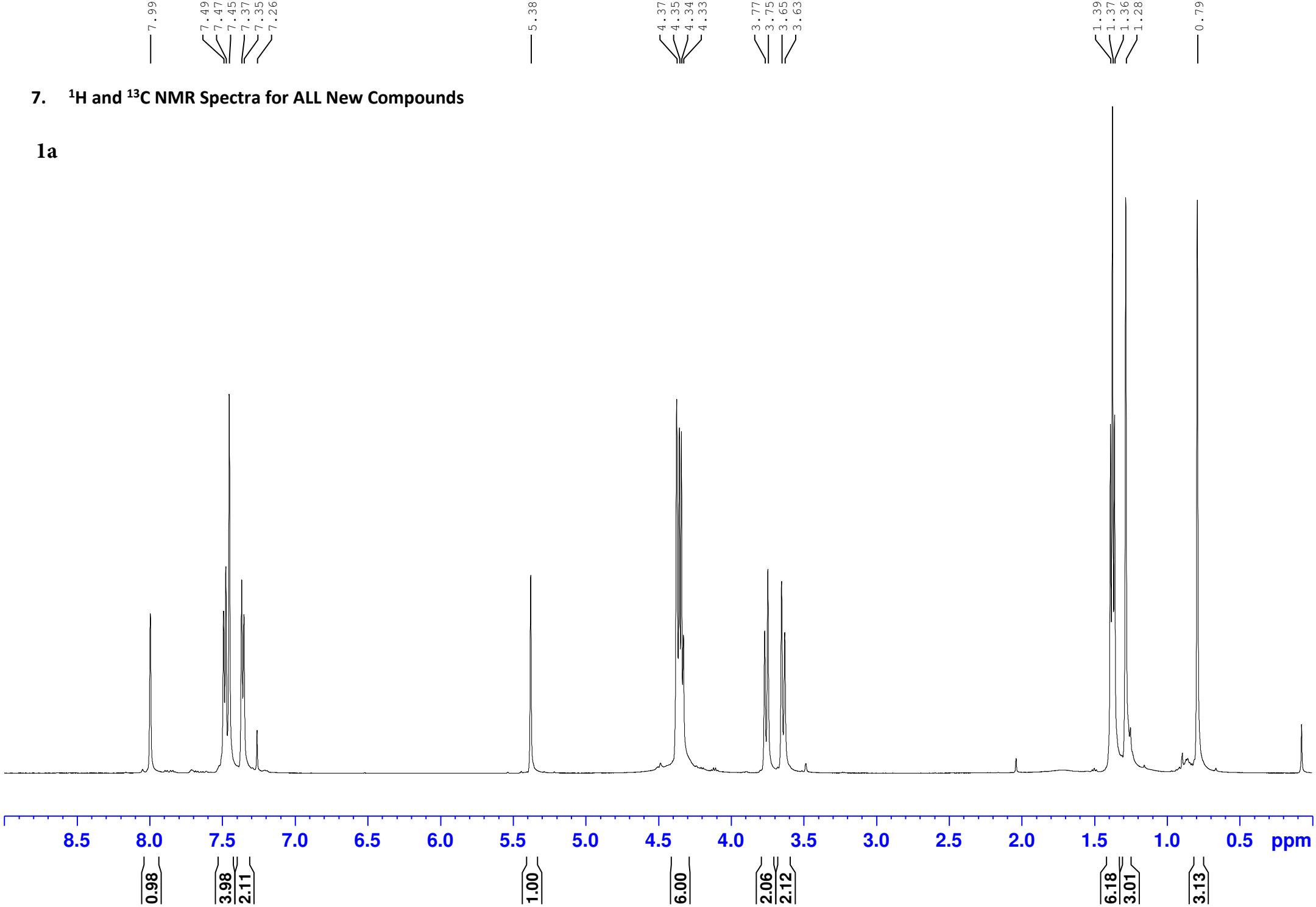
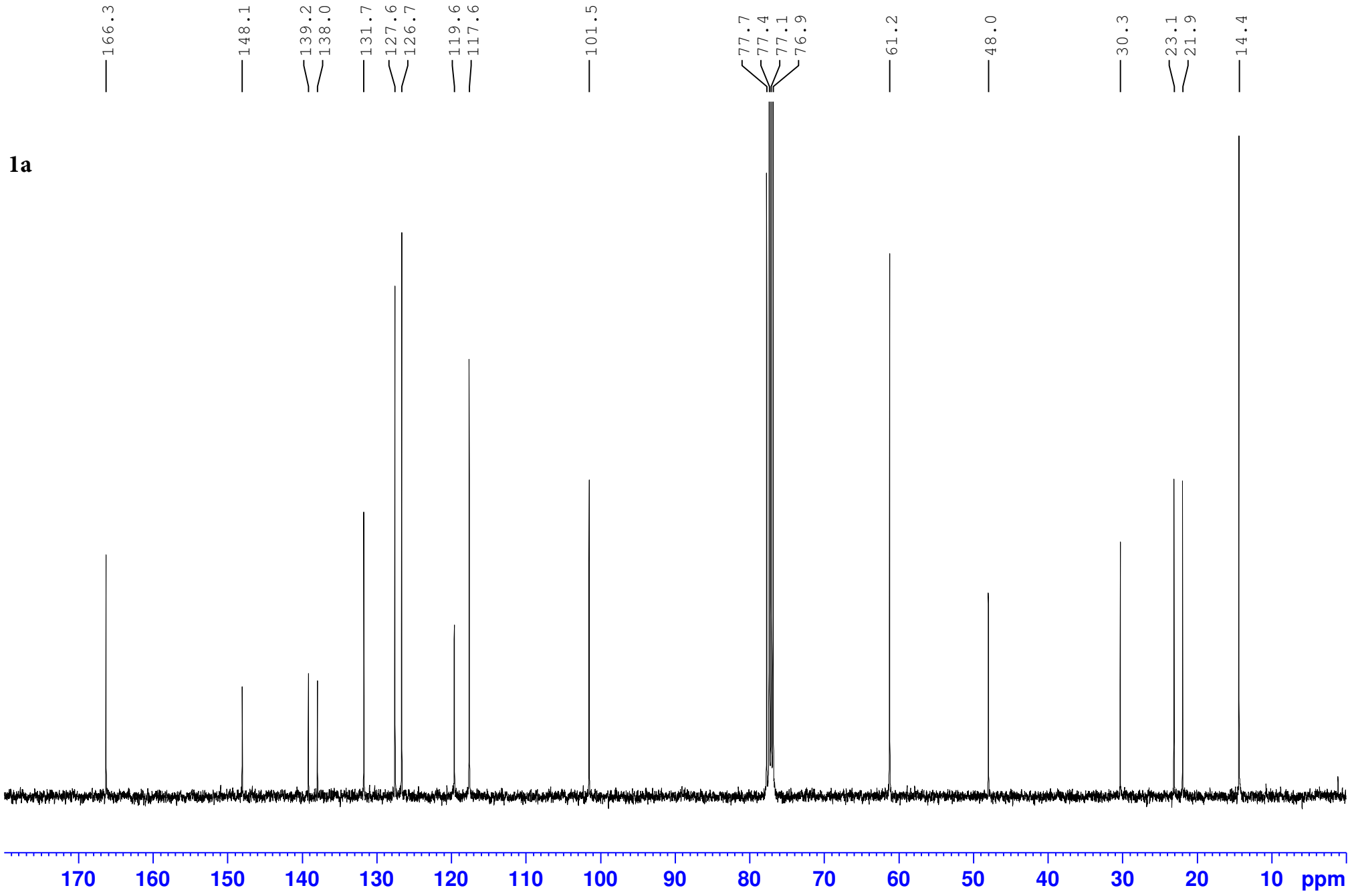
7. ^{1}H and ^{13}C NMR Spectra for ALL New Compounds

1a

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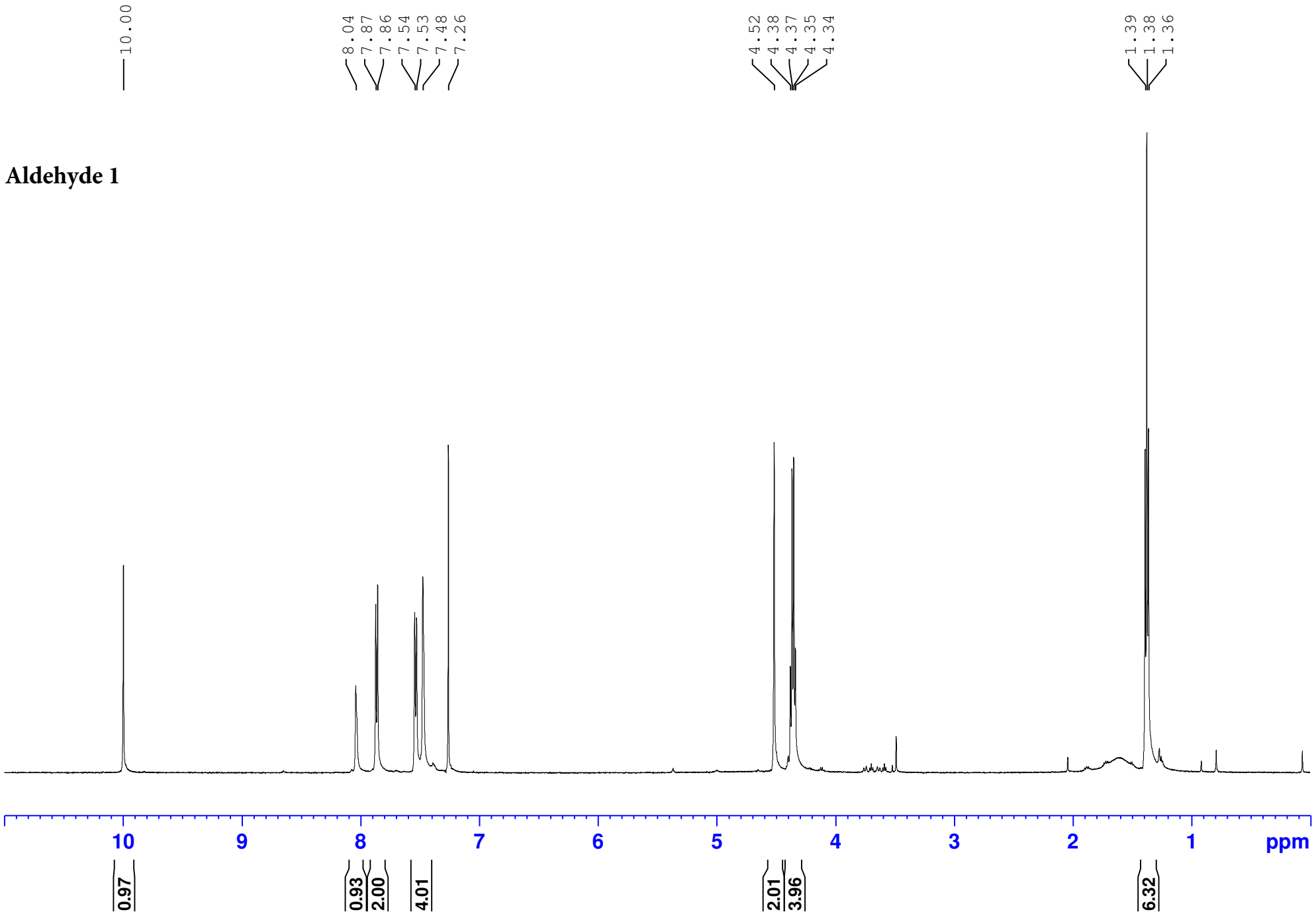
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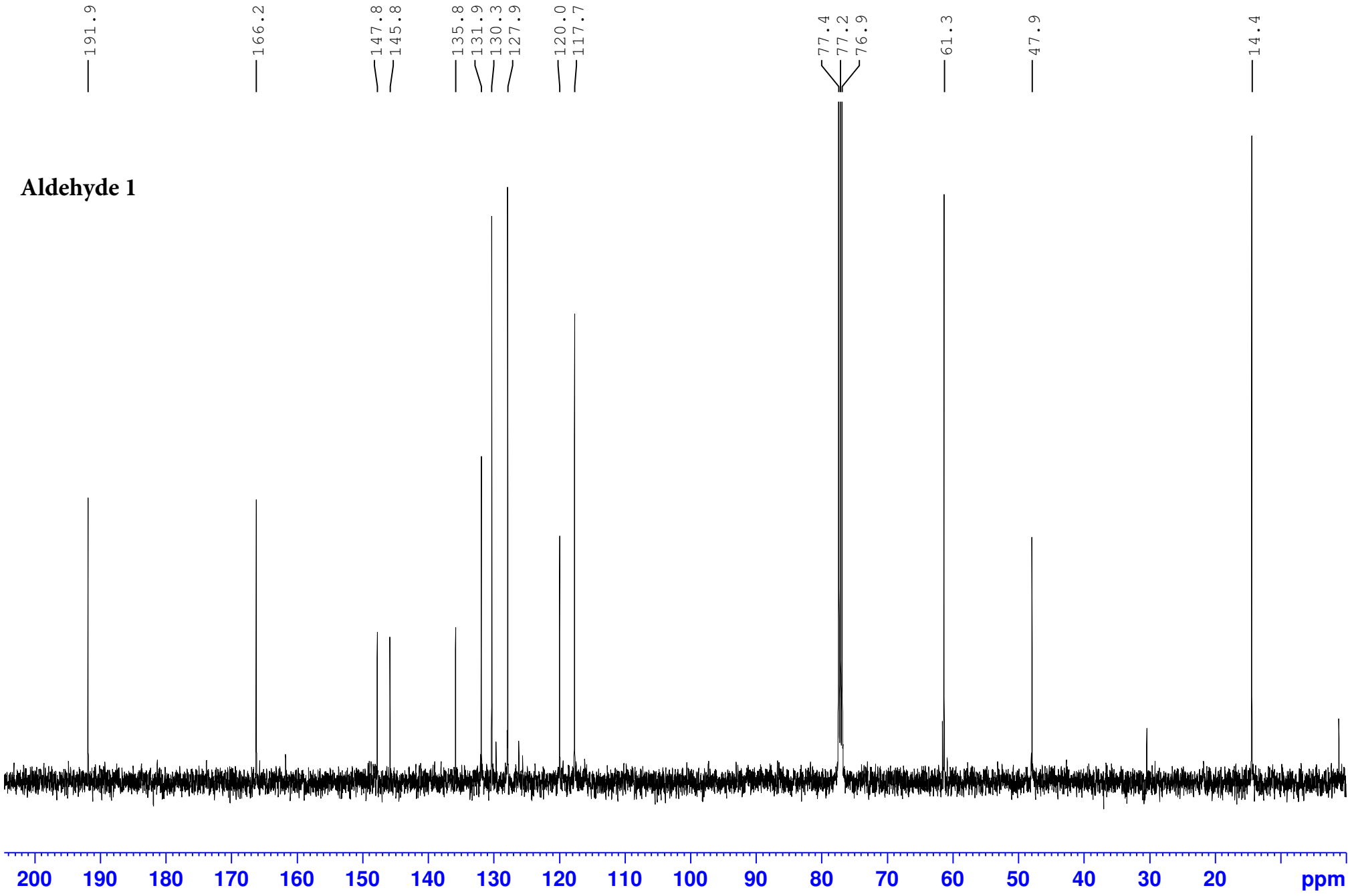
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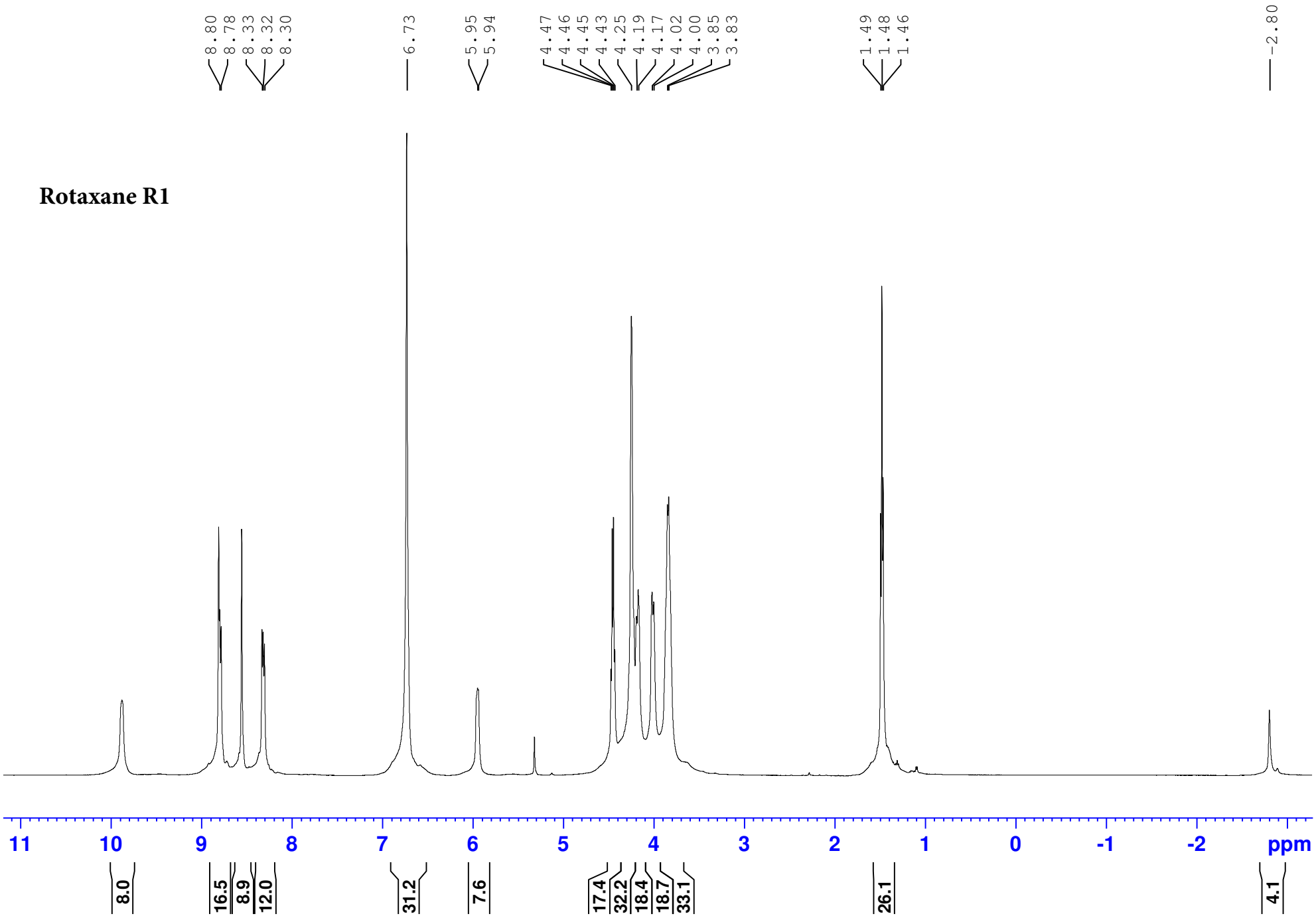
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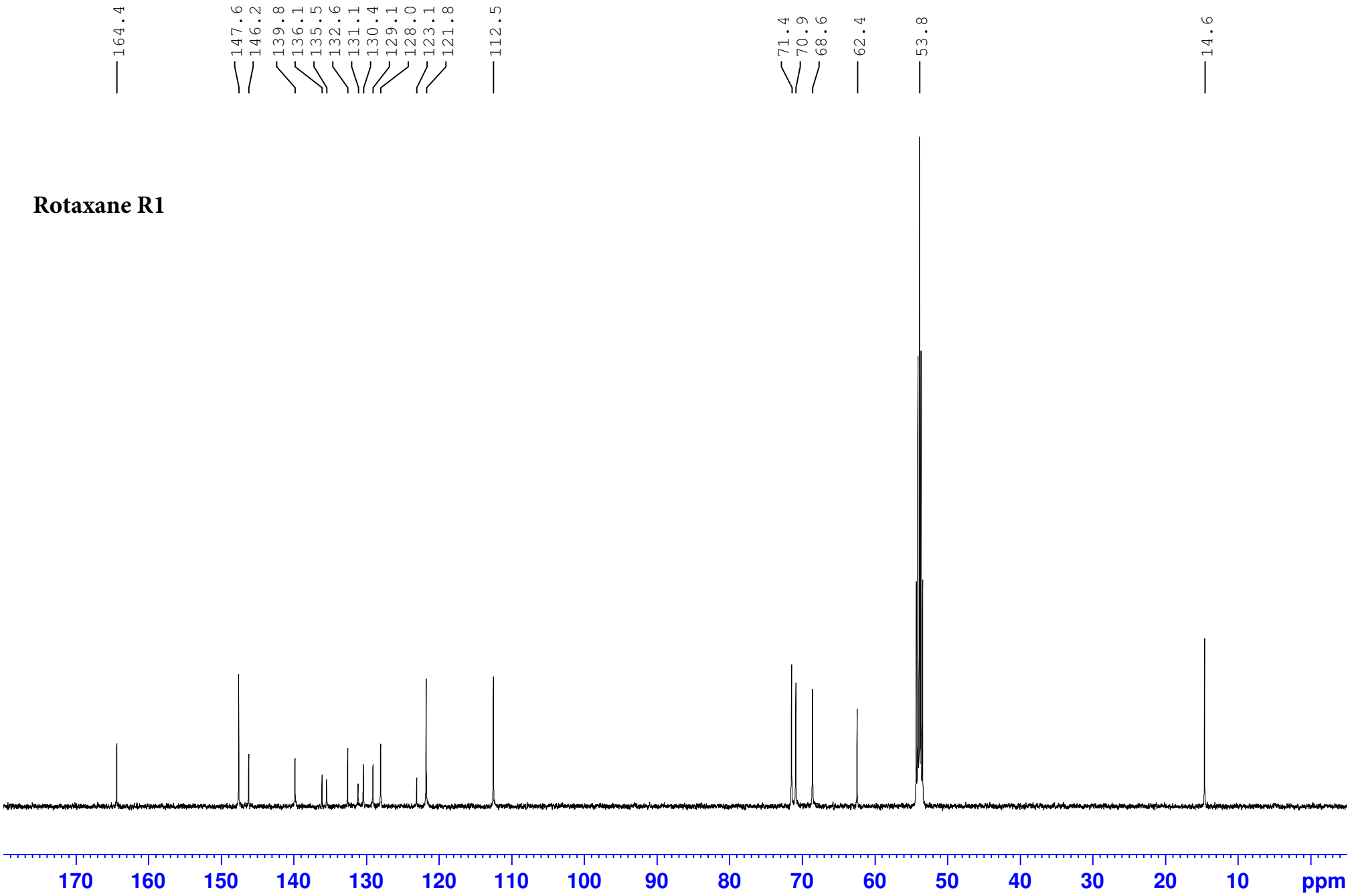
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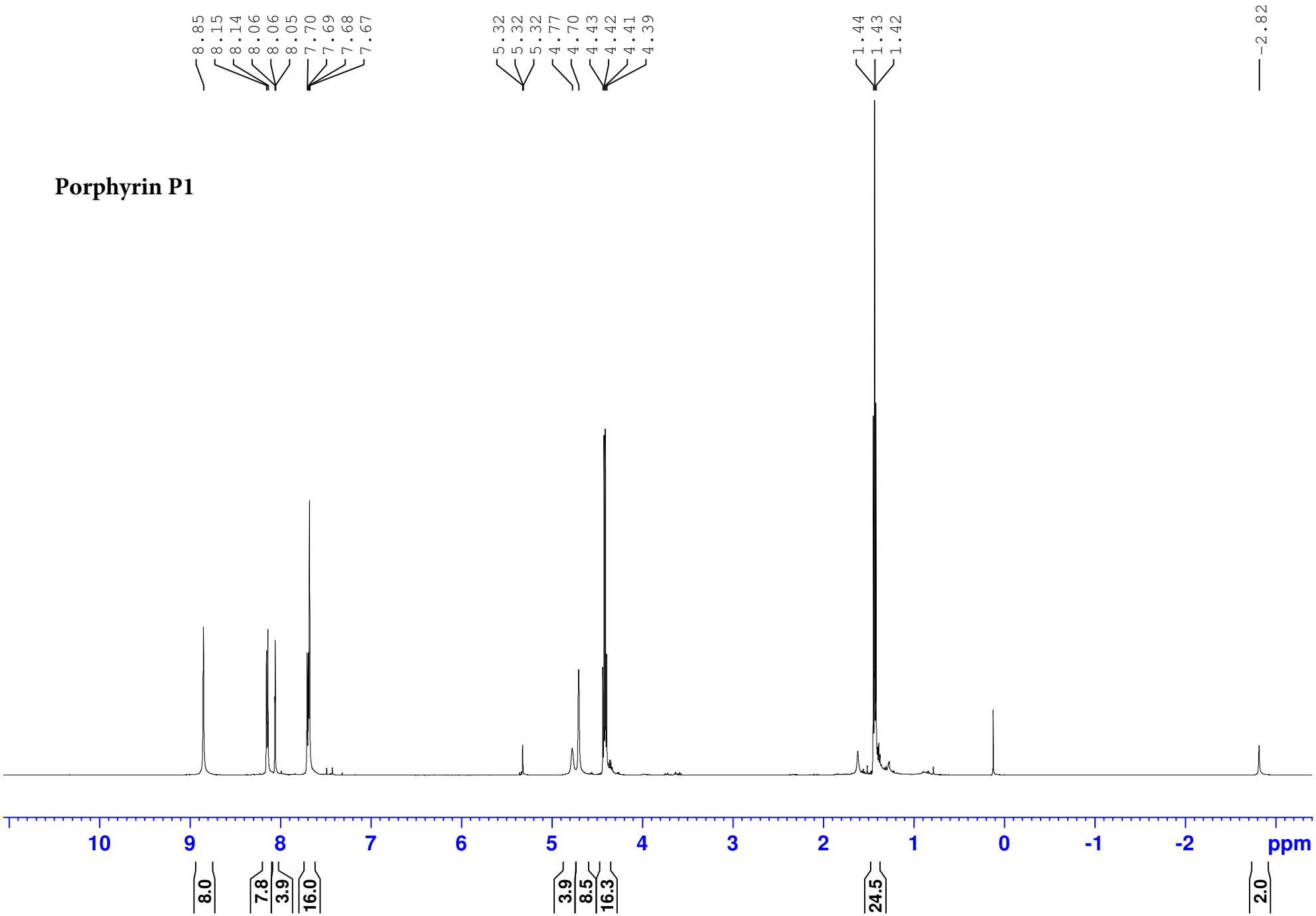
ppm

Porphyrin P1



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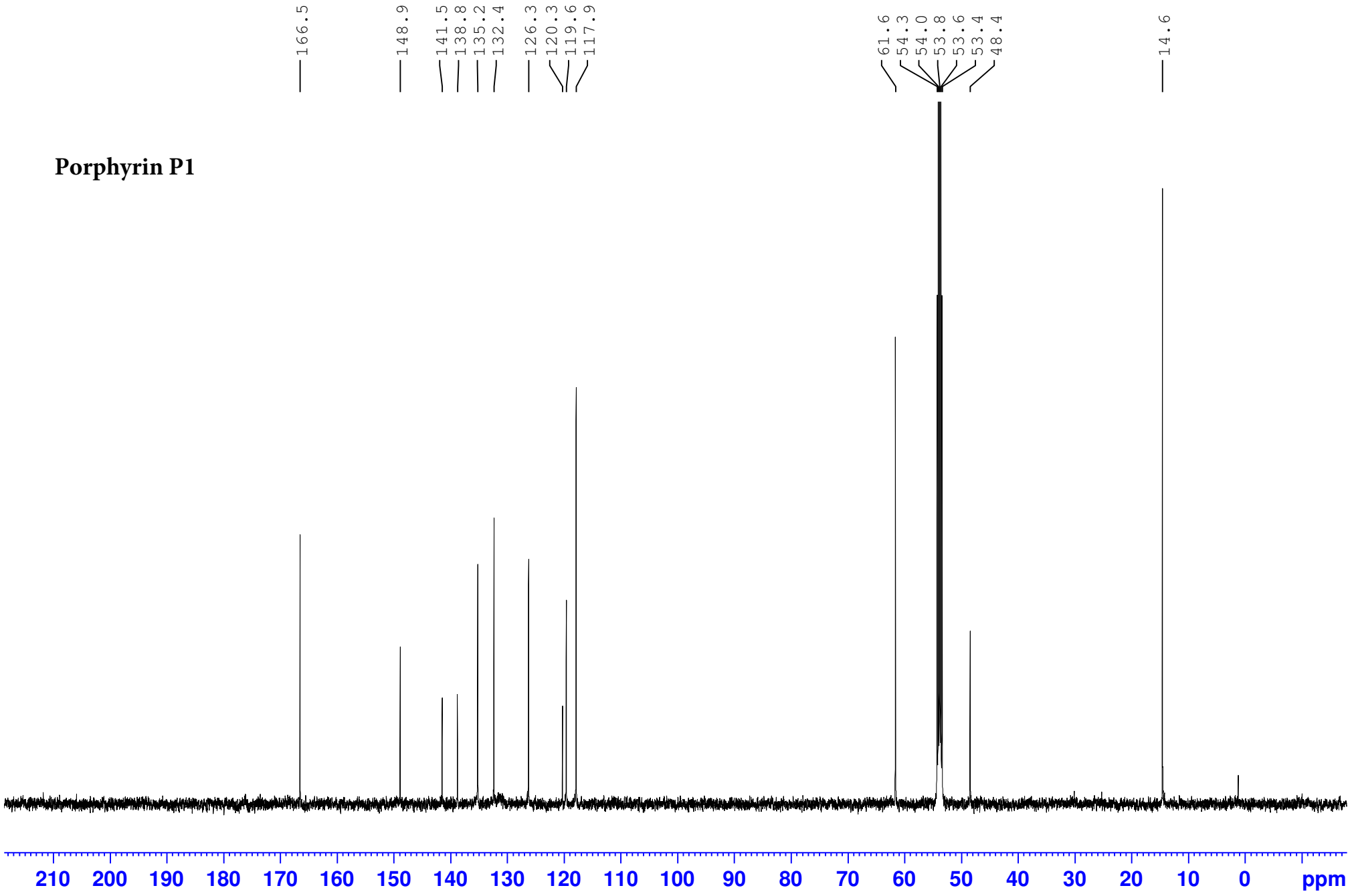

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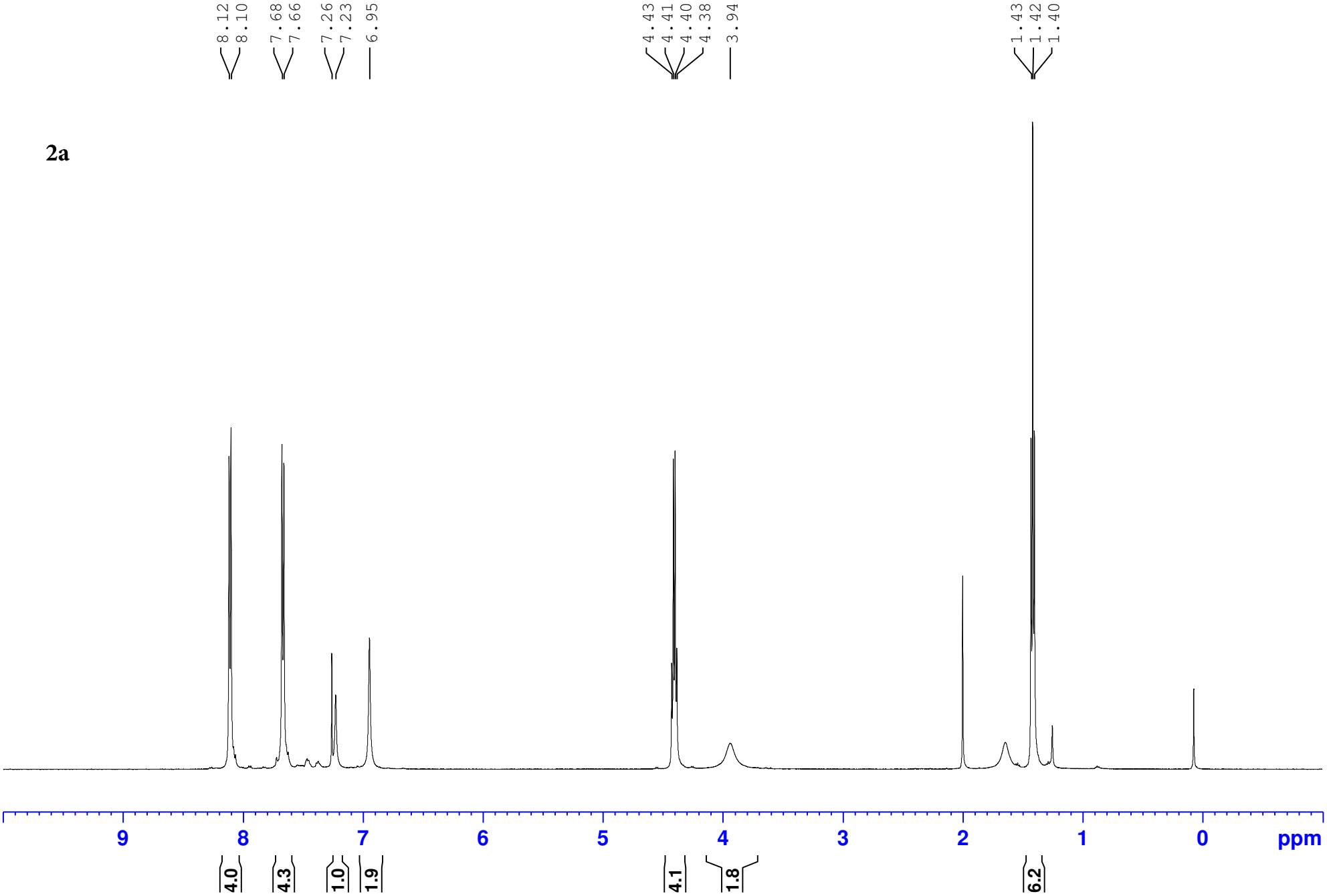
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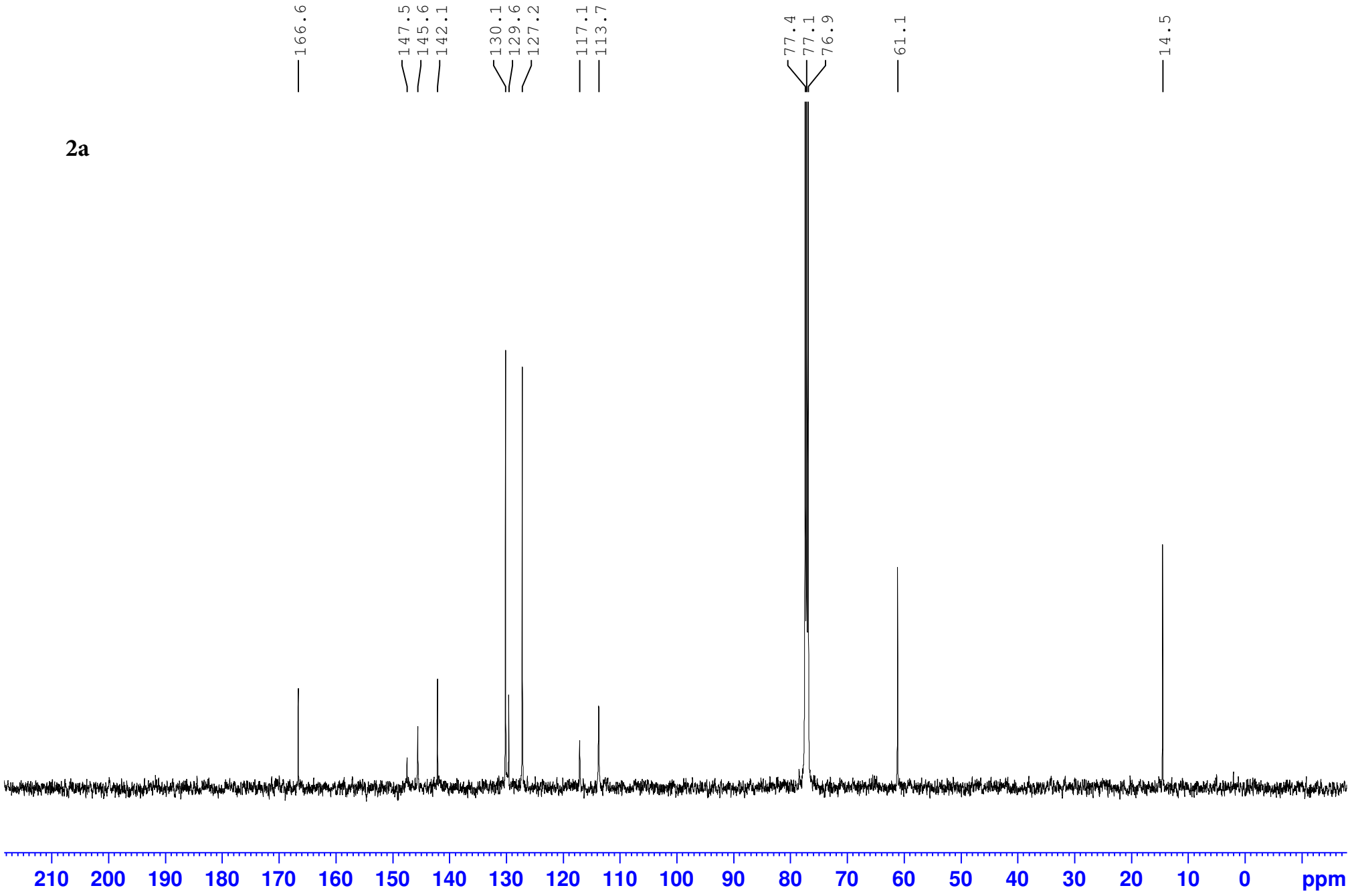
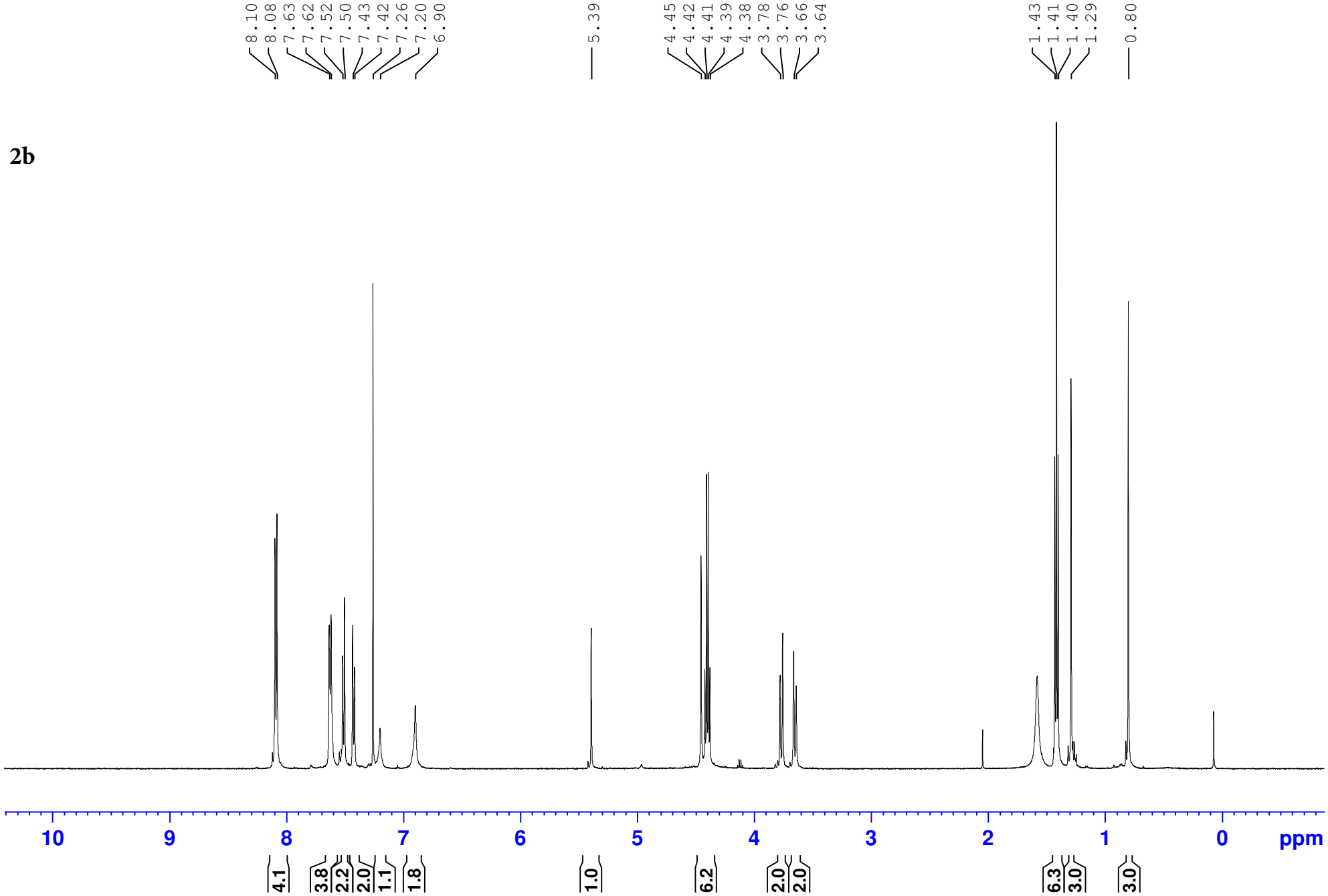
4.41
4.40
4.38
3.94
1.43
1.42
1.40
9
8
7
6
5
4
3
2
1
0
ppm
4.0
4.3
1.0
1.9
4.1
1.8
6.2

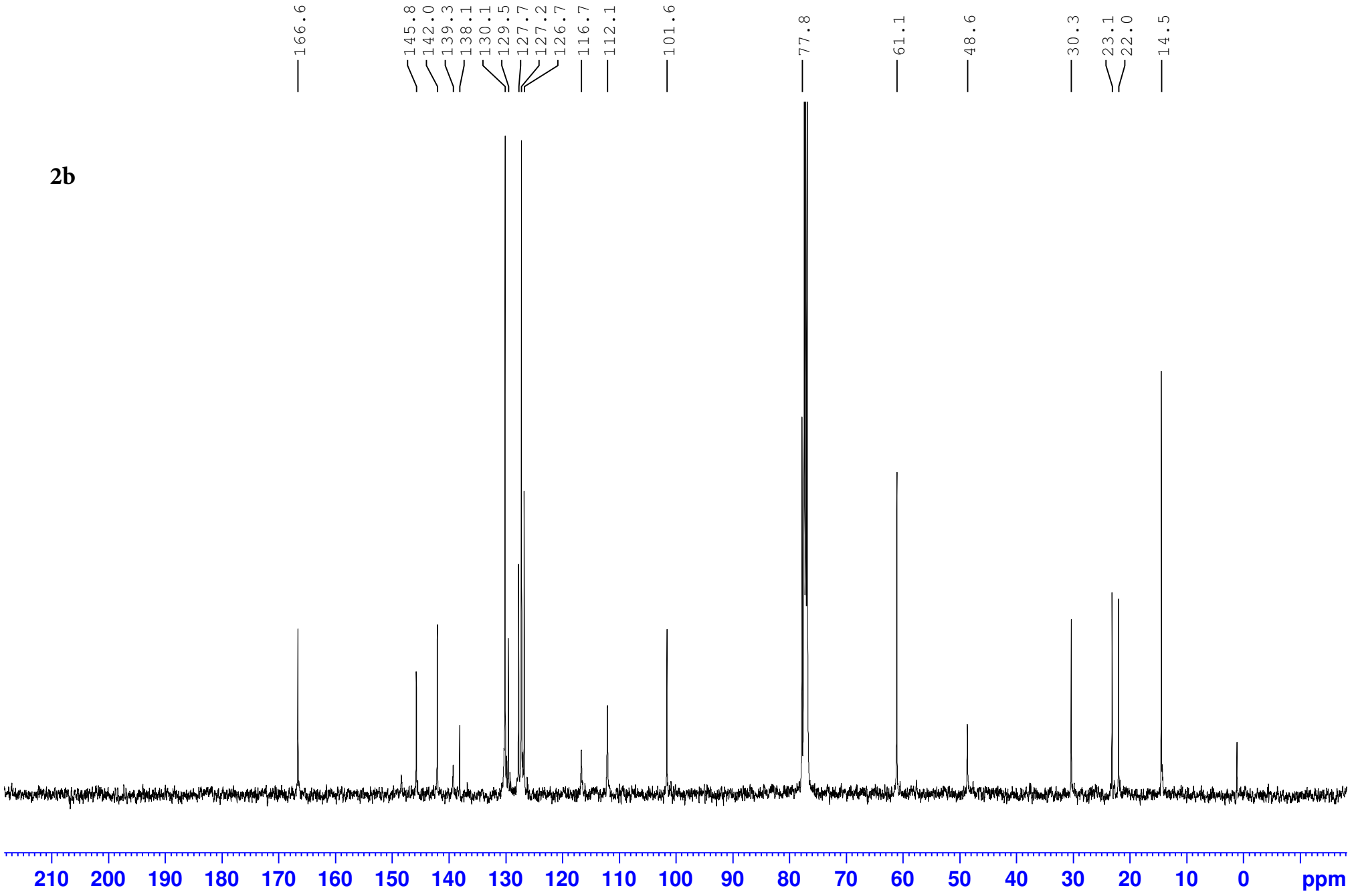
2a


166.6
147.5
145.6
142.1
130.1
129.6
127.2
117.1
113.7
77.4
77.1
76.9
61.1
14.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

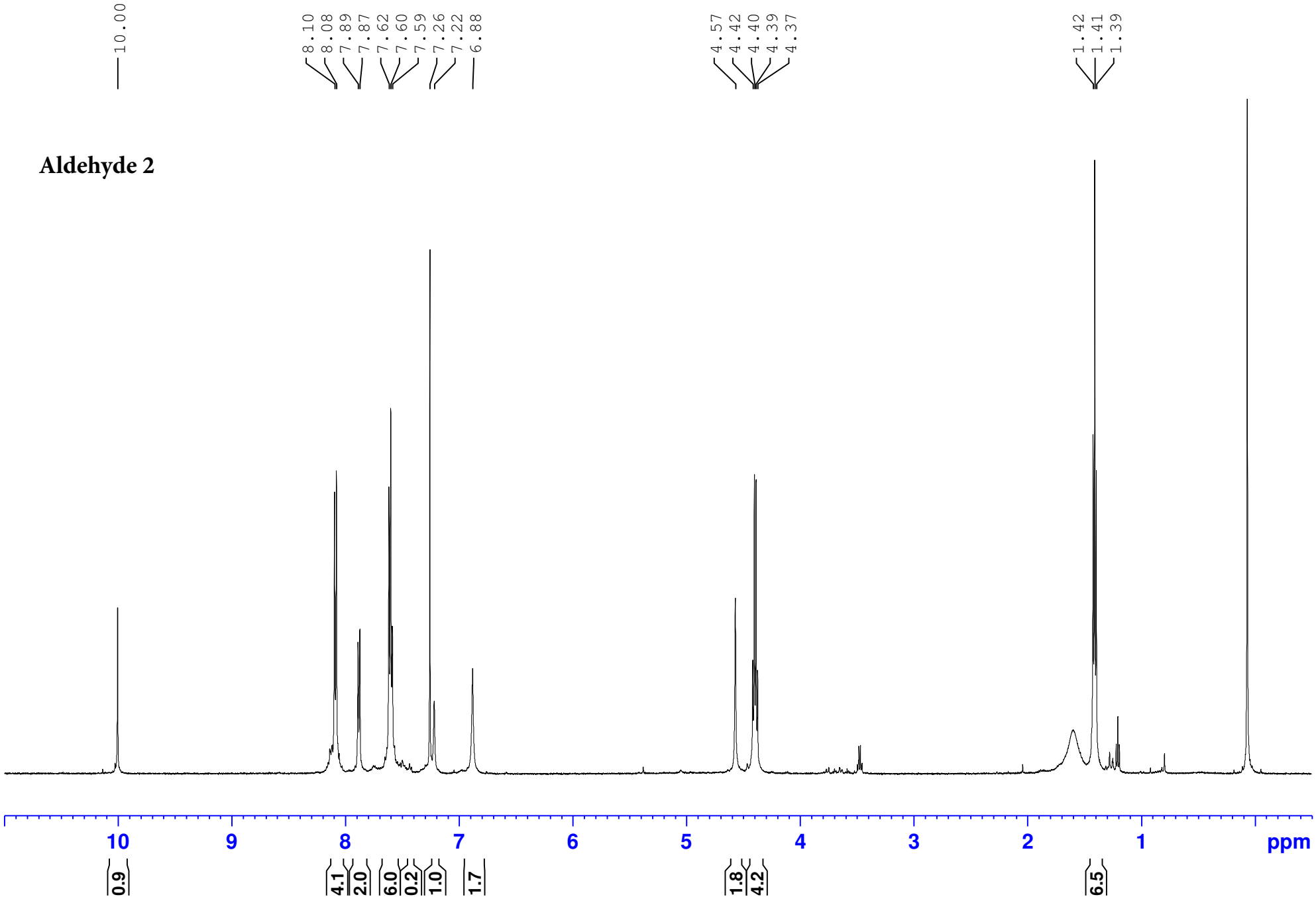
2b

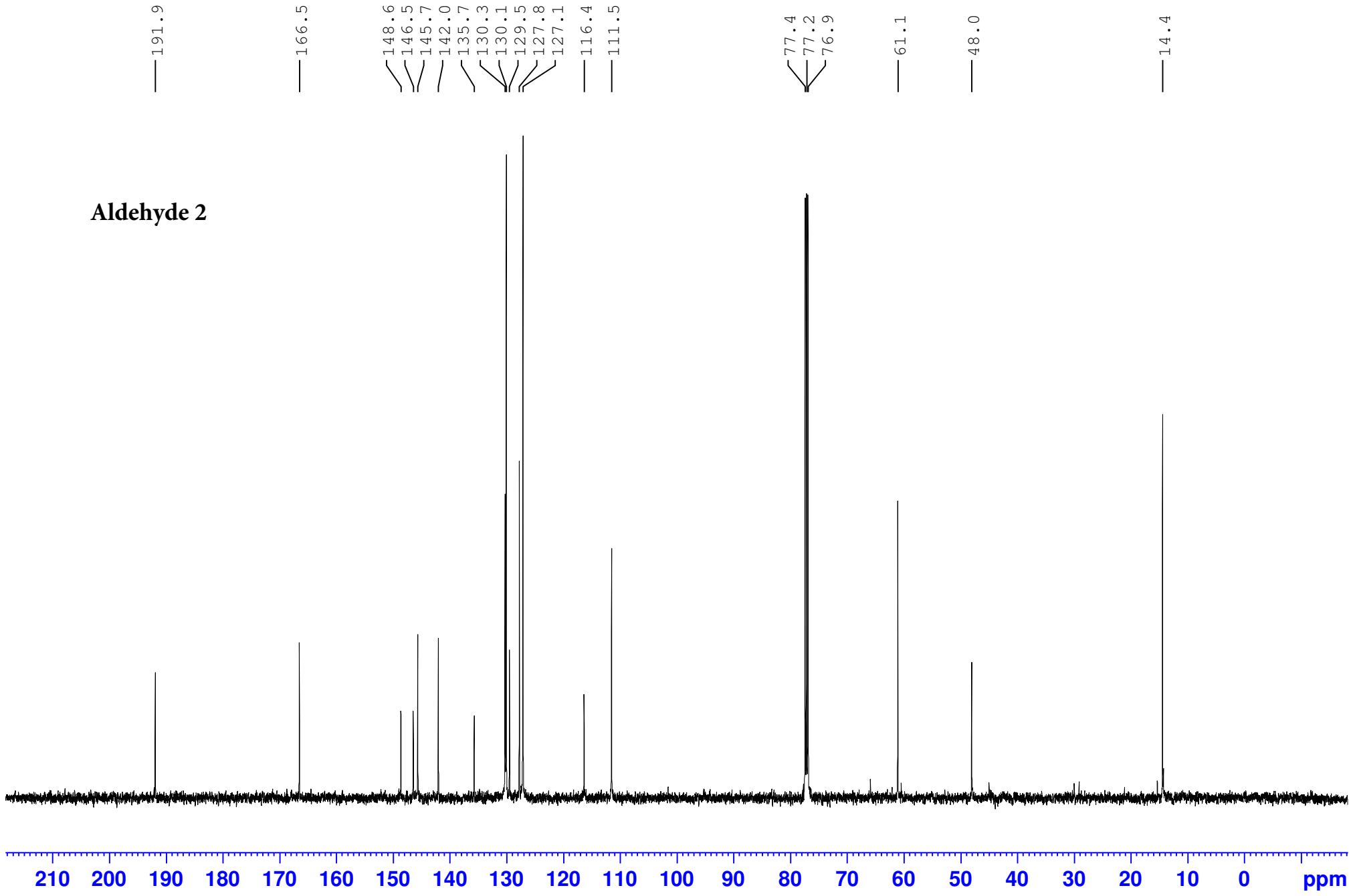

8.10
8.08
7.63
7.62
7.52
7.50
7.43
7.42
7.26
7.20
6.90
5.39
4.45
4.42
4.41
4.39
4.38
3.78
3.76
3.66
3.64
1.43
1.41
1.40
1.29
0.80
10
9
8
7
6
5
4
3
2
1
0
ppm
4.1
3.8
2.2
2.0
1.1
1.8
1.0
6.2
2.0
2.0
6.3
3.0
3.0

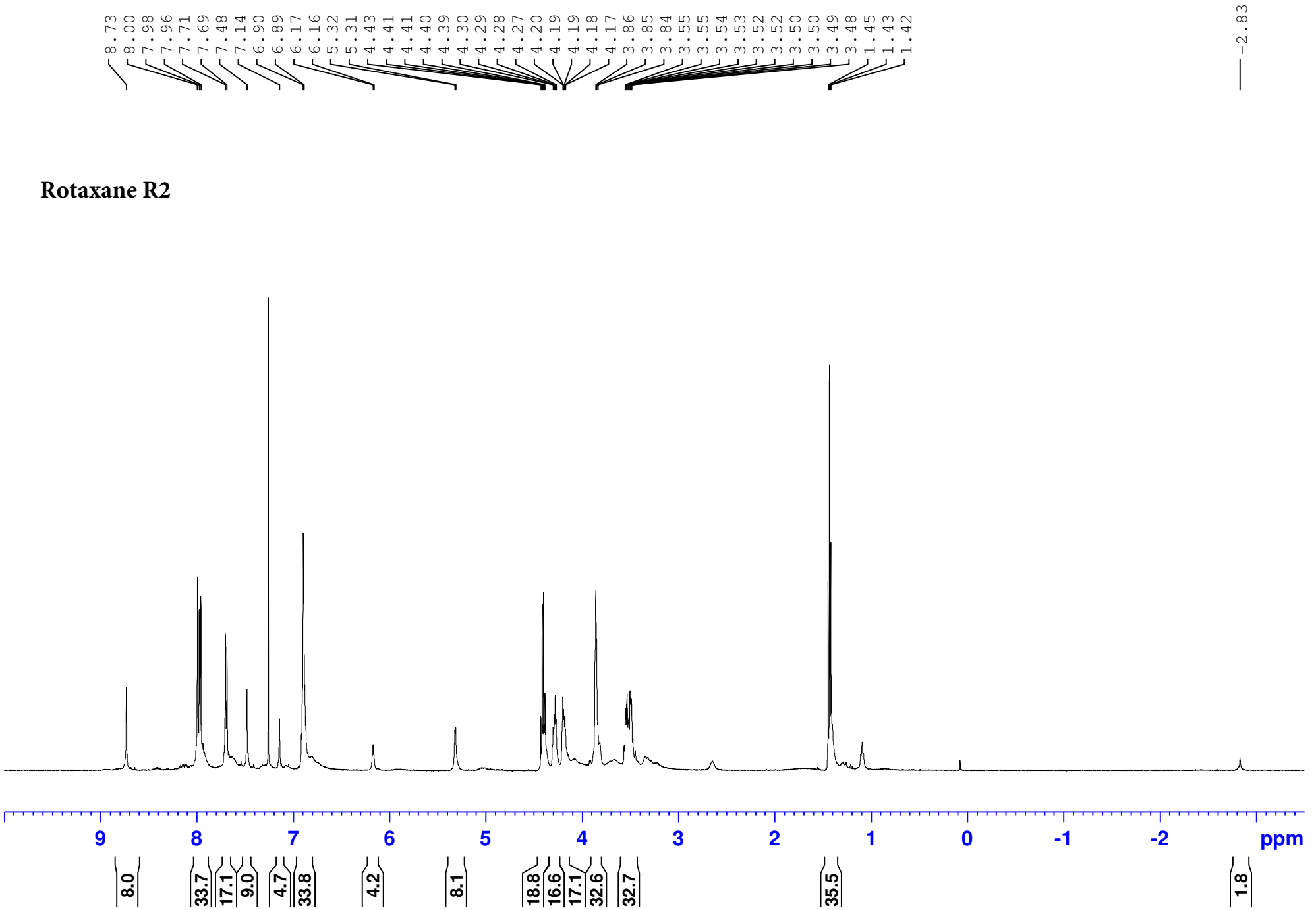
2b


166.6
145.8
142.0
139.3
138.1
130.1
129.5
127.7
127.2
126.7
116.7
112.1
101.6
77.8
61.1
48.6
30.3
23.1
22.0
14.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

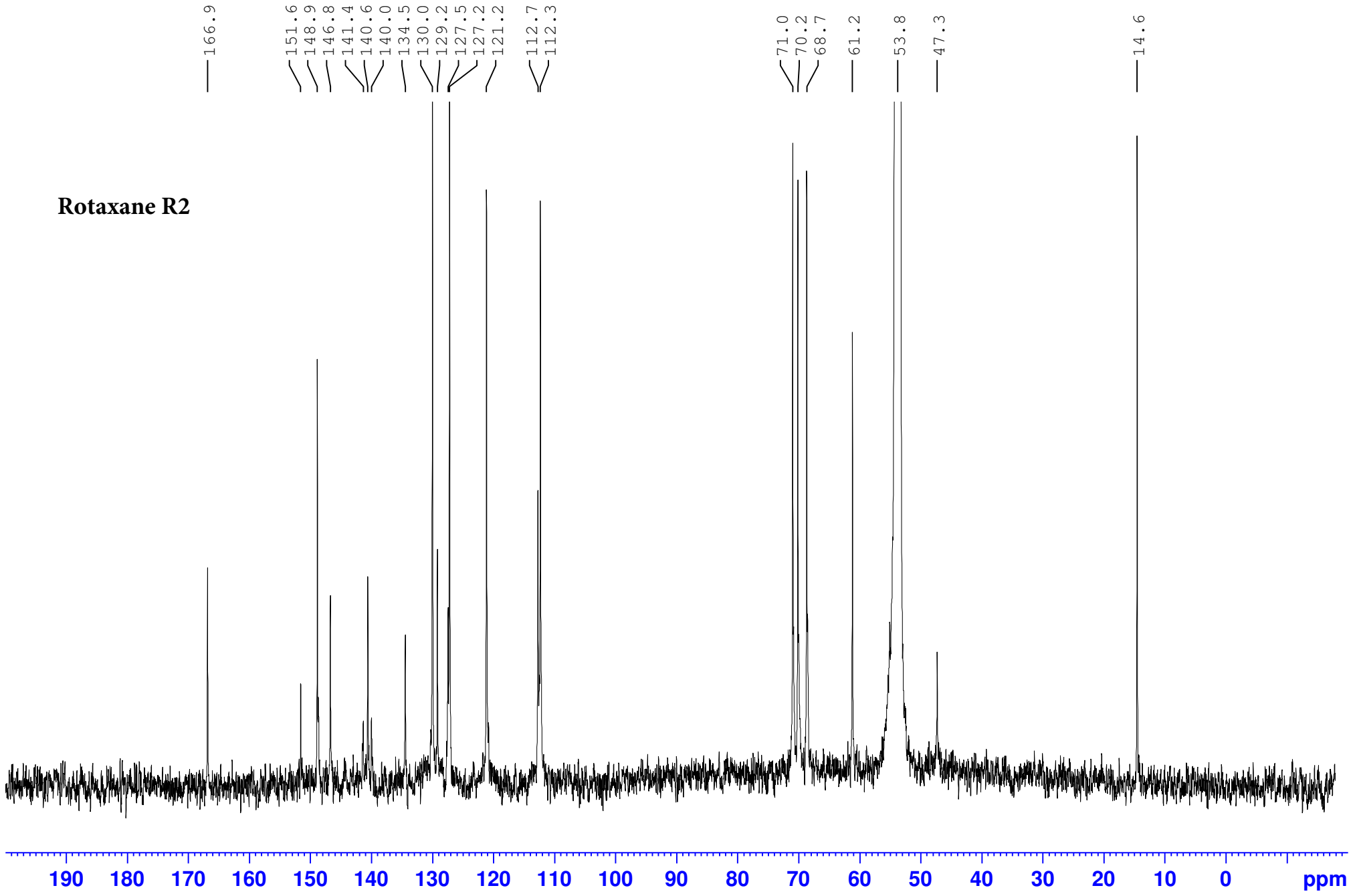
Aldehyde 2

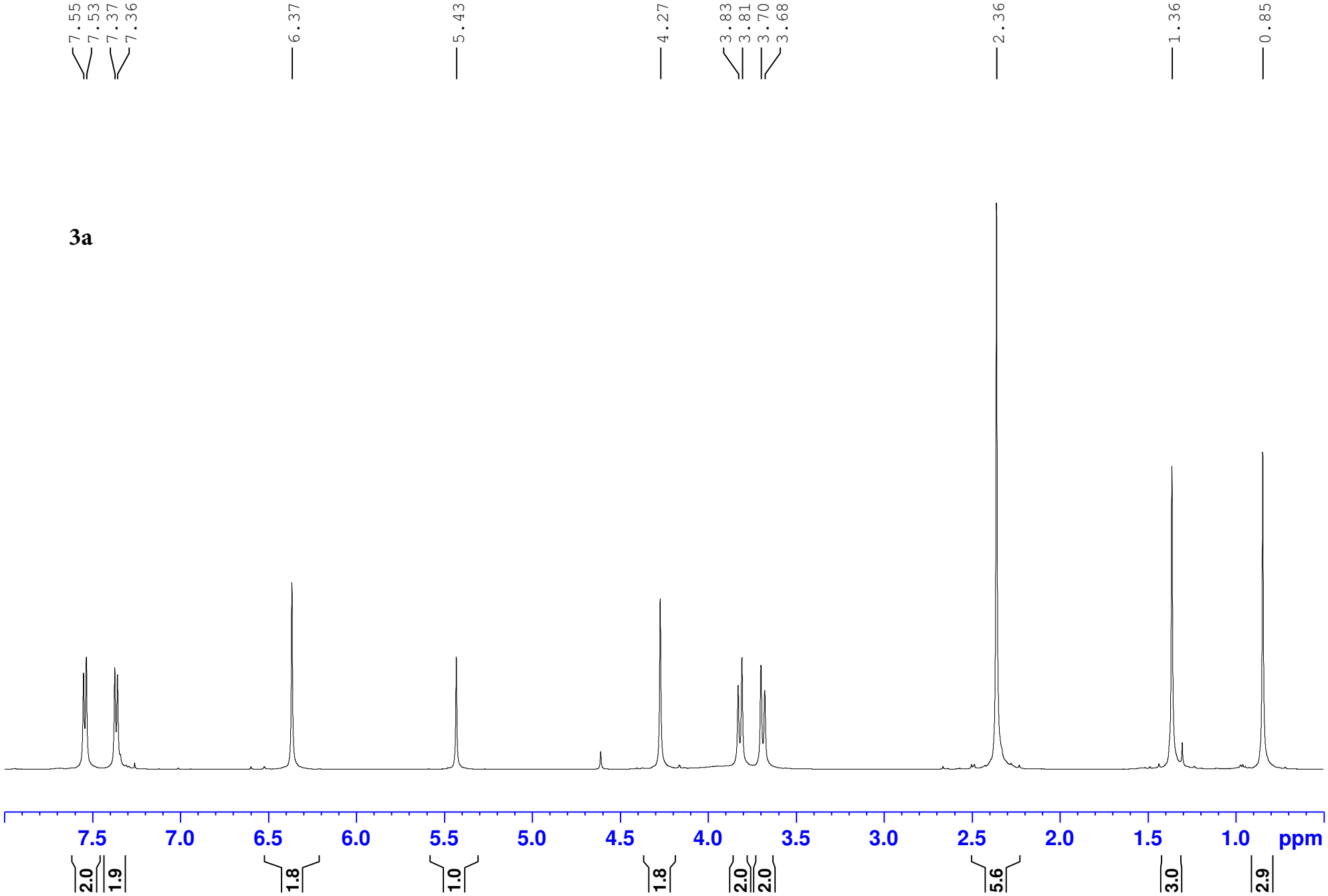

10.00
8.10
8.08
7.89
7.87
7.62
7.60
7.59
7.26
7.22
6.88
4.57
4.42
4.40
4.39
4.37
1.42
1.41
1.39
10
9
8
7
6
5
4
3
2
1
ppm
0.9
4.1
2.0
6.0
0.2
1.0
1.7
1.8
4.2
6.5

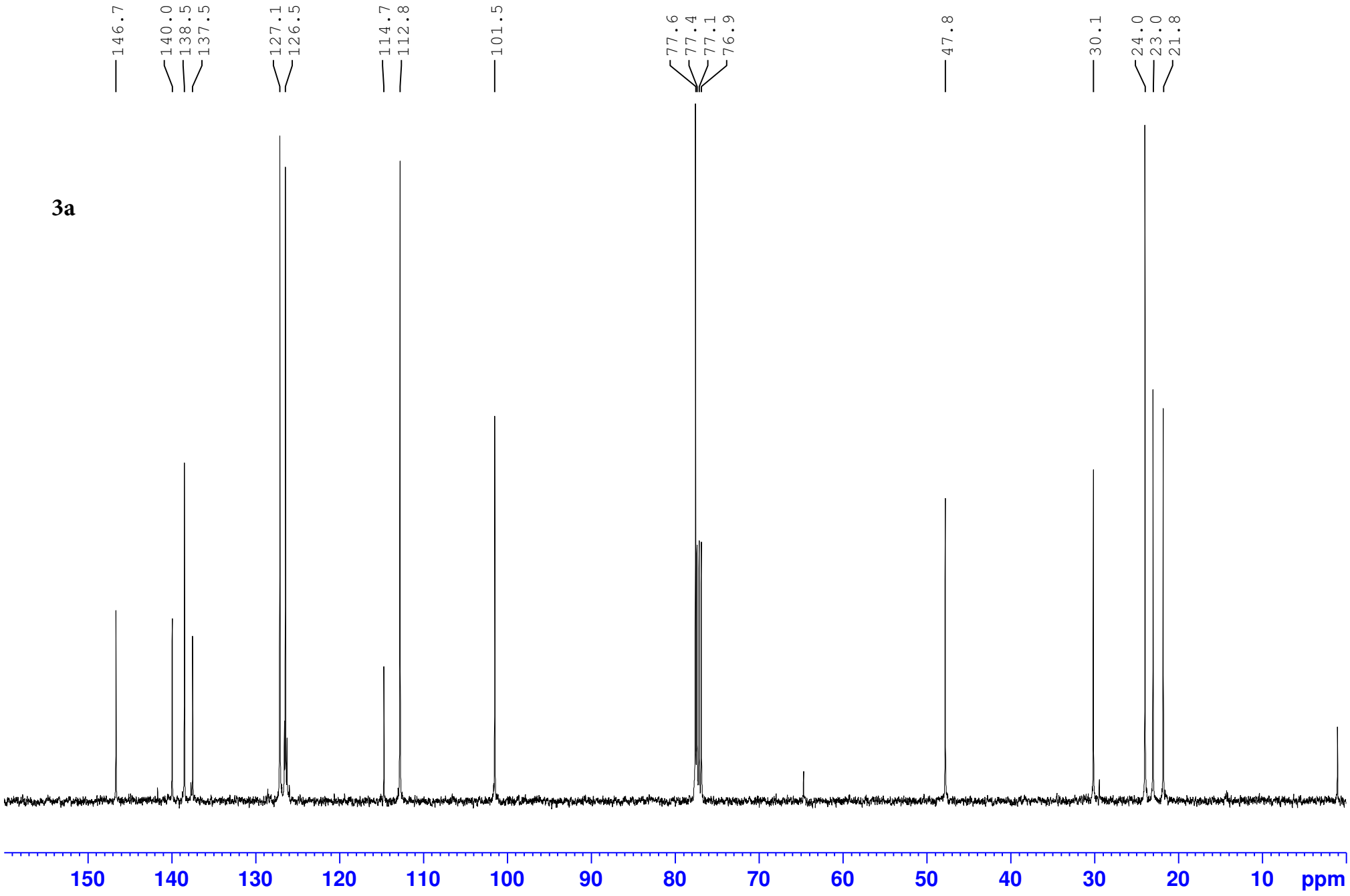

191.9
166.5
148.6
146.5
145.7
142.0
135.7
130.3
130.1
129.5
127.8
127.1
116.4
111.5
77.4
77.2
76.9
61.1
48.0
14.4
Aldehyde 2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.73
8.00
7.98
7.96
7.71
7.69
7.48
7.14
6.90
6.89
6.17
6.16
5.32
5.31
4.43
4.41
4.41
4.40
4.39
4.30
4.29
4.28
4.27
4.20
4.19
4.19
4.18
4.17
3.86
3.85
3.84
3.55
3.55
3.54
3.53
3.52
3.52
3.50
3.50
3.49
3.48
1.45
1.43
1.42
-2.83
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
8.0
33.7
17.1
9.0
4.7
33.8
4.2
8.1
18.8
16.6
17.1
32.6
32.7
35.5
1.8

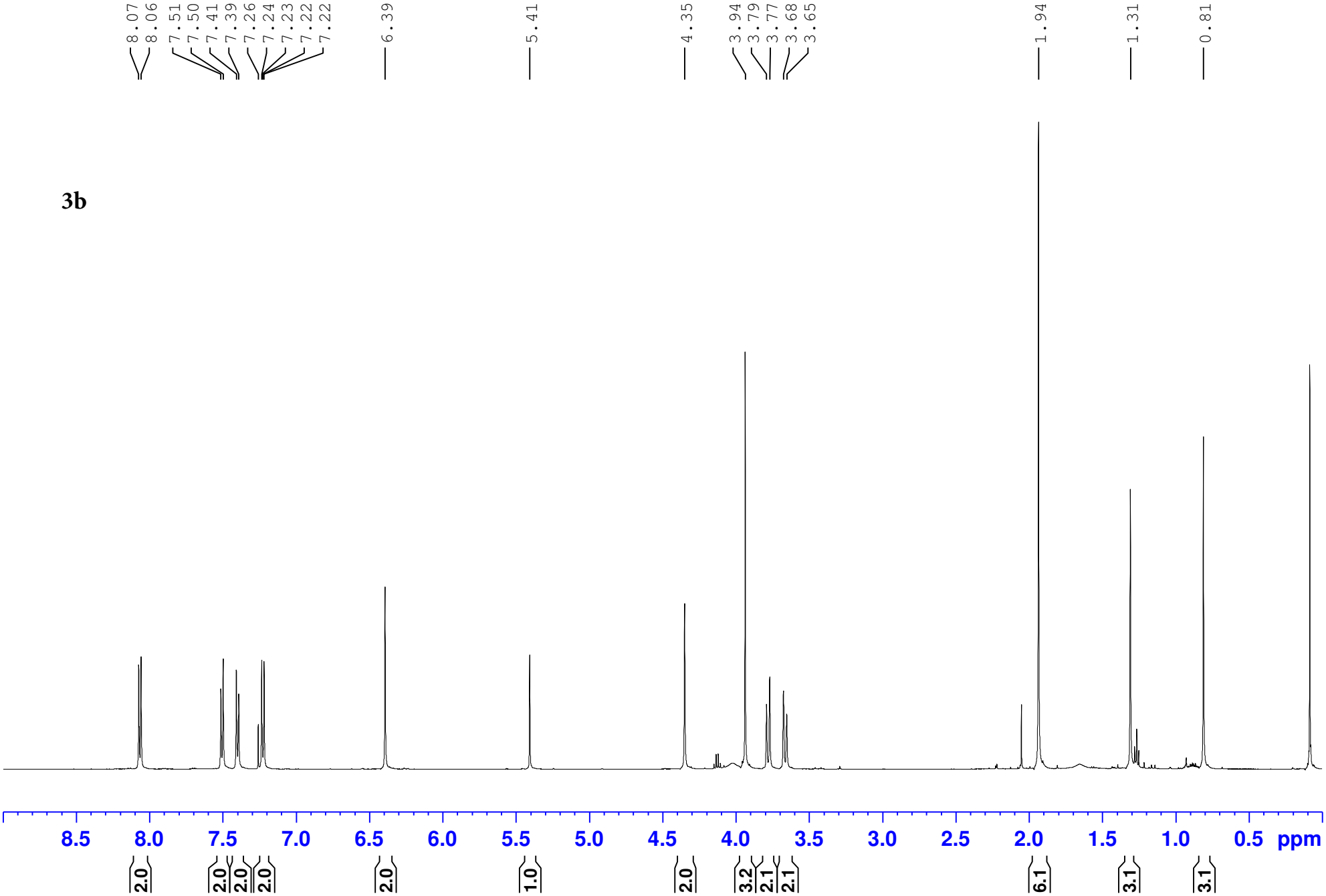
Rotaxane R2

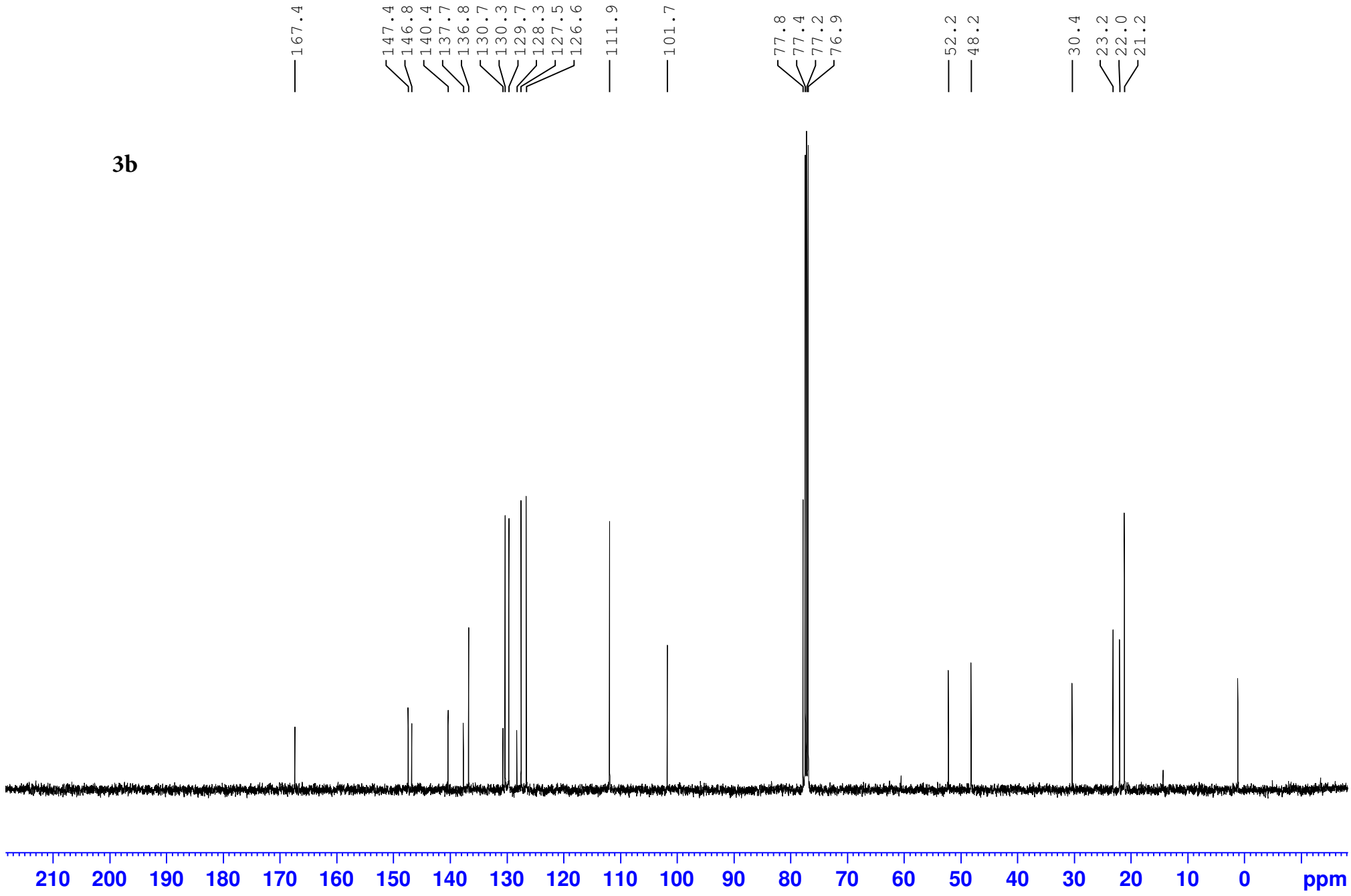

166.9
151.6
148.9
146.8
141.4
140.6
140.0
134.5
130.0
129.2
127.5
127.2
121.2
112.7
112.3
71.0
70.2
68.7
61.2
53.8
47.3
14.6
Rotaxane R2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.55
7.53
7.37
7.36
6.37
5.43
4.27
3.83
3.81
3.70
3.68
2.36
1.36
0.85
3a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.0
1.9
1.8
1.0
1.8
2.0
2.0
5.6
3.0
2.9

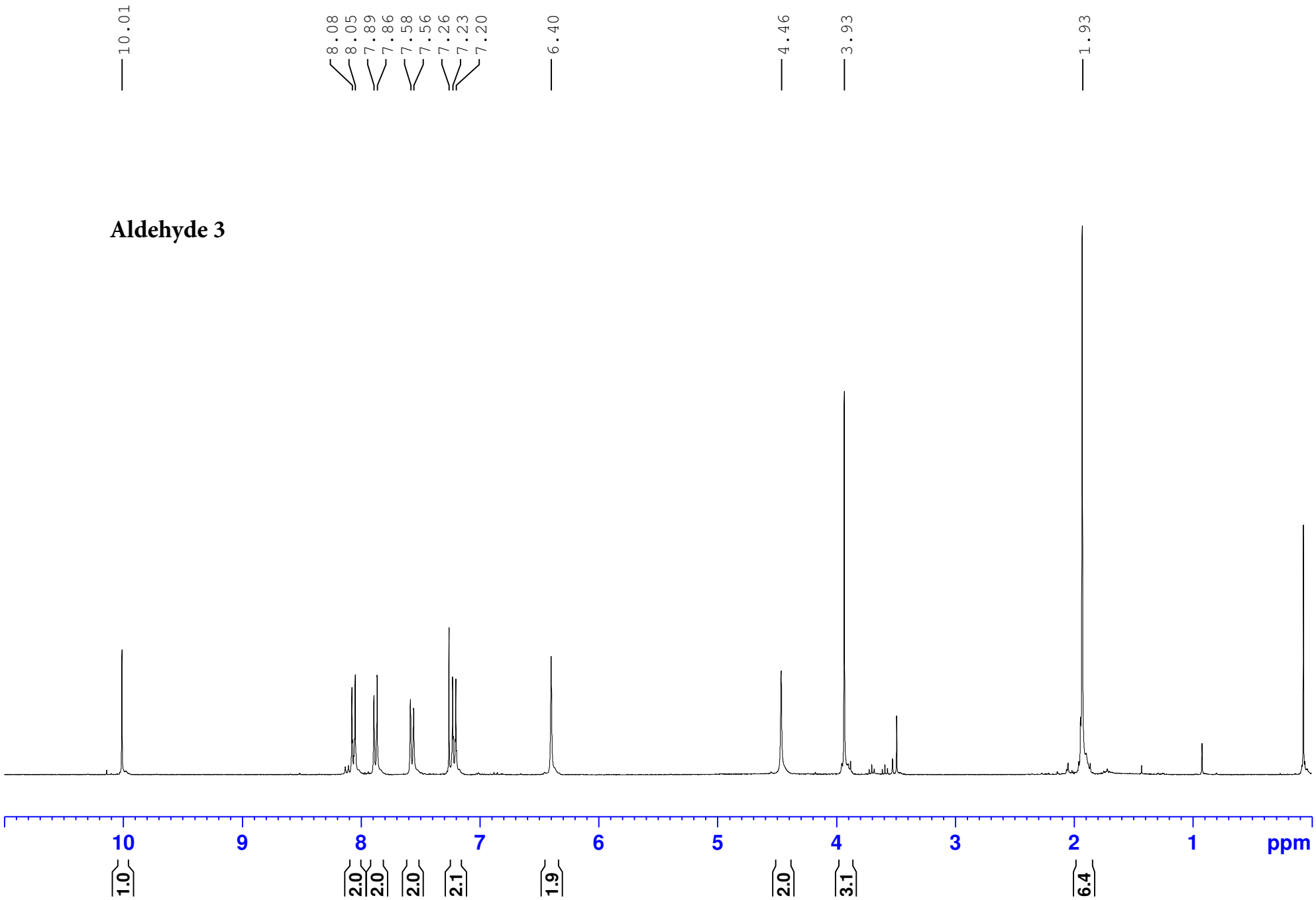

146.7
140.0
138.5
137.5
127.1
126.5
114.7
112.8
101.5
77.6
77.4
77.1
76.9
47.8
30.1
24.0
23.0
21.8
3a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3b

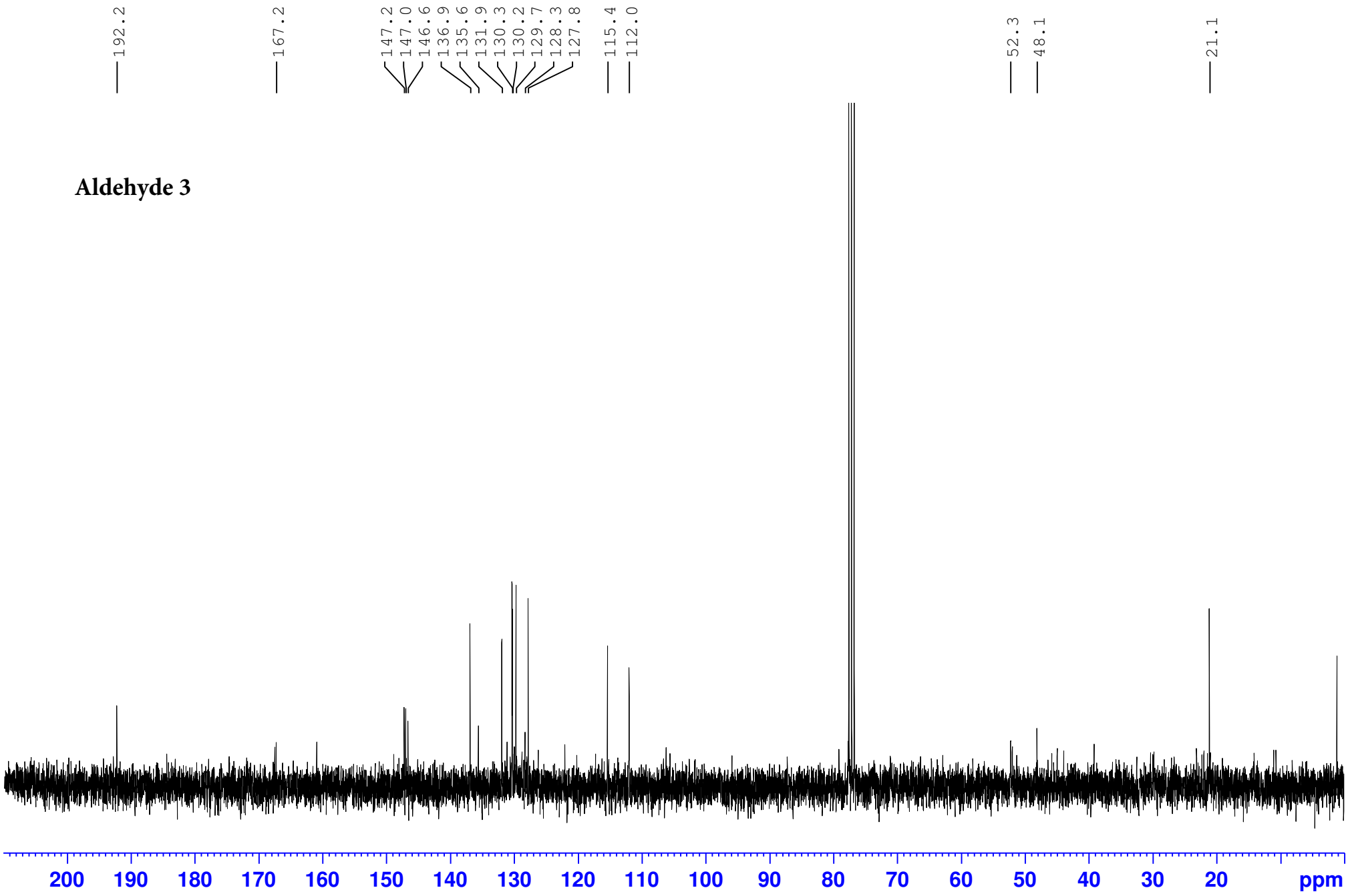

8.07
8.06
7.51
7.50
7.41
7.39
7.26
7.24
7.23
7.22
7.22
6.39
5.41
4.35
3.94
3.79
3.77
3.68
3.65
1.94
1.31
0.81
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.0
2.0
2.0
2.0
2.0
1.0
2.0
3.2
2.1
2.1
6.1
3.1
3.1

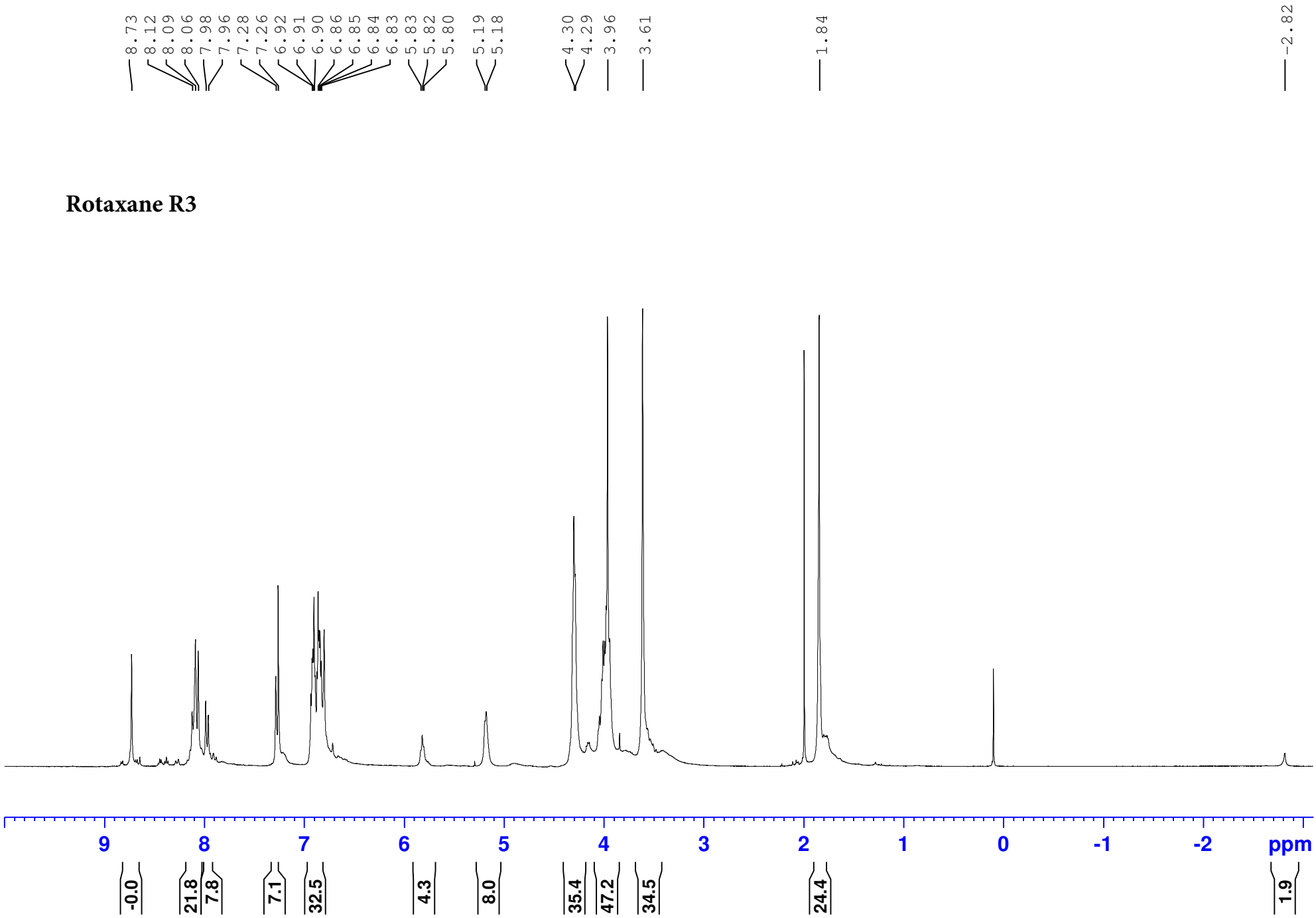

167.4
147.4
146.8
140.4
137.7
136.8
130.7
130.3
129.7
128.3
127.5
126.6
111.9
101.7
77.8
77.4
77.2
76.9
52.2
48.2
30.4
23.2
22.0
21.2
3b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Aldehyde 3

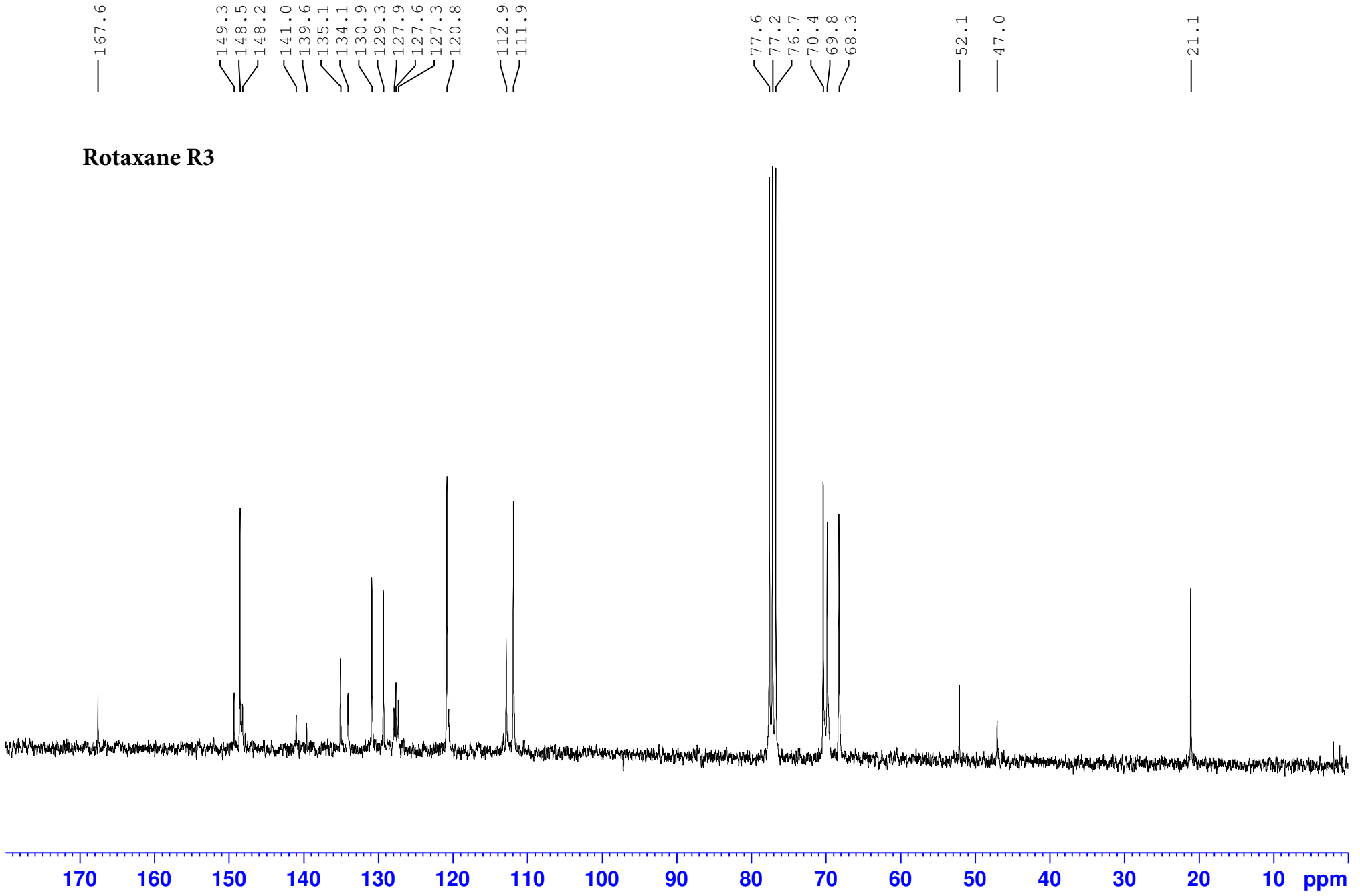

10.01
8.08
8.05
7.89
7.86
7.58
7.56
7.26
7.23
7.20
6.40
4.46
3.93
1.93
10
9
8
7
6
5
4
3
2
1
ppm
1.0
2.0
2.0
2.0
2.1
1.9
2.0
3.1
6.4

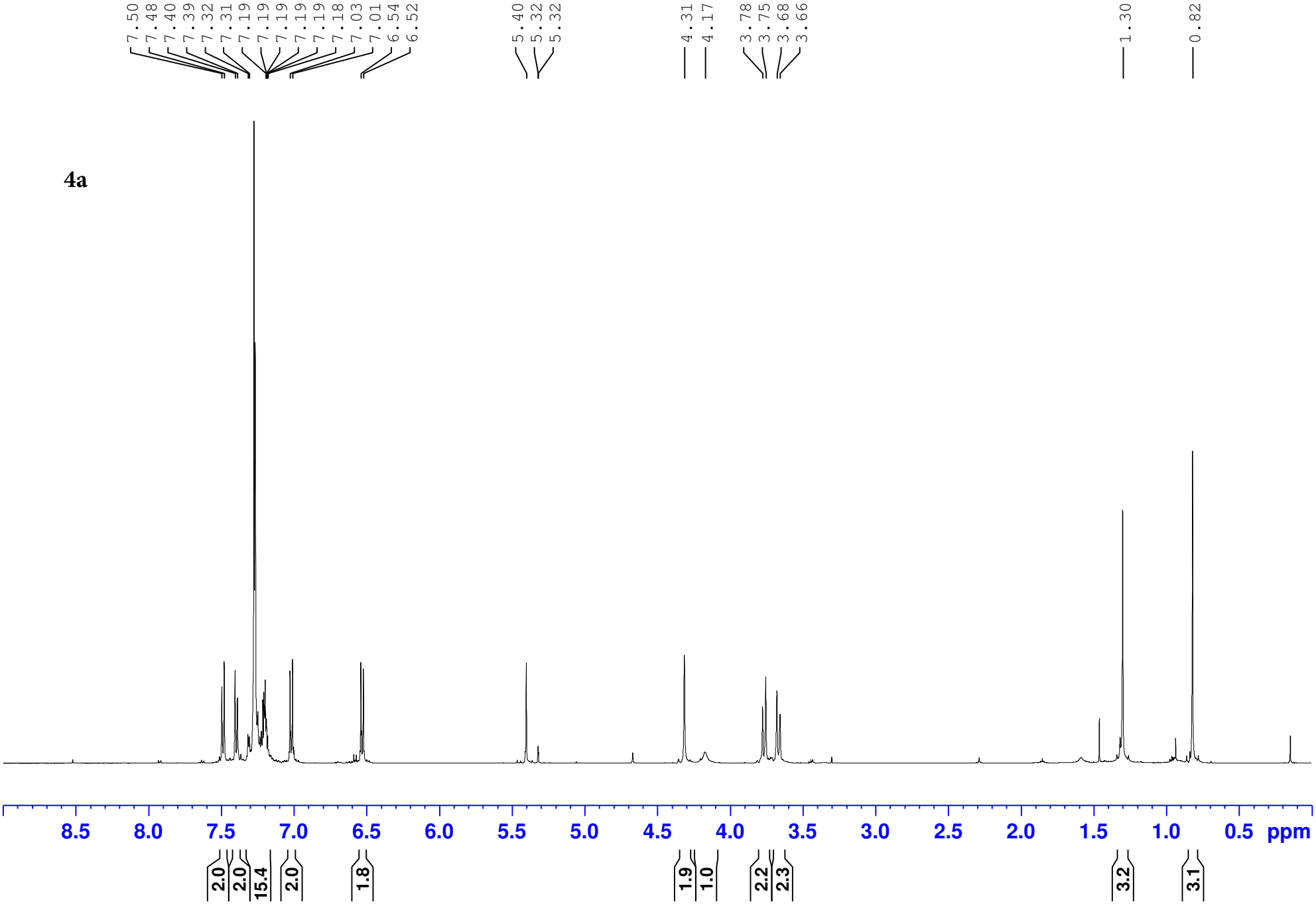
Aldehyde 3

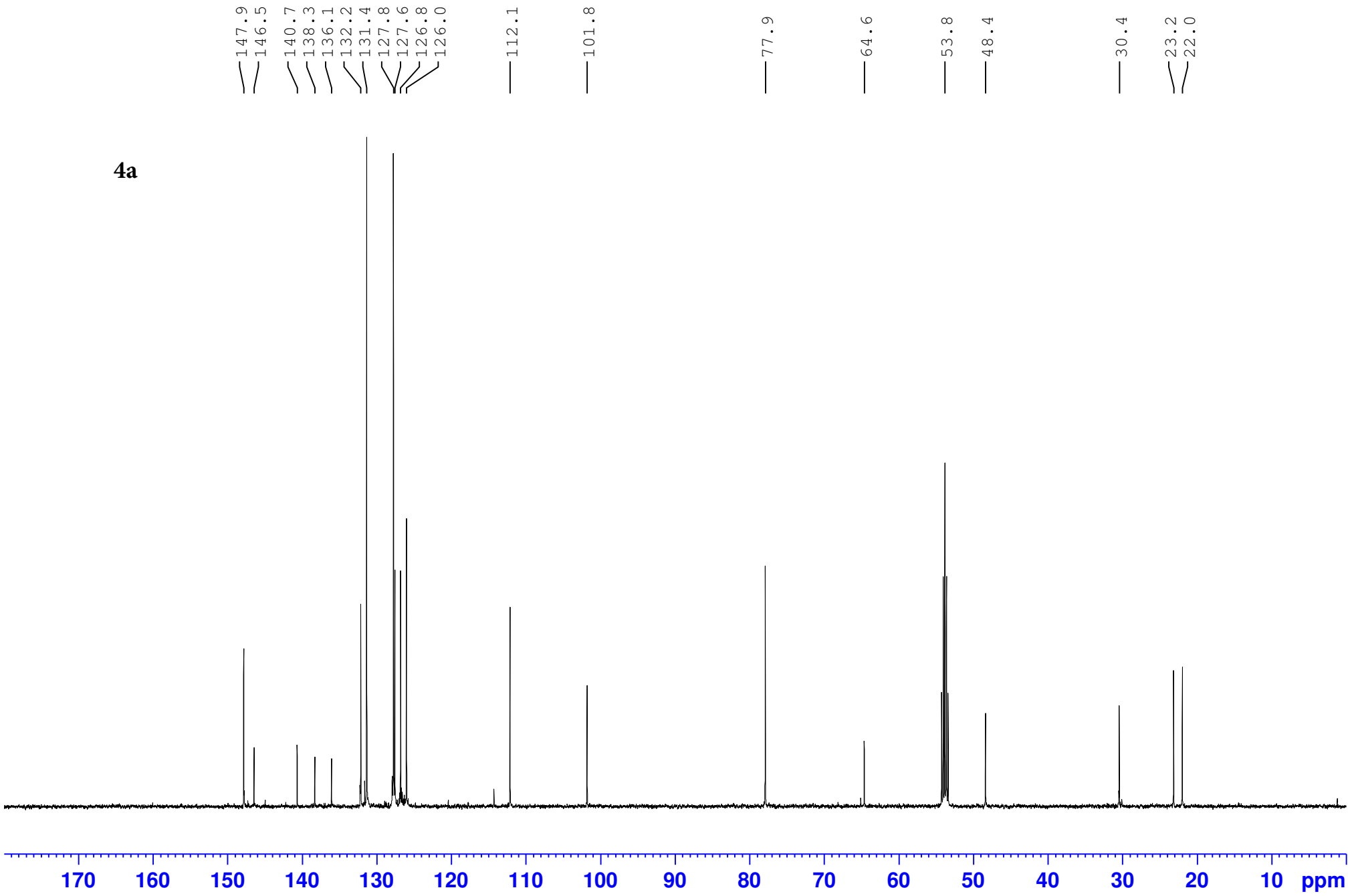

192.2
167.2
147.2
147.0
146.6
136.9
135.6
131.9
130.3
130.2
129.7
128.3
127.8
115.4
112.0
52.3
48.1
21.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

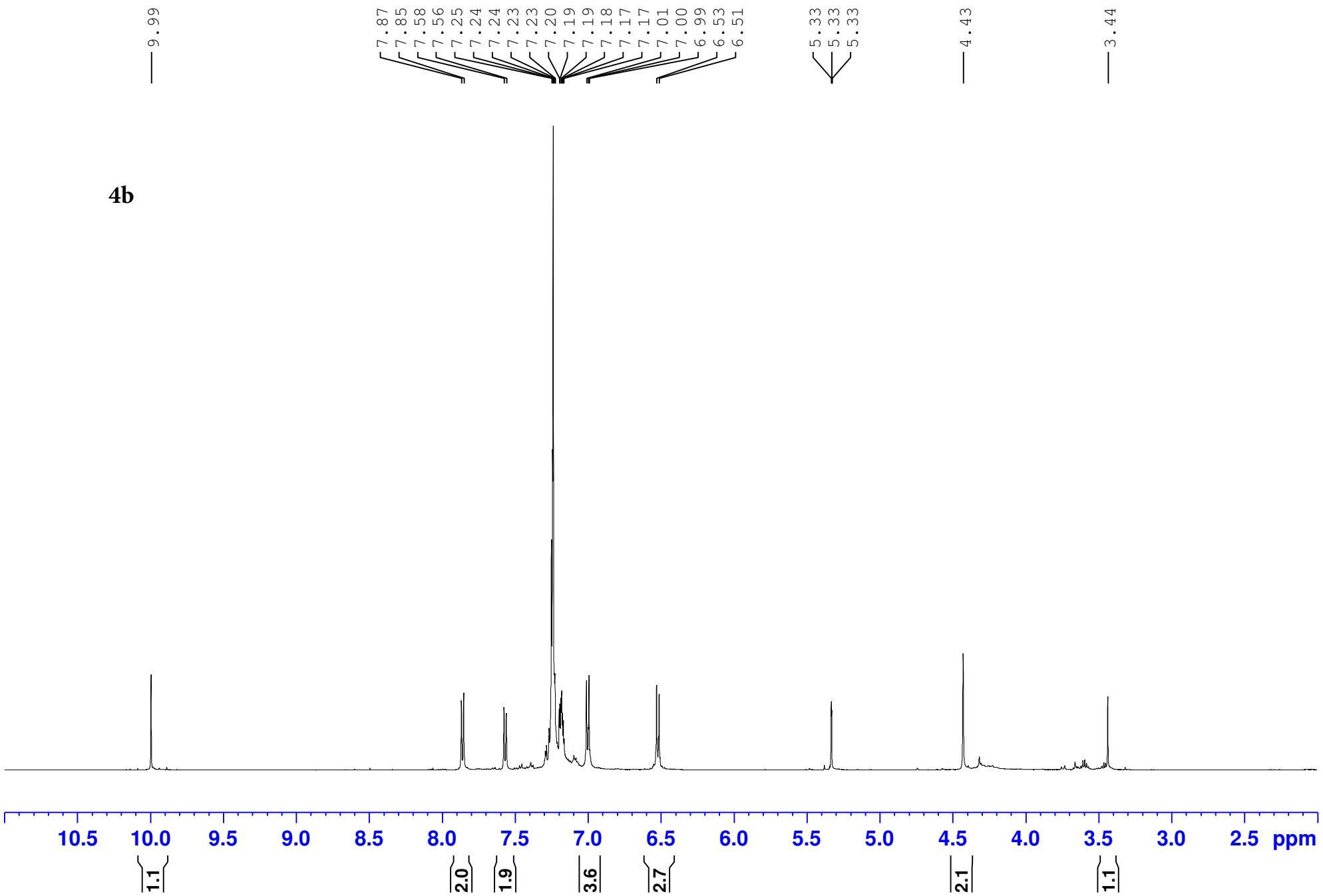

8.73
8.12
8.09
8.06
7.98
7.96
7.28
7.26
6.92
6.91
6.90
6.86
6.85
6.84
6.83
5.83
5.82
5.80
5.19
5.18
4.30
4.29
3.96
3.61
1.84
-2.82
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
-0.0
21.8
7.8
7.1
32.5
4.3
8.0
35.4
47.2
34.5
24.4
1.9

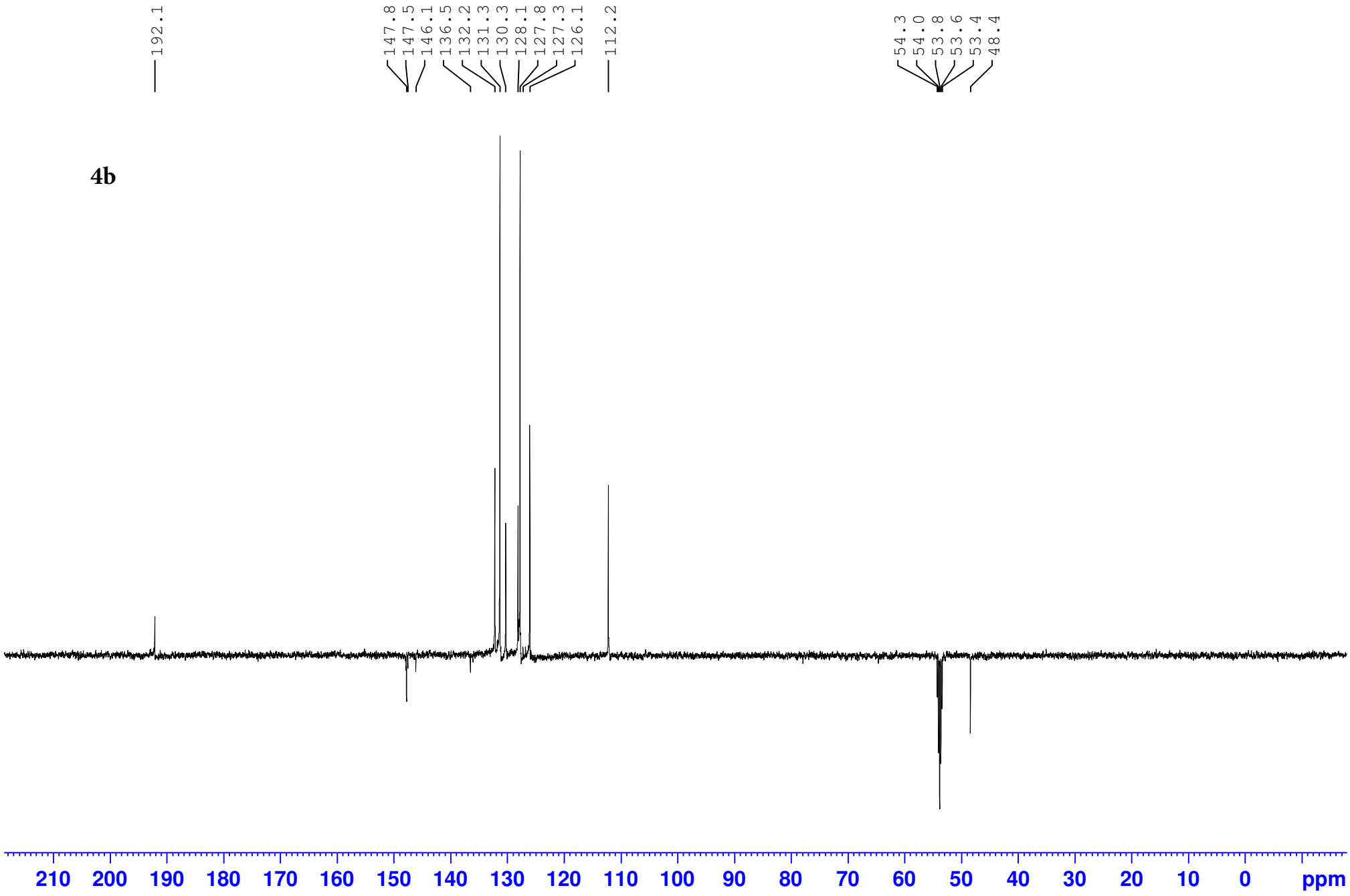
Rotaxane R3


167.6
149.3
148.5
148.2
141.0
139.6
135.1
134.1
130.9
129.3
127.9
127.6
127.3
120.8
112.9
111.9
77.6
77.2
76.7
70.4
69.8
68.3
52.1
47.0
21.1
Rotaxane R3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

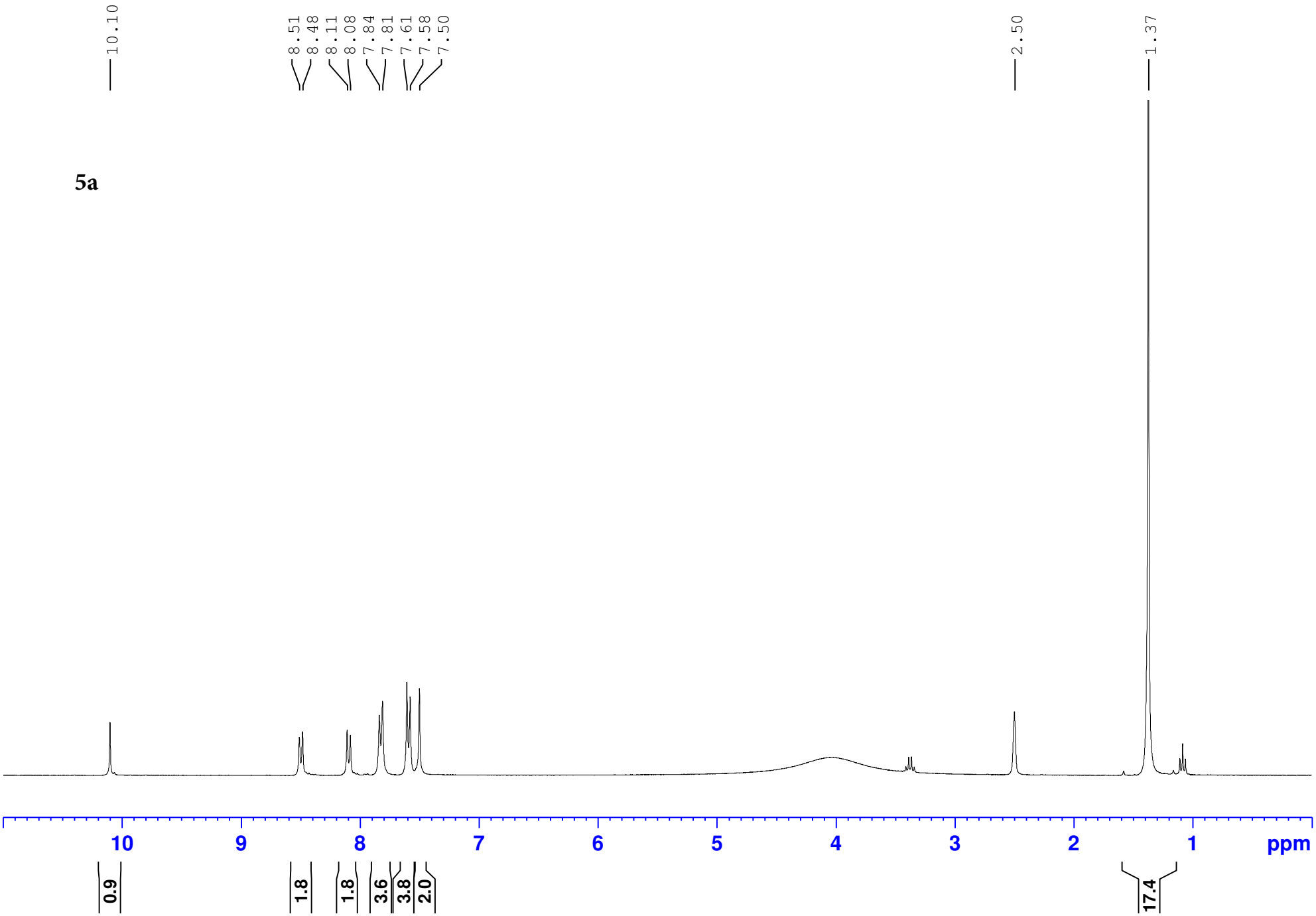

7.50
7.48
7.40
7.39
7.32
7.31
7.19
7.19
7.19
7.19
7.19
7.18
7.03
7.01
6.54
6.52
5.40
5.32
5.32
4.31
4.17
3.78
3.75
3.68
3.66
1.30
0.82
4a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.0
2.0
15.4
2.0
1.8
1.9
1.0
2.2
2.3
3.2
3.1


147.9
146.5
140.7
138.3
136.1
132.2
131.4
127.8
127.6
126.8
126.0
112.1
101.8
77.9
64.6
53.8
48.4
30.4
23.2
22.0
4a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

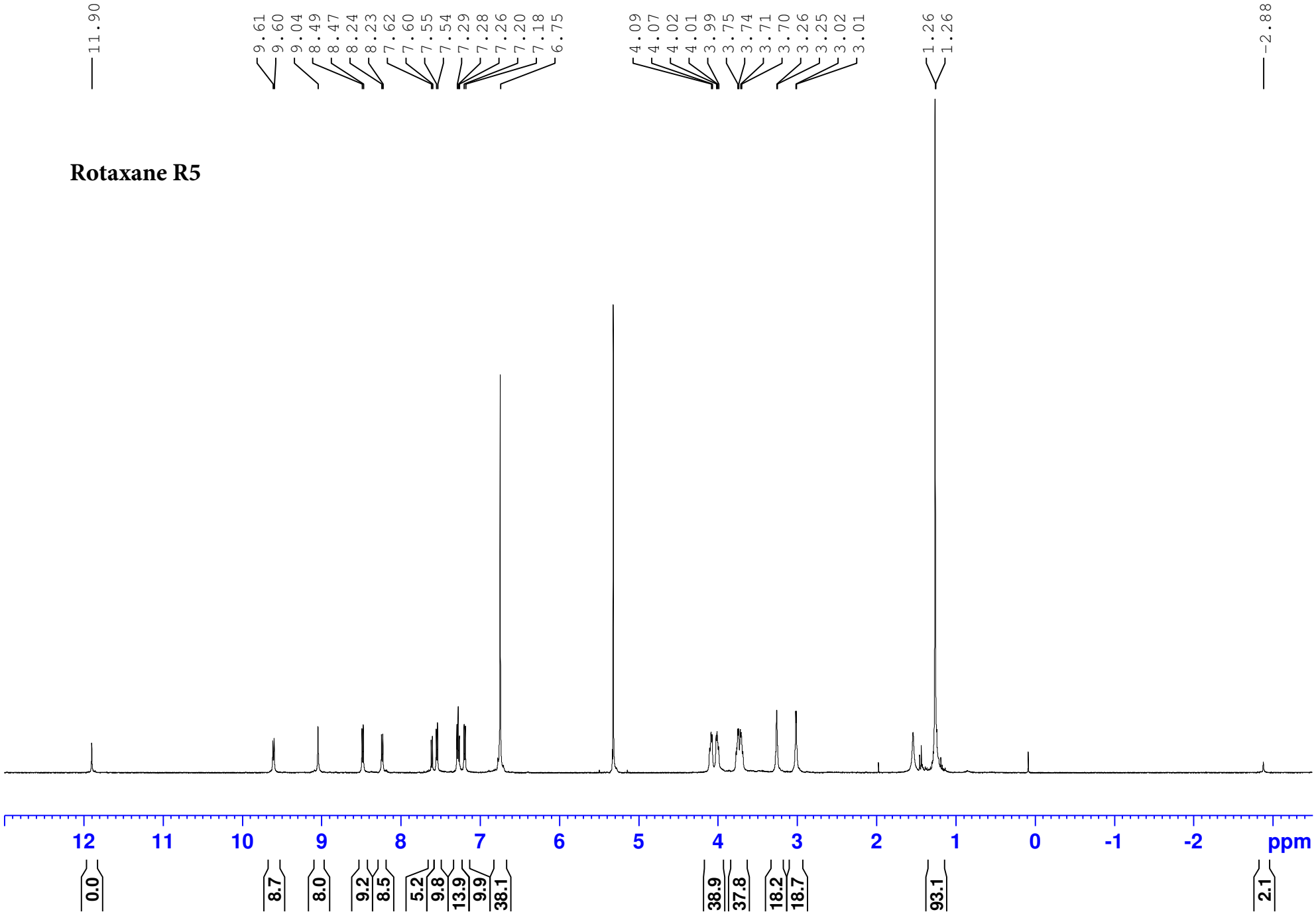

9.99
7.87
7.85
7.58
7.56
7.25
7.24
7.24
7.23
7.23
7.20
7.19
7.19
7.18
7.17
7.17
7.01
7.00
6.99
6.53
6.51
5.33
5.33
5.33
4.43
3.44
4b
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.1
2.0
1.9
3.6
2.7
2.1
1.1

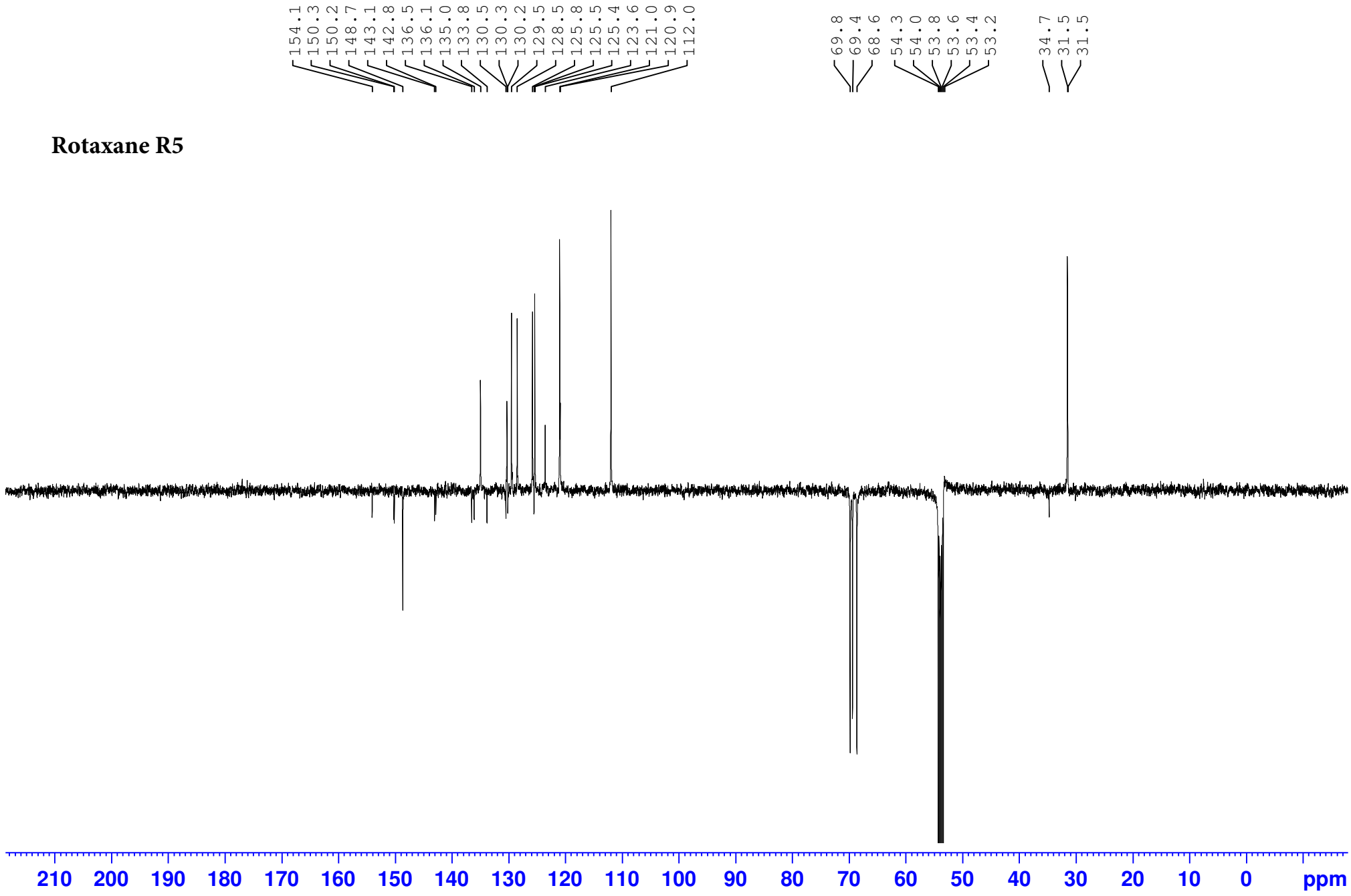

192.1
147.8
147.5
146.1
136.5
132.2
131.3
130.3
128.1
127.8
127.3
126.1
112.2
54.3
54.0
53.8
53.6
53.4
48.4
4b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

5a


10.10
8.51
8.48
8.11
8.08
7.84
7.81
7.61
7.58
7.50
2.50
1.37
10
9
8
7
6
5
4
3
2
1
ppm
0.9
1.8
1.8
3.6
3.8
2.0
17.4

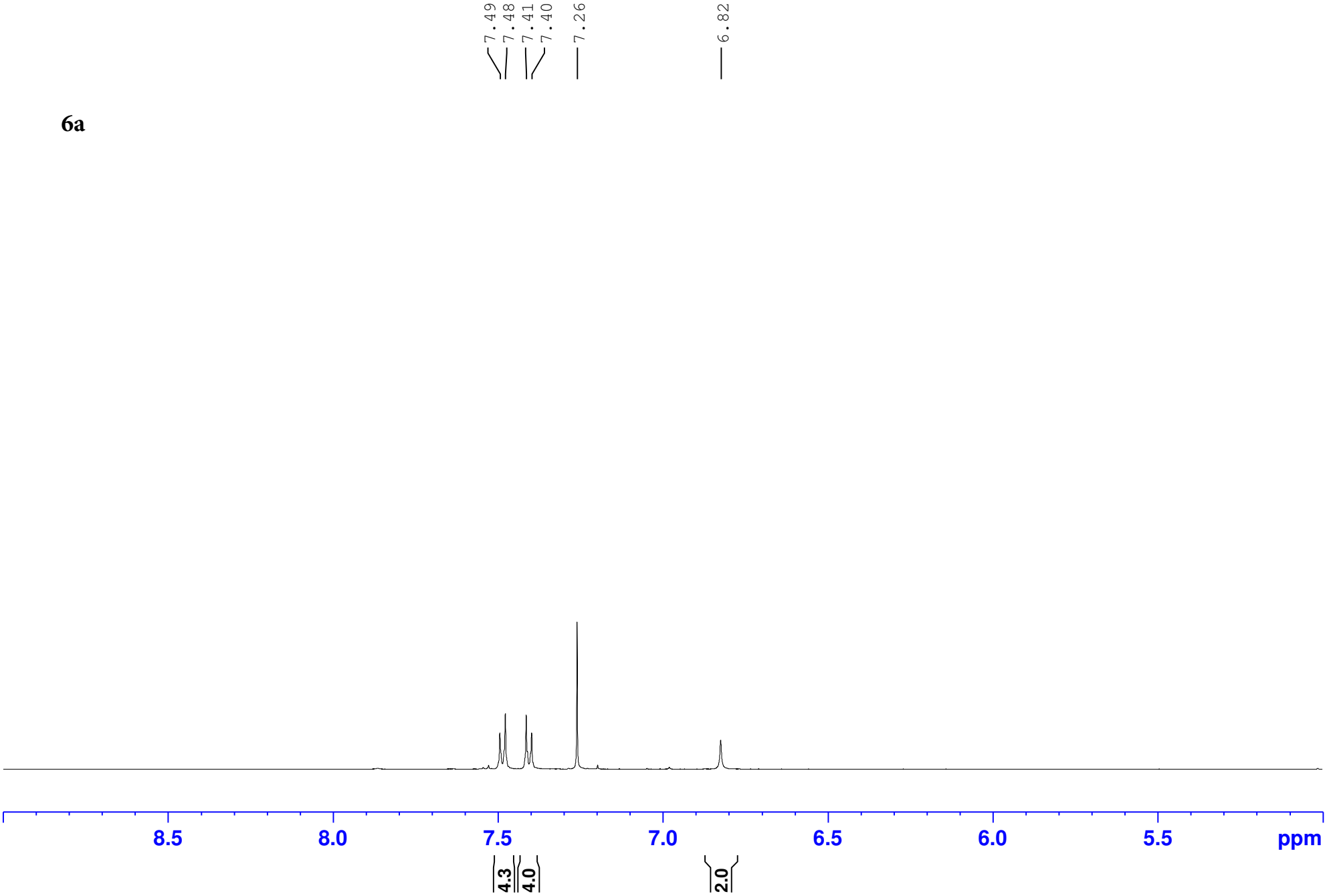
Rotaxane R5

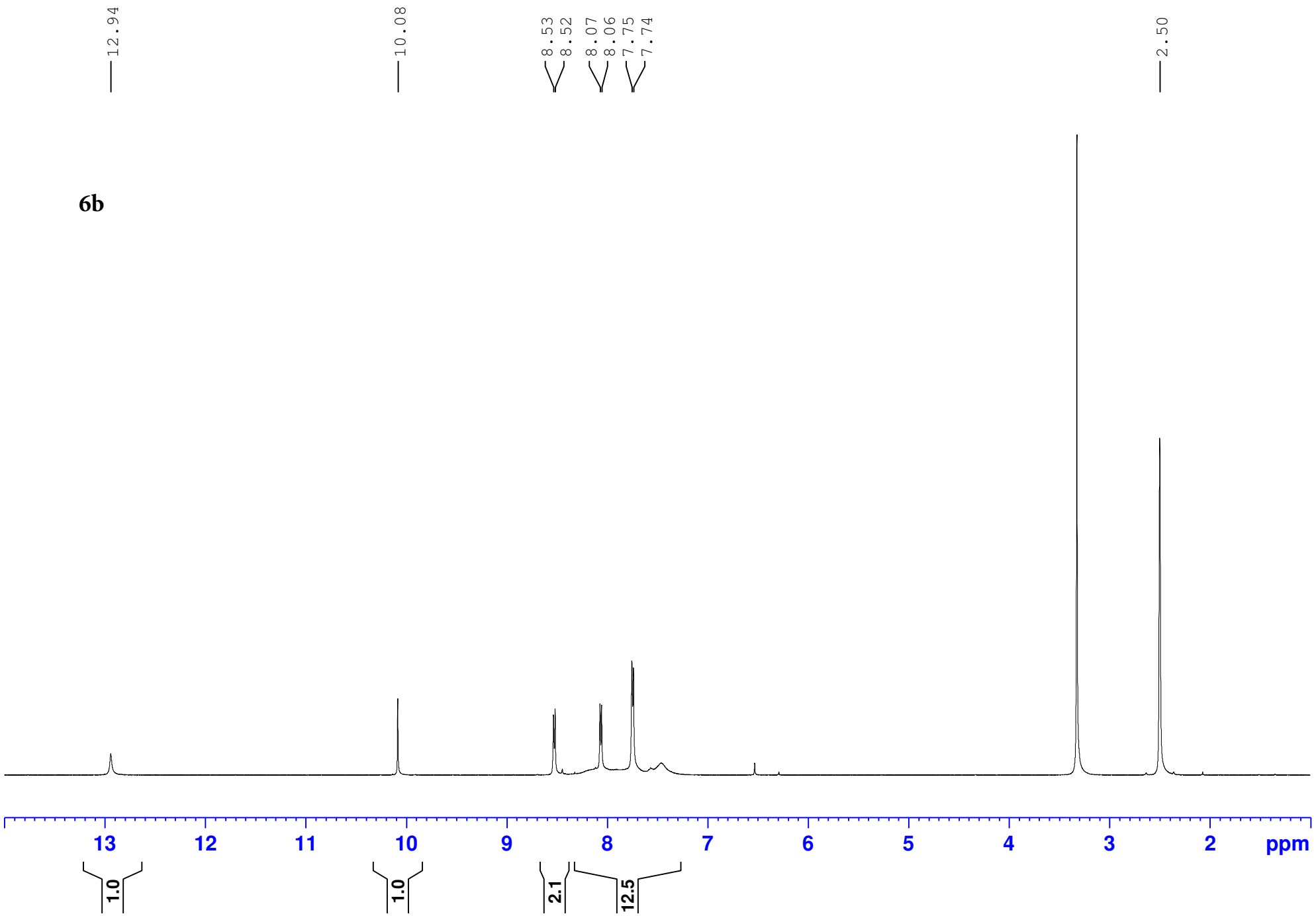

11.90
9.61
9.60
9.04
8.49
8.47
8.24
8.23
7.62
7.60
7.55
7.54
7.29
7.28
7.26
7.20
7.18
6.75
4.09
4.07
4.02
4.01
3.99
3.75
3.74
3.71
3.70
3.26
3.25
3.02
3.01
1.26
1.26
-2.88
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
0.0
8.7
8.0
9.2
8.5
5.2
9.8
13.9
9.9
38.1
38.9
37.8
18.2
18.7
93.1
2.1


154.1
150.3
150.2
148.7
143.1
142.8
136.5
136.1
135.0
133.8
130.5
130.3
130.2
129.5
128.5
125.8
125.5
125.4
123.6
121.0
120.9
112.0
69.8
69.4
68.6
54.3
54.0
53.8
53.6
53.4
53.2
34.7
31.5
31.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Rotaxane R5

6a




12.94
10.08
8.53
8.52
8.07
8.06
7.75
7.74
2.50
6b
13
12
11
10
9
8
7
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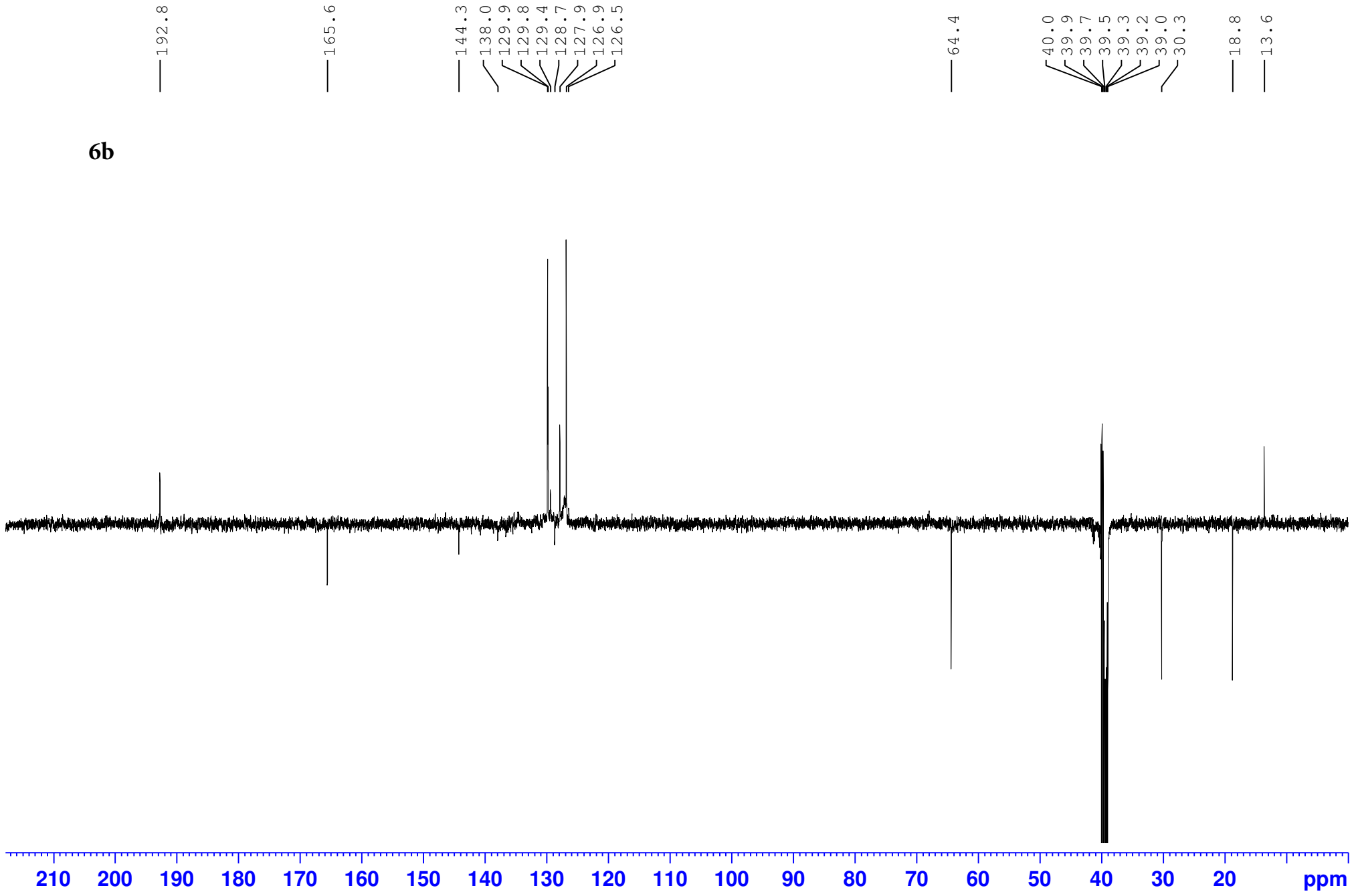
12.5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144.3
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129.9
129.8
129.4
128.7
127.9
126.9
126.5
64.4
40.0
39.9
39.7
39.5
39.3
39.2
39.0
30.3
18.8
13.6
6b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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40
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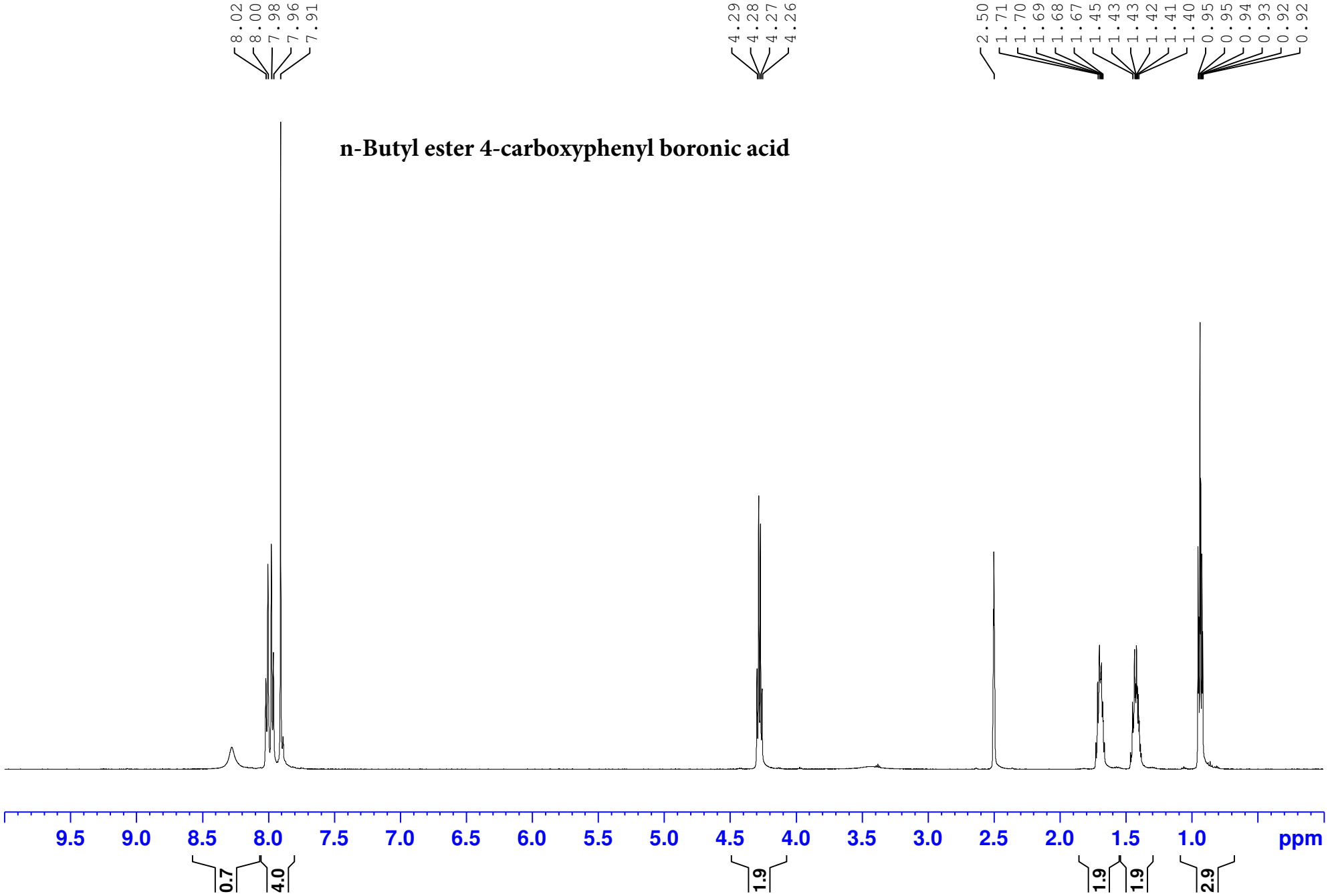
ppm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7.91
4.29
4.28
4.27
4.26
2.50
1.71
1.70
1.69
1.68
1.67
1.45
1.43
1.43
1.42
1.41
1.40
0.95
0.95
0.94
0.93
0.92
0.92
n-Butyl ester 4-carboxyphenyl boronic acid
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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ppm
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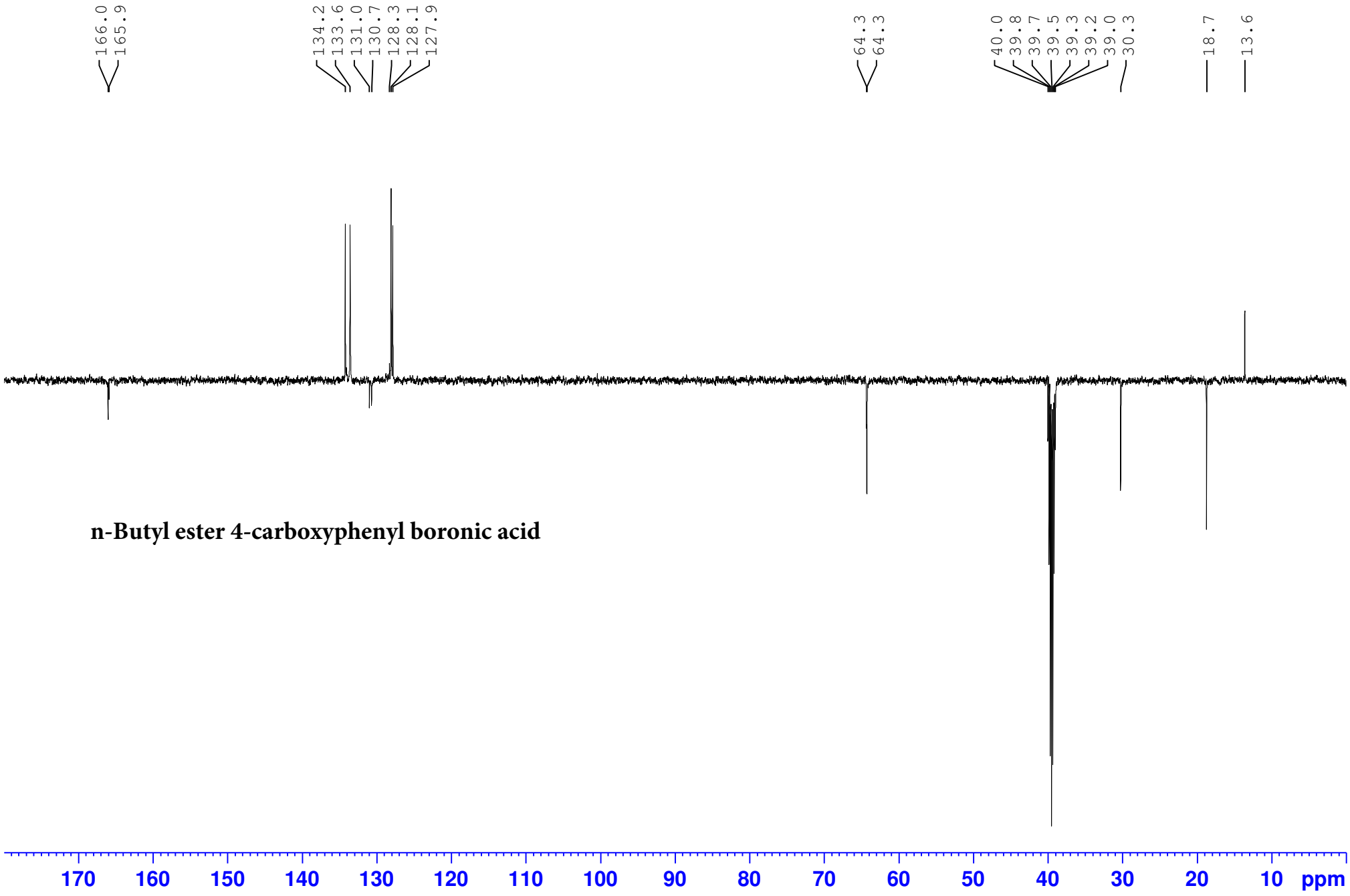
2.9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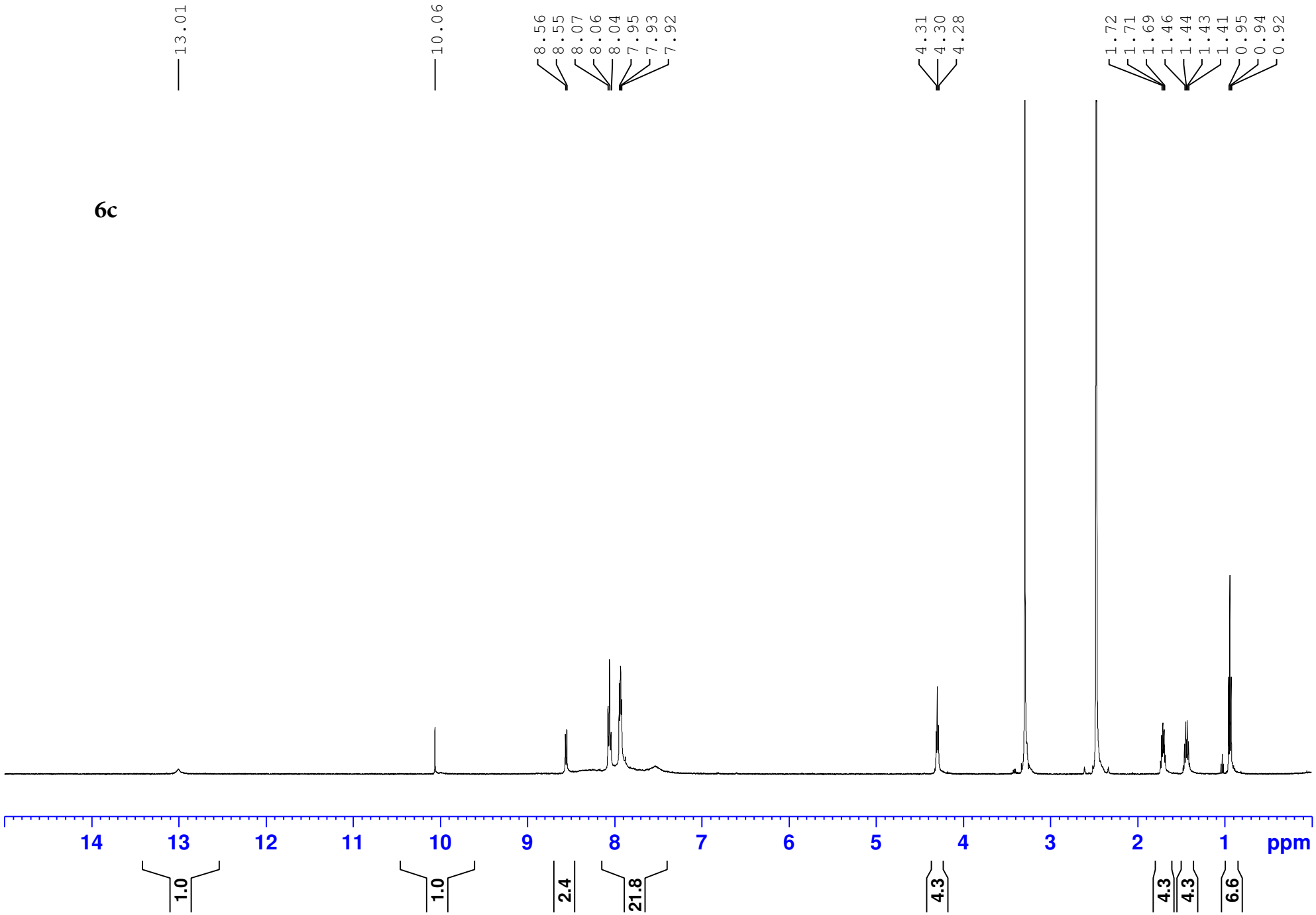
165.9
134.2
133.6
131.0
130.7
128.3
128.1
127.9
64.3
64.3
40.0
39.8
39.7
39.5
39.3
39.2
39.0
30.3
18.7
13.6
n-Butyl ester 4-carboxyphenyl boronic acid
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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10.06
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8.55
8.07
8.06
8.04
7.95
7.93
7.92
4.31
4.30
4.28
1.72
1.71
1.69
1.46
1.44
1.43
1.41
0.95
0.94
0.92
6c
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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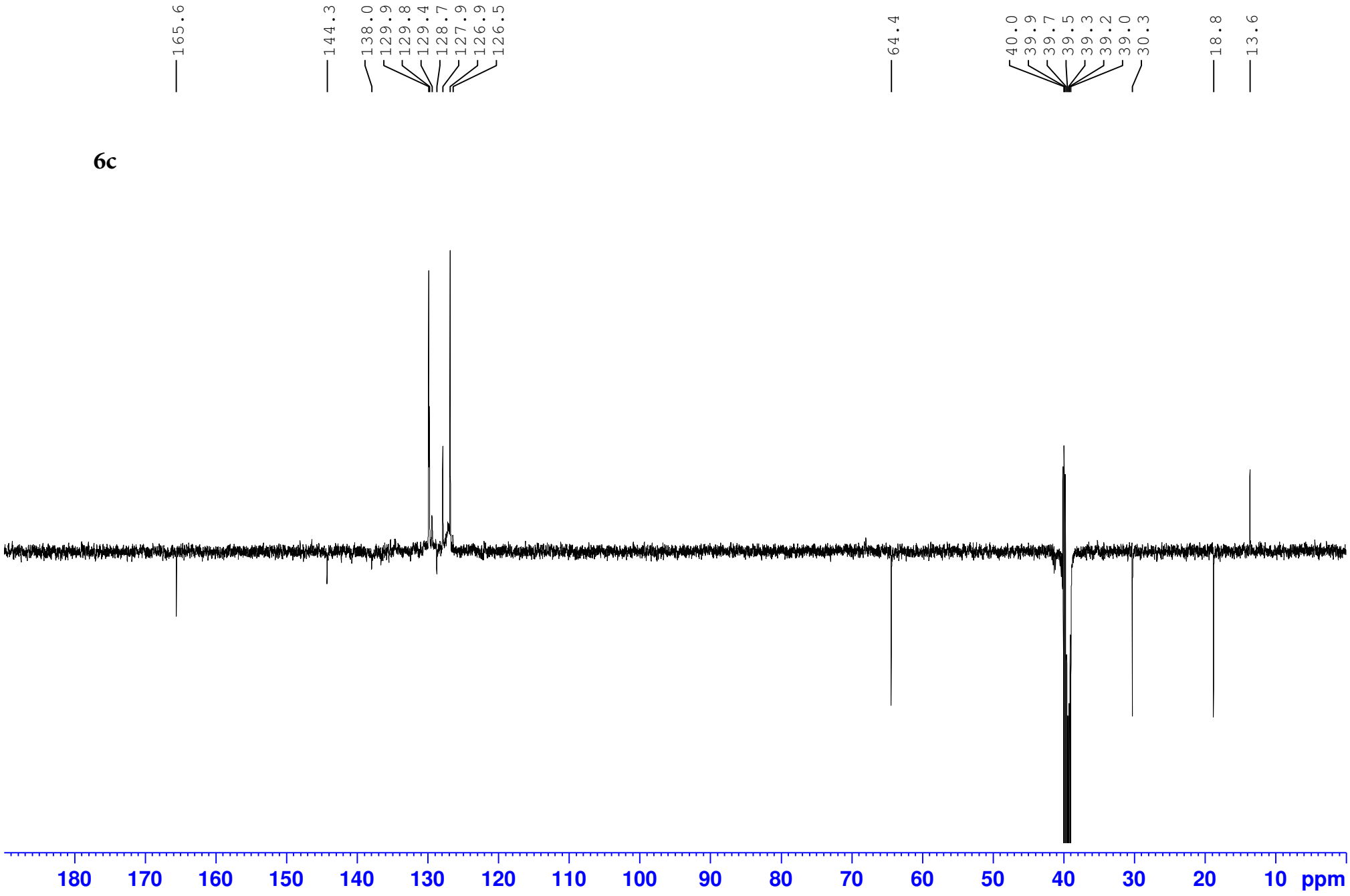
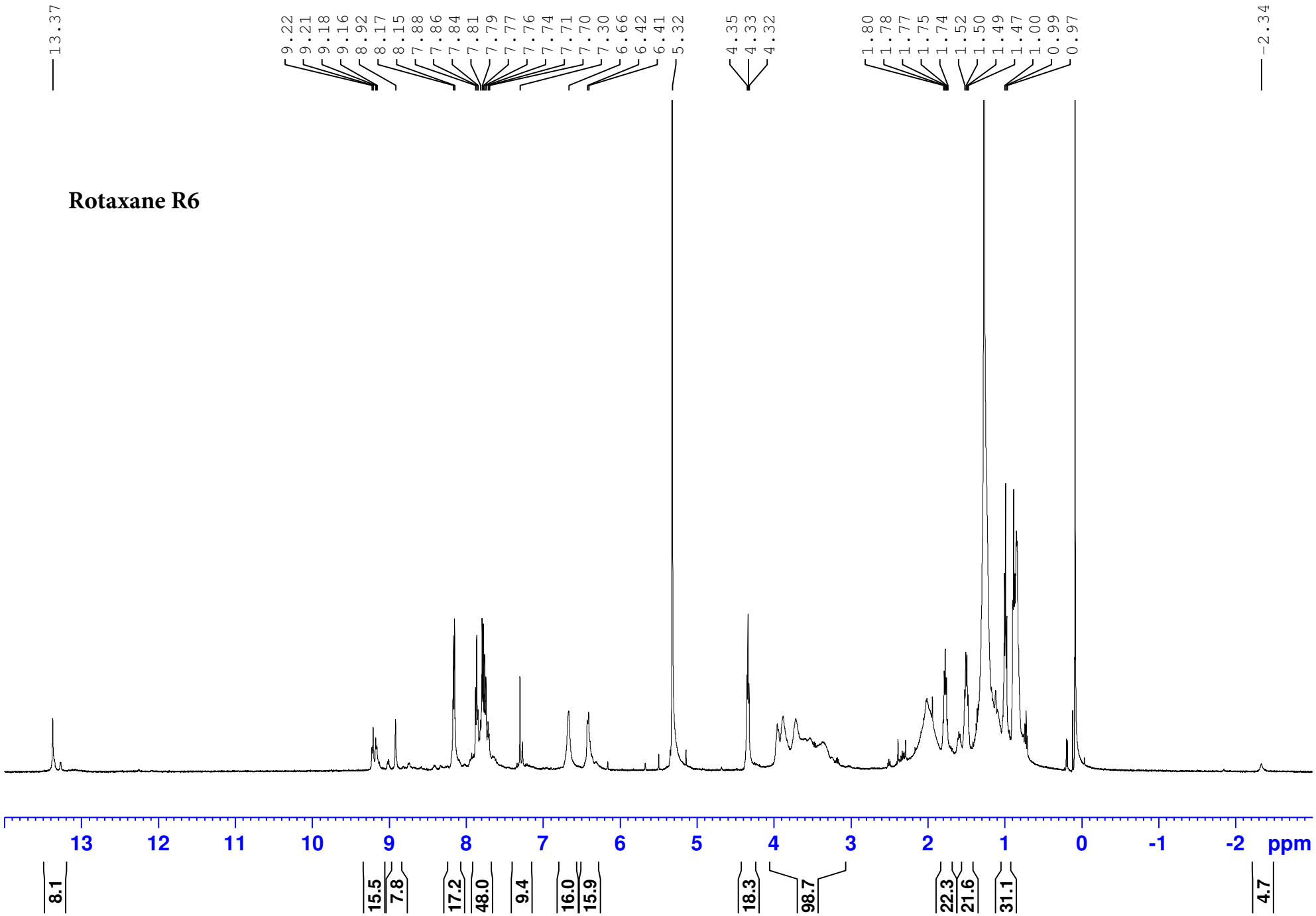
1.0
2.4
21.8
4.3
4.3
4.3
6.6


165.6
144.3
138.0
129.9
129.8
129.4
128.7
127.9
126.9
126.5
64.4
40.0
39.9
39.7
39.5
39.3
39.2
39.0
30.3
18.8
13.6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

6c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9.18
9.16
8.92
8.17
8.15
7.88
7.86
7.84
7.81
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7.77
7.76
7.74
7.71
7.70
7.30
6.66
6.42
6.41
5.32
4.35
4.33
4.32
1.80
1.78
1.77
1.75
1.74
1.52
1.50
1.49
1.47
1.00
0.99
0.97
-2.34
Rotaxane R6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
8.1
15.5
7.8
17.2
48.0
9.4
16.0
15.9
18.3
98.7
22.3
21.6
31.1
4.7