Supporting Information for

Supramolecular Polymer Nanowires: Preparation and Orthogonal Modification of Their Photophysical Properties

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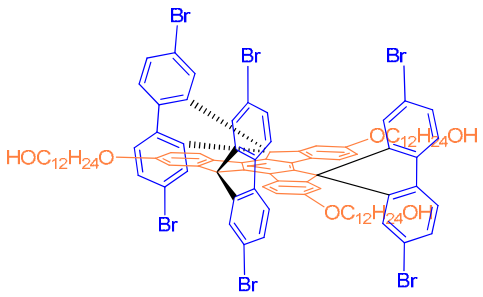
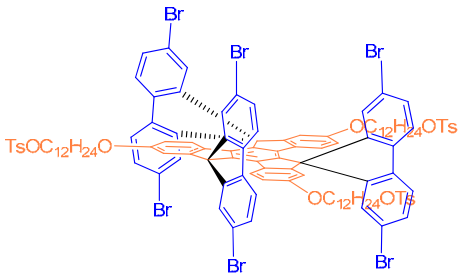
1. Synthetic Procedures and Characterization

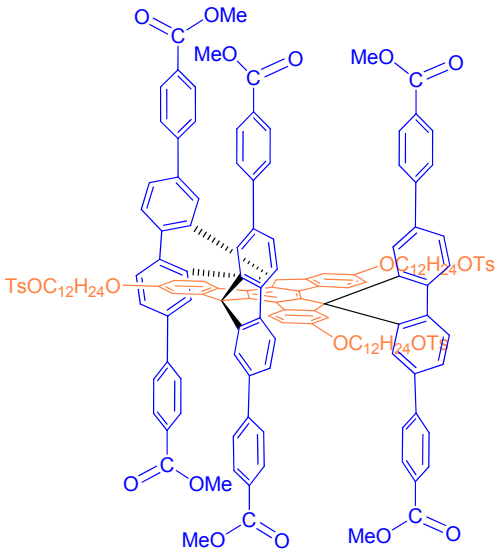
Compound **TPPOH**, **TPABTOH**, **HexBTOH**, **MeBTOH** and **DHBT** were synthesized according to the literature. [1-5]



Compound **3**. A suspension of **2** (450 mg, 0.34 mmol) in DMF (40 mL) was added K_2CO_3 (567 mg, 4.11 mmol) and heated to 100□ under nitrogen atmosphere. After 1 h, a solution of 12-bromododecanol (300 mg, 1.13 mmol) in DMF (10 mL) was added to the mixture slowly and then the mixture was stirred over night. The mixture was concentrated under reduced pressure. The residue was added dilute hydrochloric acid and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, and then dried with Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by column chromatography over silica gel (CH_2Cl_2 : EtOAc = 5:1) to afford compound **3** as a white solid in 79% yield (505 mg). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.80-7.77 (d, J = 8.1 Hz, 6H), 7.54-7.51 (dd, J = 8.1, 1.5 Hz, 6H), 7.00-6.99 (d, J = 1.5 Hz, 6H), 6.31-6.30 (d, J = 8.7 Hz, 3H), 6.22-6.18 (dd, J = 9.0, 2.4 Hz, 3H), 5.83-5.82 (d, J = 2.4 Hz, 3H), 3.66-3.59 (m, 12H), 1.58-1.52 (m, 6H), 1.28-1.22 (m, 54H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.9, 150.7, 150.1, 141.7, 139.4, 136.2, 131.4, 130.6, 127.0, 124.8, 122.7, 121.7, 112.4, 109.2, 67.8, 66.2, 63.1, 32.8, 29.53, 29.49, 29.48, 29.43, 29.37, 29.30, 29.12, 25.90, 25.70, 25.68. MALDI-TOF MS: Calcd for $C_{99}H_{102}Br_6O_6$, 1867.3; Found, 1867.6.



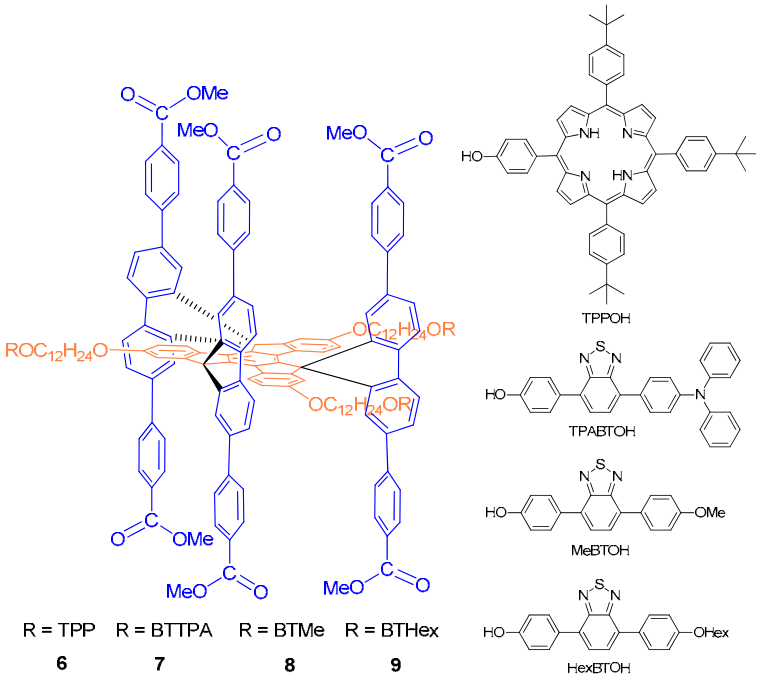
Compound **4**. To a solution of *p*-toluenesulfonyl chloride (620 mg, 3.25 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a mixture of **3** (505 mg, 0.27 mmol) and DMAP (5 mg) in CH_2Cl_2/NEt_3 (30 mL/10 mL) in ice bath. After stirred at room temperature for 5 h, the mixture was neutralized with dilute hydrochloric acid and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, and then dried with Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by column chromatography over silica gel (PE : CH_2Cl_2 = 1:1 to CH_2Cl_2) to afford **4** as a white solid in 66% yield (414 mg). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.80-7.78 (d, *J* = 8.1 Hz, 12H), 7.54-7.51 (dd, *J* = 8.1, 1.8 Hz, 6H), 7.35-7.33 (d, *J* = 8.1 Hz, 6H), 7.00-6.99 (d, *J* = 1.5 Hz, 6H), 6.31-6.28 (d, *J* = 9.0 Hz, 3H), 6.22-6.19 (dd, *J* = 9.0, 2.7 Hz, 3H), 5.83-5.82 (d, *J* = 2.4 Hz, 3H), 4.04-4.00 (t, *J* = 6.3 Hz, 6H), 3.63-3.59 (t, *J* = 6.6 Hz, 6H), 2.44 (s, 9H), 1.65-1.52 (m, 6H), 1.24-1.18 (m, 54H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 159.2, 150.8, 150.3, 144.5, 141.9, 139.6, 136.3, 133.8, 131.5, 130.7, 129.8, 127.9, 127.1, 124.9, 122.7, 121.7, 112.9, 109.2, 70.6, 68.0, 66.4, 29.41, 29.38, 29.29, 29.18, 28.91, 28.88, 25.9, 25.4, 21.5. MALDI-FTICR MS: Calcd. for $[C_{120}H_{120}Br_6O_{12}S_3 + Na]^+$, 2352.2912; Found, 2352.3009



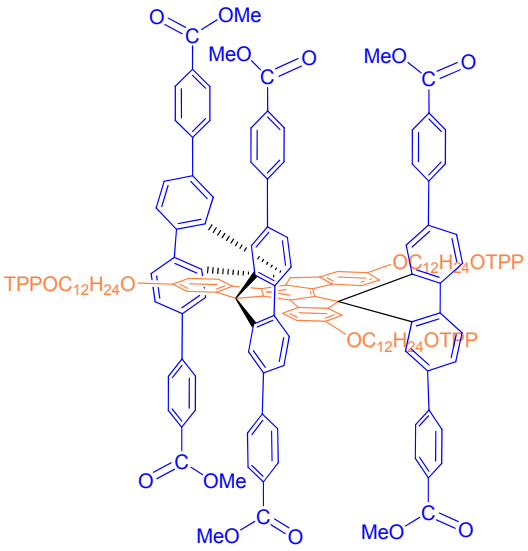
Compound **5**. A well-degassed solution of **4** (200 mg, 0.086 mmol) and 4-(methoxycarbonyl)phenylboronic pinacol ester (180 mg, 0.69 mmol) in THF (30 mL) was added premixed solution of $Pd_2(dba)_3$ (20 mg) and PCy_3 (30 mg) in THF (5 mL) and 3 mL of aqueous K_2CO_3 solution (355 mg, 2.57 mmol) under nitrogen atmosphere. After refluxed for 20 h under nitrogen atmosphere, the mixture was added water and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, and then dried with Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by column chromatography over silica gel (PE : CH_2Cl_2 : EtOAc = 10 : 4 : 1 to 3 : 3 : 1) to afford **5** as a white solid in 73% yield (167 mg). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.10-8.07 (d, J = 7.8 Hz, 6H), 7.79-7.76 (d, J = 8.1 Hz, 6H), 7.70-7.66 (dd, J = 9.3, 0.9 Hz, 6H), 7.64-7.62 (d, J = 8.1 Hz, 12H), 7.33-7.30 (d, J = 8.4 Hz, 18H), 7.17 (d, J = 1.2 Hz, 6H), 6.49-6.46 (d, J = 8.7 Hz, 3H), 6.22-6.18 (dd, J = 8.7, 2.1 Hz, 3H), 5.95-5.94 (d, J = 2.4 Hz, 3H), 4.02-3.97 (t, J = 6.3 Hz, 6H), 3.86 (s, 18H), 3.58-3.54 (t, J = 6.0 Hz, 6H), 2.42 (s, 9H), 1.64-1.55 (m, 6H), 1.50-1.43 (m, 6H), 1.25-1.13 (m, 48H). ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): δ 166.5, 158.6, 151.8, 149.8, 144.8, 144.6, 141.7, 141.1, 140.3, 137.3, 133.2, 131.1, 130.0, 129.7, 128.8,

127.8, 127.7, 126.6, 125.2, 122.0, 121.1, 112.1, 109.2, 70.7, 67.7, 66.9, 51.9, 29.35, 29.26, 29.1, 28.8, 28.7, 25.9, 25.2, 21.6. MALDI-TOF MS: Calcd. for $C_{168}H_{162}O_{24}S_3$, 2660.0; Found, 2660.4.

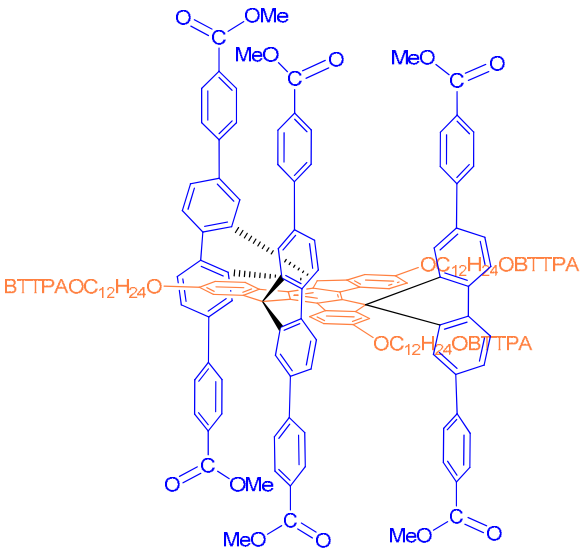
General Procedures for the Synthesis Compound 6, 7, 8 and 9



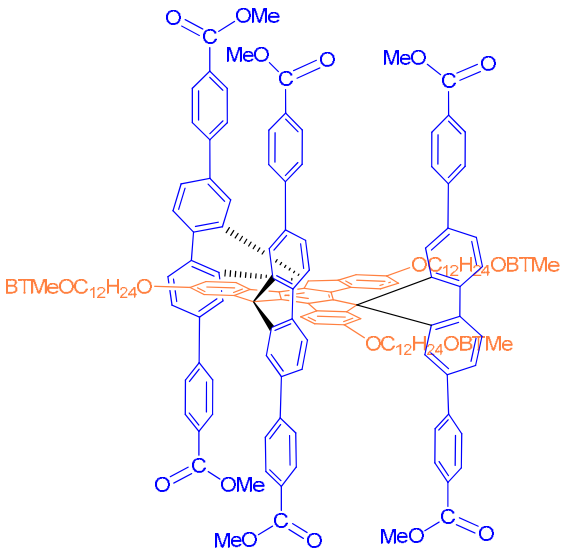
To a solution of **5** (0.038 mmol) in DMF (20 mL) was added **TPPOH**, **TPABTOH**, **MeBTOH**, or **HexBTOH** (0.15 mmol), K_2CO_3 (0.38 mmol) and KI (10 mg). After stirred at 80 ^oC under nitrogen atmosphere overnight, the mixture was concentrated under reduced pressure. The residue was added dilute hydrochloric acid and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, and then dried with Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by column chromatography over silica gel (CH_2Cl_2 to CH_2Cl_2 : EtOAc = 50 : 1).



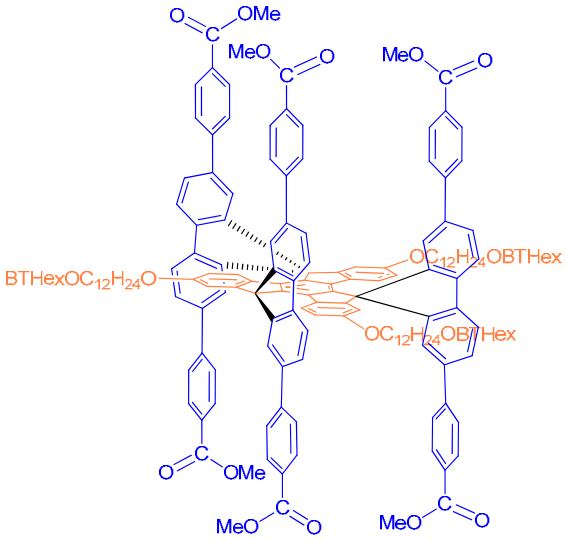
Compound **6** (Yield: 39%)**.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.87 (s, 24H), 8.15-8.09 (m, 24H), 7.94-7.91 (d, *J* = 7.8 Hz, 6H), 7.76-7.73 (d, *J* = 7.8 Hz, 18H), 7.62-7.56 (m, 18H), 7.29-7.23 (m, 18H), 7.14 (s, 6H), 6.44-6.41 (d, *J* = 9.0 Hz, 3H), 6.19-6.16 (d, *J* = 8.7 Hz, 3H), 5.92 (s, 3H), 4.21-4.17 (t, *J* = 6.3 Hz, 6H), 3.84 (s, 18H), 3.57-3.53 (t, *J* = 6.0 Hz, 6H), 1.98-1.88 (m, 6H), 1.59 (m, 81H), 1.25-1.19 (m, 60H), -2.74(s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.5, 158.9, 158.7, 150.4, 149.8, 144.8, 141.0, 140.2, 139.2, 137.3, 135.6, 134.5, 131.1, 130.0, 128.8, 127.6, 126.6, 123.6, 122.0, 121.0, 120.2, 119.9, 112.7, 68.2, 67.8, 66.9, 51.9, 34.9, 31.7, 29.7, 29.55, 29.52, 29.45, 29.36, 29.2, 26.2, 25.9. MALDI-TOF MS: Calcd. for $C_{315}H_{300}N_{12}O_{18}$, 4541.3; Found, 4541.3.



Compound **7** (Yield: 63%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.09-8.06 (d, J = 7.8 Hz, 6H), 7.92-7.85 (m, 12H), 7.72 (d, J = 0.9 Hz, 6H), 7.70-7.66 (dd, J = 8.1, 1.2 Hz, 6H), 7.63-7.60 (d, J = 8.4 Hz, 12H), 7.32-7.27 (m, 24H), 7.24-7.17 (m, 24H), 7.11-7.04 (m, 12H), 6.49-6.46 (d, J = 8.7 Hz, 3H), 6.22-6.19 (dd, J = 8.7, 2.1 Hz, 3H), 5.95-5.94 (d, J = 2.1 Hz, 3H), 4.04-4.00 (t, J = 6.6 Hz, 6H), 3.86 (s, 18H), 3.58-3.54 (t, J = 6.0 Hz, 6H), 1.84-1.75 (m, 6H), 1.51-1.40 (m, 6H), 1.27-1.17 (m, 48H). ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): δ166.5, 159.4, 158.7, 154.3, 154.1, 151.9, 149.8, 147.9, 147.5, 144.8, 141.7, 141.1, 140.3, 137.3, 132.4, 132.1, 131.1, 131.0, 130.3, 130.0, 129.9, 129.7, 129.3, 128.7, 127.7, 127.4, 127.3, 126.6, 124.9, 123.3, 122.9, 122.0, 121.1, 114.7, 112.2, 109.2, 68.1, 67.0, 52.0, 29.5, 29.40, 29.35, 29.32, 29.27, 29.1, 26.0, 25.9. MALDI-TOF MS: Calcd. for $C_{237}H_{201}N_9O_{18}S_3$, 3558.4; Found, 3558.0.

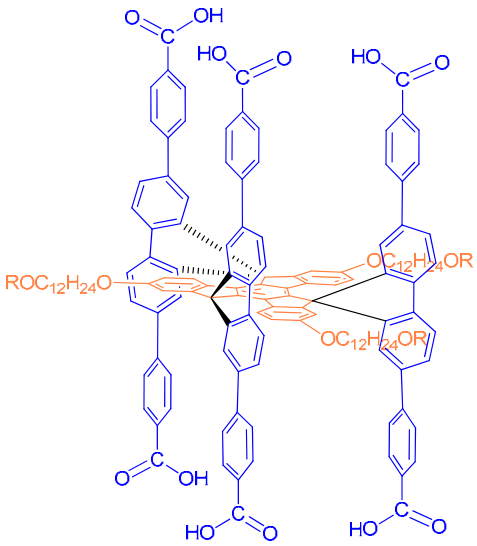


Compound **8** (Yield: 51%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.09-8.06 (d, J = 7.8 Hz, 6H), 7.93-7.89 (m, 12H), 7.70 (s, 6H), 7.69-7.66 (d, J = 8.1 Hz, 6H), 7.31-7.28 (d, J = 8.4 Hz, 12H), 7.17 (s, 6H), 7.08-7.04 (m, 12H), 6.49-6.46 (d, J = 8.7 Hz, 3H), 6.22-6.19 (dd, J = 8.7, 2.4 Hz, 3H), 5.95 (d, J = 2.1 Hz, 3H), 4.04-4.00 (t, J = 6.6 Hz, 6H), 3.88 (s, 9H), 3.86 (s, 18H), 3.58-3.54 (t, J = 6.0 Hz, 6H), 1.84-1.72 (m, 6H), 1.50-1.40 (m, 6H), 1.32-1.17 (m, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.5, 159.7, 159.3, 158.7, 154.2, 149.8, 144.8, 141.7, 141.1, 140.3, 132.4, 132.2, 130.34, 130.30, 129.98, 129.95, 129.7, 128.7, 127.7, 127.4, 127.3, 126.6, 122.0, 121.1, 114.6, 114.1, 112.2, 109.2, 68.1, 67.7, 66.9, 55.4, 51.9, 29.46, 29.43, 29.38, 29.31, 29.28, 29.23, 29.1, 26.0, 25.9. MALDI-TOF MS: Calcd. for $C_{204}H_{180}N_6O_{21}S_3$, 3147.2; Found, 3147.2.



Compound **9** (Yield: 82%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.08-8.06 (d, *J* = 7.8 Hz, 6H), 7.92-7.89 (d, *J* = 8.4 Hz 12H), 7.70 (s, 6H), 7.72 (d, *J* = 0.9 Hz, 6H), 7.65 (m, 6H), 7.63-7.60 (d, *J* = 8.4 Hz, 12H), 7.30-7.28 (d, 12H), 7.17 (d, *J* = 2.1 Hz, 6H), 7.06-7.04 (d, *J* = 6.6 Hz 12H), 6.49-6.46 (d, *J* = 8.7 Hz, 3H), 6.22-6.19 (dd, *J* = 8.7, 2.1 Hz, 3H), 5.95-5.94 (d, *J* = 2.1 Hz, 3H), 4.04-4.00 (q, 12H), 3.86 (s, 18H), 3.58-3.50 (t, *J* = 6.0 Hz, 6H), 1.85-1.75 (m, 12H), 1.48-1.26 (m, 72H), 1.17-0.92 (t, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): δ166.5, 159.4, 158.7, 154.2, 151.9, 149.8, 144.8, 141.7, 141.1, 140.3, 137.4, 132.3, 131.2, 130.3, 130.0, 129.9, 129.8, 128.8, 127.7, 127.4, 126.6, 125.2, 122.1, 121.1, 114.7, 112.2, 110.7, 109.2, 68.1, 67.8, 67.0, 52.0, 31.6, 29.51, 29.50, 29.48, 29.42, 29.35, 29.33, 29.27, 29.15, 26.0, 25.9, 25.7, 22.6, 14.1, MALDI-TOF MS: Calcd. for $C_{219}H_{210}N_6O_{21}S_3$, 3357.5; Found, 3358.0.

General Procedures for the Synthesis of Monomers



1-TPP **1-BTTPA** **1-BTMe** **1-BTHex**

A solution of **6**, **7**, **8**, or **9** (0.005 mmol) in THF (10 mL) was added aqueous LiOH (0.3 mmol) 1 mL. After refluxed for 24 h, the mixture was quenched with dilute hydochloric acid. The aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine and then dried with Na_2SO_4. After removal of the solvernts under reduced pressure, the residue was washed with ethanol and filtrated under reduced pressure to afford all the monomers.

1-TPP. (Yield: > 90%)**:** ^{1}H NMR (THF-d^8, 400 MHz, 50 ^{o}C, ppm): δ 10.59 (s, 6H), 8.81-8.79 (m, 24H), 8.12-8.09 (m, 24H), 8.05-8.03 (d, J = 8.0 Hz, 18H), 7.96-7.94 (d, J = 8.0 Hz, 18H), 7.79-7.75 (m, 18H), 7.63-7.62 (m, 18H), 7.31-7.29 (m, 12H), 7.24-7.22 (m, 12H), 6.51-6.49 (d, J = 8.4 Hz, 3H), 6.14-6.11 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 3H,), 5.92 (d, J_2 = 2.0 Hz, 3H), 4.19-4.16 (t, J = 6.4 Hz, 6H), 3.52-3.49 (t, J = 6.8 Hz, 6H), 1.93-1.86 (m, 6H), 1.59-1.57 (m, 81H), 1.43-1.20 (m, 60H), -2.58 (s, 6H). MALDI-TOF MS: Calcd. for $C_{309}H_{288}N_{12}O_{18}$, 4457.2; Found, 4457.7.

1-BTTPA: (Yield: >90%)**:** ^{1}H-NMR (DMSO-d^{6} : $C_2D_4Cl_4$ = 1 : 1, 400 MHz, 50 ^{o}C, ppm): δ 8.16-8.14 (d, *J* = 8.0 Hz, 6H), 7.86-7.81 (m, 12H), 7.72-7.67 (m, 12H), 7.54-7.52 (d, *J* = 7.6 Hz, 12H), 7.28-7.21 (m, 24H), 7.16-7.0 (m, 30H), 6.96-6.93 (m, 6H), 6.41-6.39 (d, 3H), 6.16-6.14 (d, 3H), 5.85 (s, 3H), 3.97-3.94 (t, *J* = 6.0 Hz, 6H), 3.20-3.50 (overlapped with H_2O signal, 6H), 1.73-1.70 (m, 6H), 1.53-1.51 (m, 6H), 1.49-1.11 (m, 48H). COOH hydrogen did not observed because of low solubility. MALDI-TOF MS: Calcd. for $C_{231}H_{189}N_9O_{18}S_3$, 3474.3; Found, 3474.1.

1-BTMe: (Yield: >90%)**:** ^{1}H-NMR (THF-d^{8}, 400 MHz, 50 ^{o}C, ppm): δ 10.64 (s, 6H), 8.17-8.14 (d, *J* = 8.0 Hz, 6H), 8.00-7.96 (m, 12H), 7.76-7.74 (m, 12H), 7.36-7.34 (m, 12H), 7.27 (s, 6H), 7.04-7.00 (m, 12H), 6.60-6.6.57 (d, *J* = 8.8 Hz, 3H), 6.22-6.19 (dd, *J* = 8.7 Hz, *J* = 2.4 Hz, 3H), 5.92 (d, *J* = 2.4 Hz, 3H), 4.04-4.01 (t, *J* = 6.4 Hz, 6H), 3.84 (s, 9H), 3.54-3.52 (m, 6H), 1.79-1.75 (m, 6H), 1.50-1.43 (m, 6H), 1.35-1.12 (m, 36H). MALDI-TOF MS: Calcd. for $C_{198}H_{168}N_6O_{21}S_3$, 3063.2; Found, 3063.7.

1-BTHex: (Yield: >90%): ^{1}H-NMR (DMSO-d^{6} : $C_2D_4Cl_4$ = 1 : 1, 400 MHz, 50 ^{o}C, ppm): δ 12.08 (s, broad, 2H) 8.16-8.14 (d, *J* = 8.0 Hz, 6H), 7.85-7.83 (d, *J* = 7.6 Hz 12H), 7.71-7.69 (m, 6H), 7.60 (s, 6H), 7.53-7.51 (m, 12H), 7.20-7.18 (m, 12H), 7.30-7.28 (d, 12H), 7.10 (s, 6H), 6.96-6.92 (m, 12H), 6.18-6.17 (d, *J* = 6.4 Hz, 3H), 5.87 (s, 3H), 5.46 (s, 3H), 3.96-3.93 (t, 12H), 3.52 (s, 6H), 1.75-1.70 (m, 12H), 1.41-1.11 (m, 72H), 0.90-0.86 (t, *J* = 6.7 Hz, 9H). MALDI-TOF MS: Calcd. for $C_{213}H_{198}N_6O_{21}S_3$, 3273.4; Found, $[M]^+$ 3274.0, $[M+Na]^+$ 3297.0.

Reference:

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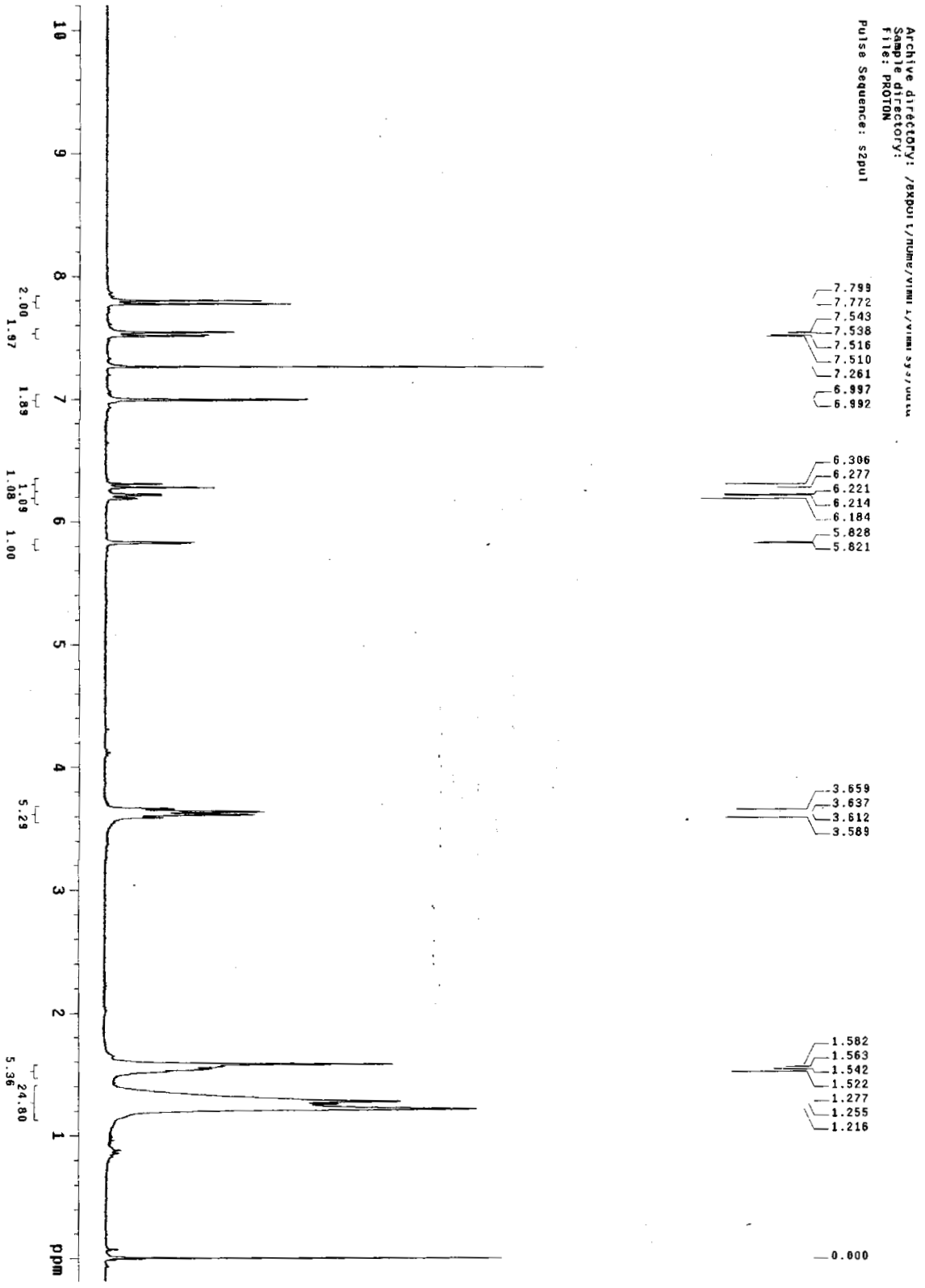
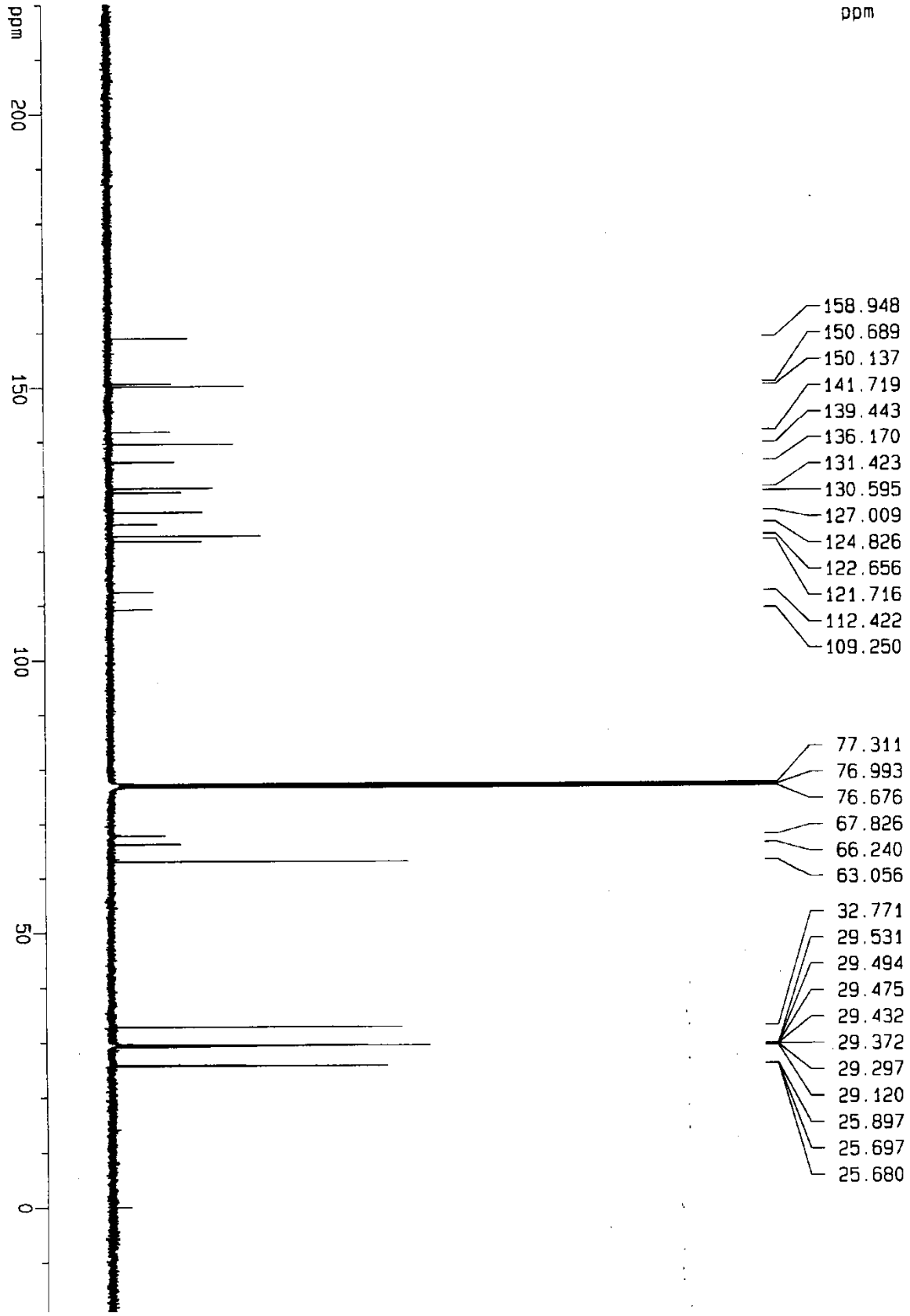
2. ^{1}H NMR and ^{13}C NMR Spectra

Compound **3**





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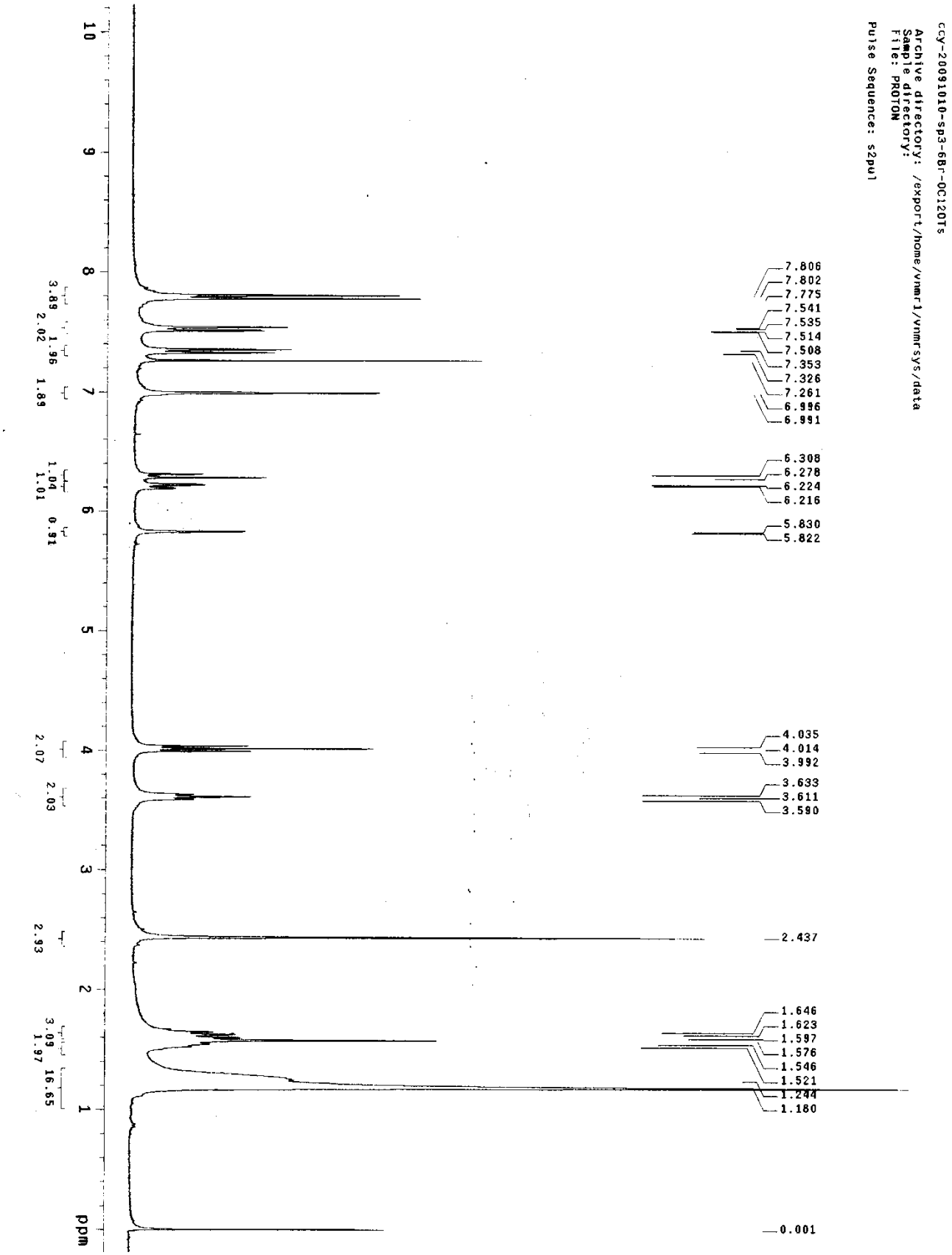
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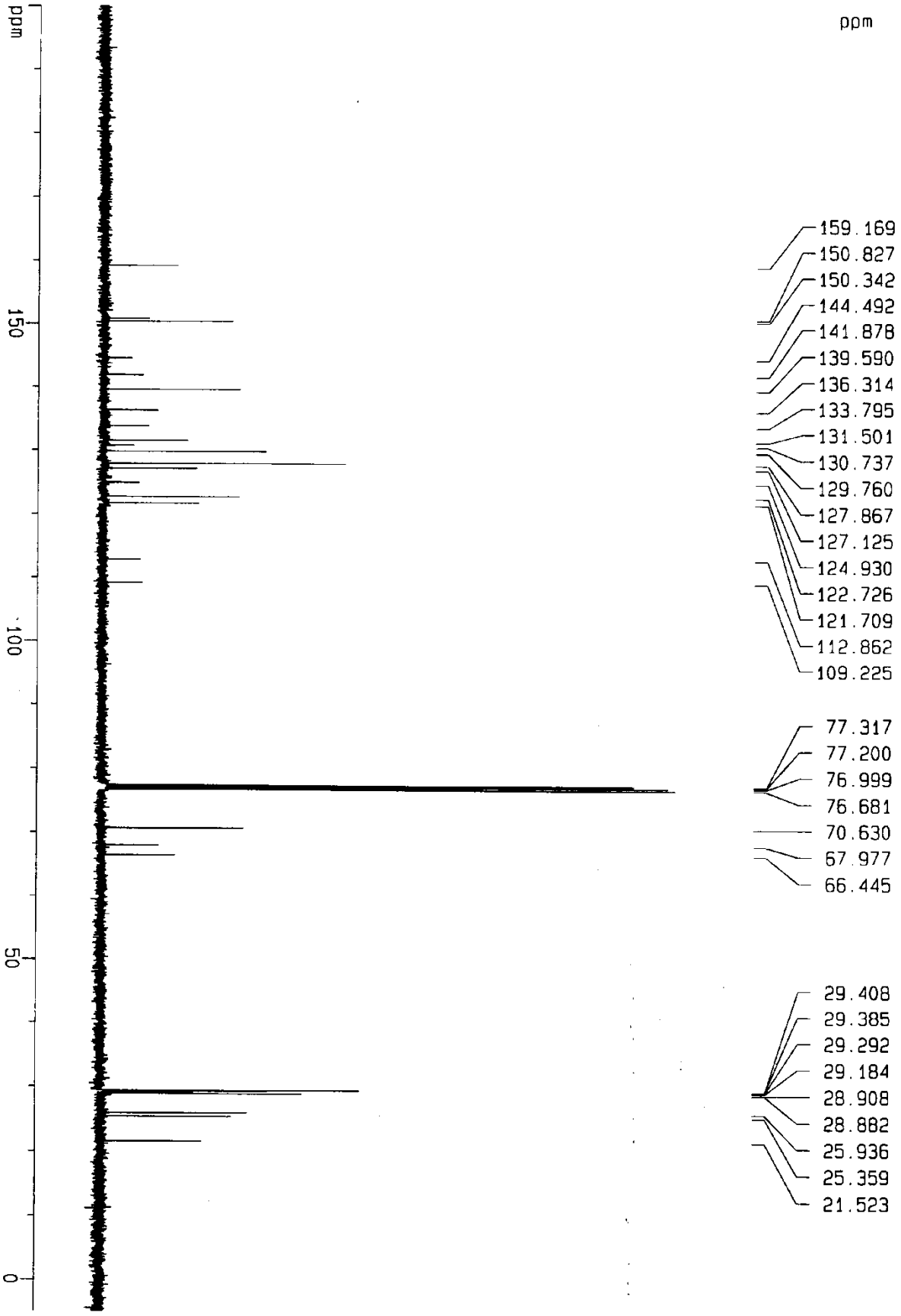
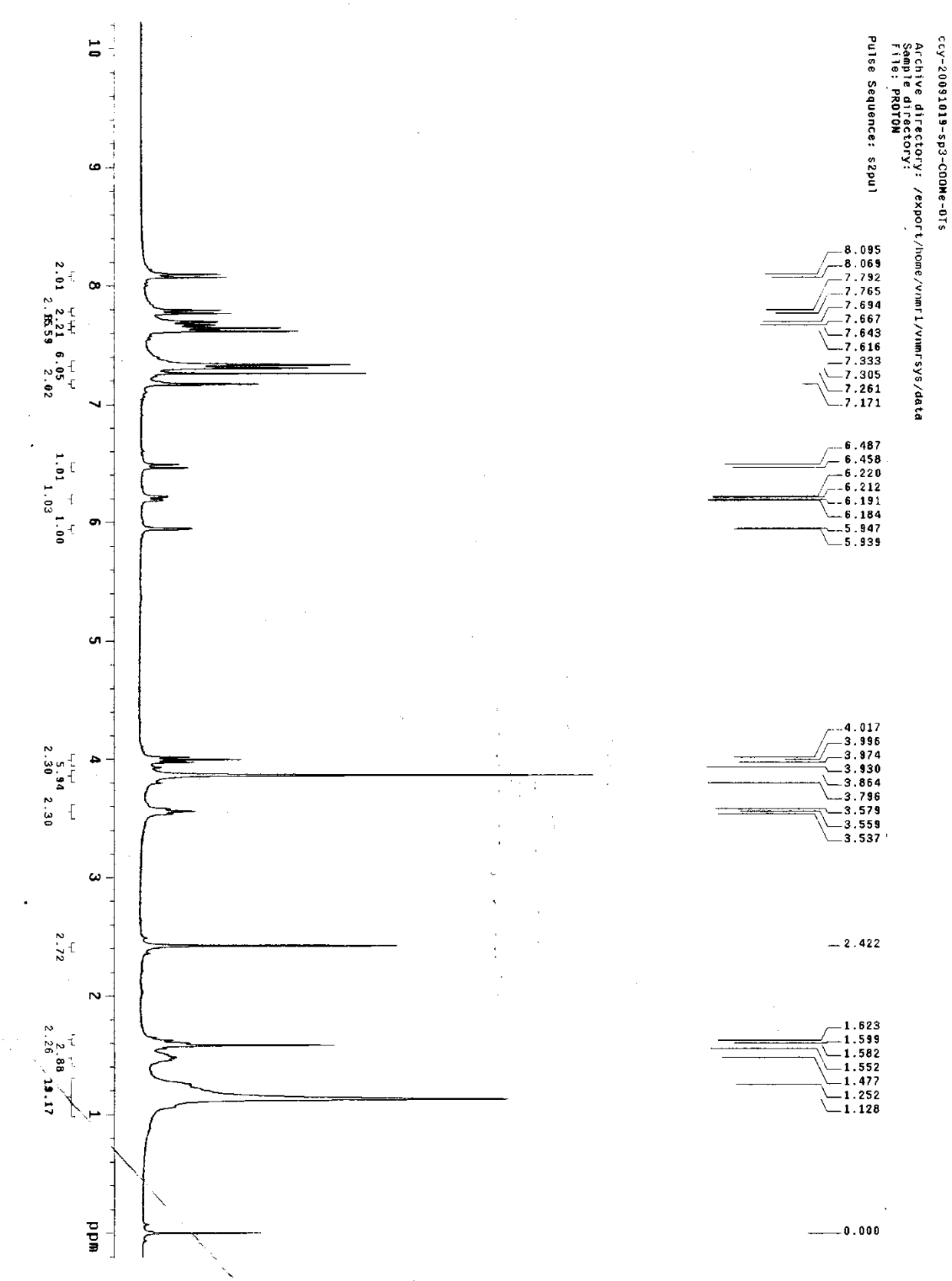
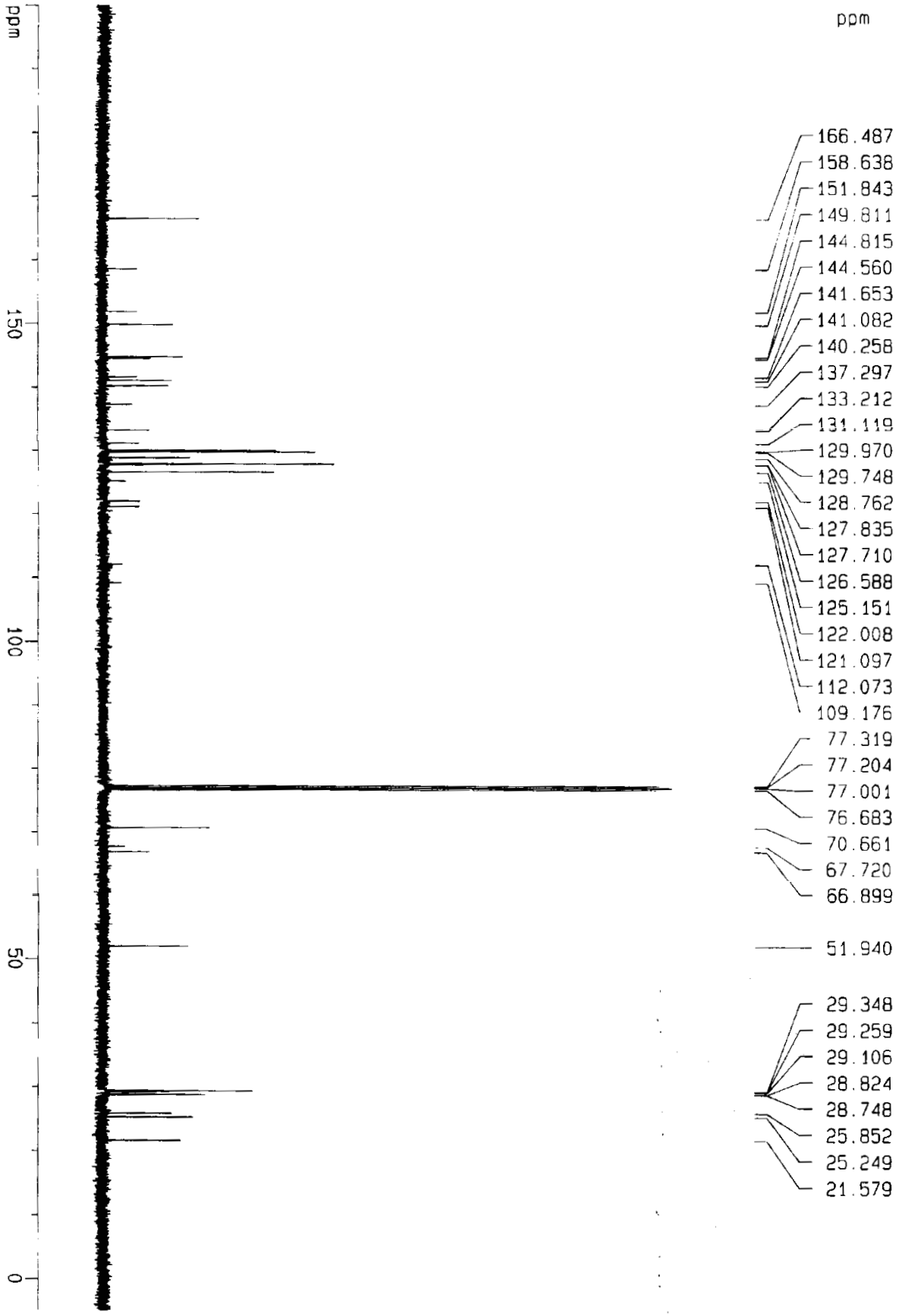
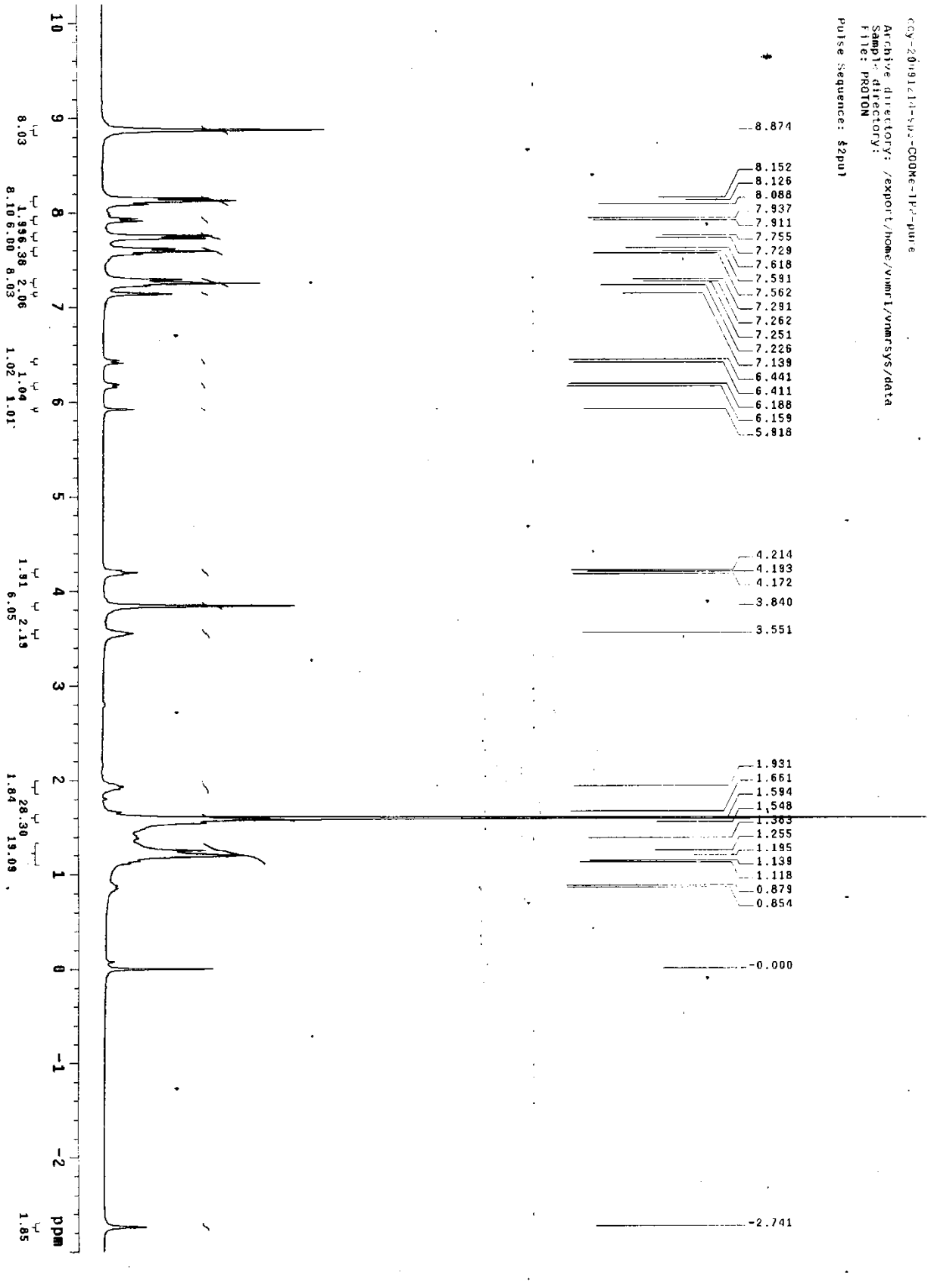


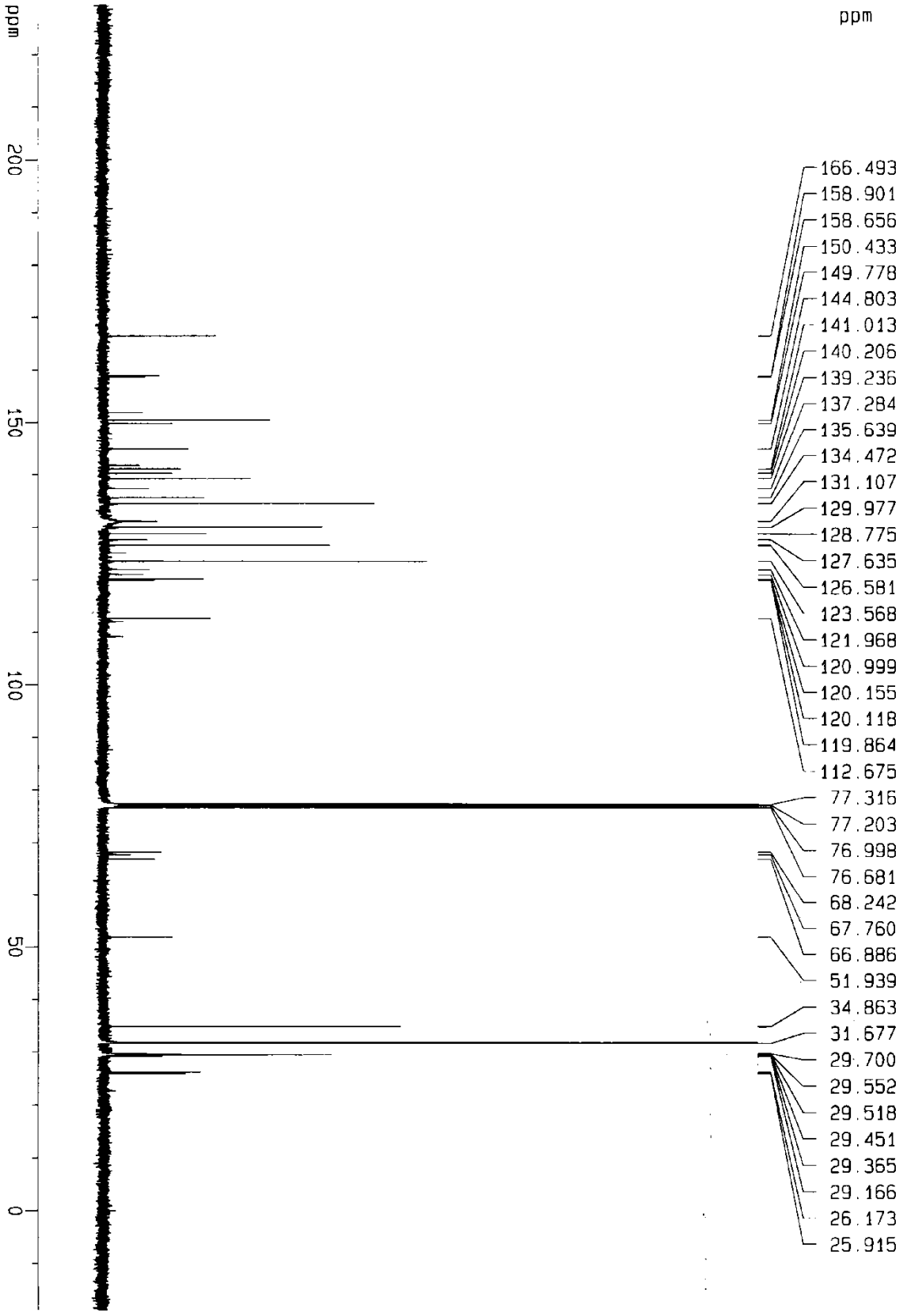
Compound **5**



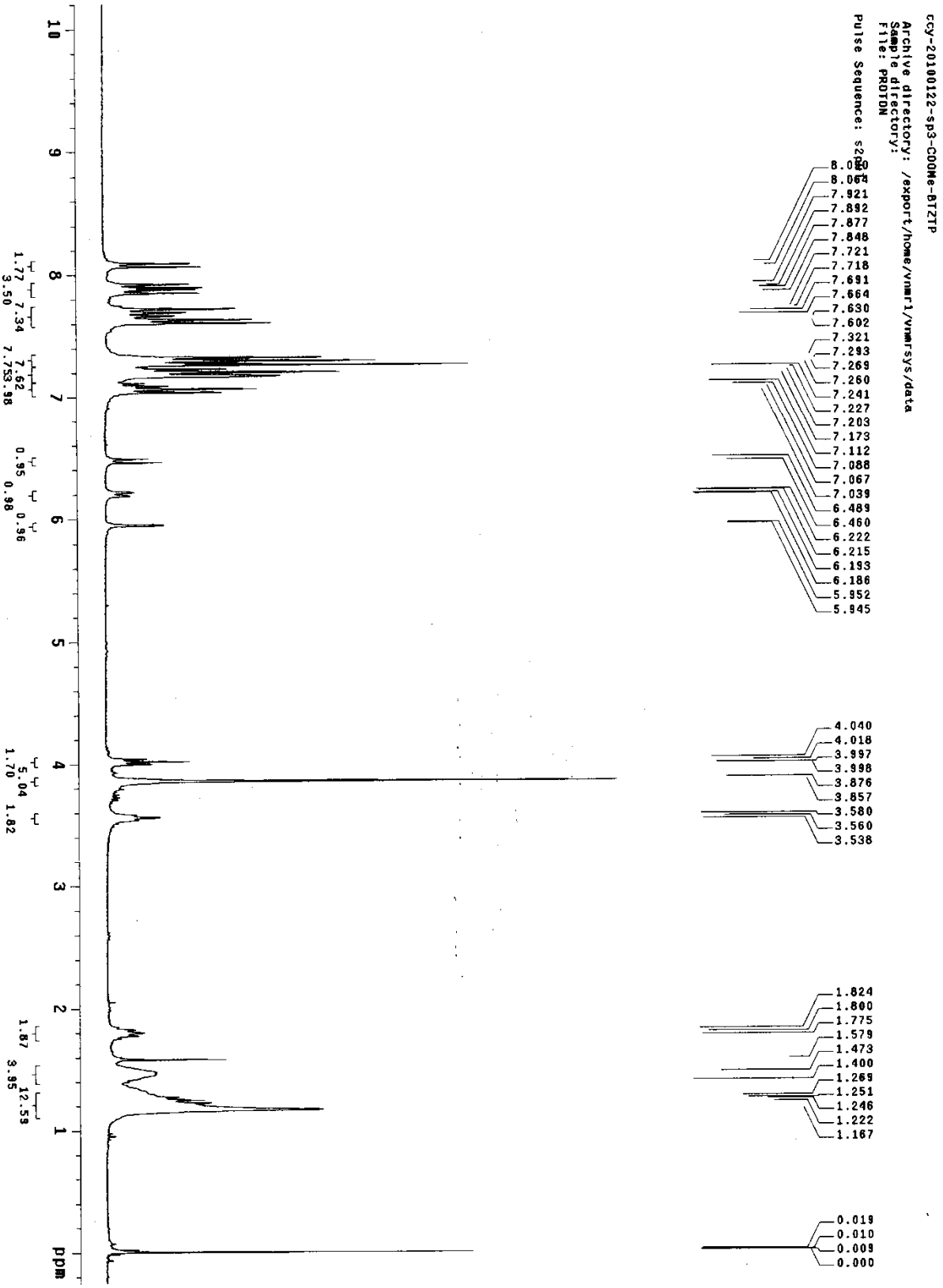


Compound **6**





Compound **7**


ccy-20100122-sp3-COOMe-BTZTP
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
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8.064
7.921
7.892
7.877
7.848
7.721
7.718
7.691
7.664
7.630
7.602
7.321
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7.269
7.260
7.241
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7.203
7.173
7.112
7.088
7.067
7.039
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6.460
6.222
6.215
6.193
6.186
5.952
5.945
4.040
4.018
3.997
3.998
3.876
3.857
3.580
3.560
3.538
1.824
1.800
1.775
1.579
1.473
1.400
1.269
1.251
1.246
1.222
1.167
0.019
0.010
0.009
0.000
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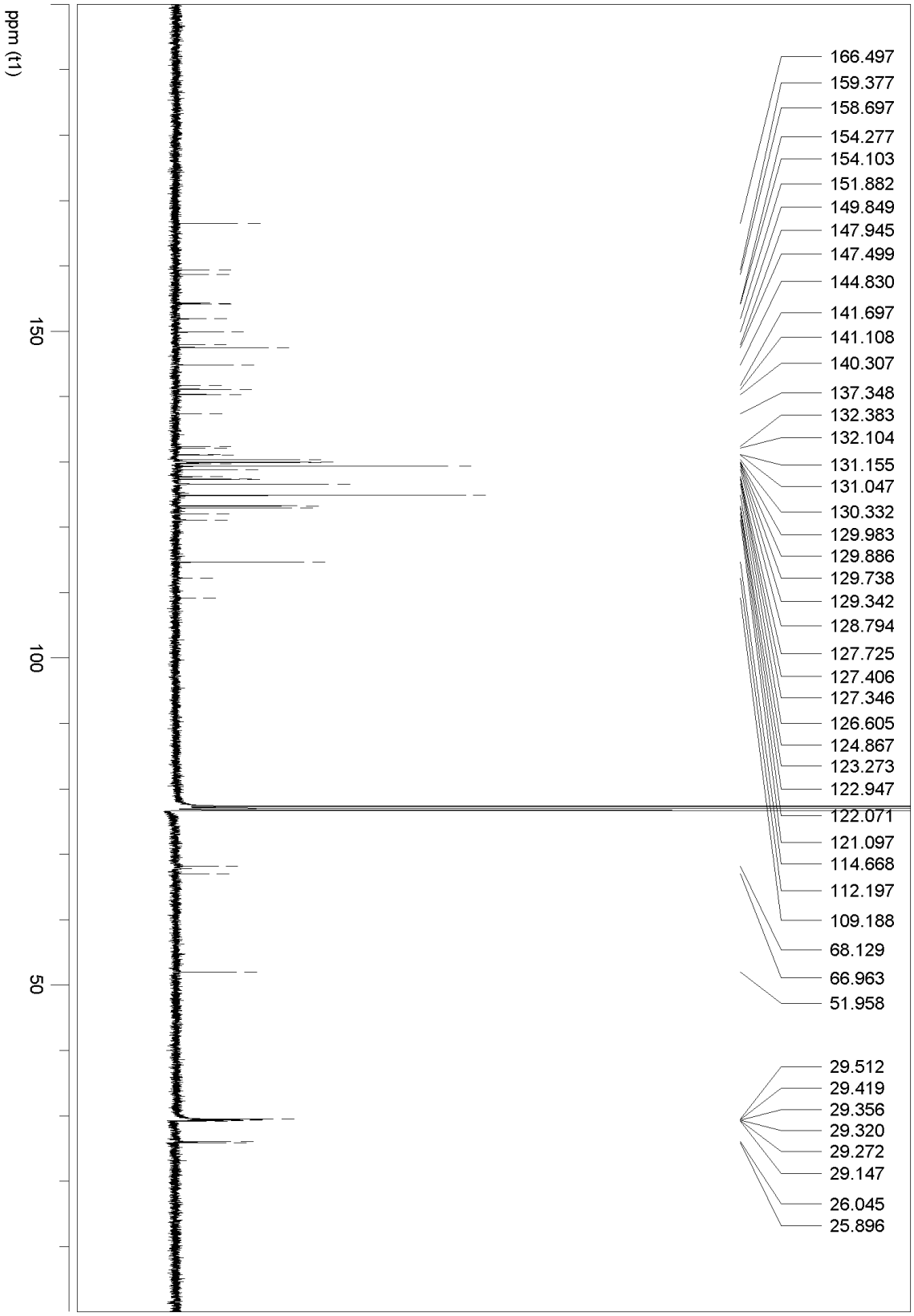
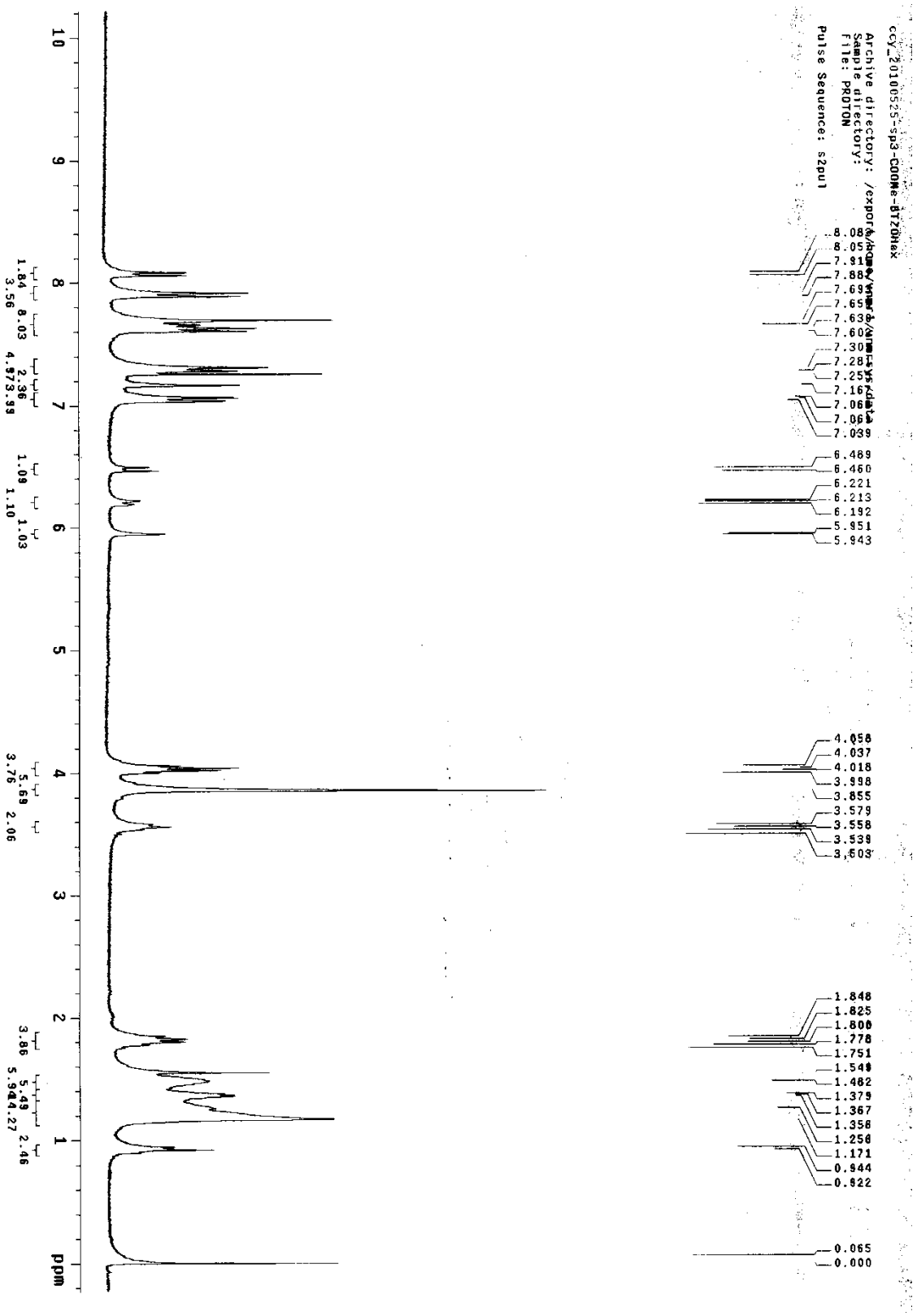
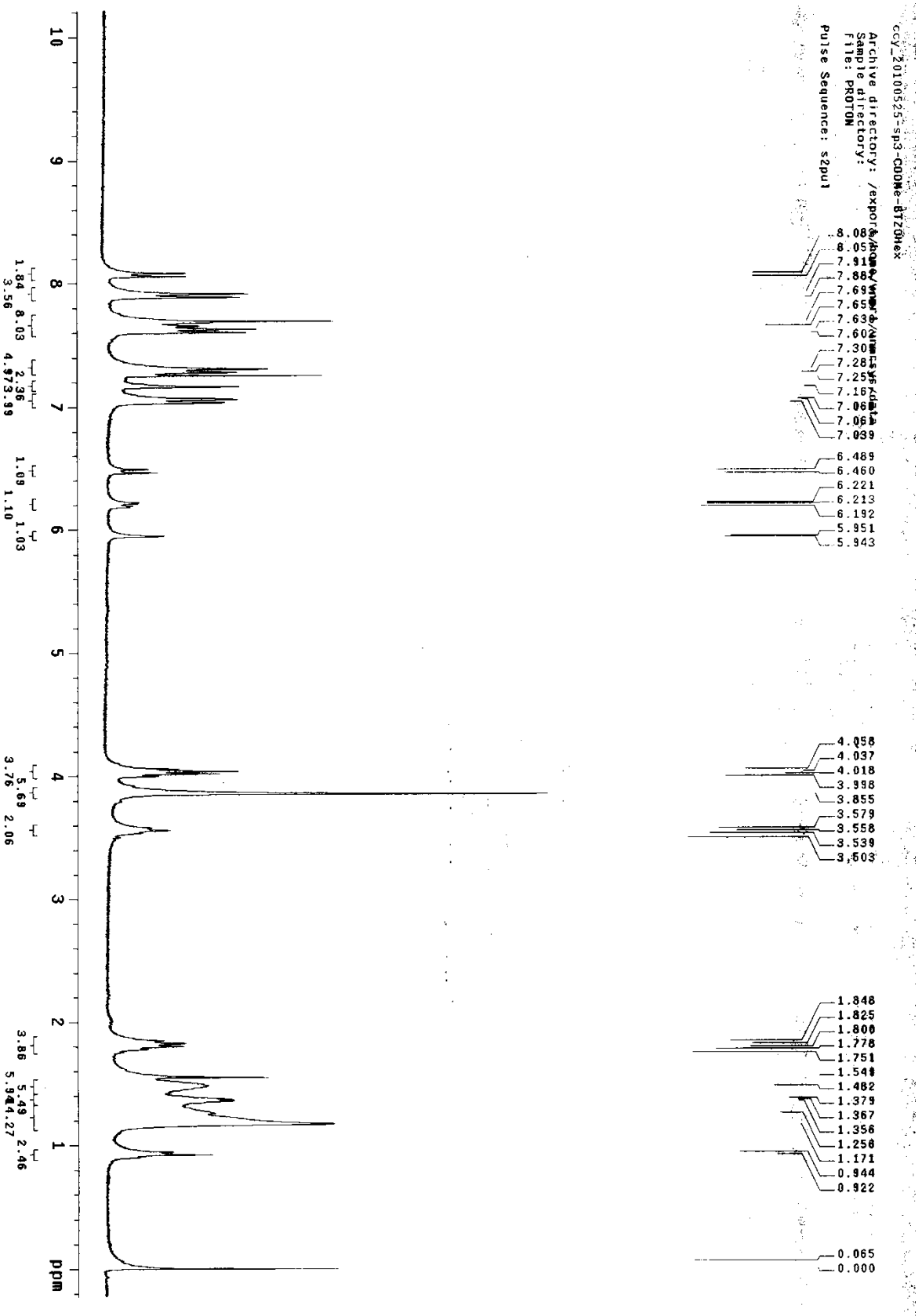
ppm

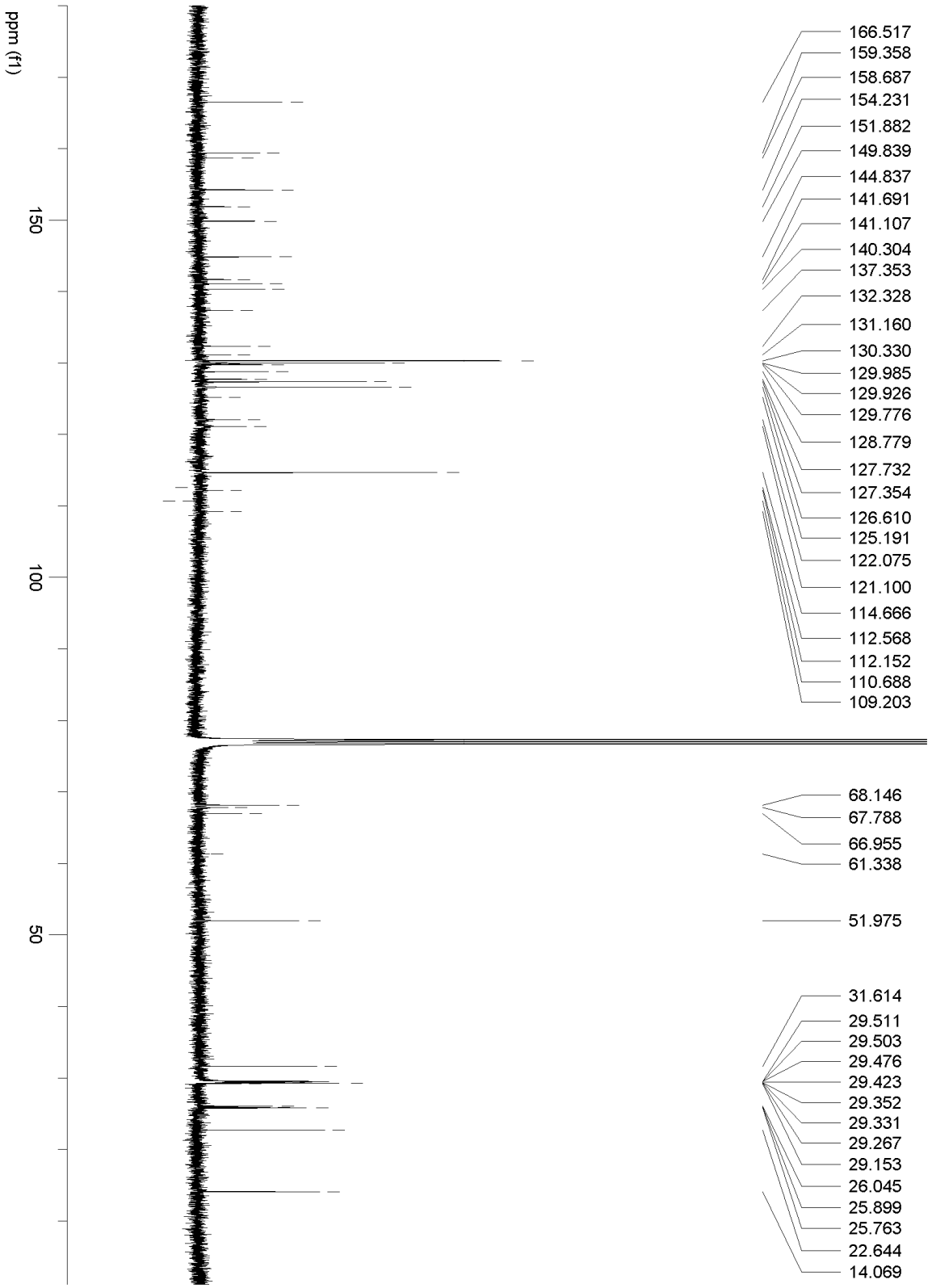


Compound **8**

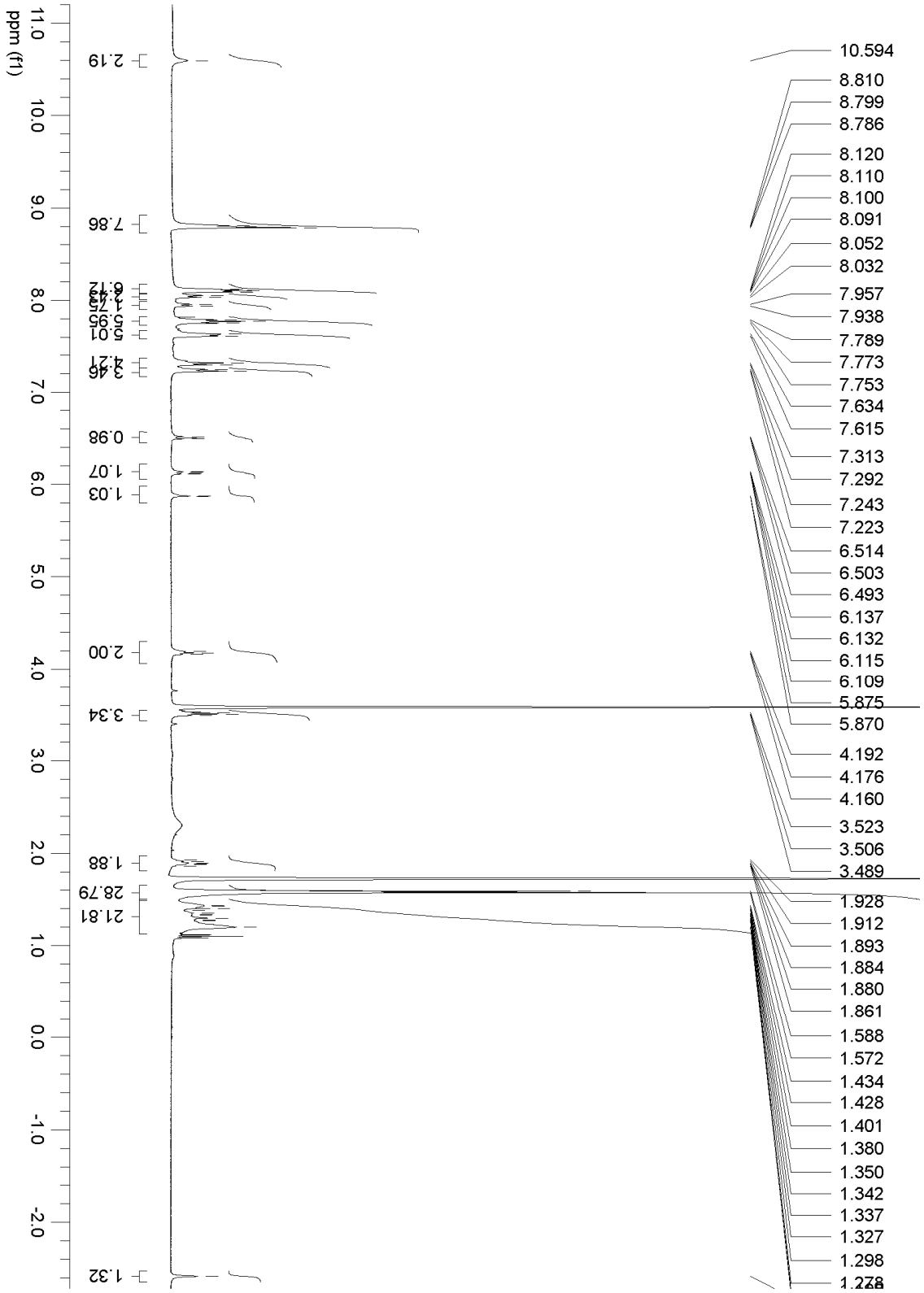


Compound **9**

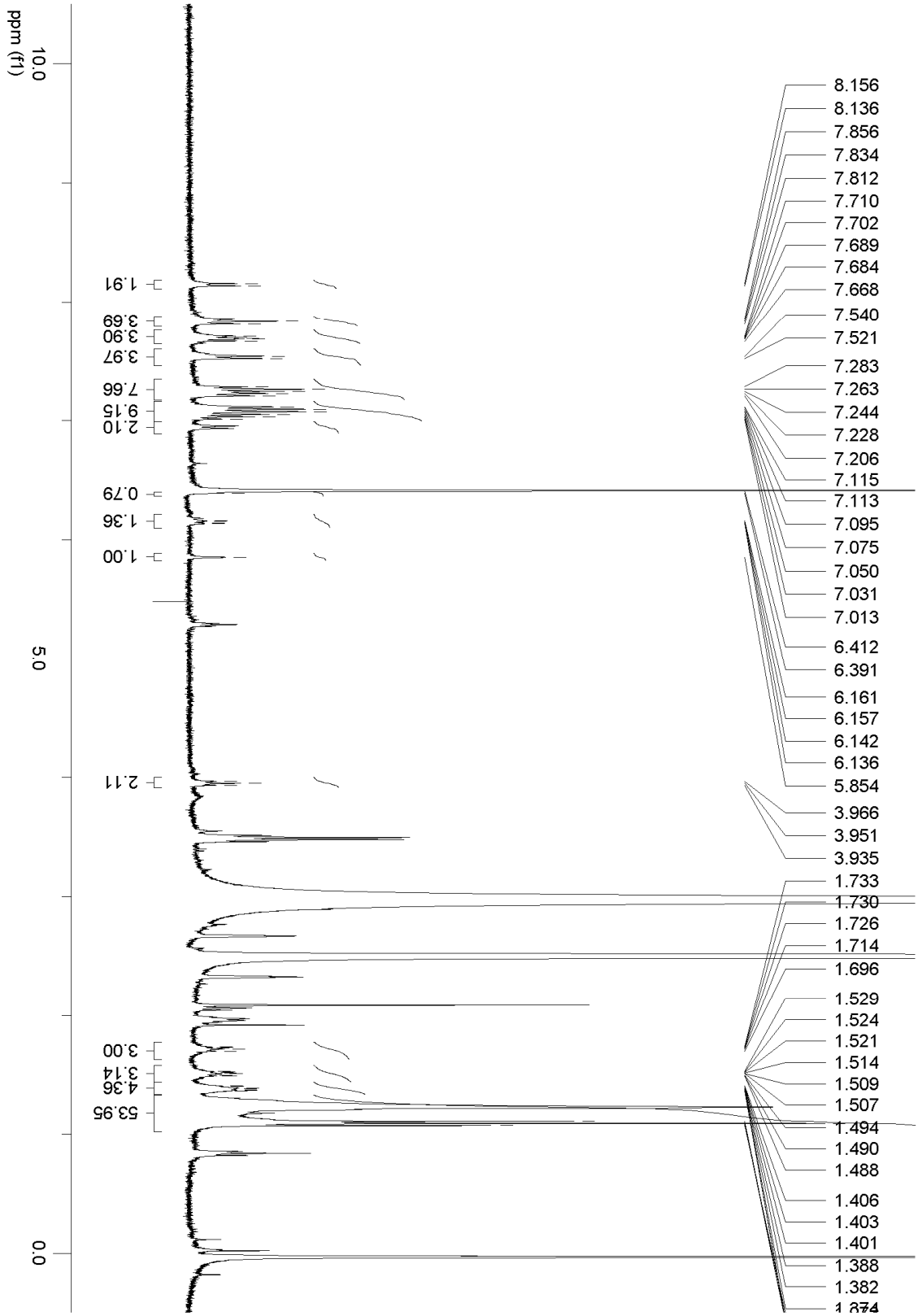




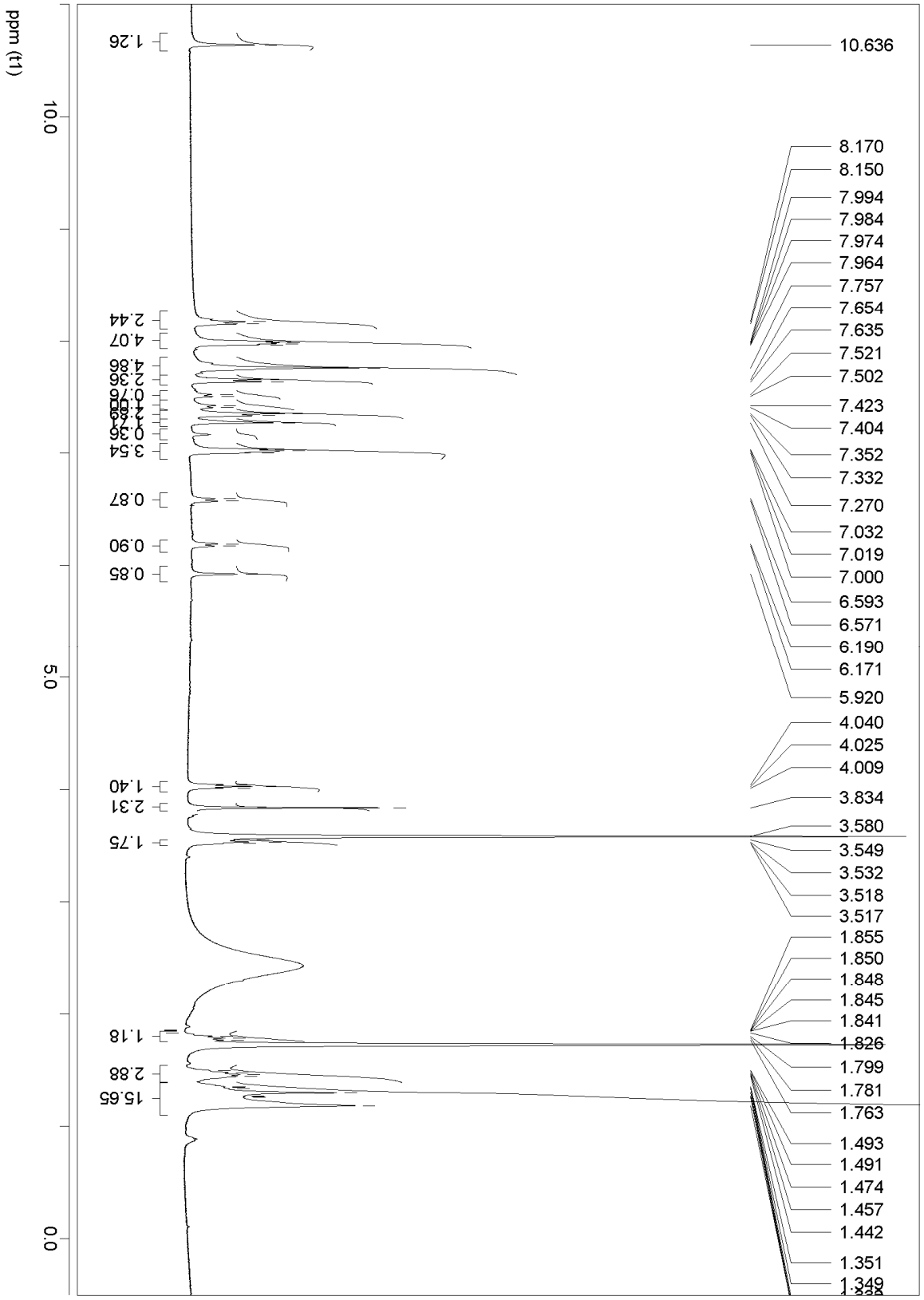
Compound **1-TPP**



Compound **1-BTTPA**



Compound **1-BTMe**



Compound **1-BTHex**