Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information (ESI)

meso-Dichloropyrimidinyl substituted expanded porphyrins

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1. Experimental procedures and data

* Expanded porphyrins 1-3

Cfr. J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 7190-7191; J.-Y. Shin, H. Furuta and A. Osuka, *Angew. Chem. Int. Ed.*, 2001, **40**, 619-621.
The reaction mixture was separated by column chromatography (silica, eluent CH_2Cl_2-petroleum ether 1-1 → CH_2Cl_2) to afford porphyrin **1** (purple solid, 10 %), pentaphyrin **2** (brown-black solid, 11 %) and hexaphyrin **3** (gold-coloured solid, 11 %) and a mixture of the higher homologues.

- Porphyrin 1

UV/VIS (DMF): λ_{max} (log ε) = 281.3 (4.841), 291.8 (4.861), 424.8 (5.374), 517.4 (4.120), 546.9 (3.362), 593.0 (3.634), 655.0 (3.093).
MS (ESI): m/z = 1203.0 $[M+H]^+$.

- Pentaphyrin 2

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 9.08 (d, ^3J = 5.1 Hz, 1H, H_β-pyr), 8.98 (d, ^3J = 5.1 Hz, 1H, H_β-pyr), 8.80-8.30 (m, 14H), 7.75-7.50 (m, 15H), 3.51 (s, 1H), -1.87 (s, 1H); some signal assignments remain unclear due to solvent impurities and overlapping signals.
UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 278.1 (4.971), 482.0 (4.677), 533.2 (4.662), 800.0 (3.869).
MS (ESI): m/z = 1502.0 $[M+H]^+$.

- Hexaphyrin 3

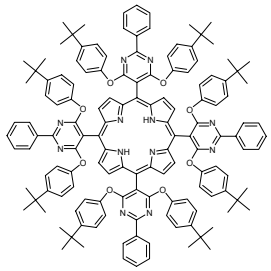
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.43 (d, ^3J = 4.8 Hz, 4H, H_β-pyr), 9.14 (d, ^3J = 4.8 Hz, 4H, H_β-pyr), 8.82 (d, ^3J = 7.2 Hz, 4H), 8.49 (d, ^3J = 7.2 Hz, 8H), 7.70 (m, 6H), 7.54 (t, ^3J = 7.6 Hz, 4H), 7.41 (t, ^3J = 7.6 Hz, 8H), -2.09 (s_{br}, 2H, NH), -2.50 (s, 4H, H_β-pyr).
^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.0, 164.9, 163.8, 162.9, 155.3, 149.1, 134.9, 134.7, 134.1, 133.0, 132.9, 132.0, 131.9, 129.6, 129.4, 129.1, 128.9, 128.7, 125.1, 122.8, 113.8.
MS (ESI): m/z = 1803.8 $[M+H]^+$.
UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 271.0 (5.039), 575.2 (5.380), 606.9 (4.961), 722.6 (4.424), 782.9 (4.009), 899.1 (3.749), 1035.1 (4.103).
Crystals could be grown from THF.

* Octasubstitution on porphyrin 1

Octafunctional porphyrin **1** (25 mg, 20.8 μmol) and 4-*t*-butylphenol (38 mg, 253 μmol) were dissolved together in DMF (5 mL). K_2CO_3 (55 mg, 400 μmol) was added and the mixture was heated at 70 °C during 24h. DMF was evaporated, the residue was dissolved in CH_2Cl_2 (25 mL), washed with water (3 x 25 mL) and the organic fraction was dried over $MgSO_4$. The octasubstituted porphyrin was, after purification by column chromatography (silica, eluent CH_2Cl_2-petroleumether 1-1), obtained in 64 % yield (28 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.21 (s, 8H, H_β-pyr), 8.36 (dd, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 8H), 7.47 (m, 12H), 7.13 (d, ^3J = 8.8 Hz, 16H), 7.02 (d, ^3J = 8.8 Hz, 16 H), 1.12 (s, 72H, *t*-Bu), -2.38 (s_{br}, 2H, NH).

^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 169.9, 163.2, 150.7, 147.4, 137.1, 131.1, 130.1 (br), 128.6, 128.5, 125.5, 120.9, 108.0, 106.1, 34.2, 31.3.
MS (ESI): m/z = 2113.0 $[M+H]^+$.
UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 258.4 (4.864), 428.0 (5.656), 520.5 (4.376), 554.5 (3.958), 595.1 (3.871), 650.9 (3.226).



*** Doubly N-fused hexaphyrins 6 and 7**

To a solution of [26]hexaphyrin **3** (50 mg, 27.7 μmol) in DMF (10 mL) were added K_2CO_3 (192 mg, 1.39 mmol) and 4-*t*-butylphenol (104 mg, 693 μmol) and the mixture was heated at 90 °C under Ar atmosphere. After 48h, DMF was evaporated and the residue was dissolved in Et_2O (25 mL) and washed with water (3 x 25 mL). The organic phase was dried over $MgSO_4$ and evaporated to dryness. The crude product was subjected to column chromatographic purification (silica, eluent CH_2Cl_2-petroleumether 1-1) and the *syn*- and *anti*-doubly N-fused hexaphyrins **6** and **7** were obtained in 13 mg (16 %) and 39 mg (49 %) yield.

- *syn*-Doubly N-fused hexaphyrin 6

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = ~16 (s_{br}, 2H, NH), 10.86 (d, ^3J = 5.7 Hz, 2H, H_β-pyr), 9.90 (d, ^3J = 5.6 Hz, 2H, H_β-pyr), 8.03 (d, ^3J = 7.3 Hz, 2H, *o*-Ph), 7.97 (d, ^3J = 7.5 Hz, 2H, *o*-Ph), 7.74 (d, ^3J = 7.5 Hz, 4H, *o*-Ph), 7.63 (m, 4H, *o*-Ph), 7.74 (d, ^3J = 8.6 Hz, 4H), 7.38-7.10 (m, 38H), 7.09 (d, ^3J = 8.5 Hz, 2H), 6.87 (m, 6H, *m*/*p*-Ph), 6.76 (d, ^3J = 8.5 Hz , 8H), 6.39 (d, ^3J = 4.4 Hz, 2H, H_β-pyr), 6.28 (d, ^3J = 4.3 Hz, 2H, H_β-pyr), 6.20 (d, ^3J = 4.2 Hz, 2H, H_β-pyr), 5.74 (d, ^3J = 4.4 Hz, 2H, H_β-pyr), 1.42 (s, 18H, *t*-Bu), 1.36 (s, 18H, *t*-Bu), 1.33 (s, 18H, *t*-Bu), 1.26 (s, 36H, *t*-Bu).
^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 169.0, 168.7, 162.6, 161.81, 161.77, 157.7 (C_α-pyr), 157.6, 155.0, 151.1 (C_α-pyr), 150.9, 150.7, 150.5, 150.4, 148.1, 147.8, 147.5, 147.4, 145.9 (C_α-pyr), 145.4 (C_α-pyr), 144.1 (C_α-pyr), 141.3 (C_α-pyr), 137.0, 136.6, 136.5 (CH_β), 136.4, 131.0 (CH), 130.4 (CH), 129.4 (CH), 128.4 (CH_β), 128.3 (CH), 128.25 (CH), 128.20 (CH), 127.72 (CH), 127.68 (CH), 127.6 (CH), 127.5 (CH_β), 126.3, 126.1 (CH), 125.9 (CH), 125.8 (CH), 125.7 (CH), 125.0 (CH_β), 121.6 (CH_β), 121.5 (CH), 121.2 (CH), 121.0 (CH), 120.6 (CH), 120.1 (CH_β), 116.0, 113.9, 108.1, 107.8, 104.2, 100.7, 34.6, 34.5, 34.42, 34.36.
MS (ESI): m/z = 2869.9 $[M+H]^+$, 1434.9 $[M+H]^{2+}$.
UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 264.0 (5.106), 547.0 (5.058).

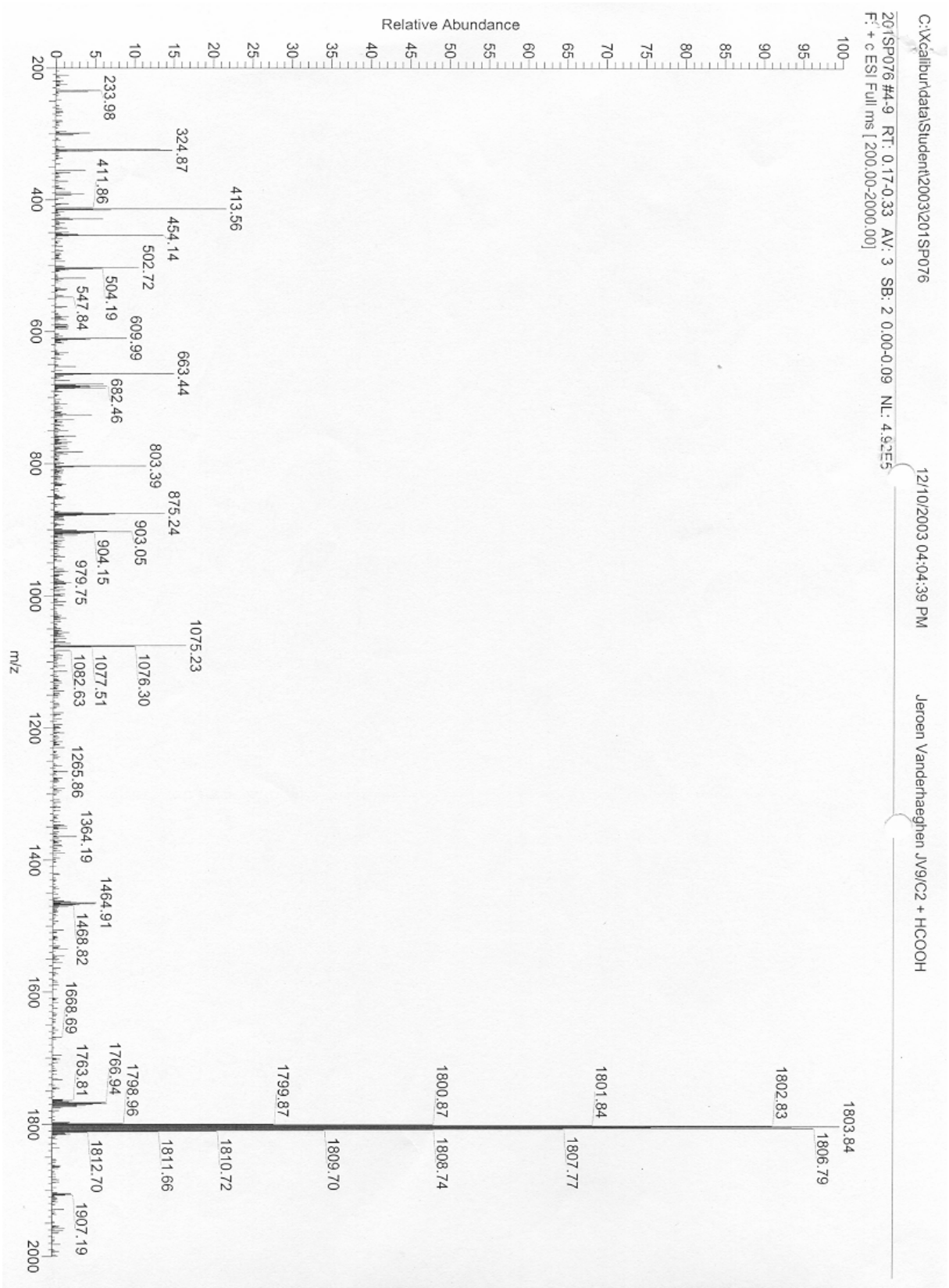
- *anti*-Doubly N-fused hexaphyrin 7

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = ~16 (s_{br}, 2H, NH), 10.82 (d, ^3J = 5.6 Hz, 2H, H_β-pyr), 10.37 (d, ^3J = 5.6 Hz, 2H, H_β-pyr), 7.97 (d, ^3J = 7.3 Hz, 4H, *o*-Ph), 7.75 (d, ^3J = 7.5 Hz, 4H, *o*-Ph), 7.62 (m, 4H, *o*-Ph), 7.46-7.08 (m, 42H), 6.89 (m, 8H, *m*/*p*-Ph), 6.69 (s_{br}, 8H), 6.31 (d, ^3J = 4.7 Hz, 2H, H_β-pyr), 6.30 (d, ^3J = 4.7 Hz, 2H, H_β-pyr), 6.25 (d, ^3J = 4.0 Hz, 2H, H_β-pyr), 5.70 (d, ^3J = 3.8 Hz, 2H, H_β-pyr), 1.39 (s, 36H, *t*-Bu), 1.34 (s, 18H, *t*-Bu), 1.25 (s, 36H, *t*-Bu).
^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 169.0, 168.6, 162.5, 161.9, 158.1 (C_α-pyr), 157.6, 154.5, 151.1 (C_α-pyr), 150.9, 150.5, 150.4, 148.6 (C_α-pyr), 148.0, 147.6, 147.3, 147.1 (C_α-pyr), 142.2 (C_α-pyr), 140.1 (C_α-pyr), 137.2, 136.6, 136.5, 136.1 (CH_β), 131.0 (CH), 130.9 (CH), 130.4, 129.5 (CH_β), 129.5 (CH), 128.3 (CH), 128.24 (CH), 128.18 (CH), 127.7 (CH), 127.5 (CH), 126.8 (CH_β), 126.7, 126.1 (CH), 125.9 (CH), 125.8 (CH_β), 125.7 (CH), 123.3 (CH_β), 121.4 (CH), 121.0 (CH), 120.4 (CH), 119.1 (CH_β), 114.3, 108.3, 107.6, 104.0, 100.8, 34.5, 34.4, 34.3.
MS (ESI): m/z = 2869.7 $[M+H]^+$, 1434.0 $[M+H]^{2+}$.
UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 262.2 (5.098), 544.3 (4.872).

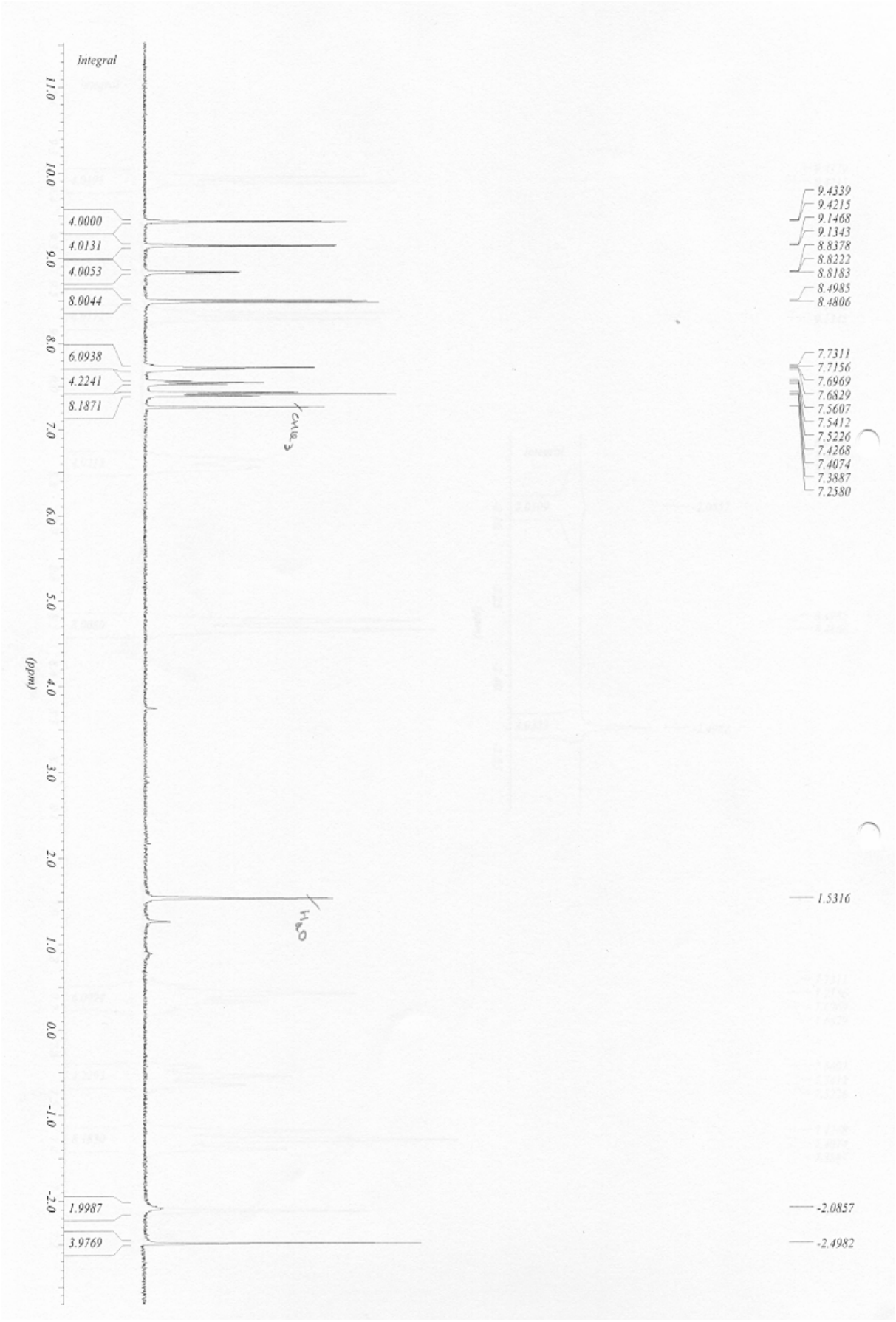
2. Spectra

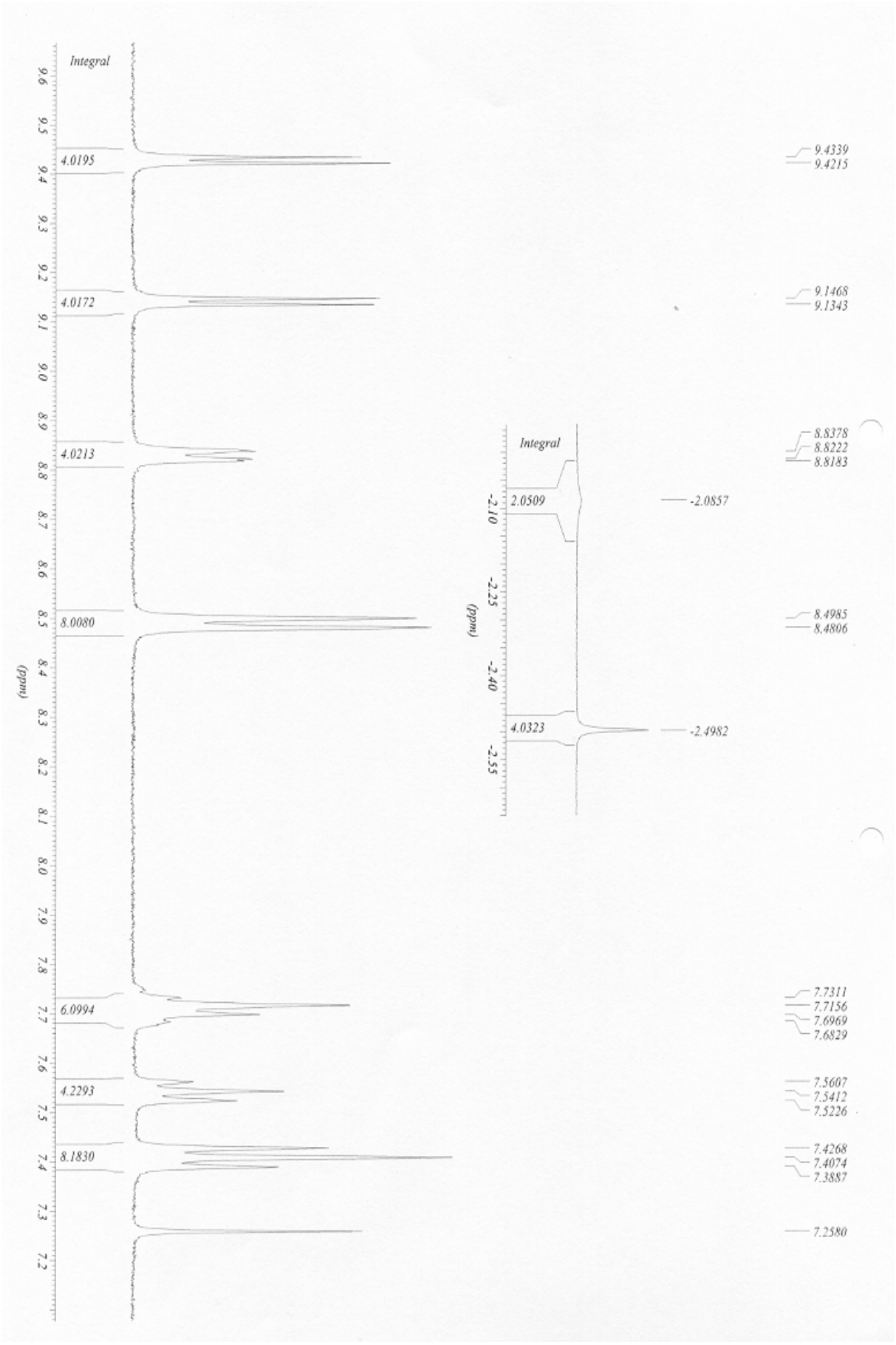
*** Hexaphyrin 3**

- ESI-MS

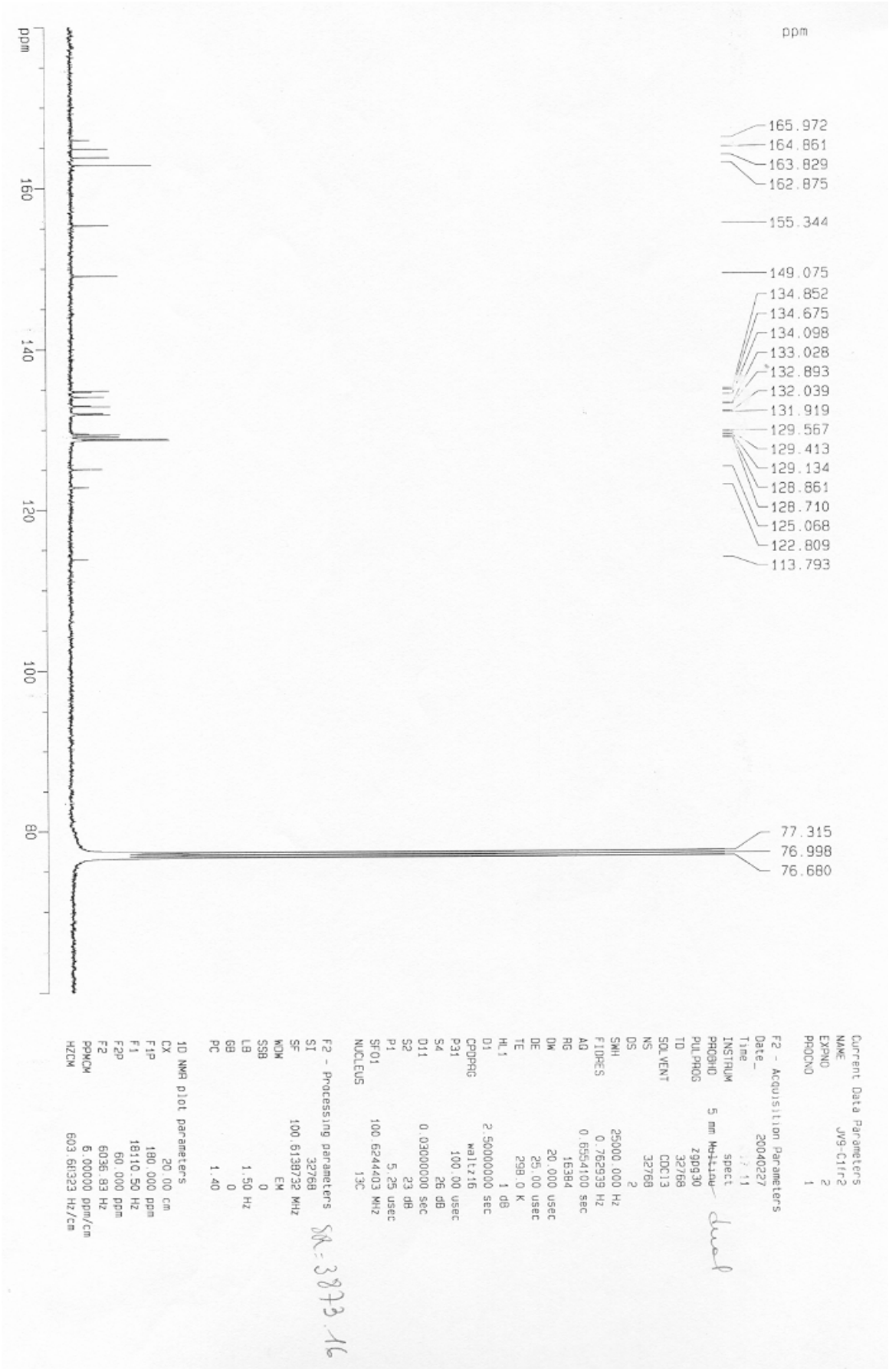


- ^{1}H NMR





- ^{13}C NMR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S2 23 dB
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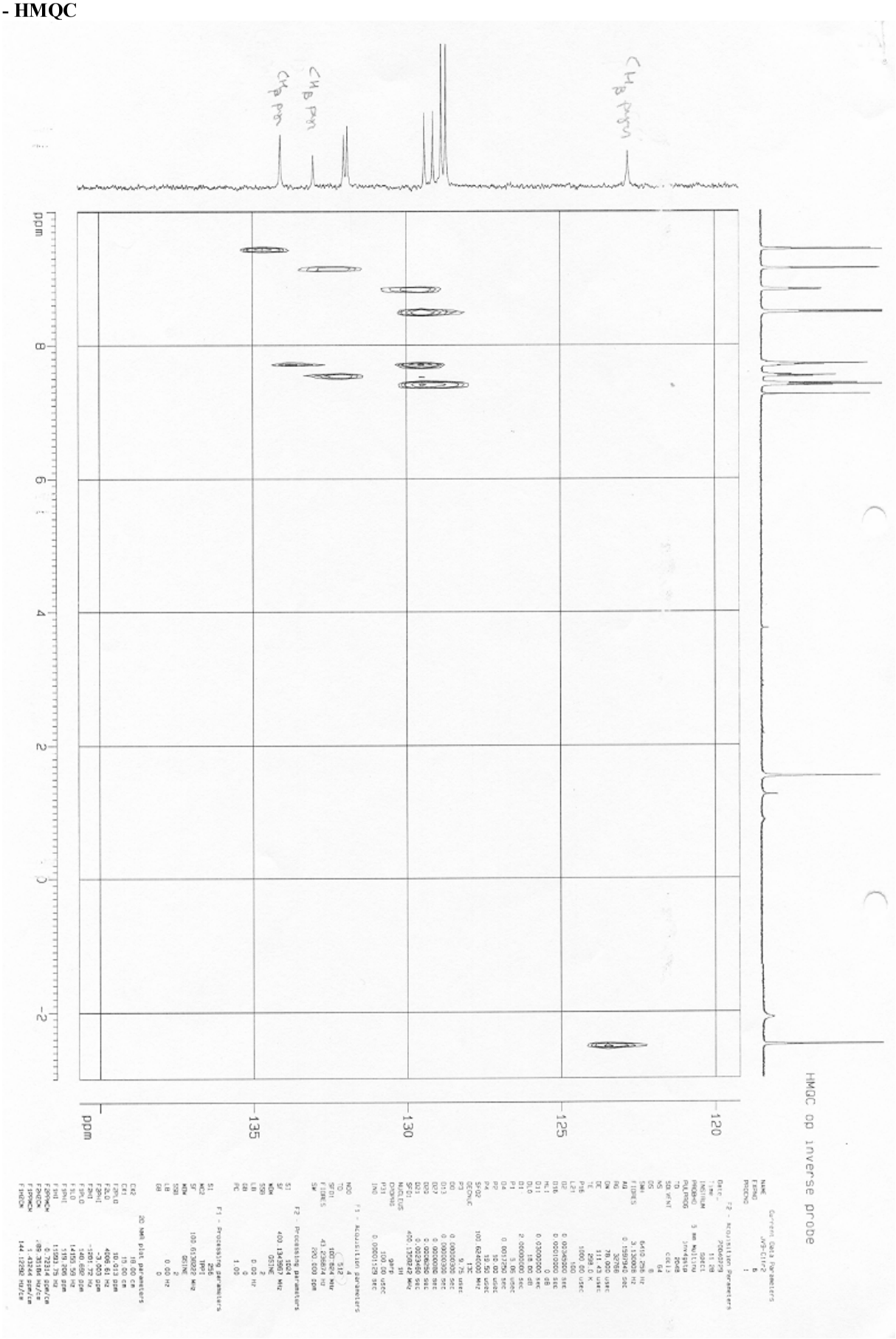
dmso

- HMQC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CH8 meta
ppm
ppm
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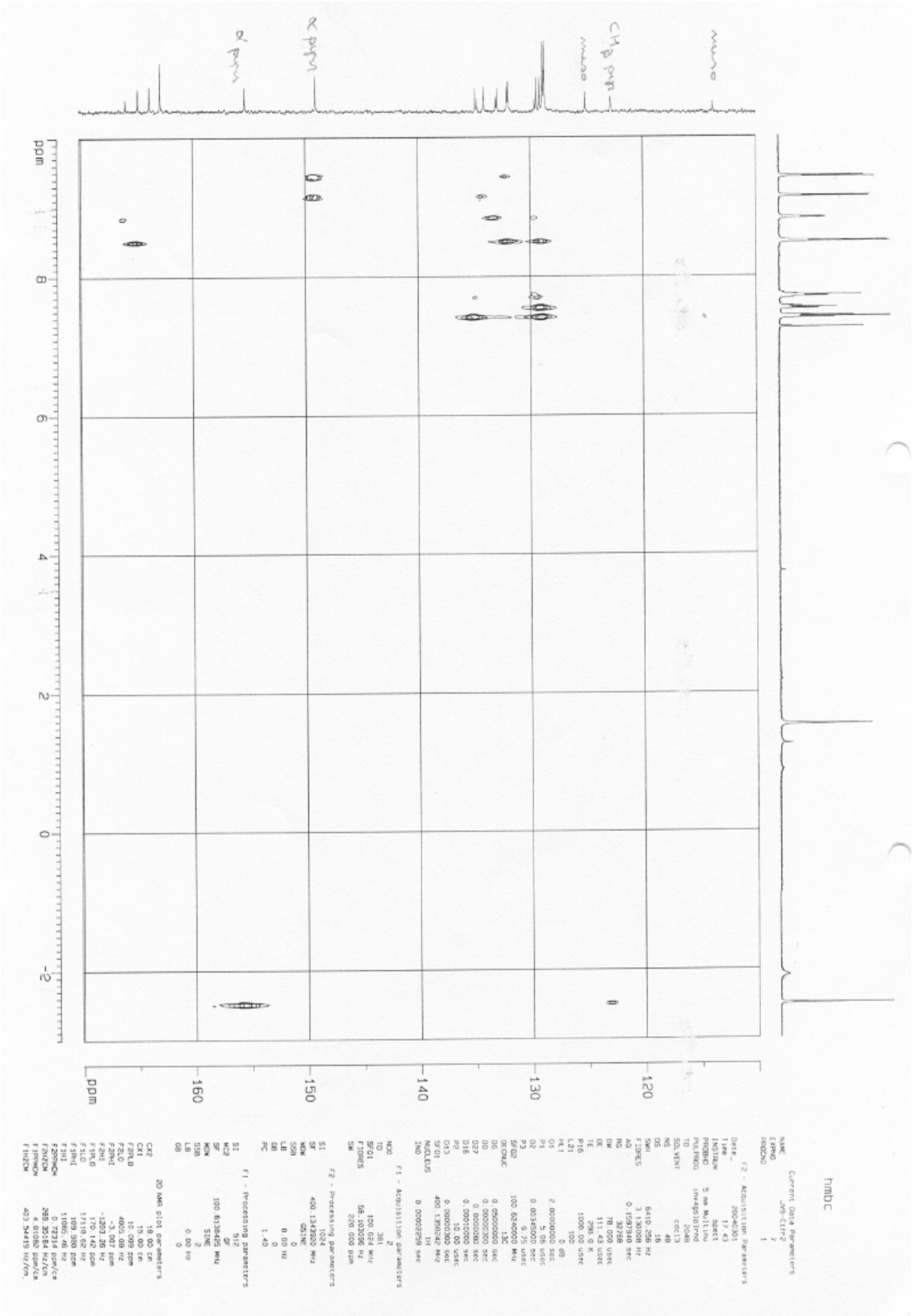
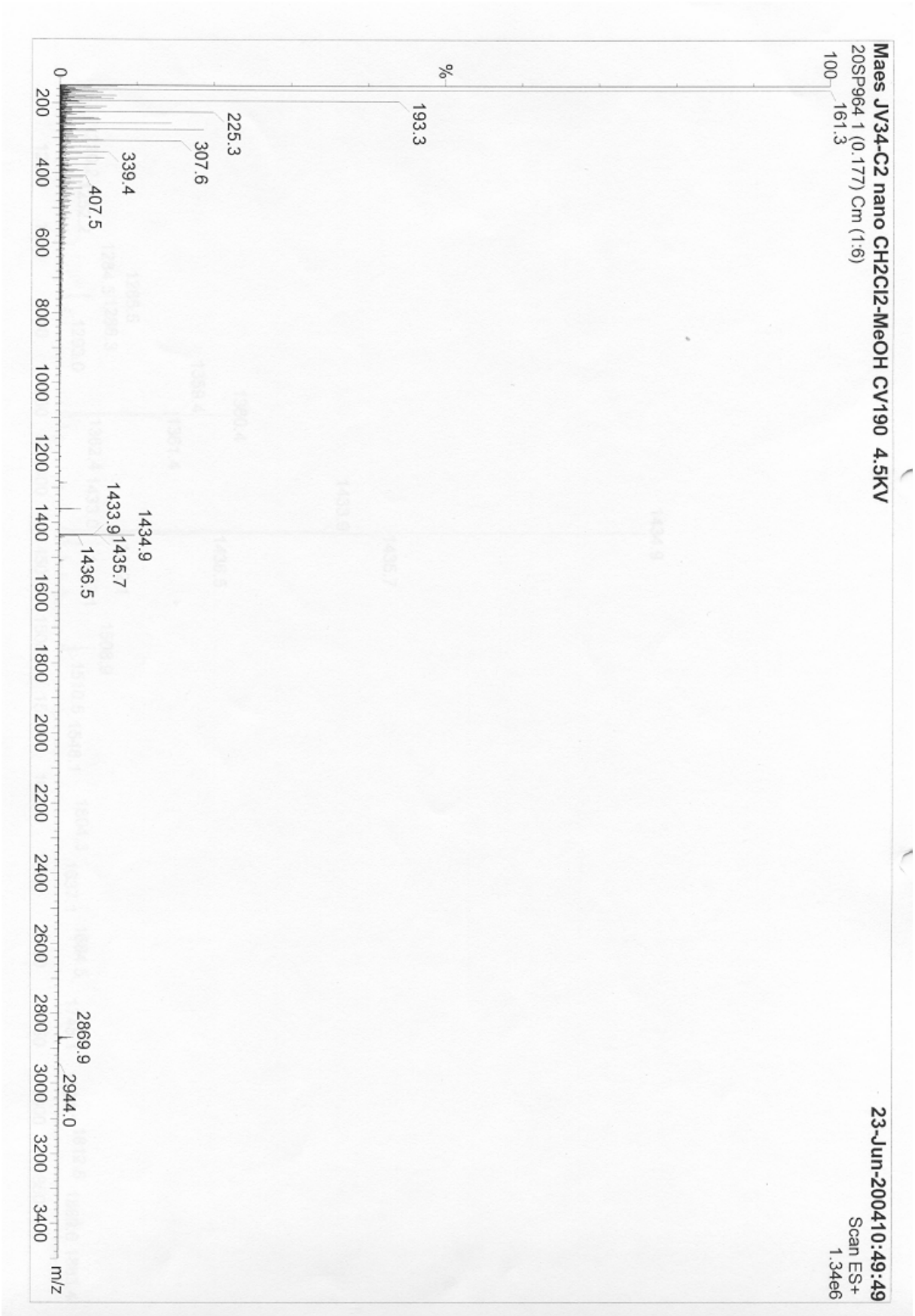
130
125
120
HMQC on inverse probe

- HMBC

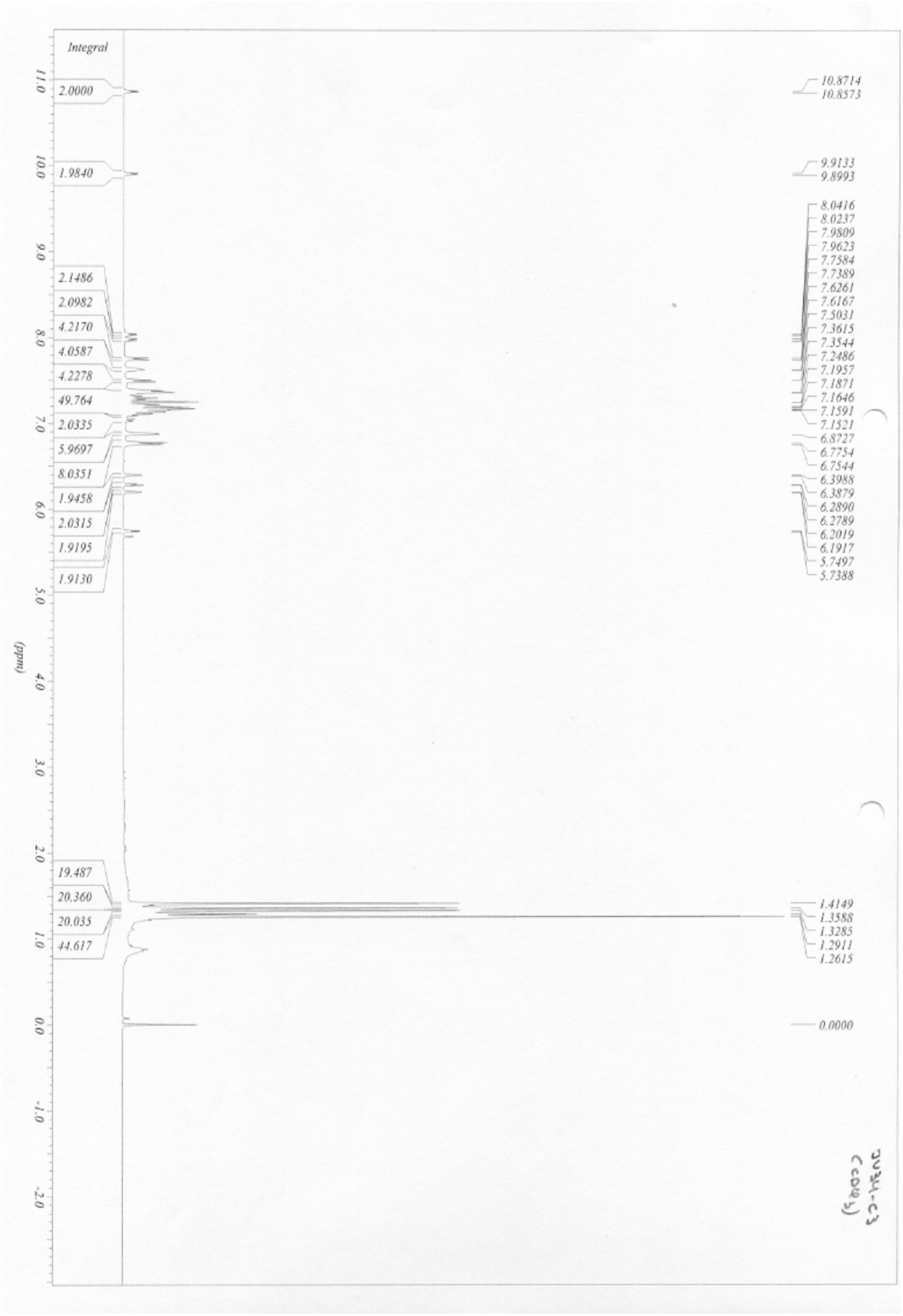


*** *syn*-Doubly N-fused hexaphyrin 6**

- ESI-MS



- ^{1}H NMR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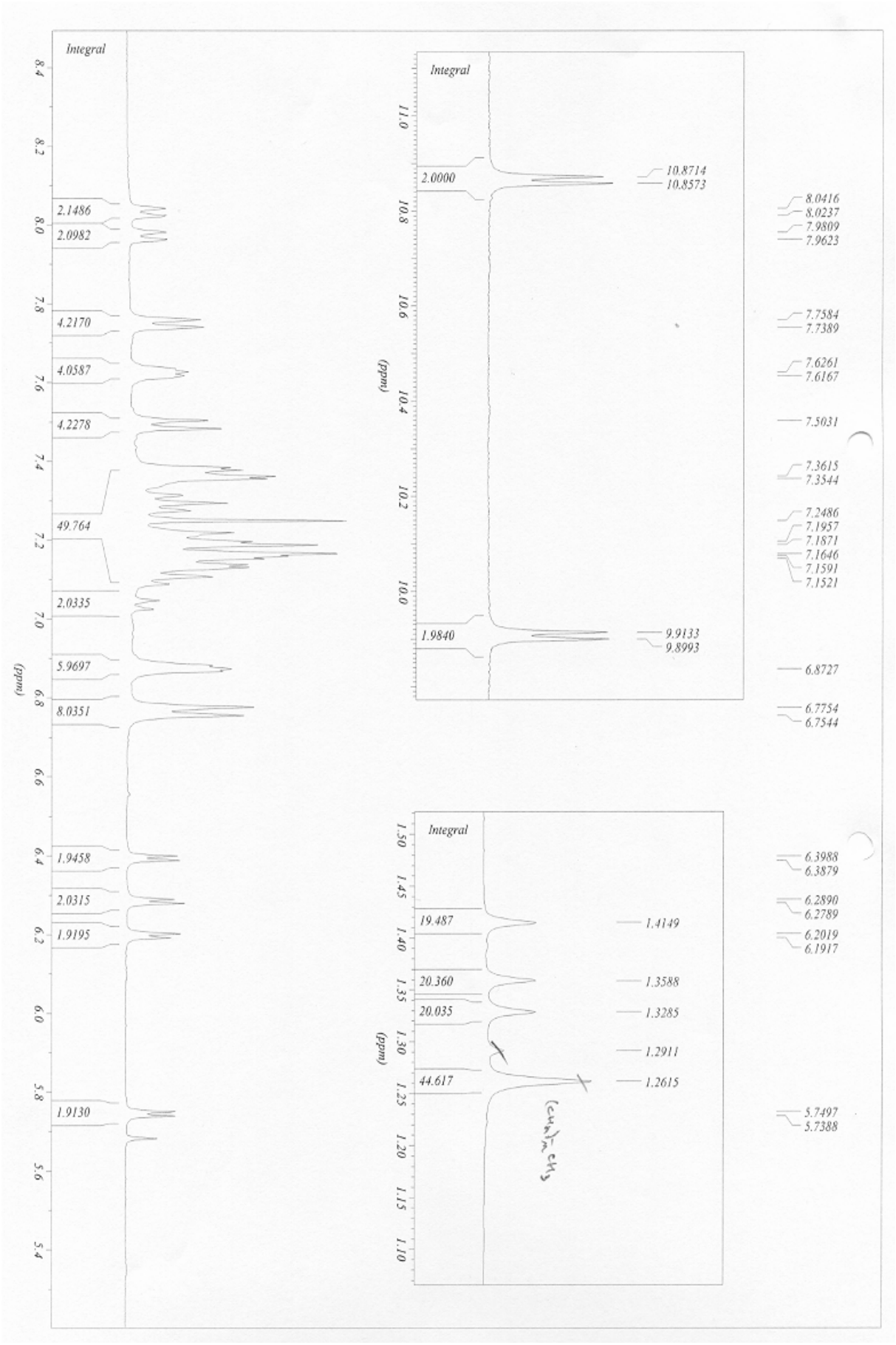
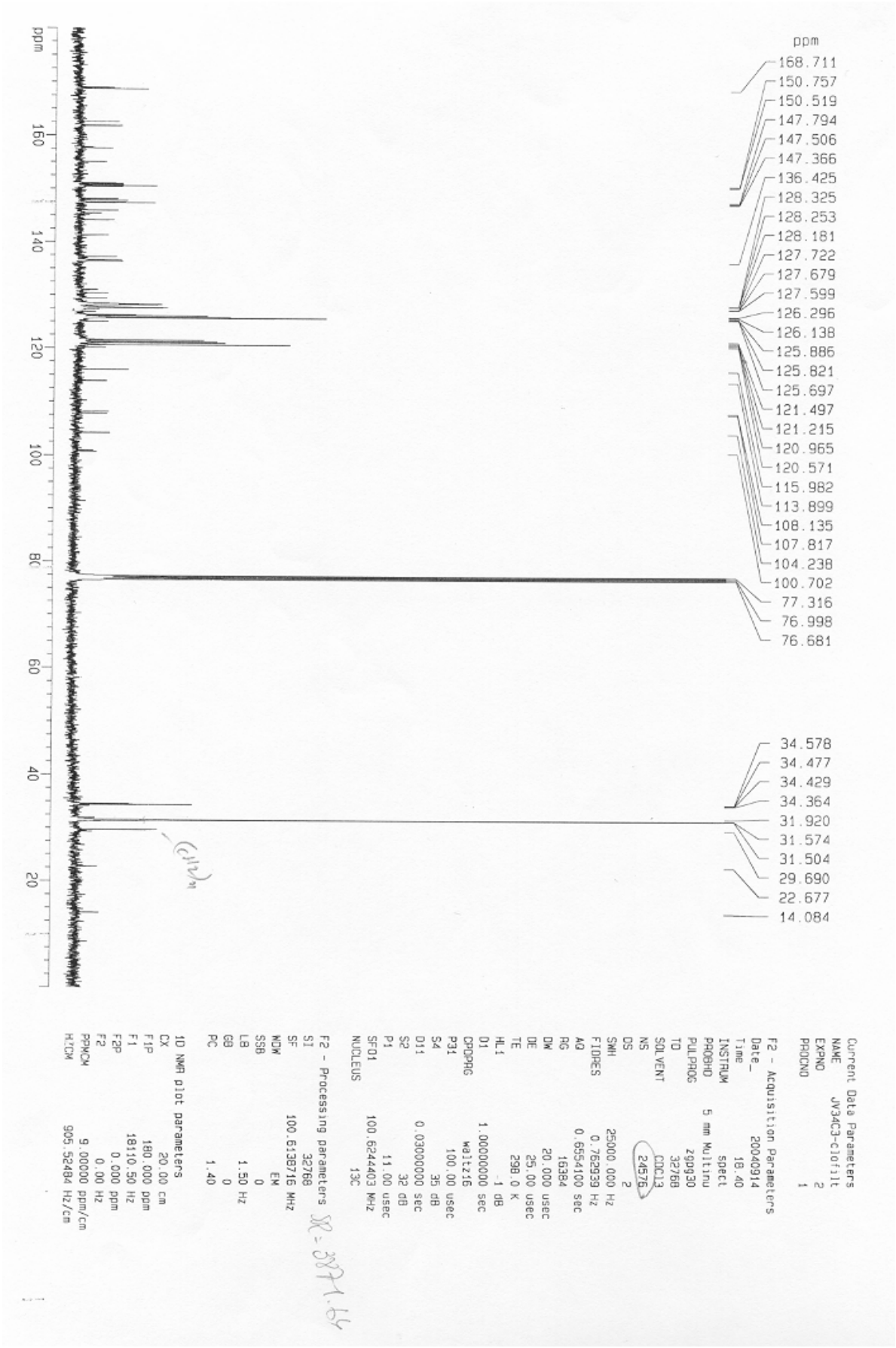


- ^{13}C NMR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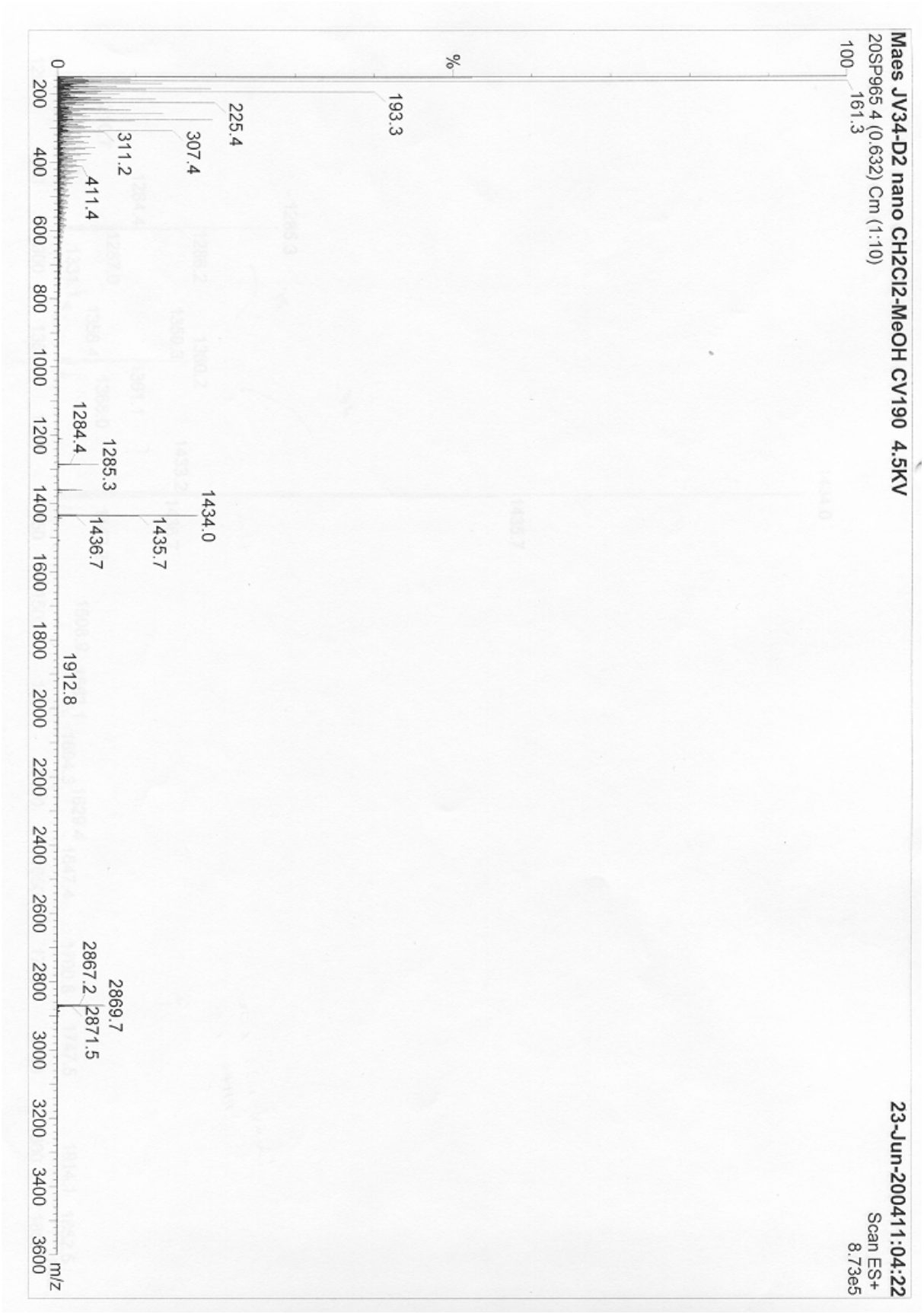
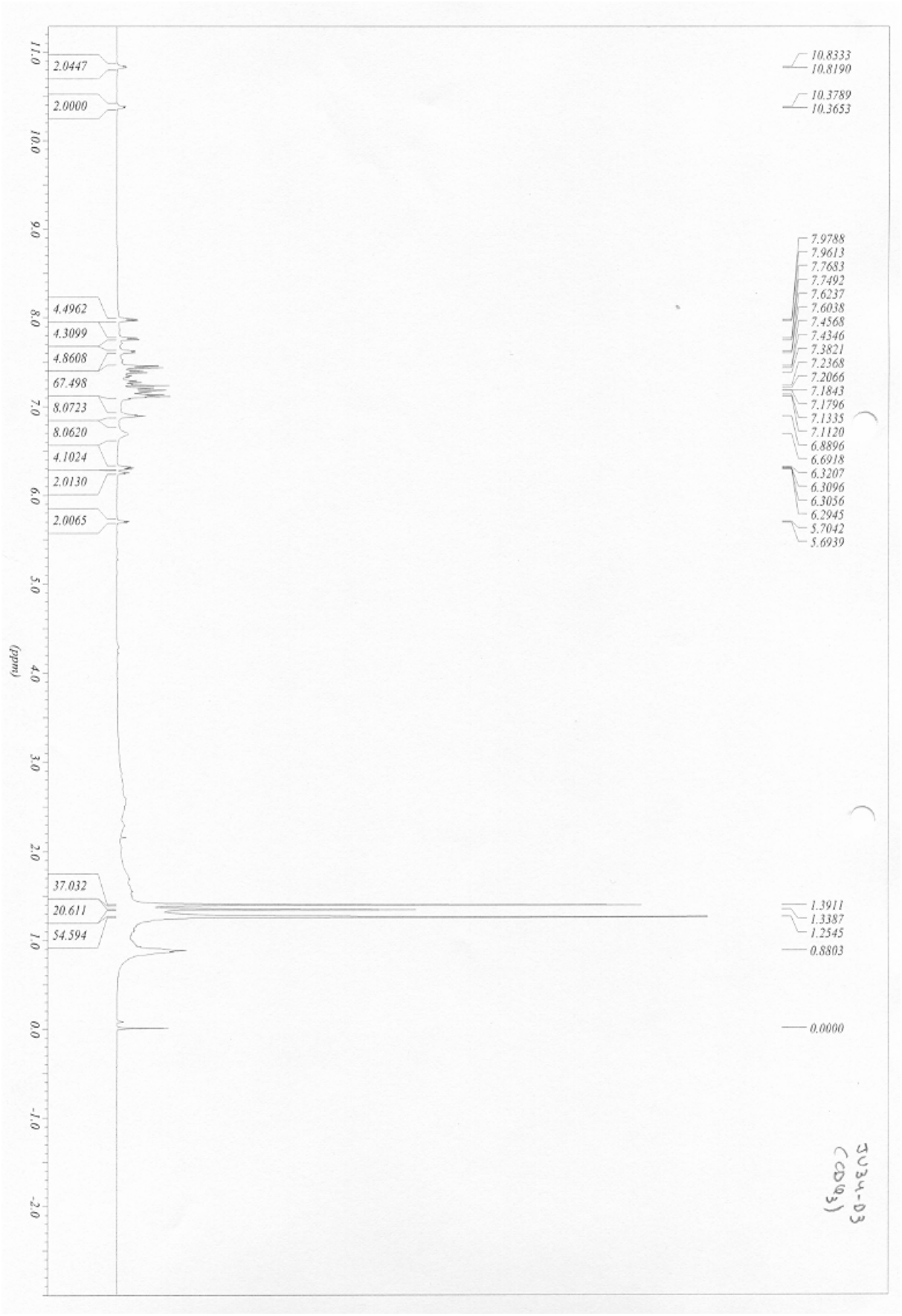
*** *anti*-Doubly N-fused hexaphyrin 7**

- ESI-MS



- ^{1}H NMR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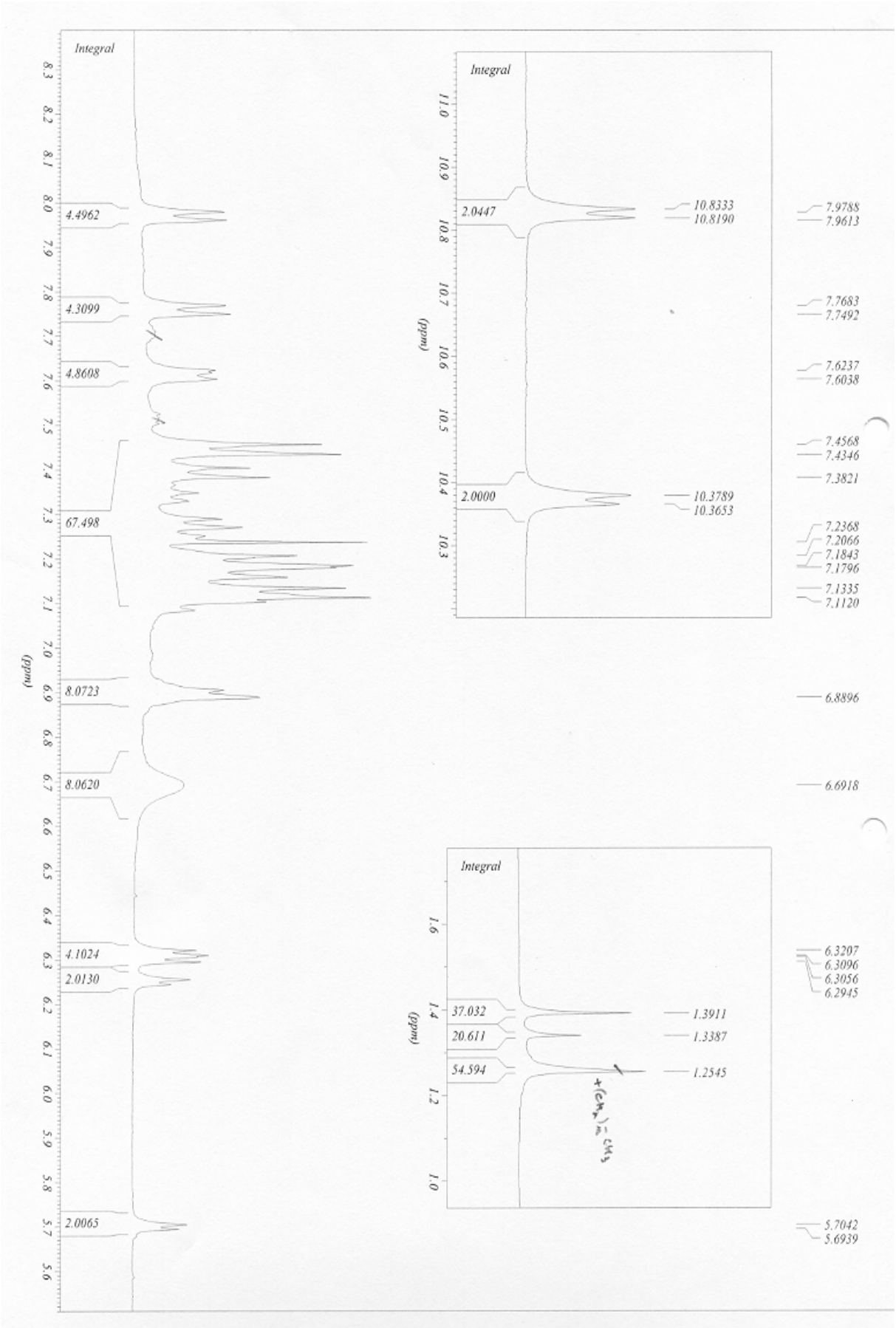
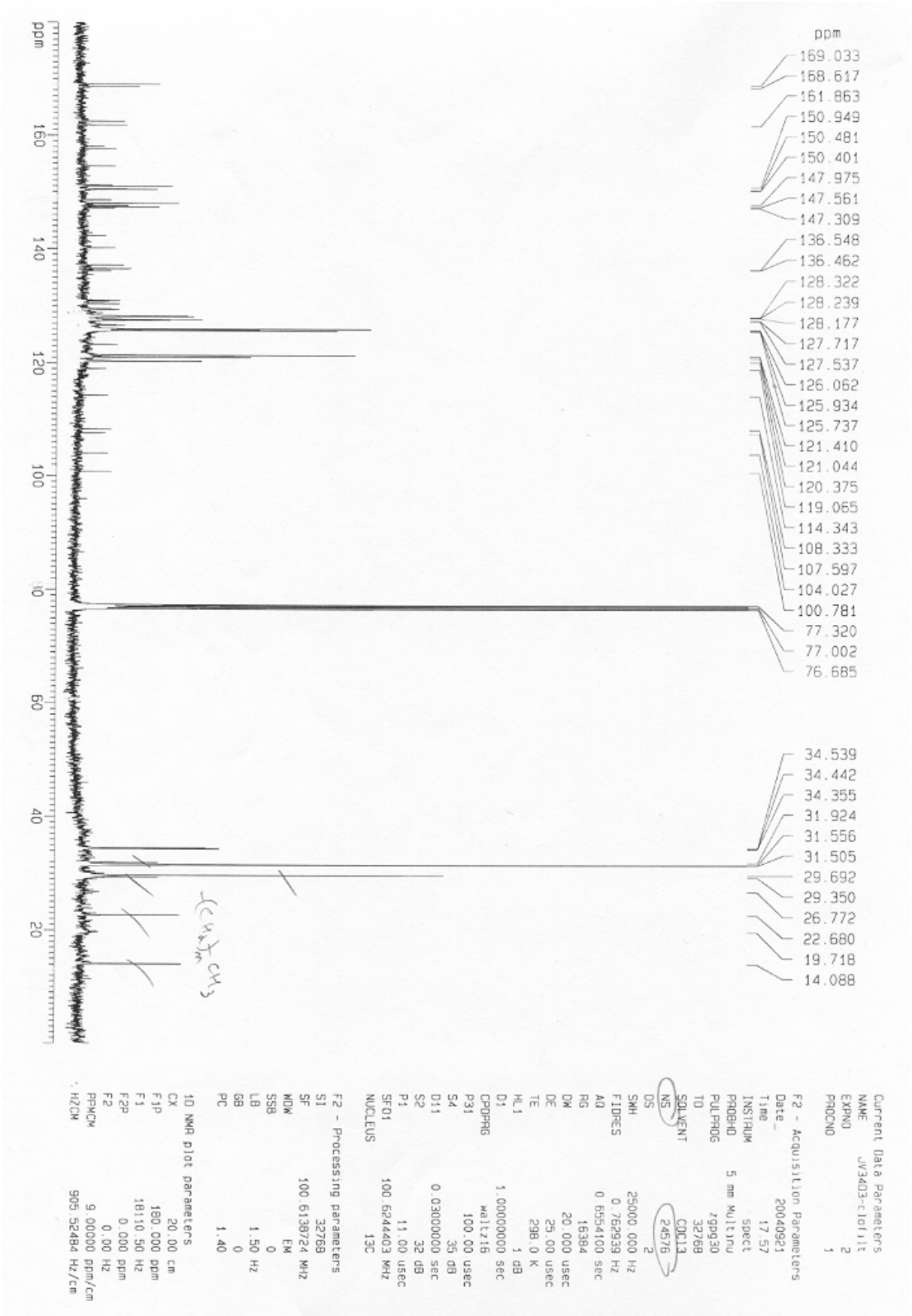


- ^{13}C NMR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D11 0.03000000 sec
S2 32 dB
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F2P 0.000 ppm
F2 0.00 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.52484 Hz/cm