Electronic Supplementary Information

Aggregation of asphaltene model compounds using a porphyrin tethered to a carboxylic acid

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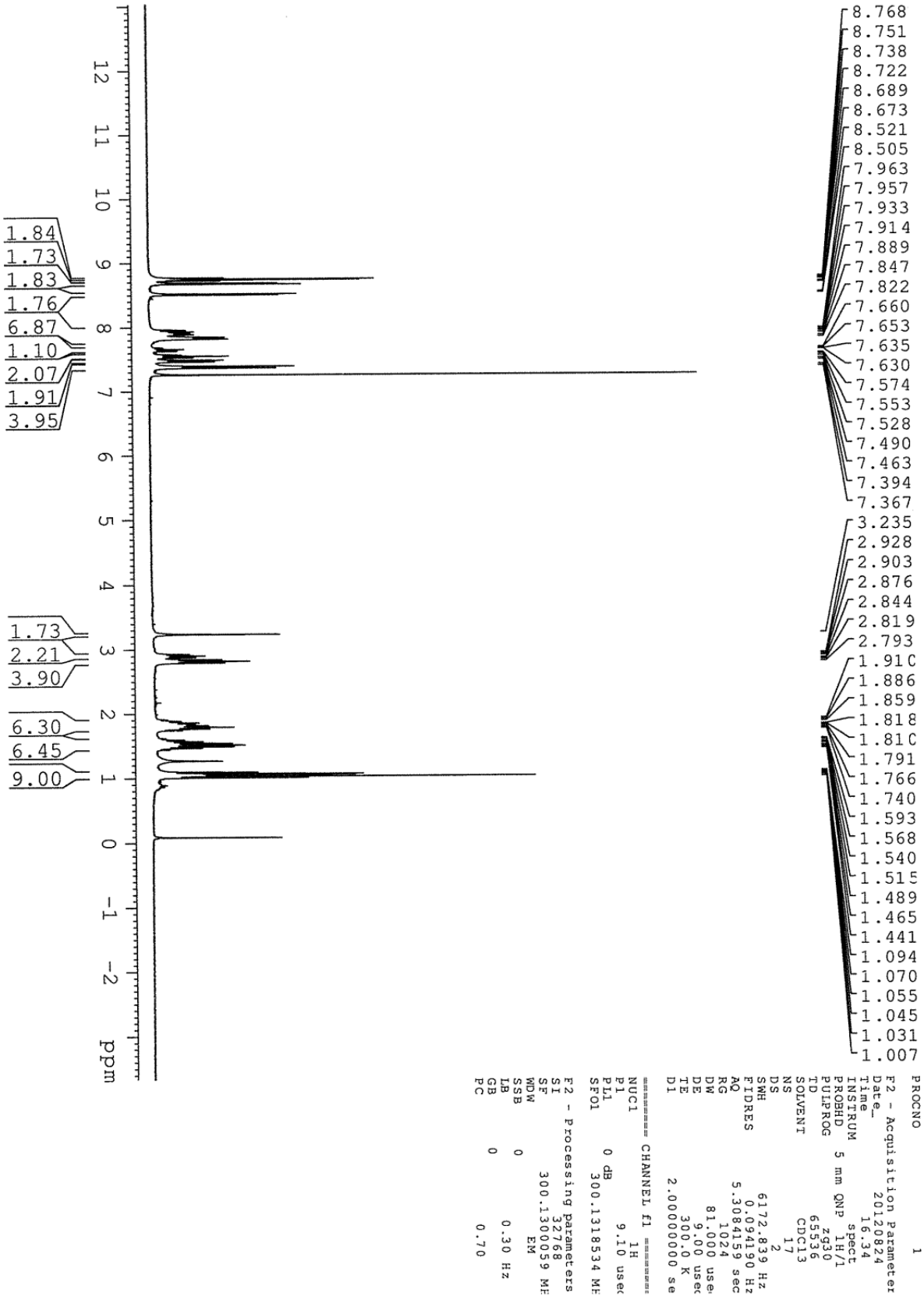
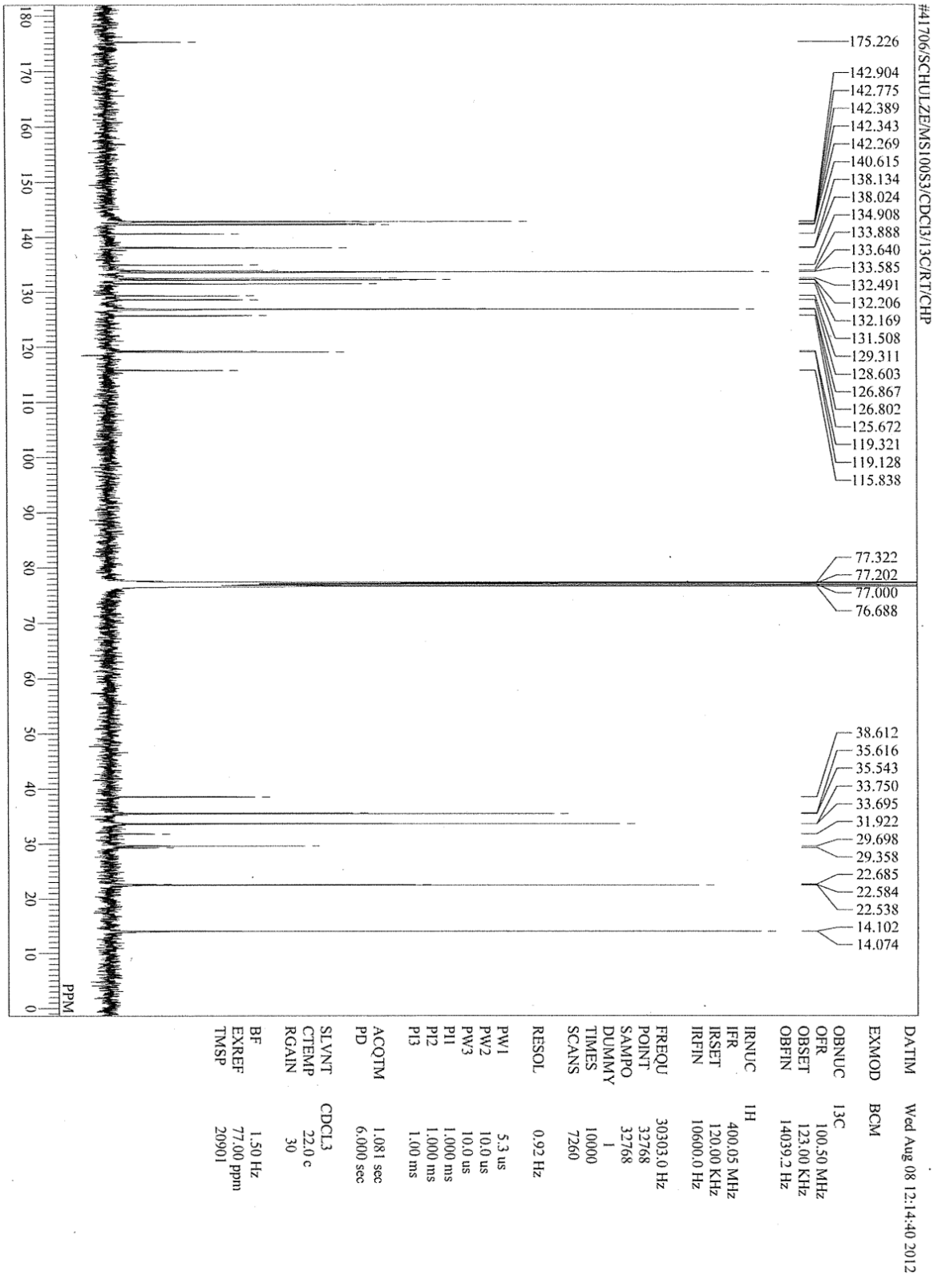
^{1}H and ^{13}C NMR spectra of compound 3–10



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of porphyrin **3**.



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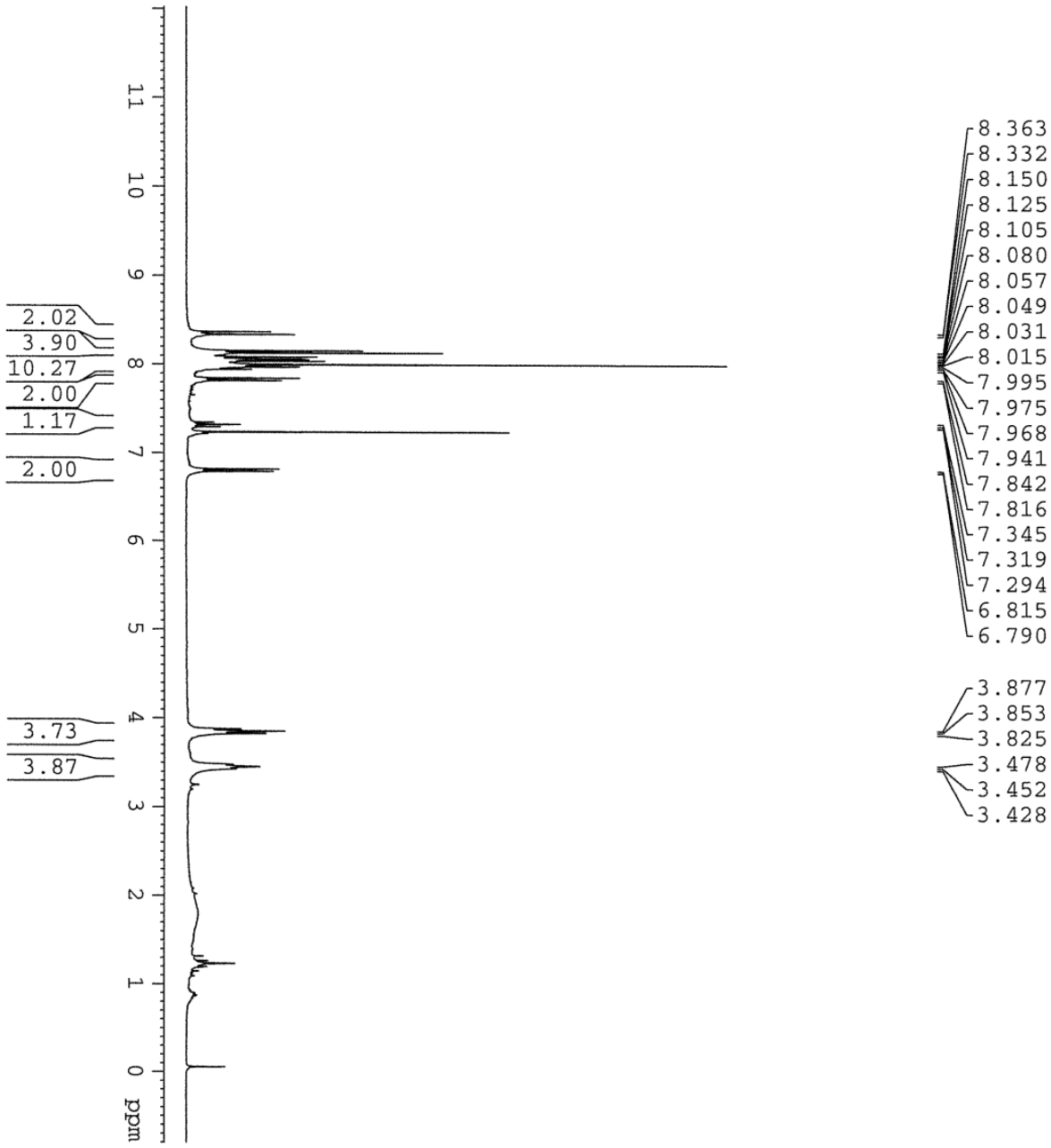

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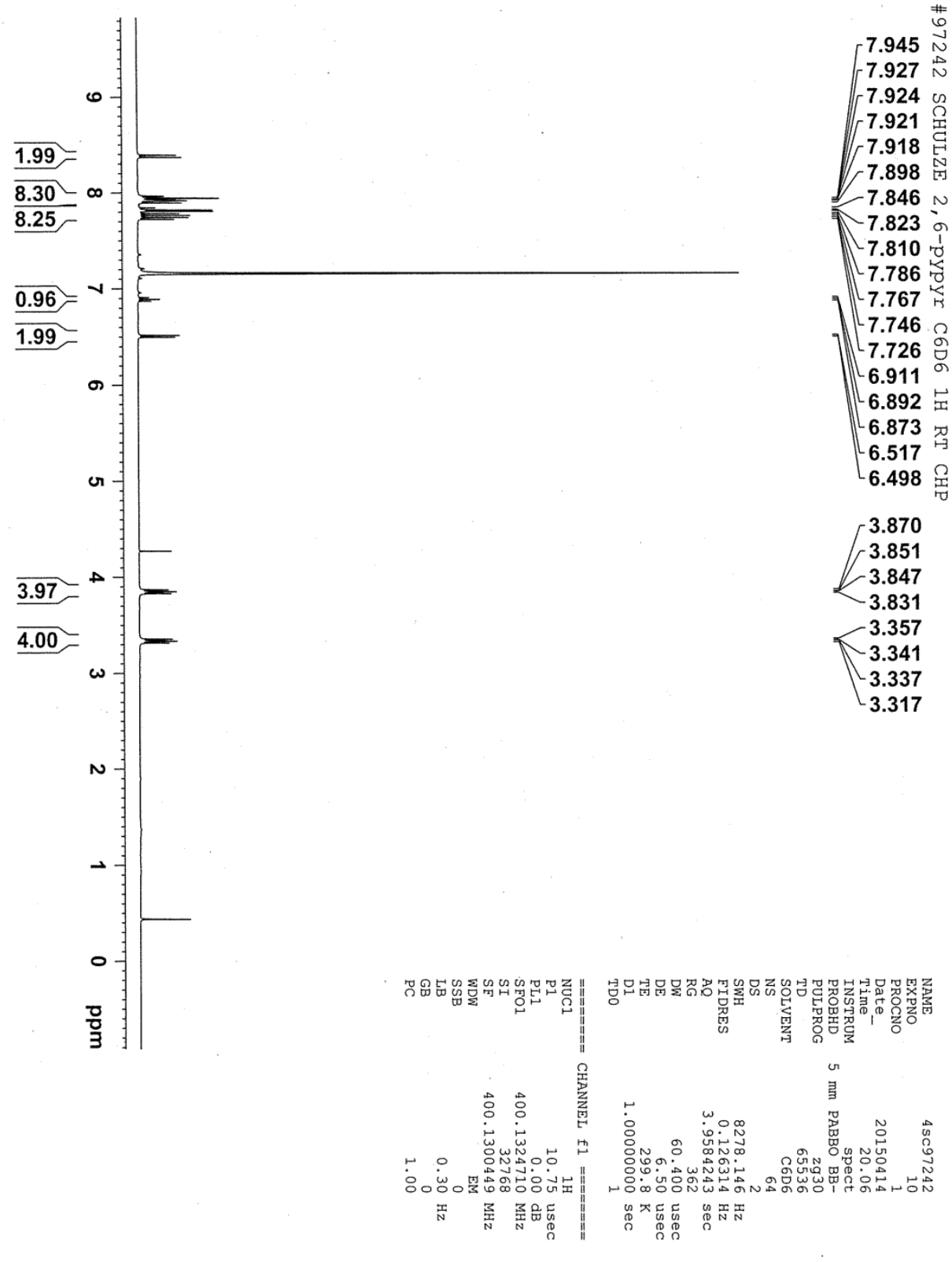

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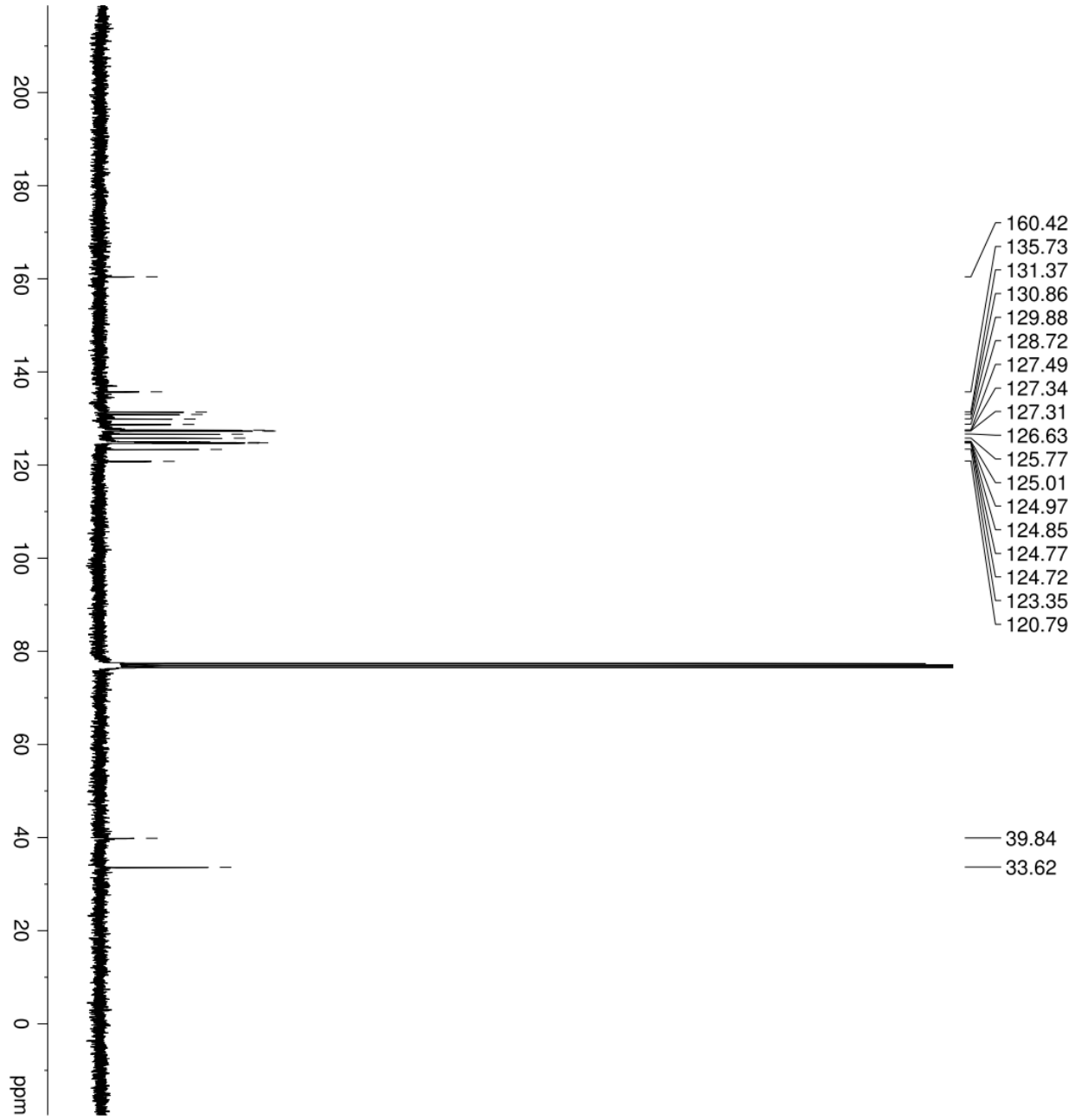

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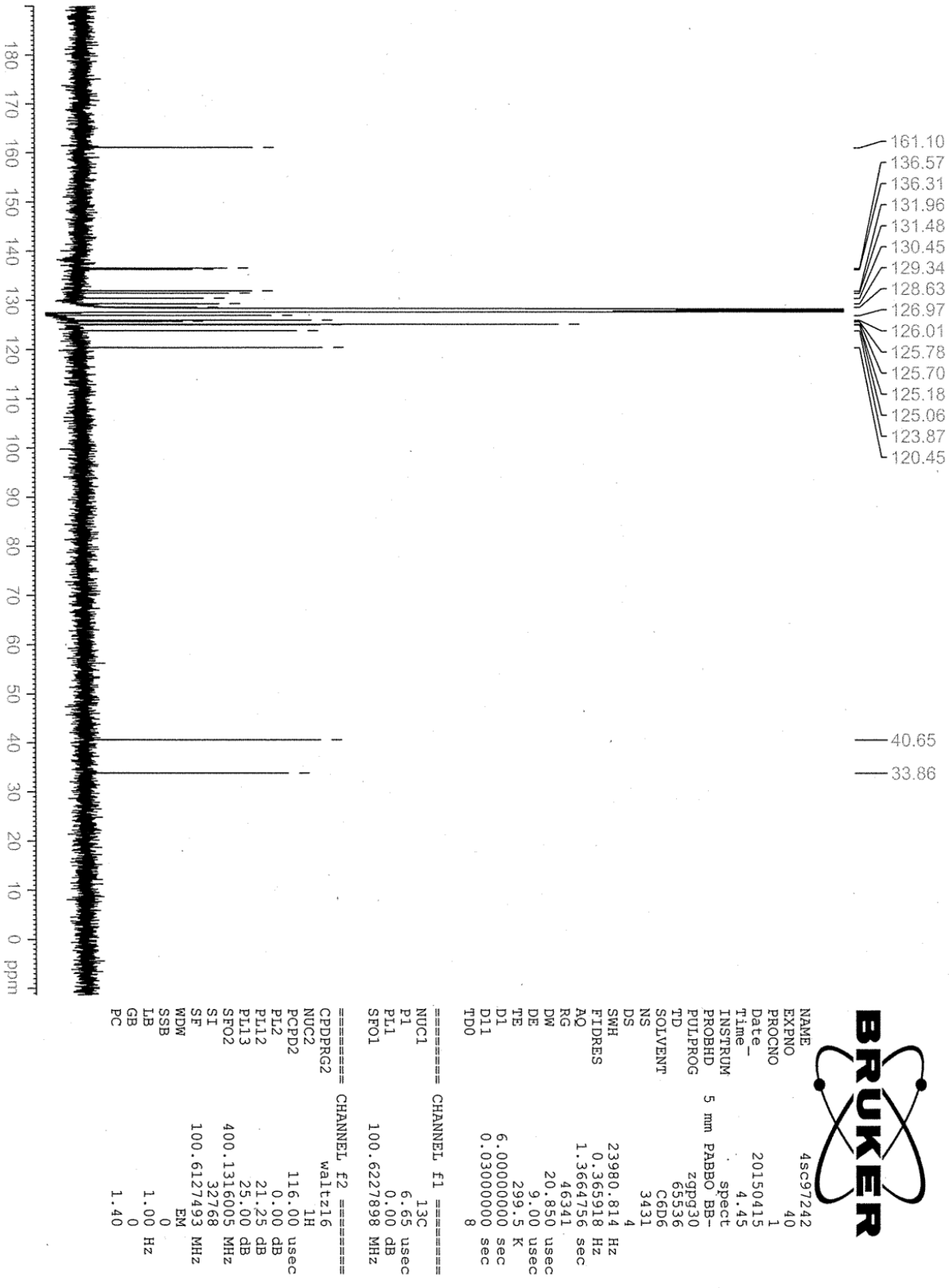

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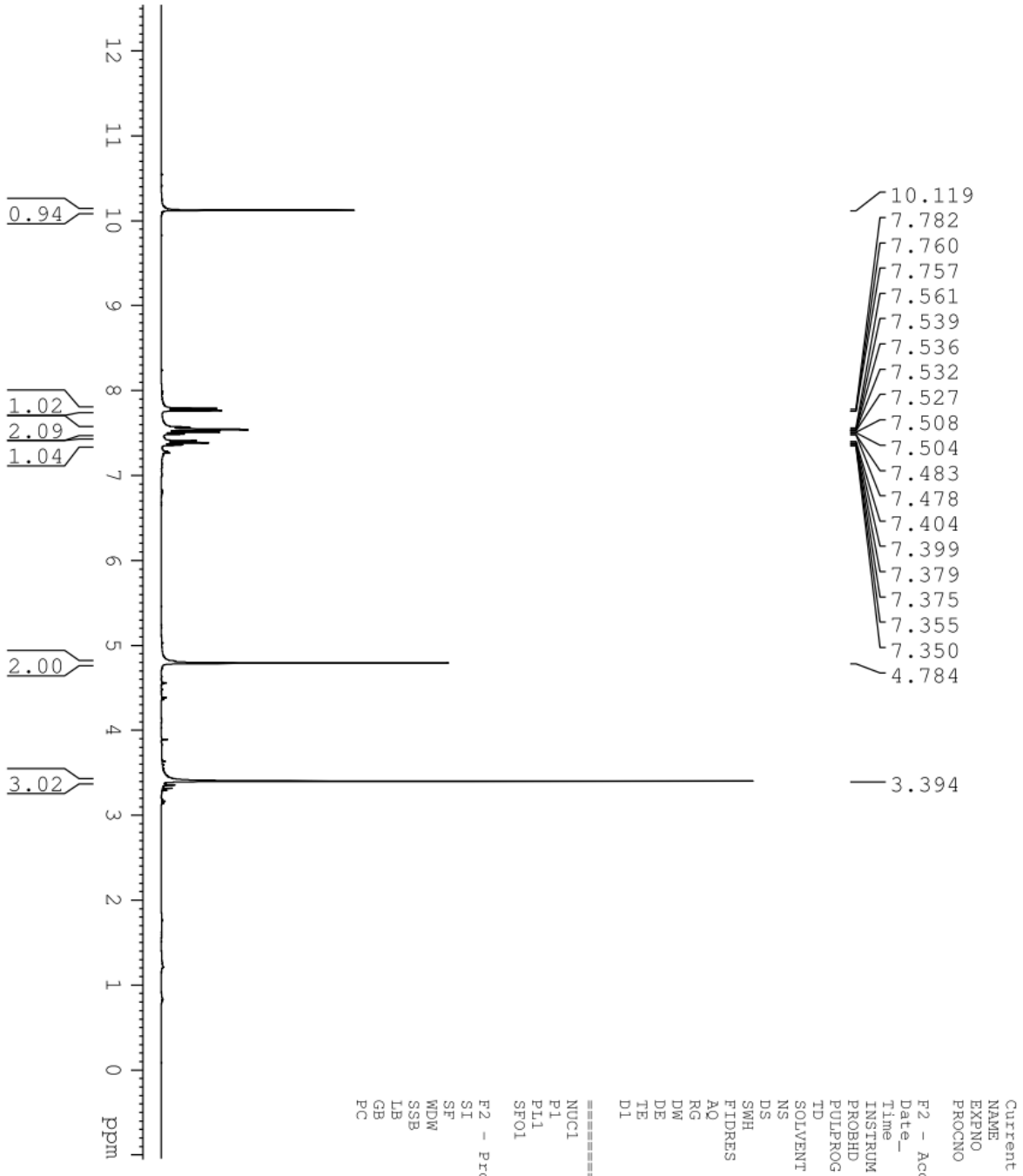

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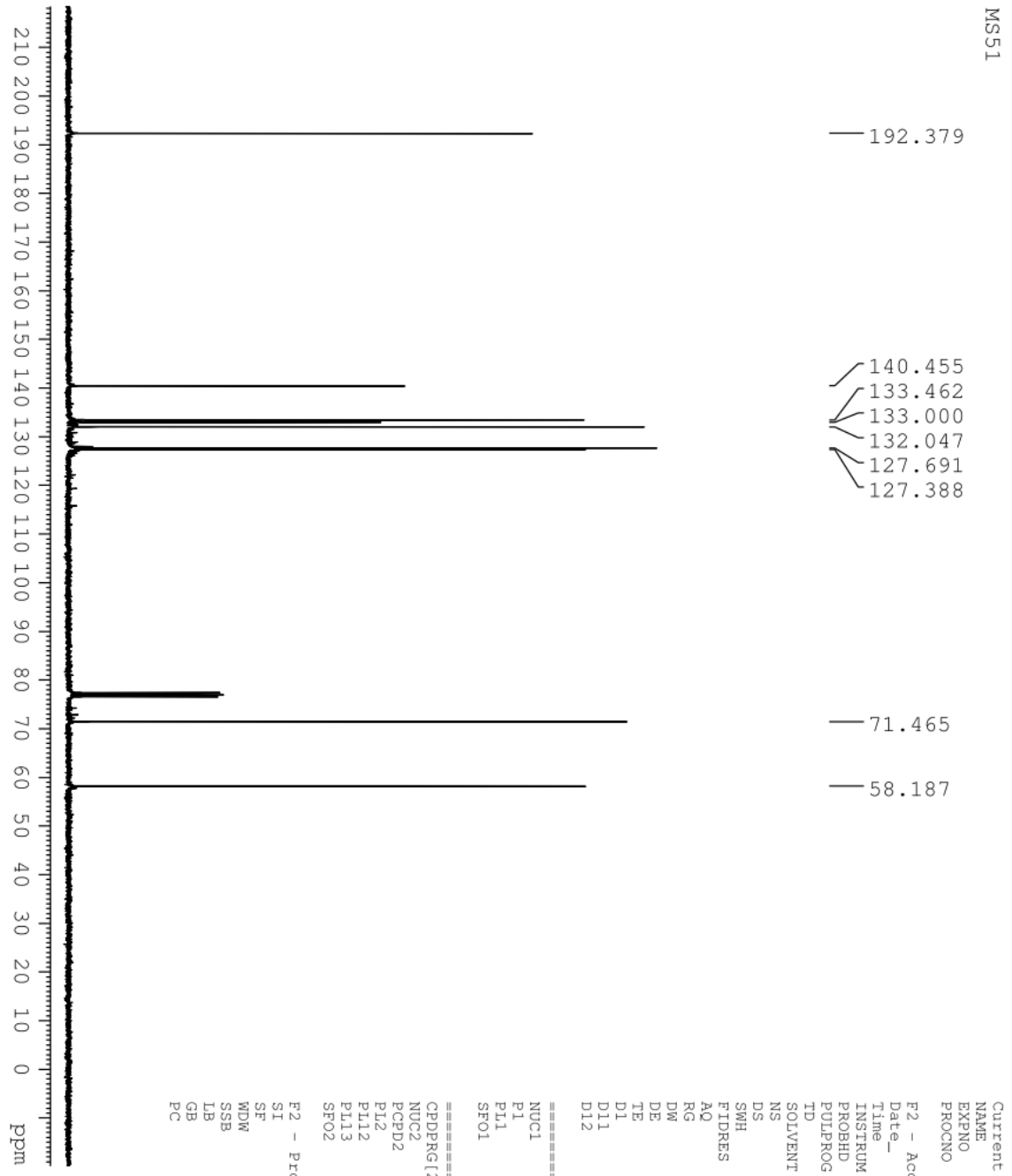

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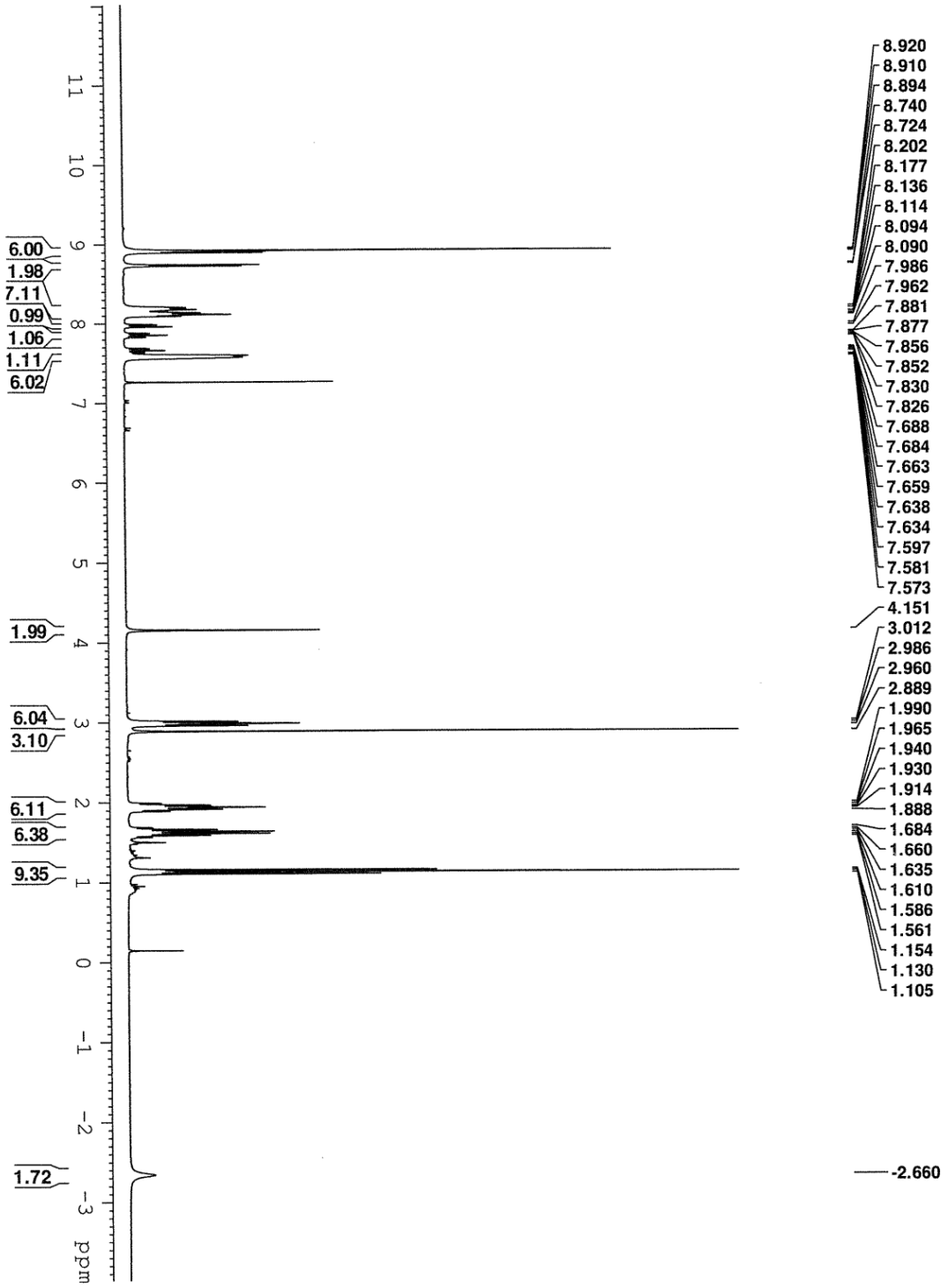

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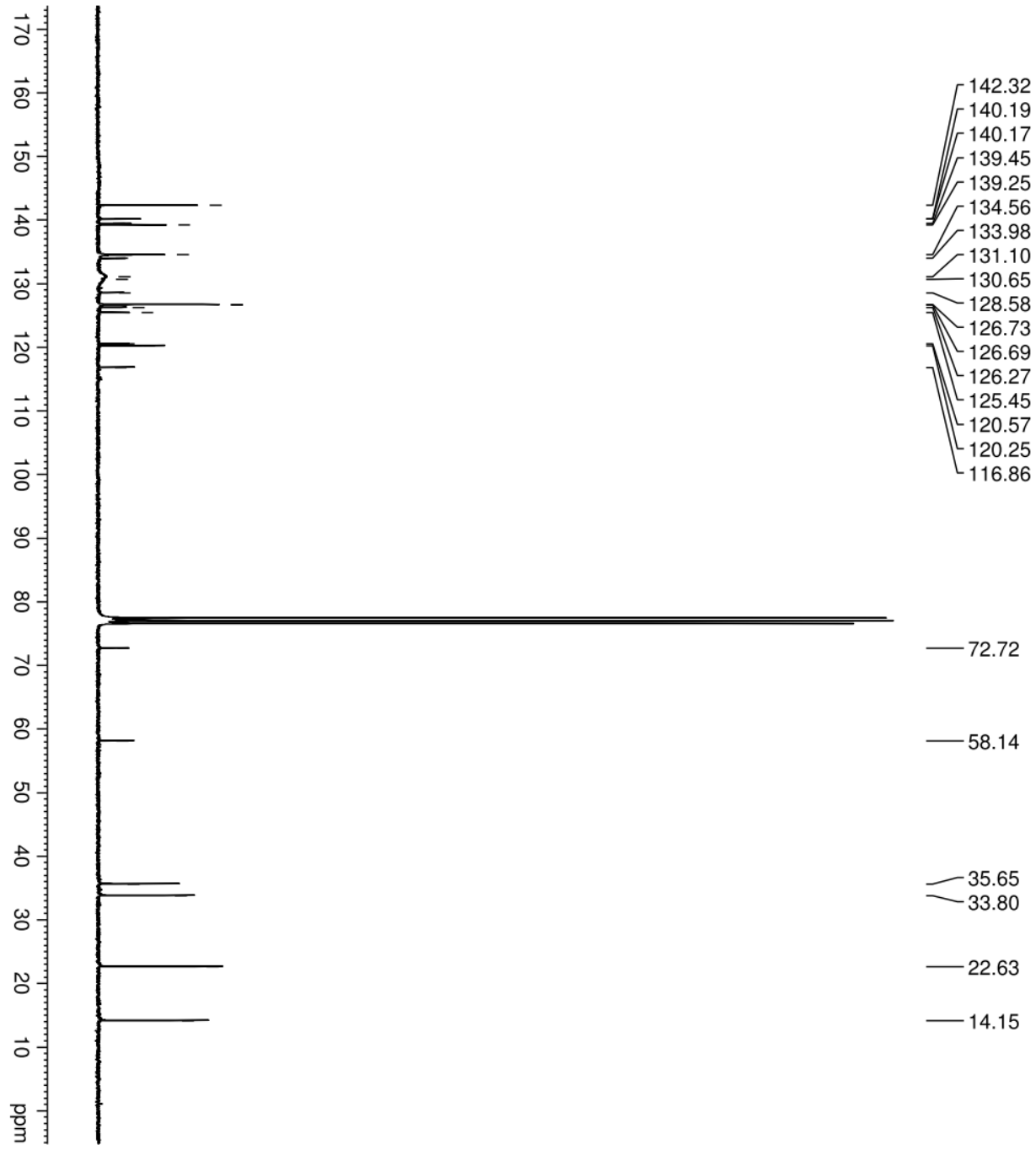


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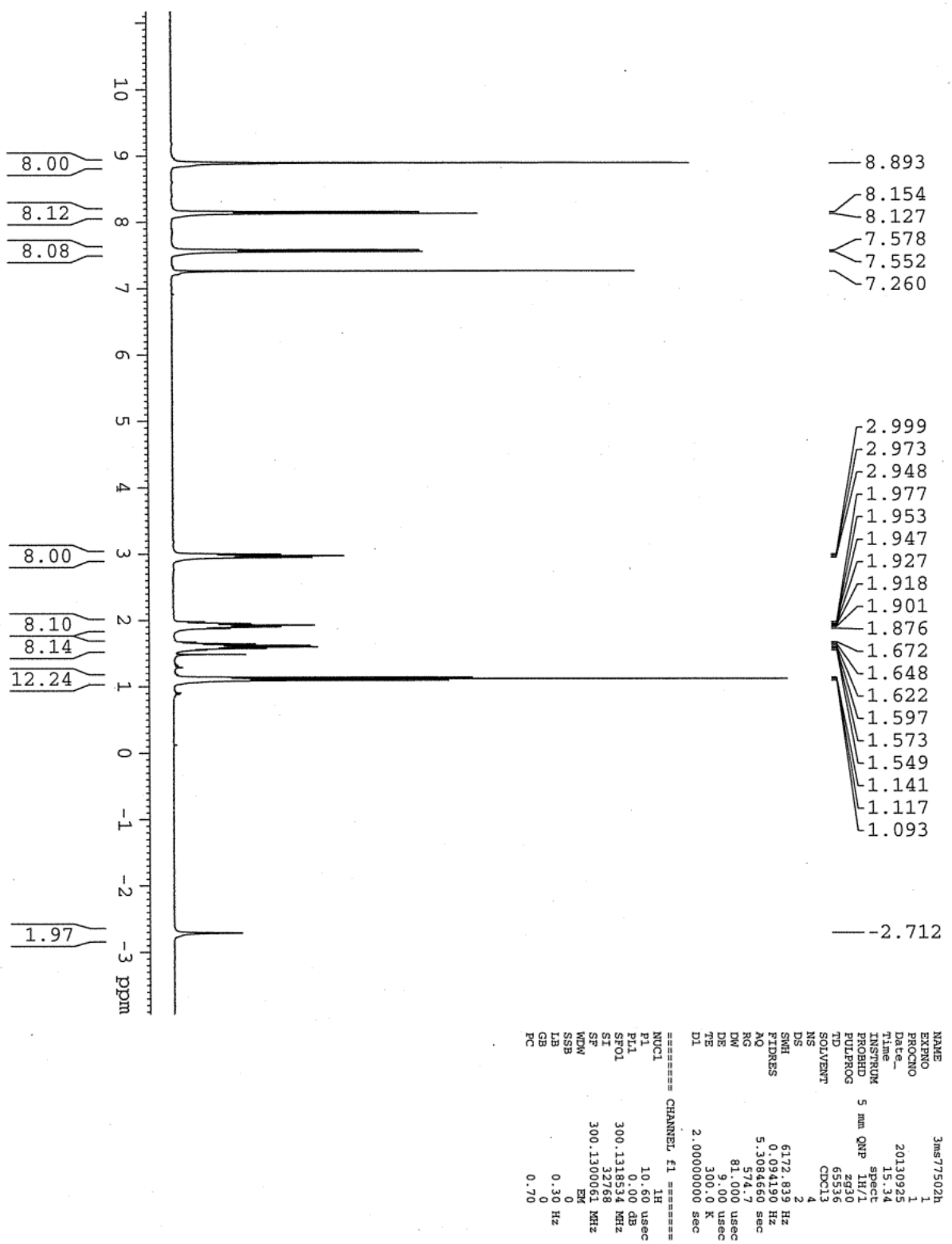

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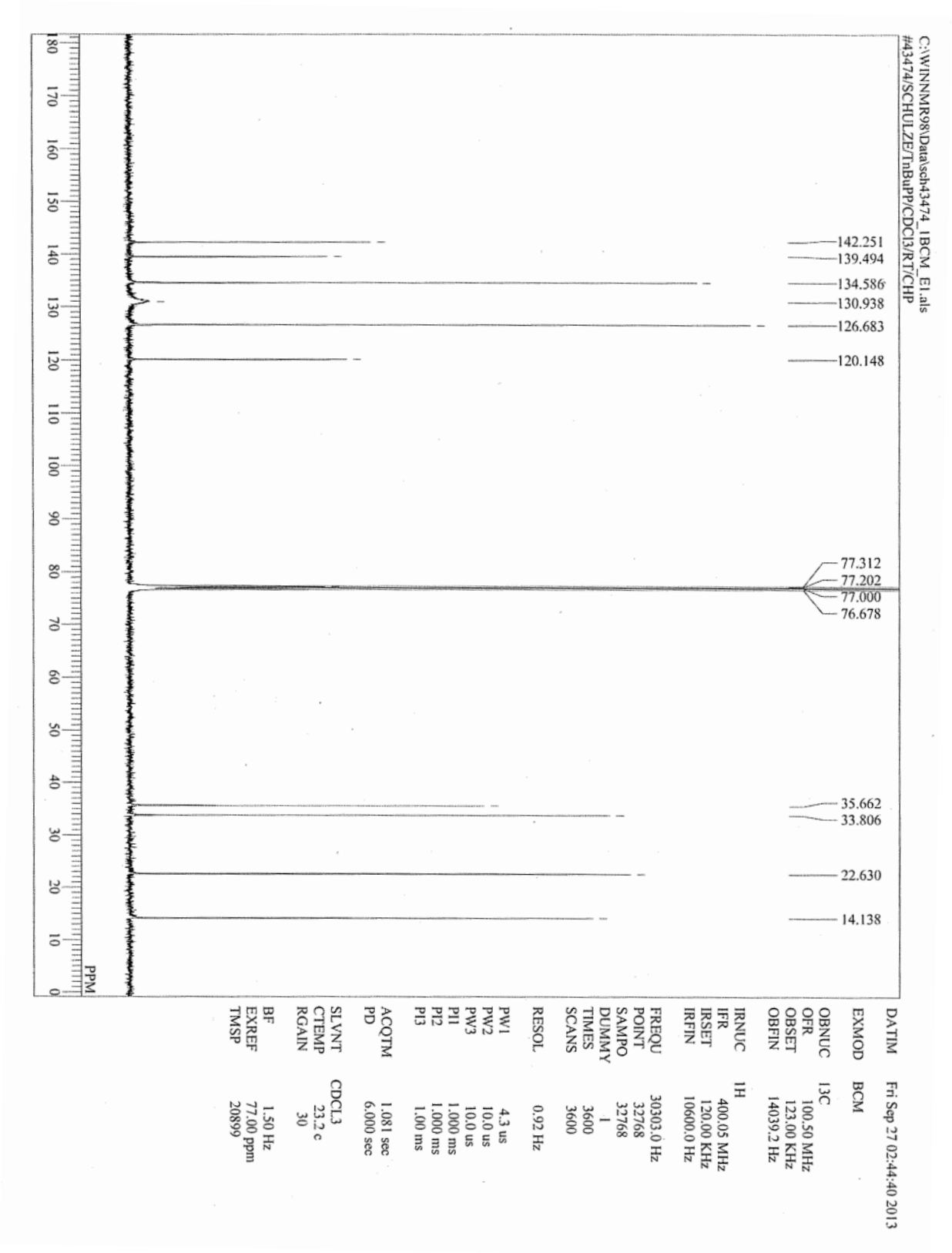

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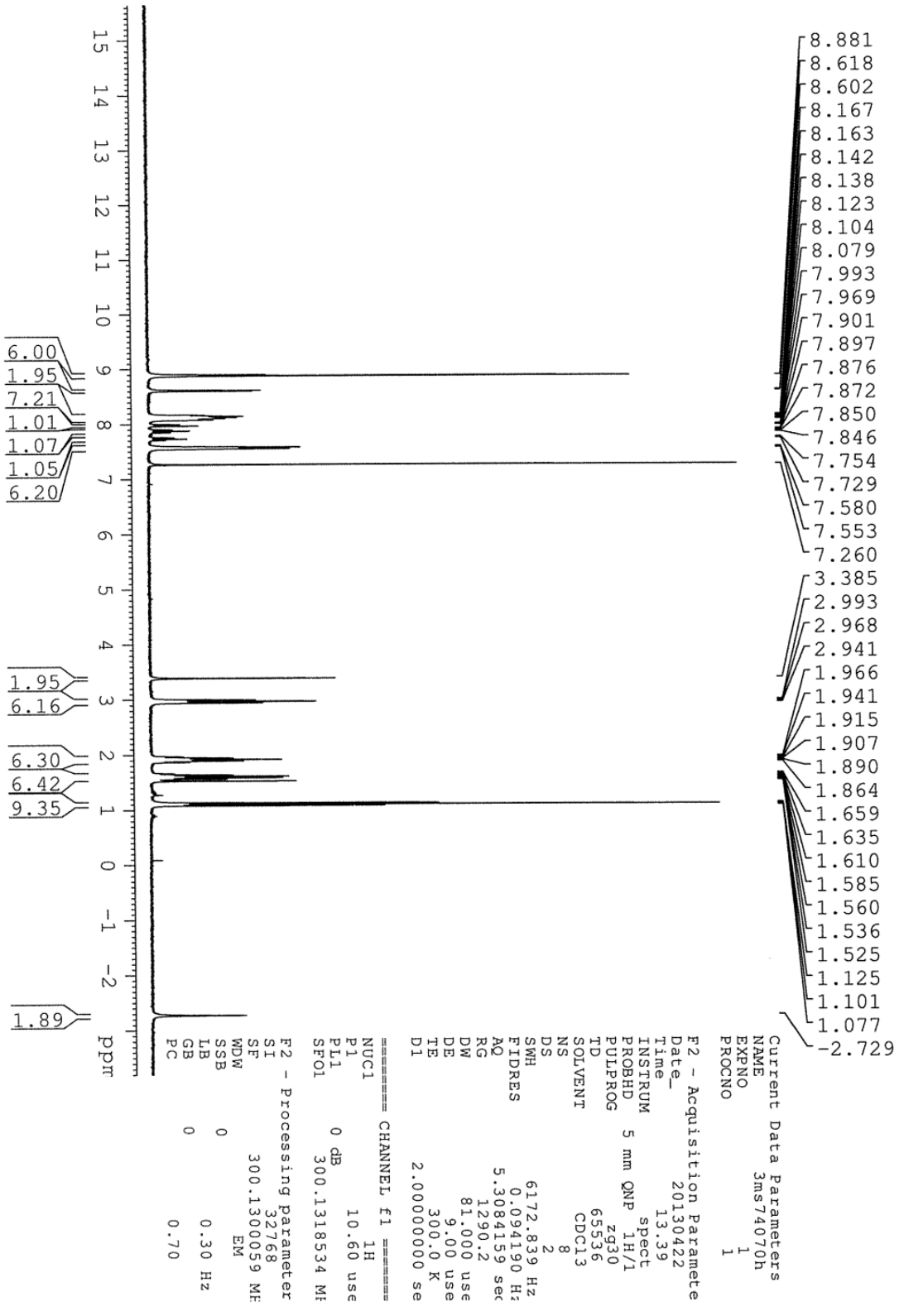

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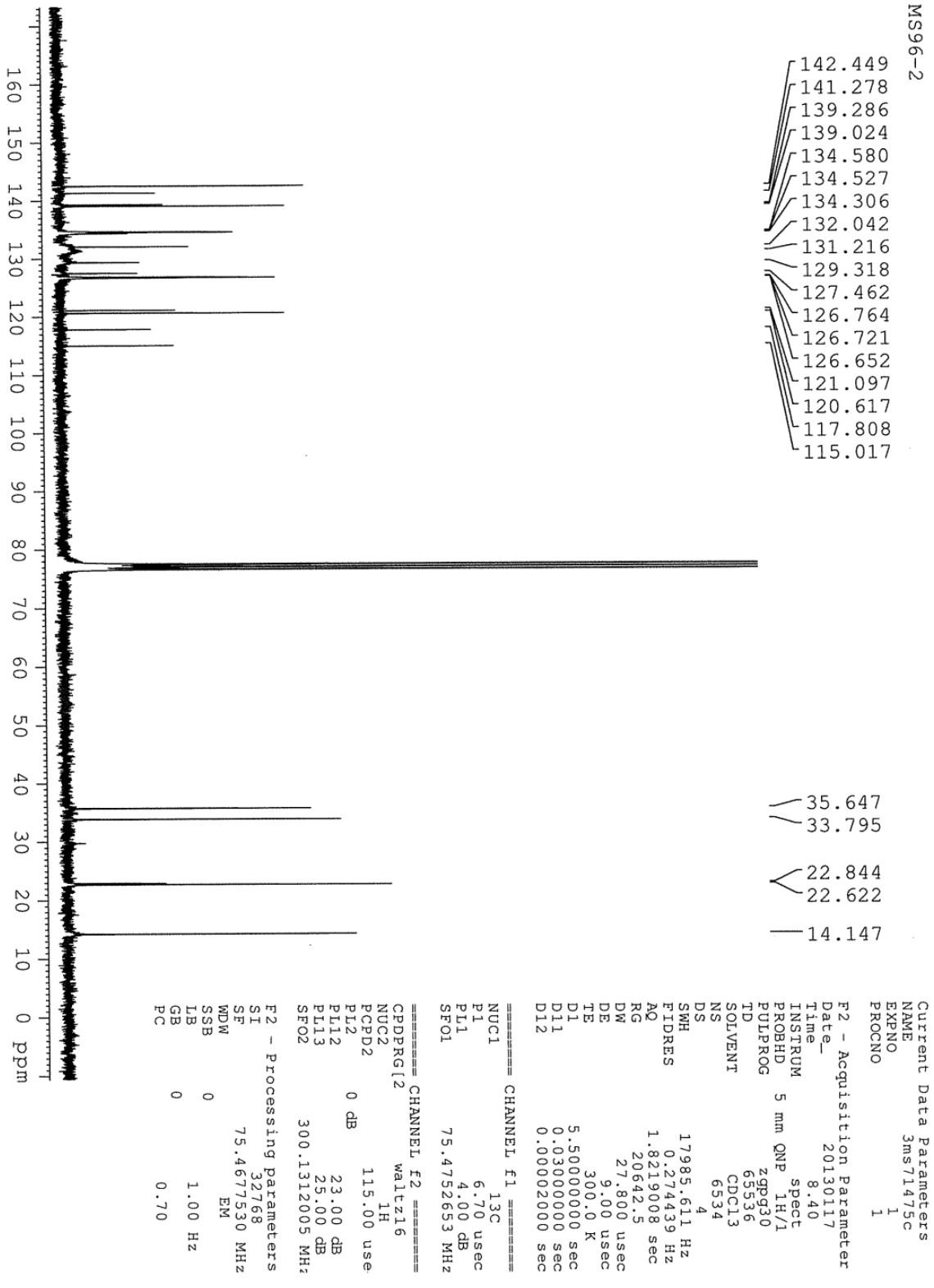

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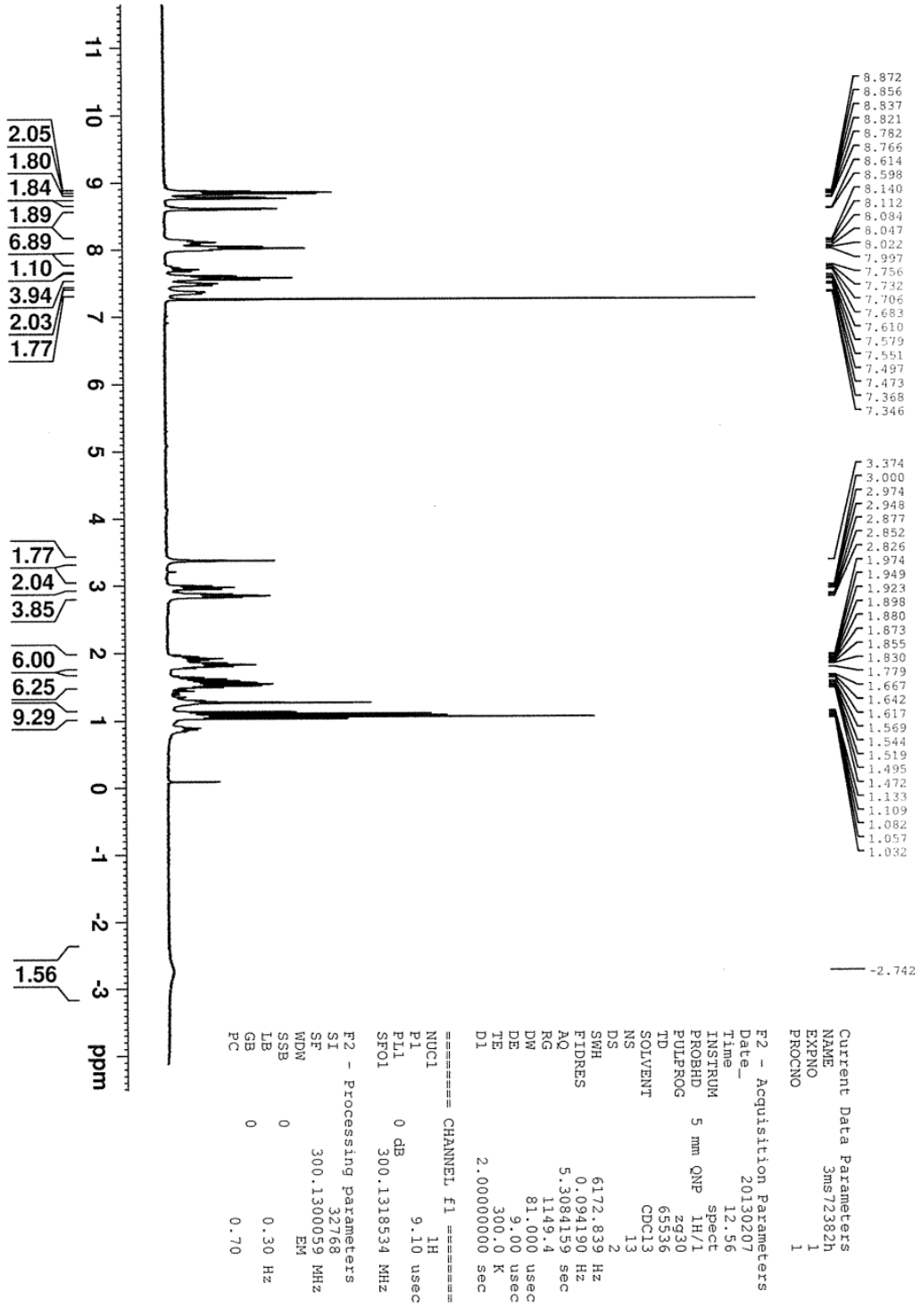

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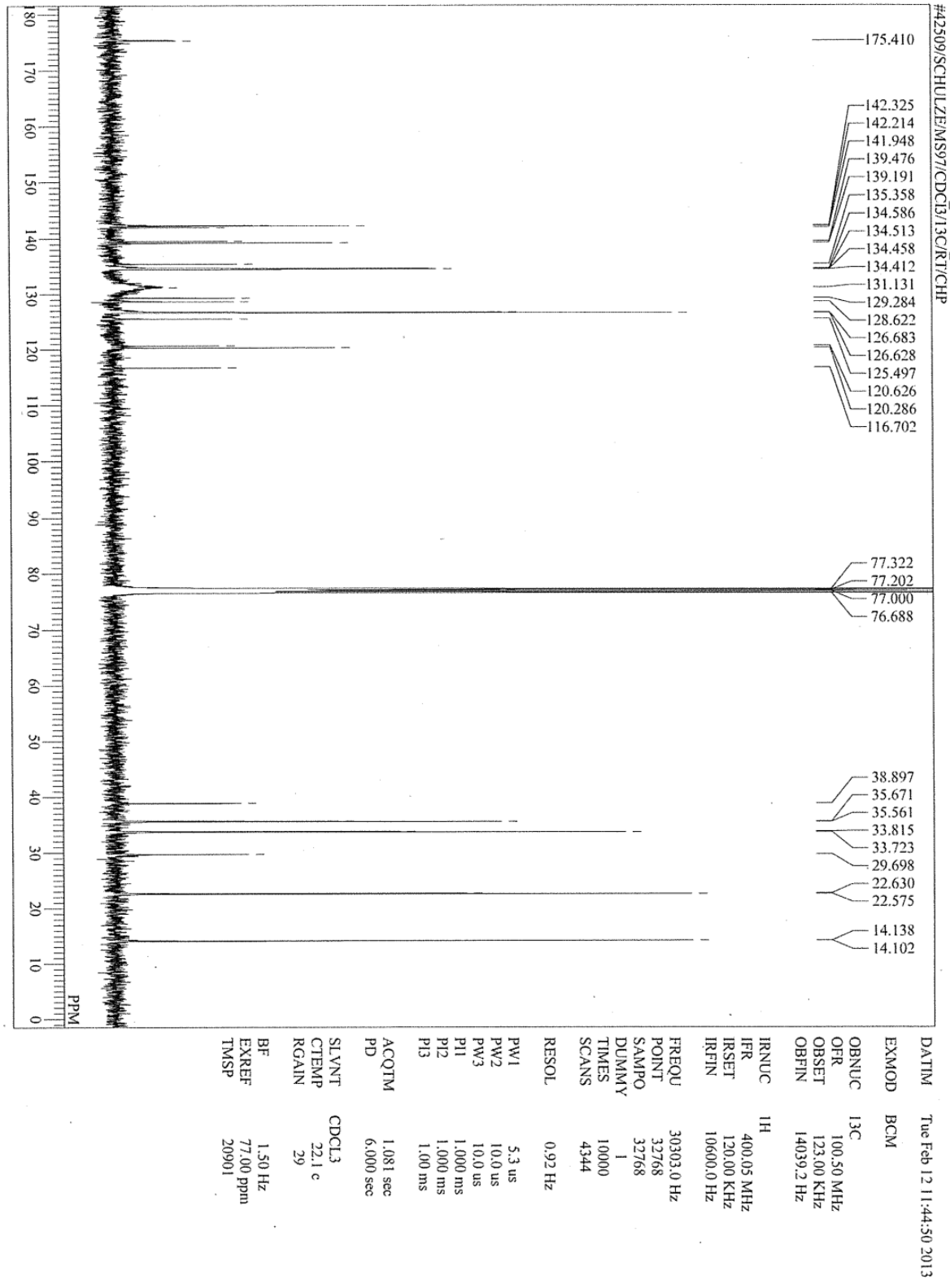
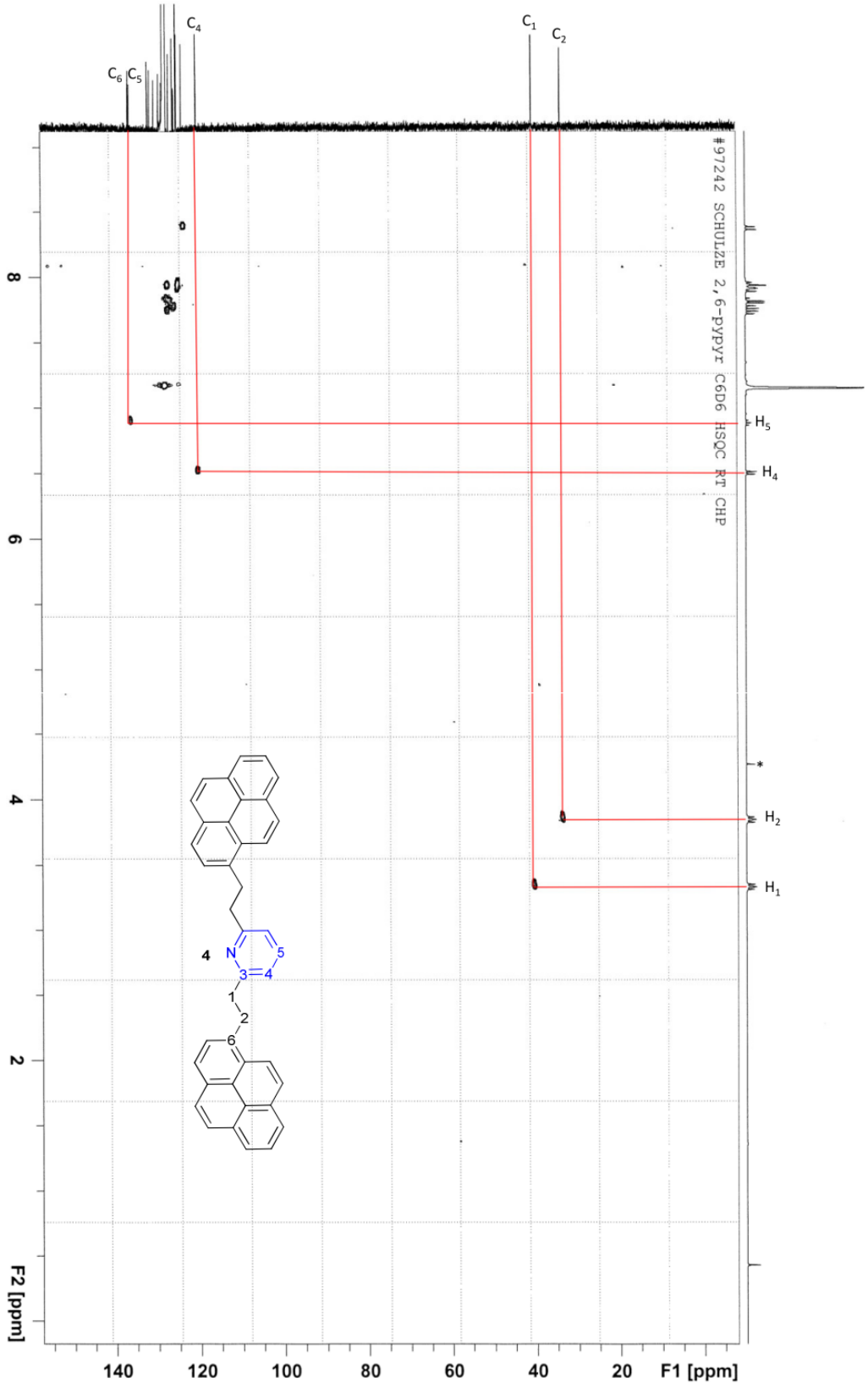
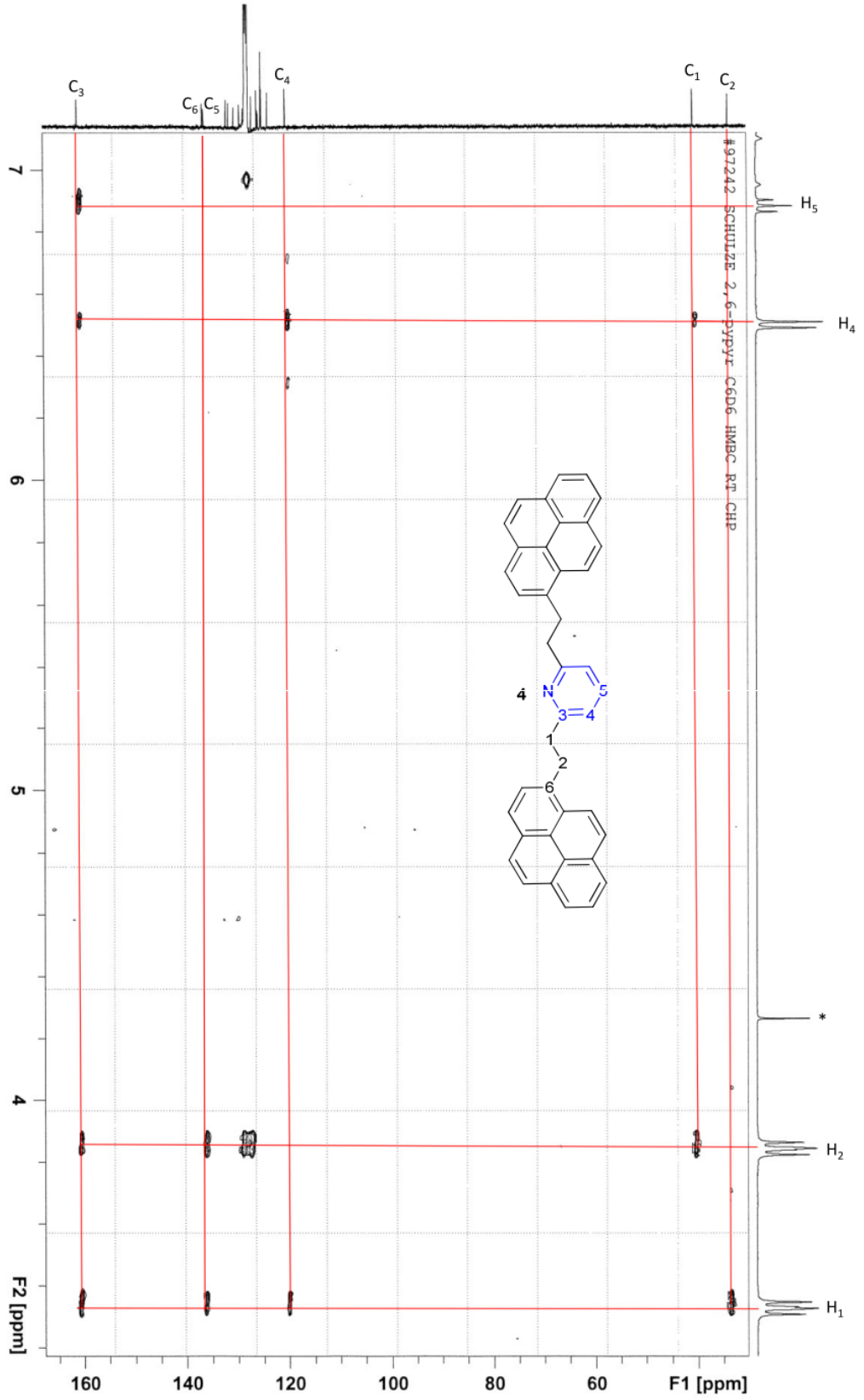


^{13}C NMR spectrum (100 MHz, $CDCl_3$) of porphyrin **10**.

2D NMR spectra of compound 4



HSQC spectrum (400 MHz, C_6D_6) of compound **4**.



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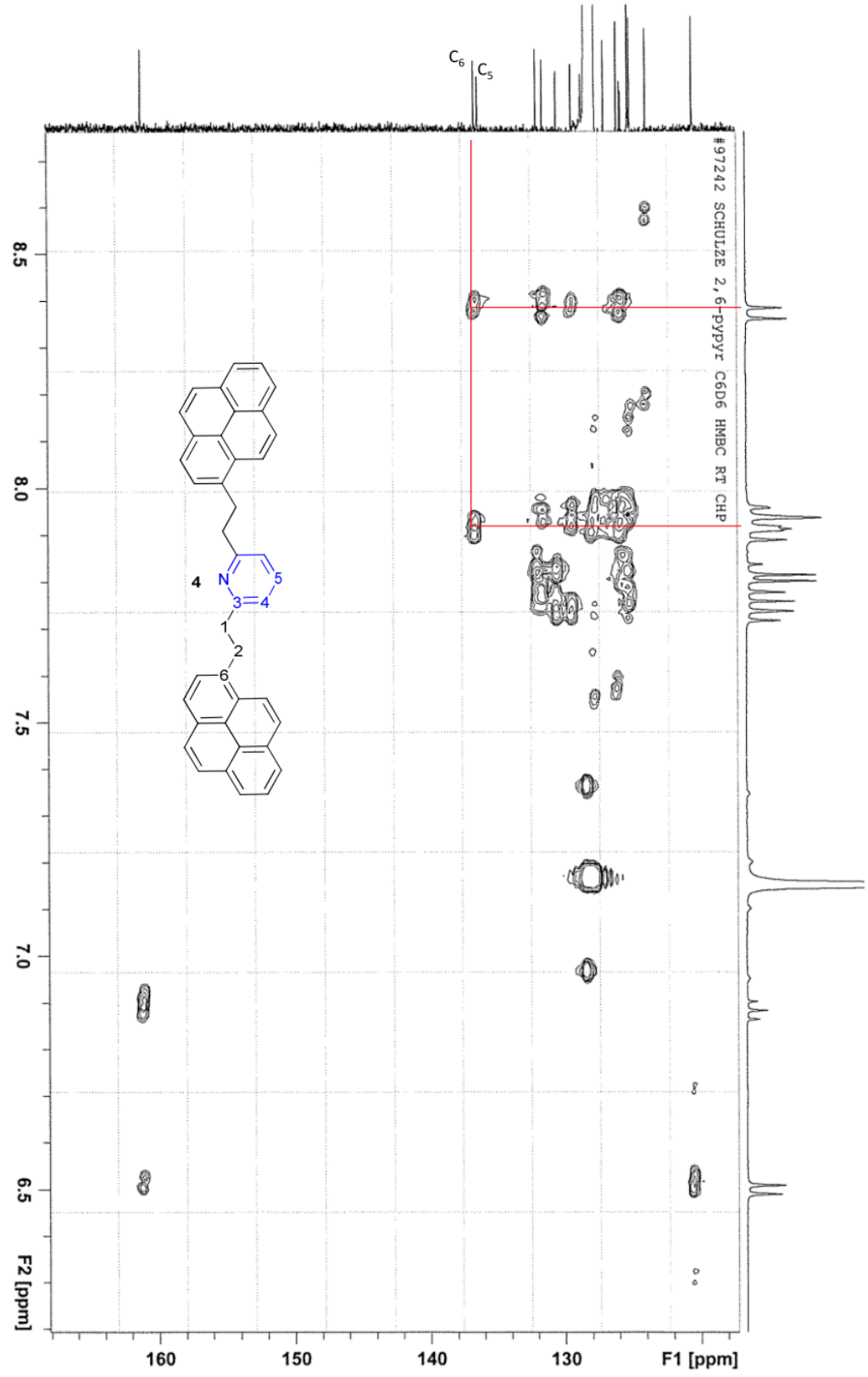

HMBC spectrum (400 MHz, C_6D_6) of compound **4**.

NMR Titration Measurements

Nonlinear curve fitting for the determination of association constants was performed with HypNMR 2008 software.[1] All titrations were analyzed using 400 MHz NMR spectrometers.

Study 1. NMR dilution titration of phenylacetic acid

Phenylacetic acid (PAA) was used as a reference carboxylic acid. In C_6D_6, no change in chemical shifts was observed by ^{1}H NMR spectroscopy over a concentration range of 0.15 M to 1 x 10^{-5} M.[2,3]

Titration 1. PAA (28.6 mg, 0.210 mmol) was dissolved in 1.40 mL C_6D_6 to give solution (a) (150 mM; Figure S1). From this solution, 0.700 mL were removed and diluted with 0.700 mL C_6D_6 to obtain solution (b) (75 mM). This procedure was repeated two times to obtain solutions with concentrations of 37.5 mM (c) and 18.75 mM (d). From solution (d), 0.374 mL were removed and diluted with 1.03 mL C_6D_6 to obtain a solution (e) (5.0 mM). From solution (e), 0.154 mL were removed and diluted with 0.62 mL C_6D_6 to obtain solution (f) (1.0 mM). From solution (f), 70 μL were removed and diluted with 0.63 mL C_6D_6 to give solution (g) (0.1 mM).

Titration 2. PAA (2.45 mg, 0.0180 mmol) was dissolved in 1.80 mL C_6D_6 to give solution (a) (10 mM; Figure S2). From this solution, 0.525 mL were removed and diluted with 0.175 mL C_6D_6 to obtain solution (b) (7.50 mM). From solution (a), 0.600 mL were removed and diluted with 0.600 mL C_6D_6 to obtain solution (c) (5.00 mM). This procedure was repeated three times to obtain solutions with the concentrations of 2.50 mM (d), 1.25 mM (e), and 0.625 mM (f). From solution (f), 0.240 mL were removed and diluted with 1.26 mL C_6D_6 to obtain solution (g) (0.1 mM). From solution (f), 22.4 μL were removed and diluted with 1.38 mL C_6D_6 to obtain solution (h) (0.01 mM).

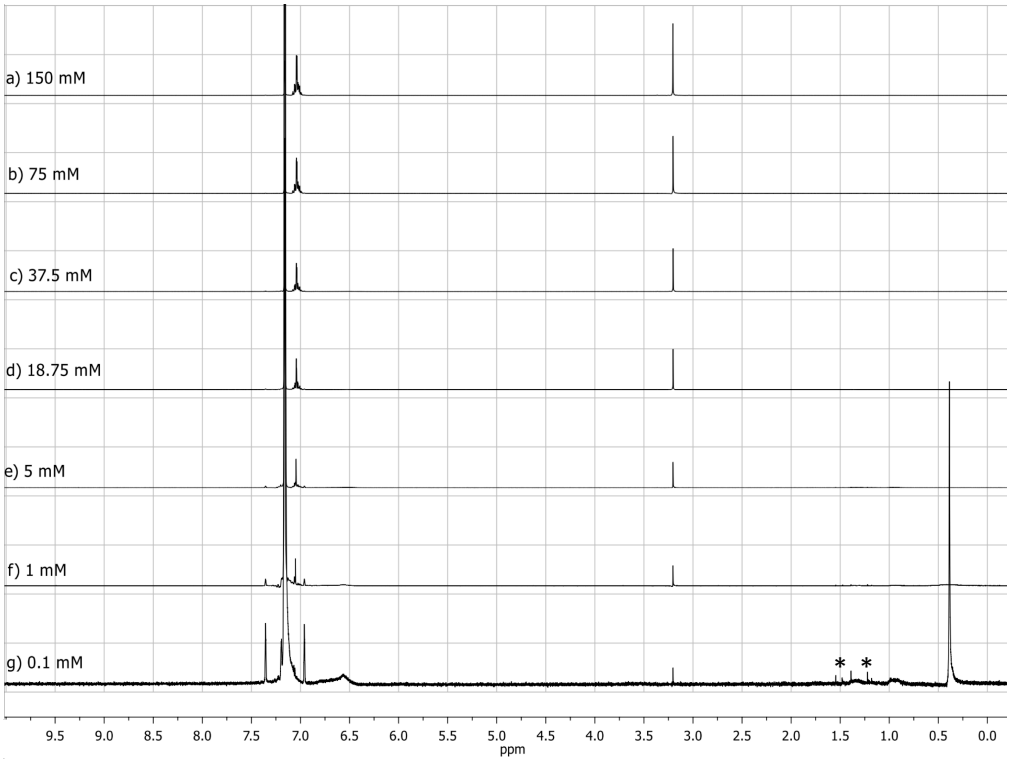

Figure S1. ^{1}H NMR spectra from PAA **Titration 1** (solutions a–g), at concentrations ranging from 150 mM to 0.1 mM (* = solvent impurities).

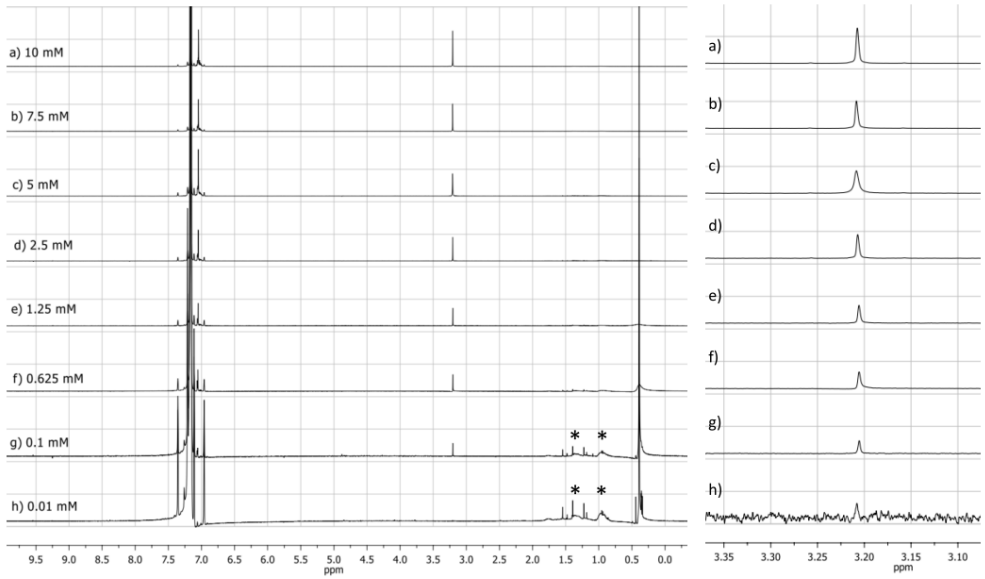

Figure S2. ^{1}H NMR spectra of PAA **Titration 1** (solutions a–h) at concentrations ranging from 10 mM to 0.01 mM (* = solvent impurities).

Study 2. NMR titration of phenylacetic acid and pyridine

A solution of pyridine (200 mM) was prepared by dissolving pyridine (16.2 μL, 15.8 mg, 0.200 mmol) in C_6D_6 (1.00 mL). From this solution, 0.450 mL were removed and diluted with 4.05 mL C_6D_6 to obtain a solution of pyridine with a concentration of 20 mM in deuterated benzene.

Next, a solution of PAA (10 mM) was prepared by dissolving PAA (5.45 mg, 40.0 μmol) into 4.00 mL C_6H_6. From this solution, 0.175 mL was removed, the solvent evaporated, and the resulting solid dried *in vacuo*. This procedure was repeated ten times, to provide eleven samples of PAA (0.24 mg, 1.8 μmol).

Finally, each sample of PAA was dissolved into a volume of the pyridine solution (20 mM) and pure C_6D_6 to obtain the following mixtures:

a) PAA (2.5 mM) / pyridine (2.5 mM)
(0.24 mg PAA + 87.5 μL pyridine solution (20 mM) + 0.613 mL C_6D_6)

b) PAA (2.5 mM) / pyridine (4.0 mM)
(0.24 mg PAA + 0.140 mL pyridine solution (20 mM) + 0.560 mL C_6D_6)

c) PAA (2.5 mM) / pyridine (6.0 mM)
(0.24 mg PAA + 0.210 mL pyridine solution (20 mM) + 0.490 mL C_6D_6)

d) PAA (2.5 mM) / pyridine (8.0 mM)
(0.24 mg PAA + 0.280 mL pyridine solution (20 mM) + 0.420 mL C_6D_6)

e) PAA (2.5 mM) / pyridine (10 mM)
(0.24 mg PAA + 0.350 mL pyridine solution (20 mM) + 0.350 mL C_6D_6)

f) PAA (2.5 mM) / pyridine (12 mM)
(0.24 mg PAA + 0.420 mL pyridine solution (20 mM) + 0.280 mL C_6D_6)

g) PAA (2.5 mM) / pyridine (14 mM)
(0.24 mg PAA + 0.490 mL pyridine solution (20 mM) + 0.210 mL C_6D_6)

h) PAA (2.5 mM) / pyridine (16 mM)
(0.24 mg PAA + 0.560 mL pyridine solution (20 mM) + 0.140 mL C_6D_6)

i) PAA (2.5 mM) / pyridine (18 mM)
(0.24 mg PAA + 0.630 mL pyridine solution (20 mM) + 70.0 μL C_6D_6)

j) PAA (2.5 mM) / pyridine (20 mM)
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All solutions were aged for 24 h at rt in the dark prior to recording a ^{1}H NMR spectrum for each sample (Figure S3).

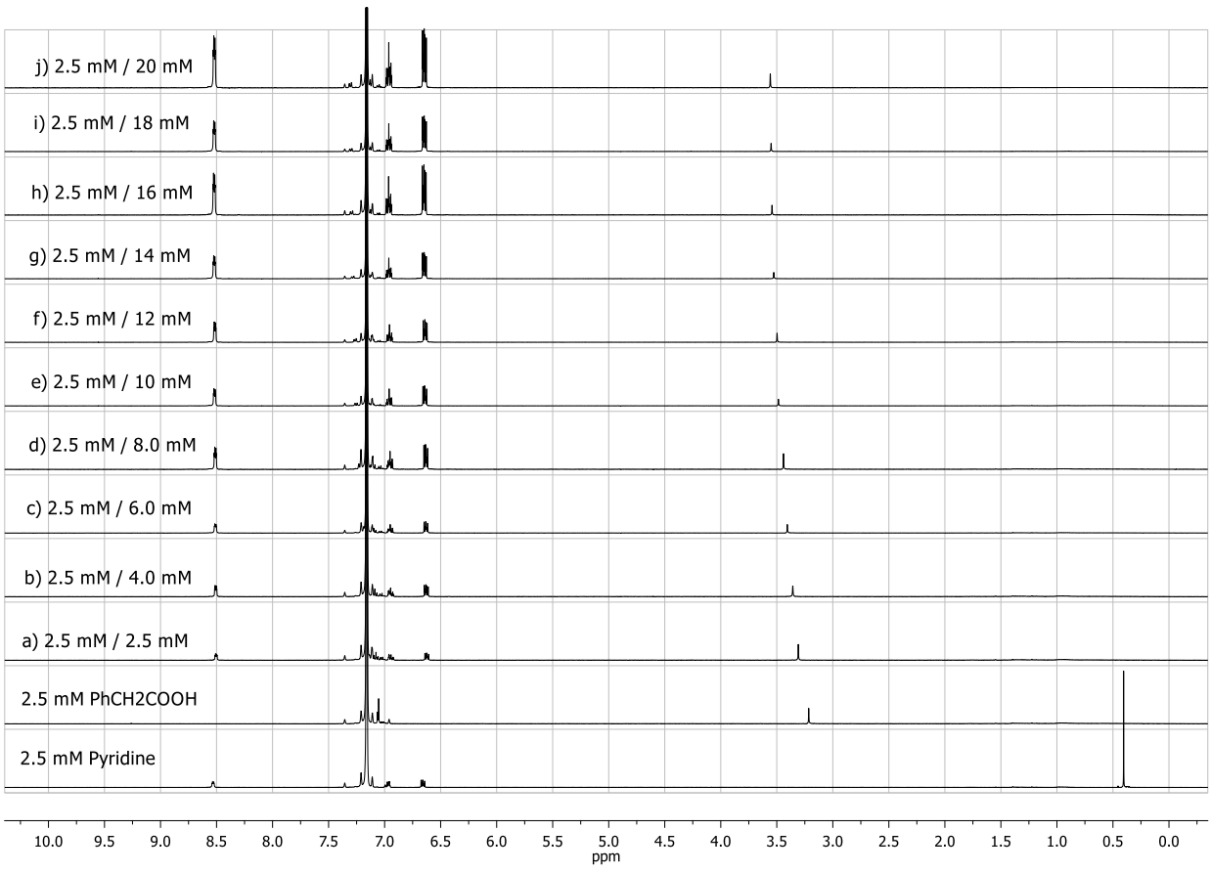

Figure S3. ^{1}H NMR spectra from the NMR titration of PAA (constant 2.5 mM) with increasing amounts of pyridine.

Addition of increasing amounts of pyridine (S) to the solution of PAA (2.5 mM; R) resulted in a shift for the signal of the methylene protons (Figure S4). Fitting this data, K_{assoc} (SR) of 123 ± 12 M^{-1} (log 2.09) was calculated for a 1:1 complex of PAA (R) and pyridine (S).[4]

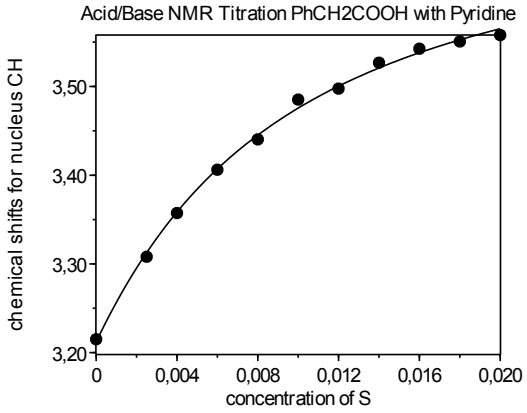

Figure S4. Binding isotherm for the NMR titration of PAA (2.5 mM) with pyridine (S) fit to a 1:1 binding model.

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Project title: Acid/Base NMR Titration PhCH2COOH with Pyridine

Converged in 4 iterations with sigma = 5,751117

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Discussion

As described in **Study 1**, dimerization of PAA was not observed in C_6D_6 based on ^{1}H NMR experiments, and it was therefore not necessary to consider K_{dim} of PAA in calculations performed to determine K_{assoc} for PAA and pyridine. Based on partition studies, however, Yamada et al. have reported K_{dim} = 48 M^{-1} for PAA in benzene.[3] An additional analysis was therefore done, considering K_{dim} = 48 M^{-1} and a reasonable value of 3.20 ppm for monomeric PAA, which gave K_{assoc} = 151 ± 15.[4] Thus, dimerization of PAA might have a slight impact on the final K_{assoc} value, but all conclusions would remain identical.

Study 3. NMR dilution titration of model compound 4

To investigate self-association of **4**, a solution of model compound **4** (10 mM; 6.43 mg, 0.0120 mmol) was prepared in deuterated benzene (1.2 mL) solution (a). From this solution, 0.6 mL was removed and diluted with 0.6 mL C_6D_6 to obtain solution (b) (5.0 mM). This procedure was repeated three times, to give solutions with concentrations of 2.5, 1.25, and 0.625 mM (c–e, respectively). From solution (e), 0.24 mL was removed and diluted with 1.26 mL C_6D_6 to obtain solution (f) (0.1 mM). A ^{1}H NMR spectrum was recorded for solutions a–f after aging for 24 h at rt in the dark and these are depicted in Figure S5. No evidence for self-association was found.[5]

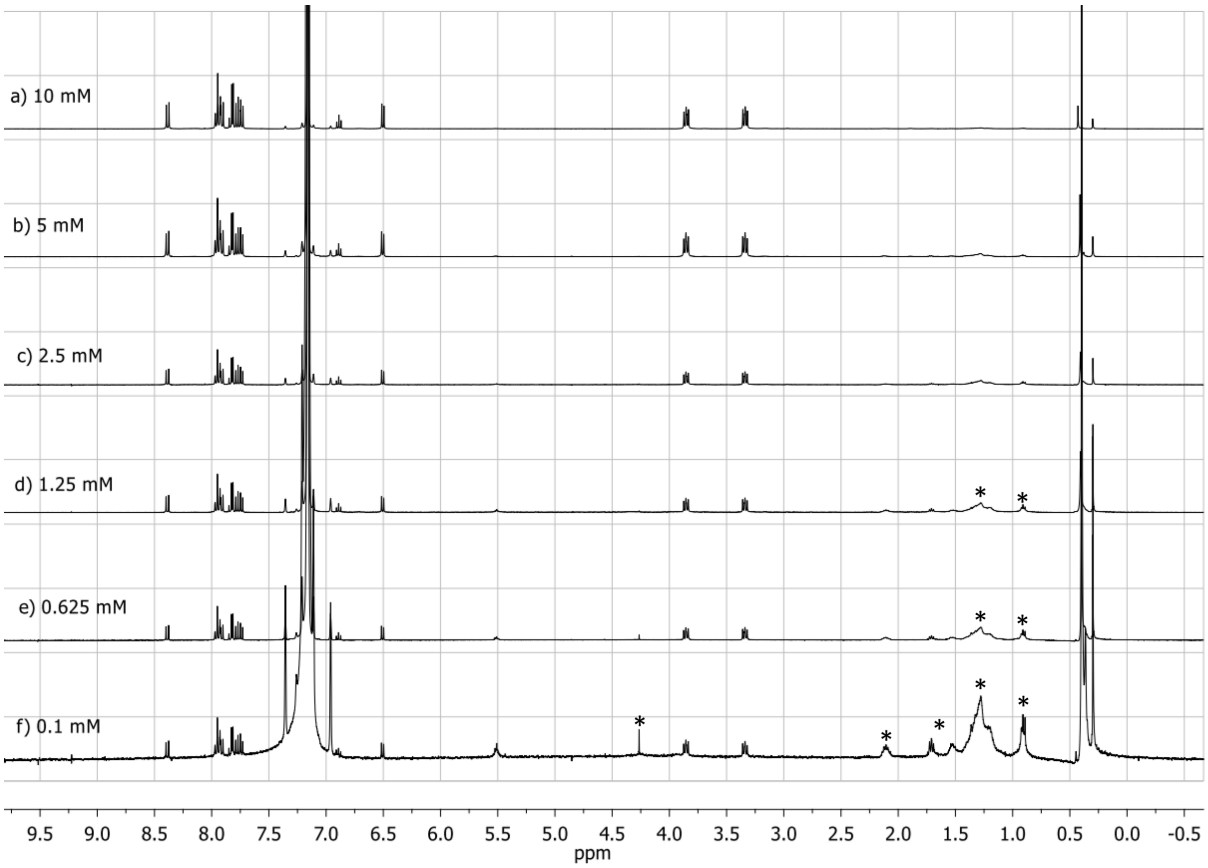

Figure S5. ^{1}H NMR spectra of model compound **4** at different concentrations (* = solvent impurities).

Study 4. NMR titration of phenylacetic acid and model compound 4

Initially, a titration series using a solution of PAA (2.5 mM) was done with compound **4**. Unfortunately, the solubility of **4** is limited, and a maximum of only four equivalents could be added to the PAA solution:

A solution of PAA (2.5 mM) in deuterated benzene was prepared by dissolving 2.04 mg (0.0150 mmol) in 6.00 mL C_6D_6. A solution of model compound **4** (10 mM; 21.4 mg, 0.0400 mmol) was prepared in 4.00 mL C_6H_6. From this solution, the volumes (0.700 mL, 0.630 mL, 0.560 mL, 0.490 mL, 0.420 mL, 0.280 mL, 0.140 mL) were removed. The solvent was evaporated and the resulting solids dried *in vacuo*. To each of these dried samples, 0.700 mL of the PAA solution (2.5 mM) was added to obtain final samples with the following concentrations of model compound **4**: 10.0 mM, 9.00 mM, 8.00 mM, 7.0 mM, 6.0 mM, 4.0 mM, 2.0 mM.

All solutions were aged for 24 h at rt in the dark prior to recording a ^{1}H NMR spectrum for each sample. Due to weak binding between PAA and model compound **4**, however, the binding isotherm (fitting the signal of the methylene protons of PAA) showed only a small deviation from linearity (Figure S6).

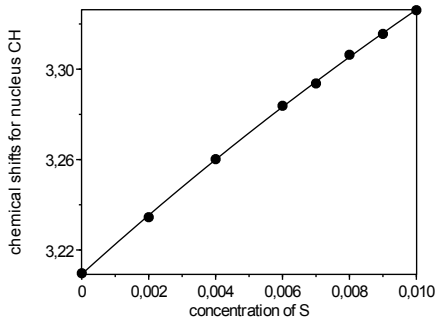

Figure S6. Binding isotherm for the NMR titration of PAA (constant 2.5 mM) with **4** (S) fit to a 1:1 binding model.

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Converged in 1 iterations with sigma = 0,782655

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Second, a titration series using a solution of PAA (1.25 mM; 1.36 mg, 0.0100 mmol, in 8.00 mL C_6D_6) was done, allowing the use of up to 8 equivalents **4** (Figure S7).

A solution of model compound **4** (10 mM; 26.8 mg, 0.0500 mmol) was prepared in 5.00 mL C_6H_6. From this solution, the volumes (87.5 μL, 0.175 mL, 0.263 mL, 0.333 mL, 0.403 mL, 0.473 mL, 0.560 mL, 0.630 mL, 0.700 mL) were removed. The solvent was evaporated and the resulting solids dried *in vacuo*. To each of these dried samples, 0.700 mL of the PAA solution (1.25 mM) was added to obtain final samples with the following concentrations of model compound **4**: 1.25 mM, 2.50 mM, 3.75 mM, 4.75 mM, 5.75 mM, 6.75 mM, 8.00 mM, 9.00 mM, and 10.0 mM (solutions a–i, respectively). All solutions were aged for 24 h at rt in the dark prior to recording a ^{1}H NMR spectrum for each sample.

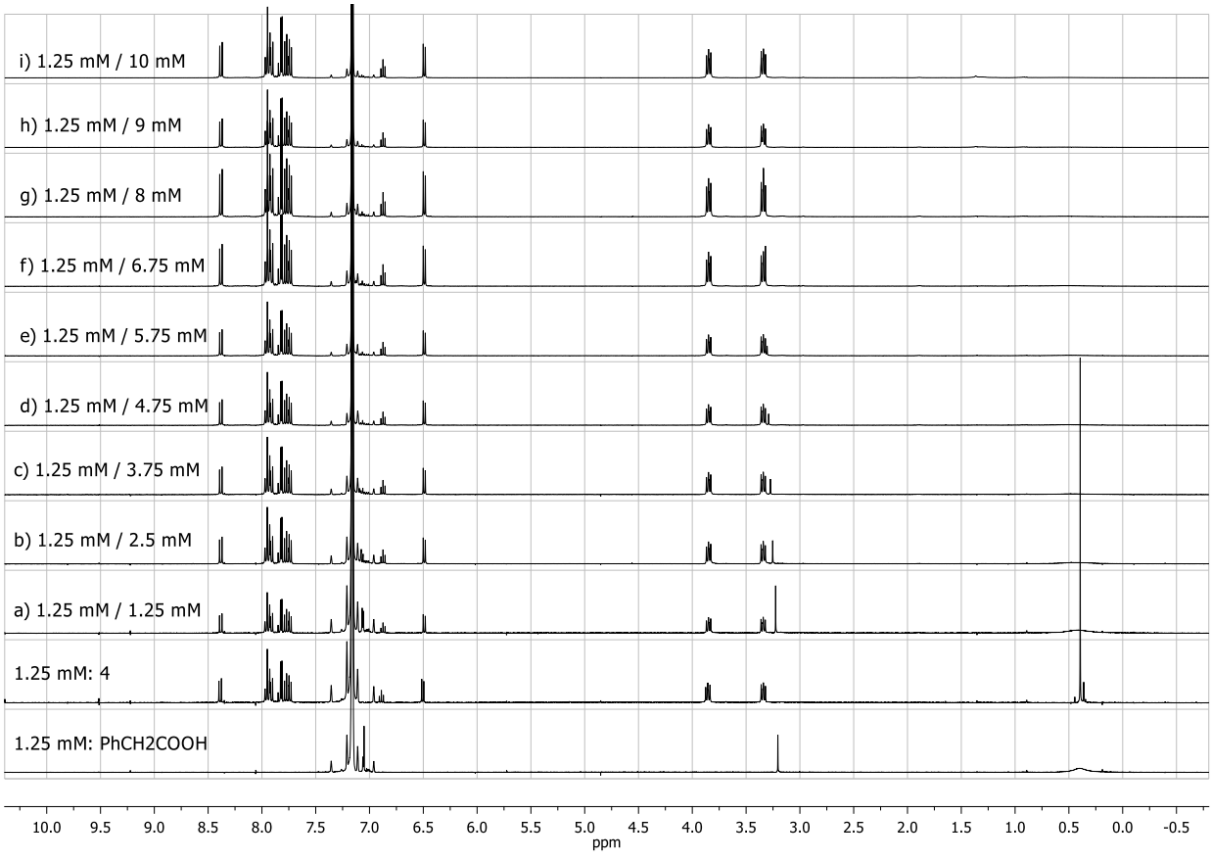

Figure S7. ^{1}H NMR spectra from the NMR titration of PAA (constant 1.25 mM) and **4**.

The results of the titration of the solution of PAA (1.25 mM) with **4** are shown in Figure S8, using the chemical shifts for the signal of the methylene protons, which gives a calculated K_{assoc} (SR) = 32 M^{-1} (log 1.5) for a 1:1 complex between PAA (R) and model compound **4** (S). The results of the titration of the solution of PAA (2.5 mM) with **4** (Figure S6) gives a calculated K_{assoc} (SR) = 16 M^{-1} (log 1.2) for a 1:1 complex between PAA (R) and model compound **4** (S).

The final association constant of K_{assoc} = 24 ± 8 M^{-1} was obtained as an average from the two titrations detailed above.

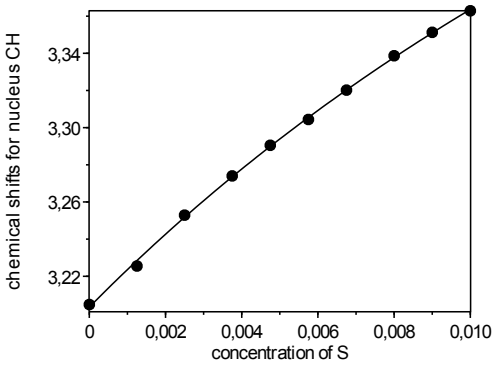

Figure S8. Binding isotherm for the NMR titration of PAA (constant 1.25 mM) with **4** (S) fit to a 1:1 binding model.

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                        standard
                value   deviation   Comments
 1 log beta(SR)  1.5008  0.064       1.5(6)
```

Discussion

As described above (**Study 2**), Yamada et al. have reported K_{dim} (48 M^{-1}) for PAA in benzene.[3] If this value is incorporated into the analysis of the titrations (1.25 and 2.5 mM PAA) and by considering a reasonable value of 3.20 ppm for the monomeric species of PAA, values of K_{assoc} = 38 M^{-1} and 31 M^{-1} are obtained (1.25 mM and 2.5 mM, respectively). Therefore, considering K_{dim} from Yamada et al. would result in the averaged association constant of K_{assoc} = 35 ± 4 M^{-1}, which is nearly identical to that determined in the absence of self-association.[4]

Study 5. NMR dilution titration of porphyrin 3

A solution of model compound **3** (10.0 mM; Figure S9) in deuterated benzene was prepared by dissolving **3** (16.2 mg, 0.0180 mmol) in C_6D_6 (1.80 mL); solution (a). From this solution, 0.525 mL was removed and diluted with 0.175 mL C_6D_6 to obtain solution (b) (7.50 mM). From solution (a), 0.600 mL was removed and diluted with 0.600 mL C_6D_6 to obtain solution (c) (5.00 mM). Dilution was continued until solutions with the concentration of 2.5 mM (d), 1.25 mM (e), and 0.625 mM (f) were obtained. From solution (f), 0.112 mL was removed and diluted with 0.588 mL C_6D_6 to obtain solution (g) (0.100 mM). All solutions were aged for 24 h at rt in the dark prior to recording a ^{1}H NMR spectrum (Figure S9).

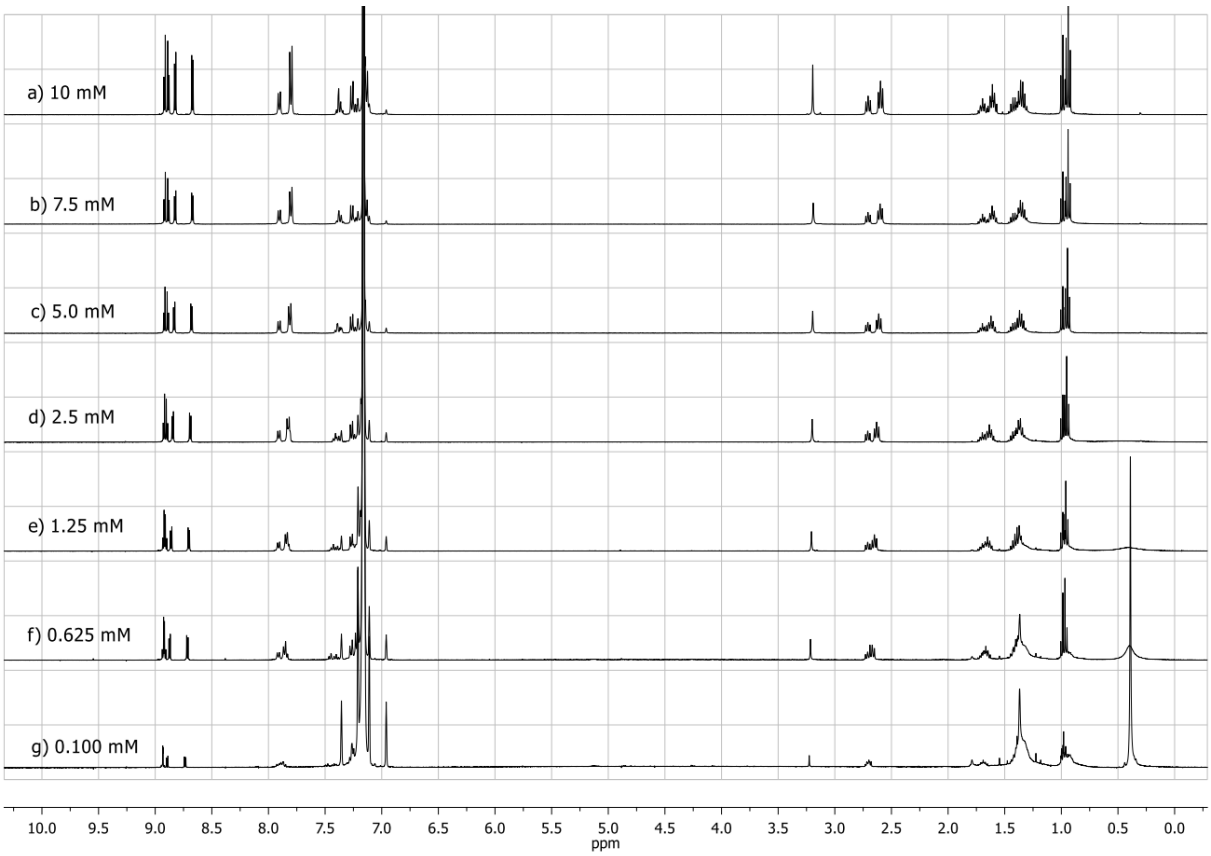

Figure S9. Dilution titration of porphyrin **3**.

From the dilution titration (Figure S9), a dimerization constant (R2) K_{dim} = 417 M^{-1} (log 2.62) was calculated for porphyrin **3** using the chemical shifts for multiple signals (two sets of pyrrole protons and the methylene protons), as depicted in Figure S10.

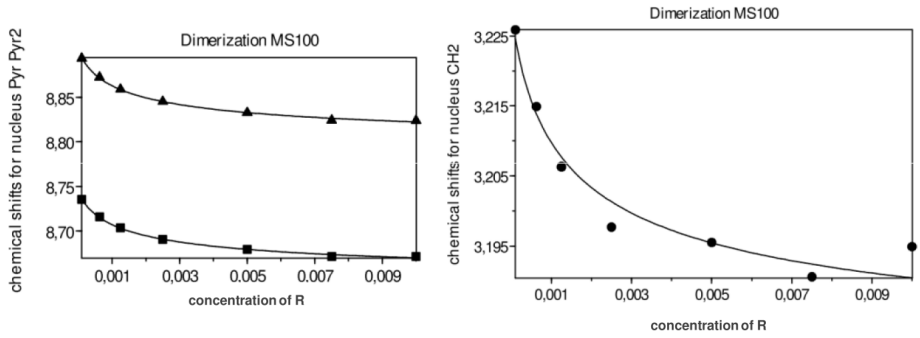

Figure S10. Binding isotherms from the signals of two sets of pyrrole protons (left) and the signal of the methylene protons (right) of porphyrin **3** (R) at various concentrations.

```
HypNMR2008
Refinement concluded at  13:56:23  on 09.03.2015
Project title: Dimerization MS100

Converged in 4 iterations with sigma = 1,010846

                      standard
                value     deviation   Comments
 1 log beta(R2)  2.617     0.064       2.62(6)
```

A second dilution titration of porphyrin **3** was carried out with solutions with the following concentrations: 10 mM, 5 mM, 2.5 mM, 1.25 mM, and 0.1 mM. A dimerization constant (R2) K_{dim} = 363 M^{-1} (log 2.56) was calculated for porphyrin **3** using the chemical shifts for multiple signals (two sets of pyrrole protons and the methylene protons), as depicted in Figure S11.

The final dimerization constant of K_{dim} = 390 ± 27 M^{-1} (log 2.59) was obtained as an average from the two dilution titrations.

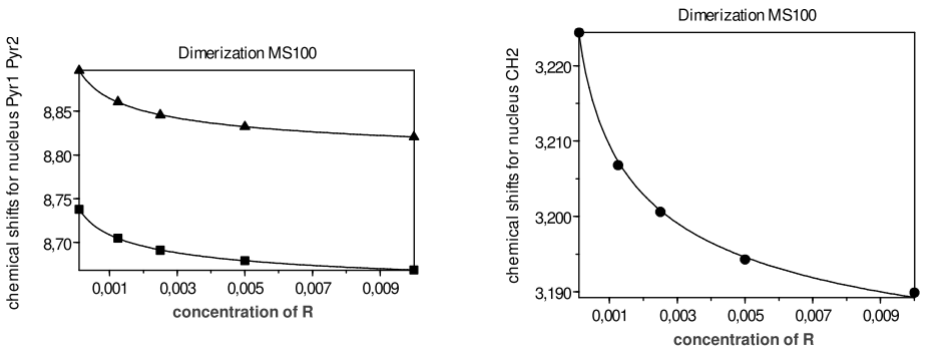

Figure S11. Binding isotherms from the signals of two sets of pyrrole protons (left) and the signal of the methylene protons (right) of porphyrin **3** (R) at various concentrations.

```
HypNMR2008
Refinement concluded at  13:54:20  on 22.04.2015
Project title: Dimerization MS100

Converged in 4 iterations with sigma = 0,226659

                          standard
                 value    deviation   Comments
 1 log beta(R2)  2.555    0.0155      2.55(2)
```

Study 6. NMR titration of porphyrin 3 and pyridine

A solution of pyridine (20 mM) in deuterated benzene was prepared in analogy to the PAA + pyridine titration (**Study 2**). A solution of porphyrin **3** (10 mM) was prepared by dissolving 35.9 mg (0.0400 mmol) in 4.00 mL C_6H_6. From this solution, 0.175 mL was removed, the solvent evaporated, and the resulting solid dried *in vacuo*. This procedure was repeated ten times, to provide eleven samples of porphyrin **3** (1.57 mg, 1.75 μmol). Finally, each porphyrin sample was dissolved into a volume of the pyridine solution (20 mM) and pure C_6D_6 to obtain the following mixtures:

a) porphyrin **3** (2.5 mM) / pyridine (2.5 mM)
1.57 mg **3** + 87.5 μL pyridine solution (20 mM) + 0.613 mL C_6D_6)

b) porphyrin **3** (2.5 mM) / pyridine (4.0 mM)
(1.57 mg **3** + 0.140 mL pyridine solution (20 mM) + 0.560 mL C_6D_6)

c) porphyrin **3** (2.5 mM) / pyridine (6.0 mM)
(1.57 mg **3** + 0.210 mL pyridine solution (20 mM) + 0.490 mL C_6D_6)

d) porphyrin **3** (2.5 mM) / pyridine (8.0 mM)
(1.57 mg **3** + 0.280 mL pyridine solution (20 mM) + 0.420 mL C_6D_6)

e) porphyrin **3** (2.5 mM) / pyridine (10 mM)
(1.57 mg **3** + 0.350 mL pyridine solution (20 mM) + 0.350 mL C_6D_6)

f) porphyrin **3** (2.5 mM) / pyridine (12 mM)
(1.57 mg **3** + 0.420 mL pyridine solution (20 mM) + 0.280 mL C_6D_6)

g) porphyrin **3** (2.5 mM) / pyridine (14 mM)
(1.57 mg **3** + 0.490 mL pyridine solution (20 mM) + 0.210 mL C_6D_6)

h) porphyrin **3** (2.5 mM) / pyridine (16 mM)
(1.57 mg **3** + 0.560 mL pyridine solution (20 mM) + 0.140 mL C_6D_6)

i) porphyrin **3** (2.5 mM) / pyridine (18 mM)

(1.57 mg **3** + 0.630 mL pyridine solution (20 mM) + 70.0 μL C_6D_6)

j) porphyrin **3** (2.5 mM) / pyridine (20 mM)

(1.57 mg **3** + 0.700 mL pyridine solution (20 mM))

All solutions were aged for 24 h at rt in the dark prior to recording the ^{1}H NMR spectra (Figure S12).

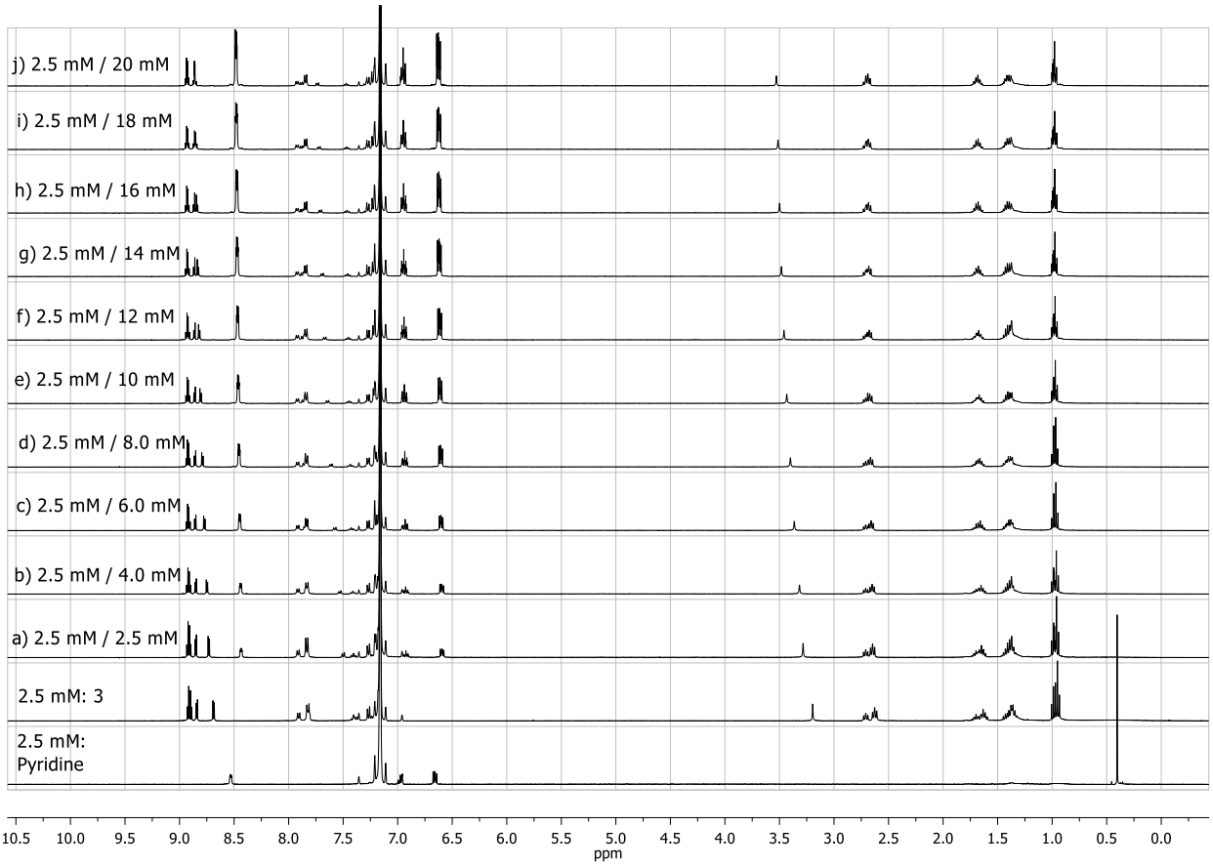

Figure S12. NMR titration of porphyrin **3** (constant 2.5 mM) with increasing amounts of pyridine.

The obtained chemical shifts of multiple signals (two sets of pyrrole protons and the methylene protons) were used for the calculation of K_{assoc} between porphyrin **3** and pyridine. The averaged dimerization constant (R2) determined for porphyrin **3** was included as a fixed value (log 2.59) in the calculation. Additionally, the calculated averaged chemical shifts of the methylene protons and the most upfield appearing pyrrole doublet for the free and dimeric species of porphyrin **3**, obtained from the NMR dilution titrations (**Study 5**), were included in the calculation. Using a 1:1 model, K_{assoc} = (SR) of 178 ± 18 M^{-1} (log 2.25) was determined (Figure S13).[4]

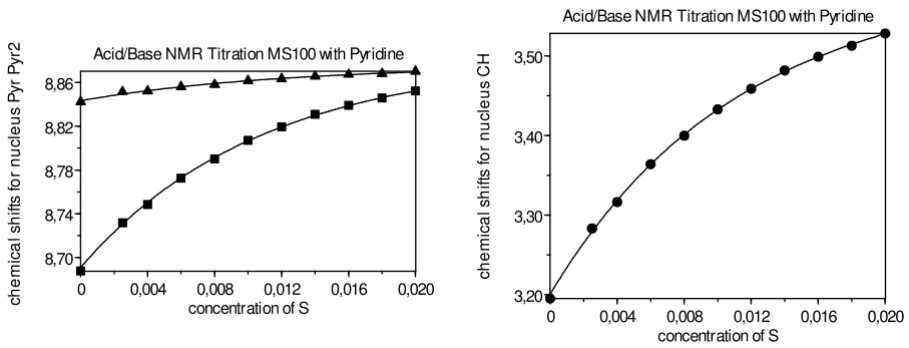

Figure S13. Binding isotherms from the titration of porphyrin **3** with pyridine (S).

```
HypNMR2008
Refinement concluded at  14:05:04  on 22.04.2015
Project title: Acid/Base NMR Titration MS100 with Pyridine

Converged in 3 iterations with sigma = 1,789513

                        standard
                value   deviation   Comments
 1 log beta(SR) 2.2492  0.009       2.249(9)
   log beta(R2) 2.59    fixed
```

Study 7. NMR titration of porphyrin 3 and model compound 4

A solution of model compound **4** (5.00 mM; 4.82 mg, 0.00900 mmol) was prepared in 1.80 mL C_6D_6. From this solution, 0.175 mL was removed, the solvent evaporated, and the resulting solid dried *in vacuo*. This procedure was repeated nine times, to provide ten samples of model compound **4** (0.469 mg, 0.875 μmol).

A solution of porphyrin **3** (2.50 mM; 1.57 mg, 0.00175 mmol) was prepared in C_6D_6 (0.700 mL). Additionally, a dried sample of compound **4** was dissolved in 0.700 mL C_6D_6. Both samples were aged for 24 h at rt in the dark and the ^{1}H NMR spectra were recorded (Figure S14).

A dried sample of compound **4** (0.469 mg, 0.875 μmol) was dissolved in the already prepared solution of porphyrin **3** (2.50 mM), maintaining a total volume of 0.7 mL, to give solution (a) (**3** / **4** = 2.5 mM / 1.25 mM; Figure S14). The solution was aged for 24 h at rt in the dark, and a ^{1}H NMR spectrum was recorded. This procedure was repeated for further seven samples of **4** until a 10 mM concentration of model compound **4** was achieved (solutions b–h, respectively).

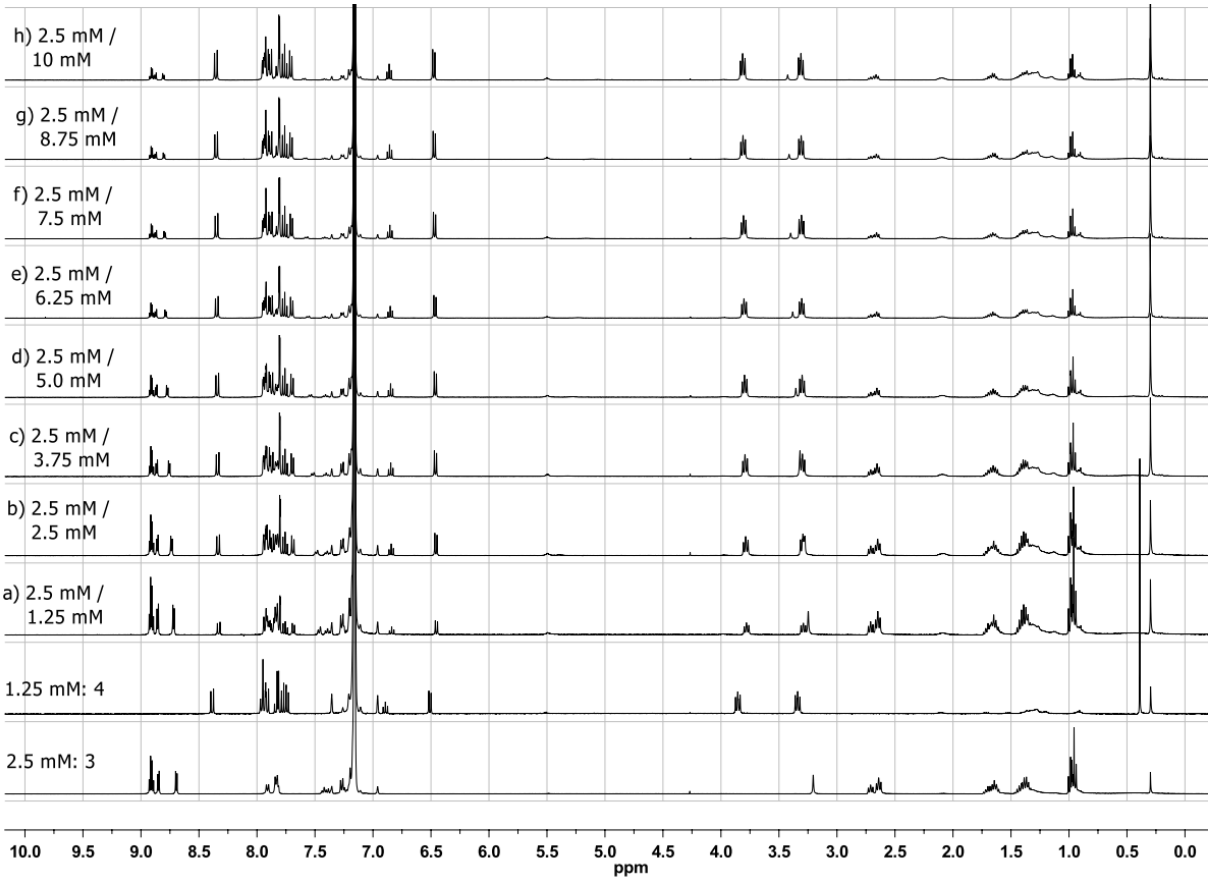

Figure S14. ^{1}H NMR spectra from the titration of porphyrin **3** (constant 2.5 mM) with compound **4**.

For the determination of the association constant between porphyrin **3** (R) and model compound **4** (S), nonlinear curve fitting with a 1:1 and a 1:2 binding isotherm (**3**:**4**) was applied. The chemical shifts of multiple signals (two sets of pyrrole protons and the methylene protons of **3**), obtained from the ^{1}H NMR titration with **4**, were used for the determination of the association constants.[4] The calculated averaged chemical shifts of the signals for the methylene protons and the most upfield appearing pyrrole doublet for the free and dimeric species of porphyrin **3**, obtained from the NMR dilution titration, were included in the calculations. Additionally, the dimerization constant (R2) determined for porphyrin **3** (**Study 5**) was included as a fixed value (log 2.59) in the calculations.

Binding Isotherms with 1:1 Model

Using a 1:1 binding isotherm, K_{assoc} (SR) of 316 ± 32 M^{-1} (log 2.50) was determined (Figure S15).

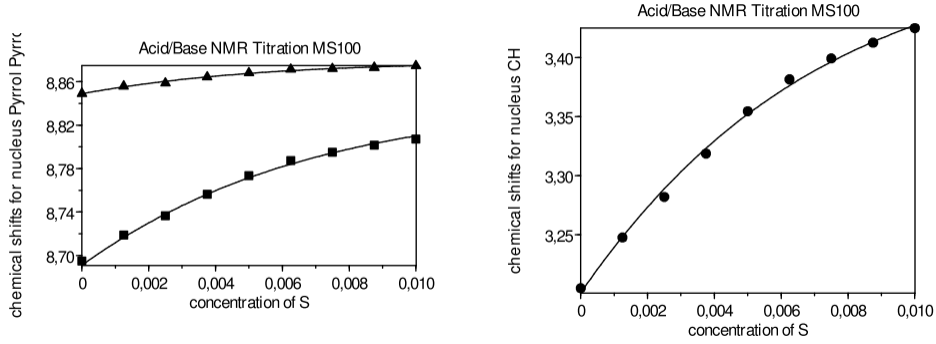

Figure S15. Binding isotherms from the titration of porphyrin **3** with compound **4** (S).

```
HypNMR2008
Refinement concluded at  14:14:17  on 22.04.2015
Project title: Acid/Base NMR Titration MS100

Converged in 4 iterations with sigma = 2,945437

                          standard
                 value    deviation   Comments
 1 log beta(SR)  2.5017   0.0312      2.5(3)
   log beta(R2)  2.59     fixed
```

Binding Isotherms with 1:2 Model

Using a 1:2 binding isotherm, an overall association constant β (S2R) of 1.23 ± 0.1 × 10^6 M^{-2} (log 6.09) was determined (Figure S16).

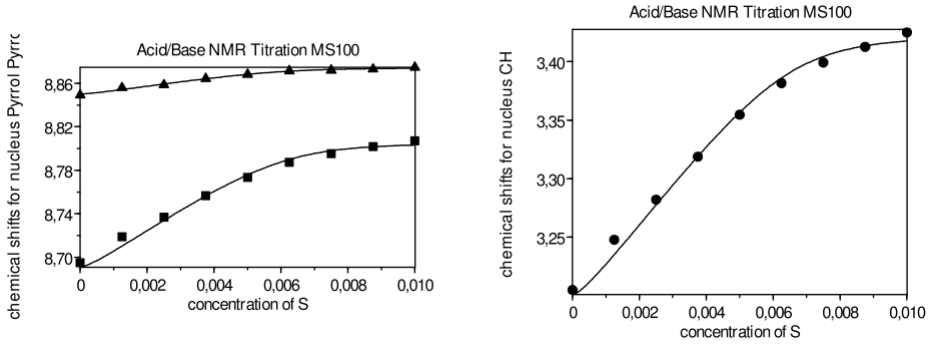

Figure S16. Binding isotherms from the titration of porphyrin **3** with compound **4** (S).

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HypNMR2008
Refinement concluded at  14:17:58  on 22.04.2015
Project title: Acid/Base NMR Titration MS100

Converged in 5 iterations with sigma = 4,584334

                          standard
                 value    deviation   Comments
 1 log beta(S2R) 6.0872   0.0771      6.09(8)
   log beta(R2)  2.59     fixed
```

Study 8. Job's Plot

Following mixtures of porphyrin **3** and model compound **4** were prepared, each in C_6D_6 (0.7 mL): a) 0.85 mM **3** (0.53 mg) / 9.15 mM **4** (3.43 mg); b) 1.2 mM **3** (0.75 mg) / 8.8 mM **4** (3.30 mg); c) 1.7 mM **3** (1.07 mg) / 8.3 mM **4** (3.11 mg); d) 2.5 mM **3** (1.57 mg) / 7.5 mM **4** (2.81 mg); e) 3.33 mM **3** (2.09 mg) / 6.66 mM **4** (2.49 mg); f) 4.1 mM **3** (2.60 mg) / 5.9 mM **4** (2.21 mg); g) 5 mM **3** (3.14 mg) / 5 mM **4** (1.88 mg); h) 6.66 mM **3** (4.18 mg) / 3.33 mM **4** (1.25 mg); i) 8.3 mM **3** (5.22 mg) / 1.7 mM **4** (0.63 mg). All solutions were aged for 24 h at rt in the dark prior to recording the corresponding ^{1}H NMR spectra (Figure S17).

Job's method of continuous variation shows formation of a 1:2 complex between **3** and **4** (Figure S18).

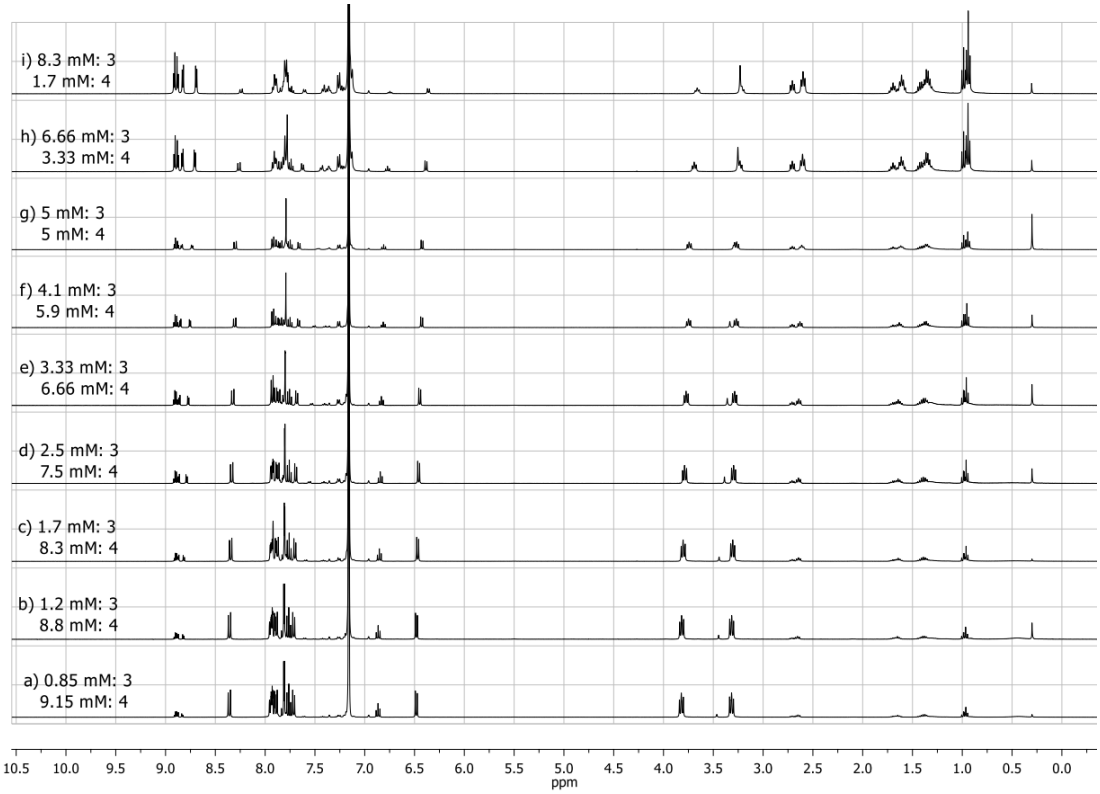

Figure S17. ^{1}H NMR spectra (400 MHz, C_6D_6) of **3** and **4**, maintaining a constant total concentration of 10 mM.

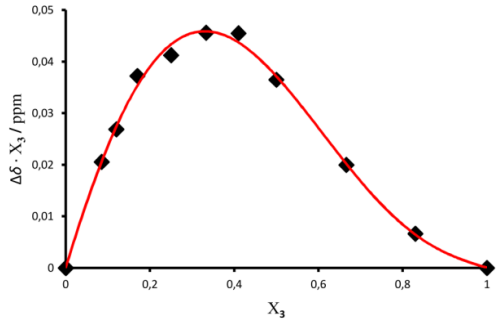

Figure S18. Job plot of porphyrin **3** and model compound **4**.

Mass spectrometry of 3•4

APPI HRMS of a mixture of **3** ($C_{58}H_{54}N_4NiO_2$) and **4** ($C_{41}H_{29}N$) shows beside the individual molecular ions a weak signal for formation of a 1:1 complex ($C_{99}H_{83}N_5NiO_2$) in the gas phase (Figure S19). Another stoichiometry was not observed.

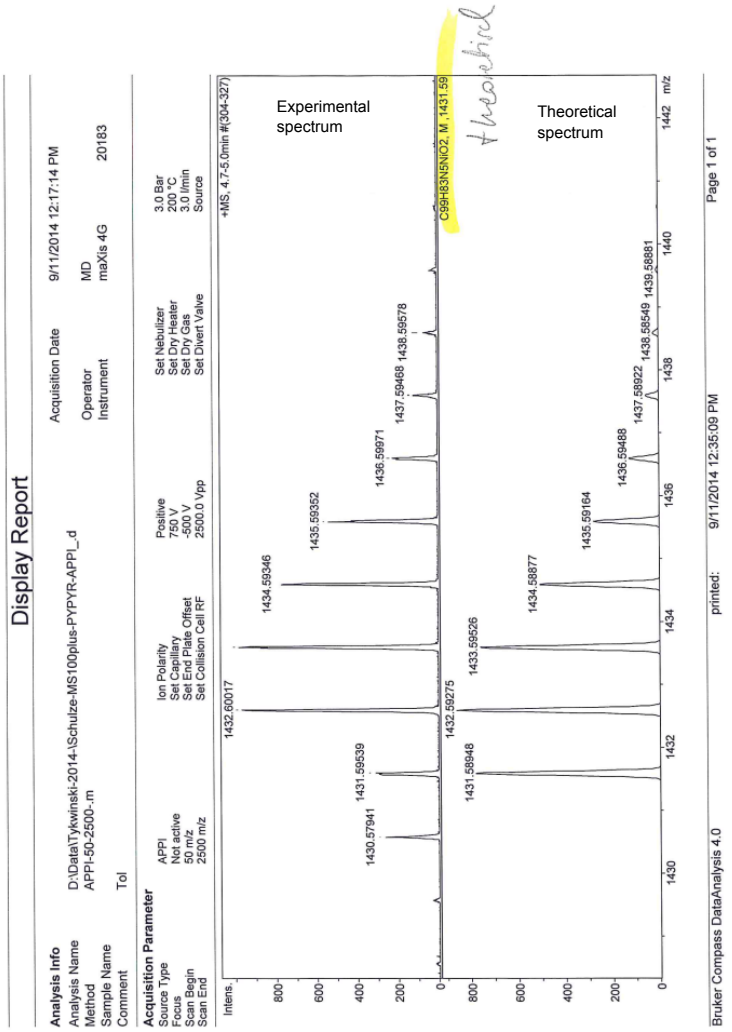

Figure S19. APPI HRMS analysis of a mixture between porphyrin **3** and model compound **4**.

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1. P. Gans, *HypNMR 2008*, Protonic Software, **2008**; http://www.hyperquad.co.uk/hypnmr.htm.
2. The dimerization of phenylacetic acid in CDCl3 has been reported Sanders and coworkers: N. Ponnuswamy, G. D. Pantoş, M. M. J. Smulders and J. K. M. Sanders, *J. Am. Chem. Soc.*, 2012, **134**, 566–573.
3. The dimerization of phenylacetic acid in C6H6 has been measured by partition: H. Yamada, Y. Taguchi and H. Wada, *Talanta*, 1994, **41**, 573–579.
4. Values are given with an estimated error of ±10%.
5. Very small concentration dependent chemical shifts (linear behavior, ca. 0.003 ppm in total comparing the 10 mM and the 0.1 mM solution) for all signals were observed.