Electronic Supplementary Material (ESI) for Chemical Communications.

Directly linked hydroporphyrin dimers

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General experimental procedures

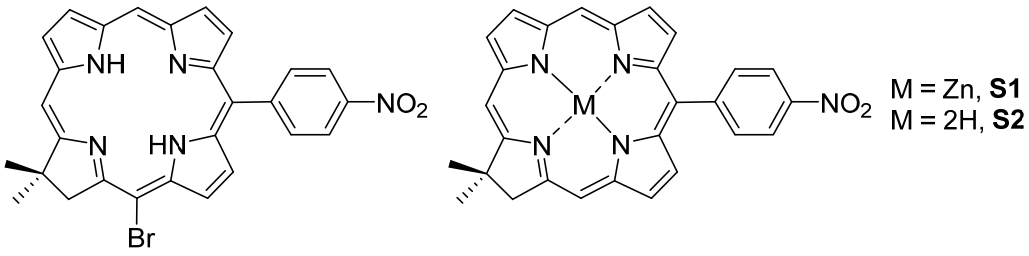
Synthesis. Microwave heating was performed using a Biotage Initiator microwave reactor. ^{1}H NMR (500 or 400 MHz) and ^{13}C NMR (125 or 100 MHz) spectra were recorded on a Bruker 500 MHz or a Bruker or a Varian 400 MHz instrument. Chemical shifts were referenced to residual solvent peaks and are given as follows: chemical shift (δ, ppm), multiplicity [s, singlet; br, broad; d, doublet, m, multiplet), coupling constant (Hz), integration]. LC-MS analysis was carried out using an Agilent 1100 and Waters micromass ZQ tandem system. HR-ESI-MS analyses were performed at the Organisch Chemisches Institut WWU Münster. All compounds displayed the expected isotope distribution pattern. Anhydrous CH_2Cl_2 was obtained by distillation from CaH_2 under an Ar atmosphere. Anhydrous THF was available from a VAC solvent purifier. **Chl**,[1] **Chl10^{Ph}**,[1] **Chl10^{Mes}**,[1] **Chl10^{PhNO2}-Zn**,[2] **Chl15^{Br}**,[3] **Chl10^{Ph}15^{Br}**,[3] **Chl10^{Mes}15^{Br}**,[3] **Chl3^{Br}**,[4] **Chl13^{Br}**,[5] and **Chl15^{Ph}** (Ref 3) were synthesized following literature methods. All other chemicals were from commercial sources and used as received.

Chromatography. Preparative chromatography was performed using silica (230–400 mesh). Thin layer chromatography was performed on silica-coated aluminum plates. Samples were visualized by UV-light (254 and 356 nm), or staining with $KMnO_4/K_2CO_3$ or cerium ammonium molybdate.

Photophysical measurements. UV-Vis absorption spectroscopy was performed on a Varian Cary 300 instrument; (sh) denotes shoulder to a peak. Steady state and time-resolved emission spectra were collected at room temperature using a Horiba Scientific FluoroMax 4 instrument equipped with a flash lamp. Phosphorescence mission intensity changes were fitted to single exponential decays using the instrument´s software (FluorEssence Version 3.5.1.20, based on Origin 8.1090). Fitting to double exponential was less suitable based on R^2 and chi.

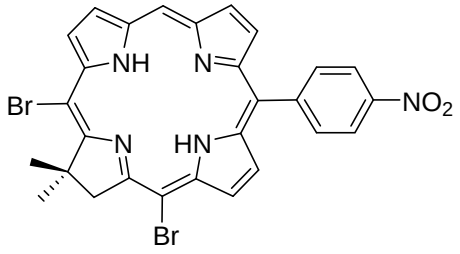
Electrochemistry. Cyclic voltammetry measurements were performed on 1 mM solutions of the analytes in dry CH_2Cl_2 using NBu_4PF_6 (0.1 M solution) as supporting electrolyte. Glassy C-electrode was used as the working electrode and $Ag/AgNO_3$ as the reference electrode. All measurements were done at ν = 100 mV/s scanning rate. All solutions were degassed by 15 min bubbling of Ar though the electrochemical cell. At the end of the measurement a small amount of ferrocene was added to each solution as external reference. All potentials are given versus $Fc^{+/0}$.

Synthesis

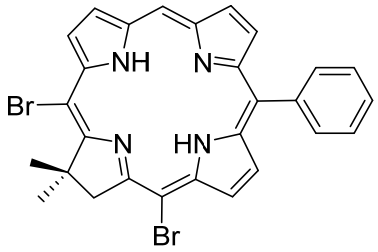


Chl10^{PhNO2}15^{Br}. Zn(II)-chlorin (**S1**,[2] 31 mg, 0.059 mmol) was dissolved in CH_2Cl_2/TFA (20 mL, 1:1), and the solution was stirred at room temperature for 12 h. The TFA was neutralized by the dropwise addition of 2 M aqueous NaOH. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 twice. The combined organic phases were washed with saturated aqueous Na_2CO_3, dried over $MgSO_4$, filtered, and eluted with heptane:CH_2Cl_2 (1:1) through a short silica column. The solvent was evaporated, and the solid residue was dried briefly under vacuum (**S2**, 23.4 mg, 86%), and then used for the bromination. A solution of the free base chlorin obtained in the previous step (20.7 mg, 0.0449 mmol) was dissolved in a mixture of CH_2Cl_2 and TFA (10:1, 11 mL), and was treated with a single portion of NBS (7.2 mg, 0.040 mmol, 0.9 equiv.). The mixture was stirred at room temperature in the dark until TLC-analysis indicated the progress of the reaction [silica, heptane:CH_2Cl_2 (2:1)]. Aqueous NaOH (2 M) was added dropwise to quench the TFA. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was washed with saturated aqueous Na_2CO_3, and was dried over $MgSO_4$, filtered, and concentrated. Purification by column chromatography [silica, heptane:CH_2Cl_2 (2:1)] yielded first the dibrominated chlorin, and then the monobrominated product as a brown solid (18 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) –2.26 (s, 1H), –2.08 (s, 1H), 2.06 (s, 6H), 4.71 (s, 2H), 8.25 (d, J = 8.8 Hz, 2H), 8.45 (d, J = 4.4 Hz, 1H), 8.57 (d, J = 8.8 Hz, 2H), 8.61 (d, J = 4.8 Hz, 1H), 8.90–8.91 (m, 2H), 8.96 (d, J = 4.8 Hz, 1H), 9.21 (d, J = 4.4

Hz, 1H), 9.25 (d, J = 4.8 Hz, 1H), 9.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 31.5, 46.3, 55.2, 95.5, 96.9, 106.7, 120.1, 121.8, 122.1, 124.7, 125.2, 127.4, 129.0, 132.4, 132.8, 133.9, 134.49, 134.54, 136.1, 138.1, 131.2, 147.7, 148.7, 150.8, 152.9, 162.8, 177.0; HR-ESI-MS calcd 540.1030 obsd 540.1039 [$(M + H)^+$, M = $C_{28}H_{22}BrN_5O_2$]; λ_{abs} = 280, 408, 505, 535, 590, 642 (CH_2Cl_2); λ_{em} = 646 nm (λ_{ex} = 408 nm, CH_2Cl_2).

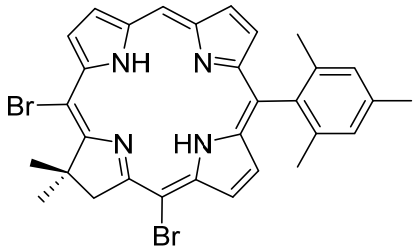


Chl10^{PhNO2}15^{Br}20^{Br}. Characterisation data for the dibrominated side-product (trace amounts formed): ^{1}H NMR (500 MHz, $CDCl_3$) –2.22 (s, 1H), –1.72 (s, 1H), 2.31 (s, 6H), 4.82 (s, 2H), 8.29 (d, J = 8.5 Hz, 2H), 8.45 (d, J = 4.1 Hz, 1H), 8.62 (d, J = 8.5 Hz, 2H), 8.66 (d, J = .2 Hz, 1H), 8.93 (d, J = 4.1 Hz, 1H), 9.22 (dd, J_1 = 4.6 Hz, J_2 = 1.7 Hz, 1H), 9.34 (d, J = 4.6 Hz, 1H), 9.46 (dd, J_1 = 4.6 Hz, J_2 = 1.7 Hz, 1H), 9.81 (s, 1H); ESI-MS calcd 617.0 obsd 617.9 [$(M + H)^+$, M = $C_{28}H_{21}Br_2N_5O_2$] λ_{abs} = 306, 370, 405, 514, 542, 598, 649 nm (CH_2Cl_2); λ_{em} = 652 nm (λ_{ex} = 405 nm, CH_2Cl_2).



Chl10^{Ph}15^{Br}20^{Br}. Characterisation data for the dibrominated species: (4 mg, 7.5%): ^{1}H NMR (500 MHz, $CDCl_3$) –2.11 (s, 1H), –1.63 (s, 1H), 2.30 (s, 6H), 4.80 (s, 2H), 7.73–7.76 (m, 3H), 8.09–8.11 (m, 2H), 8.55 (d, J = 4.6 Hz, 1H), 8.75 (d, J = 5.2 Hz, 1H), 8.88 (d, J = 4.1 Hz, 1H),

9.18 (dd, J_1 = 4.6 Hz, J_2 = 1.7 Hz, 1H), 9.27 (d, J = 4.6 Hz, 1H), 9.42 (dd, J_1 = 4.6 Hz, J_2 = 1.7 Hz, 1H), 9.77 (s, 1H); ESI-MS calcd 572.0 obsd 572.9 [$(M + H)^+$, M = $C_{28}H_{22}Br_2N_4$]; λ_{abs} = 308, 370, 405, 515, 542, 597, 649 nm (CH_2Cl_2); λ_{em} = 653 nm (λ_{ex} = 405 nm, CH_2Cl_2).



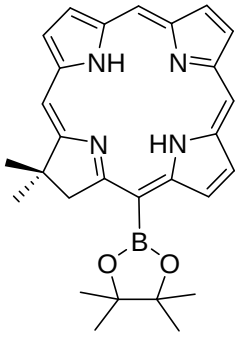
Chl10^{Mes}15^{Br}20^{Br}. Characterisation data for the dibrominated species: (10.8 mg, 14%): ^{1}H NMR (400 MHz, $CDCl_3$) –2.03 (s, 1H), –1.62 (s, 1H), 1.84 (s, 6H), 2.28 (s, 6H), 2.60 (s, 3H), 4.78 (s, 2H), 7.25 (s, 2H), 8.37 (d, J = 4.4 Hz, 1H), 8.58 (s, J = 4.8 Hz, 1H), 8.81 (d, J = 4.4 Hz, 1H), 9.13–914 (m, 1H), 9.21 (d, J = 4.8 Hz, 1H), 9.38–9.39 (m, 1H), 9.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 21.2, 29.1, 31.3, 46.1, 48.8, 60.4, 95.8, 96.8, 109.0, 121.7, 124.9, 126.0, 126.6, n127.8, 128.8, 131.7, 133.7, 135.0, 136.1, 136.9, 137.8, 138.3, 138.9, 139.1, 140.5, 151.7, 153.9, 161.8, 172.2; ESI-MS calcd 614.0 obsd 614.9 [$(M + H)^+$, M = $C_{31}H_{28}Br_2N_4$]; λ_{abs} = 308, 369, 406, 514, 540, 597, 650 nm (CH_2Cl_2); λ_{em} = 653 nm (λ_{ex} = 406 nm, CH_2Cl_2).

General procedure for chlorin borylation

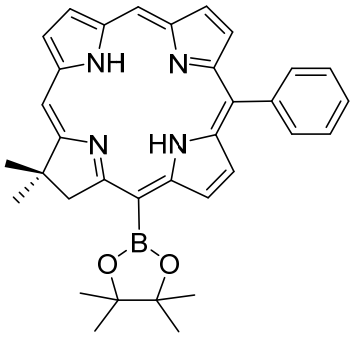
The reaction is based on a borylation described in reference 6.

A solution of bromochlorin (1.0 equiv.) in dichloroethane/Et_3N (6:1, 10 mM) was treated with $PdCl_2(PPh_3)_2$ (0.2 equiv.). The mixture was deoxygenated with three rounds of freeze-pump-thaw, the flask was back-filled with Ar, HBpin (10 equiv.) was added, and the flask was immersed into an oil bath heated at 90 °C. Heating was continued for 16 h. The reaction mixture was allowed to cool back to room temperature. Saturated aqueous NH_4Cl and CH_2Cl_2 were added. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 twice. The

combined organic phase was washed with saturated aqueous NH_4Cl, dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography [silica, heptane/CH_2Cl_2 (1:1)] yielding the borylated chlorin as a dark green-gray solid.

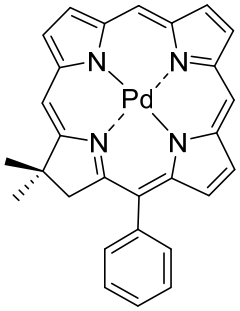


Chl15^{Bpin}, 21 mg, 70%; ^{1}H NMR (500 MHz, $CDCl_3$) −1.94 (br, 1H), −1.70 (br, 1H), 1.77 (s, 12H), 2.06 (s, 6H), 4.86 (s, 2H), 8.91–8.93 (m, 2H), 9.03 (s, 2H), 9.19 (d, J = 4.5 Hz, 1H), 9.23–9.25 (m, 1H), 9.56–9.58 (m, 1H), 9.79 (s, 1H), 9.84 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 25.4, 31.8, 46.1, 53.5, 84.5, 94.7, 107.6, 107.7, 123.6, 125.0, 127.9, 129.3, 129.6, 132.6, 132.2, 134.2, 135.0, 140.5, 145.3, 151.2, 151.5, 170.0, 175.1; HR-ESI-MS calcd 467.2618 obsd 467.2622 [$(M + H)^+$, M = $C_{28}H_{31}BN_4O_2$], calcd 489.2437 obsd 489.2448 $(M + Na)^+$; λ_{abs} = 276, 393, 495, 522, 585, 638 nm (CH_2Cl_2); λ_{em} = 643 nm (λ_{ex} = 393 nm, CH_2Cl_2).



Chl10^{Ph}15^{Bpin}, 125 mg, 86%; ^{1}H NMR (400 MHz, $CDCl_3$) −1.70 (s, 2H), 1.73 (s, 12H), 2.03 (s, 6H), 4.79 (s, 2H), 7.70–7.72 (m, 3H), 8.11 (dd, J_1 = 7.4 Hz, J_2 = 1.2 Hz, 2H), 8.52 (d, J = 4.0 Hz, 1H), 8.74 (d, J = 4.8 Hz, 1H), 8.84 (s, 1H), 8.86–8.89 (m, 2H), 9.16 (d, J = 4.4 Hz, 1H), 9.35 (d,

J = 4.8 Hz, 1H), 9.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 25.2, 31.5, 46.0, 53.2, 84.4, 94.2, 108.0, 122.3, 123.2, 124.4, 126.6, 127.5, 128.1, 129.2, 131.8, 132.1, 133.9, 134.46, 134.52, 140.9, 142.3, 144.5, 151.0, 152.3, 169.0, 175.6; HR-ESI-MS calcd 543.2932 obsd 543.2930 [$(M + H)^+$, M = $C_{34}H_{35}BN_4O_2$], calcd 565.2751 obsd 565.2759 [$(M + Na)^+$; λ_{abs} = 279, 404, 502, 529, 589, 616, 641 nm (CH_2Cl_2); λ_{em} = 646 nm (λ_{ex} = 404 nm, CH_2Cl_2).

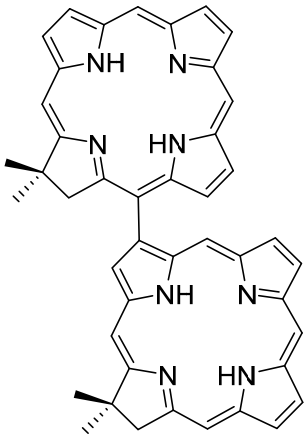


Chl15^{Ph}-Pd. A sample of **Chl15^{Ph}** (Ref 3) (6.2 mg, 0.012 mmol) in a microwave vial was dissolved in pyridine (1 mL), and the solution was treated with $Pd(acac)_2$ (18 mg, 0.06 mmol). The vial was sealed, and the reaction mixture was heated in a microwave reactor at 180 °C for 30 min. The reaction mixture was allowed to cool to room temperature, and the solvent was evaporated at reduced pressure. The dark residue was dissolved in a small amount of CH_2Cl_2, and the solution was loaded onto a silica gel chromatography column. Elution with Heptane/CH_2Cl_2 (2:1) yielded a bright red solid (6.2 mg, quant.): ^{1}H NMR (500 MHz, $CDCl_3$) 1.93 (s, 6H), 4.27 (s, 2H), 7.64–7.68 (m, 3H), 7.84–7.86 (m, 2H), 8.16 (d, *J* = 4.6 Hz, 1H), 8.77 (d, *J* = 4.6 Hz, 1H), 8.85 (s, 1H), 8.88 (d, *J* = 4.6 Hz, 1H), 8.96 (s, 1H), 9.00 (d, *J* = 4.6 Hz, 1H), 9.79 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 31.0, 45.7, 51.2, 96.6, 109.8, 110.8, 113.4, 127.1, 128.2, 128.4, 128.5, 128.7, 132.0, 133.1, 138.5, 138.8, 139.3, 139.6, 143.6, 145.8, 146.5, 146.5, 149.4, 162.5; ESI-MS calcd 520.0 obsd 520.8 [$(M)^-$, M = $C_{28}H_{22}N_4Pd$]; λ_{abs} = 275, 335, 391, 480, 546, 587 nm (THF); λ_{abs} = 269, 337, 392, 480, 548, 589 nm (CH_2Cl_2); steady-

state emission: λ_{em} = 597, 645 nm (λ_{ex} = 392 nm, CH_2Cl_2); time-resolved emission: λ_{phos} = 762 nm (77 K, λ_{ex} = 391 nm, THF); τ = 406 μs

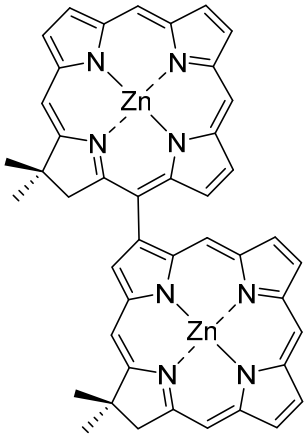
General procedure for chlorin Suzuki coupling

A solution of bromochlorin and chlorin-Bpin (1.0 equiv. each for **Chl15^{Bpin}**, 1.0 and 2.0 equiv., respectively, when **Chl10^{Ph}15^{Bpin}** was used) in toluene/DMF (4 mM and 40 mM for **Chl15^{Bpin}** and **Chl10^{Ph}15^{Bpin}**, respectively) was treated with K_2CO_3 or Cs_2CO_3 (6 or 3 equiv.) and $Pd(PPh_3)_4$ (0.25 equiv.). The mixture was deoxygenated with three rounds of freeze-pump-thaw, the flask was back-filled with Ar, and the mixture was immersed into a pre-heated oil bath heated at 85 °C. Heating was continued for 24 h. The reaction mixture was allowed to cool back to room temperature. Saturated aqueous NH_4Cl and CH_2Cl_2 were added. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 twice. The combined organic phase was washed with saturated aqueous NH_4Cl, dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography [silica, heptane/CH_2Cl_2 (1:1), then, if required, heptane:EtOAc (9:1)] yielding first the dehalogenated and proto-deborylated chlorins, and finally the chlorin dimer as a dark green-brown solid.



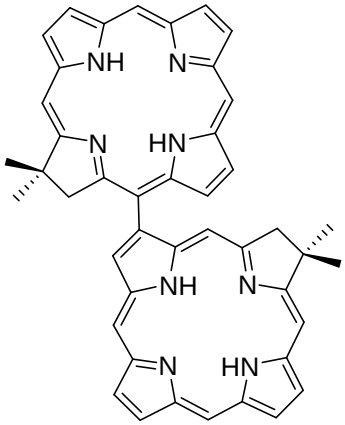
Chl$_2$3,15, 12 mg, 52%; ^{1}H NMR (400 MHz, $CDCl_3$) −1.90 (s, 1H), −1.80 (s, 1H), −2.27–(−1.72) (br, 2H), 1.85 (s, 3H), 1.97 (s, 3H), 2.22 (s, 3H), 2.24 (s, 3H), 4.24, 4.49 (ABq, *J* = 17.6 Hz, 4H),

4.79 (s, 2H), 8.40 (d, J = 4.4 Hz, 1H), 8.48 (d, J = 4.0 Hz, 1H), 8.89 (d, J = 4.4 Hz, 1H), 9.00 (d, J = 4.4 Hz, 1H), 9.05–9.08 (m, 3H), 9.16–9.17 (m, 3H), 9.27–9.28 (m, 2H), 9.31 (s, 1H), 9.34 (d, J = 4.8 Hz, 1H), 9.61 (s, 1H), 9.84 (s, 1H), 9.96 (s, 1H), 9.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, several peaks are doubled, all signals are reported) 29.4, 29.66, 29.70, 31.18, 31.25, 31.43, 31.46, 46.3, 46.8, 52.1, 52.5, 94.6, 95.0, 96.7, 103.9, 106.5, 106.6, 106.7, 107.8, 123.7, 124.1, 126.4, 127.8, 128.2, 132.2, 132.4, 132.6, 132.9, 134.5, 135.0, 135.3, 136.1, 139.0, 139.8, 140.4, 141.6, 142.3, 151.5, 151.9, 152.3, 163.4, 164.5, 175.1,175.3; HR-ESI-MS calcd 701.3112 obsd 701.3125 [$(M + Na)^+$, M = $C_{44}H_{38}N_4$]; λ_{abs} = 277, 391, 413, 498, 523, 585, 642 nm (CH_2Cl_2); λ_{em} = 646 nm (λ_{ex} = 413 nm, CH_2Cl_2).

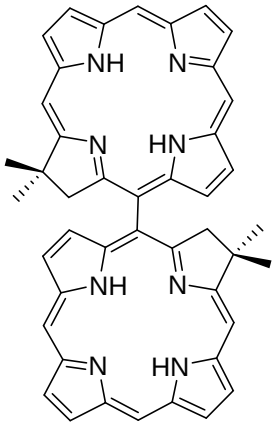


Chl$_2$3,15-Zn$_2$, 4.2 mg, quant.; ^{1}H NMR (500 MHz, $CDCl_3$) 1.78 (s, 3H), 1.93 (s, 3H), 2.18 (s, 3H), 2.19 (s, 3H), 4.13, 4.44 (ABq, J = 17.0 Hz, 2H), 4.69 (s, 2H), 8.25 (d, J = 4.0 Hz, 1H), 8.27 (d, J = 4.5 Hz, 1H), 8.71 (d, J = 4.0 Hz, 1H), 8.73 (s, 1H), 8.75 (d, J = 4.0 Hz, 1H), 8.78 (s, 1H), 8.81 (d, J = 4.0 Hz, 1H), 8.83 (d, J = 4.5 Hz, 1H), 8.91 (s, 1H), 8.97–9.00 (m, 3H), 9.10 (d, J = 4.0 Hz, 1H), 9.13 (d, J = 4.5 Hz, 1H), 9.29 (s, 1H), 9.56 (s, 1H), 9.69 (s, 1H), 9.70 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 31.5, 32.0, 32.2, 32.3, 32.4, 33.7, 46.5, 47.2, 52.4, 53.3, 95.3, 95.7, 97.5, 106.6, 109.7, 109.8, 110.7, 128.5, 128.7. 129.2, 129.4, 129.5, 129.75, 129.77, 131.9, 133.0, 134.0, 147.9, 148.06, 148.13, 148.29, 148.33, 148.6, 150.2, 151.4, 153.9, 155.0, 155.6, 156.7,

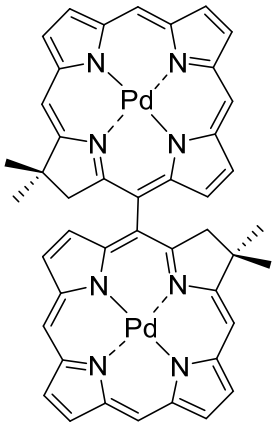
160.2, 160.8, 171.9, 172.2; HR-ESI-MS calcd 802.14948 obsd 802.14959 (M^+, M = $C_{44}H_{34}N_4Zn_2$); λ_{abs} = 281, 322, 401, 504, 575, 615 nm (CH_2Cl_2); λ_{em} = 619 nm (λ_{ex} = 401 nm, CH_2Cl_2).



Chl$_2$13,15, 4.2 mg, 32%; ^{1}H NMR (400 MHz, $CDCl_3$) −2.18 (br, 2H), −1.92 (s, 1H), −1.82 (s, 1H), 1.83 (s, 3H), 1.95 (s, 3H), 2.18 (s 3H), 2.20 (s, 3H), 4.20, 4.46 (ABq, *J* = 17.7 Hz, 2H), 4.82 (s, 2H), 8.39 (d, *J* = 4.7 Hz, 1H), 8.47 (d, *J* = 4.2 Hz, 1H), 8.90 (d, *J* = 4.2 Hz, 1H), 9.05–9.08 (m, 5H), 9.15–9.16 (m, 2H), 9.27 (s, 1H), 9.29 (d, *J* = 4.7 Hz, 1H), 9.33 (d, *J* = 4.7Hz, 1H), 9.36 (s, 1H), 9.56 (s, 1H), 9.87 (s, 1H), 9.95 (s, 1H), 9.98 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) 31.17, 31.23, 31.4, 31.9, 46.3, 46.7, 52.2, 52.5, 94.7, 95.0, 96.6, 103.9, 106.3, 106.8, 107.8, 123.6, 124.0, 124.1, 124.2, 126.4, 127.9, 128.0, 132.4, 132.9, 134.5, 134.7, 135.3, 136.4, 138.2, 140.4, 140.5, 141.5, 142.4, 151.5, 151.6, 151.8, 152.3, 163.7, 164.4, 175.0, 175.1; HR-ESI-MS calcd 679.3292 obsd 679.3267 [$(M + H)^+$, M = $C_{44}H_{38}N_4$], calcd 701.3112 obsd 701.3107 $(M + Na)^+$; λ_{abs} = 277, 392, 413, 497, 584, 642 nm (CH_2Cl_2); λ_{em} = 645 nm (λ_{ex} = 413 nm, CH_2Cl_2).

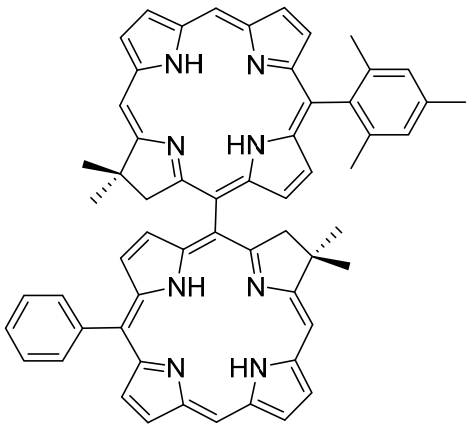


Chl$_2$15,15, 11 mg, 32%; ^{1}H NMR (400 MHz, $CDCl_3$) –1.95 (s, 2H), –1.81 (s, 2H), 1.82 (s, 6H), 1.85 (s, 6H), 3.78, 3.85 (ABq, J = 17.2 Hz, 4H), 7.92 (d, J = 4.8 Hz, 2H), 9.01 (d, J = 4.8 Hz, 2H), 9.06–9.08 (m, 4H), 9.16 (s, 4H), 9.34 (d, J = 4.8 Hz, 2H), 9.96 (s, 2H), 9.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 30.8, 31.6, 46.2, 52.6, 95.0, 106.4, 107.8, 110.8, 123.5, 124.2, 127.9, 128.0, 132.4, 132.9, 134.4, 135.4, 140.5, 142.0, 151.5, 152.4, 165.2, 174.7; HR-ESI-MS calcd 679.3293 obsd 679.3292 [$(M + H)^+$, M = $C_{44}H_{38}N_4$], calcd 701.3112 obsd 701.3113 $(M + Na)^+$; λ_{abs} = 277, 413, 500, 591, 645 nm (CH_2Cl_2); λ_{em} = 648 nm (λ_{ex} = 413 nm, CH_2Cl_2).



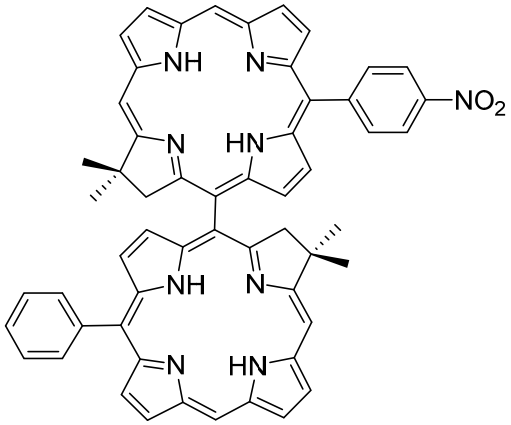
Chl$_2$15,15-Pd$_2$**. A sample of **Chl$_2$15,15 (5.2 mg, 0.0077 mmol) in a microwave vial was dissolved in pyridine (1.5 mL), and the solution was treated with $Pd(acac)_2$ (49.7 mg, 0.163 mmol). The vial was sealed, and the reaction mixture was heated in a microwave reactor at 180 °C for 30 min. The reaction mixture was allowed to cool to room temperature, and the solvent

was evaporated at reduced pressure. The dark residue was dissolved in a small amount of CH_2Cl_2, and the solution was loaded onto a silica gel chromatography column. Elution with CH_2Cl_2 yielded a dark blue solid (quant): due to the poor solubility of the compound in a range of solvents (CH_2Cl_2, $CHCl_3$, DMSO, THF, MeOH, EtOAc, toluene, acetone) we could not collect a good quality ^{1}H NMR-spectrum. ESI-MS calcd 443.1 obsd 442.8 [$(M)^{2-}$, M = $C_{44}H_{34}N_8Pd_2$]; λ_{abs} = 334, 401, 482, 514, 560, 601 nm (THF); λ_{abs} = 401, 481, 560, 601 nm (CH_2Cl_2); steady-state emission: λ_{em} = 608, 644 nm (λ_{ex} = 401 nm, CH_2Cl_2); time-resolved emission: λ_{phos} = 776 nm (77 K, λ_{ex} = 401 nm, THF); τ = 359 μs.

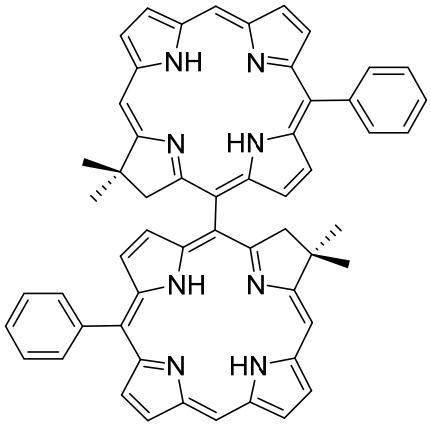


Chl$_2$15,15-PhMes, 12.5 mg, 11%; ^{1}H NMR (50 MHz, $CDCl_3$) −1.81 (s, 1H), −1.70 (s, 1H), −1.38 (s, 1H), −1.35 (s, 1H), 1.80 (s, 3H), 1.84 (s, 3H), 1.88 (s, 3H), 1.91 (s, 3H), 2.52 (s, 3H), 3.75–3.83 (m, 4H), 7.18 (m, 2H), 7.64–7.72 (m, 3H), 7.71 (d, J = 5.0 Hz, 1H), 7.81 (d, J = 5.0 Hz, 1H), 8.12–8.13 (m, 1H), 8.17–8.19 (m, 1H), 8.35 (d, J = 4.5 Hz, 1H), 8.52 (d, J = 5.0 Hz, 1H), 8.53 (d, J = 4.5 Hz, 1H), 8.69 (d, J = 4.5 Hz, 1H), 8.95–8.98 (m, 3H), 9.00–9.01 (m, 1H), 9.03 (d, J = 4.5 Hz, 1H), 9.29 (d, J = 5.0 Hz, 1H), 9.31 (d, J = 45 Hz, 1H), 9.86 (s, 1H), 9.92 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, several peaks multiplied, all signals reported) 21.5, 21.54, 21.57, 22.9, 29.5, 29.8, 29.9, 30.4, 30.8, 30.9, 31.4, 31.6, 31.7, 31.8, 32.1, 46.2, 52.8, 52.9, 94.8, 94.9, 106.8, 107.1, 110.1, 111.5, 121.5, 123.0, 123.7, 123.8, 124.0, 126.8, 127.2, 127.7, 128.3,

128.4, 128.5, 129.8, 131.7, 132.4, 132.82, 132.85, 134.0, 134.1, 134.5, 135.1, 135.23, 135.25, 137.6, 138.2, 139.18, 139.20, 141.1, 141.2, 142.1, 142.17, 142.21, 152.1, 152.6, 165.1, 165.3, 175.3, 175.5; HR-ESI-MS calcd 873.4388 obsd 873.4384 [$(M + H)^+$, M = $C_{59}H_{52}N_4$], calcd 895.4207 obsd 895.4199 $(M + Na)^+$; λ_{abs} = 283, 410, 421, 508, 534, 589, 648 nm (CH_2Cl_2); λ_{em} = 652 nm (λ_{ex} = 421 nm, CH_2Cl_2).



Chl$_2$15,15-PhNO2, 6.2 mg, 32%; ^{1}H NMR (500 MHz, $CDCl_3$) −1.92 (s, 1H), −1.80 (s, 1H), −1.46 (s, 1H), −1.34 (s, 1H), 1.80 (s x s, 2 x 3H), 1.85 (s, 3H), 1.86 (s, 3H), 3.79 (d, *J* = 1.2 Hz, 2H), 3.83 (d, *J* = 1.2 Hz, 2H), 7.63−7.68 (m, 3H), 7.74 (d, *J* = 4.5 Hz, 1H), 7.84 (d, *J* = 5.0 Hz, 1H), 811−8.14 (m, 1H), 8.17−8.19 (m, 1H), 8.32 (dd, J_1 = 8.1 Hz, 1H, J_2 = 1.7 Hz, 1H), 8.38 (dd, J_1 = 8.7 Hz, J_2 = 1.7 Hz, 1H), 8.43 (d, *J* = 4.6 Hz, 1H), 8.52−8.57 (m, 3H), 8.59 (d, *J* = 4.1 Hz, 1H), 8.69 (d, *J* = 4.5 Hz, 1H), 8.98 (s, 1H), 9.02−9.05 (m, 3H), 9.07−9.08 (m, 2H), 9.32 (d, *J* = 4.5 Hz, 1H), 9.35 (d, *J* = 4.5 Hz, 1H), 9.92 (s, 1H), 9.97 (s, 1H); ESI-MS calcd 875.4 obsd 876.3 [$(M + H)^+$, M = $C_{56}H_{45}N_9O_2$]; λ_{abs} = 280, 420, 508, 534, 591, 650 nm (CH_2Cl_2); λ_{em} = 654 nm (λ_{ex} = 420 nm, CH_2Cl_2).



Chl$_2$15,15-Ph$_2$, 17.5 mg, 16%; ^{1}H NMR (500 MHz, $CDCl_3$) –1.79 (s, 2H), –1.34 (s, 2H), 1.80 (s, 6H), 1.86 (s, 6H), 3.80 (s, 2H), 3.81 (s, 2H), 7.64–7.68 (m, 6H), 7.79 (d, J = 5.0 Hz, 2H), 8.14 (d, J = 5.0 Hz, 2H), 8.19–8.20 (m, 2H), 8.53 (d, J = 5.0 Hz, 2H), 8.70 (d, J = 4.5 Hz, 2H), 8.99 (s, 2H), 9.03–9.04 (m, 4H), 9.32 (d, J = 4.5 Hz, 2H), 9.93 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 29.7, 31.6, 46.1, 52.7, 97.7, 107.0, 111.6, 122.9, 123.5, 123.9, 126.6, 126.7, 127.6, 128.2, 128.4, 132.2, 132.7, 133.86, 133.93, 135.0, 141.1, 141.9, 142.0, 152.0, 152.5, 165.1, 175.3; HR-ESI-MS obsd 831.3899 [$(M + H)^+$, M = $C_{56}H_{46}N_8$]; λ_{abs} = 281, 411, 421, 507, 533, 590, 649 nm (CH_2Cl_2); λ_{em} = 653 nm (λ_{ex} = 421 nm, CH_2Cl_2).

Table S1. Photophysical properties of dimers and reference compounds.[a]

Compound	λ_{Soret}, λ_Q	I_B/I_Q	λ_{em} (λ_{exc})	Φ^c
$Chl_2$3,15	391, 413, 642	2.1	646	0.19
$Chl_2$13,15	392, 413, 642	2.0	645	0.16
$Chl_2$15,15	413, 645	2.6	648	0.255
$Chl_2$3,15-Zn_2	401, 615	2.6	619	0.11
$Chl_2$15^{Ph},15^{Mes}	410, 421, 648	2.6	652	0.39
$Chl_2$15^{Ph},15^{PhNO2}	420, 650	2.9	654	n.d.
$Chl_2$15^{Ph},15^{Ph}	411, 421, 649	2.9	653	0.28
Chl	398, 636[d]	2.4[d]	636[d]	0.19[d]
Chl15^{Bpin}	393, 638	4.3	643	0.21
Chl10^{Ph}15^{Bpin}	404, 641	5.6	646	n.d.
Chl15^{Ph}-Pd[b]	391, 587	1.9	n.d.	n.d.
$Chl_2$15,15-Pd_2[b]	401, 601	1.5	n.d.	n.d.

[a] In CH_2Cl_2. [b] In THF. [c] Using *meso*-tetraphenyporphyrin in toluene as standard. [d] From reference 7, measured in toluene.

VT-NMR experiments

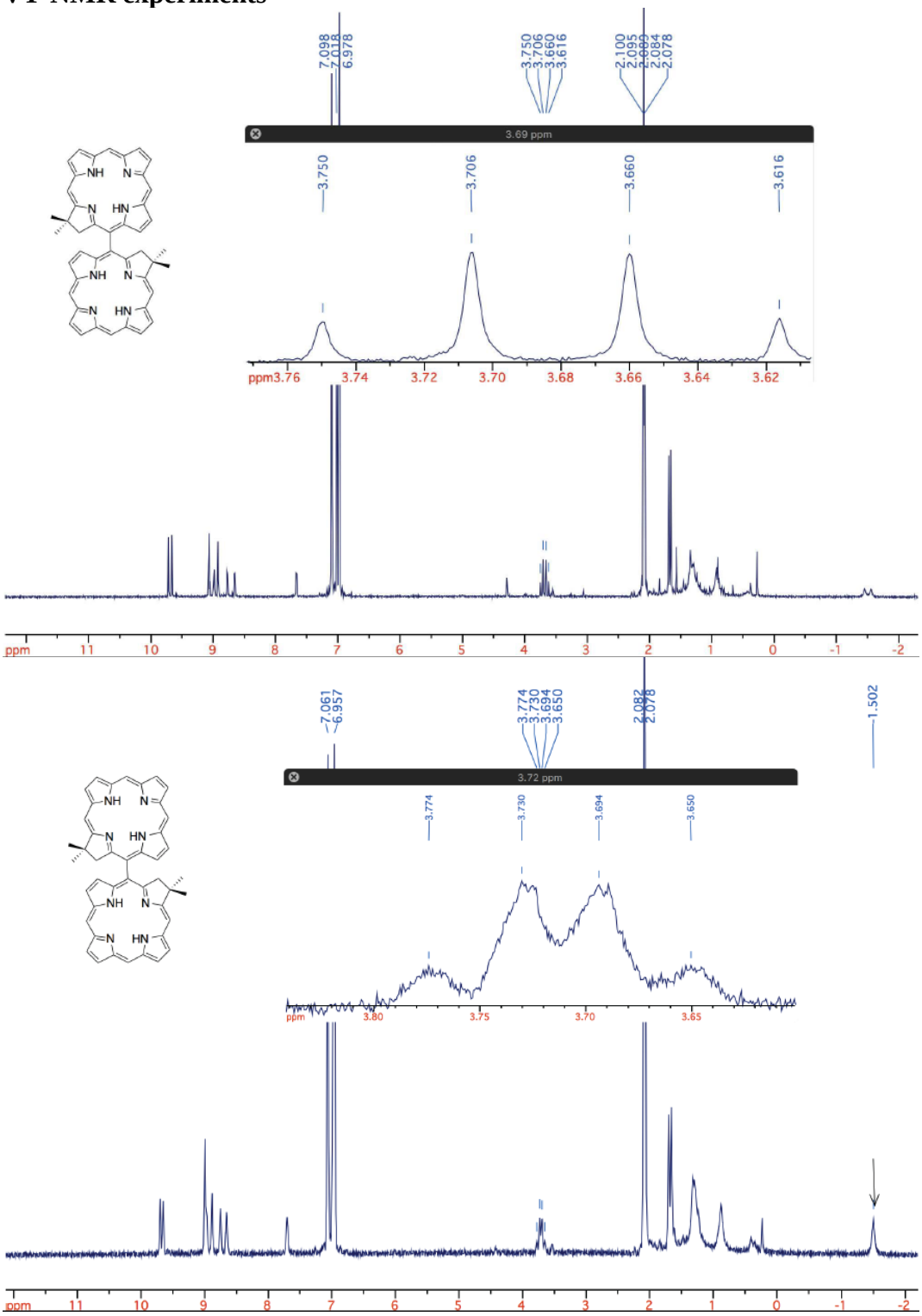


Figure S1. Spectra of **Chl$_2$13,15** at room temperature (top) and at 90 °C (bottom) in toluene-d_8, with the CH_2 ABq-signal shown separately.

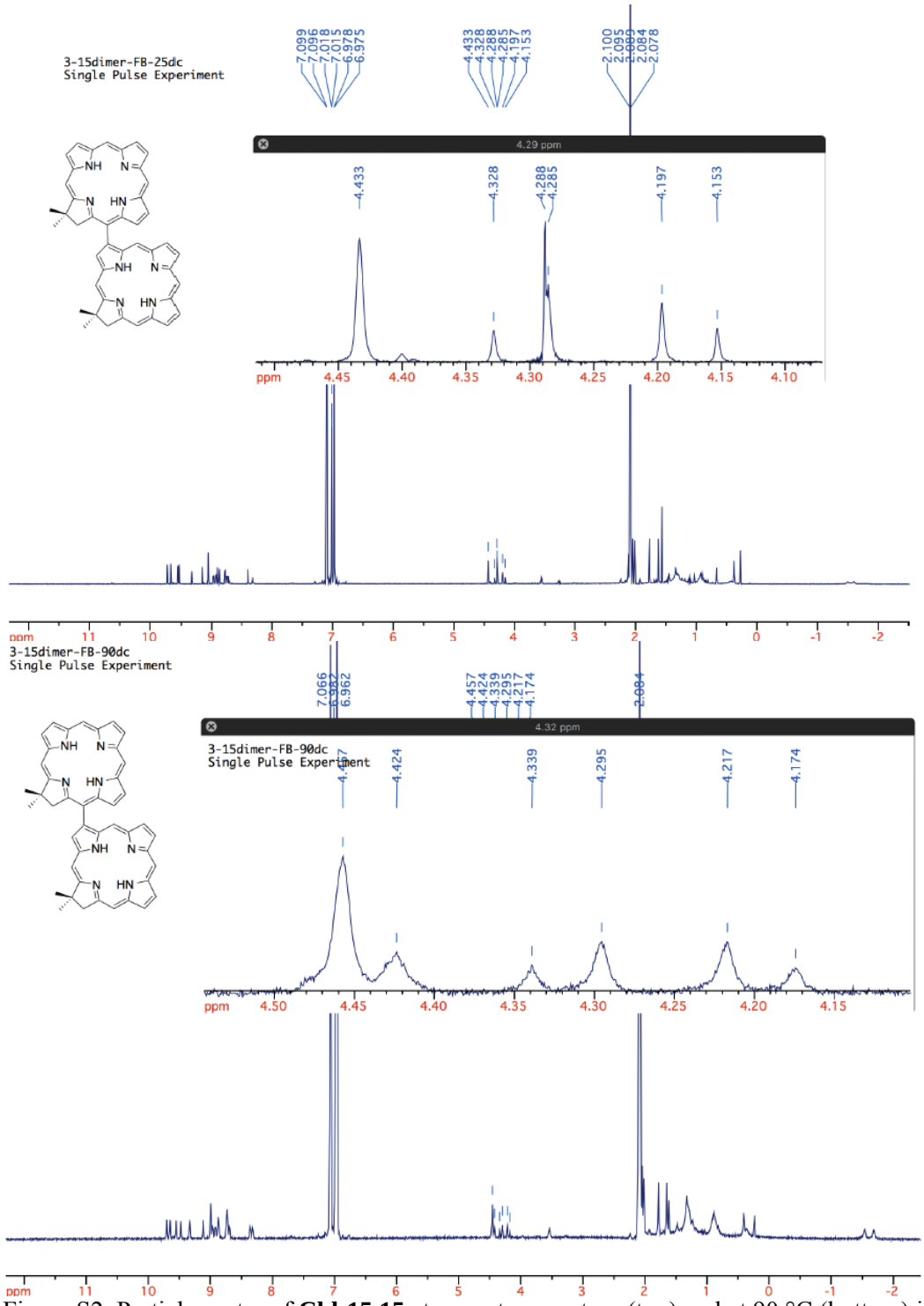


Figure S2. Partial spectra of **Chl$_2$15,15** at room temperature (top) and at 90 °C (bottom) in toluene-d_8, with the CH_2 ABq-signal shown separately.

Phosphorescence spectra of Pd-complexes

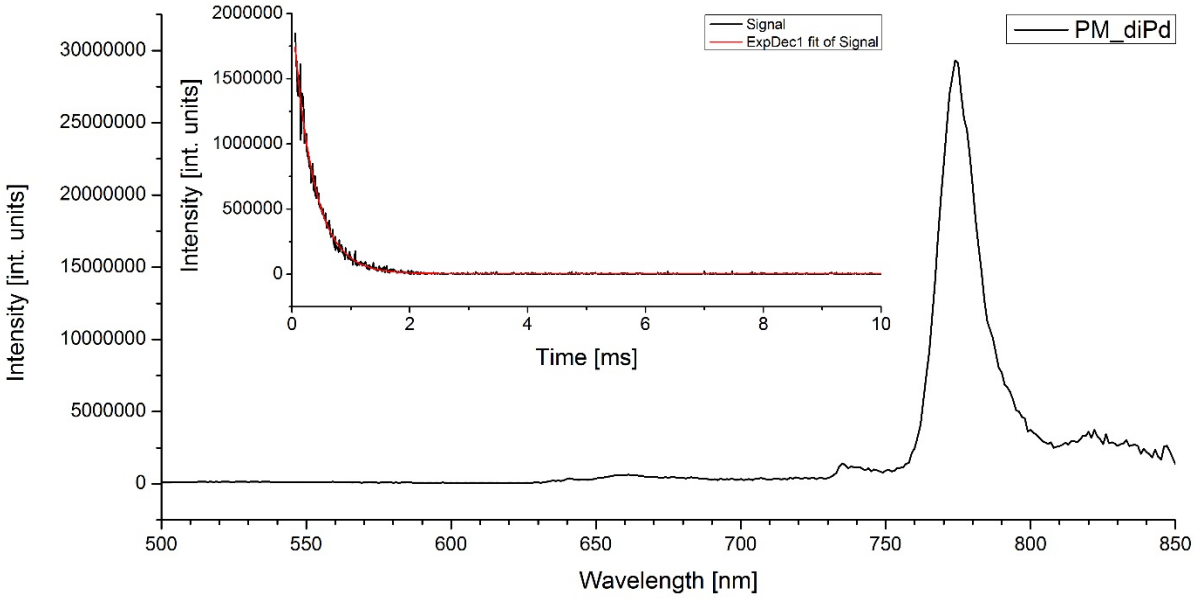


Figure S3. Time-resolved emission spectrum of **$Chl_2$15,15-Pd_2** at 77 K in THF (λ_{exc} = 401 nm, delay: 50 µs, integration time 10^5 µs). The inset shows the emission decay (λ_{exc} = 401 nm, λ_{em} = 774 nm, sample window 0.2 ms, integration time 100 ms) fitted with a monoexponential. Fitting with a biexponential did not improve the fit as judged by R^2 and χ, but yielded two lifetimes, 340 µs and 732 µs with 96% and 4% contribution, respectively.

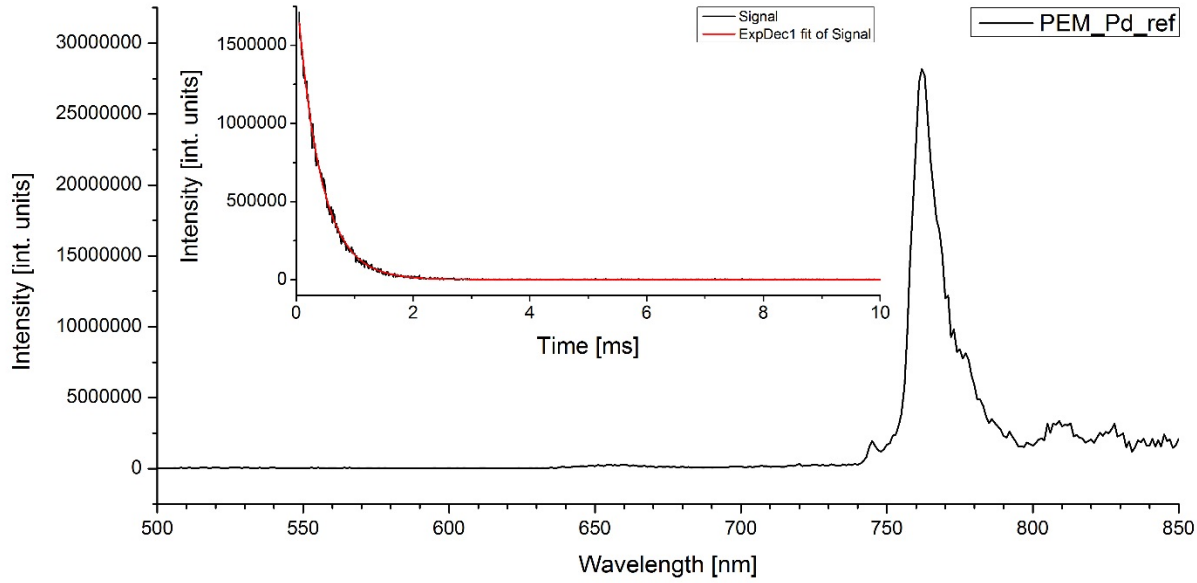


Figure S4. Time-resolved emission spectrum of **$Chl_2$15^{Ph}-Pd** at 77 K in THF (λ_{exc} = 391 nm, delay: 50 µs, integration time 10^5 µs). The inset shows the emission decay (λ_{exc} = 391 nm, λ_{em} = 762 nm, sample window 0.2 ms, integration time 100 ms) fitted with a monoexponential.

Electrochemistry

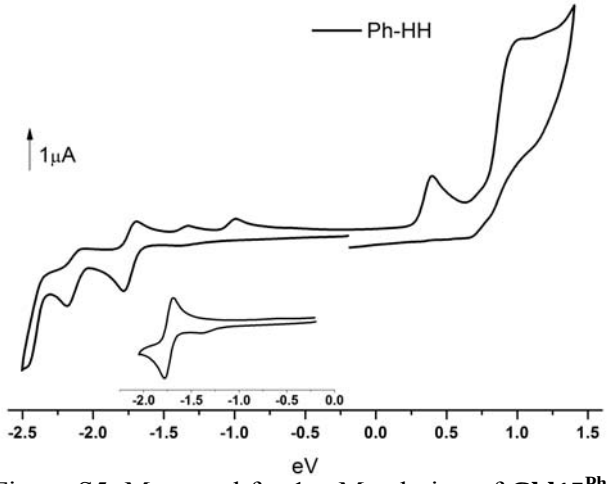


Figure S5. Measured for 1 mM solution of **Chl15^{Ph}** in CH_2Cl_2 (0.1 M NBu_4PF_6), glassy C-electrode, ν = 100 mV/s. All potentials are given versus $Fc^{+/0}$.

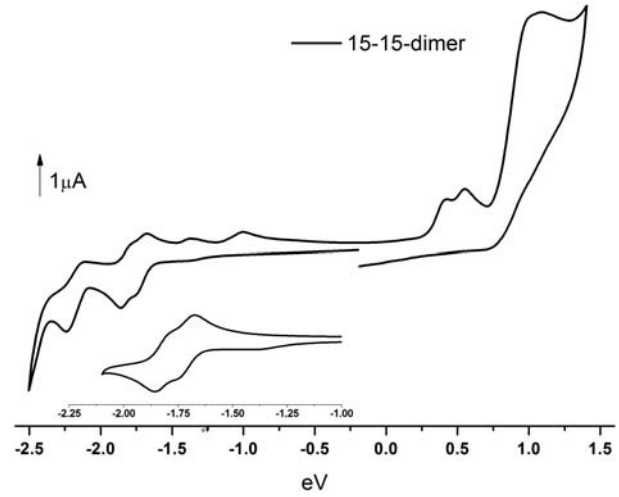


Figure S6. Measured for 1 mM solution of **Chl$_2$15,15** in CH_2Cl_2 (0.1 M NBu_4PF_6), glassy C-electrode, ν = 100 mV/s. All potentials are given versus $Fc^{+/0}$.

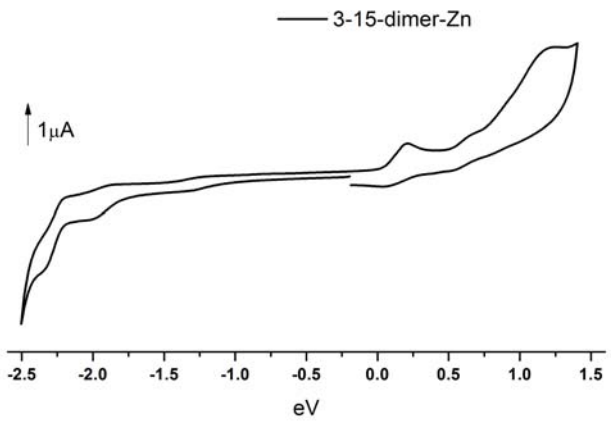


Figure S7. Measured for 1 mM solution of **$Chl_2$3,15-Zn_2** in CH_2Cl_2 (0.1 M NBu_4PF_6), glassy C-electrode, ν = 100 mV/s. All potentials are given versus $Fc^{+/0}$.

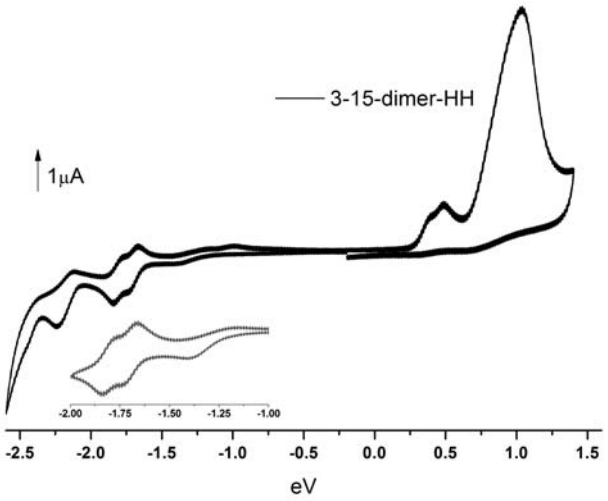


Figure S8. Measured for 1 mM solution of **$Chl_2$3,15** in CH_2Cl_2 (0.1 M NBu_4PF_6), glassy C-electrode, ν = 100 mV/s. All potentials are given versus $Fc^{+/0}$.

X-ray diffraction data

All the measurements were performed using graphite-monochromatized Mo K_α radiation at 100K using a Bruker D8 APEX-II equipped with a CCD camera. The structure was solved by direct methods (SHELXS-2014) and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014).[8] The non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C-H distances of 0.99Å.

Compound **Chl15^{Br}20^{Br}** crystallizes in the monoclinic space group C 2/c (No. 15) as dark brown blocks suitable for single crystal X-ray diffraction. The bond distances of **Chl15^{Br}20^{Br}** heterocycle are in agreement with related chlorin derivatives. The least squares planes (l.s.pl.) through the pyrrole units show significant twisting, i.e. torsion angles of adjacent range from 6.60(10)° to 12.74(11)°.

Table 2. Crystal data and structure refinement for **Chl15^{Br}20^{Br}**.

Crystal data	KEB36_095_F1
CCDC-No.	CCDC 1447589
Empirical formula	$C_{28}H_{22}Br_2N_4$
Formula weight	574.31
Crystal description	block, dark brown
Crystal size	0.3 x 0.2 x 0.18
Crystal system, space group	monoclinic, C 2/c
Unit cell dimensions: a	26.108(2)
b	8.7687(7)
c	21.6124(18)
β	112.199(2)
Volume	4581.1(7)
Z	8
Calculated density	1.665 Mg/m³
F(000)	2304
Linear absorption coefficient μ	3.565 mm^{-1}
Absorption correction	multi-scan, SADABS 2008
Max. and min. transmission	0.7456 and 0.4920
Unit cell determination	$2.0 < \Theta < 25.2°$
	4749 reflections used at 100K
Data collection	
Temperature	100(2)K
Diffractometer	Bruker APEX-II CCD
Radiation source	fine-focus sealed tube
Radiation and wavelength	MoK_α, 0.71073Å
Monochromator	Graphite
Scan type	ω scans
Θ range for data collection	2.03 to 28.09°
Index ranges	$-34 \le h \le 34, -11 \le k \le 11, -28 \le l \le 28$
Reflections collected / unique	45290 / 5531
Significant unique reflections	4749 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0271, 0.0494
Completeness to Θ_{max}	99.0%
Refinement	
Refinement method	Full-matrix least-squares on F²
Data / parameters / restraints	5531/ 317/ 0
Goodness-of-fit on F²	1.049
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0240, wR2 = 0.0538
R indices (all data)	R1 = 0.0321, wR2 = 0.0567
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$
Weighting scheme parameters a, b	0.0212, 5.9199
Largest Δ/σ in last cycle	0.003
Largest difference peak and hole	0.378 and -0.375 e/Å³
Structure Solution Program	SHELXS-2014/7 (Sheldrick, 2008)
Structure Refinement Program	SHELXL-2014 (Sheldrick, 2008)

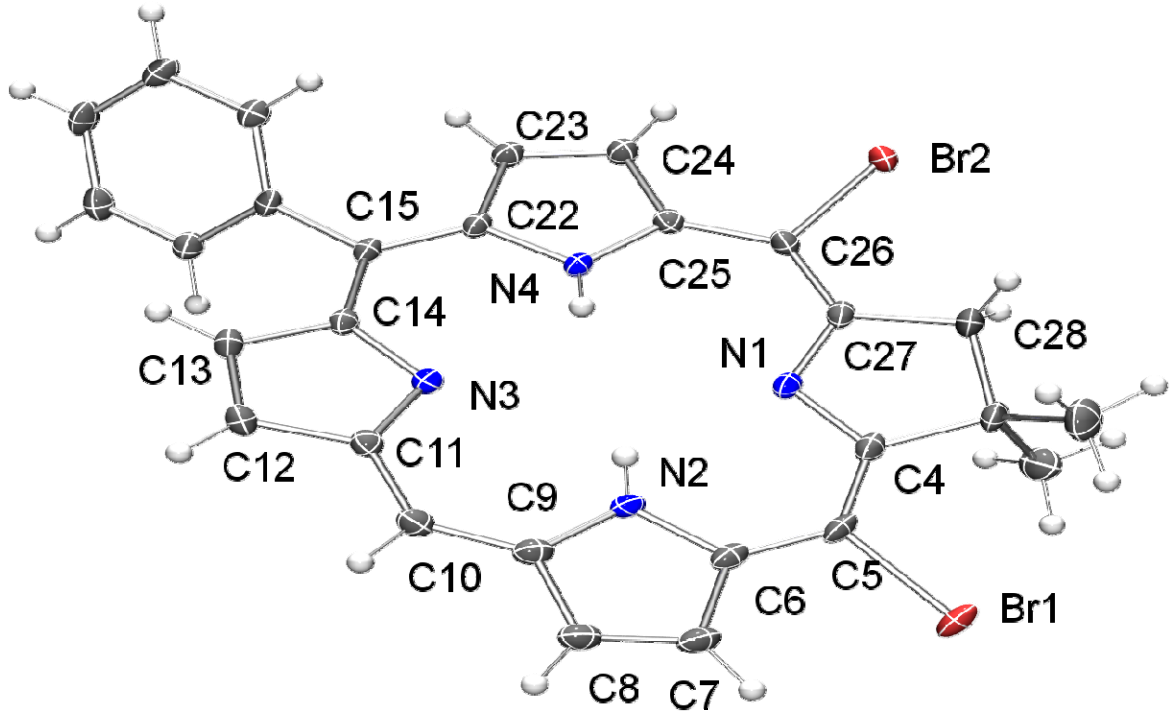


Figure S9: ORTEP representation of **Chl15^{Br}20^{Br}** with thermal ellipsoids at a probability level of 50%. Selected parameters (angles [°]): Angle between least squares planes of the pyrrole heterocycles: Plane N1 – Plane N2 12.74(11), Plane N2 –Plane N3 6.60(10), Plane N3 Plane N4 10.07(10), Plane N4 - Plane N1 12.59(10).

References

(1) Ptaszek, M.; McDowell, B. E.; Taniguchi, M.; Kim, H.-J.; Lindsey, J. S. *Tetrahedron* **2007**, *63*, 3826.

(2) Laakso, J.; Rosser, G. A.; Szijjarto, C.; Beeby, A.; Borbas, K. E. *Inorg. Chem.* **2012**, *51*, 10366.

(3) Taniguchi, M.; Ptaszek, M.; McDowell, B. E.; Lindsey, J. S. *Tetrahedron* **2007**, *63*, 3840.

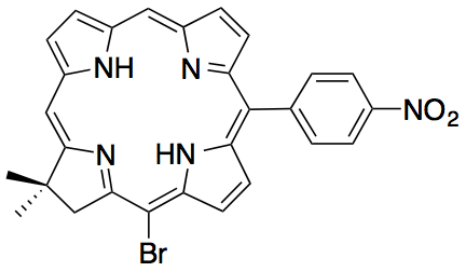
(4) Liu, M.; Ptaszek, M.; Mass, O.; Minkler, D. F.; Sommer, R. D.; Bhaumik, J.; Lindsey, J. S. *New J. Chem.* **2014**, *38*, 1717.

(5) Mass, O.; Taniguchi, M.; Ptaszek, M.; Springer, J. W.; Faries, K. M.; Diers, J. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *New J. Chem.* **2011**, *35*, 76.

(6) Ryan, A.; Gehrold, A.; Perusitti, R.; Pintea, M.; Fazekas, M.; Locos, O. B. Blaikie, F.; Senge, M. O. *Eur. J. Org. Chem.* **2011**, 5817

(7) Taniguchi, M.; Ptaszek, M.; McDowell, B. E.; Boyle, P. D.; Lindsey, J. S. *Tetrahedron* **2007**, *63*, 3850.

(8) Sheldrick, G. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112.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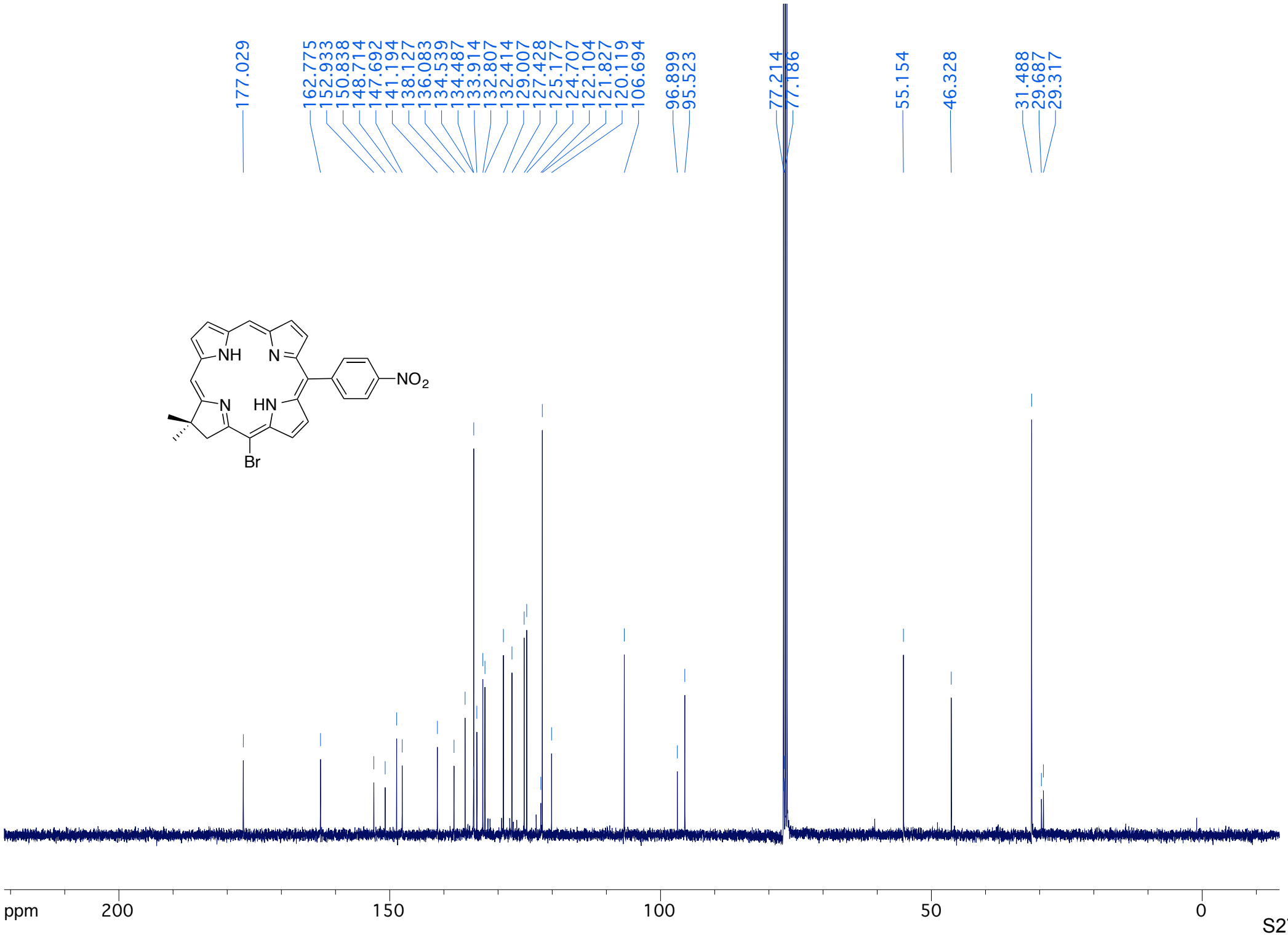
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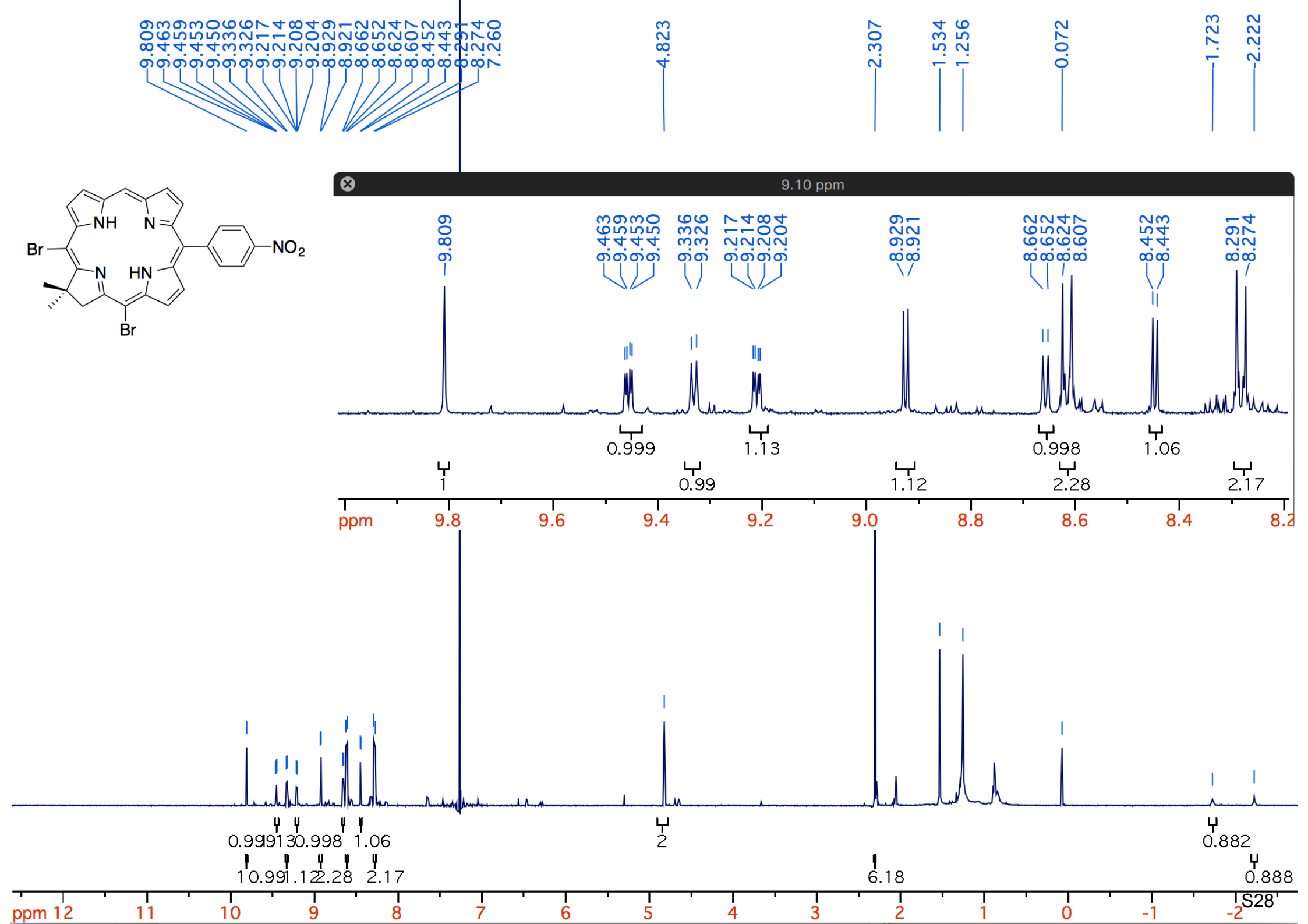
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9.459
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9.336
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9.217
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9.208
9.204
8.929
8.921
8.662
8.652
8.624
8.607
8.452
8.443
8.291
8.274
7.260
4.823
2.307
1.534
1.256
0.072
1.723
2.222
NH
N
Br
N
HN
NO2
Br
9.10 ppm
0.999
1.13
0.998
1.06
1
0.99
1.12
2.28
2.17
ppm
9.8
9.6
9.4
9.2
9.0
8.8
8.6
8.4
8.2
0.99
1.91
1.13
0.998
1.06
2
0.882
1
0.99
1.12
2.28
2.17
6.18
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ppm 12
11
10
9
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7
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5
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3
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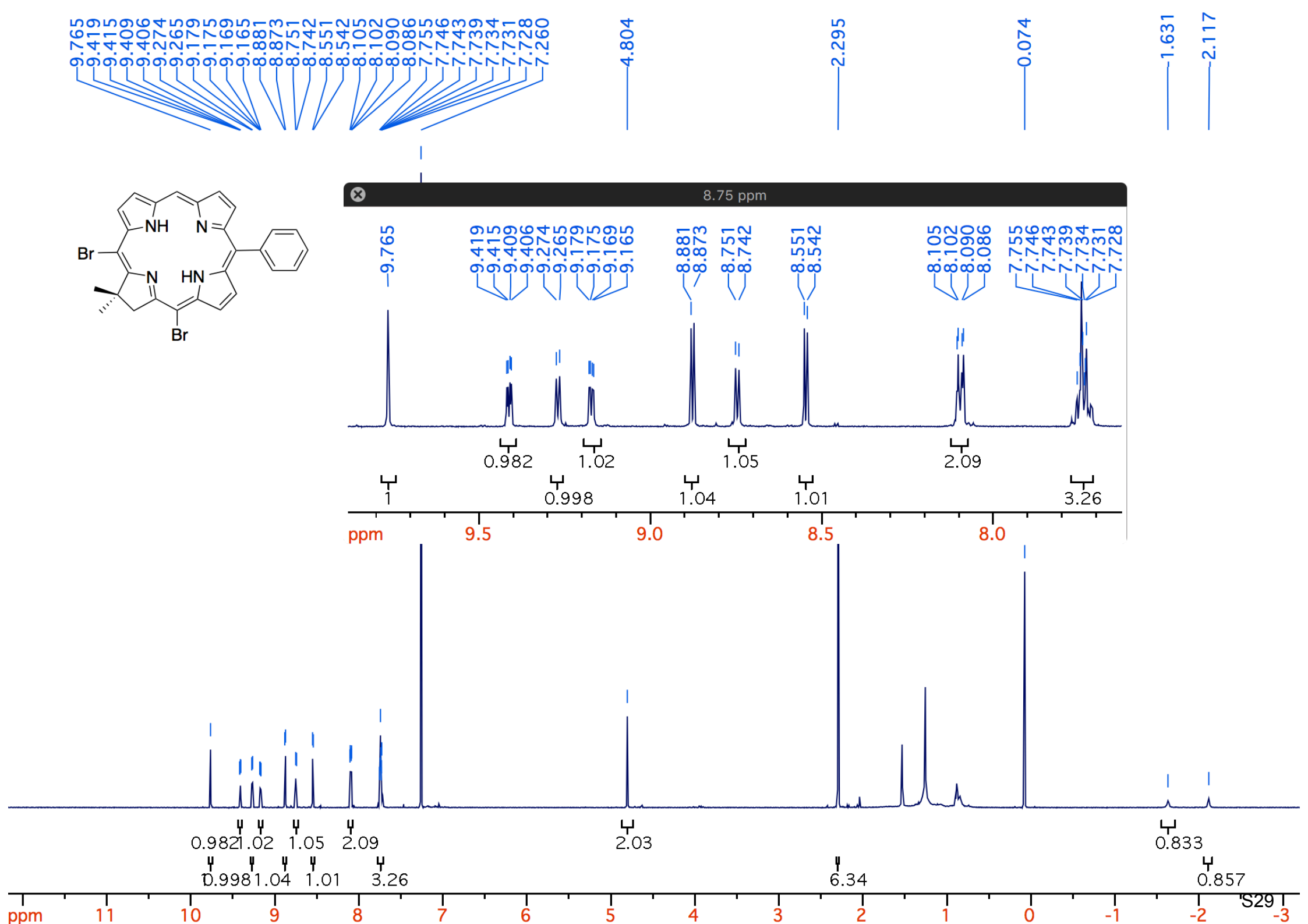
S28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8.873
8.751
8.742
8.551
8.542
8.105
8.102
8.090
8.086
7.755
7.746
7.743
7.739
7.734
7.731
7.728
7.260
4.804
2.295
0.074
1.631
2.117
NH
N
Br
N
HN
Br
8.75 ppm
0.982
1.02
1.05
2.09
1
0.998
1.04
1.01
3.26
ppm
9.5
9.0
8.5
8.0
0.982
1.02
1.05
2.09
2.03
0.833
0.998
1.04
1.01
3.26
6.34
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10
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7
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3
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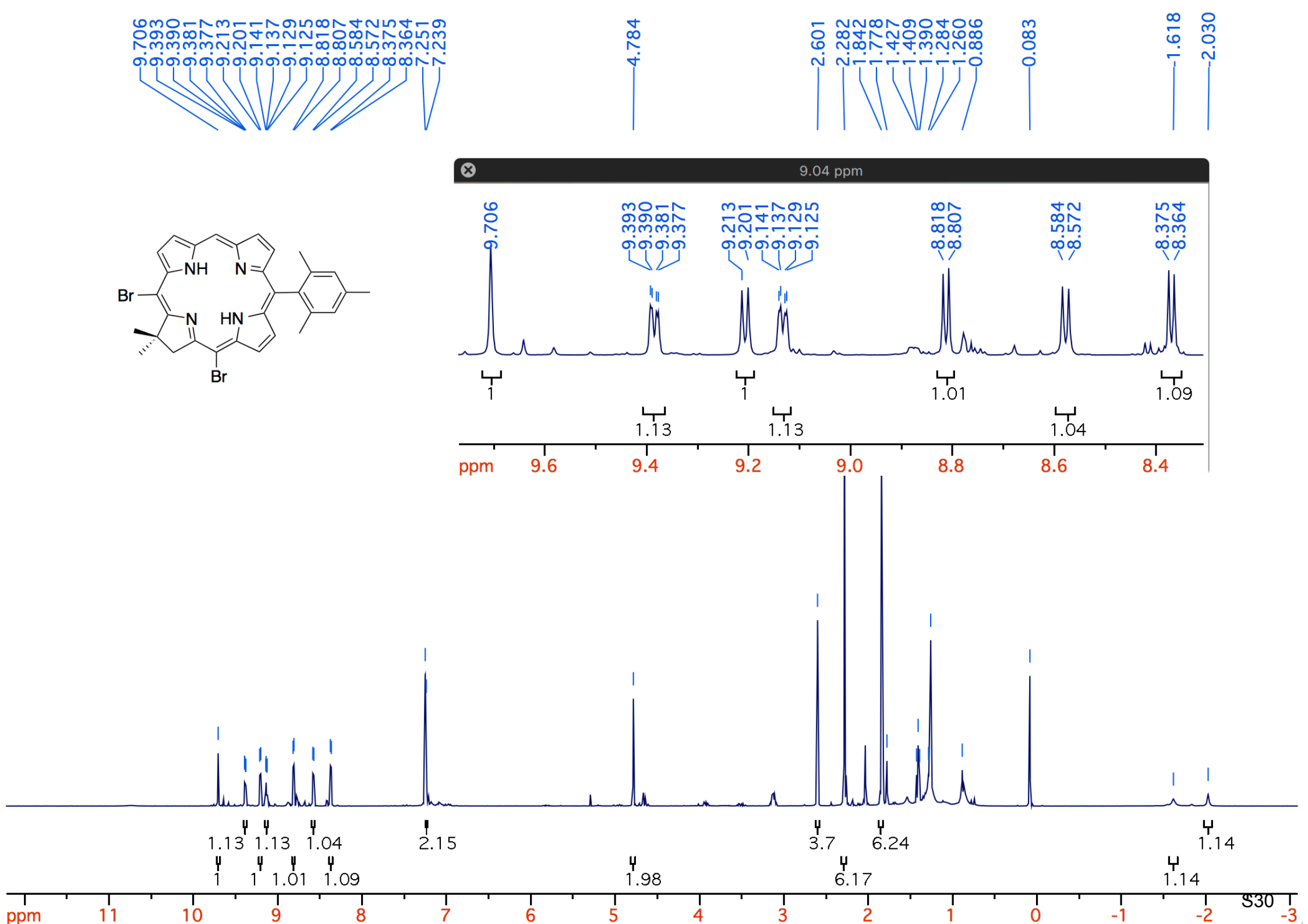
-3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9.390
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9.377
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9.201
9.141
9.137
9.129
9.125
8.818
8.807
8.584
8.572
8.375
8.364
7.251
7.239
4.784
2.601
2.282
1.842
1.778
1.427
1.409
1.390
1.284
1.260
0.886
0.083
1.618
2.030
NH
N
Br
N
HN
Br
9.04 ppm
1
1
1.01
1.09
1.13
1.13
1.04
ppm
9.6
9.4
9.2
9.0
8.8
8.6
8.4
1.13
1.13
1.04
2.15
3.7
6.24
1.14
1
1
1.01
1.09
1.98
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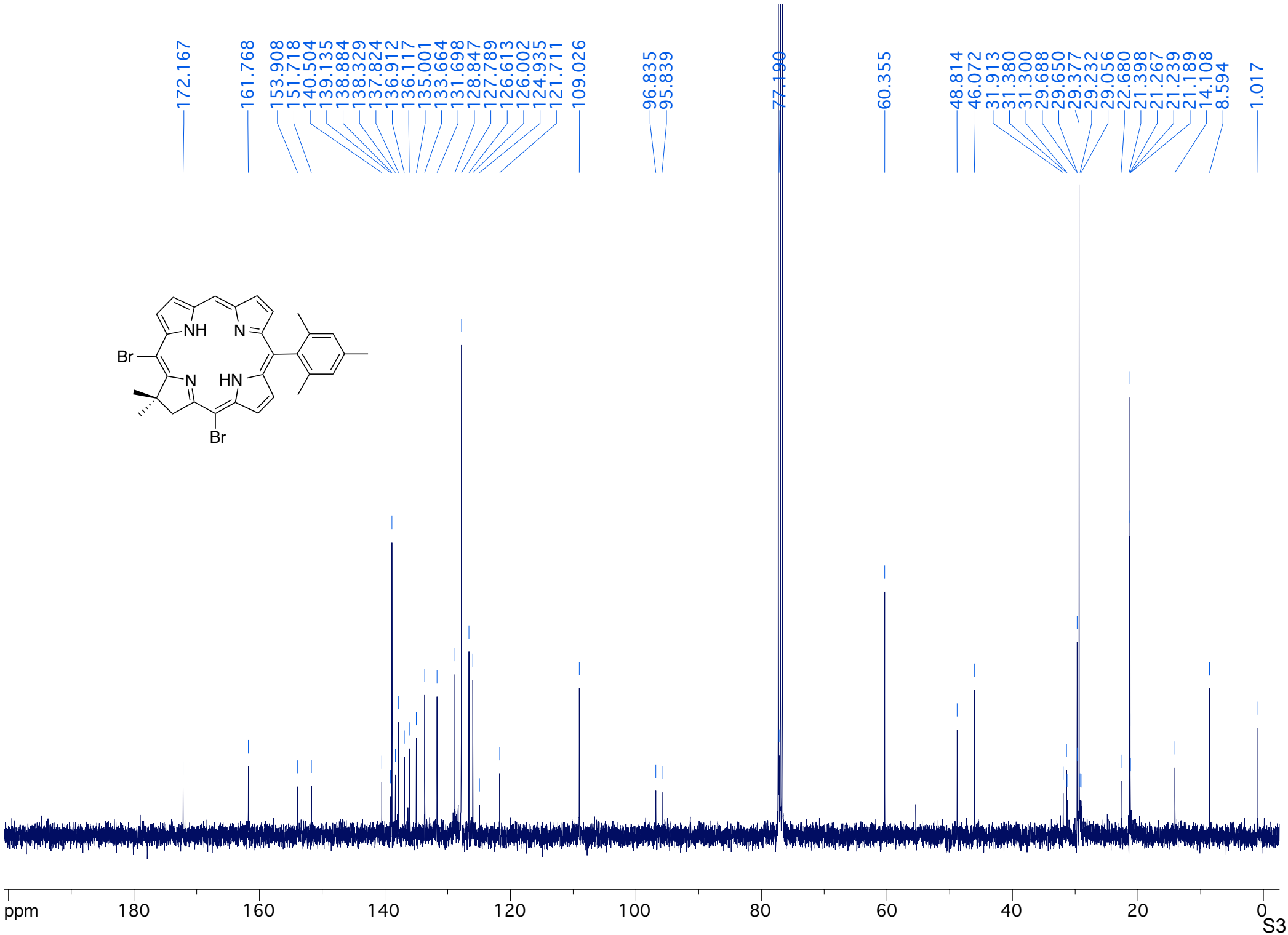
1.14
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3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135.001
133.664
131.698
128.847
127.789
126.613
126.002
124.935
121.711
109.026
96.835
95.839
77.190
60.355
48.814
46.072
31.913
31.380
31.300
29.688
29.650
29.377
29.232
29.056
22.680
21.398
21.267
21.239
21.189
14.108
8.594
1.017
NH
N
Br
N
HN
Br
ppm
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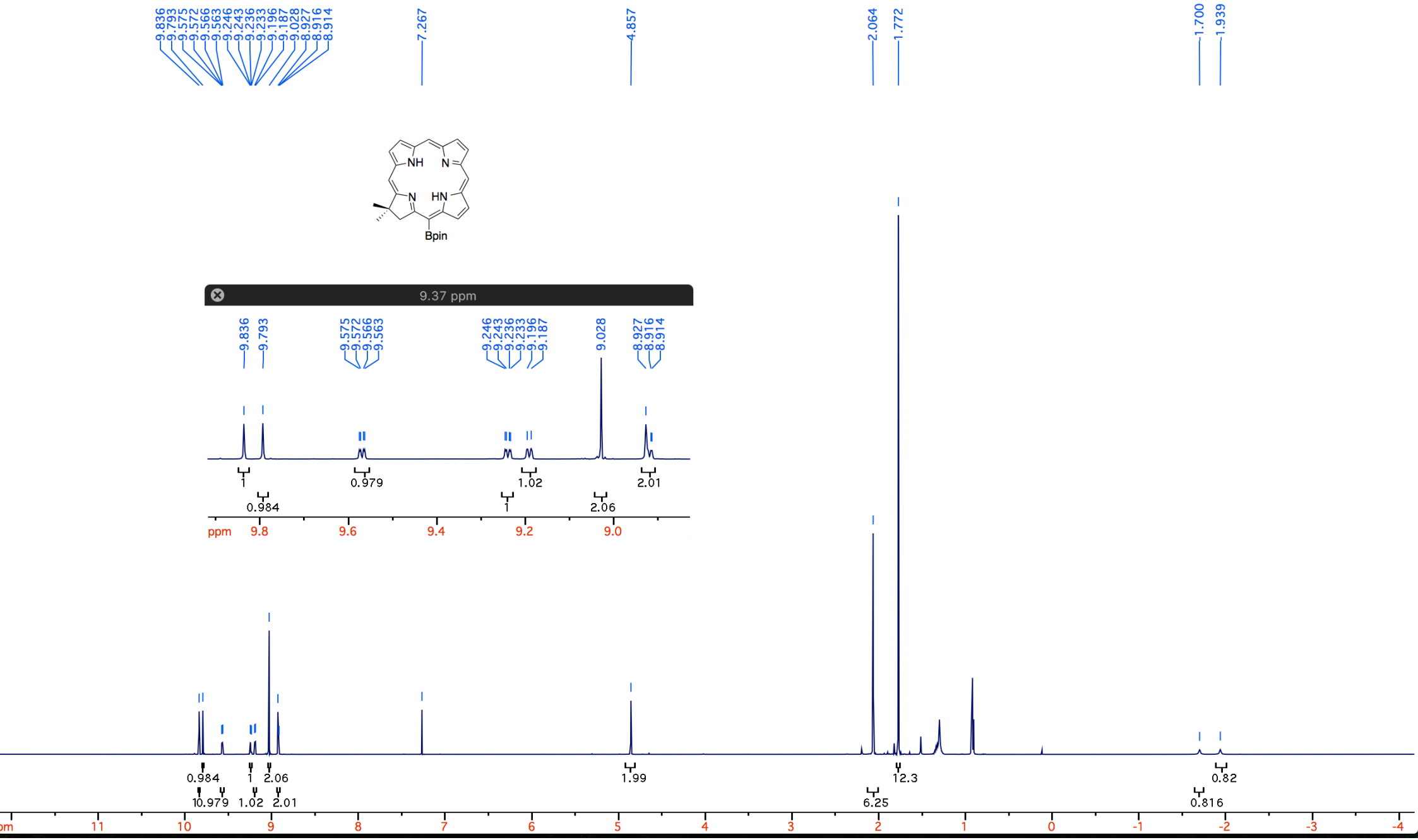
160
140
120
100
80
60
40
20
0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9.563
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9.243
9.236
9.233
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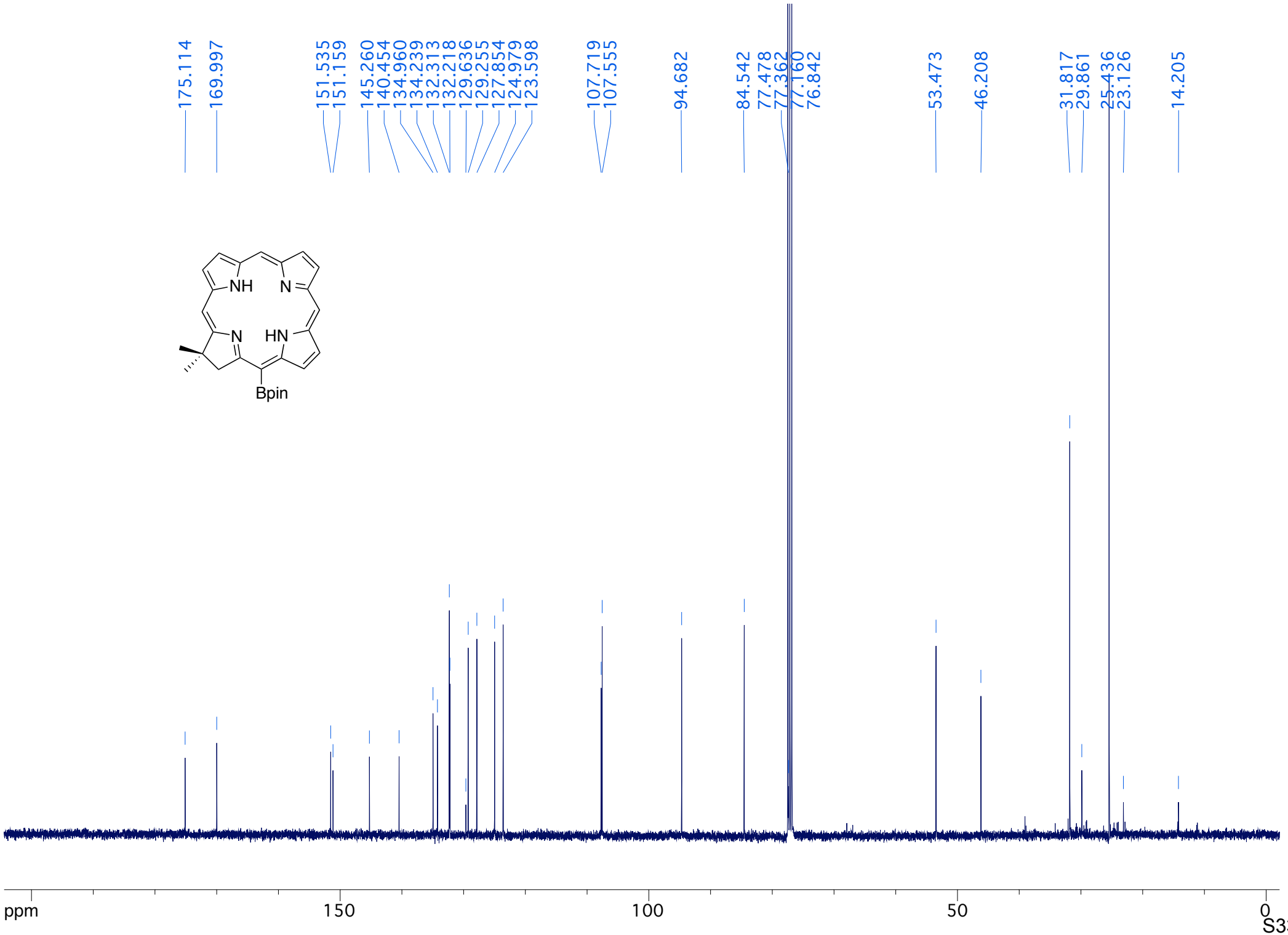
9.187
9.028
8.927
8.916
8.914
7.267
4.857
2.064
1.772
1.700
1.939
NH
N
N
HN
Bpin
9.37 ppm
0.984
0.979
1.02
2.01
1
2.06
ppm
0.984
1
2.06
1.99
12.3
0.82
10.979
1.02
2.01
6.25
0.816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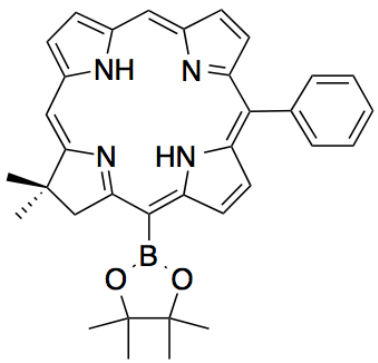
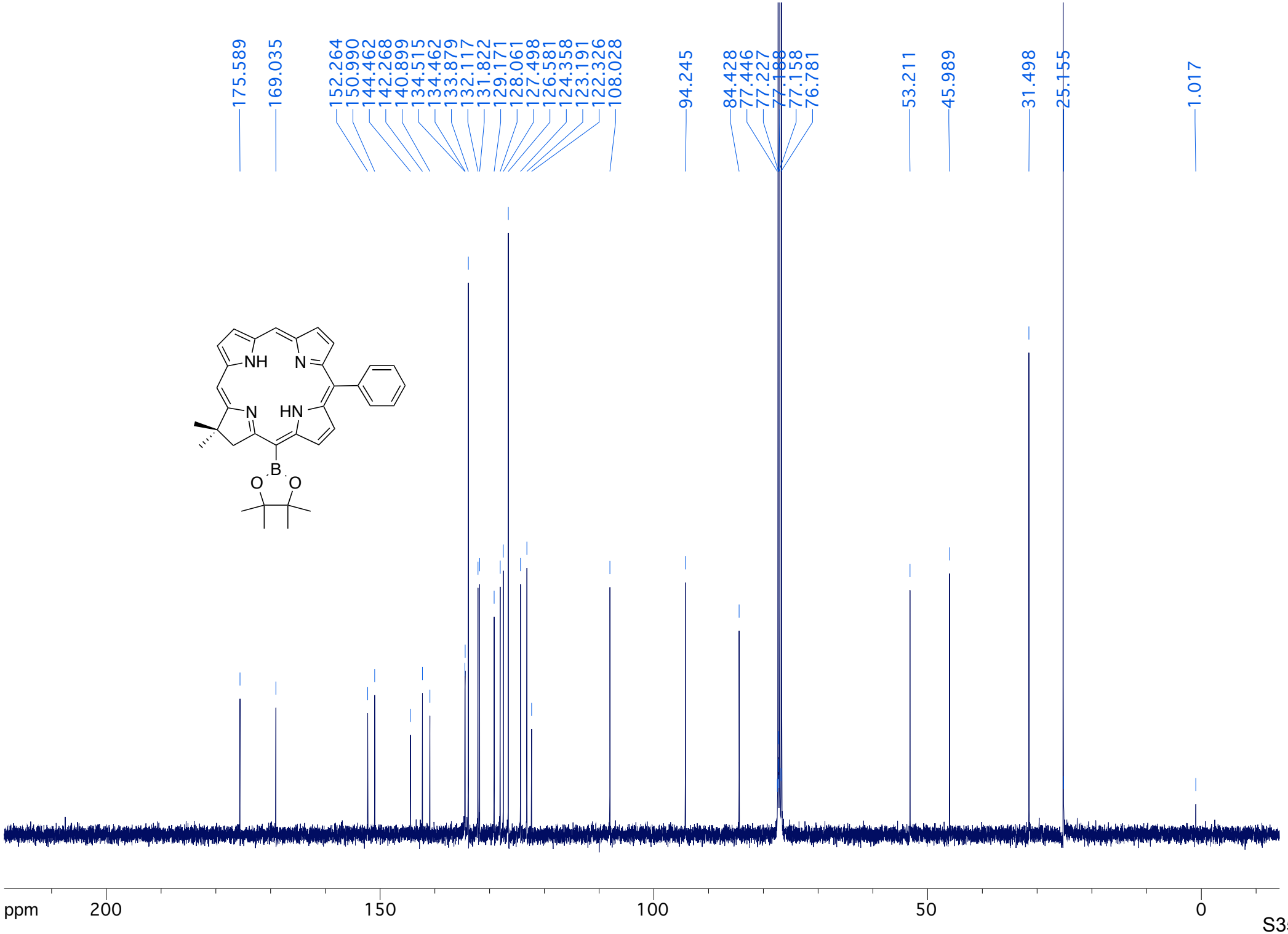
151.535
151.159
145.260
140.454
134.960
134.239
132.313
132.218
129.636
129.255
127.854
124.979
123.598
107.719
107.555
94.682
84.542
77.478
77.362
77.160
76.842
53.473
46.208
31.817
29.861
25.436
23.126
14.205
NH
N
N
HN
Bpin
ppm
150
100
50
0


NH
N
N
HN
B
O
O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134.515
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131.822
129.171
128.061
127.498
126.581
124.358
123.191
122.326
108.028
94.245
84.428
77.446
77.227
77.158
76.781
53.211
45.989
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25.155
1.017
NH
N
N
HN
B
O
O
ppm
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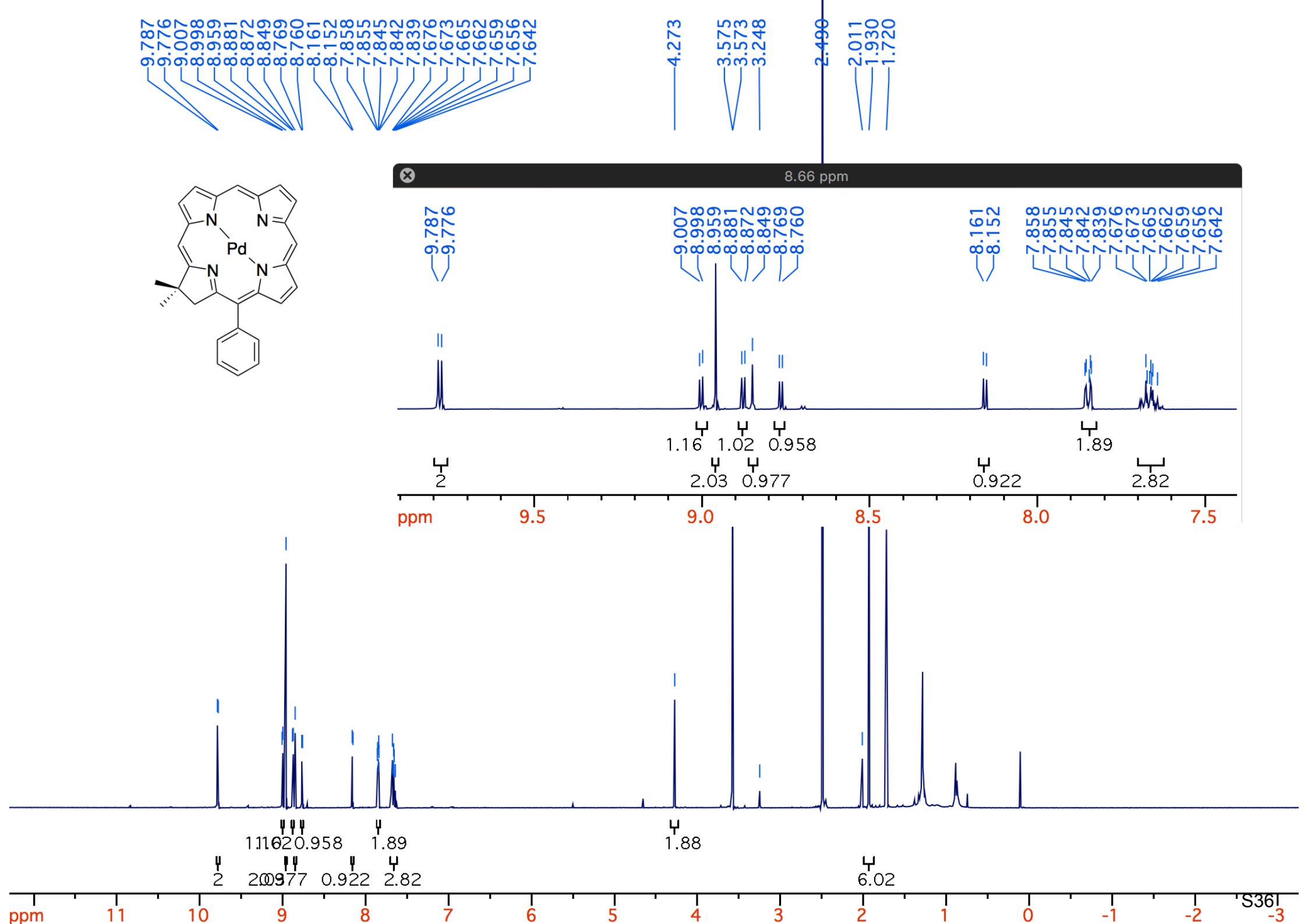
150
100
50
0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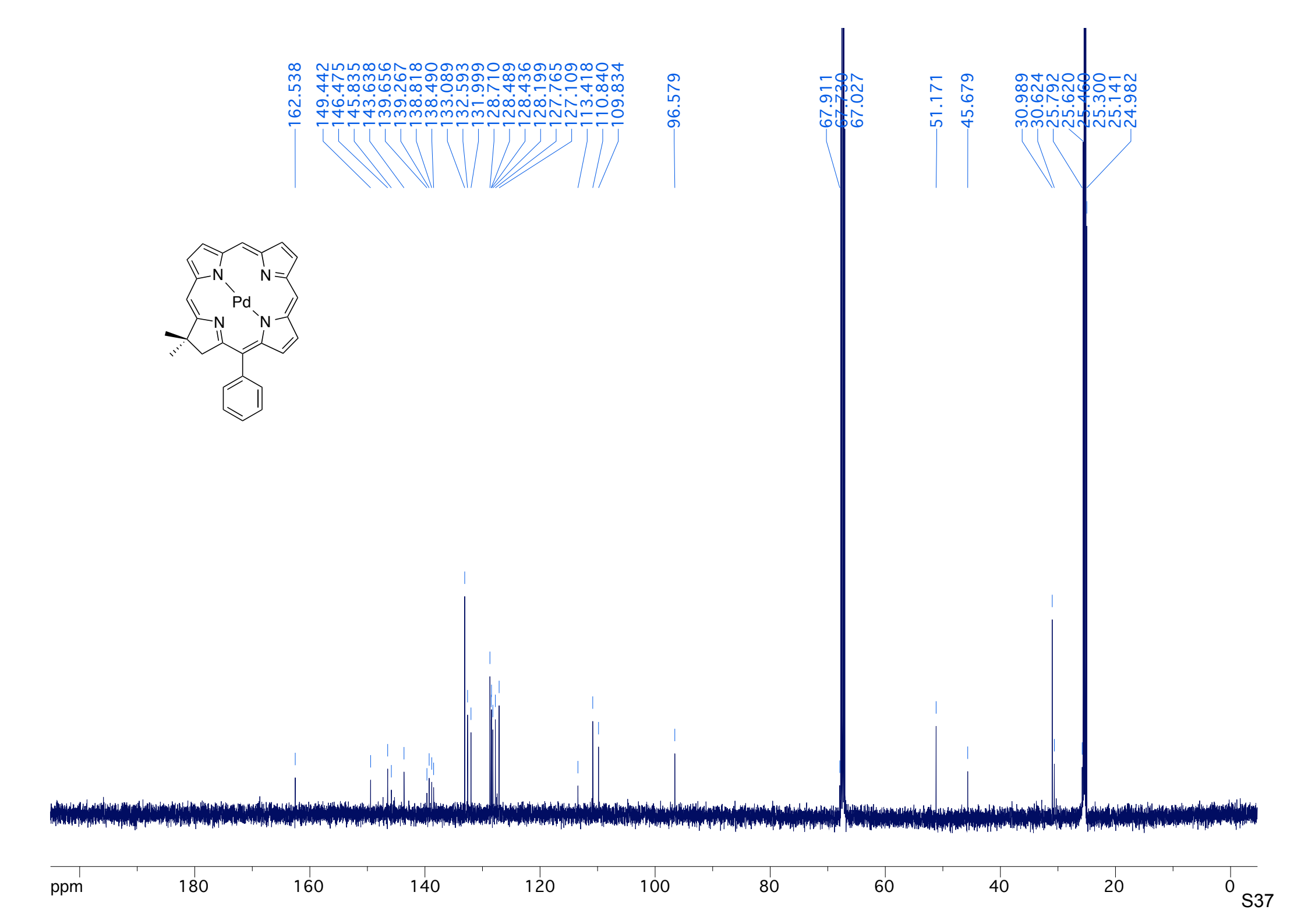
8.881
8.872
8.849
8.769
8.760
8.161
8.152
7.858
7.855
7.845
7.842
7.839
7.676
7.673
7.665
7.662
7.659
7.656
7.642
4.273
3.575
3.573
3.248
2.490
2.011
1.930
1.720
N
N
Pd
N
N
8.66 ppm
1.16
1.02
0.958
1.89
2
2.03
0.977
0.922
2.82
ppm
9.5
9.0
8.5
8.0
7.5
1.88
6.02
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3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146.475
145.835
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138.818
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132.593
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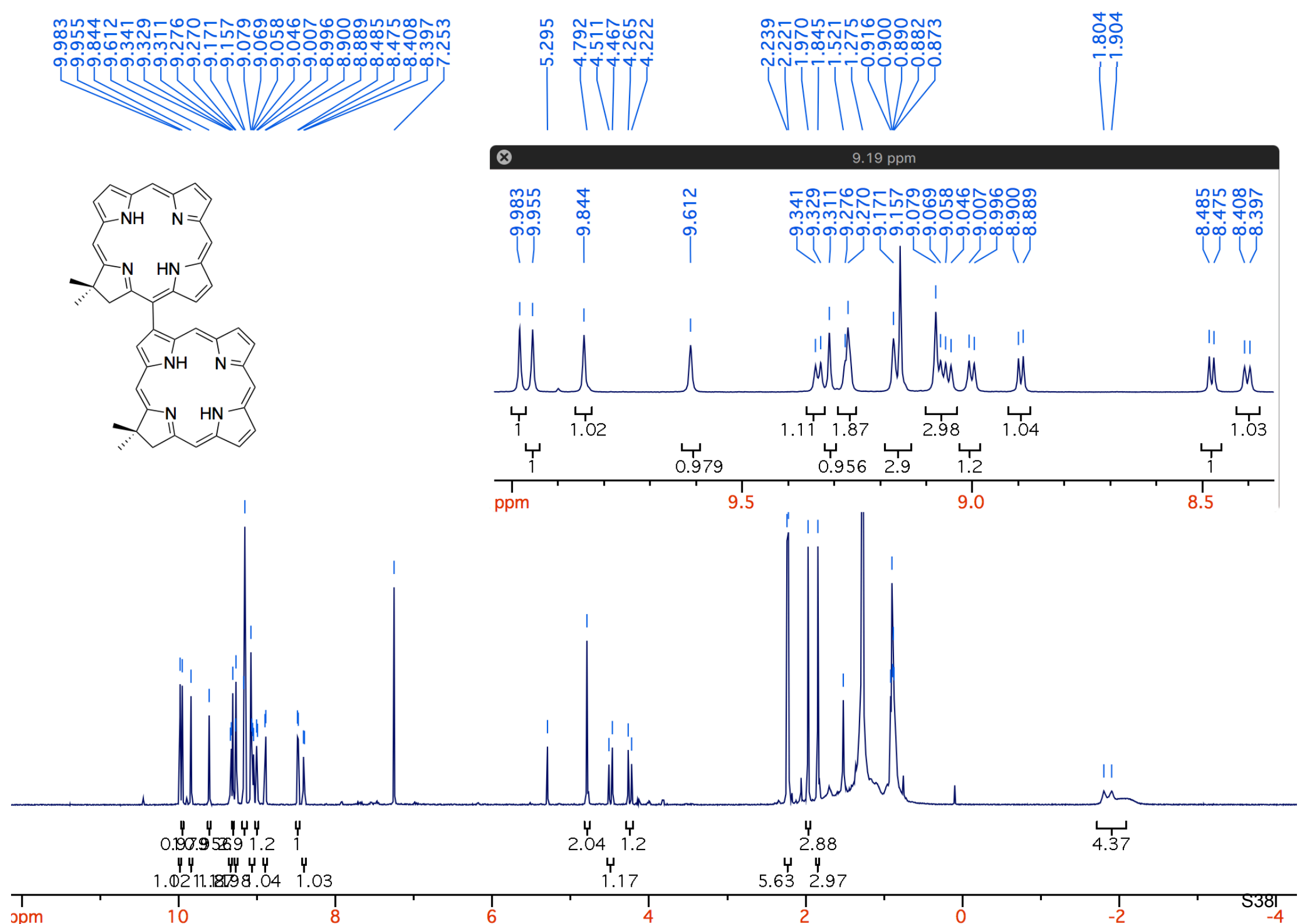
128.710
128.489
128.436
128.199
127.765
127.109
113.418
110.840
109.834
96.579
67.911
67.730
67.027
51.171
45.679
30.989
30.624
25.792
25.620
25.460
25.300
25.141
24.982
N
N
Pd
N
N
ppm
180
160
140
120
100
80
60
40
20
0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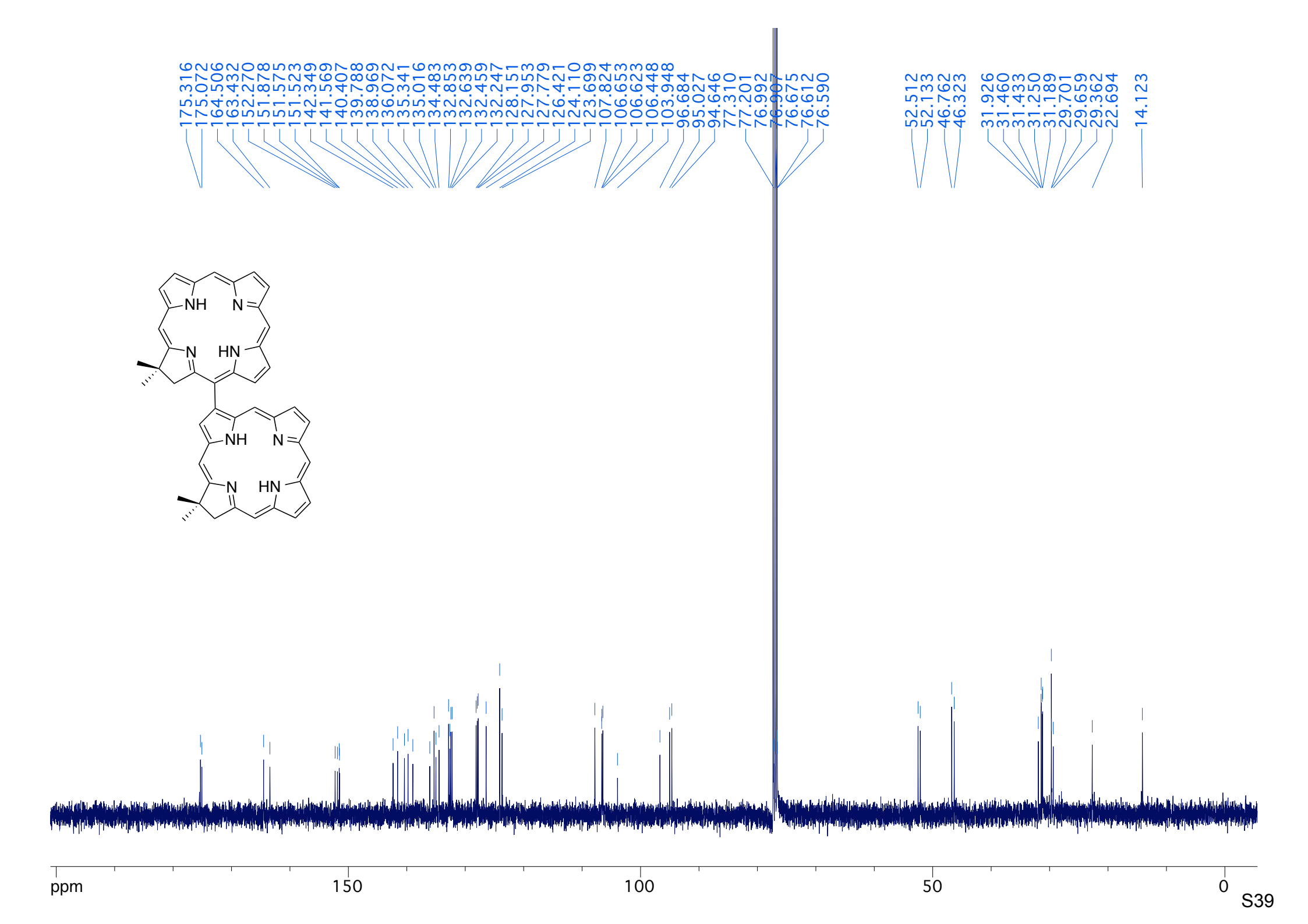
9.311
9.276
9.270
9.171
9.157
9.079
9.069
9.058
9.046
9.007
8.996
8.900
8.889
8.485
8.475
8.408
8.397
7.253
5.295
4.792
4.511
4.467
4.265
4.222
2.239
2.221
1.970
1.845
1.521
1.275
0.916
0.900
0.890
0.882
0.873
1.804
1.904
NH
N
N
HN
NH
N
N
HN
9.19 ppm
1
1.02
1.11
1.87
2.98
1.04
1.03
1
0.979
0.956
2.9
1.2
1
ppm
9.5
9.0
8.5
2.04
1.2
2.88
4.37
1.17
5.63
2.97
1.04
1.03
ppm
10
8
6
4
2
0
-2
-4
S38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164.506
163.432
152.270
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142.349
141.569
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138.969
136.072
135.341
135.016
134.483
132.853
132.639
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132.247
128.151
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127.779
126.421
124.110
123.699
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106.653
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96.684
95.027
94.646
77.310
77.201
76.992
76.907
76.675
76.612
76.590
52.512
52.133
46.762
46.323
31.926
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31.433
31.250
31.189
29.701
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N
N
HN
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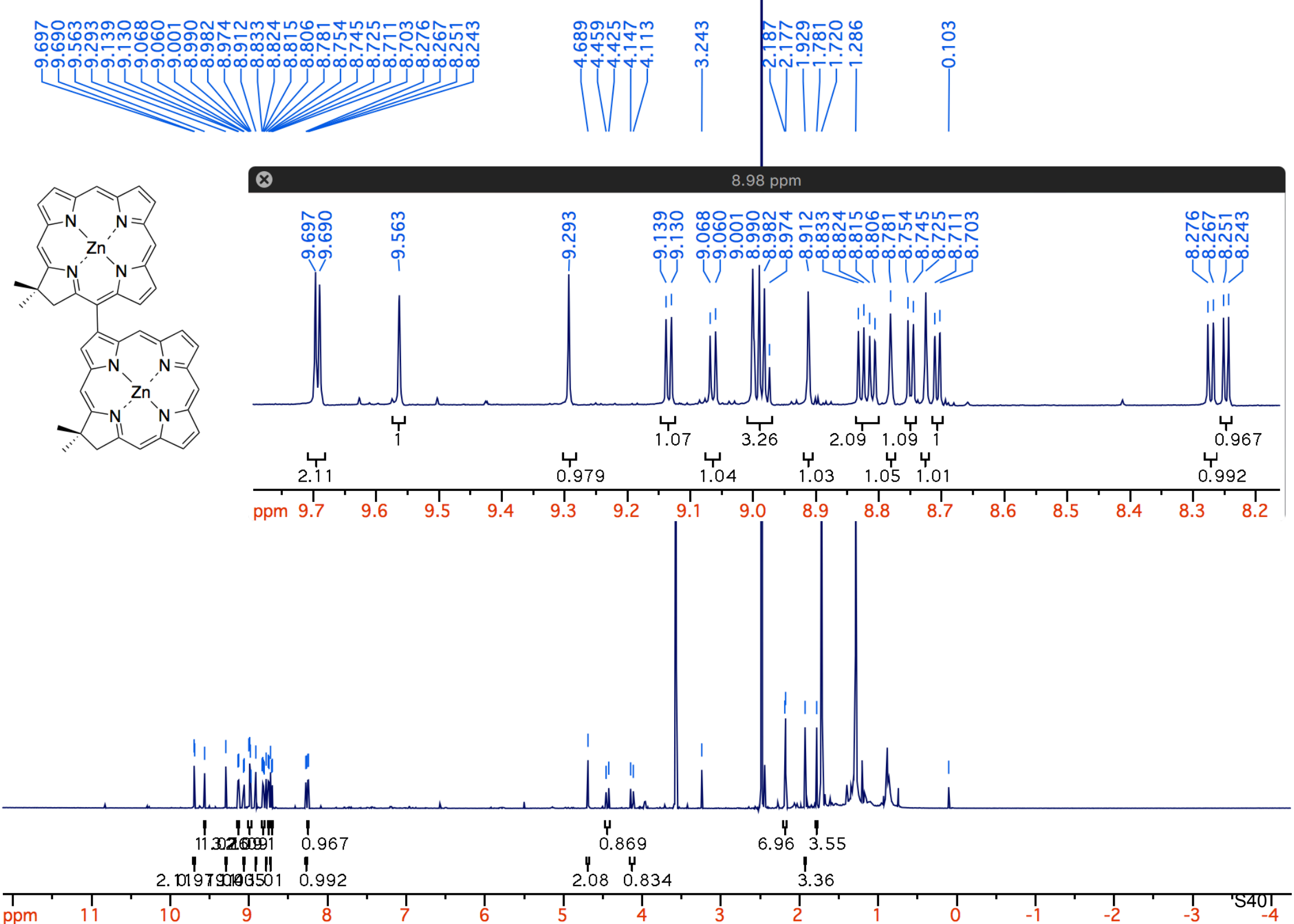
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9.068
9.060
9.001
8.990
8.982
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8.912
8.833
8.824
8.815
8.806
8.781
8.754
8.745
8.725
8.711
8.703
8.276
8.267
8.251
8.243
4.689
4.459
4.425
4.147
4.113
3.243
2.187
2.177
1.929
1.781
1.720
1.286
0.103
N
Zn
8.98 ppm
1
1.07
3.26
2.09
1.09
1
0.967
2.11
0.979
1.04
1.03
1.05
1.01
0.992
ppm
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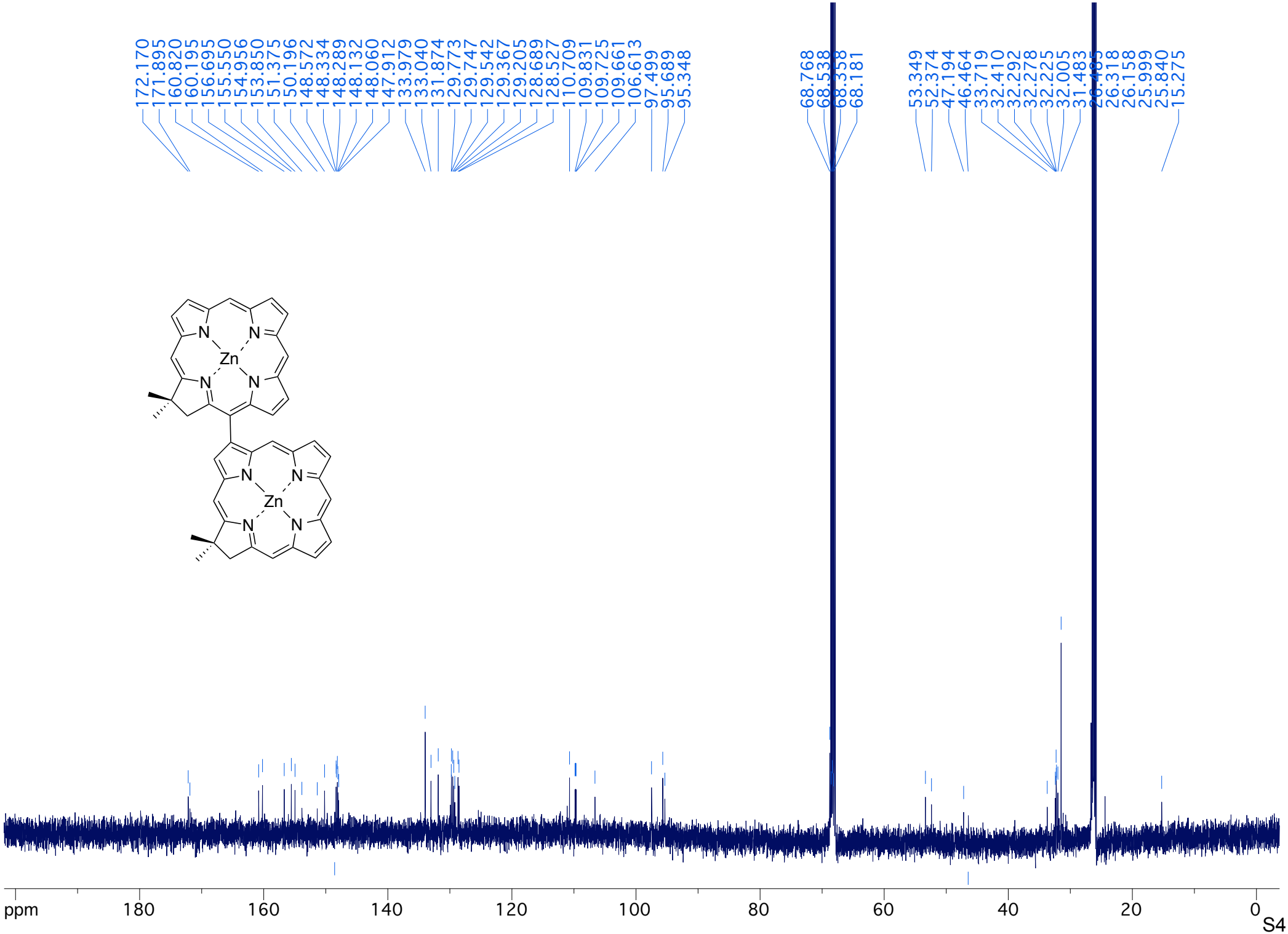
2.08
0.834
3.36
0.992
S401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153.850
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150.196
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148.289
148.132
148.060
147.912
133.979
133.040
131.874
129.747
129.542
129.367
129.205
128.689
128.527
110.709
109.831
109.725
109.661
106.613
97.499
95.689
95.348
68.768
68.538
68.358
68.181
53.349
52.374
47.194
46.464
33.719
32.410
32.292
32.278
32.225
32.005
31.483
26.485
26.318
26.158
25.999
25.840
15.275
N
N
Zn
N
N
N
N
Zn
N
N
ppm
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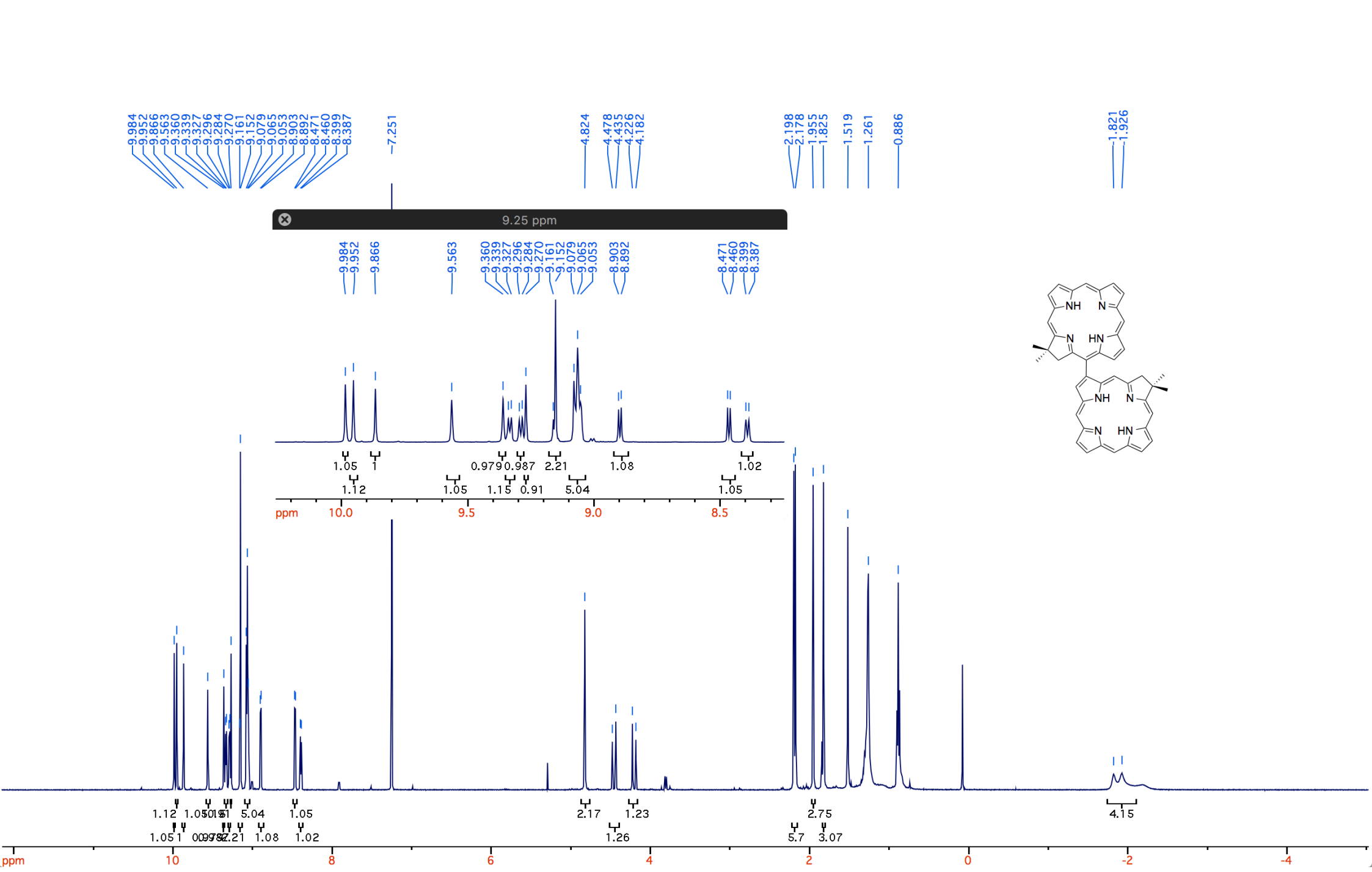
140
120
100
80
60
40
20
0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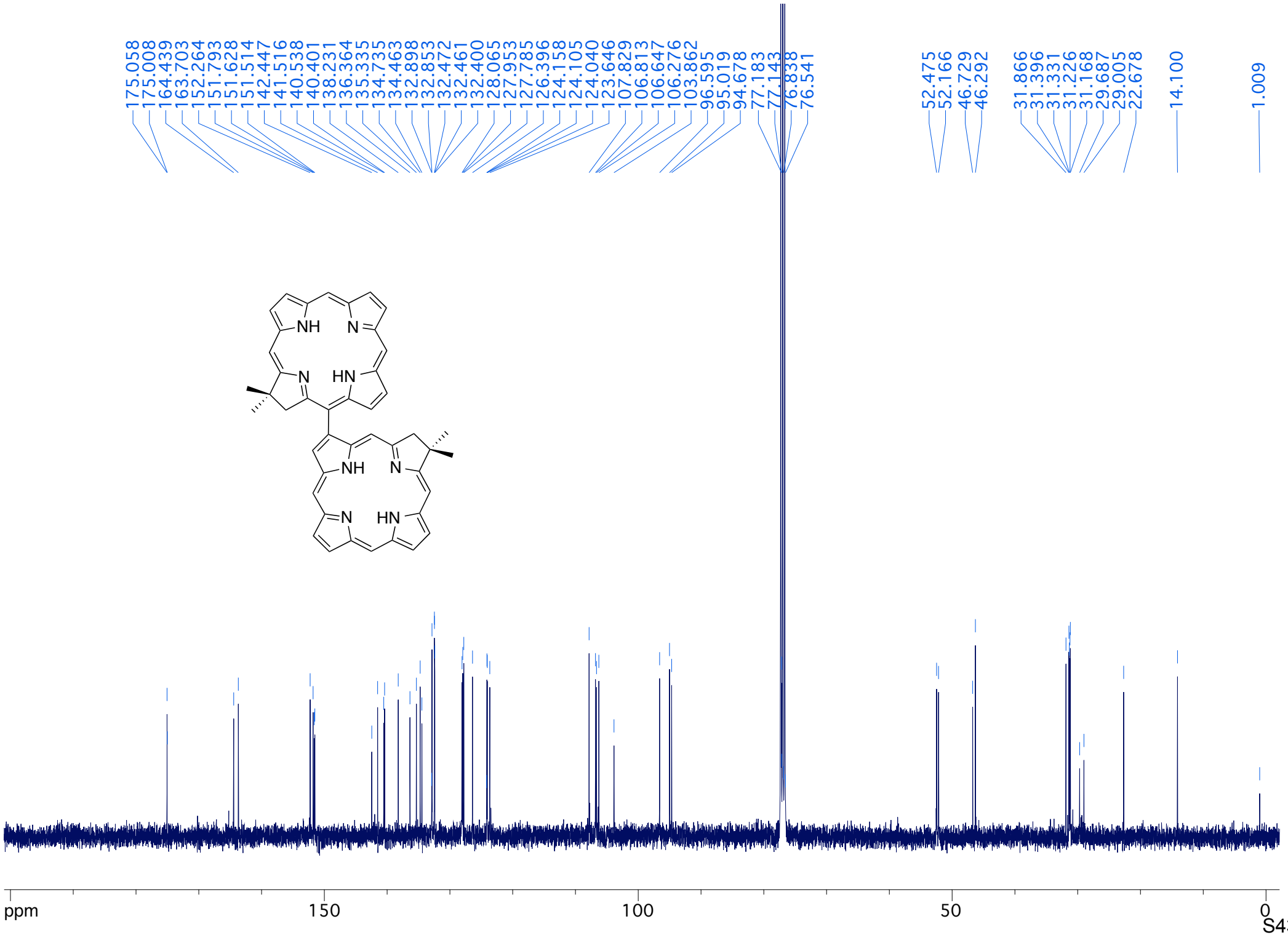
9.152
9.079
9.065
9.053
8.903
8.892
8.471
8.460
8.399
8.387
7.251
4.824
4.478
4.435
4.226
4.182
2.198
2.178
1.955
1.825
1.519
1.261
0.886
1.821
1.926
9.25 ppm
NH
N
N
HN
NH
N
N
HN
1.12 1.05 1 0.979 0.987 2.21 1.08 5.04 1.05 1.02
2.17 1.23 1.26
2.75 5.7 3.07
4.15
ppm
10
8
6
4
2
0
-2
-4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141.516
140.538
140.401
138.231
136.364
135.335
134.735
134.463
132.898
132.853
132.472
132.461
132.400
128.065
127.953
127.785
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124.158
124.105
124.040
123.646
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106.813
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106.276
103.862
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95.019
94.678
77.183
77.143
76.838
76.541
52.475
52.166
46.729
46.292
31.866
31.396
31.331
31.226
31.168
29.687
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22.678
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1.009
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N
HN
NH
N
N
HN
ppm
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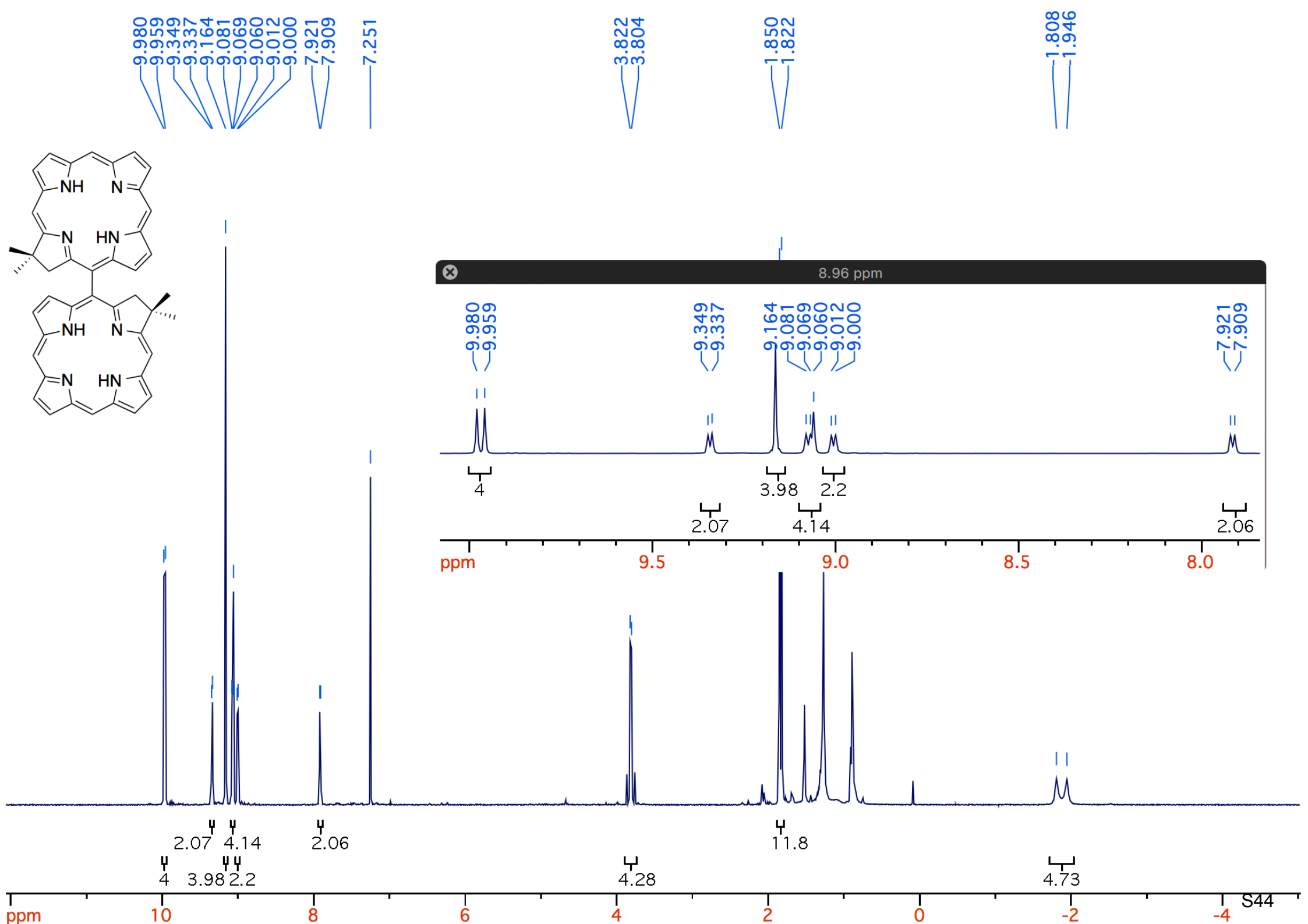
100
50
0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9.337
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9.081
9.069
9.060
9.012
9.000
7.921
7.909
7.251
3.822
3.804
1.850
1.822
1.808
1.946
NH
N
N
HN
NH
N
N
HN
8.96 ppm
9.980
9.959
9.349
9.337
9.164
9.081
9.069
9.060
9.012
9.000
7.921
7.909
4
3.98
2.2
2.07
4.14
2.06
ppm
9.5
9.0
8.5
8.0
2.07
4.14
2.06
11.8
4
3.98
2.2
4.28
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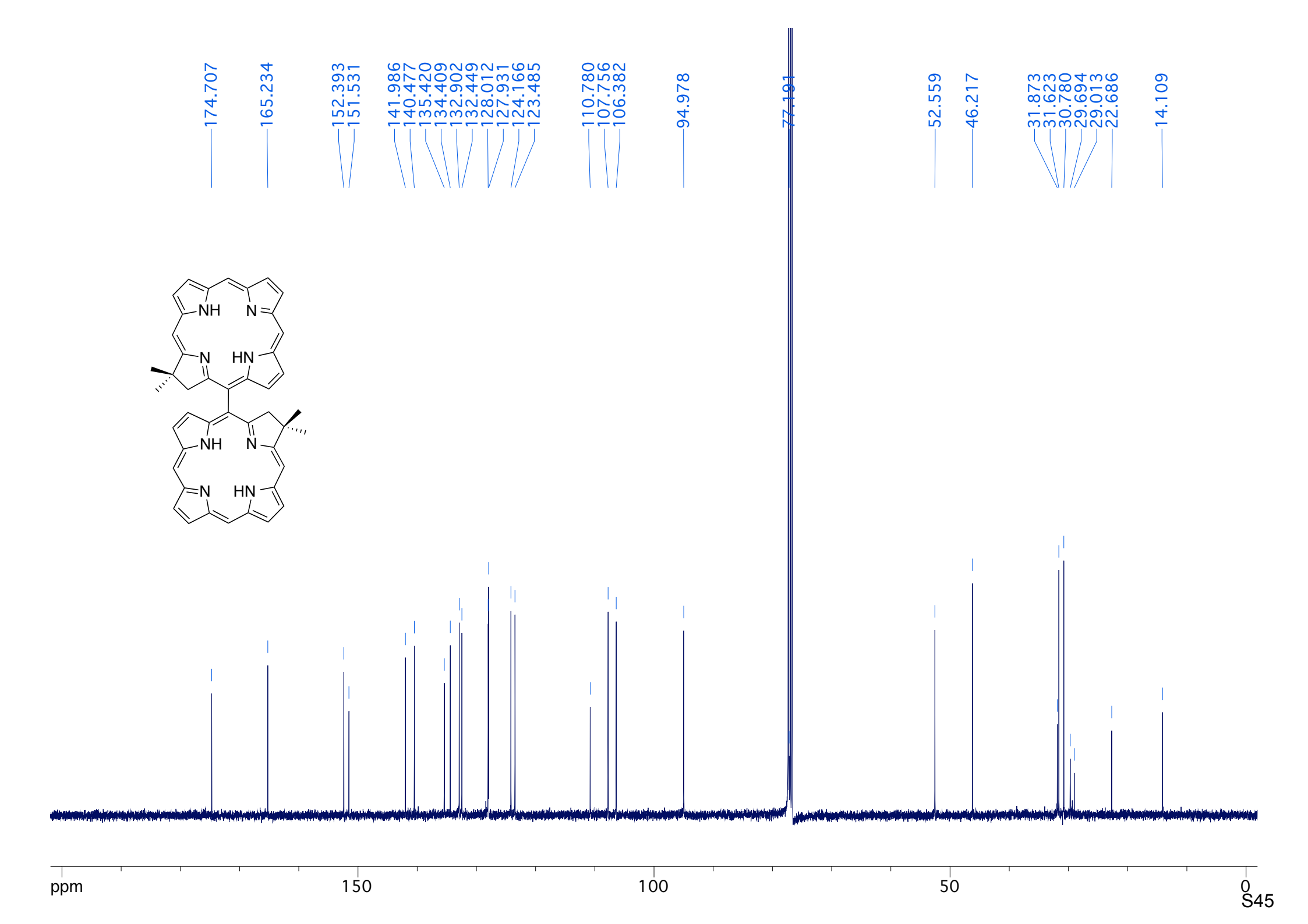
ppm
10
8
6
4
2
0
-2
-4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134.409
132.902
132.449
128.012
127.931
124.166
123.485
110.780
107.756
106.382
94.978
77.191
52.559
46.217
31.873
31.623
30.780
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29.013
22.686
14.109
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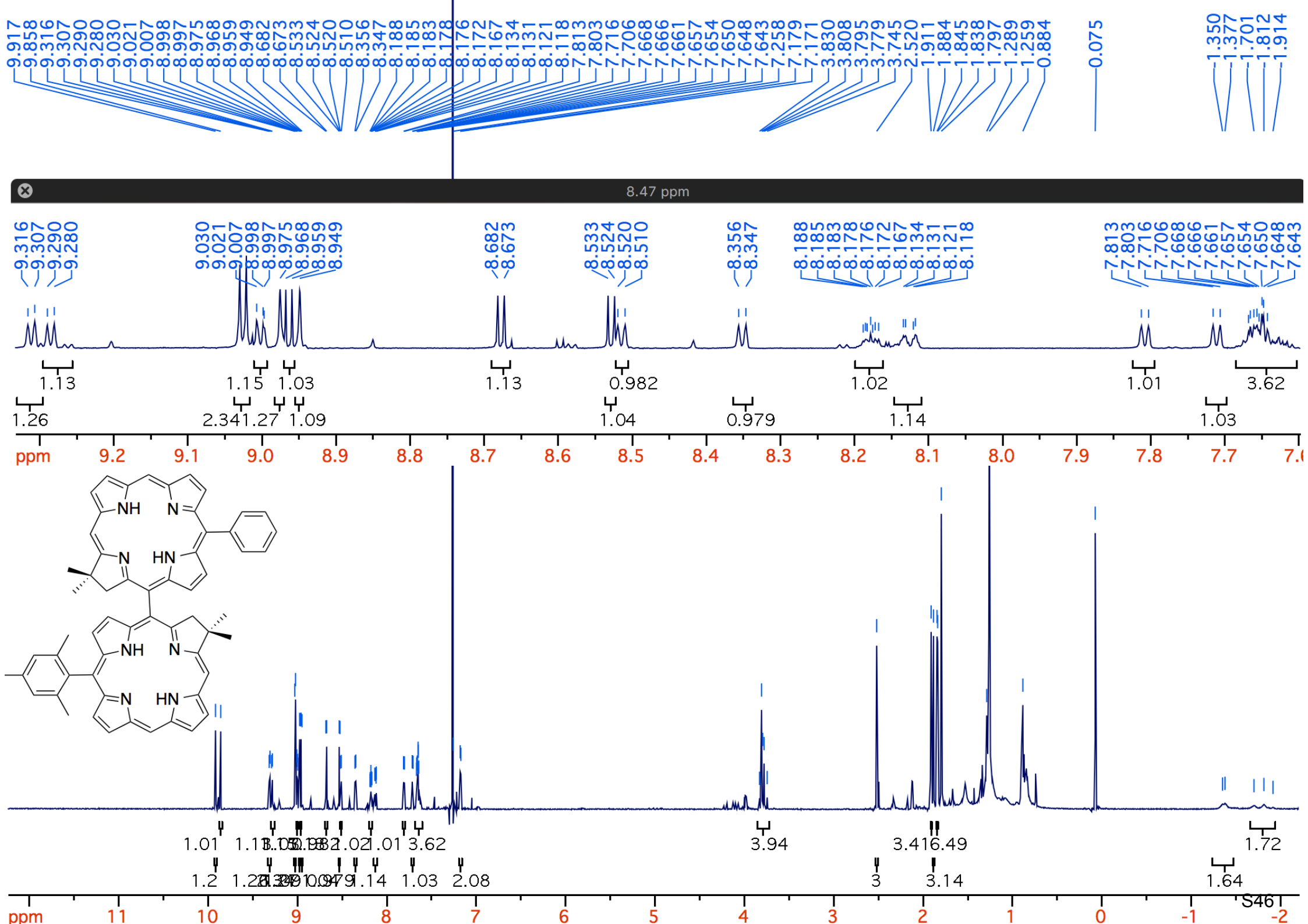
N
N
HN
NH
N
N
HN
ppm
150
100
50
0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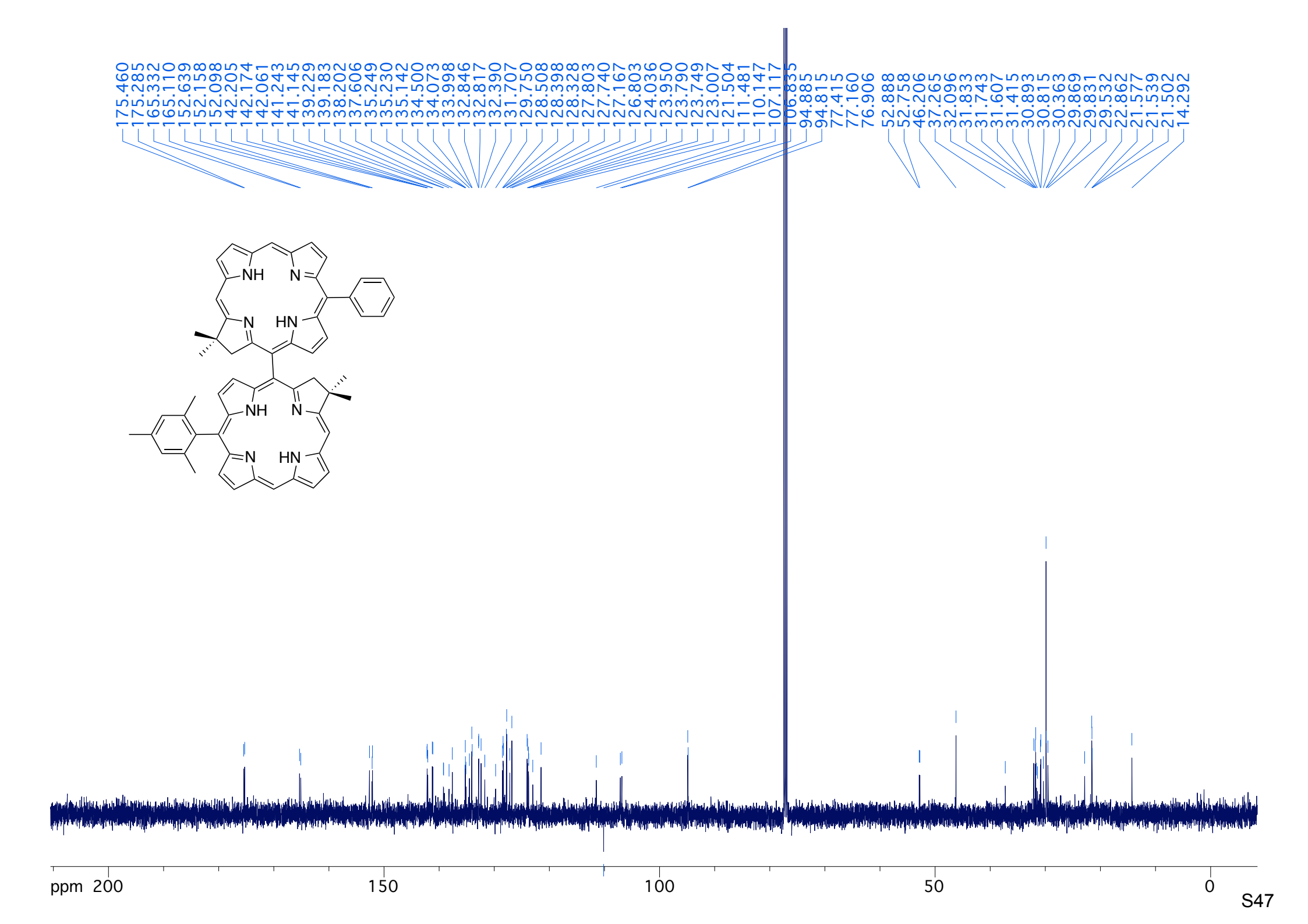
8.47 ppm
1.13 1.15 1.03 1.13 0.982 1.02 1.01 3.62
1.26 2.34 1.27 1.09 1.04 0.979 1.14 1.03
ppm 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7
NH N N HN NH N N HN
1.01 3.62 3.94 3.41 6.49 1.72
1.2 1.14 1.03 2.08 3 3.14 1.64
ppm 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
S46


175.460
175.285
165.332
165.110
152.639
152.158
152.098
142.205
142.174
142.061
141.243
141.145
139.229
139.183
138.202
137.606
135.249
135.230
135.142
134.500
134.073
133.998
132.846
132.817
132.390
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129.750
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128.398
128.328
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124.036
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121.504
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94.885
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46.206
37.265
32.096
31.833
31.743
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30.815
30.363
29.869
29.831
29.532
22.862
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N
HN
NH
N
N
HN
ppm
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50
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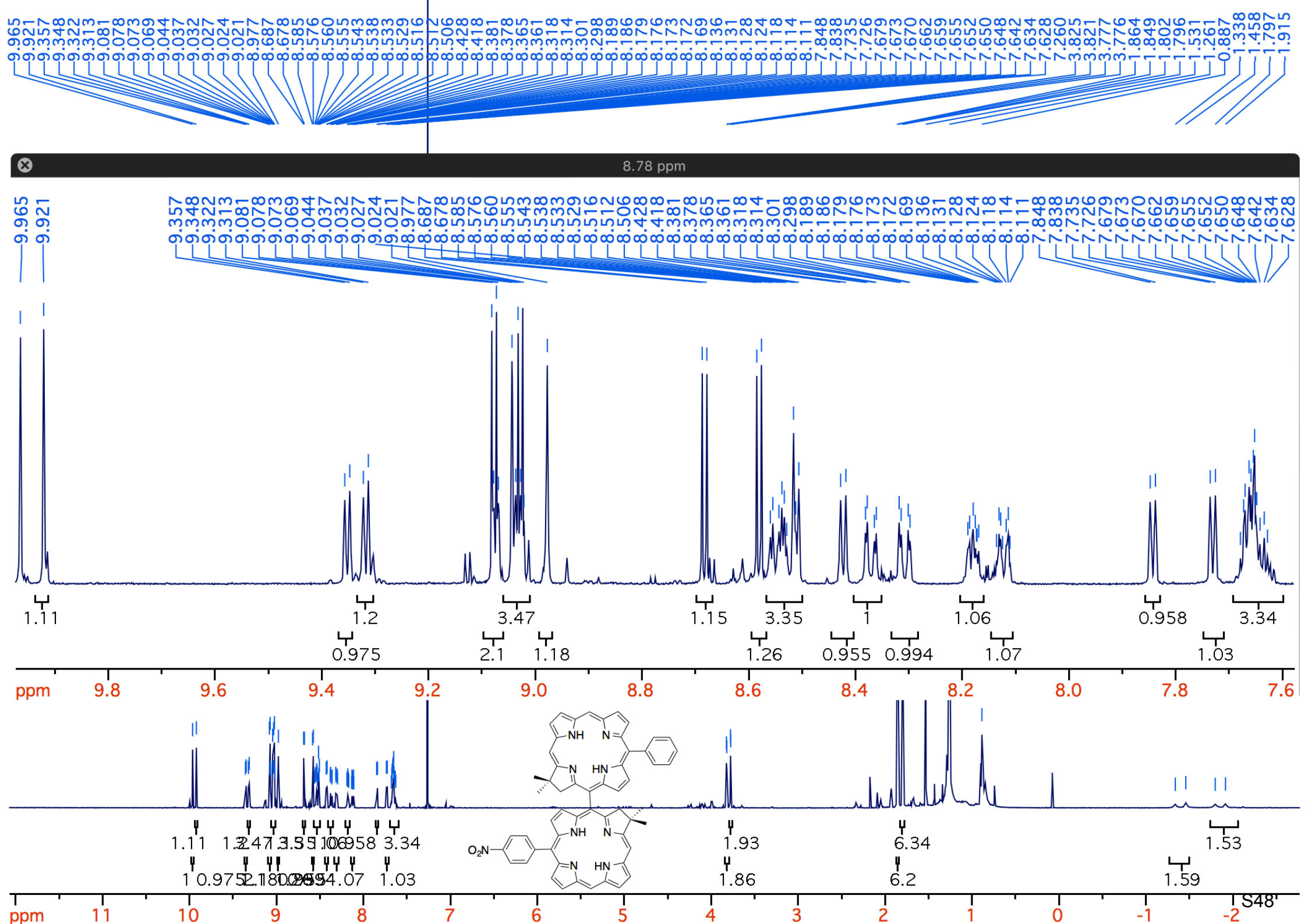
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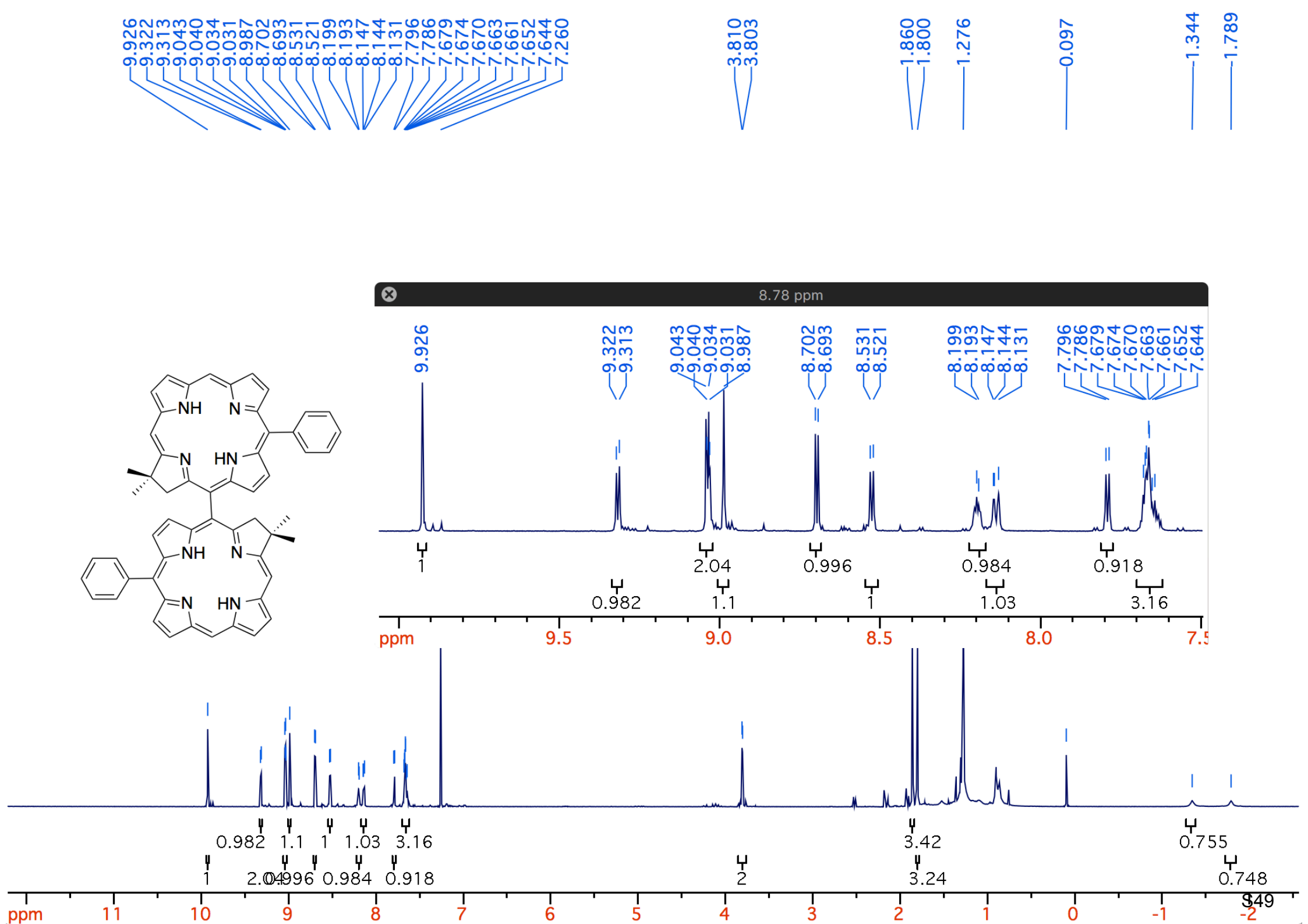
8.78 ppm
1.11 1.2 3.47 1.15 3.35 1 1.06 0.958 3.34
0.975 2.1 1.18 1.26 0.955 0.994 1.07 1.03
ppm 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6
1.11 1.93 6.34 1.53
1 0.975 1.86 6.2 1.59
ppm 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
S48'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8.199
8.193
8.147
8.144
8.131
7.796
7.786
7.679
7.674
7.670
7.663
7.661
7.652
7.644
7.260
3.810
3.803
1.860
1.800
1.276
0.097
1.344
1.789
8.78 ppm
NH
N
N
HN
NH
N
N
HN
1
2.04
0.996
0.984
0.918
0.982
1.1
1
1.03
3.16
ppm
9.5
9.0
8.5
8.0
0.982
1.1
1
1.03
3.16
3.42
0.755
1
2.04
0.996
0.984
0.918
2
3.24
0.748
ppm
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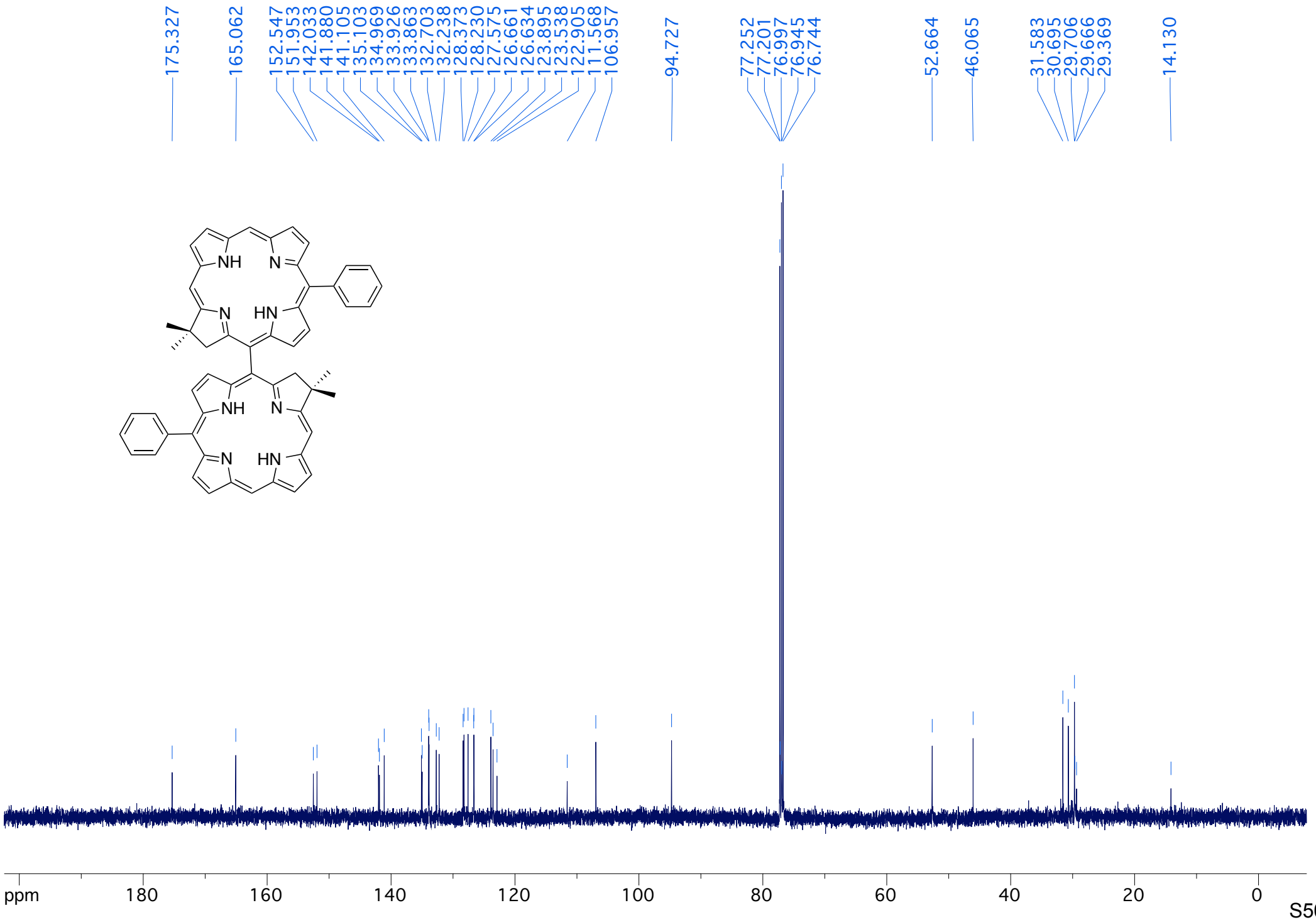
10
9
8
7
6
5
4
3
2
1
0
-1
-2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151.953
142.033
141.880
141.105
135.103
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133.863
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132.238
128.373
128.230
127.575
126.661
126.634
123.895
123.538
122.905
111.568
106.957
94.727
77.252
77.201
76.997
76.945
76.744
52.664
46.065
31.583
30.695
29.706
29.666
29.369
14.130
NH
N
N
HN
NH
N
N
HN
ppm
180
160
140
120
100
80
60
40
20
0