Electronic Supporting Information

From thioether substituted porphyrins to sulfur linked porphyrin dimers: an unusual S_NAr *via* thiolate displacement?

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1. General information

All commercial chemicals used were of analytical grade and were supplied by Sigma Aldrich and used without further purification unless otherwise stated. 2-Ethylheyl-3-mercaptopropionate was purchased from TCI chemicals. Anhydrous toluene was supplied by Acros chemicals. ^{1}H and ^{13}C NMR spectra were recorded on an Agilent 400-MR (400 MHz for ^{1}H NMR; 100.6 MHz for ^{13}C NMR) and/or Bruker AV 600 (600 MHz for ^{1}H NMR; 150.9 MHz for ^{13}C NMR). Chemical shifts are reported in ppm locked on the signal of $CDCl_3$ solvent. The assignment of signals was confirmed by 2D spectra (COSY, HSQC) except for those porphyrins with low solubility. Photophysical measurements were performed in CH_2Cl_2. UV-vis absorption measurements were performed with a Specord 250 spectrophotometer. HRMS spectra were measured on MALDI-Q-Tof Premier Micromass and Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray ionisation source (ESI). Melting points were acquired on a Stuart SMP-10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 (fluorescence indicator F254; Merck) pre-coated aluminium sheets. Flash chromatography was carried out using Fluka Silica Gel 60 (230-400 mesh). Bromoporphyrins **1a/d**[1], **1b**[2], **1c**[3], **1e**[4], **1f**[5], **1g/i**[6] **and 1h**[7]were synthesised by known methodologies and had analytical data consistent with the literature.

2. General procedures

2.1 General procedure A: *Synthesis of thiol surrogates*

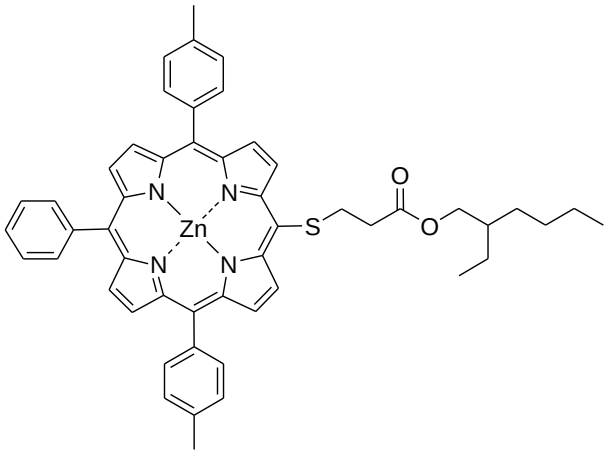
A 100 mL Schlenk tube was charged with Argon to which bromoporphyrin **1a-i** (1 eq.) was added and dried under high vacuum for 30 min. Anhydrous toluene (10-20 mL) and *N*,*N*-diisopropylethylamine (3-5 eq.) were added and the solution was degassed *via* three freeze-pump-thaw cycles. 2-Ethylheyl-3-mercaptopropionate (1.1 eq.), Xantphos (5-8 mol %) and $Pd_2(dba)_3$ (2.5-4 mol %) were added and the flask was heated to 110 °C for 4-24 h, monitoring the reaction *via* TLC analysis. The solution was cooled to room temperature and the solvent was removed *in vacuo*. The crude residue was dissolved in CH_2Cl_2 and purified through a plug of silica. The solvents were removed *in vacuo* and the product was purified by column chromatography (silica, CH_2Cl_2/*n*-hexane).

2.2 General procedure B: *Synthesis of S-linked porphyrin dimers*

A 100 ml Schlenk flask was charged with Argon and the thiol surrogate porphyrin, **2a-g** was added and dissolved in anhydrous toluene (10-15 mL). NaOEt (21 % solution in EtOH, 2 eq.) was added dropwise and the mixture was stirred at ambient temperature for 4-24 h. Upon completion, the reaction mixture was poured onto H_2O. The organic layer was extracted with CH_2Cl_2 and washed with H_2O (3 x 50 mL). The organic extracts were dried over Na_2SO_4, filtered and solvents were removed *in vacuo*. The residue was purified *via* filtration through a plug of silica using CH_2Cl_2/*n*-hexane as eluent and/or *via* column chromatography (silica, CH_2Cl_2/*n*-hexane). The isolated product(s) were recrystallized from CH_2Cl_2/MeOH.

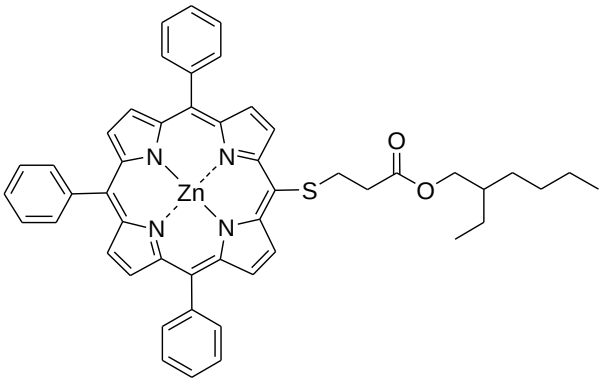
3. Synthesis and Characterisation of Substrates and Products

{5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)-15-phenylporphyrinato}zinc(II) 2a:



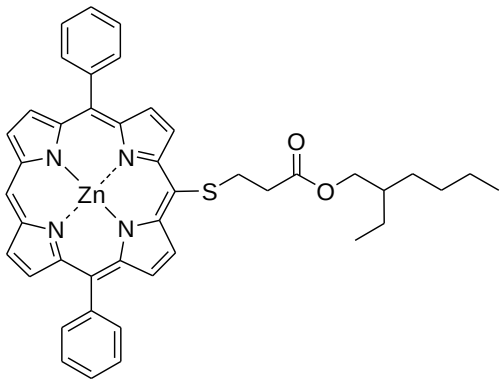
Synthesized *via* general procedure A from bromoporphyrin **1a** (110 mg, 0.155 mmol), $Pd_2(dba)_3$ (4 mg, 0.004 mmol), Xantphos (5 mg, 0.008 mmol), *N*,*N*-diisopropylethylamine (0.465 mmol, 0.08 mL) and 2-ethylhexyl-3-mercaptopropionate (0.04 mL, 0.171 mmol) in anhydrous toluene (10 mL). The reaction was stirred at 120 ºC for 24 h. Following work-up, the product was purified *via* filtration through silica plug using (*n*-hexane:CH_2Cl_2, 3:1 – 2:1 v/v) as eluent. Solvents were removed *in vacuo* and the residue was recrystallized from CH_2Cl_2/MeOH to yield **2a** as purple crystals (112 mg, 0.132 mmol, 85 %); M.p. = 135-137 °C; R_f = 0.59 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.73 (m, 6H, alkyl-CH_3), 1.12-1.30 (m, 8H, alkyl-CH_2), 1.36-1.38 (m,1H, alkyl-C*H*) 2.51 (t, *J* = 7.2 Hz, 2H, SCH_2CH$_2$COO), 2.71 (s, 6H, tolyl-CH_3), 3.68 (t, *J* = 7.2 Hz, 2H, SCH$_2$CH_2COO), 3.80-3.83 (m, 2H, COOCH_2CH), 7.55 (d, *J* = 7.8 Hz, 4H, tolyl-*o*-C*H*), 7.70-7.74 (m, 3H, phenyl-*o*/*p*-C*H*), 8.07 (d, *J* = 7.8 Hz, 4H, tolyl-*m*-C*H*), 8.16-8.18 (m, 2H, phenyl-*m*-C*H*), 8.71 (dd, *J* = 11.4, 4.7 Hz, 4H, H_β), 9.03 (d, *J* = 4.7 Hz, 2H, H_β), 10.04 ppm (d, *J* = 4.7 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 10.8, 13.9, 21.5, 22.8, 23.6, 28.8, 30.2, 34.8, 37.5, 38.5, 67.0, 110.6, 121.6, 122.5, 126.5, 127.3, 127.5, 131.9, 132.2, 133.1, 134.3, 134.4, 137.2, 139.5, 142.6, 149.8, 150.7, 150.8, 154.7, 172.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.65), 533 (4.27), 593 nm (3.64); HRMS (MALDI) *m/z* calcd. for $C_{51}H_{48}N_4O_2SZn$ $[M]^+$: 844.2789, found 844.2787.

{5-(2-Ethylhexyl-3-mercaptopropanoate)-10,15,20-triphenyporphyrinato}zinc(II) 2b:



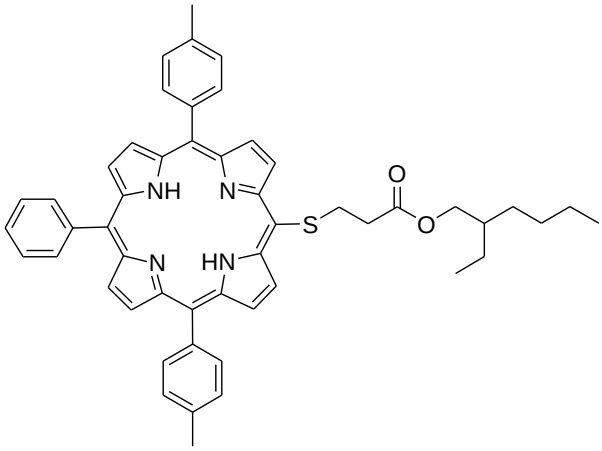
Synthesized *via* general procedure A from bromoporphyrin **1b** (200 mg, 0.294 mmol), $Pd_2(dba)_3$ (8 mg, 0.008 mmol), Xantphos (9 mg, 0.016 mmol), N,N-diisopropylethylamine (0.15 mL, 0.883 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.08 mL, 0.353 mmol) in anhydrous toluene (20 mL). The reaction was stirred at 120 ºC for 24 h. Following work-up, the product was purified by column chromatography (*n*-hexane:CH_2Cl_2, 3:1, v/v) and recrystallized from CH_2Cl_2/MeOH to yield **2b** as purple crystals (183 mg, 0.224 mmol, 76 %); M.p. = 183-185 °C; R_f = 0.54 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$:pyridine-D_5, 50:1, 25 °C): δ = 0.74-0.77 (m, 6H, alkyl-CH_3), 1.13-1.21 (m, 8H, alkyl-CH_2), 1.37-1.41 (m, 1H, alkyl-C*H*), 2.37 (t, *J* = 7.3 Hz, 2H, SCH_2CH$_2$COO), 3.63 (t, *J* = 7.3 Hz, 2H, SCH$_2$CH_2COO), 3.81-3.86 (m, 2H, COOCH_2CH), 7.65-7.75 (m, 9H, phenyl-*o*/*p*-C*H*), 8.13-8.16 (m, 6H, phenyl-*m*-C*H*), 8.77-8.81 (m, 4H, H_β), 8.90 (d, *J* = 4.6 Hz, 2H, H_β), 9.95 ppm (d, *J* = 4.6 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$:pyridine-D_5, 50:1, 25 °C): δ = 10.8, 13.9, 22.8, 23.6, 28.8, 30.2, 34.7, 37.6, 38.5, 66.9, 109.2, 121.0, 122.3, 126.2, 126.3, 127.2, 127.8, 131.4, 131.8, 131.9, 132.7, 134.4, 134.5, 143.2, 149.7, 150.3, 150.5, 154.8, 172.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.70), 552 (4.32), 592 nm (3.65); HRMS (MALDI) *m/z* calcd. for $C_{49}H_{44}N_4O_2SZn$ $[M]^+$: 816.2476, found 816.2468.

{5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-diphenylporphyrinato}zinc(II) 2c:



Synthesized *via* general procedure A from bromoporphyrin **1c** (130 mg, 0.228 mmol), $Pd_2(dba)_3$ (6 mg, 0.007 mmol), Xantphos (7 mg, 0.012 mmol), *N*,*N*-diisopropylethylamine (0.12 mL, 0.693 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.06 mL, 0.277 mmol) in anhydrous toluene (15 mL). The reaction was stirred at 120 ºC for 24 h. Following work-up, the product was purified *via* filtration through silica plug using (*n*-hexane:CH_2Cl_2, 3:1 – 2:1 v/v) as eluent. Solvents were removed *in vacuo* and the residue was recrystallized from CH_2Cl_2/MeOH to yield a purple solid **2c** (130 mg, 0.175 mmol, 76 %); M.p. = 190-191 °C; R_f = 0.43 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.73-0.81 (m, 6H, alkyl-CH_3), 1.12-1.30 (m, 8H, alkyl-CH_2), 1.37-1.40 (m, 1H, alkyl-C*H*) 2.46 (t, *J* = 7.1 Hz, 2H, SCH_2CH$_2$COO), 3.65 (t, *J* = 7.1 Hz, 2H, SCH$_2$CH_2COO), 3.75-3.80 (m, 2H, COOCH_2CH), 7.79-7.84 (m, 6H, phenyl-C*H*), 8.23 (d, *J* = 7.1 Hz, 4H, phenyl-*o*-C*H*), 9.02 (d, *J* = 4.2 Hz, 2H, H_β), 9.03 (d, *J* = 4.2 Hz, 2H, H_β), 9.30 (d, *J* = 4.2 Hz, 2H, H_β), 10.07 (d, *J* = 4.7 Hz, 2H, H_β), 10.13 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 10.8, 13.8, 22.9, 23.5, 28.7, 30.1, 34.8, 37.5, 38.5, 67.0, 107.2, 108.0, 111.3, 120.9, 126.6, 127.6, 131.9, 132.3, 132.4, 132.9. 134.5, 142.4, 149.4, 150.4, 150.6, 154.3, 172.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 416 (5.52), 546 nm (4.20); HRMS (MALDI) *m/z* calcd. for $C_{43}H_{40}N_4O_2SZn$ [M^+]: 740.2163, found 740.2185.

5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)-15-phenylporphyrin 2d: Synthesized



via general procedure A from bromoporphyrin **1d** (200 mg, 0.310 mmol), $Pd_2(dba)_3$ (10 mg, 0.011 mmol), Xantphos (15 mg, 0.026 mmol), *N*,*N*-diisopropylethylamine (0.21 mL, 1.241 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.08 mL, 0.341 mmol) in anhyrdous toluene (20 mL). The reaction was stirred at 120 ºC for 24 h. Following work-up, the product was purified *via* filtration through silica plug using (*n*-hexane:CH_2Cl_2, 3:1 – 2:1 v/v) as eluent. Solvents were removed *in vacuo* and the residue was recrystallized from CH_2Cl_2/MeOH to yield **2d** as purple crystals (169 mg, 0.215 mmol, 70 %);M.p. = 160-161 °C; R_f = 0.68 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = -2.74 (s, 2H, N-*H*) 0.74-0.77 (m, 6H, alkyl-CH_3), 1.11-1.12 (m, 8H, alkyl-CH_2), 1.39-1.40 (m, 1H, alkyl-C*H*), 2.49 (t, *J* = 7.2 Hz, 2H, SCH_2CH$_2$COO), 2.72 (s, 6H, tolyl-CH_3), 3.69 (t, *J* = 7.2 Hz, 2H, SCH$_2$CH_2COO), 3.84-3.87 (m, 2H, COOCH_2CH), 7.56 (d, *J* = 7.7 Hz, 4H, tolyl-*o*-C*H*), 7.71-7.78 (m, 3H, phenyl-*o*/*p*-C*H*), 8.08 (d, *J* = 7.7 Hz, 4H, tolyl-*m*-C*H*), 8.16-8.18 (m, 2H, phenyl-*m*-C*H*), 8.78-8.82 (m, 4H, H_β), 8.95 (d, *J* = 4.7 Hz, 2H, H_β), 9.93 ppm (d, *J* = 4.7 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 10.8, 13.9, 21.5, 22.8, 23.5, 28.8, 30.2, 34.7, 37.4, 38.5, 67.0, 109.5, 120.7, 121.7, 126.7, 127.4, 127.8, 134.4, 134.5, 137.5, 139.0, 141.9, 172.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 421 (5.56), 519 (4.19), 555 (3.89), 595 (3.70), 650 nm (3.54); HRMS (ESI) *m/z* calcd. for $C_{51}H_{51}N_4O_2S$ [M+H]$^+$: 783.3733, found 783.3732.

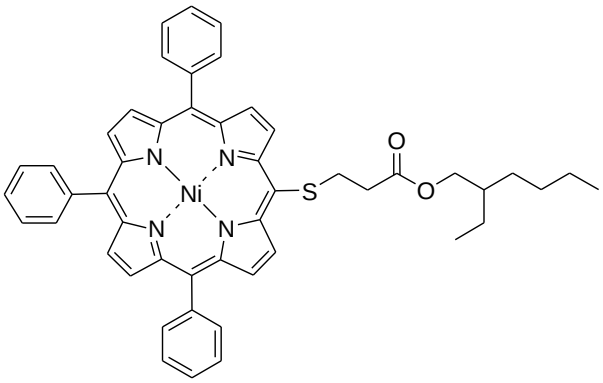
5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)porphyrin 2e. Synthesized *via* general procedure A from bromoporphyrin **1e** (130 mg, 0.228 mmol), $Pd_2(dba)_3$ (6 mg, 0.007 mmol), Xantphos (8 mg, 0.014 mmol), *N*,*N*-diisopropylethylamine (0.12 mL, 0.684 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.06 mL, 0.274 mmol) in anhydrous toluene (15 mL). The reaction was stirred at 120 ºC for 24 h. Following work-up, the product was purified *via* filtration through silica plug using (*n*-hexane:CH_2Cl_2, 3:1 – 2:1 v/v) as eluent. Solvents were removed *in vacuo* and the residue was recrystallized from CH_2Cl_2/MeOH to yield purple crystals **2e** (109 mg, 0.154 mmol, 68 %); M.p. = 175-177 °C; R_f = 0.72 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = -3.03 (s, 2H, N*H*), 0.71-0.79 (m, 6H, alkyl-CH_3), 1.09-1.15 (m, 8H, alkyl-CH_2), 1.35-1.37 (m, 1H, alkyl-C*H*) 2.48 (t, *J* = 7.2 Hz, 2H, SCH_2CH$_2$COO), 2.74 (s, 6H, tolyl-CH_3), 3.34 (t, *J* = 7.4 Hz, 2H, SCH$_2$CH_2COO), 3.84-8.87 (m, 2H, COOCH_2CH), 7.60 (d, *J* = 7.7 Hz, 4H, tolyl-*o*-C*H*), 8.12 (d, *J* = 7.7 Hz, 4H, tolyl-*m*-C*H*), 8.99-9.02 (m, 4H, H_β), 9.30 (d, *J* = 4.6 Hz, 2H, H_β), 10.03 (d, *J* = 4.9 Hz, 2H, H_β), 10.21 ppm (s, 1H, H_{meso}); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.8, 13.9, 21.5, 22.3, 22.8, 23.5, 28.8, 30.2, 34.7, 37.6, 38.5, 67.0, 106.3, 110.2, 120.2, 127.6, 131.4, 132.1, 135.6, 137.5, 138.6, 172.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 417 (5.60), 513 (4.29), 548 (3.76), 588 (3.78), 642 nm (3.33); HRMS (MALDI) *m/z* calcd. for [$C_{45}H_{46}N_4O_2S$](M^+): 706.3341, found 706.3347.

{5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)porphyrinato}nickel(II) 2f: Synthesized *via* general procedure A from bromoporphyrin **1f** (200 mg, 0.319 mmol), $Pd_2(dba)_3$ (14 mg, 0.016 mmol), Xantphos (19 mg, 0.032 mmol), *N*,*N*-diisopropylethylamine (0.17 mL, 0.958 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.15 mL, 0.641 mmol) in anhydrous toluene (20 mL). The product was purified by column chromatography (*n*-hexane:CH_2Cl_2, 2:1, v/v) and recrystallized (CH_2Cl_2/MeOH) to yield purple crystals **2f** (175 mg, 0.230 mmol, 72%); M.p. 138-140 °C; R_f = 0.31 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.69-0.77 (m, 6H, alkyl-CH_3), 1.09-1.15 (m, 9H, alkyl-CH_2/C*H*), 2.22 (t, *J* = 7.2 Hz, 2H, SCH_2CH$_2$COO), 2.66 (s, 6H, tolyl-CH_3), 3.34 (t, *J* = 7.2 Hz, 2H, SCH$_2$CH_2COO), 3.77-3.79 (m, 2H, COOCH_2CH), 7.48 (d, *J* = 7.7 Hz, 4H, tolyl-*o*-C*H*), 7.87 (d, *J* = 7.7 Hz, 4H, tolyl-*m*-C*H*), 8.83-8.86 (m, 4H, H_β), 9.06 (d, *J* = 4.9 Hz, 2H, H_β), 9.74 ppm (s, 1H, H_{meso}), 9.82 ppm (d, *J* = 4.9 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 10.8, 13.9, 21.5, 22.8, 23.5, 28.7, 30.1, 34.7, 35.8, 38.5, 66.9, 105.5, 109.5, 118.9, 127.6, 132.3, 132.4, 132.6, 133.2, 133.6, 137.5, 137.6, 142.4, 143.0, 143.2, 146.5 and 171.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 413 (5.45), 526 (4.30), 556 nm (3.98); HRMS (MALDI) *m/z* calcd. for $C_{45}H_{60}N_4NiO_2S$ $[M]^+$: 762.2546, found 762.2538.

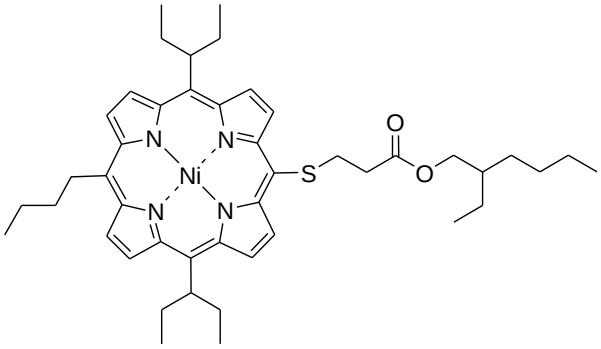
{5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)-15-phenylporphyrinato}nickel(II) 2g: Synthesized *via* general procedure A from bromoporphyrin **1g** (250 mg, 0.355 mmol), $Pd_2(dba)_3$ (16 mg, 0.018 mmol), Xantphos (21 mg, 0.036 mmol), *N*,*N*-diisopropylethylamine (0.18 mL, 1.067 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.16 mL, 0.710 mmol) in anydrous toluene (20 mL). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 3:1, v/v) and recrystallized (CH_2Cl_2/MeOH) to yield purple crystals **2g** (190 mg, 0.226 mmol, 63%); M.p. = 154-156 °C; R_f = 0.50 (CH_2Cl_2 : *n*-

hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.72-0.80 (m, 6H, alkyl-C*H*$_3$), 1.11-1.30 (m, 9H, alkyl-C*H*$_2$/C*H*), 2.21 (t, *J* = 7.2 Hz, 2H, SC*H*$_2$CH$_2$COO), 2.65 (s, 6H, tolyl-C*H*$_3$), 3.32 (t, *J* = 7.2 Hz, 2H, SCH$_2$C*H*$_2$COO), 3.80-3.82 (m, 2H, COOC*H*$_2$CH), 7.47 (d, *J* = 7.7 Hz, 4H, tolyl-*o*-C*H*), 7.64-7.67 (m, 3H, phenyl-*o*/*p*-C*H*), 7.87 (d, *J* = 7.7 Hz, 4H, tolyl-*m*-C*H*), 7.96-7.99 (m, 2H, phenyl-*m*-C*H*), 8.69-8.73 (m, 4H, *H*$_\beta$), 8.83 (d, *J* = 4.9 Hz, 2H, *H*$_\beta$), 9.78 ppm (d, *J* = 4.9 Hz, 2H, *H*$_\beta$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 10.8, 13.9, 21.5, 22.8, 23.5, 28.8, 30.2, 34.7, 35.6, 38.5, 66.9, 108.9, 119.3, 120.0, 126.9, 127.6, 127.7, 127.8, 132.2, 132.4, 132.5, 133.3, 133.5, 133.6, 137.5, 140.6, 142.3, 143.0, 146.7, 171.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 419 (5.39), 535 (4.27), 565 nm (3.88); HRMS (MALDI) *m/z* calcd. for $C_{51}H_{48}N_4NiO_2S$ $[M]^+$: 838.2851, found 838.2833.

{5-(2-Ethylhexyl-3-mercaptopropanoate)-10,15,20-triphenylporphyrinato}nickel(II) 2h: Synthesized *via* general procedure A from bromoporphyrin **1h** (200 mg, 0.296 mmol), $Pd_2(dba)_3$ (14 mg, 0.015 mmol), Xantphos (18 mg, 0.030 mmol), *N*,*N*-diisopropylethylamine (0.16 mL, 0.889 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.14 mL, 0.592 mmol) in anhydrous toluene (20 mL). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 3:1, v/v) and recrystallized (CH_2Cl_2/MeOH) to yield **2h** as purple crystals (165 mg, 0.204 mmol, 68%); M.p. = 166-167 °C; R_f = 0.44 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.69-0.77 (m, 6H, alkyl-C*H*$_3$), 1.11-1.33 (m, 9H, alkyl-C*H*$_2$/C*H*), 2.20 (t, *J* = 7.2 Hz, 2H, SC*H*$_2$CH$_2$COO), 3.30 (t, *J* = 7.2 Hz, 2H, SCH$_2$C*H*$_2$COO), 3.78-3.82 (m, 2H, COOC*H*$_2$CH), 7.64-7.67 (m, 9H, phenyl-*o*/*p*-C*H*), 7.96-7.98 (m, 6H, phenyl-*m*-C*H*), 8.68-8.69 (m, 4H, *H*$_\beta$), 8.79 (d, *J* = 4.9 Hz, 2H, *H*$_\beta$), 9.78 ppm (d, *J* = 4.9 Hz, 2H, *H*$_\beta$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 10.8, 13.9, 22.8, 23.5, 28.7, 30.1, 34.7, 35.6, 38.5, 66.9, 109.1, 119.2, 120.1, 126.8, 126.9, 127.8, 132.2, 132.5, 132.6, 133.3, 133.5, 133.6, 140.4, 140.5, 142.3, 142.8, 146.7, 171.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 418 (5.42), 534 (4.27), 566 nm (3.84); HRMS (MALDI) *m/z* calcd. for $C_{49}H_{44}N_4NiO_2S$ $[M]^+$: 810.2538, found 810.2545.



{5-Butyl-10,20-bis(2-ethylpropyl)-15-(2-ethylhexyl-3-mercaptopropanoate)porphyrinato}nickel(II) 2i: Synthesized *via* general procedure A from bromoporphyrin **1i** (200 mg, 0.321 mmol), $Pd_2(dba)_3$ (14 mg, 0.016 mmol), Xantphos (18 mg, 0.032 mmol), *N*,*N*-diisopropylethylamine (0.17 mL, 0.963 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.14 mL, 0.620 mmol) in anhydrous toluene (20 mL). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 5:1, v/v) and recrystallized (CH_2Cl_2/MeOH) to yield **2i** as purple crystals (159 mg, 0.206 mmol, 65%); M.p. = 137-138 °C; R_f = 0.53 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.73-0.81 (m, 6H, ethylhexyl-C*H*$_3$), 0.90 (t, *J* = 7.4 Hz, 12H, ethylpropyl-C*H*$_3$), 1.01 (t, *J* = 7.8 Hz, 3H, butyl-C*H*$_3$), 1.15-1.20 (m, 9H, ethylhexyl-C*H*$_2$/C*H*), 1.50-1.56 (m, 2H, butyl-CH$_2$C*H*$_2$CH$_3$), 2.13-2.19 (m, 4H, SC*H*$_2$CH$_2$COO/butyl-CH$_2$C*H*$_2$CH$_2$), 2.59-2.67 (m, 8H, ethylpropyl-C*H*$_2$), 3.16 (t, 2H, *J* = 7.2 Hz, SCH$_2$C*H*$_2$COO), 3.82-3.84 (m, 2H, COOC*H*$_2$CH), 4.24-4.27 (m, 2H, ethylpropyl-C*H*), 4.45 (t, *J* = 7.6 Hz, 2H, butyl-C*H*$_2$CH$_2$CH$_2$), 9.21 (d, *J* = 5.1 Hz, 2H, *H*$_\beta$), 9.31 (d, *J* = 5.1 Hz, 4H, *H*$_\beta$), 9.63 ppm (d, *J* = 5.1 Hz, 2H, *H*$_\beta$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 10.8, 13.9, 22.8, 23.3, 23.5, 28.8, 30.2, 33.5, 33.6, 34.7, 34.9, 38.5, 39.1, 49.3, 66.9, 106.8, 119.0, 121.1, 130.0, 130.8, 131.7, 132.5, 139.9, 141.7, 144.5, 171.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.35), 546 (4.20), 583 nm (3.69); HRMS (MALDI) *m/z* calcd. for $C_{45}H_{60}N_4NiO_2S$ $[M]^+$: 778.3790, found 778.3821.



[Bis{10,20-bis(4-methylphenyl)-15-phenyl-porphyrinato-5-yl}zinc(II)]sulfide 3a. Synthesized *via* general procedure B from thiol surrogate **2a** (50 mg, 0.059 mmol) and NaOEt (21% solution, 0.1 mL) in anhydrous toluene (15 mL). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 1:1, v/v) and recrystallized (CH_2Cl_2/*n*-hexane) to yield purple crystals (24 mg, 0.019 mmol, 63 %); M.p. > 300 °C; R_f = 0.57 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$: pyridine-d^5, 30:1, 25 °C): δ = 2.56 (s, 12H, tolyl-C*H*$_3$), 7.33 (d, *J* = 7.8 Hz, 8H, tolyl-*o*-C*H*), 7.63-7.67 (m, 6H, phenyl-*o*/*p*-C*H*), 7.82 (d, *J* = 7.7 Hz, 8H, tolyl-*m*-C*H*), 8.10 (d, *J* = 7.4 Hz, 4H, phenyl-*m*-C*H*), 8.52 (d, *J* = 4.7 Hz, 4H, H_β), 8.65 (d, *J* = 4.7 Hz, 4H, H_β), 8.69 (d, *J* = 4.7 Hz, 4H, H_β), 10.35 ppm (d, *J* = 4.8 Hz, 4H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.3, 107.5, 120.0, 120.8, 121.4, 126.2, 126.8, 127.1, 131.3, 131.4, 132.9, 134.1, 134.3, 136.6, 140.2, 143.3, 149.4, 149.8, 150.4, 153.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 410 (5.44), 419 (5.41), 566 (4.47), 621 nm (4.52); HRMS (MALDI) *m/z* calcd. for $C_{80}H_{54}N_8SZn_2$ $[M]^+$: 1286.2775, found 1286.2770.

[Bis{10,15,20-triphenyl-porphyrinato-5-yl}zinc(II)]sulfide 3b. Synthesized *via* general procedure B from thiol surrogate **2b** (50 mg, 0.061 mmol) and NaOEt (21% solution, 0.15 mL) in anhydrous toluene (15 mL). Following aqueous work-up, the product was purified by filtration through a silica plug using *n*-hexane:CH_2Cl_2, (2:1-1:1, v/v) as eluent and recrystallized from CH_2Cl_2/MeOH to yield purple crystals (21 mg, 0.016 mmol, 56%); M.p. > 300 °C; R_f = 0.46 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$: pyridine-d^5, 50:1, 25 °C): δ = 7.51-7.58 (m, 12H, phenyl-*o*/*p*-C*H*), 7.63-7.67 (m, 6H, phenyl-*o*/*p*-C*H*), 7.94 (d, *J* = 7.3 Hz, m, 8H, phenyl-*m*-C*H*), 8.10 (d, *J* = 7.3 Hz, m, 4H, phenyl-*m*-C*H*), 8.49 (d, *J* = 4.6 Hz, 4H, H_β), 8.62 (d, *J* = 4.2 Hz, 4H, H_β), 8.70 (d, *J* = 4.2 Hz, 4H, H_β), 10.33 ppm (d, *J* = 4.6 Hz, 4H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 106.3, 116.8, 117.1, 120.3, 120.7, 121.6, 126.1, 126.2, 127.0, 127.2, 131.4, 131.6, 131.9, 132.9, 134.2, 134.3, 143.2, 149.3, 149.9, 150.3, 153.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 410 (5.34), 420 (5.34), 564 (4.72), 625 nm (4.74); HRMS (MALDI) *m/z* calcd. for $C_{76}H_{46}N_8SZn_2$ $[M]^+$: 1230.2149, found 1230.2196.

[Bis{10,20-bis(4-methylphenyl)porphyrinato-5-yl}zinc(II)]sulfide 3c: Synthesized *via* general procedure B from thiol surrogate **2c** (40 mg, 0.054 mmol) and NaOEt (21% solution, 0.15 mL) in anhydrous toluene (15 mL). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 2-1-1:1, v/v) and recrystallized (CH_2Cl_2/MeOH) to yield a purple solid **3c** (16 mg, 0.015 mmol, 55 %); M.p. > 300 °C; R_f = 0.56 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$: pyridine-d^5, 50:1, 25 °C): δ = 7.55-7.59 (m, 8H, phenyl-C*H*), 7.61-7.64 (m, 4H, phenyl-C*H*), 7.99 (d, *J* = 7.1 Hz, m, 8H, phenyl-*o*-C*H*), 8.55 (d, *J* = 4.6 Hz, 4H, H_β), 8.82 (d, *J* = 4.4 Hz, 4H, H_β), 9.21 (d, *J* = 4.4 Hz, 4H, H_β), 10.03 (s, 2H, H_{meso}), 10.38 ppm (d, *J* = 4.6 Hz, 4H, H_β); ^{13}C NMR (150 MHz $CDCl_3$: pyridine-d^5, 50:1, 25 °C): δ = 106.4, 120.2, 120.9, 126.1, 127.0, 131.4, 131.9, 132.0, 132.8, 134.1, 134.3, 149.7, 150.3, 153.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 416[br] (5.31), 559 (4.42), 612 nm (4.23); HRMS (MALDI) *m/z* calcd. for $C_{64}H_{38}N_8SZn_2$ $[M]^+$: 1078.1523, found 1078.1522.

[Bis{10,20-bis(4-methylphenyl)porphyrinato-5-yl}nickel(II)]sulfide 3f: Synthesized *via* general procedure B from thiol surrogate **2f** (50 mg, 0.065 mmol) and NaOEt (21% solution, 0.1 mL) in anhydrous toluene (15 mL). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 1:1, v/v) and recrystallized (CH_2Cl_2/*n*-hexane) to yield purple crystals (0.023 mmol, 26 mg, 72 %); M.p. > 300 °C; R_f = 0.52 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.52 (s, 12H, tolyl-C*H*$_3$), 7.27 (d, *J* = 7.6 Hz, 8H, tolyl-*o*-C*H*), 7.57 (d, *J* = 7.7 Hz, 8H, tolyl-*m*-C*H*), 8.47 (d, *J* = 5.0 Hz, 4H, H_β), 8.56 (d, *J* = 4.7 Hz, 4H, H_β), 8.79 (d, *J* = 4.7 Hz, 4H, H_β), 9.43 ppm (s, 2H, H_{meso}), 9.79 ppm (d, *J* = 5.0 Hz, 4H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.3, 104.9, 115.4, 118.6, 127.4, 131.7, 131.9, 132.3, 133.4, 133.5, 137.2, 137.3, 142.1, 142.7, 144.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 405 (4.92), 452[sh] (4.59), 539 (3.66), 587 nm (3.66); HRMS (MALDI) *m/z* calcd. for $C_{68}H_{46}N_8Ni_2S$ $[M]^+$: 1122.2273, found 1122.2277.

[Bis{10,20-bis(4-methylphenyl)-15-phenylporphyrinato-5-yl}nickel(II)]sulfide 3g: Synthesized *via* general procedure B from thiol surrogate **2g** (50 mg, 0.060 mmol) and NaOEt (21% solution, 0.1 mL) in anhydrous toluene (15 mL). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 5:2, v/v) and recrystallized (CH_2Cl_2/*n*-hexane) to yield purple crystals (0.020 mmol, 26 mg, 68 %); M.p. > 300 °C; R_f = 0.27 (CH_2Cl_2 : *n*-hexane = 2:5, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.53 (s, 12H, tolyl-C*H*$_3$), 7.30 (d, *J* = 7.4 Hz, 8H, tolyl-*o*-C*H*), 7.57-7.62 (m, 14H, tolyl-*m*-C*H*/phenyl-*o*/*p*-C*H*), 7.84-7.85 (m, 4*H*, phenyl-*m*-C*H*), 8.48-8.51 (m, 12H, H_β), 9.75 ppm (d, *J* = 4.8 Hz, 4H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.3, 119.0, 119.5, 126.8, 127.4, 127.6, 131.8, 132.0, 132.1, 133.4, 133.5, 133.6, 137.2, 137.3, 140.4, 141.9, 142.0, 142.7 and 145.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 409 (5.44), 457[sh] (5.06), 547 (4.55), 596 nm (4.21); HRMS (MALDI) *m/z* calcd. for $C_{80}H_{54}N_8Ni_2S$ $[M]^+$: 1274.2899, found 1274.2947.

{5,15-Bis(4-methylphenyl)-10-methylthio-20-phenylporphyrinato}zinc(II) 4a: Thiol surrogate **2a** (50 mg, 0.059 mmol) was dissolved in anhydrous toluene (15 mL) together with methyl iodide (0.08 mL, 1.3 mmol) in a 50 mL Schlenk flask under argon. NaOEt (21 % solution, 0.2 mL) was added dropwise and the purple solution turned a green colour, before reverting to purple after 5 min. The solution was left to stir at room temperature for 20 h. The reaction was quenched by adding H_2O (20 mL) and the aqueous layer was extracted three times with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered and solvents were removed *in vacuo*. The residue was filtered through a short plug of silica using CH_2Cl_2 as eluent. Solvents were removed *in vacuo* and the title compound was obtained *via* recrystallisation from CH_2Cl_2/MeOH to yield purple crystals (31 mg, 0.046 mmol, 78 %); M.p. >300 °C; R_f = 0.61 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.73 (s, 6H, tolyl-C*H*$_3$), 3.04 (s, 3H, SC*H*$_3$), 7.57 (d, *J* = 7.8 Hz, 4H, tolyl-*o*-C*H*), 7.72-7.79 (m, 3H, phenyl-*o*/*p*-C*H*), 8.09 (d, *J* = 7.8 Hz, 4H, tolyl-*m*-C*H*), 8.18-8.20 (m, 2H, phenyl-*m*-C*H*), 8.92 (dd, *J* = 11.0, 4.6 Hz, 2H, H_β), 9.04 (d, *J* = 4.6 Hz, 2H, H_β), 10.06 ppm (d, *J* = 4.6 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.5, 26.8, 113.7, 121.5, 122.4, 126.5, 127.3, 127.5, 131.9, 132.0, 132.1, 133.1, 134.3, 134.4, 137.2, 139.6, 142.7, 149.8, 150.6, 150.8, 154.2 ppm; UV/Vis

(CH_2Cl_2): λ_{max} (log ε) = 422 (5.69), 552 (4.32), 593 nm (3.64); HRMS (MALDI) *m/z* calcd. for $C_{41}H_{30}N_4SZn$ $[M]^+$: 674.1483, found 674.1492.

{5-Butyl-10,20-bis(1-ethylpropyl)-15-methylthioporphyrinato}nickel(II) 4f: Thiol surrogate **2i** (100 mg, 0.128 mmol) was dissolved in anhydrous toluene (20 mL) together with methyl iodide (0.08 mL, 1.304 mmol). NaOEt (21 % solution, 0.2 mL) was added dropwise and the solution left to stir at room temperature for one hour. Reaction was quenched by adding H_2O (20 mL) and the aqueous layer was extracted three times with CH_2Cl_2. Title compound was obtained *via* recrystallisation (CH_2Cl_2/MeOH) to yield purple crystals (77 mg, 0.121 mmol, >95%); M.p. 215-216 °C; R_f = 0.63 (CH_2Cl_2 : *n*-hexane = 1:4, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, *J* = 7.4 Hz, 12H, ethylpropyl-C*H*$_3$), 1.00 (t, *J* = 7.4 Hz, 3H, butyl-C*H*$_3$), 1.50-1.56 (m, 2H, butyl-CH_2C*H*$_2$$CH_3$), 2.15-2.23 (m, 2H, butyl-CH_2C*H*$_2$$CH_2$), 2.55-2.69 (m, 8H, ethylpropyl-C*H*$_2$), 2.61 (s, 3H, SC*H*$_3$), 4.22-4.29 (m, 2H, ethylpropyl-C*H*), 4.44 (t, *J* = 8.0 Hz, 2H, butyl-C*H*$_2$$CH_2CH_2$), 9.19 (d, *J* = 5.1 Hz, 2H, *H*$_\beta$), 9.29-9.31 (m, 4H, *H*$_\beta$), 9.63 ppm (d, *J* = 5.1 Hz, 2H, *H*$_\beta$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.9, 23.3, 24.5, 33.4, 33.6, 39.2, 49.3, 109.8, 118.8, 120.9, 129.9, 130.7, 131.7, 132.1, 139.9, 141.7, 143.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.29), 546 (4.14), 585 nm (3.60); HRMS (MALDI) *m/z* calcd. for $C_{35}H_{42}N_4NiS$ $[M]^+$: 608.2484, found 608.2509.

{5-Hexylthio-10,20-bis(4-methylphenyl)-15-phenylporphyrinato}nickel(II) 4g: Thiol surrogate **2g** (50 mg, 0.060 mmol) was dissolved in anhydrous toluene (20 mL) together with 1-bromohexane (0.1 mL, 0.603 mmol). NaOEt (21 % solution, 0.2 mL) was added dropwise and the solution left to stir at room temperature for one hour. Reaction was quenched by adding H_2O (20 mL) and the aqueous layer was extracted three times with CH_2Cl_2. Title compound was obtained *via* recrystallisation (CH_2Cl_2/MeOH) to yield purple crystals (43 mg, 0.058 mmol, >95%); M.p. 241-243 °C; R_f = 0.54 (CH_2Cl_2 : *n*-hexane = 1:4, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.72 (t, *J* = 7.2 Hz, 3H, hexyl-C*H*$_3$), 1.02-1.04 (m, 2H, CH_2C*H*$_2$$CH_3$), 1.08-1.12 (m, 2H, C*H*$_2$$CH_2CH_3$), 1.26-1.32 (m, 4H, hexyl-C*H*$_2$), 2.64 (s, 6H, tolyl-C*H*$_3$), 3.07 (t, *J* = 7.0 Hz, 2H, SC*H*$_2$$CH_2$), 7.48 (d, *J* = 7.4 Hz, 4H, tolyl-*o*-C*H*), 7.64-7.67 (m, 3H, phenyl-*o*/*p*-C*H*), 7.87 (d, *J* = 7.7 Hz, 4H, tolyl-*m*-C*H*), 7.96-7.98 (m, 2H, phenyl-*m*-C*H*), 8.67-8.71 (m, 4H, *H*$_\beta$), 8.82 (d, *J* = 5.0 Hz, 2H, *H*$_\beta$), 9.80 ppm (d, *J* = 5.0 Hz, 2H, *H*$_\beta$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.9, 21.5, 22.4, 28.2, 29.8, 31.2, 41.5, 119.1, 126.9, 127.3, 127.6, 127.7, 127.9, 131.6, 132.1, 132.3, 132.6, 133.0, 133.2, 133.6, 137.5, 137.6, 140.7, 142.2, 142.8, 142.9 and 146.7 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 420 (5.23), 536 (4.15), 569 nm (3.77); HRMS (Maldi) *m/z* calcd. for $C_{46}H_{40}N_4NiS$ $[M]^+$: 738.2327, found 738.2364.

5-(4-bromothiophenyl)-10,20-bis(4-methylphenyl)-15-phenylporphyrin 5c: 4-Bromothiophenol (80 mg, 0.423 mmol) and K_2CO_3 (200 mg, 1.450 mmol) were dissolved in anhydrous DMF (12 mL) in a 3-necked round bottomed flask. The solution was purged with argon and was heated to 100 ºC for 2 h. Thiol surrogate **2d** (100 mg, 0.128 mmol) was added and the reaction was allowed to stir at 110 ºC for 2h, monitoring the reaction *via* TLC analysis (CH_2Cl_2/*n*-hexane 1:1, v/v). Upon completion, the reaction was allowed to cool to room temperature and was washed with H_2O (30 mL x 3) and extraction with CH_2Cl_2. Solvents were removed *in vacuo* and the residue was purified *via* column chromatography (CH_2Cl_2/*n*-hexane 1:2, v/v) to yield 2 main fractions, the first was **5c** with fraction two containing dimer **3d** (<40 %). Solvents were removed and the title compound was obtained *via* recrystallisation (CH_2Cl_2/MeOH) to yield purple

crystals (45 mg, 0.060 mmol, 47 %); M.p. >300 °C; R_f = 0.57 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = -2.61 (s, 2H, N*H*), 2.70 (s, 6H, tolyl-CH_3), 6.84 (d, *J* = 8.6 Hz, 2H, C_6H_4Br-*o*-*H*), 7.10 (d, *J* = 8.6 Hz, 2H, C_6H_4Br-*m*-*H*), 7.55 (d, *J* = 7.6 Hz, 4H, tolyl-*o*-C*H*), 7.74-7.79 (m, 3H, phenyl-C*H*), 8.06 (d, *J* = 7.6 Hz, 4H, tolyl-*m*-C*H*), 8.18 (d, *J* = 7.5 Hz, 2H, phenyl-C*H*), 8.80-8.82 (m, 4H, H_β), 8.90 (d, *J* = 4.7 Hz, 2H, H_β), 9.79 ppm (d, *J* = 4.7 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.5, 105.1, 118.4, 121.9, 122.5, 126.7, 127.5, 127.9, 131.7, 134.4, 134.5, 137.6, 138.7, 141.8, 142.7 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.57), 521 (4.29), 557 (4.00), 594 (3.81), 649 nm (3.65); HRMS (MALDI) *m/z* calcd. for $C_{46}H_{33}N_4SBr$ $[M]^+$: 752.1609, found 752.1591.

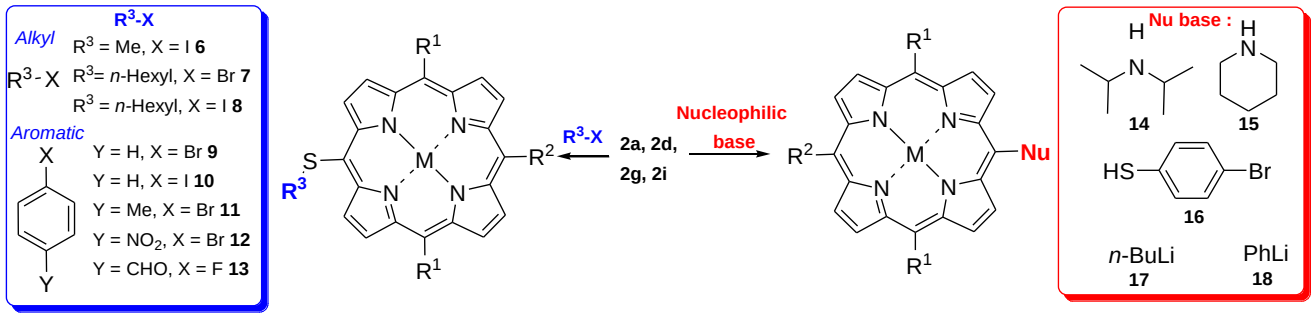
4. Note on displacement reactions:

General procedure for displacement of alkyl/aromatic halide with porphyrin thiolate:
Thiol surrogate (1 eq.) was dissolved in anhydrous toluene (20 mL) together with alkyl/aryl halide **6-13** (5-10 eq). NaOEt (21 % solution, 0.2 mL) was added dropwise and the solution left to stir at room temperature for one hour. Reaction was quenched by adding H_2O (20 mL) and the aqueous layer was extracted three times with CH_2Cl_2. The title compound and/or S-linked dimer was obtained *via* recrystallisation (CH_2Cl_2/MeOH) to yield purple crystals.

General procedure for displacement porphyrin thioether chain by N- or S-nucleophile:
Nucleophile **14, 15** or **16** (3 eq.) and K_2CO_3 (10-11 eq.) were dissolved in anhydrous DMF (12 mL) in a 3-necked round bottomed flask. The solution was purged with argon and was heated to 100 ºC for 2 h. Thiol surrogate (1 eq.) was added and the reaction was allowed to stir at 110 ºC for 2h, monitoring the reaction *via* TLC analysis (CH_2Cl_2/*n*-hexane 1:1, v/v). Upon completion, the reaction was allowed to cool to room temperature and was washed with H_2O (30 mL x 3) and was extracted with CH_2Cl_2. Solvents were removed *in vacuo* and the residue was purified *via* column chromatography (CH_2Cl_2/*n*-hexane 1:2, v/v).

General procedure for displacement porphyrin thioether chain by organolithium reagent:
Thiol surrogate (1 eq.) was added to a Schlenk flask under argon and dissolved in anhydrous THF (20-30 mL). The solution was cooled to -78 ºC before dropwise addition of organolithium reagent **17** or **18** (6 eq.). Following addition, the reaction was allowed to stir at -78 ºC for 10 min before warming to room temperature (over approx. 2h). H_2O (2 mL) was added and the solution stirred for 20 min. DDQ (6 eq.) was added and the reaction was allowed stir open to air for 1 h. The solution was then filtered through a plug of silica using CH_2Cl_2 as eluent. Solvents were removed *in vacuo* and the residue was purified *via* column chromatography (CH_2Cl_2/*n*-hexane 1:2, v/v).

Table 1: Displacement reactions: a) porphyrin thiol surrogate with alkyl/aromatic halides and b) displacement of thioether chain by nucleophilic base



Entry	R^3-X	R^1	R^2	M	Product[b]	Yield[a]	Entry	Nucleophile	R^1	R^2	M	Product	Yield[a]
1	**6**	Tolyl	Ph	Zn^{II}	**4a**	71	10	**14**	Tolyl	Ph	Zn^{II}	**5a**	n/d[d]
2	**7**	Tolyl	Ph	Zn^{II}	**4b**	trace[c]	11	**15**	Tolyl	Ph	Zn^{II}	**5b**	n/d[d]
3	**8**	Tolyl	Ph	Zn^{II}	**4c**	trace[c]	12	**16**	Tolyl	Ph	2H	**5c**	48[d]
4	**9**	Tolyl	Ph	Zn^{II}	**4d**	n/d[c]	13	**17**	Tolyl	Ph	2H	**5d**	<10%[e,f]
5	**11**	Tolyl	Ph	Zn^{II}	**4e**	n/d[c]	15	**17**	Tolyl	Ph	Ni^{II}	**5e**	Trace[e,f]
6	**6**	1-Ethylpropyl	*n*-Butyl	Ni^{II}	**4f**	95	16	**17**	Tolyl	Ph	Ni^{II}	**5e**	<10%[e,f]
7	**7**	Tolyl	Ph	Ni^{II}	**4g**	95	17	**18**	Tolyl	Ph	Ni^{II}	**5f**	n/d[f]
8	**10**	Tolyl	Ph	Ni^{II}	**4h**	n/d[c]	18	**16**	Tolyl	Ph	Ni^{II}	**5g**	>30[c,d]
9	**12**	Tolyl	Ph	Ni^{II}	**4i**	n/d[c]							

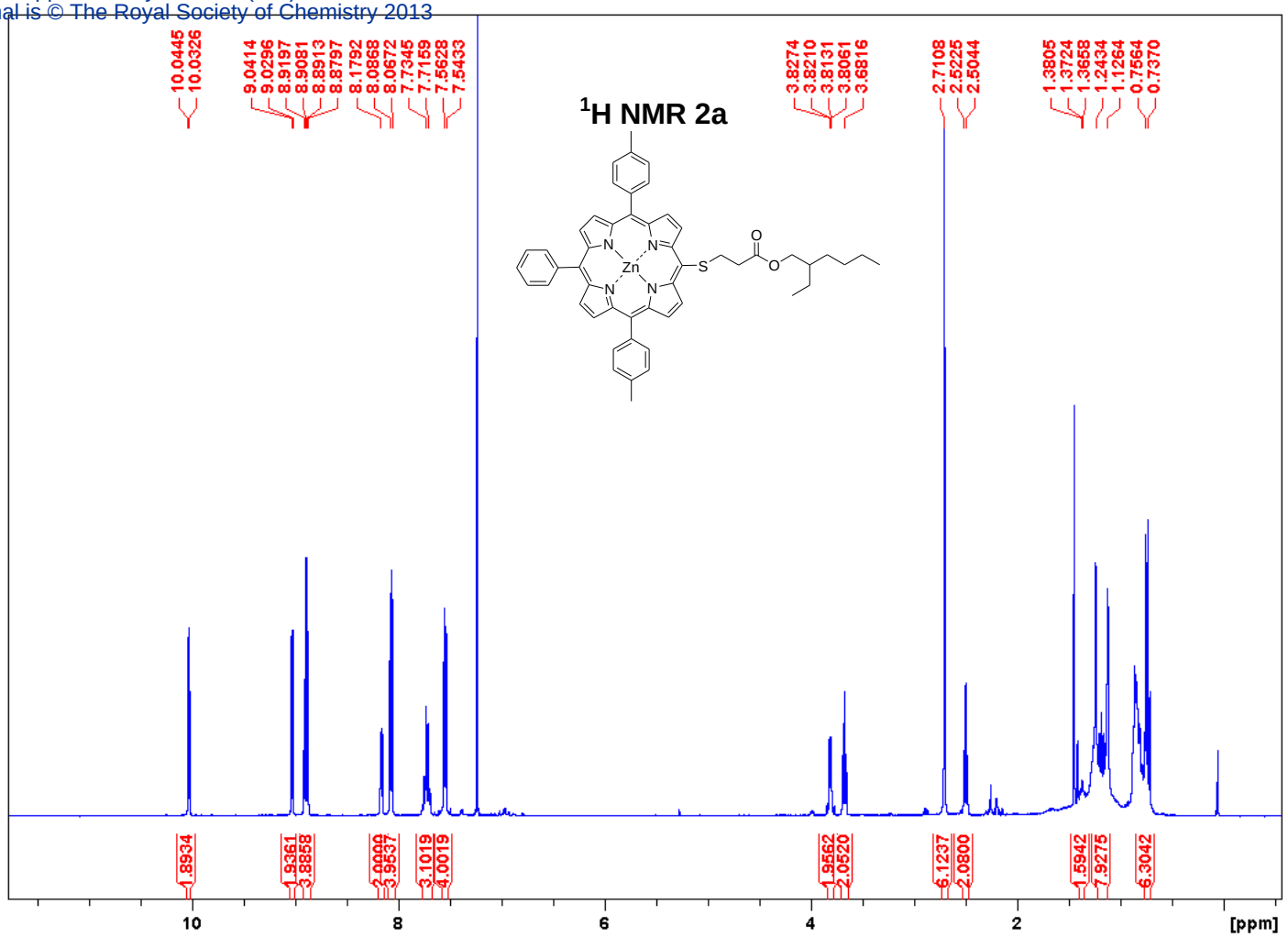
[a] Isolated yield; [b] *Reagents and conditions:* R^3-X (5-10 eq.), NaOEt (21% in EtOH), toluene, rt, Ar, 3-18 h; [c] S-linked dimer predominant product; [d] *Reagents and conditions:* i) S-/N-nucleophile (5 eq.), K_2CO_3 (10-11 eq.), DMF, 110 ºC, 2 h ii) porphyrin (1 eq.), 110 ºC, 2-16 h; [e] *Reagents and conditions:* i) porphyrin, THF, -78 ºC ii) *n*-BuLi (6 eq.), -78 ºC – rt, 2 h; [f] Predominant product was unreacted starting material;

Table 1 is an expansion of Table 3 in the main text. For alkyl and aryl halides **6-13**, numerous halide displacement attempts were made, with most success observed for alkyl derivatives **6** and **7**. For aromatic halides, no displacement was observed, with the predominant product being the S-linked dimer. This indicates that for aromatic residues the thioether chain acts as a better leaving group than halides I, Br or F. For nucleophilic displacement of the thioether chain, nucleophiles **14-18** were used. For N-nucleophiles **14** and **15**,

the predominant products observed again were S-linked dimers indicating that the nucleophilic strength of the porphyrin thiolate exceeds that of the aforementioned bases. Using organolithium reagents **17** and **18**, some success was seen with butylated products **5d** and **5e** synthesised in <10 % yield. The other products from this reaction were unreacted starting material (~40 %) and higher butylated product (<10 %). Best results were observed using S-nucleophile **16** whereby the thiolate generated from this thiophenol successfully displaced the thioether chain of porphyrin **2d**, giving **5c** in 48 % yield. This displays the potential applicability of this type of surrogate to act as a leaving group using soft nucleophiles such as **16**.

5. References

[1.] Habermeyer, B.; Takai, A.; Gros, C. P.; El Ojaimi, M.; Barbe, J.-M.; Fukuzumi, S. *Chem.-Eur. J.* **2011**, *17*, 10670.
[2.] Tomizaki, K.-y.; Lysenko, A. B.; Taniguchi, M.; Lindsey, J. S. *Tetrahedron* **2004**, *60*, 2011.
[3.] Lin, V.; DiMagno, S.; Therien, M. *Science* **1994**, *264*, 1105.
[4.] Takanami, T.; Hayashi, M.; Chijimatsu, H.; Inoue, W.; Suda, K. *Org. Lett.* **2005**, *7*, 3937.
[5.] Lu, X.-Q.; Guo, Y.; Chen, Q.-Y. *Synlett* **2011**, 77.
[6.] Plunkett, S.; Dahms, K.; Senge, M. O. *Eur. J. Org. Chem.* **2013**, 1566.
[7.] Hartnell, R. D.; Edwards, A. J.; Arnold, D. P. *J. Porphyrins Phthalocyanines* **2002**, *6*, 695.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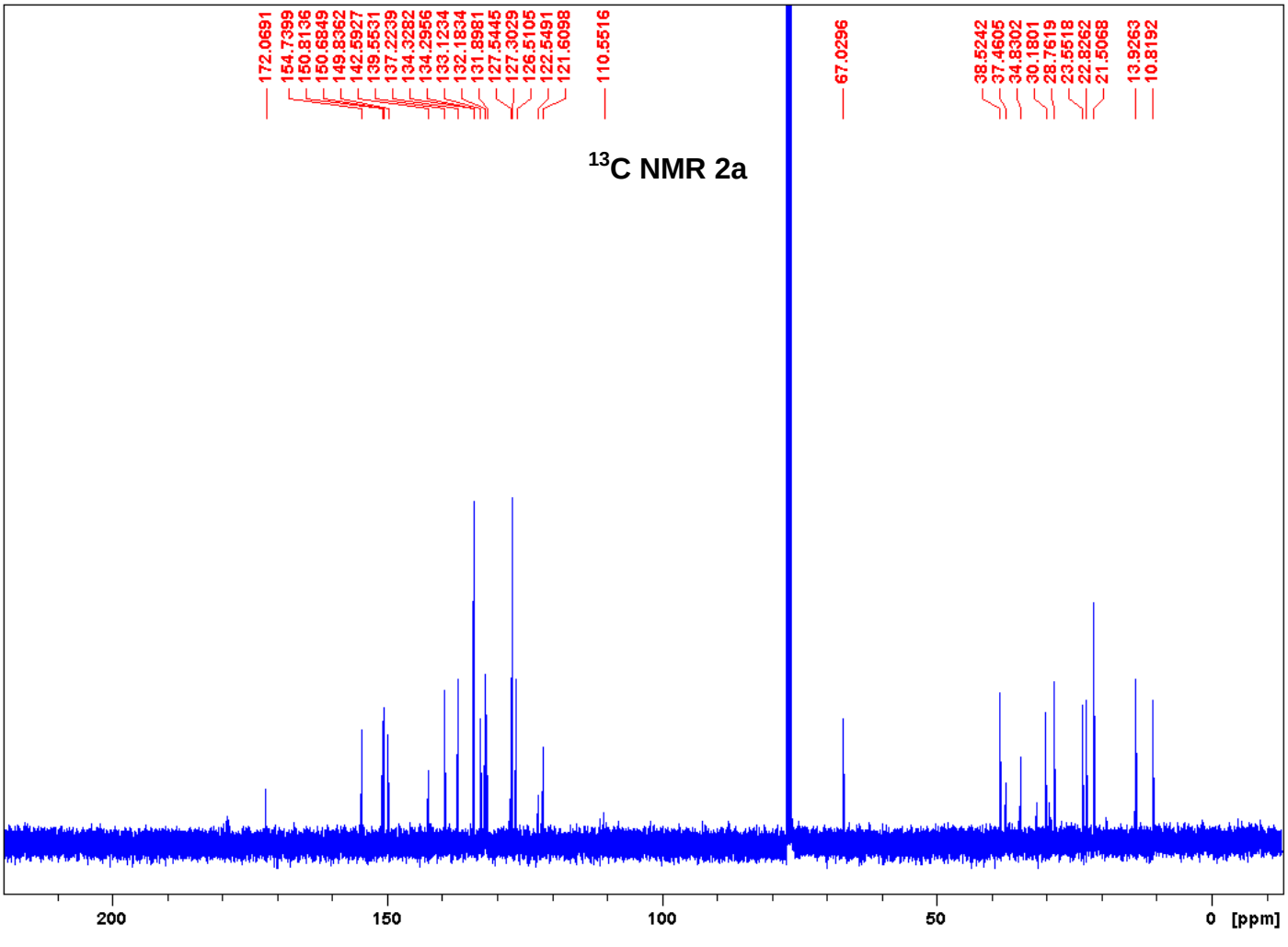
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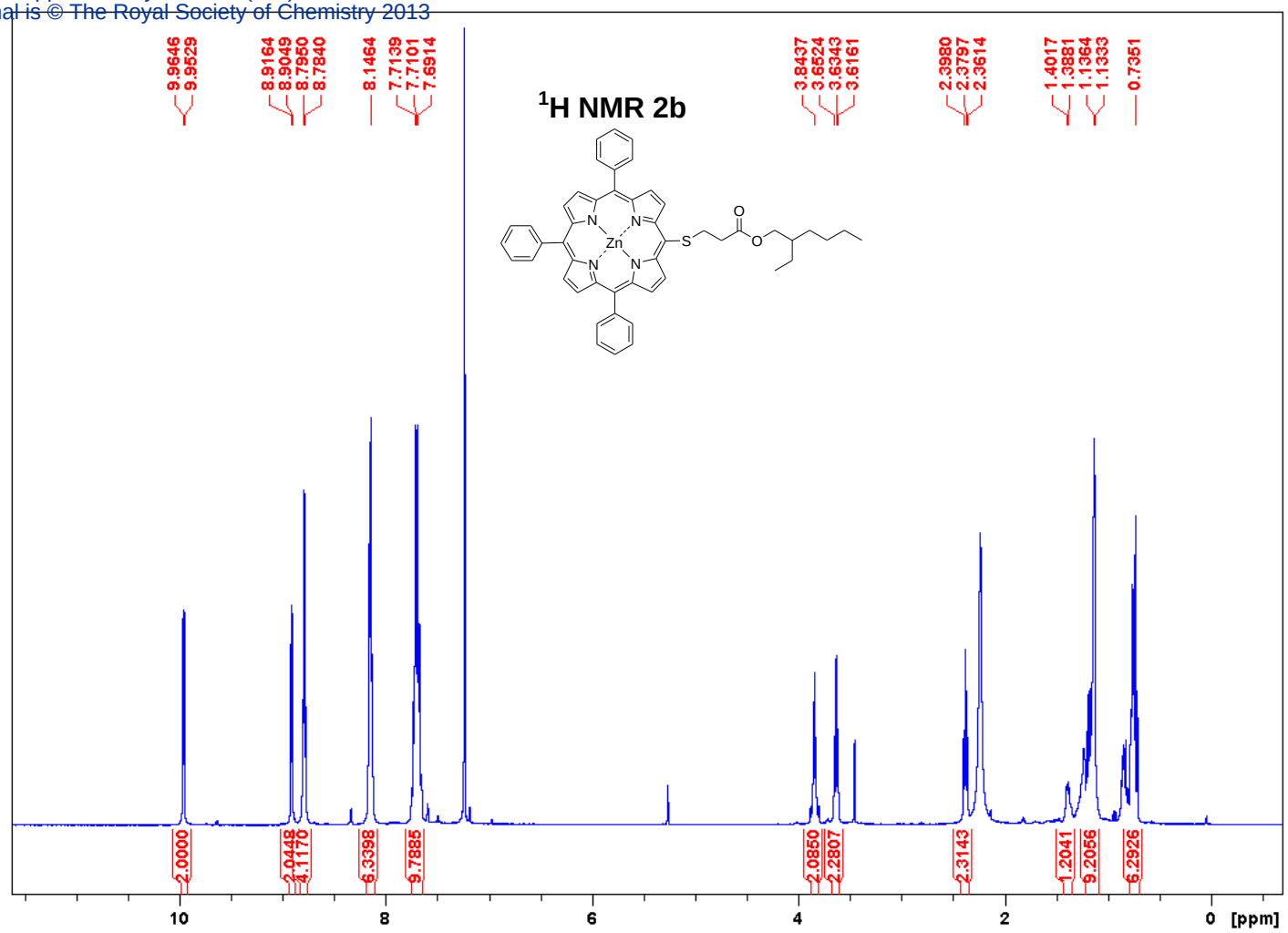

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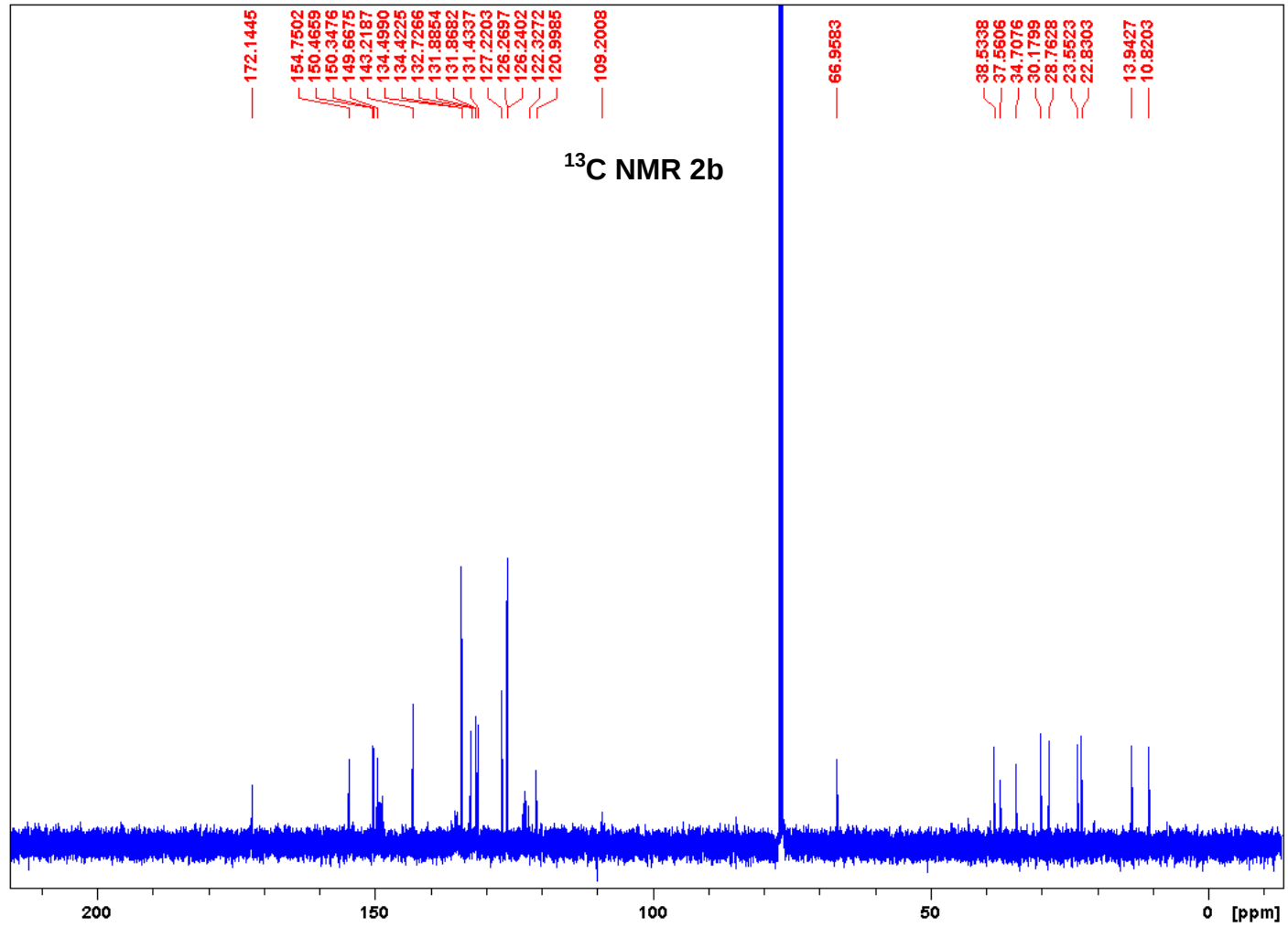

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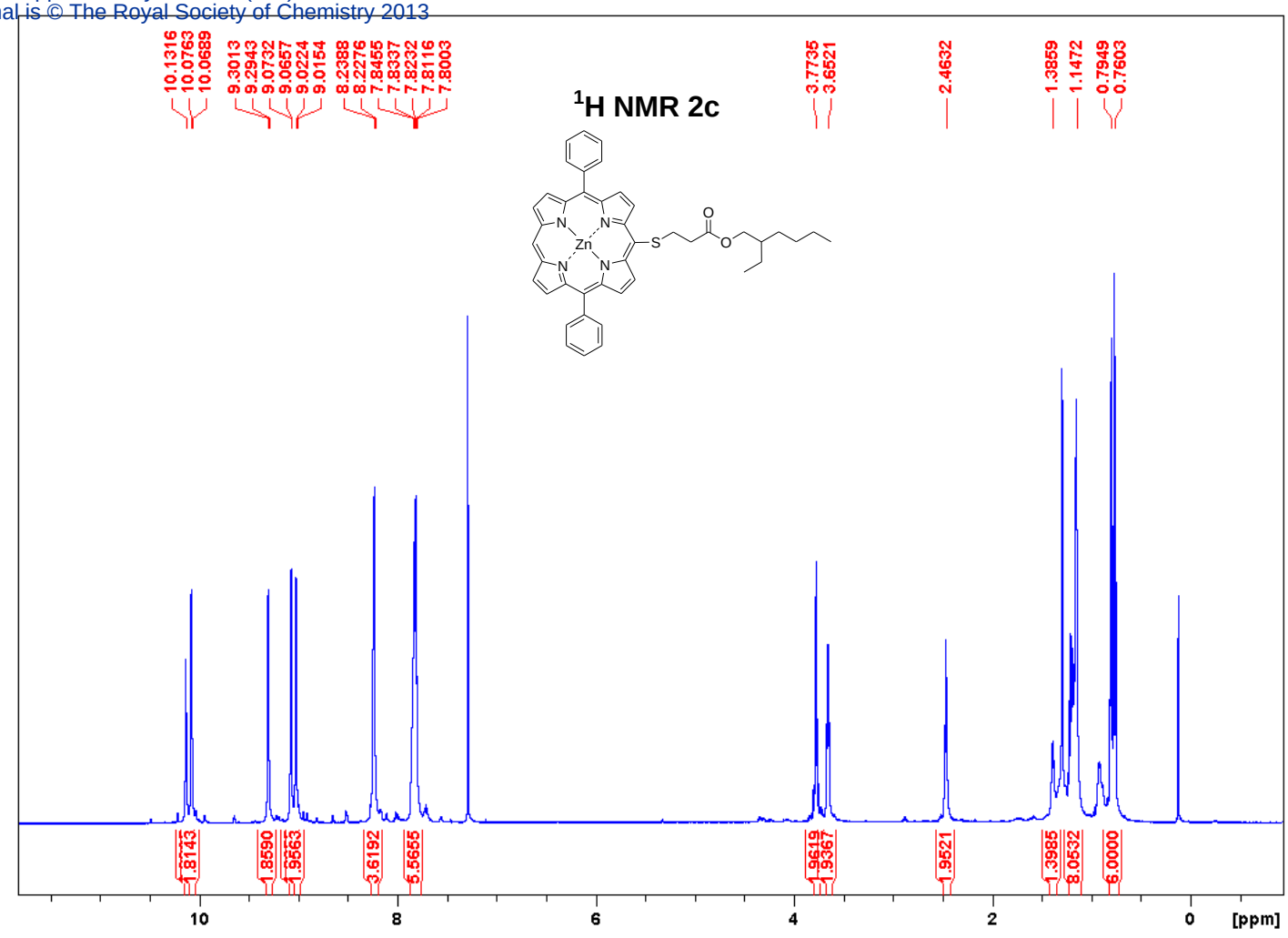
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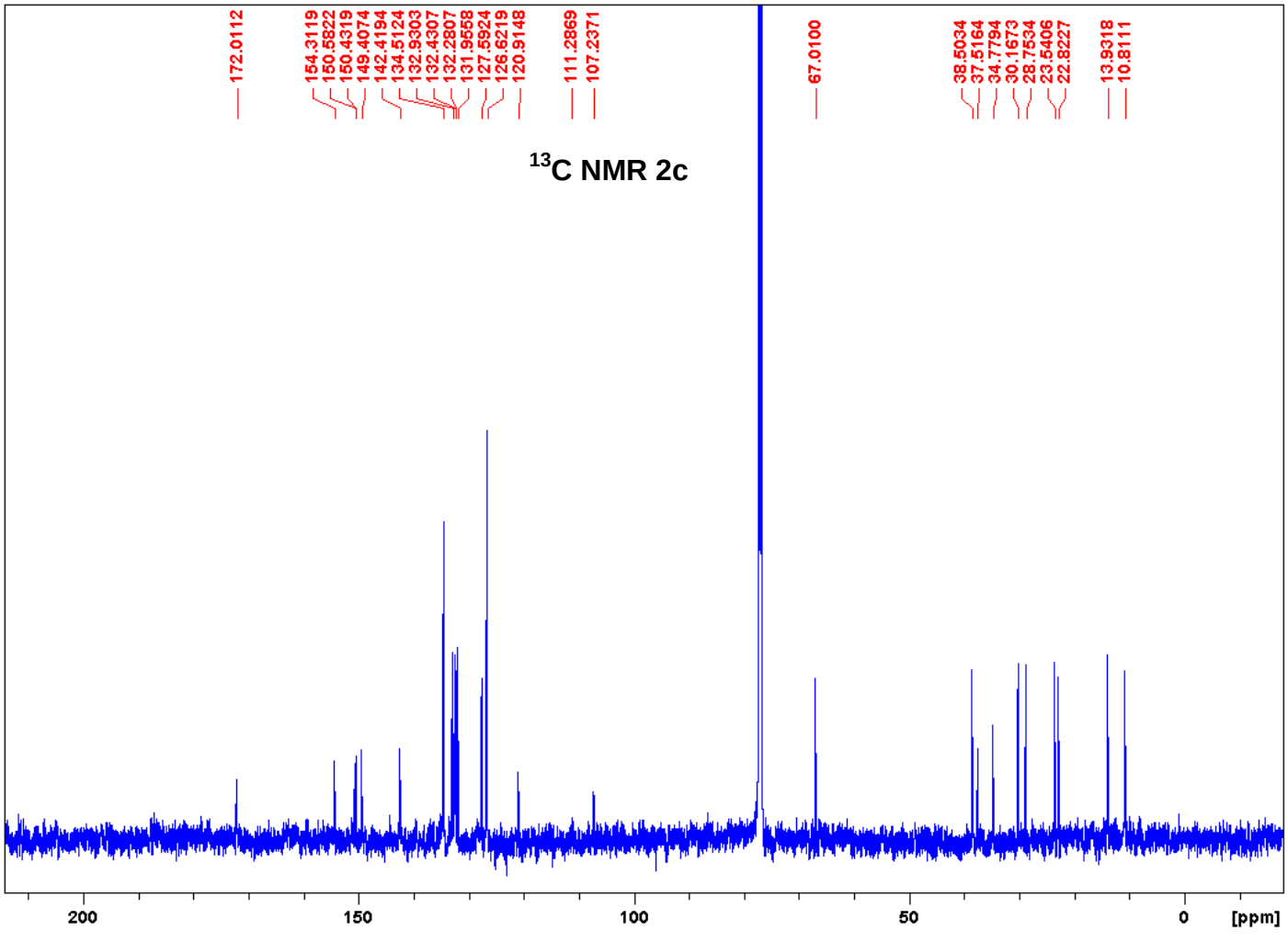
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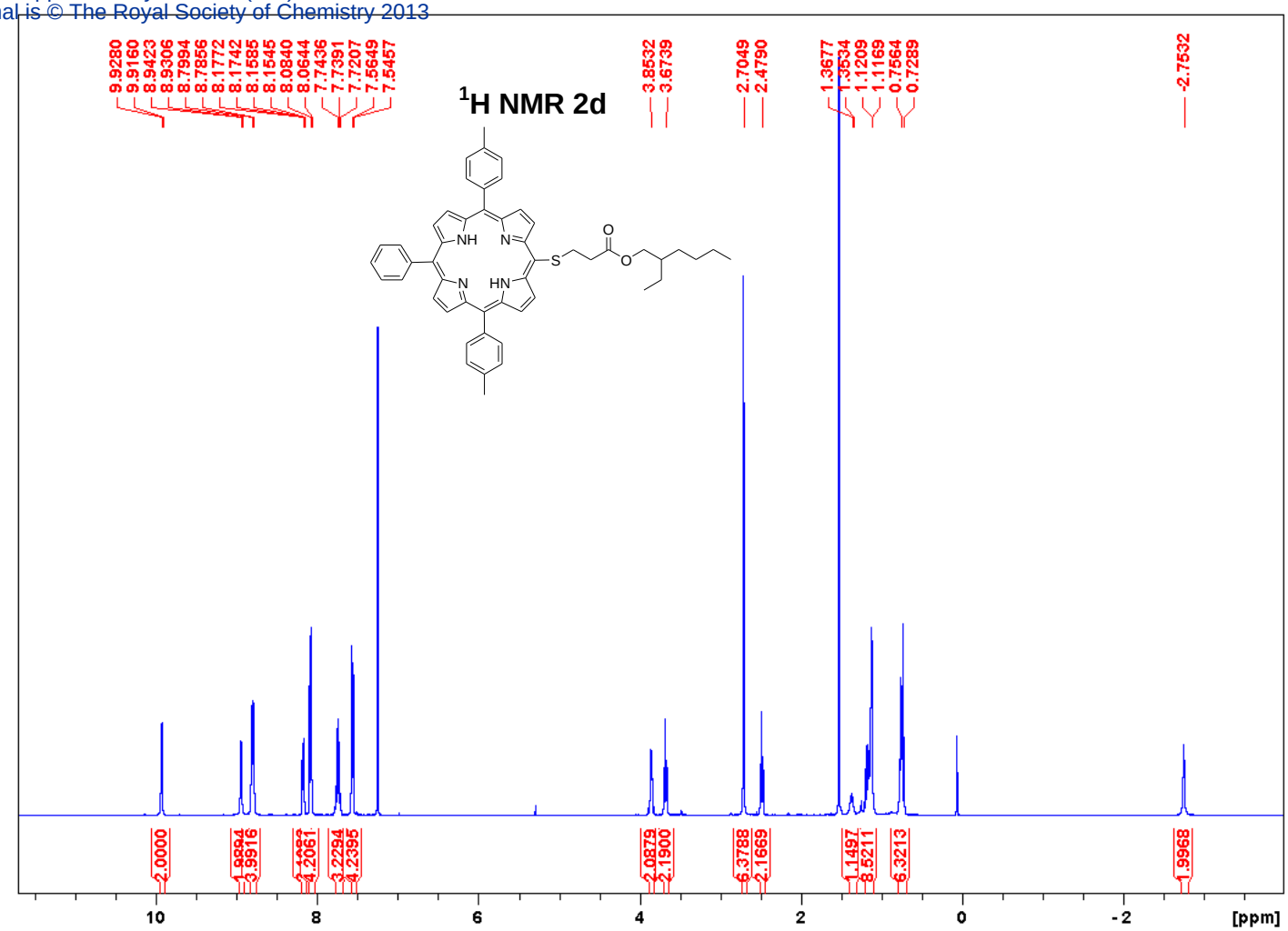
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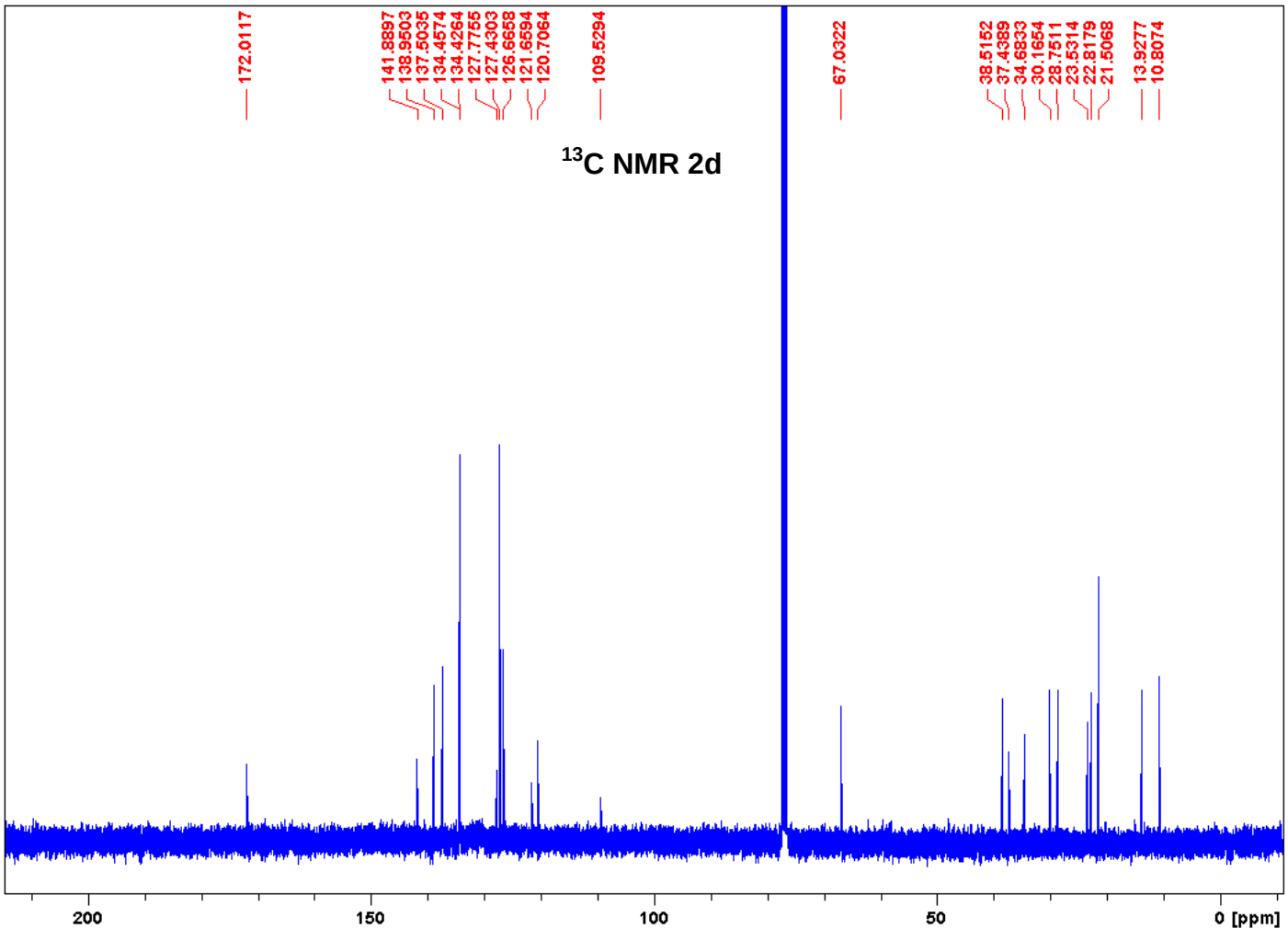
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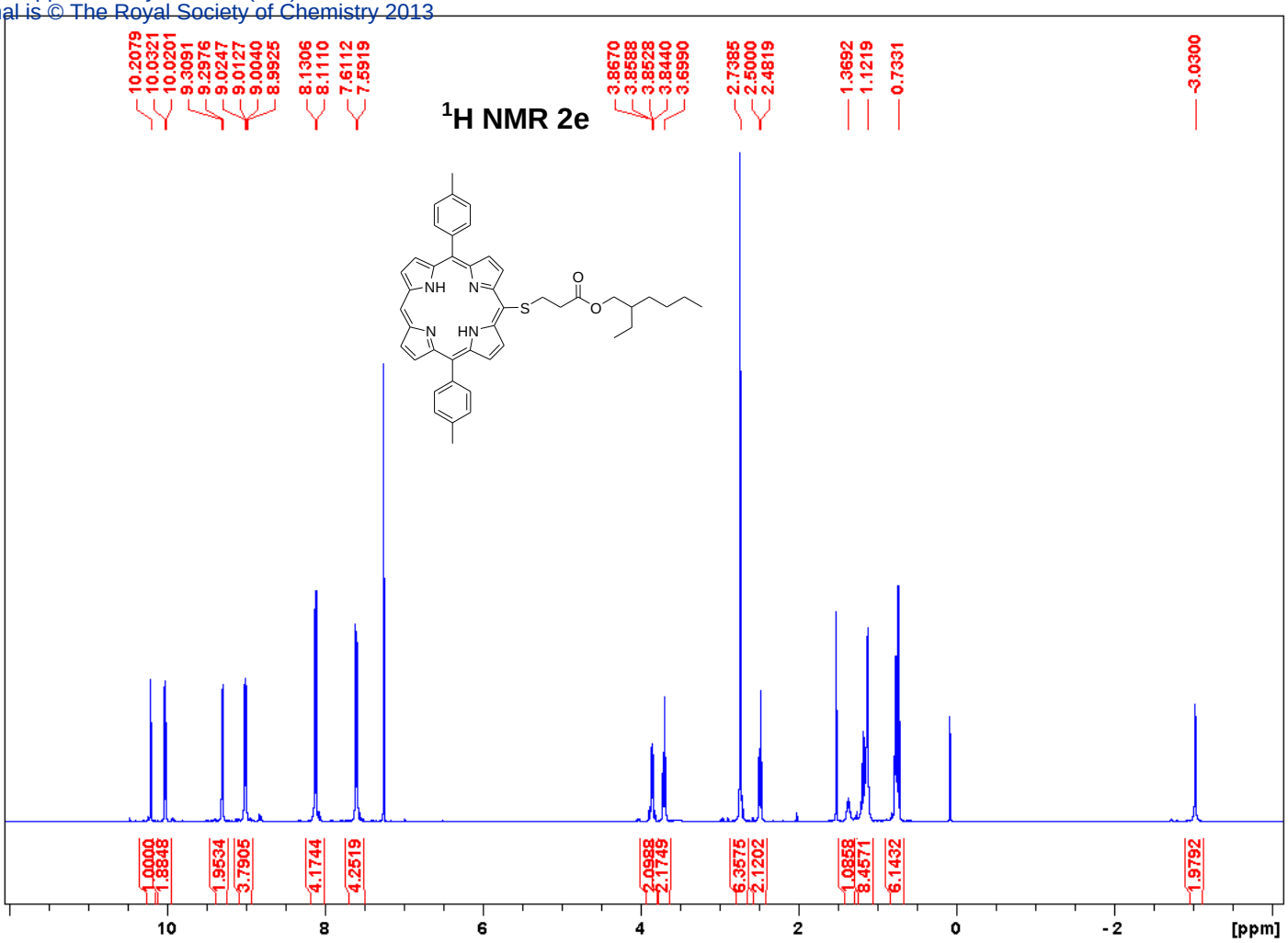
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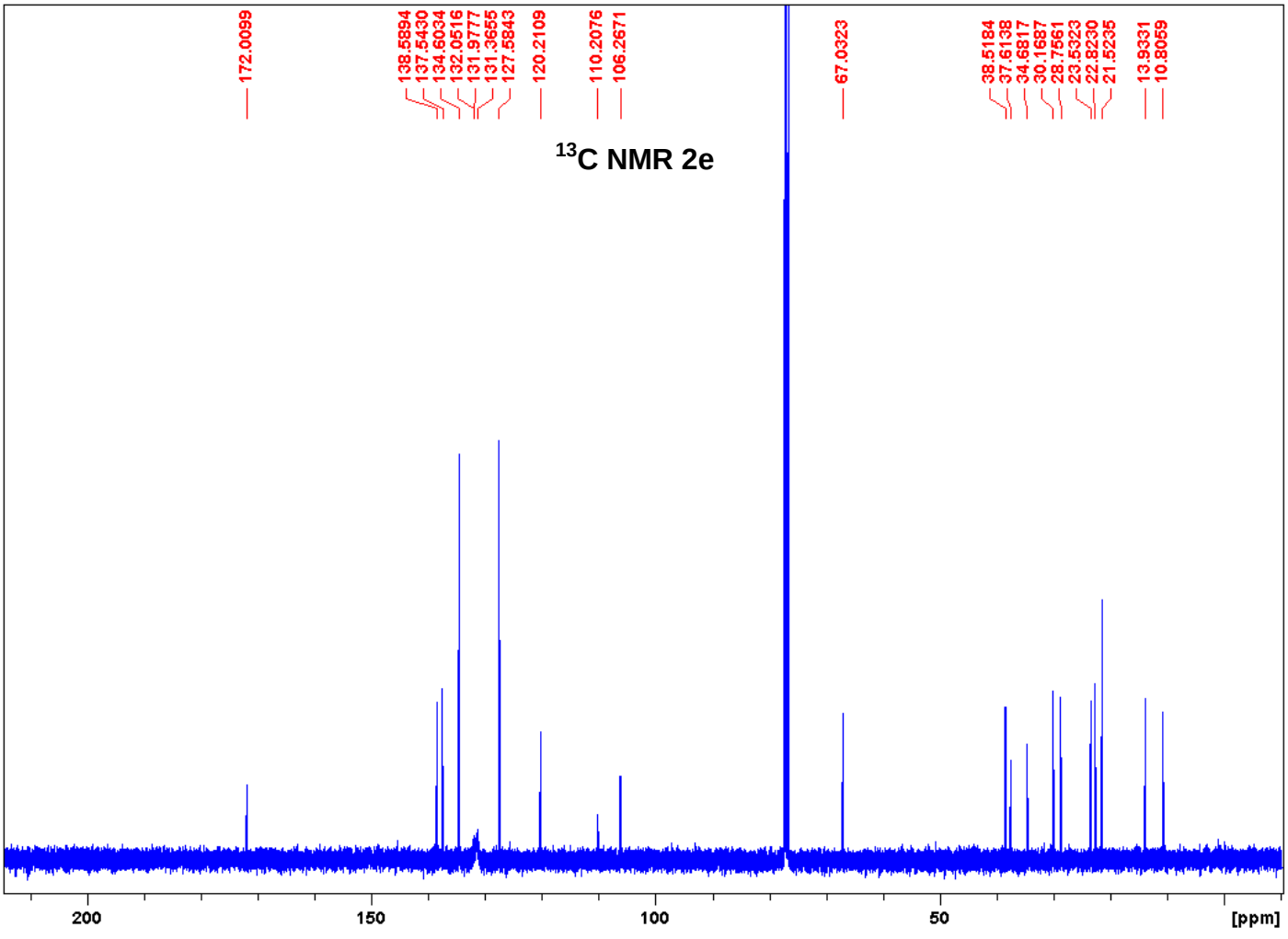
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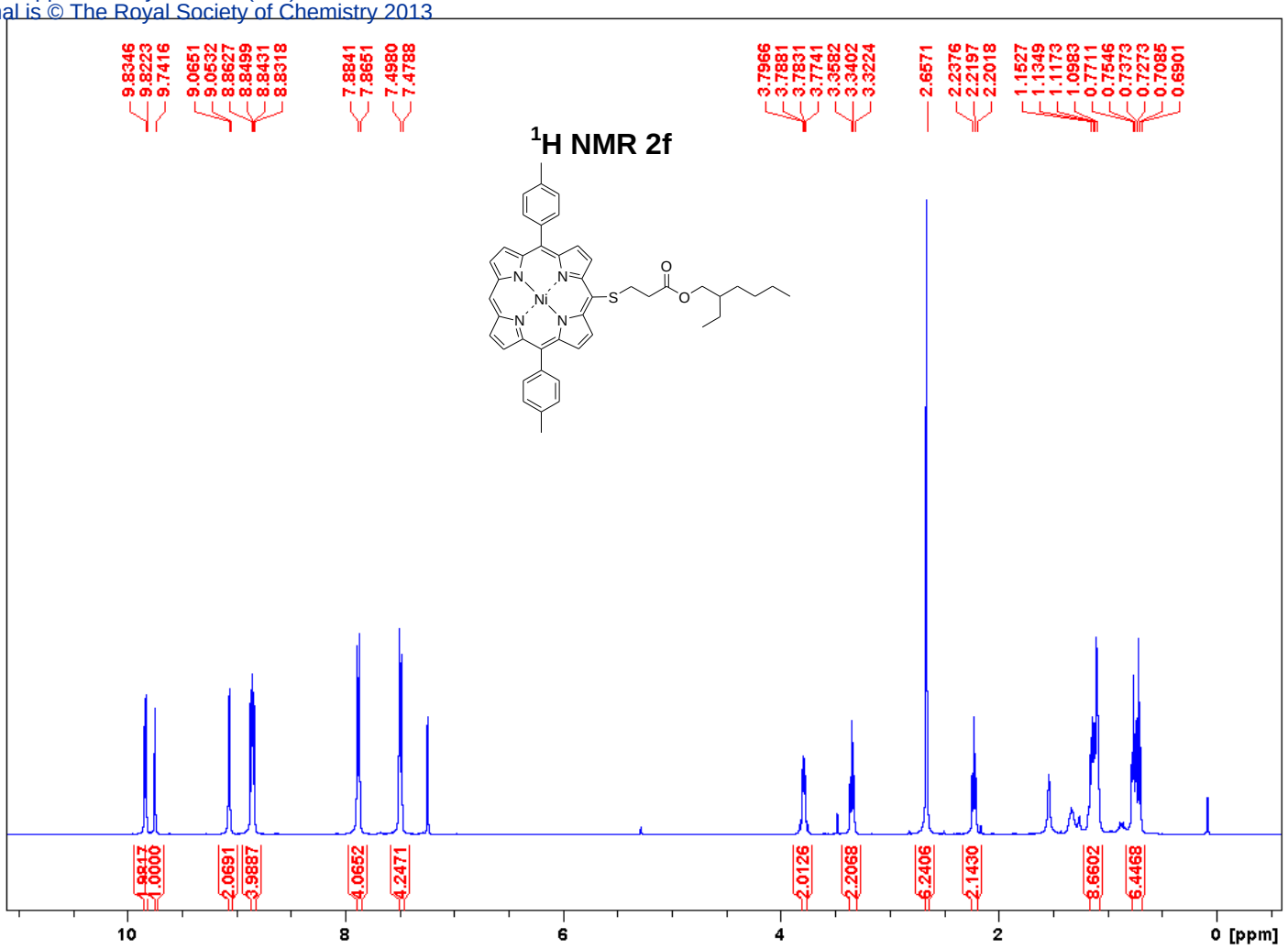
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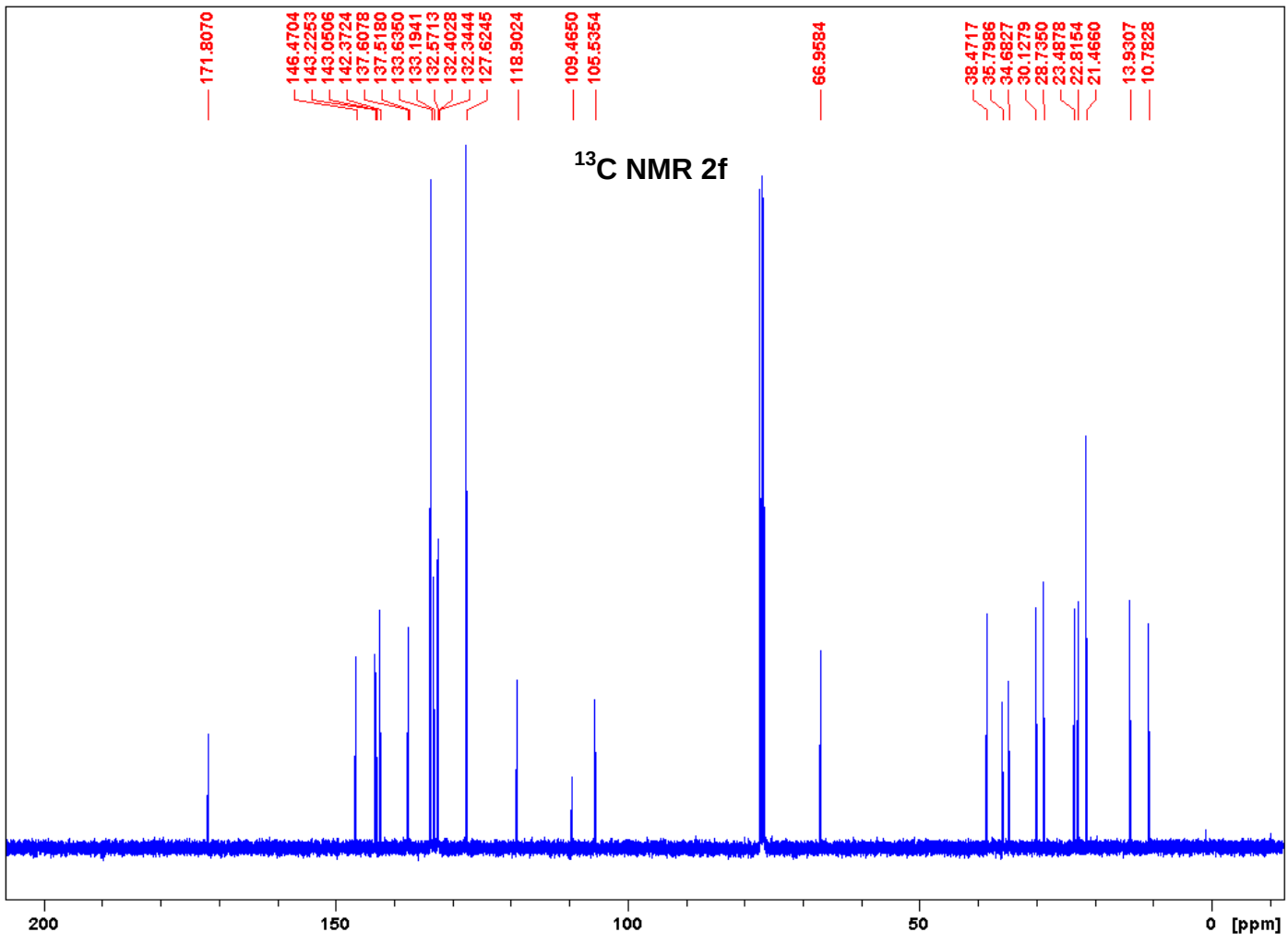
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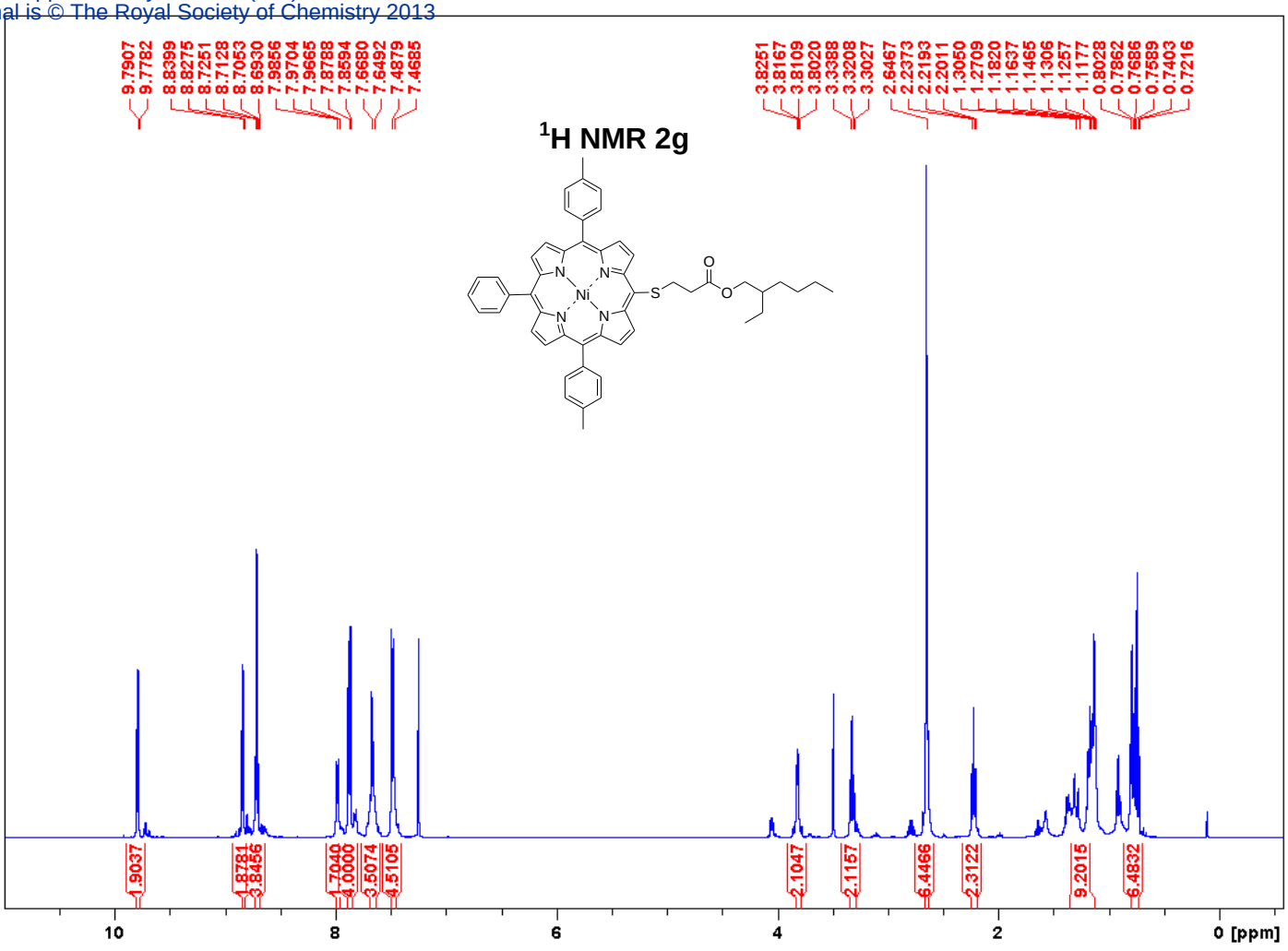

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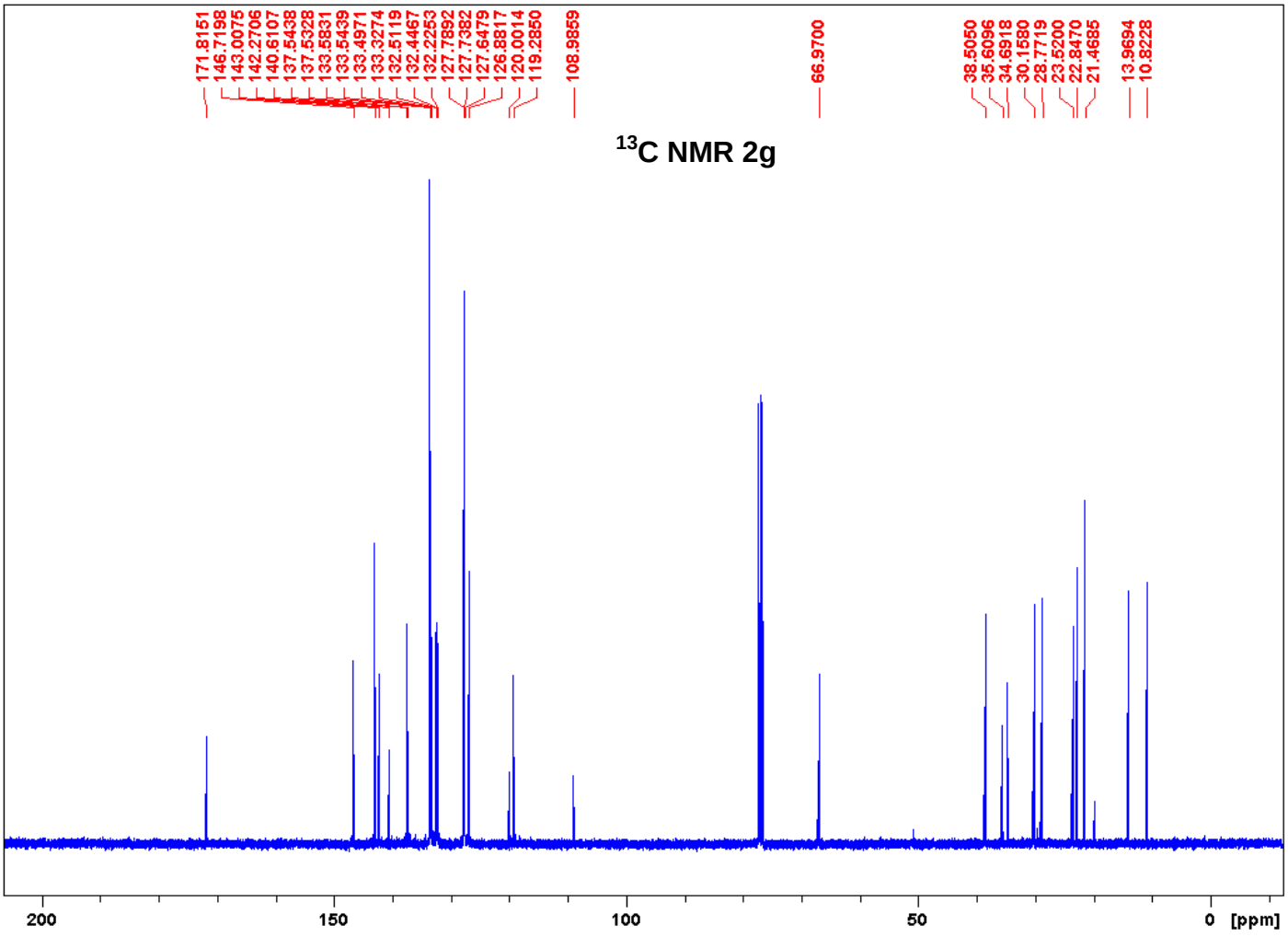

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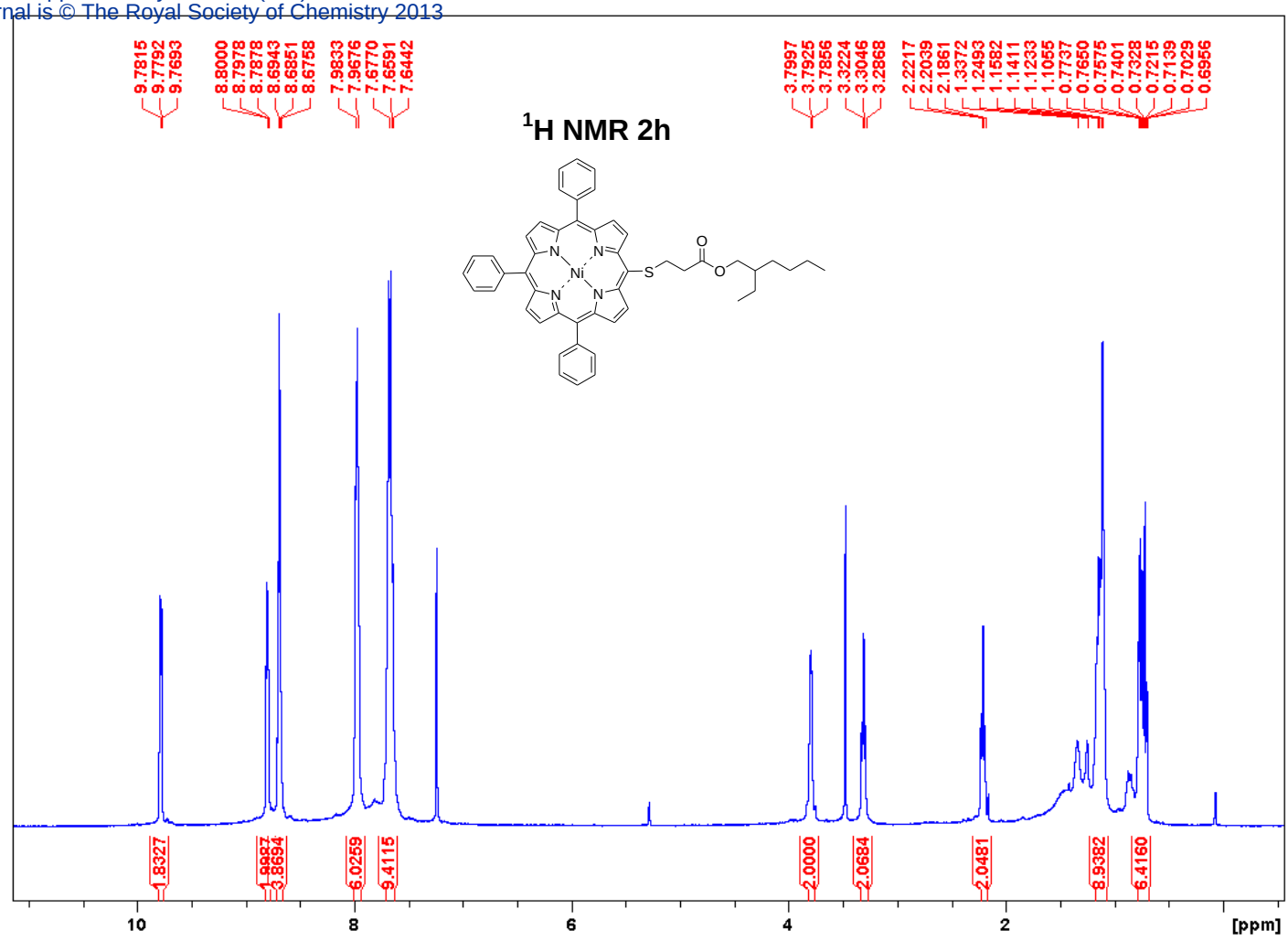
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2.2039
2.1861
1.3372
1.2493
1.1582
1.1411
1.1233
1.1055
0.7737
0.7650
0.7575
0.7401
0.7328
0.7215
0.7139
0.7029
0.6956
1H NMR 2h
N
N
Ni
N
N
S
O
O
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1.6887
3.8694
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2.0481
8.9382
6.4160
10
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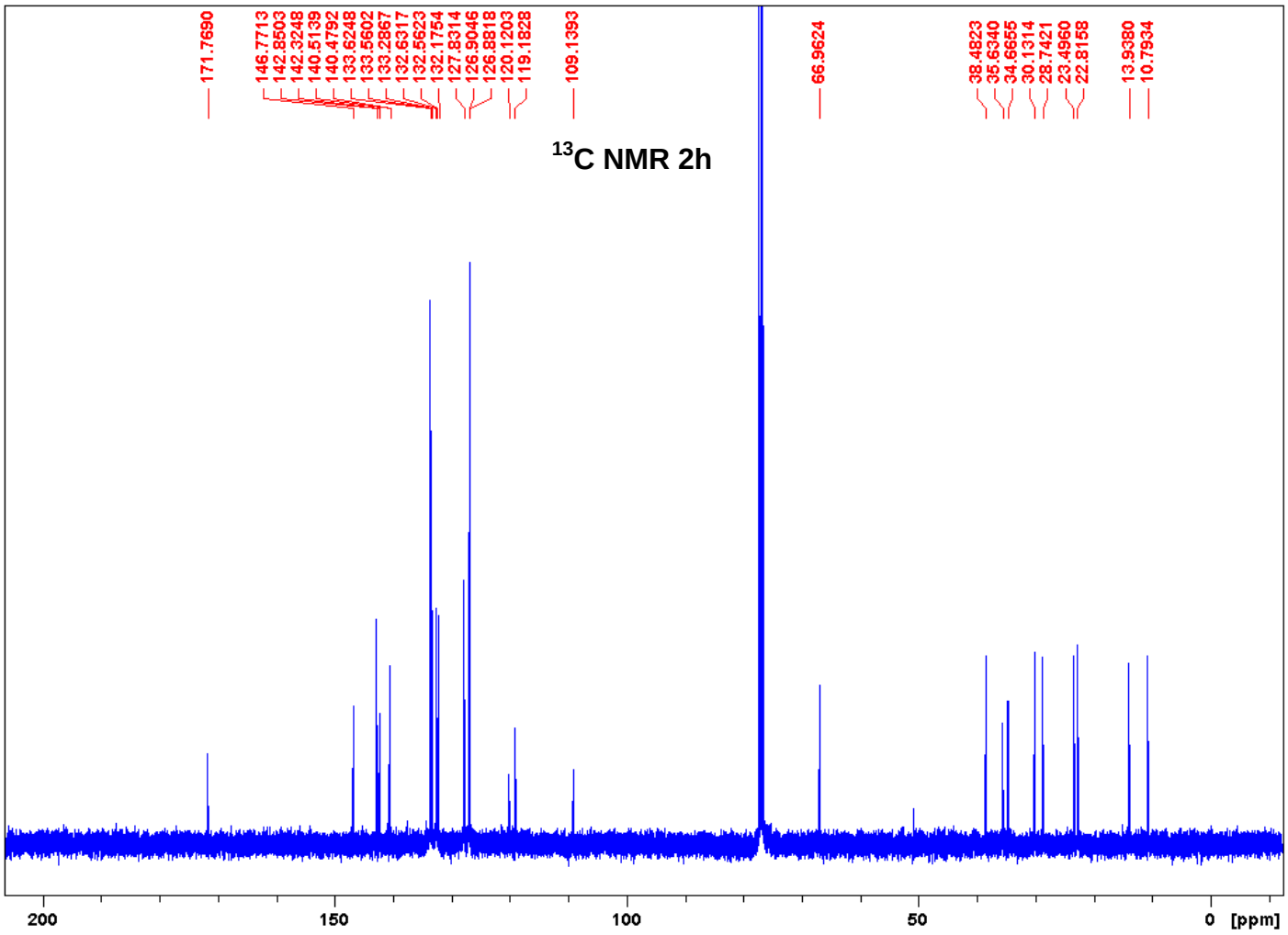
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127.8314
126.9046
126.8818
120.1203
119.1828
109.1393
66.9624
38.4823
35.6340
34.6655
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13C NMR 2h
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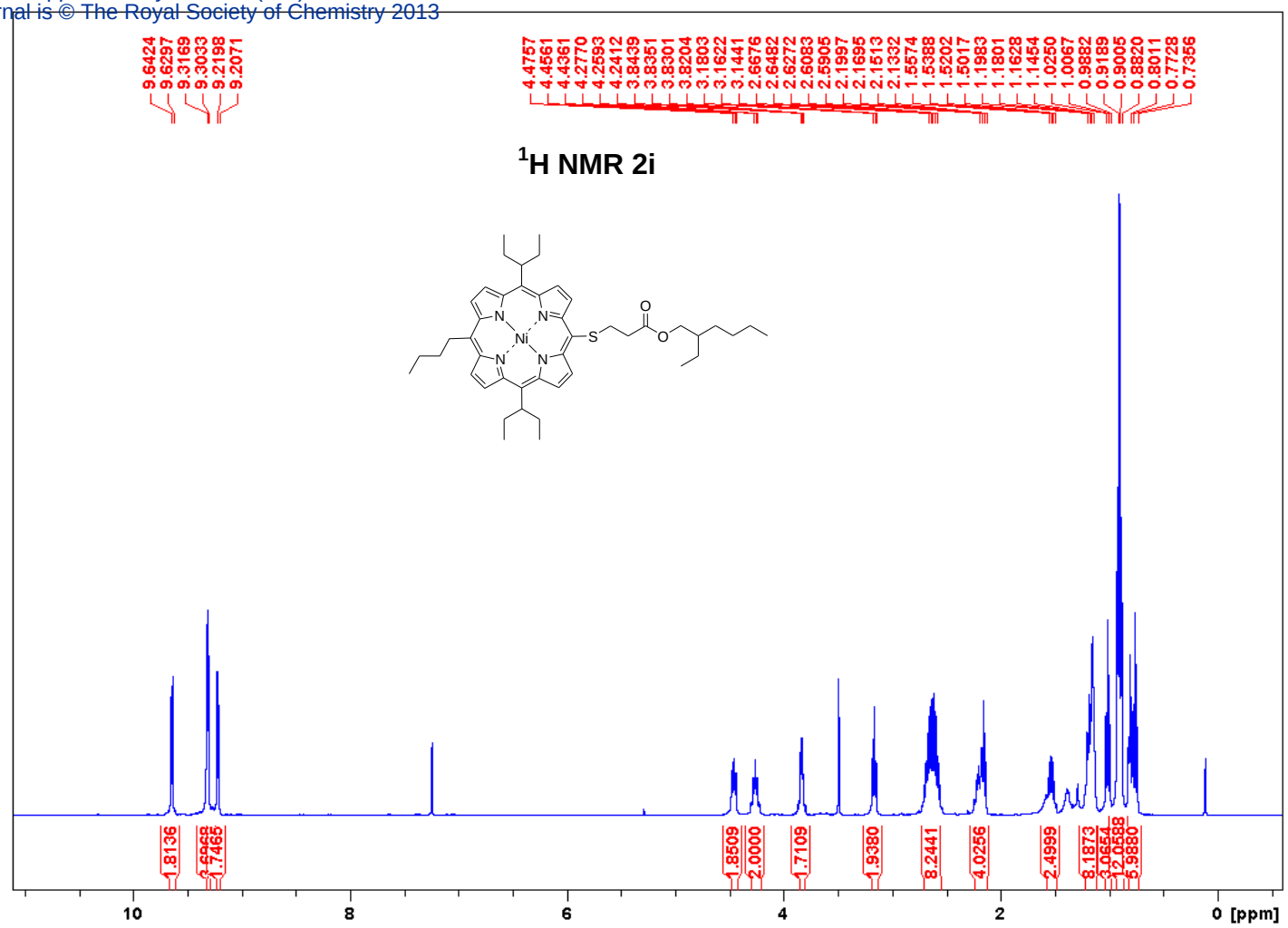
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4.2593
4.2412
3.8439
3.8351
3.8301
3.8204
3.1803
3.1622
3.1441
2.6676
2.6482
2.6272
2.6083
2.5905
2.1997
2.1695
2.1513
2.1332
1.5574
1.5388
1.5202
1.5017
1.1983
1.1801
1.1628
1.1454
1.0250
1.0067
0.9882
0.9189
0.9005
0.8820
0.8011
0.7728
0.7356
1H NMR 2i
N
N
Ni
N
N
S
O
O
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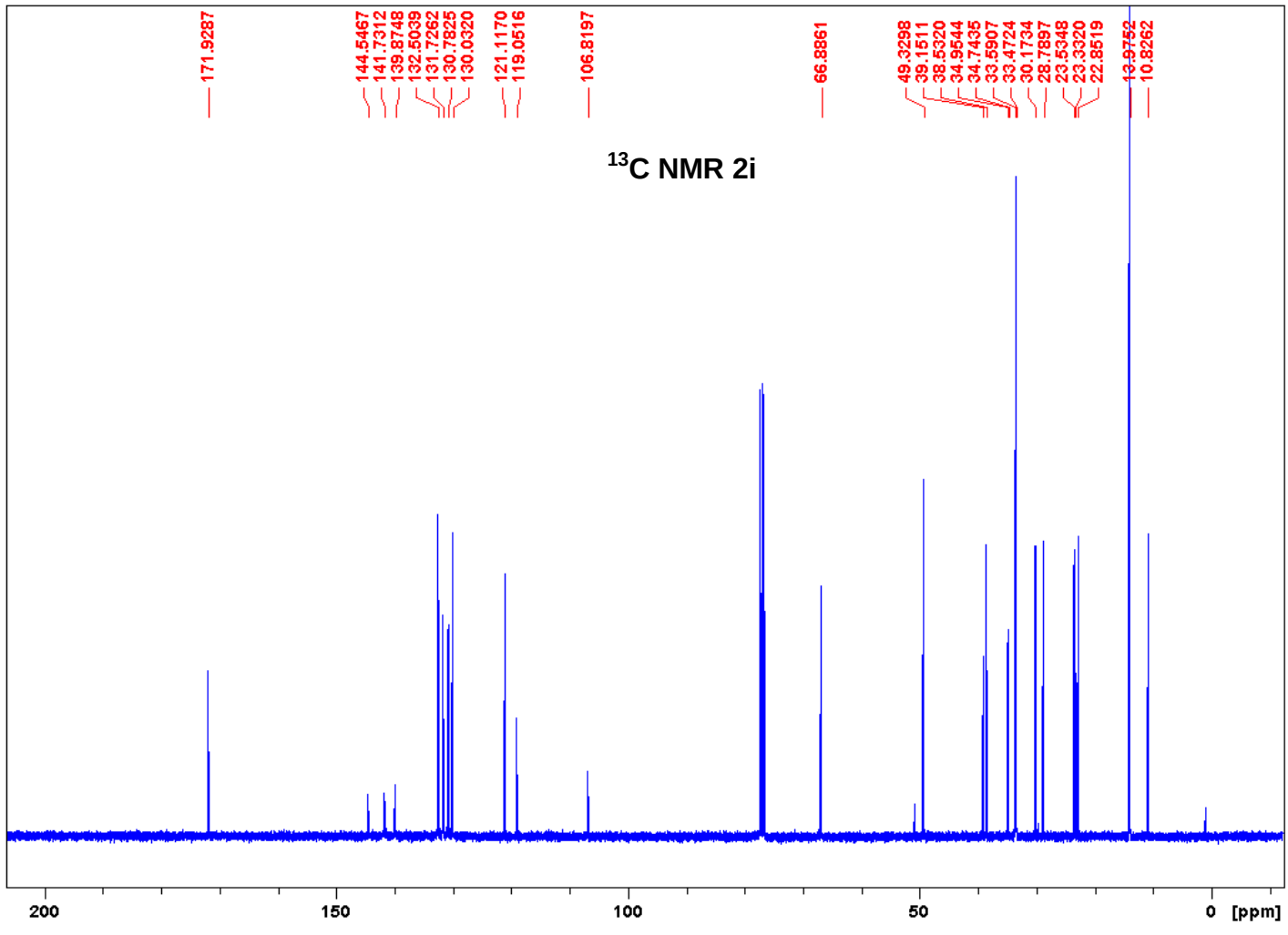
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49.3298
39.1511
38.5320
34.9544
34.7435
33.5907
33.4724
30.1734
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23.3320
22.8519
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13C NMR 2i
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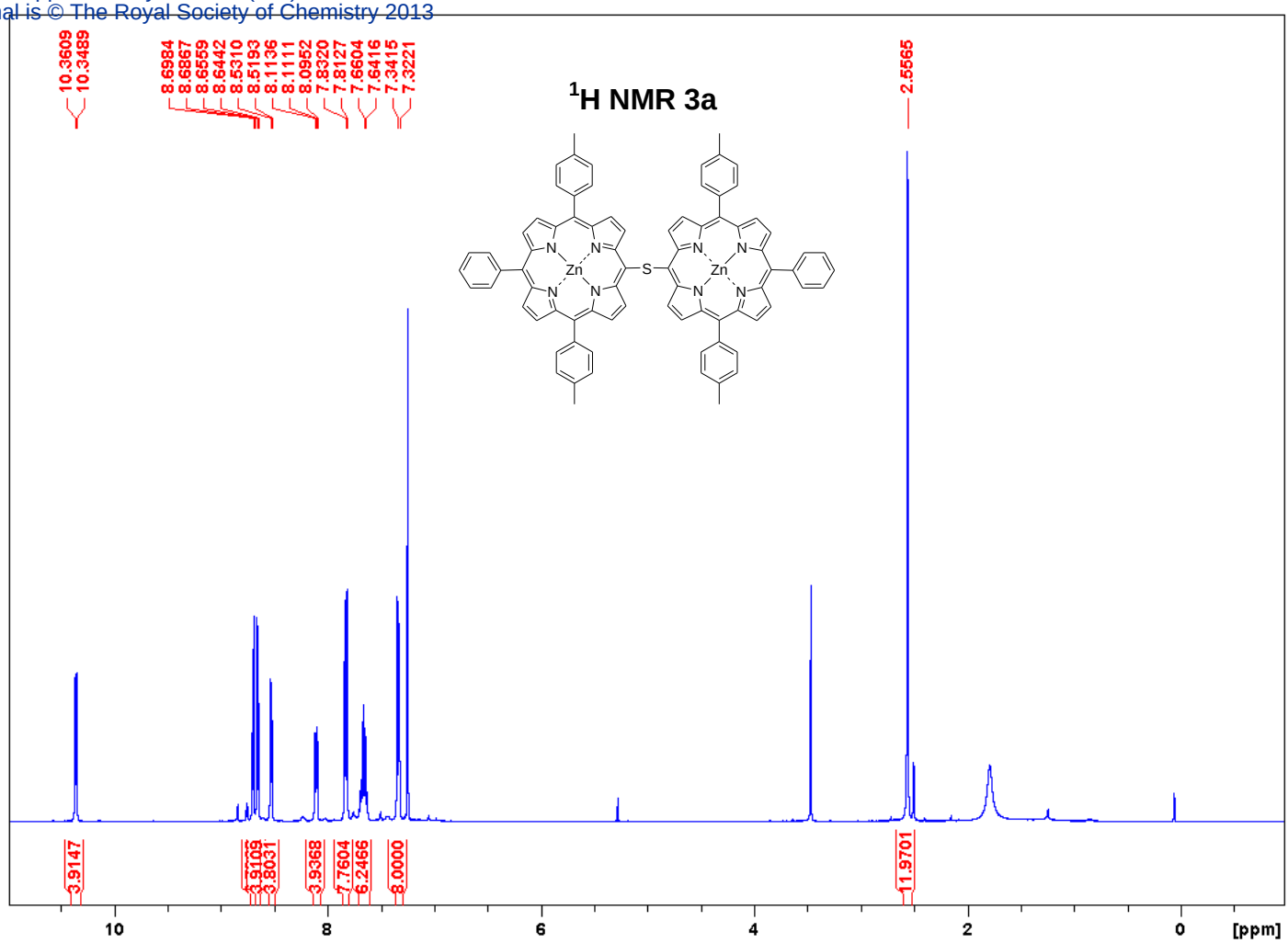
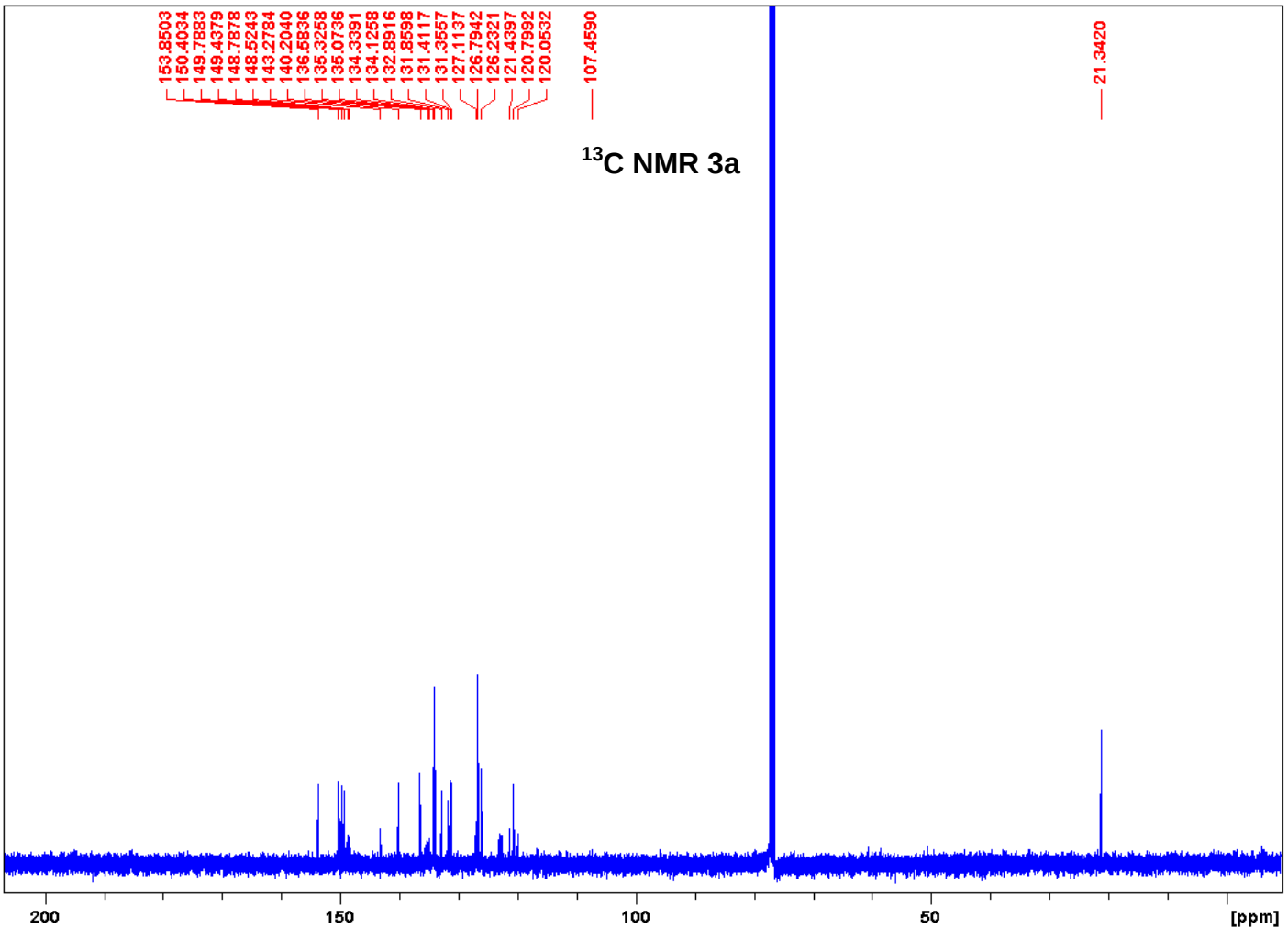
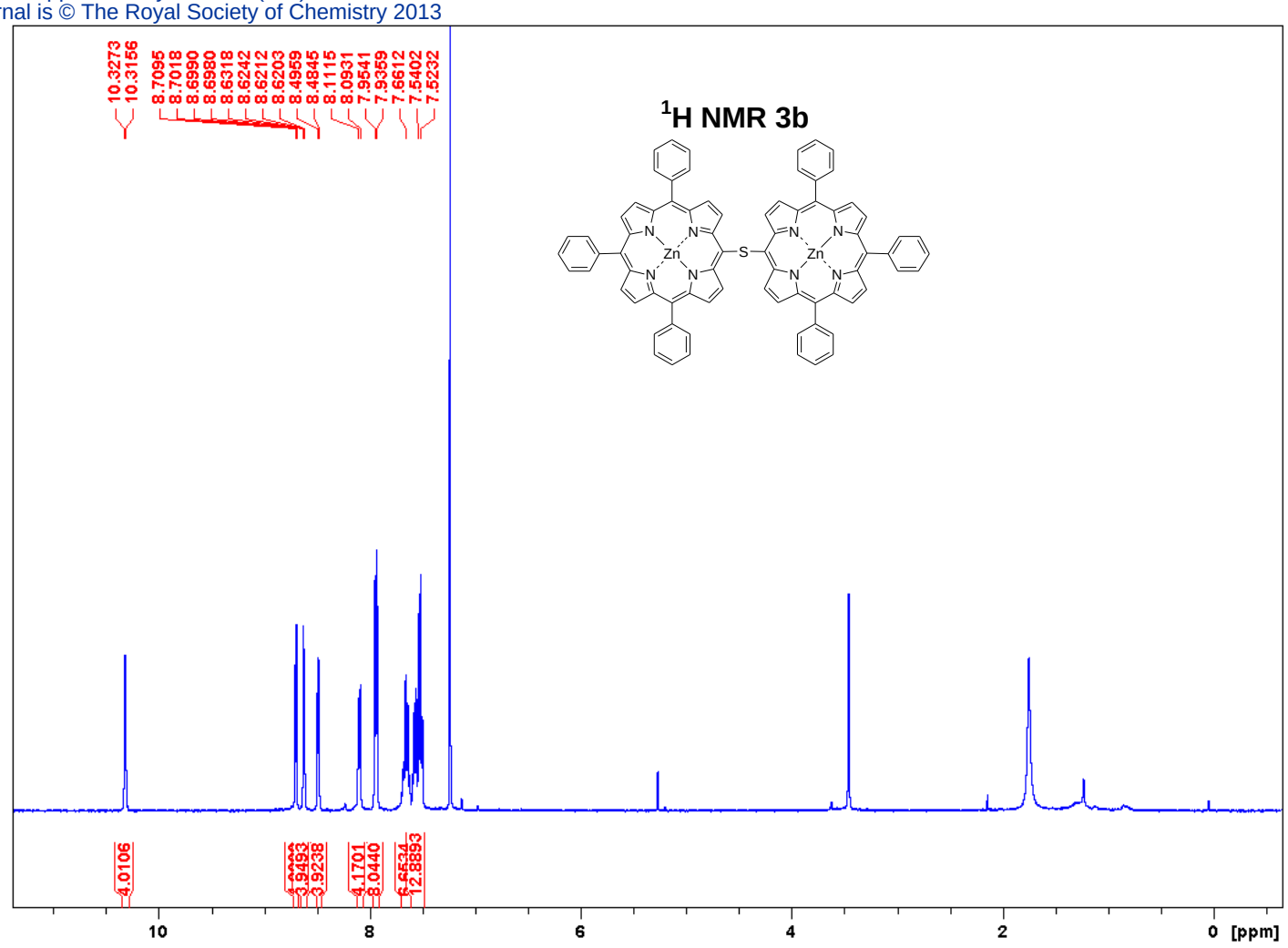


^{1}H NMR 3a



^{13}C NMR 3a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8.6990
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8.6318
8.6242
8.6212
8.6203
8.4959
8.4845
8.1115
8.0931
7.9541
7.9359
7.6612
7.5402
7.5232
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4.1701
8.0440
6.6534
12.8893
10
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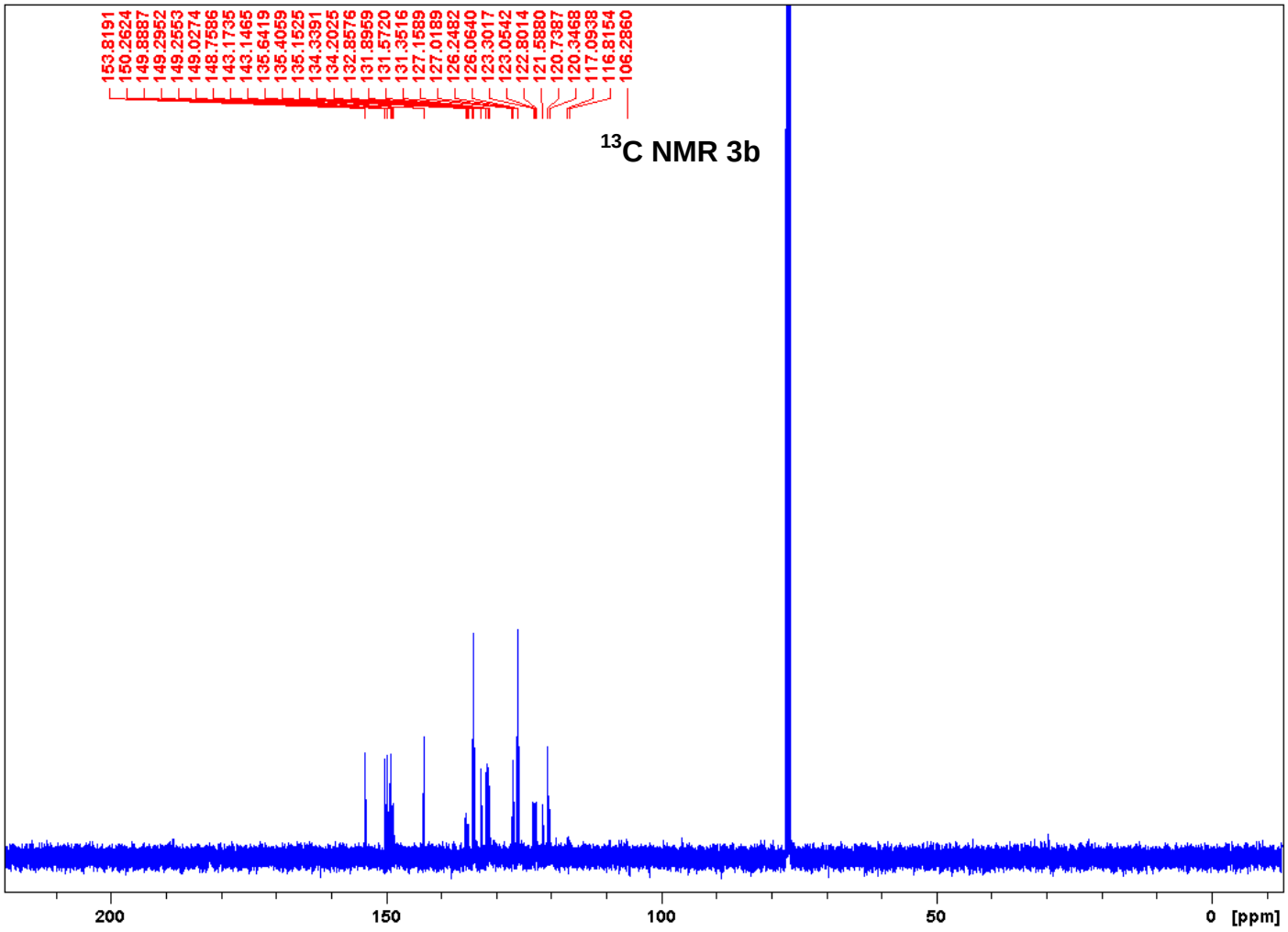
4
2
0 [ppm]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135.1525
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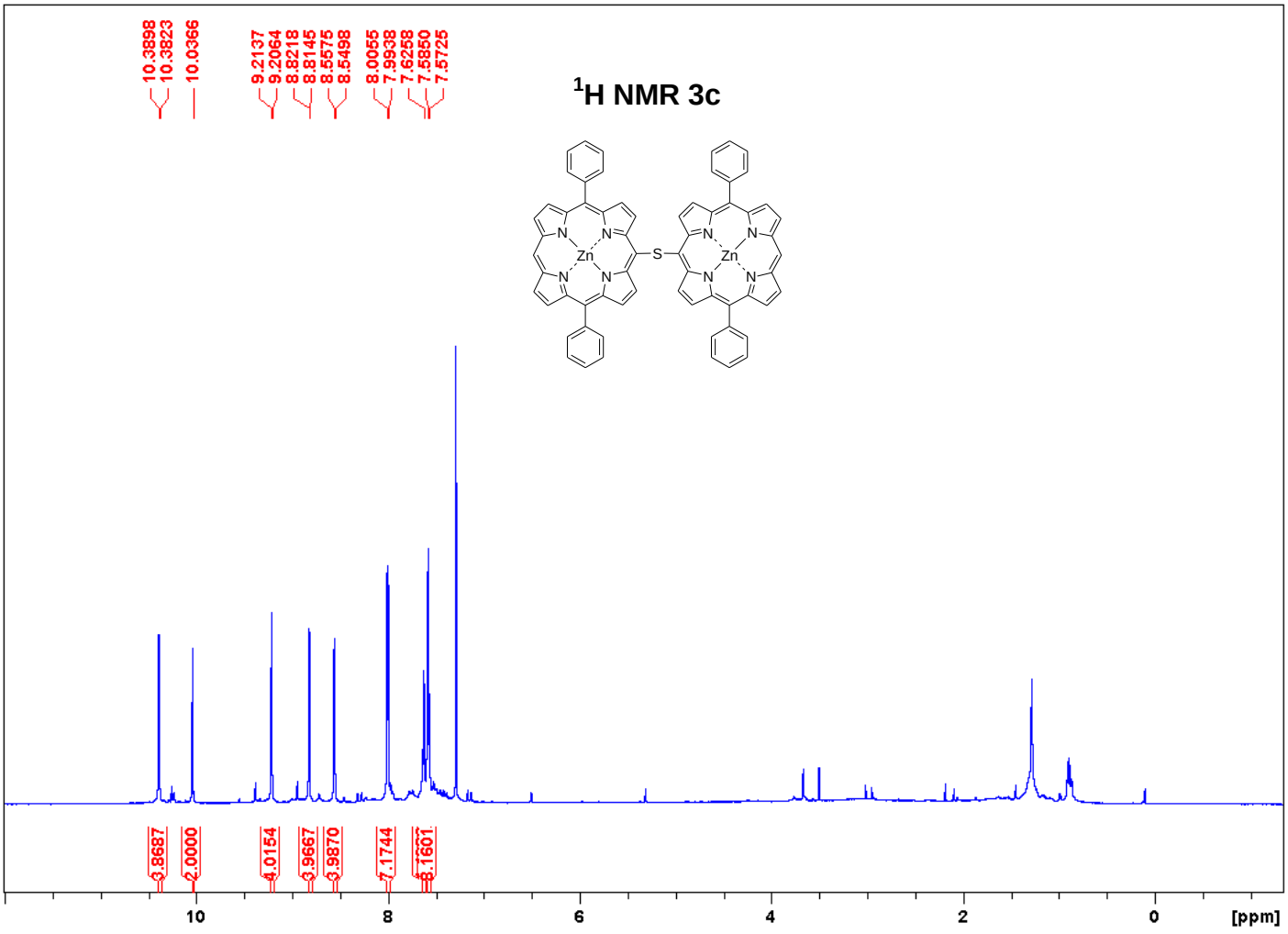
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8.0055
7.9938
7.6258
7.5850
7.5725
1H NMR 3c
Zn
Zn
S
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7.1744
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10
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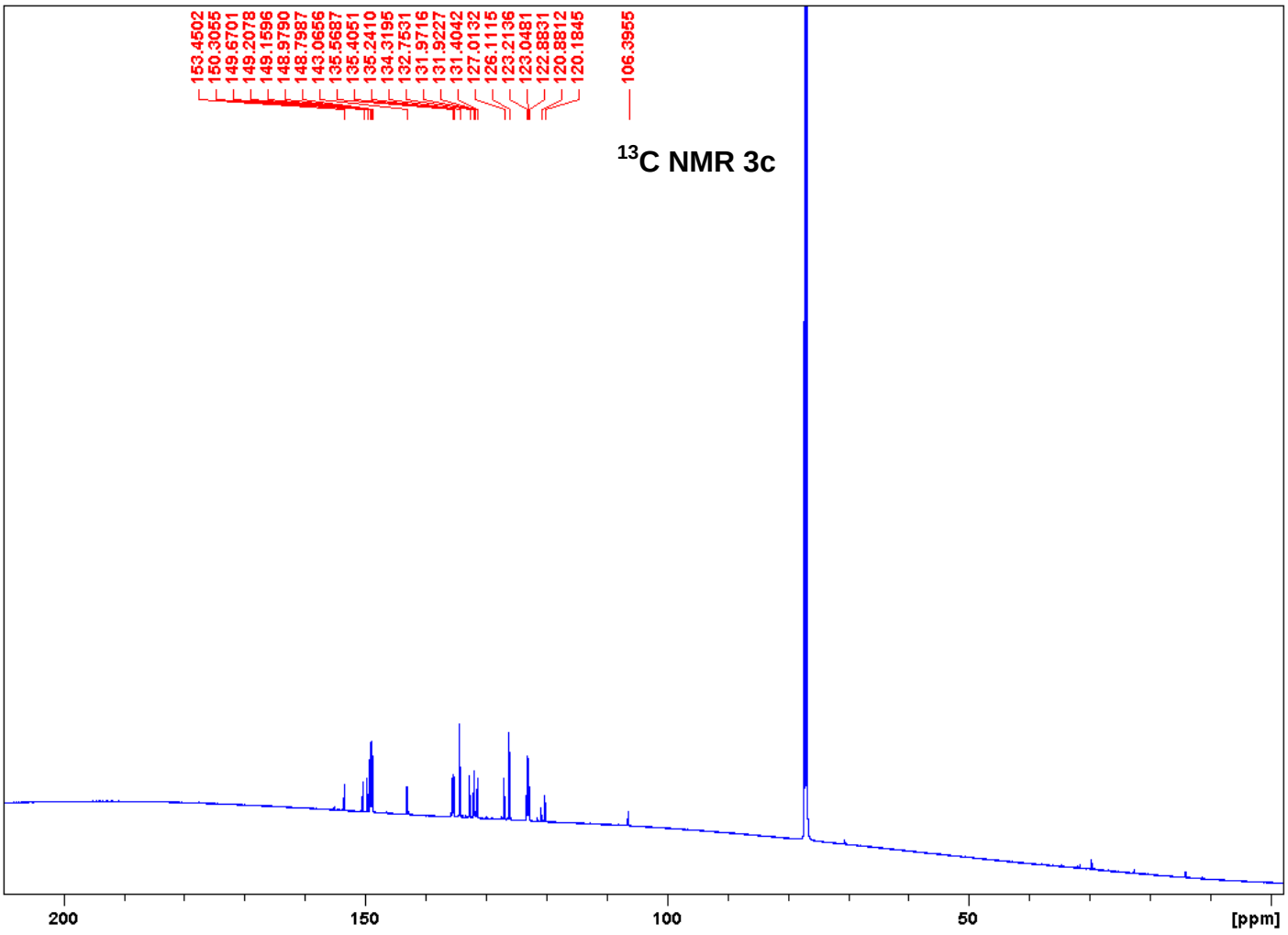
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134.3195
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131.9227
131.4042
127.0132
126.1115
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122.8831
120.8812
120.1845
106.3955
13C NMR 3c
200
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100
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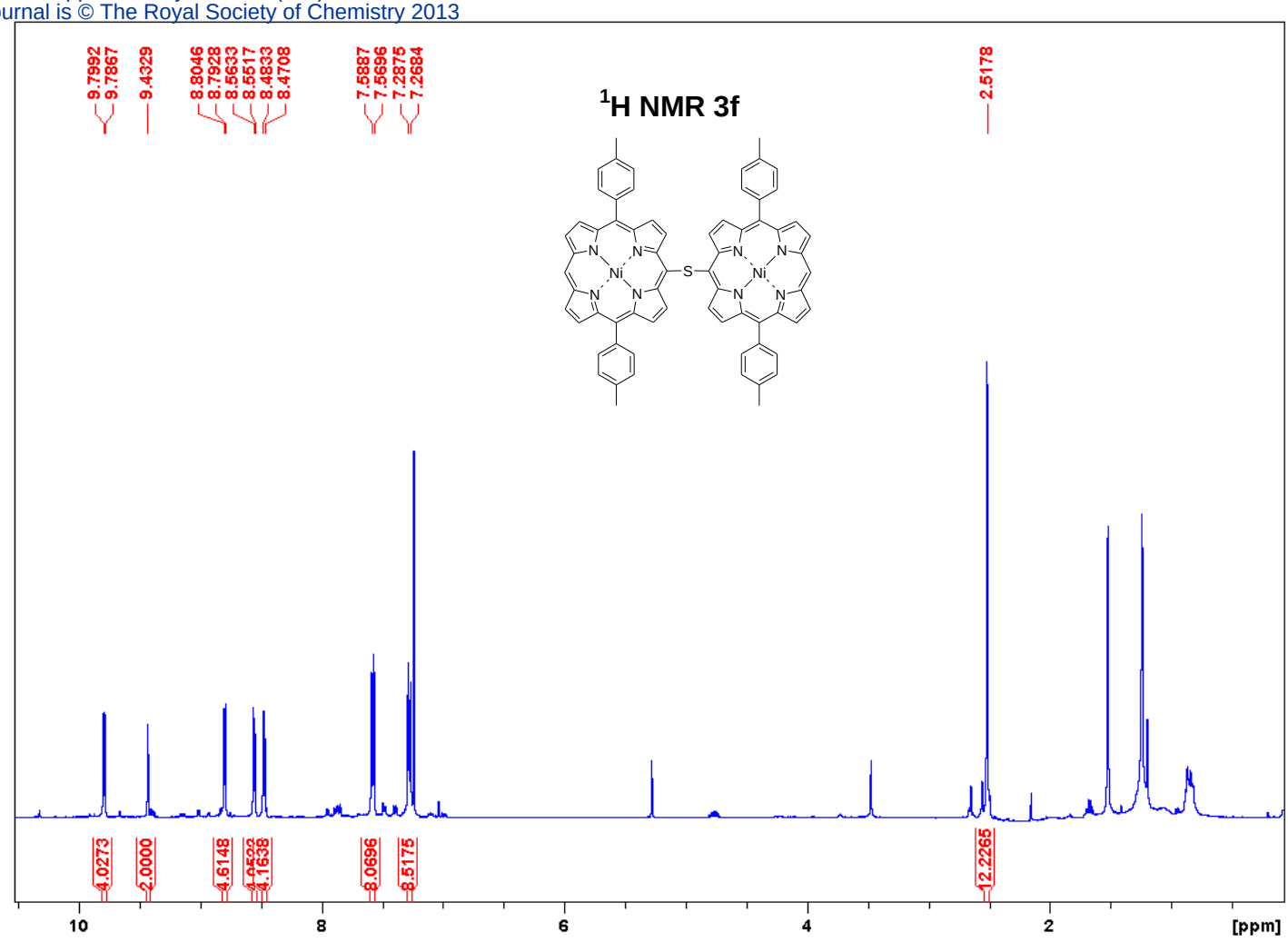
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8.5633
8.5517
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8.4708
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7.5696
7.2875
7.2684
2.5178
1H NMR 3f
Ni
S
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4
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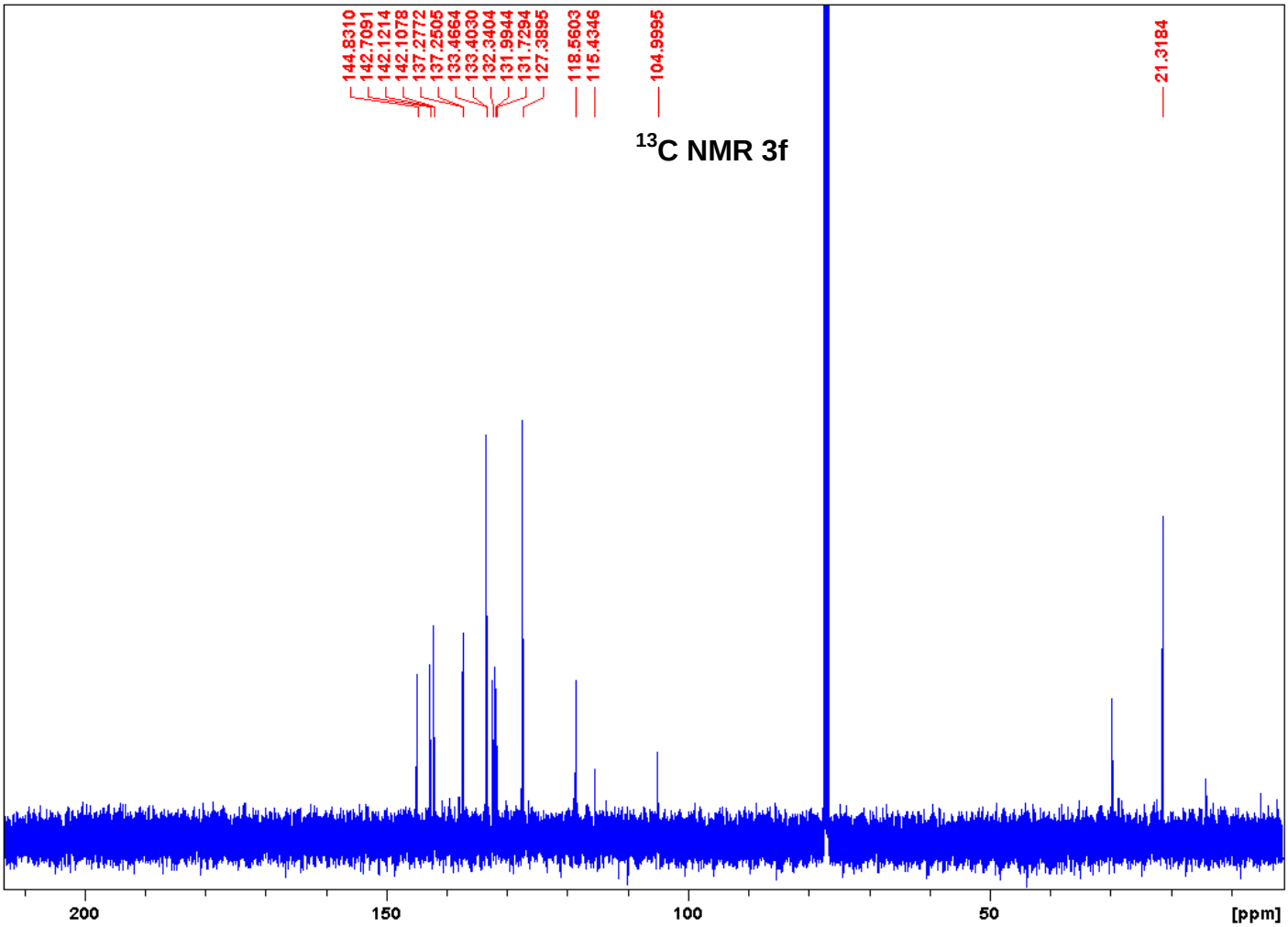
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118.5603
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104.9995
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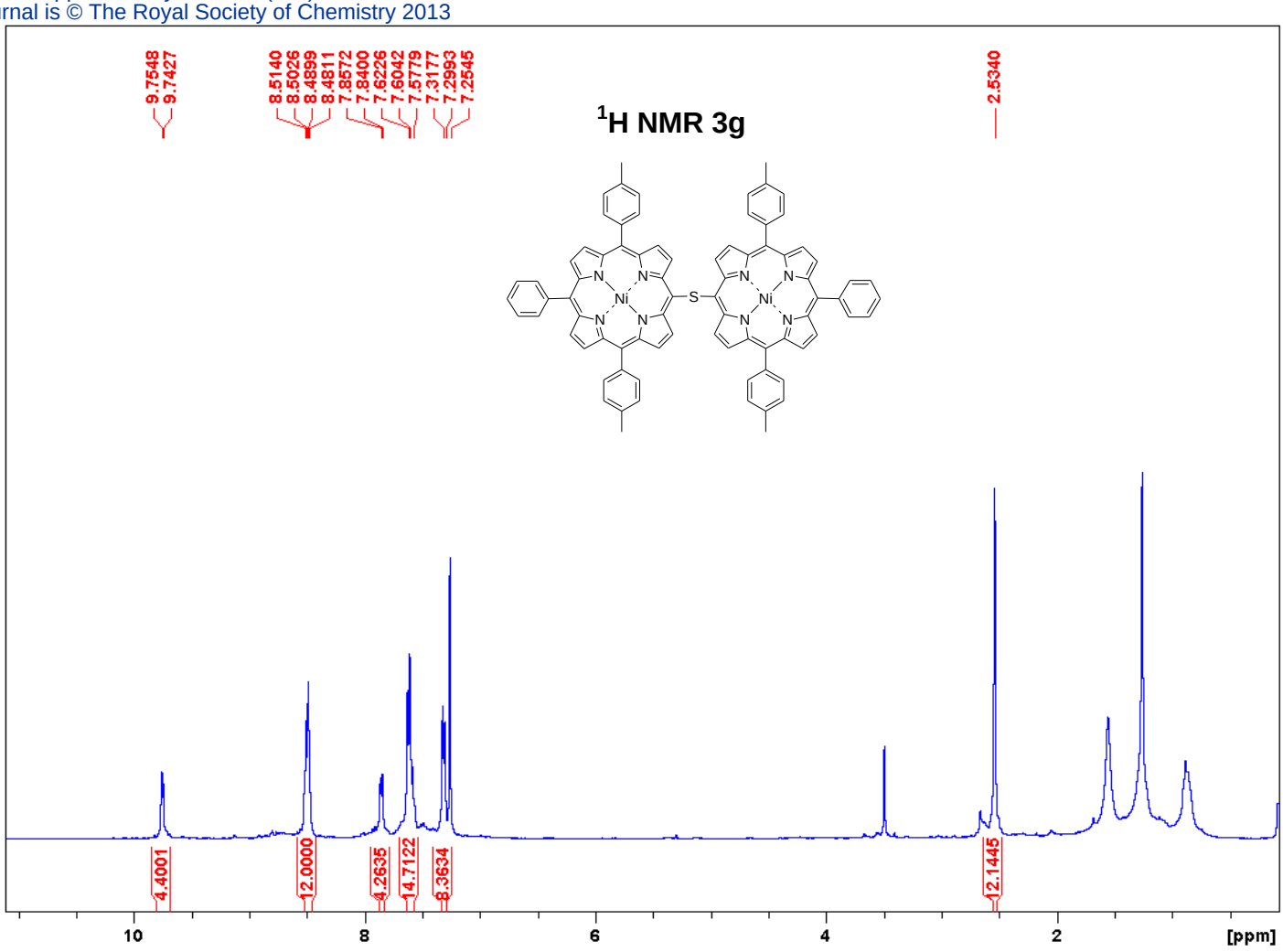
13C NMR 3f
200
150
100
50
[ppm]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7.6226
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7.5779
7.3177
7.2993
7.2545
2.5340
1H NMR 3g
Ni
Ni
S
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12.0000
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10
8
6
4
2
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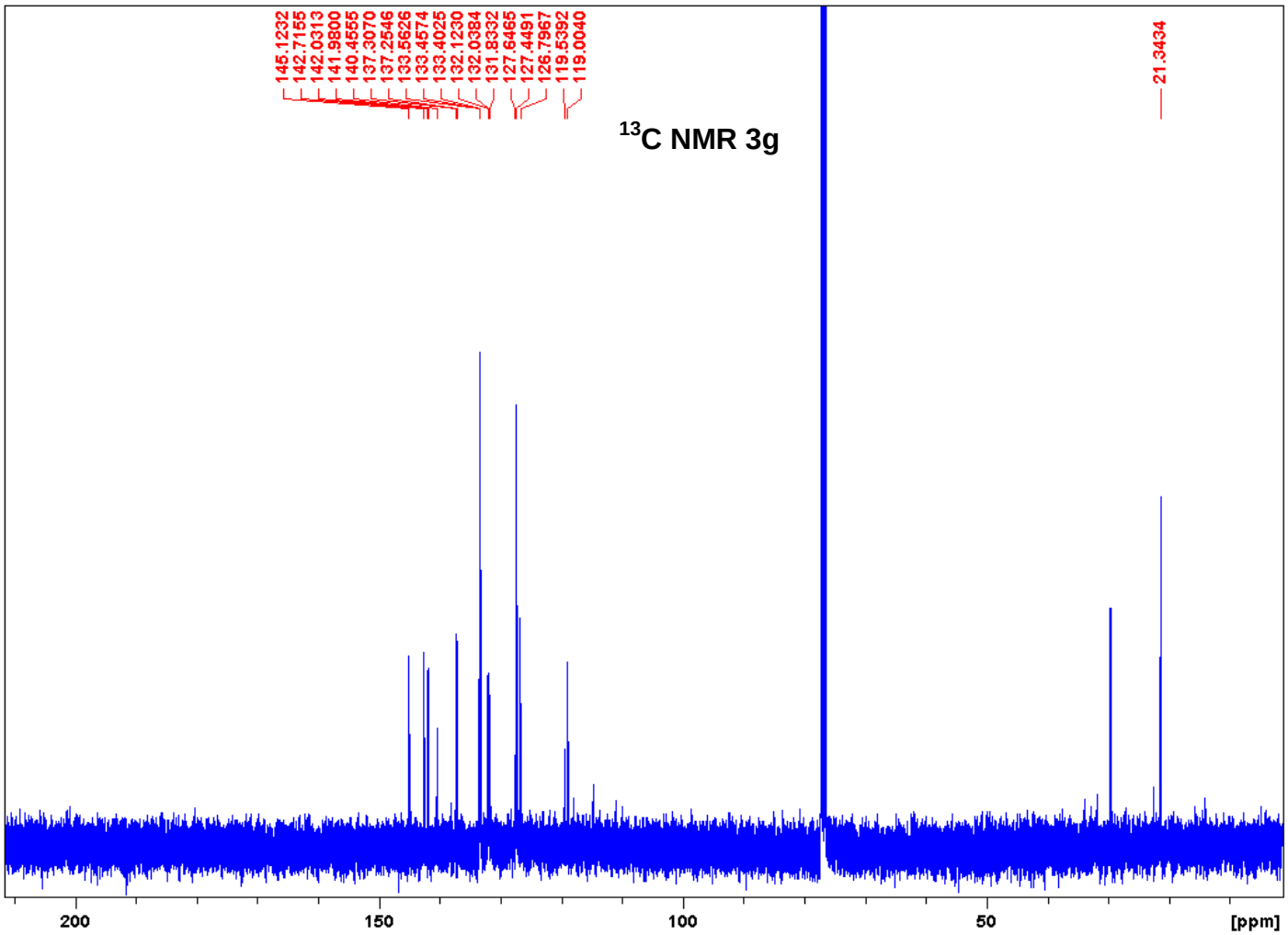
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13C NMR 3g
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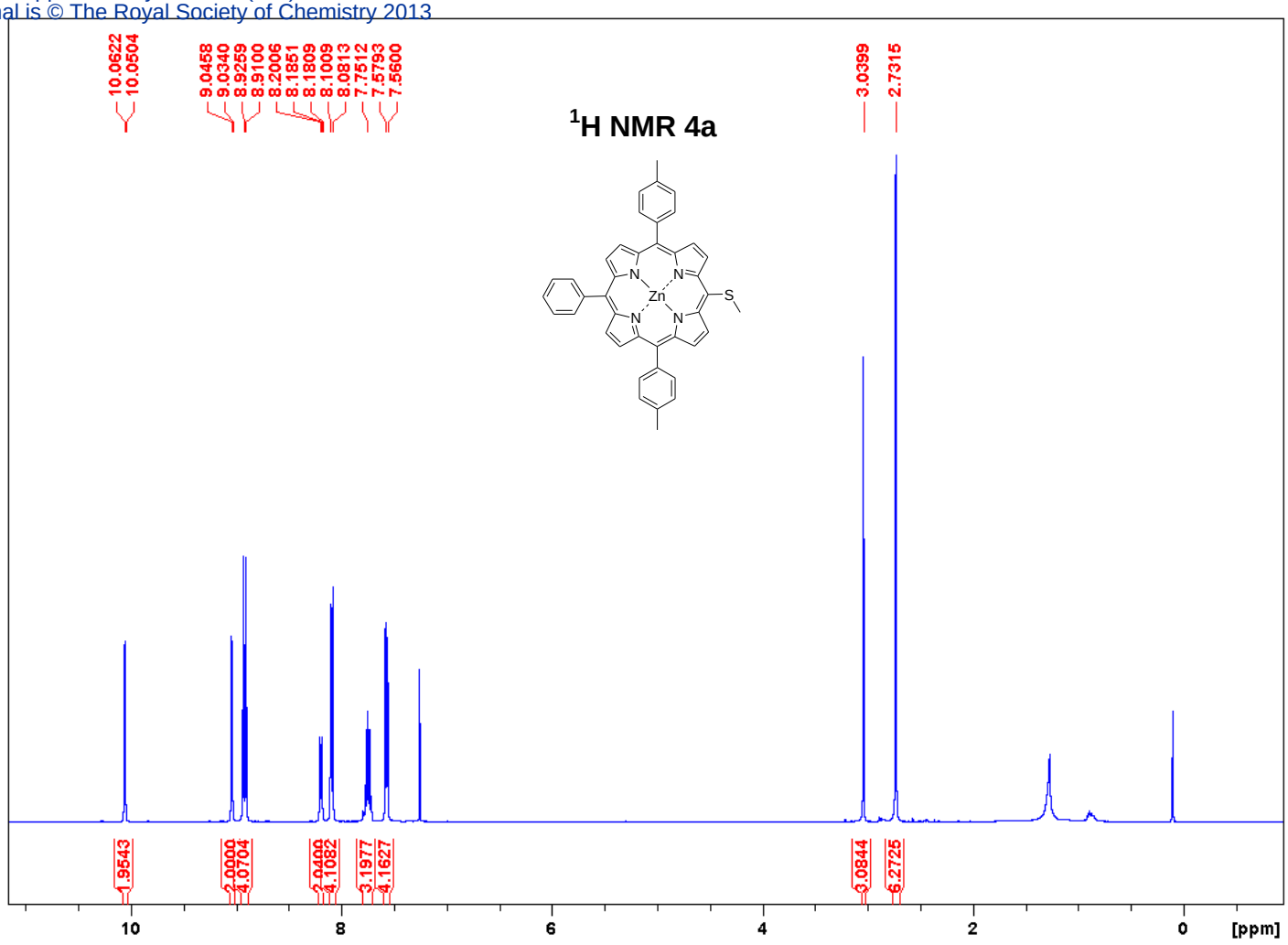
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8.1809
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8.0813
7.7512
7.5793
7.5600
3.0399
2.7315
1H NMR 4a
N
N
Zn
N
N
S
1.9543
2.0000
4.0704
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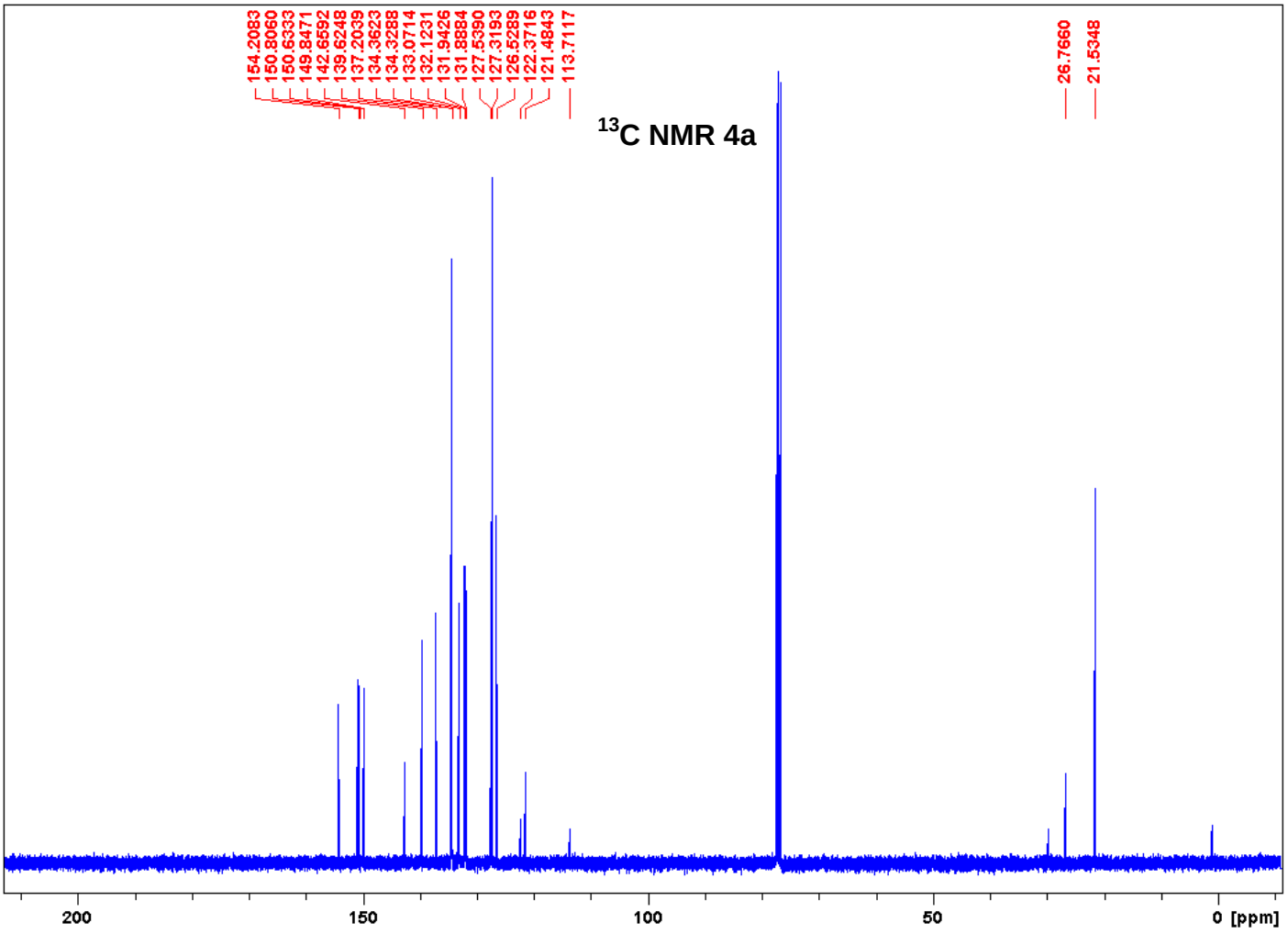
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127.5390
127.3193
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121.4843
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26.7660
21.5348
13C NMR 4a
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100
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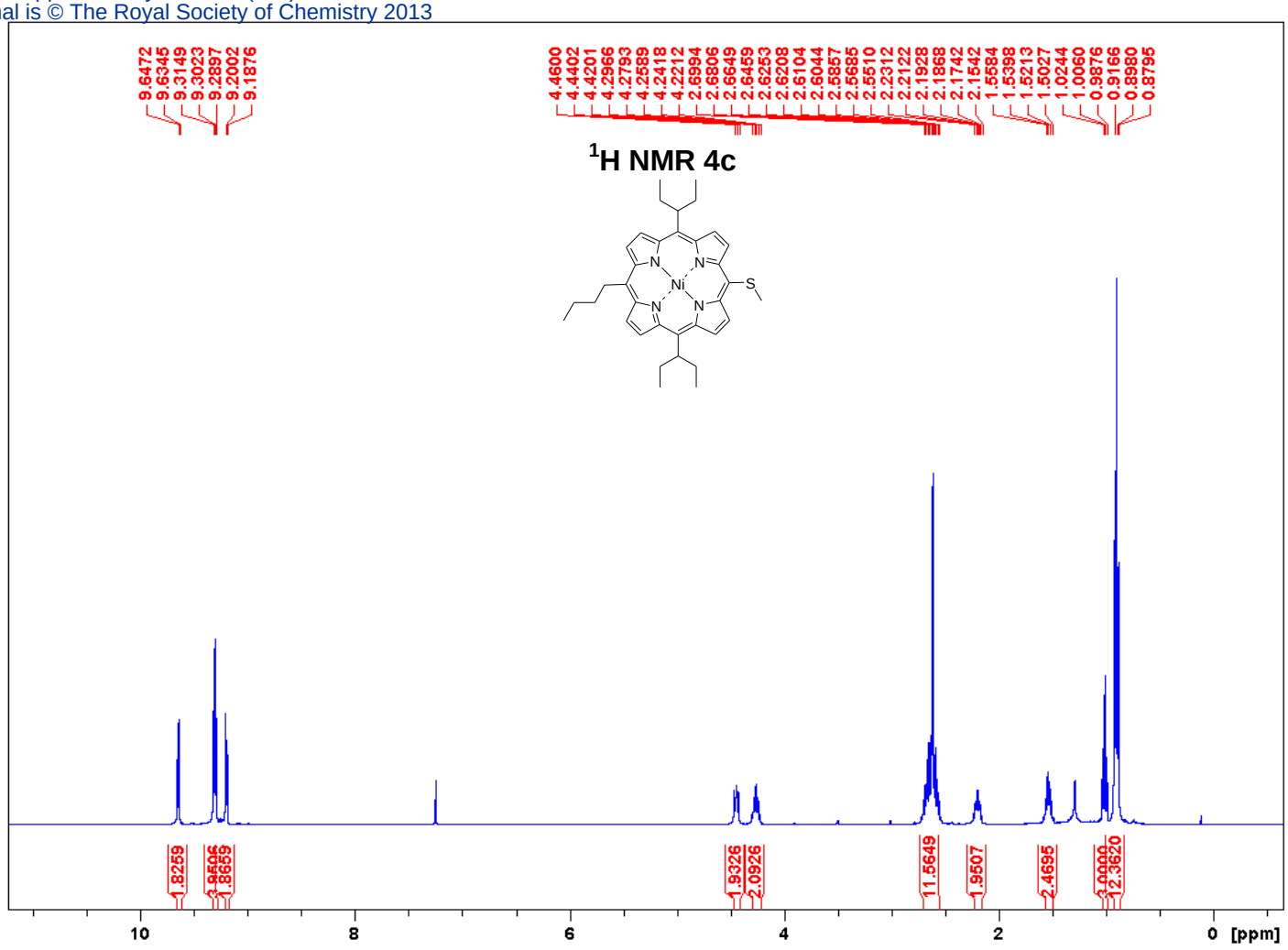
0 [ppm]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2.6208
2.6104
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2.1542
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1H NMR 4c
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N
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S
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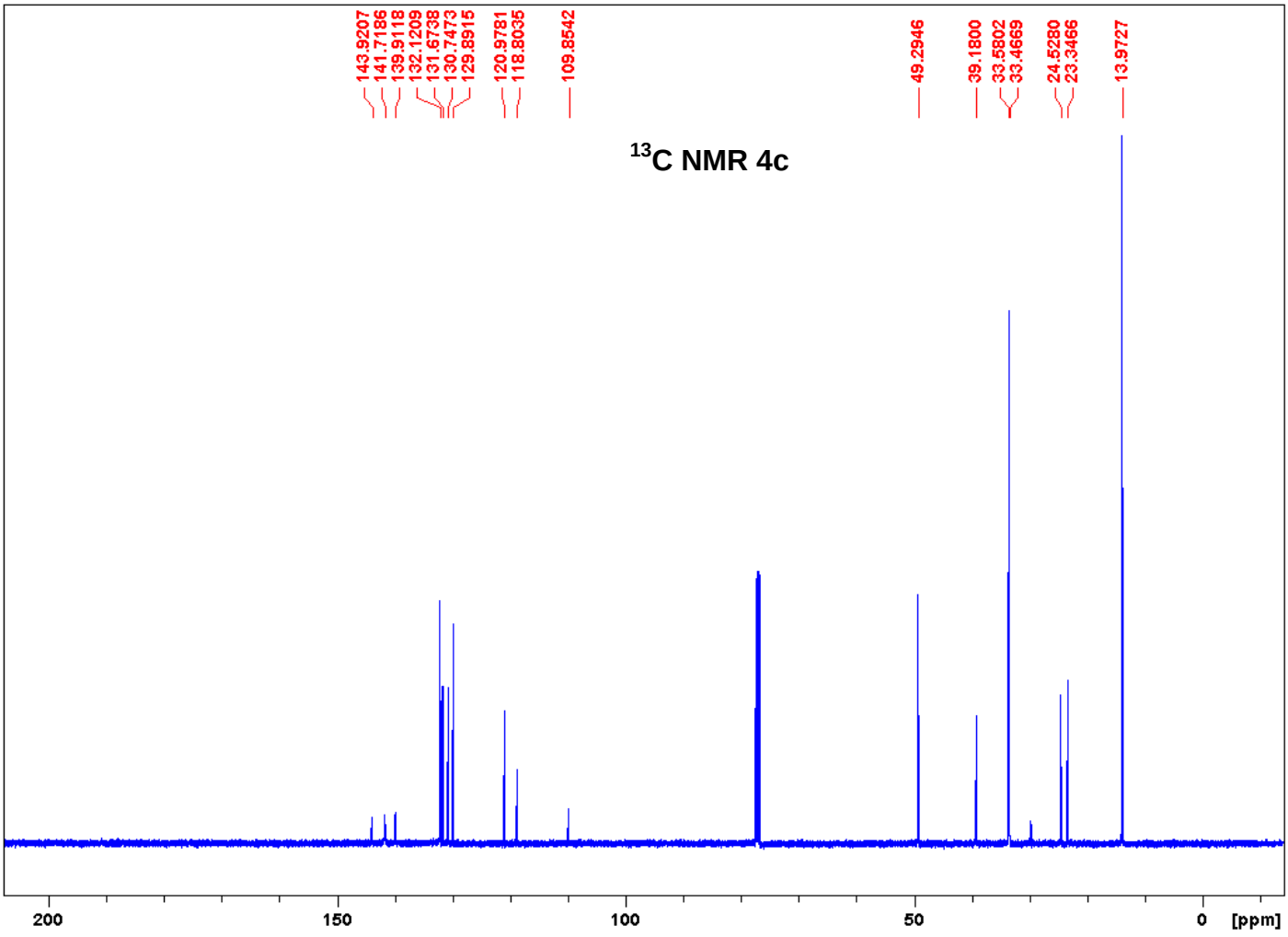
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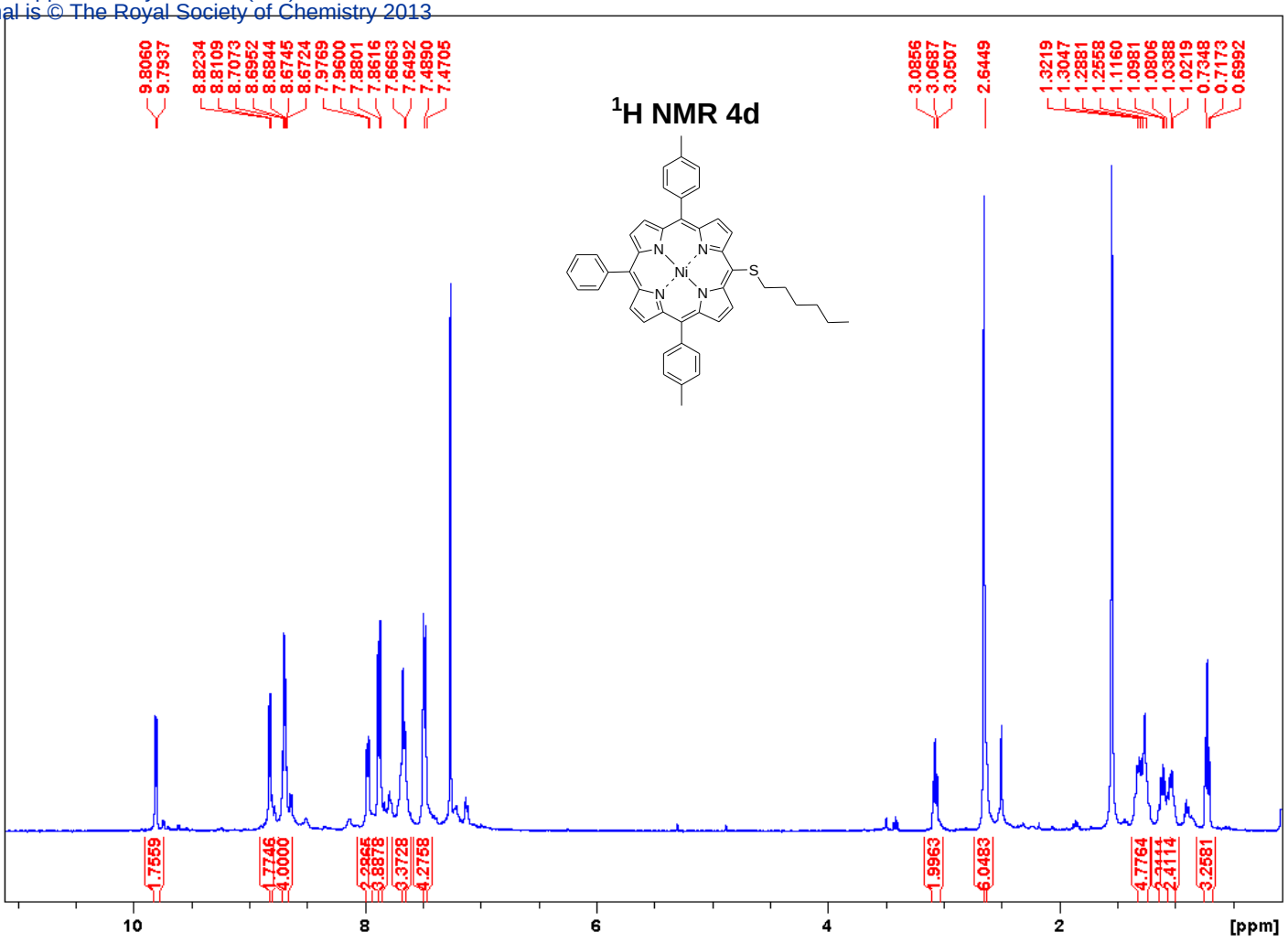
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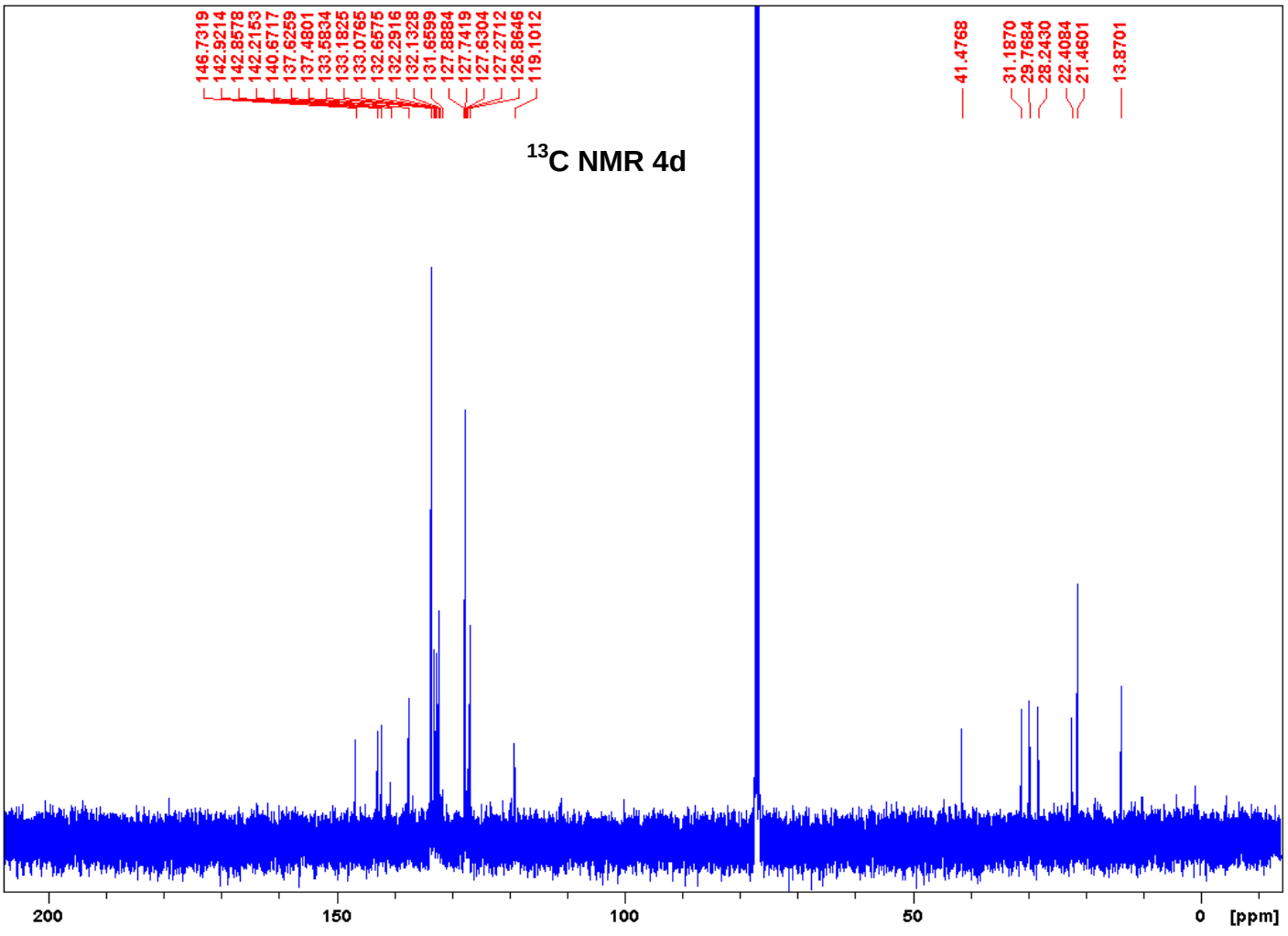
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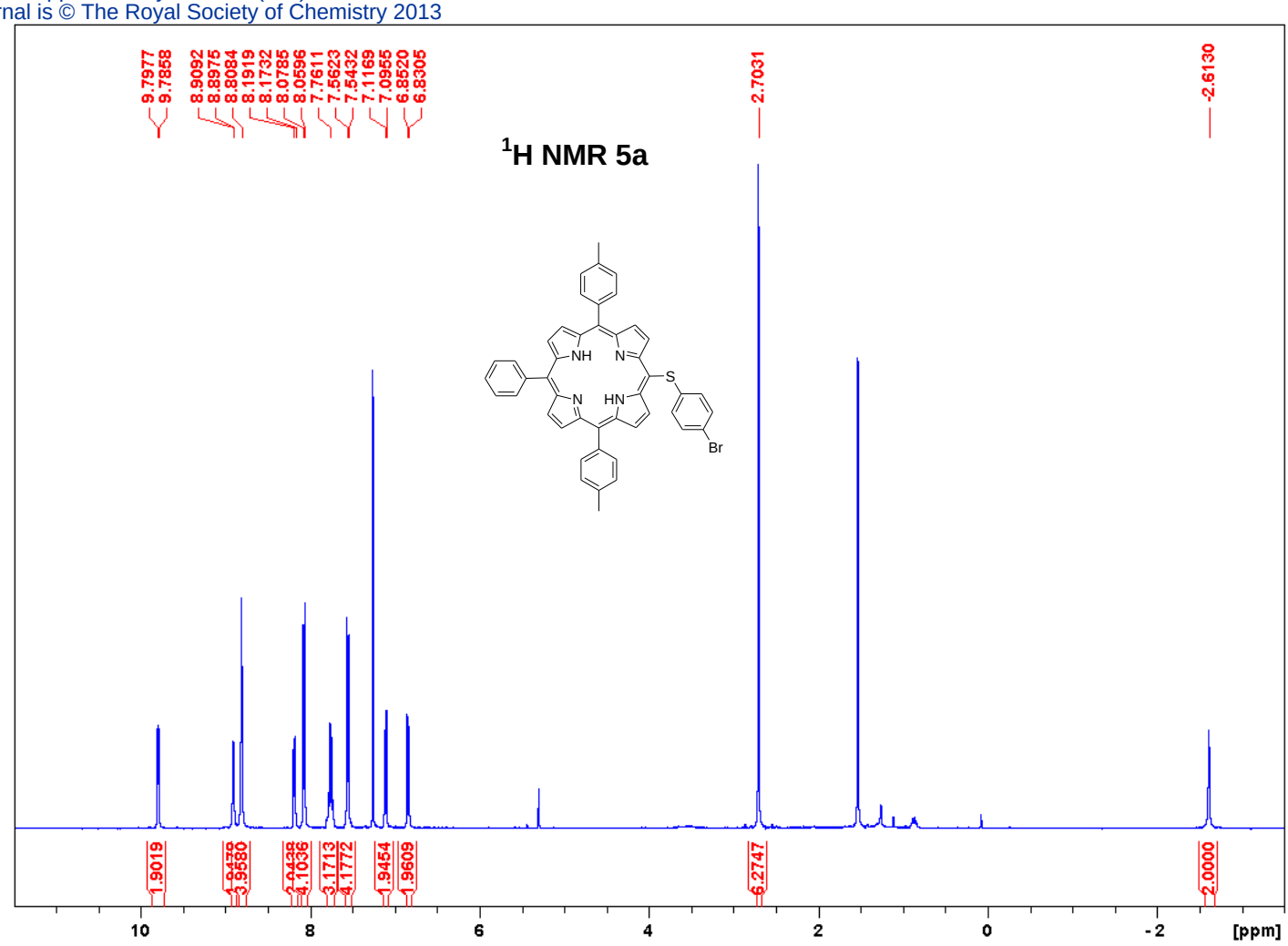
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6.8520
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1H NMR 5a
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N
HN
S
Br
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2.0438
4.1036
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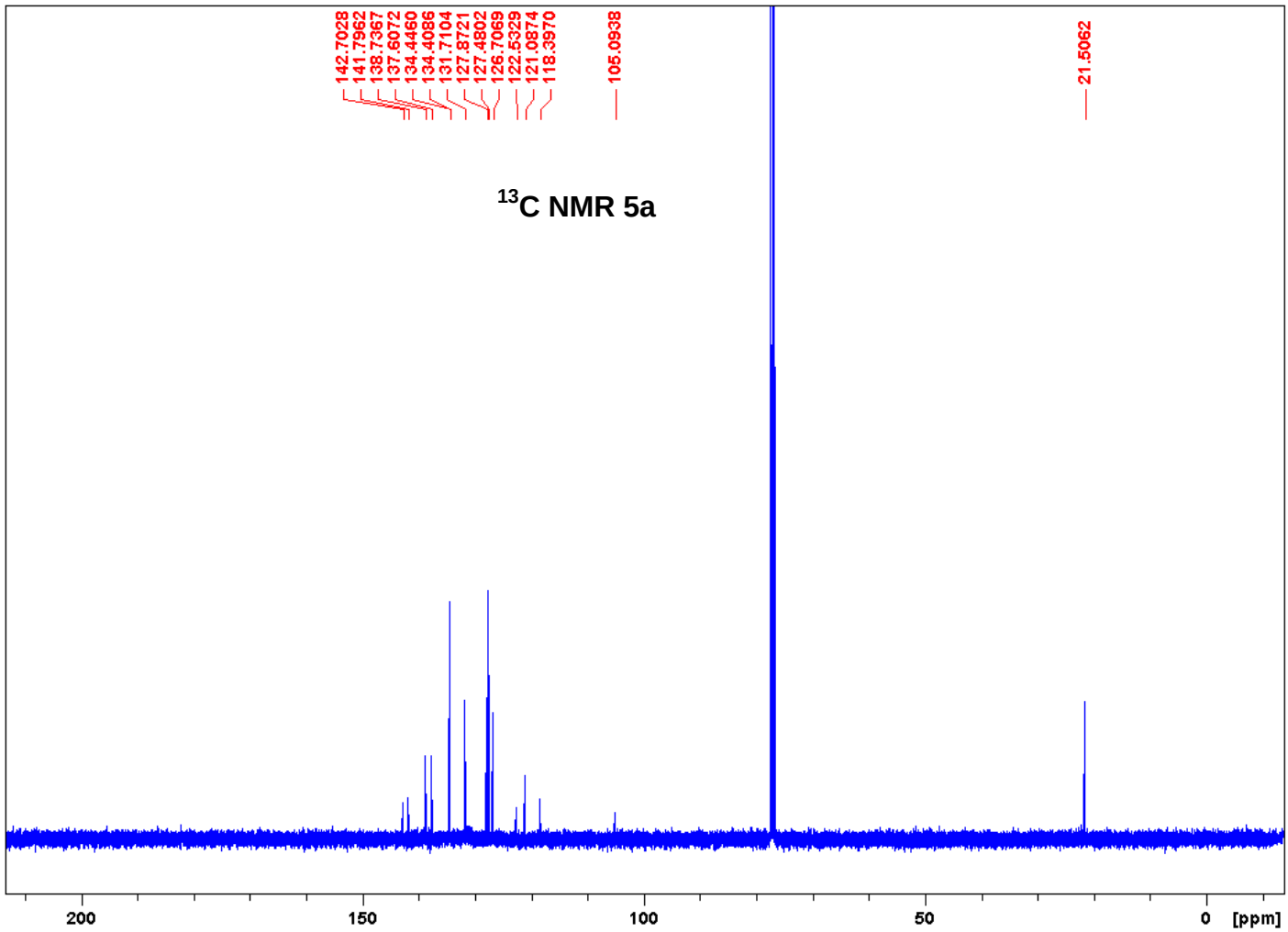
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122.5329
121.0874
118.3970
105.0938
21.5062
13C NMR 5a
200
150
100
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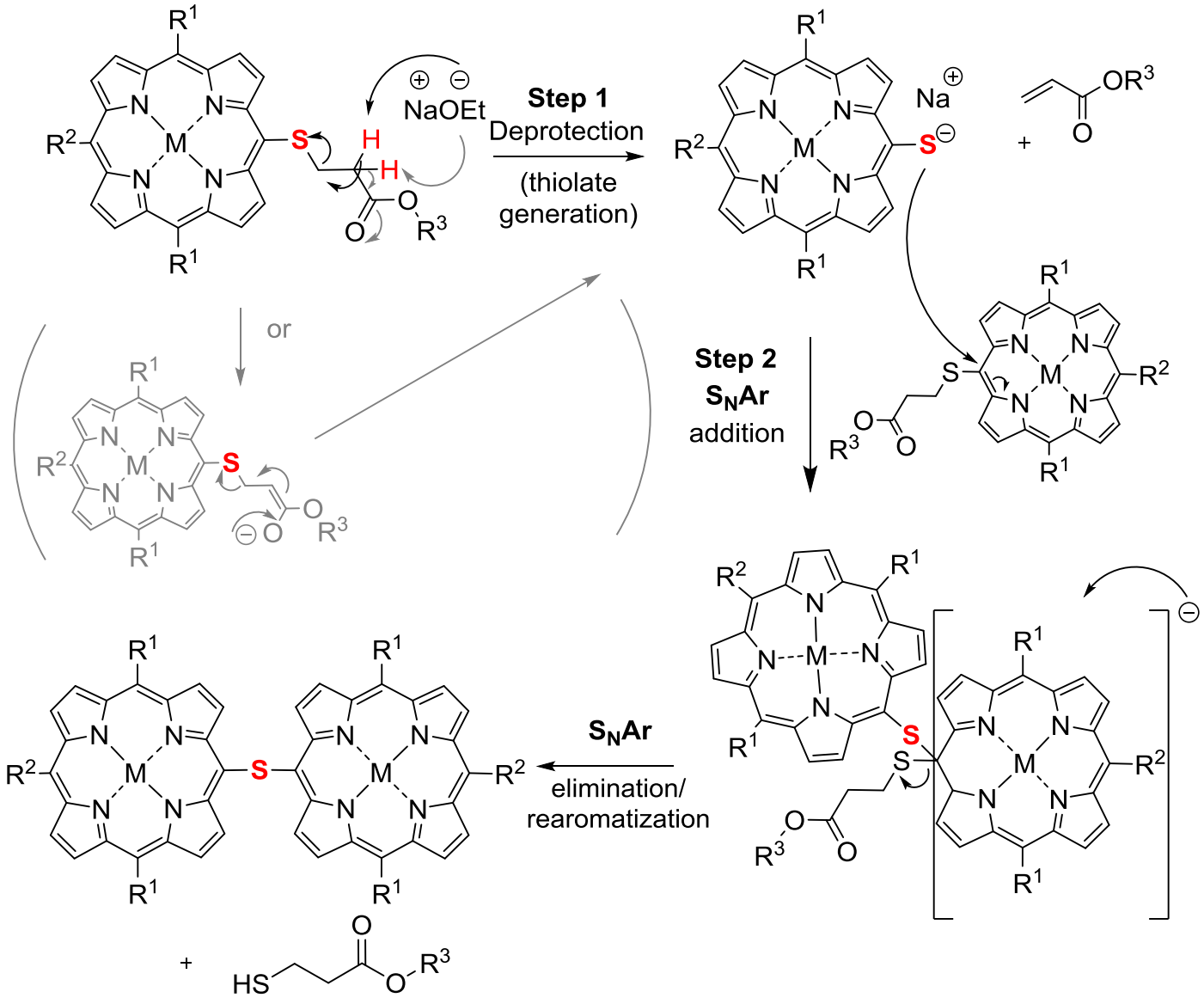
0
[ppm]

Proposed mechanism for the deprotection of the thioether chain and S_NAr for sulfur-linked bisporphyrin formation



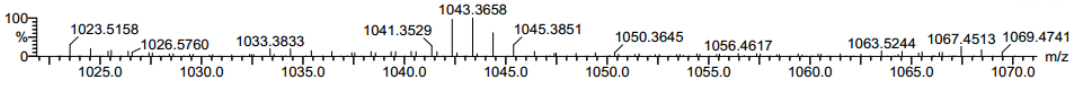
Distinguishing between sulfide- and disulfide-linked bisporphyrins 3e *via* HRMS and ^{1}H NMR

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
33 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-68 H: 0-50 N: 0-8 S: 0-2 Ni: 0-1

Aoife Ryan (MSe), AR717 in DCTB
Q-TOF20130228MF010 39 (0.720) AM (Cen,4, 80.00, Ht,10000.0,1570.68,0.70); Sm (SG, 5x5.00); Sb (15,10.00); Cm (24:88-(38:40+68:73))
28-Feb-2013
TOF MS LD+
1.60e+002



Minimum:				-1.5			
Maximum:		5.0	10.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
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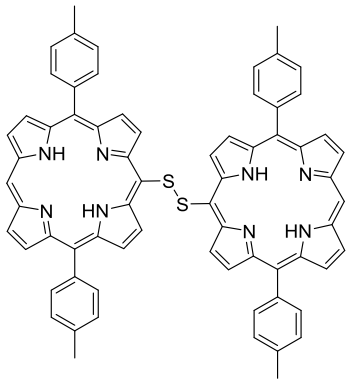


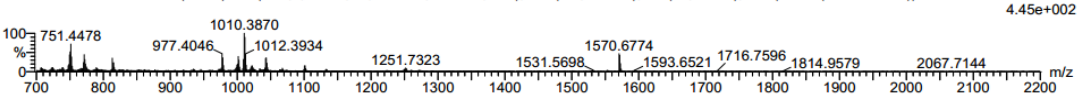
3e

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-68 H: 0-50 N: 0-8 S: 0-1 Ni: 0-1

Aoife Ryan (MSe), AR717 in DCTB
Q-TOF20130228MF010 39 (0.720) AM (Cen,4, 80.00, Ht,10000.0,1570.68,0.70); Sm (SG, 5x5.00); Sb (15,10.00); Cm (24:88-(38:40+68:73))
28-Feb-2013
TOF MS LD+
4.45e+002



Minimum:				-1.5			
Maximum:		5.0	10.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
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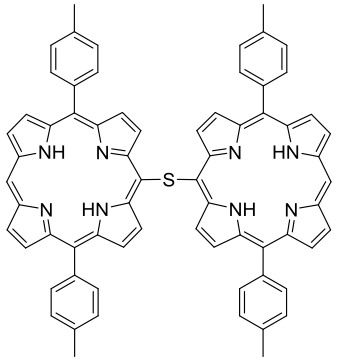
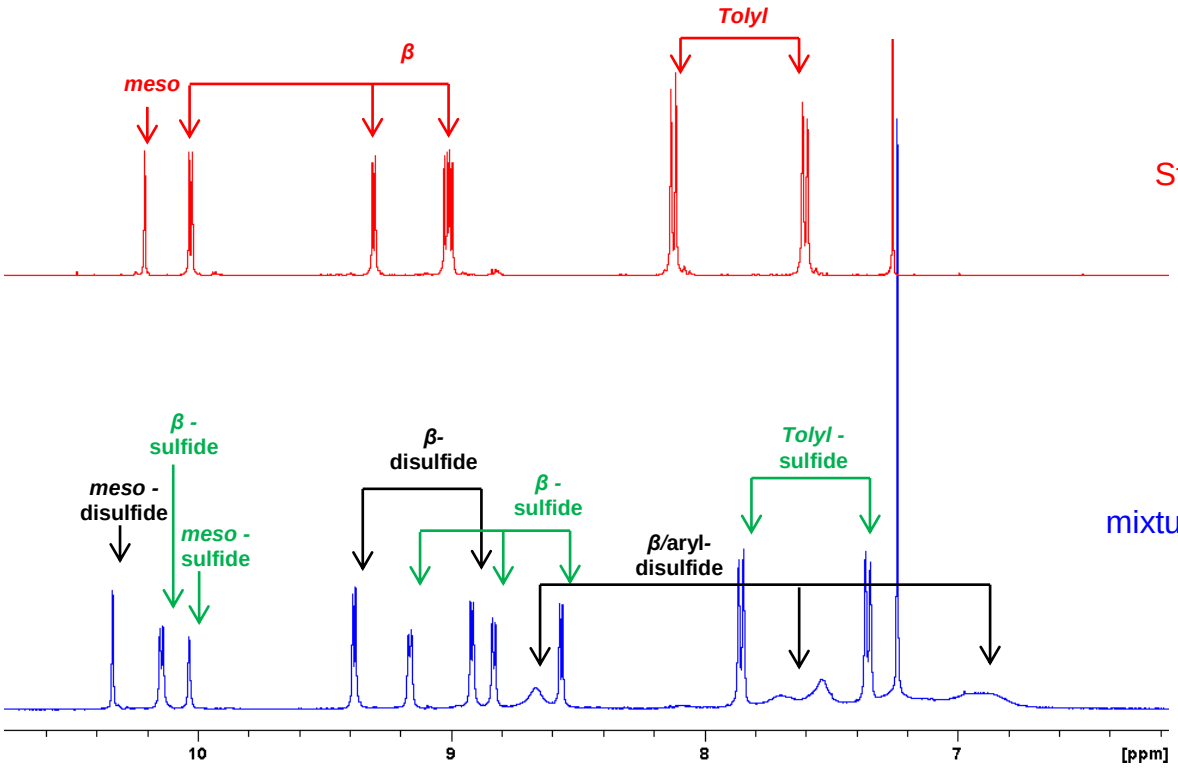


Mass spectra of **3e**: mixture of disulfide (i) and sulfide (ii) linked porphyrins



2e
Starting material

3e
mixture -S- and -S-S-

^{1}H NMR of aromatic regions of **2e** (protected thiol) and **3e** (mixture of sulfide and disulfide linked porphyrins) in $CDCl_3$ (400 MHz)

Compound **3e** contains an inseperable mixture of sulfide and disulfide linked bisporphyrins. In order to prove the presence of both materials, the HRMS and ^{1}H NMR spectra are presented on S-32. The parent ion peak at *m/z* 1042.3597 represents the disulfide linked dimer, whilst that showing a parent ion peak at *m/z* 1010.3870 indicates the sulfur linked dimer. Using ^{1}H NMR analysis, a comparison with starting material **2e** is shown and complete consumption is observed. For S-linked dimer **3e**, one set of *β*-signals, integrating for 4 protons, appears at 10.1 ppm, downfield from the meso signal and this is a common trait observed for all S-linked dimer bearing a free meso position (see ^{1}H NMR spectra of **3c** and **3f**). These reflect in inner *β*-protons and the opposite is observed for the disulfide linked dimer, whereby communication between the porphyrin units is less than that for the S-linked counterpart. Additionally, broad signals are observed for the aromatic signals in contrast to the S-linked dimer, whereby sharp signals were seen in all other compounds.

Crystal data for sulphur-linked bisporphyrin 3b

Crystal data: $C_{79}H_{52}N_8O_2SZn_2$•$0.5CH_3OH$, M = 1326.12, triclinic, space group $P\bar{1}$, a = 12.2362(6), b = 15.0184(7), c = 17.9322(9) Å, α = 99.999(2)°, β = 103.404(1)°, γ = 93.376(1)°, V = 3140.0(3) Å^3, Z = 2, T = 104 K, μ (MoK$_\alpha$) = 0.856 cm^{-1}, 26768 reflections measured, 10863 unique reflections measured (R_{int} = 0.025), 875 parameters, 8742 reflections with $I > 2.0\sigma(I)$, refinement against $|F^2|$, $R_1(I > 2.0\ \sigma\ (I))$ = 0.0855, wR_2 (all data) = 0.2226, S = 1.05, ρ_{max} = 5.99. The structure shows disorder of one axial methanol and one phenyl residue, both of which were refined with 50 % occupancy. A methanol of solvation was refined with 50 % occupancy. The residual electron density is located close to the S atom (0.8 Å). CCDC 951823.