

NIR Bacteriochlorin Chromophores Accessed by Heck and Sonogashira Cross-Coupling Reactions on a Tetrabromobacteriochlorin Derivative

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Technical Information

All reagents were purchased from Sigma-Aldrich, Vetec or Synth. When necessary, solvents and reagents were purified by routine methods.¹ ¹H-NMR, ¹³C-NMR and 2D experiments (gHSQC (¹H/¹³C), gHMBC (¹H/¹³C) and NOESY) were performed on a Bruker AVANCE 400 operating at 400.15 MHz (¹H) and 100.62 MHz (¹³C). CDCl₃ was used as solvent and tetramethylsilane (TMS) as internal reference. The chemical shifts are presented in δ (ppm) and the coupling constants (J) in Hertz (Hz). Compounds **7**^{2,3} and **13**⁴ were synthesized according to the literature.

The UV-Vis spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer using 1 cm optical length quartz cuvettes at 25°C and CH₂Cl₂ (HPLC grade) as solvent.

Fluorescence emission spectra were recorded on a Shimadzu RF-5301PC spectrofluorometer using 1 cm optical length cuvettes at 25°C and toluene (HPLC grade) as solvent.

Liquid chromatography was performed with silica-gel 70-230 mesh. Only compound **11** was purified using silica-gel 230-400 mesh. Analytical thin layer chromatography was performed on 20 x 20 cm Aluminium sheets (1mm thick)-Merck TLC silica-gel 60 F₂₅₄.

HRMS-ESI-TOF analyses of all compounds, except **17** and **19**, were performed on a Bruker Daltonics MicroTOF Q II spectrometer with capillary: 3.500 V, nebulizer gas pressure: 0.4 Bar, dry gas flow: 4.0 L/min and dry gas temperature: 180°C.

HRMS-ESI-TOF analysis of compound **17** was performed on a Bruker Daltonics MicroTOF Ic spectrometer with capillary: 4.000 V, nebulizer gas pressure: 0.4 Bar, dry gas flow: 5.0 L/min and dry gas temperature: 180°C.

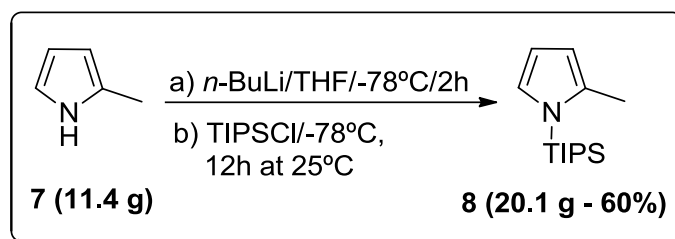
HRMS-MALDI-TOF analysis of compound **19** was performed on a Bruker Daltonics MALDI-TOF/TOF Ultraflex extreme with PIE: 110 ns, laser frequency: 1.000 Hz, IS1: 25 kV and IS2: 22.4 kV.

All DFT calculations were performed with the Gaussian 09 suite of programs using an ultrafine grid.⁵ Full optimization of ground-state geometries and population analyses were performed employing the B3LYP⁶ hybrid functional with standard 6-

31G(d) basis set for all atoms. Frequency calculations at 295.15 K (1 atm) ensured that the stationary points represent minima (no imaginary frequency) in potential energy surface. Absorption spectra were computed as vertical excitation employing the B3LYP/6-31G(d) ground-state geometries using the time-dependent DFT (TD-DFT). We considered the PBE0 functional⁷ in conjunction with 6-31+G(d,p) basis set and IEF-PCM solvent effect in CH₂Cl₂. The first 60 excited states were calculated in order to ensure that both Q- and B-bands regions are covered. All plotted orbitals and geometries were made with Gabedit.⁸ The calculated UV-VIS electronic absorption spectra were plotted with Gaussview 5.⁹

1. Synthesis

1.1. 2-methyl-1-(triisopropylsilyl)-1*H*-pyrrole (**8**)

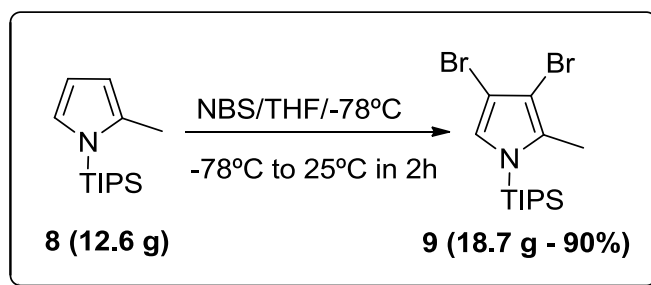


A solution of pyrrole **7** (11.4 g, 141 mmol) in anhydrous THF (100 mL) under argon atmosphere was cooled to -78°C . *n*-Butyllithium (60 mL of 2.5 M solution in hexanes, 150 mmol) was added drop-wise and the mixture was stirred for 2h at the same temperature. TIPSCl (33.0 mL, 150 mmol) was added and the mixture was slowly warmed up to room temperature over a period of 2h and stirred overnight. The mixture was concentrated to about one thirtieth of the initial volume using a N_2 flow, poured into water (200 mL) and extracted with hexane (2X 200 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure at 25°C . The crude product was purified by passing it through a plug of silica-gel (70-230 mesh) and eluted with hexanes. The desired product was obtained as a colourless oil (20.1 g, 84.5 mmol) in 60% yield.

HRMS-ESI-TOF: m/z calcd for $\text{C}_{14}\text{H}_{27}\text{NSi}$ [$\text{M} + \text{H}$] $^{+}$ 238.1991; found 238.1993.

^1H NMR (CDCl_3 , 400.15 MHz) δ (ppm): 1.12 (d, $J = 8.0$ Hz, 18H), 1.52 (sept, $J = 8.0$ Hz, 3H), 2.33 (s, 3H), 6.00 (s, 1H), 6.15 (t, $J = 2.1$ Hz, 1H), 6.74 (q, $J = 2.1$ Hz, 1H). **^{13}C NMR** (CDCl_3 , 100.62 MHz) δ (ppm): 12.9, 15.5, 18.2, 109.2, 110.9, 124.9, 133.3.

1.2. 3,4-dibromo-2-methyl-1-(triisopropylsilyl)-1H-pyrrole (9)



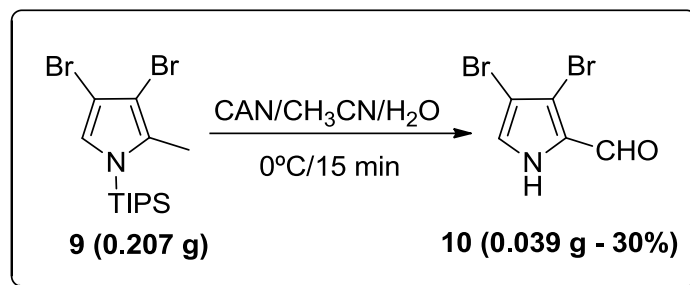
A solution of pyrrole **8** (12.6 g, 52.9 mmol) in anhydrous THF (80 mL) was cooled to -78°C and NBS (19.0 g, 106 mmol) was added. The mixture was warmed up to room temperature over a period of 2h. The mixture was diluted with cold hexane (200 mL) and washed with NaHCO₃ (saturated solution, 3x 200 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was purified by passing it through a plug of silica-gel (70-230 mesh) and eluted with hexanes. The desired product was obtained as a white solid (18.7 g, 47.3 mmol) in 90% yield.

M.P.: 64.6-66.0°C. Literature: 63°C.¹⁰

HRMS-ESI-TOF: m/z calcd for C₁₄H₂₅Br₂NSi [M + H]⁺ 396.0181; found 396.0176.

¹H NMR (CDCl₃, 400.15 MHz) δ (ppm): 1.12 (d, *J*= 7.5 Hz, 18H), 1.49 (sept, *J*= 7.6 Hz, 3H), 2.31 (s, 3H), 6.74 (s, 1H). **¹³C NMR** (CDCl₃, 100.62 MHz) δ (ppm): 12.8, 14.5, 18.0, 99.8, 102.0, 123.1, 131.1.

1.3. 3,4-dibromo-1*H*-pyrrole-2-carbaldehyde (**10**)



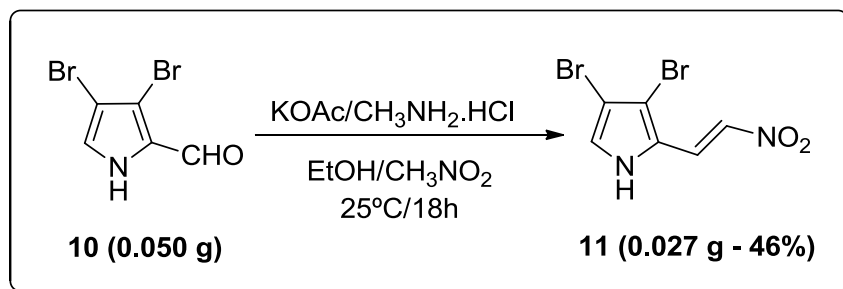
A solution of pyrrole **9** (207 mg, 0.52 mmol) in 18 mL of a mixture of CH₃CN/H₂O (5:1, v/v) was cooled to 0°C and CAN (2.16 g, 3.86 mmol) was added. The mixture was stirred for 15 min at the same temperature. The reaction was quenched by the addition of NaHCO₃ (saturated solution, 50 mL) and extracted with EtOAc (2X 30 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was purified by column chromatography using silica-gel (70-230 mesh) and hex: EtOAc (8:2) as eluent. Compound **10** was obtained as a yellow solid (39.4 mg, 0.16 mmol) in 30% yield.

M.P.: Unstable above 130°C.

HRMS-ESI-TOF: *m/z* calcd for C₅H₃Br₂NO [M + Na]⁺ 275.8459; found 275.8452.

¹H NMR (acetone-*d*₆, 400.15 MHz) δ (ppm): 7.46 (d, *J* = 1.0 Hz, 1H), 9.58 (d, *J* = 1.0 Hz, 1H), 11.55 (br.s, 1H). **¹³C NMR** (acetone-*d*₆, 100.62 MHz) δ (ppm): 101.8, 110.1, 126.9, 130.8, 178.6).

1.4. (*E*)-3,4-dibromo-2-(2-nitrovinyl)-1*H*-pyrrole (**11**)



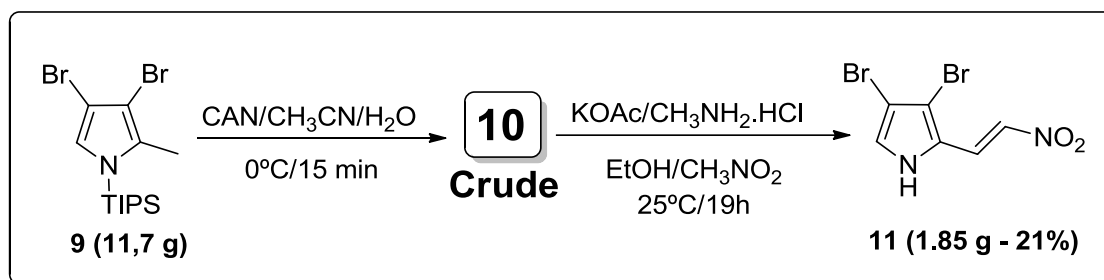
To a solution of pyrrole **10** (50.0 mg, 0.20 mmol) in anhydrous EtOH (1.0 mL), CH₃NH₂.HCl (10.7 mg, 0.16 mmol), KOAc (15.7 mg, 0.16 mmol) and CH₃NO₂ (32 μ L, 0.59 mmol) were added in this sequence. The mixture was stirred for 18h at room temperature, and then poured into water (10 mL) and extracted with EtOAc (2X 10 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 30°C. The crude product was purified by column chromatography using silica-gel (230-400 mesh) and hex: EtOAc (8:2) as eluent. Compound **11** was obtained as a yellow solid (27.0 mg, 0.09 mmol) in 46% yield.

M.P.: Unstable above 135°C.

HRMS-ESI-TOF: *m/z* calcd for C₆H₄Br₂N₂O₂ [M + H]⁺ 296.8697; found 296.8692.

¹H NMR (acetone-*d*₆, 400.15 MHz) δ (ppm): 7.46 (s, 1H), 7.87 (d, *J*= 13.6 Hz, 1H), 7.92 (d, *J*= 13.6 Hz, 1H), 11.66 (br.s, 1H). **¹³C NMR** (acetone-*d*₆, 100.62 MHz) δ (ppm): 102.5, 109.6, 126.4, 126.5, 126.7, 134.5.

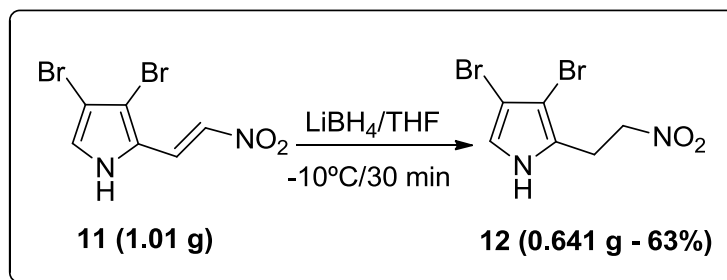
1.5. Obtainment of pyrrole 11 directly from pyrrole 9



1° Step: a solution of pyrrole **9** (11.7 g, 29.6 mmol) in 1.06 L of a mixture of CH₃CN/H₂O (4:1, v/v) was cooled to 0°C, and CAN (123 g, 220 mmol) was added. The mixture was stirred for 15 min at the same temperature. The reaction was quenched by the addition of NaHCO₃ (saturated solution, 0.6 L) and filtered under vacuum using a sintered funnel. The yellow solid was washed with EtOAc (200 mL). The organic layer was washed with NaCl (saturated solution, 2X 200 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was used without further purification in the next step.

2° Step: Crude **10** was solubilized in EtOH (24 mL), followed by the addition of CH₃NH₂·HCl (1.60 g, 23.7 mmol), KOAc (2.33 g, 23.7 mmol) and CH₃NO₂ (1.60 mL, 29.6 mmol). The mixture was stirred for 19h at room temperature, poured into water (100 mL) and extracted with EtOAc (2X 100 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 30°C. The crude product was purified by column chromatography using silica-gel (230-400 mesh) and hex:EtOAc (8:2) as eluent. Compound **11** was obtained as a yellow solid (1.85 g, 6.25 mmol) in 21% overall yield.

1.6. 3,4-dibromo-2-(2-nitroethyl)-1H-pyrrole (12)

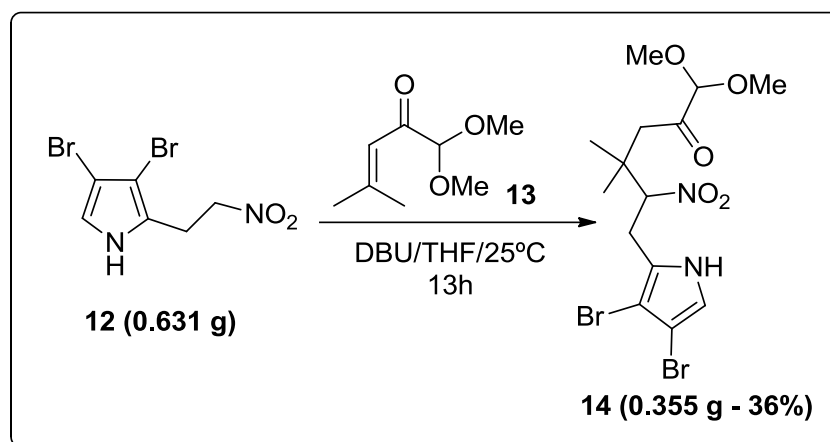


A solution of pyrrole **11** (1.01 g, 3.40 mmol) in anhydrous THF (20 mL) under argon atmosphere was cooled to -10°C and LiBH₄ (117 mg, 5.10 mmol) was added. The mixture was stirred at the same temperature for 30 min, quenched with NH₄Cl (saturated solution, 50 mL) and extracted with EtOAc (2X 50 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was purified by column chromatography using silica-gel (70-230 mesh) and hex: EtOAc (8:2) as eluent. Compound **12** was obtained as a yellow oil (641 mg, 2.15 mmol) in 63% yield.

HRMS-ESI-TOF: *m/z* calcd for C₅H₆Br₂N₂O₂ [M + Na]⁺ 320.8673; found 320.8675.

¹H NMR (CDCl₃, 400.15 MHz) δ (ppm): 3.31 (t, *J*= 6.2 Hz, 2H), 4.59 (t, *J*= 6.1 Hz, 2H), 6.76 (d, *J*= 3.0 Hz, 1H), 8.48 (br.s, 1H). **¹³C NMR** (CDCl₃, 100.62 MHz) δ (ppm): 24.6, 74.0, 99.2, 99.3, 117.7, 124.9.

1.7. 6-(3,4-dibromo-1H-pyrrol-2-yl)-1,1-dimethoxy-4,4-dimethyl-5-nitrohexan-2-one (14)

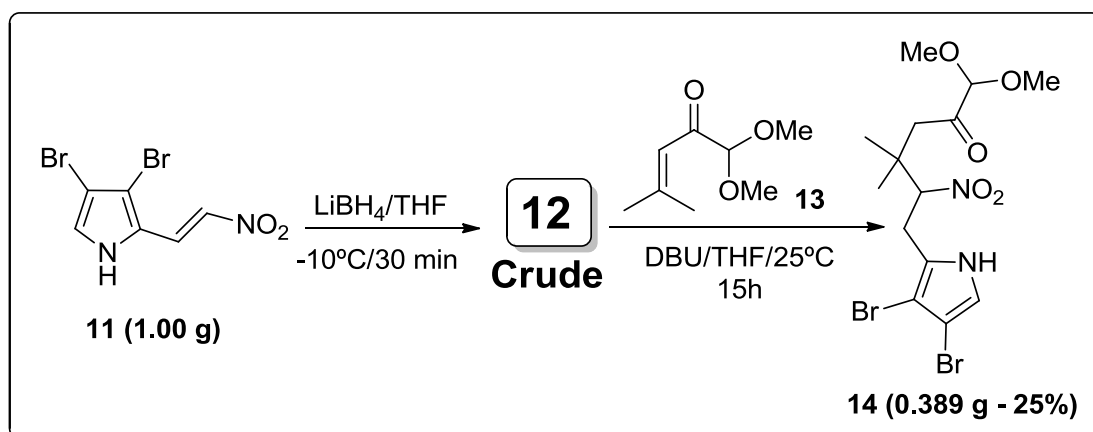


A solution of ketone **13** (2.01 g, 12.7 mmol) in anhydrous THF (8.0 mL), at room temperature, was added to **12** (631 mg, 2.12 mmol), followed by DBU (1.9 mL, 12.7 mmol). The mixture was stirred at room temperature for 13h under an argon atmosphere. The mixture was diluted with EtOAc (100 mL) and washed with NH₄Cl (saturated solution, 100 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was purified by column chromatography using silica-gel (70-230 mesh) and hex: EtOAc (8:2) as eluent. Compound **14** was obtained as a brown oil (355 mg, 0.778 mmol) in 36% yield.

HRMS-ESI-TOF: *m/z* calcd for C₁₄H₂₀Br₂N₂O₅ [M + Na]⁺ 478.9616; found 478.9604.

¹H NMR (CDCl₃, 400.15 MHz) δ (ppm): 1.15 (s, 3H), 1.27 (s, 3H), 2.62 (d, *J*= 18.8 Hz, 1H), 2.73 (d, *J*= 18.8 Hz, 1H), 3.12 (dd, *J*₁= 15.4 Hz, *J*₂= 2.7 Hz, 1H), 3.32 (dd, *J*₁= 15.4 Hz, *J*₂= 11.5 Hz, 1H), 3.42 (s, 3H), 3.43 (s, 3H), 4.37 (s, 1H), 5.18 (dd, *J*₁= 11.5 Hz, *J*₂= 2.7 Hz, 1H), 6.70 (d, *J*= 3.1 Hz, 1H), 8.47 (br.s, 1H). **¹³C NMR** (CDCl₃, 100.62 MHz) δ (ppm): 23.9, 24.2, 26.1, 36.4, 44.8, 55.1, 55.2, 93.3, 99.0, 99.4, 104.6, 117.7, 124.6, 203.4.

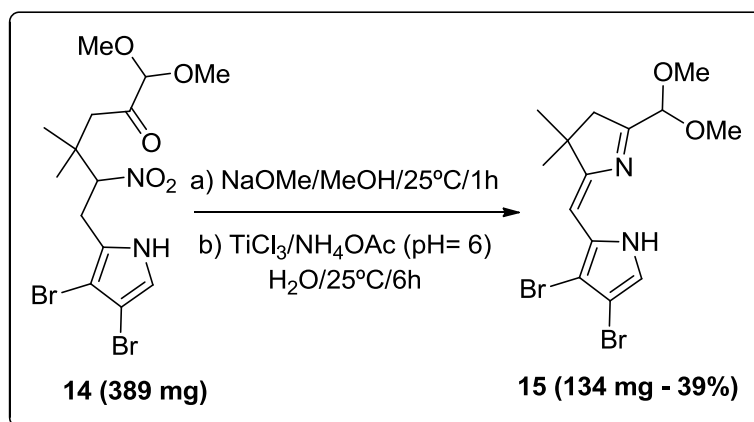
1.8. Obtainment of compound 14 directly from pyrrole 11



1° Step: a solution of pyrrole **11** (1.00 g, 3.39 mmol) in anhydrous THF (20 mL) under an argon atmosphere was cooled to -10°C, and LiBH₄ (116 mg, 5.08 mmol) was added. The mixture was stirred at the same temperature for 30 min, quenched with NH₄Cl (saturated solution, 50 mL) and extracted with EtOAc (2X 50 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was used without further purification in the next step.

2° Step: a solution of ketone **13** (3.16 g, 20.0 mmol) in anhydrous THF (13 mL), at room temperature, was added to crude **12**, followed by DBU (3.0 mL, 20.0 mmol). The mixture was stirred for 15h at room temperature. The mixture was diluted with EtOAc (200 mL) and washed with NH₄Cl (saturated solution, 200 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was purified by column chromatography using silica-gel (70-230 mesh) and hex: EtOAc (8:2) as eluent. Compound **14** was obtained as a brown oil (389 mg, 0.853 mmol) in 25% overall yield.

1.9. 7,8-Dibromo-1-(1,1-dimethoxymethyl)-3,3-dimethyl-2,3-dihydrodipyrin (**15**)

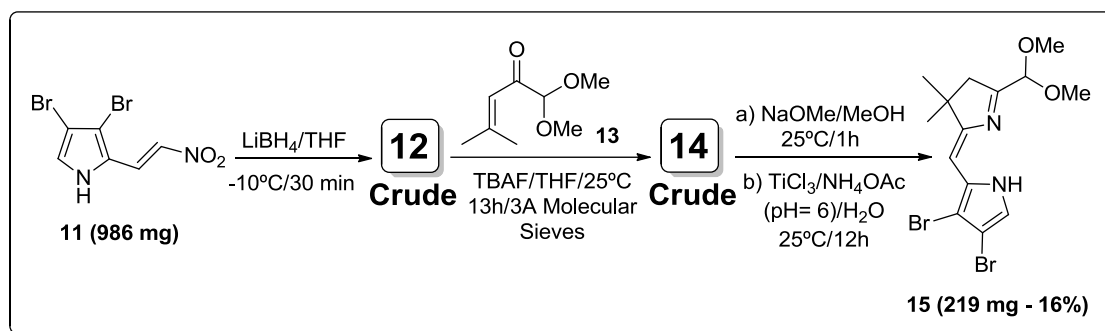


In the first flask, a solution of **14** (389 mg, 0.853 mmol) in anhydrous THF (4.0 mL) was treated with NaOMe (2.0 mL of a 2.15 M solution in MeOH, 4.3 mmol) and stirred under an argon atmosphere for 1h at room temperature. In the second flask, TiCl₃ (6.2 mL, ~10% wt in 20-30% HCl solution, 4.8 mmol) was diluted in water (34 mL, previously deoxygenated in an ultra-sonic bath and purged with argon), and NH₄OAc (26.2 g, 340 mmol) was added to buffer the solution (pH= 6). The solution in the first flask was transferred (drop-wise) to the second flask via cannula. The resulting mixture was stirred at room temperature under an argon atmosphere for 6h. The reaction was quenched by the addition of NaHCO₃ (saturated solution, 100 mL) and extracted with EtOAc (2X 100 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was purified by column chromatography using silica-gel (70-230 mesh) and hex: EtOAc (8:2) as eluent. Compound **15** was obtained as a yellow oil (134 mg, 0.330 mmol) in 39% yield.

HRMS-ESI-TOF: *m/z* calcd for C₁₄H₁₈Br₂N₂O₂ [M + Na]⁺ 428.9612; found 428.9602.

¹H NMR (CDCl₃, 400.15 MHz) δ (ppm): 1.23 (s, 6H), 2.63 (s, 2H), 3.44 (s, 6H), 5.01 (s, 1H), 5.88 (s, 1H), 6.85 (d, *J*= 3.0 Hz, 1H), 10.89 (br.s, 1H). **¹³C NMR** (CDCl₃, 100.62 MHz) δ (ppm): 29.0, 29.7, 40.4, 48.4, 54.5, 99.1, 99.3, 102.4, 104.7, 118.5, 129.1, 162.1, 176.3.

1.10. Obtainment of compound 15 directly from pyrrole 11



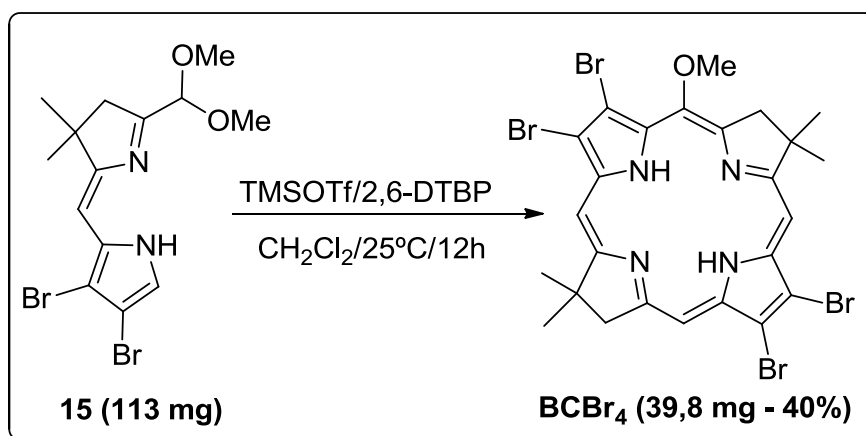
1° Step: a solution of pyrrole **11** (986 mg, 3.33 mmol) in anhydrous THF (20 mL) under an argon atmosphere was cooled to -10°C, and LiBH₄ (115 mg, 5.00 mmol) was added. The mixture was stirred at the same temperature for 30 min, quenched with NH₄Cl (saturated solution, 50 mL) and extracted with EtOAc (2X 50 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was used without further purification in the next step.

2° Step: a solution of TBAF (2.17 g, 6.66 mmol) in anhydrous THF (7.0 mL) was added to a mixture of crude **12** and ketone **13** (631 mg, 3.99 mmol) at room temperature. Powdered 3Å molecular sieves (688 mg) were added and the mixture was stirred at room temperature under an argon atmosphere for 13h. The mixture was extracted with EtOAc (2X 100 mL) and H₂O (200 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was used without further purification in the next step.

3° step: In the first flask, a solution of crude **14** in anhydrous THF (4.0 mL) was treated with NaOMe (5.0 mL of a 2.00 M solution in MeOH, 10.0 mmol) and stirred under an argon atmosphere for 1h at room temperature. In the second flask, TiCl₃ (25.8 mL, ~10% wt in 20-30% HCl solution, 20.0 mmol) was diluted in water (138 mL, previously deoxygenated in an ultra-sonic bath and purged with argon) and NH₄OAc (101.0 g, 1.31 mol) was added to buffer the solution (pH = 6). The solution in the first flask was transferred (drop-wise) to the second flask via cannula. The resulting mixture was stirred at room temperature under an argon atmosphere for 12h. The reaction was quenched by the addition of NaHCO₃ (saturated solution, 100 mL) and extracted with EtOAc (2X 100 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 25°C. The crude product was purified by column

chromatography using silica-gel (70-230 mesh) and hex: EtOAc (9:1) as eluent. Compound **15** was obtained as a yellow oil (219 mg, 0.540 mmol) in 16% overall yield.

1.11. 2,3,12,13-Tetrabromo-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (BCBr₄)



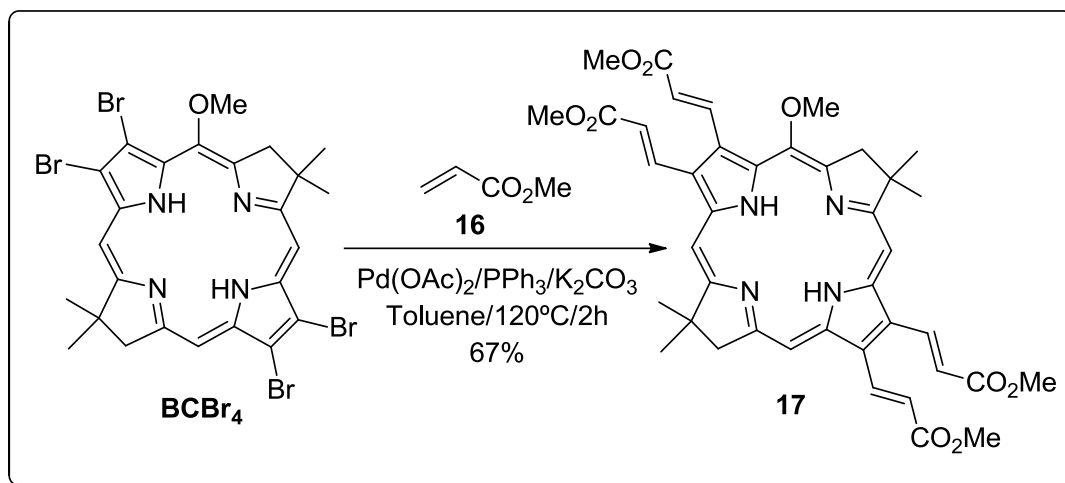
A solution of compound **15** (113 mg, 0.279 mmol) in anhydrous CH₂Cl₂ (15.5 mL) was treated first with 2,6-DTBP (1.3 mL, 5.50 mmol) and then with TMSOTf (254 μL, 1.38 mmol). The resulting mixture was stirred at room temperature under an argon atmosphere for 12h. The mixture was concentrated almost to dryness and submitted to purification by column chromatography using silica-gel (70-230 mesh) and CH₂Cl₂:hex (8:2) as eluent. After crystallization from CH₂Cl₂:MeOH, **BCBr₄** was obtained as a green solid (39.8 mg, 0.056 mmol) in 40% yield.

M.P.: Unstable above 160°C.

HRMS-ESI-TOF: *m/z* calcd for C₂₅H₂₄Br₄N₄O [M + H]⁺ 716.8721; found 716.8701.

¹H NMR (CDCl₃, 400.15 MHz) δ (ppm): -1.65 (s, 1H), -1.45 (s, 1H), 1.94 (s, 12H), 4.30 (s, 3H), 4.36 (s, 4H), 8.67 (s, 1H), 8.72 (s, 2H). **¹³C NMR** (CDCl₃, 100.62 MHz) δ (ppm): 30.8, 31.0, 45.8, 45.9, 47.3, 51.6, 64.3, 95.9, 96.0, 96.9, 107.8, 114.4, 114.6, 115.5, 126.4, 131.7, 133.4, 133.9, 135.3, 155.4, 162.1, 170.7, 171.2.

1.12. Compound 17



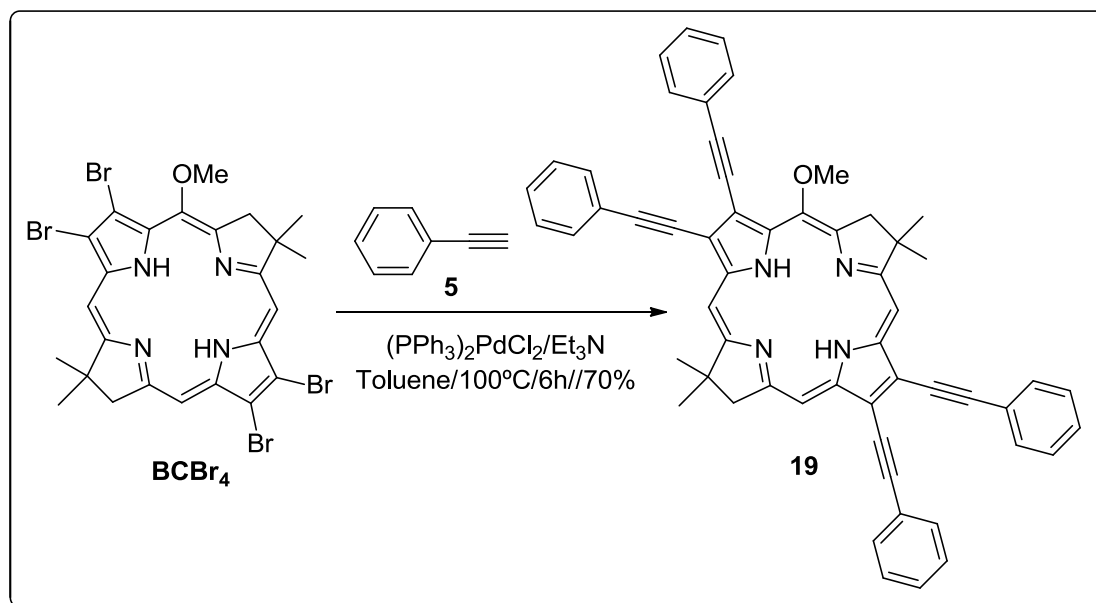
BCBr₄ (10.0 mg, 14.0 μmol), Pd(OAc)₂ (1.6 mg, 7.0 μmol), PPh₃ (4.7 mg, 18.0 μmol), K₂CO₃ (8.0 mg, 58.0 μmol) and methyl acrylate (**16**) (64 μL , 698 μmol) were added to a high pressure screw cap tube. The tube was closed with a septum and purged with argon. Anhydrous toluene (5.0 mL) was added and the mixture was deoxygenated in an ultra-sonic bath for 15 min (the purge was kept during all this time). The septum was rapidly removed and the cap was screwed on. The mixture was stirred at 120°C for 2h, concentrated to dryness and submitted to purification by column chromatography using silica-gel (70-230 mesh) and CH₂Cl₂:hex:EtOAc (6.5:3:0.5) as eluent. The resulting dark-purple solid was washed with pentane. Compound **17** was obtained as a purple solid (6.9 mg, 9.4 μmol) in 67% yield.

M.P.: Unstable above 200°C.

HRMS-ESI-TOF: m/z calcd for C₄₁H₄₄N₄O₉ [M + H]⁺ 759.3006; found 759.2996.

¹H NMR (CDCl₃, 400.15 MHz) δ (ppm): -0.97 (s, 1H), -0.74 (s, 1H), 1.91 (s, 6H), 1.93 (s, 6H), 3.98 (s, 3H), 4.01 (s, 3H), 4.02 (s, 6H), 4.20 (s, 3H), 4.33 (s, 2H), 4.34 (s, 2H), 6.63 (d, J = 16.1 Hz, 1H), 6.90 (d, J = 16.0 Hz, 1H), 6.91 (d, J = 16.1 Hz, 1H), 6.99 (d, J = 16.2 Hz, 1H), 8.64 (s, 1H), 8.68 (s, 1H), 8.72 (s, 1H), 8.78 (d, J = 16.2 Hz, 1H), 8.90 (d, J = 16.3 Hz, 1H), 8.95 (d, J = 16.2 Hz, 1H), 9.38 (d, J = 16.1 Hz, 1H). **¹³C NMR** (CDCl₃, 100.62 MHz) δ (ppm): 30.8, 45.8, 46.0, 47.7, 51.7, 51.9, 52.1, 63.6, 95.6, 96.6, 124.6, 124.7, 125.0, 126.3, 126.6, 127.0, 127.8, 129.0, 134.0, 134.6, 135.0, 136.7, 136.9, 137.0, 138.5, 140.0, 157.4, 162.4, 167.2, 167.3, 171.8, 172.4.

1.13. Compound 19



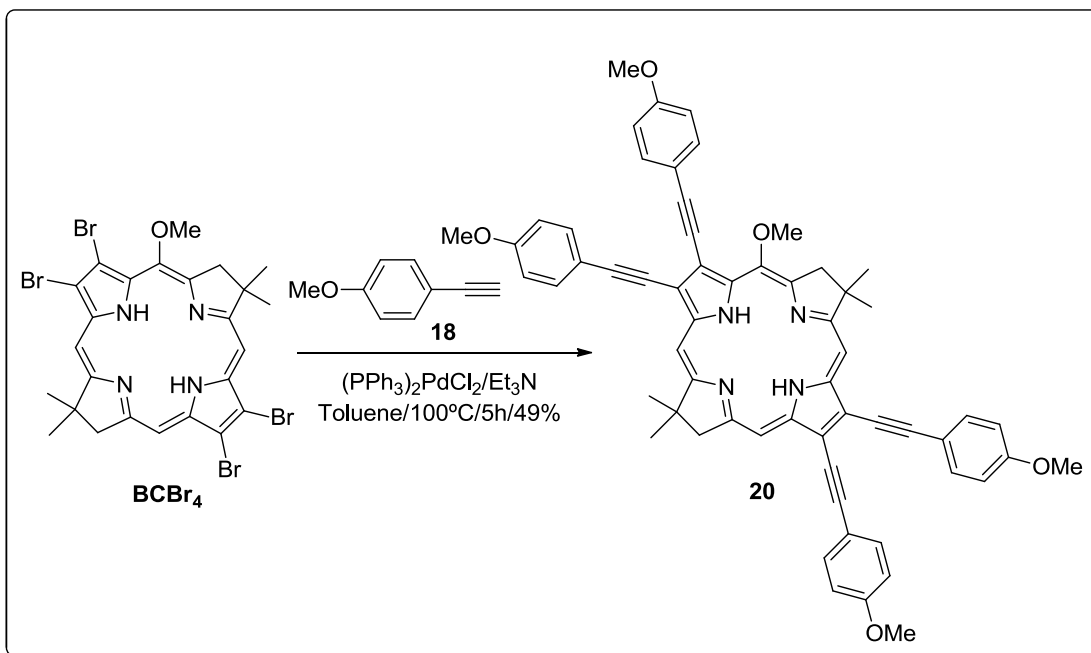
BCBr₄ (10.0 mg, 14.0 μmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (5.0 mg, 7.0 μmol) and phenylacetylene (**5**) (13 μL , 117 μmol) were added to a high pressure screw cap tube. The system was closed with a septum and purged with argon. Anhydrous toluene (2.8 mL) and triethylamine (1.4 mL) were added, and the mixture was deoxygenated in an ultra-sonic bath for 15 min (the purge was kept for all this time). The septum was rapidly removed and the cap was screwed on. The mixture was stirred at 100°C for 6h, concentrated to dryness and submitted to purification by column chromatography using silica-gel (70-230 mesh) and CH_2Cl_2 :hex (1:1) as eluent. Compound **19** was obtained as a purple solid (7.8 mg, 9.7 μmol) in 70% yield.

M.P.: Unstable above 200°C.

HRMS-MALDI-TOF: m/z calcd for $\text{C}_{57}\text{H}_{44}\text{N}_4\text{O}$ $[\text{M}]^+$ 800.3509; found 800.3473.

¹H NMR (CDCl_3 , 400.15 MHz) δ (ppm): -1.19 (s, 1H), -0.99 (s, 1H), 1.98 (s, 12H), 4.37 (s, 2H), 4.39 (s, 2H), 4.50 (s, 3H), 7.48-7.53 (m, 12H), 7.90-7.94 (m, 8H), 8.79 (s, 1H), 8.81 (s, 2H). **¹³C NMR** (CDCl_3 , 100.62 MHz) δ (ppm): 30.8, 31.0, 45.8, 47.4, 51.6, 64.4, 83.8, 83.9, 84.4, 86.5, 95.5, 95.7, 96.8, 97.6, 99.7, 100.0, 100.3, 114.3, 118.4, 118.5, 119.4, 123.6, 124.0, 124.4, 128.3, 128.5, 128.6, 128.7, 128.8, 130.8, 131.8, 131.9, 135.5, 136.1, 137.1, 137.4, 156.0, 162.3, 171.3, 171.6.

1.14. Compound 20



BCBr₄ (10.0 mg, 14.0 μmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (5.0 mg, 7.0 μmol) and 4-ethynylanisole (**18**) (30 μL , 224 μmol) were added to a high pressure screw cap tube. The system was closed with a septum and purged with argon. Anhydrous toluene (2.8 mL) and triethylamine (1.4 mL) were added, and the mixture was deoxygenated in an ultra-sonic bath for 15 min (the purge was kept for all this time). The septum was rapidly removed and the cap was screwed on. The mixture was stirred at 100°C for 5h, concentrated to dryness and submitted to purification by column chromatography using silica-gel (70-230 mesh) and CH_2Cl_2 :hex (7:3) as eluent. Compound **20** was obtained as a purple solid (6.3 mg, 6.8 μmol) in 49% yield.

M.P.: Unstable above 200°C .

HRMS-ESI-TOF: m/z calcd for $\text{C}_{61}\text{H}_{52}\text{N}_4\text{O}_5$ $[\text{M} + \text{H}]^+$ 921.4016; found 921.4017.

¹H NMR (CDCl_3 , 400.15 MHz) δ (ppm): -1.25 (s, 1H), -1.05 (s, 1H), 1.97 (s, 12H), 3.91 (s, 3H), 3.92 (s, 6H), 3.93 (s, 3H), 4.36 (s, 2H), 4.38 (s, 2H), 4.48 (s, 3H), 7.04-7.07 (m, 8H), 7.82-7.87 (m, 8H), 8.76 (s, 1H), 8.79 (s, 2H). **¹³C NMR** (CDCl_3 , 100.62 MHz) δ (ppm): 30.8, 31.0, 45.7, 45.8, 47.4, 51.6, 55.4, 64.3, 82.3, 82.8, 83.3, 95.4, 95.5, 96.6, 97.5, 99.5, 99.9, 100.2, 114.2, 114.3, 115.8, 118.4, 130.6, 133.2, 133.3, 133.4, 135.4, 136.0, 137.0, 137.4, 155.6, 159.7, 159.9, 160.0, 162.0, 170.9, 171.3.

2. NMR spectra

2.1. NMR spectra of compound 8

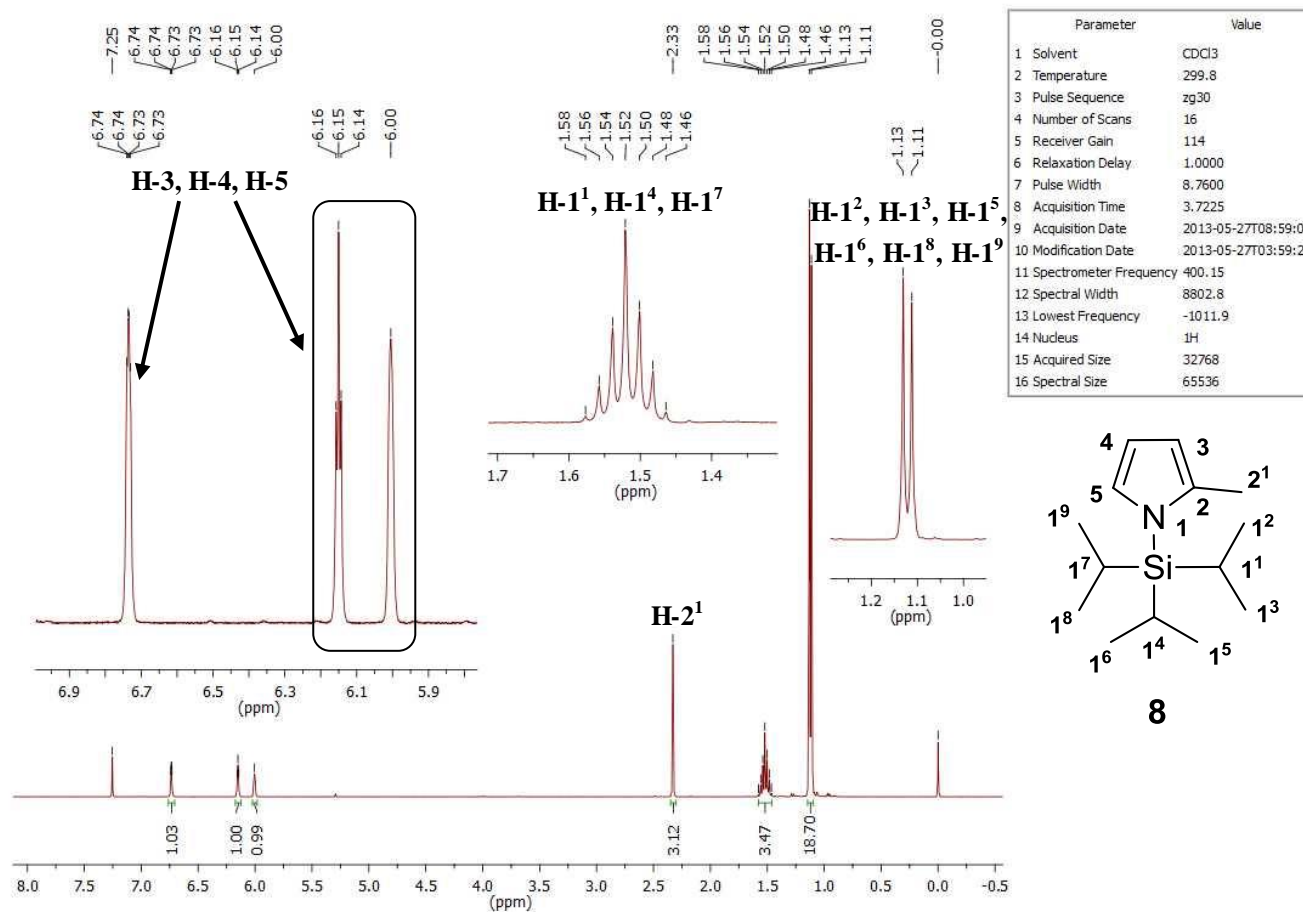


Figure S1. ^1H NMR spectrum of compound 8 in CDCl_3 .

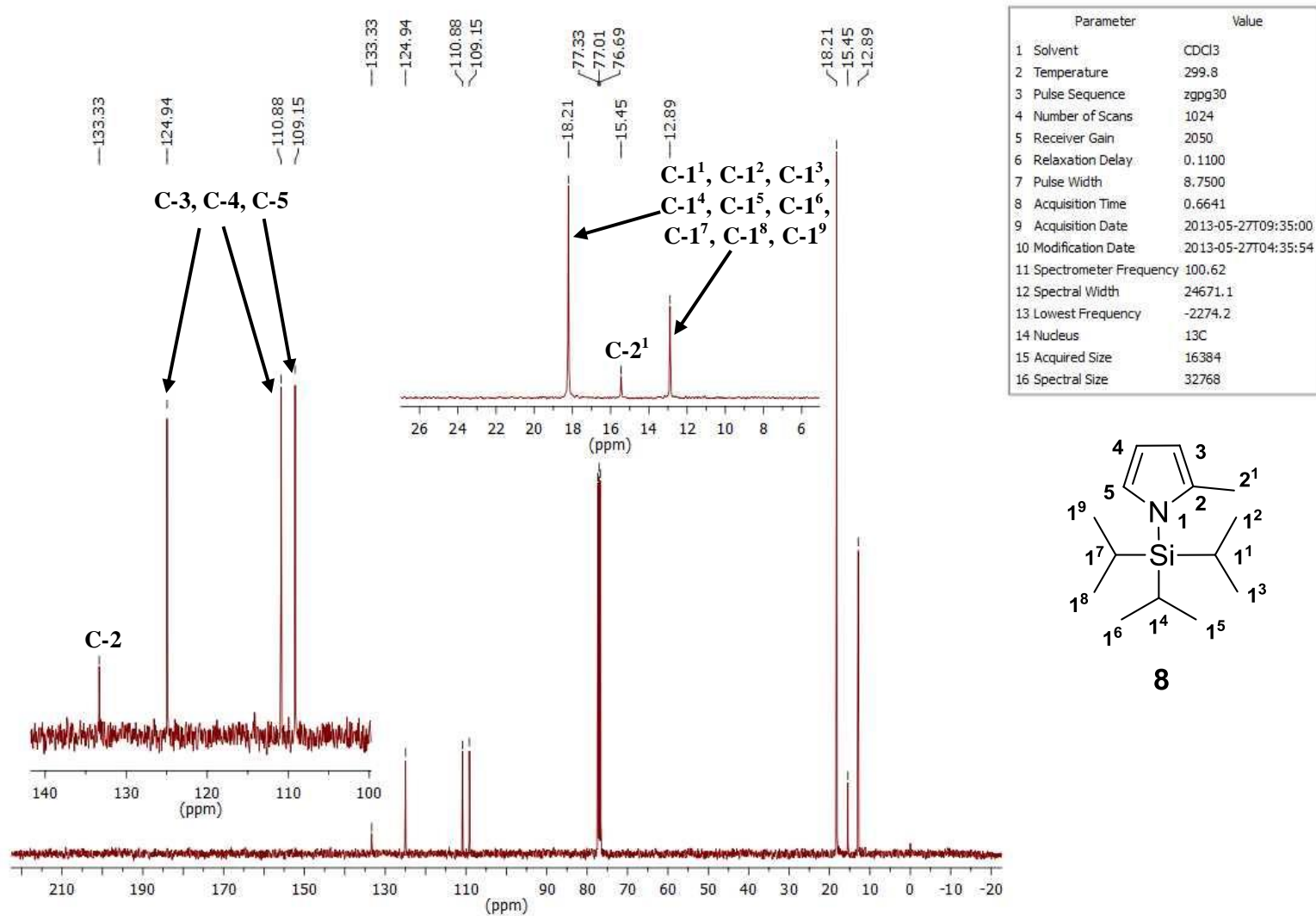


Figure S2. ¹³C NMR spectrum of compound **8** in CDCl₃.

2.2. NMR spectra of compound 9

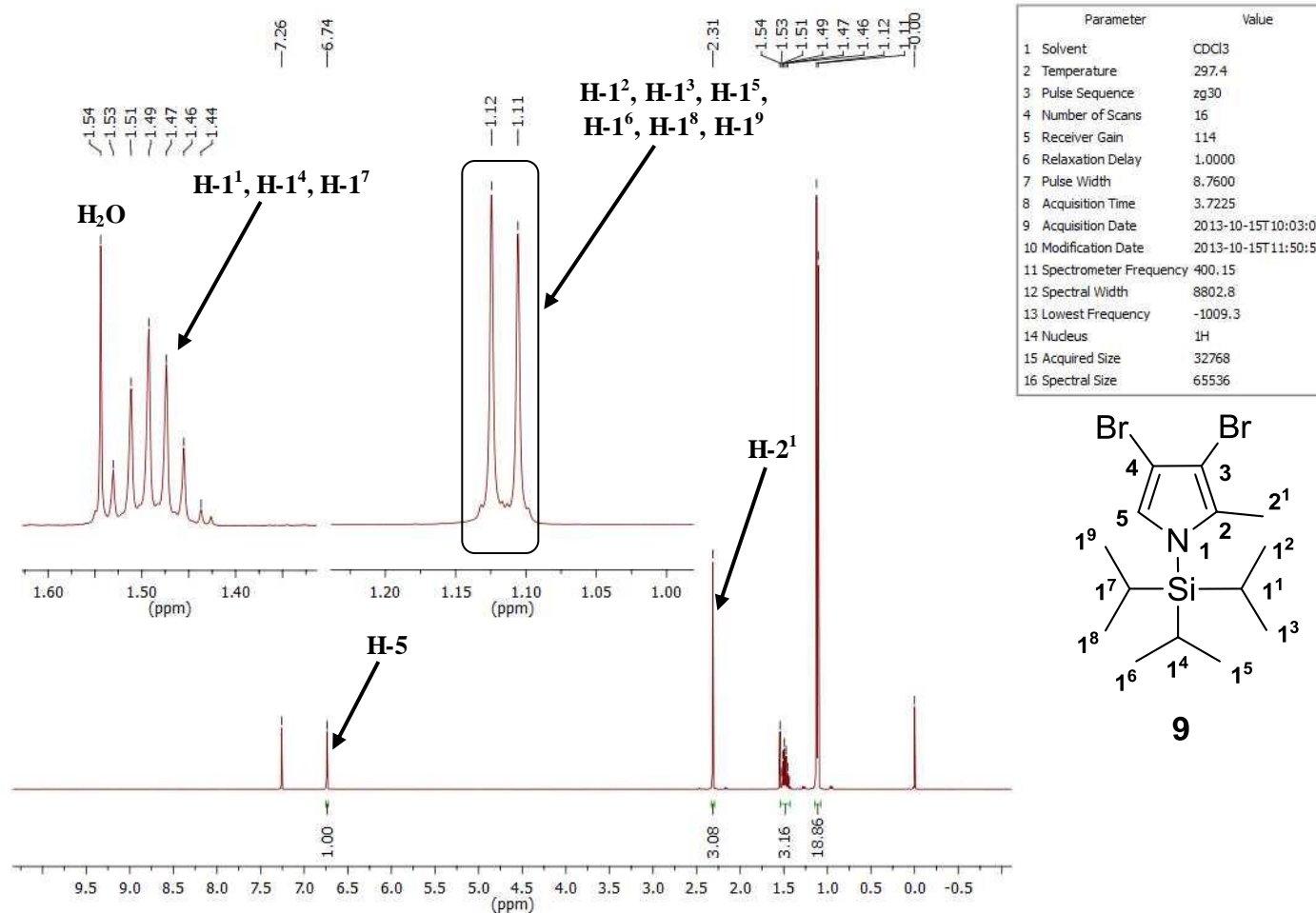


Figure S3. ^1H NMR spectrum of compound **9** in CDCl_3 .

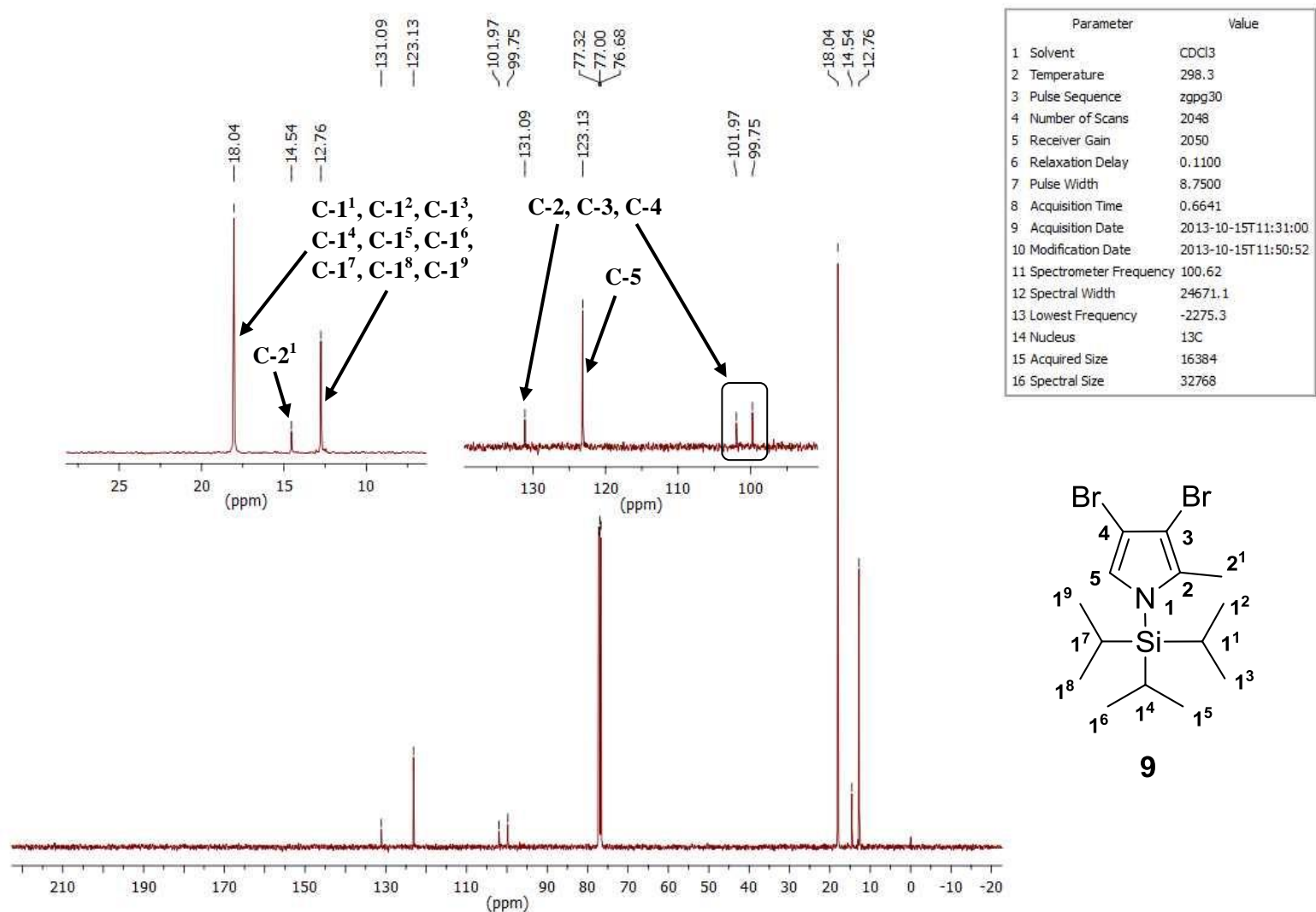


Figure S4. ¹³C NMR spectrum of compound **9** in CDCl₃.

2.3. NMR spectra of compound 10

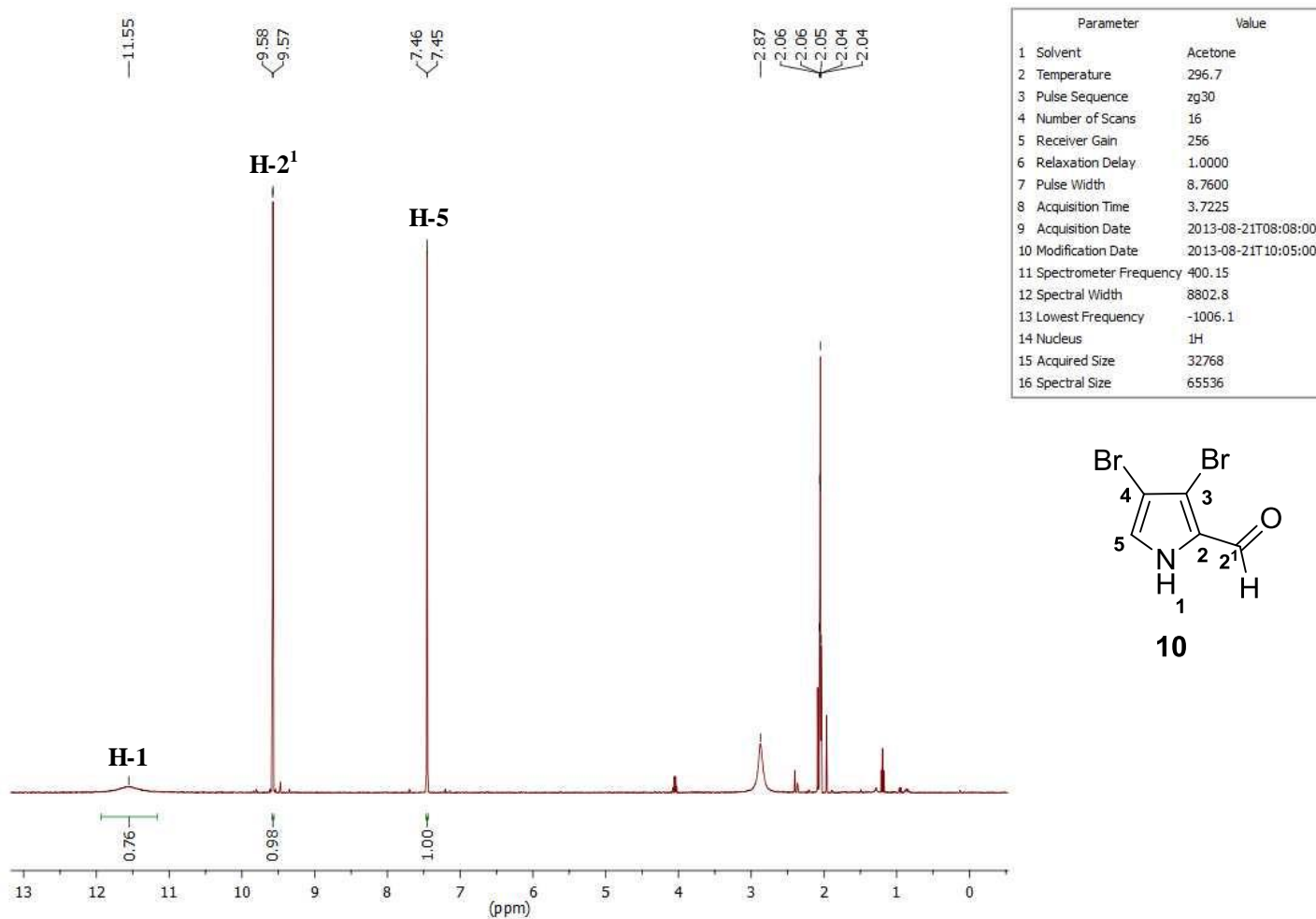


Figure S5. ¹H NMR spectrum of compound 10 in acetone-*d*₆.

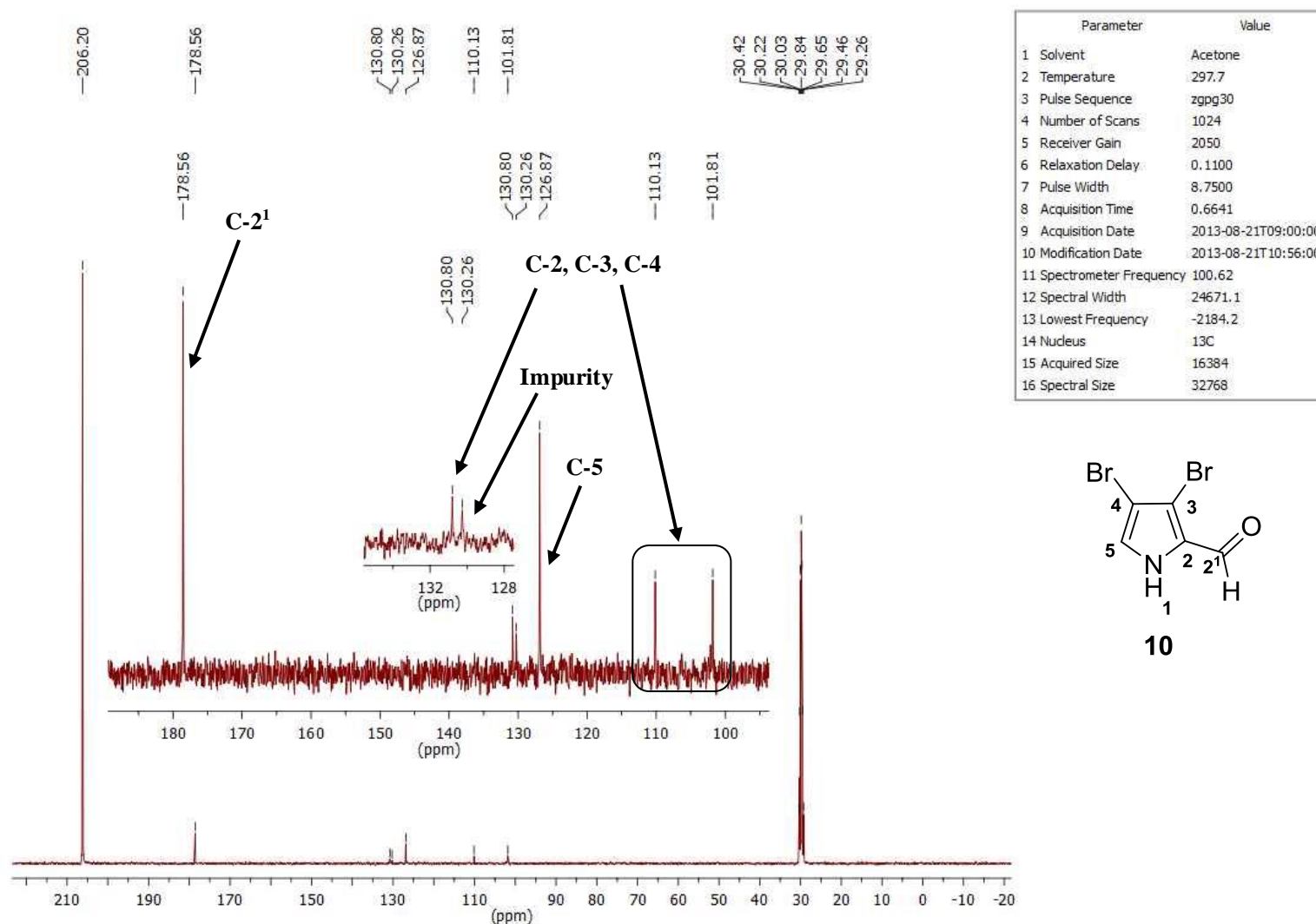


Figure S6. ^{13}C NMR spectrum of compound **10** in acetone- d_6 .

2.4. NMR spectra of compound 11

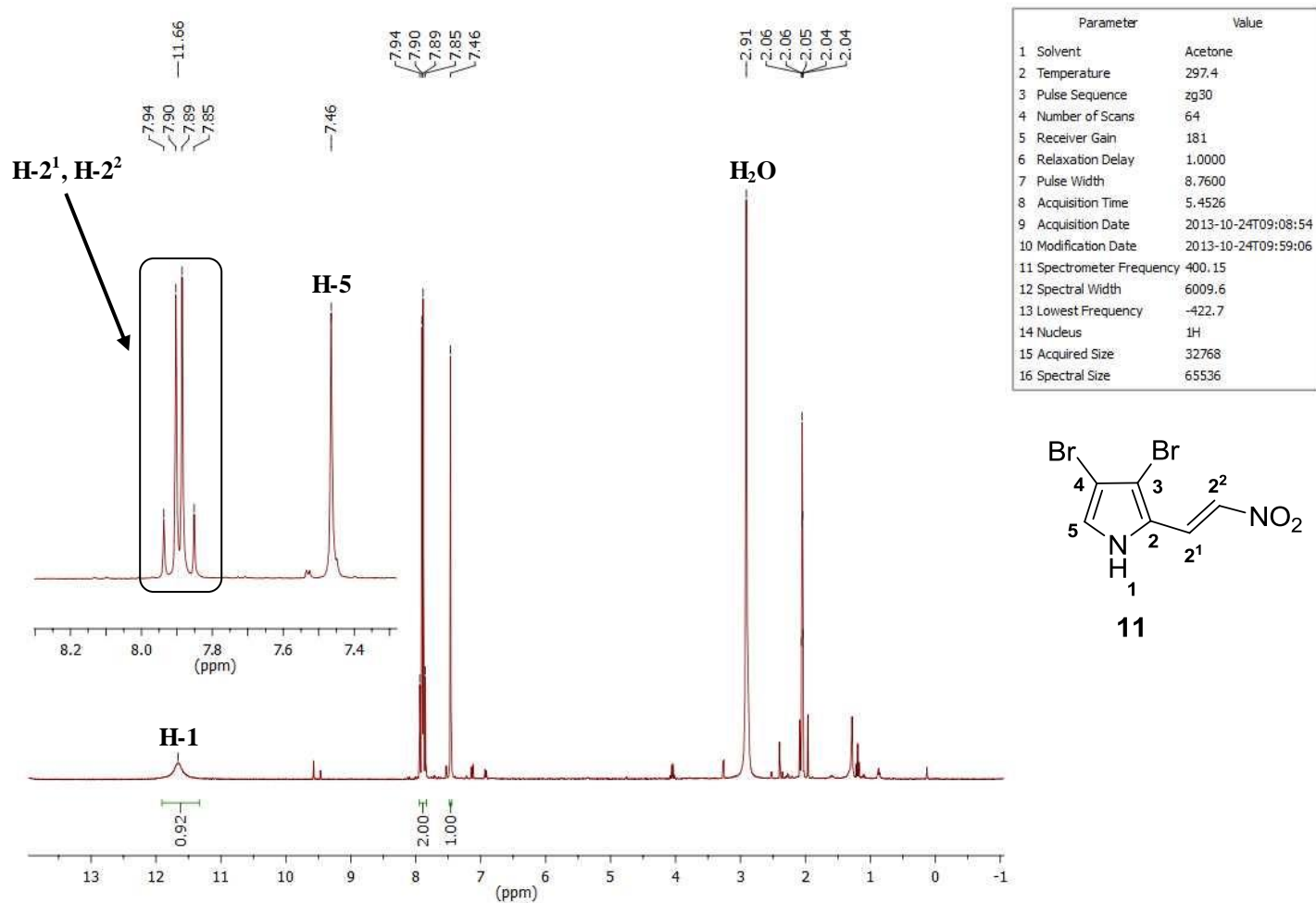


Figure S7. ^1H NMR spectrum of compound **11** in acetone- d_6 .

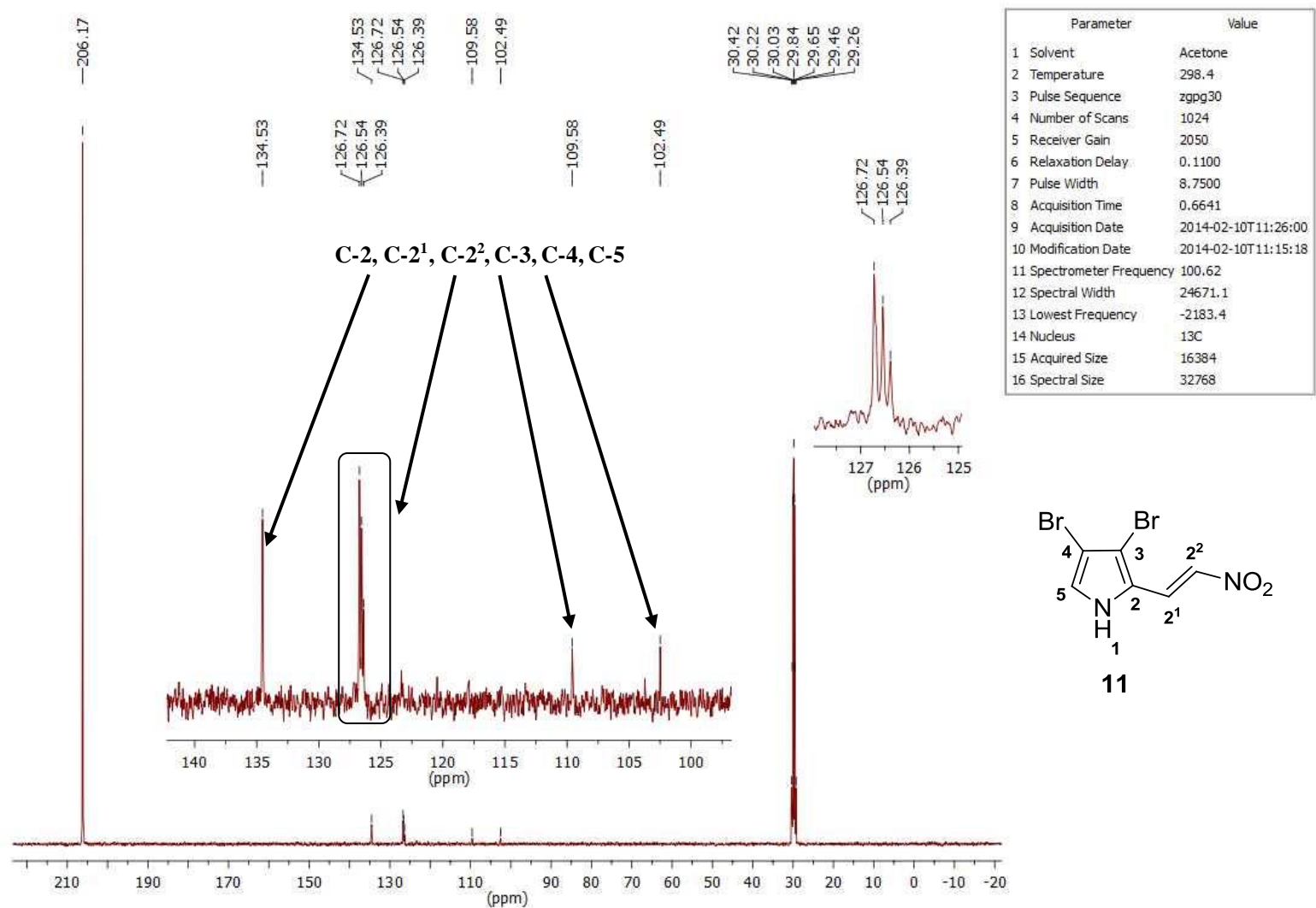


Figure S8. ¹³C NMR spectrum of compound **11** in acetone-*d*₆.

2.5. NMR spectra of compound 12

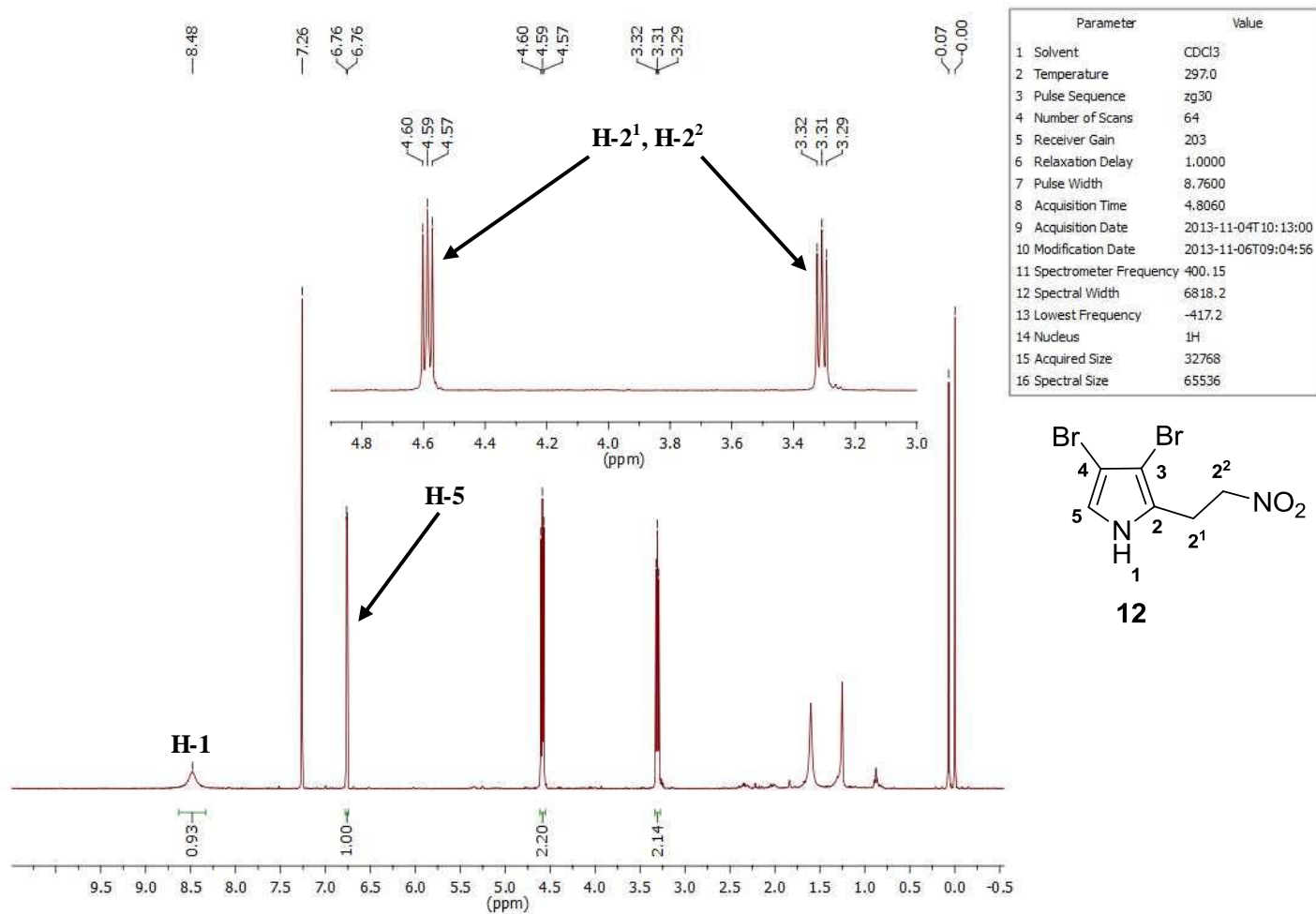
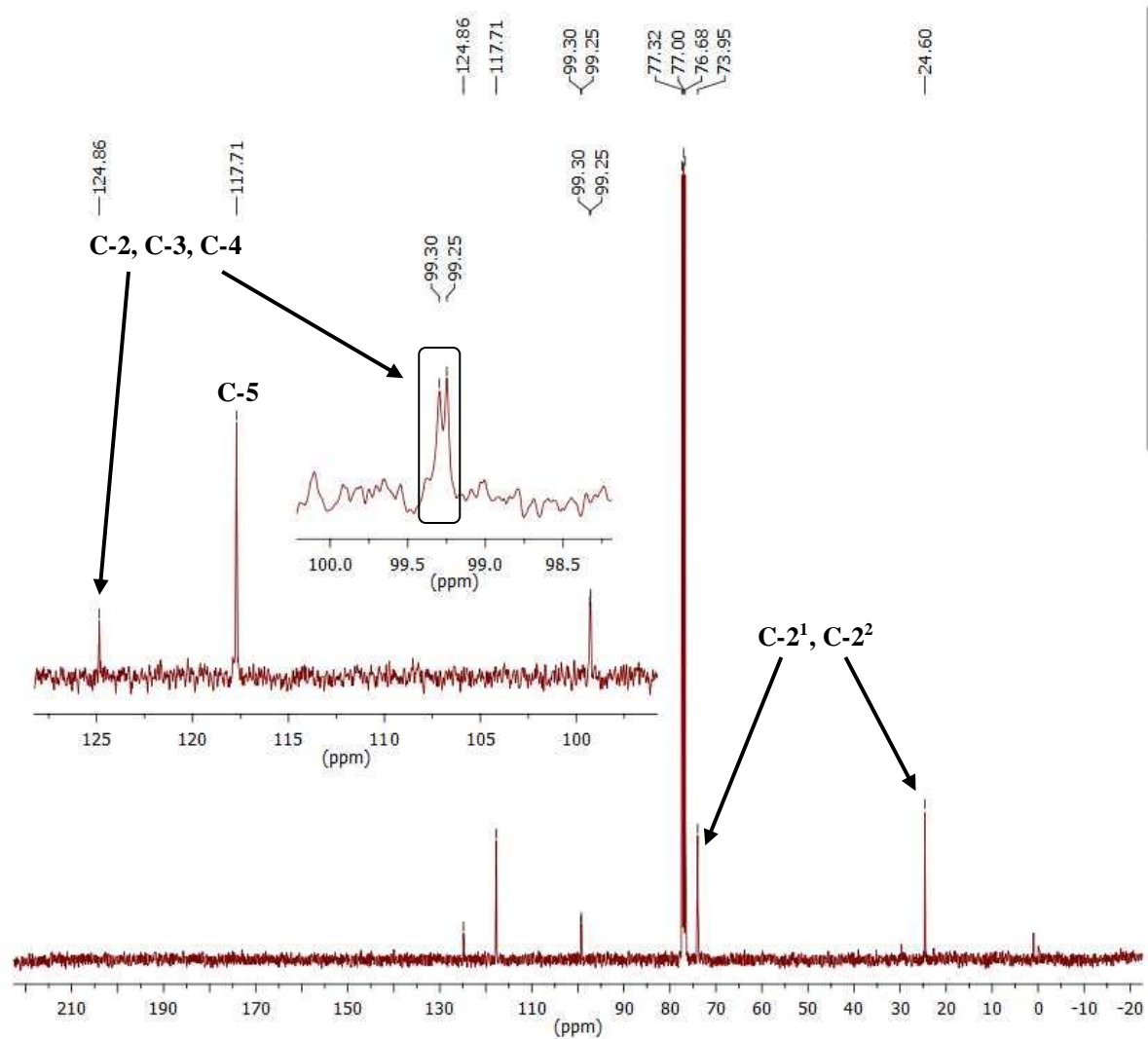


Figure S9. ^1H NMR spectrum of compound **12** in CDCl_3 .



Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.0
3 Pulse Sequence	zgpg30
4 Number of Scans	2048
5 Receiver Gain	2050
6 Relaxation Delay	0.1100
7 Pulse Width	8.7500
8 Acquisition Time	0.6641
9 Acquisition Date	2013-11-04T11:49:00
10 Modification Date	2013-11-06T09:04:36
11 Spectrometer Frequency	100.62
12 Spectral Width	24671.1
13 Lowest Frequency	-2275.9
14 Nucleus	13C
15 Acquired Size	16384
16 Spectral Size	32768

Figure S10. ^{13}C NMR spectrum of compound **12** in CDCl_3 .

2.6. NMR spectra of compound 14

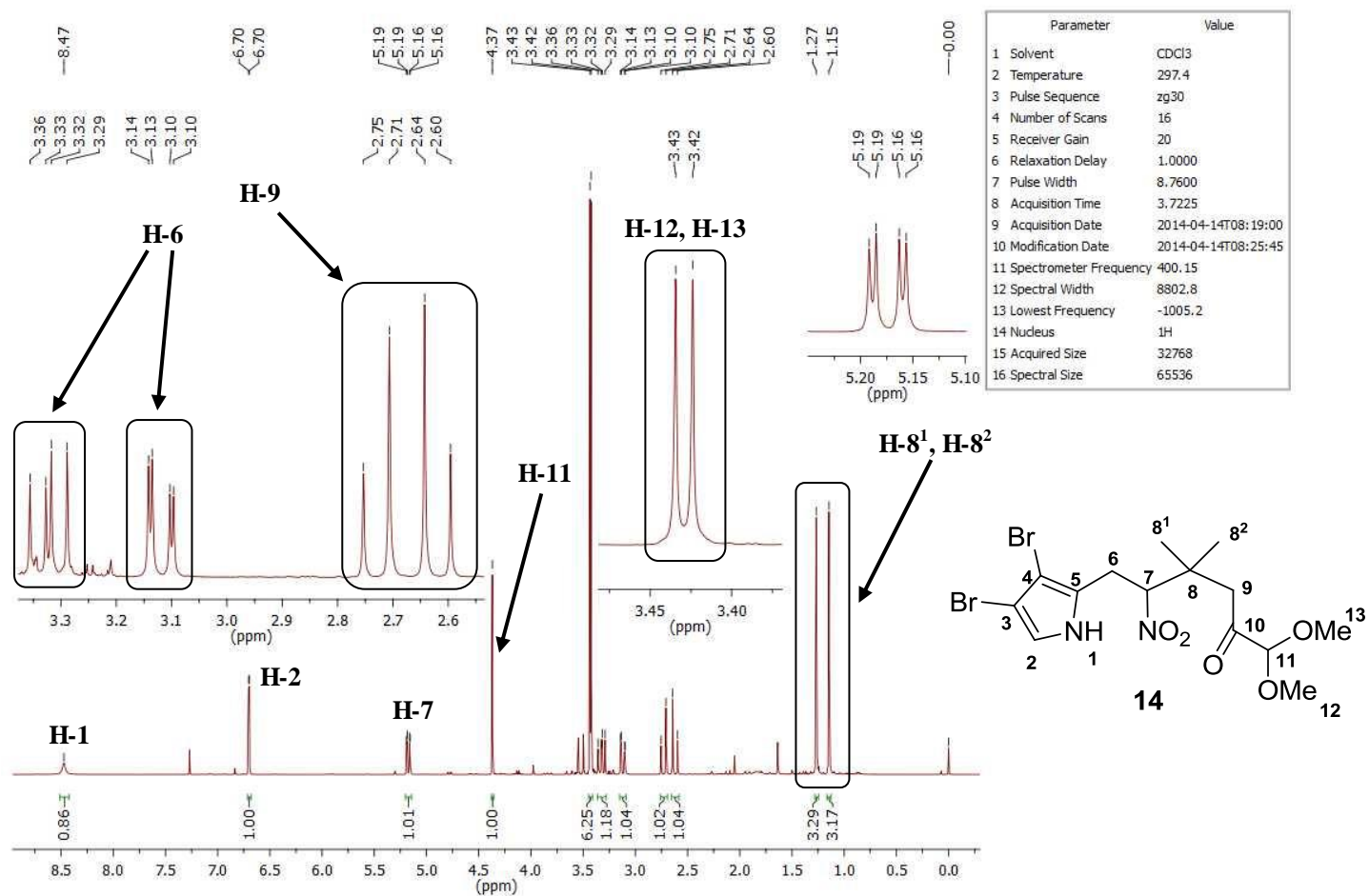


Figure S11. ¹H NMR spectrum of compound 14 in CDCl₃.

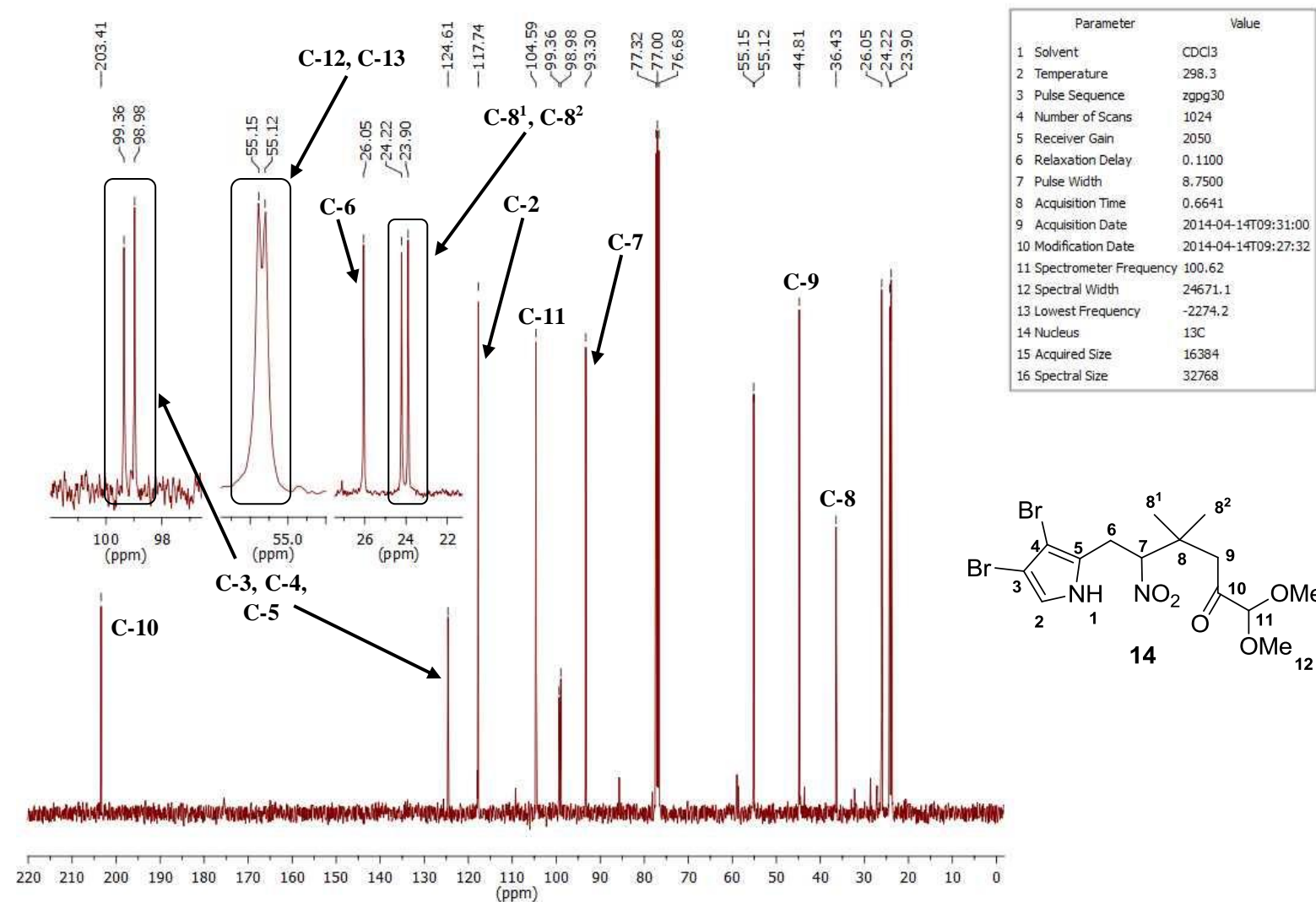


Figure S12. ^{13}C NMR spectrum of compound 14 in CDCl_3 .

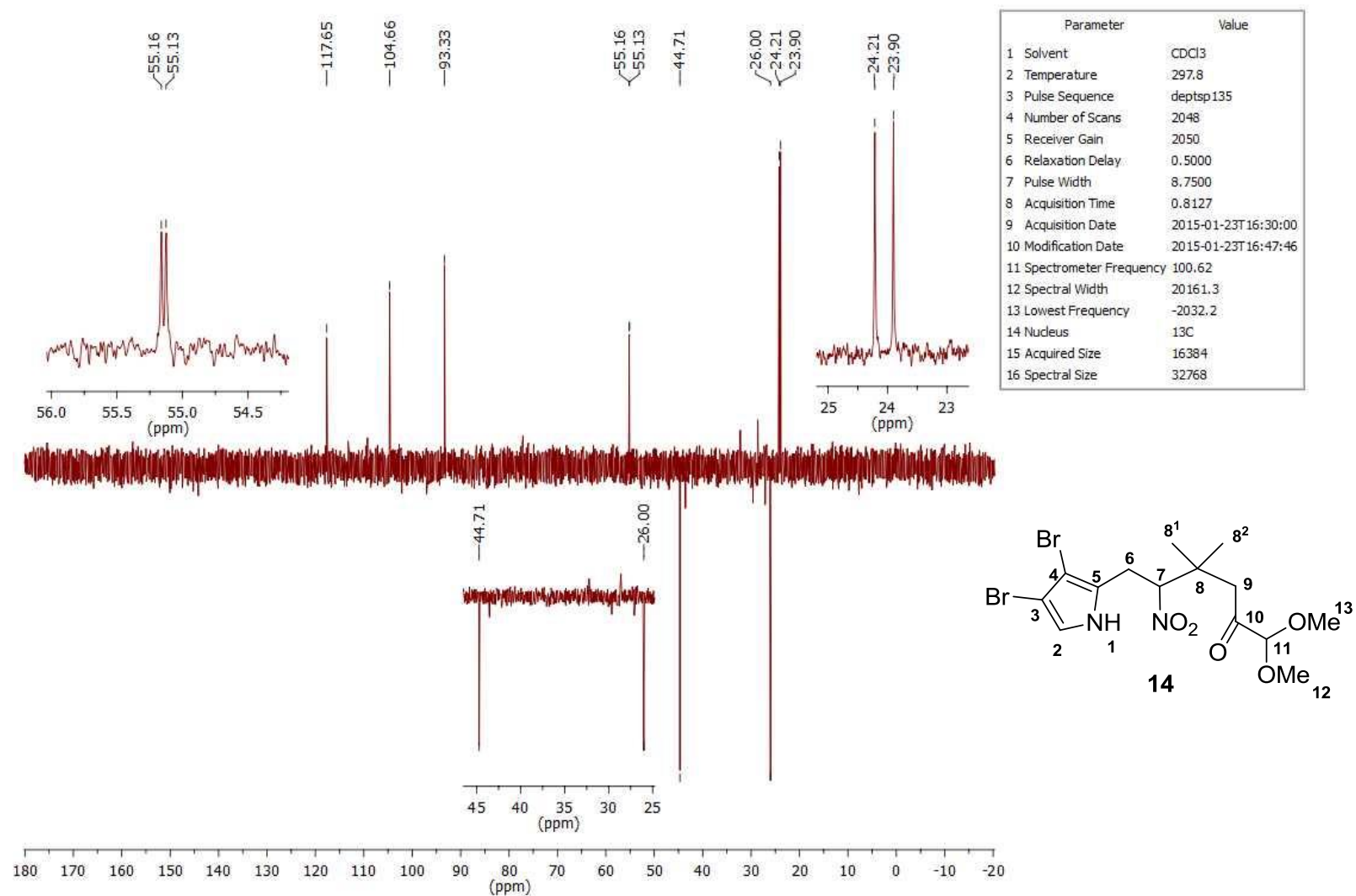
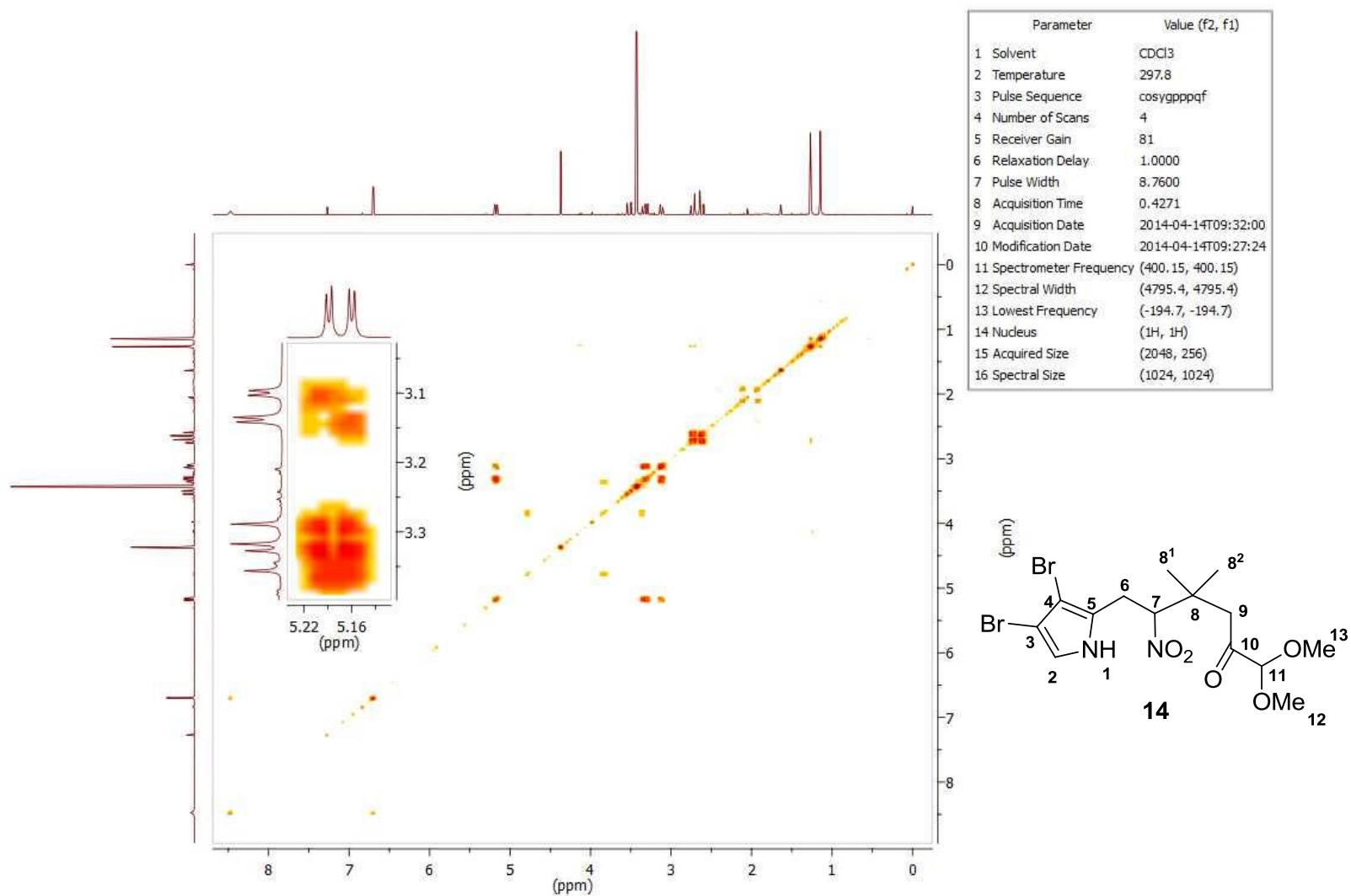


Figure S13. DEPT-135 spectrum of compound **14** in CDCl₃.



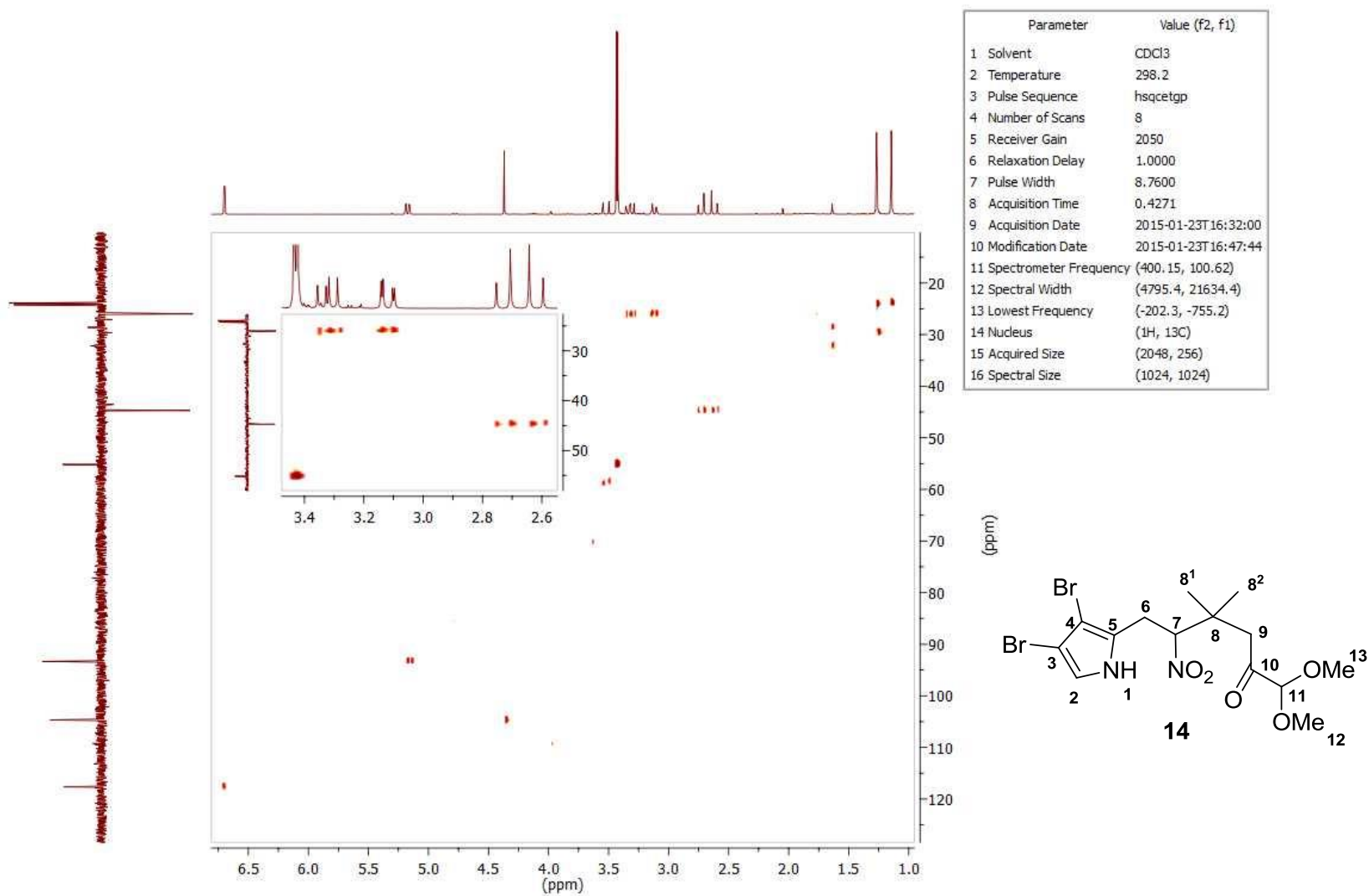


Figure S15. gHSQC spectrum of compound 14 in CDCl₃.

2.7. NMR spectra of compound 15

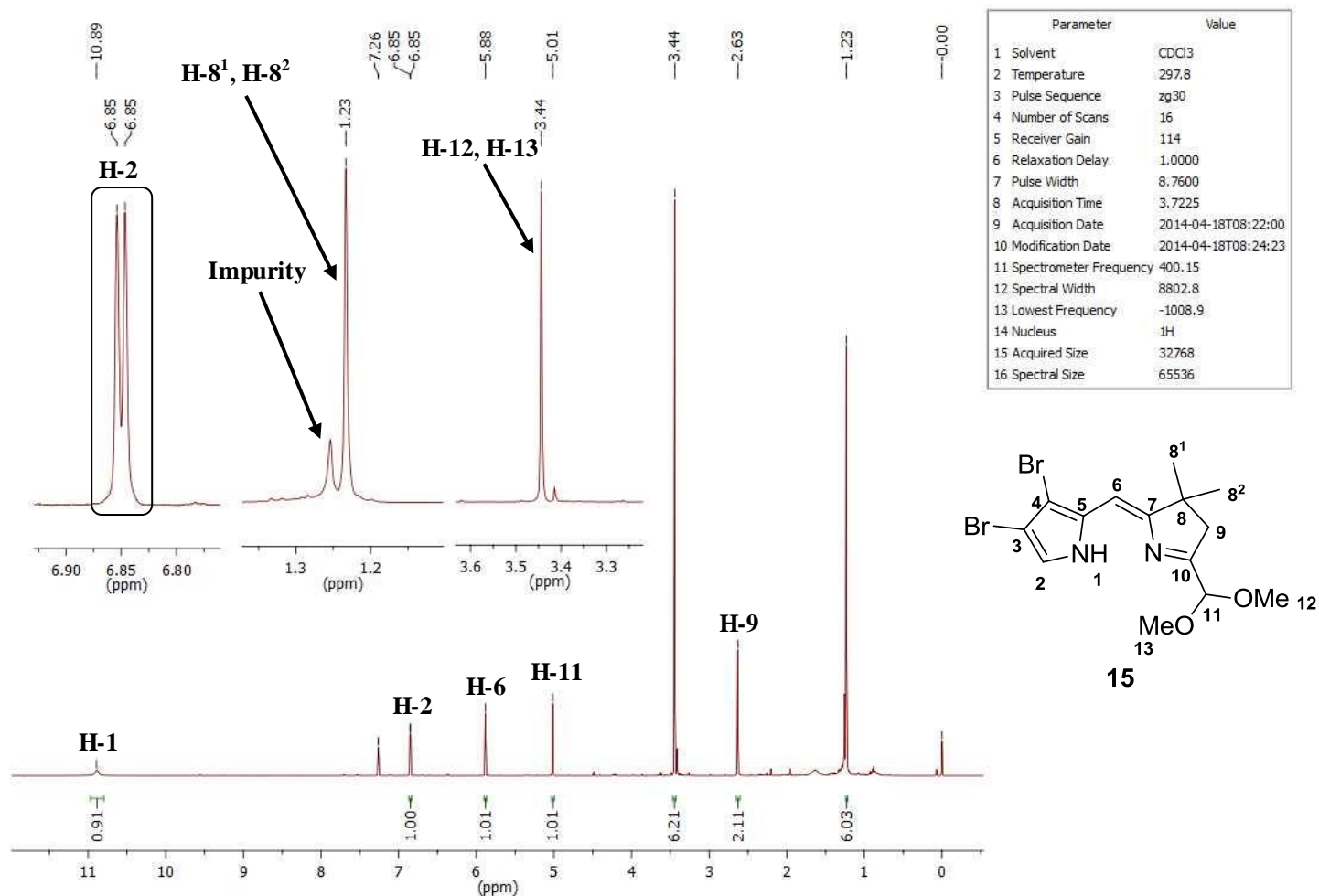


Figure S16. ¹H NMR spectrum of compound 15 in CDCl₃.

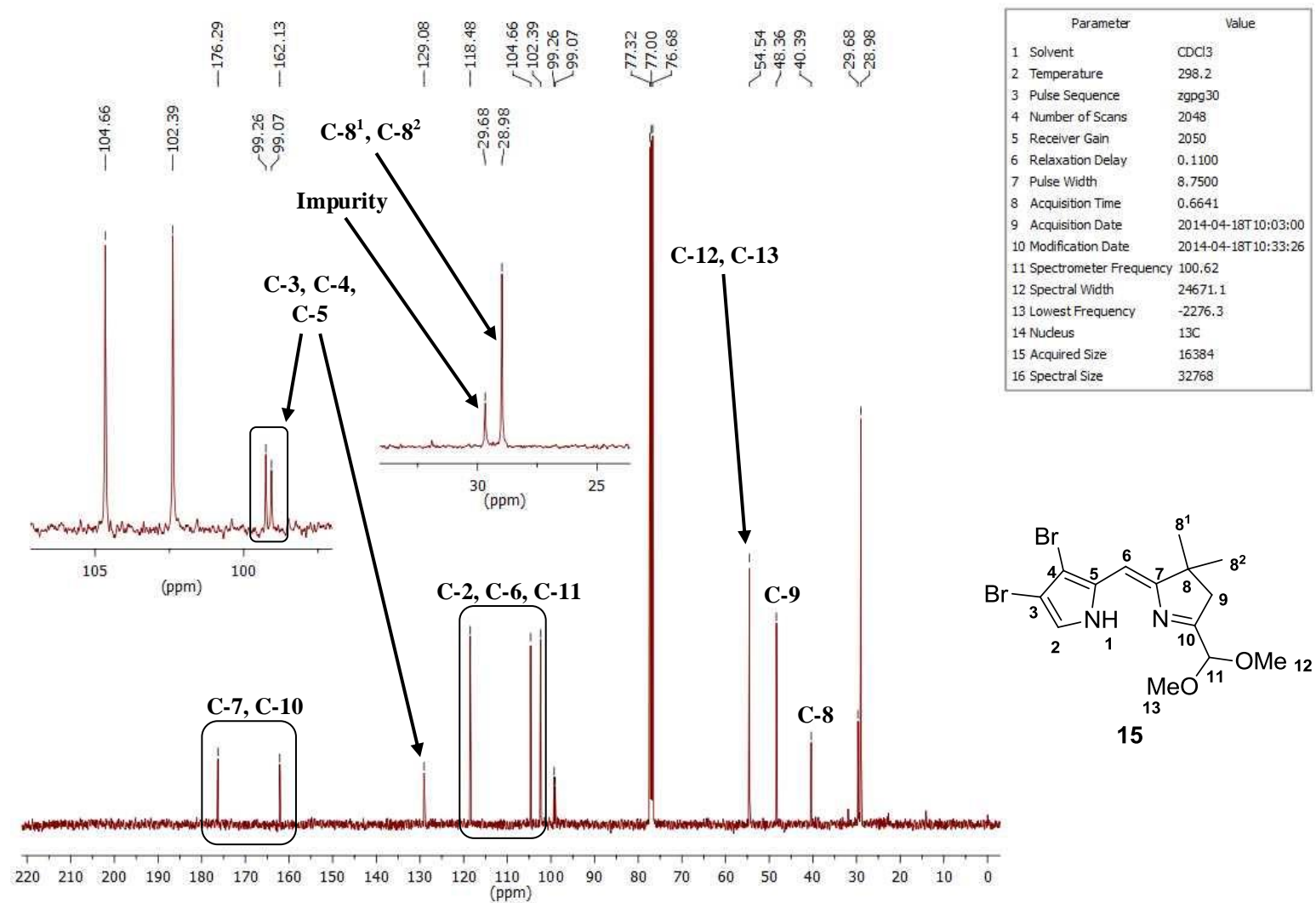


Figure S17. ¹³C NMR spectrum of compound **15** in CDCl₃.

2.8. NMR spectra of compound BCB₄

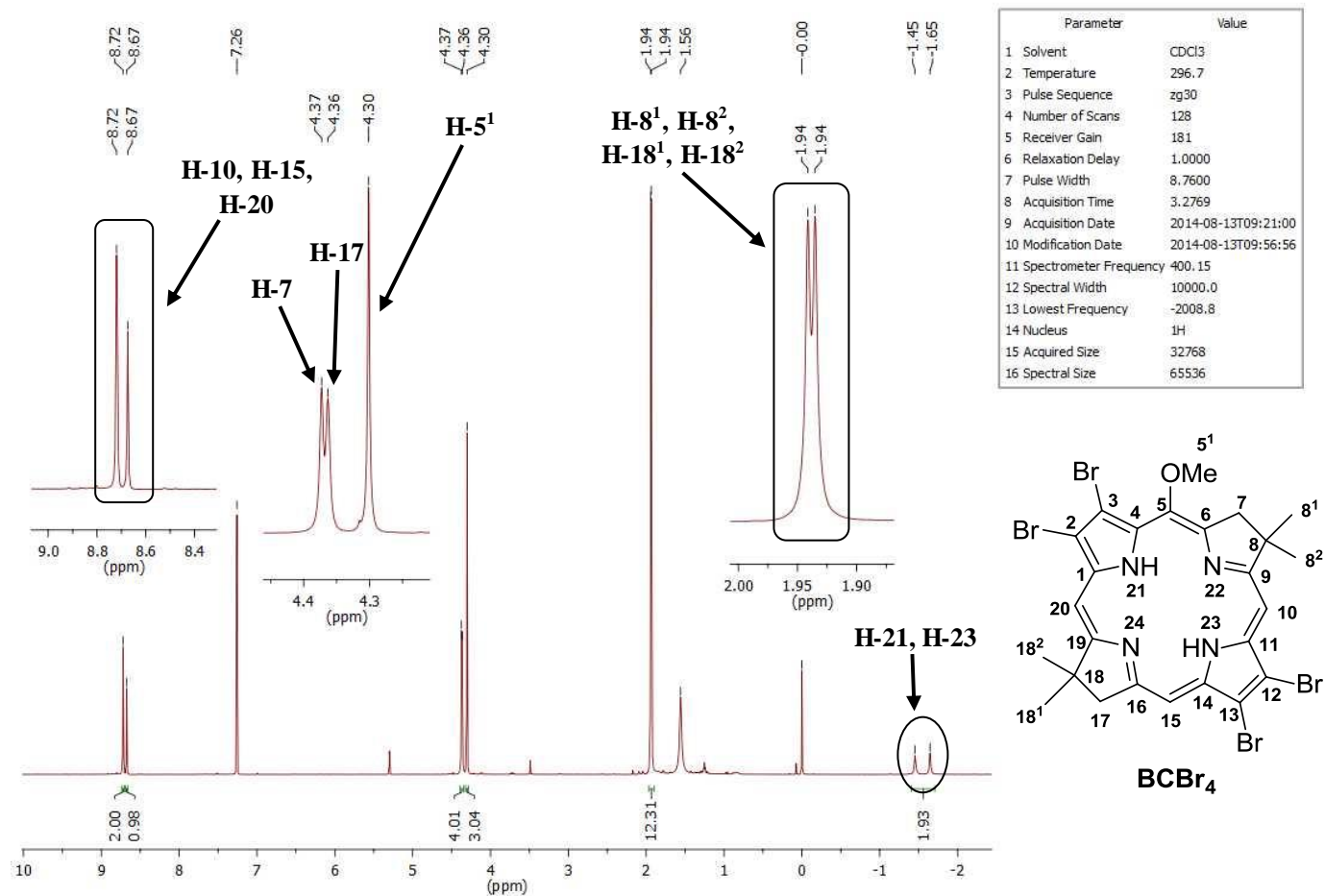


Figure S18. ¹H NMR spectrum of compound BCB₄ in CDCl₃.

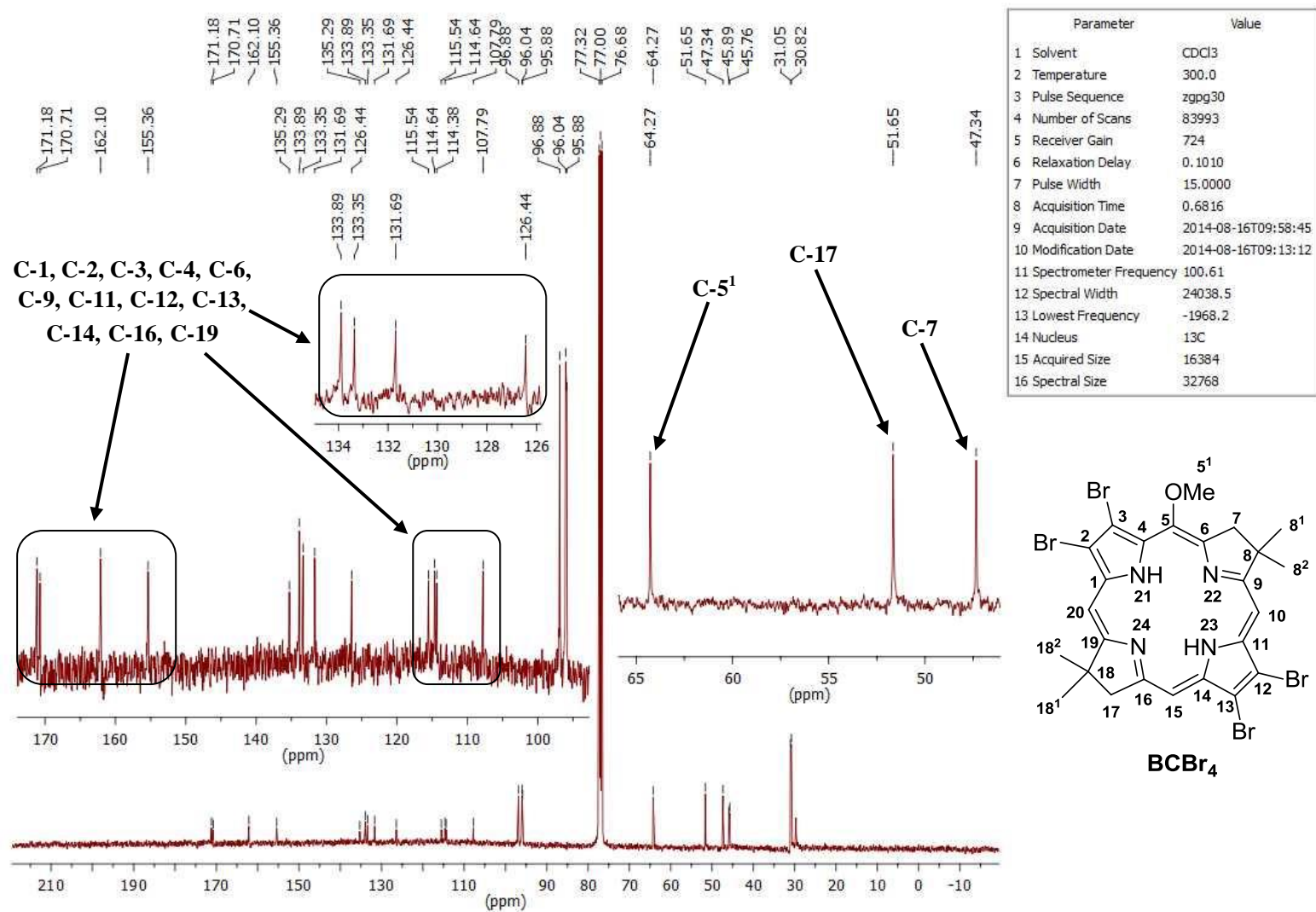


Figure S19. ¹³C NMR spectrum of compound **BCBr₄** in CDCl₃ with expansions (a).

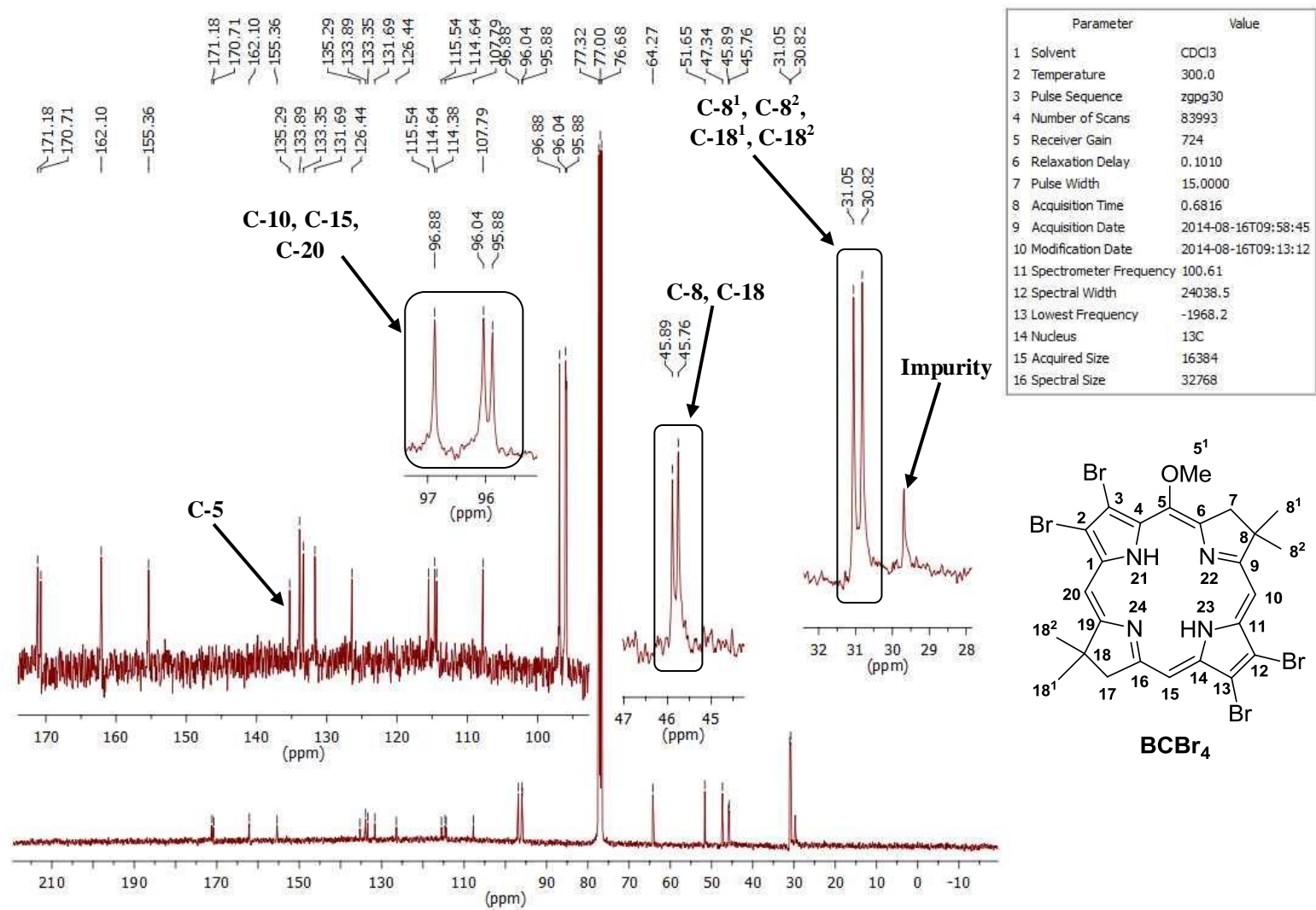


Figure S20. ¹³C NMR spectrum of compound **BCBr₄** in CDCl₃ with expansions (b).

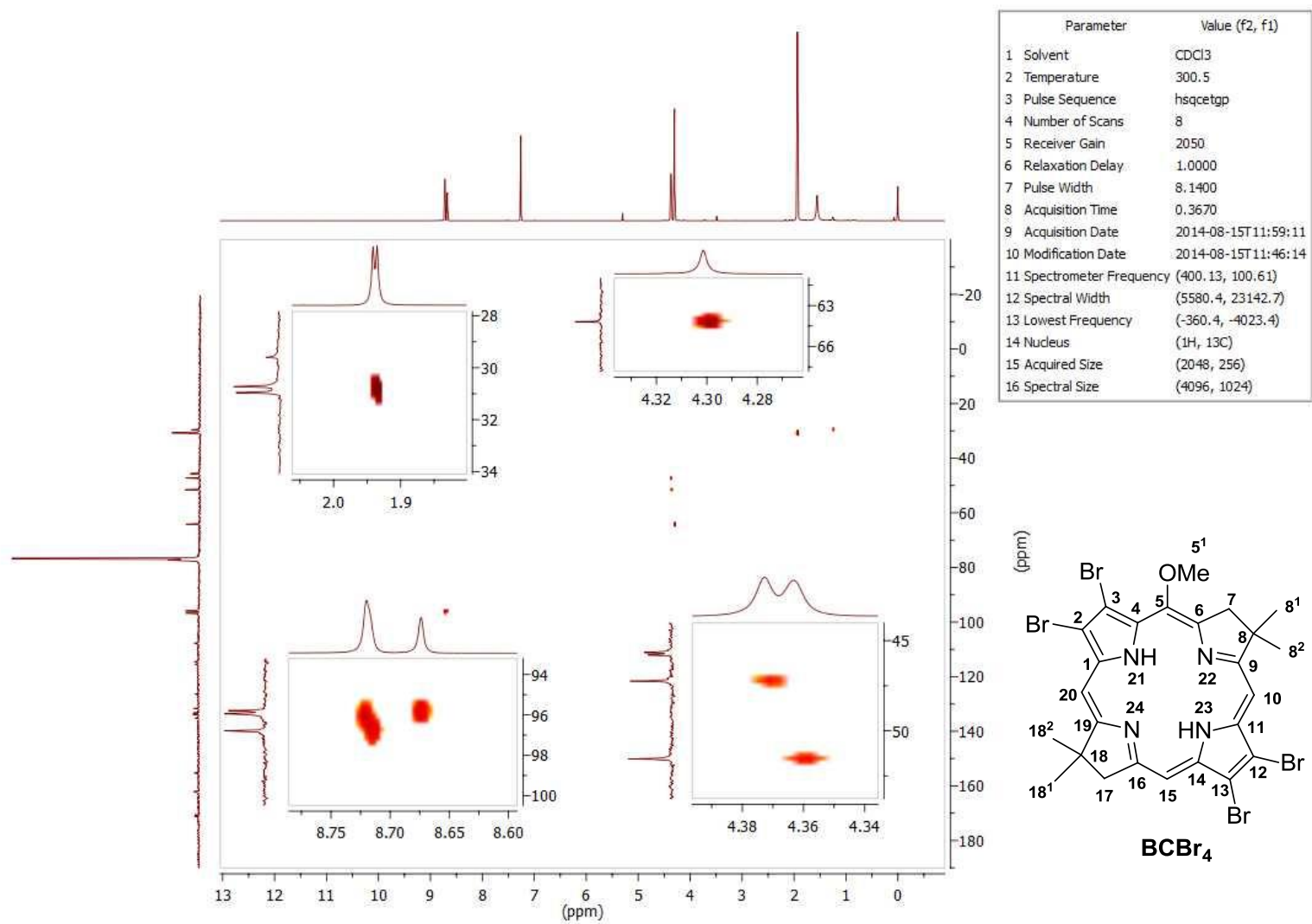


Figure S21. gHSQC spectrum of compound **BCBr₄** in CDCl₃.

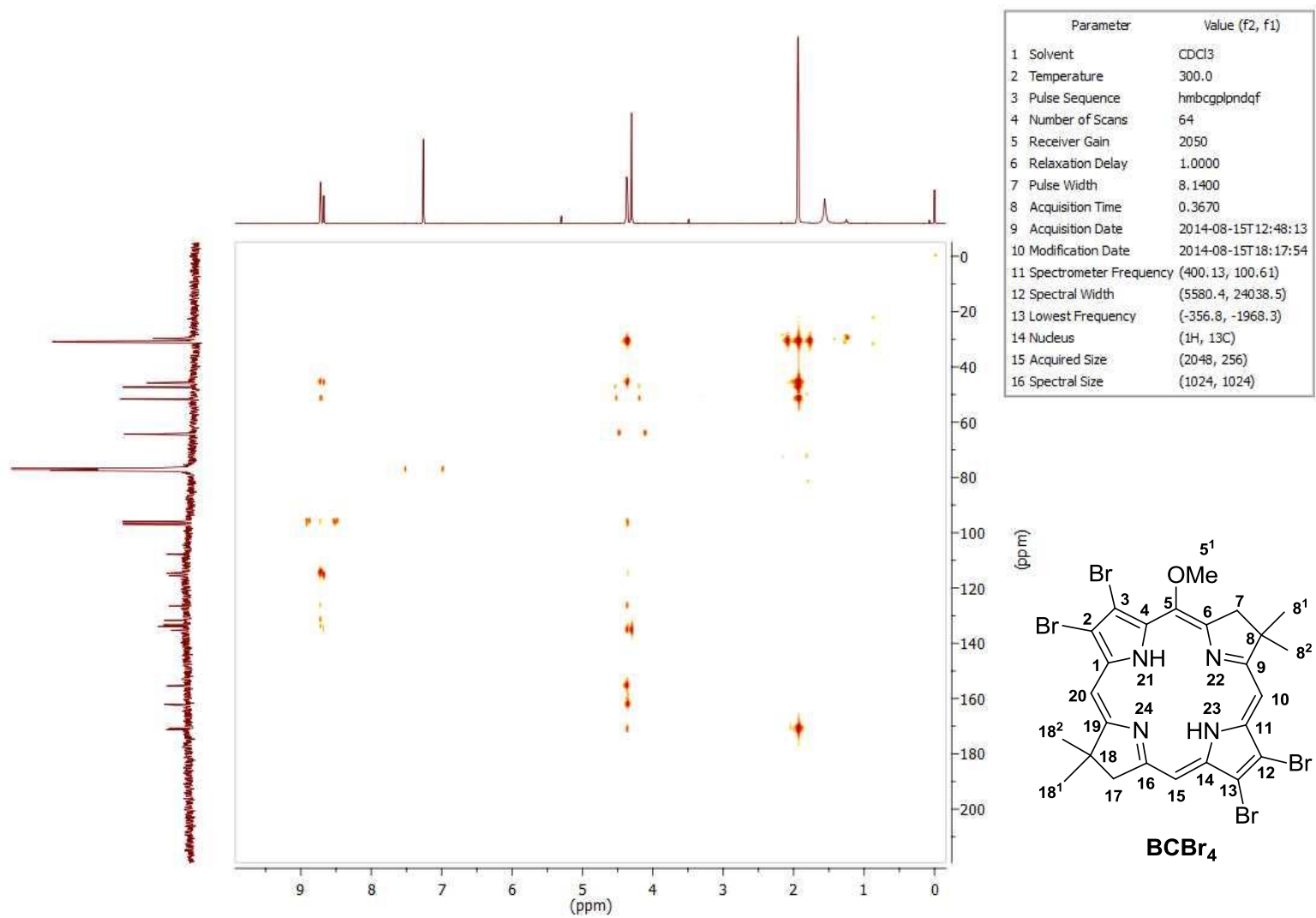
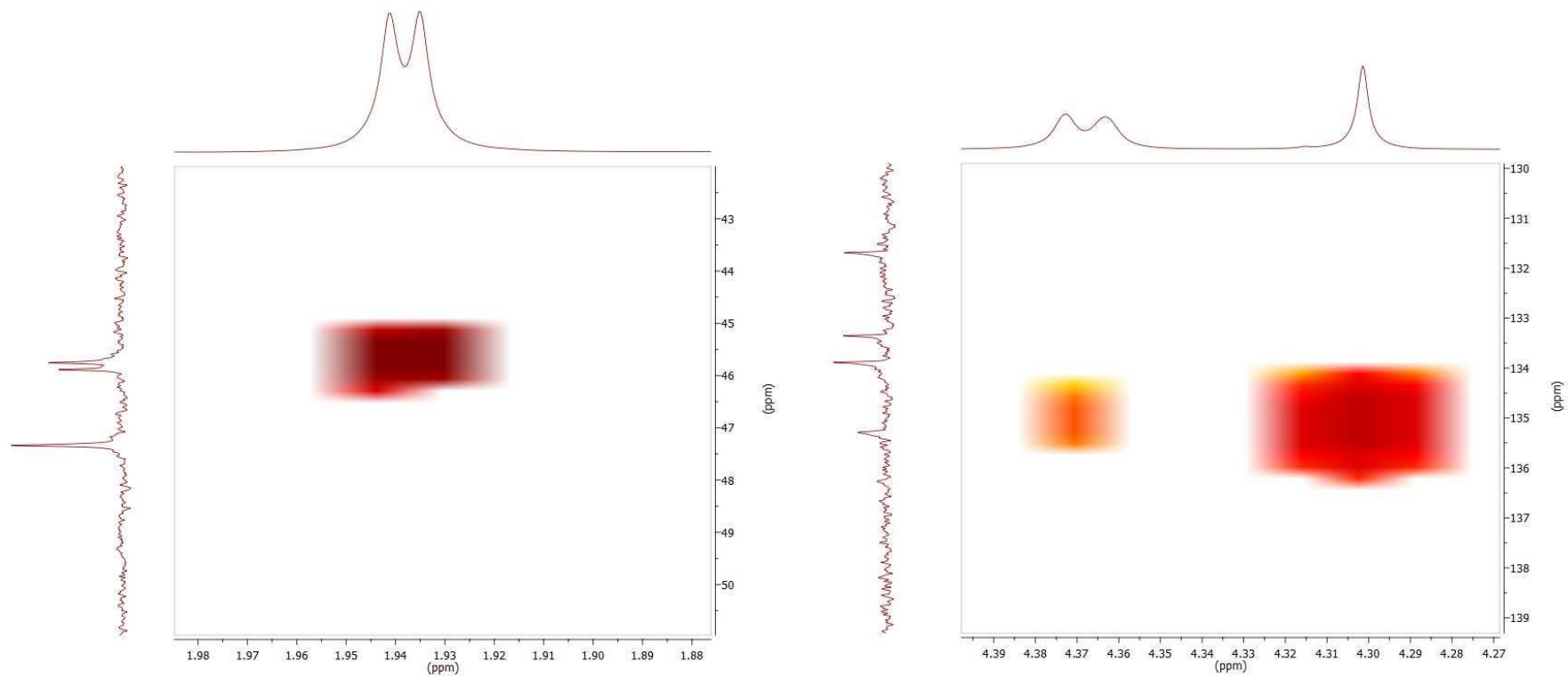


Figure S22. gHMBC spectrum of compound **BCBr₄** in CDCl₃.



Figures S23 and S24. Expansions of gHMBC spectrum of compound BCBr_4 in CDCl_3 .

2.9. NMR spectra of compound 17

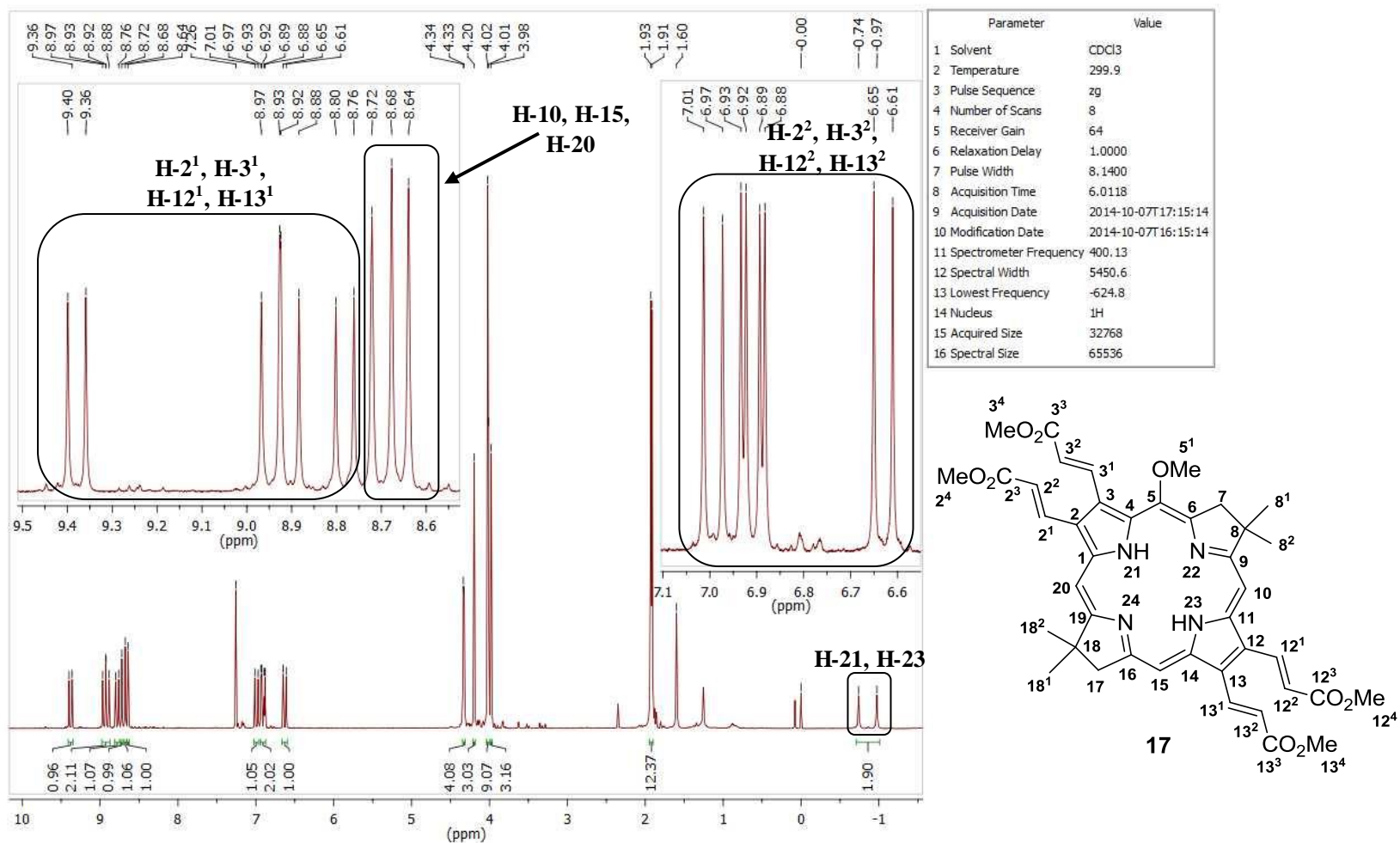


Figure S25. ¹H NMR spectrum of compound 17 in CDCl₃ with expansions (a).

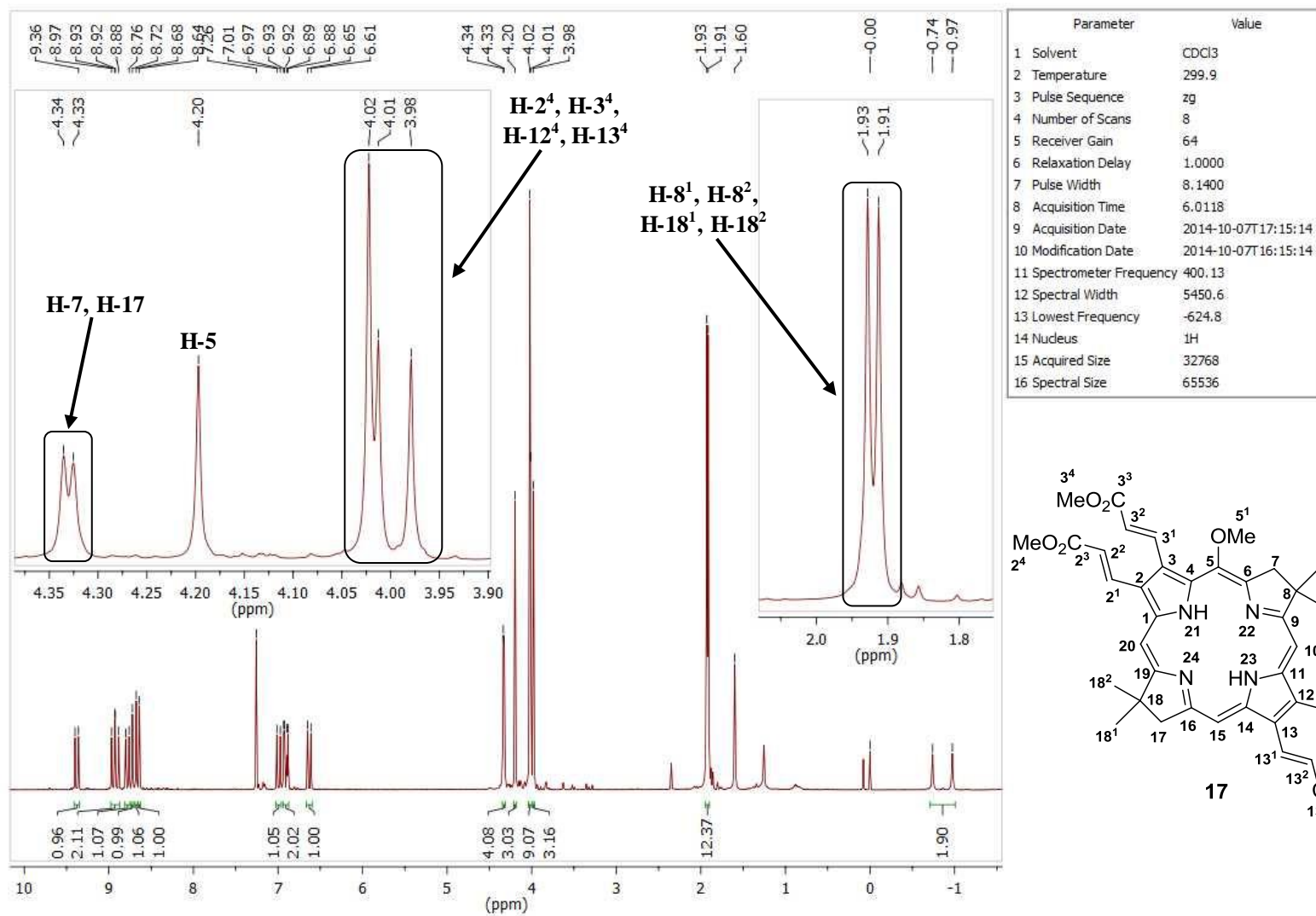


Figure S26. ^1H NMR spectrum of compound 17 in CDCl_3 with expansions (b).

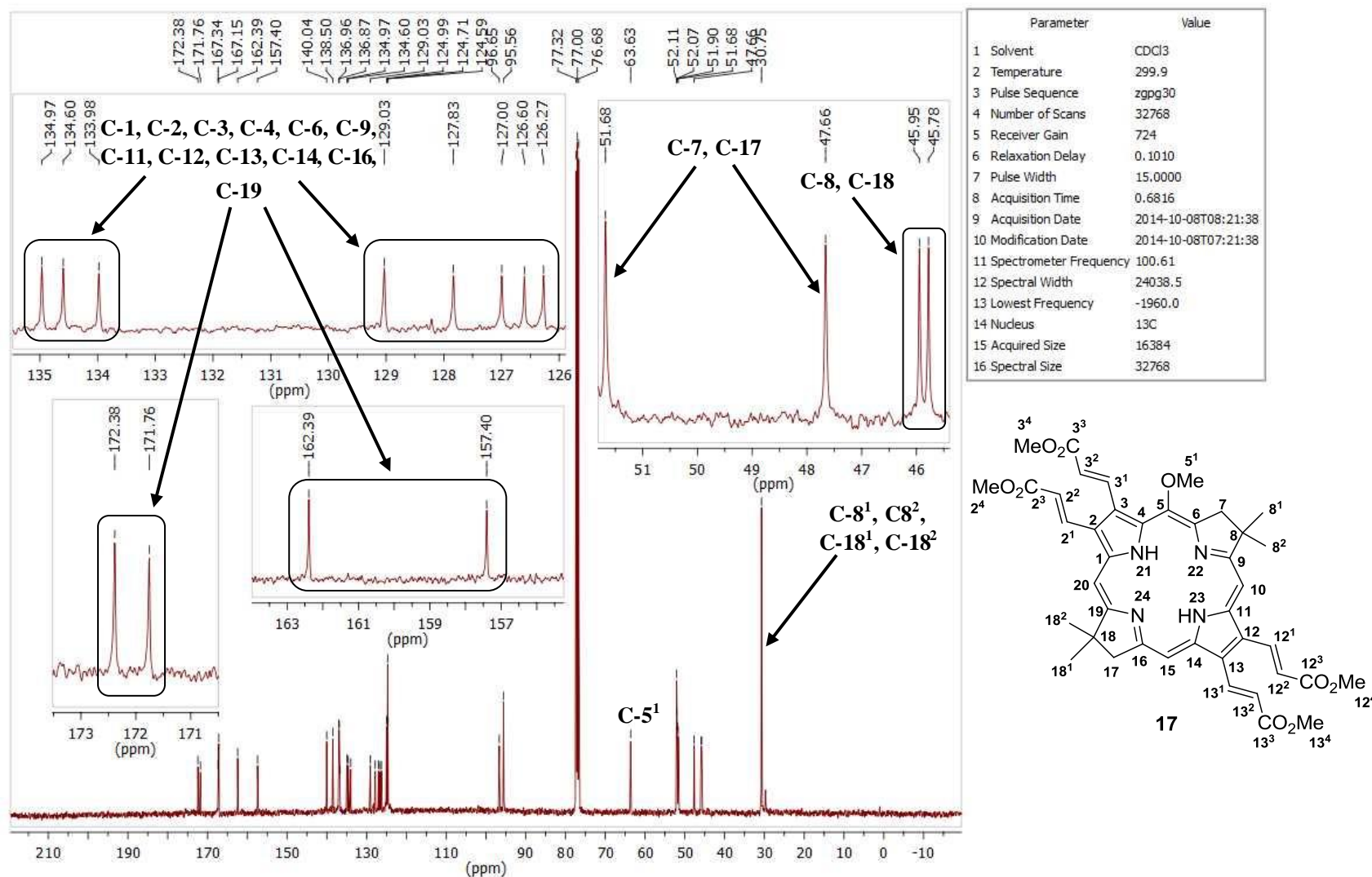


Figure S27. ¹³C NMR spectrum of compound **17** in CDCl₃ with expansions (a).

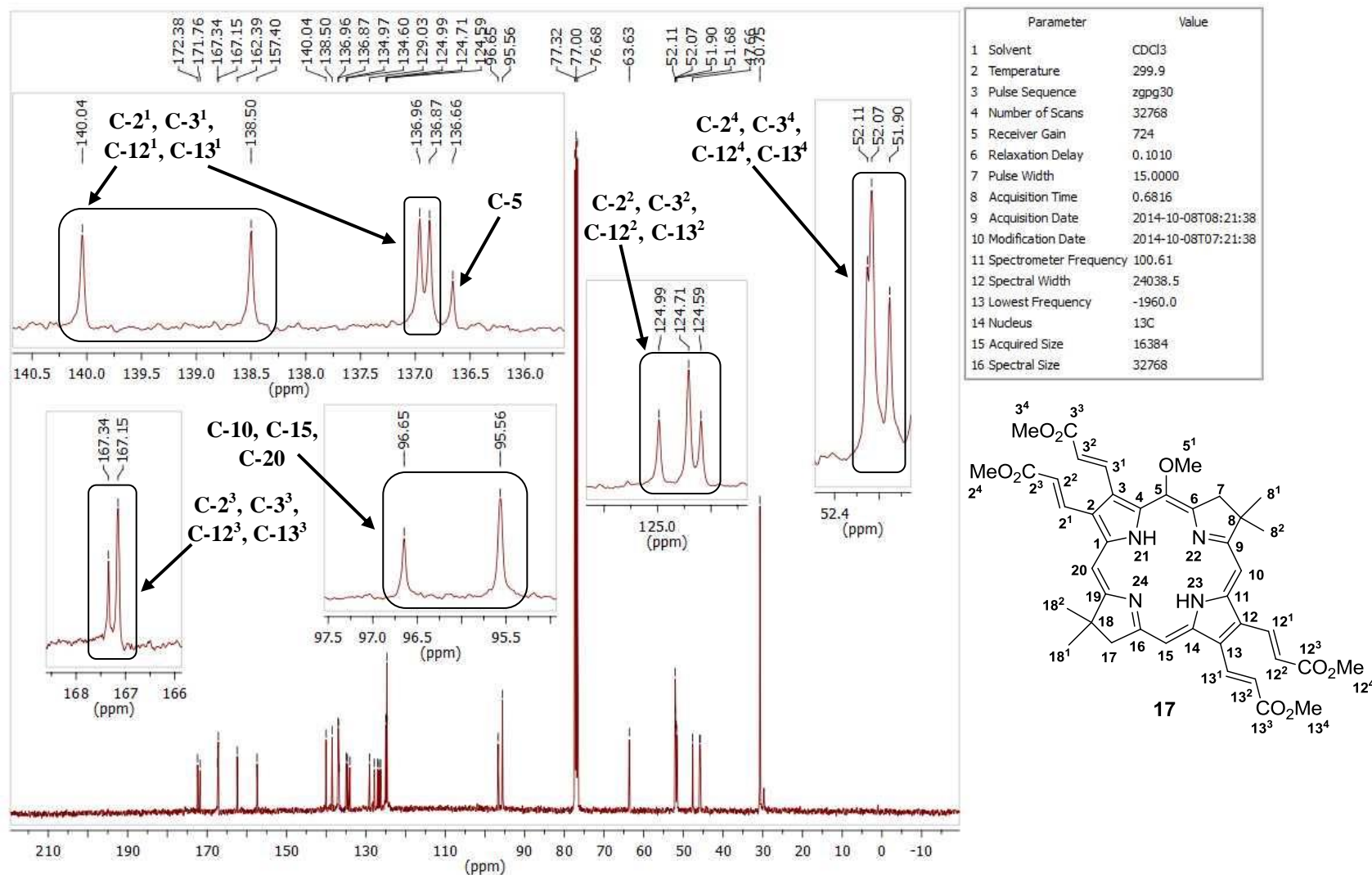


Figure S28. ^{13}C NMR spectrum of compound **17** in CDCl_3 with expansions (b).

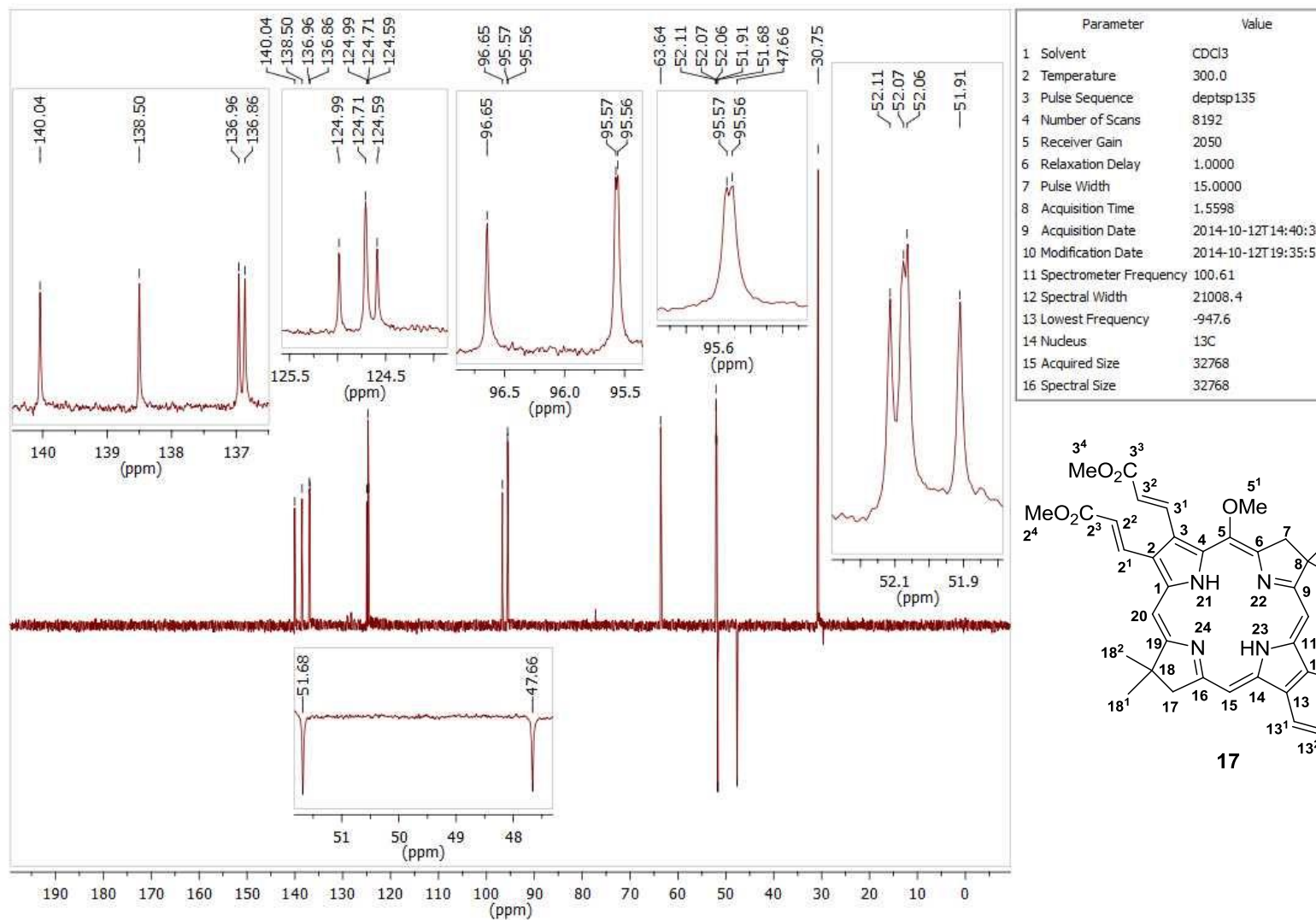
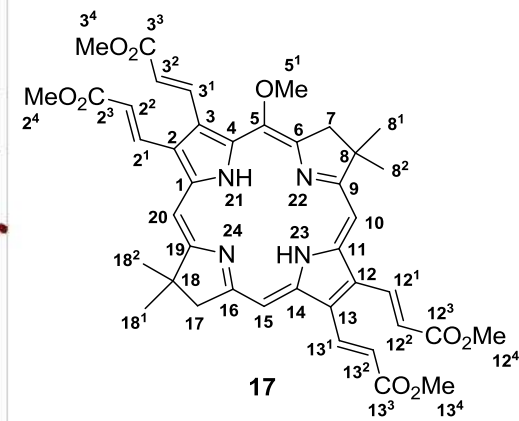


Figure S29. DEPT-135 spectrum of compound **17** in CDCl₃.



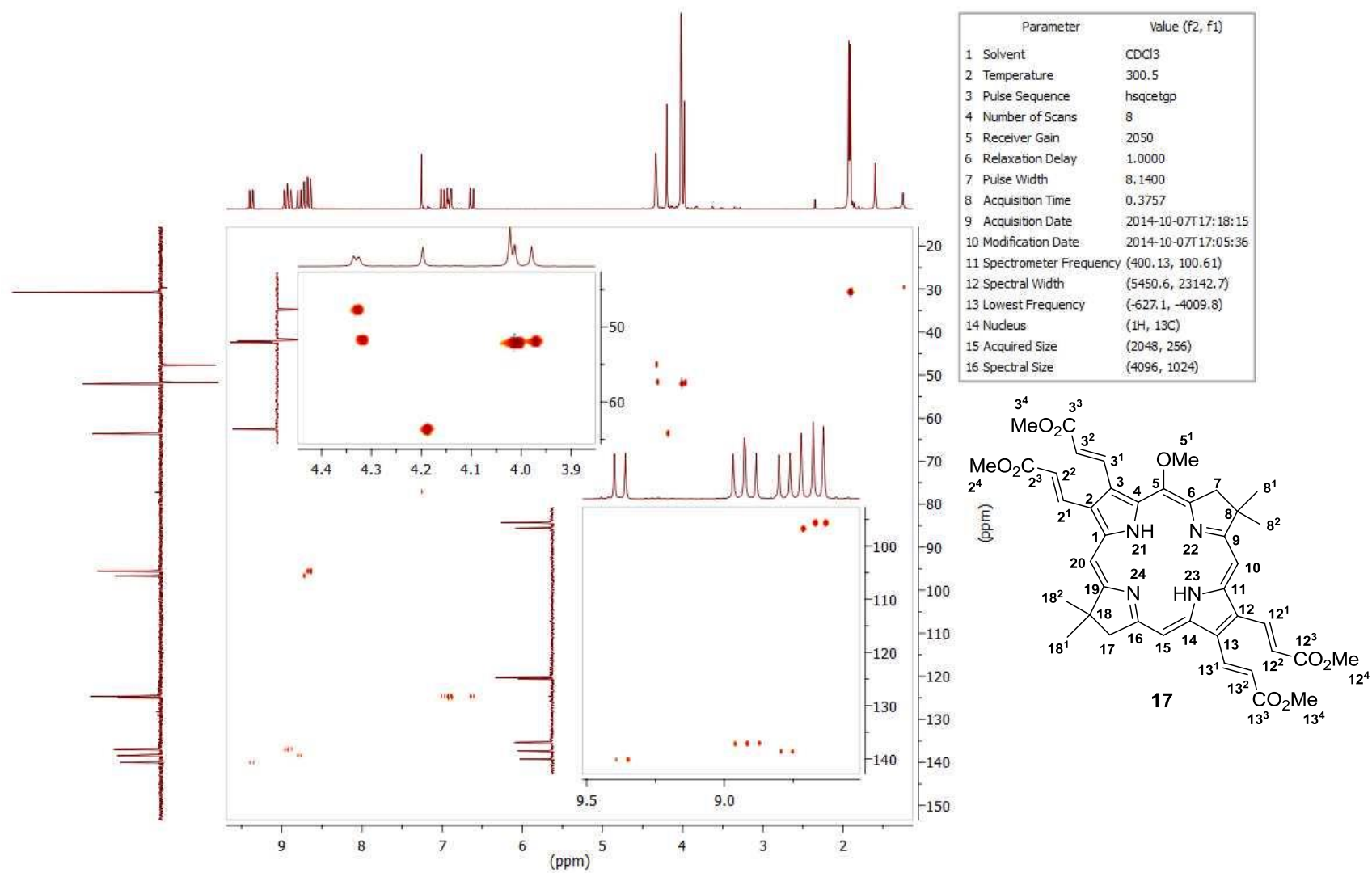


Figure S30. gHSQC spectrum of compound **17** in CDCl₃.

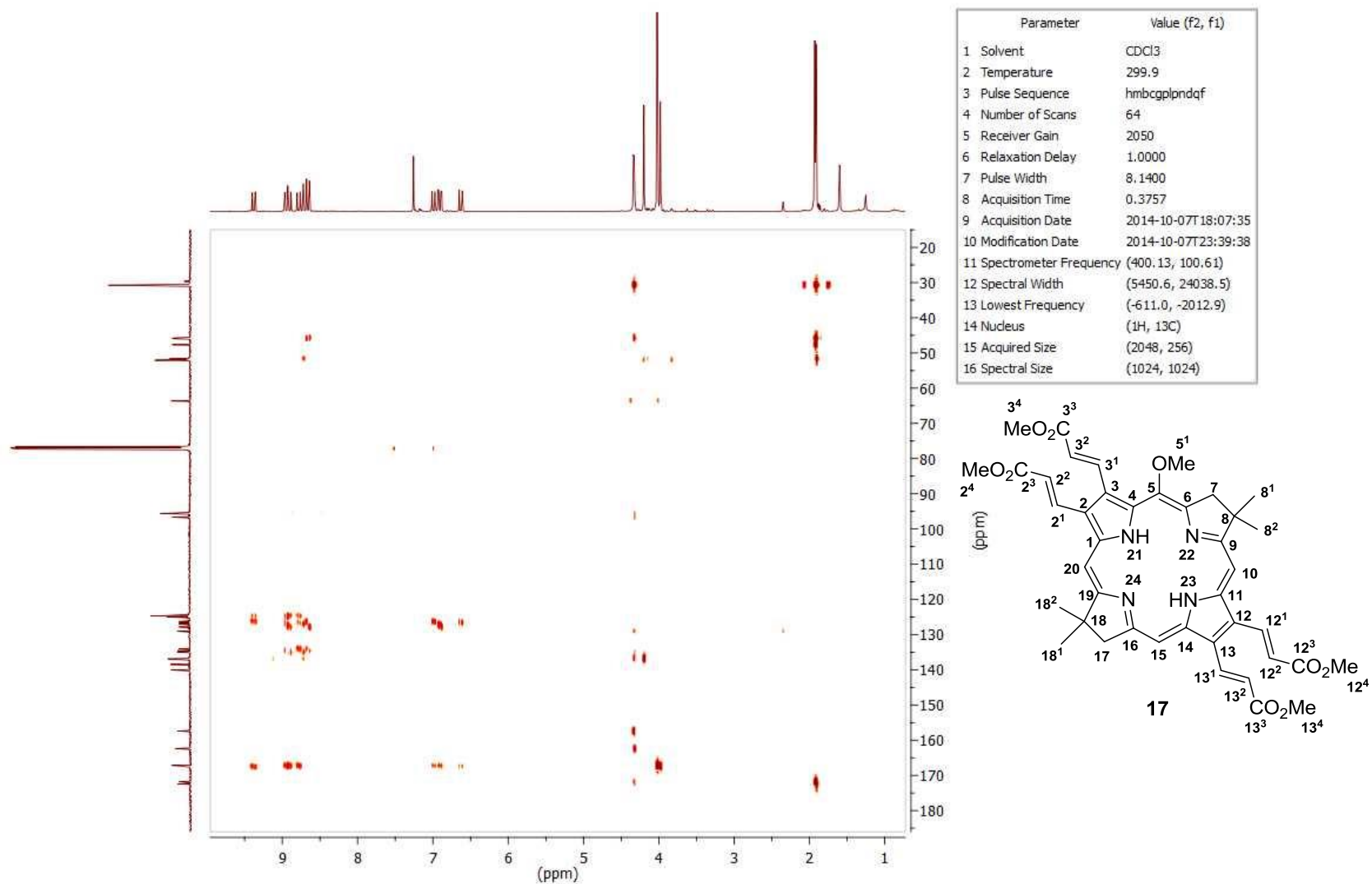
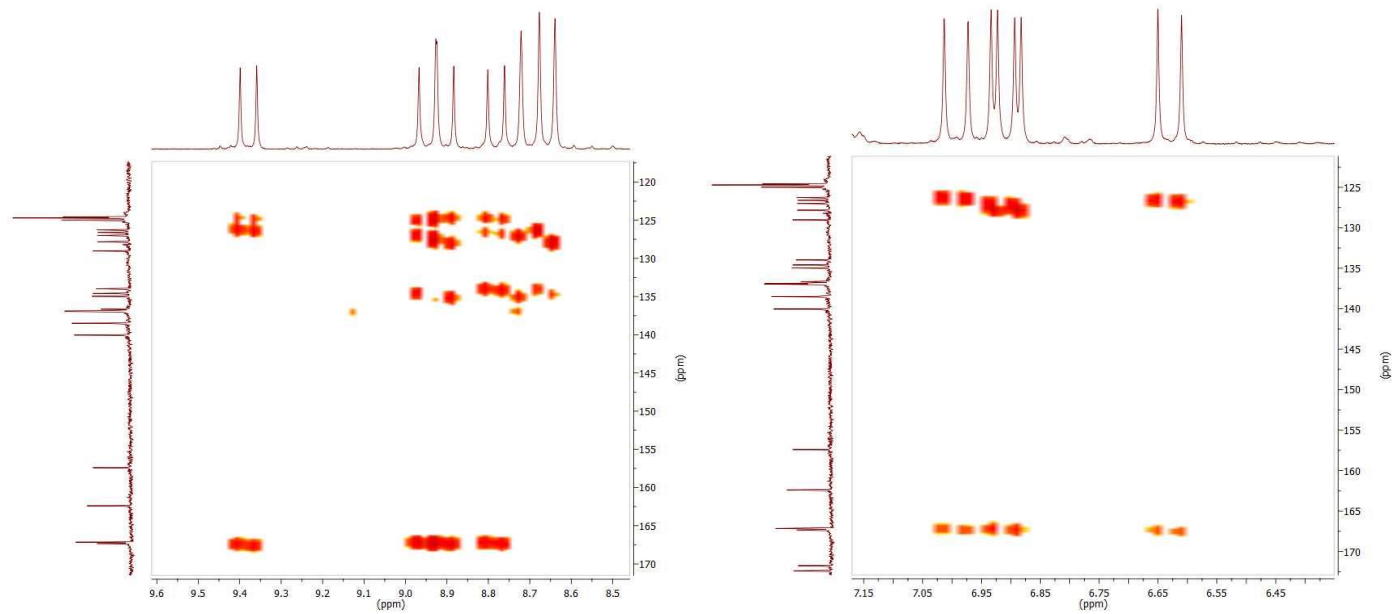


Figure S31. gHMBC spectrum of compound **17** in CDCl₃.



Figures S32 and S33. Expansions of gHMBC spectrum of compound **17** in CDCl₃.

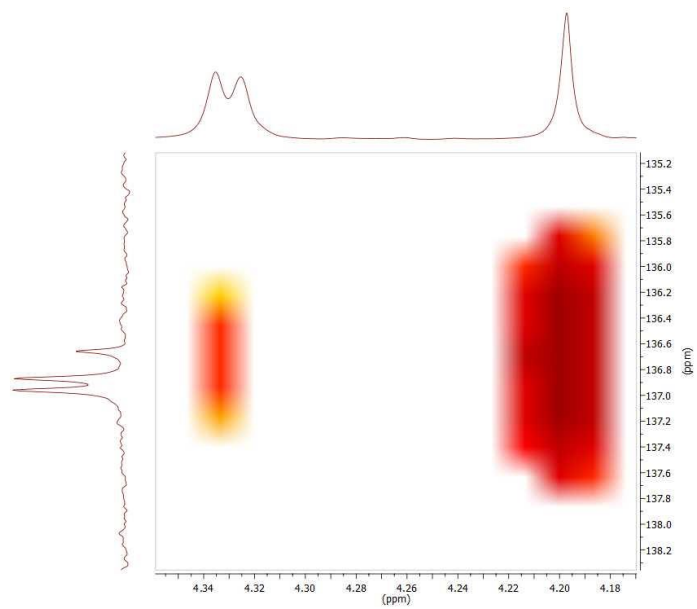


Figure S34. Expansion of gHMBC spectrum of compound **17** in CDCl_3 .

2.10. NMR spectra of compound 19

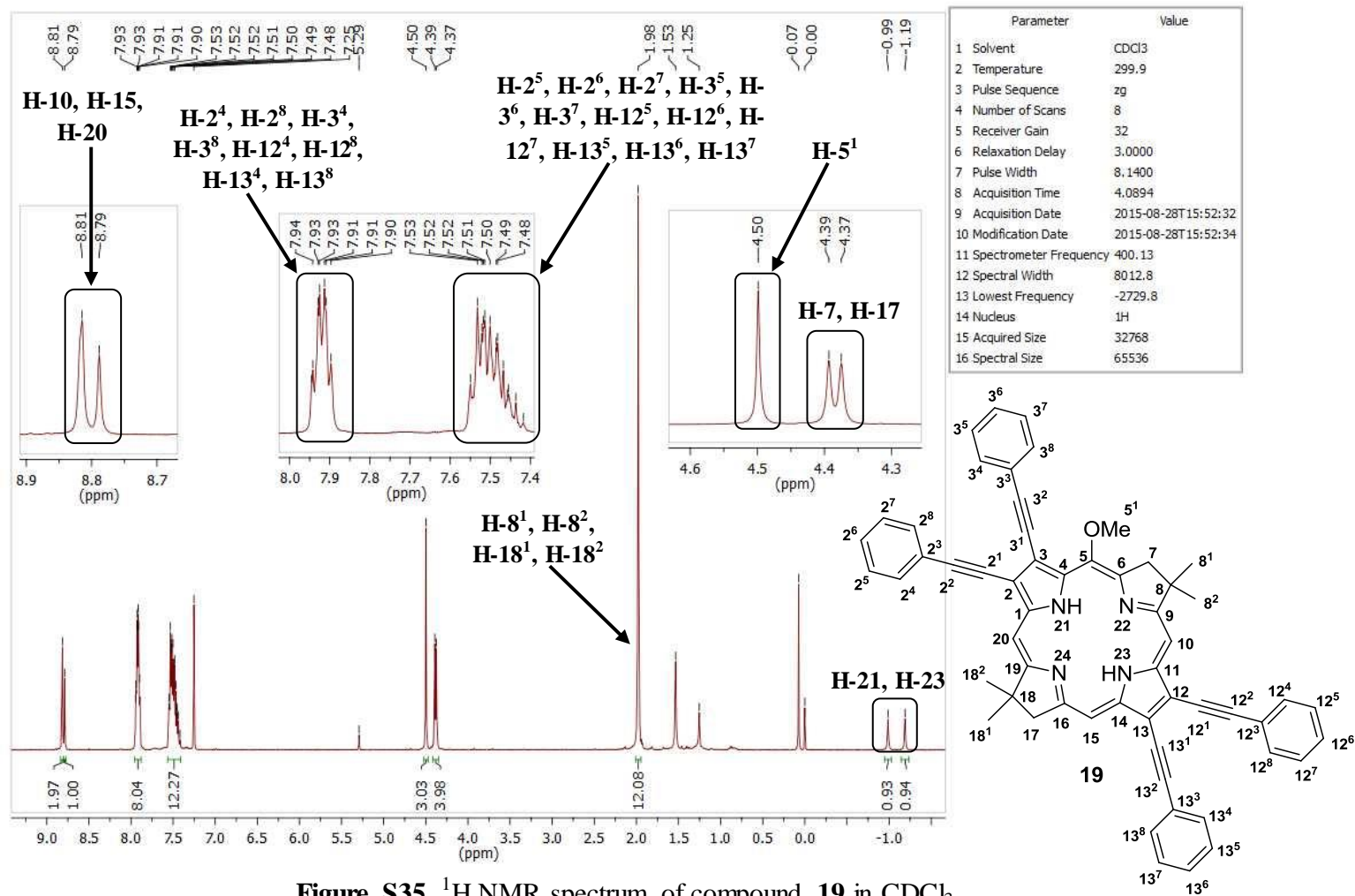


Figure S35. ¹H NMR spectrum of compound 19 in CDCl₃.

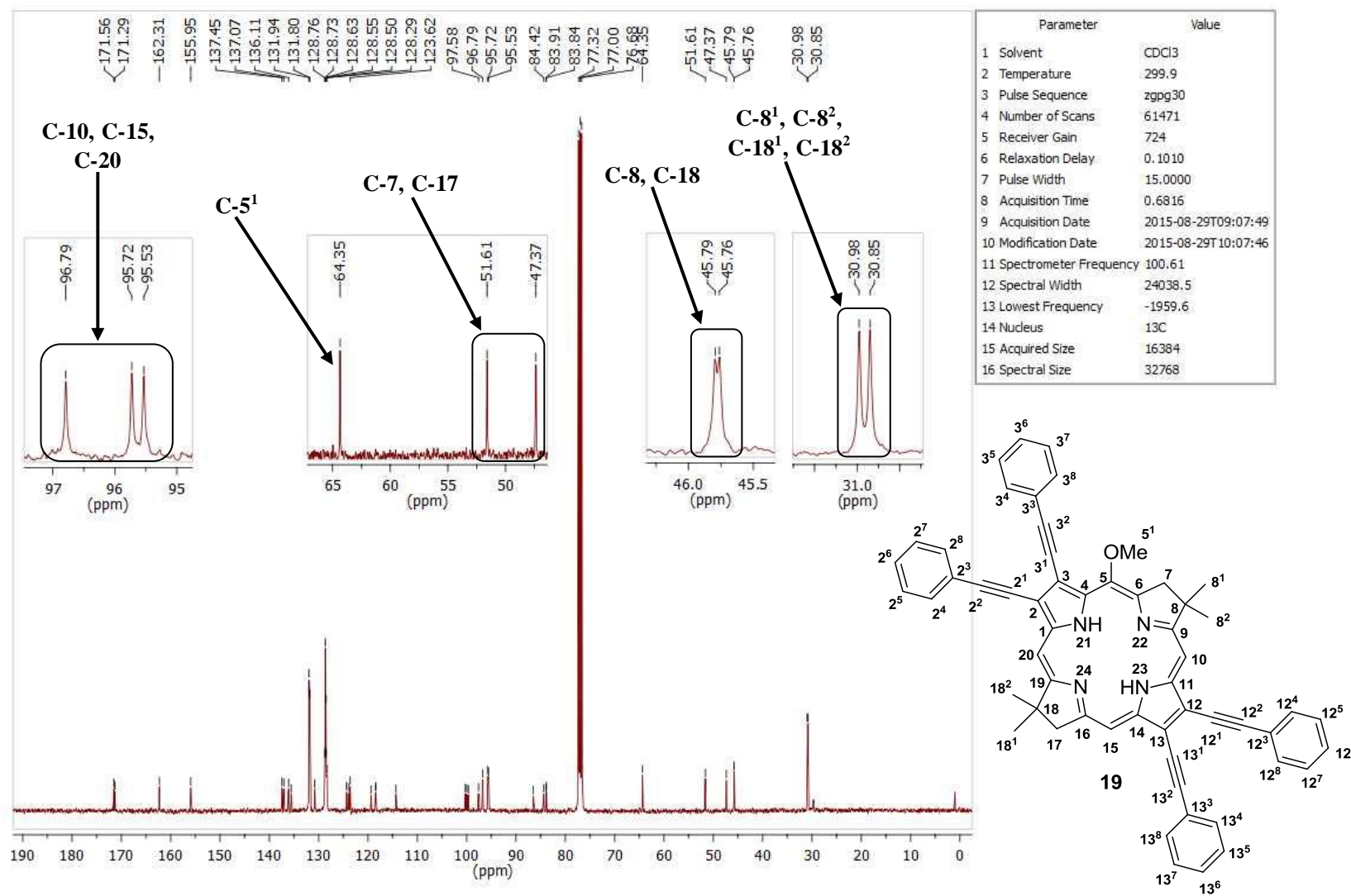


Figure S36. ^{13}C NMR spectrum of compound **19** in CDCl_3 with expansions (a).

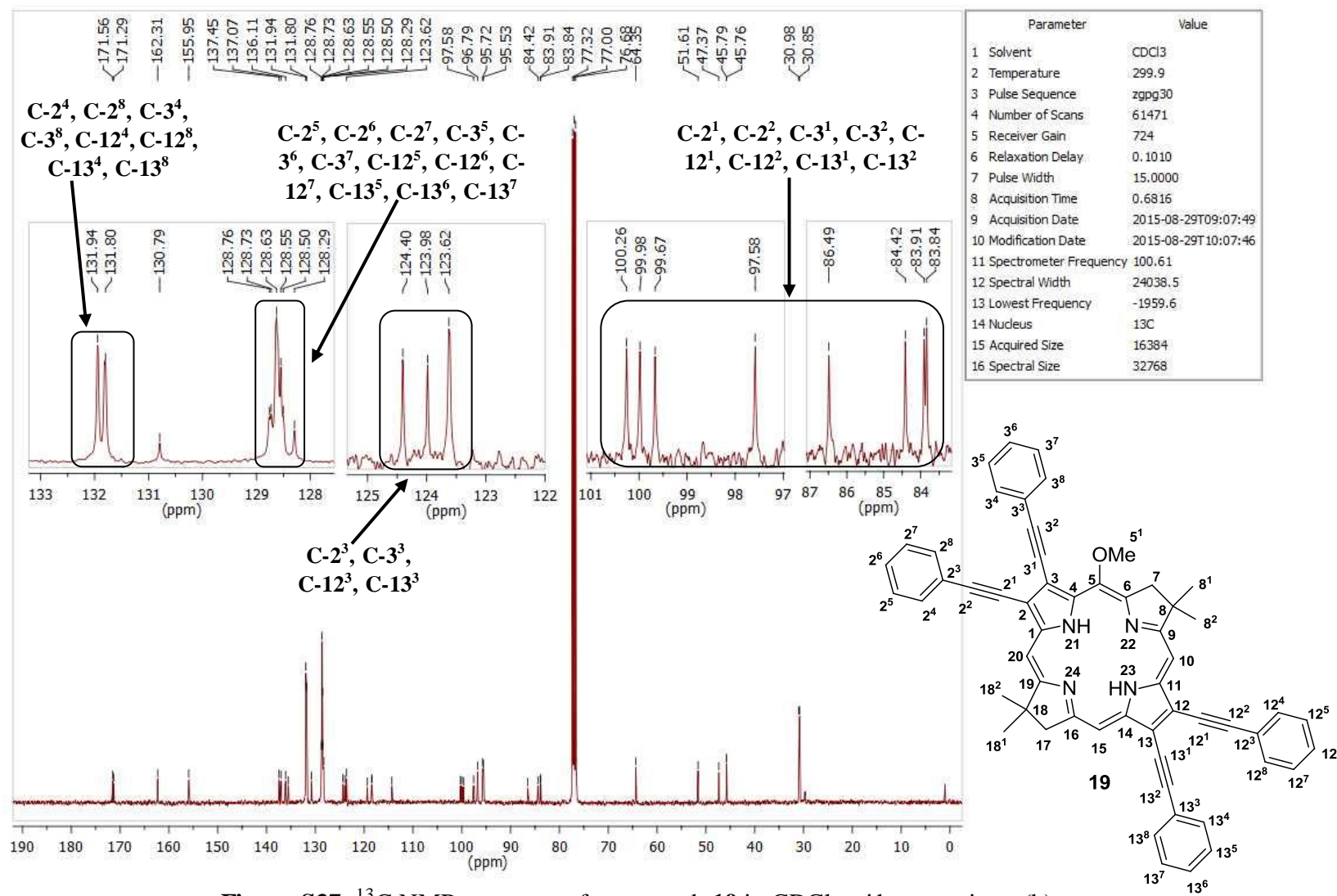


Figure S37. ^{13}C NMR spectrum of compound **19** in CDCl_3 with expansions (b).

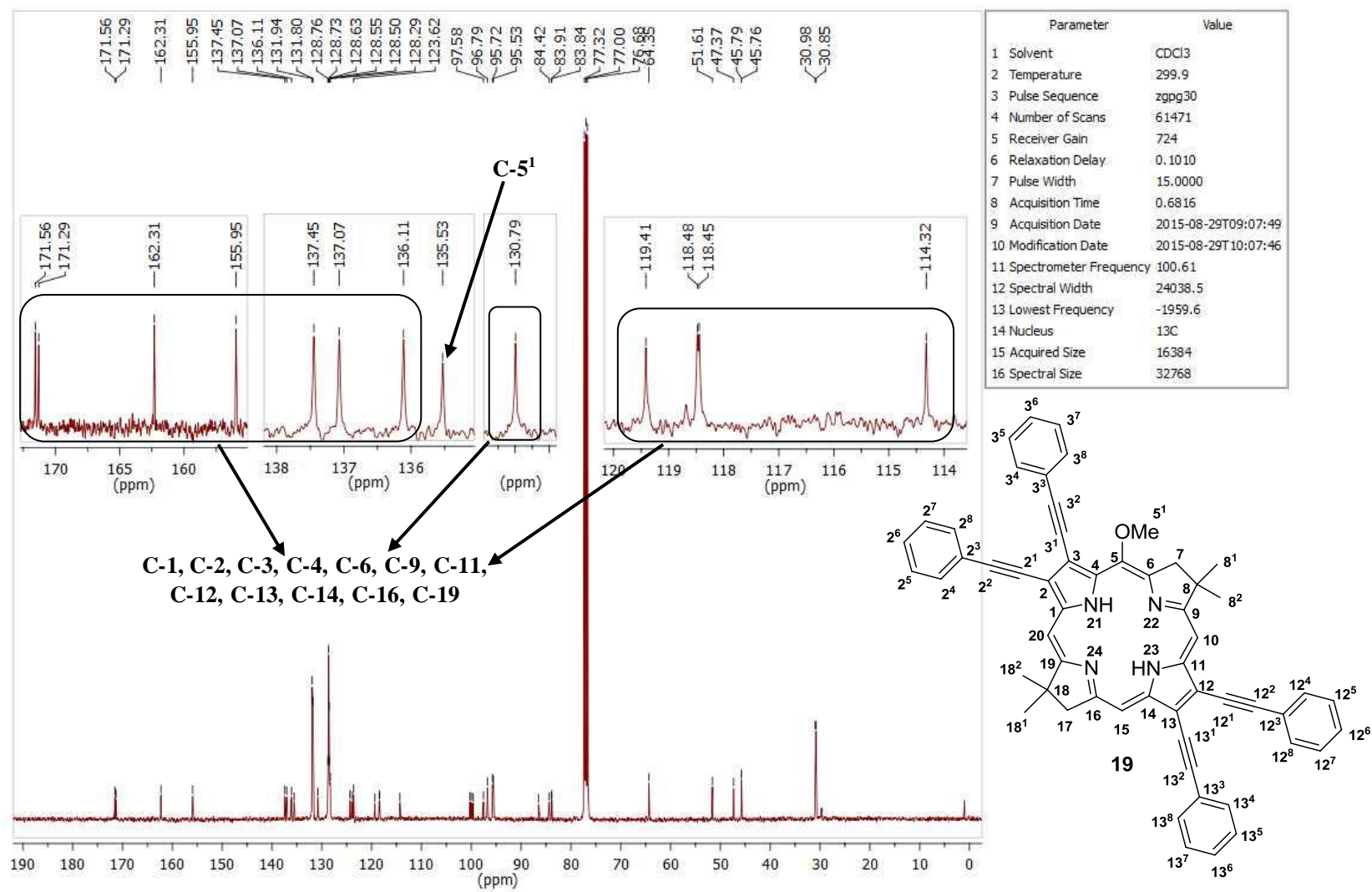
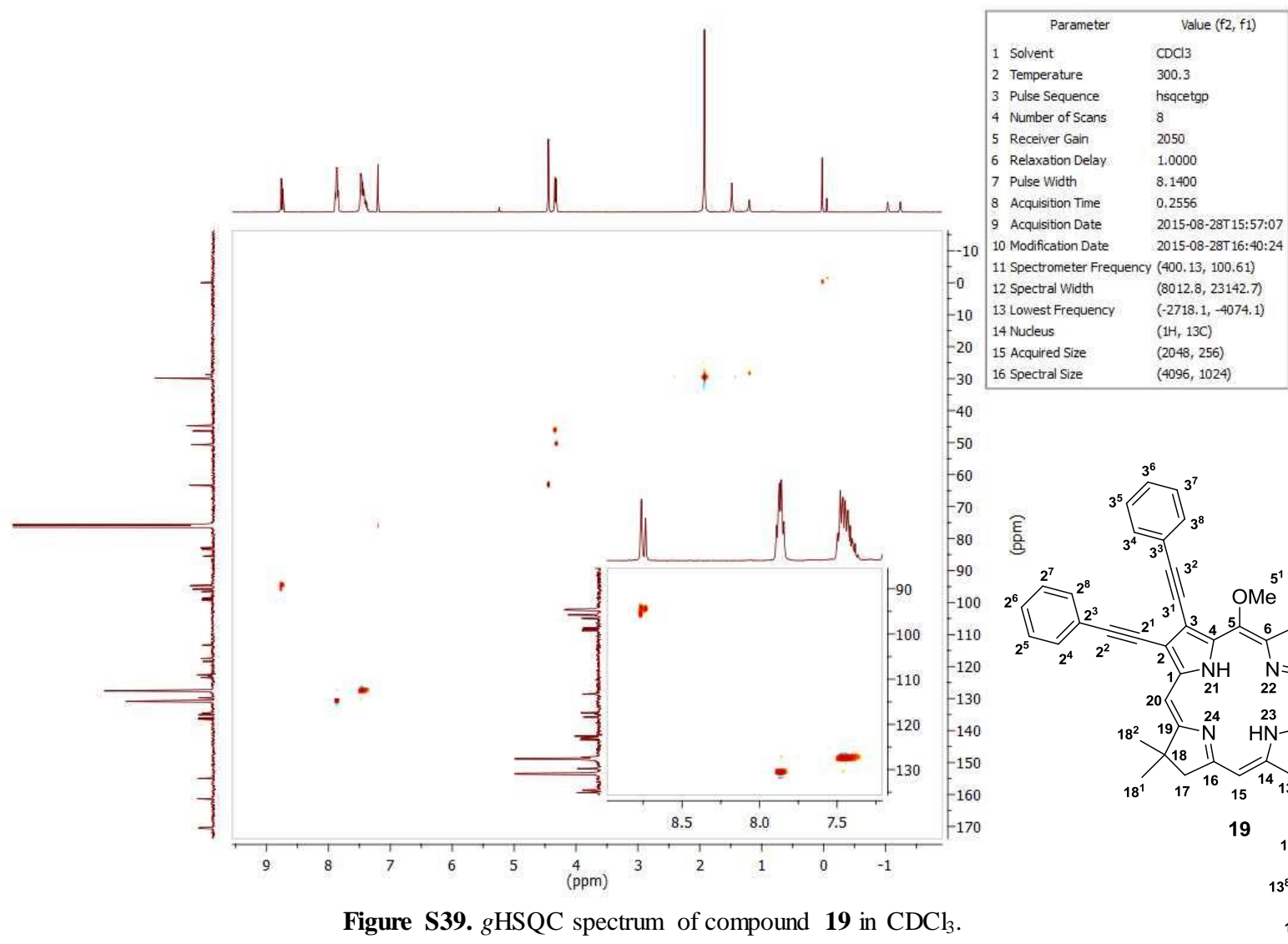


Figure S38. ^{13}C NMR spectrum of compound **19** in CDCl_3 with expansions (c).



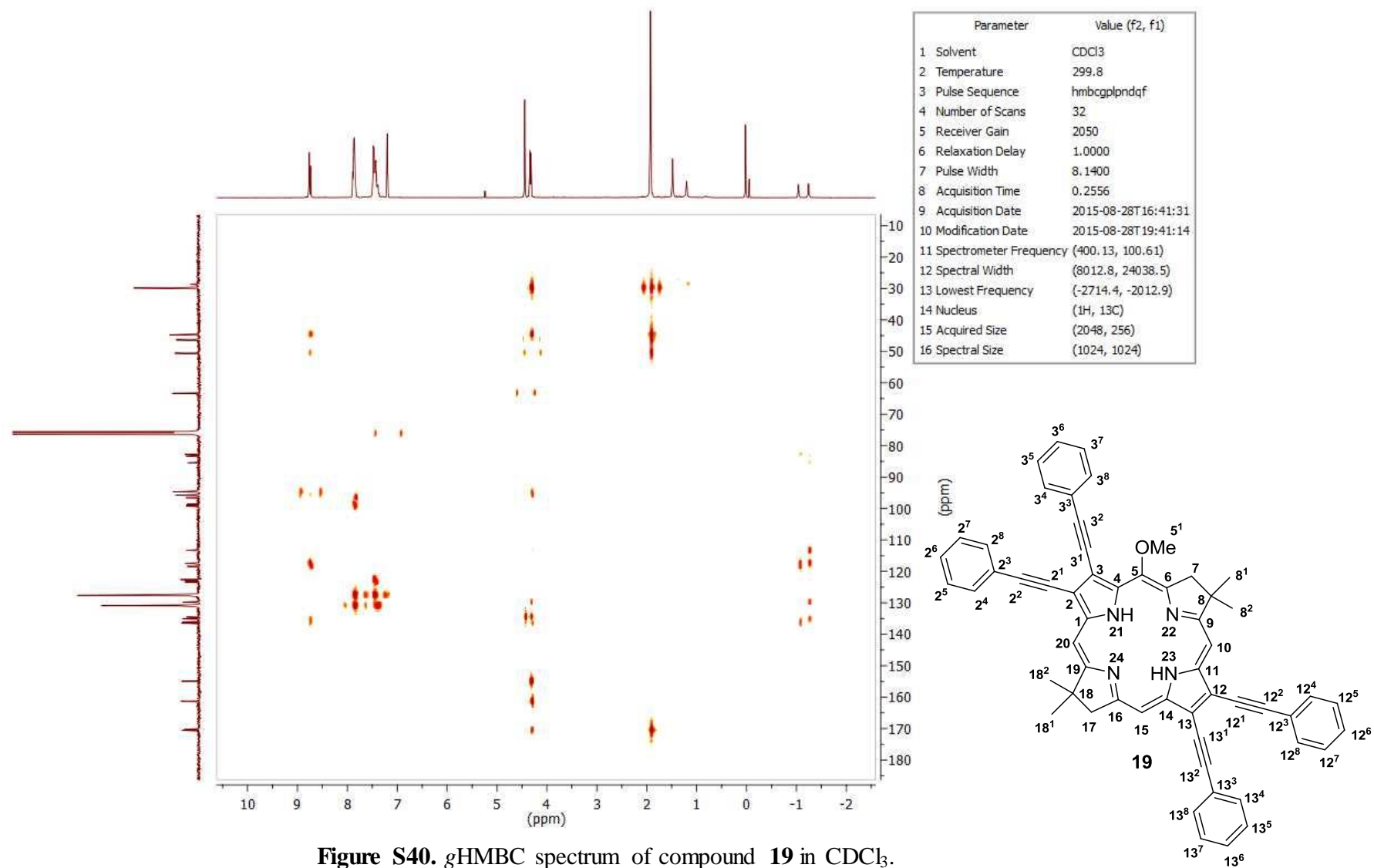


Figure S40. gHMBC spectrum of compound **19** in CDCl₃.

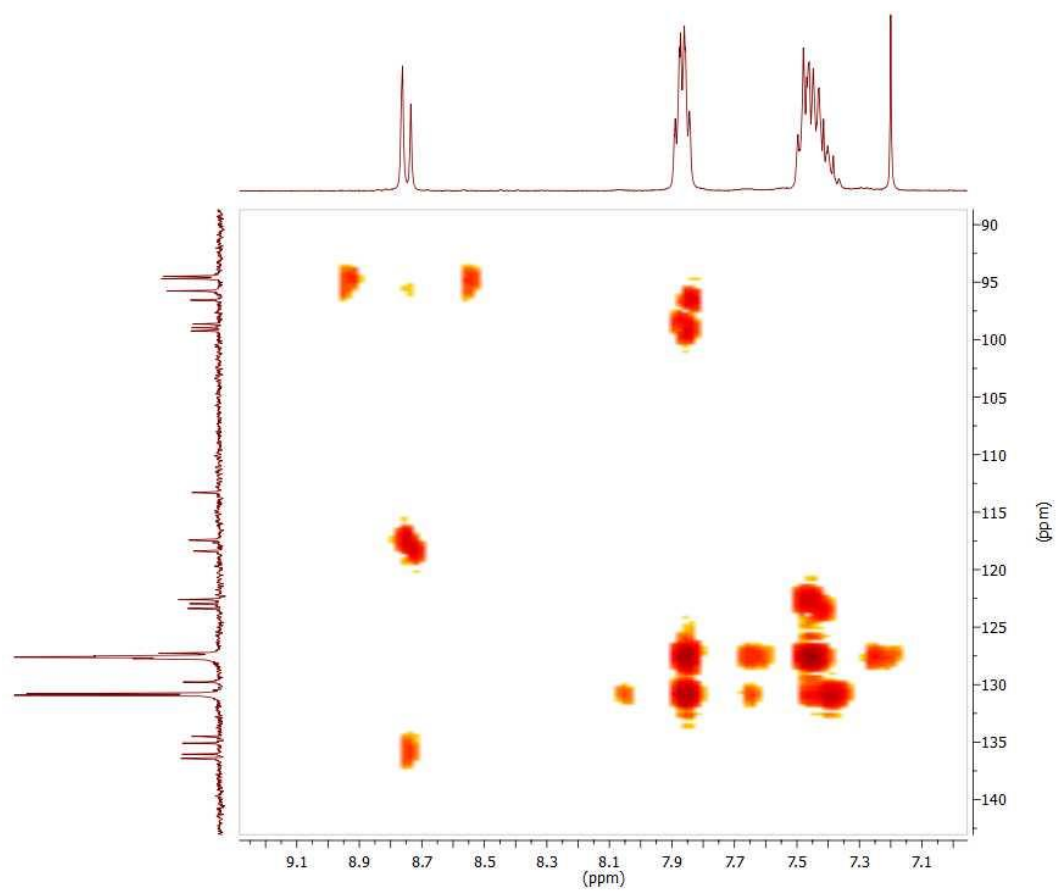
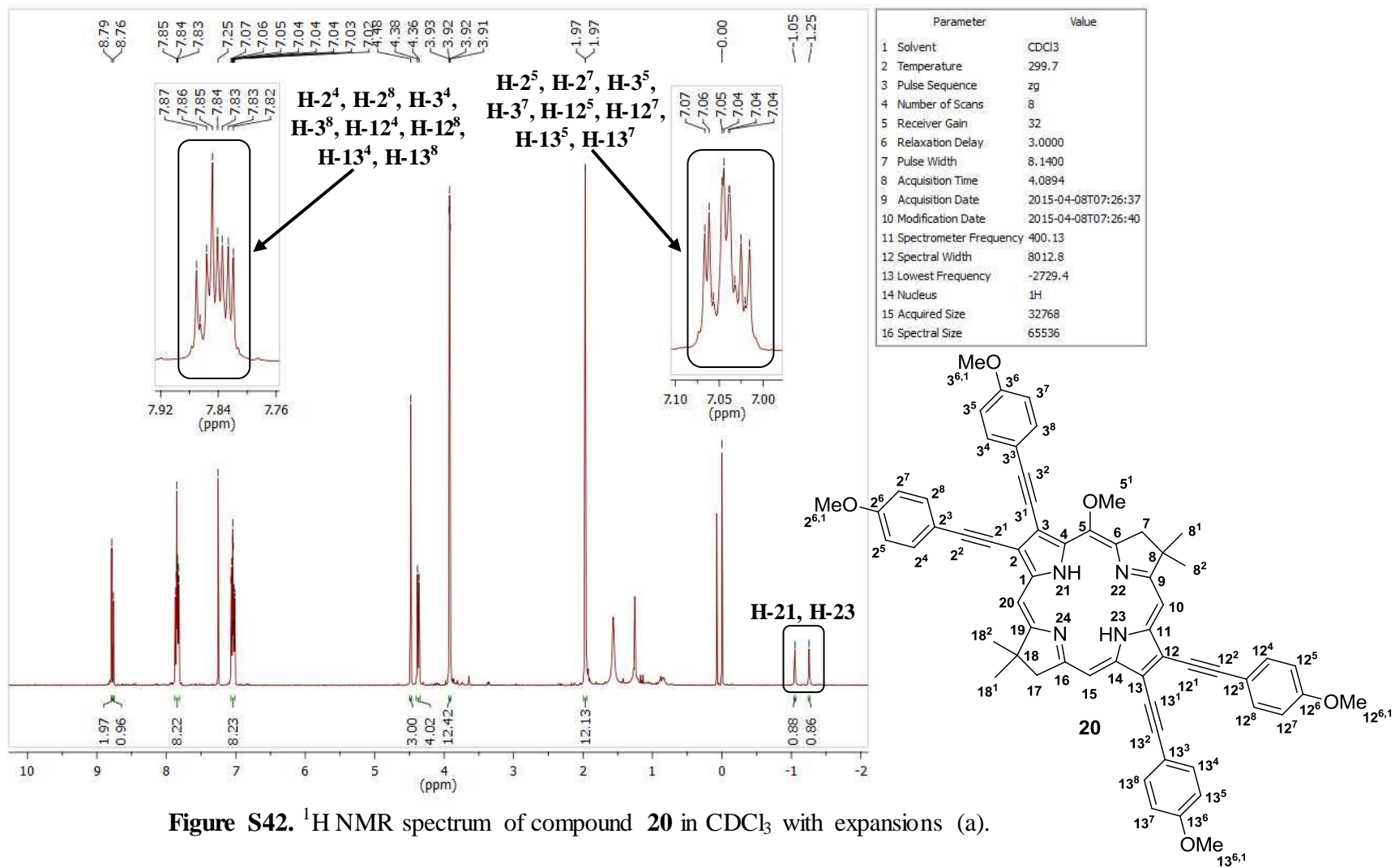


Figure S41. Expansion of gHMBC spectrum of compound **19** in CDCl₃.

2.11. NMR spectra of compound 20



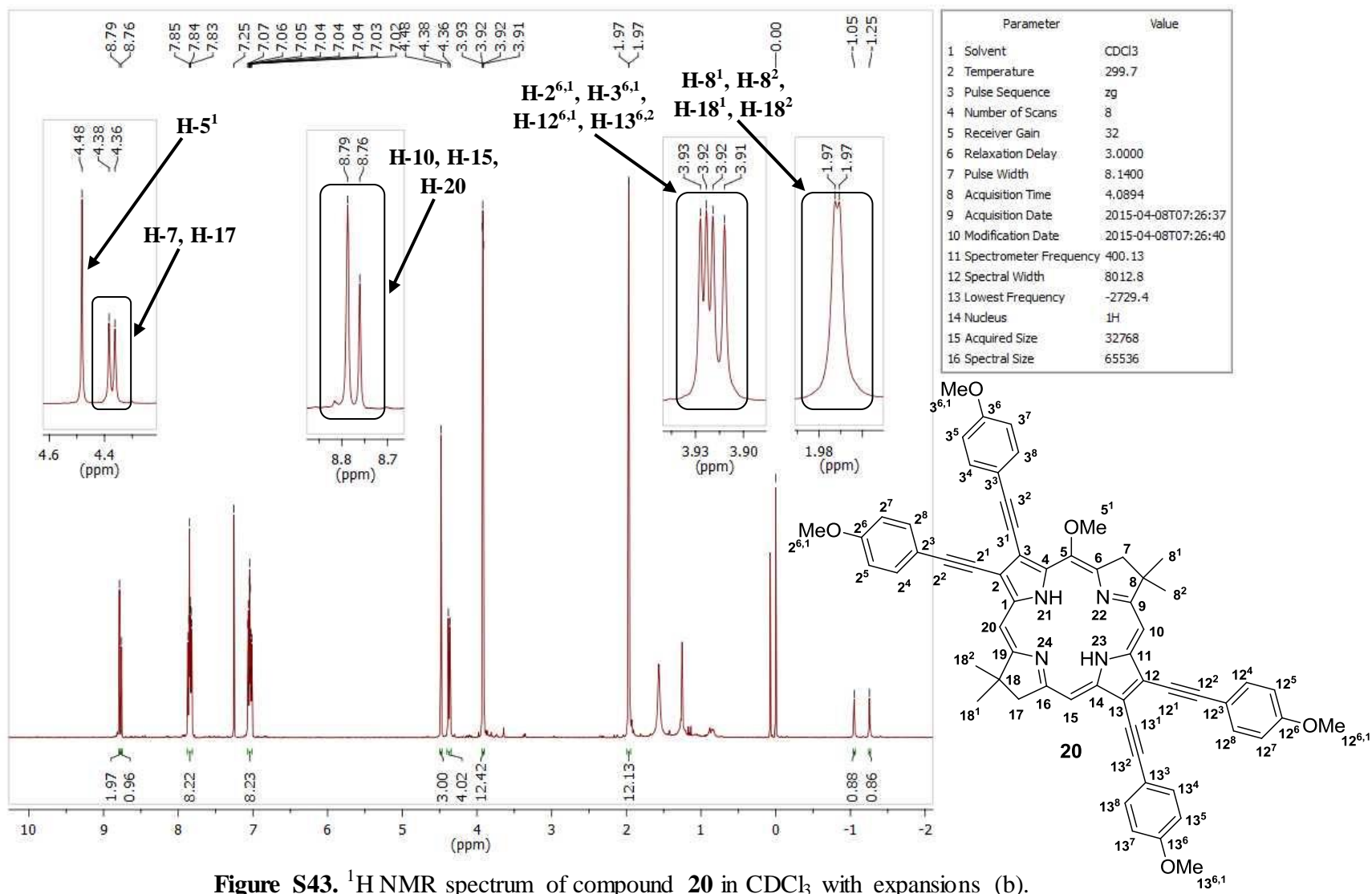


Figure S43. ^1H NMR spectrum of compound **20** in CDCl_3 with expansions (b).

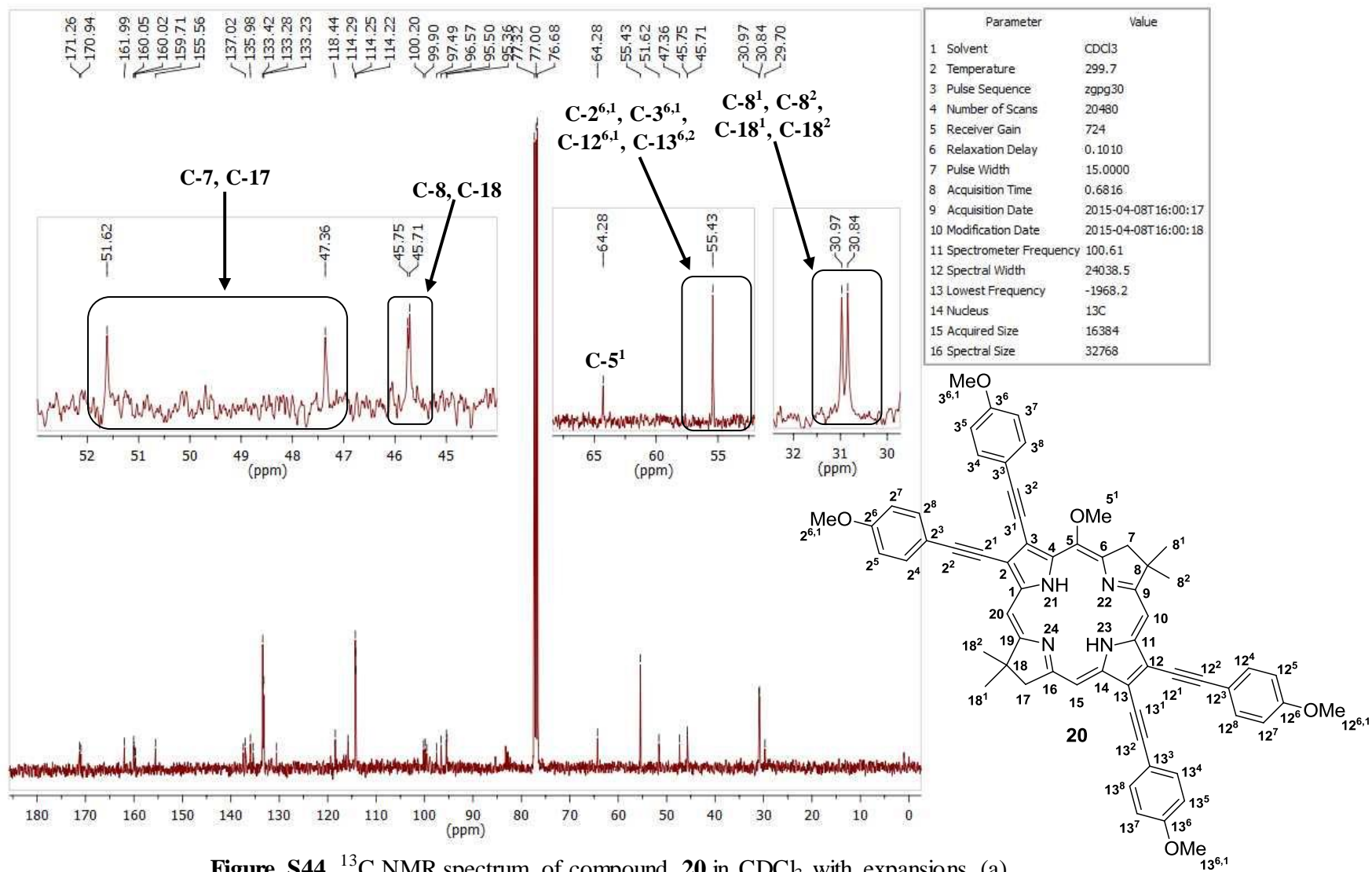


Figure S44. ¹³C NMR spectrum of compound **20** in CDCl₃ with expansions (a).

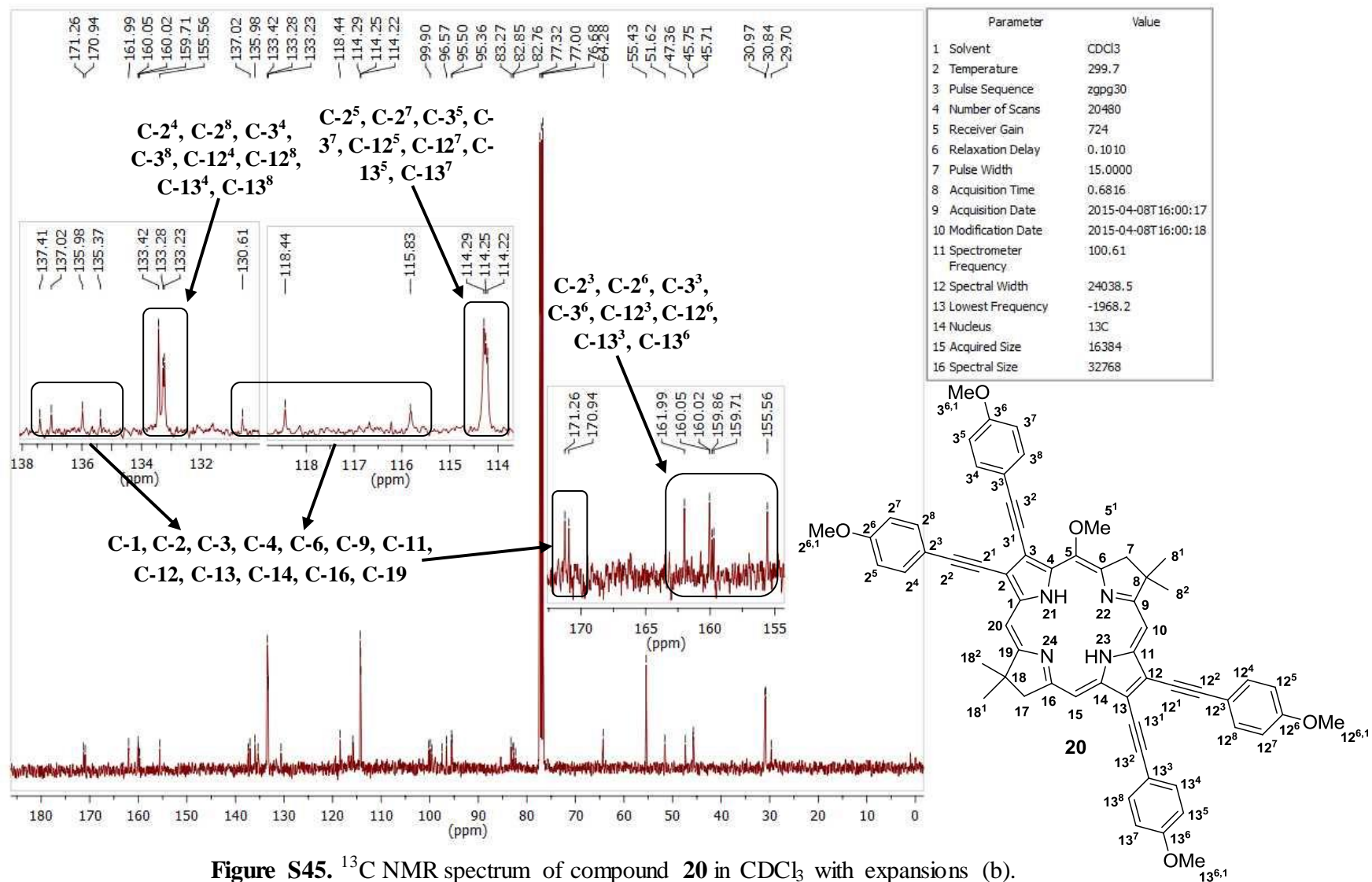


Figure S45. ¹³C NMR spectrum of compound 20 in CDCl₃ with expansions (b).

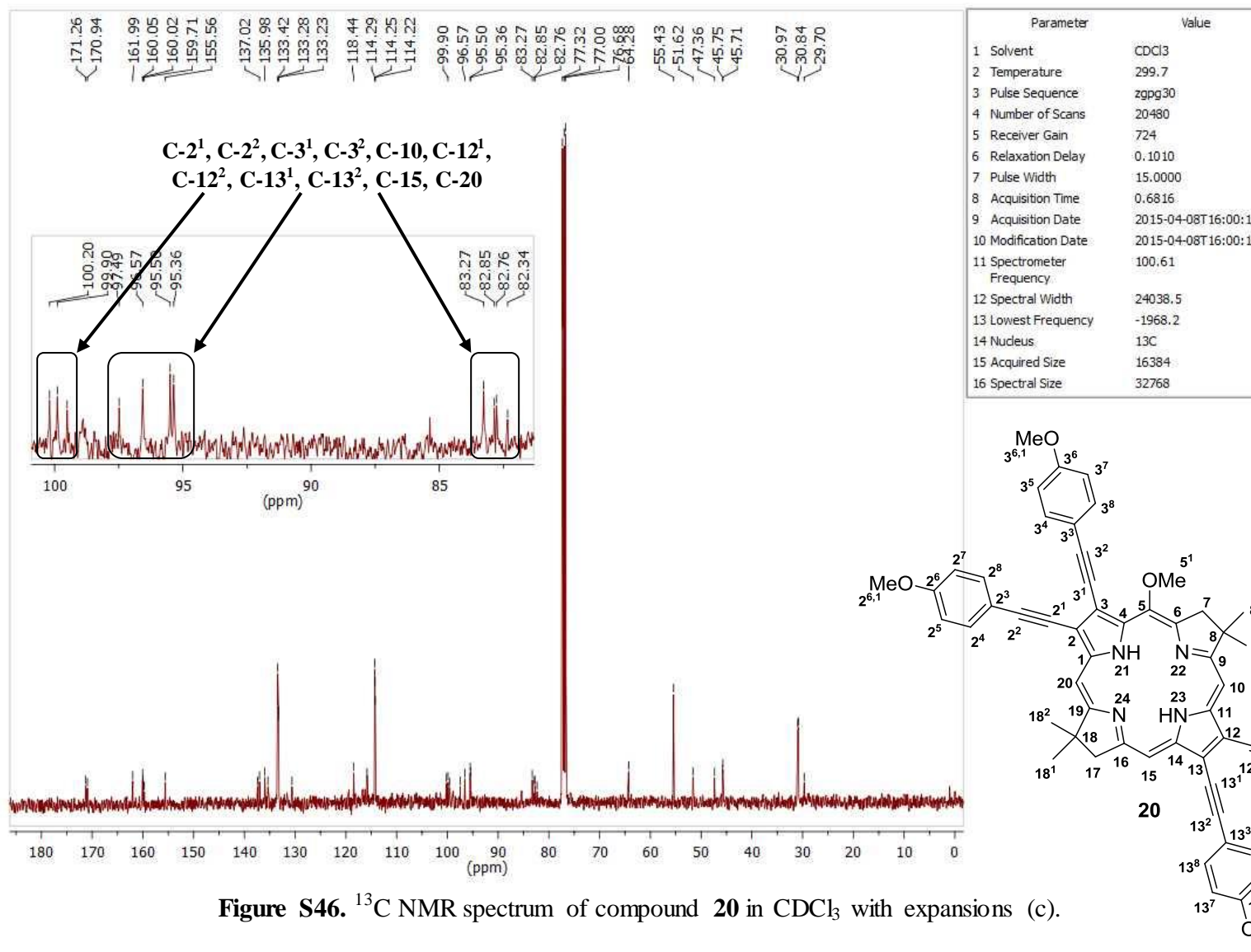
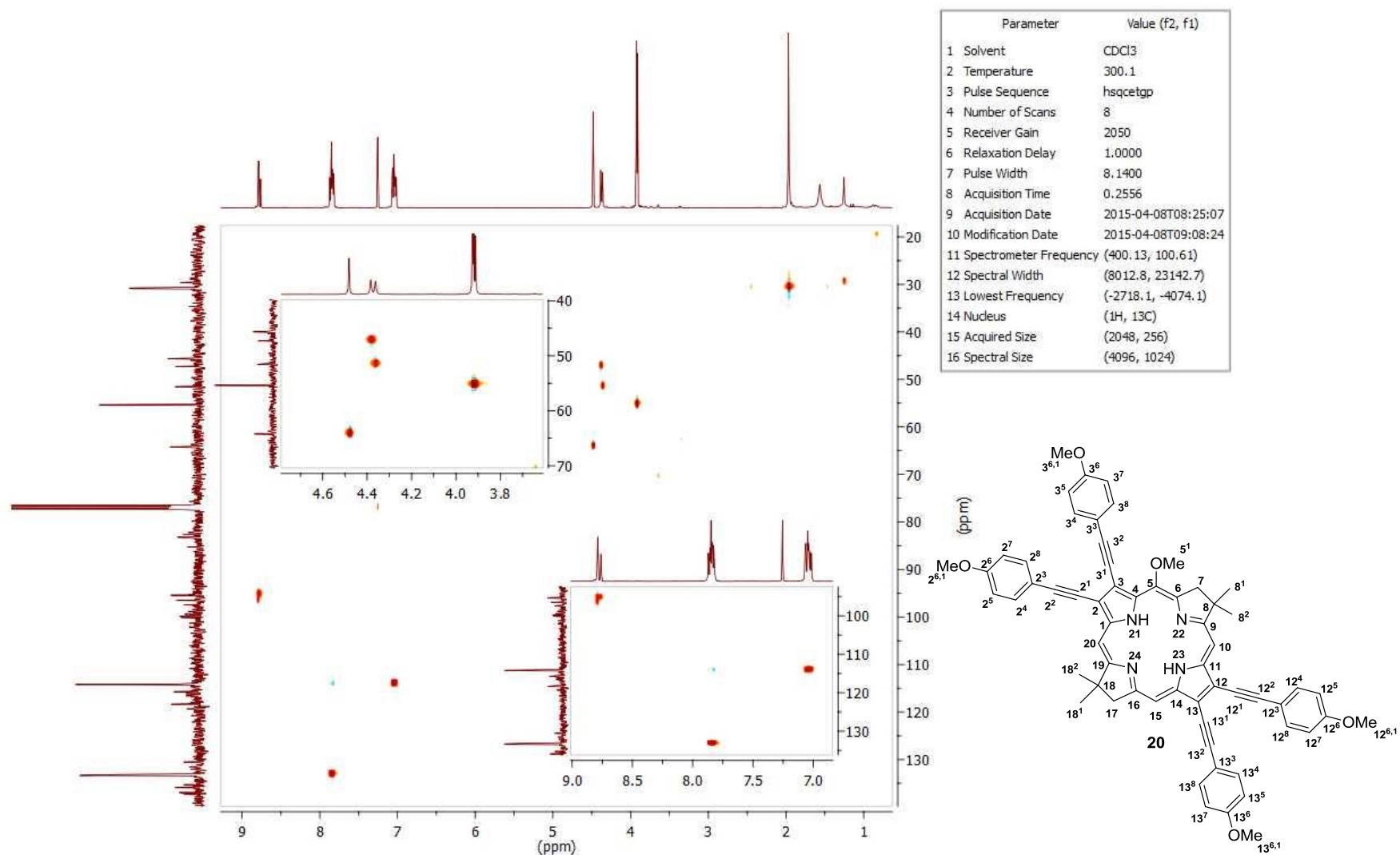
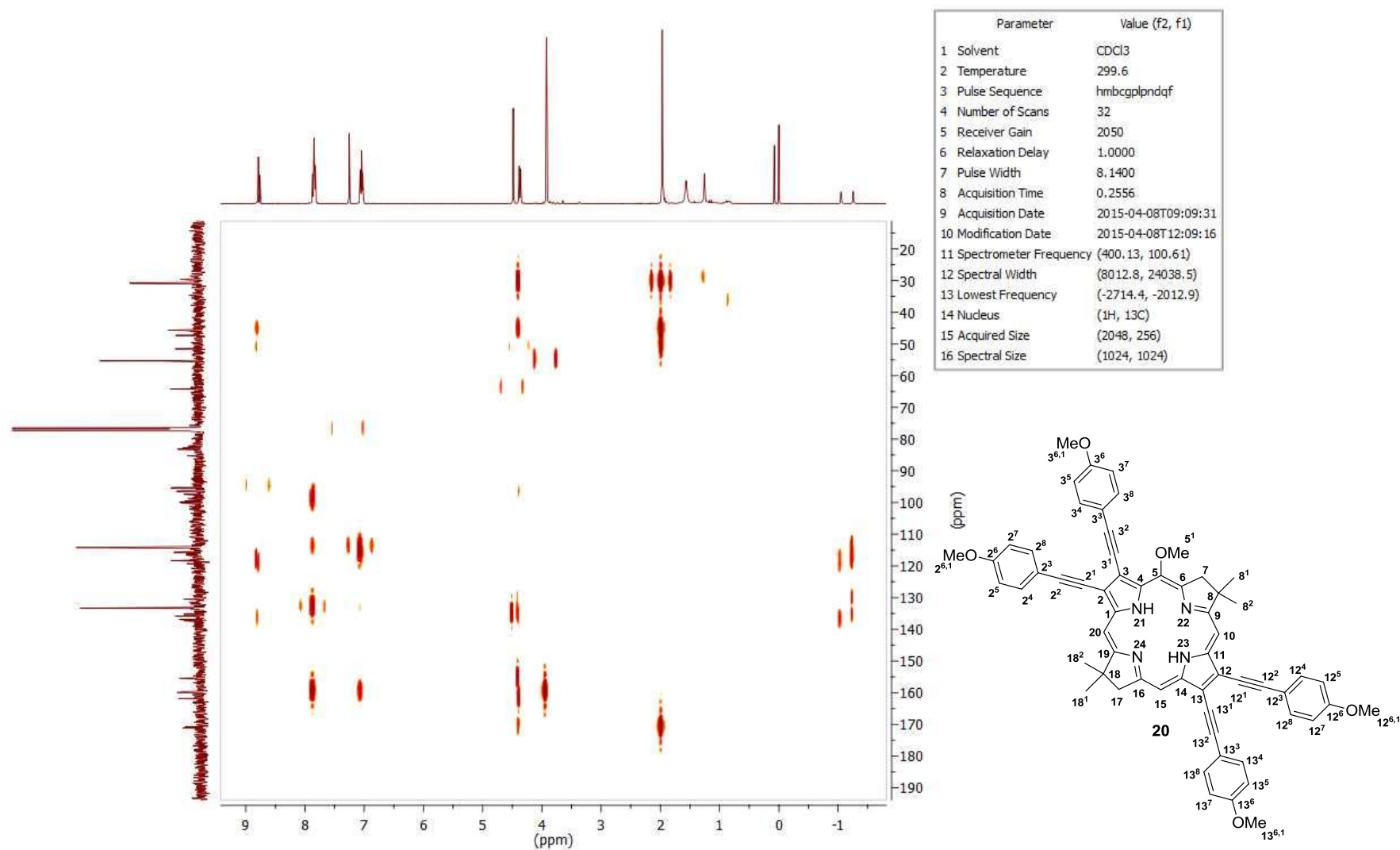
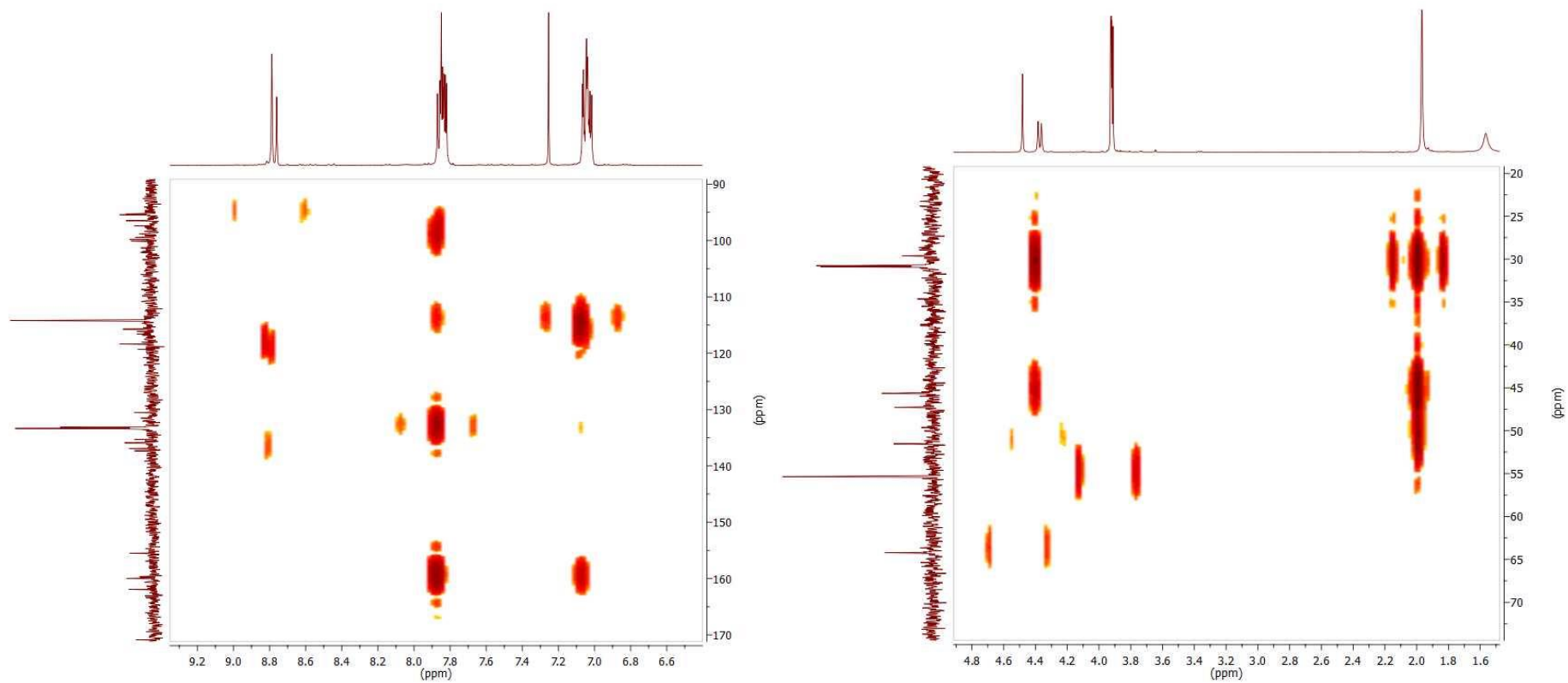


Figure S46. ¹³C NMR spectrum of compound **20** in CDCl₃ with expansions (c).







Figures S49 and S50. Expansions of gHMBC spectrum of compound 20 in CDCl₃.

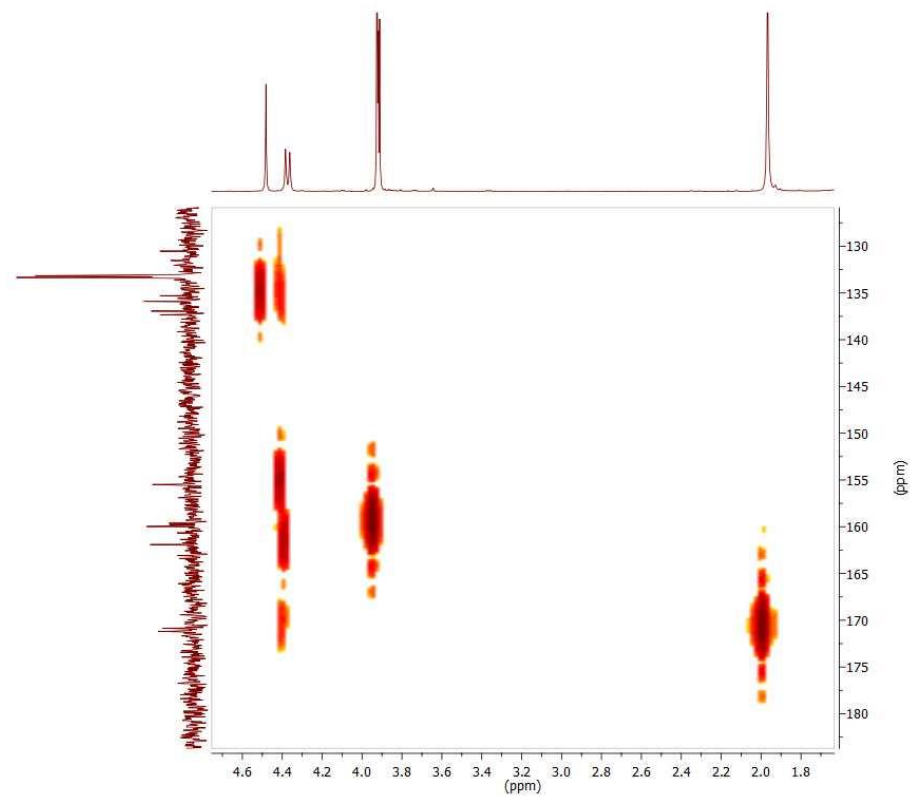


Figure S51. Expansion of gHMBC spectrum of compound **20** in CDCl₃.

3. Mass spectra

3.1. Mass spectrum of compound 8

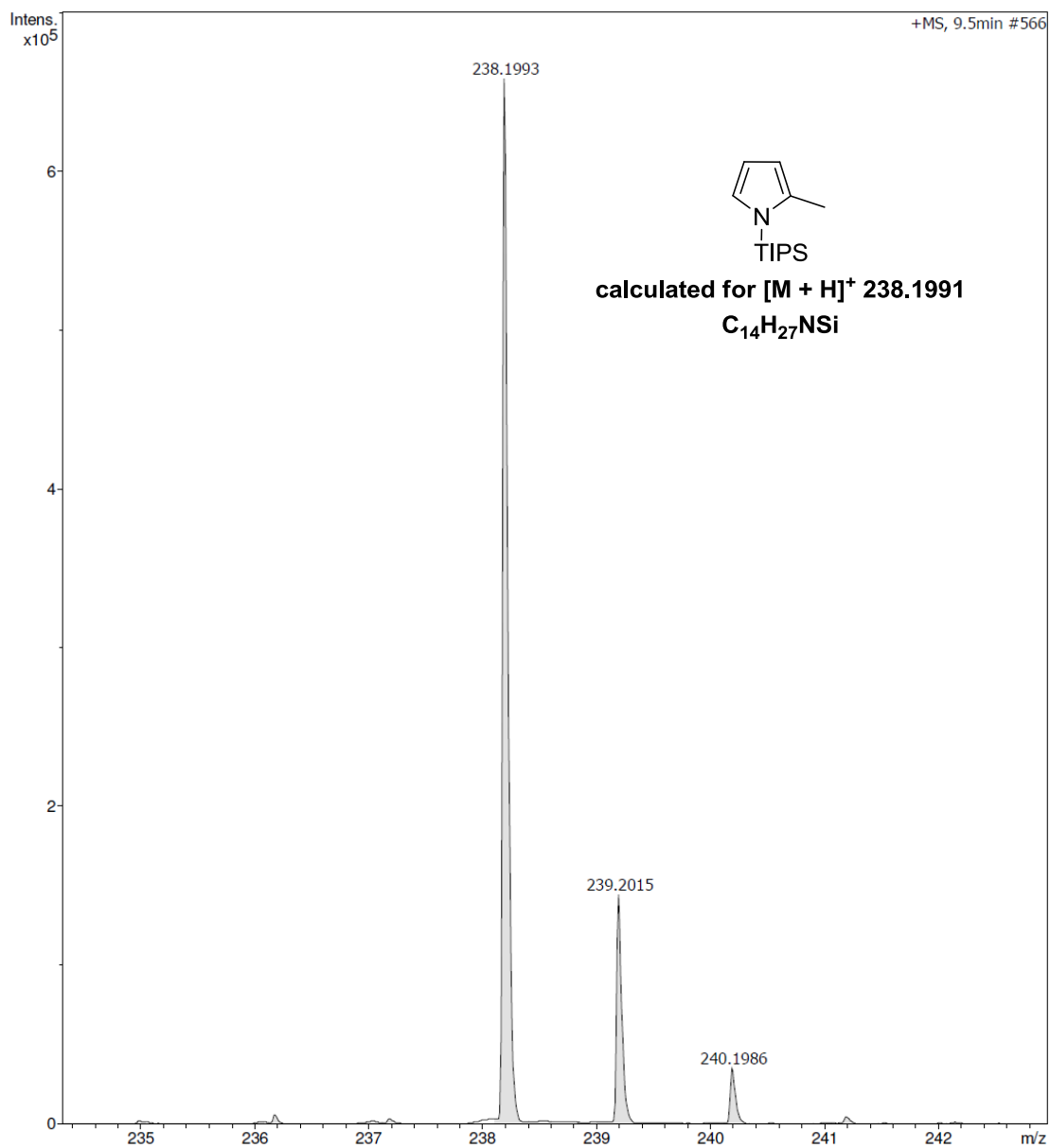


Figure S52. HRMS-ESI-TOF spectrum of compound **8**.

3.2. Mass spectrum of compound 9

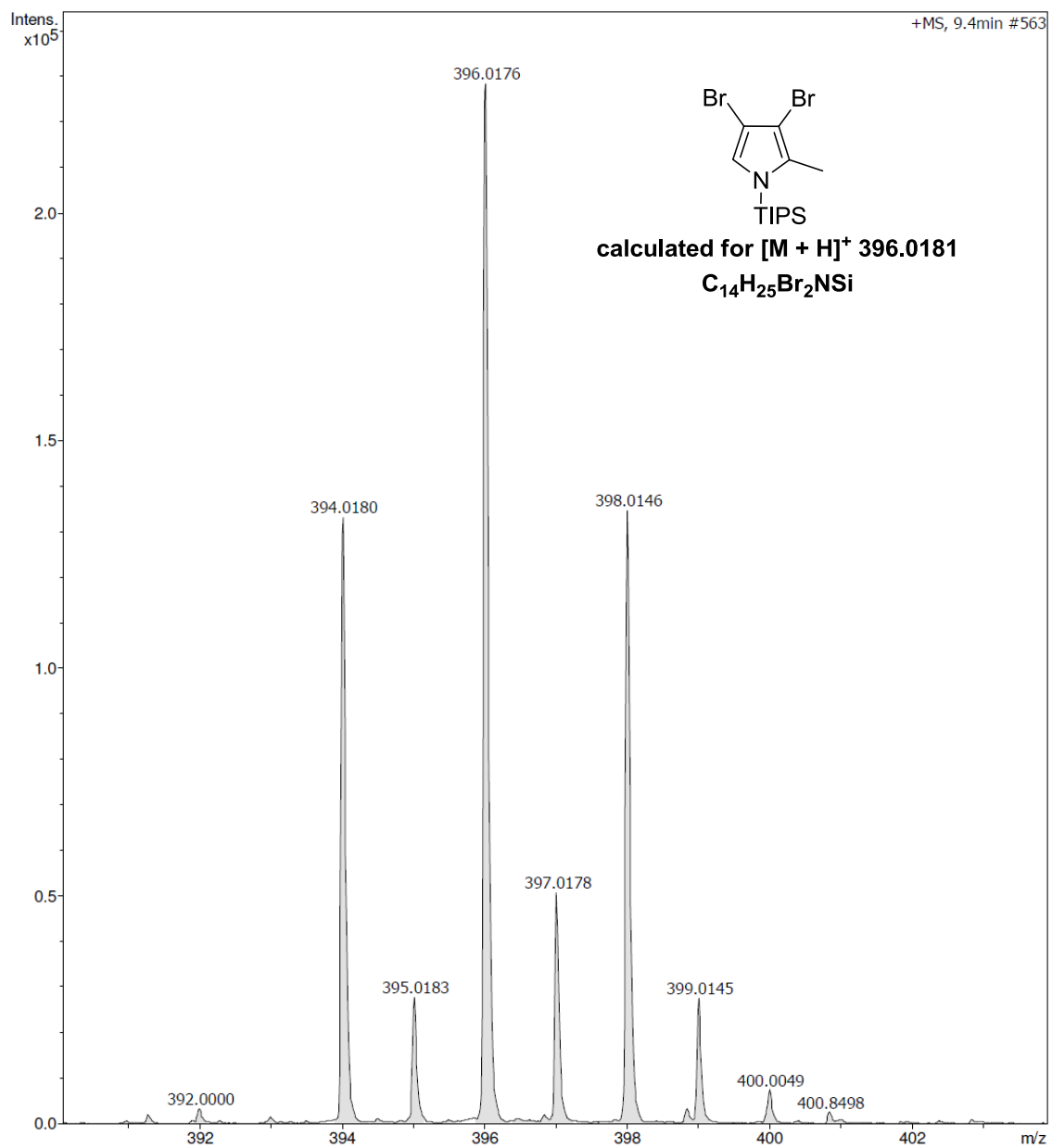


Figure S53. HRMS-ESI-TOF spectrum of compound 9.

3.3. Mass spectrum of compound 10

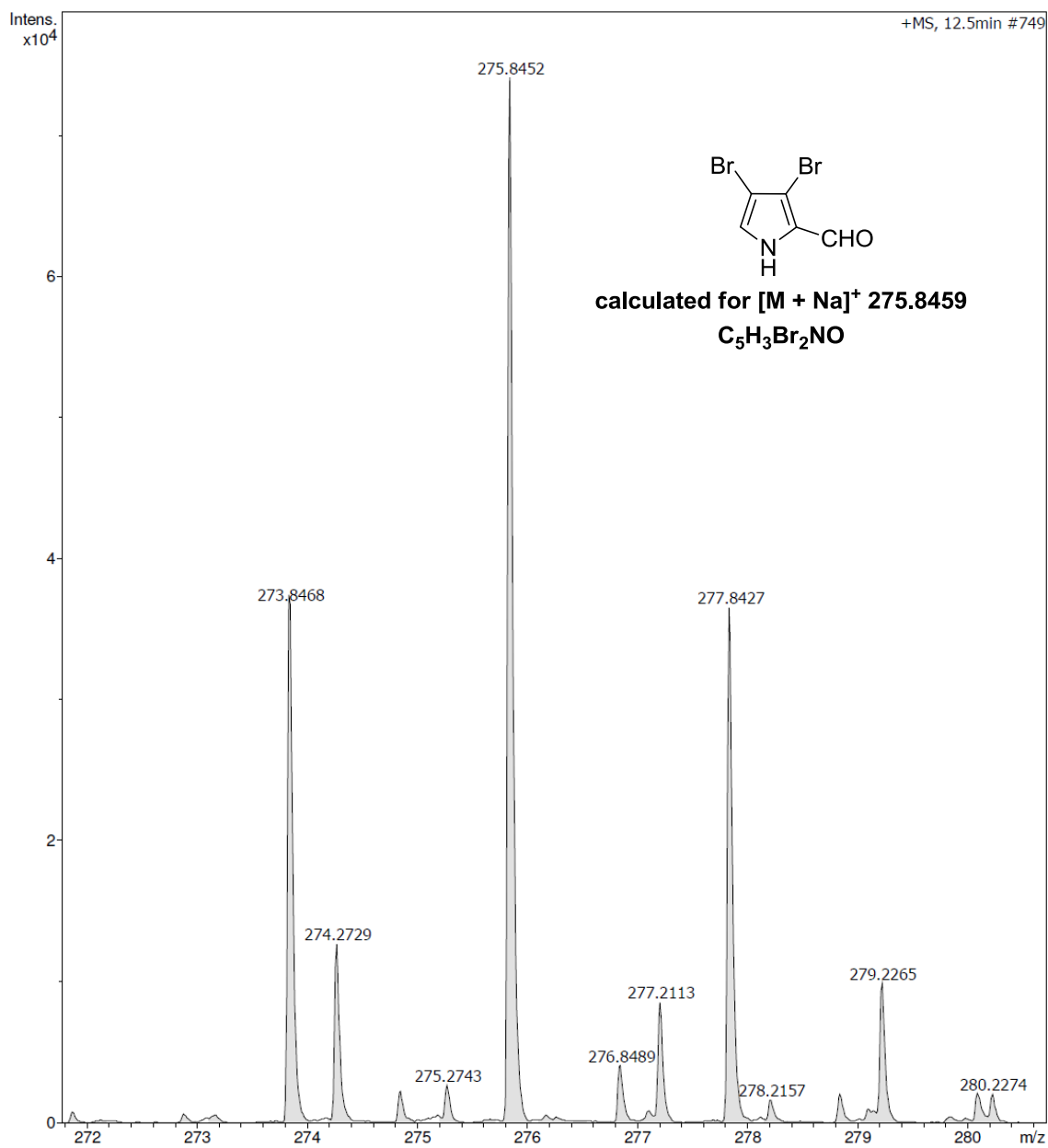


Figure S54. HRMS-ESI-TOF spectrum of compound 10.

3.4. Mass spectrum of compound 11

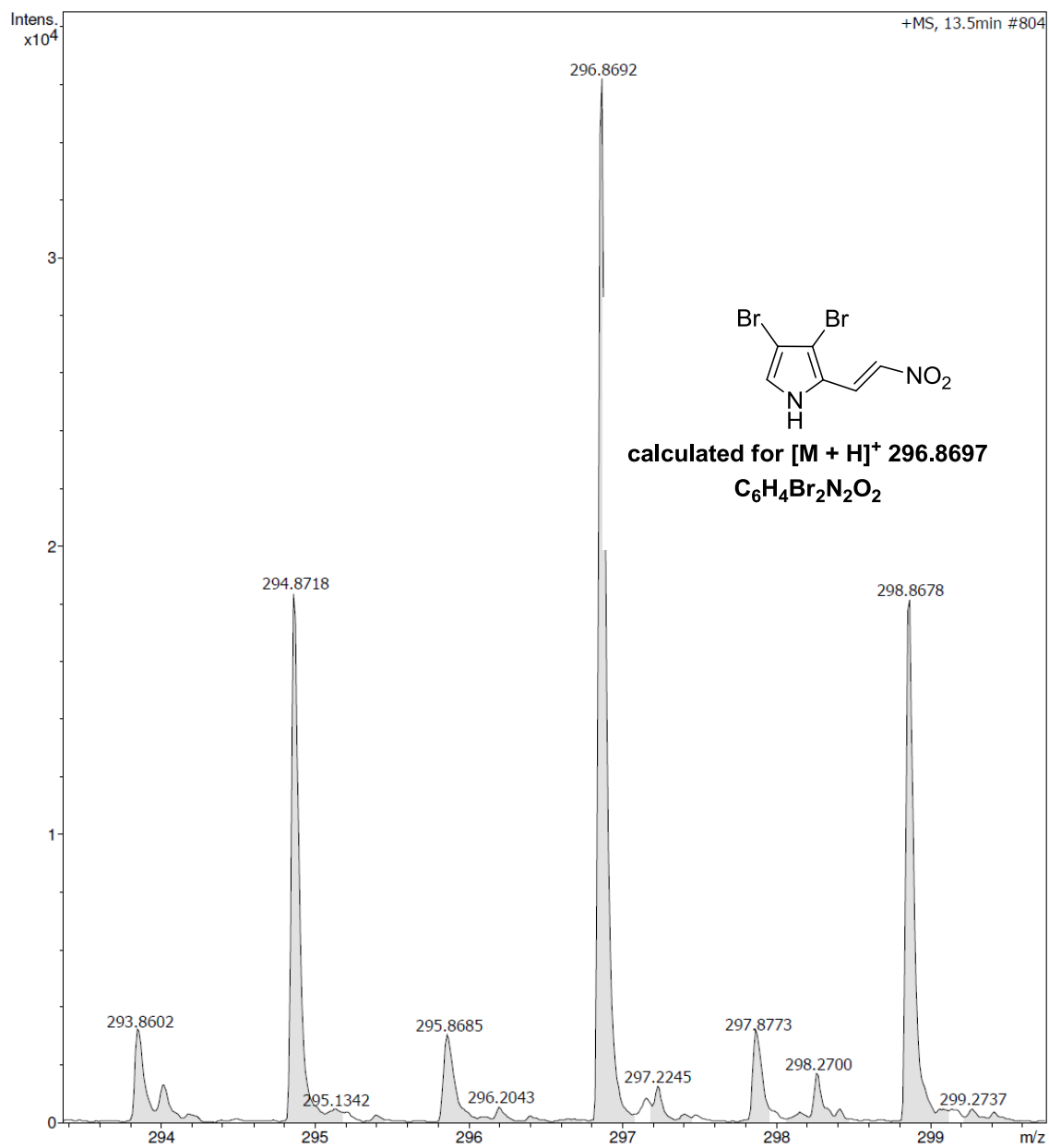


Figure S55. HRMS-ESI-TOF spectrum of compound 11.

3.5. Mass spectrum of compound 12

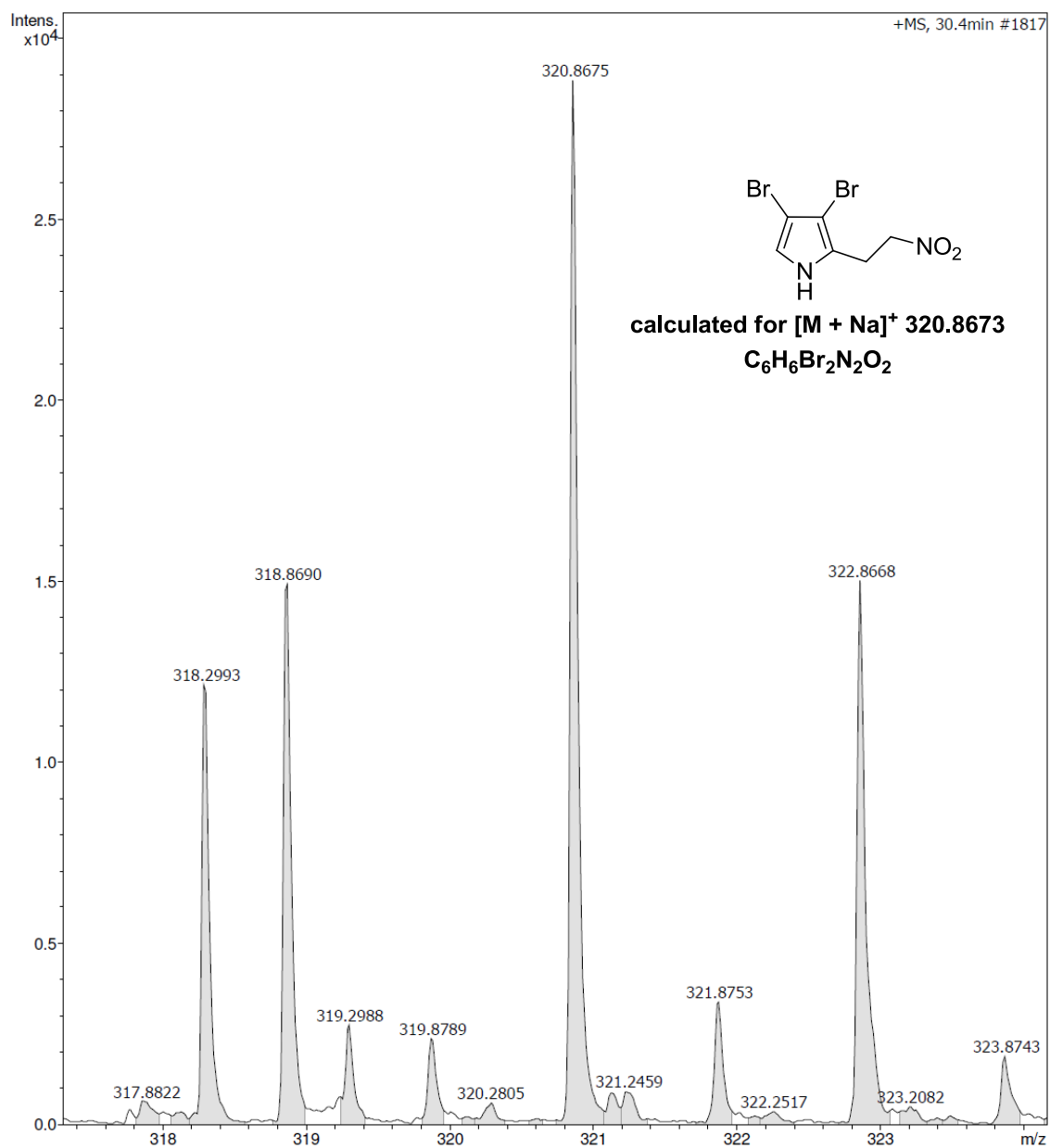


Figure S56. HRMS-ESI-TOF spectrum of compound 12.

3.6. Mass spectrum of compound 14

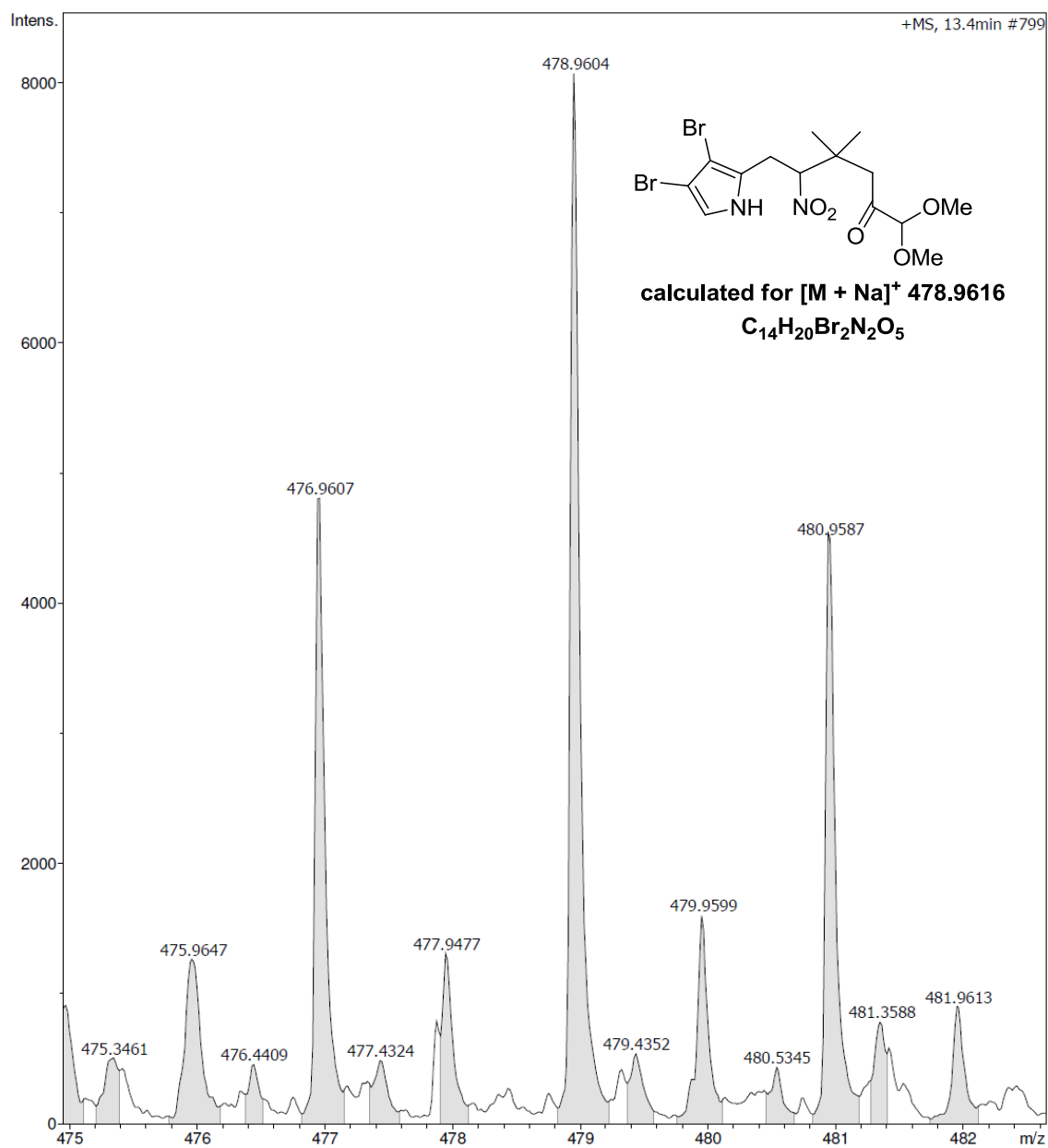


Figure S57. HRMS-ESI-TOF spectrum of compound **14**.

3.7. Mass spectrum of compound 15

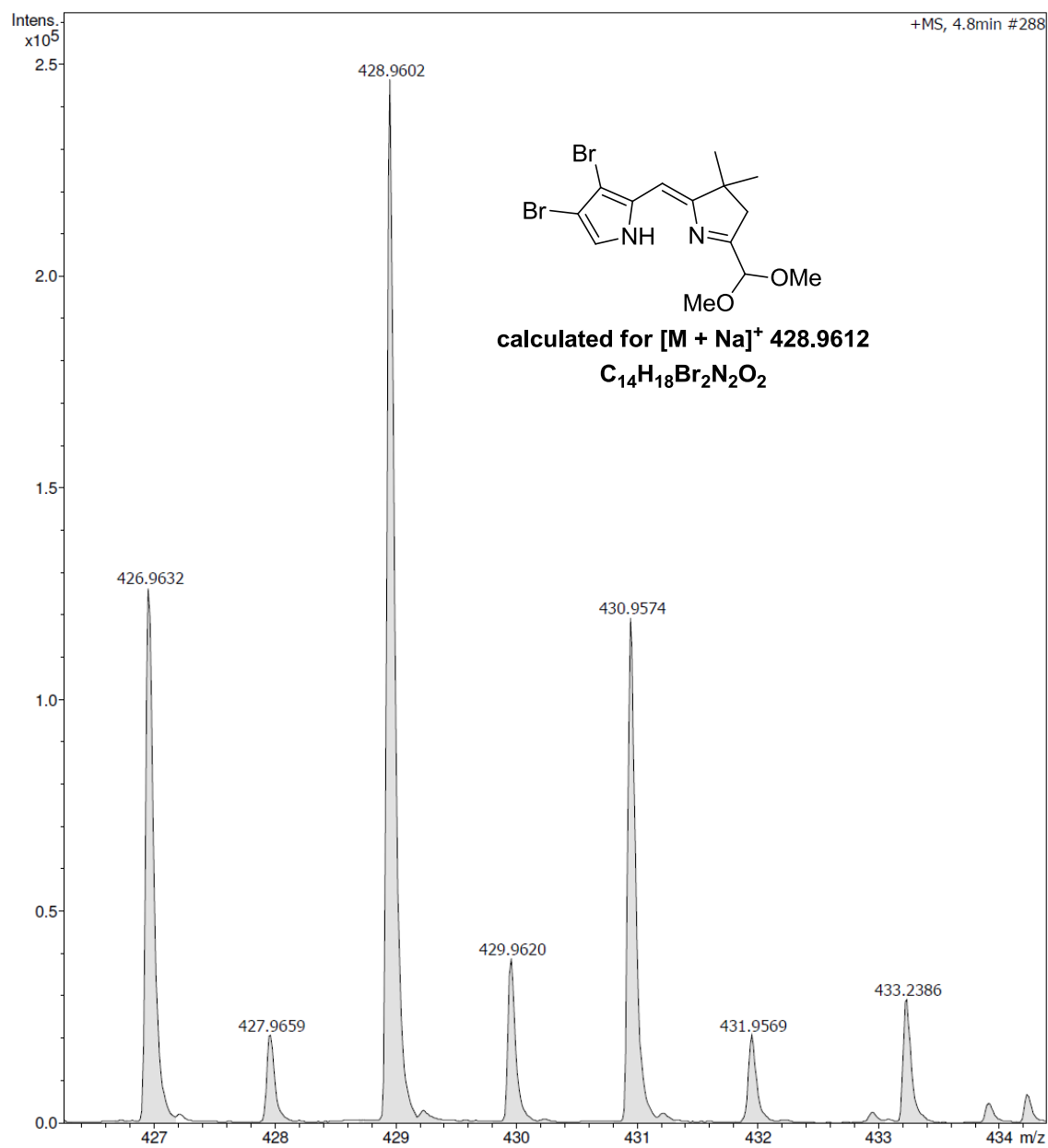


Figure S58. HRMS-ESI-TOF spectrum of compound 15.

3.8. Mass spectrum of compound BCB₄

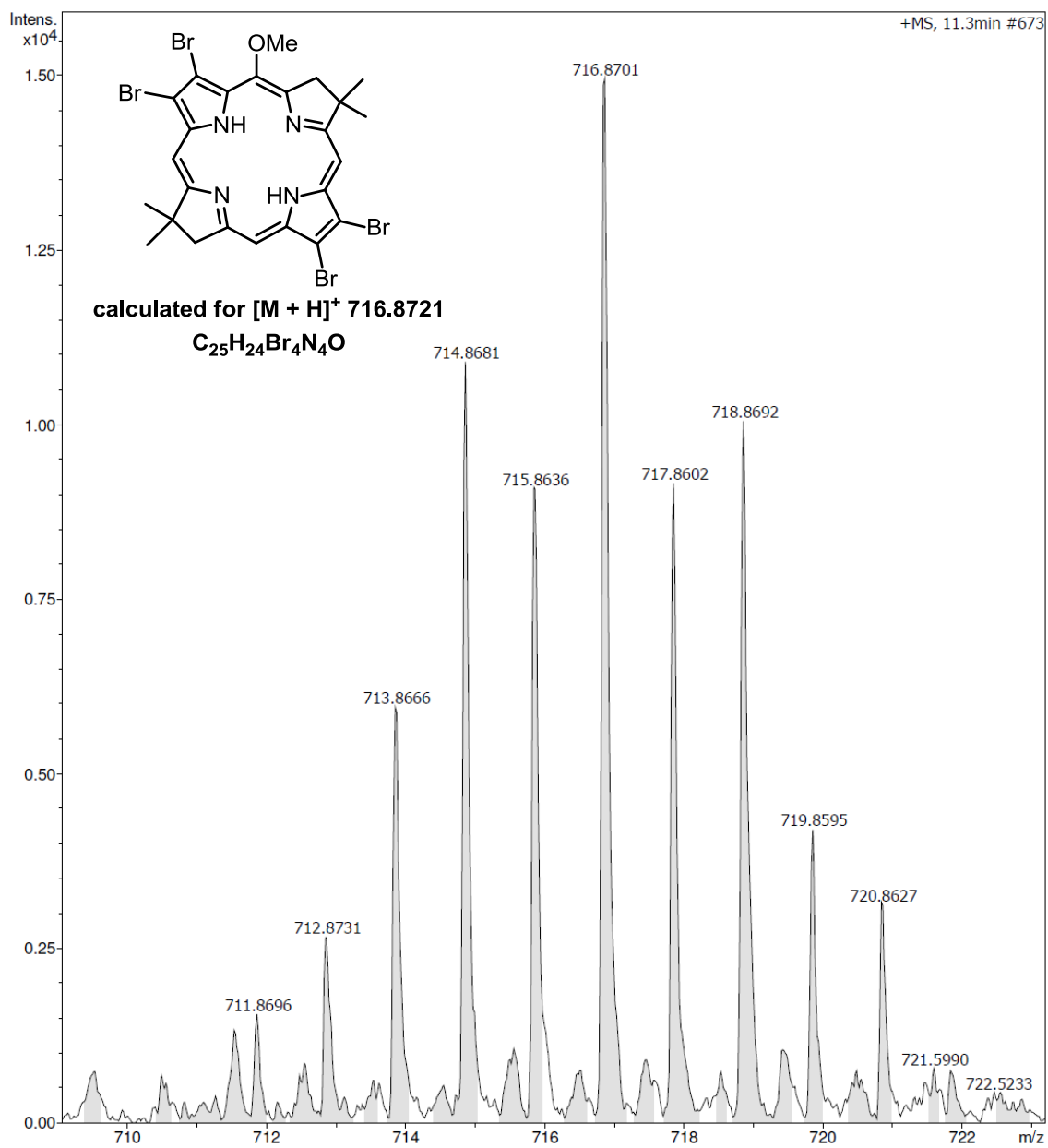


Figure S59. HRMS-ESI-TOF spectrum of compound BCB₄.

3.9. Mass spectrum of compound 17

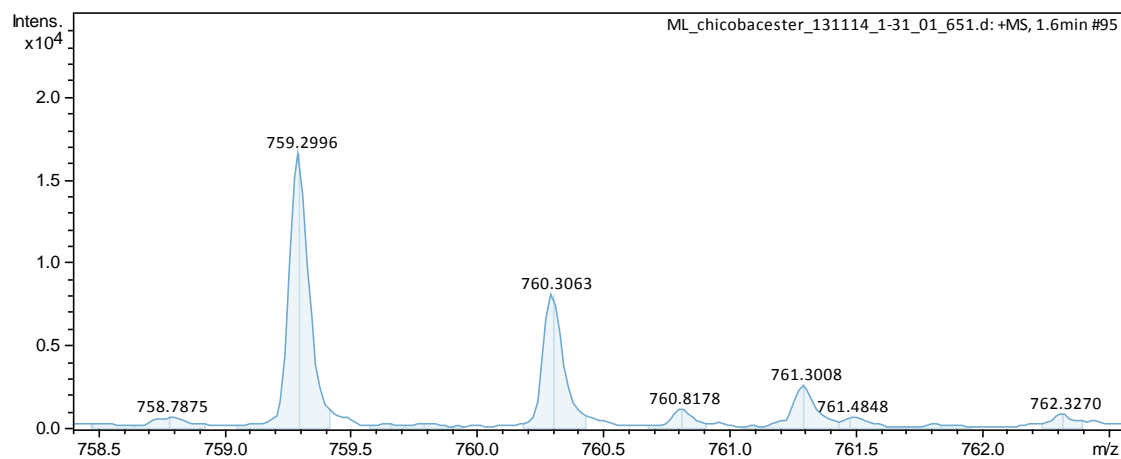
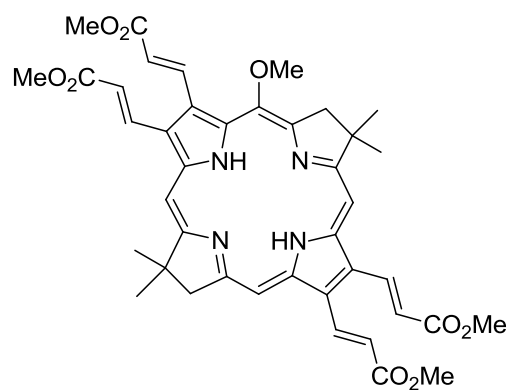


Figure S60. HRMS-ESI-TOF spectrum of compound **17**.



calculated for $[M + Na]^+$ 759.3006

$C_{41}H_{44}N_4O_9$

3.10. Mass spectrum of compound 19

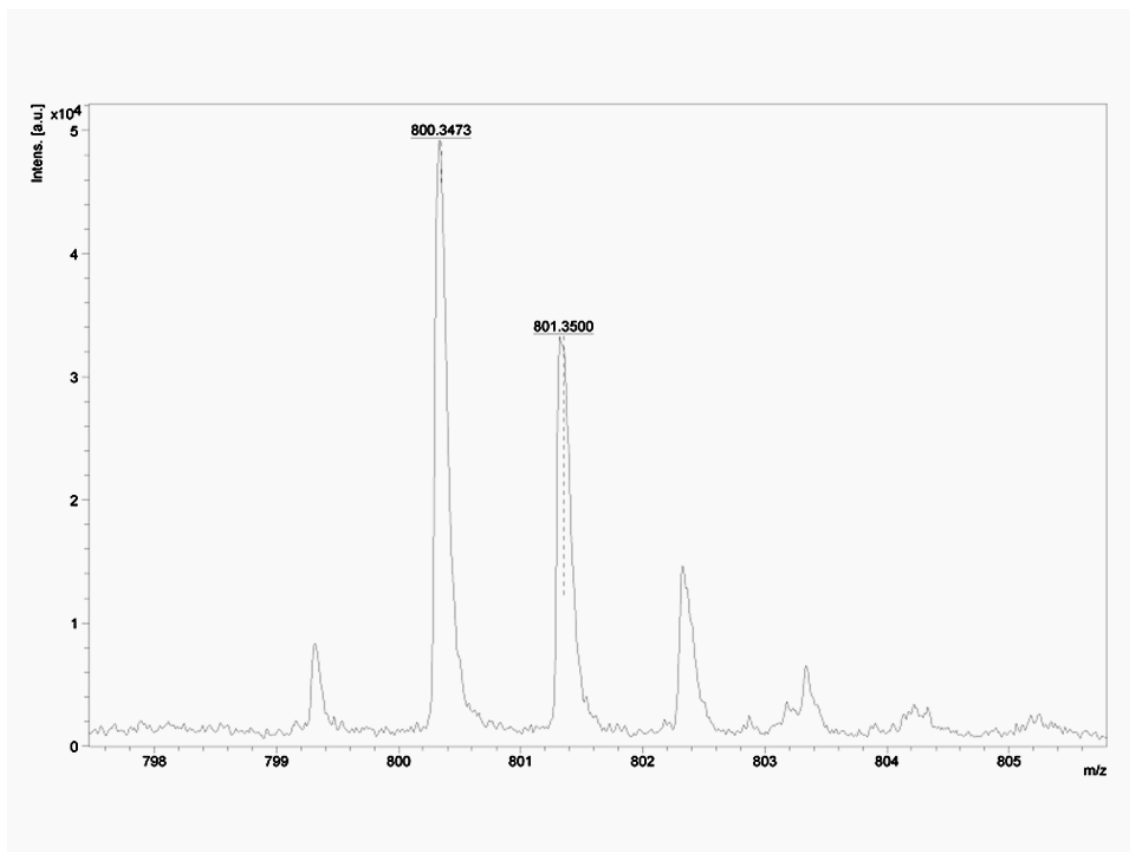
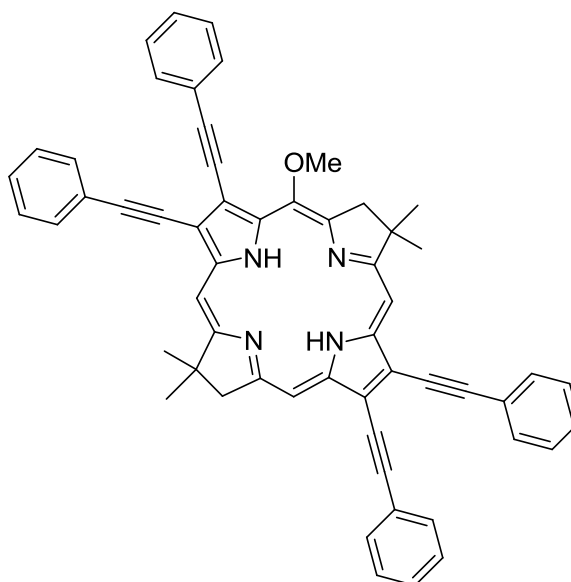


Figure S61. HRMS-MALDI-TOF spectrum of compound 19.



calculated for [M]⁺ 800.3509
C57H44N4O

3.11. Mass spectrum of compound 20

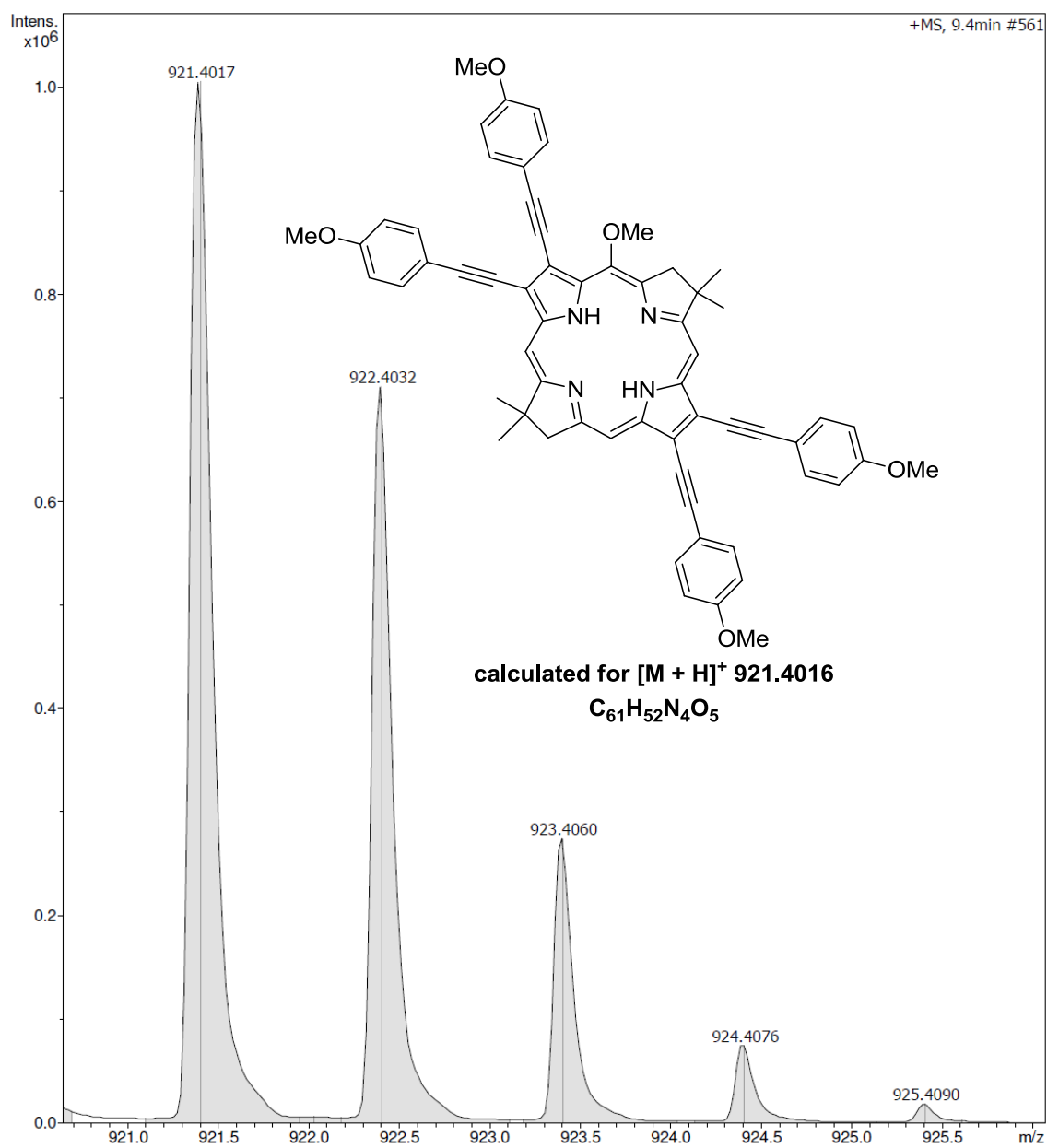


Figure S62. HRMS-ESI-TOF spectrum of compound 20.

4. Computational Details

Table S1: Optimized geometries of compounds **17**, **19**, **20**, **21**, **22**, **23** and **BCBr₄** at B3LYP/6-31G(d).

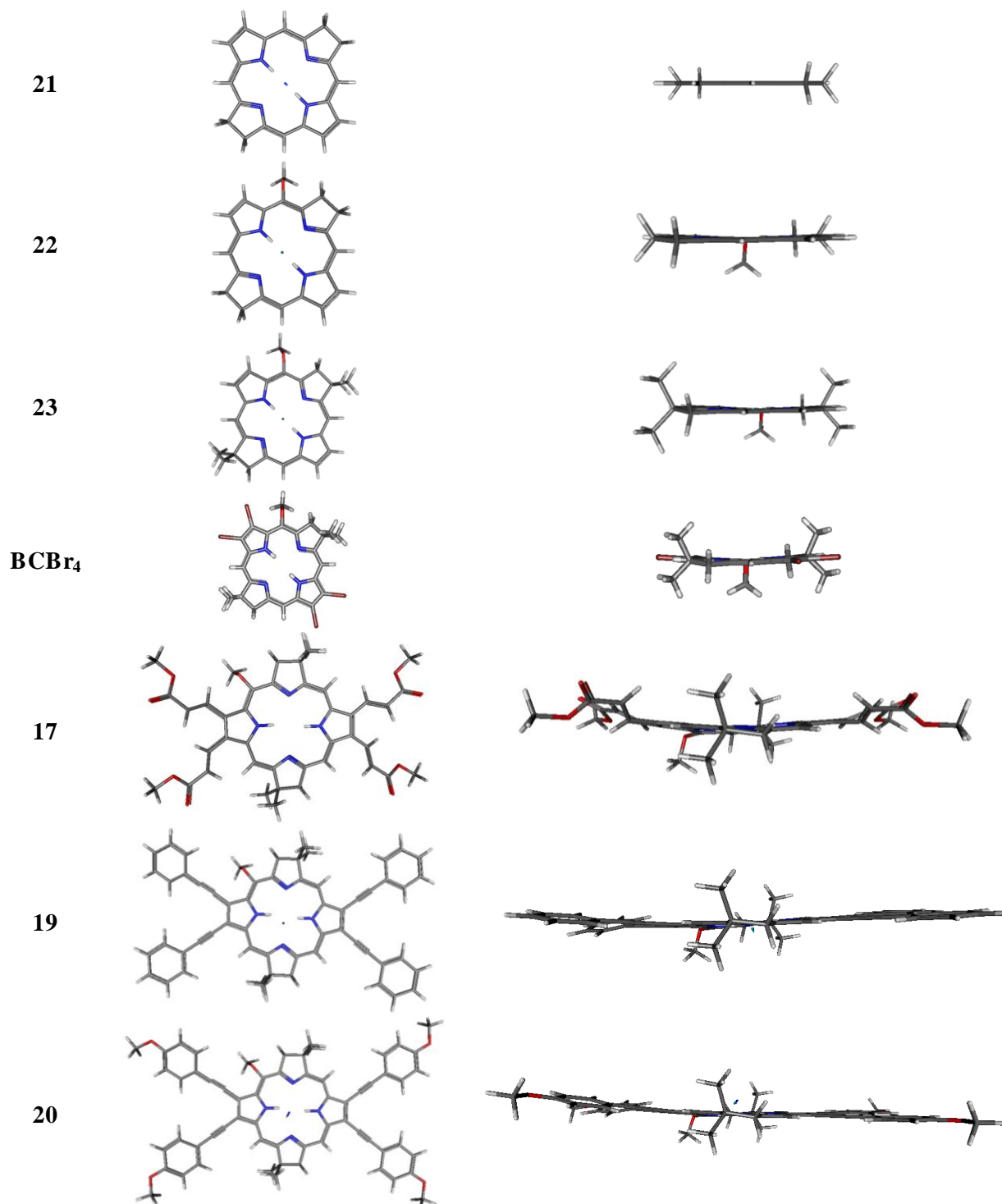


Table S2: Electronic absorption spectra for **17**, **19**, **20**, **23** and **BCBr₄** at TD-DFT PBE0/6-31+g(d,p)//B3LYP/6-31G(d) IEF-PCM [CH₂Cl₂].

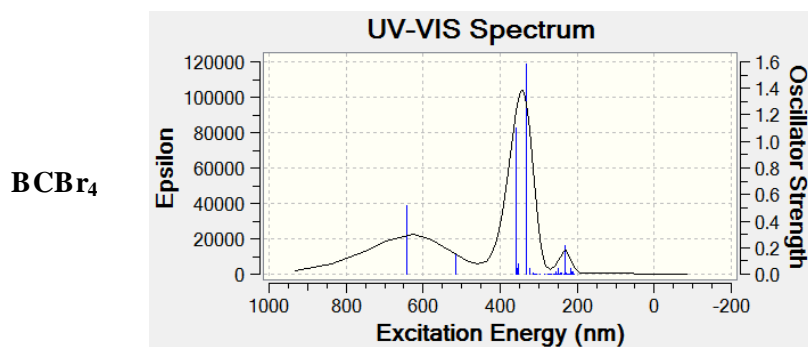
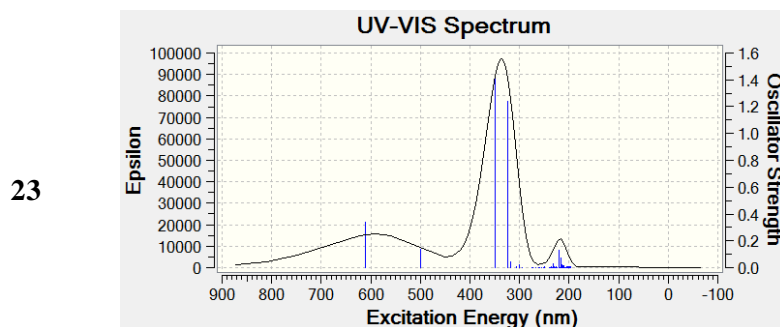
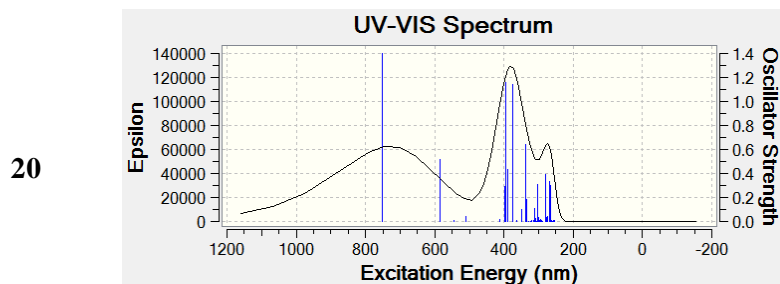
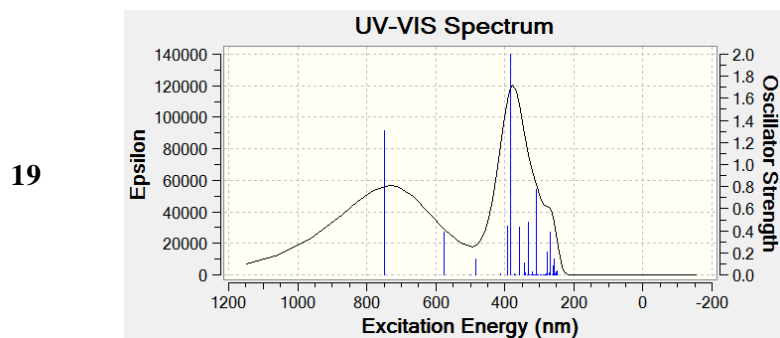
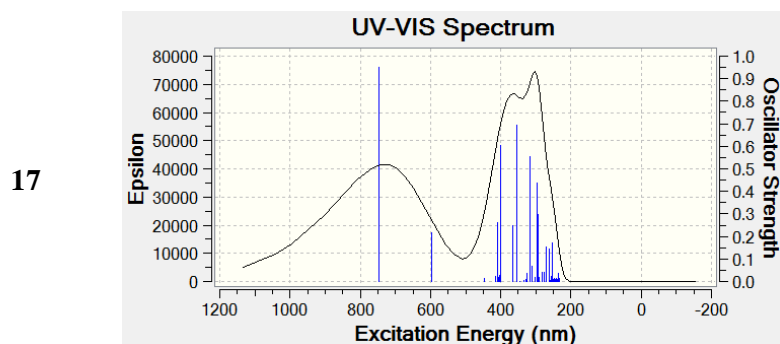


Table S3: Selected energies, oscillator strengths, and expansion coefficients for vertical transitions in **23**.

Transition	E (eV)	E (nm)	f	Assign.	Excitations (Major expansion coefficients)
1	2.03	610	0.34	Q_y	H \rightarrow L (0.67875); H-1 \rightarrow L+1 (-0.21366)
2	2.48	500	0.139	Q_x	H-1 \rightarrow L (0.63147); H \rightarrow L+1 (0.31962)
3	3.55	349	1.42	B_x	H \rightarrow L+1 (0.62925); L-1 \rightarrow L (-0.32506); L-1 \leftarrow L (0.10445)
4	3.83	324	1.24	B_y	L-1 \rightarrow L+1 (0.67432); H \rightarrow L (0.22603); H \leftarrow L (-0.11300)
32	5.61	221	0.13		H-9 \rightarrow L (0.11736); H-4 \rightarrow L+1 (0.34115); H-4 \rightarrow L+1 (0.34115); H-3 \rightarrow L+1 (0.40905); H \rightarrow L+11 (0.19673); H \rightarrow L+12 (-0.30039); H \rightarrow H+15 (-0.13238); H \rightarrow L+16 (0.13481)

Only transitions with oscillator strengths greater than 0.2 are shown.

Table S4: Selected energies, oscillator strengths, and expansion coefficients for vertical transitions in **BCBr₄**.

Transition	E (eV)	E (nm)	f	Assign.	Excitations (Major expansion coefficients)
1	1.93	642	0.52	Q_y	H-1 \rightarrow L+1 (0.19742); H \rightarrow H (0.68323)
2	2.41	514	0.15	Q_x	H-1 \rightarrow L (0.63683); H \rightarrow L+1 (-0.30815)
3	3.46	359	1.10	B_x	H-1 \rightarrow H (0.30333); H \rightarrow L+1 (0.62452)
6	3.72	333	1.58	B_y	H-1 \rightarrow L+1 (0.67715); H \rightarrow L (-0.20825); H \rightarrow L (0.10674)
37	5.34	232	0.21		H-1 \rightarrow L+1 (-0.11162); H \rightarrow L+11 (0.66253)

Only transitions with oscillator strengths greater than 0.2 are shown.

Table S5: Selected energies, oscillator strengths, and expansion coefficients for vertical transitions in **17**.

Transition	E (eV)	E (nm)	<i>f</i>	Assign.	Excitations (Major expansion coefficients)
1	1.66	747	0.95	Q _y	H-1 -> L+2 (-0.13247); H -> L (0.69566)
2	2.08	597	0.21	Q _x	H-1 -> L (0.67736); H -> L+2 (0.18924)
5	3.04	408	0.26		H-3 -> L (0.34584); H-2 -> L (-0.14096); H-1 -> L (-0.15058); H-1 -> L+1 (-0.28630); H-1 -> L+3 (0.13549); H -> L+2 (0.47894)
8	3.10	400	0.60		H-1 -> L+2 (-0.34924); H -> L+3 (0.59976)
9	3.40	365	0.25		H-4 -> L (-0.12726); H-1 -> L+2 (-0.22852); H -> L+3 (-0.12154); H -> L+4 (0.63728)
10	3.49	355	0.69		H-4 -> L (-0.25376); H-1 -> L+2 (0.51491); H -> L+3 (0.30834); H -> L+4 (0.19519)
16	3.91	317	0.55		H-7 -> L (-0.12578); H-5 -> L (0.12954); H-2 -> L+1 (-0.11231); H-1 -> L (0.10531); H-1 -> L+3 (0.35121); H-1 -> L+4 (0.17554); H -> L+2 (-0.13554); H -> L+5 (0.50818)
19	4.17	297	0.44		182 -> L (0.12255); H-3 -> L+1 (-0.26136); H-2 -> L+1 (0.47851); H-2 -> L+3 (-0.23174); H-1 -> L+5 (-0.30171)
20	4.19	296	0.35		182 -> L (-0.18942); H-9 -> L (0.16498); H-8 -> L (0.14336); H-3 -> L+3 (0.12289); H-2 -> L+1 (0.38447); H-1 -> L+5 (0.43855)
22	4.23	294	0.30		182 -> L (0.13621); 183 -> L (0.11817); H-3 -> L+1 (0.54921); H-3 -> L+3 (0.20252); H-2 -> L+1 (0.14536); H-2 -> L+3 (0.11708); H-1 -> L+5 (-0.22727)

Only transitions with oscillator strengths greater than 0.2 are shown. Molecular orbitals in **BOLD** are composed mainly by ligand moieties.

Table S6: Selected energies, oscillator strengths, and expansion coefficients for vertical transitions in **19**.

Transition	E (eV)	E (nm)	<i>f</i>	Assign.	Excitations (Major expansion coefficients)
1	1.65	749	1.30	Q _y	H-1 -> L+2 (-0.12057); H -> L (0.69528)
2	2.15	577	0.39	Q _x	H-1 -> L (0.67017); H -> L+2 (0.21291)
3	2.48	500	0.45		H-3 -> L (0.12416); H-1 -> L (-0.125); H-1 -> L+3 (0.13500); H -> L+1 (0.14432); H -> L+2 (0.62303)
7	3.23	383	2.00		H-5 -> L (-0.11740); H-1 -> L+1 (0.18961); H-1 -> L+2 (0.48155); H -> L (0.10296); H -> L+3 (-0.43841)
10	3.47	357	0.43		H-5 -> L (-0.40512); H-1 -> L+2 (0.30148); H -> L+3 (0.47058)
14	3.73	332	0.48		H-3 -> L+3 (0.11884); H-2 -> L+1 (0.44667); H-1 -> L+3 (0.44570); H -> L+5 (0.25520)
25	4.01	309	0.77		H-2 -> L+1 (-0.23924); H-2 -> L+2 (0.10724); H-1 -> L+3 (0.49036); H -> L+2 (-0.10999); H -> L+5 (-0.40231)
38	4.48	277	0.20		H-19 -> L (-0.35014); H-18 -> L (0.15693); H-15 -> L (0.12779); H-3 -> L+3 (0.50873); H-3 -> L+4 (0.10501); H-2 -> L+1 (-0.15147)
43	4.64	267	0.39		H-4 -> L+1 (-0.11190); H-3 -> L+5 (-0.28097); H-2 -> L+4 (0.59254); H-1 -> L+5 (0.13333)

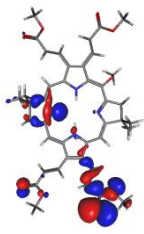
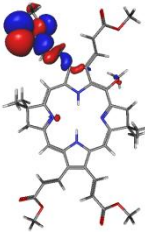
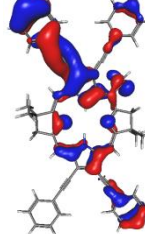
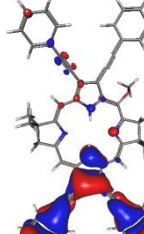
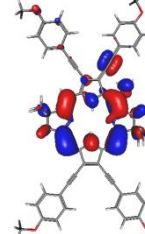
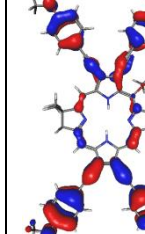
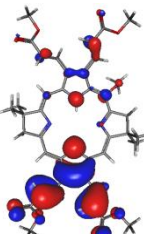
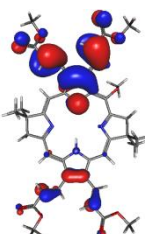
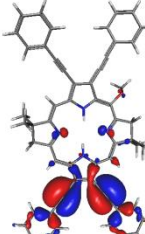
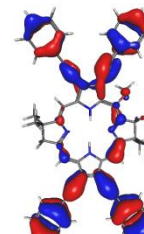
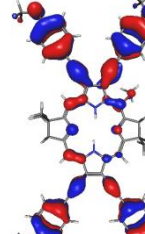
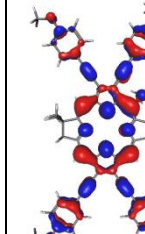
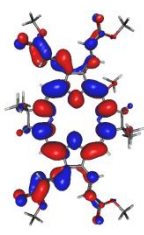
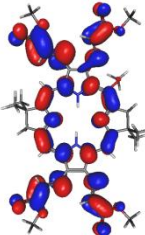
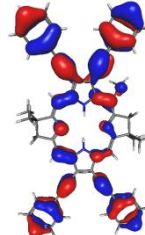
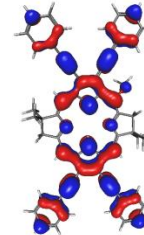
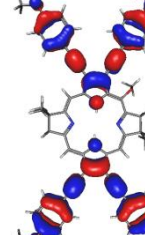
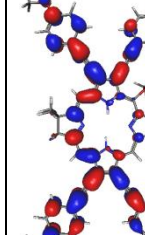
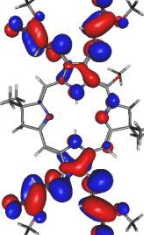
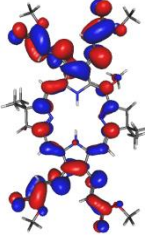
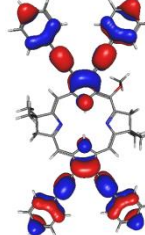
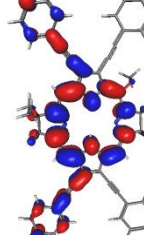
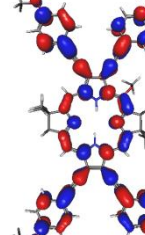
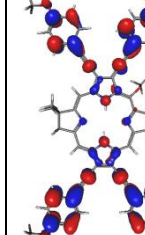
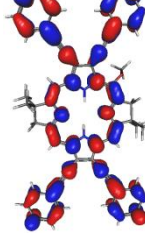
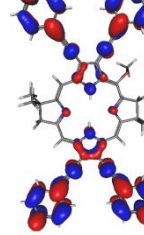
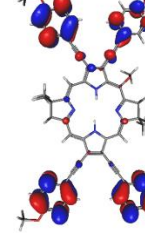
Only transitions with oscillator strengths greater than 0.2 are shown. Molecular orbitals in **BOLD** are composed mainly by ligand moieties.

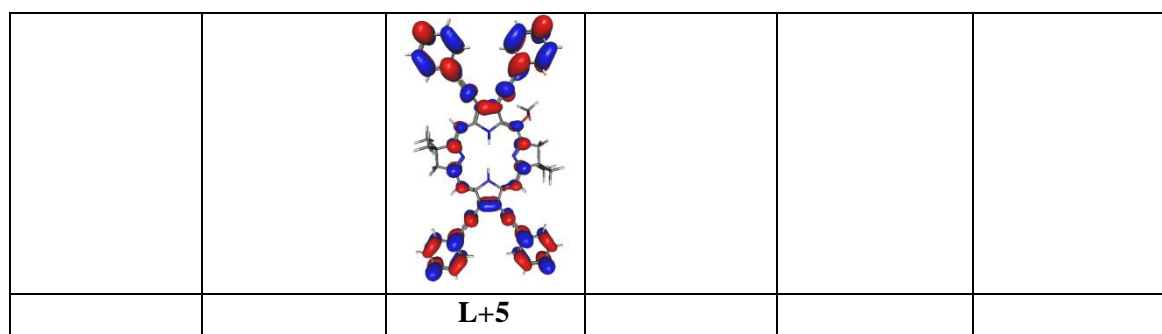
Table S7: Selected energies, oscillator strengths, and expansion coefficients for vertical transitions in **20**.

Transition	E (eV)	E (nm)	<i>f</i>	Assign.	Excitations (Major expansion coefficients)
1	1.65	752	1.40	Q _y	H-1 -> L+1 (-0.11126); H -> L (0.69535)
2	2.11	586	0.51	Q _x	H-1 -> L (0.67911); H -> L+1 (0.19033)
6	3.11	399	0.29		H-5 -> L (-0.24107); H-4 -> L (0.19152); H-1 -> L+1 (0.12002); H -> L+1 (-0.31639); H -> L+2 (0.51834)
7	3.13	396	1.16		H-5 -> L (0.49688); H-4 -> L (0.14885); H-1 -> L+1 (-0.33912); H -> L+2 (0.29042)
8	3.18	390	0.43		H-5 -> L (-0.15878); H-3 -> L (0.17580); H-1 -> L (-0.18578); H -> L+1 (0.55764); H -> L+2 (0.26L+1)
9	3.32	374	1.14		H-5 -> L (0.37183); H-1 -> L+1 (0.44614); H -> L+3 (-0.37123)
12	3.67	338	0.64		H-6 -> L (-0.11911); H-2 -> L+1 (-0.41508); H-2 -> L+2 (0.45118); H-1 -> L+3 (-0.28233)
24	4.08	304	0.31		H-8 -> L (-0.17613); H-2 -> L+2 (0.10156); H-1 -> L+3 (0.32488); H -> L+5 (0.55700)
41	4.45	279	0.39		223 -> L (-0.11488); H-3 -> L+3 (0.65464); H-2 -> L+2 (0.14931)
48	4.61	269	0.28		H-5 -> L+1 (0.54302); H-4 -> L+2 (0.27241); H-2 -> L+4 (0.12830); H-1 -> L+5 (0.14073); H-1 -> L+9 (0.13879)
49	4.62	268	0.33		H-5 -> L+1 (0.41066); H-4 -> L+2 (-0.38388); H-2 -> L+4 (-0.11805); H-1 -> L+5 (-0.23080); H-1 -> L+7 (-0.12448); H-1 -> L+9 (-0.17933)
50	4.64	267	0.30		222 -> L (0.10576); H-3 -> L+5 (0.22568); H-2 -> L+4 (0.54166); H-1 -> L+5 (-0.32316)

Only transitions with oscillator strengths greater than 0.2 are shown. Molecular orbitals in **BOLD** are composed mainly by ligand moieties.

Table S8: Molecular orbital electron distribution of bacteriochlorin compounds calculated at B3LYP/6-31G(d).

17		19		20	
					
H-9	H-7	H-19	H-18	H-6	H-5
					
H-3	H-2	H-15	H-5	H-4	H-3
					
L+2	L+3	H-4	H-3	H-2	L+2
					
L+4	L+5	H-2	L+2	L+3	L+4
					
		L+3	L+4	L+5	



Cartesian Coordinates

17 Energy: -1559276.1889885

C	-1.30802	-2.91914	-0.11635	H	-4.73775	0.64426	1.78204
C	0.95798	-2.91535	-0.00776	C	-5.14257	1.55329	-1.56307
C	2.27286	-2.44223	0.01320	H	-6.19344	1.25423	-1.65861
C	2.74452	-1.13719	-0.09481	H	-5.12135	2.63927	-1.41940
C	2.78892	1.04754	-0.34294	H	-4.63813	1.32892	-2.50964
C	2.38839	2.38390	-0.38874	C	4.80409	-1.06185	1.35578
C	1.08662	2.90791	-0.22134	H	4.71057	-2.11186	1.65519
C	-1.18062	2.87488	-0.07263	H	5.86548	-0.78938	1.40359
C	-2.97169	1.10313	-0.28139	H	4.26322	-0.45395	2.08949
C	-3.01008	-1.09574	-0.37889	C	5.05312	-1.67024	-1.08403
C	-2.60179	-2.42476	-0.30406	H	6.10213	-1.35032	-1.09570
N	-2.20900	-0.01562	-0.25568	H	5.03988	-2.73727	-0.83501
H	3.03306	-3.20943	0.10752	H	4.65211	-1.55646	-2.09743
H	-3.37971	-3.17204	-0.40625	C	3.63289	3.67011	-1.93595
C	0.52340	-4.28722	0.05059	H	4.47376	4.36733	-1.93607
C	-0.88241	-4.28877	-0.00713	H	3.87999	2.79664	-2.55227
C	-2.49841	2.40241	-0.16920	H	2.74748	4.16406	-2.35542
H	-3.24956	3.18283	-0.17482	O	3.42001	3.29764	-0.57011
C	4.25412	-0.83454	-0.06916	C	-1.72520	-5.47044	-0.03753
C	4.25648	0.67005	-0.42768	H	-1.29425	-6.34445	-0.52124
H	4.64363	0.83899	-1.44137	C	1.43483	-5.40660	0.15833
H	4.87120	1.27589	0.24464	H	2.45236	-5.22914	-0.18041
C	-4.48162	0.81037	-0.38848	C	-2.95911	-5.59969	0.49257
C	-4.46401	-0.72169	-0.60621	H	-3.43371	-4.80369	1.05589
H	-4.76739	-0.99002	-1.62710	C	1.16498	-6.63837	0.64372
H	-5.13717	-1.25646	0.07342	H	0.20077	-6.90345	1.06188
N	1.97940	-0.02713	-0.19759	C	1.20329	6.58635	0.75047
N	-0.17223	-2.14587	-0.09142	H	0.23461	6.78667	1.19229
H	-0.18354	-1.13341	-0.14033	C	-2.77548	5.47799	0.88375
N	-0.04085	2.12100	-0.20364	H	-3.14509	4.65321	1.48352
H	-0.02722	1.11348	-0.31429	C	1.52265	5.41042	0.16392
C	-5.18690	1.17501	0.93508	H	2.54891	5.28329	-0.15254
H	-5.12316	2.24961	1.13911	C	0.64947	4.26664	-0.02515
H	-6.24897	0.90530	0.88855	C	-0.75949	4.23789	0.06057
				C	-1.62359	5.39920	0.18570

H	-1.28713	6.29725	-0.32783	C	1.17867	4.17610	0.77918
C	-3.77130	-6.83009	0.41153	C	-1.90325	2.21280	0.89187
C	2.14913	-7.73577	0.69798	H	-2.64331	2.96702	1.14038
C	-3.62549	6.68360	0.94932	C	4.92581	-0.73178	-0.22687
C	2.15032	7.70613	0.90360	C	4.87804	0.81619	-0.21807
O	-4.66936	6.73622	1.57252	H	5.24230	1.23889	-1.16282
O	1.87735	8.74646	1.47383	H	5.48971	1.26093	0.57388
O	-4.88422	-6.93303	0.89272	C	-3.84935	0.55416	0.89521
O	1.90589	-8.83714	1.15424	C	-3.84089	-0.93264	0.46230
O	3.36223	-7.39753	0.18742	H	-4.35715	-1.07885	-0.49601
O	-3.15025	-7.83738	-0.25009	H	-4.33246	-1.58976	1.18910
O	-3.12357	7.72951	0.24791	N	2.63448	0.00932	-0.00749
O	3.36559	7.47007	0.34197	N	0.52739	-2.16342	-0.04330
C	4.34870	-8.43779	0.22870	H	0.48836	-1.16125	0.09688
H	4.01734	-9.30694	-0.34610	N	0.54305	2.02969	0.47935
H	5.24794	-8.00694	-0.21342	H	0.58809	1.03438	0.29703
H	4.53910	-8.74913	1.25953	C	-4.25425	0.70001	2.37720
C	-3.89338	-9.06172	-0.33610	H	-4.16204	1.73868	2.71378
H	-4.83331	-8.90488	-0.87248	H	-5.29596	0.38791	2.52292
H	-3.25172	-9.75536	-0.88031	H	-3.61988	0.08165	3.02216
H	-4.11603	-9.44771	0.66230	C	-4.77099	1.40904	0.00785
C	-3.90364	8.93252	0.30213	H	-5.81040	1.07018	0.09902
H	-3.35672	9.66255	-0.29533	H	-4.74196	2.46624	0.29462
H	-4.90096	8.76407	-0.11354	H	-4.48225	1.34006	-1.04686
H	-4.00428	9.27947	1.33402	C	5.64882	-1.27450	1.02345
C	4.31725	8.53142	0.49160	H	5.60470	-2.36870	1.06620
H	5.22573	8.18284	-0.00153	H	6.70523	-0.97874	1.01336
H	3.95221	9.44796	0.01966	H	5.19540	-0.88472	1.94161
H	4.50913	8.73329	1.54913	C	5.59441	-1.27634	-1.50240
				H	6.63985	-0.94796	-1.55433
				H	5.59002	-2.37184	-1.52657
				H	5.08113	-0.92002	-2.40258
19	Energy:	-1564136.8407830		C	4.09821	4.04426	-1.13344
C	-0.58444	-2.96701	-0.06892	H	4.88434	4.79135	-1.00366
C	1.68000	-2.88872	-0.21236	H	4.40285	3.32131	-1.90168
C	2.98346	-2.39214	-0.24980	H	3.17653	4.54401	-1.45038
C	3.42603	-1.07559	-0.16371	O	3.93461	3.40962	0.13812
C	3.40525	1.12019	-0.01345	C	1.93060	5.35822	0.91343
C	2.95571	2.42977	0.16888	C	2.50903	6.42156	1.04511
C	1.64350	2.85782	0.45334	C	-1.08500	5.13307	1.33505
C	-0.60172	2.71901	0.78759	C	-1.83268	6.04409	1.64420
C	-2.36082	0.91473	0.71990	C	2.16687	-5.34147	-0.55188
C	-2.36289	-1.25160	0.31562	C	2.93689	-6.27075	-0.72031
C	-1.90606	-2.54491	0.08365	C	-0.94582	-5.44674	-0.36163
N	-1.58308	-0.15441	0.42970	C	-1.66813	-6.42515	-0.43798
H	3.74240	-3.15705	-0.38054	C	3.23105	7.63756	1.19903
H	-2.64986	-3.33367	0.02482	C	4.63174	7.61964	1.36550
C	1.28526	-4.26408	-0.35694	C	2.56386	8.87968	1.18667
C	-0.12079	-4.31228	-0.27225				
C	-0.21651	4.08486	0.98350				

C	5.33784	8.80977	1.51431	C	2.87515	1.92721	0.98401
H	5.14649	6.66381	1.38319	C	1.61206	2.54295	0.87524
C	3.27903	10.06451	1.33594	C	-0.55661	2.82418	0.25195
H	1.48637	8.89788	1.05298	C	-2.25798	1.55161	-1.10560
C	4.66645	10.03542	1.49999	C	-2.27126	-0.36105	-2.20162
H	6.41652	8.78186	1.64385	C	-1.87150	-1.60641	-2.67597
H	2.75254	11.01516	1.32332	N	-1.52736	0.45844	-1.42769
H	5.22115	10.96240	1.61675	H	3.35009	-3.30431	-1.14820
C	-2.68188	7.12445	2.01173	H	-2.58135	-2.16069	-3.28247
C	-2.13152	8.36826	2.38587	C	1.03945	-3.79906	-2.44415
C	-4.08405	6.97503	2.01125	C	-0.26443	-3.55512	-2.92054
C	-2.96173	9.42559	2.74557	C	-0.18130	3.95804	1.04292
H	-1.05212	8.48539	2.39416	C	1.16573	3.78690	1.43544
C	-4.90587	8.03861	2.37254	C	-1.81141	2.61367	-0.33376
H	-4.51387	6.02030	1.72384	H	-2.51843	3.41499	-0.14271
C	-4.35015	9.26673	2.74037	C	4.55104	-1.34861	0.27880
H	-2.52416	10.37792	3.03293	C	4.63096	0.10003	0.82095
H	-5.98486	7.90923	2.36717	H	5.40562	0.68366	0.30802
H	-4.99498	10.09465	3.02188	H	4.86838	0.14641	1.88905
C	3.82130	-7.36697	-0.91820	C	-3.69950	1.50083	-1.65066
C	5.21749	-7.17044	-0.94989	C	-3.63509	0.22507	-2.52630
C	3.31569	-8.67288	-1.08664	H	-3.70135	0.46348	-3.59640
C	6.07636	-8.24818	-1.14383	H	-4.44632	-0.47985	-2.30952
H	5.61323	-6.16770	-0.82063	N	2.45997	-0.20869	-0.13874
C	4.18259	-9.74410	-1.28002	N	0.40056	-1.75662	-1.72990
H	2.24152	-8.82871	-1.06368	H	0.38964	-0.85167	-1.27562
C	5.56440	-9.53774	-1.30949	N	0.54465	2.00940	0.18691
H	7.15003	-8.08184	-1.16576	H	0.58005	1.12062	-0.29751
H	3.77910	-10.74491	-1.40850	C	-4.69744	1.32763	-0.48655
H	6.23805	-10.37668	-1.46059	H	-4.67022	2.18796	0.19158
C	-2.49692	-7.57745	-0.52826	H	-5.72124	1.23000	-0.86922
C	-3.90059	-7.46366	-0.45169	H	-4.46638	0.43174	0.10061
C	-1.92785	-8.85708	-0.69611	C	-4.05987	2.74901	-2.47534
C	-4.70494	-8.59587	-0.54078	H	-5.06086	2.64294	-2.91194
H	-4.34490	-6.48146	-0.32267	H	-4.06235	3.65449	-1.85814
C	-2.74059	-9.98320	-0.78414	H	-3.34698	2.90336	-3.29297
H	-0.84771	-8.94949	-0.75474	C	4.62360	-2.37850	1.42514
C	-4.13034	-9.85868	-0.70713	H	4.47767	-3.39942	1.05425
H	-5.78508	-8.49312	-0.48023	H	5.60263	-2.33445	1.91852
H	-2.28845	-10.96293	-0.91321	H	3.85367	-2.18307	2.17983
H	-4.76160	-10.74028	-0.77626	C	5.65416	-1.63252	-0.75730
				H	6.64459	-1.54634	-0.29322
				H	5.56949	-2.64290	-1.17301
				H	5.60670	-0.92320	-1.59120
				C	4.60093	3.54412	0.87288
				H	5.31630	4.02469	1.54413
				H	5.14299	3.02003	0.07444
				H	3.95392	4.30935	0.43080
20	Energy: -1851594.7113231						
C	-0.65485	-2.25270	-2.45295				
C	1.44762	-2.64298	-1.69131				
C	2.67596	-2.45850	-1.05622				
C	3.14658	-1.35294	-0.35356				
C	3.24687	0.65670	0.54009				

O	3.85033	2.62892	1.67533	O	5.19529	9.10278	6.24679
C	1.88119	4.68479	2.24934	O	-4.81844	-8.63689	-7.51206
C	2.43111	5.51206	2.95428	O	5.50685	-10.58007	-3.74933
C	-1.02367	5.03347	1.37553	C	6.81562	-10.74552	-3.22552
C	-1.75093	5.96592	1.67067	H	7.14900	-11.72940	-3.56014
C	1.82465	-4.94618	-2.65211	H	7.50300	-9.97988	-3.60860
C	2.51080	-5.93826	-2.82788	H	6.81737	-10.71577	-2.12800
C	-1.06275	-4.40484	-3.70547	C	-6.12426	-8.30182	-7.95584
C	-1.76123	-5.13566	-4.38657	H	-6.47228	-9.15935	-8.53435
C	3.11030	6.44407	3.78438	H	-6.80598	-8.13278	-7.11195
C	4.30337	6.08313	4.45180	H	-6.11597	-7.41079	-8.59731
C	2.61990	7.74952	3.96671	C	4.73615	10.42802	6.46331
C	4.96838	6.98956	5.26025	H	5.46013	10.88861	7.13783
H	4.69133	5.07667	4.32825	H	4.69806	10.99998	5.52682
C	3.28415	8.66677	4.77875	H	3.74402	10.43943	6.93347
H	1.70782	8.04603	3.45741	H	-5.60846	8.45988	1.32499
C	4.46530	8.28983	5.43127	O	-4.90937	10.33056	3.20536
H	5.88336	6.71696	5.77690	C	-6.18676	10.57071	2.63546
H	2.87656	9.66457	4.89399	H	-6.87770	9.73982	2.82966
C	-2.57580	7.06300	2.03844	H	-6.56429	11.47385	3.11817
C	-2.14987	7.98850	3.01886	H	-6.12018	10.73902	1.55251
C	-3.83510	7.26285	1.44507				
C	-2.94873	9.05967	3.38123	BCBr₄	Energy: -7246576.7163973		
H	-1.18369	7.84604	3.49320	C	-1.14977	-2.90918	-0.10191
C	-4.64422	8.33878	1.80514	C	1.12362	-2.90442	0.02171
H	-4.18077	6.56367	0.68973	C	2.44164	-2.45172	0.07831
C	-4.20330	9.24562	2.77766	C	2.92689	-1.14815	0.04044
H	-2.62683	9.77172	4.13471	C	2.98649	1.04551	-0.11502
C	3.29389	-7.10363	-3.04503	C	2.58258	2.38177	-0.16859
C	4.58770	-7.22326	-2.50619	C	1.26593	2.88449	-0.09798
C	2.79253	-8.18032	-3.81199	C	-1.01407	2.83412	-0.00697
C	5.35853	-8.36460	-2.71692	C	-2.83000	1.08278	-0.04931
H	4.99148	-6.40768	-1.91405	C	-2.88573	-1.11560	-0.16355
C	3.55293	-9.31729	-4.02540	C	-2.46247	-2.44051	-0.16706
H	1.79598	-8.10628	-4.23611	N	-2.07378	-0.03801	-0.10142
C	4.84324	-9.42065	-3.48001	H	3.17922	-3.24475	0.14550
H	6.35125	-8.42004	-2.28524	H	-3.22721	-3.20945	-0.21049
H	3.17204	-10.14632	-4.61351	C	0.67409	-4.26284	0.01355
C	-2.55934	-6.00284	-5.17994	C	-0.70027	-4.26562	-0.06586
C	-3.84905	-5.62762	-5.59775	C	-0.58617	4.19182	0.05130
C	-2.07782	-7.27256	-5.57337	C	0.79361	4.23104	-0.00270
C	-4.63476	-6.47543	-6.37573	C	-2.33827	2.37796	0.00677
H	-4.23753	-4.65652	-5.30643	H	-3.07144	3.17571	0.06409
C	-2.85310	-8.11995	-6.34628	C	4.43695	-0.85906	0.11970
H	-1.08480	-7.57988	-5.26039	C	4.45808	0.67370	-0.09868
C	-4.13906	-7.72980	-6.75496	H	4.94475	0.94087	-1.04499
H	-5.62378	-6.15107	-6.67837	H	4.99648	1.21307	0.68741
H	-2.48749	-9.09568	-6.65047	C	-4.34414	0.79551	-0.01167

C	-4.35438	-0.73671	-0.23703	H	-3.21332	-3.17975	-0.13145
H	-4.76562	-0.99947	-1.22082	C	0.67270	-4.26935	0.04688
H	-4.95387	-1.27168	0.50860	H	1.32250	-5.13384	0.08606
N	2.17096	-0.03108	-0.05046	C	-0.70252	-4.25437	-0.01159
N	-0.01448	-2.13588	-0.04911	H	-1.37246	-5.10401	-0.02706
H	-0.03313	-1.12309	-0.04710	C	-0.56491	4.19927	-0.00585
N	0.13744	2.08893	-0.08987	H	-1.21342	5.06415	0.04417
H	0.17289	1.07713	-0.13345	C	0.81423	4.18662	-0.03290
C	-4.91472	1.15827	1.37546	H	1.48556	5.03184	0.00789
H	-4.81672	2.23078	1.57731	C	-2.35889	2.41183	-0.03216
H	-5.97941	0.89982	1.43130	H	-3.09289	3.21207	-0.00096
H	-4.39066	0.61798	2.17187	C	4.46455	-0.87744	0.09965
C	-5.11267	1.54643	-1.11323	C	4.47368	0.66697	-0.04316
H	-6.17007	1.25479	-1.10662	H	4.98523	0.98851	-0.95909
H	-5.06889	2.63175	-0.96933	H	4.98513	1.16862	0.78578
H	-4.70464	1.32264	-2.10519	C	-4.36148	0.81210	-0.02211
C	4.97475	-1.23017	1.51761	C	-4.35611	-0.72855	-0.19018
H	4.87647	-2.30454	1.71018	H	-4.77897	-1.03271	-1.15708
H	6.03664	-0.96789	1.60062	H	-4.94168	-1.23923	0.58366
H	4.43021	-0.69662	2.30462	N	2.19335	-0.05994	-0.02984
C	5.23284	-1.60380	-0.96755	N	0.01044	-2.12471	-0.01468
H	6.28945	-1.31137	-0.93252	H	0.01715	-1.11356	-0.02110
H	5.18662	-2.69012	-0.83221	N	0.09622	2.05722	-0.08932
H	4.84959	-1.37390	-1.96807	H	0.08390	1.04639	-0.11510
C	3.96263	3.73788	-1.53737	C	-4.95255	1.22178	1.34274
H	4.81085	4.41545	-1.41831	H	-4.86917	2.30258	1.50420
H	4.25647	2.88802	-2.16642	H	-6.01503	0.95314	1.39889
H	3.13623	4.27592	-2.01489	H	-4.43018	0.71973	2.16486
O	3.60900	3.30838	-0.21873	C	-5.12519	1.51218	-1.16019
Br	-1.72828	5.67170	0.18968	H	-6.18133	1.21487	-1.15316
Br	1.79200	5.81534	0.09593	H	-5.08868	2.60302	-1.06037
Br	1.78758	-5.76703	0.09204	H	-4.70514	1.25124	-2.13799
Br	-1.81527	-5.76933	-0.11593	C	5.05522	-1.31765	1.45436
				H	4.97566	-2.40217	1.59204
23	Energy: -793012.9696949			H	6.11690	-1.04771	1.51665
C	-1.13065	-2.89132	-0.04864	H	4.53234	-0.83508	2.28760
C	1.13392	-2.91658	0.04302	C	5.22344	-1.55977	-1.05390
C	2.46065	-2.47569	0.08078	H	6.28288	-1.27483	-1.03719
C	2.95313	-1.17369	0.04517	H	5.17281	-2.65216	-0.98072
C	2.99875	1.02471	-0.07558	H	4.80883	-1.27033	-2.02614
C	2.56013	2.34670	-0.12120	C	3.89686	3.79299	-1.43908
C	1.23711	2.82741	-0.08844	H	4.67889	4.54383	-1.29988
C	-1.02592	2.85088	-0.04196	H	4.28187	2.98104	-2.07043
C	-2.84963	1.11393	-0.05847	H	3.03387	4.25072	-1.93906
C	-2.88093	-1.09118	-0.11874	O	3.55096	3.32385	-0.13557
C	-2.44414	-2.41243	-0.10423				
N	-2.08398	-0.00240	-0.08226	22	Energy: -694333.0337104		
H	3.19715	-3.27232	0.13617	C	-1.11844	-2.85485	0.00230

C	1.14465	-2.87335	-0.04784	21	Energy: -622474.4320919		
C	2.47527	-2.41404	-0.08523	C	-1.13331	-2.87698	0.00003
C	2.93143	-1.09827	-0.04876	C	1.13325	-2.87700	0.00006
C	2.90997	1.10381	0.04867	C	2.45512	-2.41479	0.00005
C	2.44631	2.41604	0.07474	C	2.91492	-1.10287	0.00004
C	1.12842	2.88294	0.05032	C	2.91483	1.10508	0.00002
C	-1.13748	2.89887	-0.00671	C	2.45545	2.41682	-0.00000
C	-2.91434	1.12629	-0.04116	C	1.13323	2.87937	0.00001
C	-2.90565	-1.08200	-0.00381	C	-1.13317	2.87939	0.00004
C	-2.44224	-2.38947	0.01353	C	-2.91480	1.10514	0.00002
N	-2.13059	0.02741	-0.02422	C	-2.91494	-1.10281	0.00001
H	3.20505	3.19353	0.11240	C	-2.45517	-2.41474	0.00002
H	-3.19766	-3.17066	0.03916	N	-2.13608	0.00115	0.00002
C	0.69697	-4.22436	0.00832	H	3.21303	-3.19401	0.00006
H	1.35245	-5.08202	0.04801	H	3.21293	3.19642	-0.00005
C	-0.68237	-4.21161	0.03682	H	-3.21310	-3.19395	0.00001
H	-1.34667	-5.06435	0.08740	C	0.68874	-4.23438	0.00005
C	-0.68401	4.25397	0.01519	H	1.34887	-5.09180	0.00005
H	-1.33832	5.11579	0.00507	C	-0.68883	-4.23437	0.00006
C	0.69215	4.24406	0.05194	H	-1.34897	-5.09177	0.00006
H	1.35822	5.09661	0.07589	C	-0.68895	4.23659	0.00009
C	-2.45945	2.44116	-0.03696	H	-1.34854	5.09442	0.00015
H	-3.21763	3.21971	-0.05043	C	0.68904	4.23658	-0.00005
C	4.41752	-0.75999	-0.01767	H	1.34864	5.09439	-0.00010
H	4.91170	-1.24377	0.83098	C	-2.45540	2.41687	0.00004
H	4.93086	-1.11535	-0.91849	H	-3.21287	3.19648	0.00006
C	4.40108	0.77692	0.08081	C	4.40579	-0.76859	0.00003
H	4.93276	1.26101	-0.74663	H	4.90500	-1.19081	0.88010
H	4.86092	1.14083	1.00753	H	4.90500	-1.19085	-0.88001
C	-4.40297	0.78574	-0.06554	C	4.40596	0.77087	-0.00000
H	-4.93325	1.25296	0.77208	H	4.90510	1.19304	-0.88011
H	-4.87263	1.15744	-0.98437	H	4.90514	1.19308	0.88006
C	-4.39735	-0.75172	0.01158	C	-4.40594	0.77095	0.00004
H	-4.91932	-1.22201	-0.82946	H	-4.90507	1.19312	0.88016
H	-4.87046	-1.12608	0.92741	H	-4.90512	1.19320	-0.88001
N	2.13944	-0.00309	-0.00919	C	-4.40580	-0.76850	-0.00002
N	0.01824	-2.08218	-0.04584	H	-4.90499	-1.19069	-0.88011
H	0.02768	-1.07128	-0.07298	H	-4.90505	-1.19077	0.88001
N	-0.01021	2.11165	0.01413	N	2.13608	0.00111	0.00003
H	-0.02486	1.10047	0.01400	N	-0.00002	-2.09737	0.00006
O	3.45188	-3.40510	-0.09662	H	-0.00001	-1.08597	0.00006
C	3.78868	-3.88531	-1.39857	N	0.00002	2.09972	0.00005
H	4.18403	-3.08187	-2.03450	H	0.00001	1.08827	0.00007
H	4.56012	-4.64661	-1.25718				
H	2.91836	-4.33284	-1.89498				

5. Photophysical measurements

5.1. Molar Absorption coefficient (ϵ)

General Procedure

The values for ϵ were obtained by weighing a small amount of the compound (~1.00 mg) and adding it to a volumetric flask, which was filled up to the meniscus with CH_2Cl_2 . Other solutions were prepared by making dilutions from the first one. Each one of the solutions had its absorption spectrum acquired, and the values of absorbance were plotted against concentration for each band, individually. All the graphs obtained are in agreement with the Lambert-Beer Law,¹¹ affording straight lines with $R^2 > 0,98$. From each graph the values of the angular coefficient is taken as ϵ for the corresponding band, using equation (1).

$$A = \epsilon \cdot b \cdot l \quad \text{Equation (1)}$$

In equation (1) A is the absorbance, b is the concentration and l is the optical path length. The Tables below present the data related to concentration of the solutions prepared and the values of absorbance obtained.

Table S9. Data for obtainment of ϵ for BCBr_4 .

Concentration $\times 10^{-5}$ (mol.L^{-1})	Abs B_y (353 nm)	Abs B_x (374 nm)	Abs Q_x (509 nm)	Abs Q_y (737 nm)
2.79	-	-	0.84	-
2.09	-	-	0.62	-
1.40	-	-	0.41	-
0.838	0.87	0.77	0.24	0.94
0.698	0.71	0.63	0.19	0.77
0.503	0.55	0.50	-	0.59
0.335	0.36	0.32	-	0.39

$\epsilon_{353} = 98,948 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$; $\epsilon_{374} = 86,560 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$; $\epsilon_{509} = 30,865 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$; $\epsilon_{737} = 107,118 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$.

Table S10. Data for obtainment of ϵ for 17.

Concentration x 10 ⁻⁵ (mol.L ⁻¹)	Abs B _y /B _x (398 nm)	Abs Q _x (556 nm)	Abs Q _y (802 nm)
4.78	-	0.89	-
3.58	-	0.67	-
2.39	-	0.44	-
1.19	0.83	0.22	1.06
0.952	0.66	0.17	0.84
0.669	0.45	-	0.57
0.478	0.33	-	0.41
0.287	0.19	-	0.25

$$\epsilon_{398} = 69,306 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}; \epsilon_{556} = 18,795 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}; \epsilon_{802} = 88,341 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}.$$

Table S11. Data for obtainment of ϵ for 19.

Concentration x 10 ⁻⁵ (mol.L ⁻¹)	Abs B _y /B _x (391 nm)	Abs Q _x (550 nm)	Abs Q _y (807 nm)
2.42	-	0.90	-
1.81	-	0.66	-
1.21	-	0.44	-
0.604	0.85	0.22	0.99
0.423	0.58	0.14	0.68
0.314	0.43	-	0.51
0.202	0.29	-	0.35
0.157	0.20	-	0.24

$$\epsilon_{391} = 142,333 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}; \epsilon_{550} = 37,633 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}; \epsilon_{807} = 163,582 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}.$$

Table S12. Data for obtainment of ϵ for **20**.

Concentration x 10 ⁻⁵ (mol.L ⁻¹)	Abs B _y /B _x (394 nm)	Abs Q _x (550 nm)	Abs Q _y (808 nm)
2.12		0.85	
1.59		0.63	
1.06		0.42	
0.530	0.89	0.21	0.94
0.371	0.60	0.13	0.64
0.276	0.45	0.10	0.49
0.191	0.30		0.33
0.138	0.22		0.24

$\epsilon_{394} = 170,961 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$; $\epsilon_{550} = 40,661 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$; $\epsilon_{808} = 177,847 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$.

5.2 Fluorescence quantum yield (Φ_f)

General Procedure

The values of Φ_f were obtained by comparing the areas under the fluorescence spectra of the compounds with the area under the fluorescence spectra of the standard. A solution of each compound was prepared in toluene and the absorbances at the excitation wavelength (λ_{ex}) were adjusted between 0.1 and 0.2. Oxygen was removed from the solutions by bubbling argon. The solutions had their fluorescence spectra acquired using $\lambda_{ex} = 510$ nm for **BCBr₄** and $\lambda_{ex} = 550$ nm for **17**, **19** and **20**. The *meso*-tetraphenylporphyrin (TPP) was used as standard. In the case of TPP, the fluorescence spectra were acquired without degassification for both λ_{ex} and the value of 0.07 was used as Φ_f^{Std} . The values of Φ_f were calculated using equation (2).

$$\Phi_f = \Phi_f^{Std} \frac{F \cdot A_{Std}}{F_{Std} \cdot A} \quad \text{Equation (2)}$$

In equation (2), Φ_f^{Std} is the fluorescence quantum yield of the standard, F and F_{Std} are the areas obtained from the fluorescence spectra of the sample and the standard, respectively. A and A_{Std} correspond to the absorbances. The Tables below present the data related to the values of absorbance and the area obtained for the fluorescence spectrum of each compound and also for the standard in both λ_{ex} .

Table S13. Data for obtainment of Φ_f for **BCBr₄**, **17**, **19** and **20**.

Compound	Absorbance	Area
TPP $\lambda_{ex} = 510$	0.14529	6005.189
TPP $\lambda_{ex} = 550$	0.18852	8902.858
BCBr₄	0.13014	370.905
17	0.14986	2803.559
19	0.15405	5622.031
20	0.15636	6184.829

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