

Electronic Supplementary Information

Direct C-H borylation of vinylporphyrins *via* copper catalysis

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Synthesis and characteristics of the compounds

General. Reactions were carried out under argon atmosphere using commercially available reagents that were purchased and used as received. Starting methyl pyropheophorbide-*a* (**1a**), dimethyl protoporphyrin IX, and 2,3,7,8,12,13,17,18-octaethylporphyrin were obtained from commercial sources. Heating reaction vessels was performed with oil bath. Column chromatography was performed using 40-63 μm silica gel, preparative thin layer chromatography (TLC) was performed using glass plates coated with 5-40 μm silica gel (5 mm thick). Control of the reactions was provided by TLC using aluminum-backed Silica Gel 60 F254 pre-coated plates. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance III 600 MHz spectrometer at room temperature in CDCl₃. Chemical shifts are reported relative to signals of residual protons of solvents (CDCl₃ – 7.26 ppm). Mass spectra were recorded with UltrafleXtreme mass spectrometer (Bruker Daltonics) in a positive-ion mode using reflection mode with 20 MV voltage without matrix. Electronic absorption spectra were recorded with U-2900 (Hitachi) spectrophotometer in quartz rectangular cells of 10 mm path length at concentration 10⁻⁵ M in CH₂Cl₂.

Synthesis. Zn(II) methyl pyropheophorbide-*a* (**1b**),¹ Ni(II) methyl pyropheophorbide-*a* (**1c**),^{2, 3} and methyl (*E*)-3²-bromopyropheophorbide-*a* (**2a**),⁴ Zn(II) dimethyl protoporphyrin IX (**6b**) and Ni(II) dimethyl protoporphyrin IX (**6c**)⁵ were synthesized according to reported procedures. *meso*-Vinylporphyrinoids **8** and **10** were obtained as follows. The 2,3,7,8,12,13,17,18-octaethylporphyrin was converted to the corresponding iron(III) chloride complex and reduced to the 2,3,7,8,12,13,17,18-octaethyl-17,18-*trans*-dihydroporphyrin with sodium in amyl alcohol as reported.⁶ Nickel(II) complexes of 2,3,7,8,12,13,17,18-octaethylporphyrin and 2,3,7,8,12,13,17,18-octaethyl-17,18-*trans*-dihydroporphyrin were obtained and formylated via the Vilsmeier-Haack reaction,^{7, 8} followed by the Wittig reaction with triphenylmethylphosphonium iodide to give the 5-vinyl-2,3,7,8,12,13,17,18-octaethylporphyrin (**8**) and 5-vinyl-2,3,7,8,12,13,17,18-octaethyl-17,18-*trans*-dihydroporphyrin (**10**) correspondingly.⁹

Zn(II) methyl (*E*)-3²-bromopyropheophorbide-*a* (**2b**)

A solution of Zn(OAc)₂•2H₂O (2 g, 9 mmol) in CH₃OH (25 ml) was added to a solution of methyl (*E*)-3²-bromopyropheophorbide-*a* (**2a**) (300 mg, 0.48 mmol) in CH₂Cl₂ (200 ml). The reaction was heated at reflux for 1 h, and then the crude mixture was washed with water (3 x 100 ml). The organic layer was dried over Na₂SO₄, filtered and evaporated in vacuum to give the crude product which was purified by flash column chromatography with silica gel using CH₂Cl₂ as the eluent to give the product **2b** (310 mg, 94%) as a green solid.

¹H NMR (600 MHz, CD₂Cl₂), δ , ppm: 9.18 (1H, s, 10-H), 8.83 (1H, s, 5-H), 8.48 (1H, s, 20-H), 8.30 (1H, d, *J* = 14.5 Hz, 3¹-H), 7.21 (1H, d, *J* = 14.5 Hz, 3²-H), 4.80 (1H, d, *J* = 19.0 Hz, 13²-H^a), 4.69 (1H, d, *J* = 19.0 Hz, 13²-H^b), 4.46 (1H, q, *J* = 7.5 Hz, 18-H), 4.22 (1H, m, 17-H), 3.46 (5H, m, 12-CH₃, 8¹-CH₂), 3.42 (3H, s, 17²-CO₂CH₃), 3.30 (3H, s, 2-CH₃), 3.01 (3H, s, 7-CH₃), 2.57 (1H, m, 17¹-H^a), 2.51 (1H, m, 17²-H^a), 2.25 (2H, m, 17¹-H^b, 17²-H^b), 1.87 (3H, d, *J* = 7.5 Hz, 18-CH₃), 1.57 (3H, t, *J* = 7.8 Hz, 8²-CH₃). ¹³C NMR (150 MHz, CD₂Cl₂), δ , ppm: 196.1, 173.3, 168.4, 160.9, 156.7, 150.2, 147.1, 145.8, 143.6, 136.2, 134.7, 134.4, 133.4, 131.6, 130.4, 129.6, 110.4, 106.0, 98.3, 92.7, 62.8, 51.4, 50.6, 48.6, 47.8, 30.5, 29.7, 29.5, 23.2, 19.1, 17.0, 12.3, 12.1, 10.4. HRMS (MALDI-TOF), *m/z* found: 688.1037; calc. C₃₄H₃₃BrN₄O₃Zn (M⁺): 688.1028. UV-Vis (CH₂Cl₂), λ_{max} , nm (A_{rel.}): 424 (1.00), 517 (0.05), 559 (0.06), 610 (0.12), 659 (0.69).

The borylation of methyl (*E*)-3²-bromopyrophephorbide-*a* (2)

Methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyrophephorbide-*a* (3a)

A mixture of methyl (*E*)-3²-bromopyrophephorbide-*a* (**2a**) (20 mg, 0.032 mmol), bis(pinacolato)diboron (80 mg, 0.315 mmol), Pd(PPh₃)₄ (7.3 mg, 0.006 mmol) and Cs₂CO₃ (47 mg, 0.144 mmol) in 1,4-dioxane (2 mL) was stirred at 60 °C for 24 h. Then the solvent was evaporated in vacuum, and the residue was purified by preparative TLC in a CH₂Cl₂/EtOH system (100:1) to give the product **3a** (8.6 mg, 40%) as a brown solid.

¹H NMR (600 MHz, CDCl₃), δ, ppm: 9.46 (1H, s, 10-H), 9.43 (1H, s, 5-H), 8.69 (1H, d, *J* = 18.7 Hz, 3¹-H), 8.53 (1H, s, 20-H), 6.72 (1H, d, *J* = 18.7 Hz, 3²-H), 5.20 (1H, d, *J* = 19.3 Hz, 13²-H^a), 5.05 (1H, d, *J* = 19.3 Hz, 13²-H^b), 4.42 (1H, q, *J* = 7.5 Hz, 18-H), 4.23 (1H, m, 17-H), 3.65 (2H, q, *J* = 7.8 Hz, 8¹-CH₂), 3.61 (3H, s, 12-CH₃), 3.53 (3H, s, 17²-CO₂CH₃), 3.41 (3H, s, 2-CH₃), 3.21 (3H, s, 7-CH₃), 2.63 (1H, m, 17¹-H^a), 2.49 (1H, m, 17²-H^a), 2.22 (2H, m, 17¹-H^b, 17²-H^b), 1.74 (3H, d, *J* = 7.5 Hz, 18-CH₃), 1.64 (3H, t, *J* = 7.8 Hz, 8²-CH₃), 1.43 (12H, s, CH₃(pin)), 0.10 (1H, s, NH), -1.71 (1H, s, NH). ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 196.1, 173.5, 171.1, 160.5, 155.2, 151.0, 148.9, 145.0, 141.4, 141.2, 138.0, 136.4, 135.6, 132.8, 130.6, 129.2, 128.5, 106.1, 103.9, 97.4, 93.3, 83.8, 82.7, 51.7, 51.6, 50.0, 48.0, 30.9, 29.9, 29.7, 24.9, 24.8, 23.2, 19.5, 17.4, 12.5, 11.4. HRMS (MALDI-TOF), *m/z* found: 675.3702; calc. C₄₀H₄₈BN₄O₅ (MH⁺): 675.3718. UV-Vis (CH₂Cl₂), λ_{max}, nm (A_{rel.}): 415 (1.00), 515 (0.11), 544 (0.06), 617 (0.08), 673 (0.51).

Zn(II) methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyrophephorbide-*a* (3b)

A mixture of PdCl₂(CH₃CN)₂ (1.9 mg, 0.007 mmol), dppp (3.6 mg, 0.009 mmol), Cs₂CO₃ (140 mg, 0.43 mmol) and bis(pinacolato)diboron (368 mg, 1.45 mmol) in 1,4-dioxane (15 mL) was stirred at room temperature for one hour, then it was heated to 80 °C and solution of Zn(II) methyl (*E*)-3²-bromopyrophephorbide-*a* (**2b**) (100 mg, 0.14 mmol) in 1,4-dioxane (5 mL) was added dropwise over a period of 15 min and stirred at 80 °C for 3 h. The solvent was evaporated *in vacuo*, the residue was dissolved in CH₂Cl₂ (20 mL) and washed with water (2x10 mL), then the solvent was evaporated *in vacuo* to give the crude product, which was purified by preparative TLC in a CH₂Cl₂/EtOH system (100:1) to give the product **3b** (75 mg, 70%) as a green solid.

¹H NMR (600 MHz, CDCl₃), δ, ppm: 9.10 (1H, s, 10-H), 9.08 (1H, s, 5-H), 8.69 (1H, d, *J* = 18.7 Hz, 3¹-H), 8.45 (1H, s, 20-H), 6.68 (1H, d, *J* = 18.7 Hz, 3²-H), 4.49 (1H, d, *J* = 19.3 Hz, 13²-H^a), 4.70 (1H, d, *J* = 19.3 Hz, 13²-H^b), 4.41 (1H, m, 18-H), 4.17 (1H, m, 17-H), 3.46 (2H, q, *J* = 7.8 Hz, 8¹-CH₂), 3.42 (3H, s, 12-CH₃), 3.43 (3H, s, 17²-CO₂CH₃), 3.42 (3H, s, 2-CH₃), 3.05 (3H, s, 7-CH₃), 2.51 (1H, m, 17¹-H^a), 2.44 (1H, m, 17²-H^a), 2.19 (2H, m, 17¹-H^b, 17²-H^b), 1.88 (3H, d, *J* = 7.5 Hz, 18-CH₃), 1.59 (3H, t, *J* = 7.8 Hz, 8²-CH₃), 1.55 (12H, s, CH₃(pin)). ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 196.5, 173.4, 168.0, 161.0, 156.2, 150.6, 147.1, 147.0, 144.8, 143.6, 142.4, 138.7, 136.2, 134.4, 133.5, 131.5, 106.1, 105.3, 99.2, 92.5, 83.7, 51.6, 50.6, 48.6, 47.8, 30.6, 29.7, 29.5, 25.1, 24.7, 24.6, 23.5, 19.2, 12.8, 12.4. HRMS (MALDI-TOF), *m/z* found: 737.2834; calc. C₄₀H₄₆BN₄O₅Zn (MH⁺): 737.2853. UV-Vis (CH₂Cl₂), λ_{max}, nm (A_{rel.}): 426 (1.00), 520 (0.05), 561 (0.07), 611 (0.12), 661 (0.57).

The methyl pyrophephorbide-*a* dimer (4)

A mixture of methyl (*E*)-3²-bromopyrophephorbide-*a* (**2a**) (40 mg, 0.064 mmol), bis(pinacolato)diboron (81.2 mg, 0.32 mmol), Pd(PPh₃)₄ (14.8 mg, 0.013 mmol) and Cs₂CO₃ (104 mg, 0.32 mmol) in 1,4-dioxane (3 mL) was stirred at 50 °C for 4 h, then the solvent was evaporated in vacuum, and the residue was purified by preparative TLC in a CH₂Cl₂/EtOH system (100:1) to give the product **4** (21 mg, 60%) as a brown solid.

¹H NMR (600 MHz, CDCl₃), δ, ppm: 9.49 (1H, s, 10-H), 9.48 (1H, s, 5-H), 8.69 (1H, s, 20-H), 8.09 (1H, d, *J* = 13.5 Hz, 3¹-H), 7.76 (1H, d, *J* = 13.5 Hz, 3²-H), 5.30 (1H, d, *J* = 18.7 Hz, 13²-H^a), 5.15 (1H, d, *J* = 18.7 Hz, 13²-H^b), 4.59 (1H, q, *J* = 7.8 Hz, 18-H), 4.38 (1H, m, 17-H), 3.76 (2H, q, *J* = 7.8 Hz, 8¹-CH₂), 3.68 (3H, s, 17²-CO₂CH₃), 3.60 (3H, s, 2-CH₃), 3.59 (3H, s, 12-CH₃), 3.37 (3H, s, 7-CH₃), 2.77 (1H, m, 17¹-H^a), 2.65 (1H, m, 17²-H^a), 2.38 (2H, m, 17¹-H^b и 17²-H^b), 1.93 (3H, d, *J* = 7.8 Hz, 18-CH₃), 1.77 (3H, t, *J* = 7.8 Hz, 8²-CH₃), 0.52 (1H, s, NH), -1.58 (1H, s, NH). ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 196.0, 173.5, 171.3, 160.7, 155.1, 151.0, 149.0, 145.1, 141.5, 138.1, 137.3, 136.2, 136.1, 134.9, 131.0, 130.7, 128.6, 126.0, 106.2, 104.1, 96.8, 93.2, 51.9, 51.7, 50.0, 48.1, 31.0, 29.9, 23.2, 19.6, 17.5, 12.8, 12.0, 11.4. HRMS (MALDI-TOF), *m/z* found: 1095.5516; calc. C₆₈H₇₁N₈O₆ (MH⁺): 1095.5497. UV-Vis (CH₂Cl₂), λ_{max}, nm (A_{rel.}): 413 (1.00), 514 (0.21), 554 (0.17), 625 (0.12), 692 (0.67).

General procedure of the direct borylation of vinylporphyrins.

CuSCN (0.017 mmol, 0.2 eq.) and (2-biphenyl)dicyclohexylphosphine (CyJohnPhos) (0.036 mmol, 0.44 eq.) were added to 1 mL of freshly distilled 1,2-dichloroethane and stirred at room temperature for 30 minutes, then Li^oBu (0.17 mmol, 2 eq.), Ni(II) methyl pyrophephorbide-*a* (**1c**) 50 mg (0.083 mmol, 1 eq.), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (0.33 mmol, 4 eq.), bispinacolborane ((Bpin)₂) (0.33 mmol, 4 eq.) and 4 mL of 1,2-dichloroethane were added. The reaction mixture was stirred and refluxed for 15 hours, then the solvent was evaporated and the product was purified by column chromatography with CH₂Cl₂ / MeOH (100:1) eluent, to yield 36.6 mg (60%) of Ni(II) methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyrophephorbide-*a* (**3c**) as a green powder.

Ni(II) methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyrophephorbide-*a* (3c). ¹H NMR (600 MHz, CDCl₃), δ, ppm: 9.31 (1H, s, 10-H), 9.19 (1H, s, 5-H), 8.52 (1H, d, *J* = 18.7 Hz, Bpin-CH=CH), 8.21 (1H, s, 20-H), 6.52 (1H, d, *J* = 18.7 Hz, Bpin-CH=CH), 4.87 (1H, d, *J* = 19.2 Hz, 13²-H^a), 4.8 (1H, d, *J* = 19.2 Hz, 13²-H^b), 4.30 (1H, m, 18-H), 4.01 (1H, m, 17-H), 3.62 (3H, s, 12-CH₃), 3.61 (2H, q, *J* = 7.8 Hz, 8¹-CH₂), 3.49 (3H, s, 17²-CO₂CH₃), 3.23 (3H, s, 2-CH₃), 3.17 (3H, s, 7-CH₃), 2.46 (1H, m, 17¹-H^a), 2.28 (2H, m, 17¹-H^b, 17²-H^b), 2.13 (1H, m, 17²-H^a), 1.63 (3H, t, *J* = 7.7 Hz, 8²-CH₃), 1.55 (3H, d, *J* = 7.2 Hz, 18-CH₃), 1.493 (6H, s, CH₃), 1.488 (6H, s, CH₃). ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 195.4, 173.2, 161.8, 156.3, 148.9, 147.9, 144.6, 143.8, 141.4, 140.7, 140.0, 139.4, 136.4, 134.7, 133.8, 133.0, 129.7, 106.3, 105.1,

100.3, 93.4, 83.7, 51.7, 49.2, 48.7, 47.2, 30.6, 29.7, 25.0, 22.2, 19.4, 17.2, 12.5, 11.1. HRMS (MALDI-TOF), m/z found: 730.2855; calc. $C_{40}H_{45}BN_4NiO_5$ (M^+): 730.2836. UV-Vis (CH_2Cl_2), λ_{max} , nm (log (ϵ [$L mol^{-1} cm^{-1}$])): 379 (4.56), 401 (4.68), 424 (4.67), 502 (3.43), 657 (4.72).

Zn(II) dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (7b). Yield was 13 mg (38%) (deep dark red powder) from 25 mg (0.038 mmol) of the Zn(II) dimethyl protoporphyrin IX (6b).

¹H NMR (600 MHz, $CDCl_3$), δ , ppm: 9.36 (1H, s, *meso*-H), 9.29 (1H, s, *meso*-H), 8.92 (1H, s, *meso*-H), 8.91 (1H, s, *meso*-H), 8.84 (1H, d, $J = 18.6$ Hz, Bpin-CH=CH), 8.76 (1H, d, $J = 18.6$ Hz, Bpin-CH=CH), 6.78 (1H, d, $J = 18.6$ Hz, Bpin-CH=CH), 6.73 (1H, d, $J = 18.6$ Hz, Bpin-CH=CH), 4.08 (4H, m, $CH_2CH_2COOCH_3$), 3.65 (3H, s, $CH_2CH_2COOCH_3$), 3.61 (3H, s, $CH_2CH_2COOCH_3$), 3.51 (3H, s, CH_3), 3.43 (3H, s, CH_3), 3.41 (3H, s, CH_3), 3.25 (3H, s, CH_3), 3.09 (4H, m, $CH_2CH_2COOCH_3$), 1.68 (24H, br.s, CH_3). ¹³C NMR (150 MHz, $CDCl_3$), δ , ppm: 173.6, 173.5, 147.4, 146.6, 146.2, 146.0, 145.0, 143.1, 143.0, 138.4, 138.2, 138.0, 137, 4,137.0, 136.5, 136.0, 135.8, 98.0, 97.1, 96.9, 95.4, 83.6, 51.6, 51.6, 36.8, 29, 7, 25.2, 21.7, 21.6, 13.3, 13.1, 11.7, 11.3. HRMS (MALDI-TOF), m/z found: 904.3756; calc. $C_{48}H_{58}B_2N_4ZnO_8$ (M^+): 904.3732. UV-Vis (CH_2Cl_2), λ_{max} , nm (A_{rel}): 417 (1.00), 544 (0.07), 583 (0.11).

Ni(II) dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (7c). Yield was 84 mg (49%) (maroon amorphous solid) from 123 mg (0.19 mmol) of the Ni(II) dimethyl protoporphyrin IX (6c).

¹H NMR (600 MHz, $CDCl_3$), δ , ppm: 9.52 (1H, s, *meso*-H), 9.45 (1H, s, *meso*-H), 9.38 (2H, br.s, *meso*-H), 8.70 (1H, d, $J = 18.0$ Hz, Bpin-CH=CH), 8.66 (1H, d, $J = 18.0$ Hz, Bpin-CH=CH), 6.60 (1H, d, $J = 18.0$ Hz, Bpin-CH=CH), 6.58 (1H, d, $J = 18.0$ Hz, Bpin-CH=CH), 4.10 (4H, m, $CH_2CH_2COOCH_3$), 3.71 (3H, s, $CH_2CH_2COOCH_3$), 3.70 (3H, s, $CH_2CH_2COOCH_3$), 3.45 (3H, s, CH_3), 3.41 (3H, s, CH_3), 3.38 (3H, s, CH_3), 3.34 (3H, s, CH_3), 3.10 (4H, m, $CH_2CH_2COOCH_3$), 1.58 (24H, br.s, CH_3). ¹³C NMR (150 MHz, $CDCl_3$), δ , ppm: 173.3, 141.9, 141.8, 141.6, 141.1, 140.9, 140.4, 139.5, 139.3, 139.1, 138.2, 137.7, 137.6, 137.0, 136.7, 98.3, 97.7, 97.3, 96.1, 83.6, 51.5, 36.6, 29.7, 24.9, 21.5, 13.8, 12.7, 12.6, 11.4. HRMS (MALDI-TOF), m/z found: 898.3814; calc. $C_{48}H_{58}B_2N_4NiO_8$ (M^+): 898.3794. UV-Vis (CH_2Cl_2), λ_{max} , nm (log (ϵ [$L mol^{-1} cm^{-1}$])): 406 (5.1), 528 (3.95), 566 (4.4).

Ni(II) (*E*)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (9). Yield was 9.7 mg (62%) (maroon amorphous solid) from 13 mg (0.021 mmol) of the Ni (II) 5-vinyl-2,3,7,8,12,13,17,18-octaethylporphyrin (8).

¹H NMR (600 MHz, $CDCl_3$), δ , ppm: 9.92 (1H, d, $J = 18$ Hz, Bpin-CH=CH), 9.47 (2H, br.s, *meso*-H), 9.46 (1H, s, *meso*-H), 5.04 (1H, d, $J = 18$ Hz, Bpin-CH=CH), 3.85 (16H, m, CH_2), 1.80 (12H, m, CH_3), 1.75 (6H, t, $J = 7.70$ Hz, CH_3), 1.61 (6H, t, $J = 7.70$ Hz, CH_3), 1.39 (12H, t, CH_3). ¹³C NMR (150 MHz, $CDCl_3$), δ , ppm: 144.5, 143.1, 142.8, 140.2, 139.5, 138.4, 138.3, 96.6, 95.9, 83.4, 24.8, 22.0, 19.6, 19.6, 19.5. HRMS (MALDI-TOF), m/z found: 742.3935; calc. $C_{44}H_{57}BN_4NiO_2$ (M^+): 742.3928. UV-Vis (CH_2Cl_2), λ_{max} , nm (log (ϵ [$L mol^{-1} cm^{-1}$])): 404 (5.3), 528 (4.06), 562 (4.25).

Ni(II) (*E*)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)ethenyl)-2,3,7,8,12,13,17,18-octaethyl-17,18-trans-dihydroporphyrin (11). Yield was 24.7 mg (41%) (green amorphous solid) from 50 mg (0.081 mmol) of the Ni (II) 5-vinyl-2,3,7,8,12,13,17,18-octaethyl-17,18-trans-dihydroporphyrin (10).

¹H NMR (600 MHz, $CDCl_3$), δ , ppm: 8.91 (1H, s, *meso*-H), 8.86 (1H, s, *meso*-H), 8.64 (1H, d, $J = 18.0$ Hz, Bpin-CH=CH), 7.88 (1H, s, *meso*-H), 5.29 (1H, d, $J = 18.0$ Hz, Bpin-CH=CH), 4.24 (1H, m, 17-H), 3.91 (1H, m, 18-H), 3.65-3.34 (12H, m, CH_2CH_3), 1.81 (2H, m, 18- CH_2CH_3), 1.62 (18H, m, CH_2CH_3), 1.45 (2H, m, 17- CH_2CH_3), 1.38 (6H, br.s, CH_3), 1.37 (6H, br.s, CH_3), 1.04 (3H, t, $J = 7.5$ Hz, 17- CH_2CH_3), 0.89 (3H, t, $J = 7.5$ Hz, 18- CH_2CH_3). ¹³C NMR (150 MHz, $CDCl_3$), δ , ppm: 144.4, 133.6, 143.4, 139.5, 139.3, 138.4, 138.3, 138.1, 137.6, 136.7, 135.2, 106.4, 101.9, 100.7, 93.0, 83.2, 54.2, 53.9, 29.7, 27.5, 25.6, 24.9, 24.6, 20.9, 19.4, 19.3, 19.1, 19.0, 18.1. HRMS (MALDI-TOF), m/z found: 744.4098; calc. $C_{44}H_{59}BN_4NiO_2$ (M^+): 744.4085. UV-Vis (CH_2Cl_2), λ_{max} , nm (log (ϵ [$L mol^{-1} cm^{-1}$])): 410 (4.99), 502 (3.71), 630 (4.49).

(*E*)-configuration of all the borylated C=C double bonds was confirmed by the large constant of the spin coupling between *trans*-protons (18 Hz) in the ¹H NMR spectra of the products.

Demetalation of the metal porphyrin complex

Zn(II) dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (7b) (12.8 mg, 0.014 mmol) was dissolved in CH_2Cl_2 (3 mL) and a solution of 0.15% HCl in trifluoroacetic acid (12 mL) was added, and the mixture was stirred for 5 min at ambient temperature. Then the mixture was diluted with CH_2Cl_2 (50 mL) and neutralized with aqueous $NaHCO_3$, the organic layer was dried over anhydrous sodium sulfate. The resulting supernatant was passed through a pad of silica gel and the solvent was evaporated. The residue was recrystallized from $CH_2Cl_2/MeOH$ to yield 5 mg (50%) of dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (7a) as a purple powder. ¹H NMR and UV-Vis spectra of 7a corresponds to the previously reported.¹⁰

Dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (7a). ¹H NMR (600 MHz, $CDCl_3$), δ , ppm: 10.22 (1H, s, *meso*-H), 10.18 (1H, s, *meso*-H), 10.06 (1H, s, *meso*-H), 10.01 (1H, s, *meso*-H), 9.02 (1H, d, $J = 18.6$ Hz, Bpin-CH=CH), 9.01 (1H, d, $J = 18.6$ Hz, Bpin-CH=CH), 6.90 (1H, d, $J = 18.6$ Hz, Bpin-CH=CH), 6.89 (1H, d, $J = 18.6$ Hz, Bpin-CH=CH), 4.40 (4H, t, $J = 7.86$ Hz, $CH_2CH_2COOCH_3$), 3.77 (6H, br.s, $CH_2CH_2COOCH_3$), 3.70 (3H, s, CH_3), 3.69 (3H, s, CH_3), 3.66 (3H, s, CH_3), 3.64 (3H, s, CH_3), 3.31 (4H, t, $J = 7.86$ Hz, $CH_2CH_2COOCH_3$), 1.56 (24H, br.s, CH_3), -3.89 (2H, s, NH). UV-Vis (CH_2Cl_2), λ_{max} , nm (A_{rel}): 412 (1.00), 509 (0.09), 546 (0.08), 579 (0.04), 634 (0.03).

General procedure of the Suzuki reaction on the example of methyl (*E*)-3²-phenylpyropheophorbide-*a* (**3a**)

To a 0.03M solution of borylated porphyrinoid in 1,4-dioxane 5 mol% Pd(PPh₃)₄, 2 eq. K₂CO₃ and 2 eq. aryl iodide were consecutively added, and the mixture was stirred at 80 °C for 1 h. Then the solvent was evaporated in vacuum, the residue was dissolved in CH₂Cl₂ (10 ml), washed by water (2x5 ml), the solvent was evaporated in vacuum, and the residue was purified by preparative TLC in a CH₂Cl₂/EtOH system (100:1) to give products.

Methyl (*E*)-3²-phenylpyropheophorbide-*a* (12a**).** The reaction was performed at 70 °C for 12 h. The product **12a** (12 mg, 65%) was obtained as a brown solid from (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (**3a**) (20 mg, 0.03 mmol) and iodobenzene (12 mg, 0.06 mmol). ¹H NMR spectrum of **12a** corresponds to the previously reported.⁴

¹H NMR (600 MHz, CDCl₃), δ, ppm: 9.59 (1H, s, 10-H), 9.50 (1H, s, 5-H), 8.65 (1H, s, 20-H), 8.37 (1H, d, *J* = 16.5 Hz, 3¹-H), 7.89 (2H, d, *J* = 7.5 Hz, 3^{4a}-H, 3^{4b}-H), 7.64 (1H, d, *J* = 16.5 Hz, 3²-H), 7.59 (2H, t, *J* = 7.5 Hz, 3^{5a}-H, 3^{5b}-H), 7.49 (1H, m, 3⁶-H), 5.31 (1H, d, *J* = 19.3 Hz, 13²-H^a), 5.15 (1H, d, *J* = 19.3 Hz, 13²-H^b), 4.55 (1H, q, *J* = 7.5 Hz, 18-H), 4.34 (1H, m, 17-H), 3.74 (2H, q, *J* = 7.8 Hz, 8¹-CH₂), 3.71 (3H, s, 12-CH₃), 3.65 (3H, s, 17²-CO₂CH₃), 3.49 (3H, s, 2-CH₃), 3.27 (3H, s, 7-CH₃), 2.75 (1H, m, 17¹-H^a), 2.61 (1H, m, 17²-H^a), 2.35 (2H, m, 17¹-H^b, 17²-H^b), 1.87 (3H, d, *J* = 7.5 Hz, 18-CH₃), 1.73 (3H, t, *J* = 7.8 Hz, 8²-CH₃), 0.36 (1H, s, NH), -1.65 (1H, s, NH). UV-Vis (CH₂Cl₂), λ_{max}, nm (A_{rel.}): 419 (1.00), 512 (0.11), 542 (0.09), 615 (0.08), 673 (0.44).

Zn(II) methyl (*E*)-3²-phenylpyropheophorbide-*a* (12b**).** PdCl₂(CH₃CN)₂ (1.2 mg, 0.0046 mmol) and dppp (2 mg, 0.005 mmol) were used as a precatalyst instead of Pd(PPh₃)₄. The product **12b** (14 mg, 75 %) was obtained as a green solid from Zn(II) methyl (*E*)-3²-bromopyropheophorbide-*a* (**2b**) (20 mg, 0.027 mmol) and iodobenzene (12 mg, 0.06 mmol).

¹H NMR (600 MHz, CDCl₃), δ, ppm: 9.06 (1H, s, 10-H), 8.87 (1H, s, 5-H), 8.39 (1H, s, 20-H), 8.14 (1H, d, *J* = 16.5 Hz, 3¹-H), 7.82 (2H, d, *J* = 7.5 Hz, 3^{4a}-H, 3^{4b}-H), 7.58 (2H, t, *J* = 7.5 Hz, 3^{5a}-H, 3^{5b}-H), 7.47 (1H, t, *J* = 7.5 Hz, 3⁶-H), 7.39 (1H, d, *J* = 16.5 Hz, 3²-H), 4.78 (1H, d, *J* = 18.9 Hz, 13²-H^a), 4.69 (1H, d, *J* = 18.9 Hz, 13²-H^b), 4.41 (1H, m, 18-H), 4.15 (1H, m, 17-H), 3.46 (3H, s, 17²-CO₂CH₃), 3.41 (5H, m, 12-CH₃, 8¹-CH₂), 3.32 (3H, s, 2-CH₃), 2.30 (3H, s, 7-CH₃), 2.53 (1H, m, 17¹-H^a), 2.47 (1H, m, 17²-H^a), 2.22 (2H, m, 17¹-H^b, 17²-H^b), 1.88 (3H, d, *J* = 7.5 Hz, 18-CH₃), 1.55 (3H, t, *J* = 7.7 Hz, 8²-CH₃). ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 196.5, 173.4, 168.2, 165.3, 161.1, 156.1, 153.8, 150.5, 147.2, 146.9, 144.6, 143.6, 138.3, 138.0, 134.3, 134.2, 133.8, 133.1, 129.7, 129.0, 126.7, 121.4, 106.6, 105.2, 98.6, 92.4, 62.7, 51.6, 50.5, 18.6, 47.8, 30.7, 29.7, 29.5, 25.1, 23.5, 19.1, 17.3, 12.6, 10.7. HRMS (MALDI-TOF), *m/z* found: 687.2336; calc. C₄₀H₃₉N₄O₃Zn (MH⁺): 687.2314. UV-Vis (CH₂Cl₂), λ_{max}, nm (log (ε [L mol⁻¹ cm⁻¹])): 424 (6.90), 517 (5.48), 560 (5.63), 611 (5.96), 661 (6.69).

Zn(II) methyl (*E*)-3²-(4-methylphenyl)pyropheophorbide-*a* (13b**).** The product **13b** (10 mg, 53%) was obtained as a green solid from Zn(II) methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (**3b**) (20 mg, 0.03 mmol) and 4-iodotoluene (13 mg, 0.06 mmol).

¹H NMR (600 MHz, CDCl₃), δ, ppm: 8.99 (1H, s, 10-H), 8.75 (1H, s, 5-H), 8.34 (1H, s, 20-H), 7.98 (1H, d, *J* = 16.5 Hz, 3¹-H), 7.66 (2H, d, *J* = 7.6 Hz, 3^{4a}-H, 3^{4b}-H), 7.37 (2H, d, *J* = 7.6 Hz, 3^{5a}-H, 3^{5b}-H), 7.27 (1H, d, *J* = 16.5 Hz, 3²-H), 4.79 (1H, d, *J* = 18.6 Hz, 13²-H^a), 4.69 (1H, d, *J* = 18.6 Hz, 13²-H^b), 4.40 (1H, m, 18-H), 4.13 (1H, m, 17-H), 3.50 (3H, s, 17²-CO₂CH₃), 3.41 (3H, s, 12-CH₃), 3.38 (2H, q, *J* = 7.7 Hz, 8¹-CH₂), 3.25 (3H, s, 2-CH₃), 2.91 (3H, s, 7-CH₃), 2.53 (4H, m, 3⁶-CH₃, 17¹-H^a), 2.48 (1H, m, 17²-H^a), 2.22 (2H, m, 17¹-H^b, 17²-H^b), 1.89 (3H, d, *J* = 7.4 Hz, 18-CH₃), 1.52 (3H, t, *J* = 7.7 Hz, 8²-CH₃). ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 196.5, 173.4, 168.1, 161.1, 156.1, 153.9, 146.8, 143.4, 138.1, 135.2, 135.0, 134.1, 133.8, 132.9, 129.6, 128.9, 126.6, 126.5, 120.3, 106.1, 105.2, 98.5, 92.3, 51.6, 50.6, 48.6, 47.8, 31.9, 30.7, 29.7, 29.5, 23.4, 22.7, 21.7, 21.4, 19.1, 17.2, 14.1, 12.5, 12.4, 10.6. HRMS (MALDI-TOF), *m/z* found: 701.2492; calc. C₄₁H₄₁N₄O₃Zn (MH⁺): 701.2470. UV-Vis (CH₂Cl₂), λ_{max}, nm (log (ε [L mol⁻¹ cm⁻¹])): 426 (6.69), 520 (5.40), 561 (5.49), 613 (5.77), 662 (6.52).

Methyl (*E*)-3²-(3-nitrophenyl)pyropheophorbide-*a* (14a**).** The reaction was performed at 75 °C for 22 h. The product **14a** (17 mg, 86 %) was obtained as a brown solid from methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (**3a**) (20 mg, 0.03 mmol) and 3-nitroiodobenzene (15 mg, 0.06 mmol).

¹H NMR (600 MHz, CDCl₃), δ, ppm: 9.59 (1H, s, 10-H), 9.46 (1H, s, 5-H), 8.72 (1H, m, 3⁴-H), 8.67 (1H, s, 20-H), 8.51 (1H, d, *J* = 16.5 Hz, 3¹-H), 8.31 (1H, m, 3⁶-H), 8.15 (1H, d, *J* = 7.8 Hz, 3⁸-H), 7.75 (1H, t, *J* = 7.8 Hz, 3⁷-H), 7.66 (1H, d, *J* = 16.5 Hz, 3²-H), 5.31 (1H, d, *J* = 19.2 Hz, 13²-H^a), 5.16 (1H, d, *J* = 19.2 Hz, 13²-H^b), 4.56 (1H, dq, *J* = 7.4 Hz, *J* = 1.9 Hz, 18-H), 4.36 (1H, m, 17-H), 3.75 (2H, q, *J* = 7.8 Hz, 8¹-CH₂), 3.72 (3H, s, 12-CH₃), 3.65 (3H, s, 17²-CO₂CH₃), 3.53 (3H, s, 2-CH₃), 3.30 (3H, s, 7-CH₃), 2.75 (1H, m, 17¹-H^a), 2.61 (1H, m, 17²-H^a), 2.35 (2H, m, 17¹-H^b, 17²-H^b), 1.87 (3H, d, *J* = 7.4 Hz, 18-CH₃), 1.75 (3H, t, *J* = 7.8 Hz, 8²-CH₃), 0.10 (1H, s, NH), -1.68 (1H, s, NH). ¹³C NMR (150 MHz, CDCl₃), δ, ppm: 196.0, 173.4, 171.2, 149.0, 145.1, 141.1, 139.4, 138.2, 136.2, 135.9, 134.2, 134.0, 132.5, 132.0, 130.8, 128.9, 123.9, 122.7, 121.3, 106.4, 104.2, 97.0, 93.4, 51.8, 51.7, 50.0, 48.1, 31.0, 29.9, 29.7, 23.2, 19.5, 17.4, 12.6, 12.1, 11.4. HRMS (MALDI-TOF), *m/z* found: 670.2998; calc. C₄₀H₄₀N₅O₅ (MH⁺): 670.3029. UV-Vis (CH₂Cl₂), λ_{max}, nm (A_{rel.}): 421 (1.00), 518 (0.09), 550 (0.08), 621 (0.06), 679 (0.42).

Zn(II) methyl (*E*)-3²-(3-nitrophenyl)pyropheophorbide-*a* (14b**).** The product **14b** (10 mg, 50 %) was obtained as a green solid from Zn(II) methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (**3b**) (20 mg, 0.03 mmol) and 3-nitroiodobenzene (15 mg, 0.06 mmol).

¹H NMR (600 MHz, CDCl₃), δ, ppm: 9.53 (1H, s, 10-H), 9.27 (1H, s, 5-H), 8.58 (1H, s, 3⁴-H), 8.45 (1H, s, 20-H), 8.40 (1H, d, *J* = 16.4 Hz, 3¹-H), 8.18 (1H, d, *J* = 7.8 Hz, 3⁶-H), 7.98 (1H, d, *J* = 7.8 Hz, 3⁸-H), 7.60 (1H, t, *J* = 7.8 Hz, 3⁷-H), 7.45 (1H, d, *J* = 16.4 Hz, 3²-H), 5.08 (1H, d, *J* = 18.9 Hz, 13²-CH^{2a}), 4.92 (1H, d, *J* = 18.9 Hz, 13²-CH^{2b}), 4.49 (1H, q, *J* = 7.3 Hz, 18-H), 4.29 (1H, m, 17-H), 3.76 (2H, q, *J* = 7.7 Hz, 8¹-CH₂), 3.52 (3H, s, 12-CH₃), 3.45 (3H, s, 17²-CO₂CH₃), 3.41 (3H, s, 2-CH₃), 3.28 (3H, s, 7-CH₃), 2.64 (1H, m, 17¹-CH^{2a}), 2.52 (1H, m, 17²-CH^{2a}), 2.29 (2H, m, 17¹-CH^{2b}, 17²-CH^{2b}),

1.87 (3H, d, $J = 7.3$ Hz, 18-CH₃), 1.75 (3H, t, $J = 7.7$ Hz, 8²-CH₃). ¹³C NMR (150 MHz, CDCl₃), δ , ppm: 197.0, 173.9, 168.2, 055.7, 151.3, 147.7, 147.3, 145.6, 143.9, 137.2, 135.4, 134.5, 133.6, 132.1, 131.8, 129.7, 125.0, 122.0, 121.0, 106.2, 105.3, 98.4, 92.2, 51.6, 50.7, 49.8, 49.5, 49.2, 48.8, 48.2, 31.9, 30.7, 23.5, 22.6, 19.5, 17.4, 14.0, 12.7, 12.5, 11.0. HRMS (MALDI-TOF), m/z found: 732.2176; calc. C₄₀H₃₈N₅O₅Zn (MH⁺): 732.2164. UV-Vis (CH₂Cl₂), λ_{\max} , nm (log ϵ [L mol⁻¹ cm⁻¹]): 379 (6.60), 427 (6.81), 522 (5.60), 559 (5.70), 616 (5.90), 665 (6.65).

Zn(II) methyl (*E*)-3²-(4-acetophenyl)pyropheophorbide-*a* (15b). The product **15b** (10 mg, 51%) was obtained as a green solid from methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* **3b** (20 mg, 0.03 mmol) and 4-iodoacetophenone (16 mg, 0.06 mmol).

¹H NMR (600 MHz, CDCl₃), δ , ppm: 9.15 (1H, s, 10-H), 8.87 (1H, s, 5-H), 8.40 (1H, s, 20-H), 8.17 (1H, d, $J = 16.3$ Hz, 3¹-H), 8.07 (2H, d, $J = 8.0$ Hz, 3^{5a}-H, 3^{5b}-H), 7.76 (2H, d, $J = 8.0$ Hz, 3^{6a}-H, 3^{6b}-H), 7.30 (1H, d, $J = 16.3$ Hz, 3²-H), 4.82 (1H, d, $J = 18.7$ Hz, 13²-H^a), 4.71 (1H, d, $J = 18.7$ Hz, 13²-H^b), 4.43 (1H, m, 18-H), 4.16 (1H, m, 17-H), 3.49 (5H, m, 8¹-CH₂, 17²-CO₂CH₃), 3.44 (3H, s, 12-CH₃), 3.29 (3H, s, 2-CH₃), 3.03 (3H, s, 7-CH₃), 2.70 (3H, s, 3⁷-CH₃), 2.55 (1H, m, 17¹-H^a), 2.49 (1H, m, 17²-H^a), 2.25 (2H, m, 17¹-H^b, 17²-H^b), 1.88 (3H, d, $J = 7.4$ Hz, 18-CH₃), 1.59 (3H, t, $J = 7.8$ Hz, 8²-CH₃). ¹³C NMR (150 MHz, CDCl₃), δ , ppm: 197.5, 196.5, 173.4, 168.0, 161.1, 156.3, 153.4, 147.2, 146.8, 144.9, 143.6, 142.4, 137.4, 136.2, 134.8, 134.5, 133.3, 131.6, 129.0, 126.5, 124.1, 106.2, 105.3, 98.5, 92.4, 51.6, 50.6, 48.6, 47.9, 31.9, 30.7, 29.7, 29.6, 29.4, 26.6, 22.7, 29.2, 17.3, 14.1, 12.7, 12.5, 10.8. HRMS (MALDI-TOF), m/z found: 729.2433; calc. C₄₂H₄₁N₄O₄Zn (MH⁺): 729.2419. UV-Vis (CH₂Cl₂), λ_{\max} , nm (A_{rel.}): 429 (1.00), 522 (0.03), 563 (0.05), 617 (0.12), 667 (0.74).

Ni(II) (*E*)-5-(2-(3-nitrophenyl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (16). The reaction was performed at 90 °C for 1.5 h, using 10 mol% Pd(PPh₃)₄ and 6 eq. Cs₂CO₃. The product **16** (15 mg, 50%) was obtained as a green solid from Ni(II) (*E*)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**9**) (30 mg, 0.04 mmol) and 3-nitroiodobenzene (20 mg, 0.08 mmol).

¹H NMR (600 MHz, CD₂Cl₂), δ , ppm: 9.63 (1H, d, $J = 16$ Hz, Ar-CH = CH), 9.55 (2H, br.s, *meso*-H), 9.54 (1H, s, *meso*-H), 8.44 (1H, m, 3⁴-H), 8.17 (1H, m, 3⁶-H), 7.83 (1H, m, 3⁸-H), 7.58 (1H, t, $J = 8$ Hz, 3⁷-H), 5.85 (1H, d, $J = 16$ Hz, Ar-CH = CH), 3.89 (16H, m, CH₂), 1.84 (12H, m, CH₃), 1.77 (6H, t, $J = 7.70$ Hz, CH₃), 1.69 (6H, t, $J = 7.70$ Hz, CH₃). ¹³C NMR (150 MHz, CD₂Cl₂), δ , ppm: 148.98, 145.56, 144.30, 143.47, 143.16, 140.33, 139.69, 139.03, 138.92, 138.39, 131.98, 131.06, 129.90, 122.19, 120.49, 110.20, 96.91, 96.35, 29.69, 22.17, 19.47, 17.98, 16.25. HRMS (MALDI-TOF), m/z found: 738.3342; calc. C₄₄H₅₀N₅O₂Ni (MH⁺): 738.3318. UV-Vis (CH₂Cl₂), λ_{\max} , nm (A_{rel.}): 405 (1.00), 529 (0.06), 563.5 (0.9).

Ni(II) (*E*)-5-(2-(4-methylphenyl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (17) and Ni(II) (*E*)-5-(2-phenylethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (18).¹¹ The reaction was performed at 90 °C for 1.5 h, using 10 mol% Pd(PPh₃)₄ and 6 eq. Cs₂CO₃. The mixture of products **17**, **18** (15 mg, total yield 53%) was obtained as a green solid from Ni(II) (*E*)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**9**) (30 mg, 0.04 mmol) and 4-iodotoluene (18 mg, 0.08 mmol).

¹H NMR (600 MHz, CD₂Cl₂), δ , ppm: 9.553 (1H, s, *meso*-H (**18**)), 9.545 (2H, s, *meso*-H (**17**)), 9.54 (1H, s, *meso*-H (**18**)), 9.533 (1H, s, *meso*-H (**17**)), 9.50 (1H, d, $J = 16$ Hz, Ph-CH = CH (**18**)), 9.43 (1H, d, $J = 15.9$ Hz, Ar-CH = CH (**17**)), 7.61 (2H, m, C₆H₅ (**18**)), 7.50 (2H, m, C₆H₄ (**17**)), 7.47 (2H, m, C₆H₅ (**18**)), 7.37 (1H, m, C₆H₅ (**18**)), 7.28 (2H, m, C₆H₄ (**17**)), 5.79 (1H, d, $J = 16$ Hz, Ph-CH = CH (**18**)), 5.75 (1H, d, $J = 15.9$ Hz, Ar-CH = CH (**17**)), 3.90 (16H, m, CH₂ (**17**, **18**)), 2.44 (3H, s, CH₃-C₆H₄ (**17**, **18**)), 1.84 (12H, m, CH₃ (**17**, **18**)), 1.77 (6H, m, CH₃ (**17**, **18**)), 1.71 (6H, m, CH₃ (**17**, **18**)). ¹³C NMR (150 MHz, CD₂Cl₂), δ , ppm: 148.98, 145.56, 144.30, 143.47, 143.16, 140.33, 139.69, 139.03, 138.92, 138.39, 131.98, 131.06, 129.90, 122.19, 120.49, 110.20, 96.91, 96.35, 29.69, 22.17, 19.47, 17.98, 16.25, 145.25, 145.19, 144.73, 144.69, 143.29, 143.24, 143.01, 141.07, 141.03, 140.24, 139.53, 139.49, 139.18, 139.12, 138.25, 138.22, 137.92, 137.59, 134.92, 129.54, 128.87, 127.90, 127.83, 126.87, 126.25, 126.16, 112.06, 111.75, 96.71, 96.68, 95.99, 29.70, 22.16, 20.98, 19.50, 19.45, 18.03, 17.98, 17.96, 16.59. HRMS (MALDI-TOF), m/z found: 693.3492, 707.3655; calc. **17** C₄₅H₅₃N₄Ni (MH⁺): 707.3624, **18** C₄₄H₅₁N₄Ni (MH⁺): 693.3467.

NMR spectra

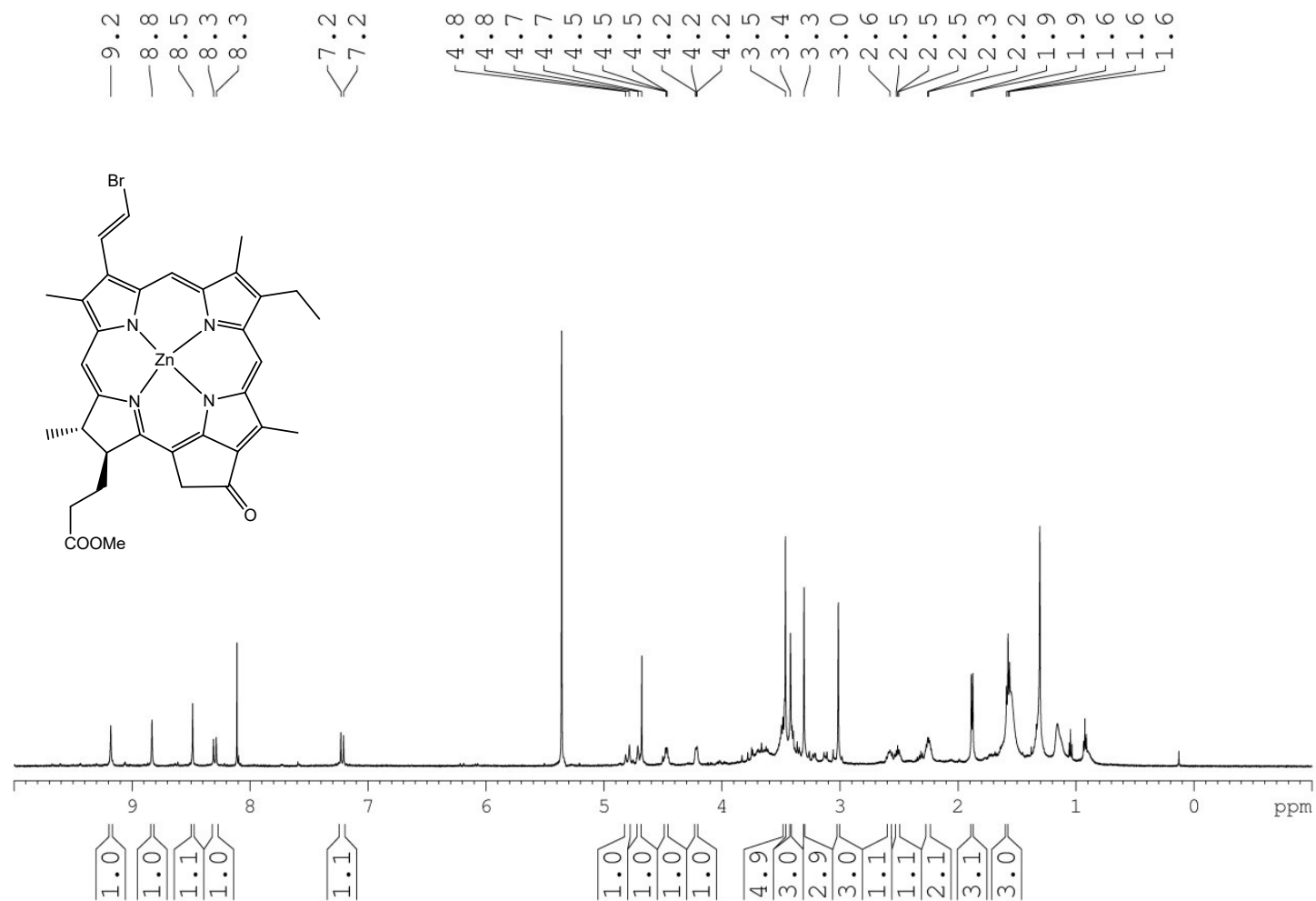


Fig. S1. ¹H NMR spectrum of Zn(II) methyl (*E*)-3²-bromopyropheophorbide-*a* (**2b**) in CDCl₃.

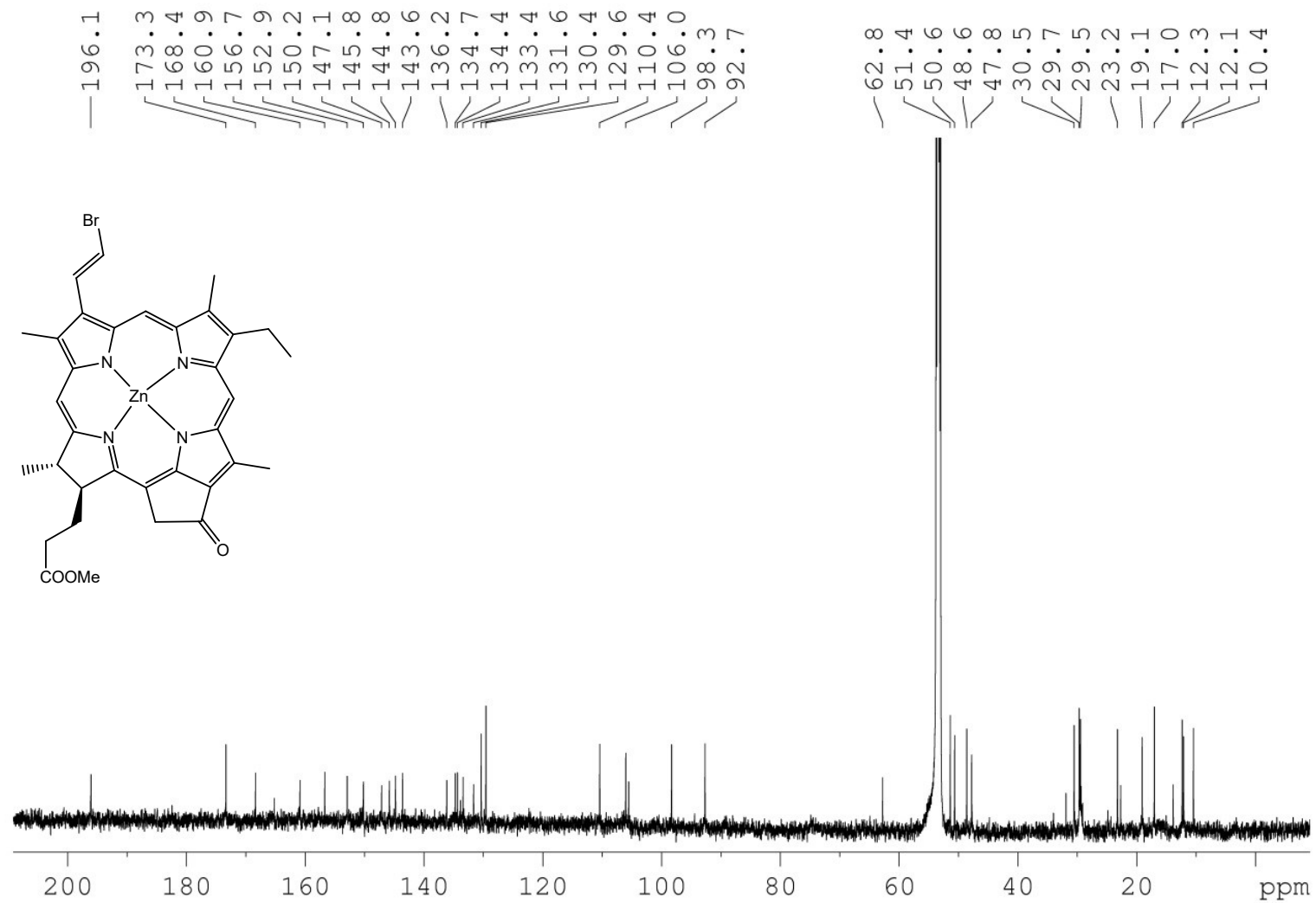


Fig. S2. ¹³C NMR spectrum of Zn(II) methyl (*E*)-3²-bromopyropheophorbide-*a* (**2b**) in CDCl₃.

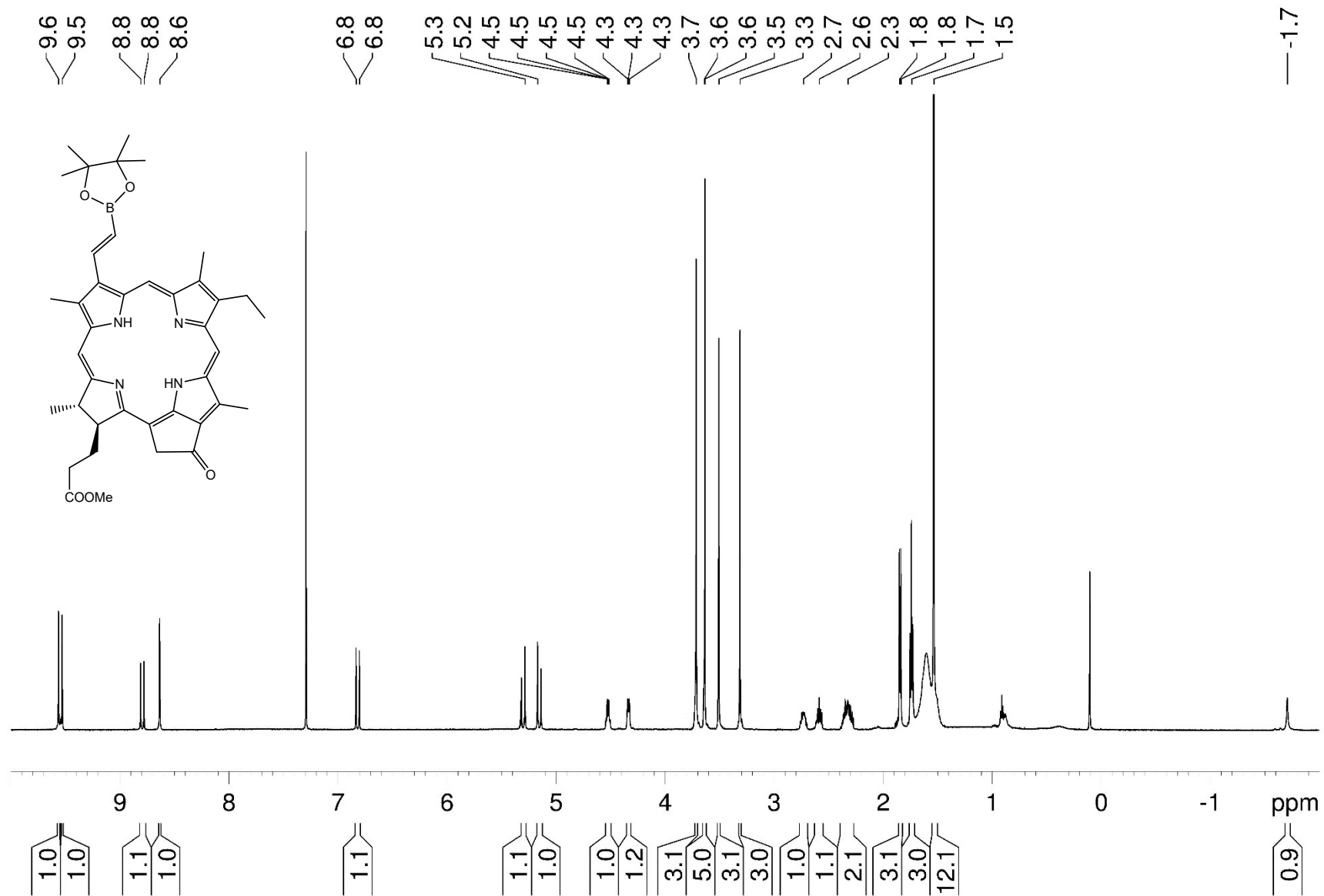


Fig. S3. ¹H NMR spectrum of methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (3a) in CDCl₃.

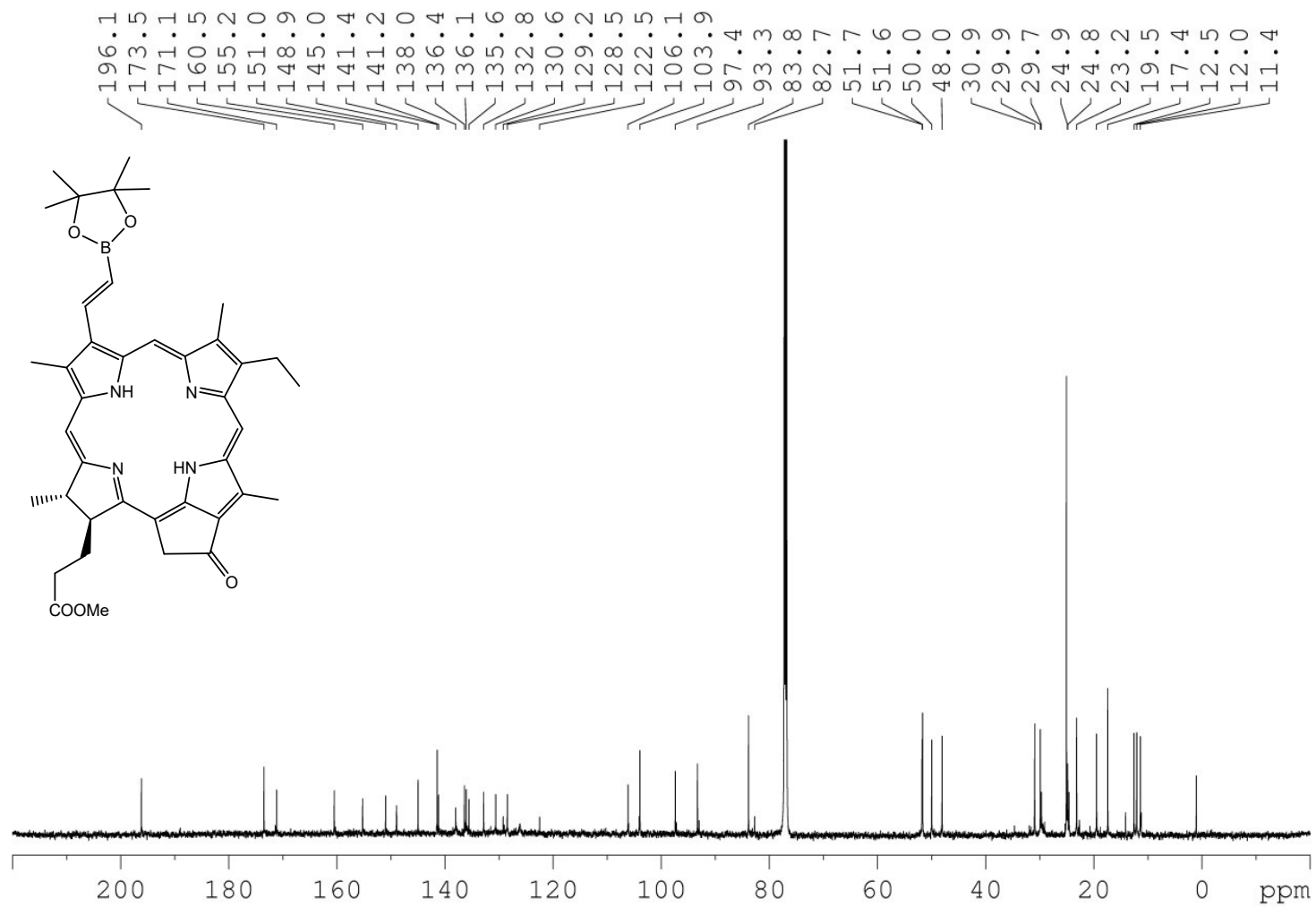


Fig. S4. ¹³C NMR spectrum of methyl (*E*)-3'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (**3a**) in CDCl₃.

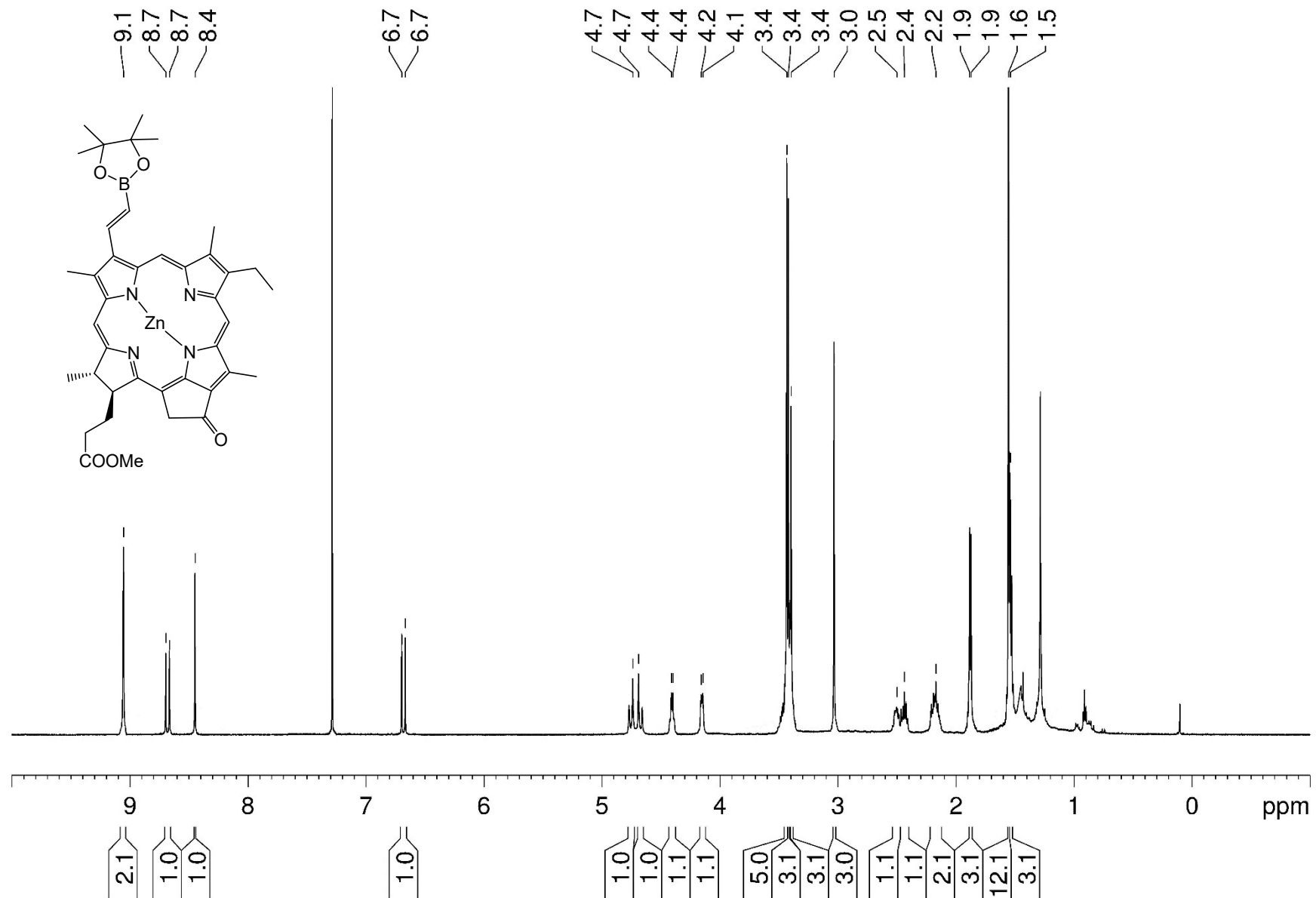


Fig. S5. ¹H NMR spectrum of Zn(II) methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (**3b**) in CDCl₃.

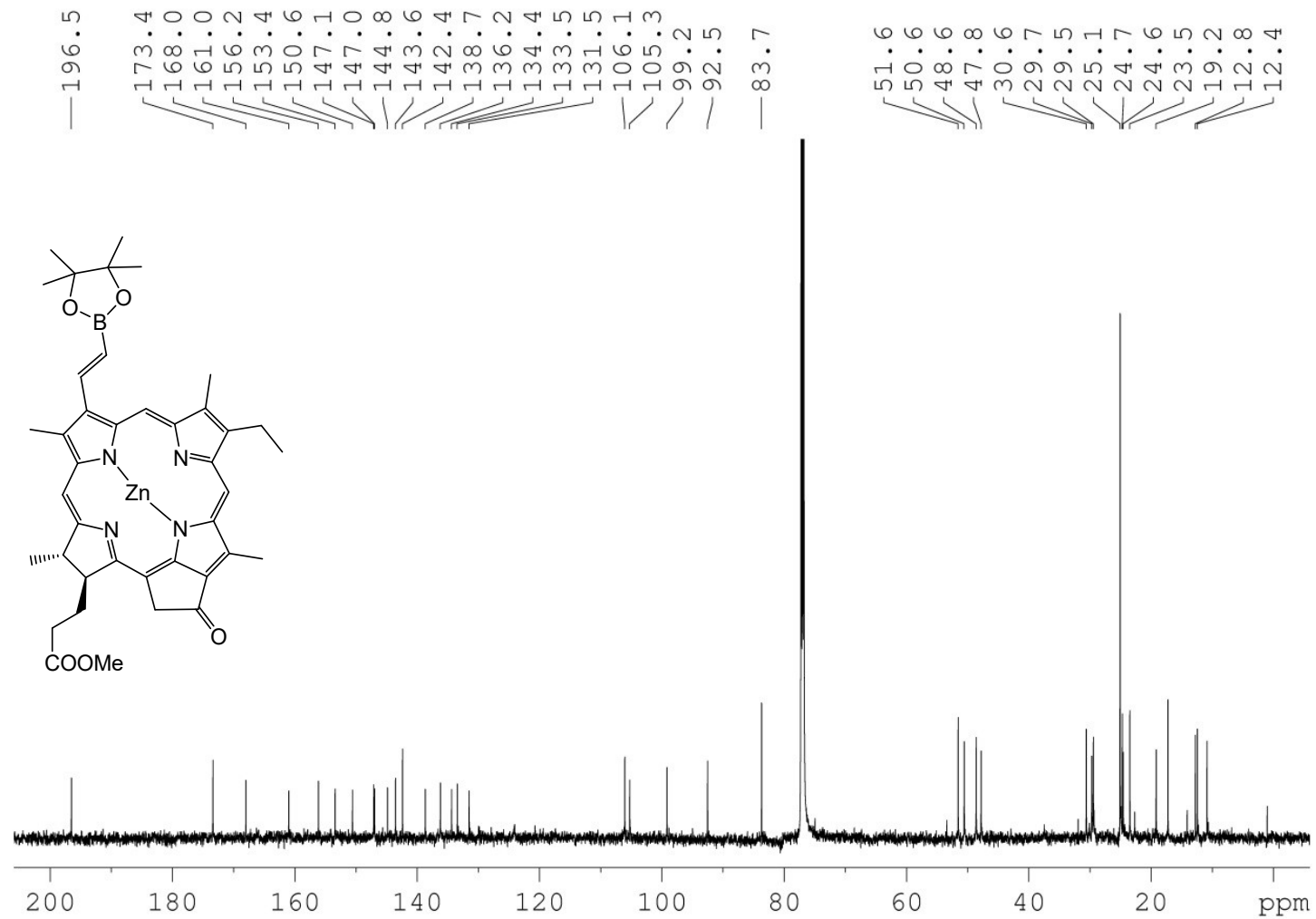


Fig. S6. ¹³C NMR spectrum of Zn(II) methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (**3b**) in CDCl₃.

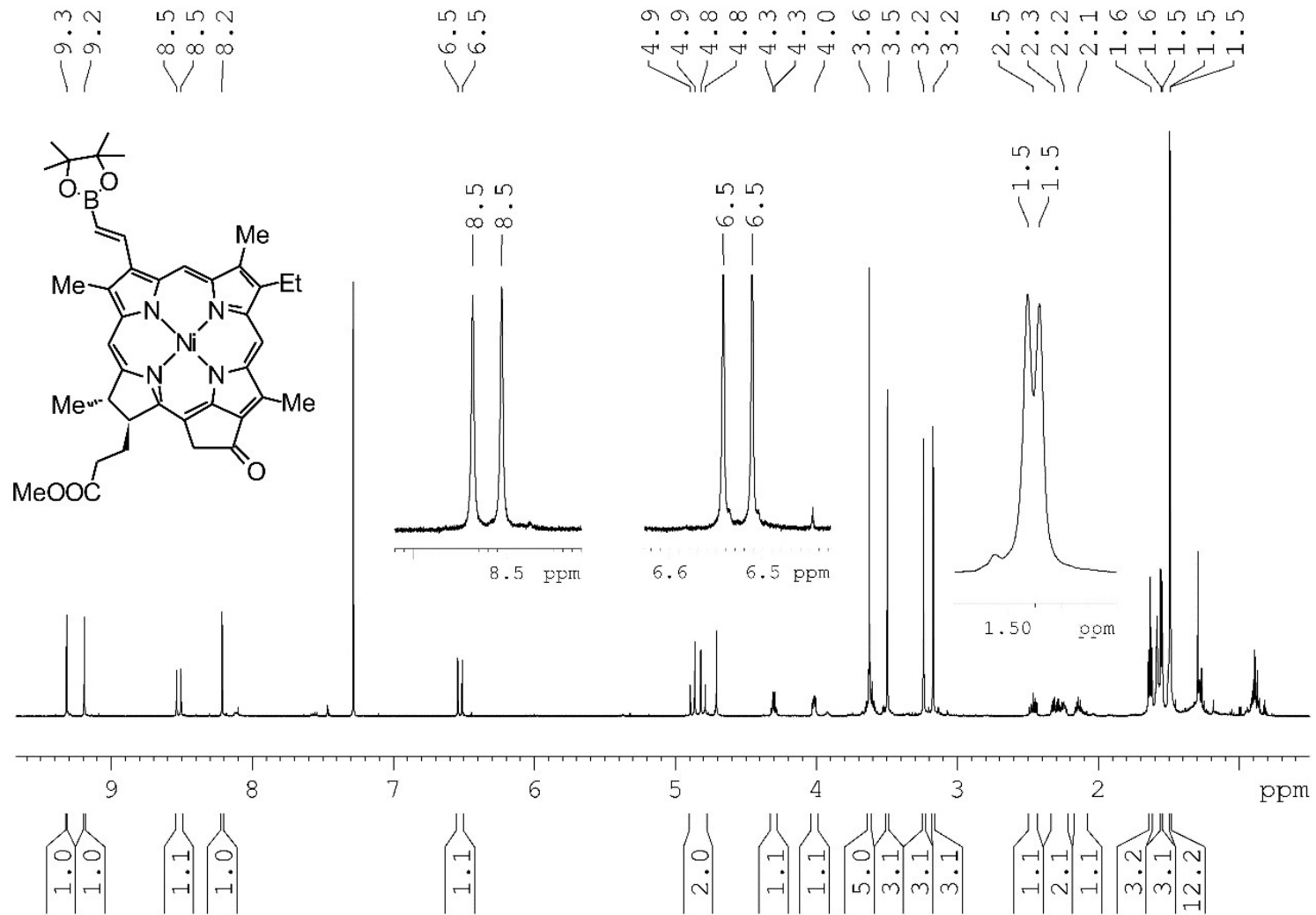


Fig. S7. ¹H NMR spectrum of Ni(II) methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (**3c**) in CDCl₃.

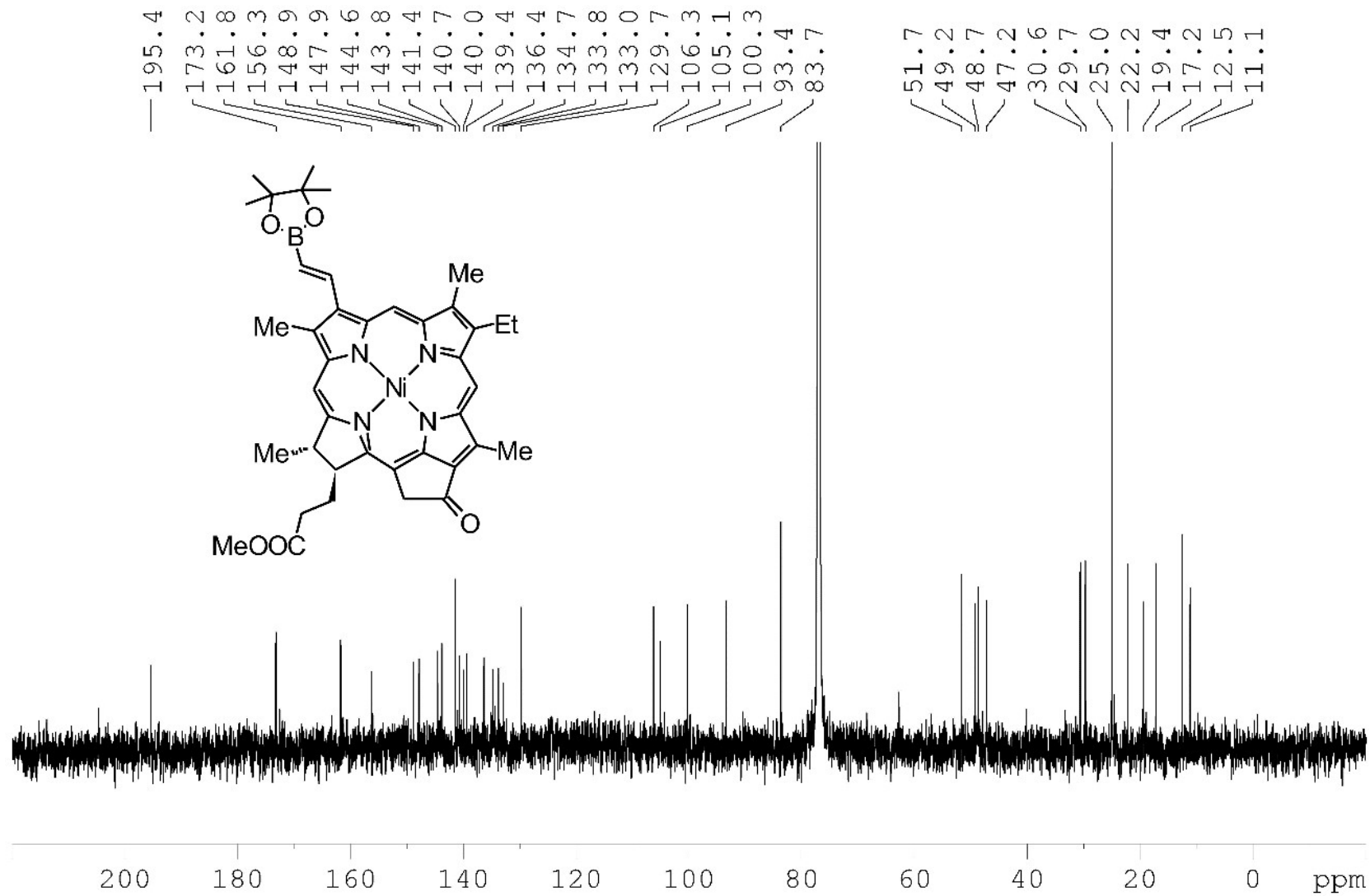


Fig. S8. ¹³C NMR spectrum of Ni(II) methyl (*E*)-3'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (3c) in CDCl₃.

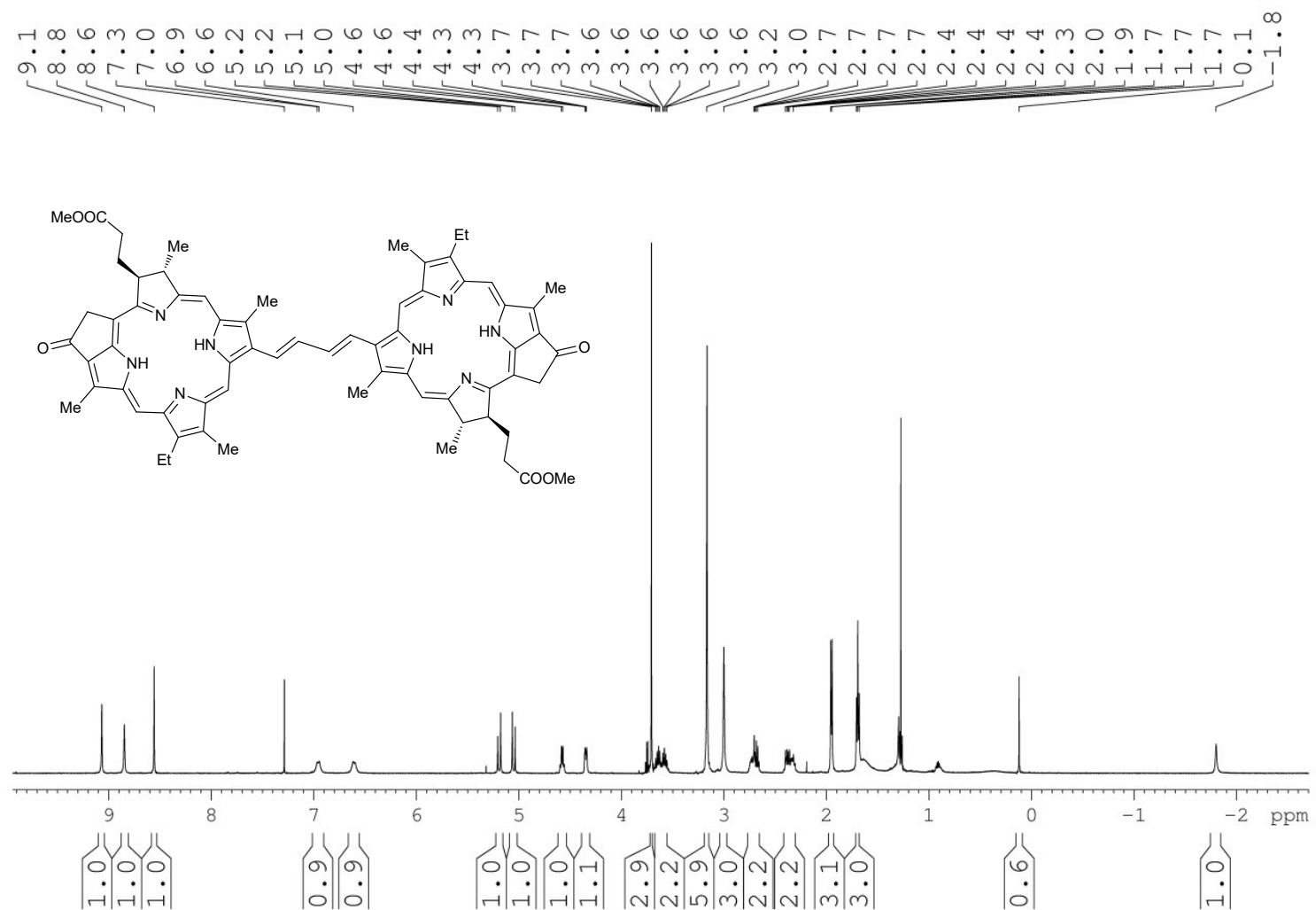


Fig. S9. ¹H NMR spectrum of methyl pyropheophorbide-*a* dimer (4) in CDCl₃.

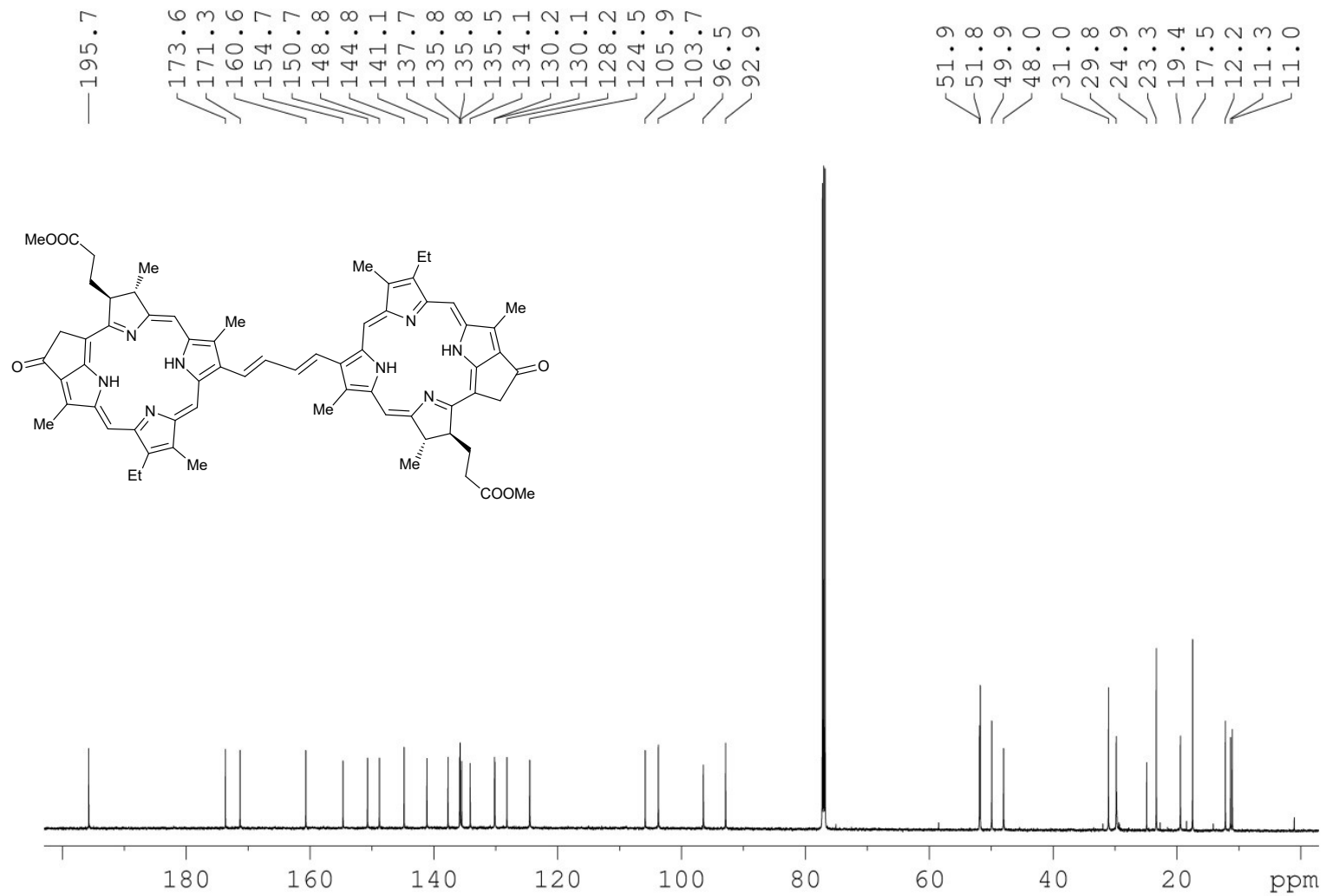


Fig. S10. ¹³C NMR spectrum of methyl pyropheophorbide-*a* dimer (**4**) in CDCl₃.

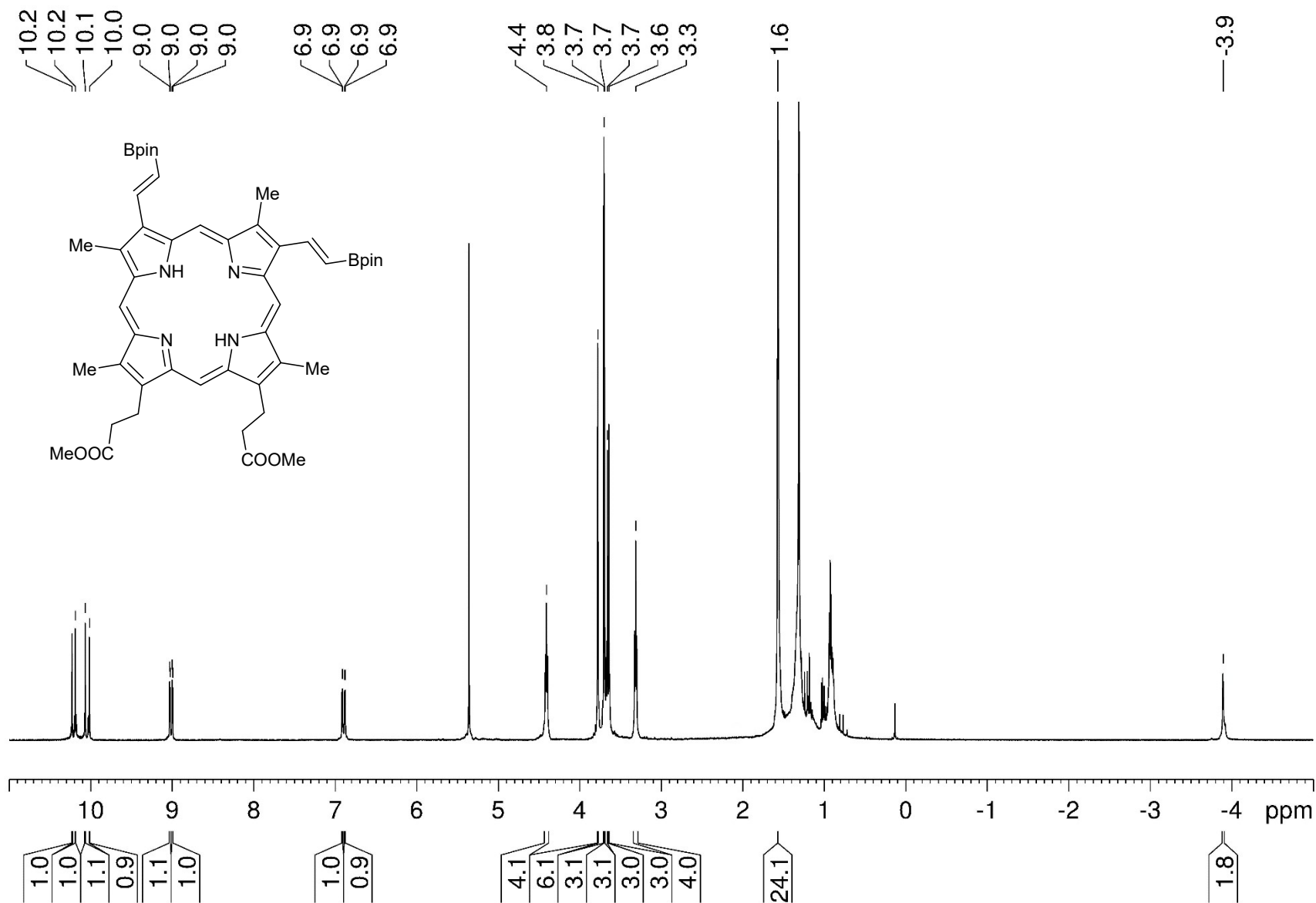


Fig. S11. ¹H NMR spectrum of dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (**7a**) in CDCl₃.

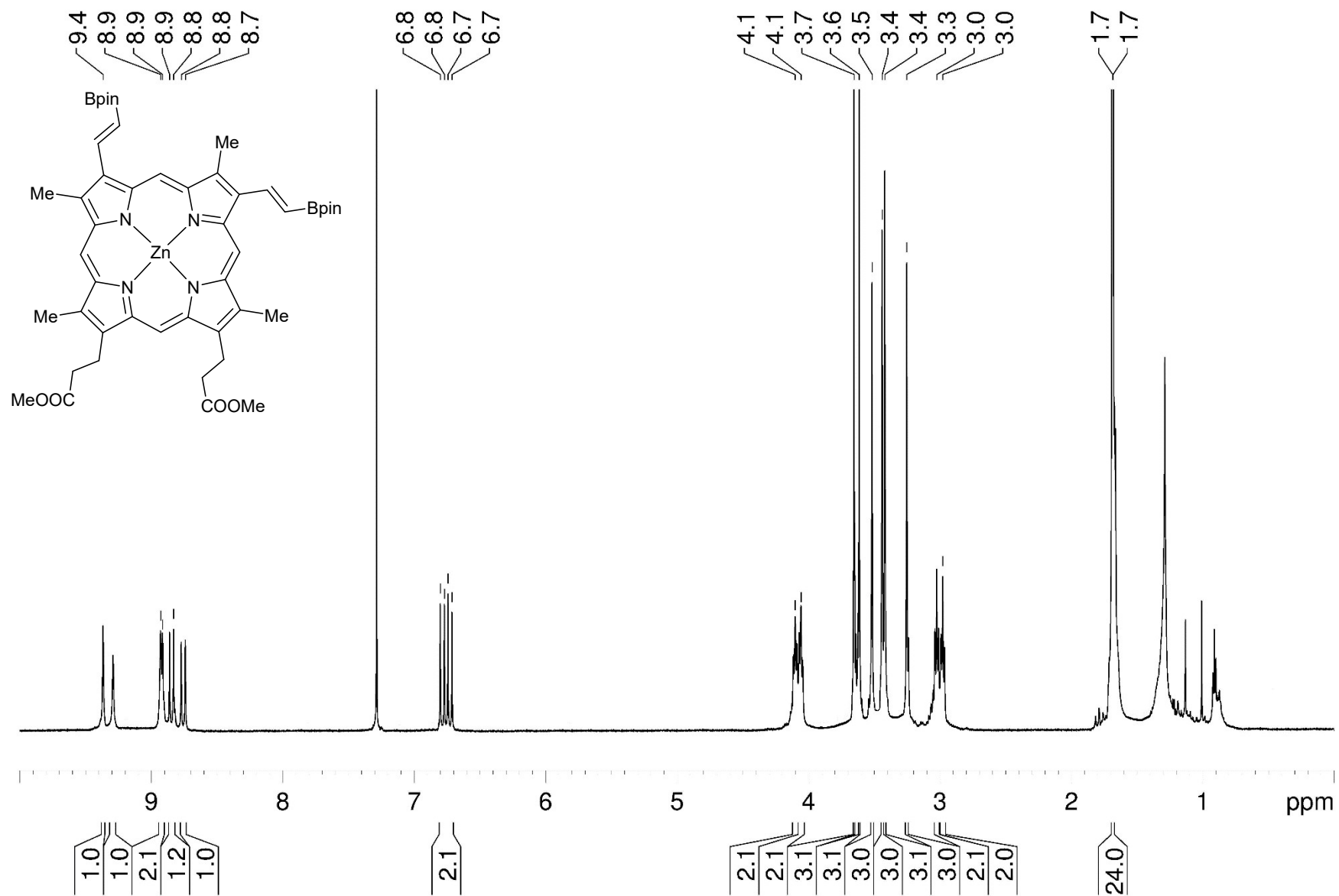


Fig. S12. ¹H NMR spectrum of Ni(II) dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (**7b**) in CDCl₃.

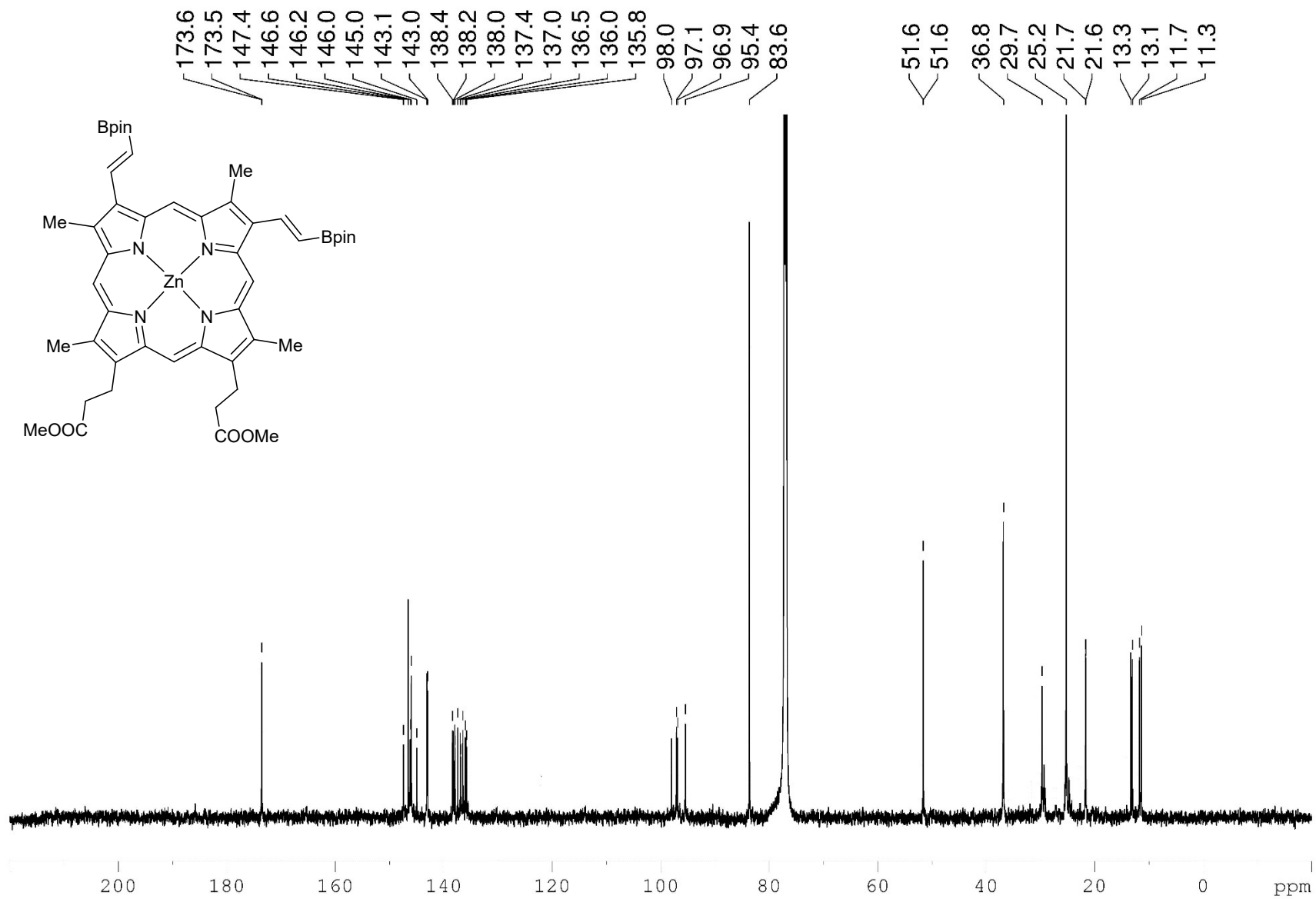


Fig. S13. ¹³C NMR spectrum of Ni(II) dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (**7b**) in CDCl₃.

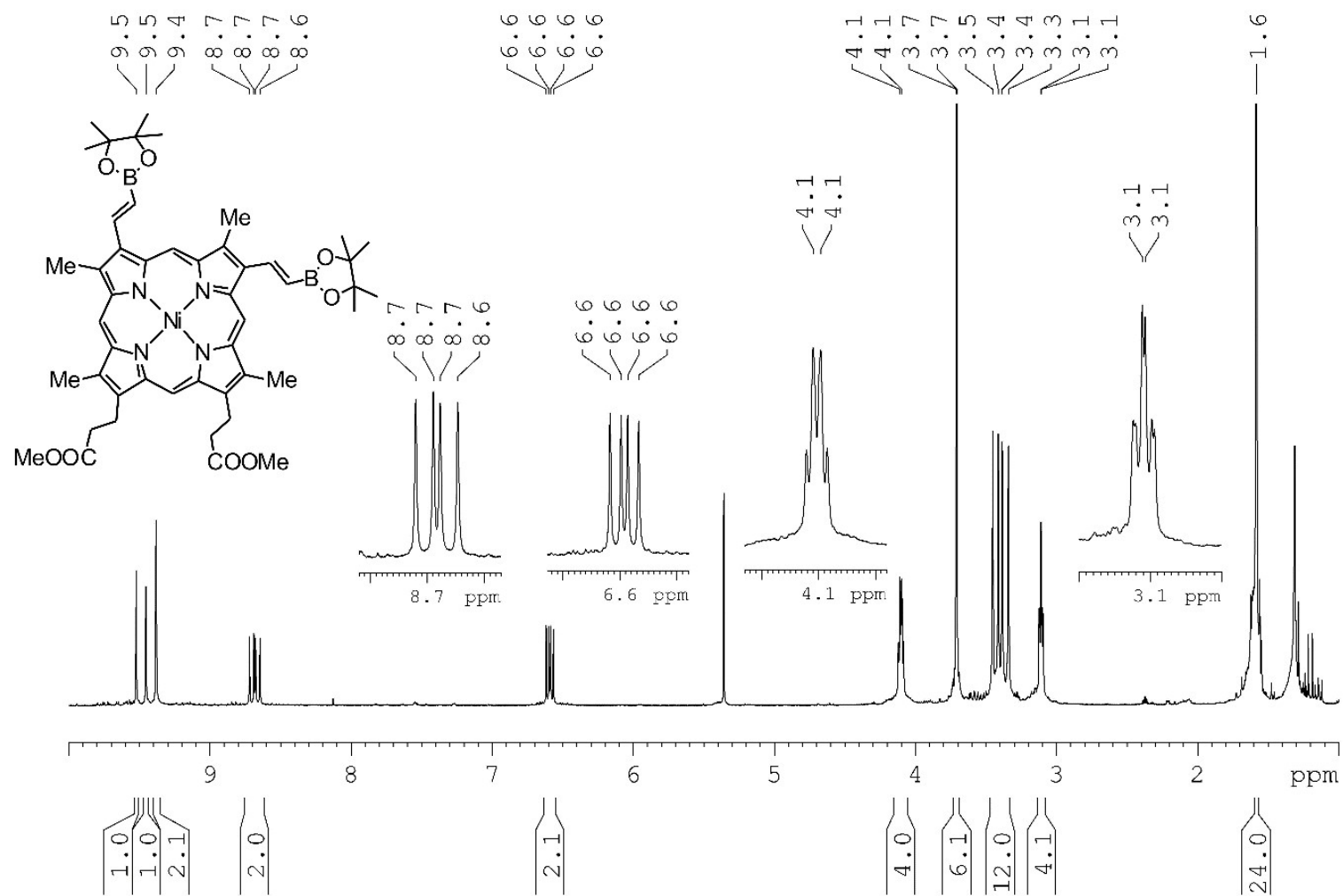


Fig. S14. ¹H NMR spectrum of Ni(II) dimethyl (*E,E*)-3,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (**7c**) in CDCl₃.

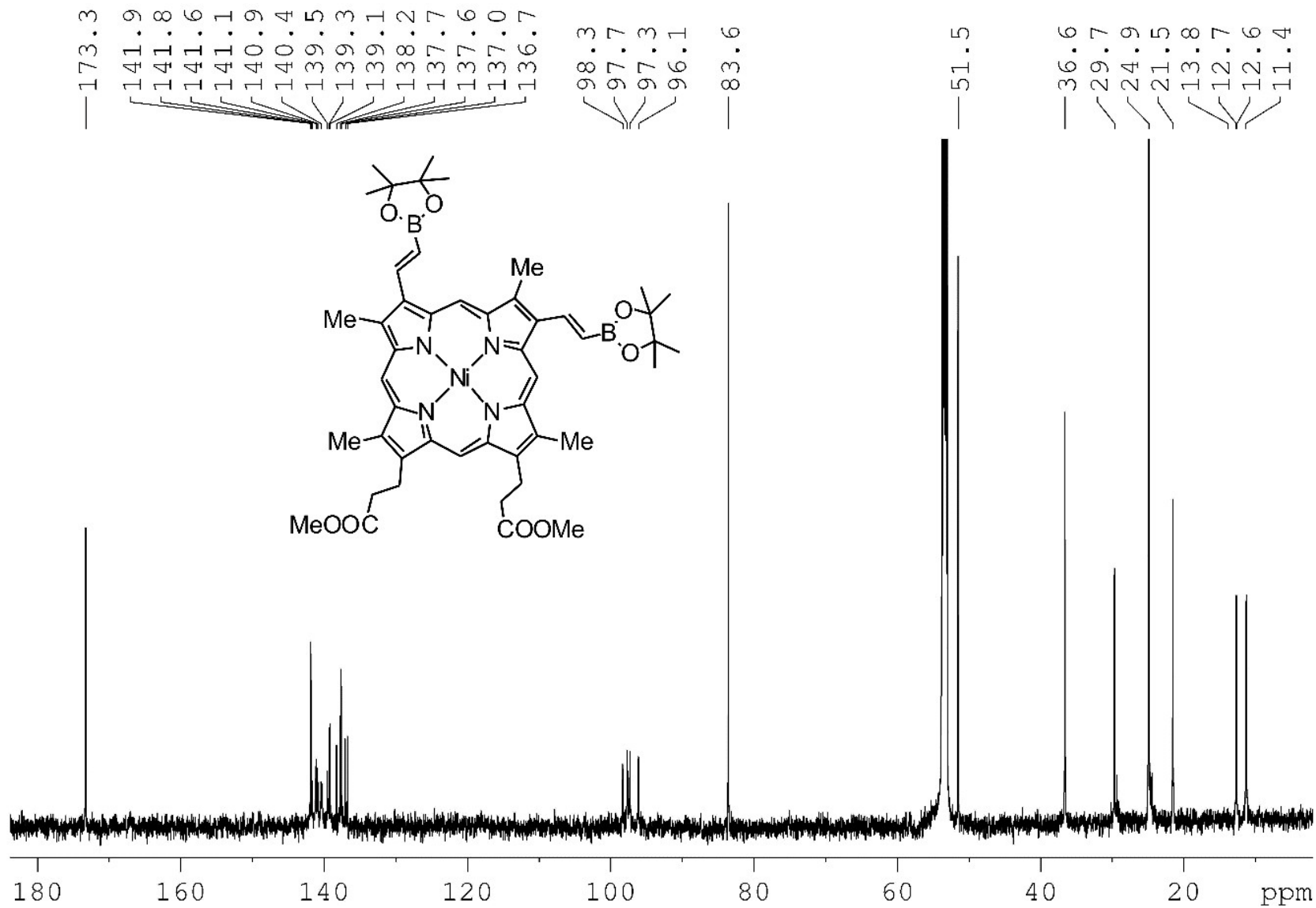


Fig. S15. ¹³C NMR spectrum of Ni(II) dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (7c) in CDCl₃.

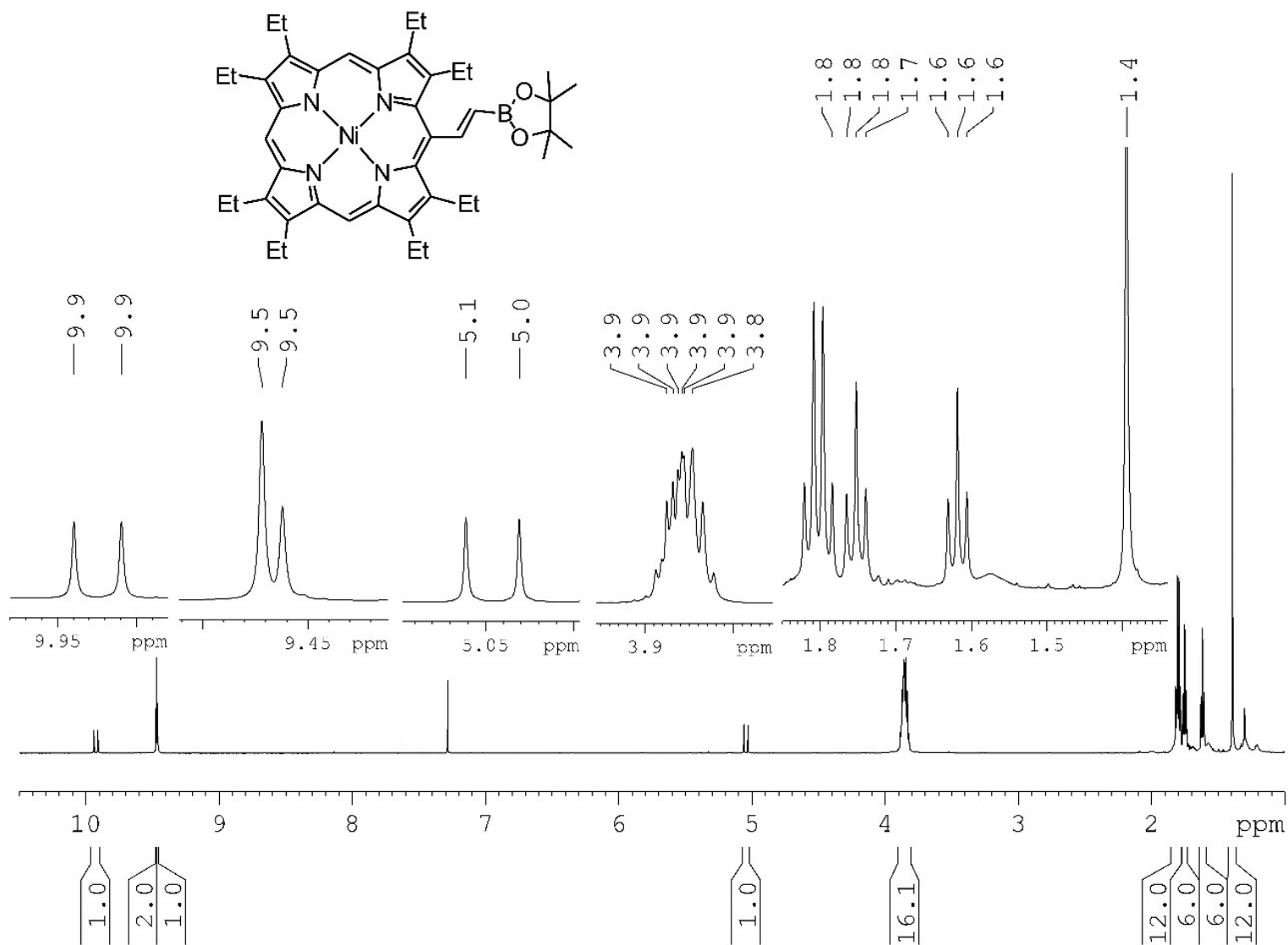


Fig. S16. ¹H NMR spectrum of Ni (II) (*E*)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)vinyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**9**) in CDCl₃.

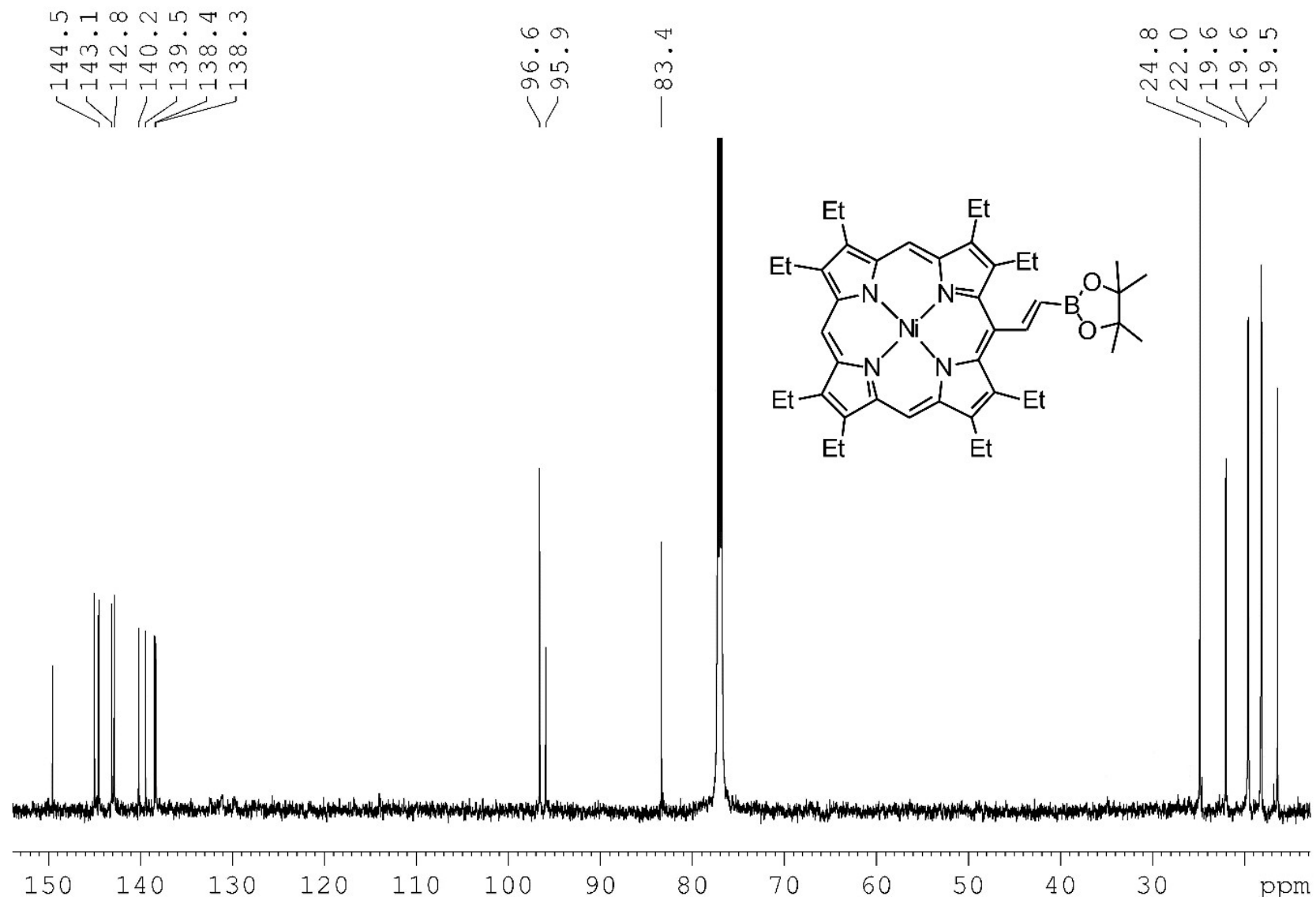


Fig. S17. ¹³C NMR spectrum of Ni (II) (*E*) 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)vinyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (9) in CDCl₃.

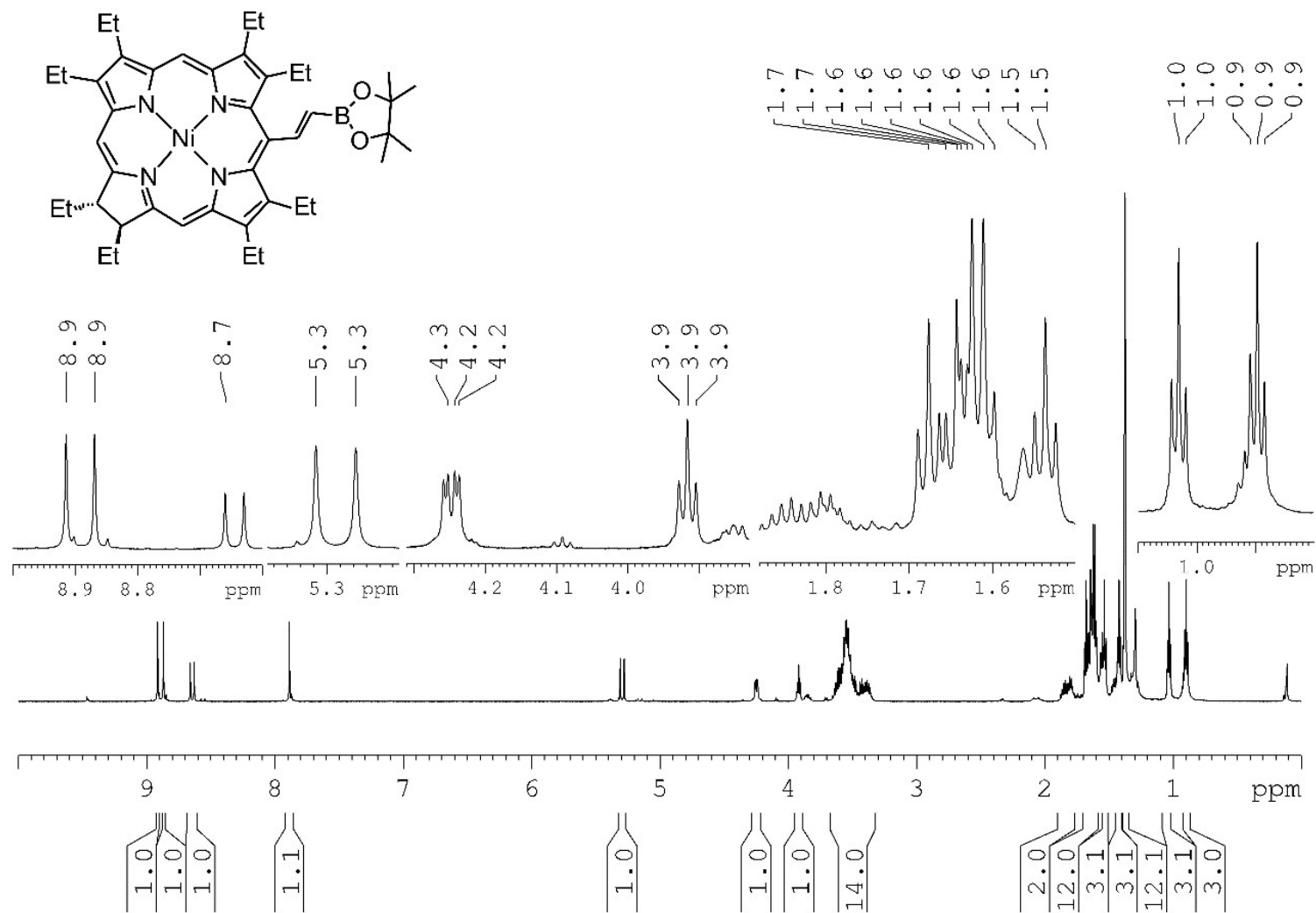


Fig. S18. ¹H NMR spectrum of Ni (II) (*E*) 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)vinyl)-2,3,7,8,12,13,17,18-octaethyl-17,18-*trans*-dihydroporphyrin (**11**) in CDCl₃.

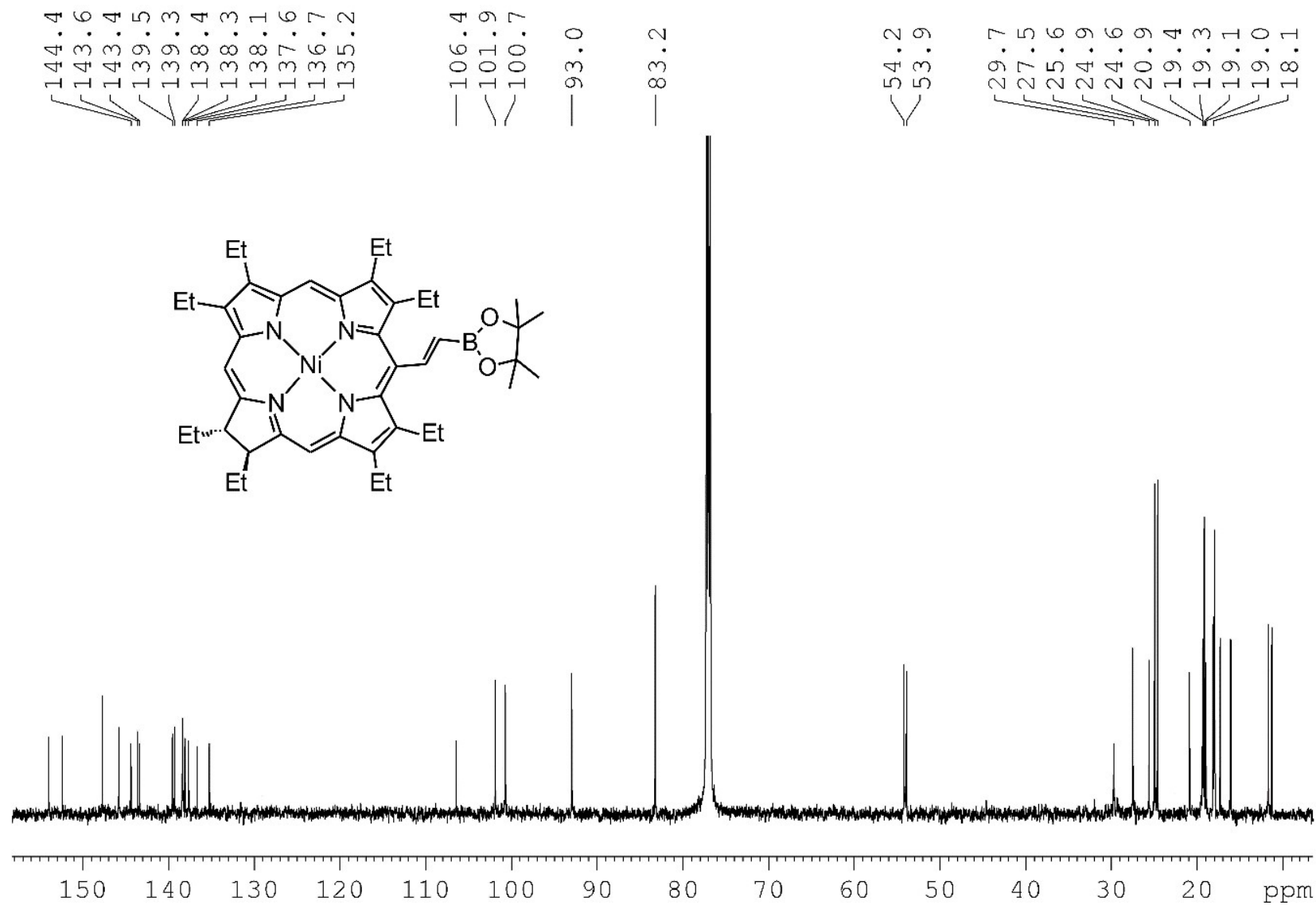


Fig. S19. ¹³C NMR spectrum of Ni(II) (*E*)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)vinyl)-2,3,7,8,12,13,17,18-octaethyl-17,18-*trans*-dihydroporphyrin (**11**) in CDCl₃.

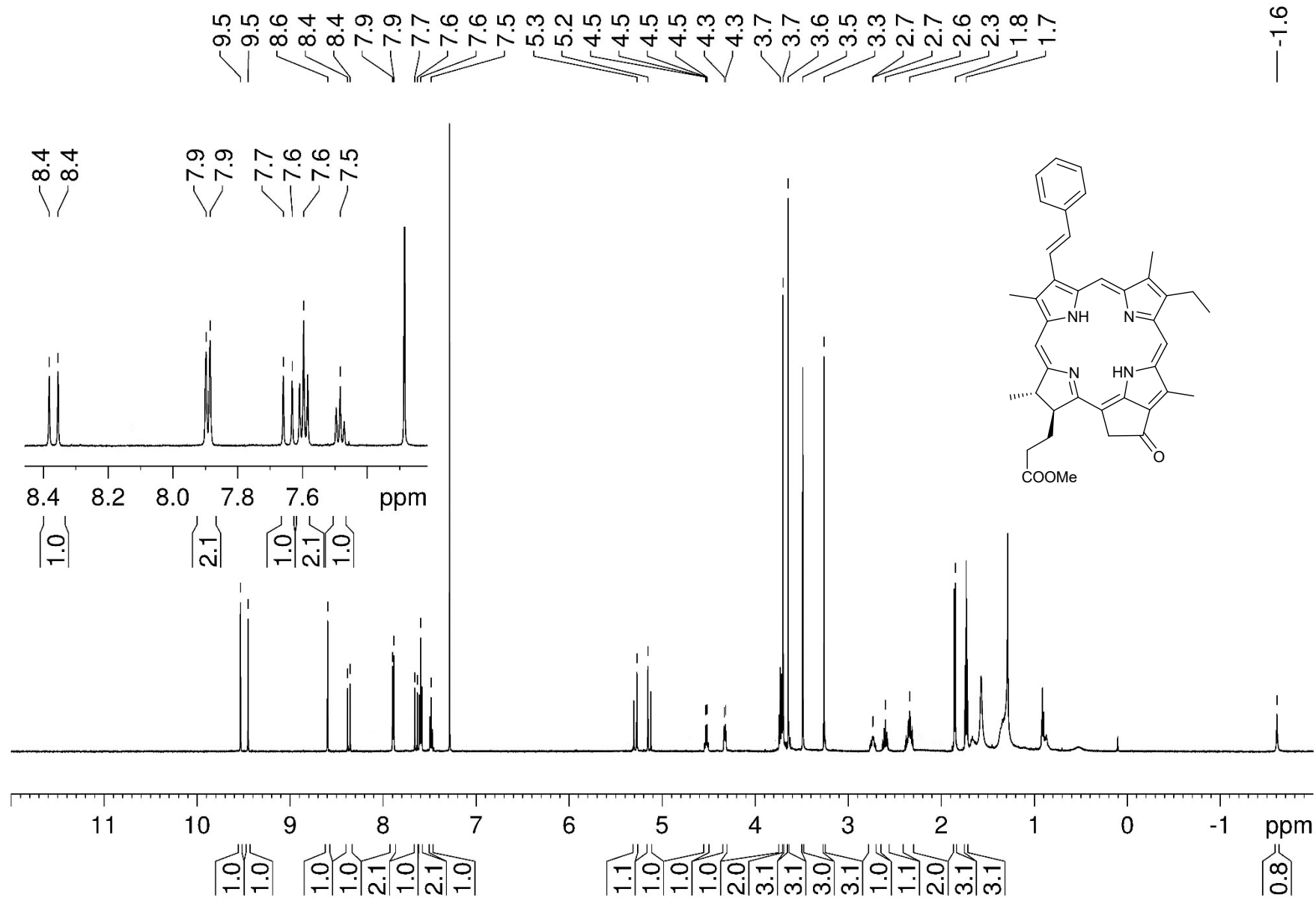


Fig. S20. ¹H NMR spectrum of methyl (*E*)-3²-phenylpyropheophorbide-*a* (12a) in CDCl₃.

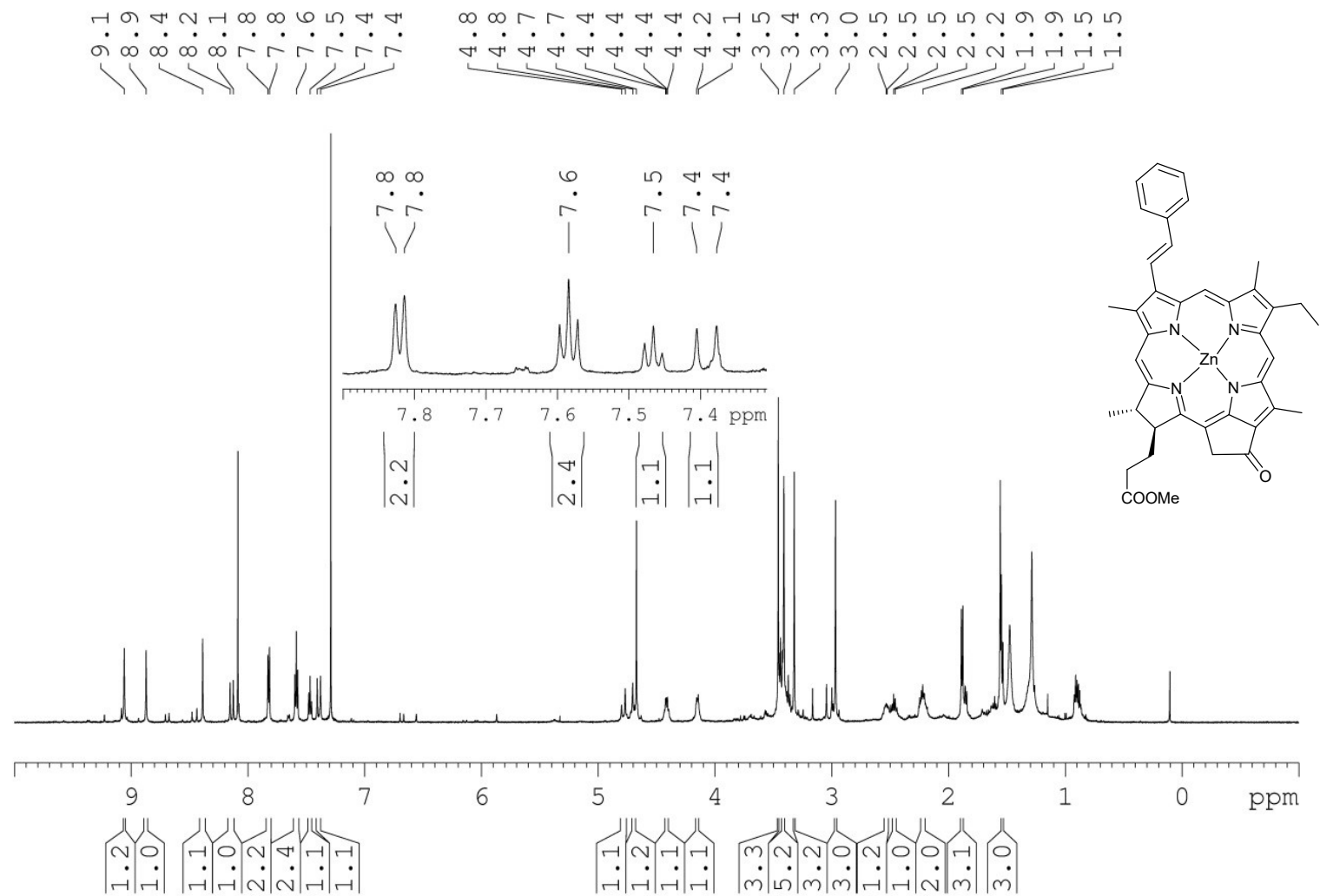


Fig. S21. ¹H NMR spectrum of Zn(II) methyl (*E*)-3²-phenylpyropheophorbide-*a* (**12b**) in CDCl₃.

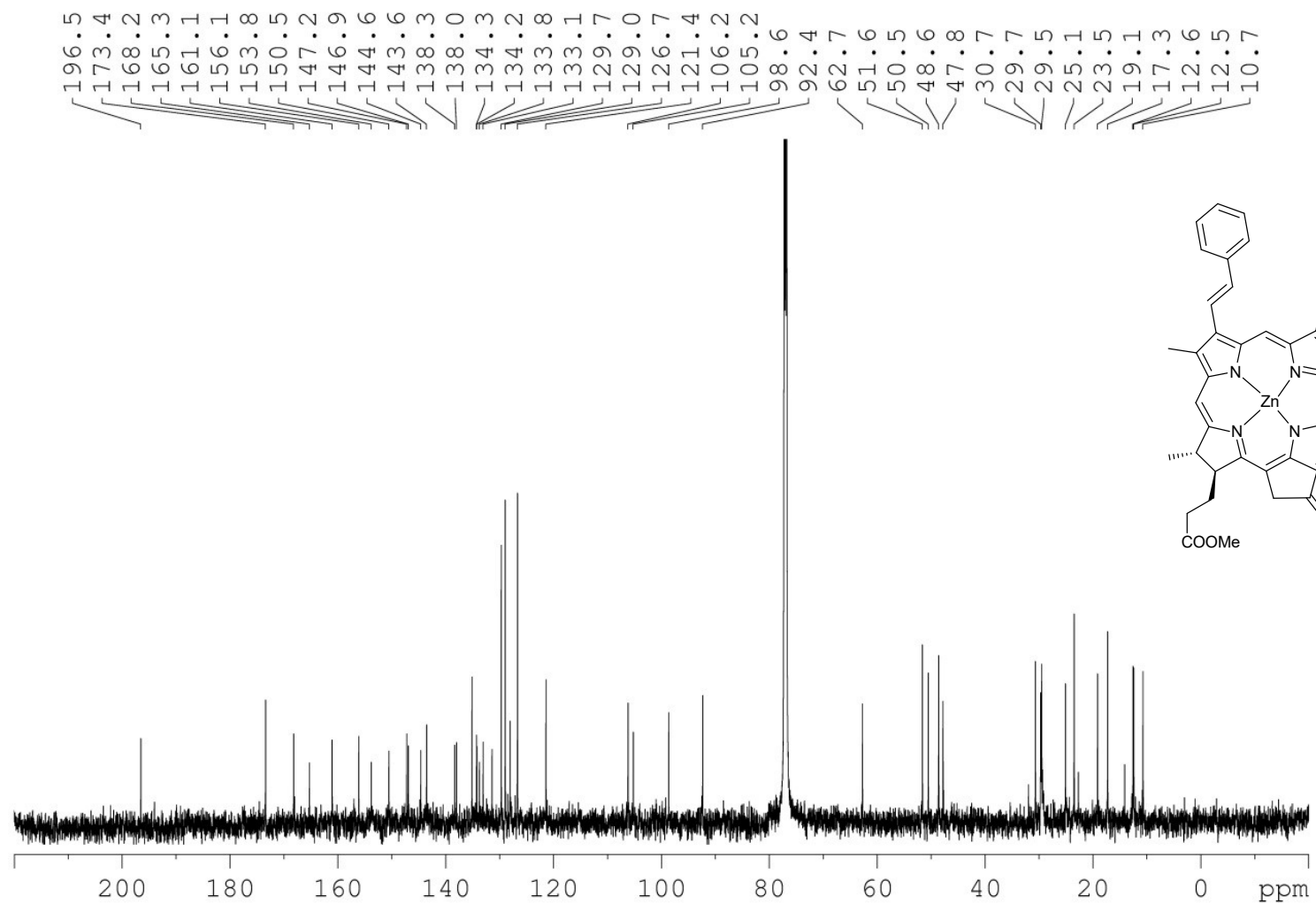


Fig. S22. ^{13}C NMR spectrum of Zn(II) methyl (*E*)-3²-phenylpyropheophorbide-*a* (**12b**) in CDCl_3 .

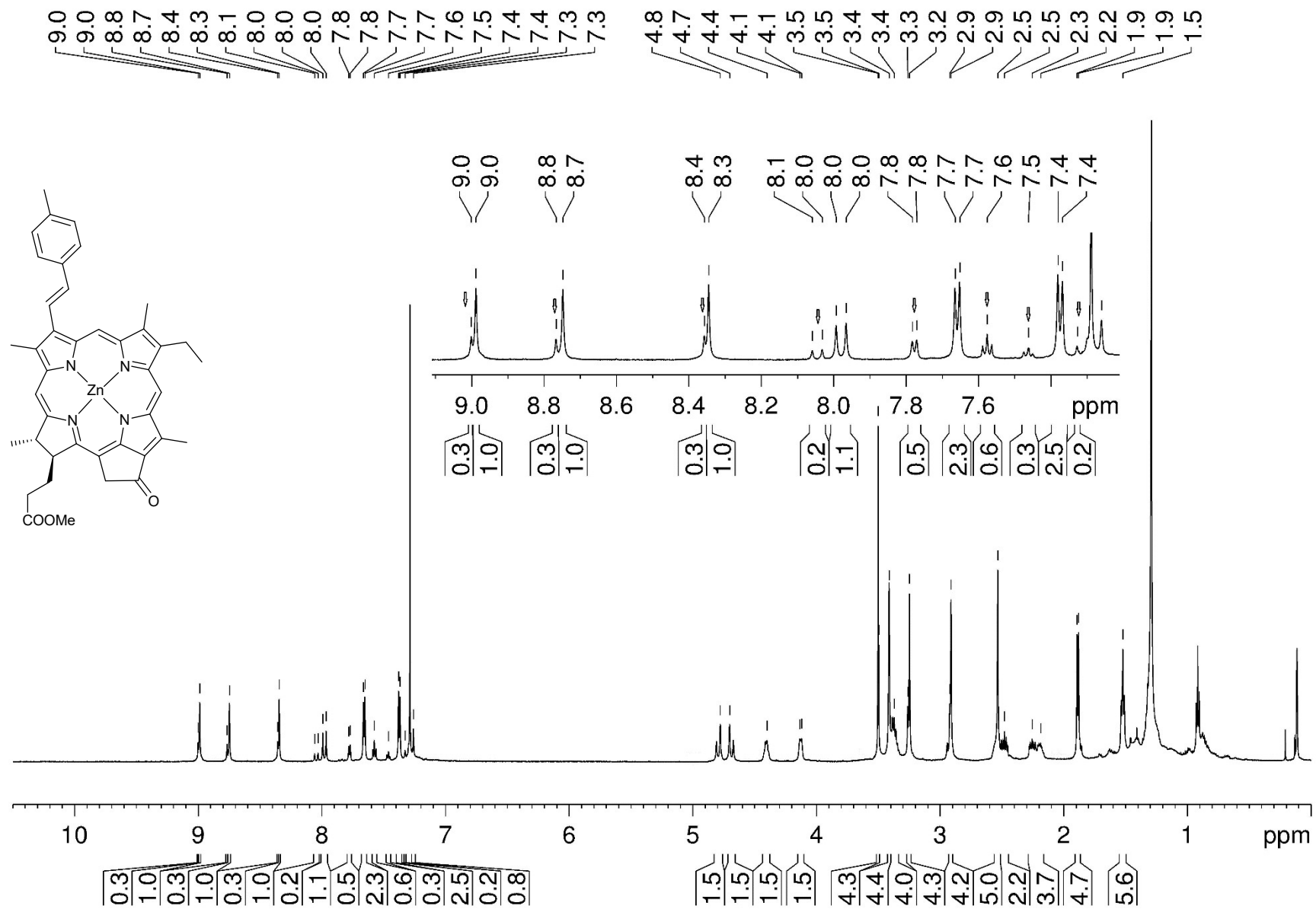


Fig. S23. ¹H NMR spectrum of Zn(II) methyl (*E*)-3²-(4-methylphenyl)pyropheophorbide-*a* (**13b**) in CDCl₃.

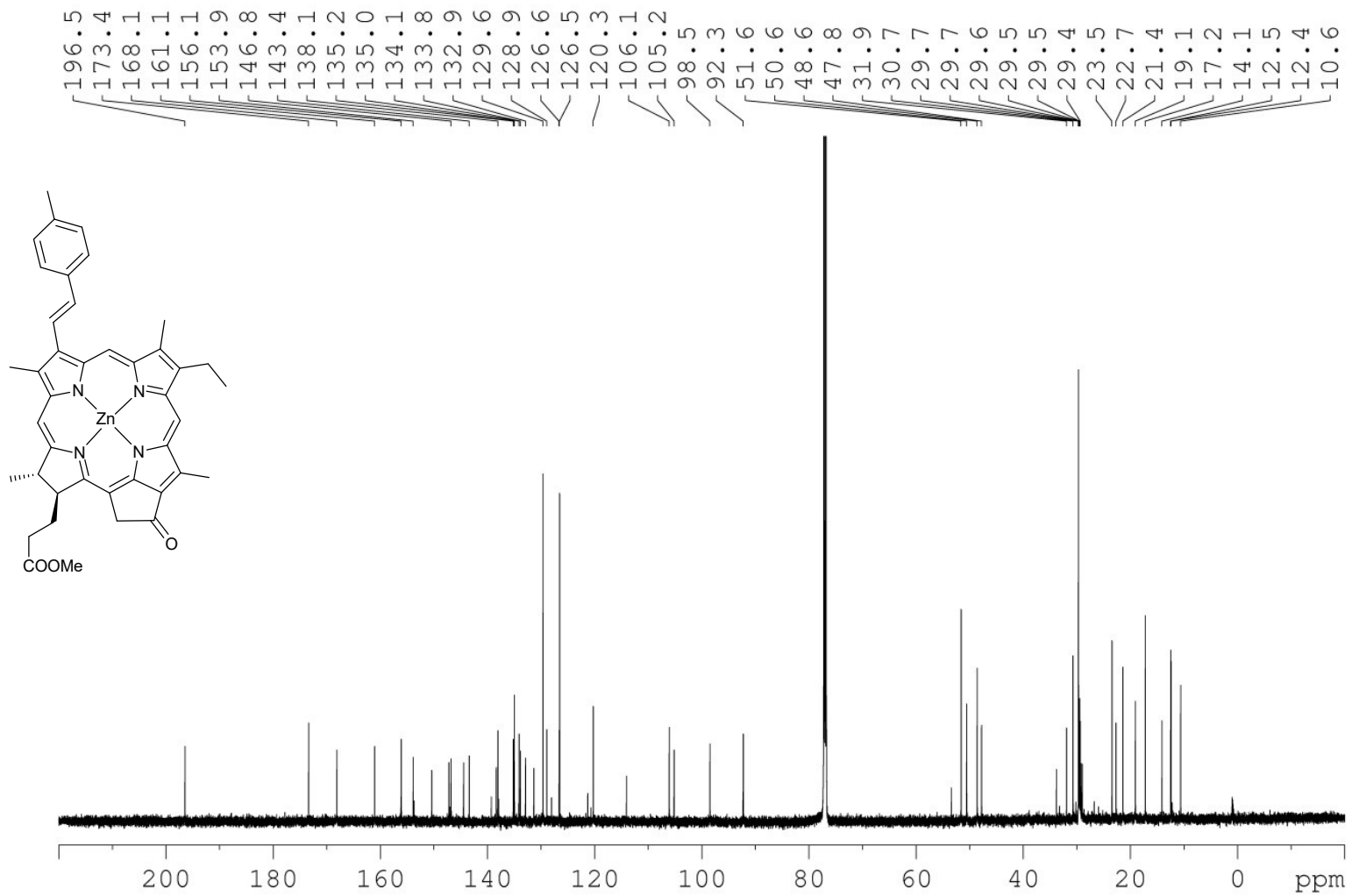


Fig. S24. ¹³C NMR spectrum of Zn(II) methyl (E)-3²-(4-methylphenyl)pyropheophorbide-*a* (**13b**) in CDCl₃.

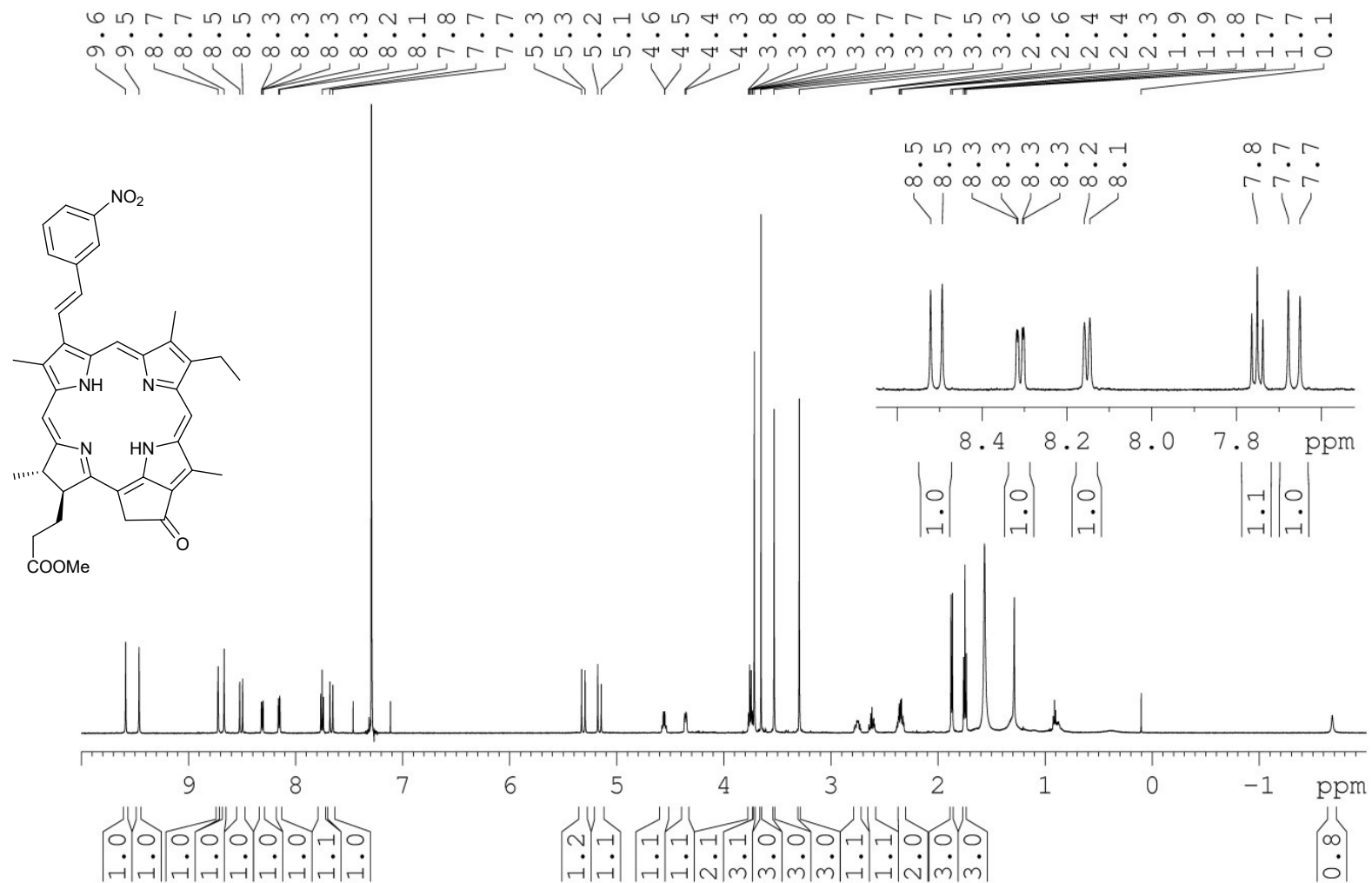


Fig. S25. ¹H NMR spectrum of methyl (*E*)-3²-(3-nitrophenyl)pyropheophorbide-*a* (**14a**) in CDCl₃.

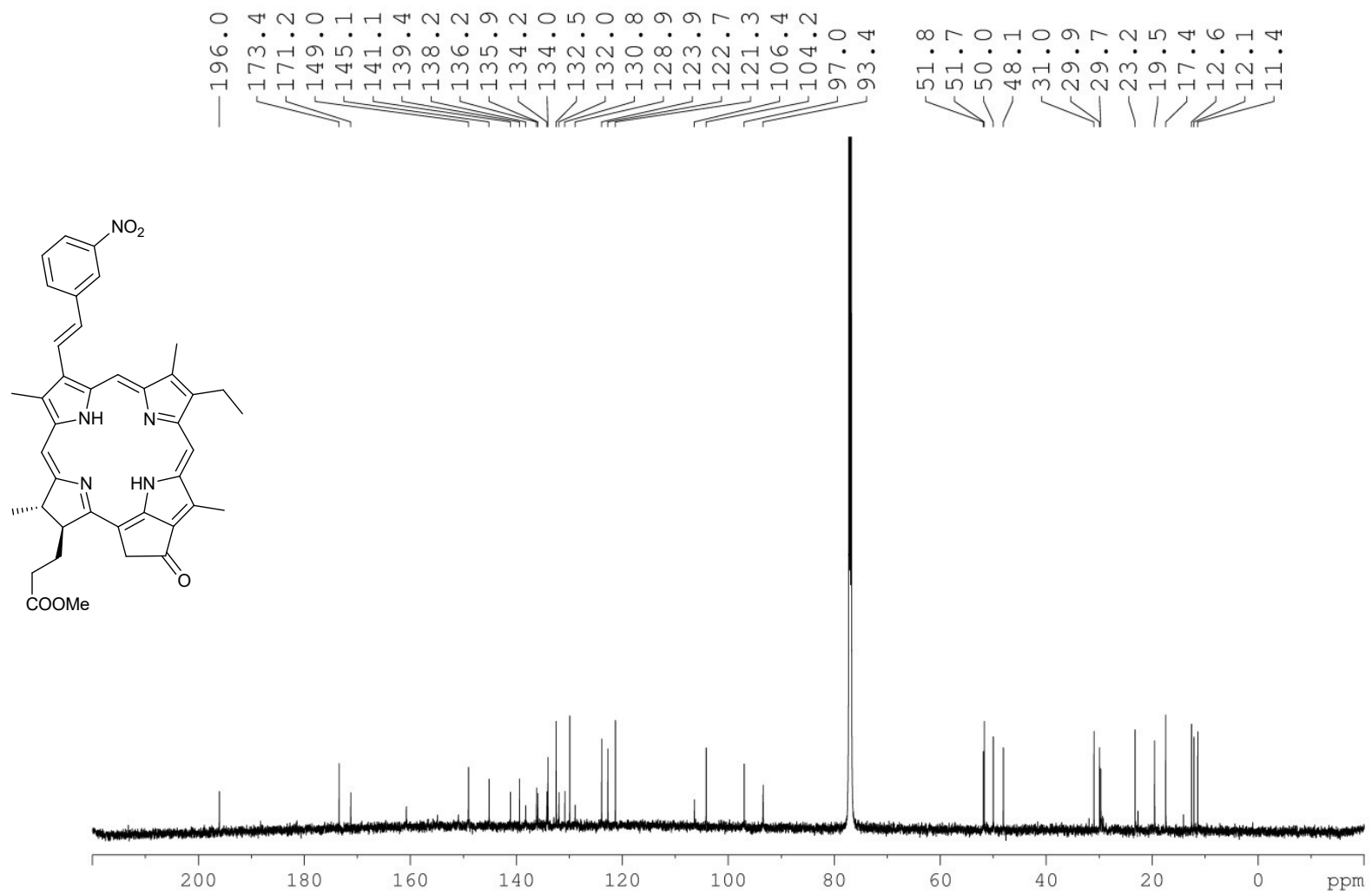


Fig. S26. ¹³C NMR spectrum of methyl (*E*)-3²-(3-nitrophenyl)pyropheophorbide-*a* (**14a**) in CDCl₃.

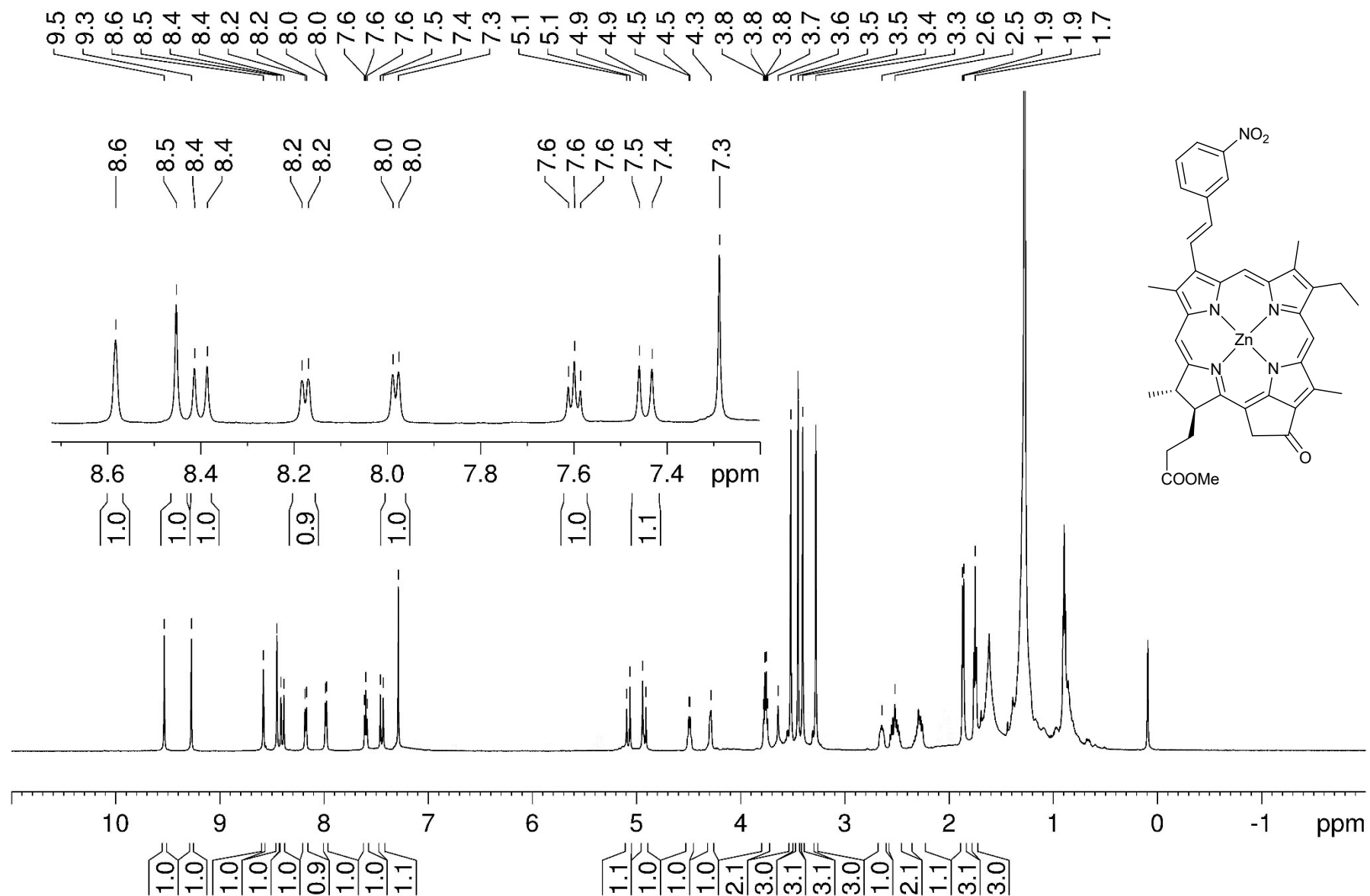


Fig. S27. ¹H NMR spectrum of Zn(II) methyl (*E*)-3²-(3-nitrophenyl)pyropheophorbide-*a* (**14b**) in CDCl₃.

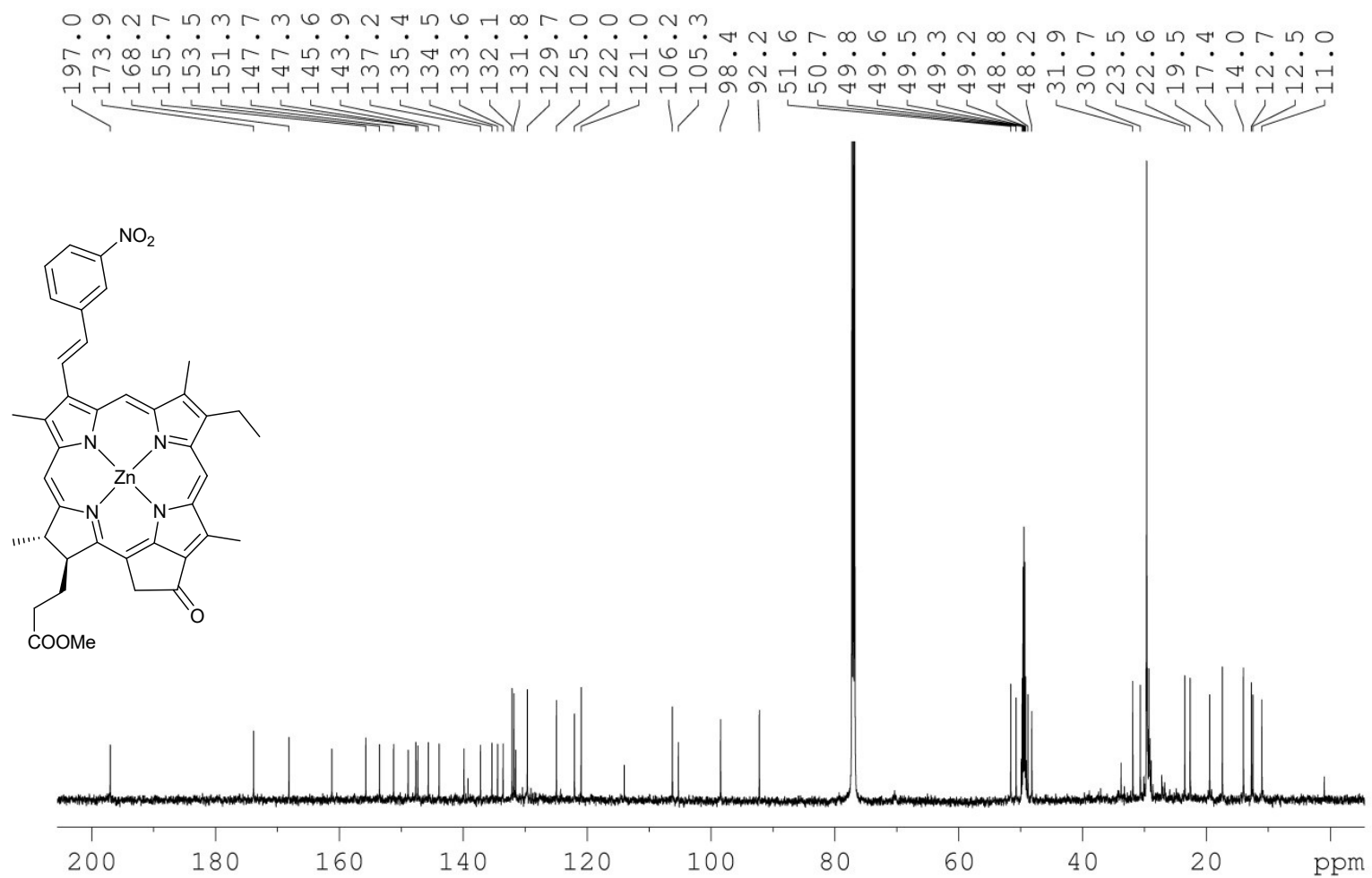


Fig. S28. ¹³C NMR spectrum of Zn(II) methyl (*E*)-3²-(3-nitrophenyl)pyropheophorbide-*a* (**14b**) in CDCl₃.

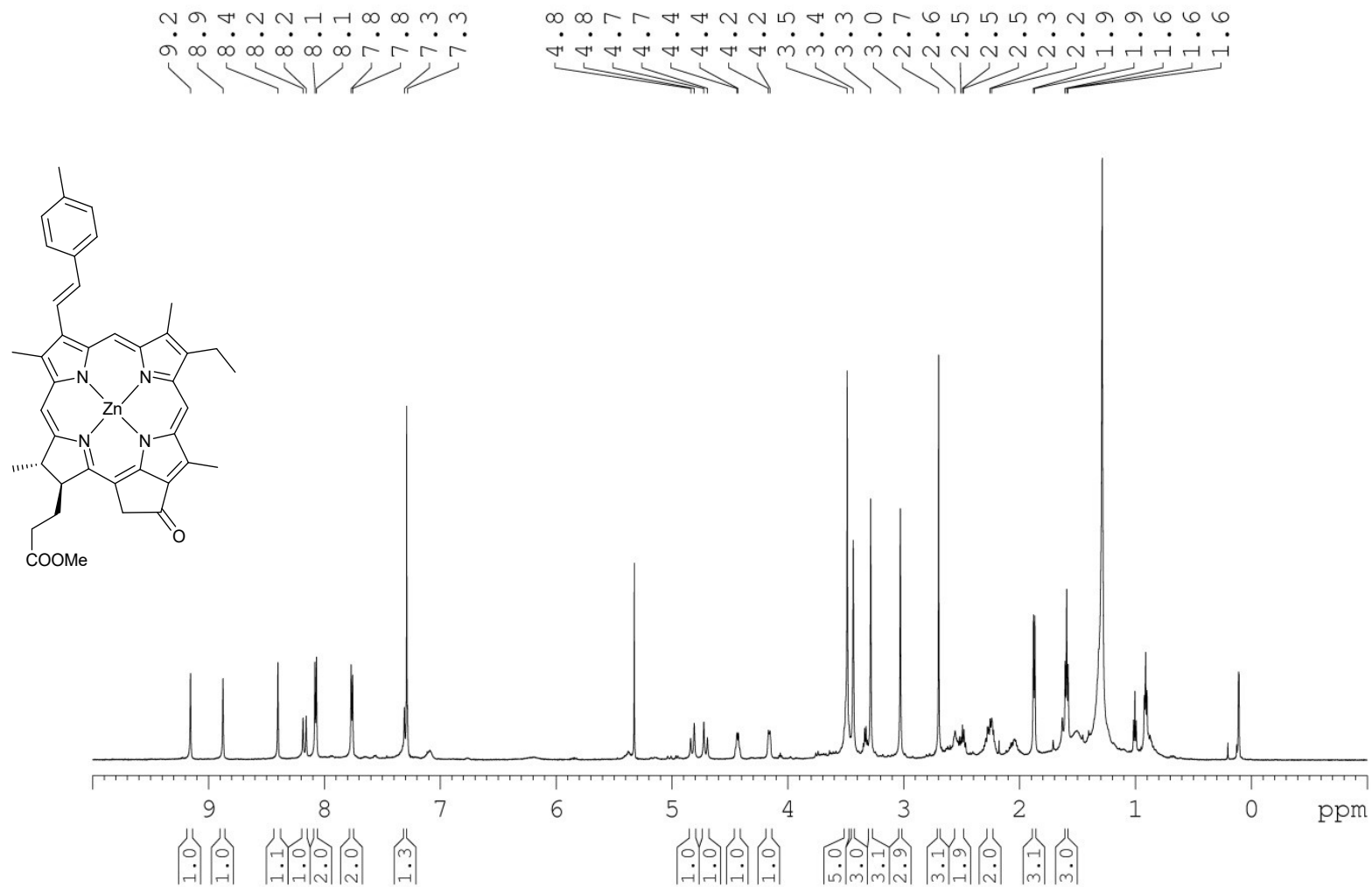


Fig. S29. ¹H NMR spectrum of Zn(II) methyl (*E*)-3²-(4-acetophenyl)pyropheophorbide-*a* (**15b**) in CDCl₃.

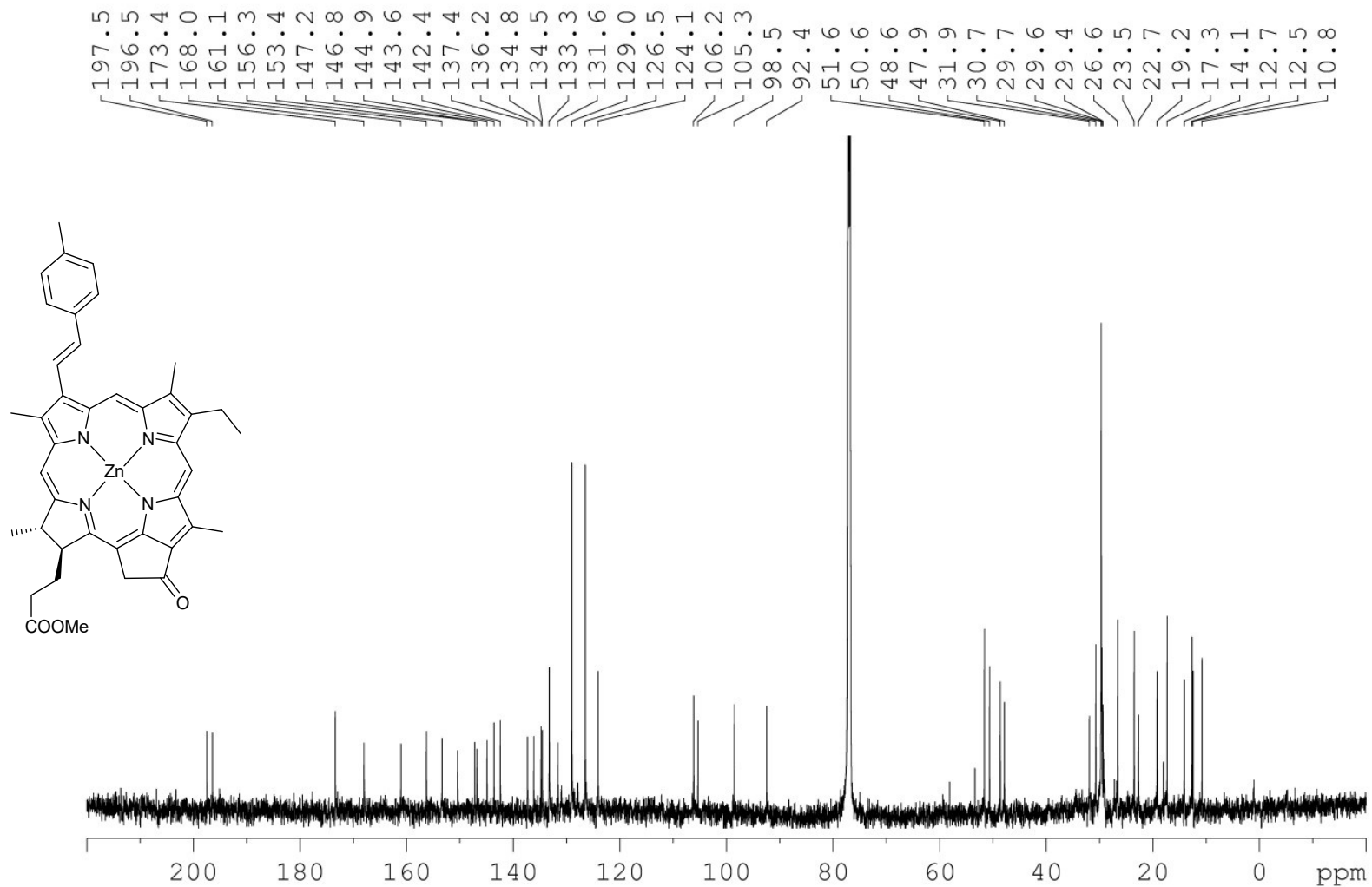


Fig. S30. ^{13}C NMR spectrum of Zn(II) methyl (*E*)-3²-(4-acetophenyl)pyropheophorbide-*a* (**15b**) in CDCl_3 .

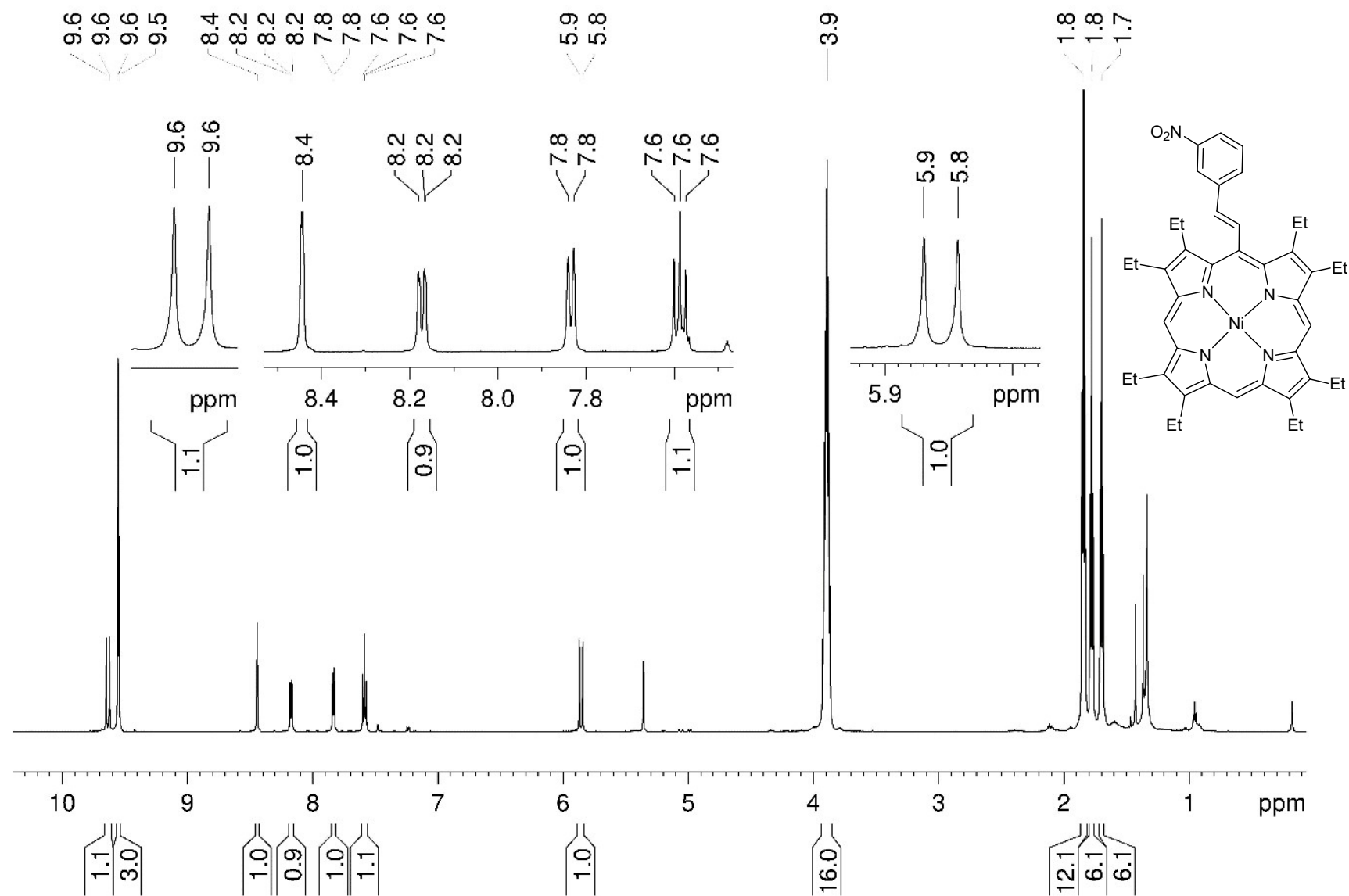


Fig. S31. ¹H NMR spectrum of Ni(II) (*E*)-5-(2-(3-nitrophenyl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**16**) in CDCl₃.

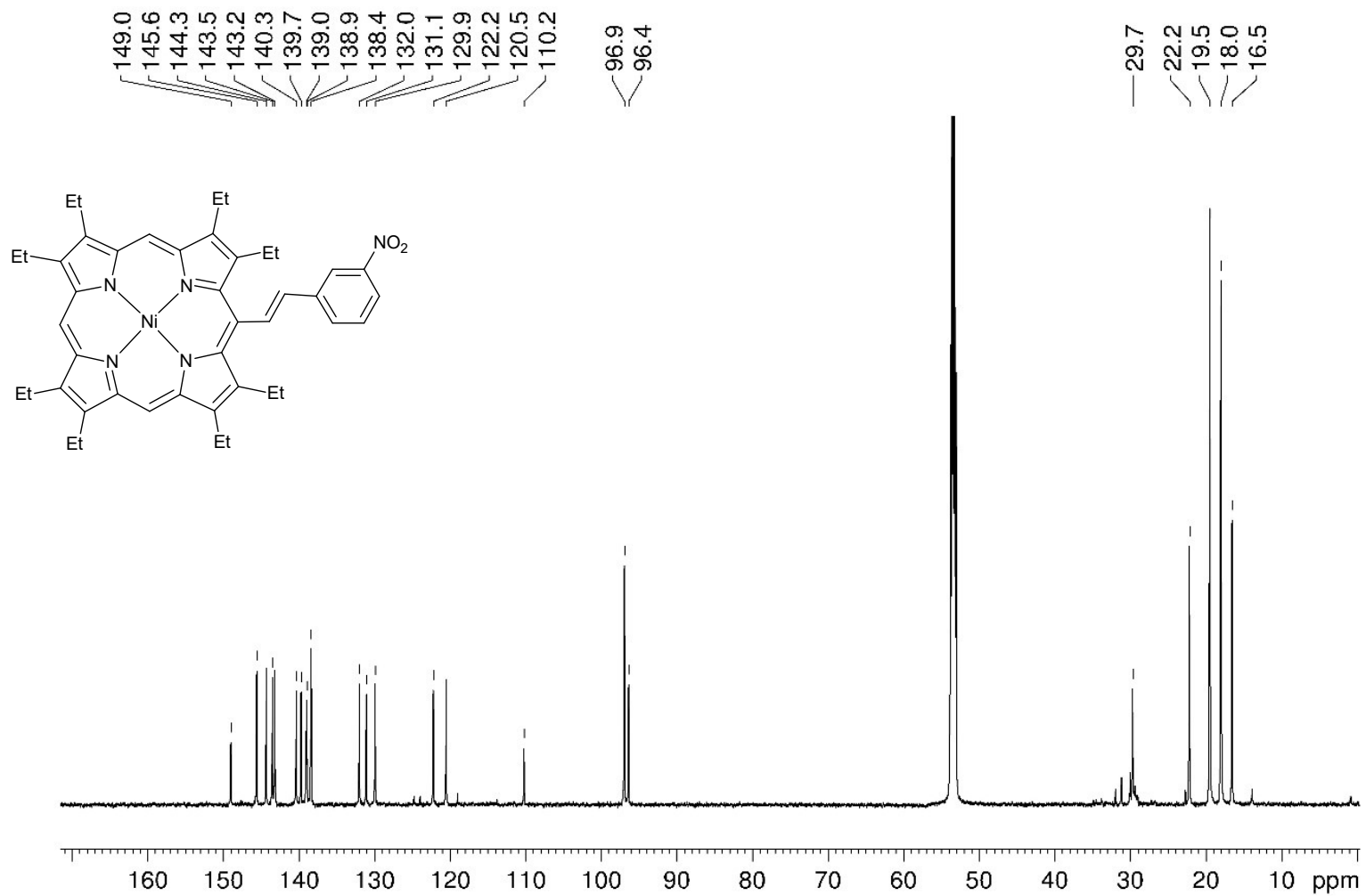


Fig. S32. ^{13}C NMR spectrum of Ni(II) (*E*)-5-(2-(3-nitrophenyl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**16**) in CDCl_3 .

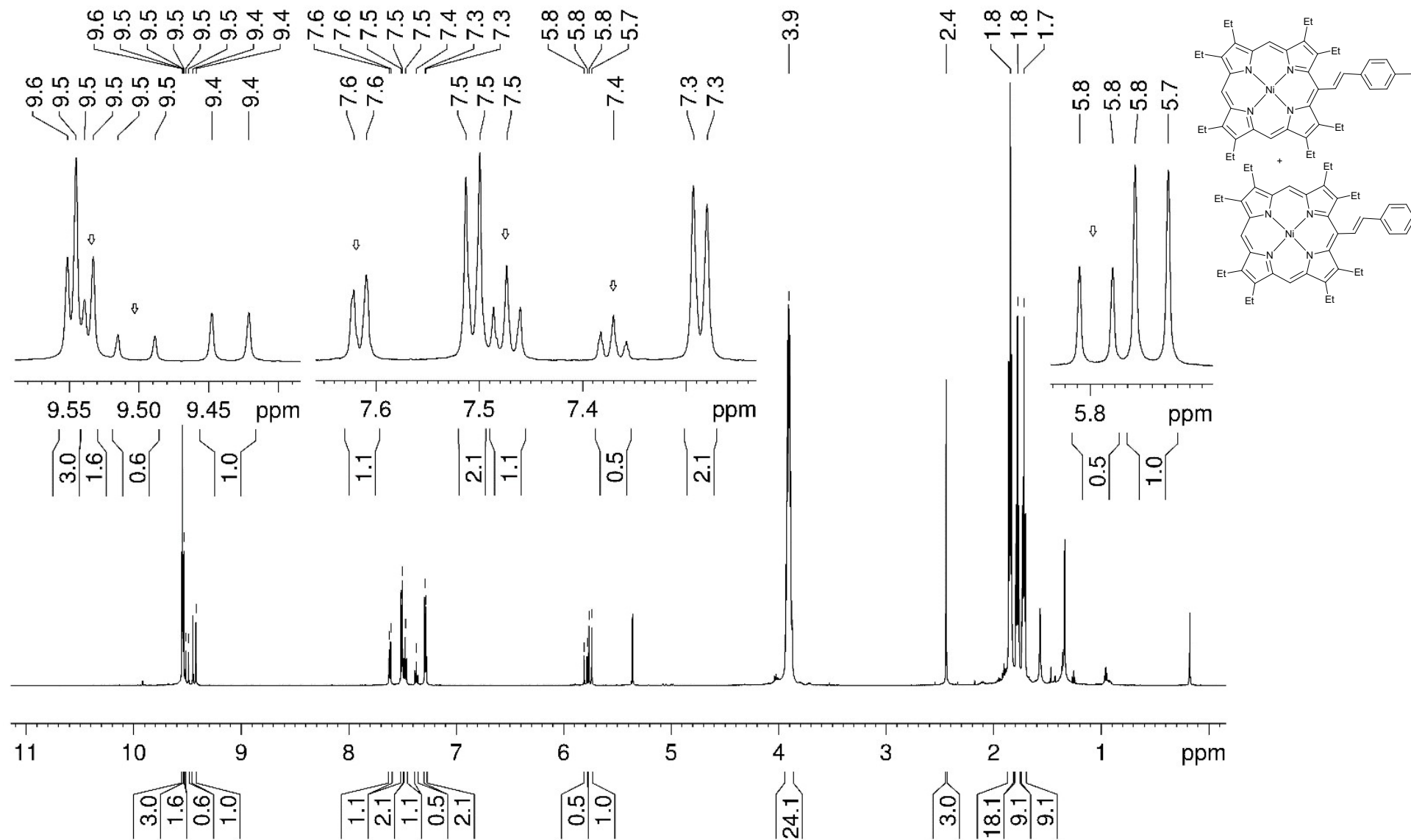


Fig. S33. ^1H NMR spectrum of the mixture of Ni(II) (*E*)-5-(2-(4-methylphenyl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**17**) and Ni(II) (*E*)-5-(2-phenylethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**18**) in CDCl_3 . Peaks of **18** are noted with arrows.

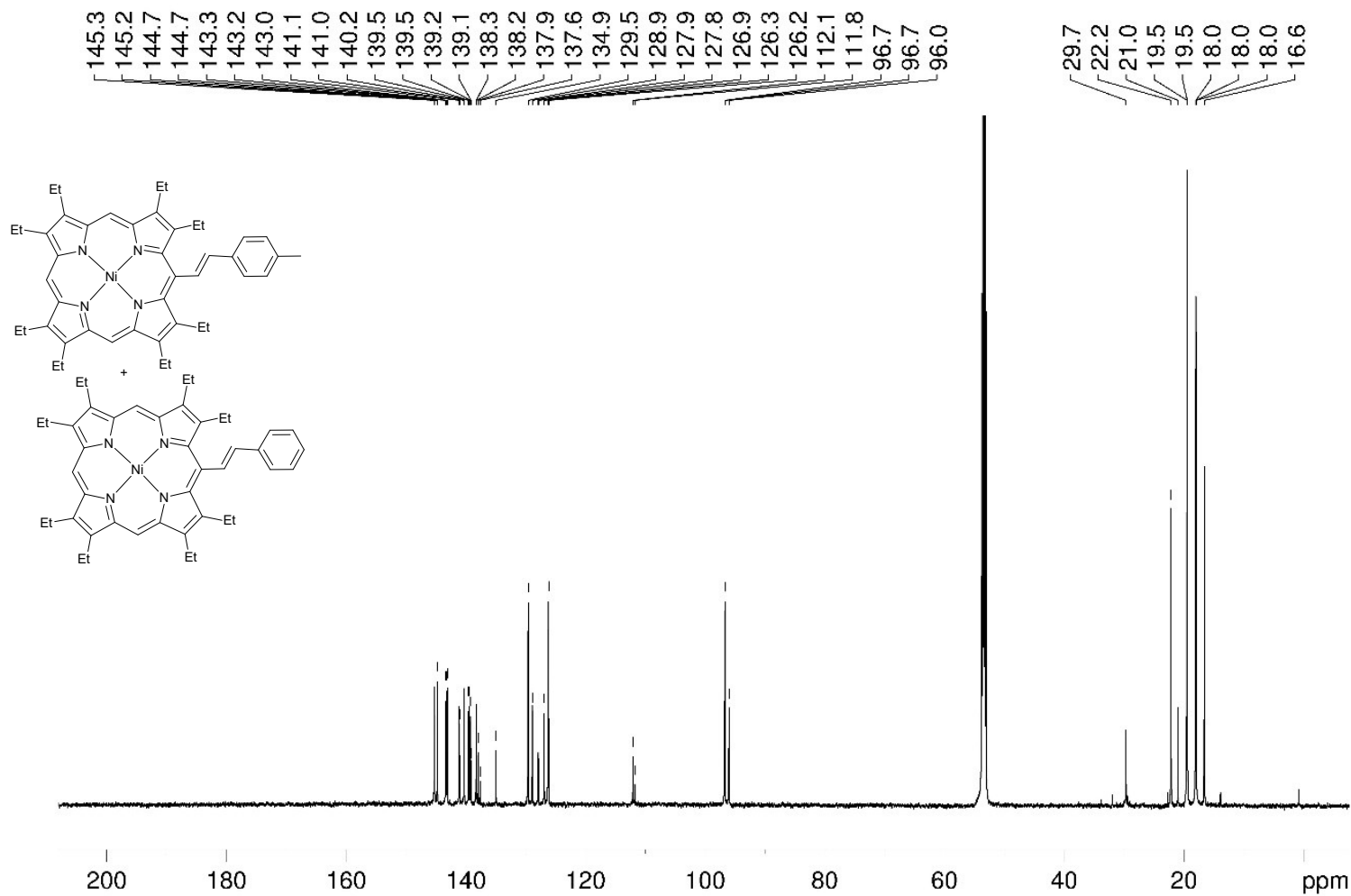


Fig. S34. ^{13}C NMR spectrum of the mixture of Ni(II) (*E*)-5-(2-(4-methylphenyl)ethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**17**) and Ni(II) (*E*)-5-(2-phenylethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**18**) in CDCl_3 .

UV-Vis absorption spectra

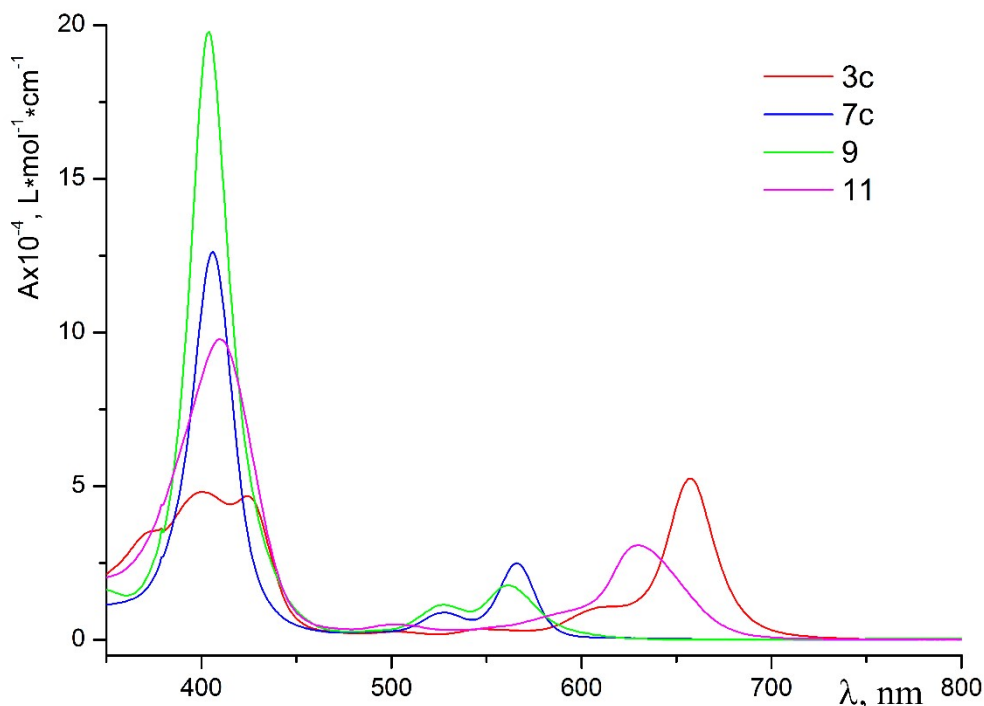


Fig. S32. Molar extinction normalized UV-Vis absorption spectra of Ni(II) methyl (*E*)-3²-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)pyropheophorbide-*a* (**3c**), Ni(II) dimethyl (*E,E*)-3²,8²-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)protoporphyrin IX (**7c**), Ni (II) (*E*) 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)viny)l)-2,3,7,8,12,13,17,18-octaethylporphyrin (**9**), Ni (II) (*E*) 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)viny)l)-2,3,7,8,12,13,17,18-octaethyl-17,18-*trans*-dihydroporphyrin (**11**) in CH₂Cl₂.

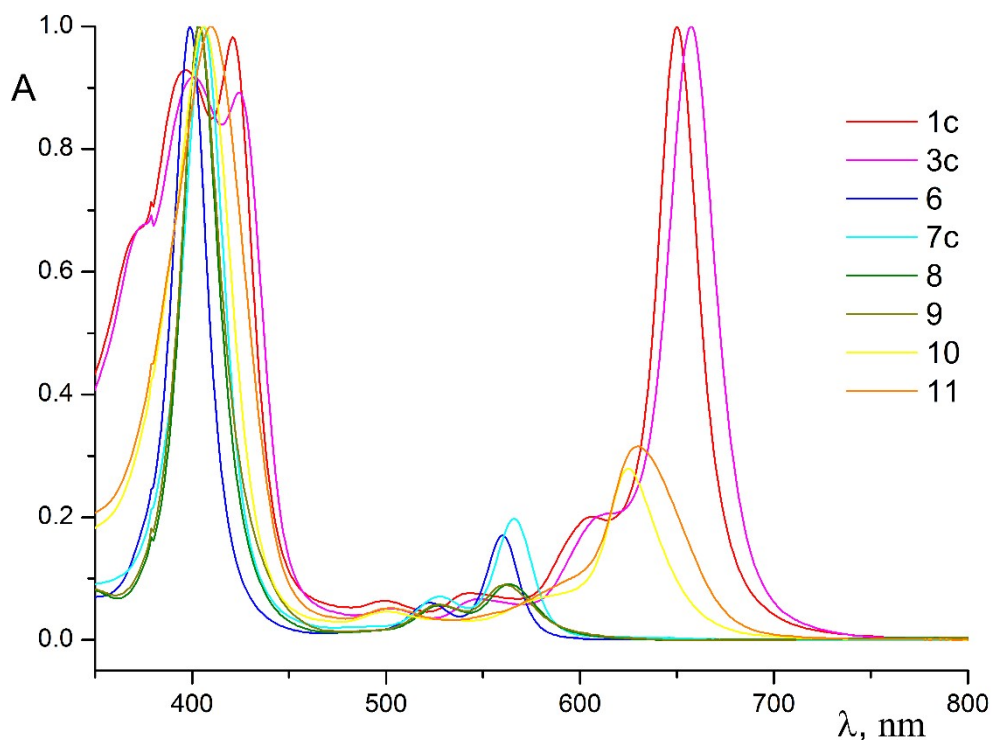


Fig. S33. Normalized UV-Vis absorption spectra of the starting vinylporphyrins **1c**, **4**, **6c**, **8** and the corresponding borylation products **3c**, **5**, **7c**, **9** in CH₂Cl₂.

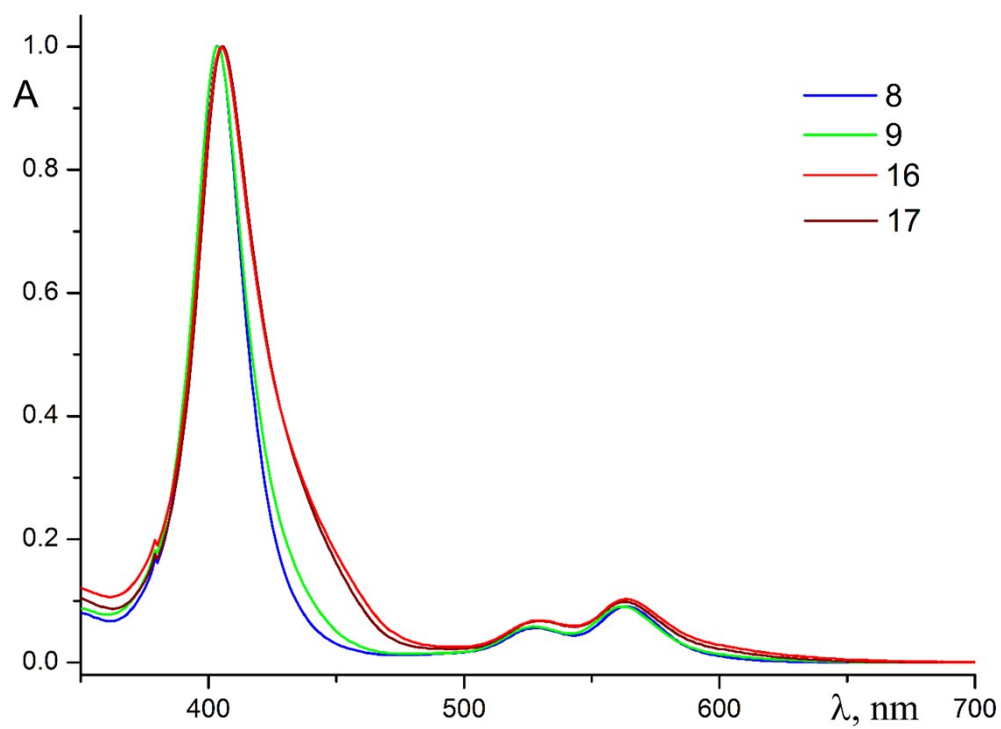


Fig. S34. Normalized UV-Vis absorption spectra of the starting vinylporphyrin **8**, its borylation product **9**, and the corresponding arylation products **16**, **17** in CH_2Cl_2 .

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