Supporting Information for

Alphabet Soup within a Porphyrinoid Cavity: Synthesis of Heterocarbaporphyrins with CNNO, CNOO, CNSO and CNSeO Cores from an Oxacarbatripyrrin

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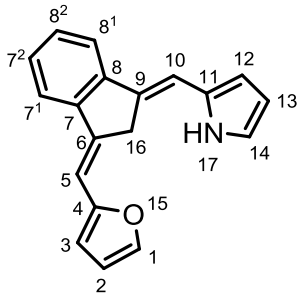
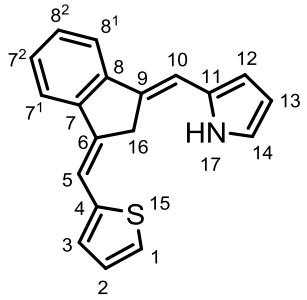
EXPERIMENTAL SECTION

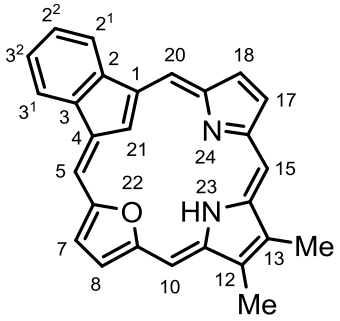
Melting points are uncorrected. NMR spectra were recorded using a 400 or 500 MHz NMR spectrometer and were run at 300 K unless otherwise indicated. ^{1}H NMR values are reported as chemical shifts δ, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; br, broad peak) and coupling constant (*J*). Chemical shifts are reported in parts per million (ppm) relative to $CDCl_3$ (^{1}H residual $CHCl_3$ δ 7.26, ^{13}C $CDCl_3$ triplet δ 77.23) or d_6-DMSO (^{1}H d_5-DMSO pentet at δ 2.49, ^{13}C d_6-DMSO septet at δ 39.7) and coupling constants were taken directly from the spectra. NMR assignments were made with the aid of ^{1}H-^{1}H COSY, HSQC, DEPT-135 and nOe difference proton NMR spectroscopy. 2D experiments were performed by using standard software. High-resolution mass spectra (HRMS) were carried out by using a double focusing magnetic sector instrument.



14-Oxa-15-carbabenzo[*g*]tripyrrin (**8b**). Dihydrofulvene **6** (1.704 g, 8.7 mmol) and freshly distilled furan-2-carbaldehyde (0.86 g, 9.0 mmol) were taken up in a solution of potassium hydroxide (0.388 g) in ethanol (18.6 mL). The resulting mixture was refluxed with stirring under nitrogen for 10 min. Upon cooling, the resulting precipitate was collected by suction filtration, washed with ethanol and dried *in vacuo* to give the tripyrrin analogue (1.860 g, 6.8 mmol, 78%) as a light brown solid, mp 178-180 ºC, dec. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.88 (2H, t, *J* = 2.3 Hz, 16-CH_2), 6.38-6.40 (1H, m, 13-H), 6.44 (1H, d, *J* = 3.3 Hz, 12-H), 6.49-6.51 (1H, m, 3-H), 6.52 (1H, dd, *J* = 1.8, 3.3 Hz, 2-H), 6.88 (2H, t, *J* = 2.3 Hz, 5,10-H), 6.90-6.92 (1H, m, 14-H), 7.22-7.28 (2H, m, 7^2,8^2-H), 7.54 (1H, d, *J* = 1.7 Hz, 1-H), 7.57-7.61 (2H, m, 7^1,8^1-H), 8.32 (1H, br, NH). ^{13}C NMR (125 MHz, CDCl3): δ 37.3 (16-CH_2), 107.4 (5- or 10-CH), 109.2 (12-CH), 109.4 (5- or 10-CH), 109.7 (3-CH), 110.8 (14-CH), 112.0 (2-CH), 118.9 (14-CH), 120.1 (7^1- or 8^1-CH), 120.6 (7^1- or 8^1-CH), 127.9 (7^2- or 8^2-CH), 128.6 (7^2- or 8^2-CH), 131.3, 135.0, 138.1, 142.3, 142.6, 143.9, 154.2. HR-MS (EI) calcd for $C_{19}H_{15}NO$ 273.11537, found 273.11499.

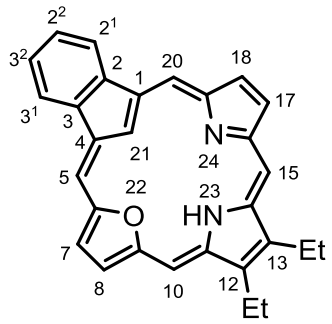


14-Thia-15-carbabenzo[*g*]tripyrrin (**8c**). Dihydrofulvene **6** (0.927 g, 4.75mmol) and thiophene-2-carbaldehyde (0.556 g, 4.96 mmol) were taken up in a solution of potassium hydroxide (0.198 g) in ethanol (10 mL). The resulting mixture was refluxed with stirring under nitrogen for 30 min. Upon cooling, the resulting precipitate was collected by suction filtration, washed with ethanol (3 mL) and dried *in vacuo* to give the tripyrrin analogue (1.333 g, 4.61 mmol, 97%) as a light yellow-brown solid, mp 189.5-190.5 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.81 (2H, t, *J* = 1.8 Hz, 16-CH_2), 6.40-6.42 (1H, m, 13-H), 6.56 (1H, br s, 12-H), 6.89-6.92 (2H, m, 10,14-H), 7.12-7.14 (1H, m, 2-H), 7.17-7.19 (1H, m, 3-H), 7.23-7.28 (2H, m, 7^2,8^2-H), 7.30 (1H, br s, 5-H), 7.40 (1H, d, *J* = 4.9 Hz, (1-H), 7.58-7.60 (1H, m, 8^1-H), 7.63-7.65 (1H, m, 7^1-H), 8.32 (1H, br s, NH). ^{13}C NMR (125 MHz, CDCl3): δ 37.6 (16-CH_2), 109.5 (10-CH), 109.7 (12-CH), 110.9 (13-CH), 112.8 (5-CH), 118.9 (14-CH), 120.1 (8^1-CH), 120.6 (7^1-CH), 125.7 (1-CH), 127.1 (3-CH), 127.6 (2-CH), 128.0 (7^2- or 8^2-CH), 128.6 (7^2- or 8^2-CH), 131.2, 134.7, 138.0, 142.4, 142.7, 143.9. HR-MS (EI) calcd for $C_{19}H_{15}NS$ 289.09252, found 289.09266.

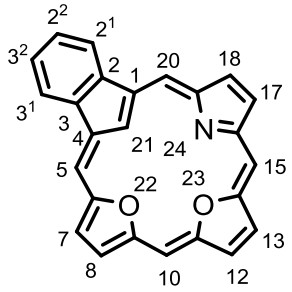


12,13-Dimethyl-22-oxa-21-carbabenzo[*b*]porphyrin (**15a**). Oxacarbatripyrrin **8b** (50.6 mg, 0.0185 mmol) and 3,4-dimethyl-2,5-pyrroledicarbaldehyde[S1] (28.0 mg, 0.0185 mmol) were dissolved in dichloromethane (19 mL). This solution was added dropwise over 15 min to TFA (1 mL) in dichloromethane (1 mL). The mixture was left to stir for an additional 30 min and washed sequentially with water and saturated aqueous sodium bicarbonate. The solvent was dried over

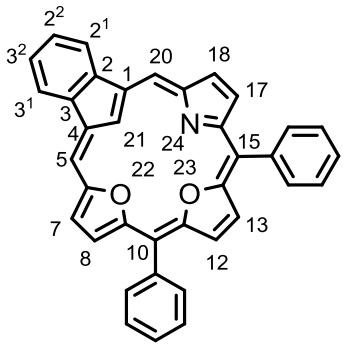
sodium sulfate, filtered, and evaporated. The crude material was purified by a grade 3 alumina column eluting with dichloromethane. A brown band was collected and the resulting material recrystallized from chloroform-hexanes to give the porphyrin (6.0 mg, 15.4 μmol, 8%) as a dark solid, mp >300 ºC. UV-Vis (1% Et_3N-CH_2Cl_2): λ_{max} (log ε) 370 (sh, 4.52), 429 (4.94), 514 (4.16), 547 (3.96), 618 (3.64), 688 nm (2.76). UV-Vis (50 equiv TFA-CH_2Cl_2): λ_{max} (log ε) 393 (4.76), 431 (4.80), 533 (4.04), 568 (sh, 3.61), 614 (3.71), 674 nm (2.98). UV-Vis (50% TFA-CH_2Cl_2): λ_{max} (log ε) 398 (4.88), 425 (4.72), 536 (4.09), 611 nm (3.82). ^{1}H NMR (500 MHz, $CDCl_3$, 50 ºC): δ -5.41 (1H, s, 21-H), -2.72 (2H, v br, 2 x NH), 3.55 (3H, s, 13-Me), 3.56 (3H, s, 12-Me), 7.67-7.73 (2H, m, 2^2,3^2-H), 8.71-8.73 (1H, m, 3^1-H), 8.78-8.80 (1H, m, 2^1-H), 9.10 (1H, d, *J* = 4.2 Hz, 17-H), 9.18 (1H, d, *J* = 4.2 Hz, 18-H), 9.48 (1H, d, *J* = 4.5 Hz, 8-H), 9.55 (1H, d, *J* = 4.5 Hz, 7-H), 9.81 (1H, s, 10-H), 9.82 (1H, s, 15-H), 10.09 (1H, s, 5-H), 10.23 (1H, s, 20-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.8, 11.9, 91.1 (10-CH), 101.6 (5-CH), 101.8 (15-CH), 111.5 (20-CH), 120.5 (3^1-CH), 120.7 (2^1-CH), 123.1 (8-CH), 125.0 (7-CH), 127.1 (2^2- or 3^2-CH), 127.4 (2^2- or 3^2-CH), 131.2 (17-CH), 133.7 (18-CH). ^{13}C NMR (125 MHz, d_6-DMSO): δ 11.0, 11.2, 62.9, 91.3, 101.4, 101.7, 110.9, 120.4, 120.5, 124.5, 126.0, 126.2, 126.3, 126.8, 126.9, 127.7, 131.1, 133.3, 134.0, 134.5, 135.3, 136.3, 140.1, 150.8, 152.8. ^{1}H NMR (500 MHz, TFA-d_6-DMSO): δ -8.69 (1H, br s, 21-H), 3.56 (3H, s, 12-Me), 3.59 (3H, s, 13-Me), 7.71-7.74 (2H, m, 2^2,3^2-H), 8.56-8.59 (1H, m, 3^1-H), 8.62-8.65 (1H, m, 2^1-H), 9.25 (1H, d, *J* = 4.3 Hz, 18-H), 9.34 (1H, d, *J* = 4.3 Hz, 17-H), 9.82 (1H, br d, 7-H), 9.86 (1H, br d, *J* = 4.4 Hz, 8-H), 10.00 (1H, br s, 5-H), 10.18 (1H, s, 20-H), 10.24 (1H, s, 10-H), 10.35 (1H, s, 15-H). ^{13}C NMR (125 MHz, TFA-d_6-DMSO): δ 11.3, 11.5, 94.1, 101.5, 104.1, 109.9, 119.8 (21-CH), 126.6, 127.6, 127.8, 128.07, 128.15, 128.3, 128.4, 129.7, 135.9, 136.3, 137.8, 138.1, 138.2, 138.8, 140.1, 142.0, 142.1, 142.9, 152.9, 153.5. HR-MS (ESI) calcd for $C_{27}H_{20}N_2O$ + H 389.1654, found 389.1647.



12,13-Diethyl-22-oxa-21-carbabenzo[*b*]porphyrin (**15b**). Oxacarbatripyrrin **8b** (50.3 mg, 0.0185 mmol) and 3,4-diethyl-2,5-pyrroledicarbaldehyde[S1] (32.8 mg, 0.0183 mmol) were reacted under the foregoing conditions. The crude material was purified as described above to yield the oxacarbaporphyrin (10.5 mg, 25.2 μmol, 14%) as a dark solid, mp >300 ºC. UV-Vis (1% Et_3N-CH_2Cl_2): λ_{max} (log ε) 372 (4.57), 430 (5.01), 515 (4.21), 547 (4.00), 618 (3.66), 679 nm (2.59). UV-Vis (50 equiv TFA-CH_2Cl_2): λ_{max} (log ε) 393 (4.82), 432 (4.90), 532 (4.10), 567 (sh, 3.61), 615 nm (3.73). UV-Vis (50% TFA-CH_2Cl_2): λ_{max} (log ε) 301 (4.52), 398 (4.94), 426 (4.80), 536 (4.13), 611 nm (3.82). ^{1}H NMR (500 MHz, $CDCl_3$): δ -5.79 (1H, s, 21-H), -3.26 (2H, br, 2 x NH), 1.83 (3H, t, *J* = 7.7 Hz, 13-CH_2CH_3), 1.86 (3H, t, *J* = 7.7 Hz, 12-CH_2CH_3), 3.92-4.01 (4H, 2 overlapping quartets, 2 x CH_2CH_3), 7.68-7.75 (2H, m, 2^2,3^2-H), 8.65-8.68 (1H, m, 3^1-H), 8.77-8.80 (1H, m, 2^1-H), 9.10 (1H, d, *J* = 4.3 Hz, 17-H), 9.17 (1H, d, *J* = 4.3 Hz, 18-H), 9.30 (1H, d, *J* = 4.6 Hz, 8-H), 9.37 (1H, d, *J* = 4.6 Hz, 7-H), 9.63 (1H, s, 10-H), 9.78 (1H, s, 15-H), 9.90 (1H, s, 5-H), 10.18 (1H, s, 20-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.1, 18.3, 19.73, 19.75, 90.8 (10-CH), 101.2 (5-CH), 101.8 (15-CH), 111.3 (20-CH), 120.4 (3^1-CH), 120.6 (2^1-CH), 120.9 (21-CH), 123.1 (8-CH), 124.9 (7-CH), 127.0 (2^2- or 3^2-CH), 127.2 (2^2- or 3^2-CH), 131.3 (17-CH), 133.6 (18-CH), 134.9, 136.3, 137.4, 139.6, 139.8, 141.0, 143.7, 144.3, 150.8, 151.7, 152.5, 152.9. ^{1}H NMR (500 MHz, TFA-$CDCl_3$): δ -7.18 (1H, br s, 21-H), -5.18 (1H, br), -4.53 (1H, br) (2 x NH), 1.88-1.94 (6H, 2 overlapping triplets, 2 x CH_2CH_3), 4.15-4.23 (4H, m, 2 x CH_2CH_3), 7.69-7.73 (2H, m, 2^2,3^2-H), 8.56-8.61 (2H, m, 2^1,3^1-H), 9.45 (1H, d, *J* = 4.5 Hz, 18-H), 9.49 (1H, d, *J* = 4.5 Hz, 17-H), 9.99 (2H, s, 7,8-H), 10.33 (1H, s, 5-H), 10.39 (1H, s, 20-H), 10.43 (1H, s, 10-H), 10.47 (1H, s, 15-H). ^{13}C NMR (125 MHz, TFA-$CDCl_3$): δ 17.7, 17.8, 19.9, 20.1, 94.8 (10-CH), 100.4 (15-CH), 105.2 (5-CH), 109.8 (20-CH), 119.2 (21-CH), 121.5, 121.8, 128.4, 128.6, 129.3, 130.4, 137.6, 137.9, 139.1, 140.3, 142.0, 142.2, 142.7, 143.2, 145.3, 153.7, 155.1. HR-MS (ESI) calcd for $C_{29}H_{24}N_2O$ + H 417.1967, found 417.1964.

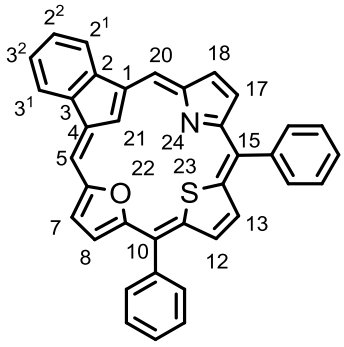


22,23-Dioxa-21-carbabenzo[*b*]porphyrin chloroform solvate (**12b·CHCl$_3$**). Oxacarbatripyrrin **8b** (49.8 mg, 0.0182 mmol) and 2,5-furandicarboxaldehyde[S2] (23.0 mg, 0.0162 mmol) were treated under the foregoing conditions. Column chromatography on grade 3 basic alumina eluting with 2% methanol-chloroform gave the product as a dark brown band. Recrystallization from chloroform-hexanes gave the heteroporphyrin (22.0 mg, 60.6 μmol, 37%) as a dark, flaky solid, mp >300 °C. UV-Vis (1% Et_3N-CH_2Cl_2): λ_{max} (log ε) 369 (sh, 4.08), 414 (sh, 4.26), 427 (4.29), 505 (3.71), 538 (3.38), 636 nm (3.22). UV-Vis (1% TFA-CH_2Cl_2): λ_{max} (log ε) 379 (sh, 3.86), 399 (4.27), 432 (3.85), 451 (sh, 3.76), 548 (3.23), 608 nm (3.10). ^{1}H NMR (500 MHz, d_6-DMSO, 70 °C): δ -4.24 (1H, s, 21-H), 7.65-7.69 (2H, m, 2^2,3^2-H), 8.23 (1H, s, $CHCl_3$), 8.78-8.82 (2H, m, 2^1,3^1-H), 9.07-9.09 (2H, collapsed AB quartet, *J* = 4.4 Hz, 17,18-H), 9.86 (1H, d, *J* = 4.5 Hz, 12-H), 9.91 (1H, d, *J* = 1.9 Hz, 8-H), 9.92 (1H, d, *J* = 1.9 Hz, 7-H), 10.01 (1H, d, *J* = 4.5 Hz, 13-H), 10.15 (1H, s, 15-H), 10.27 (1H, s, 20-H), 10.33 (1H, s, 10-H), 10.39 (1H, s, 5-H). ^{13}C (500 MHz, d_6-DMSO, 70 °C): δ 78.9 ($CHCl_3$), 91.5 (10-CH), 103.2 (5-CH), 104.7 (15-CH), 114.7 (20-CH), 120.38, 120.45 (2^1,3^1-CH), 125.1, 125.4 (21-CH), 126.4 (7- or 8-CH), 127.0 (7- or 8-CH), 127.1, 127.2 (2^2,3^2-CH), 129.4 (13-CH), 134.3 (17- or 18-CH), 134.9 (17- or 18-CH), 135.8, 139.2, 143.4, 143.7, 150.0, 151.4, 153.0, 153.3, 158.2. ^{1}H NMR (500 MHz, TFA-d_6-DMSO): δ -9.40 (1H, s, 21-H), -5.19 (1H, s, NH), 7.60-7.65 (2H, m, 2^2,3^2-H), 8.33-8.35 (1H, m, 3^1-H), 8.39-8.41 (1H, m, 2^1-H), 9.35 (1H, d, *J* = 4.4 Hz, 18-H), 9.47 (1H, d, *J* = 4.4 Hz, 17-H), 9.90 (1H, d, *J* = 4.5 Hz, 7-H), 9.98 (1H, s, 5-H), 10.06 (1H, d, *J* = 4.5 Hz, 8-H), 10.08 (1H, s, 20-H), 10.30 (1H, d, *J* = 4.6 Hz, 12-H), 10.33 (1H, d, *J* = 4.6 Hz, 13-H), 10.60 (1H, s, 15-H), 10.67 (1H, s). ^{13}C (500 MHz, TFA-d_6-DMSO): δ 79.5 ($CHCl_3$), 95.7 (10-CH), 100.9 (15-CH), 106.4 (5-CH), 111.1 (20-CH), 121.8 (3^1-CH), 121.9 (2^1-CH), 129.07 (17-CH), 129.16, 129.19 (2^2,3^2-CH), 130.2 (8-CH), 131.0 (18-CH), 131.1 (7-CH), 132.4 (12- or 13-CH), 132.6 (12- or 13-CH), 138.2, 138.5, 139.2, 141.49, 141.52, 142.0, 150.9, 152.1, 154.2, 154.7. HR-MS (ESI) calcd for $C_{25}H_{15}NO_2$ + H 362.1181, found 362.1175.



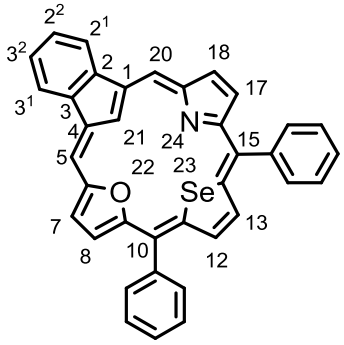
10,15-Diphenyl-22,23-dioxa-21-carbabenzo[*b*]porphyrin (**16a**). Oxacarbatripyrrin **8b** (51.6 mg, 0.0184 mmol) and furan dicarbinol **13a**[S3] (51.6 mg, 0.0184 mmol) were dissolved in dichloromethane (300 mL) under nitrogen and stirred for several minutes. A 10% $BF_3 \cdot Et_2O$ in dichloromethane (125 μL) was added dropwise over 5 minutes. The mixture was then stirred under nitrogen for two hours. DDQ (83 mg) was added and the mixture stirred for an additional 30 minutes. The solution was then washed with water, dried over sodium sulfate, and the solvent evaporated. Column chromatography using grade 3 basic alumina eluting with 2% methanol-chloroform gave a dark brown band. Recrystallization from chloroform-hexanes gave the title compound (9.0 mg, 17.5 μmol, 9.5%) as a dark solid, mp >300 °C. UV-Vis (1% Et_3N-CH_2Cl_2): λ_{max} (log ε) 302 (4.47), 358 (sh, 4.46), 429 (4.95), 517 (4.25), 546 (sh, 3.71), 602 (3.08), 649 (3.59), 717 nm (3.15). UV-Vis (1% TFA-CH_2Cl_2): λ_{max} (log ε) 303 (4.39), 415 (4.97), 434 (sh, 4.80), 494 (sh, 4.08), 557 (4.04), 623 (3.86), 684 nm (3.57). ^{1}H NMR (500 MHz, $CDCl_3$): δ -3.75 (1H, s), 7.65-7.70 (2H, m, 2^2,3^2-H), 7.72-7.85 (6H, m, *m*- and *p*-H), 8.10-8.12 (2H, m, 10-*o*-Ph), 8.14-8.16 (2H, m, 15-*o*-Ph), 8.47 (1H, d, *J* = 4.4 Hz, 17-H), 8.62-8.66 (1H, m, 3^1-H), 8.68-8.71 (1H, m, 2^1-H), 8.81 (1H, d, *J* = 4.8 Hz, 12-H), 8.85 (1H, d, *J* = 4.6 Hz, 8-H), 8.92 (1H, d, *J* = 4.4 Hz, 18-H), 9.02 (1H, d, *J* = 4.8 Hz, 13-H), 9.41 (1H, d, *J* = 4.6 Hz, 7-H), 10.00 (1H, s, 5-H), 10.16 (1H, s, 20-H). ^{13}C (500 MHz, $CDCl_3$): δ 103.8 (5-CH), 107.4, 116.1 (20-CH), 120.5 (3^1-CH), 120.8 (2^1-CH), 120.9, 125.6 (8-CH), 126.2 (21-CH), 126.3 (12-CH), 127.3, 127.5, 127.7, 128.1, 128.4, 128.9 (13-CH), 129.0, 134.0 (10-*o*-Ph), 134.2 (15-*o*-Ph), 134.7 (17-CH), 135.0 (18-CH), 137.6, 141.01, 141.02, 142.0, 144.1, 144.6, 151.5, 153.3, 154.6, 154.8. ^{1}H NMR (500 MHz, TFA-$CDCl_3$): δ -6.51 (1H, s), -4.46 (1H, br s, NH), 7.75-7.78 (2H, m, 2^2,3^2-H), 7.90-7.94 (4H, m, 4 x *m*-H), 7.96-8.01 (2H, m, 2 x *p*-H), 8.21-8.25 (4H, m, 4 x *o*-H), 8.65-8.71 (2H, m, 2^1,3^1-H), 9.17 (1H, dd, obscured by tfa, 17-H), 9.49 (1H, d, *J* = 4.9 Hz, 13-H), 9.62 (1H, d, *J* = 4.9 Hz, 12-H), 9.67 (1H, dd, *J* = 1.9, 4.8 Hz, 18-H), 10.04 (1H, d, *J* = 4.7 Hz, 7-H), 10.58 (1H, s, 5-H), 10.64 (1H, s, 20-H). ^{13}C (500 MHz, TFA-$CDCl_3$): δ 107.8 (5-CH), 110.9 (20-CH), 112.6, 117.1, 121.4 (21-H), 122.3,

128.7, 130.19, 130.22, 130.56, 130.60 (17-CH), 130.63, 131.0 (7-CH), 131.5, 131.8 (18-CH), 132.0, 132.4, 134.1, 134.6, 137.4, 138.97, 139.04, 141.8, 142.6, 142.77, 142.80, 153.3, 154.5, 156.0, 157.4. HR-MS (ESI) calcd for $C_{37}H_{23}NO_2$ + H 514.1807, found 514.1802.



10,15-Diphenyl-22-oxa-23-thia-21-carbabenzo[*b*]porphyrin (**16b**). Oxacarbatripyrrin **8b** (50.5 mg, 0.0184 mmol) and thiophene dicarbinol **8**[S3] (55.0 mg, 0.0186 mmol) were reacted under the foregoing conditions. After column chromatography using grade 3 basic alumina eluting with dichloromethane, the crude material was recrystallized from chloroform-hexanes to give the porphyrin analogue (15.7 mg, 29.6 μmol, 16%) as a red solid, mp >300 °C. UV-Vis (1% Et_3N-CH_2Cl_2): λ_{max} (log ε) 308 (4.42), 386 (sh, 4.56), 436 (5.09), 523 (4.34), 552 (sh, 3.88), 651 (3.61), 717 nm (3.23). UV-Vis (1% TFA-CH_2Cl_2): λ_{max} (log ε) 313 (4.42), 451 (5.06), 568 (4.08), 637 (3.86), 700 nm (3.93). ^{1}H NMR (500 MHz, $CDCl_3$): δ -4.00 (1H, s, 21-H), 7.69-7.74 (2H, m, 2^2,3^2-H), 7.77-7.85 (6H, m, *m*- and *p*-H), 8.18-8.23 (4H, m, 4 x *o*-Ph), 8.65 (1H, d, *J* = 4.3 Hz, 17-H), 8.71-8.74 (1H, m, 3^1-H), 8.76-8.78 (1H, m, 2^1-H), 8.99 (1H, d, *J* = 4.3 Hz, 18-H), 9.11 (1H, d, *J* = 4.6 Hz, 8-H), 9.36 (1H, d, *J* = 5.0 Hz, 12- or 13-H), 9.49 (1H, d, *J* = 4.6 Hz, 7-H), 9.59 (1H, d, *J* = 5.0 Hz, 12- or 13-H), 10.13 (1H, s, 5-H), 10.25 (1H, s, 20-H). ^{13}C (500 MHz, $CDCl_3$): δ 103.1 (5-CH), 115.9 (20-CH), 120.5 (3^1-CH), 120.8 (2^1-CH), 122.9 (21-CH), 124.4 (8-CH), 126.4 (7-CH), 127.5, 127.8, 127.9, 128.2, 128.4, 128.6, 128.9, 132.2 (12- or 13-CH), 132.9 (17-CH), 133.0, 133.7, 134.2, 135.4 (12-, 13- or 18-CH), 135.5 (12-, 13- or 18-CH), 139.7, 140.0, 140.9, 142.3, 144.3, 144.7, 146.0, 153.1, 153.4. ^{1}H NMR (500 MHz, TFA-$CDCl_3$): δ -5.90 (1H, s, 21-H), -3.85 (1H, br s, NH), 7.74-7.77 (2H, m, 2^2,3^2-H), 7.96-8.02 (6H, m, *m*- and *p*-H), 8.28-8.30 (2H, m), 8.38-8.41 (2H, m) (4 x *o*-Ph), 8.64-8.67 (2H, m, 2^1,3^1-H), 9.10 (1H, dd, *J* = 1,3, 4.6 Hz, 17-H), 9.41 (1H, br d, *J* = 4.6 Hz, 18-H), 9.68 (1H, d, *J* = 4.7 Hz, 8-H), 9.83 (1H, d, *J* = 5.0 Hz, 12- or 13-H), 9.98 (1H, d, *J* = 5.0 Hz, 12- or 13-H), 10.01 (1H, d, *J* = 4.7 Hz, 7-H), 10.50 (1H, s, 5-H), 10.55 (1H, s, 20-H). ^{13}C (500 MHz, $CDCl_3$): δ 106.7 (5-CH), 111.3 (20-CH), 118.8 (21-CH), 122.1

(2^1-CH), 122.4 (3^1-CH), 124.5, 129.1 (18-CH), 129.3, 130.2 (2^2- or 3^2-CH), 130.35 (2^2- or 3^2-CH), 130.41 (8-CH), 130.7, 130.95, 131.00 (17-CH), 131.7, 132.0 (7-CH), 134.2 (*o*-Ph), 135.8 (*o*-Ph), 137.0 (12- or 13-CH), 138.2, 138.9 (12- or 13-CH), 141.6, 142.49, 142.55, 142.61, 143.4, 143.7, 143.9, 145.1, 155.2, 156.2. HR-MS (ESI) calcd for $C_{37}H_{23}NOS$ + H 530.1579, found 530.1566.



10,15-Diphenyl-22-oxa-23-seleno-21-carbabenzo[*b*]porphyrin (**16c**). Oxacarbatripyrrin **8b** (49.9 mg, 0.0183 mmol) and selenophene dicarbinol **13c**[S3] (61.9 mg, 0.0180 mmol) were reacted under the foregoing conditions using chloroform as a solvent. The crude product was purified on a grade 3 alumina column eluting with dichloromethane and recrystallized from chloroform-hexanes to give the oxaselenaporphyrin (10.0 mg, 17.3 μmol, 9.6%) as a dark solid, mp >300 ºC. UV-Vis (1% Et_3N-CH_2Cl_2): λ_{max} (log ε) 310 (4.26), 439 (4.92), 528 (4.17), 562 (3.76), 652 (3.50), 717 nm (3.08). UV-Vis (1% TFA-CH_2Cl_2): λ_{max} (log ε) 320 (4.27), 465 (4.89), 581 (3.88), 649 (3.77), 714 nm (3.77). ^{1}H NMR (500 MHz, $CDCl_3$): δ -3.86 (1H, s, 21-H), 7.67-7.73 (2H, m, 2^2,3^2-H), 7.75-7.85 (6H, m, *m*- and *p*-H), 8.16-8.19 (2H, m) 8.23-8.25 (2H, m) (4 x *o*-Ph), 8.67-8.69 (2H, m, 2^1- and 17-H), 8.73-8.75 (1H, m, 2^1-H), 9.01 (1H, d, *J* = 4.3 Hz, 18-H), 9.09 (1H, d, *J* = 4.4 Hz, 8-H), 9.44 (1H, d, *J* = 4.4 Hz, 7-H), 9.65 (1H, d, *J* = 5.5 Hz, 12- or 13-H), 9.87 (1H, d, *J* = 5.5 Hz, 12- or 13-H), 10.15 (1H, s, 5-H), 10.24 (1H, s, 20-H). ^{13}C (500 MHz, $CDCl_3$): δ 104.0 (5-CH), 116.2 (20-CH), 120.6 (3^1-CH), 120.8 (2^1-CH), 122.9 (21-CH), 123.6 (8-CH), 124.4, 126.0 (7-CH), 127.4, 127.9, 128.08, 128.15, 128.5, 128.8, 132.0 (17-CH), 133.6, 134.25, 134.34 (12- or 13-CH), 134.9, 136.0 (18-CH), 136.5, 137.0 (12- or 13-CH), 138.7, 139.6, 140.6, 144.0, 144.7, 145.3, 150.8, 152.7, 154.2, 155.2, 157.3. ^{1}H NMR (500 MHz, TFA-$CDCl_3$): δ -5.23 (1H, s, 21-H), -3.62 (1H, br s, NH), 7.64-7.69 (2H, m, 2^2,3^2-H), 7.97-8.06 (6H, m, *m*- and *p*-H), 8.28-8.31 (2H, m, 10-*o*-Ph), 8.44-8.47 (2H, m, 15-*o*-Ph), 8.53-8.56 (2H, m, 2^1,3^1-H), 9.07 (1H, dd, *J* = 4.6 Hz, 17-H), 9.33 (1H, d, *J* = 4.6 Hz, 18-H), 9.66 (1H, d, *J* = 4.7 Hz, 8-H), 9.88 (1H, d, *J* = 5.2 Hz, 12-H), 9.97 (1H, d, *J* = 4.7 Hz, 7-H), 10.08 (1H, d, *J* = 5.2 Hz, 13-H), 10.39 (1H, s, 5-H), 10.47 (1H,

s, 20-H). ^{13}C (500 MHz, $CDCl_3$): δ 106.5 (5-CH), 111.9 (20-CH), 118.0 (21-CH), 121.9 (2^1- or 3^1-CH), 122.4 (2^1- or 3^1-CH), 125.5, 128.8 (18-CH), 129.5, 129.6, 129.8 (8-CH), 130.0, 130.2, 130.5 (17-CH), 130.7, 131.2, 132.2 (7-CH), 134.5 (10-*o*-Ph), 135.5, 136.6 (15-*o*-Ph), 137.1, 138.6 (12-CH), 140.5 (13-CH), 141.4, 142.2, 142.5, 142.7, 143.68, 143.76, 149.9, 150.3. HR-MS (ESI) calcd for $C_{37}H_{23}NOSe$ + H 578.1023, found 578.1038.

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S1 (a) C. Tardieux, F. Bolze, C. P. Gros and R. Guilard, *Synthesis*, 1998, 267-268. (b) R. Li, A. D. Lammer, G. M. Ferrence and T. D. Lash, *J. Org. Chem.*, 2014, **79**, 4078-4093.

S2 B. L. Feringa, R. Hulst, R. Rikers and L. Brandsma, *Synthesis*, 1988, 316-318.

S3 (a) C. E. Stilts, M. I. Nelen, D. G. Hilmey, S. R. Davies, S. O. Gollnick, A. R. Oseroff, S. L. Gibson, R. Hilf, M. R. Detty, *J. Med. Chem.* 2000, **43**, 2403−2410. (b) D. G. Hilmey, M. Abe, M. I. Nelen, C. E. Stilts, G. A. Baker, S. N. Baker, F. V. Bright, S. R. Davies, S. O. Gollnick, A. R. Oseroff, S. L. Gibson, R. Hilf and M. R. Detty, *J. Med. Chem.* 2002, **45**, 449−461.

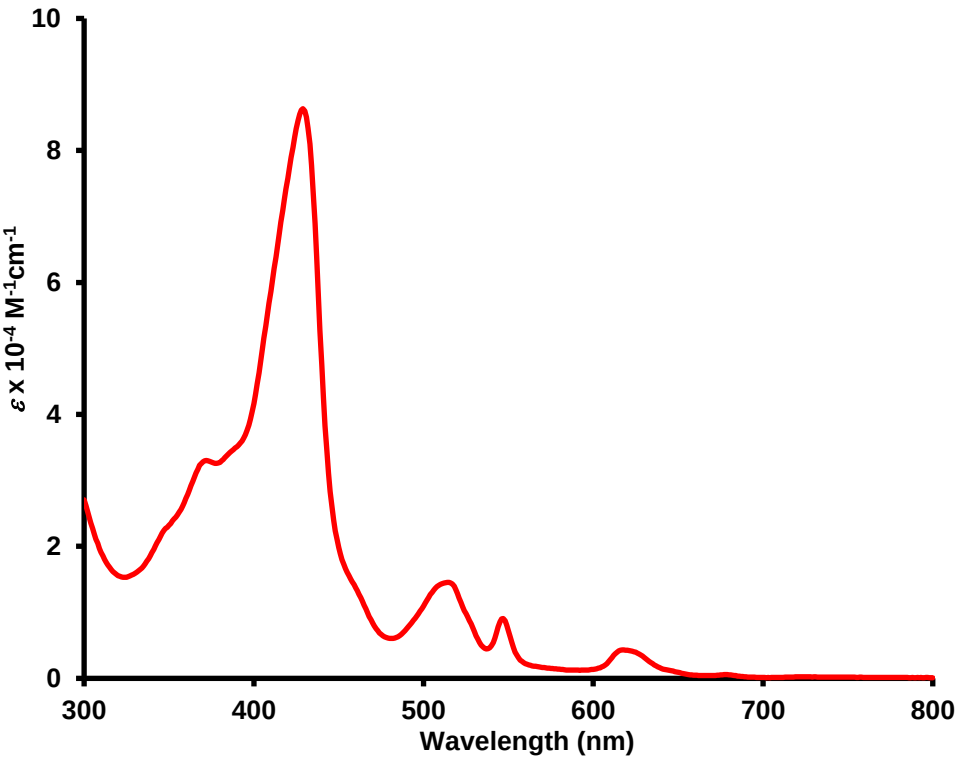

Figure S1. UV-vis spectrum of dimethyl 22-oxa-21-carbaporphyrin **15a** in 1% Et_3N-CH_2Cl_2.

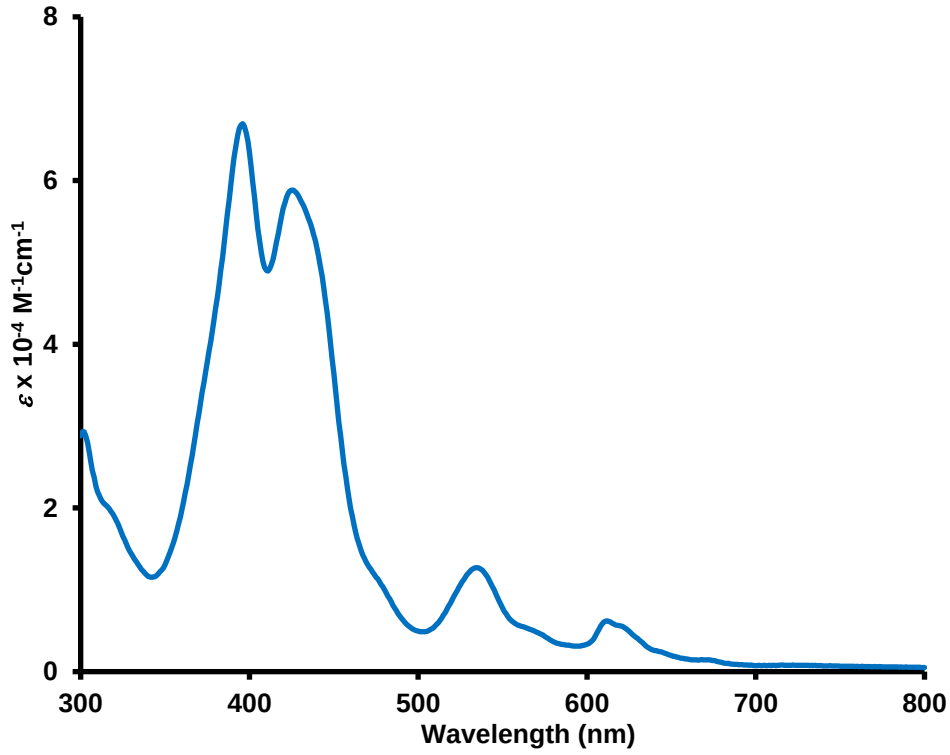

Figure S2. UV-vis spectrum of dimethyl 22-oxa-21-carbaporphyrin cation **15a**H^+ in 1% TFA-CH_2Cl_2.

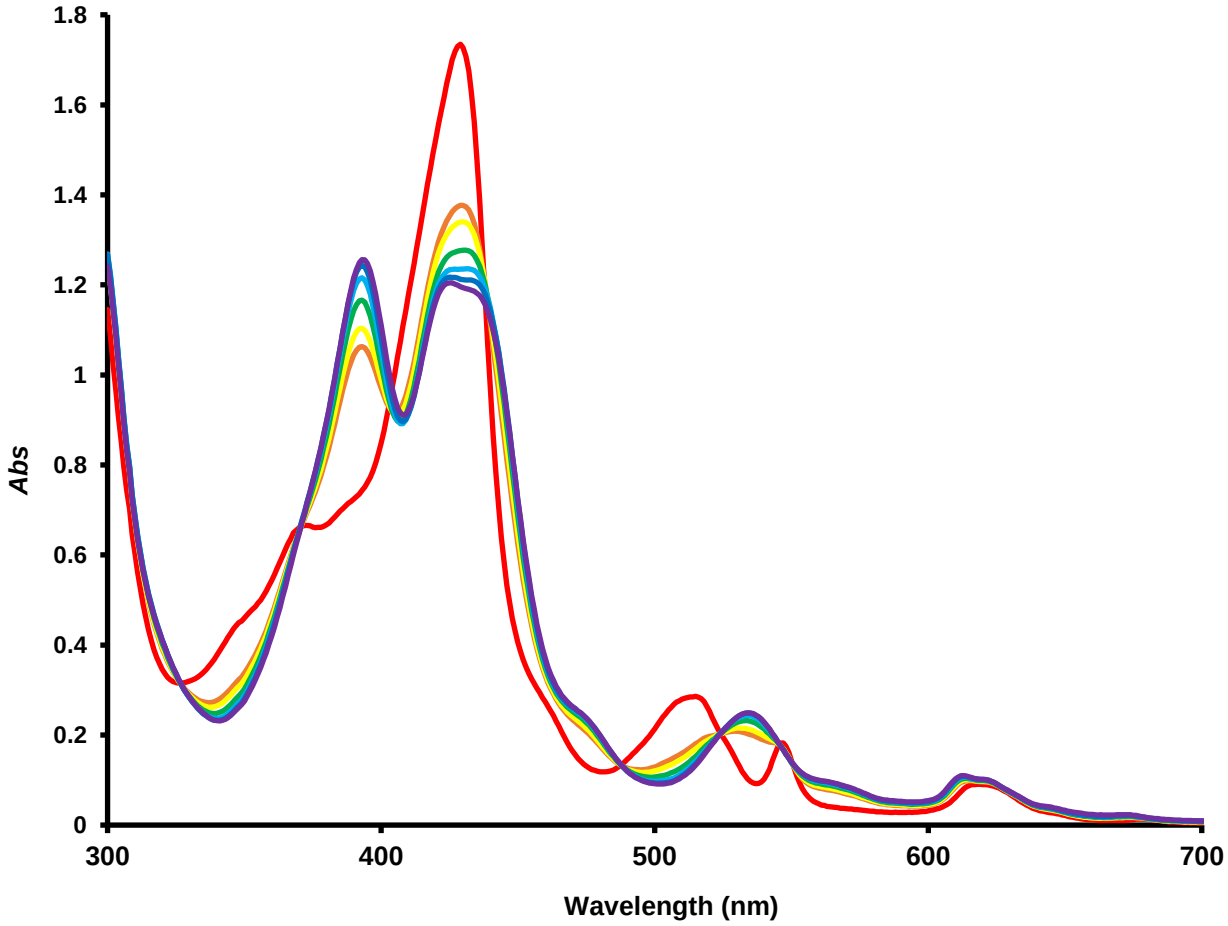

Figure S3. UV-vis spectra of dimethyl 22-oxa-21-carbaporphyrin with 0 equiv (red), 10 equiv (orange), 20 equiv (yellow), 50 equiv (green), 100 equiv (light blue), 200 equiv (dark blue) and 500 equiv of TFA (purple) in dichloromethane.

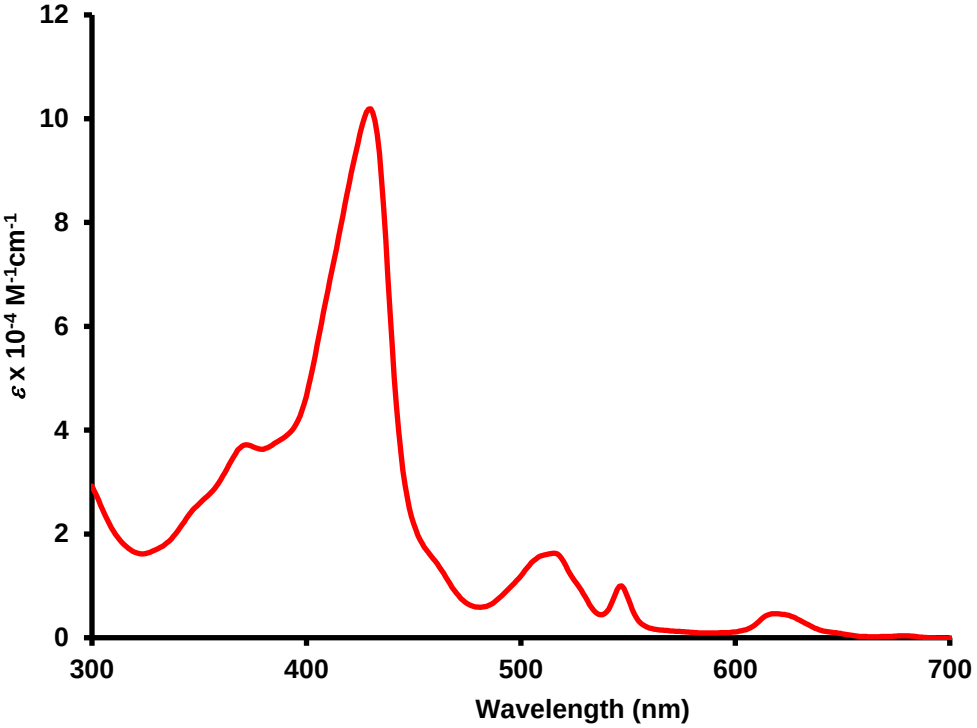

Figure S4. UV-vis spectrum of diethyl 22-oxa-21-carbaporphyrin **15b** in 1% Et_3N-CH_2Cl_2.

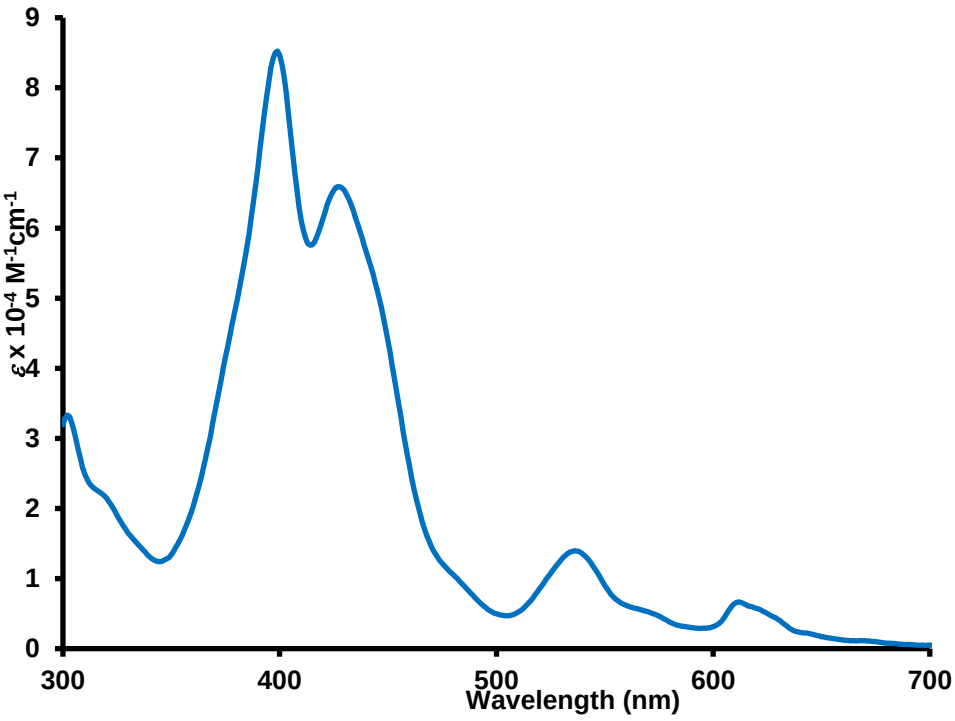

Figure S5. UV-vis spectrum of diethyl 22-oxa-21-carbaporphyrin cation **15b**H^+ in 1% TFA-CH_2Cl_2.

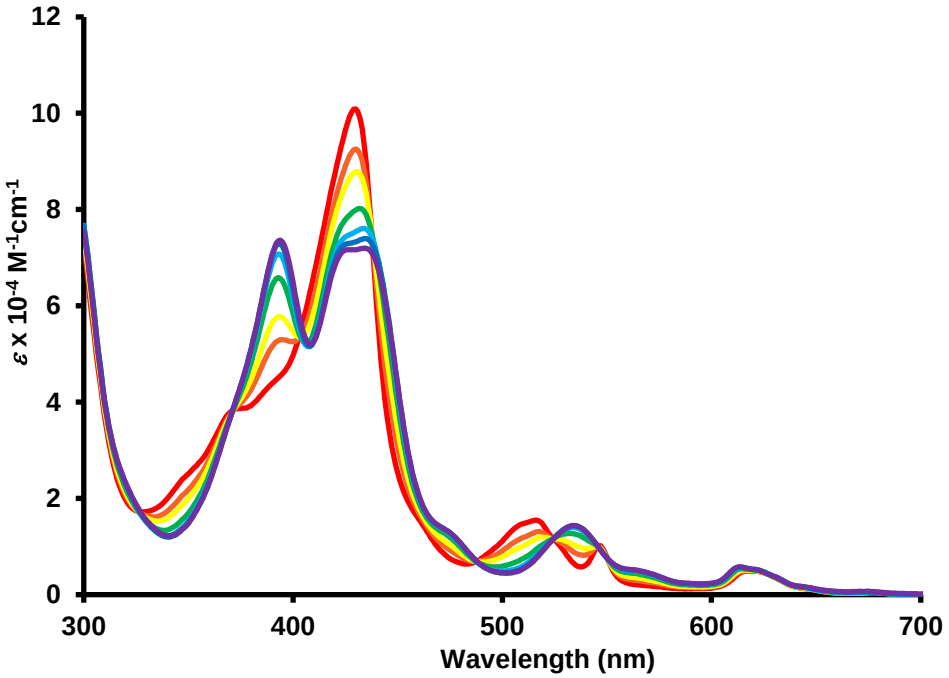

Figure S6. UV-vis spectra of diethyl 22-oxa-21-carbaporphyrin **15b** with 0 equiv (red), 10 equiv (orange), 20 equiv (yellow), 50 equiv (green), 100 equiv (light blue), 200 equiv (dark blue) and 500 equiv of TFA (purple).

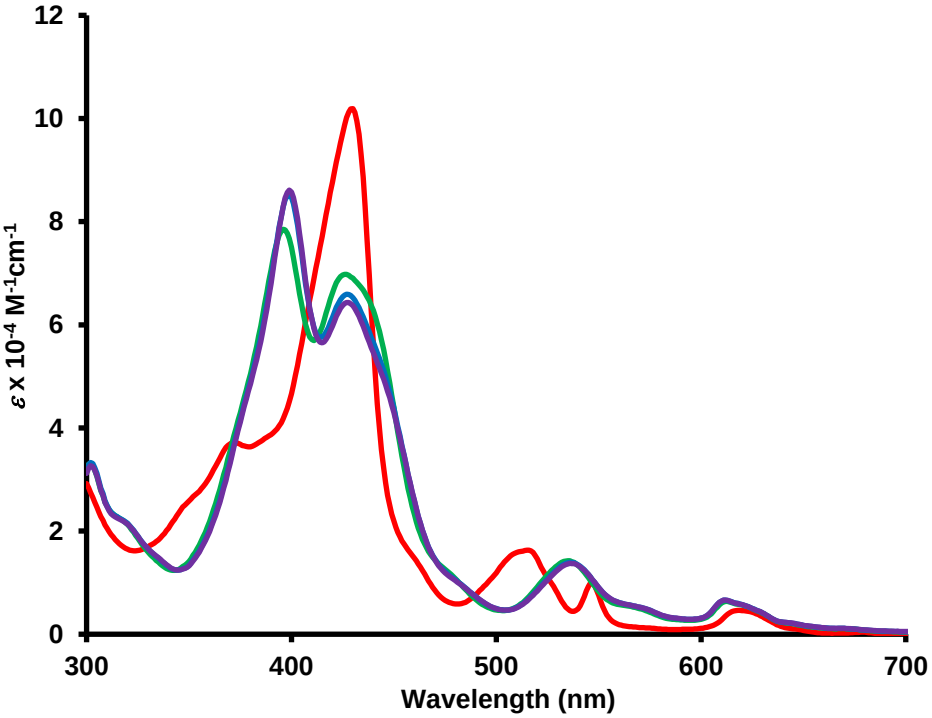

Figure S7. UV-vis spectra of diethyl 22-oxa-21-carbaporphyrin **15b** in CH_2Cl_2 with 1% Et_3N (red), 1% TFA (green), 5% TFA (blue) and 10% TFA (purple).

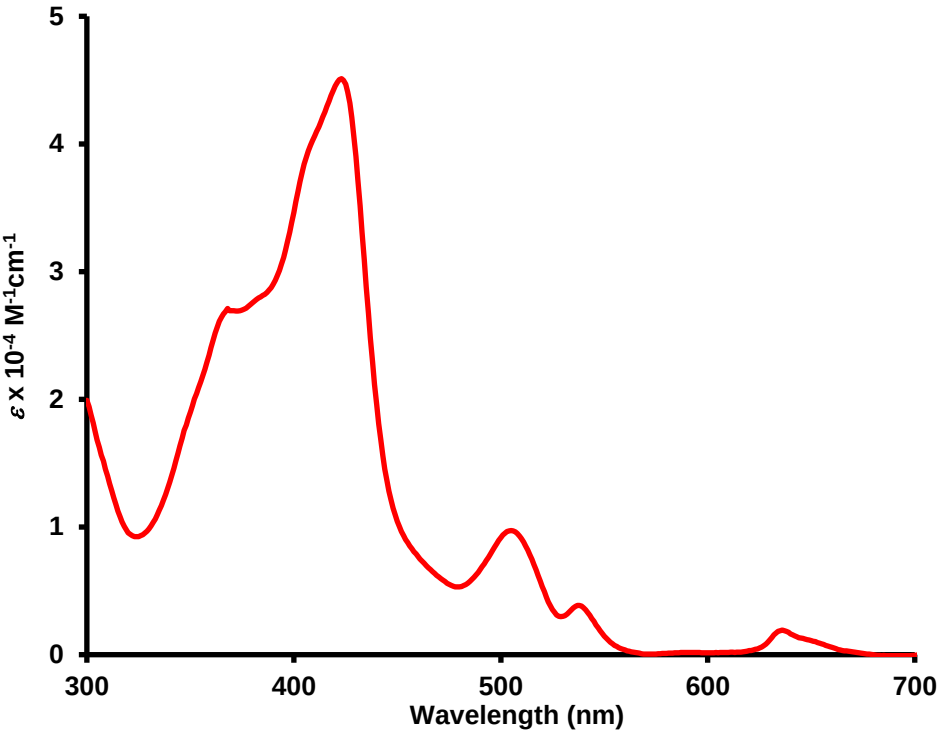

Figure S8. UV-vis spectrum of 22,23-dioxa-21-carbaporphyrin **12b** in 1% Et_3N-CH_2Cl_2.

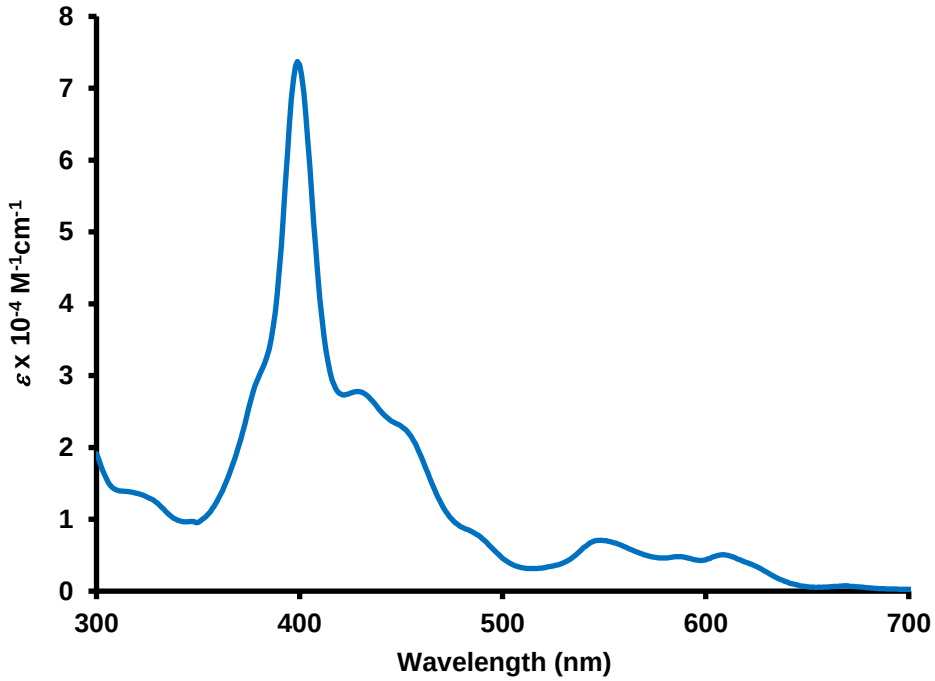

Figure S9. UV-vis spectrum of 22,23-dioxa-21-carbaporphyrin monocation **12b**H^+ in 1% TFA-CH_2Cl_2.

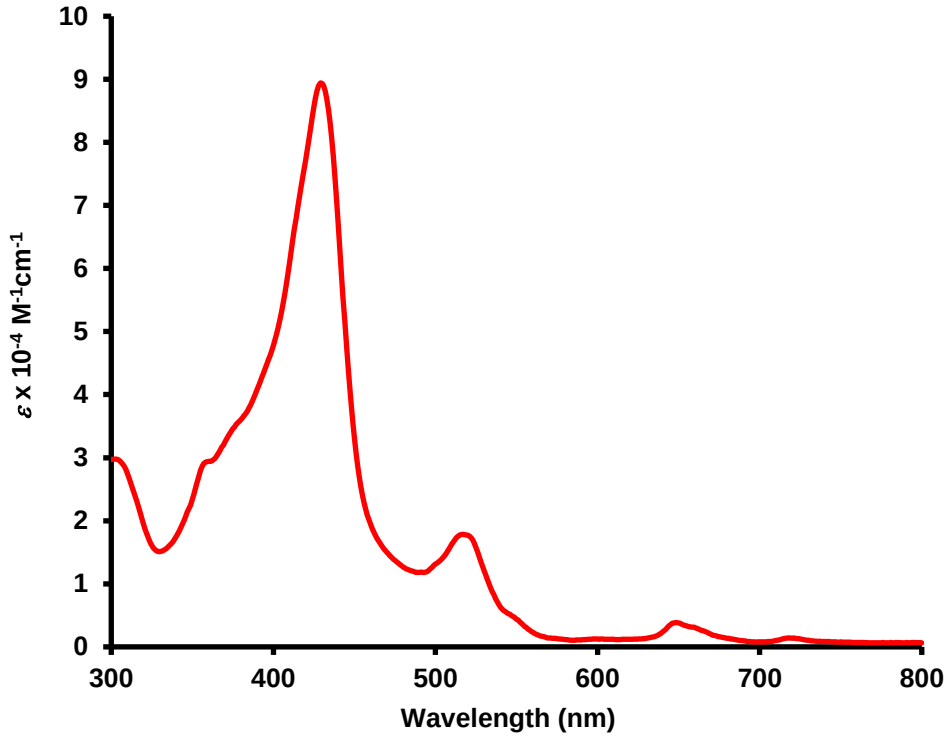

Figure S10. UV-Vis spectrum of diphenyldioxacarbaporphyrin **16a** in 1% Et_3N-CH_2Cl_2.

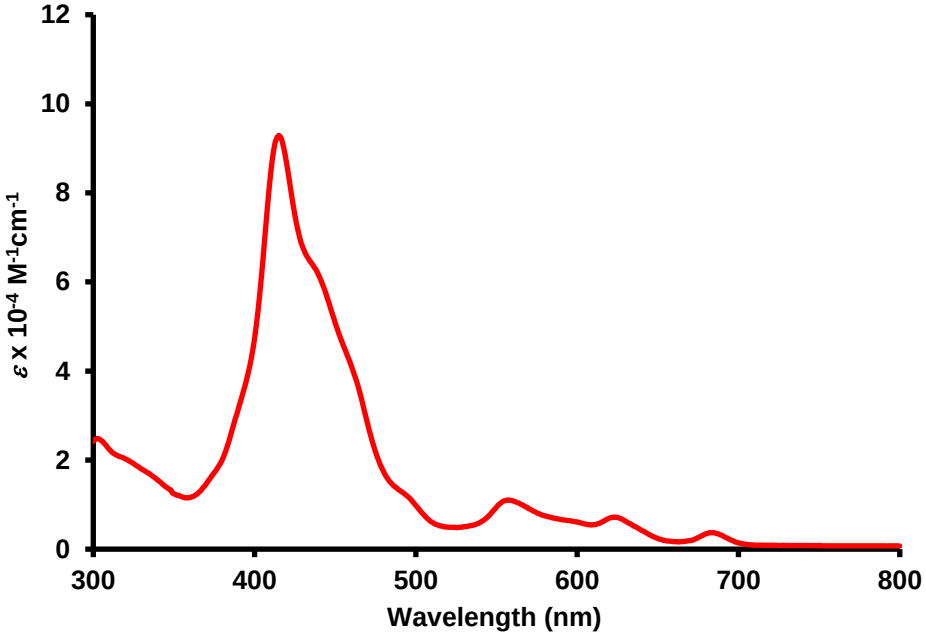

Figure S11. UV-Vis spectrum of diphenyldioxacarbaporphyrin **16a** in 1% TFA-CH_2Cl_2.

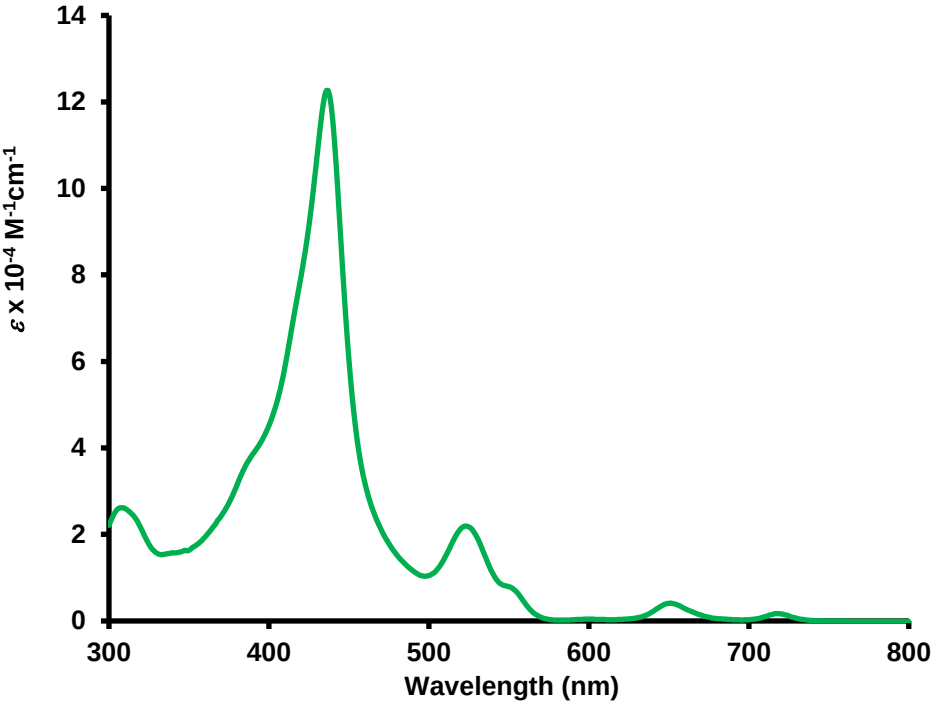

Figure S12. UV-Vis spectrum of diphenyloxathiacarbaporphyrin **16b** in 1% Et_3N-CH_2Cl_2.

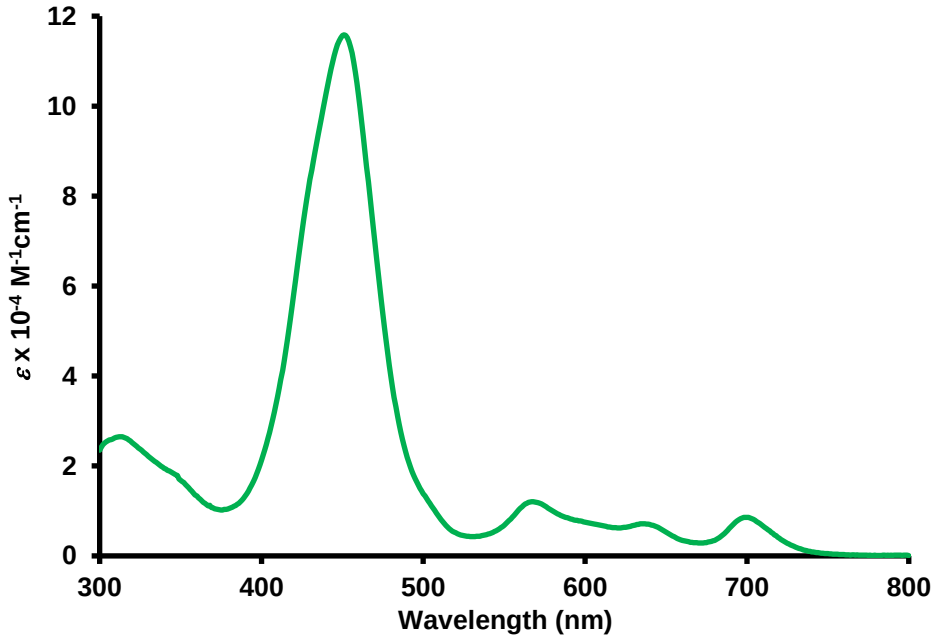

Figure S13. UV-Vis spectra of diphenyloxathiacarbaporphyrin monocation **16b** in 1% TFA-CH_2Cl_2.

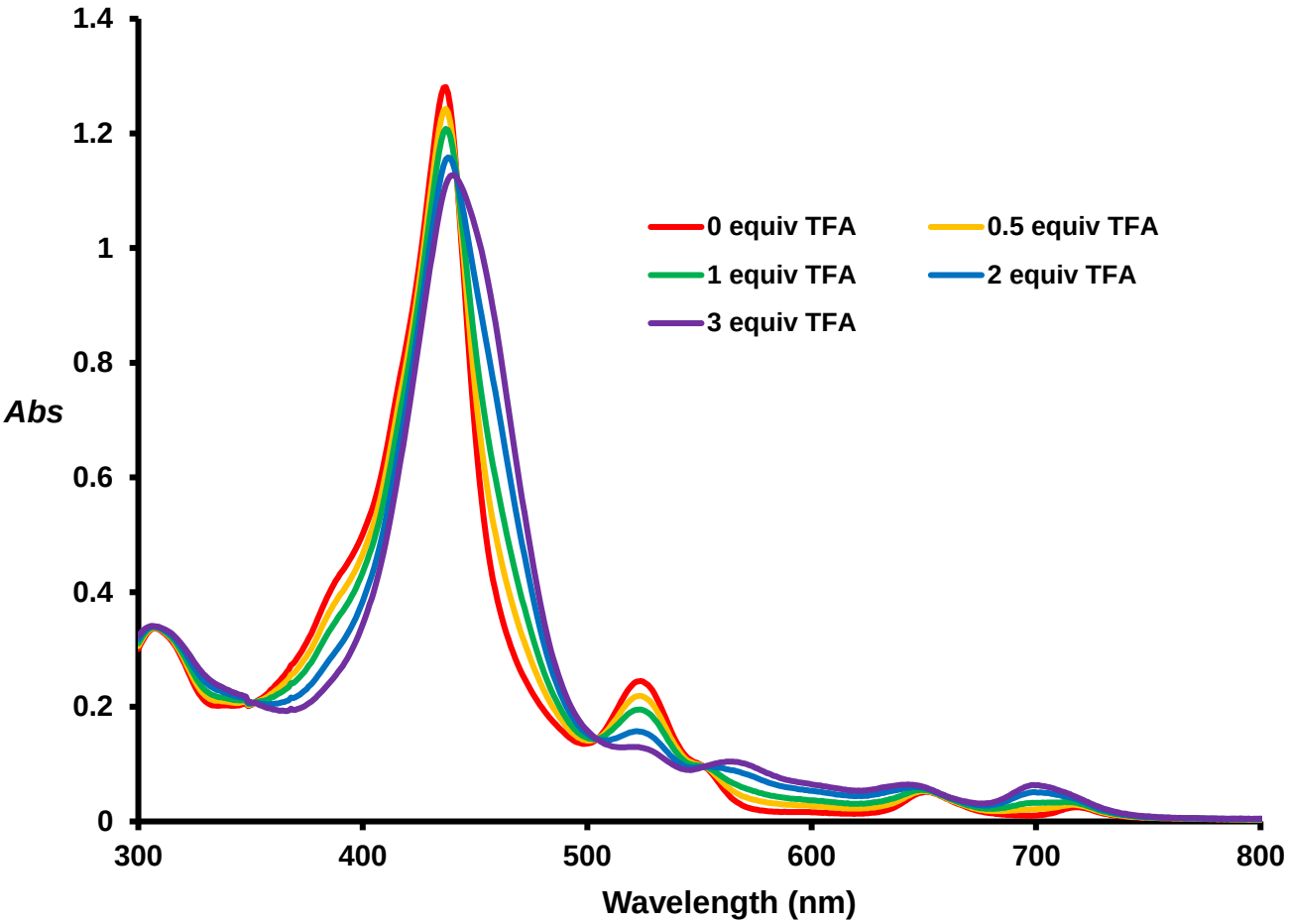

Figure S14. UV-Vis spectra of diphenyloxathiacarbaporphyrin **16b** in dichloromethane with 0-3 equivalents of TFA.

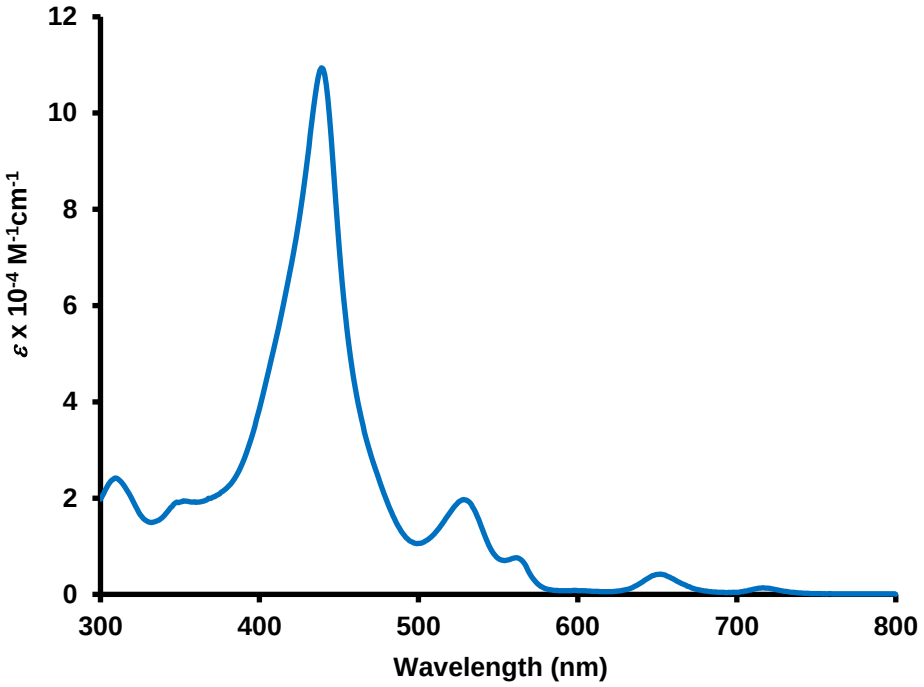

Figure S15. UV-Vis spectrum of diphenyloxaselenacarbaporphyrin **16c** in 1% Et_3N-CH_2Cl_2.

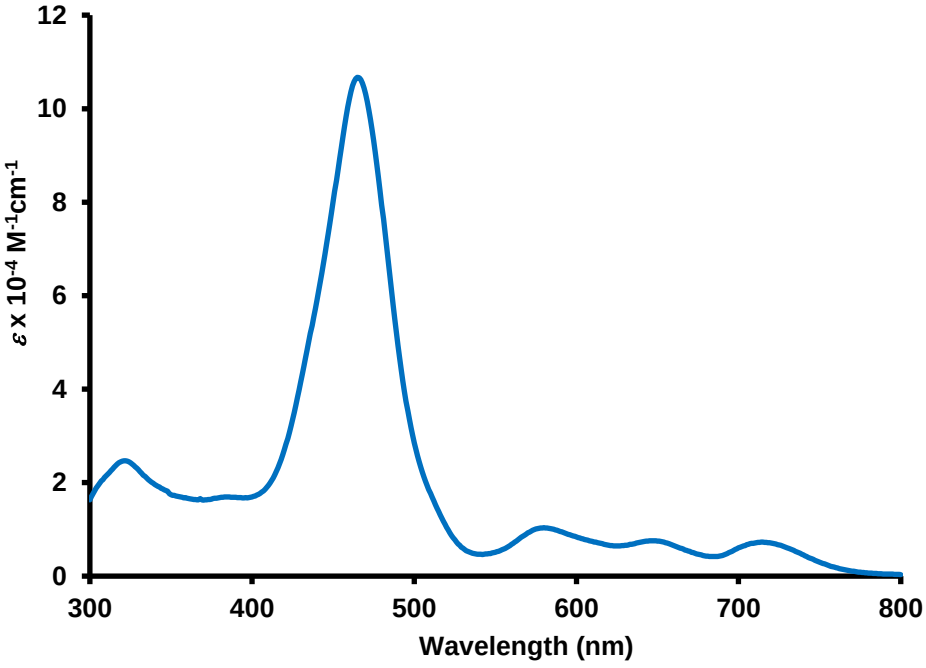

Figure S16. UV-Vis spectra of diphenyloxaselenacarbaporphyrin monocation **16c**H^+ in 1% TFA-CH_2Cl_2.

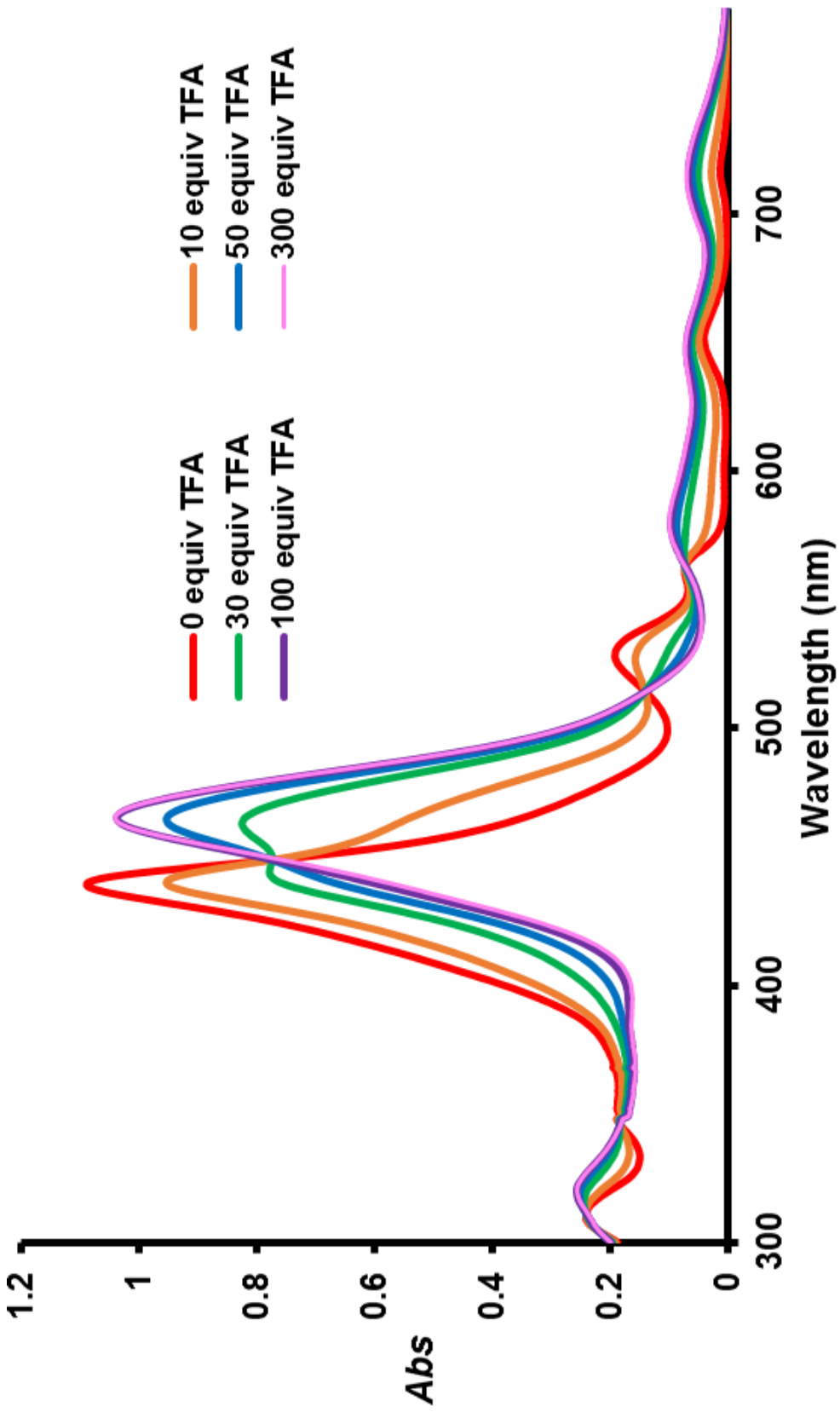

Figure S17. UV-Vis spectra of diphenylselenacarbaporphyrin **16c** in dichloromethane with 0-300 equivalents of TFA.

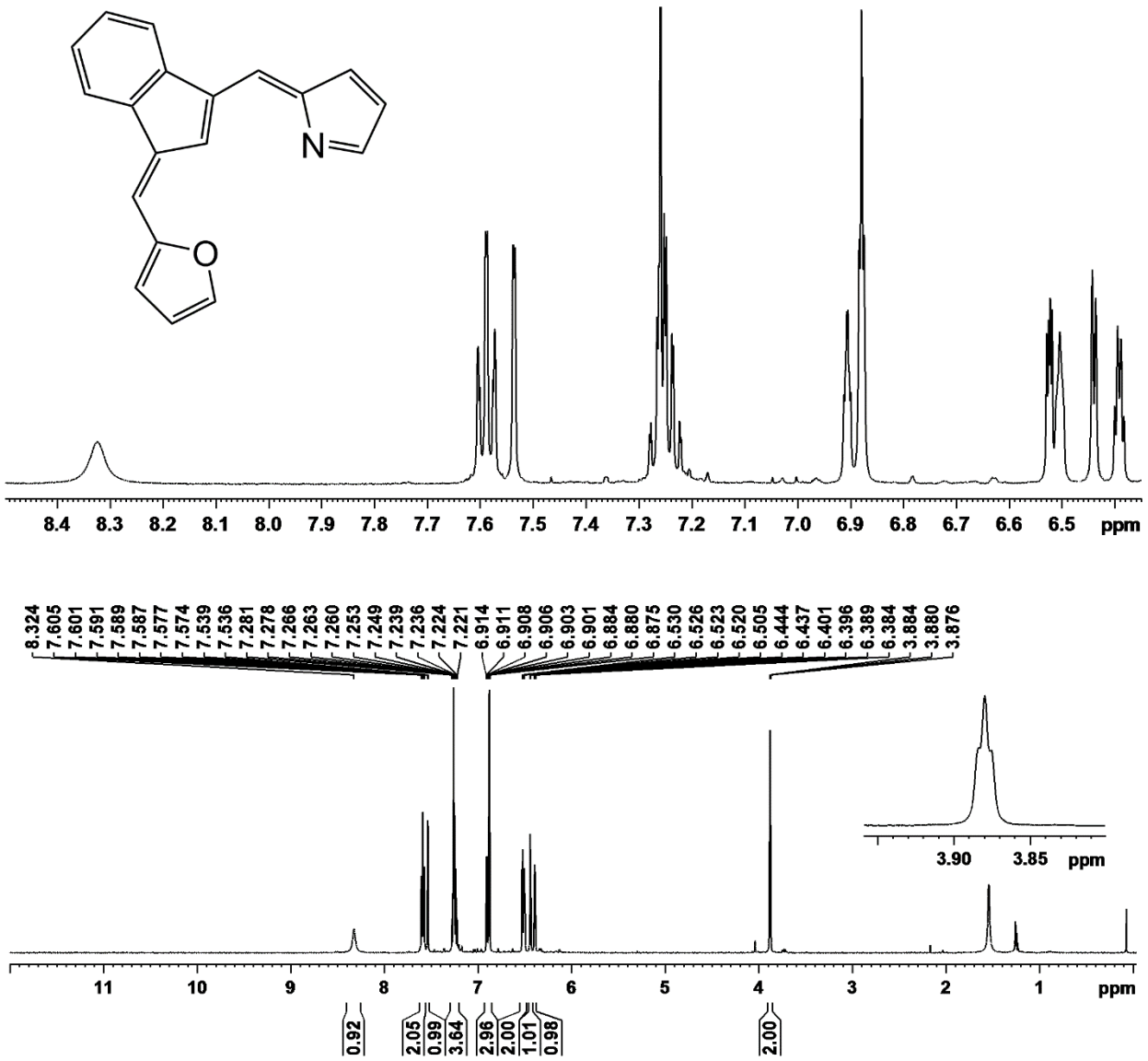

Figure S18. 500 MHz proton NMR spectrum of oxacarbatripyrrin **8b** in $CDCl_3$.

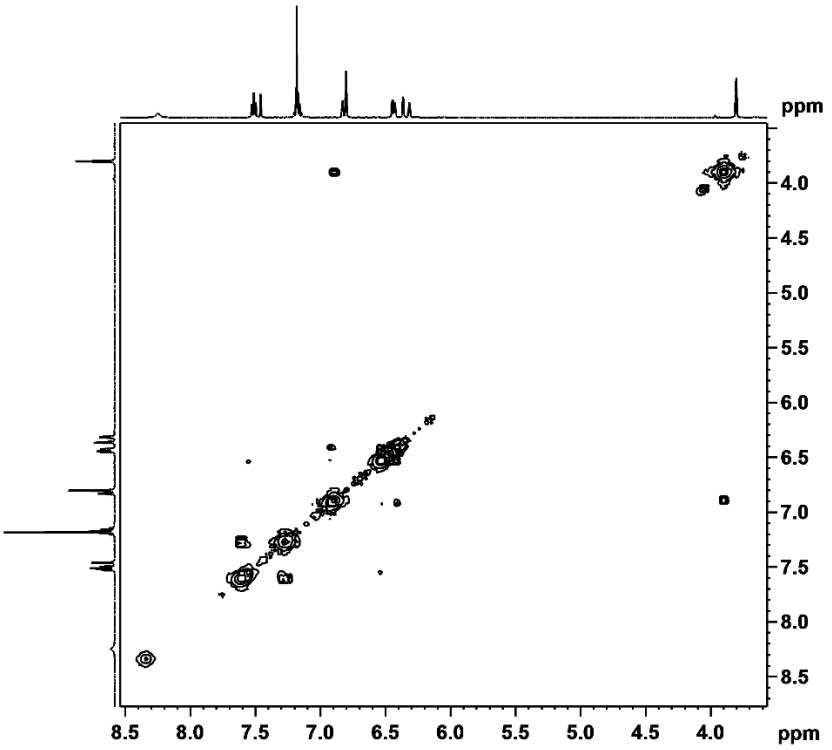

Figure S19. ^{1}H-^{1}H COSY NMR spectrum of oxacarbatripyrrin **8b** in $CDCl_3$.

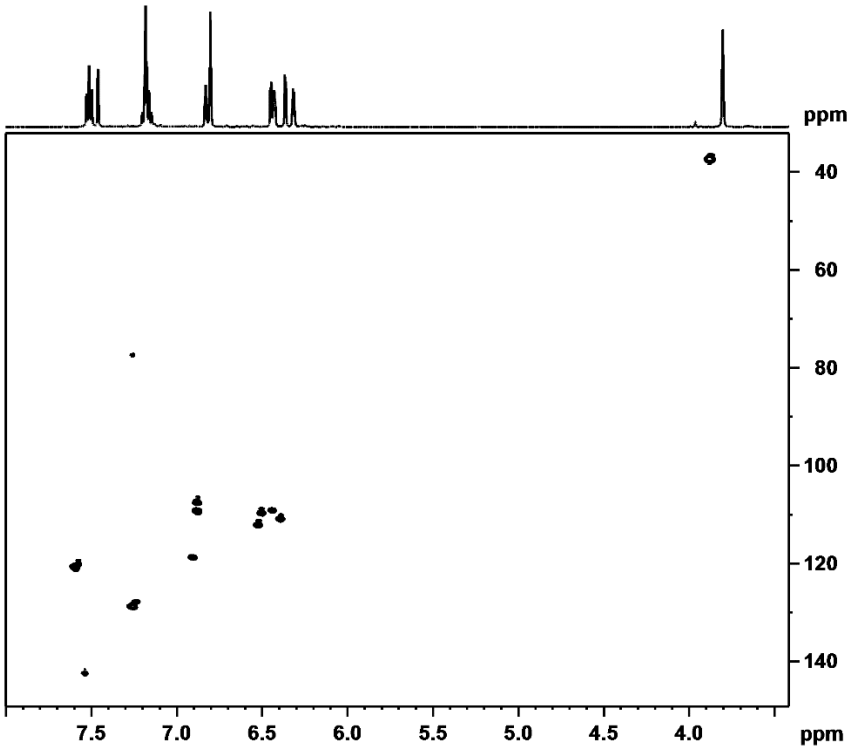

Figure S20. HSQC NMR spectrum of oxacarbatripyrrin **8b** in $CDCl_3$.

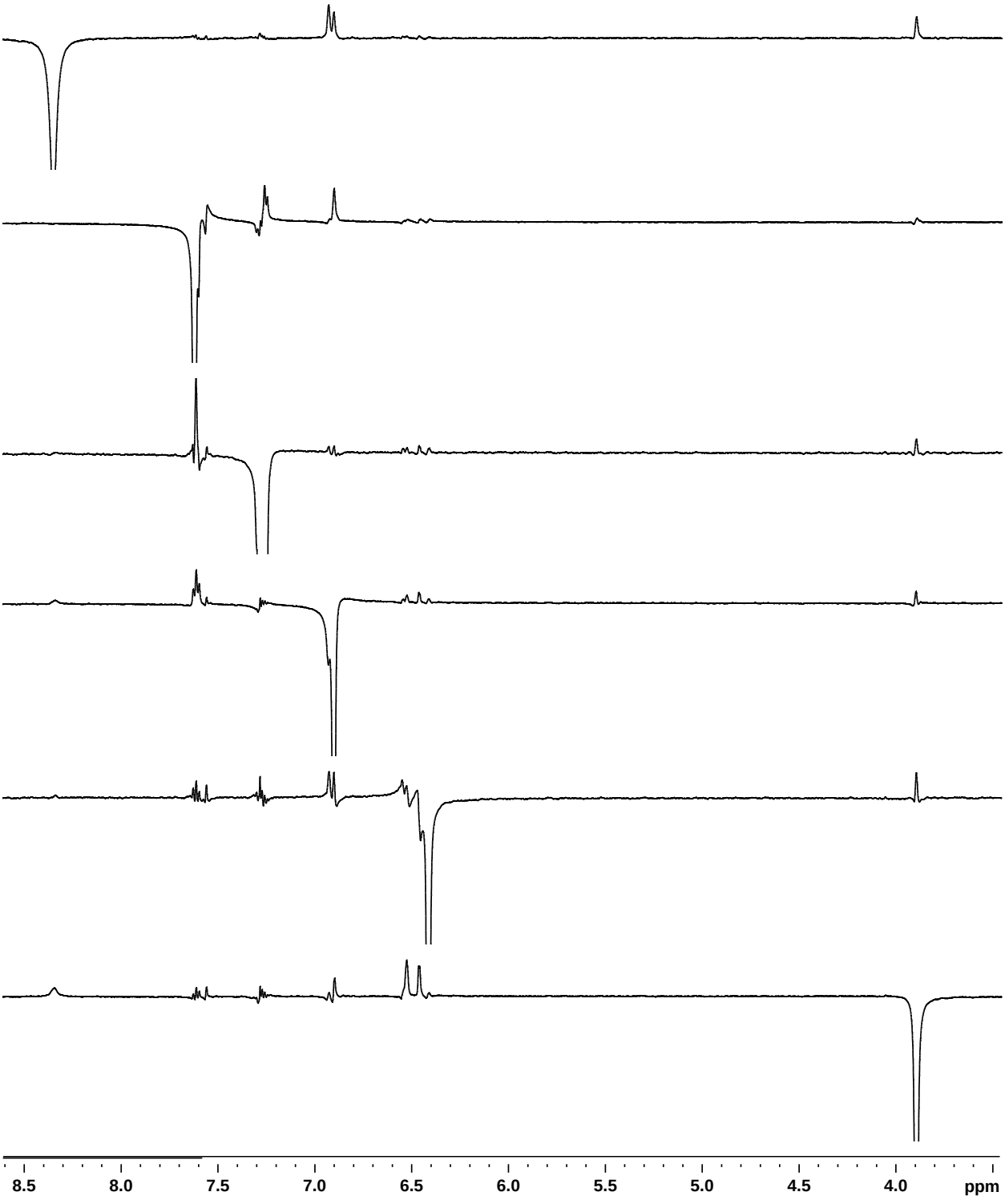

Figure S21. Selected nOe difference proton NMR spectra of oxacarbatripyrrin **8b** in $CDCl_3$.

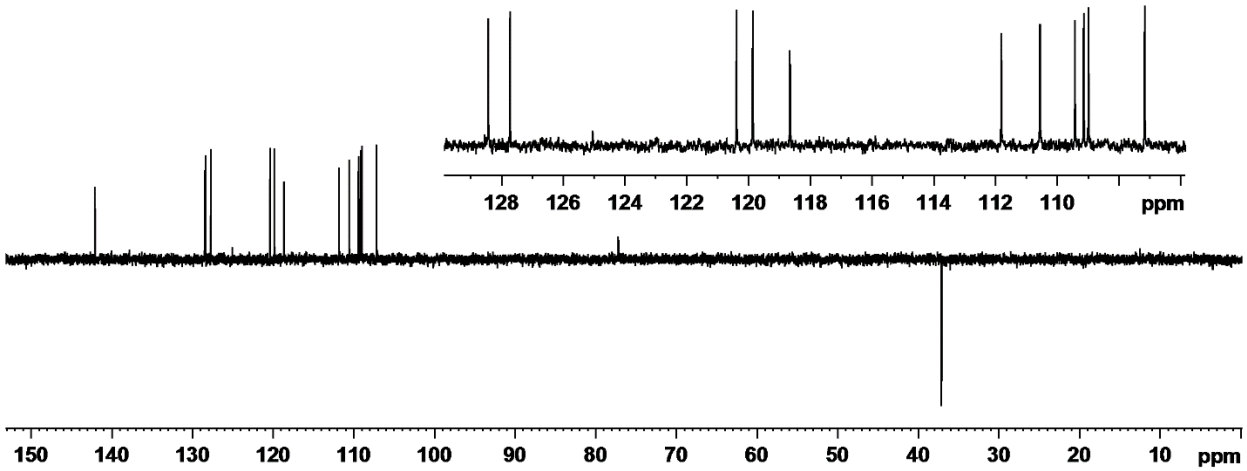

Figure S22. DEPT-135 NMR spectrum of oxacarbatripyrrin **8b** in $CDCl_3$.

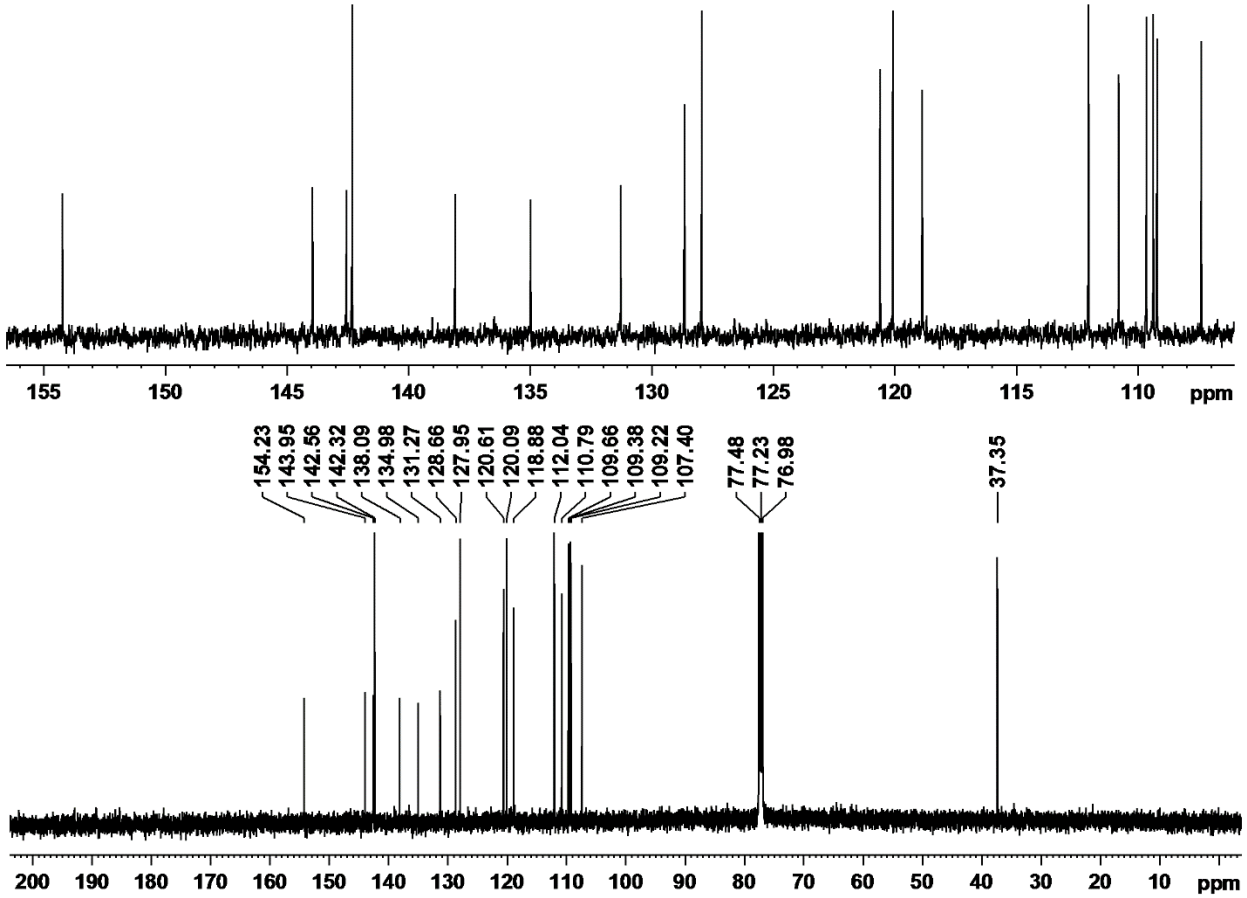

Figure S23. 125 MHz carbon-13 NMR spectrum of oxacarbatripyrrin **8b** in $CDCl_3$.

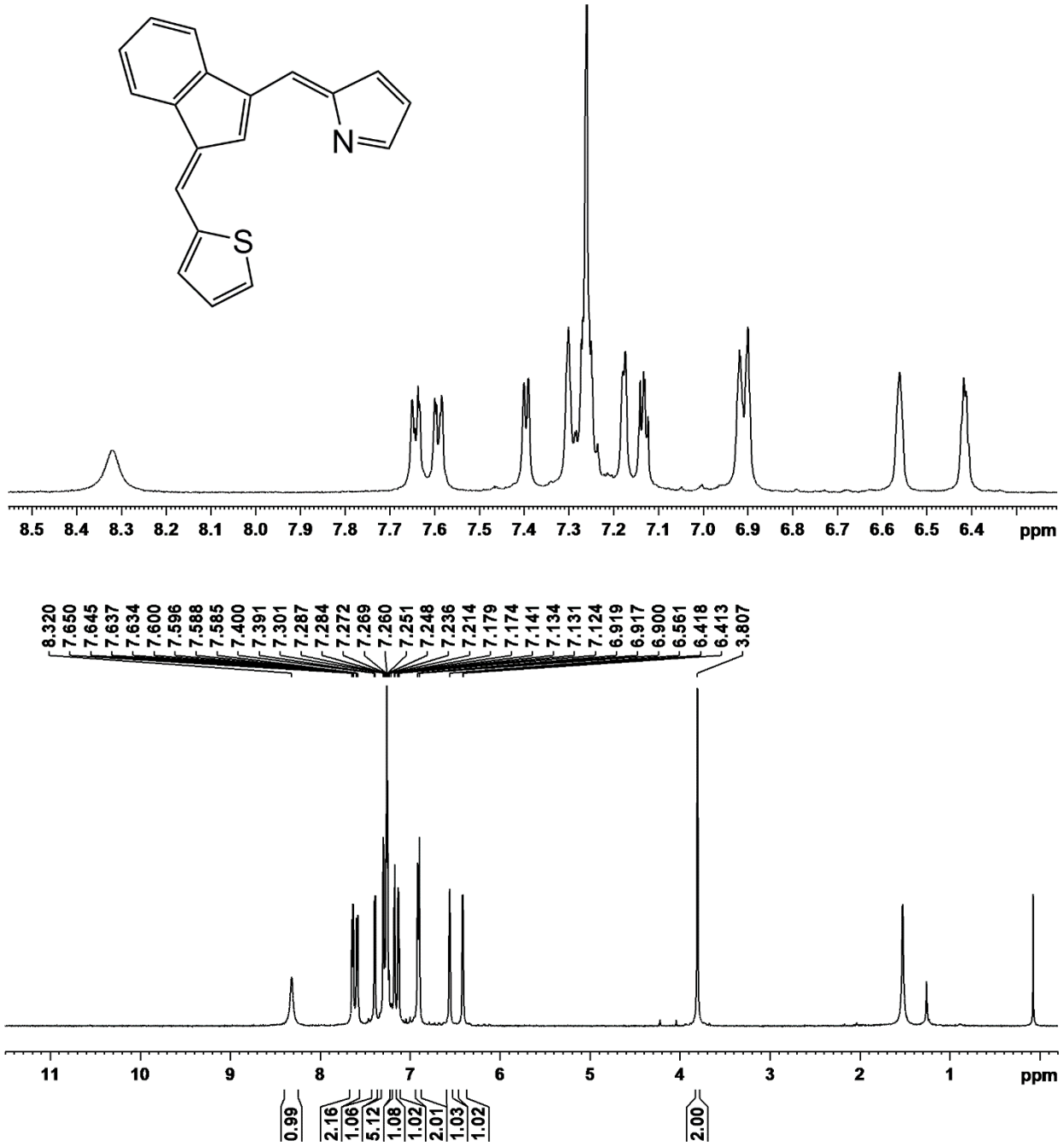

Figure S24. 500 MHz proton NMR spectrum of thiacarbatripyrrin **8c** in $CDCl_3$.

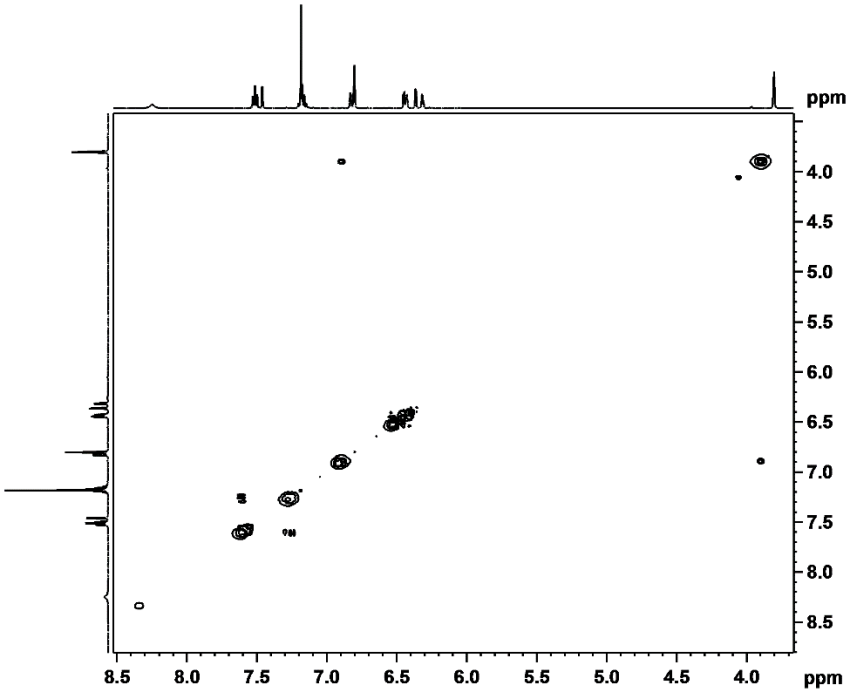

Figure S25. ^{1}H-^{1}H COSY NMR spectrum of thiacarbatripyrrin **8c** in $CDCl_3$.

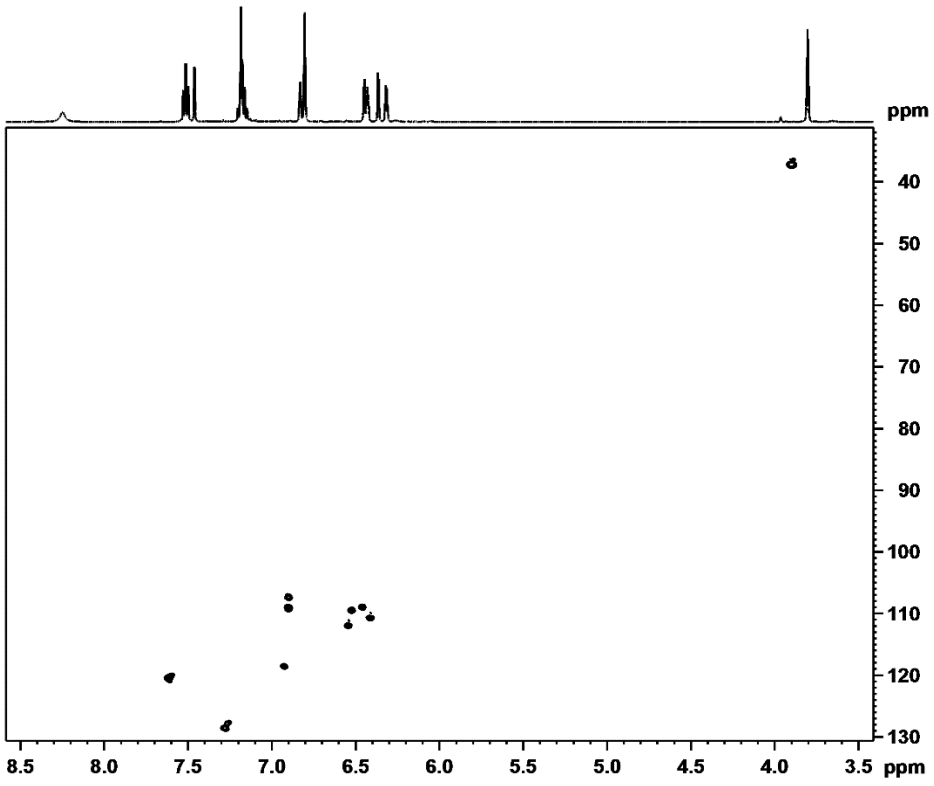

Figure S26. HSQC NMR spectrum of thiacarbatripyrrin **8c** in $CDCl_3$.

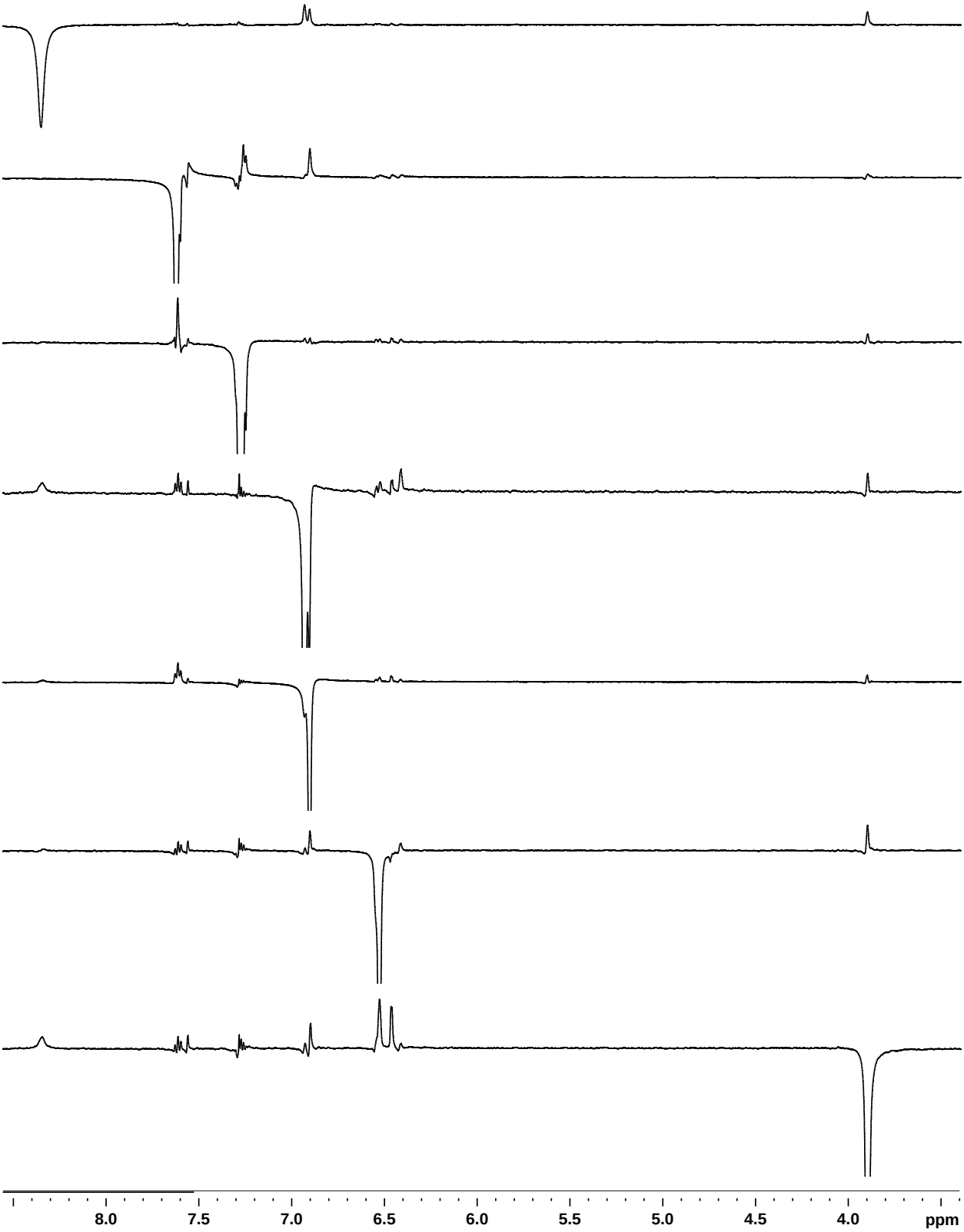

Figure S27. Selected nOe difference proton NMR spectra of thiacarbatripyrrin **8c** in $CDCl_3$.

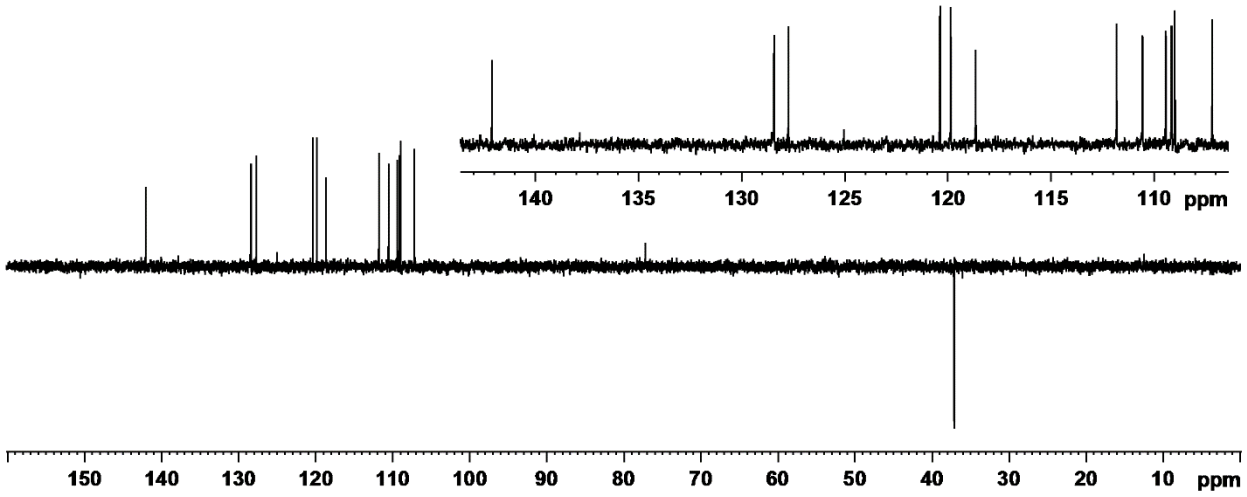

Figure S28. DEPT-135 NMR spectrum of thiacarbatripyrrin **8c** in $CDCl_3$.

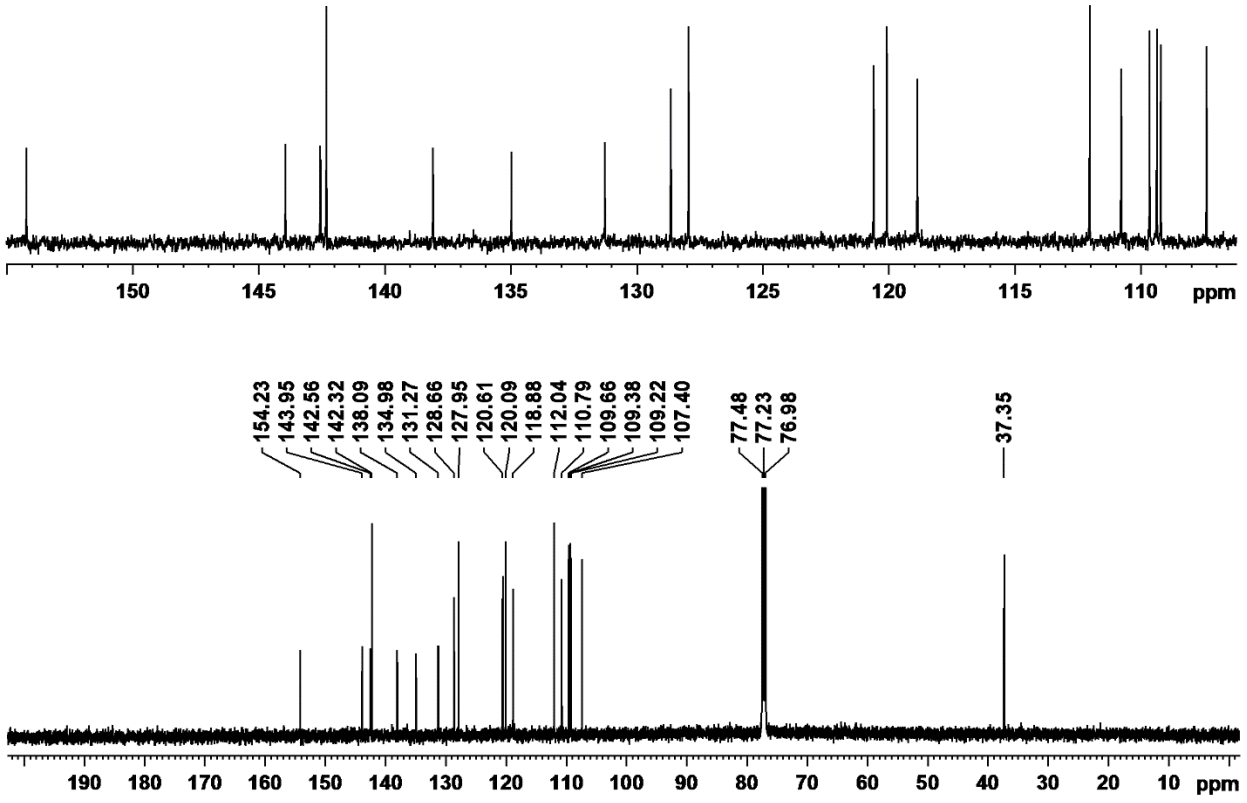

Figure S29. 125 MHz carbon-13 NMR spectrum of thiacarbatripyrrin **8c** in $CDCl_3$.

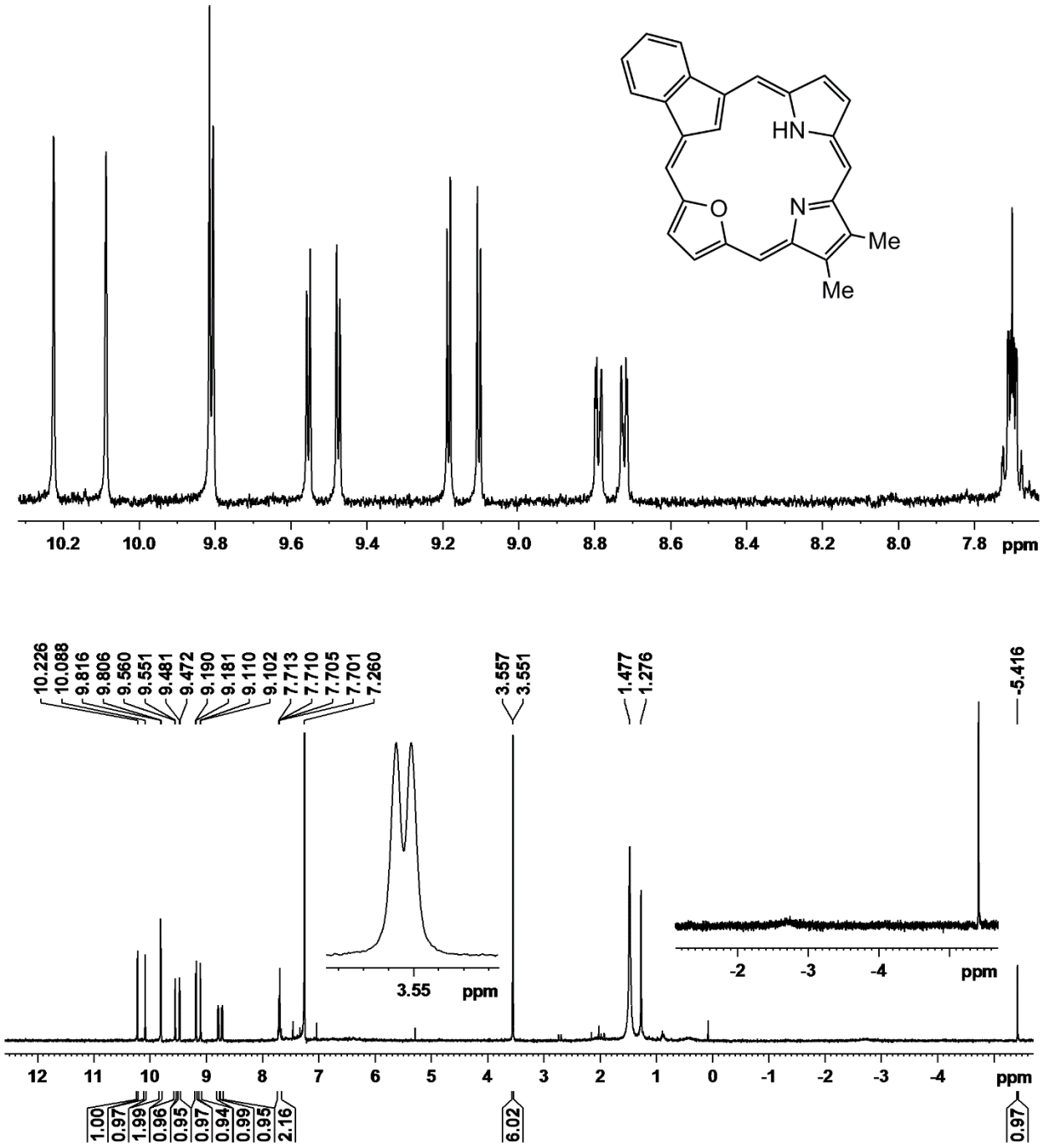

Figure S30. 500 MHz proton NMR spectrum of dimethyl oxacarbaporphyrin **15a** in $CDCl_3$ at 50 ^{o}C.

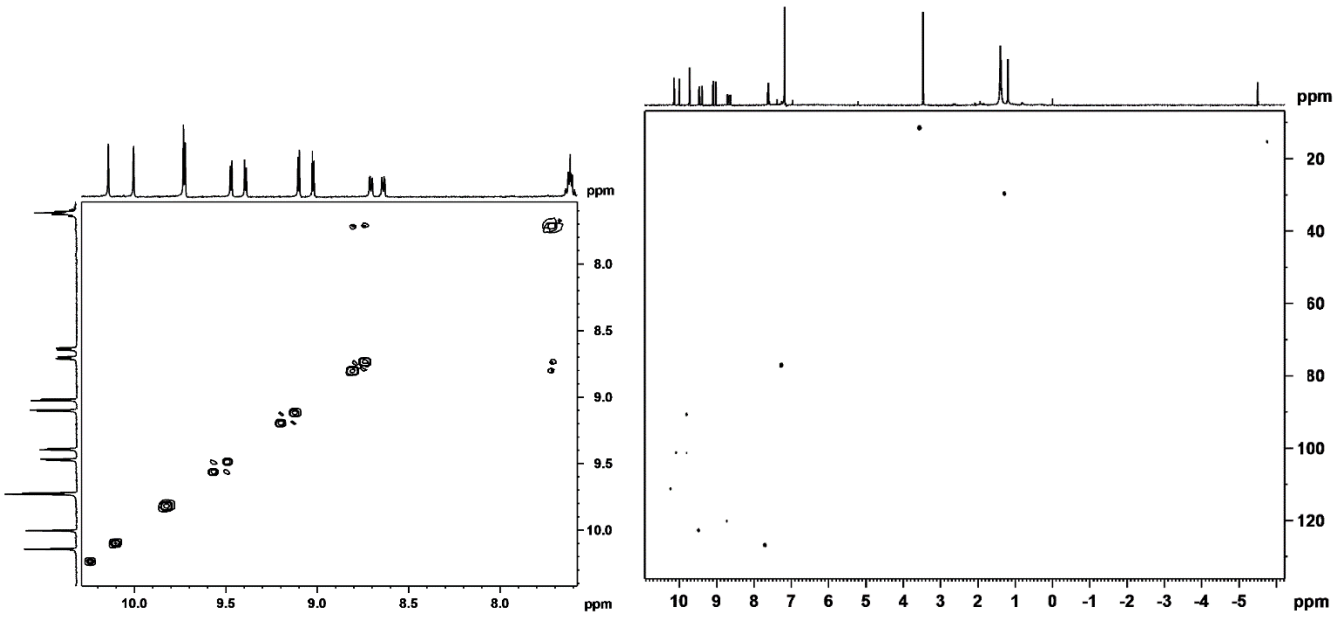

Figure S31. ^{1}H-^{1}H COSY (left) and HSQC (right) NMR spectra of dimethyl oxacarbaporphyrin **15a** in $CDCl_3$.

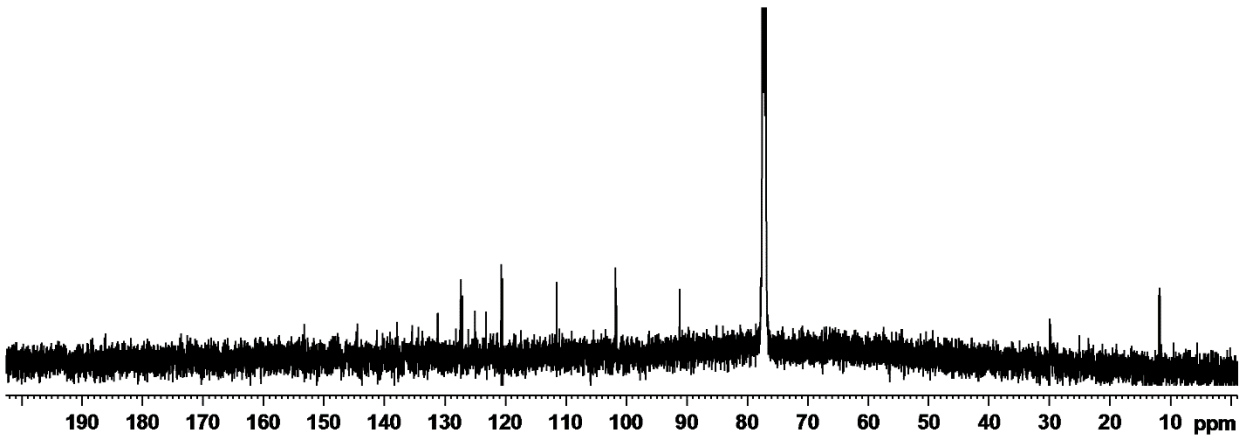

Figure S32. Poor quality 125 MHz carbon-13 NMR spectrum of dimethyl oxacarbaporphyrin **15a** in $CDCl_3$ at 50 ^{o}C. The high signal to noise ratio is due to the very low solubility of **15a**. This carbon-13 NMR spectrum required 16 hours of instrument time.

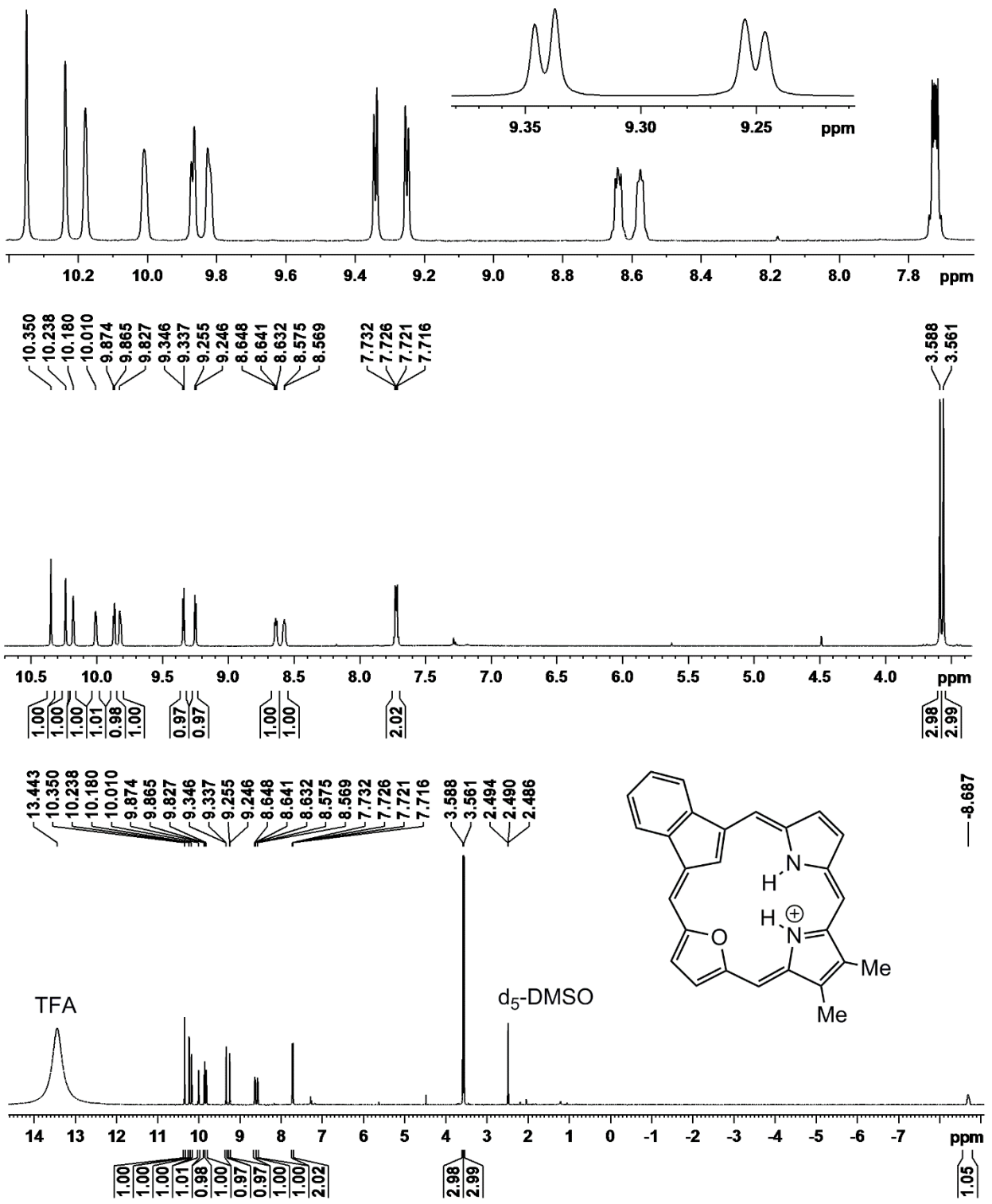

Figure S33. 500 MHz proton NMR spectrum of oxacarbaporphyrin monocation **15a**H$^+$ in TFA-*d*$_6$-DMSO at 70 ^{o}C.

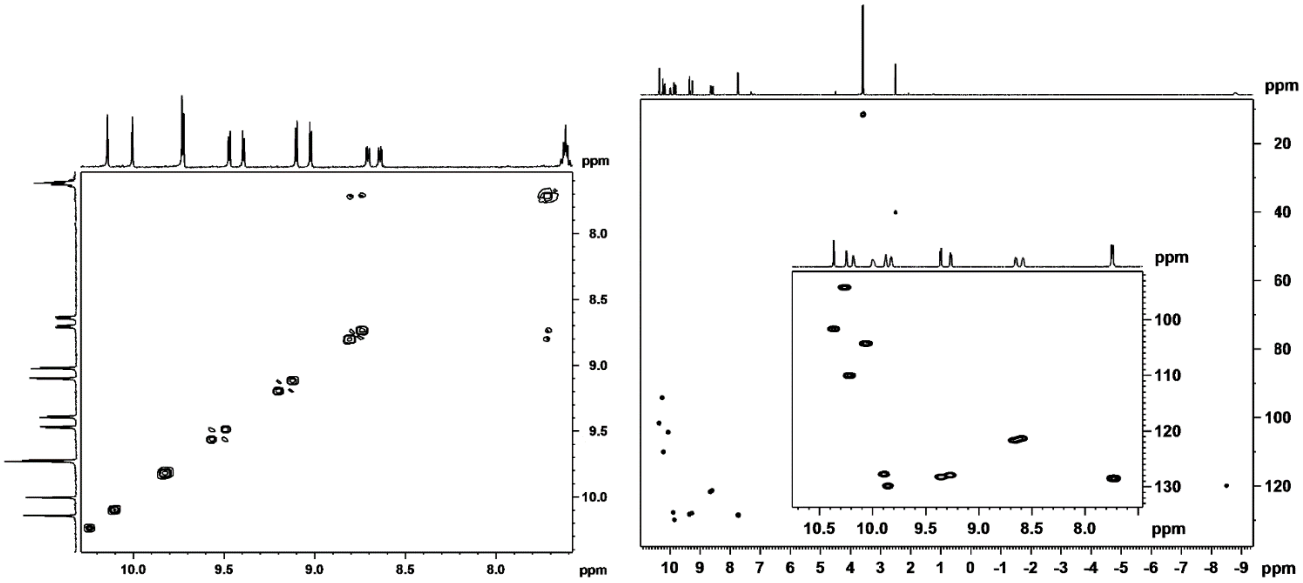

Figure S34. ^{1}H-^{1}H COSY and HSQC NMR spectra of oxacarbaporphyrin monocation **15a**H^{+} in TFA-d_6-DMSO at 70 ^{o}C.

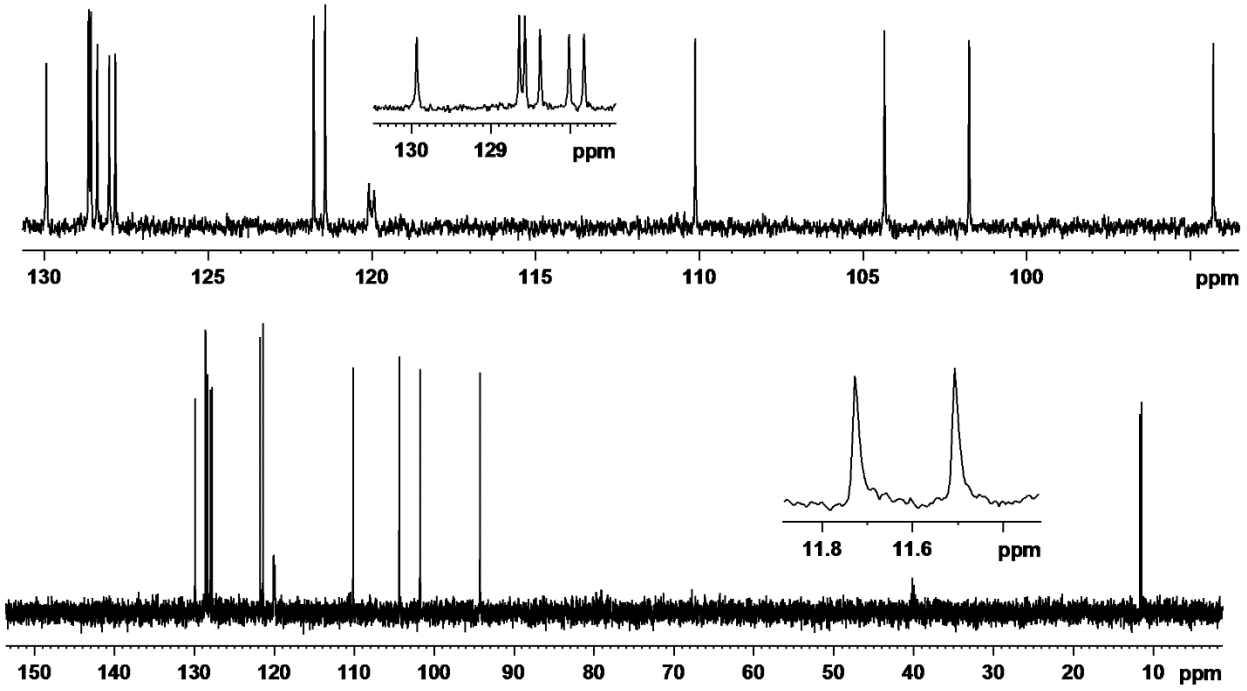

Figure S35. DEPT-135 NMR spectrum of oxacarbaporphyrin monocation **15a**H^{+} in TFA-d_6-DMSO at 70 ^{o}C.

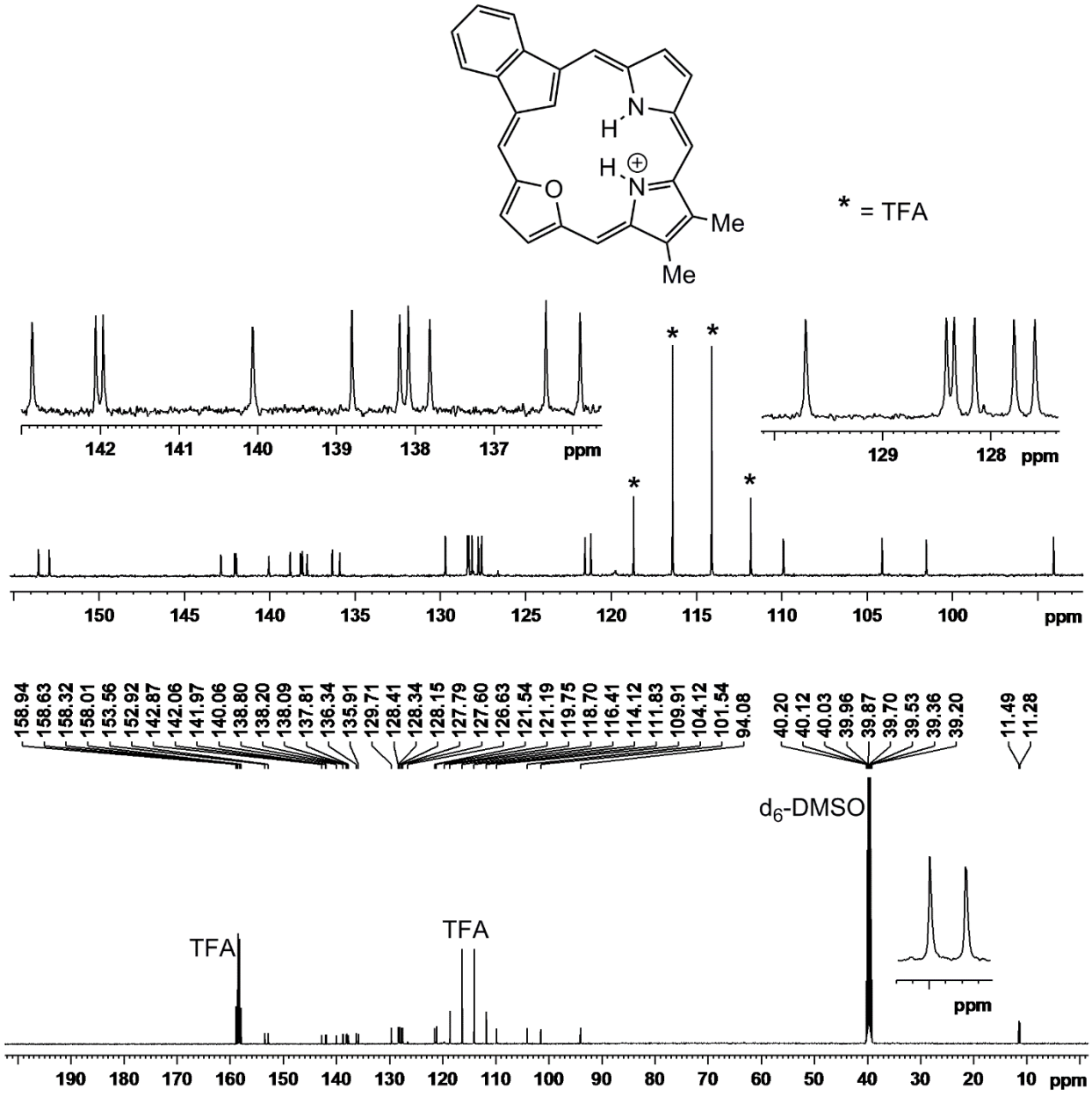

Figure S36. 125 MHz carbon-13 NMR spectrum of oxacarbaporphyrin monocation **15a**H$^+$ in TFA-d_6-DMSO at 70 ^{o}C.

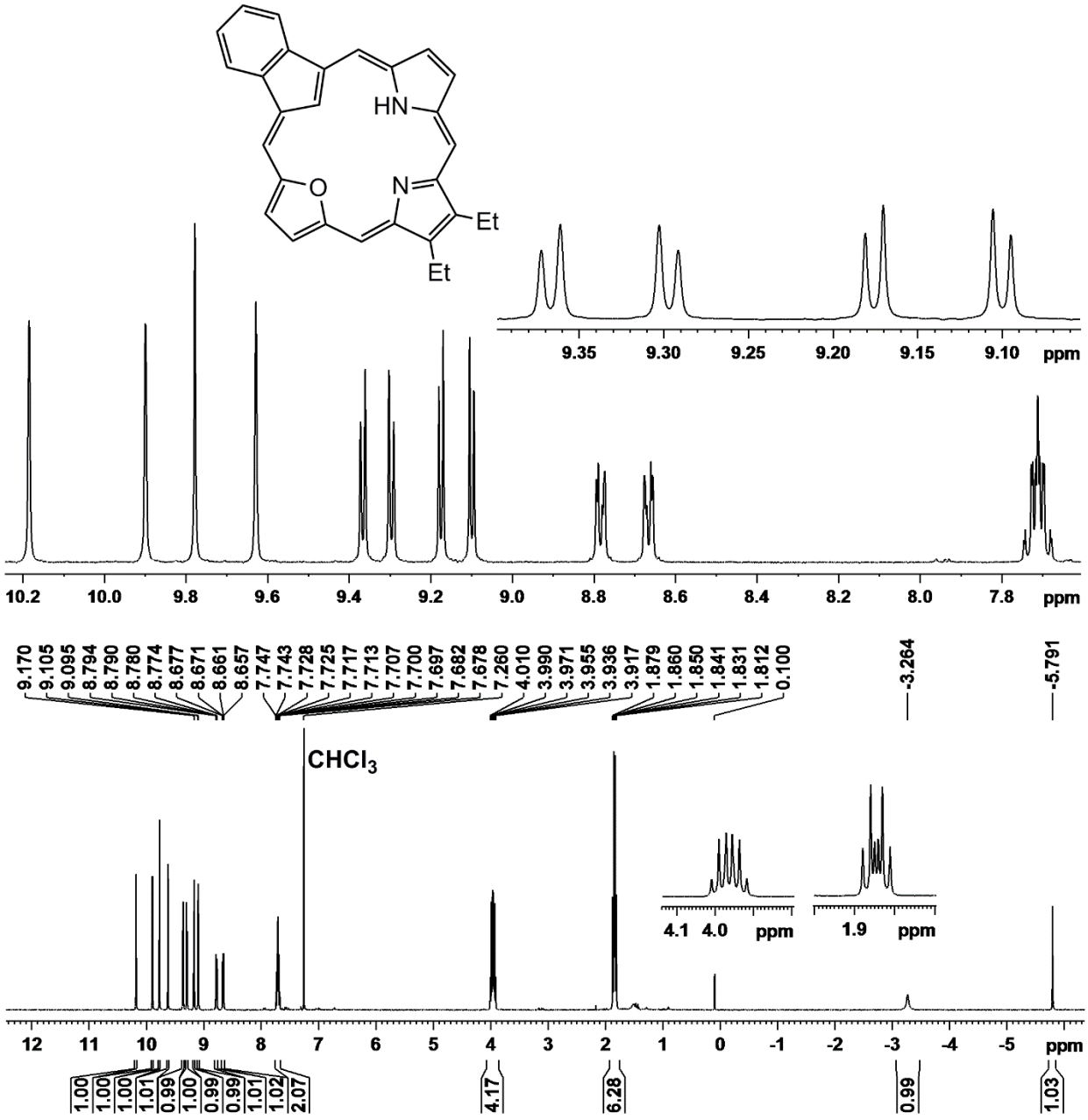

Figure S37. 500 MHz proton NMR spectrum of oxacarbaporphyrin **15b** in $CDCl_3$.

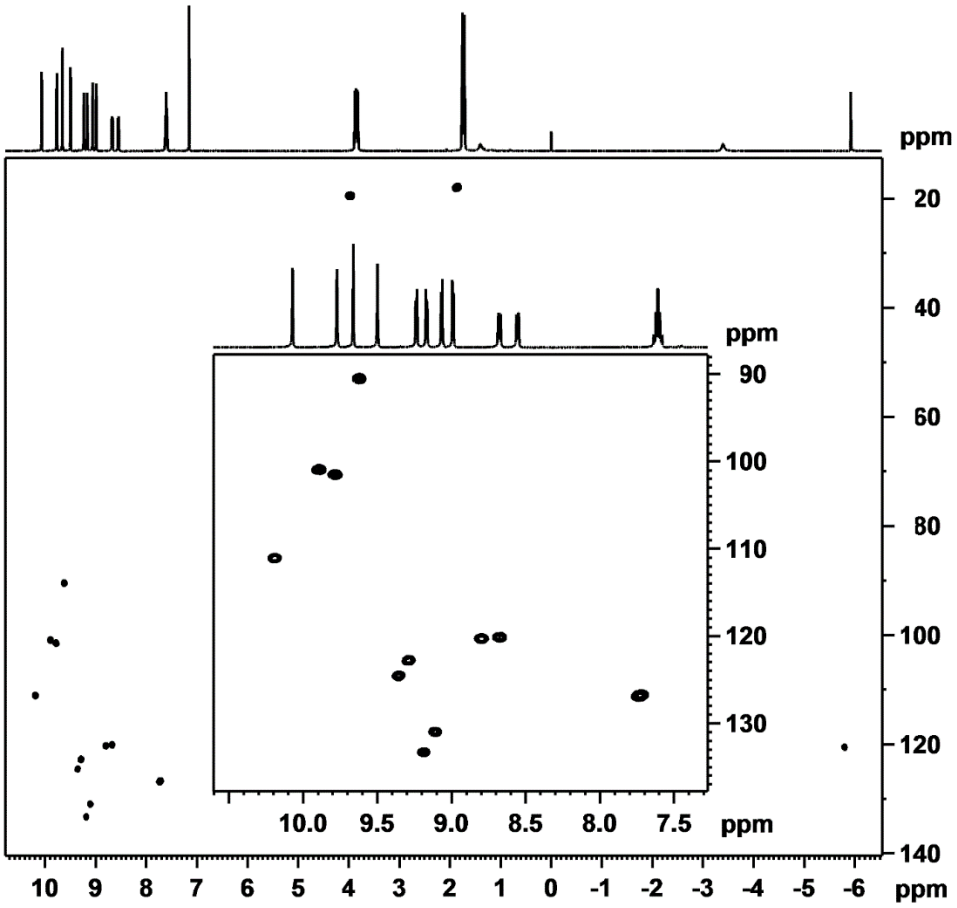

Figure S38. HSQC NMR spectrum of **15b**H^+ in $CDCl_3$.

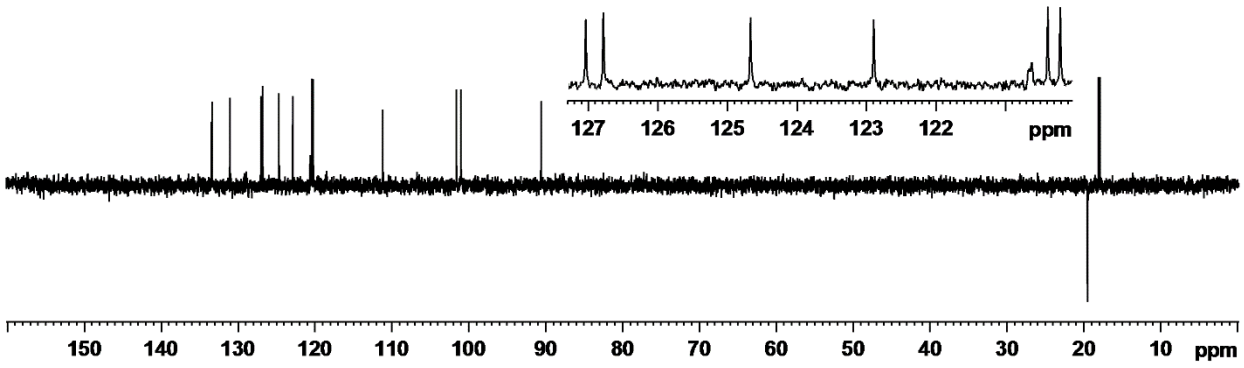

Figure S39. DEPT-135 NMR spectrum of oxacarbaporphyrin **15b** in $CDCl_3$.

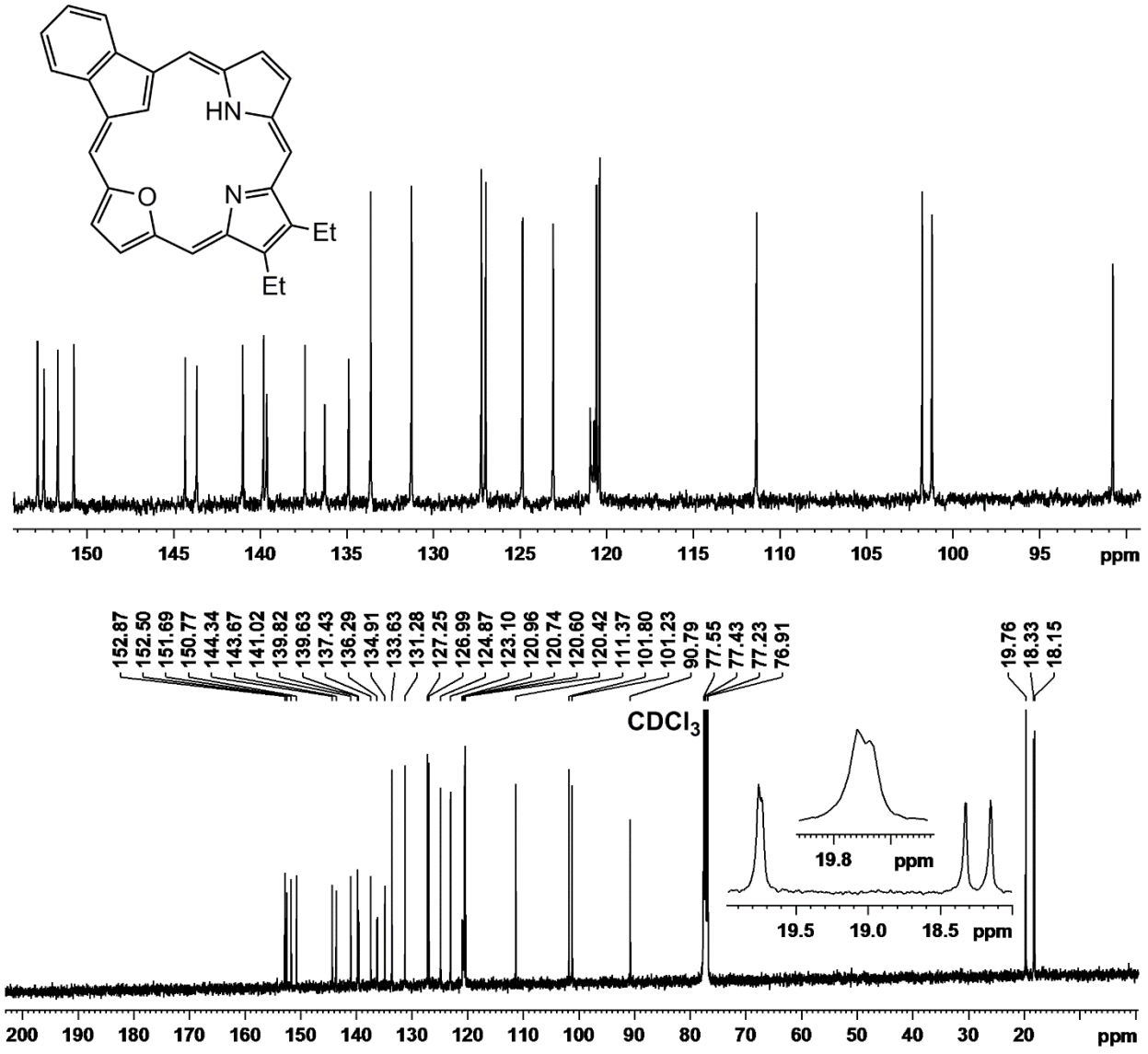

Figure S40. 125 MHz carbon-13 NMR spectrum of oxacarbaporphyrin **15b** in $CDCl_3$.

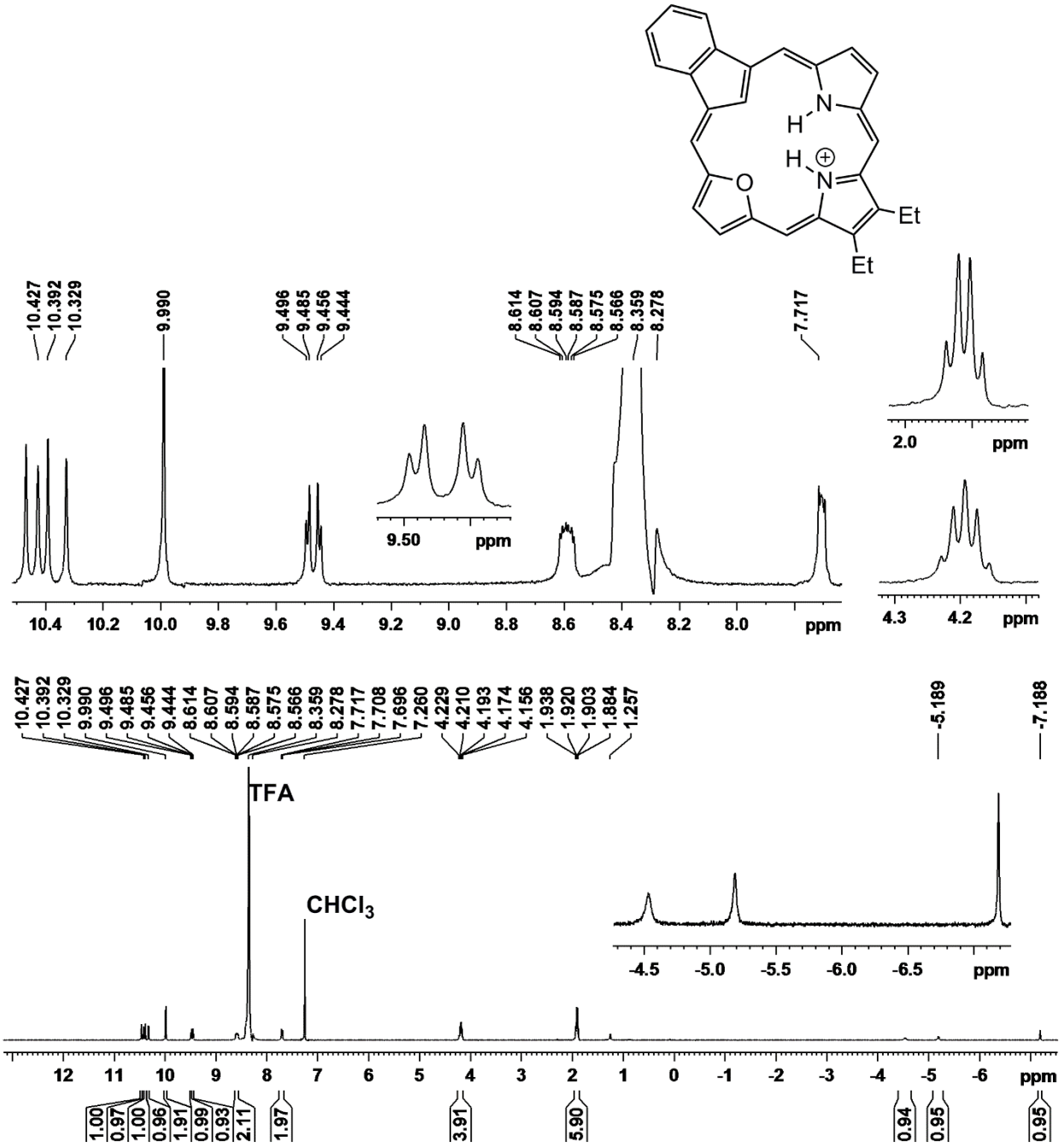

Figure S41. 500 MHz proton NMR spectrum of oxacarbaporphyrin monocation **15b**H^+ in TFA-$CDCl_3$.

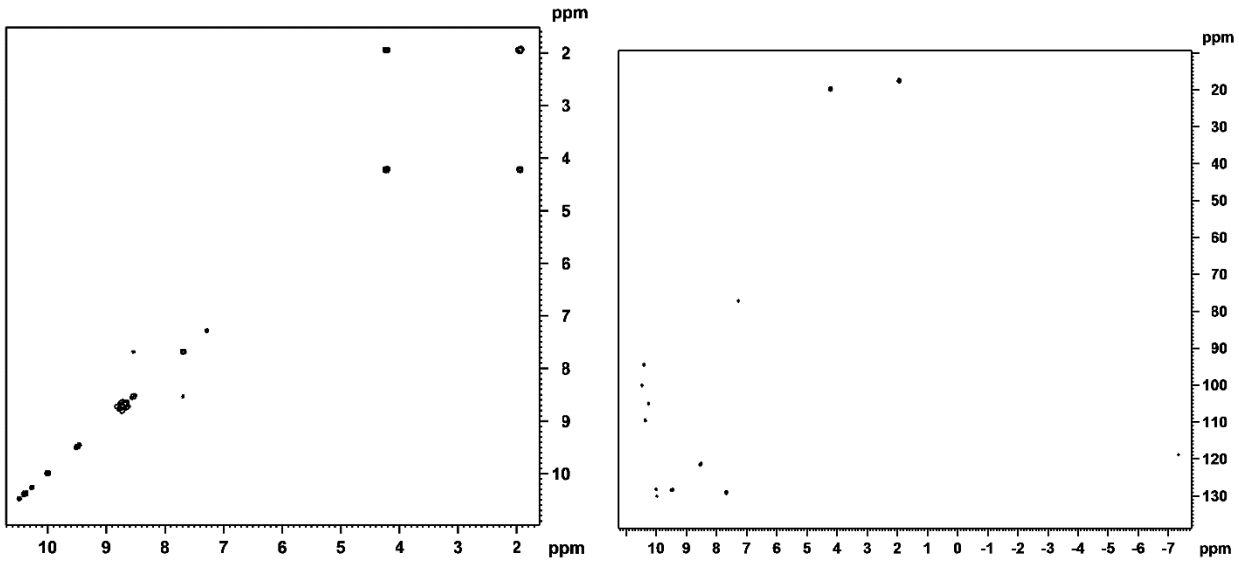

Figure S42. ^{1}H-^{1}H COSY (left) and HSQC (right) NMR spectra of oxacarbaporphyrin monocation **15b**H^{+} in TFA-CDCl$_3$.

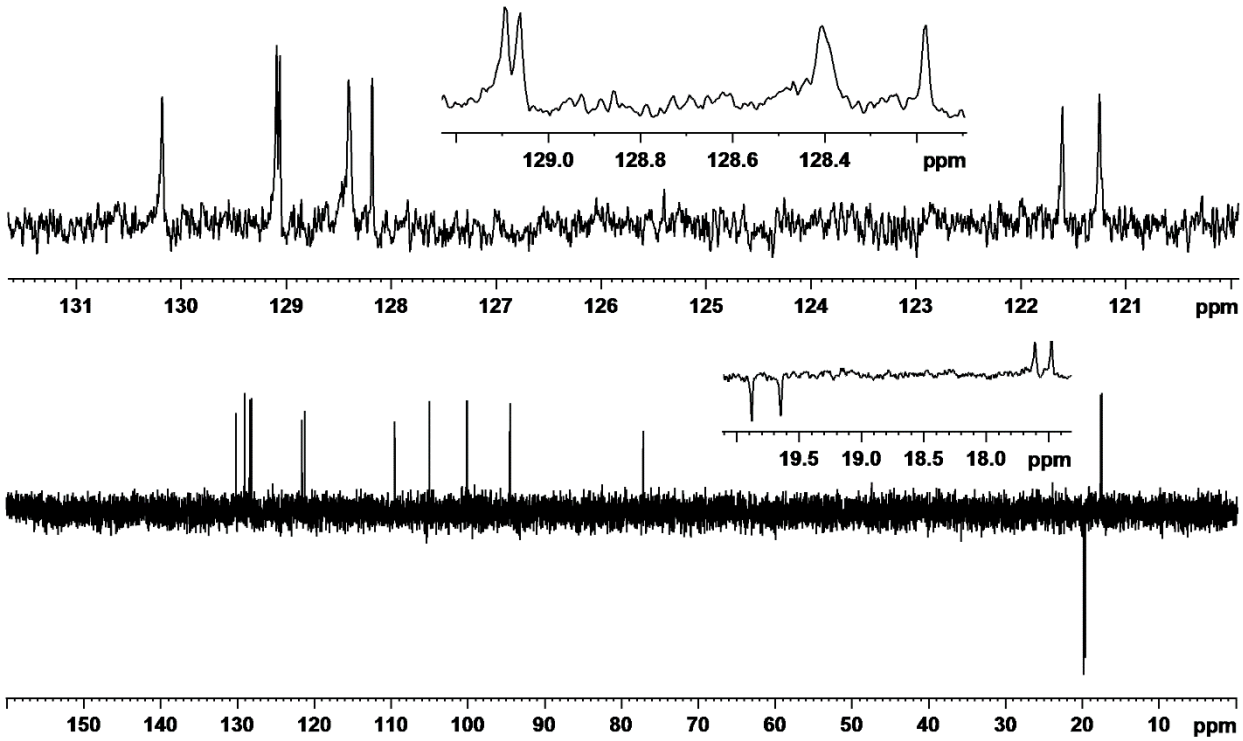

Figure S43. DEPT-135 NMR spectrum of **15b**H^{+} in TFA-CDCl$_3$.

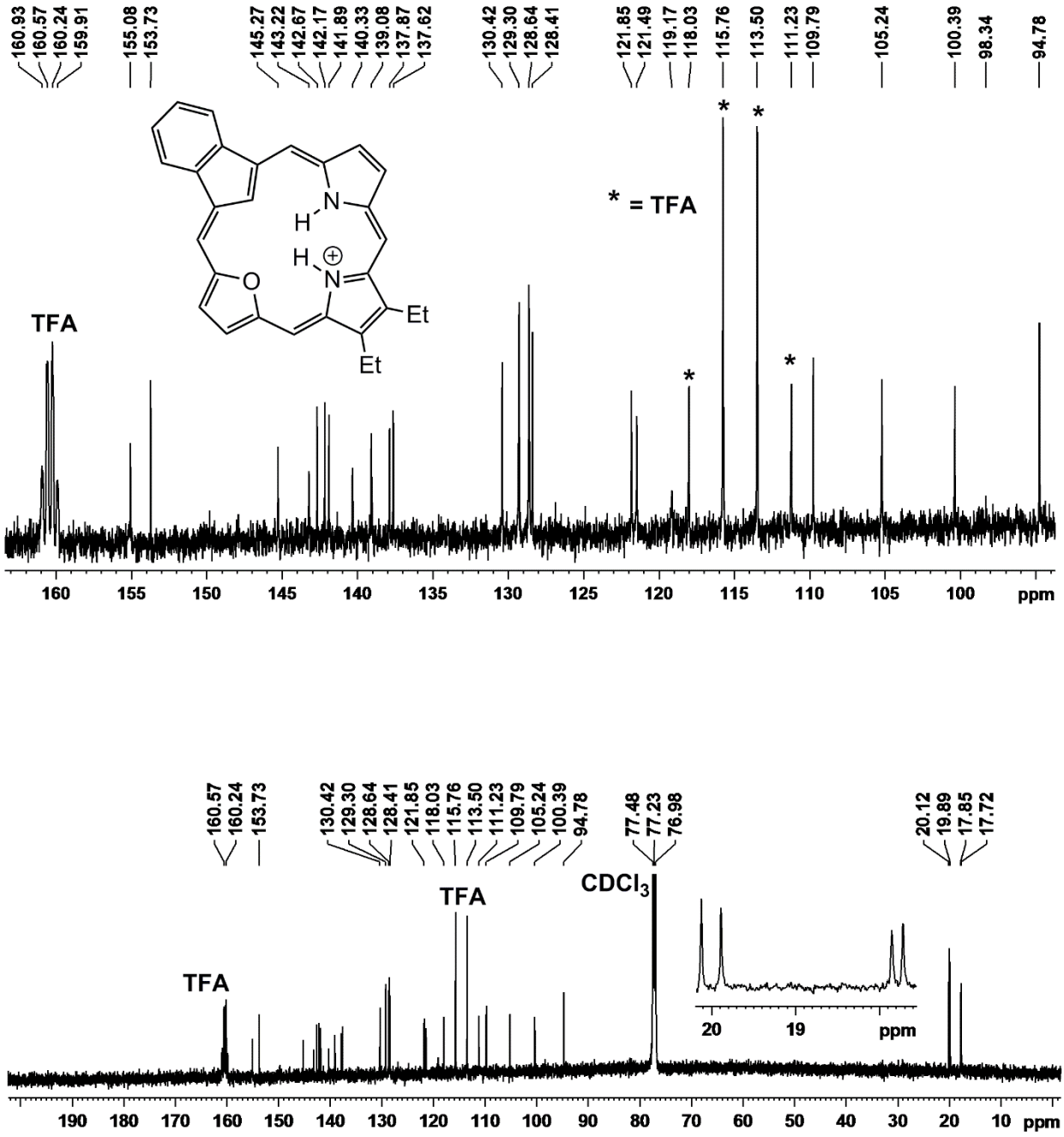

Figure S44. 125 MHz carbon-13 NMR spectrum of oxacarbaporphyrin monocation **15b**H^+ in TFA-$CDCl_3$.

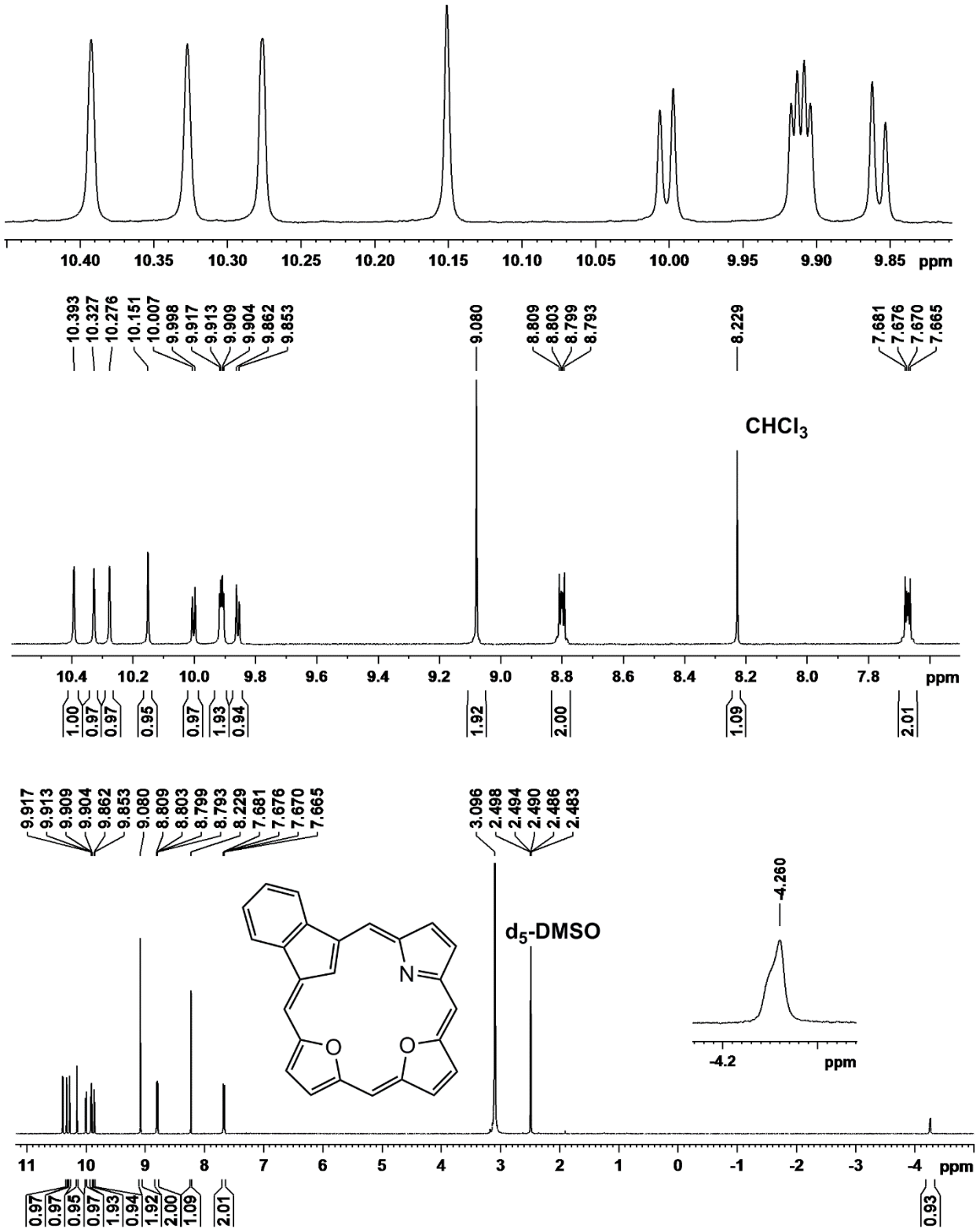

Figure S45. 500 MHz proton NMR spectrum of dioxacarbaporphyrin **12b** in d_6-DMSO at 70 ^{o}C.

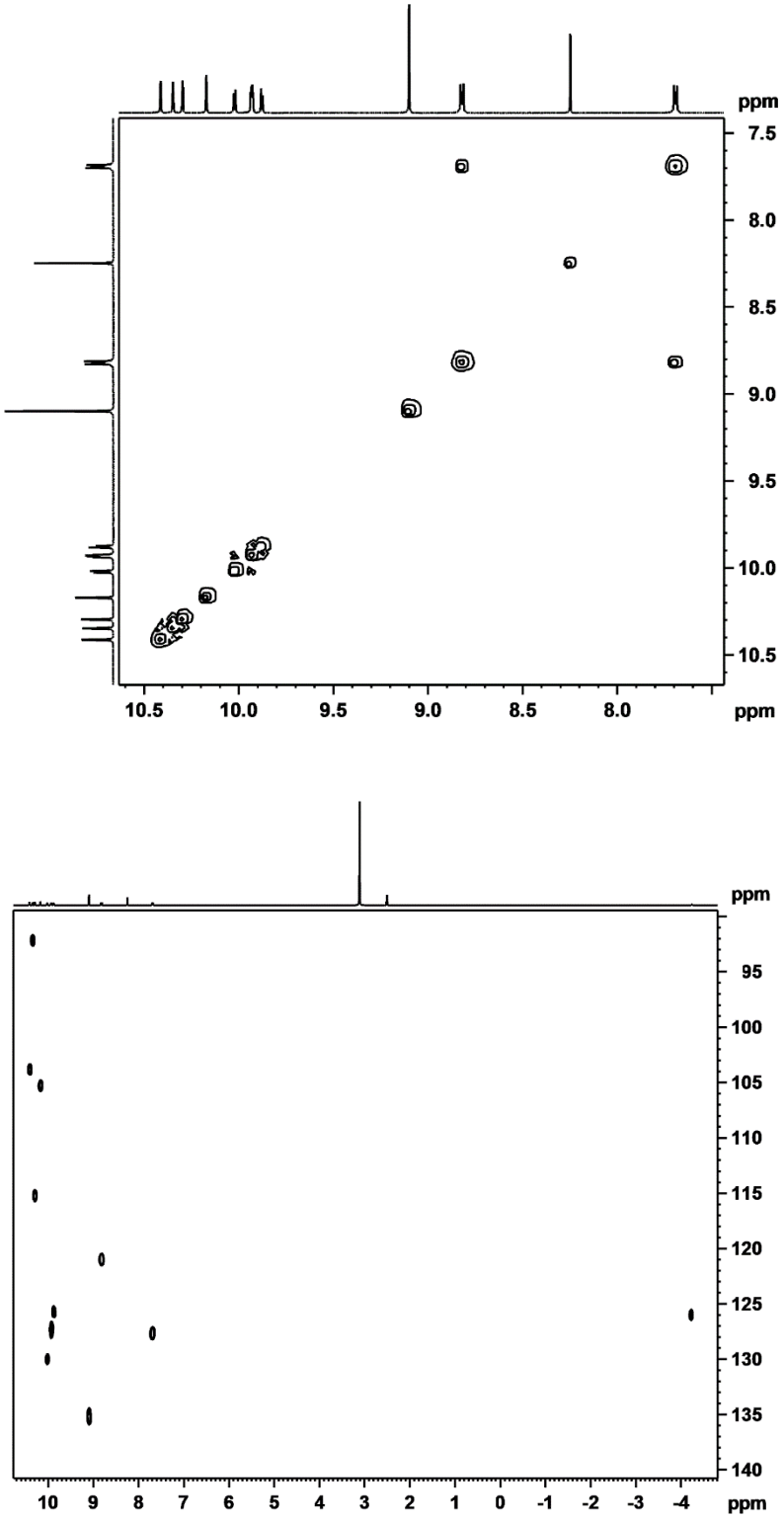

Figure S46. ^{1}H-^{1}H COSY (above) and HSQC (below) NMR spectra of **12b** in d_6-DMSO at 70 ^{o}C.

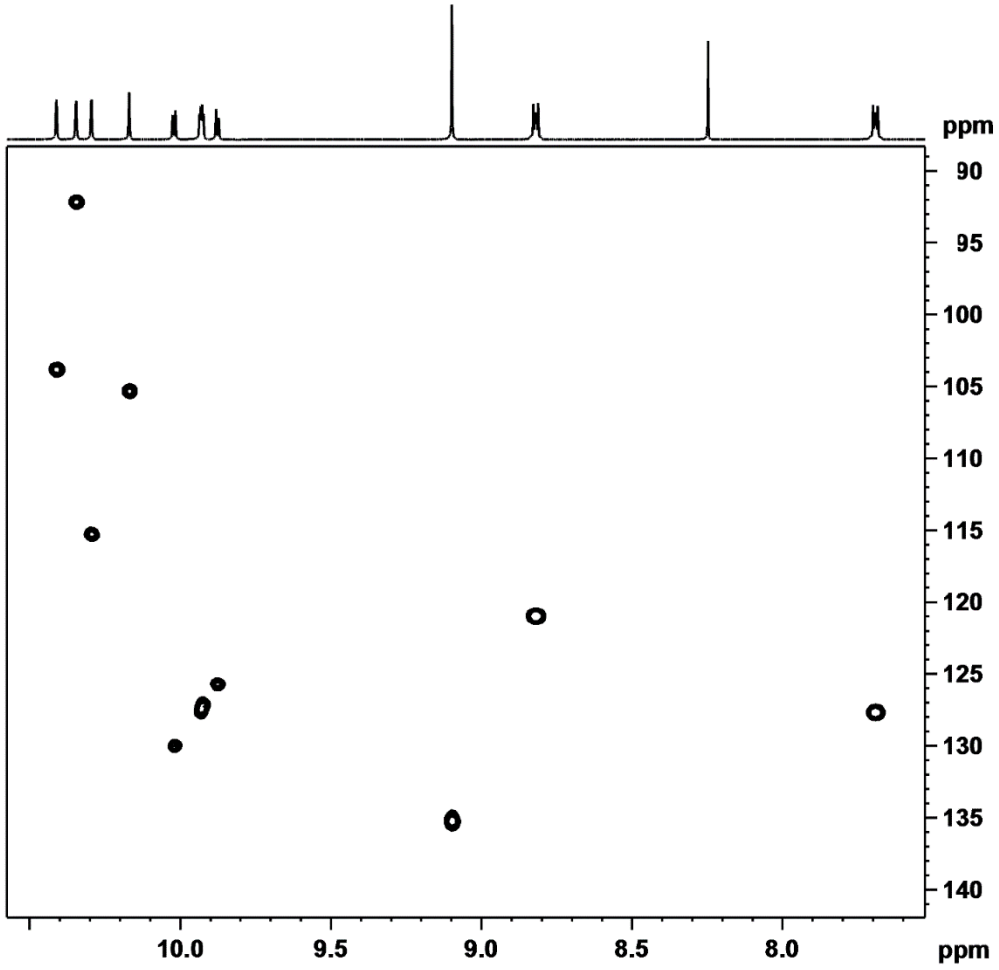

Figure S47. Expansion of previous HSQC NMR spectrum for **12b**.

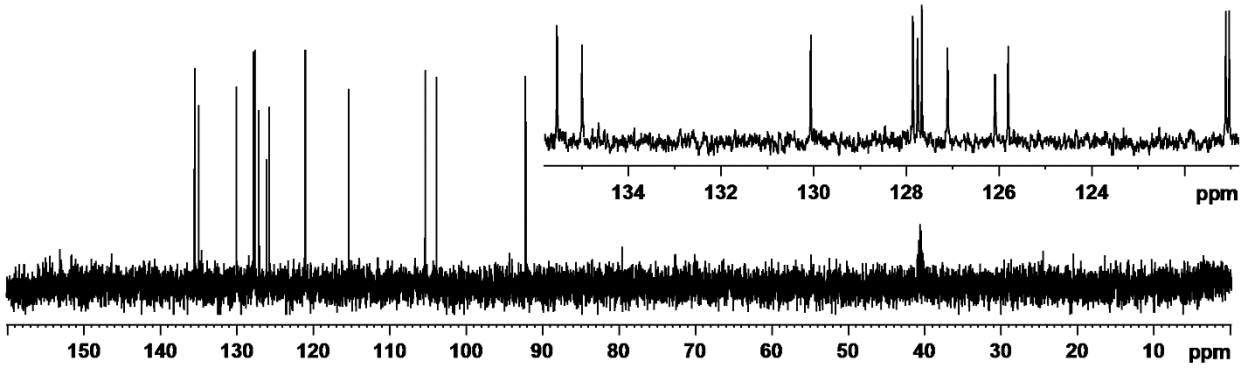

Figure S48. DEPT-135 NMR spectrum of **12b** in d_6-DMSO at 70 ^{o}C.

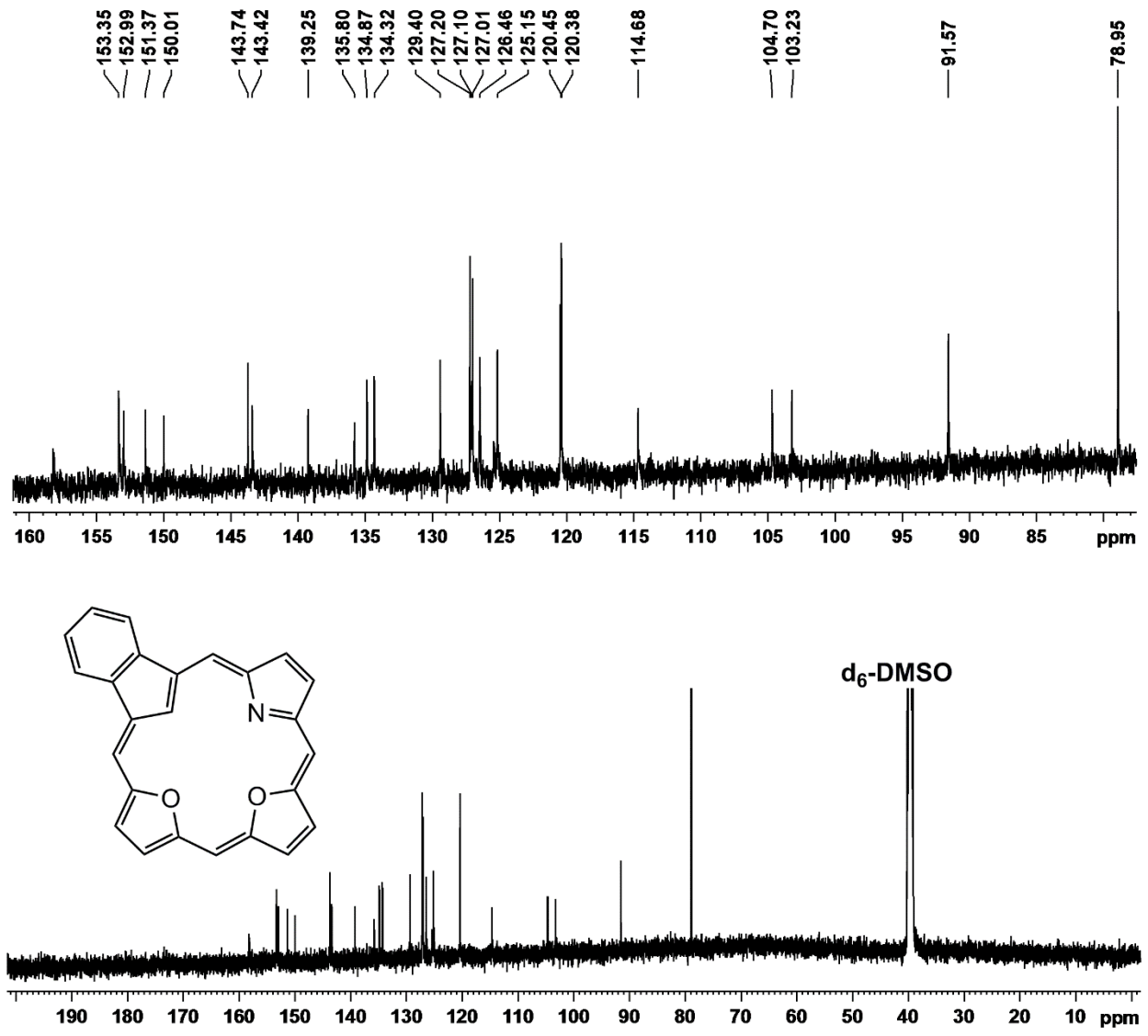

Figure S49. 125 MHz carbon-13 NMR spectrum of dioxacarbaporphyrin **12b** in d_6-DMSO at 70 ^{o}C.

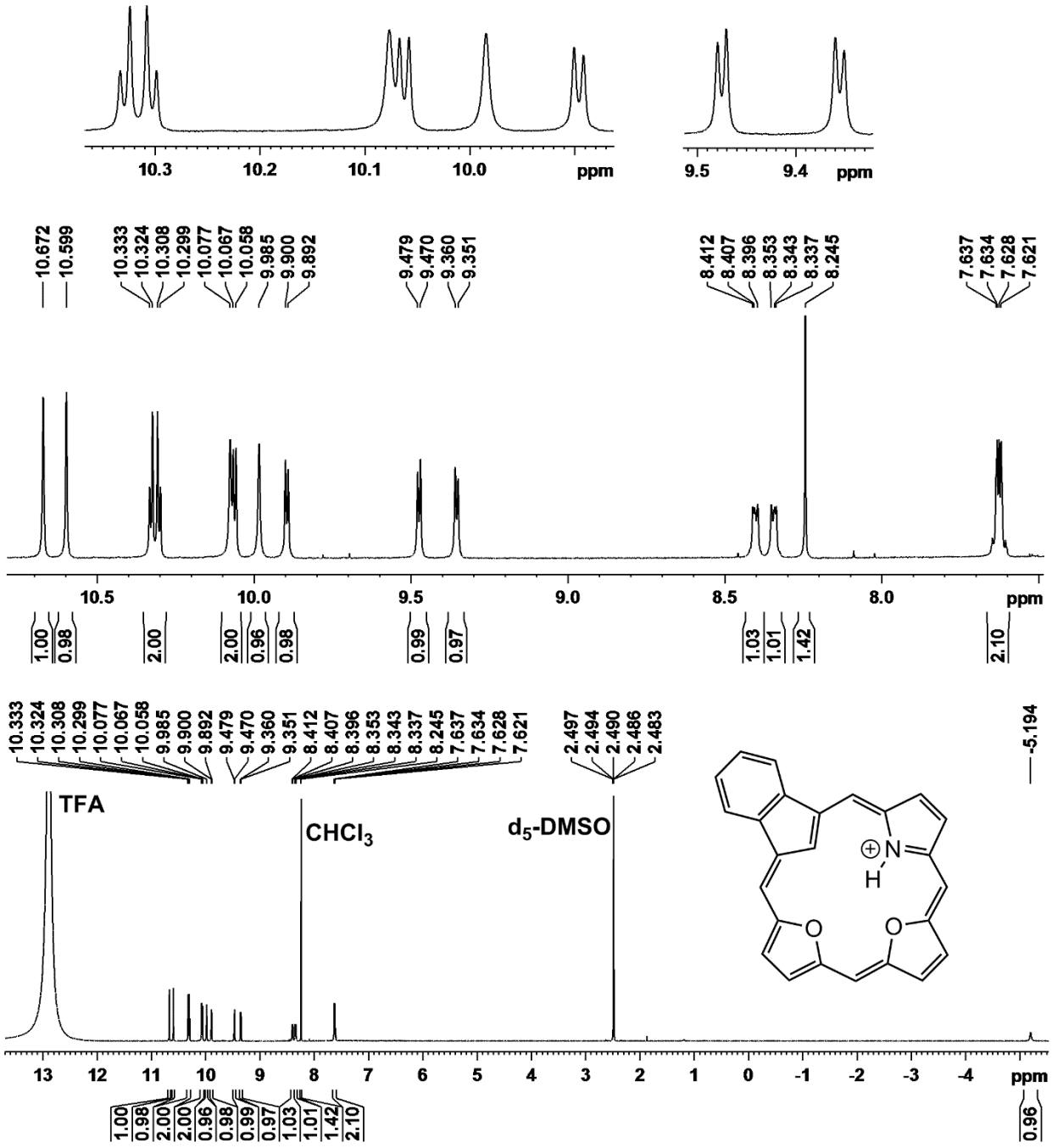

Figure S50. 500 MHz proton NMR spectrum of dioxacarbaporphyrin monocation **12b**H$^+$ in TFA-d_6-DMSO.

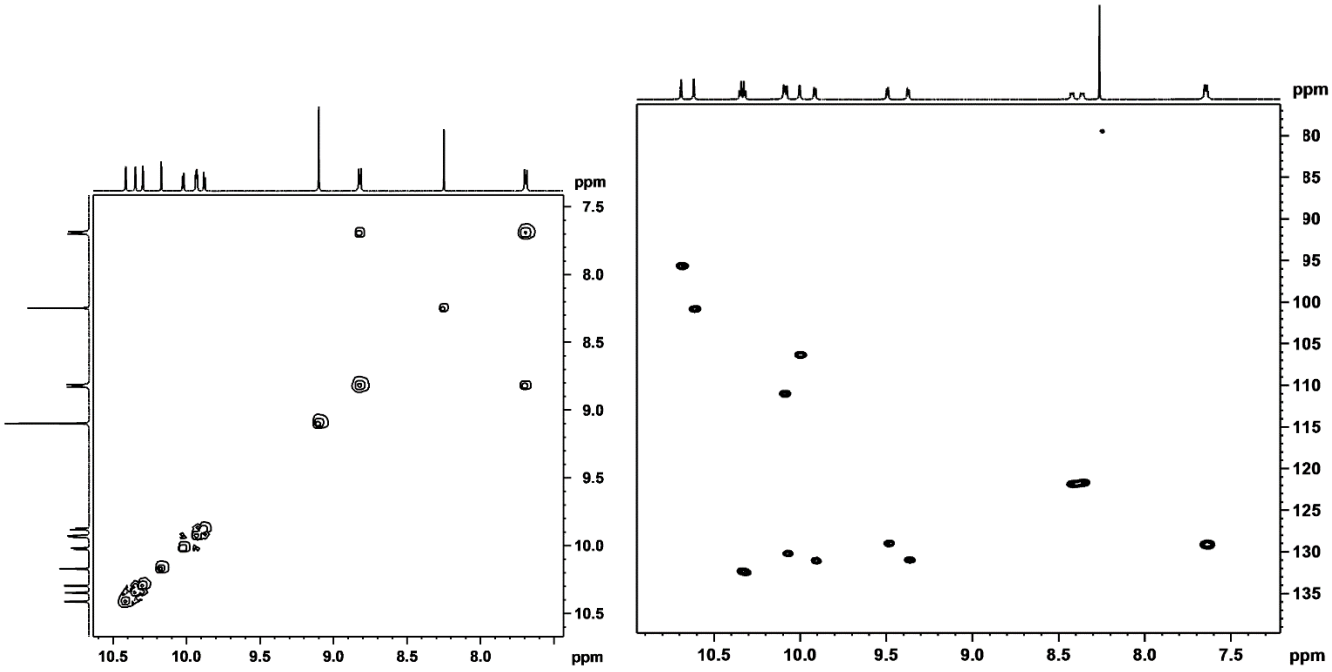

Figure S51. ^{1}H-^{1}H COSY (left) and HSQC (right) NMR spectra of dioxacarbaporphyrin monocation **12b**H^{+} in TFA-d_6-DMSO.

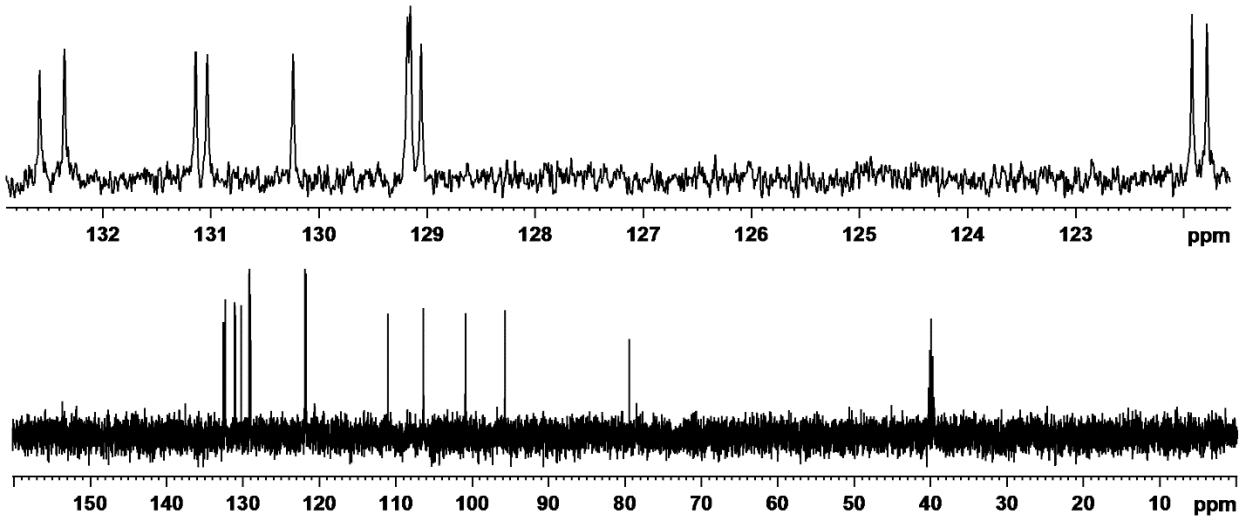

Figure S52. DEPT-135 NMR spectrum of dioxacarbaporphyrin monocation **12b**H^{+} in TFA-d_6-DMSO.

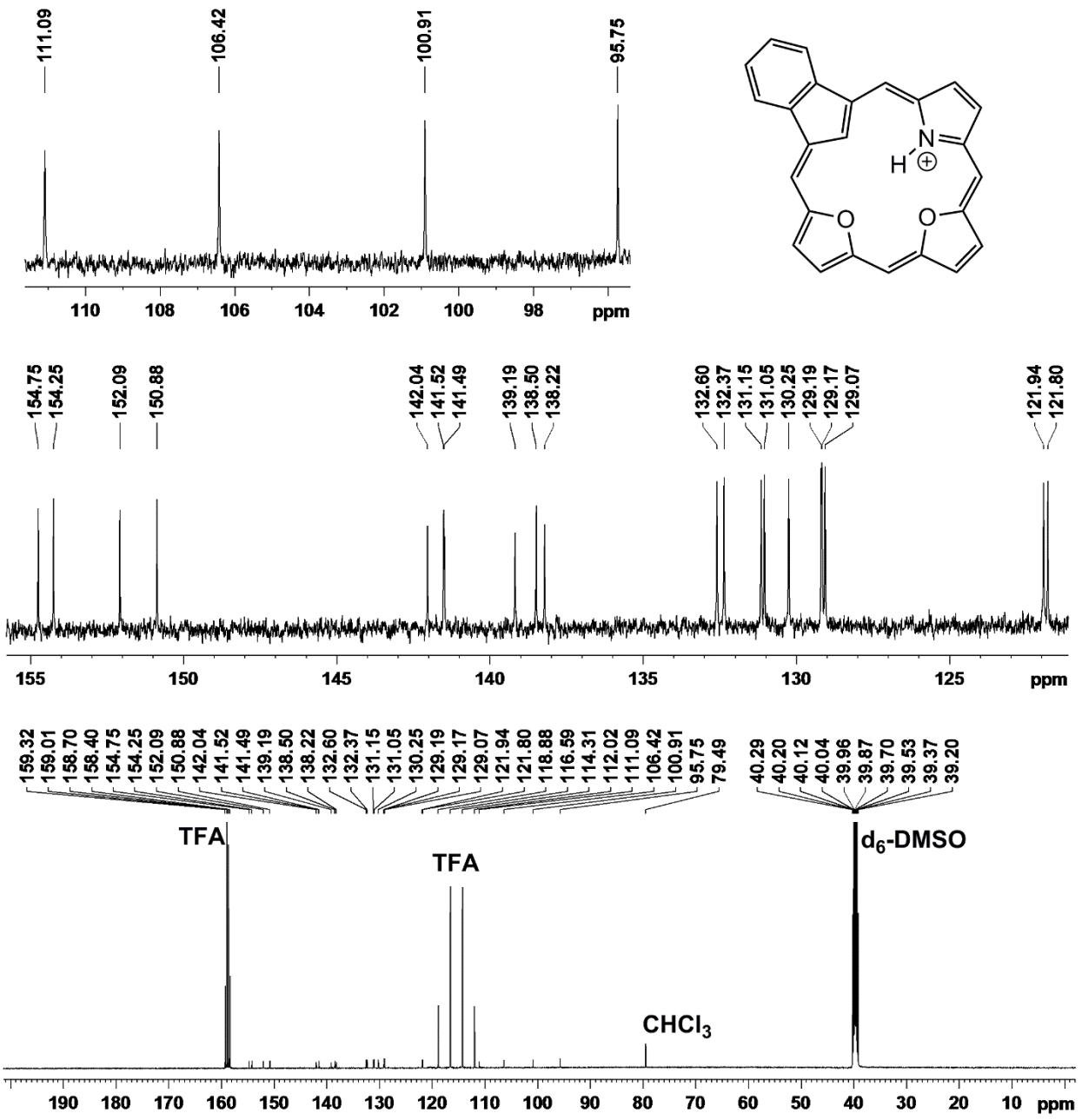

Figure S53. 125 MHz carbon-13 NMR spectrum of dioxacarbaporphyrin monocation **12b**H$^+$ in TFA-*d*$_6$-DMSO.

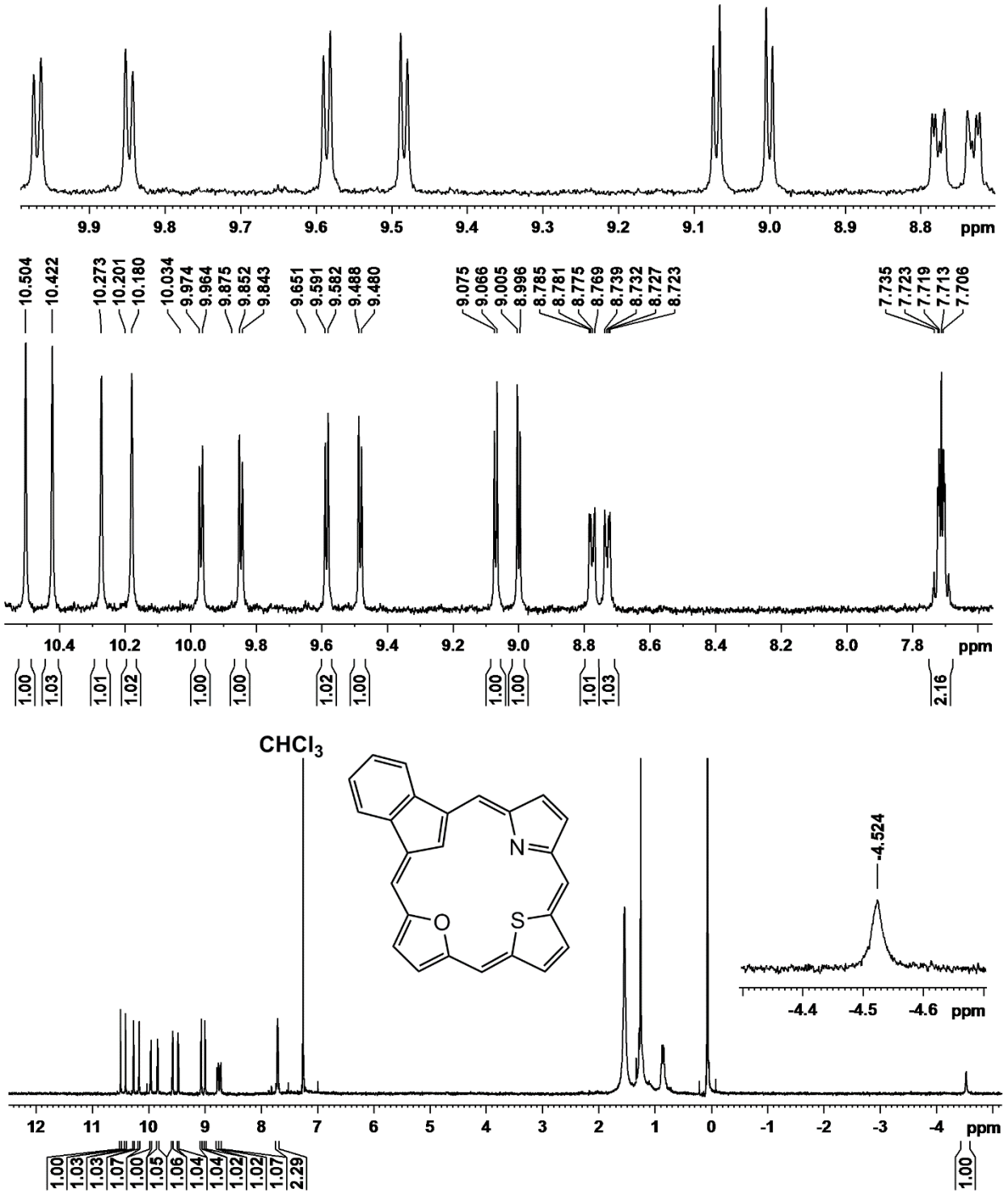

Figure S54. 500 MHz proton NMR spectrum of oxathiacarbaporphyrin **12c** in $CDCl_3$.

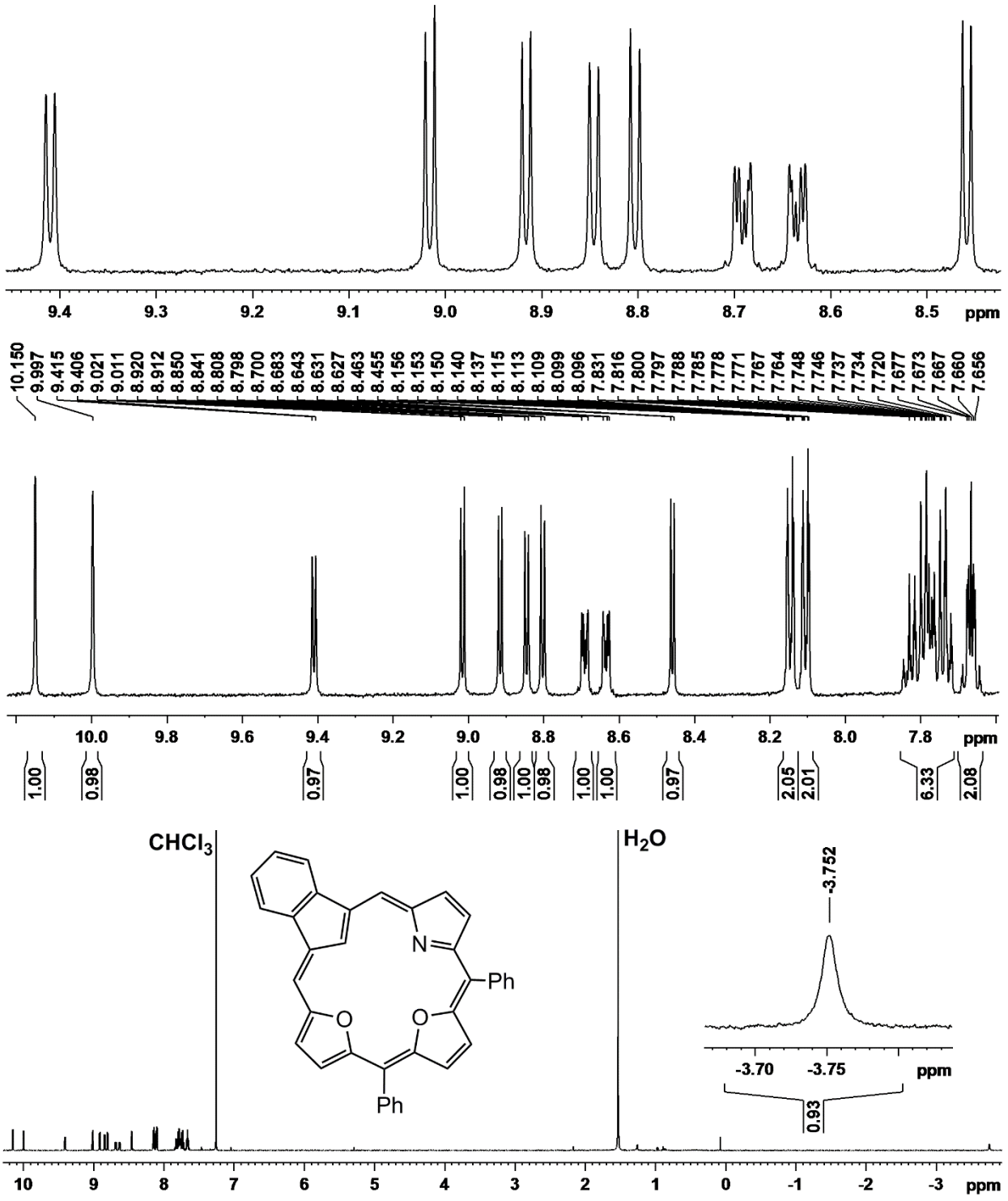

Figure S55. 500 MHz proton NMR spectrum of diphenyl dioxacarbaporphyrin **16a** in $CDCl_3$.

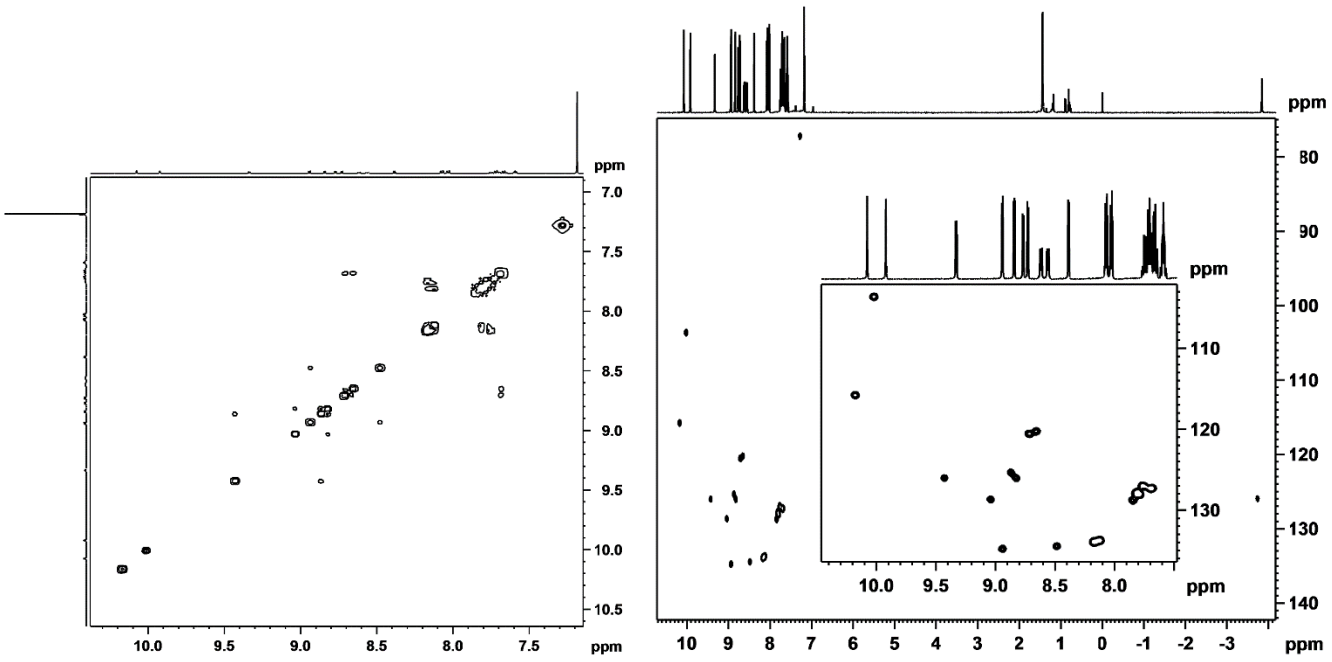

Figure S56. ^{1}H-^{1}H COSY and HSQC NMR spectra of diphenyl dioxacarbaporphyrin **16a** in $CDCl_3$.

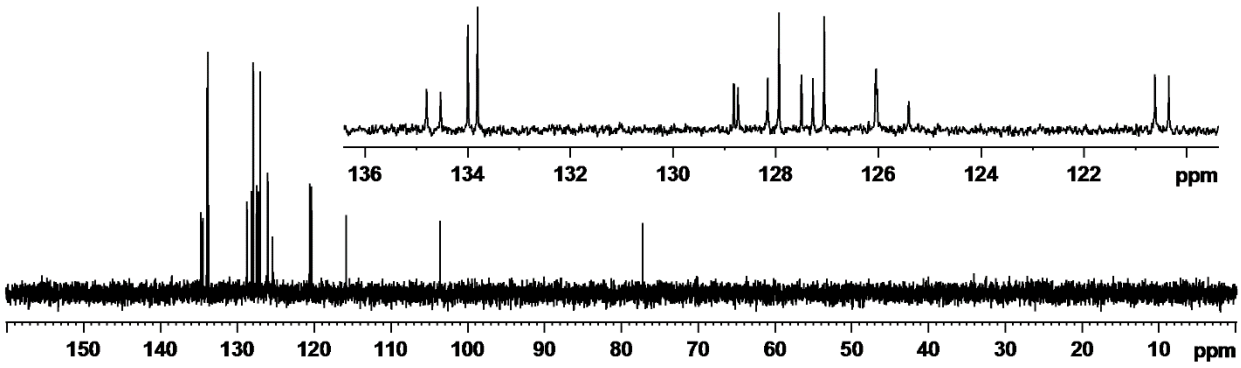

Figure S57. DEPT-135 NMR spectrum of diphenyl dioxacarbaporphyrin **16a** in $CDCl_3$.

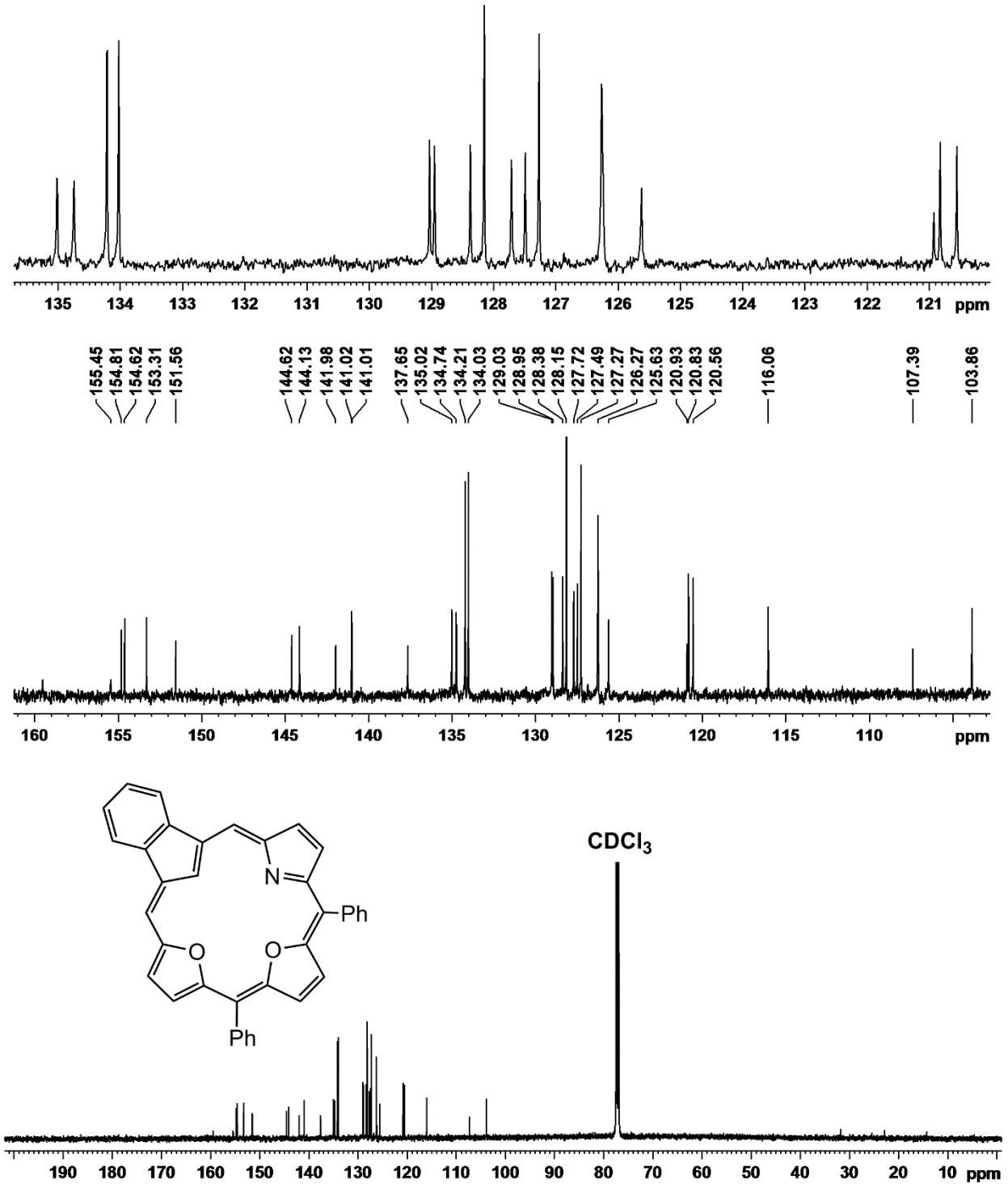

Figure S58. 125 MHz carbon-13 NMR spectrum of diphenyl dioxacarbaporphyrin **16a** in $CDCl_3$.

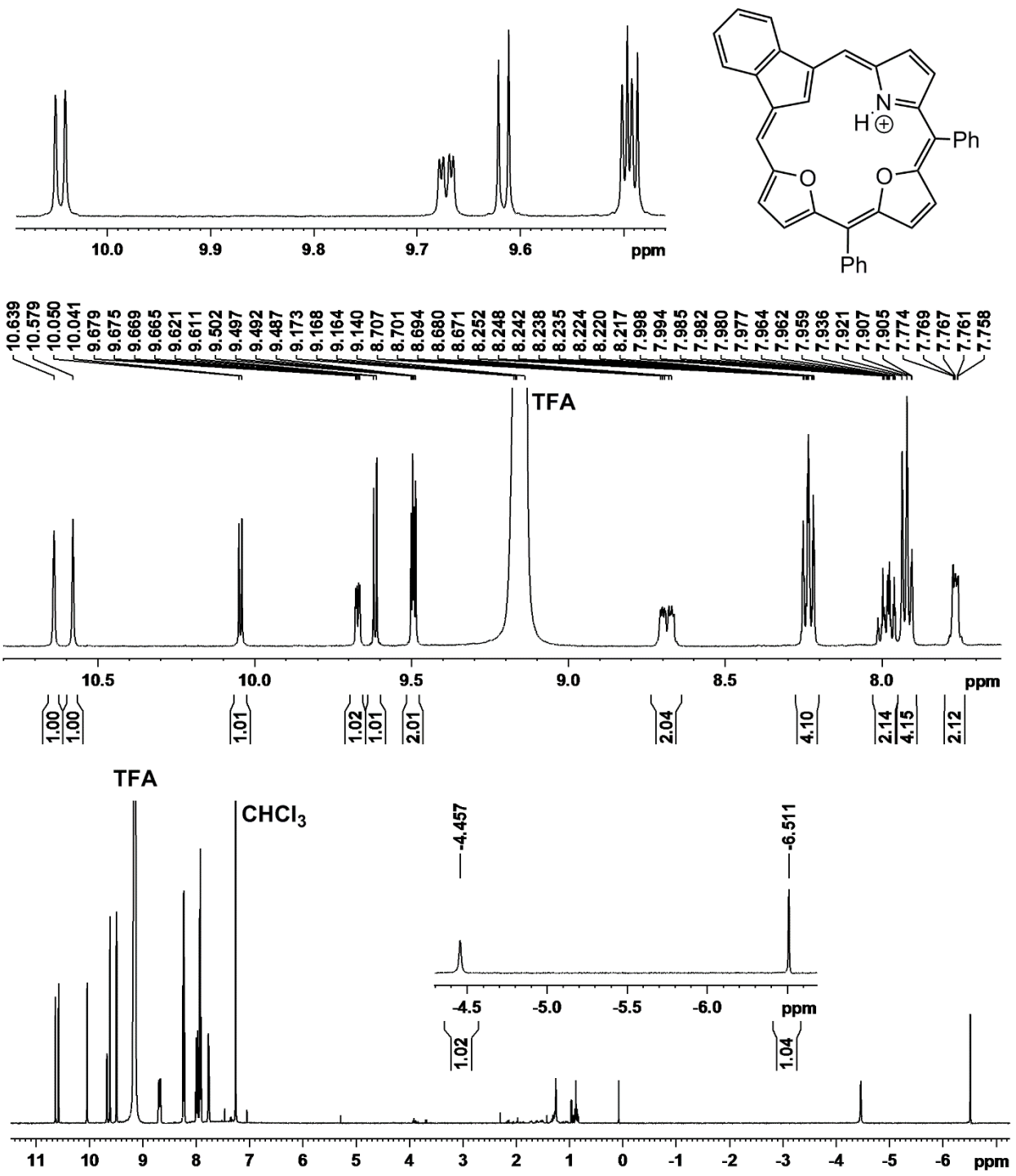

Figure S59. 500 MHz proton NMR spectrum of diphenyl dioxacarbaporphyrin monocation **16a**H^+ in TFA-$CDCl_3$.

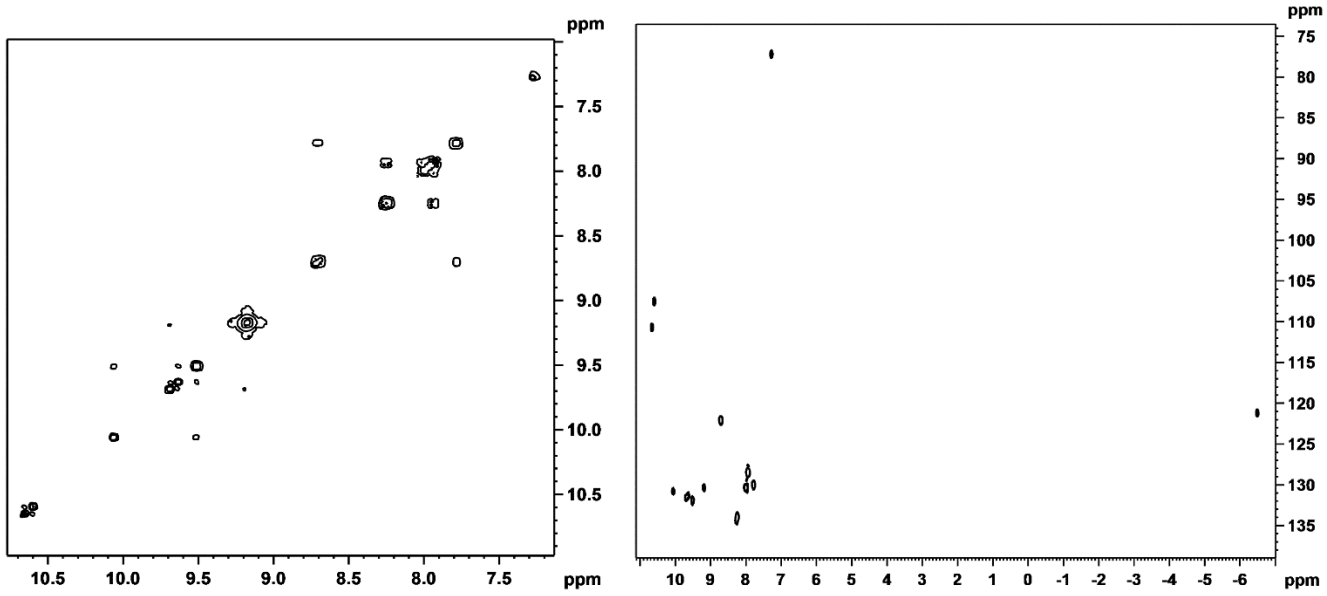

Figure S60. ^{1}H-^{1}H COSY and HSQC NMR spectra of diphenyl dioxacarbaporphyrin monocation **16a**H^{+} in TFA-CDCl$_3$.

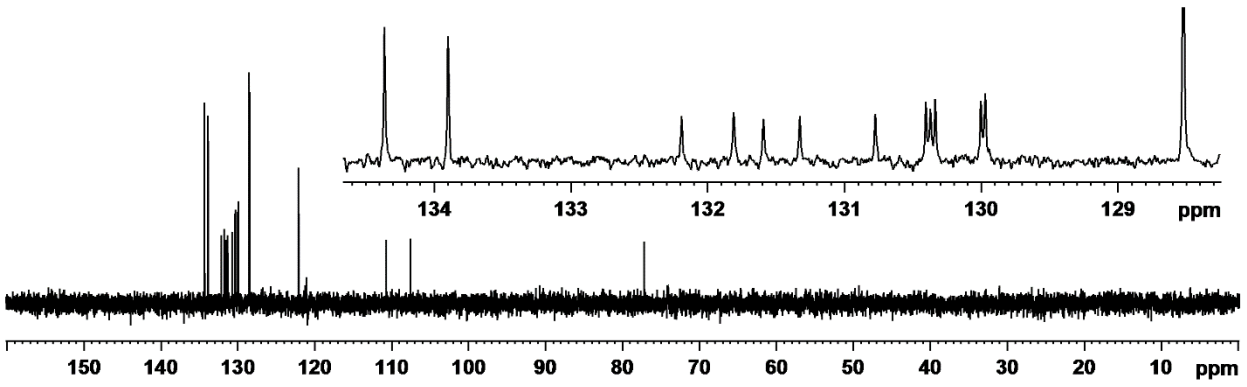

Figure S61. DEPT-135 NMR spectrum of **16a**H^{+} in TFA-CDCl$_3$.

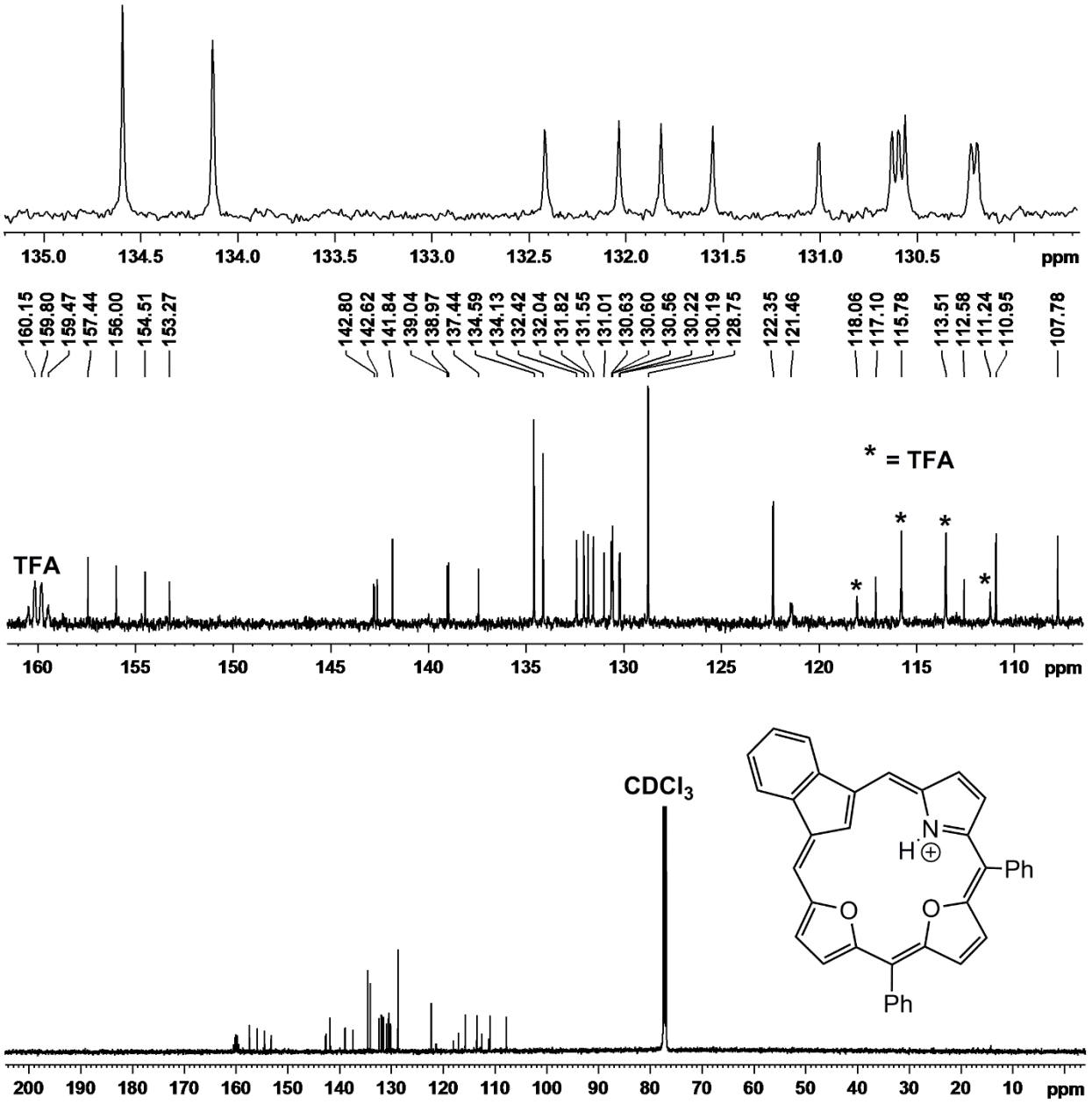

Figure S62. 125 MHz carbon-13 NMR spectrum of diphenyl dioxacarbaporphyrin monocation **16a**H^+ in TFA-$CDCl_3$.

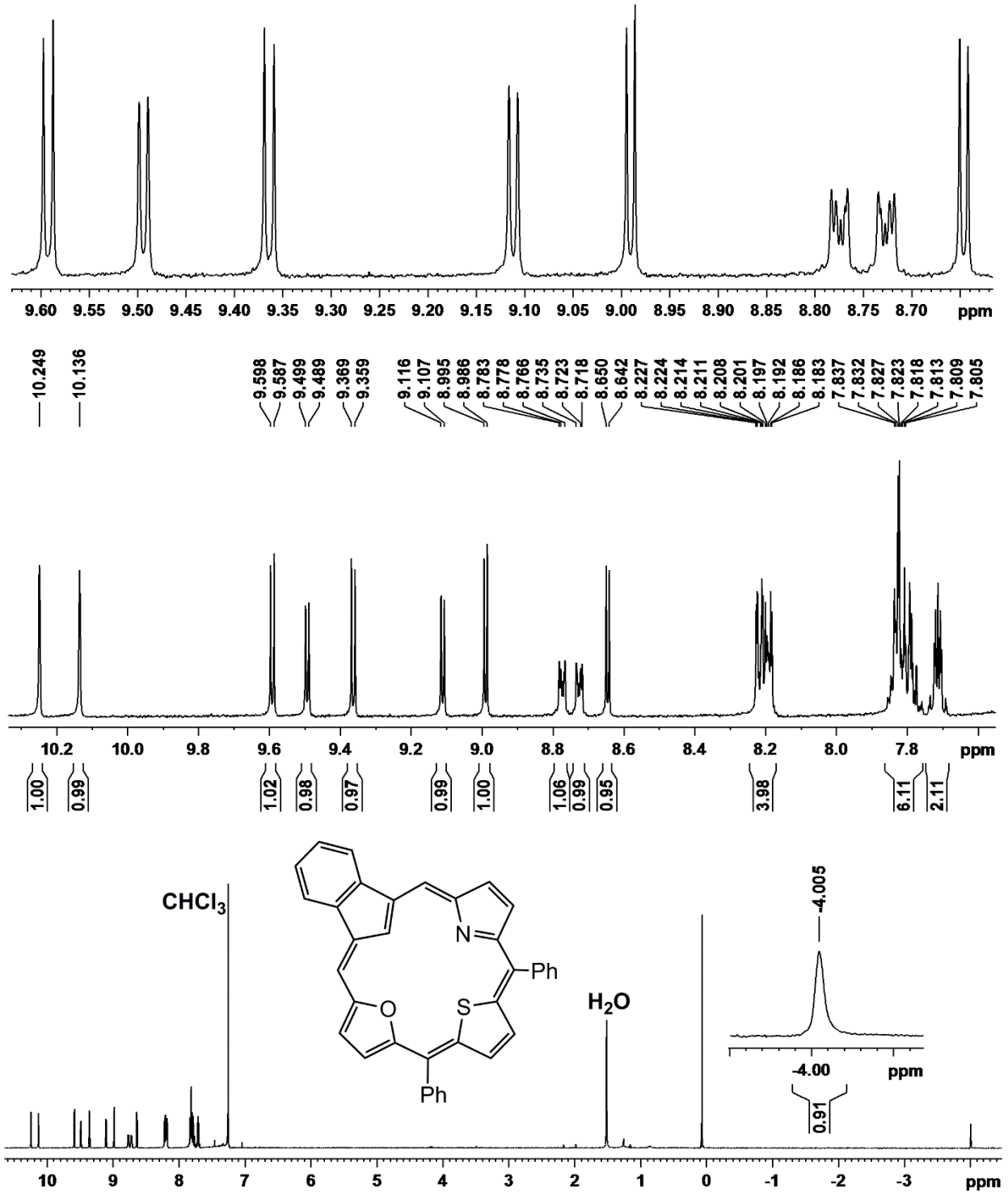

Figure S63. 500 MHz proton NMR spectrum of diphenyl oxathiacarbaporphyrin **16b** in $CDCl_3$.

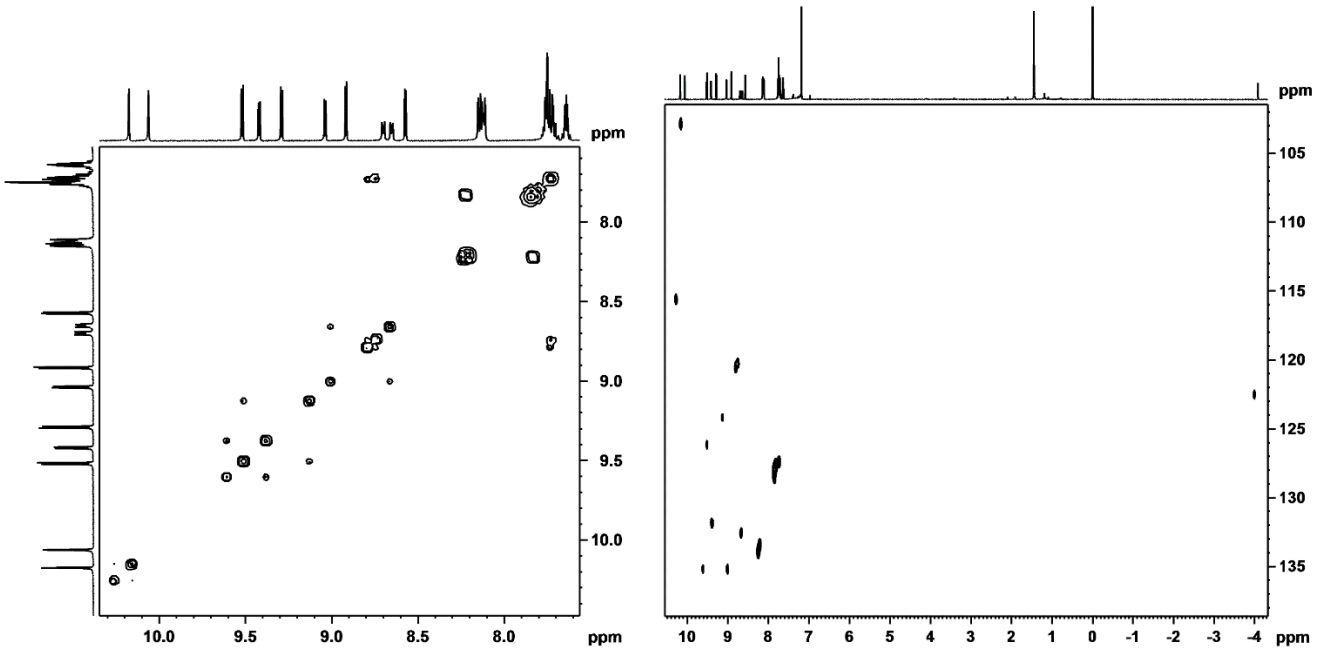

Figure S64. ^{1}H-^{1}H COSY (left) and HSQC (right) NMR spectra of **16b** in $CDCl_3$.

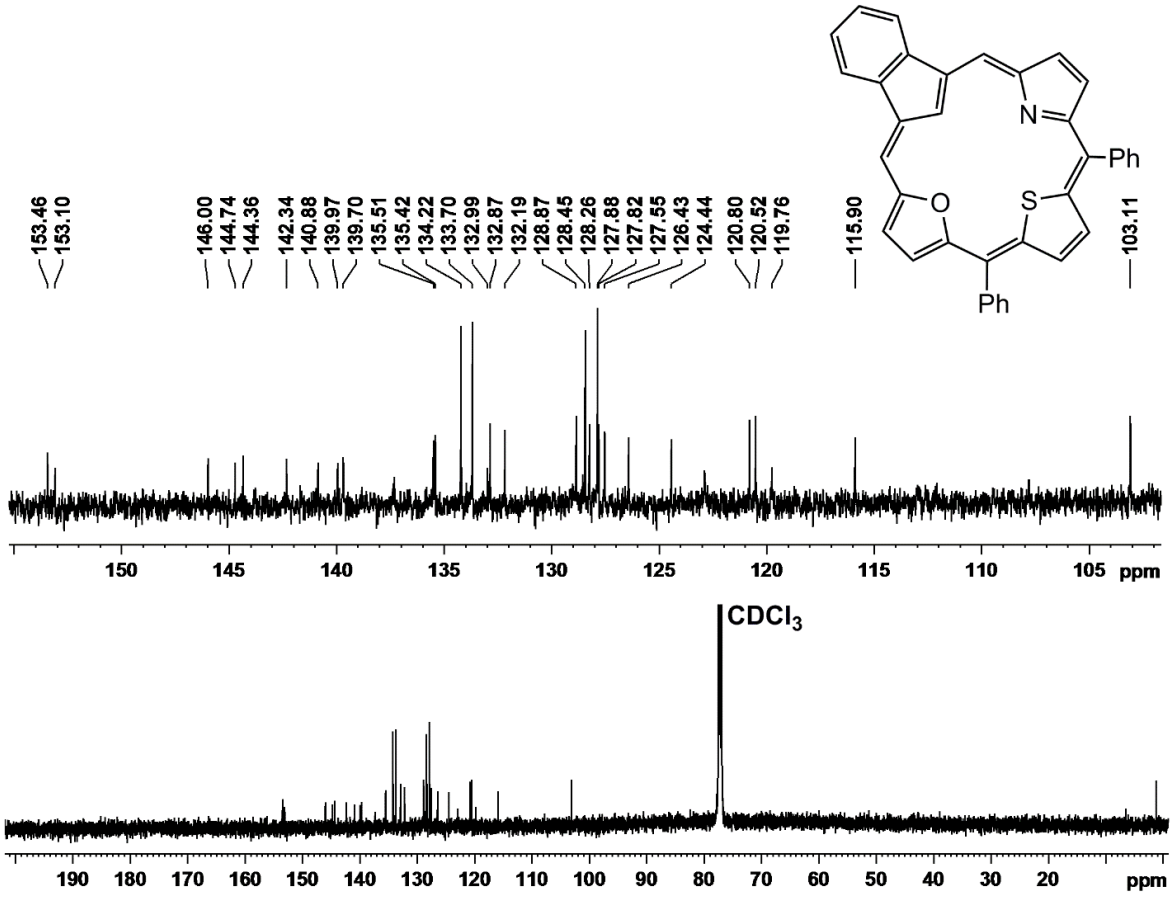

Figure S65. 125 MHz carbon-13 NMR spectrum of **16b** in $CDCl_3$.

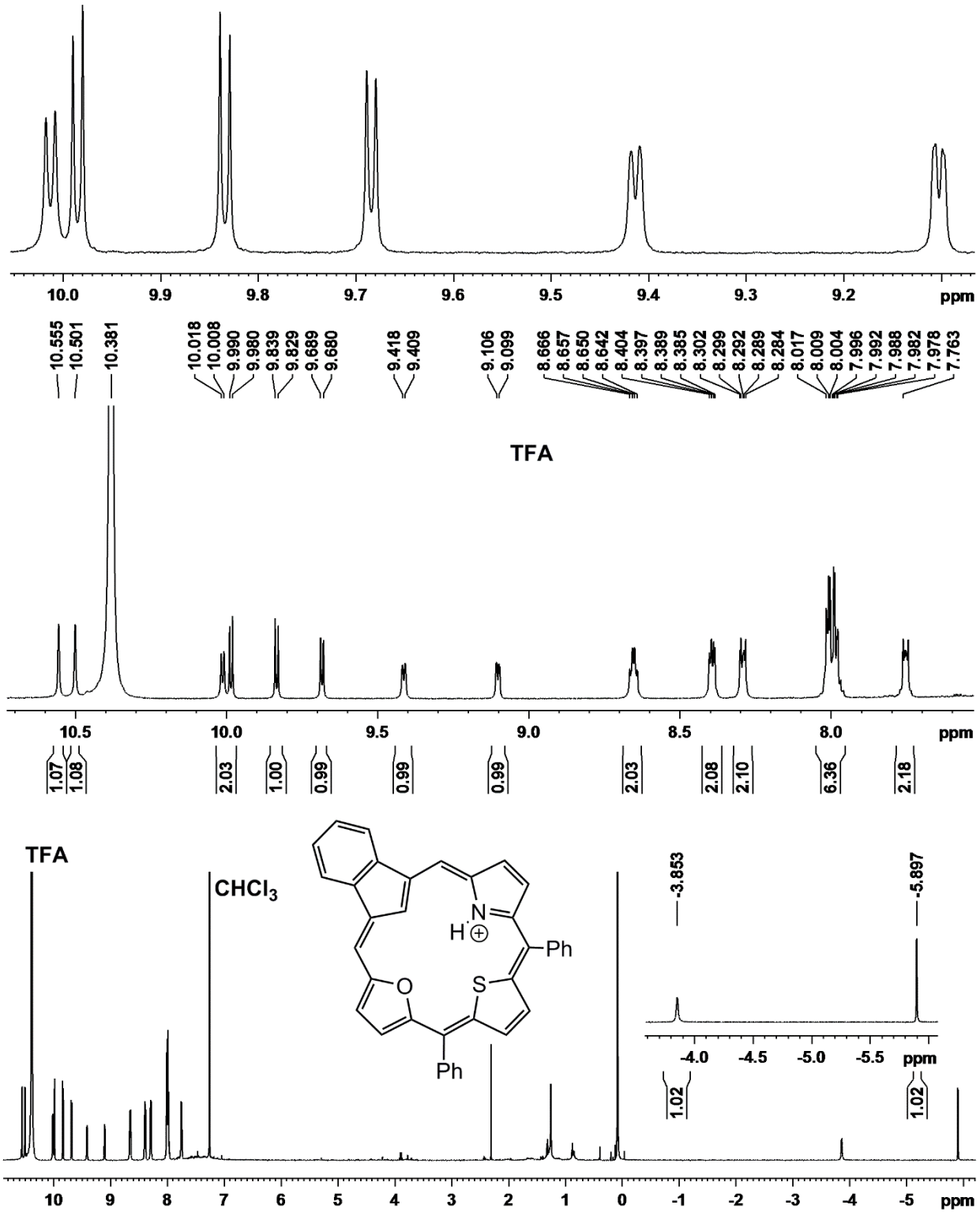

Figure S66. 500 MHz proton NMR spectrum of diphenyl oxathiacarbaporphyrin monocation **16b**H^+ in TFA-$CDCl_3$.

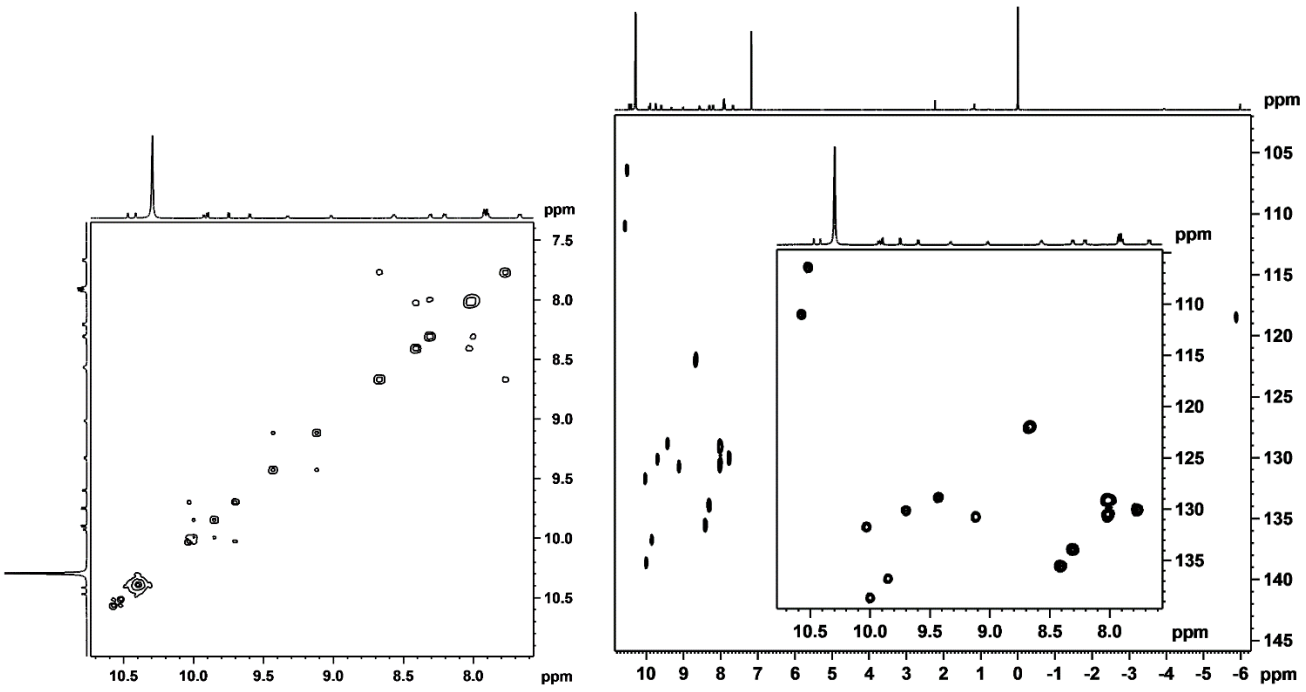

Figure S67. ^{1}H-^{1}H COSY (left) and HSQC (right) NMR spectra of **16b**H^{+} in TFA-CDCl$_3$.

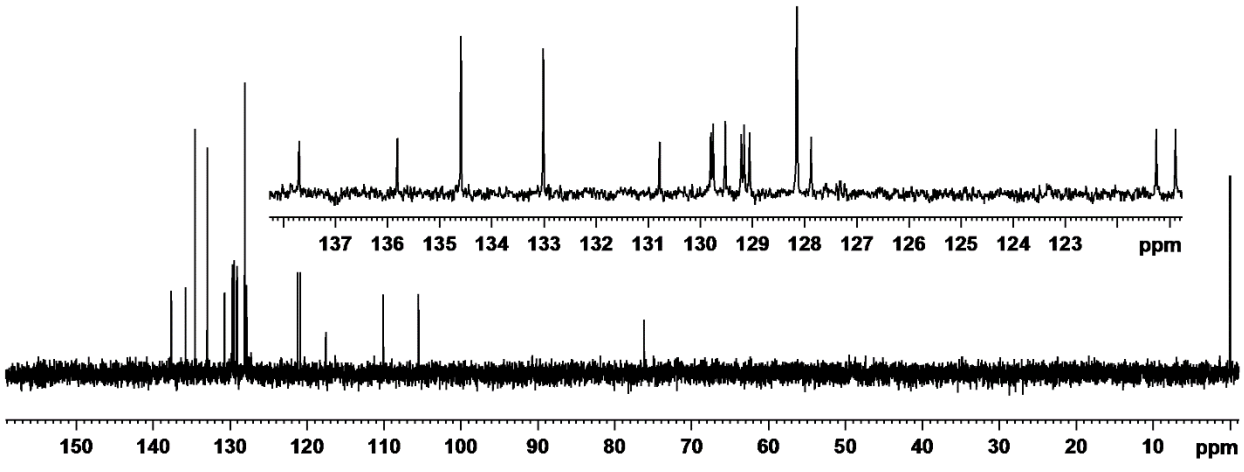

Figure S68. DEPT-135 NMR spectrum of diphenyl oxathiacarbaporphyrin monocation **16b**H^{+} in TFA-CDCl$_3$.

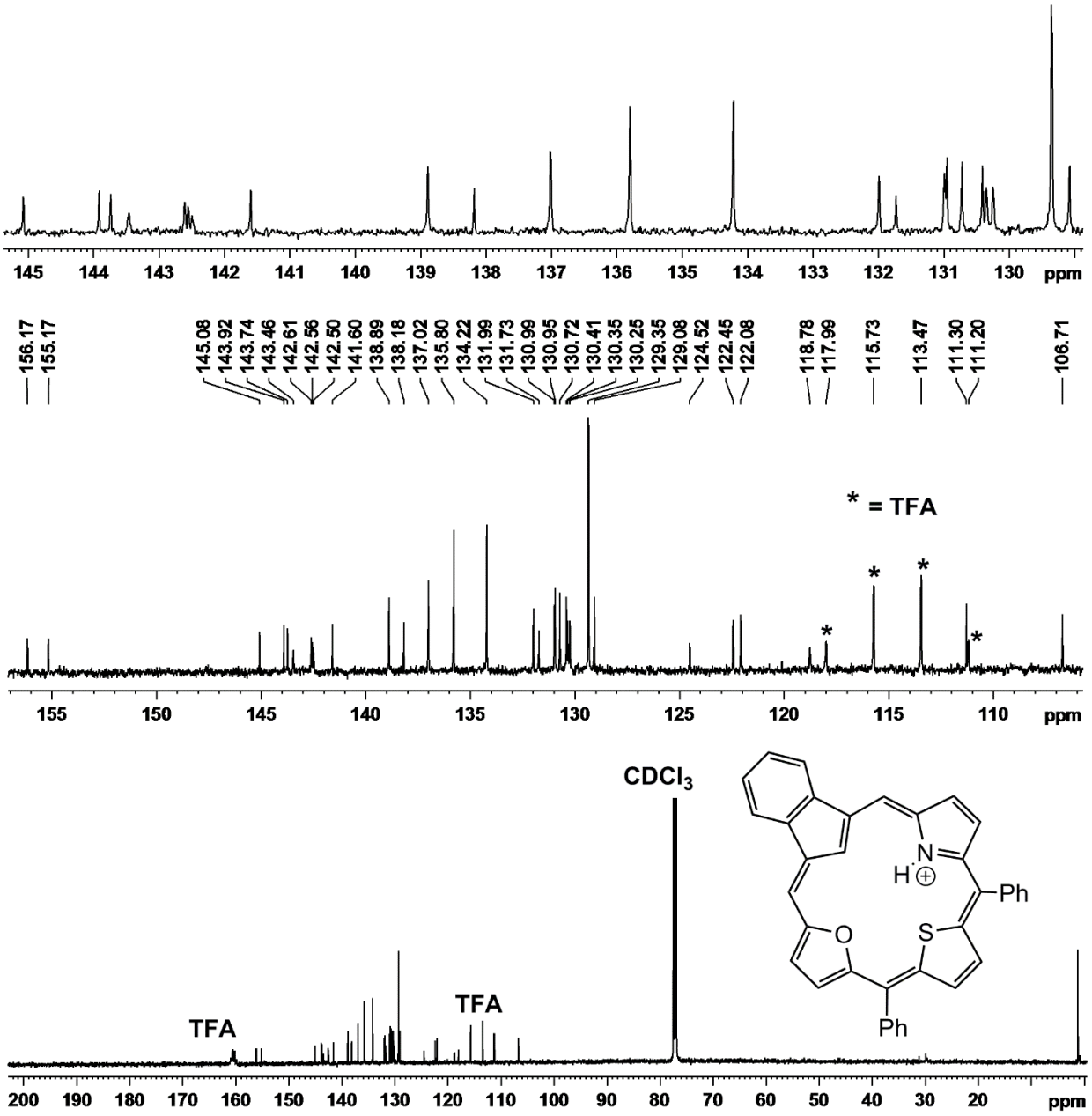

Figure S69. 125 MHz carbon-13 NMR spectrum of diphenyl oxathiacarbaporphyrin monocation **16b**H^+ in TFA-$CDCl_3$.

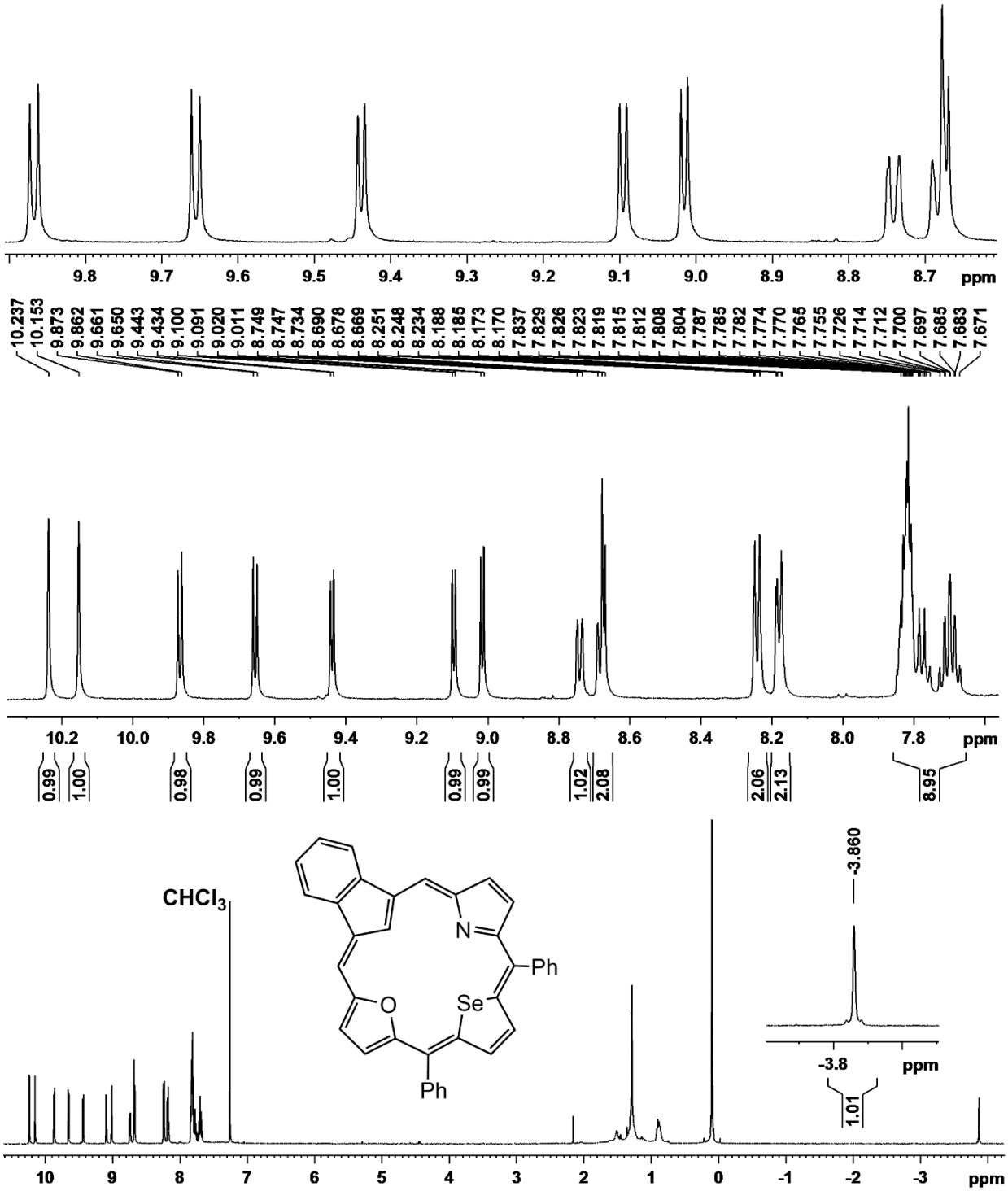

Figure S70. 500 MHz proton NMR spectrum of diphenyl oxaselenacarbaporphyrin **16c** in $CDCl_3$.

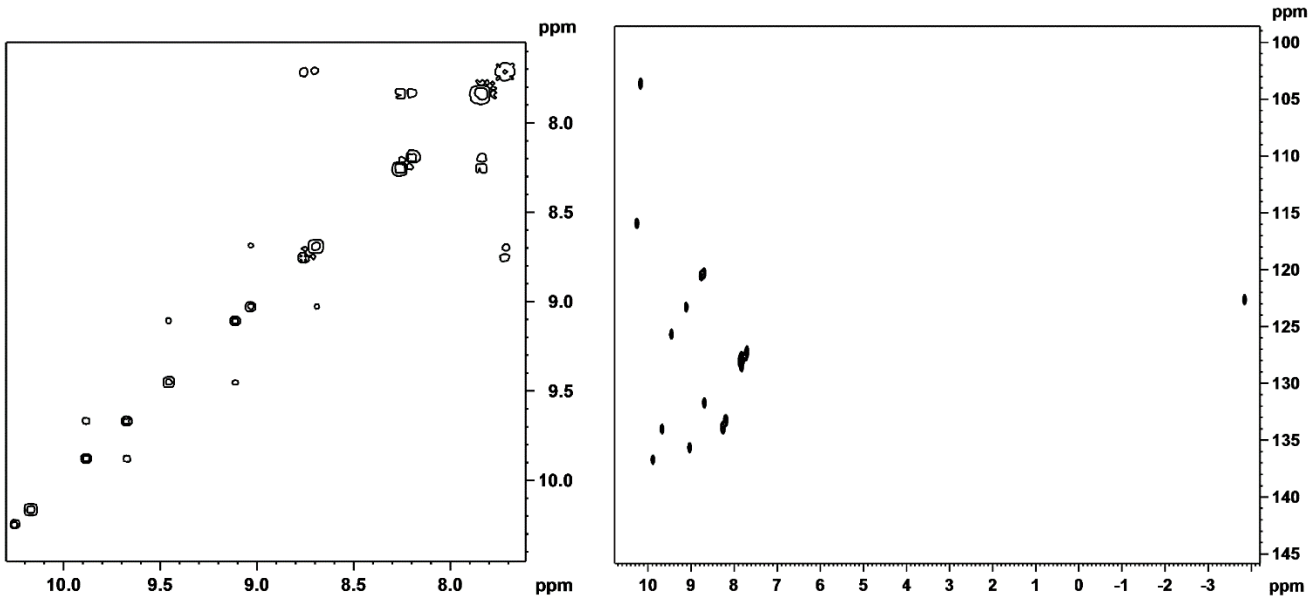

Figure S71. ^{1}H-^{1}H COSY (left) and HSQC NMR spectra of oxaselenacarbaporphyrin **16c** in $CDCl_3$.

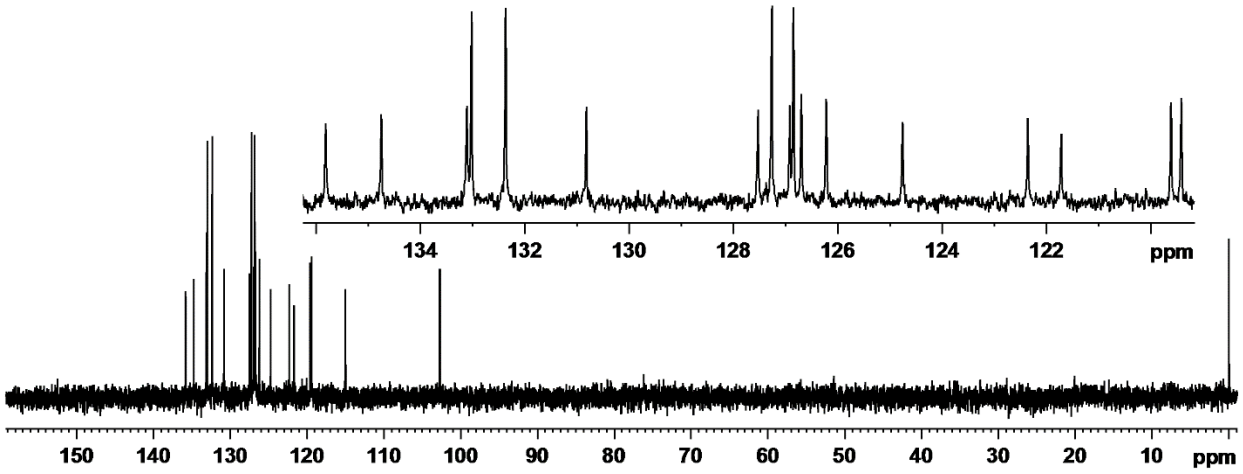

Figure S72. DEPT-135 NMR spectrum of oxaselenacarbaporphyrin **16c** in $CDCl_3$.

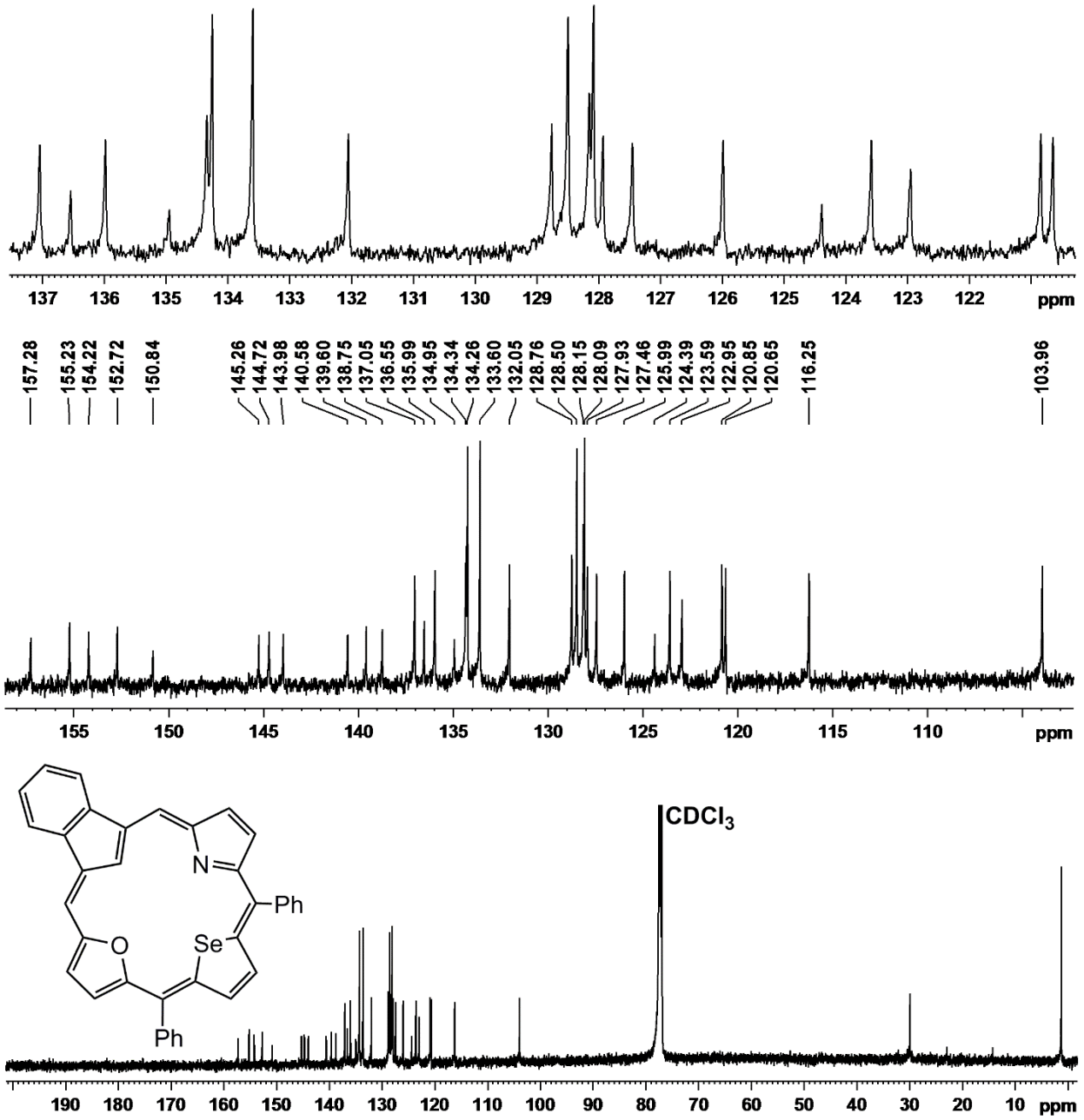

Figure S73. 125 MHz carbon-13 NMR spectrum of oxaselenacarbaporphyrin **16c** in $CDCl_3$.

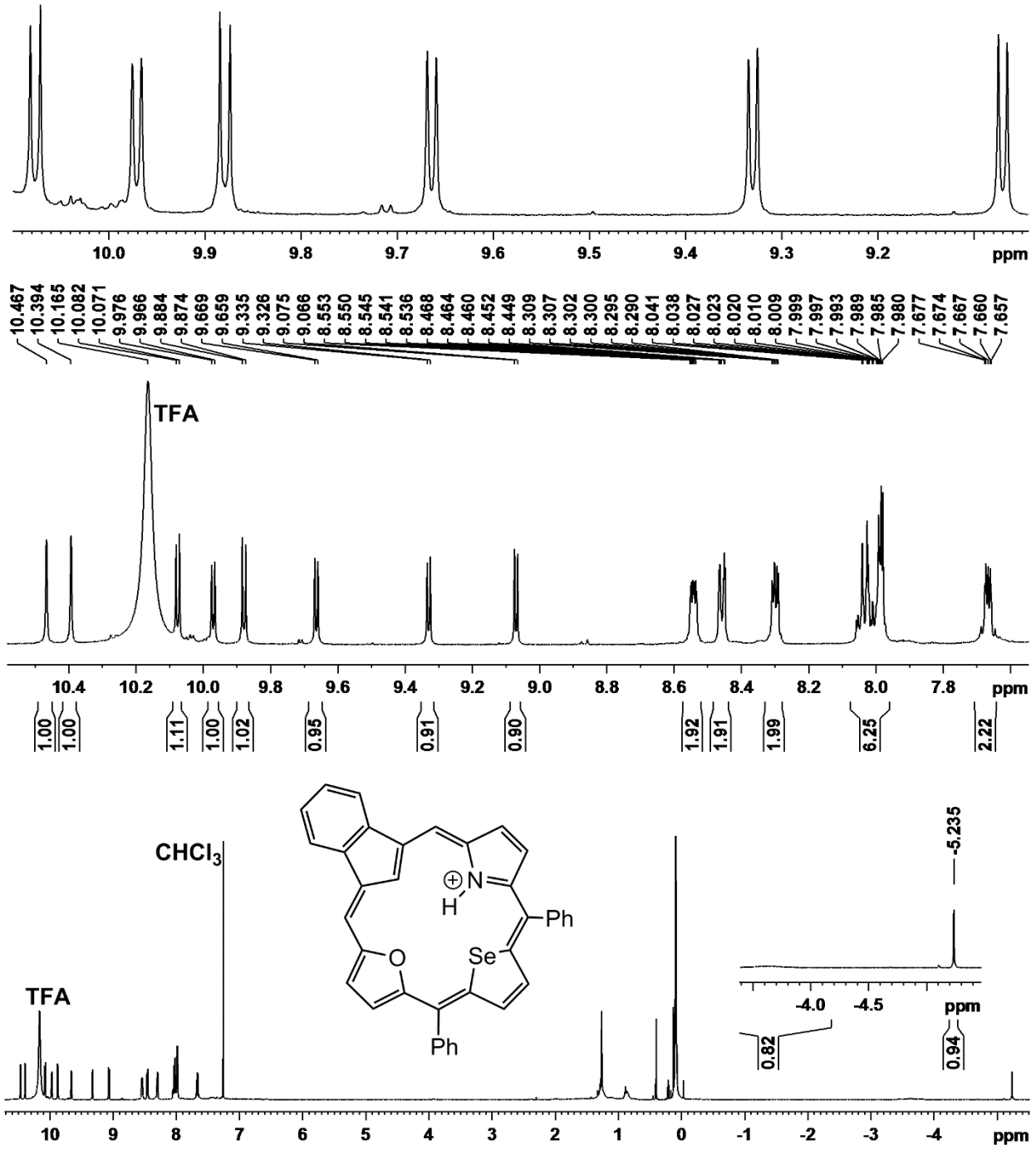

Figure S74. 500 MHz proton NMR spectrum of oxaselenacarbaporphyrin monocation **16c**H+ in $CDCl_3$ with 5 μL TFA.

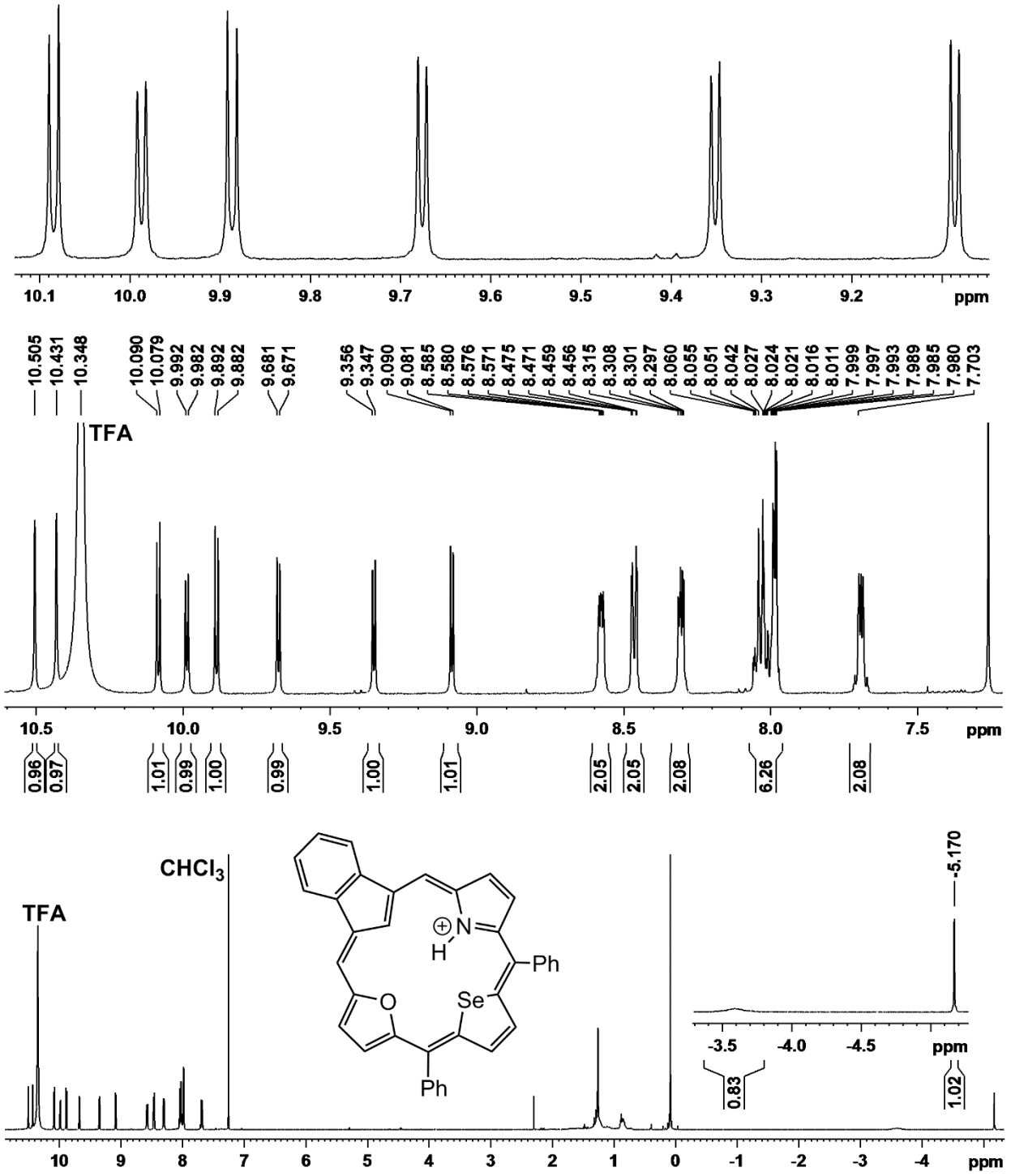

Figure S75. 500 MHz proton NMR spectrum of oxaselenacarbaporphyrin monocation **16c**H^+ in $CDCl_3$ with 2 drops of TFA.

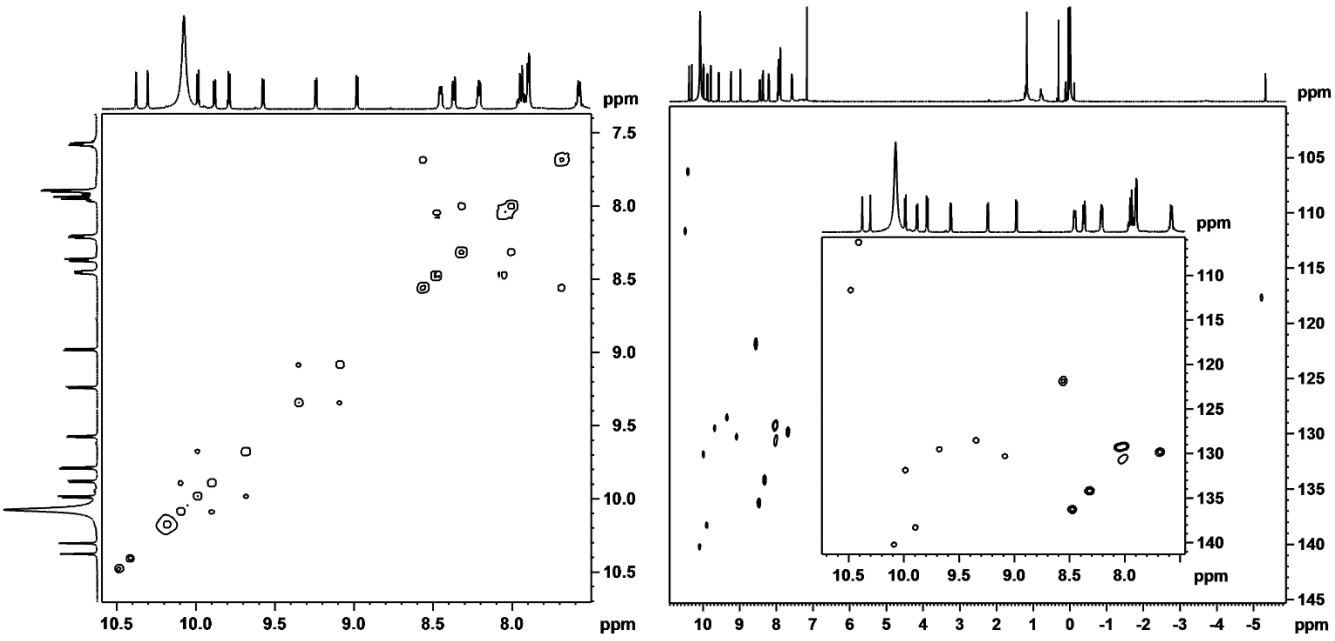

Figure S76. ^{1}H-^{1}H COSY (left) and HSQC (right) NMR spectra of oxaselenacarbaporphyrin monocation **16c**H^{+} in $CDCl_3$ with 5 μL of TFA.

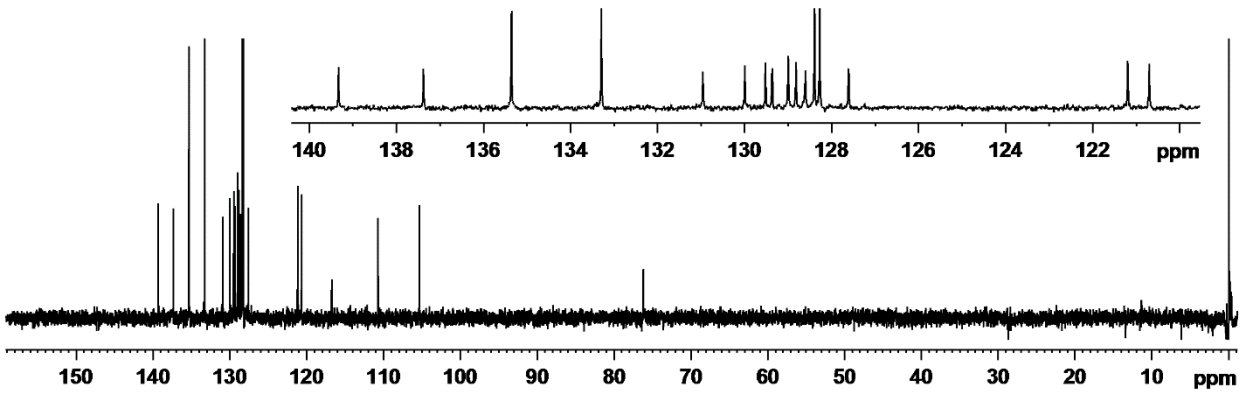

Figure S77. DEPT-135 NMR spectrum of oxaselenacarbaporphyrin monocation **16c**H^{+} in $CDCl_3$ with 5 μL of TFA.

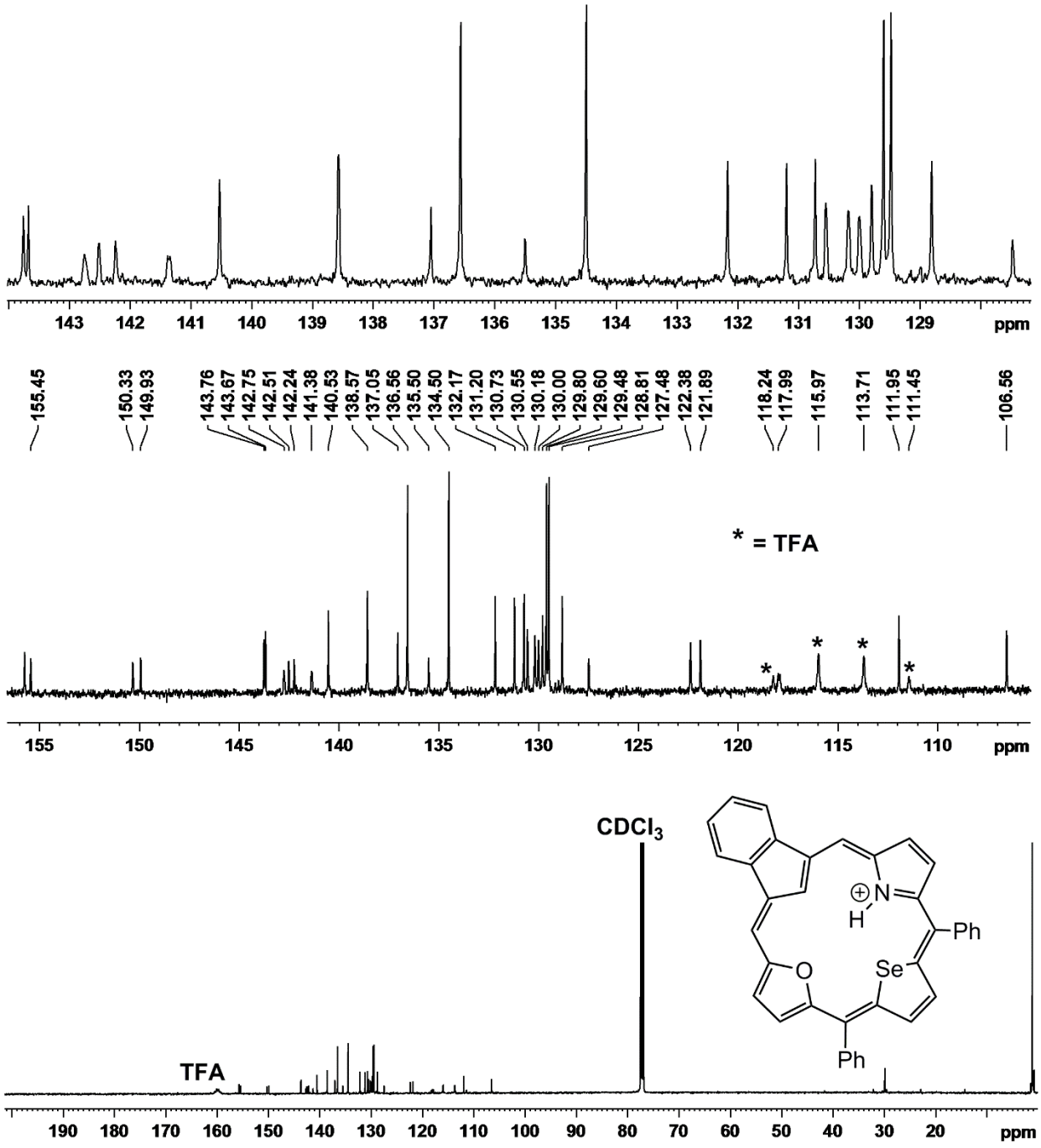

Figure S78. 125 MHz carbon-13 NMR spectrum of oxaselenacarbaporphyrin **16c**H^+ in $CDCl_3$ with 5 μL of TFA.

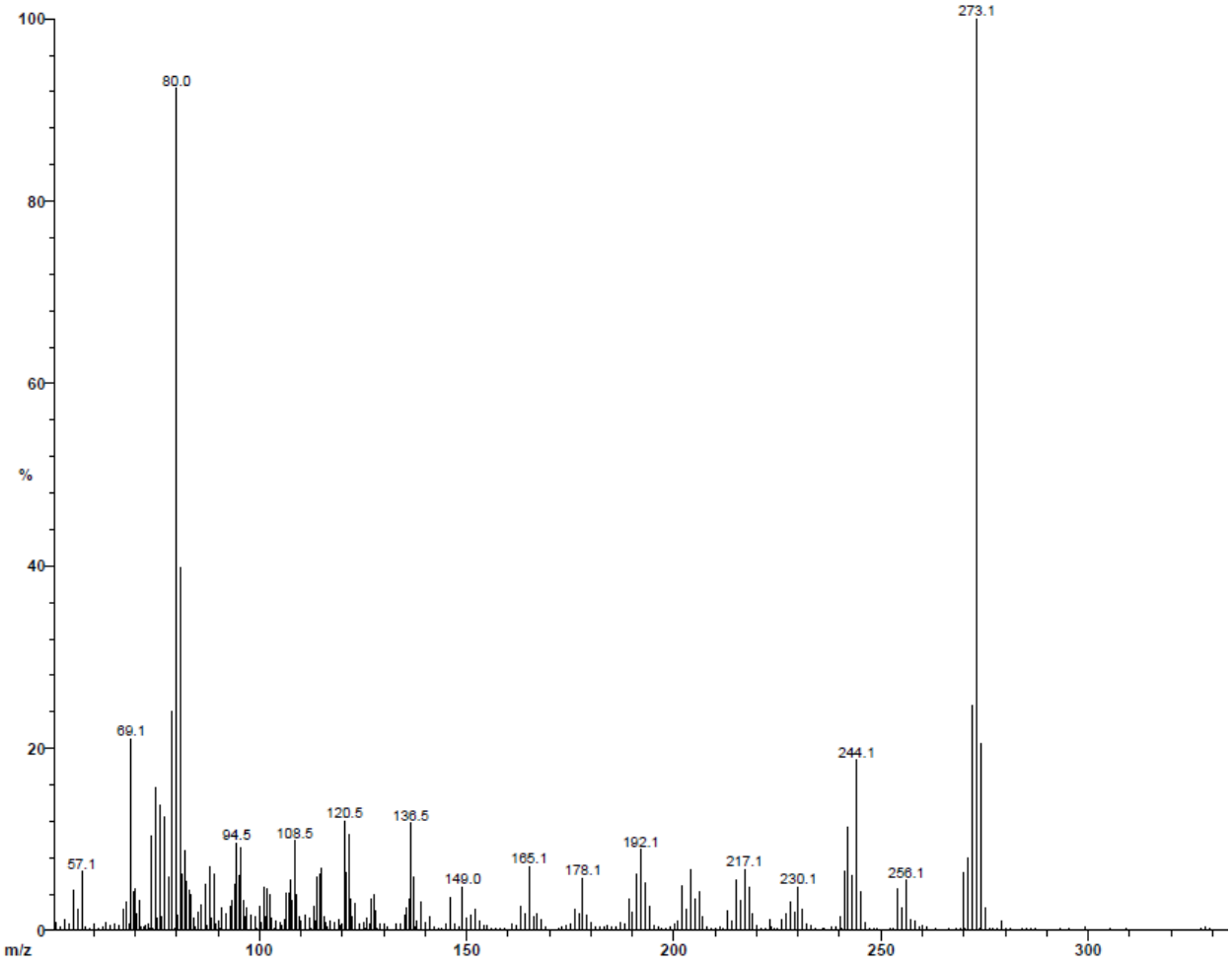

Figure S79. EI MS of oxacarbatripyrrin **8b**.

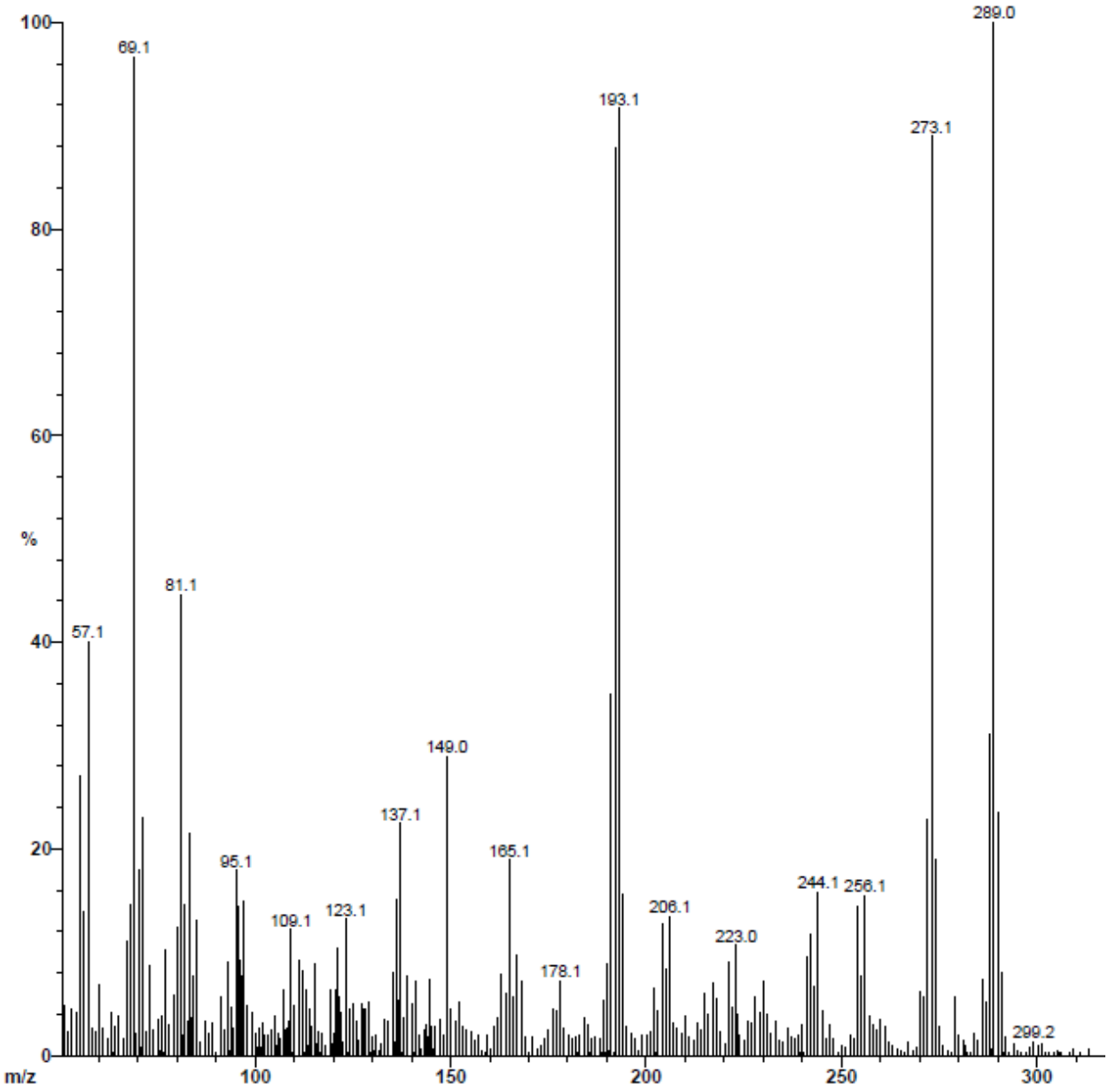

Figure S80. EI MS of thiacarbatripyrrin **8c**.

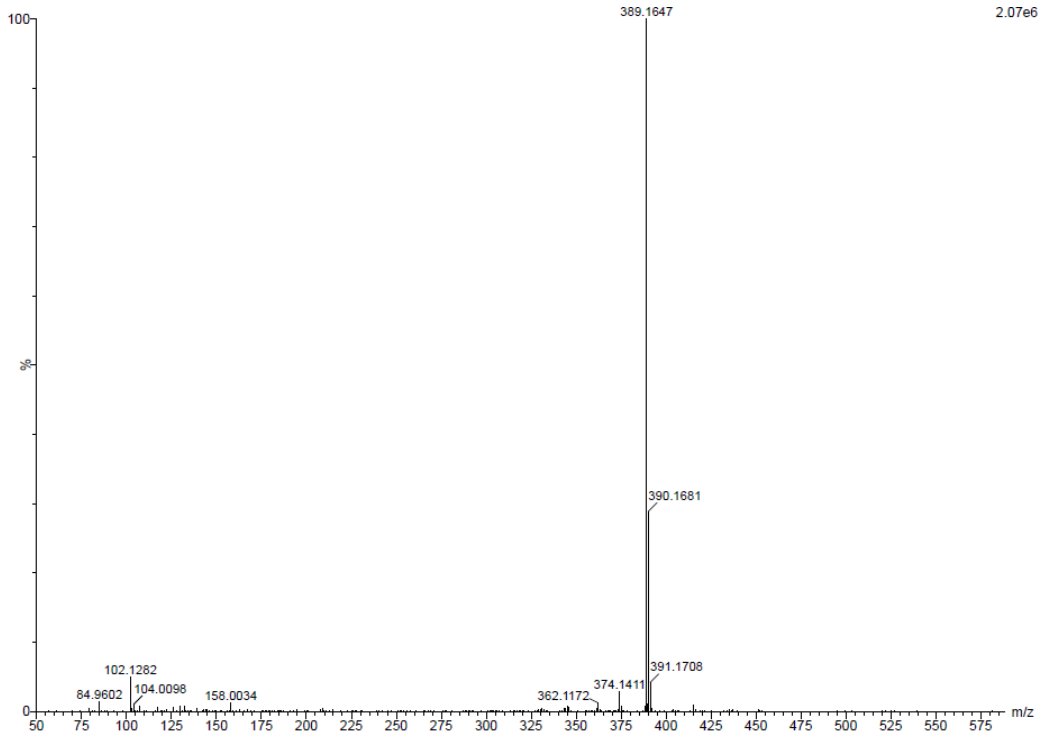

Figure S81. ESI MS of dimethyl oxacarbaporphyrin **15a**.

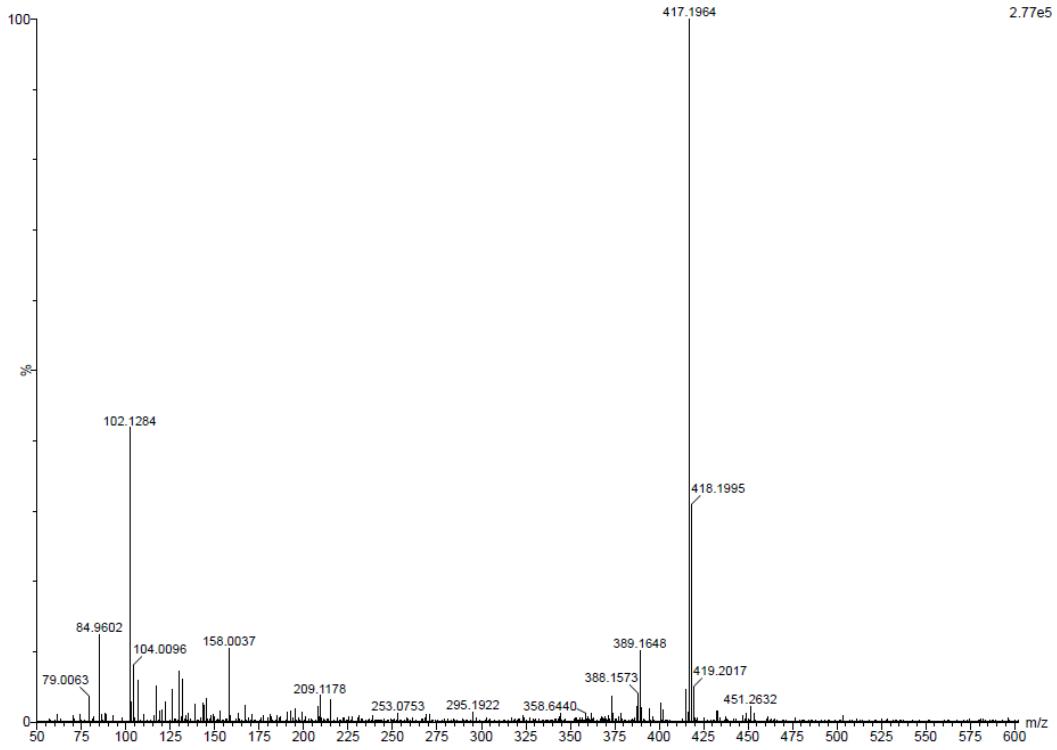

Figure S82. ESI MS of diethyl oxacarbaporphyrin **15b**.

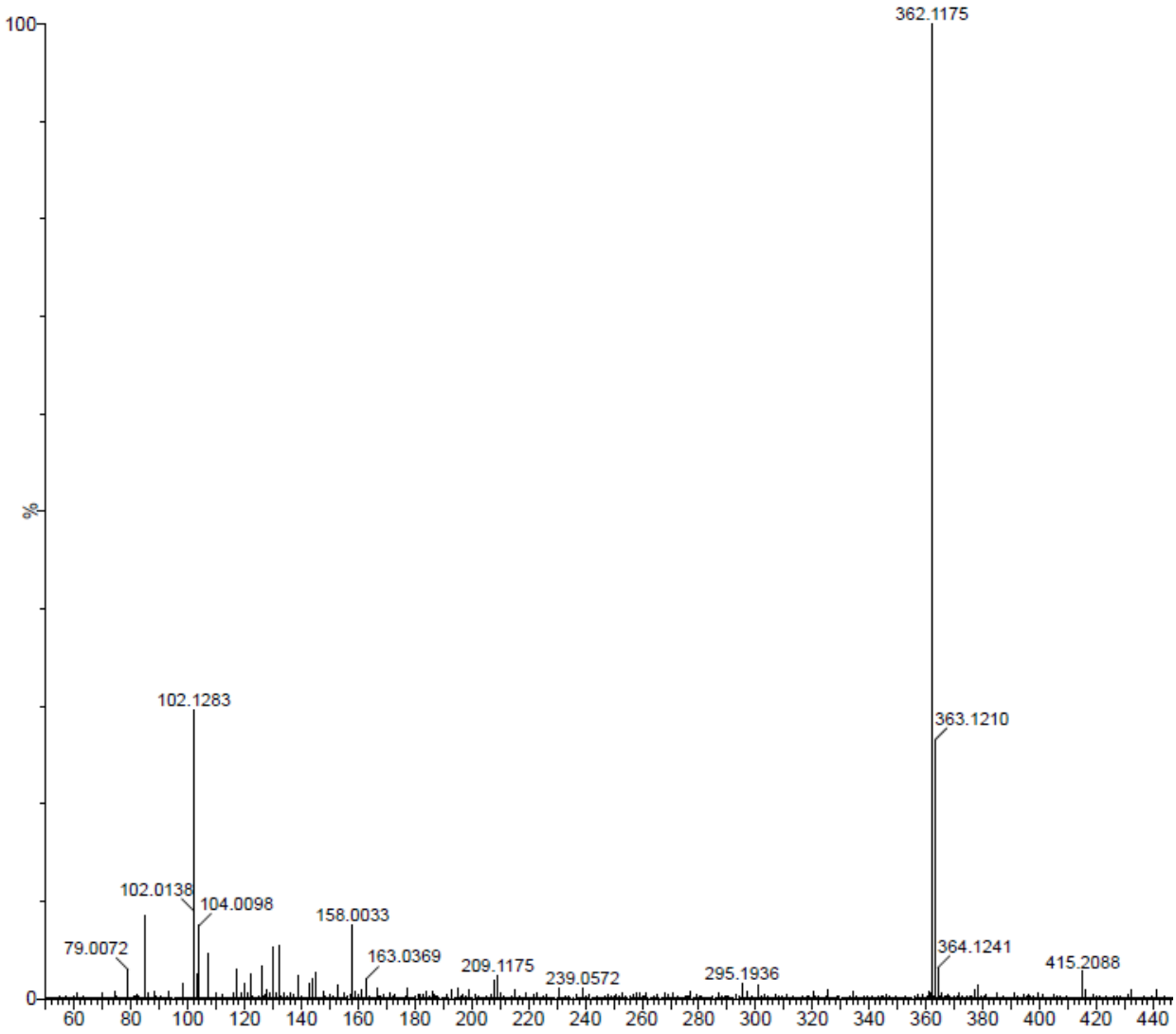

Figure S83. ESI MS of dioxacarbaporphyrin **12b**.

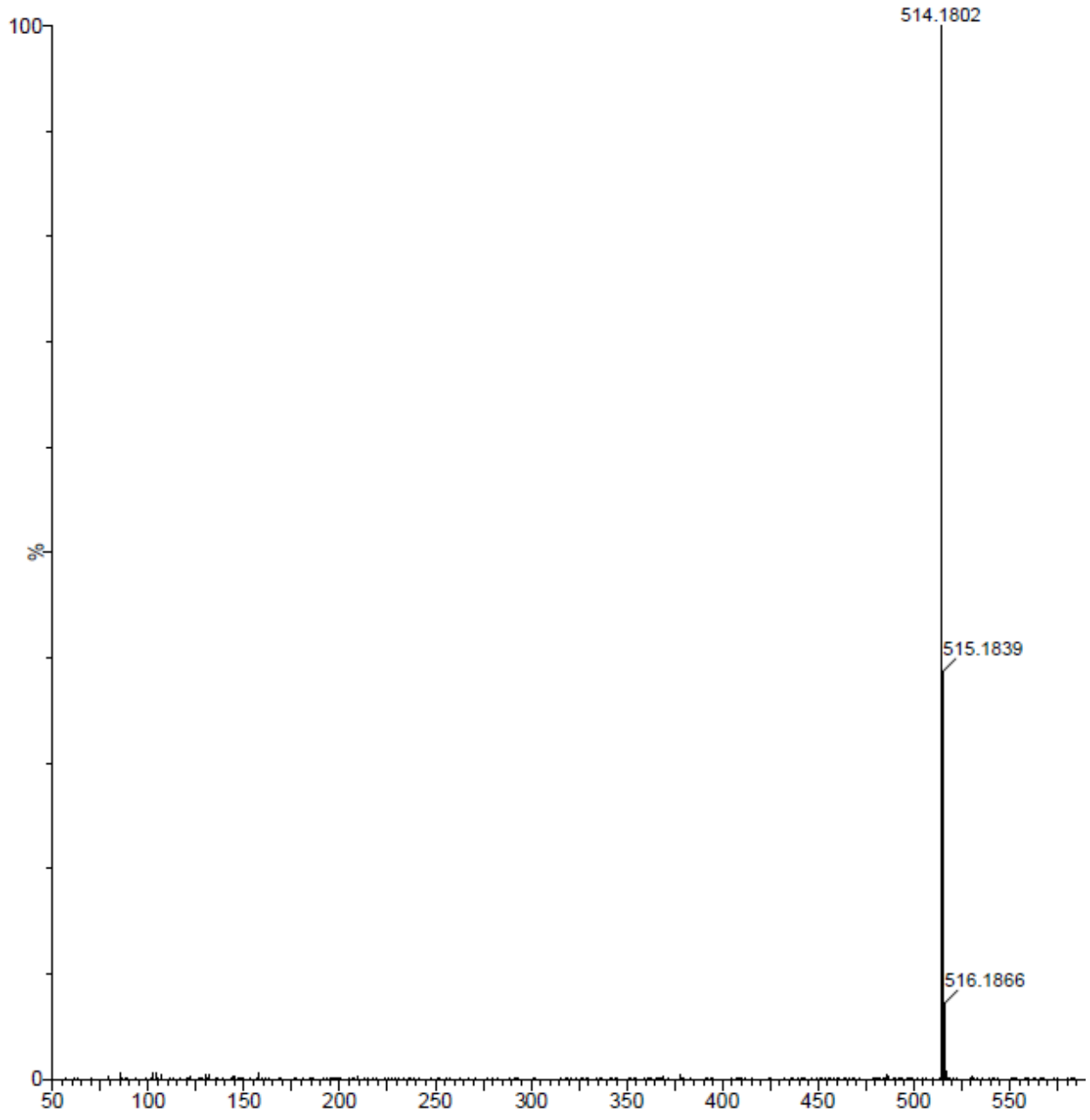

Figure S84. ESI MS of diphenyl dioxacarbaporphyrin **16a**.

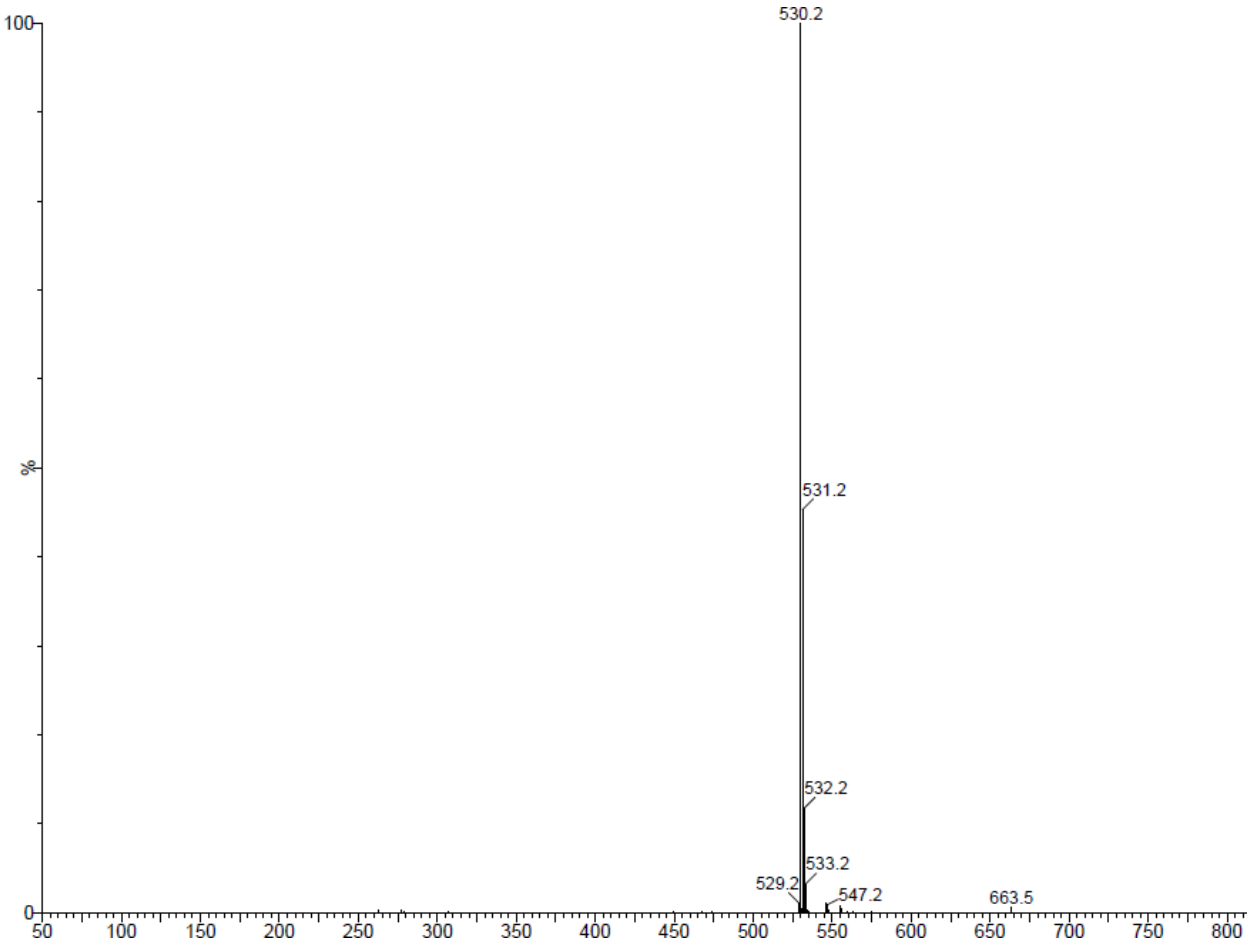

Figure S85. ESI MS of diphenyl oxathiacarbaporphyrin **16**.

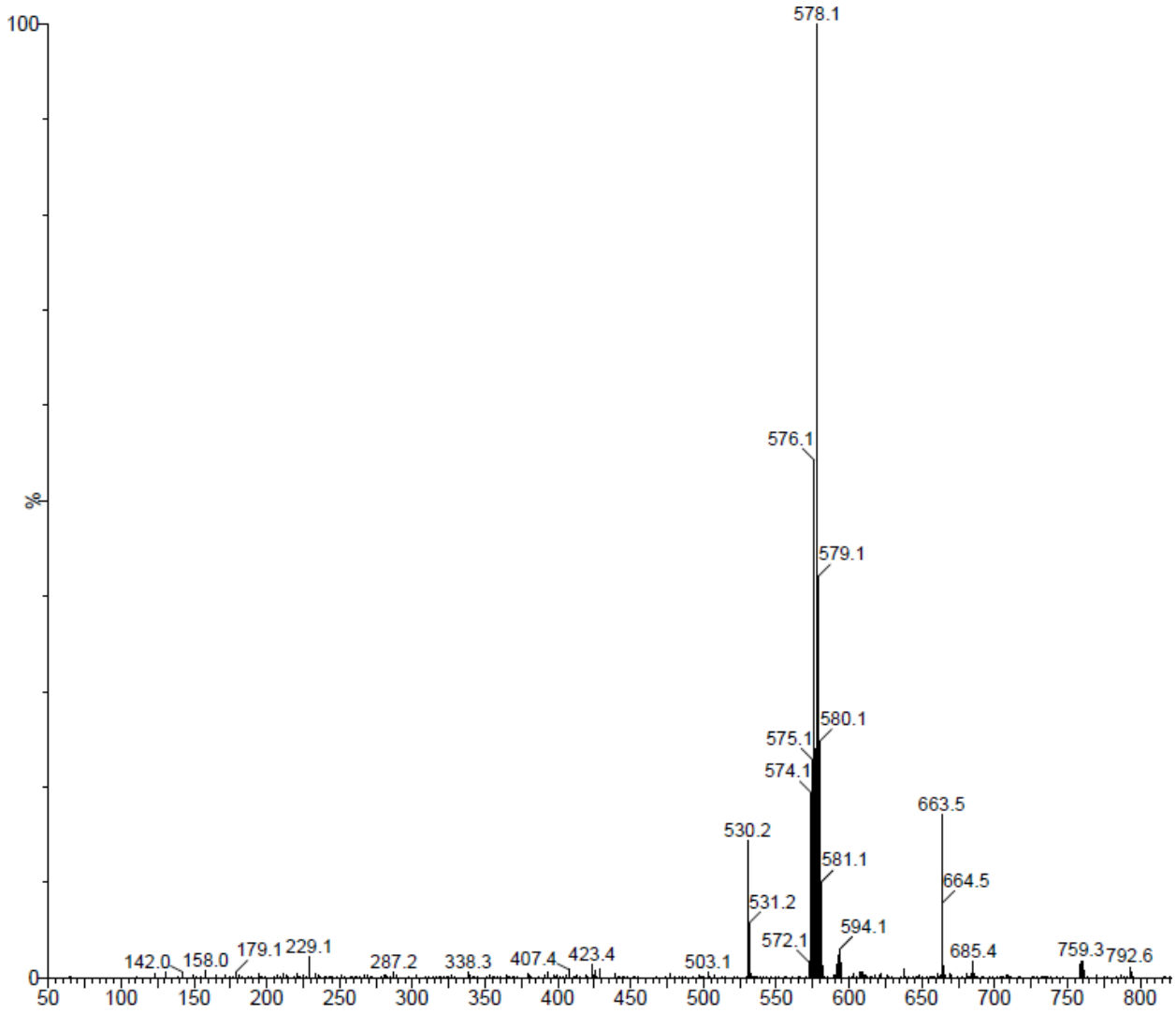

Figure S86. ESI MS of diphenyl oxaselenacarbaporphyrin **16c**.