Supporting Information to:

MTO/H_2O_2/Pyrazole-Mediated N-Oxidation of *meso*-Tetraarylporphyrins and -chlorins, and S-Oxidation of a *meso*-Tetraaryldithiaporphyrin and -chlorin

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Materials and Instruments. All solvents and reagents were used as received. Known *meso*-tetraphenylporphyrin (**2a**), *meso*-tetra(4-chlorophenyl)porphyrin (**2b**), *meso*-tetra(4-*t*-butylphenyl)porphyrin (**2c**), *meso*-tetra(3,4,5-trimethoxyphenyl)porphyrin (**2d**) were prepared according to the Adler procedure.[1] *meso*-Tetra(pentafluorophenyl)porphyrin (**2e**),[2] *meso*-tetraphenyl-*cis*-2,3-dihydroxychlorin,[3] *meso*-tetraphenyl-3-oxa-2oxo-porphyrin (**6**),[4] *meso*-tetraphenyl-21,23-dithiaporphyrin (**8**),[5] and *meso*-tetraphenyl-2,3-*cis*-dimethoxy-21,23-dithia-chlorin (**10**)[6] were also prepared according to literature procedures. Analytical TLC plates: aluminum backed, silica gel 60, 250 μm thickness); preparative plates: 20 × 20 cm, glass backed, silica gel 60, 500 or 1000 μm thickness; flash column silica gel: standard grade, 60 Å, 32-63 μm.

Octaethylporphyrin-*N*-oxide (1). Prepared in 57% yield according to the general procedure. Recovery of starting material: 30-40%. Spectroscopic data identical to those described previously.[7]

1. Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.
2. Spellane, P. J.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, Y. C. *Inorg. Chem.* **1980**, *19*, 386-391.
3. Brückner, C.; Rettig, S. J.; Dolphin, D. *J. Org. Chem.* **1998**, *63*, 2094-2098.
4. McCarthy, J. R.; Jenkins, H. A.; Brückner, C. *Org. Lett.* **2003**, *5*, 19-22.
5. Stilts, C. E.; Nelen, M. I.; Hilmey, D. G.; Davies, S. R.; Gollnick, S. O.; Oseroff, A. R.; Gibson, S. L.; Hilf, R.; Detty, M. R. *J. Med. Chem.* **2000**, *43*, 2403-2410.
6. Lara, K. K.; Rinaldo, C. K.; Brückner, C. *Tetrahedron* **2005**, *61*, 2529-2539.
7. Andrews, L. E.; Bonnett, R.; Ridge, R. J.; Appelman, E. H. *J. Chem. Soc., Perkin Trans. 1* **1983**, 103-107.

***meso*-Tetraphenylporphyrin-*N*-oxide (3a). General Procedure for the MTO/H_2O_2/Pyrazole-*N*-Oxidation of Porphyrins.** In a 50 mL round bottom flask equipped with a stirring bar, TPP (**2a**) (200 mg, 3.25×10^{-4} mol) was dissolved in CH_2Cl_2 (20 ml). In a 20 ml scintillation vial with Teflon-lined cap, MTO (20 mg, 8.1×10^{-5} mol) suspended in CH_2Cl_2 (~1 mL) is mixed with a 30% aq H_2O_2 solution (750 μL, ~6.5×10^{-3} mmol) by vigorous shaking. The yellow mixture was added at ambient temperature to the vigorously stirring porphyrin solution, followed immediately by pyrazole (44 mg, 6.4×10^{-4} mol). When the reaction had proceeded to the desired conversion (~50%, assessed by TLC), the excess H_2O_2 was quenched by addition of MnO_2 (~50 mg). After stirring for 2 min, the mixture was filtered through a glass frit (M), the organic layer was separated and dried over Na_2SO_4, and reduced by rotary evaporation. The residue was subjected to column (or preparative plate) chromatography (silica - CH_2Cl_2/1% MeOH), followed by recrystallization by solvent exchange (with pet. ether 30-60) on the rotary evaporator. Product **3a** can be isolated in 50-80% yields (100 - 160 mg). R_f (silica – CH_2Cl_2) = 0.19. ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 9.00 (d, ^3J = 4.7 Hz, 2H), 8.85 (d ^3J = 4.7 Hz, 2H), 8.67 (s, 2H), 8.28 (m, 4H), 8.21 (d, ^3J = 6.3 Hz, 4H), 7.83-7.73 (m, 12H), 7.55 (s, 2H), 1.07 (broad s, exchangeable with D_2O, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 158.2, 142.8, 141.8, 141.5, 139.4, 139.0, 136.3, 136.0, 135.3, 130.2, 129.7, 128.8, 128.3, 127.7, 127.2, 123.1, 120.3, 120.1. UV-vis (CH_2Cl_2) λ_{max} [nm] (log ε) 416 (5.21), 544 (3.80), 593 (3.87), 686 (3.39). UV-vis (CH_2Cl_2 + 2% TFA) λ_{max} [nm] (log ε) 438 (5.48), 594 (sh), 649 (4.48). MS (ESI+, 100% CH_3CN, 30 V cone voltage) *m/z* 630.7 (MH^+). HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{31}N_4O$ (MH^+) 631.2498, found 631.2440.

***meso*-Tetra(4-chlorophenyl)porphyrin-*N*-oxide (3b).** Prepared from **2b** (2.6×10^{-4} mol) in 33-39% yields, according to the general procedure; reaction time 8 h; recovery of 20-30% starting material. R_f (silica – CH_2Cl_2) = 0.29. ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 9.00 (br s, 2H), 8.85 (br s, 2H), 8.67 (s, 2H), 8.21 (d, ^3J = 8.1 Hz, 4H), 8.14 (d, ^3J = 8.1 Hz, 4H), 7.80 (d, ^3J = 8.3 Hz, 4H), 7.76 (d, ^3J = 8.3 Hz, 4H), 7.58 (s, 2H), 1.05 (broad s, exchangeable with D_2O, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 157.2, 141.8, 141.1, 139.7, 139.5, 139.0, 137.4, 136.4, 136.0, 135.7, 134.9, 130.3, 129.9, 128.1, 127.6, 121.9, 120.5, 119.0. UV-vis (CH_2Cl_2) λ_{max} [nm] (log ε) 417 (5.20), 543 (3.80), 595 (3.87), 683 (3.38). UV-vis (CH_2Cl_2 + 2% TFA) λ_{max} (nm) [log ε] 440 (5.51), 594 (3.66), 653 (4.55). MS (ESI+, 100% CH_3CN, 30 V cone voltage) *m/z* 768 (MH^+). HR-MS (ESI+, 100% CH_3CN) calculated for $C_{44}H_{27}Cl_4N_4O$ (MH^+) 769.0918, found 769.0898.

***meso*-Tetra(4-*tert*-butylphenyl)porphyrin-*N*-oxide (3c).** Prepared from **2c** (2.40×10^{-4} mol) in 34% yields, according to the general procedure; reaction time 48 h; recovery of 20-30% starting material. R_f (silica – CH_2Cl_2) = 0.19. ^{1}H NMR (400 MHz, CH_2Cl_2/CD_2Cl_2, δ): 9.02 (br s, 2H), 8.87 (d, ^3J = 4 Hz, 2H), 8.69 (s, 2H), 8.19 (br s, 4H), 8.12 (d, ^3J = 7.7 Hz, 4H), 7.82 (d, ^3J = 8 Hz, 4H), 7.77 (d, ^3J = 8 Hz, 4H), 7.52 (broad s, 2H), 1.61, 1.60 (overlapping s, 36H), 1.0 (broad s, exchangeable with D_2O, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 157.9, 151.9, 151.3, 139.7, 139.2, 136.3, 135.9, 135.2, 129.9, 129.6, 124.8, 124.3, 123.0, 120.1, 35.39, 35.37, 32.0, 31.9 (the compound possessed only marginal solubility for an optimally resolved ^{13}C NMR over the time course of 15 h). UV-vis (CH_2Cl_2) λ_{max} [nm] (log ε) 419 (5.35), 546 (3.90), 595 (4.07), 680 (3.59). UV-vis (CH_2Cl_2 + 2% TFA) λ_{max} (nm) [log ε] 445 (5.64), 665 (4.76). MS (ESI+, 100% CH_3CN, 30 V cone voltage) *m/z* 855 (MH^+). HR-MS (ESI+, 100% CH_3CN) calculated for $C_{60}H_{63}N_4O$ (MH^+) 855.5005, found 855.4944.

***meso*-Tetra(3,4,5-trimethoxyphenyl)porphyrin-*N*-oxide (3d).** Prepared from **2d** (2.00×10^{-4} mol) in 33-48% yields, according to the general procedure; reaction time 48 h; isolated by preparative plate chromatography; recovery of 30-40% starting material. R_f (silica – CH_2Cl_2/3% MeOH) = 0.18. ^{1}H NMR (400 MHz, CH_2Cl_2/CD_2Cl_2, δ): 9.13 (d, ^3J = 6.4 Hz, 2H), 8.97 (d, ^3J = 6.4 Hz, 2H), 8.79 (s, 2H), 7.68 (s, 2H), 7.56 (s, 4H), 7.46 (s, 4H), 4.08 (s, 12H), 4.00 (s, 12H), 3.99 (s, 12H), 0.9 (broad s, exchangeable with D_2O, 2H). ^{13}C NMR (100 MHz, CH_2Cl_2/CD_2Cl_2, δ): 157.8, 152.2, 151.7, 141.6, 139.1, 138.8, 138.5, 138.3, 137.7, 136.5, 135.6, 129.8, 129.4, 122.4, 119.9, 119.7, 114.4, 113.3, 61.0, 56.6, 56.5. UV-vis (CH_2Cl_2) λ_{max} [nm] (log ε) 426 (5.19), 546 (3.86), 595 (3.91), 688 (3.45). UV-vis (CH_2Cl_2 + 2% TFA) λ_{max} [nm] (log ε) 464 (5.22), 668 (3.58). MS (ESI+, 100% CH_3CN, 30 V cone voltage) *m/z* 991 (MH^+). HR-MS (ESI+, 100% CH_3CN) calculated for $C_{56}H_{55}N_4O_{13}$ (MH^+) 991.3766, found 991.3747.

***meso*-Tetra(2,3,4,5,6-pentafluorophenyl)porphyrin-*N*-oxide (3e).** Prepared from **2e** (1.2×10^{-4} mol) in 14% yield, according to the general procedure; reaction time 72 h; recovery of ~50% starting material. R_f (silica-CH_2Cl_2/hexanes-2:1) = 0.55. ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 8.98 (d, 2H, ^3J = 4 Hz), 8.93 (d, 2H, ^3J = 4Hz), 8.76 (s, 2H), 7.85 (s, 2H), NH could not be distinguished; ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 158.5, 147.8, 145.3, 140.6, 138.9, 138.7, 136.5, 135.8, 129.7, 129.5, 120.0, 115.8, 114.2, 105.5, 103.1. UV-vis (CH_2Cl_2) λ_{max} [nm] (log ε) 411 (5.12), 463 (4.24), 541 (3.77), 601 (3.30). UV-vis (CH_2Cl_2 + 2% TFA) λ_{max} [nm] (log ε) 408 (5.23), 467 (4.10), 532 (3.54), 567 (3.77). HR-MS (ESI+, 100% CH_3CN) calculated for $C_{44}H_{10}F_{20}N_4O$ (MH^+) 991.0614, found 991.0610.

***meso*-Tetraphenyl-2,3-*cis*-dimethoxychlorin (4).** [*meso*-Tetraphenyl-*cis*-2,3-dihydroxy-chlorinato]Zn(II)[8] (75 mg, 1.05×10^{-4} mol) was, under dry N_2, dissolved in dry THF (35 mL), and a four-fold molar excess of NaH (60% emulsion in oil) was added in portions. After stirring for 5 min at ambient temperature, CH_3I (16.4 μL, ~2.5 equiv) was added by syringe and the reaction was allowed to stir for 24 h. TLC showed that all starting material was converted to one major product of lesser polarity. The reaction mixture was carefully quenched by dropwise addition of H_2O. After all H_2-evolution had ceased, $CHCl_3$ (50 mL) and H_2O (50 mL) was added. The organic phase was isolated, and shaken with aq 4 M HCl (50 mL), followed by several washings with H_2O and, finally, dilute aq $NaHCO_3$. The organic phase was evaporated to dryness and the residue was chromatographed (silica – CH_2Cl_2) to provide **4** in 90% yield as purple powder. R_f (silica – CH_2Cl_2) = 0.29. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.66 (d, ^3J = 4.8 Hz, 2H), 8.53 (s, 2H), 8.36 (d, ^3J = 4.8 Hz, 2H), 8.18-8.12 (two overlapping br d, ^3J = 7.2 Hz, 6H), 7.86 (d, ^3J = 6.0, 2H), 7.63-7.76 (m, 12H), 6.06 (s, 2H), 3.02 (s, 6H), -1.88 (br s, exchangeable with D_2O, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 160.4, 153.2, 142.0, 141.9, 140.6, 135.7, 134.1, 134.0, 132.7, 131.6, 128.0, 127.7, 127.4, 127.2, 127.1, 126.8, 124.6, 122.7, 114.0, 81.8, 58.4. UV-vis (CH_2Cl_2) λ_{max} [nm] (log ε) 414 (5.15), 517 (4.08), 544 (4.05), 593 (3.75), 644 (4.27). UV-vis (CH_2Cl_2/2% TFA) λ_{max} [nm] (log ε) 433 (5.09), 584 (3.97), 639 (4.23). MS (CI) *m/z* 676 (M^+), 645 (M^+- OCH_3), 629 (M^+- OC_2H_7), 614 (M^+- $O_2C_2H_6$), 601. HR-MS (ESI+, 100% CH_3CN) calculated for $C_{46}H_{37}N_4O_2$ (MH^+) 677.2911, found 677.2903.

***meso*-Tetraphenyl-2,3-*cis*-dimethoxychlorin-22-*N*-oxide (5).** Prepared from **4** (1.4×10^{-5} mol) in 41% yields, according to the general procedure using 1 equiv MTO; reaction time 2 h,

8. Brückner, C.; Rettig, S. J.; Dolphin, D. *J. Org. Chem.* **1998**, *63*, 2094-2098.

isolation by preparative plate chromatography; recovery of ~40% starting material. R_f (silica – CH_2Cl_2/3% MeOH) = 0.30. ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 8.77 (br s, 2H), 8.31 (d, ^3J = 4.0 Hz, 2H), 8.21 (broad s, 4H), 8.12 (d, ^3J = 8 Hz, 2H), 7.88 (d, ^3J = 8 Hz, 2H), 7.8-7.62 (m, 12H), 7.43 (s, 2H), 6.00 (s, 2H), 3.00 (s, 6H); inner NH signals not traced. ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 164.2, 142.6, 142.0, 141.3, 139.9, 136.6, 135.8, 134.7, 132.2, 130.1, 128.8, 127.9, 127.8, 127.7, 127.6, 127.57, 121.8, 118.5, 116.5, 82.4, 58.8. UV-vis (CH_2Cl_2) λ_{max} [nm] (log ε) 410 (5.12), 555 (3.7), 593 (3.82), 648 (sh). UV-vis CH_2Cl_2 + 2% TFA) λ_{max} [nm] (log ε) 419 (5.02), 439 (5.02), 577 (3.9), 626 (4.94). MS (ESI+, 100% CH_3CN, 30 V cone voltage) *m/z* 693 (MH^+). HR-MS (ESI+, 100% CH_3CN) calculated for $C_{46}H_{37}N_4O_3$ (MH^+) 693.2866, found 693.2901.

***meso*-Tetraphenyl-2-oxa-3-oxoporphyrin-22-*N*-oxide (7).** Prepared from **6** (3.1×10^{-5} mol) in 45% yields scale, according to the general procedure using 1 equiv of MTO; reaction time 2 h; isolation by preparative plate chromatography; recovery of 30% starting material. R_f (silica – CH_2Cl_2) = 0.29. ^{1}H NMR (400 MHz, CH_2Cl_2/CD_2Cl_2, δ): 8.86 (d ^3J = 4.8 Hz, 1H), 8.76 (d, ^3J = 4.8 Hz, 1H), 8.65 (d, ^3J = 4.8 Hz, 1H), 8.46 (d, ^3J = 4.8 Hz, 1H), 8.21-8.15 (m, 4H), 8.12-8.07 (m, 2H), 7.98-7.94 (m, 2H), 7.81-7.71 (m, 12H), 7.41-7.36 (m, 2H), 2.6 (broad s, exchangeable with D_2O, 1H), 2.2 (broad s, exchangeable with D_2O, 1H). ^{13}C NMR (100 MHz, CH_2Cl_2/CD_2Cl_2, δ): 167.7, 156.0, 142.1, 141.8, 140.8, 140.4, 140.2, 140.0, 138.9, 138.7, 137.9, 136.8, 135.6, 135.5, 134.1, 133.1, 132.7, 131.1, 129.6, 129.4, 129.2, 128.9, 128.7, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.4, 125.2, 120.5, 120.3, 120.2, 119.7, 104.9. UV-vis (CH_2Cl_2) λ_{max} [nm] (log ε) 416 (5.25), 554 (3.78), 599 (3.98). UV-vis (CH_2Cl_2 + 2% TFA) λ_{max} [nm] (log ε) 425 (5.36), 556 (sh), 603 (4.15), 579 (sh), 633 (3.71). MS (ESI+, 100% CH_3CN, 30 V cone voltage) *m/z* 648

(MH^+). HR-MS (ESI+, 100% CH_3CN) calculated for $C_{43}H_{29}N_4O_3$ (MH^+) 649.2240, found 649.2229.

***meso*-Tetraphenyl-21,23-dithiaporphyrin-21-*S*-oxide (9).** Prepared from **8** (3.7×10^{-5} mol) in 20% yields, according to the general procedure using 1 equiv MTO; reaction time 3 h; isolation by preparative plate chromatography; recovery of ~50% starting material. R_f (silica – CH_2Cl_2/3% MeOH) = 0.14. ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 9.45 (s, 2H), 9.30 (s, 2H), 8.40 (d, ^3J = 4.1 Hz, 2H), 8.29 (d, ^3J = 4.1 Hz, 2H), 8.24 (broad s, 3H), 8.18 (broad s, 3H), 7.86-7.79 (broad s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 160.4, 155.6, 150.5, 148.8, 141.0, 140.1, 140.0, 139.4, 136.5, 136.4, 135.6, 134.7, 134.5, 134.2, 134.1, 133.3, 128.6, 128.6, 128.1, 127.6, 127.5. UV-vis (CH_2Cl_2) λ_{max} [nm] (log ε) 390 (sh), 453 (4.83), 538 (3.97), 576 (3.68), 769 (3.40). UV-vis (CH_2Cl_2 + 2%) λ_{max} [nm] (log ε) 463 (4.86), 499 (4.64), 563 (3.72), 648 (3.85), 778 (3.93). MS (ESI+, 100% CH_3CN, 30 V cone voltage) *m/z* 665 (MH^+). HR-MS (ESI+, 100% CH_3CN) calculated for $C_{44}H_{29}N_2OS_2$ (MH^+) 665.1721, found 665.1745.

***meso*-Tetratolyl-21,23-dithia-7,8-diethoxychlorin-21-*S*-oxide (11A and 11B).** Prepared from **10** (1.9×10^{-5} mol scale) in 20% yield each, according to the general procedure using 1.0 equiv MTO; reaction time 1.5 h; isolation by preparative plate chromatography (silica-CH_2Cl_2/3% MeOH); 40% recovered starting material. **Isomer I** (no assignment whether this isomer is **11A** or **11B**): R_f (silica – CH_2Cl_2/5% MeOH) 0.56. ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 9.37 (d, ^3J = 5.6 Hz, 1H), 9.13 (d, ^3J = 5.0 Hz, 1H), 9.04 (d, ^3J = 5.6 Hz, 1H), 8.76 (d, ^3J = 5.0 Hz, 1H), 8.25 (d, ^3J = 4.3 Hz, 1H), 8.10 (d, ^3J = 4.3 Hz, 1H), 8.05-7.96 (m, 4H), 7.85-7.79 (m, 4H), 7.6-7.54 (m, 8H), 5.84 (d, ^3J = 6.6 Hz, 1H), 5.70 (d, ^3J = 6.6 Hz, 1H), 3.10-3.04 (2s, 6H), 2.65-2.62 (3s, 12H). UV-vis (CH_2Cl_2) λ_{max} [nm] (rel. intensity) 436 (sh), 460 (1.00), 546 (0.16),

669 (0.02). HR-MS (ESI+, 100% CH_3CN) calculated for $C_{50}H_{43}N_2O_3S_2$ (MH^+) 783.2715, found 783.2730. **Isomer II** (no assignment whether this isomer is **11A** or **11B)**: R_f (silica – CH_2Cl_2/5% MeOH) 0.43. ^1H NMR (400 MHz, CD_2Cl_2, δ): 9.23 (d, ^3J = 5.5 Hz, 1H), 9.12 (d, ^3J = 4.7 Hz, 1H), 8.82 (d, ^3J = 5.5 Hz, 1H), 8.75 (d, ^3J = 4.7 Hz, 1H), 8.24 (d, ^3J = 4.5 Hz, 1H), 8.14 (d, ^3J = 4.5 Hz, 1H), 8.03 (broad s, 2 H), 7.98 (broad s, 2H), 7.65-7.46 (m. 12H), 5.99 (d, ^3J = 6.5 Hz, 1H), 5.92 (d, ^3J = 6.5 Hz, 1H), 3.05-3.04 (2s, 6H), 2.63-2.60 (3s, 12H). UV-vis (CH_2Cl_2) λ_{max} [nm] (rel. intensity) 460 (1.00), 544 (0.16), 667 (0.02). HR-MS (ESI+, 100% CH_3CN) calculated for $C_{50}H_{43}N_2O_3S_2$ (MH^+) 783.2715, found 783.2704.

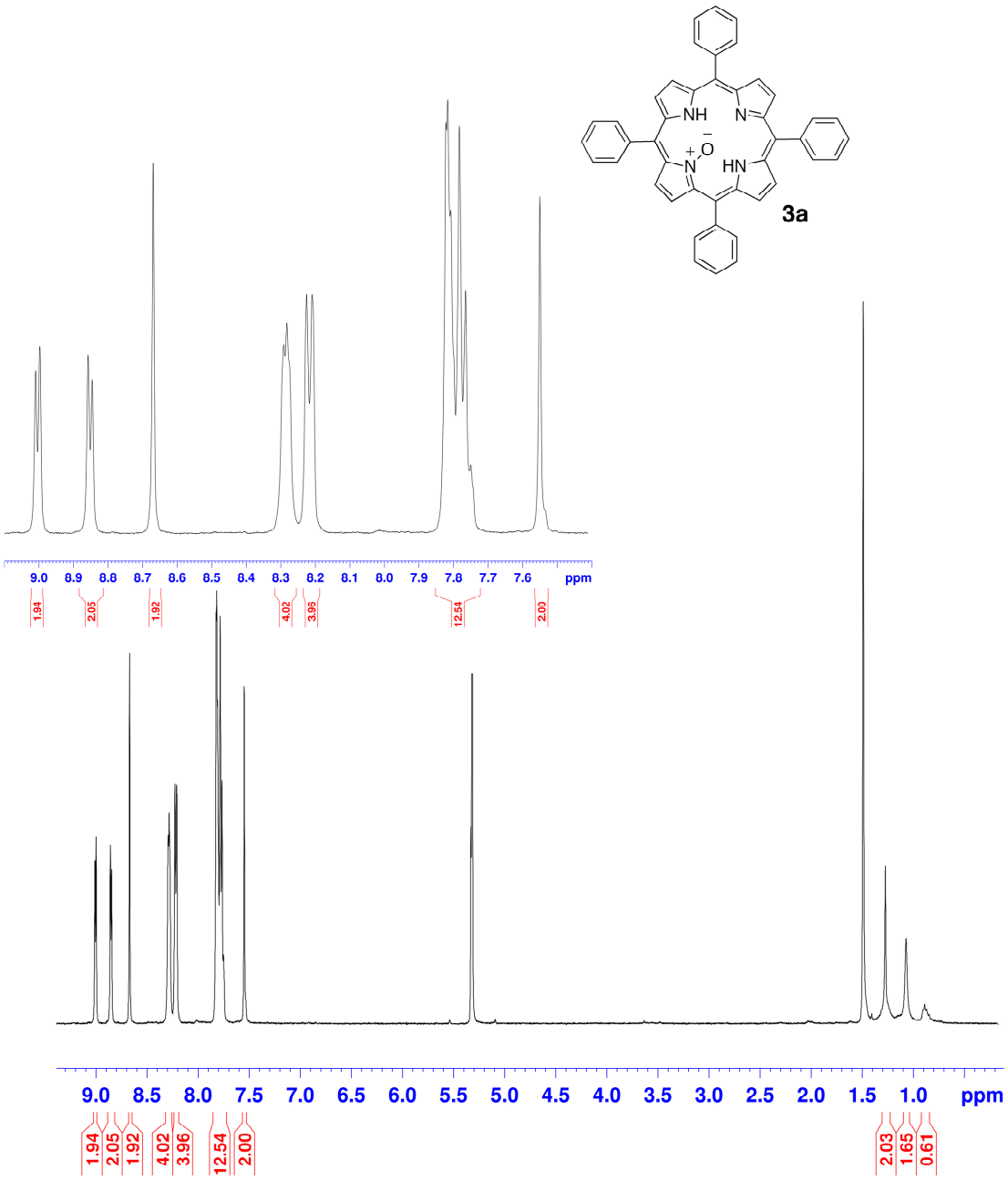

Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) of **3a**.

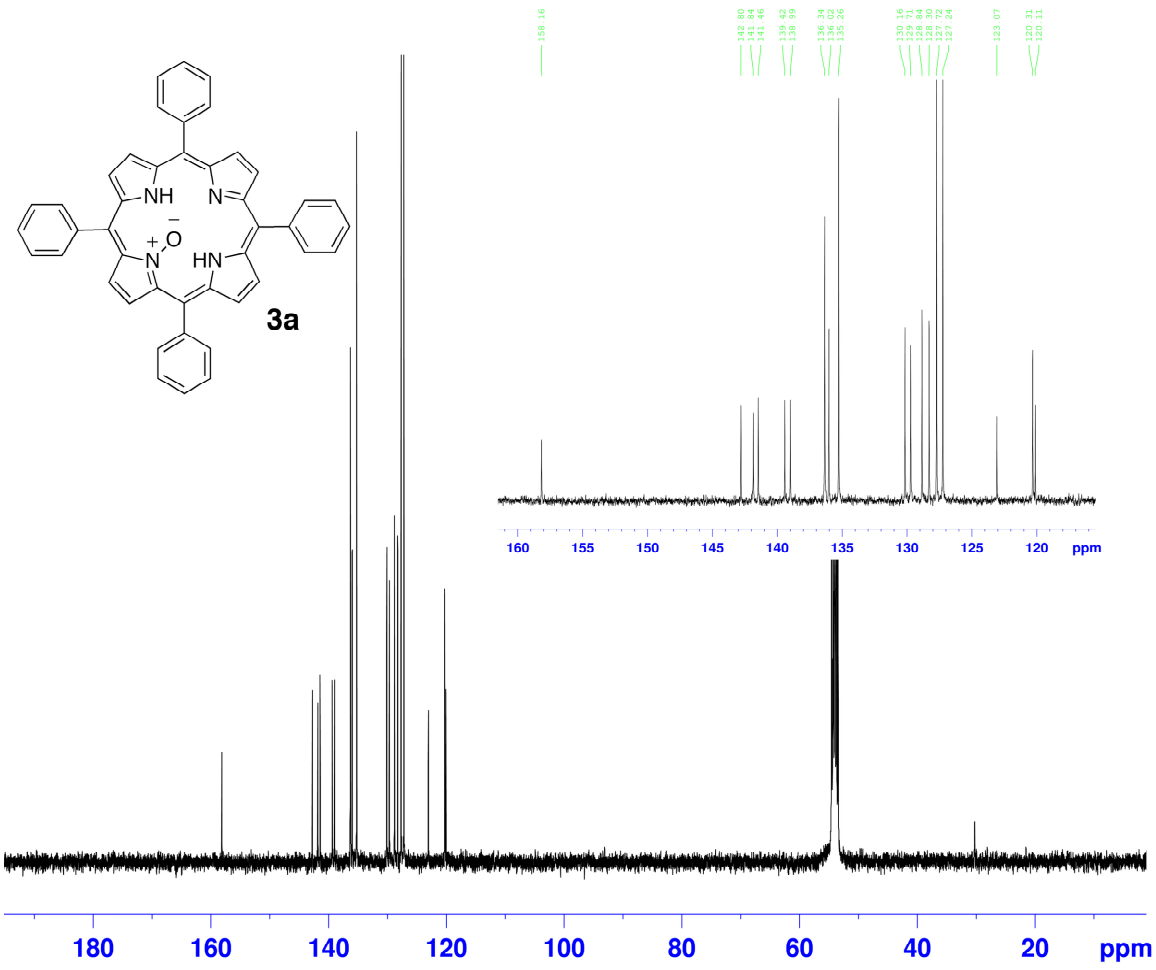

Figure S2. ^{13}C NMR (100 MHz, CD_2Cl_2, D1 = 3 s, 25 °C) of **3a**.

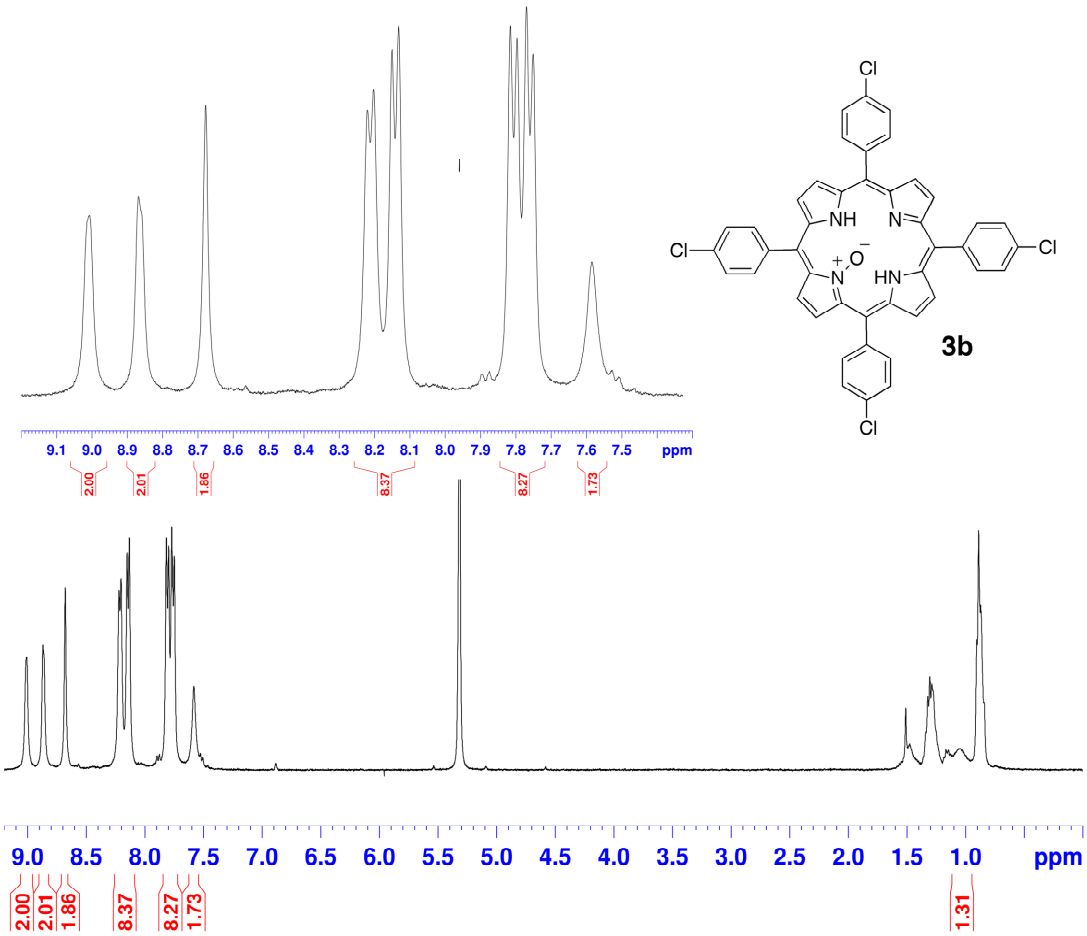

Figure S3. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) of **3b**.

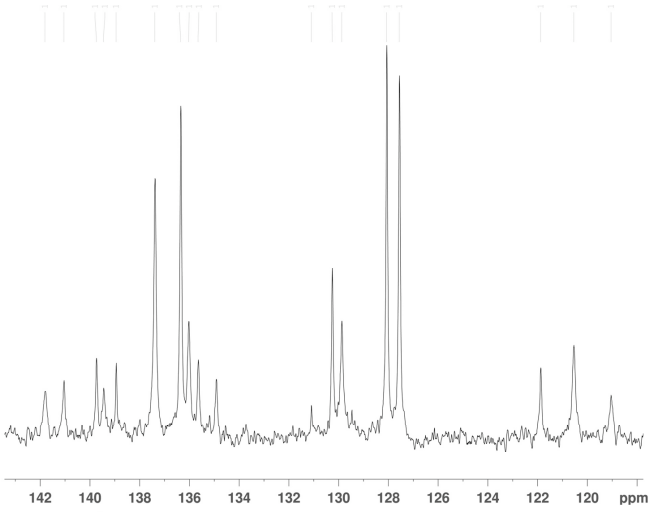

Figure S4. ^{13}C NMR (100 MHz, CD_2Cl_2, D1 = 1.5 s, 25 °C) of **3b**.

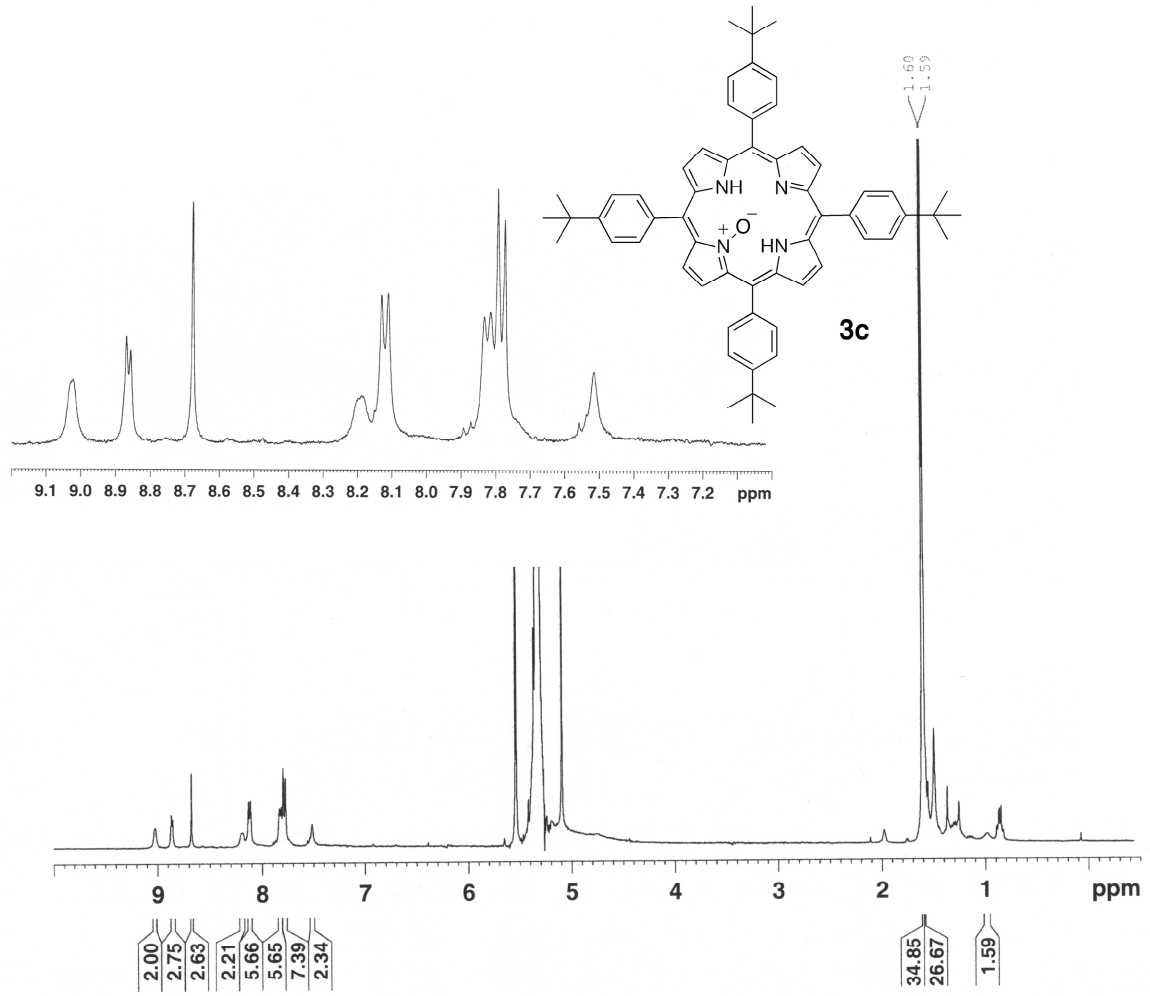

Figure S5. ^{1}H NMR (400 MHz, CH_2Cl_2/CD_2Cl_2, 25 °C) of **3c**. This compound is characterized by marginal solubility in CH_2Cl_2/CD_2Cl_2.

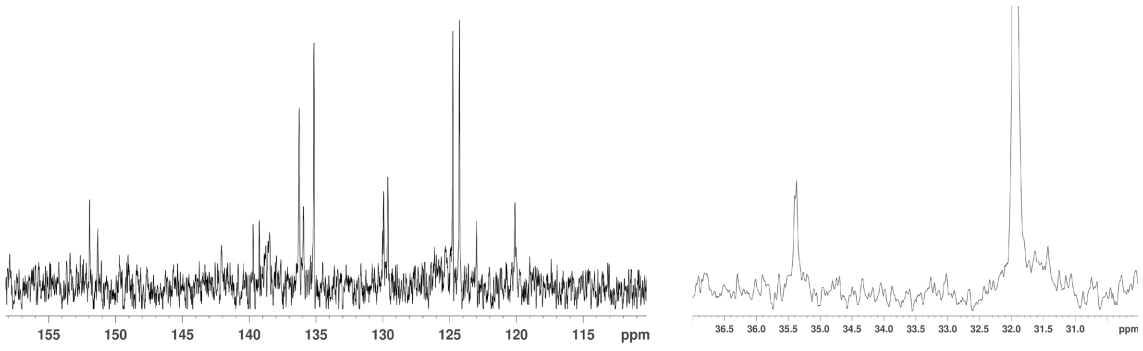

Figure S6. ^{13}C NMR (100 MHz, CD_2Cl_2, D1 = 3 s, 25 °C) of **3c**. This compound is characterized by marginal solubility in CH_2Cl_2/CD_2Cl_2.

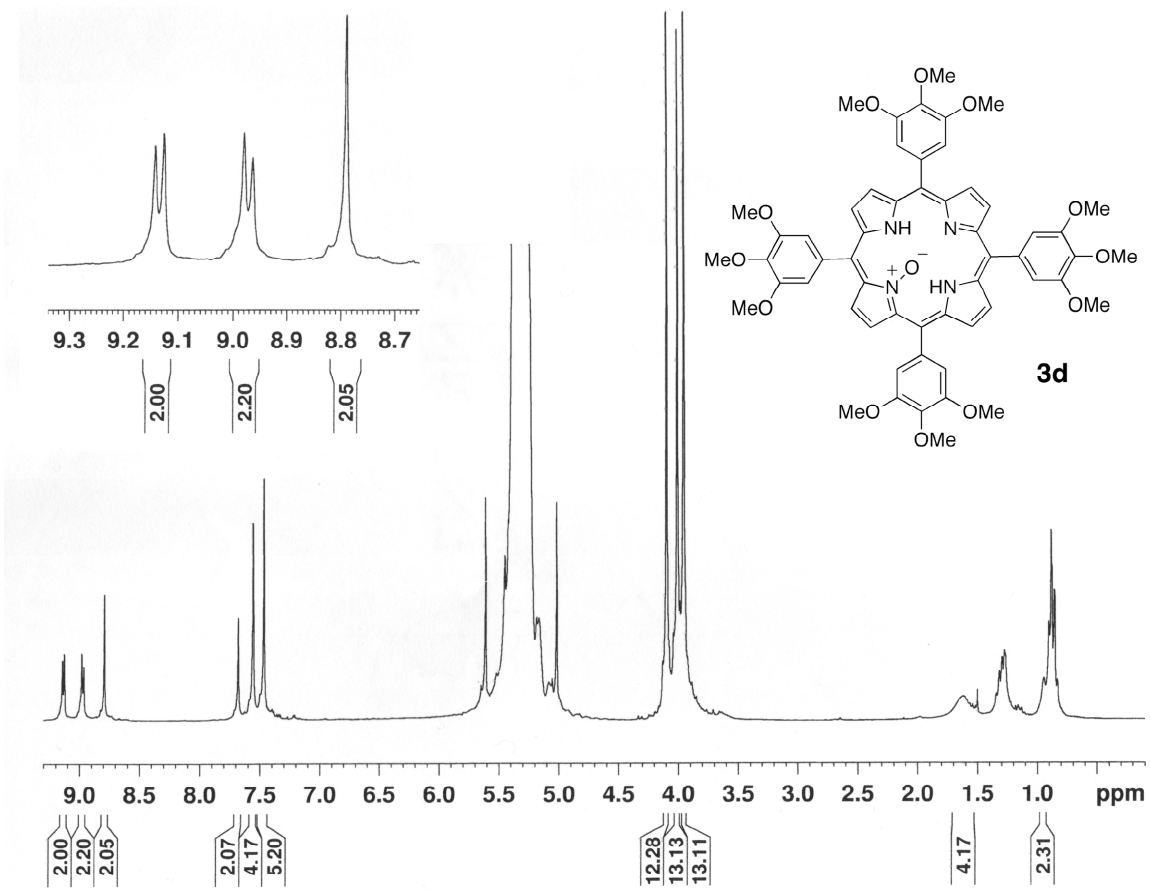

Figure S7. ^{1}H NMR (400 MHz, CH_2Cl_2/CD_2Cl_2, 25 °C) of **3d**.

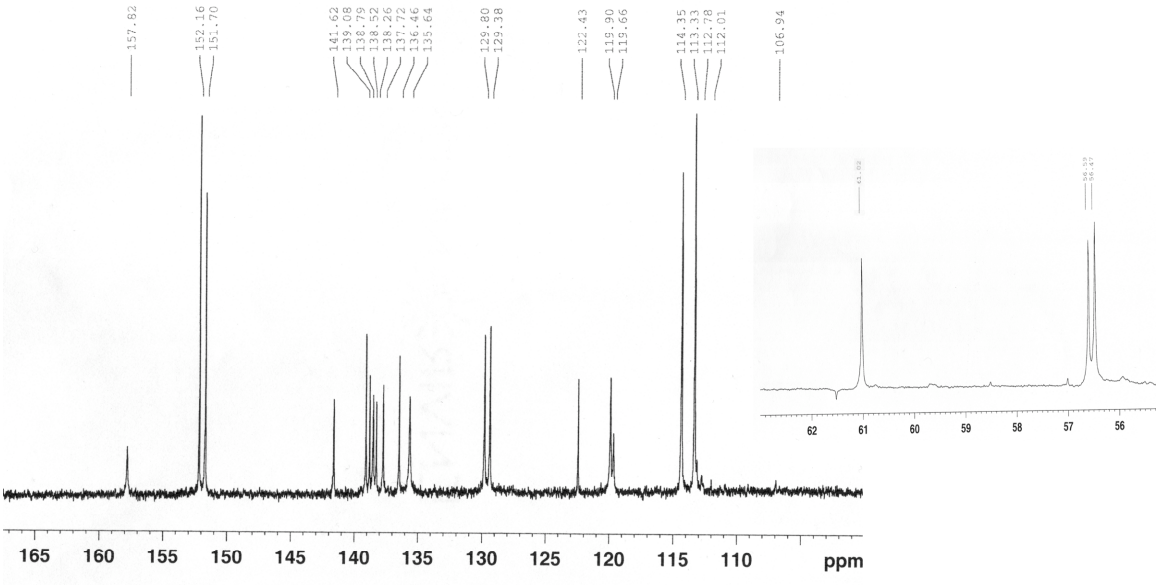

Figure S8. ^{13}C NMR (100 MHz, CH_2Cl_2/CD_2Cl_2, D1 = 1.5 s, 25 °C) of **3d**.

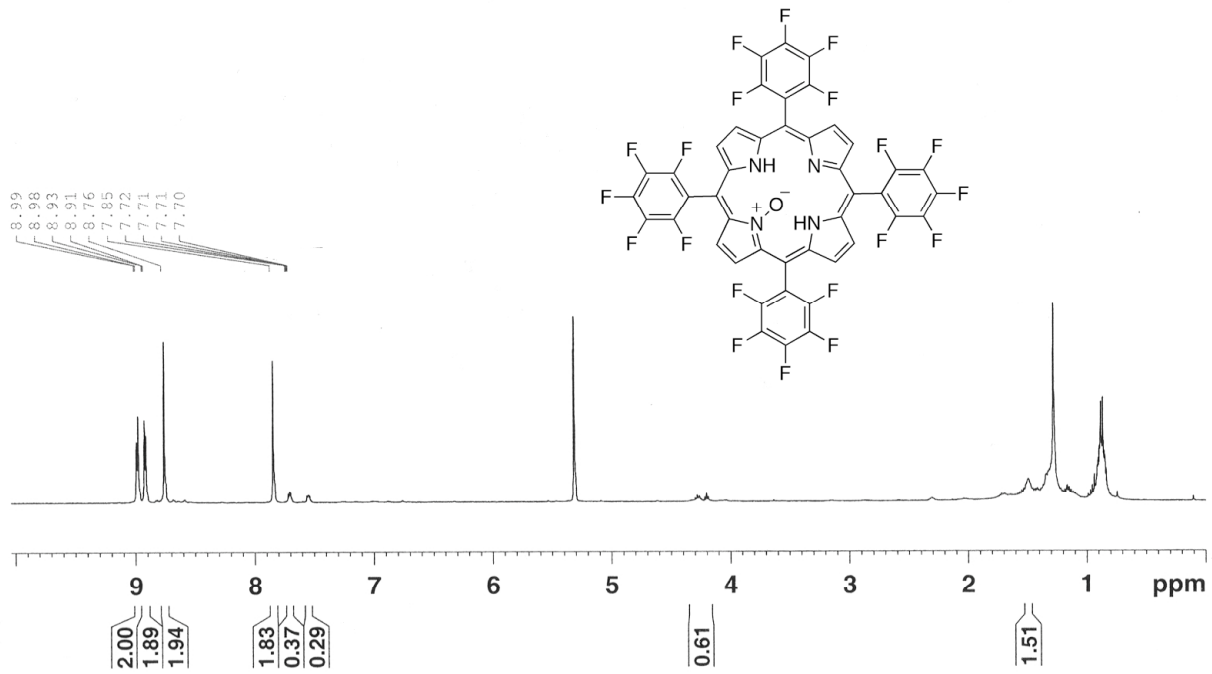

Figure S9. ^{1}H NMR (400 MHz, CH_2Cl_2, 25 °C) of **3e**.

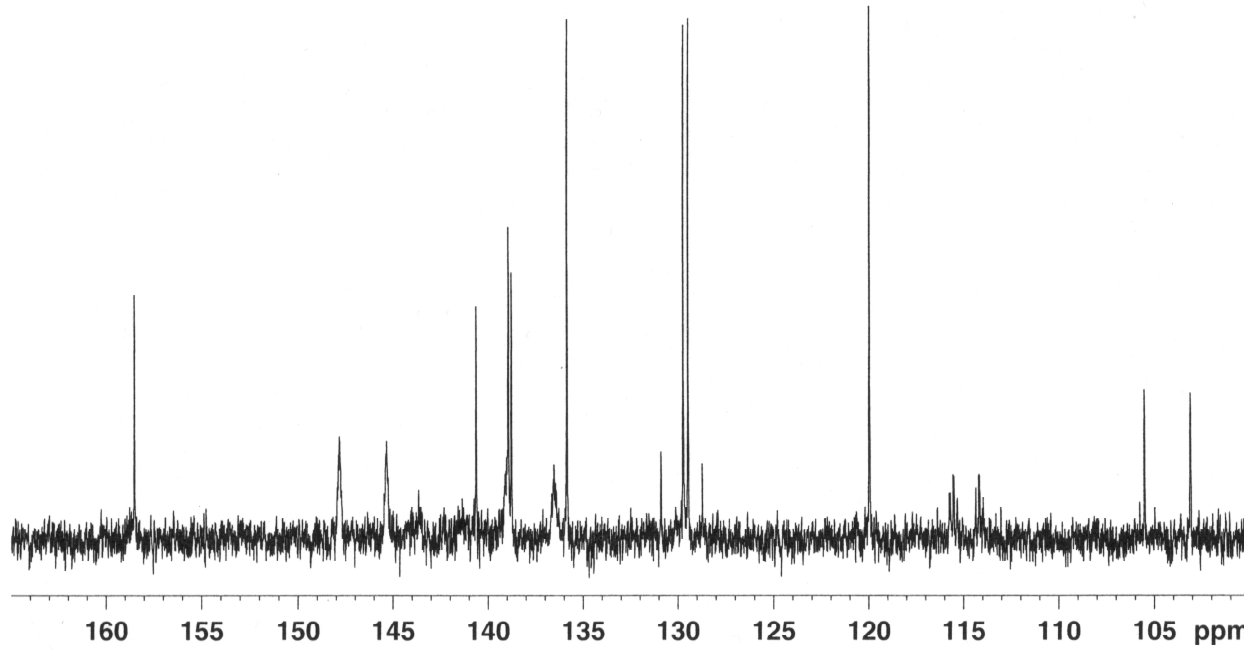

Figure S10. ^{13}C NMR (100 MHz, CH_2Cl_2, 25 °C, D1 = 2 s) of **3e**.

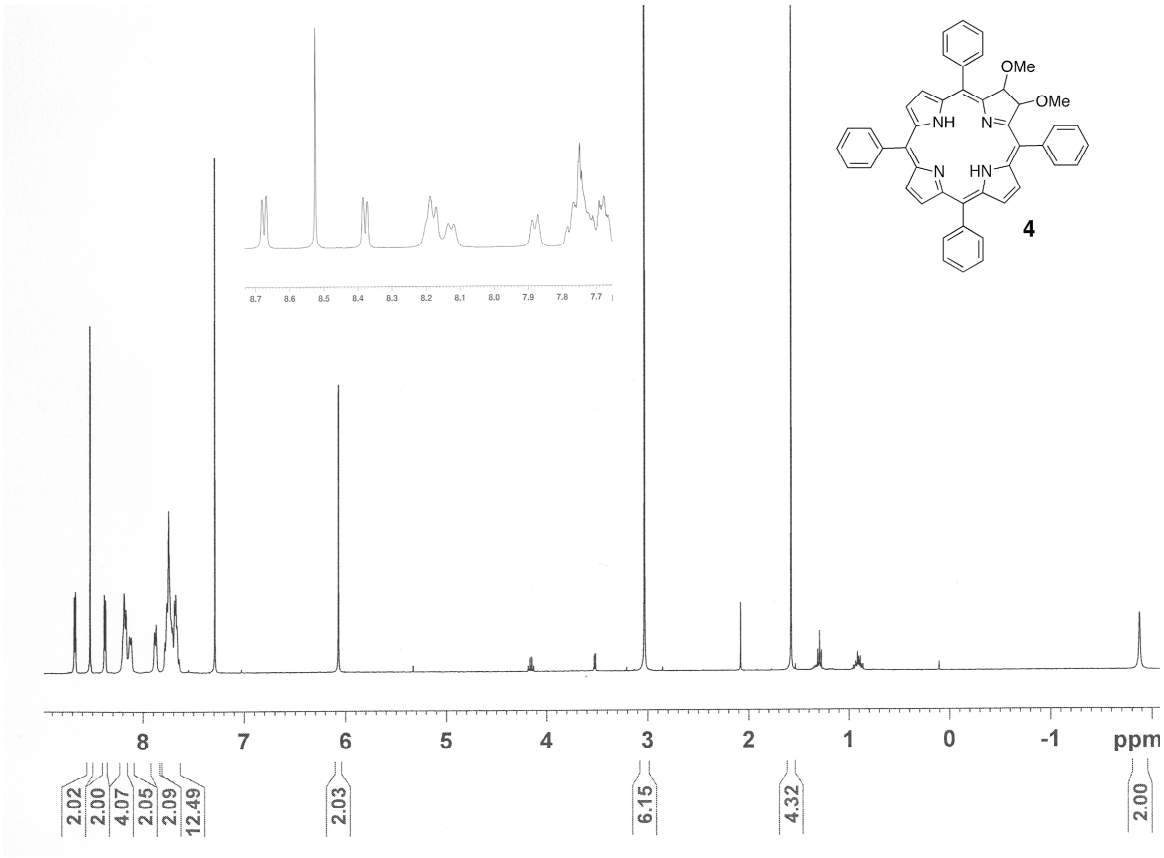

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of **4**.

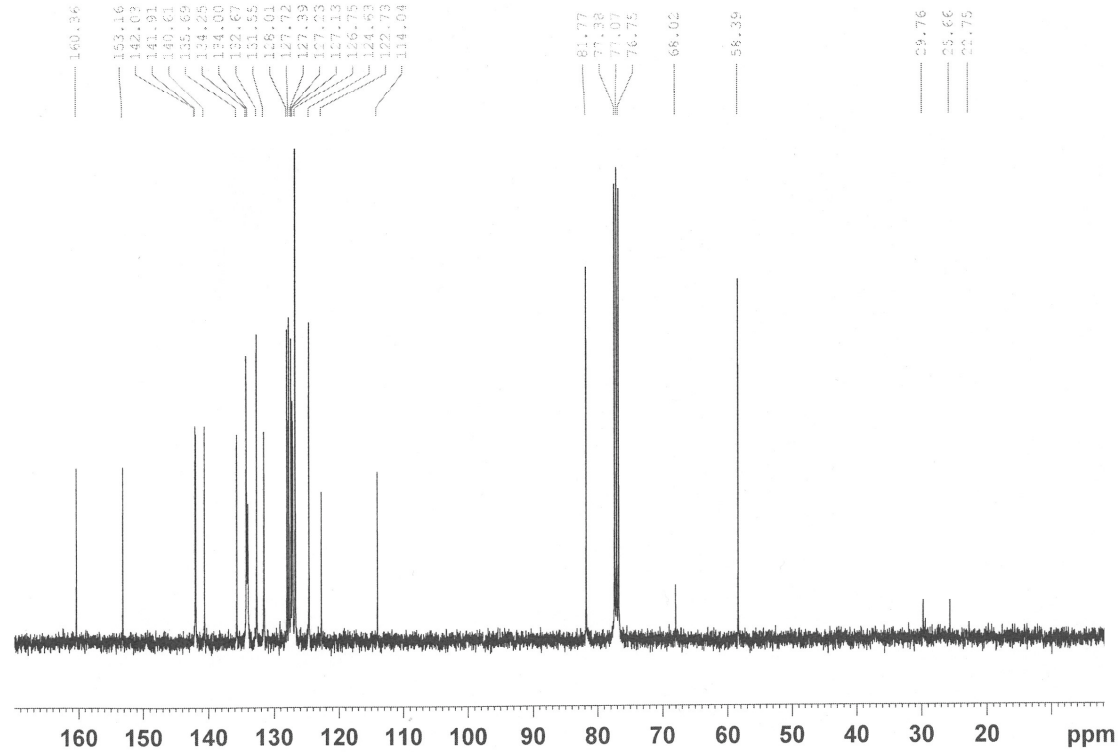

Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of **4**.

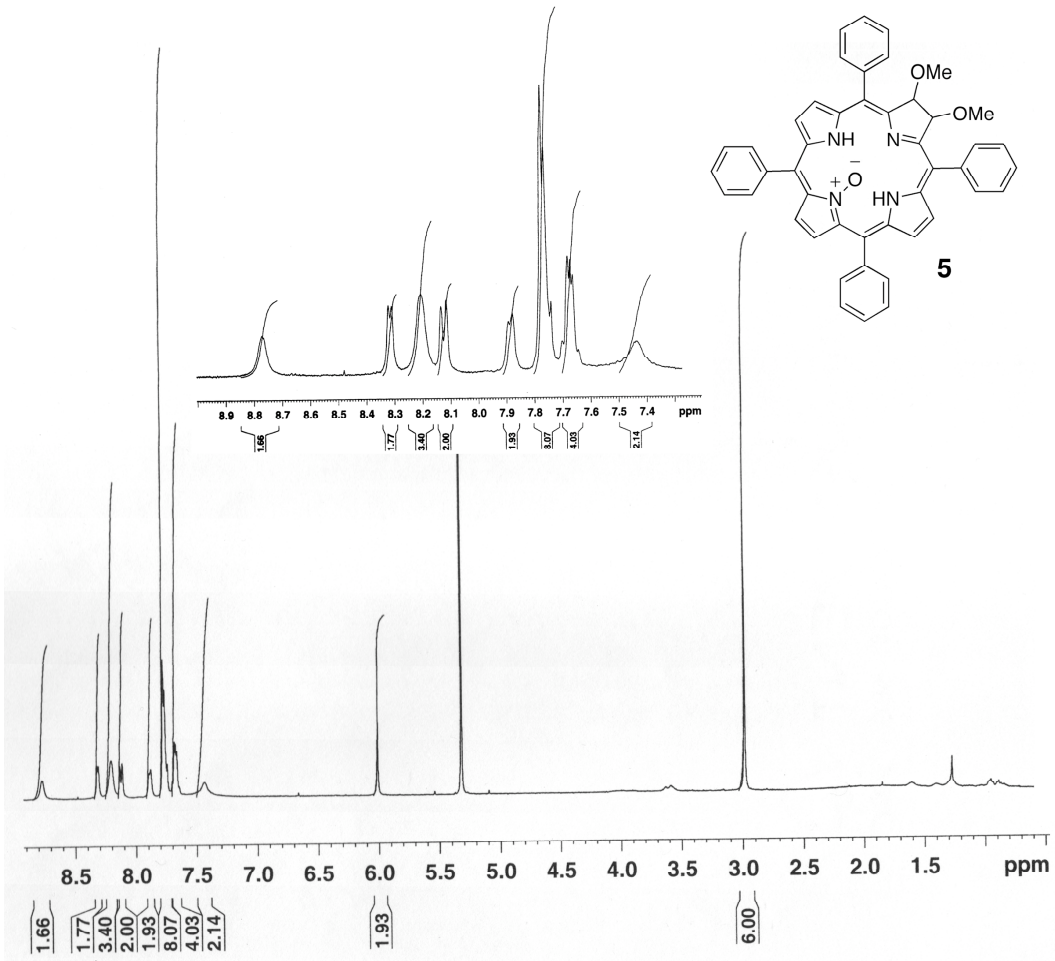

Figure S13. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) of **5**.

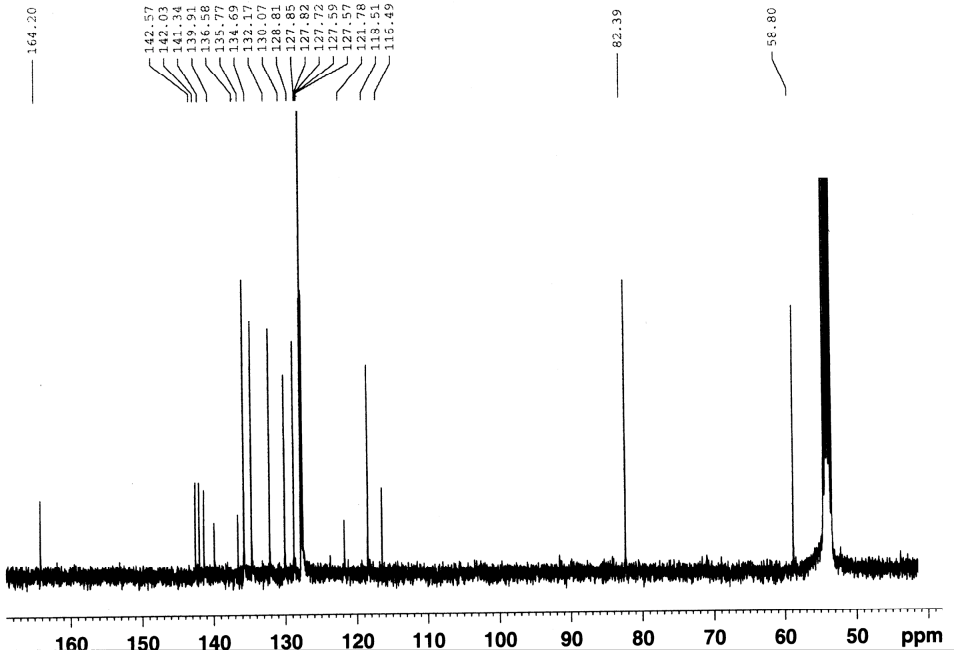

Figure S14. ^{13}C NMR (100 MHz, CD_2Cl_2, D1 = 1.5 s, 25 °C) of **5**.

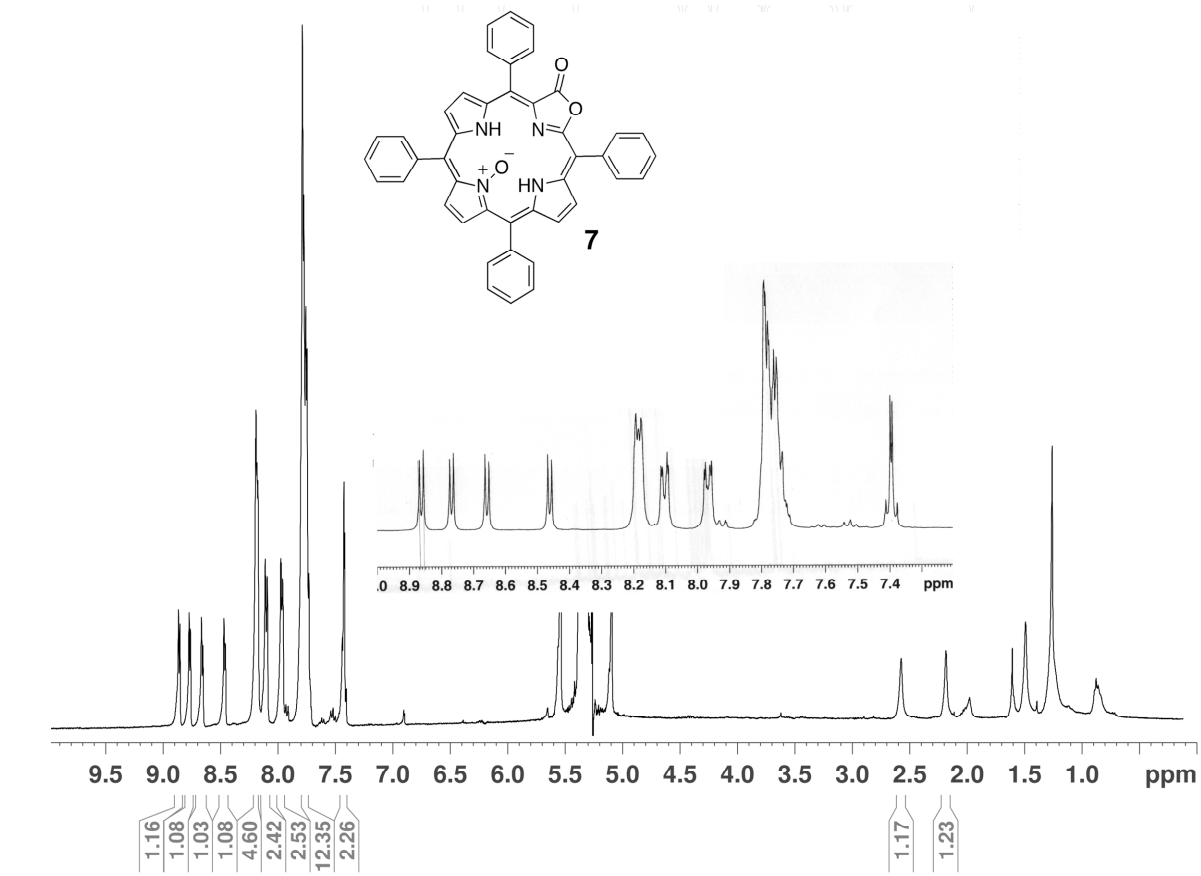

Figure S15. ^{1}H NMR (400 MHz, CH_2Cl_2/CD_2Cl_2, 25 °C) of **7**.

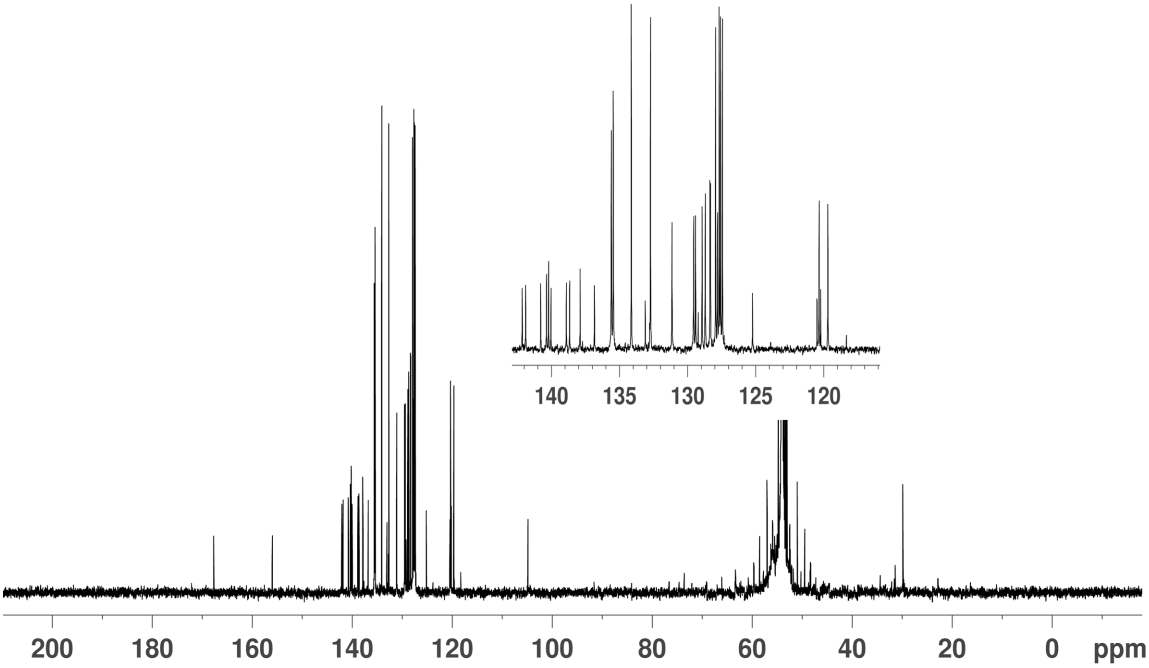

Figure S16. ^{13}C NMR (100 MHz, CH_2Cl_2/CD_2Cl_2, D1 = 1.5 s, 25 °C) of **7**.

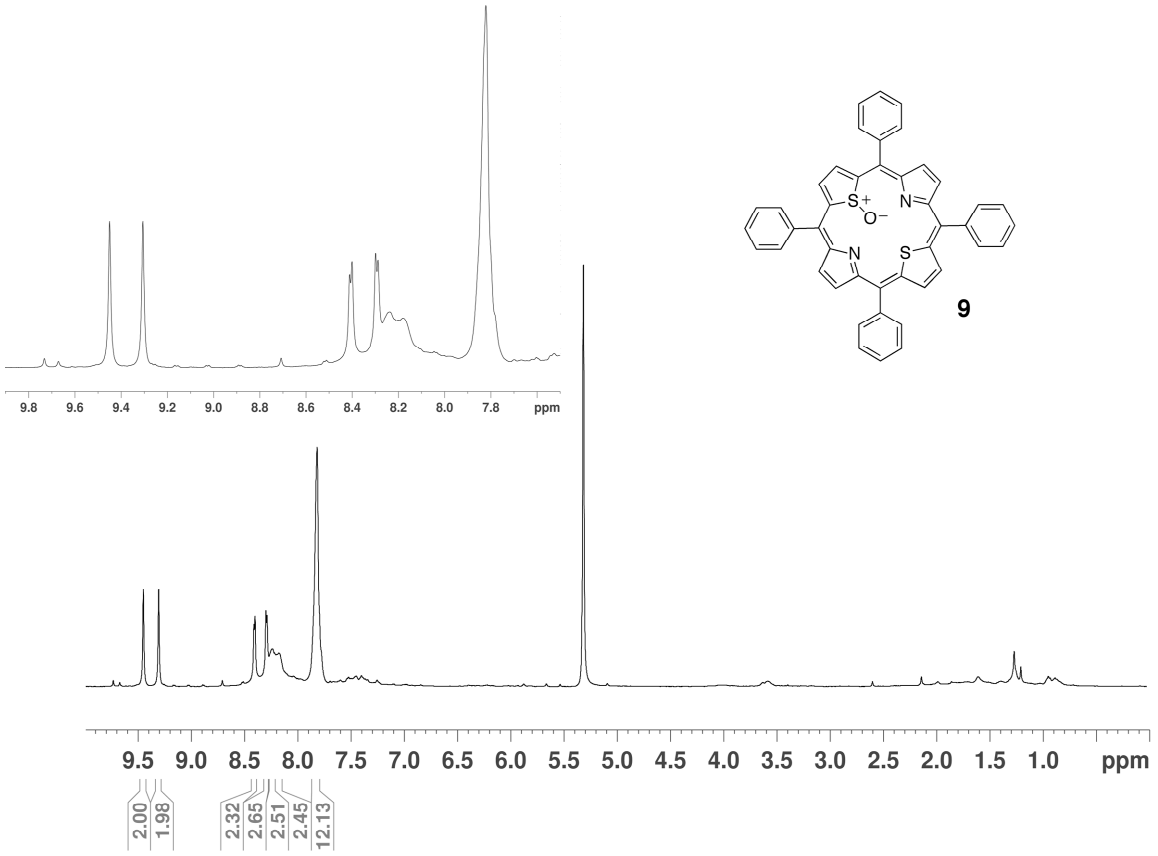

Figure S17. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) of **9**.

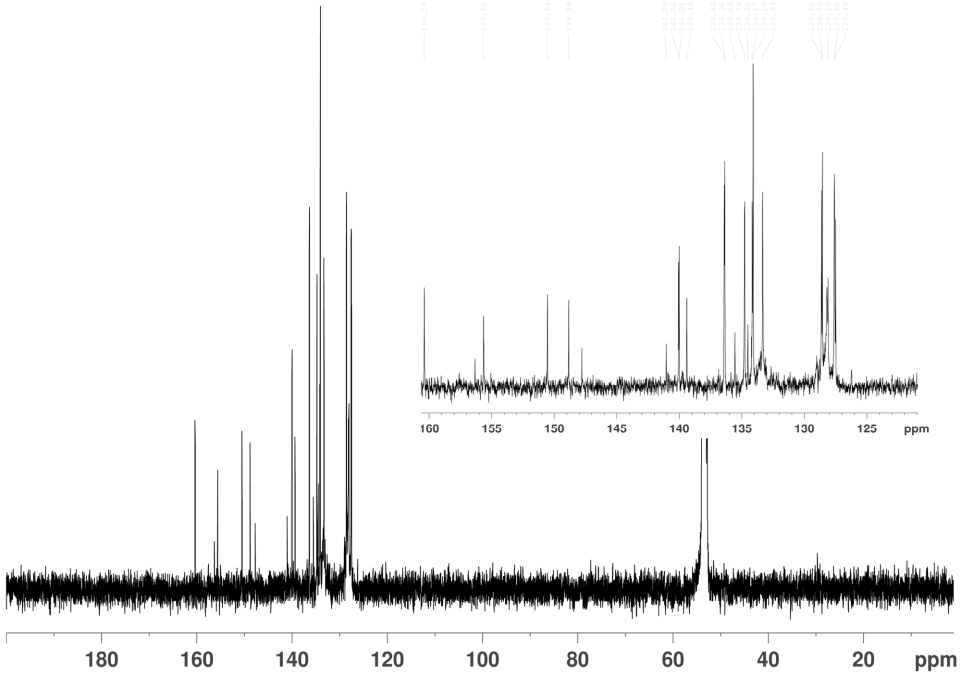

Figure S18. ^{13}C NMR (100 MHz, CD_2Cl_2, D1 = 2.0 s, 25 °C) of **9**.

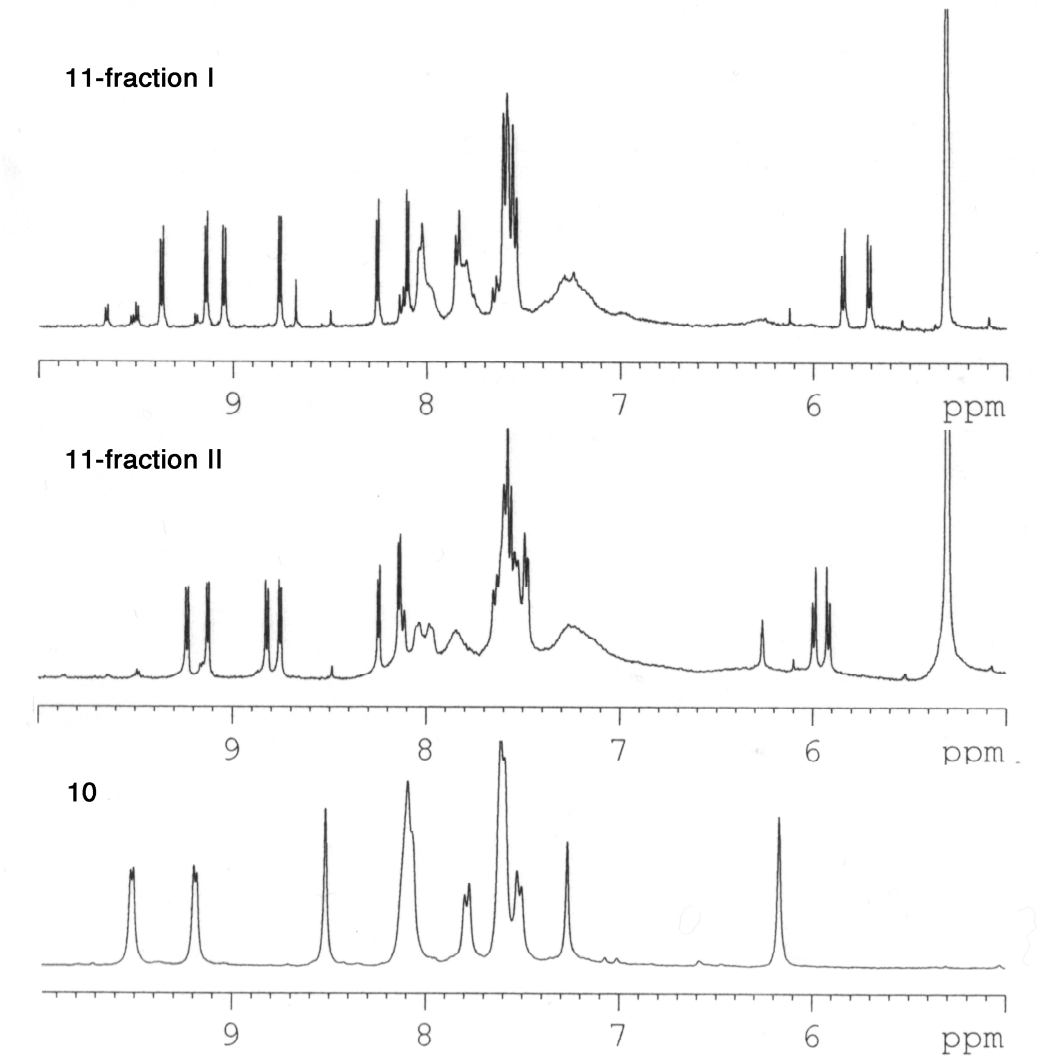

Figure S19. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) comparison, low-field region, of **10** (bottom spectrum), **11-isomer I**, and **isomer II** (top spectra). Assignment of which of the two isomers corresponds to **11A** and which to **11B** is unknown.

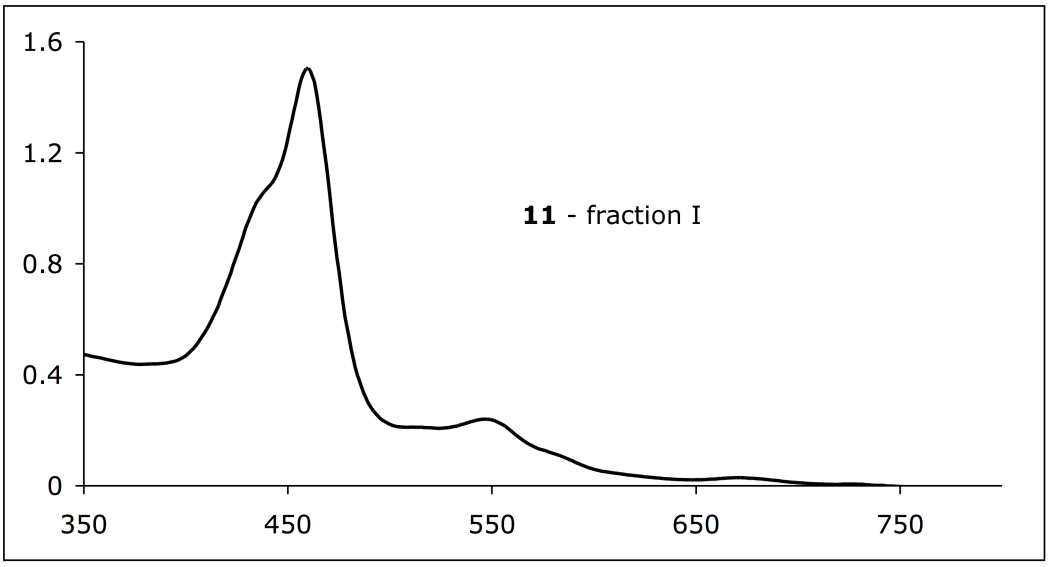

Figure S20. UV-vis spectrum (CH_2Cl_2) of **11-isomer I**.

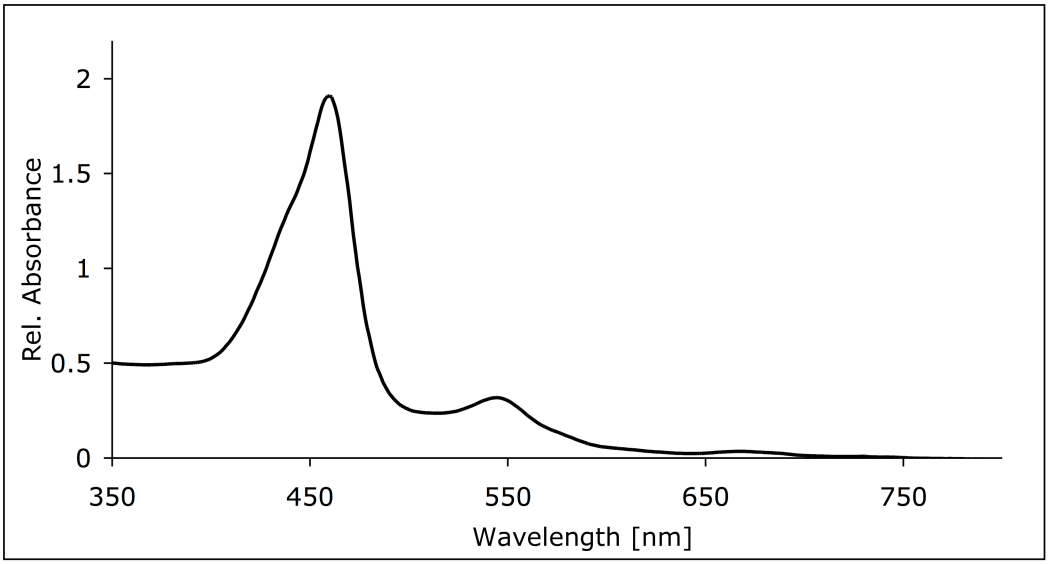

Figure S21. UV-vis spectrum (CH_2Cl_2) of **11-isomer II**.

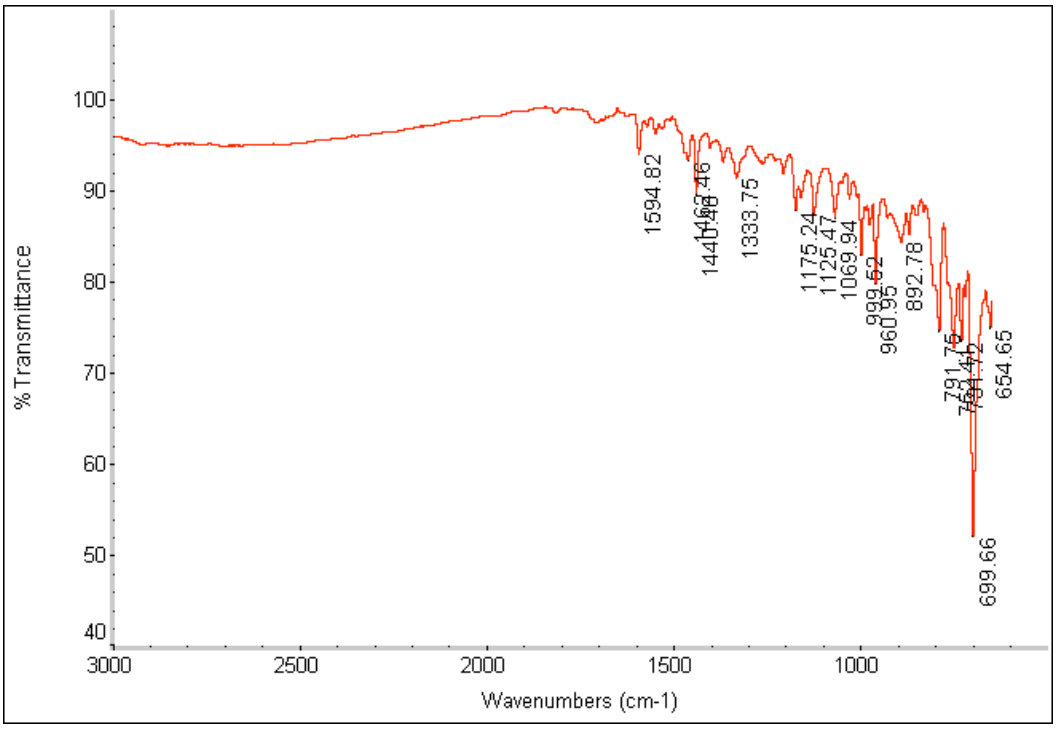

Figure S22. IR Spectrum (diffuse reflectance, neat) of **3a**.

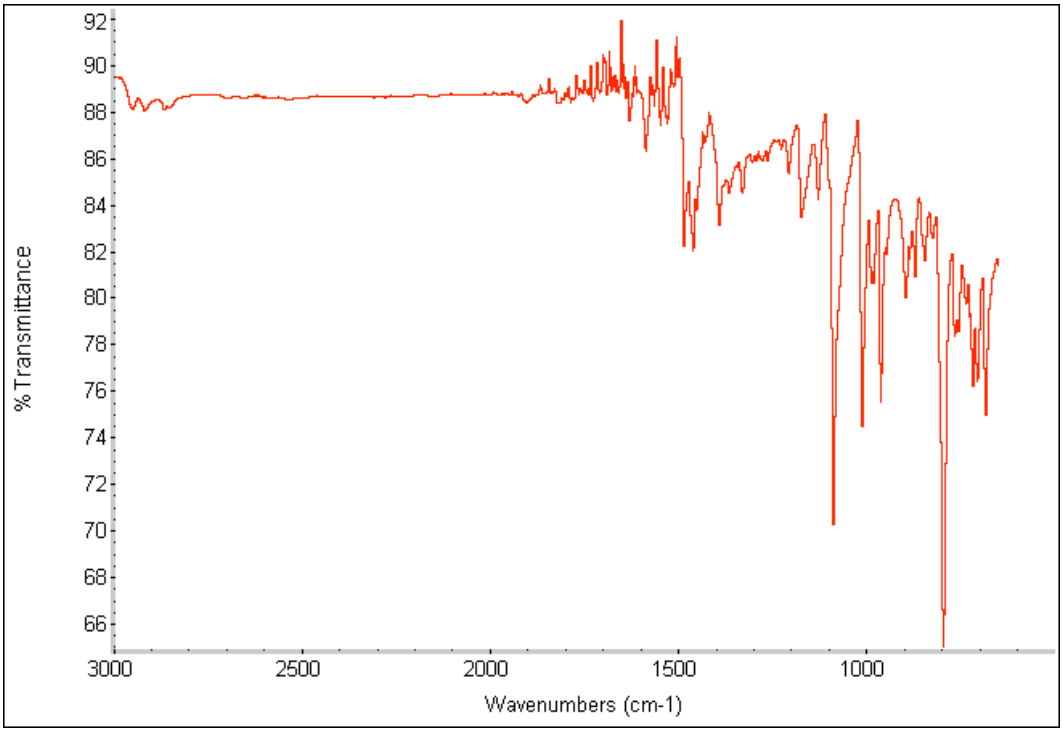

Figure S23. IR Spectrum (diffuse reflectance, neat) of **3b**.

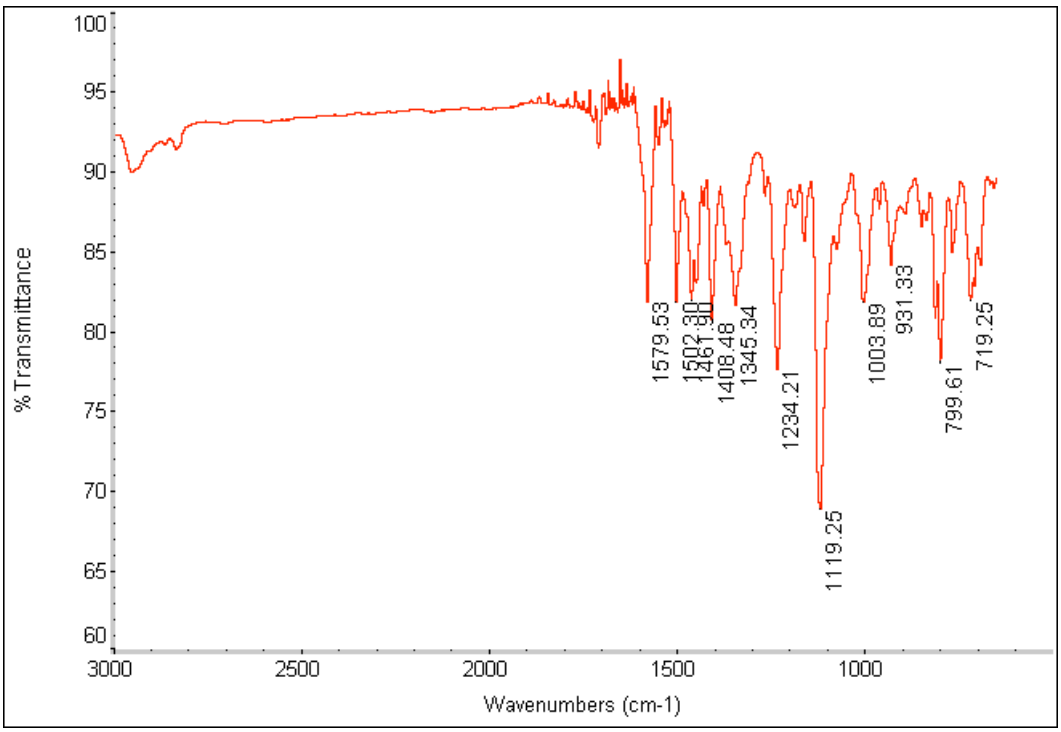

Figure S24. IR Spectrum (diffuse reflectance, neat) of **3c**.

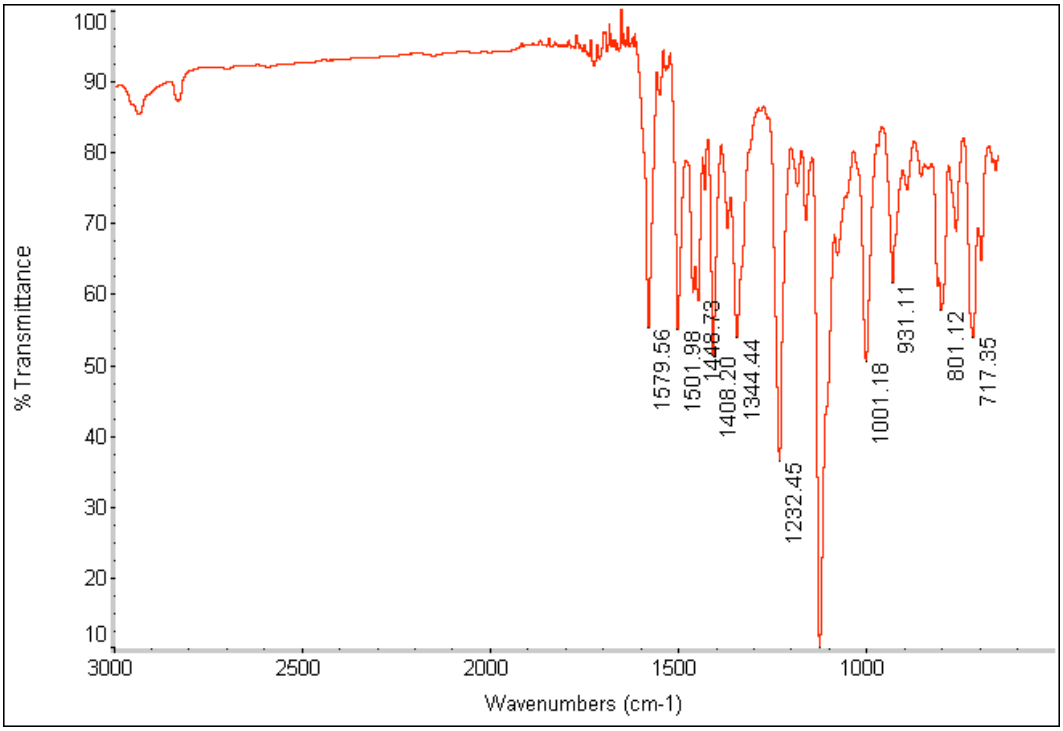

Figure S25. IR Spectrum (diffuse reflectance, neat) of **3d**.

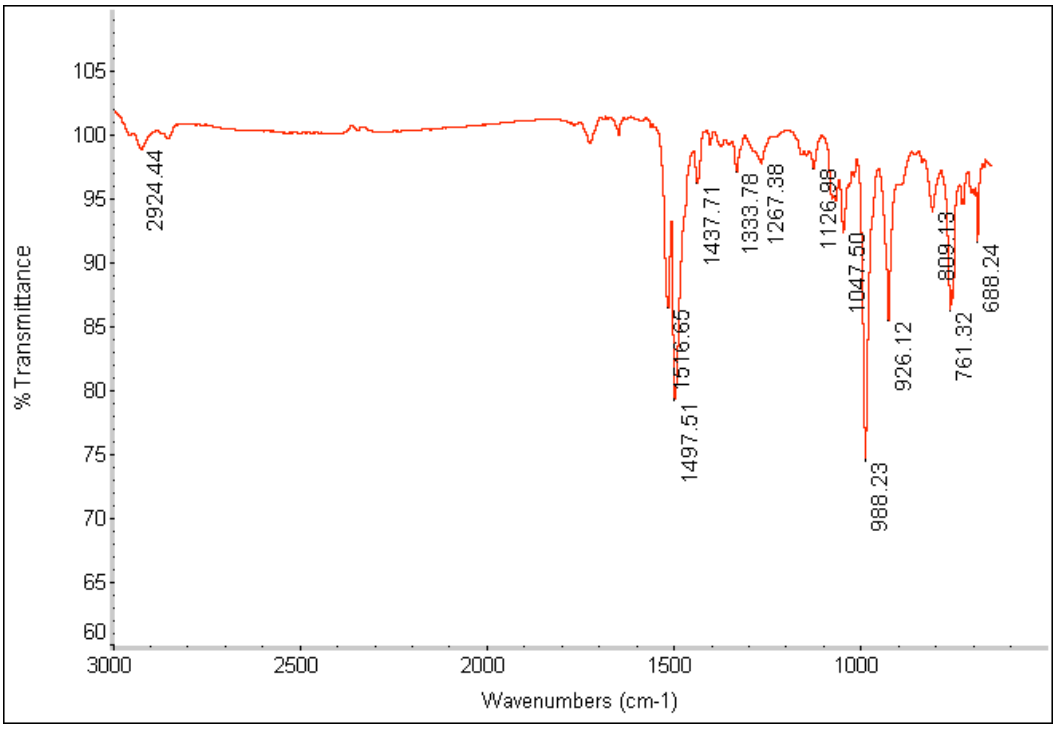

Figure S26. IR Spectrum (diffuse reflectance, neat) of **3e**.

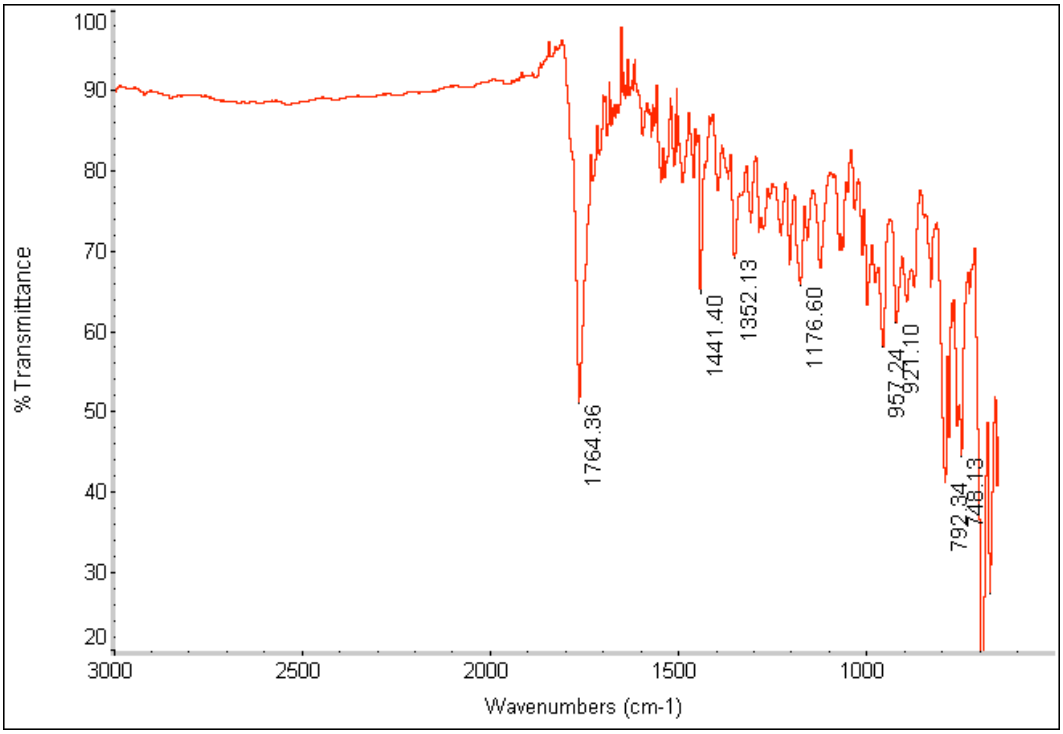

Figure S27. IR Spectrum (diffuse reflectance, neat) of **7**.

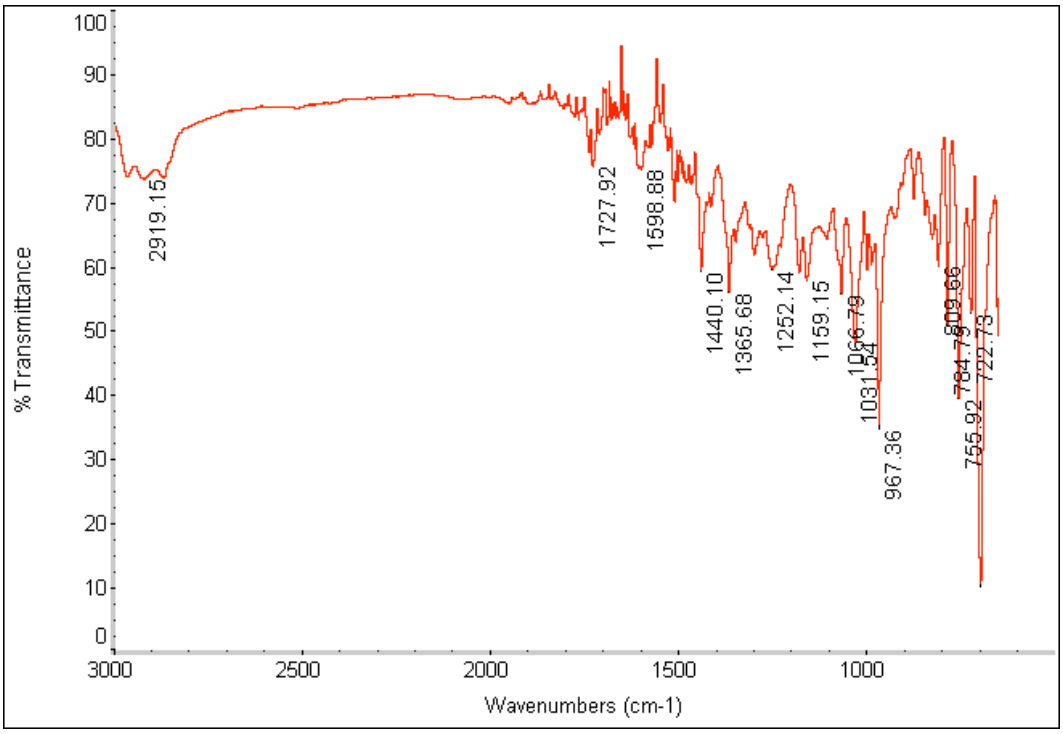

Figure S28. IR Spectrum (diffuse reflectance, neat) of **9**.

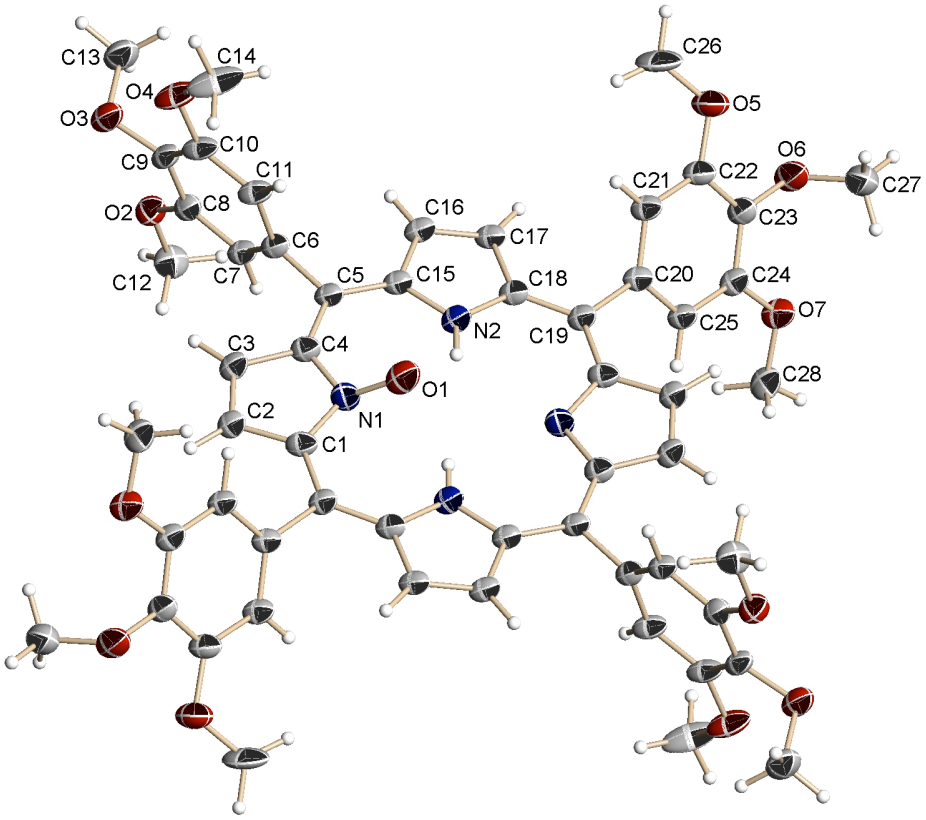

Figure S29. ORTEP Representation of the crystal structure of **3d**·CH_2Cl_2, 30% occupancy, under omission of the diosorder of the N-oxide unit showing also the numbering system used. Disordered solvent is omitted for clarity.

Black crystals of **3d** were obtained by vapor phase diffusion of petroleum ether 30-60 into a CH_2Cl_2 solution of **3d**. Diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer at 100(2) K using monochromatic Mo Kα radiation with omega scan technique. Reflections were collected. The unit cell was determined, the data were collected, integrated corrected for absorption using the Apex2 suite of programs.[1] The structure was solved by direct methods and refined by full matrix least squares against F^2 against all reflections using SHELXTL.[2] All hydrogen atoms were placed in calculated positions and were isotropically refined with a displacement parameter of 1.2 times that of the adjacent carbon atom.

Note: The oxygen atom of the N-oxide moiety is disordered over two symmetry related positions and is thus only half occupied. This disorder extends to a neighboring methylene chloride solvate molecule, which is disordered in a 1:1 ratio over two positions. The carbon atoms of the CH_2Cl_2 molecules were constrained to have identical ADPs. For further details, see .cif file.

Table S1. Crystallographic data for **3d**·CH_2Cl_2**.**

	09mz003_0m
Crystal data	
Chemical formula	$C_{58}H_{56}Cl_4N_4O_{13}$
Moiety formula	$C_{56}H_{52}N_4O_{13} \cdot 2(CH_2Cl_2)$
M_r	1158.87
Cell setting, space group	Monoclinic, $P2_1/c$
Temperature (K)	100(2)
a, b, c (Å)	14.870(5), 17.144(6), 11.875(4)
α, β, γ (°)	90.00, 113.475(5), 90.00
V (Å^3)	2776.75
Z	2
D_x (Mg m^{-3})	1.386
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.282
Crystal form, colour	plate, black
Crystal size (mm)	0.55 × 0.40 × 0.04
Data collection	
Diffractometer	Bruker AXS SMART APEX CCD diffractometer
Data collection method	ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)
T_{min}	0.497
T_{max}	0.989
No. of measured, independent and observed reflections	15185, 5277, 2282
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0956
θ_{max} (°)	25.67

Refinement

Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0823, 0.2237, 1.045
No. of relections	5277 reflections
No. of parameters	388
No. of restraints	0
H-atom treatment	Constrained to parent site
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0939P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.529, –0.407

(1) Bruker (2007). Apex2 v2.1-4. Bruker AXS Inc, Madison (WI), USA.
(2) Bruker Advanced X-ray Solutions SHELXTL (Version6.10), Bruker AXS Inc., Madison, WI, USA, 2000.