Electronic Supplementary Material (ESI) for RSC Advances

Electronic Supplementary Information

New hybrid materials with porphyrin-ferrocene and porphyrin-pyrene covalently linked to single-walled carbon nanotubes.

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Experimental Details

All solvents and reagents were purchased from Aldrich and used without further purification unless otherwise stated. Organic extracts were dried over magnesium sulphate unless indicated otherwise. Evaporation of the solvents was accomplished on a rotary evaporator. Thin layer chromatography was performed on silica gel 60 F_{254} plates. Chromatography refers to flash chromatography and was carried out on SiO_2 (silica gel 60, SDS, 70-230 mesh ASTM). ^{1}H and ^{13}C NMR spectra were recorded unless otherwise specified, as deuteriochloroform solutions using the solvent peak as internal standard on a Bruker AMX-500 MHz and on a Bruker DPX-300 MHz spectrometers. High resolution mass spectra were performed on a Bruker ultraflextreme MALDI-TOF/TOF spectrometer. Steady-state UV-Vis electronic absorption spectra were recorded on a Perkin Elmer (Lambda 19) UV-VIS-NIR spectrophotometer or on a Shimadzu Multispec-1501 instrument. Mid-infrared spectra in the region 550–4000 cm^{-1} were obtained on a Fourier Transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). Micro-Raman scattering measurements were performed at room temperature in the backscattering geometry using a RENISHAW inVia Raman microscope equipped with a CCD camera and a Leica microscope. A 2400 lines mm^{-1} grating was used for all measurements, providing a spectral resolution of ± 1 cm^{-1}. As an excitation source the Ar^{+} laser (514 nm with less than 0.5 mW laser power) was used. Measurements were taken with 60 seconds of exposure times at varying numbers of accumulations. The laser spot was focused on the sample surface using a long working distance 50x objective. Raman spectra were collected on numerous spots on the sample and recorded with Peltier cooled CCD camera. The intensity ratio I_D/I_G was obtained by taking the peak intensities following any baseline corrections. The data were collected and analyzed with Renishaw Wire and Origin software. Thermogravimetric analysis was performed using a TGA Q500 V20.2 Build 3 instrument by TA in an inert atmosphere of nitrogen. In a typical experiment, 1 mg of the material was placed in the sample pan and the temperature was equilibrated at 60 °C. Subsequently, the temperature was increased to 800 °C at a rate of 10 °C min^{-1} and the weight changes were recorded as a function of temperature. Fluorescence spectra were taken on an Aminco Bowman spectrofluorimetre (Spectronocs Co., USA) and a Fluorolog-3 Jobin Yvon-Spex spectrofluorometer (model GL3–21). Picosecond time-resolved fluorescence spectra were measured by the time-correlated single-photon counting (TCSPC) method on a NanoLog spectrofluorometer (Horiba Jobin Yvon), using a laser diode as an excitation source (NanoLED, 441 nm, 200 ps pulse width). Lifetimes were evaluated with the DAS6 Fluorescence-Decay

Analysis Software. All measurements were performed at room temperature. Electrochemistry was conducted on a Princeton Applied Research potentiostat/galvanostat model 2273 connected to a personal computer running Power Suite. The measurements were conducted using in solution using 0.1M tetrabutylammonium hexafluorophosphate 0.1M in DMF as supporting electrolyte, on a standard 3 electrode cell, with Pt disk (1.6mm diameter) as a working electrode, Pt gauze 52 mesh, 99.9% and a $Ag/AgNO_3$ reference electrode (Ag wire in 0.1M $AgNO_3$ in dry acetonitrile). Experiments were conducted in inert atmosphere using N_2 and data calibrated with ferrocene. Specifically, for the differential pulse voltammograms of materials **8** and **10** the following parameters were applied: a) reduction run: Pulse Height 0.05V, Pulse Width 70ms, Step Height 5mV and Step Time 100 ms, and b) oxidation run: Pulse Height 0.05V, Pulse Width 50ms, Step Height 5mV and Step Time 100ms, while for materials **9** and **11**, a) reduction run: Pulse Height 0.05V, Pulse Width 50ms, Step Height 5mV and Step Time 100 ms, and b) oxidation run: Pulse Height 0.05V, Pulse Width 50ms, Step Height 2mV and Step Time 100 ms.

Synthesis of 5,15-bis(4-methoxyphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin 2.

A solution of 4-methoxy-benzaldehyde (0.32 mL, 2.6 mmol) and 2,2'-(2,4,6-trimethylphenylmethylene)bis(1*H*-pyrrole) **1** (0.7 g, 2.6 mmol) in 275 mL of dichloromethane was purged with nitrogen for 5 min. Then trifluoroacetic acid (0.37 mL, 4.9 mmol) was added and the solution stirred at room temperature for 45 min. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.9 g, 3.9 mmol) was added and the solution stirred for a further 1.5 h. The mixture was filtered through an alumina (Al_2O_3) column (CH_2Cl_2). The product was eluted with dichloromethane to give **2** as a purple solid (177 mg, 18 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.85 (d, J = 5.0 Hz, 4H), 8.71 (d, J = 4.5 Hz, 4H), 8.16 (d, J = 7.5 Hz, 4H), 7.30 (m, 8H), 4.10 (s, 6H), 2.65 (s, 6H), 1.87 (s, 12H), –2.56 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 139.8, 139.0, 138.1, 135.9, 134.8, 131.8, 130.3, 128.2, 119.5, 118.6, 112.6, 56.0, 22.1, 21.9; UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 420 (473.4), 516 (18.8), 552 (9.0), 592 (5.7), 649 (5.2); HRMS (MALDI-TOF) calcd for $C_{52}H_{47}N_4O_2$ $[M+H]^+$ 759.3699, found 759.3691.

Synthesis of 5,15-bis(4-hydroxyphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin 3

To a solution of porphyrin **2** (100 mg, 0.13 mmol) in dry CH_2Cl_2 (100 mL) was added boron tribromide (6.0 mL, 60.0 mmol) and the solution was stirred at room temperature under nitrogen for 2 days. Then, CH_2Cl_2 (100 mL) was added and the mixture was cooled down to 0 ^{0}C for 30 min. After that time MeOH (70 mL) and water (140 mL) were added and left stirring fo further 30

min. The resulting solution was washed with saturated $NaHCO_3$ (3 x 50 mL) and then with H_2O (2 x 50 mL). The organic layer dried, filtered, concentrated and the residue was chromatographed on a silica gel column (CH_2Cl_2/THF). The product was eluted with THF to obtain **3** as a purple solid (85 mg, 89 %). ^{1}H NMR (300 MHz, THF-d_8): δ 8.85 (d, J = 4.5, 4H), 8.79 (s, 2H), 8.62 (d, J = 4.8 Hz, 4H), 8.00 (d, J = 8.4 Hz, 4H), 7.30 (s, 4H), 7.15 (d, J = 8.4, 4H), 2.60 (s, 6H), 1.84 (s, 12H); ^{13}C NMR (75 MHz, THF-d_8): δ 159.0, 140.3, 140.0, 138.8, 136.6, 134.0, 132.4, 130.5, 128.9, 121.0, 118.8, 114.8, 22.0, 21.8; UV/vis (toluene) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 420 (199.5), 515 (10.9), 550 (6.9), 592 (5.7), 650 (5.1); HRMS (MALDI-TOF) calcd for $C_{50}H_{43}N_4O_2$ $[M+H]^+$ 731.3386, found 731.3391.

Synthesis of 5-(4-hydroxyphenyl)-15-(4-(ferrocene-2-carbonyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin 4

To a solution of ferrocene carboxylic acid (12.6 mg, 0.05 mmol) in dry CH_2Cl_2 (1 mL) oxalyl chloride (7 µl, 0.08 mmol) was added and the solution was stirred under nitogen at 40 ^{0}C for 1h. Then the solvent and excess oxalyl chloride were removed and the mixture was dried under vacum for 1 h, to yield the ferrocene carboxylic acid chloride, which was dissolved in dry THF (4 mL). Porphyrin **3** (40 mg, 0.05 mmol) and triethylamine (0.13 mL, 0.9 mmol) were added and the solution was stirred overnight at 70 ^{0}C. After removal of the solvent the residue was obtained by chromatography (CH_2Cl_2). First the bis-ferrocene porphyrin was eluted and then the desired product **4** obtained as a purple solid (19 mg, 40 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.89 (d, J = 4.5 Hz, 2H), 8.84 (d, J = 4.5 Hz, 2H), 8.74 (d, J = 4.5 Hz, 2H), 8.71 (d, J = 4.5 Hz, 2H), 8.30 (d, J = 8.0 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.30 (s, 4H), 7.16 (d, J = 8.5 Hz, 2H), 5.15 (s, 2H), 4.61 (s, 2H), 4.44 (s, 5H), 2.65 (s, 6H), 1.87 (s, 12H), –2.57(s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 155.9, 151.2, 139.8, 138.9, 138.2, 136.1, 135.8, 134.9, 131.8, 130.6, 128.2, 120.4, 119.6, 118.8, 118.6, 114.1, 72.6, 71.2, 70.5, 22.1, 21.9; UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 419 (446.1), 447 (24.2), 515 (17.8), 550 (7.5), 591 (5.4), 647 (4.0); HRMS (MALDI-TOF) calcd for $C_{61}H_{51}FeN_4O_3$ $[M+H]^+$ 943.3311, found 943.3305.

Synthesis of 5-(4-(2-(benzyloxy)-2-oxoethoxy)phenyl)-15-(4-(ferrocene-2-carbonyloxy) phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin 6.

To a solution of porphyrin **4** (36 mg, 0.04 mmol) in dry DMF (3 mL) K_2CO_3 (7 mg, 0.05 mmol) and benzylacetylbromide (9 µl, 0.05 mmol) were added and the mixture was stirred under nitrogen at 80 ^{0}C overnight. Then CH_2Cl_2 (50 mL) was added and extracted with water (4 x 50

mL), dried, filtered and concentrated under vacuum. The resulting crude product was purified by column chromatography (CH_2Cl_2). The product was eluted with dichloromethane to obtain **6** as a purple solid (33 mg, 76 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.85 (d, J = 4.5 Hz, 2H), 8.79 (d, J = 4.5 Hz, 2H), 8.72 (t, J = 4.5 Hz, 4H), 8.26 (d, J = 8.1 Hz, 2H), 8.12 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.44 (m, 5H), 7.29 (s, 6H), 5.39 (s, 2H), 5.14 (s, 2H), 4.98 (s, 2H), 4.62 (s, 2H), 4.45 (s, 5H), 2.67 (s, 6H), 1.89 (s, 12H), -2.57 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 168.9, 157.6, 150.8, 139.4, 139.3, 138.4, 137.7, 135.5, 135.3, 135.2, 131.4, 130.0, 128.7, 128.6, 128.5, 128.4, 127.8, 120.0, 118.8, 118.3, 118.2, 117.1, 112.9, 72.1, 71.6, 70.1, 70.0, 67.2, 65.7, 21.6, 21.5; UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 419 (440.3), 447 (22.1), 515 (14.9), 550 (6.5), 591 (4.6), 647 (3.2); HRMS (MALDI-TOF) calcd for $C_{70}H_{59}FeN_4O_5$ $[M+H]^+$ 1091.3835, found 1091.3825.

Synthesis of 5-(4-hydroxyphenyl)-15-(4-(pyrene-1-carbonyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin 5

To a solution of pyrene carboxylic acid (33 mg, 0.13 mmol) in dry CH_2Cl_2 (2.0 mL) oxalyl chloride (18 µl, 0.21 mmol) was added and the solution was stirred under nitogen at 40 ^{0}C for 1h. Then the solvent and excess oxalyl chloride were removed and the mixture was dried under vacum for 1 h, to yield the pyrene carboxylic acid chloride, which was dissolved in THF (3.5 mL). Porphyrin **3** (100 mg, 0.13 mmol) and triethylamine (0.13 mL, 0.9 mmol) were added and the solution was stirred overnight at 70 ^{0}C. After removal of the solvent the residue was obtained by chromatography (CH_2Cl_2/Hexane, 7:3). First the bis-pyrene porphyrin was eluted and then the desired product **5** obtained as a purple solid (66 mg, 53 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 (d, J = 9.5 Hz, 1H), 9.13 (d, J = 8.0 Hz, 1H), 8.98 (d, J = 4.5 Hz, 2H), 8.87 (d, J = 4.5 Hz, 2H), 8.79 (d, J = 4.5 Hz, 2H), 8.75 (d, J = 4.5 Hz, 2H), 8.38 (m, 6H), 8.28 (d, J = 9.0 Hz, 1H), 8.20 (d, J = 9.0 Hz, 1H), 8.14 (t, J = 7.5 Hz, 1H), 8.09 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.33 (s, 4H), 7.15 (d, J = 8.5 Hz, 2H), 2.67 (s, 6H), 1.90 (s, 12H), –2.52 (s br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 155.8, 151.5, 140.2, 139.9, 138.9, 138.2, 136.1, 135.9, 135.6, 134.9, 132.6, 131.5, 130.9, 130.7, 130.6, 129.7, 128.2, 127.7, 127.2, 127.1, 127.0, 128.6, 125.3, 124.8, 124.6, 122.6, 120.7, 119.7, 118.8, 118.6, 114.1, 22.1, 21.9; UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 284 (32.4), 357 (33.8), 419 (356.1), 515 (15.1), 550 (6.5), 591 (4.7), 647 (3.7); HRMS (MALDI-TOF) calcd for $C_{67}H_{51}N_4O_3$ $[M+H]^+$ 959.3961, found 959.3957.

Synthesis of 5-(4-(2-(benzyloxy)-2-oxoethoxy)phenyl)-15-(4-(pyrene-1-carbonyloxy) phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin 7

To a solution of porphyrin **5** (40 mg, 0.04 mmol) in dry DMF (3 mL), K_2CO_3 (8 mg, 0.06 mmol) and benzylacetylbromide (10 µl, 0.06 mmol) were added and the mixture was stirred under nitrogen at 80 ^{0}C overnight. Then CH_2Cl_2 (50 mL) was added and extracted with water (4 x 50 mL), dried, filtered and concentrated under vacuum. The resulting crude product was purified by column chromatography (CH_2Cl_2:Hex 8/2). The product **7** was eluted as a purple solid (43 mg, 97 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.60 (d, J = 9.5 Hz, 1H), 9.12 (d, J = 8.0 Hz, 1H), 8.95 (d, J = 4.5 Hz, 2H), 8.83 (d, J = 4.5 Hz, 2H), 8.76 (d, J = 4.5 Hz, 2H), 8.73 (d, J = 5.0 Hz, 2H), 8.37 (m, 6H), 8.29 (d, J = 9.0 Hz, 1H), 8.20 (d, J = 9.0 Hz, 1H), 8.15 (m, 3H), 7.80 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.38 (d, J = 7.5 Hz, 1H), 7.32 (s, 4H), 7.29 (d, J = 8.0 Hz, 2H), 5.40 (s, 2H), 4.98 (s, 2H), 2.67 (s, 6H), 1.89 (s, 12H), –2.56 (s br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 166.9, 158.1, 151.5, 140.1, 139.8, 138.9, 138.2, 136.0, 135.9, 135.6, 135.6, 132.6, 131.5, 130.9, 130.7, 130.6, 129.6, 129.2, 129.1, 129.0, 128.2, 127.7, 127.1, 127.0, 127.0, 125.5, 125.3, 124.8, 124.6, 122.6, 120.7, 119.4, 118.8, 118.6, 113.4, 67.6, 66.2, 22.1, 21.9; UV/vis (CH_2Cl_2) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 284 (30.2), 357 (31.1), 419 (346.1), 515 (13.9), 550 (5.1), 591 (3.2), 647 (3.0); HRMS (MALDI-TOF) calcd for $C_{76}H_{59}N_4O_5$ $[M+H]^+$ 1107.4485, found 1107.4492.

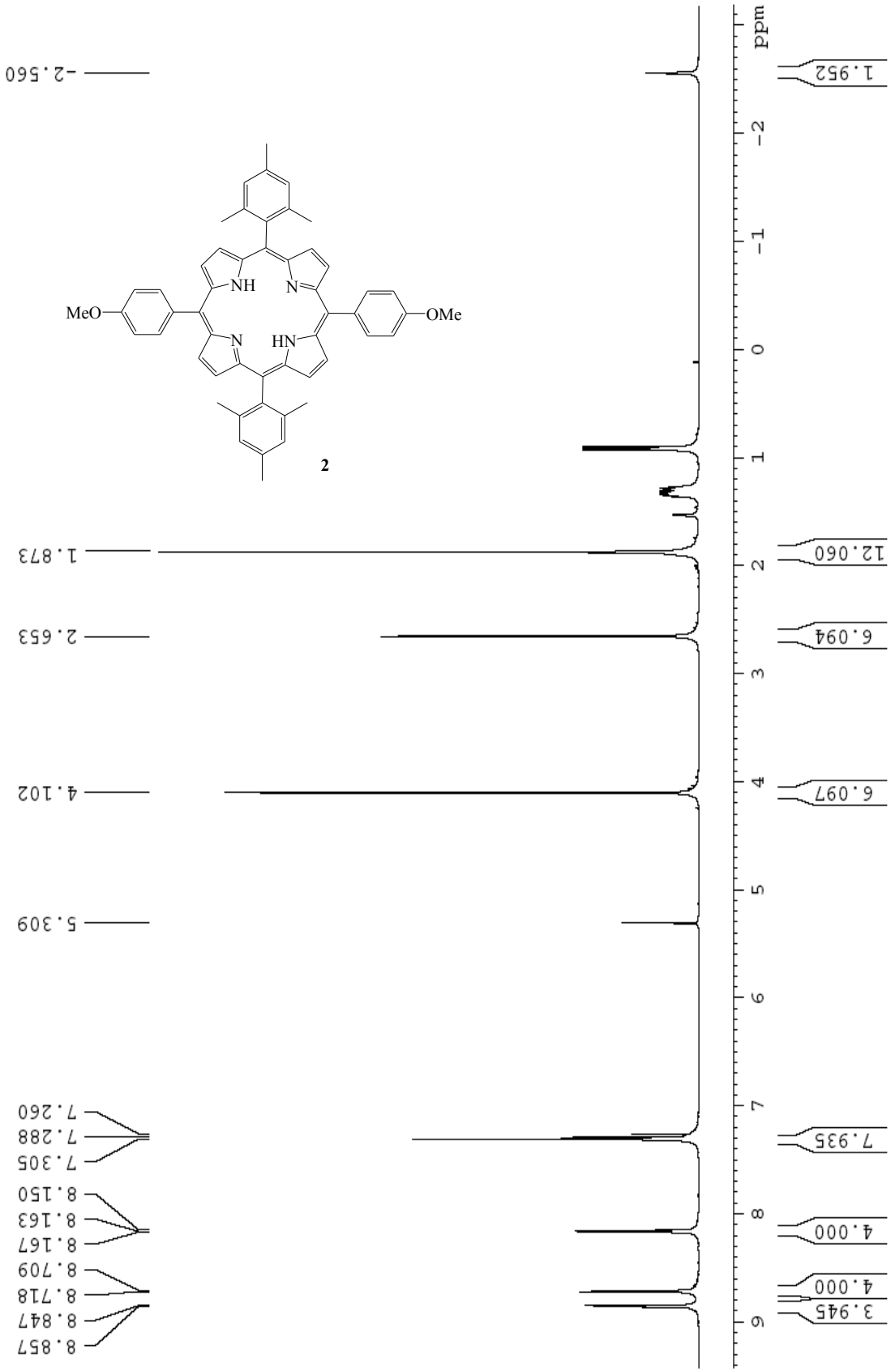

Fig. S1. ^{1}H NMR spectrum of **2** in $CDCl_3$.

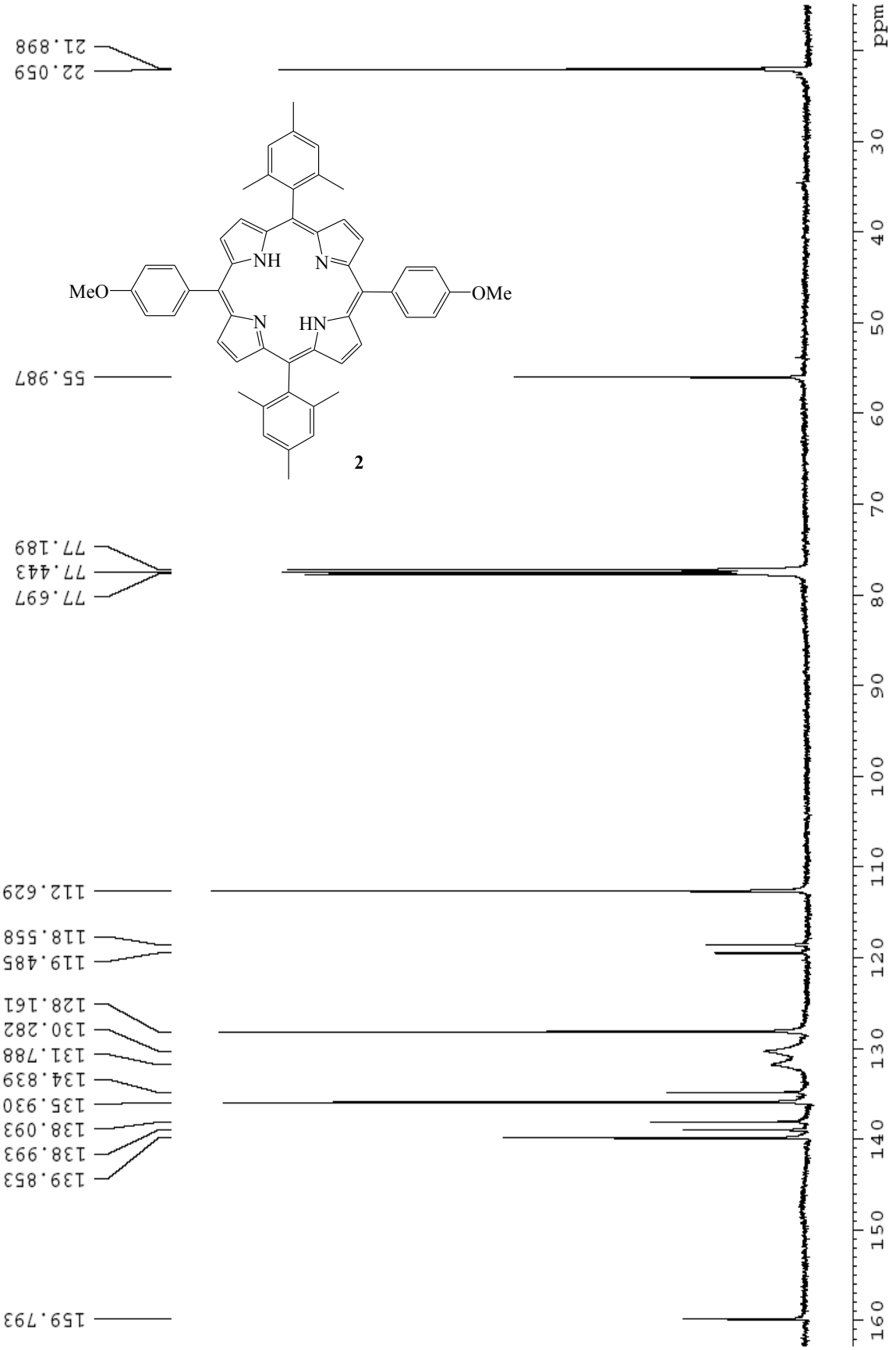

Fig. S2. ^{13}C NMR spectrum of **2** in $CDCl_3$.

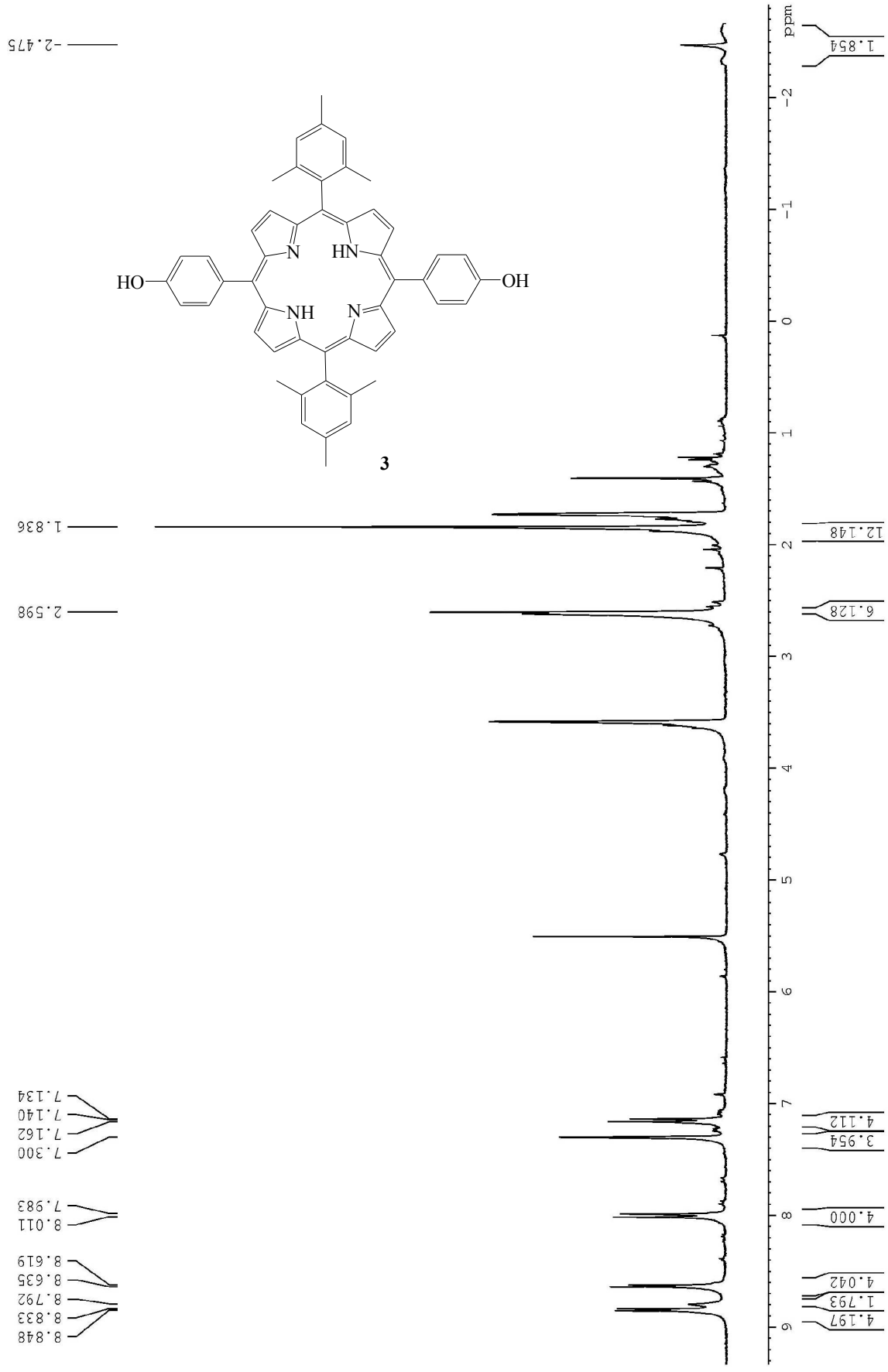

Fig. S3. ^{1}H NMR spectrum of **3** in THF-d_8.

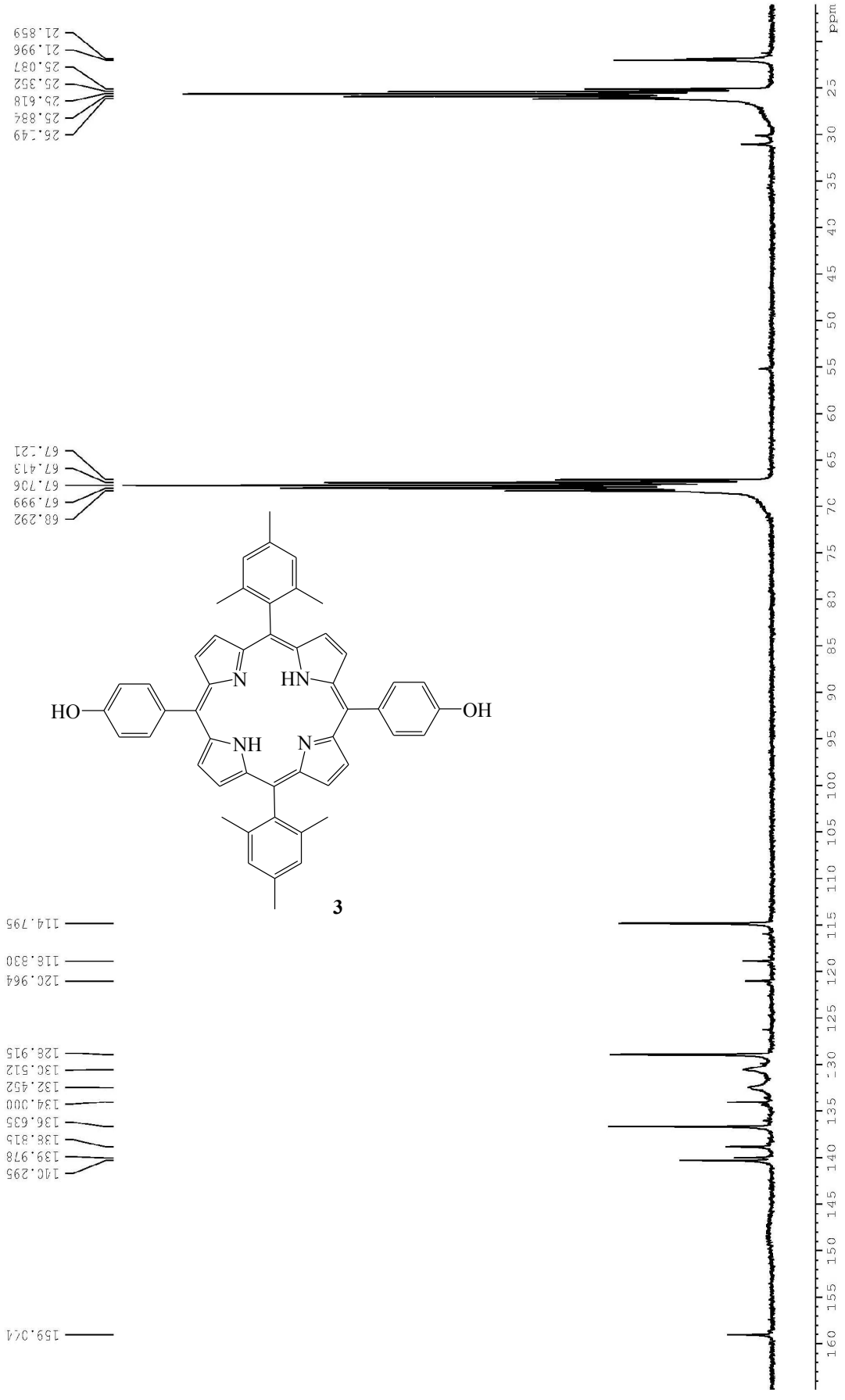

Fig. S4. ^{13}C NMR spectrum of **3** in THF-d_8.

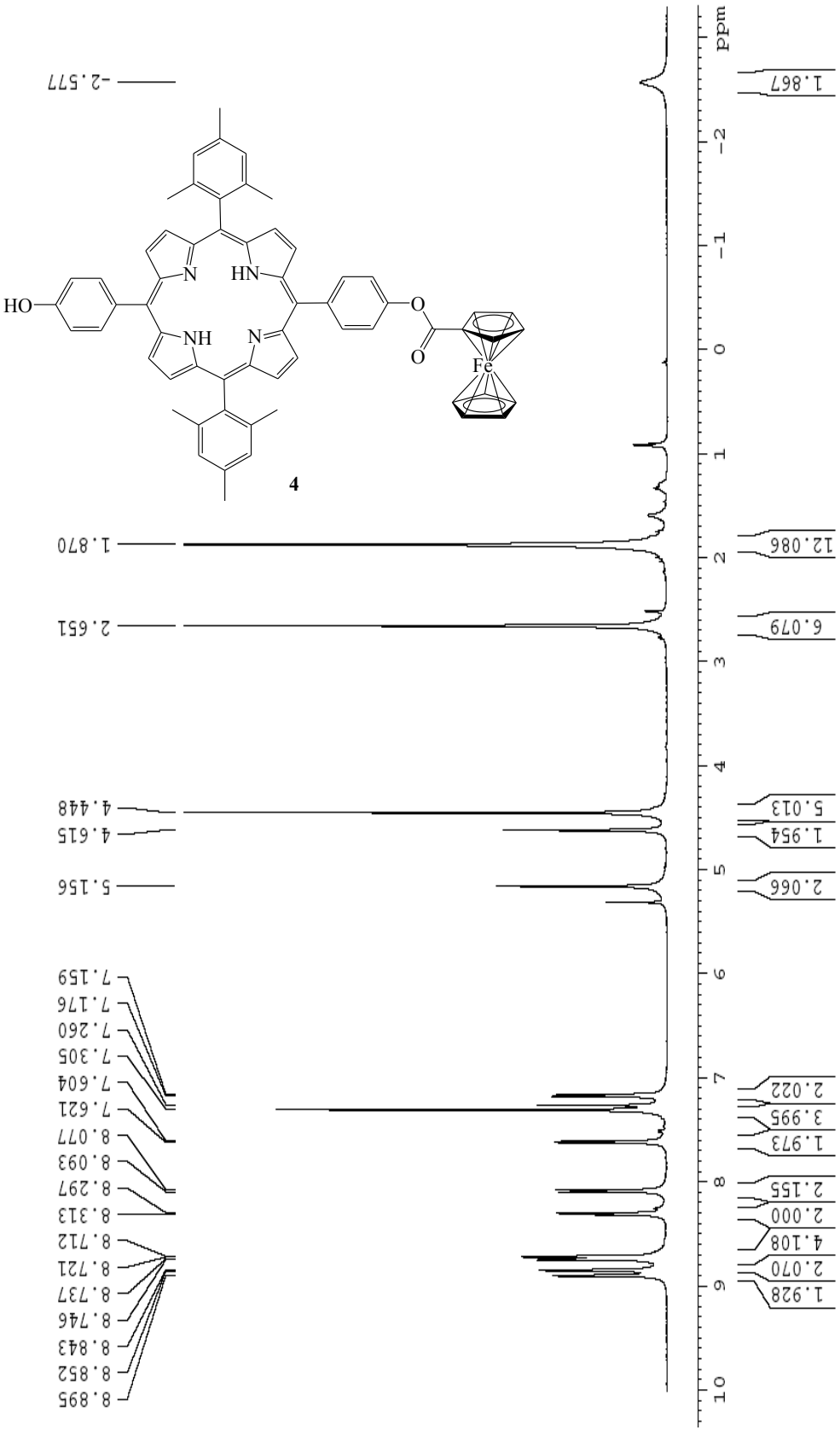

Fig. S5. ^{1}H NMR spectrum of **4** in $CDCl_3$.

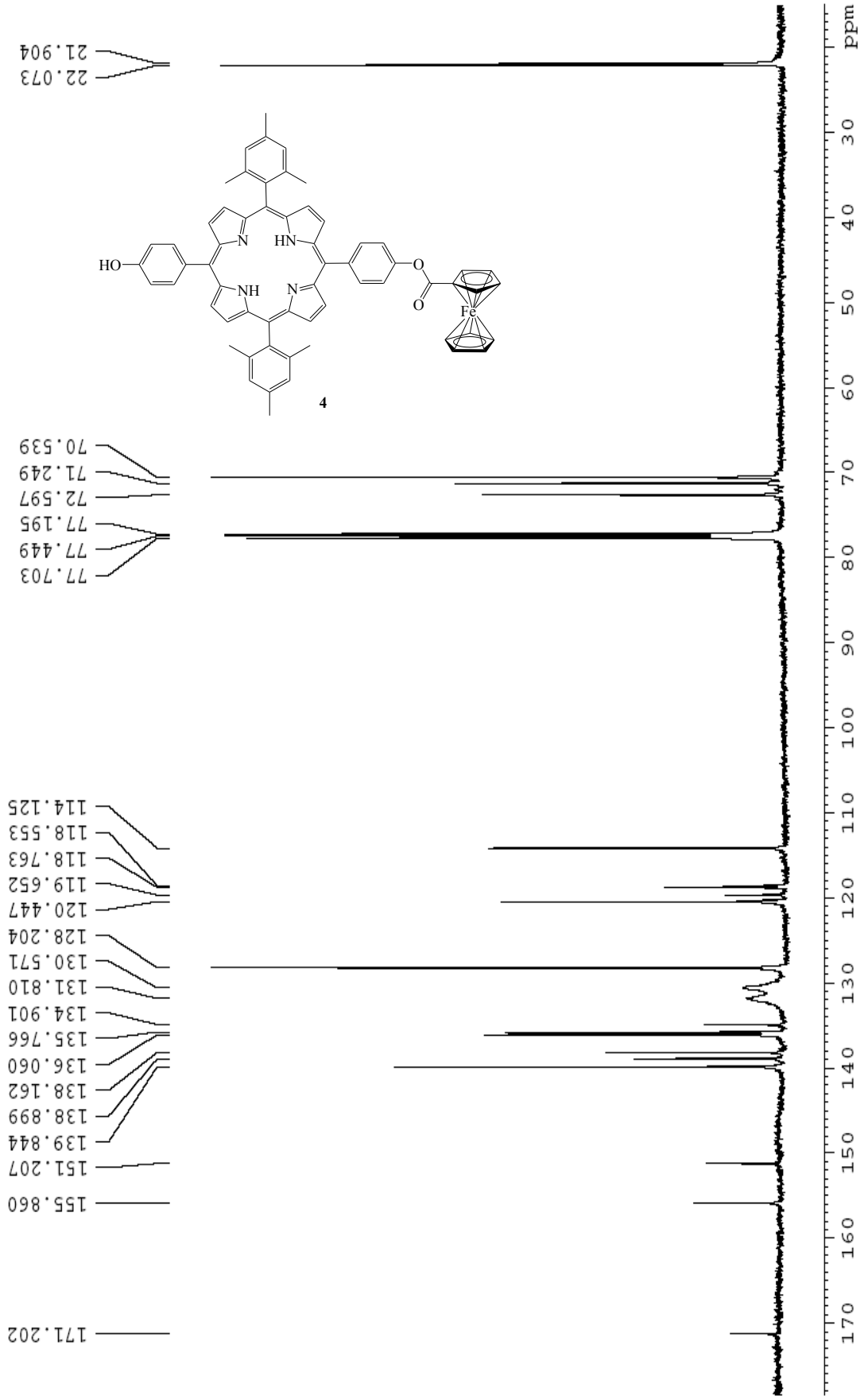

Fig. S6. ^{13}C NMR spectrum of **4** in $CDCl_3$.

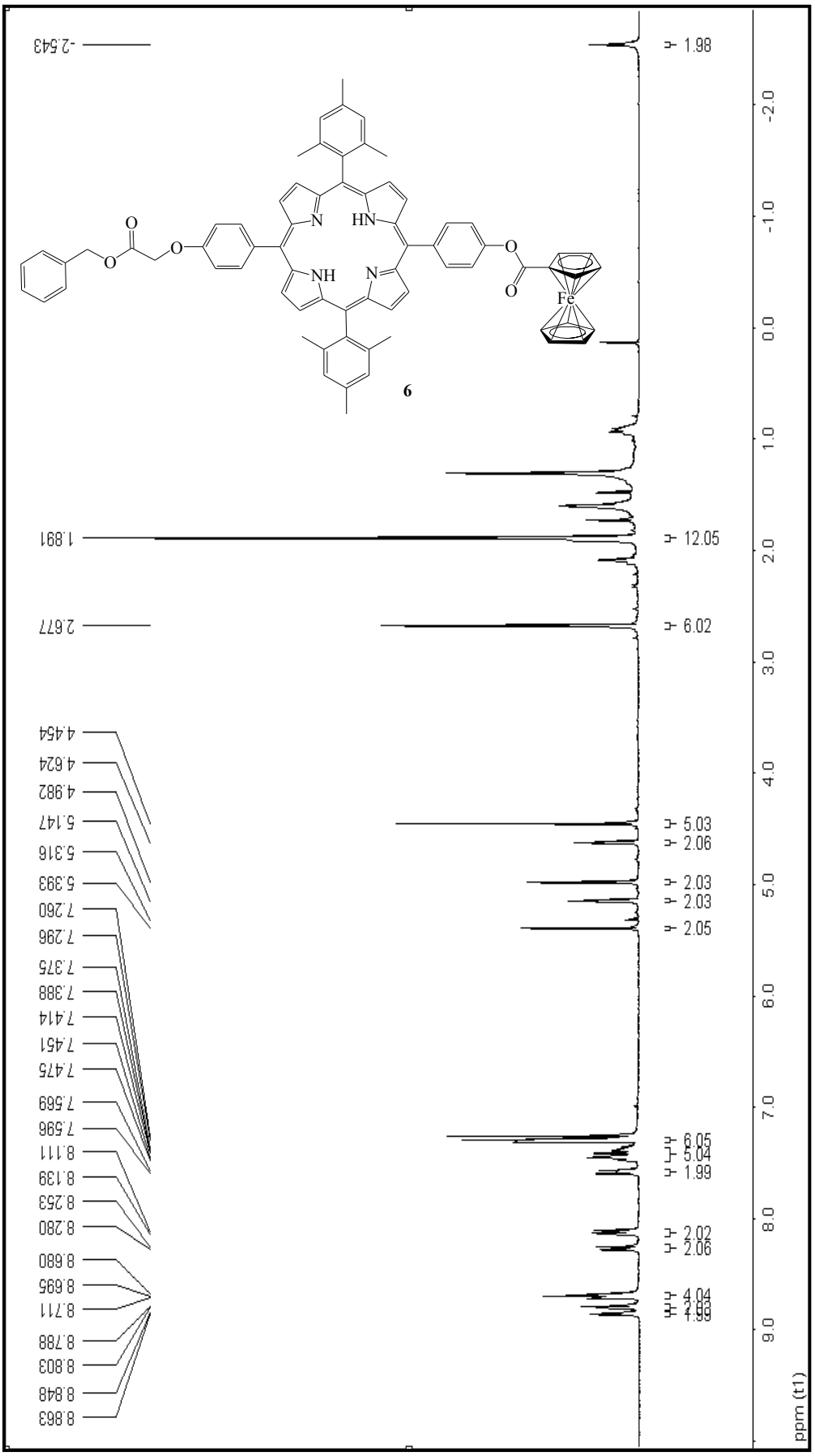

Fig. S7. ^{1}H NMR spectrum of **6** in $CDCl_3$.

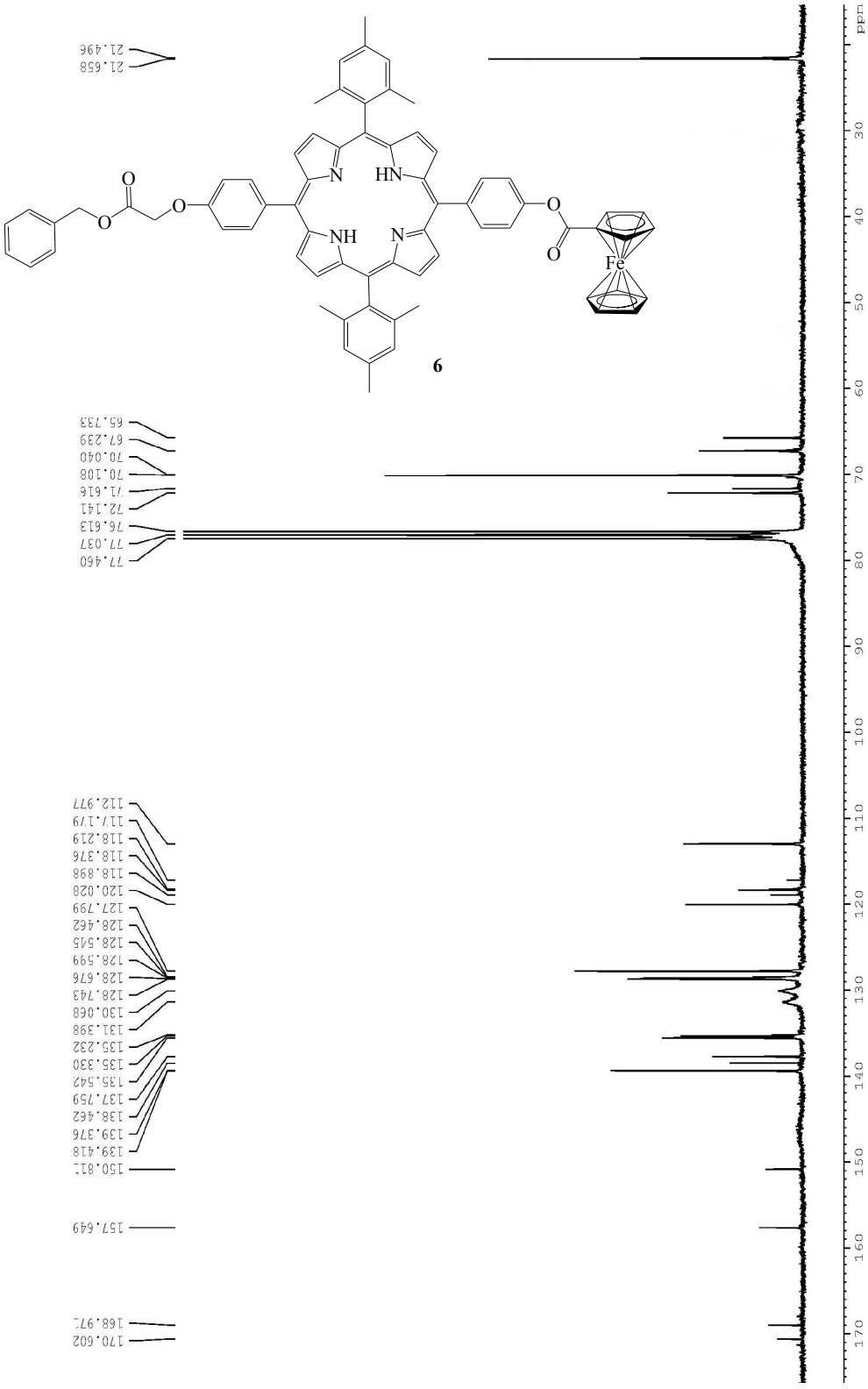

Fig. S8. ^{13}C NMR spectrum of **6** in $CDCl_3$.

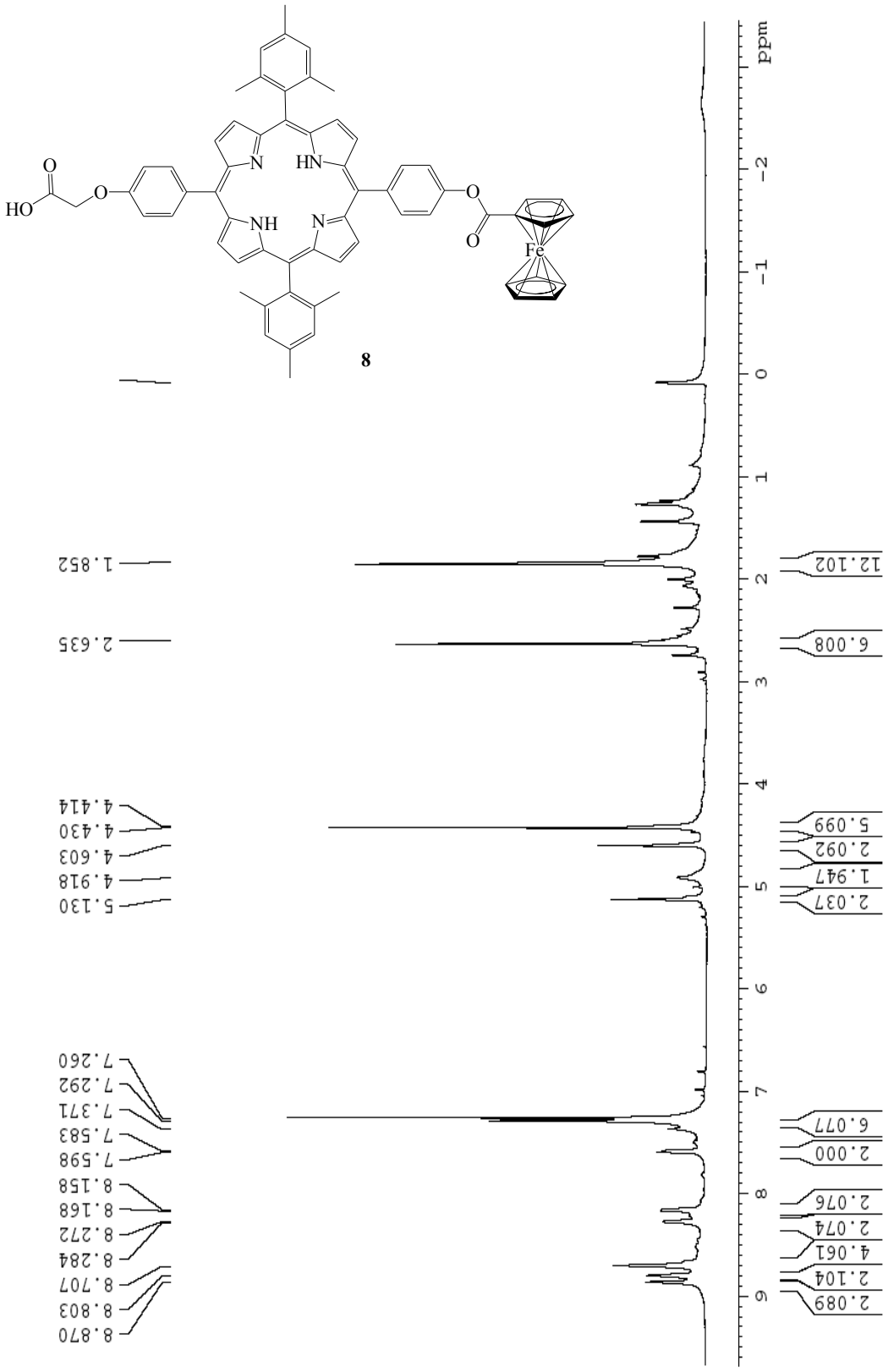

Fig. S9. ^{1}H NMR spectrum of H_2P-Fc **8** in $CDCl_3$.

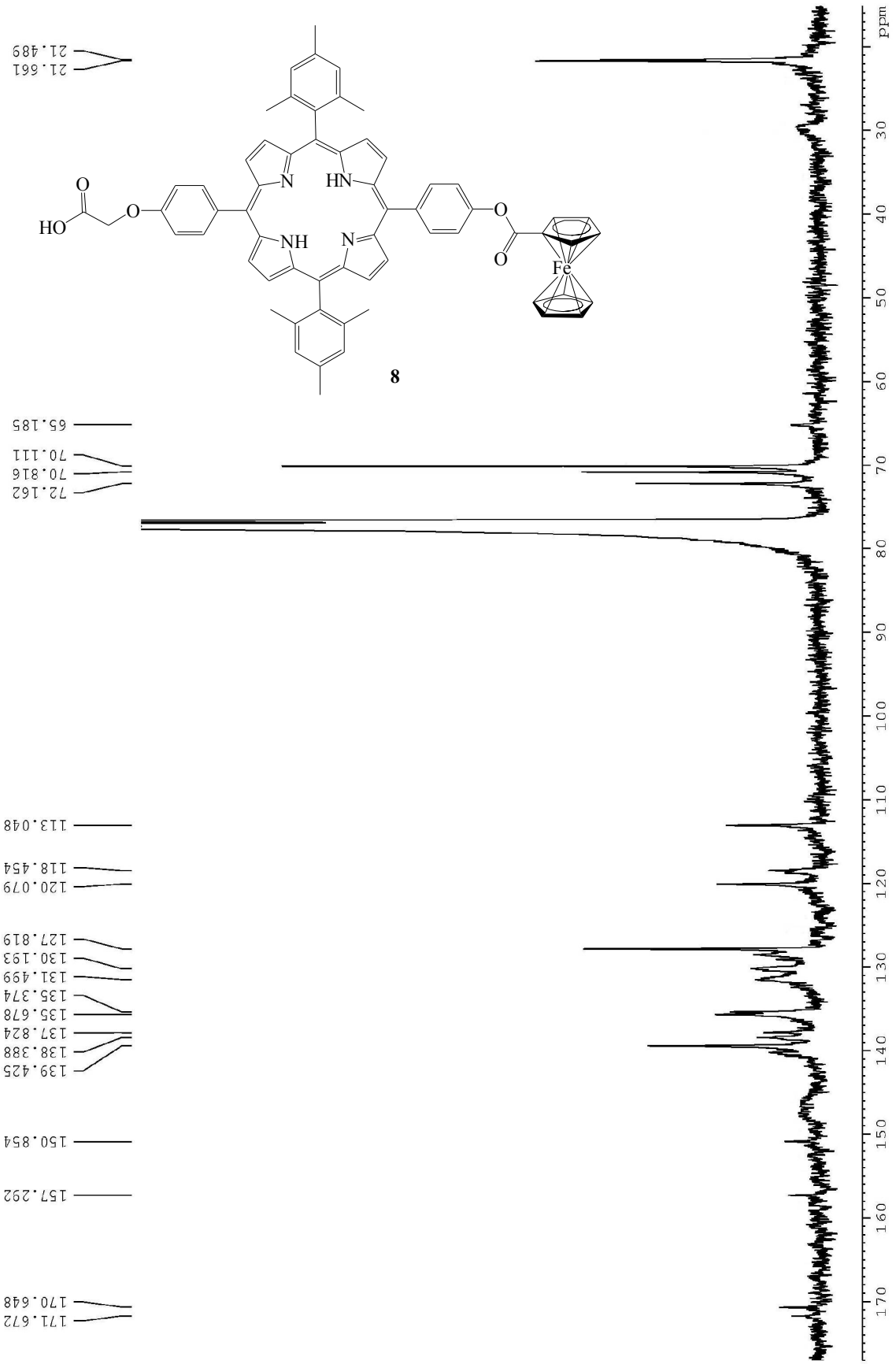

Fig. S10. ^{13}C NMR spectrum of H_2P-Fc **8** in $CDCl_3$.

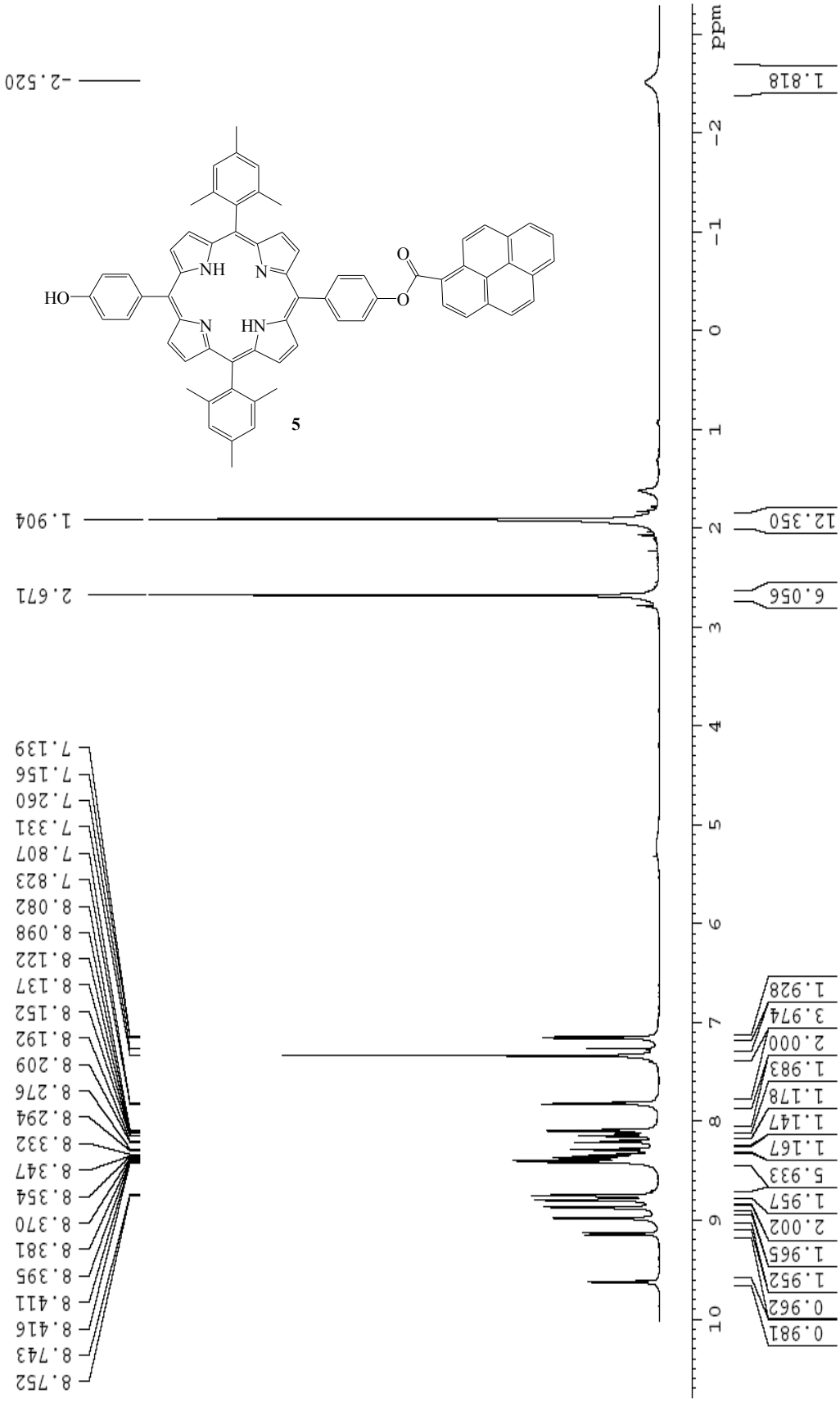

Fig. S11. ^{1}H NMR spectrum of **5** in $CDCl_3$.

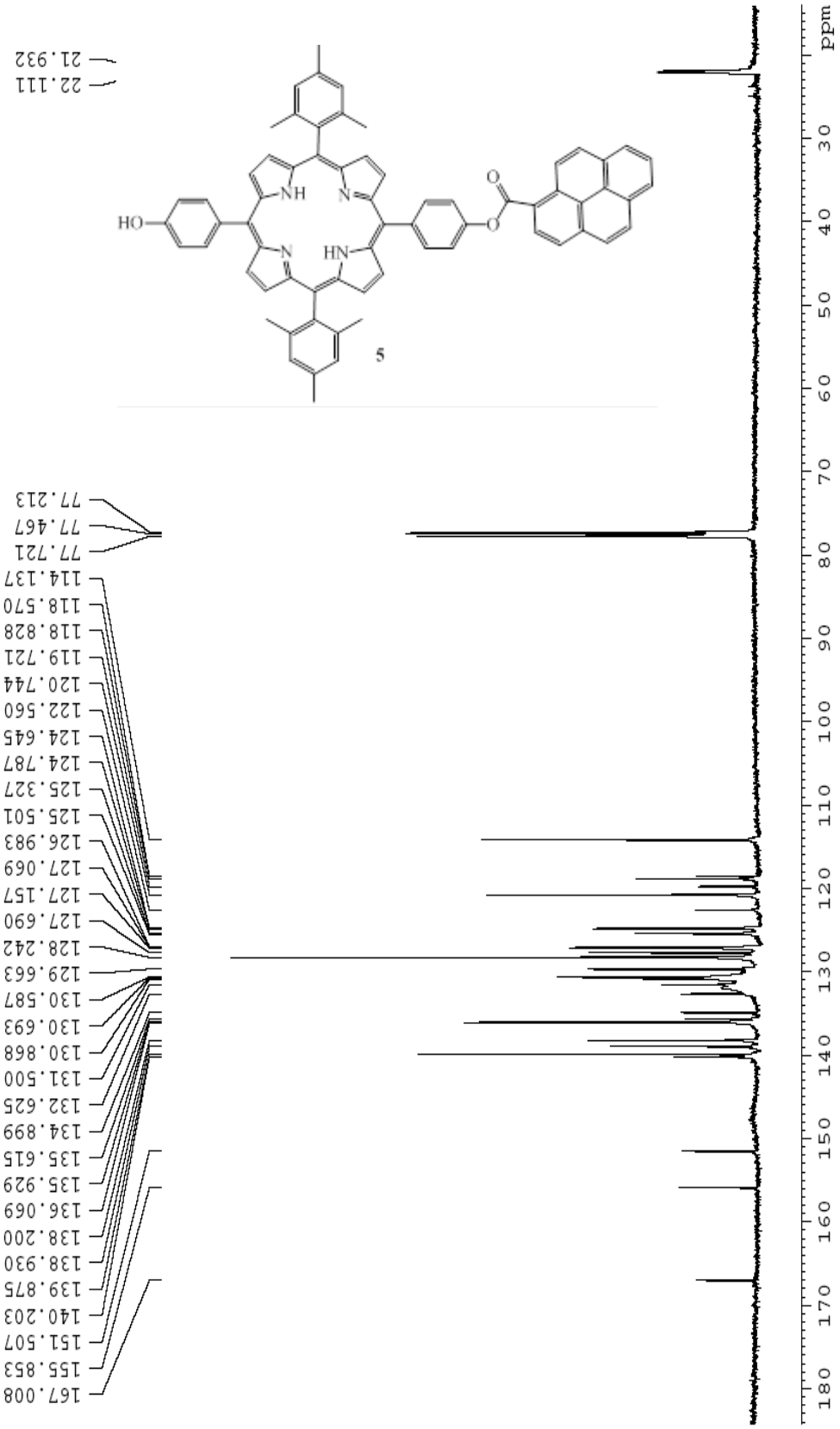

Fig. S12. ^{13}C NMR spectrum of **5** in $CDCl_3$.

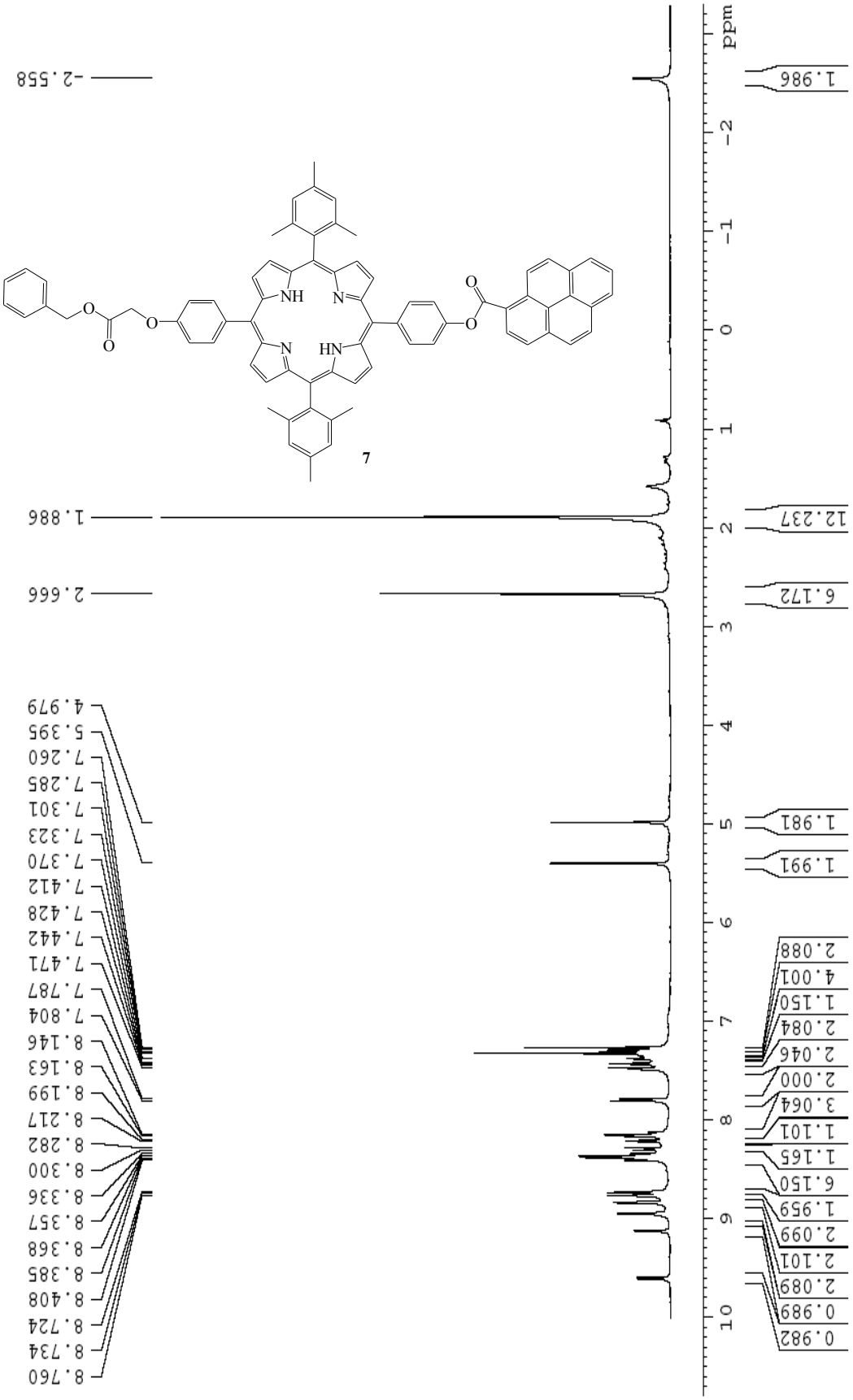

Fig. S13. ^{1}H NMR spectrum of **7** in $CDCl_3$.

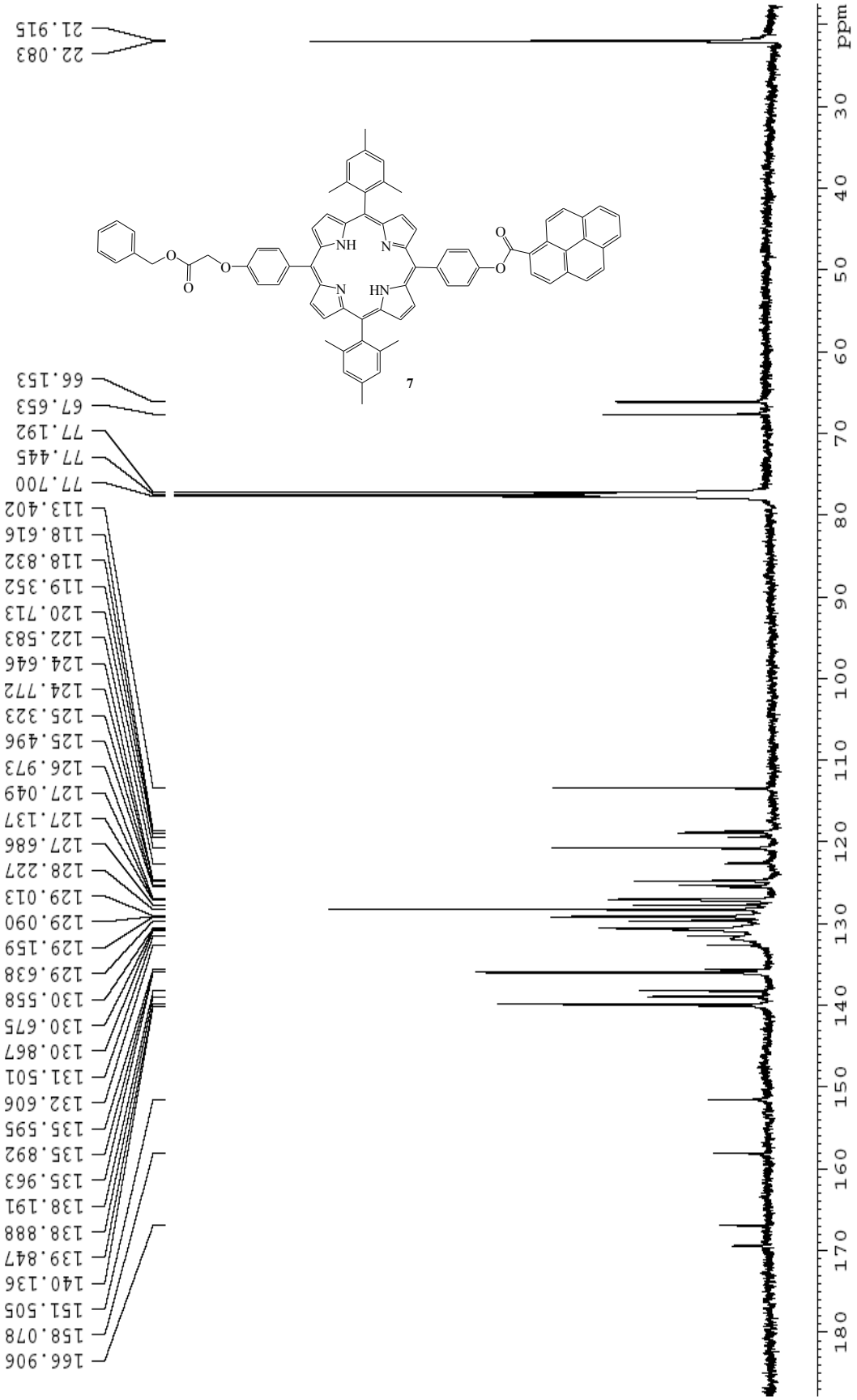

Fig. S14. ^{13}C NMR spectrum of **7** in $CDCl_3$.

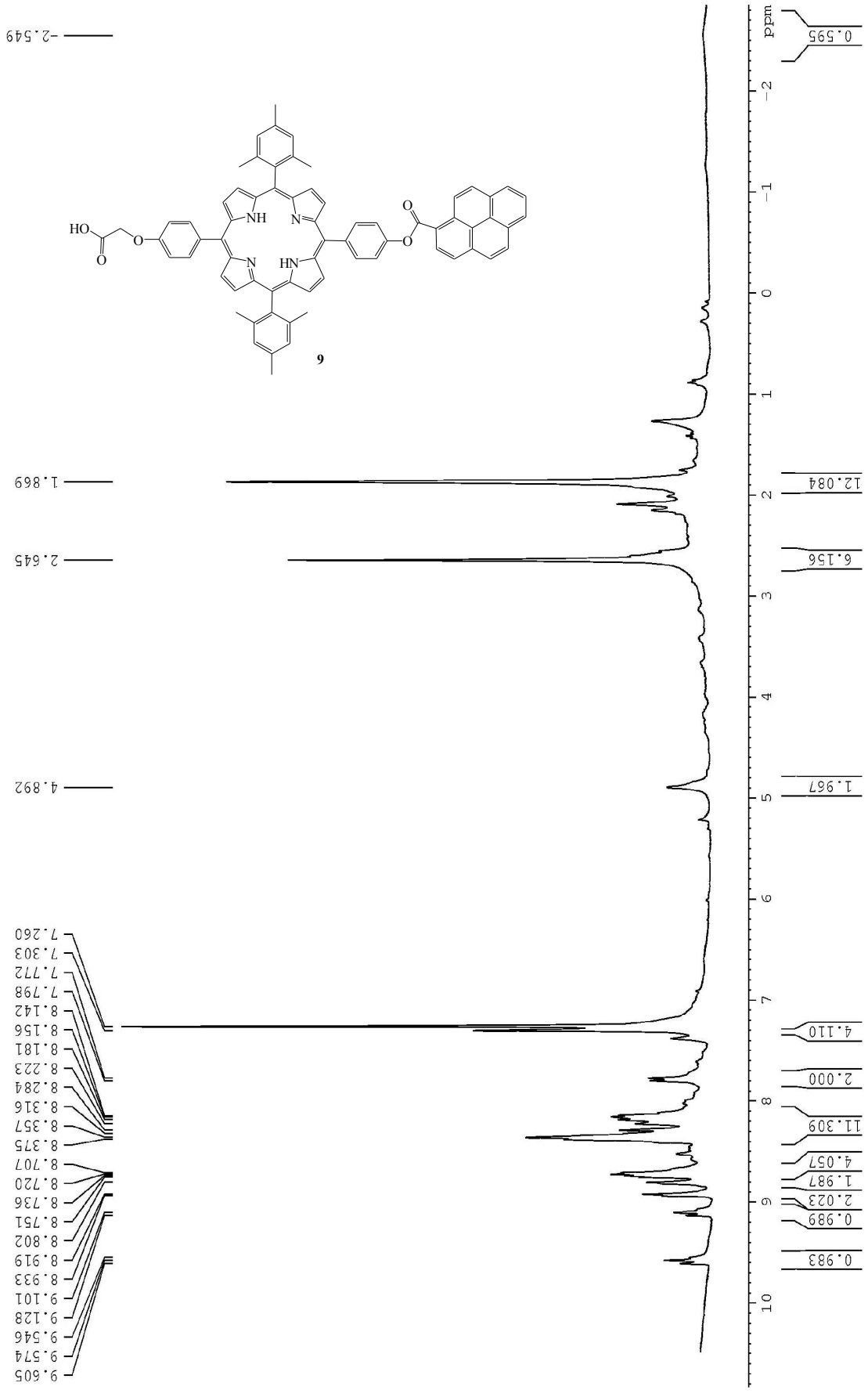

Fig. S15. ^{1}H NMR spectrum of H_2P-Fc **9** in $CDCl_3$.

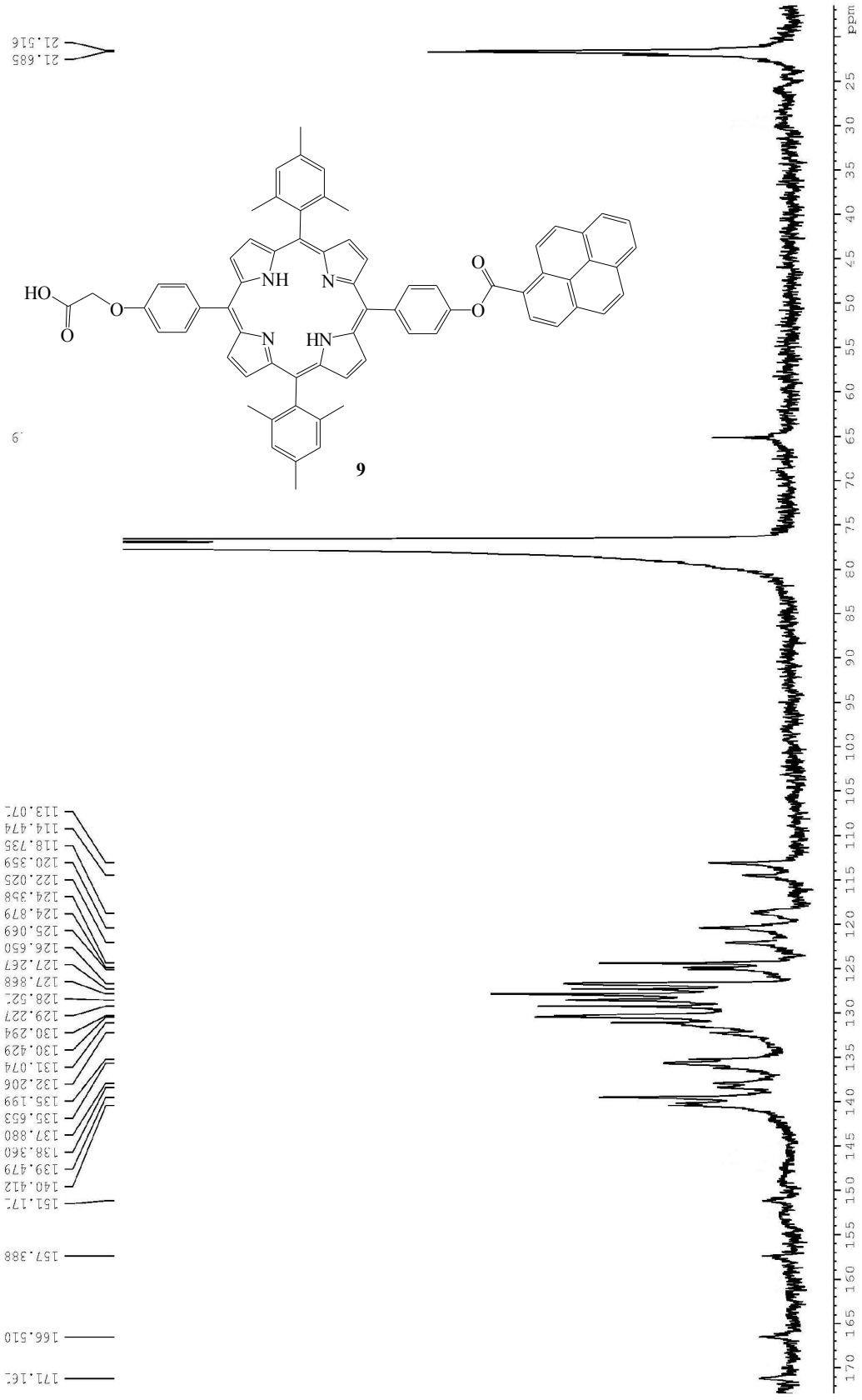

Fig. S16. ^{13}C NMR spectrum of H_2P-pyr **9** in $CDCl_3$.

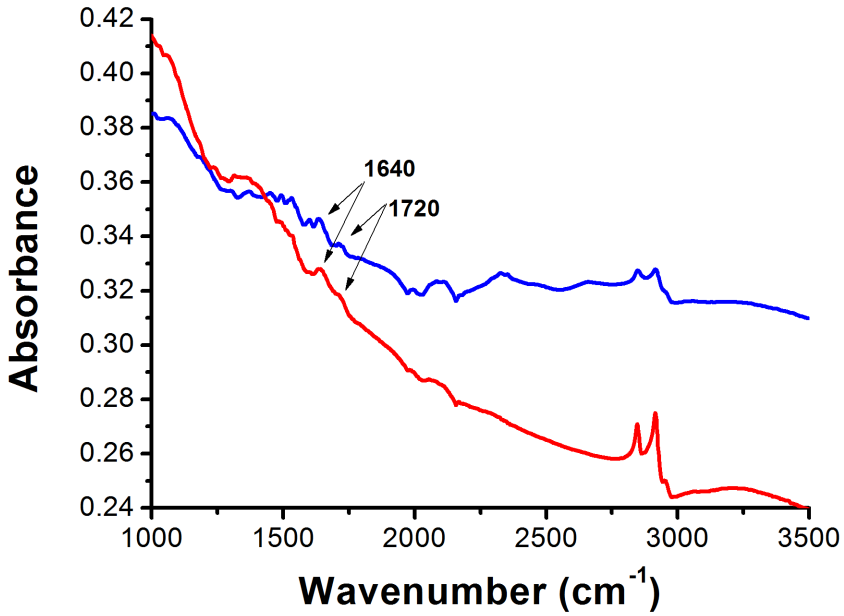

Fig. S17. ATR-IR spectra of SWCNT-(H_2P-Fc) **11** (red) and SWCNT-(H_2P-pyr) **12** (blue).

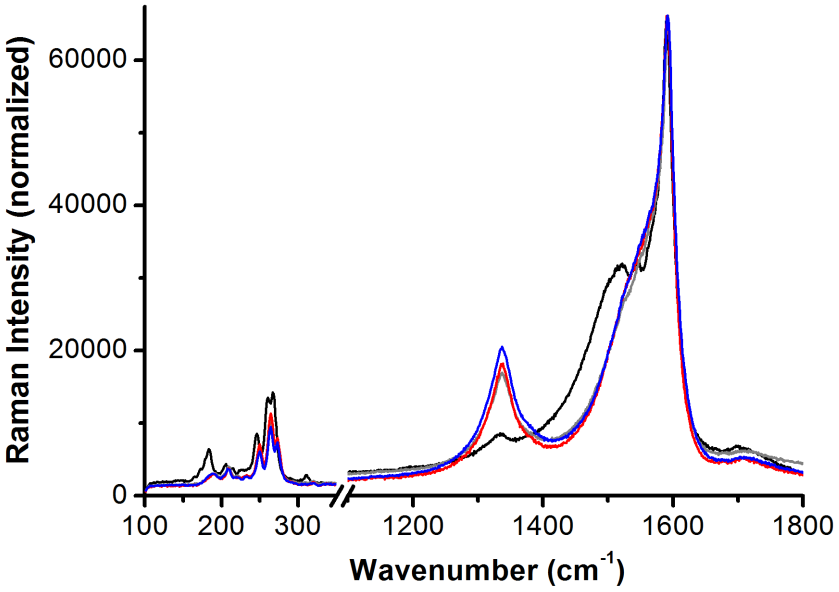

Fig. S18. Raman spectra of pristine SWCNTs (black), Boc-functionalized SWCNTs (gray), SWCNT-(H_2P-Fc) **11** (red) and SWCNT-(H_2P-pyr) **12** (blue), using 514 nm laser excitation. All intensities are normalized versus the G-band (1591 cm^{-1}) of the pristine SWCNTs.