Toward Aceneporphyrinoids: Synthesis and Transformations of Palladium(II) *meso*-Anthriporphyrin.

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Supporting Information

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Experimental section

NMR Spectroscopy. ^{1}H NMR spectra were recorded on a high-field spectrometers (^{1}H 600.15 MHz and 500.13 MHz), equipped with a broadband inverse gradient probeheads. Spectra were referenced to the residual solvent signal (chloroform-*d*, 7.24 ppm, dichloromethane-d_2, 5.32 ppm). Two-dimensional NMR spectra were recorded with 2048 data points in the t_2 domain and up to 1024 points in the t_1 domain, with a 1s recovery delay.

Mass Spectrometry. High resolution and Accurate Mass spectra were recorded on a Bruker microTOF-Q spectrometers using the electrospray technique.

UV-Vis Spectroscopy. Electronic spectra were recorded on a diode-array spectrophotometer.

X-Ray Crystallography. X-Ray quality crystals were prepared by slow evaporation of solutions of **1** dissolved in dichloromethane-methanol and [**1**-H]$^{+}$ and **2**-Cl dissolved in dichloromethane-hexane. Data were collected at 100 K on a Xcalibur PX κ-geometry diffractometer, with Mo Kα radiation (λ=0.71073 Å). Data were corrected for Lorentz, polarization and absorption (**2**-Cl) effects. Crystal data are compiled in Table S1. The structures were solved by a direct methods with SHELXS-97 and refined by full matrix least-squares method by using SHELXL-97 with anisotropic thermal parameters for the non-H atoms. Scattering factors were those incorporated in SHELXS-97.

Theoretical calculations. Geometry optimizations were carried out within unconstrained C_1 symmetry, with starting coordinates derived from molecular mechanic calculations.[4] Becke's three-parameter exchange functional with the gradient-corrected correlation formula of Lee, Yang[5-6] and Parr (DFT-B3LYP) were used with the LANL2D basis set for Pd and 6-31G** for other atoms.

Synthesis.

Synthetic procedures and analytical data.

9-benzoylanthracene was prepared as described in literature.[1]

9,10-dibenzoylanthracene 4.

In a 500 mL round-bottomed flask equipped with a magnetic stirring bar and a heating mantle, 9-benzoylanthracene (10.0 g, 0.035 mol), aluminum chloride (5.7 g, 0.043 mol) and benzoyl chloride (5.0 mL, 0.043 mol) was dissolved in 1,2-dichloroethane (300 mL). The reaction mixture was then protected from moisture (a tube with calcium chloride on the top of a condenser) and refluxed for 7 days. After this time the reaction mixture was cooled to room temperature and the reaction was quenched by cautious addition of hydrochloric acid-brine solution (100 mL, 2:3 v/v) and stirred for another hour. The organic phase was separated in a separatory funnel, washed with water and dried over anhydrous magnesium sulfate. After evaporation of the solvent the crude product was recrystallized from acetone yielding yellowish-white solid. Yield 12.6 g (92%).

^{1}H NMR (500 MHz, chloroform-*d*, 298K): δ 7.85 (d, 4H, ^{3}J=7.5 Hz), 7.76 (AA'BB' spin system, 4H), 7.60 (t, 2H, ^{3}J=7.5 Hz), 7.44 (t, 4H, ^{3}J=7.6 Hz), 7.38 (AA'BB' spin system, 4H). **^{13}C NMR** (126 MHz, chloroform-*d*, 298K) δ 199.96, 137.88, 135.92, 134.27, 130.17, 128.98, 127.99, 126.65, 125.76. **HR-MS** (ESI+, TOF) *m/z* $[M+H]^+$ 387.1380, calcd for $C_{28}H_{19}O_2^+$ 387.1380.

9,10-Bis(phenylhydroxymethyl)anthracene 5.

In a 1000 mL round-bottomed flask equipped with a magnetic stirring bar, 9,10-dibenzoylanthracene **4** (8.1 g, 0.021 mol) was dissolved in THF (300 mL) under a protective atmosphere. Solid lithium aluminum hydride (2.3 g, 2.9 equiv.) was then added in small portions, so as to avoid excessive gas evolution. The reaction mixture was then stirred for 15 minutes and then quenched by cautious addition of water (10 mL) followed by 2 M aqueous NaOH (5 mL). The reaction mixture was filtered and stripped of solvent on a rotary evaporator. The crude product was washed with cold acetone on Schott funnel and dried affording yellow solid. Yield 8.1g (~99%).

^{1}H NMR (500 MHz, dichloromethane-*d$_2$*, 298K, mixture of isomers): δ 8.45 (AA'BB' spin system, 4H), 7.46 (d, 2H, ^{3}J=3.4 Hz, C**H**(OH)), 7.40–7.37 (m: AA'BB' spin system covered with dublet, 8H), 7.29 (t, 4H, ^{3}J=7.6 Hz, *m*-Ph), 7.23 (t, 2H, ^{3}J=7.6 Hz, *p*-Ph), 2.87 (d, 2H, ^{3}J=4.0 Hz, CH(O**H**)). **^{13}C NMR** (126 MHz, dichloromethane-*d$_2$*, 298K, mixture of isomers) δ 144.42, 136.18, 130.26, 128.56, 127.05, 126.10, 125.93, 125.56, 70.58. **HR-MS** (ESI+, TOF) *m/z* $[M-OH]^+$ 373.1587, calcd for $C_{28}H_{21}O^+$ 373.1587; $[M+Ag]^+$ 497.0676, calcd for $C_{28}H_{22}AgO_2^+$ 497.0665.

5,10,15,20-Tetraphenyl-*meso*-anthriporphyrin 1.

9,10-Bis(phenylhydroxymethyl)anthracene **5** (390 mg, 1.0 mmol), pyrrole (208 µL, 3.0 mmol) and benzaldehyde (204 µL, 2.0 mmol) were added to dry dichloromethane (900 mL) under nitrogen. Boron trifluoride diethyl etherate (100 µL) was then added and the reaction mixture was protected from light and stirred for two hours. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 681 mg, 3.0 mmol) was subsequently added and the reaction mixture was stirred for another half an hour. After that time solvent was evaporated under reduced pressure and the dark residue was subjected to chromatography (grade II alumina, dichloromethane). In preliminary chromatography the desired product was eluted as one fraction with tetraphenylporphyrin and N-confused porphyrin. During subsequent chromatographies (grade II alumina) with dichloromethane-hexane as eluent (3:2 v/v) **1** was eluted as green fraction followed by N-confused porphyrin. Yield 4 mg (0.5 %).

^{1}H NMR (600 MHz, chloroform-*d*, 298K): δ 7.93 (d, 4H, ^{3}J=7.9 Hz, 5,20-*o*-Ph), 7.59 (d, 2H, ^{3}J=4.8 Hz, 7,18-H), 7.54-7.49 (m, 8H, AA'BB' and t, 2^{2},3^{2},21^{2}22^{2}-H and 5,20-*m*-Ph), 7.46 (t, 2H, ^{3}J=7.3Hz, 5,20-*p*-Ph), 7.33-3.32 (m, 6H, 10,15-*m,p*-Ph), 7.25-7.23 (m, 4H, 10,15-*o*-Ph), 7.05 (AA'BB', 4H, 2^{1},3^{1},21^{1}22^{1}-H), 6.77 (b, 1H, 24-NH, 210K; signal was detected only on spectra measured in low temperature: 220-210K), 6.52 (d, 2H, ^{3}J=4.8Hz, 8,17-H), 6.19 (s, 2H, 12,13-H). **^{13}C NMR** (151 MHz, chloroform-*d*, 298K): δ 167.24, 160.93, 146.92, 144.78, 140.96, 140.82, 137.88, 133.42, 132.70, 131.90, 131.80, 131.18, 130.08, 128.89, 128.83, 127.71, 127.17, 126.44, 124.97, 115.57. **HR-MS** (ESI+, TOF) *m/z* $[M+H]^+$ 726.2904, calcd for $C_{54}H_{36}N_3^+$ 726.2904. **UV–Vis** (CH_2Cl_2, 298K): λ_{max} (log ε) 395 (4.99), 698 (4.52) sh. 650.

5,10,15,20-Tetraphenyl-*meso*-anthriporphyrin dication [**1**-H_2]$^{2+}$.

^{1}H NMR (600 MHz, chloroform-*d*, 298K): δ 8.53 (d, 2H, ^3J=5.0 Hz, 7,18-H), 8.36 (d, 4H, ^3J=7.4 Hz, 5,20-*o*-Ph), 7.92 (t, 2H, ^3J=7.3 Hz, 5,20-*p*-Ph), 7.89 (t, 4H, ^3J=7.3 Hz, 5,20-*m*-Ph), 7.66-7.65 (m, 2H, 10,15-*p*-Ph), 7.62-7.60 (m, 10H, 8,17-H; 10,15-*o*,*m*-Ph), 7.37 (s, 2H, 12,13-H), 6.79 (AA'XX' spin system, 4H, 2^2, 3^2, 21^2, 22^2-H), 6.70 (AA'BB' spin system, 4H, 2^1, 3^1, 21^1, 22^1-H), 6.22 (b, 1H, 24-NH), 5.68 (b, 23,25-NH; increased multiplicity is accounted to complexation of TFA). **UV–Vis** (CH_2Cl_2, 298K): λ_{max} (log ε) 432 (4.94) sh 445 and 475, 506 (4.70), 549 (4.86), 784 (4.66).

Chloropalladium(II) 5,10,15,20-tetraphenyl-*meso*-anthriporphyrin **2**-Cl.

5,10,15,20-Tetraphenyl-*meso*-anthriporphyrin **1** (20.2 mg, 27.9 μmol) and palladium(II) chloride (45 mg, 0.26 mmol) were added to the solution of acetonitrile (50 mL) and dichloromethane (20 mL) under nitrogen and stirred for 48 hours. After that time solvent was evaporated under reduced pressure and the dark brown residue was subjected to chromatography (silica gel 70–230, 1% methanol-dichloromethane solution). **2**-Cl was eluted as the main, green fraction. The product was recrystallized from dichloromethane-hexane solution. Yield: 23.9 mg (99 %).

^{1}H NMR (600 MHz, chloroform-*d*, 298K): δ 7.86 (d, 4H, ^3J=8.0 Hz, 5,20-*o*-Ph), 7.64 (AA'BB' spin system, 2H, 2^1,3^1-H), 7.56 (d, 2H, ^3J=7.4 Hz, 10,15-*o*-Ph), 7.52-7.44 (m, 8H, 10,15-Ph), 7.40 (t, 4H, ^3J=7.9 Hz, 5,20-*m*-Ph), 7.34 (t, 2H, ^3J=7.5 Hz, 5,20-*p*-Ph), 7.23 (d, 2H, ^3J=4.9 Hz, 7,18-H), 7.05 (d, 2H, ^3J=4.9 Hz, 8,17-H), 7.00 (AA'BB' spin system, 2H, 2^2,3^2-H), 6.80 (s, 2H, 12,13-H), 6.23 (AA'BB' spin system, 2H, 21^2,22^2-H), 5.89 (AA'BB' spin system, 2H, 21^1,22^1-H). **^{13}C NMR** (151 MHz, chloroform-*d*, 298K): δ 168.12, 147.45, 142.29, 140.94, 140.62, 139.35, 138.51, 138.46, 138.43, 137.47, 134.24, 131.75, 131.17, 130.98, 129.00, 128.65, 128.39, 128.24, 128.08, 127.71, 127.41, 127.15, 125.40, 125.00, 124.95. **HR-MS** (ESI+, TOF) *m/z* $[M-Cl]^+$ 830.1780, calcd for $C_{54}H_{34}N_3Pd^+$ 830.1782. **UV–Vis** (CH_2Cl_2, 298K): λ_{max} (log ε) 337 (4.31), 401 (4.49), 429 (4.44), 668 (3.98), 726 (4.37).

Cleavage product **3**-Cl.

Chloropalladium(II) 5,10,15,20-tetraphenyl-*meso*-anthriporphyrin **2**-Cl (17.9 mg, 20.7 μmol) and potassium carbonate (2.1 g) was added to acetonitrile (50 mL) and stirred under nitrogen at room temperature overnight. The dark green mixture was evaporated and the residue was subjected to chromatography (silica gel 70–230, dichloromethane). Compound **3**-Cl was eluted as the first orange fraction, followed by the more polar substrate(7 mg, 39% recovery). Yield: 2.9 mg (16 %).

^{1}H NMR (600 MHz, chloroform-*d*, 220K): δ 9.83 (d, 1H, ^{3}J=7.7 Hz, 5-*o*-Ph), 9.43 (m, 1H, 3^{1}-H), 8.60 (m, 1H, 2^{2}-H), 8.48 (d, 1H, ^{3}J=8.9 Hz, 21^{1}-H), 7.92 (d, 2H, ^{3}J=7.7 Hz, 20-*o*,*o*'-Ph), 7.79 (d, 1H, ^{3}J=8.8 Hz, 22^{1}-H), 7.77-7.73 (m, 2H, 2^{1},3^{2}-H), 7.56 (d, 1H, ^{3}J=7.9 Hz, 15-*o*-Ph), 7.50 (m, 2H, 21^{2}-H, 10-Ph), 7.49-7.46 (m, 2H, 15-Ph), 7.45-7.43 (m, 2H, 15-Ph), 7.40-7.37 (m, 2H, 10-Ph, 20-*p*-Ph), 7.35 (t, ^{3}J=7.9 Hz, 10-*p*-Ph), 7.33-7.28 (m, 10-*o*-Ph, 5-*o*-Ph, 22^{2}-H), 7.26-7.22 (m, 20-*m*,*m*'-Ph), 7.15-7.13 (m, 1H, 10-*o*-Ph), 6.98 (d, 1H, ^{3}J=4.4 Hz, 18-H), 6.90 (d, 1H, ^{3}J=5.3 Hz, 13-H), 6.68 (t, 1H, ^{3}J=7.3 Hz, 5-*p*-Ph), 6.49 (d, 1H, ^{3}J=5.3 Hz, 12-H), 6.42 (d, 1H, ^{3}J=4.4 Hz, 17-H), 6.27 (d, 1H, ^{3}J=5.2 Hz, 8-H), 6.11 and 6.09 (2t, 2H, ^{3}J=7.7 Hz, 5-*m*-Ph), 5.91 (d, 1H, ^{3}J=5.2 Hz, 7-H). **^{13}C NMR** (151 MHz, chloroform-*d*, 298K): δ 185.56, 159.27, 157.29, 154.15, 144.63, 141.12, 140.21, 140.03, 138.90, 138.18, 135.54, 135.26, 134.87, 134.83, 134.07, 133.78, 132.41, 131.97, 131.47, 131.36, 130.64, 129.54, 129.36, 129.04, 128.87, 128.57, 128.12, 127.94, 127.85, 127.69, 127.33, 127.11, 126.55, 126.13, 125.00, 124.58, 123.21, 122.25, 114.92, 112.04. **HR-MS** (ESI+, TOF) *m/z* [M+H]$^{+}$ 882.1468, calcd for $C_{54}H_{35}ClN_{3}OPd^{+}$ 882.1498. **UV–Vis** (CH_2Cl_2, 298K): λ_{max} (log ε) 355 (4.52), 375 (4.51), 395 (4.50), 474 (4.44), 816 (4.25).

Bromopalladium(II) 5,10,15,20-tetraphenyl-*meso*-anthriporphyrin 2-Br and **cleavage product 3**-Br.

To the chloroform solution of **2**-Cl silver(I) tetrafluoroborate (molar excess) was added and the mixture was stirred for 5 minutes. The mixture was filtrated to the solution of sodium bromide in methanol and stirred for one hour. Subsequently the solution was evaporated to dryness. The solid residue was dissolved in dichloromethane and filtrated to remove the excess of sodium bromide. **2**-Br was subjected to cleavage conditions described for **3**-Cl affording **3**-Br as identified by ^{1}H NMR and HRMS. **HR-MS** (ESI+, TOF) *m/z* [M+H]$^{+}$ 926.0926, calcd for $C_{54}H_{35}BrN_{3}OPd^{+}$ 926.0993.

Table S1. Crystal data and structure refinement for compound **1**, [**1**-H]$^+$ and **2**-Cl.

	1	[**1**-H]$^+$	**2**-Cl
Empirical formula	$C_{54}H_{35}N_3$, 0.5(CH_2Cl_2)	$C_{54}H_{36}N_3$, $C_2F_3O_2$, 0.5($C_2F_3O_2H$)	$C_{54}H_{34}ClN_3Pd$, 0.4(C_6H_{14}), 0.1(H_2O), 1.15(CH_2Cl_2)
Formula weight	767.45	896.00	1000.63
Temperature	100K	100K	100K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Trigonal
Space group	$P\bar{1}$	$P2_1/c$	$R\bar{3}$
Unit cell dimensions			
a	9.779(3) Å	16.924(5) Å	50.222(15) Å
b	13.499(6) Å	24.465(8) Å	50.222(15) Å
c	16.963(6) Å	11.989(3) Å	9.718(3) Å
α	92.09(3)°	90.00°	90.00°
β	101.98(4)°	92.57(3)°	90.00°
γ	106.41(4)°	90.00°	120.00°
Volume	2090.4(15) Å^3	4959(3) Å^3	21227(11) Å^3
Z	2	4	18
Density (calculated)	1.211	1.201	1.409
Absorption coefficient	0.130 mm^{-1}	0.090 mm^{-1}	0.623 mm^{-1}
F(000)	796	1854	9203
Crystal size	0.4x0.2x0.01	0.47x0.43x0.03	0.08x0.13x0.35
Theta range for data collection	$2.79 \le \theta \le 36.90$	$2.55 \le \theta \le 27.50$	$4.11 \le \theta \le 38.55$
Index ranges	$-16 \le h \le 16$	$-21 \le h \le 19$	$-70 \le h \le 70$
	$-22 \le k \le 22$	$-30 \le k \le 31$	$-70 \le k \le 70$
	$-28 \le l \le 19$	$-15 \le l \le 15$	$-13 \le l \le 11$
Reflections collected	17492	11387	13715
Independent reflections	6447	6047	8722
Restraints	0	0	15
Parameters	521	585	620
Goodness-of-fit on F^2	0.774	1.107	1.060
Final R indices [$I > 2\sigma(I)$]	0.0764	0.0684	0.0424
R indices (all data)	0.1838	0.1166	0.0813

Disorder treatment and CheckCIF Alerts explanations:

1

Considering the disorder and low electron density at maxima assigned to solvent atoms (dichloromethane) we have applied the SQUEEZE routine (PLATON). Significantly the essential structural information has remained unchanged. The appropriate statement has been added to the CIF file. Original empirical formula as well as formula weight, density and F(000) are included in Table S1 and CIF.

Comments to CheckCIF Alerts:

Alert level A
PLAT051_ALERT_1_A:
Mu(calc) and Mu(CIF) Ratio Differs from 1.0 by . 48.36 Perc.

Comment: This alert arise from the fact that the highly disordered solvent could not be satisfactorily modelled. As a result, the SQUEEZE routine within PLATON was employed to remove the contribution of the solvent to the diffraction pattern. The absence of solvent from the model results in a discrepancy between calculated Mu based on assigned atoms and the actual composition including the solvent molecules.

[**1**-H]$^+$

Considering the disorder assigned to TFAH molecule atoms we have decided to apply the SQUEEZE routine (PLATON). Significantly the essential structural information on main residue has remained unchanged. The appropriate statement has been added to the CIF file. Original empirical formula as well as formula weight, density and F(000) are included in Table S1 and CIF file.

2-Cl

Disordered chloride ligand was fixed to have the same palladium-chloride bond length in both positions.

One DCM molecule was split on two parts with occupations (0.83 and 0.17). First part was refines anisotropically, the second part was refined isotropically. Distance restraints (Cl-C-Cl' moiety) of C-Cl 1.7 Å and **Cl'••• Cl** 2.9 Å were applied to the atoms of the dichloromethane. Second disordered DCM molecule (occupation 0.15) was refined isotropically with the same restraints applied.

Disordered *n*-hexane molecule (occupation 0.4) was refined istotropically. To obtain the correct geometry of molecule restraints of 1.54 Å for 1-2 distances and 2.52 Å for 1-3 distances were applied for the carbon atoms in *n*-hexane molecule during refinement.

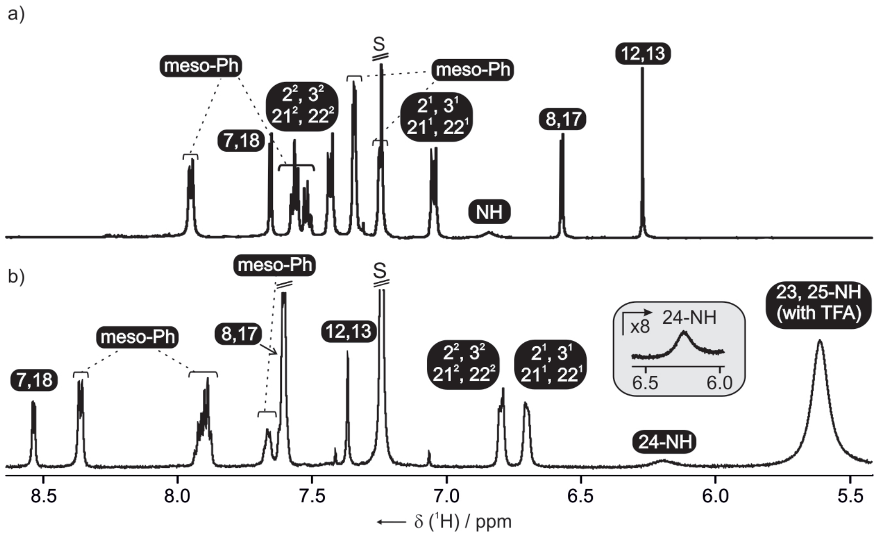

Figure S 1. ^{1}H NMR spectra of a) **1** (600 MHz, chloroform-*d*, 220 K) and b) [**1**-H_2]$^{2+}$ (600 MHz, chloroform-*d*, 300 K, 10 equiv. TFA).

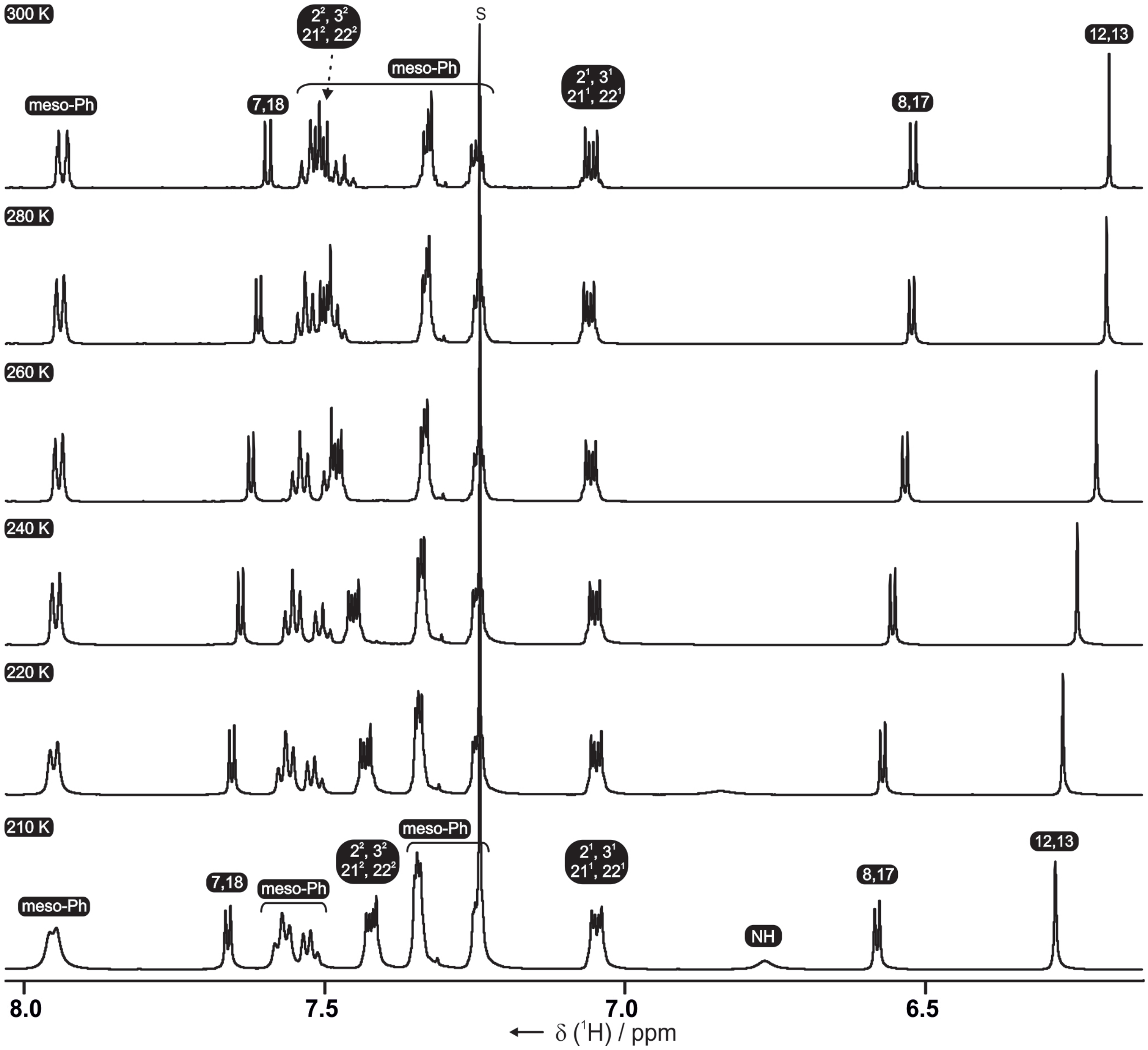

Figure S 2. ^{1}H NMR spectra of **1** recorded in 300 K – 210 K temperature range (600 MHz, chloroform-*d*).

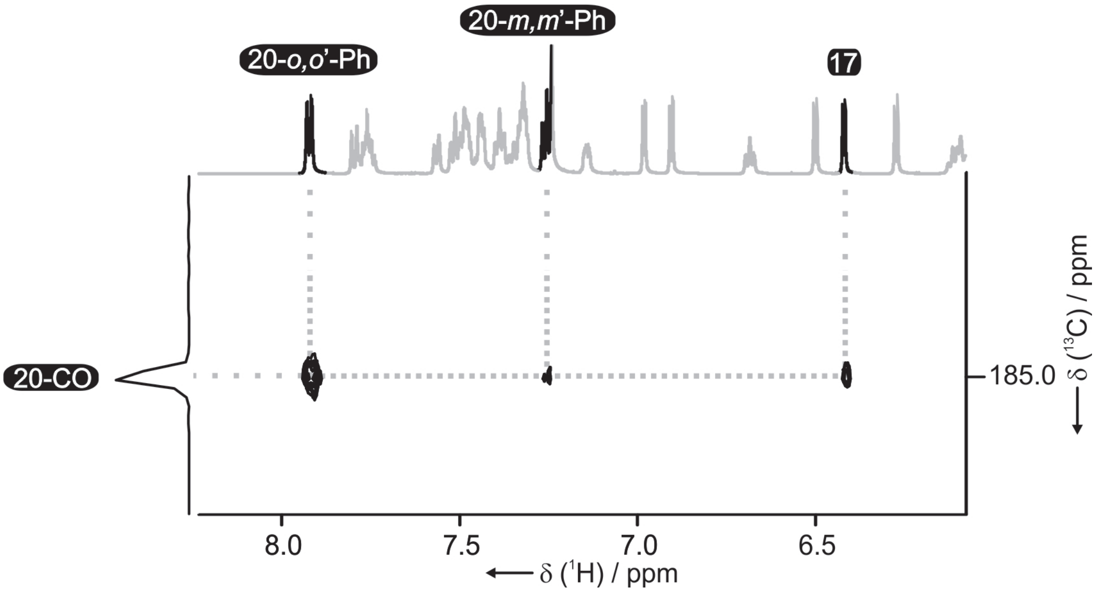

Figure S 3. Part of HMBC spectrum of **3**-Cl showing the 20-CO correlations (600 MHz, chloroform-*d*, 220 K).

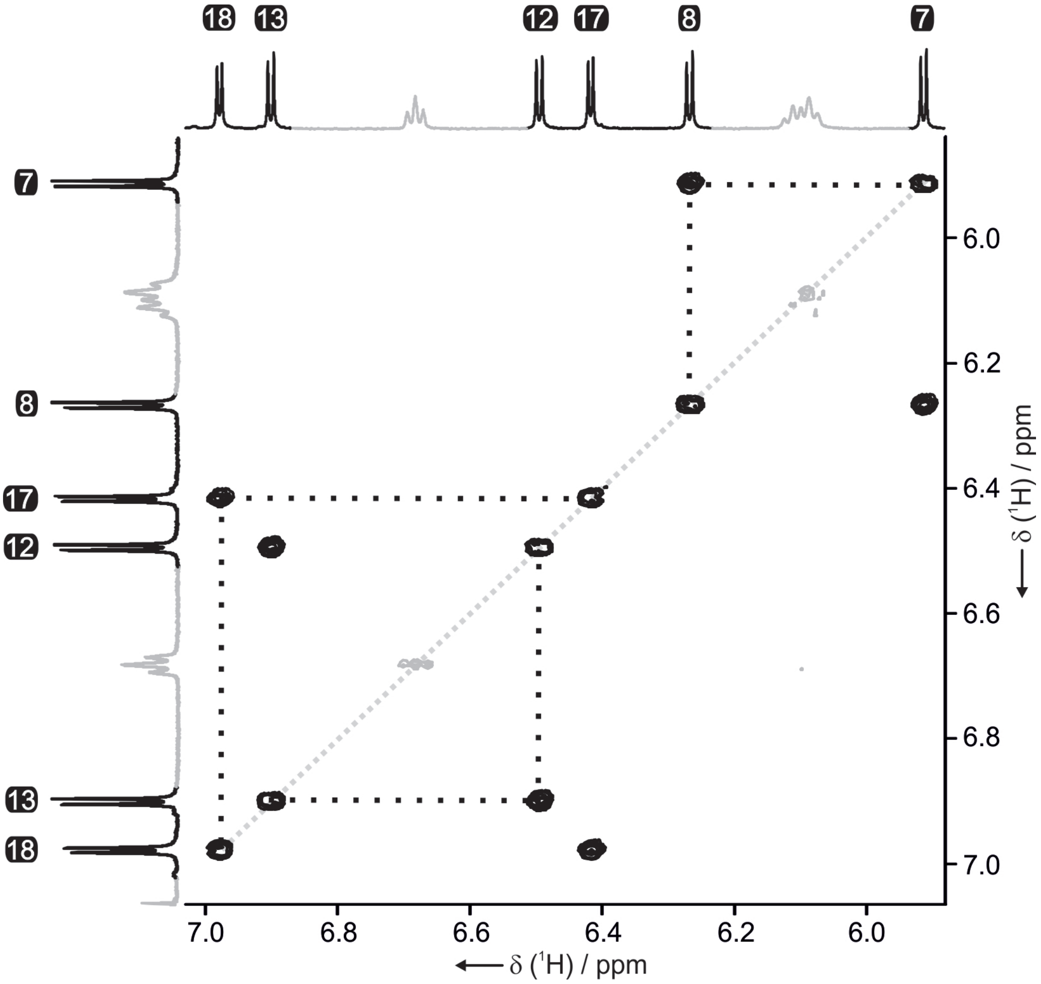

Figure S 4. Part of ^{1}H-^{1}H COSY spectrum of **3**-Cl showing the pyrrolic correlations (600 MHz, chloroform-*d*, 220 K).

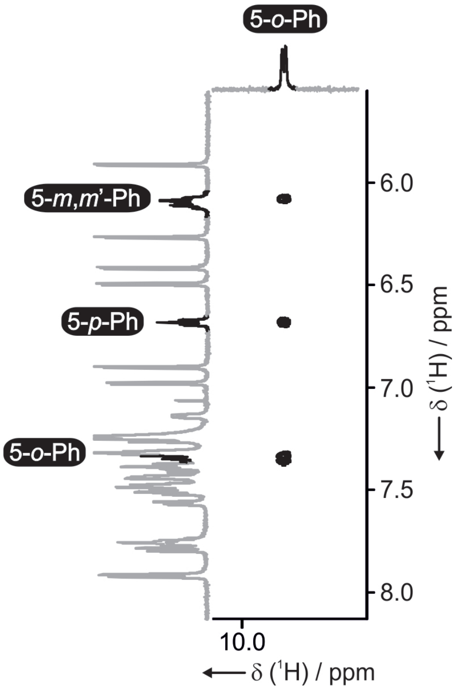

Figure S 5. Part of ^{1}H-^{1}H COSY spectrum of **3**-Cl showing the 5-*o*-Ph correlations (600 MHz, chloroform-*d*, 220 K).

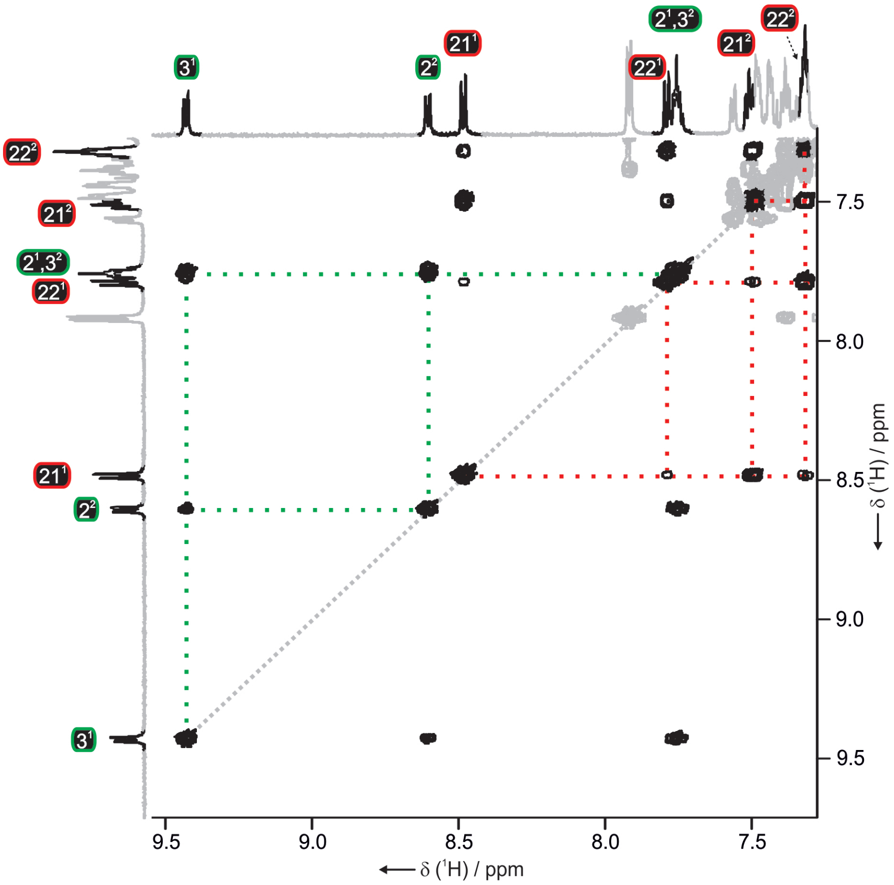

Figure S 6. Part of ^{1}H-^{1}H COSY spectrum of **3**-Cl showing the anthracenyl correlations (600 MHz, chloroform-*d*, 220 K).

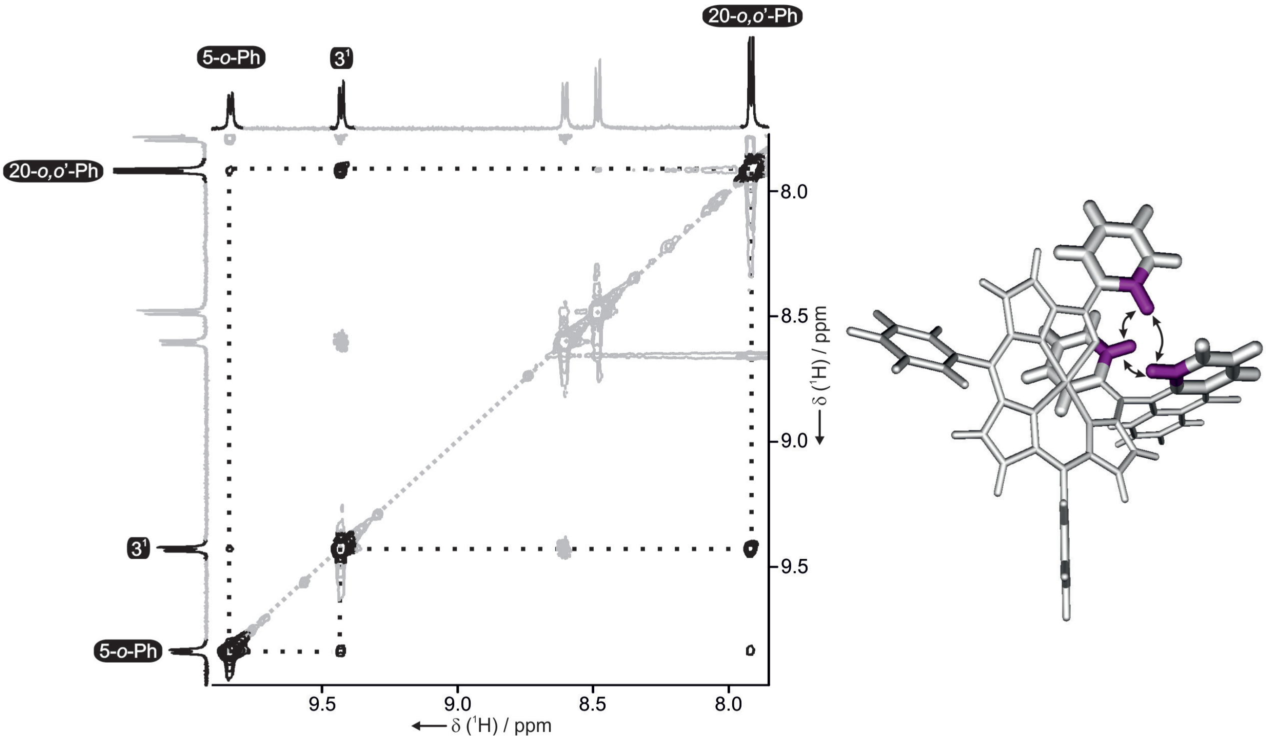

Figure S 7. Part of NOESY spectrum of **3**-Cl presenting the NOE cross peaks, which are relevant for specific 3^1 anthracenyl signal identification (600 MHz, chloroform-*d*, 220 K).

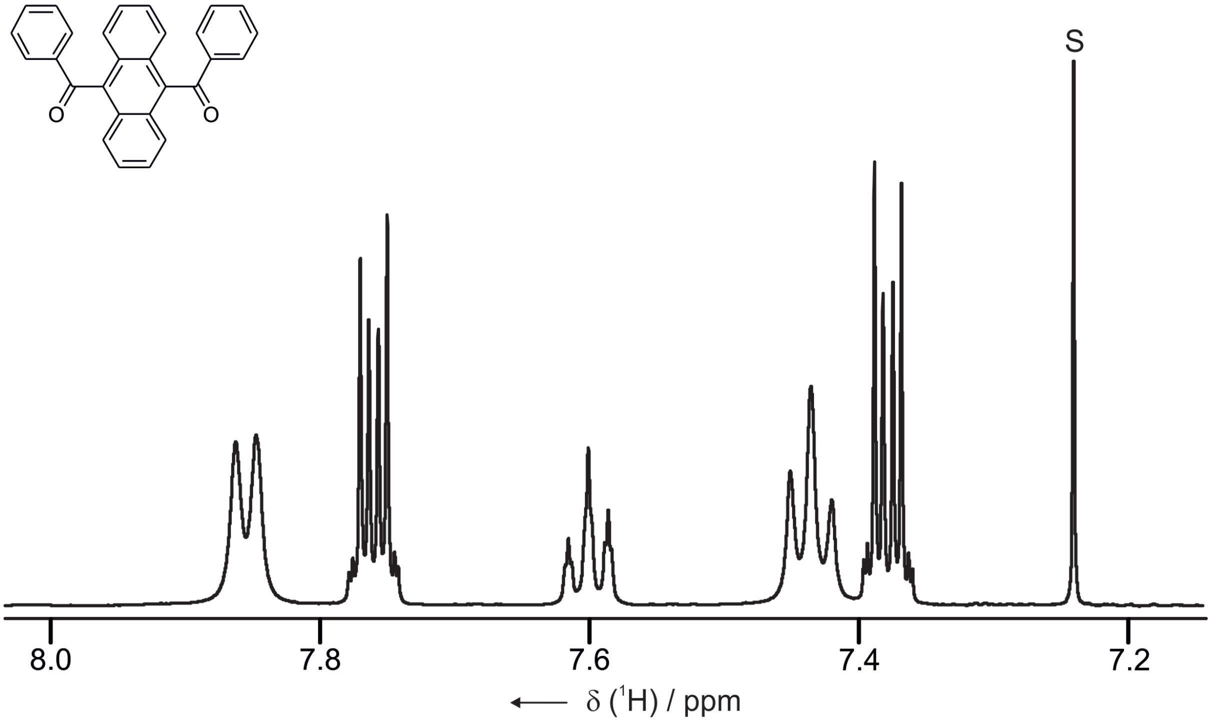

Figure S 8. ^{1}H NMR spectrum of **4** (500 MHz, chloroform-*d*, 298 K).

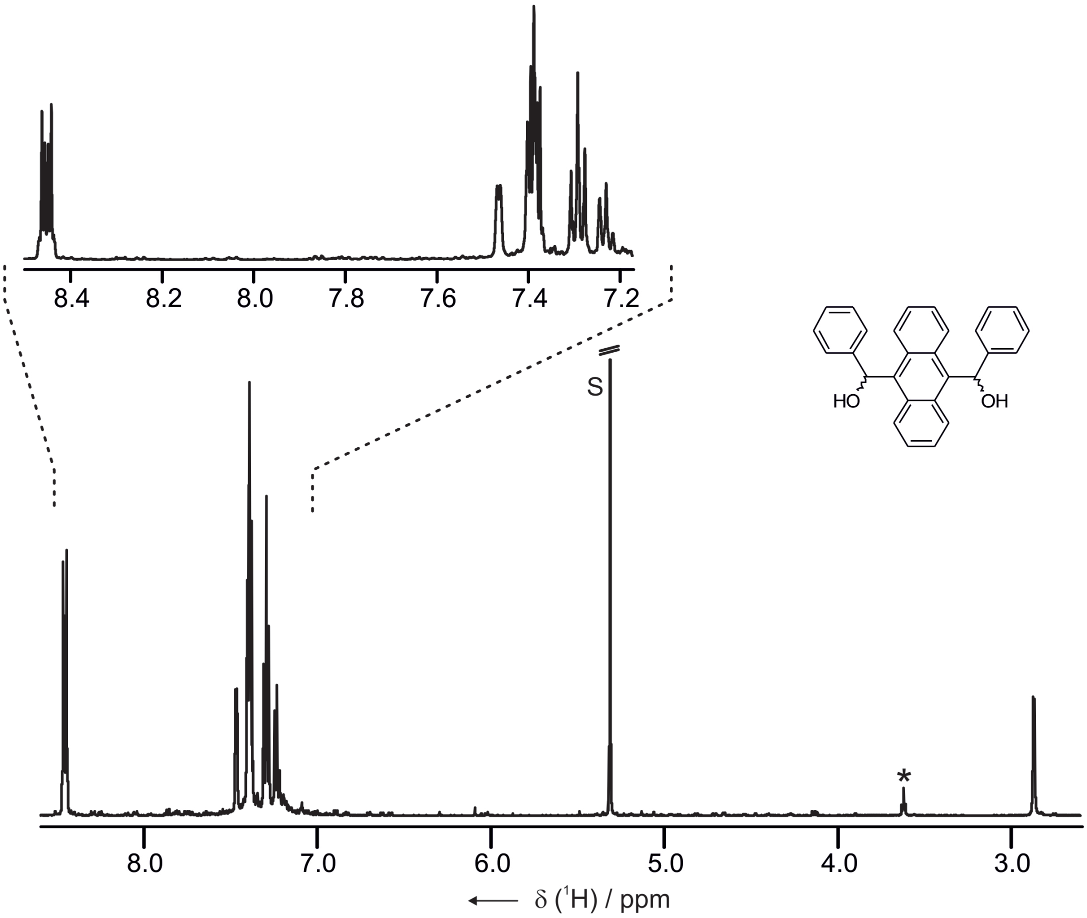

Figure S 9. ^{1}H NMR spectrum of **5** (500 MHz, dichloromethane-d_2, 298K).

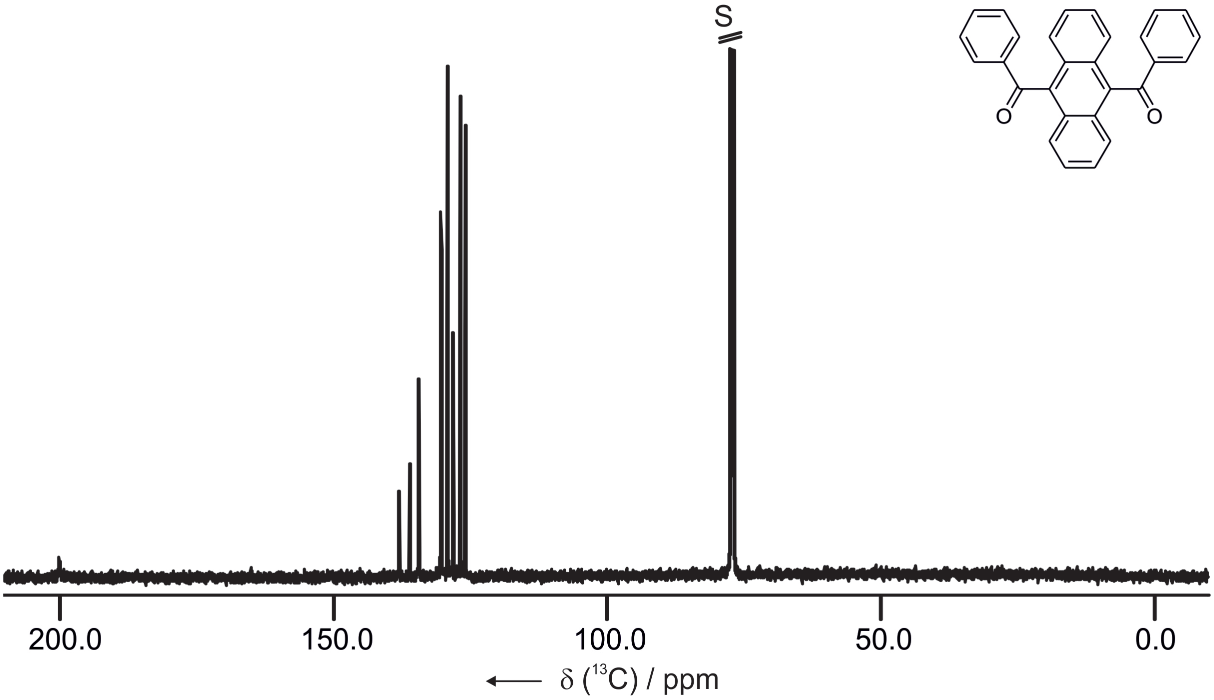

Figure S 10. ^{13}C NMR spectrum of **4** (126 MHz, chloroform-*d*, 298 K).

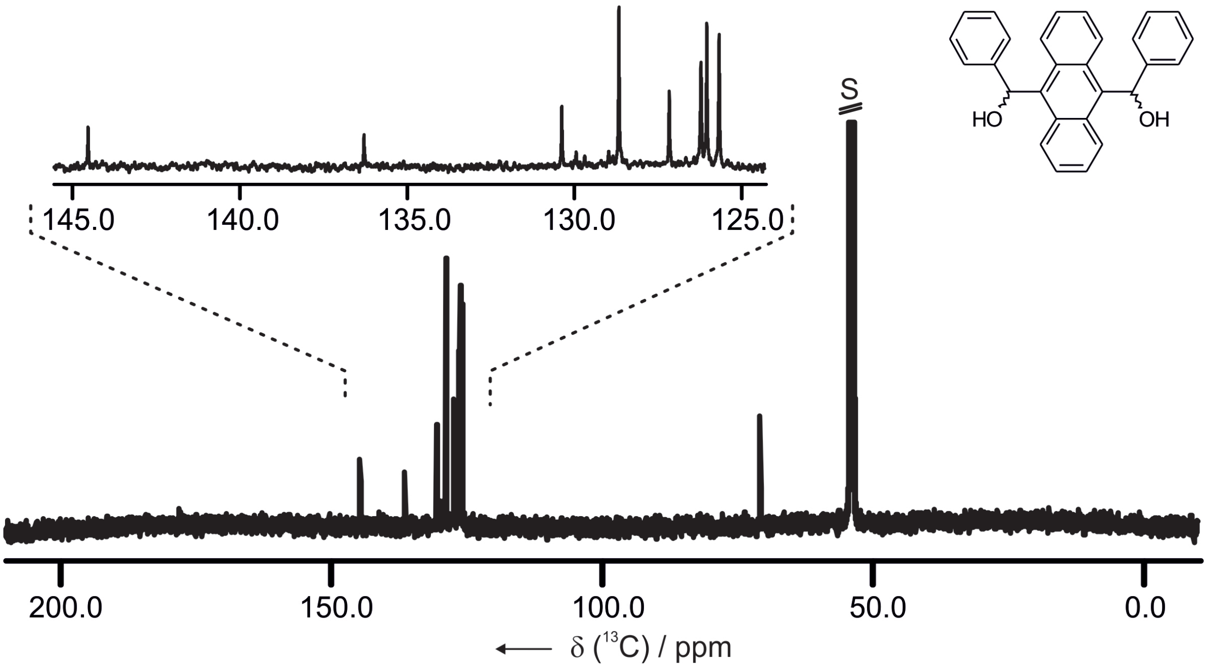

Figure S 11. ^{13}C NMR spectrum of **5** (126 MHz, dichloromethane-d_2, 298 K).

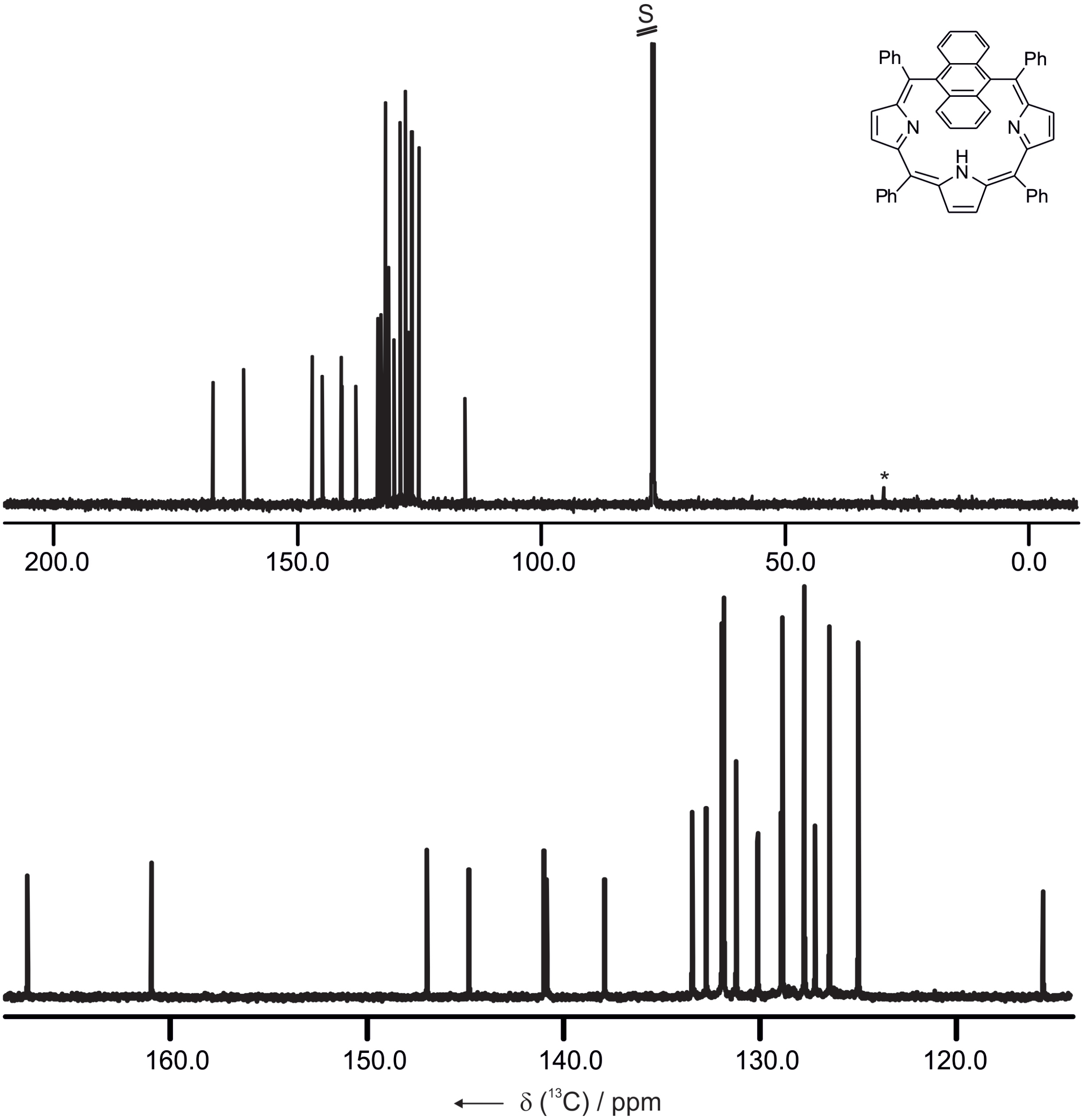

Figure S 12. ^{13}C NMR spectrum of **1** (151 MHz, chloroform-*d*, 298 K).

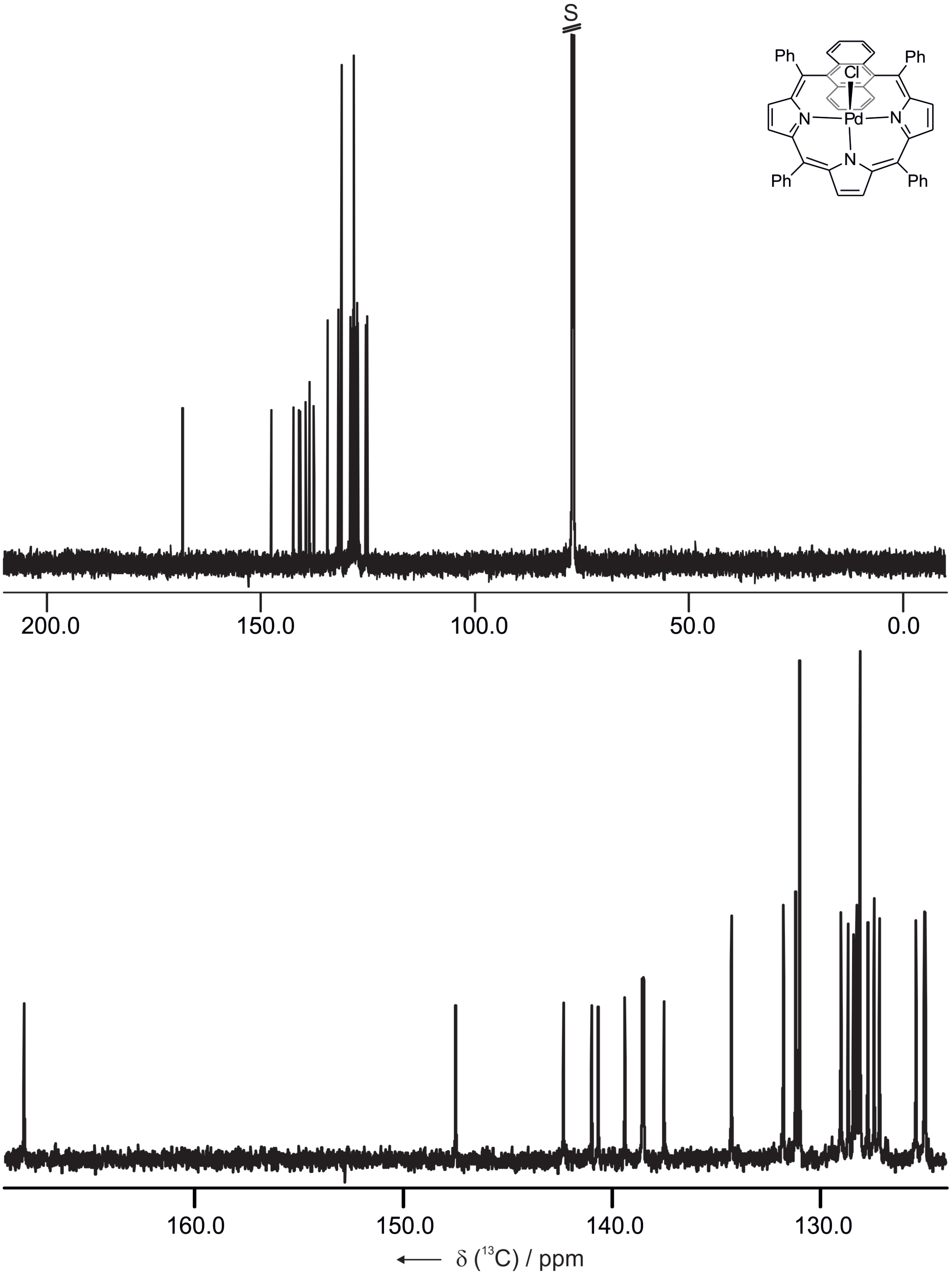

Figure S 13. ^{13}C NMR spectrum of **2**-Cl (151 MHz, chloroform-*d*, 298 K).

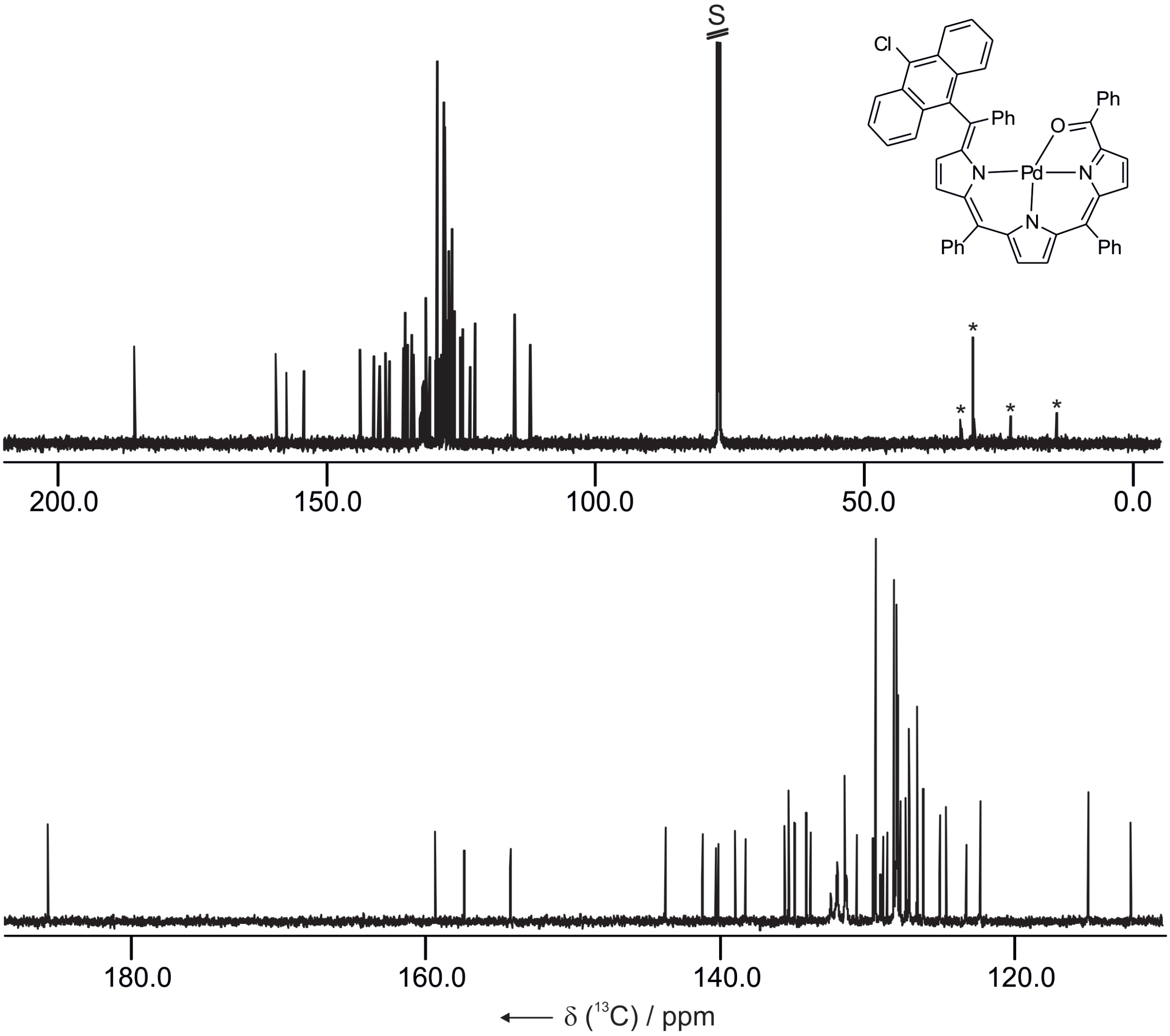

Figure S 14. ^{13}C NMR spectrum of **3**-Cl (151 MHz, chloroform-*d*, 298K).

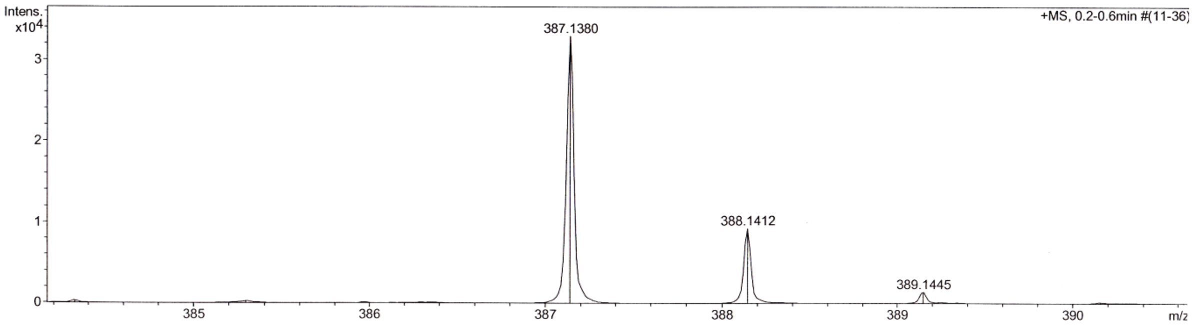

Figure S 15. HR-MS spectrum of **4** ([M+H]$^+$, ESI+, TOF).

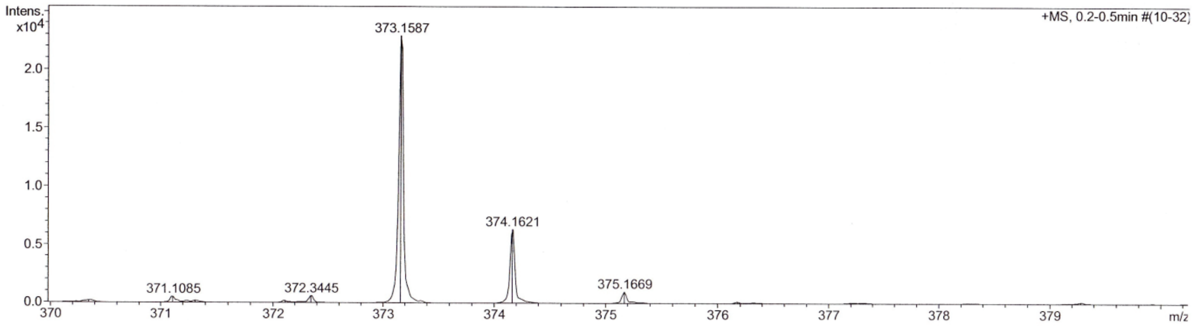

Figure S 16. HR-MS spectrum of **5** ([M-OH]$^+$, ESI+, TOF).

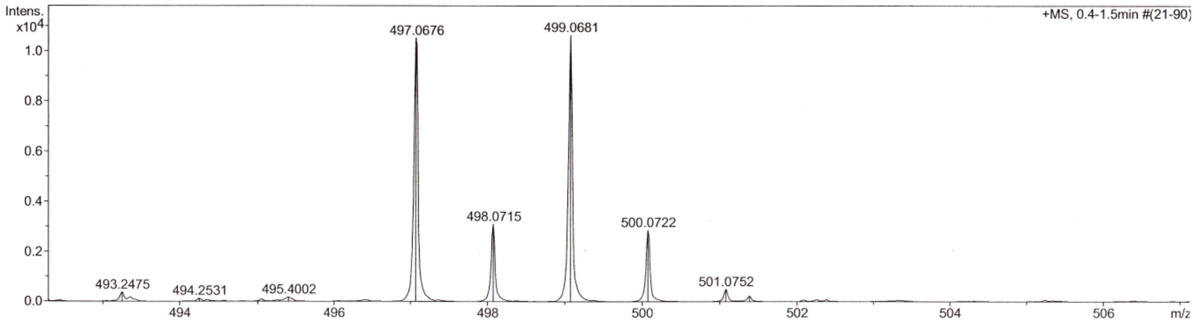

Figure S 17. HR-MS spectrum of **5** ([M+Ag]$^+$, ESI+, TOF).

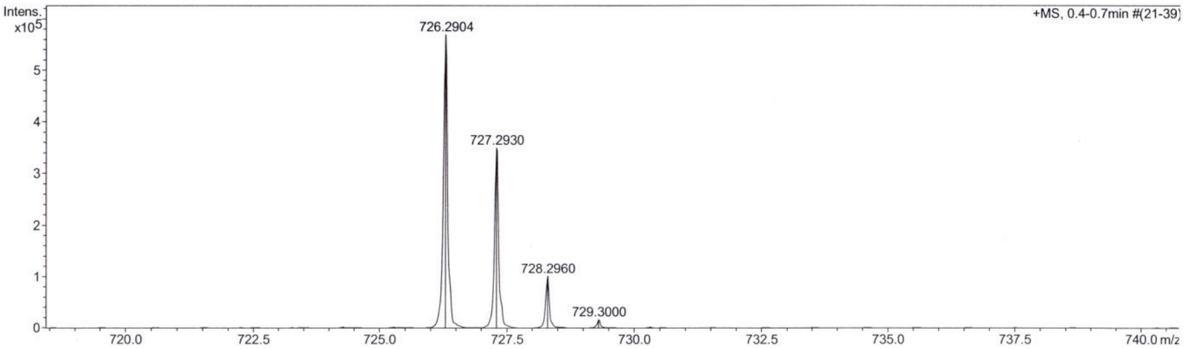

Figure S 18. HR-MS spectrum of **1** (ESI+, TOF).

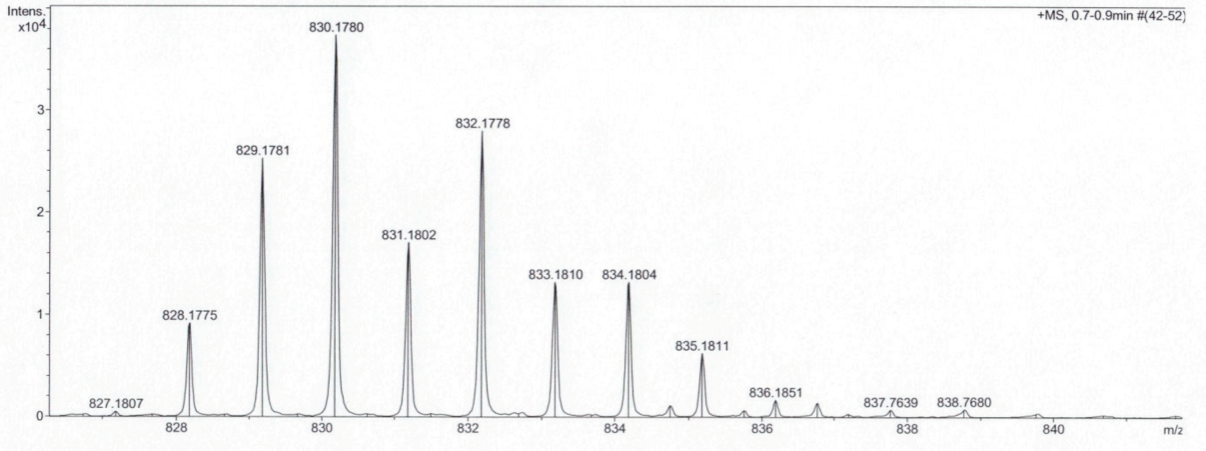

Figure S 19. HR-MS spectrum of **2**-Cl (ESI+, TOF).

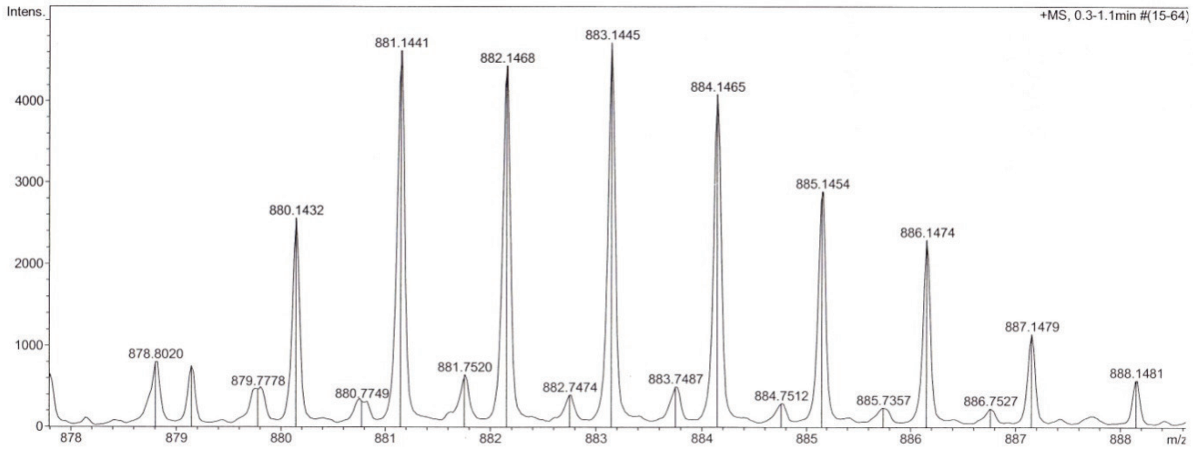

Figure S 20. HR-MS spectrum of **3**-Cl (ESI+, TOF).

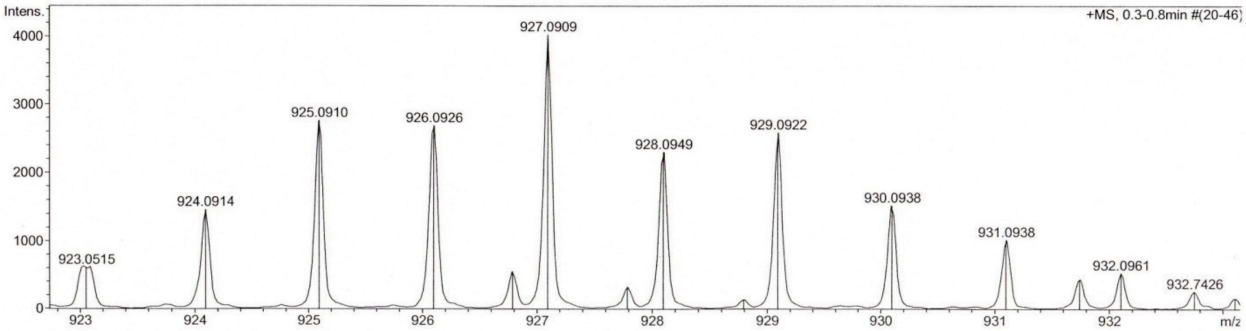

Figure S 21. HR-MS spectrum of **3**-Br (ESI+, TOF).

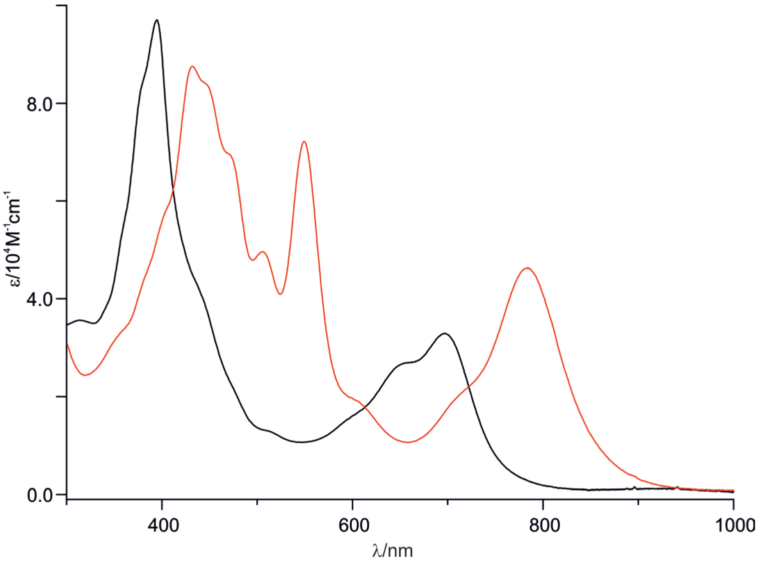

Figure S 22. The electronic absorption spectrum (dichloromethane, 298K) of **1** (black line) and [**1**-H_2]$^{2+}$ (red line).

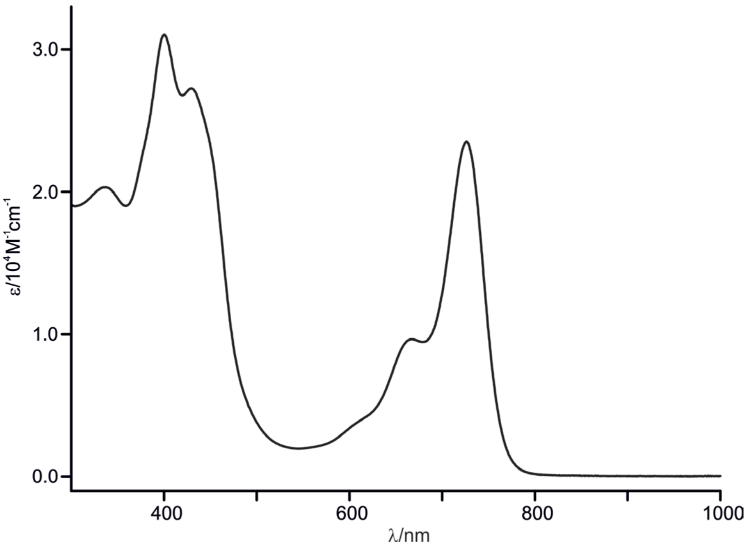

Figure S 23. The electronic absorption spectrum (dichloromethane, 298K) of **2**-Cl.

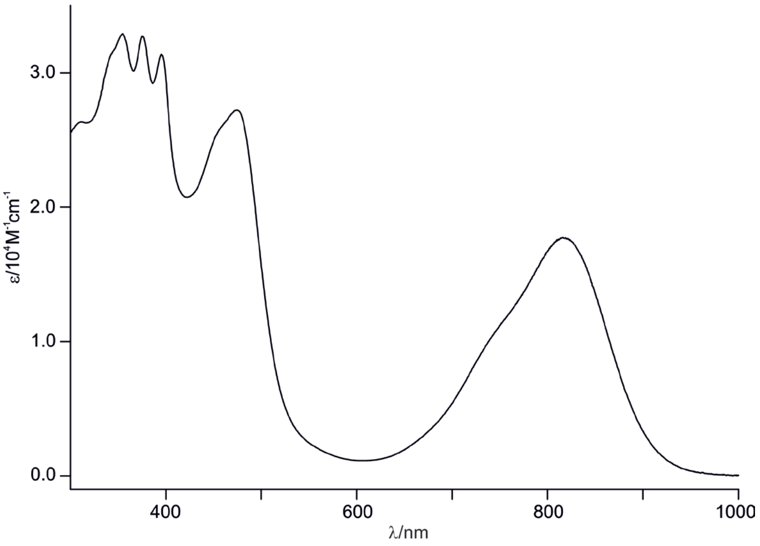

Figure S 24. The electronic absorption spectrum (dichloromethane, 298 K) of **3**-Cl.

Table S2. DFT calculated Cartesian coordinates for **3**-Cl

atom 1 - C - 0 -4.15679 -3.26541 -0.34663
atom 2 - C - 0 -2.9606 -3.93443 -0.53722
atom 3 - C - 0 -1.9211 -2.96519 -0.42004
atom 4 - N - 0 -2.50891 -1.74687 -0.1803
atom 5 - C - 0 -3.84926 -1.87956 -0.12209
atom 6 - C - 0 -4.71635 -0.7527 0.07431
atom 7 - C - 0 -4.25425 0.56202 0.12875
atom 8 - N - 0 -2.94205 1.00175 -0.02771
atom 9 - C - 0 -2.92663 2.36708 -0.04495
atom 10 - C - 0 -4.28464 2.83686 0.17449
atom 11 - C - 0 -5.08212 1.74481 0.29685
atom 12 - C - 0 -1.79925 3.18206 -0.27175
atom 13 - C - 0 -0.47086 2.69434 -0.2811
atom 14 - N - 0 -0.07785 1.44307 0.08435
atom 15 - C - 0 1.32542 1.40552 0.04483
atom 16 - C - 0 1.78807 2.6683 -0.51782
atom 17 - C - 0 0.70517 3.46885 -0.66356
atom 18 - C - 0 -0.50241 -2.9097 -0.53788
atom 19 - O - 0 0.06313 -1.75866 -0.4941
atom 20 - C - 0 0.35164 -4.10259 -0.73427
atom 21 - C- 0 -0.01445 -5.36224 -0.22976
atom 22 - C - 0 0.81596 -6.46547 -0.41909
atom 23 - C - 0 2.02023 -6.32696 -1.11248
atom 24 - C - 0 2.39871 -5.07452 -1.60435
atom 25 - C - 0 1.57606 -3.96834 -1.4108
atom 26 - C - 0 2.16082 0.46756 0.61991
atom 27 - C - 0 1.76128 -0.51561 1.64677
atom 28 - C - 0 2.4726 -1.72302 1.78923
atom 29 - C - 0 2.14891 -2.63287 2.79211
atom 30 - C - 0 1.11881 -2.35192 3.69245
atom 31 - C - 0 0.41801 -1.1478 3.58029
atom 32 - C - 0 0.73253 -0.24035 2.5724
atom 33 - C - 0 3.6088 0.50801 0.23232
atom 34 - C - 0 4.58589 0.95464 1.15563
atom 35 - C - 0 5.98539 0.97733 0.78888
atom 36 - C - 0 6.3407 0.55635 -0.50526
atom 37 - C - 0 5.39767 0.11803 -1.44972
atom 38 - C - 0 4.00132 0.08814 -1.06247
atom 39 - C - 0 4.22784 1.43209 2.45711
atom 40 - C - 0 5.17269 1.87117 3.34572
atom 41 - C - 0 6.54805 1.86925 2.98821
atom 42 - C - 0 6.94016 1.43962 1.74868
atom 43 - C - 0 3.0513 -0.39799 -2.02139
atom 44 - C - 0 3.43796 -0.7915 -3.27523
atom 45 - C - 0 4.8064 -0.73426 -3.65801
atom 46 - C - 0 5.7543 -0.29999 -2.77162
atom 47 - Cl- 0 8.04626 0.58674 -0.96415
atom 48 - C - 0 -2.02285 4.64118 -0.5019
atom 49 - C - 0 -1.44515 5.60466 0.34359
atom 50 - C - 0 -1.65517 6.96688 0.12875
atom 51 - C - 0 -2.45305 7.39577 -0.93394
atom 52 - C - 0 -3.03707 6.45163 -1.78064
atom 53 - C - 0 -2.82221 5.08954 -1.56788
atom 54 - C - 0 -6.17783 -1.02726 0.18187
atom 55 - C - 0 -7.09407 -0.47517 -0.72945
atom 56 - C - 0 -8.45848 -0.748 -0.62538
atom 57 - C - 0 -8.93308 -1.58146 0.38865
atom 58 - C - 0 -8.03275 -2.14362 1.29647
atom 59 - C - 0 -6.66883 -1.87263 1.19229
atom 60 - Pd - 0 -1.32893 -0.17977 -0.10104
atom 61 - H - 0 -5.15071 -3.68655 -0.38734
atom 62 - H - 0 -2.83811 -4.9842 -0.76145
atom 63 - H - 0 -4.57114 3.87549 0.24581
atom 64 - H - 0 -6.14508 1.72663 0.48673
atom 65 - H - 0 2.82522 2.92752 -0.67511
atom 66 - H - 0 0.68498 4.49569 -0.99714
atom 67 - H - 0 -0.92898 -5.46677 0.34277
atom 68 - H - 0 0.52718 -7.43182 -0.016
atom 69 - H - 0 2.66514 -7.18841 -1.26075
atom 70 - H - 0 3.338 -4.95928 -2.13741
atom 71 - H - 0 1.86949 -2.99283 -1.7807
atom 72 - H - 0 3.27189 -1.95318 1.09296
atom 73 - H - 0 2.70349 -3.5635 2.87106
atom 74 - H - 0 0.87102 -3.05831 4.47956
atom 75 - H - 0 -0.37252 -0.90942 4.28632
atom 76 - H - 0 0.19329 0.69703 2.50396
atom 77 - H - 0 3.18121 1.44057 2.73477
atom 78 - H - 0 4.87112 2.22553 4.32697
atom 79 - H - 0 7.29082 2.21719 3.70006
atom 80 - H - 0 7.9879 1.44964 1.47543
atom 81 - H - 0 2.00935 -0.46153 -1.7328
atom 82 - H - 0 2.69512 -1.15031 -3.98179
atom 83 - H - 0 5.10061 -1.04303 -4.65687
atom 84 - H - 0 6.79692 -0.26613 -3.06185
atom 85 - H - 0 -0.83622 5.27608 1.18081
atom 86 - H - 0 -1.20213 7.69334 0.7977
atom 87 - H - 0 -2.61829 8.45636 -1.10049
atom 88 - H - 0 -3.65479 6.77515 -2.61385
atom 89 - H - 0 -3.26711 4.35928 -2.23744
atom 90 - H - 0 -6.72645 0.15802 -1.53109
atom 91 - H - 0 -9.14936 -0.3149 -1.34328
atom 92 - H - 0 -9.99513 -1.79444 0.46919
atom 93 - H - 0 -8.39305 -2.79118 2.09092
atom 94 - H - 0 -5.97297 -2.30636 1.90416

Table S3. Experimental and DFT calculated ^{1}H NMR chemical shifts (ppm) of **3**-Cl for pyrrolic, anthracenyl and 5,20-meso-Ph protons.

Atom	δ exp	δ calc
2^1	7.75	8.81
2^2	8.60	7.83
3^1	9.43	10.01
3^2	7.75	8.02
21^1	8.48	8.67
21^2	7.50	7.57
22^1	7.79	8.09
22^2	7.30	7.32
7-H	5.91	5.84
8-H	6.27	6.33
12-H	6.49	6.50
13-H	6.90	6.92
17-H	6.42	6.26
18-H	6.98	6.85
5-*o*-Ph	7.32	6.21
5-*o*-Ph'	9.83	10.09
5-*m*-Ph	6.11	7.49
5-*m*-Ph'	6.09	6.36
5-*p*-Ph	6.68	6.92
20-*o*-Ph	7.92	7.74
20-*o*-Ph'	7.92	8.57
20-*m*-Ph	7.24	7.29
20-*m*-Ph	7.24	7.13
20-*p*-Ph	7.38	7.32

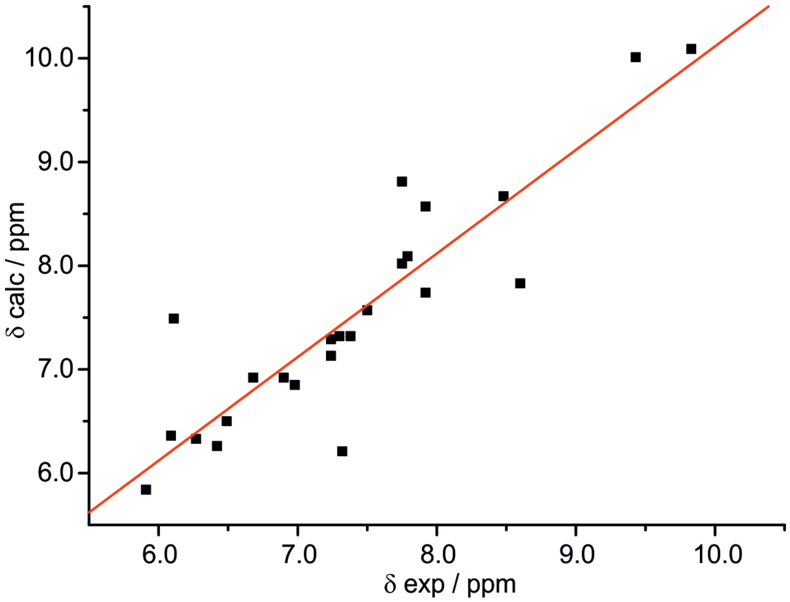

Figure S 25. Correlation between calculated and experimental chemical shifts of **3**-Cl.

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