

Electronic Supplementary Information

β -Tetrachlorotetramethoxyporphycenes: positional effect of substituents on structure and photophysical properties

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Instrumentation and reagents:

NMR spectra were recorded on Bruker Avance-400 MHz and 500 MHz FT NMR spectrometer and for ^1H NMR tetramethylsilane (TMS, $\delta = 0$ ppm) in CDCl_3 used as an internal standard at room temperature. For other deuterated solvents residual solvent peak were is used as reference in ^1H NMR and for ^{13}C NMR solvent peak was used as reference. LCMS were carried out by Shimadzu-LCMS-2010 mass spectrometer. Elemental analyses were obtained through Thermo Finnigan Flash EA 1112 analyzer. Mass spectral determinations were carried out by Bruker Maxis HRMS by ESI techniques. Melting points were determined by a Lab India MR-VIS⁺ visual melting point apparatus and uncorrected. IR spectra were recorded on NICOLET 5700 FT-IR spectrometer. All UV-VIS spectra were recorded using Perkin Elmer Lambda-750 UV-VIS spectrometer. All fluorescence spectra were recorded in Fluorolog-3-221 spectrofluorometer equipped with Hamamatsu H10330-75 TE cooled NIR detector working at -60 °C.

Fluorescence lifetime measurements were carried out using a time correlated single-photon counting (TCSPC) spectrometer (Horiba Jobin Yvon IBH). PicoBrite diode laser source (λ_{exc} 375 nm) was used as the excitation source and an MCP photomultiplier (Hamamatsu R3809U-50) as the detector. The pulse repetition rate of the laser source was 10 MHz. The width of the instrument response function, which was limited by the fwhm of the exciting pulse, was around 55 ps. The lamp profile was recorded by placing a scatterer (dilute solution of Ludox in water) in place of the sample. The time resolved emission decay profiles were collected at steady state emission spectrum maxima's 630 nm and 680 nm. Decay curves were analyzed by nonlinear least-squares iteration procedure using IBH DAS6 (Version 2.2) decay analysis software. The quality of the fit was assessed by inspection of the χ^2 values and the distribution of the residuals.

The steady-state luminescence of singlet oxygen of porphycene **1a**, **1b** and their M(II) complex was measured by using a Fluorolog-3-221 spectrofluorometer equipped with Hamamatsu H10330-75 TE cooled NIR detector working at -60 °C. Tetraphenylporphyrin (**H₂TPP**) was taken as standard (ϕ_{Δ} 0.7). All samples exhibit the emission bands ranging from 1240 to 1320 nm with the peak at about 1278 nm. The singlet oxygen quantum yields ϕ_{Δ} for all samples can be determined by using eq 1 (comparative actinometry method):^{S1}

$$\phi_{\Delta} = \phi_{\Delta}^{std} \frac{I}{I_{std}} \frac{1 - 10^{-A^{std}}}{1 - 10^{-A}} \quad (1)$$

where ϕ_{Δ}^{std} (0.7) is the singlet oxygen quantum yield of **H₂TPP** as the standard sample in aerated toluene, I and I_{std} refer to the singlet oxygen emission intensities at the peaks for the tested sample and **H₂TPP**, respectively, and A and A^{std} stand for the ground-state absorbance of the tested sample and

H₂TPP at the excited wavelength. Each sample is recorded for three times under identical condition and average value was taken to determine peak intensity.

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were done using Zahner Zennium Electrochemical Workstation and electrodes were purchased from CH Instruments Inc. All measurements were done in dichloromethane under flow of nitrogen and 0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF₆) used as a supporting electrolyte. Platinum disc as working electrode, platinum wire as counter electrode and Ag/AgCl in 1(M) KCl as reference electrode were used. Ferrocenium/Ferrocene, Fc⁺/Fc couple was used as external reference for calibration. The redox potentials were referenced vs. SCE. All cyclic voltammetric data were recorded at 50 mV/s scan rate.

Crystallographic data for **1a**, **1b**, **Zn1a.Py** and **Zn1b.Py** were collected on Oxford Gemini A Ultra diffractometer with dual source. Mo-K α ($\lambda = 0.71073 \text{ \AA}$) and Cu-K α ($\lambda = 1.54184 \text{ \AA}$) radiations were used for **Zn1a.Py** and **1a**, **1b**, **Zn1b.Py** respectively to collect the X-ray reflections of the crystal. Data reduction was performed using CrysAlisPro 171.33.55 software.^{S2} Structures were solved and refined using Olex2-1.0 with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on N were located from the Fourier map in all of the crystal structures. All C–H atoms were fixed geometrically. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. A check of the final CIF file using PLATON^{S3} did not show any missed symmetry.

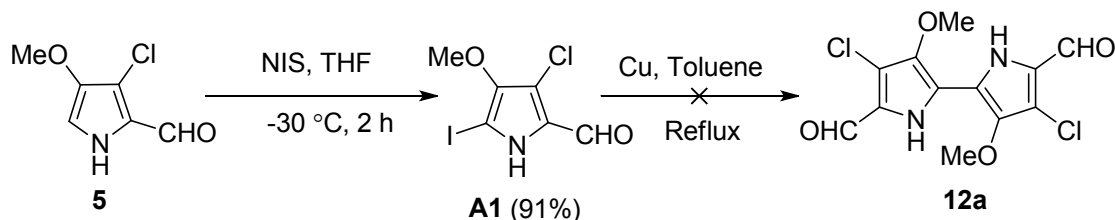
Crystallographic data for **6**, **8** and **12a** were collected on BRUKER SMART-APEX CCD diffractometer. Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation was used to collect X-ray reflections on the single crystal. Data reduction was performed using Bruker SAINT^{S4} software. Intensities for absorption were corrected using SADABS^{S5} and refined using SHELXL-97^{S6} with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on O and N were experimentally located in difference electron density maps. All C–H atoms were fixed geometrically using HFIX command in SHELX-TL. A check of the final CIF file using PLATON^{S3} did not show any missed symmetry.

Compound **6**, **8** and **12a** were crystallized by slow evaporation of chloroform solution. The compound **1a** and **1b** crystallized by the slow evaporation of chloroform solution. The compound **Zn1a.Py** was crystallized by the slow evaporation of the solution of **Zn1a** in toluene in presence of pyridine. Similarly, compound **Zn1b.Py** was crystallized by the slow evaporation of the solution of **Zn1b** in benzene in presence of pyridine. Crystallographic data (excluding the structure factor) for structures **6**, **8**, **12a**, **1a**, **1b**, **Zn1a** and **Zn1b** in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1062094-1062100. Copies of these data can be obtained free of

charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk) or via www.ccdc.cam.ac.uk/data_request/cif.

All DFT calculations were done in Gaussian09 software by using B3LYP method 6-31+G basis set.^{S7}

Reaction Scheme:



Scheme S1: Ullmann coupling protocol towards the synthesis of bipyrrole dialdehyde **12a**.

Detailed reaction procedure:

Synthesis of 3-chloro-5-iodo-4-methoxypyrrole-2-aldehyde (**A1**):

3-Chloro-4-methoxypyrrole-2-aldehyde (**5**) (3 g, 18.8 mmol) was taken in THF (75 mL) under nitrogen atmosphere. Then, N-iodosuccinimide (4.44 g, 19.7 mmol) was added at -30 °C and reaction mixture was allowed to run at that temperature for 2 h. After completion of reaction, reaction mixture was quenched by addition of sodium bicarbonate solution, organic layer was separated and aqueous layer was extracted with diethyl ether. The combined organic layer was washed with aqueous sodium thiosulphate followed by brine solution and passed through anhydrous Na₂SO₄ and evaporated to dryness under reduced pressure. Crude product was purified by silica gel column using EtOAc/hexane (1:9) as eluent to obtain **A1** (4.89 g) as crystalline white solid. Yield: 91%; m.p: 115 °C; IR (KBr): ν (cm⁻¹) 3189, 1647; ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 9.78 (br s, 1H), 9.39 (s, 1H), 3.90 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 175.96, 147.53, 129.96, 114.73, 70.99, 62.37; HRMS (ESI⁺): m/z: Calcd for C₆H₆ClINO₂ (M+H⁺): 285.9126; found: 285.9130.

Synthesis of 3-chloro-4-methoxypyrrole-2-nitrile (**7**):

3-Chloro-4-methoxypyrrole-2-aldehyde (**5**) (3 g, 18.81 mmol) and triethylamine (7.9 mL, 56.40 mmol) were taken in dry DCE (150 mL) under nitrogen. Hydroxylamine hydrochloride (1.57 g, 22.57 mmol) was added to the reaction mixture and stirred at 60 °C for 2 h. Then, phthalic anhydride (5.57 g, 37.62 mmol) was added in small portion wise and allow the reaction to stirred at reflux condition for 24 h. After reaction is over, allow the reaction mixture to reach to room temperature and washed twice with saturated

aqueous NaHCO₃ to remove phthalic acid. Aqueous layer was extracted three times with DCM (~150 ml × 3), combined organic layer was passed through anhydrous Na₂SO₄ and evaporated under reduced pressure to dryness. Crude product was washed with DCM, filtered, washed with DCM until filtrate became colorless, leaving entitled product **7** as white crystalline solid. Additional amount of compound obtained by purifying filtrate by silica gel column chromatography using EtOAc/hexane (3:7) as eluent gives entitled compound (2.46 g, combined yield). Yield: 84%. m.p: 209.8 °C; IR (neat): ν (cm⁻¹) 3299, 3122, 2217; ¹H NMR (400 MHz, DMSO-d₆), δ (ppm): 12.27 (br s, 1H), 7.00 (s, 1H), 3.71 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆), δ (ppm): 143.67, 112.64, 108.47, 108.00, 96.57, 58.48; HRMS (ESI+): m/z: calculated for C₆H₆N₂OCl (M+H⁺): 157.0163; found: 157.0177; Elemental analysis Calcd for C₅H₅N₂OCl: C, 46.03; H, 3.22; N, 17.89. Found: C, 46.12; H, 3.28; N, 17.81.

Synthesis of 3-chloro-5-formyl-4-methoxypyrrole-2-nitrile (8):

3-Chloro-4-methoxypyrrole-2-nitrile (**7**) (2 g, 12.77 mmol) was taken in DCE (140 mL) and DMF (9 mL) under nitrogen and reaction mixture was allowed to reflux to dissolve **7** completely. Under reflux condition POCl₃ (3.6 mL, 38.31 mmol) was added drop wise and stirred under reflux condition for 1 h. Then reaction mixture was cooled on ice bath and NaOAc (15.71 g, 0.19 mole) in 100 mL water added carefully and refluxed the reaction mixture for additional 2 h. After cooling the reaction mixture to room temperature organic layer was separated and water layer was extracted with DCM for three times. Combined organic layer was washed with aqueous NaHCO₃ solution. Then, organic layer was passed through anhydrous Na₂SO₄ and evaporated to dryness. Crude reaction mixture was purified by silica gel column chromatography using EtOAc/Hexane (2:8) as eluent to obtain compound **8** (1.73 g) as white crystalline solid. Yield: 73%. m.p: 138.6 °C; IR (neat): ν (cm⁻¹) 3221, 2232, 1628; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 10.62 (br s, 1H), 9.75 (s, 1H), 4.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 177.81, 150.03, 123.37, 112.85, 110.52, 106.35, 62.33; HRMS (ESI+): m/z: calculated for C₇H₆N₂O₂Cl (M+H⁺): 185.0112; found: 185.0109; Elemental analysis Calcd for C₇H₅N₂O₂Cl: C, 45.55; H, 2.73; N, 15.18. Found: C, 45.63; H, 2.71; N, 15.07.

Synthesis of 4-chloro-5-formyl-3-methoxypyrrole-2-carboxylic acid (9):

3-Chloro-5-formyl-4-methoxypyrrole-2-nitrile (**8**) (2 g, 10.84 mmol) and NaOH (4.33 g, 0.108 mole) were taken in H₂O (60 mL) and refluxed the reaction mixture for 48 h. After completion of hydrolysis, reaction mixture was placed on an ice bath and acidified with conc. HCl to pH 1 resulted precipitation of compound as white solid. Precipitate was filtered, washed with ice water and dried under vacuum leaving entitled compound **9.4H₂O** (2.47 g) as white powdery solid. Yield: 83%. m.p: 226.2 °C (dec); IR (neat): ν (cm⁻¹) 2948, 1718, 1688, 1643, 1614; ¹H NMR (400 MHz, DMSO-d₆), δ (ppm): 13.56 (br, s, 1H), 12.76

(br s, 1H), 9.69 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6), δ (ppm): 179.26, 160.07, 148.01, 122.28, 121.82, 108.03, 62.23; HRMS (ESI+): m/z: calculated for $\text{C}_7\text{H}_7\text{NO}_4\text{Cl}$ ($\text{M}+\text{H}^+$): 204.0058; found: 204.0067; Elemental analysis Calcd for $\text{C}_7\text{H}_6\text{NO}_4\text{Cl}\cdot 4\text{H}_2\text{O}$: C, 30.50; H, 5.12; N, 5.08. Found: C, 30.68; H, 5.03; N, 5.16.

Synthesis of 4-chloro-5-iodo-3-methoxypyrrole-2-aldehyde (**10**):

Sodium bicarbonate (835 mg, 9.94 mmol) in water (15 mL) was added to 4-chloro-5-formyl-3-methoxypyrrole-2-carboxylic acid (**9**) (830 mg, 3.01 mmol) at room temperature under nitrogen. After **9** were completely dissolved DCE (40 mL) was added to the reaction mixture and temperature raised to 80 °C. Then, iodine (802 mg, 3.16 mmol) and KI (1.05 g, 6.32 mmol) in water (40 mL) was added drop wise over 30 min and allowed to stir for additional 1 h at same temperature. The reaction mixture was cooled to room temperature and excess sodium thiosulphate was added in small portion to remove excess iodine and stirred for 10 min. The reaction mixture was taken in a separatory funnel and organic layer was collected. Organic layer was passed through anhydrous Na_2SO_4 and evaporated to dryness under reduce pressure. Crude reaction mixture was purified by silica gel column chromatography using EtOAc/hexane (2:8) as eluent gives entitled **10** (750 mg) as white crystalline solid. Yield: 87%. m.p: 128.6 °C; IR (neat): ν (cm^{-1}) 3381, 3221, 1616; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 9.87 (br s, 1H), 9.42 (s, 1H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 175.19, 151.07, 125.28, 111.89, 81.00, 62.29; HRMS (ESI+): m/z: calculated for $\text{C}_6\text{H}_5\text{NO}_2\text{ClNa}$ ($\text{M}+\text{Na}^+$): 307.8946; found: 307.8944; Elemental analysis Calcd for $\text{C}_6\text{H}_5\text{NO}_2\text{Cl}$: C, 25.24; H, 1.77; N, 4.91. Found: C, 25.36; H, 1.71; N, 4.98.

Synthesis of 4-chloro-3-methoxypyrrole-2-aldehyde (**6**):

Activated Zinc (1.20 g), 4-chloro-5-iodo-3-methoxypyrrole-2-aldehyde (**10**) (1.75g, 6.13 mmol) and 5%Pd/C (490 mg) were taken in acetone/water (140/140 mL) under nitrogen and reaction mixture was allowed to stir vigorously at room temperature for 18 h. The reaction mixture was quenched with DCM (~150 mL), organic layer was separated and aqueous layer washed with DCM (~50 mL) for three times. Combined organic layer was passed through celite and washed with DCM for three times. Organic layer was passed through anhydrous Na_2SO_4 and evaporated to dryness under reduce pressure. Crude reaction mixture was purified by silica gel column chromatography using EtOAc/hexane (3:7) as eluent gives entitled **6** (879 mg) as white crystalline solid. Yield: 90%. m.p: 133.4 °C; IR (neat): ν (cm^{-1}) 3077, 1621; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 9.62 (s, 1H), 9.39 (br s, 1H), 6.95 (d, 1H, $J = 3.6$ Hz), 4.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 176.63, 151.69, 123.54, 120.83, 104.46, 62.25; HRMS (ESI+): m/z: calculated for $\text{C}_6\text{H}_5\text{NO}_2\text{Cl}$ ($\text{M}+\text{H}^+$): 160.0160; found: 160.0160; Elemental analysis Calcd for $\text{C}_6\text{H}_6\text{NO}_2\text{Cl}$: C, 45.16; H, 3.79; N, 8.78. Found: C, 45.23; H, 3.84; N, 8.65.

General procedure for synthesis of ethyl 3-(3,4-disubstituted-pyrrol-2-yl)-2-cyanoacrylate (11):

3-Chloro-4-methoxypyrrole-2-aldehyde (**5**) (2 g, 25.06 mmol) was taken in toluene (60 mL) under nitrogen. Subsequently, ethyl-2-cyanoacetate (2.9 mL, 27.57 mmol) and triethylamine (3.5 mL, 25.06 mmol) were added and allowed the reaction mixture to stir at reflux condition for 4 h. The reaction mixture was allowed to come to room temperature and kept at -20 °C for 2 h result the precipitation of compound as yellow fibrous solid. The reaction mixture was filtered and washed with cold hexane leaves entitled **11a** (3 g) as yellow fibrous solid.

Ethyl 3-(3-chloro-4-methoxypyrrol-2-yl)-2-cyanoacrylate (11a):

Yield: 94%. m.p: 181.1 °C; IR (neat): ν (cm⁻¹) 3391, 2215, 1694; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.47 (br s, 1H), 8.07 (s, 1H), 6.81 (d, 1H, J = 3.6 Hz), 4.35 (d, 2H, J = 7.2 Hz), 3.85 (s, 3H), 1.38 (t, 3H, J = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 162.97, 146.52, 138.40, 121.39, 118.60, 113.19, 110.84, 93.22, 62.40, 58.90, 14.36; HRMS (ESI+): m/z : calculated for C₁₁H₁₂N₂O₃Cl (M+H⁺): 277.0350; found: 277.0354; Elemental analysis Calcd for C₁₁H₁₁N₂O₃Cl: C, 51.88; H, 4.35; N, 11.00. Found: C, 51.76; H, 4.43; N, 10.85.

Ethyl 3-(4-chloro-3-methoxypyrrol-2-yl)-2-cyanoacrylate (11b):

4-Chloro-3-methoxypyrrole-2-carbaldehyde (**6**) (850 mg, 5.33 mmol) was taken for reaction. After reaction was over, it was allowed to come to room temperature and kept at -20 °C for 2 h result the precipitation of compound. The reaction mixture was filtered and washed with cold hexane leaves entitled **11b** as reddish yellow solid. Filtrate was evaporated under reduce pressure and washed with methanol resulted another crop of compound and finally methanol washed part was purified by silica gel column chromatography by using EtOAc/hexane (2:8) as eluent resulted **11b** as yellow crystalline solid. Combined yield: 1.32 g (97%); m.p: 154.2 °C; IR (neat): ν (cm⁻¹) 3358, 2215, 1693; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.46 (br s, 1H), 8.04 (s, 1H), 7.05 (d, 1H, J = 3.6 Hz), 4.33 (d, 2H, J = 6.8 Hz), 4.07 (s, 3H), 1.37 (t, 3H, J = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 163.46, 151.61, 137.71, 125.46, 119.05, 116.52, 105.37, 90.38, 62.16, 61.93, 14.41; HRMS (ESI+): m/z : calculated for C₁₁H₁₁N₂O₃ClNa (M+Na⁺): 277.0350; found: 277.0348; Elemental analysis Calcd for C₁₁H₁₁N₂O₃Cl: C, 51.88; H, 4.35; N, 11.00. Found: C, 51.76; H, 4.28; N, 11.07.

General procedure for synthesis of 3,3'-disubstituted-4,4'-disubstituted-[2,2'-bipyrrole]-5,5'-dialdehyde (12):

Ethyl 3-(3-chloro-4-methoxypyrrol-2-yl)-2-cyanoacrylate (**11a**) (500 mg, 1.96 mmol) and FeCl₃ (954 mg, 5.88 mmol) were taken in trifluoroacetic acid (TFA) (15mL) and stirred at room temperature for 24 h. The reaction mixture was evaporated under reduce pressure, residue was dissolved in acetone and passed through anhydrous K₂CO₃ following washing with acetone and chloroform until color of solution become colorless. Combined organic layer was evaporated under reduce pressure and subjected to silica gel column chromatography by using CHCl₃ as eluent. Thus orange fluorescent fraction was collected and evaporated leaves oxidative coupled product as purple crystalline solid. Compound was used directly for hydrolysis without further characterizations. Compound obtained in the previous step was subjected to hydrolysis with aqueous 3(M) NaOH (6 mL) under reflux condition for 3 h. The reaction mixture was placed on ice bath, diluted with water (~50 ml) and neutralized with conc. HCl resulted precipitation of compound as bright golden yellow fibrous solid. Precipitated compound was filtered, washed with water and subjected to silica gel column chromatography using EtOAc/hexane (2:8) as eluent gives **12a** (122 mg) as golden yellow fibrous solid.

4,4'-dichloro-3,3'-dimethoxy-[2,2'-bipyrrole]-5,5'-dialdehyde (12a):

Yield: 122 mg (39%). m.p: 233.4 °C; IR (neat): ν (cm⁻¹) 3277, 1655; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.64 (s, 2H), 9.51 (br s, 2H), 4.11 (s, 6H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 176.55, 141.49, 125.11, 117.72, 113.71, 61.68; UV-Vis data in CHCl₃, λ_{\max} nm (log ϵ): 397 (4.57); Fluorescence in CHCl₃, λ_{\max} nm : 450; Fluorescence quantum yield in CHCl₃ (ϕ_f): 0.77; HRMS (ESI+): m/z: calculated for C₁₂H₁₁N₂O₄Cl₂ (M+H⁺): 317.0090; found: 317.0098.

3,3'-dichloro-4,4'-dimethoxy-[2,2'-bipyrrole]-5,5'-dialdehyde (12b):

Ethyl 3-(4-chloro-3-methoxypyrrol-2-yl)-2-cyanoacrylate (**11b**) (500 mg, 1.96 mmol) was taken for reaction and 9b was purified by silica gel column chromatography using EtOAc/hexane (3:7) as eluent gives **12b** (48 mg) as light yellow solid. Yield: 15%. m.p: 259.3 °C; IR (neat): ν (cm⁻¹) 3193, 1655; ¹H NMR (400 MHz, DMSO-d₆), δ (ppm): 12.30 (br s, 2H), 9.68 (s, 2H), 4.04 (s, 6H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 176.97, 149.94, 123.14, 121.08, 103.75, 62.40; UV-Vis data in CHCl₃, λ_{\max} nm (log ϵ): 365 (4.56), 384 (4.57); Fluorescence in CHCl₃, λ_{\max} nm : 402, 422; Fluorescence quantum yield in CHCl₃ (ϕ_f): 0.08; HRMS (ESI+): m/z: calculated for C₁₂H₁₁N₂O₄Cl₂ (M+H⁺): 317.0090; found: 317.0063; Elemental analysis Calcd for C₁₂H₁₀N₂O₄Cl₂: C, 45.45; H, 3.18; N, 8.83. Found: C, 45.38; H, 3.26; N, 8.72.

Synthesis of 4,4'-dichloro-3,3'-dimethoxy-[2,2'-bipyrrole]-5,5'-dialdehyde (12a) by PIFA coupling:

To a stirred solution of Ethyl 3-(3-chloro-4-methoxypropyl)-2-cyanoacrylate (**11a**) (500 mg, 1.96 mmol) in CH₂Cl₂ (50 mL), PIFA (843 mg, 1.96 mmol) and BF₃·OEt₂ (484 μL, 3.92 mmol) were quickly added at -78 °C under nitrogen. The reaction mixture was then stirred for 4 h, while the reaction temperature was maintained below -40 °C. After the reaction completion, saturated aqueous NaHCO₃ (ca. 50 mL) was added to the mixture, and then stirred for an additional 10 minutes at ambient temperature. The organic layer was separated and the aqueous phase was extracted with CH₂Cl₂. The combined extract was dried with Na₂SO₄ and evaporated to dryness and the crude reaction mixture was purified by silica gel column using CHCl₃ as eluent. Thus orange fluorescent fraction was collected and evaporated leaves oxidative coupled product as purple crystalline solid. Deprotection of cyanoacrylate groups and purification were carried out as discussed above for **12a**. Yield: 105 mg (34%).

General procedure for synthesis of β-tetrachlorotetramethoxyphycenes:

To a slurry of low-valent titanium reagent, generated by reduction of titanium tetrachloride (1.73 mL, 15.75 mmol) in dry THF (100 mL) with activated zinc (2.06 g) and CuCl (481mg, 4.86 mmol) by refluxing 3 h, a solution of **12a** (200 mg, 0.63 mmol) in dry THF (100 mL) was added dropwise slowly over 3 h under reflux condition with vigorous stirring. The reaction mixture was heated under reflux for an additional 1 h and then hydrolyzed by slow addition of 10% aqueous sodium carbonate (ca. 100 mL) to the ice cooled reaction mixture. The reaction mixture was filtered through celite to remove the excess metal, washed with CHCl₃ until color of the filtrate become colorless and organic layer was separated. Organic layer was passed through anhydrous sodium sulphate and evaporated to dryness under reduce pressure. The crude reaction mixture was purified by silica gel column chromatography using CHCl₃ as eluent yields 51 mg compound **1a** as blue purple crystalline solid.

2,7,12,17-Tetrachloro-3,6,13,16-tetramethoxyphycene (1a):

Yield: 28%. m.p: >300 °C; ¹H NMR (500 MHz, CDCl₃), δ (ppm): 9.80 (s, 4H), 4.78 (s, 12H), 0.98 (br s, 2H); UV-Vis data in CHCl₃, λ_{max} nm (log ε): 376 (5.16), 384 (5.14), 565 (4.58), 608 (4.35), 647 (4.52); Fluorescence in CHCl₃, (λ_{exc} 382 nm) nm: 655, 717; Fluorescence quantum yield in CHCl₃ (φ_f): 0.00071; HRMS (ESI+): m/z: calculated for C₂₄H₁₉N₄O₄Cl₄ (M+H⁺): 567.0155; found: 567.0165.

3,6,13,16-Tetrachloro-2,7,12,17-tetramethoxyphycene (1b):

3,3'-dichloro-4,4'-dimethoxy-[2,2'-bipyrrole]-5,5'-dialdehyde (**12b**) (60 mg, 0.19 mmol) and THF (50 mL + 50 mL) were taken and **12b** in 50 mL THF was added drop wise over 3 h. Yield: 12 mg (22%). m.p: >300 °C; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.65 (s, 4H), 4.82 (s, 12H), 0.16 (br s, 2H); UV-Vis data in CHCl₃, λ_{max} nm (log ε): 385 (5.13), 572 (4.52), 625 (4.31), 664 (4.46); Fluorescence, (λ_{exc} 572 nm) nm: 676; Fluorescence quantum yield in CHCl₃ (Φ_f): 0.00075; HRMS (ESI+): m/z: calculated for C₂₄H₁₉N₄O₄Cl₄ (M+H⁺): 567.0155; found: 567.0160; Elemental analysis Calcd for C₂₄H₁₈N₄O₄Cl₄: C, 50.73; H, 3.19; N, 9.86. Found: C, 50.65; H, 3.26; N, 9.78.

General procedure for synthesis of Zn(II)-β-tetrachlorotetramethoxyporphycenes (Zn1):

2,7,12,17-Tetrachloro-3,6,13,16-tetramethoxyporphycene (**1a**) (10 mg, 0.018 mmol) and Zn(OAc)₂·2H₂O (77 mg, 0.35 mmol) were taken in 40 mL of CHCl₃/MeOH (1:1) under nitrogen. The reaction mixture was refluxed for 4 h and solvent was evaporated under reduce pressure. Residue was purified by activated neutral alumina column chromatography using CHCl₃/MeOH (49:1) as eluent gives **Zn1a** (4 mg) as blue purple solid.

Zn(II)-2,7,12,17-tetrachloro-3,6,13,16-tetramethoxyporphycene (Zn1a):

Yield: 35%. m.p: >300 °C; ¹H NMR (400 MHz, CDCl₃ in presence of small amount of CD₃OD), δ (ppm): 9.84 (s, 4H), 4.79 (s, 12H); UV-Vis data, λ_{max} nm (log ε): 391 (5.24), 588 (4.33), 638 (4.90); Fluorescence, (λ_{exc} 390 nm) nm: 645, 706; Fluorescence quantum yield in CHCl₃ (Φ_f): 0.17; HRMS (ESI+): m/z: calculated for C₂₄H₁₇N₄O₄Cl₄Zn (M+H⁺): 628.9290; found: 628.9299.

Zn(II)-3,6,13,16-tetrachloro-2,7,12,17-tetramethoxyporphycene (Zn1b):

5 mg of **1b** was taken for reaction. After reaction was over, solvent was evaporated under reduce pressure. Residue was dissolved in CHCl₃, washed with water and chloroform layer was passed through anhydrous Na₂SO₄. Solvent was evaporated under reduce pressure gives entitled **Zn1b** (5.2 mg) as purple solid. Yield: 93%. m.p: >300 °C; ¹H NMR (400 MHz, CDCl₃ in presence of small amount of CD₃OD), δ (ppm): 9.73 (s, 4H), 4.77 (s, 12H); UV-Vis data in CHCl₃, λ_{max} nm (log ε): 391(4.90), 604 (4.14), 638 (4.61); Fluorescence, (λ_{exc} 390 nm) nm: 654, 711; Fluorescence quantum yield in CHCl₃ (Φ_f): 0.16; HRMS (ESI+): m/z: calculated for C₂₄H₁₆N₄O₄Cl₄ZnNa (M+Na⁺): 650.9109; found: 650.9115; Elemental analysis Calcd for C₂₄H₁₆N₄O₄Cl₄Zn: C, 45.64; H, 2.55; N, 8.87. Found: C, 45.58; H, 2.61; N, 8.76.

General procedure for synthesis of Pd(II)-β-tetrachloro-β-tetramethoxyporphycenes (Pd1):

2,7,12,17-Tetrachloro-3,6,13,16-tetramethoxyphycene (**1a**) (10 mg, 0.018 mmol) and Pd(OAc)₂ (40 mg, 0.18 mmol) were taken in 40 mL AcOH/DCE (1:1) and stirred under reflux condition for 4 h. The solvent was evaporated under reduce pressure and residue was washed with diethylether to remove unreacted Pd(OAc)₂. Then, residue was dissolved in CHCl₃ under reflux condition, filtered and washed repeatedly with hot CHCl₃ until color of the filtrate became colorless. Combined solvent was evaporated under reduce pressure resulted the entitled compound **Pd1a** (10.1 mg) as purple solid.

Pd(II)-2,7,12,17-tetrachloro-3,6,13,16-tetramethoxyphycene (Pd1a):

Yield: 83%. m.p: >300 °C; UV-Vis data in CHCl₃, λ_{max} nm (log ε): 389(4.94), 561 (4.14), 606 (4.70); HRMS (ESI+): m/z: calculated for C₂₄H₁₆N₄O₄Cl₄PdNa (M+Na⁺): 692.8853; found: 692.8853.

Pd(II)-3,6,13,16-tetrachloro-2,7,12,17-tetramethoxyphycene (Pd1b):

4 mg of **1b** was used for reaction. Yield: 4.4 mg (93%). m.p: >300 °C; UV-Vis data in CHCl₃, λ_{max} nm (log ε): 391(4.93), 603 (4.64), 624 (4.55); HRMS (ESI+): m/z: calculated for C₂₄H₁₆N₄O₄Cl₄PdNa (M+Na⁺): 692.8853; found: 692.8787; Elemental analysis Calcd for C₂₄H₁₆N₄O₄Cl₄Pd: C, 42.85; H, 2.40; N, 8.33. Found: C, 42.68; H, 2.32; N, 8.41.

^1H and ^{13}C NMR spectra:

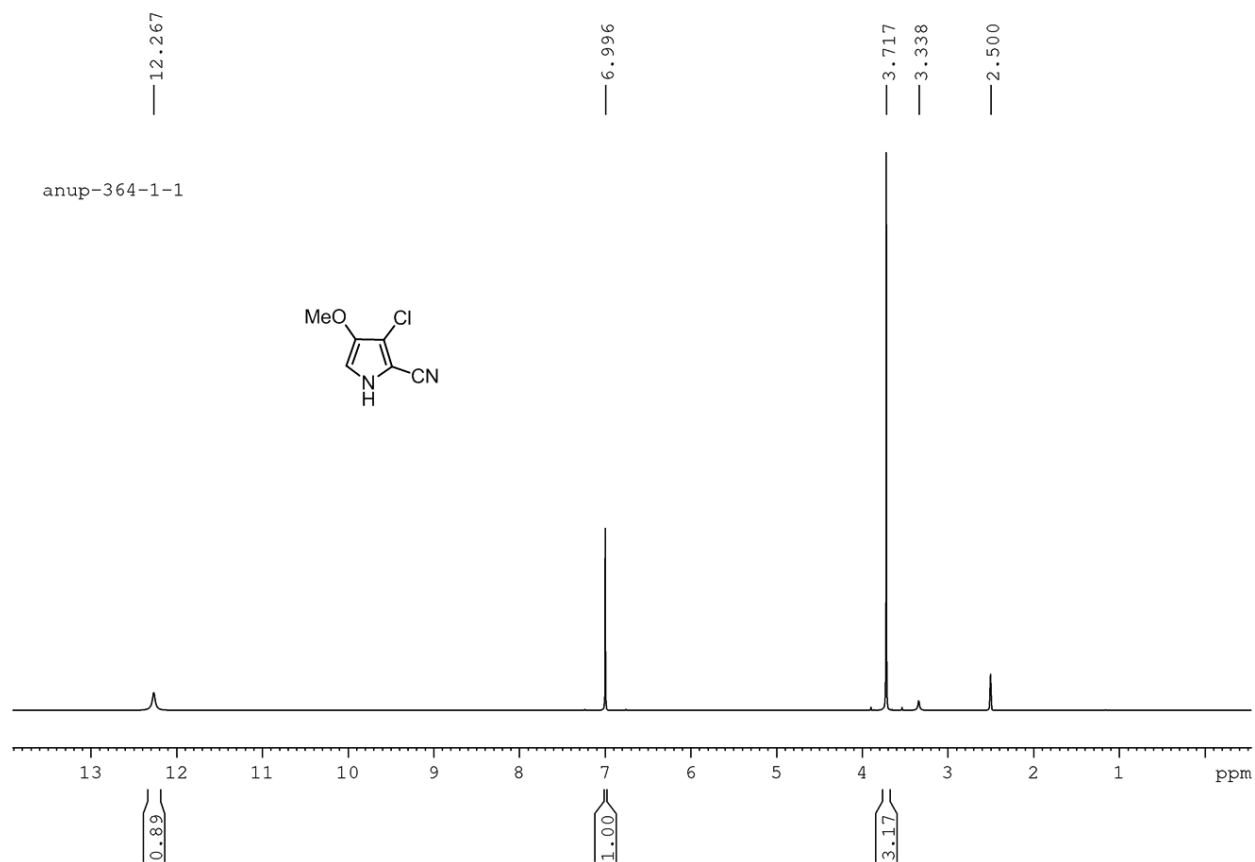


Figure S1: ^1H NMR spectrum of **7** in DMSO-d_6 .

anup-364-1-1 13C

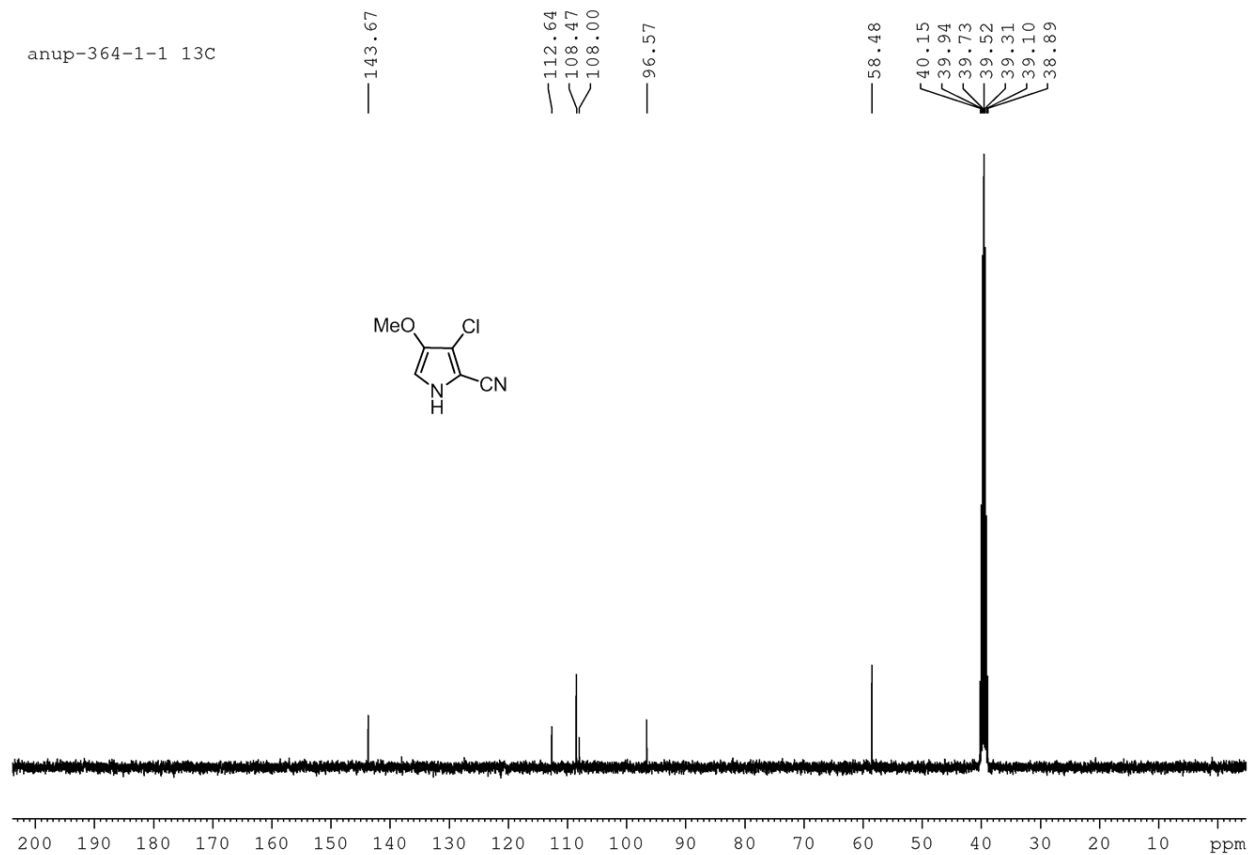


Figure S2: ¹³C NMR spectrum of 7 in DMSO-d₆.

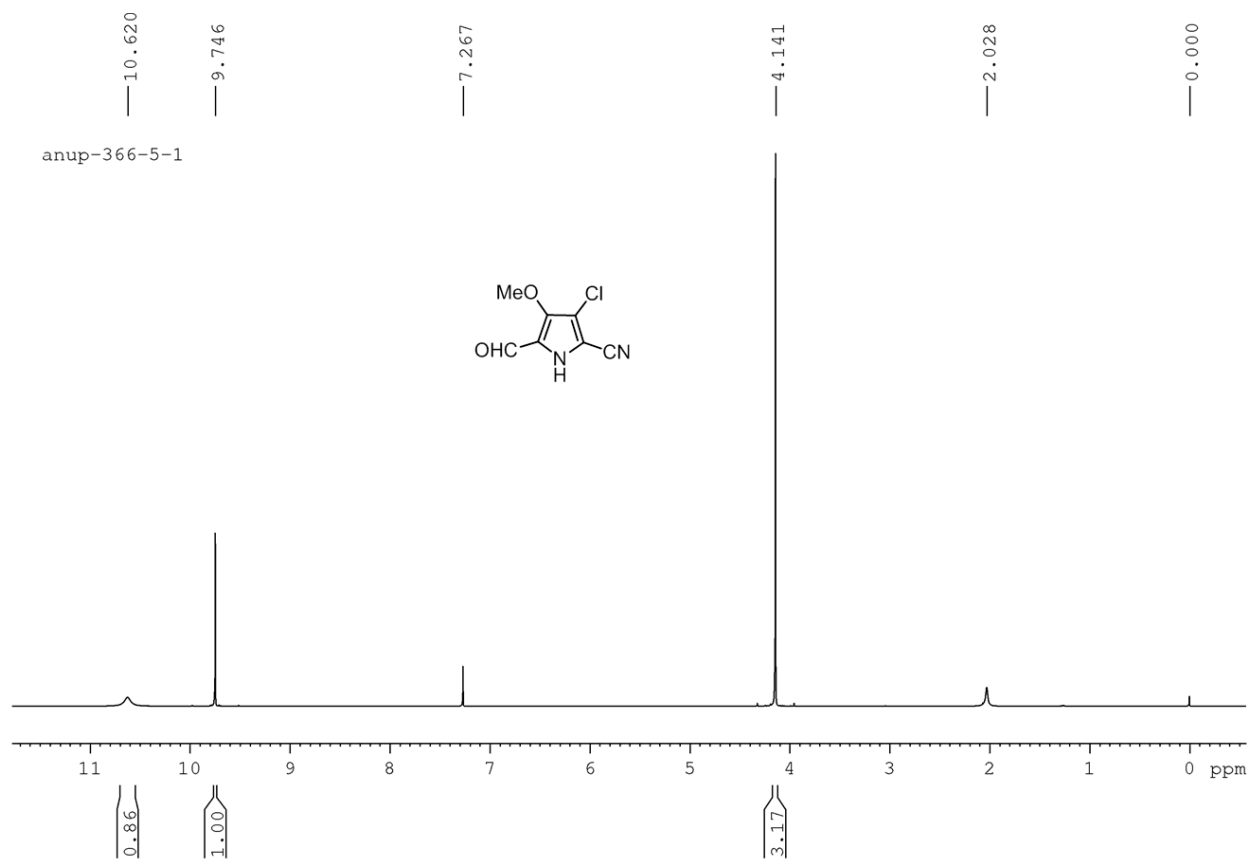


Figure S3: ^1H NMR spectrum of **8** in CDCl_3 .

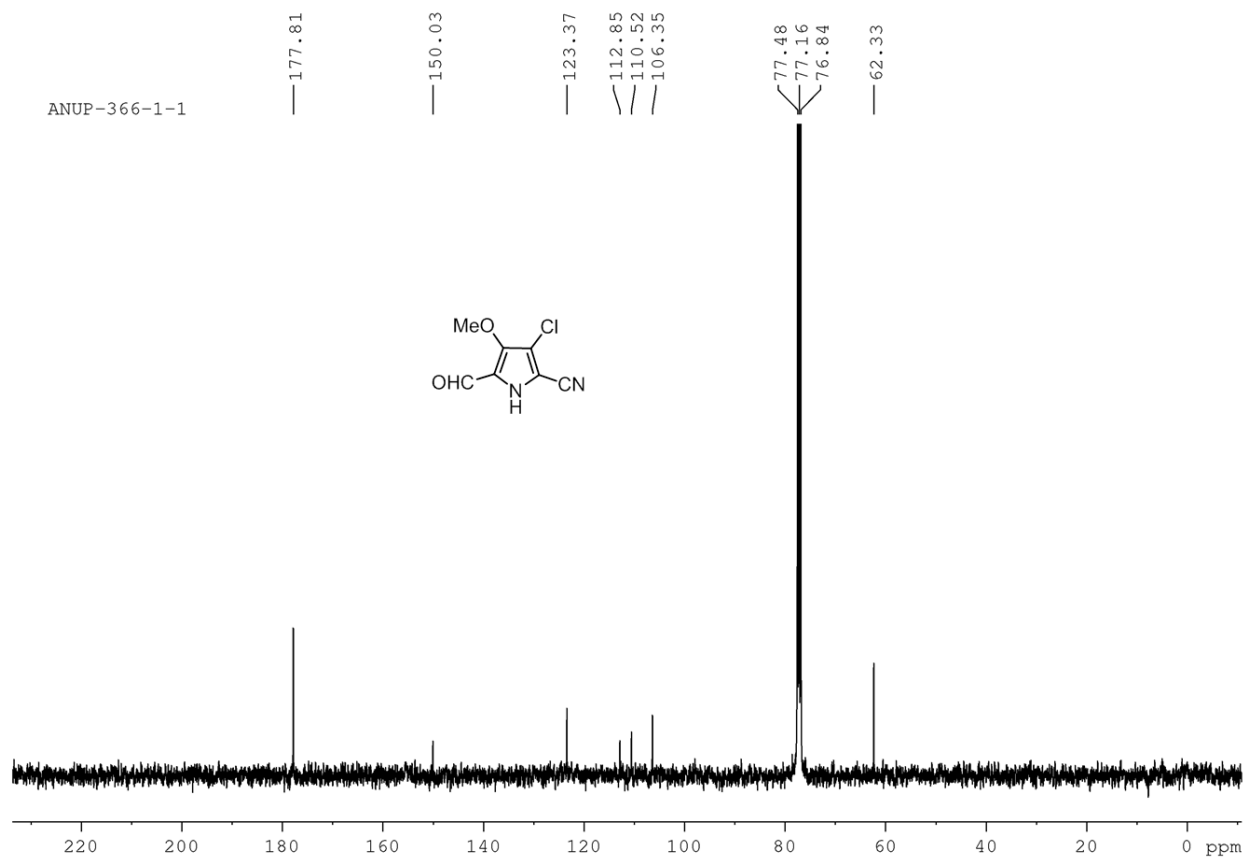


Figure S4: ^{13}C NMR spectrum of **8** in CDCl_3 .

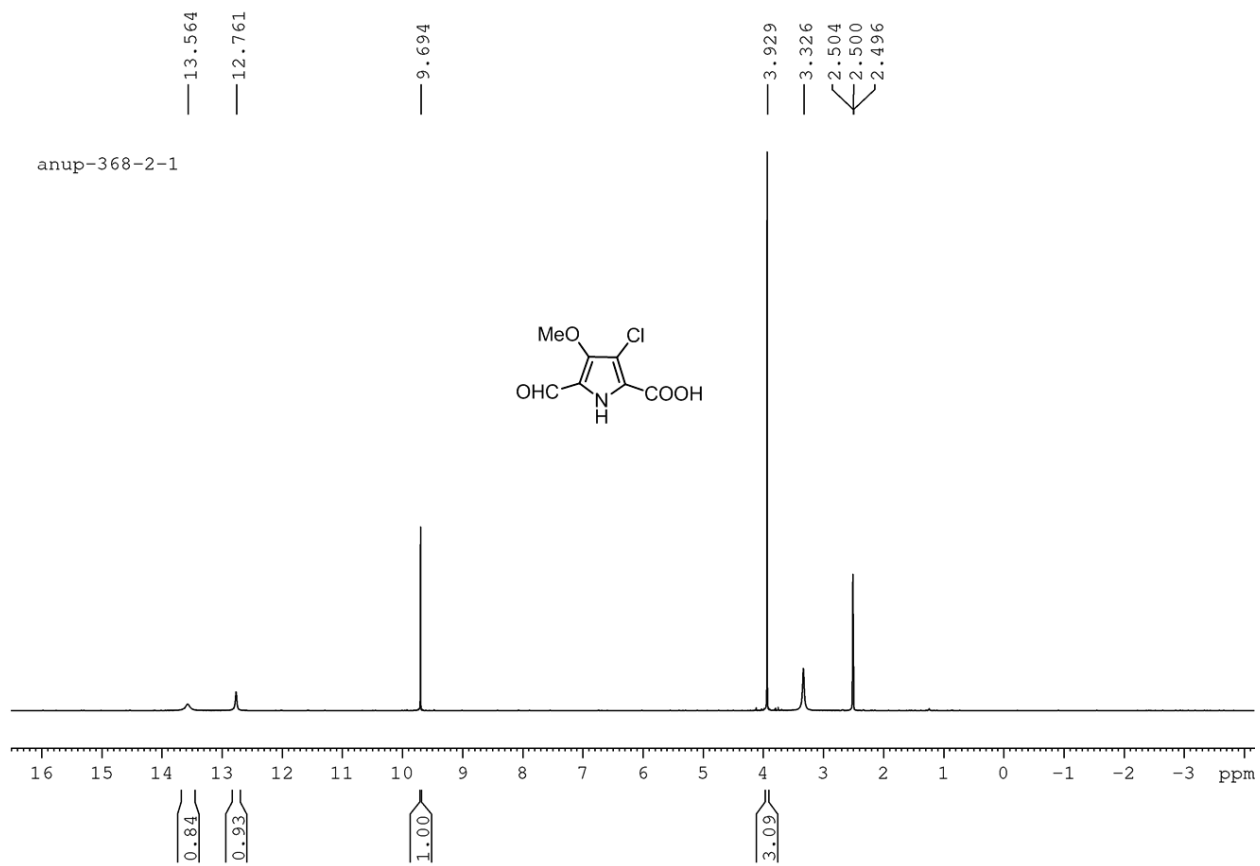


Figure S5: ^1H NMR spectrum of **9** in DMSO-d_6 .

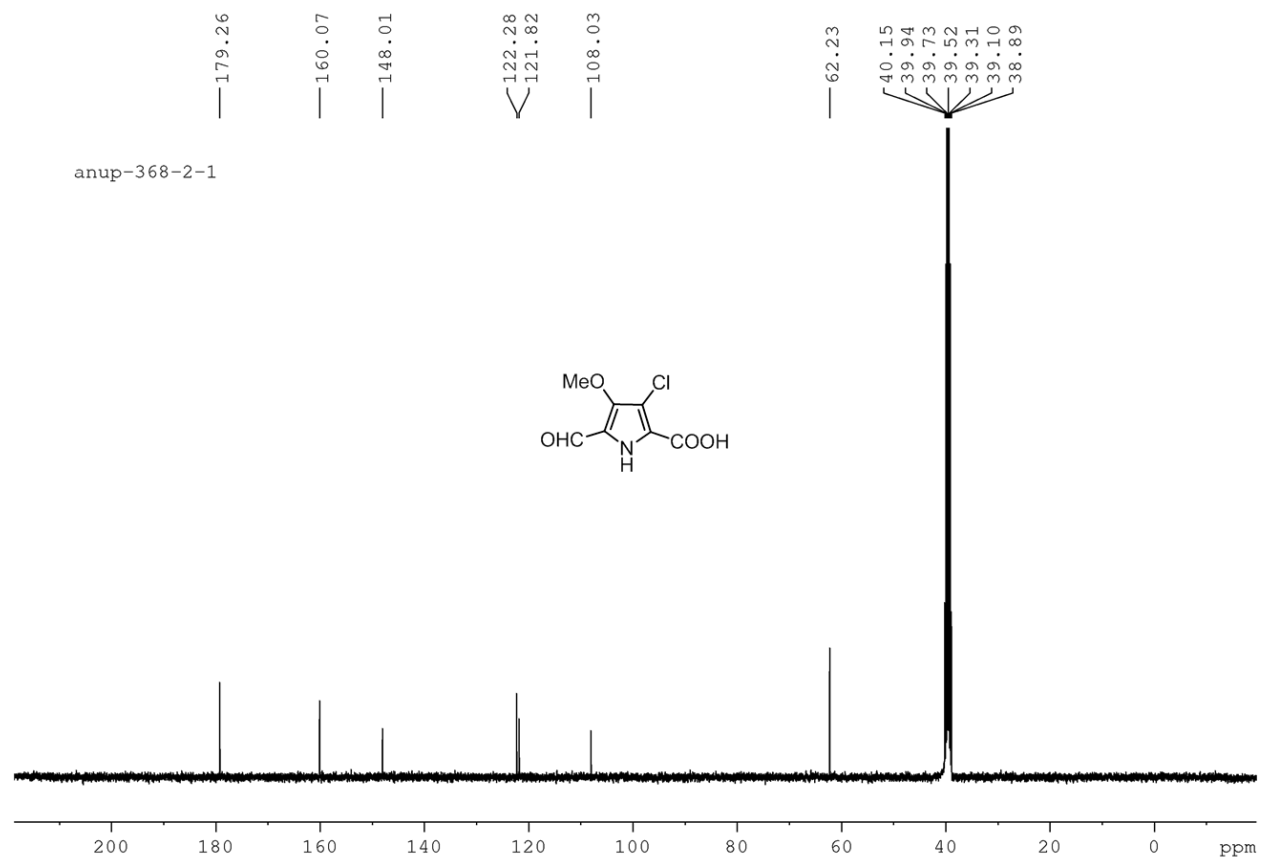


Figure S6: ^{13}C NMR spectrum of **9** in DMSO-d_6 .

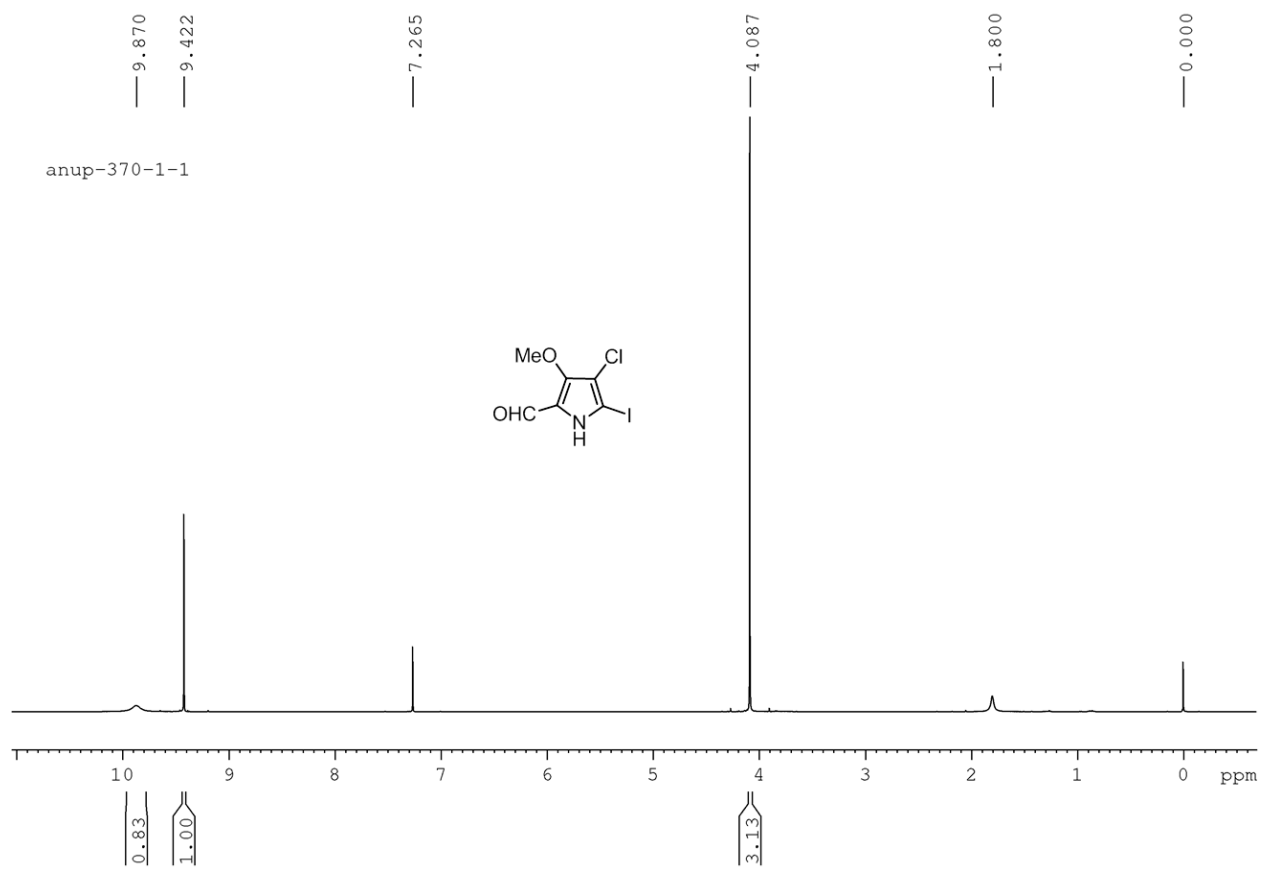


Figure S7: ^1H NMR spectrum of **10** in CDCl_3 .

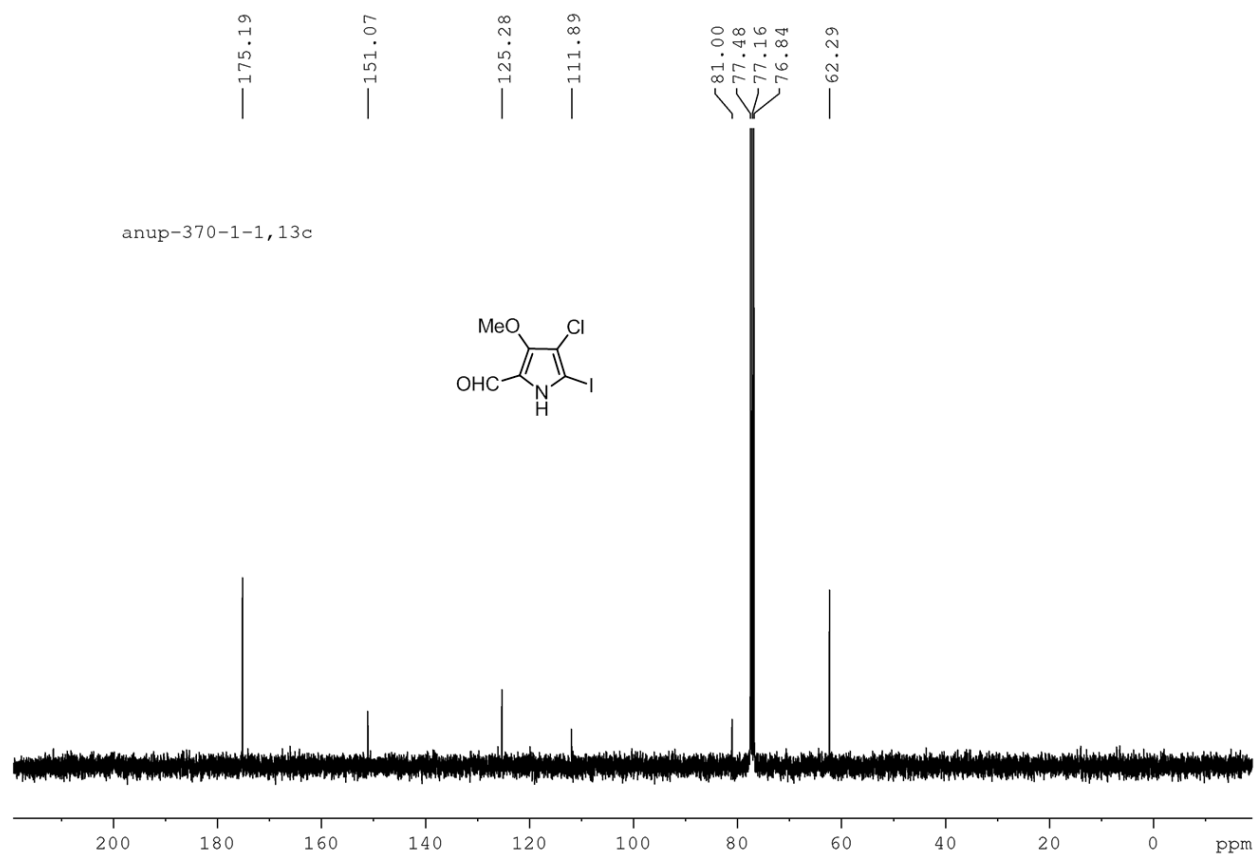


Figure S8: ^{13}C NMR spectrum of **10** in CDCl_3 .

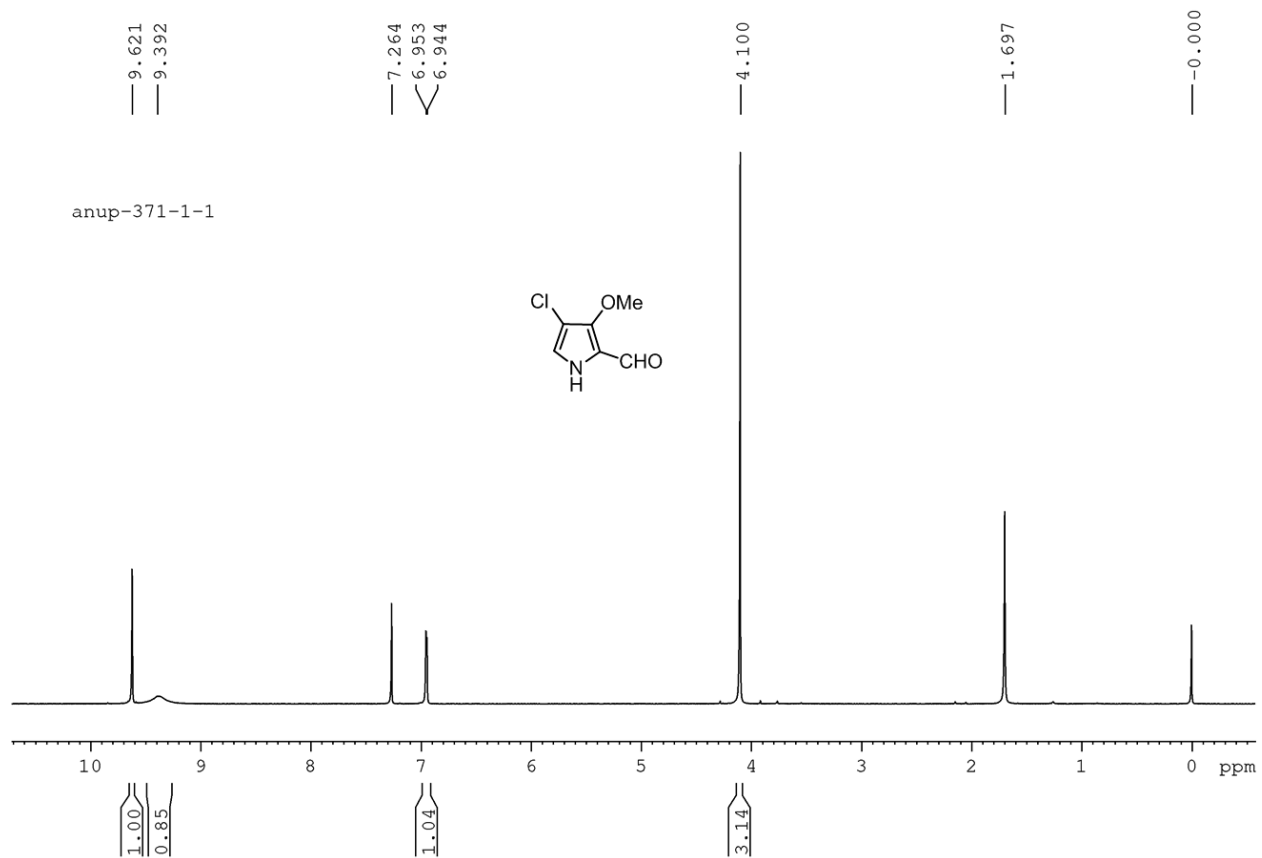


Figure S9: ^1H NMR spectrum of **6** in CDCl_3 .

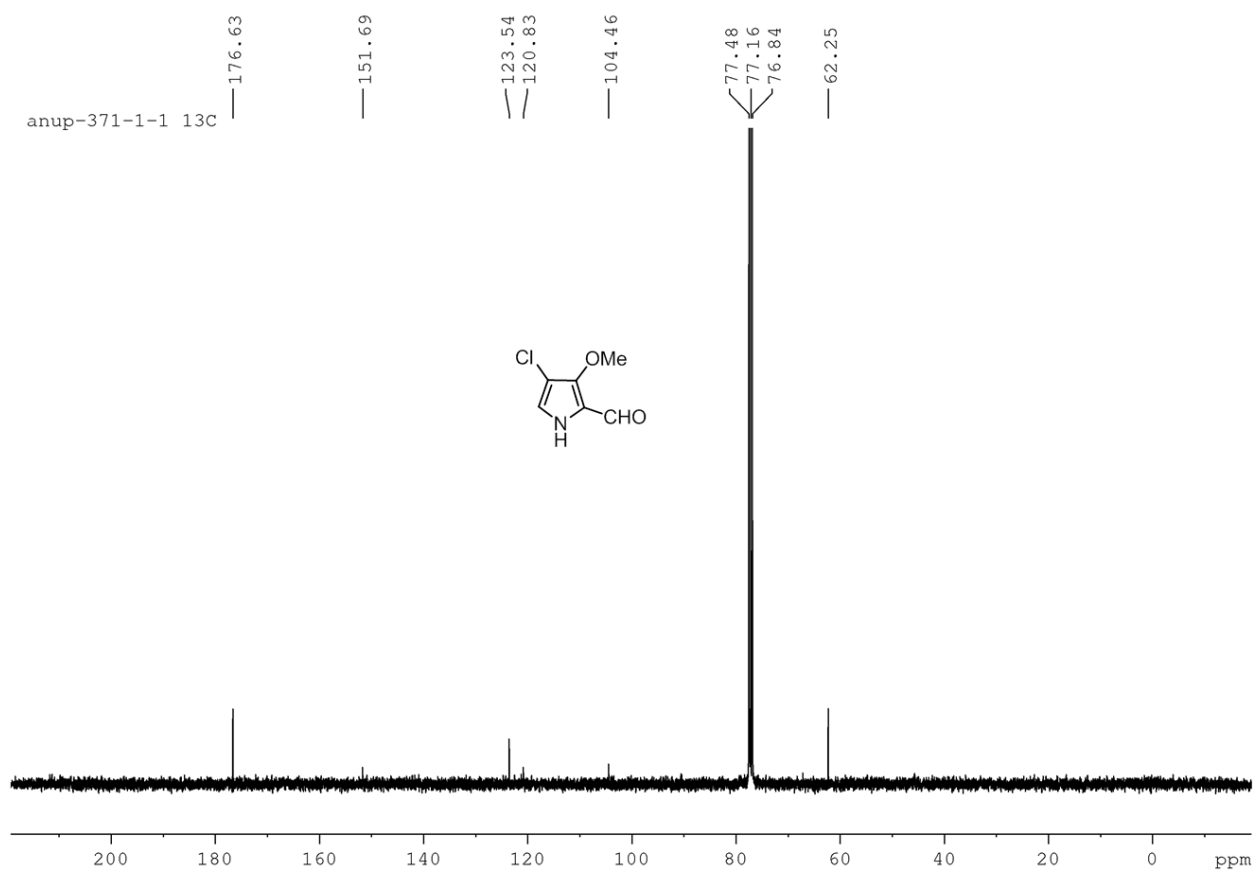


Figure S10: ¹³C NMR spectrum of **6** in CDCl₃.

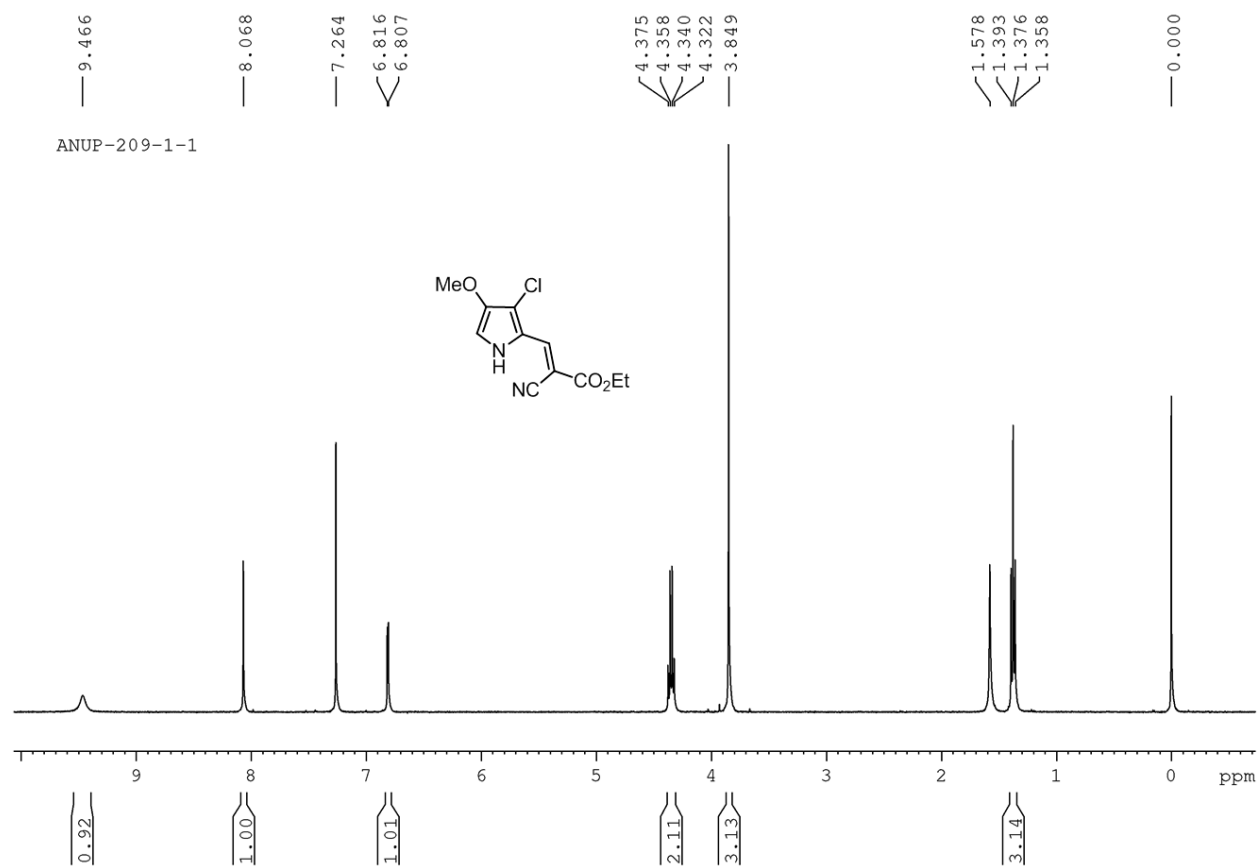


Figure S11: ^1H NMR spectrum of **11a** in CDCl_3 .

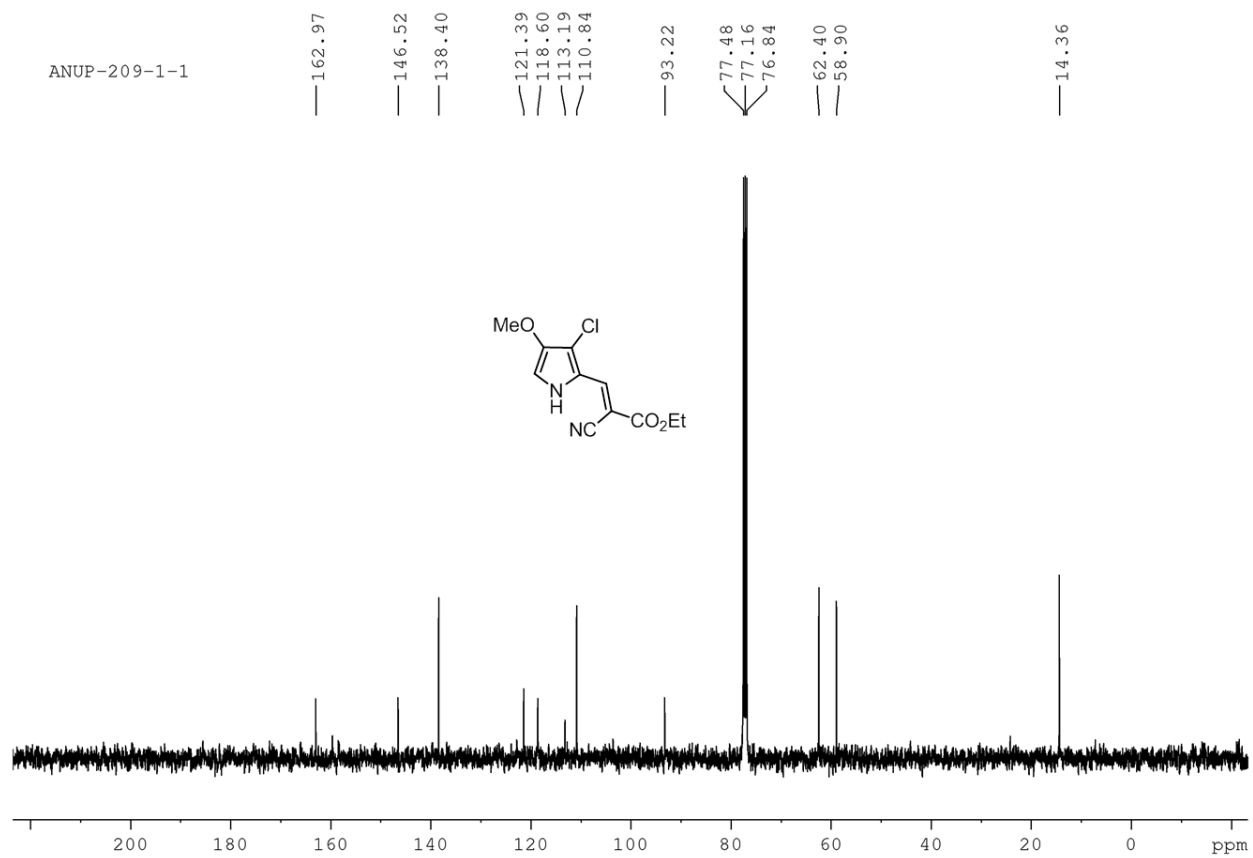


Figure S12: ^{13}C NMR spectrum of **11a** in CDCl_3 .

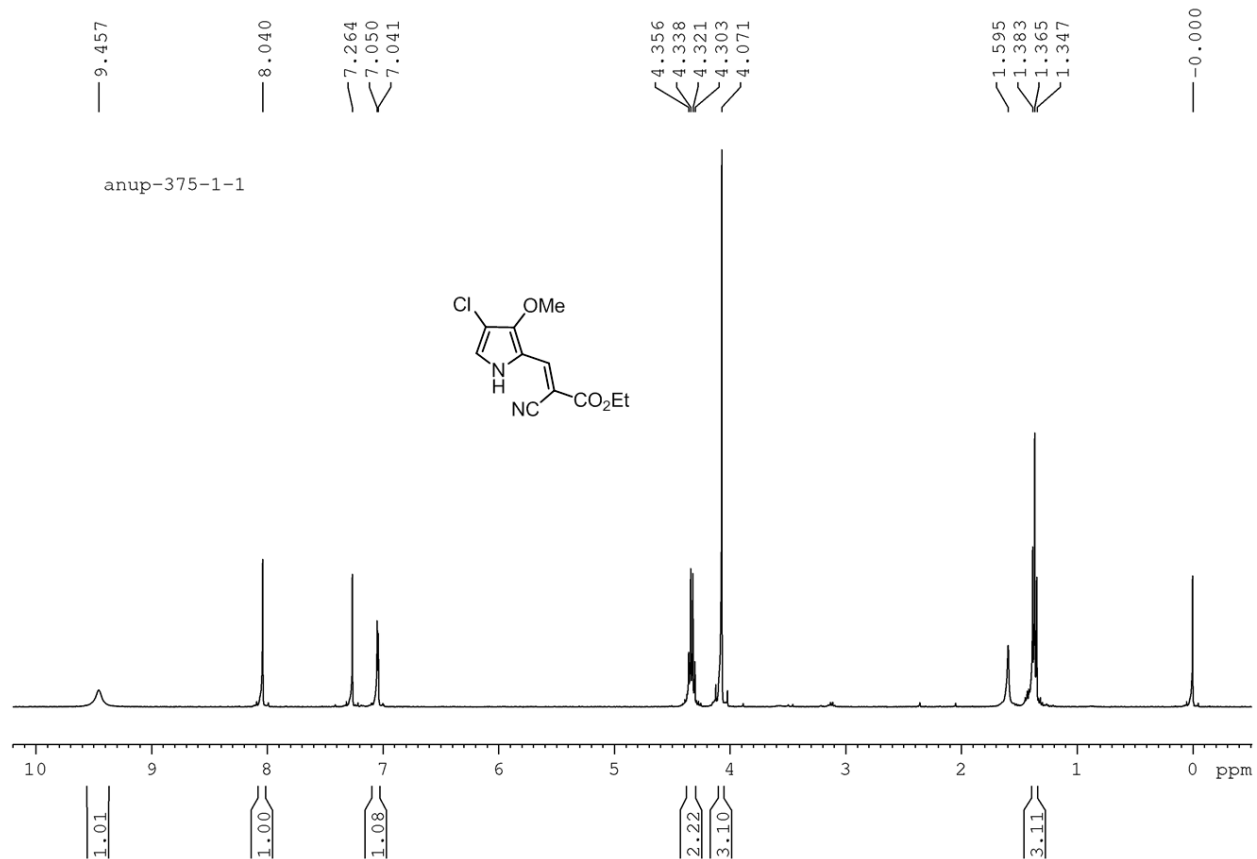


Figure S13: ^1H NMR spectrum of **11b** in CDCl_3 .

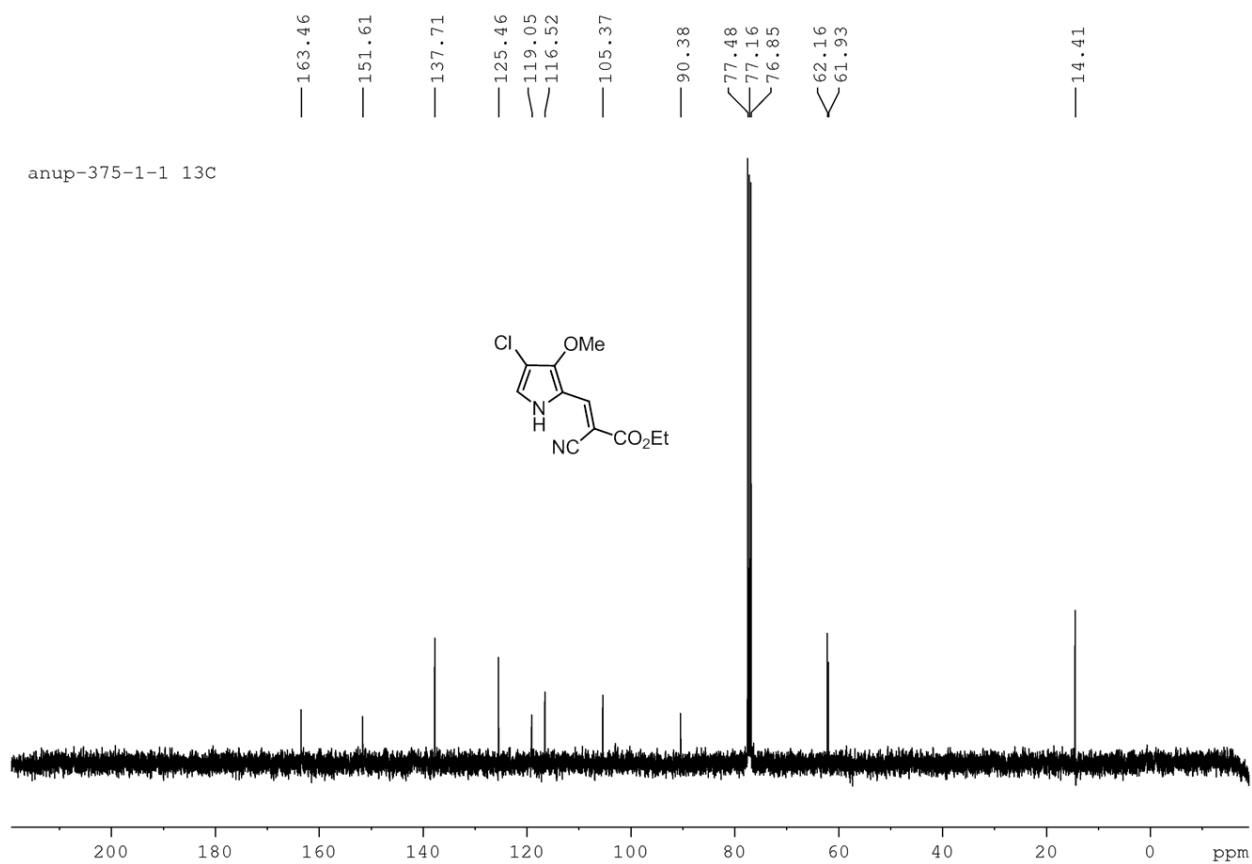


Figure S14: ^{13}C NMR spectrum of **11b** in CDCl_3 .

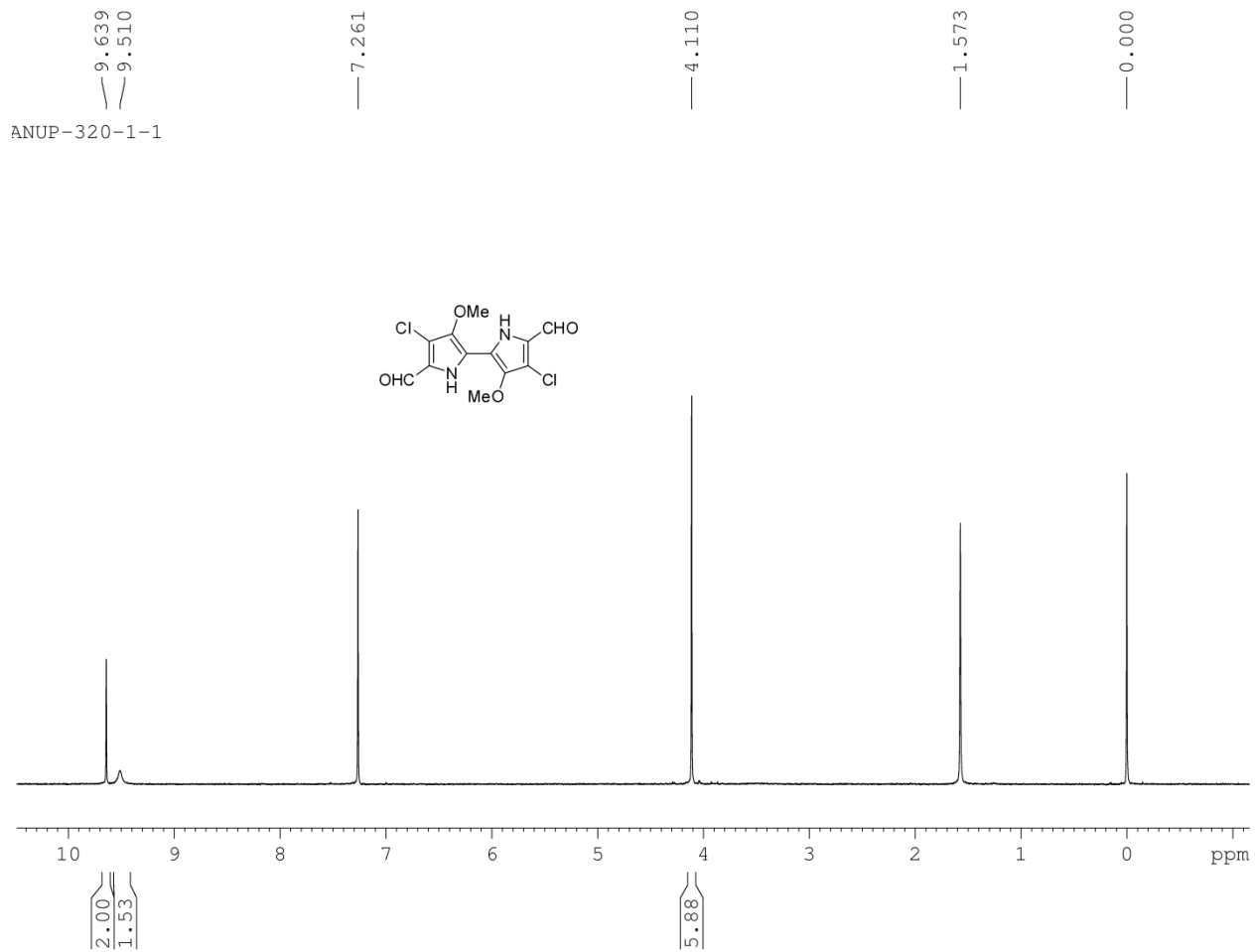


Figure S15: ^1H NMR spectrum of **12a** in CDCl_3 .

ANUP-320-1-1 (13C)

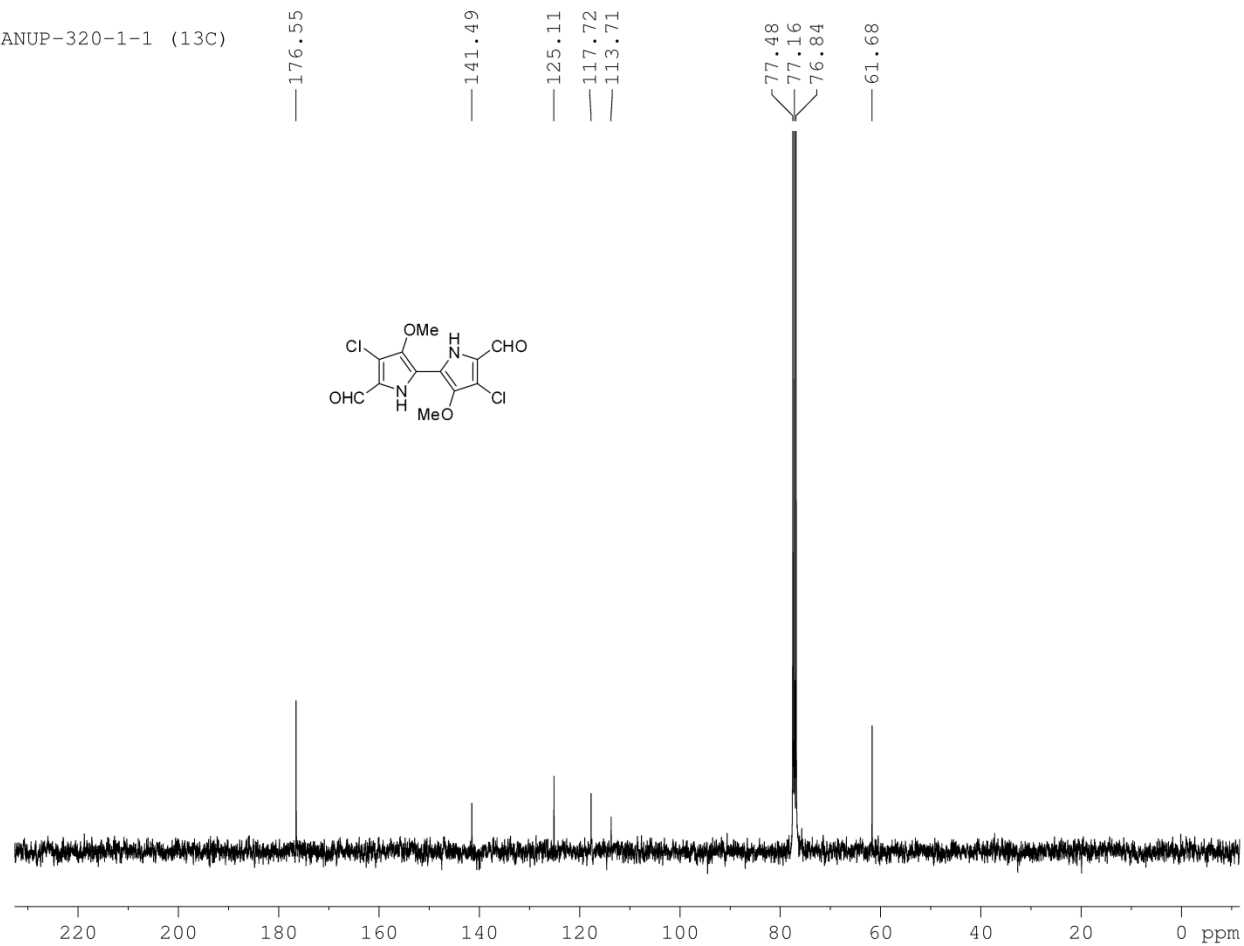


Figure S16: ^{13}C NMR spectrum of **12a** in CDCl_3 .

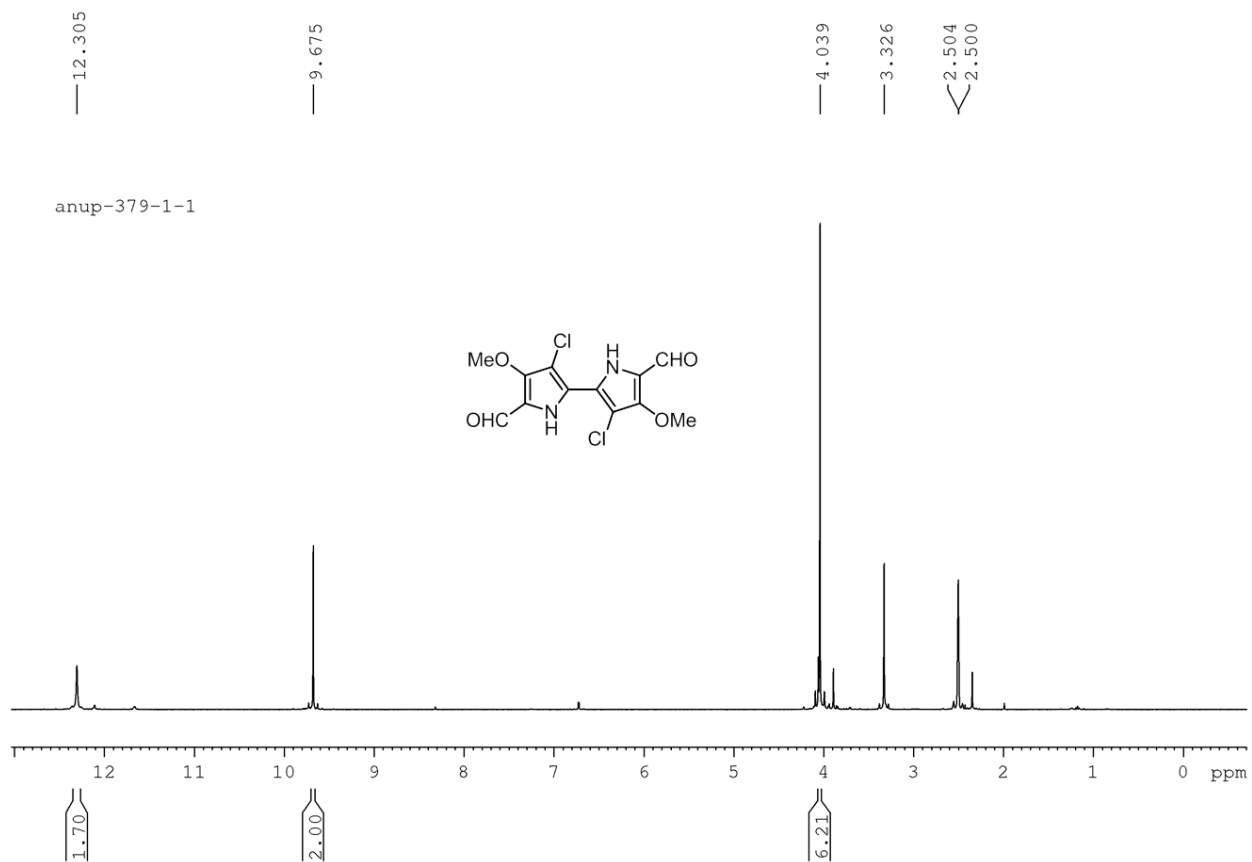


Figure S17: ^1H NMR spectrum of **12b** in DMSO-d_6 .

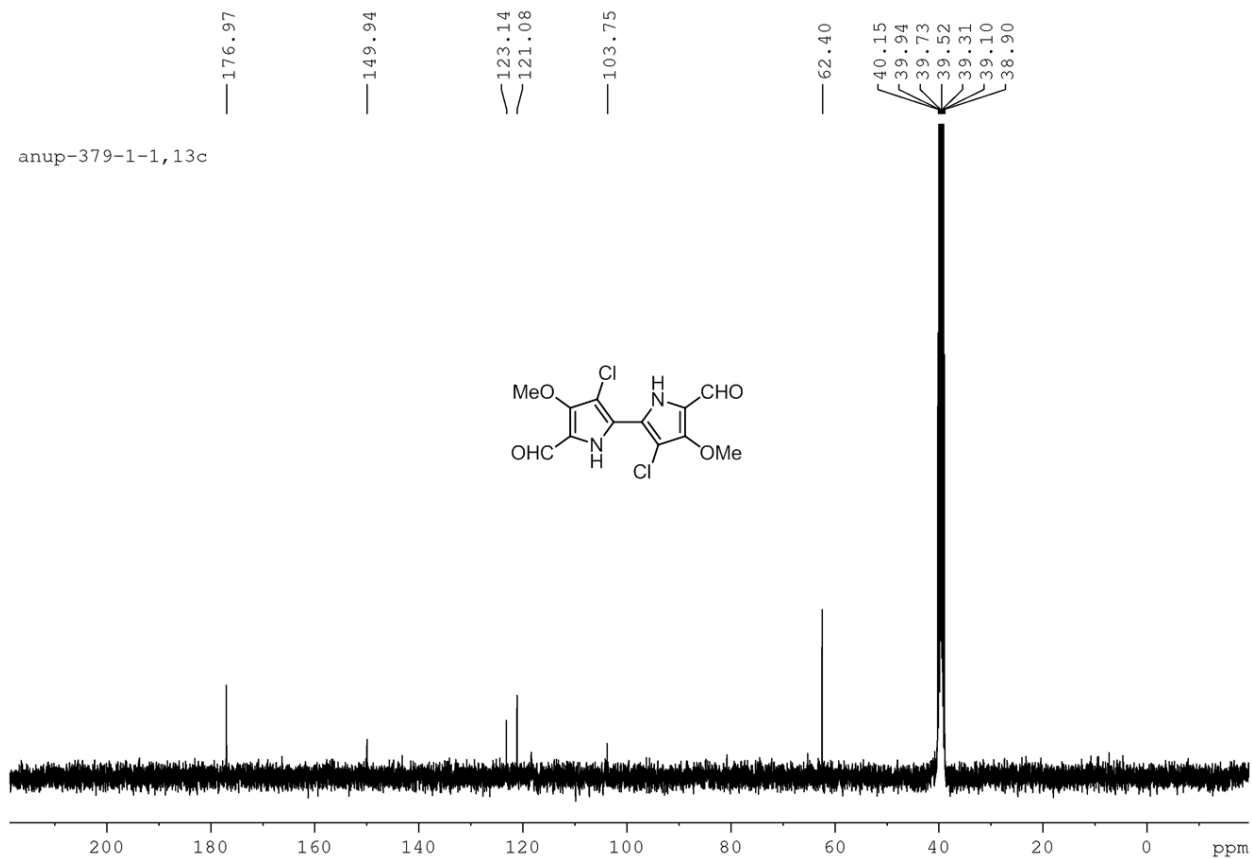


Figure S18: ^{13}C NMR spectrum of **12b** in DMSO-d_6 .

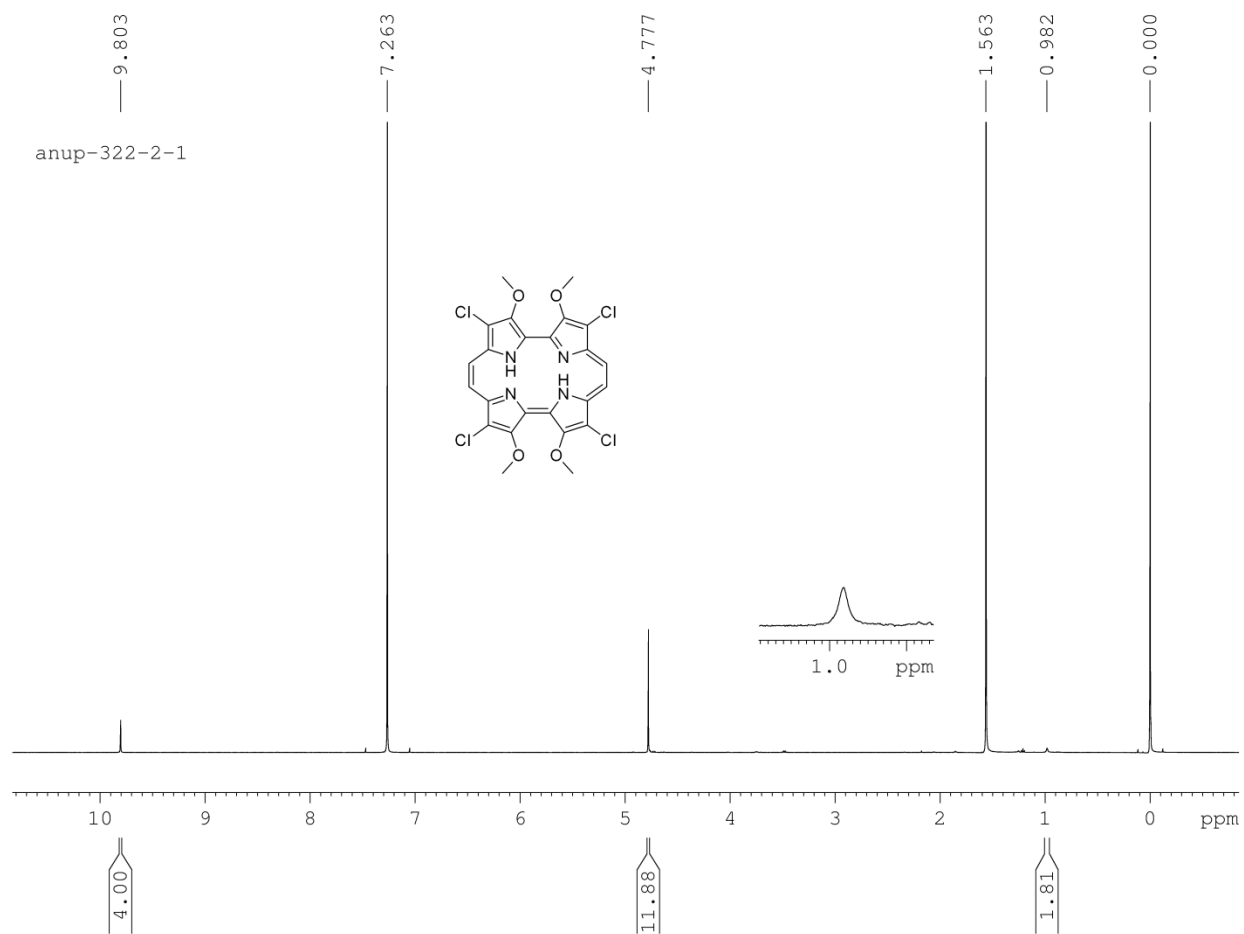


Figure S19: ^1H NMR spectrum of **1a** in CDCl_3 .

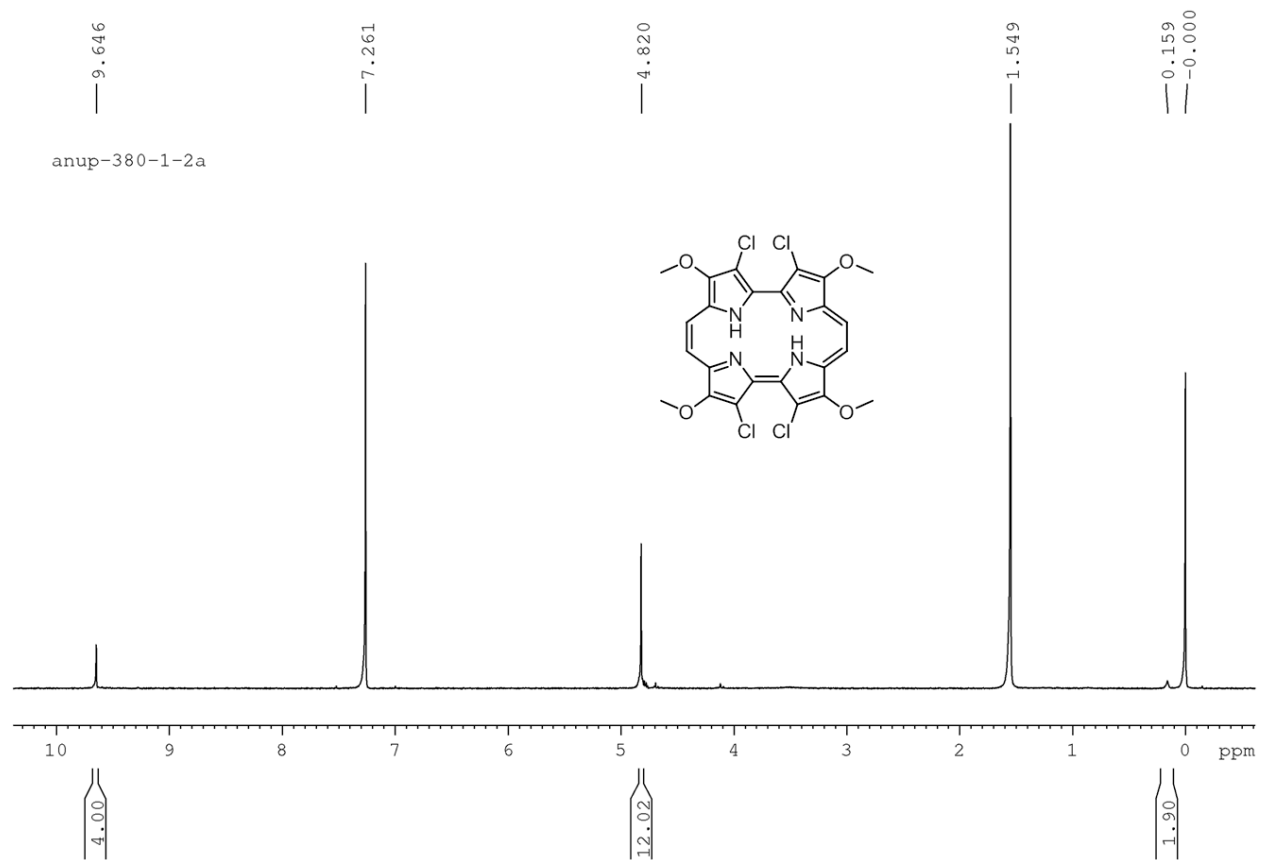


Figure S20: ¹H NMR spectrum of **1b** in CDCl₃.

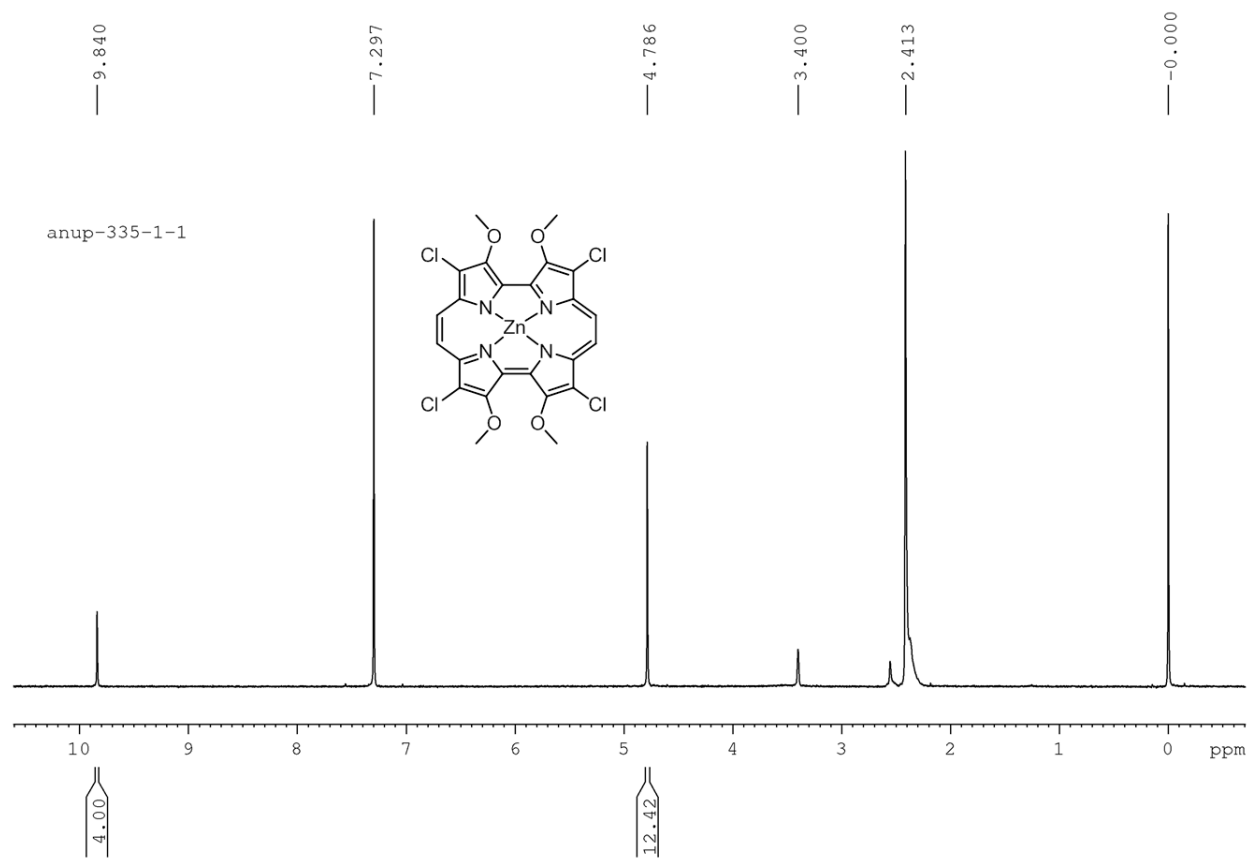


Figure S21: ^1H NMR spectrum of **Zn1a** in CDCl_3 in presence of small amount of CD_3OD .

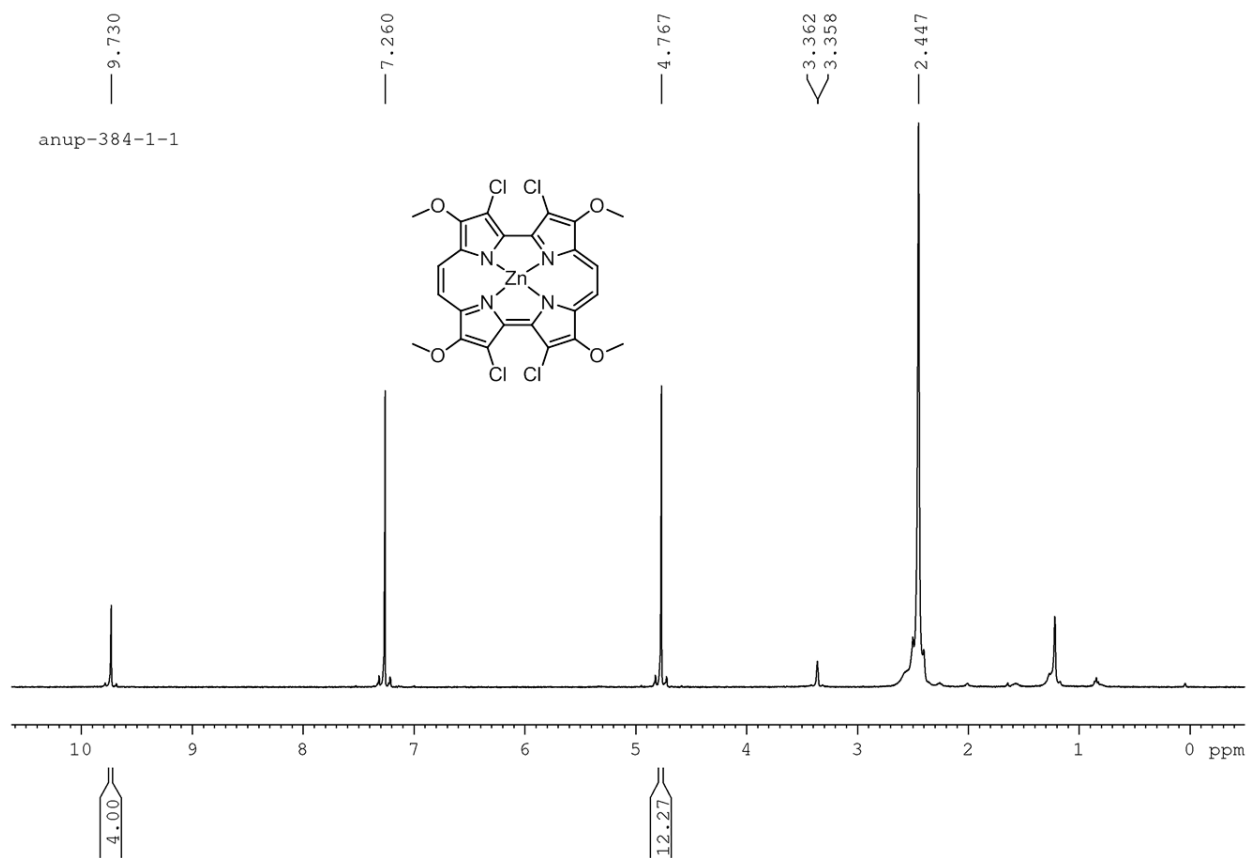


Figure S22: ^1H NMR spectrum of **Zn1b** in CDCl_3 in presence of small amount of CD_3OD .

Crystallographic Data:

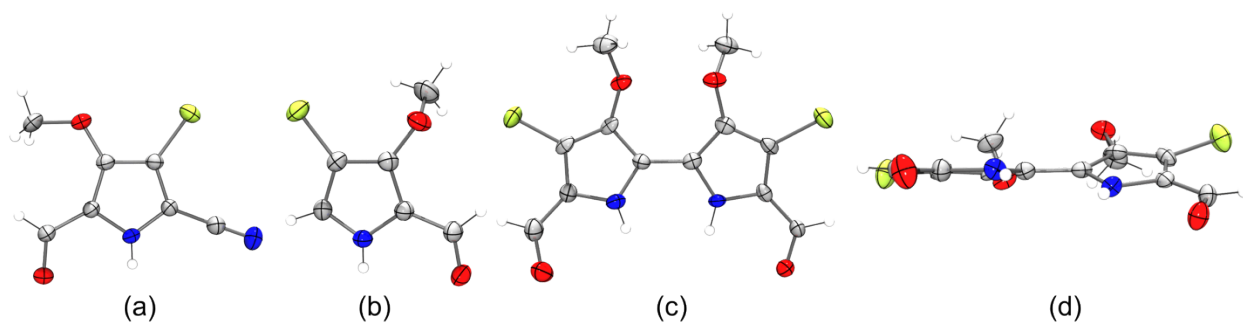


Figure S23: Molecular Structure of (a) **8**, (b) **6**, (c) front view **12a** and (d) side view of **12a** scaled in 35% probability level. Color code: C, grey; N, blue; O, red; Cl, yellow green; H, white.

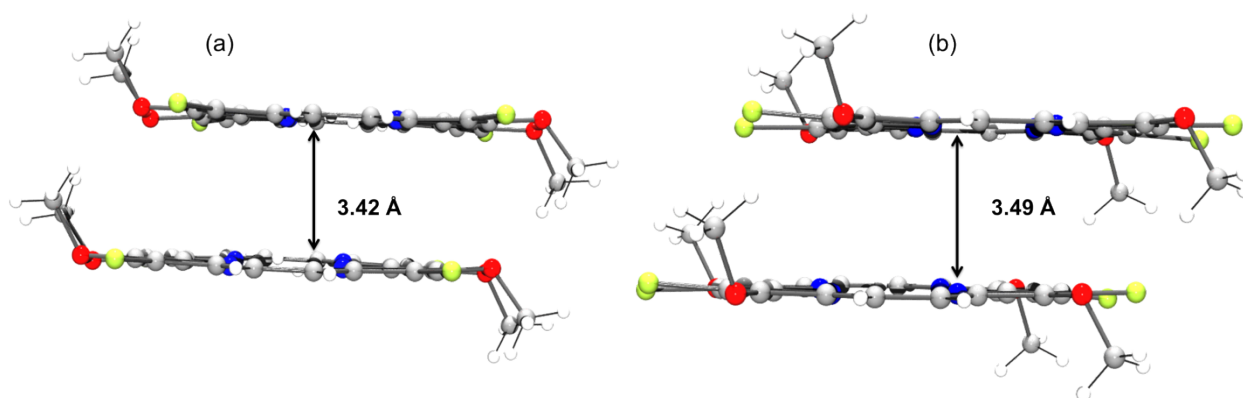


Figure S24: Distinctive π - π -stacking diagrams of (a) **1a** and (b) **1b**. Color code: C, grey; N, blue; O, red; Cl, yellow green; H, white.

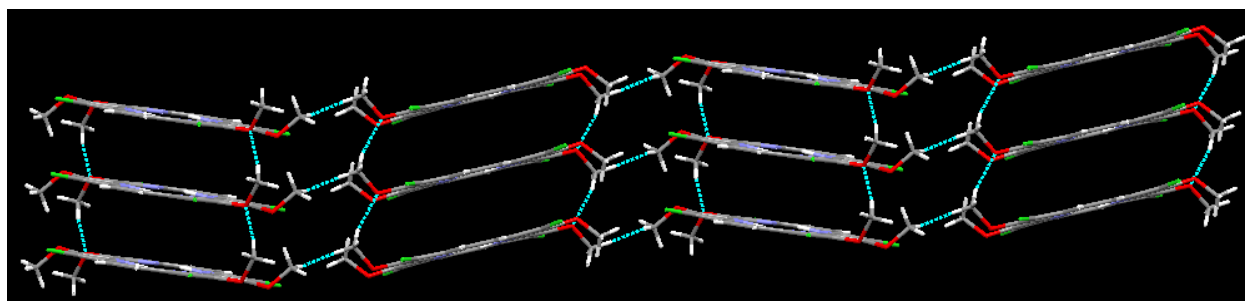


Figure S25: Crystal packing diagram of **1a** and short contact represented in cyan color. Color code: C, grey; N, blue; O, red; Cl, green; H, white.

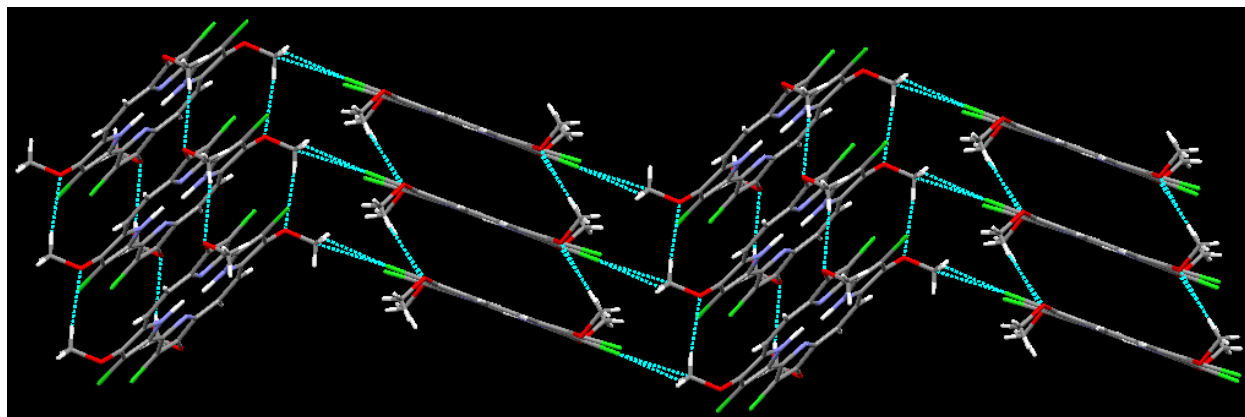


Figure S26: Crystal packing diagram of **1b** and short contact represented in cyan color. Color code: C, grey; N, blue; O, red; Cl, green; H, white.

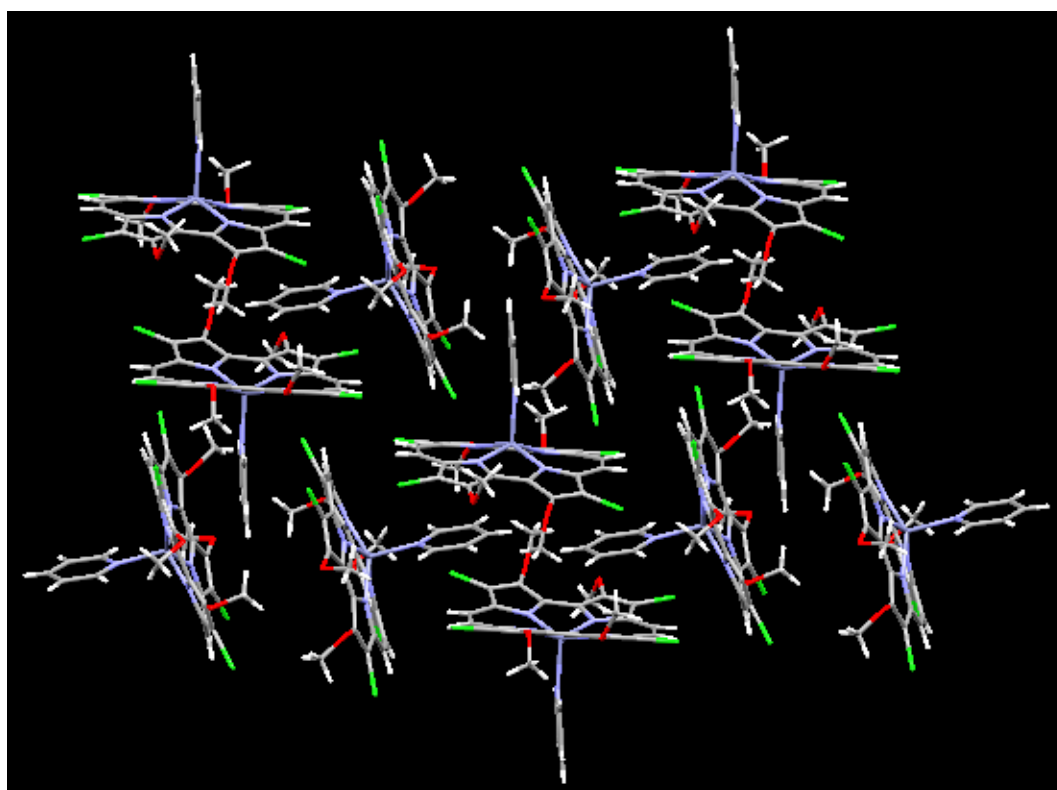


Figure S27: Crystal packing diagram of **Zn1a.Py**. Color code: C, grey; N, blue; O, red; Cl, green; H, white; Zn, steel blue.

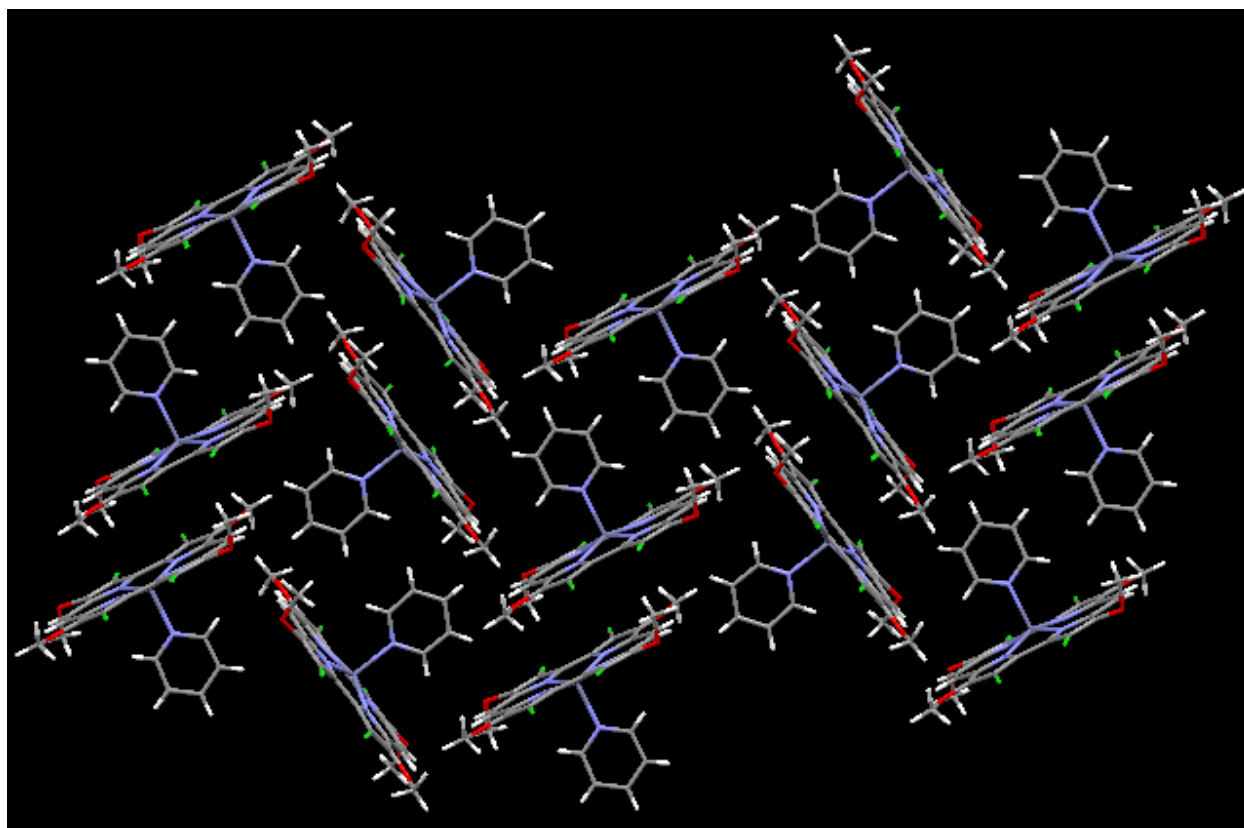


Figure S28: Crystal packing diagram of **Zn1b.Py**. Color code: C, grey; N, blue; O, red; Cl, green; H, white; Zn, steel blue.

Author's comment on IUCR check.cif alert:

For 1b:

PLAT353_ALERT_3_A Long N-H (N0.87,N1.01A) N1 - H1N ... 1.41 Ang.

Author response:

This H-atom involves in tautomerisation with opposite N-atom resulted average N-H bond distance.

Photophysical Data:

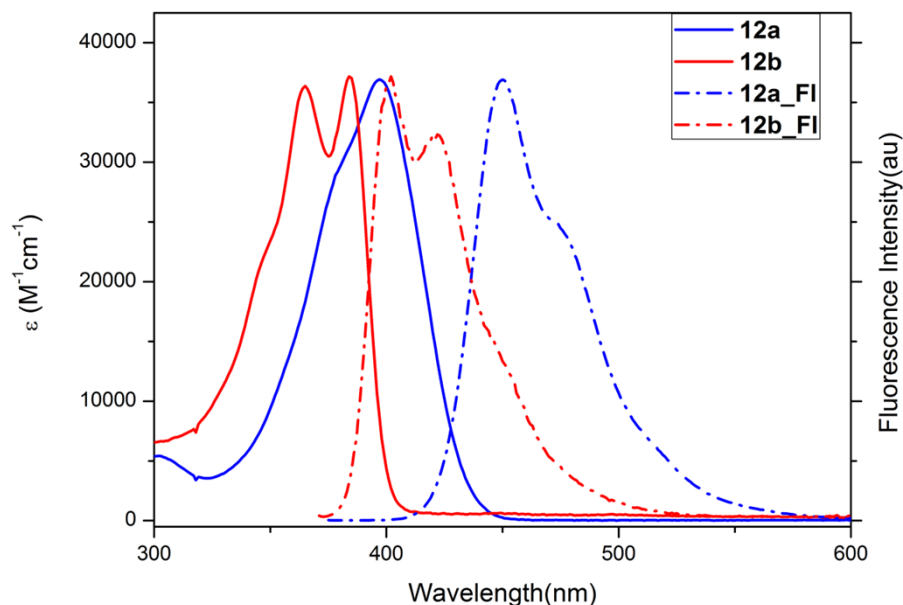


Figure S29: UV-Vis (solid line) and fluorescence (dot dash line) spectra of **12a** and **12b** in CHCl_3 at 25 °C.

Table S1: Comparative photophysical data of porphycenes in CHCl_3 at 25 °C.

Porphycene s	UV-Vis (nm, log ϵ)	Emission (λ_{max}) nm	ϕ_{fa}	τ_f ^b (ns)	k_r^c (10^8 s^{-1})	k_{nr}^d (10^8 s^{-1})
1a	376 (5.16), 384 (5.14), 565 (4.58), 608 (4.35), 647 (4.52)	655, 717	0.00071	---	---	---
Zn1a	391 (5.24), 588 (4.33), 638 (4.90)	645, 706	0.17	2.9	0.59	2.86
Pd1a	389(4.94), 561 (4.14), 606 (4.70)	---	---	---	---	---
1b	385 (5.13), 572 (4.52), 625 (4.31), 664 (4.46)	672	0.00075	---	---	---
Zn1b	391(4.90), 604 (4.14), 638 (4.61)	654, 711	0.16	2.2	0.73	3.82
Pd1b	391(4.93), 603 (4.64), 624 (4.55)	---	---	---	---	---
2^e	382 (5.09), 557 (4.40), 599 (4.24), 636 (4.34)	649	<0.0001	---	---	---
Zn2^e	390 (5.08), 618 (4.75)	632, 689	0.025	0.6	0.42	16.25
Pd2^e	390 (4.84), 590 (4.48)	---	---	---	---	---

^a fluorescence quantum yield measured by comparative actinometry method by using **H₂TPP** in toluene (ϕ_f 0.11) as standard, ^b fluorescence lifetime, ^c radiative rate constant (ϕ_f/τ_f), ^d non-radiative rate constant ($(1 - \phi_f)/\tau_f$), ^e taken from ref no. S8.

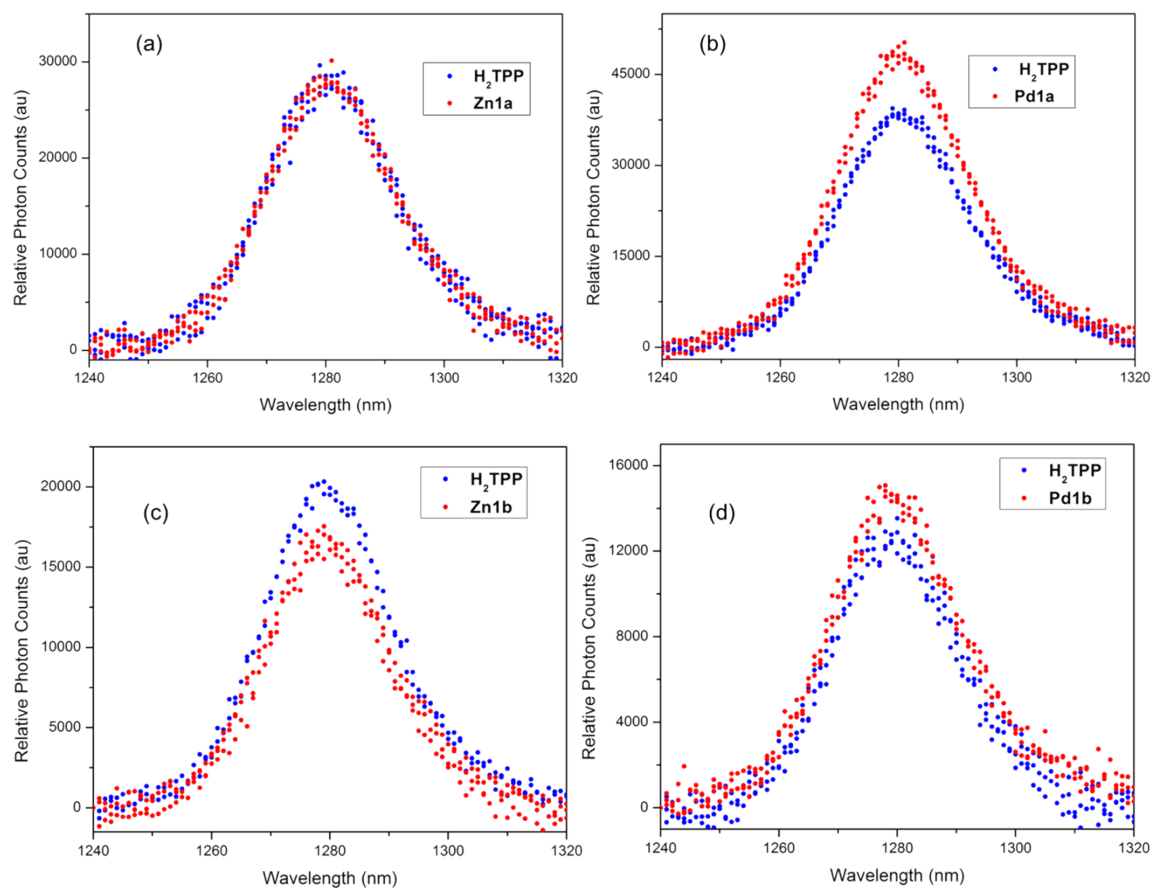


Figure S30: Singlet oxygen luminescence of optically matched (a) **H₂TPP** and **Zn1a** (b) **H₂TPP** and **Pd1a** (c) **H₂TPP** and **Zn1b** (d) **H₂TPP** and **Pd1b** in air saturated toluene at 25 °C.

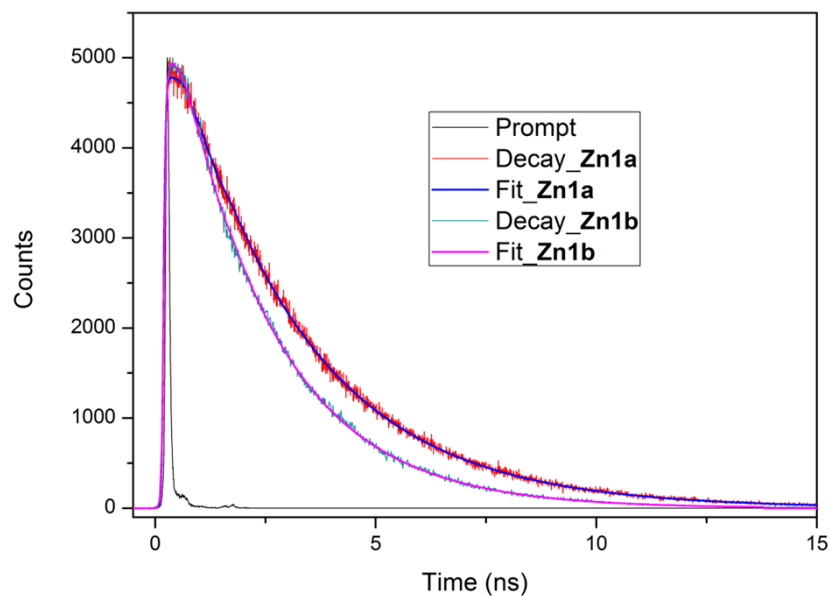


Figure S31: Fluorescence decay profiles of **Zn1a** and **Zn1b** in CHCl_3 at 25 °C.

Electrochemical Data:

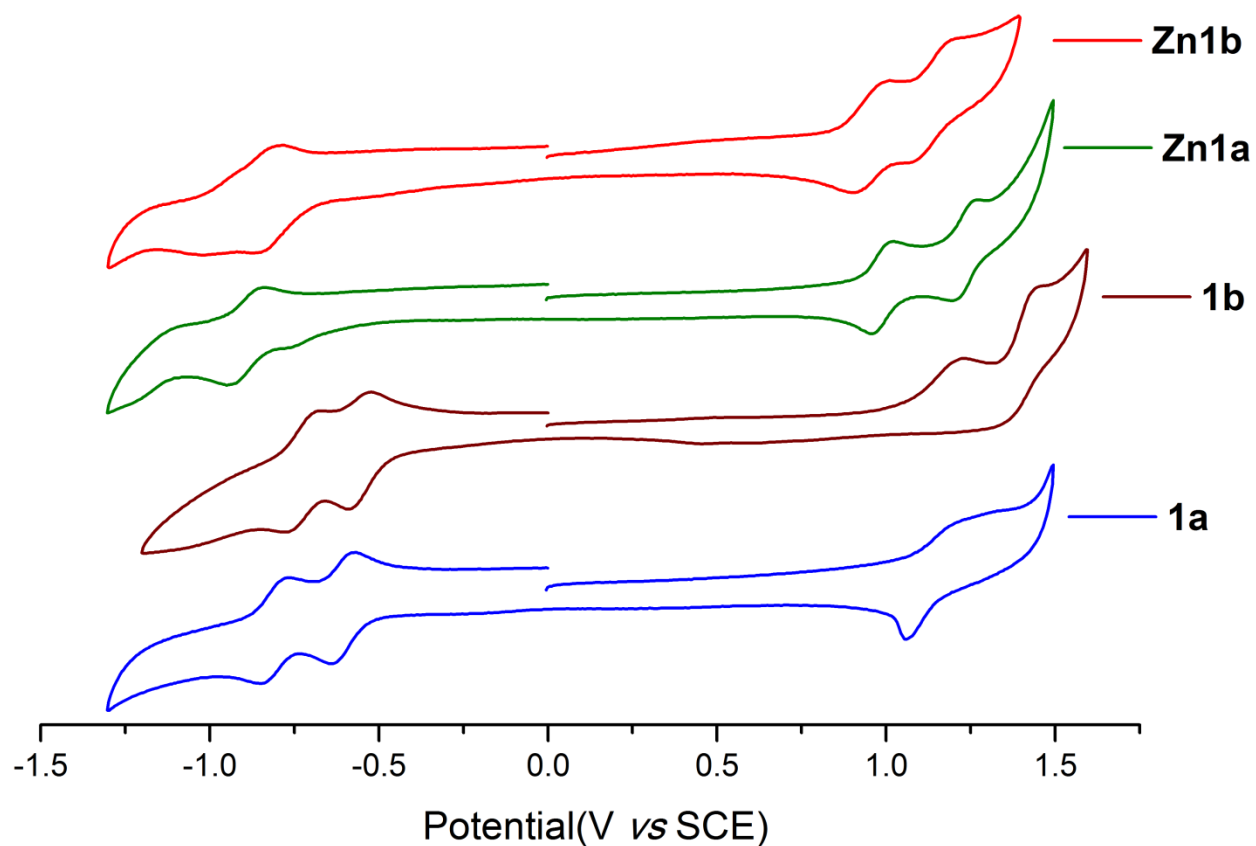


Figure S32: Cyclic voltammograms of **1a**, **1b** and their Zn(II) complexes in dichloromethane at 25 °C (scan rate 50 mV/s).

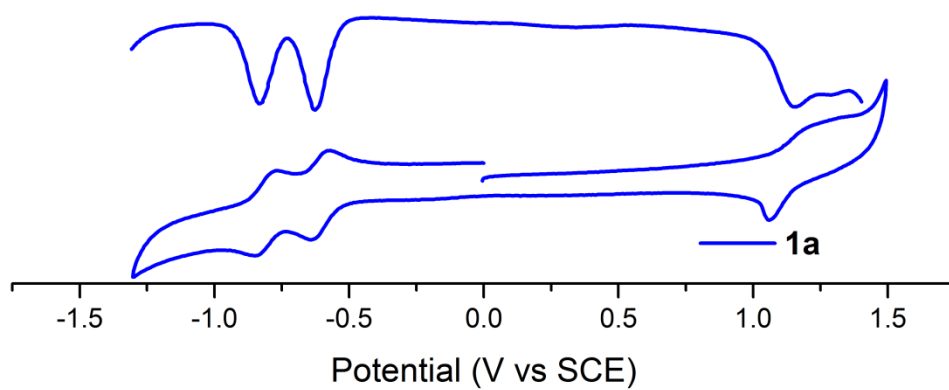


Figure S33: Combined CV (below) and DPV (above) of **1a** in dichloromethane measured at 25 °C.

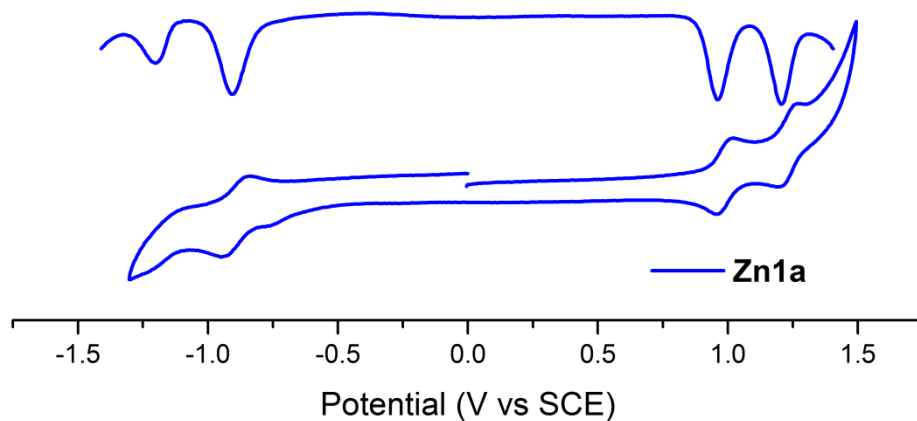


Figure S34: Combined CV (below) and DPV (above) of **Zn1a** in dichloromethane measured at 25 °C.

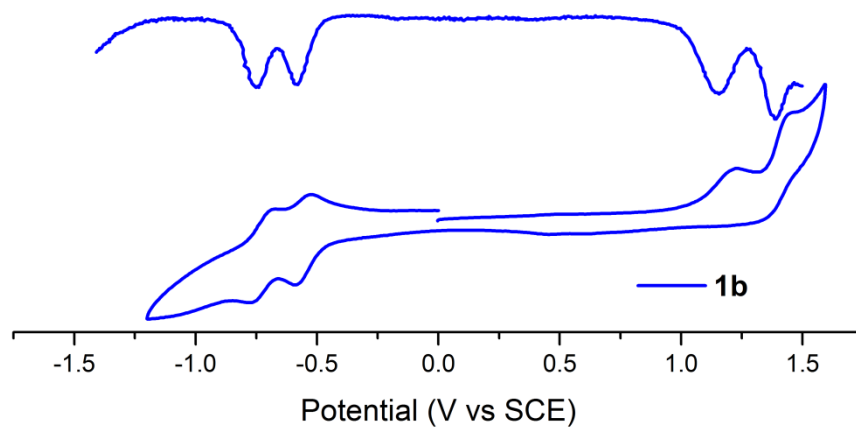


Figure S35: Combined CV (below) and DPV (above) of **1b** in dichloromethane measured at 25 °C.

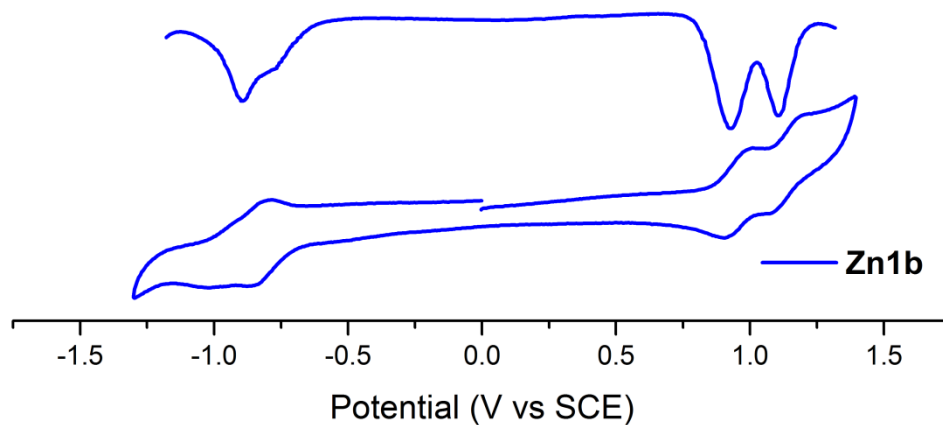


Figure S36: Combined CV (below) and DPV (above) of **Zn1b** in dichloromethane measured at 25 °C.

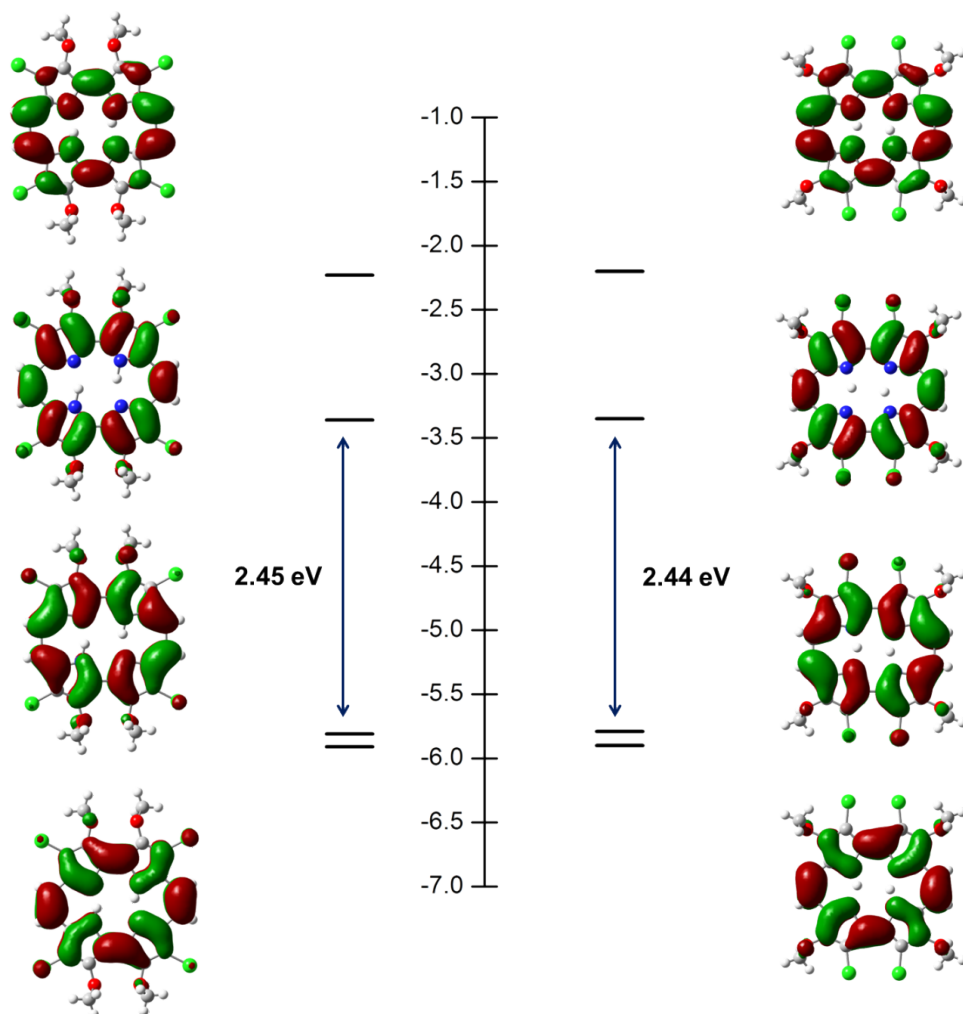


Figure S37: Molecular orbitals of **1a** (left) and **1b** obtained by single point calculation of crystal structure by using B3LYP (6-31+G) method.

Cartesian coordinates for the DFT optimized geometry:

For 1a:

Tag	Symbol	X	Y	Z
1	Cl	0.2320920	3.8247630	4.4107670
2	Cl	0.2720600	3.8348530	-4.3984040
3	N	0.0530050	1.3572160	-1.3832030
4	N	0.1642910	1.3494690	1.3948810

5	O	0.2745210	4.9250970	1.3989820
6	C	0.0373890	1.6199630	-2.7284110
7	C	0.2210930	3.6029950	-1.6536710
8	C	0.2099300	3.0107710	2.8875620
9	C	0.1580030	2.5316730	-0.7030520
10	O	0.4137020	4.9120100	-1.3431320
11	C	0.1246030	0.6732220	3.7769520
12	H	0.1531320	1.0540420	4.6249020
13	C	0.1622600	1.5928780	2.7291030
14	C	0.1733760	2.5243160	0.7149830
15	C	0.1680090	3.0416730	-2.8686630
16	C	0.2121940	3.5976270	1.6694960
17	C	-0.0531230	0.6981530	-3.7712760
18	H	-0.0668850	1.0821440	-4.6181420
19	C	-0.8843080	5.6693670	1.7715640
20	H	-1.6529830	5.3127950	1.3176960
21	H	-0.7663490	6.5889300	1.5273530
22	H	-1.0165570	5.6046090	2.7194970
23	C	-0.6099740	5.8075830	-1.7473490
24	H	-0.6979420	5.7829610	-2.7019830
25	H	-0.3821910	6.7000370	-1.4700150
26	H	-1.4403400	5.5499170	-1.3414730

27	H	-0.1014140	0.2882490	-1.1575980
28	Cl	-0.2320920	-3.8247630	-4.4107670
29	Cl	-0.2720600	-3.8348530	4.3984040
30	N	-0.0530050	-1.3572160	1.3832030
31	N	-0.1642910	-1.3494690	-1.3948810
32	O	-0.2745210	-4.9250970	-1.3989820
33	C	-0.0373890	-1.6199630	2.7284110
34	C	-0.2210930	-3.6029950	1.6536710
35	C	-0.2099300	-3.0107710	-2.8875620
36	C	-0.1580030	-2.5316730	0.7030520
37	O	-0.4137020	-4.9120100	1.3431320
38	C	-0.1246030	-0.6732220	-3.7769520
39	H	-0.1531320	-1.0540420	-4.6249020
40	C	-0.1622600	-1.5928780	-2.7291030
41	C	-0.1733760	-2.5243160	-0.7149830
42	C	-0.1680090	-3.0416730	2.8686630
43	C	-0.2121940	-3.5976270	-1.6694960
44	C	0.0531230	-0.6981530	3.7712760
45	H	0.0668850	-1.0821440	4.6181420
46	C	0.8843080	-5.6693670	-1.7715640
47	H	1.6529830	-5.3127950	-1.3176960
48	H	0.7663490	-6.5889300	-1.5273530

49	H	1.0165570	-5.6046090	-2.7194970
50	C	0.6099740	-5.8075830	1.7473490
51	H	0.6979420	-5.7829610	2.7019830
52	H	0.3821910	-6.7000370	1.4700150
53	H	1.4403400	-5.5499170	1.3414730
54	H	0.1014140	-0.2882490	1.1575980

For 1b:

Tag	Symbol	X	Y	Z
1	Cl	-0.3366640	5.3217910	-1.5026490
2	Cl	-0.1680910	5.3154060	1.6072990
3	O	-0.2312510	3.5625070	4.1664140
4	N	-0.0588660	1.3936670	-1.3690830
5	N	-0.1246280	1.3660530	1.3551540
6	O	-0.2181360	3.6393720	-4.1243600
7	C	-0.1792610	3.6079990	1.7396800
8	C	-0.1237710	0.6588440	3.7487050
9	H	-0.1756080	1.0405800	4.5965800
10	C	-0.0577480	1.6425960	-2.7105050
11	C	-0.2070420	3.6226220	-1.6765740
12	C	-0.1513430	3.0475990	-2.8964160
13	C	-0.1456260	2.5887580	-0.6863150
14	C	-0.1579540	2.5703460	0.7195930

15	C	-0.1501440	1.5838810	2.7038310
16	C	-0.1802840	2.9945450	2.9355630
17	C	-0.0344070	-0.7138630	3.7540520
18	H	-0.0354690	-1.0937050	4.6020890
19	C	1.0178640	4.0702350	4.6495720
20	H	1.6649310	3.3613990	4.6690330
21	H	0.9004490	4.4211660	5.5352600
22	H	1.3248870	4.7679990	4.0674860
23	C	0.9642960	4.3386690	-4.5211390
24	H	1.1253570	5.0659710	-3.9148430
25	H	0.8496860	4.6826460	-5.4106250
26	H	1.7124280	3.7367860	-4.5050620
27	H	-0.1020860	0.1210550	1.0177070
28	Cl	0.3366640	-5.3217910	1.5026490
29	Cl	0.1680910	-5.3154060	-1.6072990
30	O	0.2312510	-3.5625070	-4.1664140
31	N	0.0588660	-1.3936670	1.3690830
32	N	0.1246280	-1.3660530	-1.3551540
33	O	0.2181360	-3.6393720	4.1243600
34	C	0.1792610	-3.6079990	-1.7396800
35	C	0.1237710	-0.6588440	-3.7487050
36	H	0.1756080	-1.0405800	-4.5965800

37	C	0.0577480	-1.6425960	2.7105050
38	C	0.2070420	-3.6226220	1.6765740
39	C	0.1513430	-3.0475990	2.8964160
40	C	0.1456260	-2.5887580	0.6863150
41	C	0.1579540	-2.5703460	-0.7195930
42	C	0.1501440	-1.5838810	-2.7038310
43	C	0.1802840	-2.9945450	-2.9355630
44	C	0.0344070	0.7138630	-3.7540520
45	H	0.0354690	1.0937050	-4.6020890
46	C	-1.0178640	-4.0702350	-4.6495720
47	H	-1.6649310	-3.3613990	-4.6690330
48	H	-0.9004490	-4.4211660	-5.5352600
49	H	-1.3248870	-4.7679990	-4.0674860
50	C	-0.9642960	-4.3386690	4.5211390
51	H	-1.1253570	-5.0659710	3.9148430
52	H	-0.8496860	-4.6826460	5.4106250
53	H	-1.7124280	-3.7367860	4.5050620
54	H	0.1020860	-0.1210550	-1.0177070

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