Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Donor Strapped Perylene Bisimide Macrocycle and Lemniscate Dimer with Extended Charge Separation

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1. General Information

Thin-layer chromatography (TLC) was carried out using Silica Aluchrosep Silica Gel 60/UV 254 purchased from Merck Specialties Pvt Ltd and visualized either by UV Fluorescence or by an iodine chamber. Column chromatography was performed using silica gel (100-200 mesh). The bed was made using 60-120 mesh silica purchased from Spectrochem Pvt. Ltd. India, and mixtures of dichloromethane-pet ether used for elution were distilled before use. The ^{1}H, ^{13}C NMR spectra were recorded on a Bruker 400 and 500 MHz NMR spectrometer. The chemical shift values for ^{1}H (TMS as internal standard) and ^{13}C NMR are recorded in $CDCl_3$ and CD_2Cl_2. The value of the coupling constant (*J*) is stated in Hertz (Hz). All spectra were obtained at room temperature unless otherwise specified. The splitting of peaks is described as *s* (singlet), *d* (doublet), *t* (triplet), *dd* (doublet of doublets), and *m* (multiplet). Infrared spectra (I.R.) were recorded using ATR-FTIR spectra obtained on Perkin Elmer Spectrum Two spectrophotometer in the 4000-600 cm^{-1} range with a resolution of 4 cm^{-1}. The mass spectrometry experiments were conducted on Bruker ultraflex MALDI-TOF MS. The mass spectrum was recorded using 2, 5-Dihydroxybenzoic acid (DHB) as a matrix material. HRMS data were recorded on Q ExactiveHybrid^{TM} Quadrupole-Orbitrap^{TM} mass spectrometer (Thermo Scientific,^{TM}Accela 1250 pump). UV-Vis absorption spectra were recorded with a Shimadzu 1800 spectrophotometer, while all emission spectra were performed using PTI Quanta Master™ Steady State Spectrofluorometer. Lifetime measurement of dyes was recorded on Edinburgh spectrofluorometer FS5 at room temperature. Single Crystal X-ray Diffraction data were collected on a Bruker SMART APEX II CCD diffract meter with graphite-monochromatized (Mo Kα = 0.71073 Å) radiation at ambient temperature.

Materials and Methods

All chemicals, such as 1,7-Dibromo-3,4,9,10-tetracarboxylic acid dianhydride, (Triisopropylsilyl)acetylene, Bis(triphenylphosphine)palladium(II)dichloride, Trimethyltin chloride, *n*-butyllithium (1.6 M), Dichloro(1,3-bis(diphenylphosphino)propane)nickel (TCI), Cyclohexylamine, 2,6-dibromo-4-methylphenol, 2-Bromothiophene (Alfa Aeser), Potassium carbonate, Copper(I) iodide, Copper(I) chloride, Tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6), N,N,N′,N′-tetramethylethylenediamine (Aldrich), Tetrabutylammonium fluoride hydrate, diethyl ether, 3-Bromothiophene, 1-Bromohexane, *N*-Iodosuccinimide, Ethanol (Spectrochem) were used as received. The solvents such as Toluene, Dimethylformamide,

Diisopropylamine, and Triethylamine (Finar) were used after distillation. Tetrahydrofuran was distilled from sodium with benzophenone before use.

Electrochemical analysis: Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out on a CHI voltammetry analyzer at room temperature, employing a three-electrode single-compartment cell: glassy carbon electrode (company, d = 2 mm) as working electrode, a Pt wire as counter electrode and Ag/AgCl as a reference electrode. The supporting electrolyte, Tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6), was previously dried under vacuum, dichloromethane was dried and degassed before use, and all measurements were performed under a nitrogen atmosphere. Ferrocene was used as an internal standard for calibrating the potential ($E_{Fc+/Fc}$ = 0.00 V).

The formal redox potentials (half-wave potentials) were calculated using the formula:

$$E_{1/2} = (E_{pa} + E_{pc}) / 2$$

Where E_{pa} is the peak anode potential and

E_{pc} is the peak cathode potential.

HOMO energies were calculated from the first formal redox potentials (half-wave potentials) using the equation:

$$E_{HOMO} = -(4.8\ eV + E^1_{oxd}\ vs.\ Fc^+/Fc)$$

However, LUMO energies were calculated from the first formal redox potentials (half-wave potentials) using the equation:

$$E_{LUMO} = -(4.8\ eV + E^1_{red}\ vs.\ Fc^+/Fc)$$

Femtosecond transient absorption spectroscopy

The transient experiments used a Helios Fire pump-probe spectrometer set up (Ultrafast System). Ti:Sapphire amplifier system (Astrella, Coherent, 800 nm, 3mJ/pulse energy, ~ 35 fs pulse width and 1 kHz repetition rate) was used to generate ultrafast pulses. The output of the laser pulse was then splitted into two parts (95:5) to generate the pump and probe beam. The higher energy beam travels to an Optical Parametric Amplifier (OPerA-SOLO) to generate requisite pump wavelengths. The lower energy beam passes through sapphire crystal in order to generate white light. A mechanical delay stage was in place to maintain perfect delay between the pump and probe beam. The transient data was recorded, keeping the sample in a 2mm quartz cuvette and analyzed

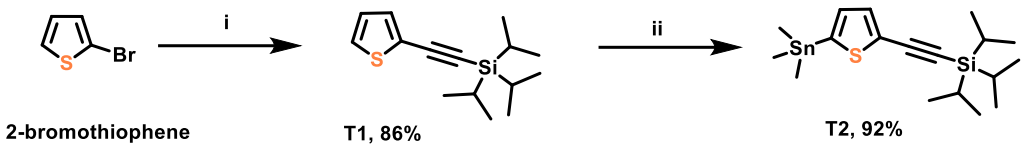
using surface xplorer software. All the experimental measurements were carried out at room temperature.

Computational Methods

All the DFT calculations were carried out by employing Gaussian09 software using B3LYP/6-31G(d) level of theory. The long alkyl chains were truncated to the methyl group to save computational cost. PCM solvation model was used to account for long-range interactions and the solvation effect of dichloromethane, respectively.

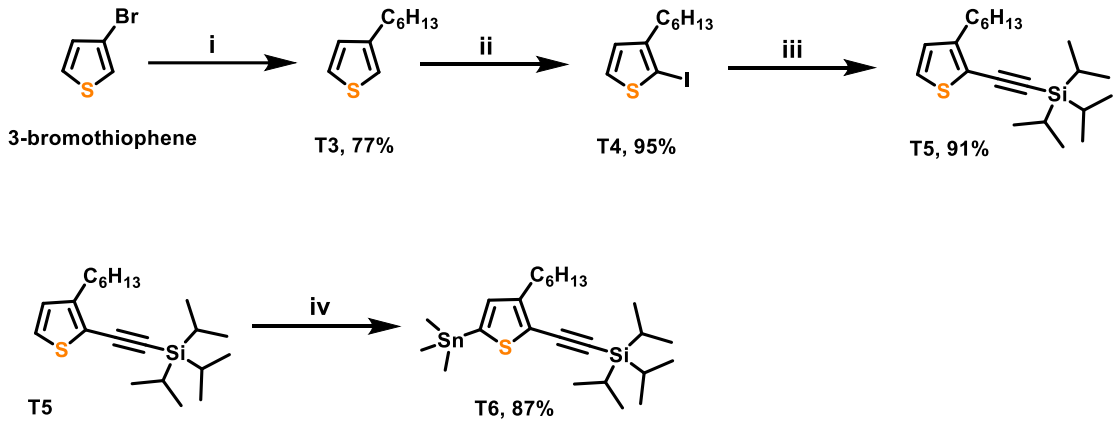
2. Experimental Procedures: Synthesis

Scheme-S1



Scheme S1: (i) (Triisopropylsilyl)acetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, RT, 12 h, (ii) **a**. *n*-BuLi, THF, -78 ^oC, 1 h; **b**. Me_3SnCl, -78 ^oC to RT, 12 h.

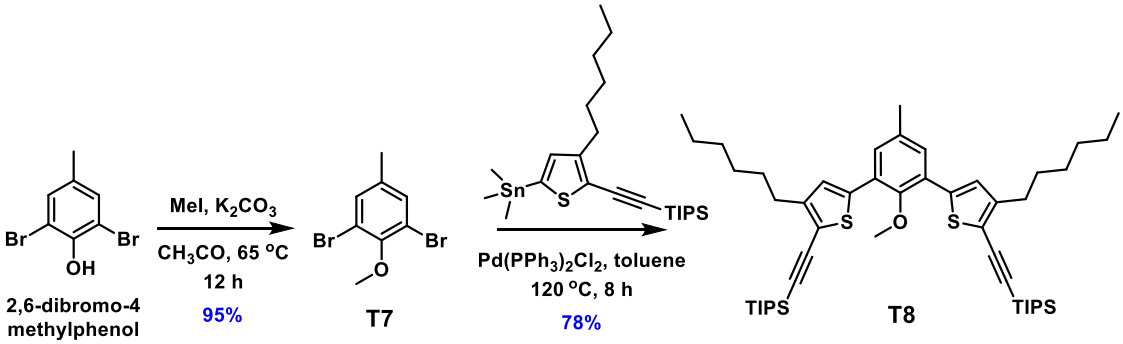
Scheme-S2



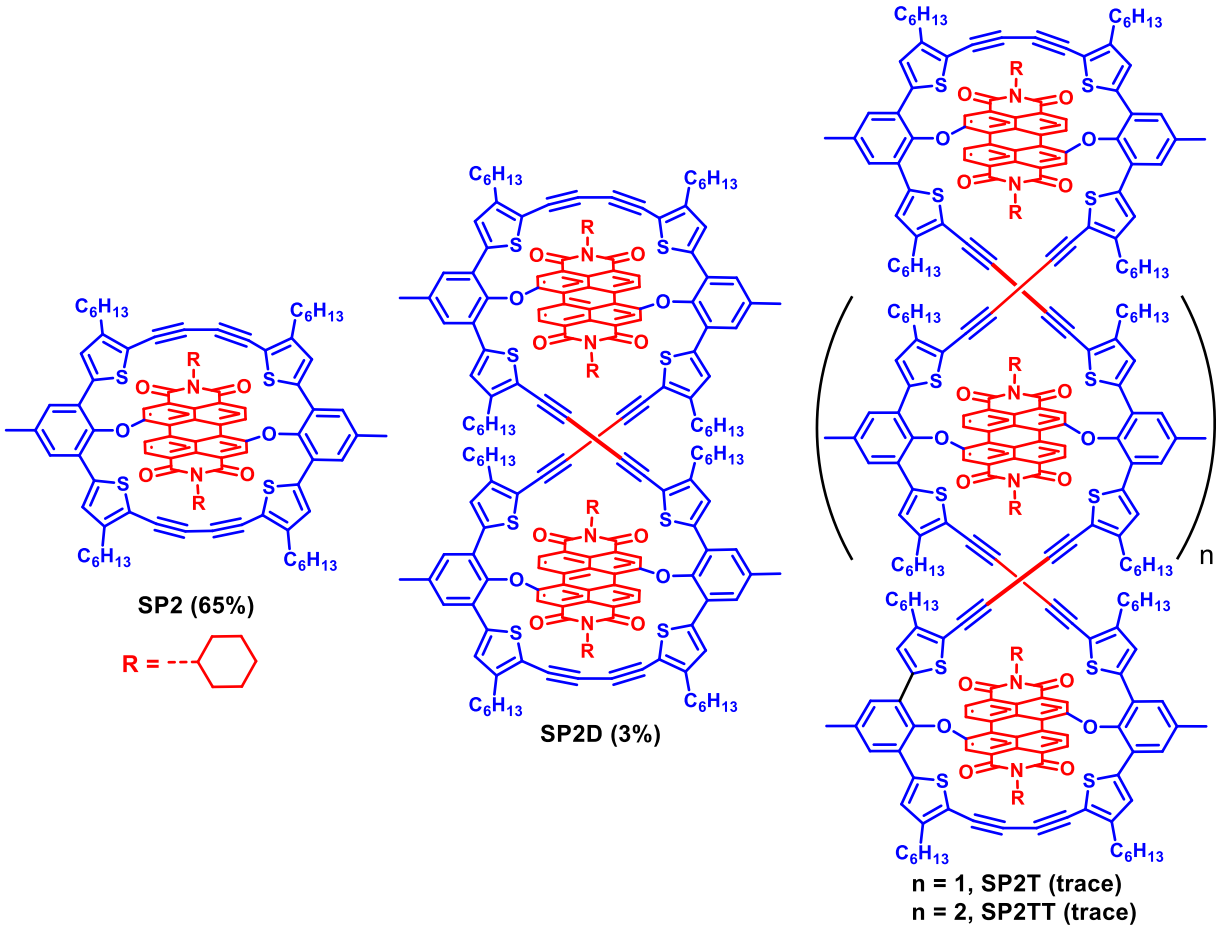
Scheme S2: (i) **a**. Mg, I_2, $C_6H_{13}Br$, THF, Reflux, 5 h; **b**. $Ni(dppp)Cl_2$, THF, Reflux, 15 h, (ii) NIS, CH_2Cl_2:AcOH (1:1), RT, 12 h, (iii) (Triisopropylsilyl)acetylene, $Pd(PPh_3)_2Cl_2$, CuI, DIPA:THF (1:1), 60 ^oC, 12 h, (iv) **a**. *n*-BuLi, THF, -78 ^oC, 45 min; **b**. Me_3SnCl, -78 ^oC to RT, 12 h.

Scheme-S3

*2,6-Dibromo-4-methylanisole (**T7**) was synthesized in quantitative yield by adapting a previously reported procedure.*[S1]



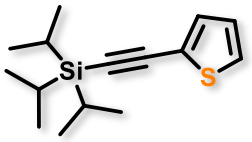
Scheme-S4



Scheme S4: Chemical Structure of **SP2**, **SP2D**, **SP2T**, and **SP2TT** molecules.

Synthesis:

Synthesis of Compound (T1):[S2]



30 mL schlenk tube was charged with 2-bromothiophene (1.5 g, 9.20 mmol), CuI (53 mg, 276.02 µmol), and $Pd(PPh_3)_2Cl_2$ (194 mg, 276.02 µmol). To that, THF (15 mL) and triethylamine (5 mL) were added, kept in an ice-cold solution, degassed for 30 min., and Triisopropylsilylacetylene (2.27 mL, 10.12 mmol) was added drop by drop. The mixture was stirred at room temperature for 12 h. After completion of the reaction, dichloromethane was added, and the resultant mixture was filtered through celite. The filtrate was extracted with water, and the solvent was removed under reduced pressure and dried over anhydrous Na2SO4. The crude product was purified by silica gel column chromatography using petroleum ether to obtain pure product triisopropyl(thiophen-2-ylethynyl)silane **T1**.

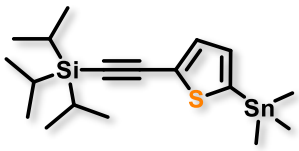
Nature and Yield: colorless oil, 2.1 g (86%).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.22-7.25 (m, 2H), 6.96 (dd, *J* = 5.0, 3.7 Hz, 1H), 1.13 (s, 21H).

^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] = 132.4, 126.9, 126.8, 123.6, 99.3, 95.3, 18.6, 11.3.

HRMS (ESI): *m/z* calculated for $C_{15}H_{25}SSi$ $[M+H]^+$: 265.1441, found: 265.1440.

Synthesis of Compound (T2):[S2]



In a 50 mL two-neck round bottom flask, a solution of triisopropyl(thiophen-2-ylethynyl)silane (1.5 g, 5.67 mmol) in 20 mL anhydrous THF was refrigerated to -78 ^{o}C under argon. To that, n-butyllithium (1.6 M, 3.9 mL, 6.24 mmol) was added dropwise over 15 minutes and stirred for 1 h at -78 ^{o}C. Later, a solution of trimethyltin chloride (1.47 g, 7.37 mmol) in THF was added dropwise, and the reaction mixture was warmed to room temperature and stirred for 12 h. The clear solution was diluted with diethyl ether and rinsed with water. The organic layer was dried over anhydrous Na_2SO_4, and the solvents were concentrated at reduced pressure. Triisopropyl((5-

(trimethylstannyl)thiophen-2-yl)ethynyl)silane (**T2**) was obtained as a light brownish oil without further purification.

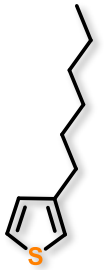
Nature and Yield: light brownish oil, 2.23 g (92%).

^{1}H NMR (200 MHz, $CDCl_3$): δ [ppm] = 7.32 (d, *J* = 3.37 Hz, 1H), 7.05 (d, *J* = 3.37 Hz, 1H) 1.11 (s, 21H), 0.36 (t, 9H).

HRMS (ESI): *m/z* calculated for $C_{18}H_{33}SSiSn$ $[M+H]^+$: 429.1089, found: 429.1098.

Scheme-S2

Synthesis of Compound (T3):[S3]



A 100 mL two-neck round bottom flask (1.04 g, 42.94 mmol) containing magnesium and I_2 was flame-dried under vacuum and filled with argon. To that, 30 mL of anhydrous THF was added and refluxed. 1-bromohexane (5.15 ml, 36.80 mmol) was added dropwise while keeping the THF refluxing. After that, the suspension was stirred for 5 h under argon until all of the magnesium had reacted. The hexylmagnesium bromide product was transferred to a second 100 mL two-neck flask chilled with ice and containing (582 mg, 1.07 mmol) of [Ni(dppp)Cl_2] and (5 g, 30.67 mmol) of 3-bromothiophene in 30 mL of anhydrous THF through a cannula needle. The reaction mixture was refluxed by stirring under argon for 15 h. After that, the reaction was cooled by pouring a solution of diluted HCl and ice. Following phase separation, the aqueous phase was extracted with ethyl acetate, and the content of organic phases was washed with (3×50 mL) of water and, one time, with 25 mL of saturated aq.$NaHCO_3$. The organic layer was dried over Na_2SO_4, and the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography using petroleum ether as the eluent to obtain the product (**T3**).

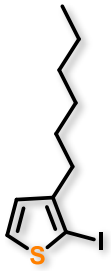
Nature and Yield: colorless oil, 4 g (77%).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.25 (dd, *J* = 5.01, 2.8 Hz, 1H), 6.93-6.96 (m, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.59-1.67 (m, 2H), 1.30-1.37 (m, 6H), 0.90 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] = 143.3, 128.3, 125, 119.7, 31.7, 30.5, 30.3, 29, 22.6, 14.1.

HRMS (ESI): *m/z* calculated for $C_{10}H_{17}S[M+H]^+$: 169.1051, found: 169.9772.

Synthesis of Compound (T4):



In a 50 mL round bottom flask, 3-hexylthiophene (**T3**) (3.1 g, 18.42 mmol) was dissolved in anhydrous dichloromethane and acetic acid (1:1, 30 mL). To that, N-iodosuccinimide (4.14 g, 18.42 mmol) was added portion-wise. The reaction mixture was stirred for 12 h at room temperature. After 12 h, the reaction was quenched with sodium thiosulfate, and the compound was extracted with ethyl acetate. The combined organic layer was washed with water (3×25 mL), dried over anhydrous Na_2SO_4, and concentrated to obtain a yellow oil. The crude product was purified by silica gel column chromatography using petroleum ether as the eluent to get the product (**T4**).

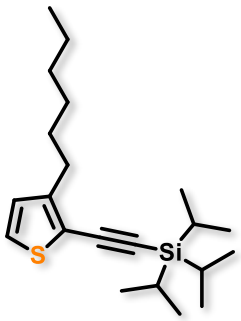
Nature and Yield: colorless oil, 5.15 g (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.39 (d, *J* = 5.5 Hz, 1H), 6.77 (d, *J* = 5.5 Hz, 1H), 2.56 (t, *J* = 6.5 Hz, 2H), 1.58 (m, 2H), 1.30-1.38 (m, 6H), 0.91 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] = 147.2, 130.3, 127.9, 73.9, 32.1, 31.6, 29.9, 28.9, 22.6, 14.1.

HRMS (ESI): *m/z* calculated for $C_{10}H_{15}IS$ $[M]^+$: 293.1939, found: 293.2957 and $C_{10}H_{16}IS$ $[M+H]^+$: 295.0017, found: 295.3023.

Synthesis of Compound (T5):



In a 30 mL Schlenk tube, 2-iodo-3-hexylthiophene (**T4**) (1 g, 3.40 mmol), CuI (26 mg, 136 μmol), $Pd(PPh_3)_2Cl_2$ (95 mg, 136 μmol) in anhydrous THF (8 mL), and diisopropyl amine (8 mL), was added. The schlenk tube was kept in an ice-cold solution, degassed for 30 min. and Triisopropylsilylacetylene (1 mL, 4.59 mmol) was added. The reaction mixture was stirred at 60 ^oC, for 12 h. Dichloromethane was added, and the resultant mixture was passed through celite before being washed with water. Under reduced pressure, the solvent was removed after drying over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography using petroleum ether as the eluent to obtain the product (**T5**).

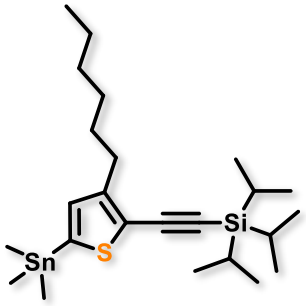
Nature and Yield: colorless oil, 1.08 g (91%).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.12 (d, *J* = 5.3 Hz, 1H), 6.84 (d, *J* = 5.3 Hz, 1H), 2.72 (t, *J* = 7.75 Hz, 2H), 1.58-1.65 (m, 2H), 1.28-1.35 (m, 6H), 1.14 (s, 21H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 148.6, 128.1, 125.5, 118.7, 99.1, 97.1, 31.7, 30.3, 29.7, 29.1, 22.6, 18.7, 14.1, 11.3.

HRMS (ESI): *m/z* calculated for $C_{21}H_{37}SSi$ $[M+H]^+$: 349.2380, found: 349.2375.

Synthesis of Compound (T6):



In a 100 mL round bottom flask, a solution of ((3-hexylthiophene-2-yl)ethynyl)triisopropylsilane (1.5 g, 4.30 mmol) in 20 mL of anhydrous THF was cooled to -78 ^oC under an argon atmosphere. Then 1.6 M n-butyllithium (3 mL, 4.73 mmol) was added dropwise and stirred for 45 minutes. The solution of trimethyl tinchloride (1.11 g, 5.59 mmol) in THF was added drop-by-drop to the reaction mixture, maintaining -78 ^oC for 30 minutes. The mixture was then warmed to room temperature and stirred for 12 h. The clear solution was diluted with diethyl ether and rinsed with water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. Triisopropyl((5-(trimethylstannyl)3-hexylthiophene-2-yl)ethynyl)silane (**T6**)

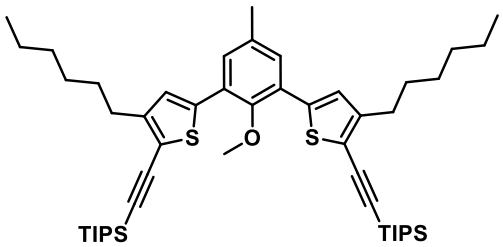
was obtained as the crude product as a light brownish oil and used directly without further purification.

Nature and Yield: light brownish oil, 1.92 g (87%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ [ppm] = 6.92 (s, 1H), 2.71 (t, *J* = 7.75 Hz, 2H), 1.59-1.65 (m, 2H), 1.29-1.36 (m, 6H), 1.13 (s, 21H), 0.88 (t, *J* = 7.17 Hz, 3H), 0.35 (t, 9H).

HRMS (ESI): *m/z* calculated for $C_{24}H_{45}SSiSn$ $[M+H]^+$: 513.2028, found: 513.2017.

Synthesis of Compound (T8):



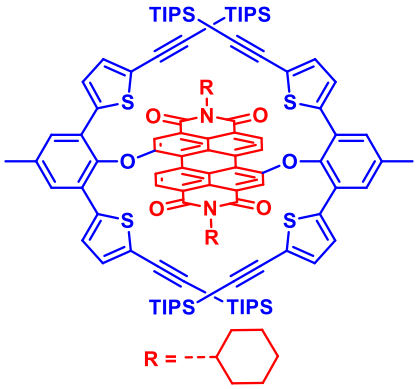
5 mL pressure tube was charged with compound 2,6-Dibromo-4-methylanisole (**T7**) (30 mg, 107.16 μmol), triisopropyl ((5-(trimethylstannyl)3-hexylthiophene-2-yl)silane (165 mg, 321.48 μmol), and $Pd(PPh_3)_2Cl_2$ (3 mg, 4.29 μmol) in 2 mL anhydrous toluene. The reaction mixture was subsequently heated to 120 ^oC for 8 h. Further, the reaction mixture was allowed to cool down to room temperature, followed by adding dichloromethane, passing through celite before water workup, and the solvent was removed by evaporation under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether to obtain pure product **T8**.

Nature and Yield: colourless semisolid, 68 mg (78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.31 (s, 2 H), 7.26 (s, 2 H), 3.56 (s, 3 H), 2.73 (t, *J* = 7.7 Hz, 4 H), 2.36 (s, 3 H), 1.67 (quin, *J* = 7.4 Hz, 4 H), 1.29 - 1.38 (m, 12 H), 1.15 (s, 43 H), 0.87 - 0.91 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 151.5, 148.6, 138.3, 134.1, 128.6, 127.9, 126.9, 119.3, 99.3, 98.2, 60.3, 31.7, 30.4, 29.9, 29.1, 22.6, 20.9, 18.7, 14.1, 11.3.

Synthesis of 2a:



10 mL pressure tube was charged with compound **1** (200 mg, 184.76 μmol), triisopropyl((5-(trimethylstannyl)thiophen-2-yl)ethynyl)silane (513 mg, 1.20 mmol), and $Pd(PPh_3)_2Cl_2$ (6.5 mg, 9.24 μmol) in 4 mL anhydrous toluene. The reaction mixture was subsequently heated to 140 ^oC for 12 h. Further, the reaction mixture was allowed to cool down to room temperature, followed by adding dichloromethane, passing through celite before water workup, and the solvent was removed by evaporation under reduced pressure. The crude product was purified by silica gel column chromatography using dichloromethane-petroleum ether (6:4 v/v) to obtain pure product **2a**.

Nature and Yield: Red solid, 296 mg (88%).

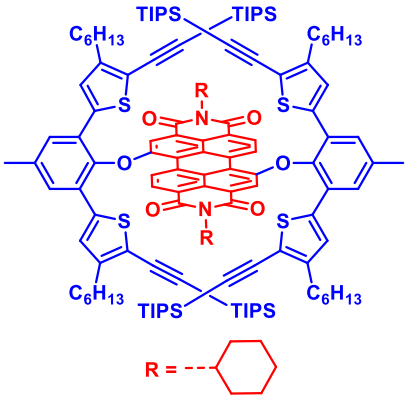
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 9.96 (d, *J* = 8.4 Hz, 2H), 8.66 (d, *J* = 8.4 Hz, 2H), 7.94 (s, 2H), 7.52 (s, 4H), 7.10 (d, *J* = 3.8 Hz, 4H), 6.83 (d, *J* = 3.8 Hz, 4H), 4.96 (t, *J* = 12.0 Hz, 2 H), 2.52 (s, 6H), 2.43-2.51 (m, 4H), 1.87 (d, *J* = 13.0 Hz, 4H), 1.70 (d, *J* = 12 Hz, 6H), 1.28-1.45 (m, 6H), 0.91-0.97 (m, 84 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] = 163.7, 163.4, 154.7, 143.5, 138.9, 137.1, 133.6, 132.5, 131.1, 129.9, 129.3, 129.2, 128.6, 126.1, 124.9, 124.3, 124, 122.5, 121.4, 118.3, 98.8, 97.2, 53.9, 29.7, 29, 26.5, 25.4, 21.1, 18.4, 11.1.

FT-IR (cm^{-1}): 2942, 2866, 2142, 1701, 1661, 1594, 1514, 1461, 1407, 1330, 1260, 1199, 882, 761, 679.

MALDI-TOF: *m/z* calculated for $C_{110}H_{131}N_2O_6S_4Si_4$ $[M+H]^+$: 1815.7967, found: 1815.75.

Synthesis of 2b:



10 mL pressure tube was charged with compound **1** (300 mg, 277.14 µmol), triisopropyl ((5-(trimethylstannyl)3-hexylthiophene-2-yl)silane (950 mg, 1.86 mmol), and $Pd(PPh_3)_2Cl_2$ (10 mg, 13.86 µmol) in 4 mL anhydrous toluene were added. The reaction mixture was subsequently heated to 140 ^oC for 12 h. Further, the reaction mixture was cooled down to room temperature, followed by adding dichloromethane and passing through celite before water workup, and the solvent was removed by evaporation under reduced pressure. The crude product was purified by silica gel column chromatography using dichloromethane-petroleum ether (5:5 v/v) to obtain pure product **2b**.

Nature and Yield: Red solid, 511 mg (86%).

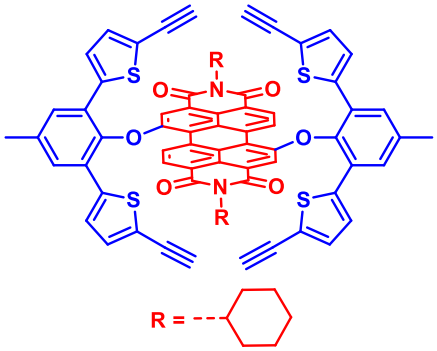
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.06 (d, *J* = 9.2 Hz, 2H), 8.70 (d, *J* = 9.2 Hz, 2H), 7.96 (s, 2H), 7.50 (s, 4H), 7.11 (s, 4H), 4.95 (t, *J* = 12.01 Hz, 2 H), 2.51 (s, 6H), 2.41-2.50 (m, 4H), 2.29 (ddd, *J* = 14.7, 9.0, 6.1 Hz, 4 H), 2.18 (ddd, *J* = 14.7, 8.6, 6.5 Hz, 4 H), 1.87 (d, *J* = 12.2 Hz, 4 H), 1.69 (d, *J* = 9.2 Hz, 6 H), 1.20-1.48 (m, 8 H), 0.94-1.00 (m, 84 H), 0.70-0.92 (m, 24 H), 0.55-0.61 (m, 6 H), 0.53 (t, *J* = 7.61 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.7, 163.2, 154.9, 148.8, 142.9, 137.3, 133.8, 130.6, 129.8, 129.2, 128.9, 127.1, 124.9, 124.2, 122.4, 120.9, 119.3, 118, 99, 98.5, 53.9, 31.2, 29.6, 29.5, 29, 28.8, 26.5, 25.4, 22.3, 21.1, 18.5, 13.9, 11.1.

FT-IR (cm^{-1}): 2922, 2856, 2136, 1702, 1655, 1599, 1469, 1403, 1329, 1263, 1198, 881, 750, 675.

MALDI-TOF: *m/z* calculated for $C_{134}H_{179}N_2O_6S_4Si_4$ $[M+H]^+$: 2152.1723, found: 2152.13.

Synthesis of 3a:



To a 25 mL round bottom flask, compound **2a** (100 mg, 55.04 μmol) was added by dissolving in 10 mL anhydrous THF under an argon atmosphere, then tetrabutylammonium fluoride hydrate (246 mg, 825.61 μmol) was added. The solution was stirred at room temperature for 15 minutes. The reaction was monitored by TLC and confirmed the product. Later, the mixture was quenched with water, and the workup was done with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, and the solvents were concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using dichloromethane-petroleum ether (8:2 v/v) as eluent, affording compound **3a**.

Nature and Yield: Red solid, 64 mg (97%).

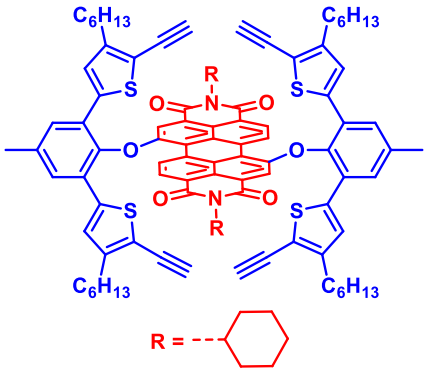
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 9.82 (d, *J* = 8.4 Hz, 2H), 8.65 (d, *J* = 8.4 Hz, 2H), 7.90 (s, 2H), 7.54 (s, 4H), 7.09 (d, *J* = 3.8 Hz, 4H), 6.91 (d, *J* = 3.8 Hz, 4H), 4.96 (t, *J* = 12.0 Hz, 2H), 3.76 (s, 1H), 3.18 (s, 3H), 2.53 (s, 6H), 2.49-2.44 (m, 4H), 1.85-1.89 (m, 4H), 1.72 (m, 6H), 1.40 (q, *J* = 12.8 Hz, 4H), 1.28-1.33 (m, 2H).

13C NMR (100 MHz, CDCl3): δ [ppm] = 163.8, 163.4, 154.8, 143.9, 139.1, 137.2, 133.4, 133.3, 131.1, 129.9, 129.4, 129.1, 128.5, 126.3, 124.8, 124.1, 122.9, 122.6, 121.7, 118.4, 82.5, 76.4, 54.0, 31.6, 29.1, 26.5, 25.4, 21.1, 14.1

FT-IR (cm^{-1}): 3309, 3253, 2957, 2929, 2873, 2095, 1767, 1721, 1693, 1655, 1590, 1459, 1329, 1263, 1193, 733.

MALDI-TOF: *m/z* calculated for $C_{74}H_{51}N_2O_6S_4$ $[M+H]^+$: 1191.2630, found: 1191.430.

Synthesis of 3b:



The synthesis of **3b** followed a similar process to that of **3a**. In 15 mL THF, **2b** (200 mg, 92.87 μmol) and Tetrabutylammonium fluoride hydrate (260 mg, 928.73 μmol) were added and stirred at room temperature for 15 minutes. The completion of the reaction was monitored by TLC. The crude product was purified by silica gel column chromatography using dichloromethane-petroleum ether (7:3 v/v) as eluent, affording compound **3b**.

Nature and Yield: Red solid, 138 mg (97%).

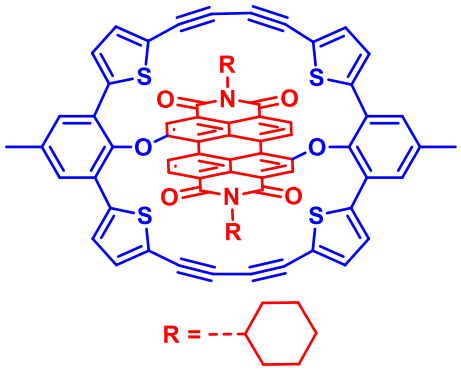
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.03 (d, *J* = 8.5 Hz, 2 H), 8.70 (d, *J* = 8.5 Hz, 2 H), 7.90 (s, 2 H), 7.54 (s, 4 H), 7.14 (s, 4 H), 4.95 (t, *J* = 12.1 Hz, 2 H), 3.29 (s, 4 H), 2.53 (s, 6 H), 2.41-2.50 (m, 4 H), 2.29-2.38 (m, 4 H), 2.20-2.28 (m, 4 H), 1.87 (d, *J* = 12.8 Hz, 4 H), 1.68 (t, *J* = 10.6 Hz, 6H), 1.31-1.47 (m, 6 H), 0.93-1.05 (m, 16 H), 0.76-0.89 (m, 16 H), 0.66 (t, *J* = 6.6 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.7, 163.3, 154.8, 149.2, 143.1, 137.5, 137.2, 133.7, 130.5, 129.9, 129.3, 129.2, 128.6, 127.2, 124.9, 124.1, 122.5, 121.3, 118.1, 117.9, 84.5, 76.2, 53.9, 31.1, 29.5, 29.2, 29.0, 28.8, 26.5, 25.4, 22.5, 21.1, 13.9

FT-IR (cm^{-1}): 3306, 3259, 2960, 2923, 2858, 2100, 1699, 1657, 1590, 1405, 1330, 1258, 1094, 1018, 796.

MALDI-TOF: *m/z* calculated for $C_{98}H_{99}N_2O_6S_4$ $[M+H]^+$: 1527.6386, found: 1527.620.

Synthesis of molecule SP1:[S4]



In a 250 mL two-neck round bottom flask, compound **3a** (50 mg, 41.97 μmol) was dissolved in 200 mL anhydrous THF. Then, copper (I) chloride (42 mg, 419.65 μmol) and N,N,N′,N′-tetramethylethylenediamine (98 mg, 839.30 μmol) were added dropwise to the solution of **3a**. The reaction mixture was stirred for 6 hours. The progress of the reaction was monitored by TLC. Once the reaction was completed, the mixture was poured into (3×40 mL) CH_2Cl_2 before being washed with water. The organic layer was dried over anhydrous Na_2SO_4, and then the solvents were concentrated an under reduced pressure. Product **SP1** (48 mg, 96%) was successfully obtained without purification. The compound solubility is very poor, and hence ^{13}C cannot be recorded.

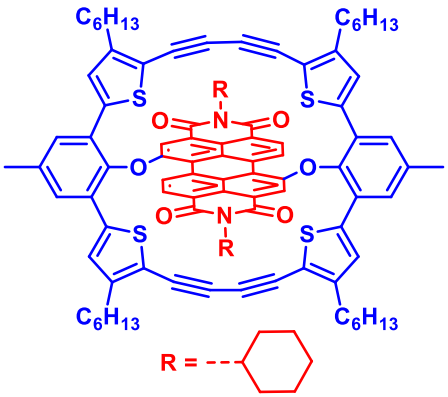
Nature and Yield: Red solid, 48 mg (96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 9.71 (d, *J* = 8.9 Hz, 2 H), 8.63 (d, *J* = 8.1 Hz, 2 H), 7.71 (s, 4 H), 7.47 (s, 2 H), 7.24 (d, *J* = 4.0 Hz, 4 H), 6.82 (d, *J* = 3.8 Hz, 4 H), 4.90-4.98 (m, 2 H), 2.62 (s, 6 H), 2.45-2.47 (s, 4 H), 1.87 (*J* = 10.4 Hz, 4 H), 1.7-1.74 (s, 6 H), 1.38-1.39 (m, 6 H).

FT-IR (cm^{-1}): 2958-2851, 2155, 2108, 1697, 1653, 1593, 1512, 1451, 1325, 1261, 1161, 811.

MALDI-TOF: *m/z* calculated for $C_{74}H_{47}N_2O_6S_4$ $[M+H]^+$: 1187.2317, found: 1187.11.

Synthesis of molecule SP2:[S4]



In a 500 mL two-neck round bottom flask, compound **3b** (100 mg, 65.44 μmol) was dissolved in 350 mL anhydrous THF. Then, copper (I) chloride (65 mg, 654.40 μmol) and N,N,N′,N′-tetramethylethylenediamine (152 mg, 1.31 mmol) were added to the solution of **3b**. The reaction mixtures were stirred for 12 hours and progress was monitored by TLC. Once the reaction was completed, the reaction mixture was poured into (5×40 mL) CH_2Cl_2 before being washed with water. The organic layer was dried over anhydrous Na_2SO_4, and then the solvents were concentrated an under reduced pressure. The crude product was purified by silica gel column chromatography using dichloromethane-petroleum ether (6:4 (v/v)) to yield **SP2** and **SP2D**.

Nature and Yield: **SP2** = Red solid, 65 mg (65%), **SP2D** = Red solid, 6 mg (3%).

SP2:

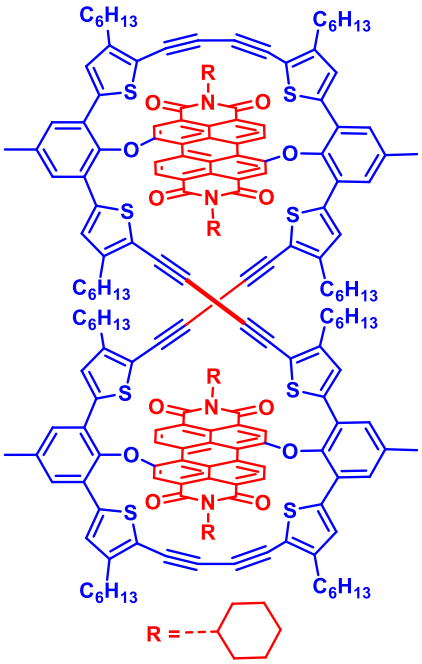
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 9.78 (d, *J* = 8.8 Hz, 2H), 8.64 (d, *J* = 8.8 Hz, 2H), 7.66 (s, 4H), 7.46 (s, 2H), 7.08 (s, 4H), 4.96 (t, *J* = 12.0 Hz, 2 H), 2.59 (s, 6H), 2.43-2.52 (m, 4 H), 2.36-2.42 (m, 8 H), 1.87 (d, *J* = 12.6 Hz, 4 H), 1.69-1.71 (m, 6H), 1.40-1.52 (m, 12 H), 1.29-1.32 (m, 2 H), 1.19 (m, 24H), 0.80-0.85 (m, 12 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] = 164, 163.6, 153.3, 146.1, 142.8, 140.8, 137.2, 133.4, 130.4, 129.8, 129.1, 128.7, 128.6, 127.9, 124.7, 123.4, 122.5, 121.5, 120.2, 116.1, 84.1, 82.7, 53.7, 31.3, 30.1, 29.7, 29, 28.7, 26.5, 25.4, 22.6, 21.6, 14.

FT-IR (cm^{-1}): 2953, 2925, 2850, 2165, 2130, 1693, 1655, 1599, 1403, 1329, 1254, 1016, 801.

MALDI-TOF: *m/z* calculated for $C_{98}H_{95}N_2O_6S_4$ $[M+H]^+$: 1523.6073, found: 1523.56.

Dimer (SP2D):



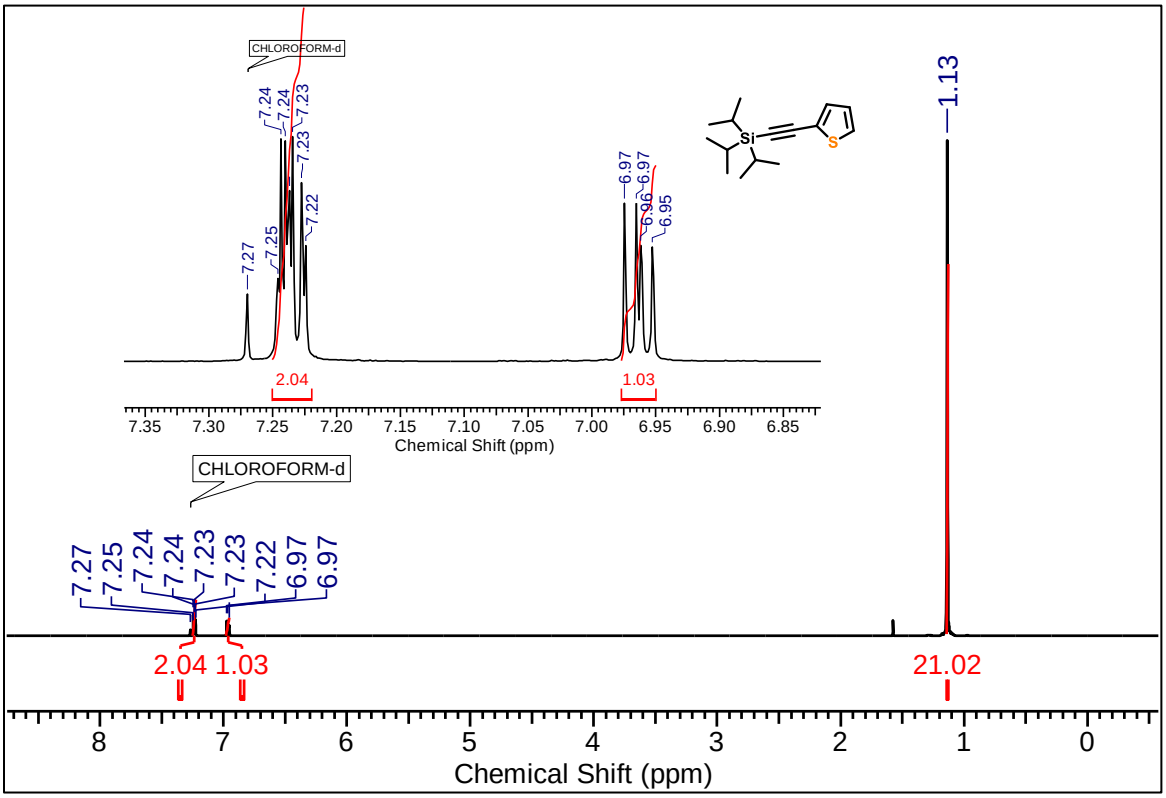
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 9.84 (d, *J* = 8.5 Hz, 2 H), 9.71 (d, *J* = 8.5 Hz, 2 H), 8.58 (dd, *J* = 8.4, 5.8 Hz, 4 H), 7.89 (d, *J* = 8.4 Hz, 4 H), 7.74 (s, 2 H), 7.72 (s, 2 H), 7.52 (s, 2 H), 7.44 (s, 2 H), 7.21 (d, *J* = 7.3 Hz, 4 H), 7.06 (s, 2 H), 6.99 (s, 2 H), 4.93 (t, *J* = 11.4 Hz, 4 H), 2.54 (s, 12 H), 2.41-2.48 (m, 16 H), 2.25-2.35 (m, 8 H), 1.83-1.85 (d, *J* = 10.4 Hz, 8 H), 1.66 (br. s., 12 H), 1.52 (br. s., 12 H), 1.31-1.42 (m, 12 H), 1.23 (br. s., 24 H), 1.04-1.08 (m, 4 H), 0.78-0.89 (m, 24 H), 0.67-0.76 (m, 12 H), 0.44-0.50 (m, 12 H).

^{13}C NMR (125 MHz, $CDCl_3$) : δ [ppm] = 163.7, 163.7, 163.5, 163.4, 155.3, 155, 151.6, 151.4, 144.8, 144.7, 142.7, 142.3, 139.6, 139.5, 139.4, 139.1, 137.1, 133.8, 133.7, 131.9, 131.4, 130.9, 130.1, 130.0, 129.9, 129.7, 129.6, 129.4, 129.2, 128.7, 128.5, 128.0, 127.9, 127.8, 127.7, 127, 126.8, 125.3, 125.2, 124.2, 124.1, 122.7, 121.6, 121.3, 119.7, 118.3, 118.2, 117.3, 117.1, 85.3, 85.2, 84.3, 81.1, 53.8 , 53.8, 31.4, 31.2, 30.2, 30.0, 29.9, 29.8, 29.8, 29.7, 29.5, 29.4, 29.4, 28.9, 28.8, 28.7, 28.5, 26.5, 25.4, 22.5, 22.2, 22.2, 21.1, 14, 13.9.

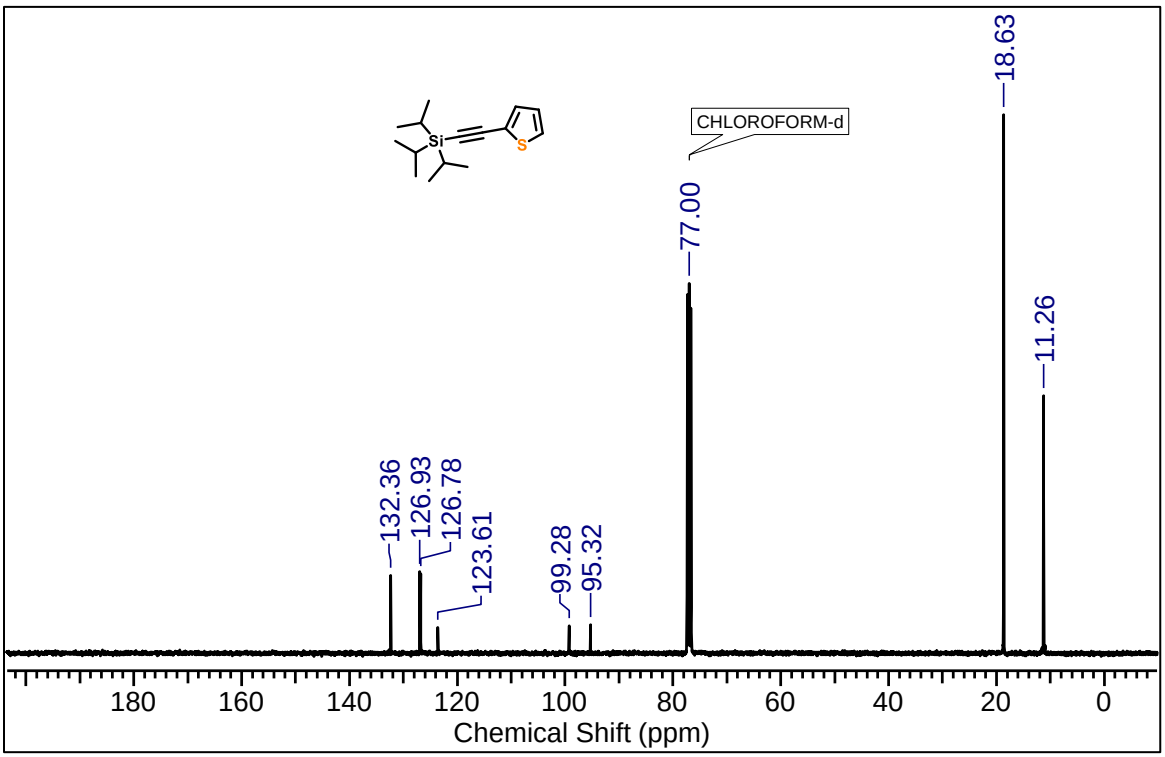
FT-IR (cm^{-1}): 2954, 2926, 2852, 2150, 2102, 1738, 1702, 1655, 1590, 1403, 1329, 1254, 1198, 750.

MALDI-TOF: *m/z* calculated for $C_{196}H_{189}N_4O_{12}S_8$ $[M+H]^+$: 3046.2067, found: 3046.6940 and $C_{196}H_{188}N_4NaO_{12}S_8$ $[M+Na]^+$: 3068.1887, found: 3068.1258

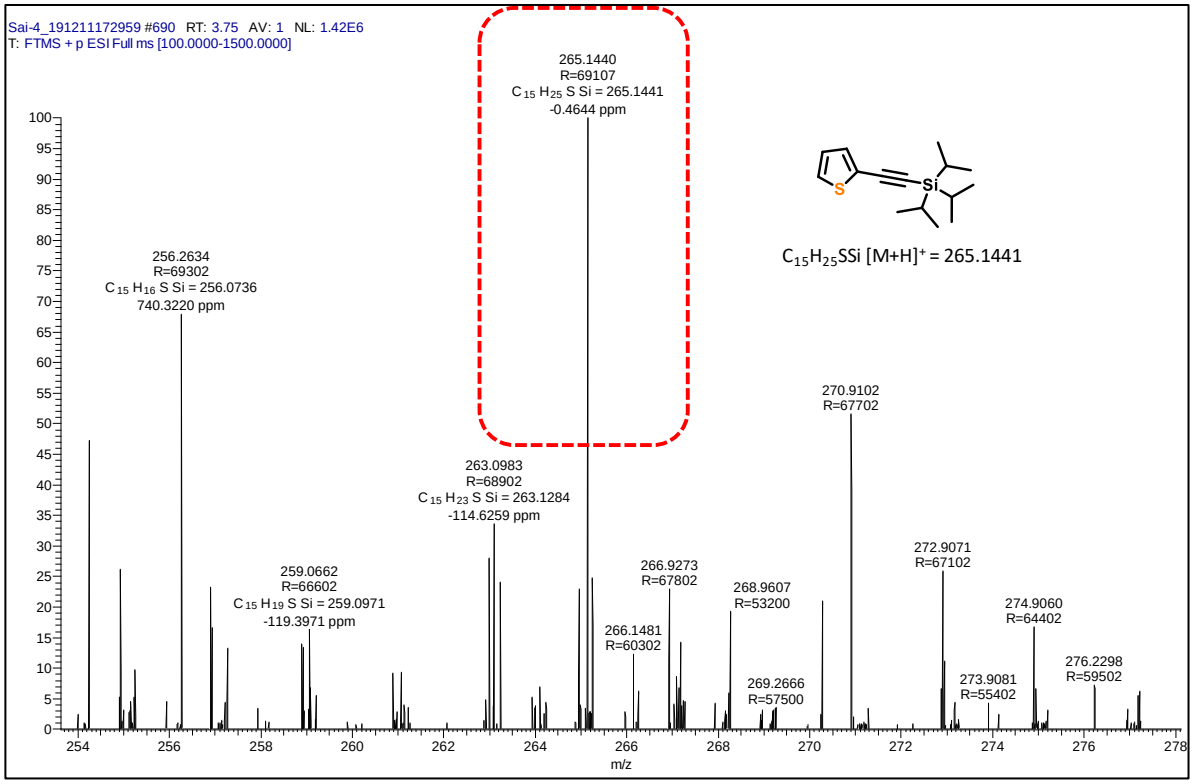
^{1}H, ^{13}C NMR Spectra, and Mass Data



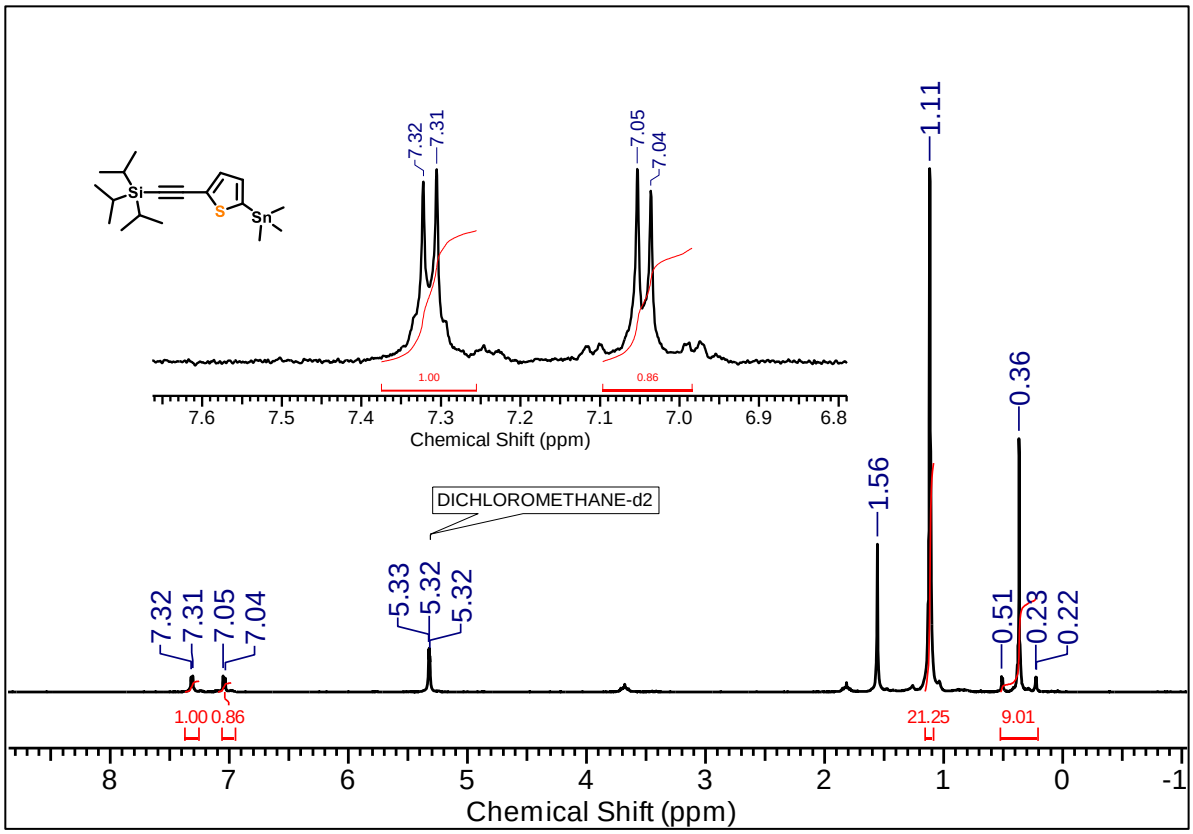
^{1}H NMR (500 MHz) spectrum of **T1** in $CDCl_3$ at 298 K.



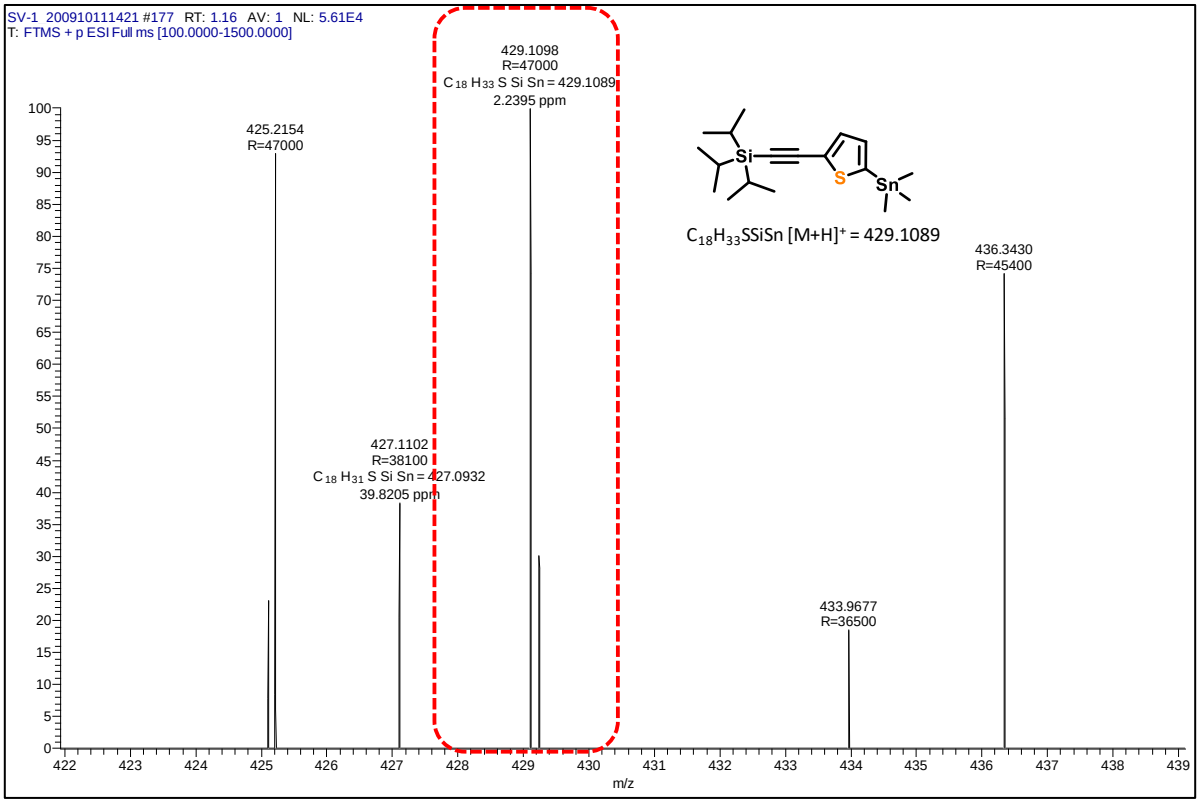
^{13}C NMR (125 MHz) spectrum of **T1** in $CDCl_3$ at 298 K.



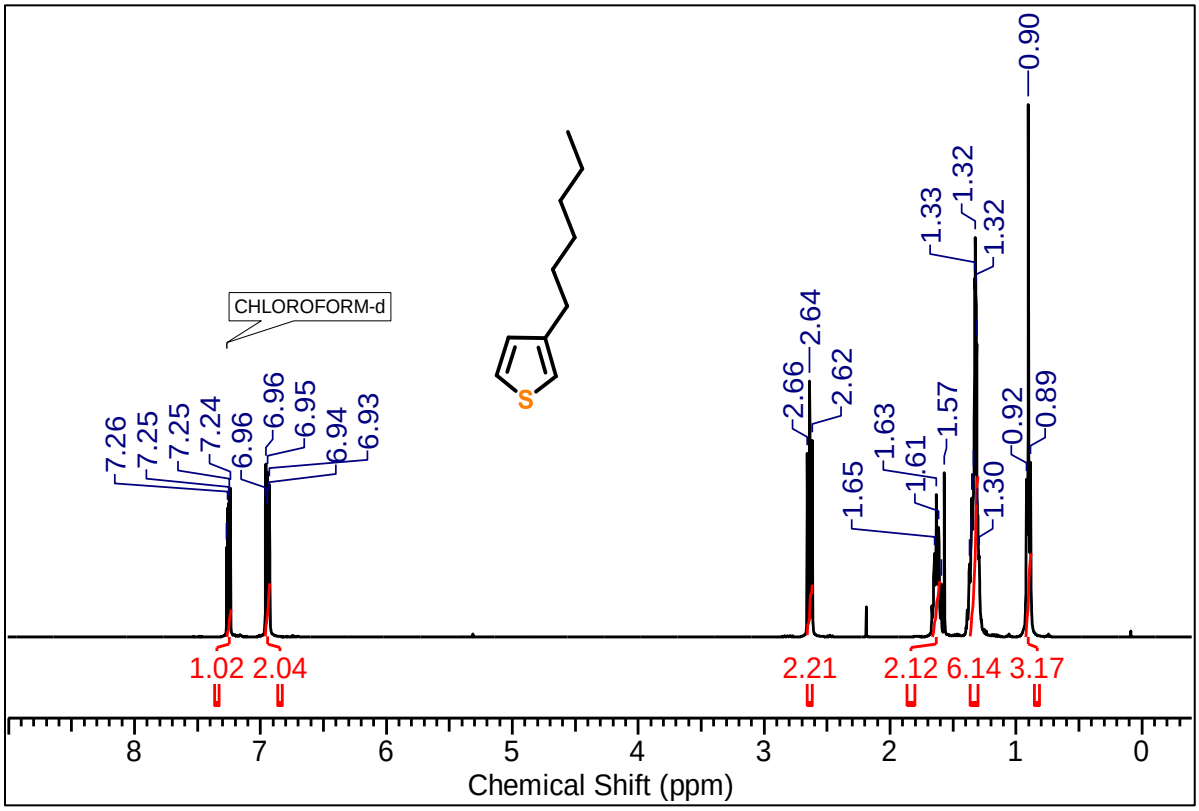
HRMS of **T1**.



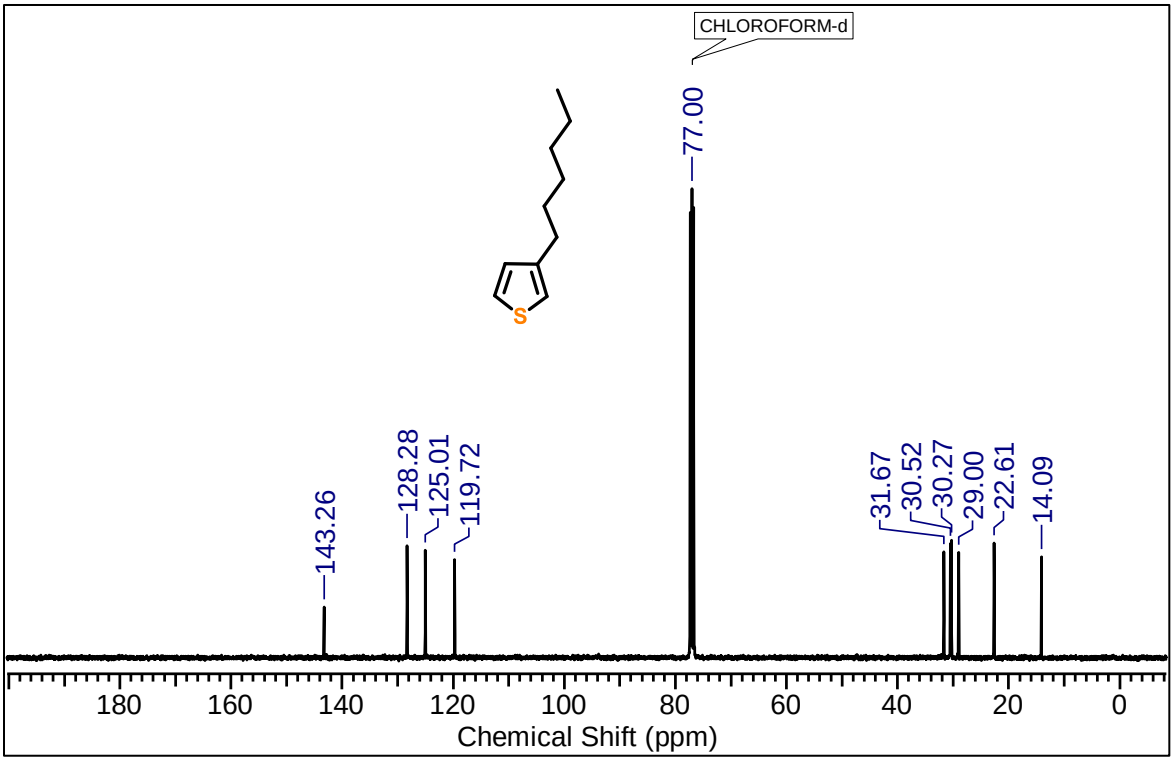
^{1}H NMR (200 MHz) spectrum of **T2** in CD_2Cl_2 at 298 K.



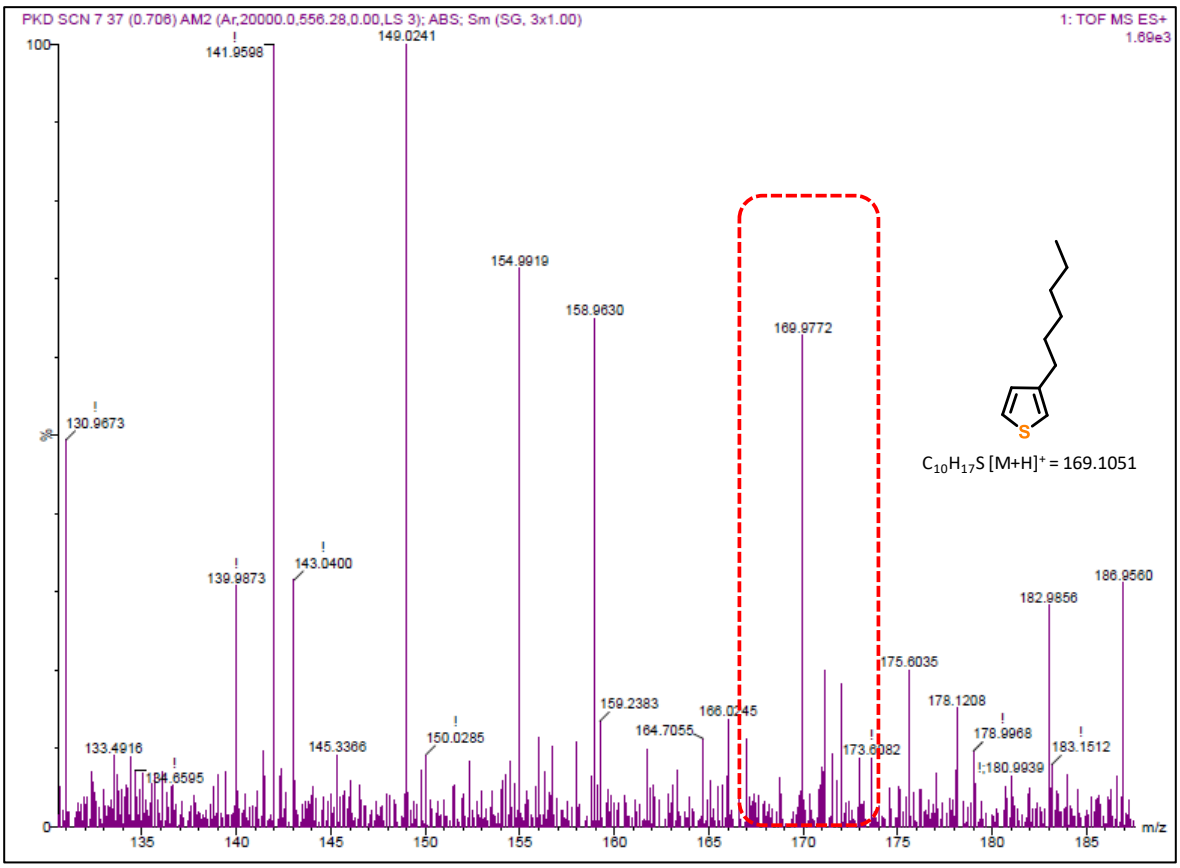
HRMS of **T2**.



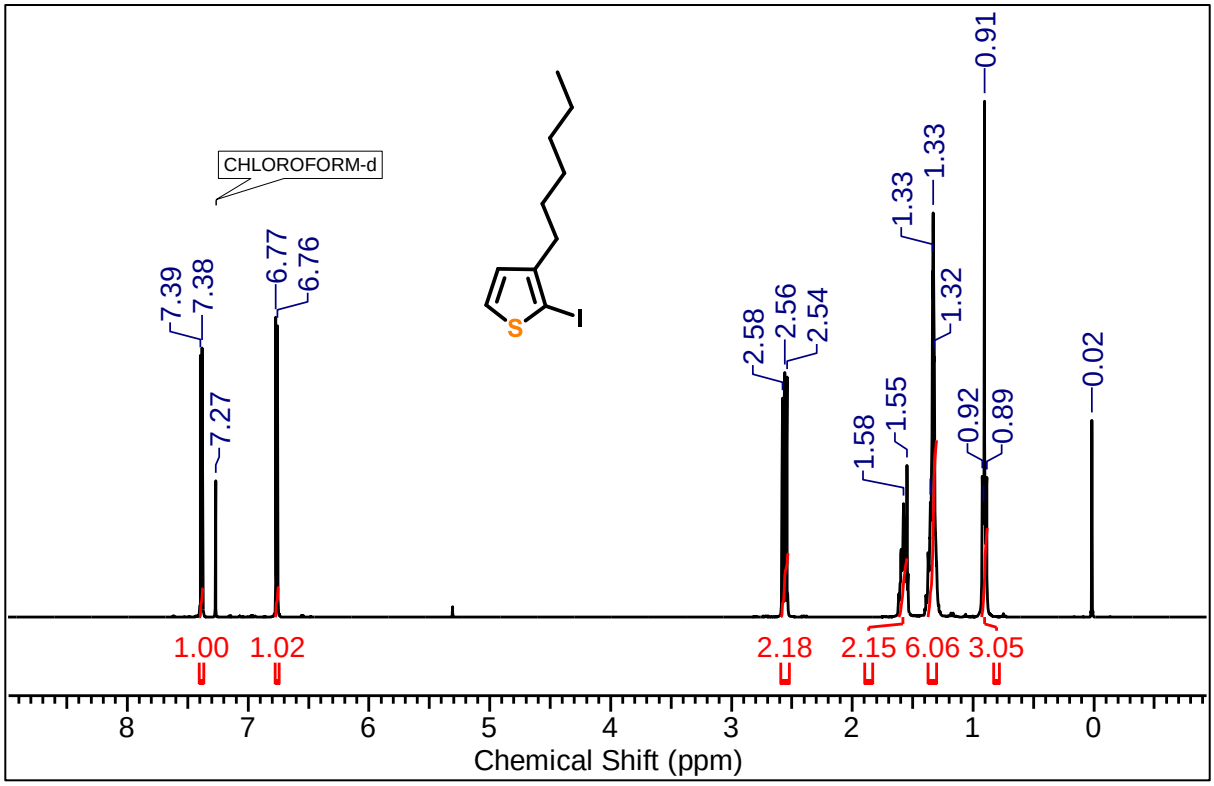
^{1}H NMR (500 MHz) spectrum of **T3** in $CDCl_3$ at 298 K.



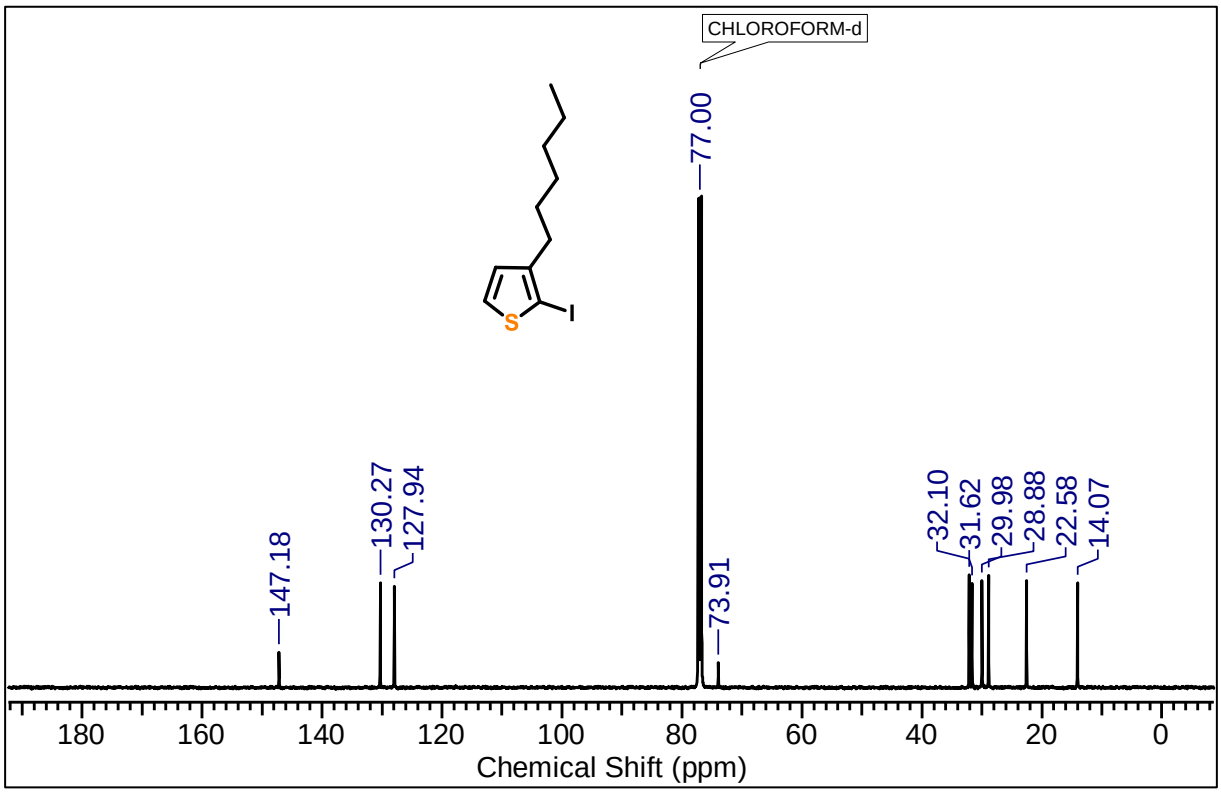
^{13}C NMR (125 MHz) spectrum of **T3** in $CDCl_3$ at 298 K.



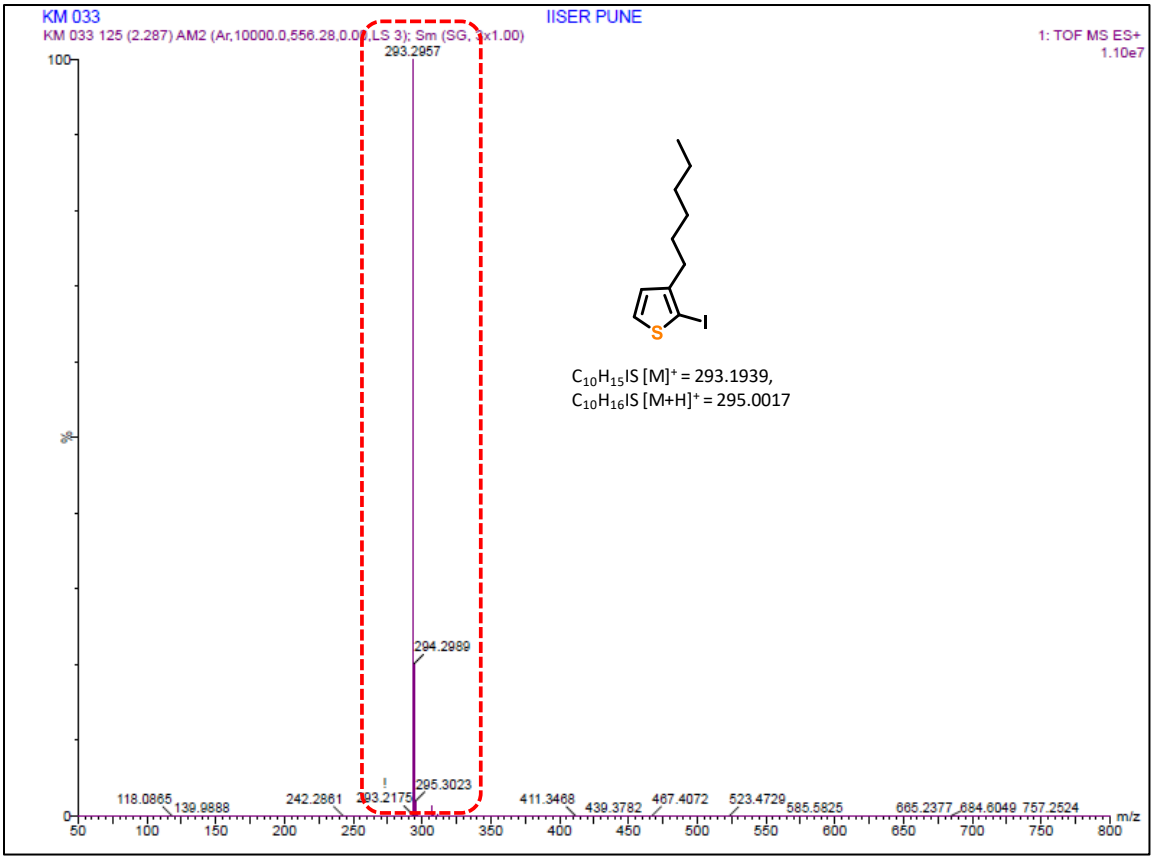
HRMS of **T3**.



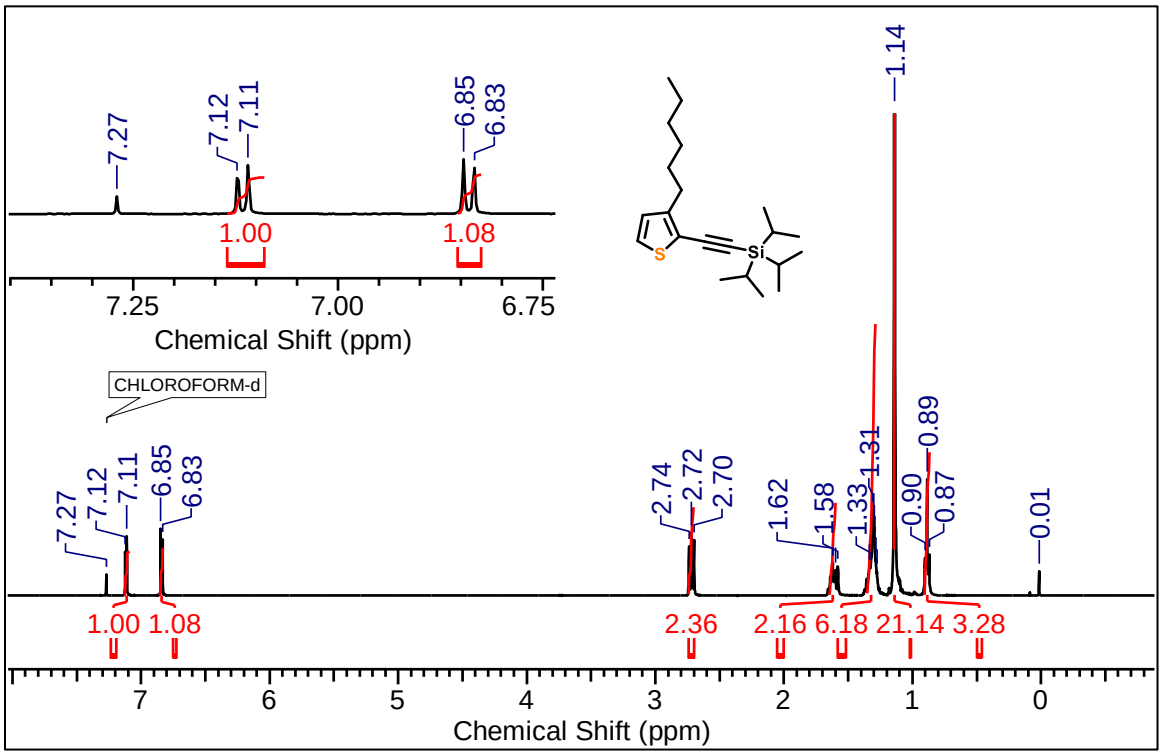
[1]H NMR (400 MHz) spectrum of **T4** in $CDCl_3$ at 298 K.



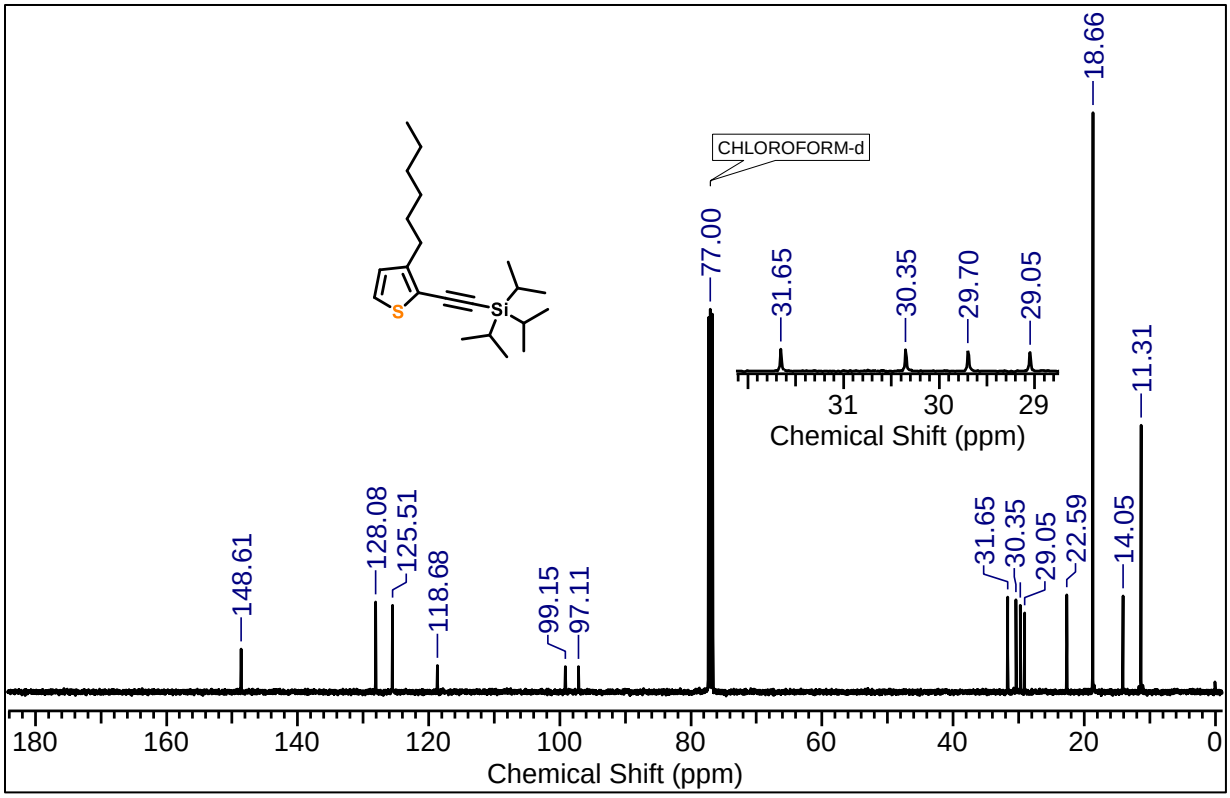
[13]C NMR (100 MHz) spectrum of **T4** in $CDCl_3$ at 298 K.



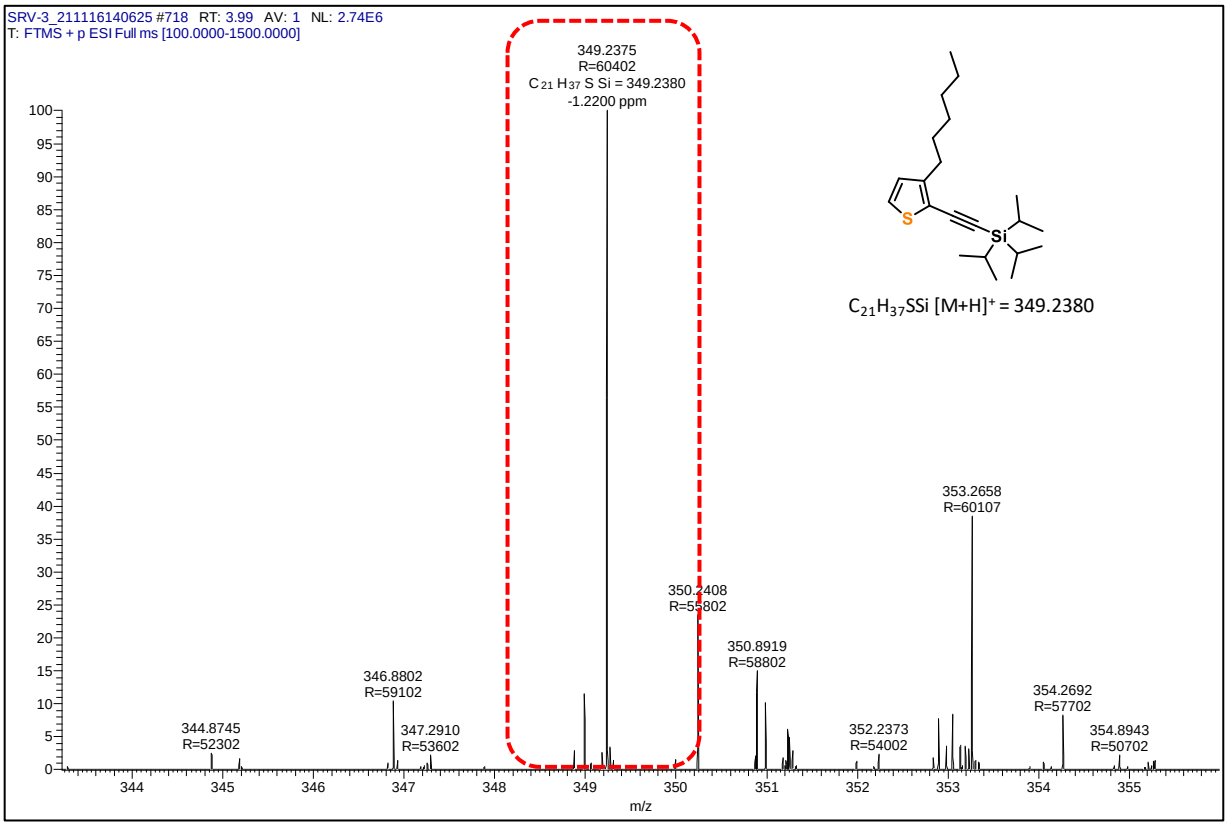
HRMS of **T4**.



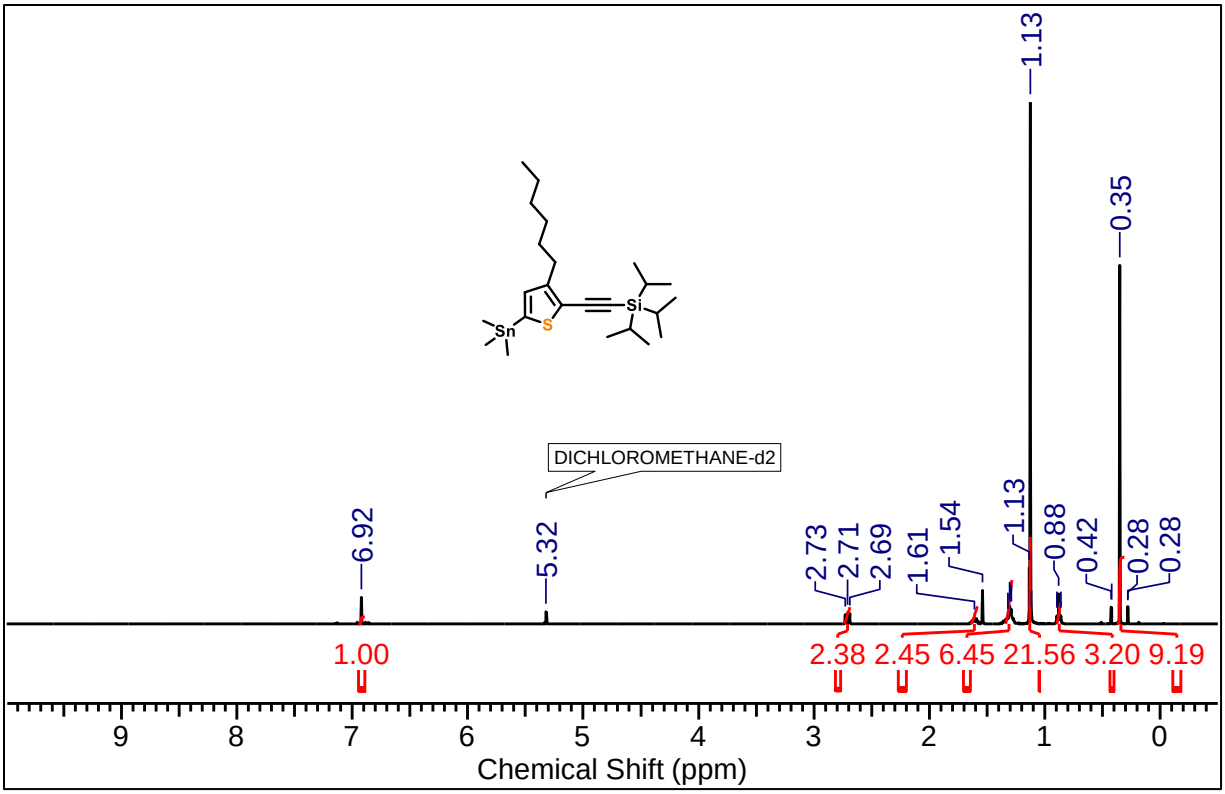
^{1}H NMR (500 MHz) spectrum of **T5** in $CDCl_3$ at 298 K.



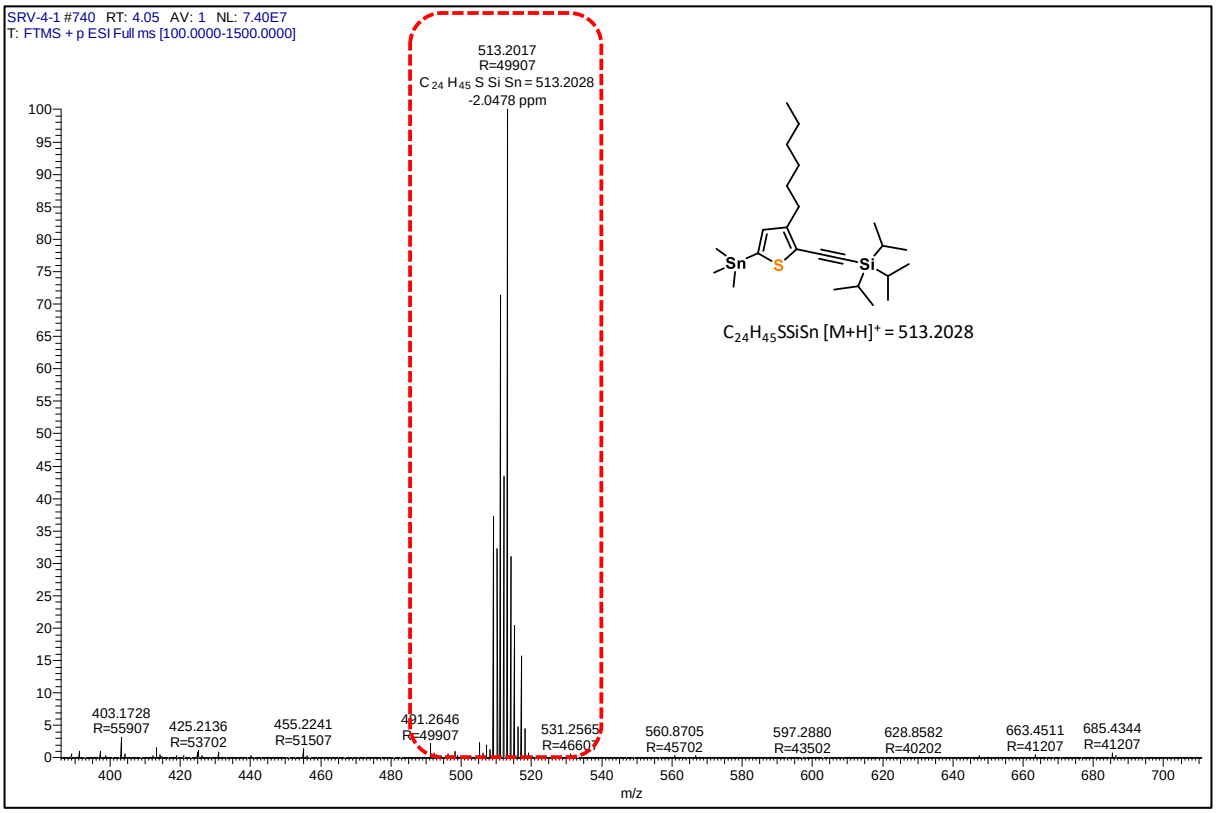
^{13}C NMR (100 MHz) spectrum of **T5** in $CDCl_3$ at 298 K.



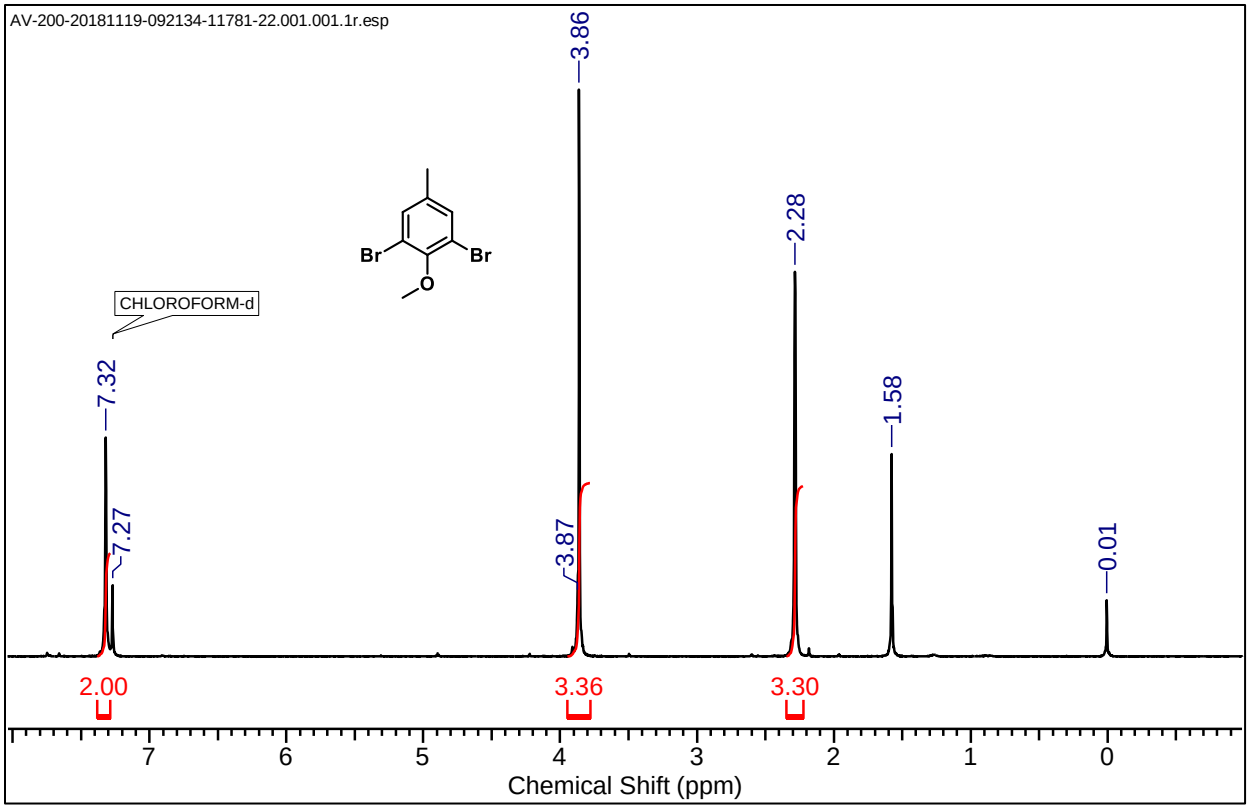
HRMS of **T5**.



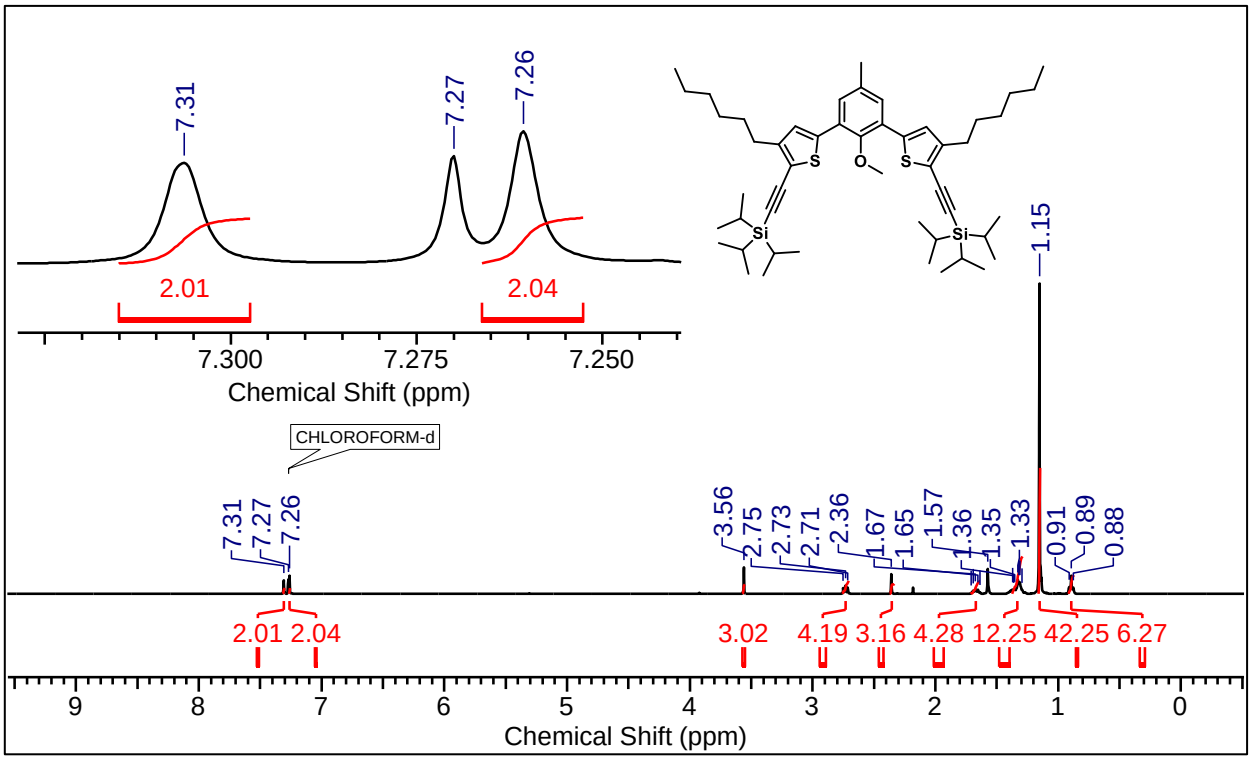
^{1}H NMR (400 MHz) spectrum of **T6** in $CDCl_3$ at 298 K.



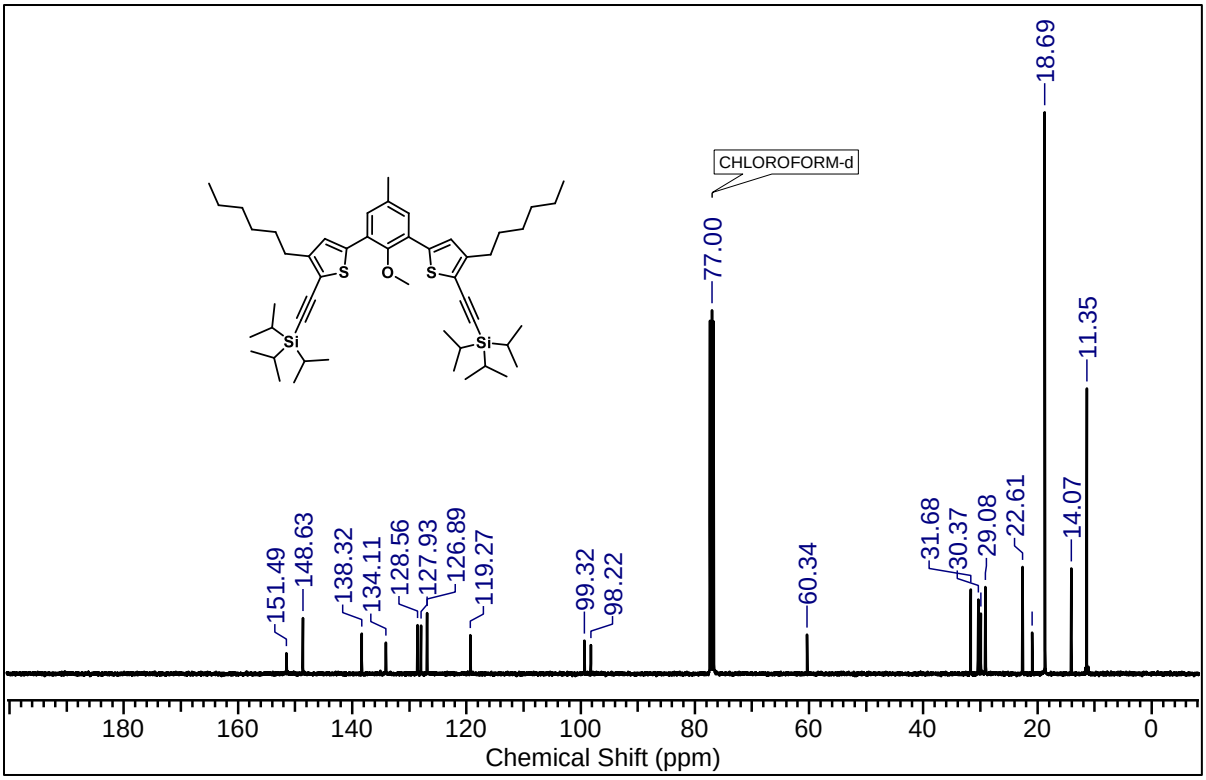
HRMS of **T6**.



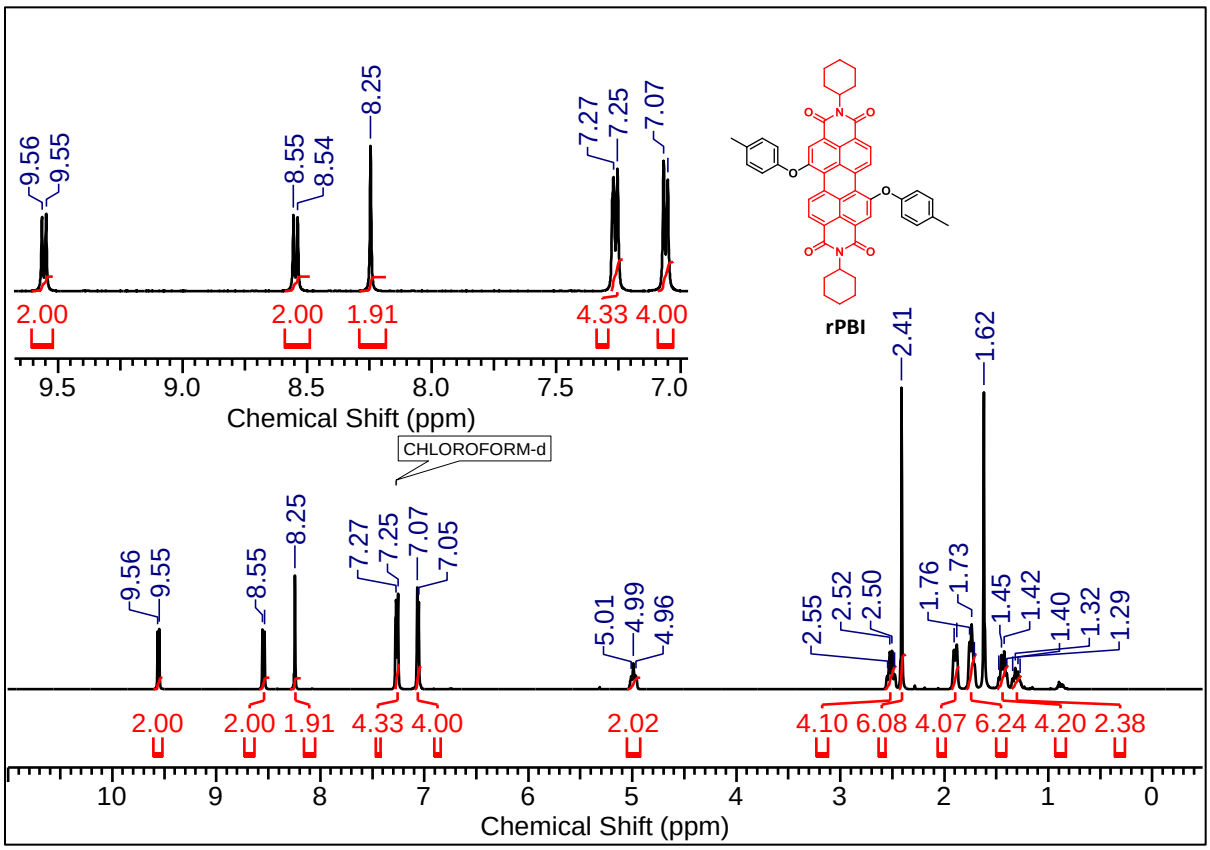
^{1}H NMR (200 MHz) spectrum of **T7** in $CDCl_3$ at 298 K.



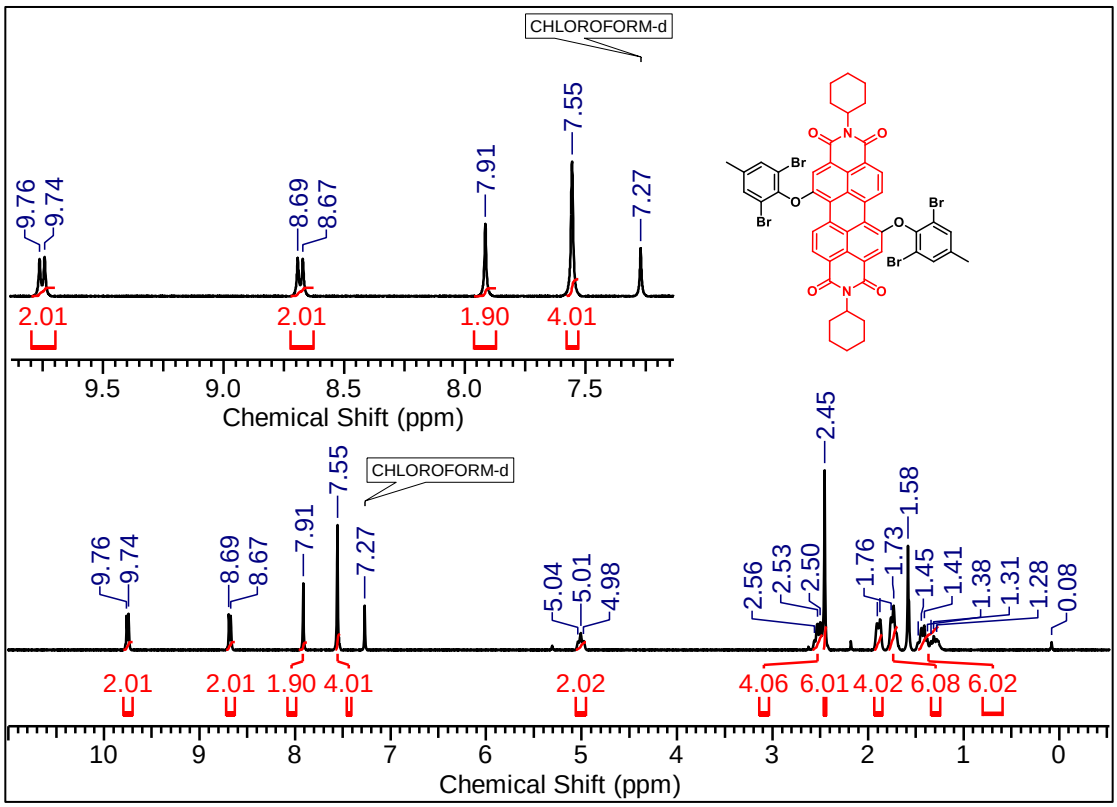
^{1}H NMR (400 MHz) spectrum of **T8** in $CDCl_3$ at 298 K.



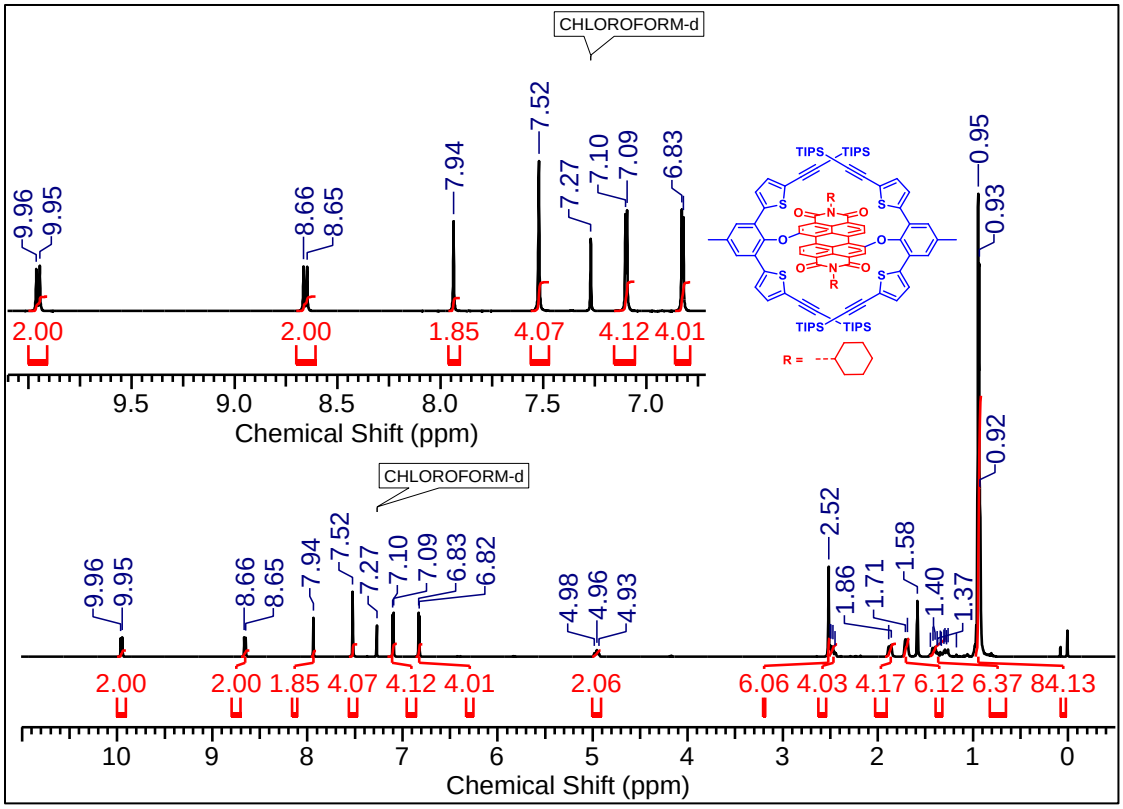
^{13}C NMR (125 MHz) spectrum of **T8** in $CDCl_3$ at 298 K.



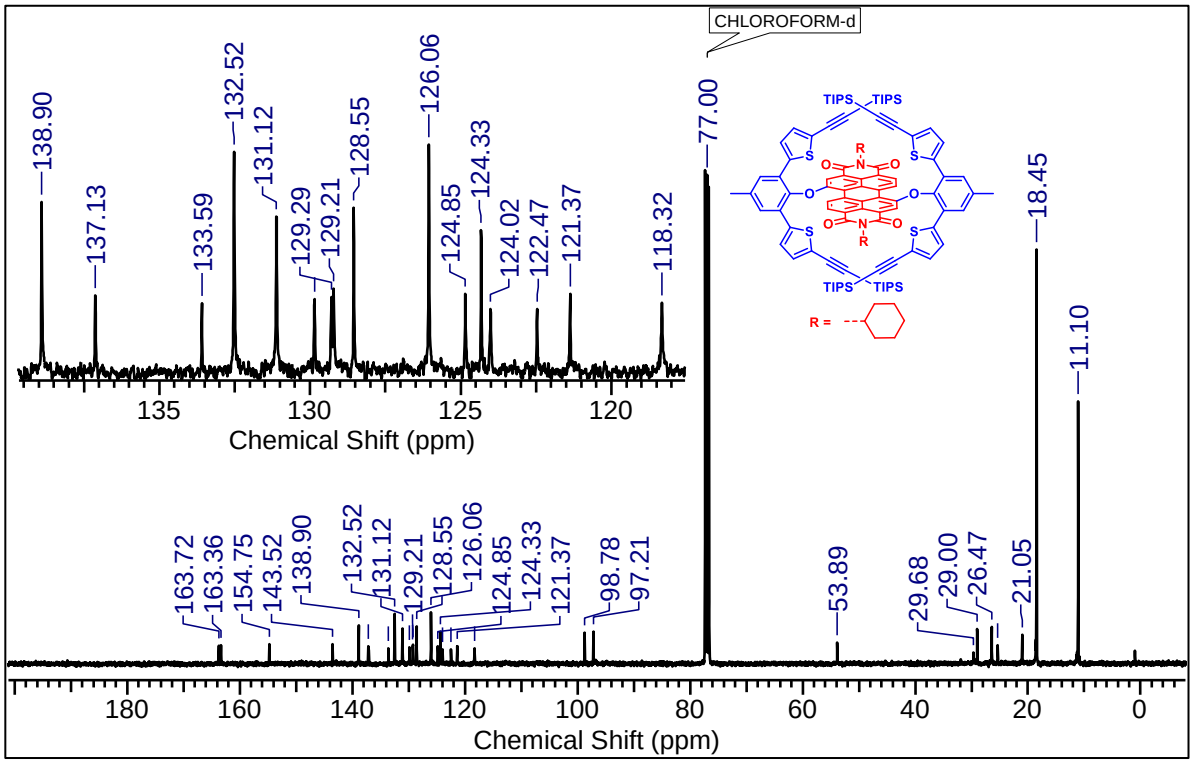
^{1}H NMR (500 MHz) spectrum of **rPBI** in $CDCl_3$ at 298 K.



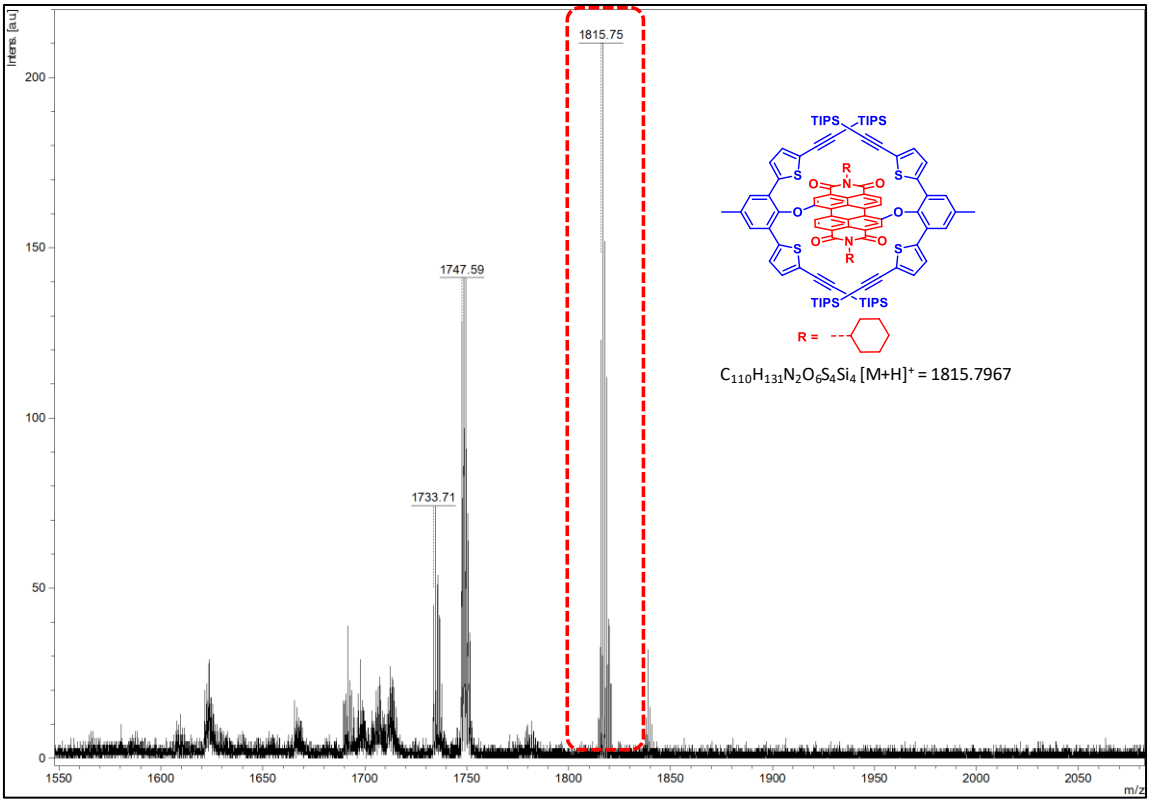
^{1}H NMR (500 MHz) spectrum of **1** in $CDCl_3$ at 298 K.



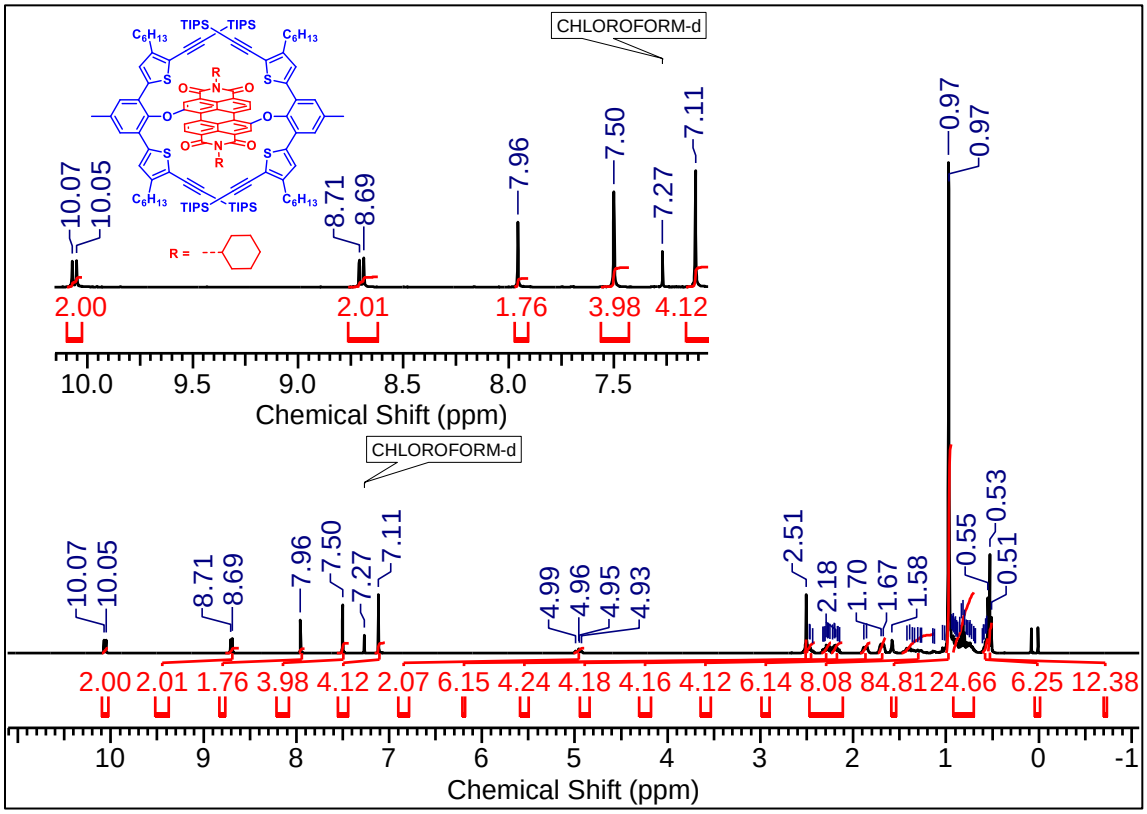
^{1}H NMR (500 MHz) spectrum of **2a** in $CDCl_3$ at 298 K.



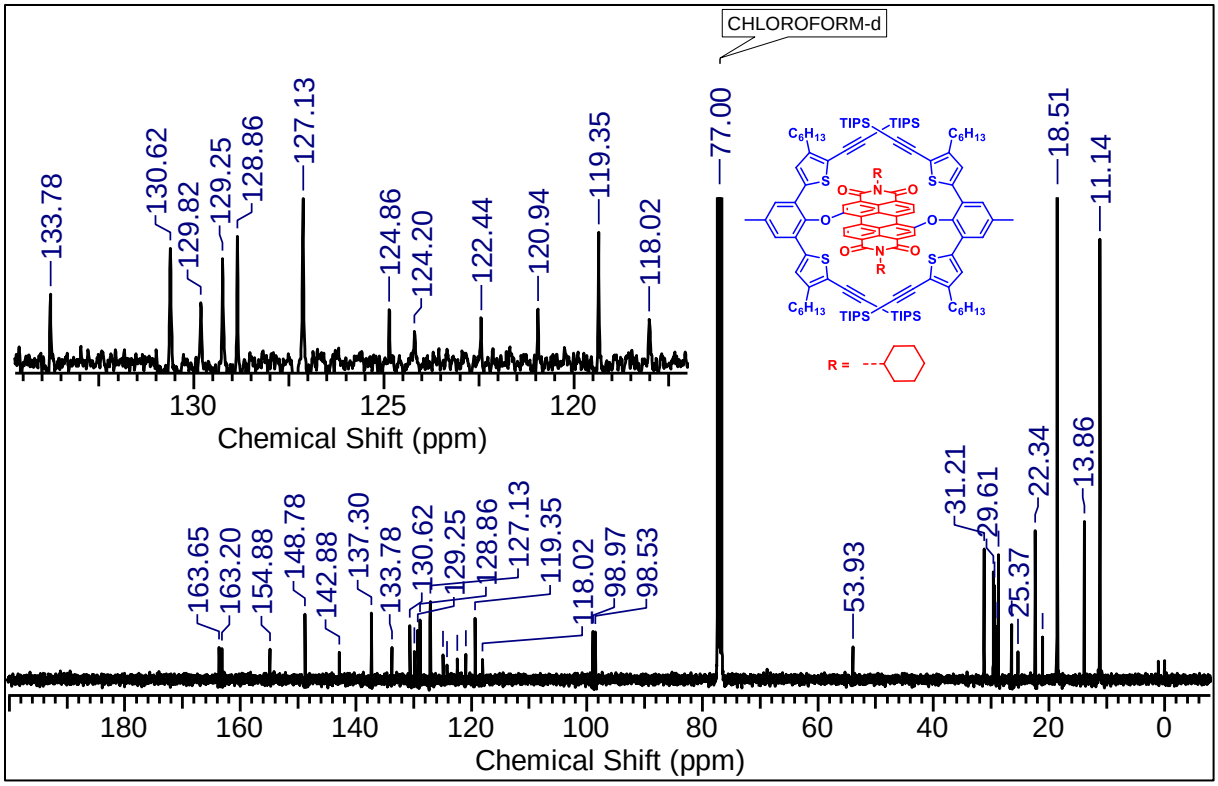
^{13}C NMR (125 MHz) spectrum of **2a** in $CDCl_3$ at 298 K.



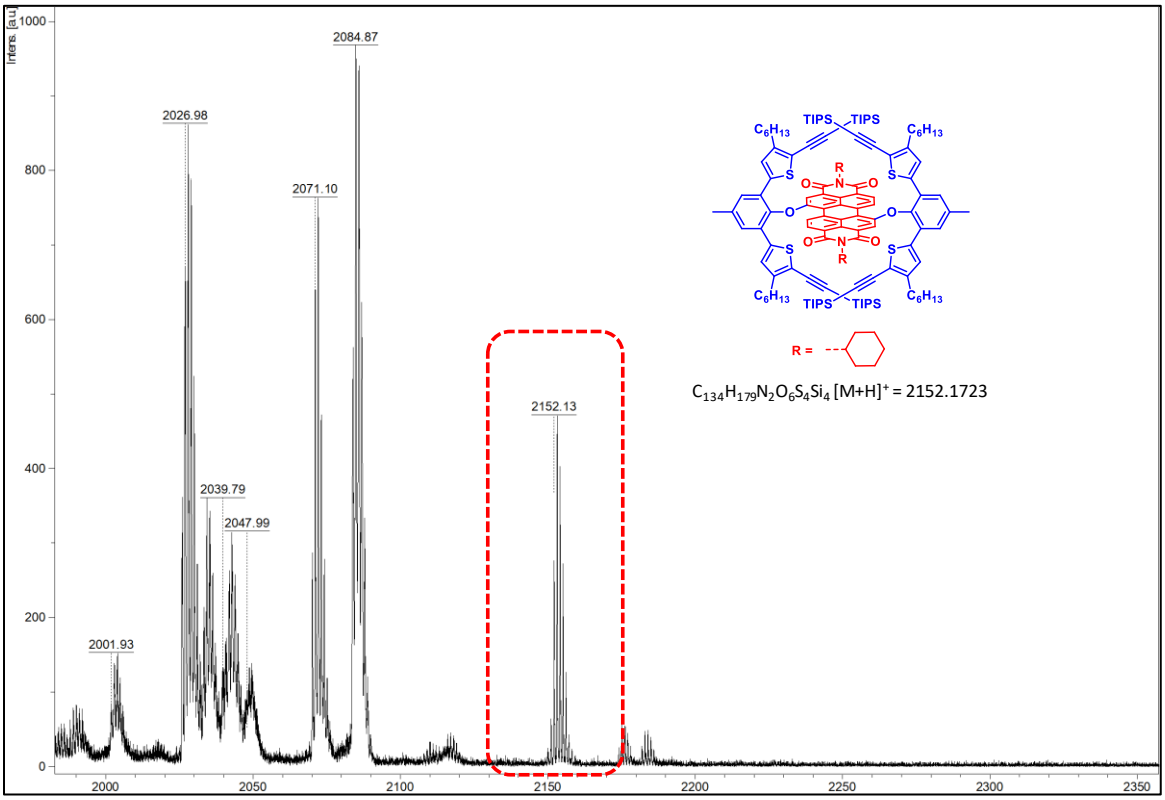
MALDI-TOF MS of compound **2a**.



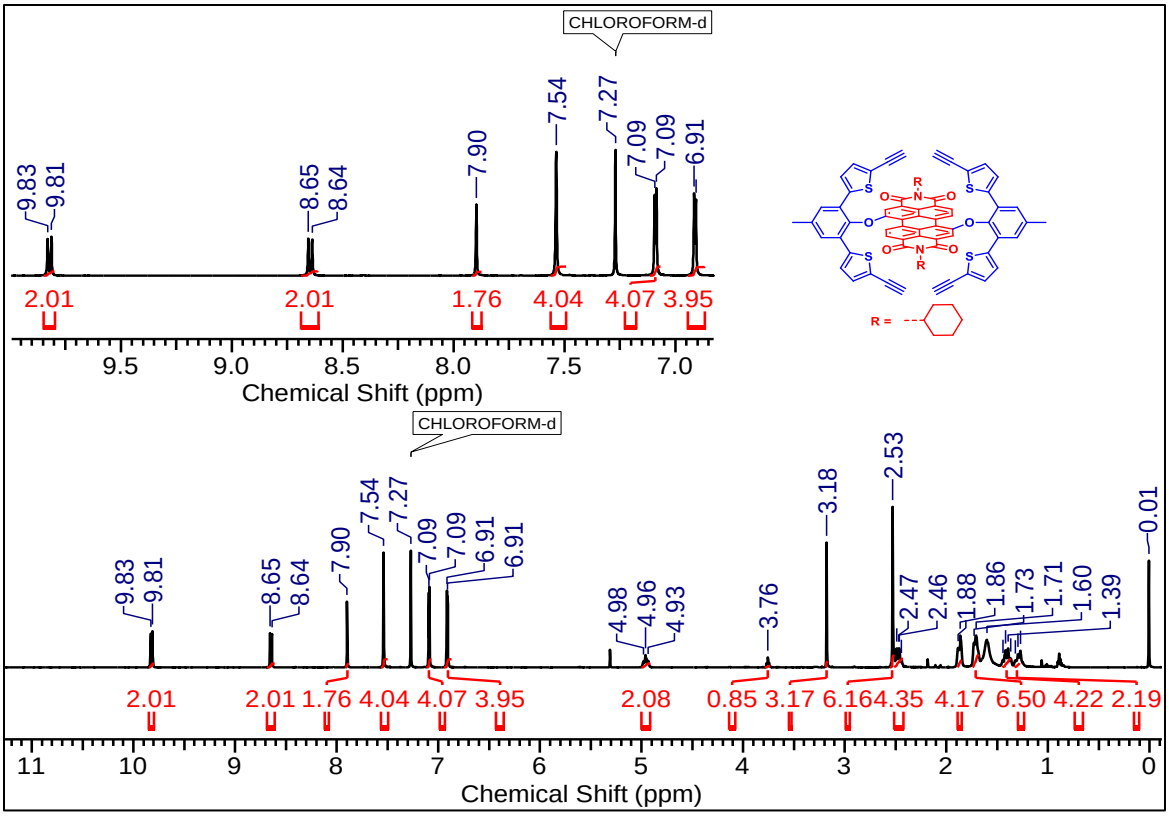
^{1}H NMR (400 MHz) spectrum of **2b** in $CDCl_3$ at 298 K.



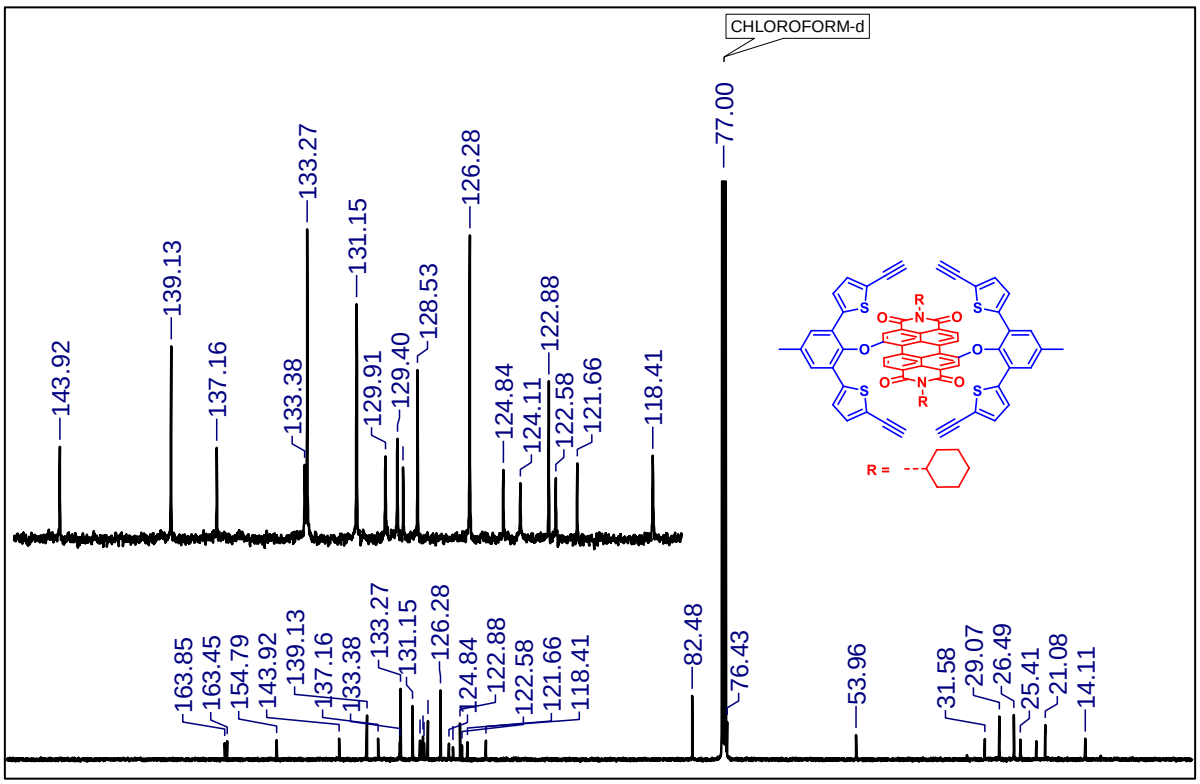
^{13}C NMR (100 MHz) spectrum of **2b** in $CDCl_3$ at 298 K.



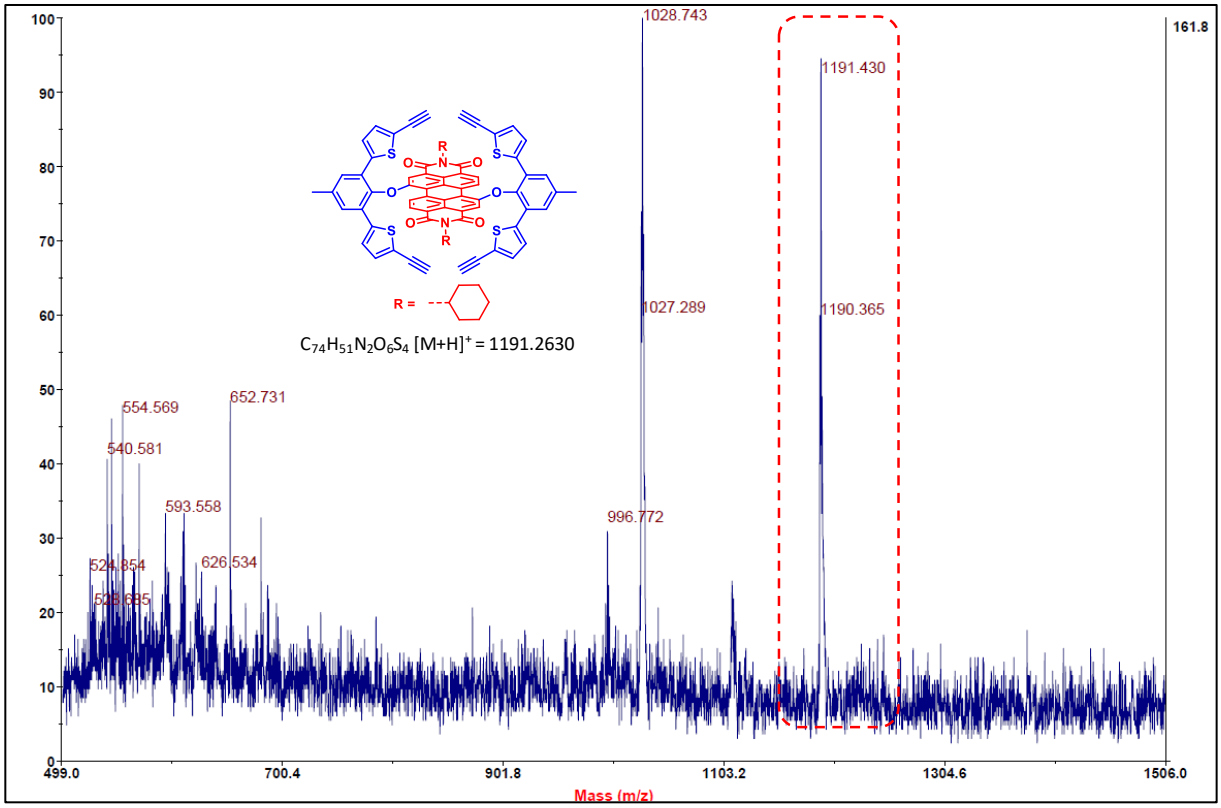
MALDI-TOF MS of compound **2b**.



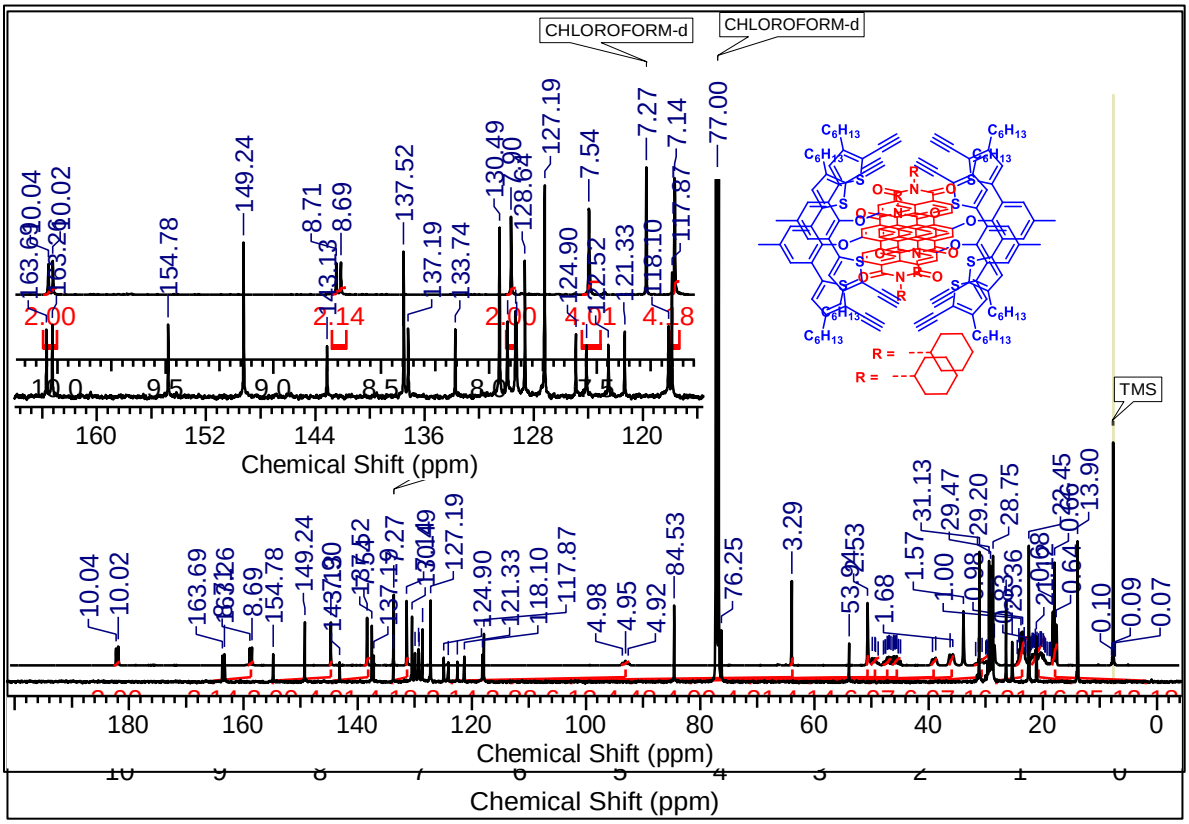
[1]H NMR (500 MHz) spectrum of **3a** in $CDCl_3$ at 298 K.



[13]C NMR (100 MHz) spectrum of **3a** in $CDCl_3$ at 298 K.

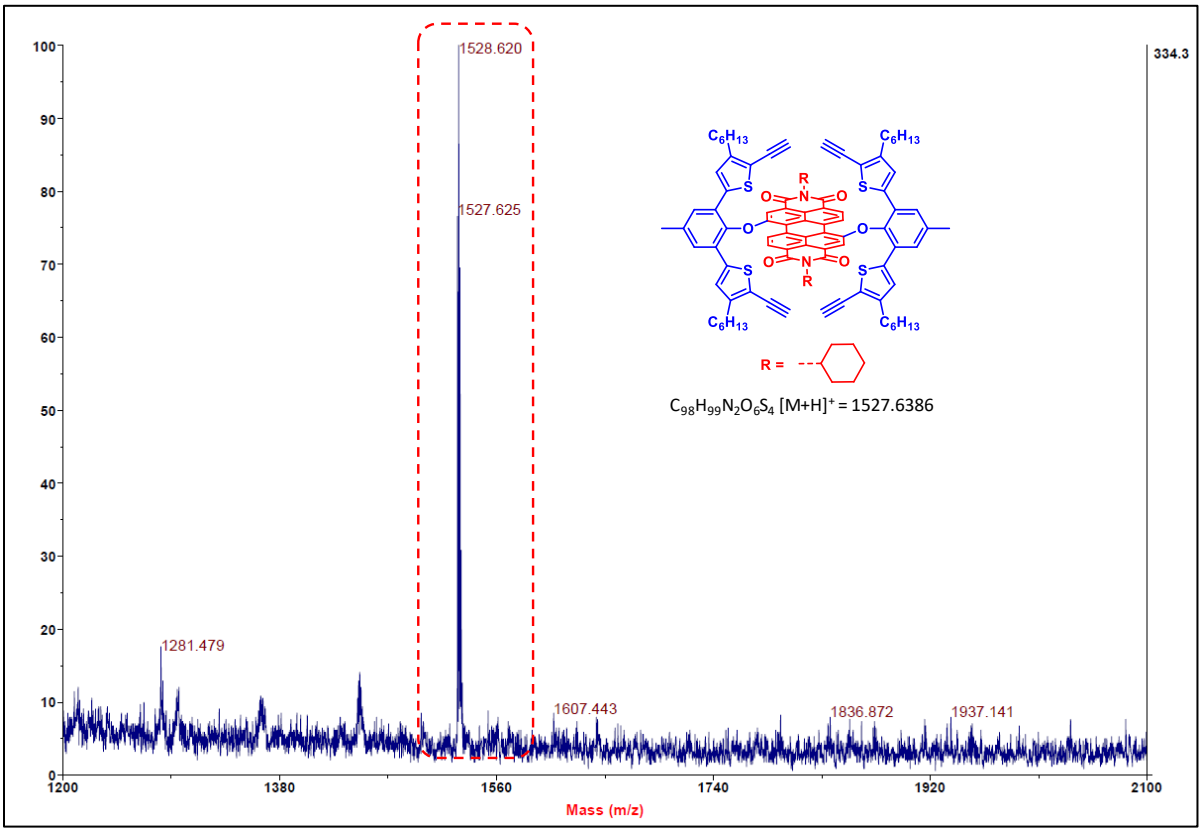


MALDI-TOF MS of compound **3a**.

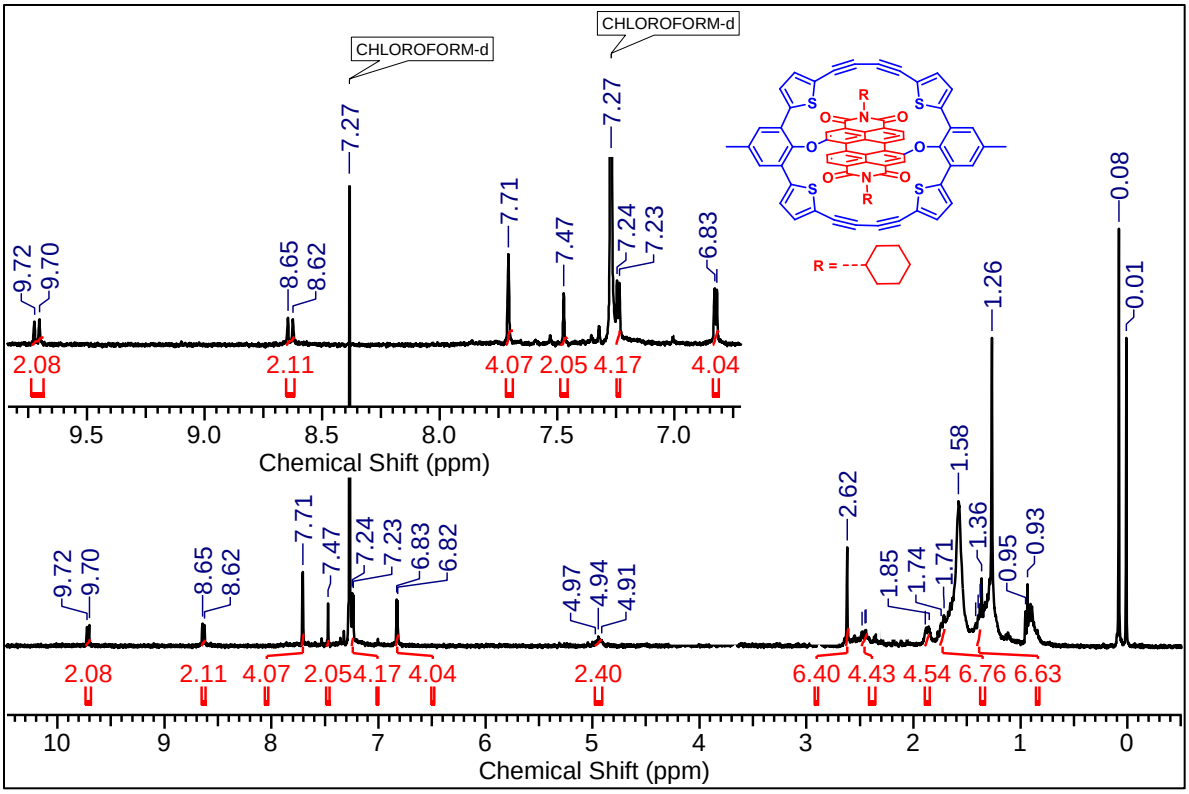


^{1}H NMR (400 MHz) spectrum of **3b** in $CDCl_3$ at 298 K.

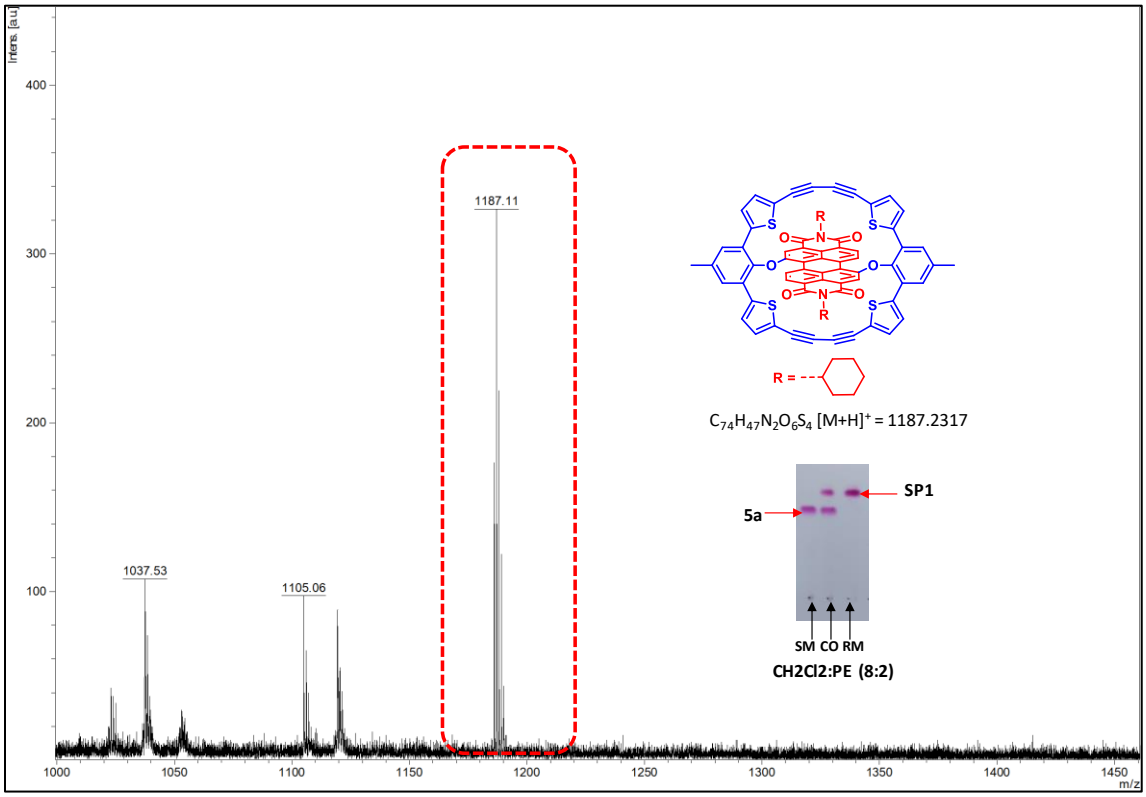
^{13}C NMR (125 MHz) spectrum of **3b** in $CDCl_3$ at 298 K.



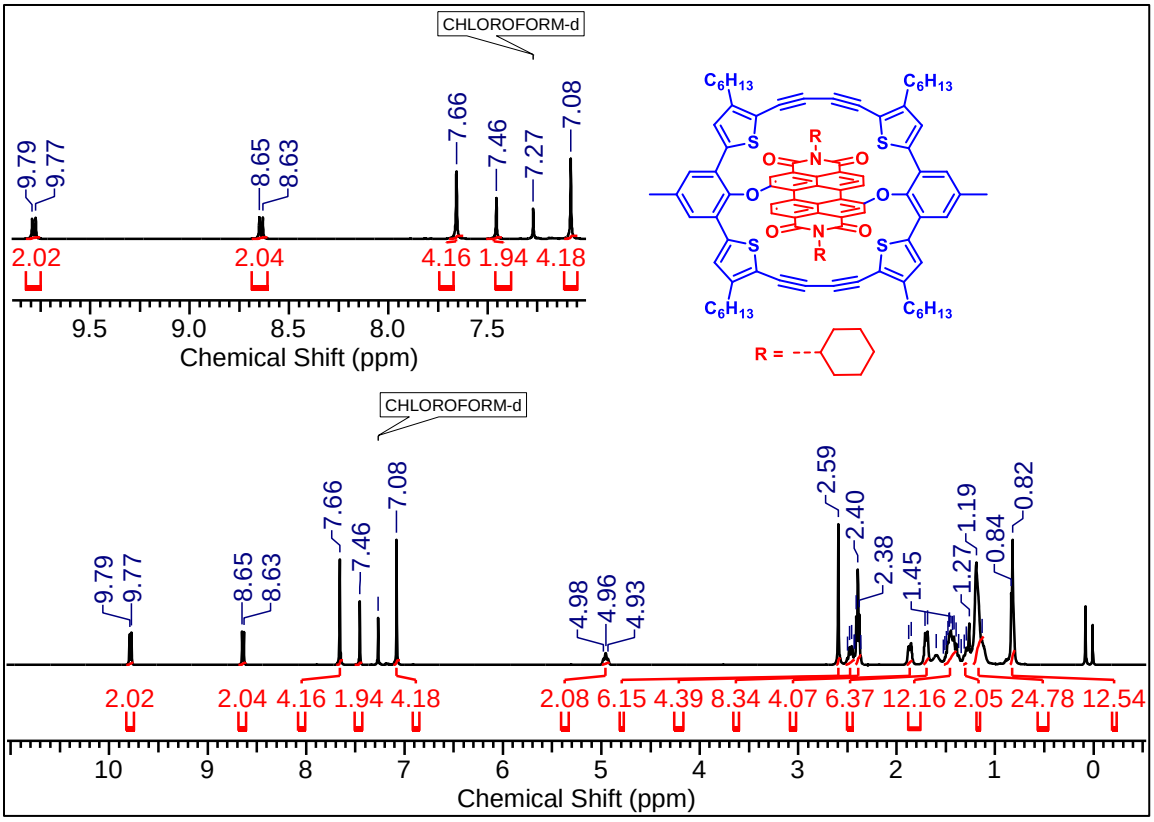
MALDI-TOF MS of compound **3b**.



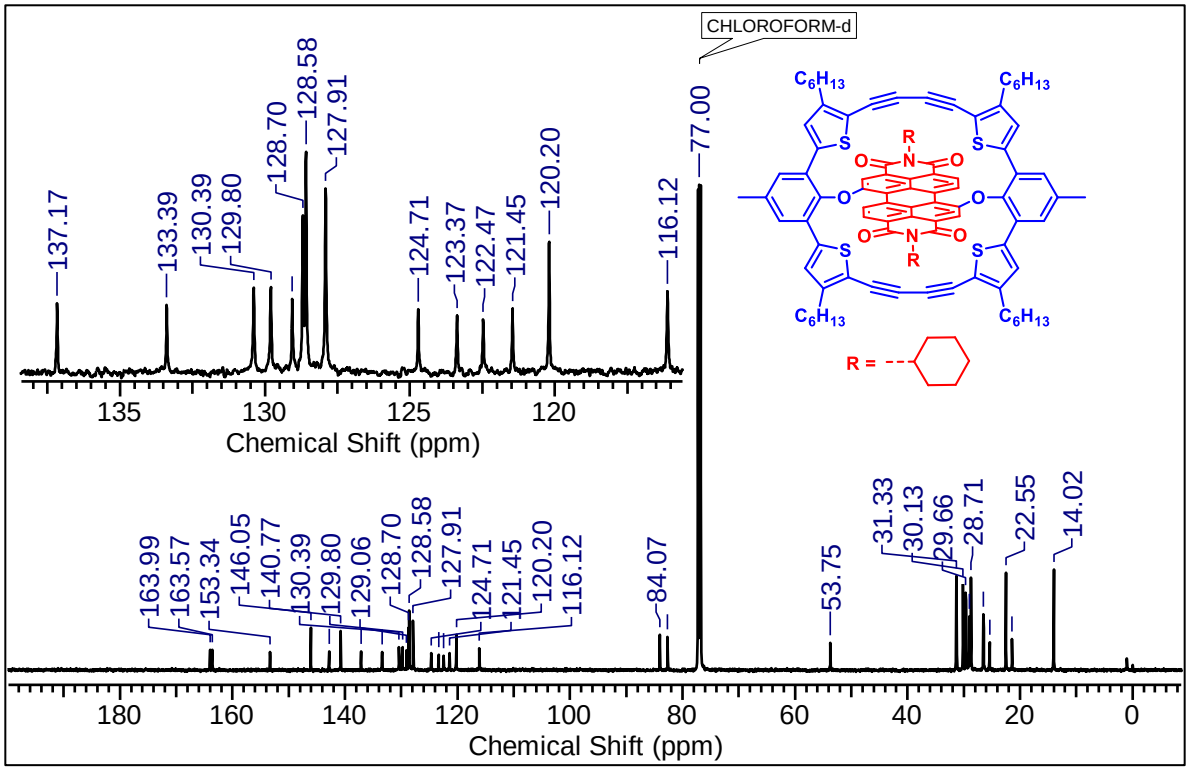
^{1}H NMR (500 MHz) spectrum of **SP1** in $CDCl_3$ at 298 K.



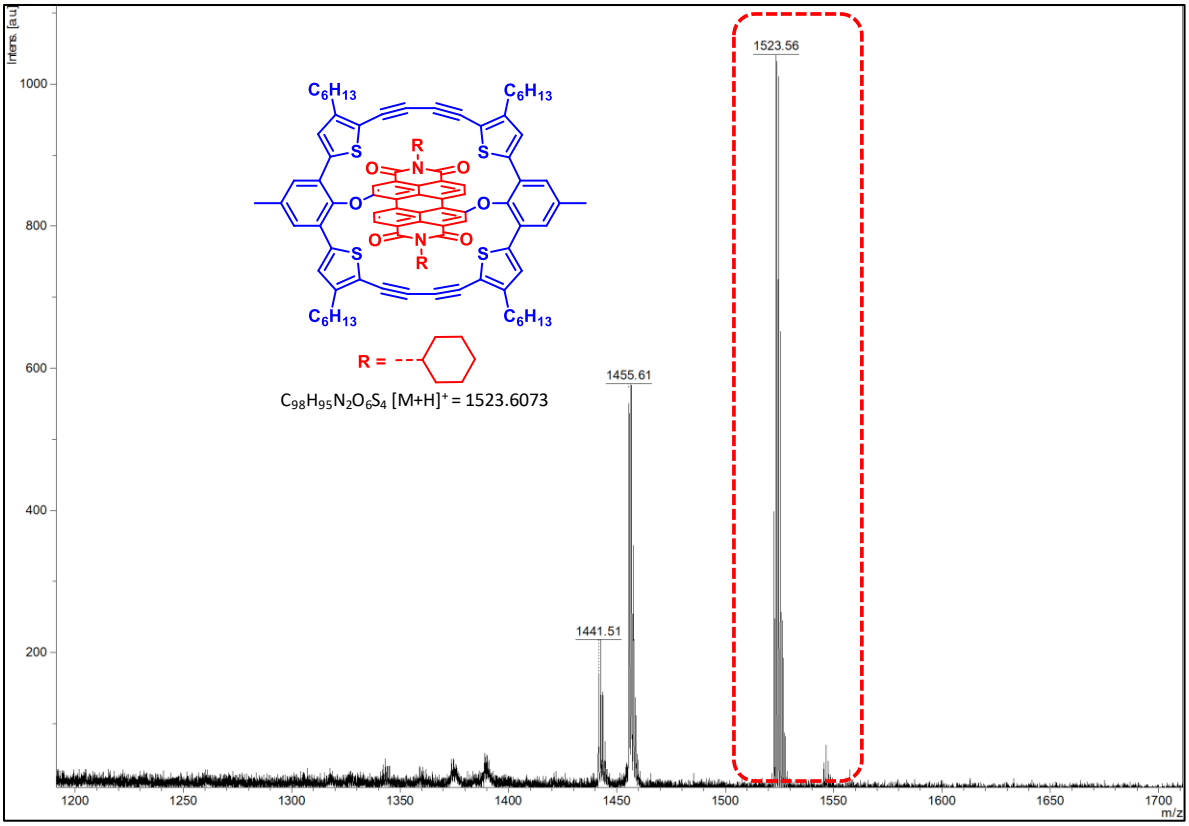
MALDI-TOF MS of compound **SP1**.



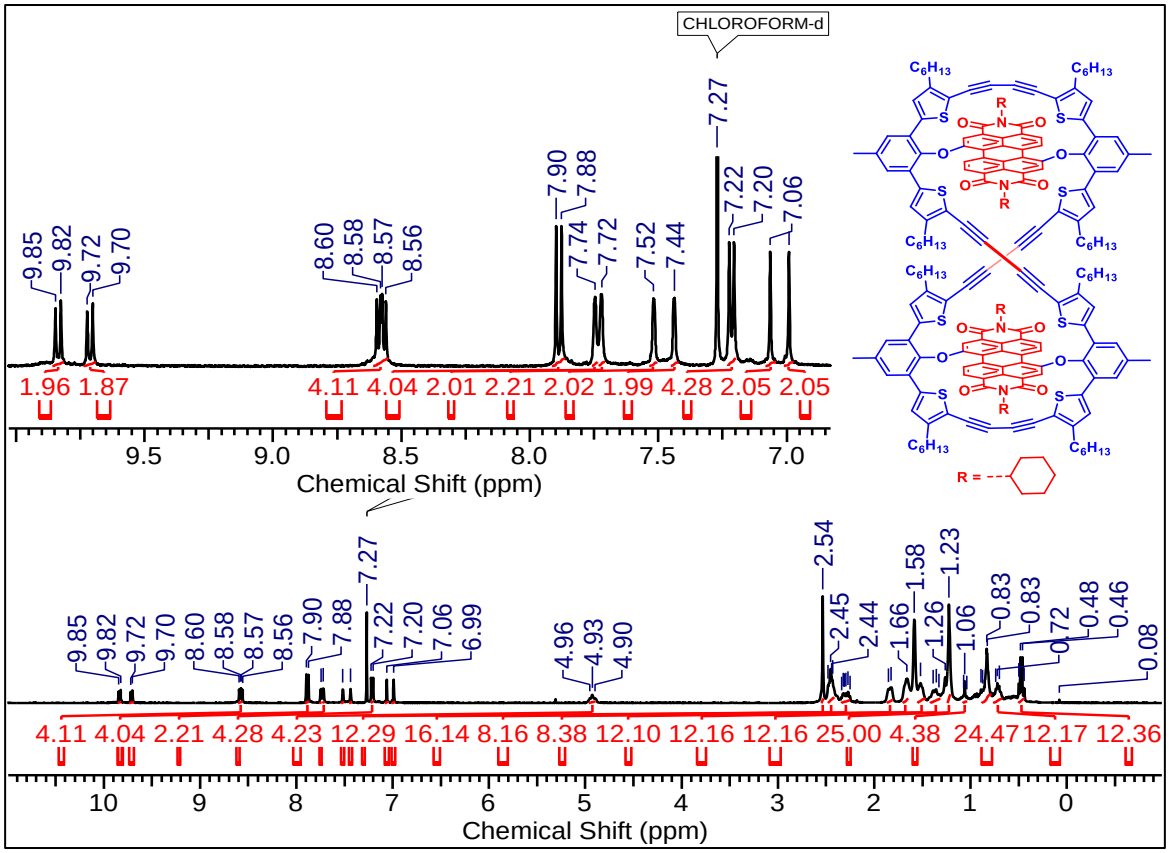
^{1}H NMR (500 MHz) spectrum of **SP2** in $CDCl_3$ at 298 K.



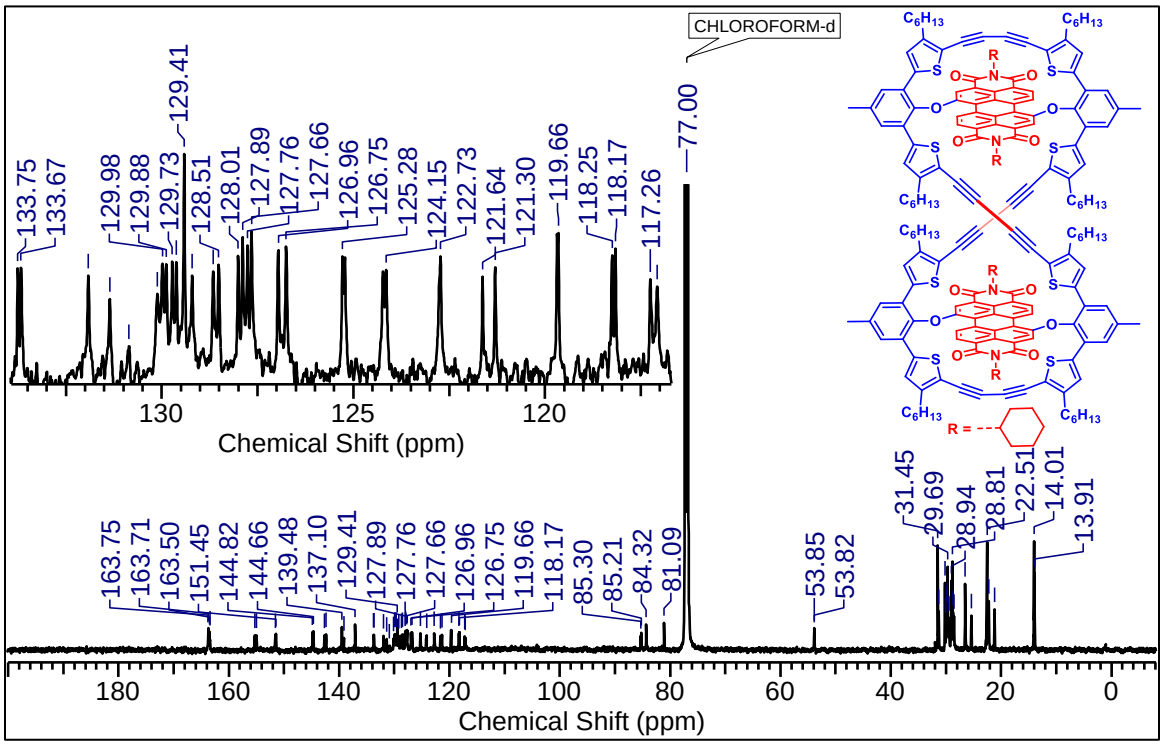
^{13}C NMR (125 MHz) spectrum of **SP2** in $CDCl_3$ at 298 K.



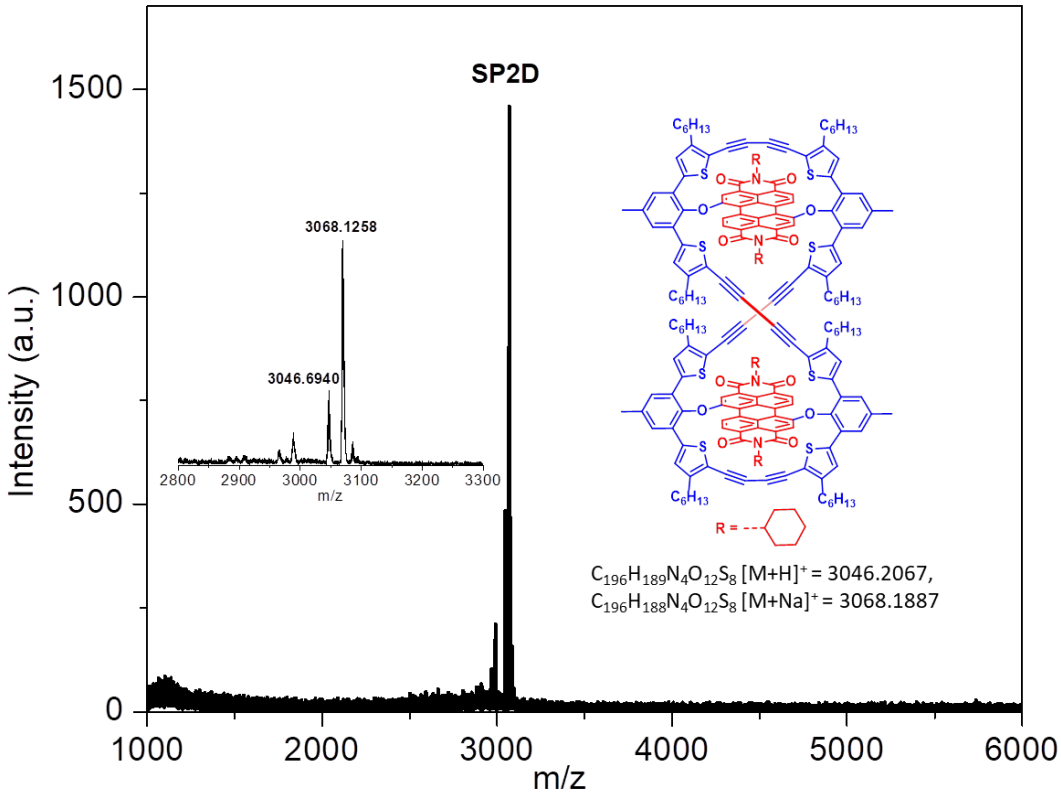
MALDI-TOF of compound **SP2**.



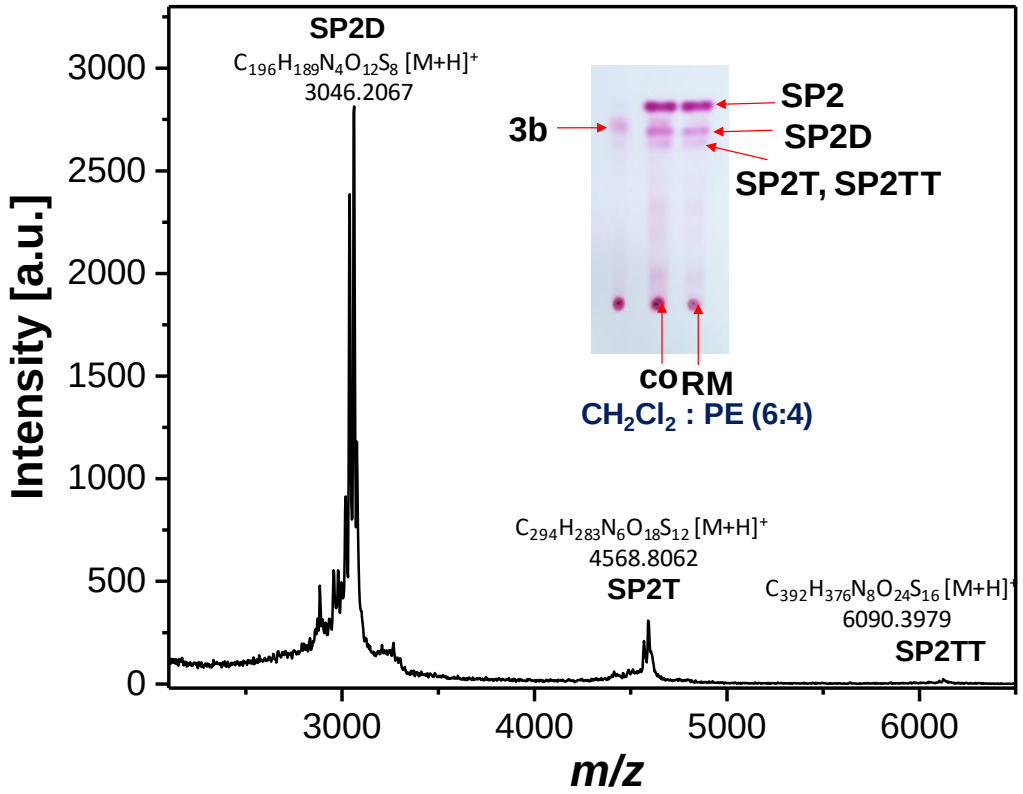
^{1}H NMR (400 MHz) spectrum of **SP2D** in $CDCl_3$ at 298 K.



^{13}C NMR (125 MHz) spectrum of **SP2D** in $CDCl_3$ at 298 K.



MALDI-TOF MS of compound **SP2D**.



MALDI-TOF MS of compound **SP2D**, **SP2T**, and **SP2TT**.

3. Figures

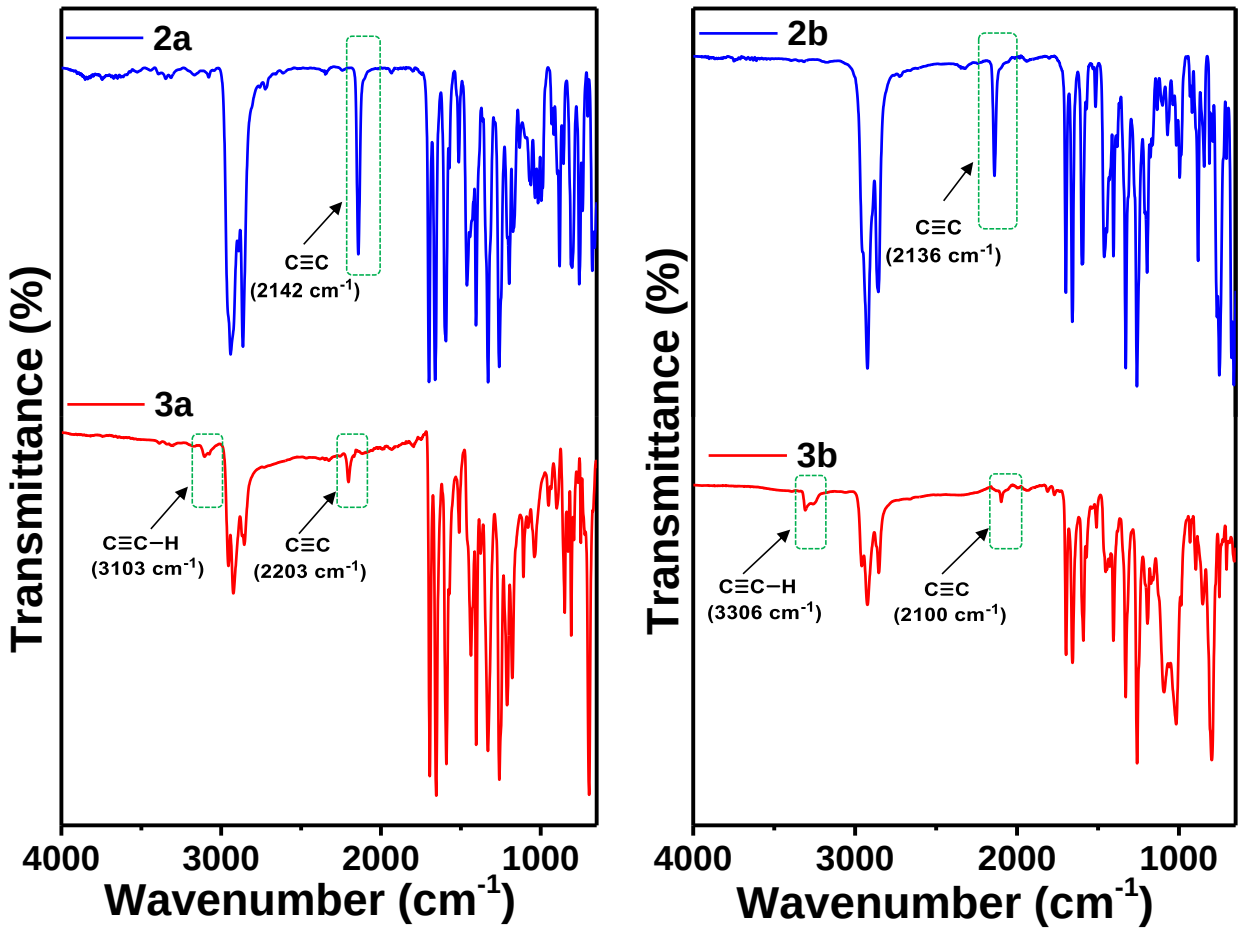


Figure S1. Comparison of the FT-IR spectra of a) **2a** and **3a**, and b) **2b** and **3b**.

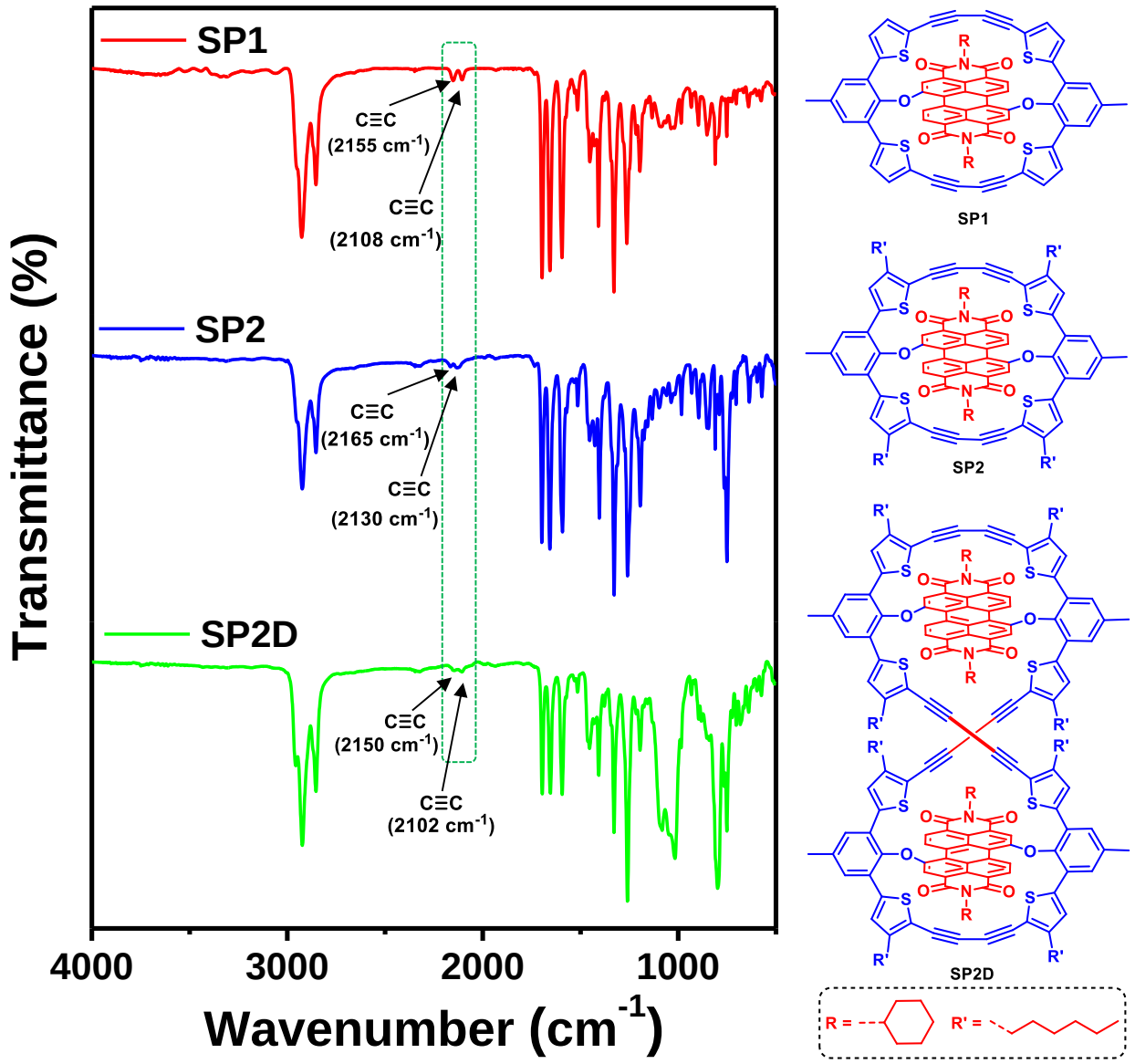


Figure S2. Comparison of the FT-IR spectra, **SP1**, **SP2,** and **SP2D** molecules.

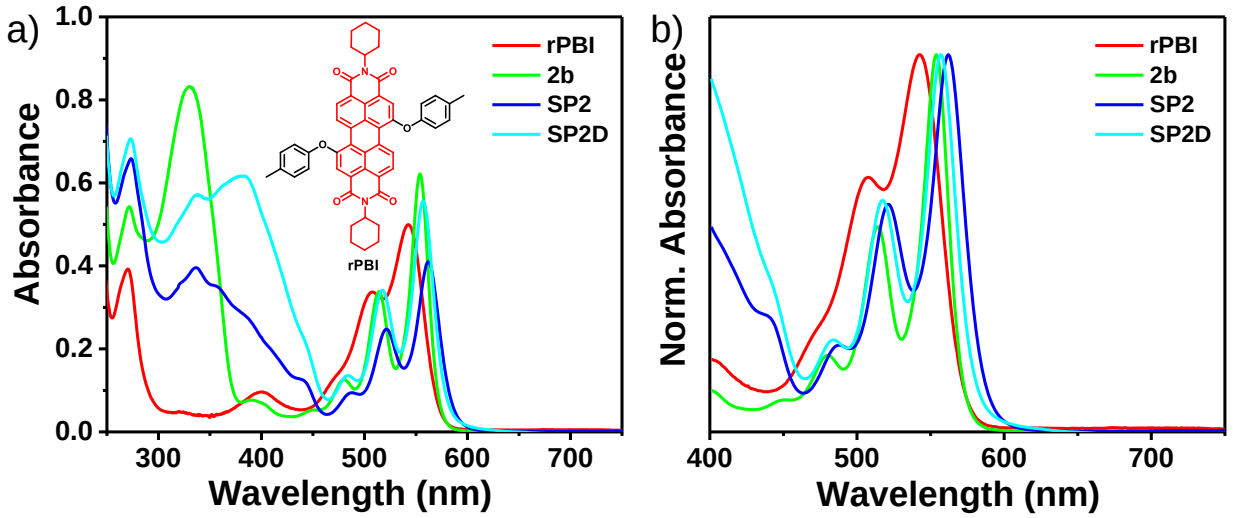


Figure S3. a) Absorption and corresponding b) normalized spectra of **rPBI**, **2b**, **SP2** and **SP2D** in CH_2Cl_2 solution (c = 1 x 10^{-5} M, l = 1 cm) at 25 ˚C. Inset shows the chemical structure of **rPBI.**[S1]

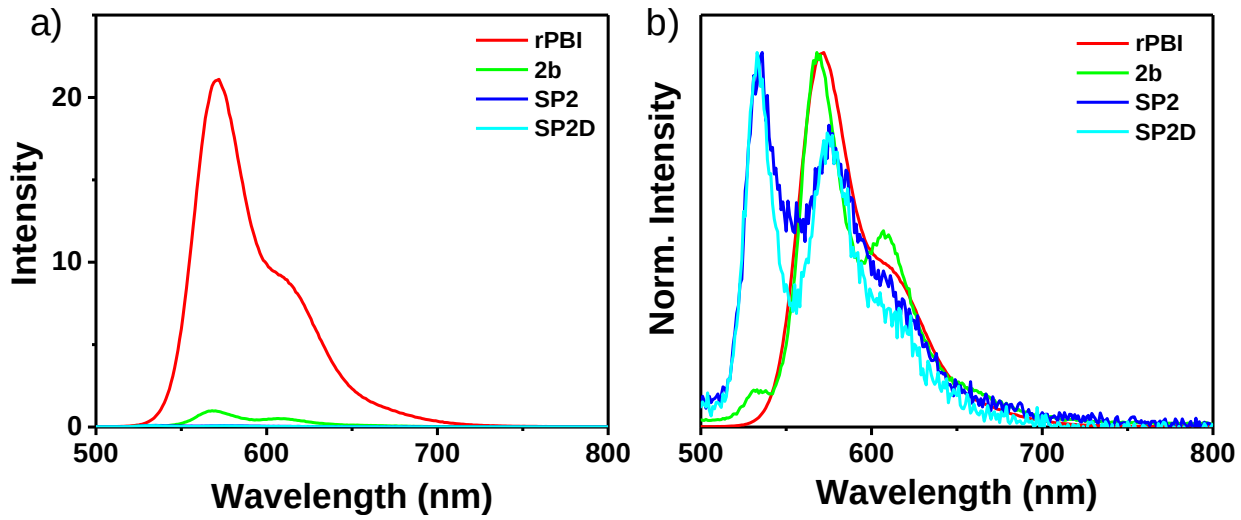


Figure S4. a) Steady-state emission and corresponding b) normalized spectra of **rPBI**, **2b**, **SP2** and **SP2D** in CH_2Cl_2 solution (c = 1 x 10^{-5} M, l = 1 cm) at 25 ˚C (λ_{ex} = 460 nm for **rPBI**, 480 nm for **2b**, and 480 nm for **SP2** and **SP2D**).

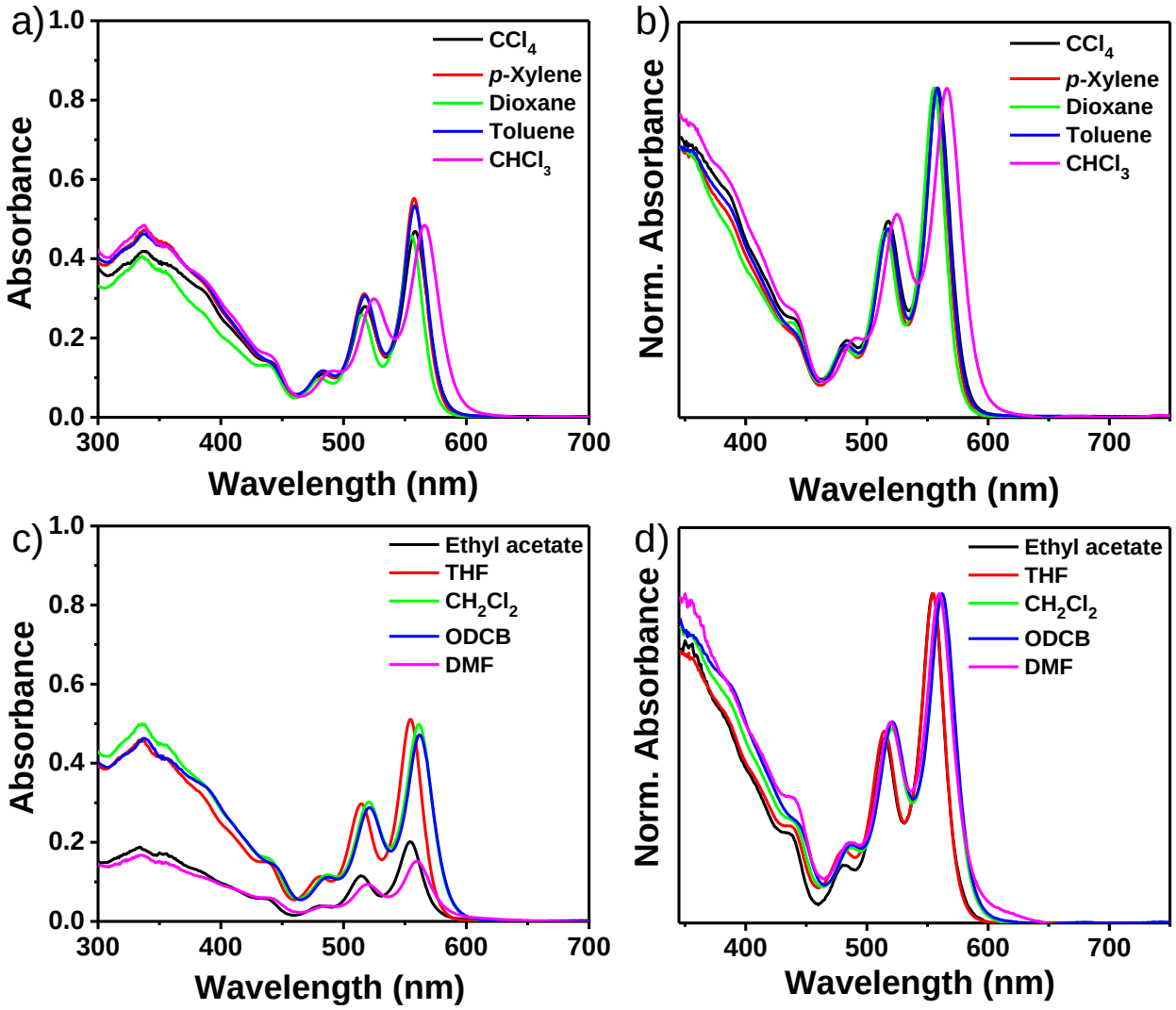


Figure S5. a) and c) Absorption and corresponding b) and d) normalized spectra of **SP2** in CCl_4, *p*-xylene, dioxane, toluene, $CHCl_3$, ethyl acetate, THF, CH_2Cl_2, ODCB, DMF solution (c = 1 x 10^{-5} M, l = 1 cm) at 25 ˚C.

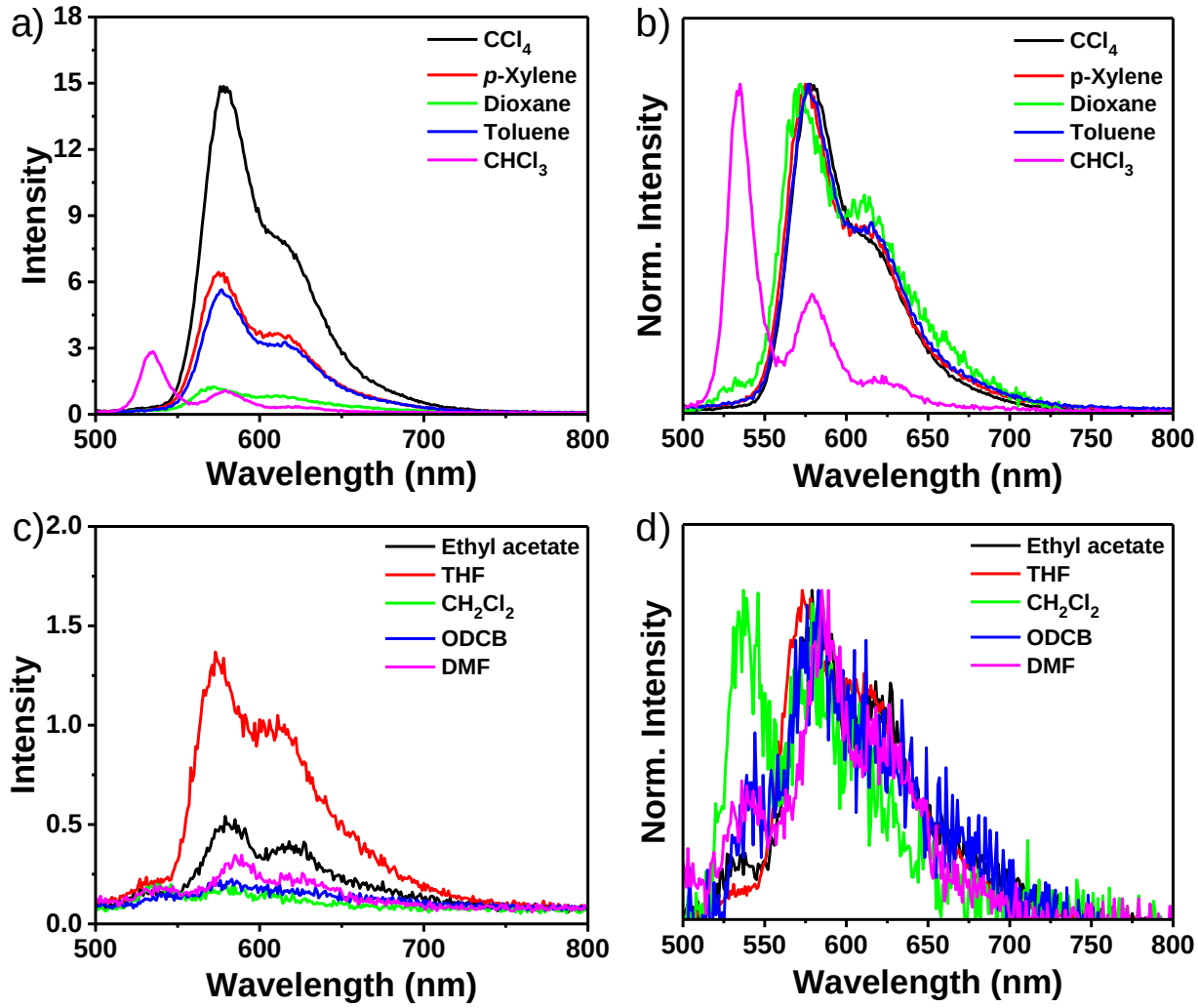


Figure S6. a) and c) Steady-state emission and corresponding b) and d) normalized spectra of **SP2**, (c = 1 x 10^{-5} M, l = 1 cm) at 25 ˚C (λ_{ex} = 480 nm for **SP2** in CCl_4, *p*-xylene, dioxane, toluene, ethyl acetate, THF, 485 nm for **SP2** in CH_2Cl_2, ODCB, DMF and 490 nm for **SP2** in $CHCl_3$ solvent).

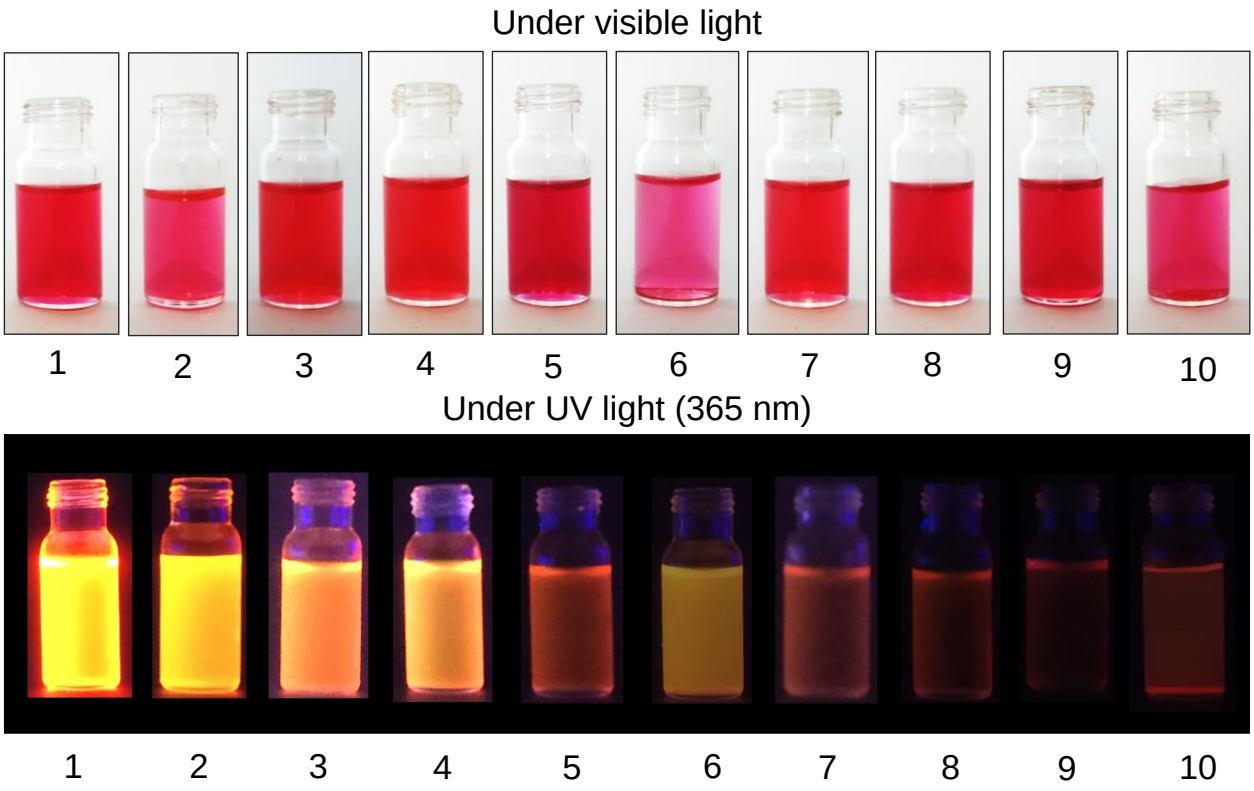


Figure S7. Photographs of **SP2**, a) visible and b) UV (365 nm) light in 1. CCl_4, 2. *p*-xylene, 3. dioxane, 4. toluene, 5. $CHCl_3$, 6. ethyl acetate, 7. THF, 8. CH_2Cl_2, 9. ODCB, 10. DMF.

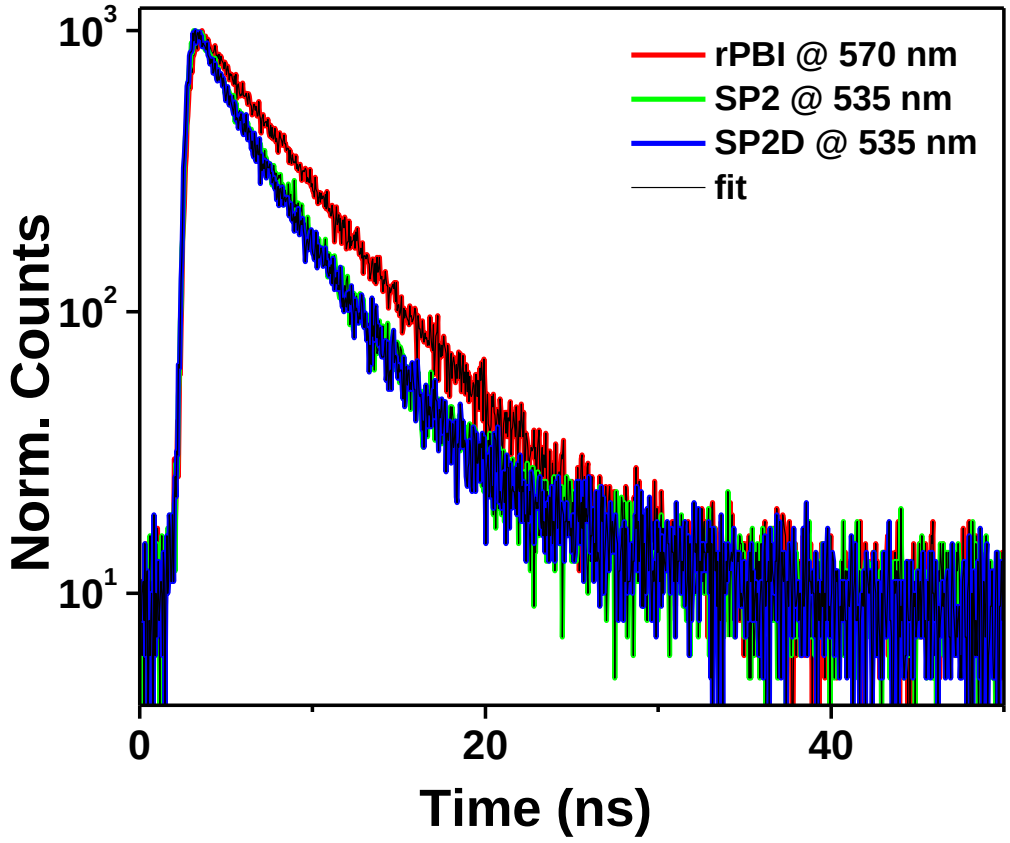


Figure S8. Fluorescence lifetime decay profile of **SP2** and **SP2D** in CH_2Cl_2 (c = 1x10^{-5} M, λ_{ex} = 448 nm).

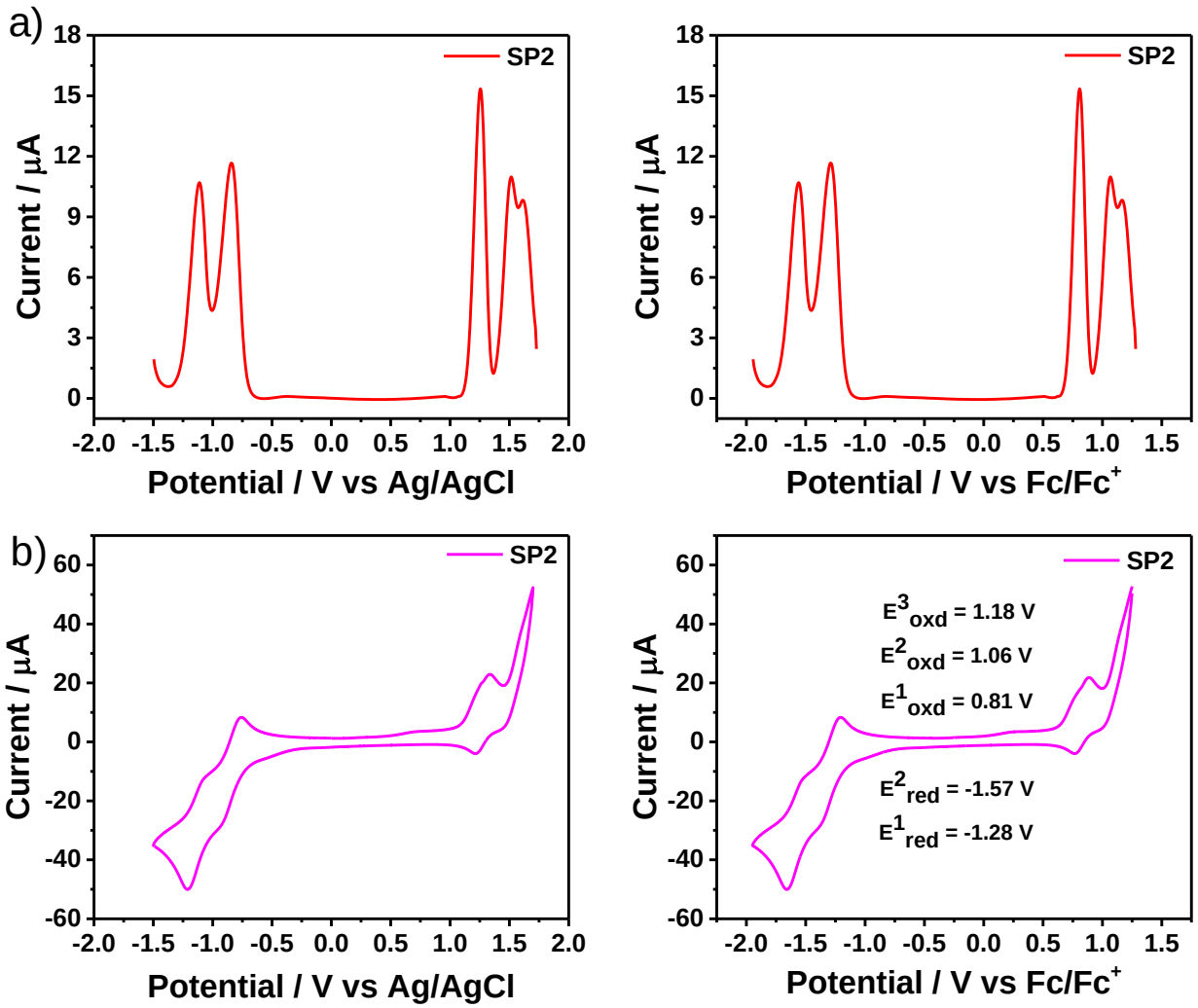


Figure S9. a) DPV measurements at 100 mV/s scan rate (left) and calculated as Ferrocene as the internal reference standard ($E_{Fc+/Fc}$ = 0.00 V) (right) of **SP2** (1mM). b) CV at 100 mV/s scan rate (left) and CV calculated as Ferrocene as the internal reference standard ($E_{Fc+/Fc}$ = 0.00 V) (right) of **SP2** (1mM).

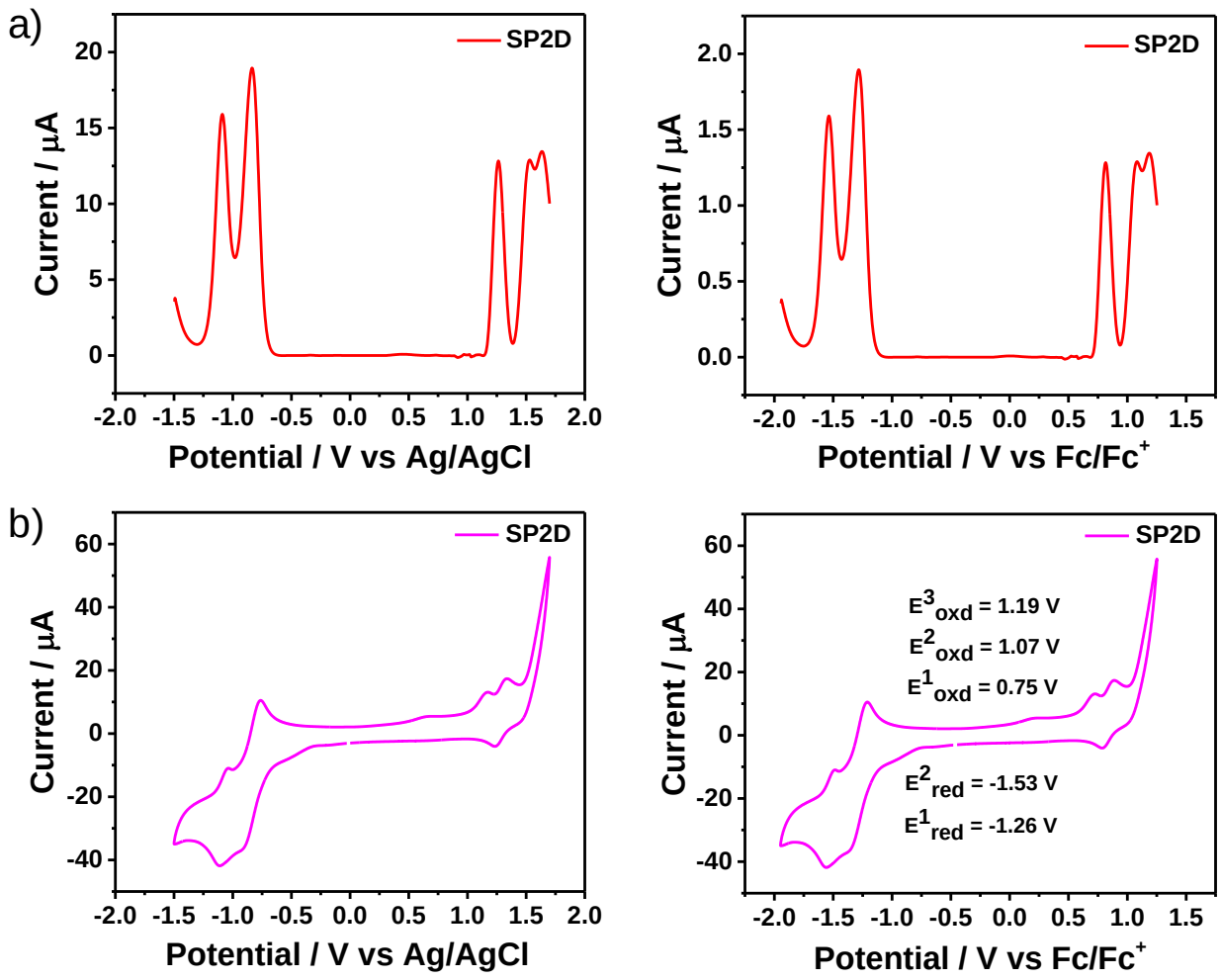


Figure S10. a) DPV measurements at 100 mV/s scan rate (left) and calculated as Ferrocene as the internal reference standard ($E_{Fc+/Fc}$ = 0.00 V) (right) of **SP2D** (1mM). b) CV at 100 mV/s scan rate (left) and CV calculated as Ferrocene as the internal reference standard ($E_{Fc+/Fc}$ = 0.00 V) (right) of **SP2D** (1mM).

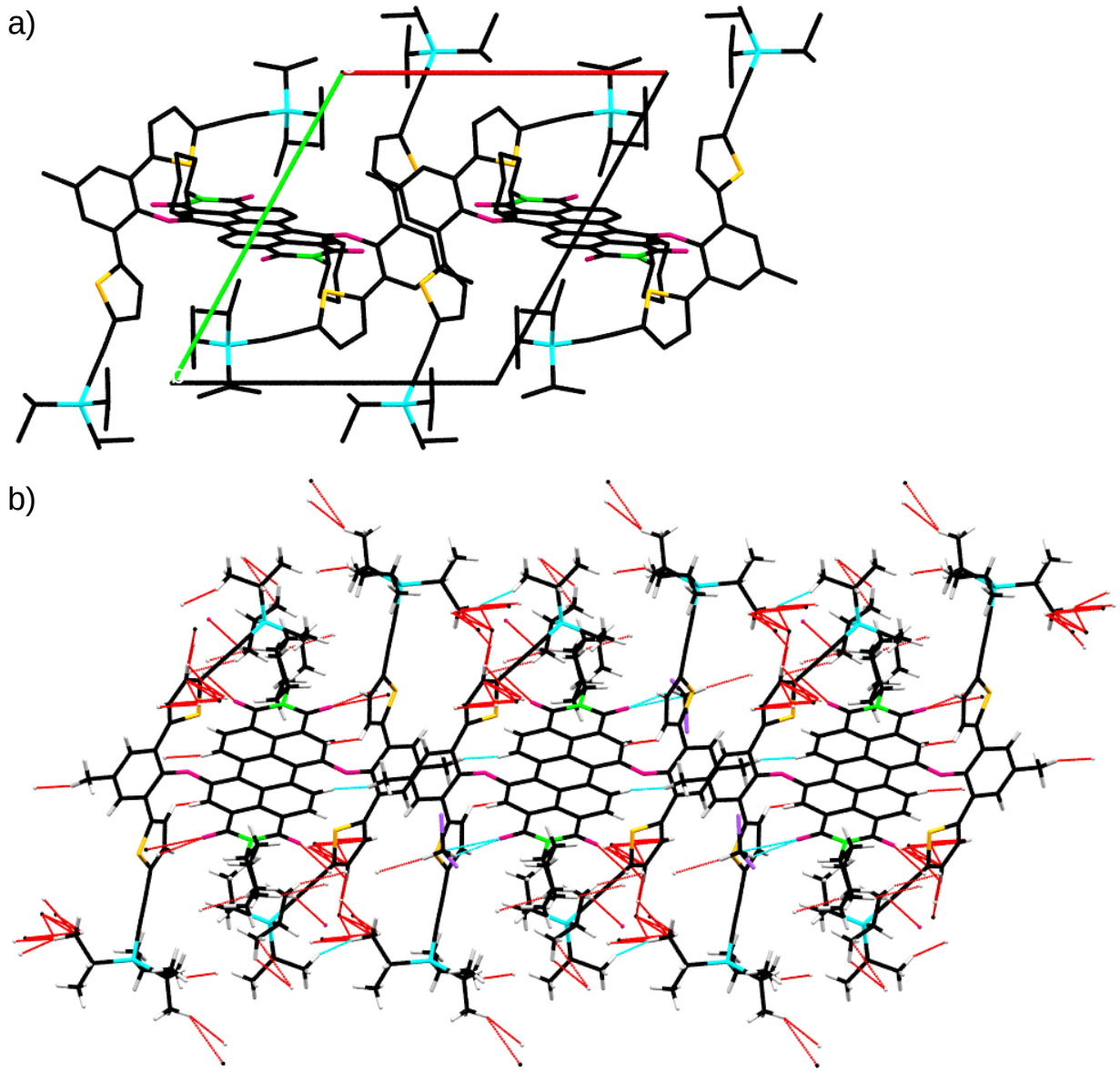


Figure S11. a) Unit cell of **2a** consists of 2 molecules. b) Extended molecular packing of **2a** using various noncovalent interactions.

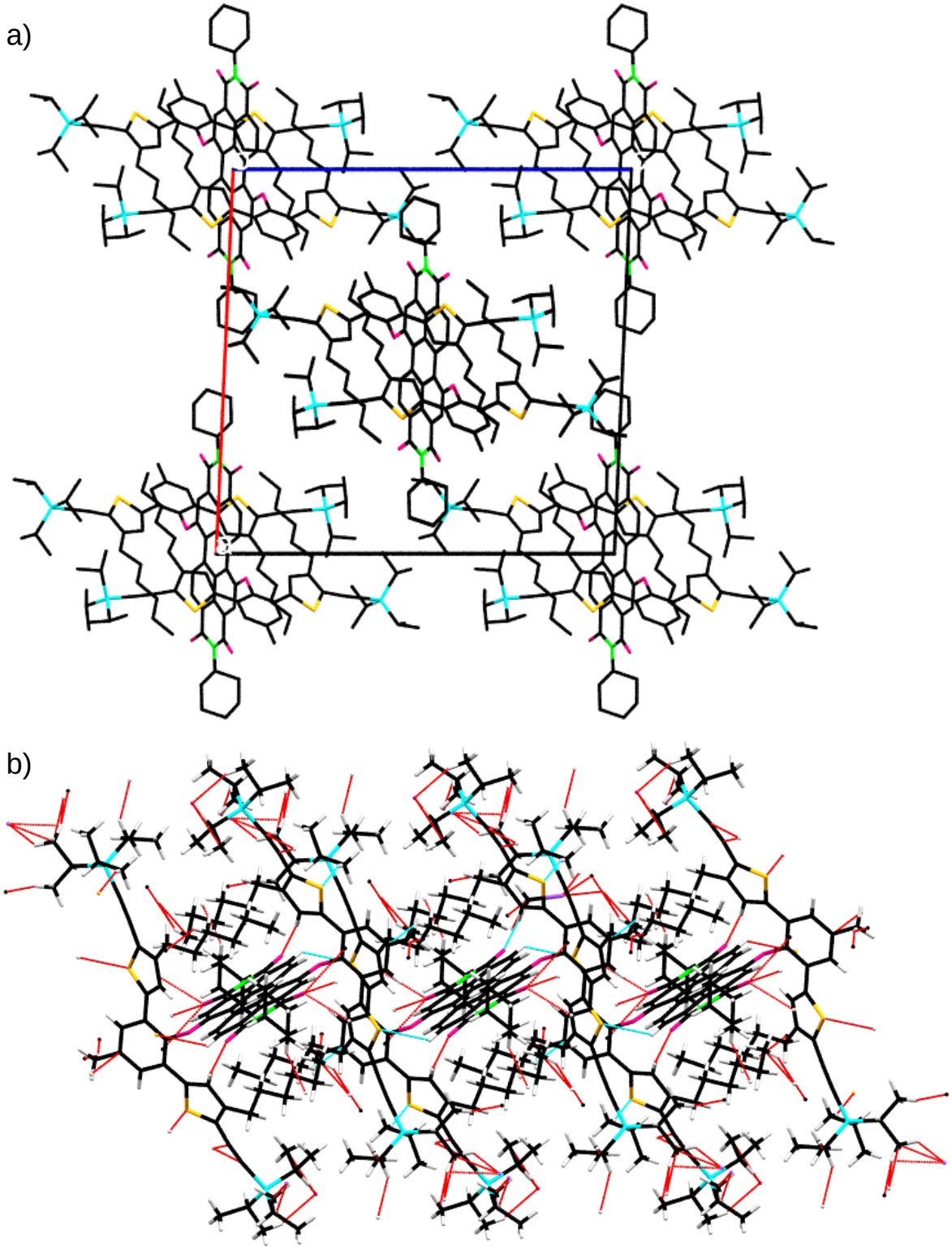


Figure S12. a) Unit cell of **2b** consists of 6 molecules. b) Extended molecular packing of **2b** using various noncovalent interactions.

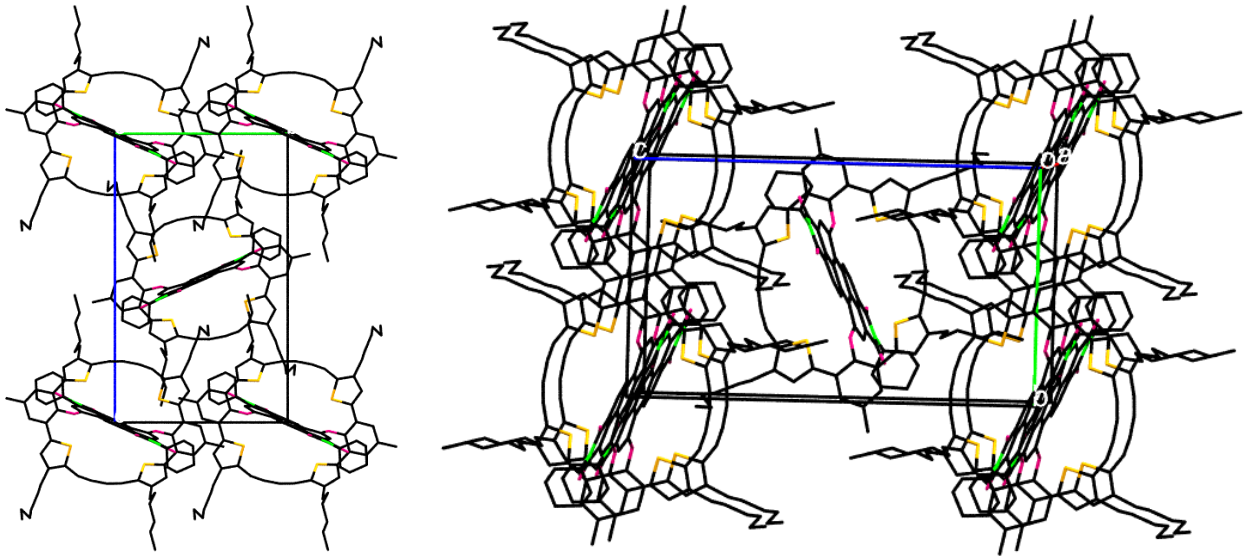


Figure S13. Unit cell of **SP2** consists of 9 molecules.

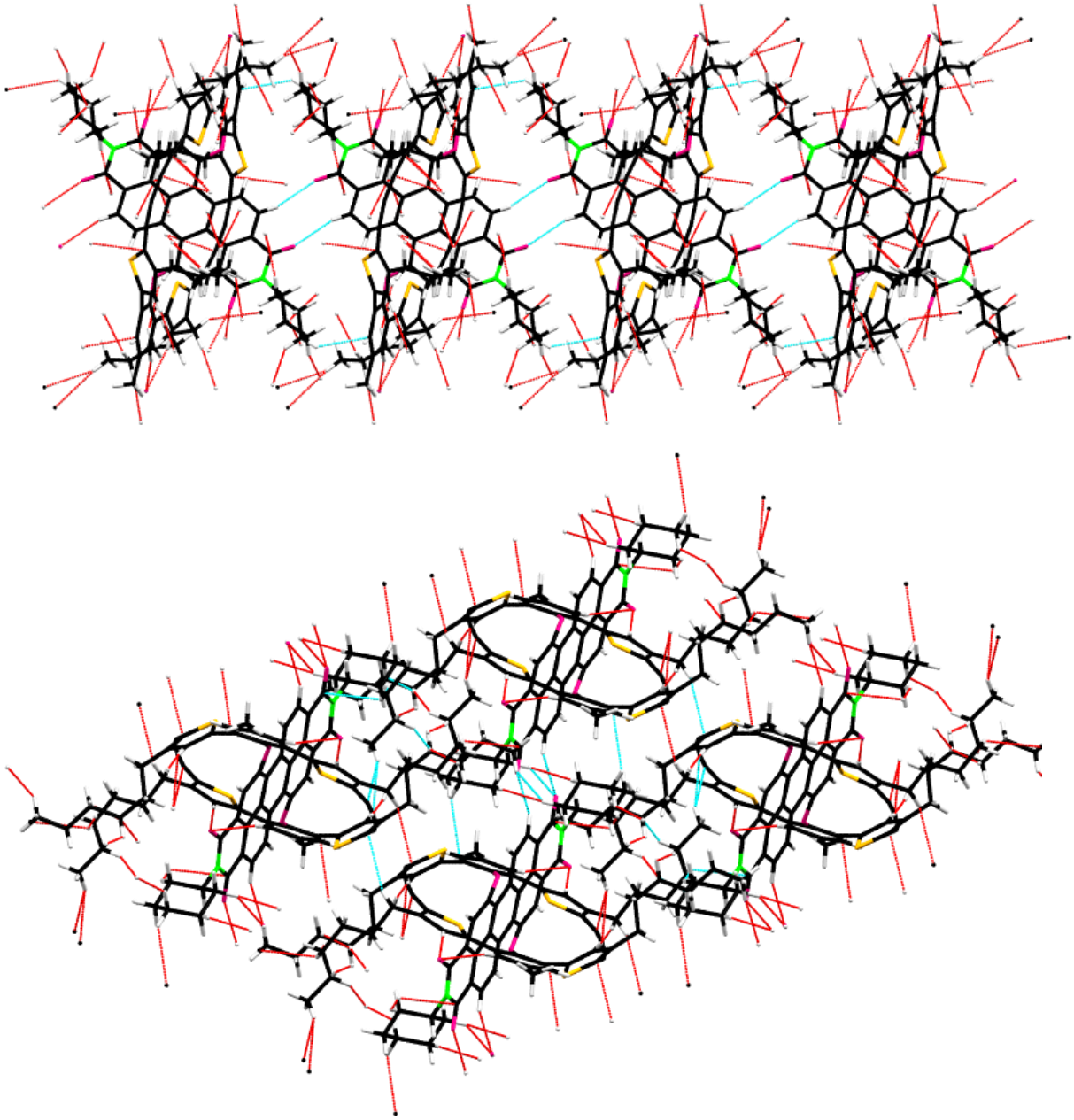


Figure S14. Extended molecular packing of **SP2** using various noncovalent interactions.

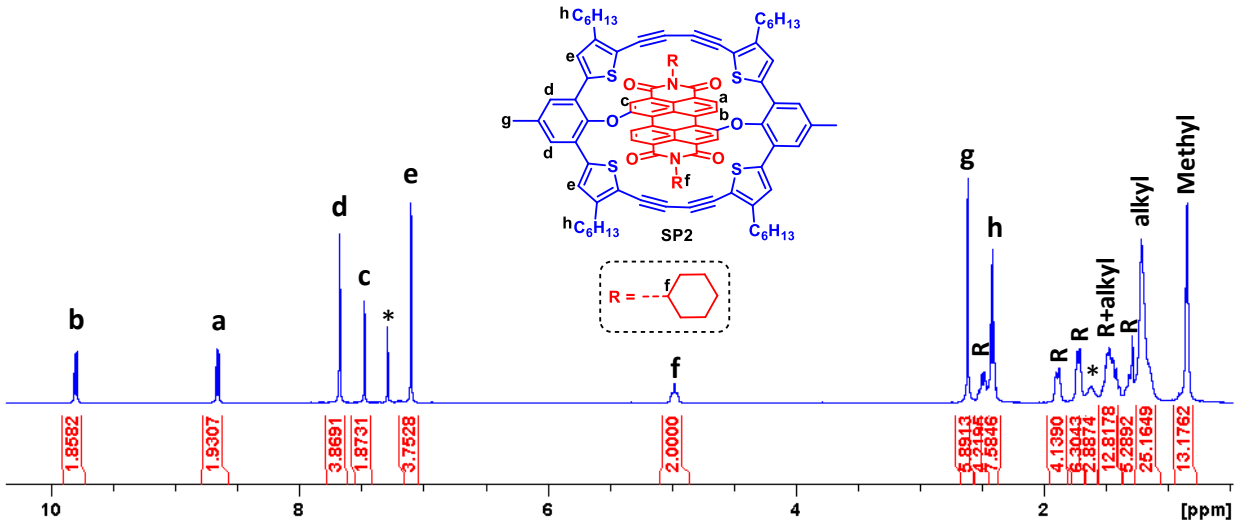


Figure S15. ^{1}H NMR spectrum of **SP2** recorded at 298K. Methylene groups of the cyclohexyl ring and the alkyl chain are labelled "R" and "alkyl", respectively. Solvent and residual water signals are indicated by asterisks.

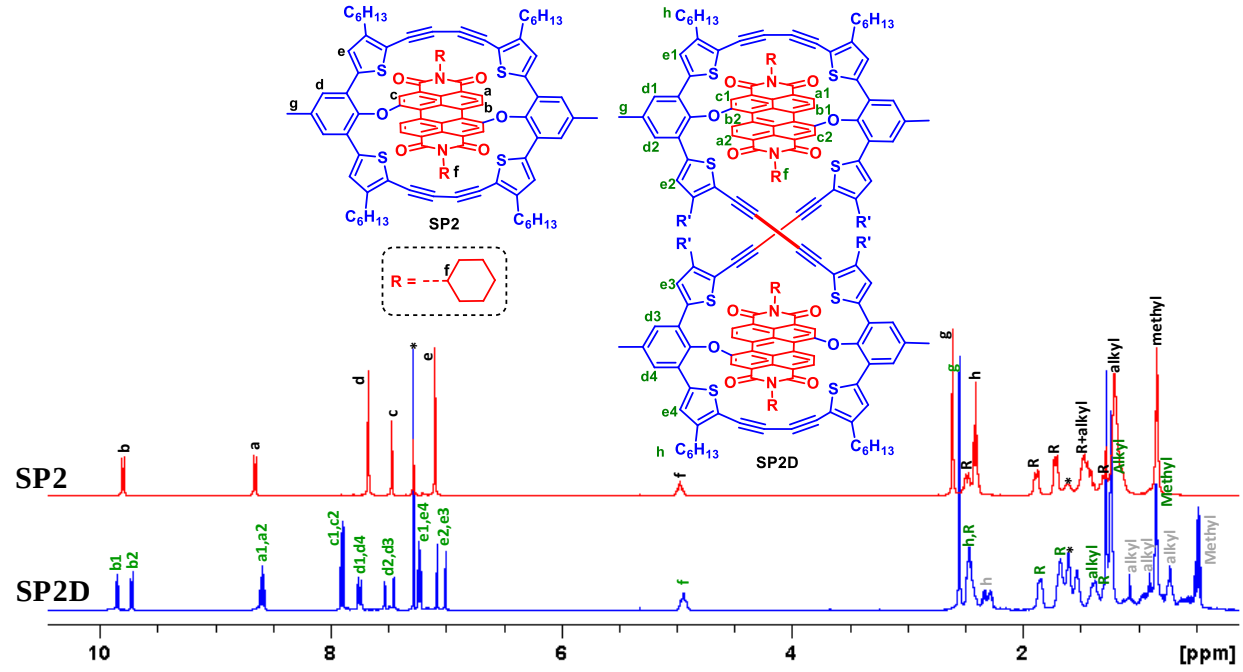


Figure S16. Comparison of ^{1}H NMR spectra of **SP2** (red) and **SP2D** (blue) recorded at 298K. All signals show doubling in **SP2D,** which implies that different environments are generated due to molecular symmetry breaking due to dimer formation. Grey labels mark additional environments in the alkyl chain of SP2D. Cyclohexyl ring "CH2" protons are labelled R. Solvent ($CDCl_3$) and asterisks indicate residual water signals.

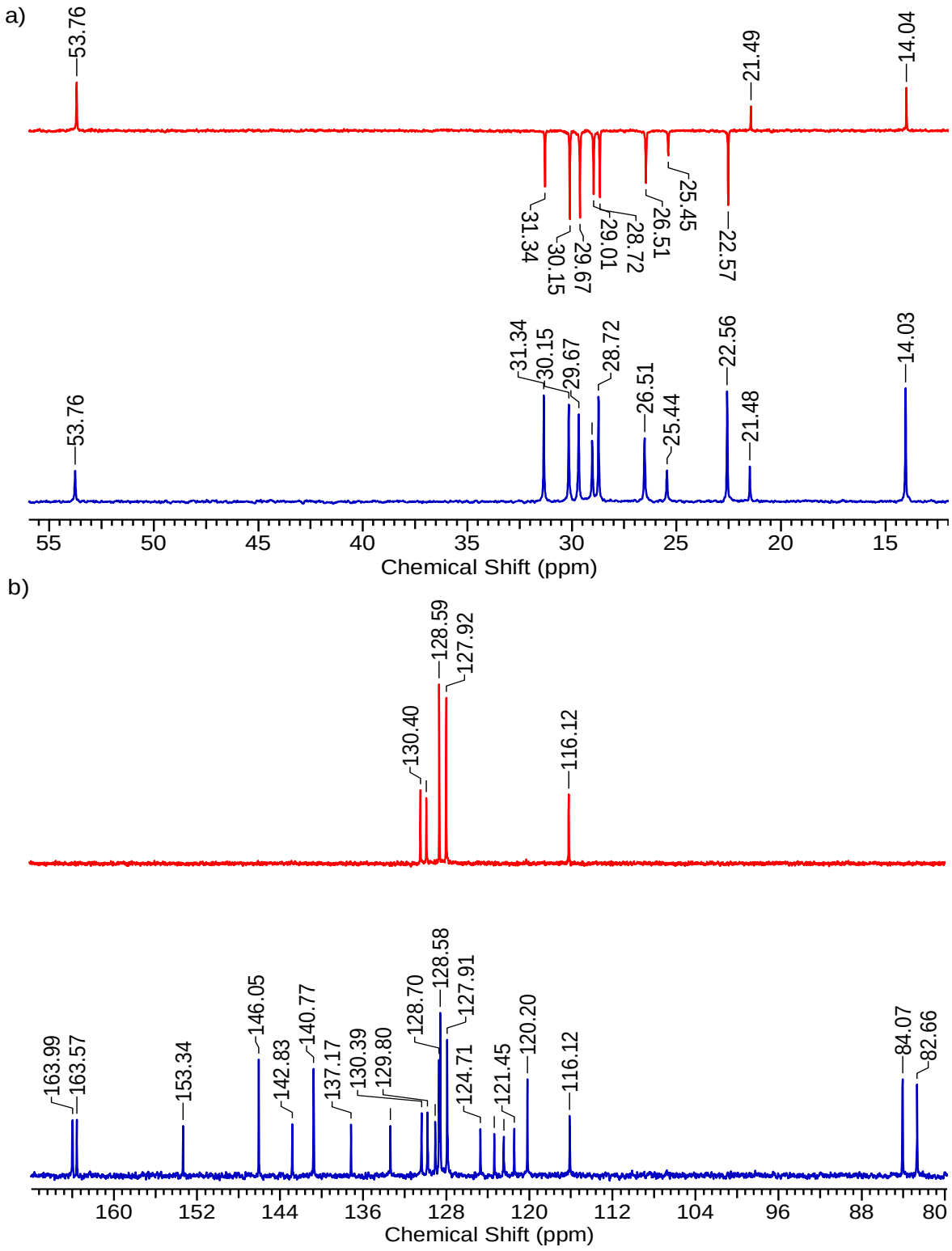


Figure S17. ^{13}C (blue) and DEPT (red) spectra of **SP2** recorded at 298 K, a) spectra range from 12 to 56 ppm, and b) spectra range from 80 to 165 ppm.

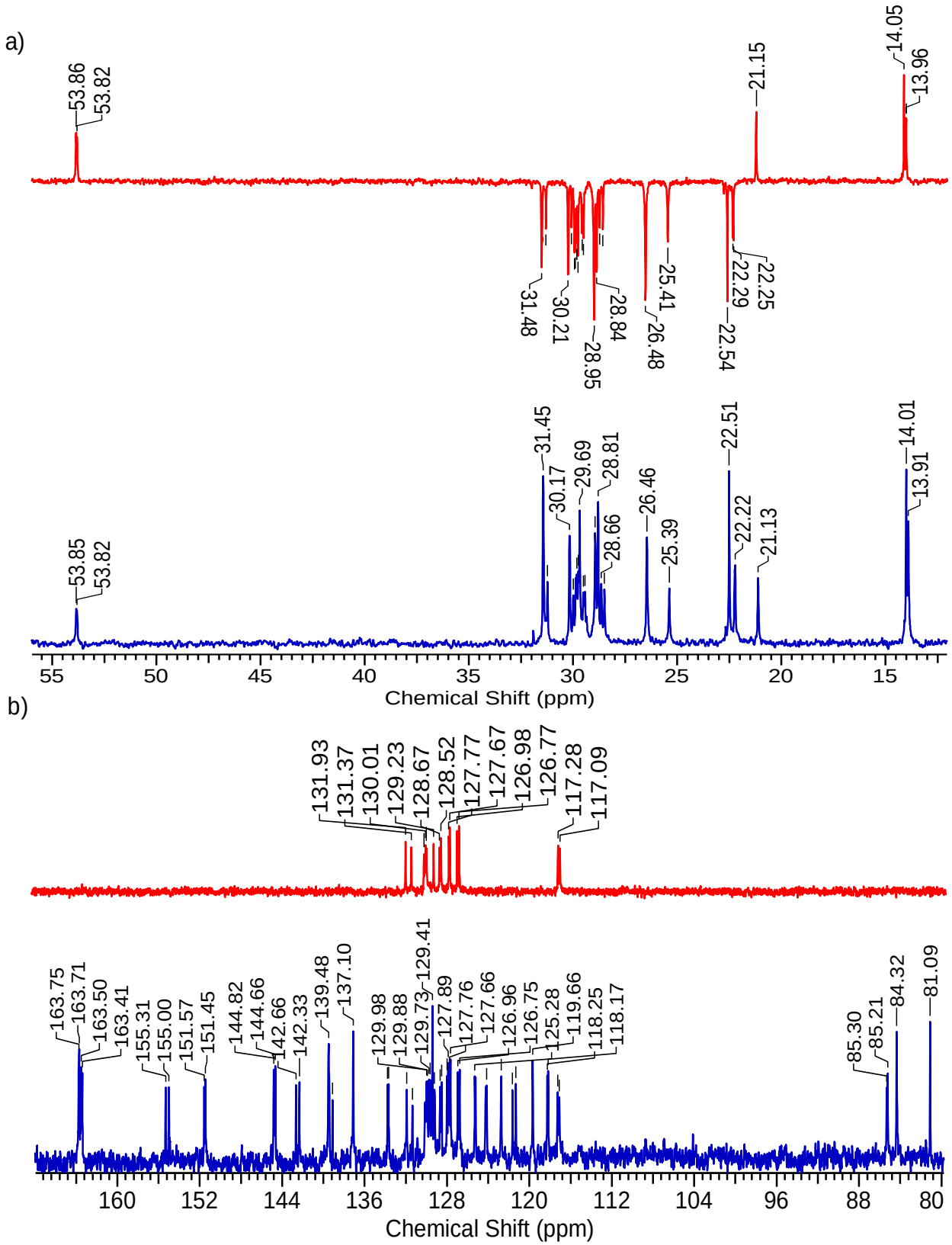


Figure S18. ^{13}C (blue) and DEPT (red) spectra of **SP2D** recorded at 298 K, a) spectra range from 12 to 56 ppm, and b) spectra range from 80 to 165 ppm.

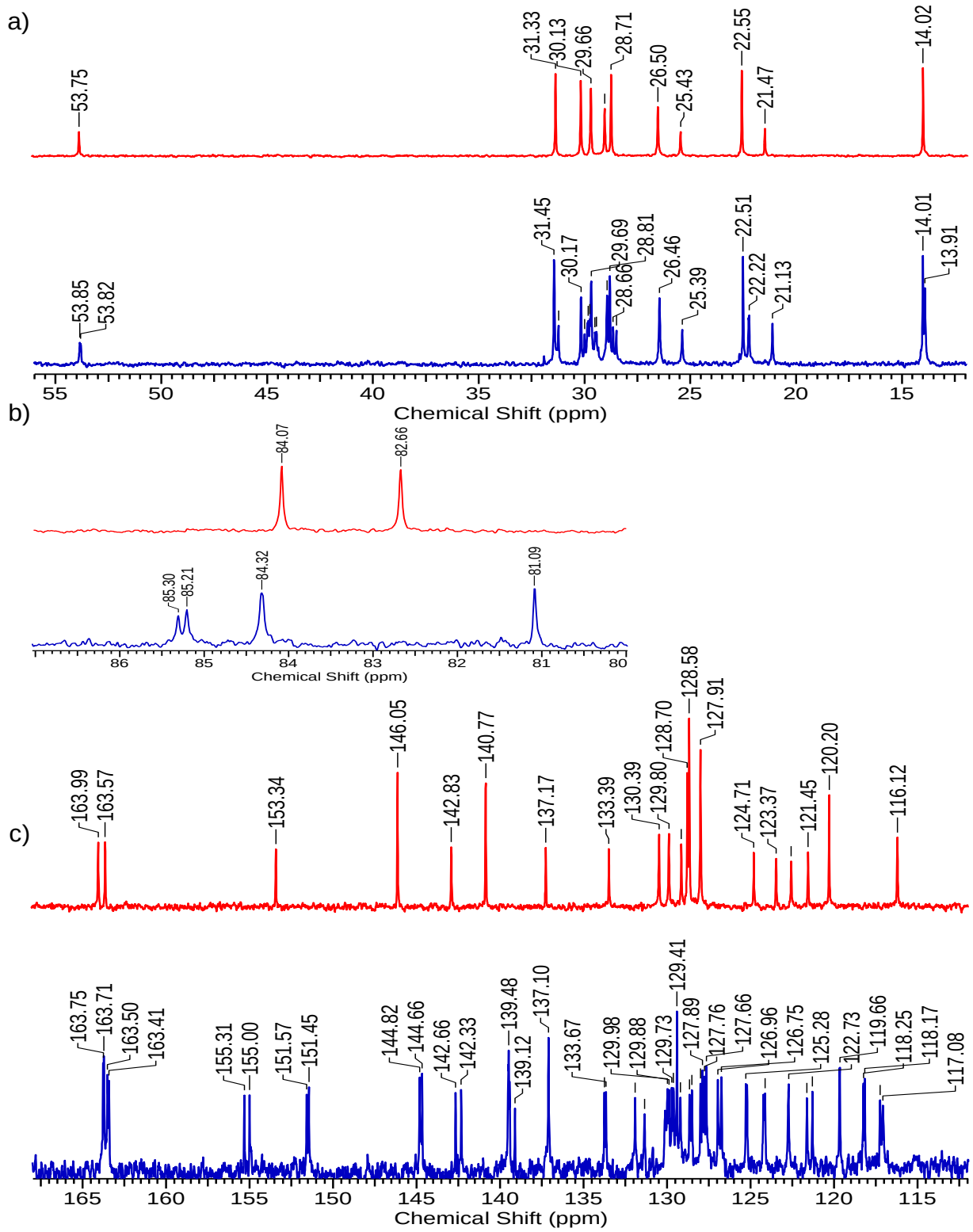


Figure S19. ^{13}C spectra of **SP2** (red) and **SP2D** (blue) recorded at 298 K, a) spectra range from 12 to 55 ppm, b) spectra range from 80 to 87 ppm, and c) spectra range from 112 to 168 ppm. Extra signals corresponding to additional environments caused by dimerization are observed in **SP2D**.

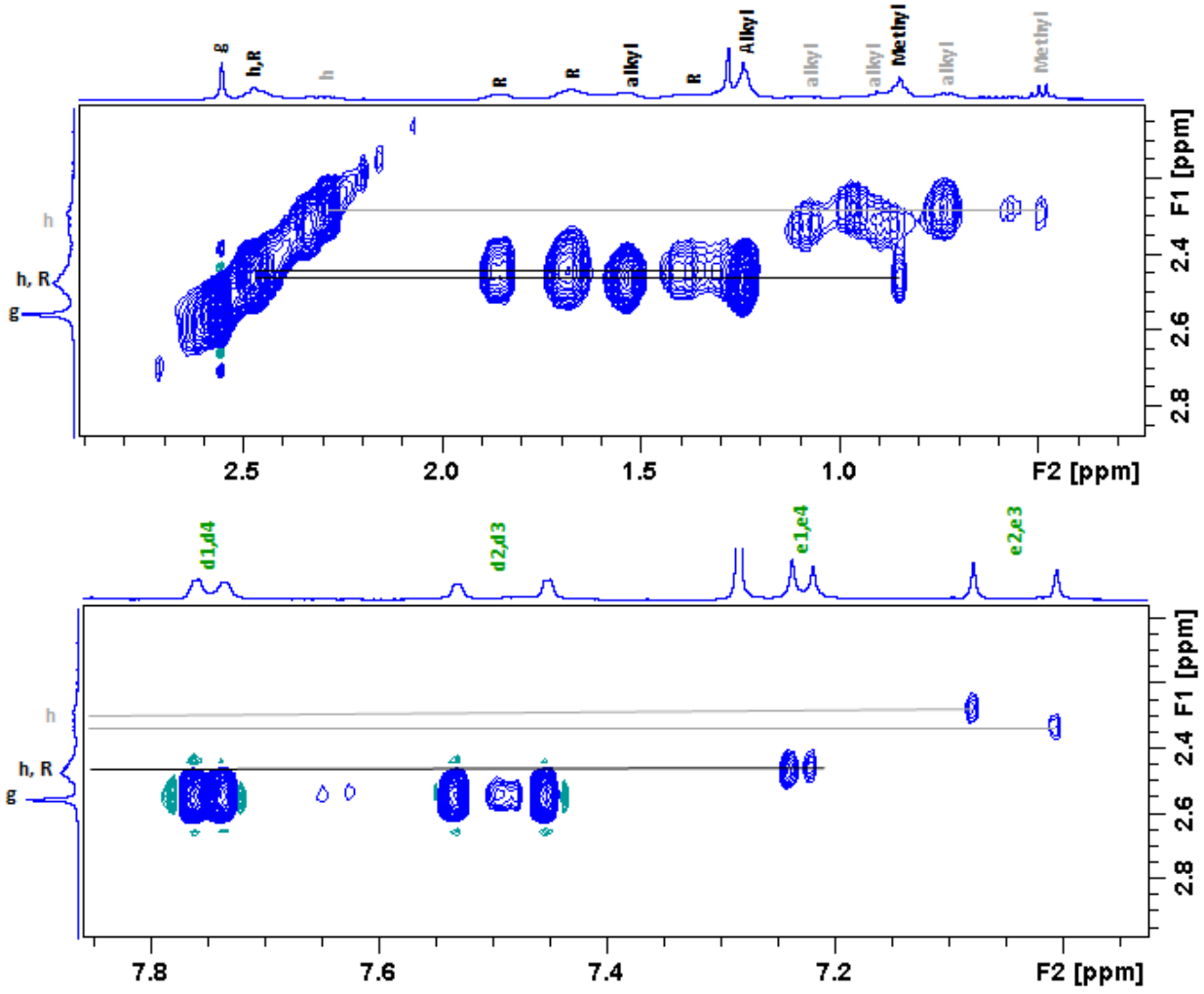


Figure S20. Regions from the TOCSY spectrum of **SP2D**. The unique correlations for different environments arising from dimerization and twisting of the outer ring are indicated in grey and black.

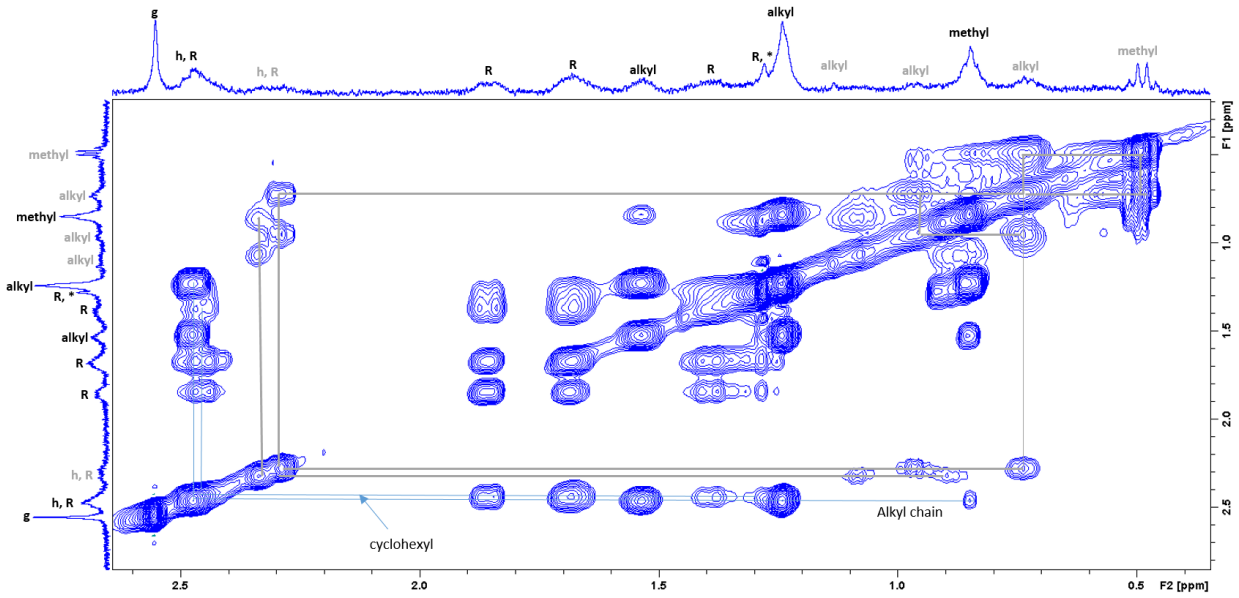


Figure S21: Alkyl region of TOCSY spectrum of **SP2D** showing aliphatic and cyclohexyl correlations. 1D traces at the top and left are from diffusion experiments where the intensity of residual water signal from the solvent is attenuated. Cyclohexyl ring protons are labelled R. Grey labels refer to additional alkyl proton environments arising from dimer formation.

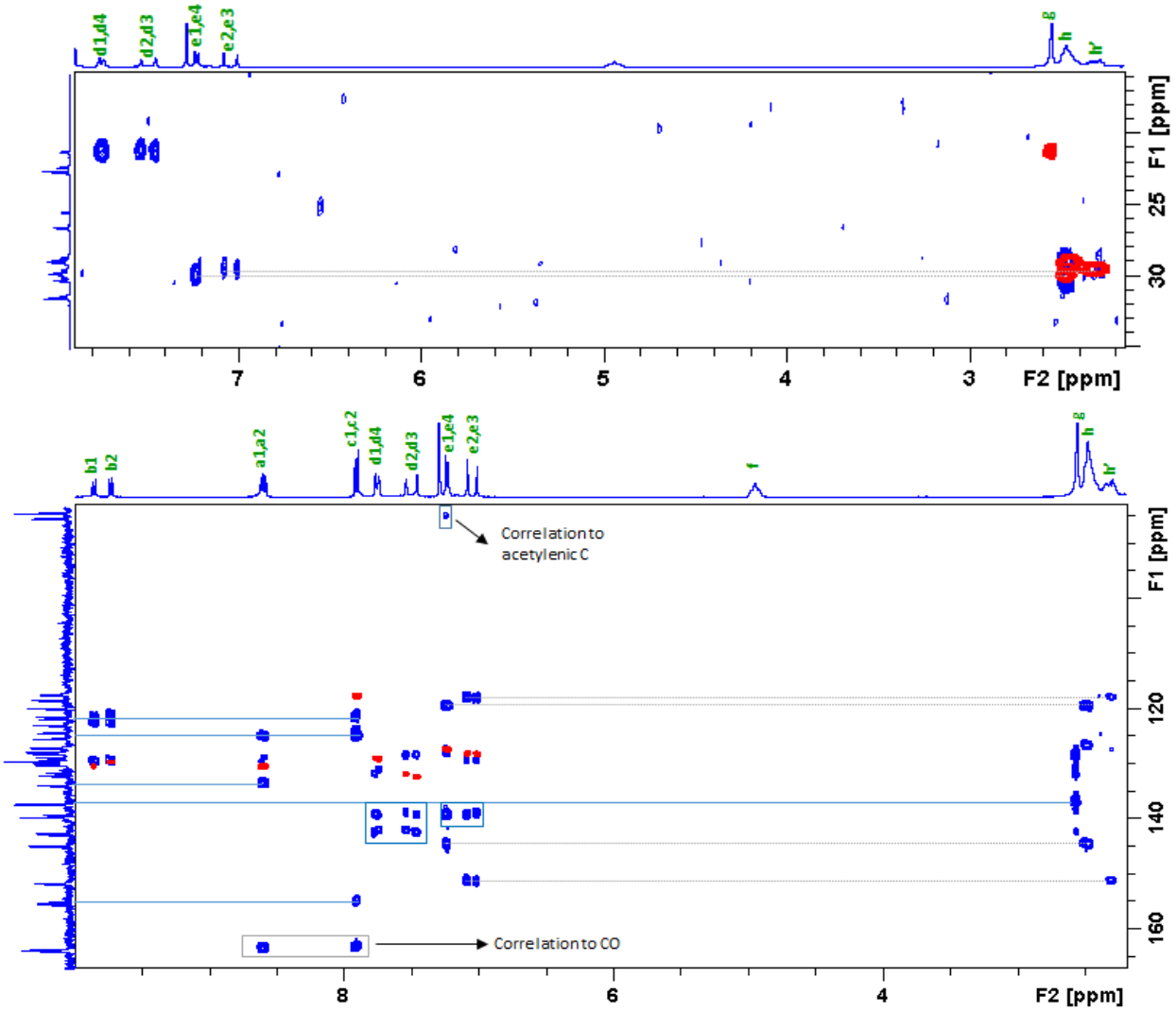


Figure S22: Overlay of ^{1}H-^{13}C HSQC (red) and HMBC (blue) spectra of **SP2D**. Non-equivalent alkyl chain protons correlating to different sets of aromatic *e* protons (grey lines) are labelled *h* and *h'*. Blue boxes/lines indicate correlations to quaternary carbons.

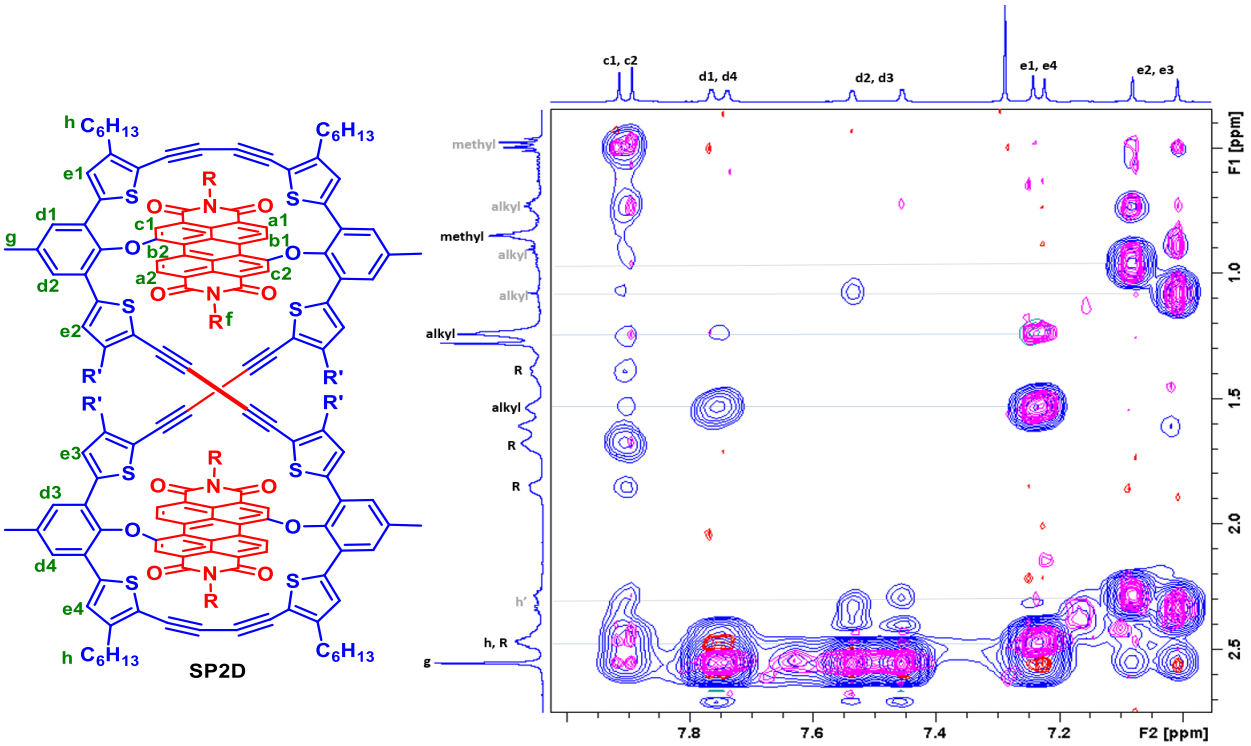


Figure S23: Overlay of NOESY (blue) and ROESY (magenta) spectral regions of **SP2D** showing aromatic to aliphatic proton correlations. Cross-peaks connect pairs of aromatic and aliphatic protons corresponding to different environments arising as a result of dimerization. Cyclohexyl ring protons are labelled R. Grey labels refer to additional alkyl proton environments arising from dimer formation, while numerals specifically indicate additional aromatic proton signals.

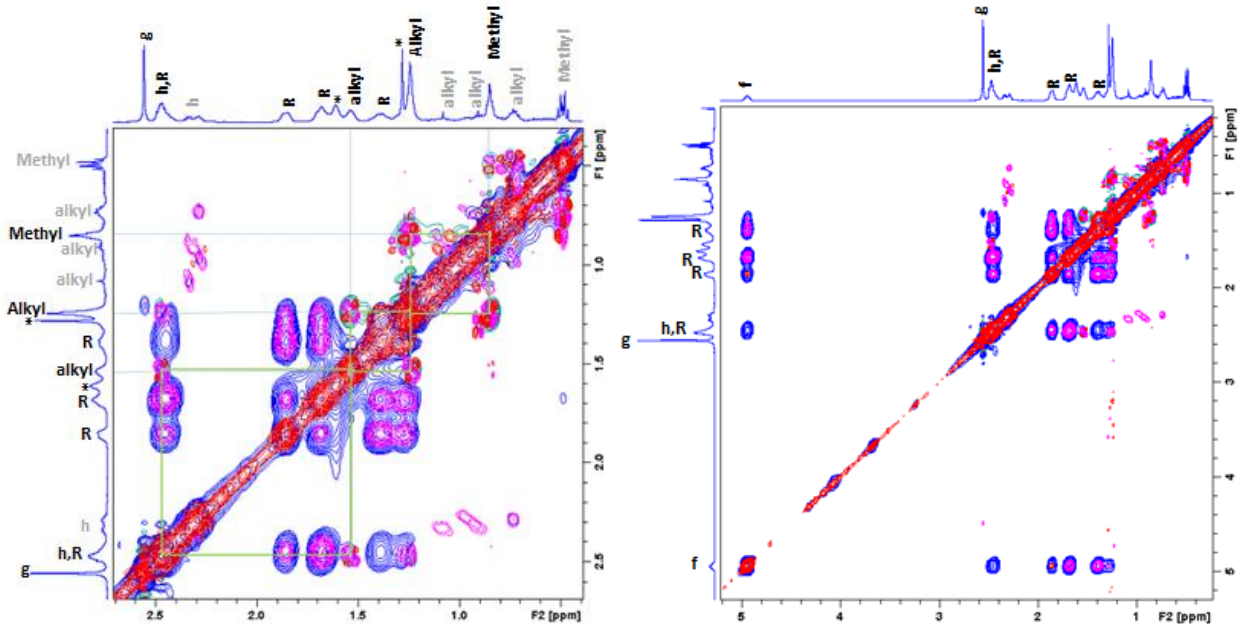


Figure S24. Overlay of NOESY (blue) and ROESY (magenta) spectral regions of **SP2D** showing aliphatic (left) and cyclohexyl (right) correlations. Grey labels correspond to alkyl proton signals which arise due to the non-degeneracy of chemical shifts induced by dimerization. Weak cross-peaks are observed between these protons, indicating alkyl chains with a different orientation. The data supports the geometry of **SP2D** shown in Figure 3d.

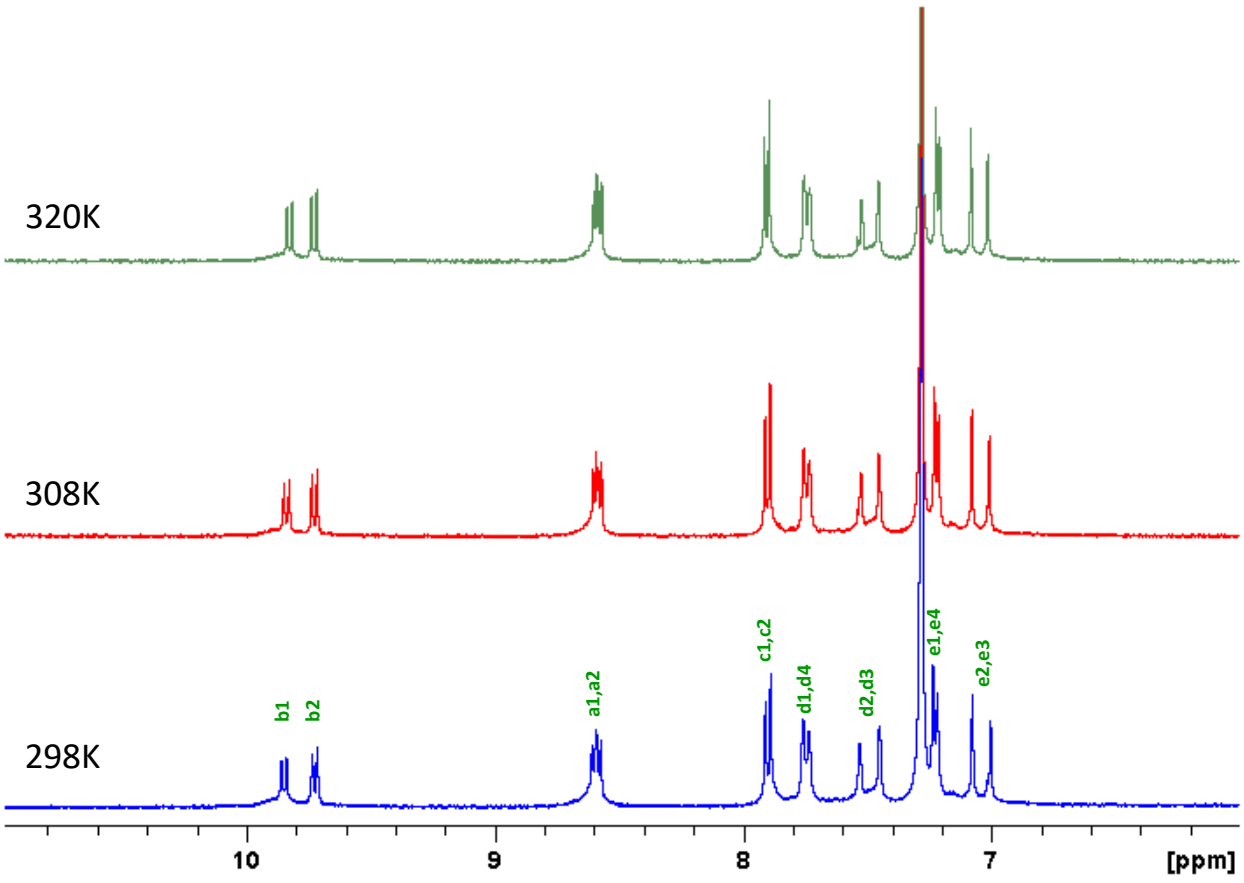


Figure S25. Aromatic region of ^{1}H NMR spectra of **SP2D** at different temperatures. Signals corresponding to different environments arising from dimerization do not undergo significant chemical shifts or linewidth changes, indicating that the dimer conformation is fairly stable.

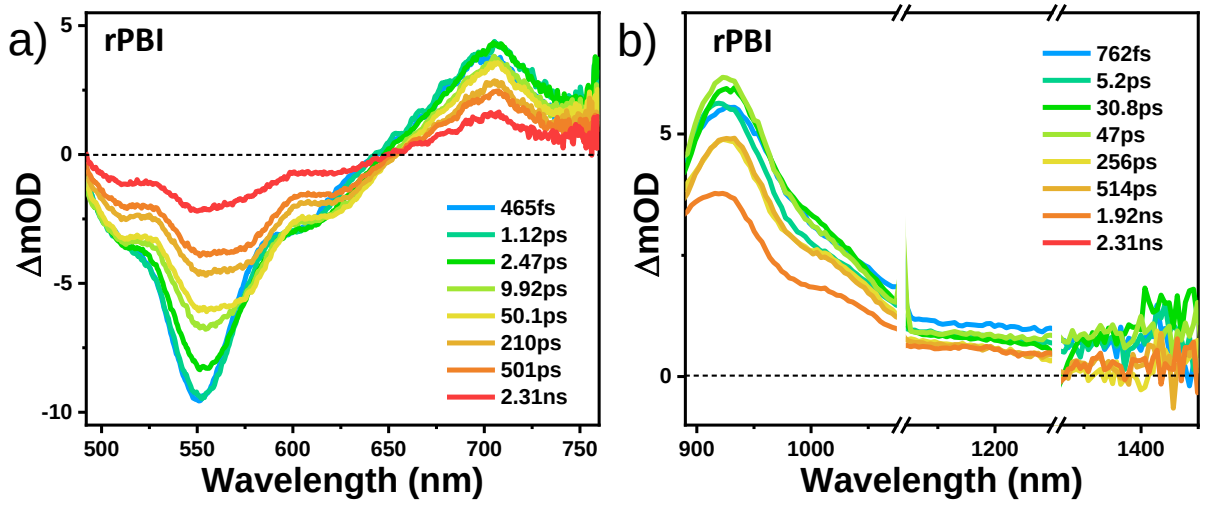


Figure S26. FTAS spectra of **rPBI** in CH_2Cl_2 a) in the visible region for 420 nm excitation and b) in the NIR region for 420 nm excitation.

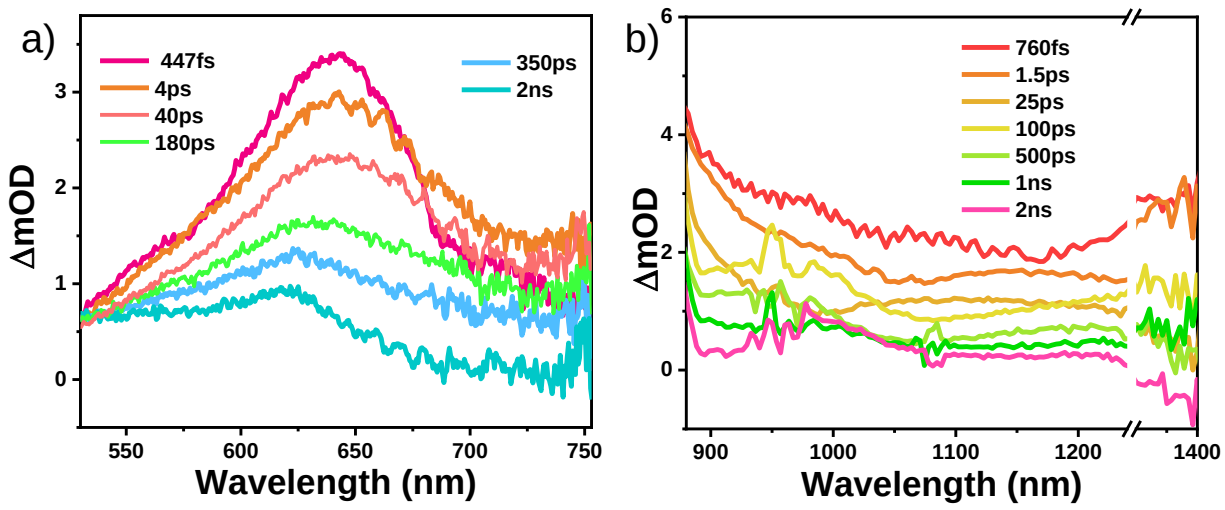


Figure 27. FTAS spectra of **T8** in CH_2Cl_2 a) in the visible region for 420 nm excitation and b) in the NIR region for 420 nm excitation.

Tables

Table S1. Optical and redox properties of **rPBI**, **SP1**, **SP2**, and **SP2D**.

Sample	$\lambda_{max,\ ab}$ (nm)	ε_{max} ($M^{-1}cm^{-1}$)	$\lambda_{max,\ em}$ (nm)	E_{ox}, 1 (eV)	E_{ox}, 2 (eV)	E_{ox}, 3 (eV)	E_{red}, 1 (eV)	E_{red}, 2 (eV)
rPBI	542	49,575	570	-	-	-	-1.14	-1.30
SP2	561	41,539	535	0.81	1.06	1.18	-1.28	-1.57
SP2D	557	55,758	535	0.75	1.07	1.19	-1.26	-1.53

Table S2. Fluorescence lifetime of **rPBI**, **SP2**, and **SP2D** in CH_2Cl_2 (c = 1x10^{-5} M).

Sample	Lifetime in ns	Contribution in %
rPBI@570 nm	5.09	100
SP2@535 nm	6.7 3.3	30 70
SP2D@535 nm	8.7 3.2	26 74

Table S3. Emission quantum yield of **rPBI**, **SP2** and **SP2D** in CH_2Cl_2 (c = 1x10^{-5} M).

Sample	PLQY (%)
rPBI	73.54
SP2	11.14
SP2D	8.52

Table S4: Fitting parameters of FTAS dynamic profiles of **SP2** and **SP2D** monitoring at both visible and NIR regions.

System	Wavelength (nm)	*Charge separation times*	*Charge recombination times*	
		τ_g (ps)	τ_1 (ps)	τ_2 (ns)
SP2 VIS	730	2.7	545 (85.6 %)	> 1 ns (14.4 %)
SP2 NIR	1460	11.8	613 (100 %)	-
SP2D VIS	738	8.4	448 (93 %)	> 1 ns (7 %)
SP2D NIR	1400	7.3	517 (100 %)	-

5. References

S1. Wang, X.; Snieckus, V. Synthetic Strategies Based on Aromatic Metalation - Cross Coupling Links. Regiospecific Synthesis of The Phenanthrene Natural Product Gymnopusin. *Tetrahedron Lett*. **1991**, *32*, 4879-4882.

S2. Liu, Q.; Ho, C. L.; Lo, Y. H.; Li, H.; Wong, W. Y. Narrow Bandgap Platinum (II)-Containing Polyynes with Diketopyrrolopyrrole and Isoindigo Spacers. *J. Inorg. Organomet. Polym. Mater*. **2015**, *25*, 159-168.

S3**.** A, Schmitt.; S, Samal.; B, C, Thompson.; Tuning the surface energies in a family of poly-3-alkylthiophenes bearing hydrophilic side-chains synthesized via direct arylation polymerization *Polym. Chem***. 2021**, *12*, 2840-2847.

S4. Hay, A. S. Oxidative Coupling of Acetylenes. *J. Org. Chem.* **1962**, *27*, 3320-3321.