Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Tetrathiafulvalene-oligofluorene star-shaped systems: new materials for fluorescent moisture indicators

Katrina Scanlan[a], Alexander L. Kanibolotskyy[b,c] , Benjamin Breig, Gordon Hedley[b] and Peter J. Skabara[b*]

[a]*WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK*

[b]*WestCHEM, Department of Pure and Applied Chemistry, University of Glasgow, Glasgow G12 8QQ, UK*

[c] Institute of Physical-Organic Chemistry and Coal Chemistry, 02160 Kyiv, Ukraine

Supplementary Information

General Experimental

Unless otherwise stated, all reagents and solvents were purchased from Sigma Aldrich or Alfa Aesar with no further purification. Dry solvents (dichloromethane, tetrahydrofuran, toluene) were obtained from a solvent purification system (SPS 400, innovative technologies) using alumina as the drying agent. Any additional dry solvents were purchased from Sigma Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance DPX400 at 400.13 and 100.61 MHz or a Bruker Advance DRX500 at 500 and 125.75 MHz. Proton and carbon NMR chemical shifts are reported as δ values in ppm. The chemical shifts are calibrated to residual solvent signals.[41] For ^{1}H NMR chemical shifts are calibrated to 7.26 ($CDCl_3$) and for ^{13}C chemical shifts are calibrated to 77.16 ($CDCl_3$). NMR data are presented as follows: chemical shift, number of nuclei based on integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet) and coupling constant(s) (*J*) are in Hz. Multiplets are reported over the range (in ppm) in which they appear. MS MALDI-TOF spectra were recorded on a Shimadzu Axima-CFR spectrometer (mass range 1-150,000 Da) and retinoic acid or dithranol was used as a matrix.

Emission spectra were recorded using the Perkin Elmer L545 or the Jasco FP-6500 fluorescence spectrometer. Both absorption and emission solutions contained compounds of ca. 10^{-6} M. Photoluminescence quantum yields were measured with the Quantaurus Plus from Hamamatsu Photonics. The sample (fused silica solution cuvette or thin film sample placed in fused silica petri dish) was placed inside a spectralon coated integrating sphere and fibre coupled excitation is provided with a high power xenon lamp, filtered for 50 nm bandwidth around the stated wavelength. Detection was made with a baffle protected fibre output port on the sphere, with light coupled into a backthinned multichannel CCD, recording both the excitation and emission spectrum. Measurements were performed by first measuring a blank to capture the power of the excitation, then with the sample to determine the amount of light absorbed and emitted. Software integration of the areas under the peaks, and correction for photometric responses of the sphere, fibres etc., all lead to a final value of the PLQY that is automatically calculated in the Hamamatsu supplied software. UV-Vis absorption spectra were recorded using the UNICAM UV 300, the Jasco V-660 or the Shimadzu UV-2600. The baseline of solvents were measured prior to analysis and the solution spectra recorded in 1 cm or 1 mm path length quartz cells between 190-900 nm (figures in the main manuscript and SI are shown for wavelengths up to 630 nm for ease of reference, but we confirm here that there are no additional bands in the region 630 – 900 nm). Cyclic voltammetry measurements were obtained using the CH Instruments 660A electrochemical workstation with iR compensation using anhydrous dichloromethane. The scan rate used for all experiments was 0.1 V s^{-1}. The electrodes used were glassy carbon, platinum wire and silver wire as the working, counter and reference electrodes, respectively. All solutions were degassed with argon and contained compounds of ca. 10^{-3} M and $TBAPF_6$ (0.1 M) as the supporting electrolyte. All measurements were referenced against $E_{1/2}$ of the Fc/Fc^+ redox couple. Thermogravimetric analysis was performed using the Perkin Elmer Thermogravimetric Analyser TGA7 under a constant flow of argon. Differential scanning calorimetry was conducted on the TA Instruments Q1000 with a RC-90 refrigerated cooling unit attached. The calibration was achieved using indium (melt temperature 156.42 °C, ΔH_f 28.42 J/g). The procedure used was a standard heat-cool-heat cycle in the range of -50 to 500 °C at a heating rate of 5 or 10 °C/min.

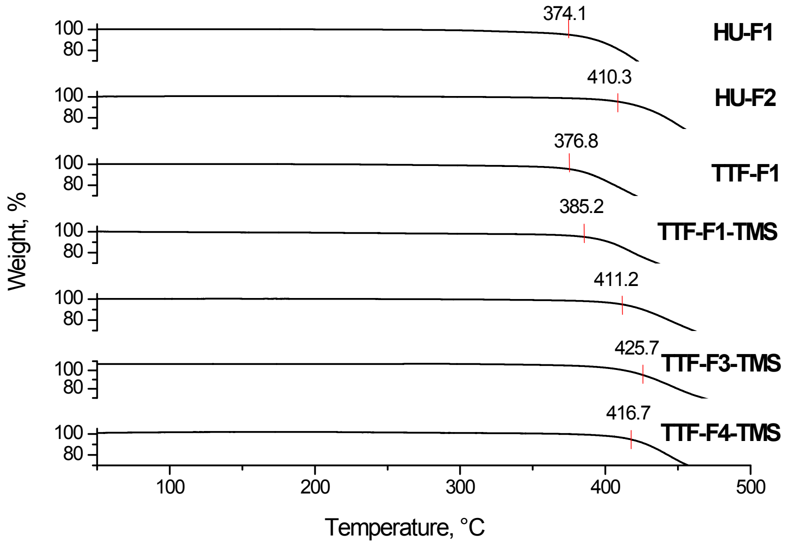


Figure S1 Thermal gravimetric analysis (TGA) showing decomposition temperature (T_d, 5% mass loss) of compounds **HU-F1-2** and **TTF-(F1-F4)-X** series.

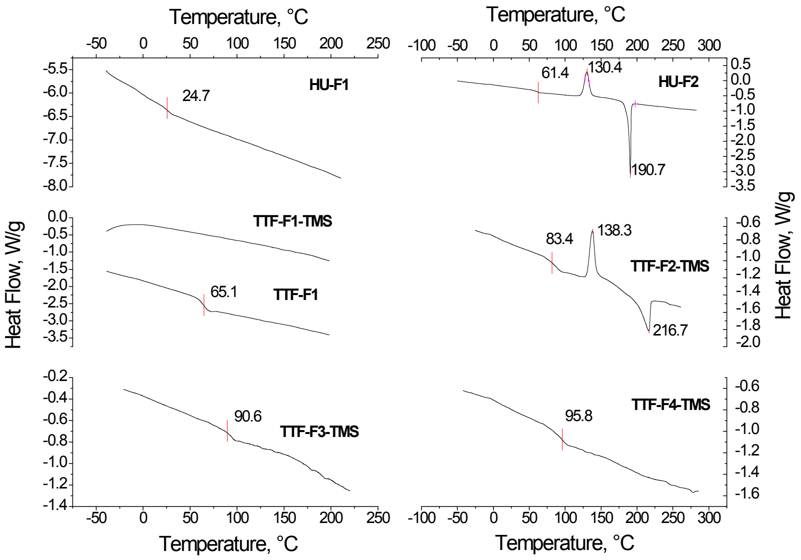


Figure S2 Differential scanning calorimetry (DSC) of compounds **HU-F1-2** and **TTF-F(1-4)-X series** showing glass transition temperatures (T_g).

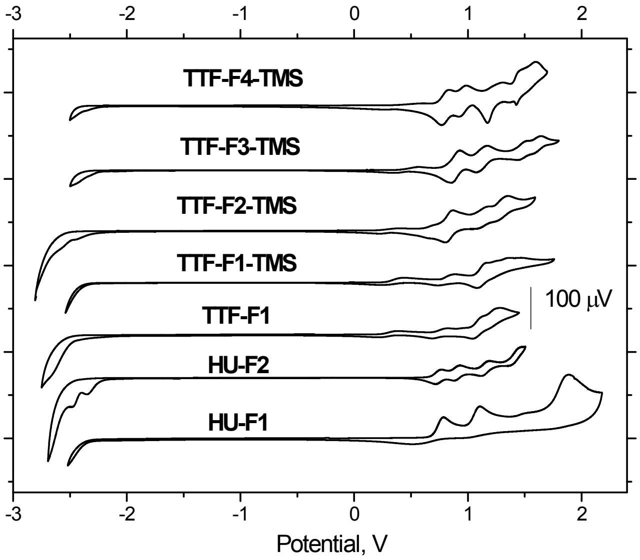


Figure S3 Cyclic Voltammetry of compounds **HU-F1-2** and **TTF-(F1-F4)-X** in CH_2Cl_2.

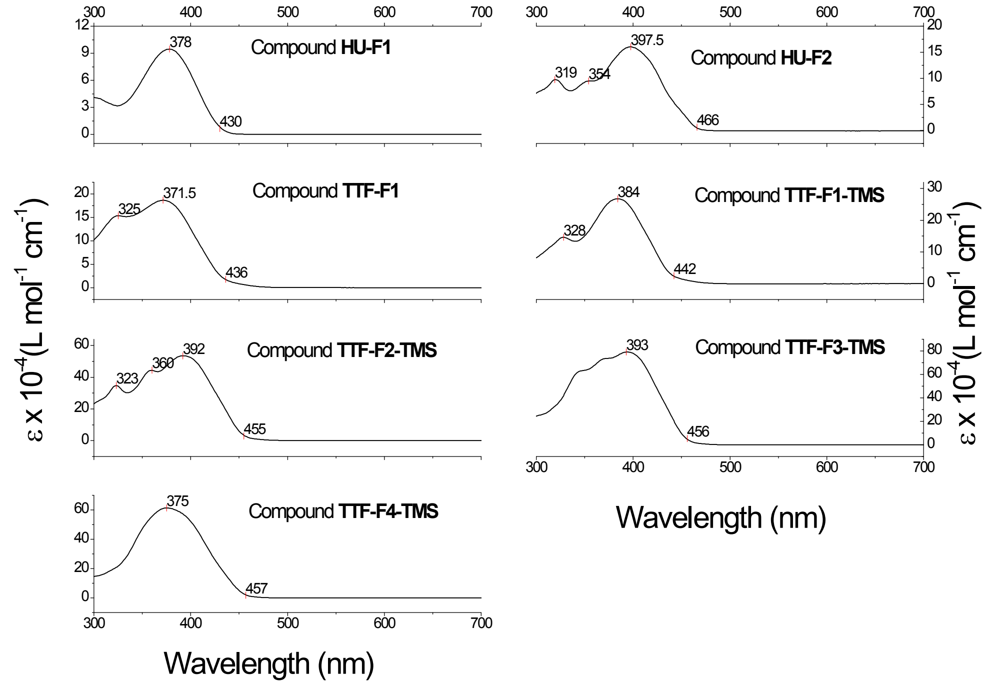


Figure S4 The spectra of compounds **HU-F1-2** and **TTF-(F1-F4)-X** (extinction coefficient versus wavelength) in dichloromethane. The onsets and positions of peaks are marked.

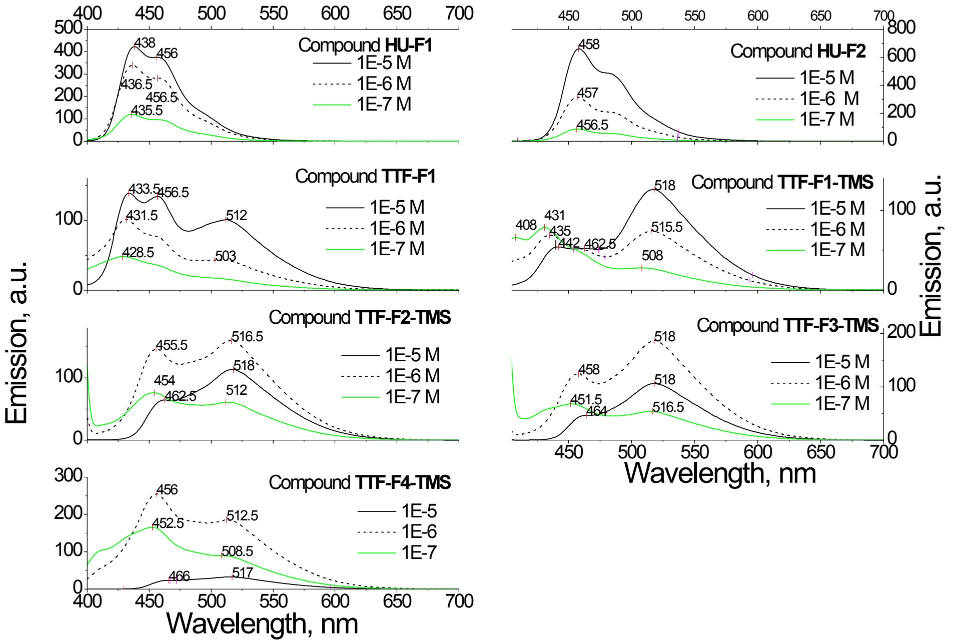


Figure S5 PL spectra of compounds **HU-F1-2** and **TTF-(F1-F4)-X** in dichloromethane at different concentrations ($1 \cdot 10^{-5}$ - $1 \cdot 10^{-7}$ M). λ_{ex} (**12**) = 378 nm, λ_{ex} (**13**) = 399 nm, λ_{ex} (**TTF-F1**) = 372 nm, λ_{ex} (**TTF-**

F1-TMS) = 384 nm, λ_{ex} (**TTF-F2-TMS**) = 392 nm, λ_{ex} (**TTF-F3-TMS**) = 396 nm, λ_{ex} (**TTF-F4-TMS**) = 378 nm. The peak positions are marked.

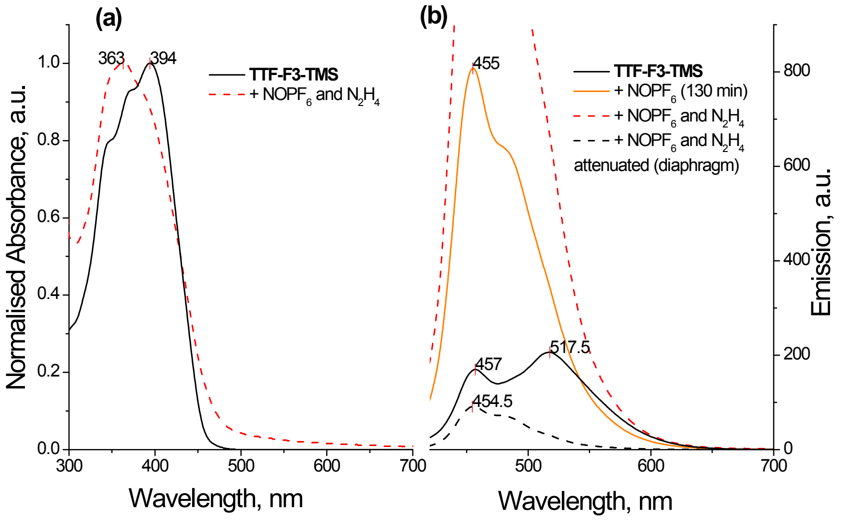


Figure S6 (a) Absorption spectra of **TTF-F3-TMS** ($1\cdot10^{-6}$ M) before and after oxidation with $NOPF_6$ followed by treatment with $N_2H_4\cdot H_2O$ (1 drop); (b) PL spectra of **TTF-F3-TMS** in neutral state, after oxidation with $NOPF_6$ (t= 130 min) and after additional treatment with $N_2H_4\cdot H_2O$ (1 drop).

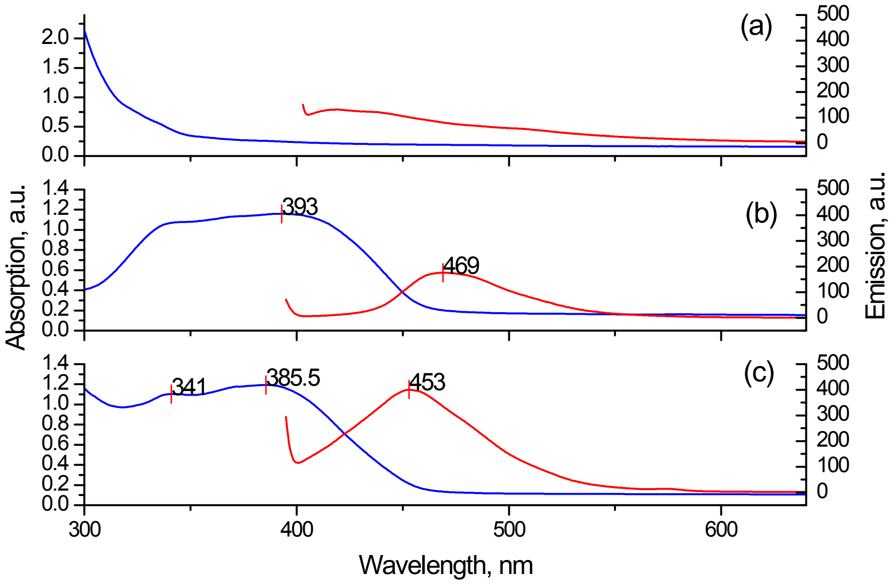


Figure S7 Absorption/emission spectra of UV cured film drop cast from blends: CHDV with 0.1 % of PAG (a); CHDV with 0.1 % of **TTF-F3-TMS** and 0.1 % of PAG before (b) and after exposure to water (c).

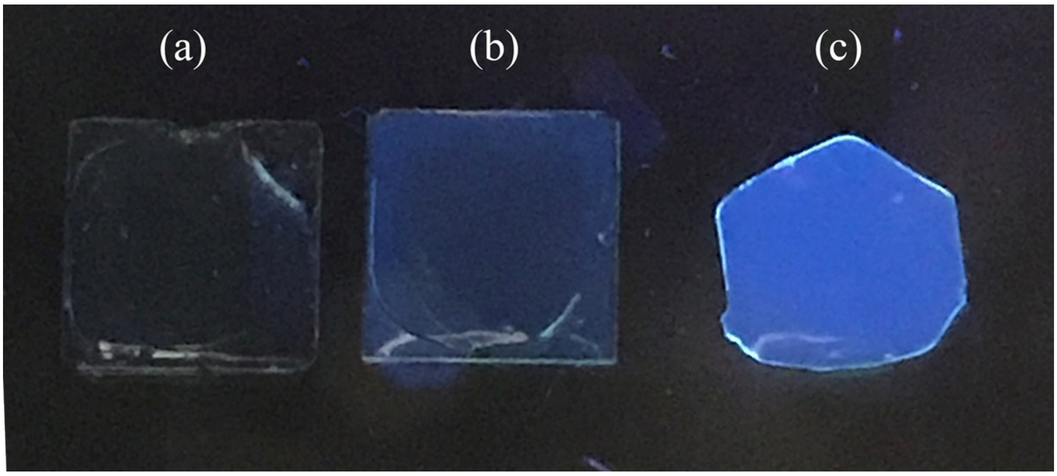
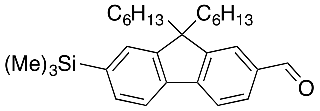


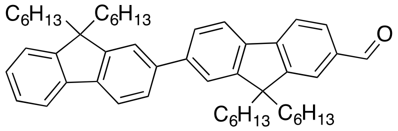
Figure S8 Photographs of the cured films prepared from blends: CHDV with 0.1 % of PAG (a); CHDV with 0.1 % of **TTF-F3-TMS** and 0.1 % of PAG before (b) and after exposure to water (c).

9,9-Dihexyl-7-(trimethylsilyl)-9*H*-fluorene-2-carbaldehyde **(3)**



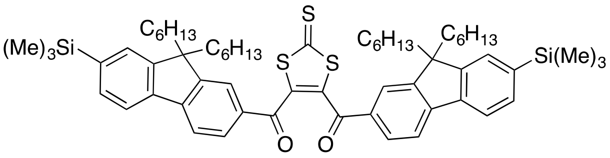
Under N_2, 2,7-dibromo-9,9-dihexyl-9*H*-fluorene (**9**) (6.00 g, 12.2 mmol, 1 equiv) was dissolved in dry THF (105 mL). The temperature of the solution was brought to -78°C and 1.58 M *n*-Buli (7.7 mL, 12.2 mmol, 1 equiv) was added dropwise. The mixture was then cooled further to -100°C and chlorotrimethylsilane (1.7 mL, 13.4 mmol, 1.1 equiv) added. The mixture was allowed to reach room temperature with stirring. The mixture was cooled to -78°C and a second portion of 1.58 M *n*-Buli (8.5 mL, 13.4 mmol, 1.1 equiv) added slowly. The temperature was further reduced to -100°C and dimethylformamide (1.2 mL, 15 mmol, 1.3 equiv) added. The mixture was allowed to reach room temperature and stirred overnight. The mixture was poured onto cold water (200 mL) and the organic layer extracted with diethyl ether (3 x 150 mL). The combined organic layers were washed with water (300 mL), dried over $MgSO_4$ and solvent evaporated under reduced pressure. The product was isolated on silica gel, eluting with a gradient of hexane: dichloromethane 9.9: 0.1 increasing to 6:4 (v/v). A colourless oil was afforded (3.4 g, 64%). ^{1}H NMR ($CDCl_3$): 10.05 (s, 1H, CHO), 7.87-7.84 (m, 3H, Ar-H), 7.75 (dd, *J* = 7.5, 0.7 Hz, 1H, Ar-H), 7.53 (dd, *J* = 7.5, 0.9 Hz, 1H, Ar-H), 7.51 (m, 1H, Ar-H), 2.05-1.98 (m, 4H, CH_2), 1.15-0.97 (m, 12H, CH_2), 0.75 (t, *J* = 7.0 Hz, 6H, CH_3), 0.65-0.56 (m, 4H, CH_2), 0.33 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$): 192.48, 151.86, 151.42, 147.73, 141.70, 140.25, 135.58, 132.23, 130.57, 127.92, 123.36, 120.28, 120.18, 55.33, 40.10, 31.46, 29.61, 23.79, 22.57, 14.08, -0.82. MALDI MS: *m/z* 435.44 $(M + H)^+$. HRMS (ASAP$^+$) calc. for $C_{29}H_{43}OSi$ theoretical mass: 435.3005, found mass: 435.3082.

9,9,9',9'-Tetrahexyl-9*H*,9'*H*-[2,2'-bifluorene]-7-carbaldehyde **(4)**



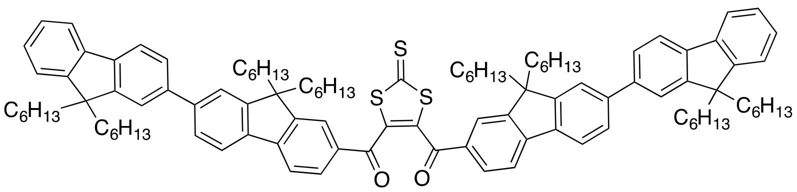
Under nitrogen, 7-Bromo-9,9,9',9'-tetrahexyl-9*H*,9'*H*-2,2'-bifluorene (**10**) (4 g, 5.36 mmol, 1 equiv) was dissolved in 55 mL of dry tetrahydrofuran. The temperature was reduced to -78°C and n-buli (2.3 mL, 5.79 mmol, 1.08 equiv) added drop-wise over 15 min. The mixture was allowed to stir for 5 min and then the temperature reduced to -90°C. Dimethylformamide (0.5 mL, 6.86 mmol, 1.28 equiv) was slowly added and the reaction was allowed to reach room temperature. Stirring continued overnight. The mixture was washed with water with water and extracted with 3 x 75 mL diethyl ether. The organic layers were combined washed with water and dried over magnesium sulphate. The solvent was evaporated under reduced pressure. The product was purified using silica gel chromatography, eluting with 99:1 mixture of hexane/ethyl acetate. The product was isolated as a yellow gum solid (2.14 g, 58%). ^{1}H NMR ($CDCl_3$): 10.08 (s, 1H, Ar-CHO), 7.92-7.85 (m, 3H), 7.86 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.79 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.76-7.73 (m, 1H, Ar-H), 7.69 (dd, *J* = 7.9, 1.6 Hz, 1H, Ar-H), 7.66-7.63 (m, 2H, Ar-H), 7.61 (d, *J* = 1.2 Hz, 1H, Ar-H), 7.38-7.30 (m, 3H, Ar-H), 2.15-1.95 (m, 8H, CH_2), 1.17-1.00 (m, 24H, CH_2), 0.80-0.60 (m, 20H, CH_3, CH_2). ^{13}C NMR ($CDCl_3$): 192.54, 153.11, 151.93, 151.71, 151.16, 147.46, 142.54, 140.90, 140.78, 140.11, 138.78, 135.37, 130.79, 127.31, 126.98, 126.65, 126.30, 123.25, 123.10, 121.74, 121.61, 121.36, 120.11, 119.95, 55.55, 55.34, 40.48, 40.34, 31.59, 29.81, 29.72, 23.91, 22.69, 22.66, 14.14; MS: MALDI 695.18 ([M + H]$^+$); HR-MS calc. for $C_{51}H_{67}O^+$ theoretical mass: 695.5186, found mass: 695.5183 ([M + H]$^+$).

(2-Thioxo-1,3-dithiole-4,5-diyl)bis((9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-yl)methanone) **(5)**



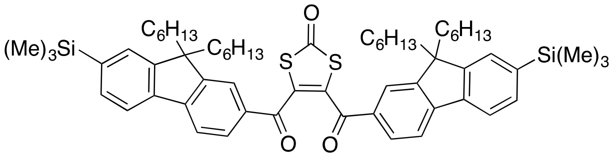
Under N_2, VTC **1** (1.36 g, 10.1 mmol, 1 equiv) was dissolved in THF (46 mL). The temperature was brought to -70°C and 1.62 M LDA.THF (7.4 mL, 12 mmol, 1.2 equiv) was added dropwise. The mixture stirred at -55°C for 30 min and 0.2 M solution of 9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluorene-2-carbaldehyde (**3**) in THF (50 mL) was added dropwise. The mixture allowed to stir for a further 30 min. The second portion of 1.62 M LDA.THF (7.4 mL, 12 mmol, 1.2 equiv) was added at -55°C and the mixture stirred for 15 min. The temperature was reduced to -80°C and a 0.2 M solution of 9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluorene-2-carbaldehyde (**3**) in THF (50 mL) was added slowly and the reaction was allowed to reach room temperature. The mixture was poured onto saturated $NaHCO_3$ solution (400 mL) to which KBr (40 g) was added. The mixture was then extracted using ethyl acetate (3 x 100 mL) and washed with water (200 mL). The mixture was dried on $MgSO_4$ and solvent evaporated under reduced pressure. The mixture was dissolved in CH_2Cl_2 (100 mL) and a 10-fold excess of MnO_2 (w/w) added. The mixture was stirred for 2 min and immediately filtered through a plug of silica. The solvent was evaporated under reduced pressure and the product isolated on silica gel, eluting with a mixture of hexane: toluene 7:3 (v/v). A yellow amorphous solid was afforded (5.1 g, 51%). ^{1}H NMR ($CDCl_3$): 7.64 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.63-7.61 (m, 1H, Ar-H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar-H), 7.55 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.49 (dd, *J* = 7.5, 0.8 Hz, 1H, Ar-H), 7.46 (s, 1H, Ar-H), 2.00-1.80 (m, 4H, CH_2), 1.15-0.95 (m, 12H, CH_2), 0.76 (t, *J* = 7.0 Hz, 6H, CH_3), 0.56-0.44 (m, 4H, CH_2), 0.30 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$): 208.82, 184.39, 151.75, 151.43, 147.88, 145.46, 142.16, 139.74, 134.56, 132.24, 129.37, 128.00, 124.00, 120.46, 120.05, 55.41, 39.78, 31.48, 29.55, 23.74, 22.63, 14.13, -0.87. MALDI MS: *m/z* 999.63 (M$^+$). Anal. Calcd for $C_{61}H_{82}O_2S_3Si_2$: C, 73.29; H, 8.27 %. Found: C, 73.16; H, 8.15%.

(2-Thioxo-1,3-dithiole-4,5-diyl)bis((9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)methanone) **(6)**



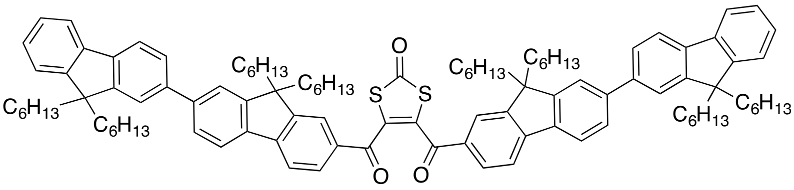
Under N_2, vinylene trithiocarbonate **1** (0.18 g, 1.35 mmol, 1 equiv) was dissolved in dry THF (6 mL). The temperature was reduced to -70°C and LDA.THF (0.76 mL, 1.61 mmol, 1.19 equiv) was added drop-wise. The mixture was stirred at -55°C for 30 min, followed by the drop-wise addition of 9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluorene]-7-carbaldehyde (**4**) (1.04 g, 1.49 mmol, 1.11 equiv) in dry tetrahydrofuran (7.25 mL). The mixture was allowed to stir for another 30 min. A second equivalent of LDA.THF (0.76 mL, 1.61 mmol, 1.19 equiv) was added and the mixture stirred for 15 min. The temperature of the mixture was reduced to -80°C and a second portion of 9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluorene]-7-carbaldehyde (**4**) (1.04 g, 1.49 mmol, 1.10 equiv) in dry tetrahydrofuran (7.25 mL) was added slowly. The reaction was allowed to reach room temperature and stirring continued overnight. The mixture was poured onto saturated $NaHCO_3$ solution (55 mL) to which KBr (6g) was added. The mixture was extracted using ethyl acetate (3 x 75 mL) and the combined organic layers washed with water. The organic layers were dried on $MgSO_4$ and solvent evaporated under reduced pressure. The mixture was dissolved in CH_2Cl_2 and a 10-fold excess (w/w) of MnO_2 added. The mixture was stirred for 1 min and filtered through silica, eluting with CH_2Cl_2. The solvent was evaporated under reduced pressure and purified on silica eluting with a mixture of 7:3 hexane: toluene, increasing to 1:1. The product was isolated as a yellow amorphous solid (0.53 g, 26%). ^{1}H NMR ($CDCl_3$): 7.79-7.72 (m, 3H, Ar-H), 7.67-7.58 (m, 7H, Ar-H), 7.38-7.30 (m, 3H, Ar-H), 2.10-1.90 (m, 8H, CH_2), 1.18-1.00 (m, 24H, CH_2), 0.80-0.52 (m, 20H, CH_3, CH_2). ^{13}C NMR ($CDCl_3$): 208.83, 184.39, 153.17, 151.84, 151.72, 151.15, 147.63, 145.45, 142.87, 141.00, 140.72, 139.97, 138.28, 134.38, 129.56, 127.36, 127.00, 126.70, 126.29, 123.95, 123.10, 121.81, 121.59, 120.12, 119.97, 55.64, 55.32, 40.47, 40.04, 31.63, 31.59, 29.80, 23.90, 22.74, 22.68, 14.17, 14.14. MS: MALDI 1519.66 ([M + H]$^+$). Mp: 88-90°C.

(2-Oxo-1,3-dithiole-4,5-diyl)bis((9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-yl)methanone) (**7**)



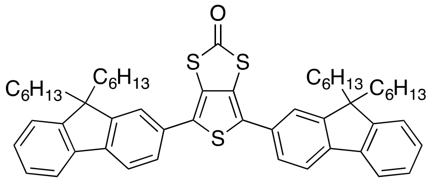
(2-Thioxo-1,3-dithiole-4,5-diyl)bis((9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-yl)methanone) (**5**) (5.14 g, 5.14 mmol, 1 equiv) was dissolved in 136 ml of CH_2Cl_2/CH_3COOH (3:1 v/v). $Hg(OAc)_2$ (2.11 g, 6.62 mmol, 1.29 equiv) was added and the mixture stirred overnight and mixture was filtered through celite with CH_2Cl_2. The mixture was washed with water (200 mL), washed with $NaHCO_3$ (3 x 200 mL) and dried over $MgSO_4$ and solvent evaporated under reduced pressure. The product was purified by reprecipitated from methanol, affording a yellow amorphous solid (4.65 g, 92%). ^{1}H NMR ($CDCl_3$): 7.69-7.64 (2H, m, Ar-H), 7.62 (1H, dd, *J* = 8.0, 1.6 Hz, Ar-H), 7.57 (1H, d, *J* = 8.0 Hz, Ar-H), 7.53-7.48 (2H, m, Ar-H), 2.02-1.84 (4H, m, CH_2), 1.18-1.00 (12H, m, CH_2), 0.78 (6H, t, J 7.0 Hz, CH_3), 0.64-0.48 (4H, m, CH_2), 0.33 (9H, s, CH_3). ^{13}C NMR ($CDCl_3$): 187.83, 185.88, 151.60, 151.35, 147.58, 141.93, 139.78, 136.55, 134.84, 132.17, 129.31, 127.93, 123.97, 120.38, 119.95, 55.33, 39.74, 31.44, 29.51, 23.68, 22.58, 14.11, -0.90. MS: MALDI 983.58 ([M + H]$^+$).

(2-Oxo-1,3-dithiole-4,5-diyl)bis((9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)methanone) **(8)**



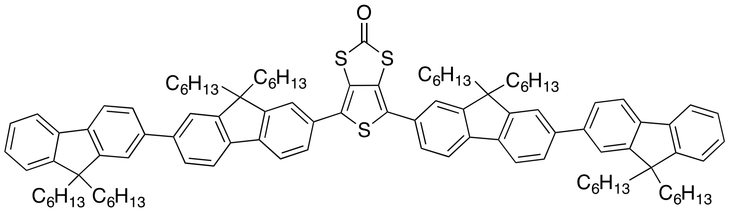
Under N_2, (2-thioxo-1,3-dithiole-4,5-diyl)bis((9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)methanone (**6**) (0.51 g, 0.34 mmol, 1 equiv) was dissolved in a mixture of dry CH_2Cl_2 (6.75 mL) and glacial acetic acid (2.25 mL) in a 3:1 (V/V) ratio. Mercury (II) acetate (0.14 g, 0.44 mmol, 1.3 equiv) was added. The reaction was stirred overnight at room temperature. The mixture was filtered through celite with CH_2Cl_2 and then washed with water (150 mL) and saturated NaHCO3 solution (2 x 150 mL). The organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The product was purified through reprecipitation using methanol yielding a yellow amorphous solid (0.40 g, 78%). ^{1}H NMR ($CDCl_3$): 7.81-7.72 (m, 3H, Ar-H), 7.70-7.56 (m, 7H, Ar-H), 7.39-7.29 (m, 3H, Ar-H), 2.09-1.90 (m, 8H, CH_2), 1.20-1.00 (m, 24H, CH_2), 0.80-0.55 (m, 20H, CH_3, CH_2). ^{13}C NMR ($CDCl_3$): 187.99, 185.93, 153.16, 151.75, 151.73, 151.17, 147.39, 142.79, 140.99, 140.75, 140.02, 138.38, 136.57, 134.70, 129.54, 127.35, 127.00, 126.68, 126.29, 123.99, 123.11, 121.83, 121.62, 121.51, 120.12, 119.96, 55.63, 55.33, 40.47, 40.05, 31.64, 31.60, 29.80, 29.71, 23.91, 22.73, 22.68, 14.16, 14.12. Mp: 80-82°C; MS: MALDI 1476.71 ($[M - 26]^+$). Anal. Calcd for $C_{105}H_{130}OS_3$: C, 83.83; H, 8.71; N, 0.00. Found: C, 83.61; H, 8.68; N, 0.00.

4,6-Bis(9,9-dihexyl-9*H*-fluoren-2-yl)thieno[3,4-*d*][1,3]dithiol-2-one **(HU-F1)**



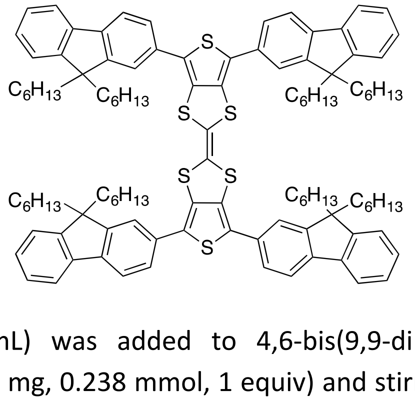
Under N_2, (2-oxo-1,3-dithiole-4,5-diyl)bis((9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-yl)methanone) (**7**) (0.50 g, 0.51 mmol, 1 equiv), P_4S_{10} (0.56 g, 1.3 mmol, 2.5 equiv) $NaHCO_3$ (0.37 g, 4.4 mmol, 8.7 equiv) and 1,4-dioxane (10.5 mL) were stirred. The mixture was heated between 60-90°C for 30 min. The mixture was further heated for 3 hr at 90°C and then allowed to cool to room temperature. Water (2 mL x 10) was added (caution – H_2S and CO_2 evolution!) and the mixture was refluxed for 1 hr and then cooled to room temperature. A brown sticky solid was produced and dissolved in a minimum amount of CH_2Cl_2. This mixture was washed with water and extracted with CH_2Cl_2 (15 mL x 3). The combined organic layers were dried over $MgSO_4$ and solvent evaporated under reduced pressure. The product was isolated on silica eluting with a mixture of 9:1 hexane/toluene, affording a yellow amorphous solid (0.20 g, 47%). ^{1}H NMR ($CDCl_3$): 7.78 (d, 7.8 Hz, 1H, Ar-H), 7.75-7.71 (m, 1H, Ar-H), 7.60-5.55 (m, 2H, Ar-H), 7.40-7.31 (m, 3H, Ar-H), 2.07-1.97 (m, 4H, CH_2), 1.20-1.00 (m, 12H, CH_2), 0.77 (t, 7.0 Hz, 6H, CH_3), 0.73-0.62 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): 193.37, 152.12, 151.22, 141.83, 140.27, 133.86, 131.26, 127.82, 127.14, 125.82, 124.61, 123.13, 121.05, 120.58, 120.17, 55.46, 40.47, 31.62, 29.81, 23.93, 22.70, 14.14.; MS: MALDI m/z 839.06 (M+H)$^+$. Anal. Calcd for $C_{55}H_{66}OS_3$: C, 78.71; H, 7.93; N, 0.00. Found: C, 78.85; H, 8.14; N, 0.00.

4,6-Bis(9,9,9',9'-Tetrahexyl-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)thieno[3,4-*d*][1,3]dithiol-2-one **(HU-F2)**



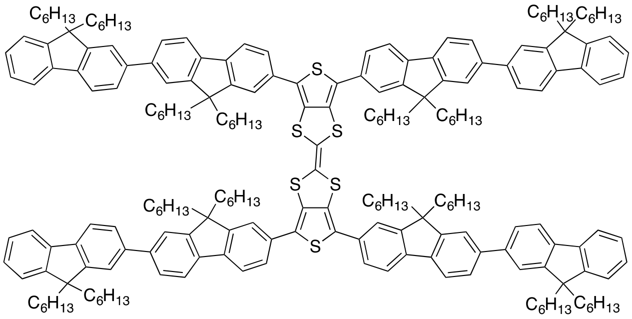
Under N_2, (2-oxo-1,3-dithiole-4,5-diyl)bis((9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)methanone) (**8**) (0.369 g, 0.245 mmol, 1 equiv), P_4S_{10} (0.27 g, 0.61 mmol, 2.49 equiv) and $NaHCO_3$ (0.11 g, 1.25 mmol. 5 equiv) were stirred in 1,4-dioxane (5 mL). The reaction was heated between 60-90°C for 30 min and then heated at 90°C for 3 hours. The mixture was cooled to room temperature and water (3 x 4 mL) added and refluxed for 1 hour. The reaction mixture was allowed to reach room temperature and then poured onto water (10 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with water (15 mL), dried over $MgSO_4$ and solvent removed under reduced pressure. The product was purified on silica using an eluent mixture of hexane/toluene 9:1 increasing to 7:3 to give the product as a yellow amorphous solid (0.25 g, 68%).^{1}H NMR ($CDCl_3$): 7.85-7.72 (m, 4H, Ar-H), 7.71-7.60 (m, 6H, Ar-H), 7.40-7.30 (m, 3H, Ar-H), 2.20-1.95 (m, 8H, CH_2), 1.20-1.05 (m, 24H, CH_2), 0.85-0.67 (m, 20H, CH_3, CH_2). ^{13}C NMR ($CDCl_3$): 193.37, 152.43, 152.02, 151.69, 151.17, 141.55, 141.42, 140.88, 140.68, 140.39, 139.42, 133.90, 131.24, 127.22, 126.97, 126.51, 126.23, 125.95, 124.66, 123.10, 121.67, 121.59, 121.11, 120.65, 120.43, 120.08, 119.91, 55.62, 55.34, 40.51, 40.47, 31.62, 29.83, 29.80, 24.01, 23.93, 22.70, 14.15. MS: MALDI 1475.35 ([M - 26]$^+$). Anal. Calcd for $C_{105}H_{130}OS_3$: C, 83.83; H, 8.71; N, 0.00. Found: C, 83.61; H, 8.68; N, 0.00.

4,4',6,6'-Tetrakis(9,9-dihexyl-9*H*-fluoren-2-yl)-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene **(TTF-F1)**



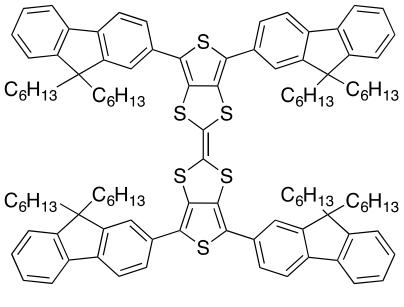
Freshly distilled $P(OEt)_3$ (12 mL) was added to 4,6-bis(9,9-dihexyl-9*H*-fluoren-2-yl)thieno[3,4-*d*][1,3]dithiol-2-one (**HU-F1**) (200 mg, 0.238 mmol, 1 equiv) and stirred under N_2 at 125 C for 3 days. The mixture was cooled to room r/t and the precipitate dissolved in CH_2Cl_2 and solvent removed under reduced pressure. The product was isolated on silica eluting with hexane/toluene (8:2 v/v) and additionally reprecipitated from methanol, affording a yellow amorphous solid (114 mg, 58 %). ^{1}H NMR ($CDCl_3$): 7.78 (1H, d, *J* = 7.9 Hz, Ar-H), 7.77-7.72 (m, 1H, Ar-H), 7.61 (dd, *J* = 7.9, 1.7 Hz, 1H, Ar-H), 7.57 (1H, d, *J* = 1.4 Hz, Ar-H), 7.42-7.31 (m, 3H, Ar-H), 2.15-1.95 (m, 4H, CH2), 1.18-1.02 (m, 12H, CH2), 0.80-0.64 (m, 10H, CH3, CH_2). 13C NMR (CDCl3): 151.96, 151.23, 141.17, 140.52, 131.16, 129.47, 127.60, 126.48, 125.16, 123.09, 120.89, 120.36, 120.07, 118.98, 55.47, 40.56, 31.64, 29.86, 23.93, 22.72, 14.17. MS: MALDI 1645.59 ([M + H] $^+$). Anal. Calcd for $C_{110}H_{132}S_6$: C, 80.24; H, 8.08%. Found: C, 80.29; H, 8.19%.

4,4',6,6'-Tetrakis(9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene **(TTF-F2)**



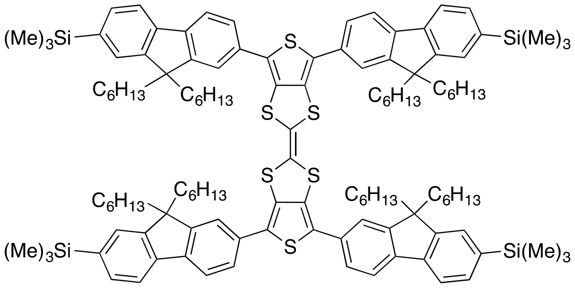
Under N_2, freshly distilled triethyl phosphite (2 mL) was added to 4,6-bis(9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)thieno[3,4-*d*][1,3]dithiol-2-one (**HU-F2**) (0.08 g, 0.05 mmol, 1 equiv). The reaction was stirred at 125°C for 3 days. The reaction was cooled to room temperature and precipitate dissolved in CH_2Cl_2 and solvent removed under reduced pressure. The product was isolated on silica eluting with a mixture of 99:1 hexane/ethyl acetate and re-precipitated from methanol. The product was obtained as a yellow amorphous solid (14.1 mg, 17.8%). ^1H NMR ($CDCl_3$): 7.88-7.58 (m, 10H, Ar-H), 7.40-7.29 (m, 3H, Ar-H), 2.20-1.95 (m, 8H, CH_2), 1.23-1.00 (m, 24H, CH_2), 0.89-0.65 (m, 20H, CH_3, CH_2). 13C NMR (CDCl3): 152.29, 152.01, 151.67, 151.17, 141.20, 140.91, 140.62, 139.68, 131.85, 131.76, 129.54, 127.19, 126.96, 126.46, 126.22, 125.28, 123.09, 121.59, 120.99, 120.44, 120.32, 120.06, 119.90, 119.03, 55.63, 55.34, 40.53, 31.63, 29.84, 24.00, 23.93, 22.71, 14.20, 14.15. Mp: 174-176 °C; (MALDI/TOF, *m/z*): 2974.50 (M^+). Anal. Calcd for $C_{210}H_{260}S_6$: C, 84.73; H, 8.80%. Found: C, 84.49; H, 8.55%. Mp: 174-176 °C.

4,4',6,6'-Tetrakis(9,9-dihexyl-9*H*-fluoren-2-yl)-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**TTF-F1**)



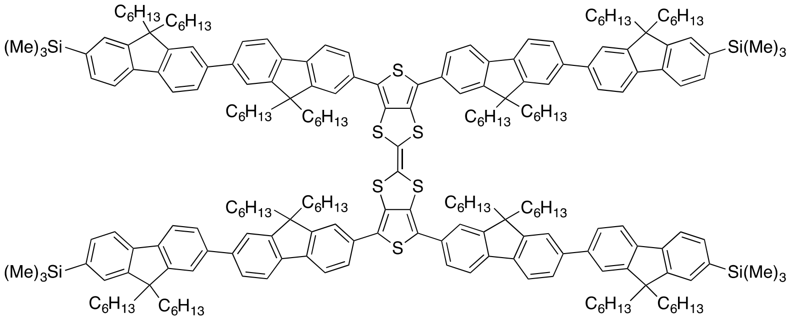
Under N_2, $Pd(PPh_3)_4$ (0.025 g, 0.022mmol, 0.2 equiv), (9,9-dihexyl-9*H*-fluoren-2-yl)boronic acid (**F_1B**) (0.20 g, 0.53 mmol, 4.8 equiv) and $Ba(OH)_2.8H_2O$ (0.28 g, 0.88 mmol, 8 equiv) were added to a mixture of perbromo-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**4**) (0.070 g, 0.11 mmol, 1 equiv) and tetrahydrofuran (2.5 mL). Water (0.6 mL) was added and the reaction mixture degassed. The mixture was placed in a microwave ramping the temperature to 80°C (20 min), then 100°C (1 h 30 min) and reducing to 80°C for a further 2 hrs. The reaction mixture was poured onto water (10 mL), extracted from CH_2Cl_2 (3 x 20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and product isolated on silica eluting with a mixture of hexane/Ethyl acetate 99:1, affording a yellow amorphous solid (0.11 g, 61%). See NMR for compound **14**.

4,4',6,6'-Tetrakis(9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-yl)-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**TTF-F1-TMS**)



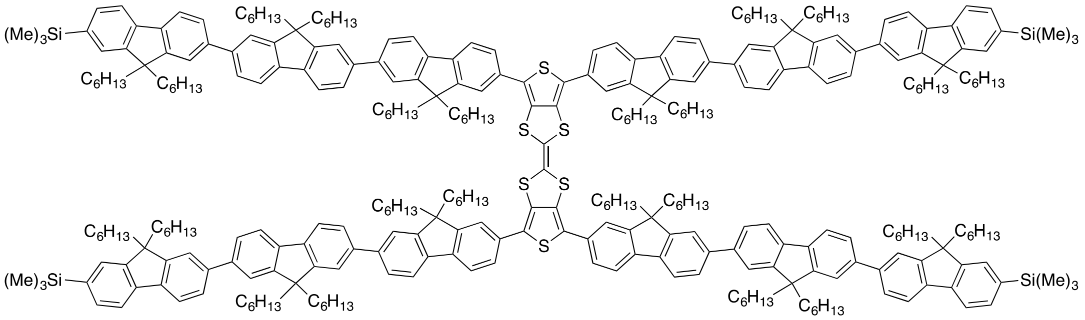
In a microwave-assisted reaction, $Pd(PPh_3)_4$ (0.04 g, 0.03 mmol, 0.2 equiv), (9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-yl)boronic acid (**SiF$_1$B**) (0.36 g, 0.79 mmol, 5 equiv) and $Ba(OH)_2.8H_2O$ (0.40 g, 1.26 mmol, 8 equiv) were added to perbromo-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**4**) (0.10 g, 0.16 mmol, 1 equiv), under N_2. Dry THF (4 mL) and degassed water (1 mL) were added. The reaction proceeded at 100°C (5 min), 120°C (5 min) and 140°C for 2 hours. The mixture was added to water (15 mL), extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic layers washed with water (40 mL). The organic mixture was dried over $MgSO_4$ and solvent evaporated under reduced pressure. The product was isolated on silica gel eluting with a gradient mixture of hexane: dichloromethane 9.9:0.1 increasing to 9.6:0.4 (v/v). The product was additionally reprecipitated from methanol, affording a yellow amorphous solid (0.20 g, 65%). ^1H NMR ($CDCl_3$): 7.78 (d, J = 7.9 Hz, 1H, Ar-H), 7.71 (d, J = 7.4, Hz, 1H, Ar-H), 7.59 (dd, J = 7.9, 1.6 Hz, 1H, Ar-H), 7.56 (d, J = 1.2 Hz, 1H, Ar-H), 7.52 (d, J = 7.9 Hz, 1H, Ar-H), 7.50 (s, 1H, Ar-H), 2.12-1.98 (m, 4H, CH_2), 1.20-1.05 (m, 12H, CH_2), 0.82-0.65 (m, 10H, CH_3, CH_2), 0.34 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$): 152.16, 150.39, 141.13, 139.79, 132.10, 131.87, 131.79, 129.50, 127.76, 125.15, 120.97, 120.47, 119.32, 118.99, 55.40, 40.30, 31.52, 29.73, 23.86, 22.65, 14.17, -0.72. Mp: 122°C; MALDI MS: *m/z* 1934.22 $(M + H)^+$. Anal. Calcd for $C_{122}H_{164}S_6Si_4$: C, 75.71; H, 8.54 %. Found: C, 75.68; H, 8.43%.

4,4',6,6'-Tetrakis(9,9,9',9'-tetrahexyl-7'-(trimethylsilyl)-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**TTF-F2-TMS**)



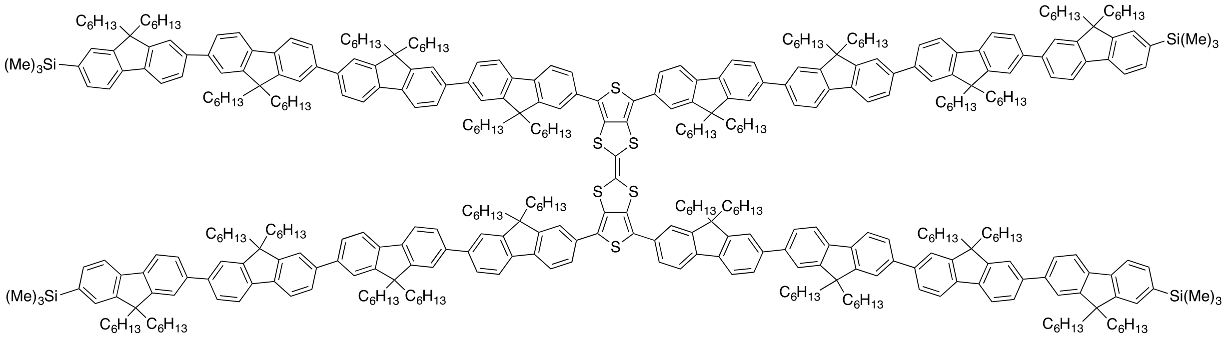
In a microwave-assisted reaction, Pd(PPh$_3$)$_4$ (0.02 g, 0.02 mmol, 0.2 equiv), (9,9,9',9'-tetrahexyl-7'-(trimethylsilyl)-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)boronic acid (**SiF$_2$B**) (0.37 g, 0.47 mmol, 5 equiv) and Ba(OH)$_2$.8H$_2$O (0.24 g, 0.76 mmol, 8 equiv) were added to perbromo-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**4**) (0.060 g, 0.095 mmol, 1 equiv), under N$_2$. Dry THF (2.5 mL) was added, followed by degassed water (0.5 mL). The reaction proceeded at 100°C for 5 min, 120°C for 5 min followed by 140°C for 2 hours. The mixture was added to water (10 mL) and extracted using CH$_2$Cl$_2$ (3 x 15 mL). The combined organic layers were dried on MgSO$_4$ and solvent evaporated under reduced pressure. The product was isolated on silica gel eluting with a mixture of hexane: toluene 9.9:0.1 increasing to 9:1 (v/v). The isolated compound was additionally reprecipitated from methanol affording a yellow amorphous solid (0.20 g, 64.5%). ^{1}H NMR (CDCl$_3$): 7.8-7.78 (m, 3H, Ar-H), 7.74 (d, J = 7.4 Hz, 1H, Ar-H), 7.72-7.58 (m, 6H, Ar-H), 7.55-7.48 (m, 2H, Ar-H), 2.21-2.00 (m, 8H, CH$_2$), 1.25-1.05 (m, 24H, CH$_2$), 0.87-0.67 (m, 20H, CH$_3$, CH$_2$), 0.34 (s, 9H, CH$_3$). ^{13}C NMR (CDCl$_3$): 152.29, 152.01, 151.89, 150.35, 141.54, 141.21, 140.91, 140.63, 140.59, 139.68, 139.21, 132.01, 131.86, 131.75, 129.54, 127.80, 126.46, 126.21, 125.29, 121.68, 120.98, 120.44, 120.32, 120.18, 119.18, 55.63, 55.27, 40.56, 40.27, 31.64, 31.50, 29.85, 29.71, 24.00, 23.87, 22.73, 22.62, 14.20, 14.15, -0.71. : MALDI MS: *m/z* 3265 (M$^+$). Anal. Calcd for C$_{222}$H$_{292}$S$_6$Si$_4$: C, 81.66; H, 9.01 %. Found: C, 81.55; H, 8.91 %.

4,4',6,6'-Tetrakis(9,9,9',9',9'',9''-hexahexyl-7''-(trimethylsilyl)-9*H*,9'*H*,9''*H*-[2,2':7',2''-terfluoren]-7-yl)-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**TTF-F3-TMS**)

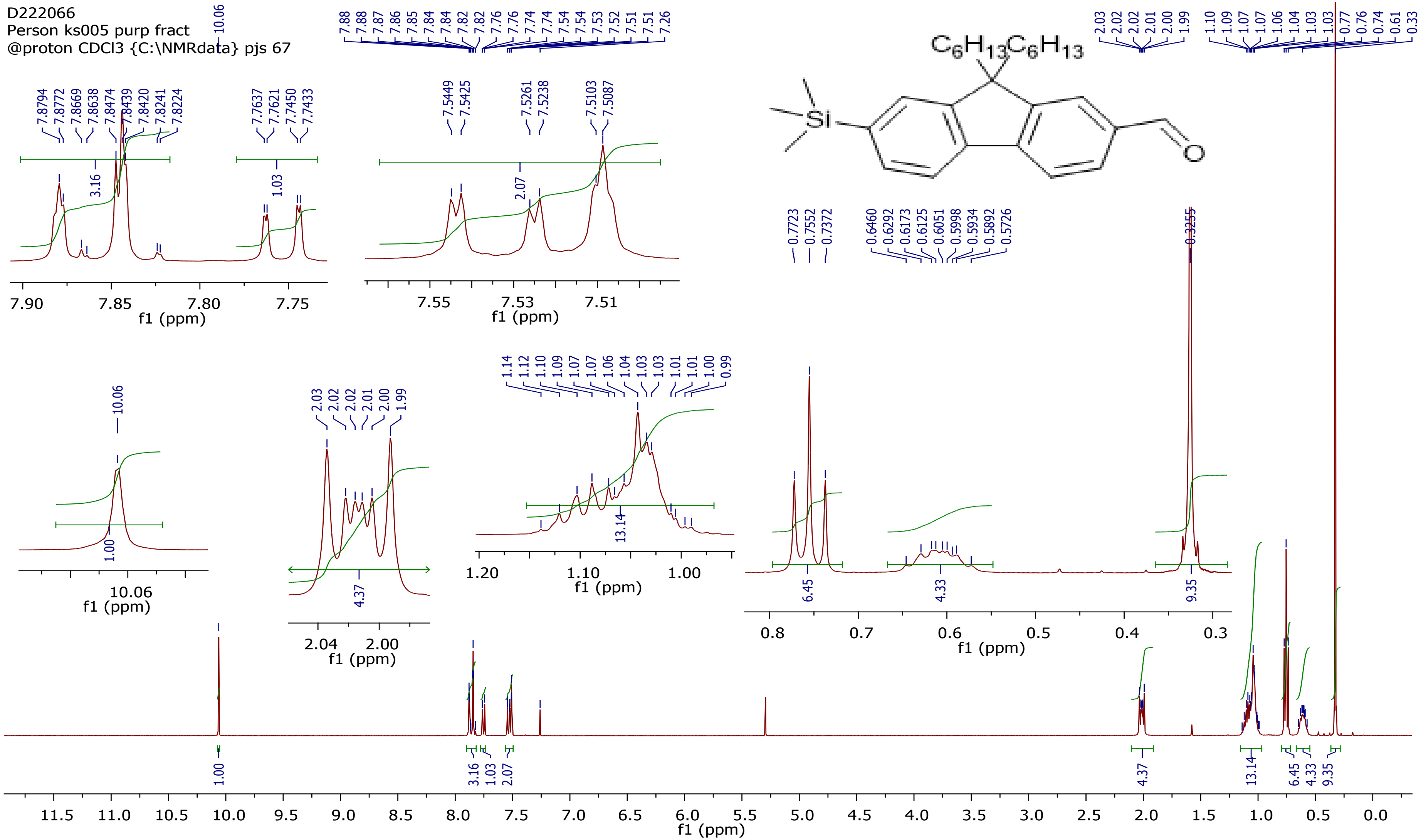


In a microwave-assisted reaction, Pd(PPh$_3$)$_4$ (0.02 g, 0.02 mmol, 0.2 equiv), (9,9,9',9',9'',9''-hexahexyl-7''-(trimethylsilyl)-9*H*,9'*H*,9''*H*-[2,2':7',2''-terfluoren]-7-yl)boronic acid (**SiF$_3$B**) (0.53 g, 0.48 mmol, 5 equiv) and Ba(OH)$_2$.8H$_2$O (0.24 g, 0.76 mmol, 8 equiv) were added to perbromo-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**4**) (0.060 g, 0.95 mmol, 1 equiv) under N$_2$. Dry THF (2.5 mL) and degassed water (0.5 mL) were added and reaction was heated to 100°C for 5 min, 120°C for 5 min and 140°C for 2 h. The mixture was added to water (20 mL) and extracted with CH$_2$Cl$_2$ (3 x 30 mL). The combined organic layers were washed with water (30 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure and isolated on silica gel eluting with a gradient of hexane: toluene 99.9: 0.1 increasing to 9.5: 0.5 (v/v). The product was additionally reprecipitated from methanol affording a yellow amorphous solid (0.28 g, 64 %). ^{1}H NMR (CDCl$_3$): 7.90-7.78 (m, 5H, Ar-H), 7.75-7.60 (m, 11H, Ar-H), 7.55-7.48 (m, 2H, Ar-H), 2.25-1.95 (m, 12H, CH2), 1.25-1.05 (m, 36 H, CH2), 0.90-0.70 (m, 30H, CH3, CH$_2$), 0.34 (s, 9H, CH3). ^{13}C NMR (CDCl$_3$): 152.31, 152.05, 152.00, 151.94, 151.87, 150.34, 141.57, 141.19, 140.91, 140.78, 140.48, 140.33, 140.10, 139.72, 139.15, 132.01, 131.87, 131.78, 129.56, 127.79, 126.34, 126.18, 125.30, 121.68, 121.02, 120.46, 120.35, 120.16, 119.16, 55.65, 55.50, 55.26, 40.52, 40.28, 31.65, 31.61, 31.50, 29.86, 29.82, 29.72, 24.00, 23.87, 22.74, 22.70, 22.63, 14.21, 14.16, -0.70. MALDI: *m/z* 4595 (M^+). Anal. Calcd for $C_{322}H_{420}S_6Si_4$: C, 84.16; H, 9.21 %. Found: C, 84.13; H, 9.25 %.

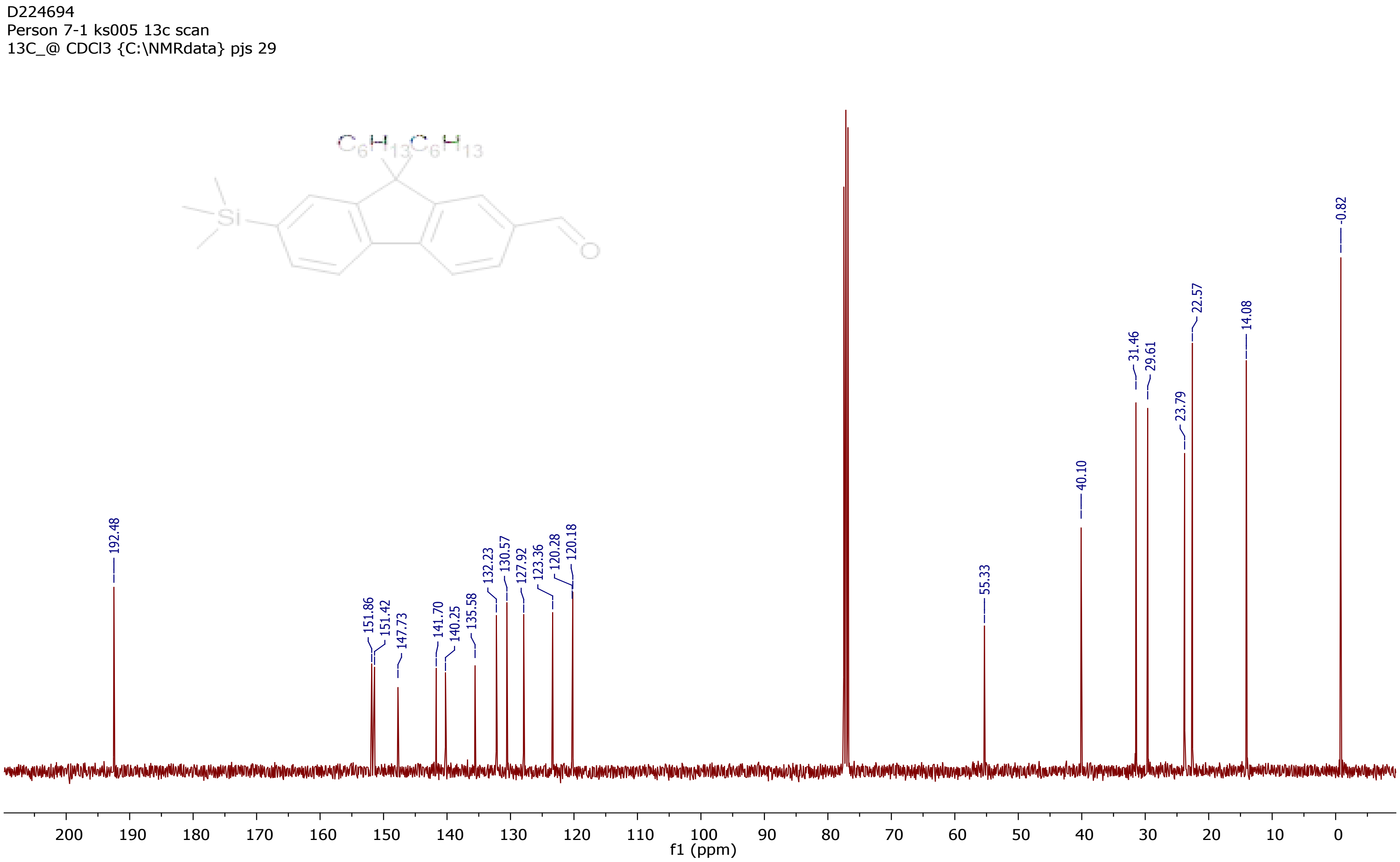
4,4',6,6'-Tetrakis(9,9,9',9',9'',9'',9''',9'''-octahexyl-7'''-(trimethylsilyl)-9*H*,9'*H*,9''*H*,9'''*H*-[2,2':7',2'':7'',2'''-quaterfluoren]-7-yl)-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**TTF-F4-TMS**)



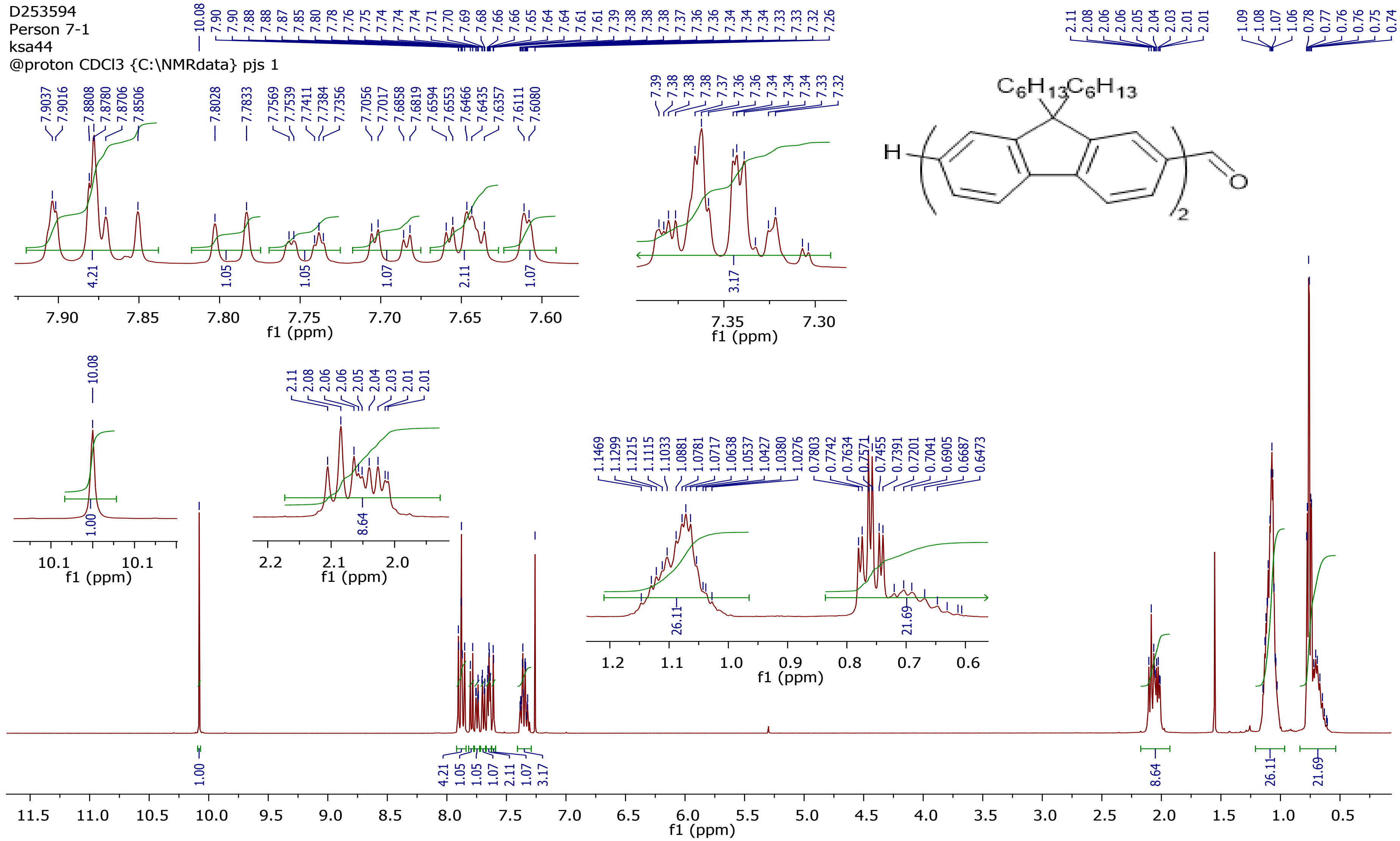
In a microwave-assisted reaction, $Pd(PPh_3)_4$ (0.02 g, 0.02 mmol, 0.2 equiv), (9,9,9',9',9'',9'',9''',9'''-octahexyl-7'''-(trimethylsilyl)-9*H*,9'*H*,9''*H*,9'''*H*-[2,2':7',2'':7'',2'''-quaterfluoren]-7-yl)boronic acid (**SiF_4B**) (0.58 g, 0.4 mmol, 5 equiv) and $Ba(OH)_2.8H_2O$ (0.20 g, 0.64 mmol, 8 equiv) were added to perbromo-2,2'-bithieno[3,4-*d*][1,3]dithiolylidene (**4**) (0.05 g, 0.08 mmol, 1 equiv) under N_2. Dry THF (2.1 mL) and degassed water (0.4 mL) were added. The reaction proceeded at 100°C (5 min), 120°C (5 min) and 140°C for 2 hours. The mixture was added to water (20 mL) and extracted with CH_2Cl_2 (3 x 40 mL). The combined organic layers were washed with water (60 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The product was isolated on silica gel eluting with a gradient mixture of hexane: toluene 9:1 increasing to 7:3 (v/v). The product was additionally reprecipitated from methanol, affording a yellow amorphous solid (0.17 g, 36%). ^1H NMR ($CDCl_3$): 7.90-7.78 (m, 7H, Ar-H), 7.77-7.60 (m, 15H, Ar-H), 7.55-7.48 (m, 2H, Ar-H), 2.28 -1.95 (m, 16H, CH2), 1.18-1.10 (m, 48H, CH2), 0.84-0.76 (m, 40H, CH3, CH2), 0.34 (s, 9H, CH3). ^{13}C NMR ($CDCl_3$): 152.31, 152.05, 152.01, 151.97, 151.86, 150.34, 141.57, 141.19, 140.92, 140.79, 140.65, 140.53, 140.47, 140.32, 140.21, 140.13, 139.73, 139.13, 132.00, 131.88, 131.79, 129.57, 127.79, 126.32, 126.17, 121.68, 121.02, 120.36, 120.16, 120.12, 119.16, 55.66, 55.51, 55.48, 55.26, 40.52, 40.28, 31.65, 31.61, 31.50, 29.86, 29.82, 29.72, 24.00, 23.87, 22.75, 22.70, 22.63, 14.22, 14.16, -0.70. MALDI: m/z 5925.18 (M^+). Anal. Calcd for $C_{422}H_{548}S_6Si_4$: C, 85.54; H, 9.32 %. Found: C, 85.32; H, 9.28 %.



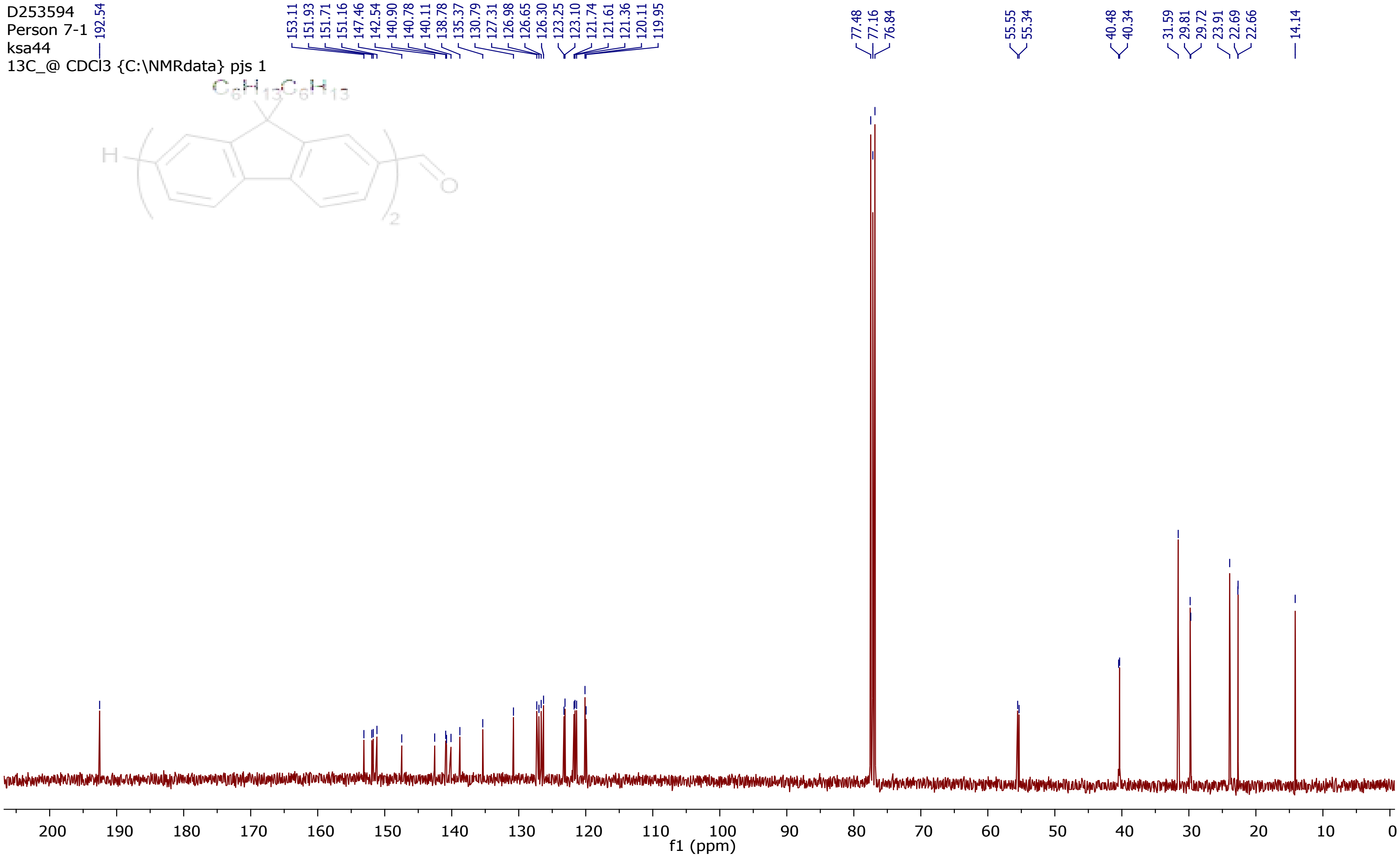
*^{1}H NMR spectra of **6** in CDCl$_3$.*



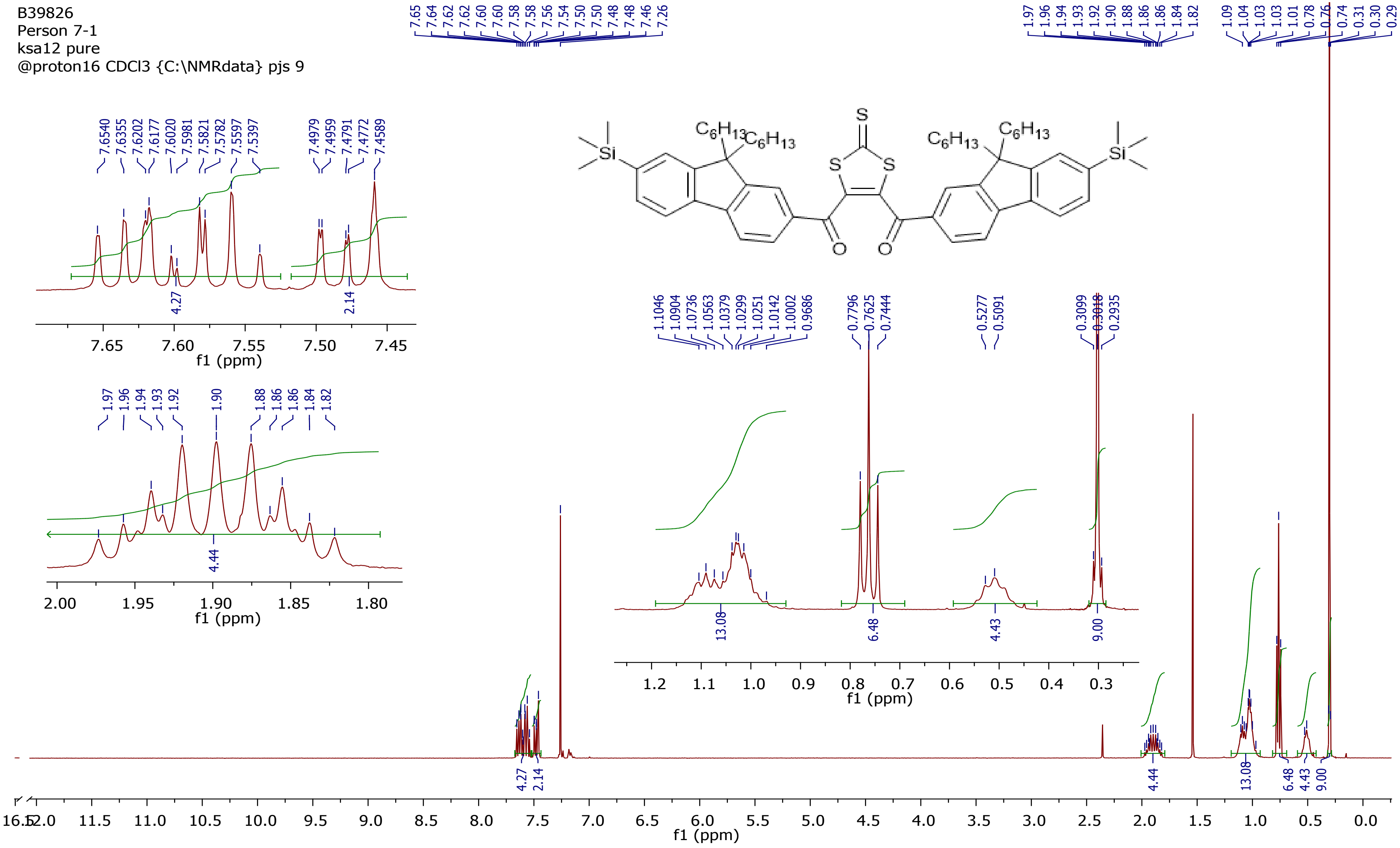
*^{13}C spectra of **6** in CDCl$_3$.*



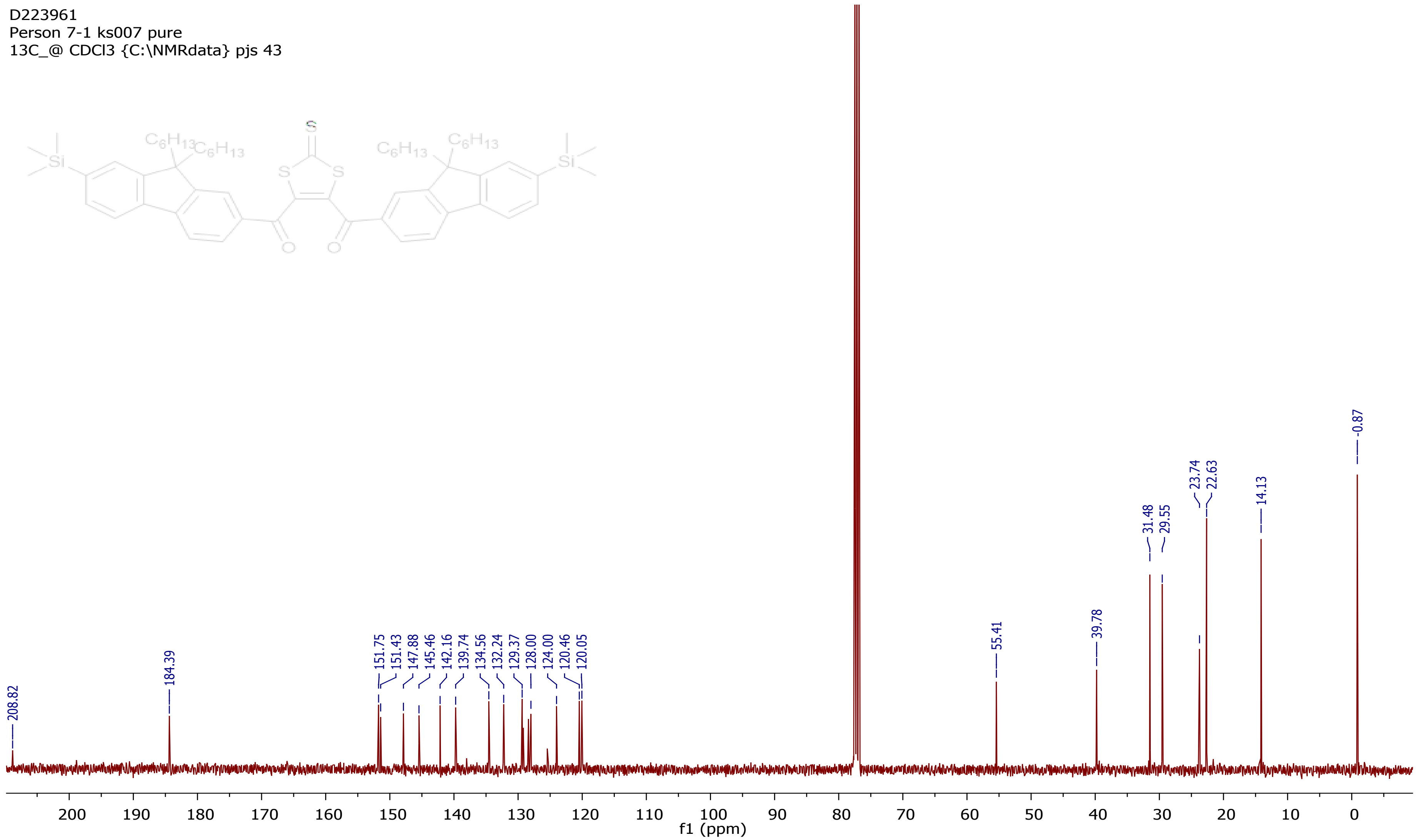
^{1}H NMR spectra of **7** in $CDCl_3$.



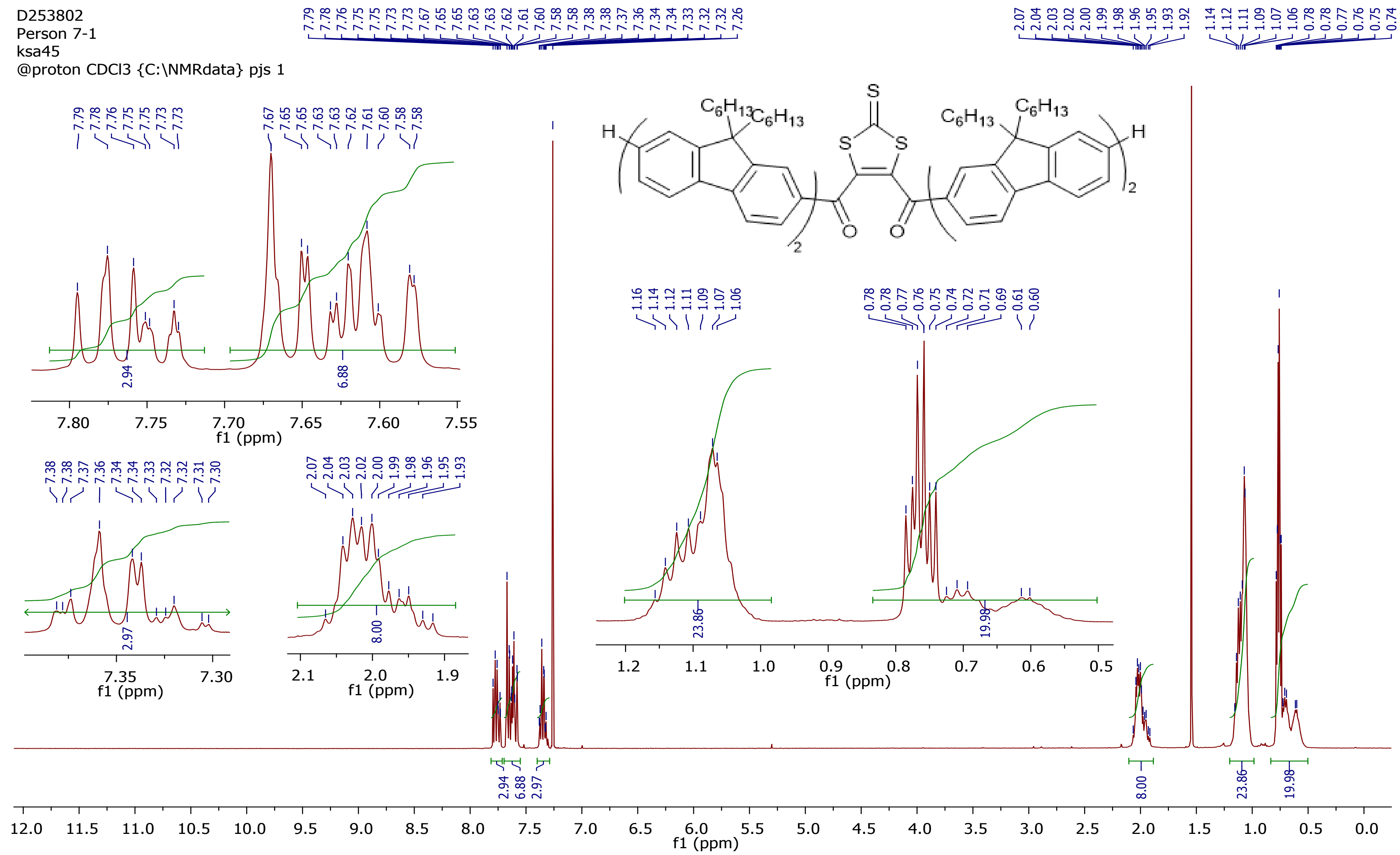
^{13}*C spectra of* ***7*** *in CDCl*$_3$.



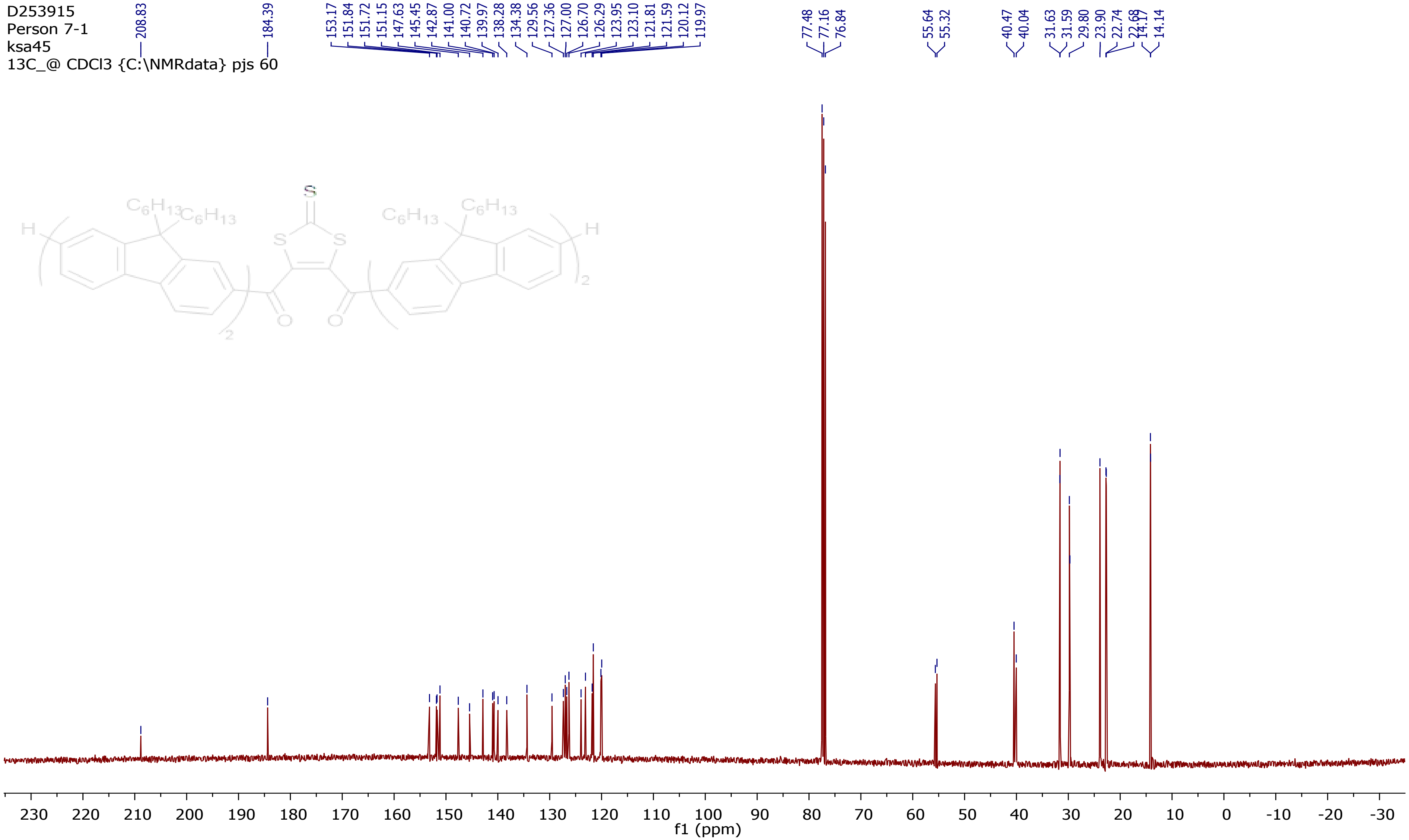
*^1H spectra of **8** in $CDCl_3$.*



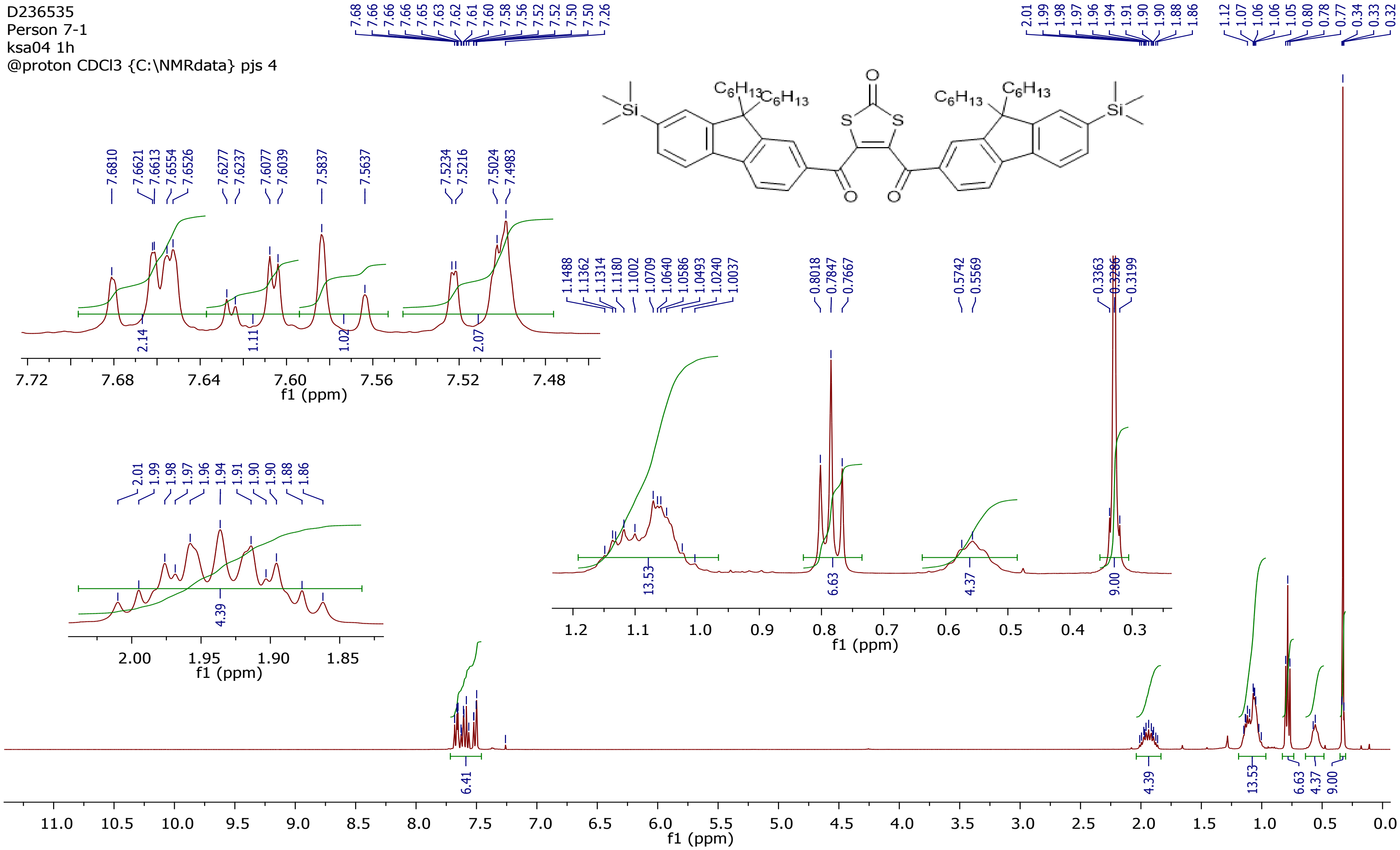
*^{13}C spectra of **8** in CDCl$_3$.*



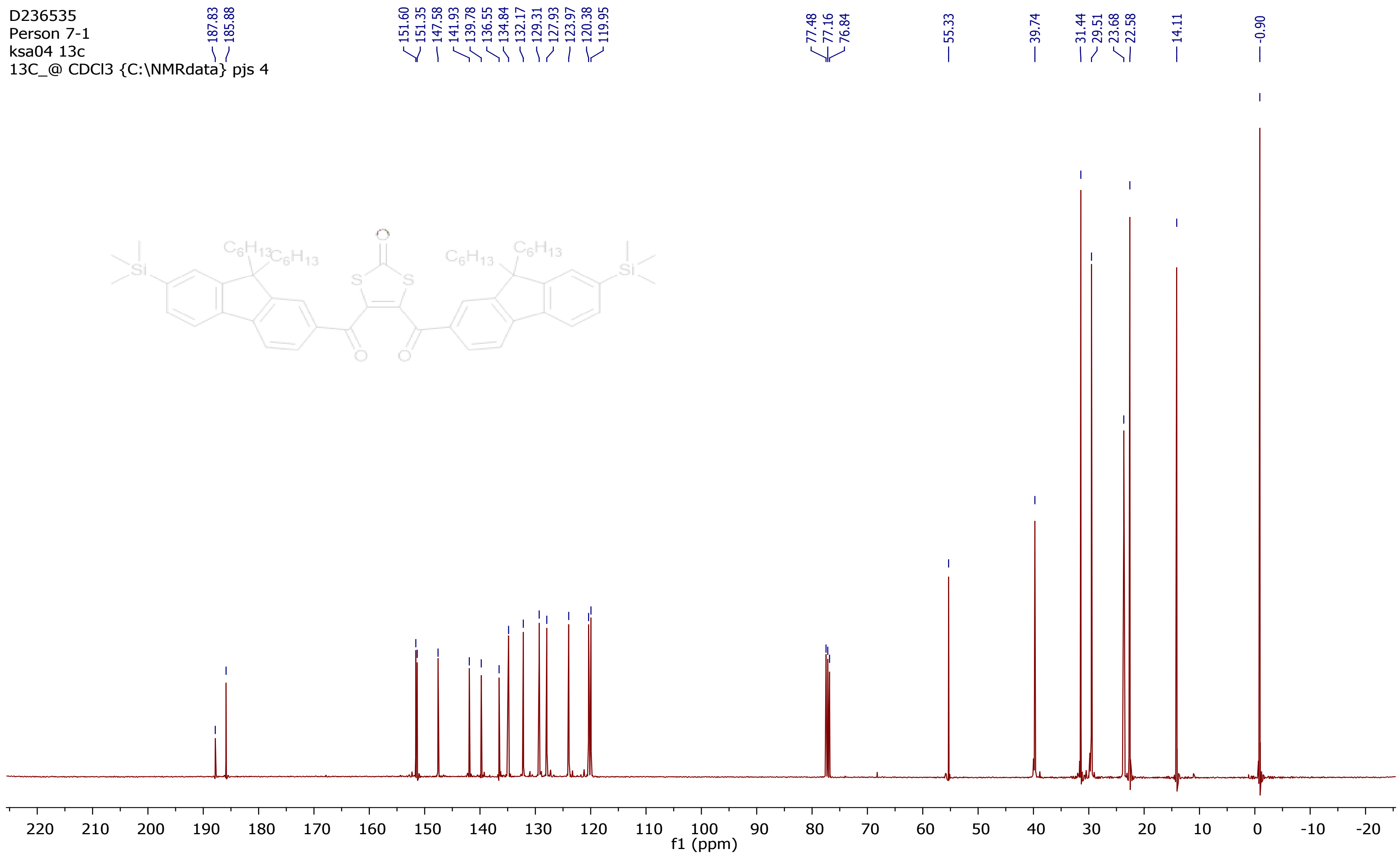
*^{1}H spectra of **9** in CDCl$_3$.*



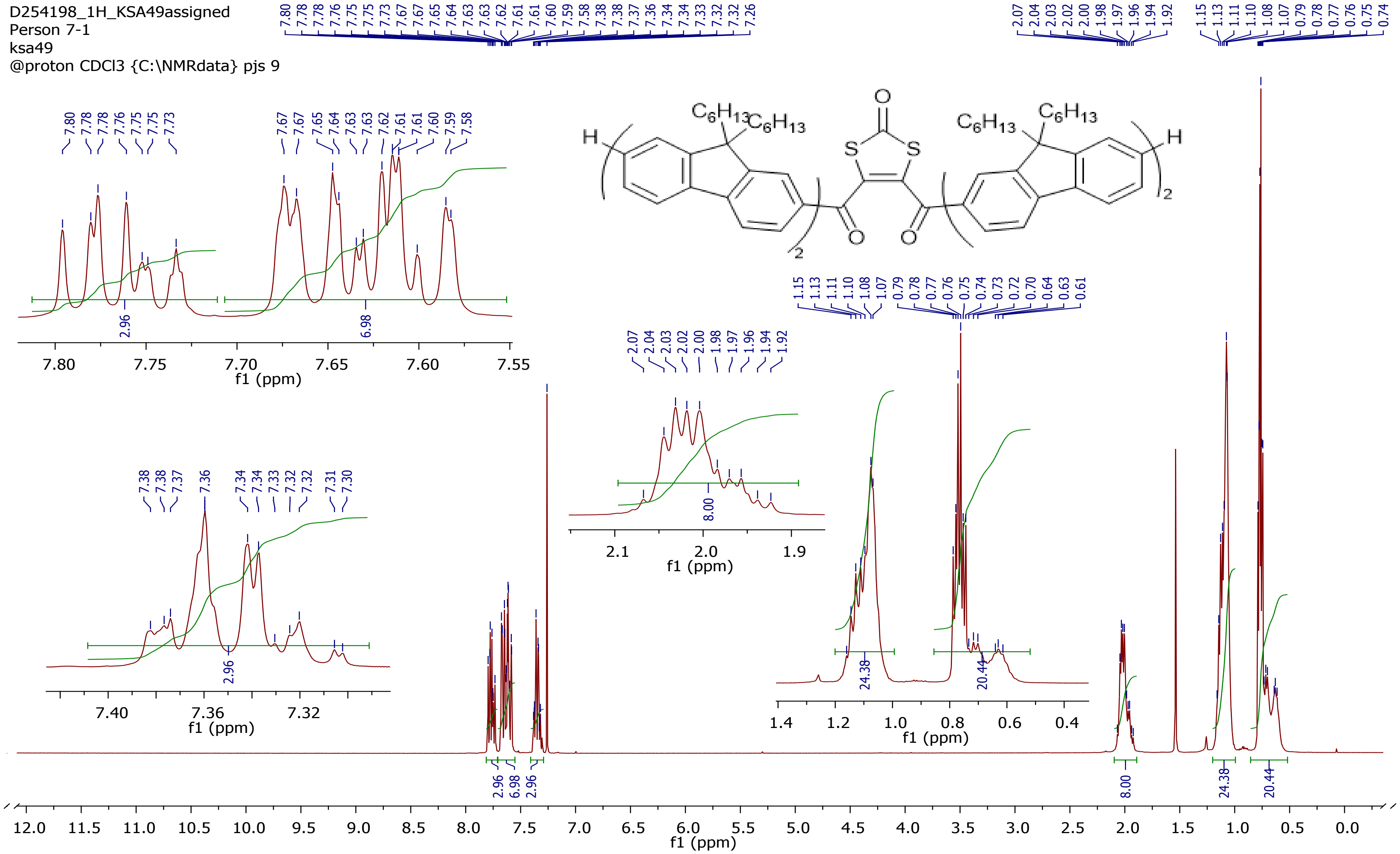
*^{13}C spectra of **9** in CDCl$_3$.*



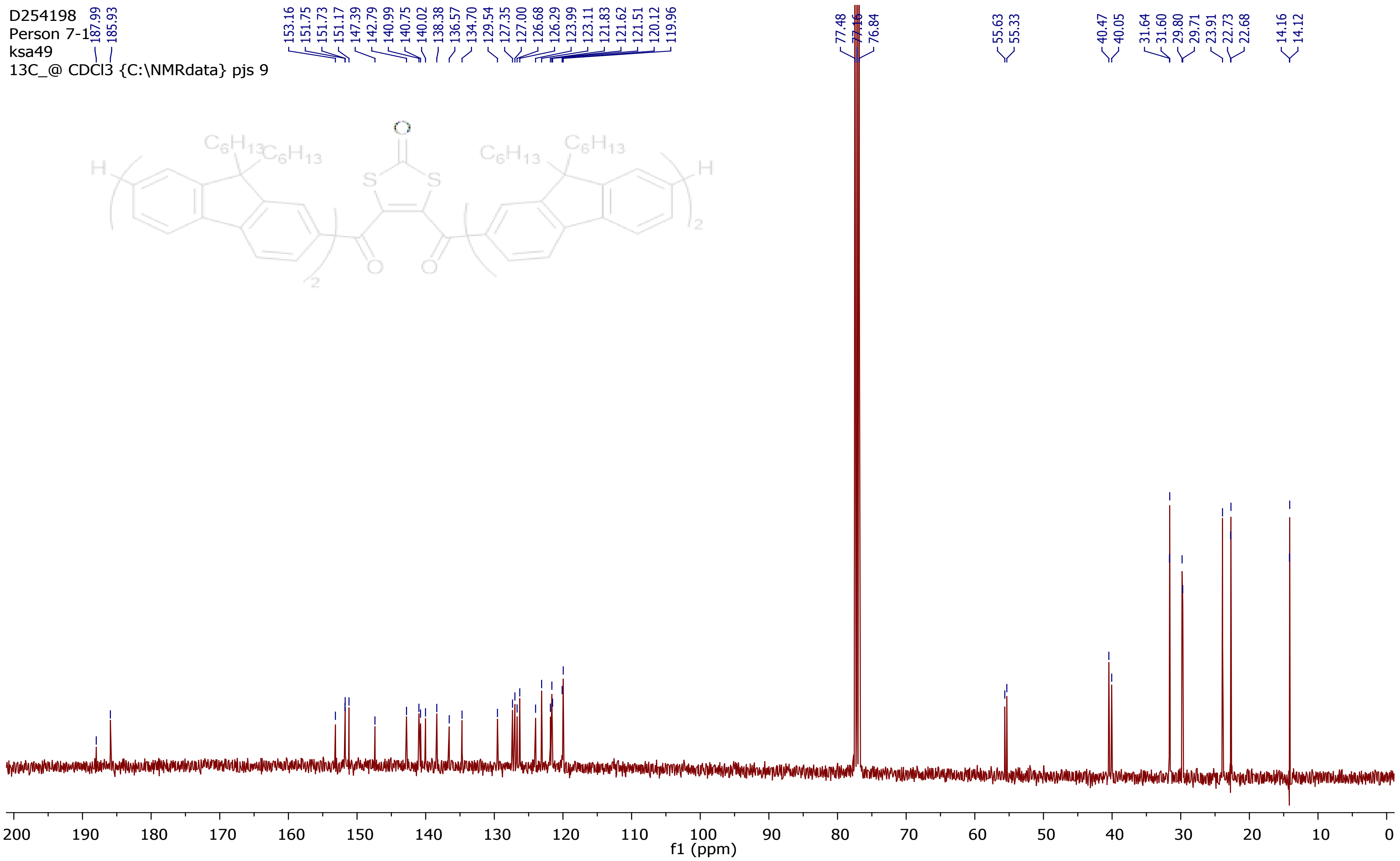
*^1H spectra of **10** in $CDCl_3$.*



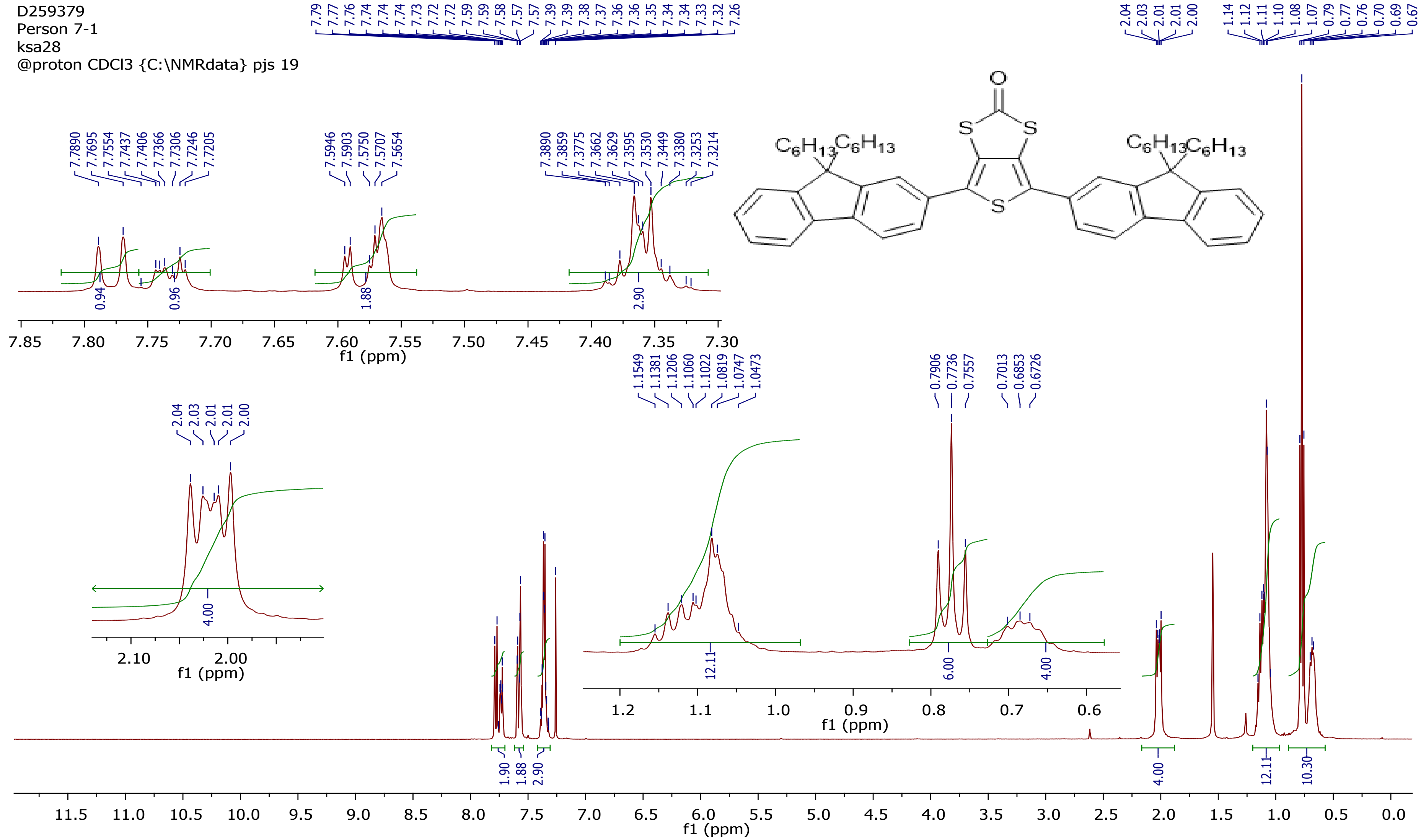
^{13}*C spectra of* ***10*** *in CDCl*$_3$*.*



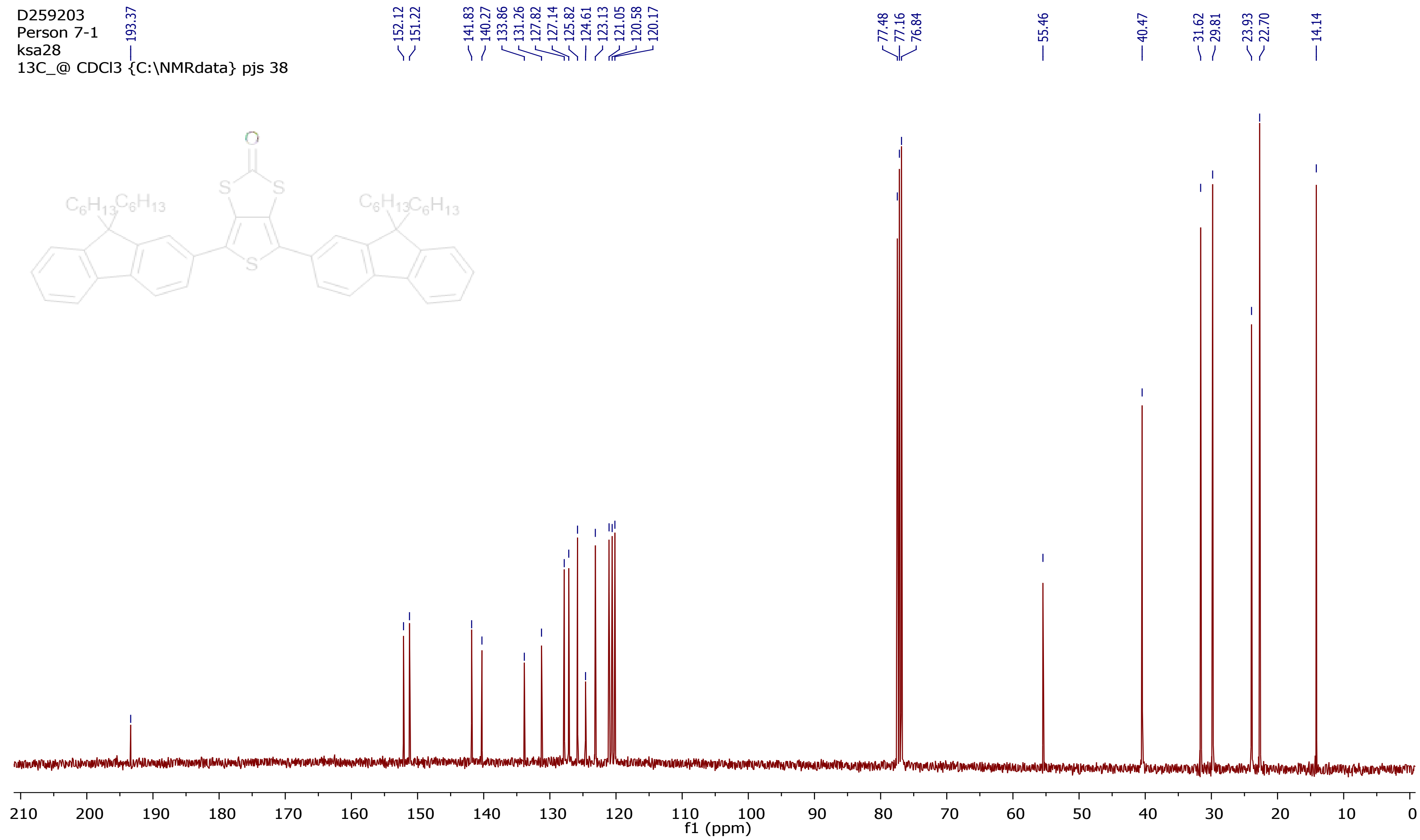
^1H *spectra of **11** in $CDCl_3$.*



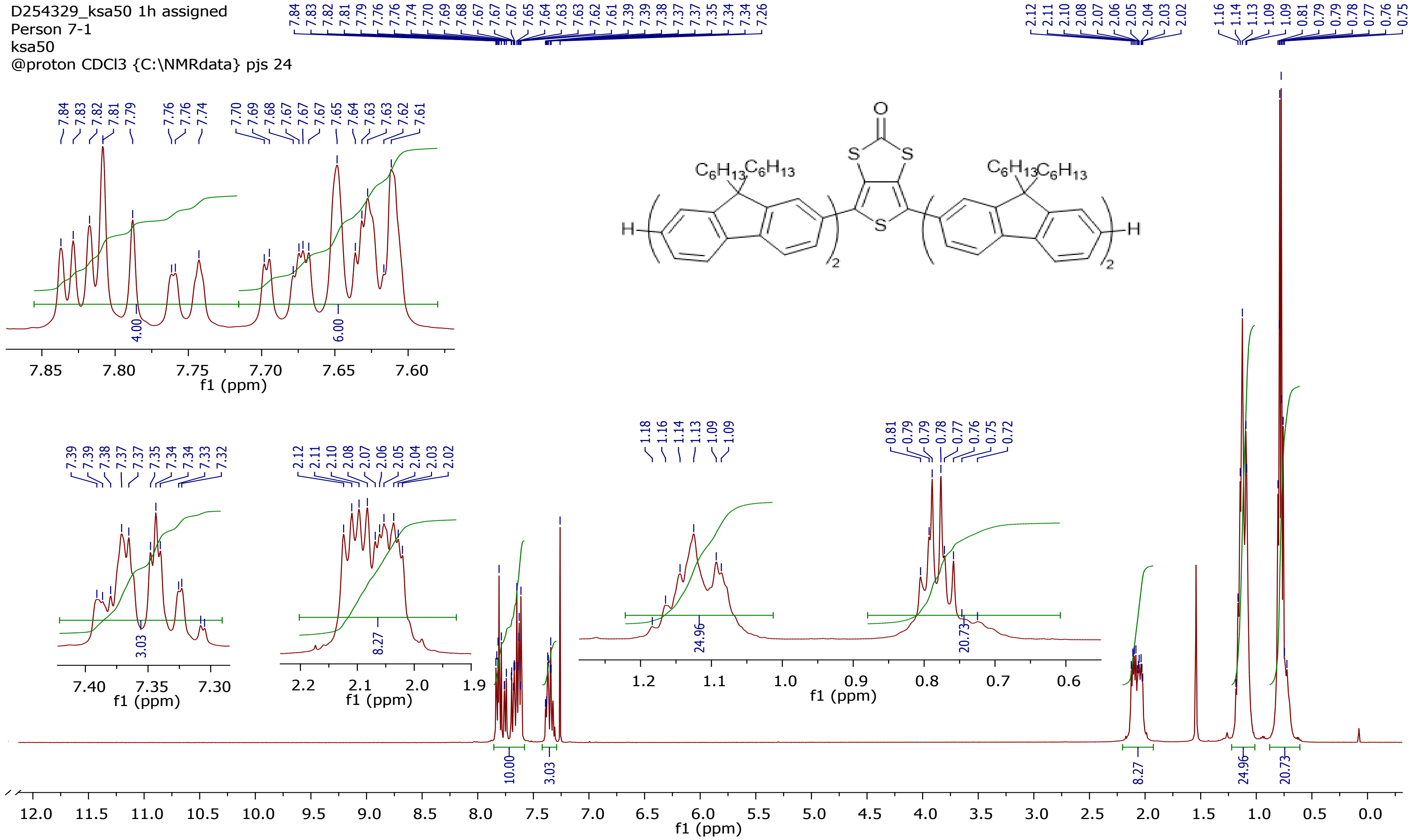
*^{13}C spectra of **11** in CDCl$_3$.*



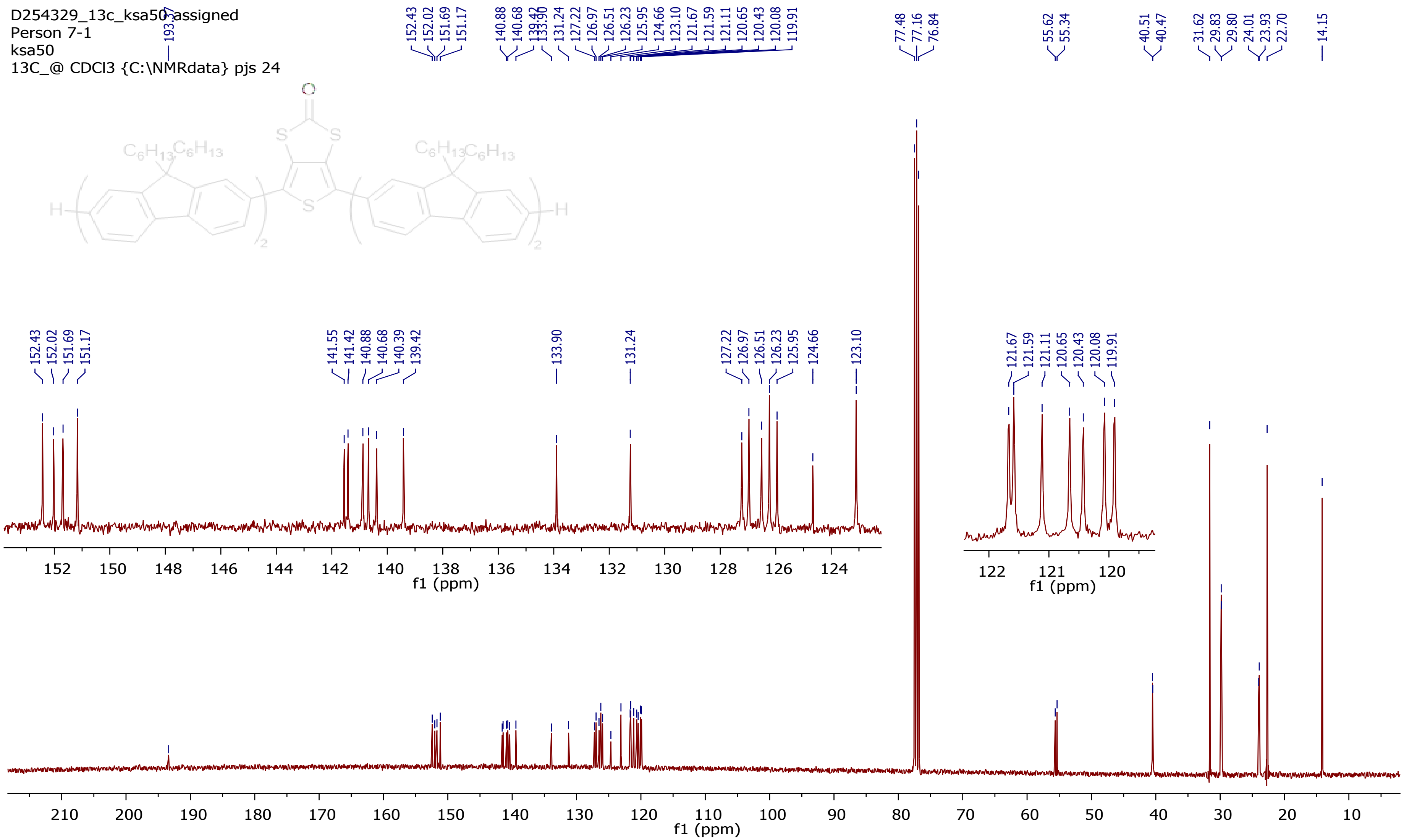
*^{1}H spectra of **12** in $CDCl_3$.*



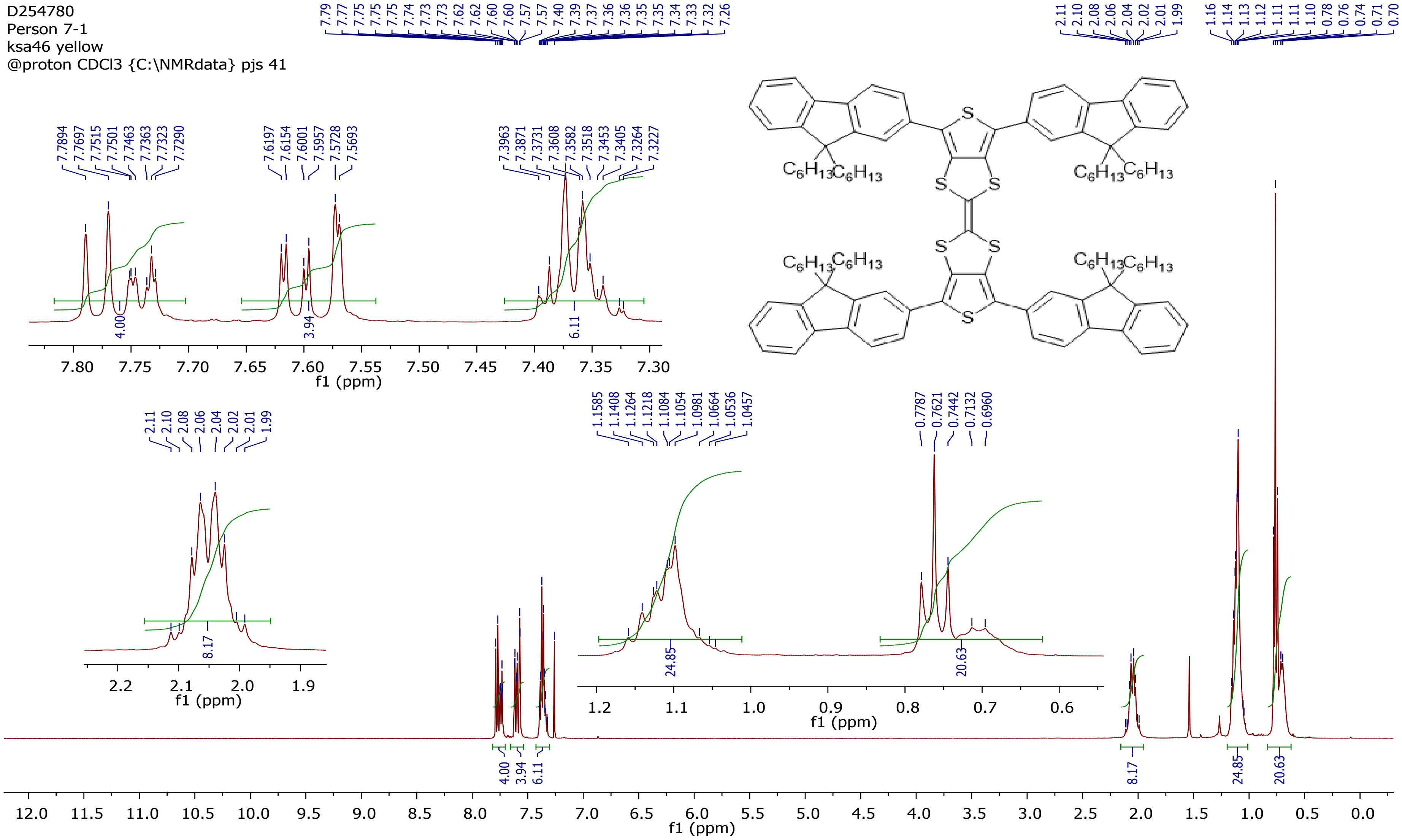
*^{13}C spectra of **12** in $CDCl_3$.*



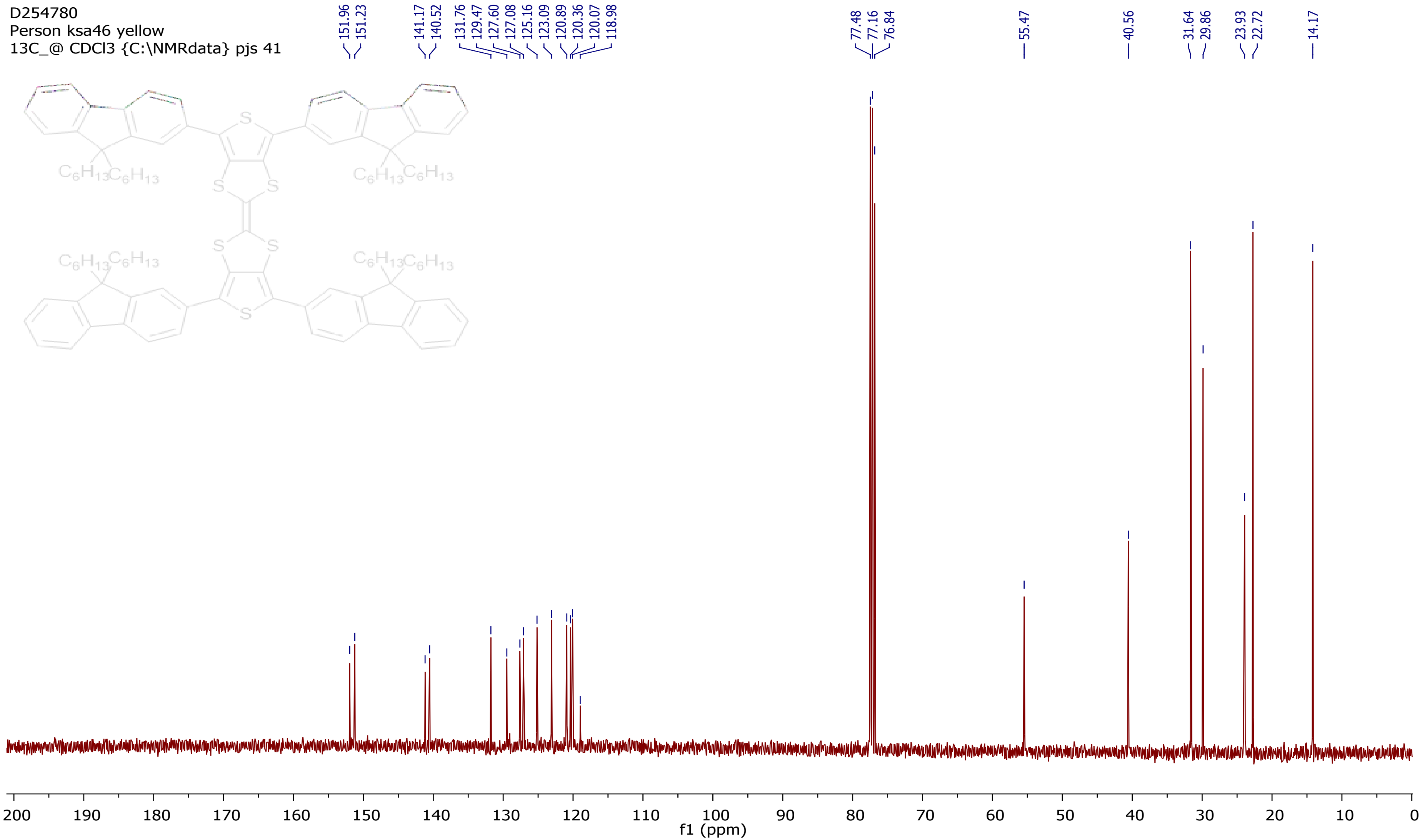
^1H *spectra of **13** in $CDCl_3$.*



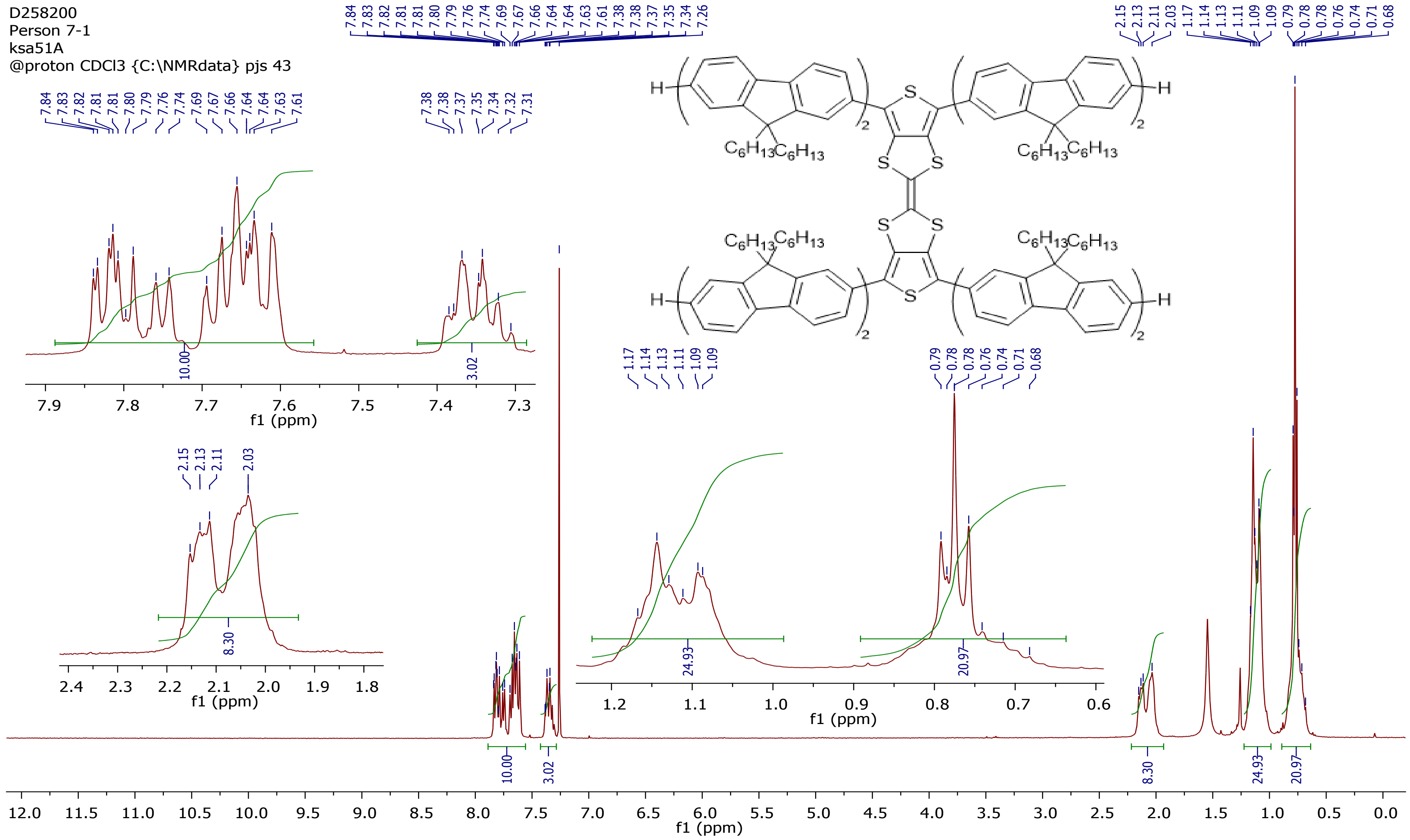
^{13}*C spectra of* ***13*** *in CDCl*$_3$*.*



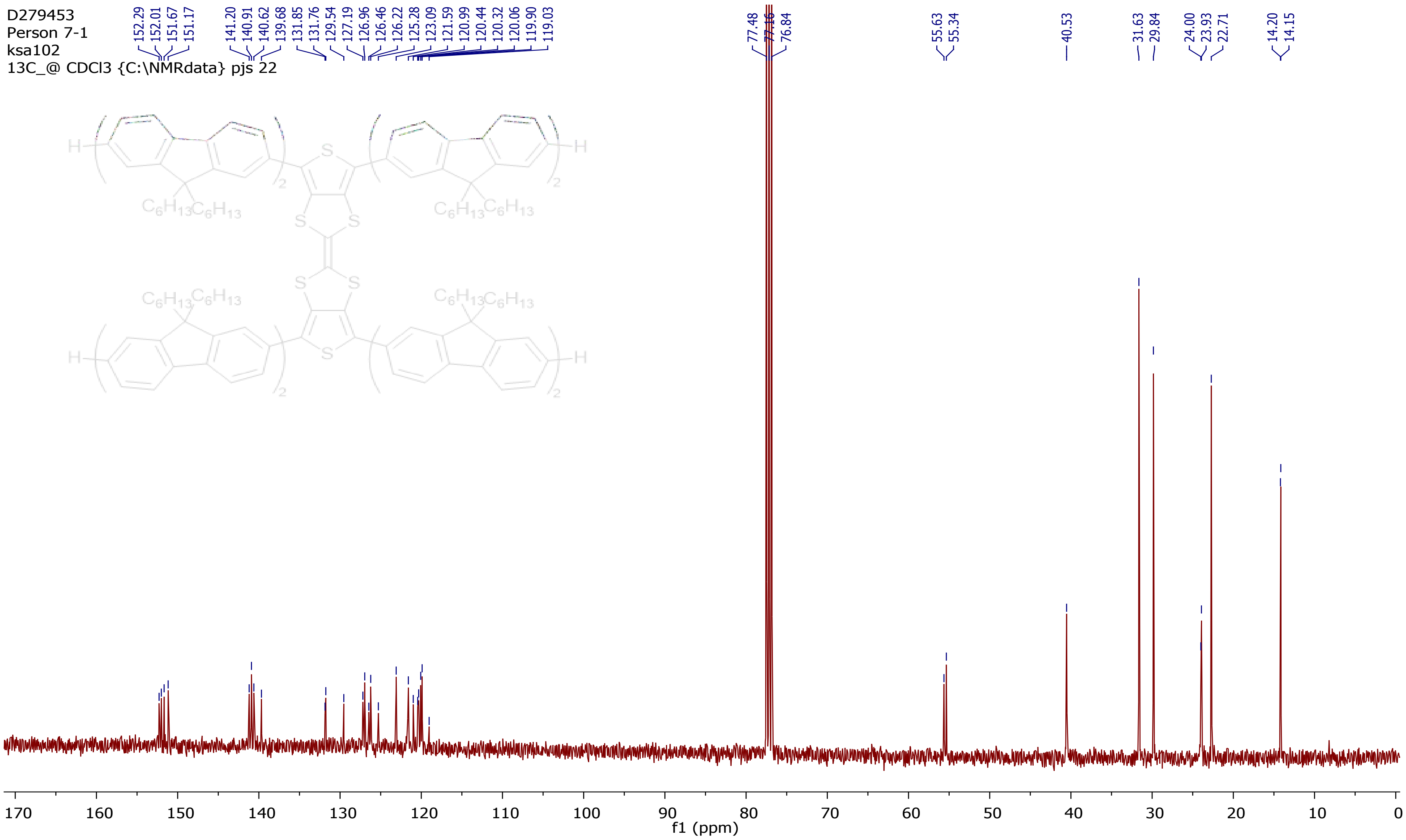
*^1H spectra of **14** in $CDCl_3$.*



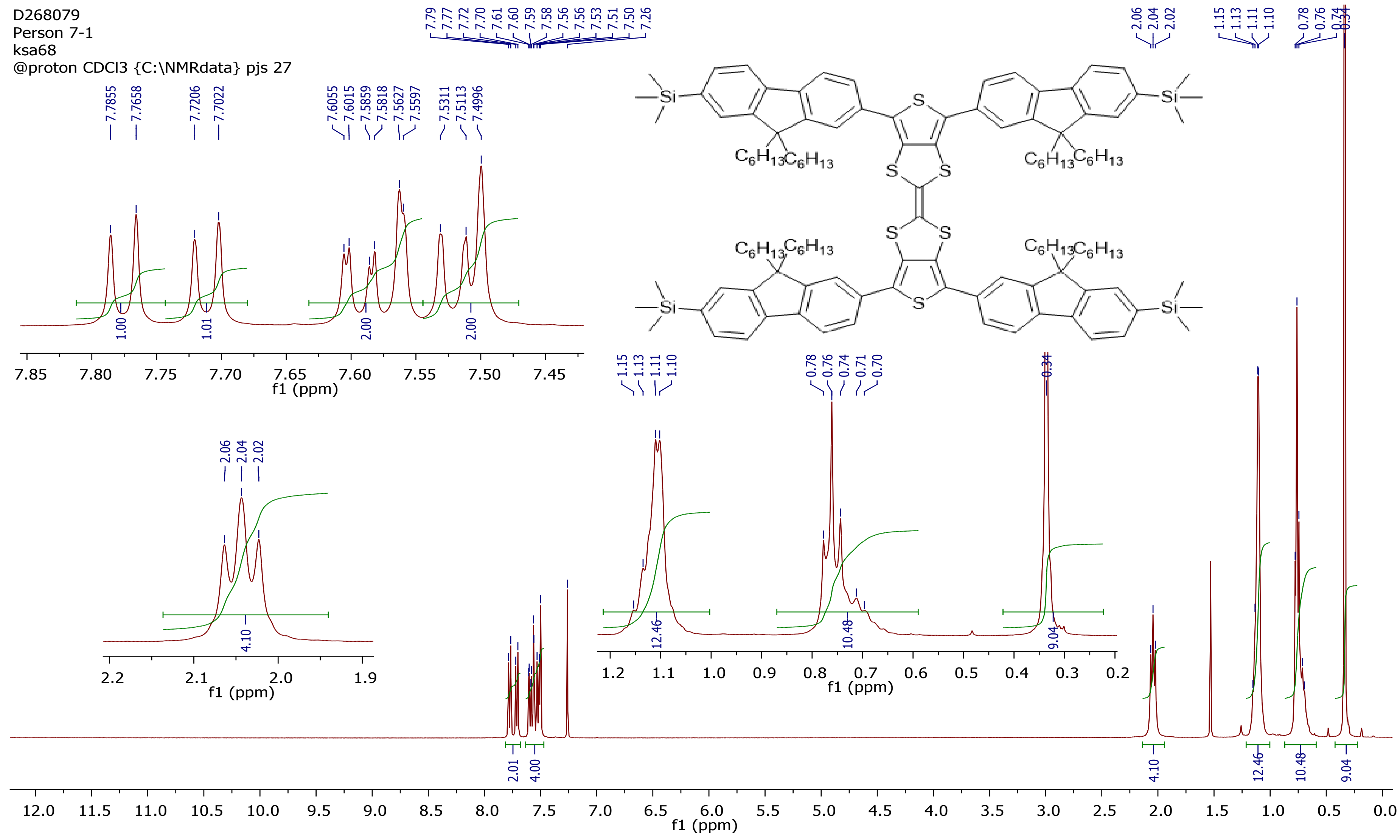
*^{13}C spectra of **14** in $CDCl_3$.*



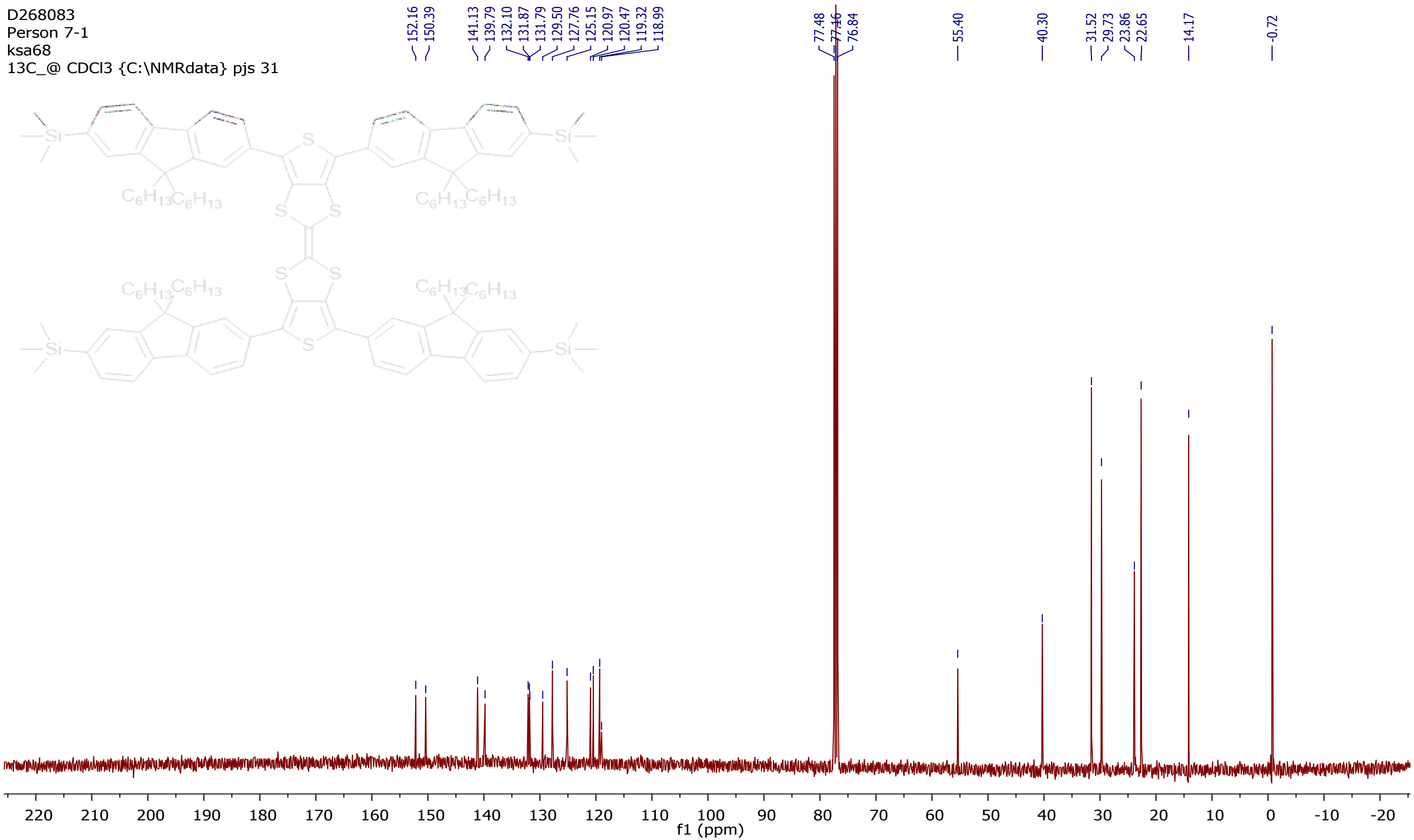
*^{1}H spectra of **15** in $CDCl_3$.*



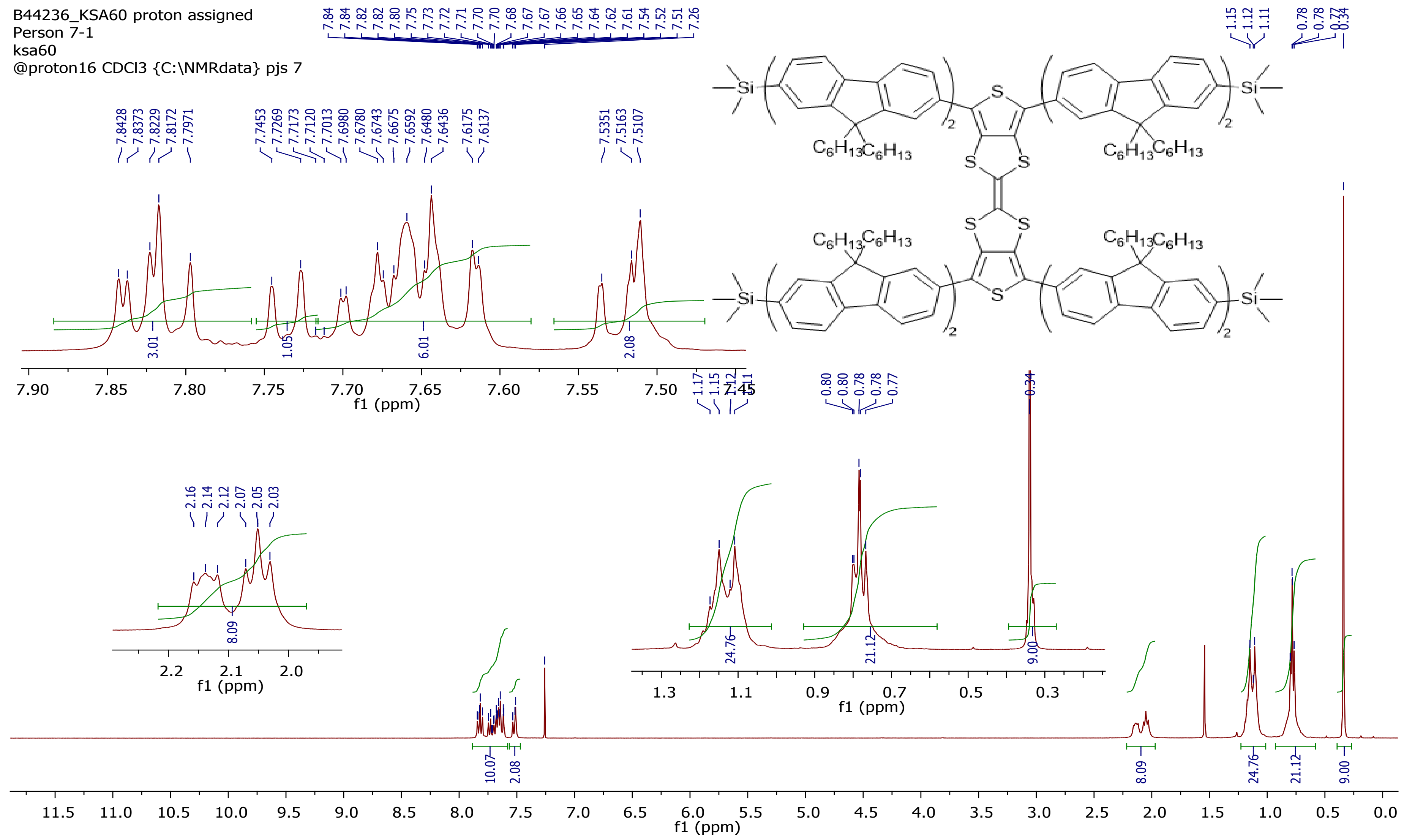
^{13}C spectra of ***15*** *in $CDCl_3$.*



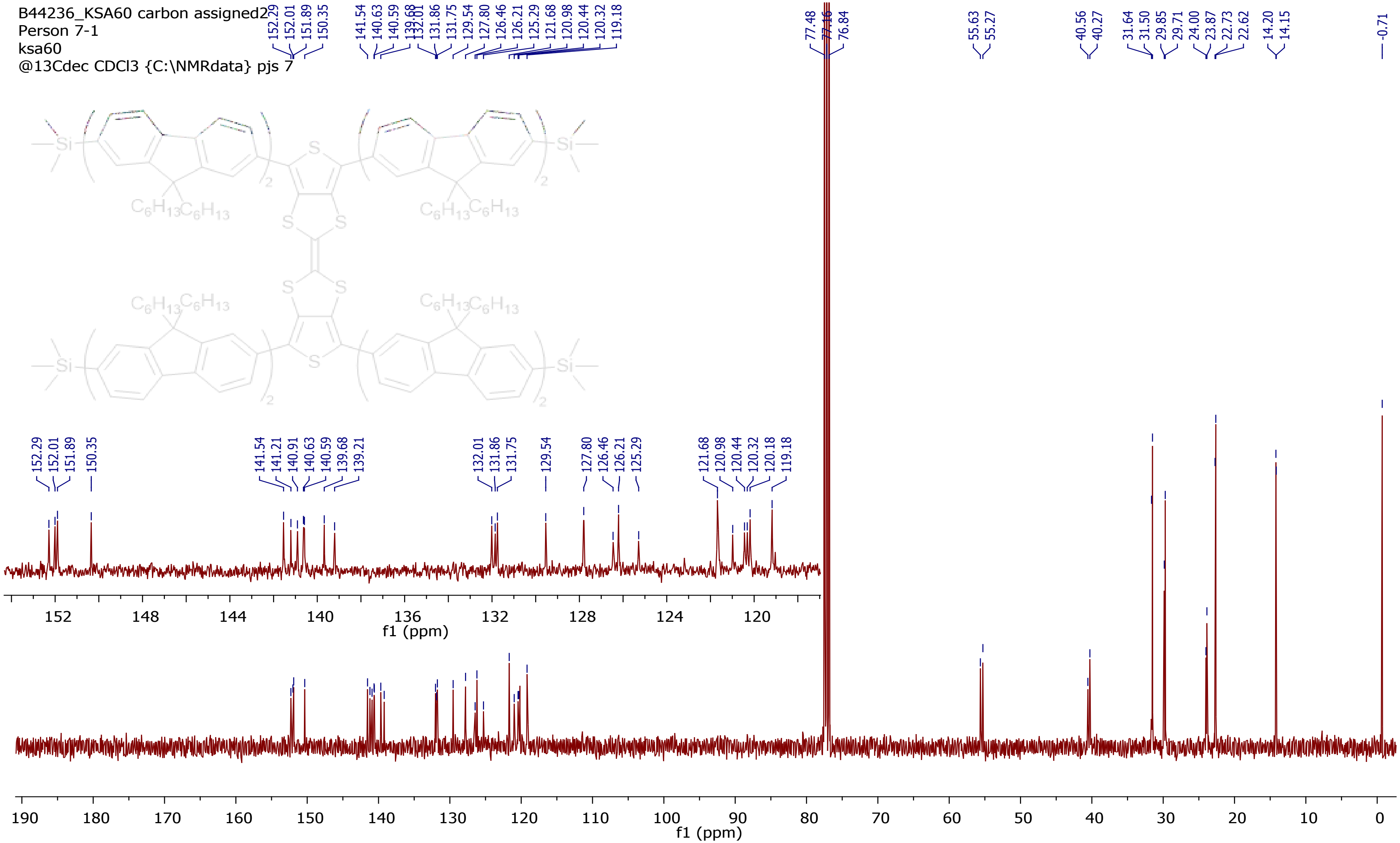
^1H *spectra of* ***TTF-F1-TMS*** *in* $CDCl_3$.



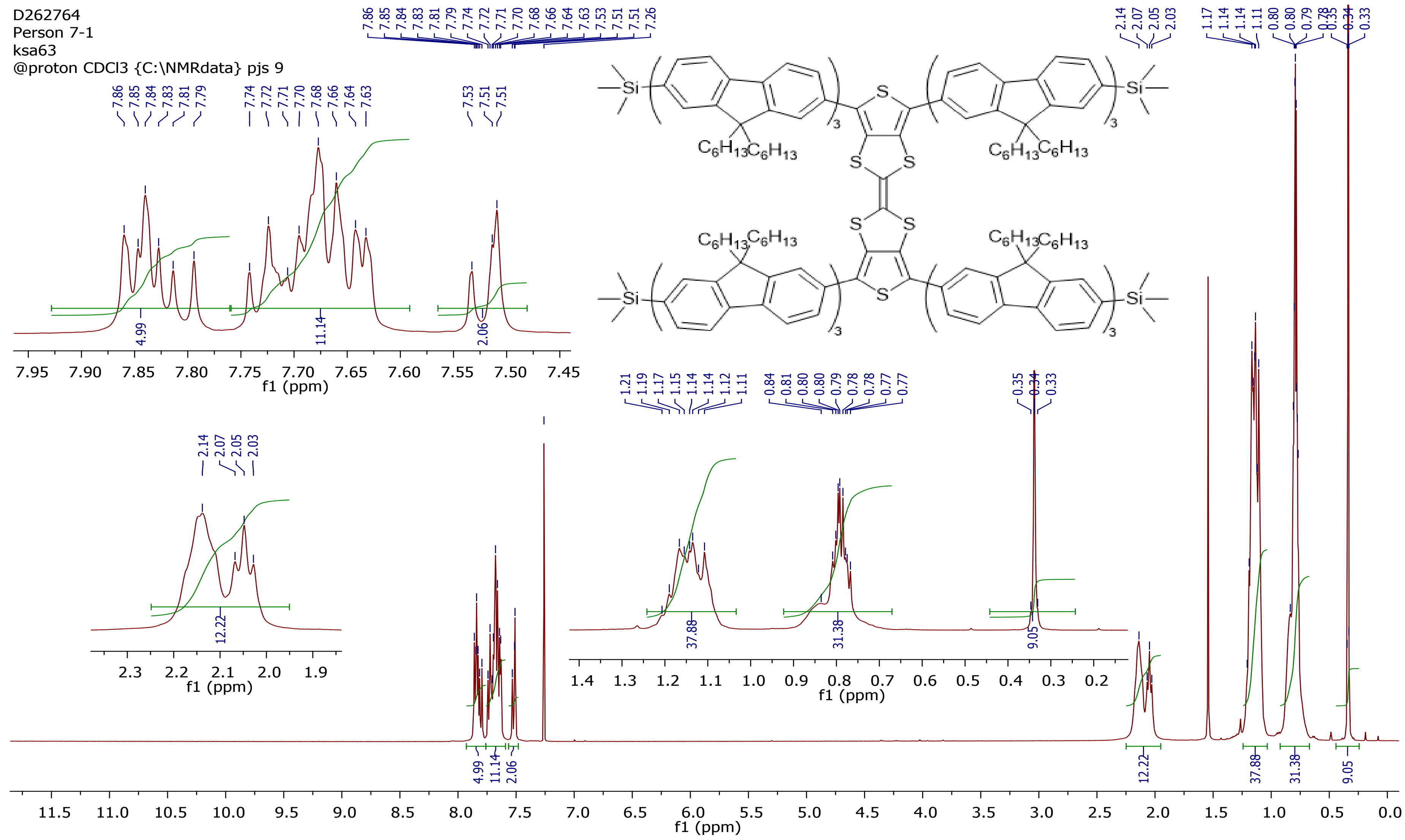
*^{13}C spectra of **TTF-F1-TMS** in CDCl$_3$.*



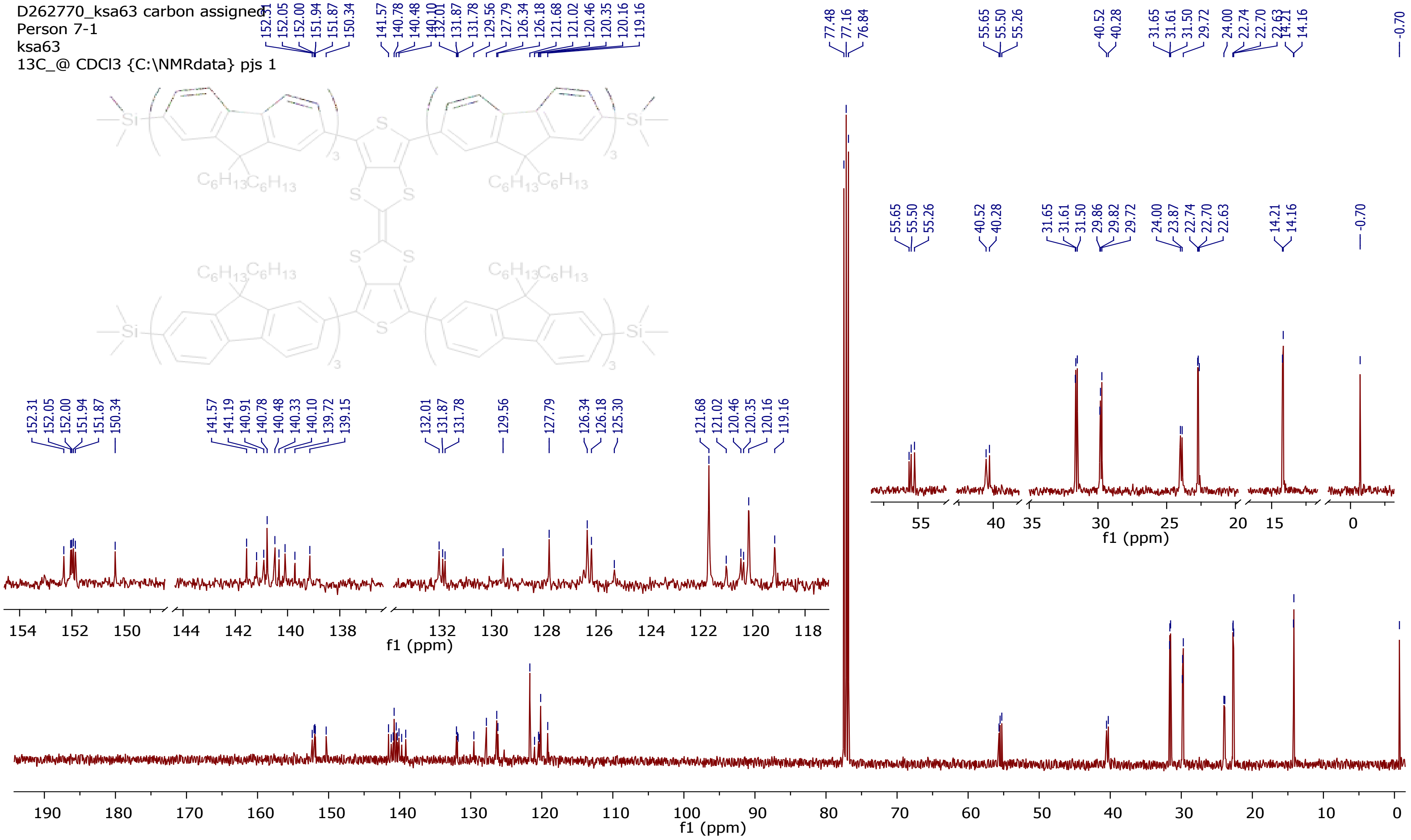
^1H *spectra of* ***TTF-F2-TMS*** *in* $CDCl_3$.



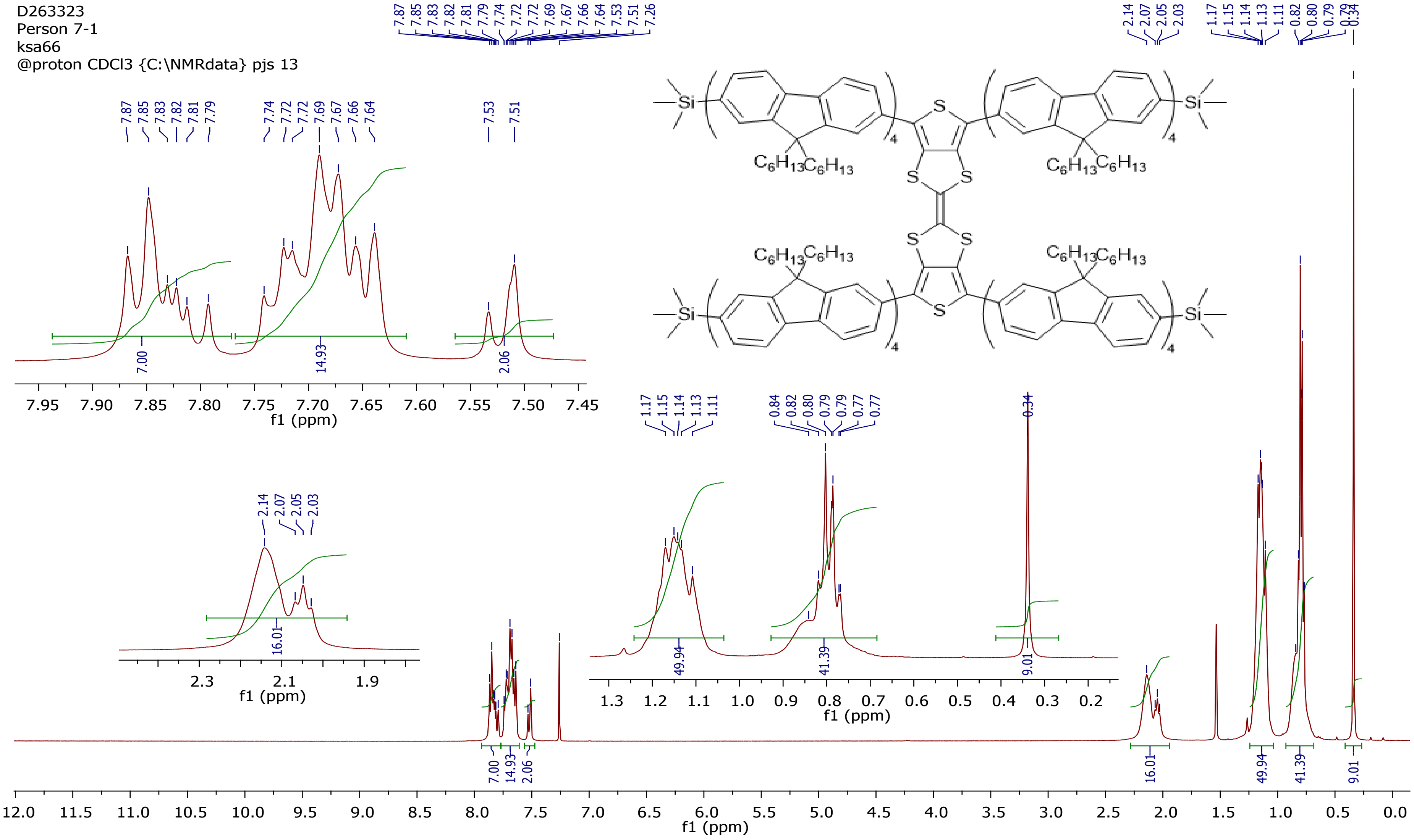
*^{13}C spectra of **TTF-F2-TMS** in $CDCl_3$.*



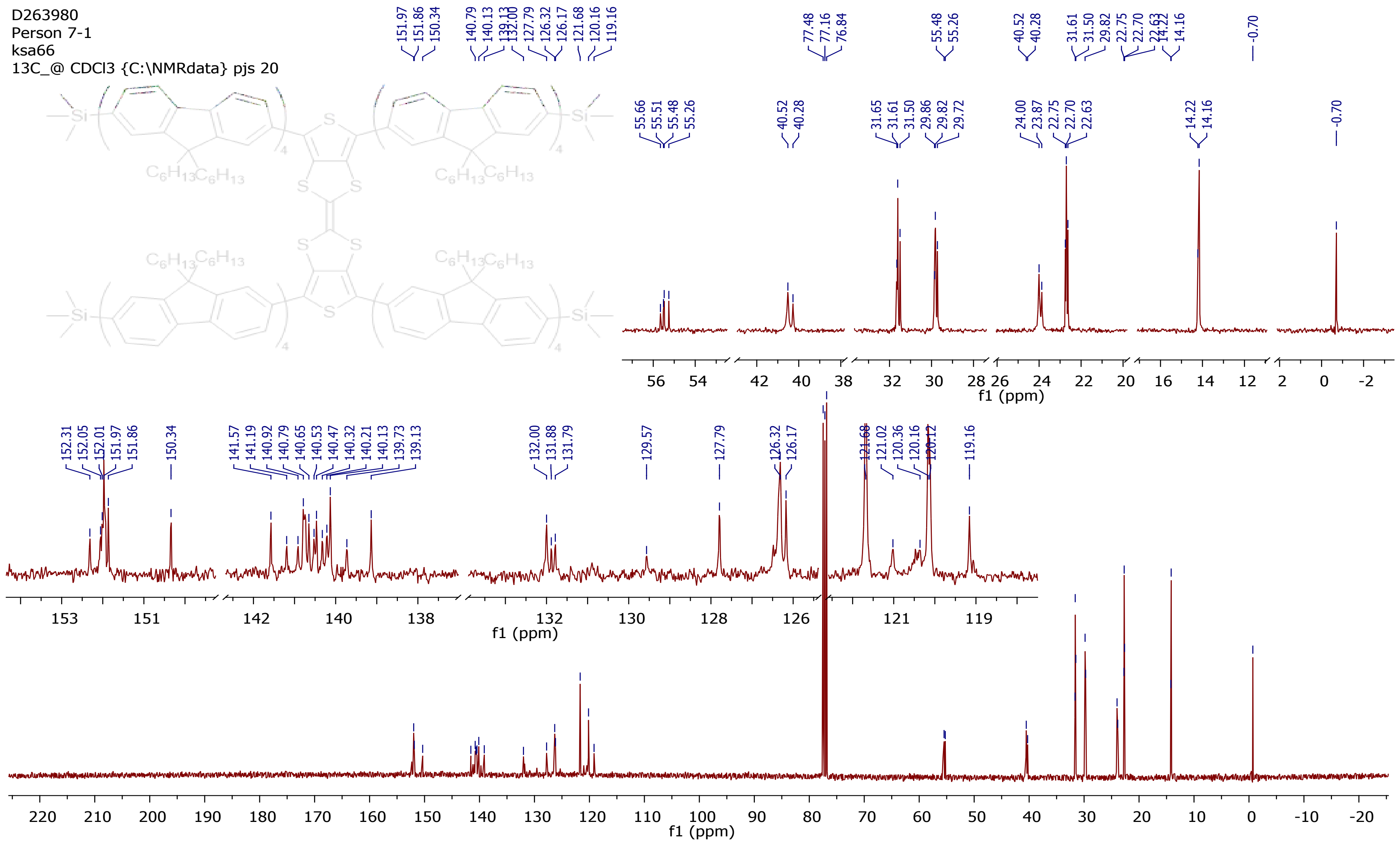
^{1}*H spectra of* ***TTF-F3-TMS*** *in* $CDCl_3$.



^{13}C spectra of **TTF-F3-TMS** in CDCl$_3$.



*^1H spectra of **TTF-F4-TMS** in $CDCl_3$.*



^{13}C *spectra of **TTF-F4-TMS** in $CDCl_3$.*