Supporting Information for:

Synthesis and Properties of Functionalized Oligo(arylene) Molecular Wires with Thiolated Termini: Competing Thiol-Au and Nitro-Au Assembly

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Contents

General. Details of equipment and procedures for the synthetic chemistry are the same as reported previously.[1] XPS data were obtained using a Kratos AXIS Ultra spectrometer and a monochromatic A1 Kα X-ray source. The instrument was operated at pressures of $<9\times10^{-7}$ Pa. Data were collected at stepintervals of 0.05 eV and the core level spectra of monolayers on gold were referenced to the Au 4f peak at 84.0 eV.

Compound 5. To a solution of **4** (3.70 g, 6.40 mmol) in anhydrous THF (100 mL) at -78 °C *n*-BuLi (2.5 M in hexane, 3.0 mL, 7.5 mmol) was added dropwise. The reaction mixture was stirred for 4 h at -78 °C, and then trimethylborate (5 mL, excess) was added. The mixture was stirred for a further 3 h at -78 °C and then slowly warmed to room temperature. The solvent was removed in vacuo and the residue was dissolved in dichloromethane (50 mL) and aqueous hydrochloric acid (1 M, 50 mL) and stirred for 1 h. The organic phase was separated and dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography (silica gel, eluent DCM: acetone, 100:3 v/v) to give **5** as a colorless oil (2.97 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.45 (s, 1H), 6.91 (s, 1H), 6.31 [bs, 2H, $B(OH)_2$], 3.98 (d, *J* = 5.6 Hz, 2H), 3.85 (d, *J* = 5.2 Hz, 2H), 1.89-1.75 (m, 1H), 1.62-1.56 (m, 1H), 1.54-1.19 (m, 25H), 0.98-0.79 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 150.6, 139.0, 137.0, 134.45, 131.6, 129.7, 120.5, 113.5, 71.7, 71.5, 46.1, 39.8, 31.1, 30.9, 30.7, 29.2, 29.1, 24.1, 24.3, 23.1, 23.1, 14.2, 11.3. Anal. Calcd for $C_{32}H_{51}BO_4S$: C, 70.83; H, 9.47. Found: C, 70.88; H, 9.46.

Compound 9. A mixture of **7** (0.428 g, 1.0 mmol), **8** (0.412g, 2.2 mmol), $Pd[PPh_3]_4$ (80 mg), CuI (20 mg), dry THF (50 mL) and triethylamine (5 mL) was stirred at room temperature for 12 h and then at 80 °C for an additional 2 h to afford a dark orange solution. The solvent was removed by vacuum evaporation and the residue was boiled with ethanol (50 mL). The mixture was suction filtered to collect a dark yellow solid, which was chromatographed on a silica column eluted with DCM. The first fraction from the column was crystallized from chlorobenzene to yield **9** as orange needles (0.33 g, 62% yield). ^{1}H NMR (500 MHz, DMSO-d_6, 363K) δ 8.54 (s, 1H), 8.47 (d, *J* = 1.5 Hz, 1H); 8.18 (d, *J* = 1.5 Hz, 1H), 8.06 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 3.33 (t, *J* = 6.8 Hz, 2H), 2.86 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (125 Hz, DMSO-d_6, 363 K) δ 186.4, 152.5, 144.3, 138.4, 137.7, 136.8, 135.7, 132.7 132.5 131.9, 131.1, 128.8, 127.9, 123.4, 121.2, 119.5, 118.10, 118.06, 99.5, 84.4, 27.4, 17.1. Anal. Calcd for $C_{24}H_{12}BrN_3O_5S$: C, 53.95; H, 2.26; N, 7.86. Found: C, 53.77; H, 2.19; N, 7.82.

A single crystal for X-ray structural analysis was obtained by slow evaporation of a 1,4-dioxane solution of **9**. *Crystal data*: $C_{24}H_{12}BrN_3O_5 \cdot ½C_4H_8O_2$, M=578.39, T=120 K, triclinic, space group $P\bar{1}$ (No. 2), a=7.7250(6), b=8.3461(5), c=19.3085(18) Å, α=79.088(12), β=82.355(12), γ=75.344(14)º, U=1177.84(16) Å^3, Z=2, μ=1.88 mm^{-1}, Mo-K_α radiation ($\bar{\lambda}$ =0.71073 Å), Bruker SMART 6K CCD area detector and SHELXTL 6.14 software, absorption correction by numerical integration, 18461 reflections with 2θ≤55º, R_{int}=0.061, $R(F)$=0.033 [4075 data with $I \geq 2\sigma(I)$], w$R(F^2)$=0.069 [all 5403 unique data]. CCDC-706327. The molecular structure is shown in Figure S1.

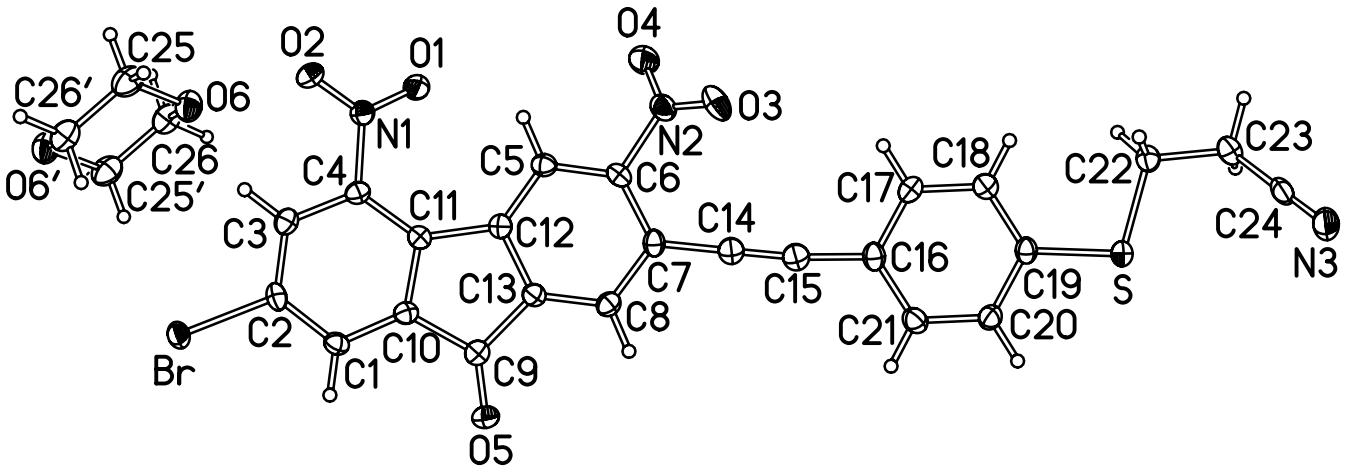
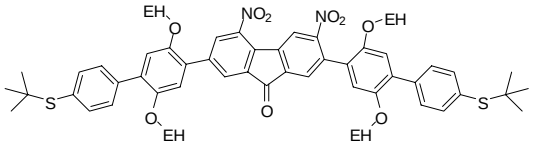


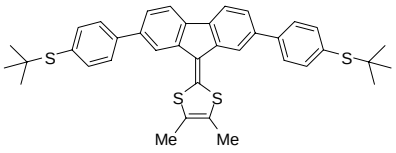
Figure S1. X-ray molecular structure of **9**·½ $C_4H_8O_2$. Thermal ellipsoids are shown at the 50% probability level. The dioxane molecule lies at a crystallographic inversion centre.

Compound 12. To a mixture of 2,7-dibromo-3,5-dinitrofluorenone **7** (64 mg, 0.15 mmol), boronic acid **5** (163 mg, 0.3 mmol), THF (7 mL), toluene (7 mL) and aqueous sodium carbonate (1 M, 1.0 mL, 1.0 mmol), $Pd(PPh_3)_4$ (12.5 mg, 0.01 mmol) was added in one portion, and the mixture was heated at reflux for 24 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (20 mL) and washed with water (10 mL). The separated red organic phase was dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography (SiO_2, eluent DCM/petroleum ether 5:1 to 10:3 v/v) to give **12** as a red solid (145 mg, 76% yield); mp 68-69 ^oC. MALDI-ToF MS: 1262.8 (M+). ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.58 (d, J = 1.2 Hz, 1H), 8.32 (d, J = 1.6 Hz, 1H), 7.93 (s, 1H), 7.61-7.54 (m, 8H), 7.05 (s, 1H), 7.04 (s, 1H), 6.98 (s, 1H), 6.93 (s, 1H), 3.97-3.77 (m, 8H), 1.77-1.59 (m, 4H), 1.43-1.07 (m, 50H), 0.97-0.77 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 153.9, 150.71, 150.66, 150.4, 149.6, 144.4, 142.0, 139.9, 138.5, 138.3, 137.0, 136.9, 136.6, 136.1, 135.9, 133.4, 132.7, 132.3, 131.8, 131.5, 129.9, 129.7, 129.56, 128.5, 125.9, 125.5, 121.9, 115.2, 114.8, 114.7, 114.1, 72.1, 72.0, 71.6, 46.1, 46.0, 39.7, 39.6, 39.2,

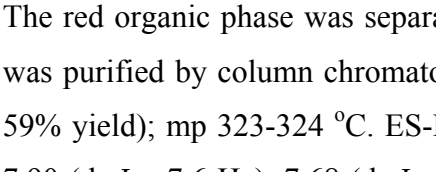


31.0, 30.7, 30.6, 30.5, 29.1, 29.0, 28.9, 24.03, 23.95, 23.8, 23.01, 22.97, 22.9, 14.03, 13.97, 11.2, 11.1. Anal. Calcd for $C_{77}H_{102}N_2O_9S_2$: C, 73.18; H, 8.14; N, 2.22. Found: C, 73.22; H, 8.18; N, 2.12.

Compound 14. To a mixture of **13** (226 mg, 0.50 mmol), **2** (210 mg, 1.0 mmol), THF (30 mL), toluene (30 mL) and aqueous sodium carbonate (1 M, 2.0 mL, 2 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) was added in one portion, and the mixture was heated at reflux for 24 h. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (40 mL) and washed with water (40 mL). The red organic phase was separated and dried over $MgSO_4$, the solvent was removed and the residue was purified by column chromatography (SiO_2, eluent DCM) to give **14** as a yellow powder (185 mg, 59% yield); mp 323-324 ^oC. ES-MS: 622.3 (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 1.6 Hz), 7.90 (d, J = 7.6 Hz), 7.68 (d, J = 8.0 Hz, 4H), 7.63 (d, J = 8.0 Hz, 4H), 7.54 (dd, 2H, J = 8.0 and 1.6 Hz), 2.19 (s, 6H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 139.1, 138.2, 137.8, 136.5, 131.5, 127.4, 124.1, 123.9, 121.5, 120.0, 46.1, 31.1, 13.2. Anal. Calcd for $C_{38}H_{38}S_4$: C, 73.26; H, 6.15. Found: C, 73.18; H, 6.24.



Compound 15. A mixture of **14** (106 mg, 0.165 mmol), dichloromethane (15 mL) and acetyl chloride (4 mL) was cooled to 0 ^oC and then BBr_3 (1.8 mL, 1.8 mmol) solution in dichloromethane (10 mL) was added in one portion. The procedure was the same as described for the preparation of **11**. Column chromatography (SiO_2, eluent DCM) gave **15** as a yellow powder (78 mg, 78% yield); mp 303-304 ^oC (dec.). ES-MS: 594.2 (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.4 Hz, 4H), 7.54-7.52 (m, 6H), 2.48 (s, 6H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 143.4, 141.6, 139.0, 138.3, 136.6, 134.8, 128.3, 126.4, 124.1, 124.0, 121.7, 120.0, 118.12, 30.3, 13.2. Anal. Calcd for $C_{34}H_{26}O_2S_4$: C, 68.65; H, 4.41. Found: C, 68.68; H, 4.38.



Compound 16. To a mixture of **13** (151 mg, 0.30 mmol), **5** (398 mg, 0.71 mmol), THF (10 mL), toluene (10 mL) and aqueous sodium carbonate (1 M, 20 mL, 2.0 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) was added in one portion, and then the mixture was heated at reflux for 48 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (20 mL) and washed with water (30 mL). The separated organic phase was dried over $MgSO_4$, evaporated and the residue was chromatographed (SiO_2, eluent DCM : acetone, 100:1 gradient to 100/3) to give **16** as a yellow crystalline solid (205 mg, 53% yield); mp 138-139 ^oC. MALDI-ToF MS: 1286.9 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 1.6 and 0.4 Hz, 2H), 7.92 (dd, J = 8.0 Hz and 0.4 Hz, 2H), 7.61 (s, 8H), 7.57 (dd, 2H, J = 8.0 and 1.6 Hz), 7.17 (s,

2H), 7.07 (s, 2H), 3.88 (d, 4H, J = 5.6 Hz), 3.85 (d, J = 5.6 Hz, 4H), 2.18 (s, 6H), 1.71-1.62 (m, 4H), 1.42-1.18 (m, 42H), 0.90-0.77 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.5, 138.5, 138.1, 136.5, 135.9, 135.3, 131.5, 130.0, 128.9, 128.7, 125.5, 123.1, 122.5, 117.9, 115.4, 115.2, 71.3, 71.0, 44.9, 38.7, 30.9, 30.0, 29.6, 28.7, 28.1, 28.0, 23.0, 22.9, 22.01, 21.97, 21.7, 13.1, 13.0, 12.1, 10.2. Anal. Calcd for $C_{82}H_{110}O_4S_4$: C, 76.46; H, 8.61. Found: C, 76.66; H, 8.66.

A single crystal for X-ray structural analysis was obtained by slow evaporation of a diethyl ether/DCM/ethanol solution of **16**. *Crystal data*: $C_{82}H_{110}O_4S_4$, M= 1287.94, T=120 K, monoclinic, space group *C2/c* (No. 15), a=52.274(4), b=8.3593(6), c=39.186(3)Å, β=118.24(1)º, U=15085(2) Å^3, Z=8, μ=0.17 mm^{-1}, Mo-K_α radiation ($\bar{\lambda}$ =0.71073 Å), Bruker SMART 6K CCD area detector and SHELXTL 6.14 software, absorption correction by numerical integration, 63511 reflections with 2θ≤50º, R_{int}=0.138, $R(F)$=0.069 [5250 data with I≥2σ(I)], w$R(F^2)$=0.220 [all 13281 unique data]. CCDC-706328. The molecular structure is shown in Figure S2.

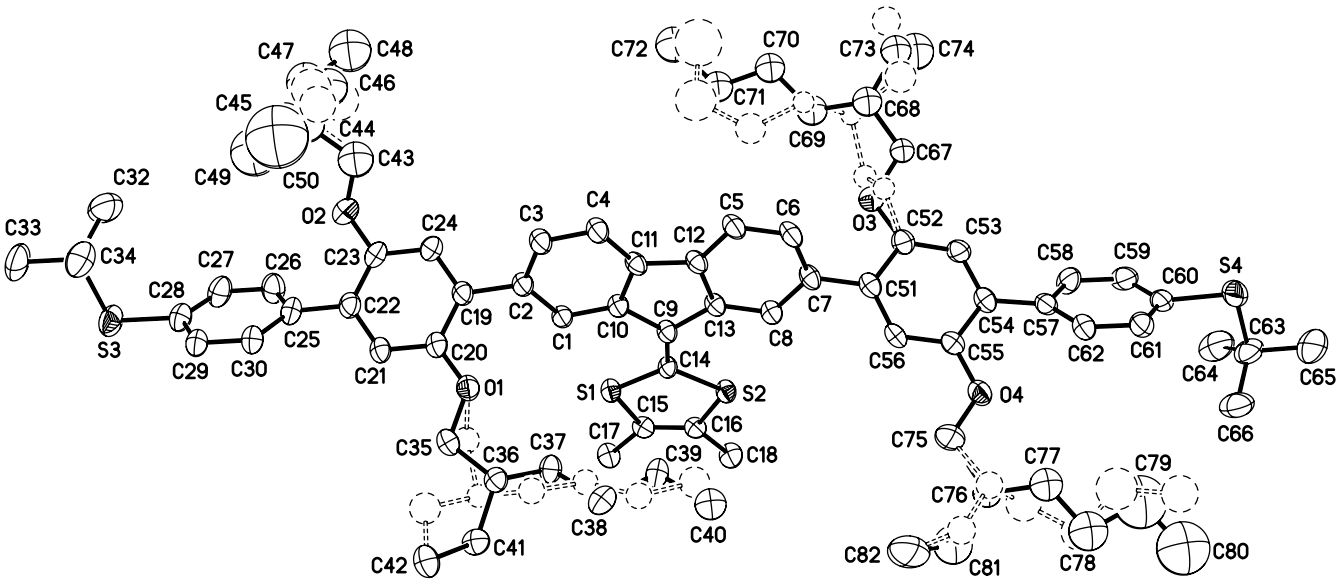
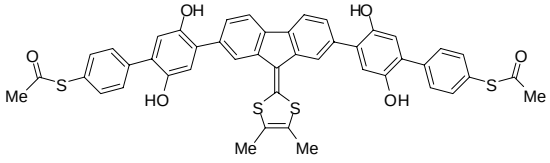


Figure S2. X-ray molecular structure of **16.** Thermal ellipsoids are drawn at the 30% probability level, hydrogen atoms are omitted. All substituents show intense disorder, which was (imperfectly) approximated by two alternative conformations (A and B) in each case.

Compound 17. A suspension of **16** (129 mg, 0.10 mmol), dichloromethane (45 mL) and acetyl chloride (3 mL) was cooled to 0 ^{o}C and then the BBr_3 (3.0 mL, 3.0 mmol) solution in dichloromethane was added in one portion. The resulting orange solution was stirred for 20 min at 0 ^{o}C, and then for 12 h at room temperature and then poured into ice. The organic layer was separated, dried over $MgSO_4$ and the residue was purified by chromatography (SiO_2, eluent DCM) to give **17** as a yellow powder (55 mg, 69% yield): mp > 240



^{o}C (dec.). MALDI-ToF MS: 810.2 (M^{+}); 833.1 ($M+Na^{+}$). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (s, 2H), 9.19 (s, 2H), 8.12 (s, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.4 Hz), 7.58 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 4H), 7.07 (s, 2H), 6.99 (s, 2H), 2.51 (s, 6H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.3, 147.6, 140.5, 140.1, 137.4, 137.0, 135.8, 134.5, 130.2, 129.1, 126.64, 126.57, 126.1, 124.5, 123.5, 120.0, 118.1, 117.8, 31.23, 13.3. Anal. Calcd for $C_{46}H_{34}O_6S_4$: C, 68.12; H, 4.23. Found: C, 68.22; H, 4.36.

Self-assembly. Monolayers were formed by immersing gold-coated substrates in a tetrahydrofuran solution of the wire molecule (0.1 mg mL^{-1}) to which aqueous ammonium hydroxide solution was added to facilitate removal of the protecting groups. The SAMs were then thoroughly rinsed with tetrahydrofuran to remove physisorbed material.

Electrical characterization. SAMs were investigated using a MultiMode scanning tunnelling microscope with a Nanoscope IV controller (Veeco Instruments, Cambridge). For *I–V* characterization, the gold probe was landed at distinct surface features distant from grain boundaries. In each case, the SAMs were investigated at several locations across the surface and the *I–V* data were averaged from multiple scans at each of these sites.

XPS data

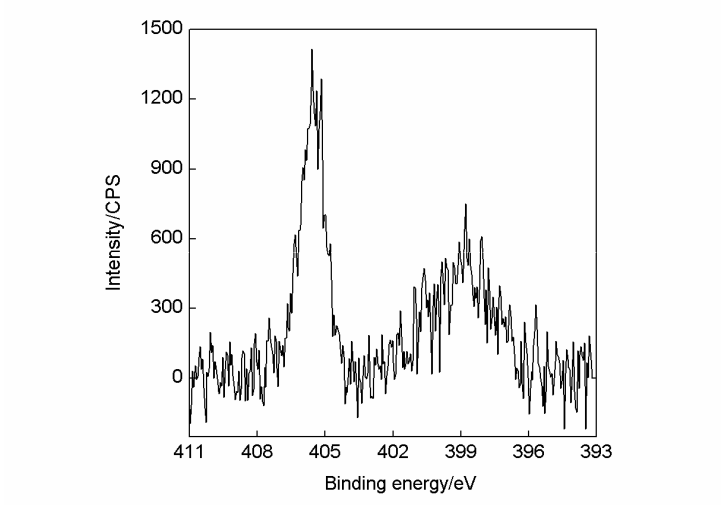
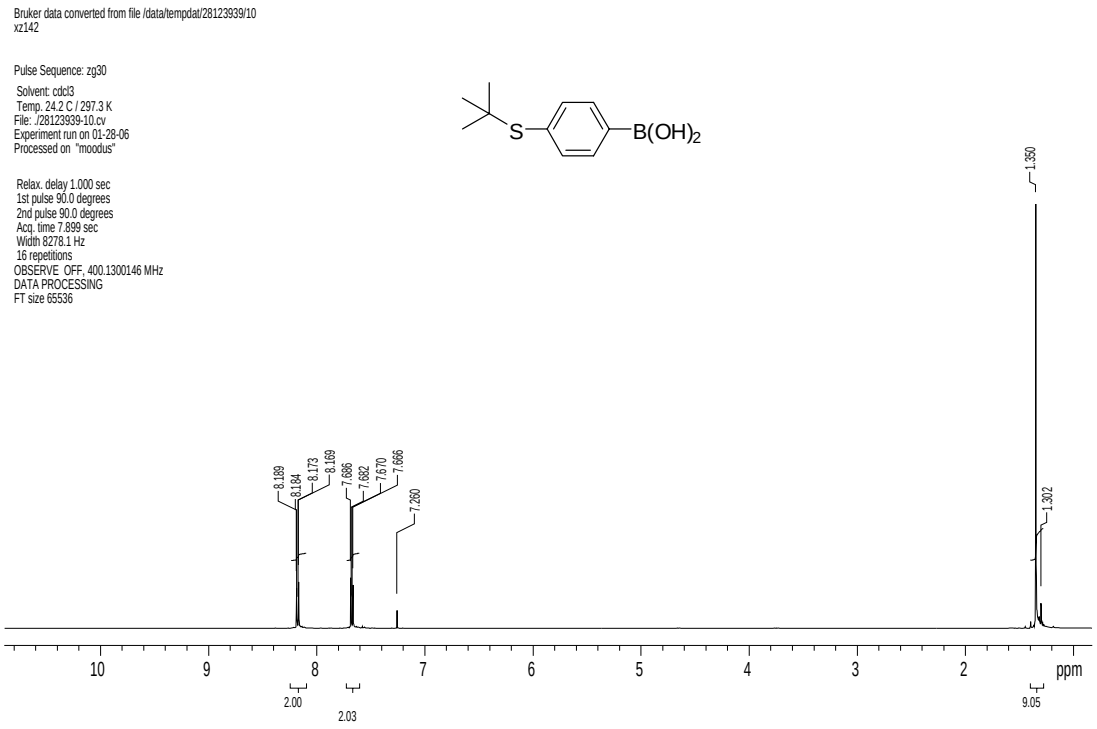
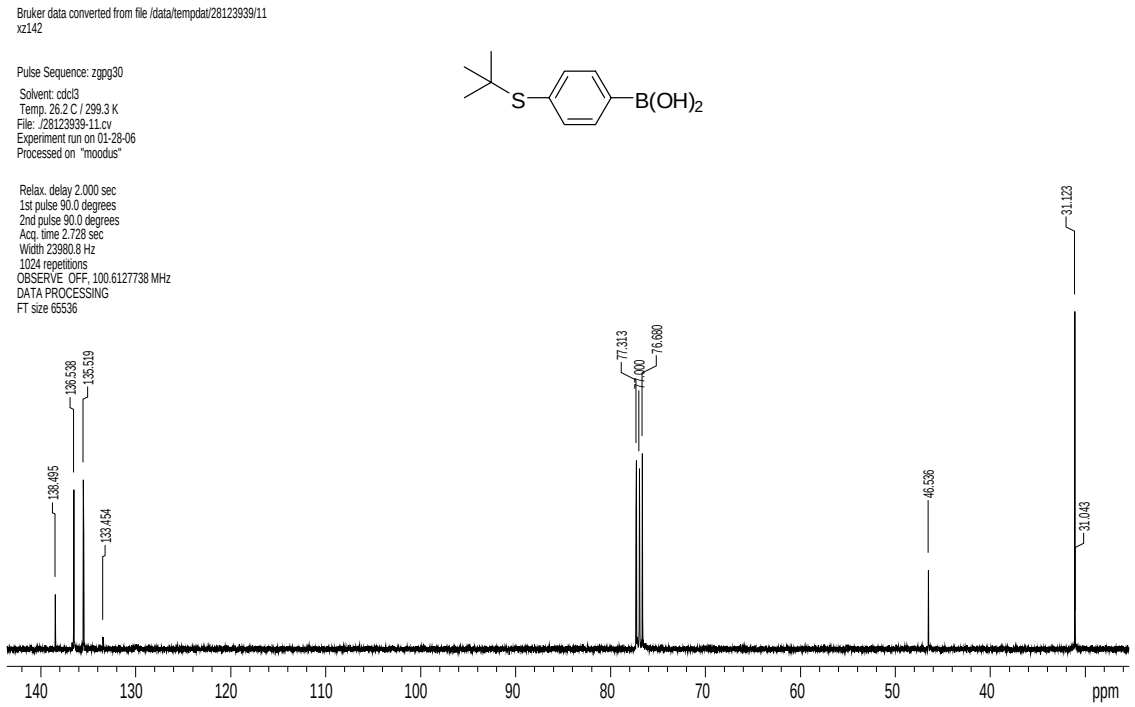


Figure S3. N 1s spectrum of a SAM of **11** showing the peak at 405.6 eV which is characteristic of NO_2 and the anomalous lower energy peak, which was observed on some occasions when using NH_4OH as a deprotecting agent.

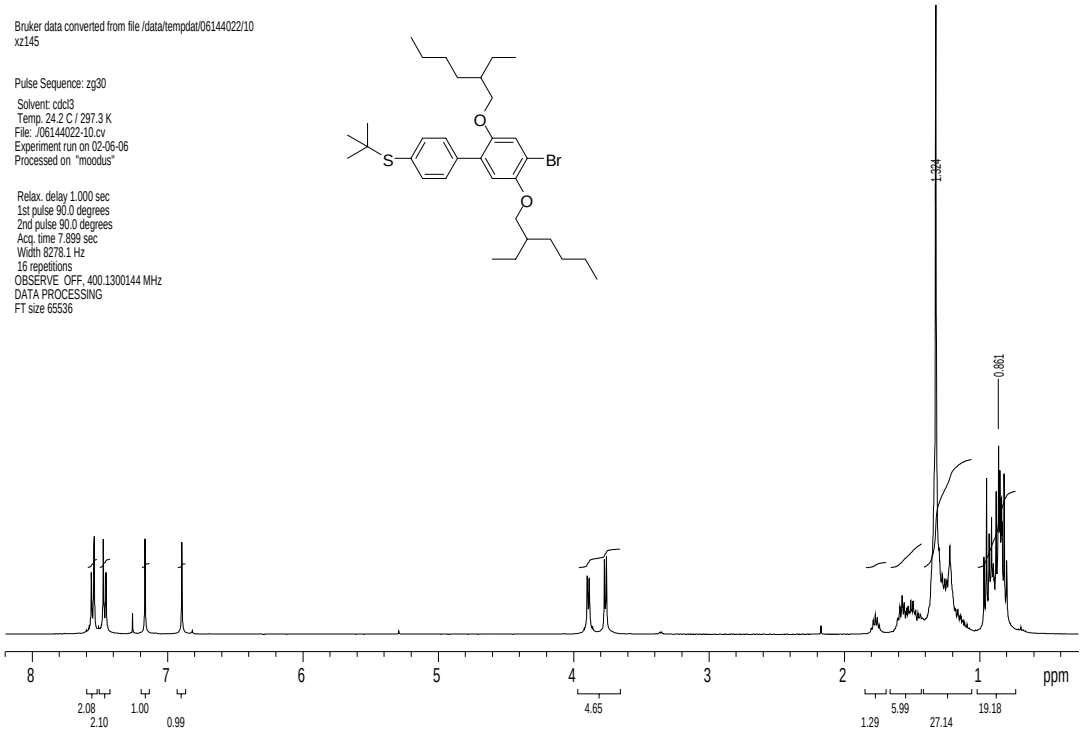
Compound **2**. ^{1}H NMR (400 MHz, $CDCl_3$)



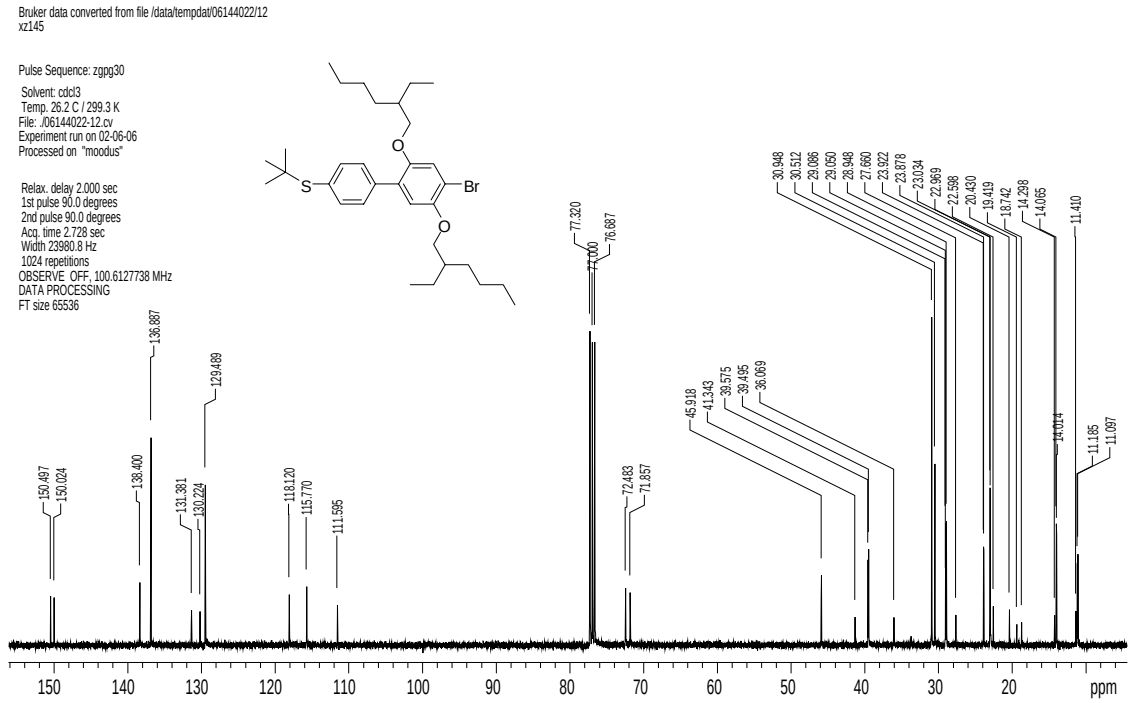
Compound **2**. ^{13}C NMR (100 MHz, $CDCl_3$)



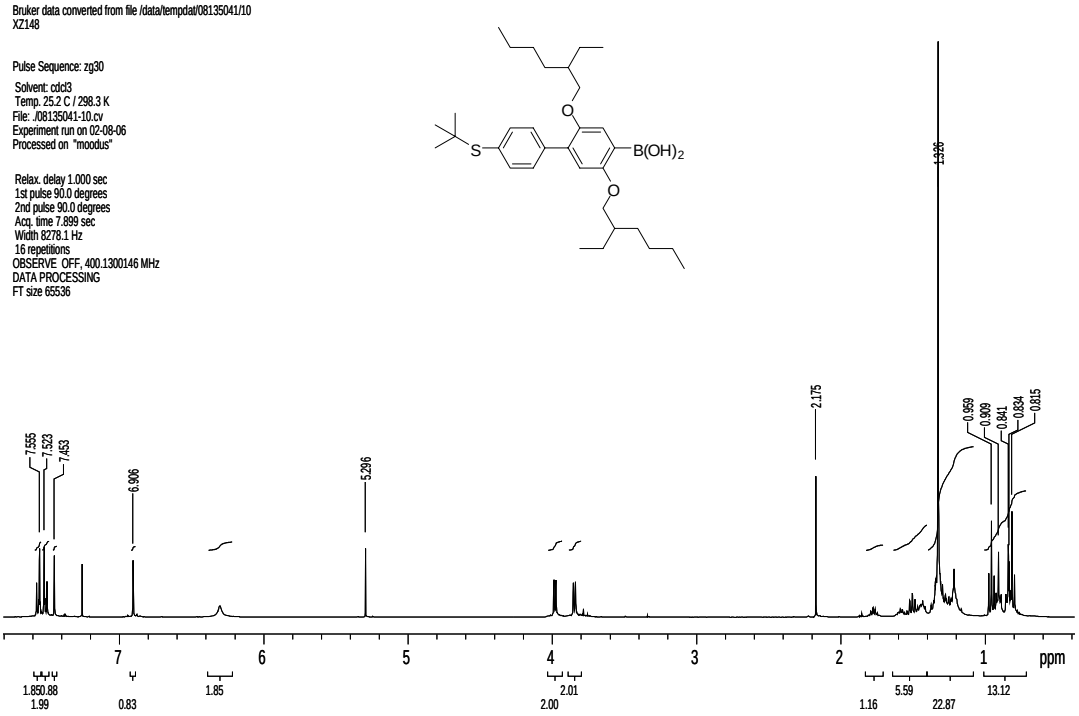
Compound **4**. ^{1}H NMR (400 MHz, $CDCl_3$)



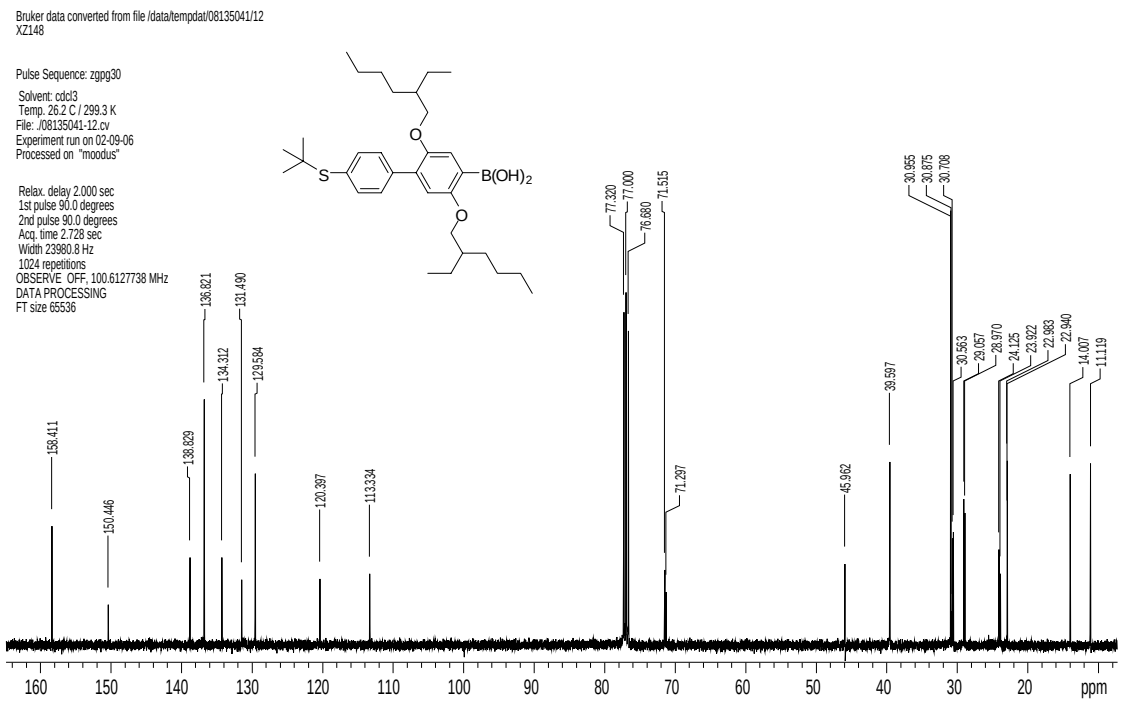
Compound **4**. ^{13}C NMR (100 MHz, $CDCl_3$)



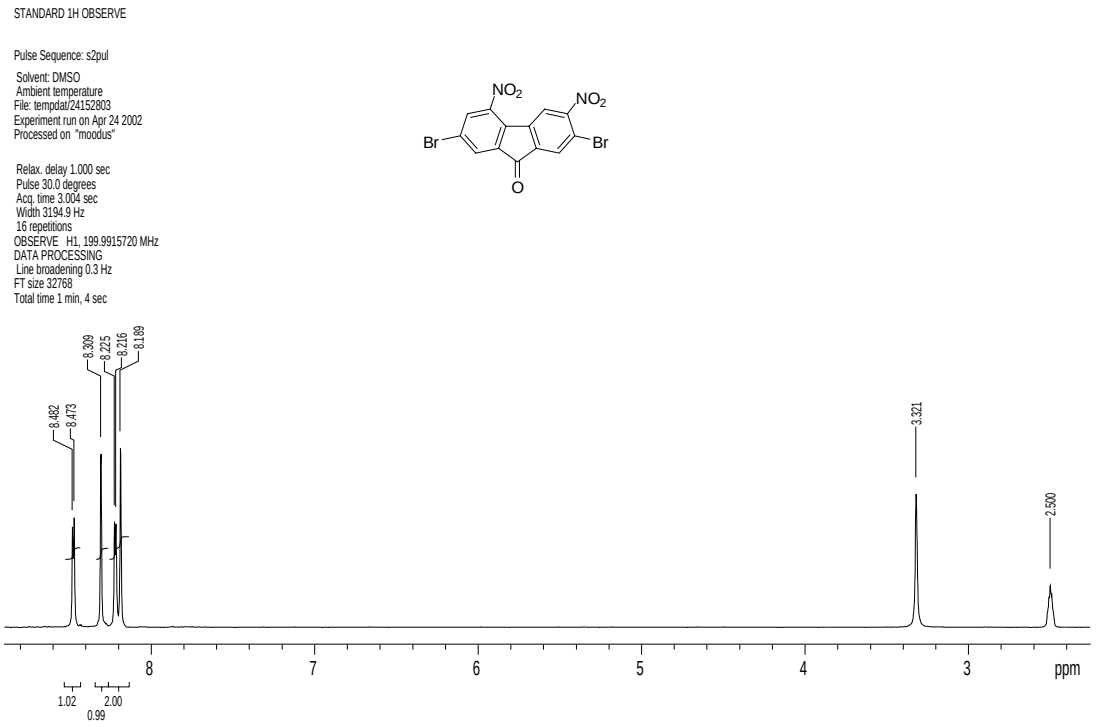
Compound **5**. ^{1}H NMR (400 MHz, $CDCl_3$)



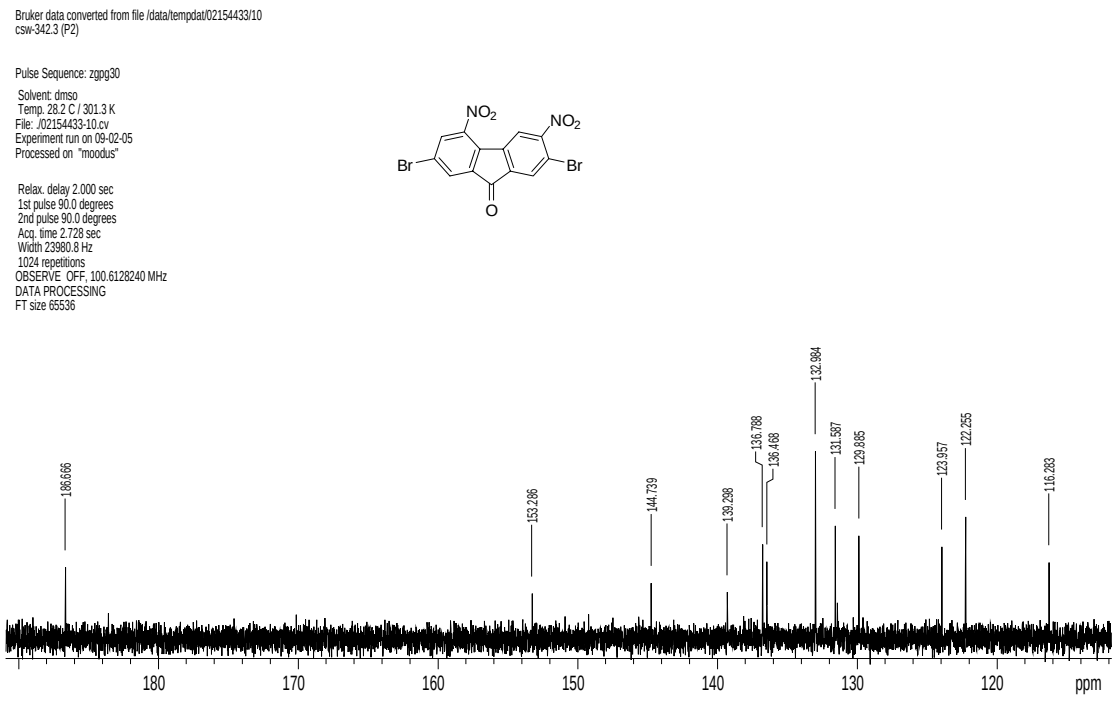
Compound **5**. ^{13}C NMR (100 MHz, $CDCl_3$)



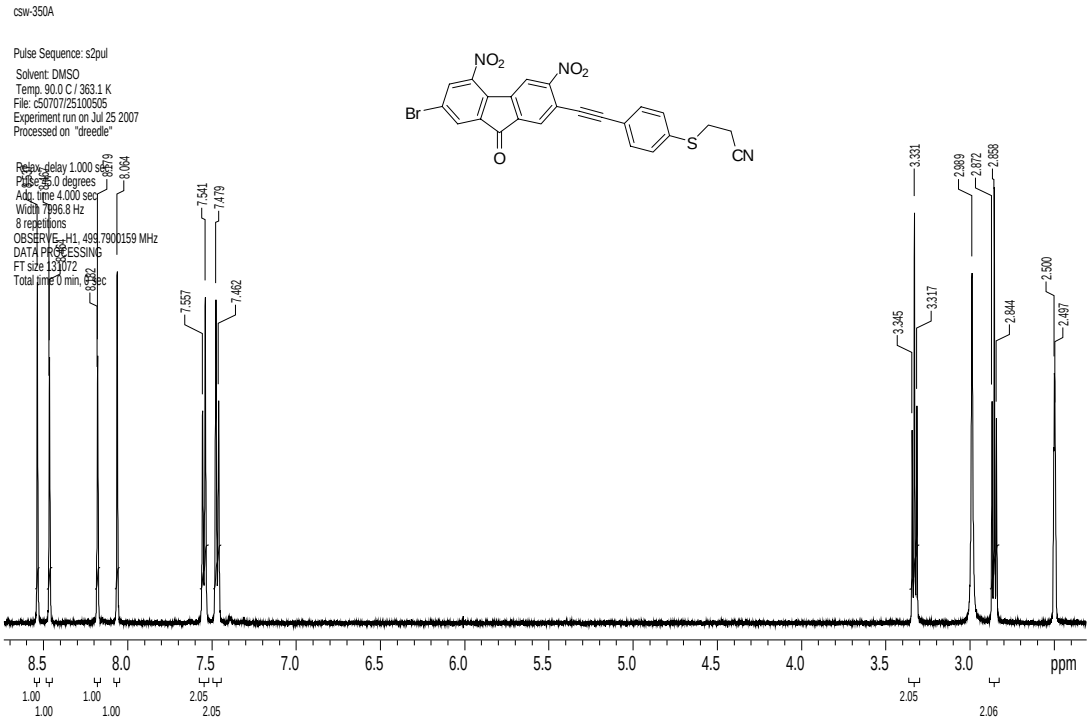
Compound **7**. ^{1}H NMR (200 MHz, DMSO-d_6)



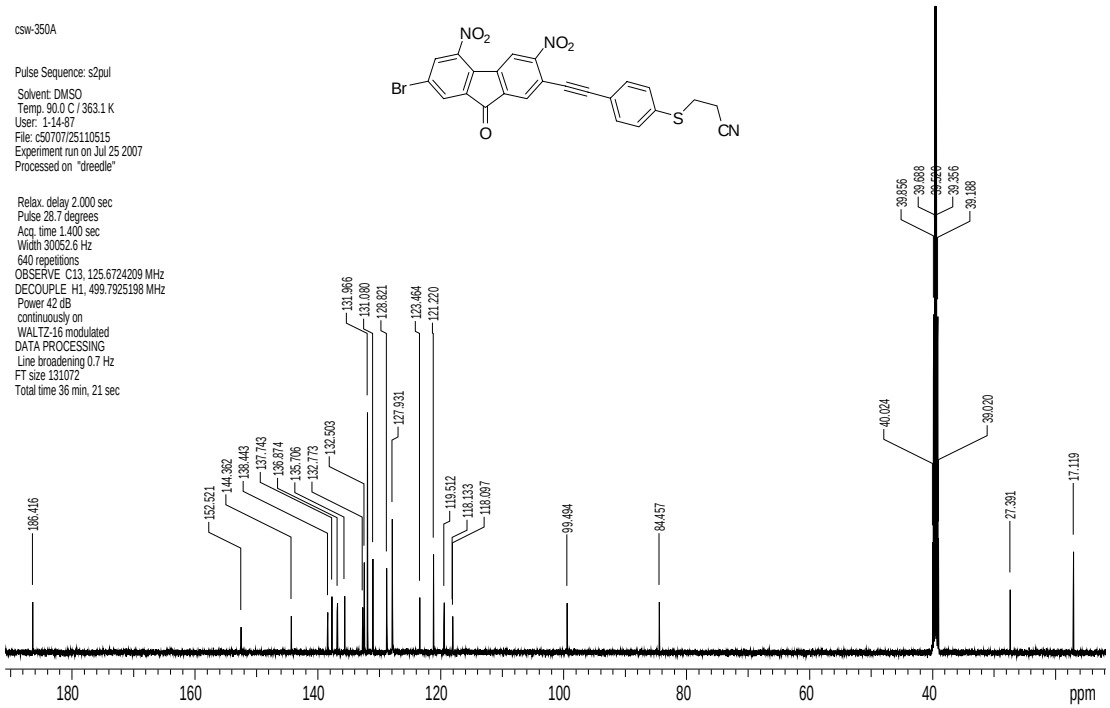
Compound **7**. ^{13}C NMR (100 MHz, DMSO-d_6)



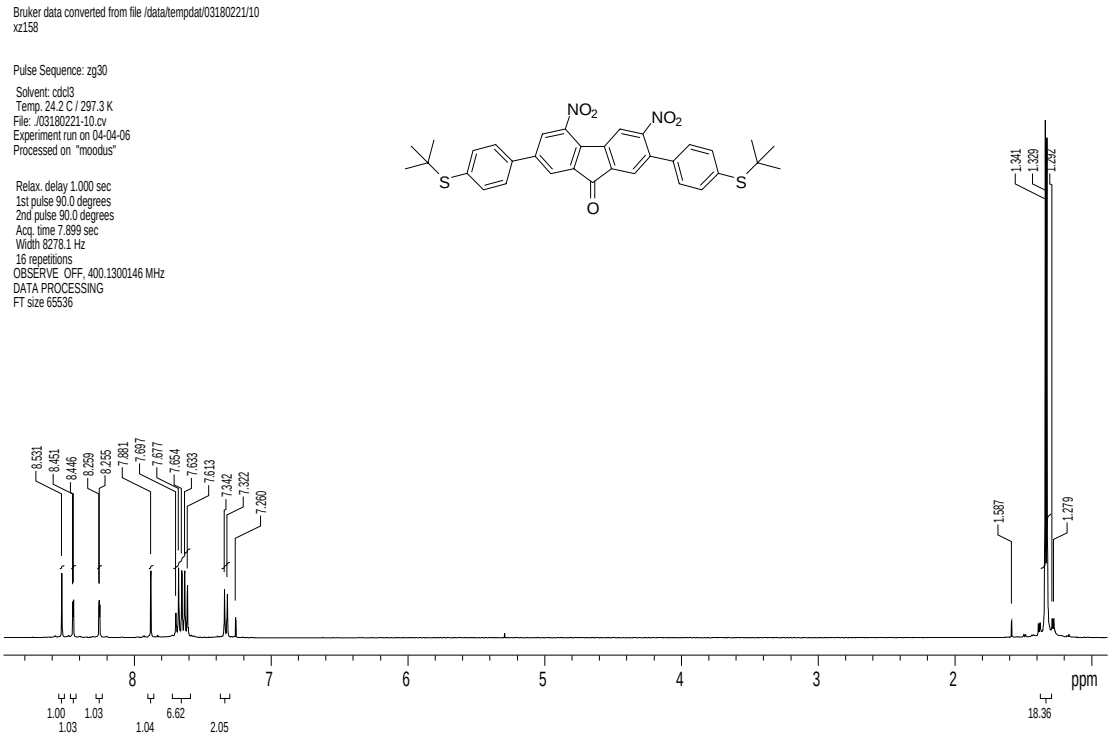
Compound **9**. ^{1}H NMR (500 MHz, DMSO-d_6, 363K)



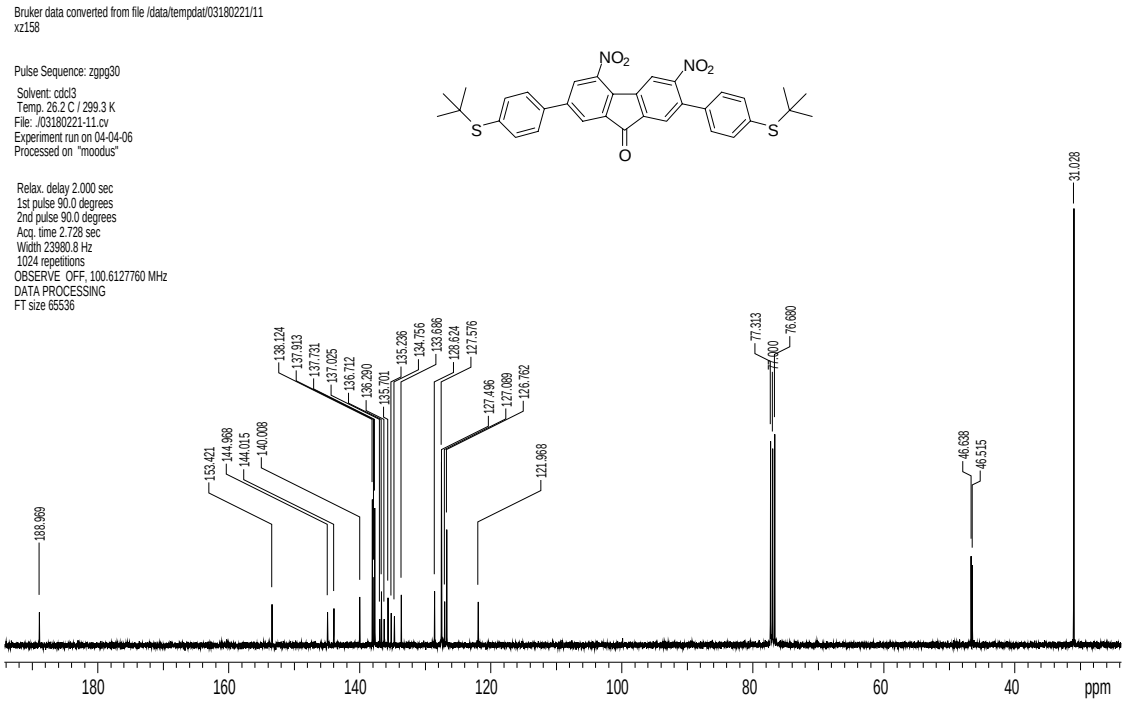
Compound **9**. ^{13}C NMR (125 MHz, DMSO-d_6, 363K)



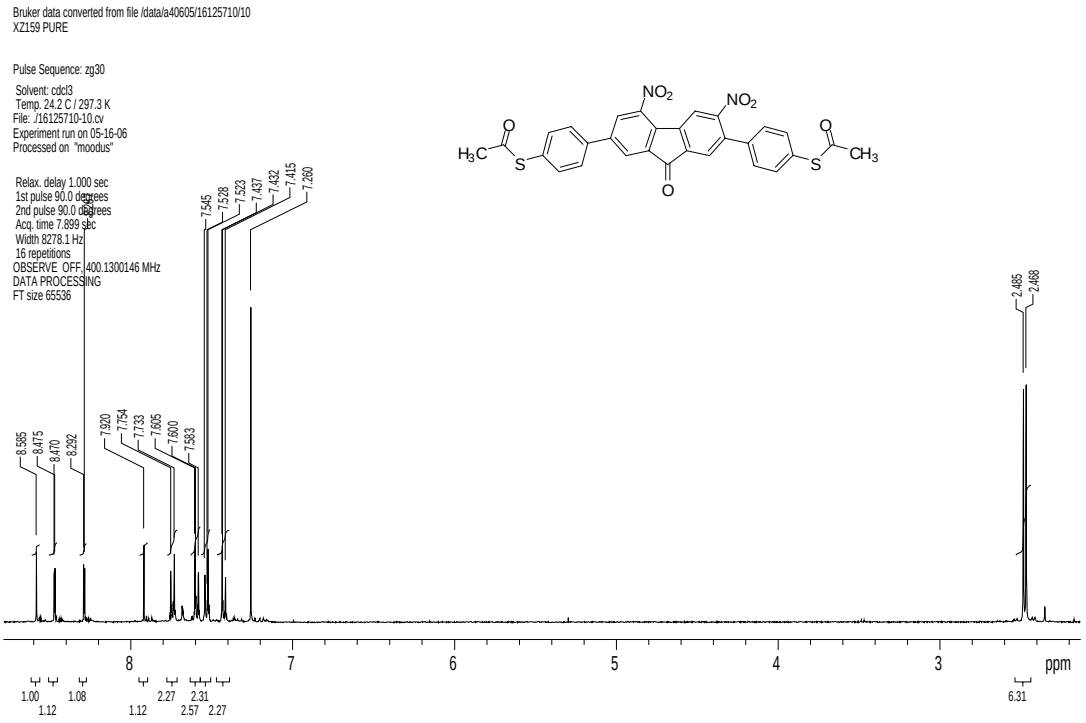
Compound **10**. ^{1}H NMR (400 MHz, $CDCl_3$)



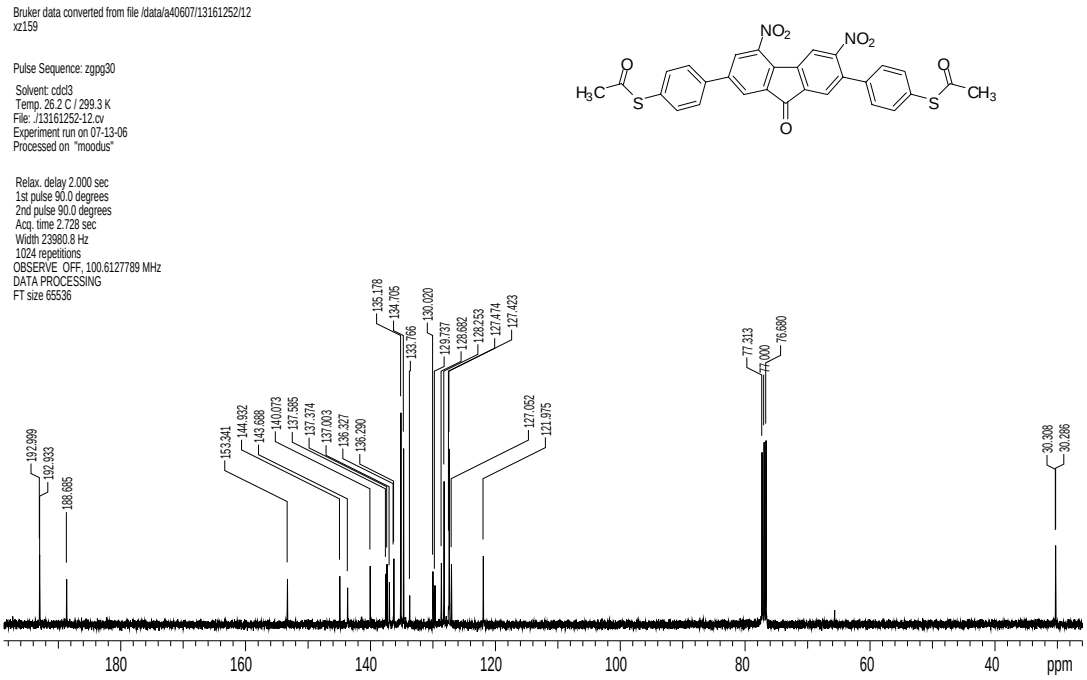
Compound **10**. ^{13}C NMR (100 MHz, $CDCl_3$)



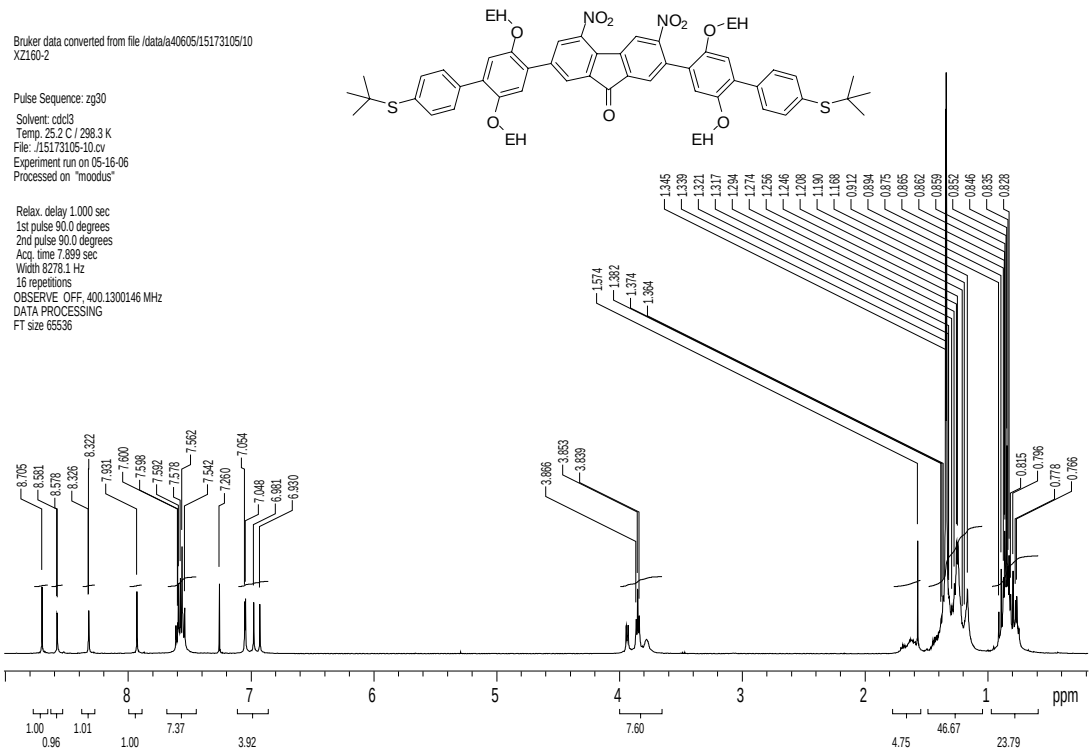
Compound **11**. ^{1}H NMR (400 MHz, $CDCl_3$)



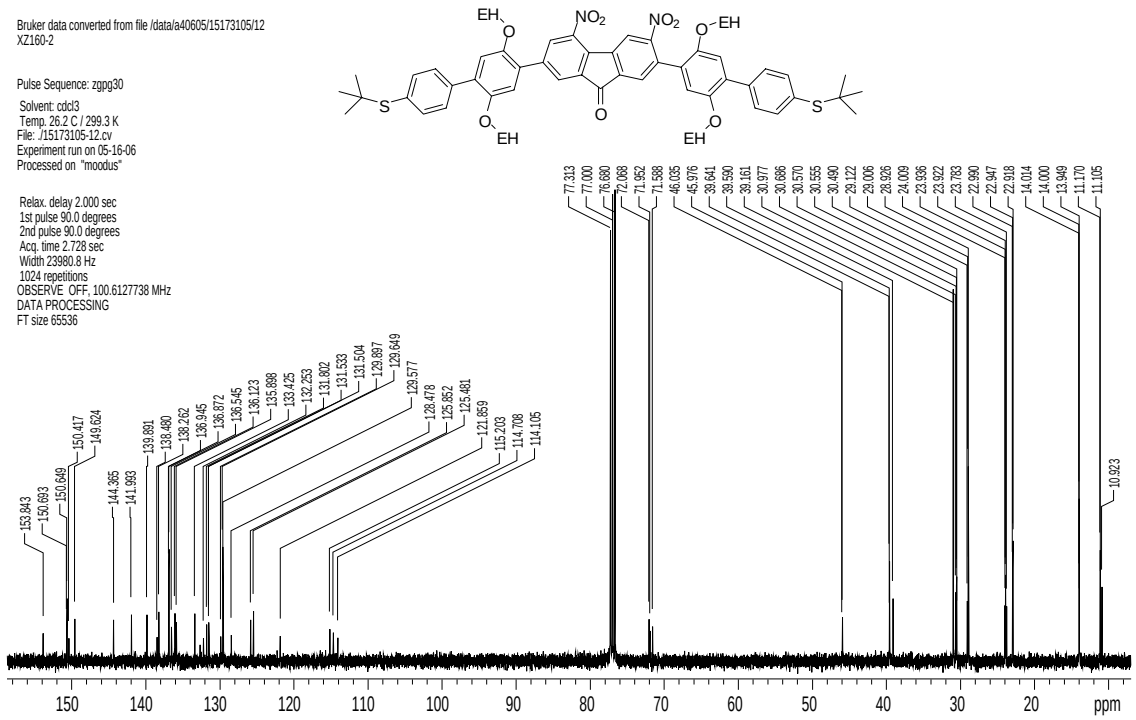
Compound **11**. ^{13}C NMR (100 MHz, $CDCl_3$)



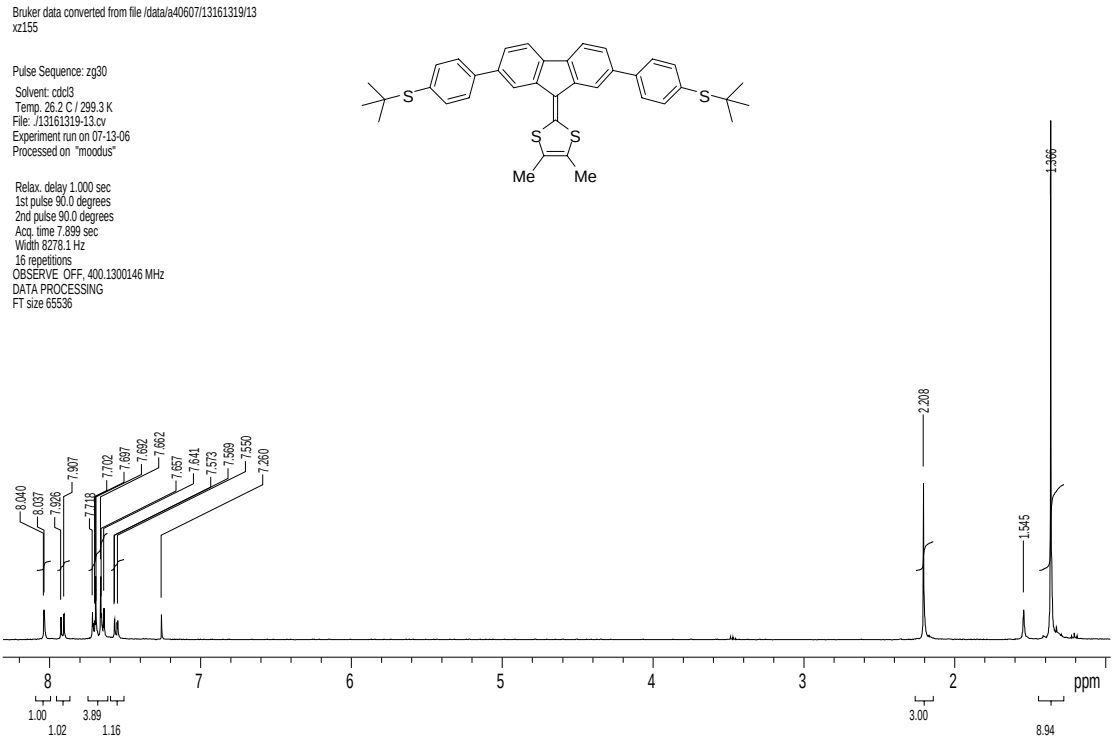
Compound **12**. ^{1}H NMR (400 MHz, $CDCl_3$)



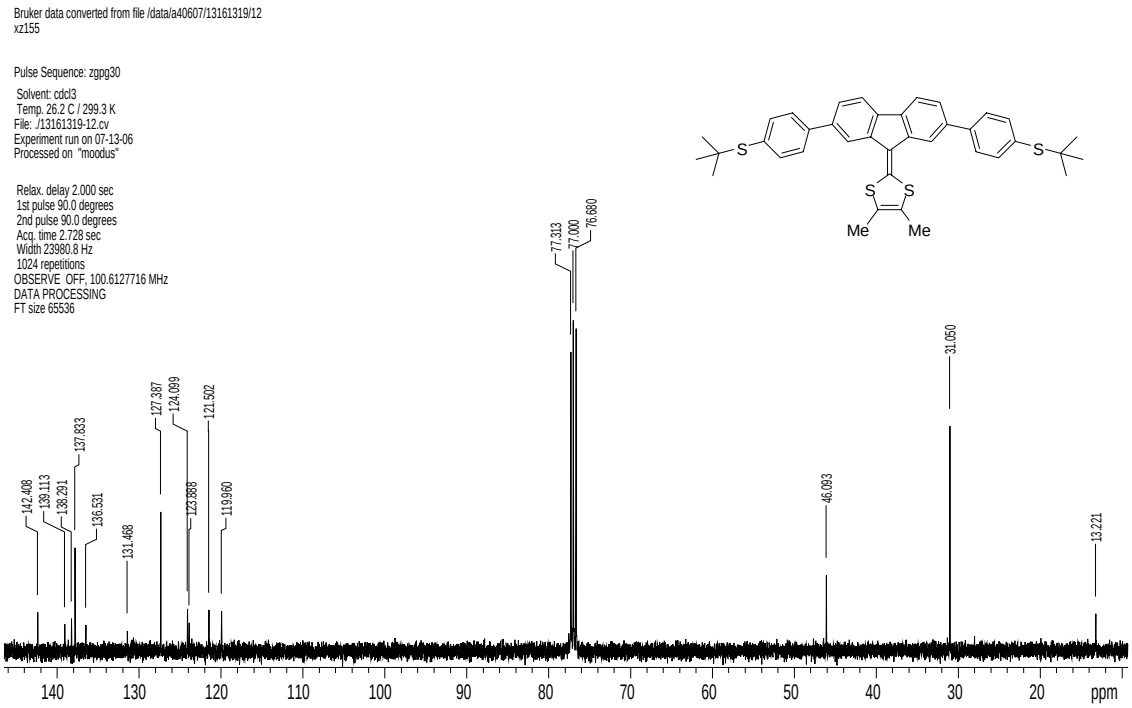
Compound **12**. ^{13}C NMR (100 MHz, $CDCl_3$)



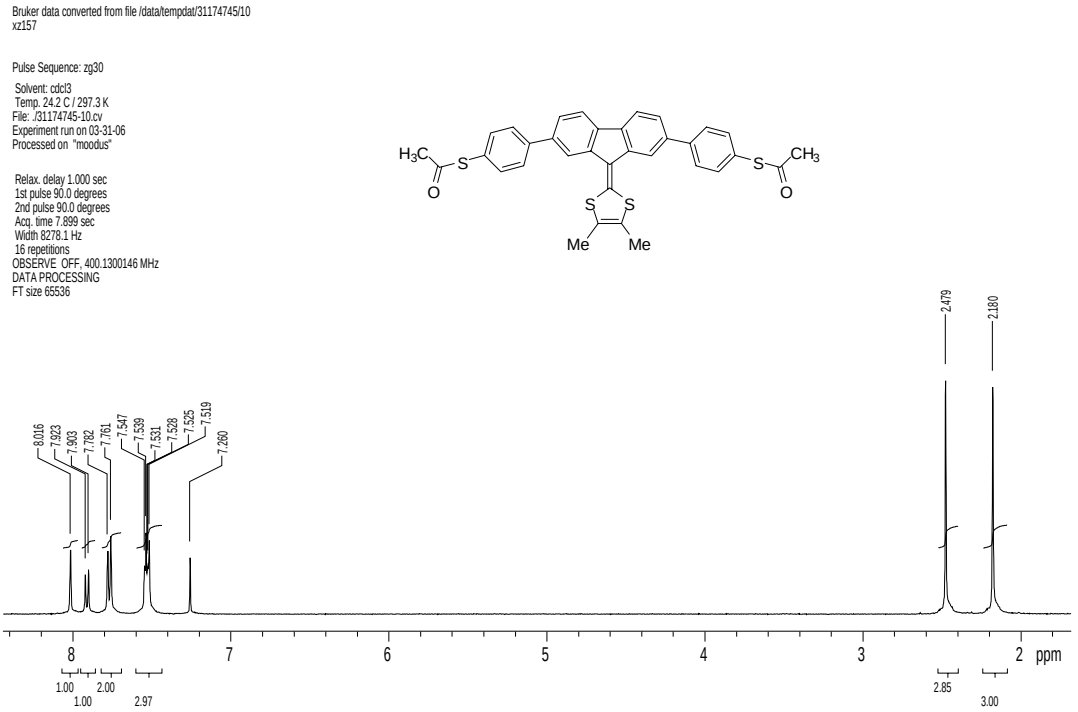
Compound **14**. ^{1}H NMR (400 MHz, $CDCl_3$)



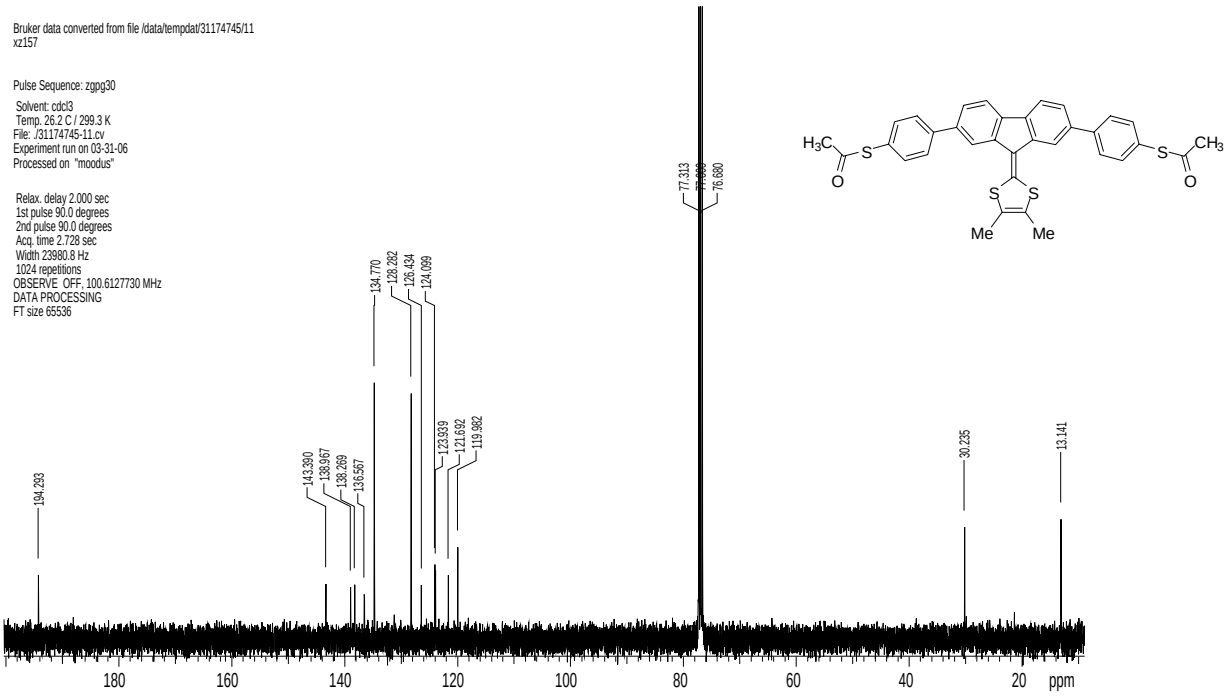
Compound **14**. ^{13}C NMR (100 MHz, $CDCl_3$)



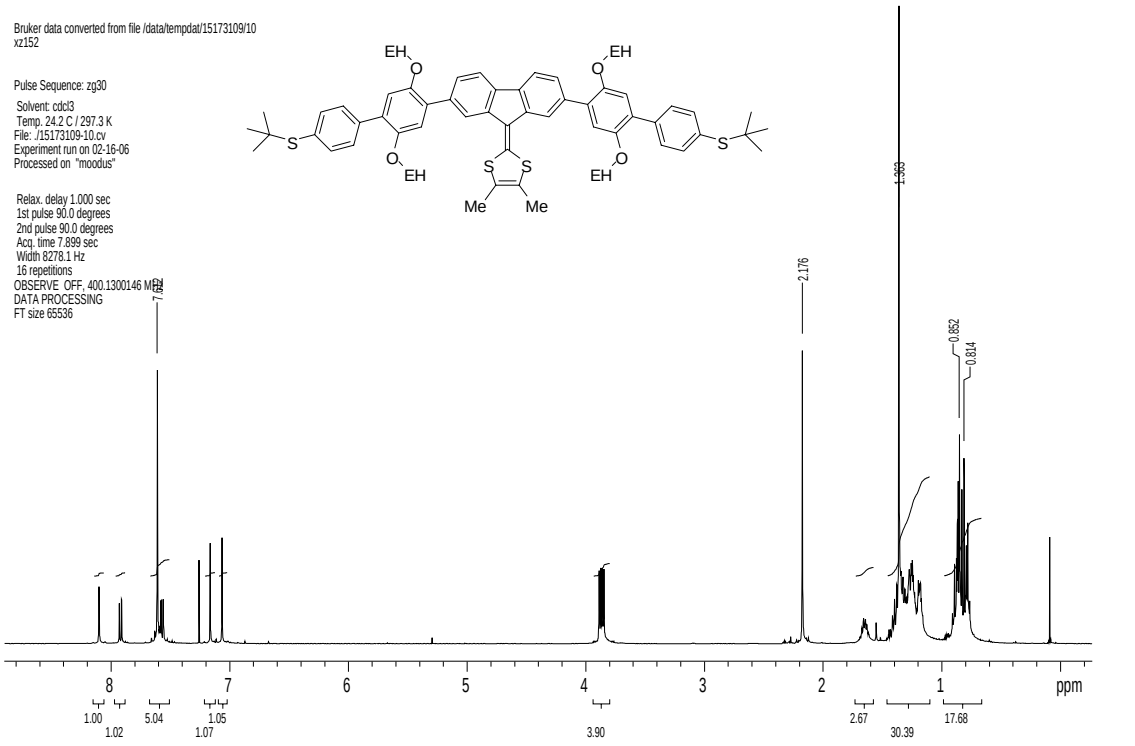
Compound **15**. ^{1}H NMR (400 MHz, $CDCl_3$)



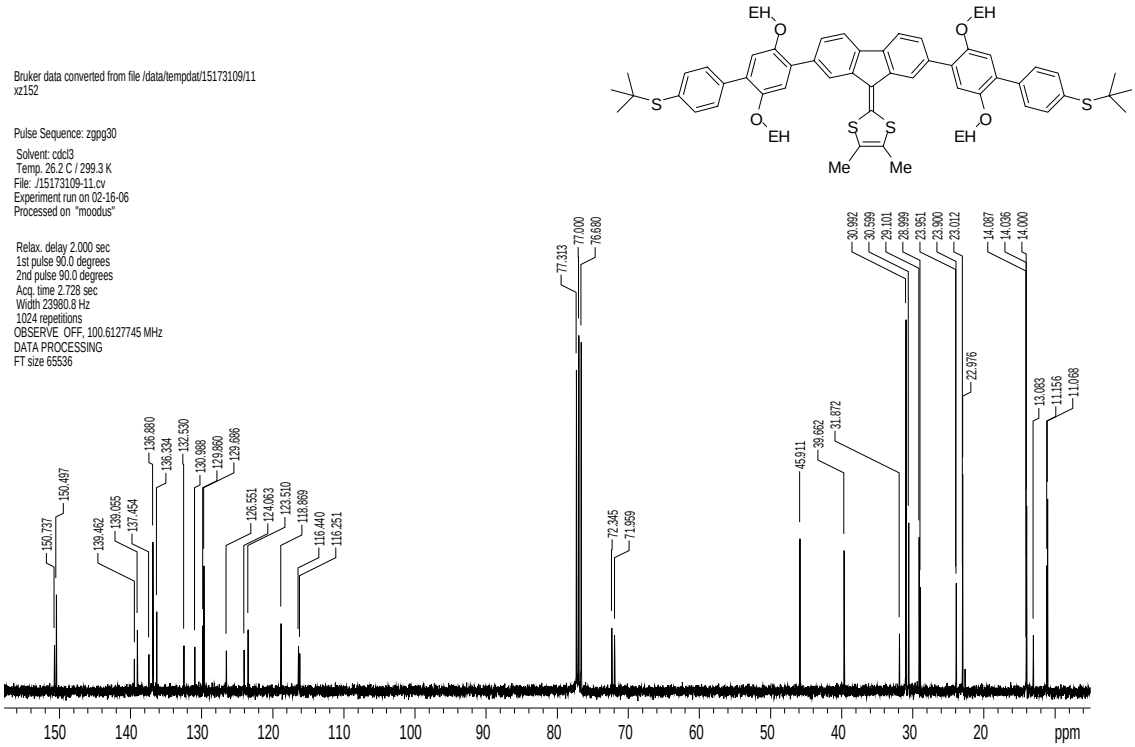
Compound **15**. ^{13}C NMR (100 MHz, $CDCl_3$)



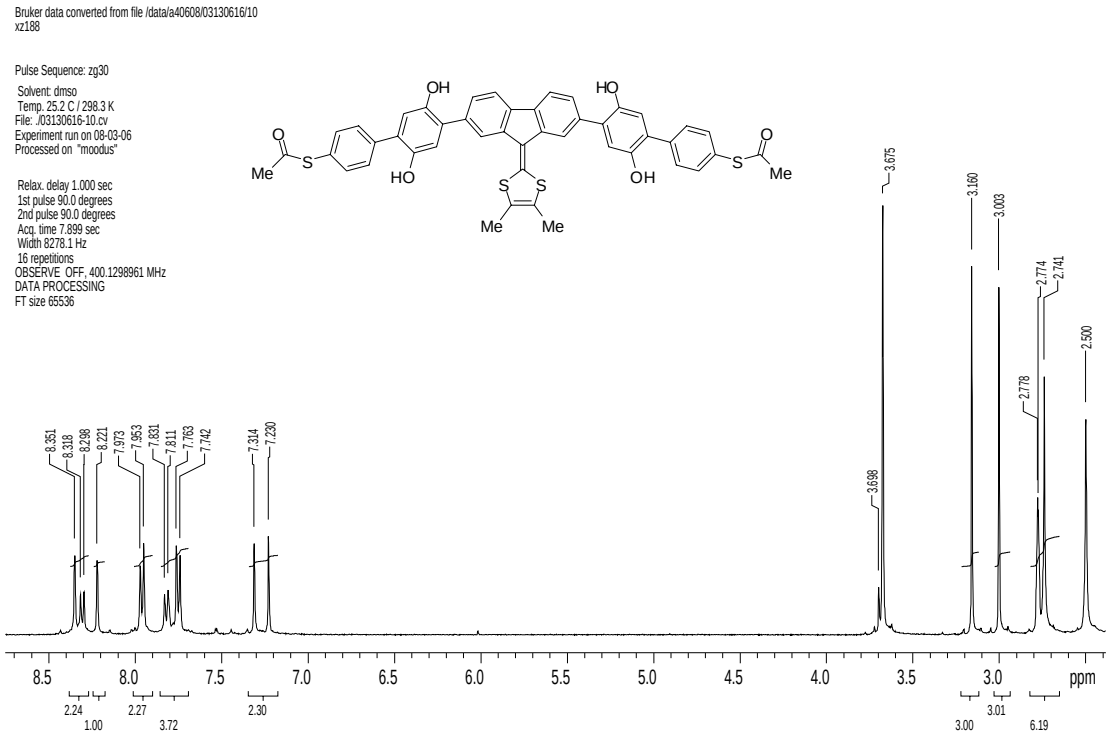
Compound **16**. ^{1}H NMR (400 MHz, $CDCl_3$)



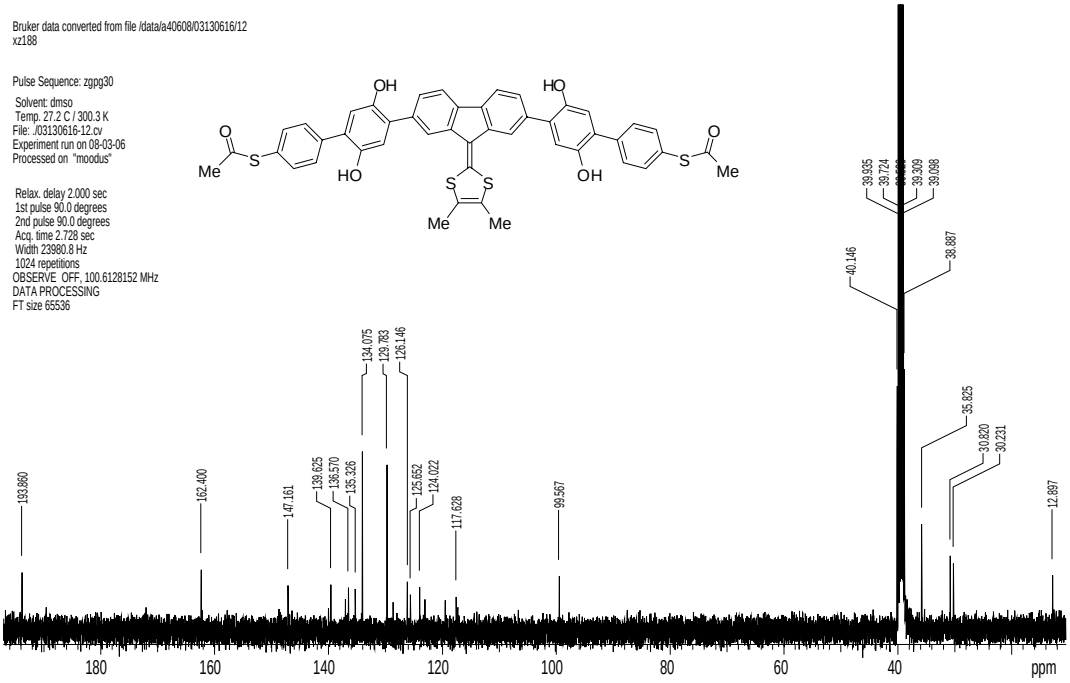
Compound **16**. ^{13}C NMR (100 MHz, $CDCl_3$)



Compound **17**. ^{1}H NMR (400 MHz, DMSO-d_6)



Compound **17**. ^{13}C NMR (100 MHz, DMSO-d_6)



References for the Supporting Information.

(1) Wang, C.; Bryce, M. R.; Gigon, J.; Ashwell, G. J.; Grace, I.; Lambert, C. J. *J. Org. Chem*. **2008**, *73*, 4810-4818.