Supporting Information

End-to-End Bent Perylene Bisimide Cyclophanes by Double Sulfur Extrusion

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1. Instrumentation and materials

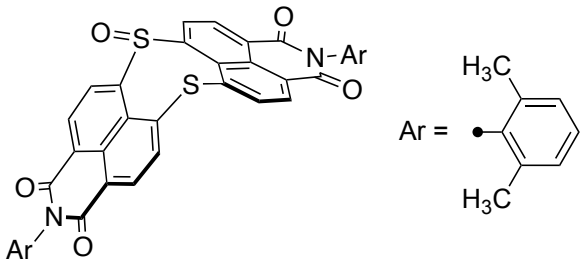
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded on a JEOL JNM-ECA600II spectrometer. Chemical shifts were reported as the delta scale in ppm relative to solvent residual signals of $CDCl_3$ (δ = 7.26 ppm), DMSO-d_6 (δ = 2.50 ppm), and 1,1,2,2-tetrachroloethane-d_2 (δ = 6.0 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm), DMSO-d_6 (δ = 39.52 ppm), and 1,1,2,2-tetrachroloethane-d_2 (δ = 74.00 ppm) for ^{13}C NMR. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCP V 770 spectrometer. Emission spectra were recorded on a Jasco FP-8550 spectrometer and absolute fluorescence quantum yields were measured by the photon-counting method using an integration sphere. Thermogravimetric analyses were recorded on a NETZSCH STA Regulus. Preparative separations were performed by silica gel column chromatography (Wako gel® C-300 or C-400). High-resolution atmospheric pressure chemical ionization time-of-flight (APCI-TOF) mass spectra were taken on a Bruker micrOTOF instrument. X-ray data were obtained using a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics. Cyclic voltammograms were obtained under the following conditions: solvent: CH_2Cl_2, electrolyte: 0.1 M Bu_4NPF_6, working electrode: glassy carbon, counter electrode: Pt, reference electrode: $Ag/AgNO_3$, scan rate: 0.05 V/s. Photo-irradiation was conducted by the USHIO OPM2-252HQ lamp house equipped with a super-high pressure mercury lamp (250 W) and an ASAHI SPECTRA LU0350 cut filter (cut range: $\lambda < 350$ nm) or L38 cut filter (cut range: $\lambda < 380$ nm).

All calculations were carried out using the Gaussian 16 software package.[1] Initial geometries of **5a**, **5b**, and **5c** were obtained from the X-ray crystal structure. Density functional theory (DFT) calculations were conducted with the restricted B3LYP[2] level, employing basis sets 6-31G(d).

Dry DMF was purchased from Wako Pure Chemical Industries, Ltd. as a dehydrated grade. Compounds **9** and **12** were prepared according to the literature.[3,4] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Experimental procedures and compound data

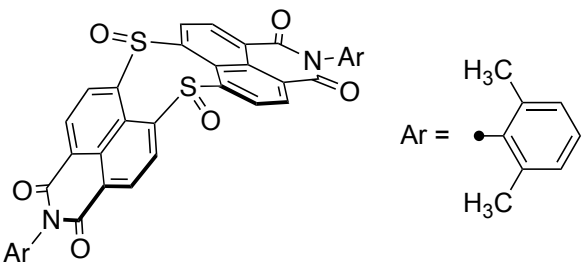
2,6-Dimethylphenyl DNDTBI *S*-oxide 10



Compound **9** (66 mg, 0.10 mmol) and CH_2Cl_2 (5.0 mL) were placed in a round-bottom flask and cooled to 0 °C. To the flask, *m*-CPBA (containing ca. 30 wt% water, 29 mg, 0.12 mmol) was added, and the mixture was stirred for 1 h at 0 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. After the reaction, the solution was separated by silica gel column chromatography (eluent: CH_2Cl_2/ethyl acetate = 30/1). After removal of the solvent in vacuo, recrystallization from CH_2Cl_2/CH_3OH afforded **10** (50 mg, 74 μmol, 74%) as a yellow solid.

^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ = 8.79 (d, J = 8.0 Hz, 2H), 8.76 (d, J = 8.0 Hz, 2H), 8.62 (d, J = 7.7 Hz, 2H), 8.58 (d, J = 7.7 Hz, 2H), 7.27 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.2 Hz, 2H), 7.17 (d, J = 7.3 Hz, 2H), 2.02 (s, 6H), 1.88 (s, 6H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6, 298 K): δ = 161.9, 161.8, 153.4, 138.0, 137.2, 135.42, 135.37, 133.5, 131.9, 130.2, 128.6, 128.2, 124.25, 124.19, 123.6, 17.3, 17.2 ppm (Three signals due to sp^2 carbon are missing due to overlapping.); HRMS (APCI): $[M+H]^+$ Calcd for $C_{40}H_{27}N_2O_5S_2$ 679.1356; Found 679.1332.

2,6-Dimethylphenyl DNDTBI *S*,*S*'-dioxide 11

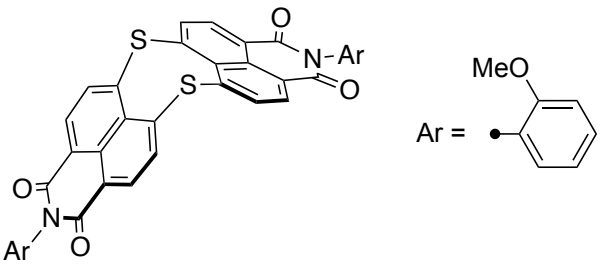


Compound **9** (66 mg, 0.10 mmol), $Na_2WO_4 \cdot 2H_2O$ (6.6 mg, 20 μmol), phenylphosphonic acid (3.2 mg, 20 μmol), $MeN(Oct)_3 \cdot HSO_4$ (9.3 mg, 20 μmol), toluene (2.5 mL), and H_2O_2 aq. (ca. 30

wt%, 1.0 mL, ca. 9 mmol) were placed in a round-bottom flask. The mixture was stirred under light-shielded conditions for 16 h at 80 °C. After the reaction, the mixture was cooled to room temperature and extracted with water and CH_2Cl_2. The organic layer was dried over Na_2SO_4. After removal of the solvent in vacuo, recrystallization from CH_2Cl_2/CH_3OH afforded **11** (50 mg, 73 μmol, 73%) as a yellow solid.

^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ = 8.78 (d, J = 8.0 Hz, 4H), 8.65 (d, J = 8.1 Hz, 4H), 7.27 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 7.2 Hz, 2H), 7.17 (d, J = 7.3 Hz, 2H), 2.02 (s, 6H), 1.88 (s, 6H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6, 298 K): δ = 161.7, 151.2, 135.4 (overlap), 133.4, 132.0, 129.8, 128.6 (overlap), 128.2, 124.8, 122.6, 122.1, 17.4, 17.3 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{40}H_{27}N_2O_6S_2$ 695.1305; Found 695.1294.

_o_-Anisyl DNDTBI 13

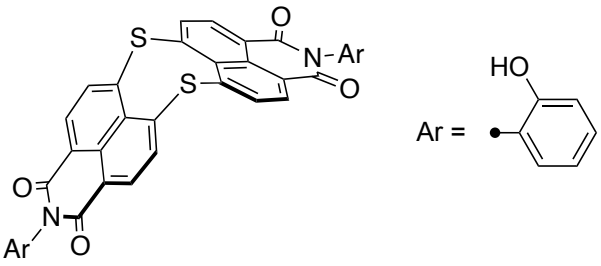


Compound **12** (1.8 g, 4.9 mmol) and DMF (0.40 L) were placed in a round-bottom flask. To the flask, Na_2S (0.70 g, 9.0 mmol) was added. The mixture was stirred for 3 h at room temperature. After the reaction was completed, 1 M HCl aq. was added. After removal of the solvent in vacuo, the residue was collected by filtration. The solid was washed with water, methanol, and Et_2O, affording a brown solid (1.2 g). The obtained brown solid (1.2 g), propionic acid (14 mL), *N*-methylpyrrolidone (NMP, 14 mL), and *o*-anisidine (2.8 mL, 25 mmol) were placed in a round-bottom flask, and the mixture was refluxed for 3 h at 170 °C. After the reaction mixture was cooled to room temperature, water was added to the mixture. The precipitate was filtered and washed with CH_3OH and Et_2O. The solid was dissolved in CH_2Cl_2, and insoluble yellow solids were removed by filtration. The filtrate was purified by silica gel column chromatography (eluent: CH_2Cl_2) to afford **13** (0.20 g, 0.30 mmol, 12%) as a yellow solid. Compound **13** was obtained as the mixture of the rotational isomers due to the *o*-anisyl groups.

^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ = 8.55–8.45 (m, 8H), 7.49–7.42 (m, 2H), 7.38–7.32 (m, 1H), 7.26–7.13 (m, 3H), 7.13–7.02 (m, 2H), 3.74–3.57 (m, 6H) ppm; HRMS (APCI): $[M+H]^+$

Calcd for $C_{38}H_{23}N_2O_6S_2$ 667.0992; Found 667.0975.

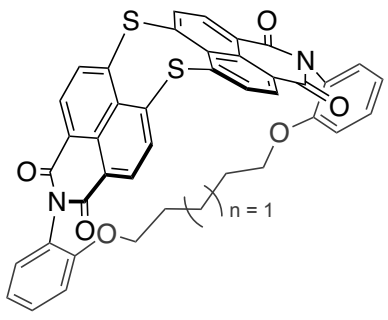
_o_-Hydroxyphenyl DNDTBI 14



Compound **8** (0.83 g, 1.2 mmol) was placed in a round-bottom flask under argon. To the flask, CH_2Cl_2 (0.11 L, dried) was added, and the solution was cooled to 0 °C. BBr_3 (ca.1 M CH_2Cl_2 solution, 15 mL, 15 mmol) was added to the flask under argon. The solution was allowed to warm to room temperature and stirred for 1 h. After the reaction, excess NH_3 aqueous was added. The precipitate was filtered and washed with water and CH_3OH to afford **14** (0.74 g, 1.2 mmol, 93%) as an orange solid. Compound **14** was obtained as the mixture of the rotational isomers due to the *o*-hydroxyphenyl groups.

^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ = 8.55–8.45 (m, 8H), 7.30–6.80 (m, 8H) ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{36}H_{19}N_2O_6S_2$ 639.0679; Found 639.0671.

C5-tethered DNDTIBI 15a

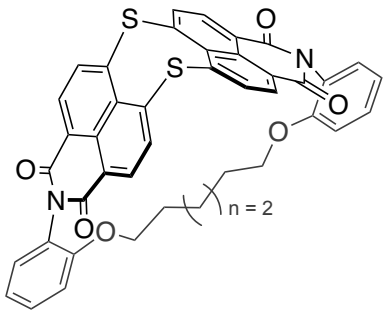


Compound **14** (0.59 g, 0.93 mmol) and K_2CO_3 (0.32 g, 2.3 mmol) were placed in a round-bottom flask under argon. To the flask, DMF (0.75 L, dried) and 1,5-dibromopentane (0.15 mL, 1.1 mmol) were added under argon, and the solution was stirred for 3 days at 40 °C. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 and washed with water. The

organic layer was dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography (eluent: CH_2Cl_2/ethyl acetate = 50/1). After removal of the solvent in vacuo, recrystallization from CH_2Cl_2/MeOH afforded **15a** (0.11 g, 0.15 mmol, 17%) as an orange solid.

^{1}H NMR (500 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 8.48 (d, J = 7.7 Hz, 4H), 8.35 (d, J = 7.7 Hz, 4H), 7.45–7.41 (m, 4H), 7.14 (t, J = 7.5 Hz, 2H), 6.87 (d, J = 7.5 Hz, 2H), 3.54 (br, 4H), 0.64 (br, 6H) ppm; ^{13}C NMR (126 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 163.8, 152.7, 142.3, 137.6, 132.4, 131.5, 131.0, 130.5, 130.3, 125.1, 124.0, 120.9, 112.5, 67.0, 29.2, 19.8 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{41}H_{27}N_2O_6S_2$ 707.1305; Found 707.1287.

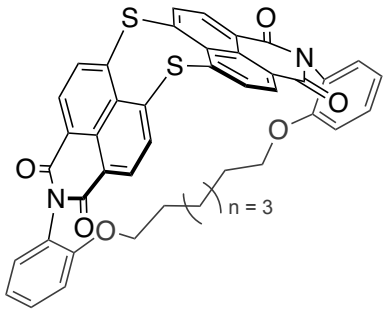
C6-tethered DNDTIBI 15b



Compound **14** (0.48 g, 0.76 mmol) and K_2CO_3 (0.26 g, 1.9 mmol) were placed in a round-bottom flask under argon. To the flask, DMF (250 mL, dried) and 1,6-dibromohexane (0.14 mL, 0.91 mmol) were added. The solution was stirred for 3 days at 40 °C. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography (eluent: CH_2Cl_2/ethyl acetate = 50/1). After removal of the solvent in vacuo, recrystallization from CH_2Cl_2/MeOH afforded **15b** (0.13 g, 0.18 mmol, 24%) as an orange solid.

^{1}H NMR (500 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 8.49 (d, J = 7.7 Hz, 4H), 8.35 (d, J = 7.7 Hz, 4H), 7.46 (t, J = 8.0 Hz, 2H), 7.35 (dd, J = 7.8 Hz, 1.3 Hz, 2H), 7.14 (t, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 3.69 (t, J = 6.3 Hz, 4H), 1.06 (br, 4H), 0.70 (br, 4H) ppm; ^{13}C NMR (126 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 163.2, 153.8, 142.1, 137.6, 132.4, 131.6, 131.0, 130.5, 130.2, 124.3, 124.0, 121.2, 113.8, 69.3, 28.7, 25.6 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{42}H_{29}N_2O_6S_2$ 721.1462; Found 721.1445.

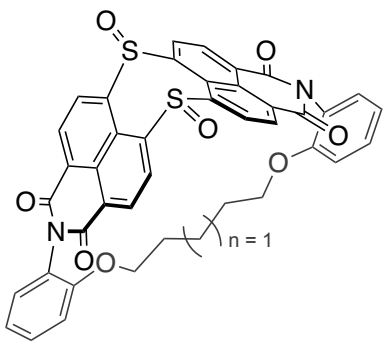
C7-tethered DNDTIBI 15c



Compound **14** (0.16 g, 0.25 mmol) and K_2CO_3 (84 mg, 0.61 mmol) were placed in a round-bottom flask under argon. To the flask, DMF (200 mL, dried) and 1,7-dibromoheptane (47 μL, 0.28 mmol) were added. The solution was stirred for 4 days at 40 °C. After removal of the solvent in vacuo, the residue was extracted with water and CH_2Cl_2. The organic layer was dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography (eluent: CH_2Cl_2/ethyl acetate = 50/1). After removal of the solvent in vacuo, recrystallization from CH_2Cl_2/hexane afforded **15c** (65 mg, 89 μmol, 36%) as an orange solid.

^{1}H NMR (500 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 8.51 (d, J = 7.7 Hz, 4H), 8.40 (d, J = 7.7 Hz, 4H), 7.46 (t, J = 7.2 Hz, 2H), 7.41 (dd, J = 7.2 Hz, 1.2 Hz, 2H), 7.15 (t, J = 7.2 Hz, 2H), 6.95 (d, J = 7.2 Hz, 2H), 3.68 (t, J = 4.8 Hz, 4H), 1.01 (q, J = 4.8 Hz, 4H), 0.34 (q, J = 4.8 Hz, 4H), –0.39 (q, J = 4.8 Hz, 4H) ppm; ^{13}C NMR (126 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 163.6, 153.2, 141.6, 137.6, 132.5, 131.5, 130.8, 130.6, 130.1, 124.8, 124.2, 121.0, 113.1, 67.6, 28.6, 27.6, 22.7 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{43}H_{31}N_2O_6S_2$ 735.1618; Found 735.1587.

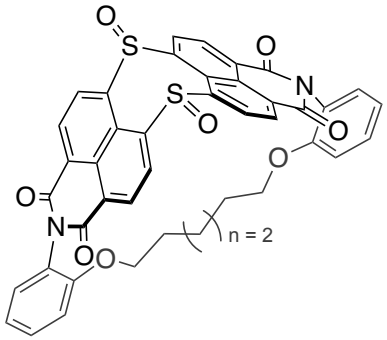
C5-tethered DNDTIBI *S*,*S*'-dioxide 4a



Compound **15a** (83 mg, 0.12 mmol), $Na_2WO_4 \cdot 2H_2O$ (39 mg, 0.12 mmol), phenylphosphonic acid (19 mg, 0.12 mmol), $MeN(Oct)_3 \cdot HSO_4$ (55 mg, 0.12 mmol), toluene (80 mL), and H_2O_2 aq. (ca. 30wt%, 10 mL, 8.8 mmol) were placed in a round-bottom flask. The mixture was stirred under light-shielded conditions for 23 h at 80 °C. The mixture was cooled to room temperature. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography (eluent: CH_2Cl_2/ethyl acetate = 10/1). After removal of the solvent in vacuo, the solid material was washed with CH_2Cl_2 (ca. 3 mL), affording **4a** (78 mg, 0.11 mmol, 90%) as a pink solid.

^{1}H NMR (600 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 8.73 (d, J = 8.2 Hz, 4H), 8.65 (d, J = 8.2 Hz, 4H), 7.46 (td, J_1 = 7.7 Hz, J_2 = 1.2 Hz, 2H), 7.39 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 2H), 7.15 (t, J = 7.8 Hz, 2H), 6.90 (d, J = 7.8 Hz, 2H), 3.59 (t, J = 6.9 Hz, 4H), 0.77 (quin, J = 6.9 Hz, 4H), 0.60 (quin, J = 6.9 Hz, 2H) ppm; ^{13}C NMR (150 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 162.8, 152.8, 151.3, 132.3, 130.8, 130.1, 130.0, 125.4, 124.2, 122.0, 121.5, 121.0, 112.5, 66.4, 28.4, 19.3 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{41}H_{27}N_2O_8S_2$ 739.1203; Found 739.1196.

C6-tethered DNDTIBI *S*,*S*'-dioxide 4b

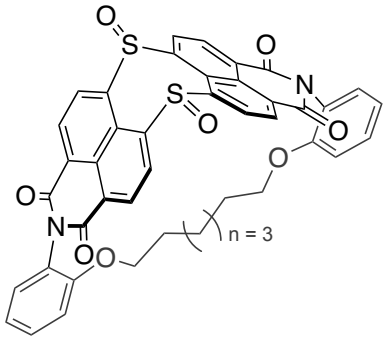


Compound **15b** (0.10 g, 0.14 mmol), $Na_2WO_4 \cdot 2H_2O$ (46 mg, 0.14 mmol), phenylphosphonic acid (22 mg, 0.14 mmol), $MeN(Oct)_3 \cdot HSO_4$ (65 mg, 0.14 mmol), toluene (95 mL), and H_2O_2 aq. (ca. 30wt%, 12 mL, 11 mmol) were placed in a round-bottom flask. The mixture was stirred under light-shielded conditions for 22 h at 80 °C. The mixture was cooled to room temperature. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography (eluent: CH_2Cl_2/ethyl acetate = 20/1). After

removal of the solvent in vacuo, recrystallization from CH_2Cl_2/MeOH afforded **4b** (64 mg, 85 μmol, 61%) as a pink solid.

^{1}H NMR (500 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 8.75 (d, J = 7.9 Hz, 4H), 8.67 (d, J = 7.9 Hz, 4H), 7.48 (td, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 2H), 7.31 (dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 2H), 7.15 (td, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 3.72 (t, J = 6.4 Hz, 4H), 1.13 (br, 4H), 0.78 (br, 4H) ppm; ^{13}C NMR (126 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 162.3, 153.8, 151.0, 132.4, 130.8, 130.0, 129.9, 125.4, 123.7, 122.2, 121.7, 121.2, 113.6, 69.1, 28.6, 25.4 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{42}H_{29}N_2O_8S_2$ 753.1360; Found 753.1356.

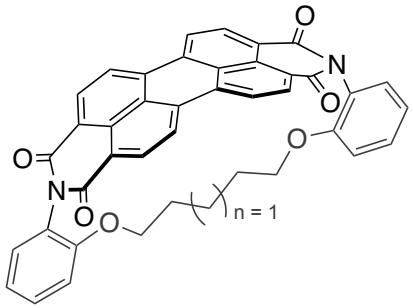
C7-tethered DNDTIBI *S*,*S*'-dioxide 4c



Compound **15c** (25 mg, 34 μmol), $Na_2WO_4 \cdot 2H_2O$ (13 mg, 40 μmol), phenylphosphonic acid (5.0 mg, 32 μmol), $MeN(Oct)_3 \cdot HSO_4$ (15 mg, 32 μmol), toluene (23 mL), and H_2O_2 aq. (ca. 30wt%, 4 mL, 2.8 mmol) were placed in a round-bottom flask. The mixture was stirred under light-shielded conditions for 23 h at 80 °C. After the reaction, the mixture was cooled to room temperature and extracted with water and CH_2Cl_2. The organic layer was dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography (eluent: from CH_2Cl_2 to CH_2Cl_2/ethyl acetate = 25/1). After removal of the solvent in vacuo, recrystallization from CH_2Cl_2/hexane afforded **4c** (13 mg, 17 μmol, 49%) as a pink solid.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.85 (d, J = 8.0 Hz, 4H), 8.71 (d, J = 8.0 Hz, 4H), 7.42 (td, J_1 = 7.5 Hz, J_2 = 1.8 Hz, 2H), 7.31 (dd, J_1 = 7.5 Hz, J_2 = 1.8 Hz, 2H), 7.10 (t, J = 7.5 Hz, 2H), 6.95 (d, J = 7.5 Hz, 2H), 3.77 (t, J = 5.5 Hz, 4H), 1.30–1.10 (m, 4H), 0.64 (quin, J = 7.5 Hz, 4H), 0.29 (quin, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 162.5, 153.9, 150.7, 132.2, 130.8, 130.3, 129.9, 126.0, 124.0, 122.6, 122.4, 121.2, 113.6, 68.6, 29.4, 29.0, 24.2 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{43}H_{31}N_2O_8S_2$ 767.1516; Found 767.1480.

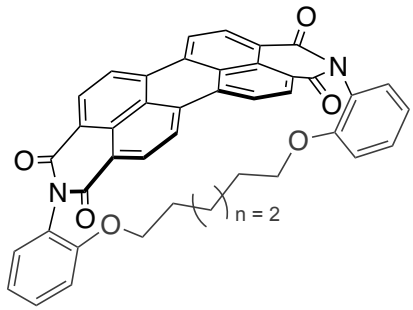
C5-tethered PBIphane 5a



Compound **4a** (7.2 mg, 9.8 μmol) and CH_2Cl_2 (0.10 L) were placed in a round-bottom flask. The mixture was stirred under photo irradiation (λ > 350 nm) for 2 h at room temperature. The crude mixture was directly loaded on silica gel column pre-eluted with CH_2Cl_2. The mixture was purified by the subsequent elution with CH_2Cl_2/ethyl acetate (33/1 to 20/1). After removal of the solvent in vacuo, recrystallization from CH_2Cl_2/MeOH afforded **5a** (4.2 mg, 6.5 μmol, 67%) as a red solid.

^{1}H NMR (500 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 8.64 (d, J = 8.5 Hz, 4H), 8.62 (d, J = 8.5 Hz, 4H), 7.72 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 2H), 7.35 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 2H), 7.13 (t, J = 7.5 Hz, 2H), 6.93 (d, J = 7.5 Hz, 2H), 3.16 (t, J = 8.0 Hz, 4H), 0.37 (br, 2H), –0.53 (br, 4H) ppm; ^{13}C NMR (126 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 166.7, 152.3, 135.3, 132.2, 132.0, 131.9, 130.4, 129.3, 127.5, 124.1 (overlap), 120.8, 111.7, 66.8, 29.6, 19.0 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{41}H_{27}N_2O_6$ 643.1864; Found 643.1881.

C6-tethered PBIphane 5b

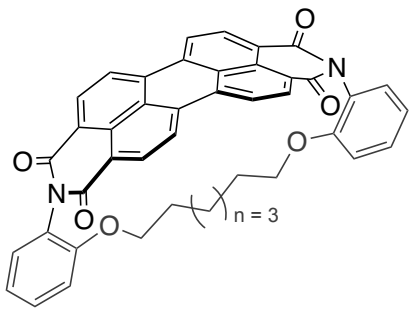


Compound **4b** (7.9 mg, 10 μmol) and CH_2Cl_2 (0.10 L) were placed in a round-bottom flask. The mixture was stirred under photo irradiation (λ > 350 nm) for 2 h at room temperature. The

crude mixture was directly loaded on silica gel column pre-eluted with CH_2Cl_2. The mixture was purified by the subsequent elution with CH_2Cl_2/ethyl acetate (50/1 to 30/1). After removal of the solvent in vacuo, recrystallization from CH_2Cl_2/MeOH afforded **5b** (4.9 mg, 7.5 μmol, 71%) as a reddish orange solid.

^{1}H NMR (500 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 8.67 (d, J = 8.5 Hz, 4H), 8.65 (d, J = 8.5 Hz, 4H), 7.72 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.5 Hz, 2H), 6.85 (d, J = 7.5 Hz, 2H), 3.25 (t, J = 6.5 Hz, 4H), 0.26 (br, 4H), –0.08 (br, 4H) ppm; ^{13}C NMR (126 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 165.9, 152.9, 135.0, 131.9, 131.5, 131.3, 130.3, 129.2, 127.0, 123.8, 123.6, 121.7, 115.1, 70.2, 29.6, 26.0 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{42}H_{29}N_2O_6$ 657.2020; Found 657.1994.

C7-tethered PBIphane 5c



Compound **4c** (7.1 mg, 9.3 μmol) and CH_2Cl_2 (0.10 L) were placed in a round-bottom flask. The mixture was stirred under photo irradiation (λ > 350 nm) for 2 h at room temperature. The crude mixture was directly loaded on silica gel column pre-eluted with CH_2Cl_2. The mixture was purified by the subsequent elution with CH_2Cl_2/ethyl acetate (30/1 to 20/1). After removal of the solvent in vacuo, recrystallization from CH_2Cl_2/MeOH afforded **5c** (5.2 mg, 7.8 μmol, 84%) as an orange solid.

^{1}H NMR (600 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 8.71 (d, J = 7.8 Hz, 4H), 8.69 (d, J = 7.8 Hz, 4H), 7.70 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 2H), 7.42 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 2H), 7.21 (t, J = 7.8 Hz, 2H), 6.86 (d, J = 7.8 Hz, 2H), 3.35 (t, J = 7.2 Hz, 4H), 0.30–0.13 (m, 8H), –0.40 (quin, J = 7.2 Hz, 2H) ppm; ^{13}C NMR (150 MHz, 1,1,2,2-tetrachroloethane-d_2, 298 K): δ = 165.8, 152.6, 135.2, 132.1, 131.4, 131.1, 130.5, 128.9, 127.1, 124.0, 123.9, 121.7, 114.8, 69.3, 32.6, 31.6, 24.3 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{43}H_{31}N_2O_6$ 671.2177; Found 671.2152.

3. NMR spectra

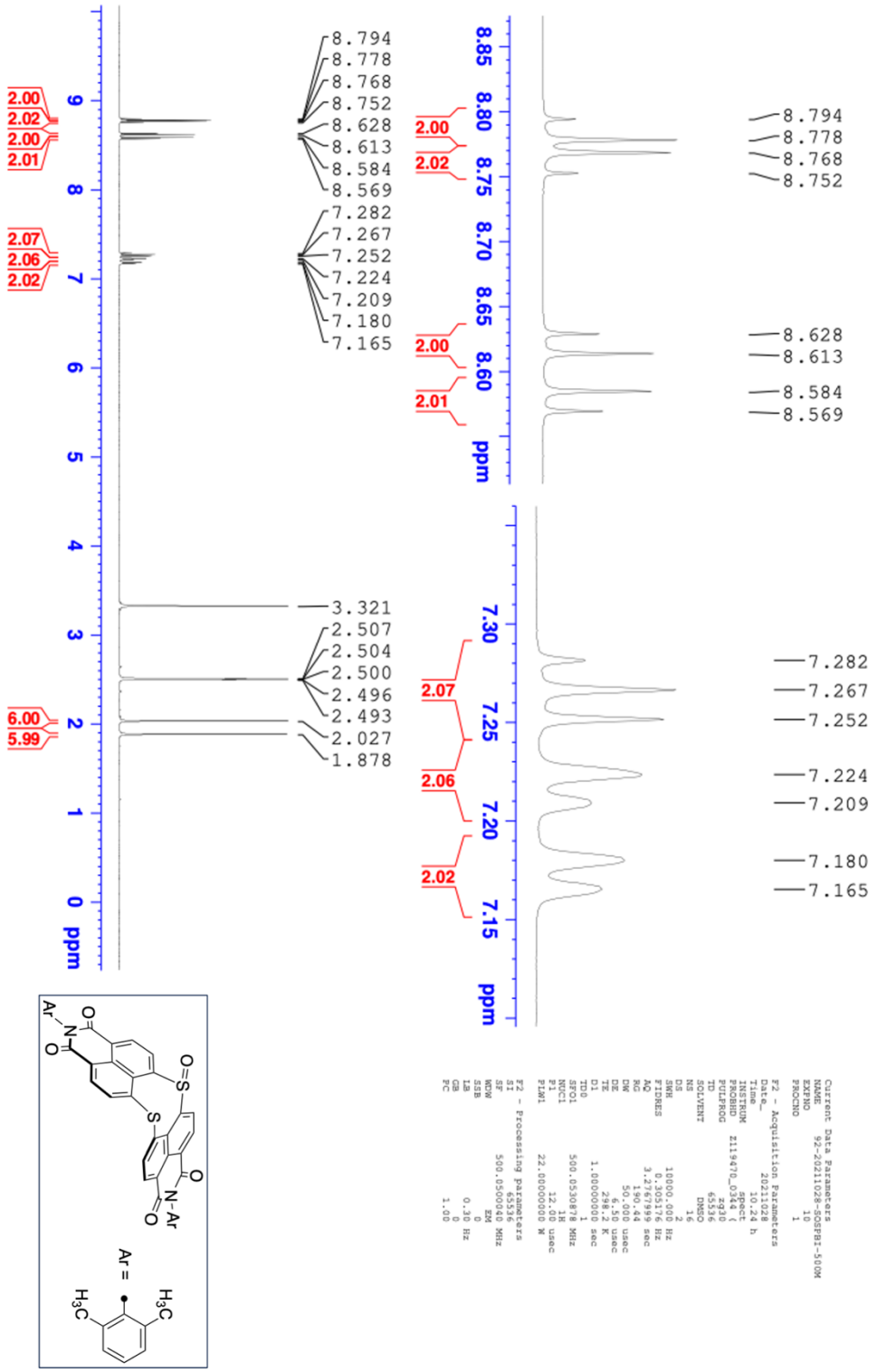


Figure S1. [1]H NMR spectrum of **10** in DMSO-d_6 at 25 °C.

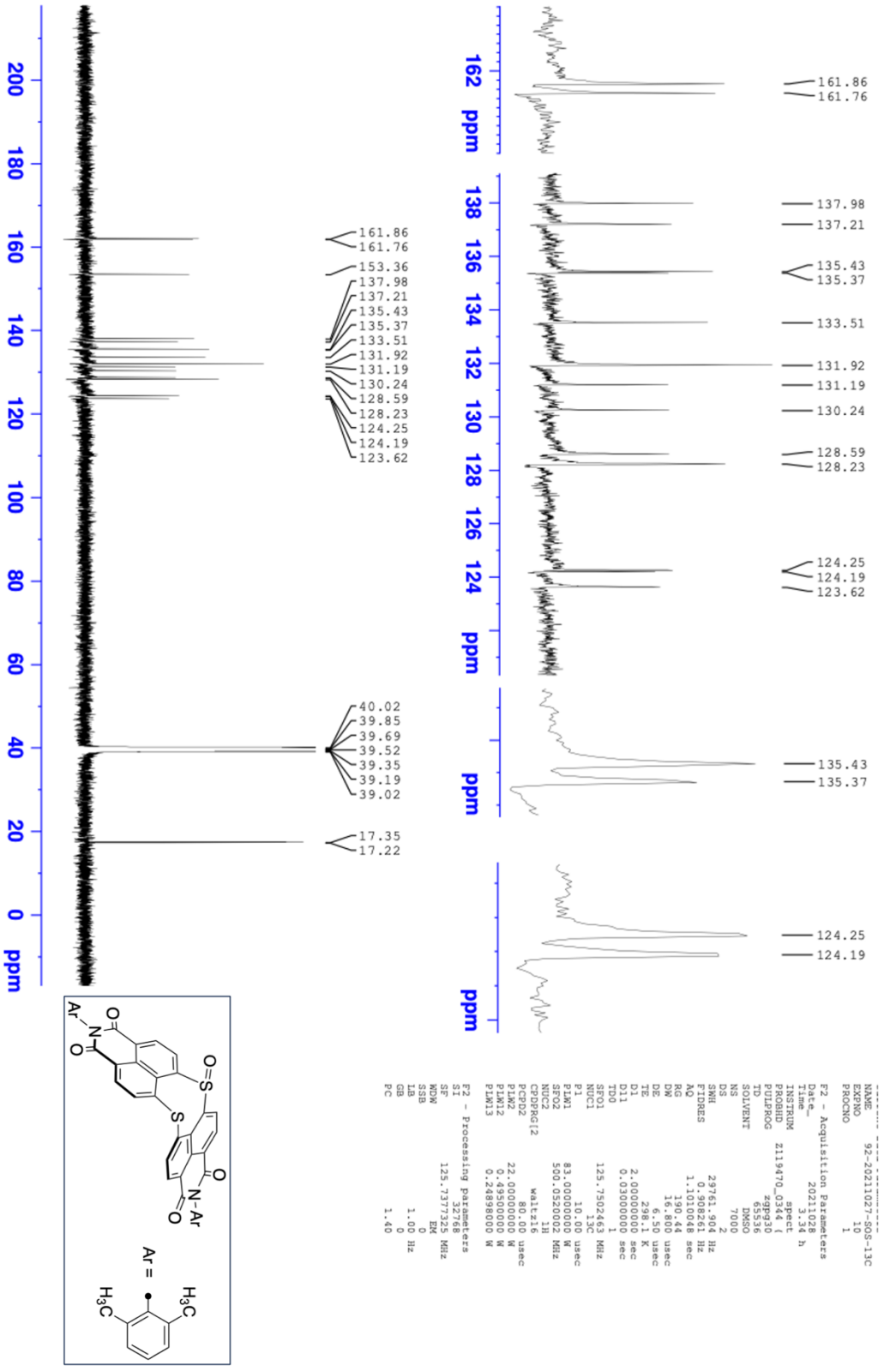


Figure S2. ^{13}C NMR spectrum of **10** in DMSO-d_6 at 25 °C.

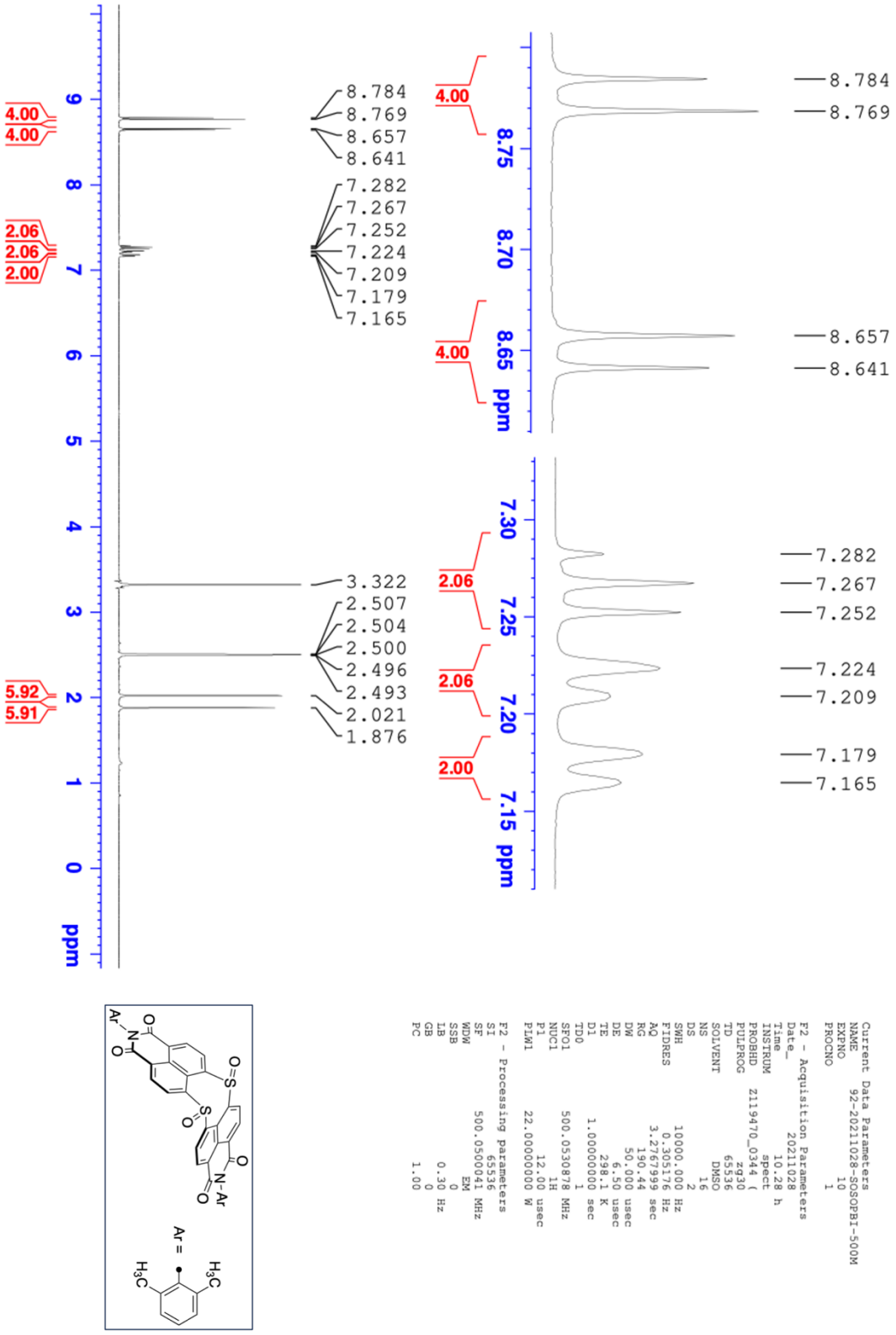


Figure S3. ^{1}H NMR spectrum of **11** in DMSO-d_6 at 25 °C.

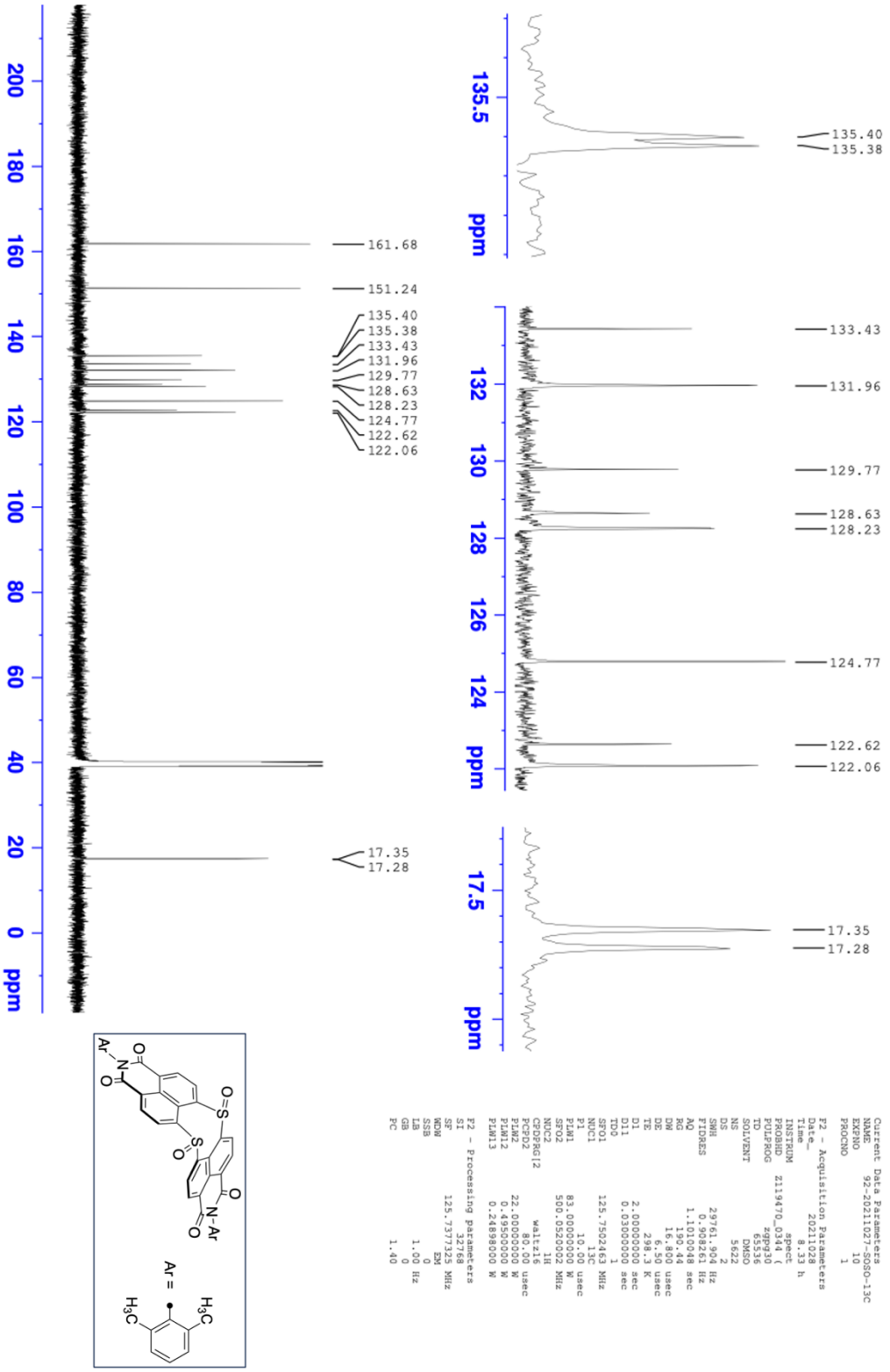


Figure S4. ^{13}C NMR spectrum of **11** in DMSO-d_6 at 25 °C.

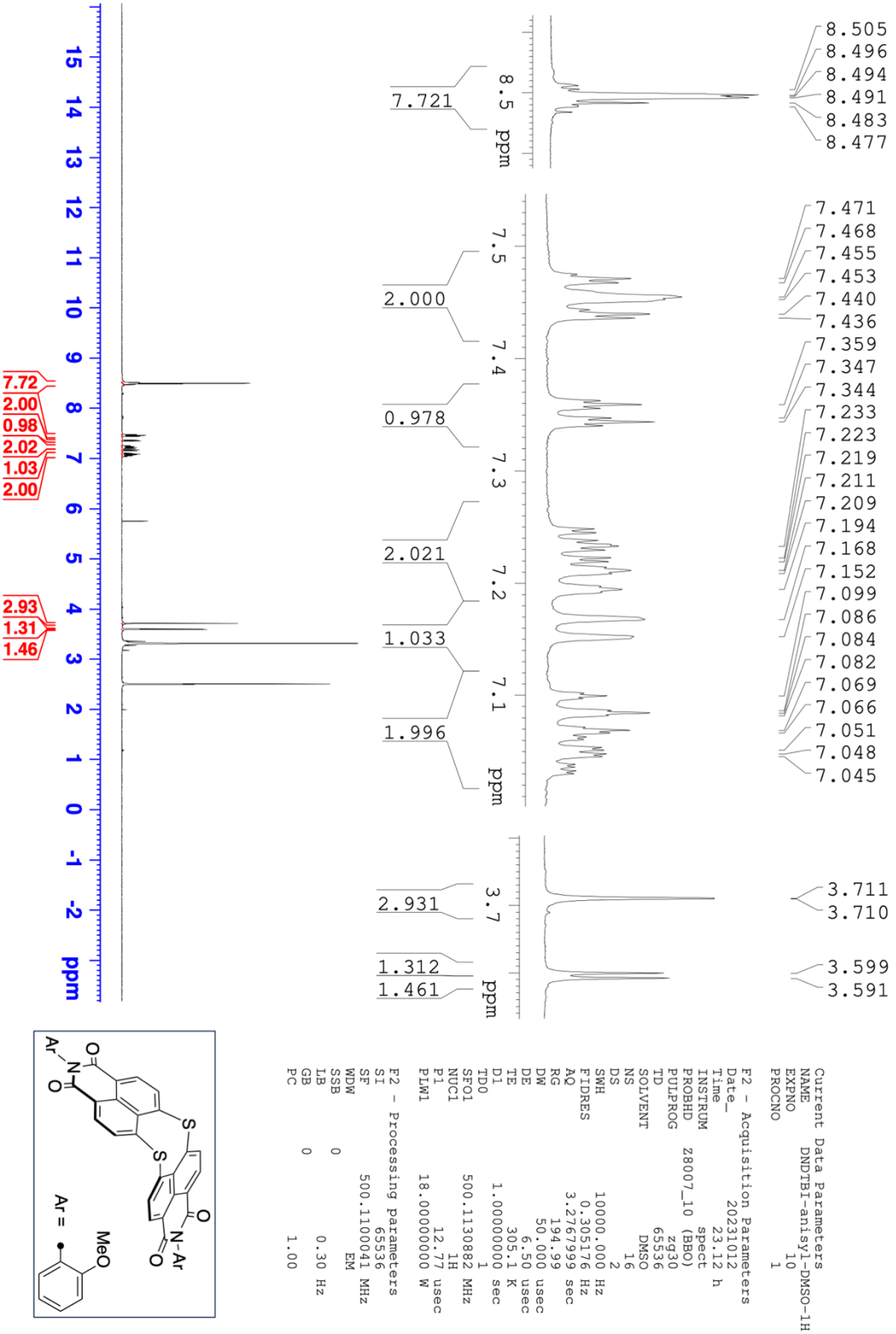


Figure S5. ^{1}H NMR spectrum of **13** in DMSO-d_6 at 25 °C.

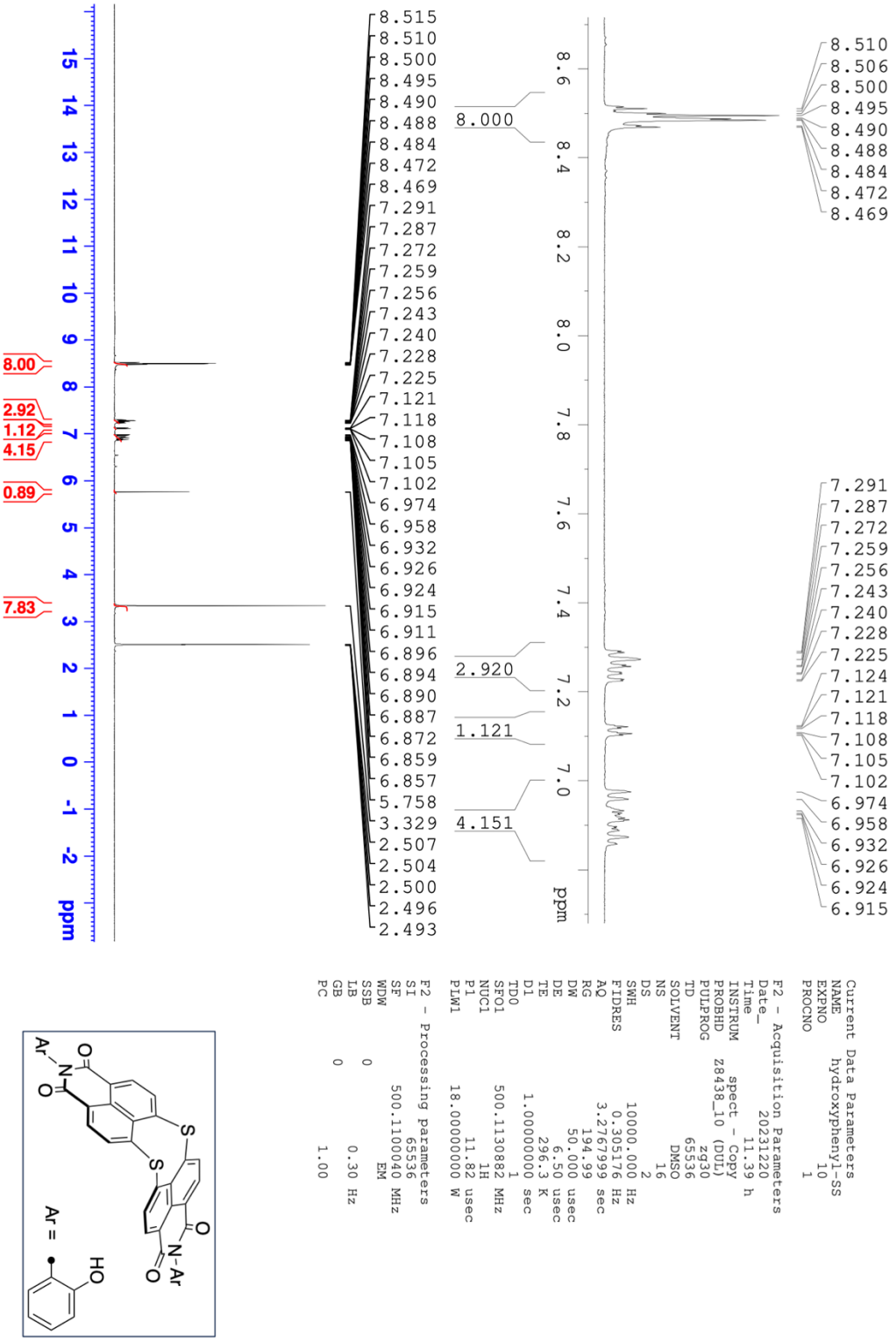


Figure S6. ^{1}H NMR spectrum of **14** in DMSO-d_6 at 25 °C.

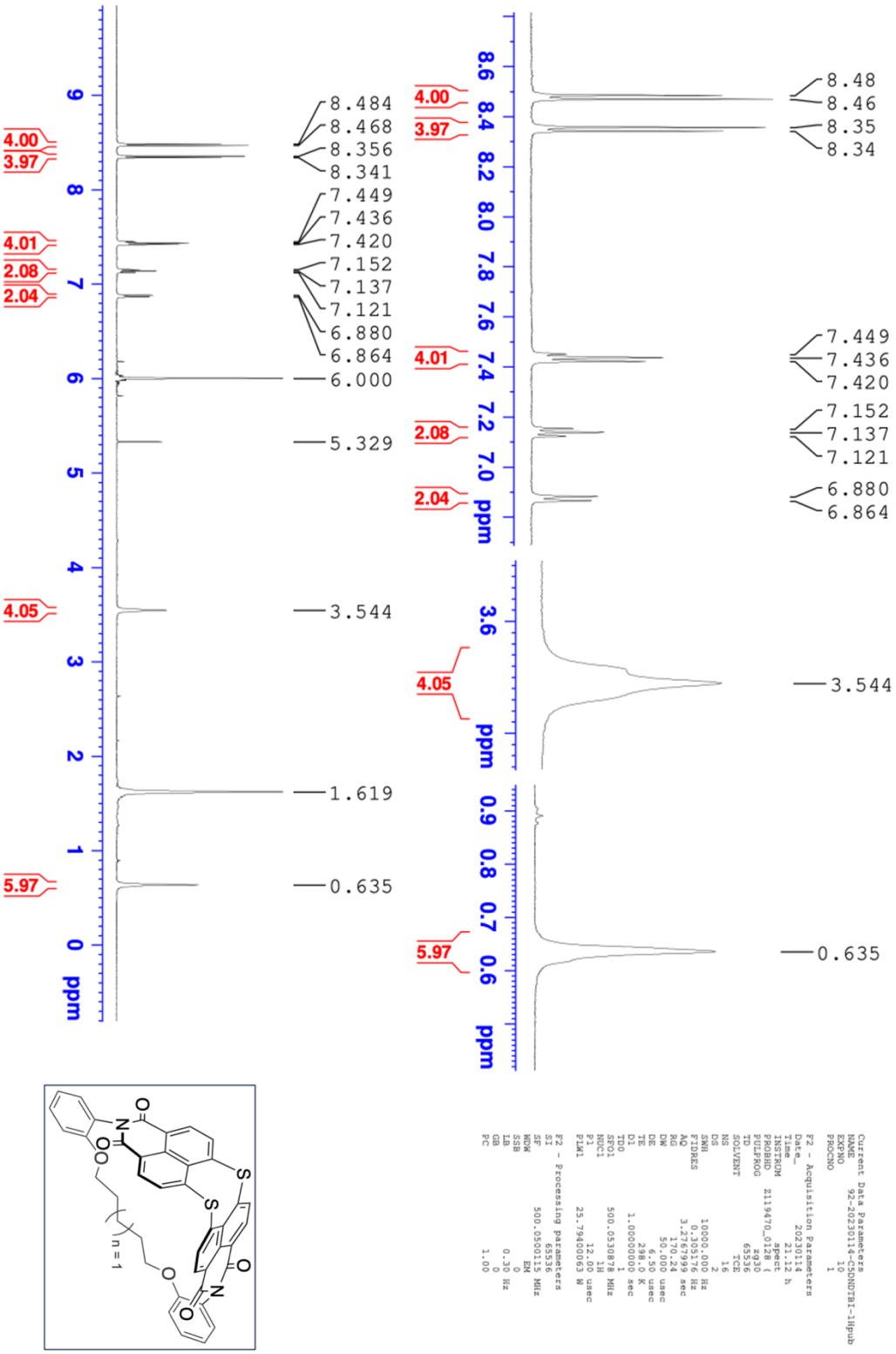


Figure S7. ^{1}H NMR spectrum of **15a** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

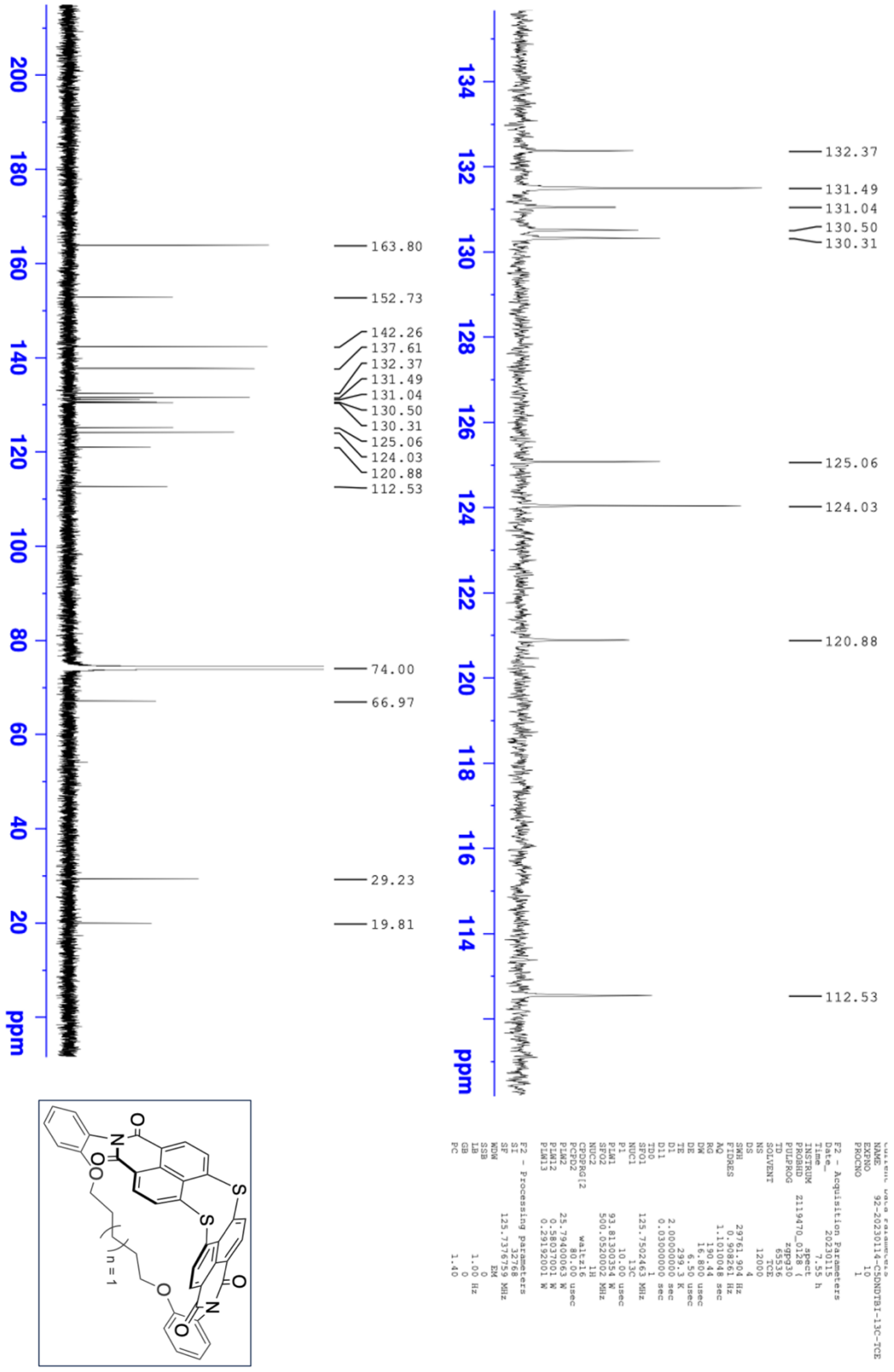


Figure S8. ^{13}C NMR spectrum of **15a** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

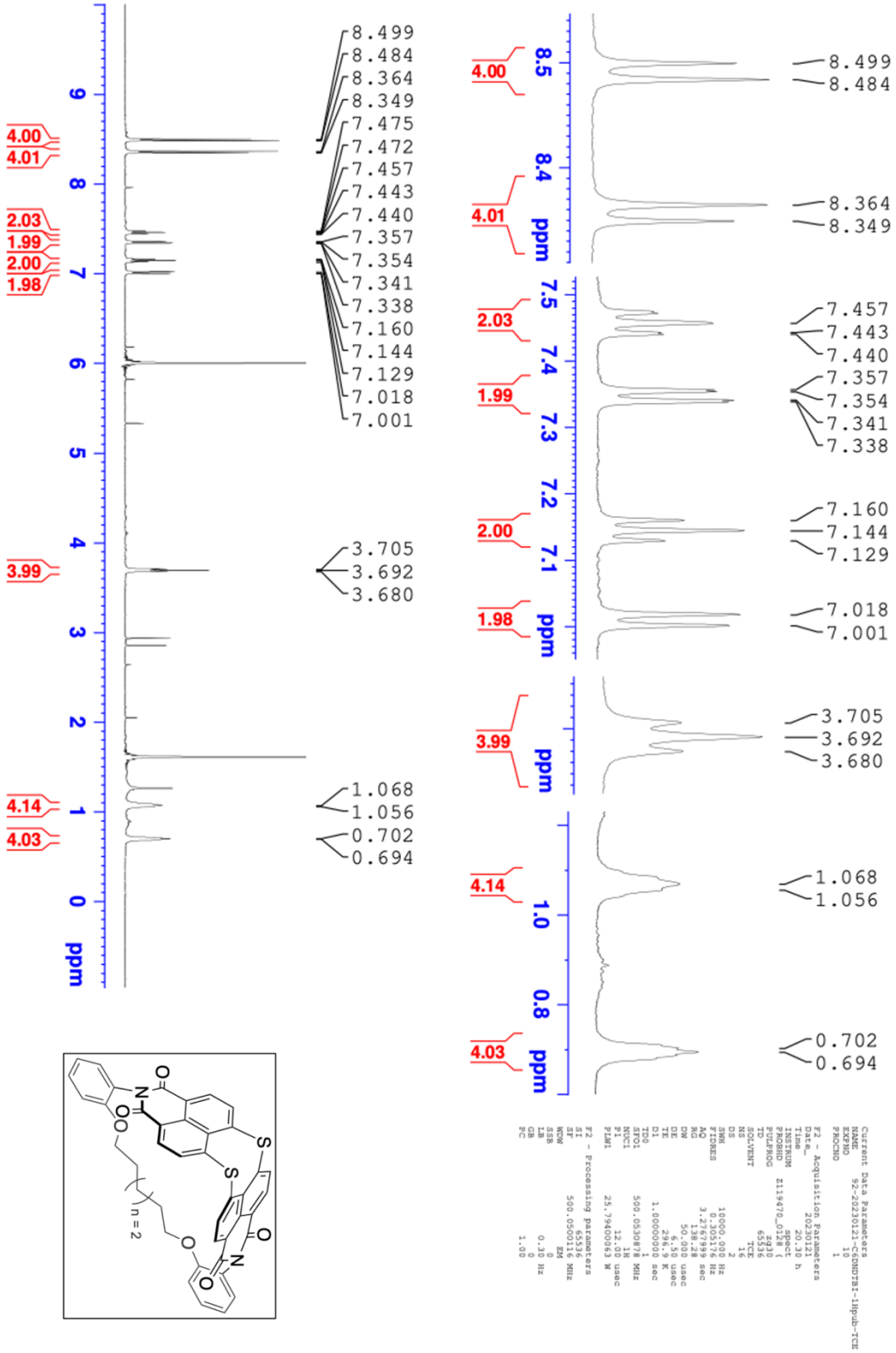


Figure S9. [1]H NMR spectrum of **15b** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

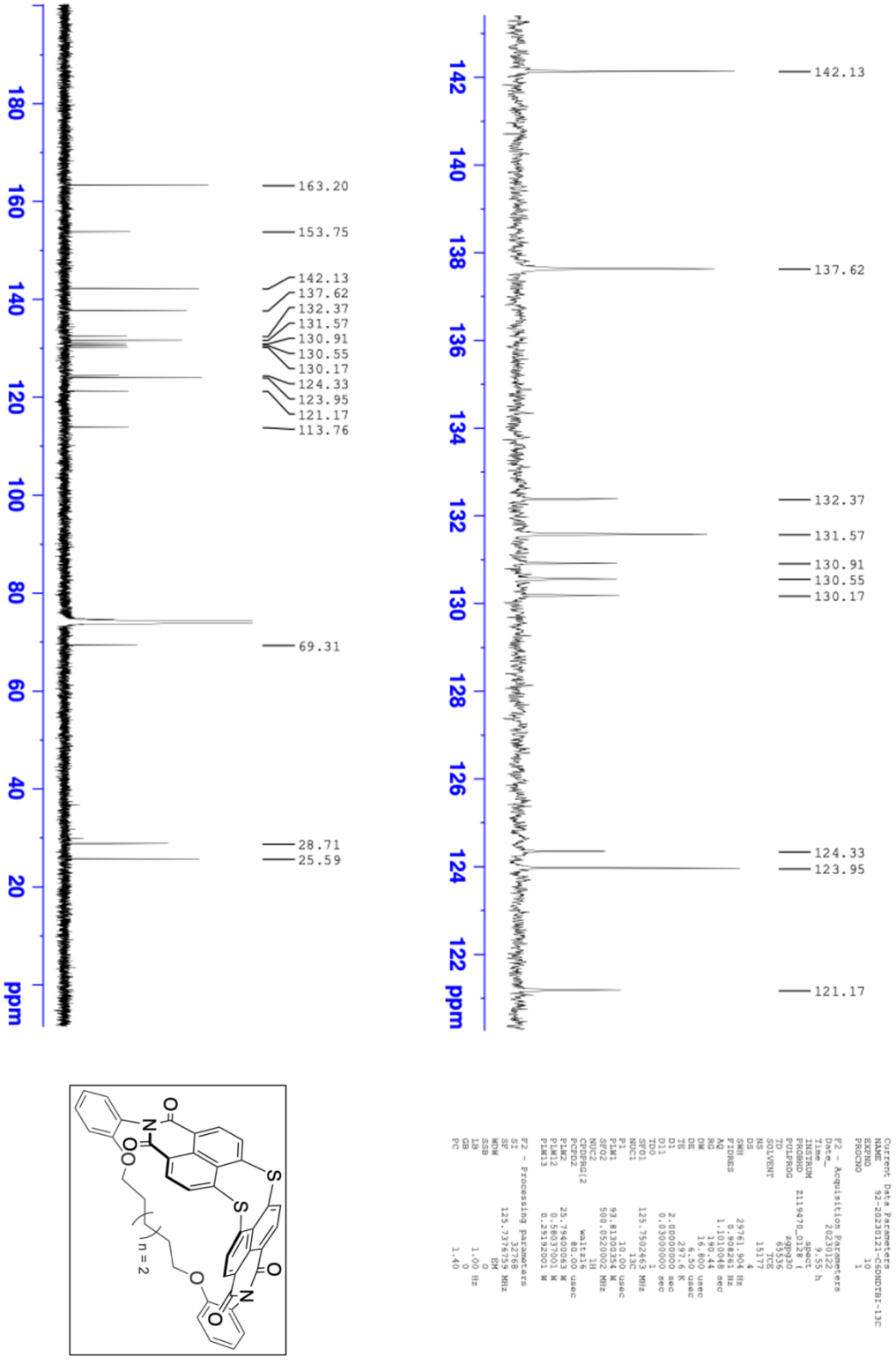


Figure S10. ^{13}C NMR spectrum of **15b** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

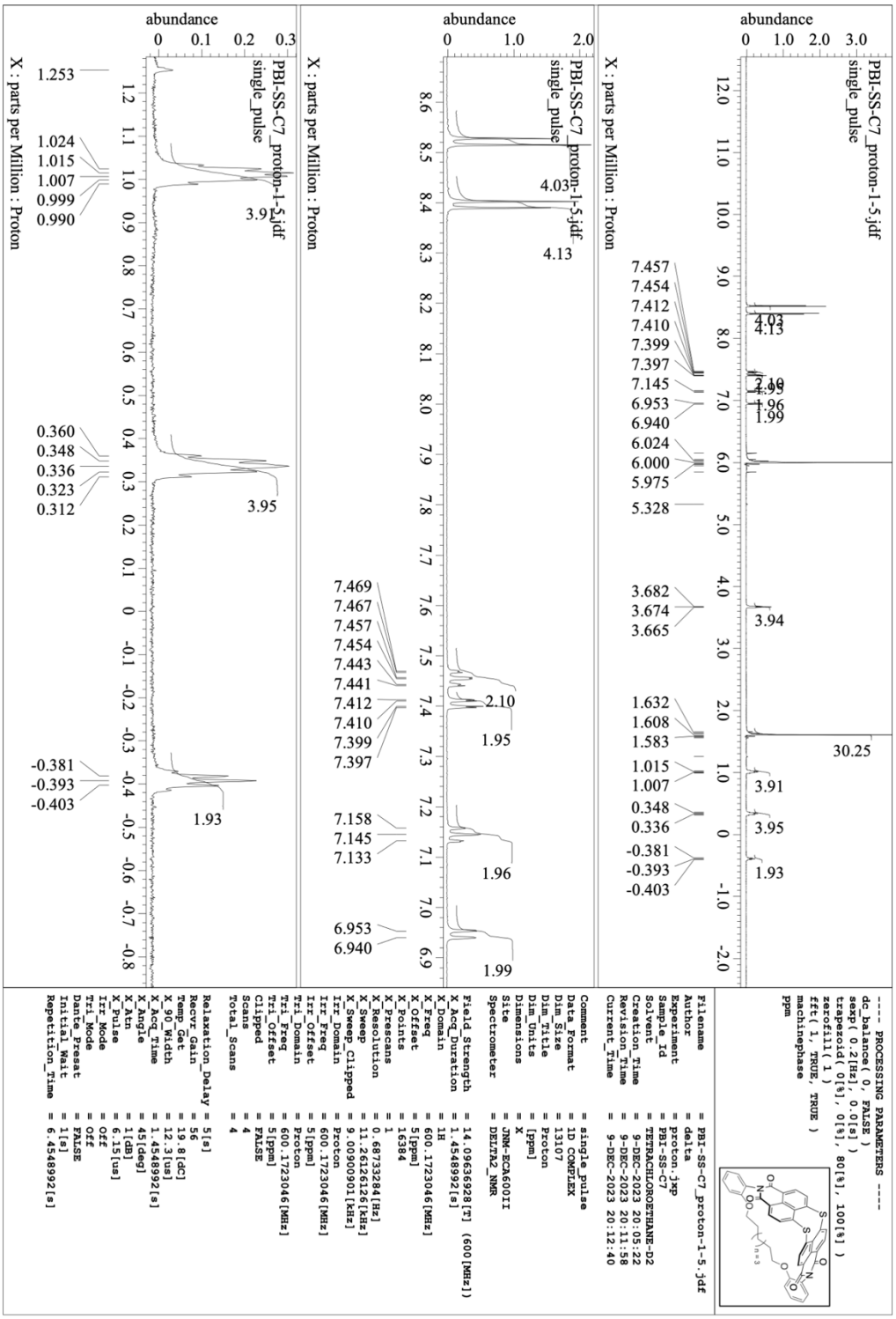


Figure S11. ^{1}H NMR spectrum of **15c** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

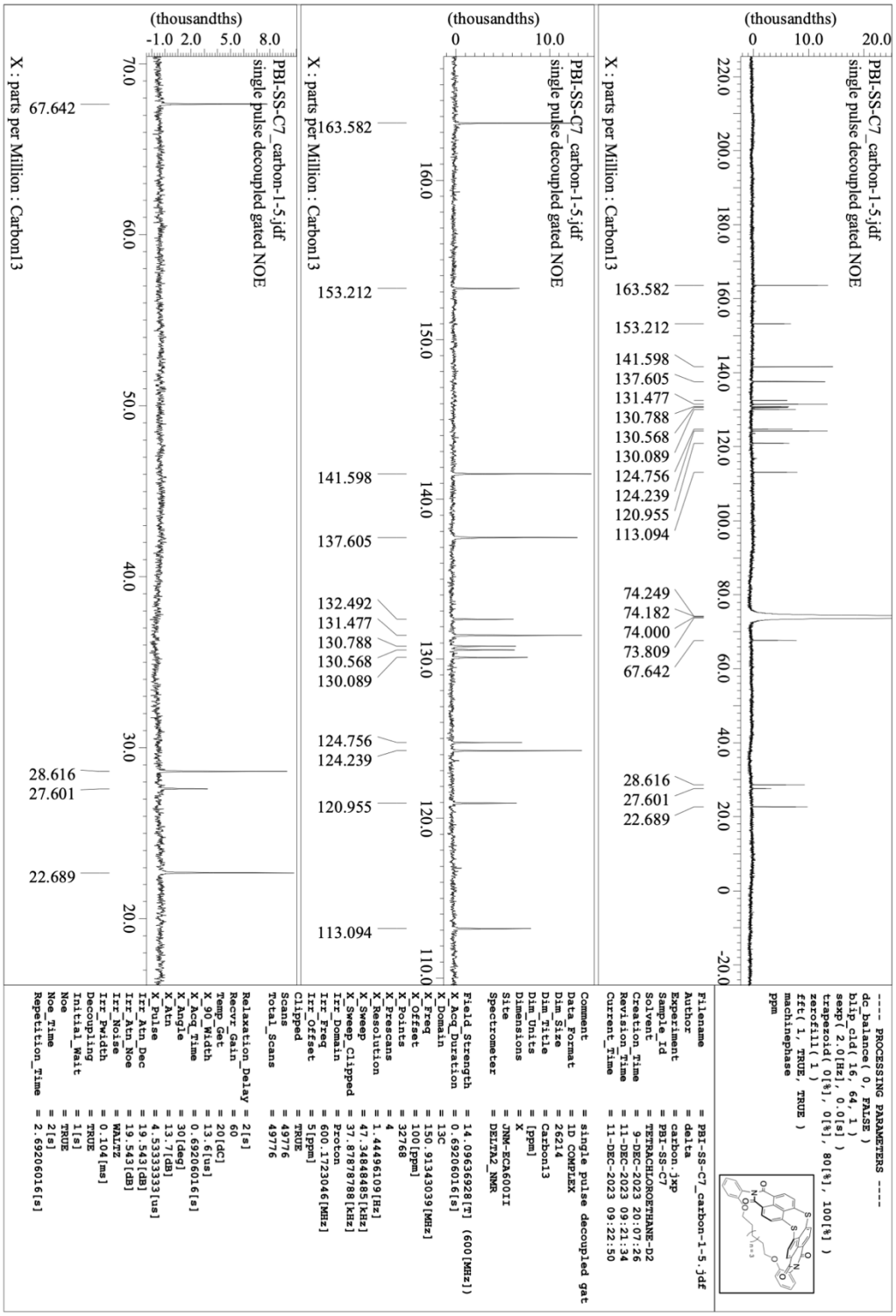


Figure S12. ^{13}C NMR spectrum of **15c** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

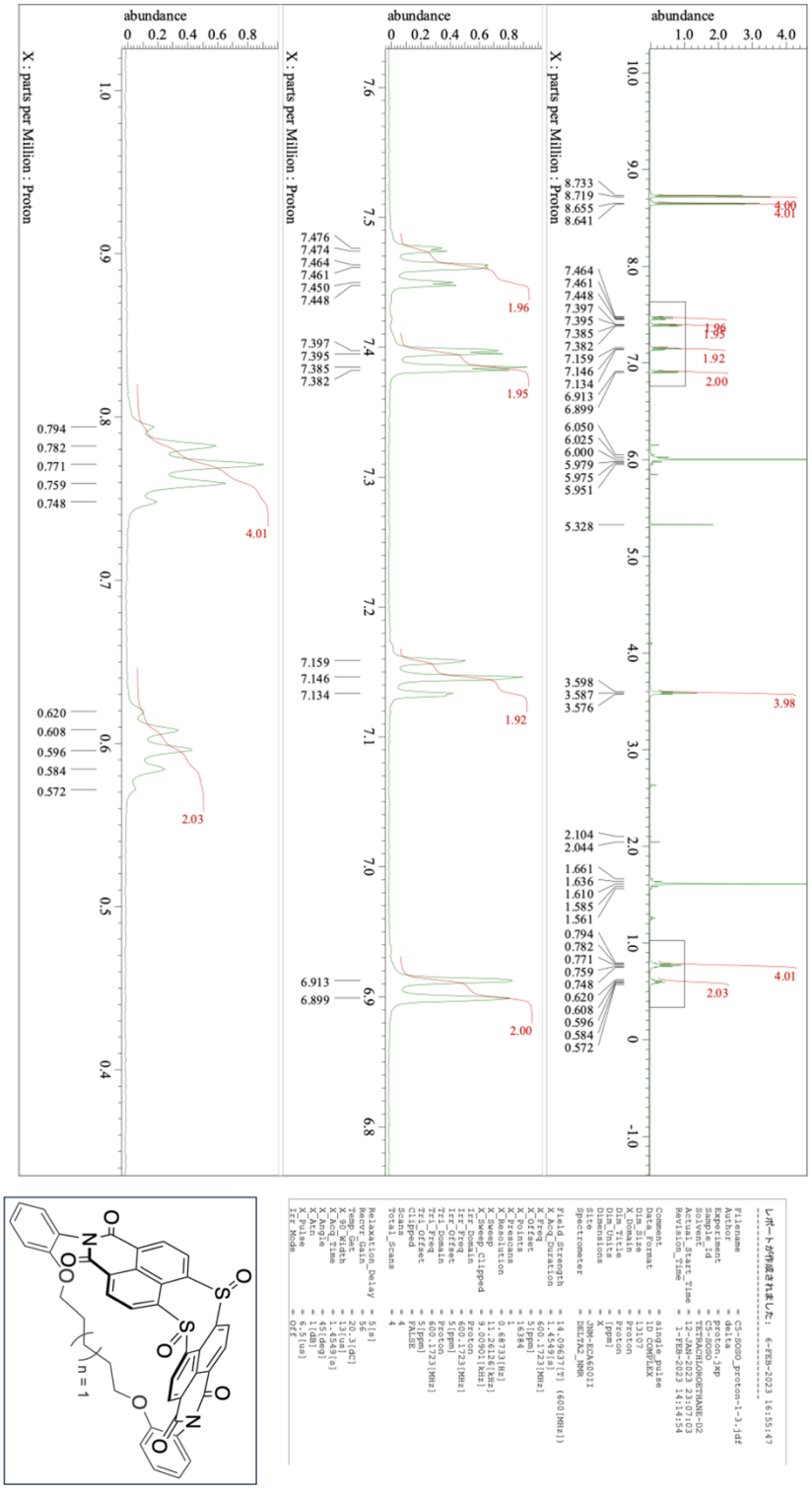


Figure S13. ^{1}H NMR spectrum of **4a** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

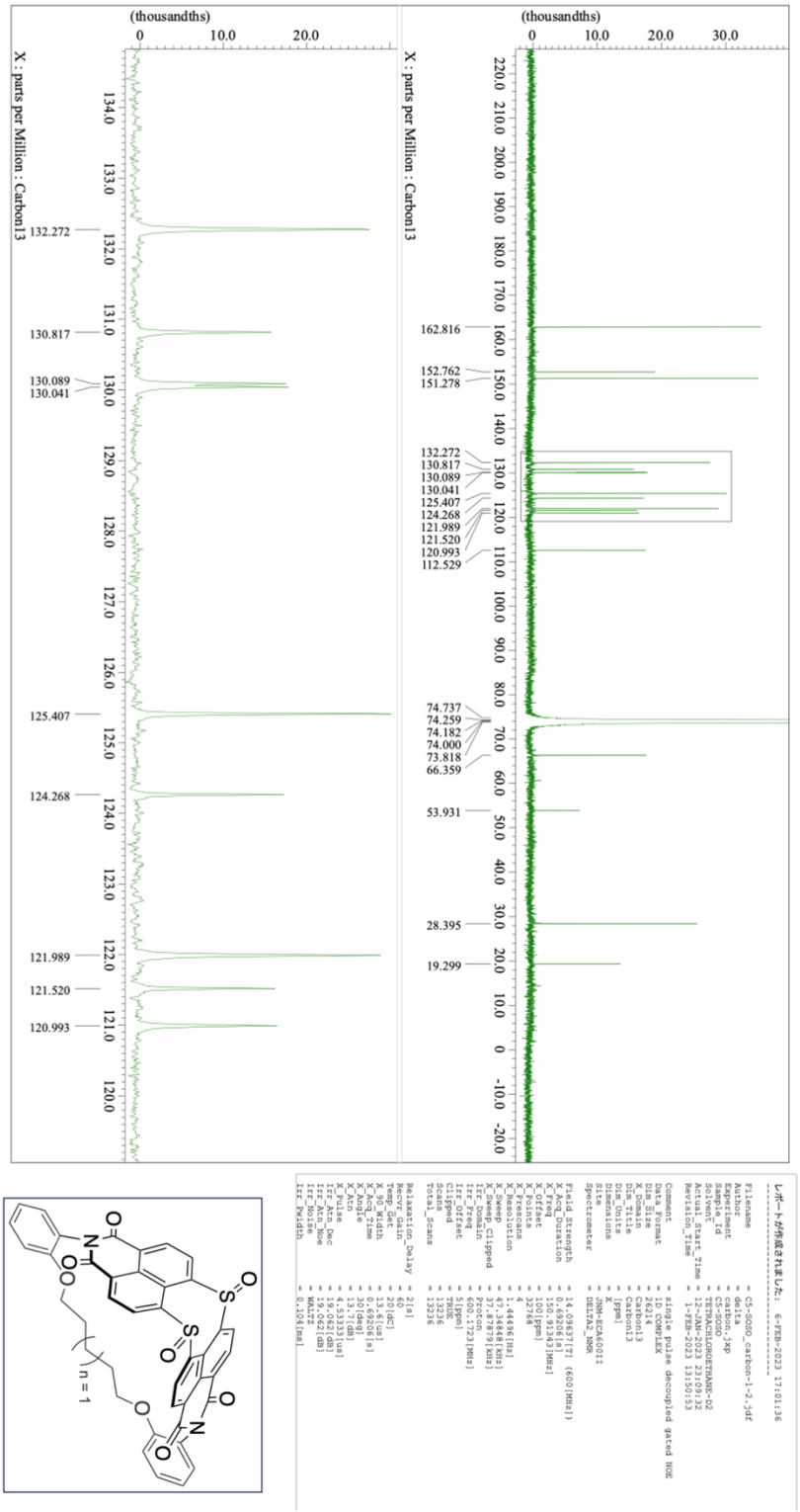


Figure S14. ^{13}C NMR spectrum of **4a** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

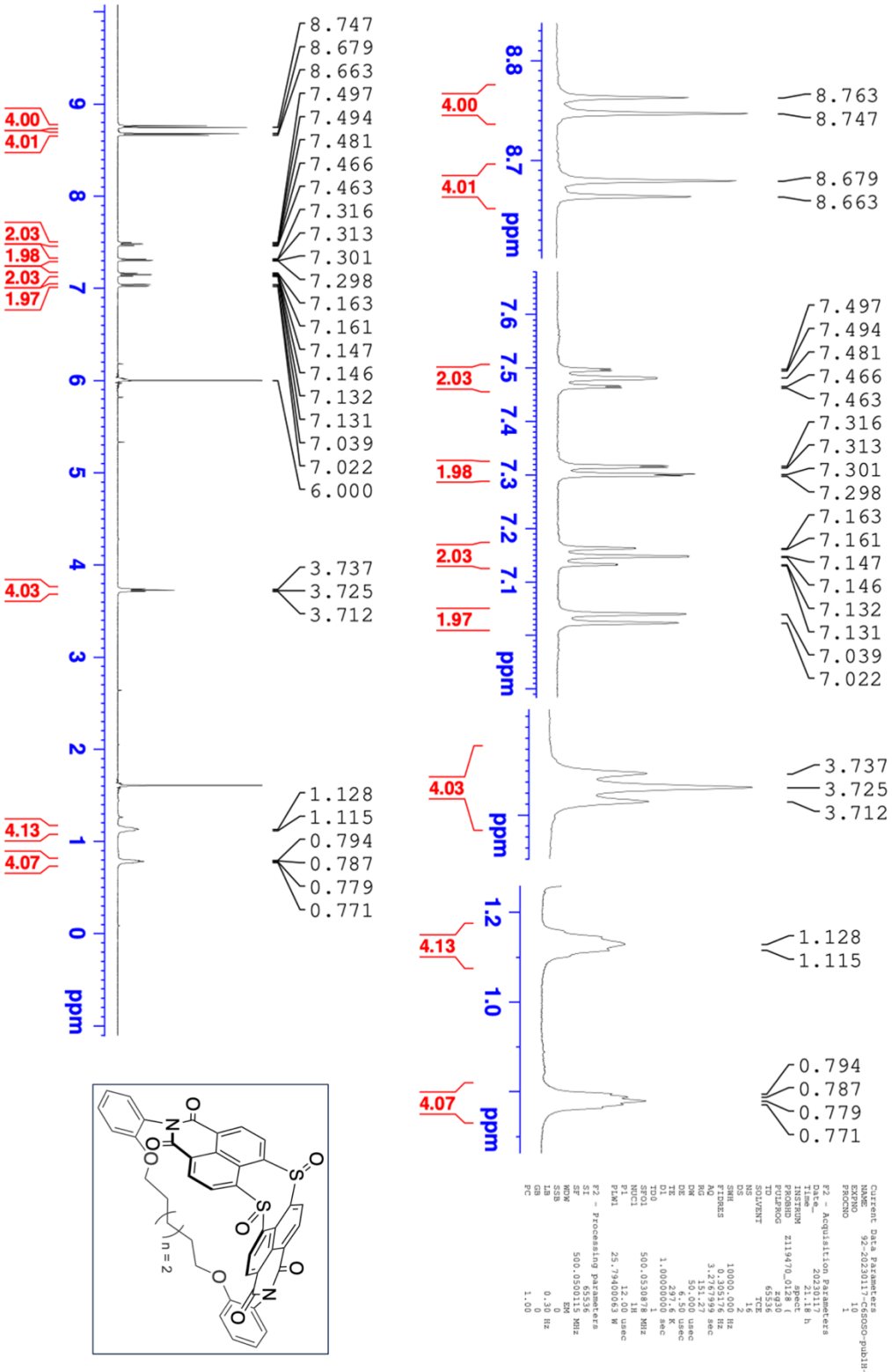


Figure S15. ^{1}H NMR spectrum of **4b** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

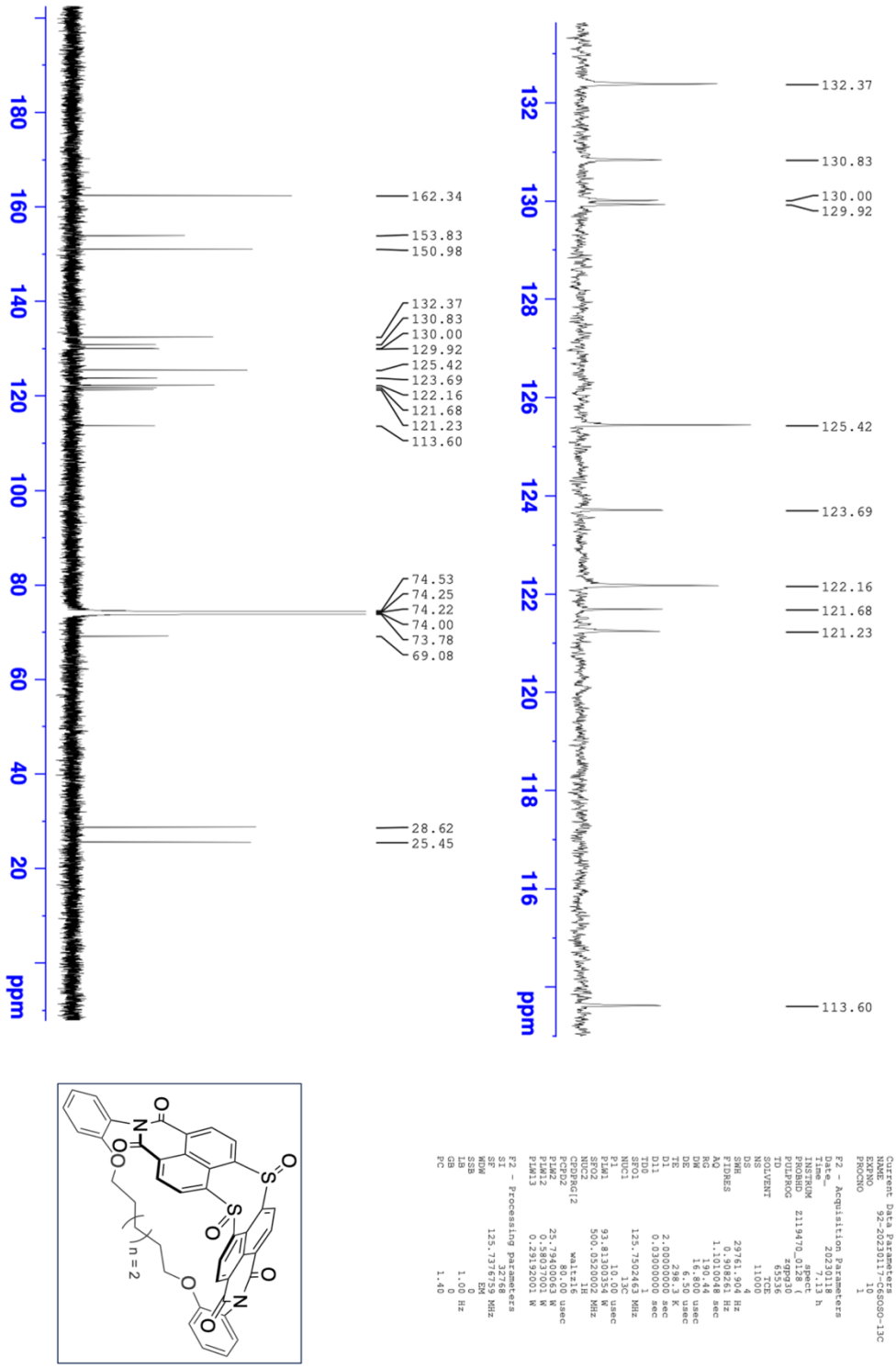


Figure S16. ^{13}C NMR spectrum of **4b** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

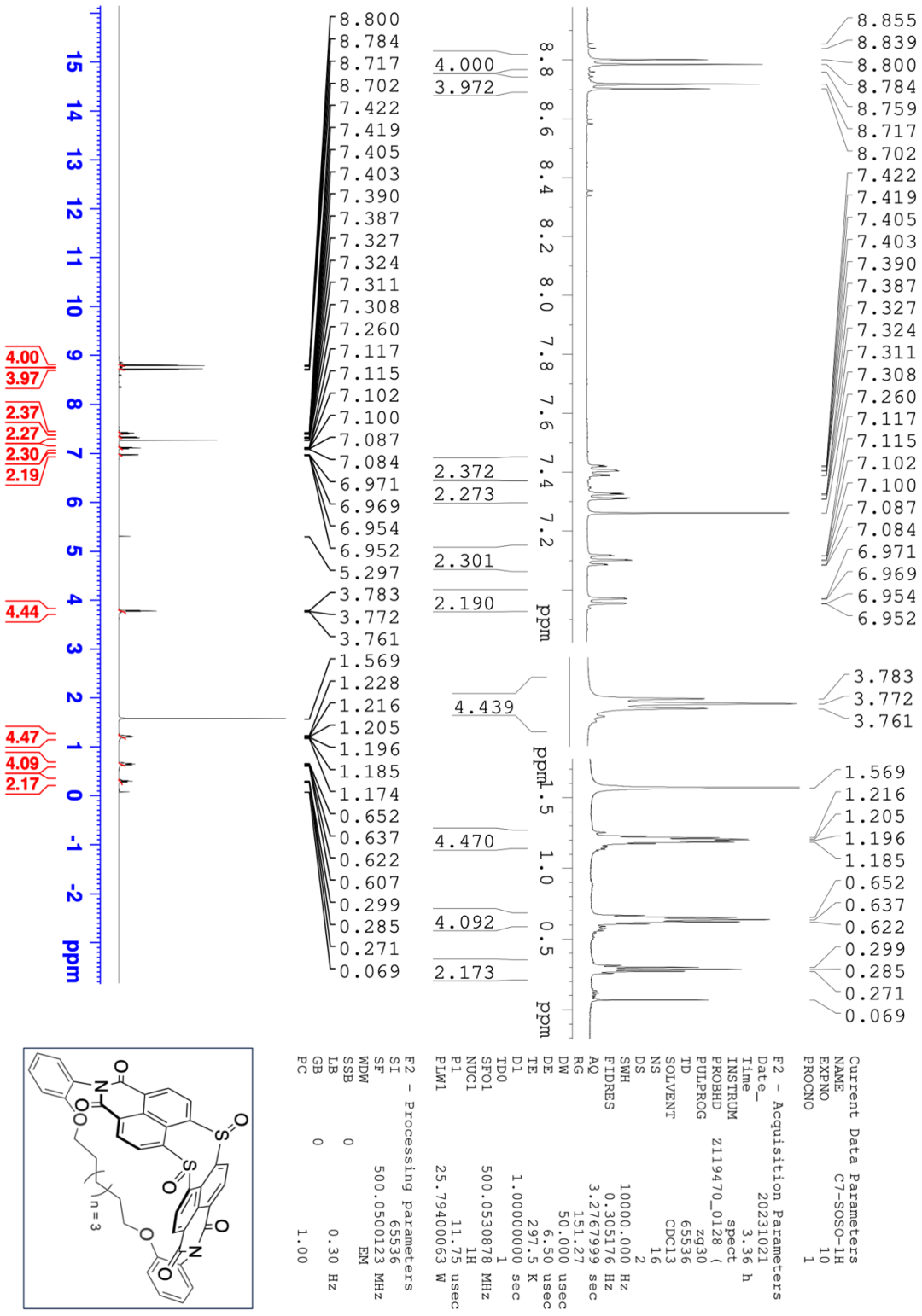


Figure S17. ^{1}H NMR spectrum of **4c** in $CDCl_3$ at 25 °C.

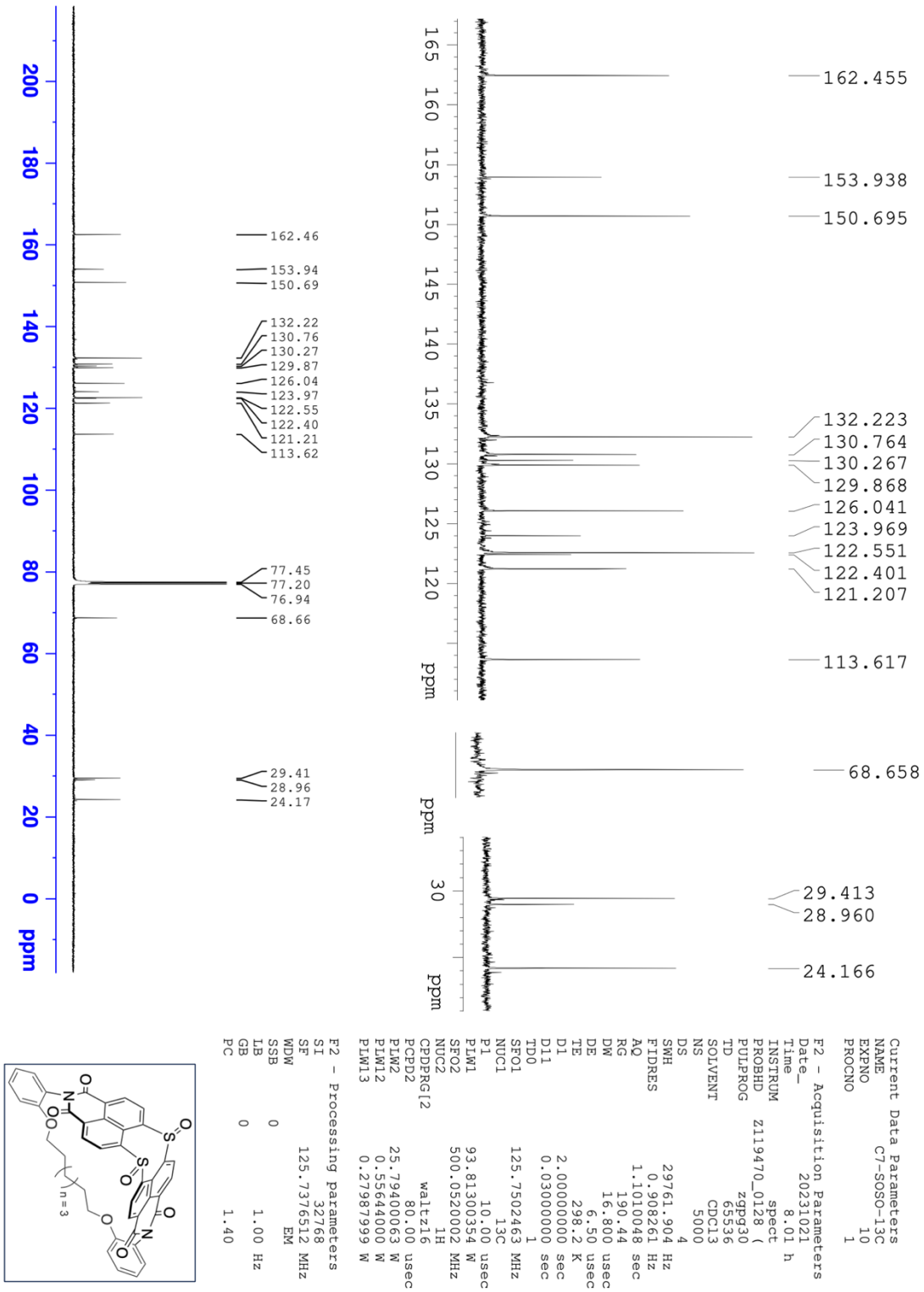


Figure S18. ^{13}C NMR spectrum of **4c** in $CDCl_3$ at 25 °C.

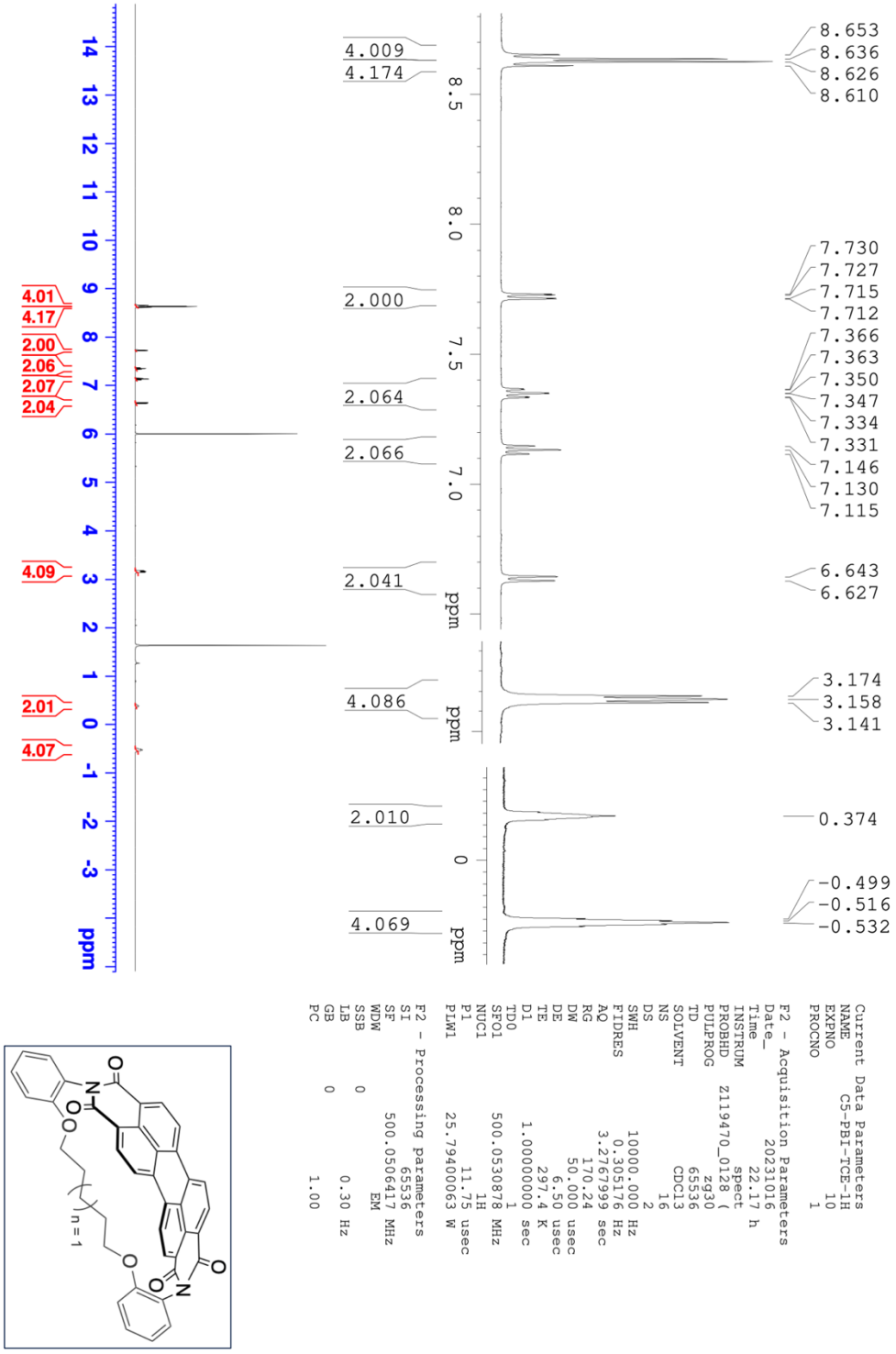


Figure S19. ^{1}H NMR spectrum of **5a** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

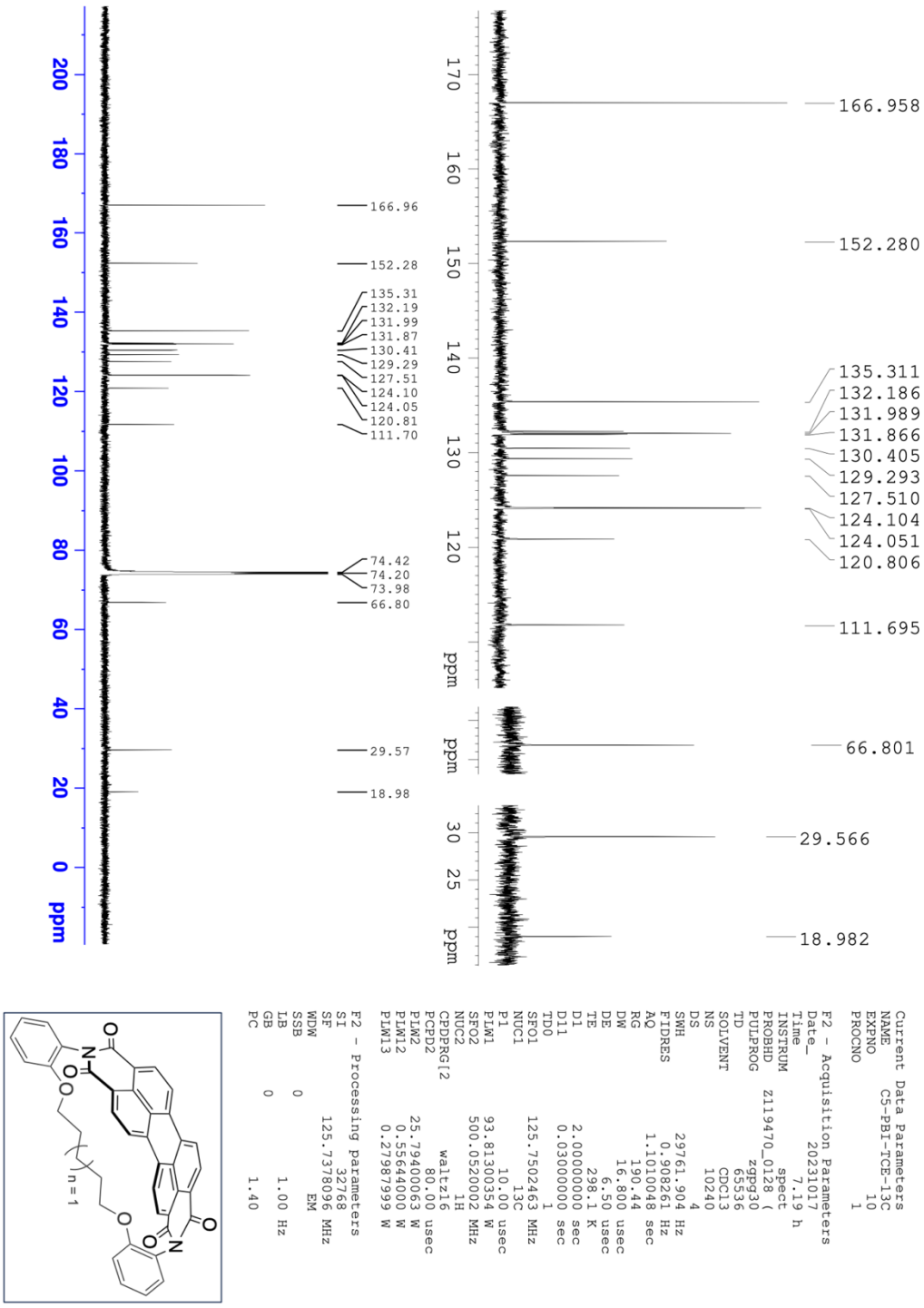


Figure S20. ^{13}C NMR spectrum of **5a** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

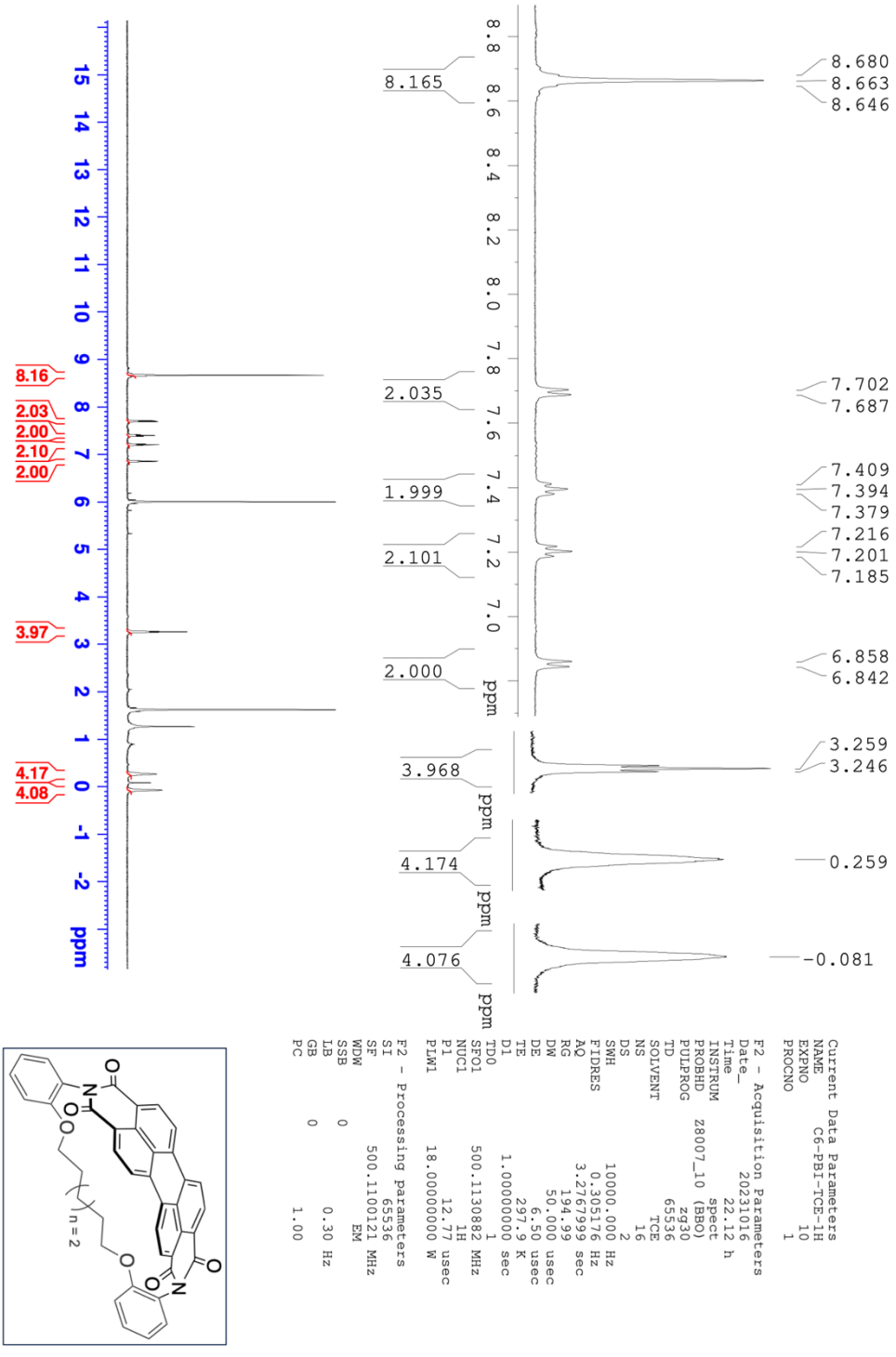


Figure S21. [1]H NMR spectrum of **5b** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

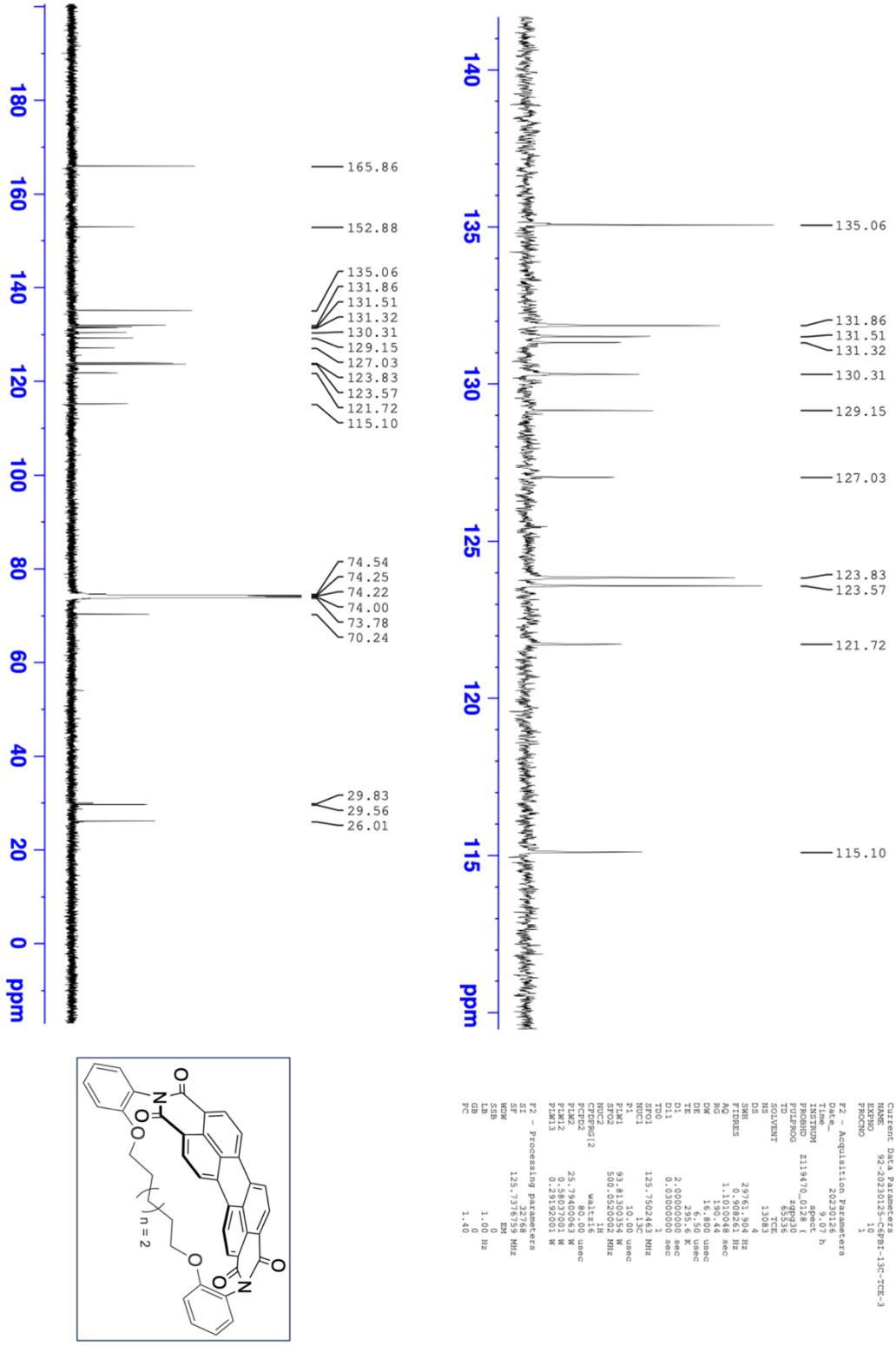


Figure S22. ^{13}C NMR spectrum of **5b** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

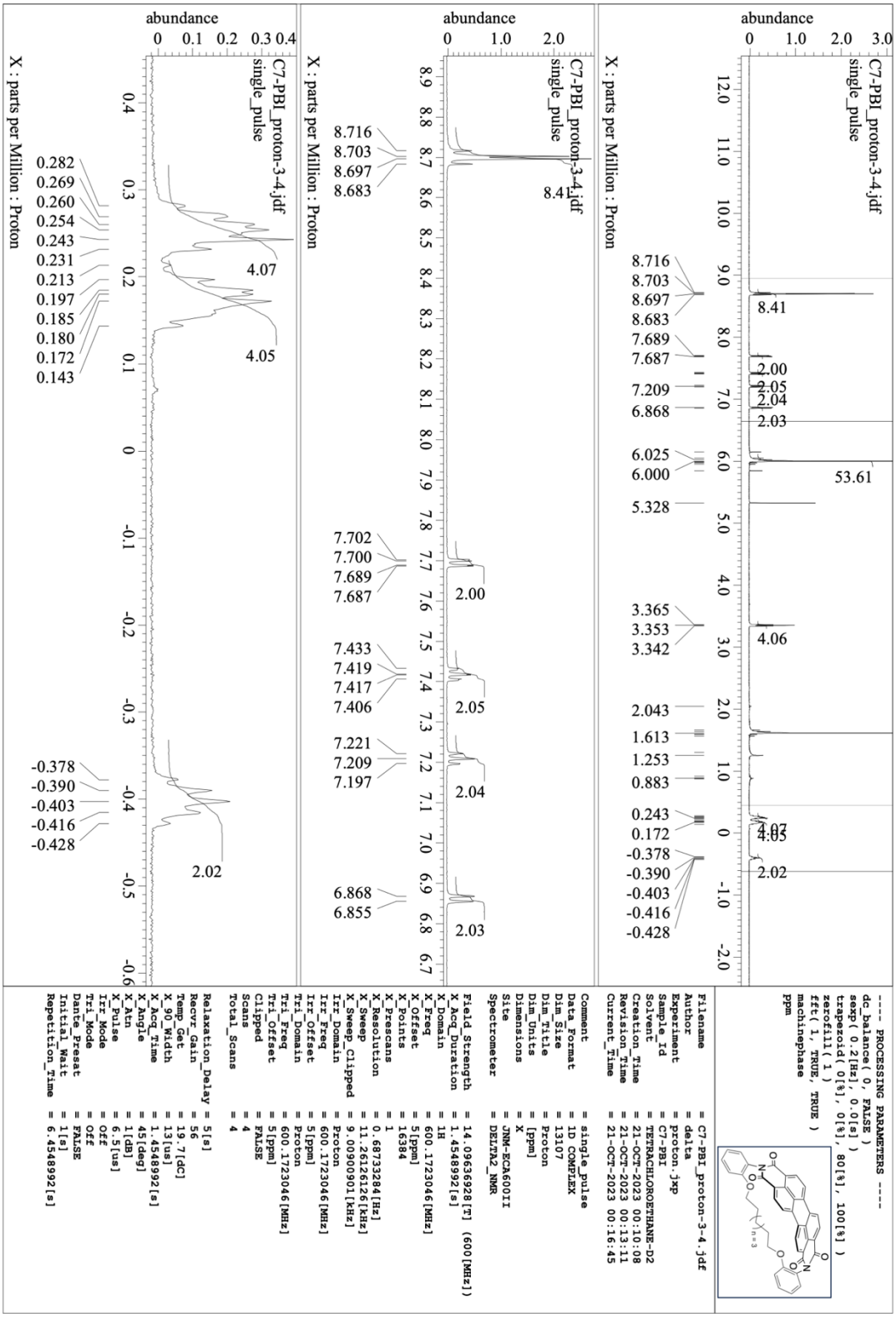


Figure S23. ^{1}H NMR spectrum of **5c** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

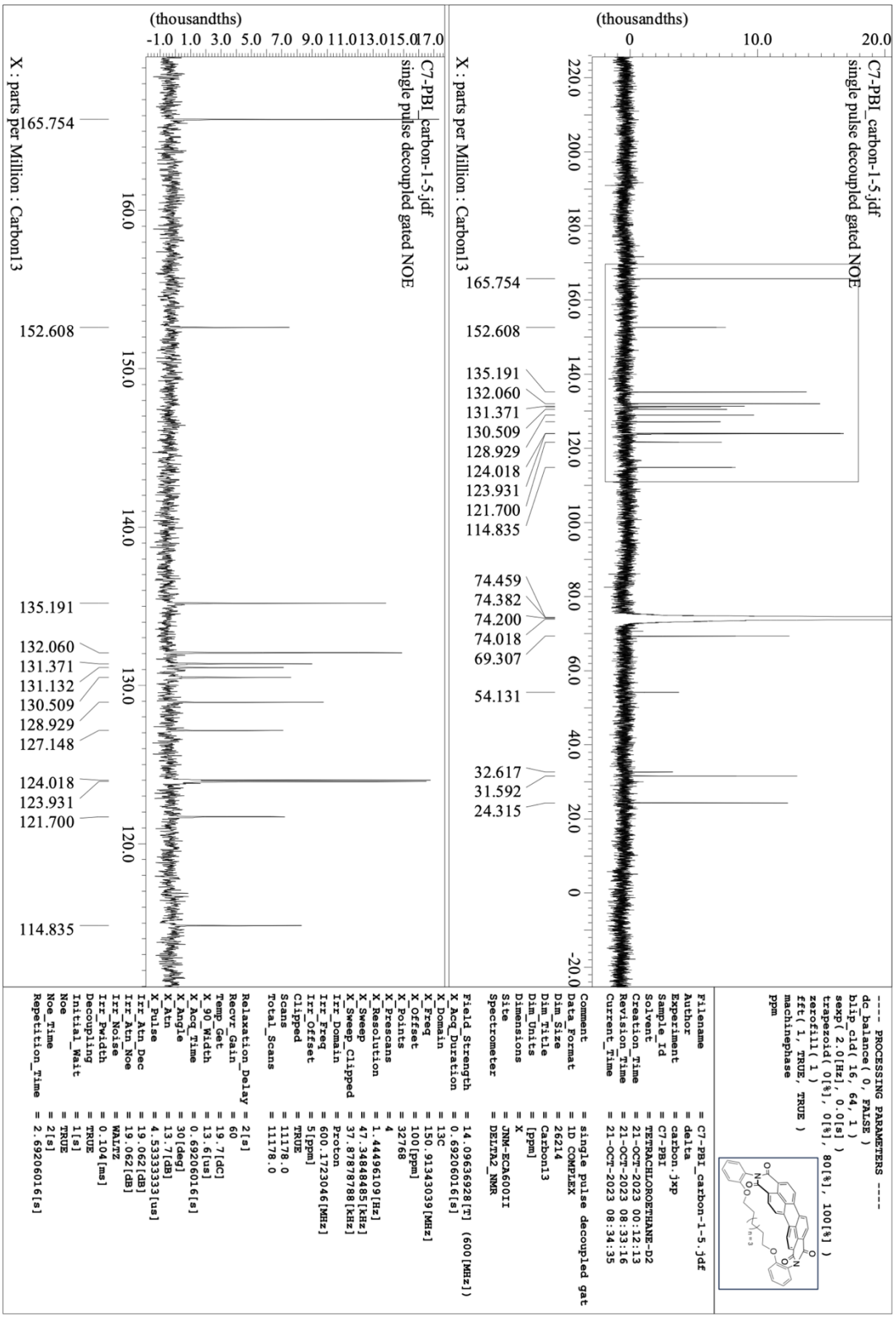


Figure S24. ^{13}C NMR spectrum of **5c** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

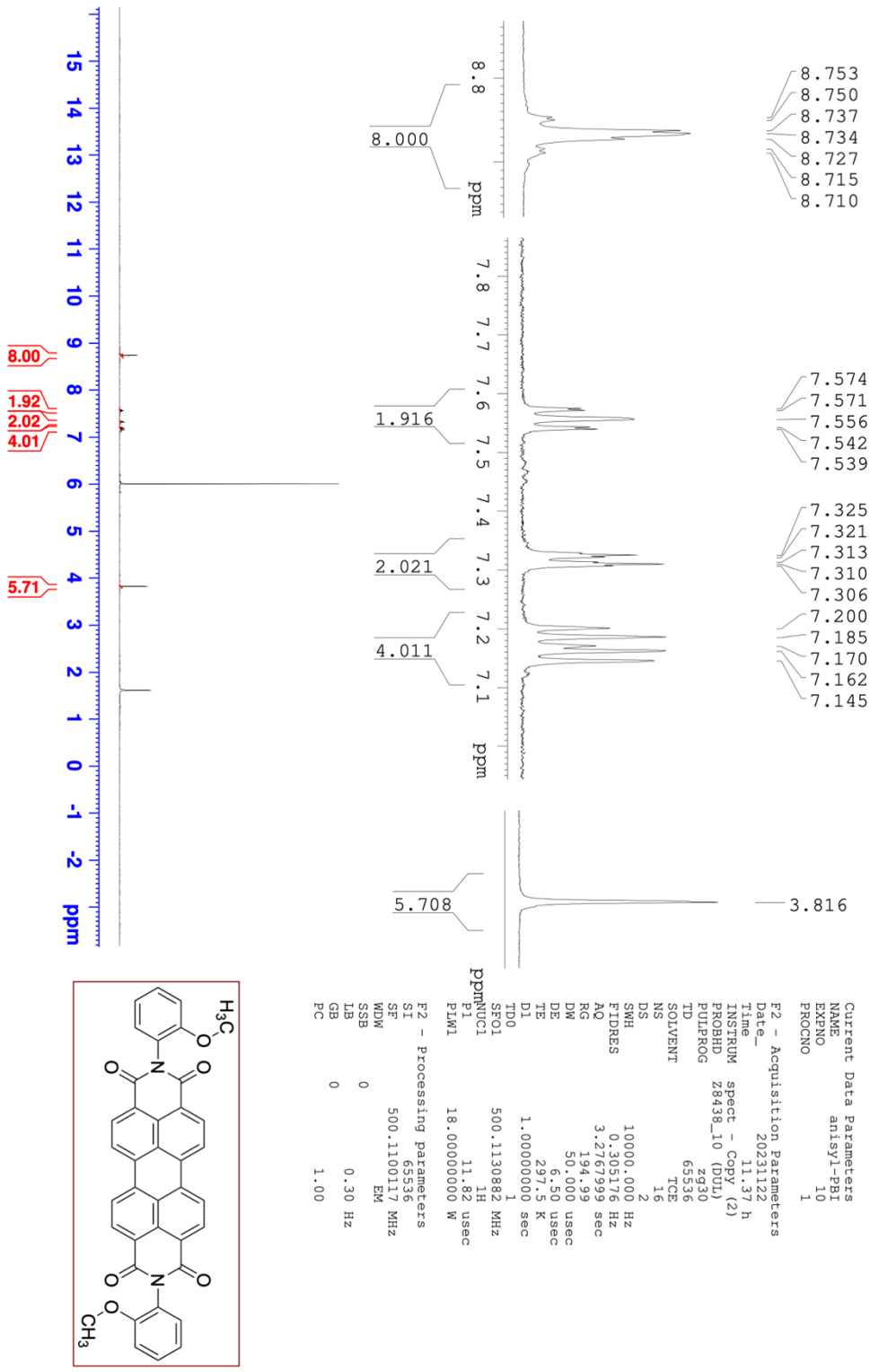


Figure S25. ^{1}H NMR spectrum of **3″** in 1,1,2,2-tetrachroloethane-d_2 at 25 °C.

4. Mass spectra

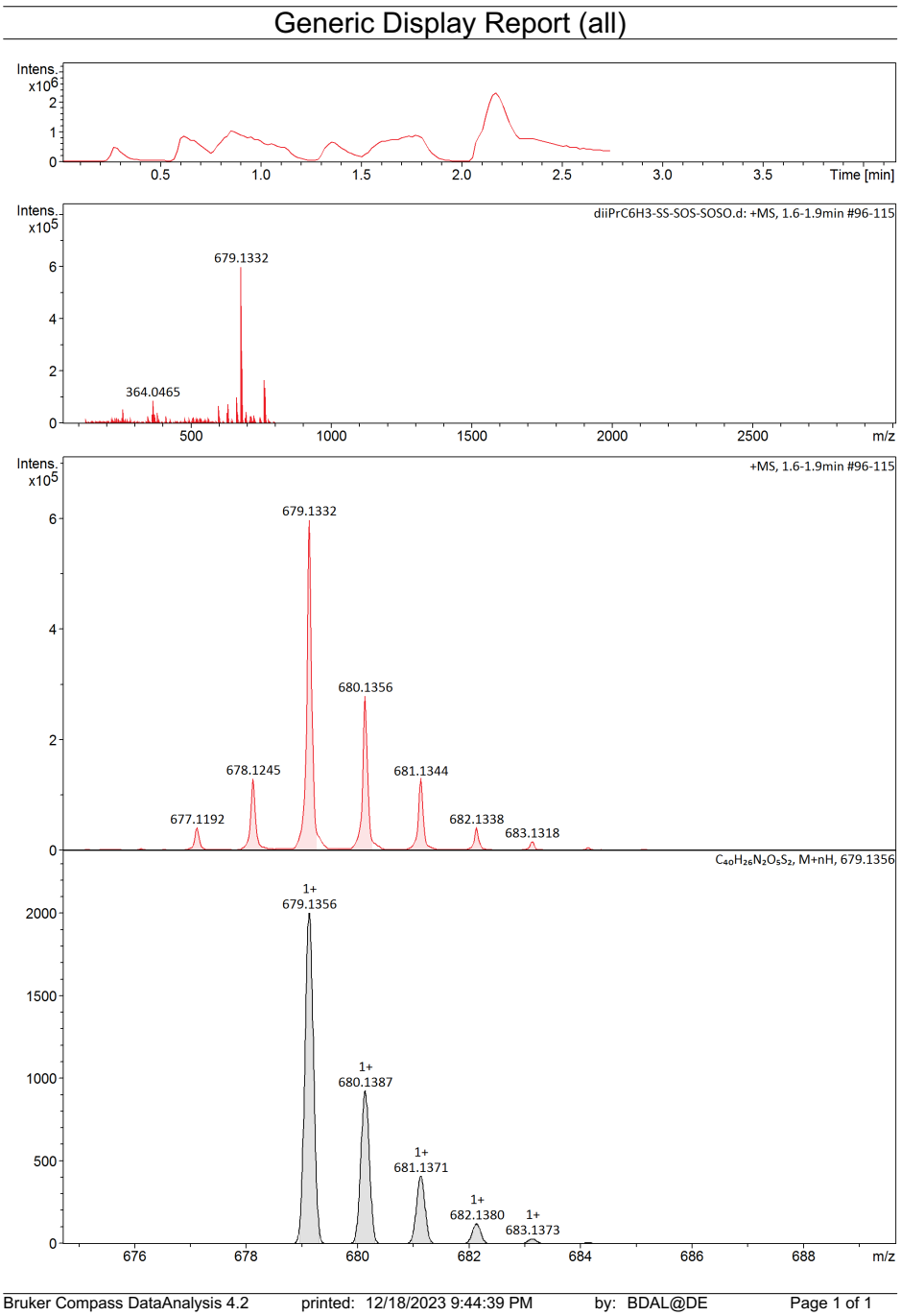


Figure S26. APCI-TOF mass spectrum of **10**.

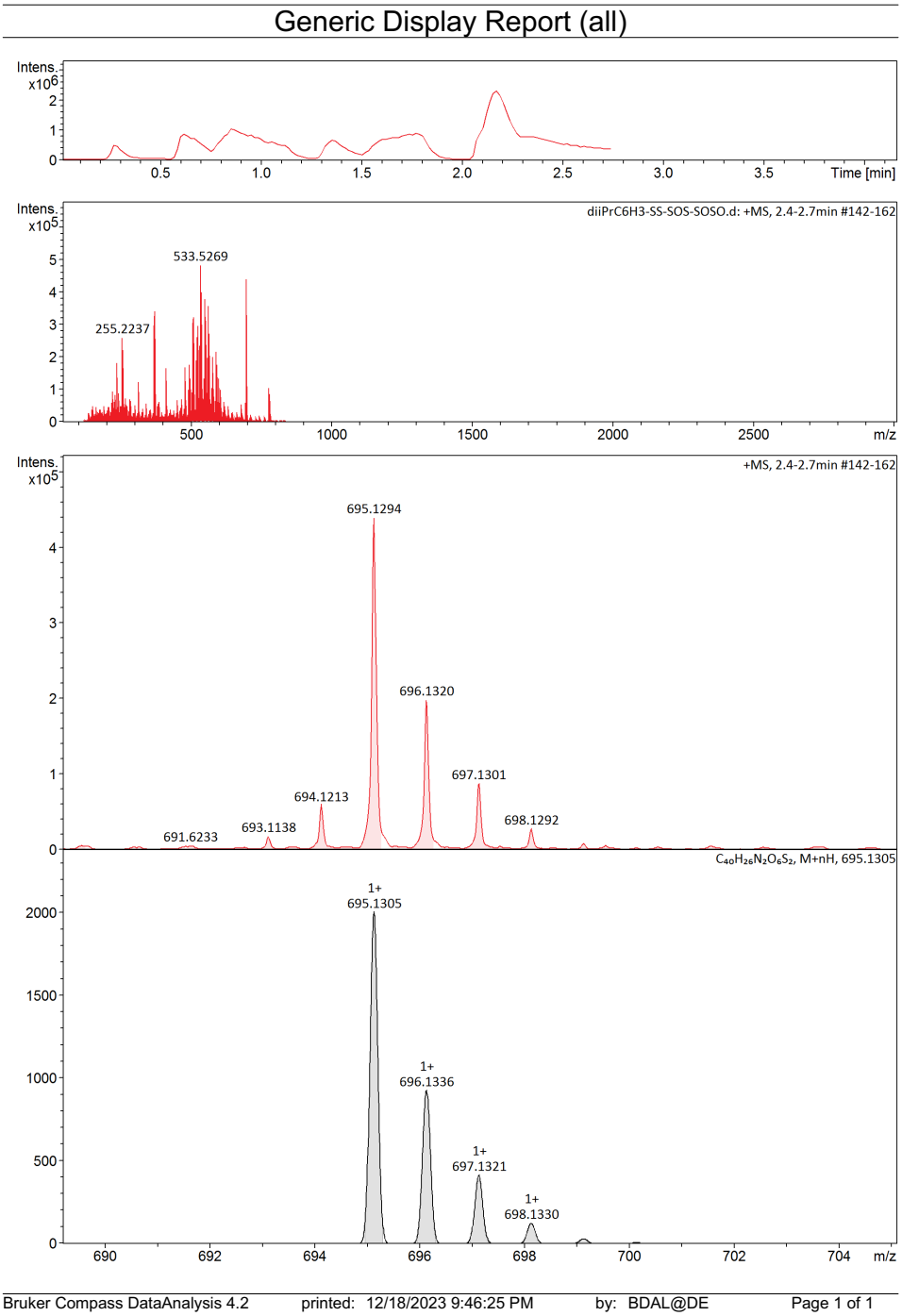


Figure S27. APCI-TOF mass spectrum of **11**.

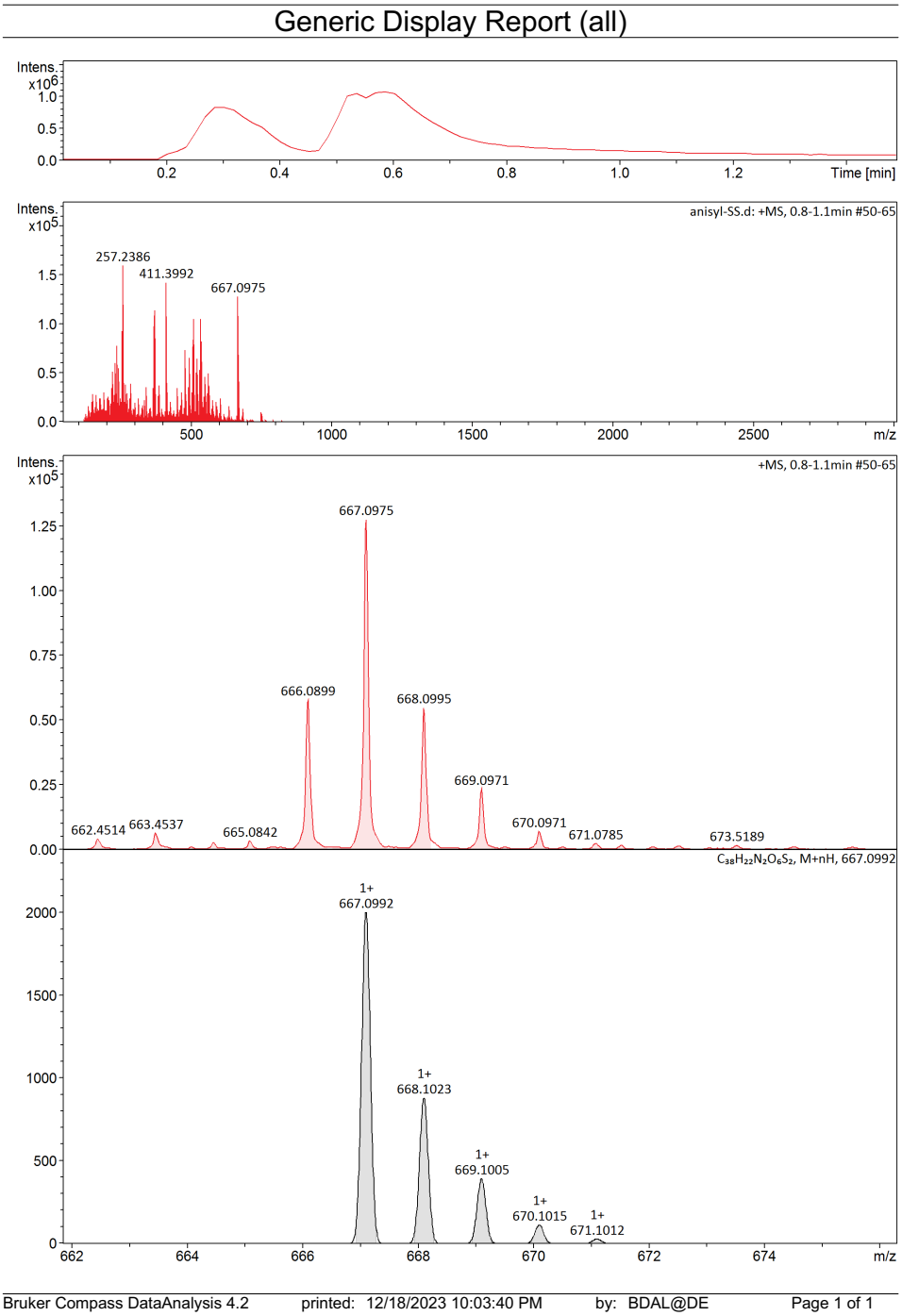


Figure S28. APCI-TOF mass spectrum of **13**.

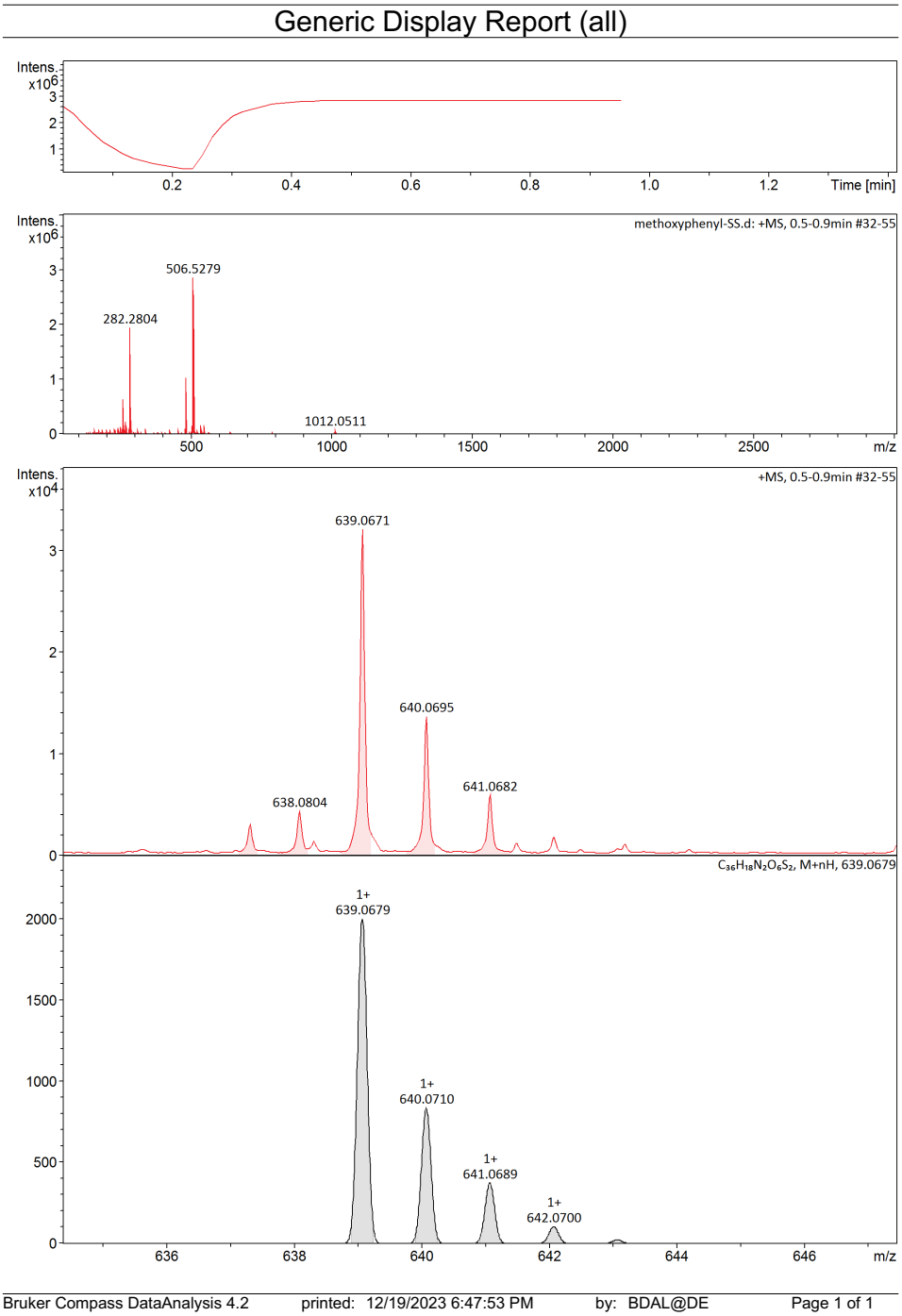


Figure S29. APCI-TOF mass spectrum of **14**.

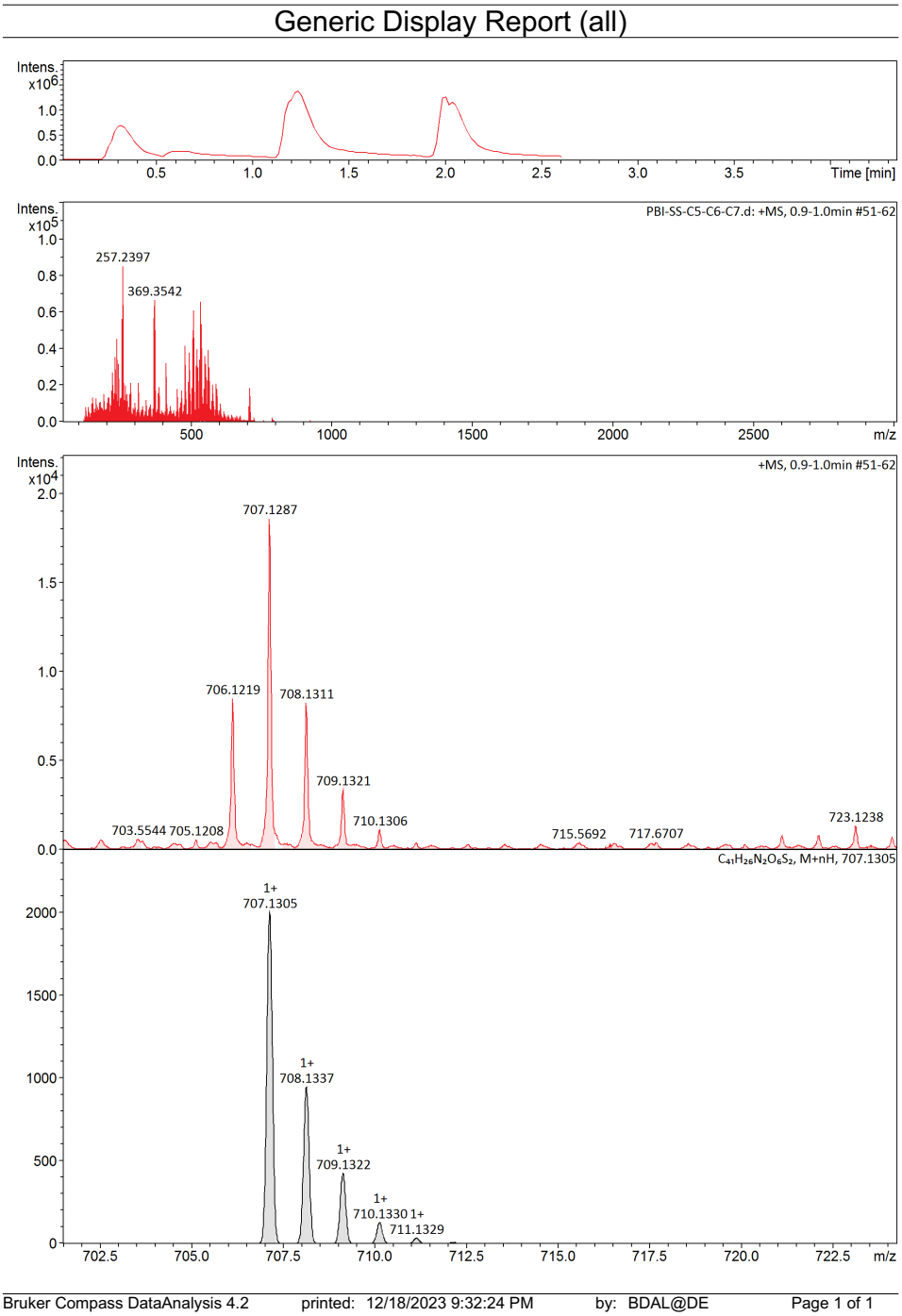


Figure S30. APCI-TOF mass spectrum of **15a**.

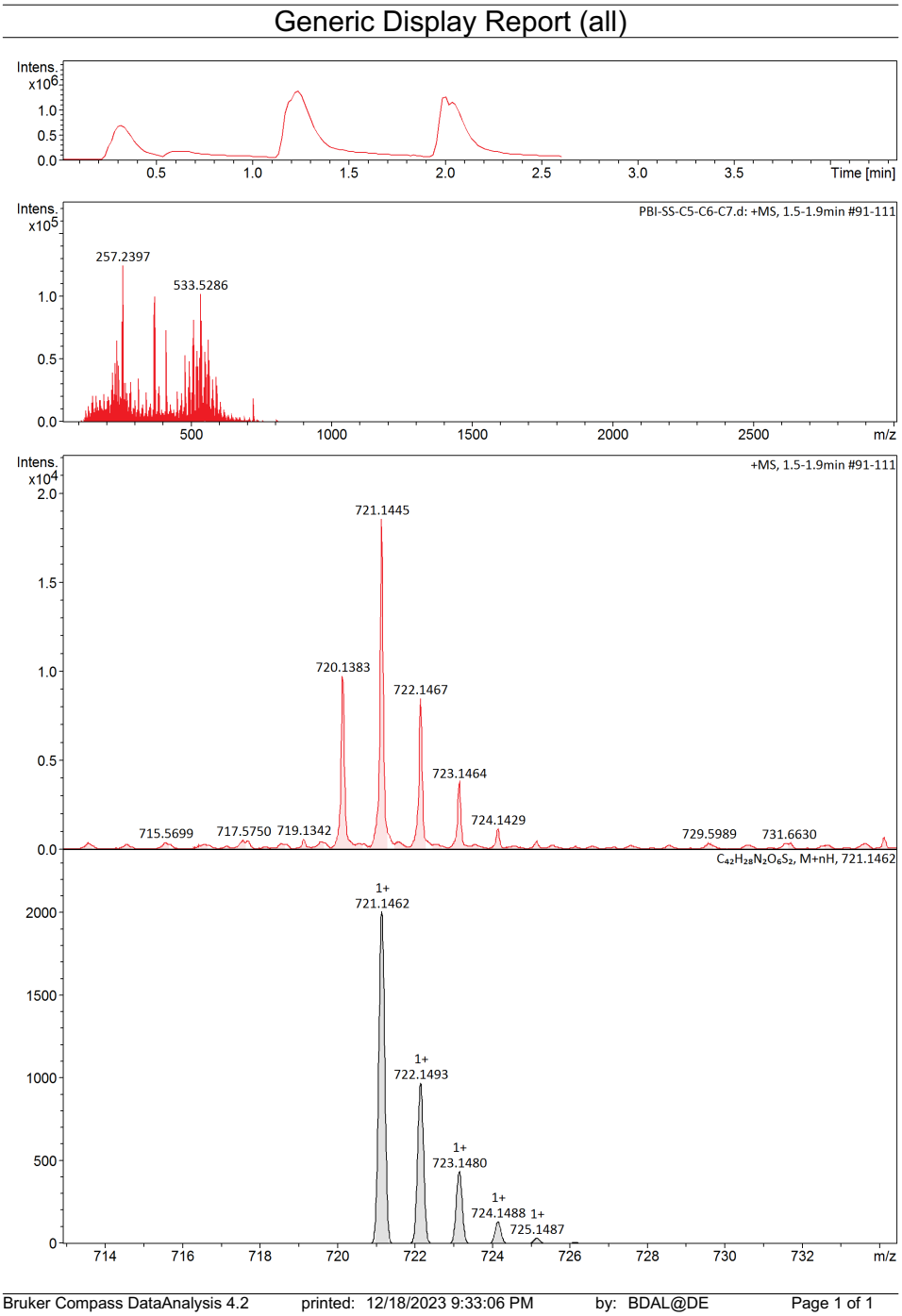


Figure S31. APCI-TOF mass spectrum of **15b**.

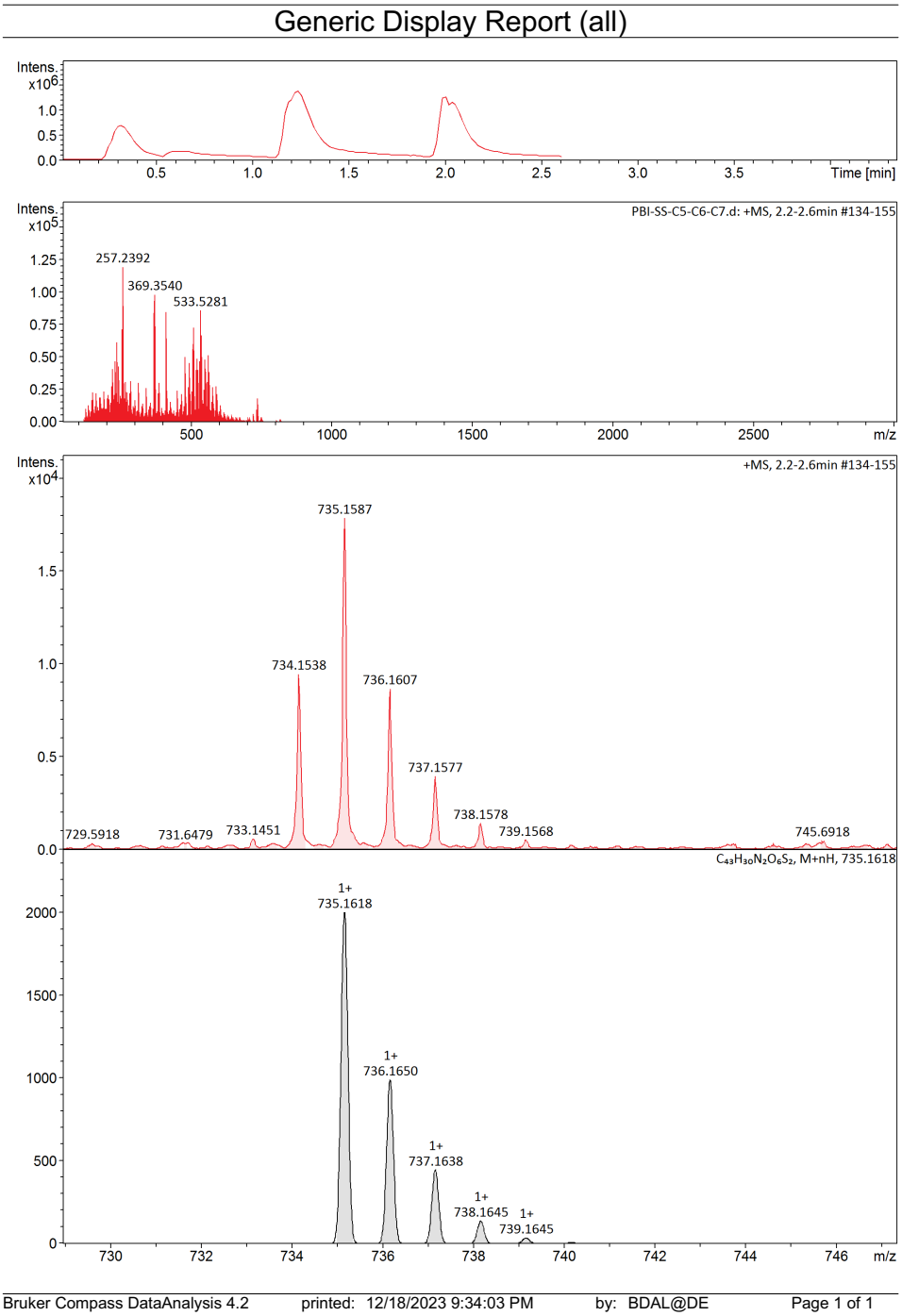


Figure S32. APCI-TOF mass spectrum of **15c**.

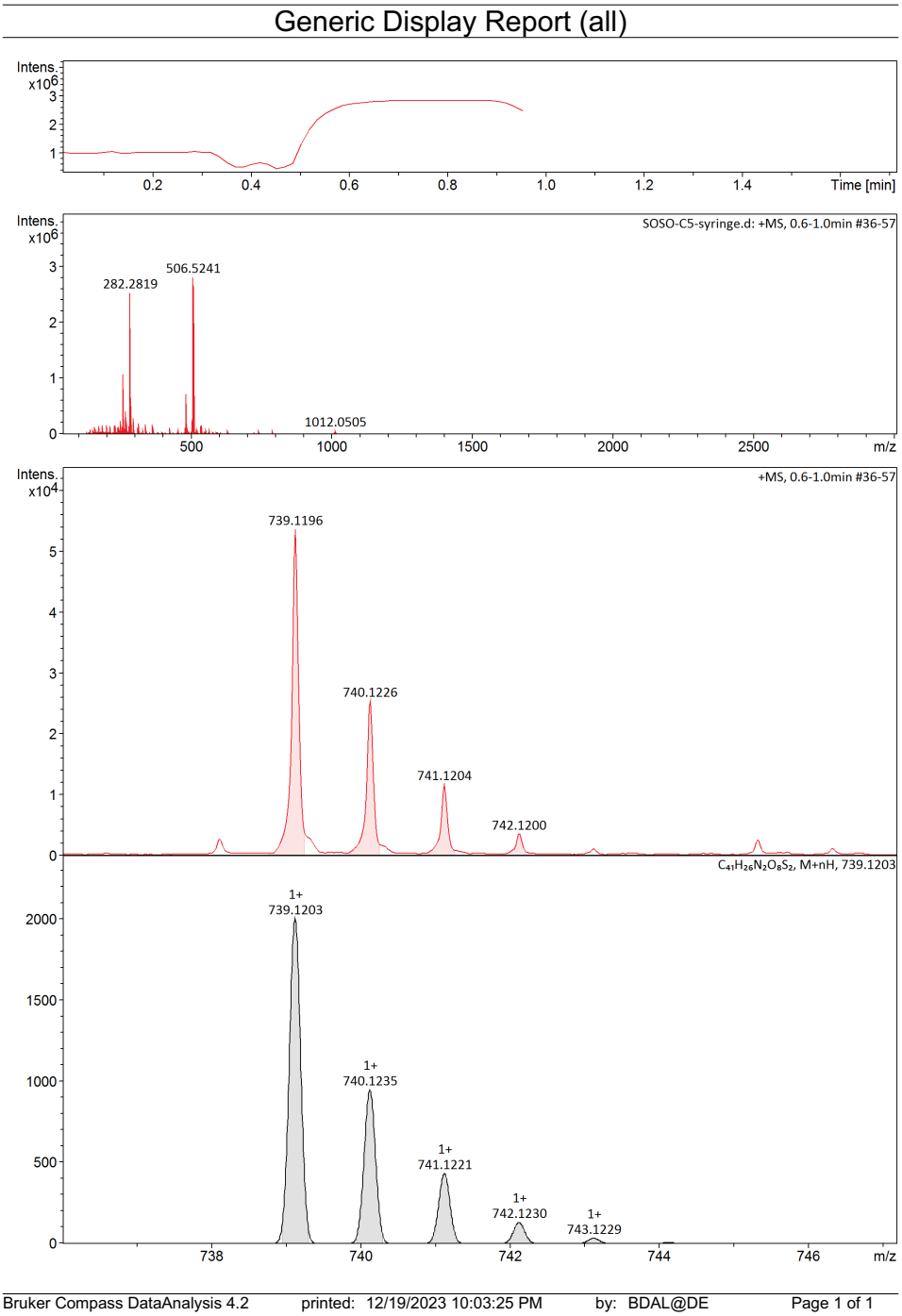


Figure S33. APCI-TOF mass spectrum of **4a**.

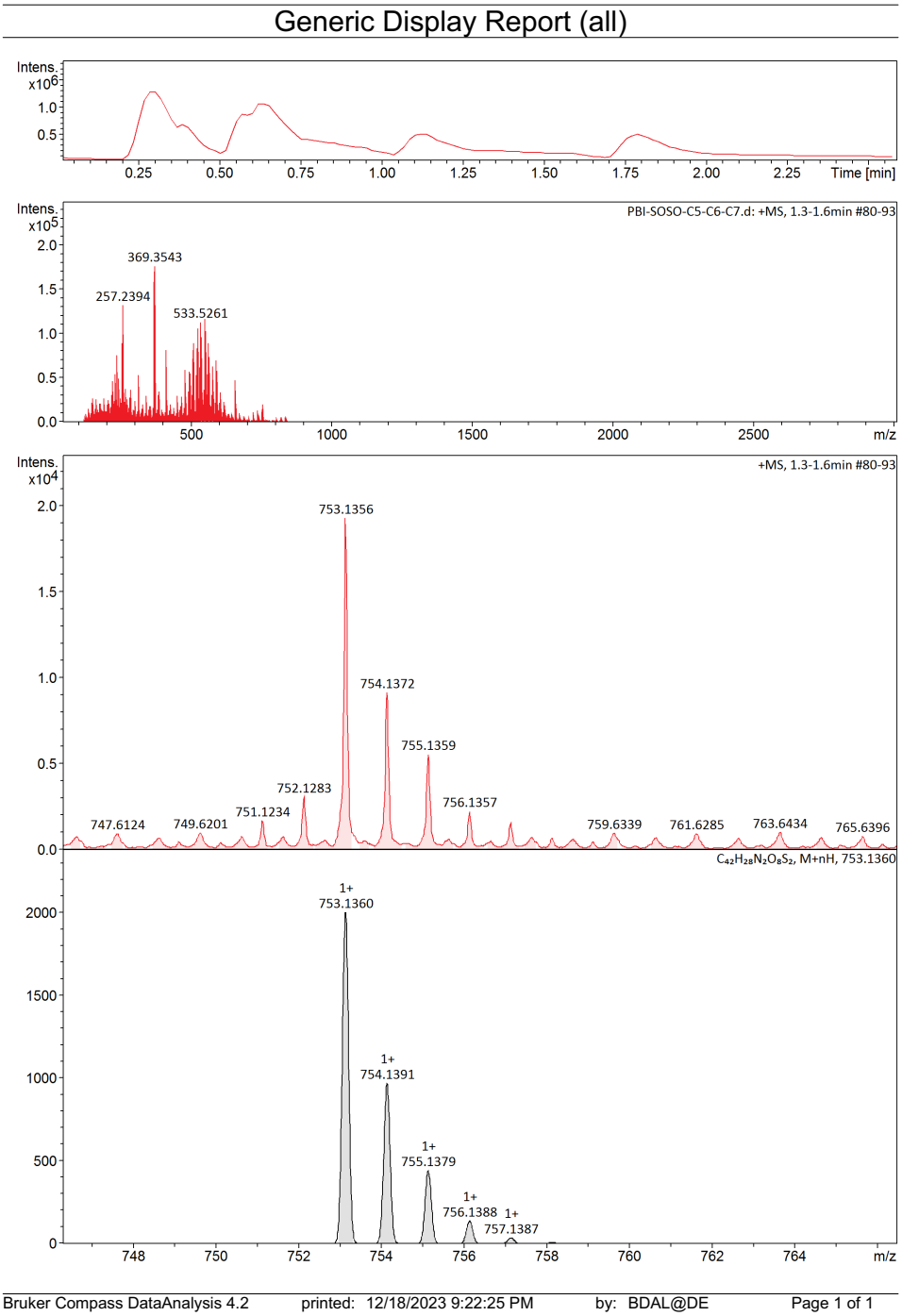


Figure S34. APCI-TOF mass spectrum of **4b**.

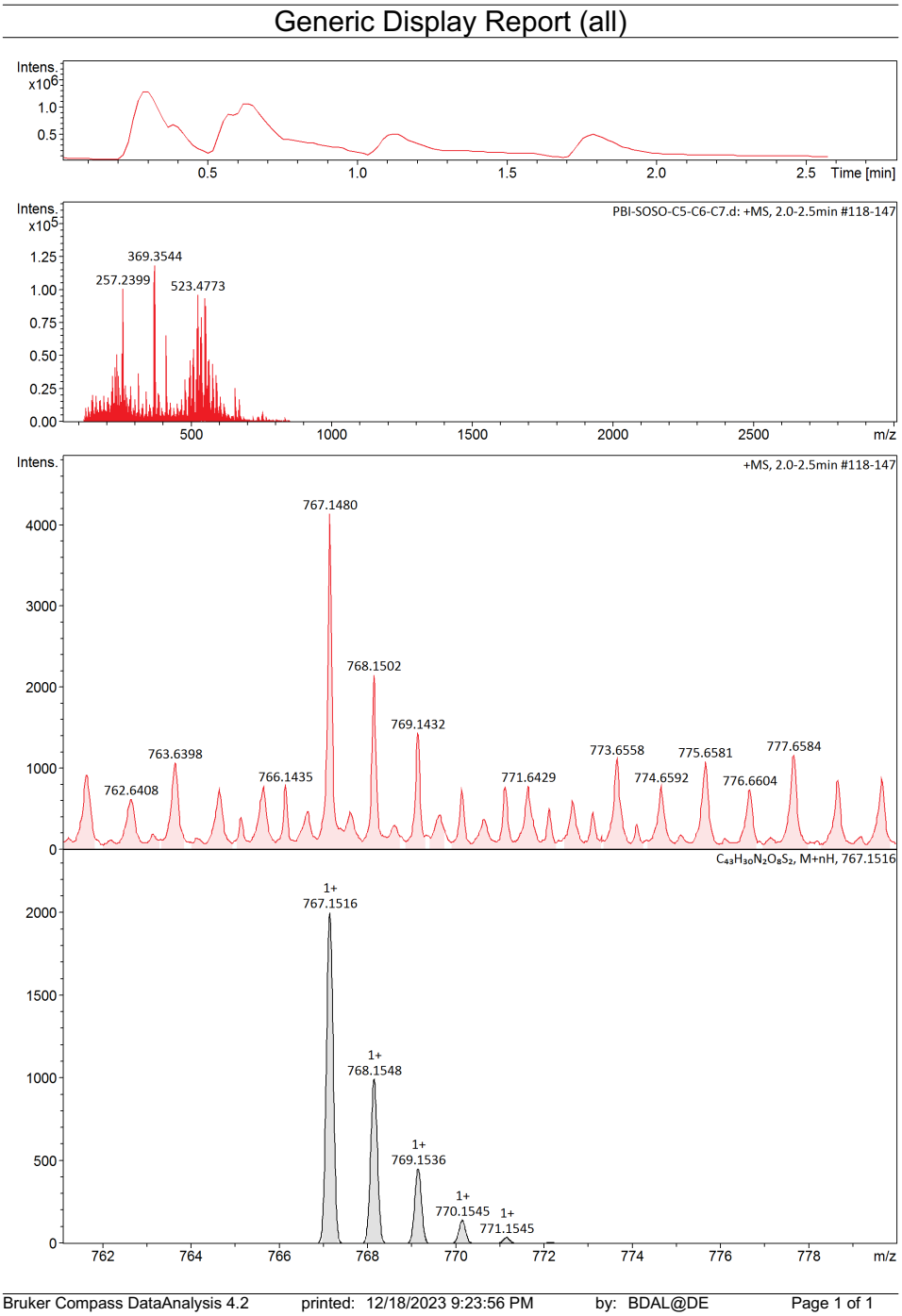


Figure S35. APCI-TOF mass spectrum of **4c**.

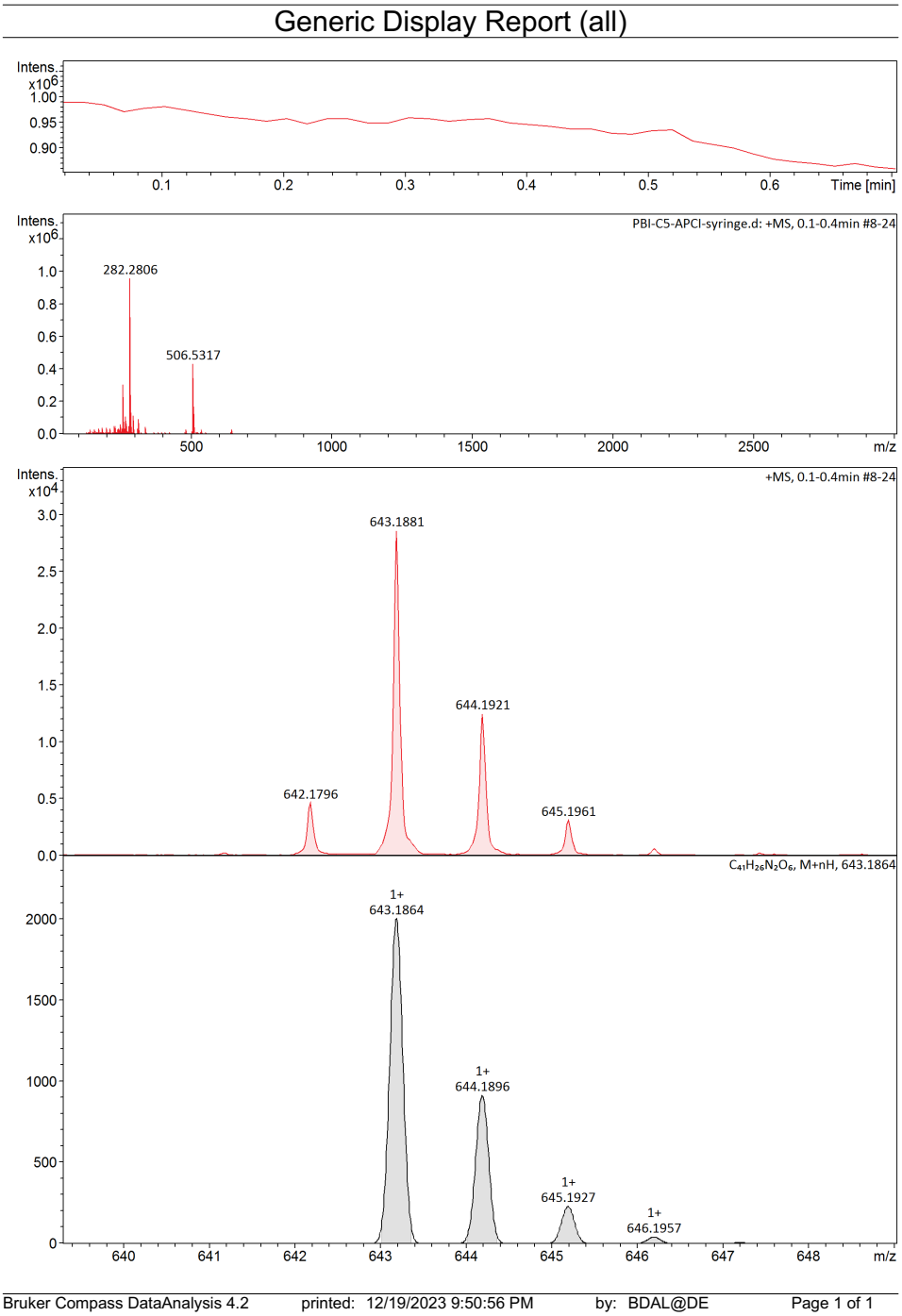


Figure S36. APCI-TOF mass spectrum of **5a**.

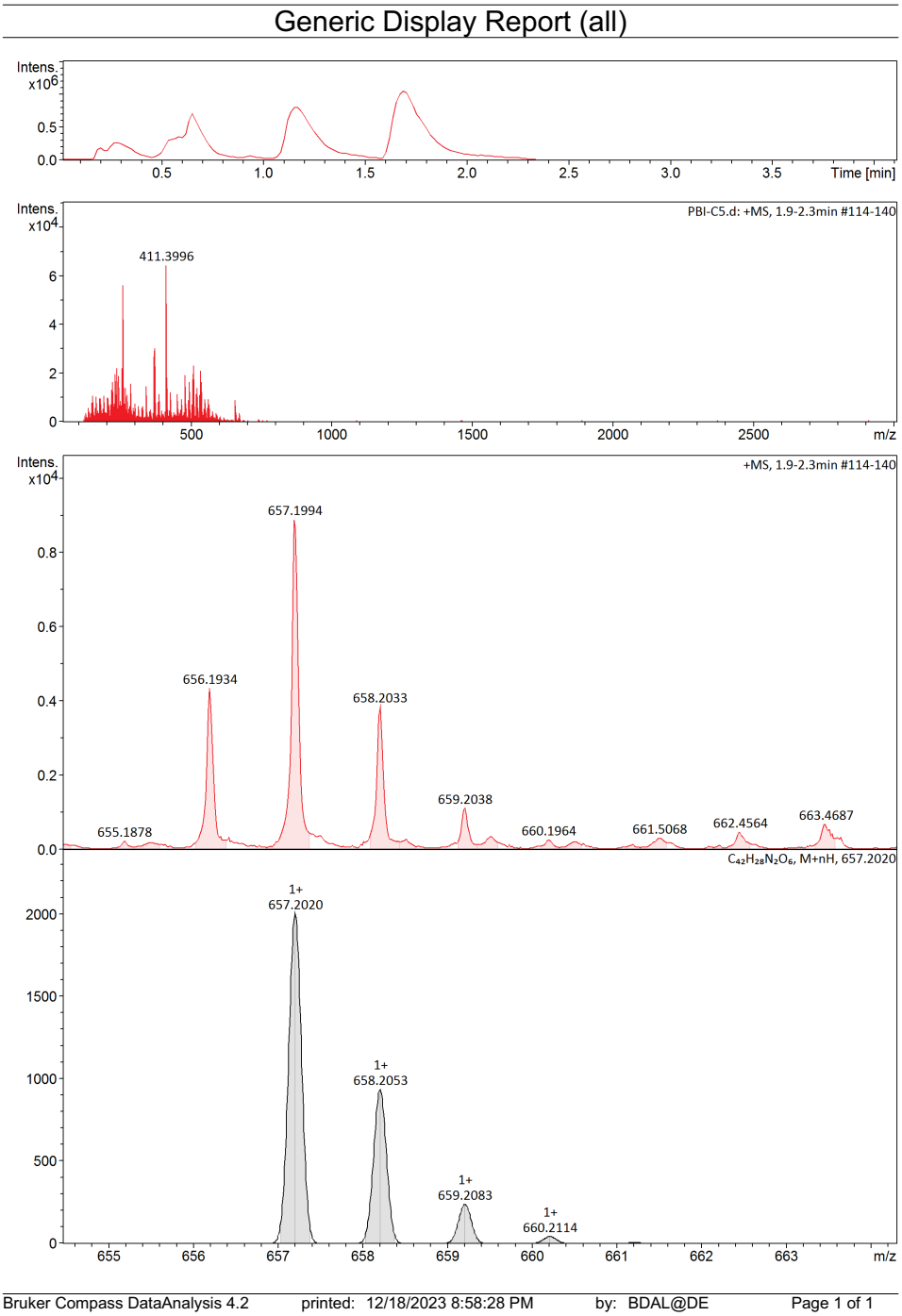


Figure S37. APCI-TOF mass spectrum of **5b**.

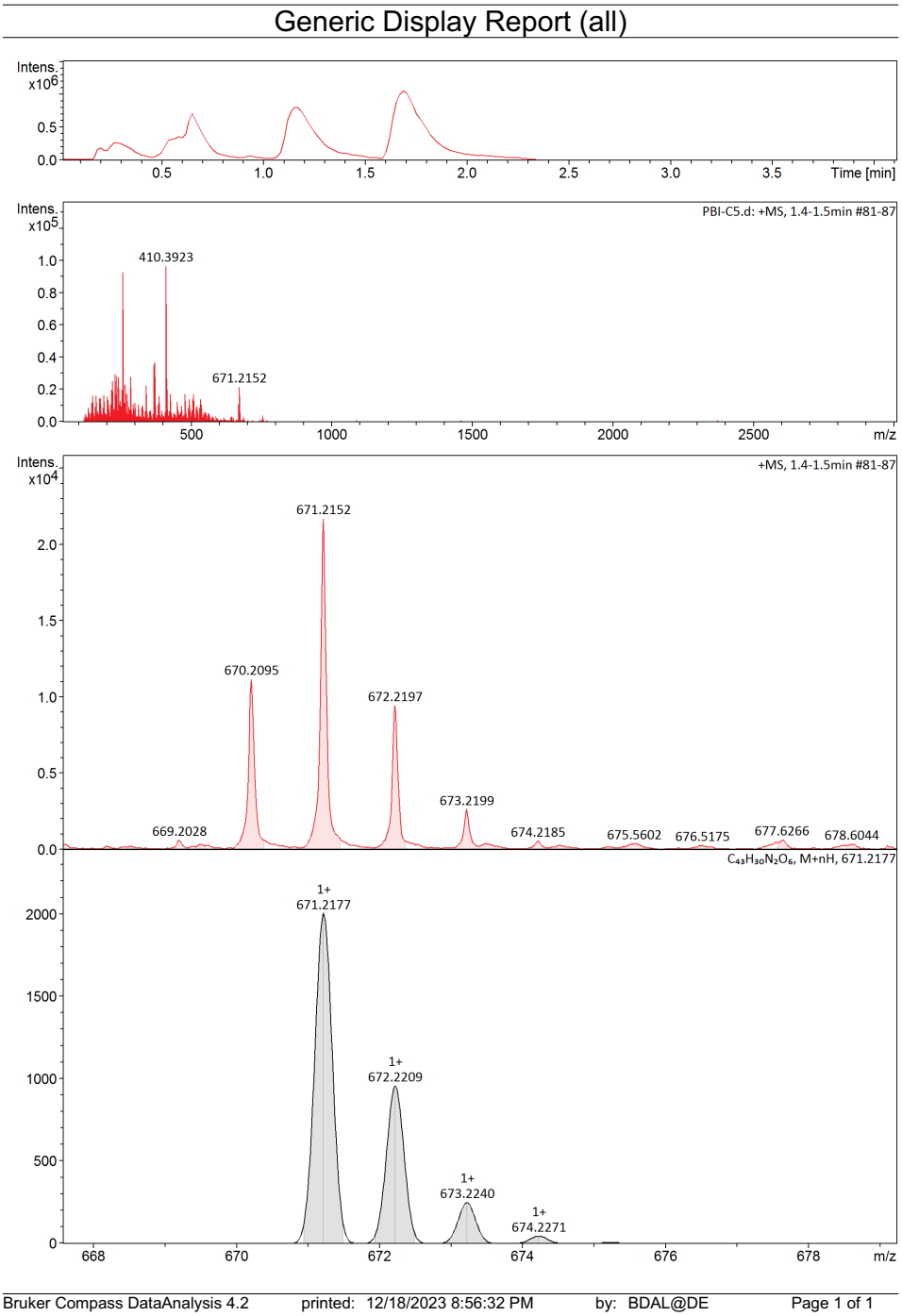


Figure S38. APCI-TOF mass spectrum of **5c**.

5. Crystal data

Table S1. Crystallographic data of **5a**, **5b**, and **5c**.

Compound	**5a**	**5b**	**5c**
Formula	$C_{41}H_{26}N_2O_6$	$C_{42}H_{28}N_2O_6$, $CHCl_3$	$2(C_{43}H_{30}N_2O_6)$
Formula weight	642.64	776.03	1341.38
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*I*12/a1 (No. 15)	$P2_1/a$ (No. 14)	$P12_1/n1$ (No. 14)
Crystal color	red	red	red
Crystal description	plate	plate	block
a [Å]	15.7272(6)	11.8210(5)	13.6337(3)
b [Å]	11.3327(3)	24.9798(9)	11.8657(3)
c [Å]	20.9939(8)	12.1425(5)	19.1562(5)
α [°]	—	—	—
β [°]	109.582(4)	106.628(4)	98.107(2)
γ [°]	—	—	—
V [Å^3]	3525.4(2)	3435.6(2)	3067.99(13)
Z	4	4	2
d_{calcd} [g cm^{-3}]	1.328	1.500	1.452
R_1 ($I > 2\sigma(I)$)	0.0499	0.0619	0.0562
wR_2 (all data)	0.1238	0.1800	0.1435
Goodness-of-fit	1.013	1.146	1.029
Temperature [K]	93(2)	93(2)	93(2)
CCDC No.	2348376	2348377	2348378

Table S2. Crystallographic data of **10** and **11**.

Compound	**10**	**11**
Formula	$C_{40}H_{26}N_2O_4S_2$, 2.73($CH_3C_6H_5$), 0.27(CH_2Cl_2)	$C_{40}H_{26}N_2O_6S_2$
Formula weight	593.20	933.48
Crystal system	triclinic	triclinic
Space group	*P*–1 (No. 2)	*P*–1 (No. 2)
Crystal color	yellow	colorless
Crystal description	plate	block
a [Å]	12.9868(4)	10.1116(10)
b [Å]	13.0586(5)	13.6115(9)
c [Å]	14.4262(4)	15.4513(13)
α [°]	80.800(3)	83.734(6)
β [°]	81.409(3)	73.598(8)
γ [°]	74.562(3)	68.554(7)
V [Å^3]	2313.21(14)	1898.8(3)
Z	2	2
d_{calcd} [g cm^{-3}]	1.369	1.633
R_1 ($I > 2\sigma(I)$)	0.0835	0.0781
wR_2 (all data)	0.2766	0.2468
Goodness-of-fit	1.044	1.037
Temperature [K]	93(2)	93(2)
CCDC No.	2348379	2348380

6. Electrochemical properties

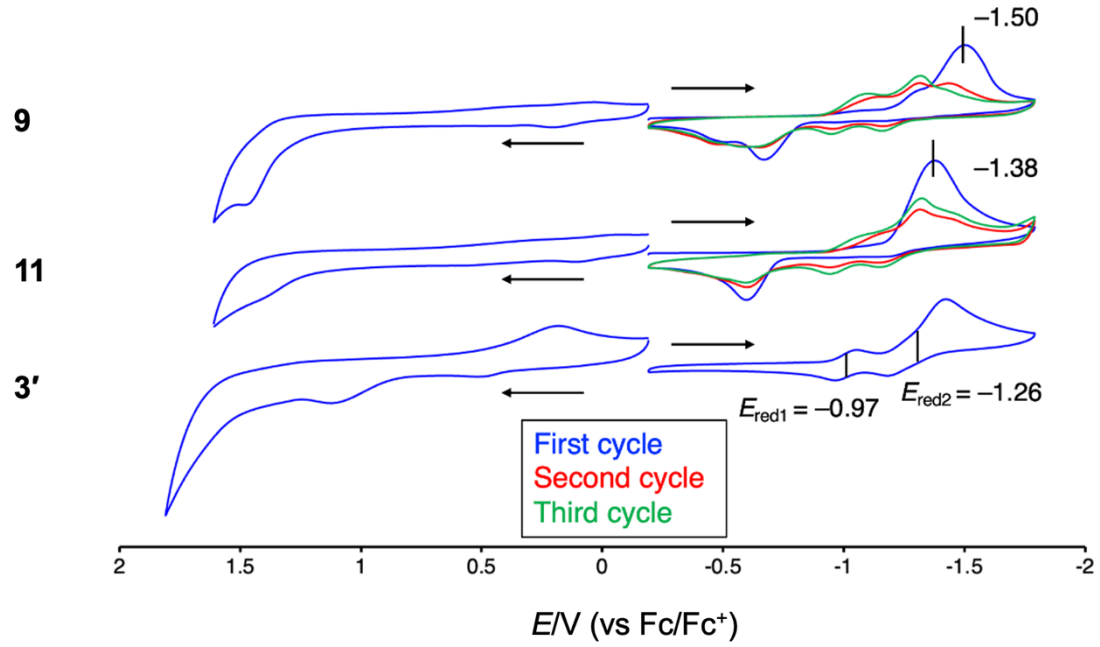


Figure S39. Cyclic voltammograms of **3′**, **9**, and **11**.

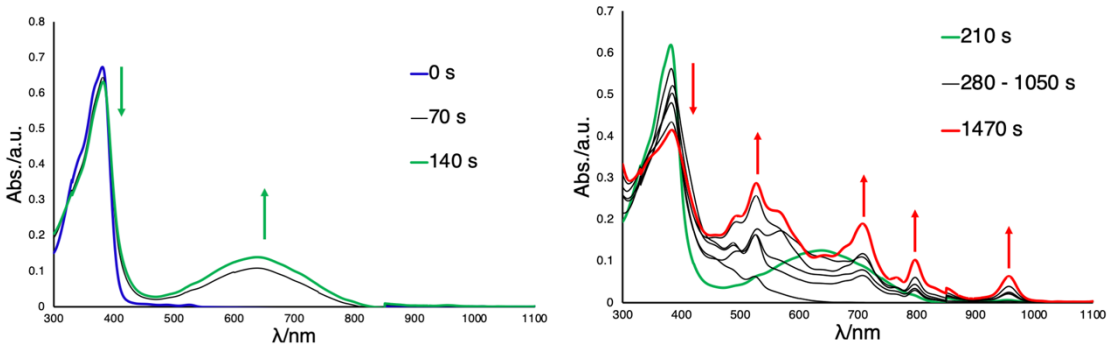


Figure S40. Spectroelectrochemical absorption spectra of **11** in CH_2Cl_2 using $[Bu_4N][PF_6]$ as the supporting electrolyte at −1.2 V (vs Fc/Fc^+).

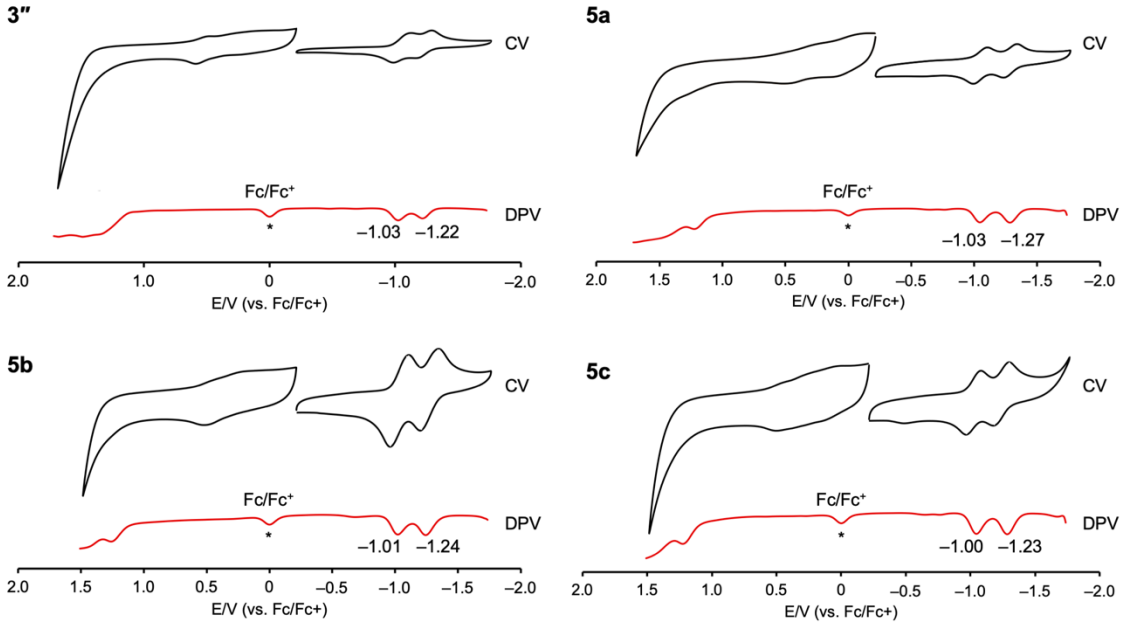


Figure S41. Cyclic voltammograms of **3′**, **5a**, **5b**, and **5c**.

7. Thermal analysis

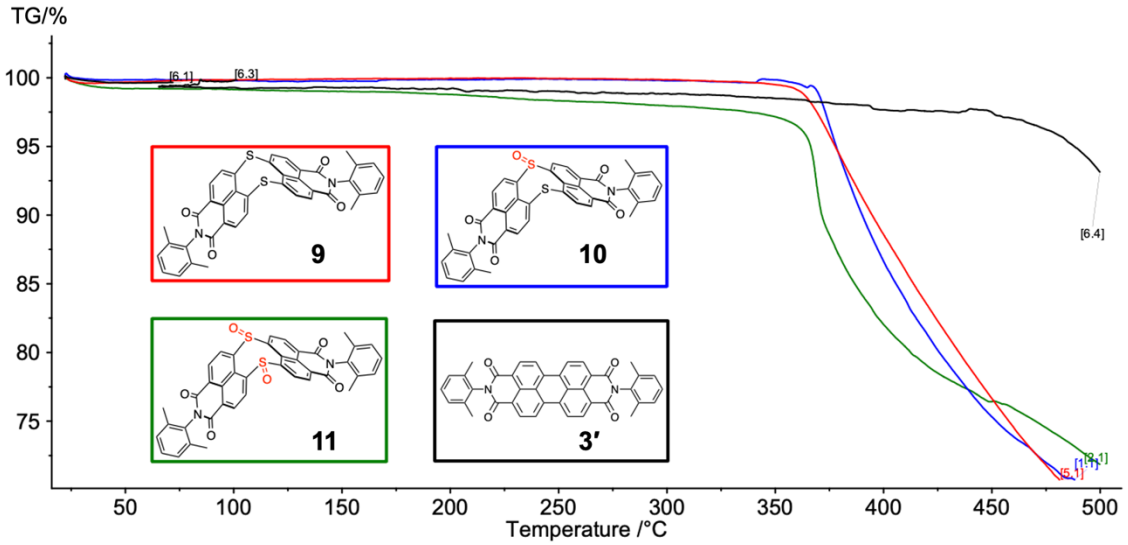


Figure S42. Thermogravimetric analysis (TGA) profiles of **3′**, **9**, **10**, and **11**.

8. DFT Calculations

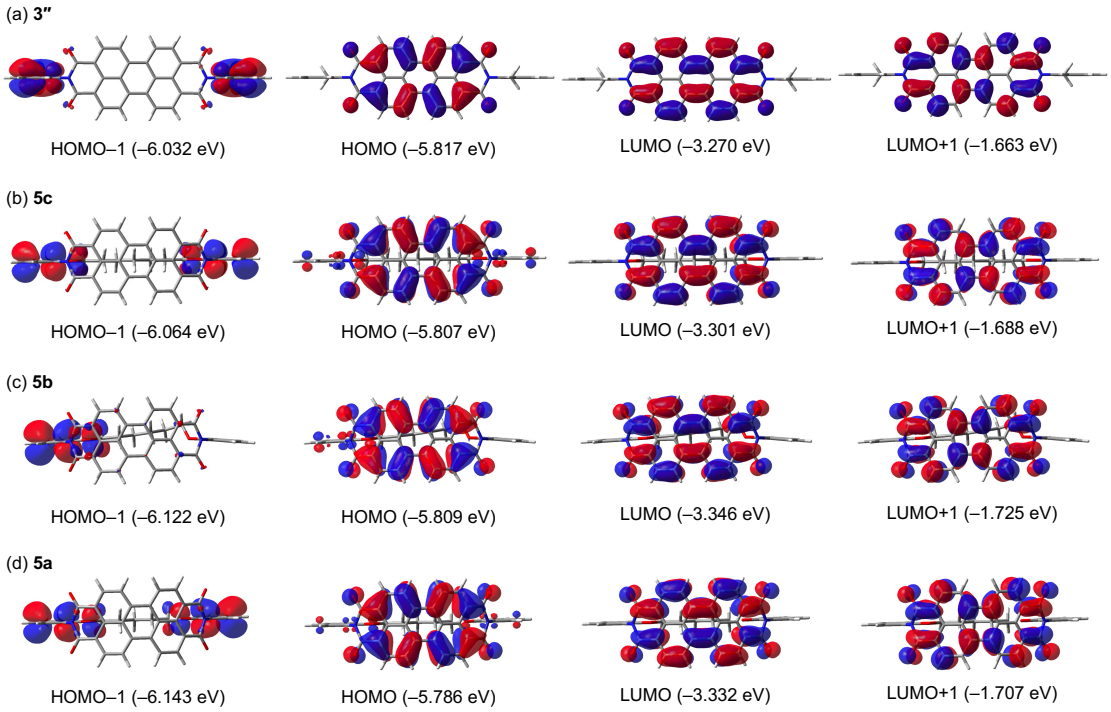


Figure S43. Calculated molecular orbitals of **3″**, **5a**, **5b**, and **5c** (isovalue = 0.02, B3LYP/6-31G(d)).

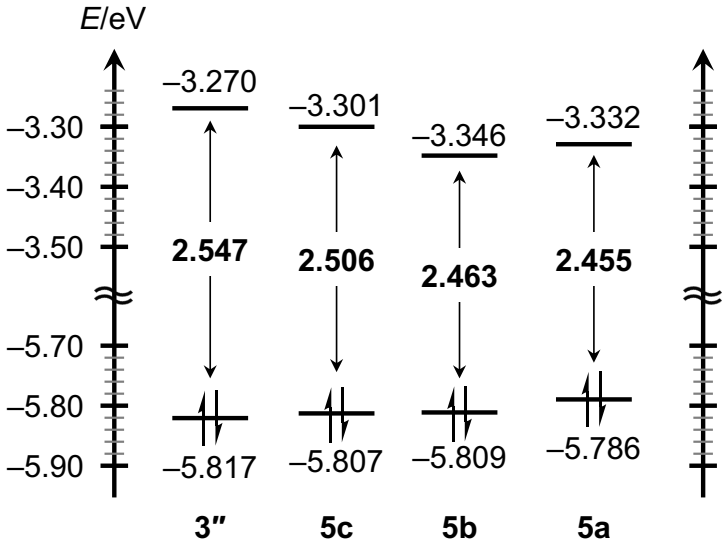


Figure S44. Energy diagrams of **3″**, **5a**, **5b**, and **5c** (B3LYP/6-31G(d)).

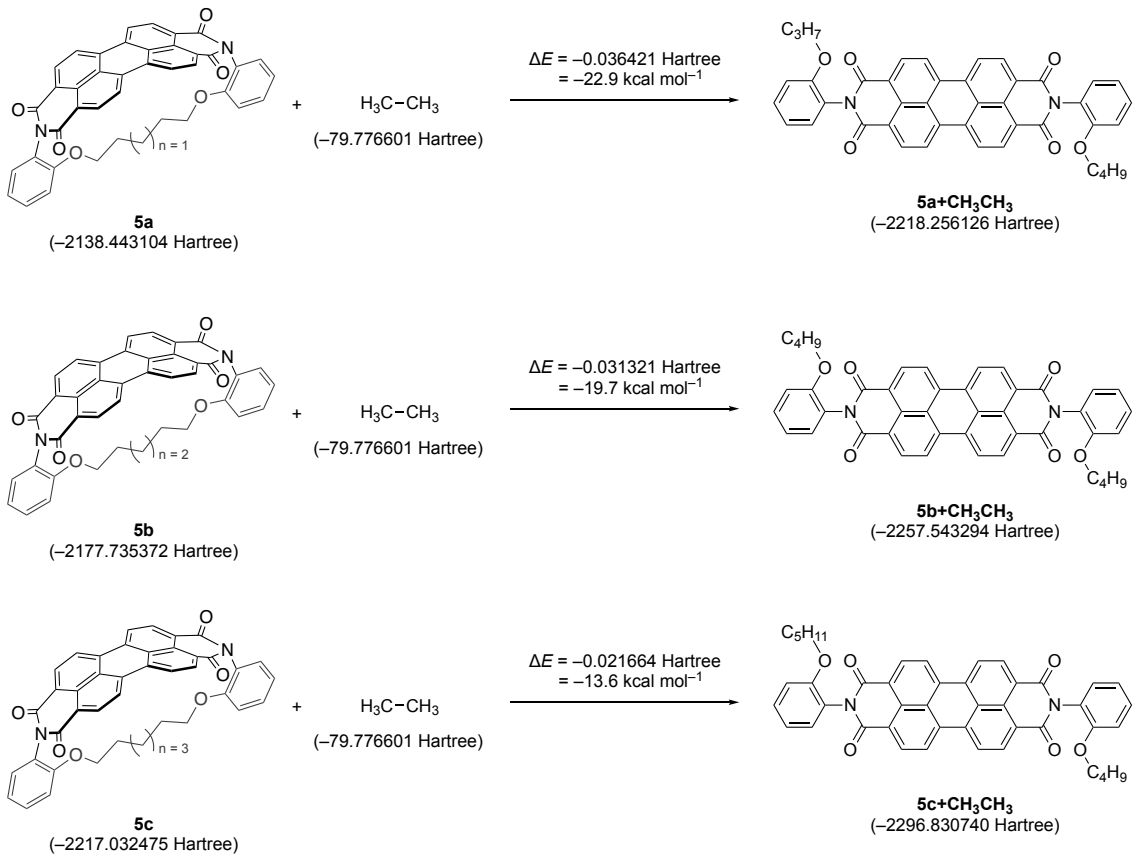
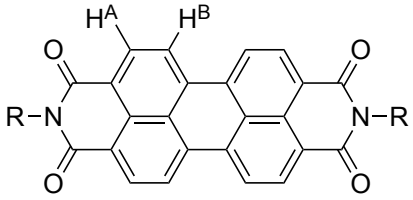


Figure S45. Hypothetical homodesmotic reactions (B3LYP/6-31G(d)).

Table S3. Simulated ^{1}H NMR chemical shifts calculated at the B3LYP/6-31G(d) level. The chemical shifts were averaged for four equivalent protons.



	H^A (ppm)	H^B (ppm)
5a	8.49	8.28
5b	8.52	8.30
5c	8.54	8.35
3	8.60	8.40

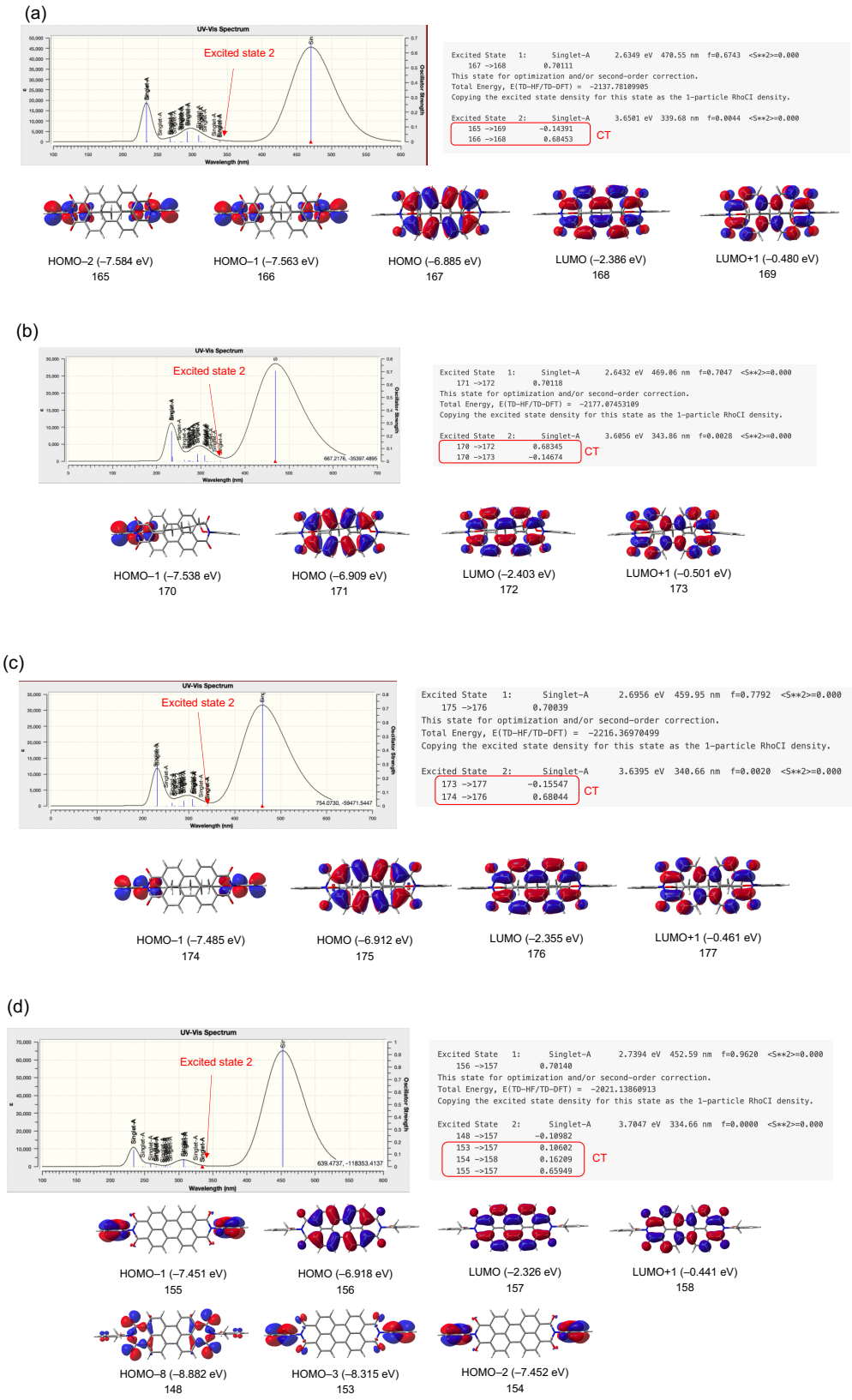


Figure S46. Results of TD-DFT calculations of (a) **5a**, (b) **5b**, (c) **5c**, and (d) **3″**. (B3LYP/6-31G(d)//CAM-B3LYP/6-31G(d)).

Table S4. Cartesian coordinate and geometry of **3″**.

O	6.966945	-0.002646	-2.005822
O	-6.966827	-0.001912	-2.005845
O	5.697872	-2.288734	0.325989
O	5.697776	2.289732	0.322241
N	-5.707245	0.000323	0.380448
C	3.57503	-1.223641	0.345645
O	-5.697805	-2.288948	0.325821
O	-5.697887	2.289522	0.32279
N	5.707226	0.000544	0.380435
C	2.862731	0.000457	0.345739
C	-3.575006	-1.223774	0.34565
C	-2.862753	0.000352	0.345804
C	0.735411	-1.249595	0.344822
C	7.78682	-0.001175	-0.919813
C	-7.147641	0.000267	0.333219
C	-7.786775	-0.000923	-0.919882
C	-3.57505	1.224449	0.343907
C	1.481747	-2.429635	0.344432
H	0.982539	-3.39126	0.344273
C	-9.923338	0.00019	0.215654
H	-11.008618	0.000155	0.160255
C	3.574983	1.224581	0.34374
C	-0.735386	-1.249622	0.344823
C	-1.432681	0.000377	0.344795
C	7.147621	0.000521	0.333247
C	0.735364	1.250427	0.342928
C	2.880576	2.421526	0.340446
H	3.443349	3.348965	0.337632
C	9.184333	-0.001204	-0.970334
H	9.700742	-0.002471	-1.923152
C	-9.184281	-0.00096	-0.97048
H	-9.700652	-0.001878	-1.923318
C	-2.880687	2.421421	0.340657
H	-3.443496	3.348838	0.337951
C	1.481656	2.430493	0.340712
H	0.982414	3.392099	0.339096
C	5.058795	1.250232	0.342369
C	-5.058861	1.250045	0.342642
C	-0.735433	1.2504	0.342969
C	1.432659	0.00043	0.344763
C	9.287508	0.00216	1.454572
H	9.865929	0.003453	2.373118
C	-9.287587	0.001385	1.454424
H	-9.866054	0.002293	2.372942
C	5.05884	-1.249236	0.344388
C	-5.058817	-1.249423	0.344342
C	7.891856	0.002175	1.5047
H	7.368462	0.003475	2.456006
C	-2.880599	-2.420723	0.344153
H	-3.443372	-3.348164	0.342751
C	9.923328	0.00046	0.215831
H	11.008611	0.000423	0.160494
C	-7.891932	0.001417	1.504629

H	-7.368596	0.002331	2.455967
C	-1.481768	2.430439	0.340843
H	-0.982559	3.392062	0.33924
C	2.880666	-2.420617	0.344191
H	3.443474	-3.348037	0.34284
C	-1.481679	-2.42969	0.344409
H	-0.982436	-3.391297	0.344243
C	7.560131	-0.004809	-3.295689
H	8.174175	-0.900734	-3.453446
H	6.730254	-0.006052	-4.004392
H	8.17408	0.890643	-3.456495
C	-7.559927	-0.003432	-3.295751
H	-8.173965	0.892041	-3.456106
H	-6.730006	-0.004191	-4.004404
H	-8.173866	-0.899335	-3.454046

Negative frequency = zero

Sum of electronic and thermal free energies = –2021.807876 Hartree

Table S5. Cartesian coordinate and geometry of **5a**.

O	-3.60828	1.697052	-0.000915
O	3.608299	1.697071	-0.000842
O	-5.291216	-0.545418	2.284631
O	-5.29172	-0.545629	-2.284193
N	5.19382	-0.389193	-0.000097
C	-3.460201	-1.626067	1.224832
O	5.291689	-0.546081	2.28428
O	5.291235	-0.545012	-2.284551
C	0.000015	2.846974	-0.000249
H	0.000245	3.504342	0.880833
H	-0.000206	3.504334	-0.881337
N	-5.19383	-0.389193	0.000215
C	-2.789115	-1.859369	0.00003
C	3.460339	-1.626236	1.224546
C	2.789106	-1.859372	-0.000211
C	-0.734322	-2.380918	1.250594
C	-4.935664	2.015595	-0.000203
C	5.818537	0.910688	0.000112
C	1.262959	1.966427	-0.000598
H	1.247884	1.309193	-0.879135
H	1.248032	1.30865	0.877537
C	4.935702	2.015616	-0.000263
C	-2.598305	2.711803	-0.000163
H	-2.70556	3.347026	0.890526
H	-2.704836	3.347618	-0.89053
C	3.460184	-1.625817	-1.224973
C	-1.48267	-2.313415	2.428285
H	-1.002875	-2.462522	3.388752
C	6.845163	3.490285	0.000849
H	7.244338	4.500989	0.001089
C	-3.460351	-1.625986	-1.224683
C	0.734423	-2.380973	1.250514
C	1.416623	-2.246552	-0.000202
C	-5.818537	0.91069	0.000212
C	-1.262966	1.966462	0.000054
H	-1.248004	1.308752	-0.878128
H	-1.247939	1.309181	0.878549
C	-0.73444	-2.380756	-1.25081
C	-2.828451	-1.927468	-2.419347
H	-3.366034	-1.769263	-3.348402
C	-5.457495	3.309666	-0.000048
H	-4.797082	4.170064	-0.000418
C	5.45755	3.309664	0.000066
H	4.797164	4.170075	-0.000281
C	2.828168	-1.927153	-2.419607
H	3.365633	-1.768764	-3.348704
C	-1.482924	-2.313204	-2.428411
H	-1.003236	-2.462243	-3.38894
C	-4.728927	-0.859353	-1.248794
C	4.728683	-0.859028	-1.249103
C	0.734315	-2.380695	-1.250886
C	-1.416633	-2.246544	-0.000065
C	-7.711917	2.400137	0.000859

H	-8.78662	2.552998	0.001301
C	7.711957	2.400087	0.001312
H	8.786665	2.552921	0.00197
C	-4.728724	-0.859283	1.249098
C	4.728937	-0.859592	1.24879
C	2.598284	2.711775	-0.000427
H	2.705115	3.347528	-0.890801
H	2.70516	3.347071	0.890259
C	-7.190069	1.102585	0.000715
H	-7.840923	0.234554	0.001032
C	2.828424	-1.927897	2.419156
H	3.366011	-1.769866	3.348243
C	-6.845093	3.490315	0.000489
H	-7.244244	4.501028	0.000617
C	7.190069	1.102537	0.000955
H	7.840906	0.234492	0.001338
C	1.482661	-2.31295	-2.428566
H	1.002867	-2.461863	-3.389062
C	-2.828181	-1.92763	2.419406
H	-3.365642	-1.769443	3.34854
C	1.48289	-2.313594	2.428139
H	1.003172	-2.462744	3.388637

Negative frequency = zero

Sum of electronic and thermal free energies = –2138.443104 Hartree

Table S6. Cartesian coordinate and geometry of **5b**.

O	-3.81405	1.63562	-0.157626
O	4.150358	1.946422	-0.259296
O	-5.548973	-0.353018	2.247532
O	-5.489376	-0.852852	-2.291855
N	5.114665	-0.586462	-0.018498
C	-3.682506	-1.503579	1.333846
O	5.08447	-0.189118	2.23563
O	5.246456	-1.180151	-2.228557
C	-0.277563	2.973344	-0.004593
H	-0.452377	3.745466	0.759614
H	-0.243408	3.502203	-0.9682
N	-5.416627	-0.437992	-0.038846
C	-2.99531	-1.862527	0.149236
C	3.254983	-1.413382	1.350553
C	2.597496	-1.848073	0.174581
C	-0.942921	-2.18005	1.465432
C	-5.139334	1.953552	-0.251565
C	6.048127	0.493089	-0.207941
C	1.092202	2.316665	0.261957
H	1.303376	1.562622	-0.506793
H	1.054068	1.779984	1.221089
C	5.51731	1.793031	-0.297392
C	-2.816045	2.66238	-0.184767
H	-3.004645	3.383591	0.623111
H	-2.865151	3.201797	-1.141461
C	3.29411	-1.861635	-1.058015
C	-1.702598	-1.996102	2.622914
H	-1.228707	-2.024792	3.597386
C	7.761788	2.647352	-0.591324
H	8.427626	3.491752	-0.747505
C	-3.657468	-1.783871	-1.099851
C	0.524169	-2.138035	1.47068
C	1.217506	-2.204885	0.22102
C	-6.031213	0.857584	-0.187788
C	-1.456229	1.984409	-0.002825
H	-1.327447	1.242763	-0.801126
H	-1.475646	1.42807	0.943058
C	-0.923945	-2.507685	-1.014012
C	-3.009407	-2.210271	-2.246428
H	-3.53825	-2.163815	-3.192622
C	-5.653014	3.242826	-0.401979
H	-4.988927	4.098397	-0.455108
C	6.38784	2.868842	-0.49153
H	5.98512	3.872602	-0.587898
C	2.663605	-2.336864	-2.195674
H	3.221263	-2.369289	-3.12574
C	-1.66076	-2.582201	-2.198254
H	-1.170335	-2.836167	-3.13085
C	-4.934685	-1.041036	-1.222408
C	4.62785	-1.22869	-1.178595
C	0.544362	-2.526812	-1.000245
C	-1.617084	-2.221495	0.204442
C	-7.911875	2.34386	-0.425154

H	-8.984127	2.498811	-0.493378
C	8.280362	1.35443	-0.508456
H	9.34932	1.184965	-0.594684
C	-4.964947	-0.764953	1.259614
C	4.555477	-0.712367	1.265776
C	2.233356	3.347922	0.30377
H	2.338074	3.829744	-0.677445
H	1.963825	4.143852	1.013595
C	-7.399719	1.051397	-0.274588
H	-8.055216	0.18837	-0.224033
C	2.600787	-1.480898	2.568879
H	3.12859	-1.163591	3.462085
C	-7.037589	3.426161	-0.487283
H	-7.428333	4.433361	-0.604761
C	7.4166	0.275596	-0.320673
H	7.793805	-0.73974	-0.256364
C	1.304753	-2.669864	-2.162956
H	0.830662	-2.965786	-3.091701
C	-3.057421	-1.650762	2.56034
H	-3.608933	-1.401128	3.460699
C	1.255354	-1.85781	2.627601
H	0.762244	-1.834728	3.592361
C	3.605152	2.83354	0.738287
H	4.281084	3.68421	0.882626
H	3.545782	2.289614	1.691052

Negative frequency = zero

Sum of electronic and thermal free energies = –2177.735372 Hartree

Table S7. Cartesian coordinate and geometry of **5c**.

O	5.533952	-0.871727	-2.288384
O	-5.533814	-0.867552	2.288808
O	-5.534158	-0.872258	-2.288239
O	-4.643618	1.661017	-0.002126
O	5.534016	-0.867958	2.288691
O	4.643577	1.660923	-0.000353
N	5.51733	-0.777917	0.000086
N	-5.51723	-0.777845	0.000191
C	-2.836824	-1.722271	0.000975
C	-4.933361	-1.084896	-1.248115
C	-0.735214	-2.038152	-1.249084
C	-1.427121	-1.955265	0.001152
C	-6.000898	1.589223	-0.00202
C	6.509833	0.271197	-0.000845
C	-0.735172	-2.036123	1.251497
C	-2.863762	-1.771186	-2.418714
H	-3.417025	-1.676076	-3.347082
C	4.933334	-1.082612	1.248913
C	-3.535374	-1.582824	-1.222887
C	-7.875048	0.042781	-0.000583
H	-8.239526	-0.979304	0.000397
C	2.836852	-1.722252	0.000892
C	-6.880463	2.670741	-0.003096
H	-6.501949	3.687687	-0.004137
C	0.735245	-2.036148	1.251469
C	4.933276	-1.084666	-1.248259
C	2.863686	-1.771011	-2.418808
H	3.416901	-1.675806	-3.347195
C	3.53534	-1.582692	-1.222997
C	1.483719	-2.000099	2.43006
H	0.992125	-2.092707	3.391451
C	-3.535319	-1.580659	1.224626
C	2.8638	-1.767207	2.420646
H	3.417047	-1.670524	3.348862
C	0.735199	-2.038121	-1.249111
C	3.535404	-1.58075	1.224518
C	-6.509805	0.271193	-0.000775
C	-2.863671	-1.767046	2.420739
H	-3.416874	-1.670284	3.348974
C	-1.483669	-2.004002	-2.427741
H	-0.992057	-2.098086	-3.388978
C	-8.759513	1.12716	-0.00162
H	-9.830911	0.952485	-0.001472
C	-8.258739	2.427264	-0.002865
H	-8.943043	3.27145	-0.003712
C	-1.483597	-1.99999	2.430114
H	-0.991971	-2.092547	3.391494
C	1.483607	-2.003901	-2.427795
H	0.991964	-2.097979	-3.389018
C	-4.933215	-1.082451	1.249032
C	6.000859	1.5892	-0.001263
C	7.875088	0.042844	-0.001556
H	8.239587	-0.979232	-0.001255

C	1.427149	-1.955254	0.001103
C	-3.916113	2.893148	-0.002053
H	-4.169311	3.484818	0.888781
H	-4.165913	3.482789	-0.895207
C	6.880382	2.670755	-0.002465
H	6.501838	3.687689	-0.002857
C	8.258667	2.427337	-0.003168
H	8.942927	3.271559	-0.004097
C	8.759507	1.127258	-0.002709
H	9.830914	0.952638	-0.003282
C	-2.460791	2.429611	0.001264
H	-2.338322	1.77653	-0.872303
H	-2.340404	1.781612	0.878908
C	-1.330823	3.470616	-0.000678
H	-1.39765	4.118269	-0.885923
H	-1.400417	4.125037	0.879353
C	3.916048	2.893047	-0.001091
H	4.166135	3.482263	-0.894441
H	4.168955	3.48513	0.889553
C	2.460735	2.429512	0.002014
H	2.338431	1.776221	-0.871418
H	2.340137	1.781737	0.879791
C	-0.000026	2.699196	0.004272
H	0.000057	2.02678	-0.865955
H	-0.000135	2.037042	0.88232
C	1.330799	3.470562	-0.000404
H	1.397899	4.118081	-0.885728
H	1.400186	4.125105	0.879551

Negative frequency = zero

Sum of electronic and thermal free energies = –2217.032475 Hartree

Table S8. Cartesian coordinate and geometry of **5a+CH_3CH_3**.

O	-7.461078	-1.006329	0.000235
O	7.142053	0.735386	-0.000094
O	-5.740397	1.009149	-2.289423
O	-5.740214	1.010575	2.289107
N	5.419825	-1.341834	0.000121
C	-3.658487	0.595929	-1.224093
O	5.422029	-1.281999	-2.289171
O	5.422102	-1.281099	2.289389
N	-5.737918	1.070418	-0.000177
C	-2.960862	0.451682	-0.000096
C	3.340232	-0.868211	-1.223903
C	2.642664	-0.723338	0.000044
C	-0.879018	0.014089	-1.250074
C	-8.039856	0.223902	0.000005
C	6.839577	-1.590852	0.000149
C	7.979659	1.892285	-0.000152
H	8.625842	1.882933	0.889492
H	8.625906	1.8828	-0.889748
C	7.721424	-0.494496	0.00004
C	-8.298473	-2.162767	0.000385
H	-8.944786	-2.154658	-0.889343
H	-8.944799	-2.154424	0.890104
C	3.340278	-0.867701	1.224025
C	-1.610135	0.164304	-2.430073
H	-1.121971	0.05988	-3.391708
C	9.579438	-2.045605	0.000201
H	10.653037	-2.214088	0.000222
C	-3.658391	0.596684	1.223867
C	0.560744	-0.28647	-1.250035
C	1.243051	-0.42979	0.00001
C	-7.157576	1.319865	-0.000201
C	-0.878934	0.01479	1.249986
C	-2.979315	0.451946	2.420854
H	-3.53075	0.56493	3.348234
C	-9.418242	0.462836	-0.000026
H	-10.11928	-0.363469	0.000129
C	9.099906	-0.733046	0.00007
H	9.800702	0.093453	-0.000017
C	2.661272	-0.72242	2.420977
H	3.212768	-0.834954	3.348374
C	-1.609951	0.165767	2.429951
H	-1.121708	0.061949	3.391612
C	-5.111135	0.899516	1.249273
C	4.793064	-1.170473	1.249487
C	0.560806	-0.285879	1.25002
C	-1.561254	0.158089	-0.000061
C	-9.020741	2.857491	-0.000447
H	-9.398091	3.875303	-0.000617
C	8.703221	-3.127866	0.000305
H	9.080922	-4.145549	0.000408
C	-5.111236	0.898738	-1.24957
C	4.793022	-1.170972	-1.249294
C	-7.644719	2.61946	-0.000422

H	-6.936766	3.44275	-0.000572
C	2.661181	-0.723425	-2.420889
H	3.212648	-0.836318	-3.348259
C	-9.897349	1.775547	-0.000252
H	-10.970887	1.944389	-0.000271
C	7.327118	-2.890284	0.000277
H	6.619428	-3.713803	0.000357
C	1.291893	-0.436272	2.430012
H	0.803702	-0.33201	3.391653
C	-2.979506	0.450453	-2.421044
H	-3.531019	0.562843	-3.348449
C	1.291795	-0.437319	-2.429991
H	0.803569	-0.333447	-3.391656
C	7.07684	3.117879	-0.000275
H	6.423514	3.07233	-0.881171
H	6.423413	3.072425	0.880551
C	7.869377	4.431451	-0.0003
H	8.528839	4.461419	0.878538
H	8.529027	4.461276	-0.879003
C	-7.39581	-3.388644	0.000551
H	-6.743651	-3.342117	-0.879994
H	-6.743426	-3.34168	0.880907
C	-8.196451	-4.694683	0.000981
H	-7.527273	-5.561208	0.000899
H	-8.838496	-4.771557	0.886833
H	-8.83903	-4.771826	-0.884465
C	6.965526	5.66849	-0.000498
H	6.3179	5.685593	0.884346
H	7.555423	6.591751	-0.000499
H	6.318108	5.685459	-0.885497

Negative frequency = zero

Sum of electronic and thermal free energies = –2218.256126 Hartree

Table S9. Cartesian coordinate and geometry of **5b+CH_3CH_3**.

O	7.323942	0.654976	0.000139
O	-7.323815	-0.655177	0.000015
O	5.544969	-1.309376	-2.289395
O	5.544853	-1.310072	2.289145
N	-5.540967	1.370182	-0.000004
C	3.476231	-0.834671	-1.22407
O	-5.544999	1.310145	-2.289282
O	-5.545038	1.309776	2.289264
N	5.540803	-1.370158	-0.000135
C	2.783185	-0.669704	-0.000098
C	-3.476297	0.835204	-1.223994
C	-2.783291	0.669953	-0.000037
C	0.715111	-0.171159	-1.250101
C	7.86656	-0.591552	-0.000001
C	-6.952732	1.661071	0.000009
C	-8.195239	-1.786801	0.000045
H	-8.840882	-1.75826	0.889674
H	-8.840908	-1.758289	-0.889565
C	-7.866609	0.591278	0.00002
C	8.195536	1.786465	0.000235
H	8.841202	1.7579	-0.889375
H	8.841174	1.757776	0.889863
C	-3.476322	0.834986	1.223935
C	1.441445	-0.343123	-2.430082
H	0.956526	-0.224582	-3.391725
C	-9.677981	2.196579	0.000033
H	-10.746128	2.396735	0.000045
C	3.476172	-0.835029	1.223859
C	-0.715163	0.17175	-1.250086
C	-1.392935	0.335259	-0.000052
C	6.952533	-1.661218	-0.000143
C	0.71506	-0.171483	1.249951
C	2.801677	-0.67022	2.420834
H	3.349555	-0.799329	3.348216
C	9.237364	-0.870883	-0.000006
H	9.962341	-0.065489	0.0001
C	-9.237455	0.87042	0.000037
H	-9.962319	0.064927	0.000056
C	-2.801859	0.669938	2.420894
H	-3.349766	0.79884	3.348287
C	1.441334	-0.34381	2.429917
H	0.956367	-0.225554	3.391571
C	4.919371	-1.180609	1.249271
C	-4.919534	1.180509	1.249378
C	-0.715199	0.171488	1.249966
C	1.392835	-0.334981	-0.000083
C	8.769736	-3.252866	-0.000286
H	9.117061	-4.281313	-0.000395
C	-8.770152	3.252467	0.000015
H	-9.11762	4.280866	0.000009
C	4.919435	-1.180231	-1.249513
C	-4.91951	1.180719	-1.249406
C	7.401281	-2.974546	-0.000283

H	6.669466	-3.776703	-0.00039
C	-2.801808	0.670368	-2.420968
H	-3.3497	0.79942	-3.34835
C	9.677708	-2.197105	-0.000148
H	10.745829	-2.397402	-0.000149
C	-7.401662	2.974338	0.000003
H	-6.669959	3.776597	-0.000009
C	-1.44151	0.343551	2.429947
H	-0.956569	0.225099	3.391591
C	2.801794	-0.669513	-2.421029
H	3.34972	-0.798337	-3.348422
C	-1.441454	0.344004	-2.430051
H	-0.956495	0.225718	-3.391706
C	-7.329076	-3.038564	0.000047
H	-6.674705	-3.012476	-0.880865
H	-6.674573	-3.012377	0.880857
C	-8.160187	-4.328081	0.000186
H	-8.820205	-4.338393	0.879058
H	-8.82048	-4.338419	-0.878479
C	7.32956	3.038357	0.000301
H	6.67525	3.012455	-0.880662
H	6.674988	3.012174	0.88106
C	8.16086	4.327753	0.000642
H	8.820794	4.337886	0.879578
H	8.82124	4.338087	-0.877959
C	-7.293397	-5.591355	0.000066
H	-6.646514	-5.627553	0.884877
H	-7.910391	-6.49673	0.000191
H	-6.646816	-5.62759	-0.884964
C	7.294246	5.591149	0.000557
H	6.647767	5.627564	-0.88454
H	6.647272	5.627344	0.885301
H	7.911364	6.49644	0.000845

Negative frequency = zero

Sum of electronic and thermal free energies = –2257.543294 Hartree

Table S10. Cartesian coordinate and geometry of **5c+CH_3CH_3**.

O	7.530352	0.518102	-0.001002
O	-7.160304	-0.225245	-0.001152
O	5.676285	-1.373451	-2.287579
O	5.675351	-1.377835	2.29094
N	-5.298905	1.728396	0.002455
C	3.627146	-0.820332	-1.222179
O	-5.304556	1.671477	-2.286898
O	-5.306074	1.664964	2.291633
N	5.669348	-1.435874	0.001614
C	2.940708	-0.629946	0.001832
C	-3.2561	1.115519	-1.221698
C	-2.570324	0.92215	0.002214
C	0.893509	-0.051334	-1.248051
C	8.023791	-0.748692	0.000032
C	-6.698146	2.074576	0.00248
C	-8.075774	-1.321719	-0.003322
H	-8.720064	-1.269121	0.886138
H	-8.719388	-1.266161	-0.89309
C	-7.653462	1.041601	0.000579
C	8.445555	1.614609	-0.003713
H	9.088829	1.559161	-0.893781
H	9.090339	1.562313	0.885459
C	-3.256886	1.112127	1.226215
C	1.612907	-0.250126	-2.428071
H	1.133034	-0.112346	-3.389683
C	-9.400139	2.717087	0.002491
H	-10.459569	2.959195	0.002483
C	3.626622	-0.822797	1.225752
C	-0.522508	0.346384	-1.247953
C	-1.193847	0.534305	0.002118
C	7.06864	-1.781803	0.001503
C	0.892909	-0.054079	1.252
C	2.958705	-0.633304	2.422763
H	3.501052	-0.78412	3.350122
C	9.382642	-1.081388	-0.000167
H	10.13855	-0.304955	-0.001365
C	-9.012257	1.374597	0.000602
H	-9.768308	0.598306	-0.00084
C	-2.589629	0.919743	2.423128
H	-3.132463	1.068396	3.350549
C	1.61185	-0.255073	2.431925
H	1.131591	-0.119135	3.393606
C	5.055474	-1.223588	1.251086
C	-4.685717	1.513049	1.251729
C	-0.523228	0.34321	1.252095
C	1.564203	-0.242187	0.001927
C	8.822236	-3.443261	0.002811
H	9.129108	-4.484495	0.003926
C	-8.45141	3.736377	0.004366
H	-8.758085	4.777669	0.005827
C	5.055986	-1.221131	-1.247697
C	-4.684892	1.516589	-1.247018
C	7.465711	-3.11168	0.002923

H	6.703106	-3.884623	0.004096
C	-2.588079	0.926442	-2.41871
H	-3.130292	1.077762	-3.346064
C	9.770783	-2.423806	0.001222
H	10.830255	-2.665723	0.001072
C	-7.094951	3.404531	0.004347
H	-6.332193	4.177325	0.005781
C	-1.242794	0.541419	2.432108
H	-0.763055	0.403181	3.393721
C	2.959725	-0.628492	-2.419093
H	3.502436	-0.777562	-3.346521
C	-1.241282	0.547986	-2.427873
H	-0.760919	0.412438	-3.389558
C	-7.259538	-2.60663	-0.005134
H	-6.604278	-2.603846	-0.885667
H	-6.605113	-2.606874	0.876027
C	-8.141272	-3.861838	-0.007709
H	-8.802936	-3.849126	0.871107
H	-8.801872	-3.846253	-0.887276
C	7.629268	2.899447	-0.005277
H	6.973465	2.897416	-0.885506
H	6.975151	2.900695	0.876211
C	8.510466	4.155265	-0.008429
H	9.17145	4.141171	0.869666
H	9.169587	4.138055	-0.887866
C	-7.332065	-5.165462	-0.009347
H	-6.67203	-5.181516	0.869253
H	-6.670925	-5.178629	-0.887164
C	7.694078	5.451672	-0.00986
H	7.048321	5.511753	-0.894193
H	7.050229	5.514907	0.875644
H	8.346242	6.332051	-0.01213
C	-8.211737	-6.419492	-0.011961
H	-7.605316	-7.332203	-0.01308
H	-8.859921	-6.451456	0.872451
H	-8.858809	-6.448547	-0.897288

Negative frequency = zero

Sum of electronic and thermal free energies = –2296.830740 Hartree

Table S11. Cartesian coordinate and geometry of ethane.

C	0	0	0.765306
H	-0.510273	0.884352	1.16449
H	1.021008	-0.000267	1.16449
H	-0.510735	-0.884085	1.16449
C	0	0	-0.765306
H	0.510735	-0.884085	-1.16449
H	-1.021008	-0.000267	-1.16449
H	0.510273	0.884352	-1.16449

Negative frequency = zero

Sum of electronic and thermal free energies = –79.776601 Hartree

9. Photophysical properties

Method to determine quantum yields of the triplet generations: To obtain quantum yields of the intersystem crossings (ISC), we conducted transient absorption (TA) spectroscopic analysis of **5b** and **5c** (Figure SX). The nanosecond transient absorption data were obtained using a nanosecond time-resolved optical absorption spectrometer system (UNISOKU, TSP-1000-KK) at room temperature. For the light excitation of 532 nm light, a Nd: YAG laser (Continuum Minilite II, fwhm = 5 ns, pulse energy = 0.3 mJ/pulse, pulse repetition frequency = 10 Hz) was employed. The excitation wavelength was the second harmonics (532 nm) of the 1064 nm pump laser. The sample solutions were deoxygenated by the freeze-pump-thaw cycle in the CH_2Cl_2 solutions.

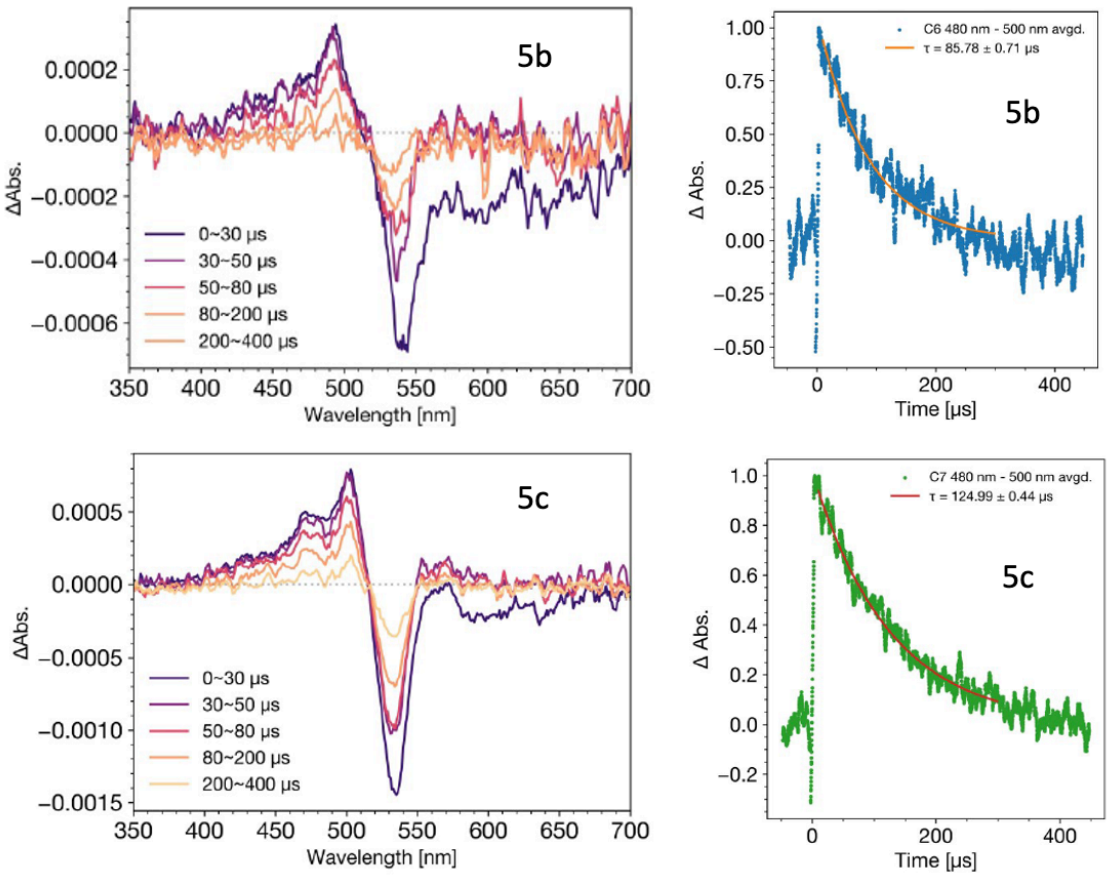


Figure S477. TA spectra of **5b** and **5c** by the 532 nm laser irradiations. Time profiles of the absorbance changes in the 480–500 nm regions are shown in the right panels.

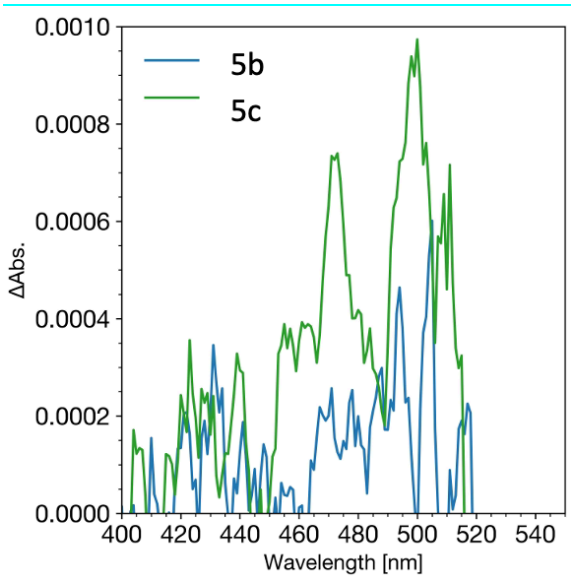


Figure S488. TA spectra of **5b** and **5c** at 1 μs after the 532 nm laser irradiations.

The TA spectra In Figure S47 are almost identical with the reported TA spectra[5] of the excited triplet states of **3‴**. Thus, these bands originate from the triplet exatons generated by the ISC.

The optical densities of the 532 nm absorptions are determined from the light pathlengths of l = 0.1 [cm] in the UV-VIS measurements and the actual path (0.45 cm) employed with the TA measurements. The absorbances were A_{532} = 0.1128 (**5b**) and 0.1259 (**5c**) in the UV-VIS. Thus, for the TA experimental setups, the following absorbances were obtained:

$$A_{532nm,5b} = 0.56655$$
$$A_{532nm,5c} = 0.5076$$

The S_1 state concentration [S_1] is determined using the numbers (mol) of the laser photons ($N_{Ph} = 8.0346\ldots\times 10^{14}$) per pulse and the rate of the absorption ($1-10^{-A_{532nm}}$) by the followings:

$$N_{S1,5b} = \frac{N_{Ph}\times\left(1-10^{-A_{532}nm,5b}\right)}{N_A} = \frac{8.0346\ldots\times 10^{14}\times(1-10^{-0.56655})}{6.022\times 10^{23}[mol^{-1}]}$$
$$= 9.7256024\ldots\times 10^{-10}[mol]$$
$$N_{S1,5c} = \frac{N_{Ph}\times(1-10^{-A_{532,5c}})}{N_A} = \frac{8.0346\ldots\times 10^{14}\times(1-10^{-0.5076})}{6.022\times 10^{23}[mol^{-1}]}$$
$$= 9.1991906\ldots\times 10^{-10}[mol]$$

$[S_1]$ is thus obtained as,

$$[S_1]_{5b} = N_{S1,5b}/V = 3.05754\ldots \times 10^{-5}[M]$$
$$[S_1]_{5c} = N_{S1,5c}/V = 2.89204\ldots \times 10^{-5}[M]$$

where irradiation volume (V) is estimated from the irradiation path ($0.45[cm]$) and the radius of the laser spot, as, $V = \pi r^2 l = \pi \times 0.15[cm] \times 0.15[cm] \times 0.45[cm] = 3.18086\ldots \times 10^{-5}[L^{-1}]$.

From Figure S49, the absorbance peak tops around 500 nm are $Abs.(\mathrm{T1})_{5b} = 0.0005$ and $Abs.(\mathrm{T1})_{5c} = 0.001$, respectively. Using the reported difference of the molar excitation coefficients $(\varepsilon_T - \varepsilon_{S0}) \approx 40000\,[M^{-1}cm^{-1}]$ between the triplet state and the ground state absorption[5], the triplet concentrations are estimated as follows:

$$[T]_{5b} = \frac{Abs.(TT)_{5b}}{(\varepsilon_T - \varepsilon_{S0}) \times l} = \frac{0.0005}{40000 \times 0.45\ [cm]} = 2.8 \times 10^{-8}[M]$$

$$[T]_{5c} = \frac{Abs.(TT)_{5c}}{(\varepsilon_T - \varepsilon_{S0}) \times l} = \frac{0.001}{40000 \times 0.45\ [cm]} = 5.6 \times 10^{-8}[M]$$

Thus, the triplet yields in Table 2 are estimated as follows:

$$\Phi_{T,5b} = \frac{[T]_{5b}}{[S_1]_{5b}} = \frac{2.8 \times 10^{-8}[M]}{3.05754\ldots \times 10^{-5}[M]} \approx 0.0009$$

$$\Phi_{T,5c} = \frac{[T]_{5c}}{[S_1]_{5c}} = \frac{5.6 \times 10^{-8}[M]}{2.89204\ldots \times 10^{-5}[M]} = \approx 0.0019$$

10. References

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