Supporting Information

Facile two-step Synthesis of *para*-Dithienopyrazines

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1 Experimental Procedures

1.1 General Information

Chemicals were bought from commercial suppliers (abcr, Acros, Alfa Aesar, BLDPharm, Carbolution, Chempur, Fluka, Merck, Sigma Aldrich and TCI) and used as delivered. Anhydrous solvents were dispensed from a solvent purification system MB SPS-800. Solvents were degassed by freeze-pump-thaw technique. Deuterated solvents were bought from Eurisotop and Sigma Aldrich.

Melting points (mp) were measured in open glass capillaries on a Stuart SMP10 melting point apparatus and are uncorrected.

R_f-values were determined by analytical thin layer chromatography (TLC) on aluminium sheets coated with silica gel produced by Macherey-Nagel (ALUGRAM® Xtra SIL G/25 UV_{254}). Detections was accomplished using UV-light (254 and 365 nm) or a TLC staining solution (vanillin and ninhydrine).

Nuclear magnetic resonance (NMR) spectra were, if not mentioned otherwise, recorded at room temperature at the organic chemistry department of Heidelberg University under the supervision of Dr. J. Graf on the following spectrometers: Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Fourier 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz), Bruker Avance III 600 (600 MHz), Bruker Avance NEO 700 (700 MHz). Chemical shifts δ are given in ppm and coupling constants *J* in Hz. Spectra were referenced to residual solvent protons according to Fulmer *et al.*[1] or for TCE-d_2 to 6.00 ppm (^{1}H) and 73.8 ppm (^{13}C) respectively. The following abbreviations were used to describe the observed multiplicities: for ^{1}H NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sext = sextet, sept = septet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, br = broad signal; for ^{13}C{^{1}H} NMR spectra: s = quarternary carbon, d = CH carbon, t = CH_2 carbon and q = CH_3 carbon. ^{13}C{^{1}H} NMR spectra are proton decoupled and interpreted with help of DEPT- and 2D spectra. All spectra were integrated and processed using MestreNova software.

High-resolution mass spectra (HR-MS) were recorded at the chemistry department of Heidelberg University under the supervision of Dr. J. Gross on the following spectrometers: JEOL AccuTOF GCx (EI), Bruker ApexQe hybrid 9.4 T FT-ICR (ESI, MALDI, DART), Finnigan LCQ (ESI), Bruker AutoFlex Speed (MALDI) and Bruker timsTOFfleX (ESI, MALDI).

Infrared spectra were recorded from a neat powder or oil on a FT-IR spectrometer (Bruker LUMOS) with a Germanium ATR-crystal. For the most significant bands the wave numbers are given.

UV-Vis spectra were recorded on a Jasco UV-Vis V-670. Fluorescence spectra were recorded on a Jasco FP6500. Quantum yields (QY) were recorded on a Jasco FP-8600 fluorescence spectrometer equipped with a ILF-835 100 mm dia. Integrating sphere or determined according to the publication from C. Würth *et al.* using quinine sulfate dihydrate as standard.[2]

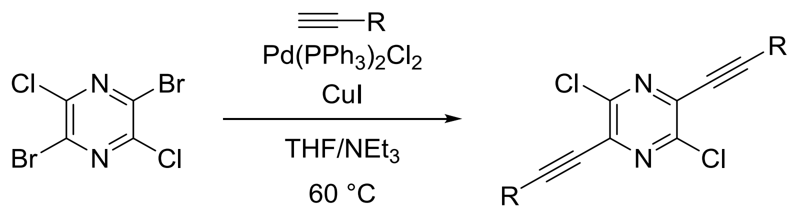
Cyclic voltammograms were measured on a VERSASTAT3-200 potentiostat, using a glassy carbon working electrode, a silver reference electrode and a platinum/titanium counter electrode. Measurements were carried out in a 0.1 M tetrabutylammonium hexafluorophosphate solution in anhydrous and degassed DCM. Ferrocene/ferrocenium was used as internal standard.

X-ray crystallography was carried out at the chemistry department of Heidelberg University under the supervision of Dr. F. Rominger on the following instruments: Bruker Smart APEX II Quazar (with Mo-microsource) and Stoe Stradivari (with Co-microsource and Pilatus detector). The structures were processed with Mercury 4.3.0.

For flash column chromatography silica gel (Sigma-Aldrich, pore size 60 Å, 70-230 mesh, 63-200 µm) or aluminium oxide (Honeywell, pore size 60 Å, activated, neutral) was used as stationary phase. As eluents different mixtures of petroleum ether (PE), ethyl acetate (EA) or dichloromethane (DCM) were used.

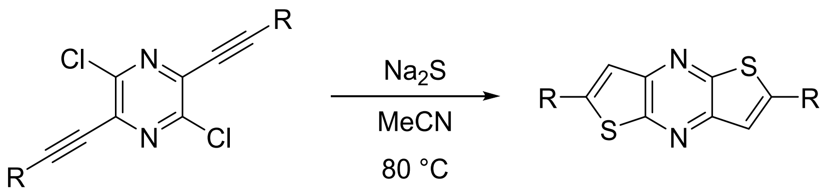
1.2 General Procedures

General Procedure 1 (GP1): Sonogashira cross coupling



In a heat gun-dried Schlenk flask under an atmosphere of nitrogen, 2,5-dibromo-3,6-dichloropyrazine (1.00 eq.), $Pd(PPh_3)_2Cl_2$ (3 mol %) and CuI (3 mol %) were dissolved in a degassed mixture of THF (20 ml) and triethylamine (20 ml). After stirring for 5 min, the corresponding alkyne (2.05 eq.) was added. The mixture was stirred at 60 °C overnight. The reaction was cooled and solvents were removed under reduced pressure. The crude product was purified by flash column chromatography.

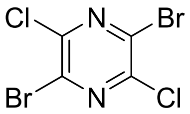
General Procedure 2 (GP2): Nucleophilic cyclization to Dithienopyrazines



In a 15 ml sealed crimp-vial, bis-ethynylpyrazine (1.00 eq.) and Na_2S (6.00 eq.) were suspended in MeCN (10 ml). The mixture was stirred at 80 °C overnight. The reaction was cooled, saturated NH_4Cl solution was added and the aqueous phase was extracted with DCM (3 x 50 ml). The combined organic phase was dried over Na_2SO_4 and the crude product was purified by precipitation or column chromatography.

1.3 Synthesis of Compounds

2,5-dibromo-3,6-dichloropyrazine (1)

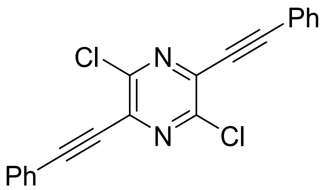


To a solution of 5-bromo-6-chloropyrazin-2-amine (10.0 g, 48.0 mmol, 1.00 eq.) in MeOH (100 ml) was added N-chlorosuccinimide (7.05 g, 52.8 mmol, 1.10 eq.) and the resulting mixture was stirred at 50 °C over night. Water (500 ml) was added and the colorless precipitate was collected by filtration and dried under reduced pressure. The compound was dissolved in HBr (48 wt%, 320 ml) and THF (160 ml). The mixture was cooled to 0 °C and $NaNO_2$ (8.21 g, 119 mmol, 2.50 eq.) was added in small portions. The reaction mixture was stirred at rt for 1 h. Afterwards, KOH was added until neutralization of the mixture and the crude product was extracted with EA, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel, PE/EA 30:1) yielded a colorless solid (8.10 g, 26.4 mmol, 56 %).

R_f: 0.50 (silica gel, PE/EA = 50:1); **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 146.8 (s), 136.5 (s) ppm.

The spectroscopic data correspond to those previously reported in the literature.[3]

2,5-Dichloro-3,6-bis(phenylethynyl)pyrazine (2a)

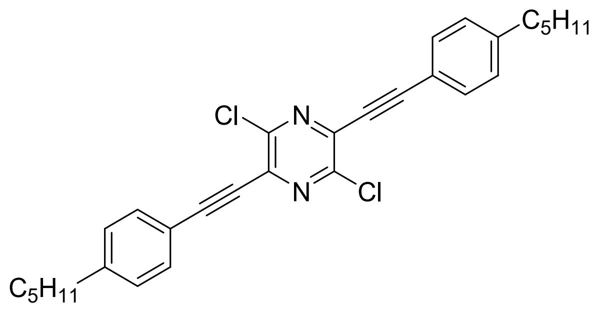


The reaction was carried out according to **GP1** with **1** (3.00 g, 9.78 mmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (206 mg, 294 μmol, 0.03 eq.), CuI (55.9 mg, 294 μmol, 0.03 eq.) and phenylacetylene (2.10 g, 20.5 mmol, 2.05 eq.). Purification by column chromatography (silica gel, PE/DCM 5:1 → DCM) yielded a pale yellow solid (3.40 g, 9.74 mmol, 99 %).

R_f: 0.60 (silica gel, PE/EA = 10:1); **^1H NMR** (300 MHz, $CDCl_3$): δ = 7.70 – 7.63 (m, 4H), 7.52 – 7.36 (m, 6H) ppm.

The spectroscopic data correspond to those previously reported in the literature.[4]

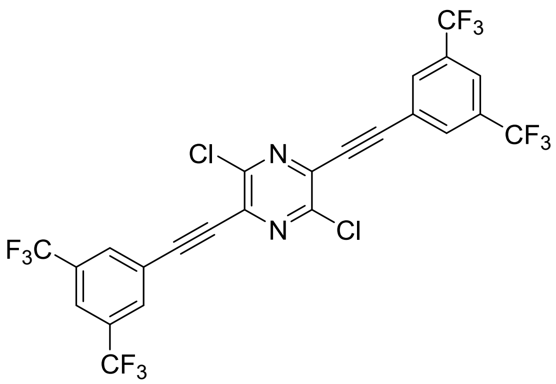
2,5-Dichloro-3,6-bis(4-n-pentylphenylethynyl)pyrazine (2b)



The reaction was carried out according to **GP1** with **1** (500 mg, 1.63 mmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (34.3 mg, 48.9 μmol, 0.03 eq.), CuI (9.31 mg, 48.9 μmol, 0.03 eq.) and 4-n-pentylphenylacetylene (576 mg, 3.34 mmol, 2.05 eq). Purification by column chromatography (silica gel, PE/DCM 10:1) yielded a yellow solid (585 mg, 1.20 mmol, 73 %).

Mp: 126-129 °C; **R*f***: 0.33 (silica gel, PE/DCM = 5:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.1 Hz, 4H), 7.22 (d, J = 8.2 Hz, 4H), 2.64 (t, J = 7.8 Hz, 4H), 1.63 (qui, J = 7.5 Hz, 4H), 1.38 – 1.28 (m, 8H), 0.90 (t, J = 7.0 Hz, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 147.52 (s), 146.16 (s), 135.95 (s), 132.58 (d), 128.93 (d), 118.20 (s), 101.04 (s), 84.22 (s), 36.21 (t), 31.56 (t), 30.98 (t), 22.65 (t), 14.16 (q) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{30}H_{30}N_2Cl_2]^+$, $[M]^+$: 488.17806, found: 488.17750; **IR** (ATR): ν [cm^{-1}] = 2951, 2926, 2857, 2222, 2199, 1604, 1512, 1467, 1424, 1374, 1299, 1239, 1223, 1160, 1107, 1018, 853, 812, 731, 678, 639; **UV-VIS** (DCM): λ_{max} [nm] = 313, 393; **Fluorescence** (DCM): λ_{ex} [nm] = 395, λ_{max} [nm] = 431; **Quantum yield** (DCM): Φ = 51 %.

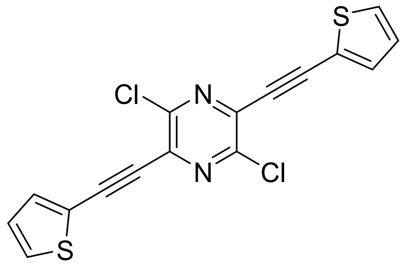
2,5-Dichloro-3,6-bis(3,5-bis(trifluoromethyl)phenylethynyl)pyrazine (2c)



The reaction was carried out according to **GP1** with **1** (250 mg, 815 μmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (17.2 mg, 24.5 μmol, 0.03 eq.), CuI (4.67 mg, 24.5 μmol, 0.03 eq.) and 3,5-bis(trifluoromethyl)phenylacetylene (398 mg, 1.67 mmol, 2.05 eq.). Purification by column chromatography (silica gel, PE/DCM 5:1) yielded a yellow solid (453 mg, 729 μmol, 89 %).

Mp: 246-255 °C; **R*f***: 0.42 (silica gel, PE/DCM = 5:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 8.09 (s, 4H), 7.96 (s, 2H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 148.17 (s), 135.94 (s), 132.66 (s), 132.39 (d), 123.96 (d), 123.2 (s), 122.79 (s), 96.32 (s), 86.43 (s) ppm; **^{19}F NMR** (283 MHz, $CDCl_3$): δ = 63.16 (s, 6F) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{24}H_6N_2F_{12}Cl_2]^+$, $[M]^+$: 619.97109, found: 619.96935; **IR** (ATR): ν [cm^{-1}] = 3076, 2223, 1850, 1830, 1614, 1470, 1426, 1366, 1304, 1278, 1175, 1132, 1112, 938, 905, 850, 748, 699, 683; **UV-VIS** (DCM): λ_{max} [nm] = 297, 368; **Fluorescence** (DCM): λ_{ex} [nm] = 390, λ_{max} [nm] = 399; **Quantum yield** (DCM): Φ = 12 %.

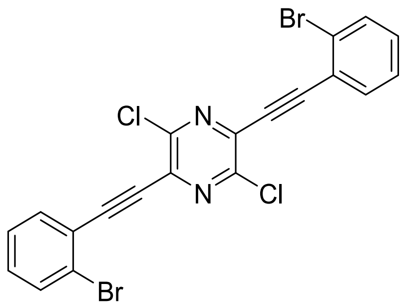
2,5-Dichloro-3,6-bis(2-thienylethynyl)pyrazine (2d)



The reaction was carried out according to **GP1** with **1** (500 mg, 1.63 mmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (34.3 mg, 48.9 μmol, 0.03 eq.), CuI (9.31 mg, 48.9 μmol, 0.03 eq.) and 2-ethynylthiophene (362 mg, 3.34 mmol, 2.05 eq.). Purification by column chromatography (silica gel, PE/DCM 10:1) yielded a red solid (562 mg, 1.56 mmol, 96 %).

Mp: 210-212 °C; **R_f**: 0.23 (silica gel, PE/DCM = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.52 – 7.47 (m, 4H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 2H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 147.23 (s), 135.69 (s), 135.40 (d), 130.90 (d), 127.84 (d), 120.93 (s), 94.15 (s), 88.53 (s) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{16}H_6N_2S_2Cl_2]^+$, $[M]^+$: 359.93440, found: 359.93816; **IR** (ATR): ν [cm^{-1}] = 3110, 3092, 2198, 1523, 1445, 1422, 1393, 1337, 1301, 1263, 1230, 1184, 1165, 1098, 1071, 1042, 856, 831, 797, 741, 702, 675, 649; **UV-VIS** (DCM): λ_{max} [nm] = 284, 324, 414; **Fluorescence** (DCM): λ_{ex} [nm] = 325, λ_{max} [nm] = 448; **Quantum yield** (DCM): Φ = 8 %.

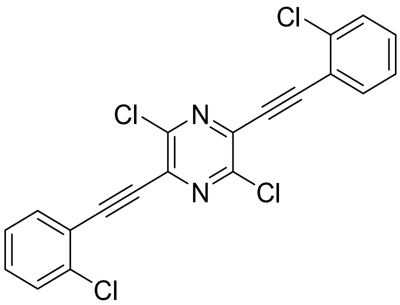
2,5-Dichloro-3,6-bis(2-bromophenylethynyl)pyrazine (2e)



The reaction was carried out according to **GP1** with **1** (500 mg, 1.63 mmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (34.3 mg, 48.9 μmol, 0.03 eq.), CuI (9.31 mg, 48.9 μmol, 0.03 eq.) and 2-bromophenylacetylene (605 mg, 3.34 mmol, 2.05 eq.). Purification by column chromatography (silica gel, PE/DCM 5:1 → DCM) yielded a yellow solid (551 mg, 1.08 mmol, 67 %).

Mp: 223-226 °C; **R_f**: 0.20 (silica gel, PE/DCM = 5:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.68 (td, *J* = 7.7, 1.5 Hz, 4H), 7.37 (td, *J* = 7.6, 1.3 Hz, 2H), 7.31 (td, *J* = 7.7, 1.8 Hz, 2H) ppm; **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$): δ = 148.06 (s), 136.08 (s), 134.70 (d), 133.03 (d), 131.58 (d), 127.42 (d), 126.46 (s), 123.56 (s), 98.41 (s), 88.15 (s) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{20}H_8N_2Cl_2Br_2]^+$, $[M]^+$: 503.84258, found: 503.84202; **IR** (ATR): ν [cm^{-1}] = 2372, 2220, 2193, 1932, 1811, 1584, 1556, 1477, 1425, 1410, 1302, 1279, 1244, 1220, 1159, 1110, 1046, 1027, 944, 860, 750, 707, 681, 647; **UV-VIS** (DCM): λ_{max} [nm] = 302, 382; **Fluorescence** (DCM): λ_{ex} [nm] = 300, λ_{max} [nm] = 416; **Quantum yield** (DCM): Φ = 5 %.

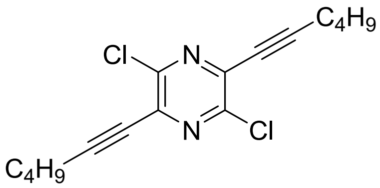
2,5-Dichloro-3,6-bis(2-chlorophenylethynyl)pyrazine (2f)



The reaction was carried out according to **GP1** with **1** (500 mg, 1.63 mmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (34.3 mg, 48.9 μmol, 0.03 eq.), CuI (9.31 mg, 48.9 μmol, 0.03 eq.) and 2-chlorophenylacetylene (456 mg, 3.34 mmol, 2.05 eq.) was added. Purification by column chromatography (silica gel, PE/DCM 10:1 → 5:1 → DCM) yielded a yellow solid (539 mg, 1.29 mmol, 79 %).

Mp: 218-220 °C; **R*f***: 0.25 (silica gel, PE/DCM = 5:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.69 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.49 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.39 (td, *J* = 7.8, 1.7 Hz, 2H), 7.32 (td, *J* = 7.6, 1.2 Hz, 2H) ppm; **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$): δ = 148.02 (s), 137.26 (s), 136.06 (s), 134.46 (d), 131.54 (d), 129.84 (d), 126.88 (d), 121.26 (s), 96.87 (s), 88.76 (s) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{20}H_8N_2Cl_4]^+$, $[M]^+$: 415.94361, found: 415.94448; **IR** (ATR): ν [cm^{-1}] = ; **UV-VIS** (DCM): λ_{max} [nm] = 262, 296, 387; **Fluorescence** (DCM): λ_{ex} [nm] = 300, λ_{max} [nm] = 425; **Quantum yield** (DCM): Φ = 6 %.

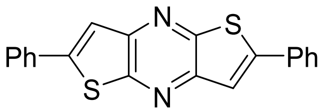
2,5-Dichloro-3,6-bis(4-butylethynyl)pyrazine (2g)



The reaction was carried out according to **GP1** with **1** (500 mg, 1.63 mmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (34.3 mg, 48.9 μmol, 0.03 eq.), CuI (9.31 mg, 48.9 μmol, 0.03 eq.) and hexyne (275 mg, 3.34 mmol, 2.05 eq.). Purification by column chromatography (silica gel, PE/DCM 10:1 → 5:1 → 2:1) yielded an orange solid (430 mg, 1.39 mmol, 85 %).

Mp: 60-62 °C; **R*f***: 0.19 (silica gel, PE/DCM = 5:1); **^{1}H NMR** (700 MHz, $CDCl_3$): δ = 2.54 (t, *J* = 7.1 Hz, 4H), 1.65 (qui, *J* = 7.3 Hz, 4H), 1.51 (sext, *J* = 7.4 Hz, 4H), 0.95 (t, *J* = 7.4 Hz, 6H) ppm; **^{13}C{^{1}H} NMR** (176 MHz, $CDCl_3$): δ = 147.37 (s), 136.02 (s), 103.19 (s), 76.30 (s), 30.08 (t), 22.14 (t), 19.67 (t), 13.68 (q) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{16}H_{18}N_2Cl_2]^+$, $[M]^+$: 308.08416, found: 308.08245; **IR** (ATR): ν [cm^{-1}] = 2954, 2932, 2871, 2230, 1467, 1419, 1377, 1364, 1299, 1246, 1157, 1144, 1014, 951, 806, 643; **UV-VIS** (DCM): λ_{max} [nm] = 276, 342; **Fluorescence** (DCM): λ_{ex} [nm] = 275, λ_{max} [nm] = 379; **Quantum yield** (DCM): Φ = 8 %.

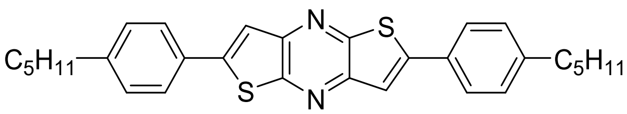
2,2'-Diphenyldithieno[2,3-b:2',3'-e]pyrazine (3a)



The reaction was carried out according to **GP2** with **2a** (3.40 g, 9.74 mmol, 1.00 eq.) and Na_2S (4.56 g, 58.4 mmol, 6.00 eq.) in MeCN (50 ml). The crude product was precipitated with PE to yield a brown solid (1.05 g, 3.05 mmol, 31 %).

Mp: >300 °C; **R*f***: 0.75 (silica gel, DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.83 – 7.78 (m, 4H), 7.73 (s, 2H), 7.54 – 7.42 (m, 6H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 154.38 (s), 148.87 (s), 147.64 (s), 133.68 (s), 129.92 (d), 129.41 (d), 126.74 (d), 117.21 (d) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{20}H_{12}N_2S_2]^+$, $[M]^+$: 344.04364, found: 344.04282; **IR** (ATR): ν [cm^{-1}] = 3057, 3024, 2923, 2852, 2362, 1962, 1944, 1887, 1872, 1815, 1738, 1661, 1597, 1535, 1490, 1435, 1299, 1265, 1220, 1188, 1144, 1099, 1072, 1028, 963, 931, 906, 825, 753, 687; **UV-VIS** (DCM): λ_{max} [nm] = 302, 381; **Fluorescence** (DCM): λ_{ex} [nm] = 300, λ_{max} [nm] = 415; **Quantum yield** (DCM): Φ = 16 %.

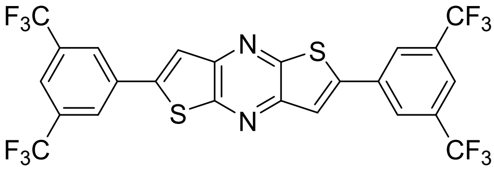
2,2'-Bis(4-n-pentylphenyl)dithieno[2,3-b:2',3'-e]pyrazine (3b)



The reaction was carried out according to **GP2** with **2b** (200 mg, 409 μmol, 1.00 eq.) and Na_2S (191 mg, 2.45 mmol, 6.00 eq.). Purification by column chromatography (silica gel, PE/DCM 10:1 → 1:1 → DCM) yielded a light brown solid (111 mg, 229 μmol, 56 %).

Mp: 210-215 °C; **R*f***: 0.65 (silica gel, PE/DCM = 1:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.2 Hz, 4H), 7.68 (s, 2H), 7.30 (d, *J* = 8.2 Hz, 4H), 2.67 (t, *J* = 7.9 Hz, 4H), 1.66 (qui, *J* = 7.3 Hz, 4H), 1.41 – 1.30 (m, 8H), 0.91 (t, *J* = 7.1 Hz, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 154.13 (s), 148.93 (s), 147.52 (s), 145.32 (s), 131.05 (s), 129.44 (d), 126.60 (d), 116.42 (d), 35.91 (t), 31.60 (t), 31.15 (t), 22.69 (t), 14.18 (q) ppm; **HR-MS** (DART+): *m/z* calculated for $[C_{30}H_{33}N_2S_2]^+$, $[M + H]^+$: 485.20800, found: 485.20840; **IR** (ATR): ν [cm^{-1}] = 3022, 2955, 2927, 2855, 1607, 1542, 1504, 1465, 1455, 1412, 1371, 1311, 1288, 1228, 1185, 1143, 1016, 933, 900, 802, 728, 689, 672, 635; **UV-VIS** (DCM): λ_{max} [nm] = 259, 303, 396; **Fluorescence** (DCM): λ_{ex} [nm] = 305, λ_{max} [nm] = 434; **Quantum yield** (DCM): Φ = 28 %.

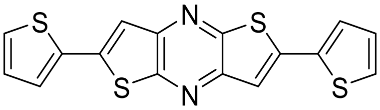
2,2'-Bis(3,5-bis(trifluoromethyl)phenyl)dithieno[2,3-b:2',3'-e]pyrazine (3c)



The reaction was carried out according to **GP2** with **2c** (150 mg, 242 μmol, 1.00 eq.) and Na_2S (113 mg, 1.45 mmol, 6.00 eq.). The crude product was filtered over silica to yield a dark brown solid (37.0 mg, 60.0 μmol, 25 %).

Mp: 171-172 °C; **R*f***: 0.63 (silica gel, PE/DCM = 1:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 8.20 (s, 4H), 7.96 (s, 2H), 7.90 (s, 2H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 154.83 (s), 147.65 (s), 145.89 (s), 135.67 (s), 133.09 (s), 126.66 (d), 123.30 (d), 123.08 (s), 119.76 (d) ppm; **^{19}F NMR** (283 MHz, $CDCl_3$): δ = -62.97 (s, 6F) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{24}H_8N_2S_2F_{12}]^+$, $[M]^+$: 615.99318, found: 615.99093; **IR** (ATR): ν [cm^{-1}] = 2928, 1619, 1467, 1370, 1276, 1174, 1129, 998, 896, 847, 701, 682; **UV-VIS** (DCM): λ_{max} [nm] = 264, 290, 378, 438; **Fluorescence** (DCM): λ_{ex} [nm] = 380, λ_{max} [nm] = 449; **Quantum yield** (DCM): Φ = 3 %.

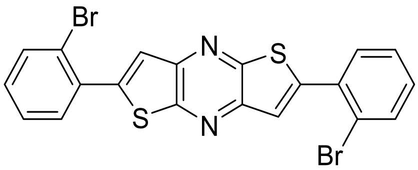
2,2'-Bis(2-thienyl)dithieno[2,3-b:2',3'-e]pyrazine (3d)



The reaction was carried out according to **GP2** with **2d** (200 mg, 554 μmol, 1.00 eq.) and Na_2S (260 mg, 3.32 mmol, 6.00 eq.). Purification by recrystallization (PE/DCM) yielded a dark brown solid (88.0 mg, 247 μmol, 45 %).

Mp: >300 °C; **R*f***: 0.31 (silica gel, PE/DCM = 1:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.54 (s, 2H), 7.46 (dd, *J* = 3.7, 1.1 Hz, 2H), 7.44 (dd, *J* = 5.0, 1.1 Hz, 2H), 7.14 (dd, *J* = 5.1, 3.7 Hz, 2H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 154.32 (s), 147.42 (s), 141.99 (s), 137.18 (s), 128.71 (d), 127.95 (d), 126.82 (d), 116.98 (d) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{16}H_8N_2S_4]^+$, $[M]^+$: 355.95648, found: 355.95893; **IR** (ATR): ν [cm^{-1}] = 3105, 3083, 3058, 1539, 1503, 1412, 1356, 1303, 1265, 1182, 1140, 1076, 1048, 838, 823, 739, 694, 671; **UV-VIS** (DCM): λ_{max} [nm] = 263, 310, 410, 426; **Fluorescence** (DCM): λ_{ex} [nm] = 310, λ_{max} [nm] = 456; **Quantum yield** (DCM): Φ = 26 %.

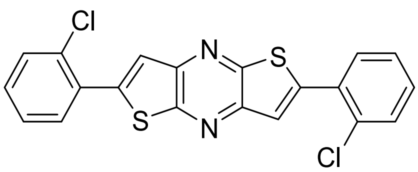
2,2'-Bis(2-bromophenyl)dithieno[2,3-b:2',3'-e]pyrazine (3e)



The reaction was carried out according to **GP2** with **2e** (200 mg, 395 μmol, 1.00 eq.) and Na_2S (185 mg, 2.37 mmol, 6.00 eq). Purification by recrystallization (PE/DCM) yielded a light brown solid (60.0 mg, 120 μmol, 30 %).

Mp: 239-240 °C; **R*f***: 0.29 (silica gel, PE/DCM = 1:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.75 (s, 2H), 7.62 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.45 (td, *J* = 7.5, 1.2 Hz, 2H), 7.32 (td, *J* = 7.7, 1.7 Hz, 2H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 154.82 (s), 147.52 (s), 146.97 (s), 134.85 (s), 134.37 (d), 132.30 (d), 130.88 (d), 128.06 (d), 123.08 (s), 122.67 (d) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{20}H_{10}N_2S_2Br_2]^+$, $[M]^+$: 499.86467, found: 499.86264; **IR** (ATR): ν [cm^{-1}] = 2873, 2212, 1702, 1510, 1468, 1432, 1377, 1301, 1254, 1187, 1143, 1119, 1053, 1026, 932, 832, 745, 715, 701, 670, 639; **UV-VIS** (DCM): λ_{max} [nm] = 262, 279, 366; **Fluorescence** (DCM): λ_{ex} [nm] = 370, λ_{max} [nm] = 444; **Quantum yield** (DCM): Φ = 3 %.

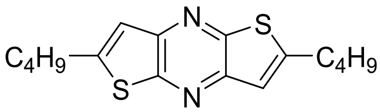
2,2'-Bis(2-chlorophenyl)dithieno[2,3-b:2',3'-e]pyrazine (3f)



The reaction was carried out according to **GP2** with **2f** (200 mg, 478 μmol, 1.00 eq.) and Na_2S (224 mg, 2.87 mmol, 6.00 eq.). The crude product was filtered over silica to yield a light brown solid (80.0 mg, 194 μmol, 41 %).

Mp: 270-274 °C; **R*f***: 0.43 (silica gel, PE/DCM = 1:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.83 (s, 2H), 7.67 (dd, *J* = 7.0, 2.3 Hz, 2H), 7.57 (dd, *J* = 7.2, 2.2 Hz, 2H), 7.40 (tt, *J* = 7.4, 5.5 Hz, 4H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 154.60 (s), 146.93 (s), 145.71 (s), 133.05 (s), 132.57 (s), 131.83 (d), 131.09 (d), 130.52 (d), 127.45 (d), 122.45 (d) ppm; **HR-MS** (DART+): *m/z* calculated for $[C_{20}H_{11}N_2S_2Cl_2]^+$, $[M + H]^+$: 412.97350, found: 412.97350; **IR** (ATR): ν [cm^{-1}] = 3108, 3055, 2925, 2852, 1953, 1921, 1888, 1805, 1563, 1536, 1470, 1421, 1302, 1253, 1210, 1187, 1143, 1058, 1039, 933, 850, 833, 744, 715, 682, 641; **UV-VIS** (DCM): λ_{max} [nm] = 263, 283, 370; **Fluorescence** (DCM): λ_{ex} [nm] = 370, λ_{max} [nm] = 424; **Quantum yield** (DCM): Φ = 6 %.

2,2'-Dibutyldithieno[2,3-b:2',3'-e]pyrazine (3g)



The reaction was carried out according to **GP2** with **2g** (200 mg, 647 μmol, 1.00 eq.) and Na_2S (303 mg, 3.88 mmol, 6.00 eq.). The crude product was filtered over silica to yield a light brown solid (115 mg, 378 μmol, 59 %).

Mp: 72-74 °C; **R*f***: 0.54 (silica gel, PE/DCM = 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.16 (s, 2H), 2.99 (t, *J* = 6.9 Hz, 4H), 1.79 (qui, *J* = 7.4 Hz, 4H), 1.46 (sext, *J* = 7.4 Hz, 4H), 0.98 (t, *J* = 7.4 Hz, 6H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 153.48 (s), 152.17 (s), 146.66 (s), 118.53 (d), 32.76 (t), 31.97 (t), 22.35 (t), 13.90 (q) ppm; **HR-MS** (EI+): *m/z* calculated for $[C_{16}H_{20}N_2S_2]^+$, $[M]^+$: 304.10624, found: 304.10585; **IR** (ATR): ν [cm^{-1}] = 2956, 2929, 2871, 2859, 2229, 1551, 1459, 1377, 1298, 1247, 1197, 1143, 1076, 964, 843, 730, 663; **UV-VIS** (DCM): λ_{max} [nm] = 262, 346; **Fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 394.

2 NMR Spectra

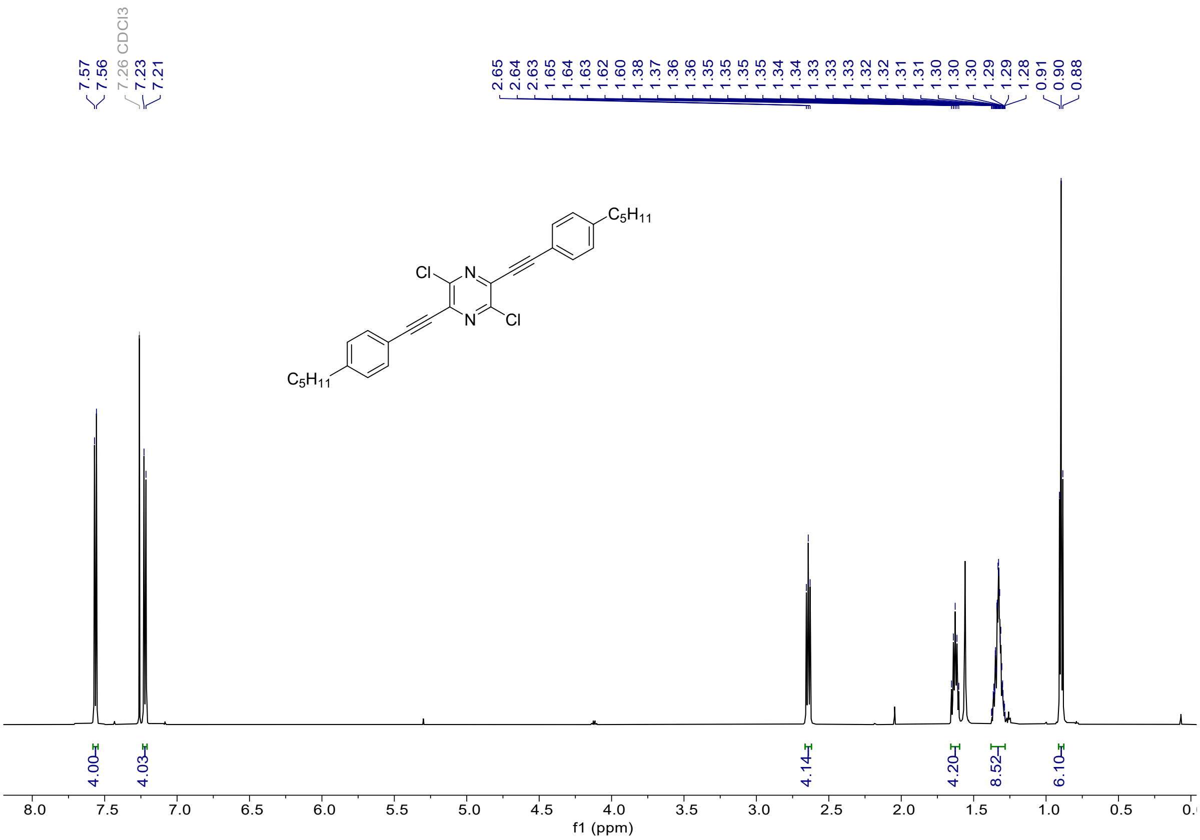


Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2b**.

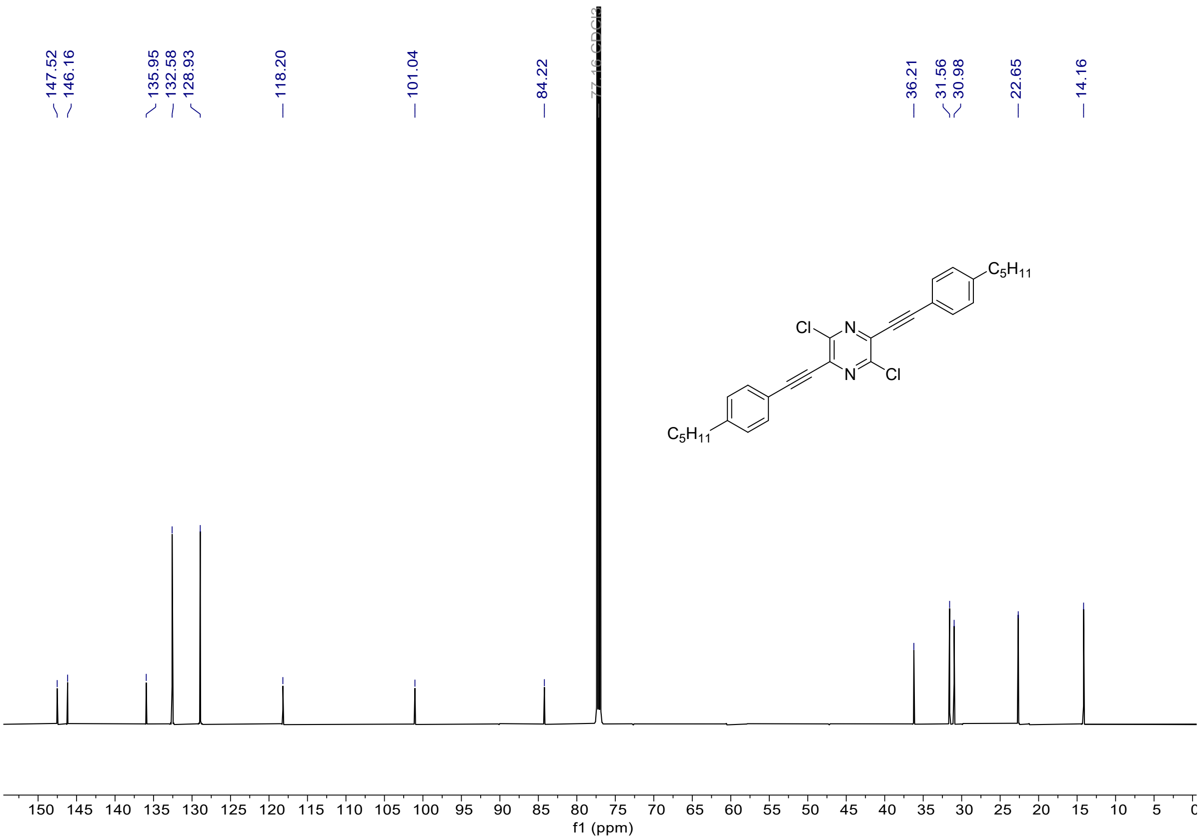


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **2b**.

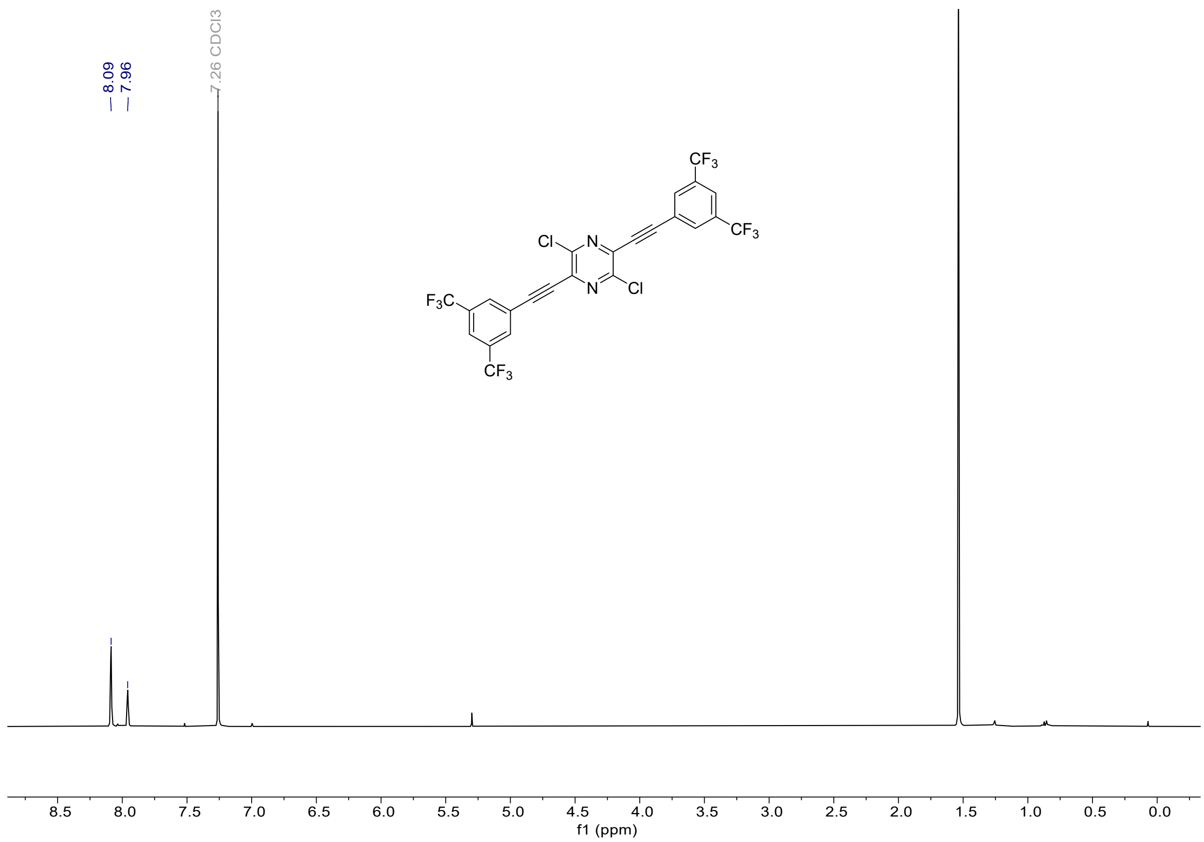


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2c**.

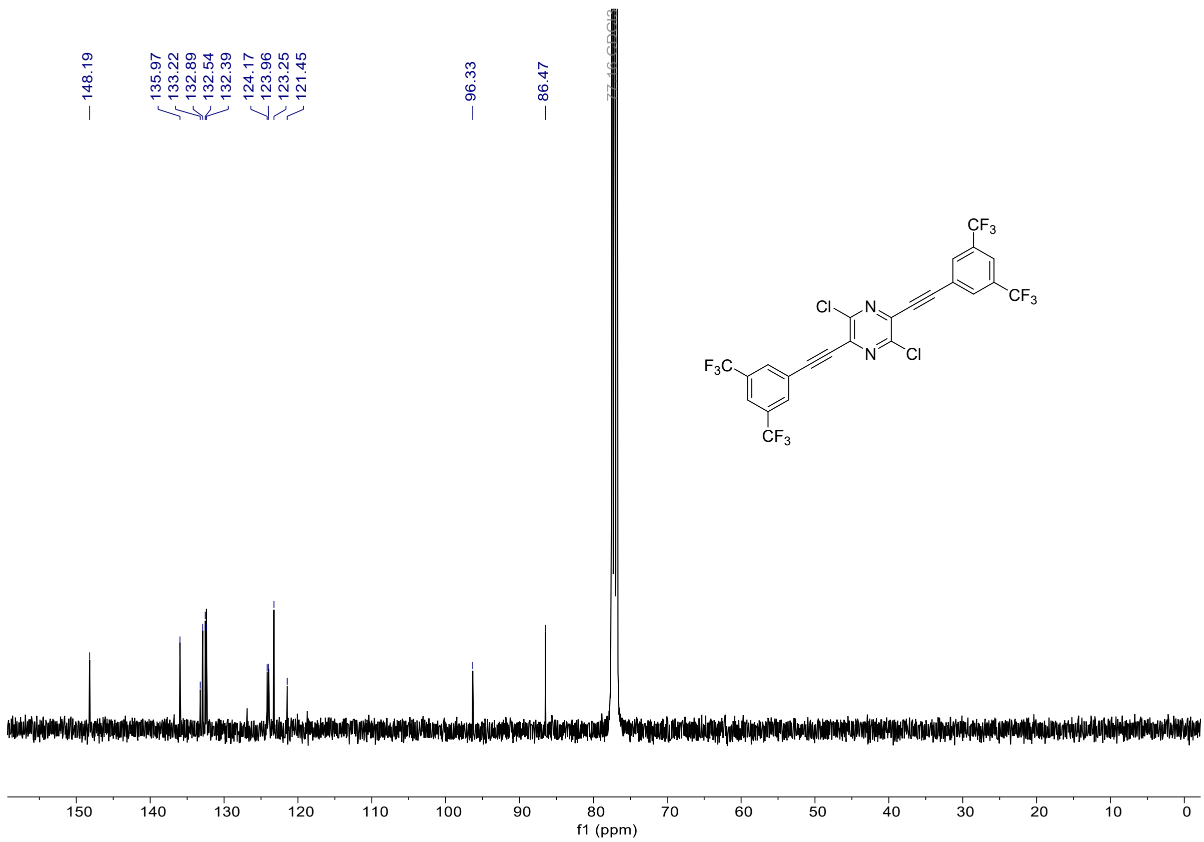


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2c**.

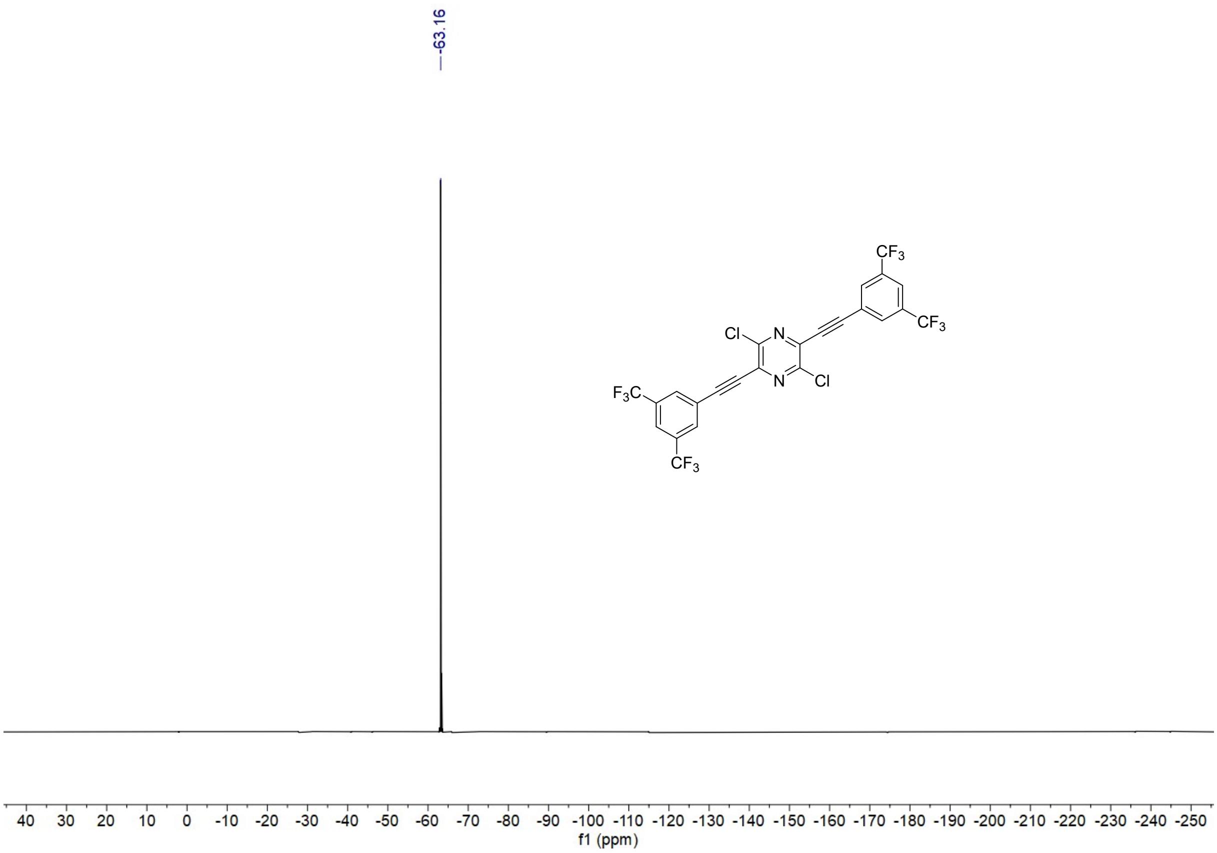


Figure S5. $^{19}F\{^{1}H\}$ NMR spectrum (283 MHz, $CDCl_3$) of **2c**.

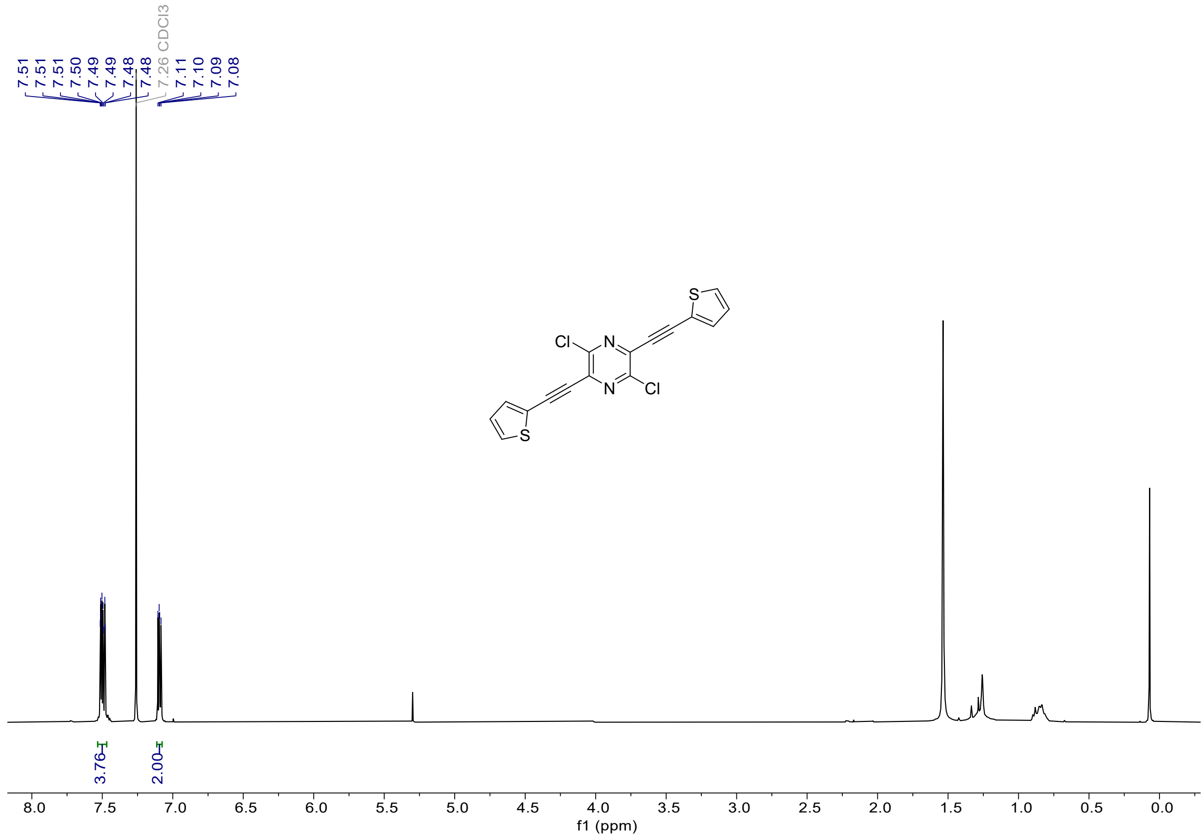


Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2d**.

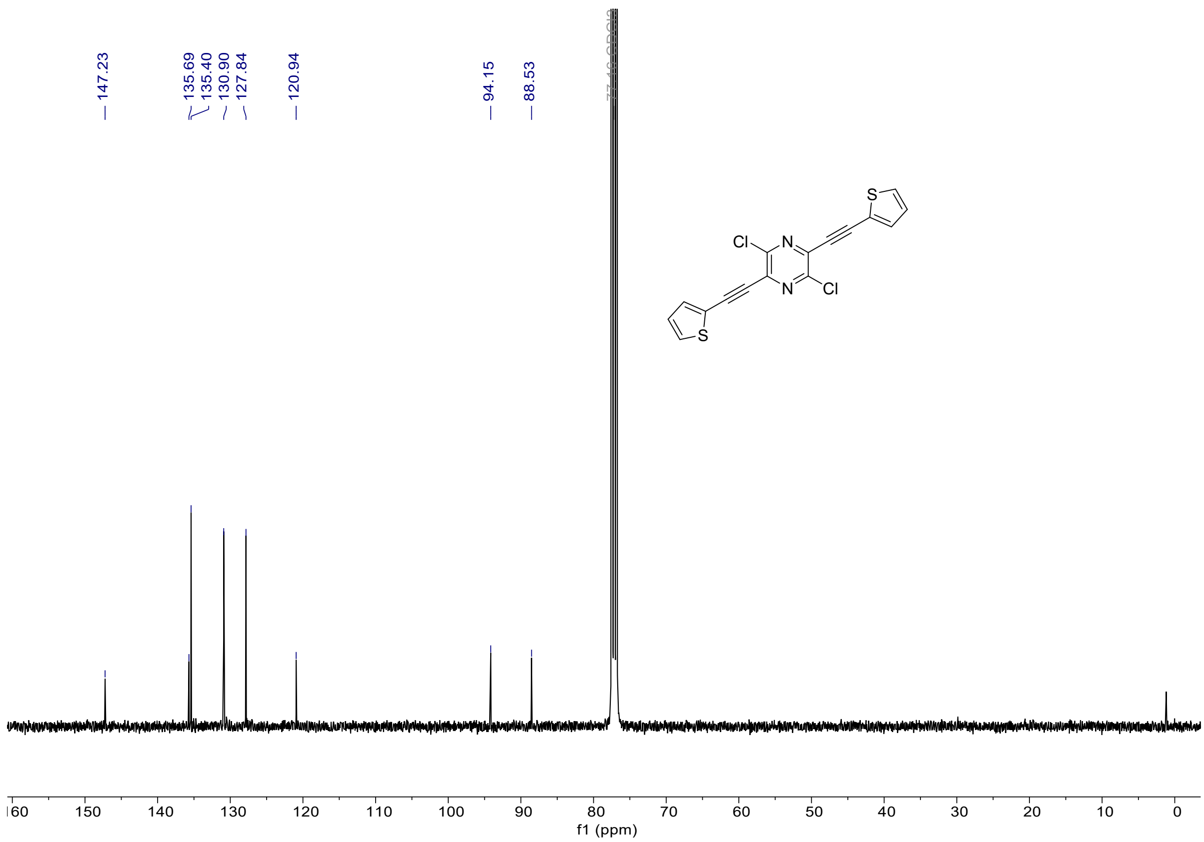


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2d**.

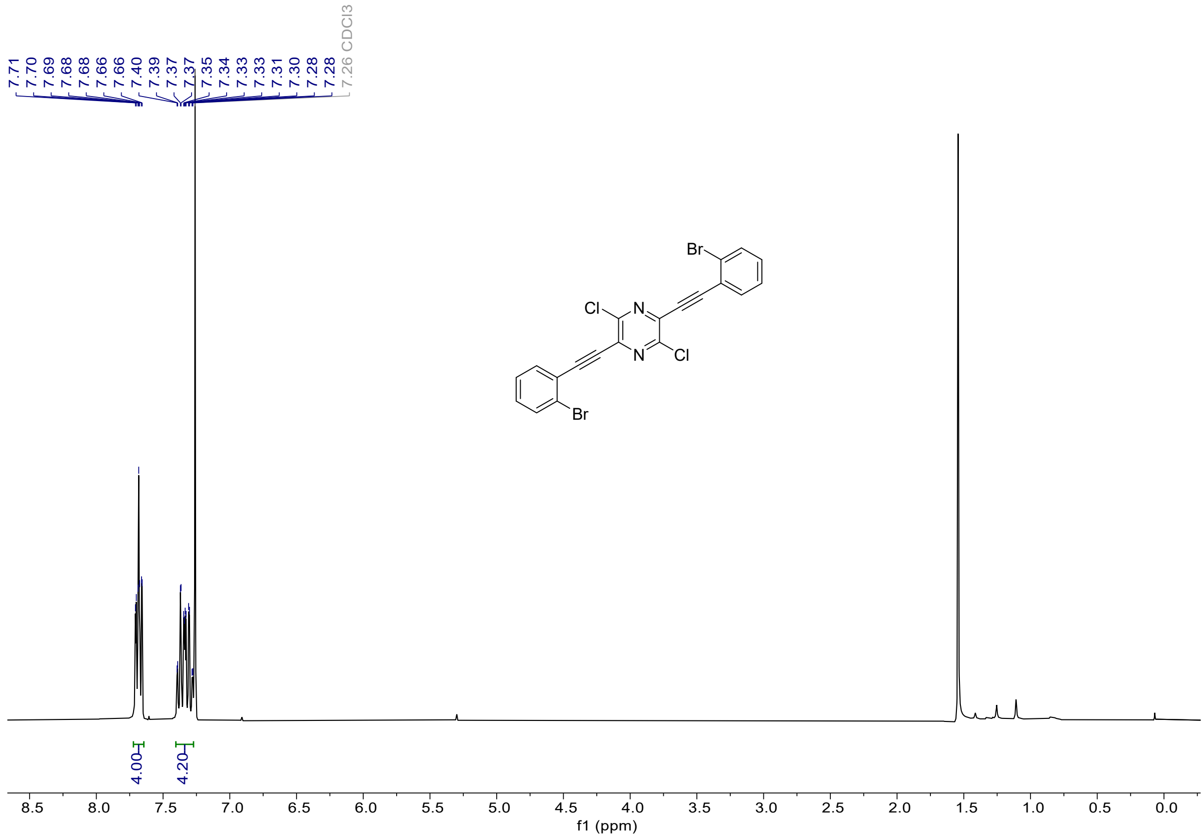


Figure S8. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2e**.

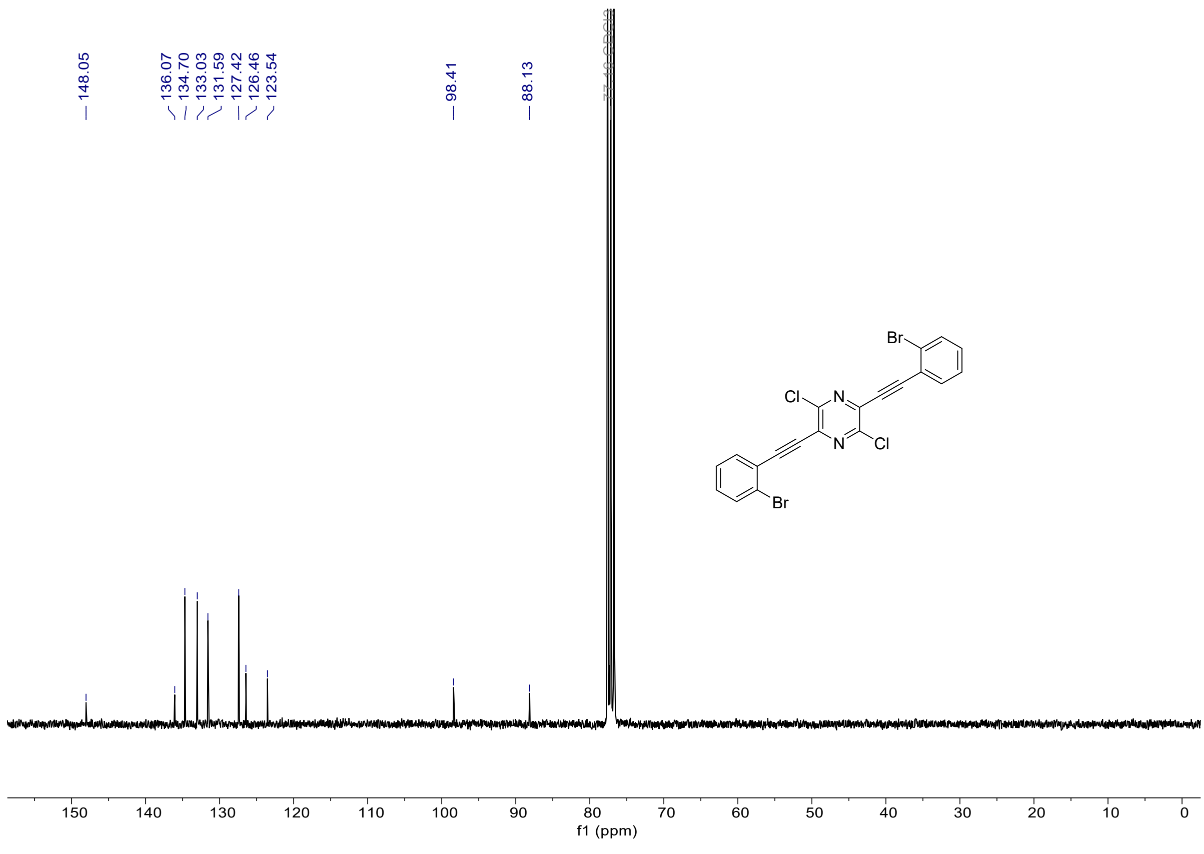


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (76 MHz, $CDCl_3$) of **2e**.

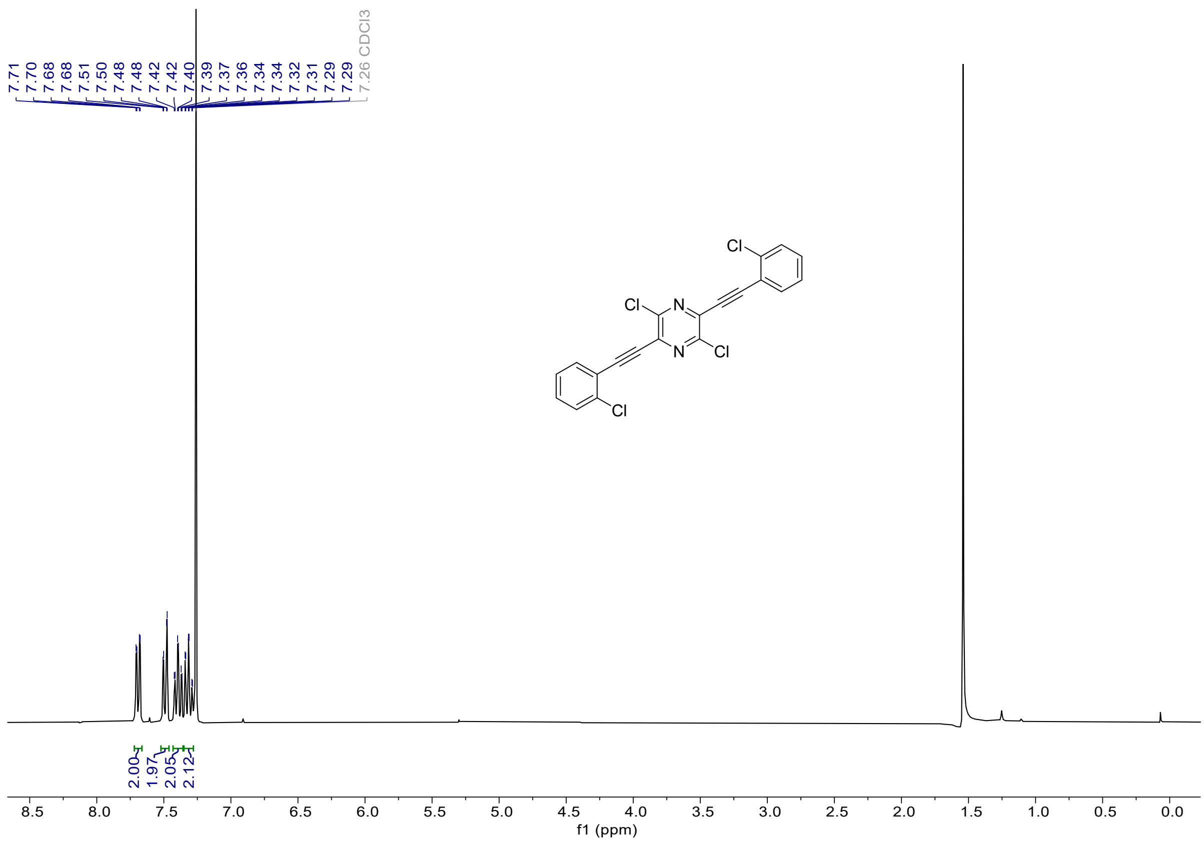


Figure S10. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2f**.

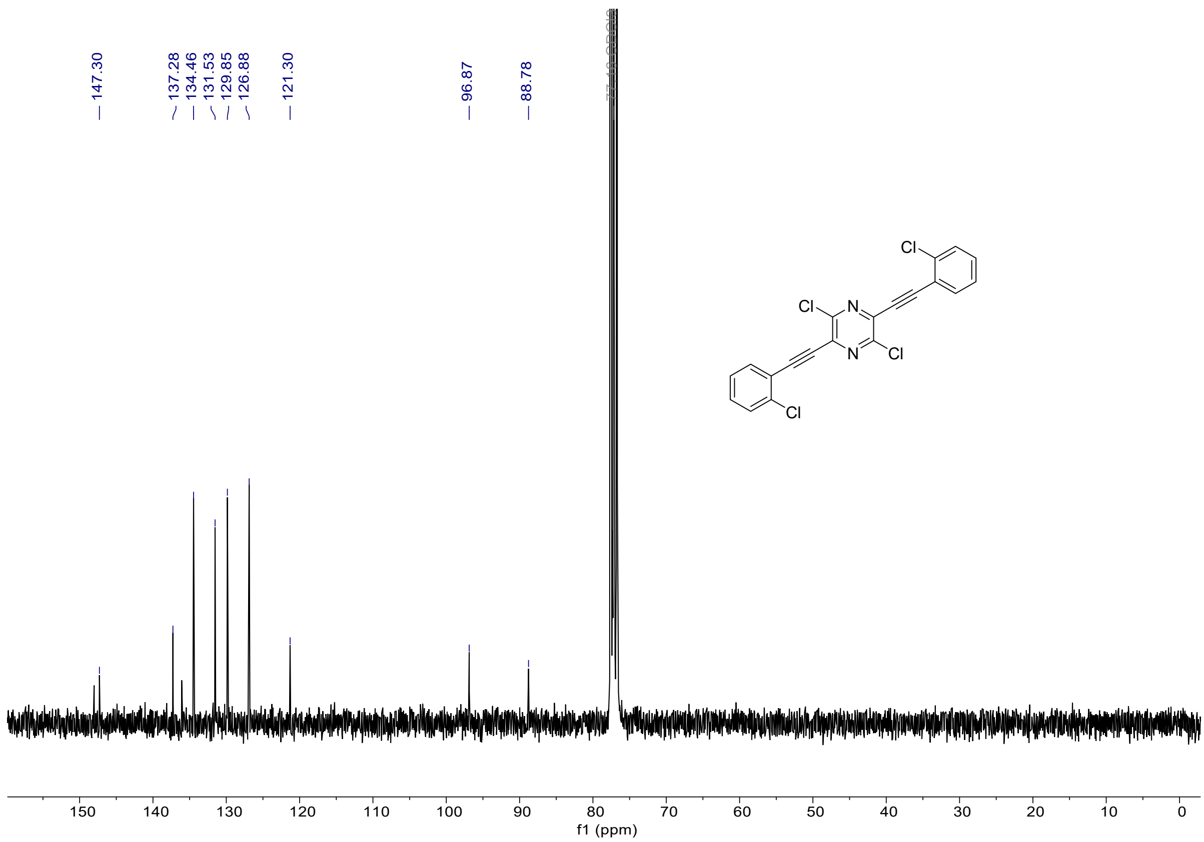


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (76 MHz, $CDCl_3$) of **2f**.

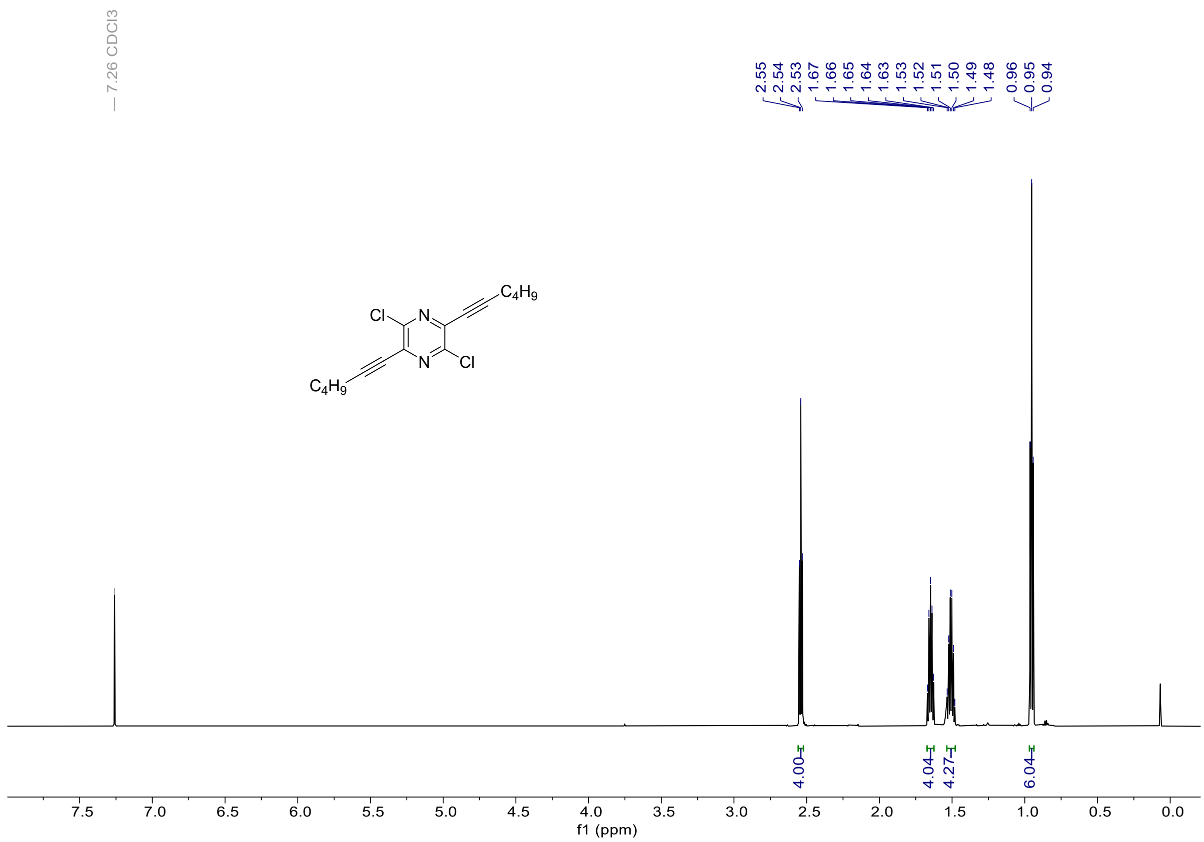


Figure S12. ^{1}H NMR spectrum (700 MHz, $CDCl_3$) of **2g**.

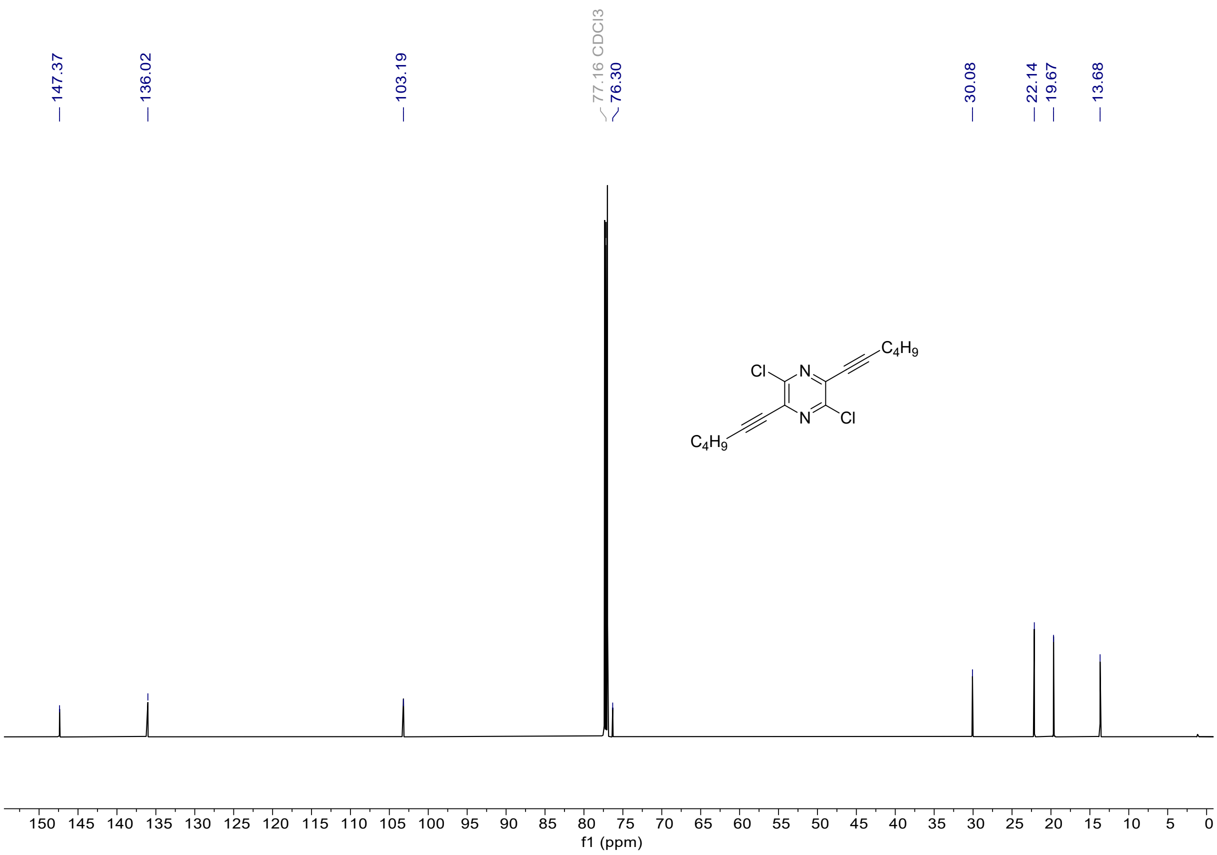


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (176 MHz, $CDCl_3$) of **2g**.

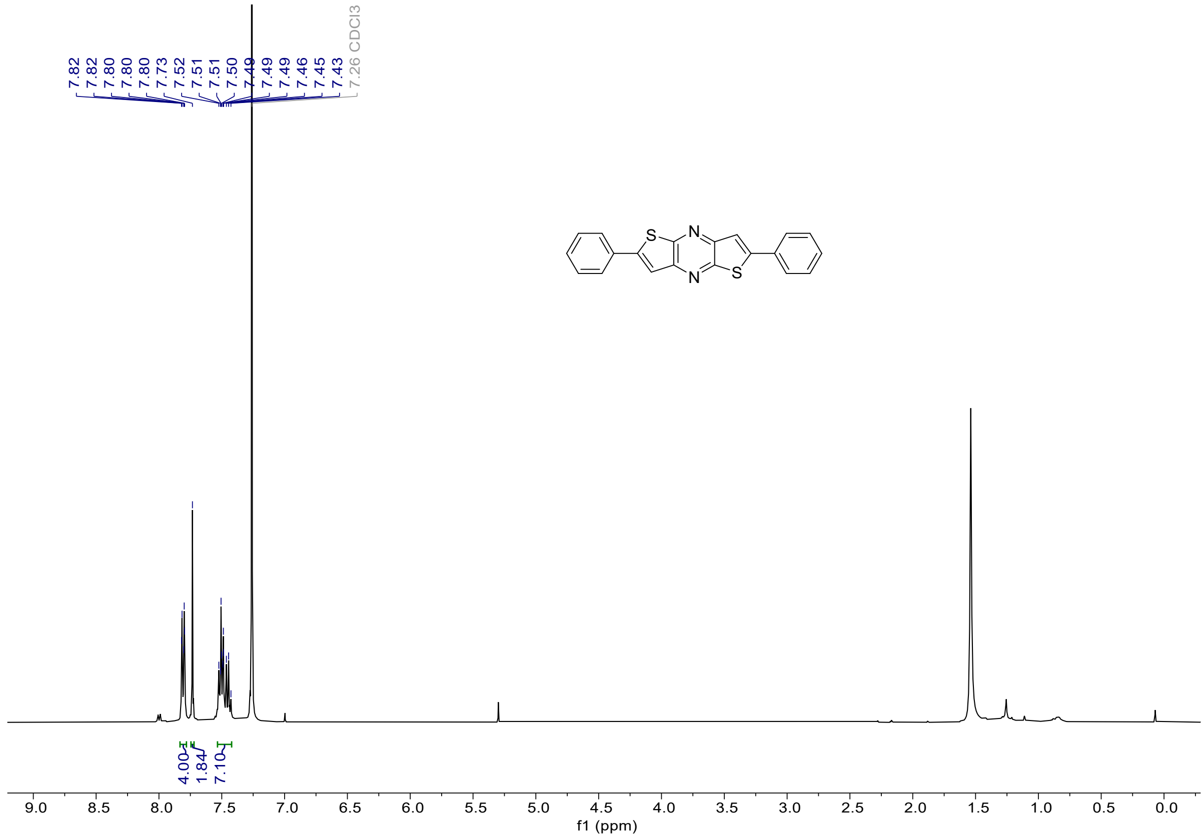


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**.

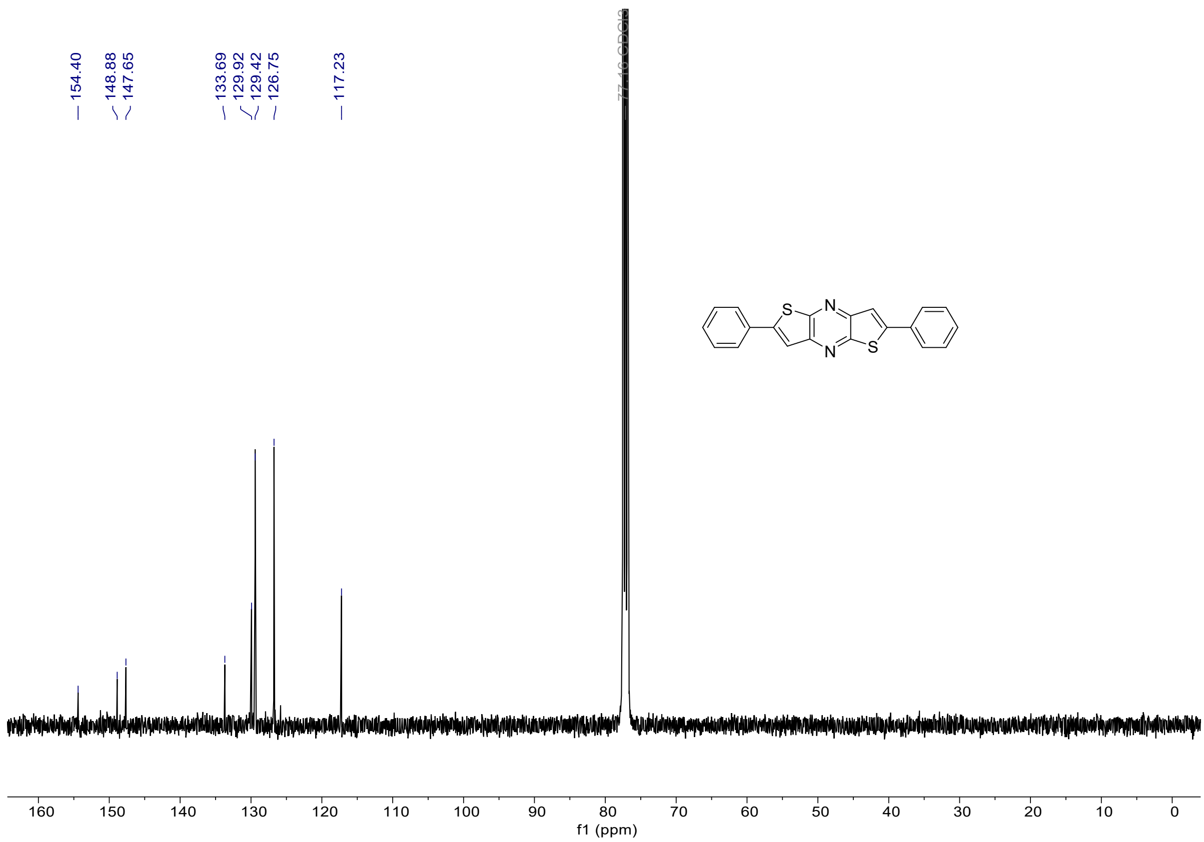


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3a**.

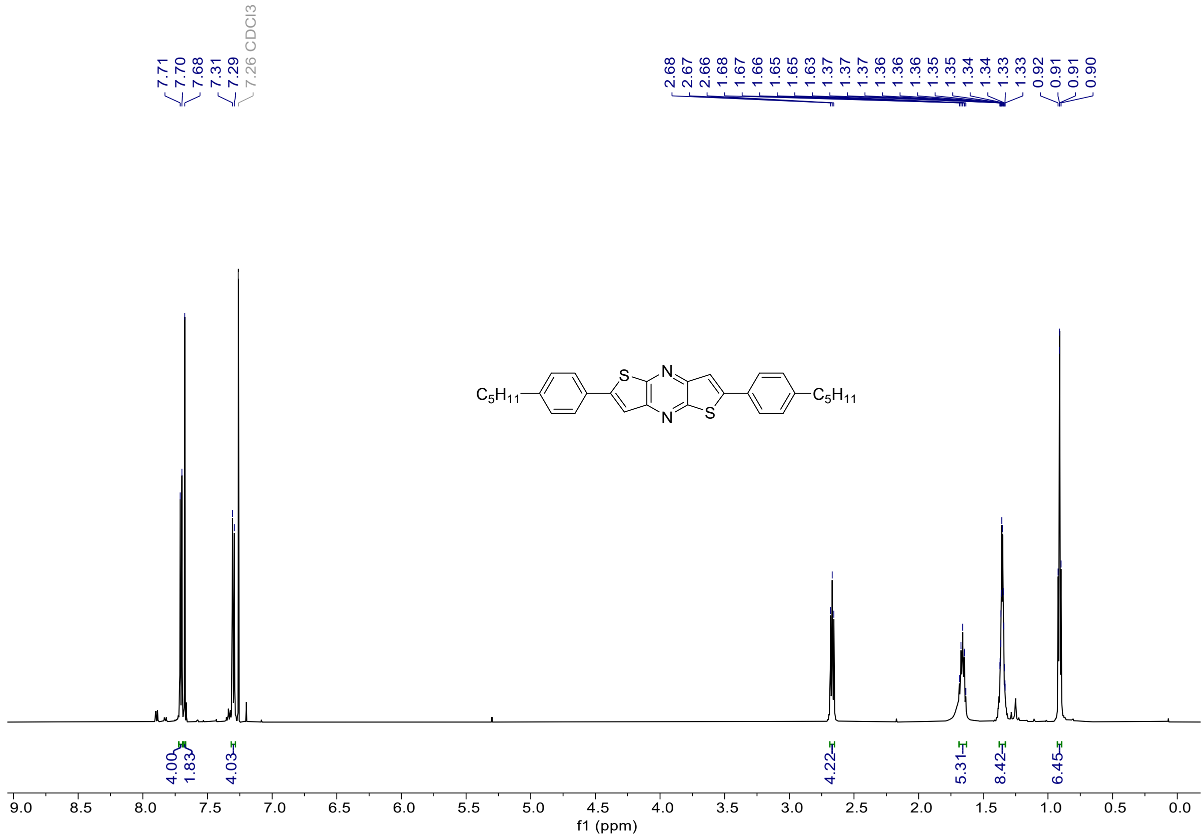


Figure S16. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3b**.

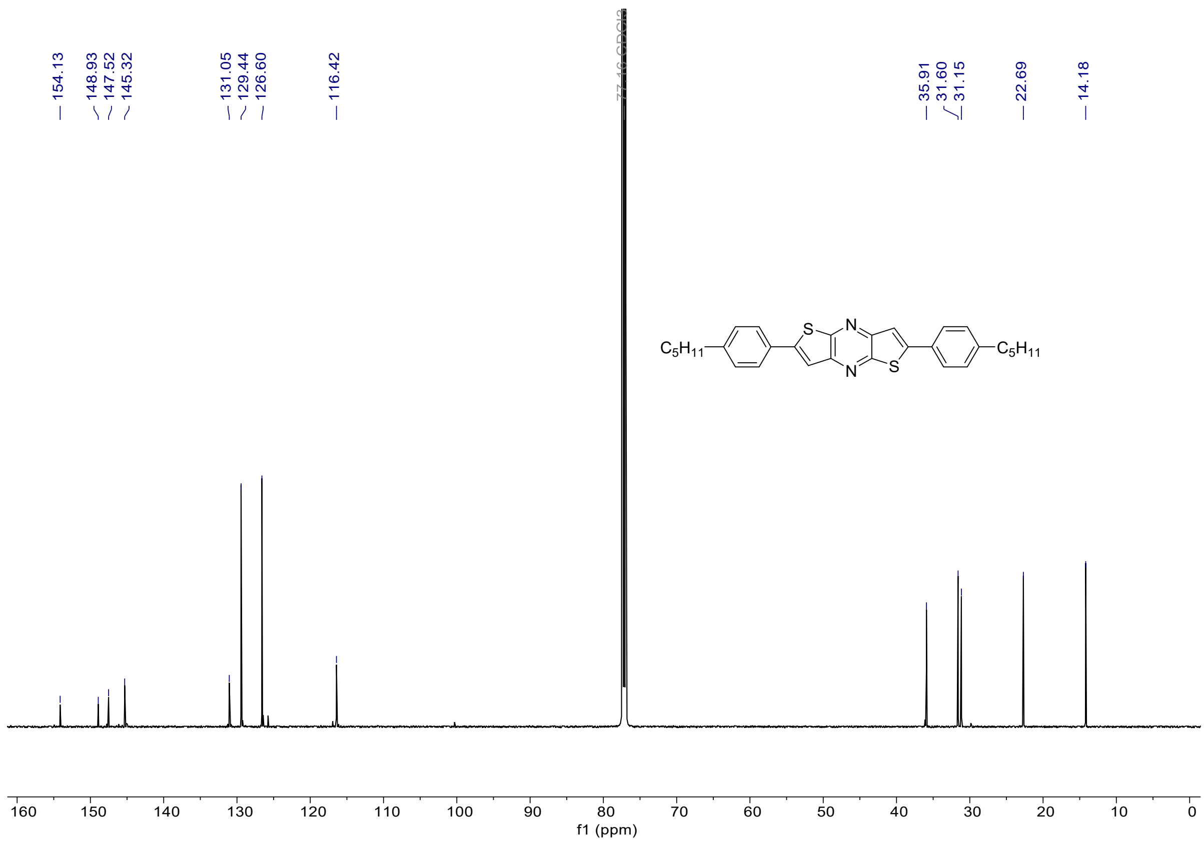


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **3b**.

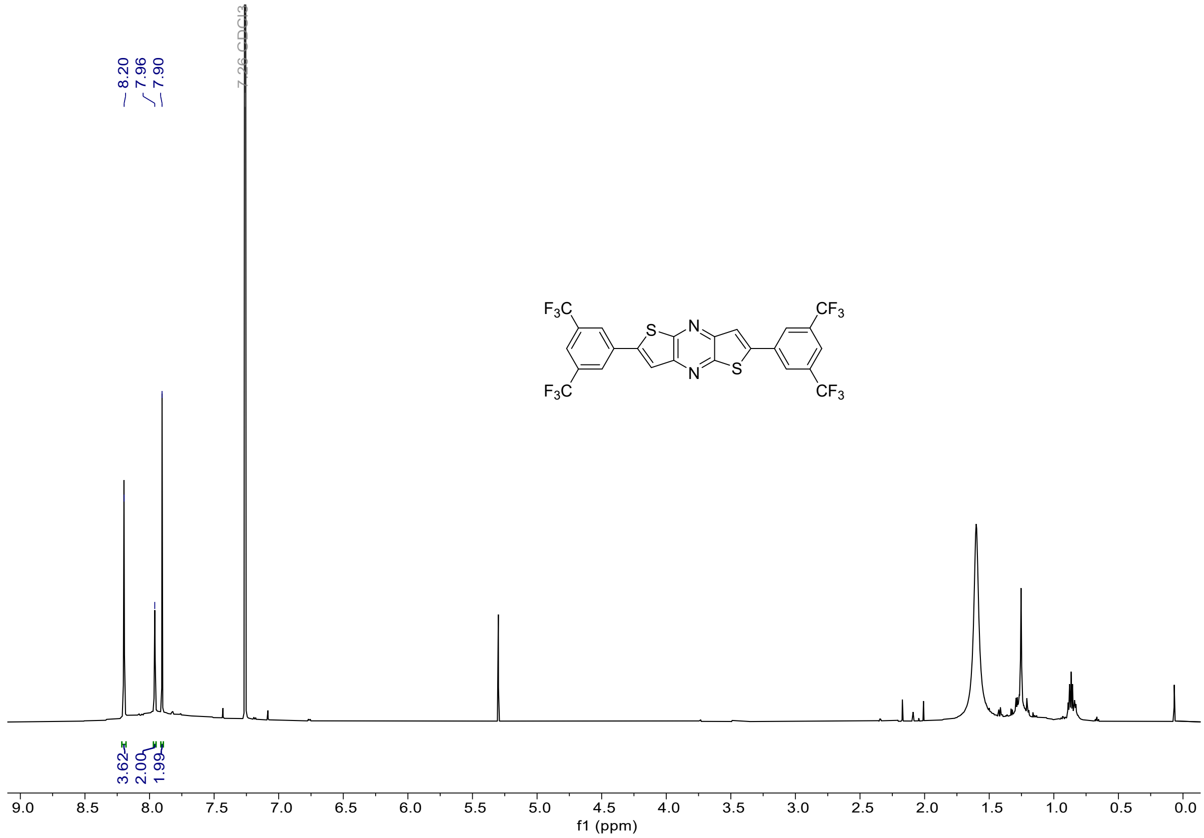


Figure S18. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3c**.

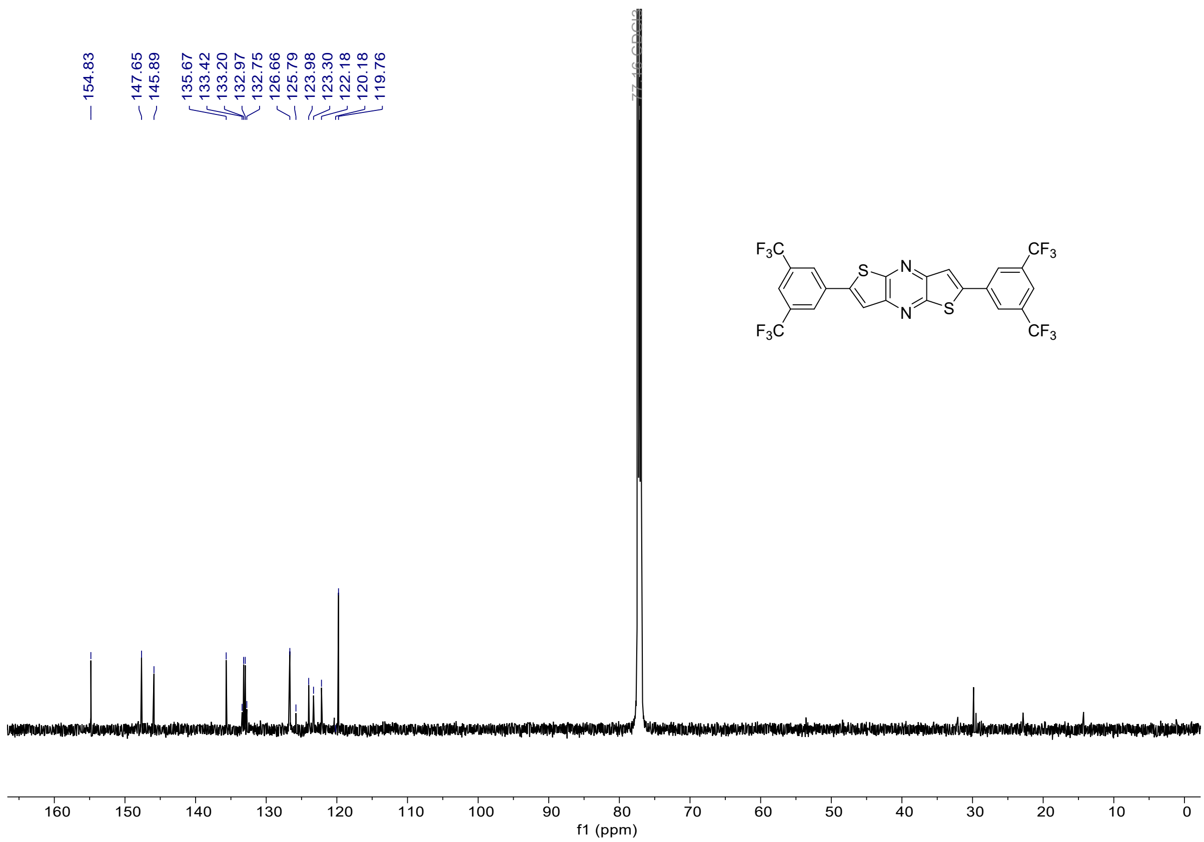


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **3c**.

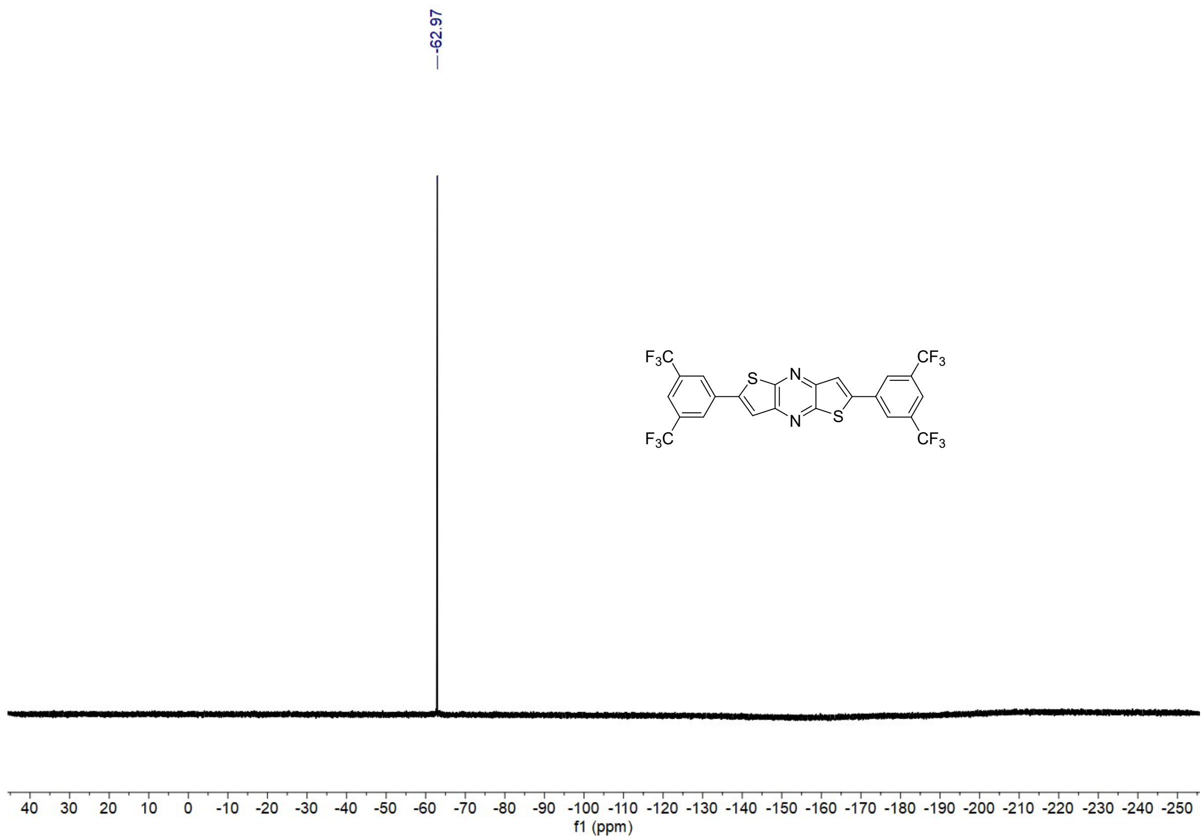


Figure S20. $^{19}F\{^{1}H\}$ NMR spectrum (283 MHz, $CDCl_3$) of **3c**.

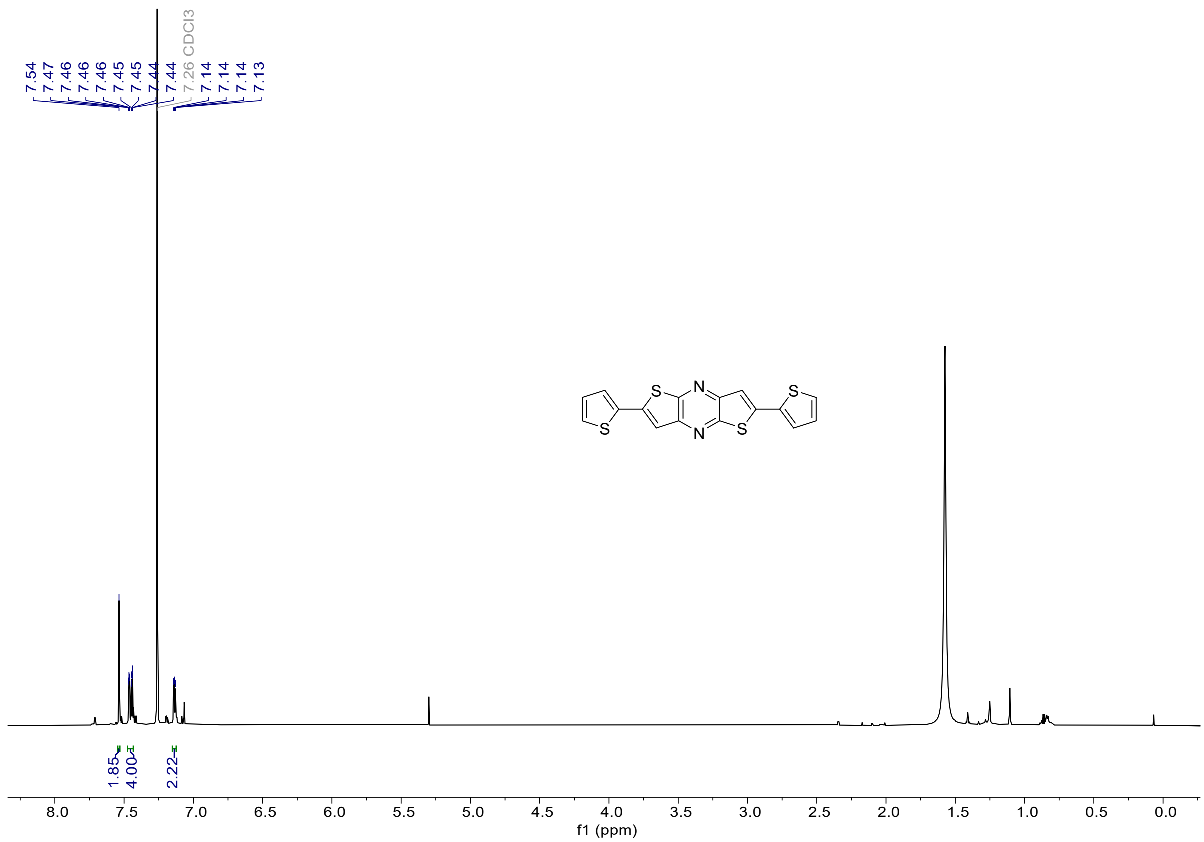


Figure S21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3d**.

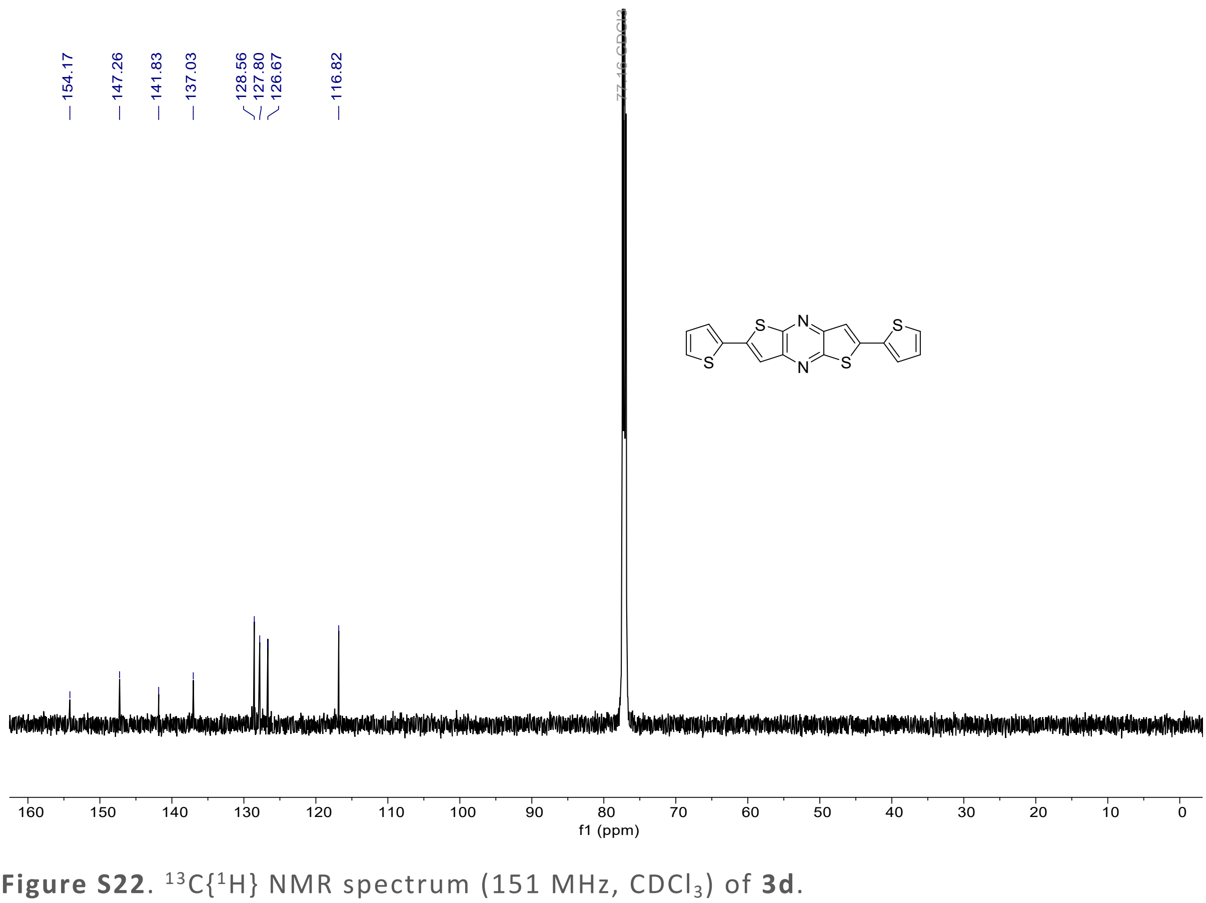


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **3d**.

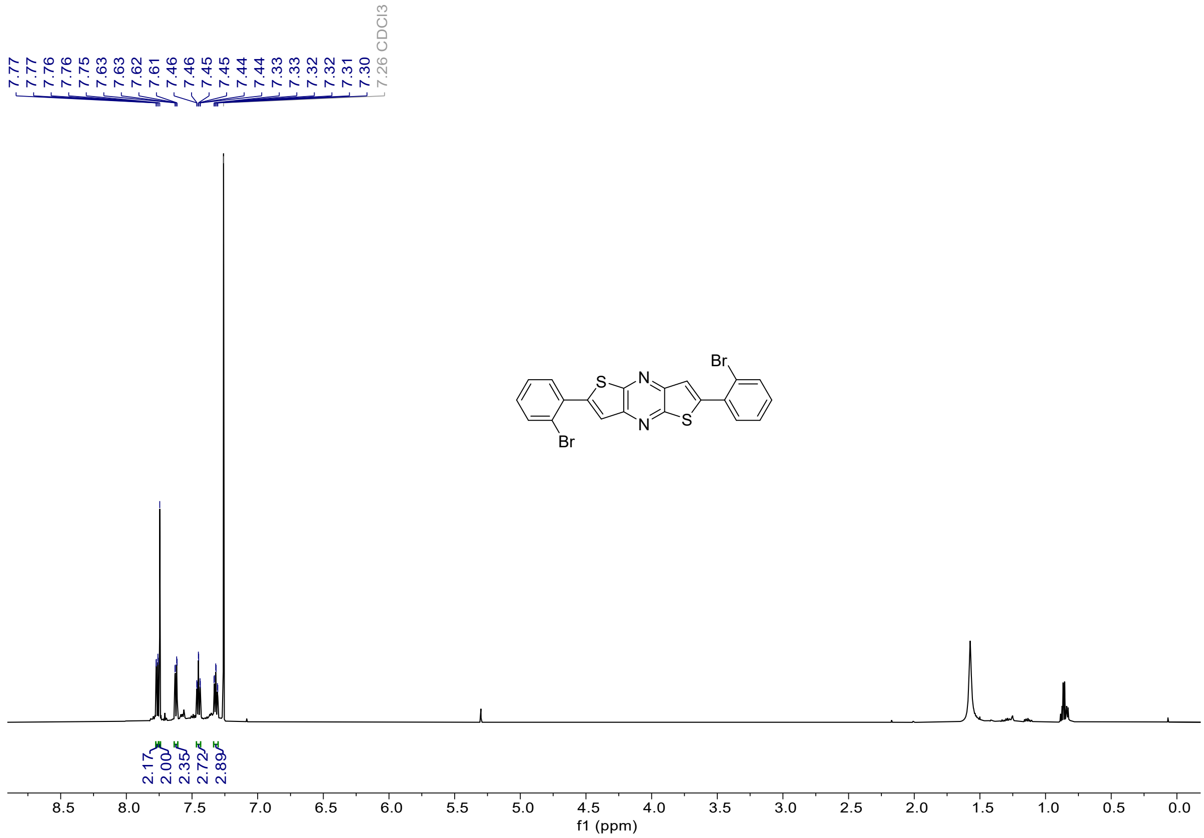


Figure S23. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3e**.

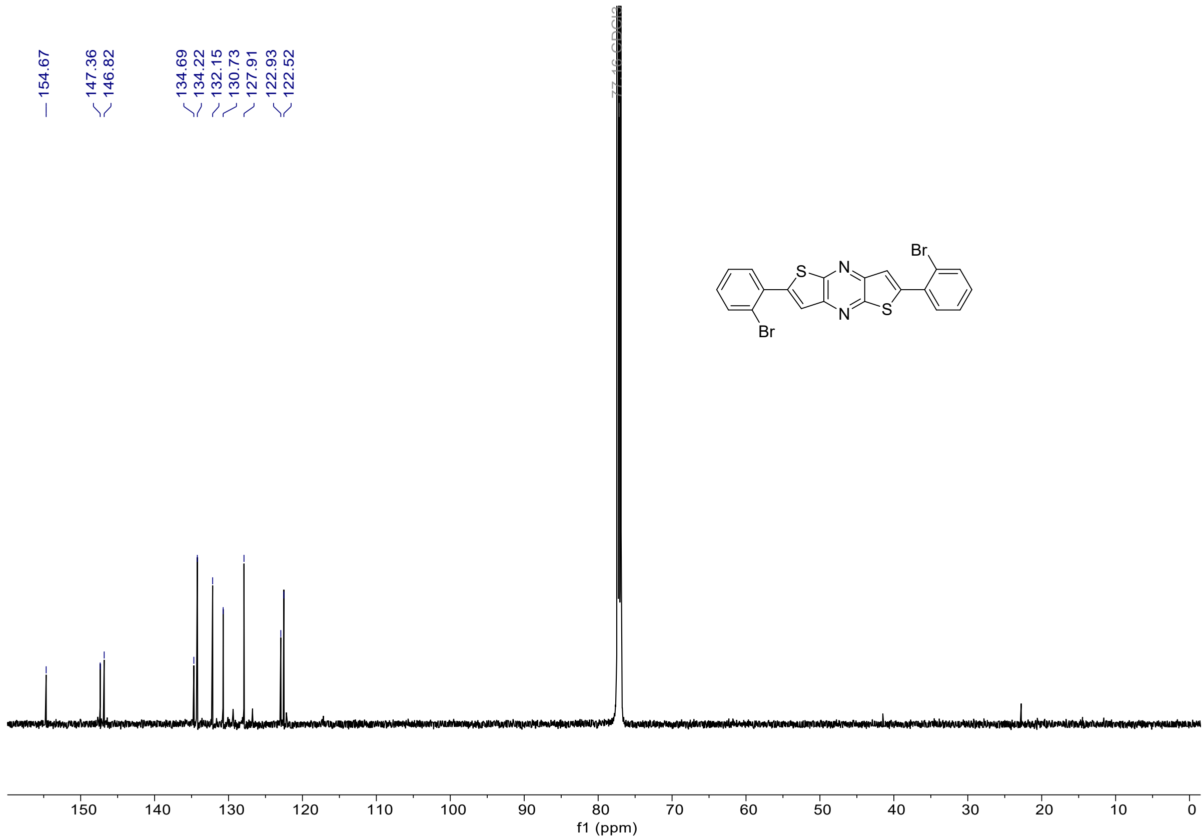


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **3e**.

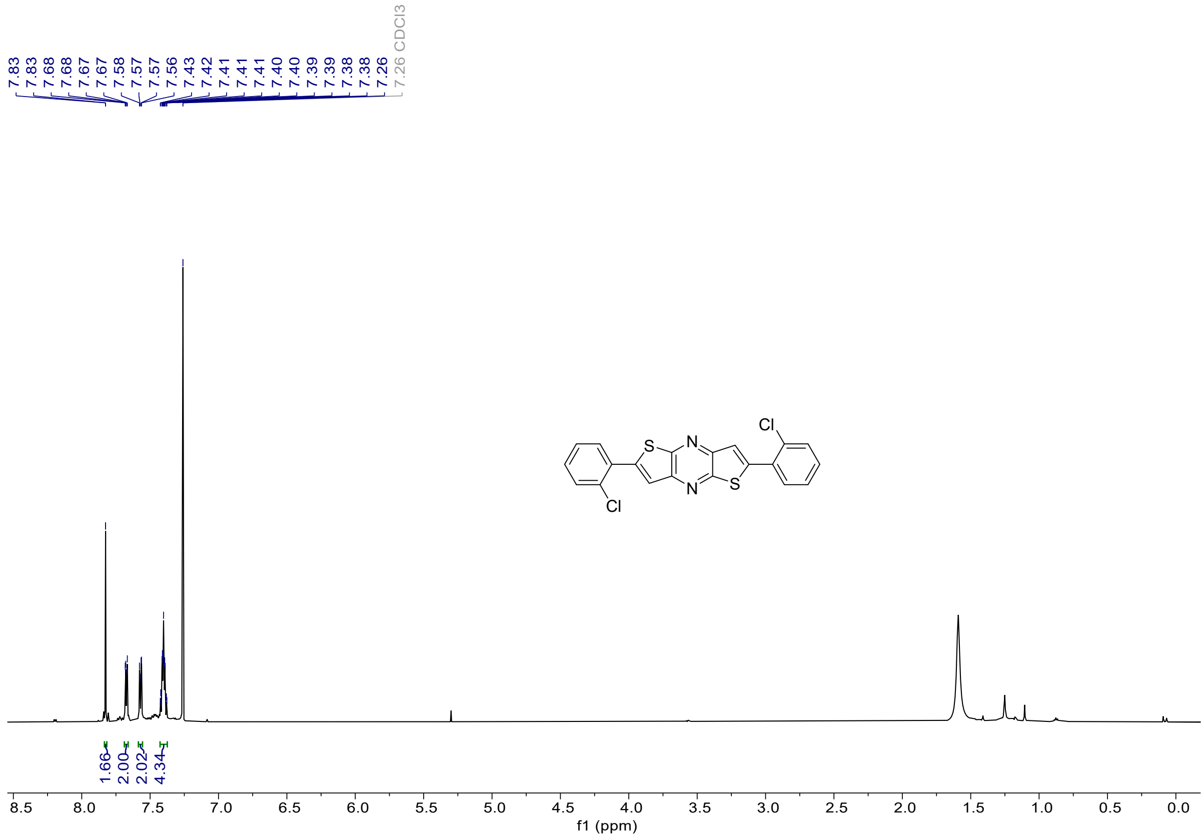


Figure S25. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3f**.

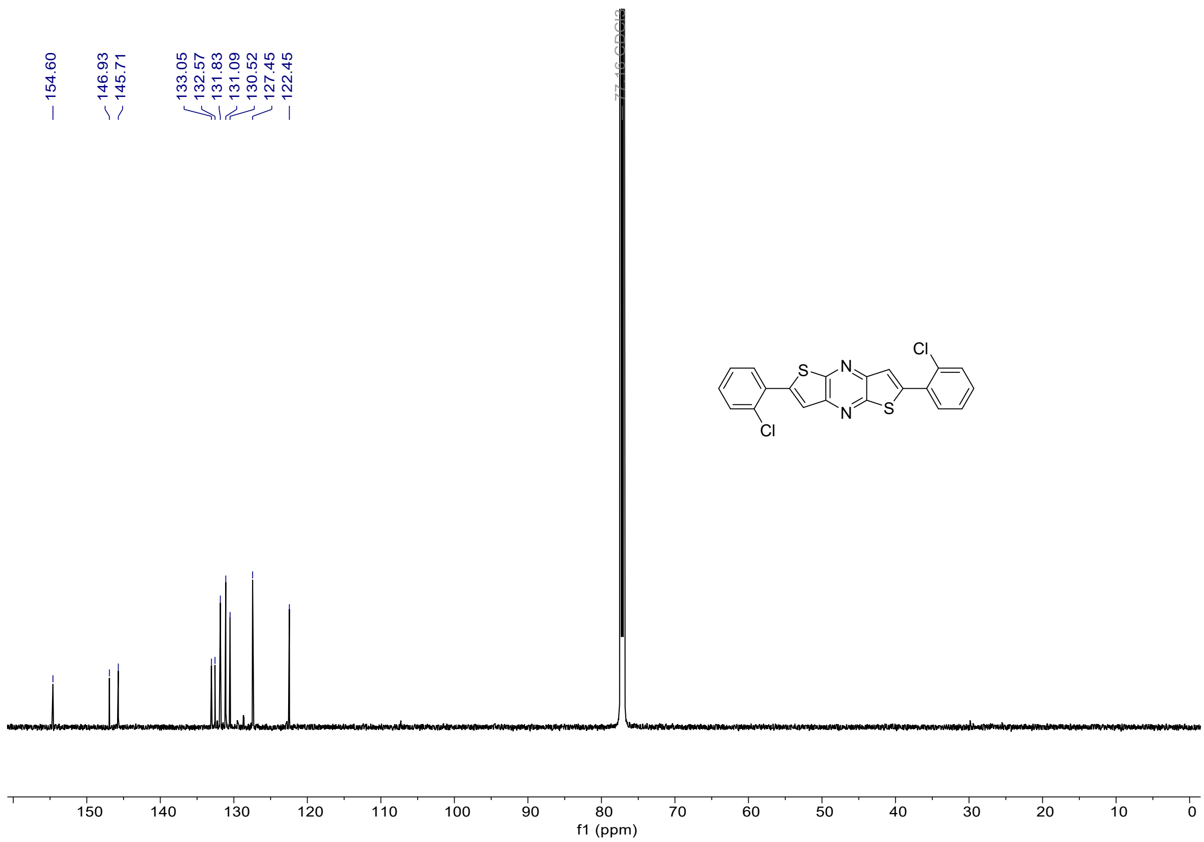


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **3f**.

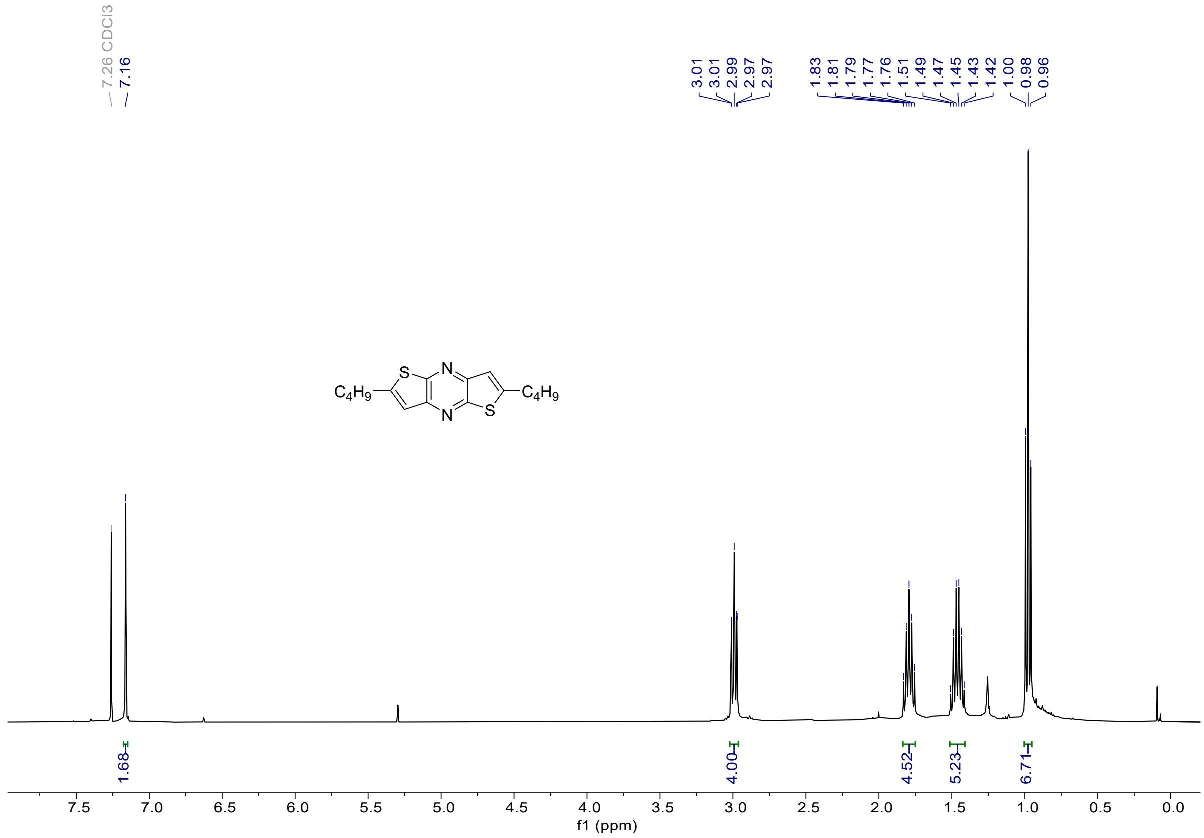


Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3g**.

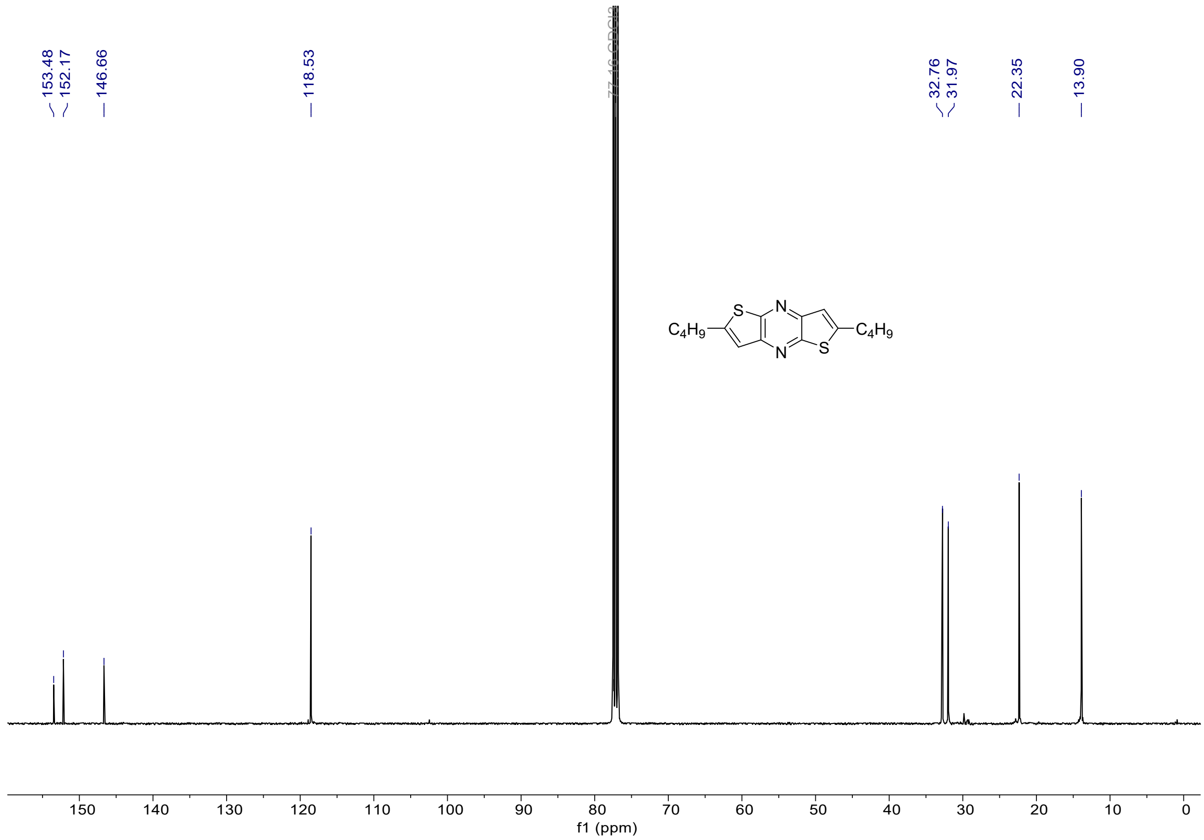


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3g**.

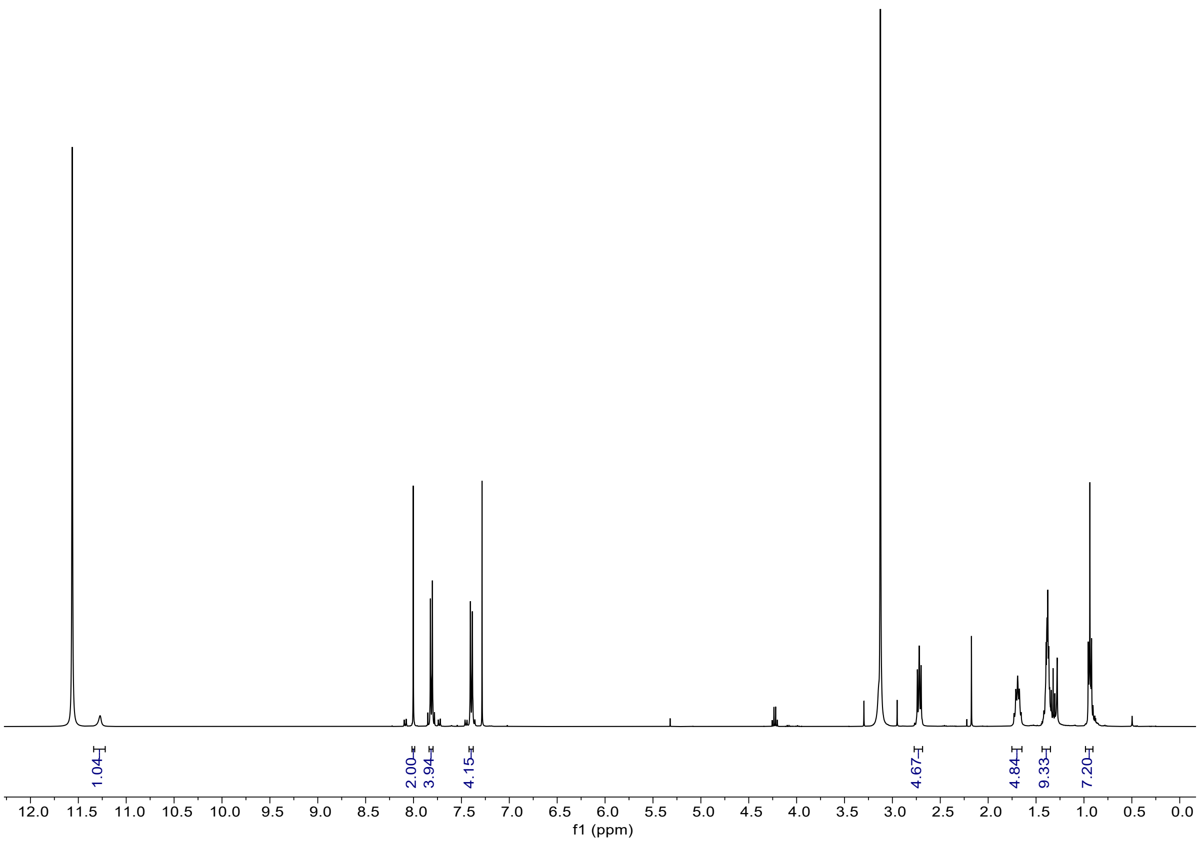


Figure S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b** with addition of $MeSO_3H$ (2 eq.).

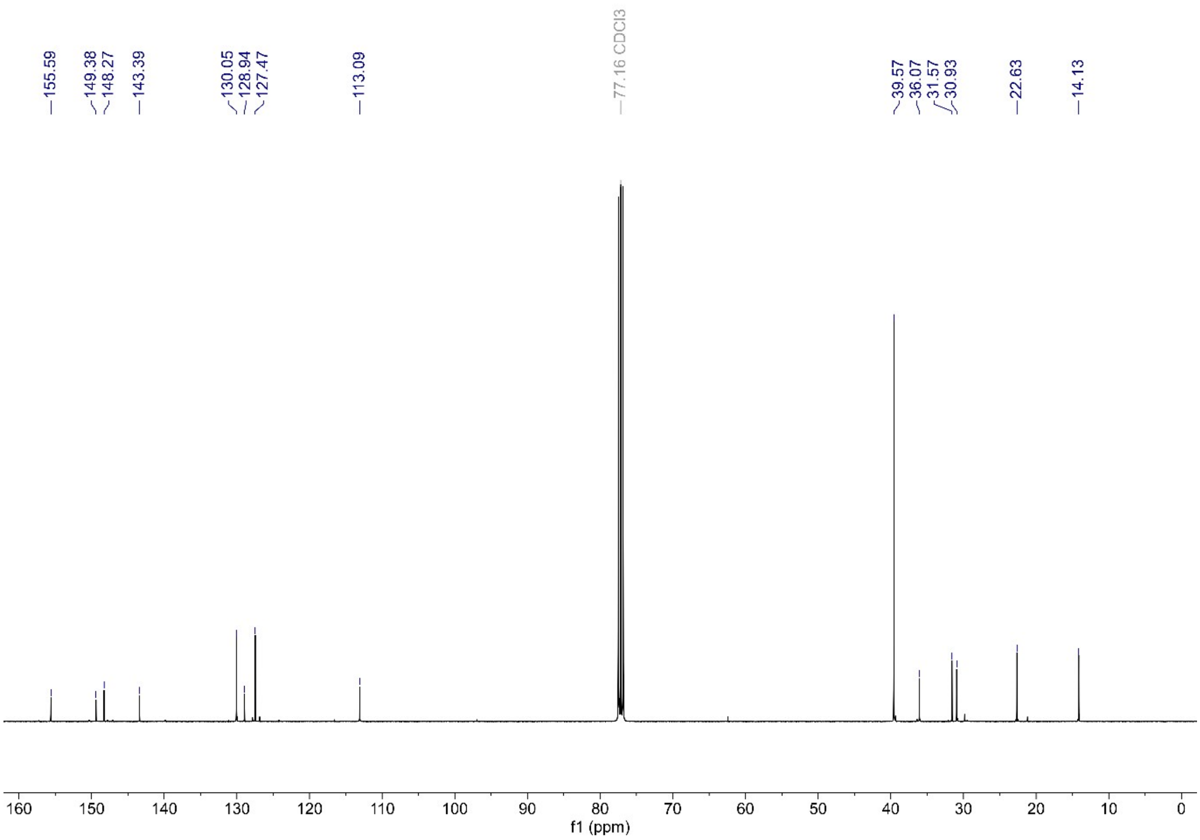


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **3b** with addition of $MeSO_3H$ (2 eq.).

3 UV-Vis and Fluorescence Spectra

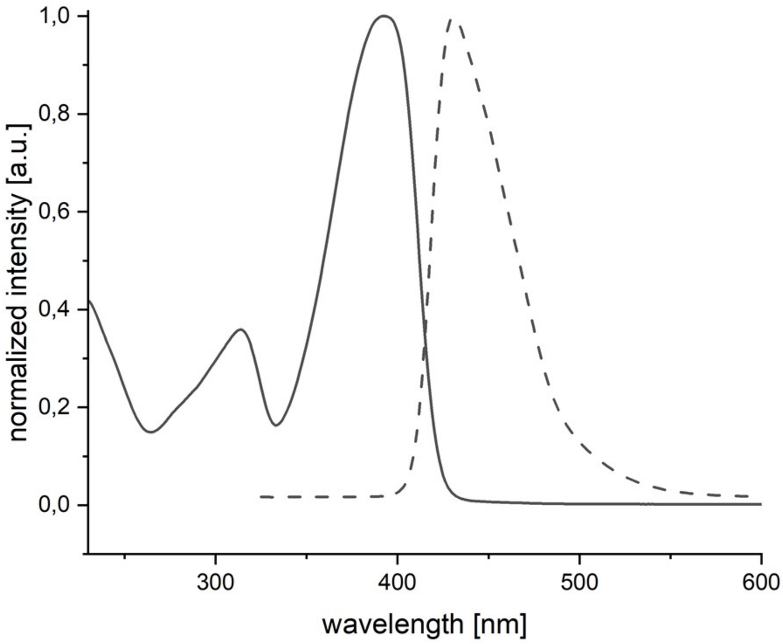


Figure S31. Absorption (solid line) and emission (dashed line) spectra of **2b** in DCM.

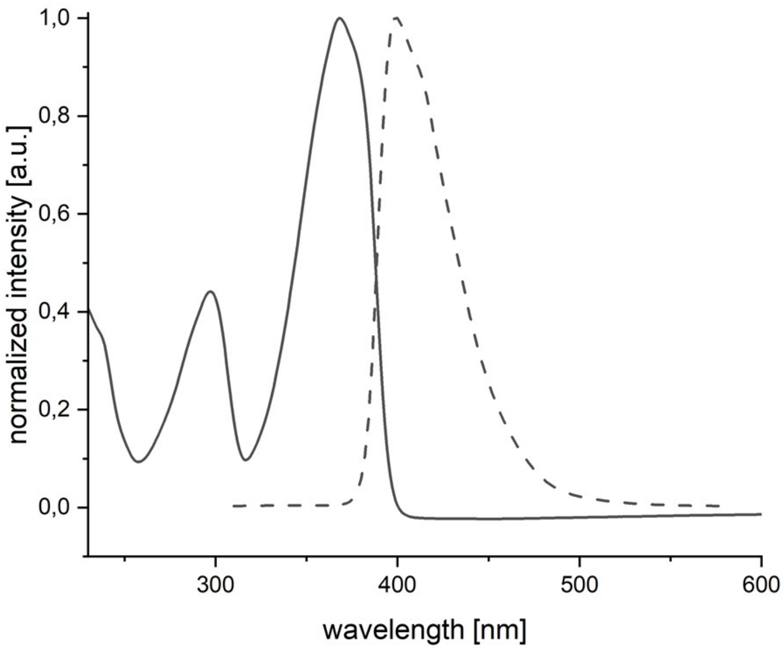


Figure S32. Absorption (solid line) and emission (dashed line) spectra of **2c** in DCM.

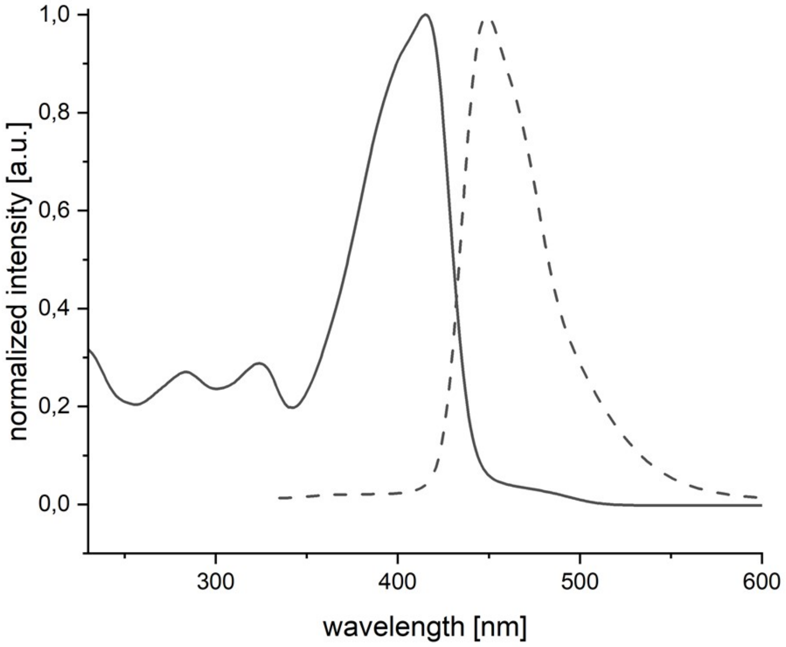


Figure S33. Absorption (solid line) and emission (dashed line) spectra of **2d** in DCM.

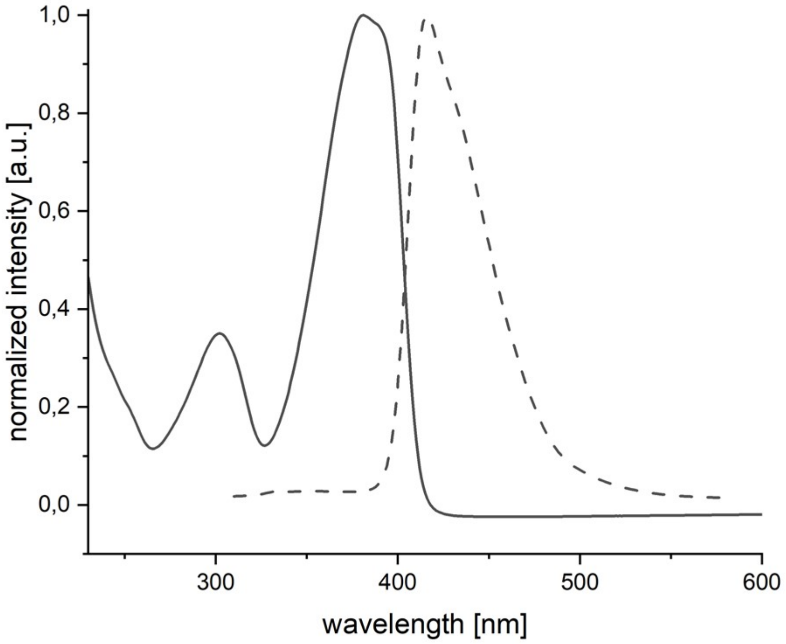


Figure S34. Absorption (solid line) and emission (dashed line) spectra of **2e** in DCM.

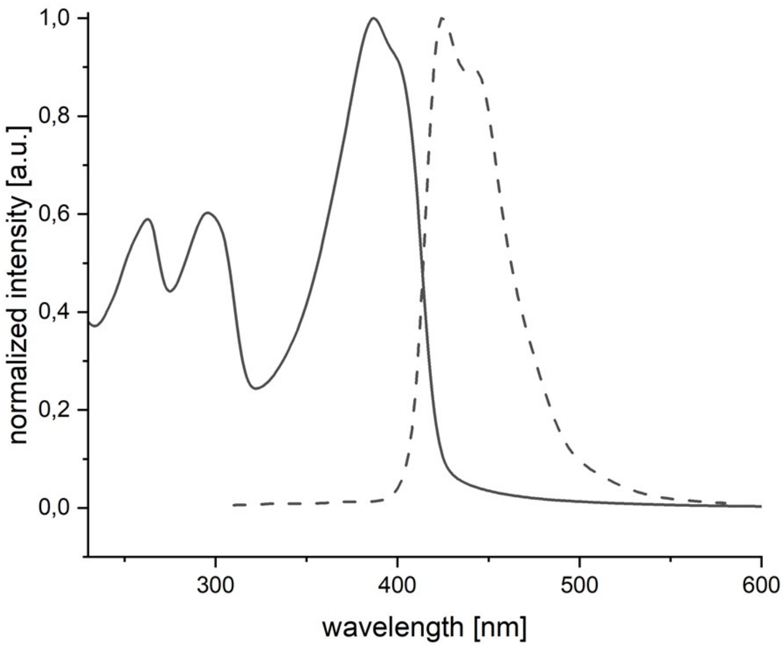


Figure S35. Absorption (solid line) and emission (dashed line) spectra of **2f** in DCM.

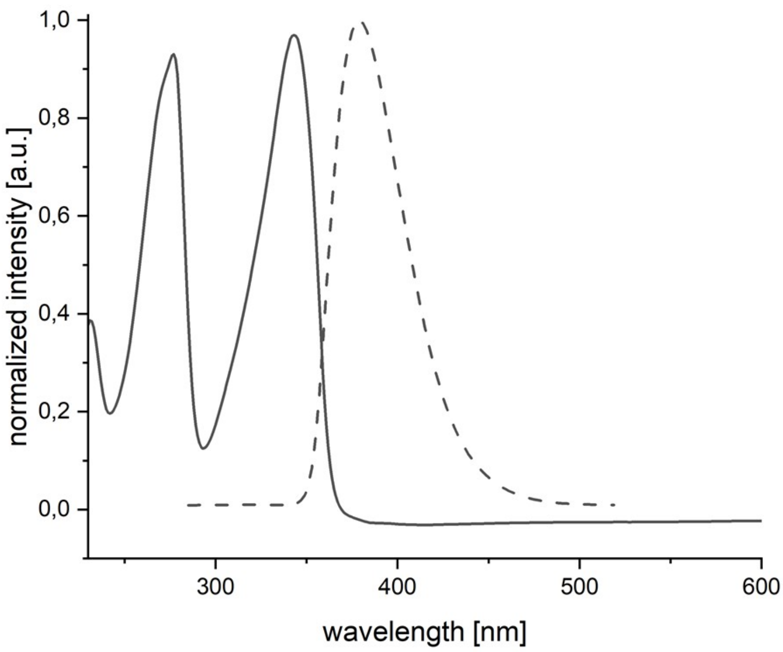


Figure S36. Absorption (solid line) and emission (dashed line) spectra of **2g** in DCM.

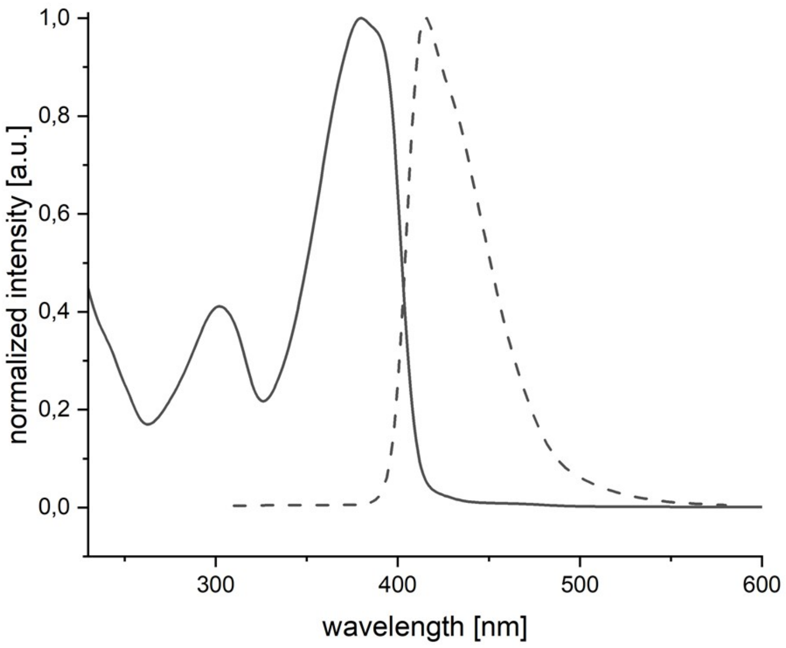


Figure S37. Absorption (solid line) and emission (dashed line) spectra of **3a** in DCM.

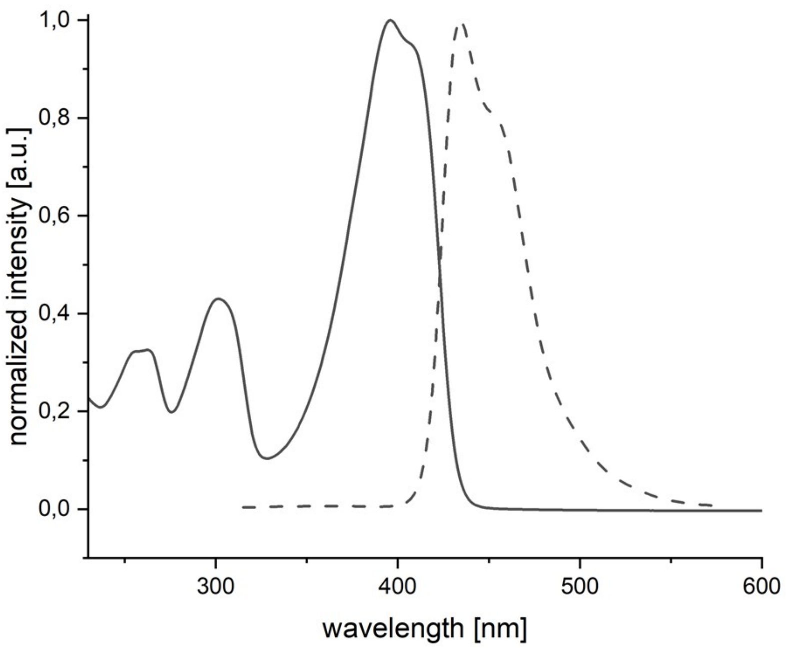


Figure S38. Absorption (solid line) and emission (dashed line) spectra of **3b** in DCM.

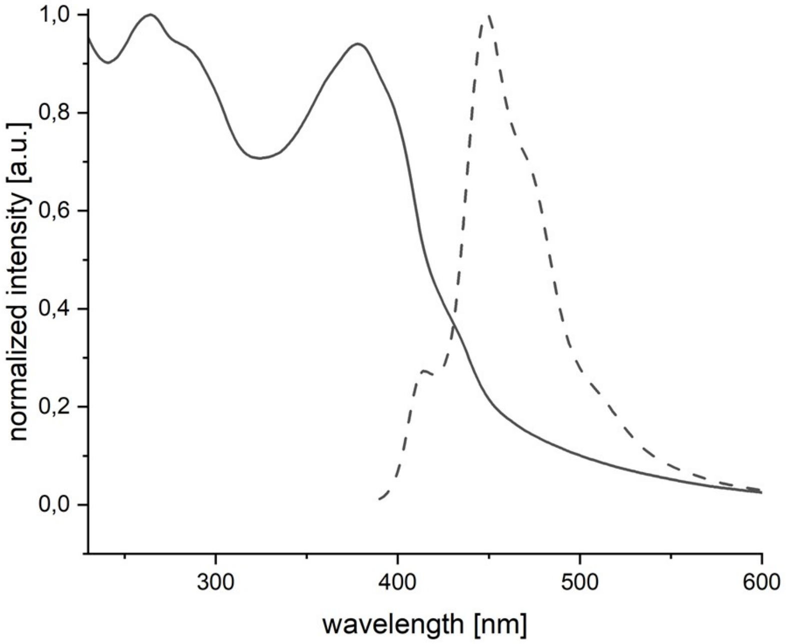


Figure S39. Absorption (solid line) and emission (dashed line) spectra of **3c** in DCM.

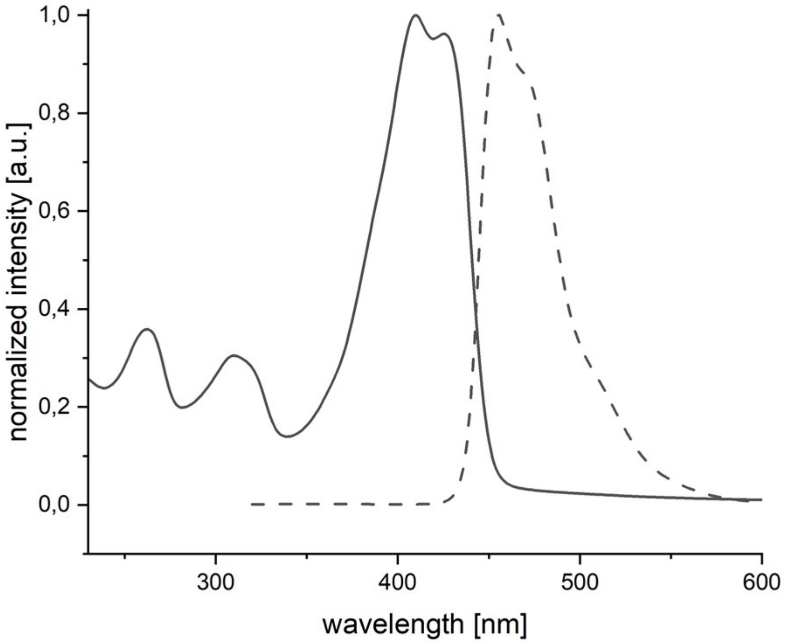


Figure S40. Absorption (solid line) and emission (dashed line) spectra of **3d** in DCM.

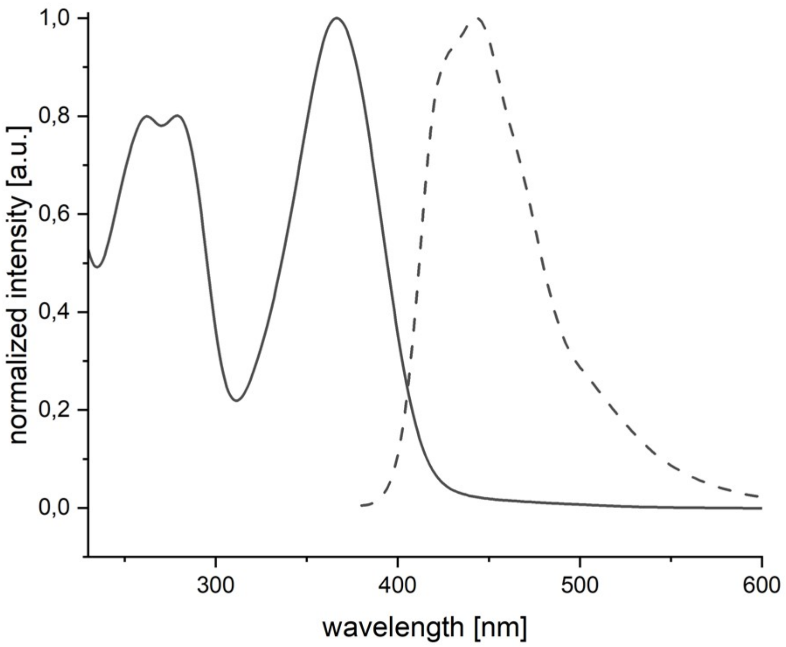


Figure S41. Absorption (solid line) and emission (dashed line) spectra of **3e** in DCM.

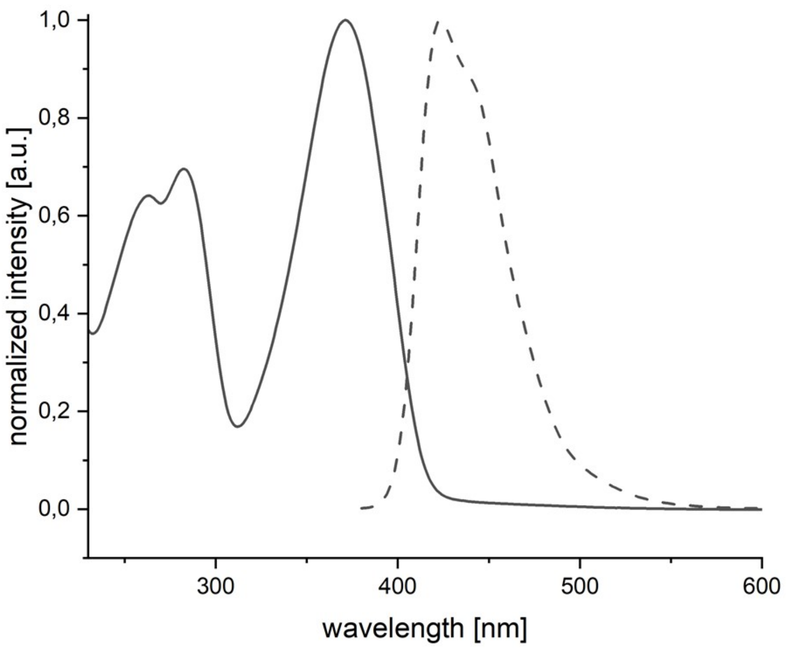


Figure S42. Absorption (solid line) and emission (dashed line) spectra of **3f** in DCM.

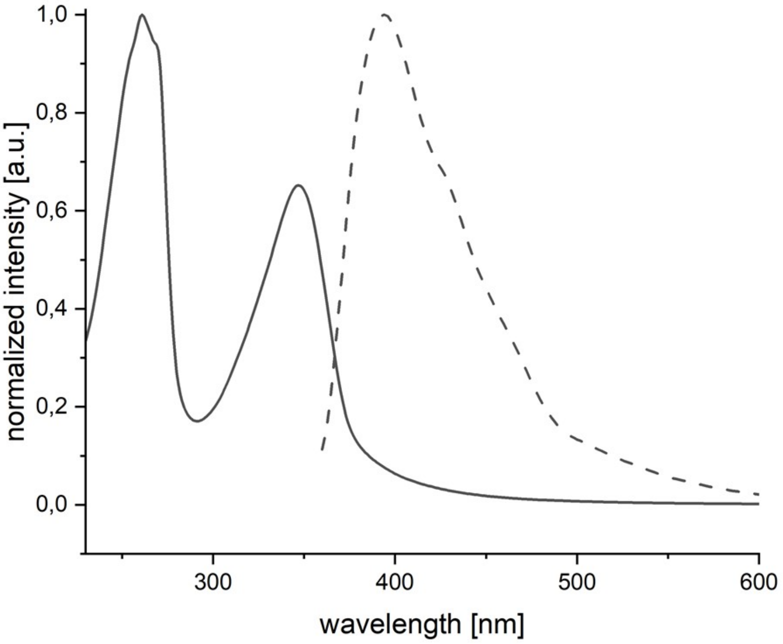


Figure S43. Absorption (solid line) and emission (dashed line) spectra of **3g** in DCM.

4 Electrochemical Data

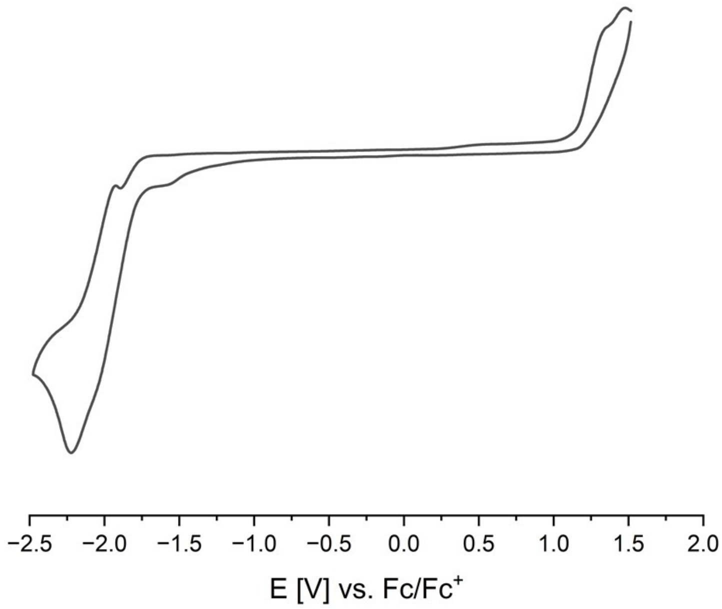


Figure S44. Cyclic voltammogram of **3a** in DCM/tetrabutylammonium hexafluorophosphate (0.1 M), scan speed 500 mV/s at r.t.

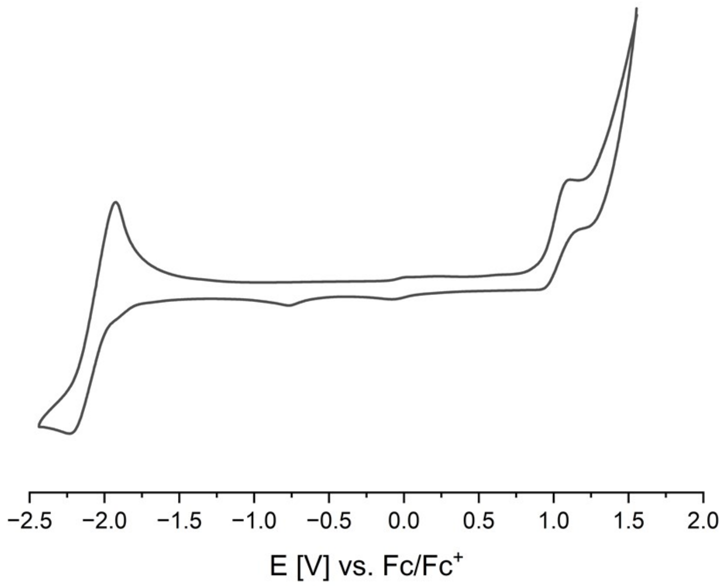


Figure S45. Cyclic voltammogram of **3b** in DCM/tetrabutylammonium hexafluorophosphate (0.1 M), scan speed 500 mV/s at r.t.

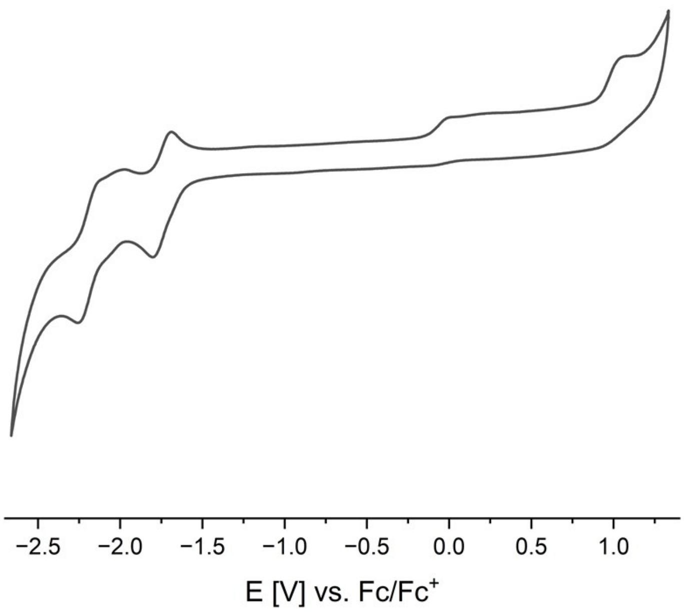


Figure S46. Cyclic voltammogram of **3c** in DCM/tetrabutylammonium hexafluorophosphate (0.1 M), scan speed 500 mV/s at r.t.

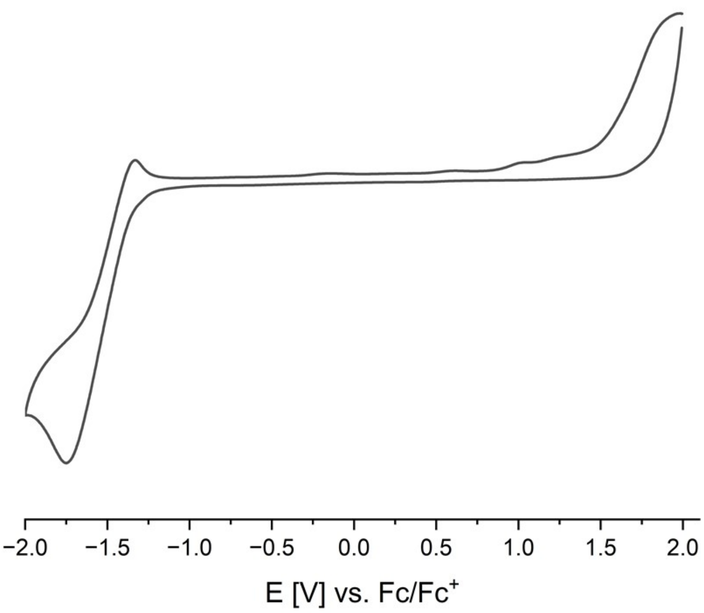


Figure S47. Cyclic voltammogram of **3e** in DCM/tetrabutylammonium hexafluorophosphate (0.1 M), scan speed 500 mV/s at r.t.

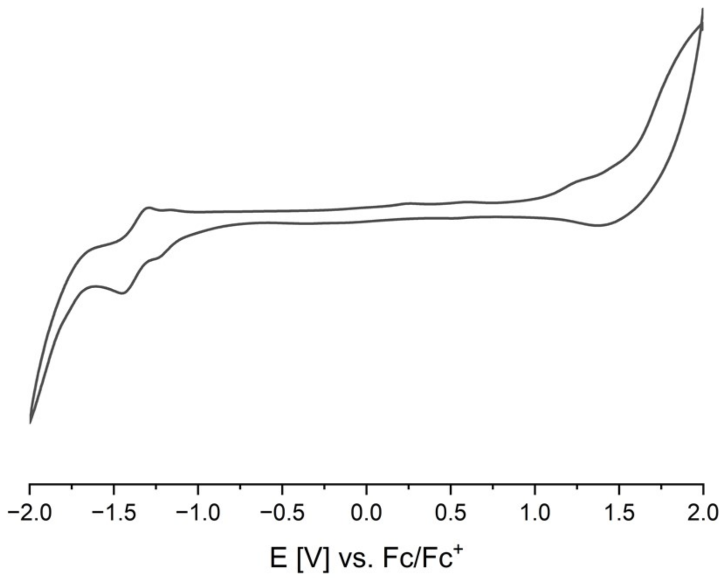


Figure S48. Cyclic voltammogram of **3f** in DCM/tetrabutylammonium hexafluorophosphate (0.1 M), scan speed 500 mV/s at r.t.

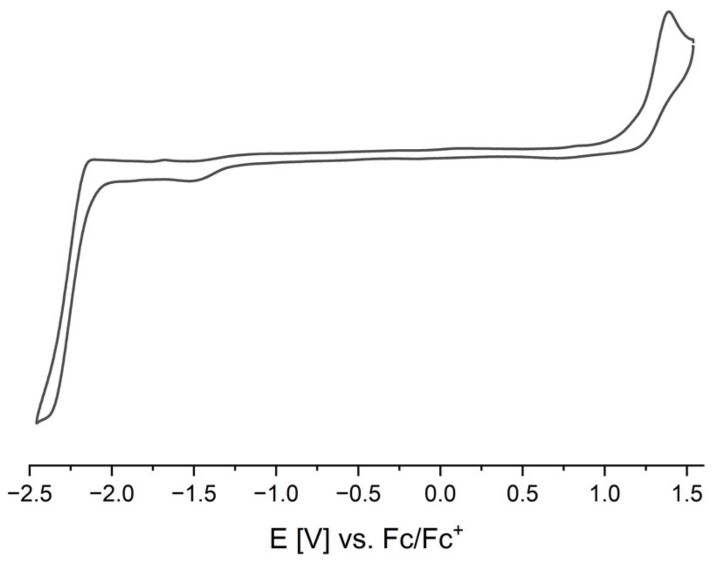
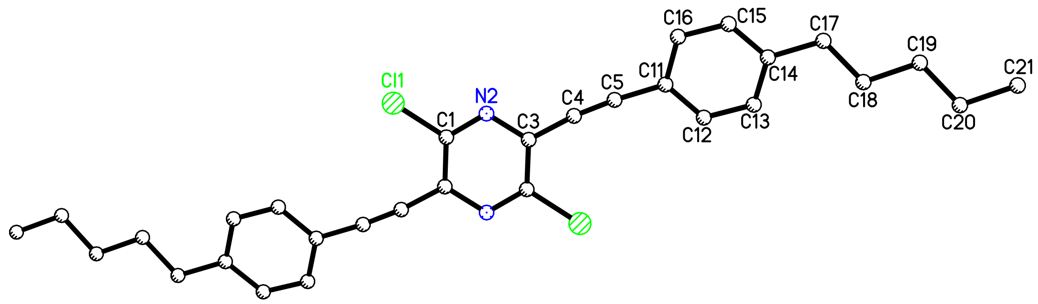


Figure S49. Cyclic voltammogram of **3g** in DCM/tetrabutylammonium hexafluorophosphate (0.1 M), scan speed 500 mV/s at r.t.

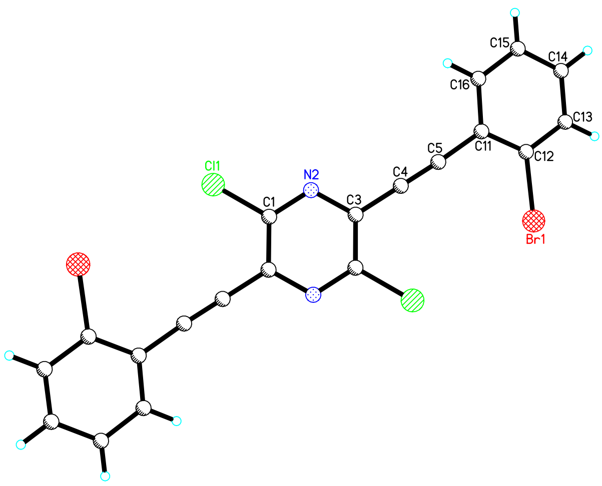
5 Crystallographic Data

Table S1. Crystal structure, crystal data and structure refinement of **2b** (CCDC 2260642).



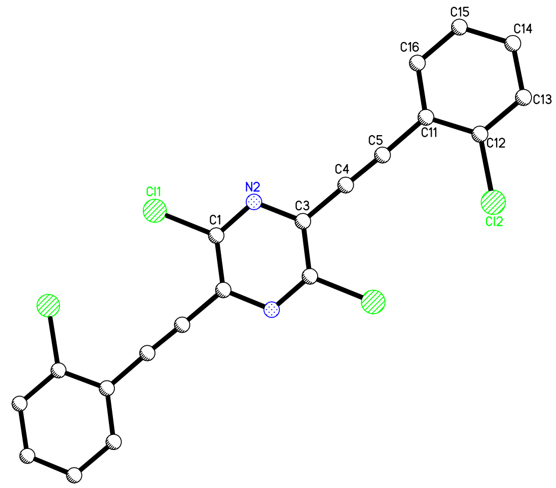
Empirical formula	$C_{30}H_{30}Cl_2N_2$	
Formula weight	489.46	
Temperature	270(2) K	
Wavelength	1.54178 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Z	2	
Unit cell dimensions	a = 8.3303(6) Å	α = 68.470(6) deg.
	b = 12.1997(9) Å	β = 74.945(6) deg.
	c = 14.8086(11) Å	γ = 80.004(6) deg.
Volume	1346.76(18) $Å^3$	
Density (calculated)	1.21 g/cm^3	
Absorption coefficient	2.31 mm^{-1}	
Crystal shape	irregular	
Crystal size	0.070 x 0.050 x 0.022 mm^3	
Crystal colour	yellow	
Theta range for data collection	3.9 to 56.9 deg.	
Index ranges	$-9\leq h\leq 5$, $-13\leq k\leq 13$, $-15\leq l\leq 16$	
Reflections collected	9334	
Independent reflections	3566 (R(int) = 0.0410)	
Observed reflections	2004 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.97 and 0.83	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3566 / 307 / 327	
Goodness-of-fit on F^2	1.00	
Final R indices (I>2sigma(I))	R1 = 0.050, wR2 = 0.110	
Largest diff. peak and hole	0.20 and -0.18 eÅ-3	

Table S2. Crystal structure, crystal data and structure refinement of **2e** (CCDC 2260643).



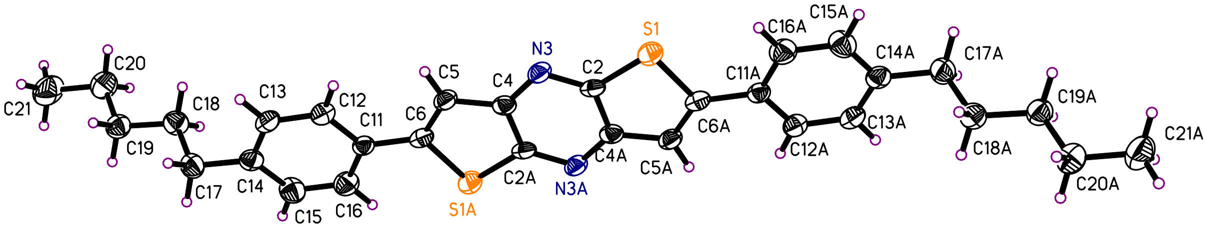
Empirical formula	$C_{20}H_8Br_2Cl_2N_2$	
Formula weight	507.00	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Z	1	
Unit cell dimensions	a = 3.8978(4) Å	α =102.910(2) deg.
	b = 10.0989(10) Å	β = 97.478(2) deg.
	c = 12.0105(12) Å	γ = 99.650(2) deg.
Volume	447.34(8) $Å^3$	
Density (calculated)	1.88 g/cm^3	
Absorption coefficient	4.84 mm^{-1}	
Crystal shape	plank	
Crystal size	0.139 x 0.055 x 0.018 mm^3	
Crystal colour	yellow	
Theta range for data collection	1.8 to 27.3 deg.	
Index ranges	$-5 \le h \le 5$, $-12 \le k \le 12$, $-15 \le l \le 15$	
Reflections collected	6293	
Independent reflections	1873 (R(int) = 0.0493)	
Observed reflections	1327 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.93 and 0.80	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1873 / 0 / 123	
Goodness-of-fit on F^2	1.04	
Final R indices (I>2sigma(I))	R1 = 0.038, wR2 = 0.056	
Largest diff. peak and hole	0.39 and -0.46 $eÅ^{-3}$	

Table S3. Crystal structure, crystal data and structure refinement of **2f** (CCDC 2260644).



Empirical formula	$C_{20}H_8Cl_4N_2$	
Formula weight	418.08	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	2	
Unit cell dimensions	a = 3.8745(6) Å	α = 90 deg.
	b = 11.2406(18) Å	β = 91.300(4) deg.
	c = 20.211(3) Å	γ = 90 deg.
Volume	880.0(2) $Å^3$	
Density (calculated)	1.58 g/cm^3	
Absorption coefficient	0.68 mm^{-1}	
Crystal shape	plank	
Crystal size	0.402 x 0.095 x 0.028 mm^3	
Crystal colour	yellow	
Theta range for data collection	2.0 to 27.2 deg.	
Index ranges	$-4 \le h \le 4$, $-14 \le k \le 14$, $-25 \le l \le 25$	
Reflections collected	9089	
Independent reflections	1913 (R(int) = 0.0573)	
Observed reflections	1597 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.79	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1913 / 94 / 152	
Goodness-of-fit on F^2	1.30	
Final R indices (I>2sigma(I))	R1 = 0.077, wR2 = 0.151	
Largest diff. peak and hole	0.28 and -0.39 $eÅ^{-3}$	

Table S4. Crystal structure, crystal data and structure refinement of **3b** (CCDC 2260645).



Empirical formula	$C_{30}H_{32}N_2S_2$				
Formula weight	484.69				
Temperature	200(2) K				
Wavelength	0.71073 Å				
Crystal system	Triclinic				
Space group	P-1				
Z	1				
Unit cell dimensions	a =	4.7524(8) Å	□ =	102.232(6) deg.	
	b =	8.7141(17) Å	□ =	91.437(4) deg.	
	c =	15.891(3) Å	□ =	99.209(4) deg.	
Volume	633.68(19) $Å^3$				
Density (calculated)	1.27 g/cm^3				
Absorption coefficient	0.23 mm^{-1}				
Crystal shape	column				
Crystal size	0.384 x 0.043 x 0.028 mm^3				
Crystal colour	yellow				
Theta range for data collection	1.3 to 20.7 deg.				
Index ranges	-4≤h≤4, -8≤k≤8, -15≤l≤15				
Reflections collected	5536				
Independent reflections	1316 (R(int) = 0.0541)				
Observed reflections	1044 (I > 2\s(I))				
Absorption correction	Semi-empirical from equivalents				
Max. and min. transmission	0.75 and 0.63				
Refinement method	Full-matrix least-squares on F^2				
Data/restraints/parameters	1316 / 0 / 155				
Goodness-of-fit on F2	1.04				
Final R indices (I>2□(I))	R1 = 0.040, wR2 = 0.085				
Largest diff. peak and hole	0.15 and -0.26 $eÅ^{-3}$				

6 Computational Investigation

6.1 Computational Details

All geometry optimizations, subsequent frequency analyses, and calculations concerning transition states were performed in the gas phase using Orca 5.0.3[5] on the bwForCluster Justus 2. The B3LYP functional and the 6-31G(d,p)[6] basis set were employed. Additionally, the 6-311G(d,p)[7] basis set was employed for bromine.

6.2 Overview of the Computed Molecules

Table S5. Energies of all computed structures.

Compound	E_{HOMO} [eV]	E_{LUMO} [eV]	$E_{g(calc)}$ [eV]
3a	-5.59	-2.07	3.52
3b	-5.40	-1.94	3.46
3c	-6.29	-2.70	3.55
3d	-5.38	-2.24	3.13
3e	-5.96	-2.02	3.94
3f	-5.88	-2.08	3.79
3g	-5.80	-1.55	4.24

6.3 Coordinates of the Optimized Geometries

3a

Xyz

0 1

6 -0.826638000 1.134571000 -0.003290000

6 -1.212522000 -0.244686000 0.000254000

7 0.422178000 1.570946000 -0.004351000

6 1.346555000 0.591652000 0.000298000

7 -0.288145000 -1.223981000 -0.004453000

6 0.960671000 -0.787606000 -0.003347000

16 -2.237574000 2.185258000 -0.000058000

6 -3.317408000 0.774441000 -0.007739000

6 -2.632311000 -0.410886000 -0.003924000

16 2.371607000 -1.838292000 -0.000173000

6 3.451441000 -0.427475000 -0.007744000

6 2.766343000 0.757851000 -0.003852000

1 -3.105902000 -1.383943000 -0.034781000

1 3.239935000 1.730911000 -0.034635000

6 -4.769343000 0.967419000 -0.009368000

6 -5.350577000 2.143712000 -0.513588000

6	-5.615576000	-0.035944000	0.497262000
6	-6.997265000	0.128968000	0.485779000
6	-7.563160000	1.301671000	-0.020788000
6	-6.733543000	2.308435000	-0.517274000
1	-4.715839000	2.923839000	-0.923365000
1	-7.163540000	3.222884000	-0.914939000
1	-7.634217000	-0.655249000	0.884217000
1	-8.641290000	1.430697000	-0.024079000
1	-5.182684000	-0.936230000	0.921164000
6	4.903376000	-0.620453000	-0.009372000
6	5.484615000	-1.796709000	-0.513672000
6	5.749603000	0.382874000	0.497340000
6	6.867581000	-1.961431000	-0.517357000
6	7.697193000	-0.954703000	-0.020790000
6	7.131292000	0.217963000	0.485859000
1	5.316707000	1.283128000	0.921304000
1	8.775323000	-1.083727000	-0.024080000
1	7.768240000	1.002151000	0.884361000
1	4.849881000	-2.576806000	-0.923512000
1	7.297583000	-2.875850000	-0.915085000

3b

Xyz

0 1

6	-0.607434000	1.269740000	-0.272469000
6	-1.038009000	-0.089434000	-0.408933000
7	0.653305000	1.657996000	-0.174209000
6	1.544647000	0.648951000	-0.214028000
7	-0.147138000	-1.099207000	-0.439756000
6	1.113677000	-0.710814000	-0.343191000
16	-1.981736000	2.368330000	-0.255558000

6	-3.106669000	1.002660000	-0.414907000
6	-2.460822000	-0.202892000	-0.485655000
16	2.488055000	-1.809314000	-0.361452000
6	3.611955000	-0.445331000	-0.181920000
6	2.966713000	0.761284000	-0.123949000
1	-2.967963000	-1.156631000	-0.557742000
1	3.470801000	1.709781000	0.011102000
6	-4.548713000	1.247266000	-0.460985000
6	-5.120141000	2.396755000	0.104179000
6	-5.409224000	0.317965000	-1.076405000
6	-6.779513000	0.533512000	-1.105690000
6	-7.355206000	1.681330000	-0.536045000
6	-6.497380000	2.608266000	0.065354000
1	-4.992537000	-0.564602000	-1.551136000
6	5.053125000	-0.691172000	-0.118753000
6	5.573339000	-1.922441000	0.306241000
6	5.964326000	0.318932000	-0.482497000
6	6.949033000	-2.136675000	0.374009000
6	7.856073000	-1.131407000	0.022645000
6	7.332139000	0.099256000	-0.406720000
1	5.591006000	1.270907000	-0.846194000
1	-7.422760000	-0.197356000	-1.590259000
1	-6.900189000	3.507202000	0.518799000
1	8.015528000	0.894003000	-0.696698000
1	7.310951000	-3.101067000	0.713019000
1	-4.484650000	3.125132000	0.599511000
1	4.896553000	-2.716498000	0.608192000
6	-8.858701000	1.863553000	-0.600375000
6	9.359722000	-1.314360000	0.080742000
6	9.862856000	-2.671027000	0.577764000
1	9.780541000	-0.523523000	0.717975000

1	9.771657000	-1.126579000	-0.921190000
6	-9.419865000	3.132502000	0.044345000
1	-9.334011000	0.988076000	-0.135287000
1	-9.167713000	1.832697000	-1.655021000
6	-10.944723000	3.222468000	-0.066500000
1	-8.970269000	4.016910000	-0.426692000
1	-9.132429000	3.166748000	1.103796000
6	-11.524908000	4.484708000	0.579508000
1	-11.396989000	2.335499000	0.399862000
1	-11.236159000	3.189887000	-1.126081000
6	-13.049246000	4.567462000	0.466254000
1	-11.071815000	5.369841000	0.112650000
1	-11.231713000	4.515433000	1.637736000
1	-13.367124000	4.570636000	-0.582762000
1	-13.438294000	5.477030000	0.935353000
1	-13.527807000	3.709857000	0.953092000
6	11.391775000	-2.755246000	0.607074000
1	9.469408000	-3.470022000	-0.064850000
1	9.470903000	-2.863614000	1.585509000
6	11.914039000	-4.105491000	1.108282000
1	11.788863000	-1.953012000	1.245412000
1	11.787054000	-2.564430000	-0.400929000
6	13.442653000	-4.182394000	1.135041000
1	11.515735000	-4.905867000	0.469943000
1	11.517687000	-4.294066000	2.115293000
1	13.862691000	-4.028780000	0.134302000
1	13.789821000	-5.155775000	1.496605000
1	13.864688000	-3.412555000	1.791342000

3c

Xyz

0 1

6	-0.870221000	1.085308000	0.068096000
6	-1.250718000	-0.288753000	-0.074952000
7	0.377053000	1.520833000	0.127632000
6	1.303596000	0.548525000	0.042625000
7	-0.324606000	-1.262073000	-0.148951000
6	0.922577000	-0.826595000	-0.088539000
16	-2.283183000	2.129846000	0.146573000
6	-3.353390000	0.723538000	-0.004391000
6	-2.669842000	-0.457264000	-0.112599000
16	2.334198000	-1.871713000	-0.168043000
6	3.405701000	-0.466371000	-0.017009000
6	2.723216000	0.716139000	0.079698000
1	-3.141575000	-1.429028000	-0.186195000
1	3.195058000	1.682477000	0.205663000
6	-4.807206000	0.907178000	-0.009424000
6	-5.409149000	2.005669000	0.623179000
6	-5.630330000	-0.030745000	-0.654401000
6	-7.013331000	0.123069000	-0.651117000
6	-7.607919000	1.214044000	-0.015916000
6	-6.794953000	2.152436000	0.617422000
1	-4.799047000	2.742945000	1.133465000
1	-8.684582000	1.332223000	-0.018510000
1	-5.188491000	-0.873564000	-1.172339000
6	4.858796000	-0.655901000	-0.010332000
6	5.435924000	-1.859833000	0.418030000
6	5.706894000	0.381130000	-0.436624000
6	6.821374000	-2.019168000	0.422759000
6	7.657567000	-0.986216000	0.008294000
6	7.087751000	0.215512000	-0.418371000
1	5.285277000	1.308156000	-0.806491000

1	8.732528000	-1.114995000	0.010962000
1	4.806342000	-2.669509000	0.771873000
6	-7.425214000	3.297724000	1.366763000
6	-7.874751000	-0.854561000	-1.407515000
6	7.397416000	-3.345306000	0.846699000
6	7.985026000	1.358294000	-0.817007000
9	-7.674401000	2.962433000	2.651867000
9	-8.601051000	3.665144000	0.815844000
9	-6.621636000	4.381973000	1.386995000
9	-9.083570000	-1.002806000	-0.826382000
9	-7.299495000	-2.073862000	-1.480560000
9	-8.090329000	-0.438757000	-2.674948000
9	6.790166000	-3.810120000	1.960525000
9	8.719302000	-3.263281000	1.101340000
9	7.227439000	-4.280836000	-0.113334000
9	9.130595000	0.917766000	-1.378240000
9	8.329423000	2.104815000	0.255636000
9	7.383312000	2.183386000	-1.699841000

3d

Xyz

0 1

6	-0.017520000	1.450650000	0.330793000
6	-0.873400000	0.356139000	-0.017818000
7	1.287258000	1.361071000	0.520739000
6	1.783751000	0.118823000	0.358407000
7	-0.376879000	-0.886068000	-0.180347000
6	0.927878000	-0.975669000	0.009719000
16	-0.930370000	2.948889000	0.476855000
6	-2.434821000	2.093146000	0.071563000
6	-2.236595000	0.754976000	-0.156876000

16	1.840615000	-2.474016000	-0.135816000
6	3.345227000	-1.618111000	0.268519000
6	3.147004000	-0.279964000	0.497104000
1	-3.026864000	0.061346000	-0.417327000
1	3.937474000	0.413877000	0.756381000
6	4.583052000	-2.359454000	0.320430000
6	-3.672624000	2.834494000	0.019236000
6	-3.878927000	4.180940000	0.243214000
16	-5.188839000	2.040668000	-0.368345000
6	-6.061790000	3.530490000	-0.221223000
6	-5.238538000	4.574880000	0.105932000
6	4.791516000	-3.703095000	0.082073000
6	6.971007000	-3.057116000	0.568067000
6	6.150436000	-4.097977000	0.223422000
1	-7.130258000	3.545038000	-0.385088000
1	-5.589714000	5.590599000	0.244329000
1	6.503055000	-5.111807000	0.075193000
1	-3.076580000	4.863996000	0.498165000
1	3.991342000	-4.383338000	-0.186842000
16	6.096264000	-1.569572000	0.727301000
1	8.038410000	-3.072995000	0.738618000

3e

Xyz

0 1

6	-0.862634000	0.960171000	-0.449136000
6	-1.236589000	-0.151853000	0.372763000
7	0.376498000	1.233144000	-0.828493000
6	1.294952000	0.362184000	-0.374345000
7	-0.318133000	-1.022814000	0.826910000
6	0.920999000	-0.749841000	0.447555000

16	-2.262530000	1.928071000	-0.888340000
6	-3.321151000	0.843417000	0.031646000
6	-2.647216000	-0.189864000	0.617983000
16	2.320897000	-1.717740000	0.886759000
6	3.379519000	-0.633070000	-0.033221000
6	2.705581000	0.400192000	-0.619576000
1	-3.125817000	-0.952040000	1.220187000
1	3.184169000	1.162367000	-1.221792000
6	-4.785037000	1.012639000	0.024279000
6	-5.464735000	2.161385000	0.466180000
6	-5.566921000	-0.059825000	-0.444568000
6	-6.956239000	0.008907000	-0.477974000
6	-7.602368000	1.167105000	-0.045712000
6	-6.856408000	2.244455000	0.430277000
1	-8.685395000	1.236768000	-0.072448000
1	-5.052786000	-0.947221000	-0.798766000
6	4.843400000	-0.802337000	-0.025840000
6	5.523047000	-1.951085000	-0.467812000
6	5.625320000	0.270057000	0.443101000
6	6.914714000	-2.034226000	-0.431889000
6	7.660715000	-0.956944000	0.044192000
6	7.014636000	0.201255000	0.476526000
1	5.111219000	1.157454000	0.797346000
1	8.743738000	-1.026660000	0.070944000
1	-7.529889000	-0.834774000	-0.848191000
1	-7.347952000	3.143083000	0.784433000
1	7.588323000	1.044880000	0.846814000
1	7.406225000	-2.932852000	-0.786096000
35	-4.515569000	3.651857000	1.214766000
35	4.573798000	-3.441455000	-1.216491000

3f

Xyz

0 1

6	-0.846486000	1.016729000	-0.360347000
6	-1.245210000	-0.179492000	0.318914000
7	0.401481000	1.319671000	-0.683226000
6	1.303740000	0.390976000	-0.318128000
7	-0.342951000	-1.108185000	0.684015000
6	0.905015000	-0.805242000	0.361132000
16	-2.227780000	2.048490000	-0.700373000
6	-3.316828000	0.870882000	0.057269000
6	-2.658968000	-0.230112000	0.532883000
16	2.286439000	-1.836538000	0.702048000
6	3.375219000	-0.659926000	-0.057527000
6	2.717441000	0.441363000	-0.532554000
1	-3.153011000	-1.052534000	1.034989000
1	3.211378000	1.263578000	-1.035104000
6	-4.779275000	1.035976000	0.040886000
6	-5.467403000	2.195407000	0.443890000
6	-5.558030000	-0.054490000	-0.393024000
6	-6.947251000	0.002776000	-0.423036000
6	-7.601030000	1.169085000	-0.024609000
6	-6.859770000	2.265655000	0.410397000
1	-8.684512000	1.230365000	-0.049986000
1	-5.041089000	-0.947752000	-0.727218000
6	4.837601000	-0.825663000	-0.042423000
6	5.524831000	-1.985509000	-0.445756000
6	5.617230000	0.264540000	0.390546000
6	6.917193000	-2.056412000	-0.413446000
6	7.659343000	-0.960081000	0.020649000

6	7.006454000	0.206629000	0.419362000
1	5.101009000	1.158138000	0.724959000
1	8.742818000	-1.021860000	0.045097000
1	-7.515328000	-0.855665000	-0.766941000
1	-7.350893000	3.175826000	0.735228000
1	7.575225000	1.064895000	0.762555000
1	7.407595000	-2.966902000	-0.738470000
17	-4.604228000	3.595074000	1.059592000
17	4.660431000	-3.384935000	-1.060290000

3g

Xyz

0 1

6	-0.213785000	1.510870000	0.176430000
6	-1.078505000	0.387840000	-0.013580000
7	1.106105000	1.443729000	0.257387000
6	1.602006000	0.198623000	0.144620000
7	-0.582603000	-0.857266000	-0.126343000
6	0.737287000	-0.924408000	-0.045387000
16	-1.141656000	3.003980000	0.289404000
6	-2.657782000	2.107271000	0.082439000
6	-2.462717000	0.767152000	-0.061984000
16	1.665165000	-2.417507000	-0.158445000
6	3.181280000	-1.520815000	0.048676000
6	2.986217000	-0.180692000	0.193053000
1	-3.259613000	0.047998000	-0.199866000
1	3.783107000	0.538463000	0.330970000
6	4.472778000	-2.286732000	0.044947000
6	-3.949286000	2.873178000	0.086260000
6	-5.196442000	2.003232000	-0.099338000

6	-6.489783000	2.824457000	-0.088663000
1	-5.236605000	1.248257000	0.696436000
1	-5.120542000	1.453595000	-1.046442000
6	-7.739760000	1.960519000	-0.273515000
1	-6.444168000	3.582361000	-0.882337000
1	-6.559887000	3.377389000	0.857793000
1	-7.708932000	1.421397000	-1.227196000
1	-8.650724000	2.567417000	-0.262372000
1	-7.825181000	1.214742000	0.525002000
6	5.719923000	-1.416804000	0.230712000
6	7.013257000	-2.238041000	0.220160000
1	5.643920000	-0.867192000	1.177822000
1	5.760183000	-0.661806000	-0.565037000
6	8.263224000	-1.374113000	0.405126000
1	7.083445000	-2.790977000	-0.726287000
1	6.967560000	-2.995940000	1.013834000
1	8.348742000	-0.628357000	-0.393401000
1	9.174182000	-1.981023000	0.394098000
1	8.232300000	-0.834966000	1.358790000
1	-4.030847000	3.431654000	1.029543000
1	-3.915044000	3.635790000	-0.704660000
1	4.438454000	-3.049386000	0.835825000
1	4.554428000	-2.845159000	-0.898356000

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