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SUPPORTING INFORMATION

3,4-Phenylenedioxythiophenes (PheDOTs) functionalized with electron-withdrawing groups and their analogs for organic electronics. Remarkably efficient tuning the energy levels in flat conjugated polymers

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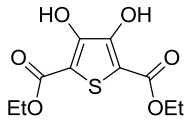
CONTENTS

Experimental Part

Materials

All starting materials were purchased from Aldrich, Fisher Scientific or Alfa Aesar and were used without further purification. Diethyl 3,4-dihydroxy-2,5-dicarboxylate (**1**) and dimethyl 3,4-dihydroxy-2,5-dicarboxylate (**27**) were synthesized according to the method described by Hinsberg[1] (syntheses by this protocol have also been described in later publications[2]). Disodium 2,5-bis(methoxycarbonyl)thiophene-3,4-bis(olate) (**26**) was obtained as an intermediate in synthesis of compound **27** by this method.



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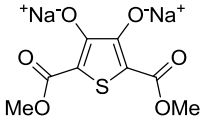

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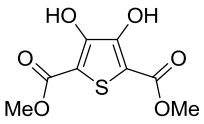

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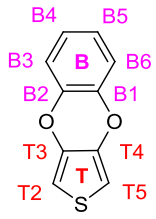
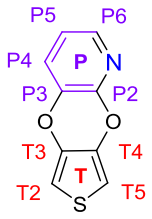
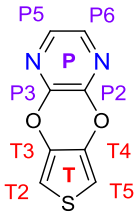
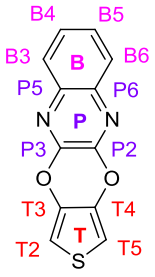
Instruments

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded using a Bruker Avance 400 instrument in $CDCl_3$. Tetramethylsilane (TMS) (δ_H , δ_C = 0.00 ppm) and C_6F_6 (δ_F = –163.0 ppm) were used as internal standards. For assigning H and C signals, DEPTQ and 2D NMR (^{1}H-^{1}H COSY, ^{13}C-^{1}H HSQC and HMBC spectroscopy have been used). Enumerations of H and C atoms used in description of ^{1}H and ^{13}C NMR spectra are shown below:









Electron impact mass spectra (positive mode) were recorded on a GC-MS system consisting of a HP 5890 gas chromatograph with a HP 8971 EI-MS detector, operating at 70KeV. Thin layer chromatography (TLC) was carried out throughout all syntheses using Merck TLC silica gel 60 aluminium sheets. Microwave assisted reactions were carried out in a CEM Discover SP microwave reactor, with a maximum power output of 300 W and controlling the temperature of the reaction mixture. Purification of synthesised compounds by flash chromatography was performed manually on glass columns or on Teledyn ISCO Combiflash Rf 200 flash chromatograph on silica gel 40-60 μm (40–250 mesh). UV-Vis electron absorption spectra of **ArDOT** monomers were recorded on a Shimadzu UV-3600 spectrophotometer in dichloromethane in quartz cells of 10 mm path length.

Computational methodology

Computational studies were carried out using density functional theory (DFT) with the Gaussian 09[3] package of programs. Becke's three-parameter hybrid exchange functional[4] with the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP)[5] and Pople's 6-31G split valence basis set supplemented by d-polarization functions for heavy atoms were employed [B3LYP/6-31G(d)]. The restricted Hartree-Fock formalism was used. The geometries of the oligomers, **(ArDOT)$_n$**, were fully optimized for isolated molecules in a gas phase, with no constraints, and the electronic structures for the optimised geometries were calculated at the same level of theory.

Optimization of the geometries of the polymers, **p[ArDOTs]**, and calculation of their electronic structures were performed using periodic boundary conditions formalism (PBC) at the PBC/B3LYP/6-31G(d) level, which generally gives a good estimate of the band gaps of conjugated

polymers, including polythiophenes.[6] The unit cells for PBC calculations of the polymers presented in the paper have been prepared from the optimized structures of corresponding dimers. Presented in the paper PBC calculations of non-symmetrical **ArDOTs** (as in the case of **p[4R-PheDOT]** and **p[5CF$_3$-PyDOT]**) from the dimers as unit cells, are for head-to-tail (HT) connectivity of the monomer units in all the cases. For comparison, we also performed calculations for head-to-head/tail-to-tail (HH-TT) arrangement of the monomer units in the polymer backbone.The results show that in the absence of steric repulsions between the side aromatic moieties, which are on the same side of the polymer backbone (as in the case of **p[4R-PheDOT]** and **p[5CF$_3$-PyDOT]**), the calculations of the polymers with HT and HH-TT arrangement give very close total energies (differencies are 0.00 – 0.39 kcal/mol), as well as HOCO, LUCO and E_g (differences are 0 – 5 meV) (Table S1). Of course, these differences are substantially higher in the case of polymers with substantial steric repulsion between the the side moieties, i.e. **p[3NO$_2$,5CF$_3$-PheDOT]**, **p[3NO$_2$,5CF$_3$-PheDOT]** and **p[F$_6$-NaphDOT(1,2)]**, and PBC calculations for these polymer were not performed.

Table S1. Total energies (E_{total}), HOCO/LUCO energy levels and the band gaps (E_g,) of regioisomeric **p[ArDOTs]** by PBC/B3LYP/6-31G(d) calculations in the gas phase

Polymer	Regio-isomer[a]	E_{total}, hartree	ΔE_{total} (HT–HHTT), kcal/mol	HOCO, eV	LUCO, eV	E_g, eV
p[4Me-PheDOT]	HT	–1942.8090085	–0.08	–4.270	–2.147	2.123
	HHTT	–1942.8088779		–4.268	–2.139	2.129
p[4F-PheDOT]	HT	–2062.6355280	0.00	–4.644	–2.511	2.133
	HHTT	–2062.6355222		–4.644	–2.512	2.132
p[4Br-PheDOT]	HT	–7006.3793017	0.00	–4.770	–2.631	2.139
	HHTT	–7006.3793007		–4.770	–2.631	2.140
p[4Cl-PheDOT]	HT	–2783.3613276	0.00	–4.790	–2.650	2.140
	HHTT	–2783.3613268		–4.790	–2.650	2.140
p[4CF$_3$-PheDOT]	HT	–2538.2463064	–0.39	–4.953	–2.809	2.144
	HHTT	-2538.246926		–4.955	–2.806	2.149
p[4MeSO$_2$-PheDOT]	HT	–3039.9466487	–0.09	–4.980	–2.831	2.149
	HHTT	–3039.9465101		–4.982	–2.834	2.147
p[4CN-PheDOT]	HT	–2048.6563942	–0.01	–5.324	–3.173	2.152
	HHTT	–2048.6563817		–5.325	–3.174	2.151
p[4NO$_2$-PheDOT]	HT	–2273.1744023	–0.03	–5.370	–3.230	2.140
	HHTT	–2273.1743528		–5.371	–3.235	2.136
p[5CF3-PyDOT]	HT	–2570.3264606	–0.10	–5.055	–2.887	2.169
	HHTT	–2570.32631		–5.055	–2.891	2.164

[a]HT – head-to-tail arrangement of 4R groups in the polymer backbone. [a]HH-TT – head-to-head / tail-to-tail arrangement of 4R groups in the polymer backbone.

The PBC calculated HOCO/LUCO and E_g of **p[ArDOTs]** were compared with the results based on the oligomers approach of extrapolations of HOMO/LUMO energies and the HOMO–LUMO energy gaps (ΔE_{HL}) of **(ArDOT)$_n$** to the infinite chain length to ($n = \infty$) by linear fitting of E vs $1/(n + 0.1n^2)$, showing good coincidence.

X-Ray crystallography

Single crystals of studied **ArDOTs** have been obtained by recrystallization of pure samples from appropriate solvents (petrol ether, dichloromethane, toluene, ethylacetate or their mixtures) or by slow evaporation of their solution at room temperature. The X-ray single crystal data have been collected using λMoKα radiation (λ = 0.71073Å) on a Bruker D8Venture (Photon100 CMOS detector, IμS-microsource, focusing mirrors; compounds **F$_4$-23, 36F$_2$-PheDOT**, and **PzDOT**) and Agilent XCalibur (Sapphire-3 CCD detector, fine-focus sealed tube, graphite monochromator; comounds **F$_4$-PheDOT**, **3NO$_2$5CF$_3$-PheDOT**, **56Cl$_2$-PyDOT**, **5CF$_3$-PyDOT** and **QxDOT**) diffractometers equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 120.0(2) K. The crystals of compound **3NO$_2$5CF$_3$-PheDOT** shuttered during the flash-freezing, so the crystal of this compound was placed on a goniometer at 250 K and slowly cooled down to 200 K where the data were collected. All structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2[7] and SHELXTL[8] software. All non-disordered non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the structures of **F$_4$-PheDOT** and **PzDOT** were placed in the calculated positions and refined in riding mode. The hydrogen atoms in the other structures were refined isotropically. The disordered atoms in the structure of **3NO$_2$5CF$_3$-PheDOT** were refined isotropically with fixed SOF = 0.5. Crystal data and parameters of refinement are listed in Table S4 and molecular structures and crystal packings are shown in Figures S3 and S4.

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1553610–1553517.

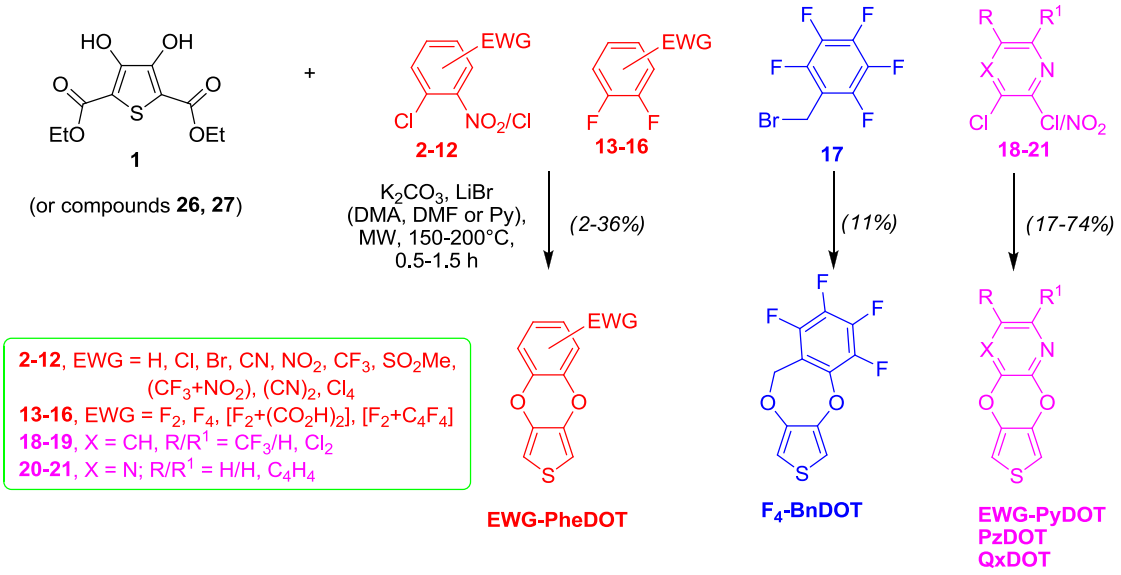
Electrochemistry and Vis-NIR electron absorption spectroscopy of polymers.

Electrochemical experiments were carried out using an Autolab PGSTAT-302N potentiostat-galvanostat. Cyclic voltammetry (CV) measurements were performed in a three-electrode cell equipped with a platinum disk (d = 1.6 mm) as the working electrode, platinum wire as a counter electrode and a non-aqueous Ag/Ag^+ reference electrode (0.01 M $AgNO_3$ and 0.1 M Bu_4NPF_6 in MeCN). Cyclic voltammograms of monomers **PheDOT** and **4CF$_3$-PheDOT** were recorded at room temperature in dichloromethane (DCM) at low concentrations (~ 1mM) with 0.2 M Bu_4NPF_6 as supporting electrolyte, with ohmic drop compensation (Figure S9a,c). The potentials were corrected with ferrocene/ferrocenium redox pair (Fc/Fc^+) as an internal standard. At such low monomer concentrations, no electropolymerization was observed on cycling (we have observed previously that electropolymerization of **PheDOT** is more difficult than **EDOT** and requires higher concentrations of the monomer[9,10]). Their electropolymerization was performed under potendiodynamic conditions in 0.2 M Bu_4NPF_6 / DCM at higher monomer concentrations of ~100 mM, cycling between 0 and + 1.3 V for **PheDOT**, and between 0 and +1.6 V for **4CF$_3$-PheDOT** (vs. Ag/Ag^+ reference electrode) (Figure S9b,d). After being electrodeposited onto working electrodes, the films of the polymers **p[PheDOT]** and **p[4CF$_3$-PheDOT]** were rinsed with acetonitrile and their electrochemical response was recorded in dry acetonitrile with 0.1 M Bu_4NPF_6 as supporting electrolyte.

For measurements of Vis-NIR electron absorption spectra, the films of **p[PheDOT]** and **p[4CF$_3$-PheDOT]** were electrodeposited on ITO glass substrate working electrodes in the same manner as described above. As the polymers have low oxidation potentials, they can be partly self-doped under air. Therefore, their Vis-NIR spectra were measured (Shimadzu UV-3600 spectrophotometer) in a spectroelectrochemical setup (0.1 M Bu_4NPF_6 / acetonitrile, ITO working

electrode, Ag wire reference electrode) applying potentials corresponding to the neutral state of the polymers.

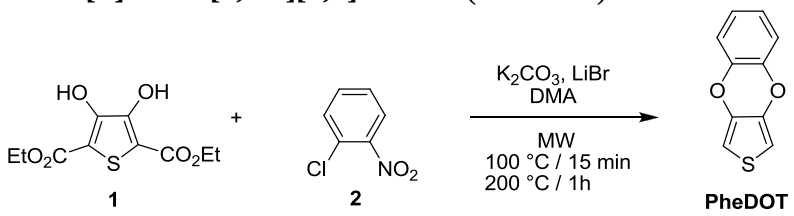
Synthesis



Microwave-assisted synthesis of PheDOTs and their analogs. General procedure.

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.000 g, 3.84 mmol, 1.00 eq.), K_2CO_3 (531 mg, 3.84 mmol, 1.00 eq.), electrophilic reagent **2–21** (1.0–1.3 eq.) and LiBr (210 mg, 2.42 mmol, 0.60 eq.) were combined in a 35 mL microwave tube, and DMA (10–12 mL) was added. The tube was sealed and bubbled with N_2 under stirring for ca. 5–10 min. The mixture was then heated with stirring in a microwave reactor (initially for 5–20 min at 80–100°C (for dissolution and homogenization of the reaction mixture), then at 150–200 °C for 0.5–1.5 h). After cooling to room temperature, the dark brown mixture was diluted with water (100 mL) and extracted with DCM (3 × 100 mL). The combined organic layers were washed with water (2–3 times), dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silicagel with an appropriate solvent as an eluent (PE, toluene, DCM, PE/DCM or PE/EA).

Benzo[b]thieno[3,4-e][1,4]dioxine (PheDOT)



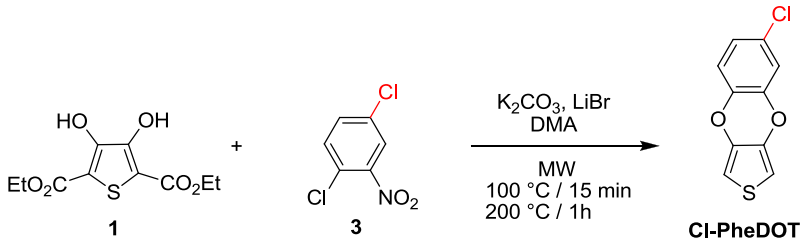
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.004 g, 3.86 mmol, 1.00 eq.), K_2CO_3 (0.533 g, 3.86 mmol, 1.00 eq.), 1-chloro-2-nitrobenzene (**2**) (0.632 g, 4.01 mmol, 1.04 eq.), LiBr (0.200 g, 2.30 mmol, 0.60 eq.) and DMA (10 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min, 4) 200 °C / 1 h. The reaction was repeated at the same conditions using diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.002 g, 3.85 mol, 1.00 eq.), K_2CO_3 (0.548 g, 3.97 mol, 1.03 eq.), 1-chloro-2-nitrobenzene (**2**) (0.653 g, 4.14 mol, 1.08eq.) and LiBr (0.211 g, 2.43 mol, 0.63 eq.) in DMA (10 mL). The combined mixtures from both syntheses were poured into water (200 mL), stirred and the precipitate was filtered off. The solid was dissolved in DCM (200 mL), stirred for 1 h, dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: PE) to yield compound **PheDOT** (24.1 mg, 1.6%) as a white solid.

Analytical data (^{1}H and ^{13}C NMR, MS) were consistent with the data published in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.92 (4H, m, $H^{B1–4}$), 6.43 (2H, s, $H^{T2,5}$).

FTIR (cm^{-1}): 3102, 3075.

6-Chlorobenzo[b]thieno[3,4-e][1,4]dioxine (4Cl-PheDOT)



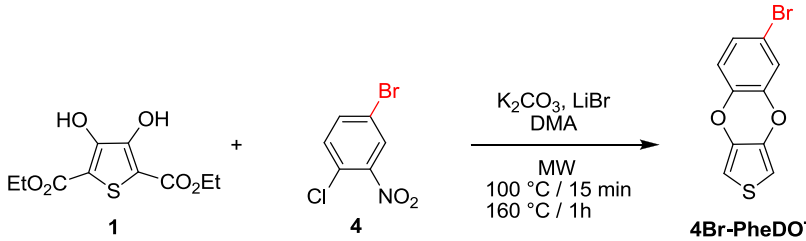
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.001 g, 3.85 mmol, 1.00 eq.), K_2CO_3 (0.542 g, 3.92 mmol, 1.02 eq.), 2,5-dichloronitrobenzene (**3**) (0.804 g, 4.19 mmol, 1.09 eq.), LiBr (0.218 g, 2.51 mmol, 0.65 eq.) and DMA (10 mL) were placed in a 35 mL MW reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min, 4) 200 °C / 1 h. After cooling to room temperature, the mixture was poured into DCM (100 mL) and stirred for 1 h before adding water (100 mL). The mixture was filtered, the organic layer was separated, washed with water (4 × 50 mL), dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by flash chromatography on silica gel (eluent: PE) to yield compound **4Cl-PheDOT** (0.145 g, 16.8%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.93 (1H, d, $J_{B3–B5}$ = 2.3 Hz, H^{B3}), 6.90 (1H, dd, $J_{B5–B6}$ = 8.6 Hz, $J_{B3–B5}$ = 2.3 Hz, H^{B5}), 6.84 (1H, d, $J_{B5–B6}$ = 8.6 Hz, H^{B6}), 6.46 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 6.44 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$).

^{13}C NMR (DEPTQ, 100 MHz, $CDCl_3$): δ (ppm) 141.29, 139.70, 138.61, 138.32, 128.16 (C^{B4}), 123.55 (CH, C^{B5}), 117.57 (CH, C^{B6}), 117.07 (CH, C^{B3}), 101.57 (CH, $C^{T2/5}$), 101.38 (CH, $C^{T2/5}$).

MS (EI+): *m/z* 223.95 (M^+, 100%), 225.95 (37.61%); calcd. for $C_{10}H_5ClO_2S$: 223.97 (100.0%), 225.97 (37.0%).

6-Bromobenzo[b]thieno[3,4-e][1,4]dioxine (**4Br-PheDOT**)



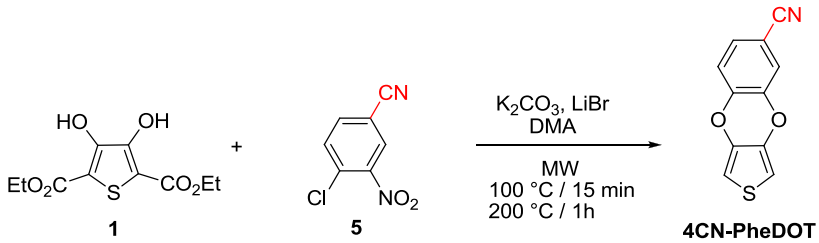
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.500 g, 5.76 mmol, 1.00 eq.), K_2CO_3 (0.840 g, 6.08 mmol, 1.05 eq.), 2-chloro-5-bromonitrobenzene (**4**) (1.781 g, 6.34 mmol, 1.10 eq.), LiBr (0.320 g, 3.68 mmol, 0.64 eq.) and DMA (15 mL) were placed in a 35 mL MW reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min, 4) 160 °C / 1 h. The mixture was cooled to room temperature, diluted with DCM (100 mL) and filtered. The filtrate was washed with water (3 × 200 mL), dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by flash chromatography on silica gel (eluent: PE) to yield compound **4Br-PheDOT** (139 mg, 9.0%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.07 (1H, d, $J_{B3–B5}$ = 2.3 Hz, H^{B3}), 7.03 (1H, dd, $J_{B5–B6}$ = 8.6 Hz, $J_{B3–B5}$ = 2.3 Hz, H^{B5}), 6.79 (1H, d, $J_{B5–B6}$ = 8.6 Hz, H^{B6}), 6.46 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 6.44 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$).

^{13}C NMR (DEPTQ, 100 MHz, $CDCl_3$): δ (ppm) 141.5 ($C^{B1/2}$), 140.2 ($C^{B1/2}$), 138.6 ($C^{T3/4}$), 138.3 ($C^{T3/4}$), 126.5 (CH,C^{B4}), 119.9 (CH, C^{B3}), 118.0 (CH, C^{B6}), 115.1 (C^{B4}), 101.6 (CH, $C^{T2/5}$), 101.4 (CH, $C^{T2/5}$).

MS (EI+): *m/z* 267.95 (M^+, 100.0%, ^{79}Br), 270.00 (M^+, 99.47%, ^{81}Br); calcd. for $C_{10}H_5BrO_2S$: 267.92 (97.8%, ^{79}Br), 269.92 (100.0%, ^{81}Br).

Benzo[b]thieno[3,4-e][1,4]dioxine-6-carbonitrile (**4CN-PheDOT**)



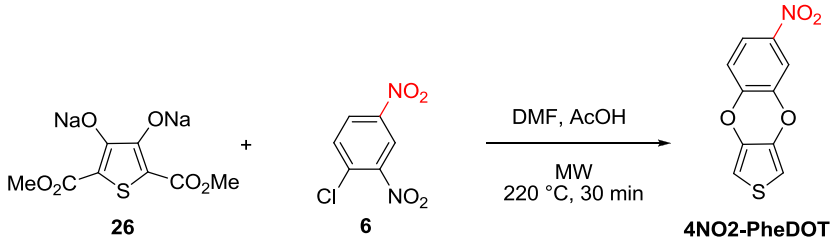
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.508 g, 5.79 mmol, 1.00 eq.), K_2CO_3 (0.802 g, 5.80 mmol, 1.00 eq.), 1-chloro-2-nitro-4-cyanobenzene (**5**) (1.150 g, 6.30 mmol, 1.09 eq.), LiBr (0.215 g, 2.48 mmol, 0.43 eq.) and DMA (15 mL) were placed in a 35 mL MW reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C/ 15 min; 3) 100 °C/ 15 min, 4) 200 °C / 1 h. After cooling, the mixture was diluted with DCM (100 mL), filtered and the filtrate was washed with water (5 × 100 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified by flash chromatography on silica gel (eluent: toluene) to yield compound **4CN-PheDOT** (242 mg, 19.4%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.24 (1H, dd, $J_{B5–B6}$ = 8.4 Hz, $J_{B3–B5}$ = 1.9 Hz, H^{B5}), 7.19 (1H, d, $J_{B3–B5}$ = 1.9 Hz, H^{B3}), 6.98 (d, $J_{B5–B6}$ = 8.4 Hz, H^{B6}), 6.52 (d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 6.50 (d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.68 ($C^{B1/2}$), 141.30 ($C^{B1/2}$), 137.75 ($C^{T3/4}$), 137.67 ($C^{T3/4}$), 128.24 (CH, C^{B5}), 120.63 (CH, C^{B3}), 117.95 (CN), 117.85 (CH, C^{B6}), 107.17 (C^{B4}), 102.53(CH, $C^{T2/5}$), 102.27 (CH, $C^{T2/5}$).

MS (EI+): *m/z* 214.95 (M^+, 100.0%); calcd. for $C_{11}H_5NO_2S$: 215.00.

6-Nitrobenzo[b]thieno[3,4-e][1,4]dioxine (4NO$_2$-PheDOT)



26 **6** **4NO2-PheDOT**

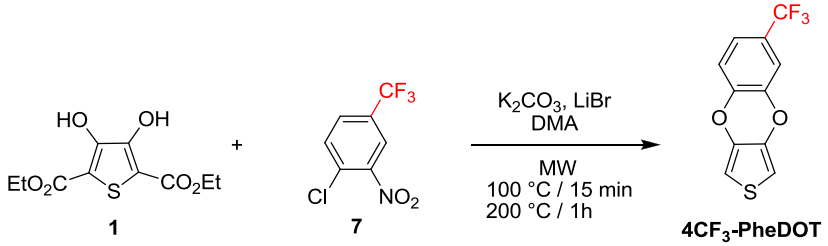
Dimethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate disodium salt (**26**) (201 mg, 0.73 mmol, 1.00 eq.), 1-chloro-2,4-dinitrobenzene (**6**) (147 mg, 0.73 mmol, 1.00 eq.), acetic acid (44 mg, 0.73 mmol, 1.00 eq.) and DMF (5 mL) were placed in a 10 mL microwave tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor at 220 °C for 30 min. After cooling, the mixture was poured into water (25 mL) and extracted with ethyl acetate (2 × 20 mL). The organic layer was dried over $MgSO_4$, evaporated to dryness and purified by flash chromatography on silica gel (eluent: toluene) to afford **4NO$_2$-PheDOT** (23.6 mg, 15%) as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87 (1H, dd, $J_{B5–B6}$ = 8.9 Hz, $J_{B3–B5}$ = 2.6 Hz, 1H^{B5}), 7.82 (1H, d, $J_{B3–B5}$ = 2.6 Hz, H^{B3}), 7.02 (1H, d, $J_{B5–B6}$ = 8.9 Hz, H^{B6}), 6.56 (1H, d, $J_{T2–T5}$ = 3.6 Hz, H$^{T2/5}$), 6.54 (1H, d, $J_{T2–T5}$ = 3.6 Hz, H$^{T2/5}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 146.08, 143.52, 140.92, 137.55, 137.10 (C^{B4}), 119.72 (CH, C$^{B3/5/6}$), 116.99 (CH, C$^{B3/5/6}$), 112.96 (CH, C$^{B3/5/6}$), 102.81 (CH, C$^{T2/5}$), 102.43 (CH, C$^{T2/5}$).

MS (EI+): *m/z* 235.05 (M$^+$, 100%); calcd. for: $C_{10}H_5NO_4S$: 234.99.

6-(Trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine (4CF$_3$-PheDOT)



1 **7** **4CF$_3$-PheDOT**

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.009 g, 3.88 mmol, 1.00 eq.), K_2CO_3 (0.536 g, 3.88 mmol, 1.00 eq.), 4-chloro-3-nitrobenzotrifluoride (**7**) (0.964 g, 4.27 mmol, 1.10 eq.), LiBr (0.267 g, 3.07 mmol, 0.79 eq.) and DMA (10 mL) were placed in a 35 mL MW tube The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min, 4) 200 °C / 1 h. Another batch of diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.021 g, 3.92 mmol, 1.00 eq.), K_2CO_3 (0.537 g, 3.89 mmol, 1.01 eq.), 4-chloro-3-nitrobenzotrifluoride (**7**) (0.976 g, 4.33, 1.12 eq.), LiBr (0.221 g, 2.54, 0.66 eq.), DMA (10 mL) was run under the same conditions. The two reaction mixtures were combined, diluted with DCM (200 mL), stirred and filtered to remove insoluble material. The filtrate was washed with water (6 × 150 mL), dried over $MgSO_4$ and the solvent was evaporated to dryness. The crude product was purified by flash chromatography on silica gel (eluent: PE) to yield compound **4CF$_3$-PheDOT** (0.715 g, 35.8%) as a white solid.

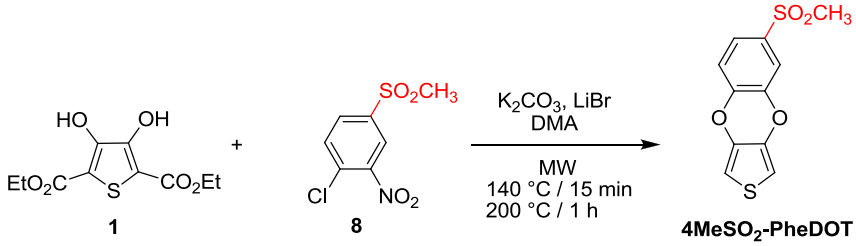
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19 (2H, m, H^{B3,5}), 6.98 (1H, d, $J_{B5–B6}$ = 8.4 Hz, H^{B6}), 6.49 (1H, d, $J_{T2–T5}$ = 3.6 Hz, H$^{T2/5}$), 6.48 (1H, d, $J_{T2–T5}$ = 3.6 Hz. H$^{T2/5}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.46 (C$^{B1/2}$), 141.00 (C$^{B1/2}$), 138.24 (C$^{T3/4}$), 138.18 (C$^{T3/4}$), 126.12 (q, $^2J_{C–F}$ = 33.4 Hz, C^{B4}), 123.51 (q, $^1J_{C–F}$ = 271.6 Hz, CF_3), 120.89 (CH, q, $^3J_{C–F}$ = 3.9 Hz, C^{B5}), 117.21 (CH, C^{B6}), 114.44 (CH, q, $^3J_{C–F}$ = 3.9 Hz, C^{B3}), 101.97 (CH, C$^{T2/5}$), 101.82 (CH, C$^{T2/5}$).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –63.52 (s, CF_3).

MS (EI+): *m/z* 258.05 (M$^+$, 100%); calcd. for $C_{11}H_5F_3O_2S$: 258.00.

6-(Methylsulfonyl)benzo[b]thieno[3,4-e][1,4]dioxine (4MeSO$_2$-PheDOT)



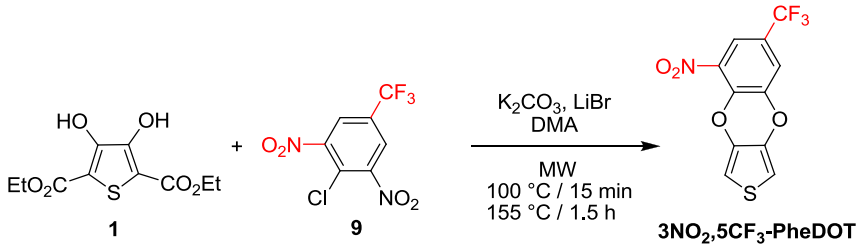
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.001 g, 3.85 mmol, 1.00 eq.), K_2CO_3 (0.566 g, 4.10 mmol, 1.06 eq.), 2-chloro-5-methylsulfonyl-1-nitrobenzene (**8**) (1.009 g, 4.28 mmol, 1.11 eq.), LiBr (0.217 g, 2.49 mmol, 0.65 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 140 °C / 15 min (80 W), 2) 200 °C / 1 h. After cooling, the mixture was diluted with DCM (50 mL) and water (100 mL) and filtered. The organic phase was washed with water (3 × 50 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The residue was dissolved in hot toluene (50 mL) and passed through a short silica gel column eluting with DCM. After solvent evaporation the solvent, the crude product was purified by flash chromatography on silica gel (eluent: DCM) to afford compound **4MeSO$_2$-PheDOT** (216 mg, 20.9 %) as a white solid (purity 98%, by ^{1}H NMR). Analytically pure product (193 mg, 18.7%) was obtained by recrystallization from heptane/chloroform (7:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (1H, dd, $J_{B5–B6}$ = 8.4 Hz, $J_{B3–B5}$ = 2.0 Hz, H^{B5}), 7.50 (1H, d, $J_{B3–B5}$ = 2.0 Hz, H^{B3}), 7.07 (1H, d, $J_{B5–B6}$ = 8.4 Hz, H^{B6}), 6.54 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 6.52 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 3.05 (3H, s, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.19, 141.32, 137.84, 137.71, 135.69, 123.39, 117.74, 116.57, 102.51, 102.27, 44.63 (CH_3).

MS (EI+): *m/z* 268.10 (M^+, 100%); calcd. for $C_{11}H_8O_4S_2$: 267.99.

5-Nitro-7-(trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine (3NO$_2$,5CF$_3$-PheDOT)



Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.004 g, 3.86 mmol, 1.00 eq.), K_2CO_3 (0.531 g, 3.84 mmol, 1.00 eq.), 4-chloro-3,5-dinitrobenzotrifluoride (**9**) (1.144 g, 4.23 mmol, 1.10 eq.), LiBr (0.200 mg, 2.30 mmol, 0.60 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) and heated with stirring in a microwave reactor in 2 steps: 1) 100 °C / 10 min, 2) 155 °C / 1.5 h). After cooling, the mixture was diluted with DCM (50 mL) and water (50 mL), stirred and filtered to remove insoluble material. The organic layer was washed with water (3 × 50 mL), dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by flash chromatography on silica gel (eluent: PE:DCM, 7:3) to yield compound **3NO$_2$,5CF$_3$-PheDOT** (150 mg, 12.8%) as a light yellow solid.

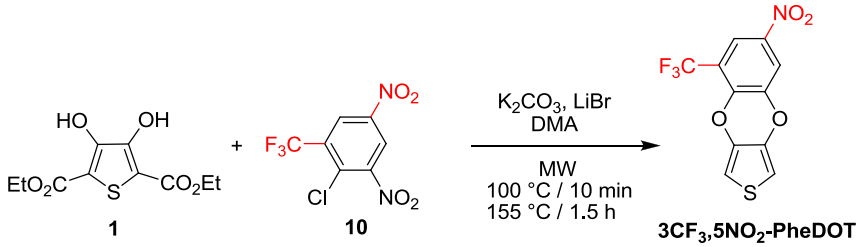
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (1H, d, $J_{B3–B5}$ = 2.0 Hz, $H^{B3/5}$), 7.39 (1H, d, $J_{B3–B5}$ = 2.0 Hz, $H^{B3/5}$), 6.72 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 6.59 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.92, 138.56, 138.25, 136.76, 136.02, 122.35 (q, $^1J_{C-F}$ = 272.7 Hz, CF_3), 125.31 (q, $^2J_{C–F}$ = 35.2 Hz, C^{B4}), 118.13 (CH, q, $^3J_{C–F}$ = 3.5 Hz, $C^{B3/5}$), 117.24 (CH, q, $^3J_{C–F}$ = 4.0 Hz, $C^{B3/5}$), 104.50, 103.07.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –64.13 (s, CF_3).

MS (EI+): *m/z:* 303.05 (100; calcd. for $C_{11}H_4F_3NO_4S$: 302.98.

7-Nitro-5-(trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine (3CF$_3$,5NO$_2$-PheDOT)



Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.007 g, 3.87 mmol, 1.00 eq.), K_2CO_3 (0.537 g, 3.89 mmol, 1.00 eq.), 2-chloro-3,5-dinitrobenzotrifluoride (**10**) (1.144 g, 4.23 mmol, 1.09 eq.), LiBr (0.217 mg, 2.50 mmol, 0.65 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 100 °C / 10 min, 2) 155 °C / 1.5 h. After cooling, the mixture was diluted with DCM (70 mL) and water (50 mL), stirred and filtered to remove insoluble material. The organic layer was washed with water (2 × 50 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: DCM) to yield compound **3CF$_3$,5NO$_2$-PheDOT** (175 mg, 14.9%) as a light yellow solid. An analytically pure sample was obtained by recrystallization from heptane (154 mg, 13.1%).

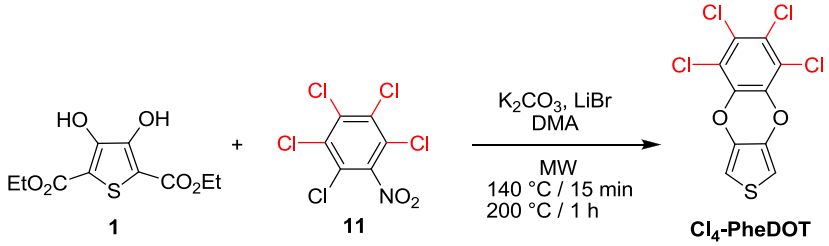
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16 (1H, d, $J_{B3–B5}$ = 2.6 Hz, $H^{B3/5}$), 7.98 (1H, d, $J_{B3–B5}$ = 2.6 Hz, $H^{B3/5}$), 6.71 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 6.60 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.35, 142.39, 142.02, 136.65, 136.20, 121.55 (q, $^1J_{C–F}$ = 273.8 Hz, CF_3), 119.18 (CH, q, $^2J_{C–F}$ = 34.0 Hz, C^{B5}), 117.28 (q, $^3J_{C–F}$ = 5.3 Hz, C^{B4}), 115.95, 104.34 (CH, $C^{T2/5}$), 103.17 (CH, $C^{T2/5}$).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –63.63 (s, CF_3).

MS (EI+): *m/z* 303.05 (M^+, 100%); calcd. for $C_{11}H_4F_3NO_4S$: 302.98.

5,6,7,8-Tetrachlorobenzo[b]thieno[3,4-e][1,4]dioxine (Cl$_4$-PheDOT)



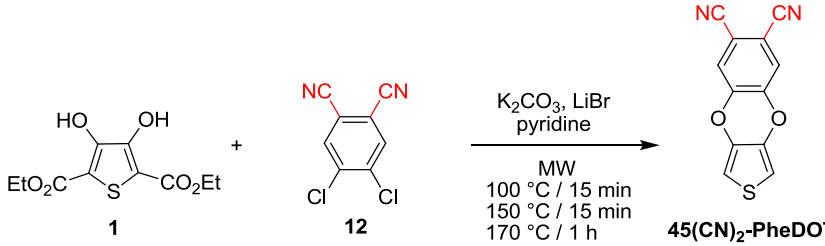
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (904 mg, 3.47 mmol, 1.00 eq.), K_2CO_3 (486 mg, 3.52 mmol, 1.01 eq.), pentachloronitrobenzene (**11**) (112 mg, 0.38 mmol, 1.09 eq.), LiBr (187 mg, 2.15 mmol, 0.62 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 140 °C / 15 min (80 W), 2) 200 °C / 1 h. After cooling, the mixture was diluted with DCM (100 mL), washed with water (3 × 50 mL), dried with $MgSO_4$, and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: hot heptane) to yield compound **Cl$_4$-PheDOT** (105 mg, 9.2%) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.65 (1H, s, $H^{T2,5}$).

^{13}C NMR (DEPTQ, 100 MHz, $CDCl_3$): δ (ppm) 137.87, 136.91, 127.08, 120.40, 103.16 (CH, $C^{T2,5}$).

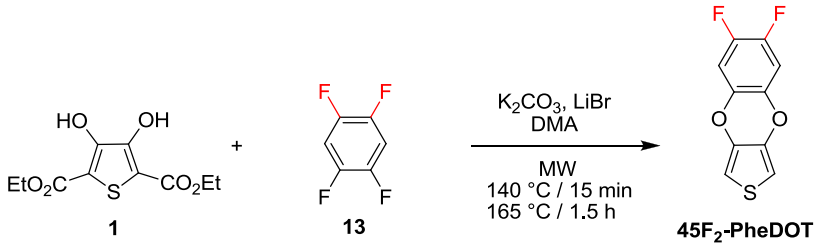
MS (EI+): *m/z* 325.90 (80%), 327.95 (100%), 329.90 (51%) [M^+ with ^{35}Cl/^{37}Cl distribution]; calcd. for $C_{10}H_2Cl_4O_2S$ (for natural ^{35}Cl/^{37}Cl distribution): 325.85 (78.2%), 327.85 (100.0%), 329.85 (47.9%).

Benzo[b]thieno[3,4-e][1,4]dioxine-6,7-dicarbonitrile (45(CN)$_2$-PheDOT)



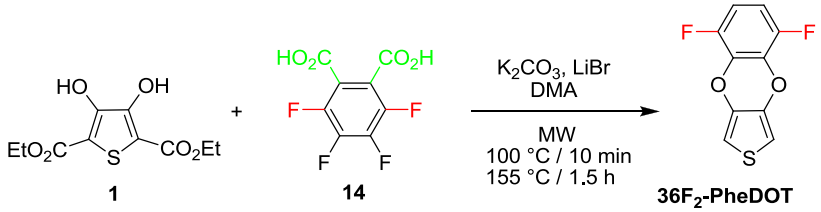
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.502 g, 5.77 mmol, 1.00 eq.), 4,5-dichlorophthalonitrile (**12**) (1.238 g, 6.28 mmol, 1.09 eq.), K_2CO_3 (0.797 g, 5.77 mmol, 0.99 eq.), LiBr (0.220 g, 2.55 mmol, 0.44 eq.) and pyridine (15 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps (MW 150 W): 1) 100 °C / 10 min, 150 °/ 15 min, 170 °C / 1 h. After cooling, the mixture was diluted with water (100 mL) and extracted with DCM (8 × 25 mL). The combined DCM layers were washed with concentrated HCl (4 mL), water (2 × 25 mL) and filtered through a silica gel plug. The solvent was evaporated to yield the crude product (750 mg, 54%) as an orange solid. The crude product was purified by flash chromatography on silica gel (eluent: toluene) to yield pure compound **45(CN)$_2$-PheDOT** (208 mg (15 %) as a light yellowish solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.29 (2H, s, $H^{B3,6}$), 6.61 (2H, s, $H^{T2,5}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.65, 136.54, 122.12, 114.56, 111.32, 103.85.
^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 144.23, 136.14, 122.67, 115.22, 110.25, 104.37.
MS (EI+): *m/z* 240.08 (M^+, 100%); calcd for $C_{12}H_4N_2O_2S$: 240.00.

6,7-Difluorobenzo[b]thieno[3,4-e][1,4]dioxine (45F$_2$-PheDOT)



Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.001 g, 3.86 mmol, 1.00 eq.), K_2CO_3 (0.562 g, 4.07 mmol, 1.06 eq.), 1,2,4,5-tetrafluorobenzene (**13**) (0.640 g, 4.26 mmol, 1.11 eq.), LiBr (0.199 g, 2.29 mmol, 0.60 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 140 °C/ 15 min, 2) 165 °C / 1 h. After cooling, the mixture was diluted with DCM (100 mL) and filtered to remove insoluble material. The filtrate was washed with water (3 × 50 mL), dried with $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by flash chromatography on silica gel (eluent: PE) to yield compound **45F$_2$-PheDOT** (17 mg, 2%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.78 (2H, dd, J = 9.2 Hz, 8.8 Hz, $H^{B3,6}$), 6.45 (2H, s, $H^{T2,5}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.70 (dd, $^1J_{C-F}$ = 246.1 Hz, $^2J_{C-F}$ = 15.8 Hz, $C^{B4,5}$), 138.06 ($C^{T3,4}$), 136.53 (dd, J = 6.4 Hz, J = 6.3 Hz), 105.74 (m), 101.62 (CH, $C^{T2,5}$).
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –143.85 (s, $F^{B4,5}$).
MS (EI+): 226.00 (M^+, 100%); calcd. for $C_{10}H_4F_2O_2S$: 225.99.

5,8-Difluorobenzo[b]thieno[3,4-e][1,4]dioxine (36F$_2$-PheDOT)



Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.005 g, 3.86 mmol, 1.00 eq.), K_2CO_3 (0.546 g, 3.95 mmol, 1.02 eq.), tetrafluorophthalic acid (**14**) (1.021 g, 0.004 mmol, 1.11 eq.), LiBr (0.207 g, 2.38 mmol, 0.62 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 100 °C / 10 min (80 W), 2) 155 °C / 1.5 h. After cooling, the mixture was diluted with DCM (100 mL) and water (100 mL), stirred and filtered to remove insoluble material. The filtrate was acidified with a few drops of concentrated HCl, organic layer was separated, washed with water (3 × 50 mL), dried with $MgSO_4$, filtered and the solvent evaporated. The crude product was purified by flash chromatography on silica gel (eluent: PE to PE:EA, 95:5) to yield compound **36F$_2$-PheDOT** (58.5 mg, 6.7%)* as a white powder.

***Note:** The yield in the reaction is low (lower than e.g. in the case of **F$_4$-PheDOT**, see below). We can't guarantee that full decarboxylation took place in the reaction and possibly the products with one or two CO_2H on the benzene ring were formed as well but were lost with a tag during the column chromatography purification. Thus, CO_2H group at the benzene ring of **PheDOT** seems to be more stable toward decarboxylation than those at the 2,5-positions of the thiophenes ring.*

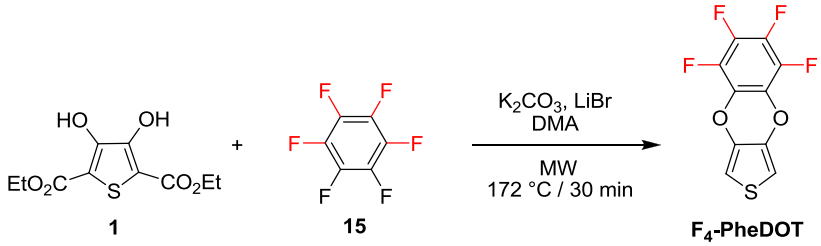
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.74–6.69 (2H, m, $H^{B4,5}$), 6.60 (2H, s, $HT^{2,5}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 146.92 (dd, $^1J_{C–F}$ =245.0 Hz, $^4J_{C–F}$ = 3.9 Hz, $C^{B3,6}$), 137.27 ($C^{T3,4}$), 131.52 (dd, $^2J_{C–F}$ = 12.6 Hz, $^3J_{C–F}$ = 6.8 Hz, $C^{B2,3}$), 109.25 (CH, dd, $^2J_{C–F}$ = 16.8 Hz, $^3J_{C–F}$ = 11.2 Hz, $C^{B4,5}$), 102.71 (CH, $C^{T2,5}$).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –140.53 (s, $F^{B3,6}$).

MS (EI+): *m/z* 226.05 (M^+, 100%); calcd. for $C_{10}H_4F_2O_2S$: 225.99 (100.0%).

5,6,7,8-Tetrafluorobenzo[b]thieno[3,4-e][1,4]dioxine (F$_4$-PheDOT)



Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (2.002 g, 7.69 mmol, 1.00 eq.), K_2CO_3 (1.068 g, 7.73 mmol, 1.00 eq.), hexafluorobenzene (**15**) (1.837 g, 9.87 mmol, 1.28 eq.), LiBr (0.400 g, 4.61 mmol, 0.60 eq.) and DMA (20 mL) were placed in a 35 mL microwave reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor at 172 °C for 30 min. The mixture was cooled down to room temperature, poured into DCM (100 mL) and filtered to remove insoluble material. The filtrate was washed with water (5 × 50 mL), dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by flash chromatography on a silica gel (eluent: toluene) to yield compound **F$_4$-PheDOT** (0.719 g, 35.6% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.63 (2H, s, $H^{T2,5}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 138.16 (m, $C^{3,6/4,5}$), 136.42 (s, $C^{T3,4}$), 135.76 (m, $C^{3,6/4,5}$), 128.28 (m, $C^{B1,2}$), 103.27 (CH, s, $C^{T2,5}$).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –163.27 – 163.43 (m, 2F), –166.23 – 166.39 (m, 2F).

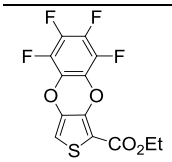
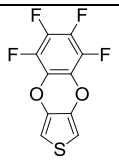
^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) –(163.35–163.5) (m, 2F), –(166.3–166.5) (m, 2F).

MS (EI+): *m/z* 262.05 (M^+, 100%); calcd. for $C_{10}H_2F_4O_2S$: 261.97.

Optimization of the reaction conditions in synthesis of F_4-PheDOT

For more detailed studies in our initial experiments, the reaction of thiophene **1** was tested with hexafluorobenzene (**15**) with monitoring by GC-MS (Table S2). No product **F_4-PheDOT** or intermediates **F_4-22** or **F_4-23** were detected in the reaction with conventional heating even at prolonged time at 100 °C (Table S2, entries 1, 2).[11] In MW-assisted conditions, heating with K_2CO_3 in DMA at 220 °C showed formation of the target product **F_4-PheDOT** along with intermediate **F_4-23** (entries 3, 4). However, the yield was drastically decreased when the temperature was raised to 245 °C indicating decomposition of **F_4-PheDOT** at higher temperatures (entry 5). Addition of LiBr substantially increased the rate of decarboxyethylation of intermediate **F_4-23**, giving the yields of **F_4-PheDOT** of ca. 30% (entries 6, 7), although entry 8 indicates that decomposition of **F_4-PheDOT** occurs upon prolonged heating at 220 °C. Finally, variations in the amount of DMA solvent showed that the highest yields are achieved when the reaction temperature does not exceed 200 °C and ca. 10 mL of a solvent is used per 1 g of thiophene **1** (entries 10, 11).

Table S2. Reaction of thiophene **1** with hexafluorobenzene (**15**) at different conditions.[a]

Entry	T, °C	Time, h	LiBr, eq.	$V_{DMA}/1$[c] mL/g	Yield,[b] %	
					 **F_4-23**	 **F_4-PheDOT**
1[d]	100	16	0	60	0	0
2[e]	100	18	0	25	0	0
3	220	1.5	0	25	19.2	14.8
4	220	3	0	25	11.4	17.3
5	245	1.5	0	25	0	2.1
6	200	1.5	0.6	30	10.5	29.3
7	220	0.5	0.6	25	0	31.5
8	220	1.5	0.6	25	0	10.4
9	200	1.5	0.6	6	0	19.9
10	200	1	0.6	10	0	34.3
11	200	0.5	0.6	9.5	0	34.5

[a]Reaction conditions: thiophene **1** (1.0 eq.), hexafluorobenzene **15** (1.1 eq.), K_2CO_3 (1.0 eq.), LiBr (0–0.6 eq.), in DMA, MW irradiation. [b]Yields by GC-MS analysis. The intermediate **F_4-22** (with two CO_2Et groups at the thiophenes ring) was not detected in any experiment.[12] [c]Amount of DMA per 1 g of thiophene **1**. [d]In DMF, conventional heating. [e]In DMF, conventional heating, 3 eq. Cs_2CO_3 instead of 1 eq. K_2CO_3.

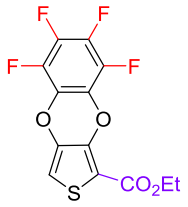
Microwave irradiation is an important factor for the reaction: performing the reaction under similar conditions with conventional heating resulted in substantially lower yields of **F_4-PheDOT** (0–7%, Table S3) and incomplete decarboxyethylation: apart from the target product **F_4-PheDOT**, substantial amount of the intermediate **F_4-23** was formed. It was isolated and is characterized below.

Table S3. Optimization of the reaction conditions and the yields of **F$_4$-PheDOT** in MW-asisted reaction of thiophene **1** with hexafluorobenzene (**15**):[a]

Entry.	Thiophene **1**	C_6F_6 (**15**)	Base (1.0 eq.)	Solvent: DMA	MW, temp. / time	Yield,[b] %	Number of reactions
1	2.00 g	1.1 eq.	K_2CO_3	20 mL	172 °C / 0.5 h	35.6%	1
2	1.50 g	1.1 eq.	*t*-BuOK	10 mL	178 °C / 1 h	31.7%	1
3	2.00 g	1.1 eq.	K_2CO_3	20 mL	160–170 °C / 1 h	32.3%	4
4	1.50 g	1.1 eq.	K_2CO_3	10 mL	164 °C / 1 h	29.3%	3
5	1.00 g	1.1 eq.	K_2CO_3	10 mL	190–200 °C / 1 h	23%	3
6[c]	2.00 g	1.0 eq.	K_2CO_3	20 mL	120 °C / 38 h 140 °C / 18 h	4%	1
7[c]	1.00 g	1.1 eq.	K_2CO_3	9 mL	160 °C / 2.5 h	7%	1
8[c]	8.00 g	1.1 eq.	K_2CO_3	72 mL	180 °C / 2.5 h	6%	1
9[c]	5.00 g	1.5 eq.	K_2CO_3	40 mL (DMF)	149 °C / 28 h	0%	1

[a]0.6 eq. LiBr has been used in all reactions. [b]Isolated yields. Average yields from several reactions (where appropriate). [c]Conventional heating in an autoclave.

Ethyl 5,6,7,8-tetrafluorobenzo[b]thieno[3,4-e][1,4]dioxine-1-carboxylate (F$_4$-23)



F$_4$-23

Compound **F$_4$-23** was isolated from a tag after an isolation of **F$_4$-PheDOT**. After purification of **F$_4$-PheDOT**, the resiude from the column was washed with DCM, the crude product was collected and was purified twice by flash chromatography on a silica gel (eluent: gradient from PE to PE:DCM, 1:1) to afford pure compound **F$_4$-23**.

R_f (PE:DCM, 1:1) = 0.32.

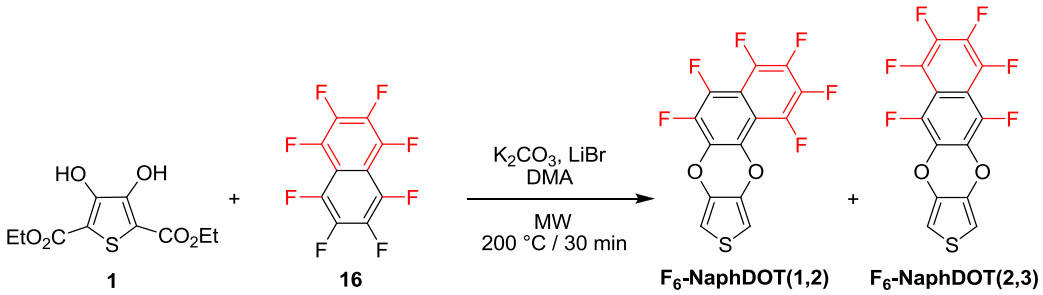
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.83 (1H, s, H^{T5}), 4.38 (2H, q, *J* = 7.1 Hz, CH_2), 1.40 (3H, t, *J* = 7.1 Hz, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) {only thiophene aromatic carbons have been detected; benzene carbons appear as very low intensity multiplets due to H–F coupling}, 160.12 (s, C=O), 139.00 (s, C), 139.0–137.8 (m, C–F, C^B)136.36 (s, C), 137.0–135.5 (m, C–F, C^B), 128.2–127.8 (m, C–F, C^B), 108.12 (s, CH, C^{T5}), 61.65 (CH_2), 14.19 (CH_3).

^{19}F NMR (376 MHz, $CDCl_3$); δ (ppm) –161.64 (1F, ddd, *J* = 21.6, 5.7, 2.9 Hz, $F^{B3/6}$), –163.13 (1F, ddd, *J* = 21.5, 5.6, 3.3 Hz, $F^{B3/6}$), –164.75 (1F, td, *J* = 21.7, 2.8 Hz, $F^{B4/5}$), –165.30 (1F, td, *J* = 21.7, 3.3 Hz, $F^{B4/5}$).

MS (EI+): *m/z* 334.01; calcd for $C_{13}H_6F_4O_4S$: 333.99.

1,2,3,4,5,6-Hexafluoronaphtho[2,1-b]thieno[3,4-e][1,4]dioxine {F_6-NaphDOT(1,2)}
and
5,6,7,8,9,10-hexafluoronaphtho[2,3-b]thieno[3,4-e][1,4]dioxine {F_6-NaphDOT(2,3)}

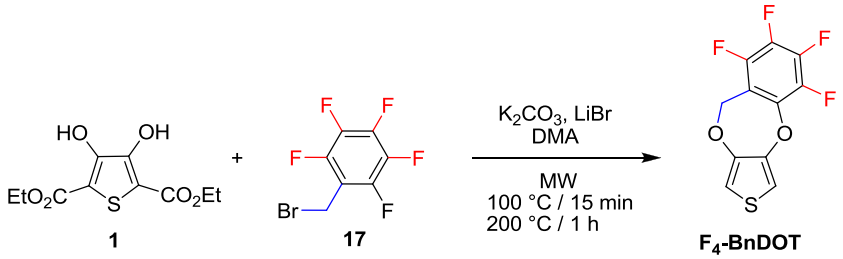


Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (101 mg, 0.39 mmol, 1.00 eq.), K_2CO_3 (55.7 mg, 0.40 mmol, 1.03 eq.), octafluoronaphthalene (**16**) (115 mg, 0.42 mmol, 1.09 eq.), LiBr (20 mg, 0.23 mmol, 0.60 eq.) and DMA (1.0 mL) were placed in a 10 mL MW reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor at 200 °C for 30 min. The mixture was cooled to room temperature and poured into DCM (20 mL). The solution was filtered from insoluble material, the filtrate was washed with water (5 × 15 mL), dried over $MgSO_4$, filtered and the solvent was removed by evaporation. The residue, which contains a mixture of isomers **F_6-NaphDOT(1,2)** and **F_6-NaphDOT(2,3)** (two closely spaced spots on TLC in non-polar solvents, which are not separated in more polar solvents) was purified by column chromatography on silica gel (eluent: PE) first eluting compound **F_6-NaphDOT(1,2)** (16.6 mg, 12.2% yield, white solid), followed by compound **F_6-NaphDOT(2,3)** (28.9 mg, 21.3% yield, white solid). The total combined yield of both isomers was 33.5% (with a ratio of **F_6-NaphDOT(1,2):F_6-NaphDOT(2,3)** ≈ 1:2). Both isomers, especially **F_6-NaphDOT(2,3)**, are very insoluble materials, so their flash chromatography separation can only be performed on a small scale.

Non-symmetric compound **F_6-NaphDOT(1,2):**
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.64 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 6.62 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.22, 136.40, 103.32 (2C, $C^{T2,5}$), {identification of other peaks in the region of 133–144 ppm was difficult because of low solubility of the compound and low intensity of the signals due to C–F coupling}.
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –144.0–144.2 (m, 1F), –144.5–147.9 (m, 1F), –150.3–150.6 (m, 1F), –155.1–155.2 (m, 1F), –157.0–157.2 (m, 1F), –157.4–157.6 (m, 1F).
MS (EI+): *m/z* 348.01 (M^+, 100.0%); calcd. for $C_{14}H_2F_6O_2S$: 347.97.

Symmetric compound **F_6-NaphDOT(2,3):**
^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 6.74 (2H, s, $H^{T2,5}$).
^{13}C NMR (DEPTQ, 100 MHz, $CDCl_3$): δ (ppm) 103.5 (2C, $C^{T2,5}$), {an identification of other peaks was difficult because of very low solubility of the compound and low intensity of the signals due to C–F coupling}.
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –146.5–146.8 (m, 2F), –147.7–148.1 (m, 2F), –157.6–157.8 (m, 2F).
MS (EI+): *m/z* 348.05 (M^+, 100.0%); calcd. for $C_{14}H_2F_6O_2S$: 347.97.

5,6,7,8-Tetrafluoro-9H-benzo[e]thieno[3,4-b][1,4]dioxepine (F$_4$-BnDOT)



Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.018 g, 3.91 mmol, 1.00 eq.), K_2CO_3 (0.558 g, 4.04 mmol, 1.03 eq.), 2,3,4,5,6-pentafluorobenzylbromide (**17**) (1.170 g, 4.48 mmol, 1.15 eq.), LiBr (0.215 g, 2.48 mmol, 0.63 eq.) and DMA (10 mL) were placed in a 35 mL MW tube The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min, 4) 200°C / 1 h. After cooling, the mixture was diluted with water (100 mL), stirred for 1h and the solid was filtered off by suction. The solid was transferred into DCM (150 mL), stirred for 30 min, dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: PE) to yield compound **F$_4$-BnDOT** (0.120 g, 11.1%) as a white solid.

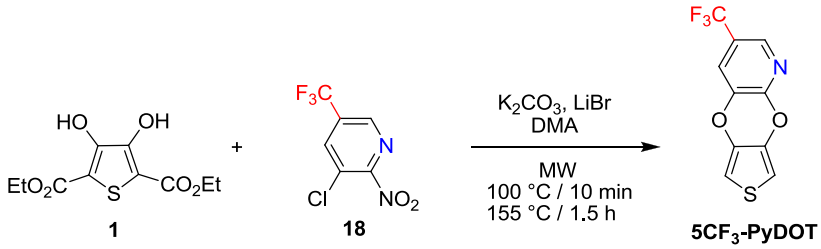
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.87 (1H, d, $J_{T2–T5}$ = 4.2 Hz, $H^{T2/5}$), 6.44 (1H, d, $J_{T2–T5}$ = 4.2 Hz, $H^{T2/5}$), 5.24 (2H, d, $J_{H–F}$ = 1.5 Hz, CH_2).

^{13}C NMR (100 MHz $^{13}C\{^1H\}$): δ (ppm) 145.35 (s), 145.0 (m), 142.7 (m), 142.31 (s), 140.8 (m), 140.3 (m), 138.5 (m), 136.2 (m), 114.40 (dd, *J* =16.1 Hz, *J* = 3.6 Hz), 108.76 (CH, s, $H^{T2/5}$), 104.39 (CH, s, $C^{T2/5}$), 60.38 (d, $^3J_{C–F}$ = 4.3 Hz, CH_2).

^{19}F NMR (376 Hz): δ (ppm) –146.16 (1F, ddd, *J* = 22.5 Hz, 11.1 Hz, 1.9 Hz), –154.91 (1F, td, *J* = 20.8 Hz, 1.9 Hz), –157.61 (1F, dd, *J* = 21.1 Hz, 10.5 Hz), –162.65 (1F, dd, *J* = 22.2 Hz, 20.7 Hz).

MS (EI+): *m/z* 276.05 (M^+, 100%); calcd. for $C_{11}H_4F_4O_2S$: 275.99.

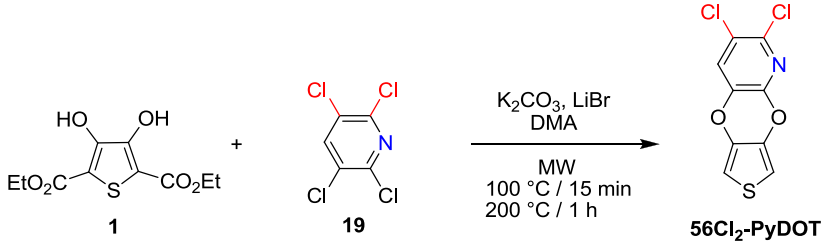
3-Trifluoromethylthieno[3',4':5,6][1,4]dioxino[2,3-b]pyridine (5CF$_3$-PyDOT)



Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.000 g, 3.84 mmol, 1.00 eq.), K_2CO_3 (531 mg, 3.84 mmol, 1.00 eq.), 2,3-difluoro-6-trifluoromethylpyridine (**18**) (778 mg, 4.25 mmol, 1.11 eq.), LiBr (210 mg, 2.42 mmol, 0.63 eq.) and DMA (11 mL) were placed in a 35 mL MW tube The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 100°C / 10 min, 155°C / 90 min. After cooling, a clear, almost colorless layer was formed at the bottom of the tube. The mixture was partitioned between DCM (80 mL) and water (70 mL) (full dissolution was observed). The organic layer was separated, washed with water (3 × 25 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was analyzed by GC-MS, which showed the desired product, together with small amount of one by-product. The crude product was purified by flash chromatography on silica gel (eluent: PE to PE:EA, 9:1) to yield a relatively pure sample of compound **5CF$_3$-PyDOT** (841 mg, 96%) followed by an impure fraction (71 mg). The first fraction was additionally purified by flash chromatography on silica gel (eluent: PE:EA, 1:1) to afford pure compound **5CF$_3$-PyDOT** (641 mg, 74%) as a white solid.

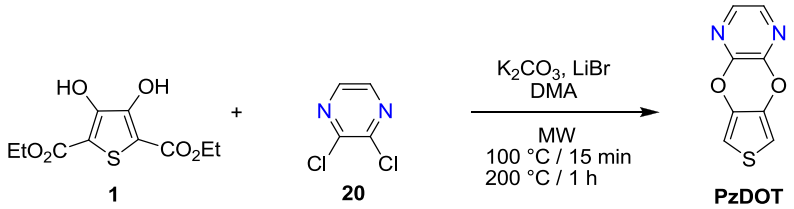
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16 (br.s, $H^{P5/6}$), 7.44 (d, $J_{P4–P6}$ = 1.9 Hz, $H^{P5/6}$), 6.65 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 6.55 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.55 (C^{P2}), 139.02 (CH, q, $^{3}J_{C–F}$ = 4.5 Hz, $C^{P4/6}$), 137.90 ($C^{T3/4}$), 137.04 ($C^{T3/4}$), 136.89 (C^{P3}), 124.00 (q, $^{2}J_{C–F}$ = 33.8 Hz, C^{P5}), 122.79 (q, $^{1}J_{C–F}$ = 272.0 Hz, CF_3), 121.92 (CH, q, $^{3}J_{C–F}$ = 3.3 Hz, $C^{P4/6}$), 103.75 (CH, $C^{T2/5}$), 102.61 (CH, $C^{T2/5}$).
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –63.18 (s, CF_3).
MS (EI+): *m/z* 259.00 (M^+, 100%); calcd. for $C_{10}H_4F_3NO_2S$: 258.99.

2,3-Dichlorothieno[3',4':5,6][1,4]dioxino[2,3-b]pyridine (56Cl$_2$-PyDOT)



Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.001 g, 3.85 mmol, 1.00 eq.), K_2CO_3 (0.544 g, 3.94 mmol, 1.02 eq.), 2,3,5,6-tetrachloropyridine (**19**) (0.920 g, 4.24 mmol, 1.10 eq.), LiBr (0.222 g, 2.56 mmol, 0.66 eq.) and DMA (10 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min, 2) 80 °C / 15 min, 3) 100 °C / 15 min, 4) 200°C / 1 h. After cooling, the mixture was poured into water (100 mL) and stirred for 1 h. The solid was filtered off, dissolved in DCM (150 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: toluene) to yield compound **56Cl$_2$-PyDOT** (166 mg, 16.6%) as light-yellow crystals. An analytically pure sample was obtained by repeated flash chromatography with PE:DCM, 2:1.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (1H, s, H^{P4}), 6.61 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$), 6.53 (1H, d, $J_{T2–T5}$ = 3.6 Hz, $H^{T2/5}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.50 ($C^{P2/3/5/6}$), 139.01 ($C^{P2/3/5/6}$), 137.76 ($C^{T3/4}$), 136.85 ($C^{T3/4}$), 136.01 ($C^{P2/3/5/6}$), 127.06 (CH, C^{P4}), 124.89 ($C^{P2/3/5/6}$), 103.66 (CH, $C^{T2/5}$), 102.71 (CH, $C^{T2/5}$).
MS (EI+): *m/z* 259.00 (M^+, 100%, $^{35}Cl/^{35}Cl$), 261.00 (68%, $^{35}Cl/^{37}Cl$), 262.95 (13%, $^{37}Cl/^{37}Cl$), calcd. for $C_9H_3Cl_2NO_2S$: 258.93 (100.0%), 260.92 (68.4%), 262.92 (13.2%).

Thieno[3',4':5,6][1,4]dioxino[2,3-b]pyrazine (PzDOT)



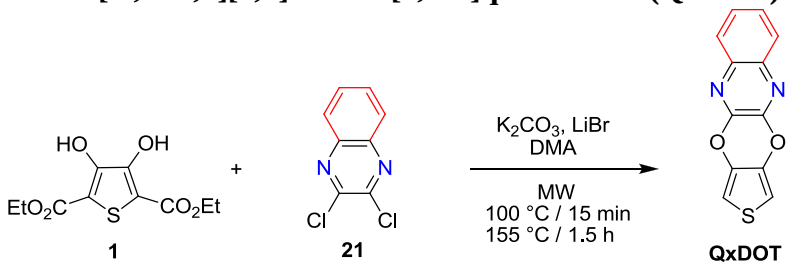
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.001 g, 3.85 mmol, 1.00 eq.), K_2CO_3 (0.531 g, 3.84 mmol, 1.00 eq.), 2,3-dichloropyrazine (**20**) (0.594 g, 3.99 mmol, 1.04 eq.), LiBr (0.205 g, 2.36 mmol, 0.61 eq.) and DMA (10 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min, 2) 80 °C / 15 min, 3) 100 °C / 15 min, 4) 200 °C / 1 h. After cooling, the mixture was diluted with DCM (100 mL), stirred for 1 h and filtered to remove insoluble materials. The filtrate was washed with water (6 × 150 mL), dried over $MgSO_4$, filtered and the solvent was evaporated to dryness. The crude product was purified by flash chromatography on silica gel (eluent: PE:EA, 9:1) to yield compound **PzDOT** (0.283 g, 38.2%) as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.88 (2H, s, $H^{P5,6}$), 6.66 (2H, s, $H^{T2,5}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.91 ($C^{P2,3}$), 137.51 ($C^{T3,4}$), 137.09 (CH, $C^{P5,6}$), 103.54 (CH, $C^{T2,5}$).

MS (EI+): *m/z* 192.01 (100%); calcd. for $C_8H_4N_2O_2S$: 192.00.

Thieno[3',4':5,6][1,4]dioxino[2,3-b]quinoxaline (QxDOT)



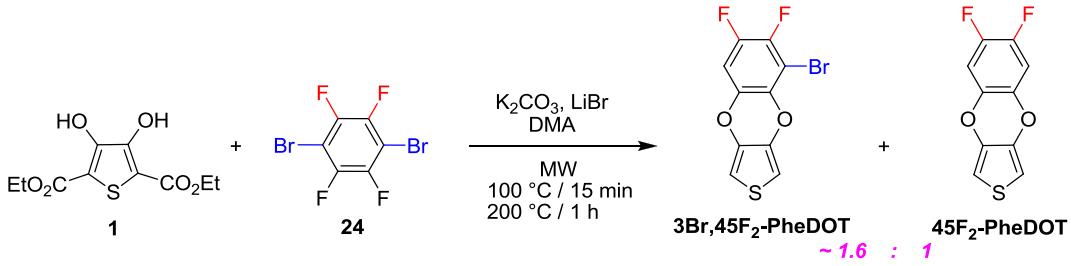
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (999 mg, 3.84 mmol, 1.00 eq.), K_2CO_3 (534 mg, 3.86 mmol, 1.01 eq.), 2,3-dichloroquinoxaline (**21**) (839 mg, 4.22 mmol, 1.10 eq.), LiBr (195 mg, 2.25 mmol, 0.6 eq.) and DMA (12 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min, 2) 80 °C / 5 min, 3) 100 °C / 15 min, 4) 155 °C / 1.5 h. After cooling, the mixture was diluted with DCM (120 mL) and water (25 mL), stirred and filtered through glass wool to remove insoluble materials. The organic layer was separated, washed with water (3 × 25 mL), dried with $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography on a silica gel (eluent: gradient from PE to DCM) to yield compound **QxDOT** (388 mg, 41.7%) as a yellowish powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85 (2H, dd, *J* = 6.3 Hz, 3.5 Hz, $H^{B3,6/B4.5}$), 7.62 (2H, dd, *J* = 6.3 Hz, 3.5 Hz, $H^{B3,6/B4,5}$), 6.75 (2H, s, $H^{T2,5}$).

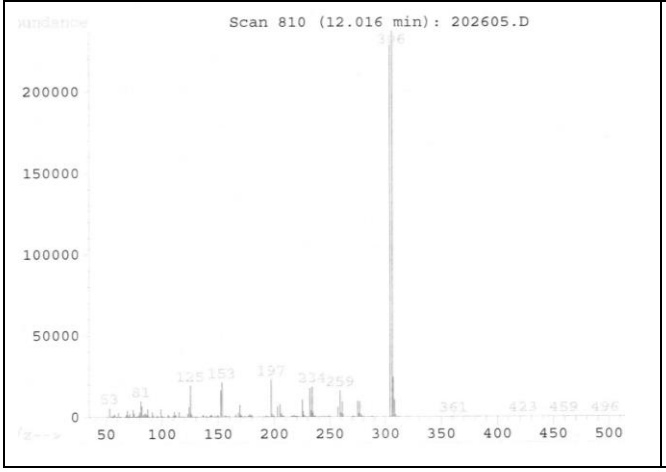
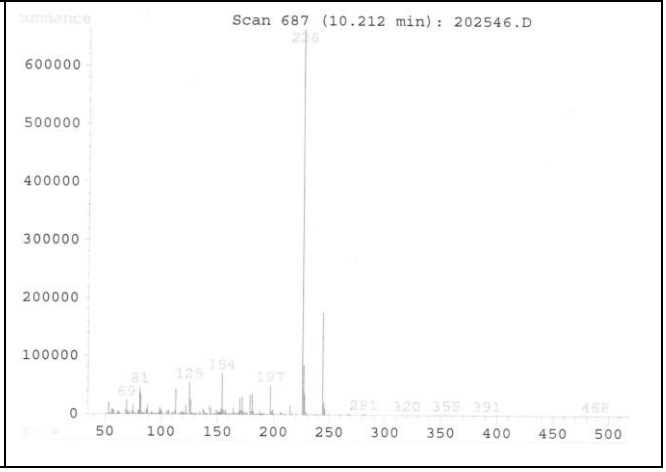
^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 143.15 ($C^{P2,3}$), 138.66 ($C^{P5,6}$), 137.18 ($C^{T3,4}$), 129.09 (CH, $C^{B3,5/B4,5}$), 127.34 (CH, $C^{B3,5/B4,5}$), 103.70 (CH, $C^{T2,5}$).

MS (TOF EI+): *m/z* 242.09 (M^+, 100%); calcd for $C_{12}H_6N_2O_2S$: 242.01.

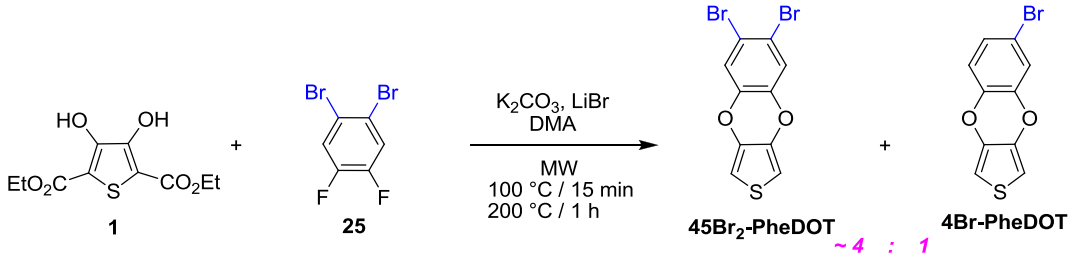
6-Bromo-5,8-difluorobenzo[b]thieno[3,4-e][1,4]dioxine (**3Br,45F$_2$-PheDOT**) and **5,8-difluorobenzo[b]thieno[3,4-e][1,4]dioxine** (**45F$_2$-PheDOT**)



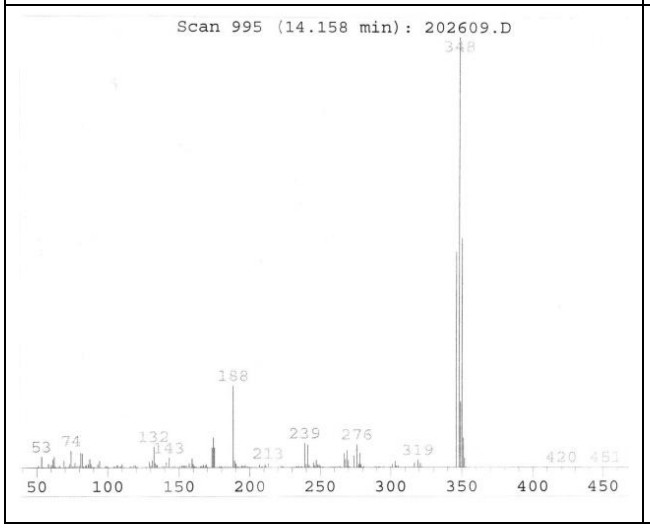
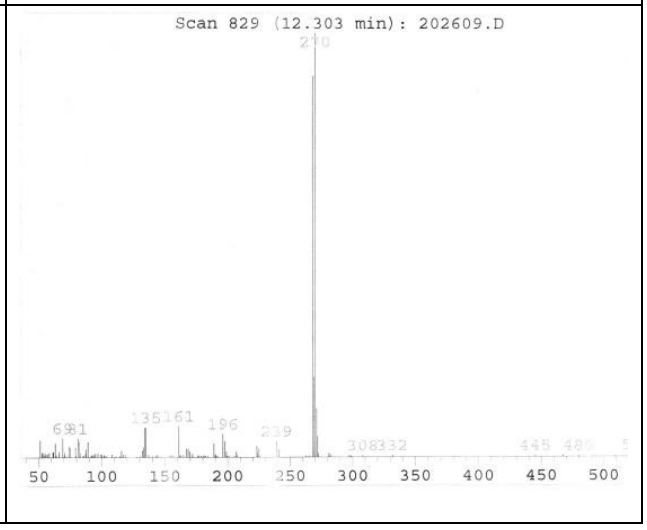
Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.031 g, 3.96 mmol, 1.00 eq.), K_2CO_3 (0.546 g, 3.95 mmol, 1.00 eq.), 1,4-dibromo-2,3,5,6-tetrafluorobenzene (**24**) (1.216 g, 3.95 mmol, 1.00 eq.), LiBr (0.208 g, 2.40 mmol, 0.61 eq.) and DMA were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor (80 W) in 4 steps: 1) 50 °C / 5 min, 2) 80 °C/ 5 min, 3) 100 °C/ 15 min, 4) 200 °C / 1 h. After cooling, the reaction mixture was transferred into water (100 mL), stirred for 1 h and the precipitate was filtered off. This solid was transferred into DCM (150 mL), stirred for 1 h for dissolution, dried over $MgSO_4$, filtered and the solvent was evaporated. The crude was purified by column chromatography on silica gel (eluent: PE) to yield a light-cream color solid (0.055 g, ~5%). The GC-MS analysis of the sample showed a mixture of two products, **3Br,45F$_2$-PheDOT** and **45F$_2$-PheDOT**, in a ratio of ca. 1.6:1. The sample showed one spot on TLC (with the same R_f as authentic **45F$_2$-PheDOT** synthesized independently in another experiment, see above) and we were unable to separate these products by flash chromatography. As the yield was low, partial debromination occurred during the reaction and the experiment did not give the expected **36Br$_2$,45F$_2$-PheDOT**, we did not make further attempts to separate the products.

3Br,45F$_2$-PheDOT:	***45F$_2$-PheDOT:***
MS (EI+): *m/z* 305.95 (M^+, 100%, ^{79}Br), 303.90 (95.5%, ^{81}Br); calcd. for $C_{10}H_3BrF_2O_2S$: 305.90 (100.0%, ^{79}Br), 303.90 (97.8%, ^{81}Br).	MS (EI+): *m/z* 226.00 (M^+, 100%); calcd. for $C_{10}H_4F_2O_2S$: 225.99.
	

6,7-Dibromobenzo[b]thieno[3,4-e][1,4]dioxine (**45Br$_2$-PheDOT**), and **6-bromobenzo[b]thieno[3,4-e][1,4]dioxine** (**4Br-PheDOT**)



Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.013 g, 3.89 mmol, 1.00 eq.), K_2CO_3 (0.552 g, 3.99 mmol, 1.03 eq.), 1,2-dibromo-4,5-difluorobenzene (**25**) (1.106 g, 4.07 mmol, 1.04eq.), LiBr (0.222 g, 2.56 mmol, 0.66 eq.) and DMA (10 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor (80 W) in 4 steps: 1) 50 °C / 5 min, 2) 80 °C / 5 min, 3) 100 °C / 15 min, 4) 200 °C/ 1 h. Another batch of diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (**1**) (1.012 g, 3.89 mmol, 1.00 eq.), K_2CO_3 (0.539 g, 3.90 mmol, 1.00 eq.), 1,2-dibromo-4,5-difluorobenzene (**29**) (1.137 g, 4.18 mmol, 1.08eq.), LiBr (0.209 g, 2.41 mmol, 0.62 eq.) and DMA (10 mL) was run at the same conditions. After cooling, the combined reaction mixtures were poured into water (200 mL), stirred for 1 h and the precipitate was filtered off. This solid was transferred into DCM (200 mL), stirred for 1 h, dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: PE) to yield an off-white (light cream color) solid (0.258 g, ~10%). The GC-MS and ^{1}H NMR analyses of the sample showed a mixture of two products, **45Br$_2$-PheDOT** and **4Br-PheDOT**, in a ratio of ca. 4:1. The sample showed one spot on TLC and we were unable to separate these products by flash chromatography. In the ^{1}H NMR of the mixture, partly debrominated compound **4Br-PheDOT** was identified by comparison with an authentic sample prepared independently (see above) and **45Br$_2$-PheDOT** was identified by comparison with an authentic sample prepared by reaction of 4,5-dibromocatechol with 3,4-dimethoxythiophene.[13] As partial debromination occurred during the reaction and the experiment did not give the expected **45Br$_2$-PheDOT** in a pure form, we did not make further attempts to separate these products.

45Br$_2$-PheDOT:	***4Br-PheDOT:***
MS (EI+): *m/z* 347.95 (M^+, 100%, ^{79}Br/^{79}Br), 349.90 (53.3%, ^{79}Br/^{781}Br), 345.90 (50.2%, ^{81}Br/^{81}Br); calcd. for C10H4Br2O2S: 347.83 (100.0%, ^{79}Br/^{79}Br), 345.83 (50.1%, ^{79}Br/^{81}Br), 349.83 (48.4%, ^{81}Br/^{81}Br).	MS (EI+): *m/z* 270.00 (M^+, 100%, ^{79}Br), 267.95 (90.0%, ^{81}Br); calcd. for $C_{10}H_5BrO_2S$: 269.92 (100.0%, ^{79}Br), 267.92 (97.8%, ^{81}Br).
	

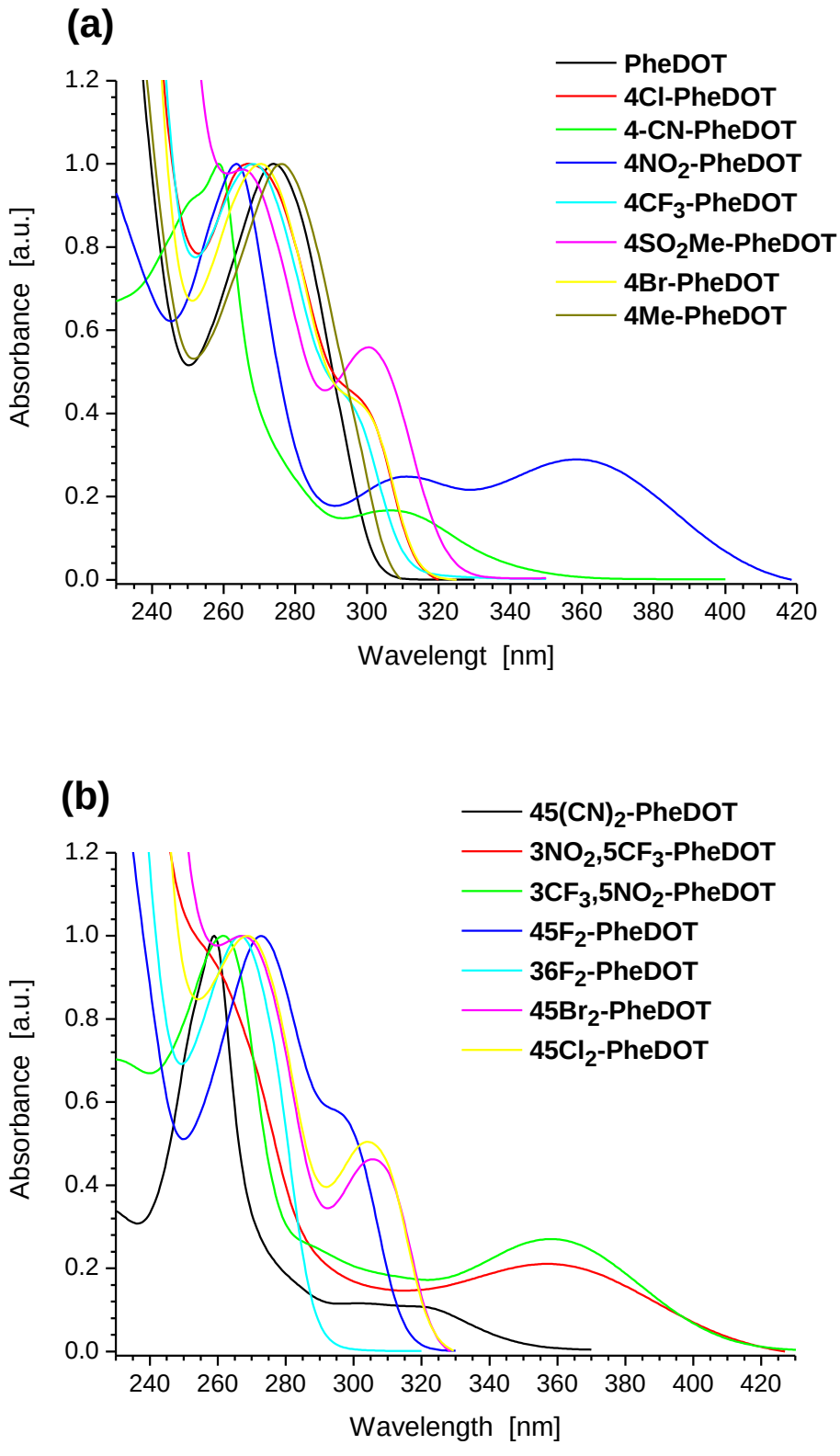


Figure S1. UV-Vis electron absorption spectra of mono- and disubstituted (at the benzene ring) **EWG-PheDOT** monomers in dichloromethane. The spectra are normalized to the maxima in the region of 260–280 nm (**45Br$_2$-PheDOT** and **45Cl$_2$-PheDOT** have been synthesized according to Ref. 13).

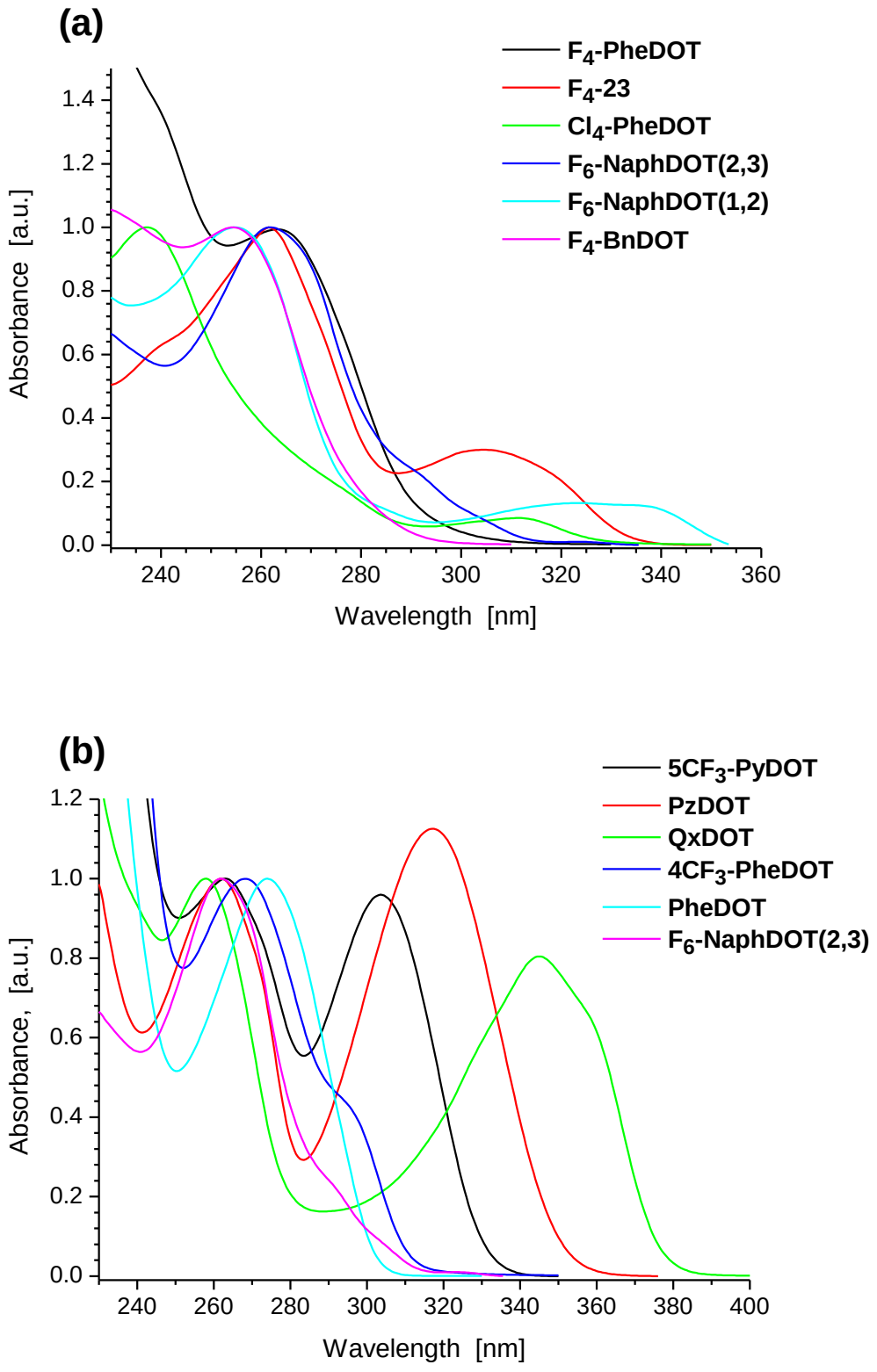
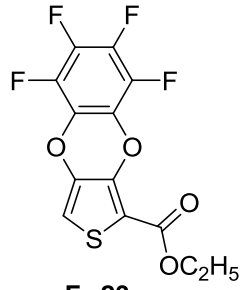


Figure S2. UV-Vis electron absorption spectra of **ArDOT** monomers in dichloromethane. The spectra are normalized to the maxima in the region of 240–280 nm.

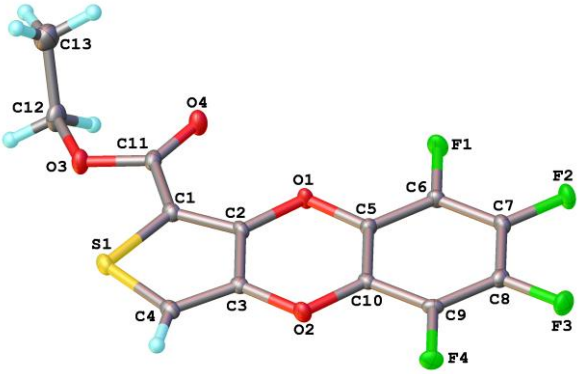
Table S4. Crystal data and structure refinement parameters.

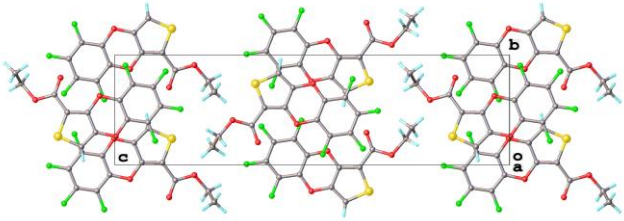
Compound	**F_4-23**	**36F_2-PheDOT**	**F_4-PheDOT**	**3NO_2,5CF_3-PheDOT**	**5CF_3-PyDOT**	**56Cl_2-PyDOT**	**PzDOT**	**QxDOT**
Empirical formula	$C_{13}H_6F_4O_4S$	$C_{10}H_4F_2O_2S$	$C_{10}H_2F_4O_2S$	$C_{11}H_4F_3NO_4S$	$C_{10}H_4F_3NO_2S$	$C_9H_3Cl_2NO_2S$	$C_8H_4N_2O_2S$	$C_{12}H_6N_2O_2S$
Formula weight	334.24	226.19	262.18	303.21	259.20	260.08	192.19	242.25
Temperature/K	120.0	120.0	120.0	200.0	120.0	120.0	120.0	120.0
Crystal system	orthorhombic	orthorhombic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	Pnma	P-1	P-1	$P2_1/n$	C2/c	$P2_1/c$	$P2_1/n$
a/Å	6.2517(5)	19.8371(6)	5.8022(9)	6.2118(10)	6.0124(2)	18.0302(5)	17.3384(3)	4.43002(16)
b/Å	7.3716(5)	11.5899(4)	7.6384(9)	7.0519(13)	22.0636(7)	5.89058(13)	6.74570(10)	21.1250(7)
c/Å	26.471(2)	3.70810(10)	11.243(2)	14.316(2)	7.2454(3)	18.9311(6)	14.5495(4)	10.8195(3)
α/°	90.00	90.00	108.558(15)	79.354(14)	90.00	90.00	90.00	90.00
β/°	90.00	90.00	94.513(15)	79.598(13)	97.282(3)	110.094(3)	114.8015(15)	92.714(3)
γ/°	90.00	90.00	104.161(12)	65.073(16)	90.00	90.00	90.00	90.00
Volume/$Å^3$	1219.94(16)	852.53(5)	451.33(13)	555.18(15)	953.39(6)	1888.26(9)	1544.75(6)	1011.40(6)
Z	4	4	2	2	4	8	8	4
$\rho_{calc}g/cm^3$	1.820	1.762	1.929	1.814	1.806	1.830	1.653	1.591
μ/mm^{-1}	0.335	0.384	0.407	0.348	0.373	0.880	0.378	0.308
F(000)	672.0	456.0	260.0	304.0	520.0	1040.0	784.0	496.0
Reflections collected	25897	15895	5934	5400	14144	14968	34104	14911
Independent reflections, R_{int}, R_σ	3576, 0.0302, 0.0175	1181, 0.0762, 0.0325	2173, 0.0568, 0.0713	2411, 0.0331, 0.0501	2527, 0.0473, 0.0353	2764, 0.0440, 0.0320	4513, 0.0729, 0.0542	2675, 0.0634, 0.0498
Data/restraints/parameters	3576/0/224	1181/0/78	2173/0/154	2411/21/192	2527/0/170	2764/0/148	4513/0/236	2675/0/178
Goodness-of-fit on F^2	1.071	1.060	1.019	1.054	1.044	1.048	1.032	1.018
R_1 indexes [I≥2σ (I)]	0.0259	0.0370	0.0581	0.0830	0.0357	0.0309	0.0433	0.0438
wR_2 indexes [all data]	0.0690	0.0910	0.1554	0.2398	0.0864	0.0743	0.0952	0.1033
Flack parameter	0.00(5)							

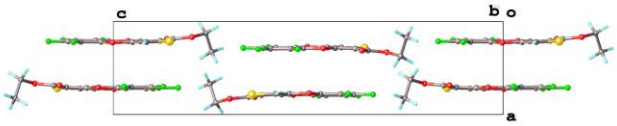
Figure S3 *(4 pages)*: Molecular and crystal structures of compounds **F_4-23, 36F_2-PheDOT, F_4-PheDOT, 3NO_2,4CF_3-PheDOT, 56Cl_2PyDOT, 5CF_3-PheDOT, PzDOT** and **QxDOT**.

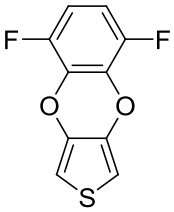


F_4-23



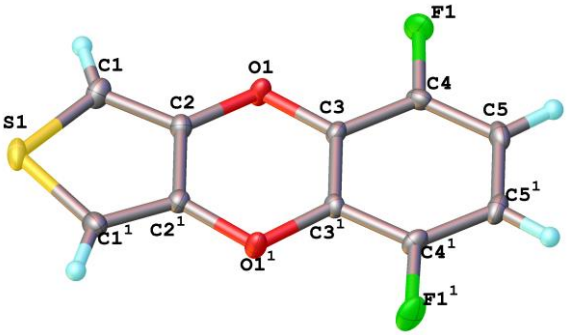


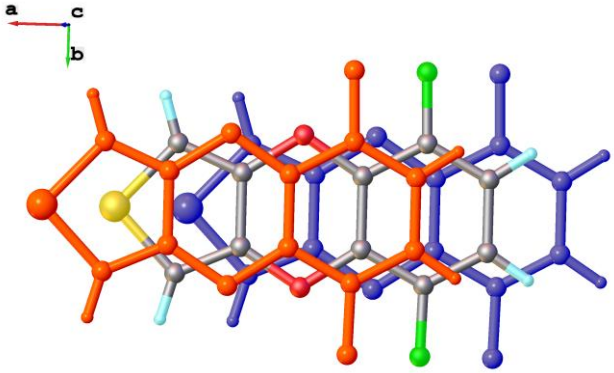


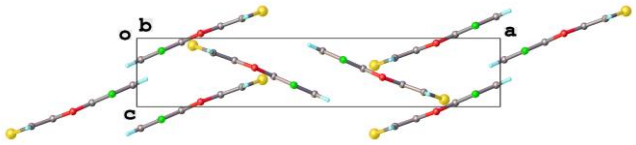


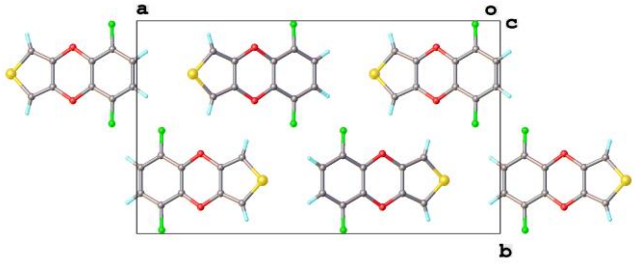
36F_2-PheDOT

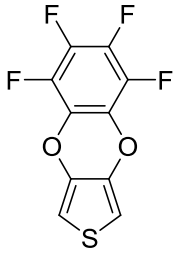
(non-centrosymmetric structure; second polymorph crystal is seen)



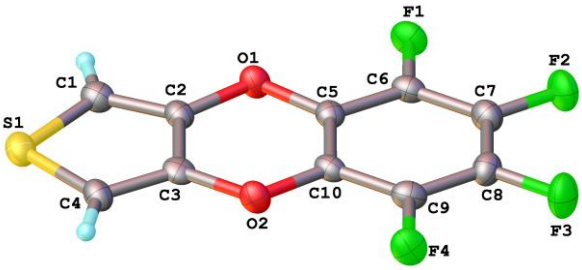


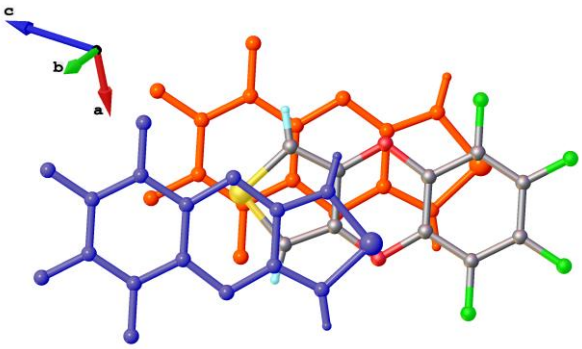


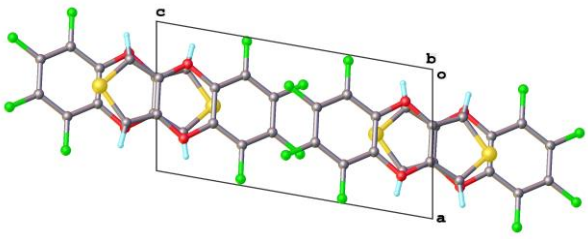


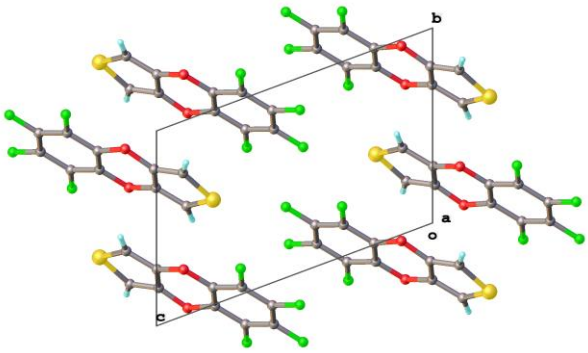


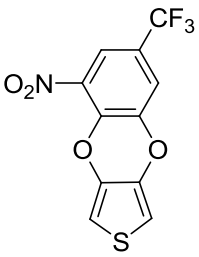
F_4-PheDOT





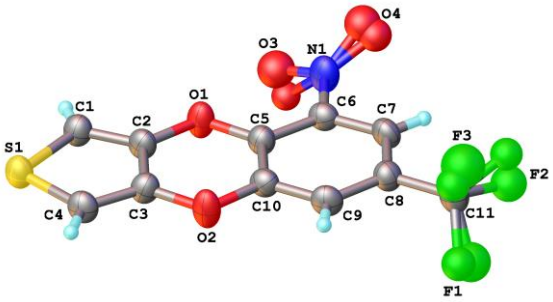


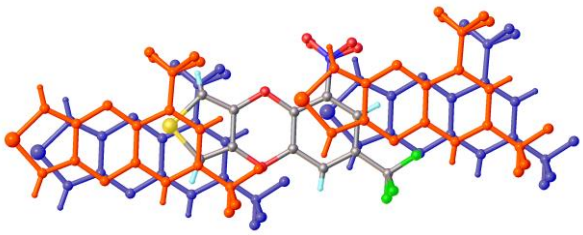


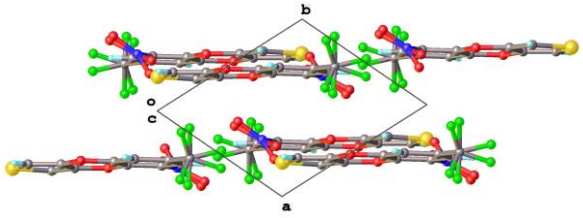


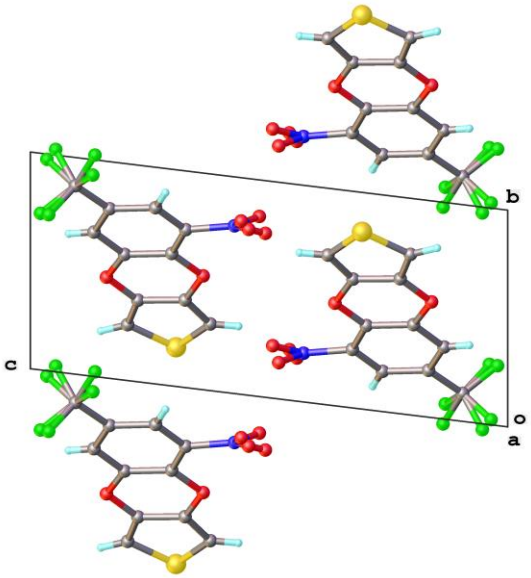
$3NO_2,4CF_3$-PheDOT

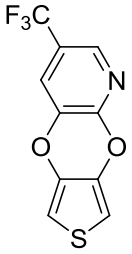
(some disorder of NO_2/CF_3 in a crystal)



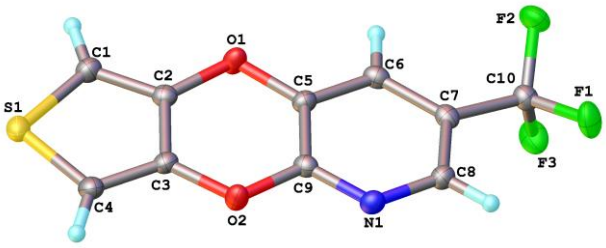


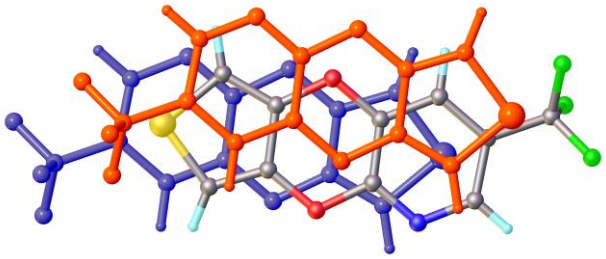


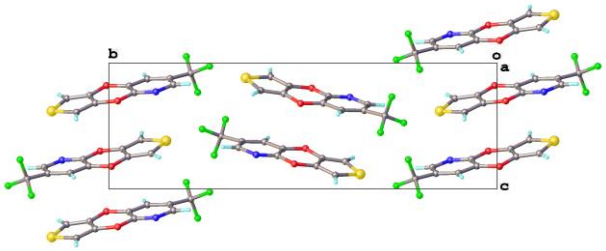


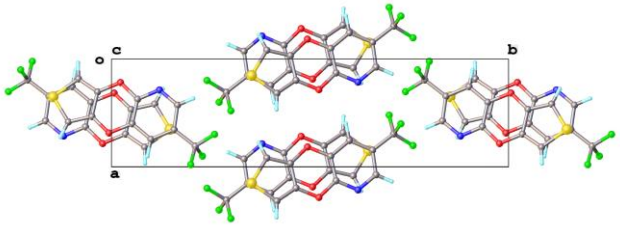


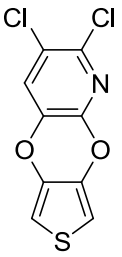
5CF$_3$-PyDOT



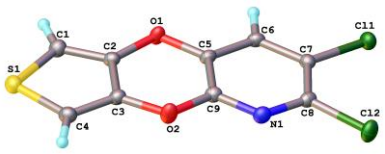


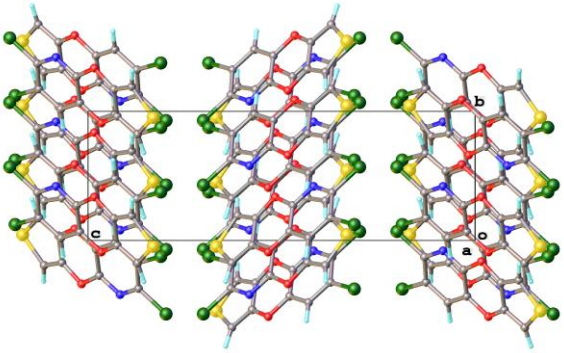


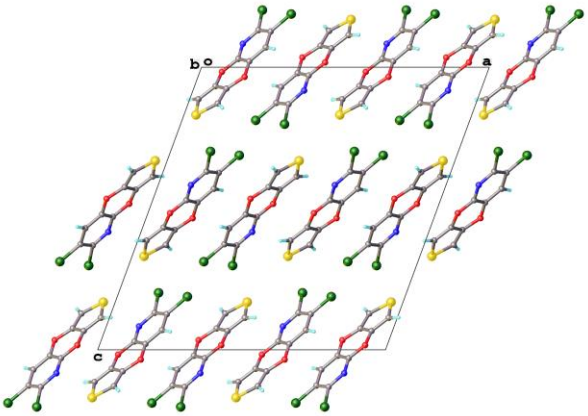


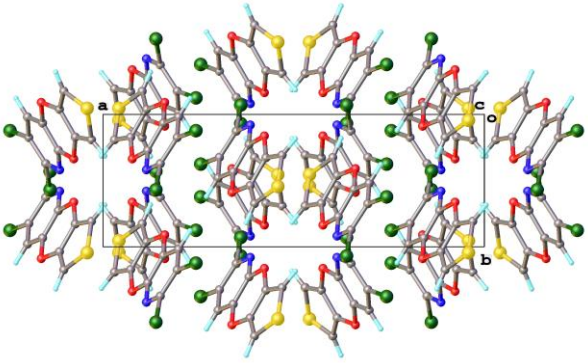


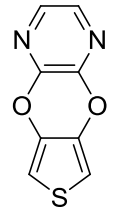
56Cl$_2$-PyDOT





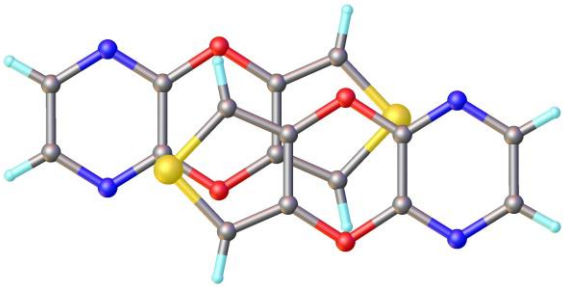


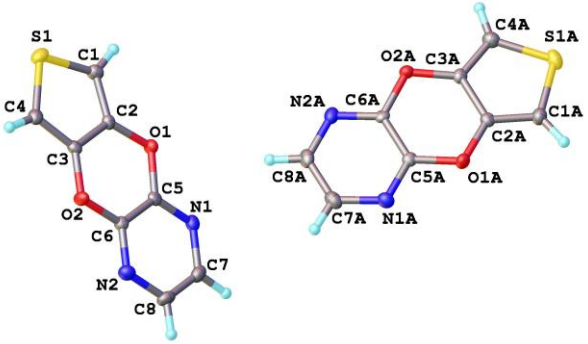


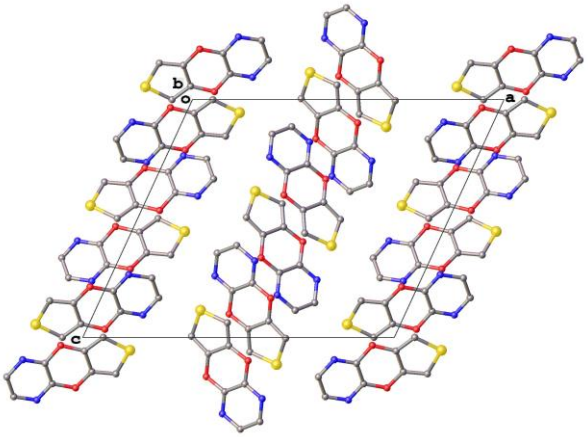


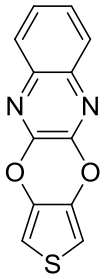
PzDOT

(twin crystals; two independent molecules in a unit cell)

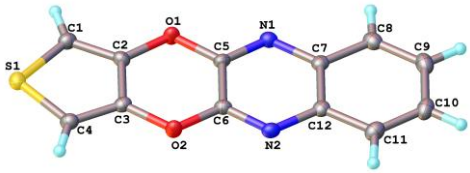


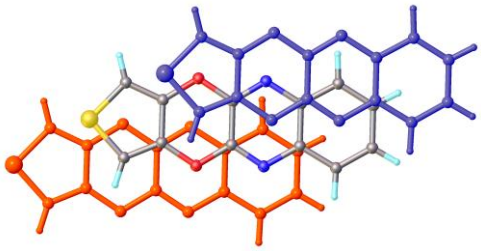


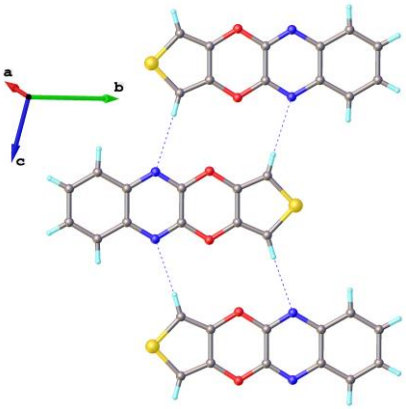


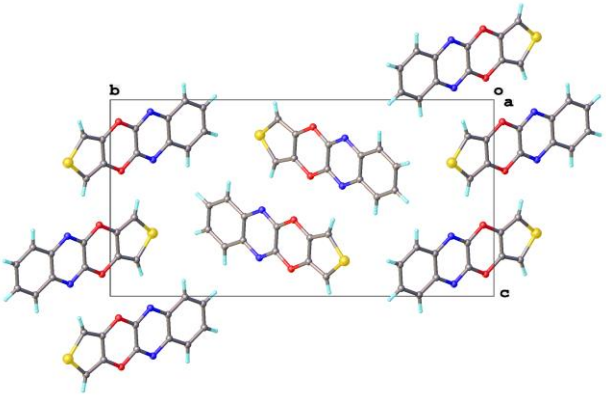


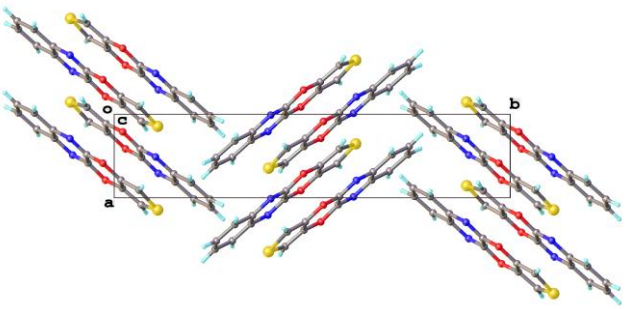
QxDOT











We were also able to isolate the **F4-23** intermediate from the reaction mixture in synthesis by Scheme 1 in the paper, and its structure was confirmed by a single crystal X-Ray diffraction (Figure S4). In the crystal structure of **F4-23** planar (with the exception of the terminal methyl group) molecules are arranged in layers perpendicular to the c-axis. Each layer is formed out of anti-parallel chains of molecules linked by C(thiophene)–H···O and F···O contacts. Weaker C(methylene)–H···S contacts exist between the layers. The polycyclic fragments of the molecules in adjacent parallel chains do not overlap, meaning the absence of "classical" aromatic π···π stacking in the structure. Nevertheless, the distance between molecules in parallel chains is quite short: the shortest interatomic distance is O···O 3.132(1) Å. Most probably electrostatic interactions between numerous heteroatoms are responsible for such an unusual (for planar tricyclic molecules) packing arrangement. A proper analysis of these interactions requires quantum-chemical calculations and is impossible on the basis of geometrical information obtained by X-ray method only.

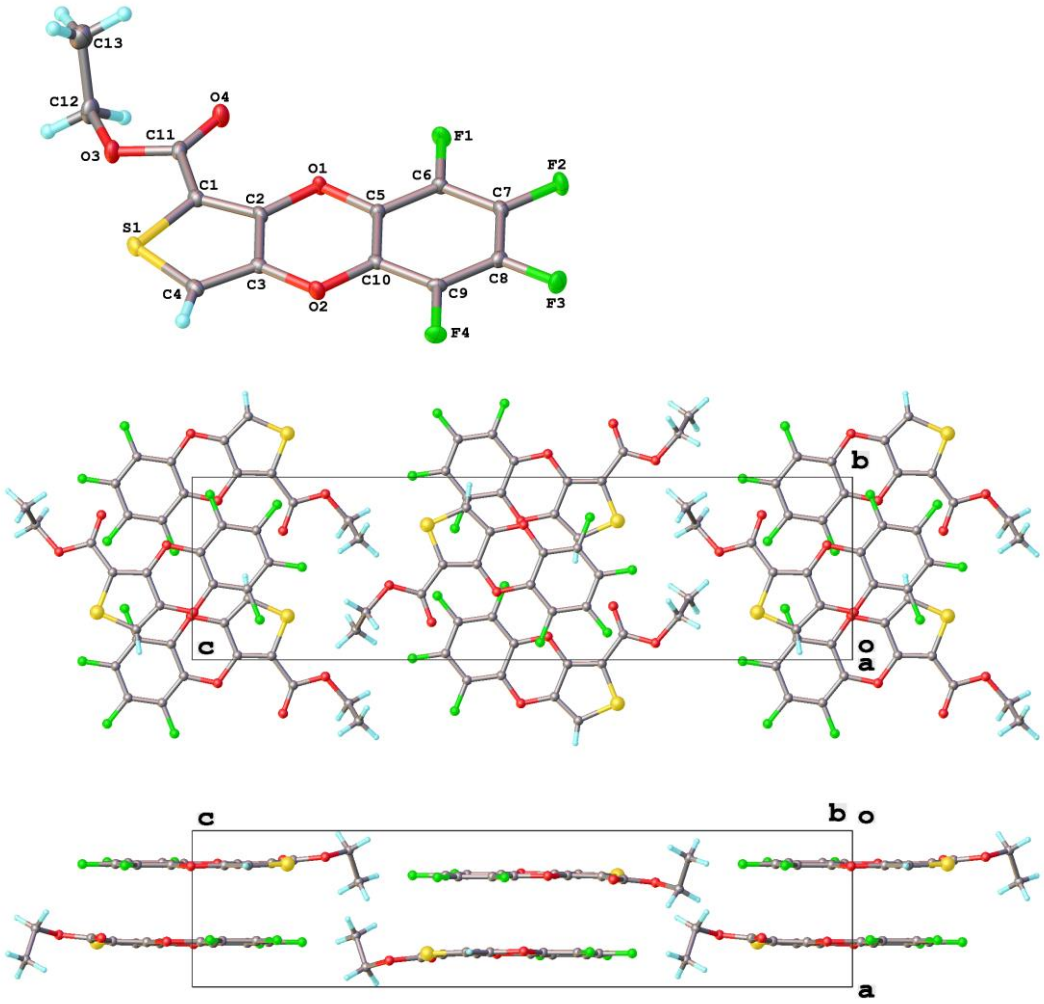


Figure S4. Molecular structure and crystal packing of compound **F4-23**.

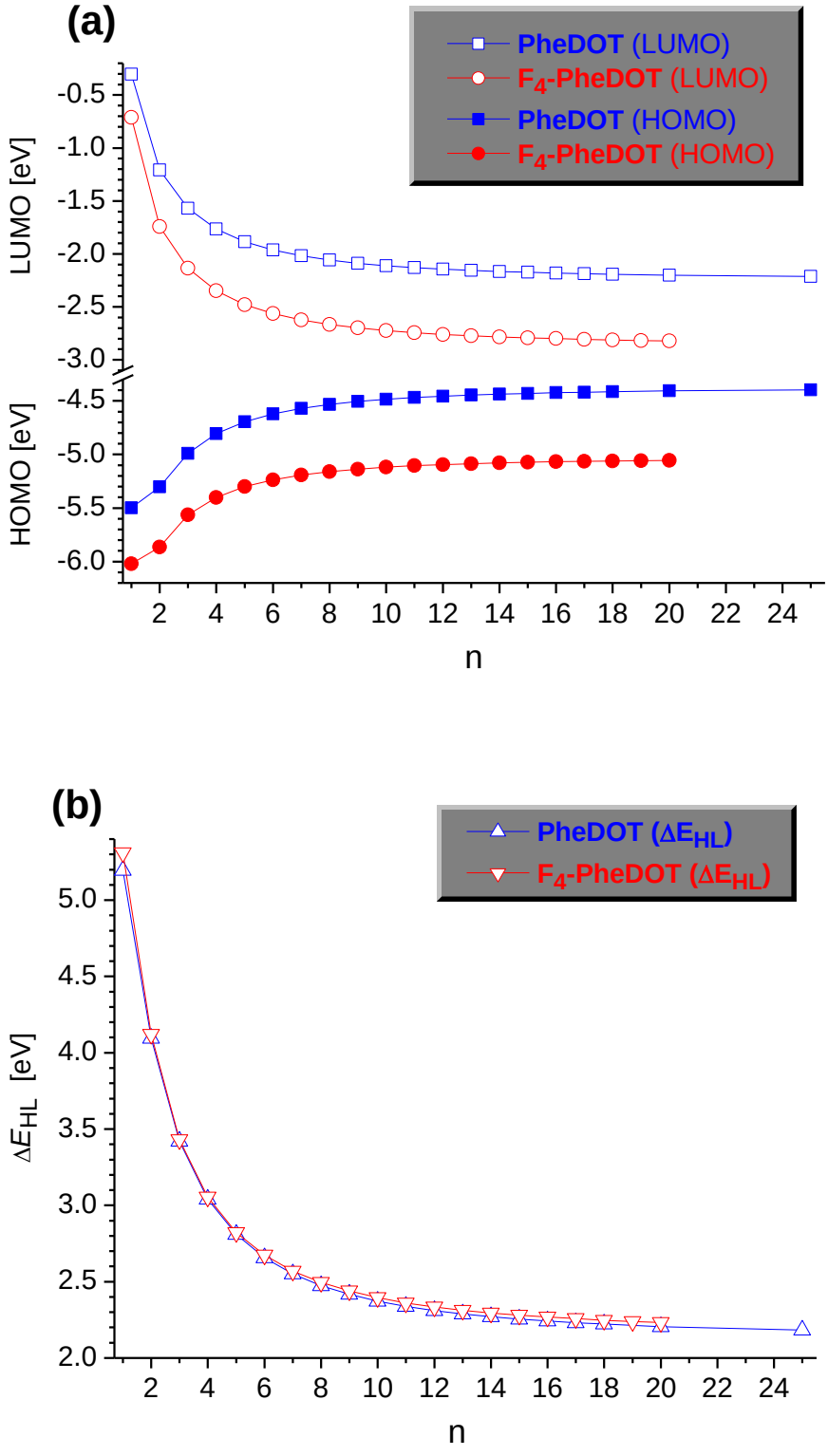


Figure S5. Chain length dependences of (a) HOMO and LUMO energies and (b) HOMO–LUMO energy gaps ΔE_{HL} for B3LYP/6-31G(d) optimized geometries (in the gas phase) of **(PheDOT)$_n$** and **(F$_4$-PheDOT)$_n$** oligomers, plotted versus a number of repeating units "n".

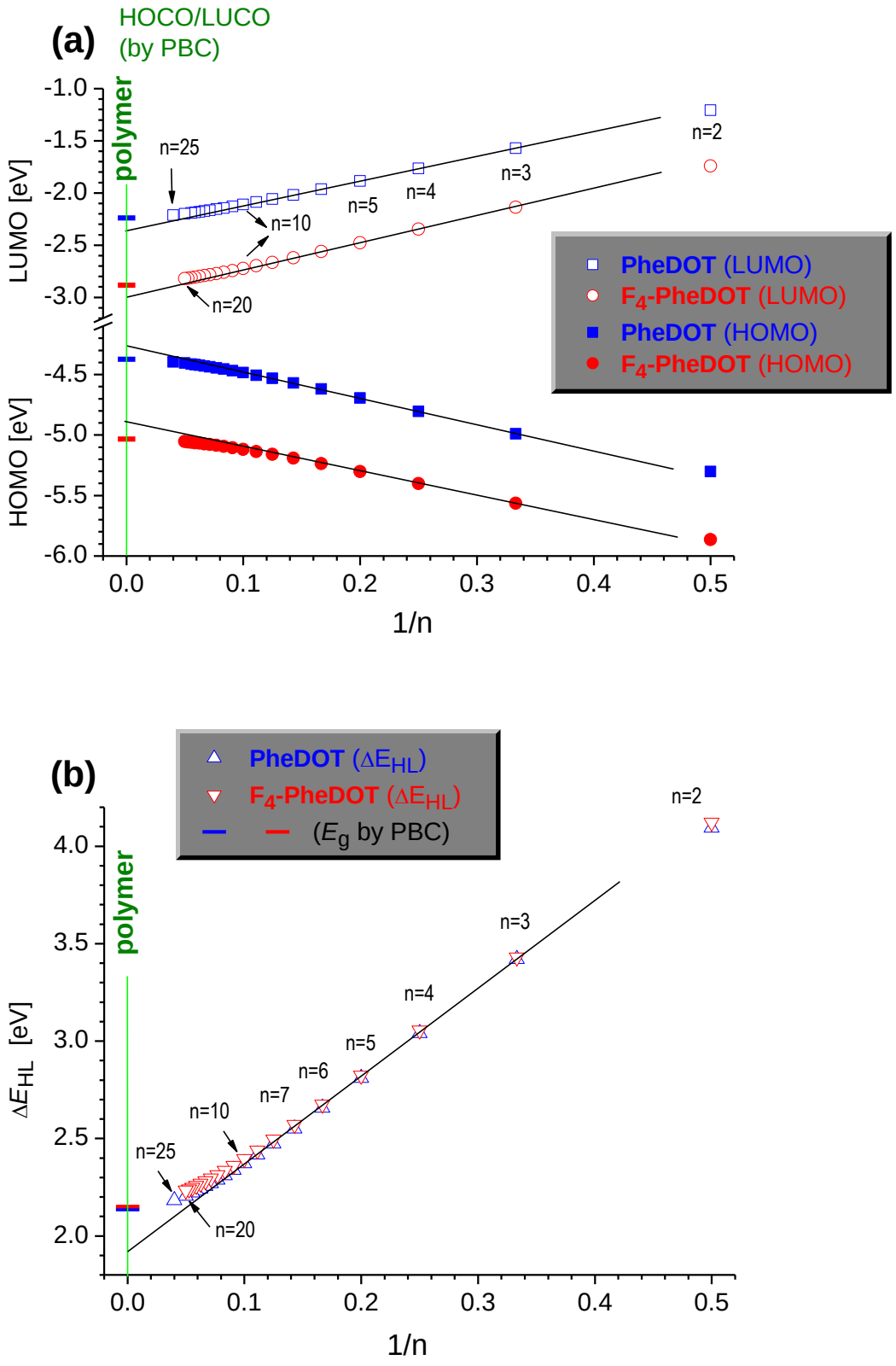


Figure S6. Chain length dependences of (a) HOMO and LUMO energies and (b) HOMO–LUMO energy gaps ΔE_{HL} for B3LYP/6-31G(d) optimized geometries (in the gas phase) of **(PheDOT)$_n$** and **(F$_4$-PheDOT)$_n$** oligomers, plotted versus a reciprocal number of repeating units, 1/n. Symbols — and — correspond to the energies (HOCO, LUCO, E_g) for polymers calculated by PBC/B3LYP/6-31G(d).

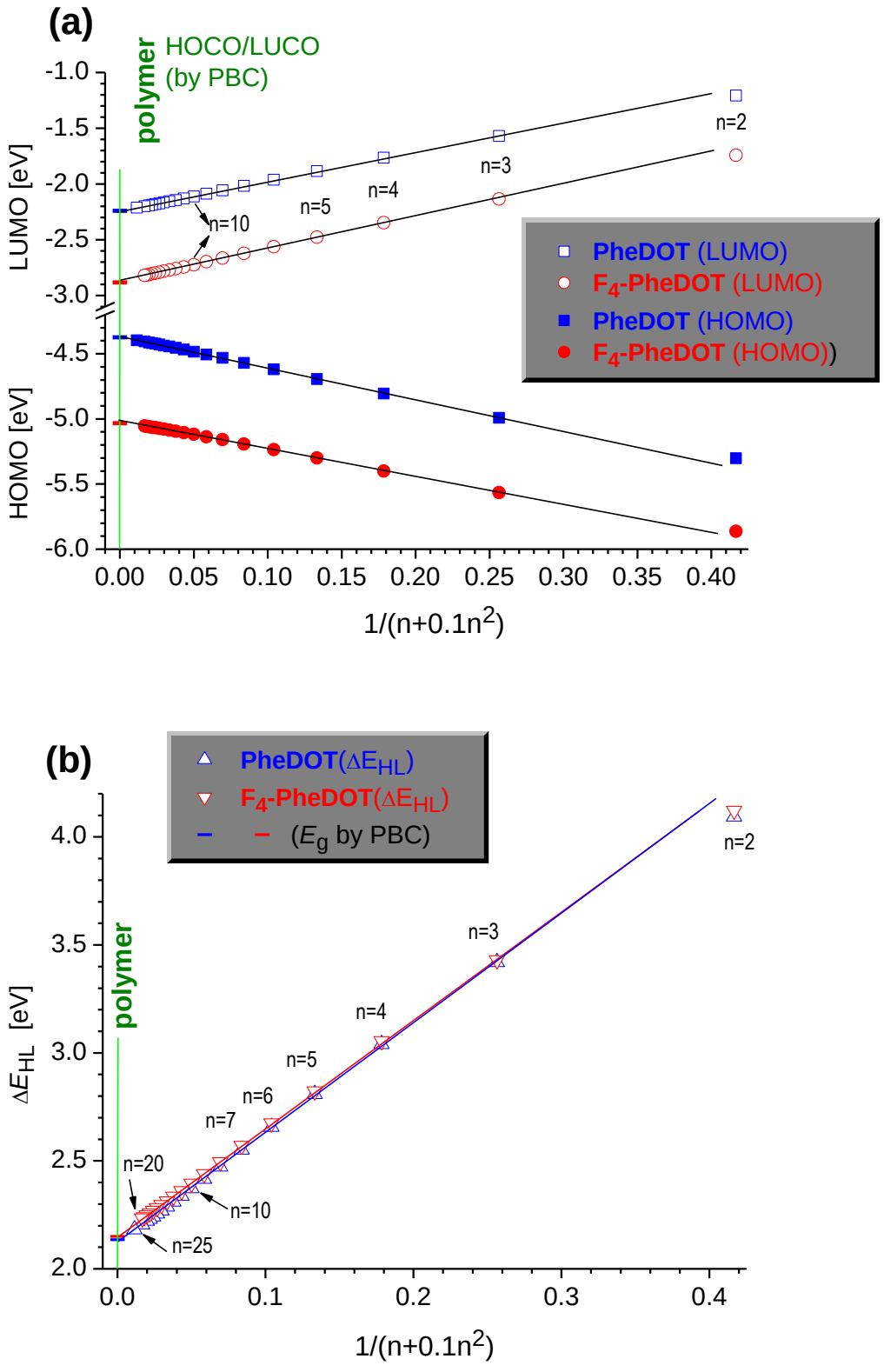


Figure S7. Chain length dependences of (a) HOMO and LUMO energies and (b) HOMO–LUMO energy gaps ΔE_{HL} for B3LYP/6-31G(d) optimized geometries (in the gas phase) of **(PheDOT)$_n$** and **(F$_4$-PheDOT)$_n$** oligomers, plotted as a function of $1/(n + 0.1n^2)$.
Symbols — and — correspond to the energies (HOCO, LUCO, E_g) for polymers calculated by PBC/B3LYP/6-31G(d).

In contrast to dependences of energies (HOMO, LUMO, ΔE_{HL}) versus 1/n, which show deviation from the linearity (saturation) with an elongation of the oligomers length, the use of the function **$1/(n + 0.1n^2)$**) gives excellent linear dependences (see Figure S7 for magnified graphs) with correlation coefficients $R \geq 0.9998$, and the extrapolated (to the infinite polymer length, $n = \infty$) energies excellently coincide with the energies for the polymers calculated by PBC/B3LYP/6-31G(d).

$$E_n = E_{n=\infty} + \alpha \cdot [1/(n + 0.1n^2)]$$

(PheDOT)$_n$:

LUMO [eV] = **–(2.244** ± 0.001) + (2.655 ± 0.011)·[1/(n + 0.1n^2)]
R = 0.9999, N = 18 (points n = 3...18, 20, 25)

HOMO [eV] = **–(4.364** ± 0.001) – (2.454 ± 0.008)·[1/(n + 0.1n^2)]
R = 0.9999, N = 18 (points n = 3...18, 20, 25)

ΔE_{HL} [eV] = (**2.120** ± 0.002) + (5.109 ± 0.017) ·[1/(n + 0.1n^2)]
R = 0.9999, N = 18 (points n = 3...18, 20, 25)

p[PheDOT], calculations by PBC:

LUCO = **–2.239** eV
HOCO = **–4.374** eV
E_g = **2.135**eV

(F_4-PheDOT)$_n$:

LUMO [eV] = **–(2.868** ± 0.002) + (2.889 ± 0.012)·[1/(n + 0.1n^2)]
R = 0.9999, N = 18 (points n = 3...20)

HOMO [eV] = **–(5.015** ± 0.001) – (2.143 ± 0.010)·[1/(n + 0.1n^2)]
R = 0.9998, N = 18 (points n = 3...20)

ΔE_{HL} [eV] = (**2.147** ± 0.001) + (5.032 ± 0.015) ·[1/(n + 0.1n^2)]
R =0.9999 , N = 18 (points n = 3...20)

p[F_4-PheDOT], calculations by PBC:

LUCO = **–2.882** eV
HOCO = **–5.033** eV
E_g = **2.151**eV

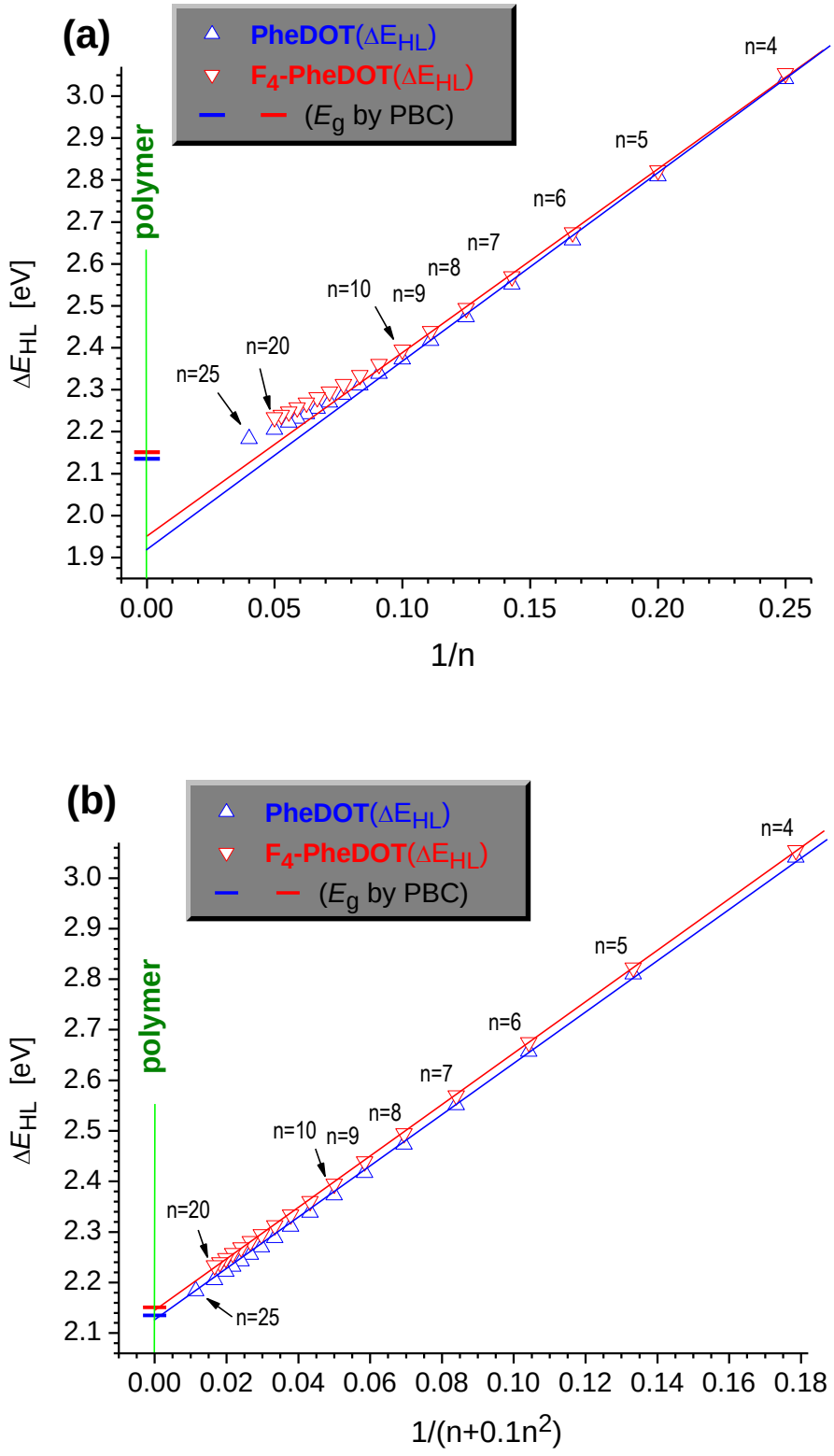


Figure S8. Magnified graphs (for n = 4 – 25, from Figures S4 and S5) of B3LYP/6-31G(d) calculated energy gaps ΔE_{HL} for **(PheDOT)$_n$** and **(F$_4$-PheDOT)$_n$**: comparison of correlations versus (a) 1/n and (b) $1/(n + 0.1n^2)$.

Table S5. Total energies, HOMO/LUMO energy levels and the HOMO–LUMO gaps for **(PheDOT)$_n$** and **(F$_4$-PheDOT)$_n$** oligomers by B3LYP/6-31G(d) calculations in the gas phase.

(PheDOT)$_n$

n	1/n	$1/(n+0.1n^2)$	Total energy, hartree	HOMO, eV	LUMO, eV	ΔE_{HL}, eV
1	1	0.9091	–933.27336120	–5.499	–0.304	5.196
2	0.5000	0.4167	–1865.3590544	–5.303	–1.208	4.095
3	0.3333	0.2564	–2797.4456125	–4.991	–1.571	3.420
4	0.2500	0.1786	–3729.5318205	–4.806	–1.764	3.041
5	0.2000	0.1333	–4661.6187163	–4.695	–1.885	2.810
6	0.1667	0.1042	–5593.7044558	–4.620	–1.963	2.657
7	0.1429	0.0840	–6525.7918588	–4.570	–2.018	2.551
8	0.1250	0.0694	–7457.8778554	–4.532	–2.058	2.473
9	0.1111	0.0585	–8389.9650029	–4.506	–2.088	2.417
10	0.1000	0.0500	–9322.0512785	–4.484	–2.111	2.373
11	0.0909	0.0433	–10254.1381466	–4.468	–2.123	2.339
12	0.0833	0.0379	–11186.2245524	–4.455	–2.144	2.311
13	0.0769	0.0334	–12118.3112902	–4.445	–2.156	2.289
14	0.0714	0.0298	–13050.3978619	–4.437	–2.166	2.271
15	0.0667	0.0267	–13982.4844337	–4.429	–2.174	2.256
16	0.0625	0.0240	–14914.5709395	–4.423	–2.181	2.242
17	0.0588	0.0218	–15846.6575770	–4.418	–2.187	2.232
18	0.0556	0.0198	–16778.7441030	–4.414	–2.192	2.222
25	0.0400	0.0114	–23303.3501514	–4.396	–2.213	2.183

(F$_4$-PheDOT)$_n$

n	1/n	$1/(n+0.1n^2)$	Total energy, hartree	HOMO, eV	LUMO, eV	ΔE_{HL}, eV
1	1	0.9091	–1330.1652878	–6.022	–0.710	5.311
2	0.5000	0.4167	–2659.1424162	–5.864	–1.741	4.122
3	0.3333	0.2564	–3988.1206097	–5.565	–2.136	3.429
4	0.2500	0.1786	–5317.0989362	–5.401	–2.347	3.054
5	0.2000	0.1333	–6646.0773958	–5.301	–2.478	2.823
6	0.1667	0.1042	–7975.0556120	–5.236	–2.562	2.675
7	0.1429	0.0840	–9304.0341761	–5.192	–2.622	2.570
8	0.1250	0.0694	–10633.0124079	–5.150	–2.665	2.494
9	0.1111	0.0585	–11961.9910497	–5.137	–2.698	2.439
10	0.1000	0.0500	–13290.9693471	–5.119	–2.724	2.395
11	0.0909	0.0433	–14619.9478397	–5.105	–2.745	2.361
12	0.0833	0.0379	–15948.9261401	–5.094	–2.760	2.334
13	0.0769	0.0334	–17277.9045610	–5.086	–2.773	2.313
14	0.0714	0.0298	–18606.8829648	–5.078	–2.783	2.295
15	0.0667	0.0267	–19935.8614073	–5.073	–2.791	2.281
16	0.0625	0.0240	–21264.8398646	–5.068	–2.799	2.269
17	0.0588	0.0218	–22593.8182640	–5.064	–2.806	2.258
18	0.05556	0.01984	–23922.7954363	–5.060	–2.812	2.248
19	0.05263	0.01815	–25251.7721790	–5.058	–2.818	2.240
20	0.0500	0.0167	–26580.7515697	–5.055	–2.821	2.234

Table S6. HOMO, LUMO energy levels and the HOMO–LUMO energy gaps (ΔE_{HL}) of dimers **(ArDOT)$_2$** by B3LYP/6-31G(d) calculations in the gas phase.

	Dimers **(ArDOT)$_2$**	Total energy, hartree	HOMO, eV	LUMO, eV	ΔE_{HL},[a] eV
1	**[(4MeO)$_2$-PheDOT]$_2$**	–2323.4326423	–4.895	–1.040	3.855
2	**(4MeO-PheDOT)$_2$**	–2094.4015000	-5.142	-1.134	4.008
3	**(4Me-PheDOT)$_2$**	–1943.9948689	–5.225	–1.148	4.077
4	**(PheDOT)$_2$**	–1865.3590543	–5.303	–1.208	4.095
5	**(36F$_2$-PheDOT)$_2$**	–2262.2632089	–5.577	–1.465	4.111
6	**(4F-PheDOT)$_2$**	–2063.8215136	–5.464	–1.368	4.096
7	**(4Br-PheDOT)$_2$**	–7007.5652927	–5.563	–1.463	4.100
8	**(4Cl-PheDOT)$_2$**	–2784.5474279	–5.572	–1.468	4.104
9	**(45F$_2$-PheDOT)$_2$**	–2262.2698477	–5.612	–1.512	4.100
10	**(4CF$_3$-PheDOT)$_2$**	–2539.4325592	–5.701	–1.582	4.119
11	**(4MeSO$_2$-PheDOT)$_2$**	–3041.1303425	–5.843	–1.729	4.114
12	**(F4-PheDOT)$_2$**	–2659.1424161	–5.864	–1.742	4.122
13	**(45Cl$_2$-PheDOT)$_2$**	–3703.7258360	–5.766	–1.658	4.108
14	**(Cl$_4$-PheDOT)$_2$**	–5542.0642800	–5.990	–1.869	4.120
15	**(3NO$_2$,5CF$_3$-PheDOT)$_2$**	–2948.4047350	–6.148	–2.842	3.306
16	**(4CN-PheDOT)$_2$**	–2049.8433341	–5.917	–1.845	4.073
17	**(4NO$_2$-PheDOT)$_2$**	–2274.3601970	–6.003	–2.587	3.416
18	**(3CF$_3$,5NO$_2$-PheDOT)$_2$**	–2352.9989481	–5.947	–2.513	3.434
19	**(45(CN)$_2$-PheDOT)$_2$**	–2234.3133927	–6.415	–2.582	3.833
20	**(NaphDOT(2,3))$_2$**	–2172.6473759	–5.260	–1.313	3.947
21	**[F$_6$-NaphDOT(2,3)]$_2$**	–3363.3433721	–5.773	–1.874	3.899
22	**[F$_6$-NaphDOT(1,2)]$_2$**	–3363.3378313	–5.798	–1.918	3.881
23	**(PyDOT)$_2$**	–1897.4408713	–5.509	–1.365	4.145
24	**(5CF$_3$-PyDOT)$_2$**	–2571.5109075	–5.899	–1.754	4.145
25	**(56Cl$_2$-PyDOT)$_2$**	–3735.8092468	–5.966	–1.825	4.141
26	**(PzDOT)$_2$**	–1929.5159146	–5.764	–1.641	4.124
27	**(QxDOT)$_2$**	–2236.8167607	–5.701	–1.968	3.734
28	**(F$_4$-BnDOT)$_2$** cisoid[b]	–2737.7710399	–5.437	–1.340	4.097
29	**(F$_4$-BnDOT)$_2$** transoid[b]	–2737.7710008	–5.439	–1.343	4.096

[a] ΔE_{HL} = LUMO – HOMO.

[b] "Cisoid" and "transoid" belongs to the relative orientation of non-planar seven-member rings in the dimers.

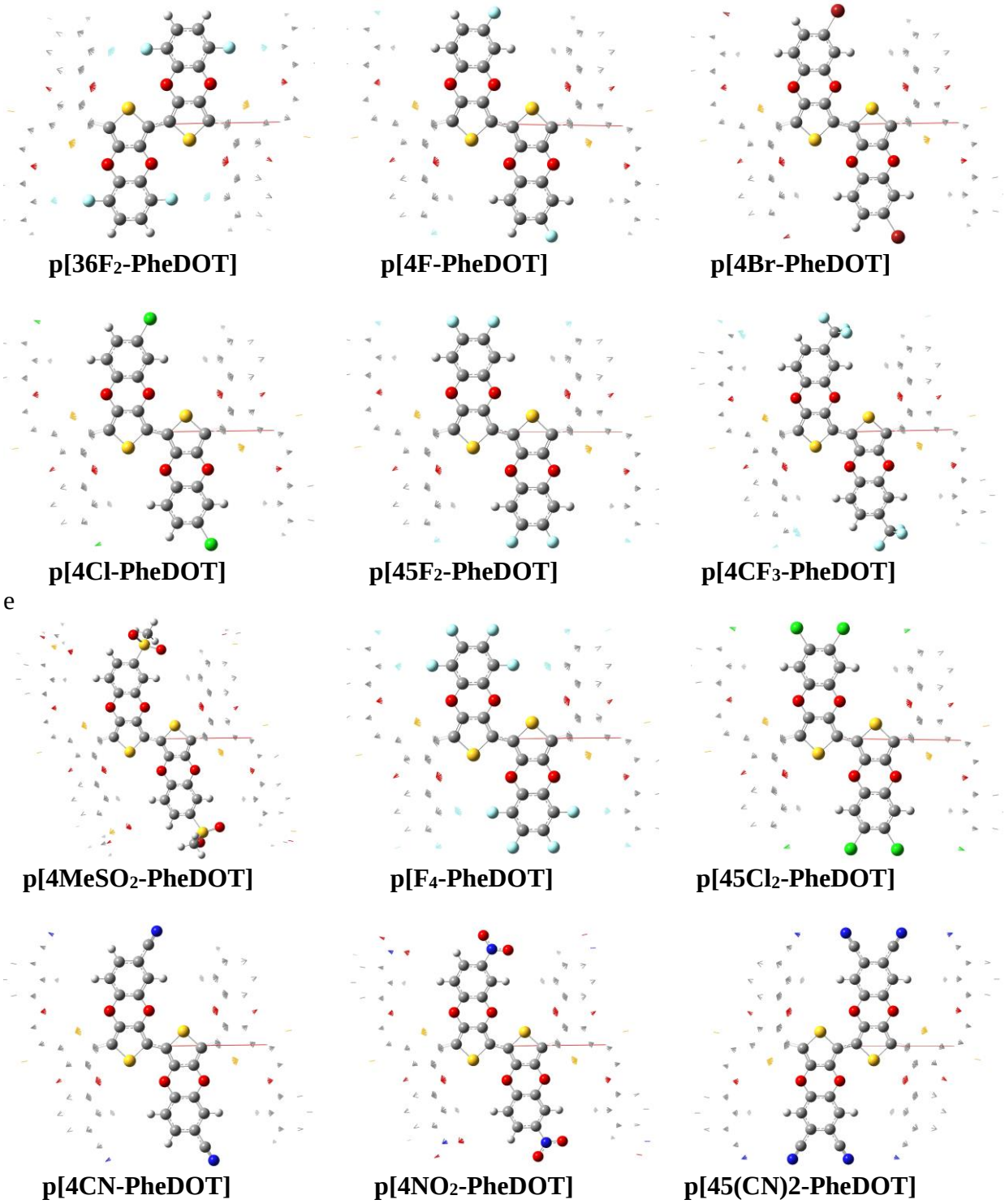
Table S7. HOCO, LUCO energy levels and the band gaps (E_g,) of **p[ArDOT]** polymers by PBC/B3LYP/6-31G(d) calculations in the gas phase

p[ArDOT]	Total energy,[a] hartree	HOCO, eV	LUCO, eV	E_g,[b] eV	ΔHOCO,[c] eV	ΔE_g,[d] meV
p[4MeO-PheDOT]	–2093.2153646	–4.329	–2.204	2.126	0.040	–10
p[4Me-PheDOT]	–1942.8090085	–4.270	–2.147	2.123	0.104	–13
p[PheDOT]	–1864.1731432	–4.374	–2.239	2.135	**0**	**0**
p[36F$_2$-PheDOT]	–2261.0764465	–4.552	–2.390	2.162	–0.178	26
p[4F-PheDOT]	–2062.6355280	–4.644	–2.511	2.133	-0.27	–2
p[4Br-PheDOT]	–7006.3793017	–4.770	–2.631	2.139	–0.396	4
p[4Cl-PheDOT]	–2783.3613276	–4.790	–2.650	2.140	–0.416	5
p[45F$_2$-PheDOT]	–2261.0829434	–4.893	–2.755	2.138	–0.519	2
p[4CF$_3$-PheDOT]	–2538.2463064	–4.953	–2.809	2.144	–0.579	9
p[4MeSO$_2$-PheDOT]	–3039.9466487	–4.980	–2.831	2.149	–0.606	14
p[F$_4$-PheDOT]	–2657.9557189	–5.033	–2.882	2.151	–0.659	16
p[45Cl$_2$-PheDOT]	–3702.5384442	–5.059	–2.919	2.140	–0.685	5
p[4CN-PheDOT]	–2947.2281140	–5.324	–3.173	2.152	–0.950	16
p[4NO$_2$-PheDOT]	–2048.6563942	–5.370	–3.230	2.140	–0.996	5
p[45(CN)2-PheDOT]	–2273.1744023	–6.017	–3.847	2.170	–1.643	35
p[NaphDOT(2,3)]	–2351.8121007	–4.393	–2.364	2.029	–0.019	–106
p[F$_6$-NaphDOT(2,3)]	–2233.1177820	–4.950	–2.913	2.037	–0.576	–98
p[PyDOT]	–2171.4611856	–4.471	–2.315	2.156	–0.097	21
p[5CF$_3$-PyDOT]	–3362.1576614	–5.055	–2.887	2.169	–0.681	33
p[56Cl$_2$-PyDOT]	–3362.1542424	–5.157	–2.988	2.169	–0.783	34
p[PzDOT]	–1896.2573156	–4.684	–2.507	2.177	–0.310	41
p[QxDOT]	–2570.3264606	–4.639	–2.583	2.056	–0.265	–79

[a] Absolute energies per unit cell.
[b] E_g = LUCO – HOCO.
[c] ΔHOCO = HOCO(**p[ArDOT]**) – HOCO(**p[PheDOT]**)
[d] ΔE_g = E_g(**p[ArDOT]**) – E_g(**p[PheDOT]**)

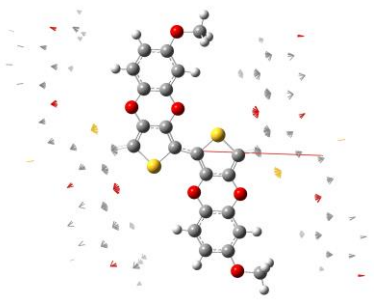
Table S8. Short S···O contacts and selected bond distances in **p[ArDOTs]** for optimized polymer structures by PBC/B3LYP/6-31G(d).

p[ArDOT]	S···O	(Ph)C1–O (Ph)C2–O	O–C3(Th) O–C4(Th)	(Th–Th) C2–C5'	Thiophene C2–C3	Thiophene C3–C4
p[4MeO-PheDOT]	2.944 2.949	1.385	1.372	1.437	1.378	1.413
p[4Me-PheDOT]	2.947	1.384	1.372	1.437	1.379	1.413
p[PheDOT]	2.947	1.384	1.372	1.437	1.379	1.413
p[36F$_2$-PheDOT]	2.951	1.377	1.374	1.442	1.378	1.413
p[4F-PheDOT]	2.947	1.383	1.373	1.437	1.378	1.412
p[4Br-PheDOT]	2.943 2.952	1.382	1.373	1.436	1.378	1.412
p[4Cl-PheDOT]	2.944 2.951	1.382	1.373	1.437	1.378	1.412
p[45F$_2$-PheDOT]	2.947	1.382	1.373	1.437	1.378	1.412
p[4CF$_3$-PheDOT]	2.943 2.954	1.381	1.373	1.437	1.378	1.412
p[4MeSO$_2$-PheDOT]	2.894 2.996	1.380	1.375	1.435	1.378	1.411
p[F$_4$-PheDOT]	2.951	1.376	1.375	1.441	1.378	1.413
p[45Cl$_2$-PheDOT]	2.948	1.380	1.373	1.437	1.378	1.412
p[4CN-PheDOT]	2.934 2.965	1.380	1.373	1.437	1.378	1.411
p[4NO$_2$-PheDOT]	2.916 2.980	1.379	1.373	1.436	1.378	1.411
p[45(CN)2-PheDOT]	2.955	1.376	1.374	1.438	1.378	1.411
p[NaphDOT(2,3)]	2.950	1.382	1.371	1.436	1.379	1.411
p[F$_6$-NaphDOT(2,3)]	2.951	1.374	1.373	1.438	1.379	1.410
p[PyDOT]	2.948 2.932	1.380	1.374	1.435	1.378	1.411
p[5CF$_3$-PyDOT]	2.944 2.938	1.376	1.375	1.435	1.378	1.410
p[56Cl$_2$-PyDOT]	2.935 2.946	1.375	1.375	1.436	1.378	1.411
p[PzDOT]	2.942	1.374	1.376	1.438	1.378	1.411
p[QxDOT]	2.945	1.373	1.374	1.437	1.379	1.409
RANGE (lowest-highest)	*2.894–2.996*	*1.373–1.385*	*1.371–1.376*	*1.435–1.442*	*1.378–1.379*	*1.409–1.413*



e

Figure S9. Unit cells for the optimized structures of **p[EWG-PheDOT]** polymers calculated at PBC/B3LYP/6-31G(d). Replication of the unit cells is shown as shadow atoms/bonds. Absolute energies (per unit cell), HOCO and LUCO energies and the band gaps E_g are given in the Table S7.



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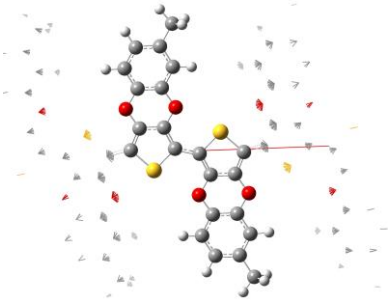
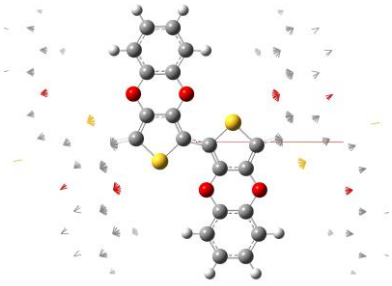
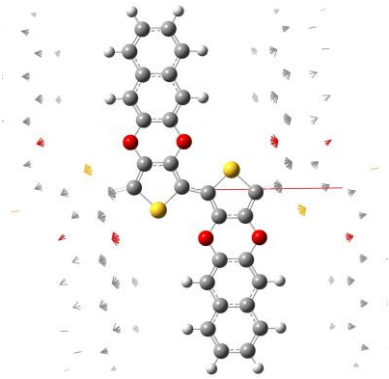


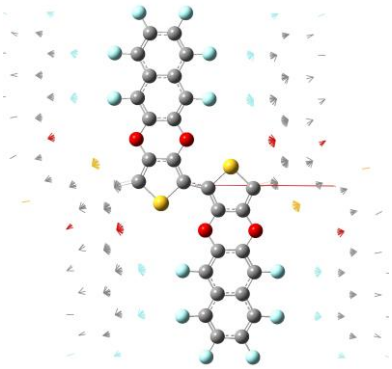
p[4Me-PheDOT]



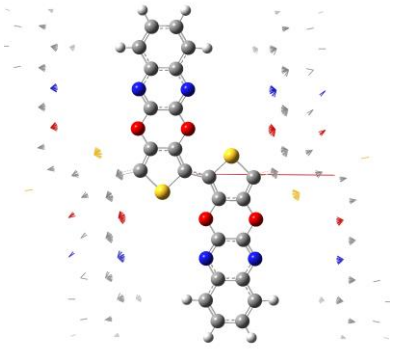
p[PheDOT]



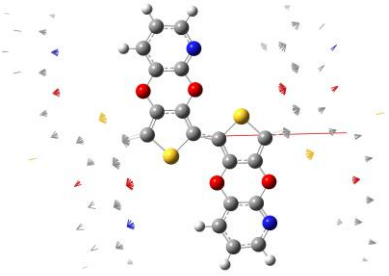
p[NaphDOT(2,3)]



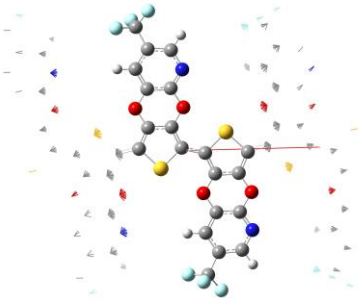
p[F$_6$-NaphDOT(2,3)]



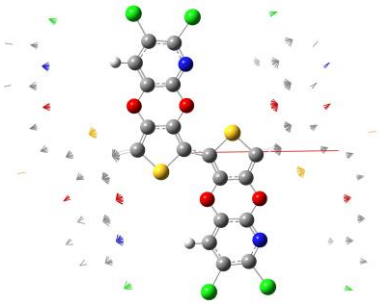
p[QxDOT]



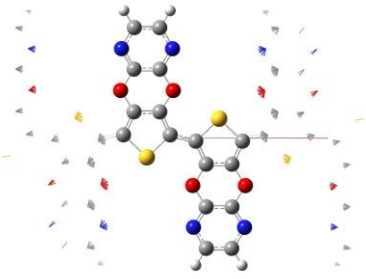
p[PyDOT]



p[5CF$_3$-PyDOT]



p[56Cl$_2$-PyDOT]



p[PzDOT]

Figure S10. Unit cells for the optimized structures of other **p[Ar-DOT]** polymers calculated at PBC/B3LYP/6-31G(d). Replication of the unit cells is shown as shadow atoms/bonds. Absolute energies (per unit cell), HOCO and LUCO energies and the band gaps E_g are given in the Table S7.

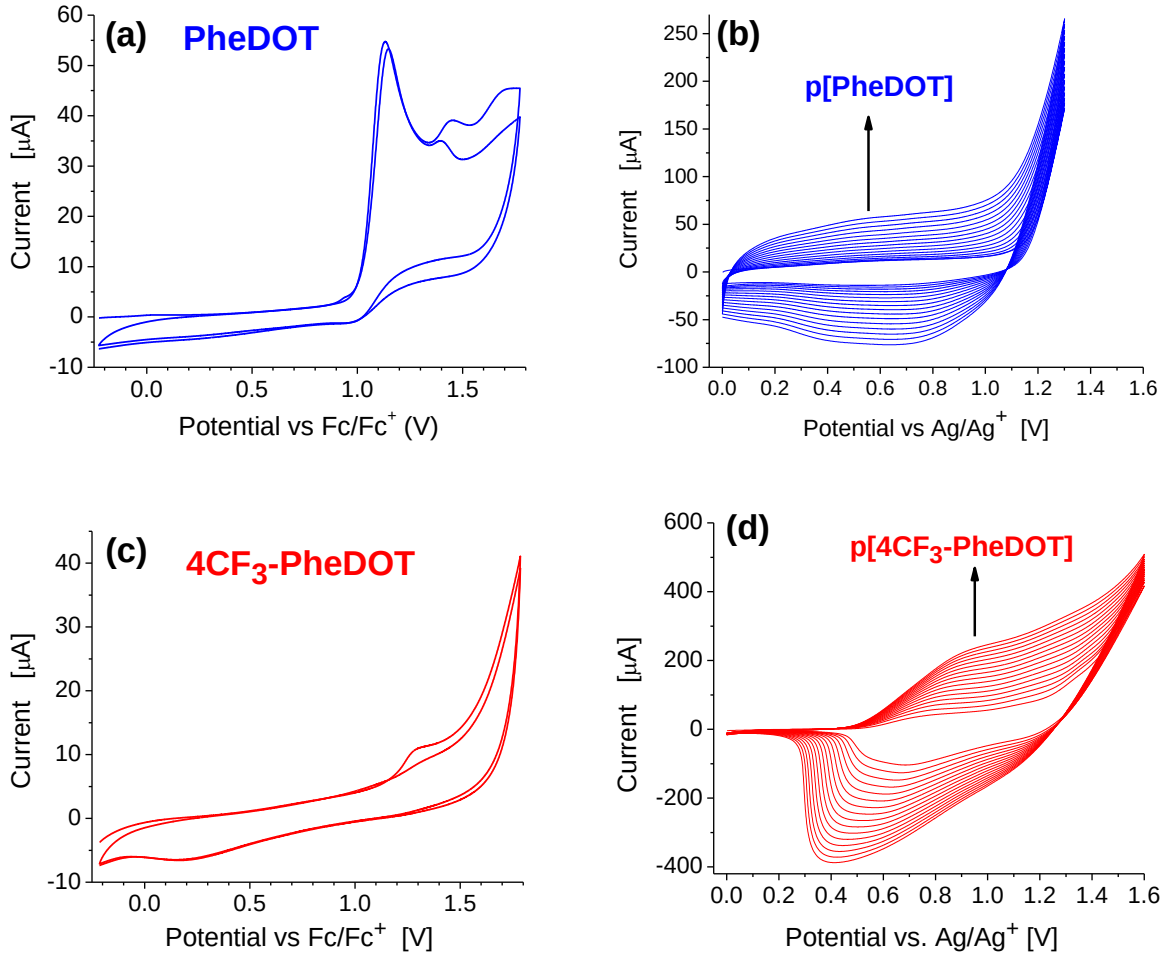


Figure S11. (a,c) Cyclic voltammograms of **PheDOT** and **4CF$_3$-PheDOT** (~1 mM) in dichloromethane, 0.2 M Bu_4NPF_6, scan rate 100 mV/s. (b,d) Potentiodynamic electropolymerization of **PheDOT** and **4CF$_3$-PheDOT** (~100 mM) in dichloromethane, 0.2 M Bu_4NPF_6, scan rate 100 mV/s.

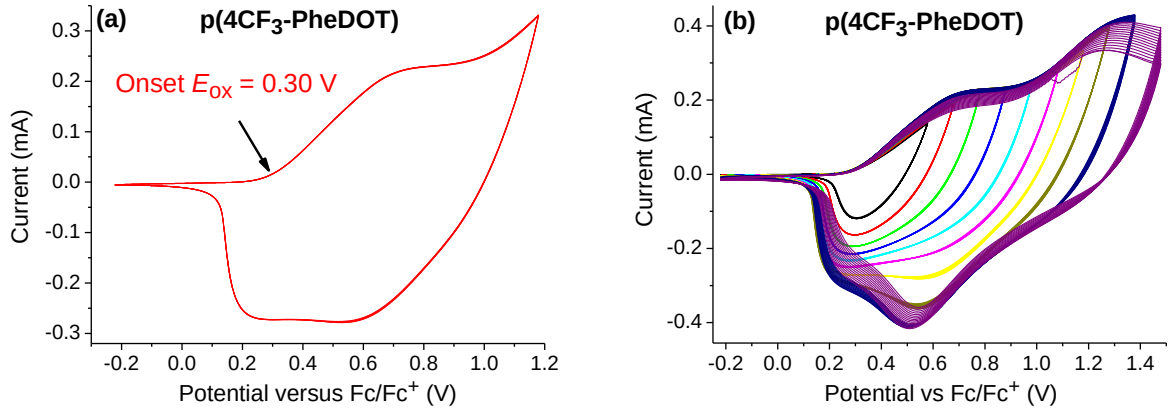


Figure S12. Cyclic voltammograms of **p[4CF$_3$-PheDOT]** films in DCM solution, 0.1 M Bu_4NPF_6, scan rate 100 mV/s. (a) Six consecutive scand on p-doping / dedoping. (b) Recurrent p-doping / dedoping of **p[4CF$_3$-PheDOT]** to different maximal p-doping potentials: the polymer shows good reversibility and stability on cycling up to potentials of ~1.2–1.3 V. Overdoping the films by applying the potentials of >1.4 V leads to some degradation of the polymer films.

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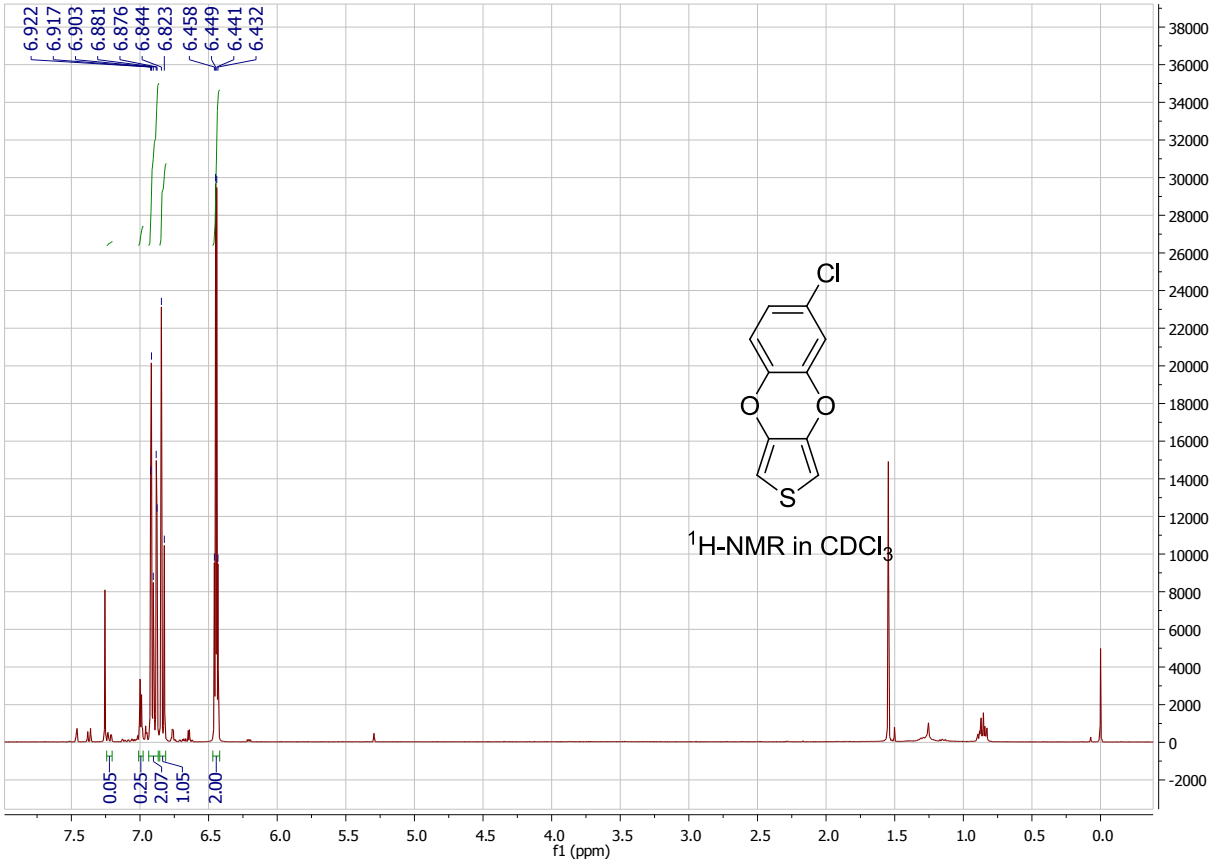
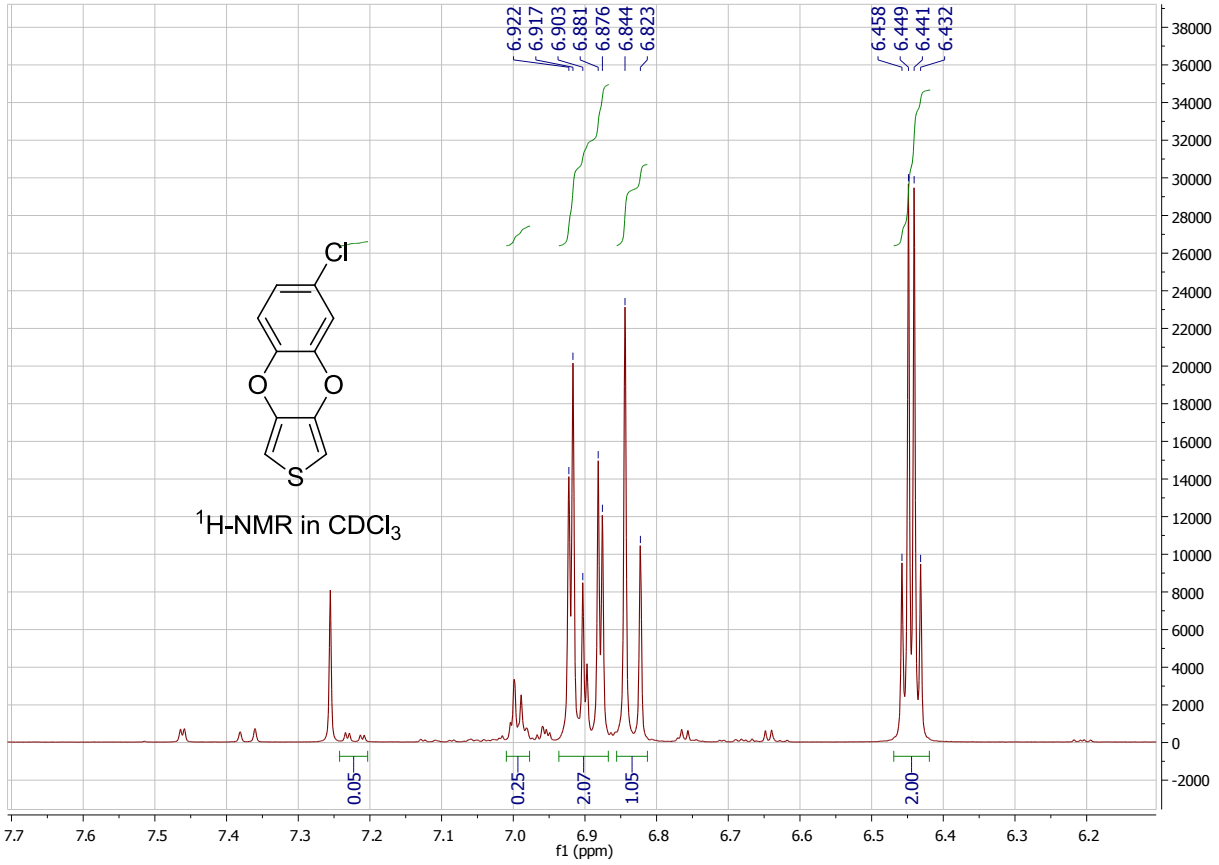
11 We have isolated an intermediate **F_4-23** when the reaction was performed at higher temperature of 140–160 °C (see below).

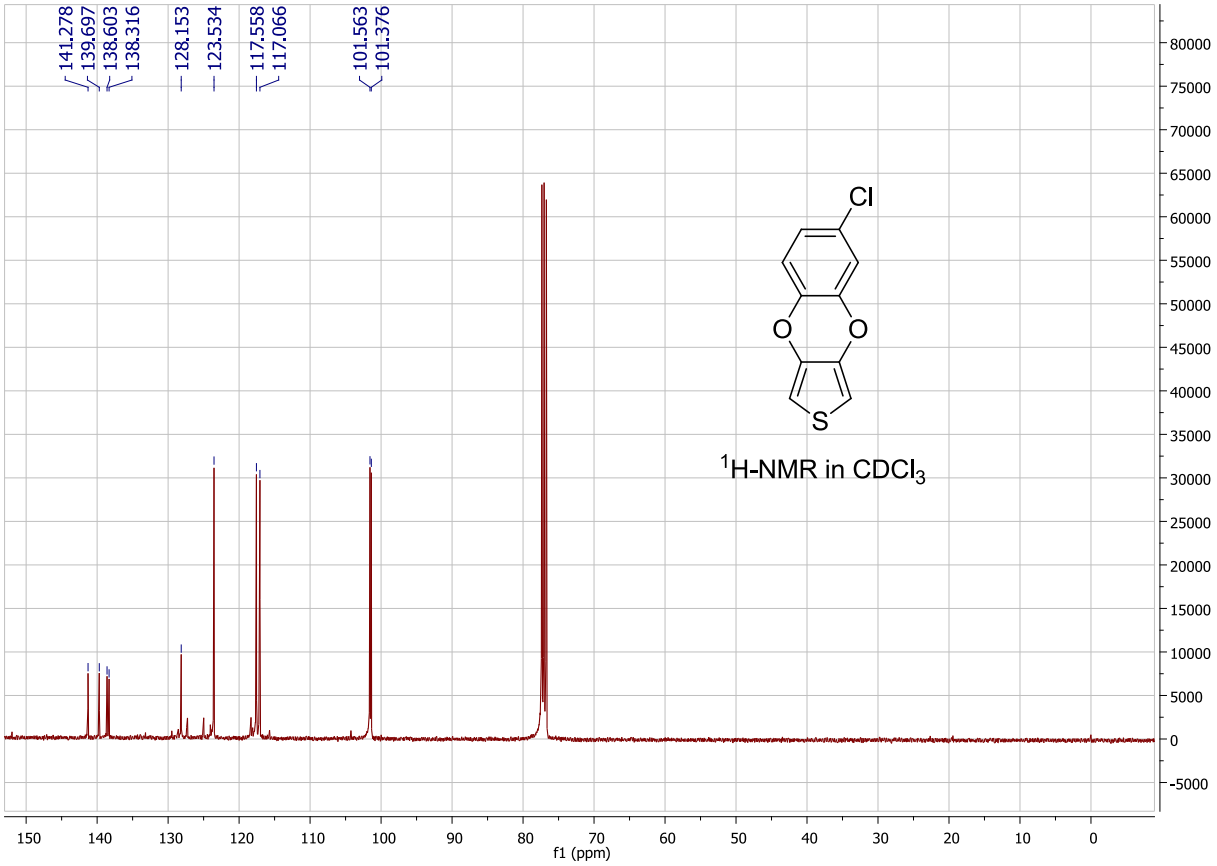
12 Easier decarboxyethylation of the first CO_2Et group in the intermediate **22** (without EWG) was observed before [Ref. 9 above]: in conventional heating reaction of thiophene **1** with o-chloronitrobenzene (**2**) at 100 °C, a mixture of mono- and disubstituted thiophenes (**22** and **23**) were formed. An absence of such products in the reaction with hexafluorobenzene (**15**) (Table S2, entries 1, 2) is indicative of its substantially lower reactivity in S_NAr reaction.

13 **45Br_2-PheDOT** and **45Cl_2-PheDOT** were synthesized by reflux of 4,5-dibromocatechol or 4,5-dibromocatechol with 3,4-dimethoxythiophene in benzene or toluene in the presence of *p*-toluenesulfonic acid, similarly to unsubstituted **PheDOT** (Ref. 6a, 9) and isolated with low yields of 1.3 and 5%, respectively (M. P. Krompiec, S. N. Baxter and I. F. Perepichka, unpublished results).

6-Chlorobenzo[b]thieno[3,4-e][1,4]dioxine (**4Cl-PheDOT**)



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O
S
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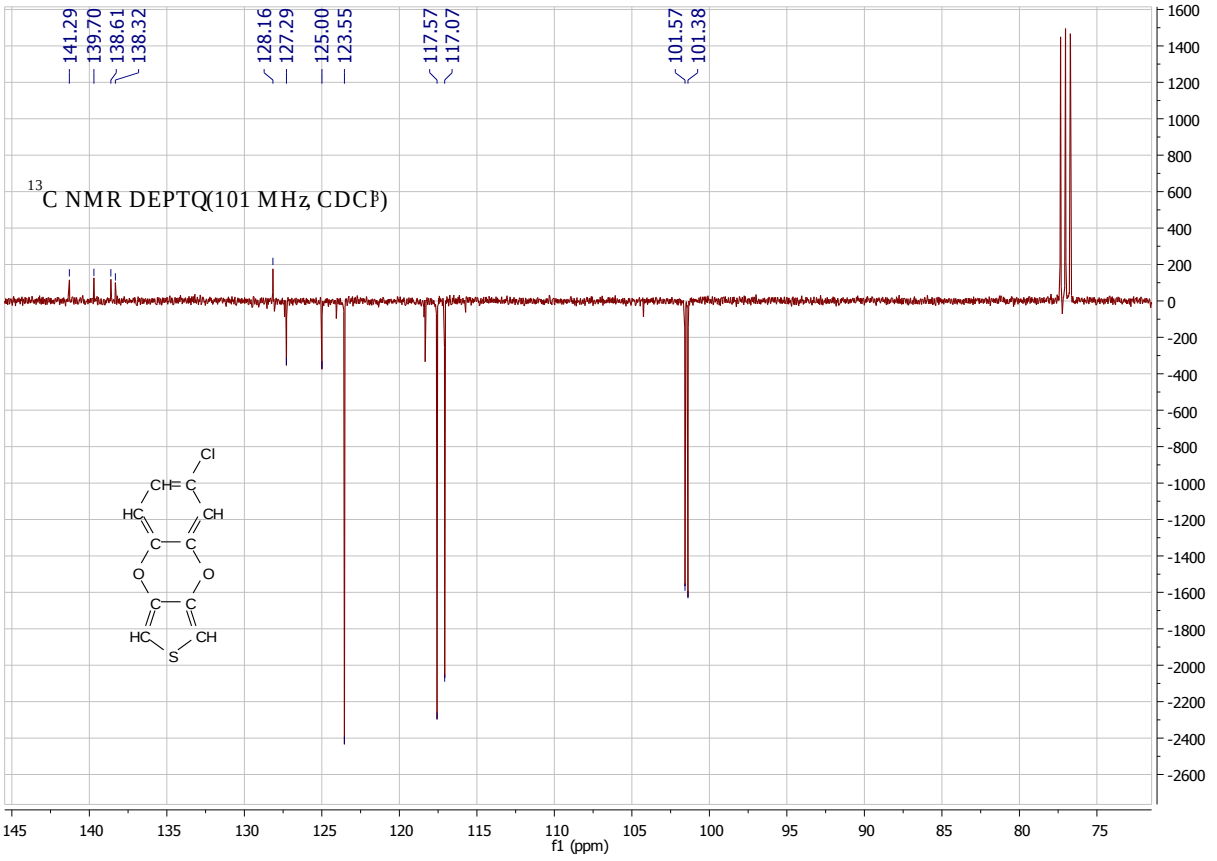
f1 (ppm)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HC
CH
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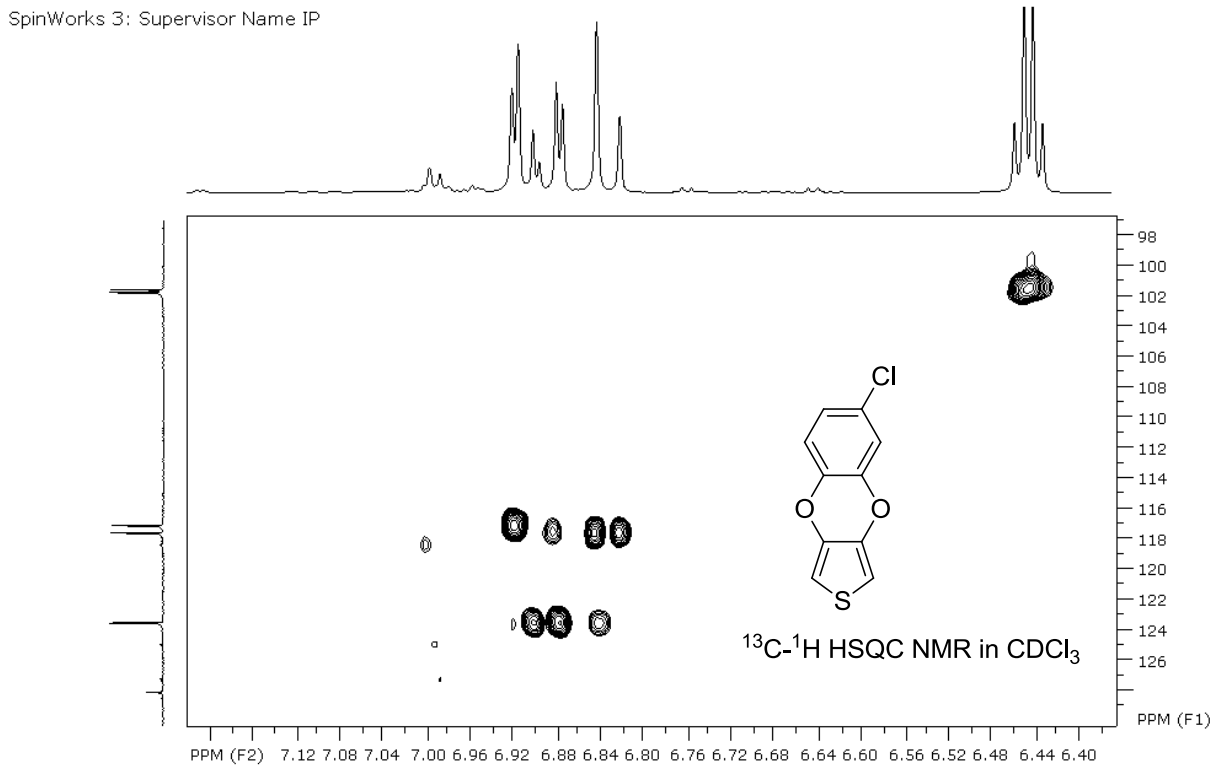
C
O
O
C
C
HC
CH
S
f1 (ppm)



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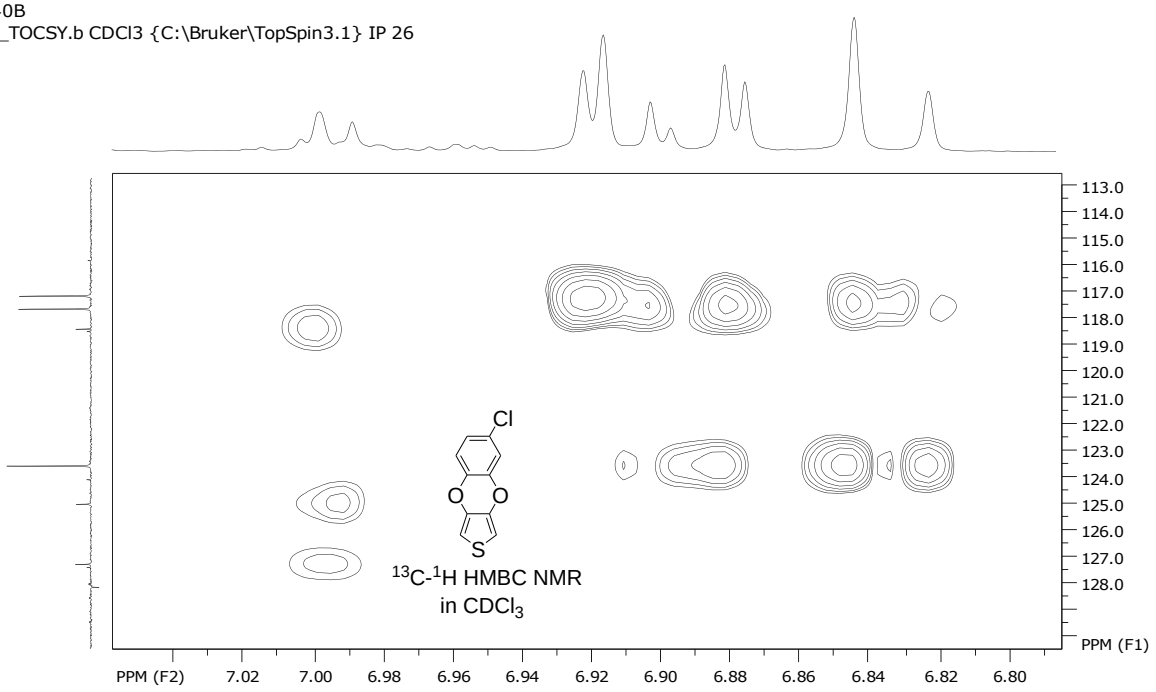

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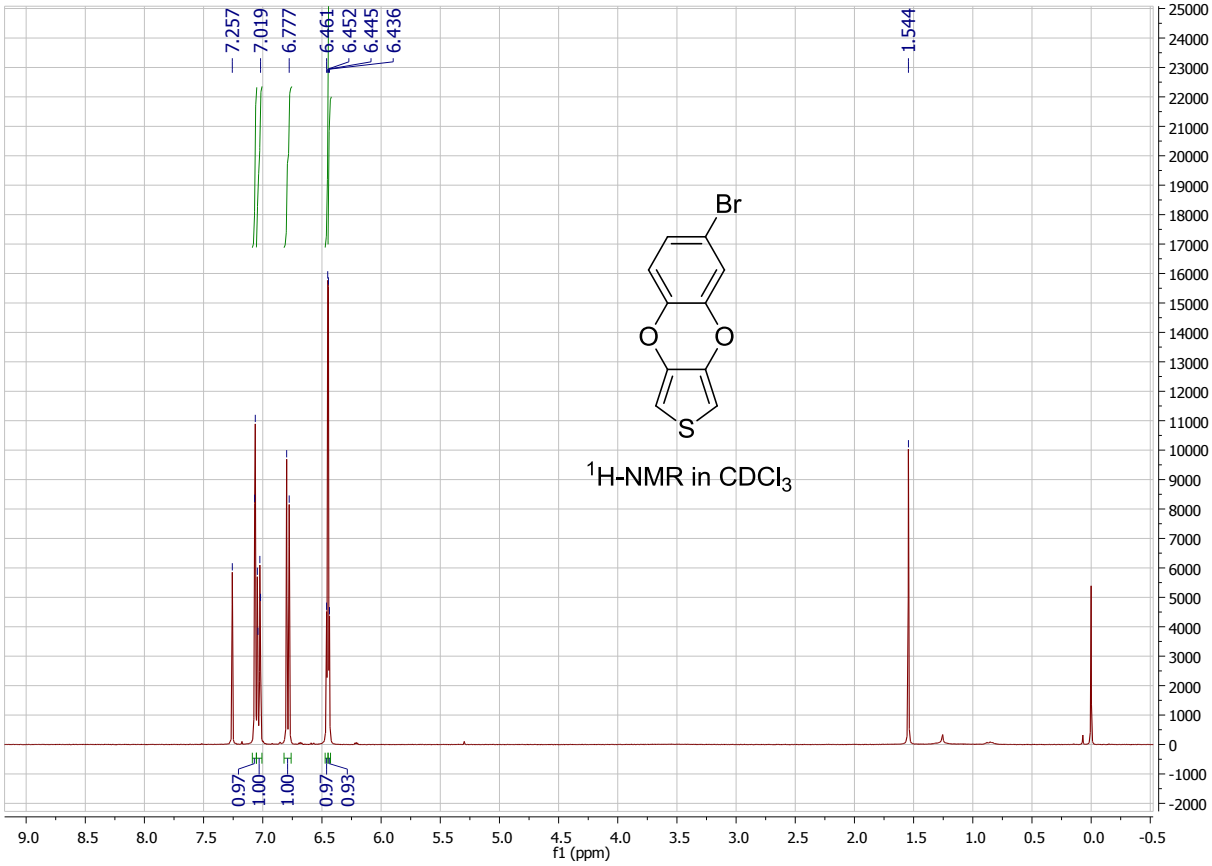
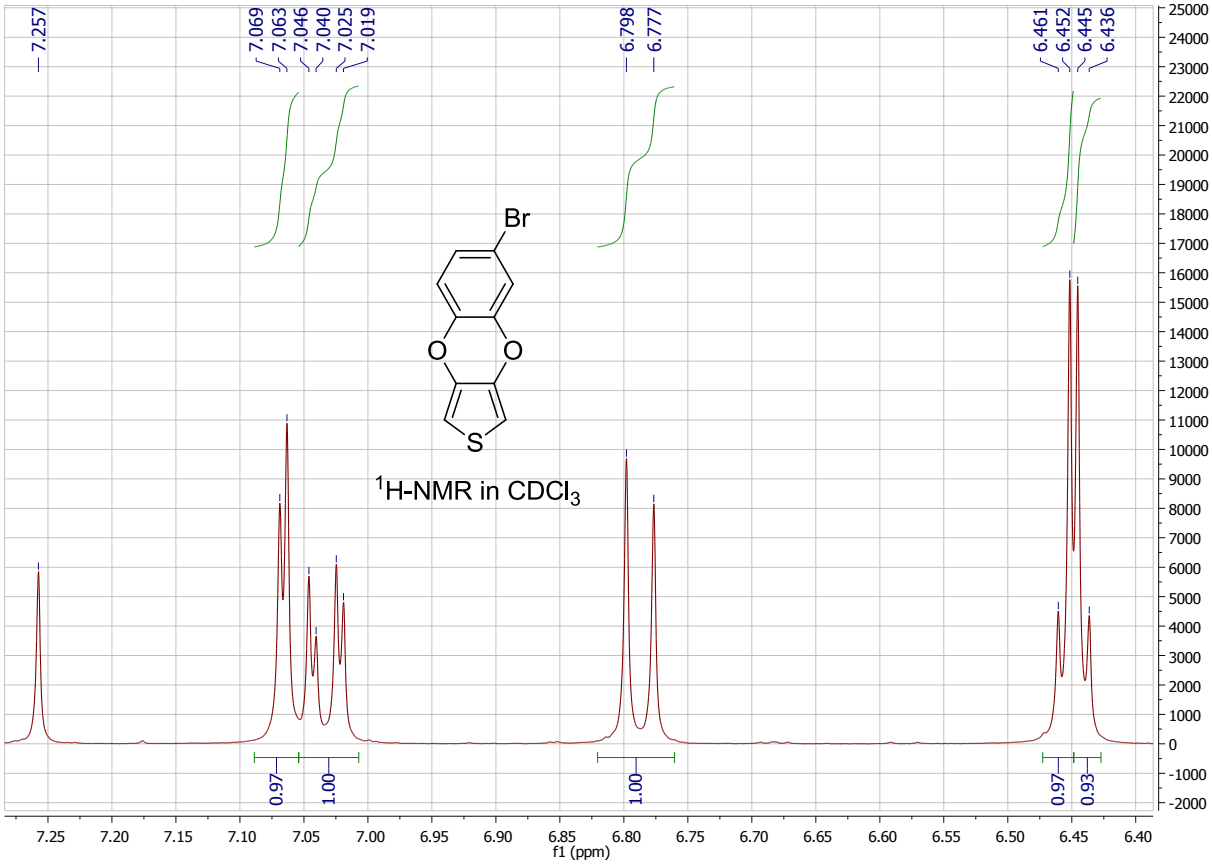
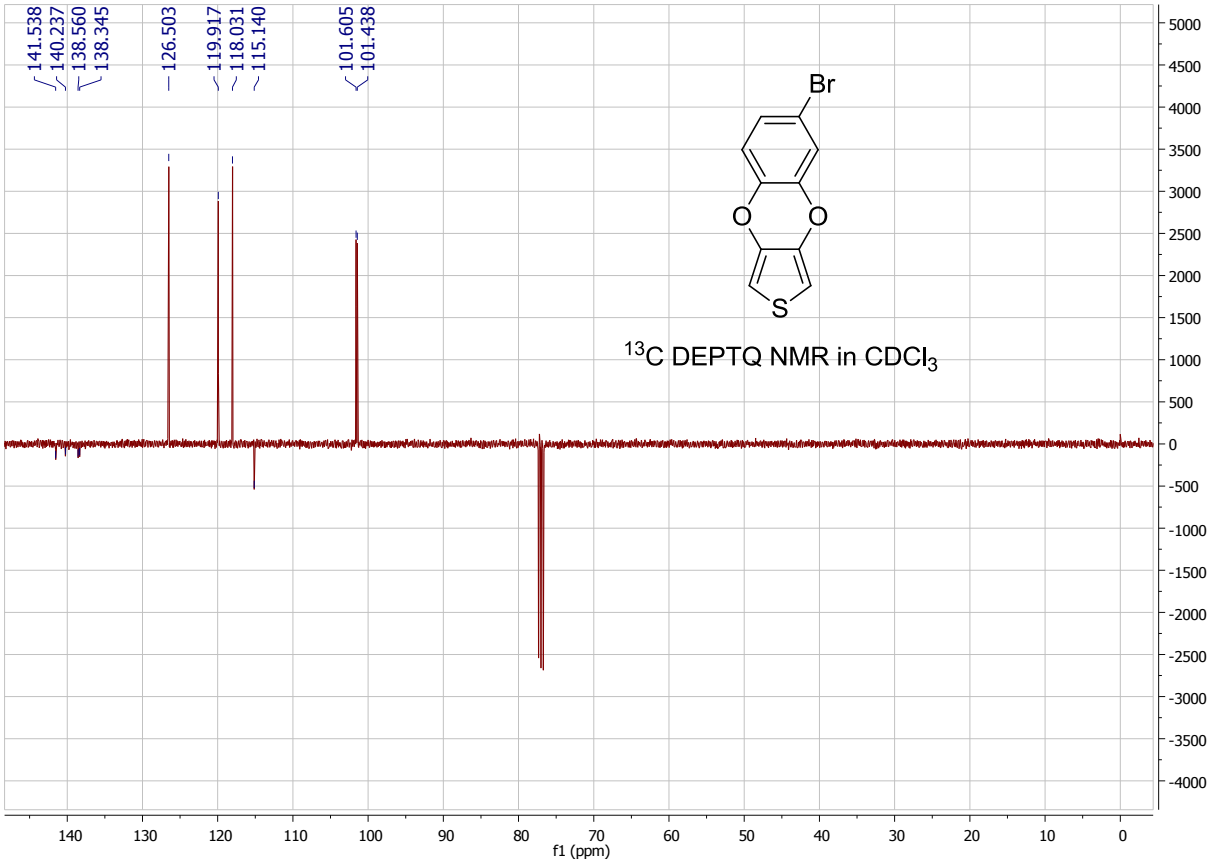
6-Bromobenzo[b]thieno[3,4-e][1,4]dioxine (**4Br-PheDOT**)



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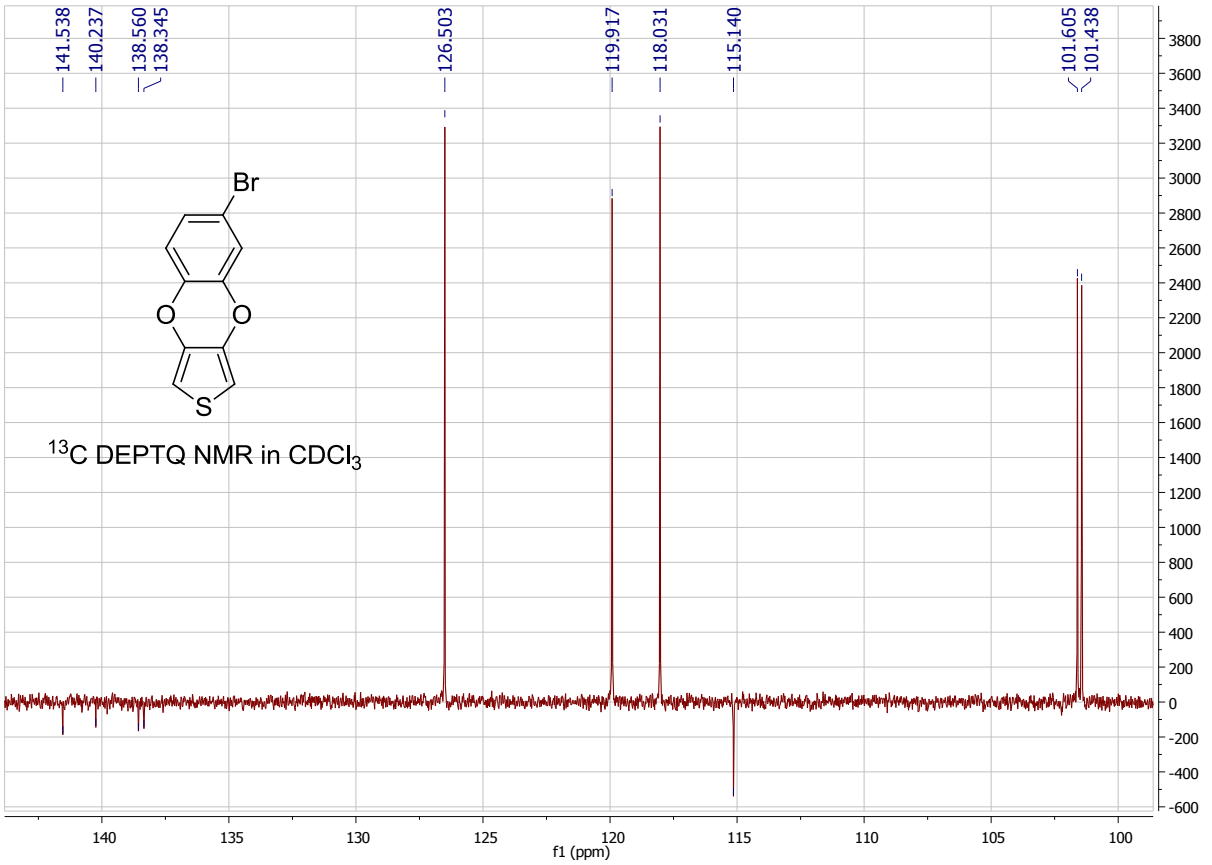
O
O
S
13C DEPTQ NMR in CDCl3
f1 (ppm)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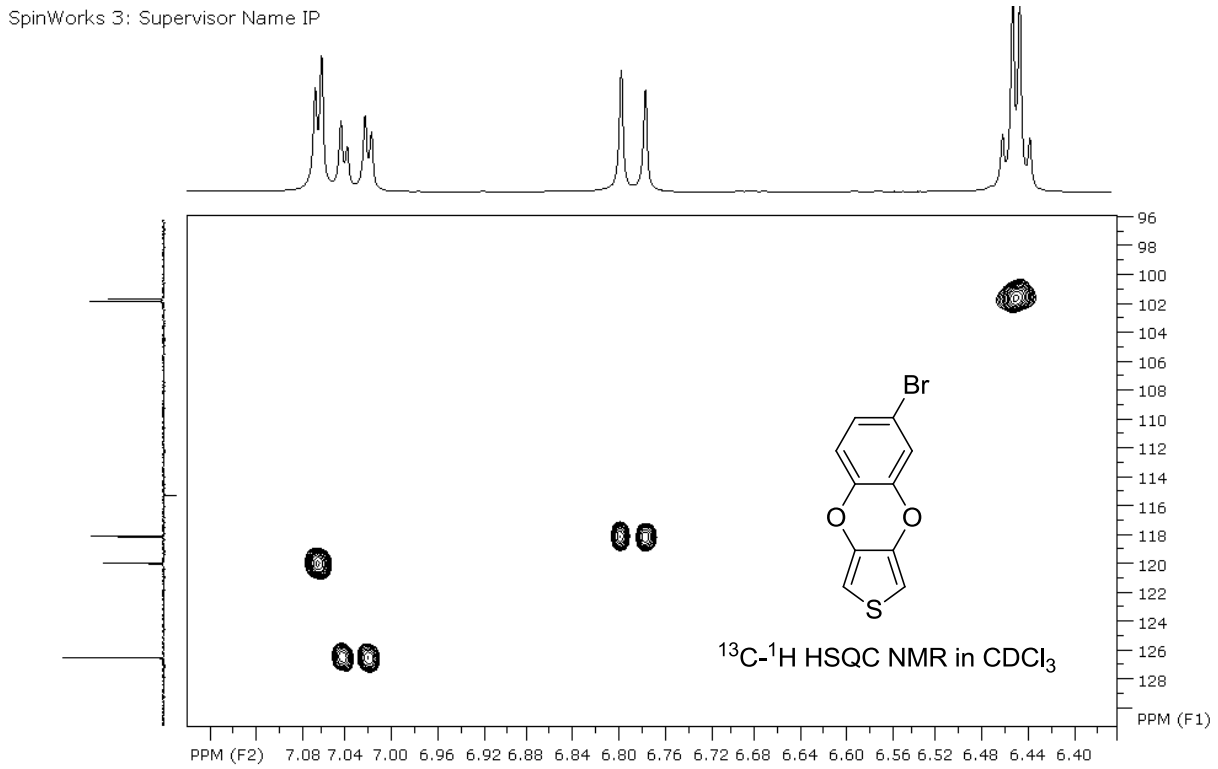

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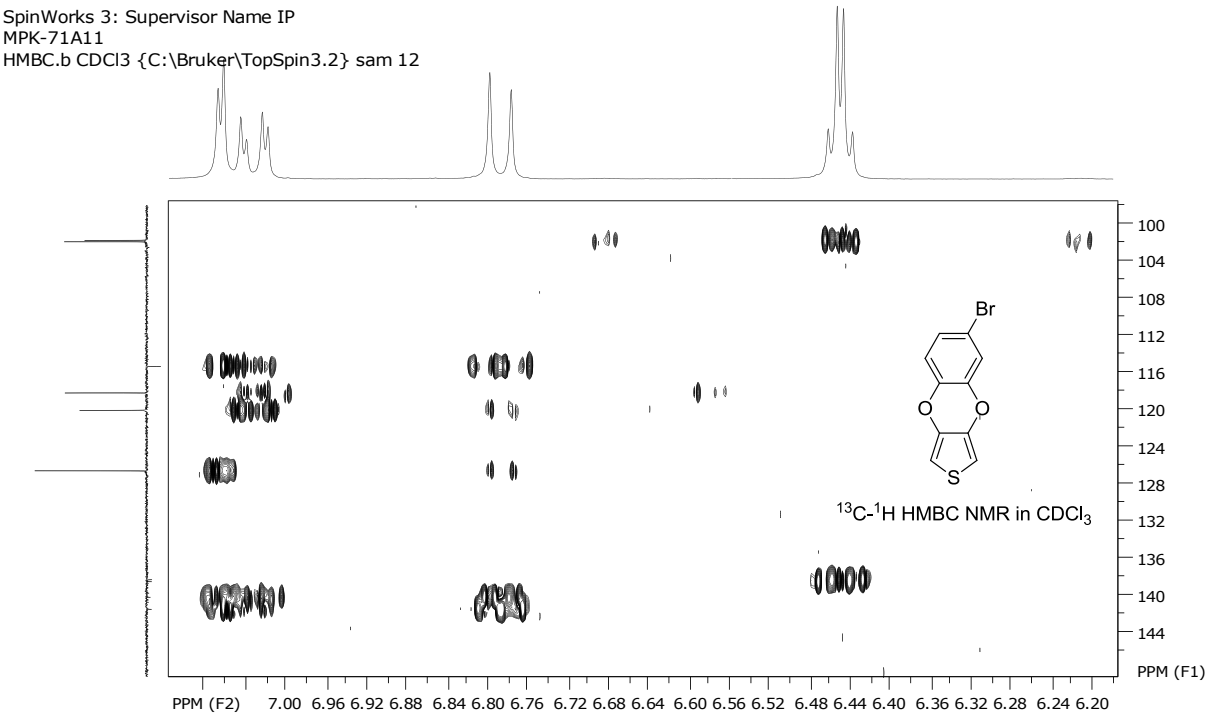

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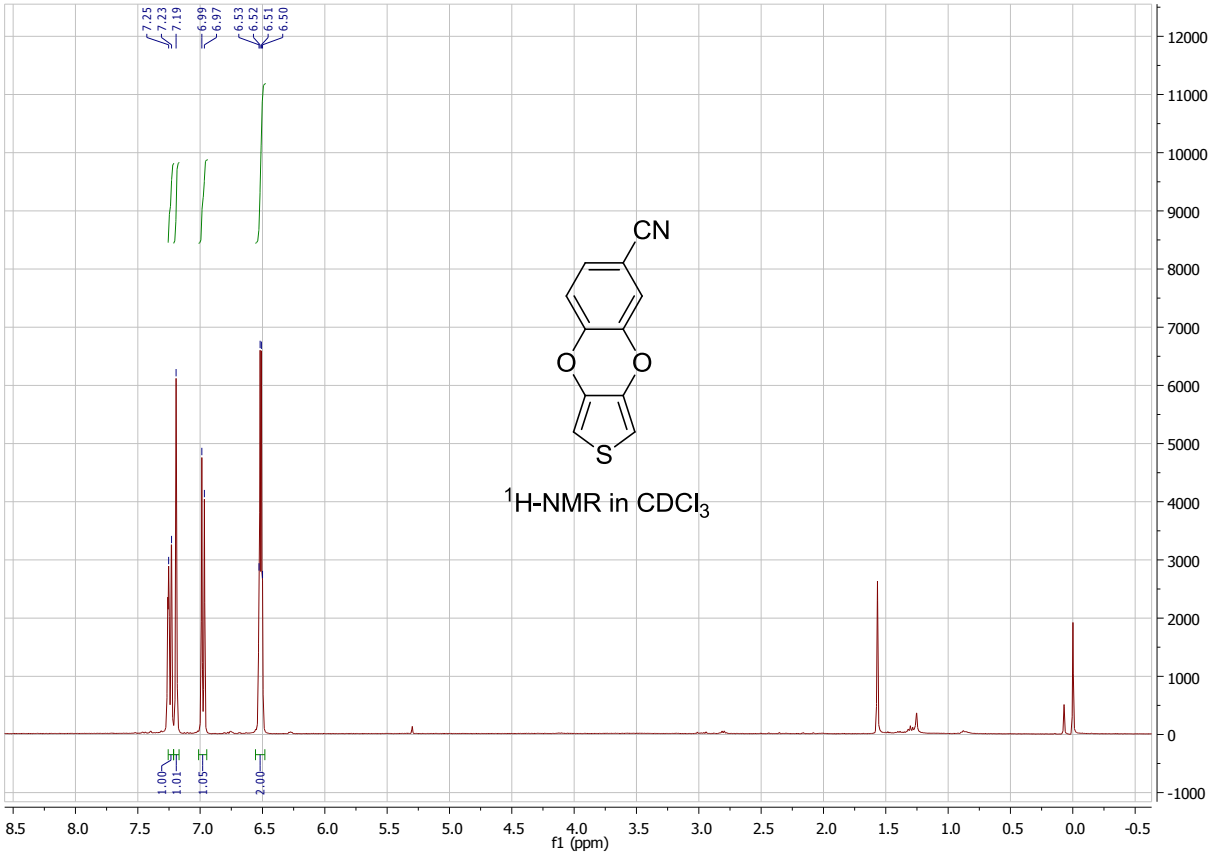
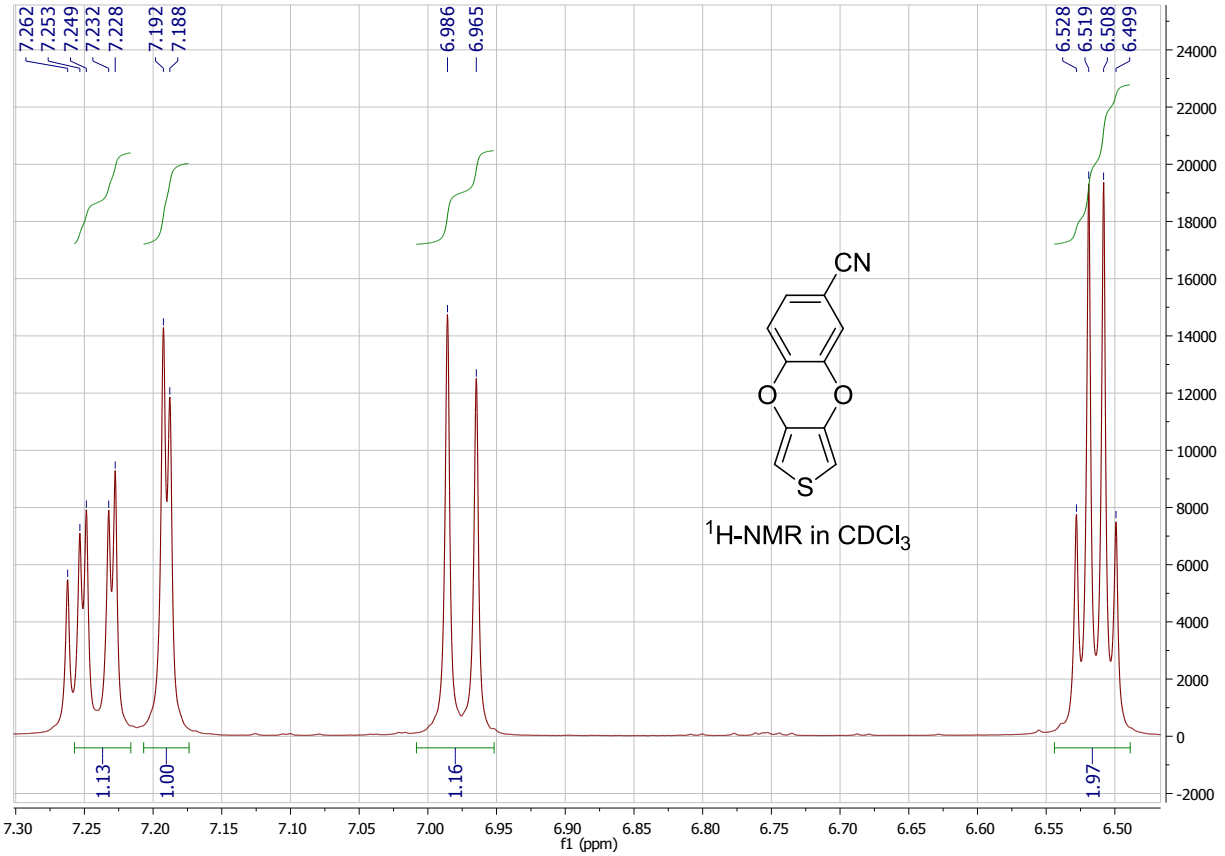
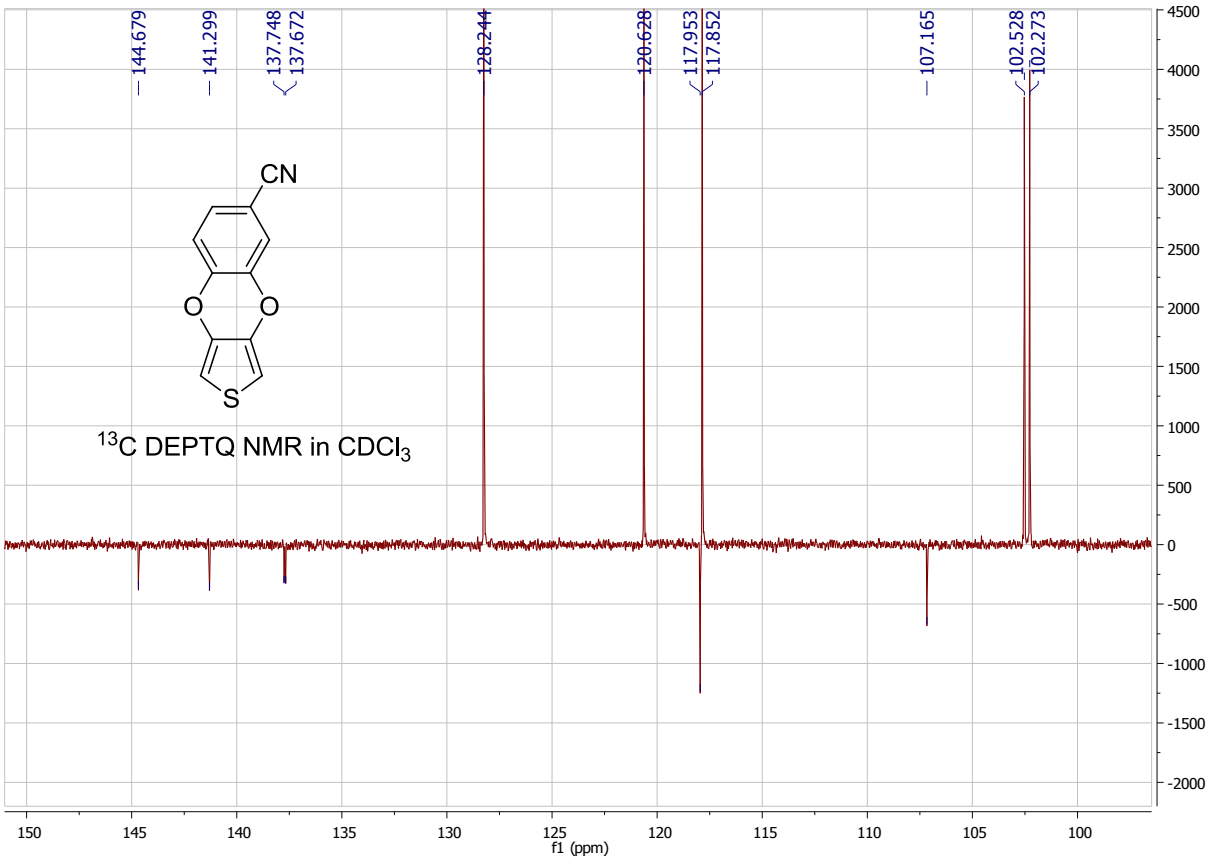
Benzo[b]thieno[3,4-e][1,4]dioxine-6-carbonitrile (**4CN-PheDOT**)



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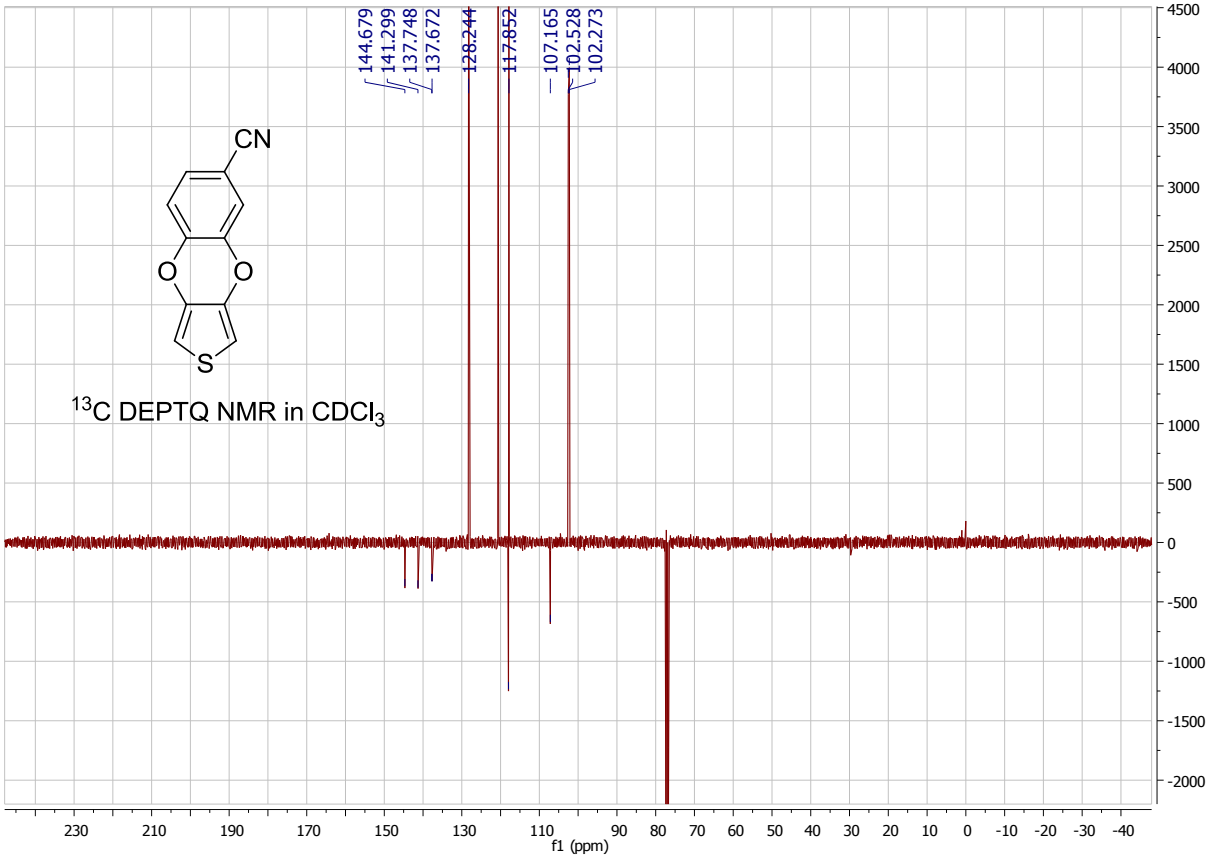
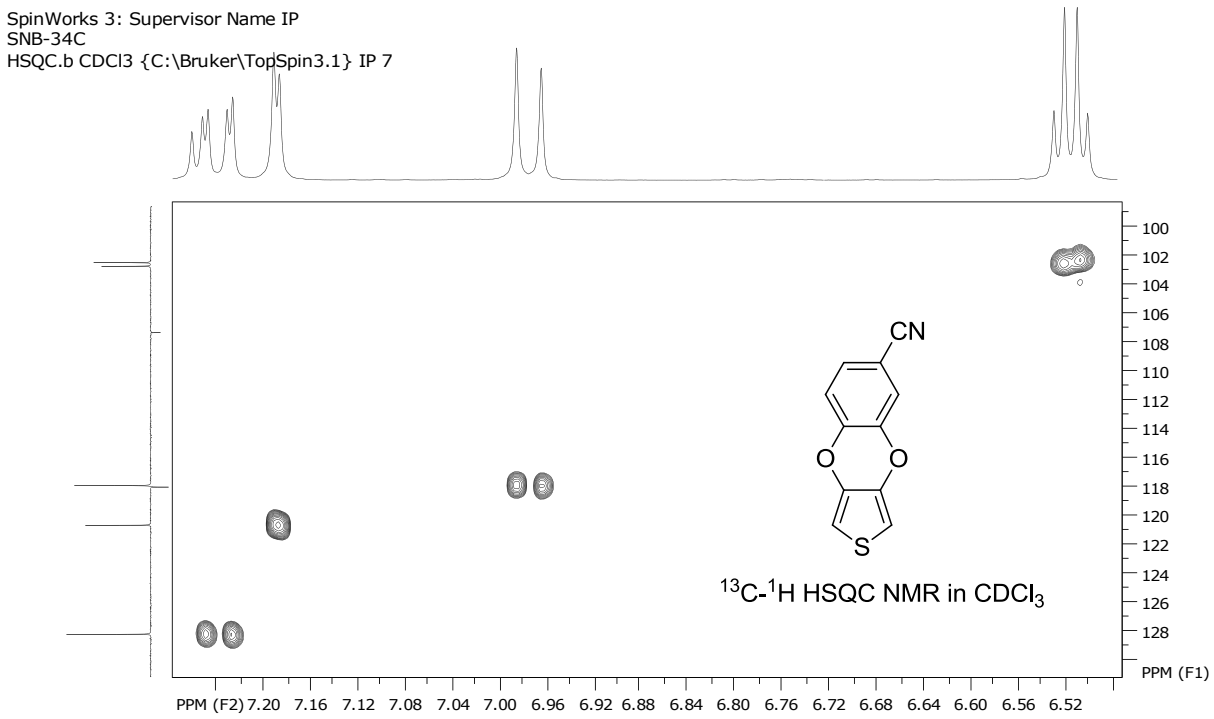
O
S
13C DEPTQ NMR in CDCl3
f1 (ppm)


144.679
141.299
137.748
137.672
128.244
117.852
107.165
102.528
102.273
CN
O
O
S
13C DEPTQ NMR in CDCl3
f1 (ppm)

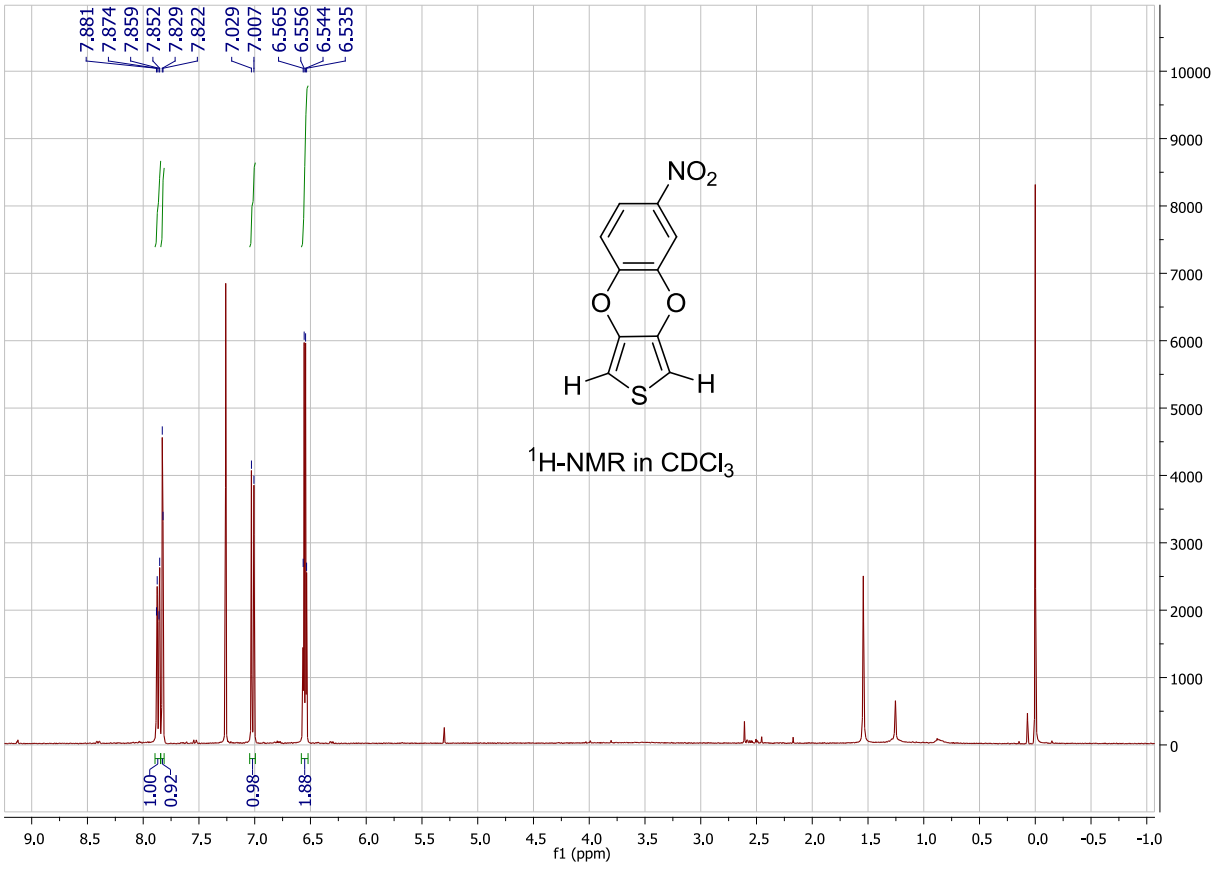


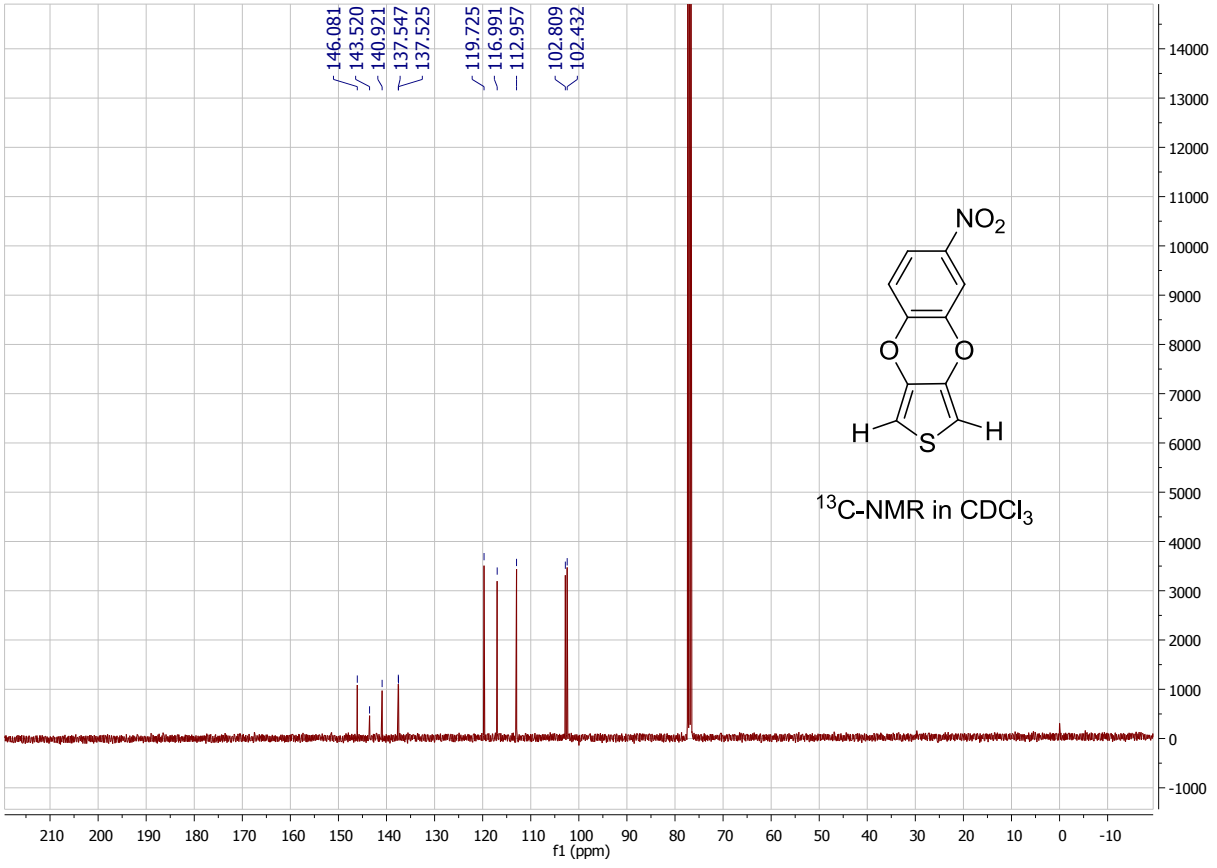
file: ...ated\SNB-34C\53-SNB-34C-HSQC.b\ser
expt: <hsqcedetgpsisp2.3>
transmitter freq: 400.131656 MHz
time domain size: 2048 by 256 points
width (F2): 2994.01 Hz = 7.4826 ppm = 1.4619 Hz/pt
number of scans: 2

F2: freq. of 0 ppm: 400.1300088 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 14.649 ppm/cm: 0.03661

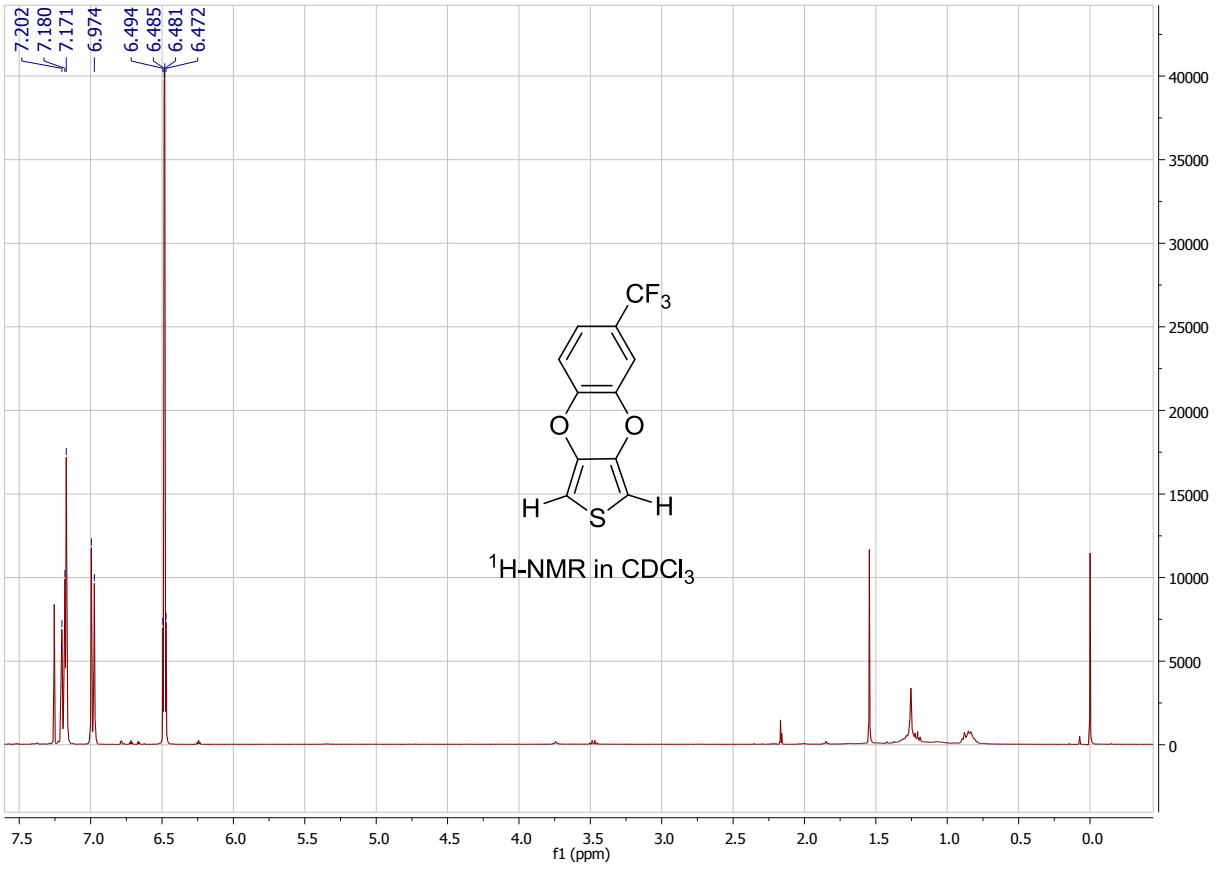
F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 301.160 ppm/cm: 2.99305

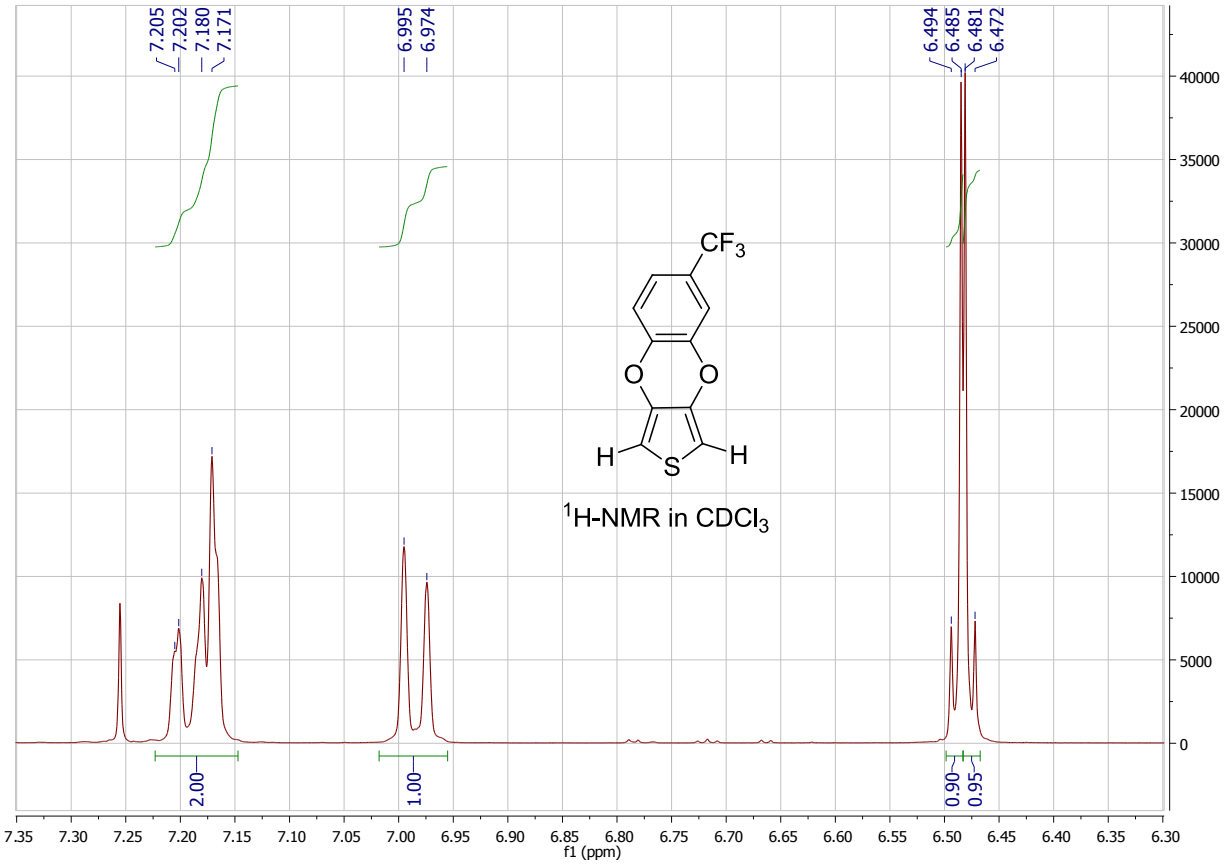
6-Nitrobenzo[b]thieno[3,4-e][1,4]dioxine (**4NO$_2$-PheDOT**)

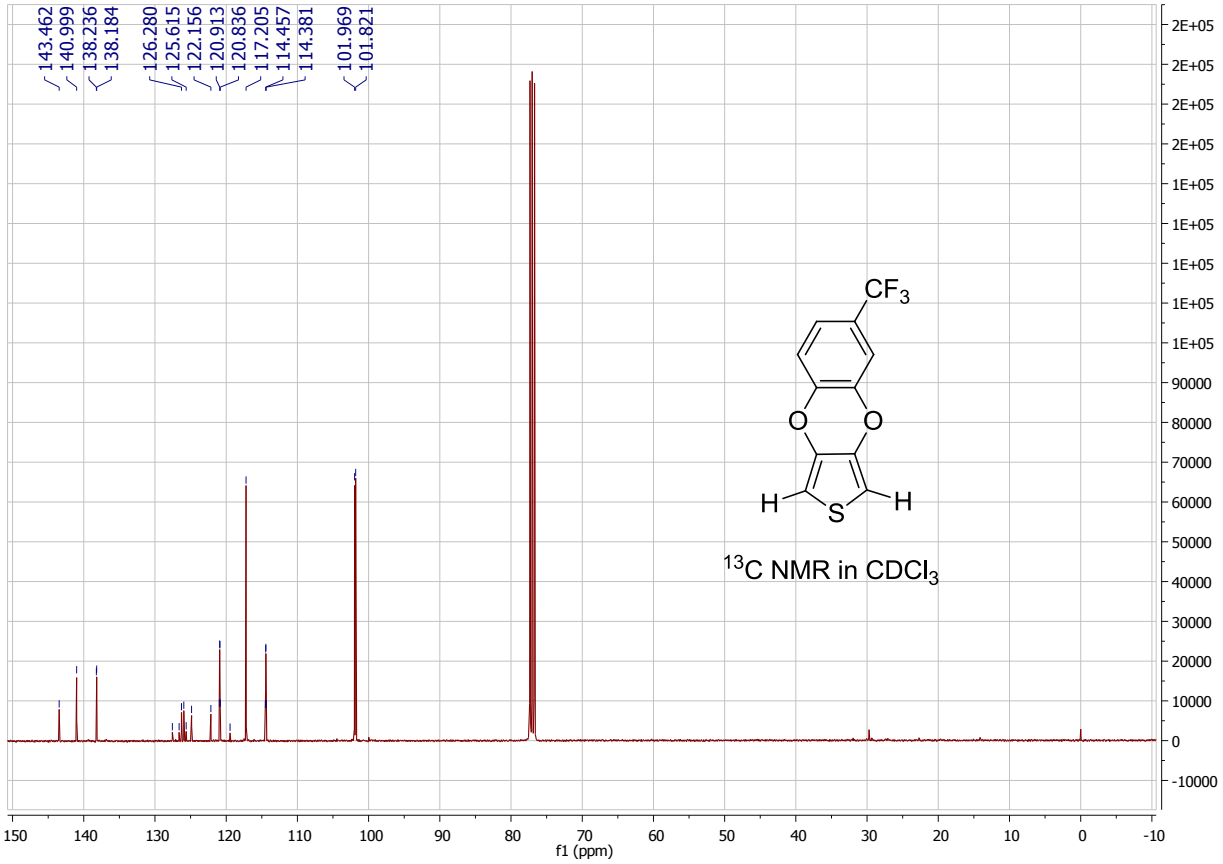


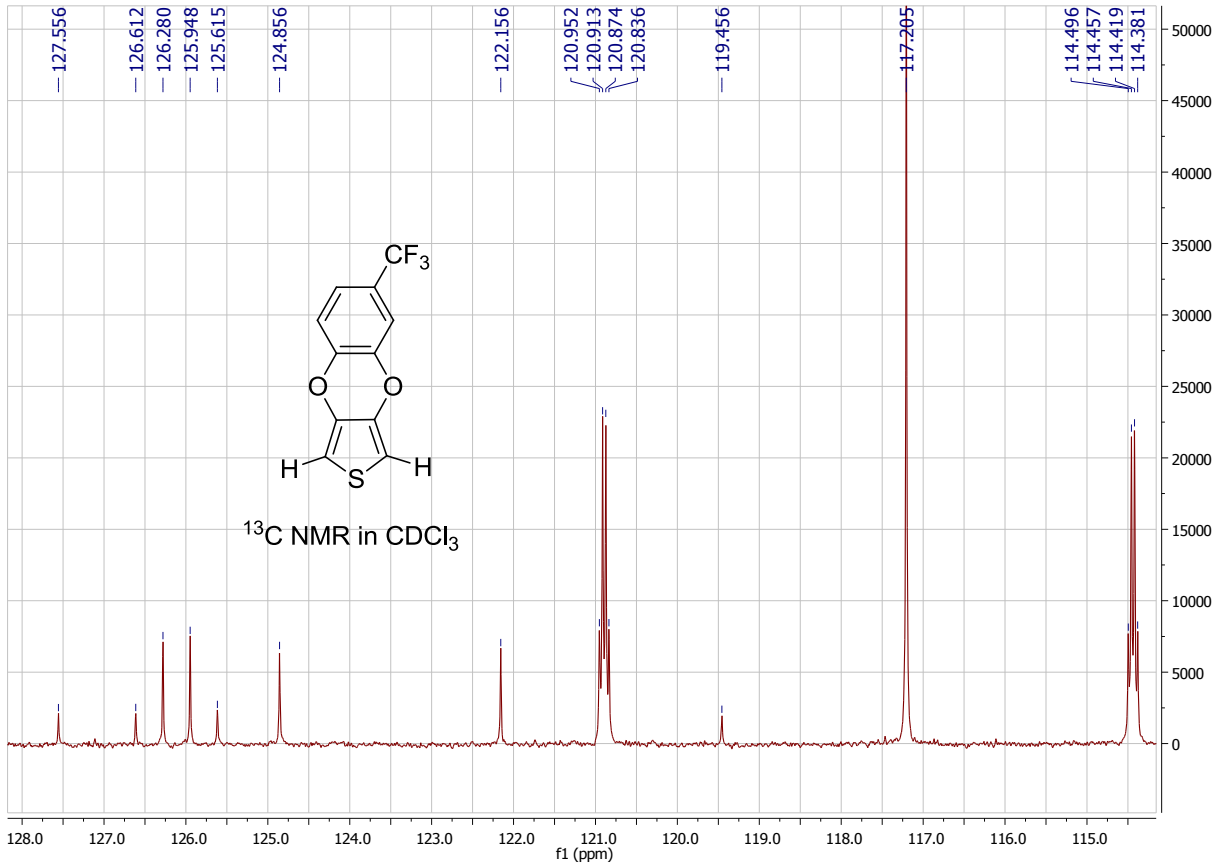


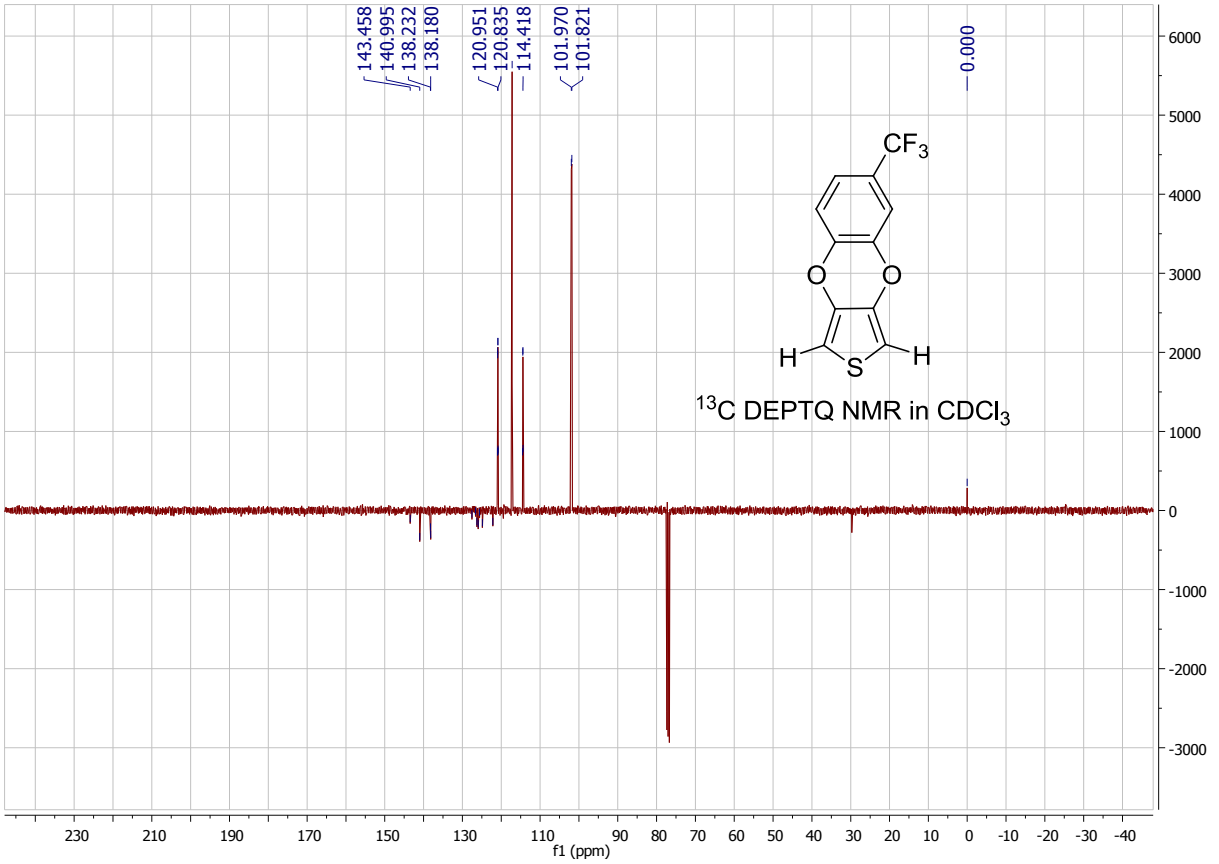
6-(Trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine (**4CF$_3$-PheDOT**)

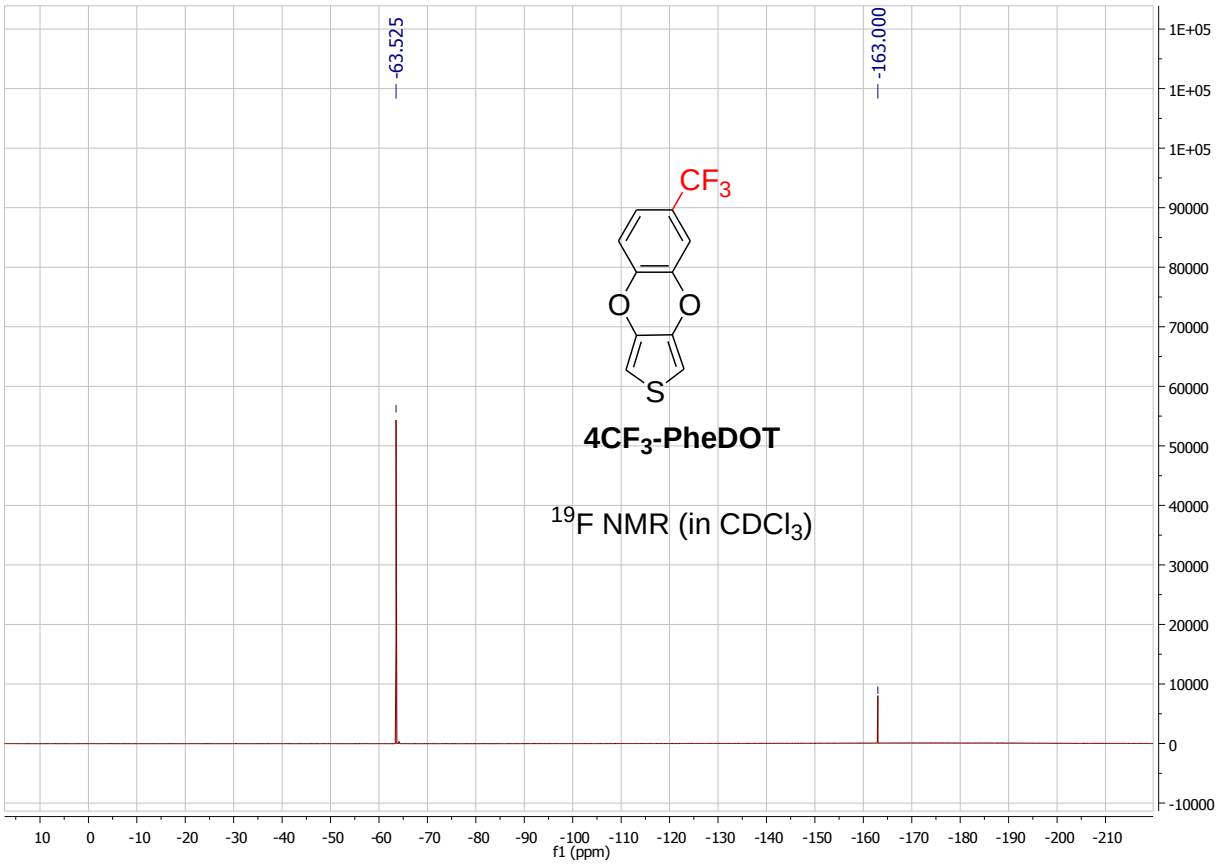




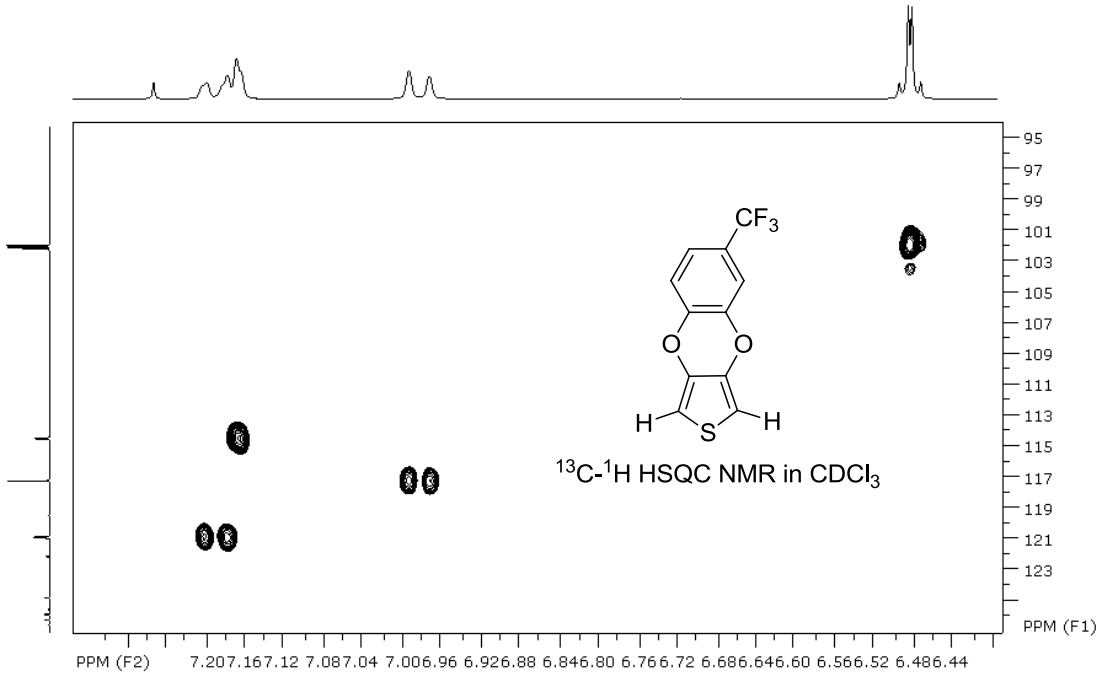

143.462
140.999
138.236
138.184
126.280
125.615
122.156
120.913
120.836
117.205
114.457
114.381
101.969
101.821
CF3
O
O
H
S
H
13C NMR in CDCl3
f1 (ppm)


127.556
126.612
126.280
125.948
125.615
124.856
122.156
120.952
120.913
120.874
120.836
119.456
117.205
114.496
114.457
114.419
114.381
CF3
O
O
H
S
H
13C NMR in CDCl3
f1 (ppm)


143.458
140.995
138.232
138.180
120.951
120.835
114.418
101.970
101.821
0.000
CF3
O
O
H
S
H
13C DEPTQ NMR in CDCl3
f1 (ppm)


-63.525
-163.000
CF3
O
O
S
4CF3-PheDOT
19F NMR (in CDCl3)
f1 (ppm)

SpinWorks 3: Supervisor Name IP

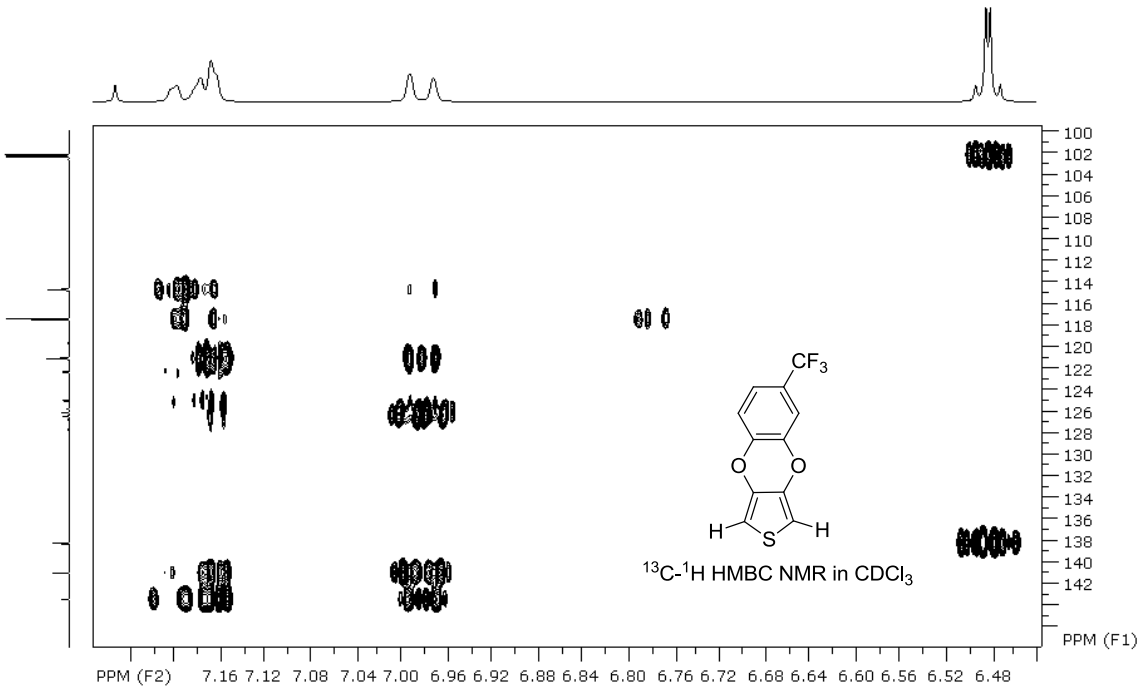


file: ...eated\snb38B\11-SNB-38B-HSQC.b\ser
expt: <hsqcedetgpsisp2.3>
transmitterfreq: 400.131644 MHz
time domain size: 2048 by 256 points
width (F2): 3012.05 Hz = 7.5276 ppm = 1.4707 Hz/pt
number of scans: 2

F2: freq. of 0 ppm: 400.1300117 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 18.913 ppm/cm: 0.04727

F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 303.030 ppm/cm: 3.01164

SpinWorks 3: Supervisor Name IP

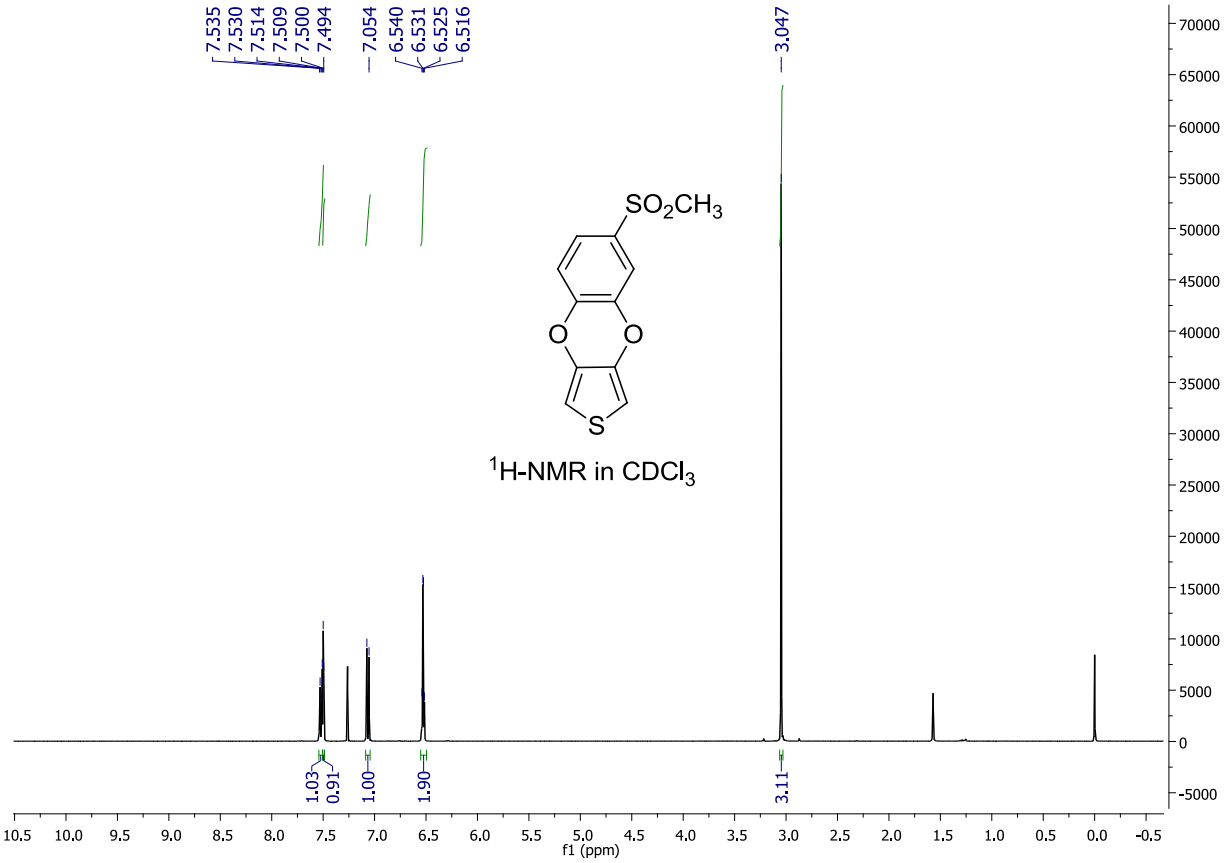


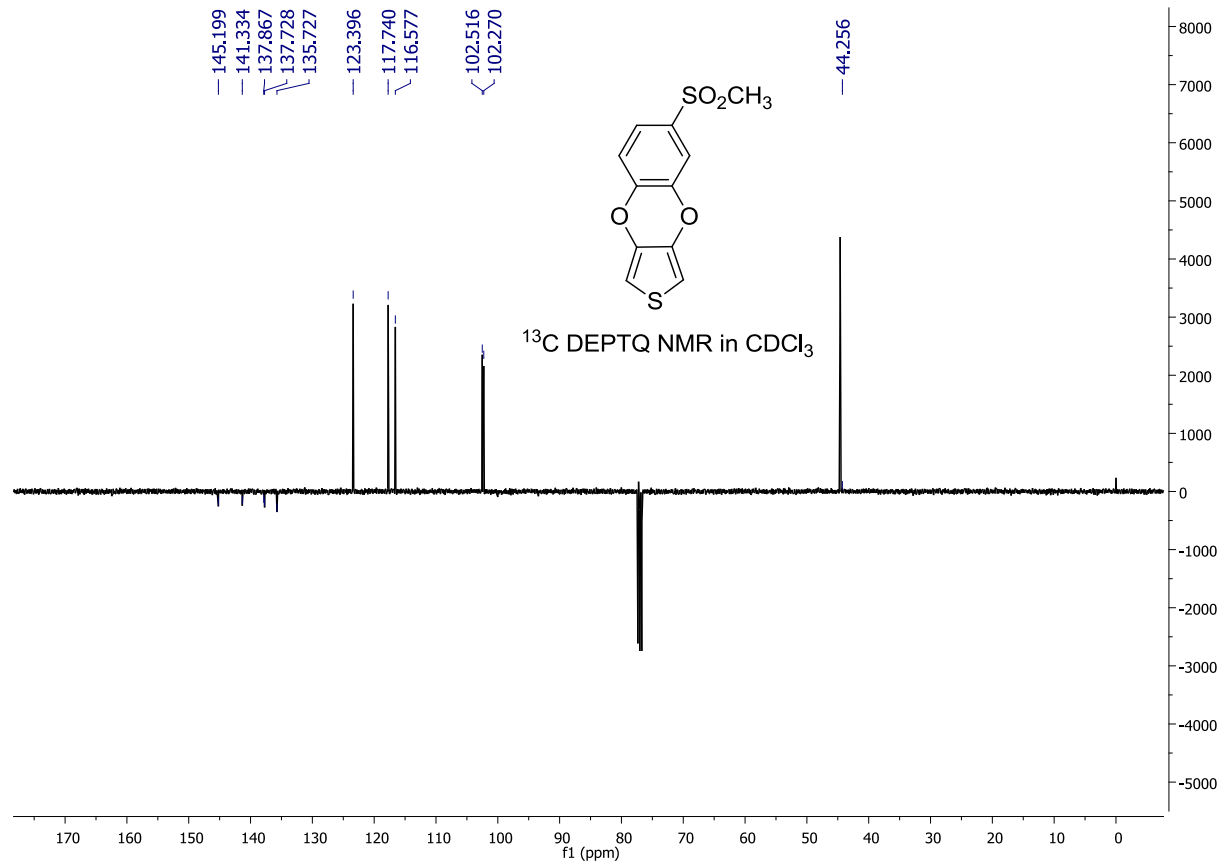
file: ...eated\snb38B\12-SNB-38B-HMBC.b\ser
expt: <hmbcetgpl3nd>
transmitterfreq: 400.131644 MHz
time domain size: 4096 by 256 points
width (F2): 3012.05 Hz = 7.5276 ppm = 0.7354 Hz/pt
number of scans: 4

F2: freq. of 0 ppm: 400.1300117 MHz
processed size: 2048 complex points
window function: Sine
shift: 45.0 degrees
Hz/cm: 16.726 ppm/cm: 0.04180

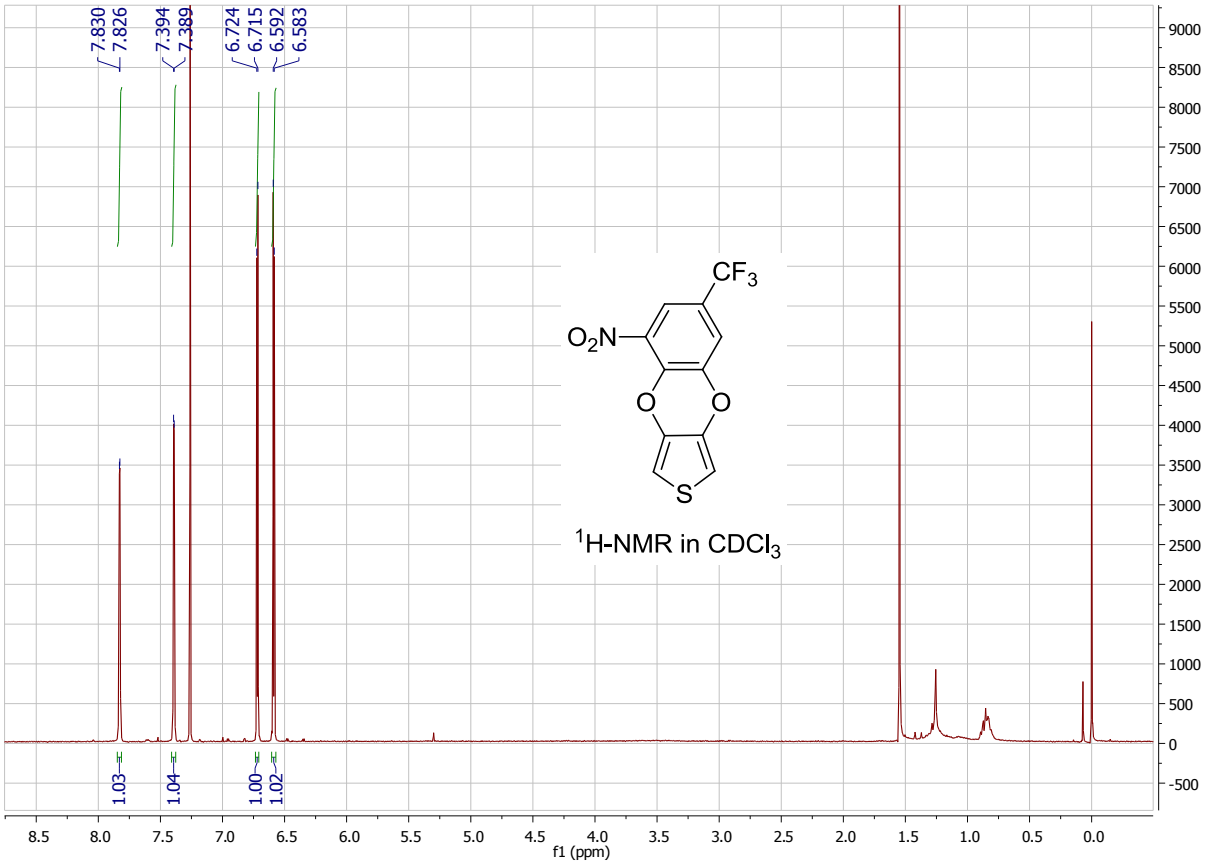
F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 442.769 ppm/cm: 4.40029

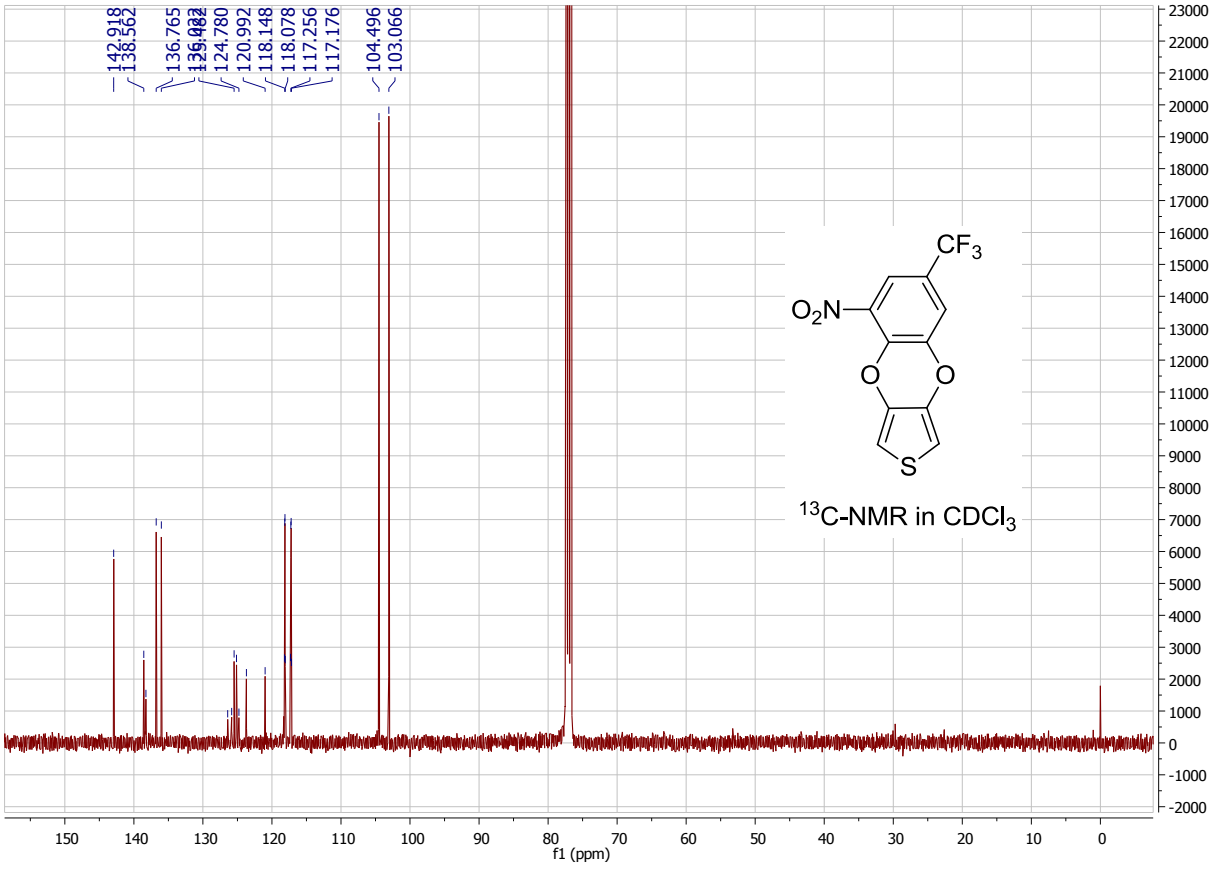
6-(Methylsulfonyl)benzo[b]thieno[3,4-e][1,4]dioxine **(4MeSO$_2$-PheDOT)**

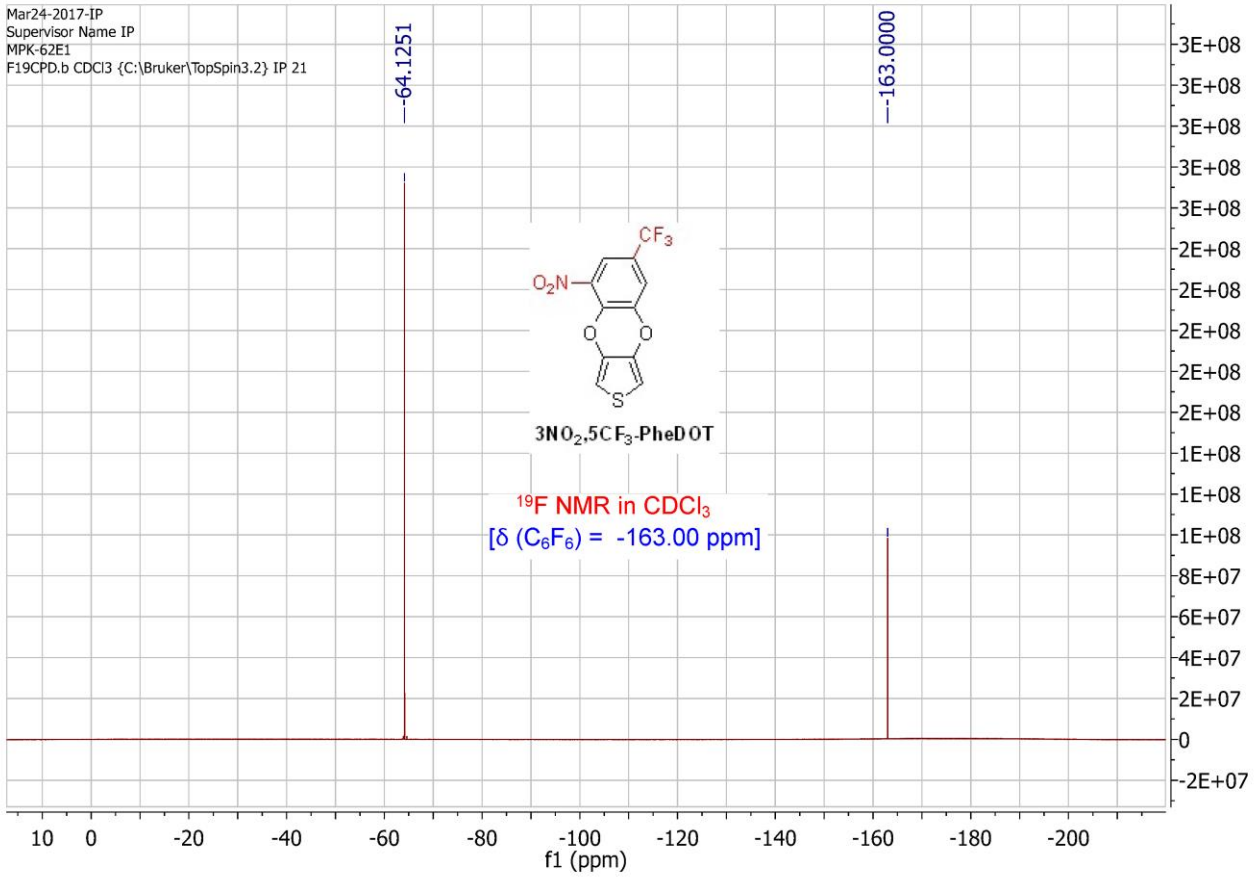




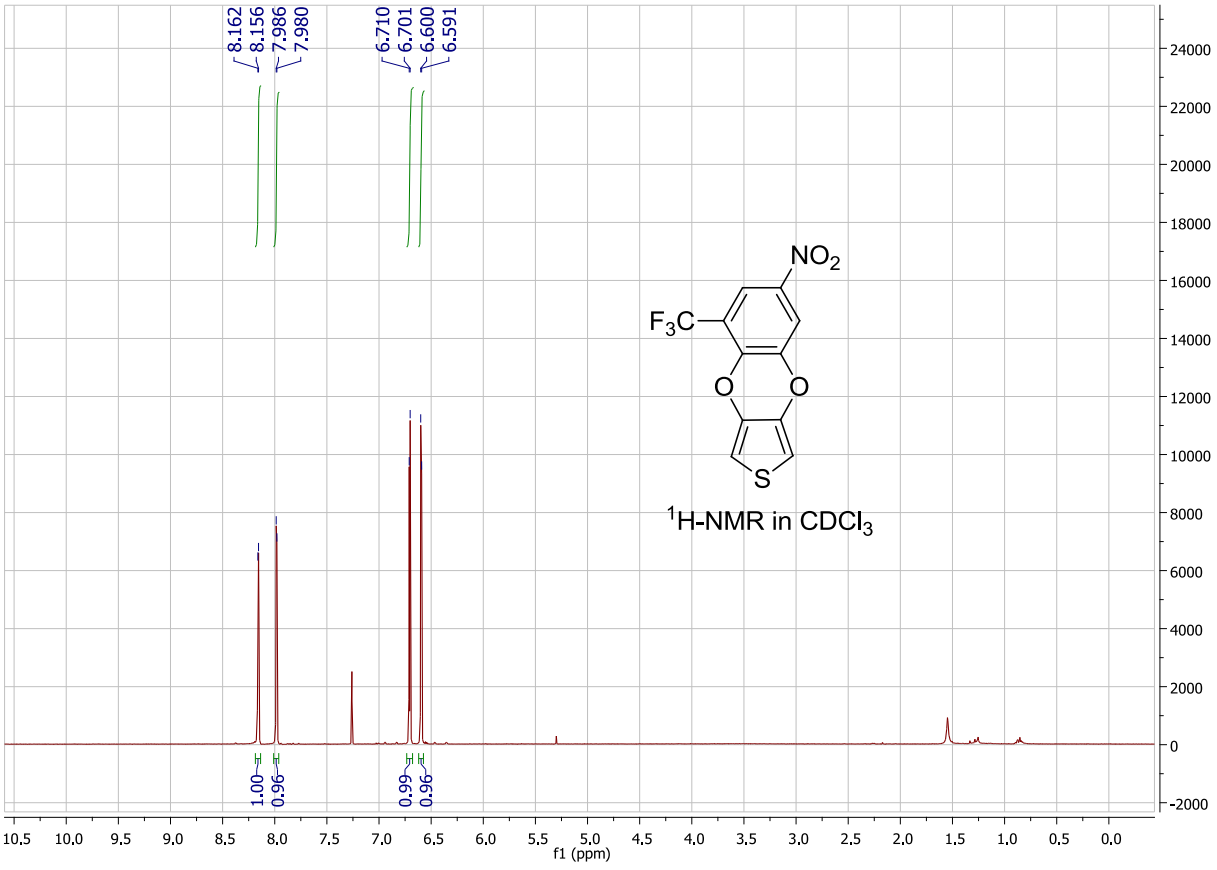
5-Nitro-7-(trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine (**3NO$_2$,5CF$_3$-PheDOT**)

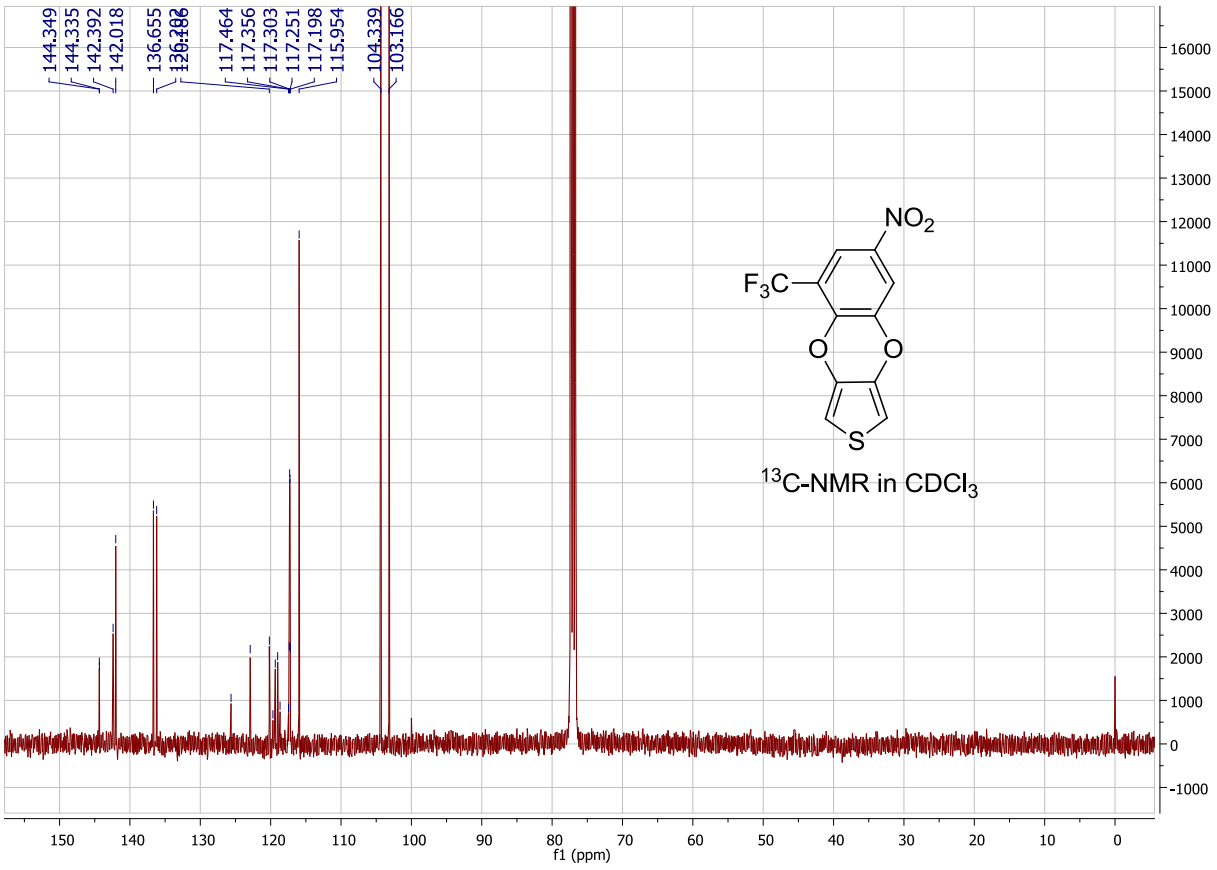


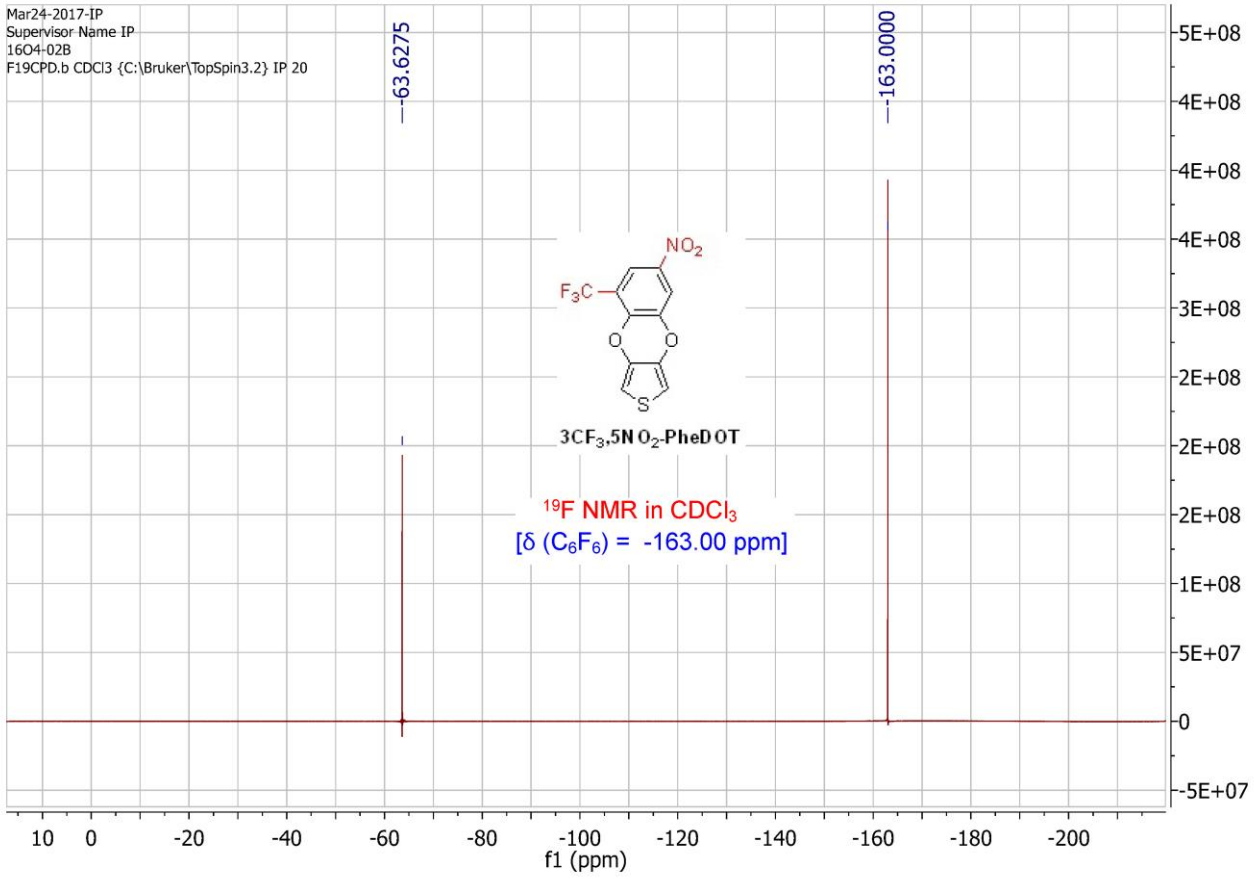



Mar24-2017-IP
Supervisor Name IP
MPK-62E1
F19CPD.b CDCl3 {C:\Bruker\TopSpin3.2} IP 21
-64.1251
-163.0000
3E+08
3E+08
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)
CF3
O2N
O
O
S
3NO2,5CF3-PheDOT
19F NMR in CDCl3
[δ (C6F6) = -163.00 ppm]

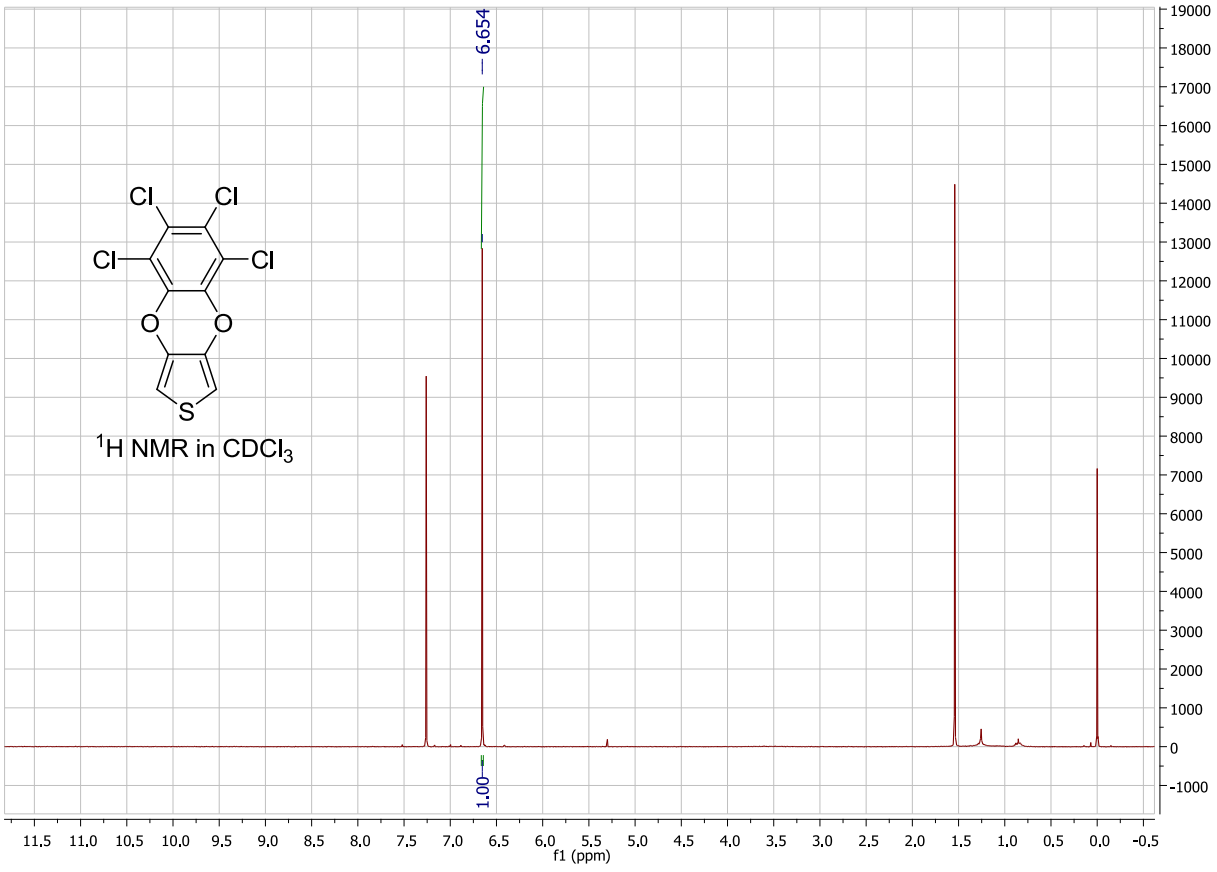
7-Nitro-5-(trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine **(3CF$_3$,5NO$_2$-PheDOT)**

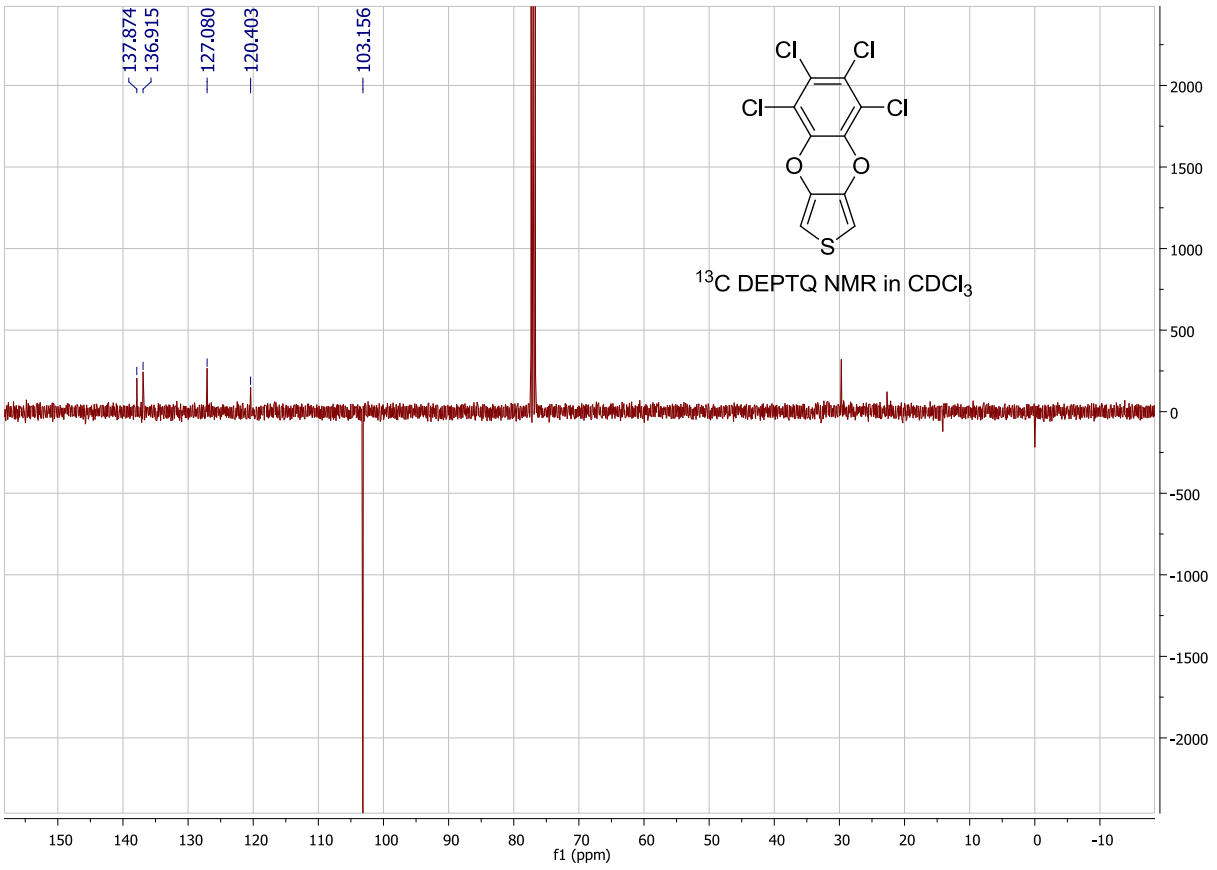




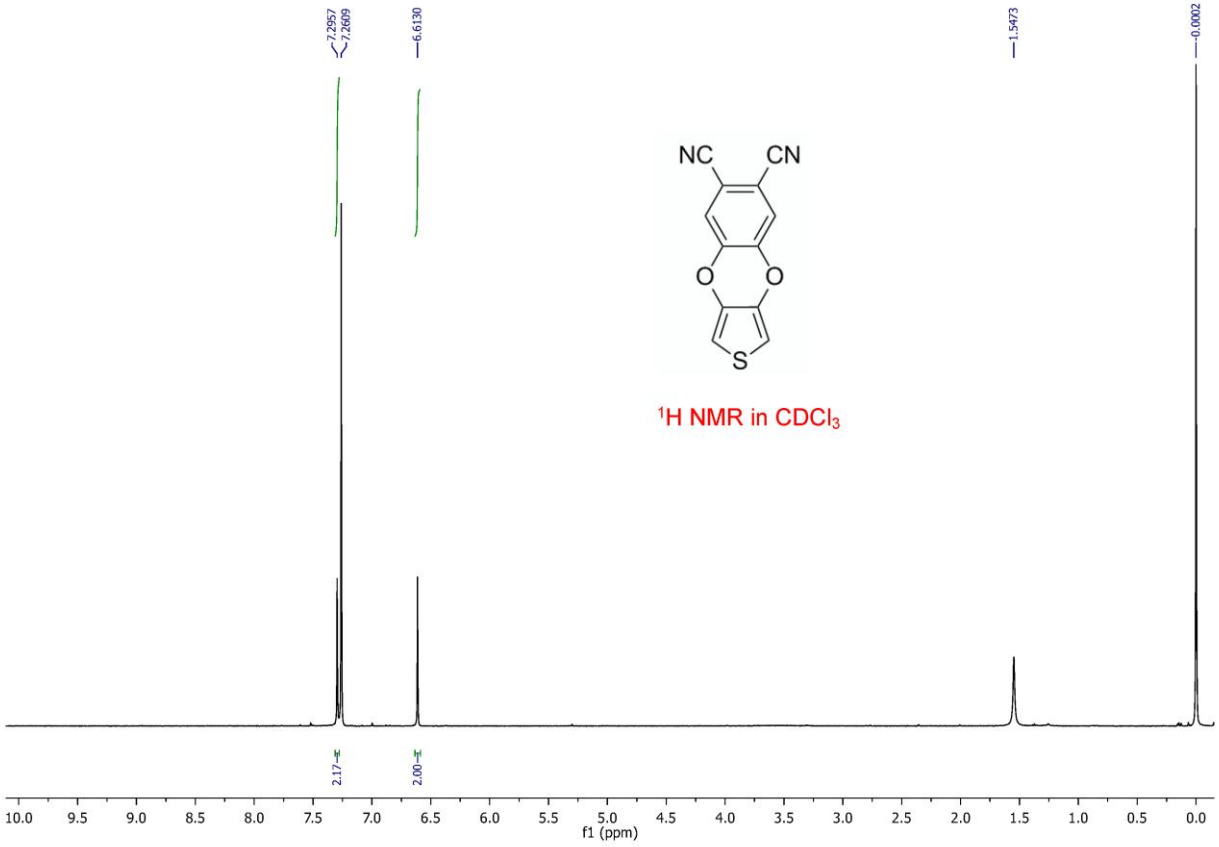

Mar24-2017-IP
Supervisor Name IP
16O4-02B
F19CPD.b CDCl3 {C:\Bruker\TopSpin3.2} IP 20
-63.6275
-163.0000
NO2
F3C
O
O
S
3CF3,5NO2-PheDOT
19F NMR in CDCl3
[δ (C6F6) = -163.00 ppm]
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

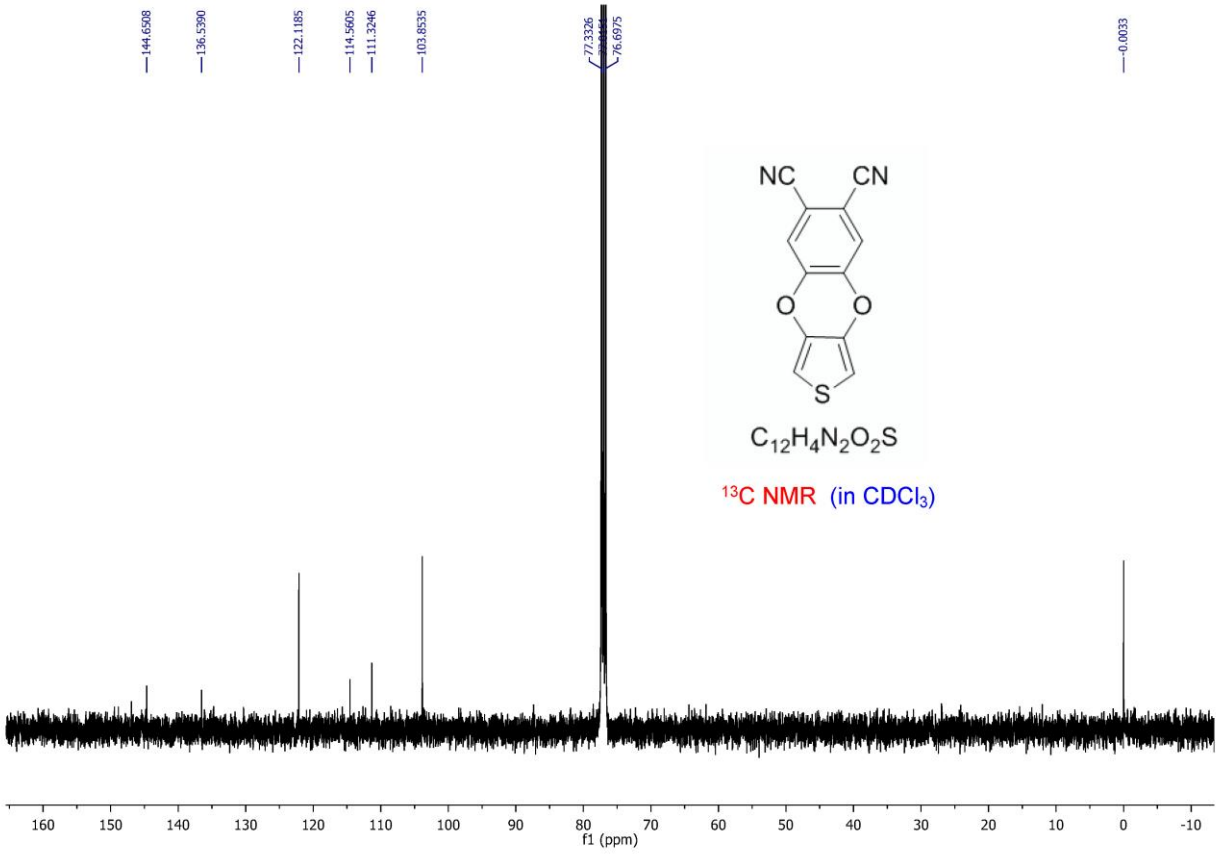
5,6,7,8-Tetrachlorobenzo[b]thieno[3,4-e][1,4]dioxine **(Cl4-PheDOT)**

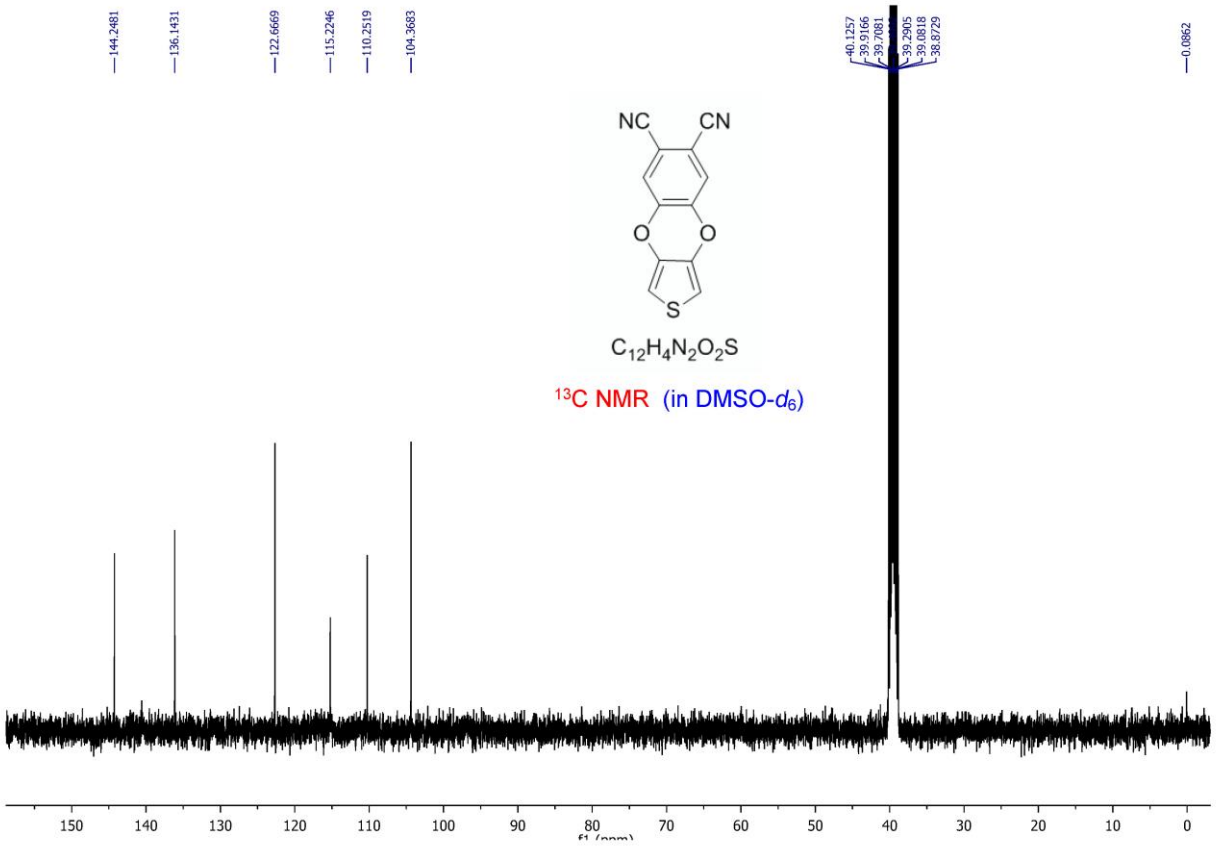




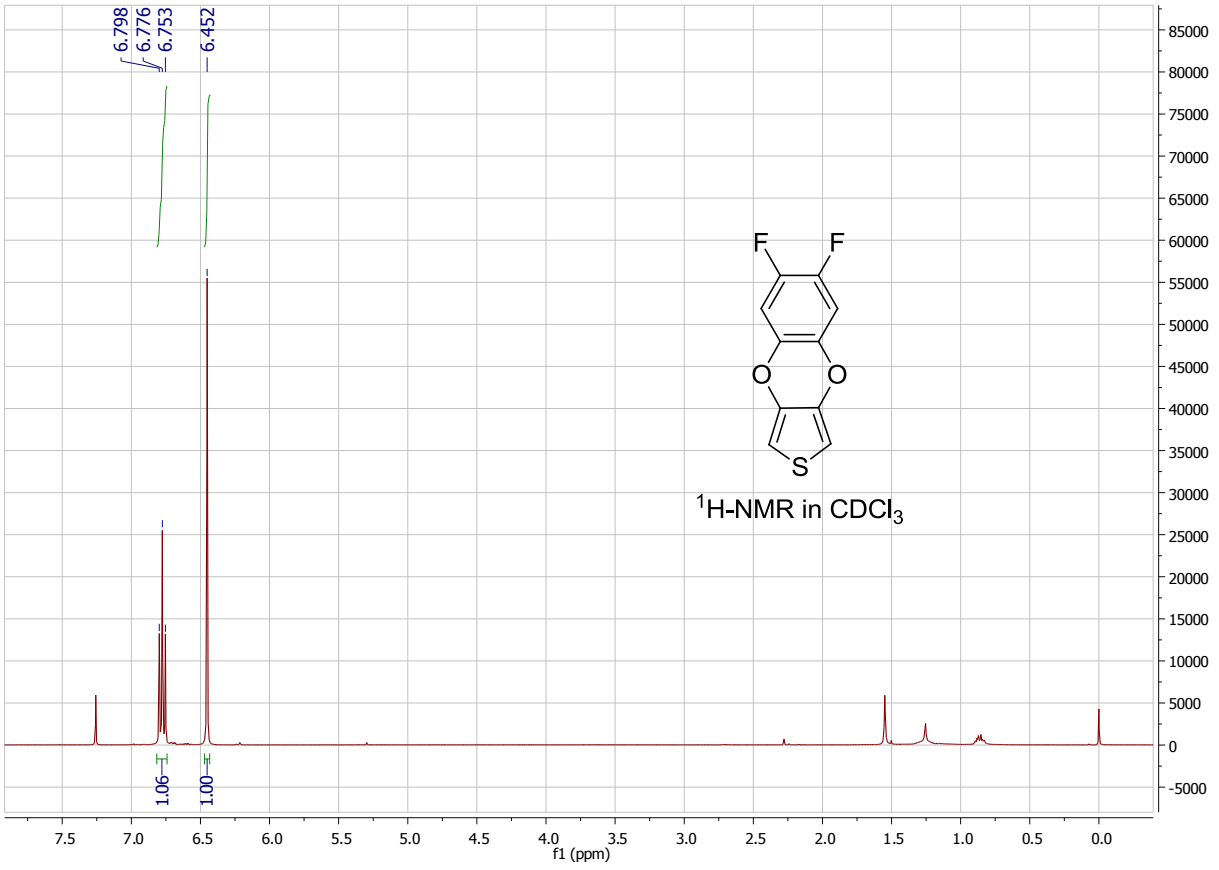
Benzo[b]thieno[3,4-e][1,4]dioxine-6,7-dicarbonitrile **(45(CN)$_2$-PheDOT)**

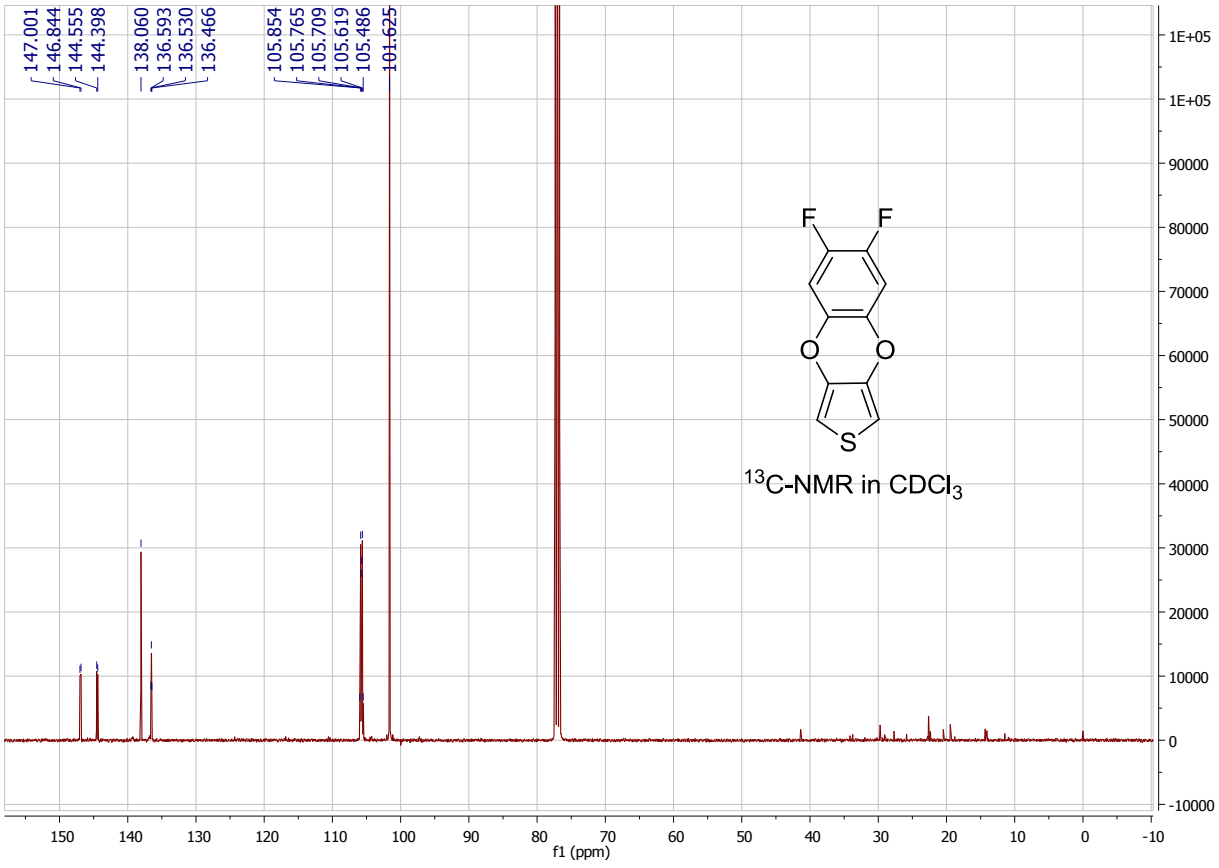


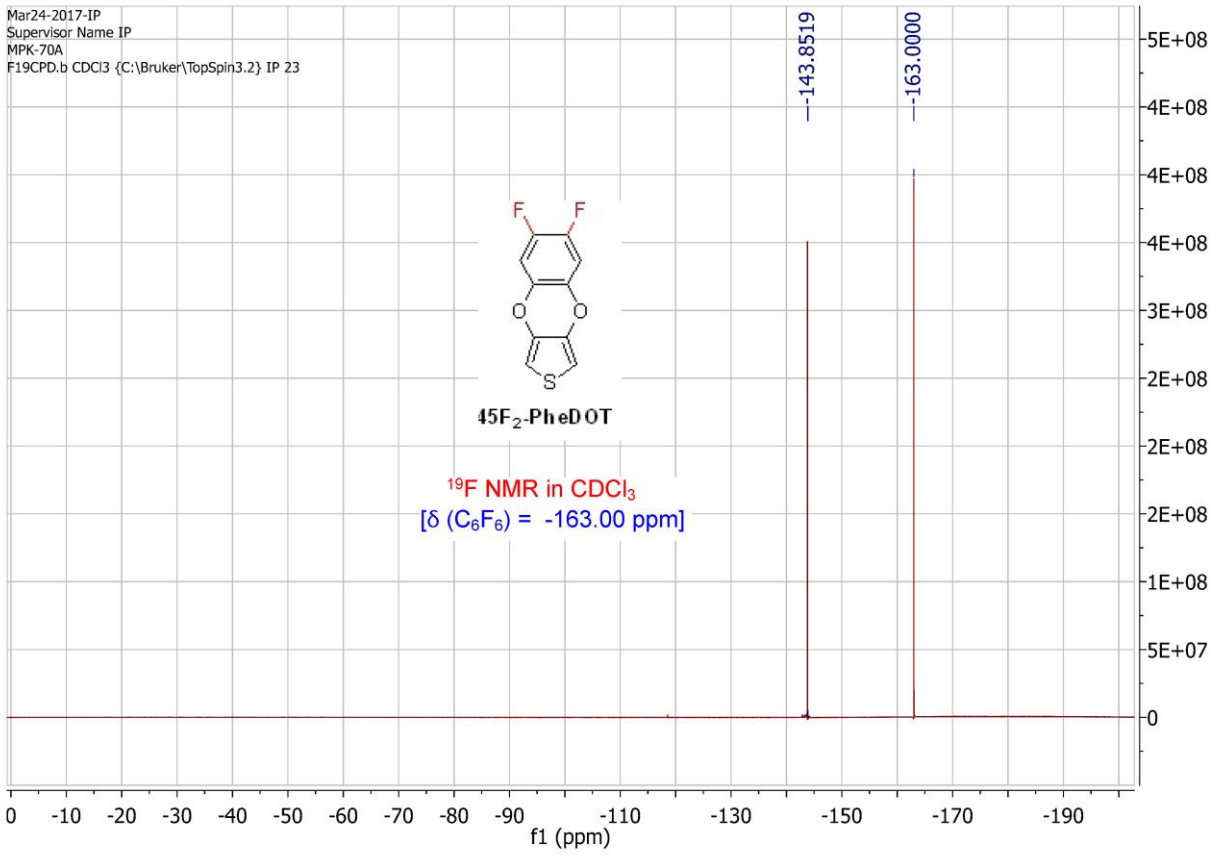



144.2481
136.1431
122.6669
115.2246
110.2519
104.3683
40.1257
39.9166
39.7081
39.2905
39.0818
38.8729
0.0862
NC
CN
O
O
S
C12H4N2O2S
13C NMR (in DMSO-d6)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

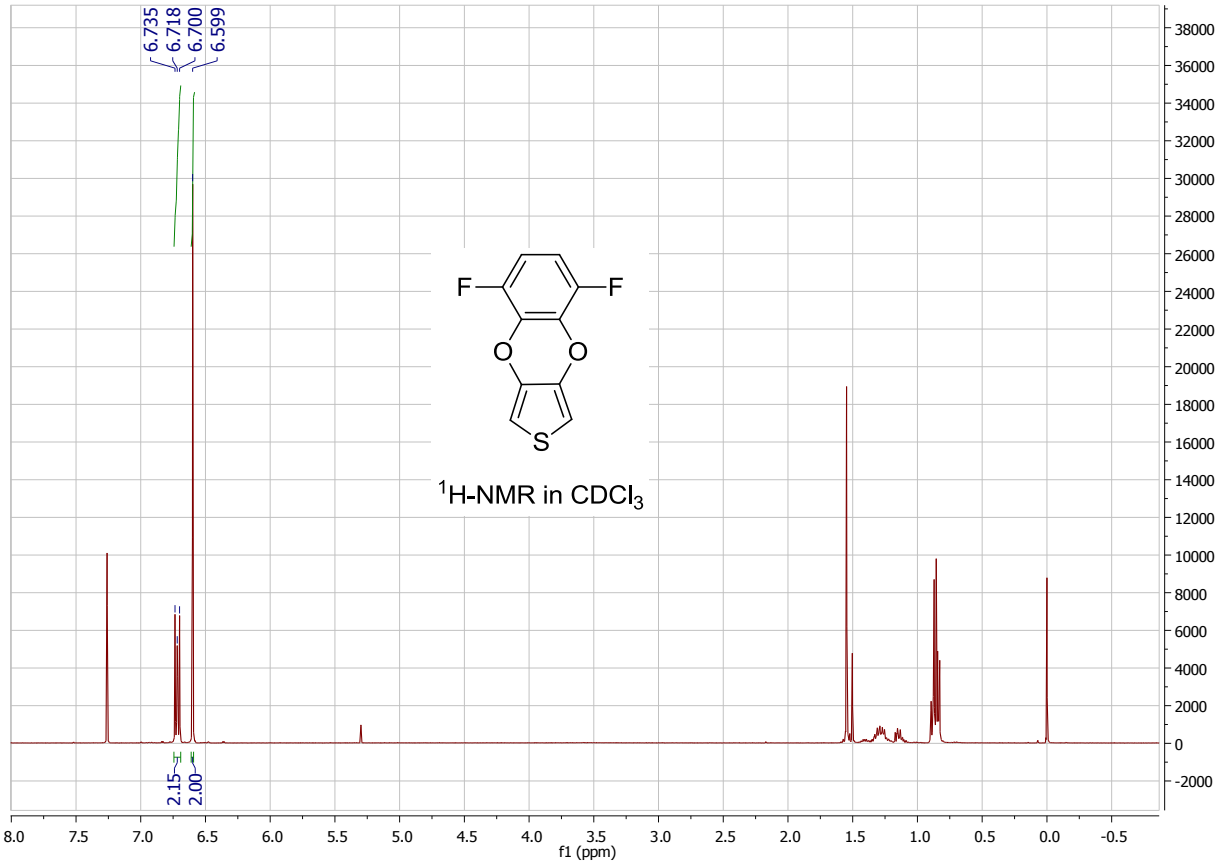
6,7-Difluorobenzo[b]thieno[3,4-e][1,4]dioxine **(45F$_2$-PheDOT)**

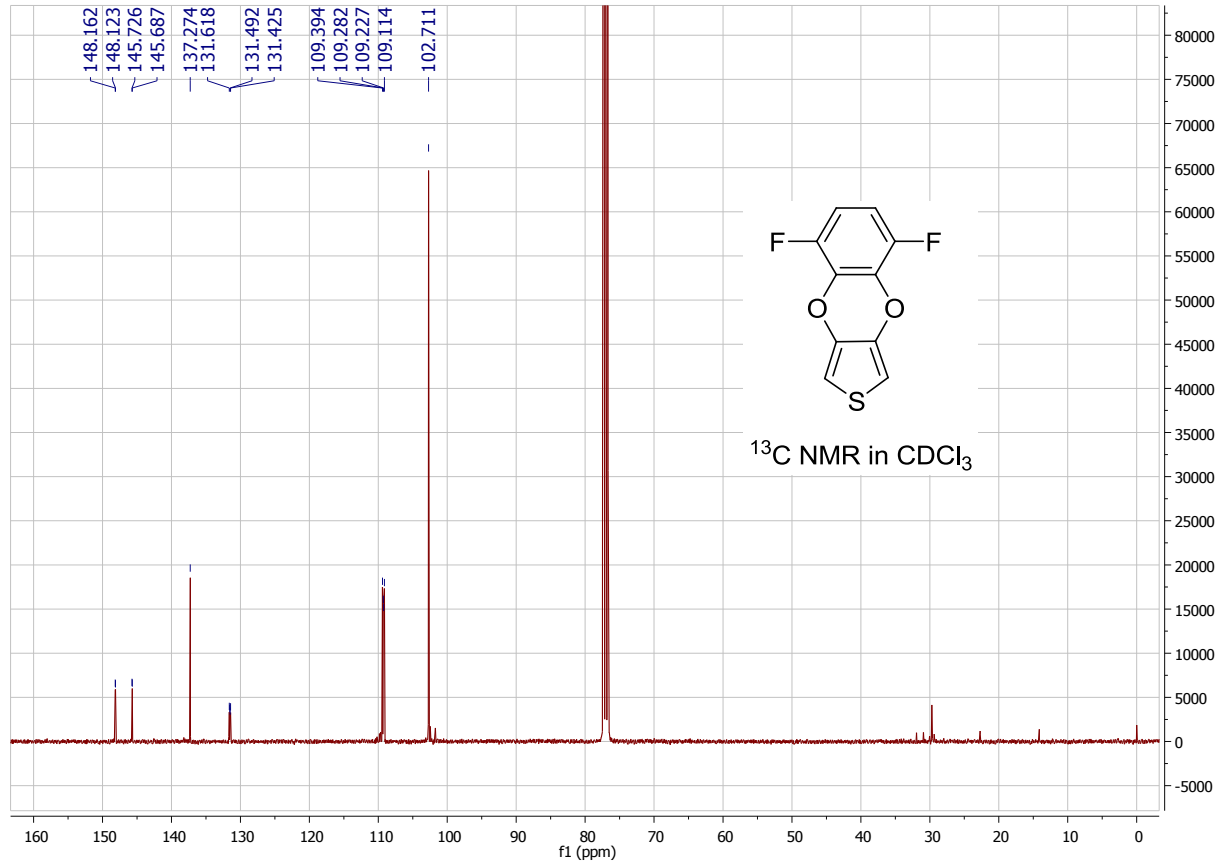


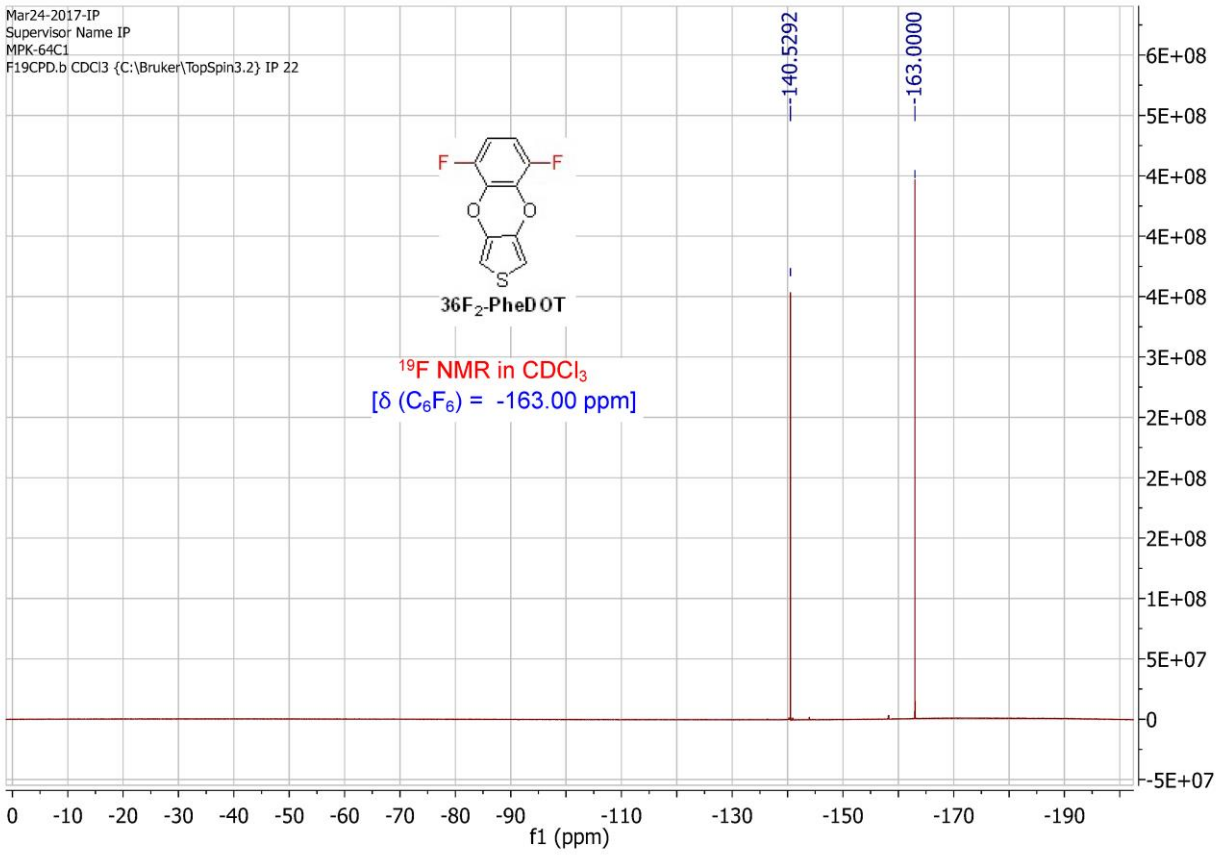



Mar24-2017-IP
Supervisor Name IP
MPK-70A
F19CPD.b CDCl3 {C:\Bruker\TopSpin3.2} IP 23
-143.8519
-163.0000
F
F
O
O
S
45F2-PheDOT
19F NMR in CDCl3
[δ (C6F6) = -163.00 ppm]
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

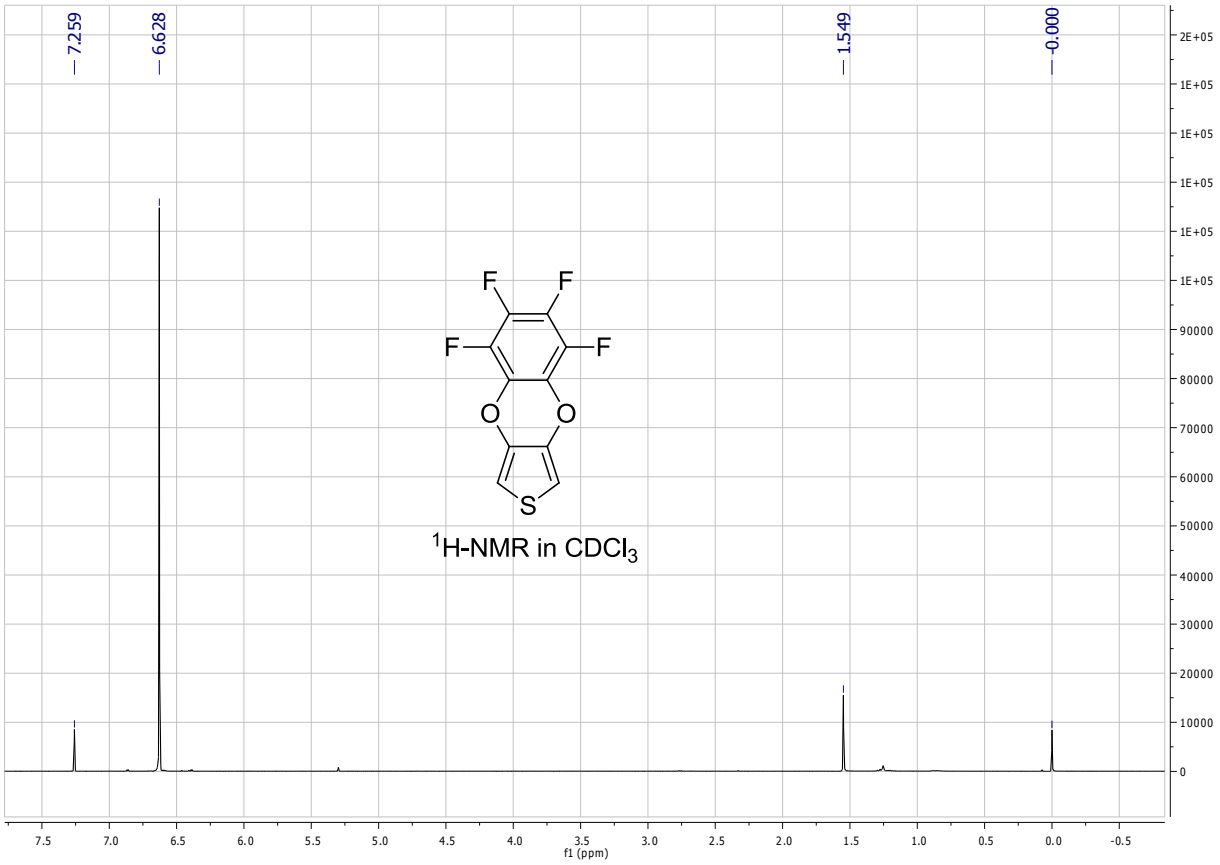
5,8-Difluorobenzo[b]thieno[3,4-e][1,4]dioxine **(36F$_2$-PheDOT)**

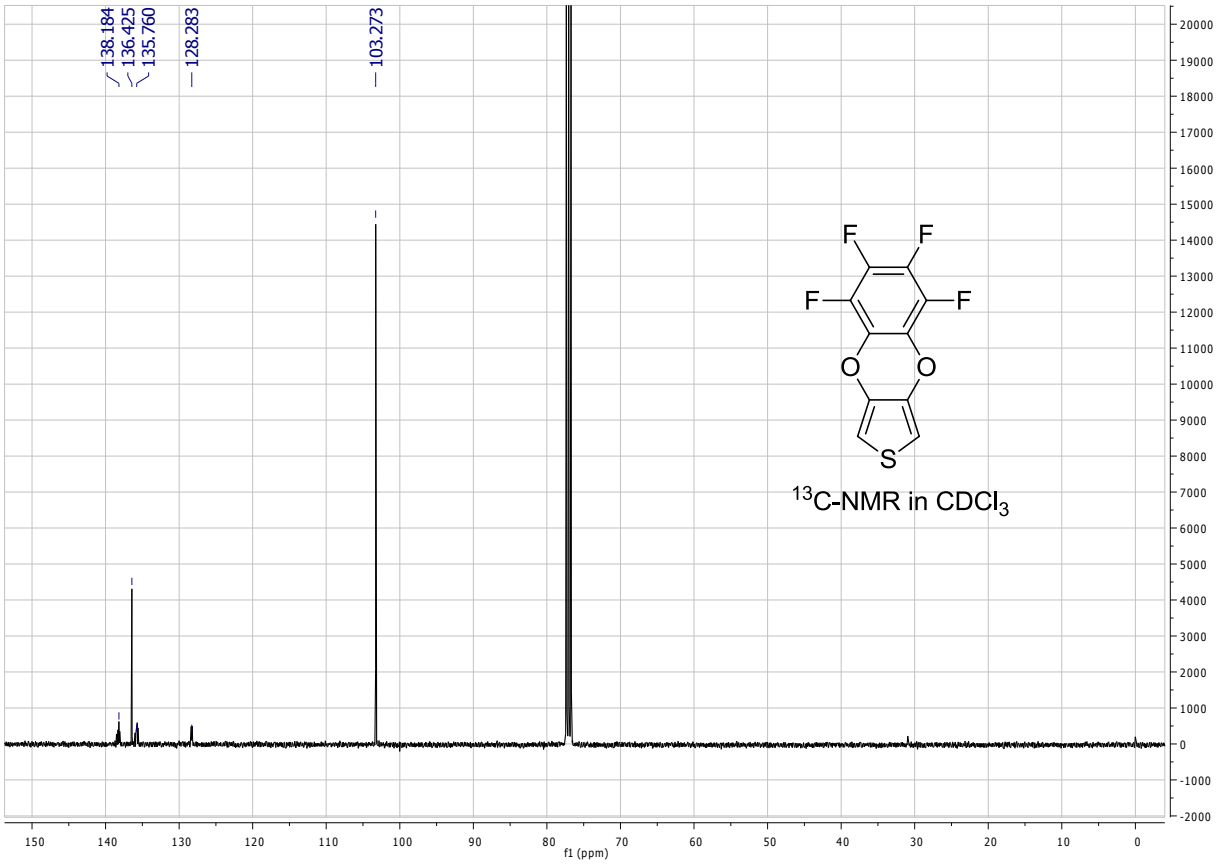


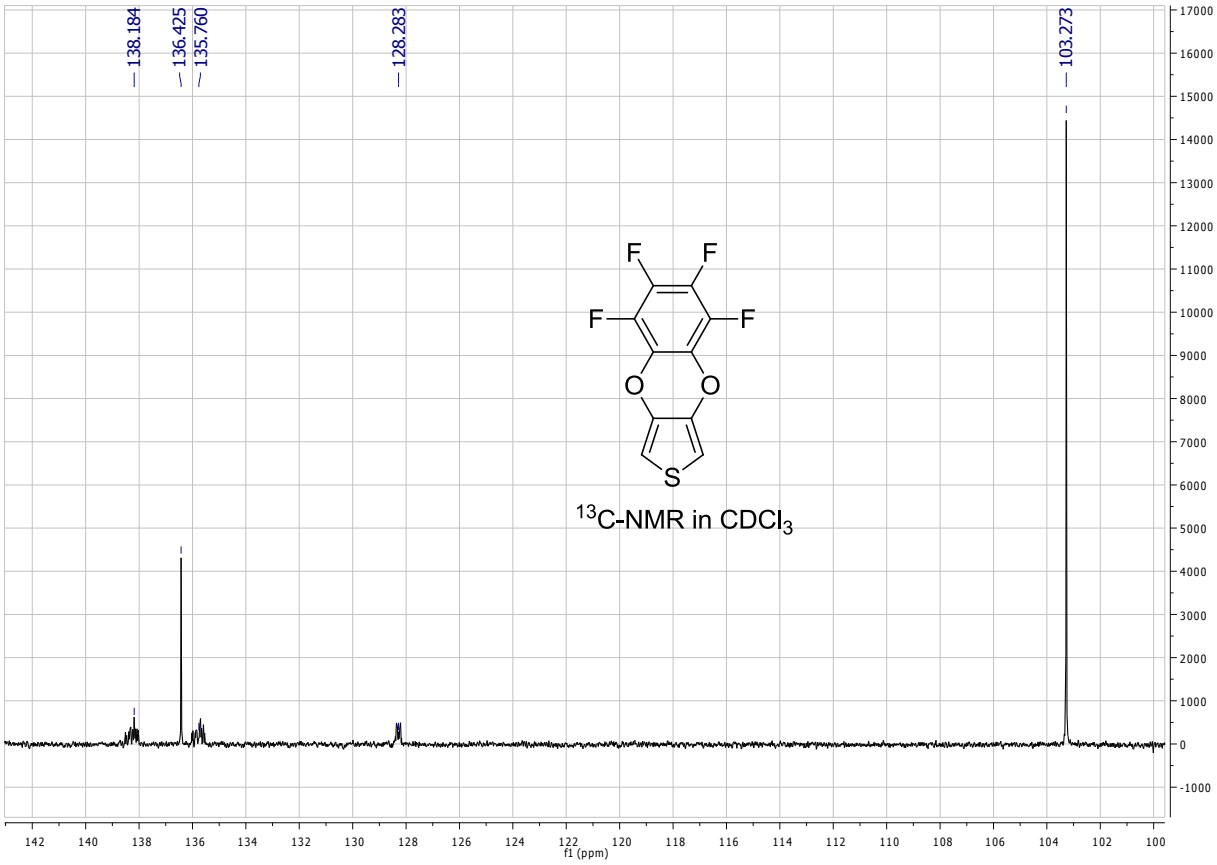


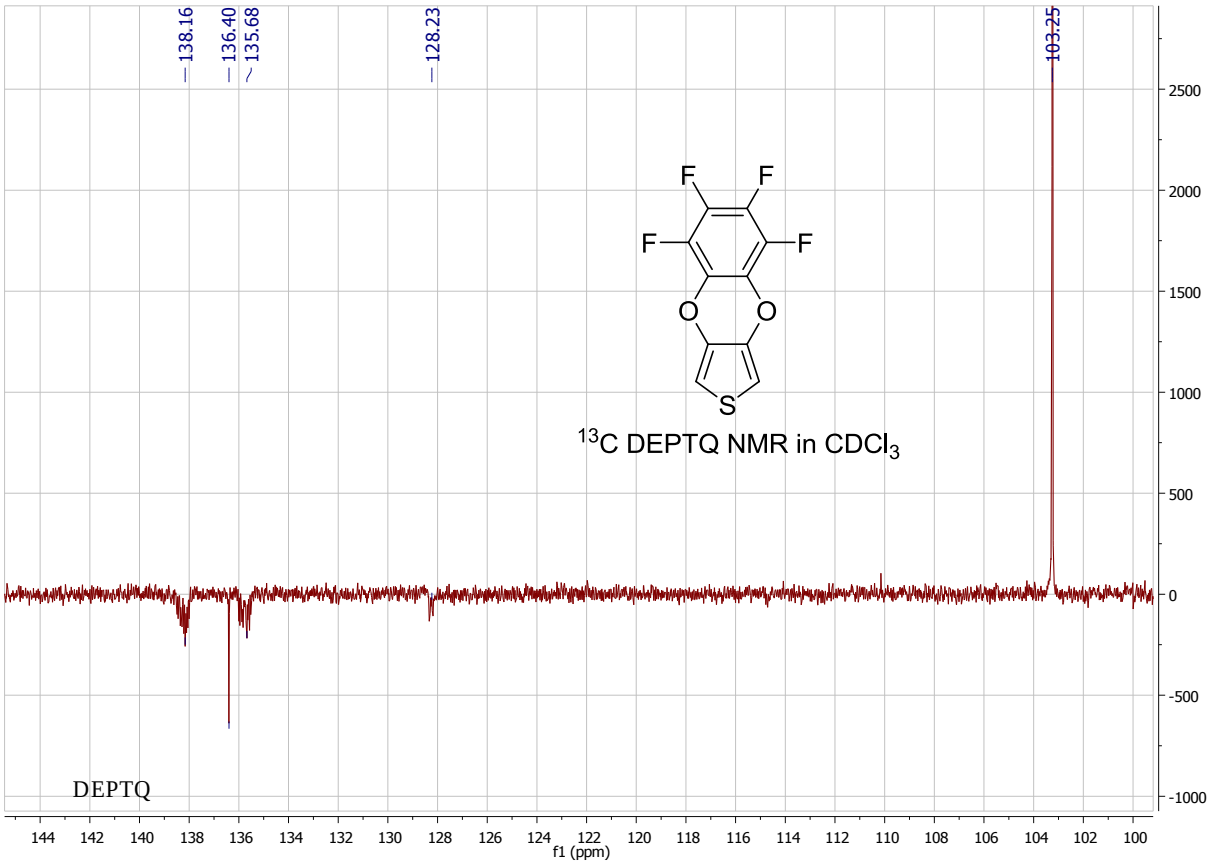

Mar24-2017-IP
Supervisor Name IP
MPK-64C1
F19CPD.b CDCl3 {C:\Bruker\TopSpin3.2} IP 22
-140.5292
-163.0000
F
F
O
O
S
36F2-PheDOT
19F NMR in CDCl3
[δ (C6F6) = -163.00 ppm]
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

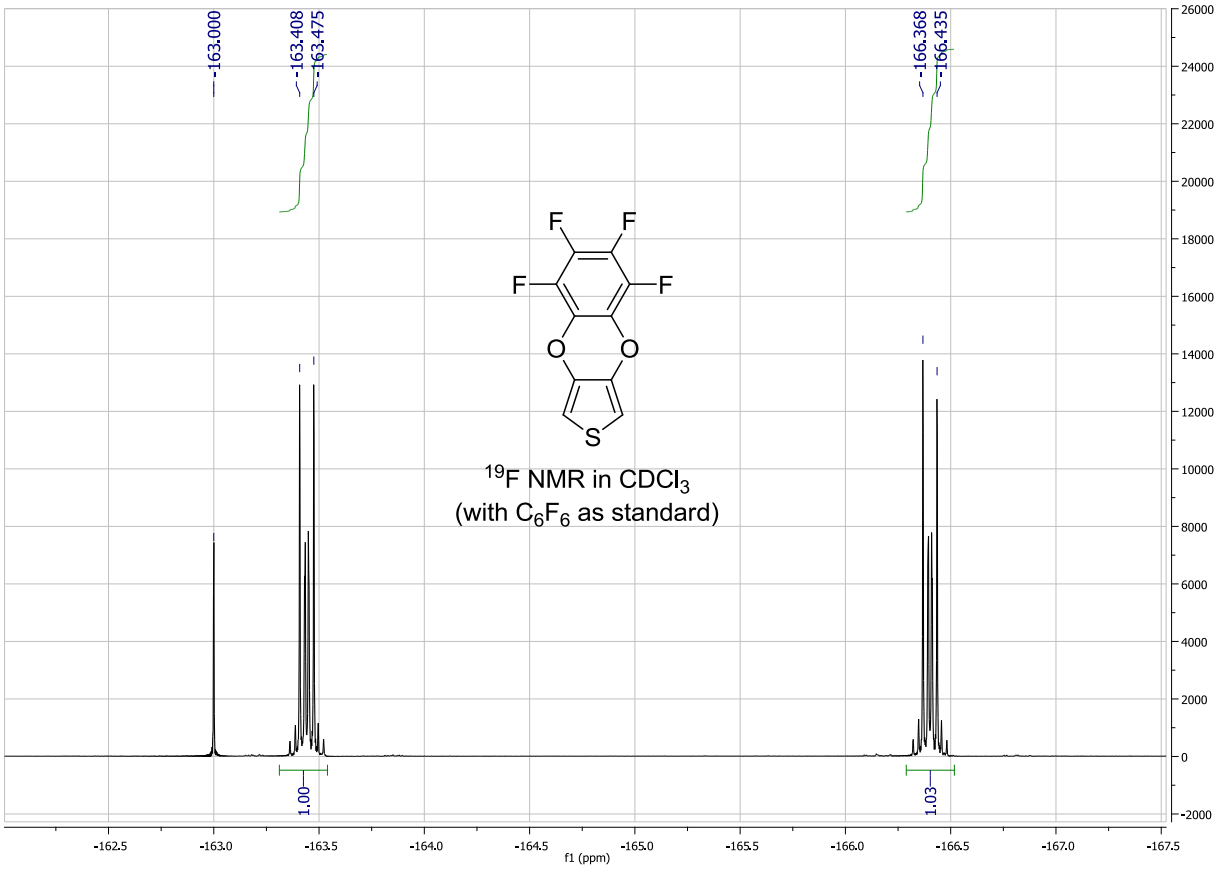
5,6,7,8-Tetrafluorobenzo[b]thieno[3,4-e][1,4]dioxine (**F$_4$-PheDOT**)

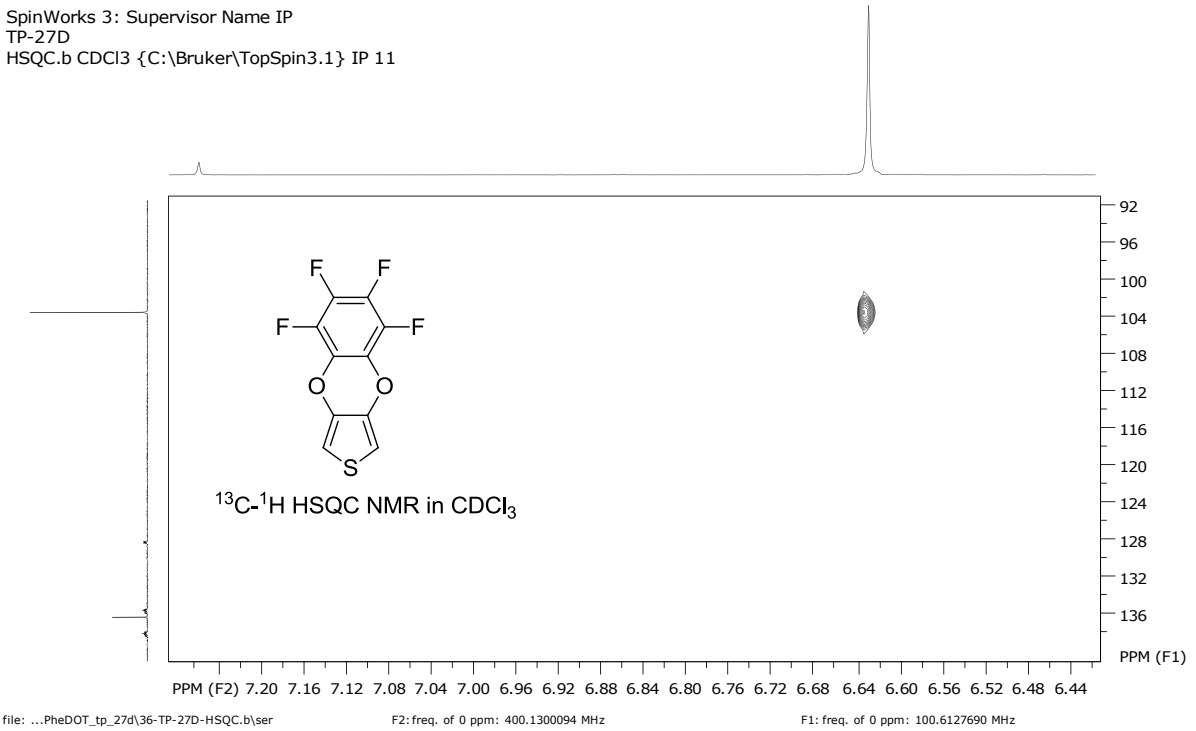





138.184
136.425
135.760
128.283
103.273
F
F
F
F
O
O
S
^{13}C-NMR in CDCl$_3$
f1 (ppm)


138.16
136.40
135.68
128.23
103.25
F
F
F
F
O
O
S
^{13}C DEPTQ NMR in CDCl$_3$
DEPTQ
f1 (ppm)



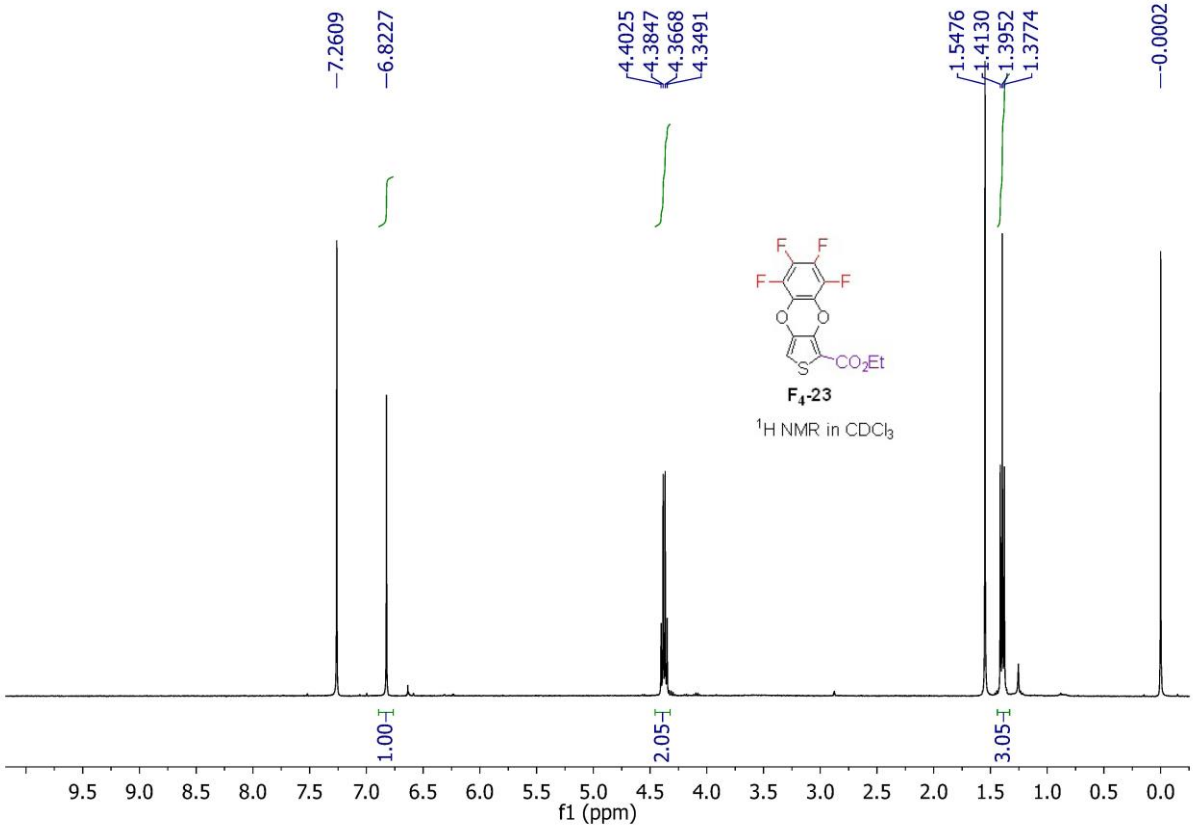


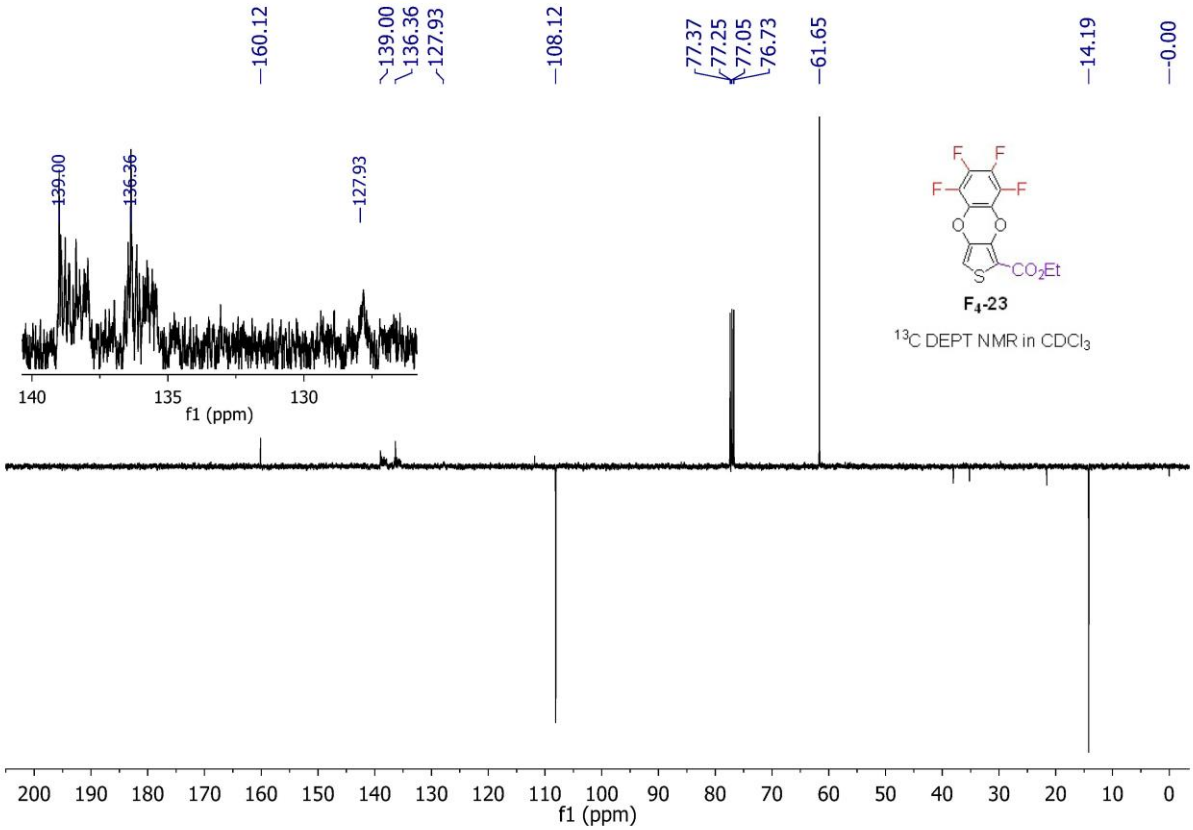
file: ...PheDOT_tp_27d\36-TP-27D-HSQC.b\ser
expt: <hsqcedetgpsisp2.3>
transmitter freq: 400.131549 MHz
time domain size: 2048 by 256 points
width (F2): 2762.43 Hz = 6.9038 ppm = 1.3488 Hz/pt
number of scans: 2

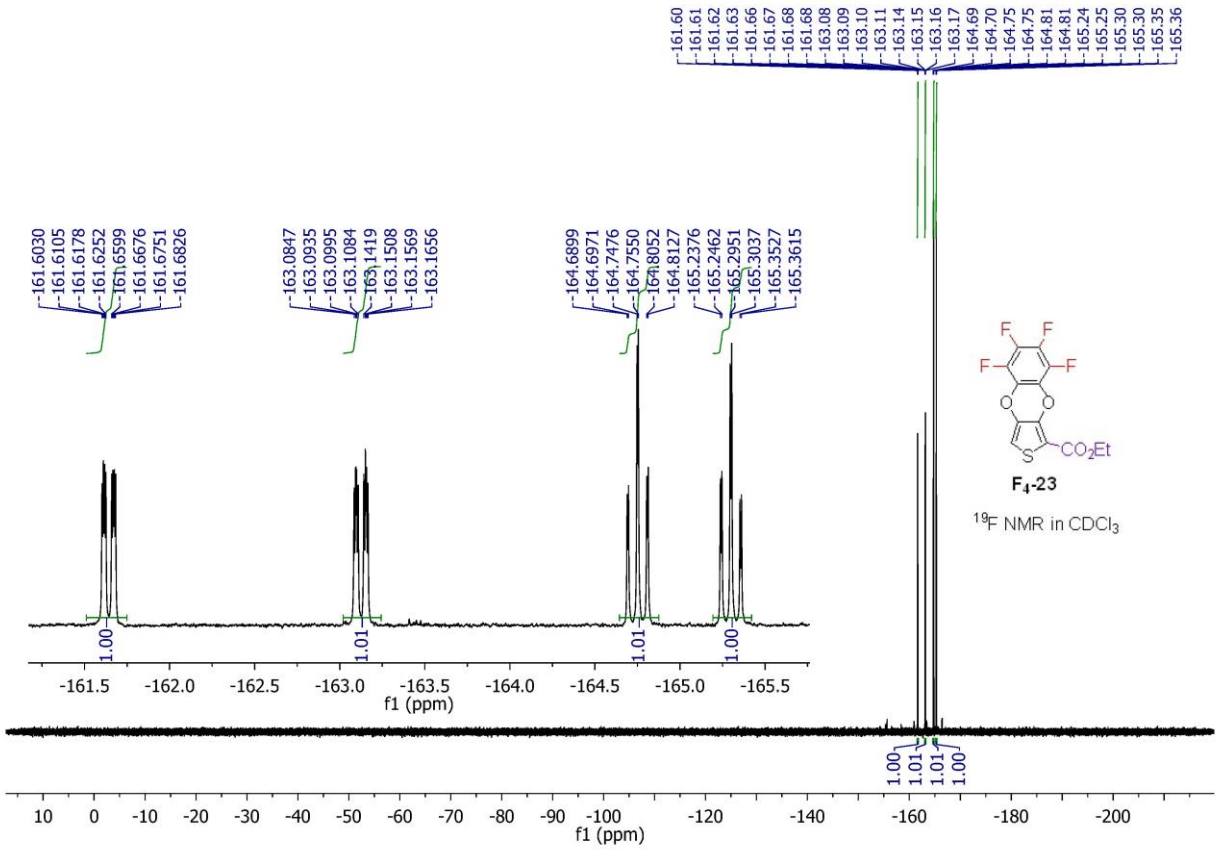
F2: freq. of 0 ppm: 400.1300094 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 15.901 ppm/cm: 0.03974

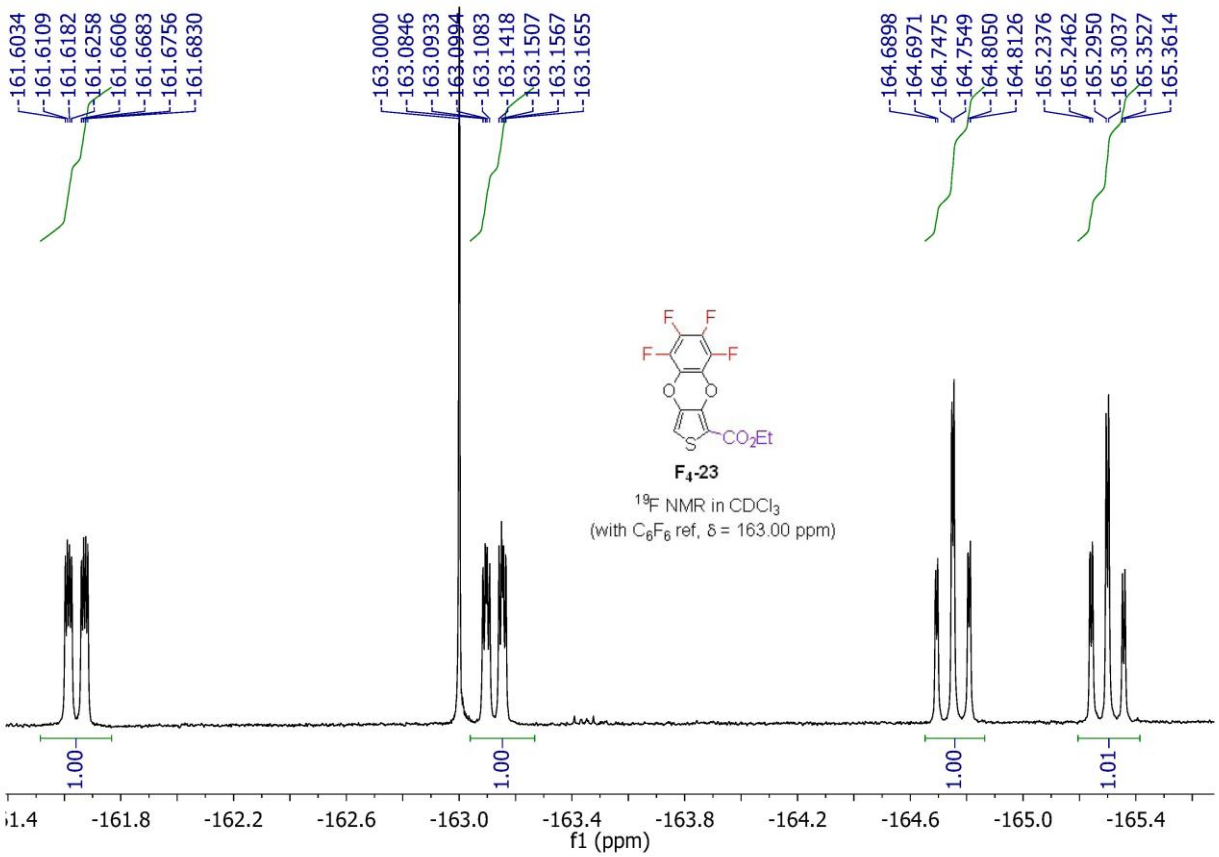
F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 459.036 ppm/cm: 4.56208

Ethyl 5,6,7,8-tetrafluorobenzo[b]thieno[3,4-e][1,4]dioxine-1-carboxylate (**F_4-23**)

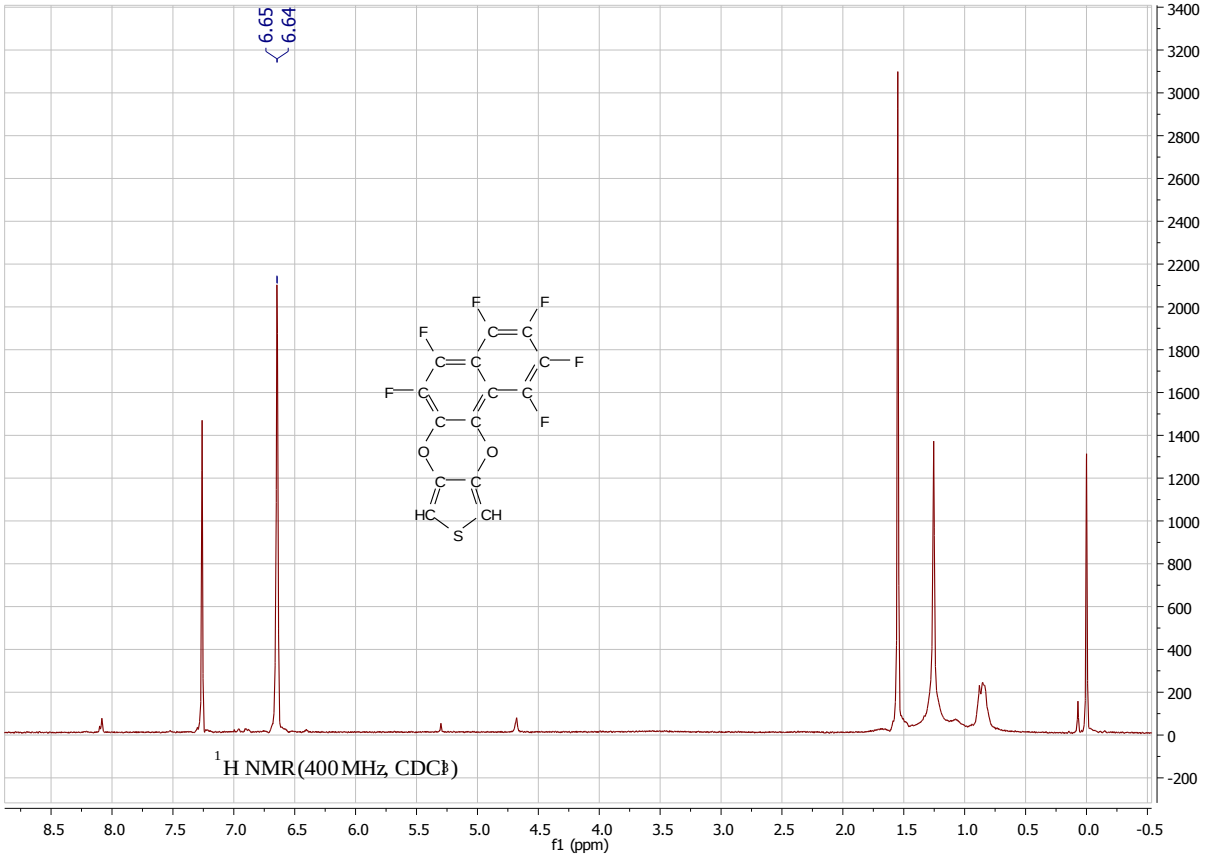


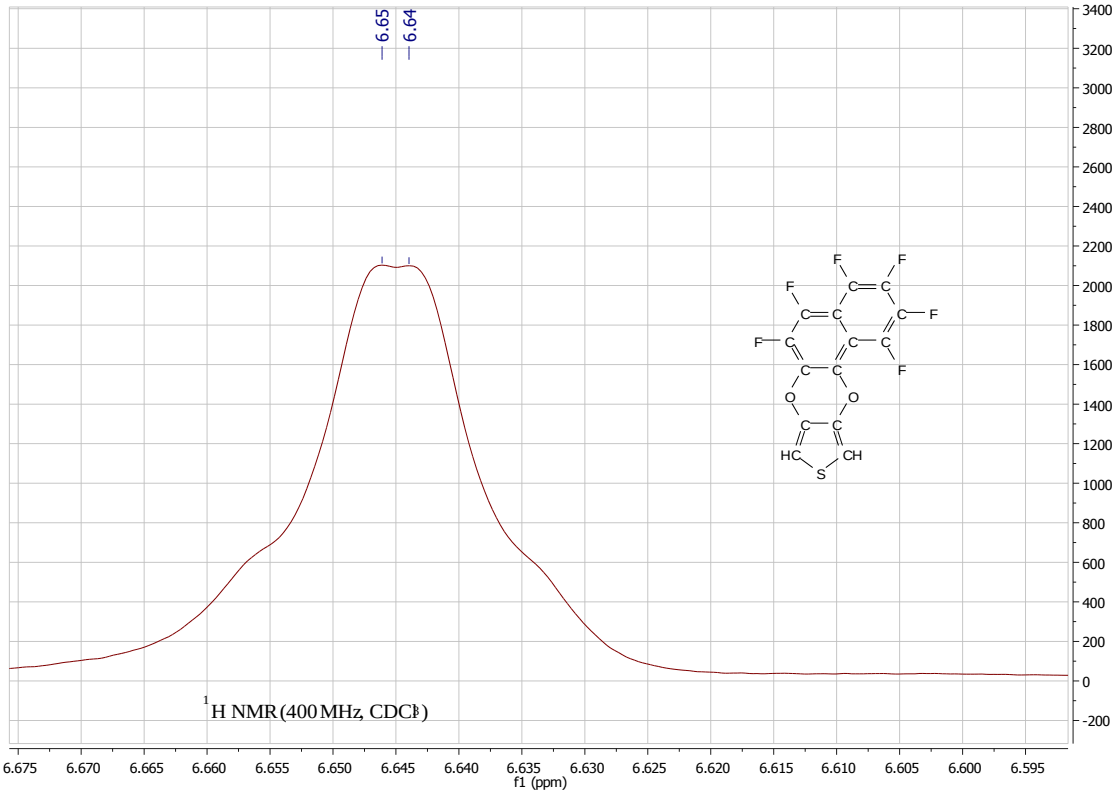


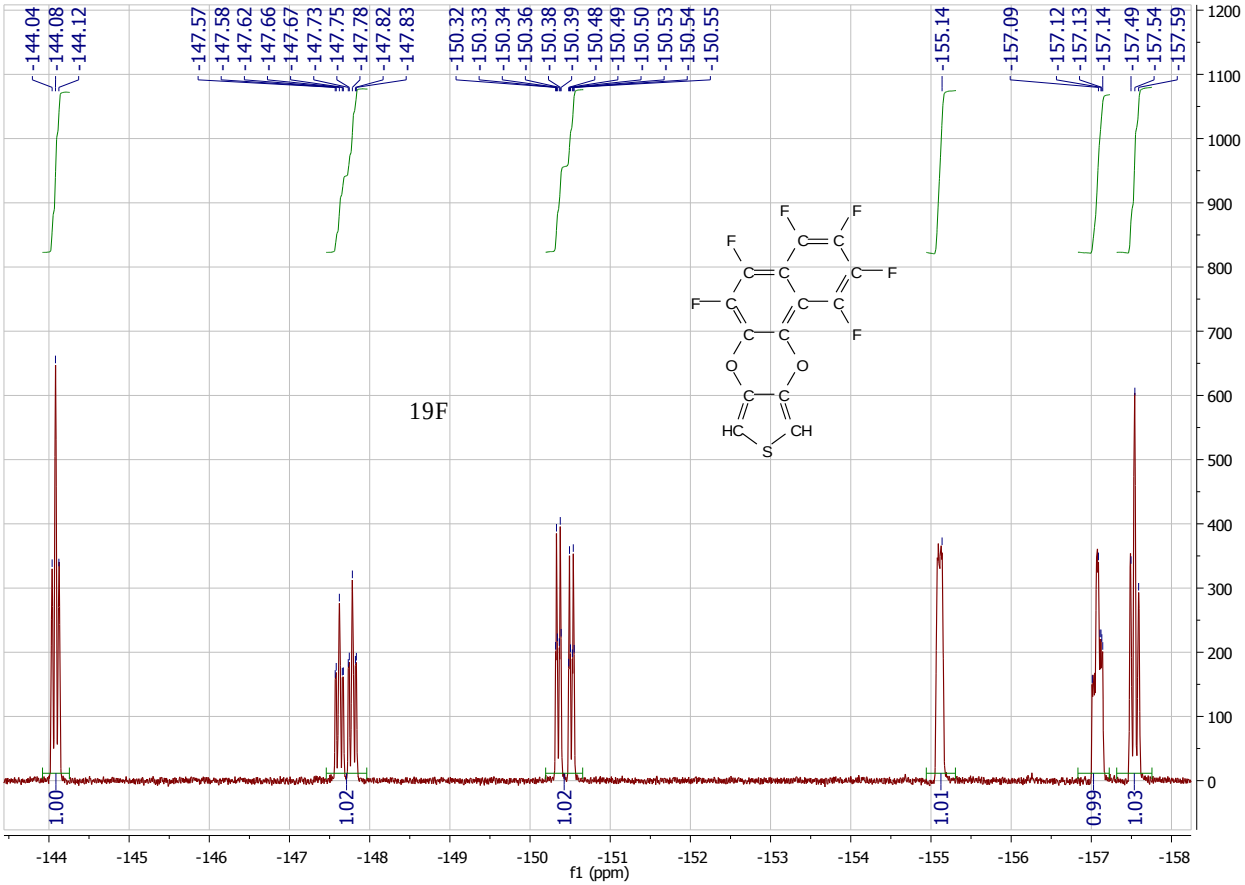

F4-23
19F NMR in CDCl3
f1 (ppm)


F4-23
19F NMR in CDCl3
(with C6F6 ref, δ = 163.00 ppm)
f1 (ppm)

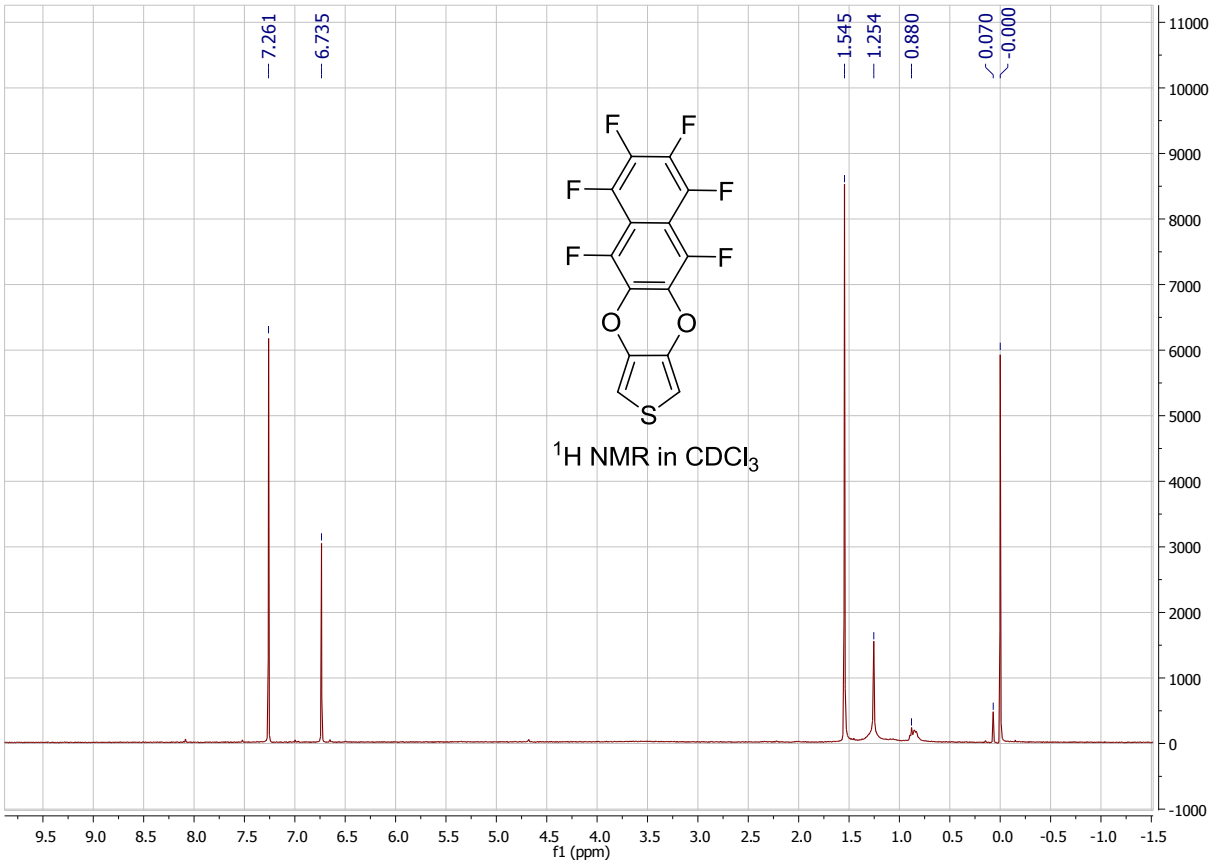
1,2,3,4,5,6-Hexafluoronaphtho[1,2-b]thieno[3,4-e][1,4]dioxine **{F_6-NaphDOT(1,2)}**

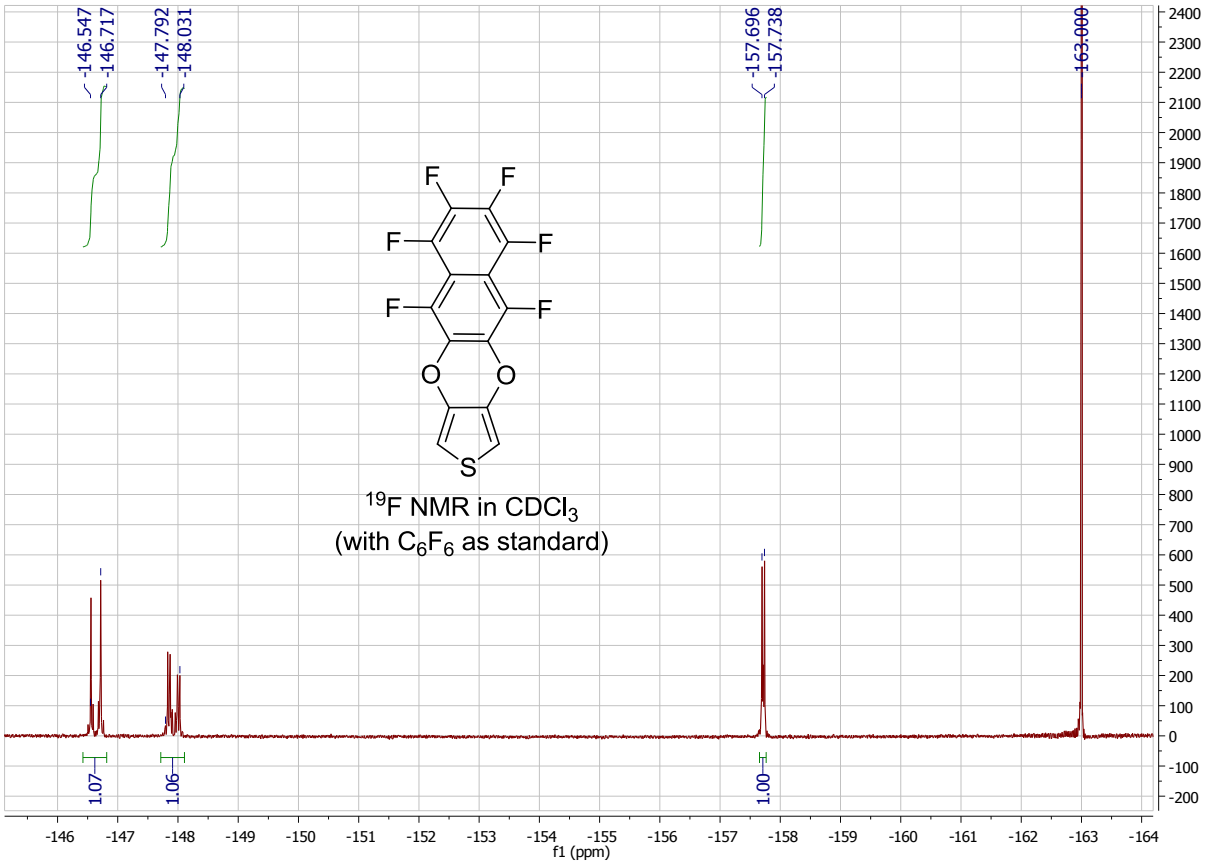


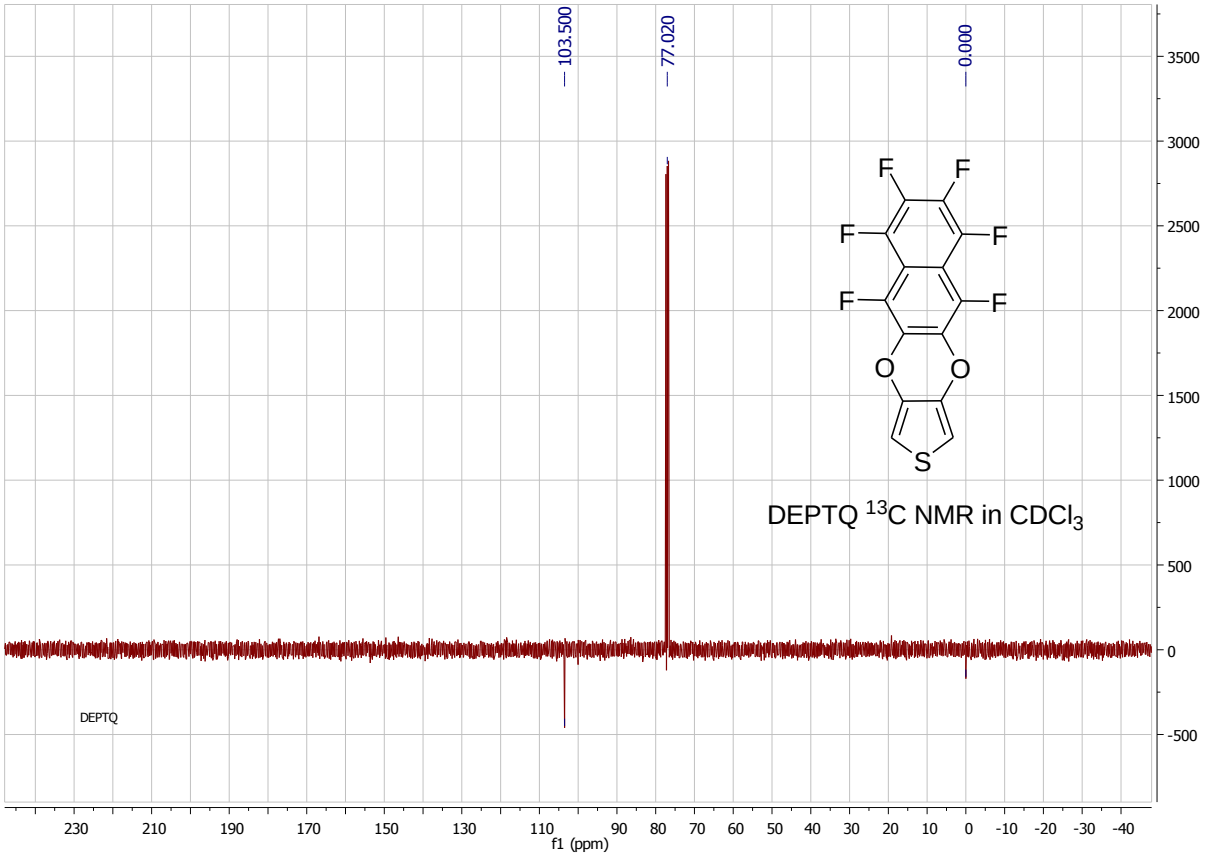



-144.04
-144.08
-144.12
-147.57
-147.58
-147.62
-147.66
-147.67
-147.73
-147.75
-147.78
-147.82
-147.83
-150.32
-150.33
-150.34
-150.36
-150.38
-150.39
-150.48
-150.49
-150.50
-150.53
-150.54
-150.55
-155.14
-157.09
-157.12
-157.13
-157.14
-157.49
-157.54
-157.59
19F
1.00
1.02
1.02
1.01
0.99
1.03
f1 (ppm)

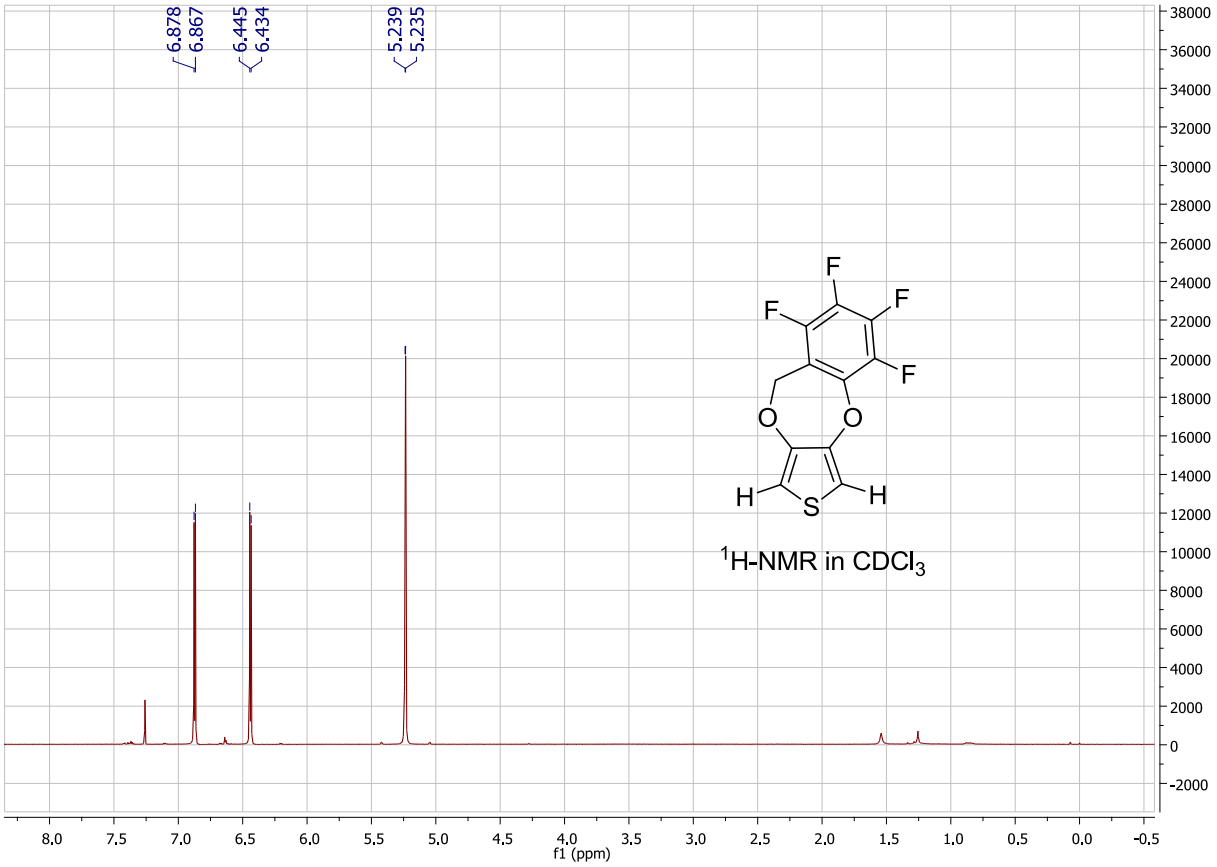
5,6,7,8,9,10-Hexafluoronaphtho[2,3-b]thieno[3,4-e][1,4]dioxine **{F6-NaphDOT(2,3)}**

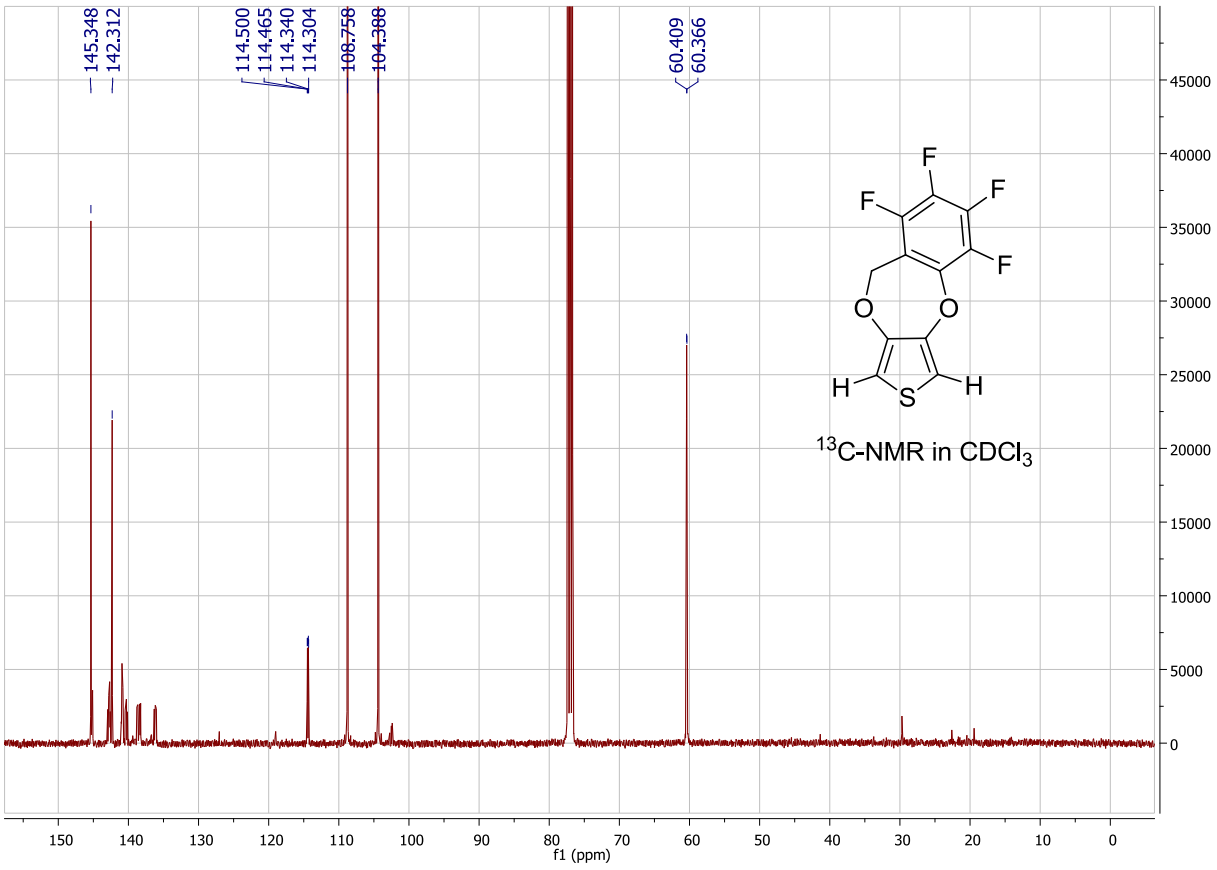


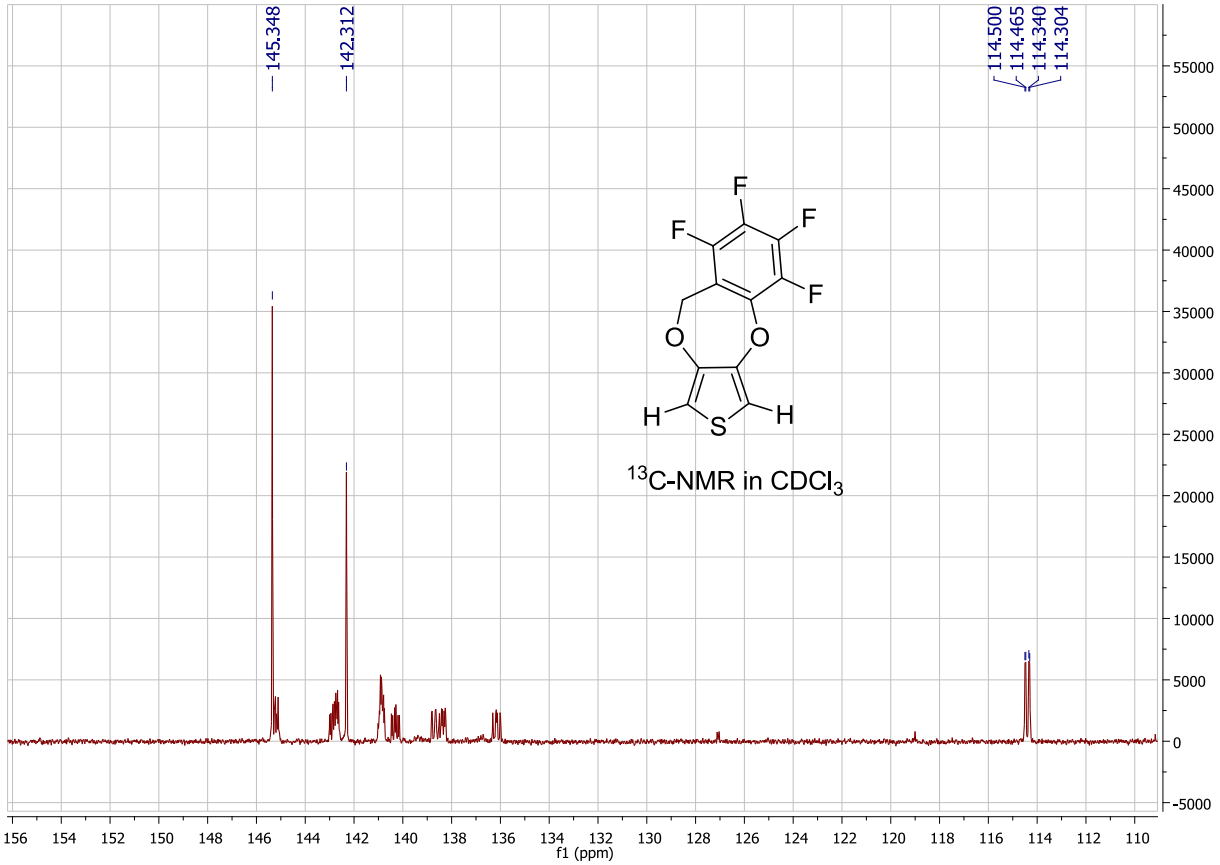


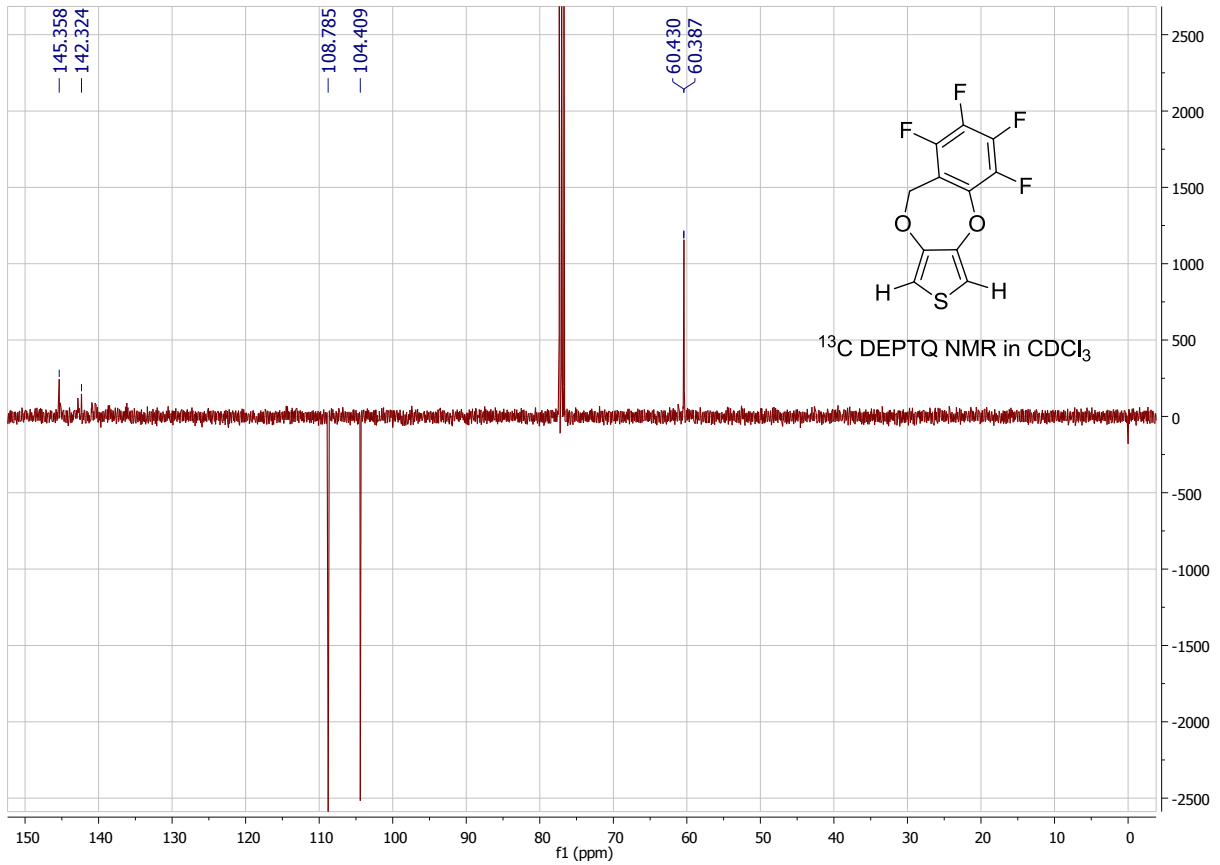

103.500
77.020
0.000
F
F
F
F
F
F
O
O
S
DEPTQ ^{13}C NMR in $CDCl_3$
DEPTQ
3500
3000
2500
2000
1500
1000
500
0
-500
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

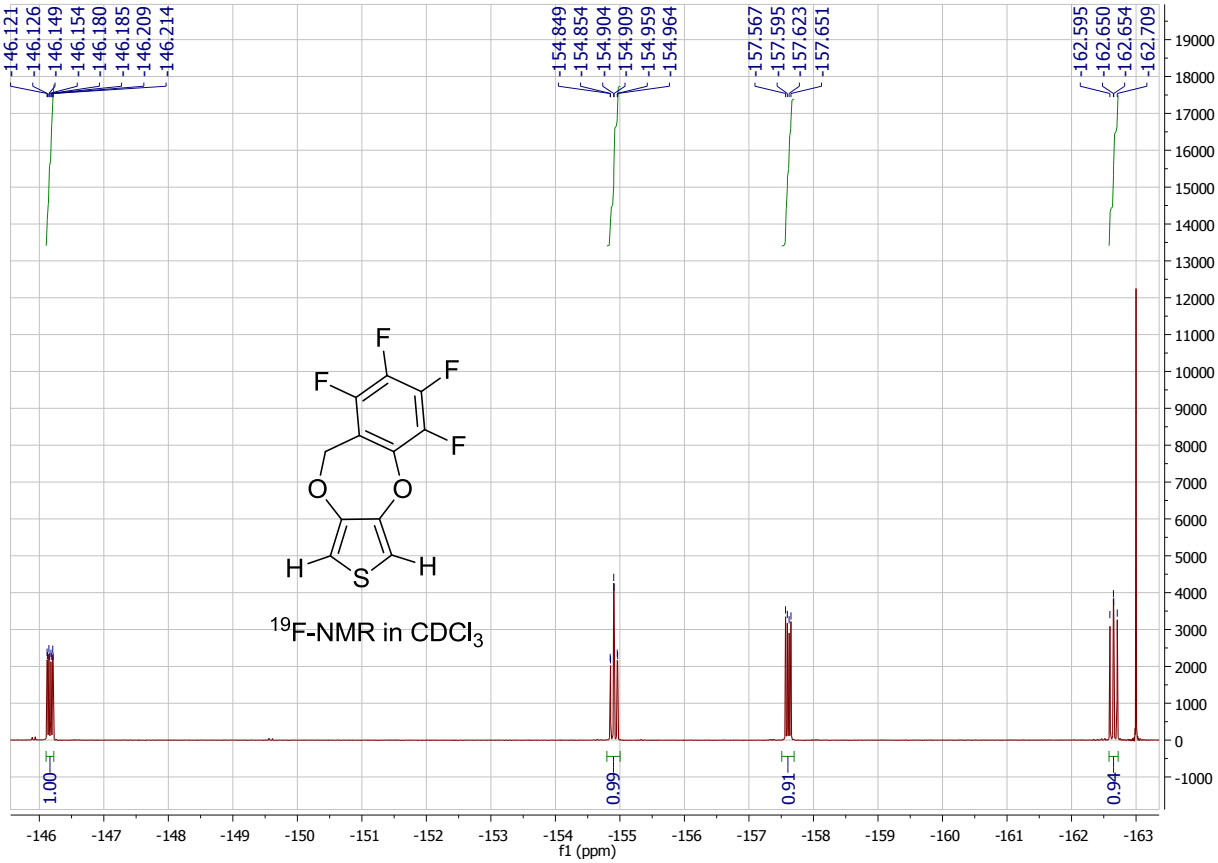
5,6,7,8-Tetrafluoro-9H-benzo[e]thieno[3,4-b][1,4]dioxepine (**F4-BnDOT**)

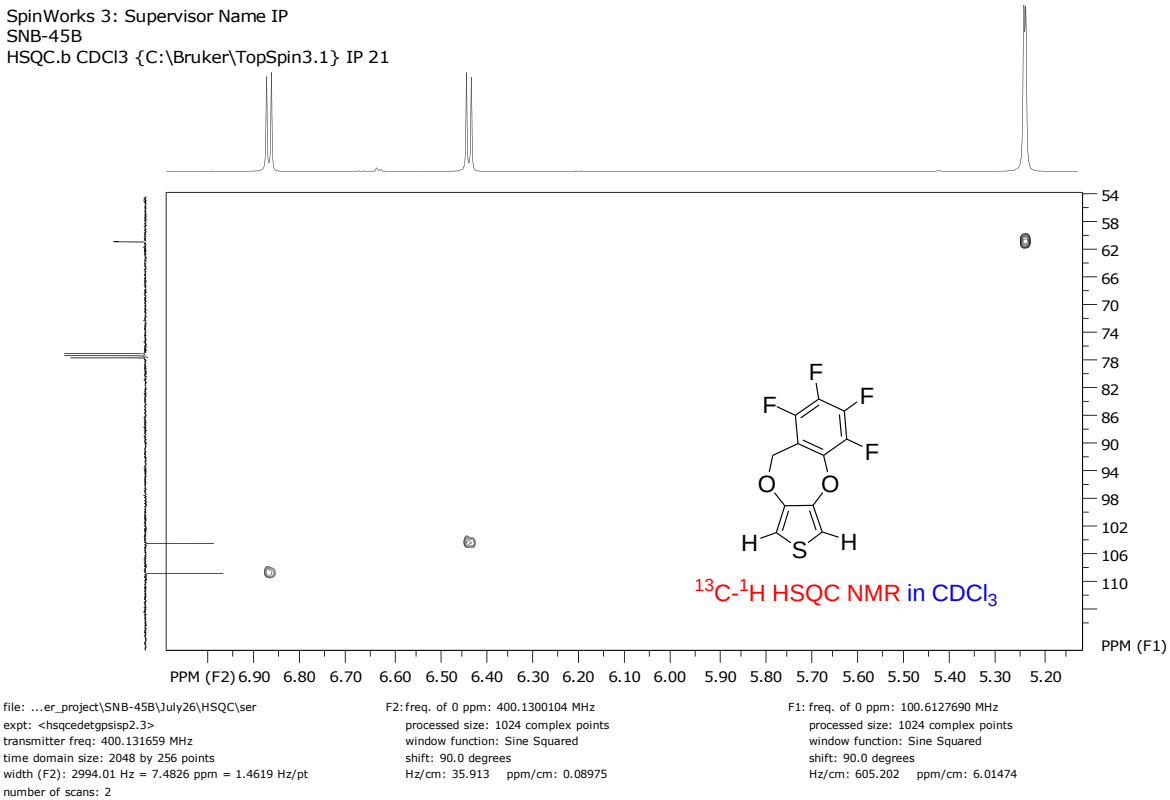





145.348
142.312
114.500
114.465
114.340
114.304
F
F
F
F
O
O
H
S
H
^{13}C-NMR in CDCl$_3$
f1 (ppm)


145.358
142.324
108.785
104.409
60.430
60.387
F
F
F
F
O
O
H
S
H
^{13}C DEPTQ NMR in CDCl$_3$
f1 (ppm)



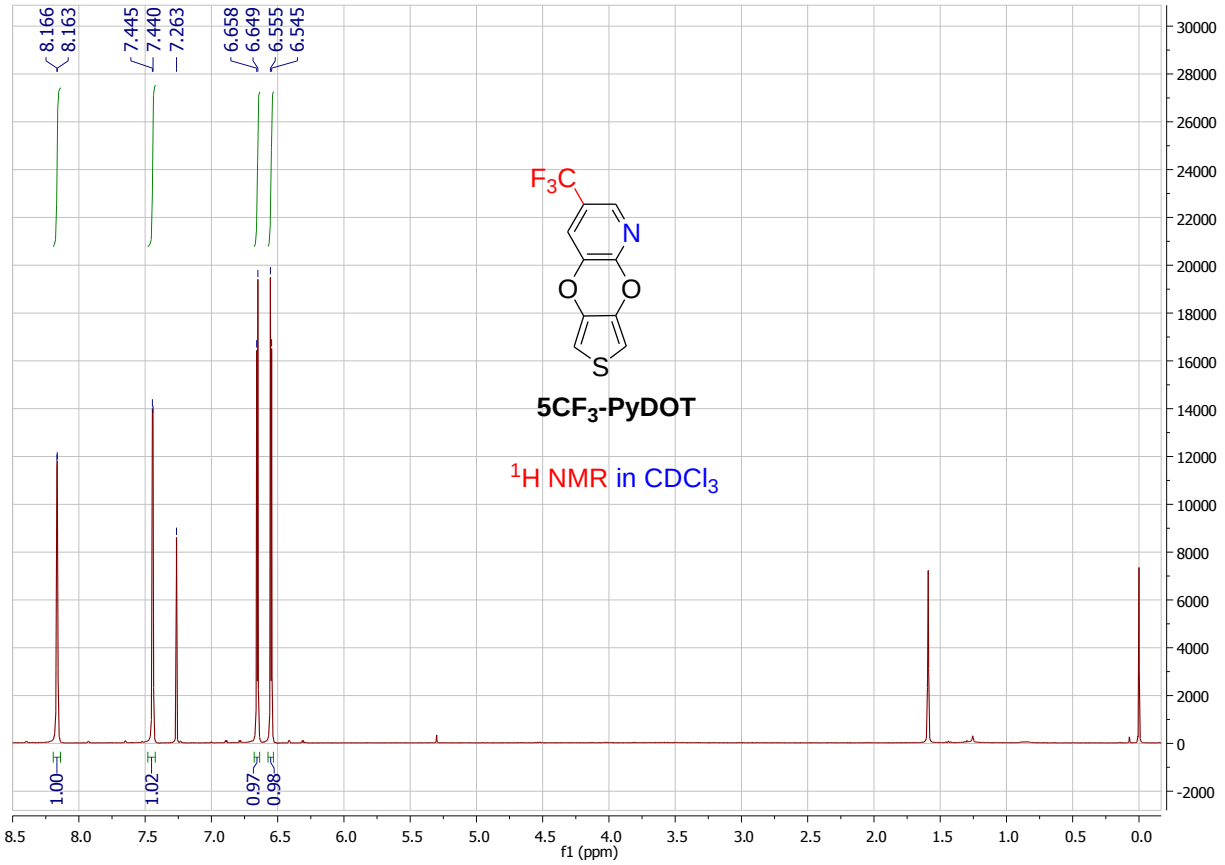


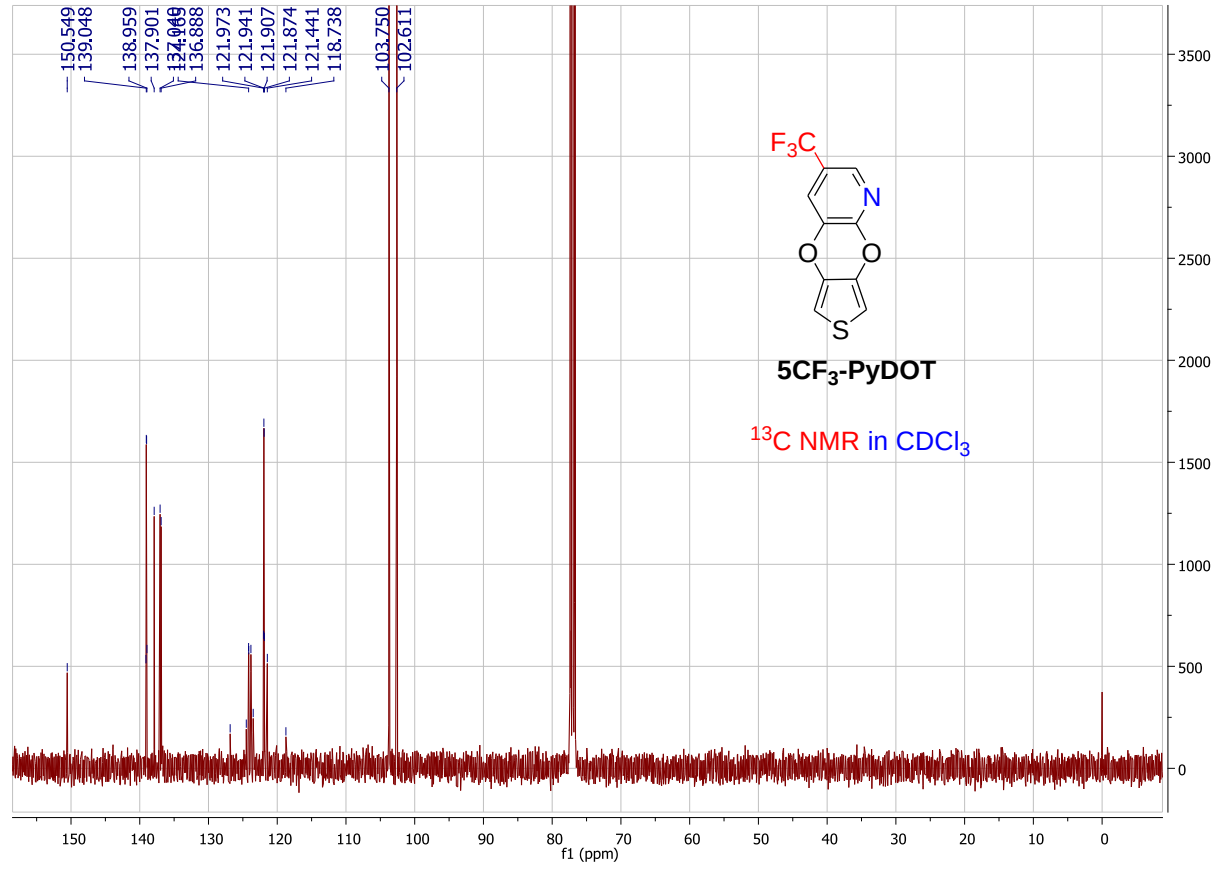
file: ...er_project\SNB-45B\July26\HSQC\ser
expt: <hsqcedetgpsisp2.3>
transmitter freq: 400.131659 MHz
time domain size: 2048 by 256 points
width (F2): 2994.01 Hz = 7.4826 ppm = 1.4619 Hz/pt
number of scans: 2

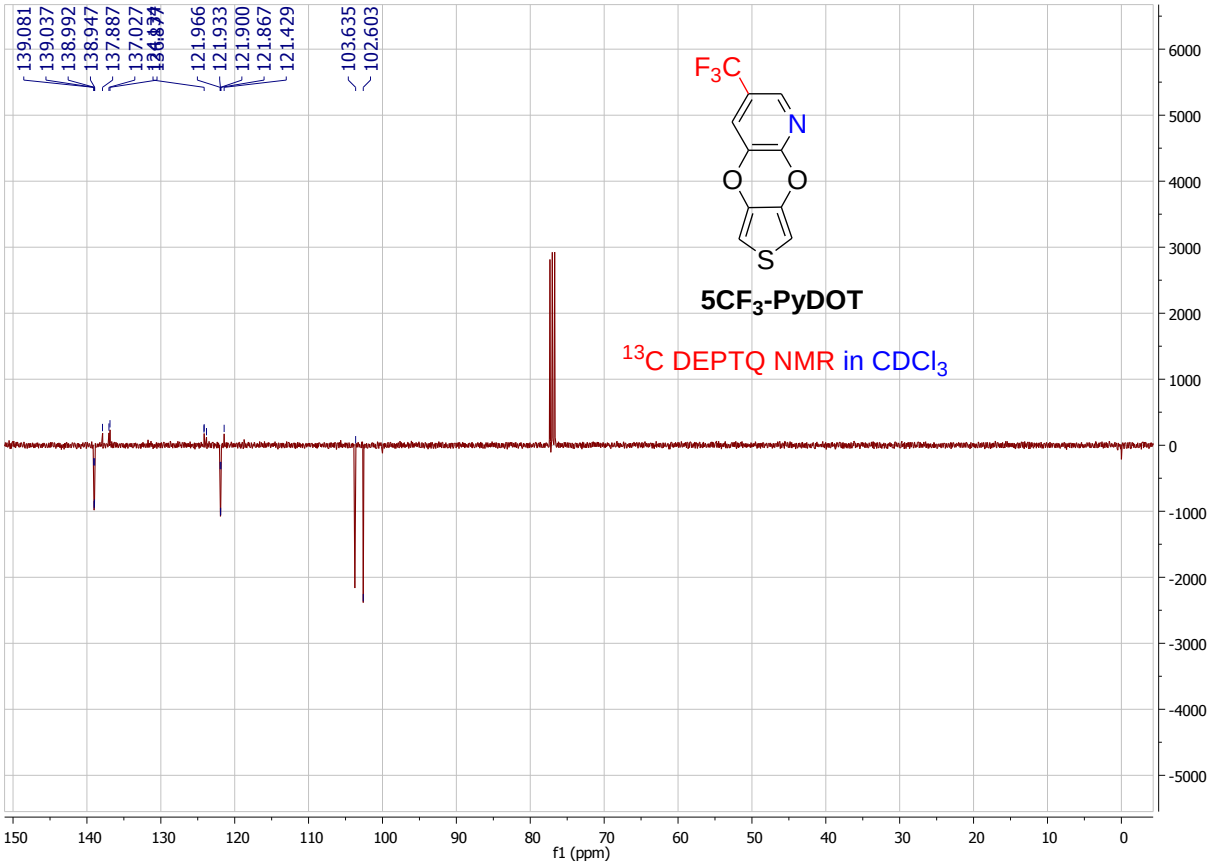
F2: freq. of 0 ppm: 400.1300104 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 35.913 ppm/cm: 0.08975

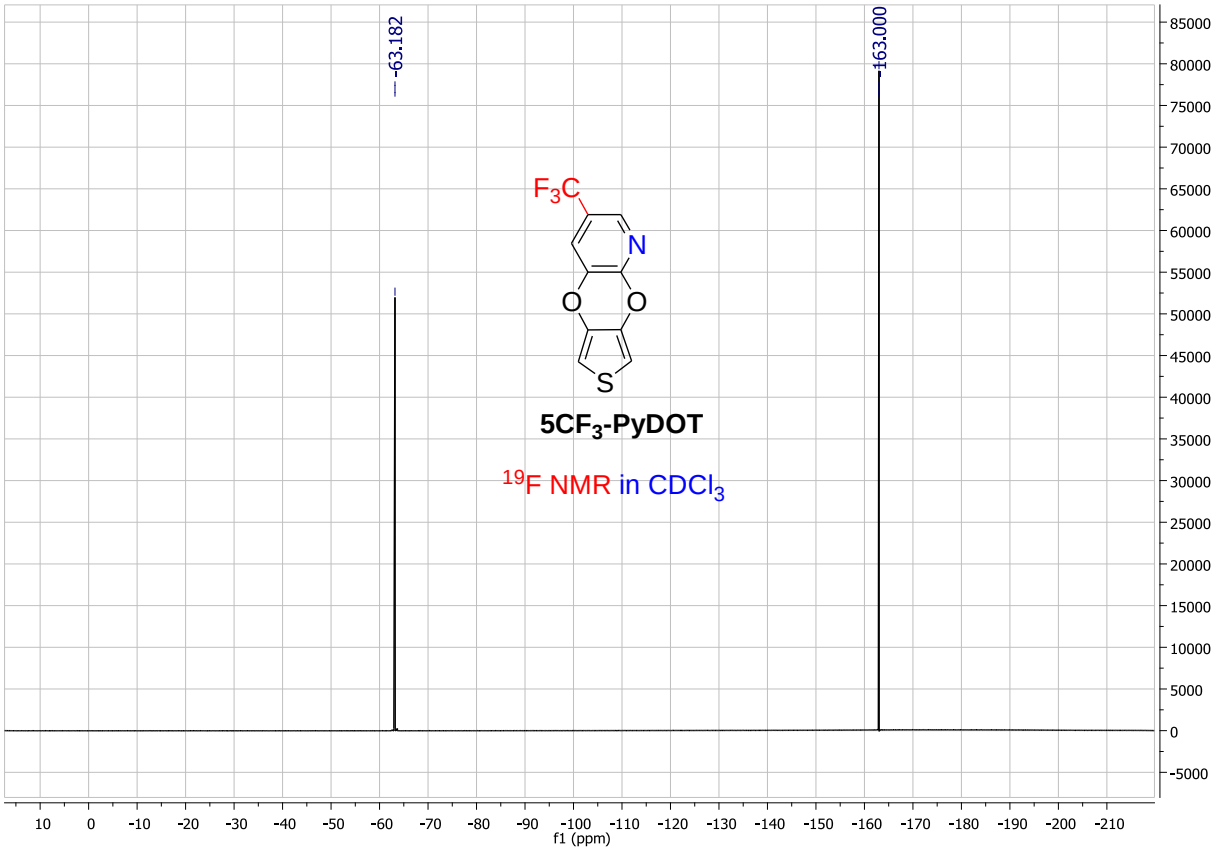
F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 605.202 ppm/cm: 6.01474

3-Trifluoromethylthieno[3',4':5,6][1,4]dioxino[2,3-b]pyridine (**5CF$_3$-PyDOT**)

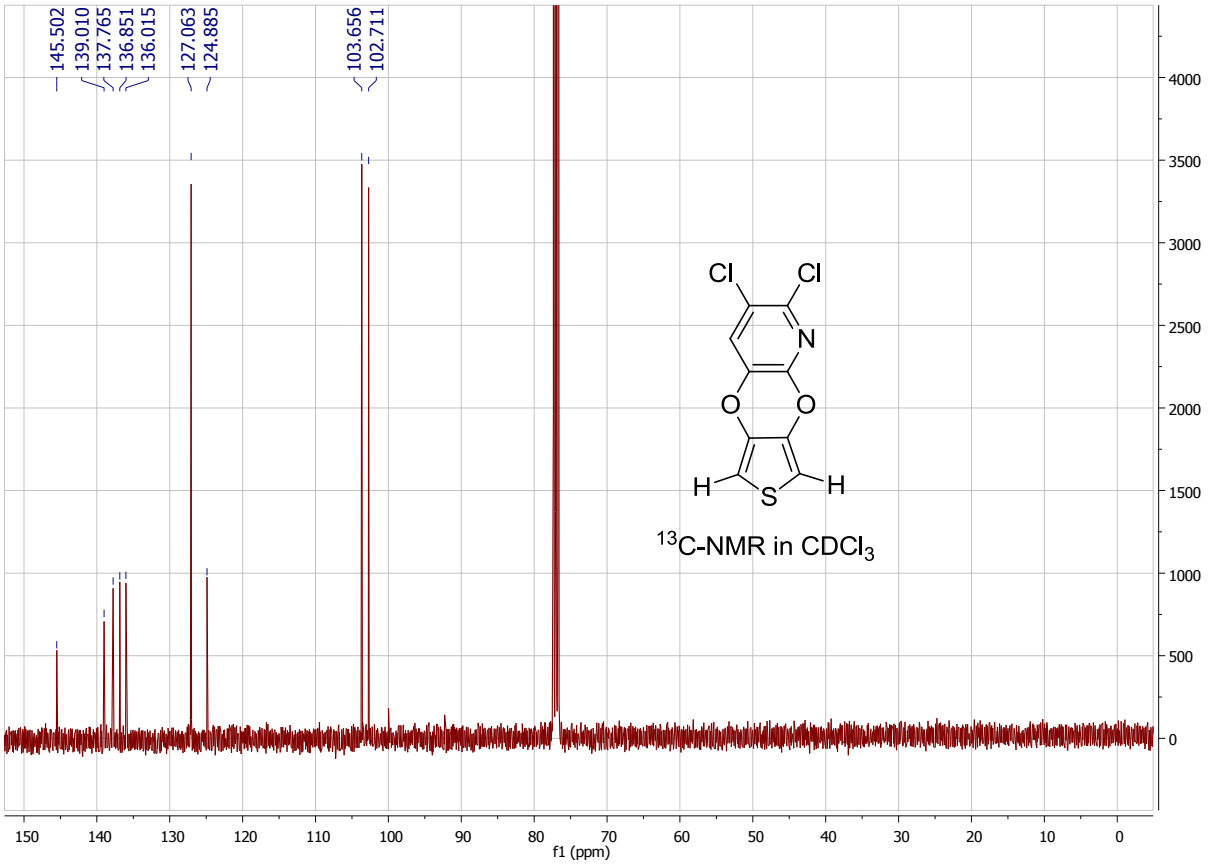


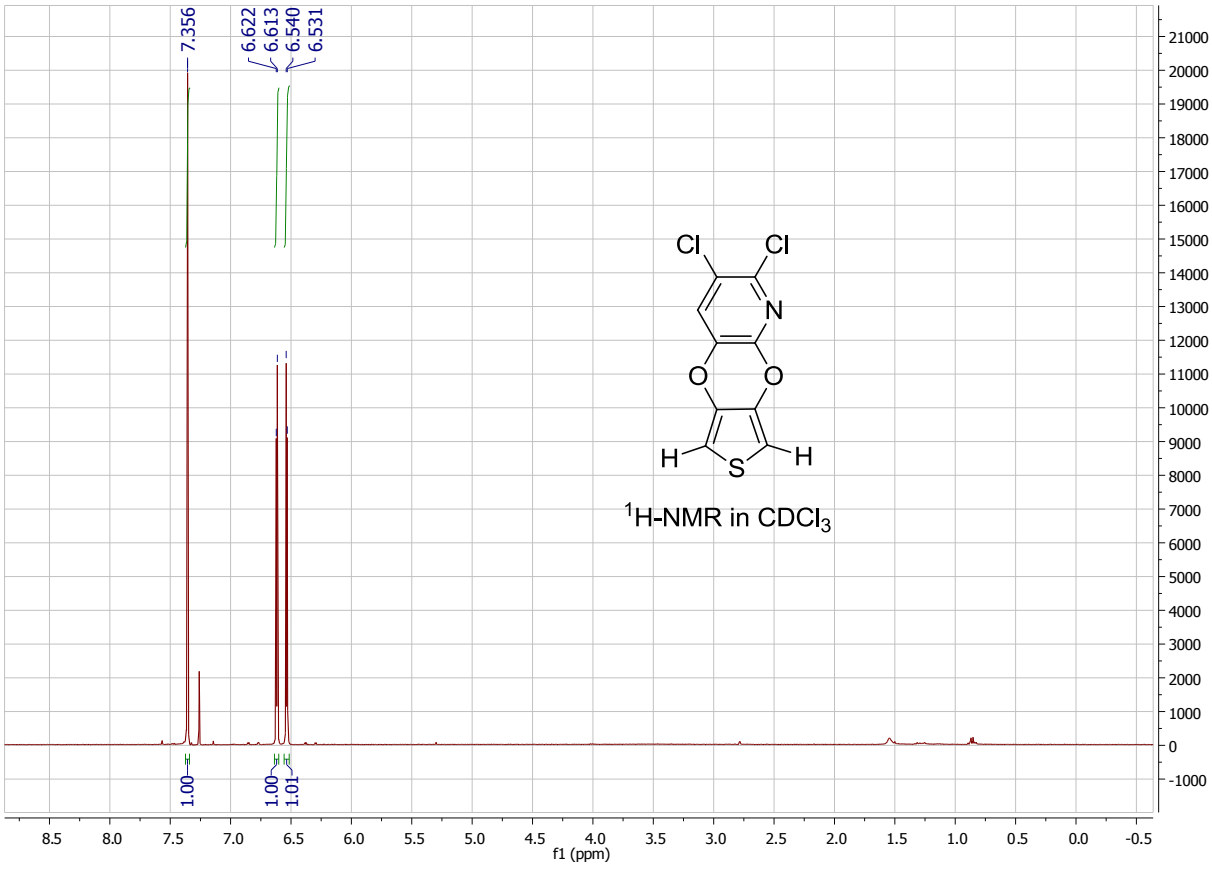



139.081
139.037
138.992
138.947
137.887
137.027
121.966
121.933
121.900
121.867
121.429
103.635
102.603
F3C
N
O
O
S
5CF3-PyDOT
13C DEPTQ NMR in CDCl3
f1 (ppm)

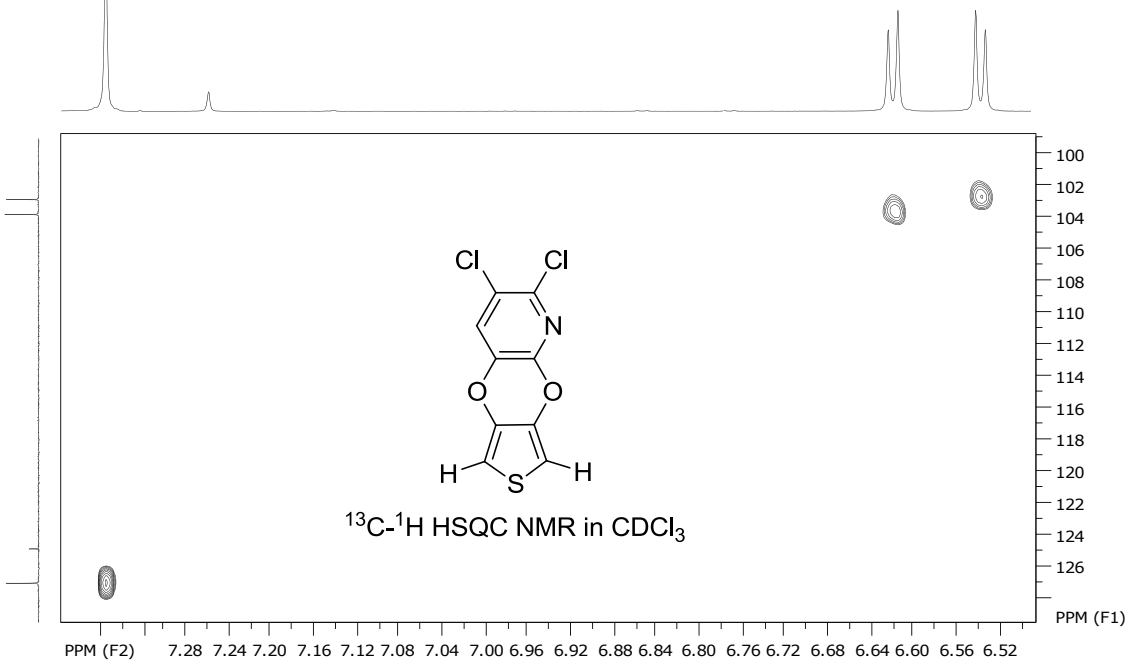

-63.182
-163.000
F3C
N
O
O
S
5CF3-PyDOT
19F NMR in CDCl3
f1 (ppm)

2,3-Dichlorothieno[3',4':5,6][1,4]dioxino[2,3-b]pyridine (**56Cl$_2$-PyDOT**)





SpinWorks 3: Supervisor Name IP
SNB-47BP
HSQC.b CDCl3 {C:\Bruker\TopSpin3.2} sam 10

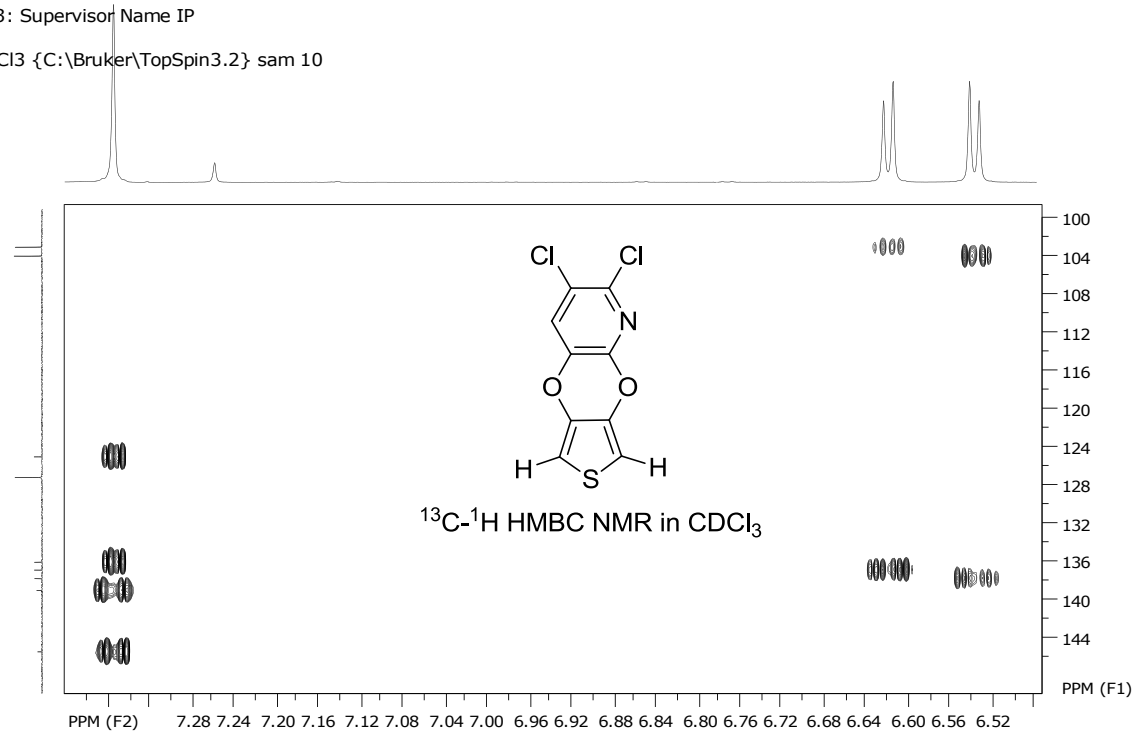


file: ...d\snb_47bp\101-SNB-47BP-HSQC.b\ser
expt: <hsqcedetgpsisp2.3>
transmitter freq: 400.131694 MHz
time domain size: 2048 by 256 points
width (F2): 3048.78 Hz = 7.6194 ppm = 1.4887 Hz/pt
number of scans: 2

F2: freq. of 0 ppm: 400.1300097 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 16.571 ppm/cm: 0.04141

F1: freq. of 0 ppm: 100.6127684 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 281.170 ppm/cm: 2.79438

SpinWorks 3: Supervisor Name IP
SNB-47BP
HMBC.b CDCl3 {C:\Bruker\TopSpin3.2} sam 10

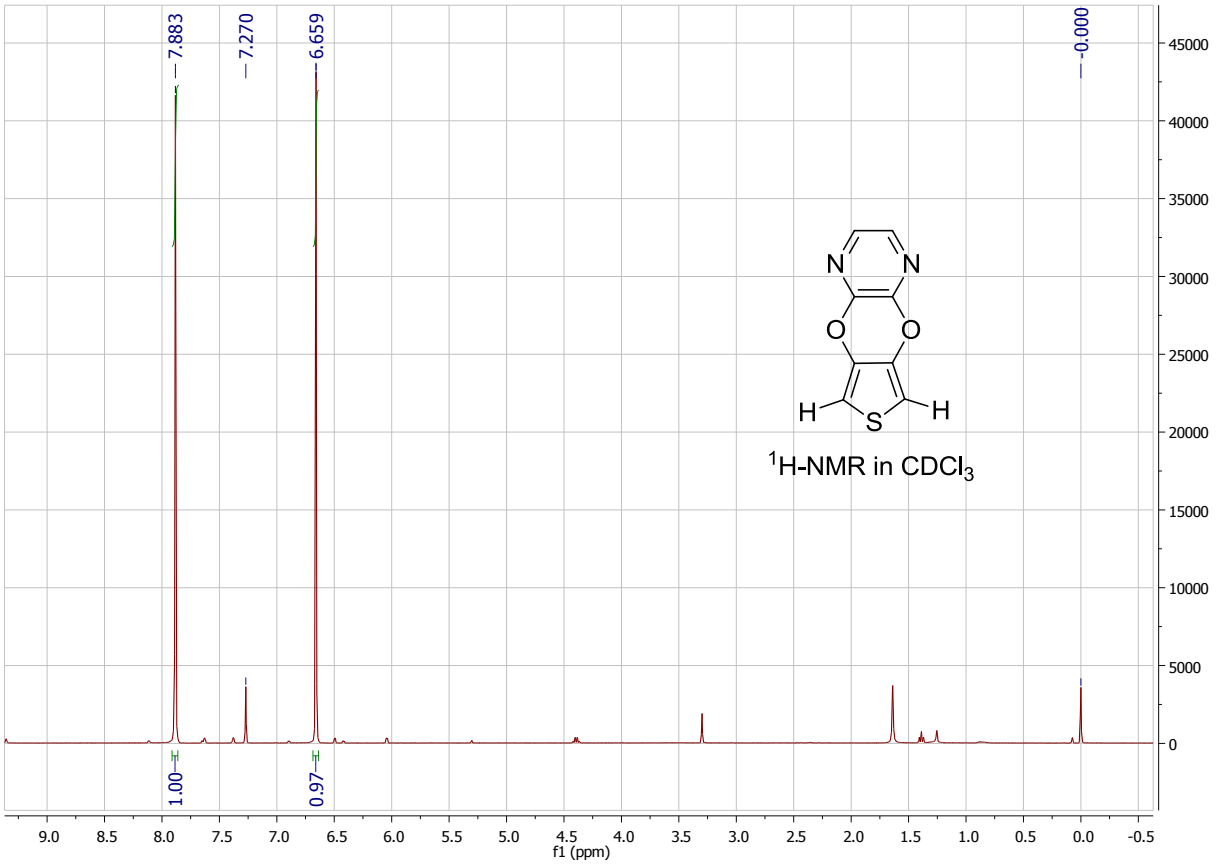


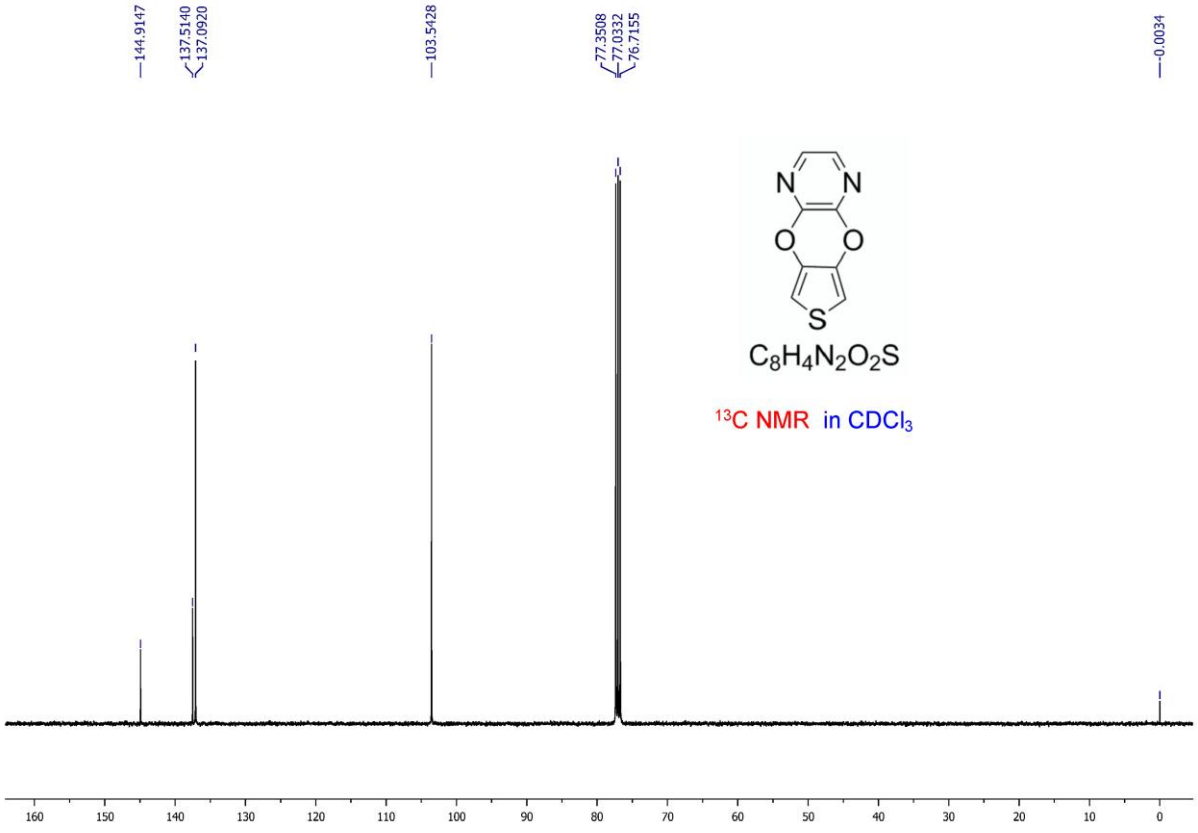
file: ...d\snb_47bp\102-SNB-47BP-HMBC.b\ser
expt: <hmbcetgpl3nd>
transmitter freq: 400.131694 MHz
time domain size: 4096 by 256 points
width (F2): 3048.78 Hz = 7.6194 ppm = 0.7443 Hz/pt
number of scans: 4

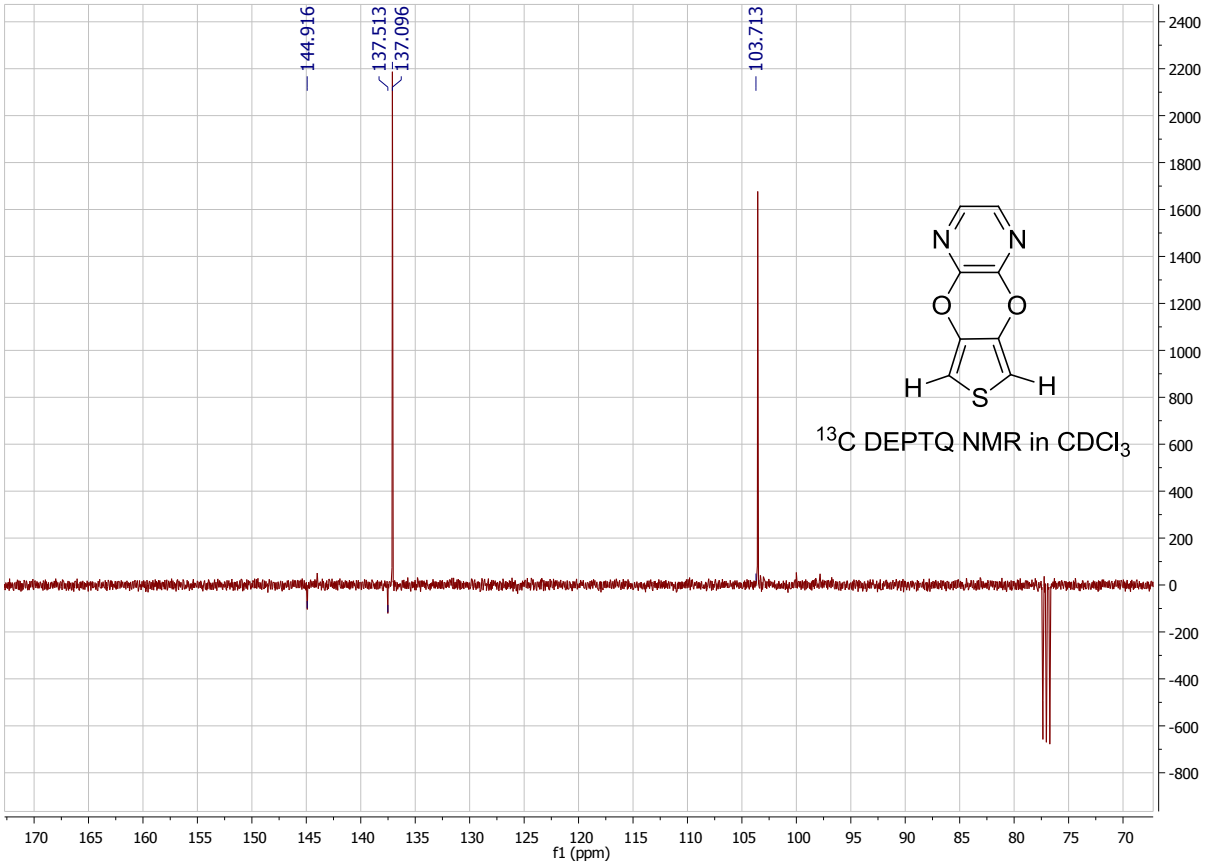
F2: freq. of 0 ppm: 400.1300098 MHz
processed size: 2048 complex points
window function: Sine
shift: 45.0 degrees
Hz/cm: 16.881 ppm/cm: 0.04219

F1: freq. of 0 ppm: 100.6127679 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 468.609 ppm/cm: 4.65708

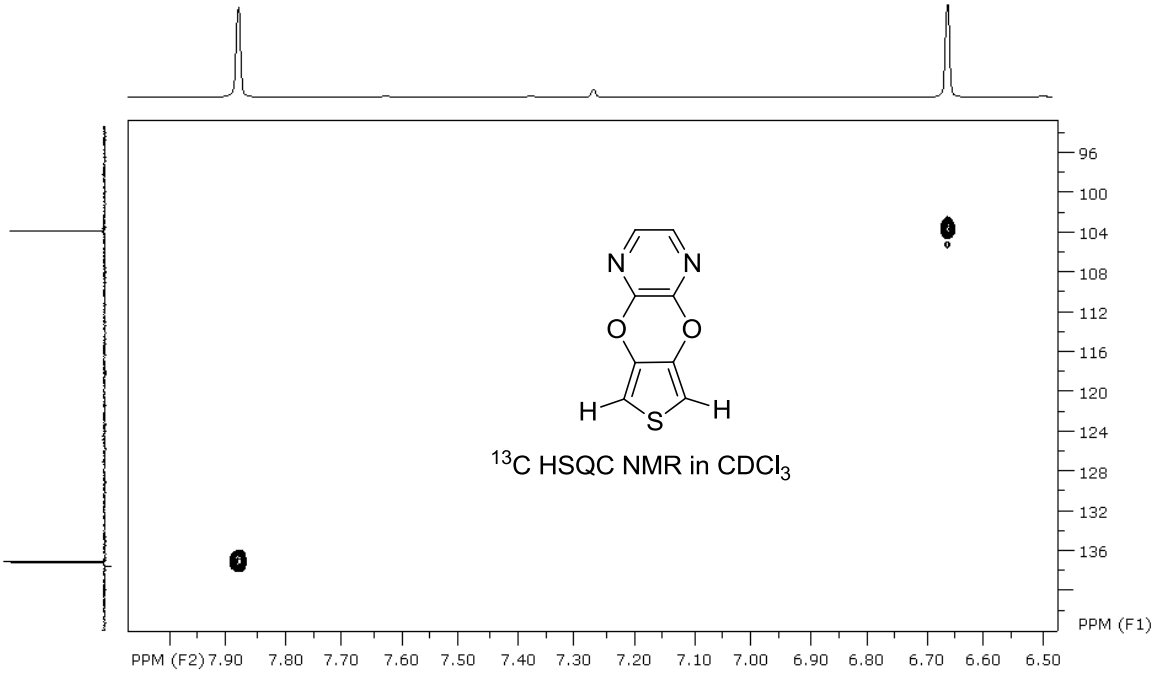
Thieno[3',4':5,6][1,4]dioxino[2,3-b]pyrazine **(PzDOT)**






144.916
137.513
137.096
103.713
N
N
O
O
H
S
H
^{13}C DEPTQ NMR in CDCl$_3$
f1 (ppm)

SpinWorks 3: Supervisor Name IP

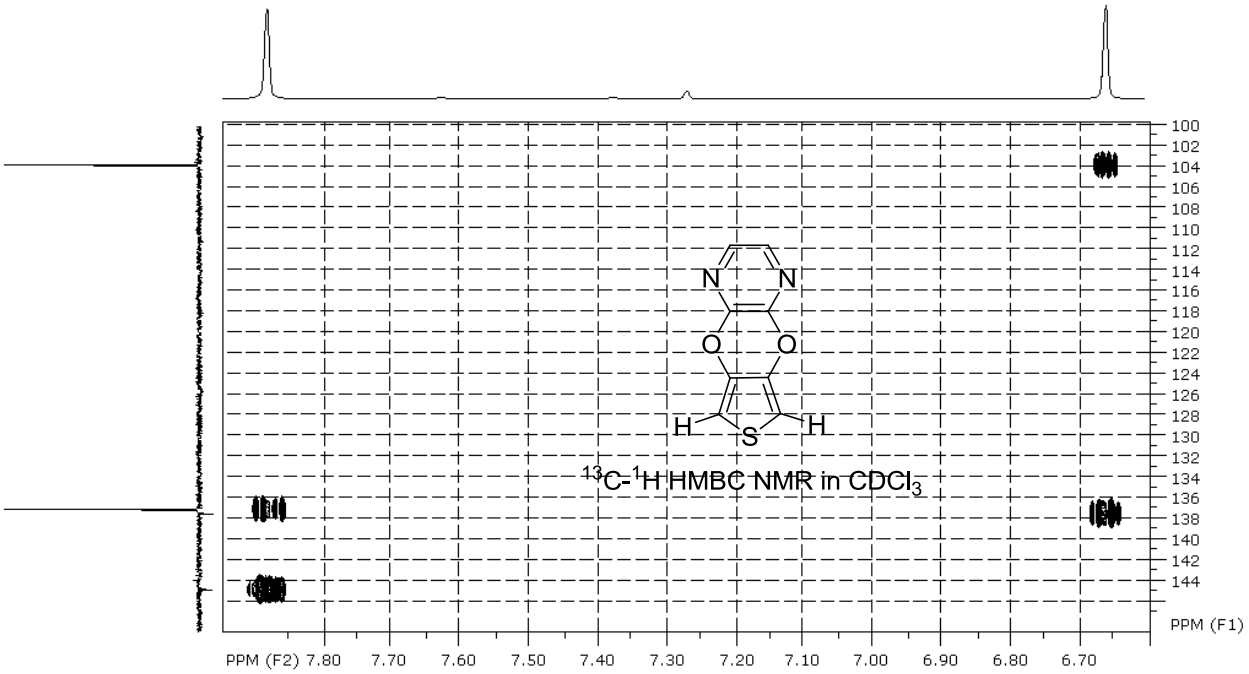


file: ...r_project\SNB-39B\July 19\HSQC\ser
expt: <hsqcedetgpsisp2.3>
transmitter freq: 400.132054 MHz
time domain size: 2048 by 256 points
width (F2): 3846.15 Hz = 9.6122 ppm = 1.8780 Hz/pt
number of scans: 2

F2: freq. of 0 ppm: 400.1300057 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 31.945 ppm/cm: 0.07984

F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 469.355 ppm/cm: 4.66464

SpinWorks 3: HMBC spectrum of SNB-39B

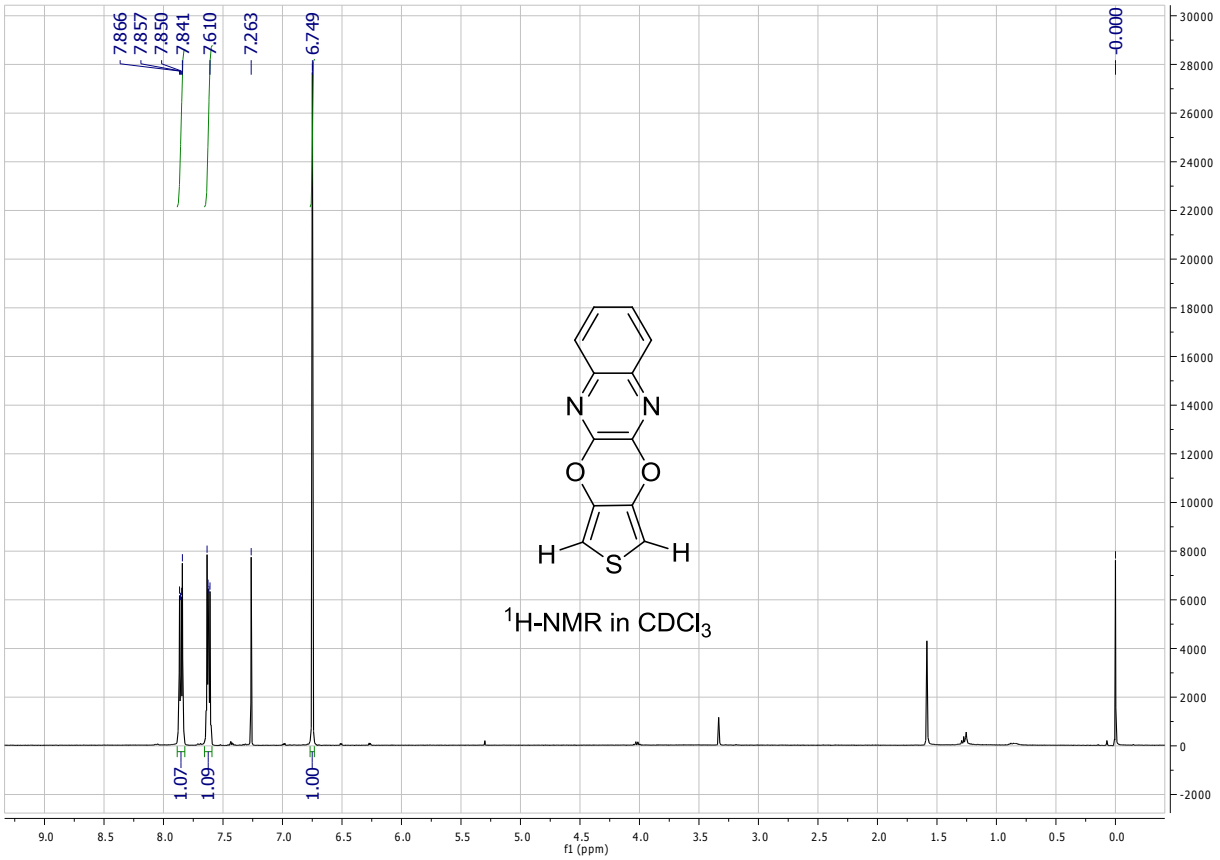


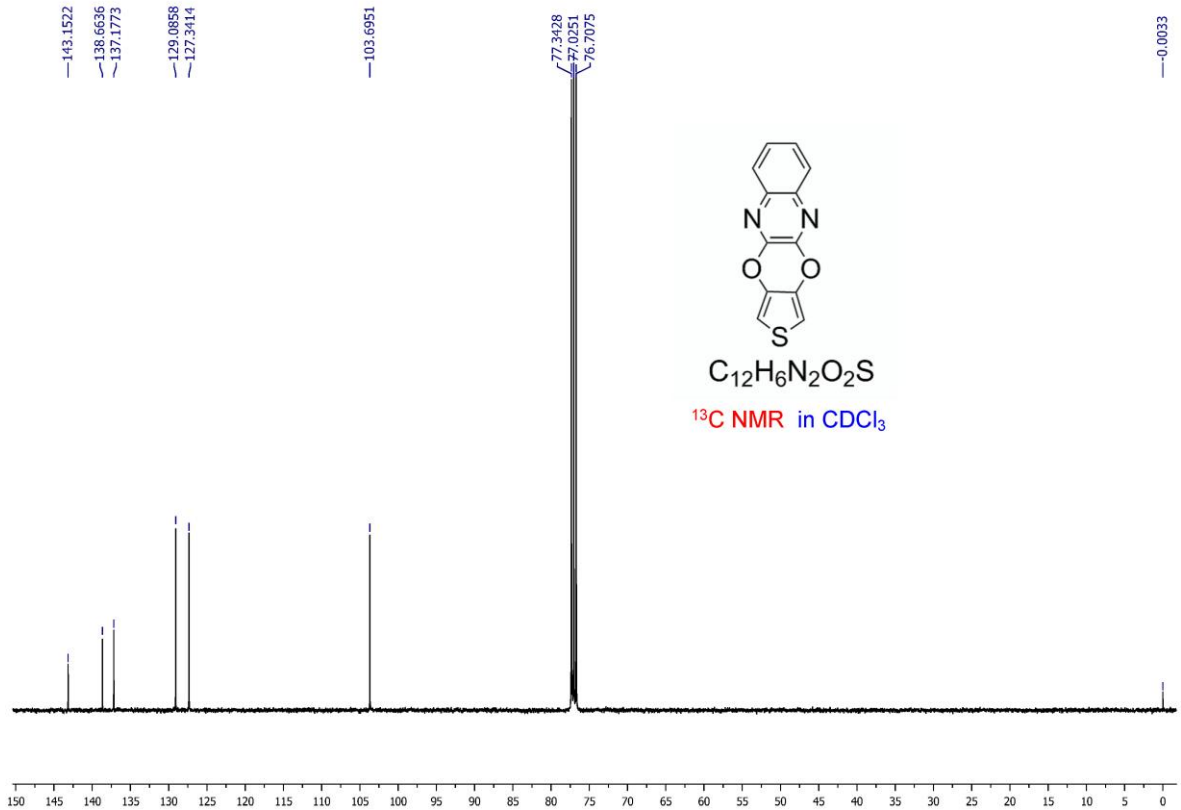
file: ...r_project\SNB-39B\July 19\HMBC\ser
expt: <hmbcetgpl3nd>
transmitter freq: 400.132054 MHz
time domain size: 4096 by 256 points
width (F2): 3846.15 Hz = 9.6122 ppm = 0.9390 Hz/pt
number of scans: 4

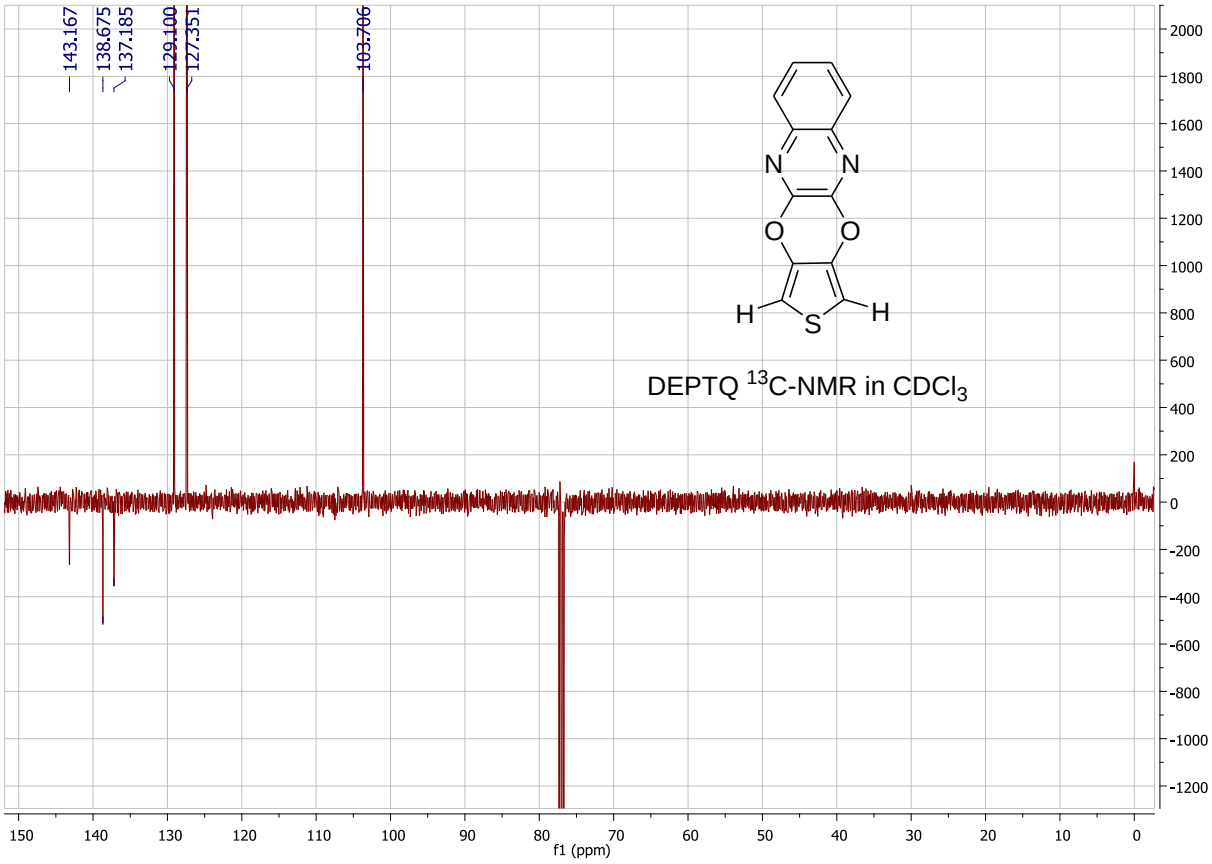
F2: freq. of 0 ppm: 400.1300057 MHz
processed size: 2048 complex points
window function: Sine
shift: 45.0 degrees
Hz/cm: 26.938 ppm/cm: 0.06732

F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 450.079 ppm/cm: 4.47293

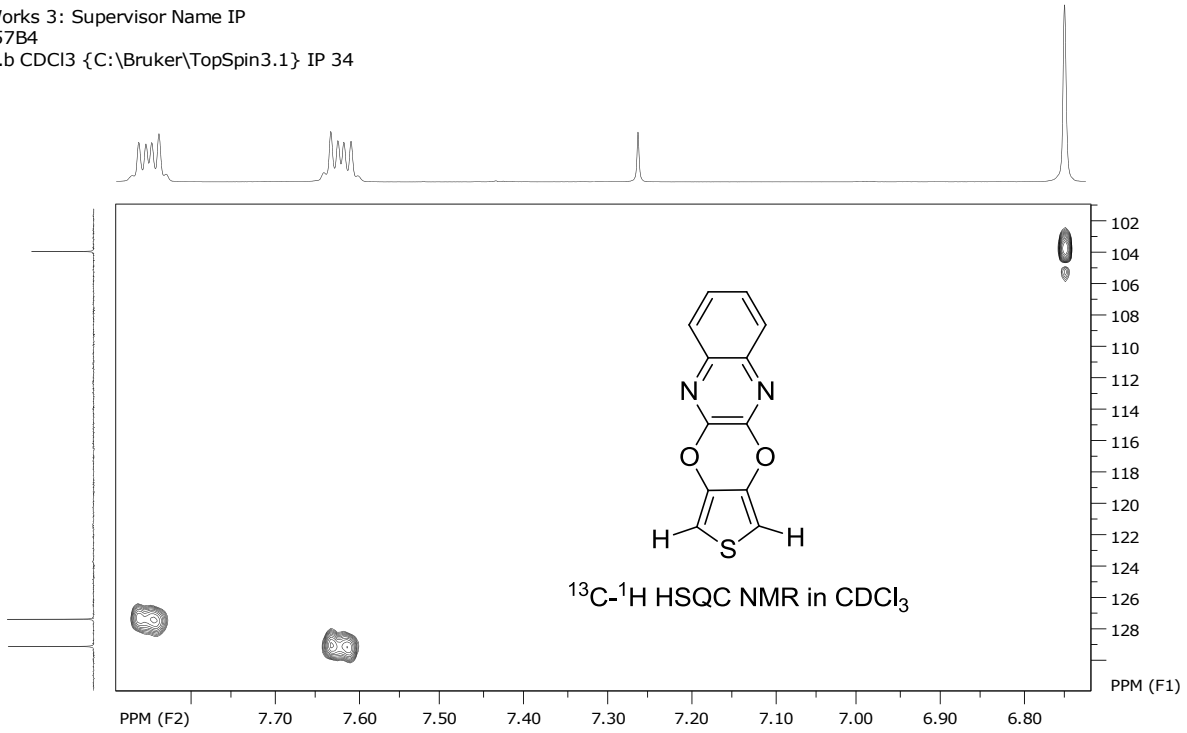
Thieno[3',4':5,6][1,4]dioxino[2,3-b]quinoxaline **(QxDOT)**






143.167
138.675
137.185
129.100
127.351
103.706
N
N
O
O
H
S
H
DEPTQ 13C-NMR in CDCl3
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
-1200
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

SpinWorks 3: Supervisor Name IP
MPK-57B4
HSQC.b CDCl3 {C:\Bruker\TopSpin3.1} IP 34

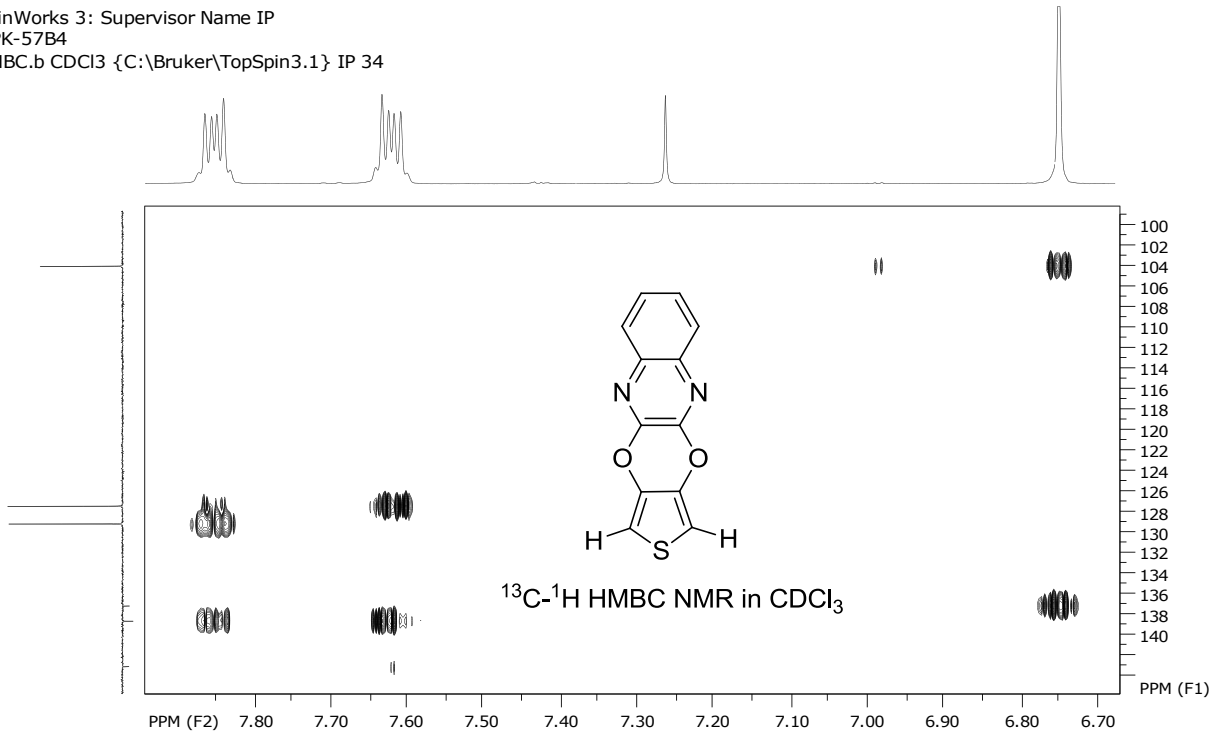


file: ...0-60\mpk_57\53-MPK-57B4-HSQC.b\ser
expt: <hsqcedetgpsisp2.3>
transmitter freq: 400.131763 MHz
time domain size: 2048 by 256 points
width (F2): 3184.71 Hz = 7.9592 ppm = 1.5550 Hz/pt
number of scans: 2

F2: freq. of 0 ppm: 400.1300084 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 21.302 ppm/cm: 0.05324

F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 283.687 ppm/cm: 2.81940

SpinWorks 3: Supervisor Name IP
MPK-57B4
HMBC.b CDCl3 {C:\Bruker\TopSpin3.1} IP 34



file: ...0-60\mpk_57\54-MPK-57B4-HMBC.b\ser
expt: <hmbcetgpl3nd>
transmitter freq: 400.131763 MHz
time domain size: 4096 by 256 points
width (F2): 3184.71 Hz = 7.9592 ppm = 0.7775 Hz/pt
number of scans: 4

F2: freq. of 0 ppm: 400.1300084 MHz
processed size: 2048 complex points
window function: Sine
shift: 45.0 degrees
Hz/cm: 23.096 ppm/cm: 0.05772

F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 435.681 ppm/cm: 4.32984