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Supporting Information for

Thioether- and sulfone-functionalized dibenzopentalenes as n-channel semiconductors for organic field-effect transistors

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Table of contents

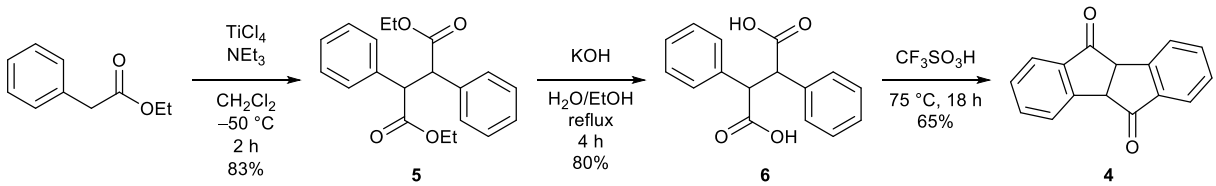
1. Materials and methods S3
2. Synthetic manipulations S5
   2.1 Synthesis of of diketone precursor **6** S5
3. NMR spectra S7
4. Thermal measurements S17
   4.1 Thermogravimetric analysis of **2a–d** and **3** S17
   4.2 Differential scanning calorimetry of **2a–d** and **3** S17
5. Cyclic voltammograms S19
6. FET device fabrication S24
7. Single-crystal X-ray diffraction S25
   7.1 Experimental setup S25
   7.2 Single-crystal X-ray diffraction data for **2b** S25
      7.2.1 Solution and refinement S26
   7.3 Single-crystal X-ray diffraction data for **2c** S27
      7.3.1 Solution and refinement S27
8. DFT calculations S29
   8.1 Cartesian coordinates of calculated structures S29
9. References S33

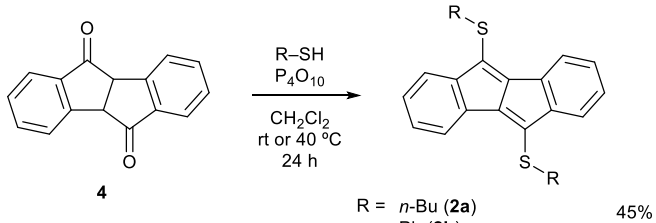
1. Materials and methods

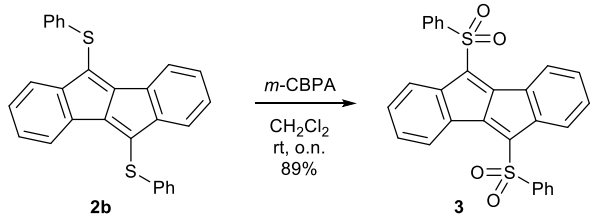
Chemicals were purchased from ABCR, Acros-Organics, Alfa-Aesar, ChemPur, Flurochem, Roth, Sigma-Aldrich or TCI and used directly without further purification unless otherwise noted. Moisture- or oxygen-sensitive reactions were carried out in dried glassware, heated under vacuum (10^{-3} mbar), using standard Schlenk techniques in a dry argon atmosphere (Argon 5.0 from Sauerstoffwerke Friedrichshafen). Anhydrous solvents (CH_2Cl_2) were obtained from an M. BRAUN solvent purification system (MB-SPS-800) and stored over 3 Å molecular sieves for a minimum duration of 48 h before use. Other anhydrous solvents were obtained by drying over activated molecular sieves (3 Å) for several days.[1] Cyclohexane for flash chromatography were purchased in technical grade and purified by distillation using a rotary evaporator. Other solvents were purchased and used in analytical or HPLC grade. Analytical thin layer chromatography was carried out using silica gel-coated aluminum plates with a fluorescence indicator (Merck 60 F_{254}). Detection was carried out by using short wave UV light (λ_{max} = 254 nm). Flash column chromatography was carried out using silica gel 60, grain size 40–63 µm (230–400 mesh) from Machery-Nagel. NMR spectra were recorded at 300 K, unless otherwise noted, on the following spectrometers: Bruker *Avance III HD* [300.1 MHz (^{1}H), 282.4 MHz (^{19}F)], Bruker *Avance II* [400.1 MHz (^{1}H), 100.6 MHz (^{13}C), 376.5 MHz (^{19}F)] and Bruker *Avance III HD* [500.3 MHz (^{1}H), 125.8 MHz (^{13}C), 470.8 MHz (^{19}F)]. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the signal of tetramethylsilane (δ = 0.00 ppm). ^{1}H NMR spectra are referenced to tetramethylsilane as an internal standard or the residual solvent signal of the respective solvent: $CDCl_3$: δ = 7.26 ppm; CD_2Cl_2: δ = 5.32 ppm, DMSO-d_6: δ = 2.50 ppm, ^{13}C NMR spectra are referenced to the following signals: $CDCl_3$: δ = 77.16 ppm; CD_2Cl_2: δ = 53.84 ppm DMSO-d_6: δ = 39.52 ppm.[2] ^{19}F NMR spectra are referenced to tetramethylsilane following the IUPAC recommendations.[3] Analysis followed first order, and the following abbreviations for multiplets were used: singlet (s), broad singlet (br. s), doublet (d), triplet (t), quartet (q), septet (sept), multiplet (m) and combinations thereof *i.e.* doublet of doublets (dd). Coupling constants (*J*) are given in Hertz [Hz]. High resolution mass spectra were measured on a Thermo Fisher Scientific inc. Exactive or LCQ Advantage via electron spray ionization (ESI) or atmospheric pressure chemical ionization (APCI) with an orbitrap analyzer. UV/Vis absorption spectra were measured on a Perkin Elmer Lambda 950. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 C/CD and differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204 F1 Phoenix. Cyclic voltammograms (CVs) were measured inside an argon filled glovebox using a PGSTAT128N by Metrohm Autolab. As working electrode a glassy carbon disc electrode (2 mm diameter) was used, as counter electrode a platinum rod and as reference electrode a Ag/$AgNO_3$ electrode containing a silver wire immersed in an inner chamber filled with 1 M $AgNO_3$ and 0.1 M *n*-Bu_4NPF_6 in anh. CH_3CN. The analyte solution contained 10 mL of solvent (anh. CH_2Cl_2) with 0.1 M *n*-Bu_4NPF_6 and the specified analyte concentration. The

ferrocene/ferrocenium redox couple was used as internal reference. HOMO and LUMO levels were calculated using the following equations: E_{LUMO} (eV) = $-(E_{i,Fc}+x_{Red})$ (with $E_{i,Fc}$ = 4.8 eV (ionization energy of ferrocene)[4]; x_{Red} = onset of the first reduction peak, calibrated vs. Fc/Fc^+ in eV), E_{HOMO} (eV) = $-(E_{i,Fc}+x_{Ox})$ (with x_{Ox} = onset of the first oxidation peak, calibrated vs. Fc/Fc^+ in eV).

2. Synthetic manipulations

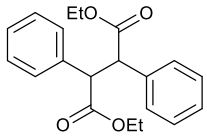






2.1 Synthesis of of diketone precursor 6

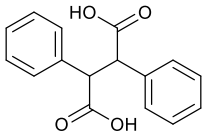
Diethyl 2,3-diphenylsuccinate (5)



The synthesis was carried out following a procedure by MATSUMURA *et al.*[5] $TiCl_4$ (15.0 mL, 26.0 g, 137 mmol, 2.05 eq.) was slowly added to a solution of ethyl phenylacetate (10.0 g, 66.6 mmol) in anh. CH_2Cl_2 (100 mL) at −50 °C. The reaction was kept at −50 °C for 45 min. Anh. NEt_3 (19.5 mL, 14.0 g, 141 mmol, 2.11 eq.) was added to the yellow suspension, which turned black and was stirred for another 1.5 h at −50 °C. The reaction was quenched with sat. aq. NH_4Cl (50 mL) and was slowly warmed to rt afterwards. The dark purple mixture was extracted with CH_2Cl_2 (4 × 100 mL), dried ($MgSO_4$) and evaporated to dryness. Flash chromatography (cyclohexane/ethyl acetate: 8/1, 5/1, 3/1) yielded diester **5** as a colorless solid (8.90 g, 83%).

***R*f** 0.62/0.54 (*d*/*l*- and *meso*-isomer; cyclohexane/EtOAc: 5/1); **^{1}H NMR** (500 MHz, $CDCl_3$, mixture of diastereomers): δ 7.20–6.95 (m, 10H), 4.25–4.06 (m, 6H), 1.20 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$, main diastereomer): δ 173.2, 136.0, 128.5, 128.5, 127.5, 61.3, 55.1, 14.2; **HRMS** (pos. ESI): *m/z* calcd for $C_{20}H_{22}O_4Na$ 349.1410 $[M+Na]^+$, found 349.1413.

2,3-Diphenylsuccinic acid (6)



Diester **5** (8.80 g, 27.0 mmol) and KOH (11.0 g, 196 mmol, 7.30 eq.) were refluxed in a mixture of EtOH (100 mL) and H_2O (100 mL) for 4 h. EtOH was removed under vacuum and the remaining aq. solution was cooled to 0 °C. After addition of aq. HCl (10% w/w) a yellowish solid precipitated, which was filtered over a fritted funnel. The residue was washed with H_2O (100 mL) and *n*-pentane (20 mL). After drying under reduced pressure, diacid **6** could be obtained as a light yellow solid (5.83 g, 80%). **^{1}H NMR** (400 MHz, DMSO-d_6, mixture of diastereomers): δ 12.47 (br. s, 2H), 7.49–7.06 (m, 10H), 4.26–4.14 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6, main diastereomer): δ 173.9, 136.5, 128.3, 128.1, 126.9, 53.8; **HRMS** (pos. ESI): *m/z* calcd for $C_{16}H_{14}O_4Na$ 293.0784 $[M+Na]^+$, found 293.0788; **HRMS** (neg. ESI): *m/z* calcd for $C_{16}H_{13}O_4$ 269.0819 $[M-H]^-$, found 269.0818.

3. NMR spectra

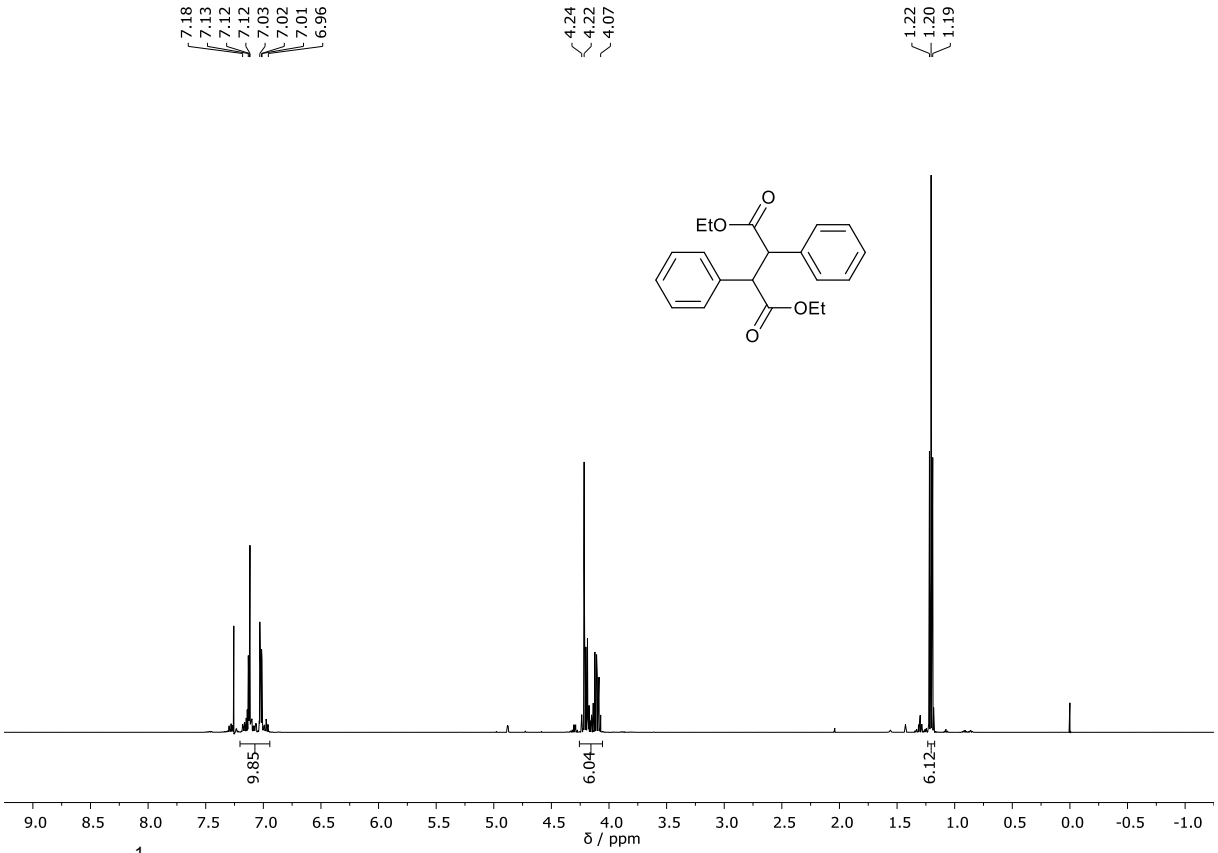


Figure S1. ^{1}H NMR spectrum of **5** ($CDCl_3$, 500 MHz).

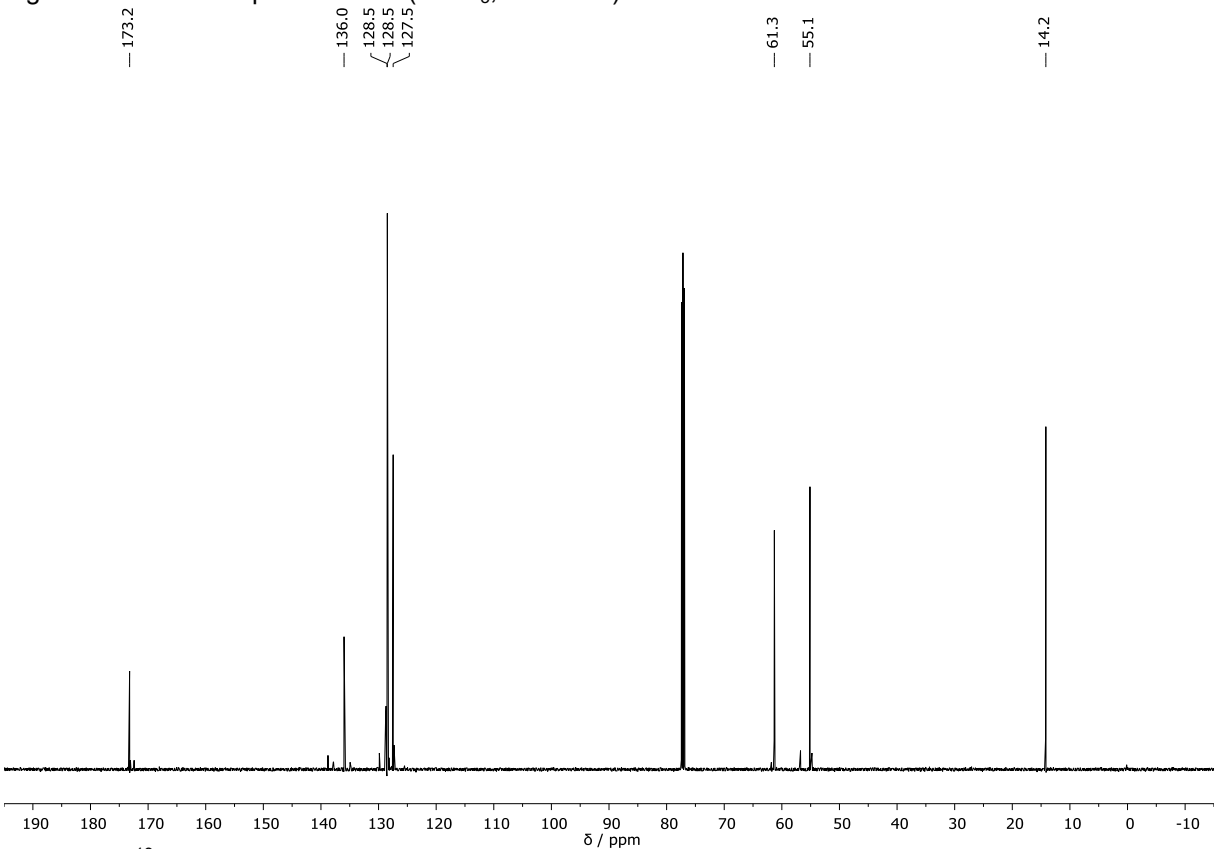


Figure S2. ^{13}C NMR spectrum of **5** ($CDCl_3$, 126 MHz).

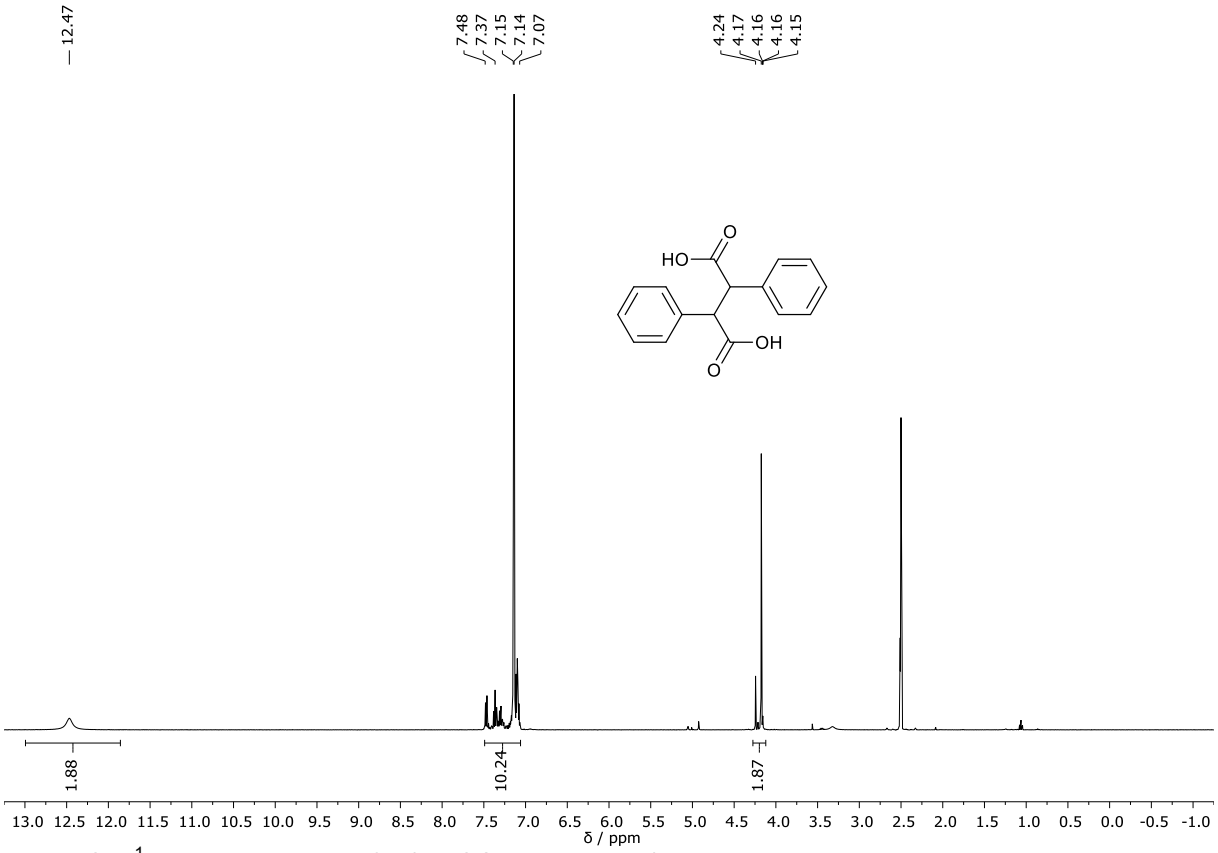


Figure S3. ^{1}H NMR spectrum of **6** (DMSO-d_6, 400 MHz).

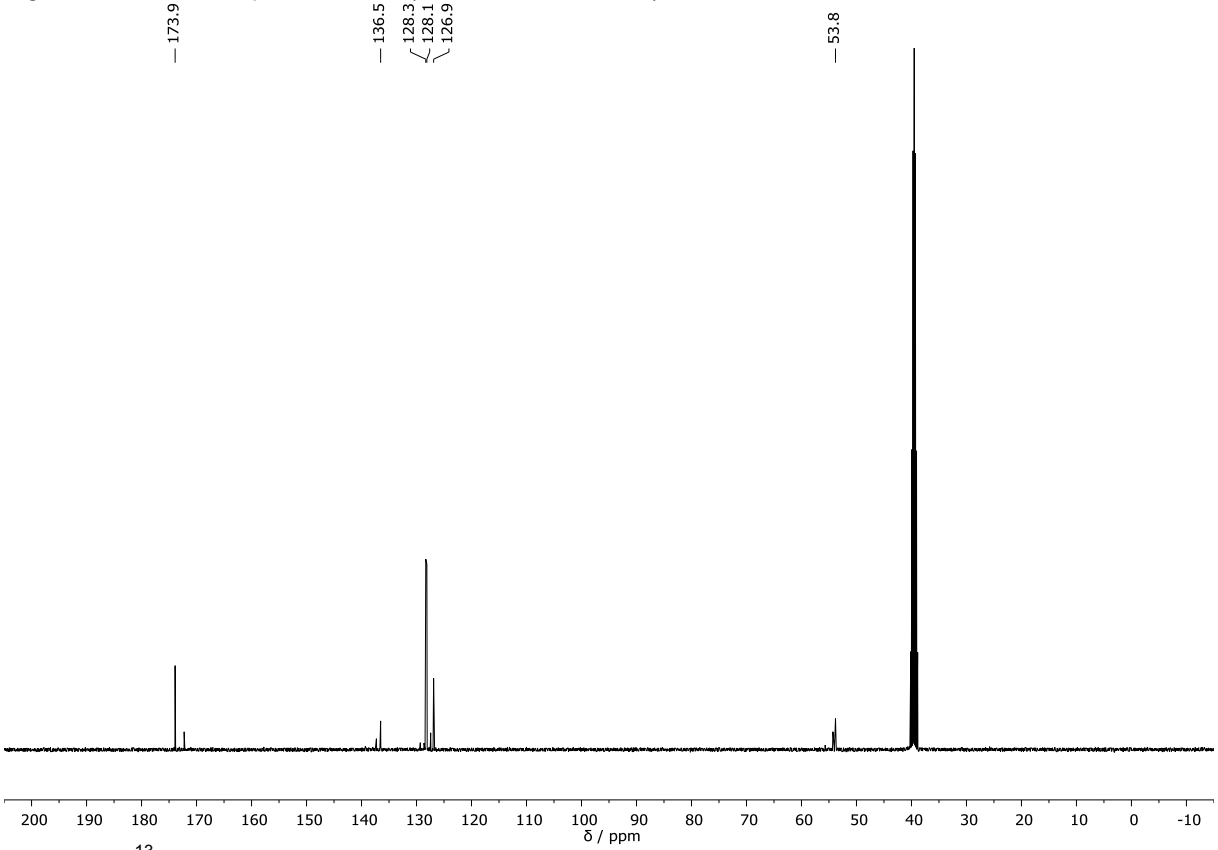


Figure S4. ^{13}C NMR spectrum of **6** (DMSO-d_6, 101 MHz).

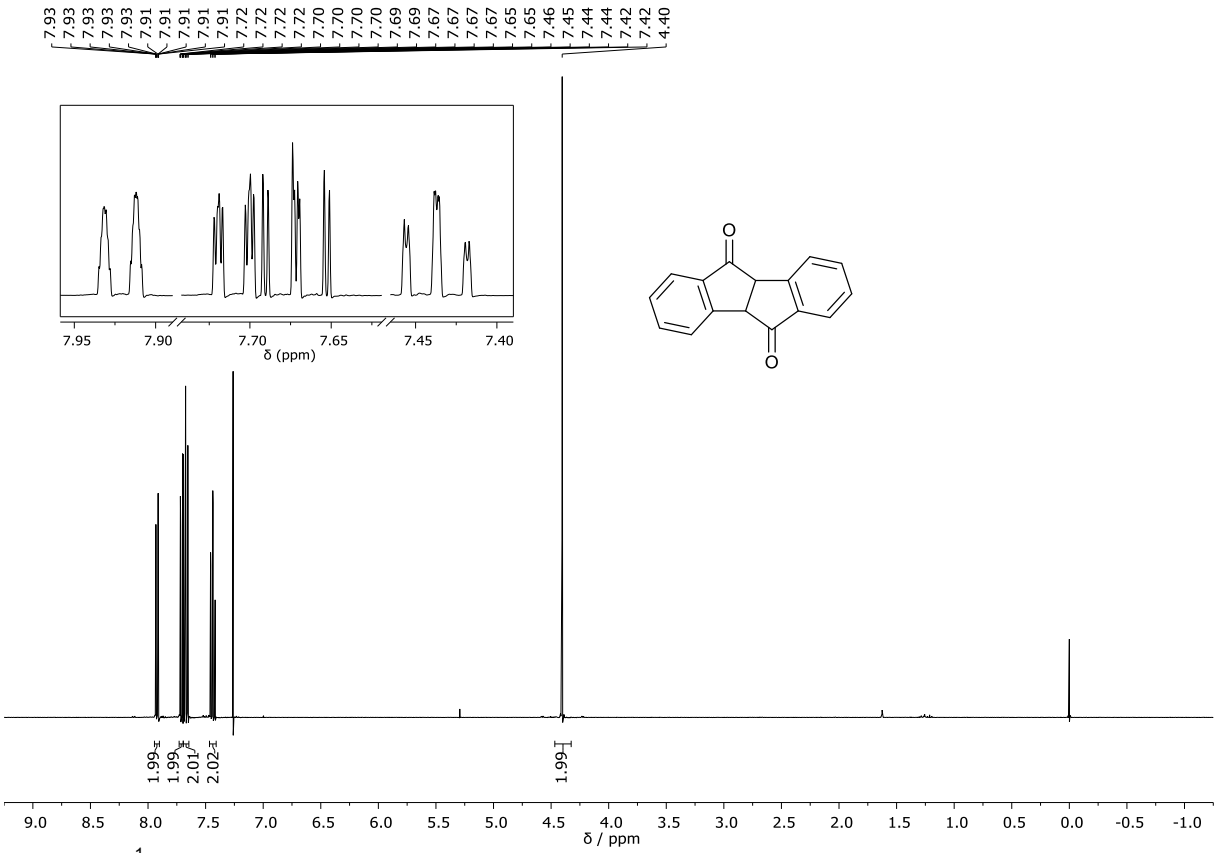


Figure S5. ^{1}H NMR spectrum of **4** ($CDCl_3$, 400 MHz).

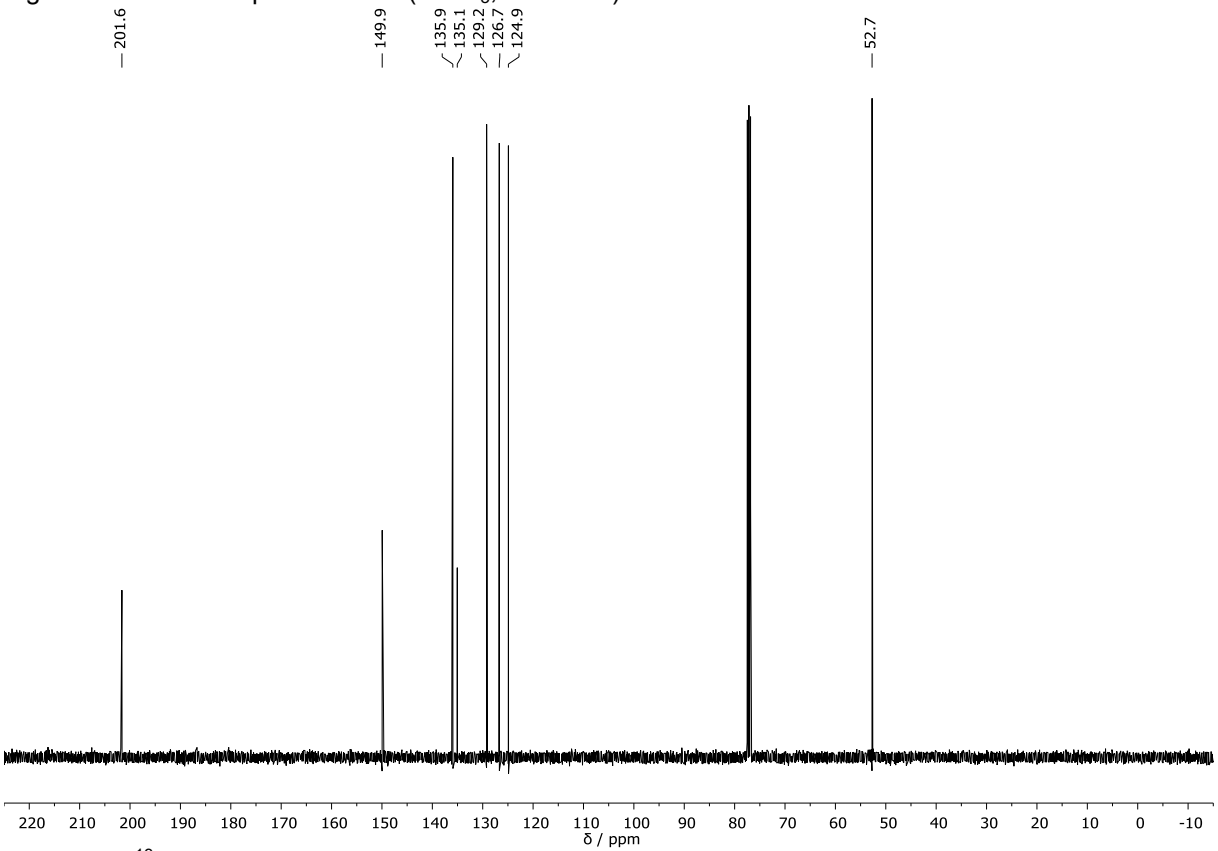


Figure S6. ^{13}C NMR spectrum of **4** ($CDCl_3$, 101 MHz).

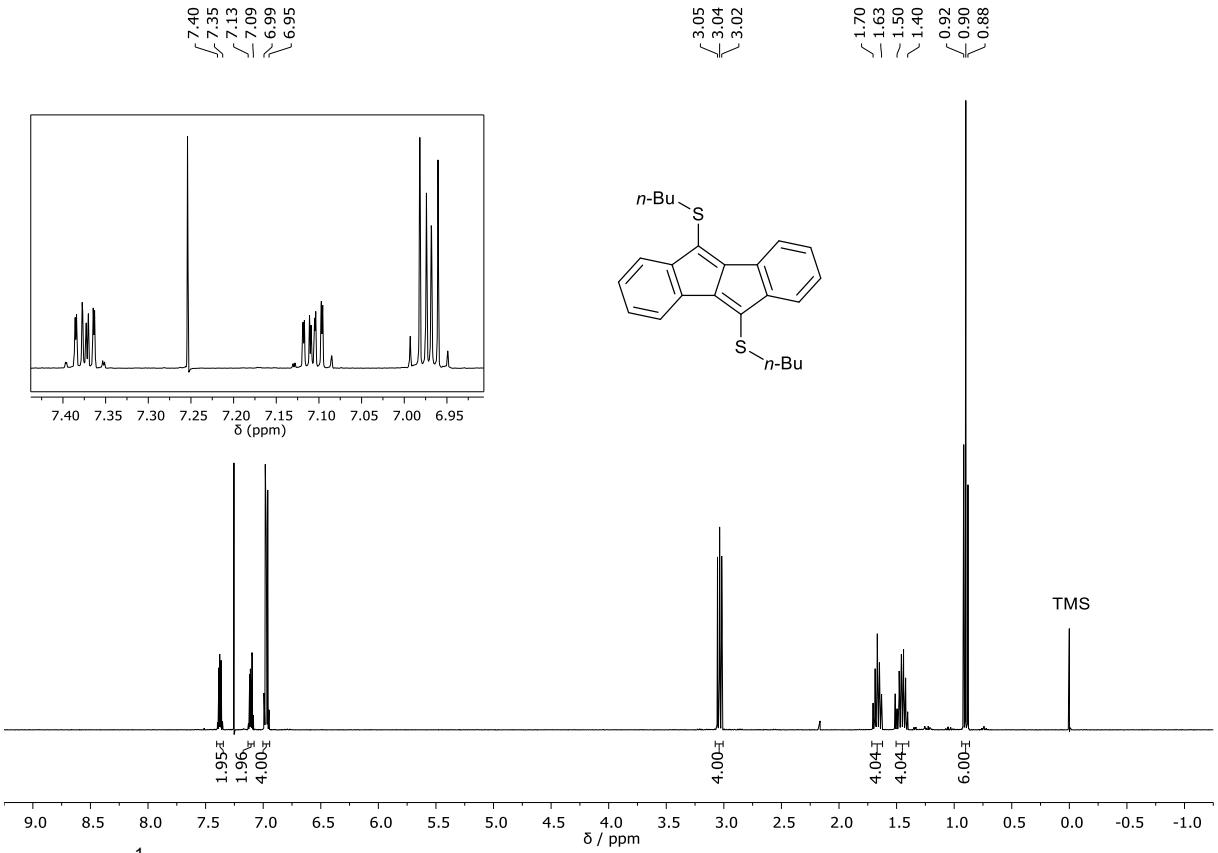


Figure S7. ^{1}H NMR spectrum of **2a** ($CDCl_3$, 400 MHz).

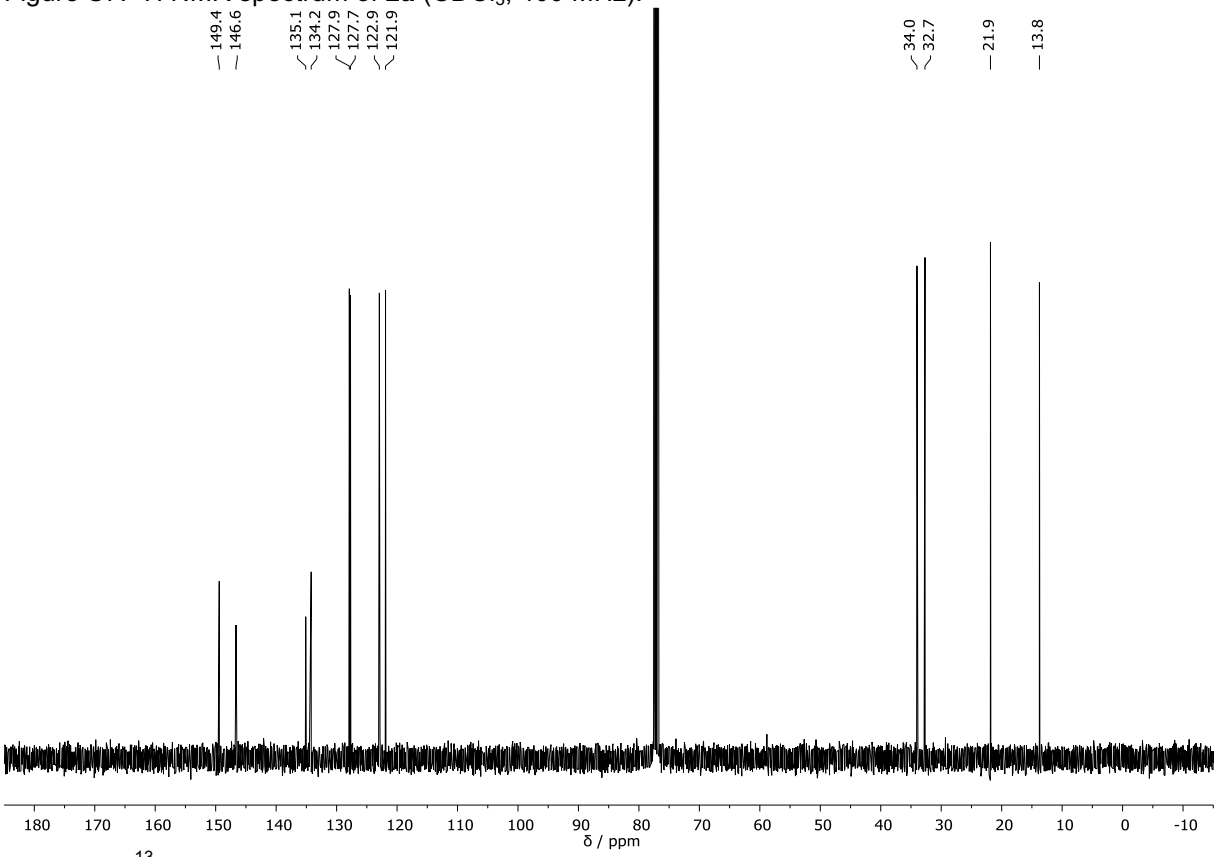


Figure S8. ^{13}C NMR spectrum of **2a** ($CDCl_3$, 101 MHz).

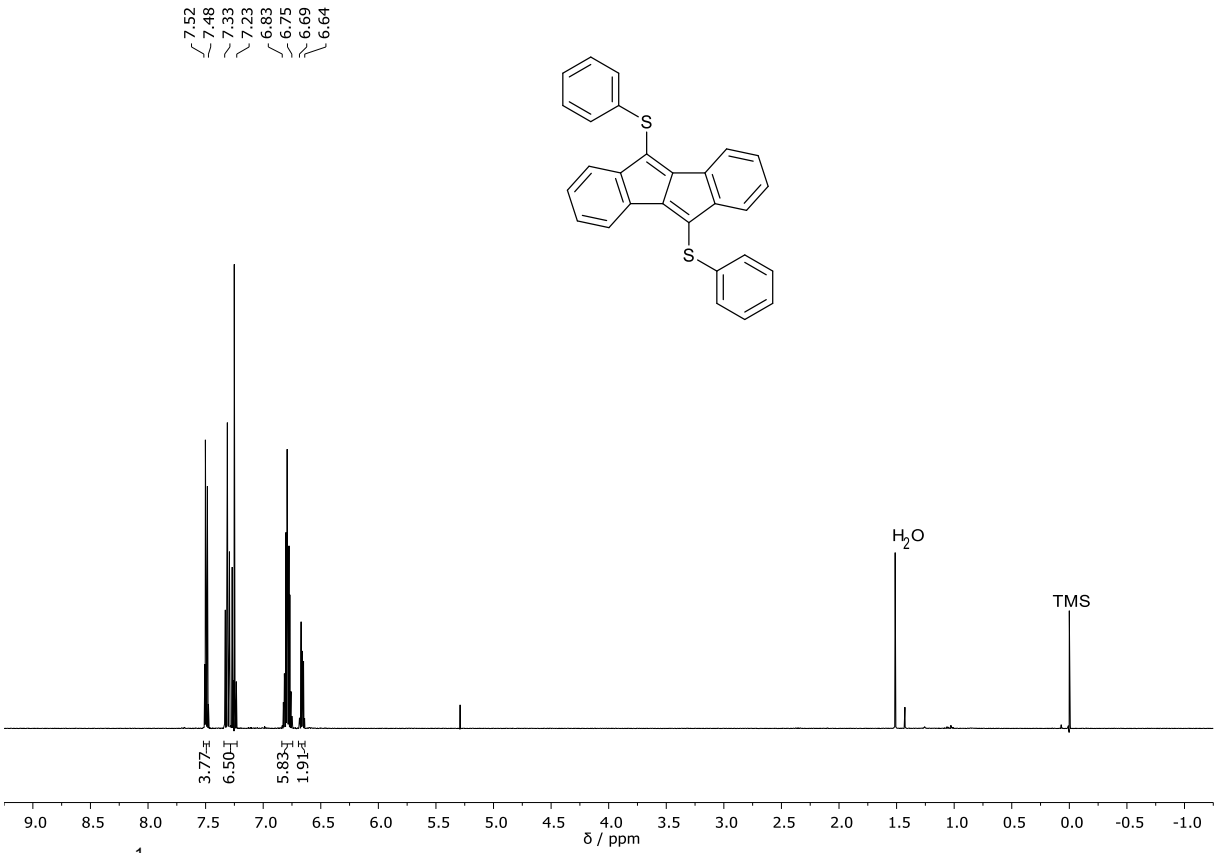


Figure S9. ^{1}H NMR spectrum of **2b** ($CDCl_3$, 400 MHz).

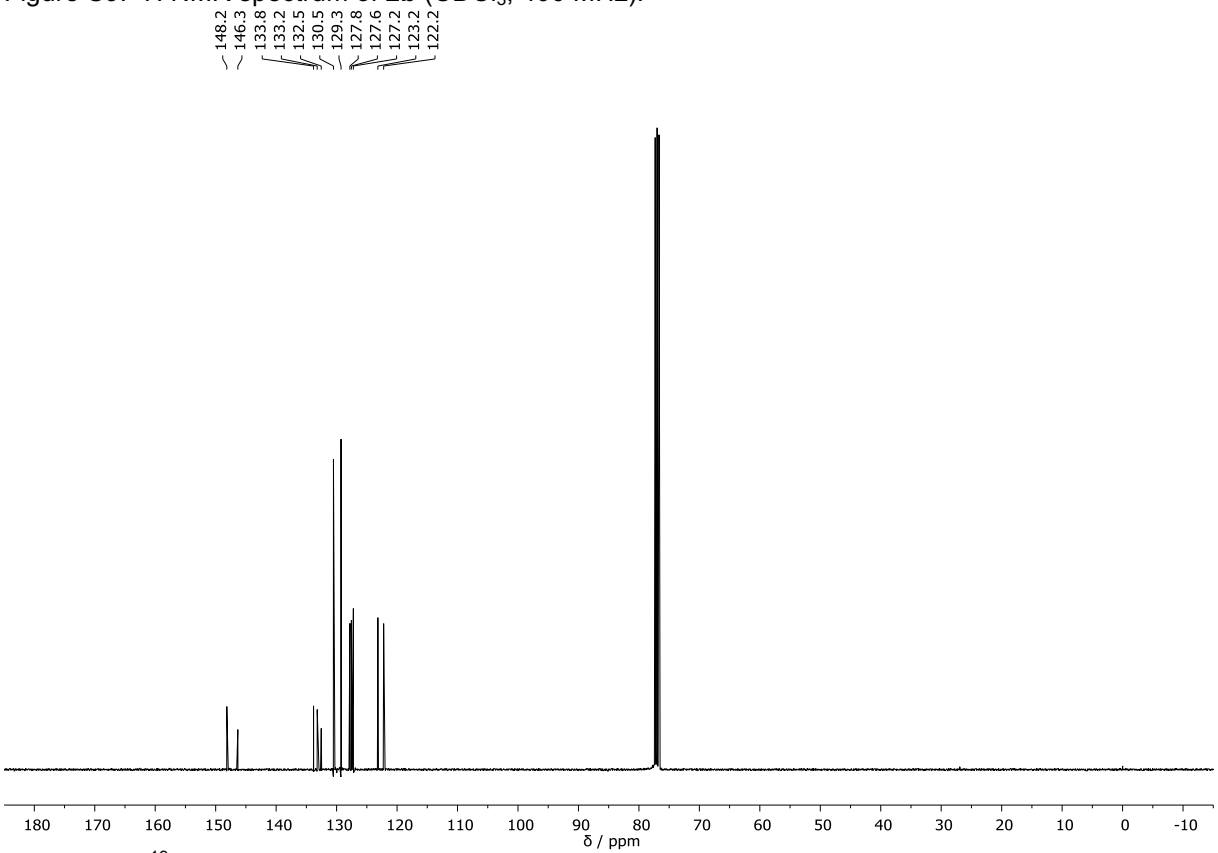


Figure S10. ^{13}C NMR spectrum of **2b** ($CDCl_3$, 101 MHz).

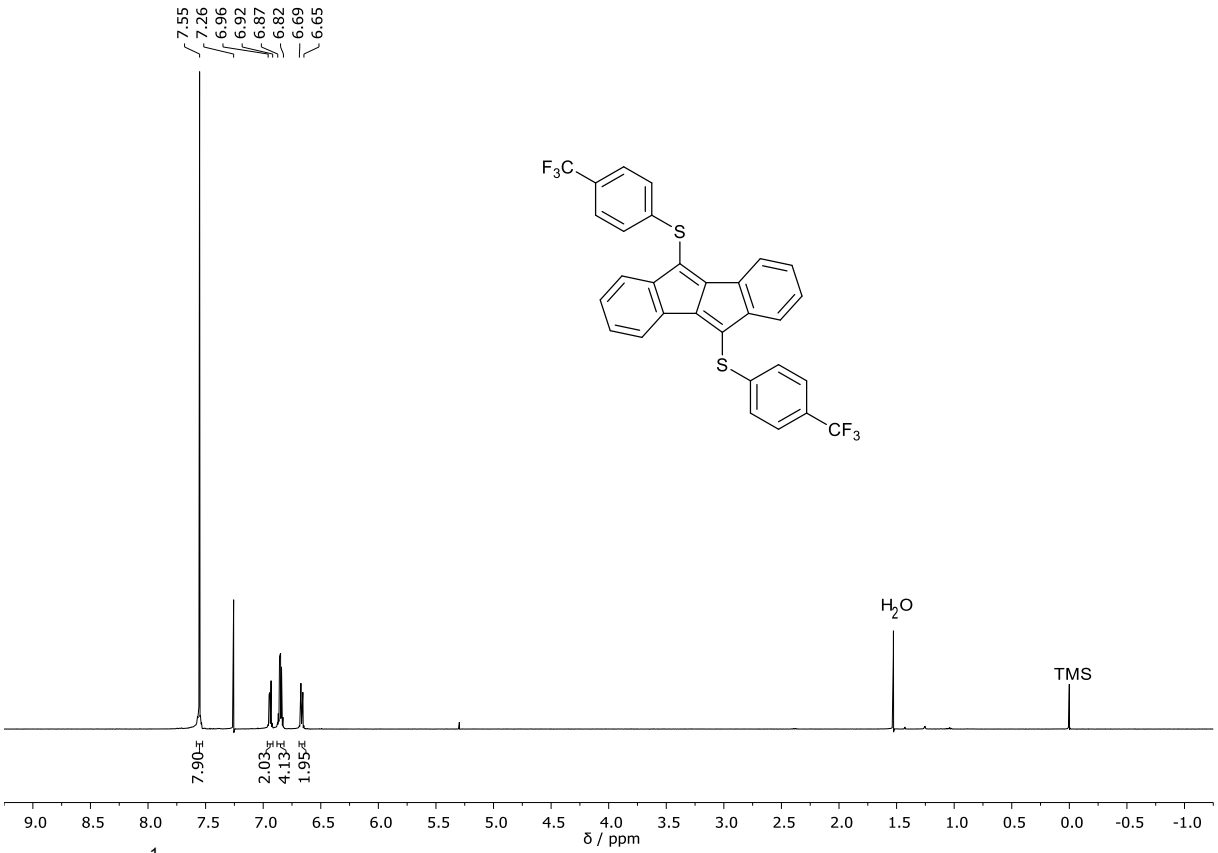


Figure S11. ^{1}H NMR spectrum of **2c** ($CDCl_3$, 500 MHz).

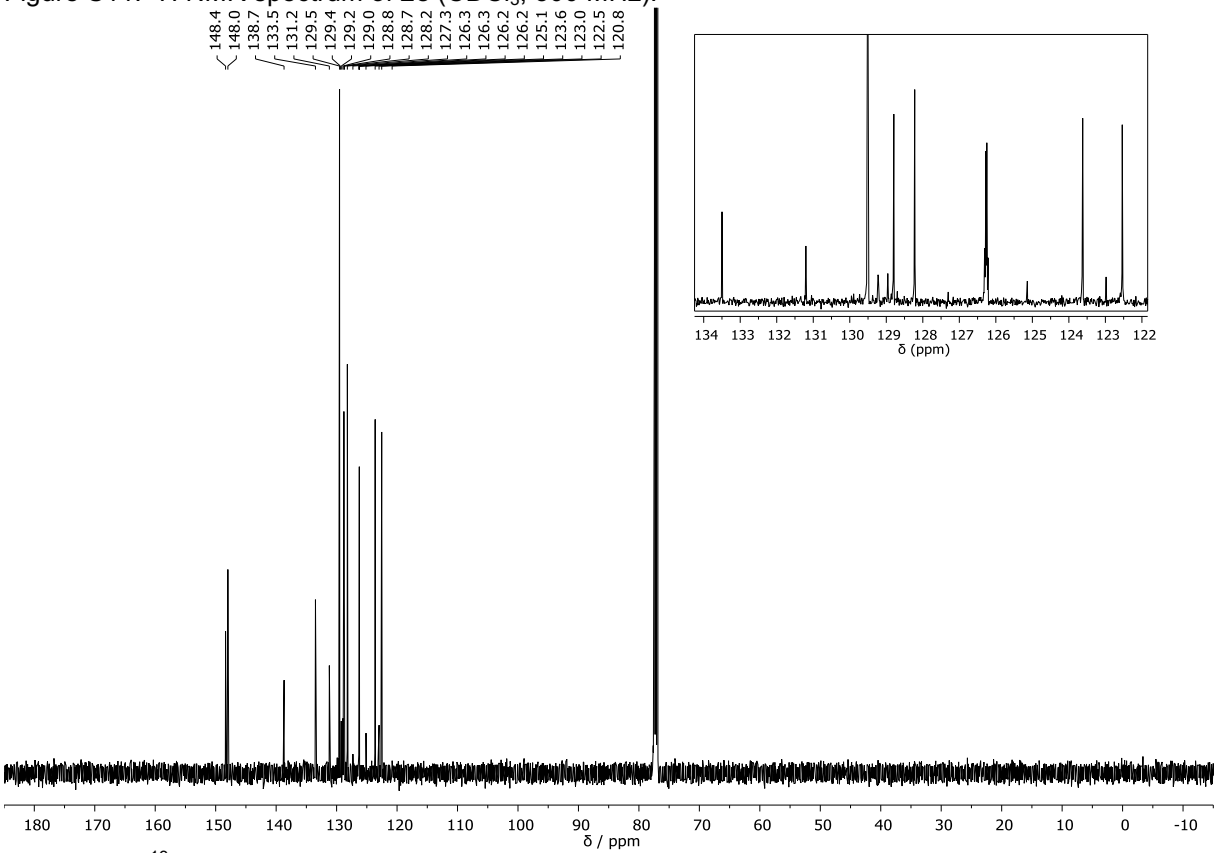


Figure S12. ^{13}C NMR spectrum of **2c** ($CDCl_3$, 126 MHz).

Figure S13. ^{19}F NMR spectrum of **2c** ($CDCl_3$, 471 MHz).

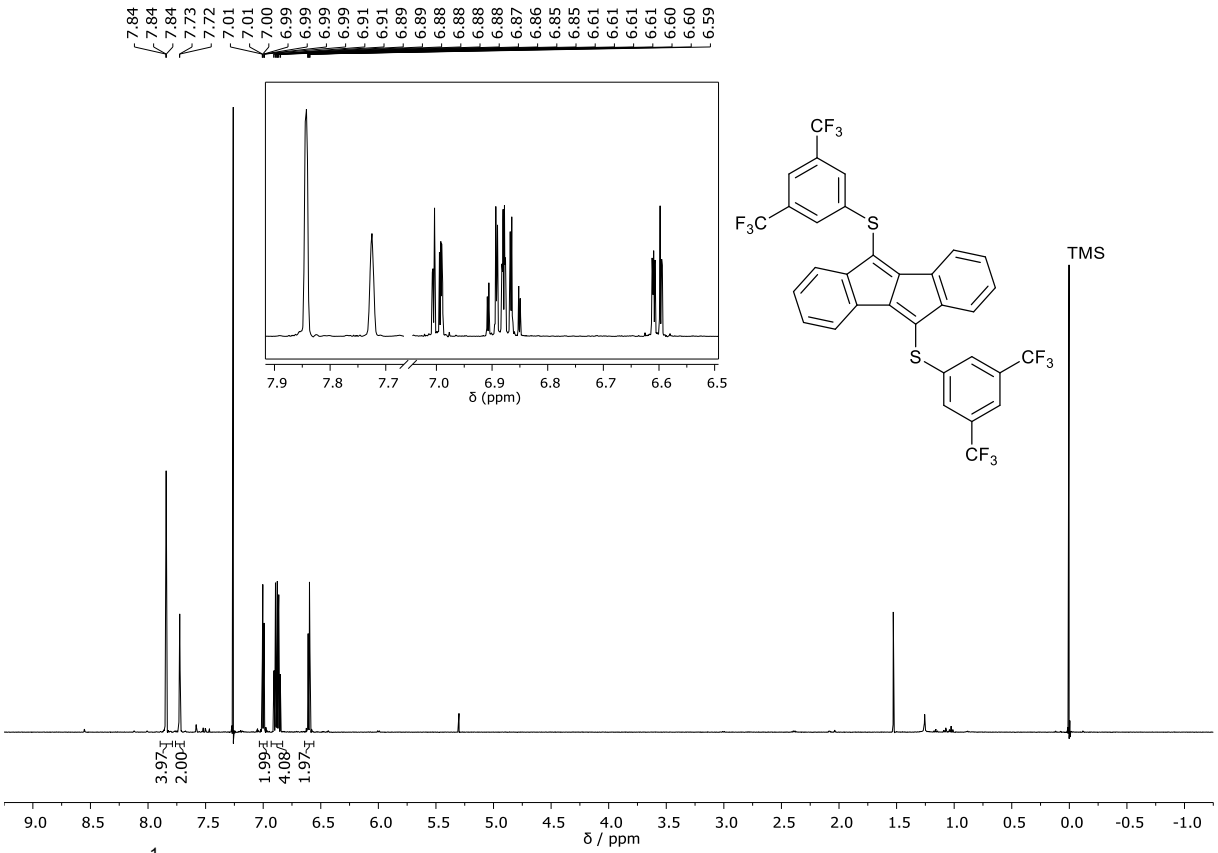


Figure S14. ^{1}H NMR spectrum of **2d** ($CDCl_3$, 500 MHz).

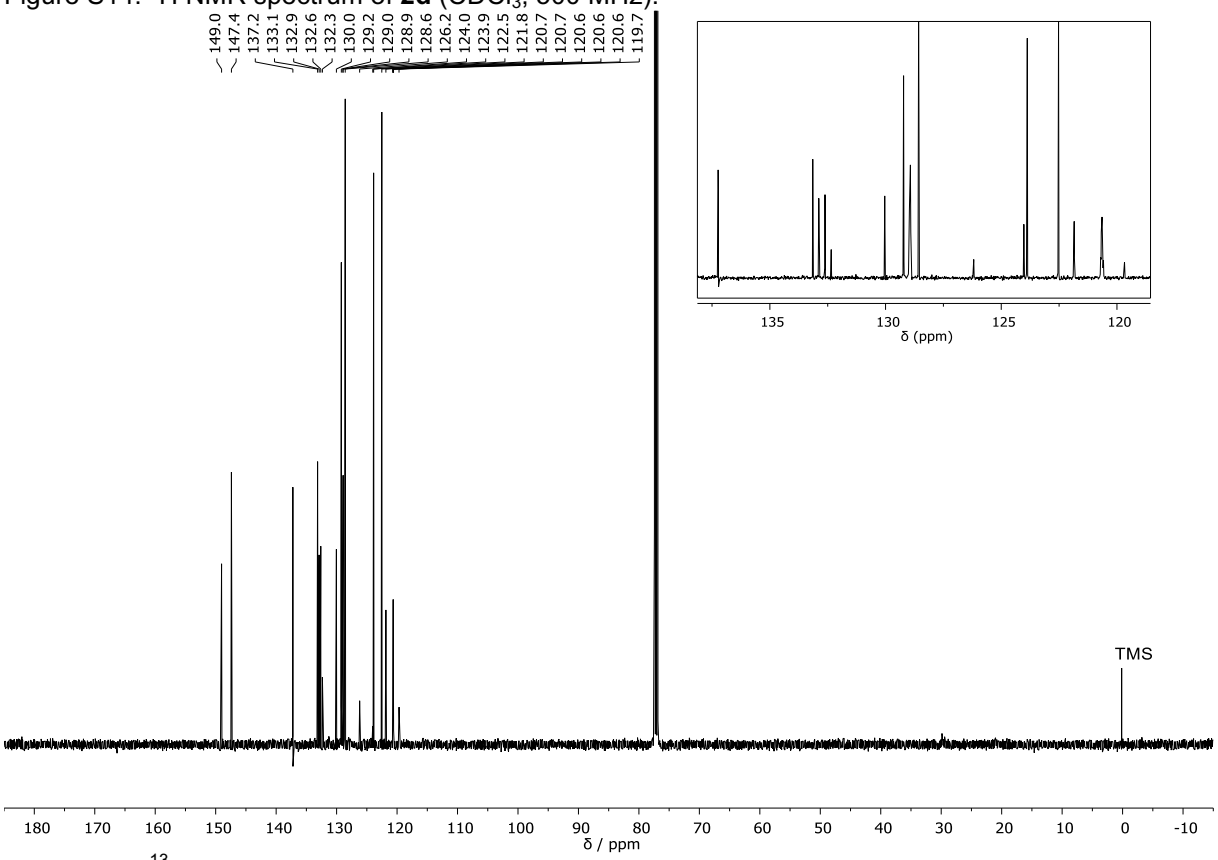


Figure S15. ^{13}C NMR spectrum of **2d** ($CDCl_3$, 126 MHz).

Figure S16. ^{19}F NMR spectrum of **2a** ($CDCl_3$, 471 MHz).

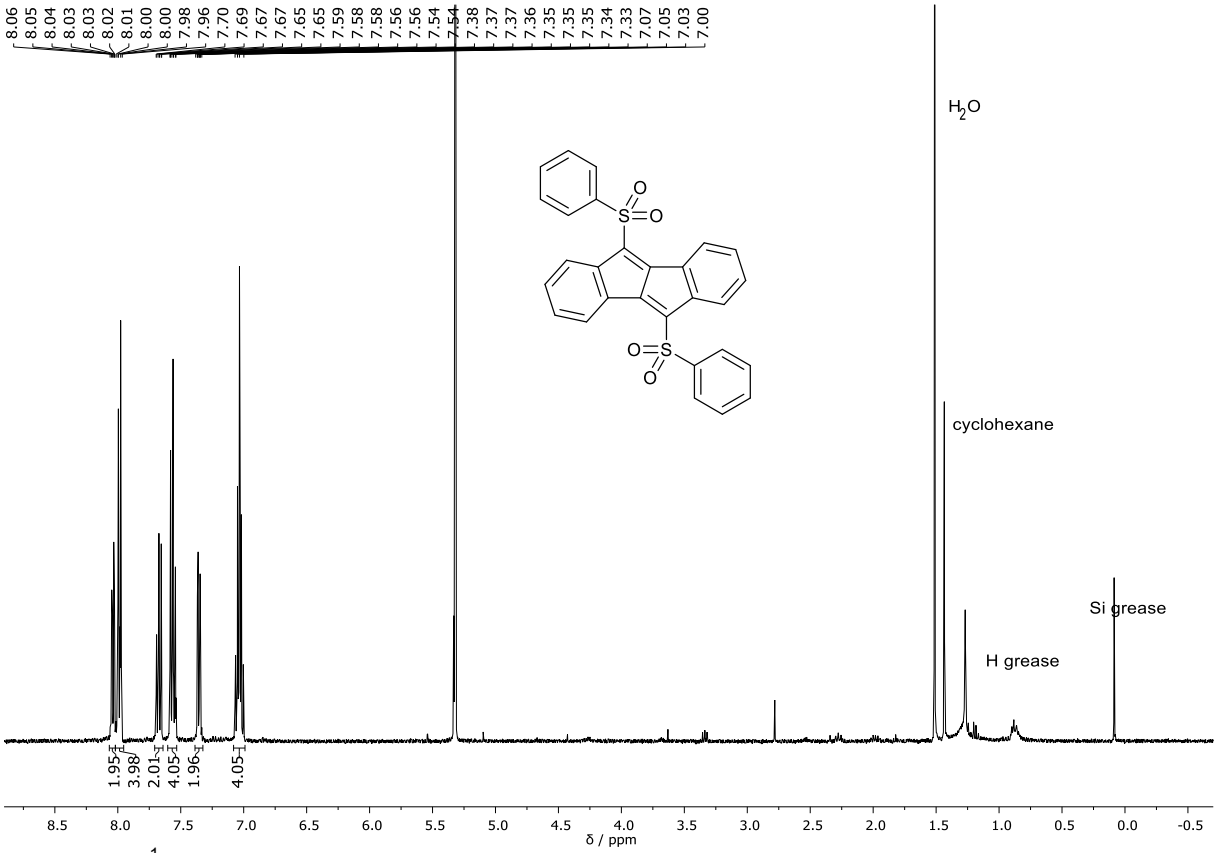


Figure S17. ^{1}H NMR spectrum of **3** (CD_2Cl_2, 400 MHz).

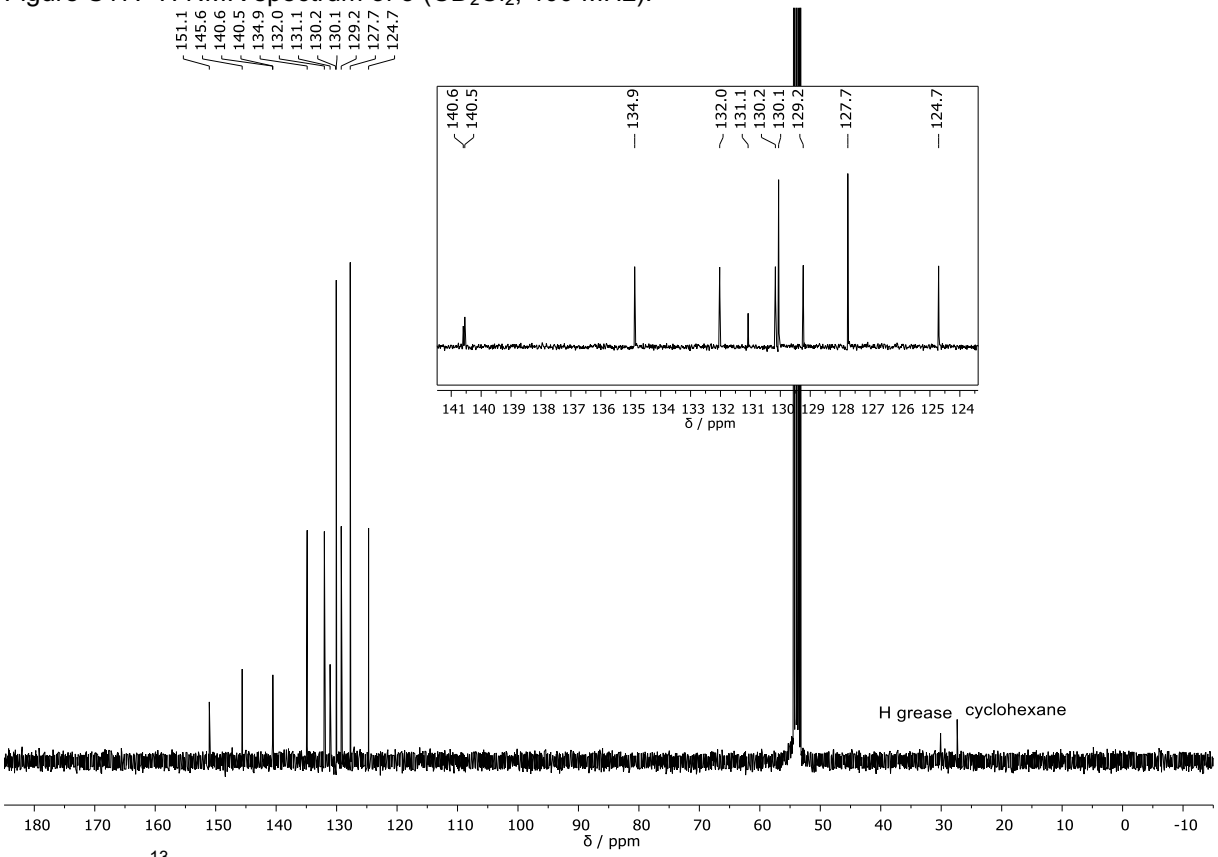


Figure S18. ^{13}C NMR spectrum of **3** (CD_2Cl_2, 101 MHz).

4. Thermal measurements

4.1 Thermogravimetric analysis of 2a–d and 3

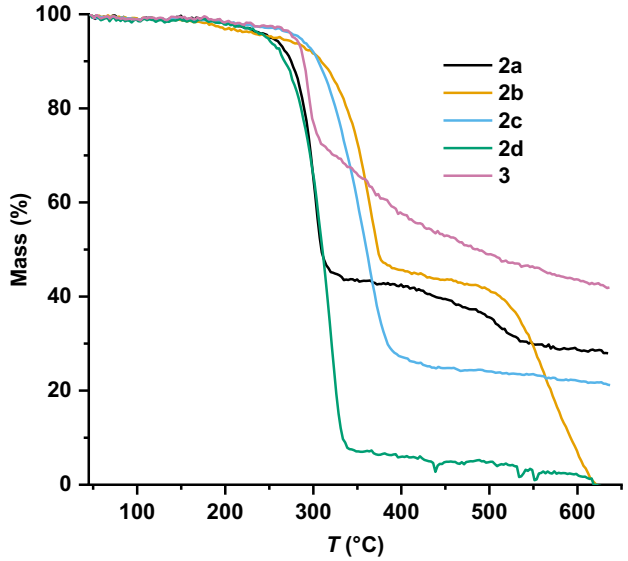


Figure S19. TGA measurement of thioether-DBPs **2a–d** and sulfone **3** under inert N_2 atmosphere at a heating rate of 10 K min^{-1}.

4.2 Differential scanning calorimetry of 2a–d and 3

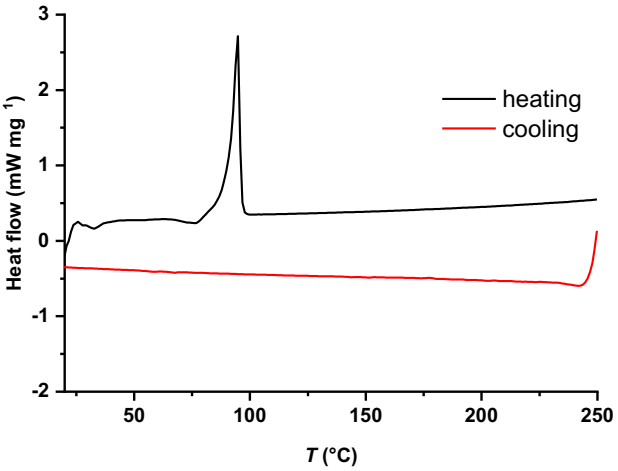


Figure S20. DSC of **2a** at a heating rate of 10 K min^{-1}.

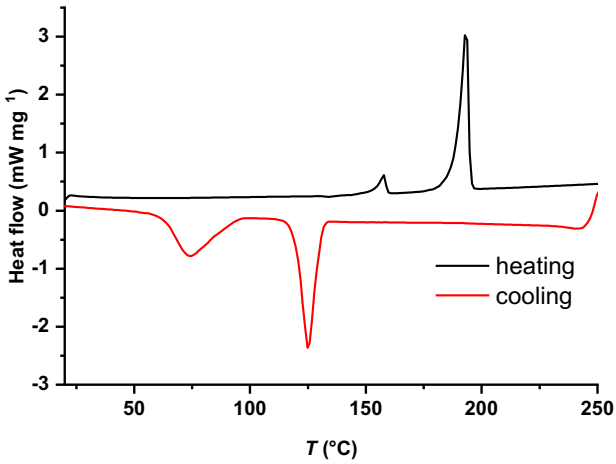


Figure S21. DSC of **2b** at a heating rate of 10 K min^{-1}.

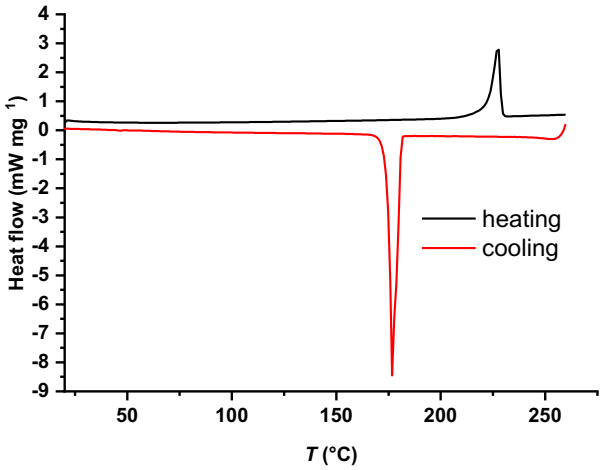


Figure S22. DSC of **2c** at a heating rate of 10 K min^{-1}.

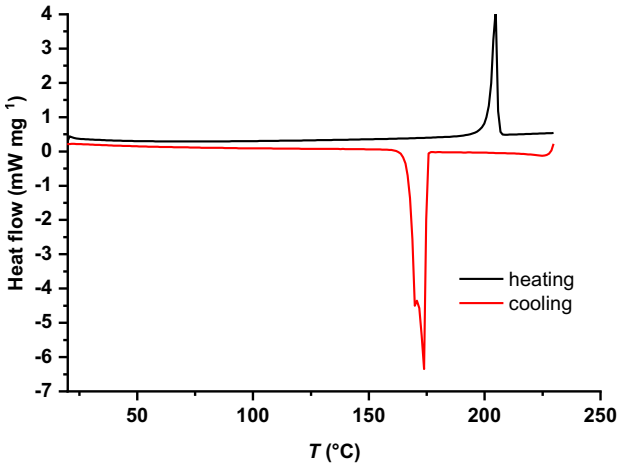


Figure S23. DSC of **2d** at a heating rate of 10 K min^{-1}.

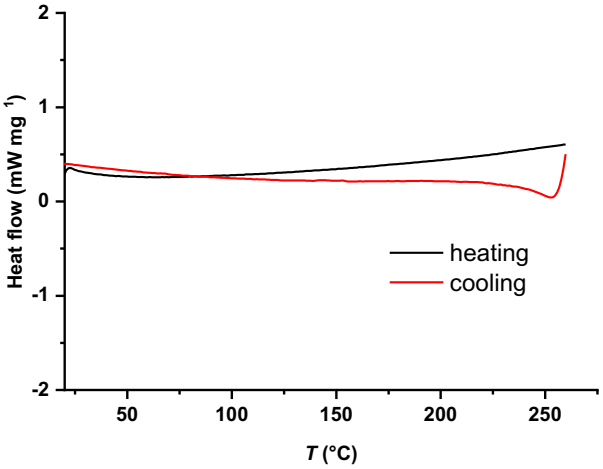


Figure S24. DSC of **3** at a heating rate of 10 K min^{-1}.

5. Cyclic voltammograms

All cyclic voltammetry measurements were performed in CH_2Cl_2 solution (1 mM substance concentration) with a glassy carbon working electrode and 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte. Sulfone **3** was measured in CH_2Cl_2 as well as THF.

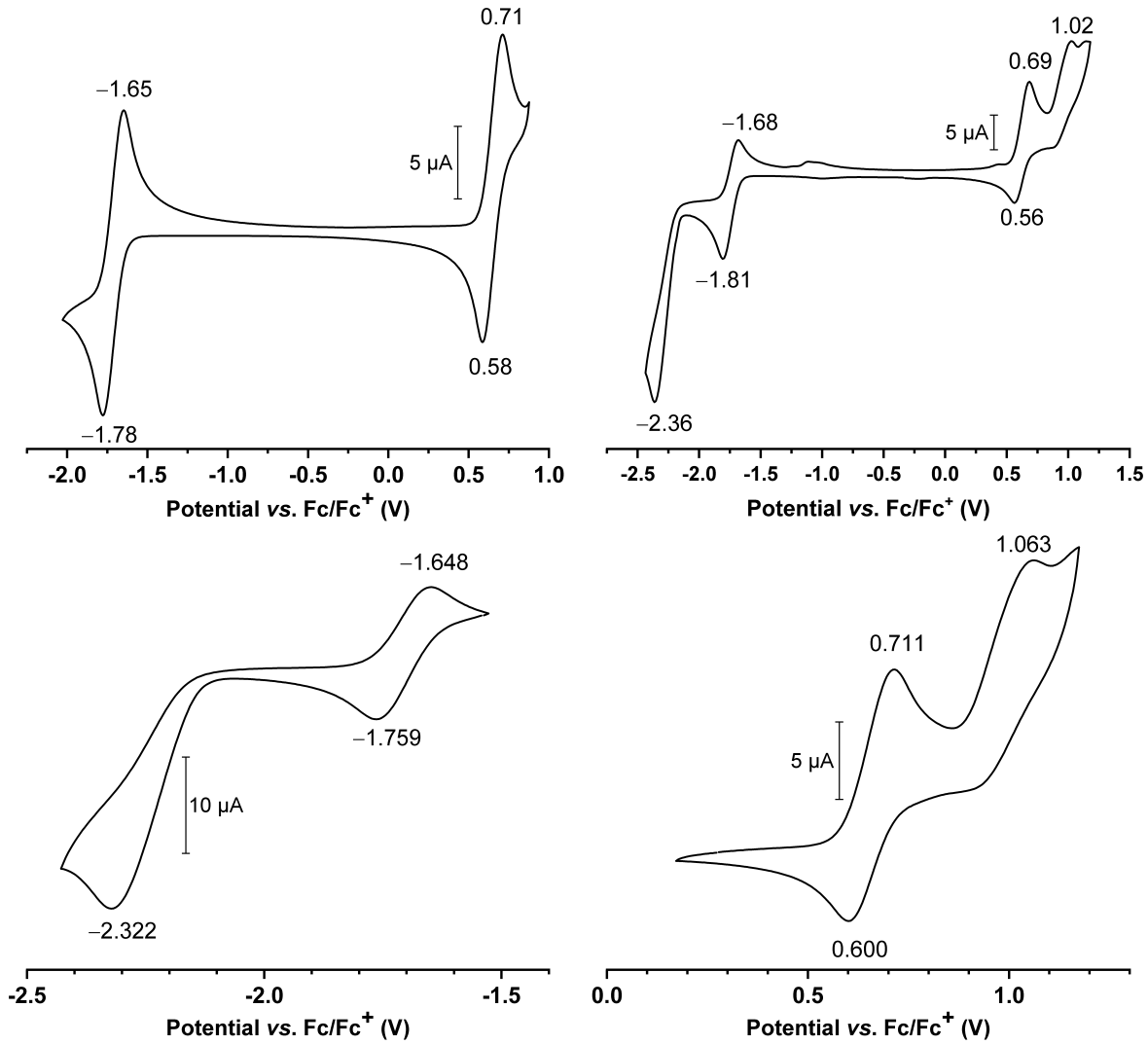


Figure S25. Cyclic voltammograms of **2a** in CH_2Cl_2 at 100 mV/s scan rate.

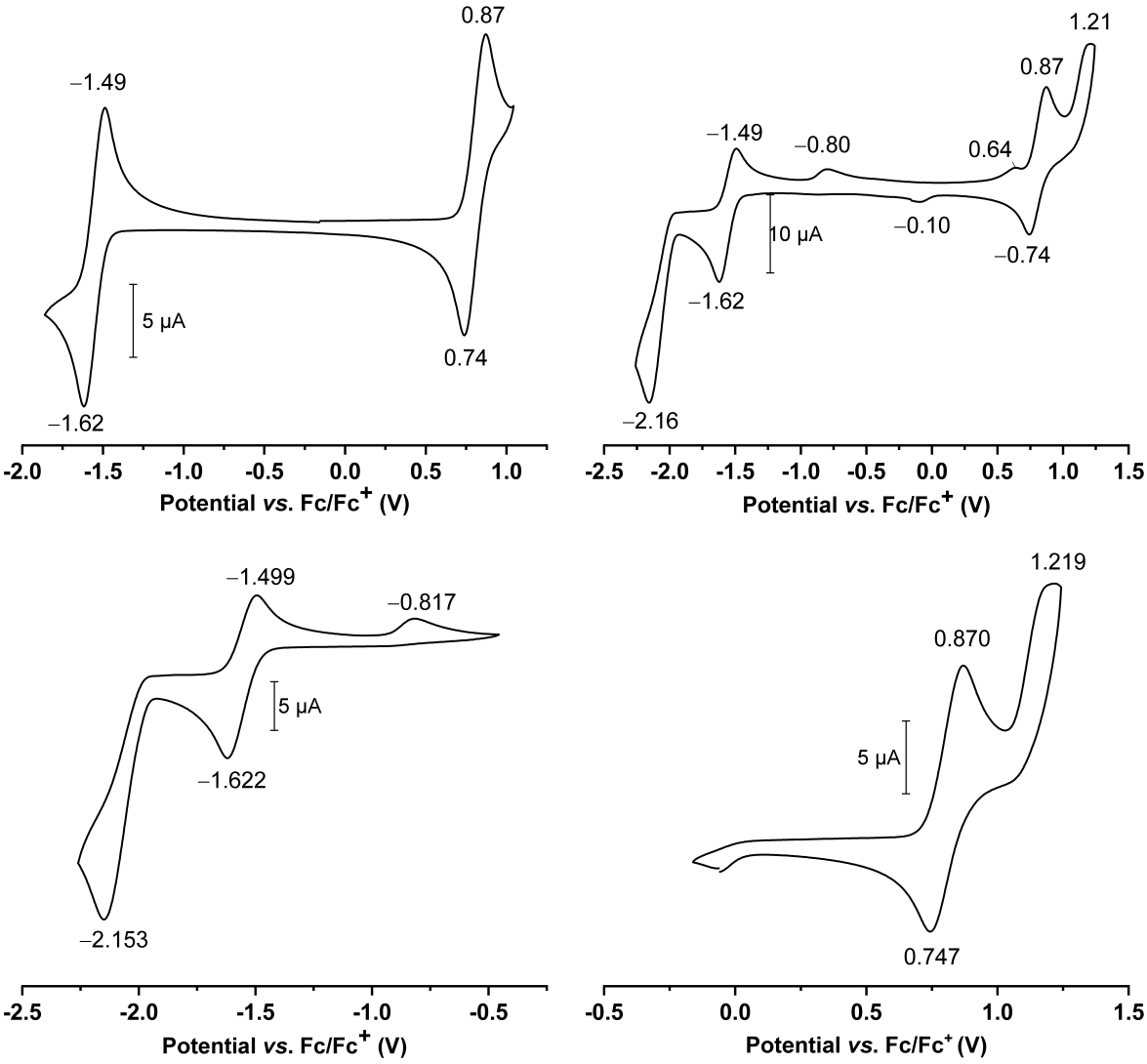


Figure S26. Cyclic voltammograms of **2b** in CH_2Cl_2 at 100 mV/s scan rate.

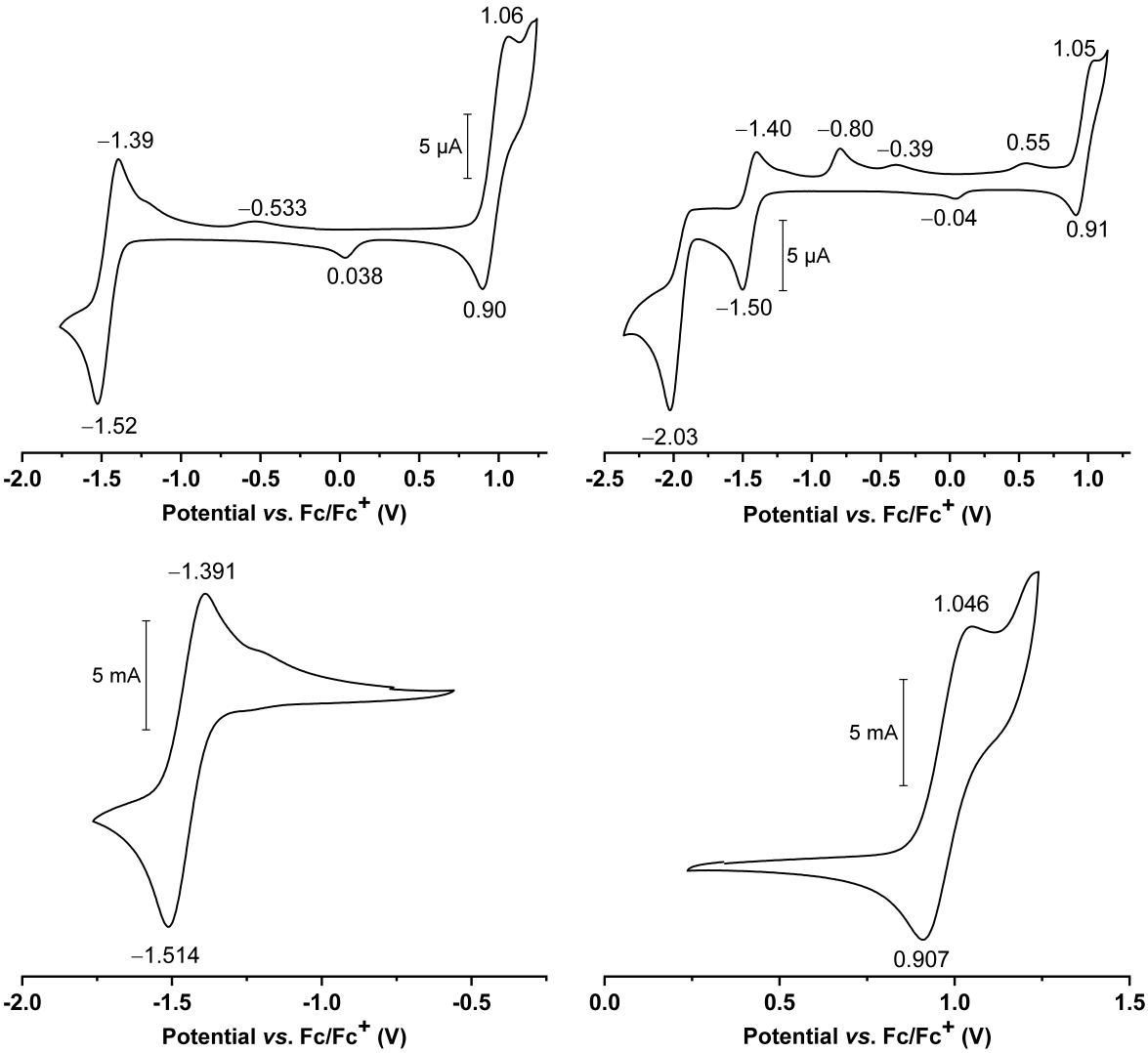


Figure S27. Cyclic voltammograms of **2c** in CH_2Cl_2 at 100 mV/s scan rate.

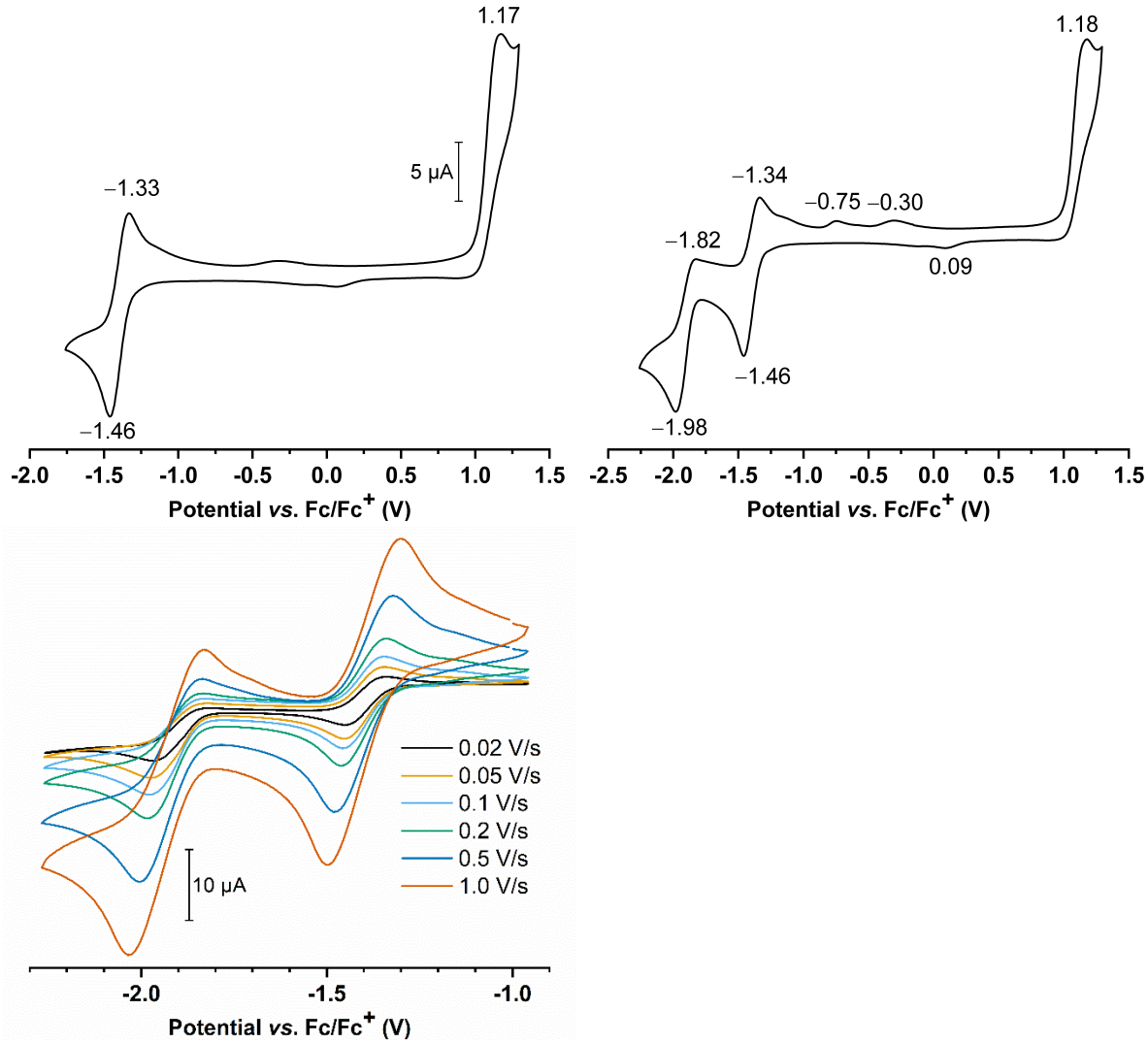


Figure S28. Cyclic voltammograms of **2d** in CH_2Cl_2 at 100 mV/s scan (top) rate and various scanrates (bottom).

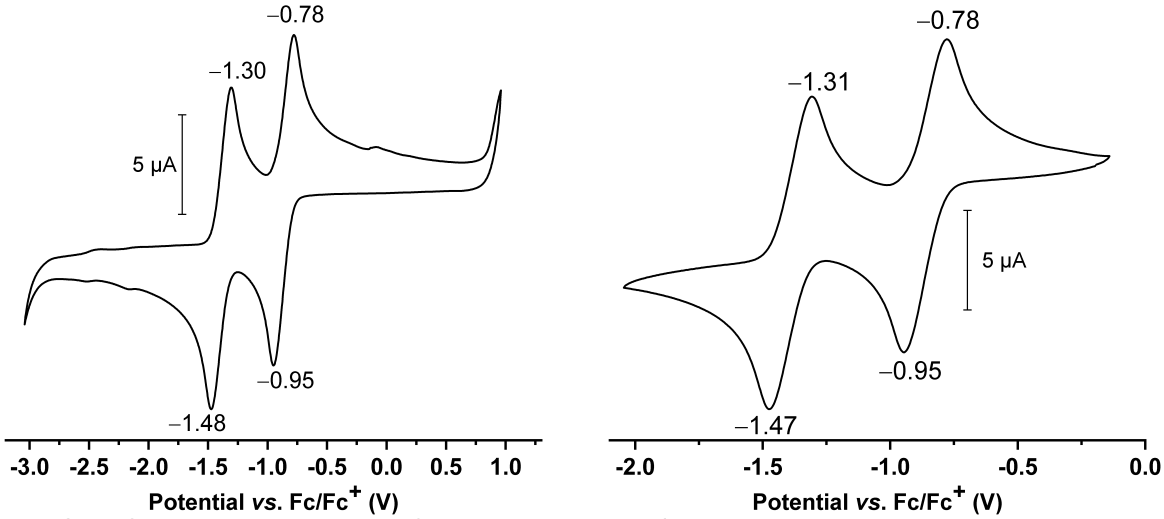


Figure S29. Cyclic voltammograms of **3** in THF at 100 mV/s scan rate.

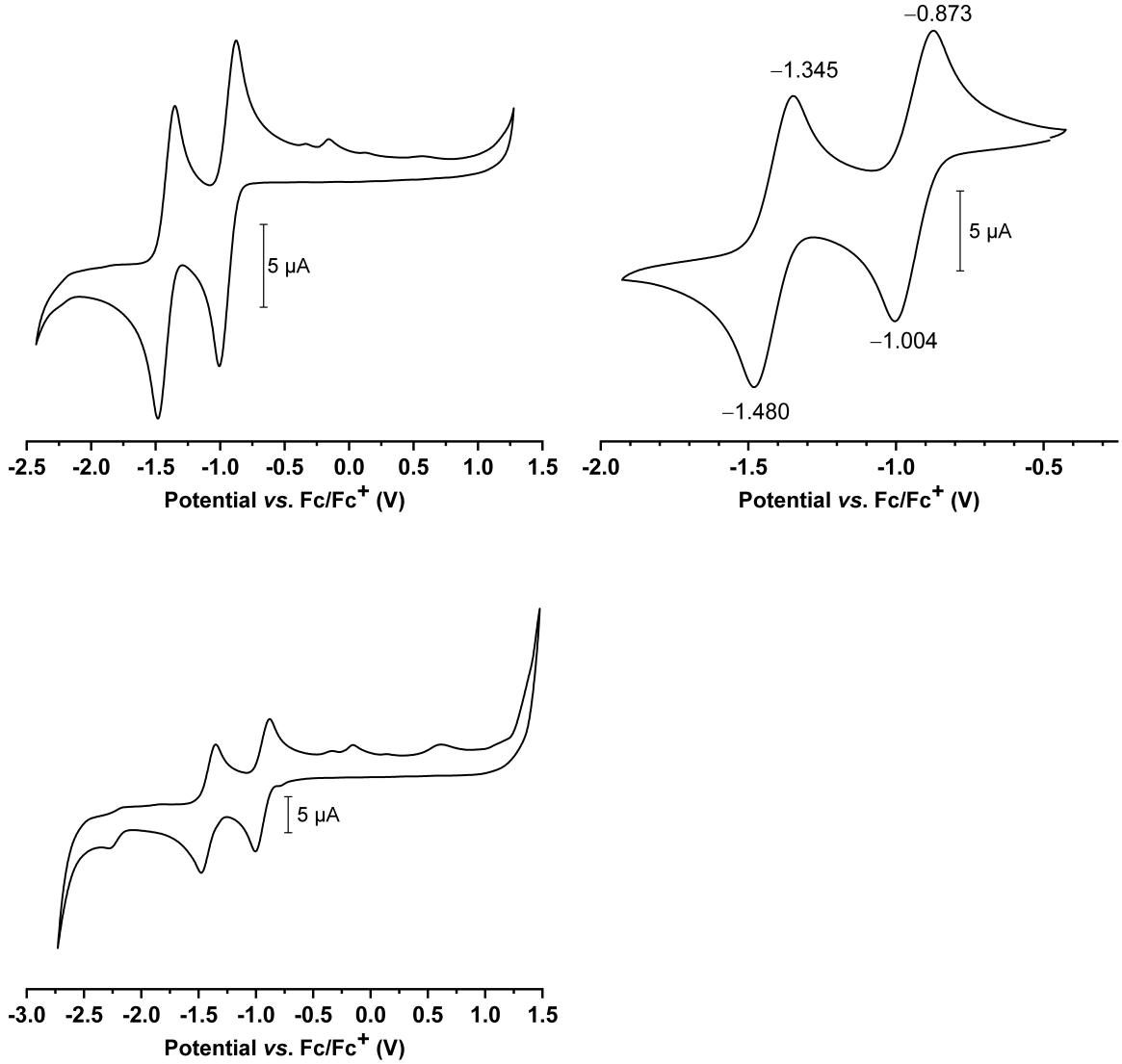


Figure S30. Cyclic voltammograms of **3** in CH_2Cl_2 at 100 mV/s scan rate.

6. FET device fabrication

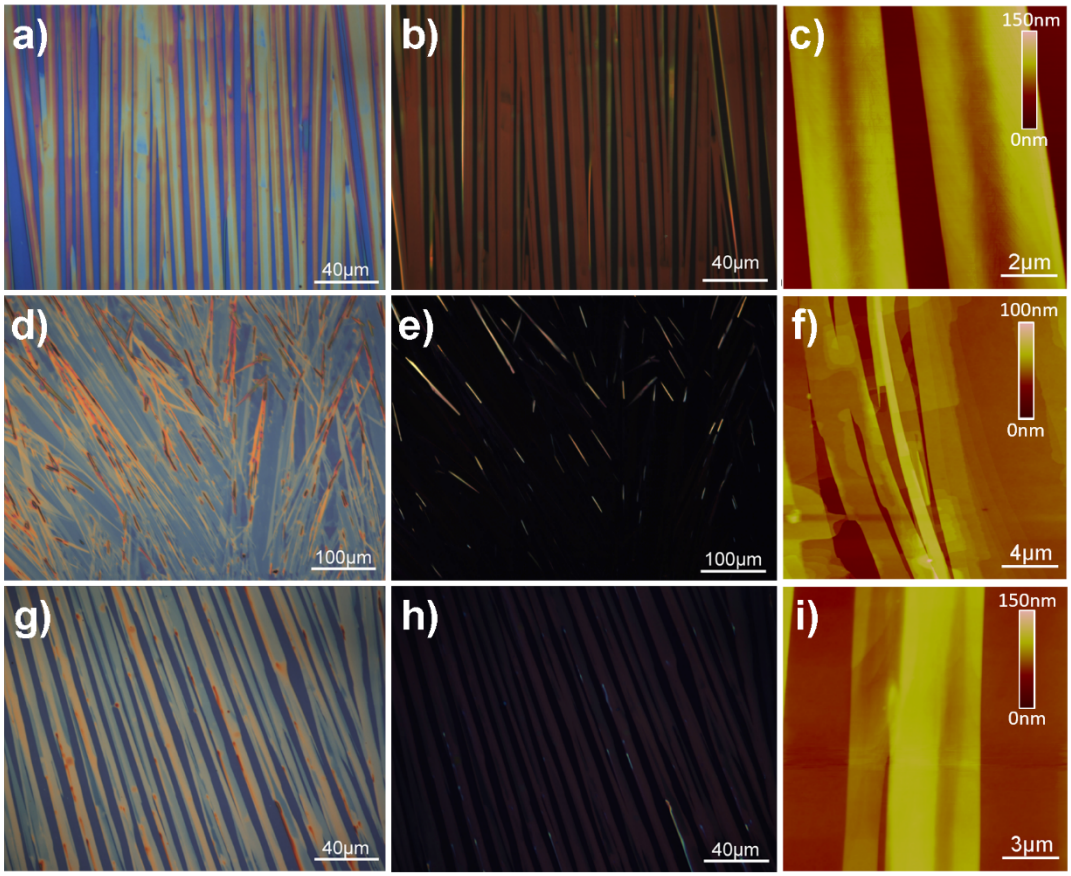


Figure S31. Morphologies of **2c** (a–c), **2d** (d–f) and **3** crystals (g–i) grown by the DPC method. (a, d and g) Optical microscopy images, (b, e and h) cross-polarized optical microscopy images and (c, f and i) AFM images of aligned crystals. These aligned crystals were used for FET device fabrication.

7. Single-crystal X-ray diffraction

7.1 Experimental setup

The crystals were mounted on a MITIGEN holder in perfluoroether oil. X-ray diffraction data were collected using a Bruker SMART APEXII QUAZAR diffractometer equipped with an Oxford Cryosystems 800 low-temperature device, operating at T = 100 K.

Data were measured using ω and ϕ scans scans using MoK_α radiation (microfocus sealed X-ray tube, 50 kV, 0.6 mA). The total number of runs and images was based on the strategy calculation from the program APEX2 (Bruker).

Cell parameters were retrieved using the SAINT software and refined using SAINT.[6] Data reduction was performed using the SAINT[6] software which corrects for Lorentz polarisation. Scaling and absorption correction was performed by SADABS.[7] Disorder was modelled using DSR[8] in ShelXle[9] or Olex2[10].

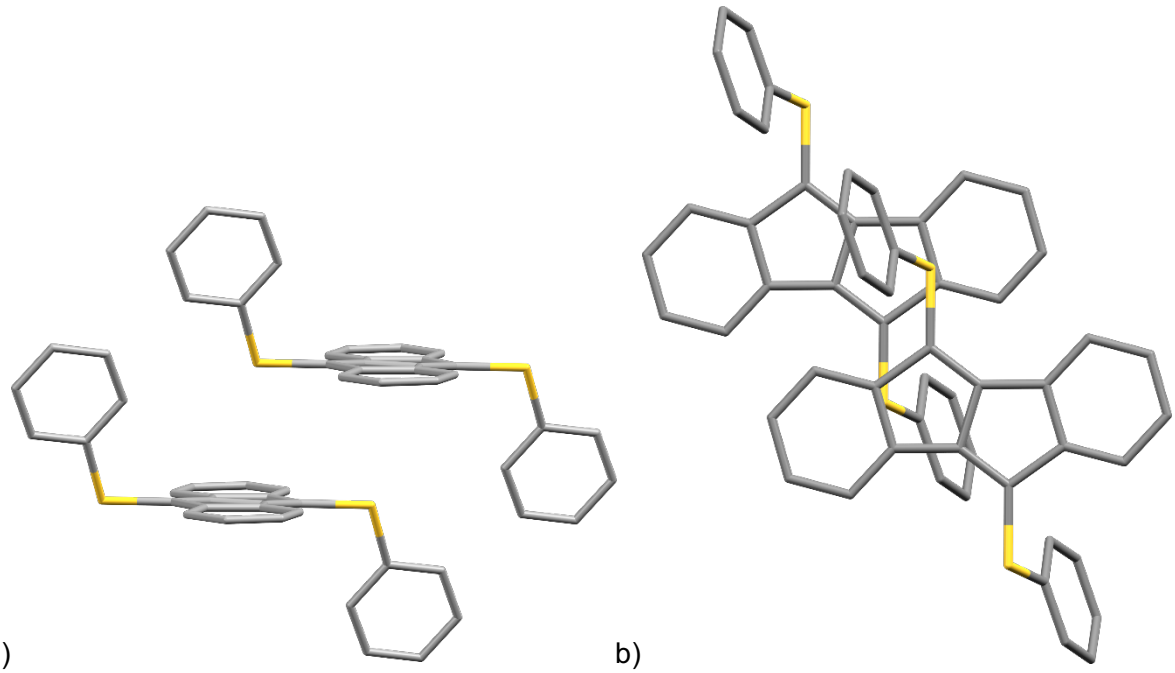
Compound	**2b**	**2c**
CCDC	1532986	1582024
Formula	$C_{28}H_{18}S_2$	$C_{30}H_{16}F_6S_2$
$D_{calc.}$ / g cm^{-3}	1.387	1.579
μ / mm^{-1}	0.279	0.296
Formula Weight	418.54	554.55
Color	brown	red
Shape	block	plate
Size / mm^3	0.31×0.20×0.11	0.33×0.11×0.04
T / K	100(2)	100(2)
Crystal System	monoclinic	triclinic
Space Group	$P21/n$	$P\bar{1}$
a / Å	12.307(3)	8.951(5)
b / Å	5.5294(14)	9.552(5)
c / Å	15.071(5)	14.344(9)
α / °	90	103.52(2)
β / °	102.214(10)	91.36(2)
γ /°	90	101.337(15)
V / Å^3	1002.4(5)	1166.0(11)
Z	2	2
Z'	0.5	1
Wavelength / Å	0.710730	0.710730
Radiation type	MoK_α	MoK_α
Θ_{min} / °	1.946	1.464
Θ_{max} /°	27.108	26.372
Measured Refl.	8126	17667
Independent Refl.	2191	4758
Reflections Used	2027	4034
R_{int}	0.0178	0.0242
Parameters	136	371
Restraints	0	180
Largest Peak	0.792	0.563
Deepest Hole	−0.495	−0.385
GooF	1.058	1.038
wR_2 (all data)	0.0880	0.0948
wR_2	0.0864	0.0899
R_1 (all data)	0.0392	0.0430
R_1	0.0365	0.0352

7.2 Single-crystal X-ray diffraction data for 2b

7.2.1 Solution and refinement

The structure was solved in the space group $P21/n$ (# 14) by Intrinsic Phasing using the ShelXT 2015/5[11] structure solution program and refined by Least Squares using version 2016/6 of ShelXL[12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using a riding model.

SADABS-2016/2[7] was used for absorption correction. wR_2(int) was 0.1156 before and 0.0349 after correction. The Ratio of minimum to maximum transmission is 0.9453. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.



a) b)

Figure S32. Single crystal X-ray structure of **2b**, a) view from the side and b) view from the top. The distance between the two planes amounts to 3.254 Å.

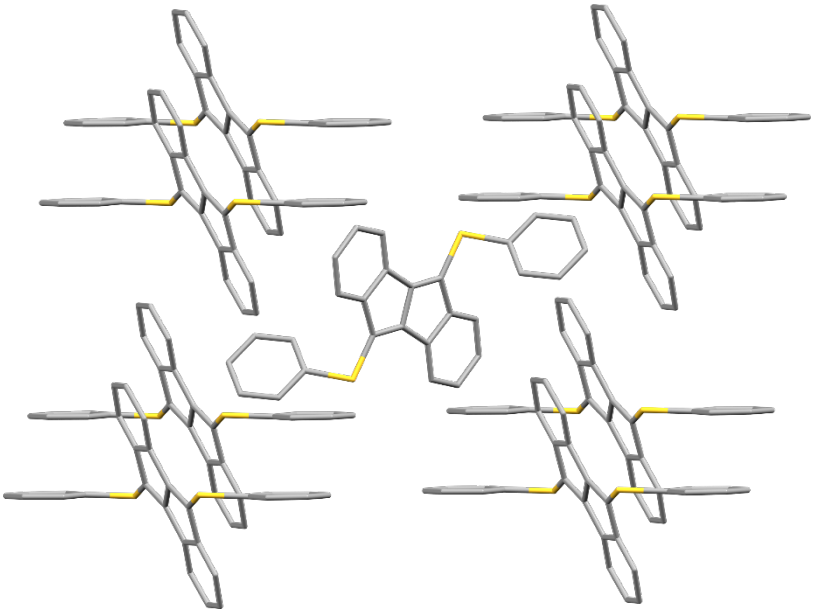


Figure S33. Herringbone packing of **2b**.

7.3 Single-crystal X-ray diffraction data for 2c

7.3.1 Solution and refinement

The structure was solved in the space group $P\bar{1}$ (# 2) by direct methods using the ShelXT 2014/5[11]) structure solution program and refined by Least Squares using version 2016/6 of ShelXL[12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using a riding model. The rotationally disordered CF_3-group was modelled using DSR.[8]

SADABS-2016/2[7] was used for absorption correction. wR_2(int) was 0.1341 before and 0.0376 after correction. The Ratio of minimum to maximum transmission is 0.9353. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

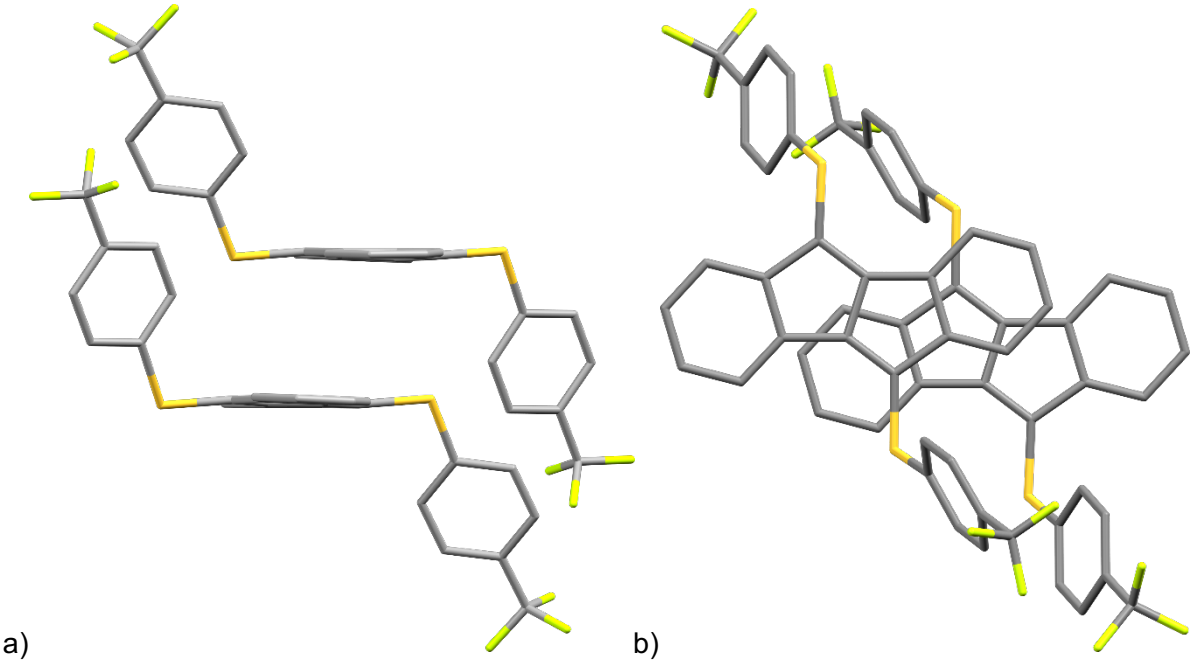


Figure S34. Single crystal X-ray structure of **2c**, a) view from the side and b) view from the top. The distance between the two planes amounts to 3.504 Å.

8. DFT calculations

8.1 Cartesian coordinates of calculated structures

The following Cartesian coordinates are listed in angstrom.

Table S1. Coordinates of the calculated structure of **2a*** (B3LYP-D3/def2-TZVP).

	x	y	z
S	2.5893988	0.4075331	8.7307246
C	2.3695279	0.8308322	10.4830225
C	3.9165959	1.463162	8.3165864
C	3.8957195	2.4650444	7.4121634
C	5.2966851	1.3510196	8.8369432
C	5.8509295	0.452966	9.722373
H	5.2541845	−0.3384624	10.1586479
C	7.2089037	0.5672224	10.0269715
H	7.6589901	−0.1276963	10.7234716
C	1.1327158	3.9632232	5.2725803
H	0.0848225	3.88653	5.0148154
C	1.683745	3.0650097	6.1884852
H	1.0741559	2.2995154	6.6502965
C	3.0216029	3.180455	6.4984794
S	6.5232892	5.1297252	6.0091651
C	6.7467513	4.7147461	4.255168
C	5.1982242	4.0689612	6.4173577
C	5.2207408	3.0623343	7.3163215
C	3.81842	4.1801234	5.8961571
C	3.2638979	5.0781517	5.0109948
H	3.8586872	5.874217	4.5806675
C	1.9085647	4.9566208	4.6977145
H	1.4584939	5.6506978	4.0003784
C	7.9872526	1.5540686	9.4442682
H	9.037636	1.6237055	9.6936891
C	7.4357314	2.453944	8.5303454
H	8.0468255	3.2148047	8.0629671
C	6.0953165	2.3458502	8.2288723
H	7.5308711	5.3674003	3.875751
H	5.8407516	4.8853972	3.6788855
H	7.0607626	3.6799631	4.1422924
H	1.5826874	0.183392	10.8657323
H	2.0604428	1.8675692	10.5917552
H	3.2752463	0.6583535	11.0593359

Table S2. Coordinates of the calculated structure of **2b** (B3LYP-D3/def2-TZVP).

	x	y	z
S	−2.0799237	−2.1863793	1.4319546
C	−2.1588695	−2.1407531	5.9773855
H	−2.1888839	−2.1390278	7.0586849
C	−2.4647186	−3.2960482	5.2740351
H	−2.7325066	−4.2006041	5.8038955
C	−2.4121929	−3.3048934	3.888386
H	−2.6241521	−4.2144488	3.3408726
C	−2.0715873	−2.1446202	3.2022676
C	−0.7030461	−1.2041889	1.0320396
C	−0.6764494	−0.254459	0.0692734
C	−1.7822009	−0.9789467	3.9032789
H	−1.5275503	−0.0728019	3.3691548
C	−1.8137225	−0.9865943	5.2879973
H	−1.5761289	−0.0811176	5.830446
C	0.6688219	−1.3536672	1.5657589
C	1.1790465	−2.203027	2.5242271
H	0.5434827	−2.9057648	3.0460336
C	2.5425666	−2.1374598	2.8139723
H	2.9569614	−2.7942201	3.5671905
C	−3.3703816	1.2444364	−2.1526909
H	−4.4245999	1.2122236	−2.3935729
C	−2.8615212	0.3876079	−1.1766405
H	−3.511049	−0.3022461	−0.6539496
C	−1.5145186	0.4464366	−0.8865345
S	2.0799237	2.1863793	−1.4319546
C	2.1588695	2.1407531	−5.9773855
H	2.1888839	2.1390278	−7.0586849
C	2.4647186	3.2960482	−5.2740351
H	2.7325066	4.2006041	−5.8038955
C	2.4121929	3.3048934	−3.888386
H	2.6241521	4.2144488	−3.3408726
C	2.0715873	2.1446202	−3.2022676
C	0.7030461	1.2041889	−1.0320396
C	0.6764494	0.254459	−0.0692734
C	1.7822009	0.9789467	−3.9032789
H	1.5275503	0.0728019	−3.3691548
C	1.8137225	0.9865943	−5.2879973
H	1.5761289	0.0811176	−5.830446
C	−0.6688219	1.3536672	−1.5657589
C	−1.1790465	2.203027	−2.5242271
H	−0.5434827	2.9057648	−3.0460336
C	−2.5425666	2.1374598	−2.8139723
H	−2.9569614	2.7942201	−3.5671905
C	3.3703816	−1.2444364	2.1526909
H	4.4245999	−1.2122236	2.3935729
C	2.8615212	−0.3876079	1.1766405
H	3.511049	0.3022461	0.6539496
C	1.5145186	−0.4464366	0.8865345

Table S3. Coordinates of the calculated structure of **2c** (B3LYP-D3/def2-TZVP).

	x	y	z
S	2.8022444	−0.7264728	−1.7029436
C	1.1495094	−0.6115972	−1.1736328
C	0.0050292	−1.3718588	−1.7217865
S	−2.7892933	0.6438135	1.6907956
C	−0.0705931	−2.250634	−2.7803448
H	0.7986185	−2.4796164	−3.3824826
F	−1.9161342	−1.327724	8.0222225
C	−1.3009984	−2.8453163	−3.0642339
H	−1.3789361	−3.5331007	−3.8954693
F	−3.7139565	−0.1603913	8.2318224
C	−2.4211974	−2.5665032	−2.2981027
H	−3.3641252	−3.0399609	−2.5366065
C	−2.3481926	−1.683958	−1.2198805
H	−3.2225272	−1.4757363	−0.6172851
F	−1.7962753	0.809106	8.2322695
C	−1.1360316	−1.0911358	−0.9363382
C	−0.700582	−0.1704271	0.0986878
C	−1.1347476	0.5317722	1.1689353
C	0.0085983	1.2978607	1.7130213
C	0.0824649	2.1877655	2.7626339
H	−0.7873978	2.4238088	3.3610602
C	1.312283	2.7857645	3.0424098
C	2.4339705	2.4994081	2.2813799
H	3.3763985	2.9753309	2.5168672
C	2.3625213	1.6072191	1.2110852
H	3.2371815	1.3939641	0.6107833
C	1.1508684	1.0117833	0.931069
C	0.7164059	0.0876329	−0.1013173
C	2.6591461	−0.4098979	−3.4360805
C	3.5350084	−1.0624962	−4.295309
H	4.2447004	−1.7804704	−3.9052608
C	3.4947017	−0.8050272	−5.6552744
H	4.1868859	−1.3195246	−6.3073779
C	2.5692306	0.0931627	−6.167955
C	1.6895886	0.7392324	−5.3069843
H	0.9654391	1.4469251	−5.6874859
C	1.740213	0.5007976	−3.9462526
H	1.0641037	1.023808	−3.2831855
C	2.4745394	0.3309303	−7.6437794
F	3.6233712	0.0625412	−8.2703187
F	2.1530838	1.5976534	−7.9231732
C	−2.6554916	0.3826407	3.4331293
C	−3.5633795	1.0346092	4.2609081
H	−4.2929164	1.7136635	3.838946
C	−3.5276268	0.8273623	5.6281511
H	−4.2438262	1.3402082	6.2558753
C	−2.5749426	−0.0182168	6.1824478
C	−1.6669986	−0.6648531	5.354119
H	−0.9216897	−1.3315607	5.7653171
C	−1.714303	−0.4790959	3.9837416
H	−1.0147491	−1.0038317	3.3468887
C	−2.5013601	−0.1803974	7.6696186
F	1.5339651	−0.441215	−8.2018863
H	1.388201	3.4822552	3.8665616

Table S4. Coordinates of the calculated structure of **2d** (B3LYP-D3/def2-TZVP).

	x	**y**	**z**
S	−2.0320052	−2.3713208	1.2423117
C	−2.2221207	−2.3796306	5.7798304
H	−2.2790042	−2.3927338	6.8609647
C	−2.5567524	−3.5096396	5.0497551
C	−2.9924602	−4.7392484	5.7930963
C	−2.468933	−3.5017703	3.6664882
H	−2.7012345	−4.3882405	3.0917018
C	−2.0654569	−2.3463354	3.0098144
C	−0.6930086	−1.3177328	0.892161
C	−0.7040699	−0.3157078	−0.0140012
C	−1.7478633	−1.2032434	3.7332198
H	−1.4491918	−0.3041731	3.2115509
C	−1.8137505	−1.231618	5.1159972
C	0.6820915	−1.4489866	1.4231089
C	1.2185585	−2.3331415	2.3333316
H	0.6105573	−3.0953188	2.8024527
C	2.5762909	−2.2287889	2.6409523
H	3.0119016	−2.9114731	3.3579902
C	−3.438229	1.212426	−2.1686138
H	−4.48931	1.1593853	−2.4184442
C	−2.9070399	0.3179362	−1.2383678
H	−3.5379742	−0.4204261	−0.7612349
C	−1.564778	0.4053489	−0.9359027
S	1.9582483	2.2946745	−1.4128452
C	2.1488722	1.7679572	−5.9394583
C	2.2283862	1.6279644	−7.4297749
C	2.4369041	3.001968	−5.3724485
H	2.7090598	3.8337998	−6.0076261
C	2.3681337	3.1822405	−4.0016973
C	2.6297289	4.5411051	−3.4159334
C	2.017496	2.1079174	−3.1758815
C	0.6251786	1.2432454	−1.0304959
C	0.6339953	0.2493054	−0.1162411
C	1.7449865	0.8744557	−3.7519461
H	1.4886022	0.0330087	−3.1226814
C	1.7987498	0.7052573	−5.1240465
H	1.5751851	−0.2664589	−5.5409658
C	−0.7491389	1.3763561	−1.5584933
C	−1.2795399	2.2657507	−2.4664133
H	−0.66641	3.0303035	−2.9257619
C	−2.6387979	2.1711286	−2.7697714
H	−3.0730188	2.859199	−3.482494
C	3.370644	−1.2643787	2.0430319
H	4.4197947	−1.2014432	2.298375
C	2.8348688	−0.3738615	1.1118315
H	3.459781	0.3725113	0.6392588
C	1.4945857	−0.4717558	0.8049289
C	−1.456305	−0.0238785	5.9343958
F	−3.2881294	−5.7478849	4.9725369
F	−4.0748669	−4.4945165	6.5364338
F	−2.0358054	−5.1644673	6.6237891
F	−1.1068368	1.0152961	5.1782539
F	−0.4357099	−0.2872336	6.7559139
F	−2.4832318	0.3599638	6.6985623
F	1.929231	0.3938816	−7.8367699
F	3.4545382	1.9134576	−7.8793391
F	1.3861447	2.4677879	−8.0408793
F	3.0903806	5.3992691	−4.3262611
F	3.5337008	4.4834706	−2.4331782
F	1.5143769	5.0690366	−2.9040714

Table S5. Coordinates of the calculated structure of **3** (B3LYP-D3/def2-TZVP).

	x	y	z
C	−2.6245706	0.0884836	−3.4920269
C	−2.1962904	−1.2198038	−3.3750774
C	−1.3308694	−1.6010642	−2.3483324
C	−0.9090258	−0.6449039	−1.4469605
C	−1.3365178	0.6956132	−1.5795557
C	−2.1981435	1.0649385	−2.5900345
C	−0.0391475	−0.683806	−0.2750768
C	0.0391475	0.683806	0.2750768
C	−0.7143983	1.4894691	−0.5013903
C	0.7143983	−1.4894691	0.5013903
C	1.3365178	−0.6956132	1.5795557
C	0.9090258	0.6449039	1.4469605
C	2.1981435	−1.0649385	2.5900345
C	2.6245706	−0.0884836	3.4920269
C	2.1962904	1.2198038	3.3750774
C	1.3308694	1.6010642	2.3483324
S	0.902556	−3.2414424	0.3615474
S	−0.902556	3.2414424	−0.3615474
C	−0.2263031	−3.8080092	1.6101425
C	0.2263031	3.8080092	−1.6101425
O	−2.2520215	3.5888296	−0.7714866
O	−0.3937221	3.6584851	0.9321172
O	0.3937221	−3.6584851	−0.9321172
O	2.2520215	−3.5888296	0.7714866
C	1.590734	3.7327201	−1.3611913
C	2.4745494	4.1744145	−2.3297103
C	1.9946093	4.695558	−3.5245053
C	0.6300702	4.7771656	−3.7548342
C	−0.2660621	4.3313293	−2.7947729
C	−1.590734	−3.7327201	1.3611913
C	−2.4745494	−4.1744145	2.3297103
C	−1.9946093	−4.695558	3.5245053
C	−0.6300702	−4.7771656	3.7548342
C	0.2660621	−4.3313293	2.7947729
H	−3.3009518	0.3648061	−4.2897752
H	−2.5316465	−1.9624838	−4.0863074
H	−0.9923786	−2.6220058	−2.2732213
H	−2.5574238	2.0786005	−2.6814426
H	2.5574238	−2.0786005	2.6814426
H	3.3009518	−0.3648061	4.2897752
H	2.5316465	1.9624838	4.0863074
H	0.9923786	2.6220058	2.2732213
H	1.9619548	3.3332842	−0.4263163
H	3.5394587	4.1168828	−2.1505664
H	2.6896179	5.0419837	−4.2777259
H	0.2592023	5.1907642	−4.6827199
H	−1.3318278	4.4013691	−2.9623875
H	−1.9619548	−3.3332842	0.4263163
H	−3.5394587	−4.1168828	2.1505664
H	−2.6896179	−5.0419837	4.2777259
H	−0.2592023	−5.1907642	4.6827199
H	1.3318278	−4.4013691	2.9623875

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