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Electronic coupling mediated by furan, thiophene, selenophene and tellurophene in a homologous series of organic mixed valence compounds

Supporting Information

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Synthesis and product characterization data

10,10'-biphenothiazinyl-2,5-furan, compound **1**. This is a modified version of a synthetic procedure reported earlier:[1] Commercially available 2,5-dibromofuran (100 µL, 0.96 mmol), 10*H*-phenothiazine (381 mg, 1.91 mmol), sodium *tert*-butoxide (1.84 g, 19.12 mmol), $Pd(dba)_2$ (43.8 mg, 5 mol-%), tri-*tert*-butylphosphonium tetrafluoroborate (13.9 mg, 5 mol-%) and dry toluene (30 mL) were placed in a 2-neck flask under N_2 atmosphere. The reaction was heated to 80 °C for 24 h. After cooling to room temperature the reaction was filtered over celite, and the latter was washed with CH_2Cl_2. After the solvent was removed, the crude product was purified by column chromatography (silica, eluted first with pentane and then with pentane/acetone 10:1). Due to minor impurities a second purification by column chromatography (silica, eluted with pentane/acetone 30:1) was performed. The final product was obtained as a shiny white solid (42 mg, 0.09 mmol, 10%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 7.13 (dd, $J_{H,H}$ = 7.6, 1.6 Hz, 4H), 7.09 (ddd, $J_{H,H}$ = 8.1, 7.6, 1.6 Hz, 4H), 6.98 (td, $J_{H,H}$ = 7.6, 1.2 Hz, 4H), 6.78 (dd, $J_{H,H}$ = 8.1, 1.2 Hz, 4H), 6.58 (s, 2H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ (ppm) = 145.94, 143.75, 127.90, 127.57, 124.51, 123.21, 117.42, 109.26. ESI-MS calculated (m/z) for $C_{28}H_{18}N_2OS_2$: 462.0855; found: 462.0856. EA calculated (%) for $C_{28}H_{18}N_2OS_2$: C 72.70, H 3.92, N 6.06; found: C 72.91, H 4.53, N 5.80.

10,10'-biphenothiazinyl-2,5-thiophene, compound **2**. This is a modified version of a synthetic procedure reported earlier for the analogous compound with furan instead of thiophene (see above):[1] Commercially available 2,5-dibromothiophene (100 µL, 0.89 mmol), 10*H*-phenothiazine (350 mg, 1.76 mmol), sodium *tert*-butoxide (1.69 g, 17.57 mmol), $Pd(dba)_2$ (40.2 mg, 5 mol-%), tri-*tert*-butylphosphonium tetrafluoroborate (12.8 mg, 5 mol-%) and dry toluene (30 mL) were placed in a 2-neck flask under N_2 atmosphere. The reaction was heated to 80 °C for 24 h. After cooling to room temperature the reaction was filtered over celite, and the latter was washed with CH_2Cl_2. After the solvent was removed, the crude product was purified by column chromatography (silica, eluted with pentane/CH_2Cl_2 5:1). The final product was obtained as a yellow crystalline solid (276 mg, 0.58 mmol, 65%). ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) = 6.93 (dd, $J_{H,H}$ = 7.6, 1.6 Hz, 4H), 6.86 (dd, $J_{H,H}$ = 8.2, 1.2 Hz, 4H), 6.75 (td, $J_{H,H}$ = 8.2, 7.6, 1.6 Hz, 4H), 6.63 (td, $J_{H,H}$ = 7.6, 1.2 Hz, 4H), 6.45 (s, 2H). ^{13}C NMR (C_6D_6, 100 MHz): δ (ppm) = 144.23, 142.58, 127.40, 127.38, 126.03, 124.06, 123.43, 118.00. ESI-MS calculated (m/z) for $C_{28}H_{18}N_2S_3$: 478.0627; found: 478.0630. EA calculated (%) for $C_{28}H_{18}N_2S_3$: C 70.26, H 3.79, N 5.85; found: C 70.22, H 4.05, N 5.86.

10,10'-biphenothiazinyl-2,5-selenophene, compound **3**. Commercially available 2,5-dibromo-selenophene (100 µL, 0.87 mmol), 10*H*-phenothiazine (345 mg, 1.73 mmol), sodium *tert*-butoxide (1.66 g, 17.31 mmol), $Pd(dba)_2$ (39.6 mg, 5 mol-%), tri-*tert*-butylphosphonium tetrafluoroborate (12.6 mg, 5 mol-%) and dry toluene (30 mL) were placed in a 2-neck flask under N_2 atmosphere. The reaction was heated to 80 °C for 24 h. After cooling to room temperature the reaction was filtered over celite, and the latter was washed with CH_2Cl_2. After the solvent was removed, the crude product was purified by column chromatography (silica, eluted with pentane/CH_2Cl_2 5:1). The final product was obtained as an orange-yellow solid (351 mg, 0.67 mmol, 77%). ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) = 7.05 (dd, $J_{H,H}$ = 8.2, 1.3 Hz, 4H), 6.93 (dd, $J_{H,H}$ = 7.6, 1.6 Hz, 4H), 6.81-6.72 (m, 4H), 6.64 (td, $J_{H,H}$ = 7.6, 1.3 Hz, 4H), 6.51 (s, 2H). ^{13}C NMR (C_6D_6, 100 MHz): δ (ppm) = 149.33, 144.05, 127.39, 127.37, 126.57, 124.26, 123.91, 118.88. ESI-MS calculated (m/z) for $C_{28}H_{18}N_2S_2Se$: 526.0071; found: 526.0069. EA calculated (%) for $C_{28}H_{18}N_2S_2Se$: C 63.99, H 3.45, N 5.33; found: C 63.89, H 3.79, N 5.40.

Tellurophene. This is a modified version of a previously described procedure:[2]
Flask A: Under N_2 atmosphere tellurium powder (17.40 g, 136 mmol) was placed together with dry, oxygen-free ethanol (700 mL) in a 1L flask. Sodium borohydride (26.73 g, 710 mmol) was added in one portion and the reaction was brought to reflux for 2.5 h. Every 30 minutes an additional portion of sodium borohydride (4 × 5 g, 528 mmol) was added until the solution became almost colorless. When the tellurium reduction was finished, the solution was cooled in an ice bath.
Flask B: In a second flask under N_2 atmosphere, fitted with a condenser and a closed gas injection to flask A, a solution of KOH (68.88 g, 1.23 mol) in water (200 mL) was brought to reflux. A solution of 1,4-dichloro-2-butyne (40 mL, 409 mmol) in dry, oxygen-free 1,4-dioxane (60 mL) was added to the refluxing solution to produce in situ butadiyne gas.
The gas injection between flask A and B was opened. As soon as the first butadiyne gas arrived in flask A, the ice bath was removed. The gas was allowed to bubble through the solution of flask A for 2 h. Then the reaction mixture was diluted with pentane (280 mL) and quenched with brine (200 mL). After filtration over celite the organic layer was separated, and the aqueous layer was extracted with pentane. The combined organic phases were washed with brine (3×) and dried over anhydrous Na_2SO_4. After the solvent was removed, the crude product was purified by column chromatography (silica, eluted with pentane). Due to the product's low boiling point, the solvent was not fully removed. The final product was obtained as dark orange oil (3.85 g, 21.44 mmol, 16%). ^{1}H NMR ($CDCl_3$, 400 MHz): AA'XX' spin system with resonances at 8.97 ppm (2 H) and at 7.85 ppm (2 H), coupling constants: $J_{H,H}$ = 7.8 Hz, $J_{Te,H}$ = 3.0 Hz.

2,5-dibromotellurophene. This is an adapted version of a previously described procedure:[3]
Tellurophene (600 mg, 3.34 mmol) and TMEDA (1.05 mL, 7.01 mmol) were dissolved in dry hexane (30 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and *sec*-butyllithium (1.3 M in cyclohexane/hexane 92:8, 5.39 mL, 7.01 mmol) was added dropwise. The reaction mixture was heated to 65 °C for 45 minutes. Then the reaction mixture was cooled to -78 °C and 1,2-dibromo-tetrachloroethane (2.175 g, 6.68 mmol) dissolved in dry Et_2O (35 mL) was added. While stirring over night the reaction was allowed to warm up to room temperature. Then the reaction was quenched by addition of water. After extraction with pentane, the combined organic layers were dried over Na_2SO_4, and the solvent was removed. The crude product was purified by column chromatography (silica, eluted with pentane). The product was obtained as a pale yellow solid (288 mg, 0.83 mmol, 25%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.34 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 140.23, 109.75. EI-MS (m/z, %): 337.8 ($C_4H_2Br_2$, 100), 258.8 (C_4H_2Br, 38), 208.8 (40), 129.9 (Te, 46), 50 (27). EA calculated (%) for $C_4H_2Br_2Te \cdot 1/8$ pentane: C 16.03, H 1.02, N 0.00; found: C 15.96, H 0.98, N 0.00.

10,10'-biphenothiazinyl-2,5-tellurophene, compound **4**. 2,5-dibromotellurophene (111 mg, 0.33 mmol), 10*H*-phenothiazine (130 mg, 0.65 mmol), sodium *tert*-butoxide (632 mg, 6.58 mmol), $Pd(dba)_2$ (15.1 mg, 5 mol-%), tri-*tert*-butylphosphonium tetrafluoroborate (4.77 mg, 5 mol-%) and dry toluene (20 mL) were placed in a 2-neck flask under N_2 atmosphere. The reaction was heated to 80 °C for 24 h. After cooling to room temperature the reaction was filtered over celite, and the latter was washed with CH_2Cl_2. After the solvent was removed, the crude product was extracted with CH_2Cl_2 against water. The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed. The final product was obtained as dark brown solid (134 mg, 0.23 mmol, 71%) in a mixture with a side-product (~9%). The poor stability of compound **4** precluded further purification. Mass-spectrometry and EPR spectroscopy suggest that the side-product is a tellurium-free species. ^{1}H NMR (acetone-d_6, 500 MHz): δ (ppm) = 7.33 (dd, $J_{H,H}$ = 8.5, 1.2 Hz, 4H), 7.21-7.15 (m, 8H), 7.10 (s, 2H), 7.06 (td, $J_{H,H}$ = 7.6, 1.2 Hz, 4H). ^{13}C NMR (acetone-d_6, 125 MHz): δ (ppm) = 147.95, 144.42, 130.53,

128.32, 127.87, 125.35, 125.09, 121.12. ESI-MS calculated (m/z) for $C_{28}H_{18}N_2S_2Te$: 575.9968; found: 575.9966. EA calculated (%) for $C_{28}H_{18}N_2S_2Te$: C 65.76, H 3.75, N 5.48; found: C 62.80 H 4.40, N 4.63. We have been unable to obtain satisfactory results from elemental analysis due to difficulties associated with the purification of this product, see comment above. The ^{1}H NMR spectrum clearly shows that the desired product is the majority product (~91%) resulting from this synthesis.

Experimental methods/ apparatus

^{1}H and ^{13}C NMR spectra were recorded either on a Bruker 400 MHz Avance III spectrometer or on a Bruker 500 MHz Avance III spectrometer. Chemical shifts are reported in ppm relative to residual proton and carbon signals of the solvent as is common practice.[4] High-resolution electron spray mass spectrometry (ESI-MS) was measured on a Bruker maXis 4G QTOF instrument. The EI mass spectrum was recorded with a Finnigan MAT 8200. Elemental analyses were performed by Ms. Sylvie Mittelheisser in the analytical laboratory of the Department of Chemistry at Universität Basel using an Elementar Vario Micro Cube instrument. Chemical oxidation of compounds **1** – **4** to their monocationic and dicationic forms was effected with $Cu(ClO_4)_2$ in CH_3CN or with $SbCl_5$ in CH_2Cl_2. This is a common procedure for generating triarylamine radical cations.[5] Cyclic voltammetry was performed using a potentiostat from Princeton Applied Research (Versastat3-200) with a glassy carbon disk working electrode and two separate silver wires as counter and quasi-reference electrodes. Optical absorption spectra were measured on a Cary 5000 instrument from Varian. UV-Vis and cyclic voltammetry data were analyzed using the Igor Pro software (version 6.3.2.3) from WaveMetrics. Electron paramagnetic resonance (EPR) measurements were performed on a Bruker CW EPR Elexsys-500 spectrometer equipped with a variable temperature unit. The spectra were recorded at 297 K with the following parameters: microwave power 2 mW, number of scans up to 20, modulation amplitude 2 G, and sweep width 80 G. Working frequencies were 9.458569 GHz for $\mathbf{1}^+$, 9.517391 GHz for $\mathbf{2}^+$, 9.461641 GHz for $\mathbf{3}^+$, and 9.455617 GHz for $\mathbf{4}^+$, respectively. EPR spectra were simulated using the WinSim (NIEHS/NIH) simulation package. For spectra resulting from a superposition of contributions of paramagnetic species, the fit determined the relative intensity of each component with a typical error of 5%. (http://www.niehs.nih.gov/research/resources/software/tools/index.cfm).

Additional optical absorption data

The integrals of the orange bands in Figure 1 were used to determine μ_{ge} (equation 1).

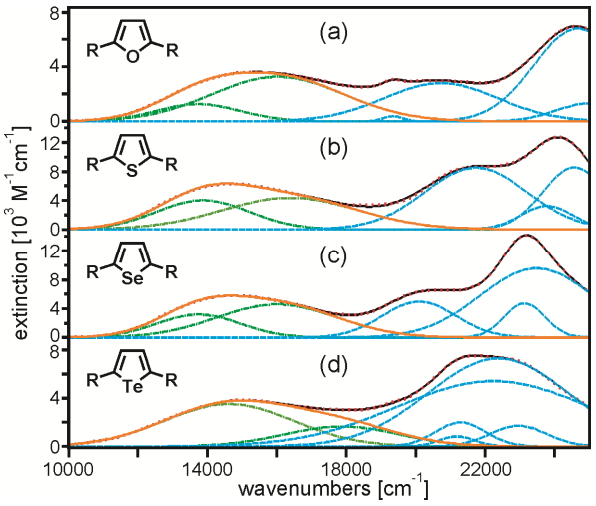


Figure S1. Solid black traces: Experimental absorption spectra of the various chalcogenophene monocations $\mathbf{1}^+$ – $\mathbf{4}^+$. Dotted red traces: Simulated absorption spectra representing the sum of several Gaussian functions. Dashed blue and green traces: Individual Gaussian functions used to simulate the experimental absorption spectra; their sums correspond to the dotted red traces. Solid orange traces: Sum of the green traces, i. e., the Gaussian functions used to simulate the IVCT contribution to the overall absorption spectra.

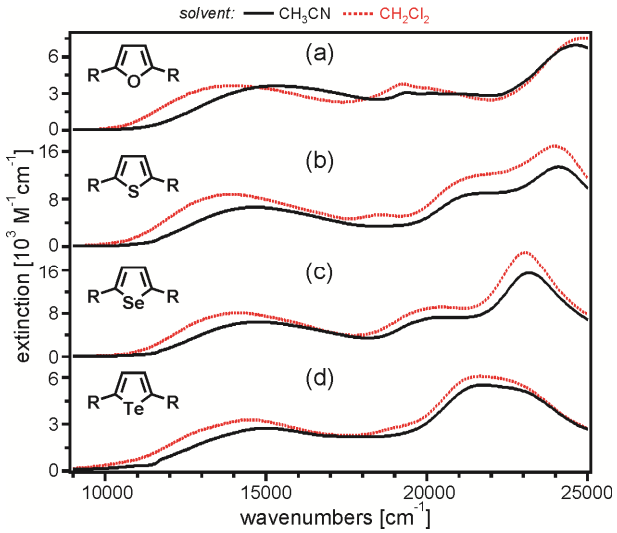


Figure S2. Solvent dependence of the optical absorption spectra of $\mathbf{1}^+$ – $\mathbf{4}^+$.

Additional EPR data

As noted above, compound **4** contains about 10% of an impurity which is likely to be a tellurium-free species. We speculate that this impurity is the compound shown in the inset of Figure S3c (R = phenothiazine residue).

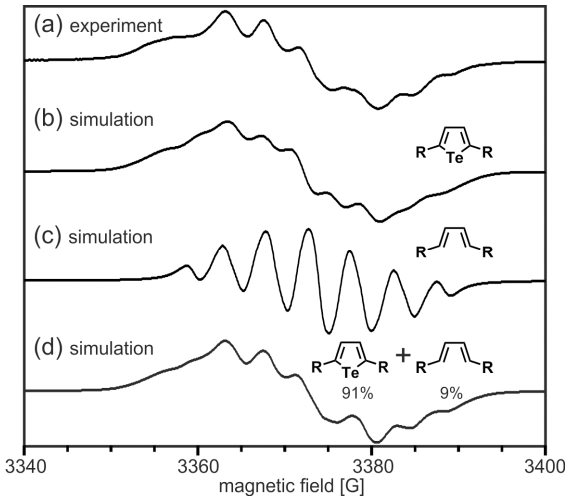


Figure S3. Experimental and simulated EPR spectra for compound $\mathbf{4}^+$.

The simulated EPR spectrum shown as the dotted orange trace in Figure 4d (also shown in Figure S3d) is the sum of the simulation spectra obtained for the tellurophene cation $\mathbf{4}^+$ (Figure S3b) and the cation of the molecule shown as an inset in Figure S3c.

The EPR spectra of $\mathbf{1}^+ - \mathbf{4}^+$ can be satisfactorily simulated by taking into account hyperfine interactions with the ^{14}N nuclei of phenothiazine and the ^{1}H nuclei of the chalcogenophene bridges (Table 3). For $\mathbf{1}^+ - \mathbf{3}^+$, hyperfine interactions with the chalcogenophene heteroatom (O, S, Se) can be excluded. For $\mathbf{4}^+$, a simulation with a_{Te} = 4.8 G and a_N = 4.1 G yields the spectrum shown in Figure S4b. From comparison with the experimental spectrum in Figure S4a we conclude that in the case of monocation $\mathbf{4}^+$ hyperfine interaction with the tellurium nucleus cannot be rigorously excluded.

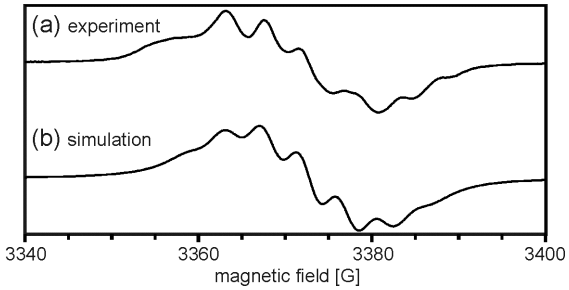
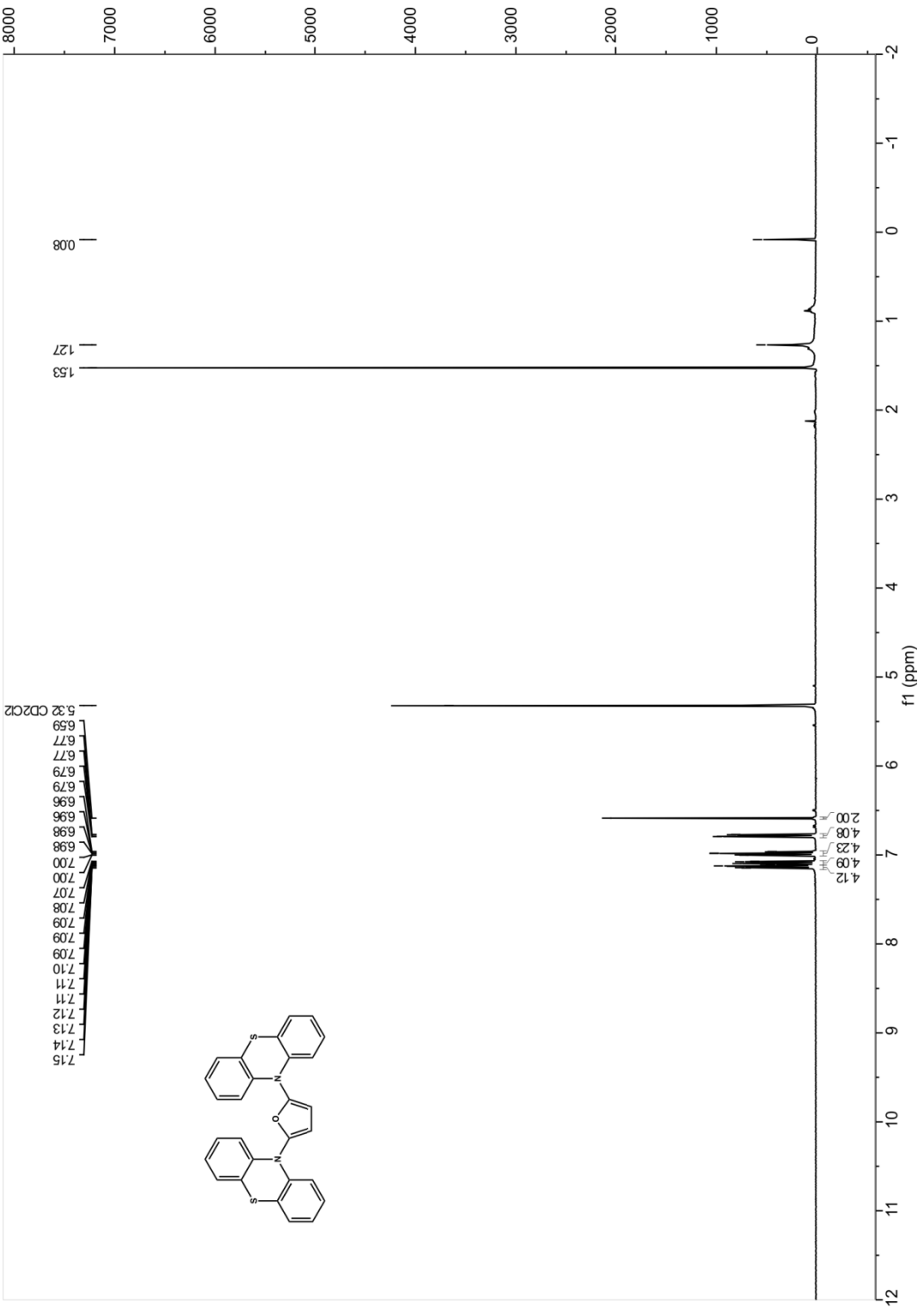
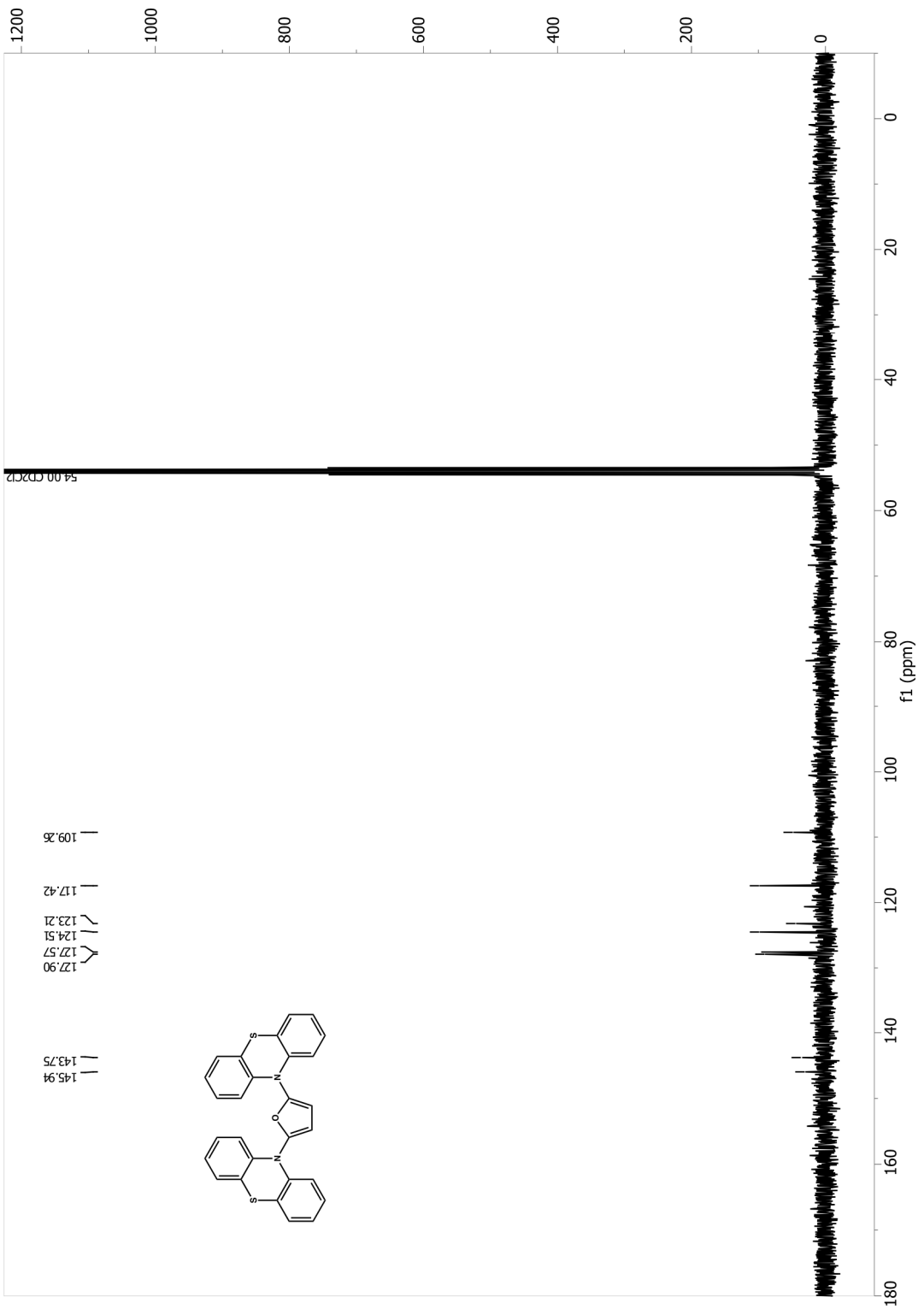
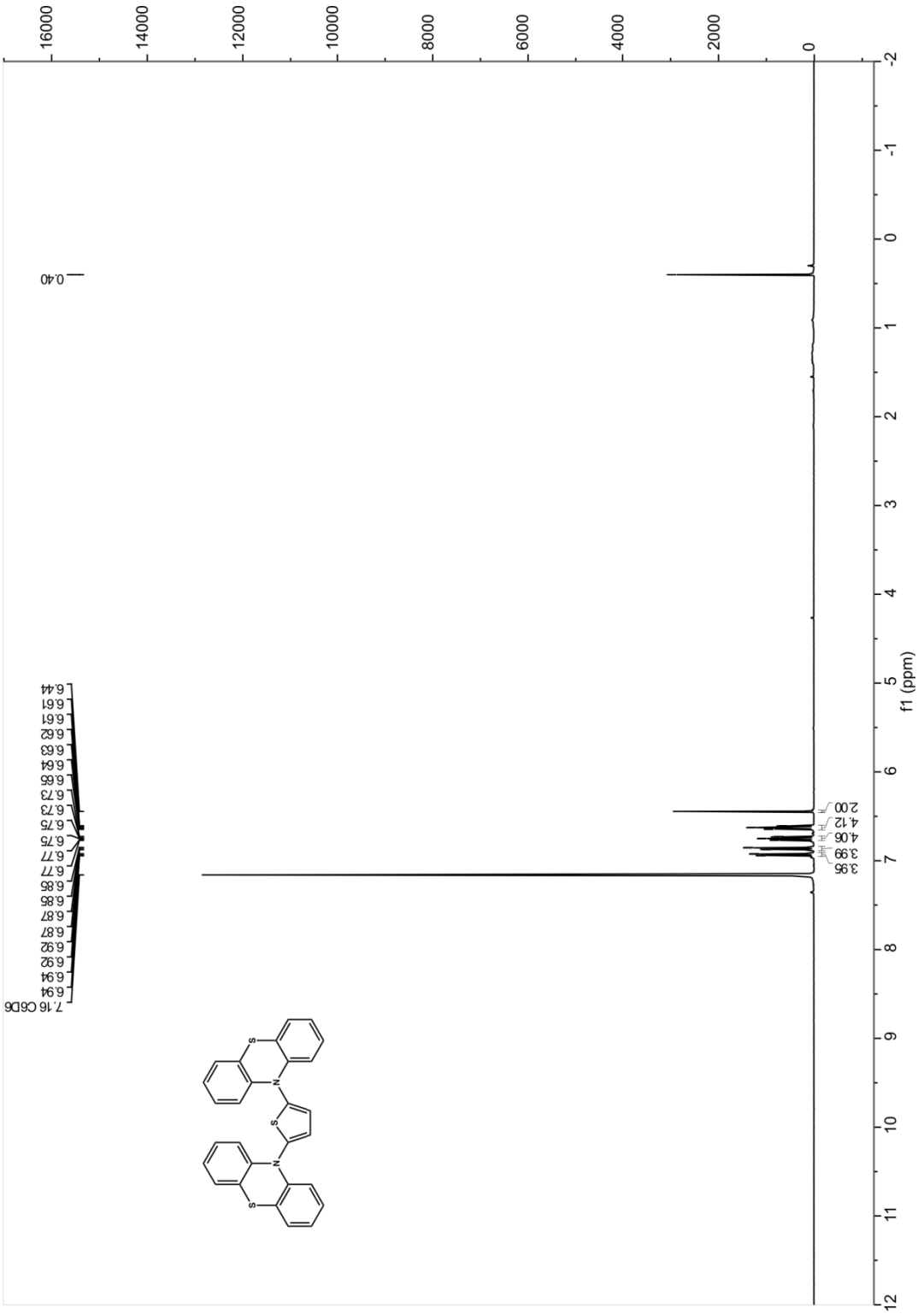


Figure S4. Experimental and simulated EPR spectra of $\mathbf{4}^+$.



This ^{1}H NMR spectrum contains resonances due to a grease impurity (0.08 and 1.27 ppm).


145.94
143.75
127.90
127.57
124.51
123.21
117.42
109.26
54.00 CD2Cl2
f1 (ppm)


16000
14000
12000
10000
8000
6000
4000
2000
0
-2
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
f1 (ppm)
0.40
2.00
4.12
4.06
3.99
3.96
7.16 C6D6
6.94
6.94
6.92
6.92
6.87
6.87
6.85
6.85
6.77
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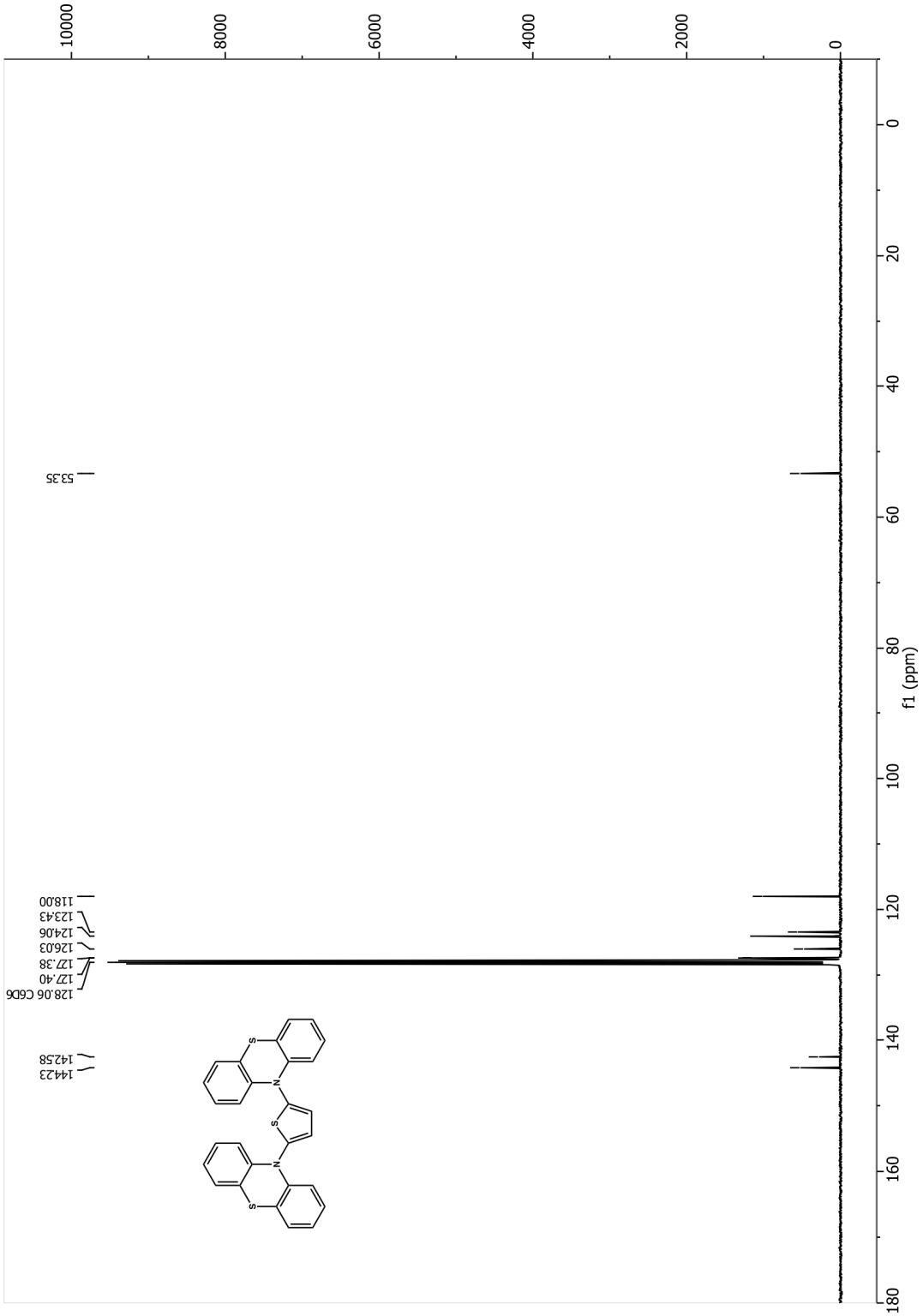
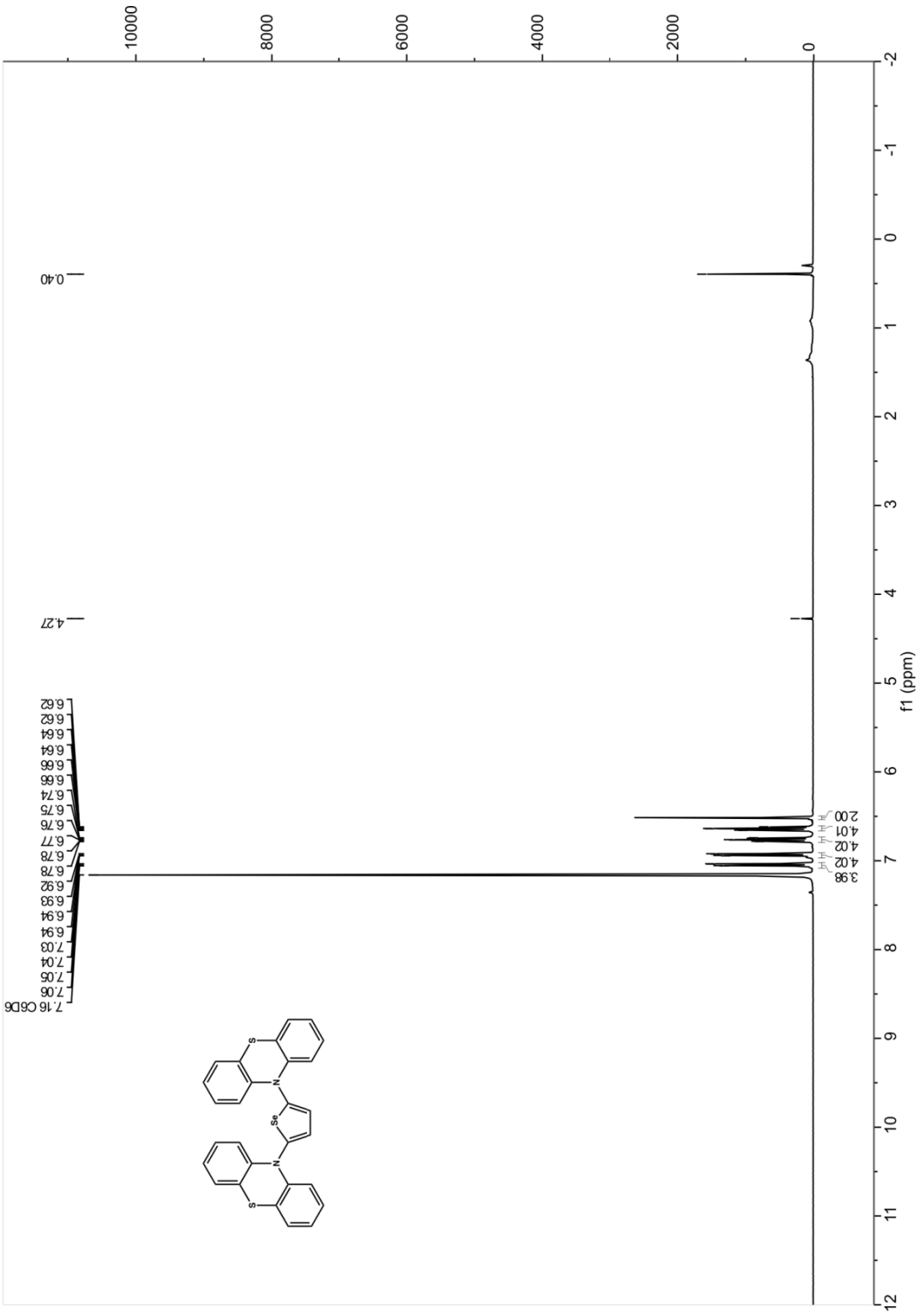
6.64
6.63
6.62
6.61
6.61
6.44



This ^{13}C NMR spectrum contains resonances due to a dichloromethane impurity (53.35 ppm).


10000
8000
6000
4000
2000
0
-2
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
f1 (ppm)
0.40
4.27
7.16 C6D6
7.06
7.05
7.04
7.03
6.94
6.94
6.93
6.92
6.78
6.78
6.77
6.76
6.75
6.74
6.66
6.66
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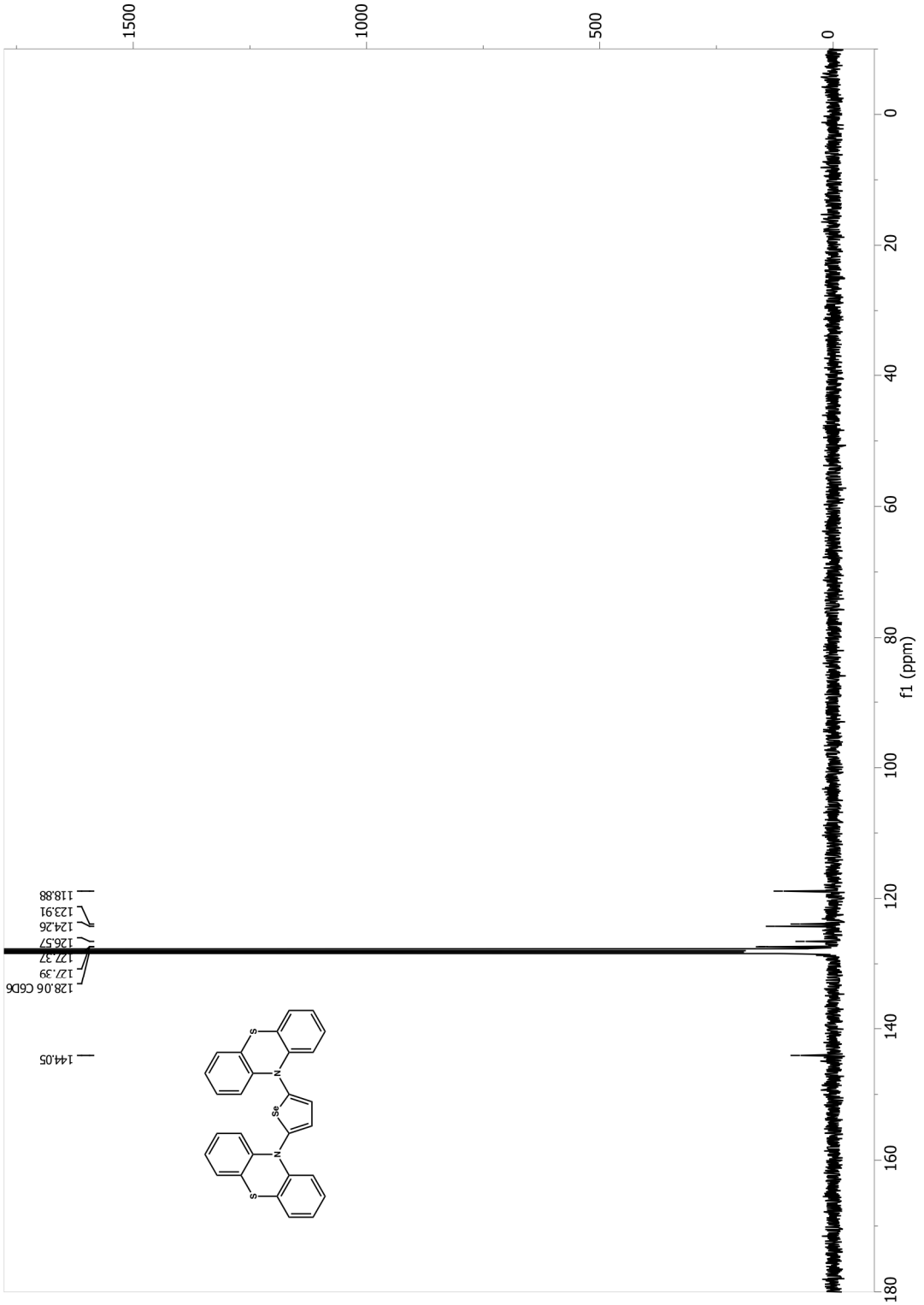
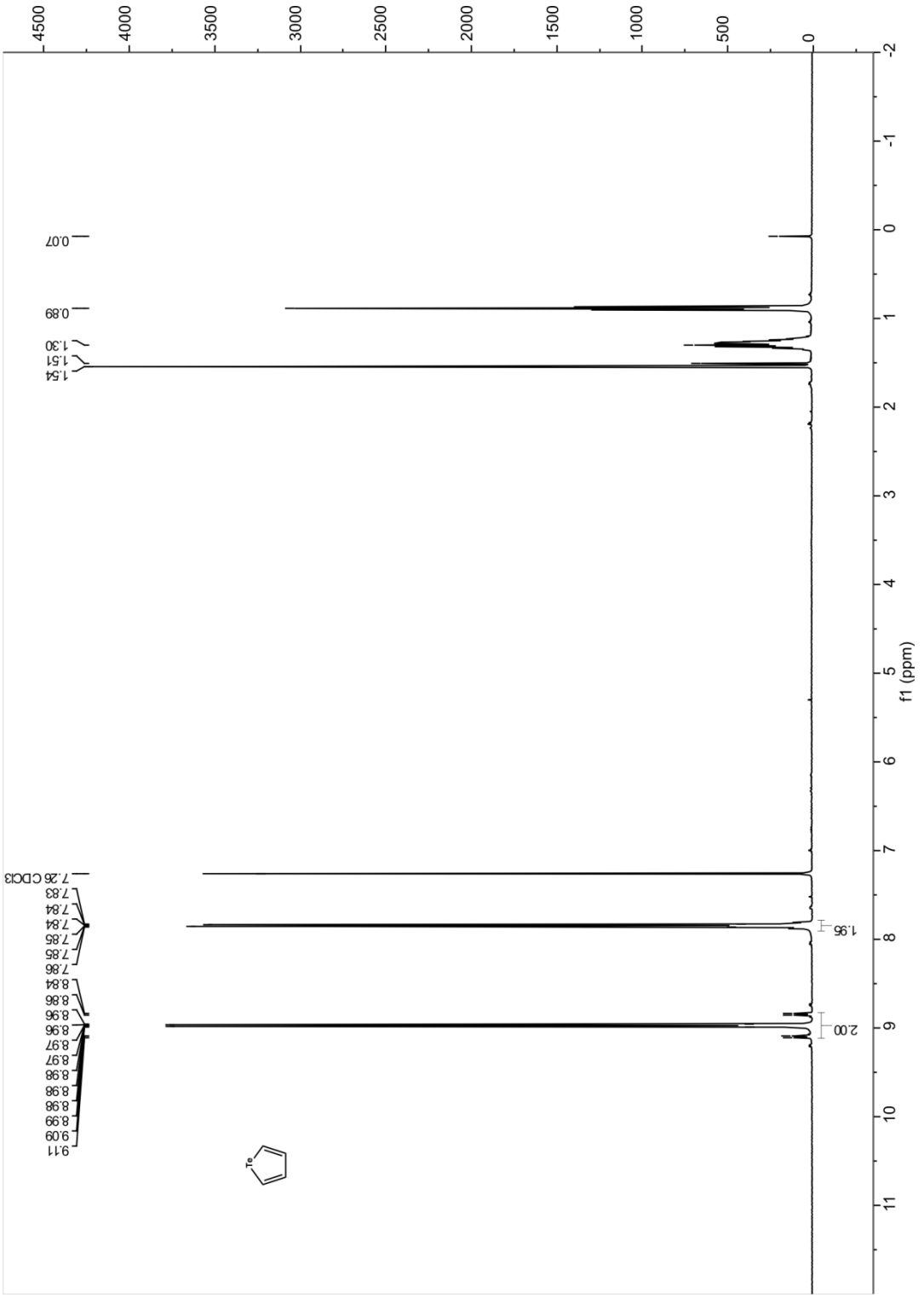
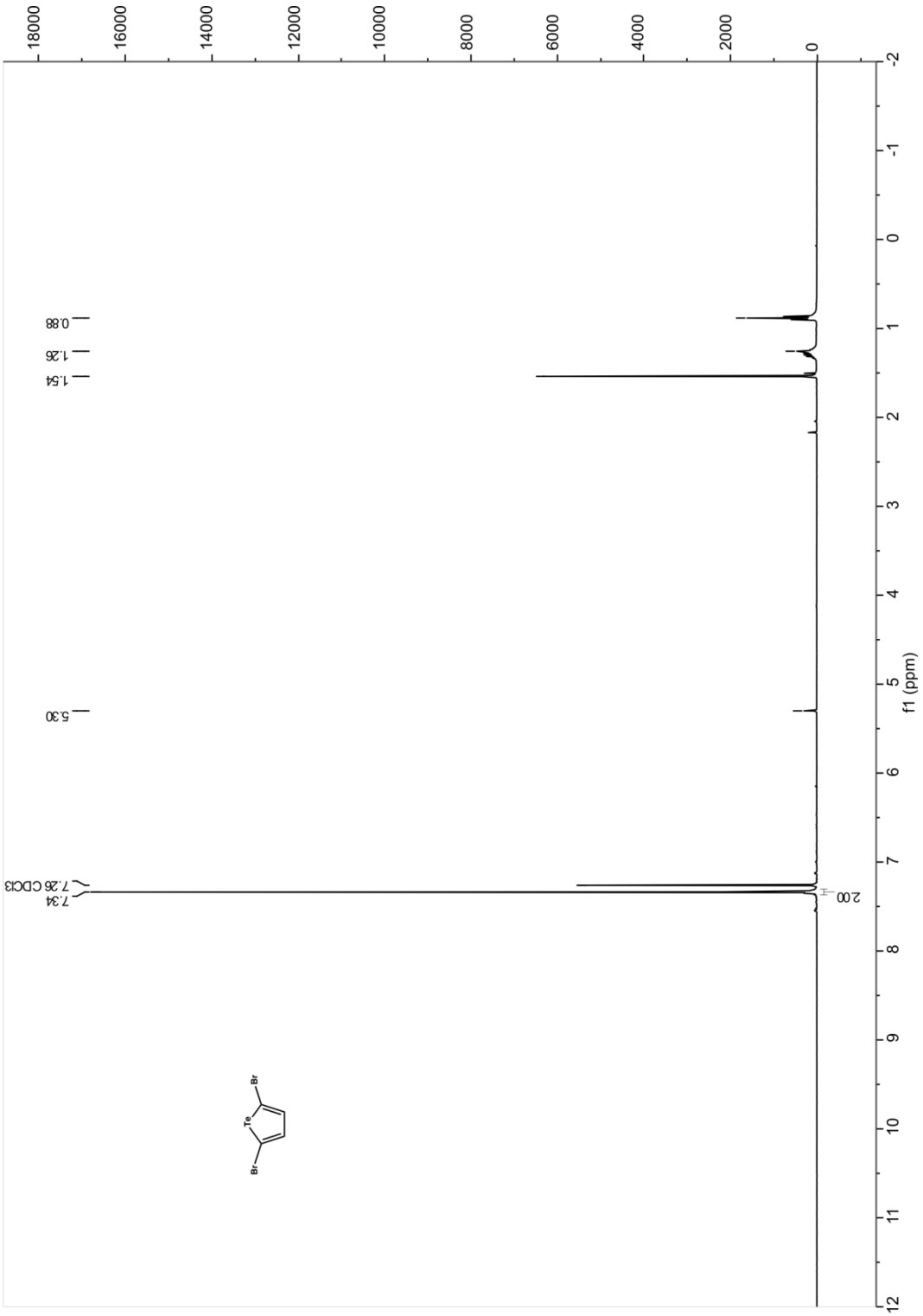
4.02
4.01
2.00
S
N
Se
N
S

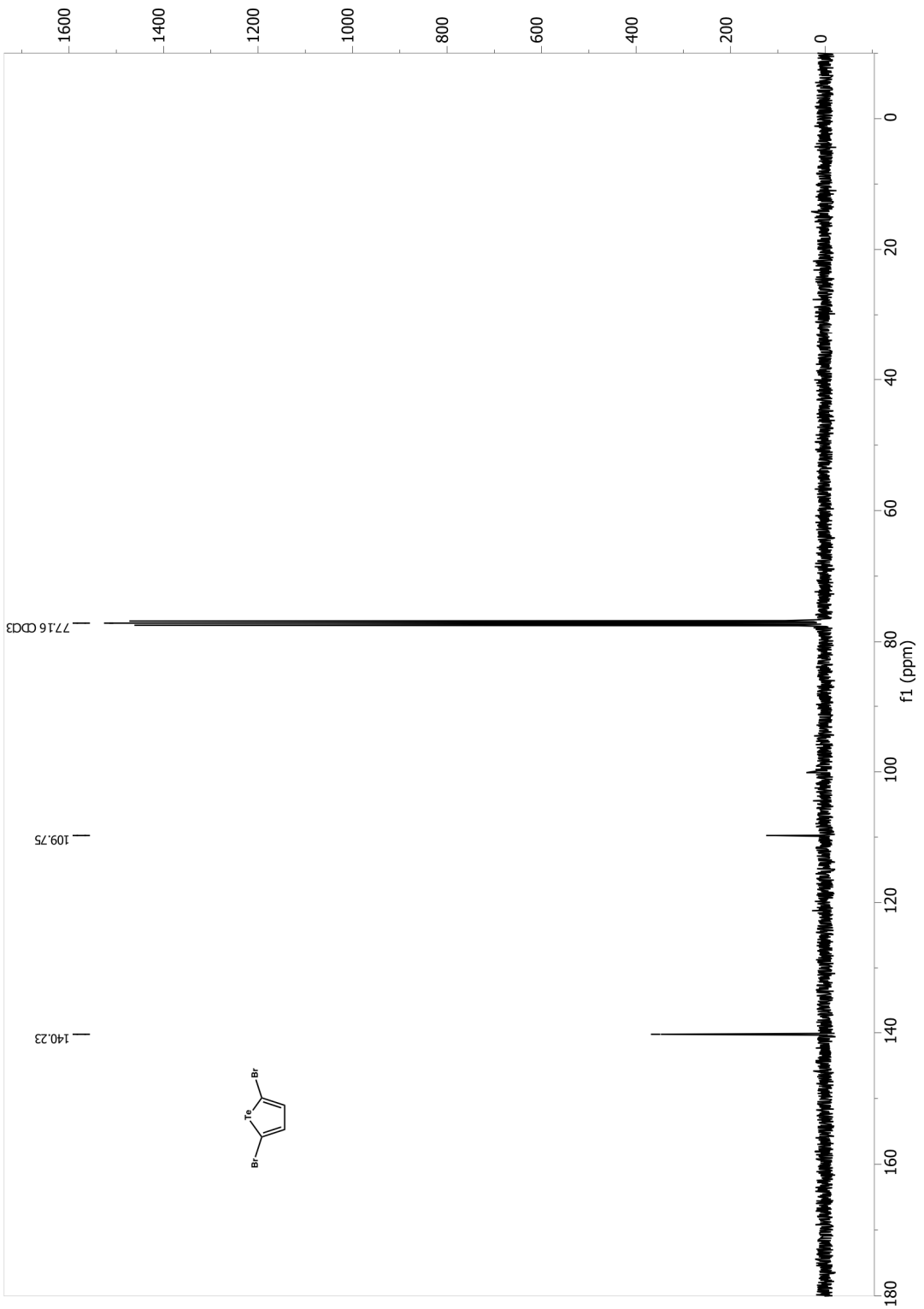

1500
1000
500
0
144.05
128.06 C6D6
127.39
127.37
126.57
124.26
123.91
118.88
S
N
Se
N
S
0
20
40
60
80
100
120
140
160
180
f1 (ppm)

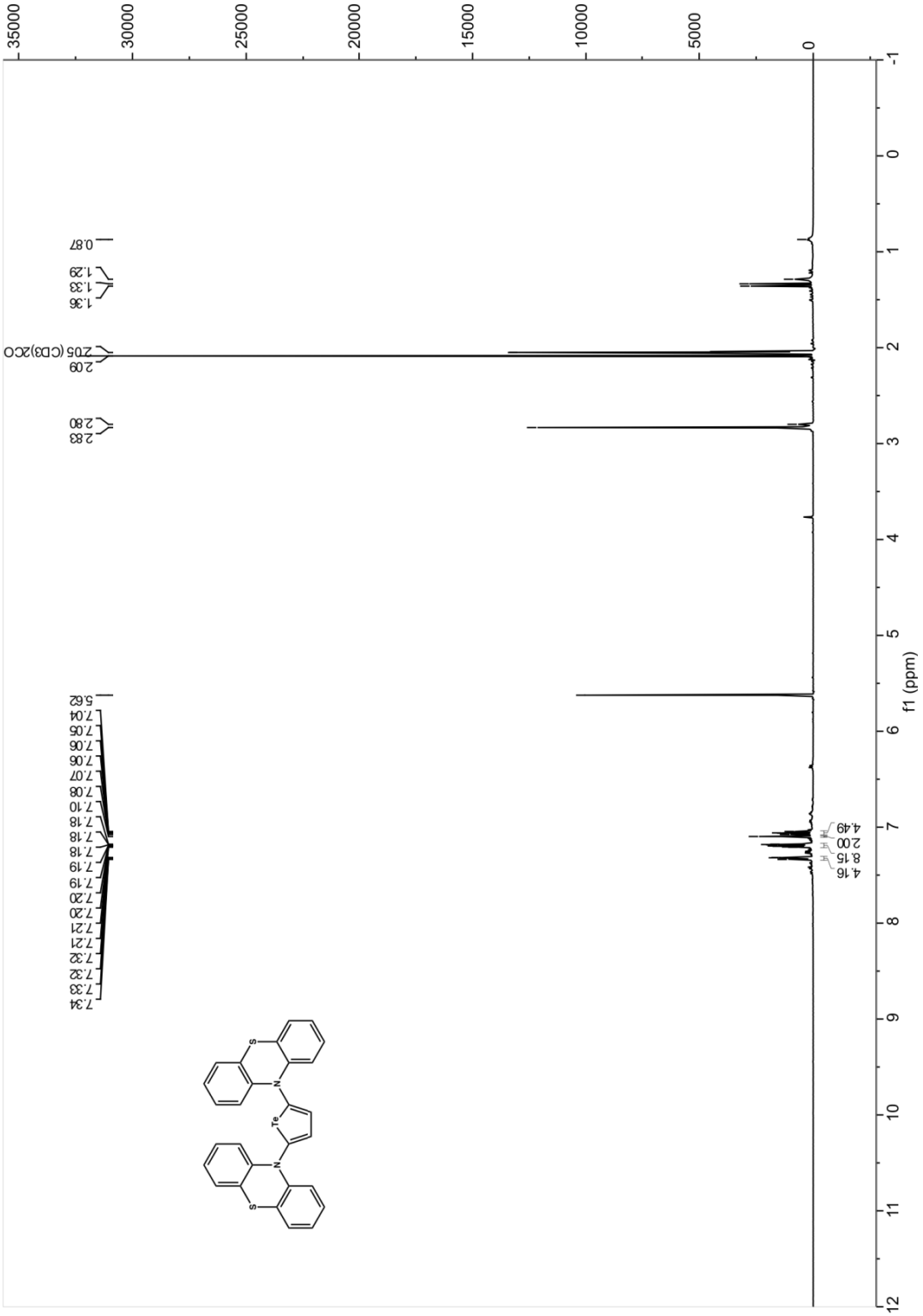


This ^{1}H NMR spectrum contains resonances due to a residue of pentane (0.89 and 1.30 ppm) and a grease impurity (0.07 and 1.30 ppm).

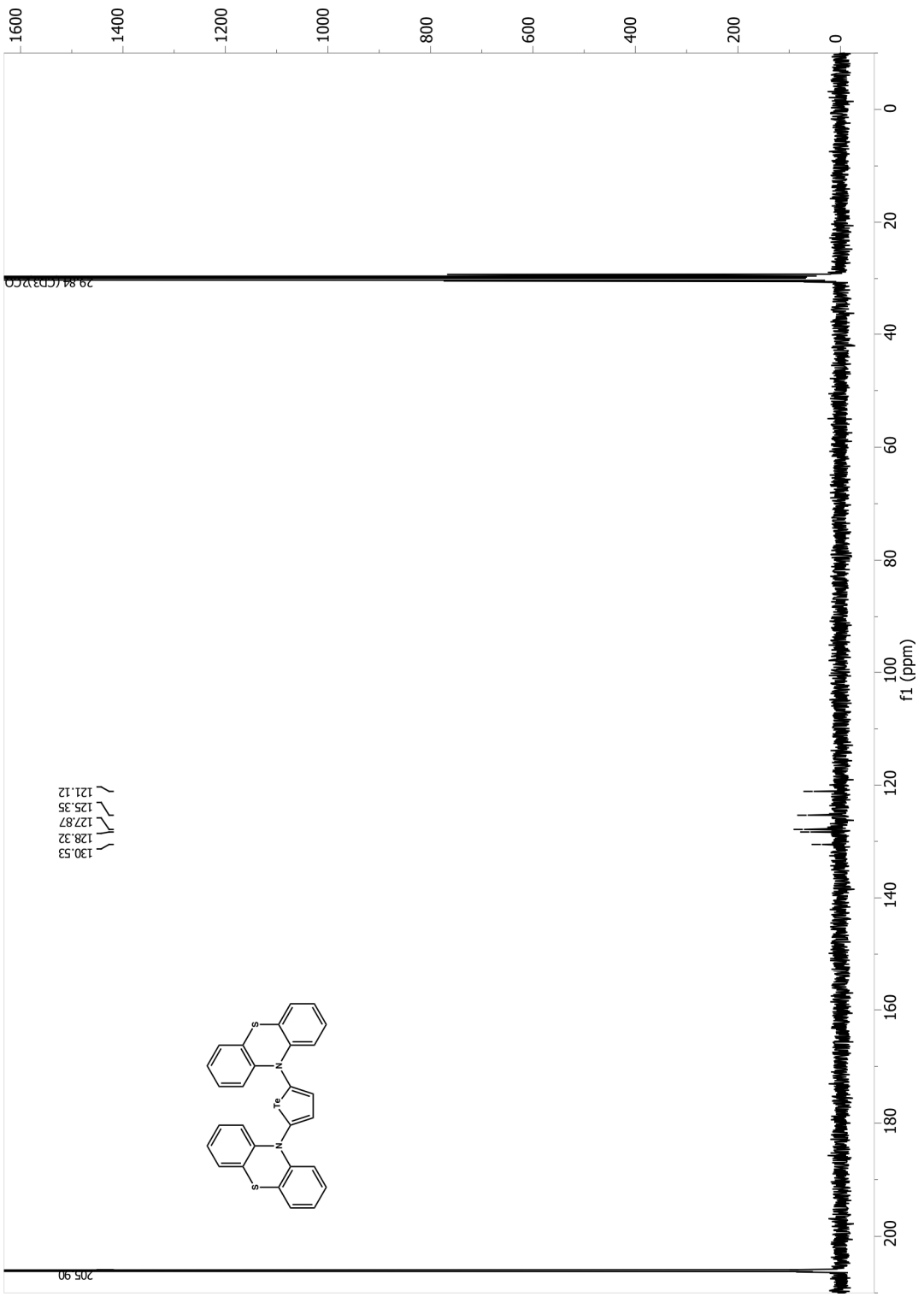


This ^{1}H NMR spectrum contains resonances due to a pentane impurity (0.88 and 1.26 ppm).


1600
1400
1200
1000
800
600
400
200
0
0
20
40
60
80
100
120
140
160
180
f1 (ppm)
77.16 CDCl3
109.75
140.23
Br
Te
Br



This ^{1}H NMR spectrum displays some resonances at 1.36-1.29 ppm which we assign to a decomposition product, see comments above. The resonance at 5.62 ppm is due to CH_2Cl_2.



For the quaternary carbon atoms no resonances could be detected with ordinary 1D ^{13}C NMR spectroscopy. Using 2D NMR spectroscopy we were able to find the resonances of the quaternary carbon atoms at 147.95, 144.47 and 125.09 ppm.

References

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