

Supporting Information

1. Synthesis

Synthetic procedures given in the ESI are according to literature procedures with minor adaptations.

1.1. 3,5-Dibromo-2-methylthiophene (**2**)^{1,2}

In a 1 L three-necked flask 35.60 g (200 mmol, 2.00 eq.) *N*-bromo succinimide are suspended in 250 mL glacial acetic acid. A solution of 9.68 mL (100 mmol, 1.00 eq.) 2-methylthiophene **1** in 50 mL glacial acetic acid is added dropwise in 30 min and the reaction mixture is stirred for 18 h while developing an orange color. A mixture of 400 mL water and 400 mL *n*-hexane are added and the organic phase is separated. The aqueous layer is extracted with *n*-hexane twice. The combined organic layers are washed with Na₂CO₃ solution and brine, dried with Na₂SO₄ and concentrated in vacuo. The crude product is purified by column chromatography (*n*-hexane) to yield 21.45 g (83.8 mmol, 83 %) 3,5-dibromo-2-methylthiophene **2** as a colorless liquid.

¹H-NMR: (CDCl₃, 300 MHz, 300K): δ = 6.86 (s, 1H, H₁), 2.34 (s, 3H, H₂) ppm.

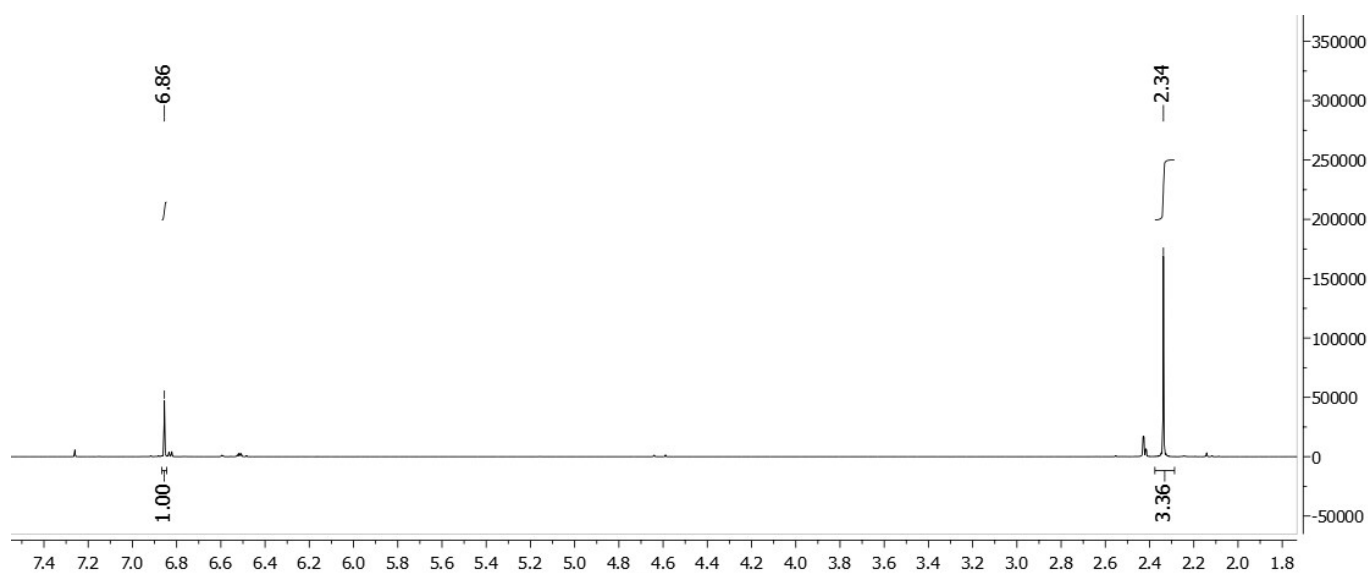
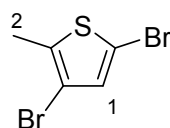


Fig S1 ¹H-NMR-spectrum of 3,5-dibromo-2-methylthiophene in CDCl₃ at 300 K.

1.2. 3-Bromo-2-methyl-5-thienylboronic acid (**3**)^{3,4}

In a flame-dried and argon flushed 250 mL Schlenk flask 20 g (78.14 mmol, 1.00 eq.) 3,5-dibromo-2-methylthiophene **2** are dissolved in 200 mL absolute diethyl ether. The solution is cooled to -78 °C and 32.82 mL of a *n*-BuLi solution in hexanes (2.5 M, 82.04 mmol, 1.05 eq.) are added. After stirring for an hour at low temperature, 22.56 mL tributyl borate (83.61 mmol, 1.07 eq.) are added over 10 min. The mixture is stirred for 15 min at -78°C and 1 h at room temperature. Afterwards, 20 mL of 2 M HCl are added and the mixture stirred for 20 min. The organic layer is separated and extracted with 2 M NaOH solution three times. The aqueous layers are washed with *n*-hexane twice. The aqueous layer is acidified with 2 M HCl leading to a precipitation of 15.04 g (70.98 mmol, 90 %) of the colorless solid product **3** which is collected by filtration, washed with water and dried in an air flow.

¹H-NMR: (CDCl₃, 300 MHz, 300 K) δ =7.34 (s, 1H, H₁), 4.62 (s, 2H, H₃), 2.45 (s, 3H, H₂) ppm.

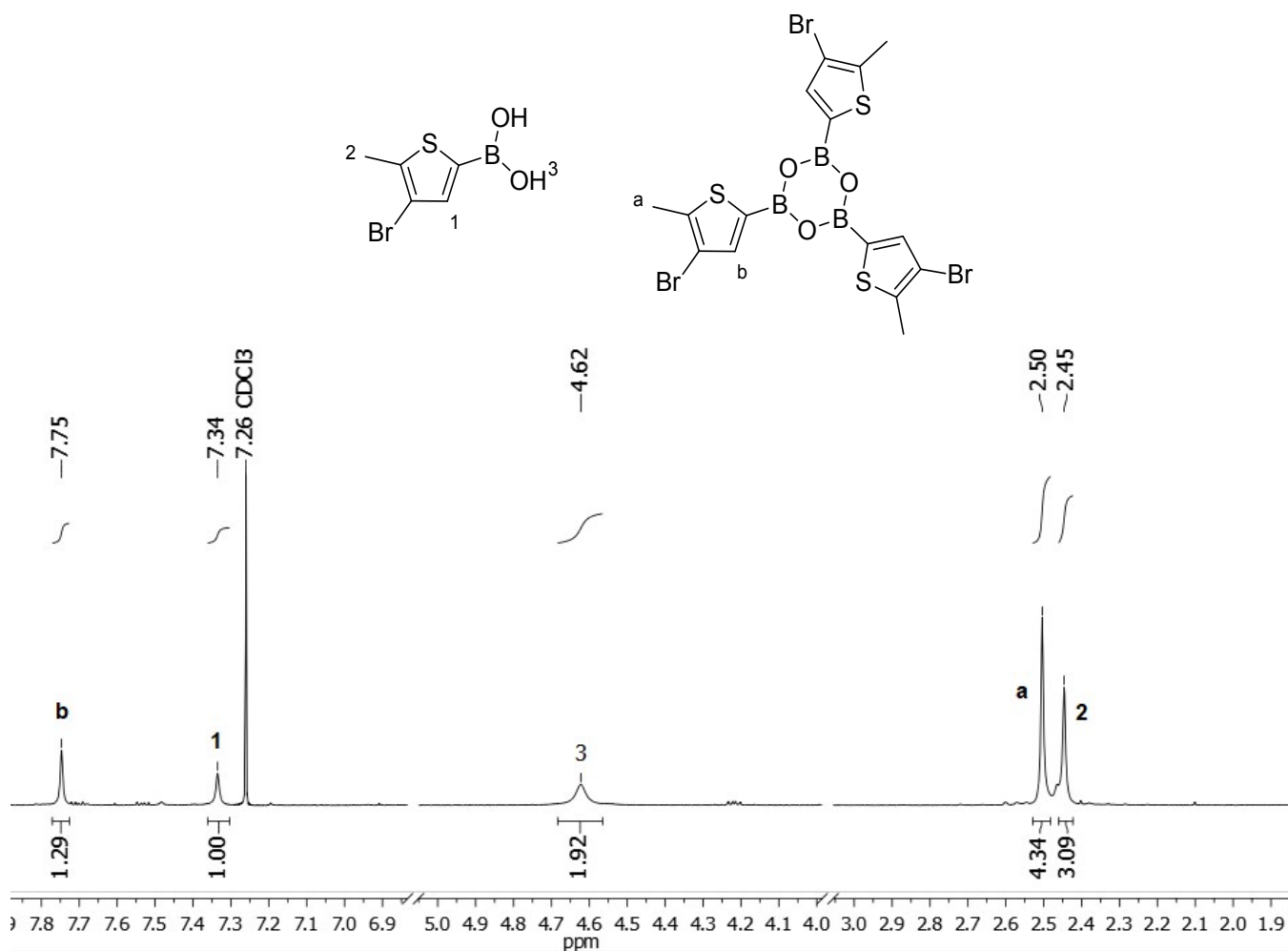


Fig S2 ¹H-NMR-spectrum of 3-bromo-2-thienylboronic acid in CDCl₃ at 300 K.

1.3. 4-Iodothioanisole (**4**)⁵

In a flame-dried and argon flushed 500 mL Schlenk flask 4.06 g (20.00 mmol, 1.00 eq.) 4-bromothioanisole are dissolved in 60 mL abs. diethyl ether. The solution is cooled to $-78\text{ }^{\circ}\text{C}$, 23.53 mL *t*-BuLi (1.7 M in *n*-pentane, 40.00 mmol, 2.00 eq.) are added dropwise and the solution stirred for 45 min. In a separate flask 6.09 g (24.00 mmol, 1.20 eq.) iodine is dissolved in 150 mL abs. diethyl ether and the resulting solution is cooled to $-78\text{ }^{\circ}\text{C}$. The iodine solution is added in portions over 15 min and the reaction mixture stirred for another 25 min at $-78\text{ }^{\circ}\text{C}$ and 25 min at $0\text{ }^{\circ}\text{C}$. The reaction mixture is poured into a mixture of 300 mL diethyl ether and an aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution. The phases are separated and the organic layer is washed twice with a $\text{Na}_2\text{S}_2\text{O}_3$ solution and brine. After drying over Na_2SO_4 and concentration in vacuo, recrystallization leads to 4.04 g (16.15 mmol, 81 %) 4-iodothioanisole **4** as a beige solid.

$^1\text{H-NMR}$: (CDCl_3 , 300 MHz, 300 K) δ = 7.59 - 7.56 (d, 2H, J = 8.42 Hz, H_1), 7.00 - 6.98 (d, 2H, J = 8.46 Hz, H_2), 2.46 (s, 3H, H_3) ppm.

$^{13}\text{C-NMR}$: (CDCl_3 , 300 MHz, 300 K) δ = 138.80, 137.80, 128.46, 89.36, 15.86 ppm.

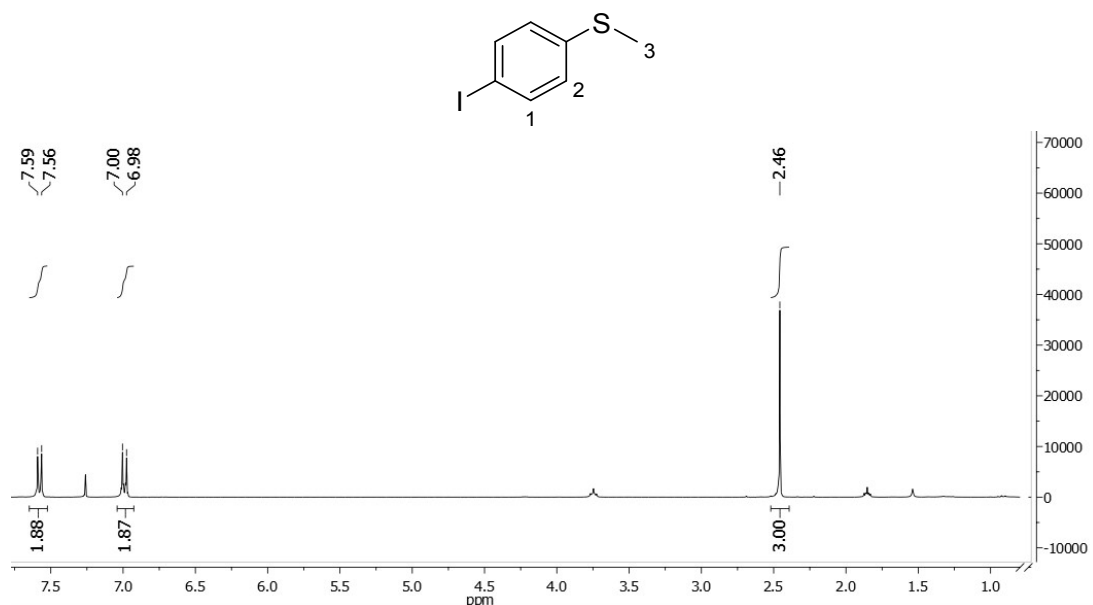


Fig S3 $^1\text{H-NMR}$ -spectrum of 4-iodothioanisole in CDCl_3 at 300 K.

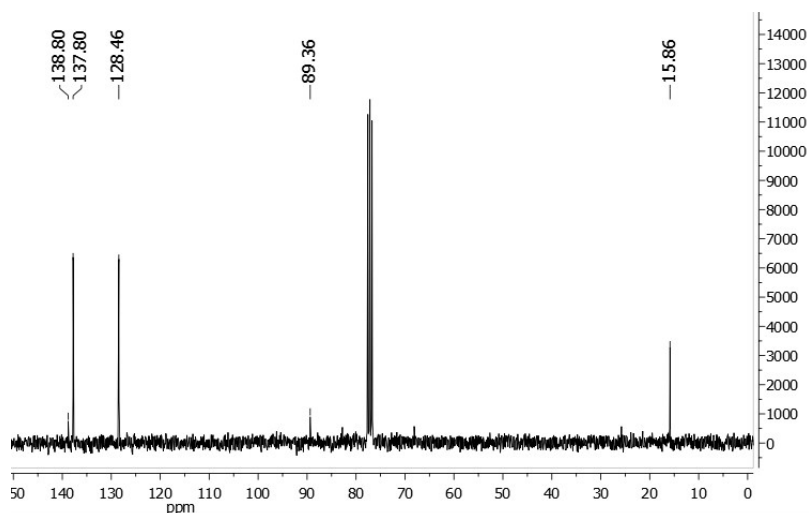


Fig S4 $^{13}\text{C-NMR}$ -Spectrum of 4-iodothioanisole in CDCl_3 at 300 K.

1.4. 3-Bromo-2-methyl-5-(4-(methylthio) phenyl) thiophene (5)⁶

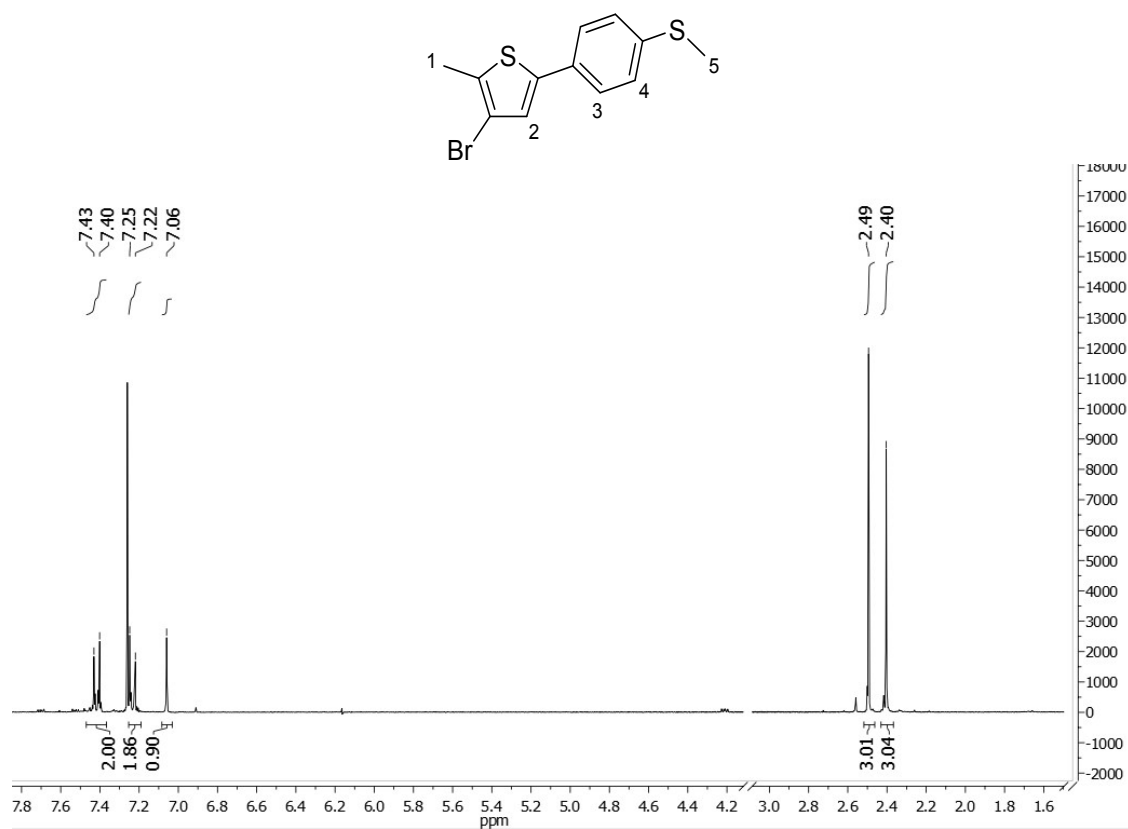


Fig S5 ¹H-NMR-spectrum of 3-bromo-2-methyl-5-(4-(methylthio) phenyl) thiophene in CDCl₃ at 300 K.

1.5. 1,2-Dibromocyclopent-1-ene (7)⁷

In an argon flushed 500 mL Schlenk flask 55.0 g (264 mmol, 1.10 eq.) phosphorous pentachloride are suspended in 120 mL abs. toluene and 21.2 mL (240 mmol, 1.00 eq.) cyclopentanone are added carefully over 30 min. The mixture is cooled to -20 °C and 12.3 mL (240 mmol, 1.00 eq.) bromine are added dropwise. After full addition the reaction is stirred at room temperature for 18 h. The solvent is evaporated and the remaining solid collected in 40 ml *n*-hexane. The solution is cooled to -25°C and 27.8 g (248 mmol, 1.03 eq.) KO^tBu in 150 mL THF are added dropwise. The reaction mixture is stirred for 30 min at room temperature. Afterwards, 120 mL water, 60 mL *n*-hexane and 16 g celite are added and the mixture is filtered through a plug of celite. The phases are separated, the organic phase is dried over MgSO₄ and the solvent is evaporated. The remaining liquid is distilled in fractions in vacuo. The collected product 1,2-dibromocyclopent-1-ene **7** (16.27 g, 72.03 mmol, 30 %) is dried over CaH₂ and cryo-transferred in vacuo prior to use.

¹H-NMR: (CDCl₃, 300 MHz, 300 K) δ = 2.67 – 2.62 (t, 4H, *J* = 7.52 Hz, H₁), 2.13 – 2.03 (m, 2H, H₂) ppm.

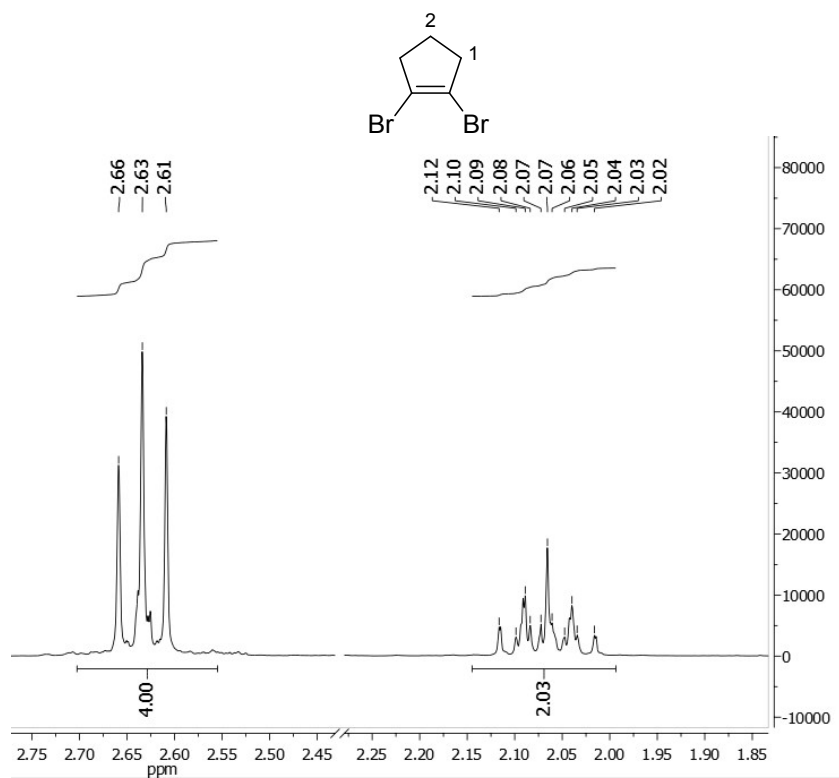
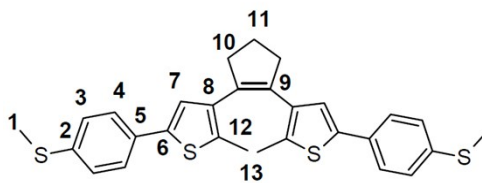


Fig S6 ¹H-NMR-spectrum of 1,2-dibromocyclopent-1-ene in CDCl₃ at 300 K.

1.6. 1,2-Bis (2-methyl-5-(4-(methylthio) phenyl) thiophene-3-yl) cyclopent-1-ene (DTE 1)



NMR spectroscopic data can be found in section 4 of the SI.

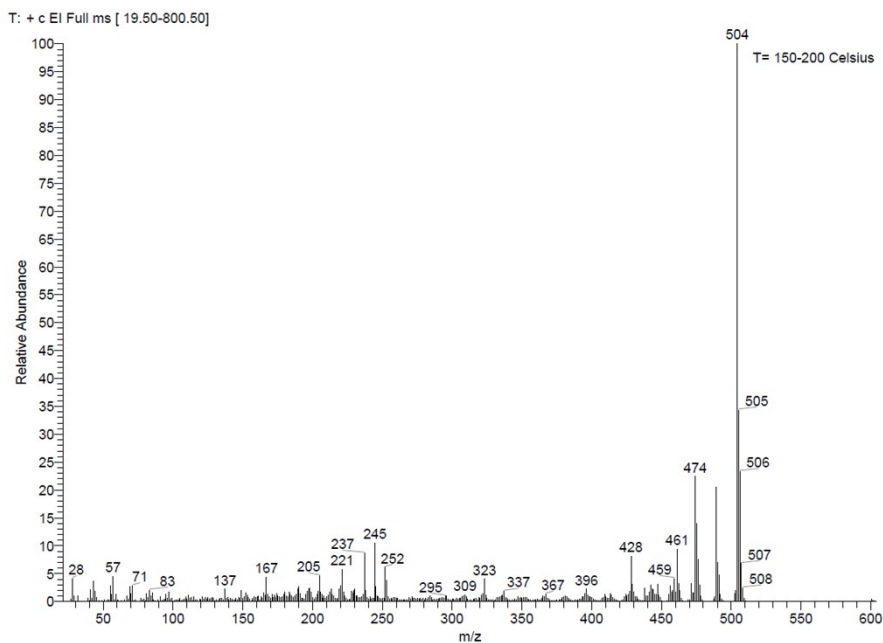
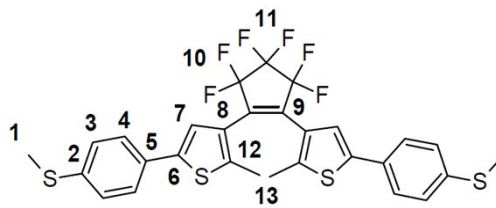


Fig S7 EI-LRMS of 1,2-bis (2-methyl-5-(4-(methylthio) phenyl) thiophene-3-yl) cyclopent-1-ene. T = 150-200°C.

1.7. 1,2-Bis (2-methyl-5-(4-(methylthio) phenyl) thiophene-3-yl) perfluorocyclopent-1-ene (DTE 2)



NMR spectroscopic data can be found in section 4 of the SI.

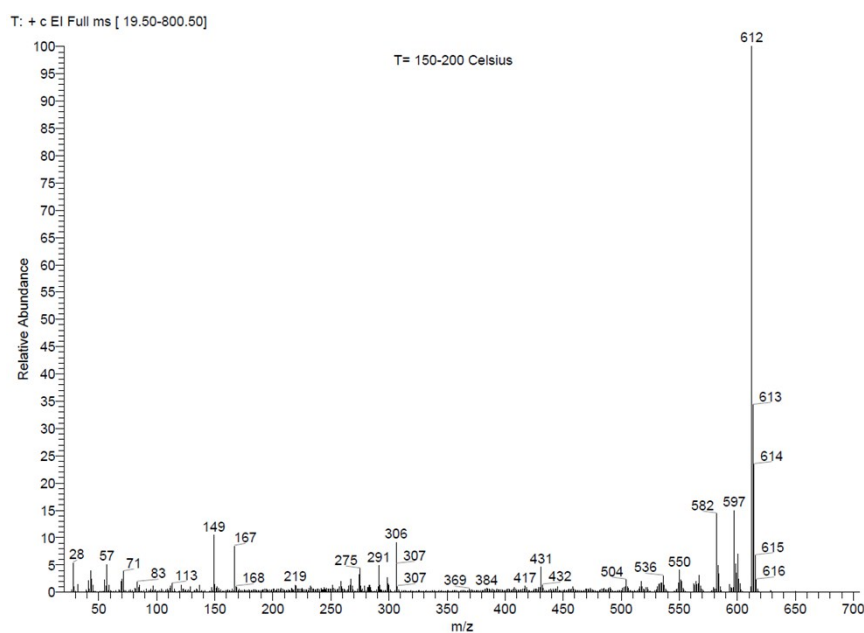


Fig S8 EI-LRMS of 1,2-bis (2-methyl-5-(4-(methylthio) phenyl) thiophene-3-yl) perfluorocyclopent-1-ene. T = 150-200°C.

2. UV/Vis Spectra

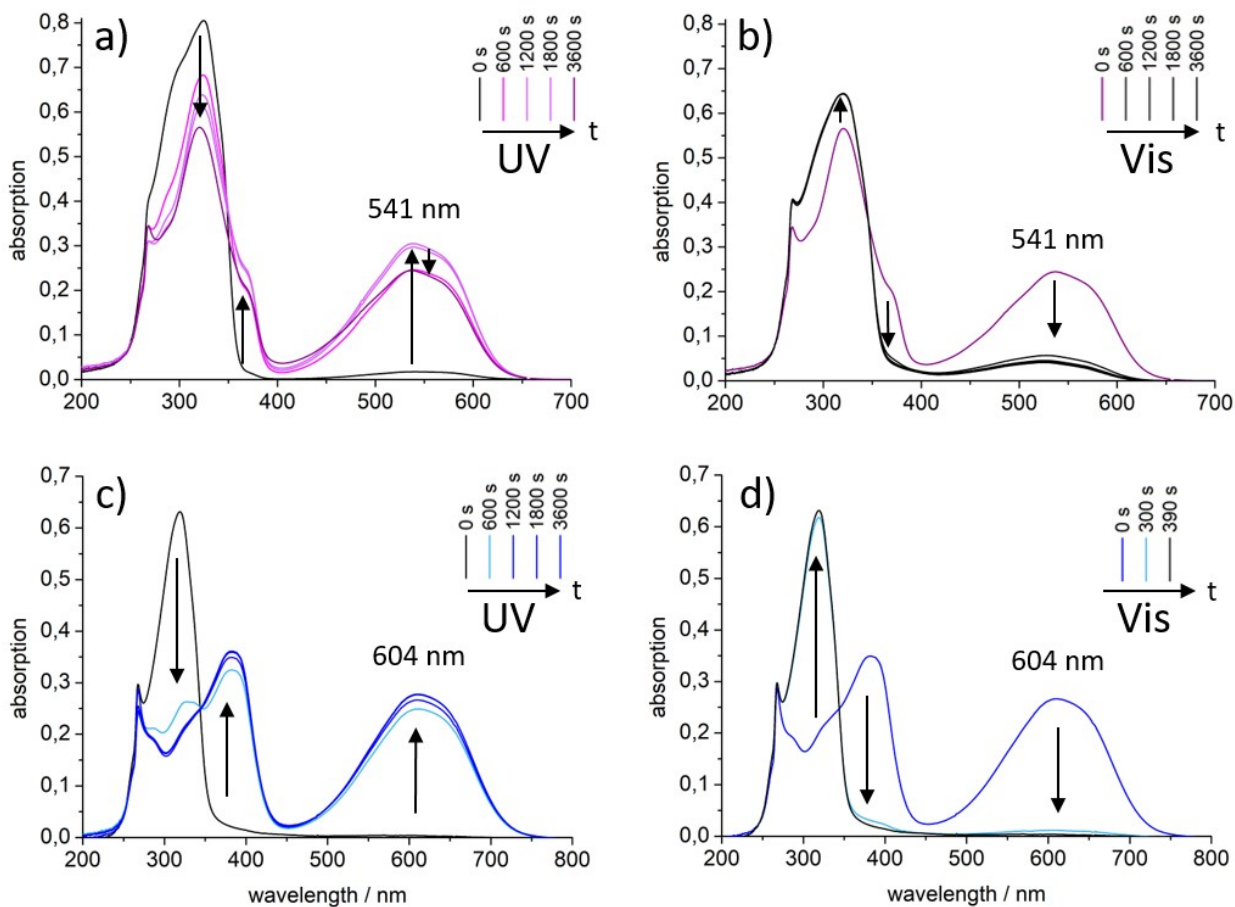


Fig S9 UV/Vis spectra of **DTE 1** (a) and **DTE 2** (c) after exposure to UV light for 1 h and subsequent Vis-light irradiation show remnant absorption for the **DTE 1** at 541 nm (b) while the absorption in the visible region of **DTE 2** (604 nm) vanishes completely (d).

Overview of the maxima of both DTE assigned to the respective photoreactions.

	DTE 1	DTE 2
UV (o → c)	230 – 370 nm (max. 333 nm)	240 – 370 nm (max. 319 nm)
Vis (c → o)	400 – 650 nm (max. 541 nm)	450 – 650 nm (max. 604 nm)
UV (c → irr)	230 – 400 nm (max. unknown)	–

3. FT-IR

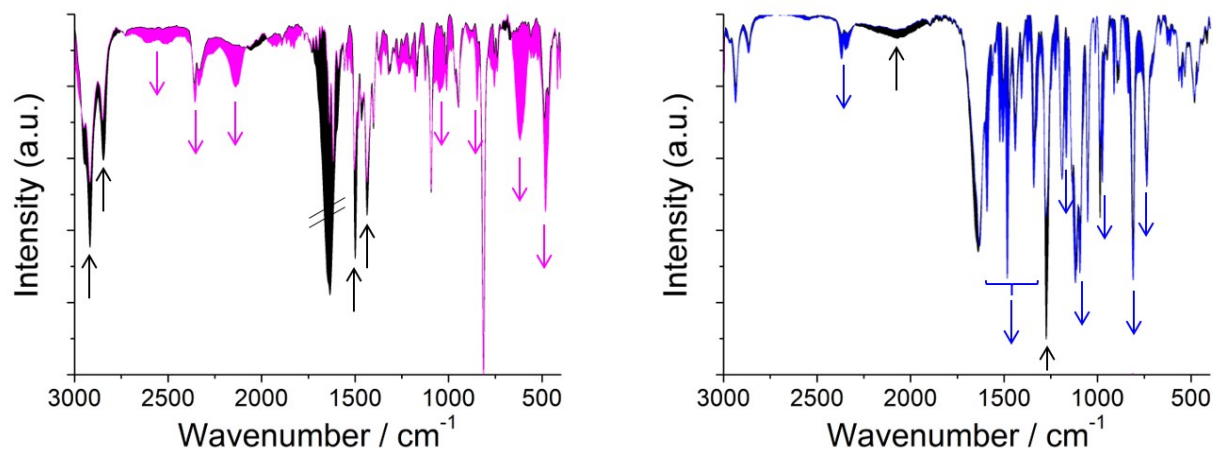


Fig S10 FT-IR spectra of **DTE 1** (left) and **DTE 2** (right) in an overlay fashion. The white filled curve corresponds to the ring open isomers recorded after decyclization with visible light. Colored areas (blue/magenta) show the bands where absorption increases upon irradiation with UV-light and black areas show bands where absorption decreases upon irradiation with UV-light.

4. NMR Spectroscopic Data

4.1. Experimental Details

¹H-NMR spectra series

¹H-NMR spectra series were recorded with the pulse program *zg2d*, which records multiple 1D ¹H-NMR spectra as a pseudo-2D experiment measuring proton signal in the direct and using a time delay in the indirect dimension. The FID received, consisting of 65536 data points within a spectral width of 20.5 ppm over 2.66 s, was Fourier transformed using the *EM* window function (LB = 0.30 Hz) without zero-filling. The measurement was performed using a single scan. A ¹H-NMR spectrum was recorded every minute automatically. From this pseudo 2D-experiment the 1D-¹H-NMR spectra were extracted via a macro using the *rsr* command and phase and baseline correction were applied automatically. With suitable integration regions for each DTE respectively the peak areas for the observed species were obtained by using the *intser* command without global scaling. For **DTE 1** the integration was performed on 13-H signal at 2.01 ppm for the open form, the 7-H signal at 6.83 ppm for the closed one and the signal 7-H at 6.71 ppm for the irreversible one. For **DTE 2** the signals 7-H were used for both open and closed species, with 7.57 ppm (open) and 7.08 ppm (closed) respectively. From these integrals the molar fraction *x* of each species was calculated by:

$$x(A) = \frac{I(A) \cdot n^{-1}}{\sum_i I(A) \cdot n^{-1}}$$

With *I(A)* being the integral of the observed species, *n* the number of protons associated with the signal and *i* being the group of all observed species.

2D-Experiments

2D-correlation spectra have been recorded to identify proton- and carbon-chemical shifts of the different dithienyl species. In addition to the chemical shift reference, the phase correction was done manually. Furthermore, the sin² window function and zero-filling (see below) was used to process the data. The relevant parameters are shown in the table below.

PARAMETER	HSQC	COSY	NOESY	HMBC	¹⁹ F COSY	¹⁹ F HMQC
PULSE PROGRAM	hsqcetgpsp.2	cosygppqf	noesygpshzs	hmbcgpndqf	cosygpmfqqf	hmqcetgp
DATA POINTS (F2)	1200	2048	2048	4096	1024	2048
INCREMENTS (F1)	512	512	512	512	128	512
SW F2 / PPM	15.0	14.0	13.3	14.0	53.1	49.9
SW F1 / PPM	180	14.0	13.3	222	52.7	165.1
AQ. TIME F2 / S	0.07	0.12	0.13	0.24	0.0295	0.0623
# OF SCANS	8	4	8	32	2	8
ZERO-FILLING F2	2048	-	4096	-	2048	2048
ZERO-FILLING F1	2048	1024	1024	2048	1024	2048

Sample preparation

Approximately 1 mg of the DTEs was suspended directly in an NMR-tube (Wilmad LabGlass, 507-PP) in 450 μL DMF-*d*₇ and dissolved using an ultrasonic bath.

In situ irradiation

In order to observe the DTEs' photochemical (de-)cyclization, continuous irradiation during the NMR-experiments was used.^{8,9,10} A glass coaxial insert (Wilmad; WGS-5BL) containing a glass fiber (Thorlabs; TECS-Clad Multimode Optical Fiber) was placed within in the NMR-tubes, as shown in **Fig S3**. The end of the glass fiber was roughened with sand paper to distribute the light homogenously within the sample and a light source was connected at the other end of the glass fiber. Different LEDs of individual emission wavelengths were used as light sources. For the cyclization reaction a 365 nm LED (Nichia, NVSU233A UV SMD-LED, 1030 mW) was used. A 525 nm (LUMILED, Luxeon CZ, 100 mW) LED was used to induce the ring opening reaction.

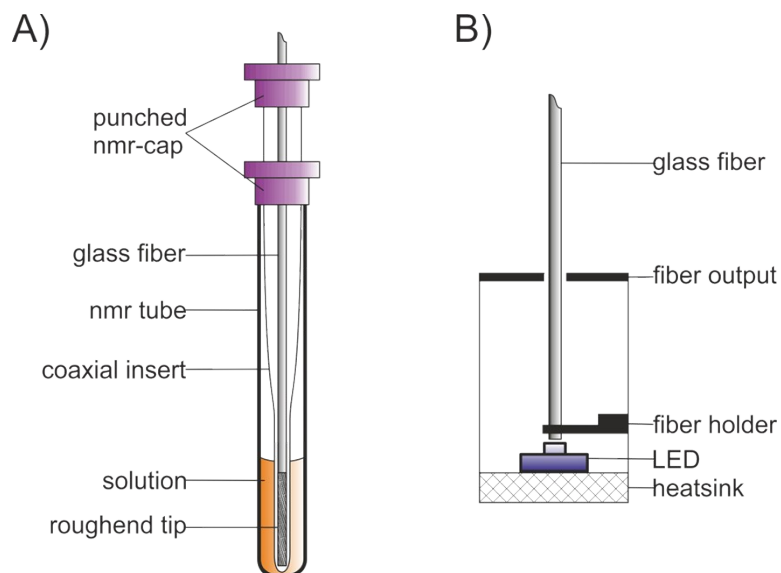
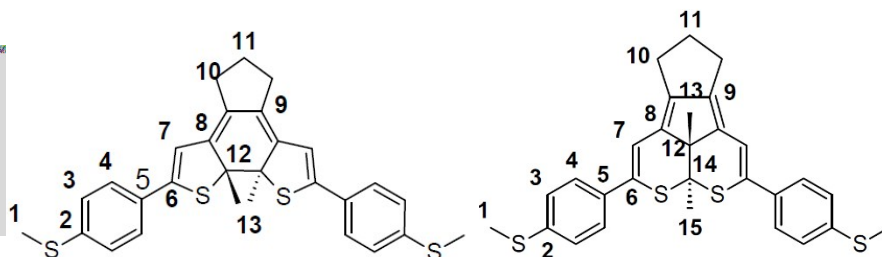
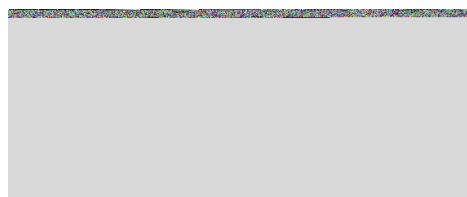


Fig S11 *in situ* irradiation NMR spectroscopy approach.⁸ A) detailed setup of the NMR tube with a coaxial insert and glass fiber to guide light into the reaction sample. B) schematic setup of the LEDs used to show how the light is coupled into the fiber.

4.2. NMR chemical shift tables

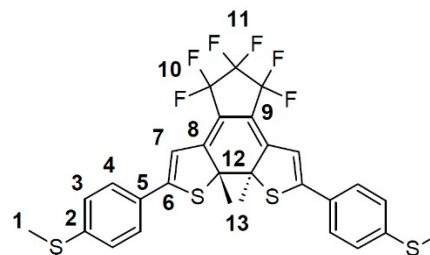


1o		
#	¹ H shift /ppm	¹³ C shift /ppm
1	2.54	15.2
2	-	139.7
3	7.31	127.3
4	7.56	126.0
5	-	131.8
6	-	140.1
7	7.31	124.8
8	-	138.4
9	-	136.0
10	2.89	38.7
11	2.08	23.2
12	-	134.4
13	2.01	14.8

1c		
#	¹ H shift /ppm	¹³ C shift /ppm
1	2.57	15.2
2	-	140.8
3	7.35	126.6
4	7.59	127.2
5	-	131.8
6	-	145.7
7	6.83	116.9
8	-	142.2
9	-	135.3
10	2.54	30.5
11	1.89	25.9
12	-	66.6
13	1.98	27.7

1irr		
#	¹ H shift /ppm	¹³ C shift /ppm
1	2.55	15.2
2	-	140.4
3	7.32	126.6
4	7.55	126.9
5	-	n.d.
6	-	133.1
7	6.71	115.5
8	-	136.1
9	-	152.8
10	2.29	24.5
10'	2.42	24.5
11	2.12	30.5
11'	2.21	30.5
12	-	59.4
13	2.47	24.2
14	-	67.1
15	2.53	30.0

n.d.: Not determined due to absence of signals in HMBC spectra.



2o			
#	¹ H shift /ppm	¹³ C shift /ppm	¹⁹ F shift /ppm
1	2.56	14.6	-
2	-	139.2	-
3	7.66	126.0	-
4	7.36	126.7	-
5	-	130.0	-
6	-	142.1	-
7	7.57	122.7	-
8	-	141.5	-
9	-	137.0	-
10	-	116 ¹	-110.2
11	-	112 ¹	-132.1
12	-	125.9	-
13	2.09	13.8	-

2c			
#	¹ H shift /ppm	¹³ C shift /ppm	¹⁹ F shift /ppm
1	2.61	13.9	-
2	-	144.0	-
3	7.78	127.7	-
4	7.43	125.7	-
5	-	129.2	-
6	-	158.1	-
7	7.08	113.4	-
8	-	150.0	-
9	-	115.6	-
10	-	115 ¹	-112.1 ² and -113.5 ²
11	-	113 ¹	-133.7
12	-	65.8	-
13	2.18	24.8	-

¹ determined by ¹⁹F-¹³C-HMQC

² ³J coupling between 10 and 11 is not resolved in the 1D ¹⁹F spectrum. Additionally, the resonance of 10 splits up into two resonances (10 and 10') due to the diastereotopic relationship of these fluorine atoms in the cyclized product. Hence, two (roofed) doublets with a ²J coupling constant of approximately 255 Hz are observed.

Typically, photochemical cyclisation of DTEs occurs via conrotatory electrocyclozation¹¹ according to the Woodward-Hoffmann rules¹². Hence, it is assumed that **DTE 1c** and **DTE 2c** are C₂ symmetric (methyl groups 13 and 13' *anti*). The configuration of compound **1irr**, however, could not be determined by NMR spectroscopy. The only 'evidence' for the *anti*-configuration is the missing NOE between protons of methyl groups 13 and 15 in the NOESY spectrum of **1irr** (see SI 25), which would have been proof for the *syn* product. For a related (fluorinated) compound, there is evidence by x-ray crystallographic analysis for the *anti*-configuration of the irreversibly closed byproduct.¹³

4.3. DTE 1o

All spectra shown in the following sections are acquired using DMF-*d*₇ as solvent. Residual proton resonances of the solvent are labeled as DMF.

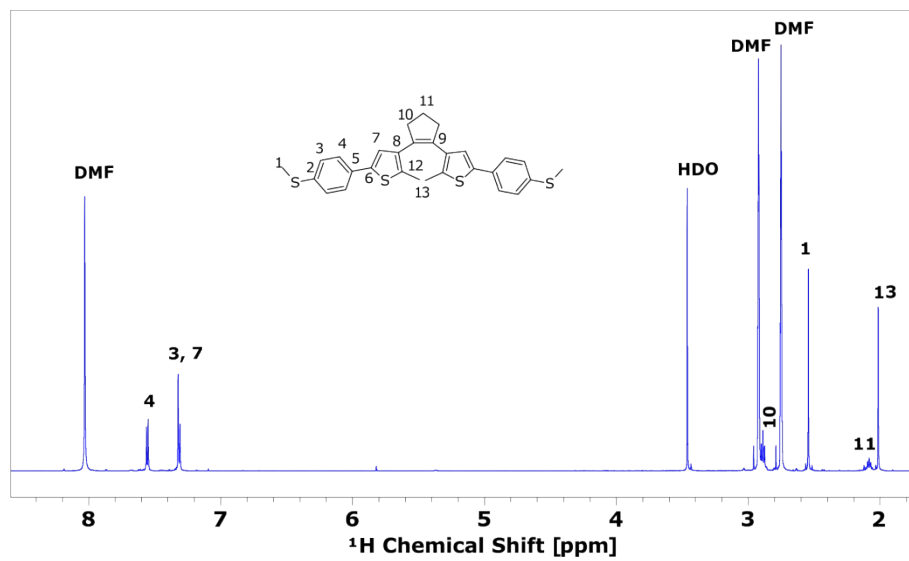


Fig S12 ¹H-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1o in DMF-*d*₇ at 300 K.

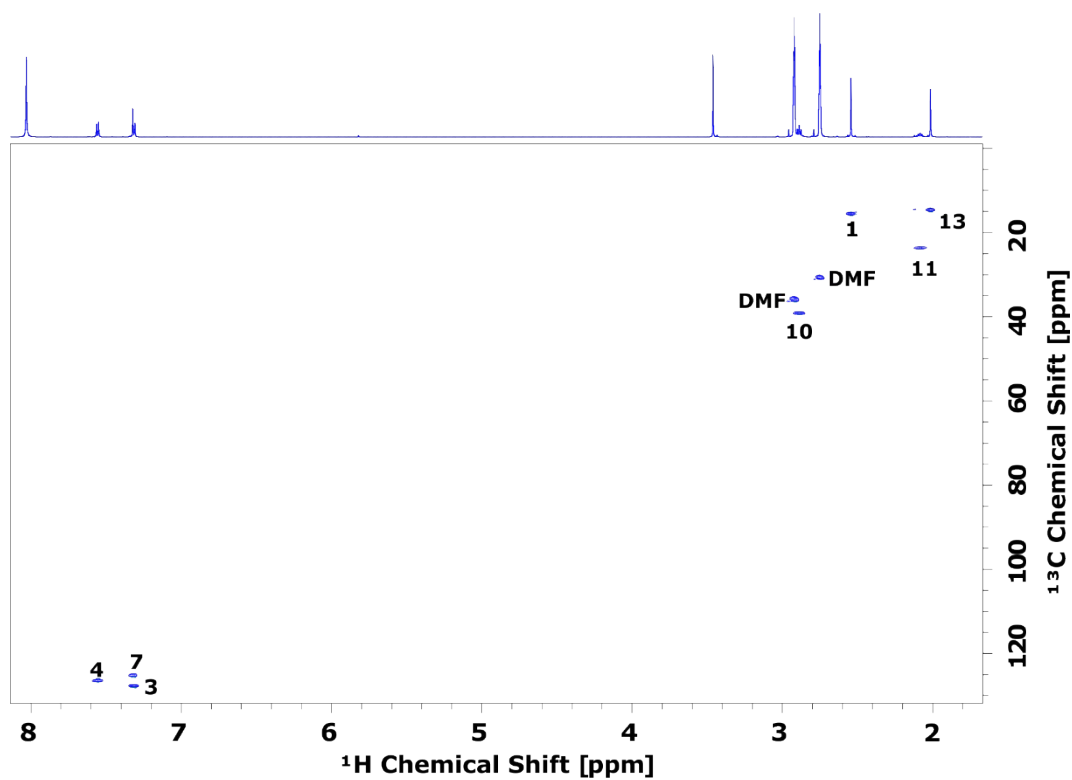


Fig S13 ¹H-¹³C-HSQC-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1o in DMF-*d*₇ at 300 K.

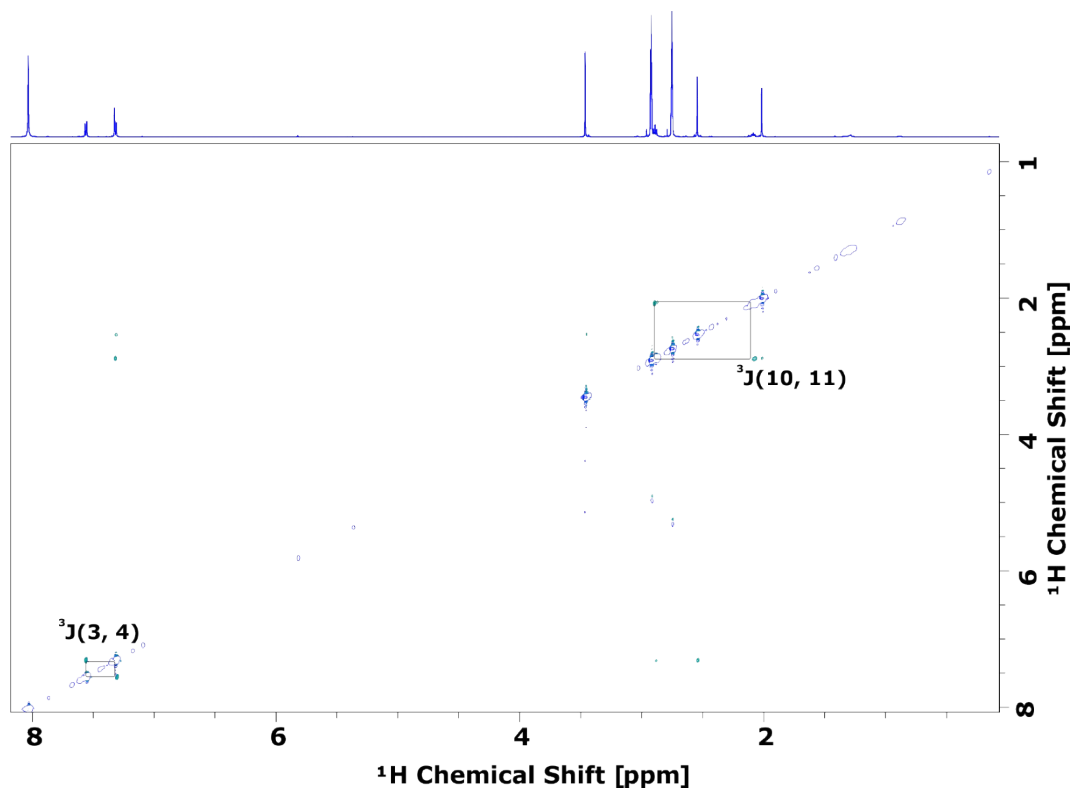


Fig S14 ^1H - ^1H -COSY-NMR-spectrum (600 MHz proton resonance frequency) of DTE **1o** in $\text{DMF-}d_7$ at 300 K.

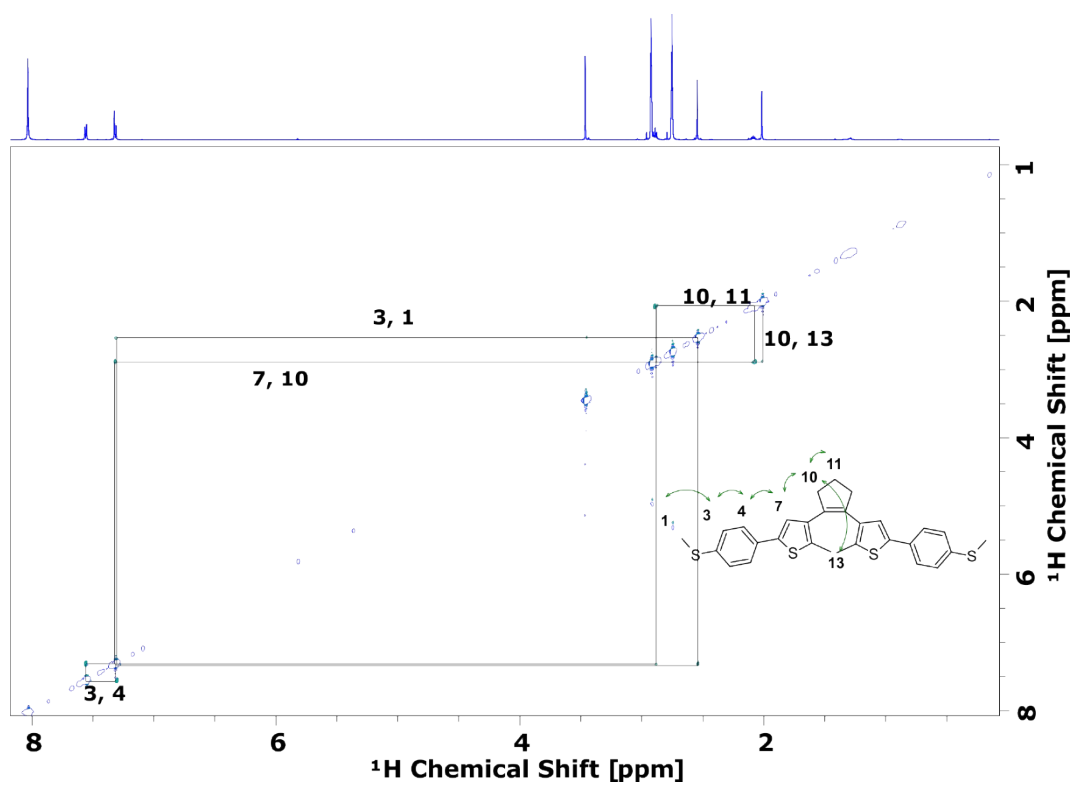


Fig S15 ^1H - ^1H -NOESY-NMR-spectrum (600 MHz proton resonance frequency) of DTE **1o** in $\text{DMF-}d_7$ at 300 K.

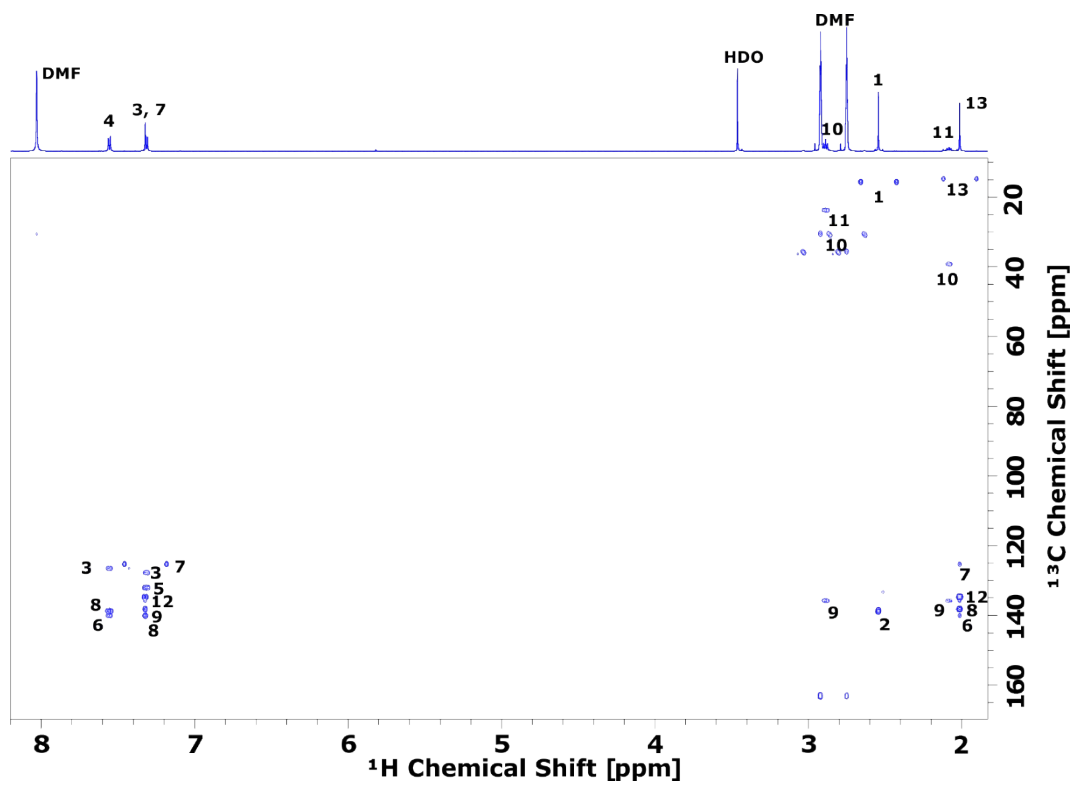


Fig S16 ^1H - ^{13}C -HMBC-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1o in $\text{DMF-}d_7$ at 300 K.

4.4. DTE 1c

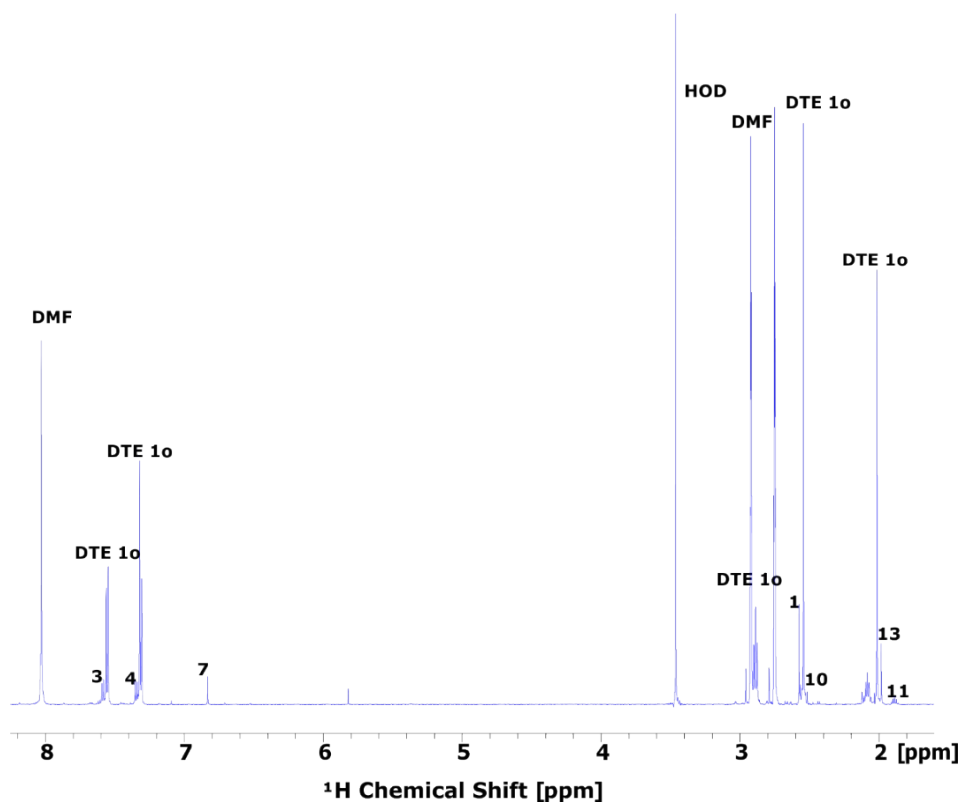


Fig S17 ^1H -NMR-spectrum (600 MHz proton resonance frequency) of DTE 1c in $\text{DMF-}d_7$ at 300 K.

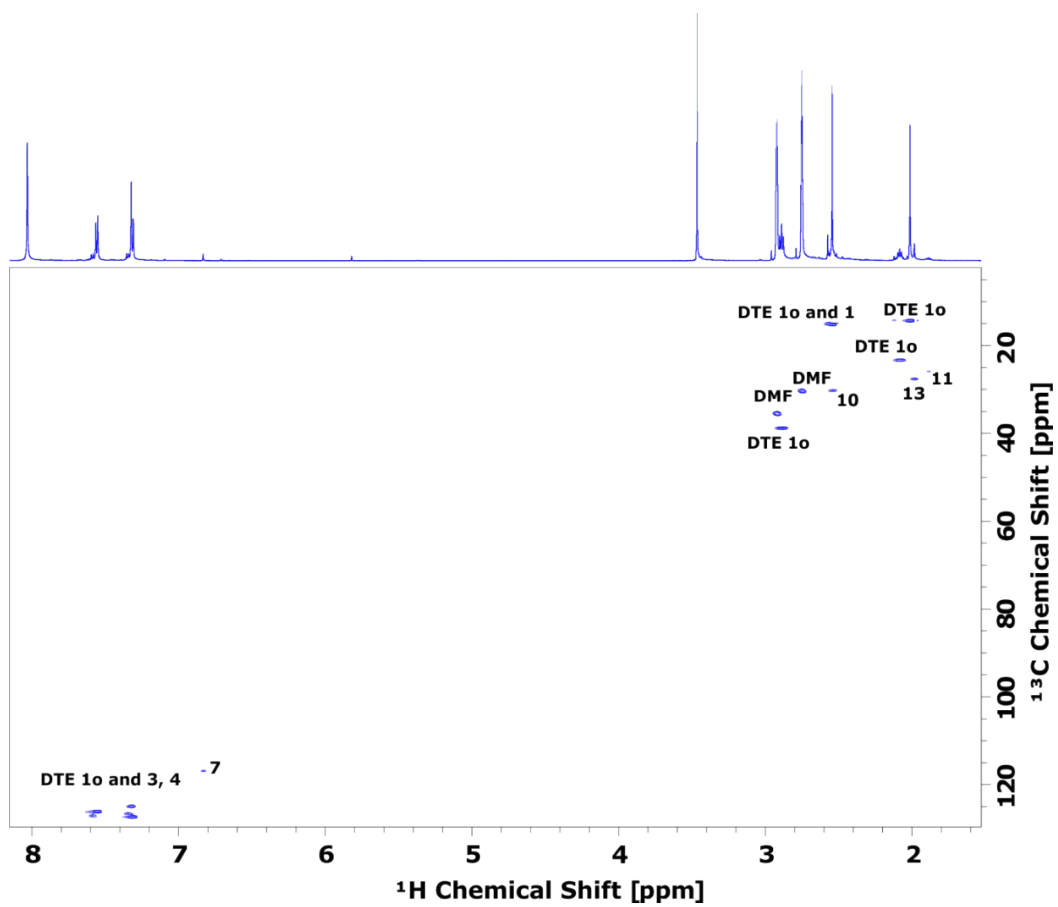


Fig S18 ^1H - ^{13}C -HSQC-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1c in $\text{DMF-}d_7$ at 300 K.

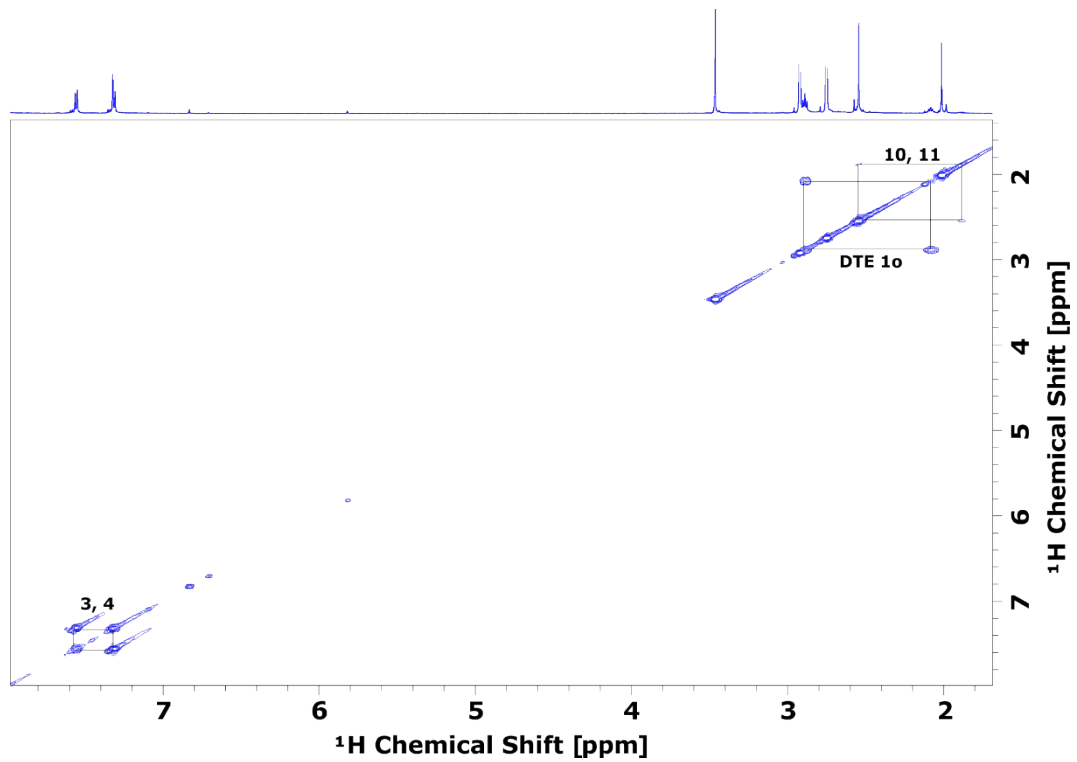


Fig S19 ^1H - ^1H -COSY-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1c in $\text{DMF-}d_7$ at 300 K.

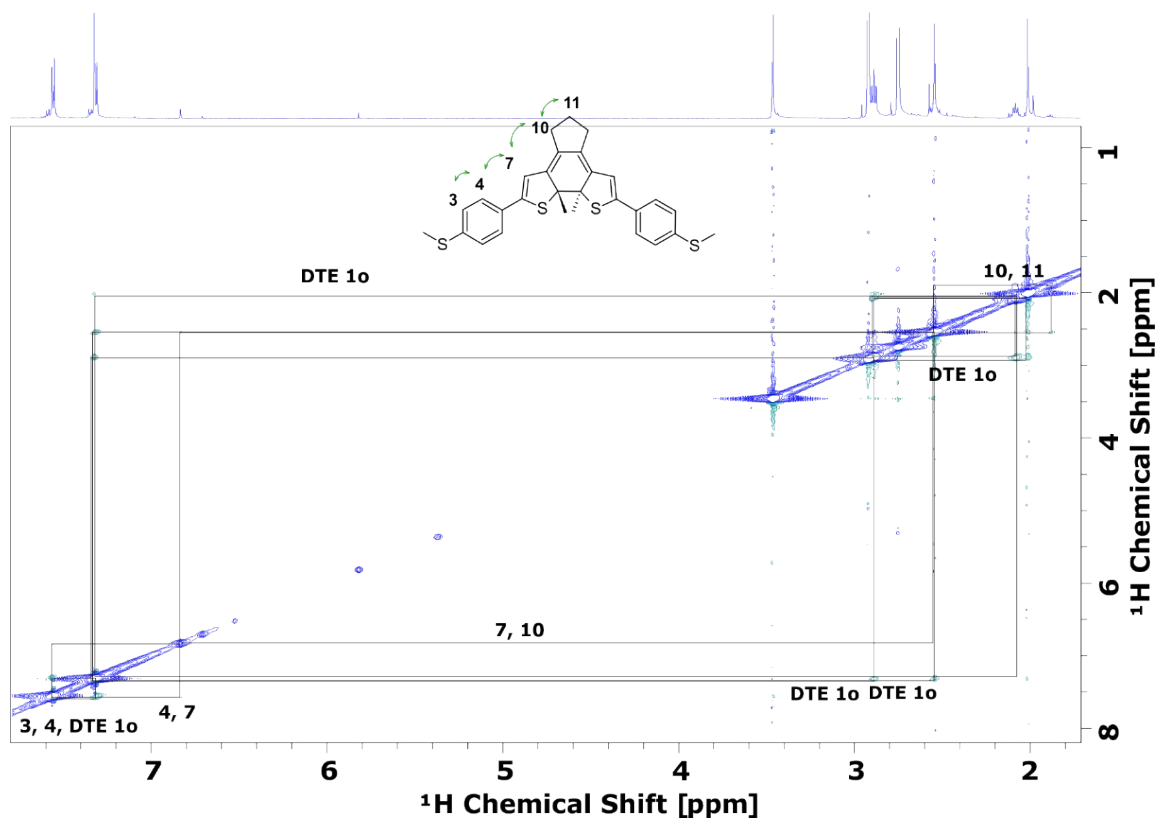


Fig S20 ^1H - ^1H -NOESY-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1c in $\text{DMF-}d_7$ at 300 K.

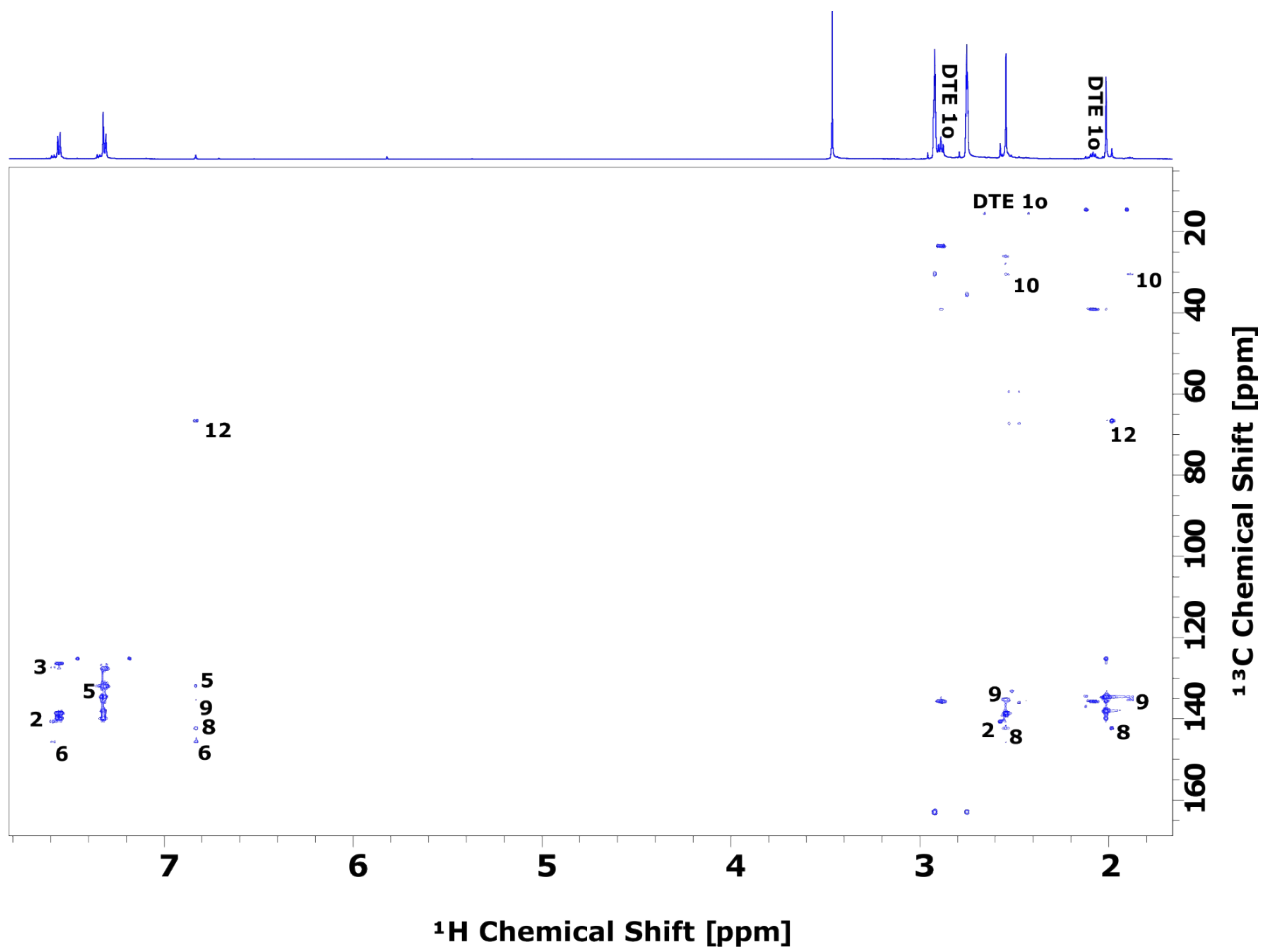


Fig S21 ¹H-¹³C-HMBC-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1c in DMF-*d*₇ at 300 K.

4.5. DTE 1irr

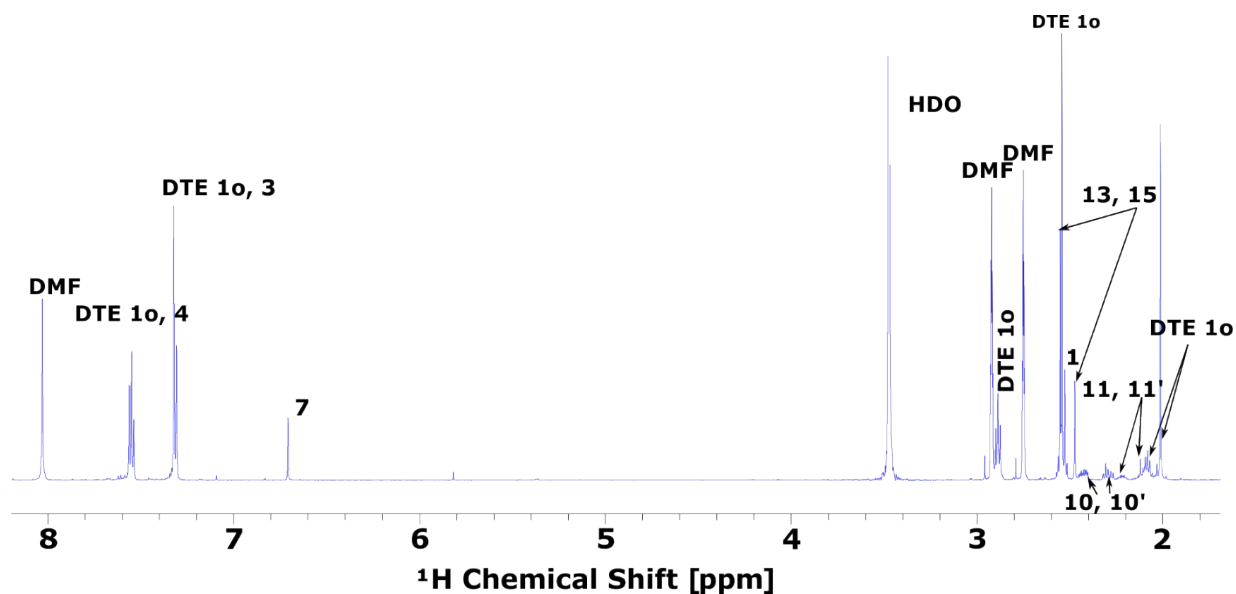


Fig S22 ^1H -NMR-spectrum (600 MHz proton resonance frequency) of DTE 1o and DTE 1irr in $\text{DMF-}d_7$ at 300 K after irradiation with green light (525 nm) to completely remove DTE 1c.

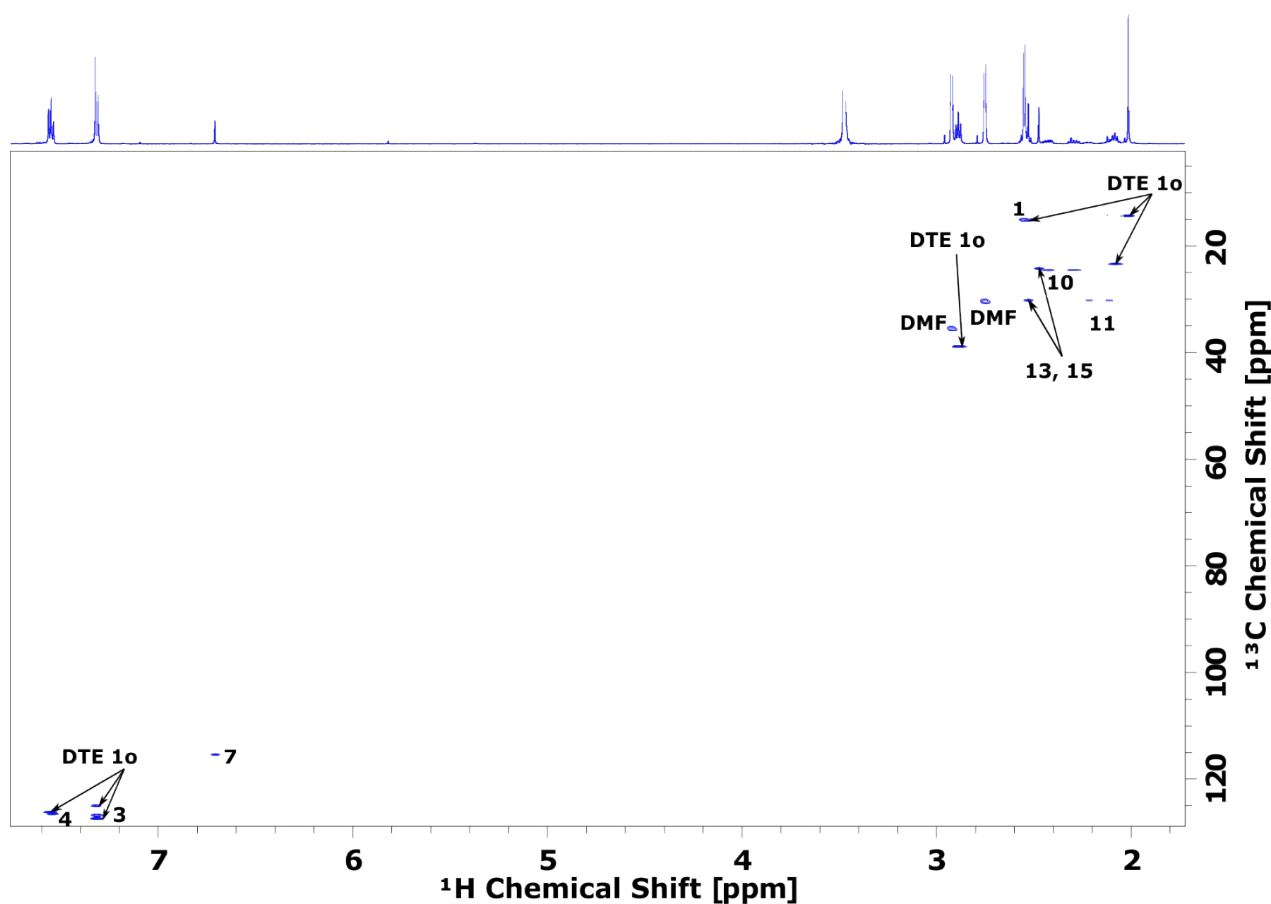


Fig S23 ^1H - ^{13}C -HSQC-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1o and DTE 1irr in $\text{DMF-}d_7$ at 300 K after irradiation with green light (525 nm) to completely remove DTE 1c.

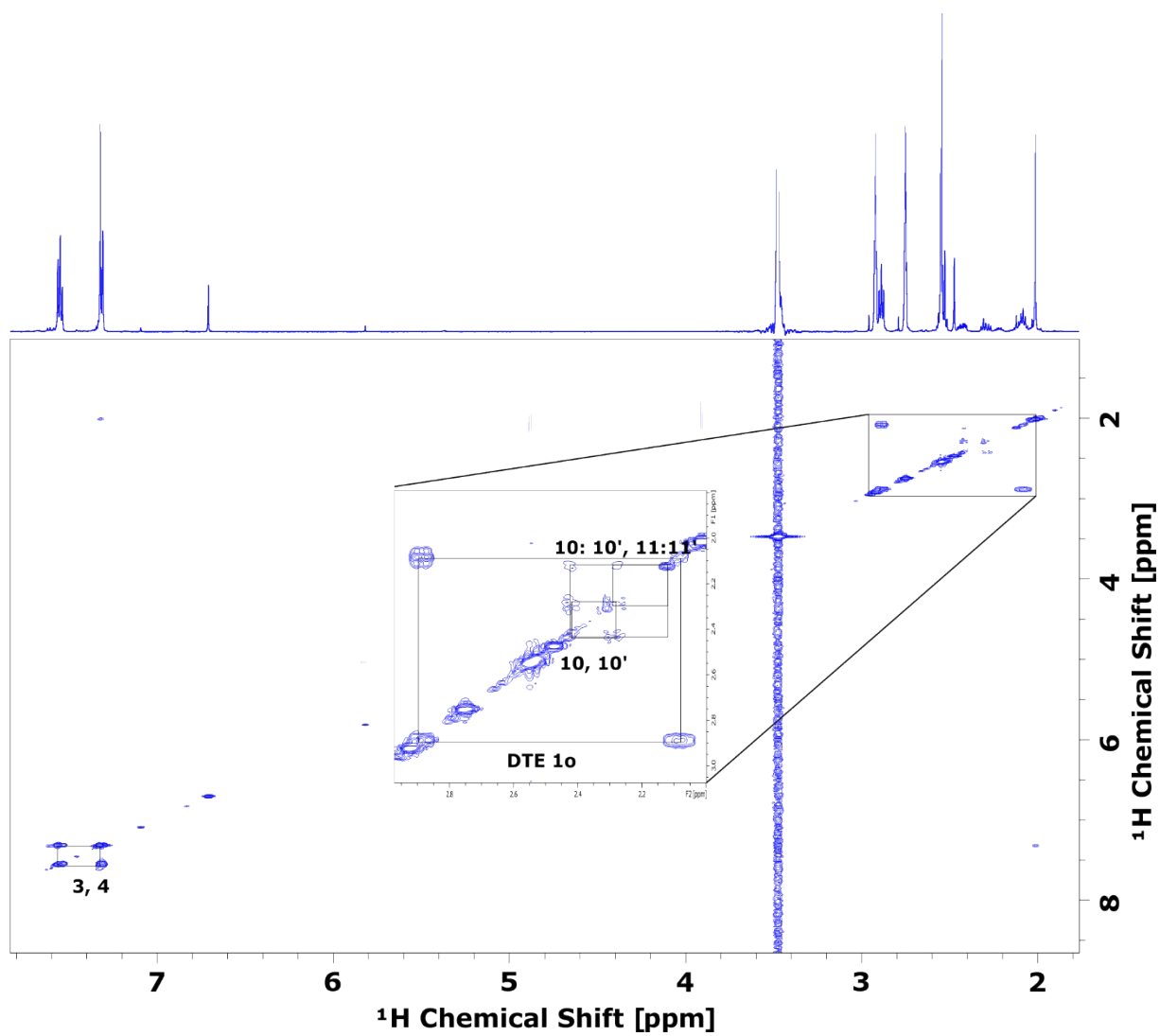


Fig S24 ^1H - ^1H -COSY-NMR-spectrum (600 MHz proton resonance frequency) of DTE **1o** and DTE **1irr** in $\text{DMF-}d_7$ at 300 K after irradiation with green light (525 nm) to completely remove DTE **1c**.

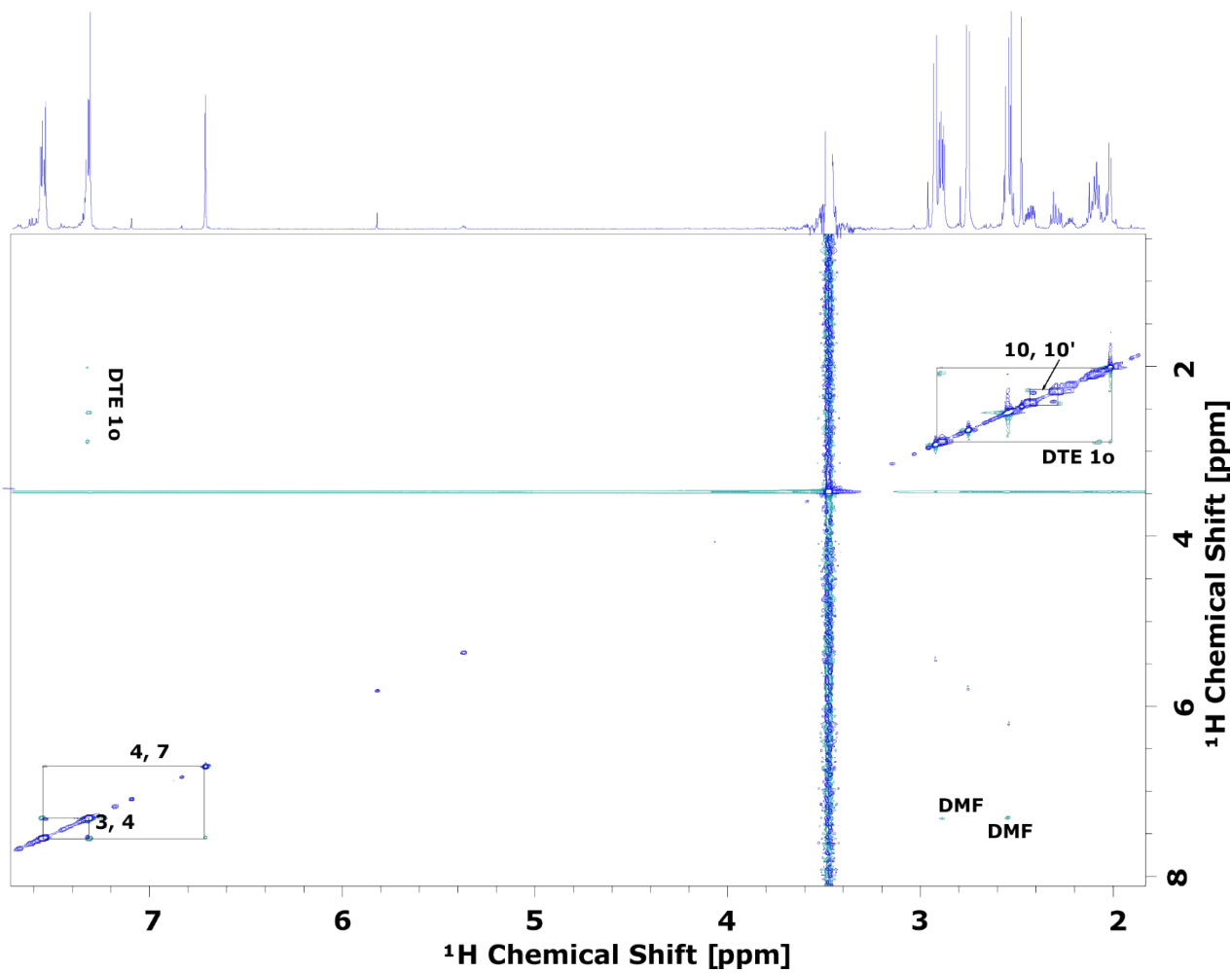


Fig S25 ^1H - ^1H -NOESY-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1o and DTE 1irr in $\text{DMF-}d_7$ at 300 K after irradiation with green light (525 nm) to completely remove DTE 1c.

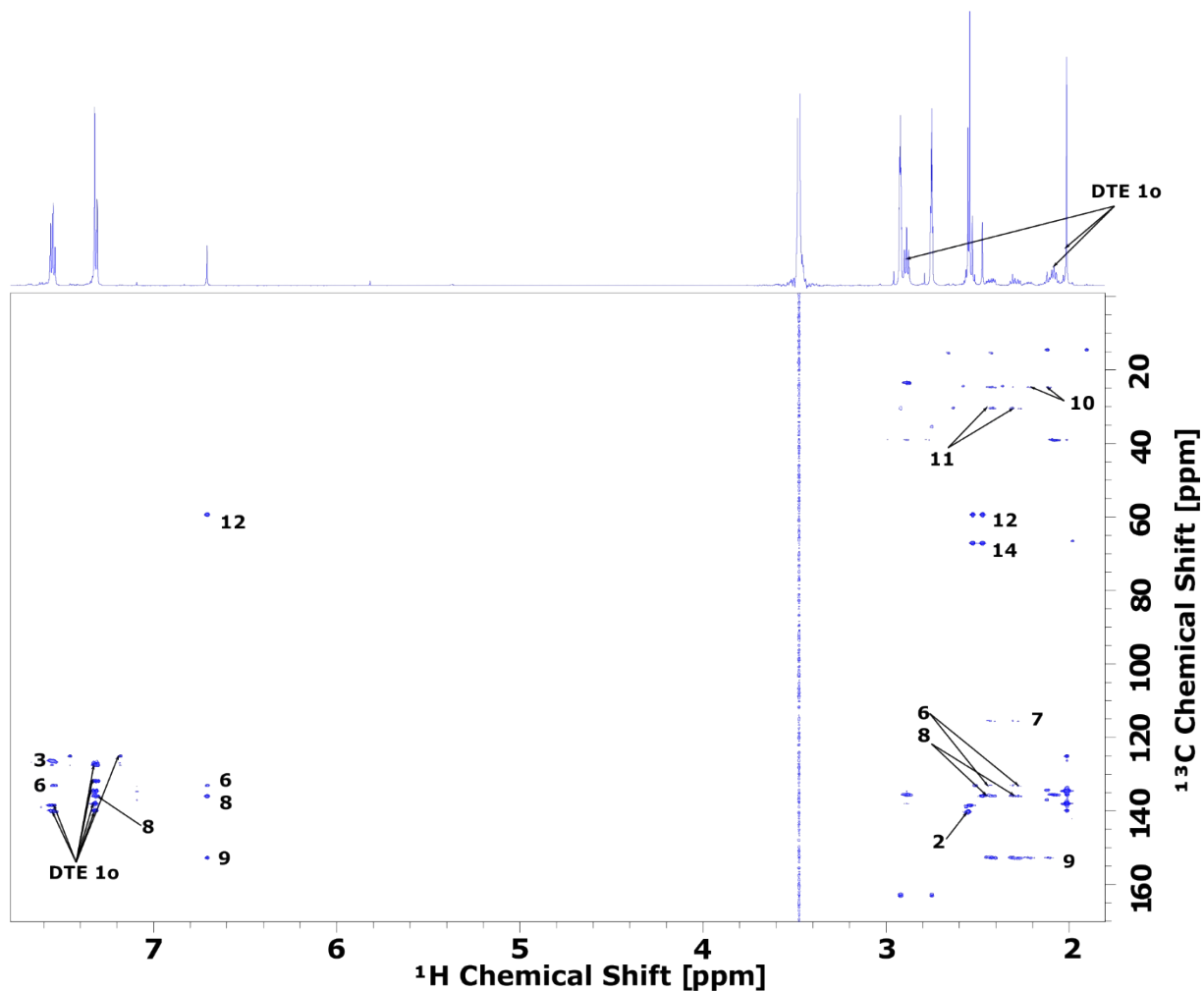


Fig S26 ^1H - ^{13}C -HMBC-NMR-spectrum (600 MHz proton resonance frequency) of DTE 1o and DTE 1irr in $\text{DMF-}d_7$ at 300 K after irradiation with green light (525 nm) to completely remove DTE 1c.

4.6. DTE 2o/c

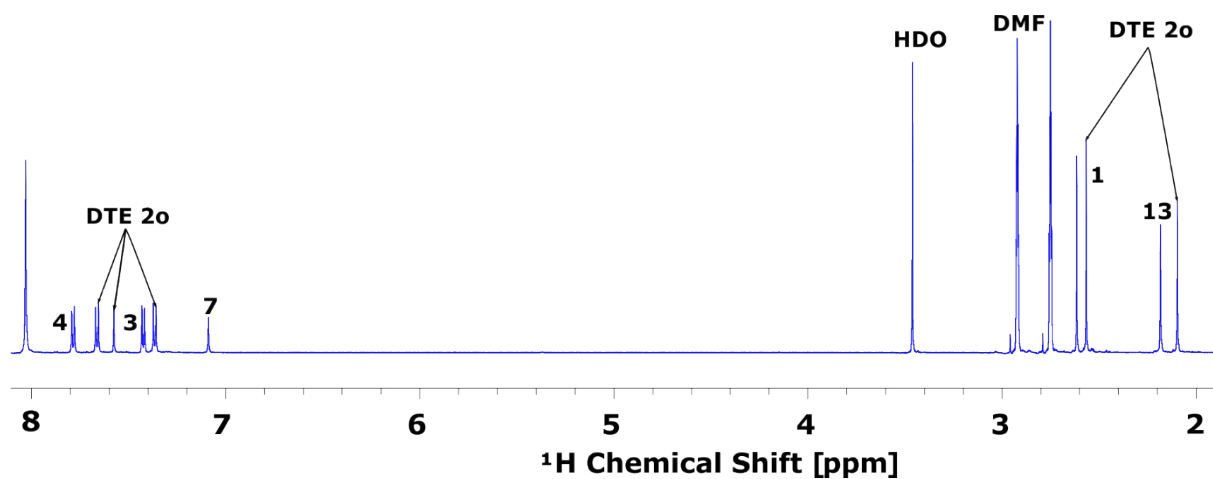


Fig S27 ^1H -NMR-spectrum (600 MHz proton resonance frequency) of a mixture of DTE 2o and DTE 2c in $\text{DMF-}d_7$ at 300 K.

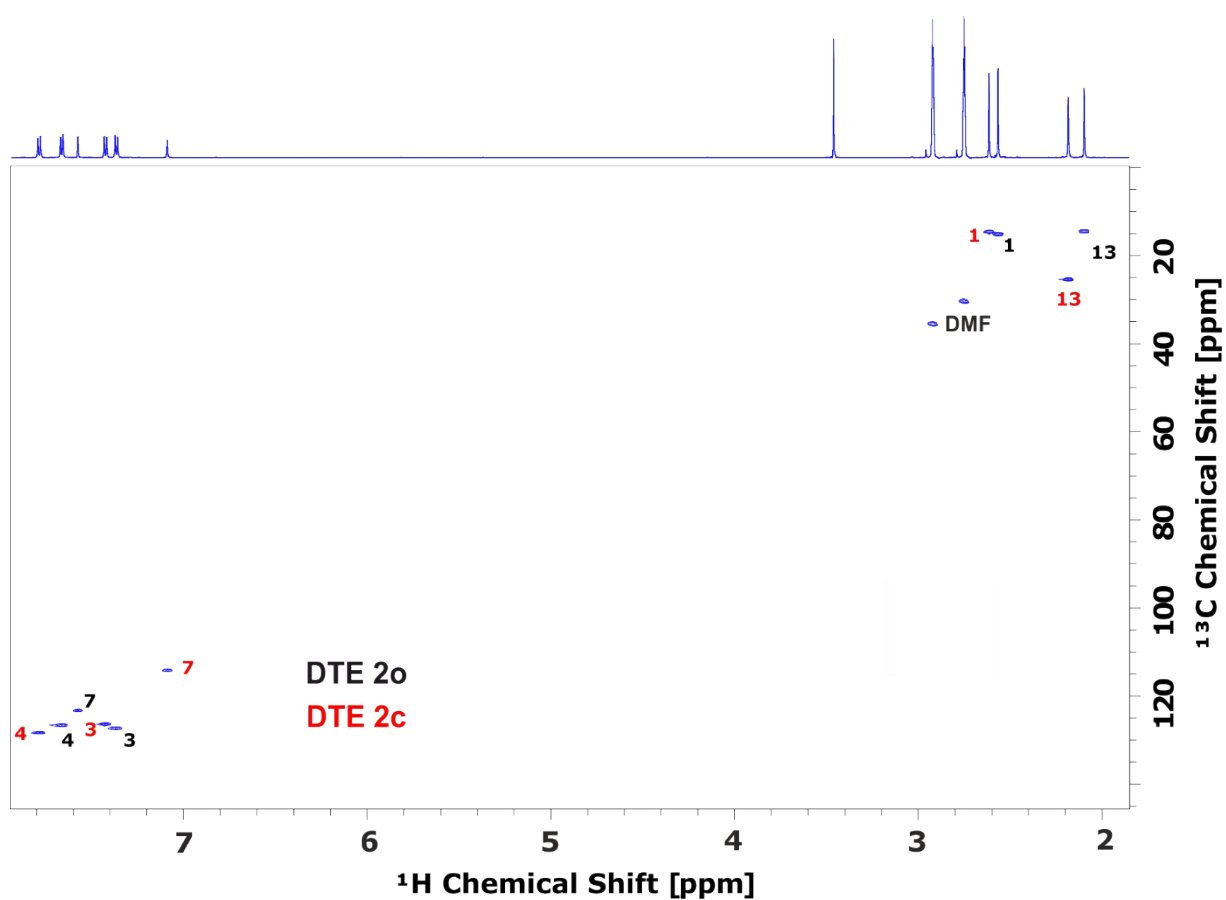


Fig S28 ^1H - ^{13}C -HSQC-NMR-spectrum (600 MHz proton resonance frequency) of a mixture of DTE 2o and DTE 2c in $\text{DMF-}d_7$ at 300 K.

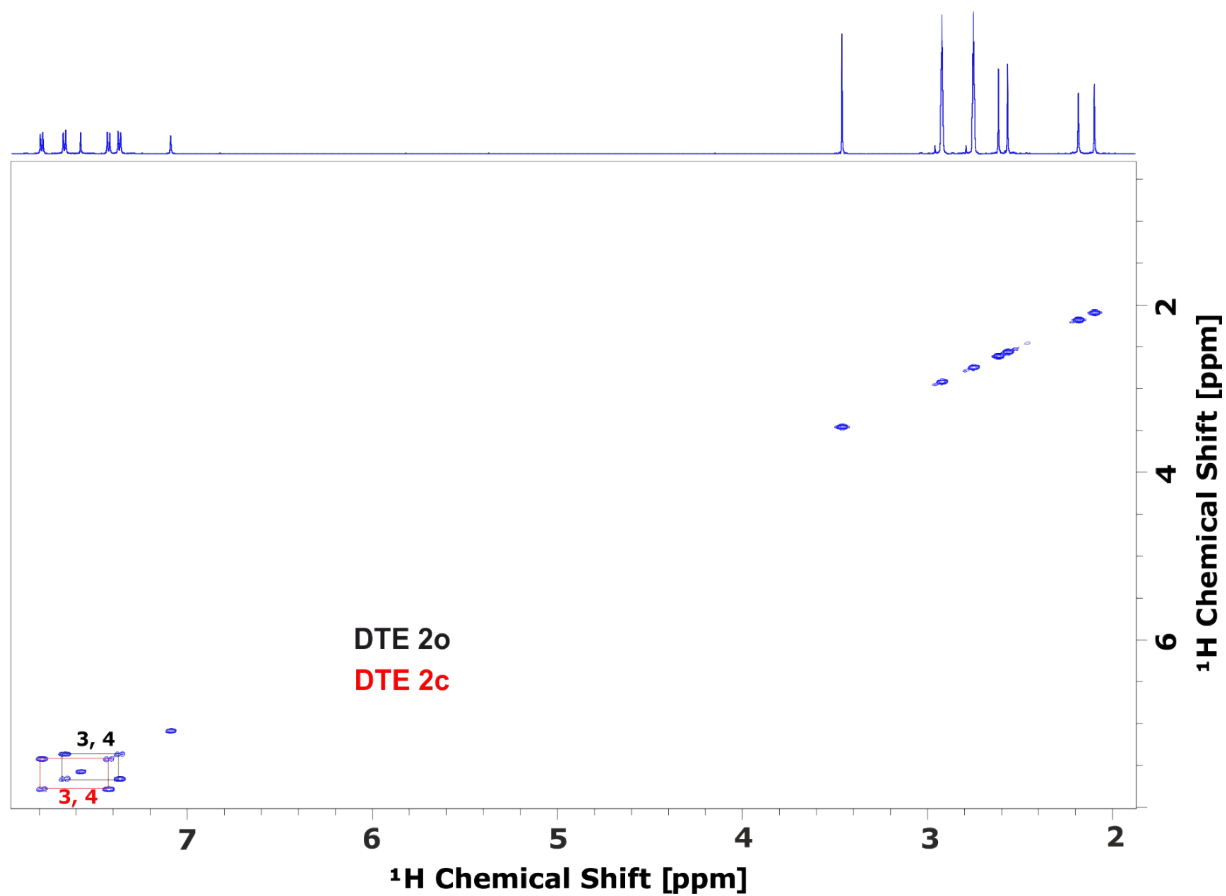


Fig S29 ^1H - ^1H -COSY-NMR-spectrum (600 MHz proton resonance frequency) of a mixture of DTE 2o and DTE 2c in $\text{DMF-}d_7$ at 300 K.

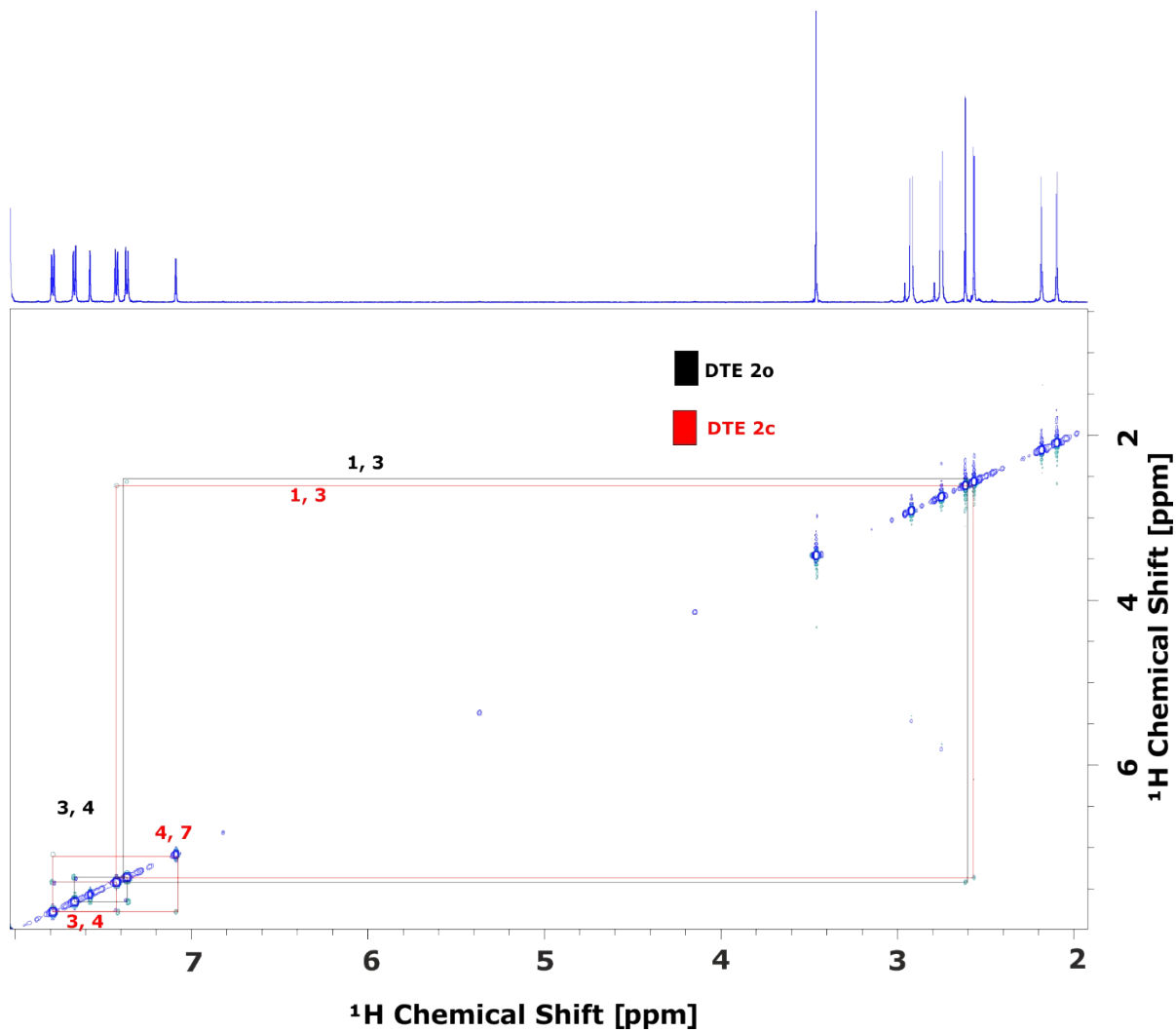


Fig S30 ¹H-¹H-NOESY-NMR-spectrum (600 MHz proton resonance frequency) of a mixture of DTE 2o and DTE 2c in DMF-*d*₇ at 300 K.

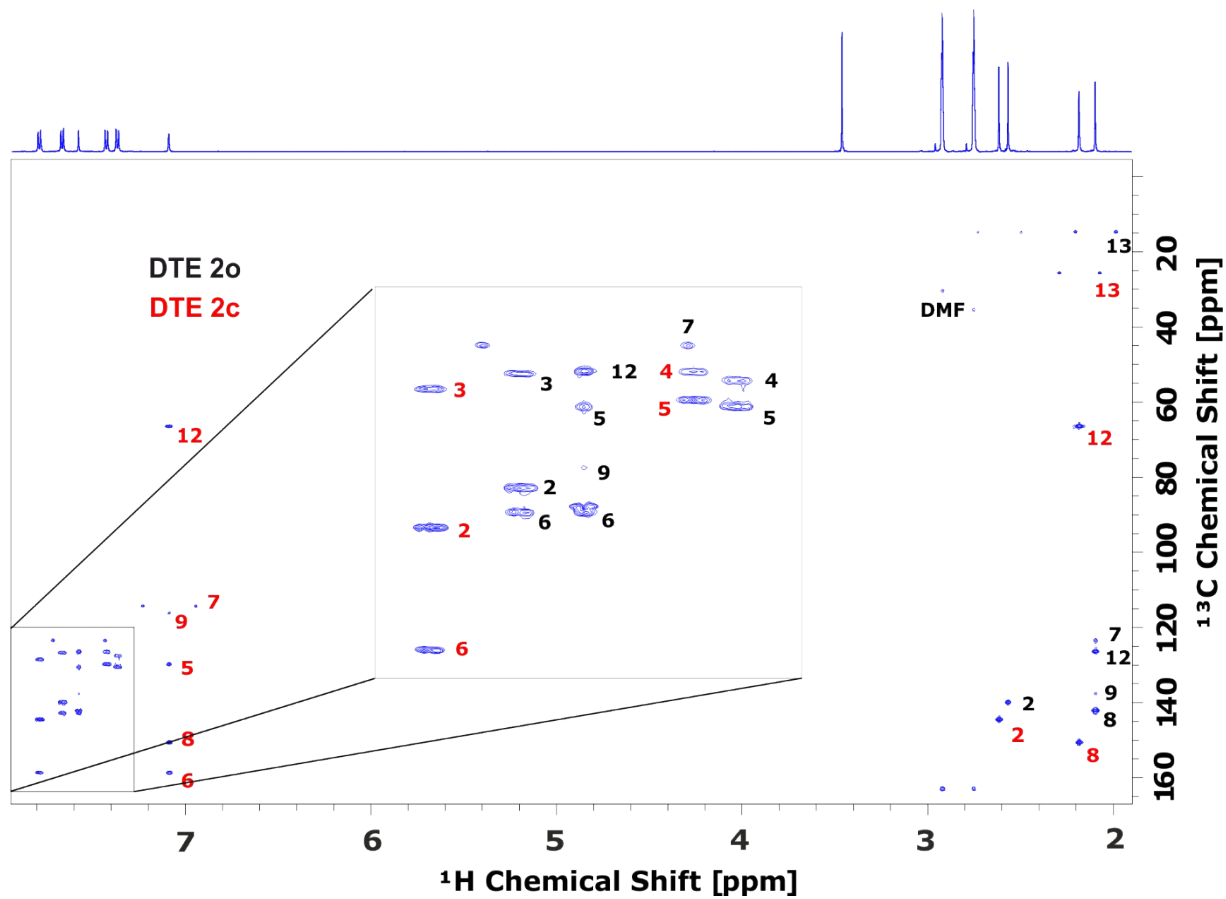


Fig S31 ¹H-¹³C-HMBC-NMR-spectrum (600 MHz proton resonance frequency) of a mixture of DTE 2o and DTE 2c in DMF-*d*₇ at 300 K.

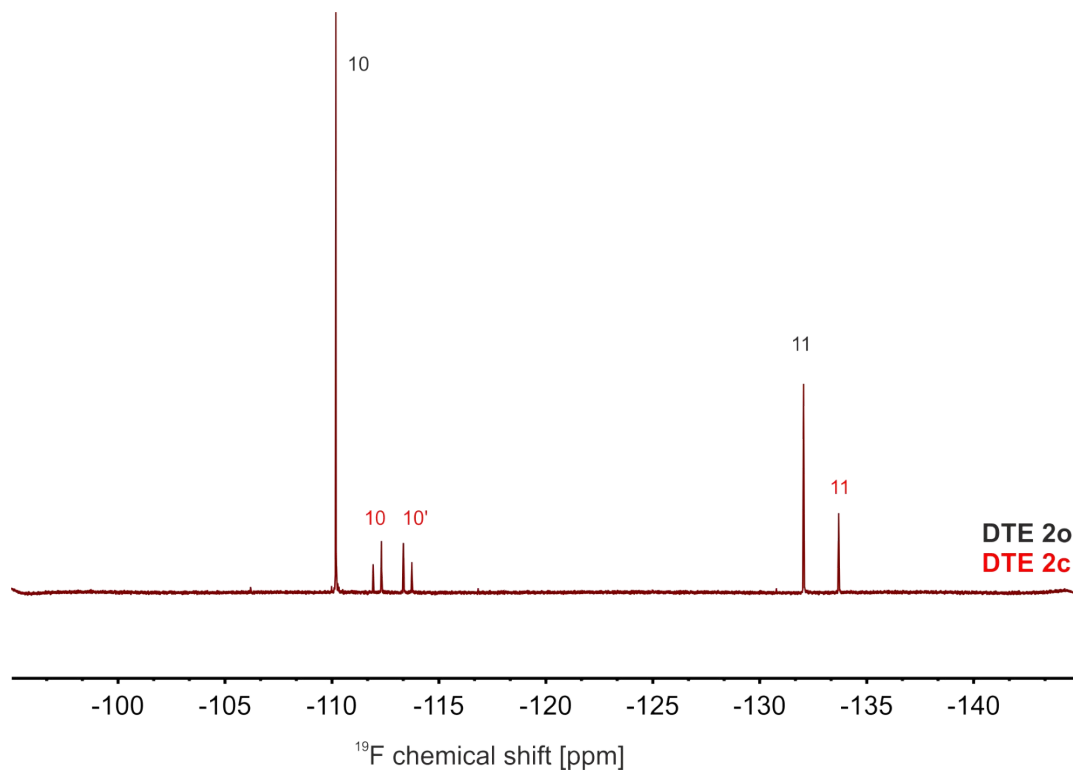


Fig S32 ¹⁹F NMR-spectrum (700 MHz proton resonance frequency) of a mixture of DTE 2o and DTE 2c in DMF-*d*₇ at 300 K.

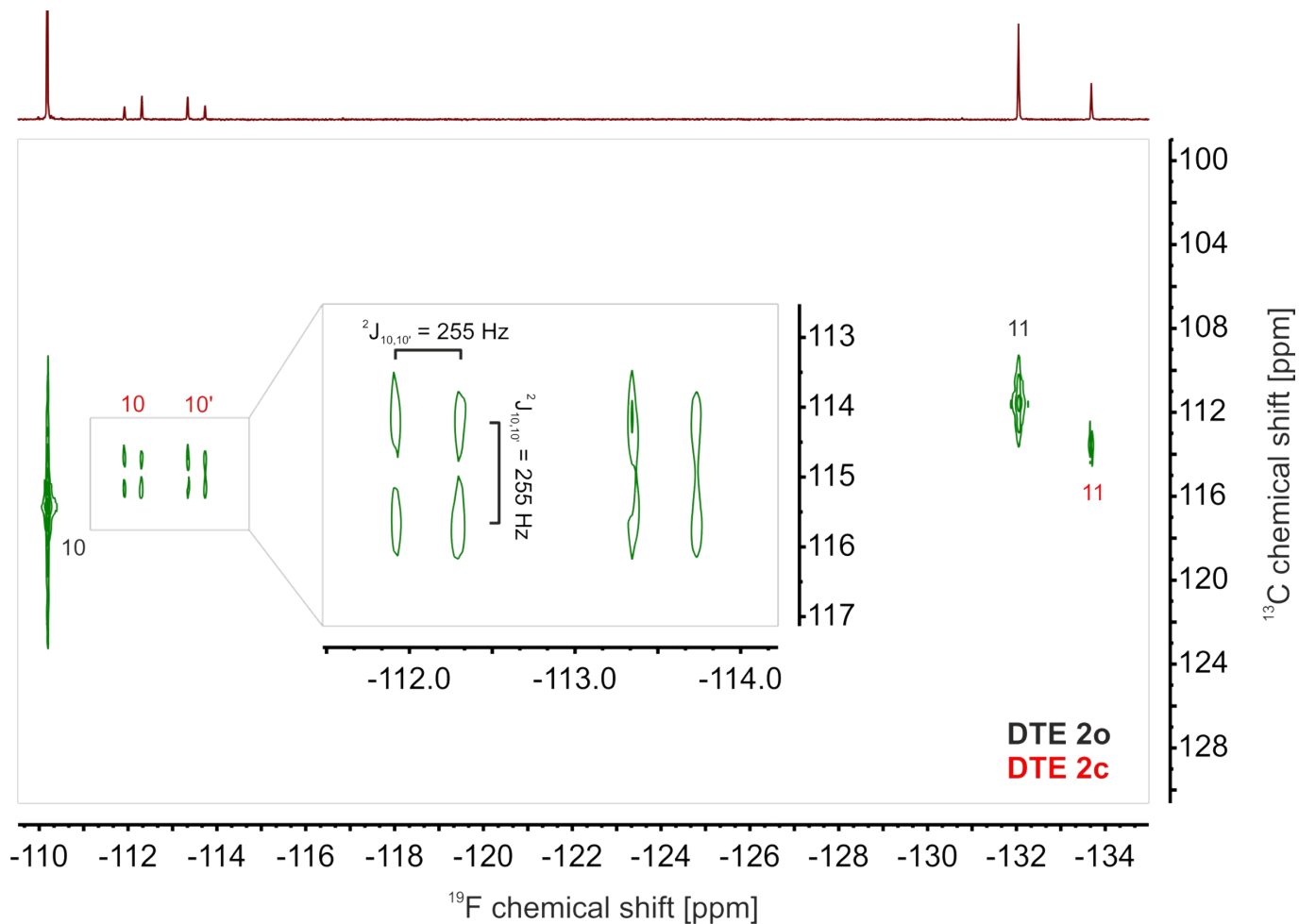


Fig S33 ${}^{19}\text{F}$ - ${}^{13}\text{C}$ -HMOC NMR-spectrum (700 MHz proton resonance frequency) of a mixture of DTE 2o and DTE 2c in $\text{DMF-}d_7$ at 300 K.

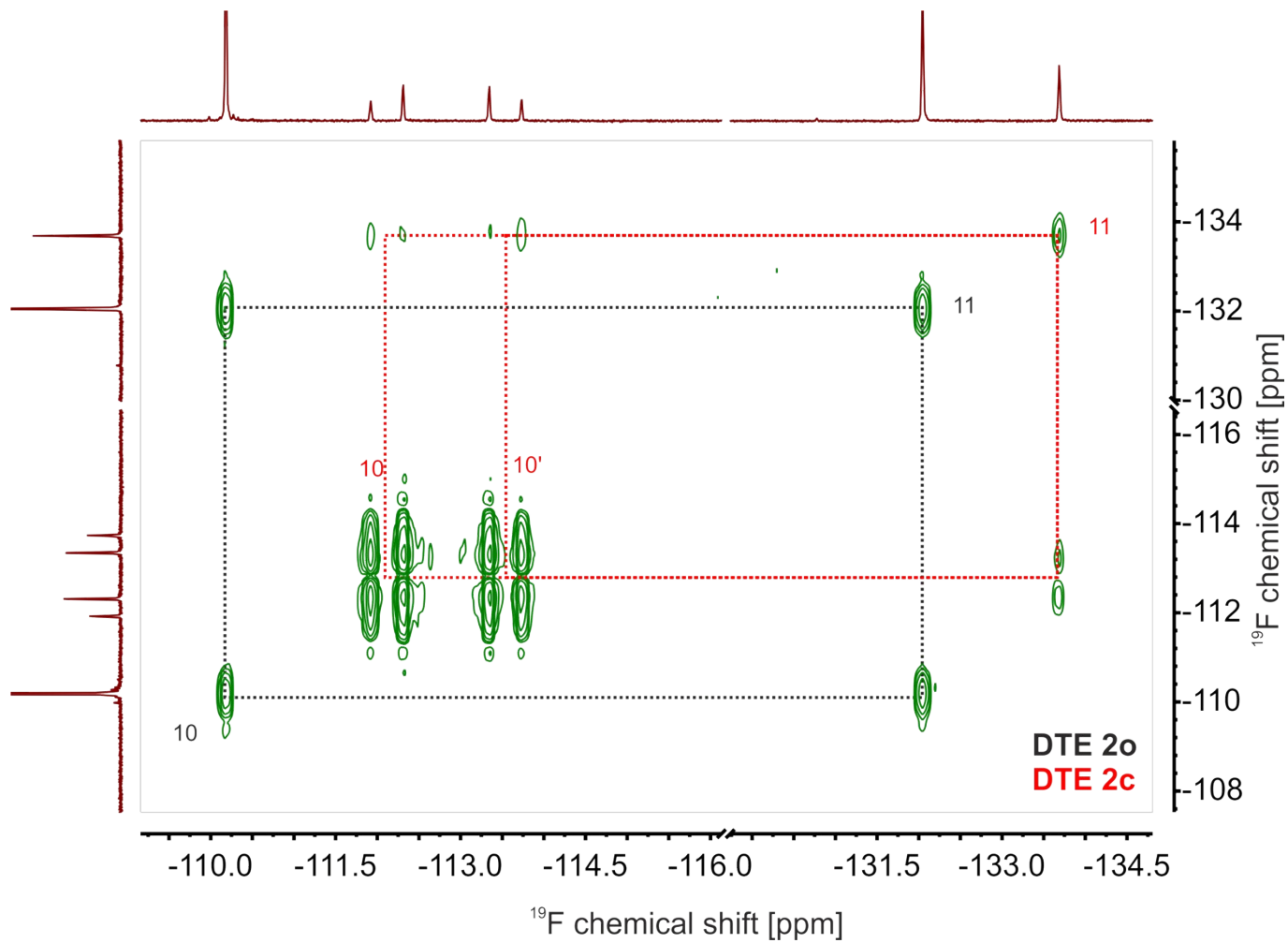


Fig S34 ^{19}F - ^{19}F -COSY NMR-spectrum (700 MHz proton resonance frequency) of a mixture of **DTE 2o** and **DTE 2c** in $\text{DMF-}d_7$ at 300 K.

5. Cyclic Voltammetry

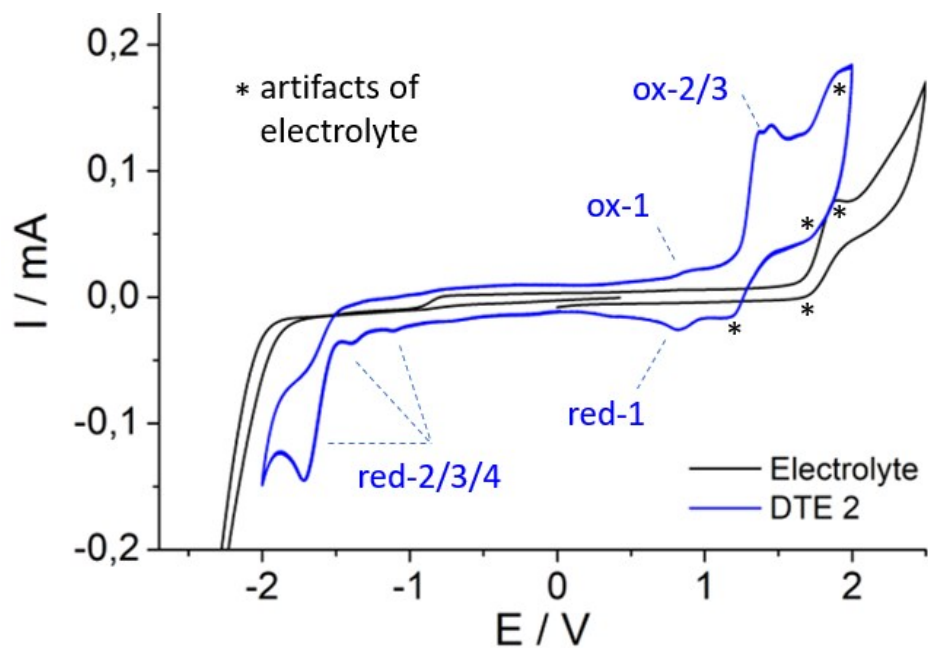


Fig S35 Cyclic Voltammetry (CV) of DTE 2 in a DCM/ $(n\text{Bu}_4\text{N})\text{PF}_6$ electrolyte (0.1 M).

Electrochemical process	E (V)
ox-1	0.92
ox-2/3	1.35/1.47
red-1	0.82
red-2	-1.11
red-3	-1.37
red-4	-1.67

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