The electrical properties of biphenylenes

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Supplementary Information

General Information:

Chemicals: Solvents, inorganic salts, and organic reagents were purchased from commercial sources and used without further purification unless otherwise mentioned.

Chromatography: Merck pre-coated 0.25 mm silica plates containing a 254 nm fluorescence indicator were used for analytical thin-layer chromatography. Flash chromatography was performed on 230-400 mesh silica (SiliaFlash® P60) from Silicycle.

Preparative HPLC was run on a Waters 600 liquid chromatography system equipped with a Waters^{TM} 600 pumping system and a Waters 2489 UV-Vis detector. Samples were collected manually. A Waters XBridge^{TM} C18 reverse phase preparative column (particle size 5 μm, 19x150 mm) was used as stationary phase.

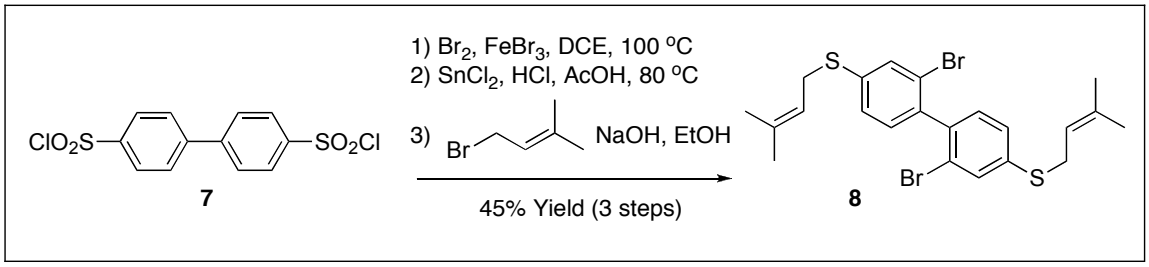
Spectroscopy: NMR spectra were obtained on a Bruker DPX 300 or 400 MHz spectrometer. Spectra were analyzed with the MestreNova Software (Version 6.1). CI-MS spectra were taken on a Nermag R-10-10 instrument. FAB MS spectra were taken on a JEOL JMS-DX-303 HF instrument using either glycerol or p-nitrobenzyl alcohol as matrices. Matrix assisted laser desorption ionization (MALDI) mass spectra were acquired using an Applied Biosystems Voyager DE Pro time-of-flight mass spectrometer. Positive ion mass spectra were acquired in the linear mode using a nitrogen laser (337nm). Instrument settings were as follows: accelerating voltage, 21,000 volts; grid voltage, 95%; guide wire, 0.05%; extraction delay time, 200 nsec. All data processing was performed using Applied Biosystems Data Explorer v 4.0.0.0.

Theoretical Methods:

The DFT-based studies were performed using the generalized gradient approximation (GGA) as formulated by Perdew, Burke and Ernzerhof (PBE)[1]. The molecular calculations were done with Jaguar v7.5 using a 6-31g** basis for the light atoms and a lacvp** basis for Au[2, 3]. For each species studied, the geometry was fully relaxed. Calculations representing **4** were done for 2,7-Dithiomethoxybiphenylene and those representing **5** were done for 2,7-Dithiomethoxyfuorene. The ionization potential was calculated with the geometry frozen from the ground state (vertical ionization potential). To probe the trends in tunnel coupling and conductance, the undercoordinated Au

binding site on each electrode is simulated by a cluster consisting of a single Au atom. For the complex consisting of the core molecule coordinated by an Au atom bonded to each N or S link atom, the geometry was fully relaxed. Both cis and trans configurations of the Au-N or Au-S link bond (same side of the molecule or opposite) were investigated. The differences in total energy and tunnel coupling were not significant.

Synthesis of biphenylene derivatives

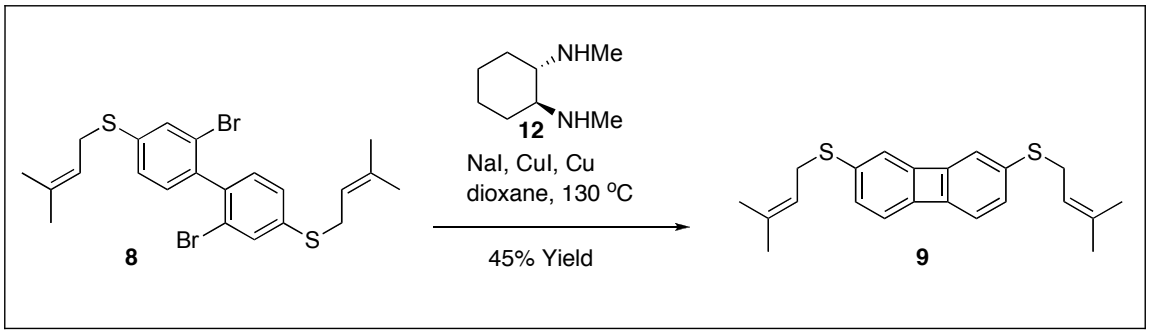


(2,2'-dibromobiphenyl-4,4'-diyl)bis((3-methylbut-2-enyl)sulfane) (8):

Commercially available 4,4'-biphenyldisulfonyl chloride (**7,** 5.00 g, 14.2 mmol) was dissolved in dry DCE (25 ml). Bromine (8 ml, 155 mmol) and iron(III) bromide (0.3 g, 1.0 mmol) were added and the reaction mixture was stirred at 100 °C for 8 days in a high pressure sealed tube with teflon screw-cap. The reaction mixture was then allowed to cool to room temperature. 1.0 ml of the reaction mixture (out of about 33 ml) were transferred to a 25 ml round bottom flask and excess bromine as well as the DCE were evaporated on the rotavap. The dark brown oily residue was dried on the high vacuum for 2 hours. The residue (about 0.43 mmol, assuming 100% yield in the first stage and a 1/33 dilution after the first stage) was dissolved in a HCl solution (1.0 M, 5.0 ml) in acetic acid and anhydrous stannous chloride (1.75 g, 9.23 mmol) was added. The reaction mixture was then stirred at 80 °C for 1 hour. During the reaction time, the reaction mixture became colorless. The reaction mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was dissolved in 10 ml EtOH and a solution of NaOH (0.50 g, 12.5 mmol) in 1 ml 50 % EtOH/H_2O was slowly added at room temperature under argon. The reaction mixture was stirred for 5 min at room temperature and then 3,3-dimethylallyl bromide (0.13 ml, 1.11 mmol) was added

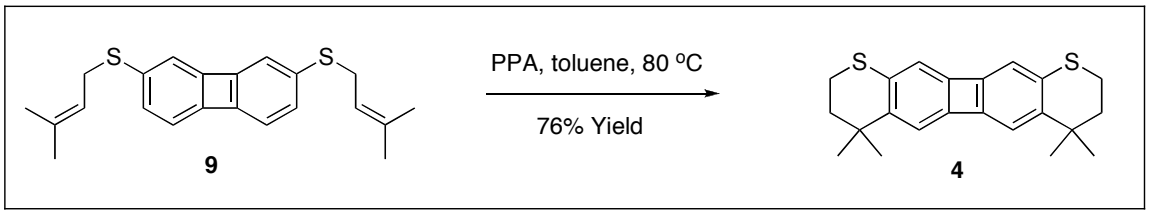
and the reaction mixture was warmed to 45 °C for 1 hour under argon. The solvent was evaporated on the rotavap and the residue was taken up in DCM. The organic phase was then washed with H_2O, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting oil was purified by flash colum chromatography on silica gel (10% DCM in hexanes) to afford **8** (100 mg, 0.195 mmol, 45% yield, 3 steps, assuming a 1/33 dilution after the first stage) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.8 Hz, 2H), 7.29 (dd, *J* = 8.1, 1.9 Hz, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.52 – 5.22 (m, 2H), 3.59 (d, *J* = 7.5 Hz, 4H), 1.75 (s, 6H), 1.64 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.13, 138.99, 137.39, 132.50, 131.12, 127.88, 123.83, 118.81, 32.11, 25.83, 17.99; MS (FAB+, *m/z*) 510; HRMS calcd for $C_{22}H_{24}Br_2S_2$: 509.9686; found 509.9709.



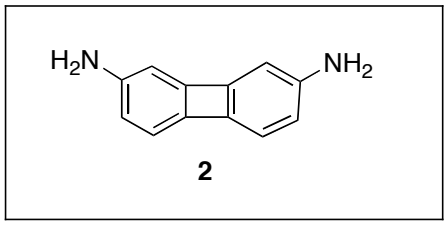
2,7-bis(3-methylbut-2-enylthio)biphenylene (9): A mixture of **8** (100 mg, 0.195 mmol), CuI (35 mg, 0.184 mmol), NaI (100 mg, 0.667 mmol) and copper powder (100 mg, 1.574 mmol) was dried for 12 hours under high vacuum in a 10 ml high pressure reaction vessel. The reaction vessel was then backfilled three times with argon and the reagents were suspended in anhydrous dioxane (2 ml). Diamine ligand **12** (25 mg, 0.17 mmol) was added and the reaction mixture was purged with argon for 15 min. The high pressure reaction vessel was sealed with a teflon screw cap and the reaction mixture was heated to 130 °C for 75 hours. The reaction mixture was cooled to room temperature, diluted with DCM, and washed with aqueous NH_4OH (10 ml, 2 N). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting oil was purified with flash column chromatography on silica gel (10% DCM in hexanes)

to afford **9** (31 mg, 0.088 mmol, 45% yield) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 7.2, 1.3 Hz, 2H), 6.67 (s, broad, 2H), 6.54 (dd, *J* = 7.2, 0.5 Hz, 2H), 5.37 – 5.25 (m, 2H), 3.48 (d, *J* = 7.7 Hz, 4H), 1.73 (s, 7H), 1.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.91, 148.68, 136.71, 130.01, 129.78, 119.83, 119.29, 117.67, 32.73, 25.83, 17.91; MS (FAB+, *m/z*) 352; HRMS calcd for $C_{22}H_{24}S_2$: 352.1319; found 352.1330.



Cyclic biphenylene 4:. Polyphosphoric acid (PPA, 1.0 ml) was added to an oven-dried Schenk tube with stirring bar and the Schlenk tube was backfilled with argon three times. Then, a solution of **9** (30 mg, 0.085 mmol) in toluene (3 ml, purged with argon for 15 minutes) was added to the Schlenk tube and the reaction mixture was heated to 80 °C and stirred vigorously for 16 hours. The reaction mixture was cooled to room temperature and the toluene phase was decanted. The leftover PPA was hydrolyzed with H_2O (15 ml) and the resulting phosphoric acid solution was extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting oily residue was purified with flash column chromatography on silica gel (10% DCM in hexanes) to afford cyclic biphenylene **4** (23 mg, 0.065 mmol, 76% yield, single isomer) as a yellow solid: Mp. 182–185 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.69 (s, 2H), 6.35 (s, 2H), 2.96 (s, broad, 4H), 1.97–1.86 (m, 4H), 1.25 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.65, 146.95, 140.52, 130.02, 116.49, 115.81, 38.33, 33.46, 30.22, 23.40; MS (FAB+, *m/z*) 352; HRMS calcd for $C_{22}H_{24}S_2$: 352.1319; found 352.1306.

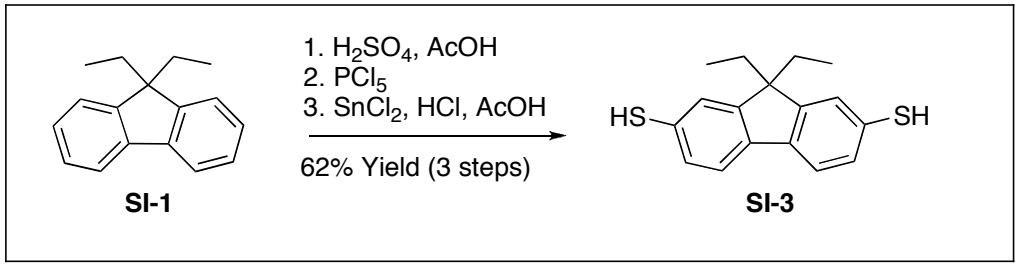
About 2 mg of biphenylene **4** were repurified by preparative HPLC (liquid phase: 20% H_2O in acetonitrile; flow rate: 10 ml/min; compound injected as a solution in 50 μL THF, retention time: 22 minutes). The repurified compound was used for the single molecule conductance measurements.



2

2,7-Diaminobiphenylene (2). The compound was synthesized following a procedure by Larkem and coworkers.[4] Larkem and coworkers only reported a melting point and low resolution MS data. Due to the facile decomposition of **2** in air, we were not able to get a highly pure sample. A ^{1}H NMR of an impure sample is shown in the spectral section of the supplementary information. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (d, J = 7.3 Hz, 2H), 6.14 (d, J = 1.5 Hz, 2H), 5.96 (dd, J = 7.3, 1.7 Hz, 2H), 3.57 (s, 4H). CV traces of impure samples of **2** only showed irreversible oxidation/reduction peaks.

Synthesis of fluorene derivatives

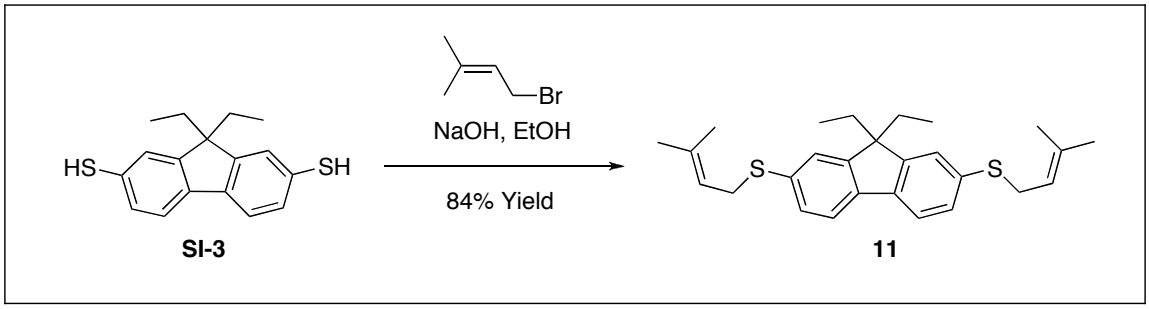


SI-1 **SI-3**

9,9-diethyl-9*H*-fluorene-2,7-dithiol (SI-3). To a stirred solution of 9,9-diethyl-9*H*-fluorene, **SI-1**,[5] (7.5 g, 0.033 mol) in acetic acid (50 mL), chlorosulfonic acid (15 mL) was added dropwise at 0 °C. The reaction mixture was refluxed for 2 h, cooled, and poured into a saturated aqueous solution of NaCl (200 mL) containing NaOH (5.0 g, 0.13 mol). The precipitate was washed with a saturated solution of NaCl (3 x 30 mL) and dried overnight at 60 °C in vacuo to give sodium 9,9-diethyl-9*H*-fluorene-2,7-disulfonate. The salt was mixed with phosphorus pentachloride (24 g, 0.116 mol) and stirred at 120

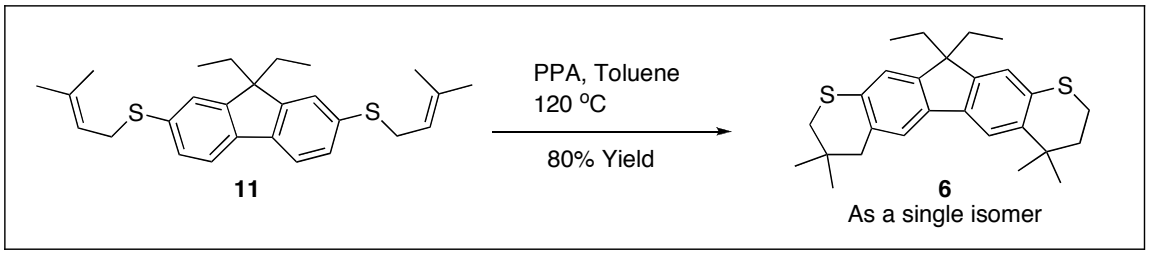
°C for 2h. The phosphorus oxychloride formed during the reaction was distilled off, and the resulting dry residue was pulverized in a mortar and then treated with water. The precipitate was filtered off and washed with water to give 9,9-diethyl-9*H*-fluorene-2,7-disulfonyl dichloride (**SI-2**, 12 g, 0.028 mol) with 84% yield (two steps) as a light-reddish-brown powder. MS (FAB+, *m/z*) 417, 419. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.15 (d, *J* = 7.8 Hz, 2H), 8.12 (s, 2 H), 8.05 (d, *J* = 7.8 Hz, 2H), 2.19 (q, *J* = 7.5 Hz, 4H), 0.36 (t, *J* = 7.5 Hz, 6H).

Stannous chloride dihydrate (12.7 g, 67.14 mmol) was dissolved in a mixture of acetic acid (30 mL) and concentrated HCl (15 mL). The mixture was heated to 90 °C and 9,9-diethyl-9*H*-fluorene-2,7-disulfonyl dichloride (1.4 g, 3.35 mmol) was added with stirring. The reaction temperature was kept at 90 °C for 2 h. The reaction mixture was then allowed to cool to 20 °C and poured into water (25 mL) containing concentrated HCl (15 mL). The light-yellow precipitate was filtered, washed with water, and dried to yield dithiol **SI-3** (0.717 g, 74%). ^{1}H NMR ($CDCl_3$, 300MHz) *δ* 7.54 (d, *J* = 7.8 Hz, 2H), 7.30-7.29 (m, 4H), 3.58 (s, 2H), 2.01 (q, *J* = 7.2 Hz, 4H), 0.35 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 150.8, 139.1, 129.0, 128.5, 124.4, 120.1, 56.4, 32.8, 8.6; MS (FAB+, *m/z*) 286; HRMS calcd for $C_{17}H_{18}S_2$: 286.0850; found: 286.0858.



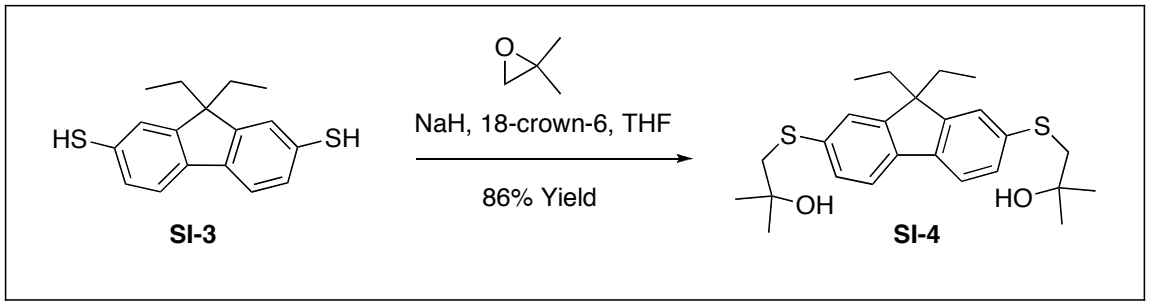
9,9-diethyl-2,7-bis(3-methylbut-2-enylthio)-9*H*-fluorene (11). To a stirred solution of **SI-3** (340 mg, 1.188 mmol) in ethanol (10 mL), 1-bromo-3-methylbut-2-ene (553 ml, 4.755 mmol) and sodium hydroxide (142.6 mg, 3.755 mmol) were added at room temperature. The mixture was heated at 90 °C for 3 hours and then the solvent evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography (hexane : EtOAc =100:1) to provide **11** with 84% yield (420 mg,

0.995 mmol).[1]H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.30 (s, 2H), 5.32 (m, 2H), 3.56 (d, J = 7.6 Hz, 4H), 1.98 (q, J = 7.2 Hz, 4H), 1.70 (s, 6H), 1.57 (s, 6H), 0.31 (t, J = 7.2 Hz, 6H); [13]C NMR ($CDCl_3$, 100MHz) δ 150.4, 139.7, 136.1, 135.1, 129.5, 125.3, 119.9, 119.8, 56.2, 33.1, 32.8, 25.7, 17.8, 8.6; MS (FAB+, *m/z*) 422; HRMS calcd for $C_{27}H_{34}S_2$: 422.2102; found: 422.2099.

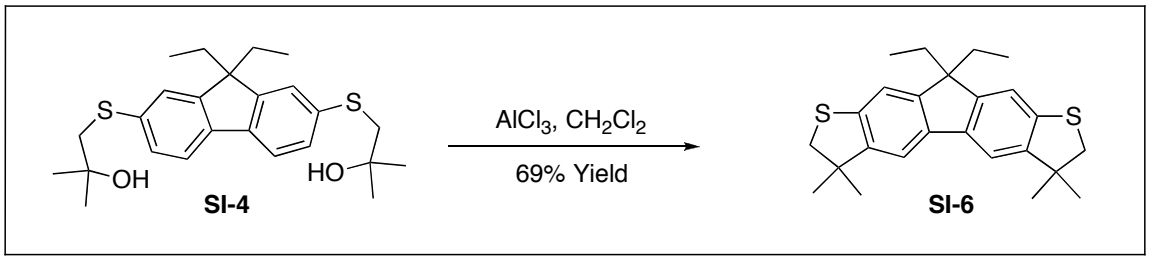


9,9-diethyl-2,7-cyclicthioether9*H*-fluorene (6). To a stirred solution of **11** (350 mg, 0.829 mmol) in toluene (10 mL), PPA (3 ml) was added at room temperature. The mixture was heated at 120 °C until the starting material was consumed (followed by [1]H NMR, after 36 hours).

The reaction mixture was then allowed to cool to room temperature and poured into an aqueous solution of sodium hydroxide. The organic layer was separated and the aqueous layer was extracted three times with DCM. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude reaction mixture was purified by column chromatography (hexane : EtOAc =50:1) to provide **6** as a single isomer with 80% yield (280 mg, 0.663 mmol) as a colorless solid: Mp. 278–281 °C; [1]H NMR ($CDCl_3$, 300 MHz) δ 7.64 (s, 2H), 7.02 (s, 2H), 3.10 (m, 4H), 2.03–1.89 (m, 8H), 1.45 (s, 12H), 0.41 (m, 6H); [13]C NMR ($CDCl_3$, 75MHz) δ 147.6, 140.6, 138.2, 129.6, 121.0, 116.9, 55.3, 38.2, 33.4, 32.8, 30.6, 23.4, 8.9; MS (FAB+, *m/z*) 422; HRMS calcd for $C_{27}H_{34}S_2$: 422.2102; found: 422.2099.

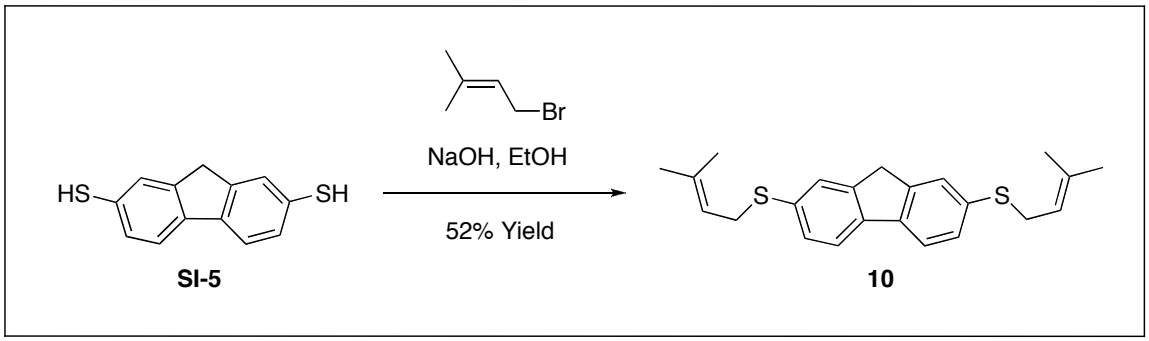


1,1'-(9,9-diethyl-9*H*-fluorene-2,7-diyl)bis(sulfanediyl)bis(2-methylpropan-2-ol) (SI-4). To a stirred solution of **SI-3** (410 mg, 1.433 mmol) in THF (10 mL), 2,2-dimethyloxirane (306 ml, 3.440 mmol), 18-crown-6 (27.5 mg, 0.143 mmol) and sodium hydroxide (82.6 mg, 3.440 mmol) were added at 0 °C. The mixture was stirred at 0 °C for one hour, and then at room temperature for 17 hours. Four drops of water were added, the mixture was passed through small pad of silica gel, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography (hexane : EtOAc =1:1) to provide **SI-4** with 86% yield (530 mg, 1.232 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, J = 8.0 Hz, 2H), 7.39 (m, 4H), 3.15 (s, 4H), 2.51 (s, 2H), 1.98 (q, J = 7.2 Hz, 4H), 1.32 (s, 12H), 0.32 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 150.7, 139.6, 135.7, 128.8, 124.5, 120.1, 71.0, 56.3, 49.2, 32.7, 32.6, 28.8, 8.5; MS (FAB+, *m/z*) 430; HRMS calcd for $C_{27}H_{34}O_2S_2$: 430.2000; found: 430.2013.

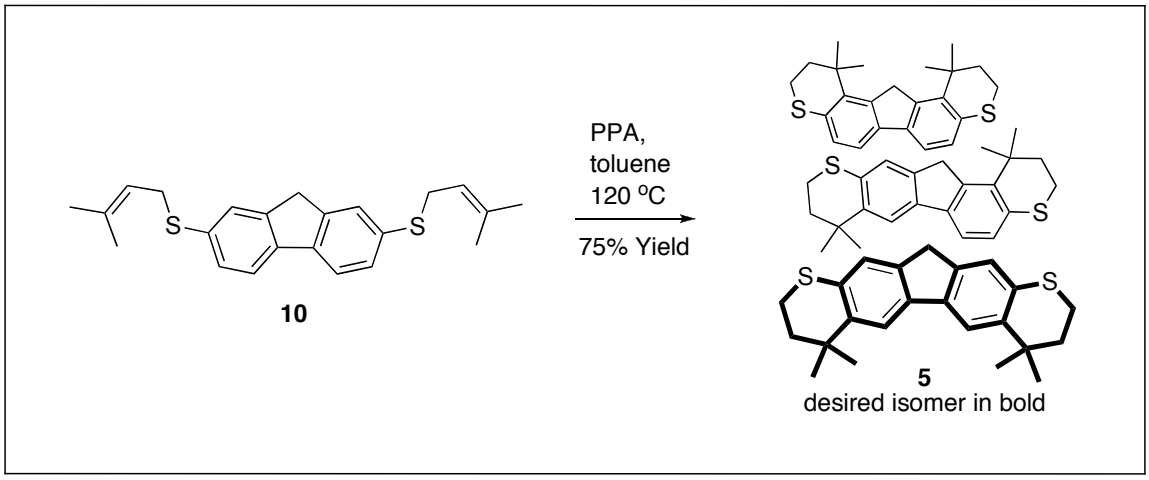


Fluorene derivative SI-6. To a stirred solution of **SI-4** (120 mg, 0.279 mmol) in dry DCM (10 mL), aluminum(III) chloride (223.0 mg, 1.672 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature for 17 hours and then passed through small pad of silica gel using DCM as the liquid phase. The solvent was then evaporated

under reduced pressure. The crude reaction mixture was purified by column chromatography (hexane : EtOAc =50:1) to provide **SI-6** with 69% yield (76 mg, 0.192 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (s, 2H), 7.08 (s, 2H), 3.23 (s, 4H), 1.90 (q, J = 7.2 Hz, 4H), 1.44 (s, 12H), 0.36 (t J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.8, 146.8, 138.7, 138.6, 117.1, 113.3, 55.3, 47.7, 47.1, 32.8, 27.7, 8.8; MS (FAB+, *m/z*) 394; HRMS calcd for $C_{25}H_{30}S_2$: 394.1789; found: 394.1790.



2,7-bis(3-methylbut-2-enylthio)-9*H*-fluorene (10). To a stirred solution of **SI-5**[6] (300 mg, 1.304 mmol) in ethanol (10 mL), 1-bromo-3-methylbut-2-ene (607 ml, 5.217 mmol) and sodium hydroxide (156.5 mg, 3.912 mmol) were added at room temperature. The mixture was heated at 90 °C for 4 hours and then the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography (hexanes:EtOAc = 100:1) to provide **10** with 52% yield (250 mg, 0.683 mmol). ^{1}H NMR ($CDCl_3$, 400MHz) δ 7.63 (d, J = 8.0 Hz, 2H), 7.51 (s, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.32 (m, 2H), 3.84 (s, 2H), 3.58 (d, J = 7.6 Hz, 4H), 1.72 (s, 6H), 1.59 (s, 6H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 143.8, 139.7, 136.4, 135.1, 129.0, 126.9, 120.0, 119.5, 36.7, 33.0, 25.8, 17.8; MS (FAB+, *m/z*) 366; HRMS calcd for $C_{27}H_{34}S_2$: 366.2102; found: 366.2099.



Cyclic fluorene 5. To a stirred solution of **10** (140 mg, 0.382 mmol) in toluene (10 mL), PPA (1 ml) was added at room temperature. The mixture was heated at 120 °C until the starting material was consumed (followed by ^{1}H NMR, after 24 hours). The reaction mixture was allowed to cool to 20 °C and poured into aqueous solution of sodium hydroxide. The organic layer was separated and the aqueous layer was extracted three times with DCM. The organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography (hexanes:EtOAc = 50:1) to provide an inseparable mixture of cyclic isomers **5** with 75% yield (105 mg, 0.287 mmol).

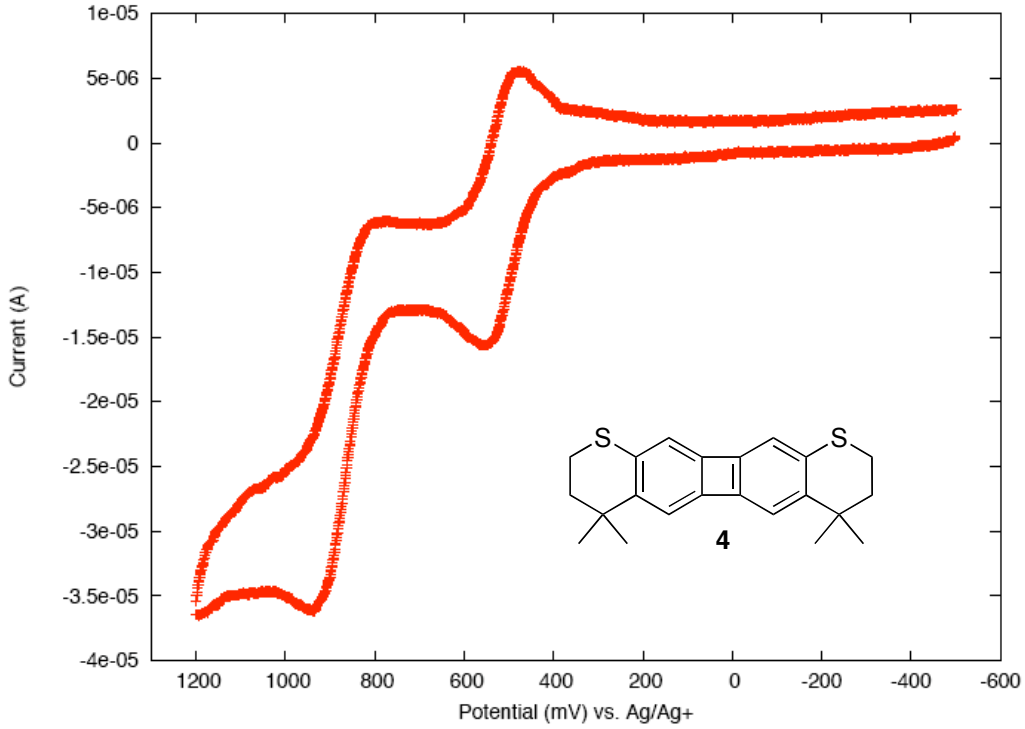
About 2 mg of the mixture of isomers was separated via preparative HPLC (liquid phase: 20% H_2O in acetonitrile; flow rate: 10 ml/min; Compound injected as a solution in 50 μL THF, retention time: 24 minutes) to afford **5** as a single isomer (isolated isomer shown in bold) as a colorless solid: Mp. 173–175 C; ^{1}H NMR (300 MHz, CD_3OD) δ 7.84 (s, 2H), 7.19 (s, 2H), 3.72 (s, 2H), 3.16–2.91 (m, 4H), 2.10–1.86 (m, 4H), 1.47 (s, 12H); ^{13}C NMR (75 MHz, CD_3OD) δ 142.44, 142.04, 139.74, 131.07, 123.67, 118.25, 39.37, 36.29, 34.34, 30.80, 23.89; MS (FAB+, *m/z*) 366; HRMS calcd for $C_{23}H_{26}S_2$: 366.1476; found 366.1469.

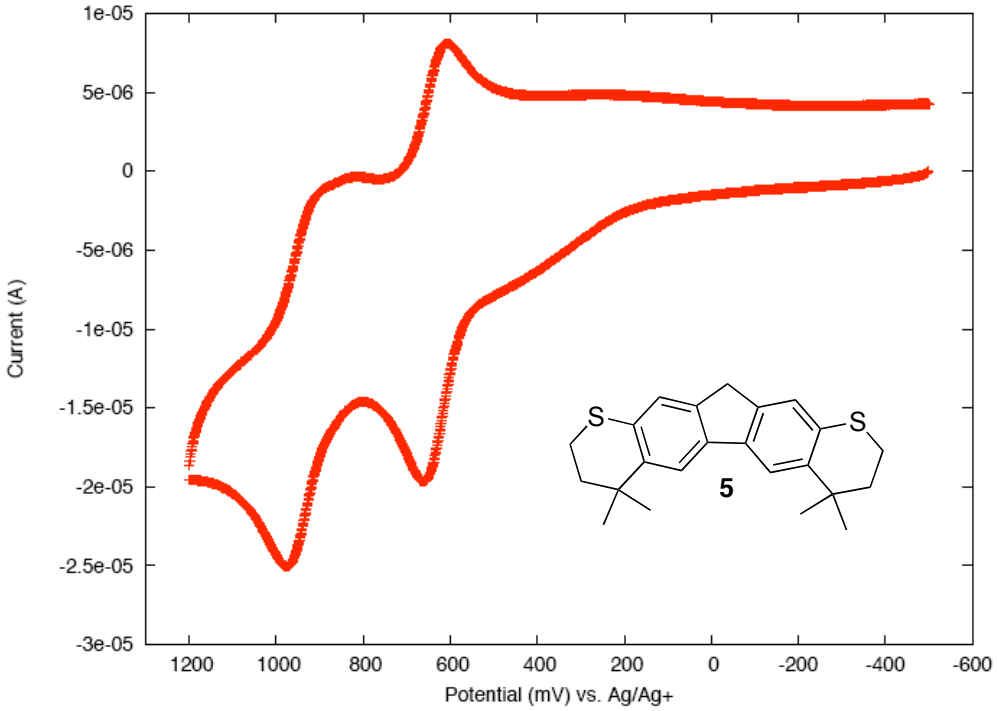
Cyclic Voltametry (CV) Measurements:

Electrochemistry was performed on a BAS CV-50W voltammetric analyzer with a three

electrode cell. Each analyte was dissolved in acetonitrile containing 0.100 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte to give 1.0 mM final concentration in analyte. Sample solutions were sparged with argon for 5 min. prior to use. A platinum disc working electrode (BAS, d = 1.6 mm) and a platinum wire counter electrode were used. The reference electrode contained a silver wire with 10 mM silver nitrate in TBAP electrolyte solution. Cyclic voltammetry experiments were carried out at ambient temperature and were recorded at 100 mV/s. Potentials were swept from -500 mV to 1200 mV or from -2000 mV to 2000 mV. Ferrocene was used as an external calibrator and gave $E_{1/2}$ = 90 mV (vs $Ag/AgNO_3$) for each experiment.

CV Voltamogramms:

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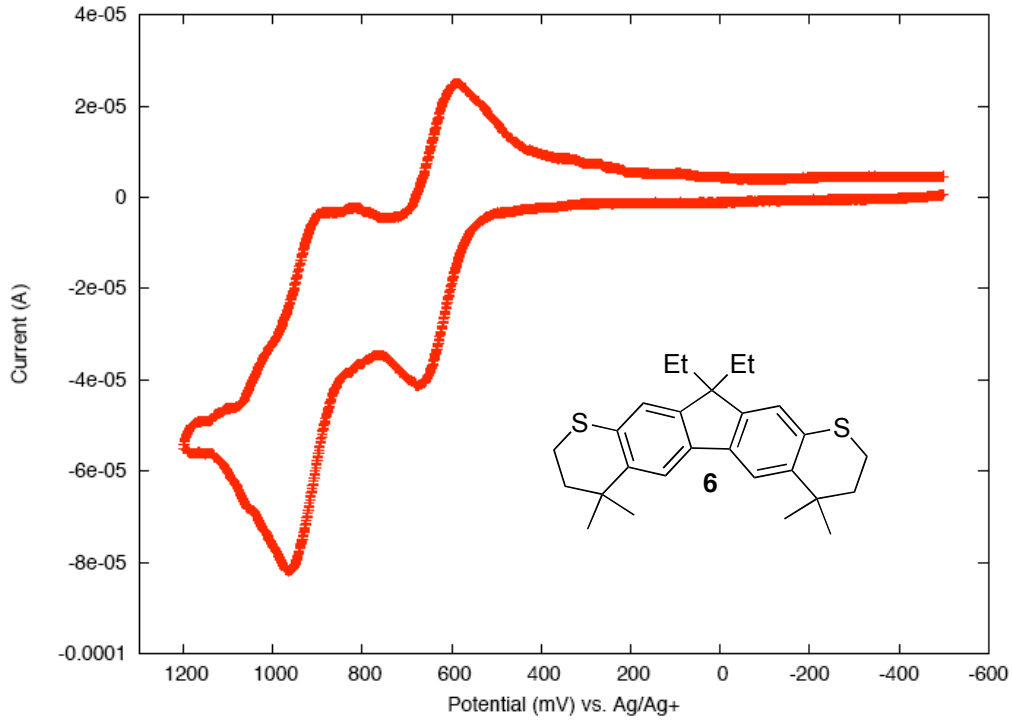
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0
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Potential (mV) vs. Ag/Ag+
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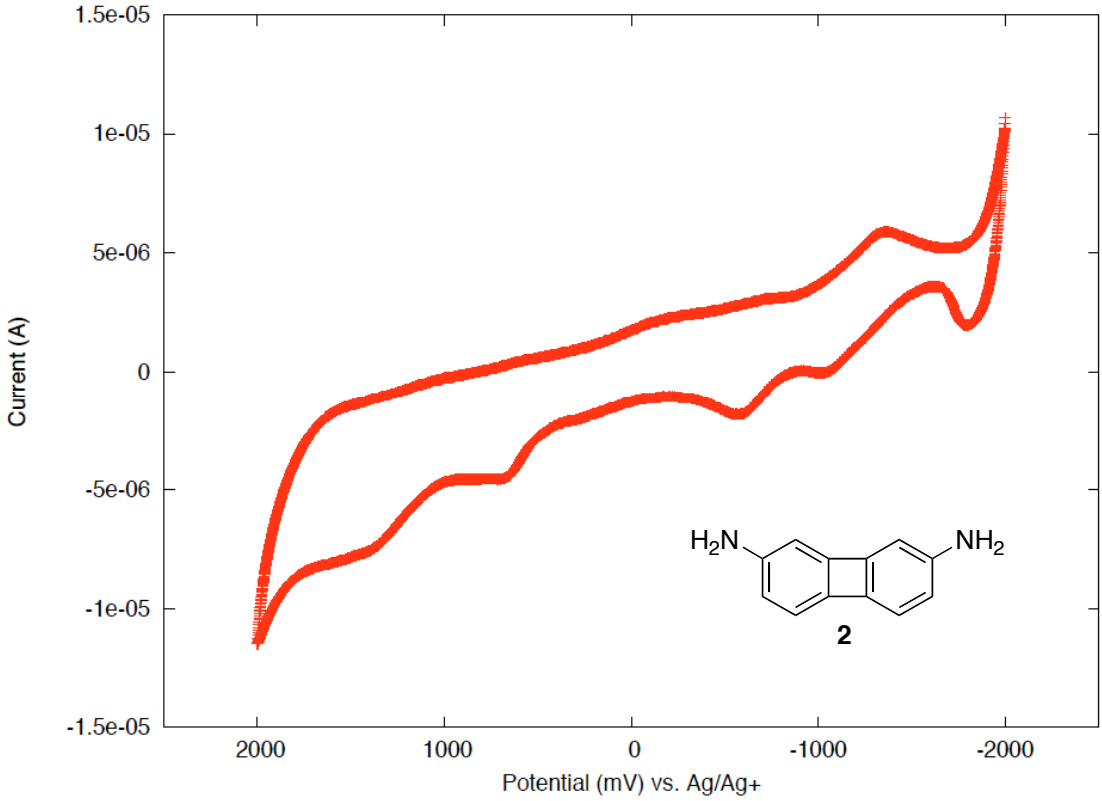
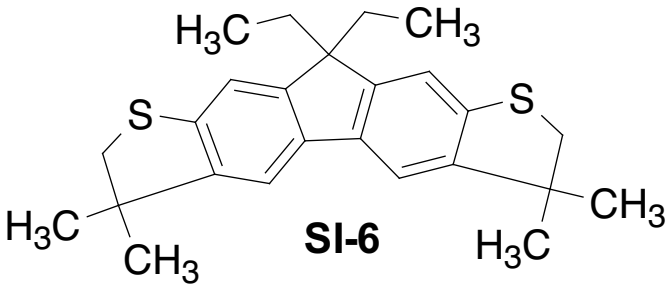
Et
S
S
6



NMR-Spectra:

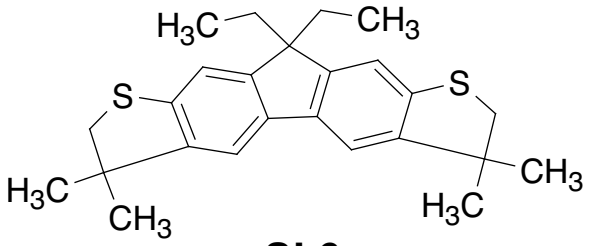
[1] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996**, *77*, 3865.
[2] Jaguar v7.5; Schrodinger, L.L.C., New York, NY 2008.
[3] Wadt, W. R.; Hay, P. J. *Journal of Chemical Physics* **1985**, *82*, 284.
[4] Larkem, A.; Larkem, H. *Indian J. Chem., Sec. B* **2002**, *41*, 175.
[5] Mohanakrishnan, A. K.; Kumar, N. S.; Amaladass, P. *Tetrahedron Lett.* **2008**, *49,* 4792.
[6] De Boer, B.; Meng, H.; Perepichka, D. F.; Zheng, J.; Frank, M. M.; Chabal, Y. J.; Bao, Z. *Langmuir* **2003**, *19*, 4272.

Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	D2O
3 Temperature	300.0
4 Pulse Sequence	zg
5 Experiment	1D
6 Number of Scans	32
7 Acquisition Date	2009-11-14T17:15:00
8 Spectrometer Frequency	399.92
9 Nucleus	1H



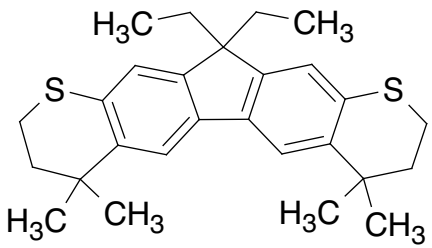
SI-6

Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	CDCl3
3 Temperature	696.5
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	2689
7 Acquisition Date	2009-11-23T17:16:00
8 Spectrometer Frequency	75.47
9 Nucleus	13C



SI-6

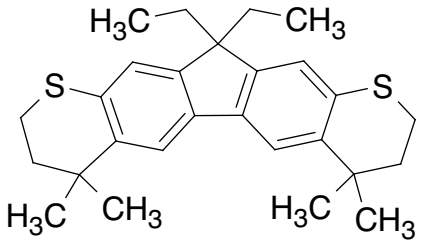
Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	D2O
3 Temperature	300.0
4 Pulse Sequence	zg
5 Experiment	1D
6 Number of Scans	32
7 Acquisition Date	2009-11-12T09:51:00
8 Spectrometer Frequency	399.92
9 Nucleus	1H



6

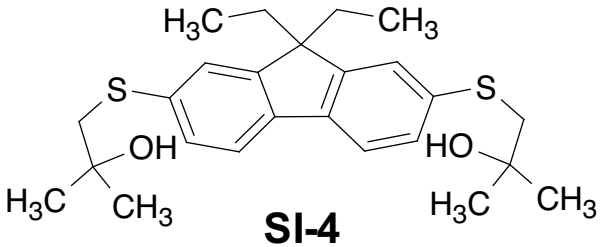
Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	Aceton
3 Temperature	300.0
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	469
7 Acquisition Date	2009-11-12T09:58:00
8 Spectrometer Frequency	100.56
9 Nucleus	13C

147.62
140.60
138.24
129.59
121.04
116.89
77.48
77.16
76.84
55.34
38.23
33.43
32.78
30.61
23.42
8.88



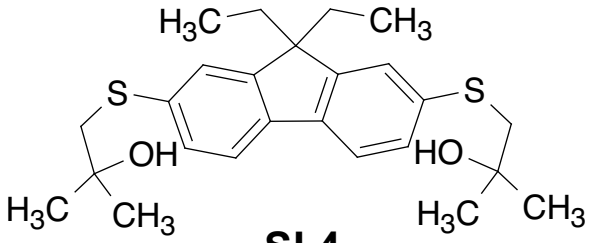
6

Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	D2O
3 Temperature	300.0
4 Pulse Sequence	zg
5 Experiment	1D
6 Number of Scans	32
7 Acquisition Date	2009-11-13T09:50:00
8 Spectrometer Frequency	399.92
9 Nucleus	1H



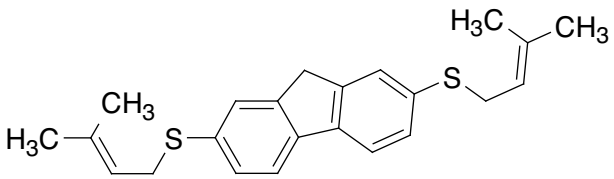
SI-4

Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	Aceton
3 Temperature	300.0
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	291
7 Acquisition Date	2009-11-13T09:59:00
8 Spectrometer Frequency	100.56
9 Nucleus	13C



SI-4

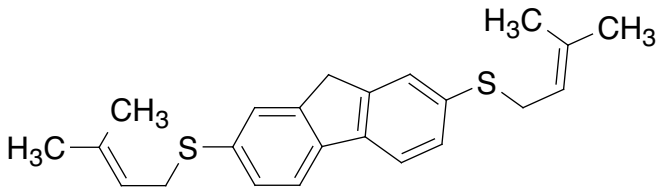
Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	D2O
3 Temperature	300.0
4 Pulse Sequence	zg
5 Experiment	1D
6 Number of Scans	32
7 Acquisition Date	2009-10-09T17:38:00
8 Spectrometer Frequency	399.92
9 Nucleus	1H



10

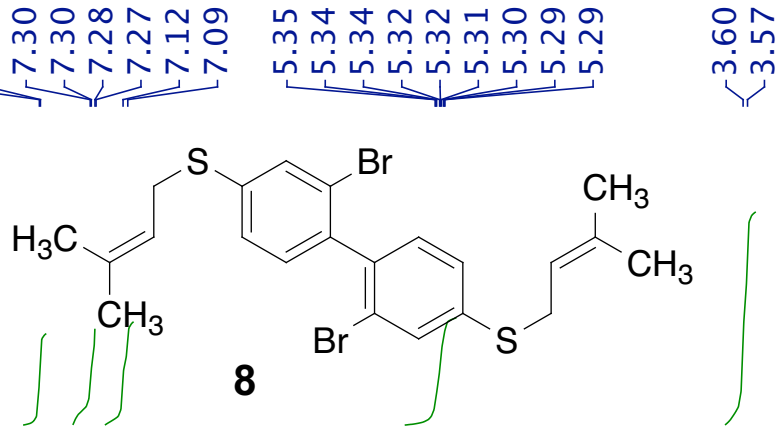
Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	CDCl3
3 Temperature	300.0
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1600
7 Acquisition Date	2009-10-12T19:18:00
8 Spectrometer Frequency	75.47
9 Nucleus	13C

143.76
139.72
136.45
135.08
128.97
126.88
119.99
119.51
77.57
77.14
76.72
36.69
32.98
25.78
17.83



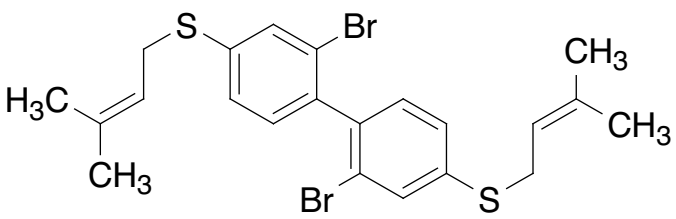
10

Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	Chloroform
Temperature	296.9
Pulse Sequence	zg
Experiment	1D
Number of Scans	64
Acquisition Date	2009-11-19T 15:37:00
Spectrometer Frequency	300.13
Nucleus	1H



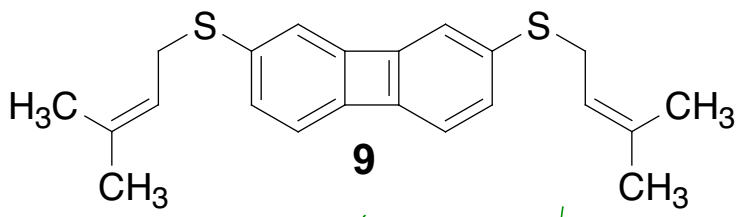
8

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1515
Acquisition Date	2010-06-11T15:40:28
Spectrometer Frequency	100.61
Nucleus	13C



8

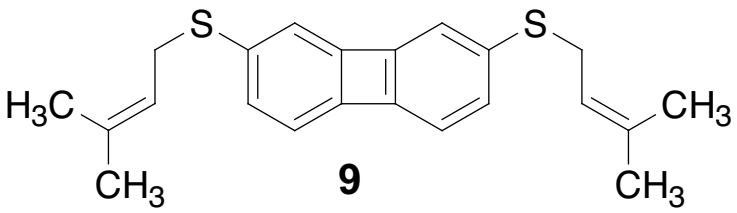
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	299.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	9
Acquisition Date	2010-02-08T 08:35:00
Spectrometer Frequency	399.92
Nucleus	1H



9

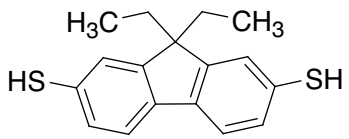
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	514
Acquisition Date	2010-02-08T08:22:00
Spectrometer Frequency	100.56
Nucleus	13C

150.91
148.68
136.71
130.01
129.78
119.83
119.29
117.67
32.73
25.83
17.91



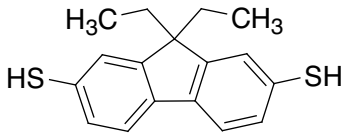
9

Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	Aceton
3 Temperature	296.1
4 Pulse Sequence	zg
5 Experiment	1D
6 Number of Scans	32
7 Acquisition Date	2009-11-10T09:40:00
8 Spectrometer Frequency	300.13
9 Nucleus	1H



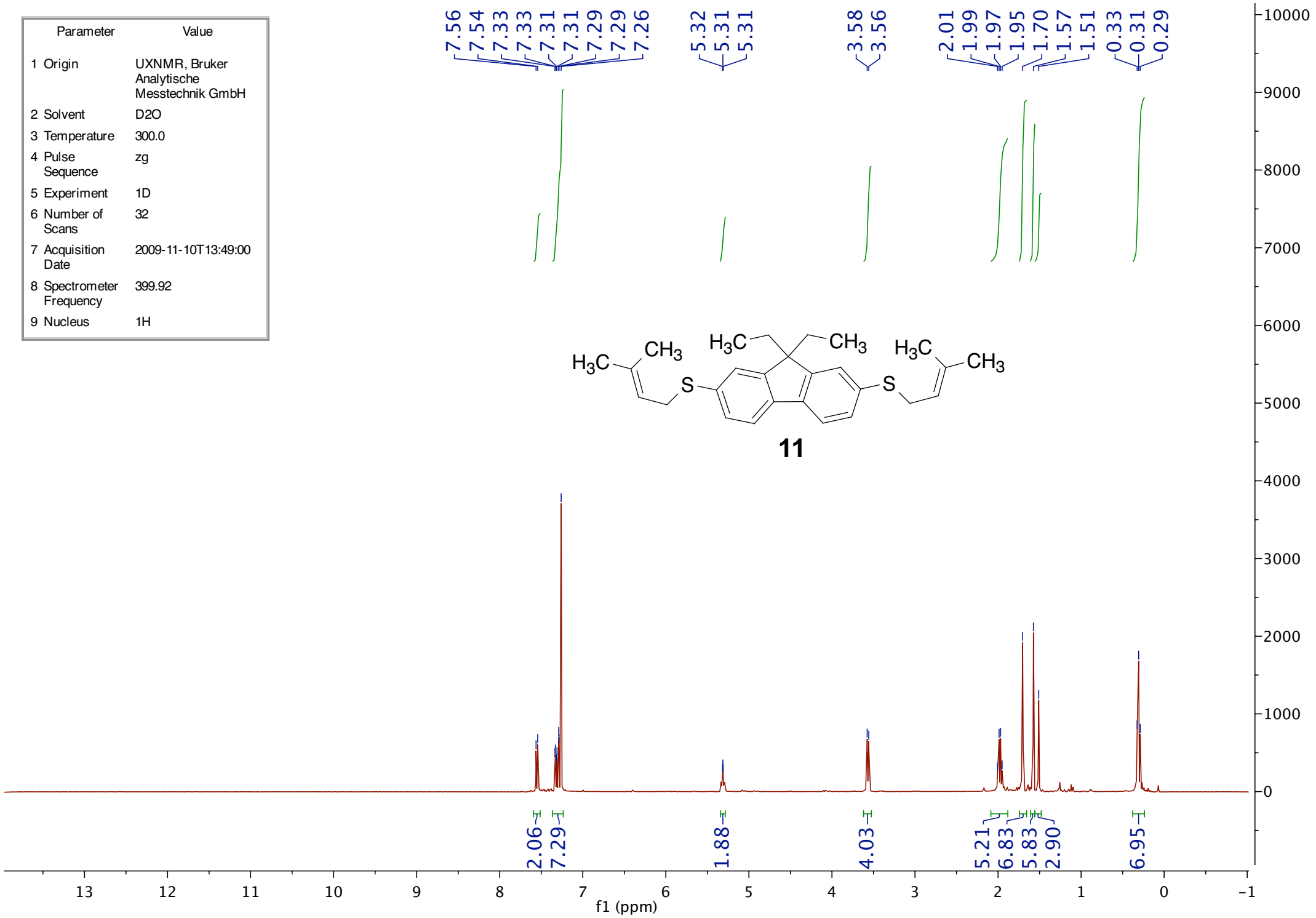
SI-3

Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	CDCl3
3 Temperature	300.0
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	627
7 Acquisition Date	2009-11-10T18:56:00
8 Spectrometer Frequency	75.47
9 Nucleus	13C

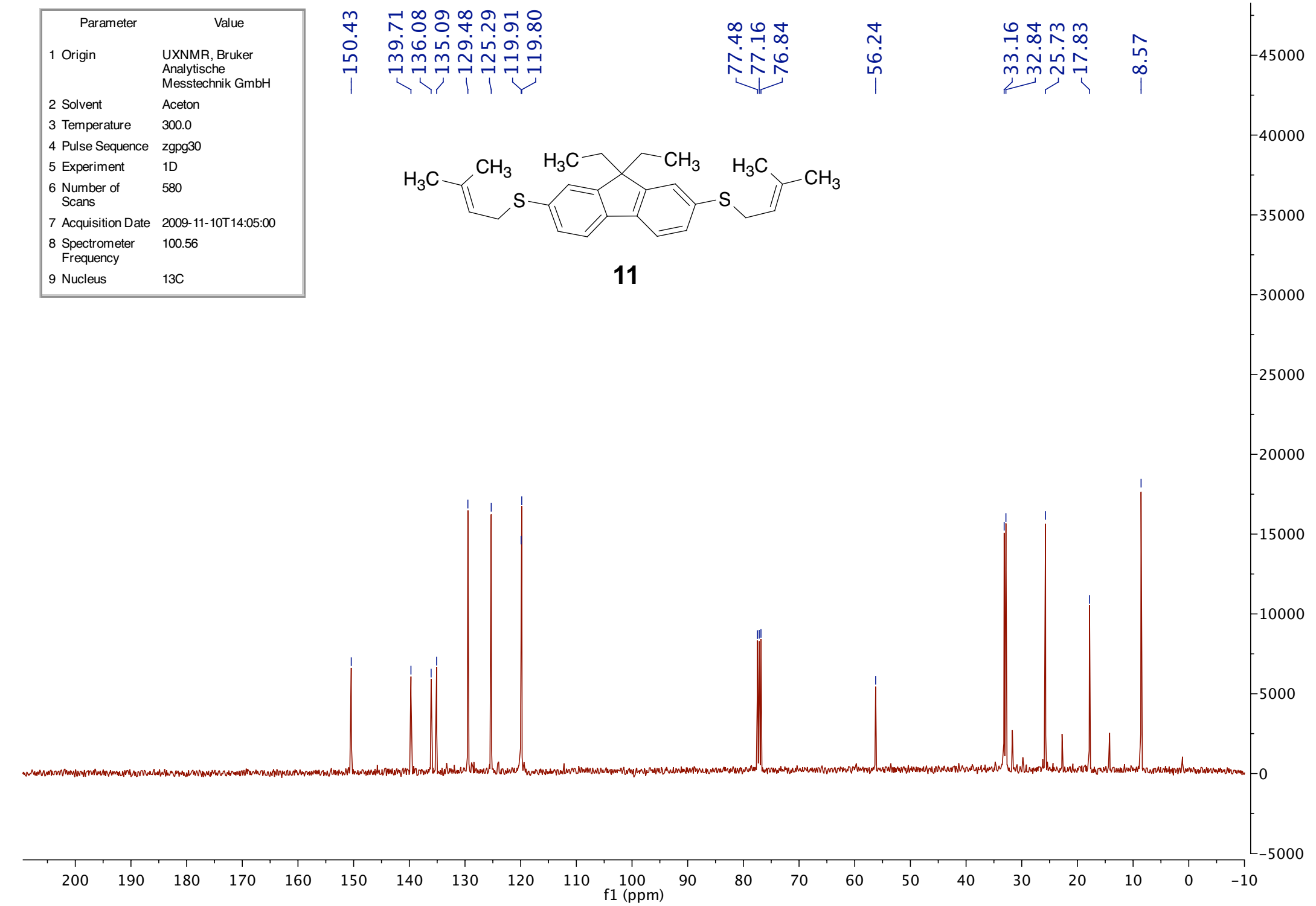


SI-3

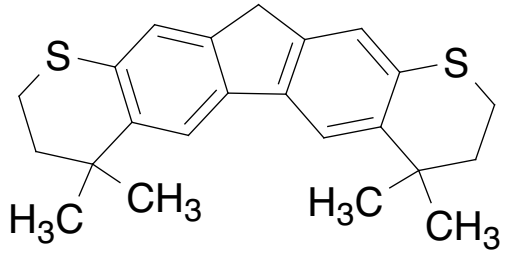
Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	D2O
3 Temperature	300.0
4 Pulse Sequence	zg
5 Experiment	1D
6 Number of Scans	32
7 Acquisition Date	2009-11-10T13:49:00
8 Spectrometer Frequency	399.92
9 Nucleus	1H



Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Solvent	Aceton
3 Temperature	300.0
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	580
7 Acquisition Date	2009-11-10T14:05:00
8 Spectrometer Frequency	100.56
9 Nucleus	13C

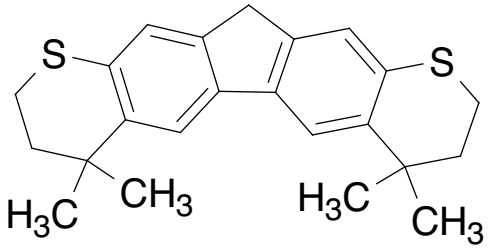


Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	Aceton
Temperature	300.0
Pulse Sequence	zg
Experiment	1D
Number of Scans	32
Acquisition Date	2010-05-05T 22:07:09
Spectrometer Frequency	300.13
Nucleus	1H



5

Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	25723
Acquisition Date	2010-05-05T2 2:11:00
Spectrometer Frequency	75.47
Nucleus	13C



5

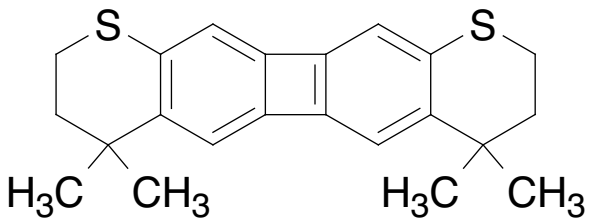
142.44
142.04
139.74
131.07
123.67
118.25
39.37
36.29
34.34
30.80
23.89

55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

270 250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30

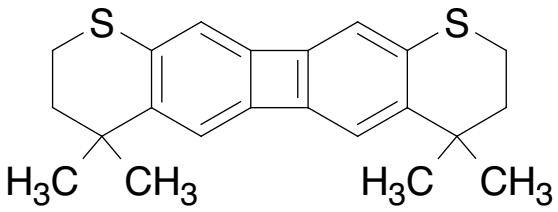
f1 (ppm)

Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	Aceton
Temperature	296.3
Pulse Sequence	zg
Experiment	1D
Number of Scans	19
Acquisition Date	2010-02-10T 07:30:02
Spectrometer Frequency	300.13
Nucleus	1H



4

Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	296.3
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	6896
Acquisition Date	2010-02-10T0 7:31:00
Spectrometer Frequency	75.47
Nucleus	13C



4

Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	Aceton
Temperature	300.0
Pulse Sequence	zg
Experiment	1D
Number of Scans	32
Acquisition Date	2007-06-27T 11:15:00
Spectrometer Frequency	300.13
Nucleus	1H