Electronic Supplementary Information

ESI

Multigram Synthesis of Bis[(trimethylsilyl)ethynyl]benzenes suitable for Post-Polymerization Modification

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1. Synthetic Part

1.1. General procedures and methods.

All reactions were performed in oven-dried glassware. Reagents were purchased from common commercial sources and used without further purification. Anhydrous solvents were prepared by filtration through drying columns. Column chromatography was performed on silica 60 (Merck, 40-63 µm) using distilled solvents as given.

NMR spectra were recorded at 400 MHz for ^{1}H and 100 MHz for ^{13}C on a Bruker Avance DRX-400 Spectrometer for all monomers and at 200 MHz for ^{1}H and 50 MHz for ^{13}C on a Bruker Avance 200 for intermediates and polymers. Data for ^{1}H NMR are reported as follows: chemical shift in parts per million from TMS (tetramethylsilane) with the residual solvent signal as an internal reference ($CDCl_3$ δ = 7.26 ppm, CD_2Cl_2 δ = 5.32 ppm) multiplicity (s = singlet, d = doublet, t = triplet and m = multiplet; br = broad), coupling constant in Hz and integration. ^{13}C NMR spectra are reported in ppm from TMS using the central peak of the solvent as reference ($CDCl_3$ δ = 77.0 ppm, CD_2Cl_2 δ = 54.0 ppm); multiplicity with respect to proton (deduced from APT experiments, s = quaternary C, d = CH, t = CH_2, q = CH_3).

FT-IR spectra were recorded on a Bruker Tensor 27. Measurements were carried out with an ATR MicroFocusing MVP-QL with a diamond crystal using OPUS version 4.0 software for analysis. Resolution was set to 4 cm^{-1} in a range from 4000 to 600 cm^{-1} recording 32 scans.

The absorption spectra were recorded on a Perkin Elmer Lambda 750 using Suprasil glass cuvettes. The measurements were performed of sample solutions in dry DCM (5 µM (concentration of small molecules / polymer repeating units)) at room temperature.

The fluorescence spectra were recorded on an Edinburgh FLS920 system using Suprasil glass cuvettes. The measurements were performed of sample solutions in dry DCM (5 µM (concentration of polymer repeating units)) at room temperature. Quantum yields of polymers were determined on the same system using a spherical setup (Ulbricht sphere). These

measurements were also performed in dry DCM (5 μM and additionally at 50 μM investigate concentration dependence).

Gel permeation chromatography was carried out in THF on a Waters/Viscotek system (Waters 515 HPLC pump, Waters 717plus autosampler, Waters 2410 RI detector, Waters temperature Controller, OmniSec Software) equipped with three columns (Styragel HR 0.5 THF, Styragel HR 3 THF, Styragel HR 4 THF). Polystyrene standards were used for calibration.

Microwave-assisted reactions were carried out in a BIOTAGE Initiator EXP EU 355301 microwave reactor. Pre-stirring was set to 10 seconds, fixed hold time and cooling-while-heating (cwh) was applied.

HR-MS data was obtained from matrix-assisted laser desorption/ionization (MALDI) measurements using a system provided by Thermo Scientific (MALDI LTQ Orbitrap and LTQ Orbitrap XL). α-Cyano-4-hydroxycinnamic acid (CHCA) was applied as matrix for all given HR-MS measurements.

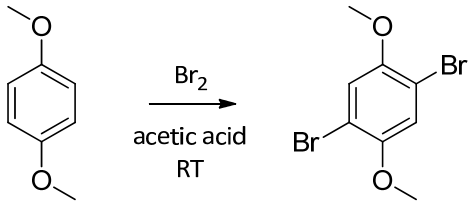
Elemental analyses were performed at the “Mikroanalytisches Laboratorium” (University of Vienna, Mag. J. Theiner).

Cyclic voltammetry (CV) data was recorded using a Metrohm Autolab B.V equipment (PGSTAT128N, ADC164, DAC164, External, DI048 potentiostat). The measurements were performed of sample + supporting electrolyte solutions in dry DCM (0.25 mM sample + 0.1 M tetrabutylammonium tetrafluoroborate (*n*-Bu_4NBF_4) as supporting electrolyte). These solutions were purged with nitrogen for 15 minutes prior to measurement. A three electrode configuration consisting of platinum working and counter electrodes and a silver chloride coated silver reference electrode was used. HOMO energy levels were calculated from the oxidation onsets.

1.2. Experimental procedures

The synthesis of dimethyldioxirane (DMDO)[1] was performed in analogy to published protocols.

*1.2.1. 1,4-Dibromo-2,5-dimethoxybenzene **2***



1
$C_8H_{10}O_2$
138.16

2
$C_8H_8Br_2O_2$
295.96

Synthesis according to published protocol [2]:

1 (27.63 g, 200 mmol, 1.0 eq) was dissolved in 57 ml acetic acid. Br_2 (63.92 g, 400 mmol, 2.0 eq) in 20 ml acetic acid was added dropwise to the stirred solution. The temperature was kept below 30°C using an ice bath during addition.

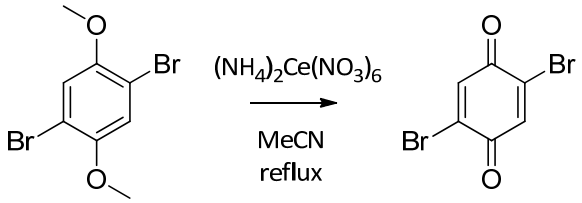
After stirring overnight at room temperature, the reaction was cooled and the fine, off-white precipitate **2** (52.83 g, 178.5 mmol, 89 %) was obtained by vacuum filtration and washing with water. **2** was applied for the reaction toward **3** without further purification.

Yield 52.83 g (89 %)

^{1}H NMR 200 MHz, $CDCl_3$ δ = 7.10 (s, 2H), 3.84 (s, 6H) ppm.

^{13}C NMR 50 MHz, $CDCl_3$ δ = 150.5 (s), 117.1 (d), 110.5 (s), 57.0 (q) ppm.

*1.2.2. 2,5-Dibromobenzo-1,4-quinone **3***



2
$C_8H_8Br_2O_2$
295.96

3
$C_6H_2Br_2O_2$
265.89

Synthesis according to published protocol [2]:

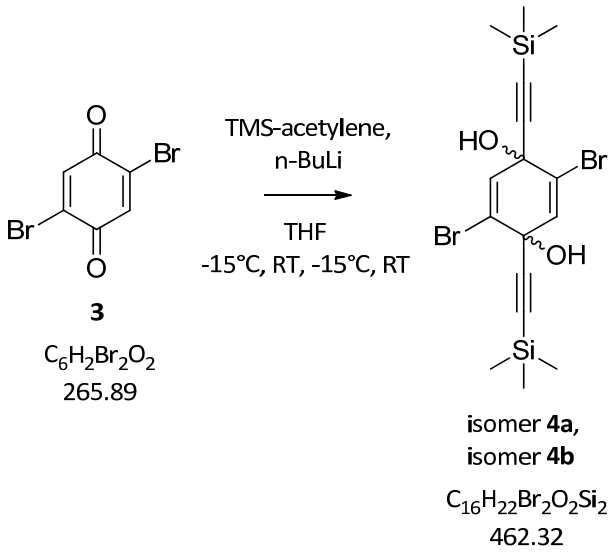
2 (48.83 g, 165 mmol, 1.0 eq) was dissolved in 550 ml MeCN (0.3 M) and heated to reflux temperature. Ceric ammonium nitrate (199.02 g, 363 mmol, 2.2 eq) in 726 ml water (0.5 M) was added dropwise to the solution.

After completion of the addition, the reaction was allowed to slowly cool to room temperature while stirring. The suspension was then cooled with an ice bath to further promote precipitation.

The yellow solid was collected by vacuum filtration and washed with MeCN twice. Drying in vacuo yielded 31.07 g (117 mmol, 71 %) of **3**.

Yield	31.07 g	(71 %)
^{1}H NMR	200 MHz, $CDCl_3$	δ = 7.48 (s, 2H) ppm.
^{13}C NMR	50 MHz, $CDCl_3$	δ = 177.0 (s), 137.8 (s), 137.0 (d) ppm.

1.2.3. 2,5-Dibromo-1,4-bis[2-(trimethylsilyl)ethynyl]cyclohexa-2,5-diene-1,4-diol ***4a*** *and* ***4b***



The procedure of VanVeller, et al. [3] was used with modifications:

(Trimethylsilyl)acetylene (11.30 g, 115.0 mmol, 2.3 eq) was dissolved in 500 ml dry THF under argon atmosphere. The solution was cooled to -15°C before adding *n*-BuLi (44 ml, 2.5 M in hexane, 110.0 mmol, 2.2 eq) in such a manner that the temperature was always kept below -5°C. After addition, the reaction mixture was allowed to warm to room temperature and stirred for another 30 min.

3 (13.29 g, 50.0 mmol, 1.0 eq) was added in one portion after again cooling to -15°C. The solution was allowed to warm to room temperature and was stirred for 3 h.

The reaction was quenched with 300 ml saturated aqueous NH_4Cl solution and stirred for another 15 min.

After extraction with PE once and DCM three times the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was dissolved in PE:EE 3:1 and filtrated through a thick pad of silica gel (PE:EE 3:1).

Following evaporation of the solvent yielded a slightly yellow solid which was further purified by trituration in 100 ml boiling *n*-hexane. The white solid was collected by

vacuum filtration and washed twice with *n*-hexane to finally yield 19.54 g (42.3 mmol, 85 %) of **4**.

Since this reaction yields stereoisomers a 3:1 mixture of **4a** and **4b** was obtained.

Yield	19.54 g (85 %)	
^{1}H NMR	200 MHz, $CDCl_3$	δ = 6.41 (s, 1.5H), 6.37 (s, 0.5H), 2.95 (s, 0.5H), 2.86 (s, 1.5H), 0.19 (s) and 0.18 (s, together 18H) ppm.
^{13}C NMR	50 MHz, $CDCl_3$	δ = 130.4 (d), 129.9 (d), 127.2 (s), 126.9 (s), 101.8 (s), 101.6 (s), 92.9 (s), 67.4 (s), 67.2 (s), -0.4 (q), -0.5 (q) ppm.

The two isomers were separated by column chromatography (PE:EE 4 % → 15 %) for individual characterization. Generally, separation is easily possible but not required for the following reactions.

Isomer **4a** (less polar):

^{1}H NMR	200 MHz, $CDCl_3$	δ = 6.40 (s, 2H), 2.90 (s, 2H), 0.18 (s, 18H) ppm.
^{13}C NMR	50 MHz, $CDCl_3$	δ = 130.4 (d), 127.2 (s), 101.8 (s), 92.9 (s), 67.4 (s), -0.5 (q) ppm.

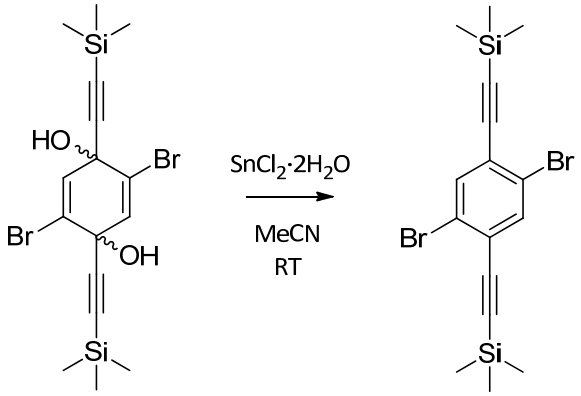
Anal. Calcd for $C_{16}H_{22}Br_2O_2Si_2$: C, 41.57; H, 4.80; found: C, 41.41; H, 4.88.

Isomer **4b** (more polar):

^{1}H NMR	200 MHz, $CDCl_3$	δ = 6.37 (s, 2H), 3.01 (s, 2H), 0.19 (s, 18H) ppm.
^{13}C NMR	50 MHz, $CDCl_3$	δ = 129.9 (d), 126.9 (s), 101.6 (s), 92.5 (s), 67.2 (s), -0.4 (q) ppm.

Anal. Calcd for $C_{16}H_{22}Br_2O_2Si_2$: C, 41.57; H, 4.80; found: C, 41.64; H, 5.00

*1.2.4. 1,4-Dibromo-2,5-bis[2-(trimethylsilyl)ethynyl]benzene **5***



isomer **4a**,
isomer **4b**
$C_{16}H_{22}Br_2O_2Si_2$
462.32

5
$C_{16}H_{20}Br_2Si_2$
428.31

Synthesis according to published protocol [3]:

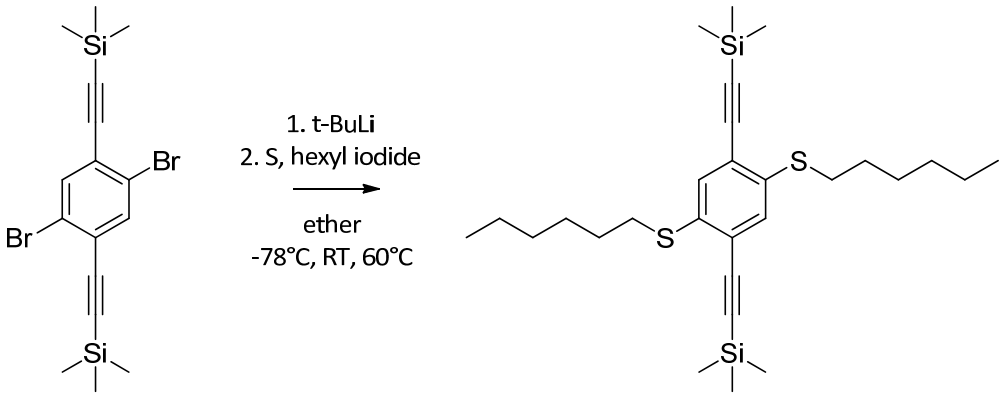
A mixture of **4a** and **4b** (13.87 g, 30.0 mmol, 1.0 eq) was added to 600 ml degassed MeCN (0.05 M) together with $SnCl_2 \cdot 2H_2O$ (27.08 g, 120 mmol, 4.0 eq).

The solution was then stirred at room temperature under argon atmosphere until TLC analysis (PE:EE 9:1) indicated completion of the reaction after 11h.

The reaction mixture was extracted with PE three times and the combined PE layers were washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent yielded 12.06 g (28.2 mmol, 94 %) white solid **5**.

Yield	12.06 g (94 %)	
^{1}H NMR	200 MHz, $CDCl_3$	δ = 7.67 (s, 2H), 0.27 (s, 18H) ppm.
^{13}C NMR	50 MHz, $CDCl_3$	δ = 136.4 (d), 126.4 (s), 123.7 (s), 103.0 (s), 101.3 (s), -0.31 (q) ppm.

1.2.5. 1,4-Bis(hexylthio)-2,5-bis[2-(trimethylsilyl)ethynyl]benzene ***6a***



5
$C_{16}H_{20}Br_2Si_2$
428.31

6a
$C_{28}H_{46}S_2Si_2$
502.97

5 (3.43 g, 8.0 mmol, 1.0 eq) was dissolved in degassed dry Et_2O (80 ml, 0.1 M) under argon atmosphere in a pressure resistant glass vial. The solution was cooled to -78°C and *t*-BuLi (18.8 ml, 1.7 M in pentane, 32.0 mmol, 4.0 eq) was slowly added. The resulting mixture was stirred for 45 min at -78°C before allowing the solution to warm up above 0°C.

Sulfur (539 mg, 16.8 mmol, 2.1 eq) was then added and the yellow suspension was stirred for 3 h at room temperature. Hexyl iodide (3.73 g, 17.6 mmol, 2.2 eq) was added and the suspension was stirred at 60°C overnight.

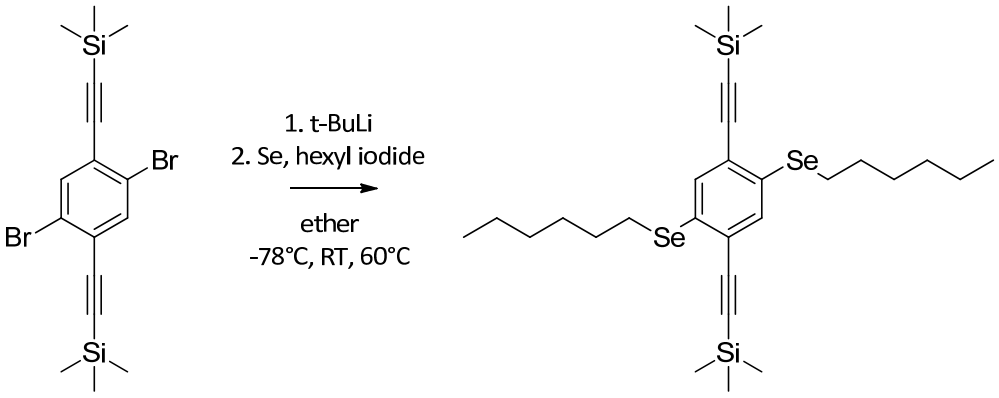
The solution was poured on water and extracted three times with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by column chromatography (PE) and by following crystallization from EtOH. 2.52 g (5.0 mmol, 63 %) of the slightly yellow solid **VIa** were obtained.

Single crystals were obtained by solvent evaporation of a solution in *n*-hexane.

Alternatively, purification can also be achieved by crystallization from EtOH and following trituration in hot EtOH instead of column chromatography and following crystallization, leading to slightly lower yields of 2.25 g (4.5 mmol, 56 %).

Yield	2.52 g	(63 %)
^{1}H NMR	400 MHz, CD_2Cl_2	δ = 7.27 (s, 2H), 2.93 (t, J = 7.4 Hz, 4H), 1.65 (quint, J = 7.4 Hz, 4H) 1.45 (quint, J = 7.2 Hz, 4H), 1.35 – 1.26 (m, 8H), 0.90 (t, J = 6.6 Hz, 6H), 0.27 (s, 18H) ppm.
^{13}C NMR	100 MHz, CD_2Cl_2	δ = 137.6 (s), 131.6 (d), 123.8 (s), 103.3 (s), 102.5 (s), 33.1 (t), 31.9 (t), 29.2 (t), 29.1 (t), 23.1 (t), 14.3 (q), 0.1 (q) ppm.
HR-MS	Anal Calcd for $C_{28}H_{46}S_2Si_2$: *m/z* 502.2580 $[M]^+$. Found: MS (MALDI, CHCA): *m/z* 502.2600 $[M]^+$.	

1.2.6. 1,4-Bis(hexylseleno)-2,5-bis[2-(trimethylsilyl)ethynyl]benzene ***6b***



5
$C_{16}H_{20}Br_2Si_2$
428.31

6b
$C_{28}H_{46}Se_2Si_2$
596.76

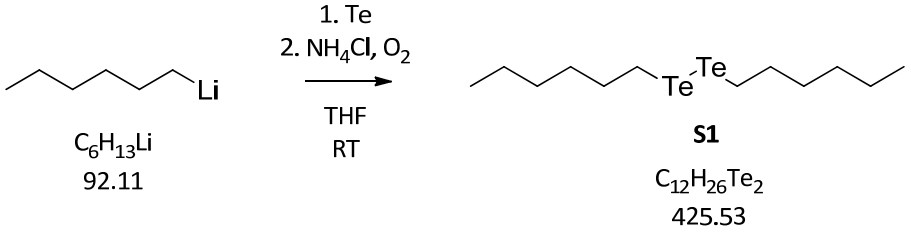
5 (1.713 g, 4.0 mmol, 1.0 eq) was dissolved in degassed dry ether (40 ml, 0.1 M) under argon atmosphere in a pressure resistant glass vial. The solution was cooled to -78°C and *t*-BuLi (9.4 ml, 1.7 M in pentane, 16.0 mmol, 4.0 eq) was slowly added. The resulting mixture was stirred for 45 min at -78°C before allowing the solution to warm up above 0°C.

Selenium (0.662 g, 8.4 mmol, 2.1 eq) was then added and the yellow suspension was stirred for 1 h at room temperature and 2 h at 60°C. Hexyl iodide (1.866 g, 8.8 mmol, 2.2 eq) was added and the suspension was stirred at 60°C overnight.

The solution was poured on water and extracted three times with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. Purification by column chromatography (PE) yielded 1.743 g (2.92 mmol, 73 %) of the yellow solid **VIb**. Single crystals were obtained by solvent evaporation of a solution in *n*-hexane.

Yield	1.743 g	(73 %)
^{1}H NMR	400 MHz, CD_2Cl_2	δ = 7.36 (s, 2H), 2.95 (t, J = 7.4 Hz, 4H), 1.72 (quint, J = 7.4 Hz, 4H), 1.44 (quint, J = 6.9 Hz, 4H), 1.33 – 1.29 (m, 8H), 0.89 (t, J = 6.6 Hz, 6H), 0.27 (s, 18H) ppm.
^{13}C NMR	100 MHz, CD_2Cl_2	δ = 133.7 (d), 133.0 (s), 125.7 (s), 103.3 (s), 102.8 (s), 31.8 (t), 30.2 (t), 30.1 (t), 26.9 (t), 23.1 (t), 14.4 (q), 0.1 (q) ppm.
HR-MS	Anal Calcd for $C_{28}H_{46}Se_2Si_2$: *m/z* 598.1469 $[M]^+$. Found: MS (MALDI, CHCA): *m/z* 598.1492 $[M]^+$.	

*1.2.7. Dihexylditelluride **S1***



$C_6H_{13}Li$
92.11

S1
$C_{12}H_{26}Te_2$
425.53

Synthesis according to published procedure [4]:

Tellurium (5.10 g, 40.0 mmol, 1.0 eq) was added to ~270 ml degassed dry THF (0.15M) under argon atmosphere. The suspension was cooled to 0°C prior to dropwise addition of *n*-HxLi (19.4 ml, 2.47 M in hexane, 48.0 mmol, 1.2 eq). The reaction mixture was then allowed to warm to room temperature and stirred for 3h.

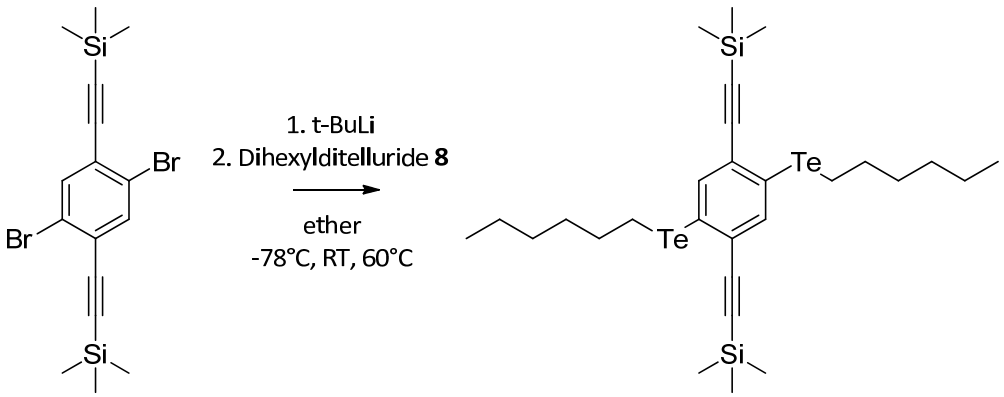
~70 ml saturated aqueous NH_4Cl solution were slowly added and the reaction flask was then opened to the atmosphere. After stirring for another 3h, the aqueous phase was separated from the organic phase and extracted with Et_2O once. The combined organic layers were dried over anhydrous Na_2SO_4 and filtrated through a pad of celite.

Evaporation of the solvent yielded 5.44 g (12.8 mmol, 64 %) of the red liquid which was used for the following reactions without further purification. Purity was controlled by GC-MS analysis.

Yield 5.44 g (64 %)

GC-MS single peak at 11.18 min, 100-280°C;
Anal Calcd for $C_{12}H_{26}Te_2$: *m/z:* 430.17 $[M]^+$. Found: MS (EI): *m/z* 430.02 $[M]^+$.

1.2.8. 1,4-Bis(hexyltelluro)-2,5-bis[2-(trimethylsilyl)ethynyl]benzene ***6c***



5
$C_{16}H_{20}Br_2Si_2$
428.31

6c
$C_{28}H_{46}Si_2Te_2$
694.04

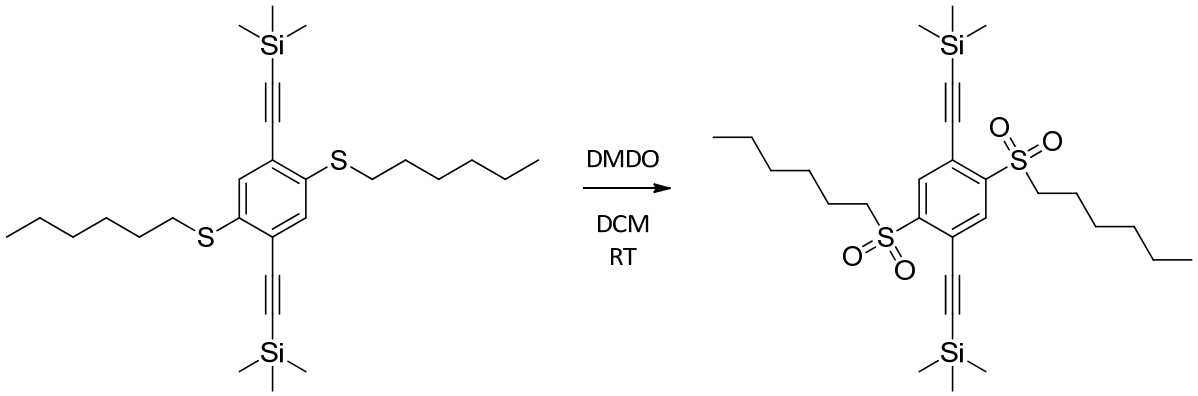
5 (1.713 g, 4.0 mmol, 1.0 eq) was dissolved in degassed dry ether (40 ml, 0.1 M) under argon atmosphere in a pressure resistant vial. The solution was cooled to -78°C and *t*-BuLi (9.4 ml, 1.7 M in pentane, 16.0 mmol, 4.0 eq) was slowly added. The resulting mixture was stirred for 45 min at -78°C before allowing the solution to warm up above 0°C.

Dihexylditelluride (3.574 g, 8.4 mmol, 2.1 eq) was then added and the yellow suspension became an orange solution.

After stirring for 3 h at room temperature, the solution was poured on water and extracted three times with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. Purification by column chromatography (PE) yielded 1.479 g (2.13 mmol, 53 %) of the yellow solid **VIc**.

Yield	1.479 g	(53 %)
^{1}H NMR	400 MHz, CD_2Cl_2	δ = 7.43 (s, 2H), 2.94 (t, J = 7.6 Hz, 4H), 1.83 (quint, J = 7.5 Hz, 4H), 1.46 – 1.39 (m, 4H), 1.34 – 1.28 (m, 8H), 0.89 (t, J = 6.8 Hz, 6H), 0.28 (s, 18H) ppm.
^{13}C NMR	100 MHz, CD_2Cl_2	δ = 137.2 (d), 129.3 (s), 118.0 (s), 105.3 (s), 102.1 (s), 32.4 (t), 31.72 (t), 31.70 (t), 23.1 (t), 14.4 (q), 8.3 (t), 0.1 (q) ppm.
HR-MS	Anal Calcd for $C_{28}H_{46}Te_2Si_2$: *m/z* 698.1263 $[M]^+$. Found: MS (MALDI, CHCA): *m/z* 698.1289 $[M]^+$.	

*1.2.9. 1,4-Bis(hexylsulfonyl)-2,5-bis[2-(trimethylsilyl)ethynyl]benzene **6d***



6a
$C_{28}H_{46}S_2Si_2$
502.97

6d
$C_{28}H_{46}O_4S_2Si_2$
566.96

Oxidation according to Lumpi [5]:

6a (50.3 mg, 0.10 mmol, 1.0 eq) was dissolved in DCM (8.3 ml, 0.012 M). DMDO (12.0 ml, 0.035 M in acetone, 0.42 mmol, 4.2 eq) was added dropwise and the

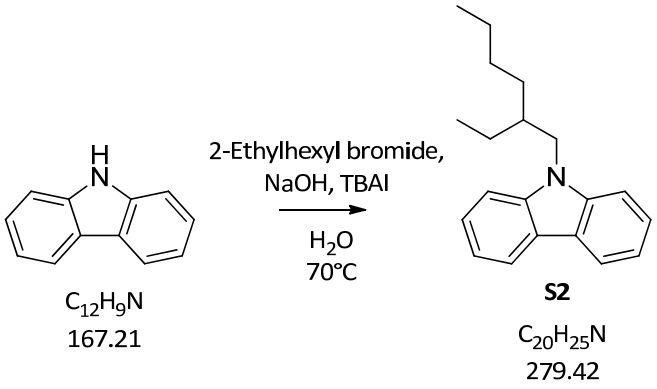
solution stirred for 20 min at room temperature. Evaporation of the solvent yielded 55.6 mg (0.098 mmol, 98%) of **6d** as a white solid.

Single crystals were obtained by solvent evaporation of a solution in EtOH.

Yield	55.6 mg (98 %)	
^{1}H NMR	400 MHz, CD_2Cl_2	δ = 8.27 (s, 2H), 3.47 (t, J = 8.1 Hz, 4H), 1.65 (quint, J = 7.7 Hz, 4H), 1.38 (quint, J = 7.2 Hz, 4H), 1.30 – 1.24 (m, 8H), 0.87 (t, J = 6.7 Hz, 6H), 0.30 (s, 18H) ppm.
^{13}C NMR	100 MHz, CD_2Cl_2	δ = 144.7 (s), 136.2 (d), 122.6 (s), 109.9 (s), 99.7 (s), 54.0 (t, DEPT), 31.7 (t), 28.5 (t), 22.84 (t), 22.81 (t), 14.2 (q), -0.5 (q) ppm.
HR-MS	Anal Calcd for $C_{28}H_{46}O_4S_2Si_2$: *m/z* 567.2456 $[M+H]^+$. Found: MS (MALDI, CHCA): *m/z* 567.2467 $[M+H]^+$.	

*1.2.10. Synthetic route towards 3,6-Diazido-9-(2-ethylhexyl)-9H-carbazole **7***

*1.2.10.1. 9-(2-Ethylhexyl)-9H-carbazole **S2***



Synthesis according to published protocol [6]:

Carbazole (10.87 g, 65.0 mmol, 1.0 eq) and tetra-*n*-butylammonium iodide (TBAI, 2.40 g, 6.5 mmol, 0.1 eq) were dissolved in 130 ml aq. NaOH (50 %). 2-Ethylhexyl bromide (37.66 g, 195.0 mmol, 3.0 eq) was added and the solution was heated to 70°C for 4 h.

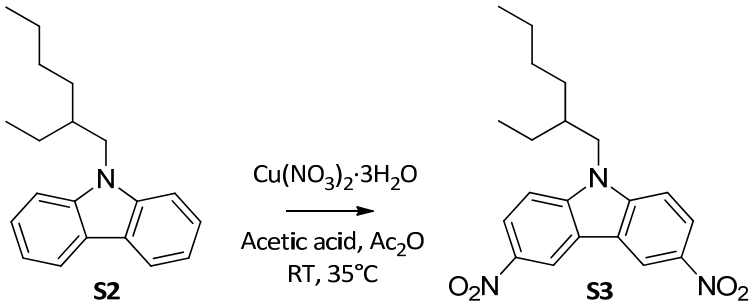
After extraction with $CHCl_3$, the combined organic layers were dried over anhydrous Na_2SO_4. Evaporation of the solvent yielded a red oil, which was purified by column

chromatography (PE, 180 g SG). 17.01 g (60.9 mmol, 94%) of **S2** were obtained as a slightly yellow, highly viscous liquid which crystallized at 5°C overnight.

Yield 17.01 g (94 %)

Physical data in accordance to literature [7, 8]

*1.2.10.2. 9-(2-Ethylhexyl)-3,6-dinitro-9H-carbazole **S3***



Synthesis similar to published protocol [9]:

$Cu(NO_3)_2 \cdot 3H_2O$ (31.41 g, 130.0 mmol, 2.6 eq) was added to 120 ml of a mixture of glacial acetic acid (45 ml) and acetic anhydride (75 ml) at room temperature. The resulting blue mixture was stirred for 1 h.

S2 (13.97 g, 50.0 mmol, 1.0 eq) was then added in portions while keeping the temperature below 35°C with a water bath. The reaction stirred for another 2 h without further cooling until TLC analysis indicated complete conversion.

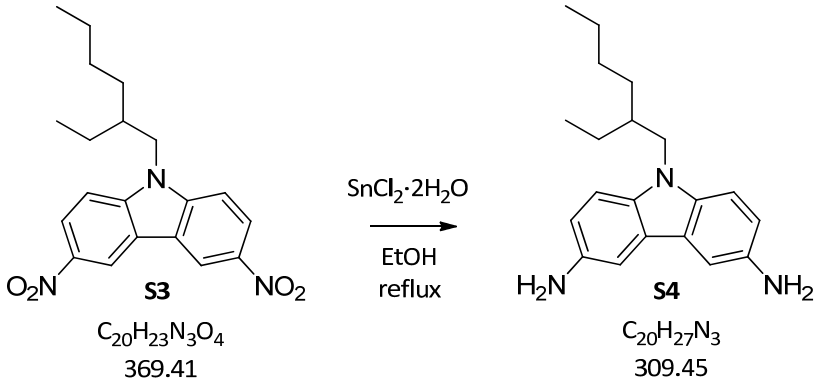
The reaction was then poured on water and the formed yellow precipitate was collected by vacuum filtration, washed three times with water and finally triturated in 500 ml boiling EtOH. The light yellow solid was again collected by vacuum filtration, washed once with EtOH and dried in vacuo overnight to afford **S3** (16.87 g, 45.67 mmol, 91 %) as a dry yellow powder.

Yield 16.87 g (91 %)

^{1}H NMR 200 MHz, $CDCl_3$ δ = 9.09 (d, J = 2.2 Hz, 2H), 8.48 (dd, J^1 = 9.1 Hz, J^2 = 2.2 Hz, 2H), 7.51 (d, J = 9.1 Hz, 2H), 4.29 (d, J = 7.5 Hz, 2H), 2.12 – 1.98 (m, 1H), 1.43 – 1.20 (m, 8H), 0.98 – 0.82 (m, 6H) ppm.

^{13}C NMR 50 MHz, $CDCl_3$ δ = 145.1 (s), 141.8 (s), 122.9 (d), 122.4 (s), 117.6 (d), 109.8 (d), 48.4 (t), 39.5 (d), 30.9 (t), 28.6 (t), 24.3 (t), 22.9 (t), 13.9 (q), 10.8 (q) ppm.

*1.2.10.3. 9-(2-Ethylhexyl)-9H-carbazole-3,6-diamine **S4***



Synthesis according to published protocol [10]:

S3 (12.19 g, 33.0 mmol, 1.0 eq) was dissolved in 165 ml EtOH (0.2 M). $SnCl_2 \cdot 2H_2O$ (52.13 g, 231.0 mmol, 7.0 eq) was added and the reaction was heated to reflux overnight.

The solution was then alkalinized with aq. NaOH (50 %) and extracted three times with DCM. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo.

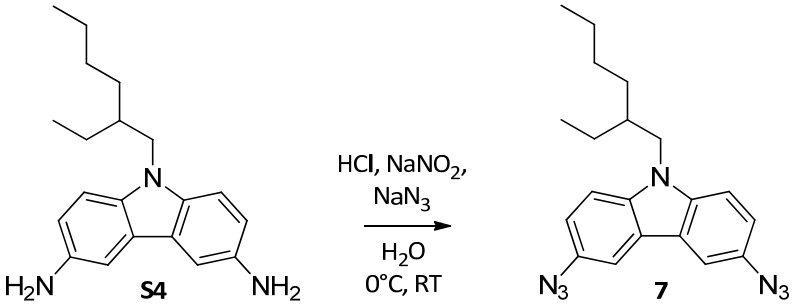
The residue was purified by column chromatography (PE:EE 20%) to yield 7.78 g (25.14 mmol, 76 %) **S4**.

Yield 7.78 g (76 %)

^{1}H NMR 200 MHz, $CDCl_3$ δ = 7.31 (d, J = 2.2 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.87 (dd, J^1 = 8.6 Hz, J^2 = 2.2 Hz, 2H), 4.03 (d, J = 7.4 Hz, 2H), 3.55 (bs, 4H), 2.07 – 1.95 (m, 1H), 1.40 – 1.21 (m, 8H), 0.93 – 0.83 (m, 6H) ppm.

^{13}C NMR	50 MHz, $CDCl_3$	δ = 138.1 (s), 136.1 (s), 122.8 (s), 115.5 (d), 109.3 (d), 106.1 (d), 47.4 (t), 39.4 (d), 30.9 (t), 28.8 (t), 24.3 (t), 23.0 (t), 14.0 (q), 10.9 (q) ppm.

*1.2.10.4. 3,6-Diazido-9-(2-ethylhexyl)-9H-carbazole **7***



Synthesis according to published protocol [11]:

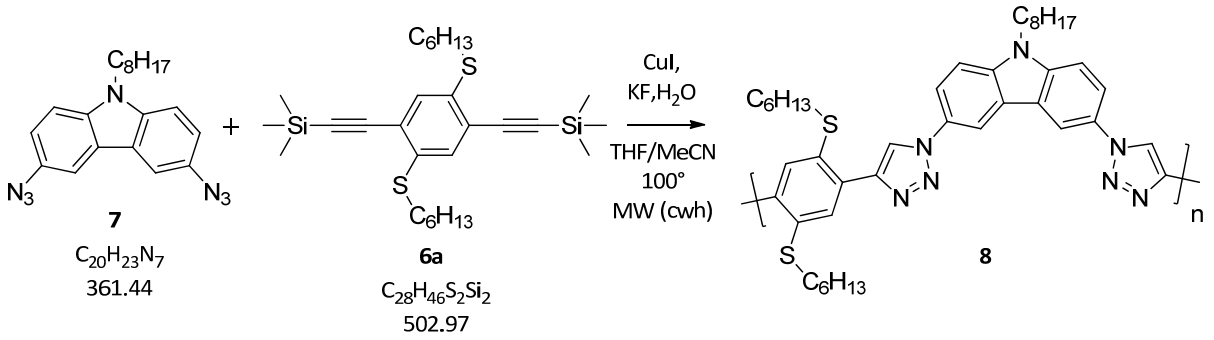
23 (2.91 g, 9.4 mmol, 1.0 eq) was dissolved in 175 ml aq. HCl (6 %). After cooling to 5°C (ice-water bath) $NaNO_2$ (2.85 g, 41.3 mmol, 4.4 eq) in 14 ml H_2O (~3 M) was added dropwise while keeping the temperature constant. The reaction was stirred for 25 min at 5°C.

NaN_3 (1.83 g, 28.2 mmol, 3.0 eq) was then added dropwise as a solution in 28 ml H_2O (1 M). The reaction was allowed to warm to room temperature and stirred for another 2 h.

Vacuum filtration afforded a solid which was purified by silica filtration (PE:Et_2O 20%). Evaporation of the solvent finally yielded **7** (2.18 g, 6.03 mmol, 64 %) as an orange solid.

Yield	2.18 g	(64 %)
^{1}H NMR	200 MHz, $CDCl_3$	δ = 7.69 (d, J = 2.2 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 7.14 (dd, J^1 = 8.7 Hz, J^2 = 2.2 Hz, 2H), 4.12 (d, J = 7.5 Hz, 2H), 2.07 – 1.92 (m, 1H), 1.37 – 1.20 (m, 8H), 0.94 – 0.81 (m, 6H) ppm.
^{13}C NMR	50 MHz, $CDCl_3$	δ = 138.8 (s), 131.1 (s), 122.7 (s), 117.7 (d), 110.2 (d), 110.1 (d), 47.5 (t), 39.3 (d), 30.9 (t), 28.7 (t), 24.3 (t), 22.9 (t), 13.9 (q), 10.8 (q) ppm.

*1.2.11. 3,6-Diazido-9-(2-ethylhexyl)-9H-carbazole, polymer with 1,4-bis(hexylthio)-2,5-diethynylbenzene **8***



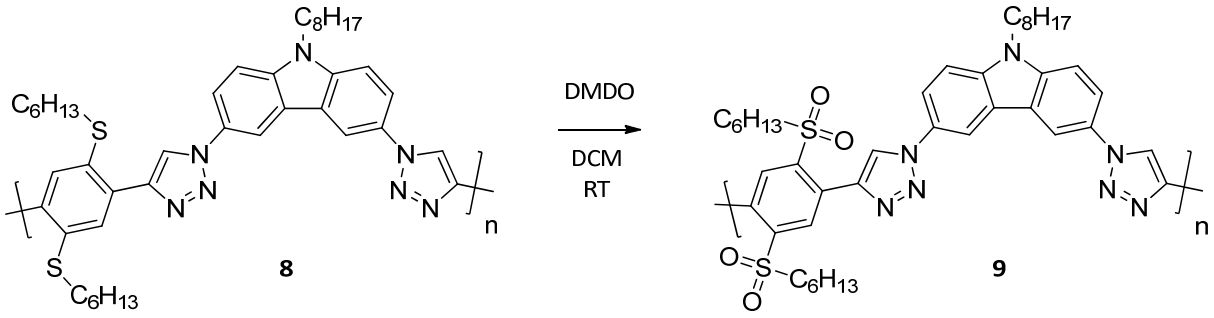
6a (377.23 mg, 0.750 mmol, 1.0 eq) and **7** (271.08 mg, 0.750 mmol, 1.0 eq) were weighed in into separate vials on a high precision scale (d = 0.01 mg). CuI (14.3 mg, 0.075 mmol, 10 mol%), KF (130.7 mg, 2.25 mmol, 3.0 eq) and H_2O (108.1 mg, 6.00 mmol, 8.0 eq) were added to **6a** and the vial was sealed and flushed with argon. **7** was dissolved in 5 ml degassed THF/MeCN (4:1, 0.15 M) and added completely to the other reagents via a syringe. The reaction mixture was then heated to 100°C (cooling while heating mode) in the reaction microwave for 6 h.

The solution was added dropwise to degassed 50 ml methanol using a syringe. The reaction vial was flushed with some degassed THF which was then also added to the degassed methanol.

The precipitate was collected by vacuum filtration, dried in a constant flow of nitrogen, washed three times with water and twice with MeOH and again dried in a flow of nitrogen to yield 443.9 mg (82 %) of the yellow-orange solid **8**.

Yield	443.9 mg (82 %)	
GPC	M_n = 3.6 kDa, M_w = 7.2 kDa, PDI = 2.0	
^{1}H NMR	200 MHz, $CDCl_3$	δ = 8.93 – 8.77 (br), 8.63 – 8.29 (br), 8.21 – 8.13 (br), 8.05 – 7.84 (br), 7.68 – 7.40 (br), 4.38 – 4.09 (br), 3.20 – 2.92 (br), 2.25 – 1.93 (br), 1.84 – 1.56 (br), 1.56 – 1.06 (br), 1.06 – 0.64 (br) ppm.

*1.2.12. 3,6-Diazido-9-(2-ethylhexyl)-9H-carbazole, polymer with 1,4-bis(hexylsulfonyl)-2,5-diethynylbenzene **9***



Oxidation according to Lumpi [5]:

8 (108.0 mg, 1 eq) was dissolved in 18.8 ml DCM (0.008 M). 18.0 ml DMDO (0.035 M in acetone, 0.63 mmol, 4.2 eq) was added dropwise and the solution stirred for 20 min at room temperature. Simple evaporation of the solvents yielded 117.3 mg (100 %) of **9** as a yellow-orange solid.

Yield	117.3 mg (100 %)	
GPC	M_n = 3.5 kDa, M_w = 7.5 kDa, PDI = 2.1	
^{1}H NMR	200 MHz, $CDCl_3$	δ = 8.83 – 8.39 (br), 8.23 – 8.12 (br), 8.04 – 7.78 (br), 7.69 – 7.33 (br), 4.40 – 4.04 (br), 3.46 – 3.18 (br), 2.21 – 1.88 (br), 1.88 – 1.56 (br), 1.56 – 1.03 (br), 1.03 – 0.35 (br) ppm.

1.3. Spectral Data

1.3.1 ^{1}H-, ^{13}C(APT)- NMR spectra

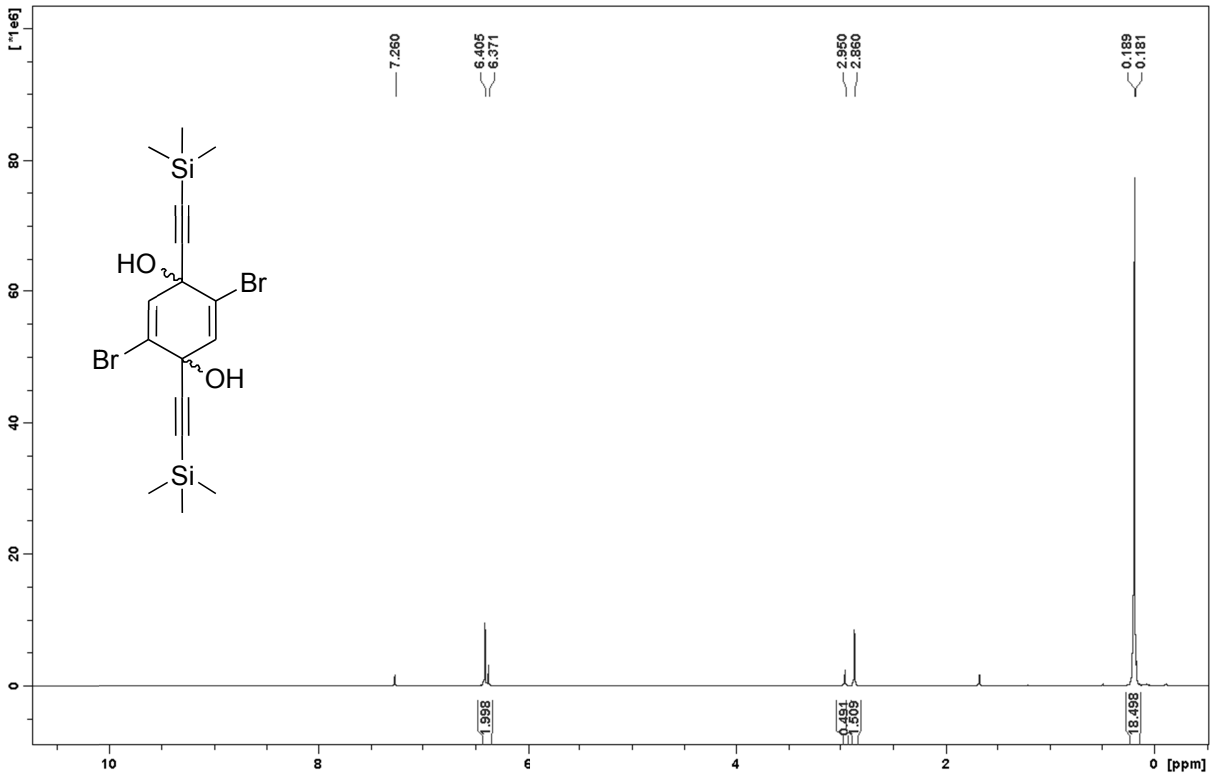


Figure S1: ^{1}H NMR (200 MHz, $CDCl_3$) of compounds 4a and 4b (mixture of isomers)

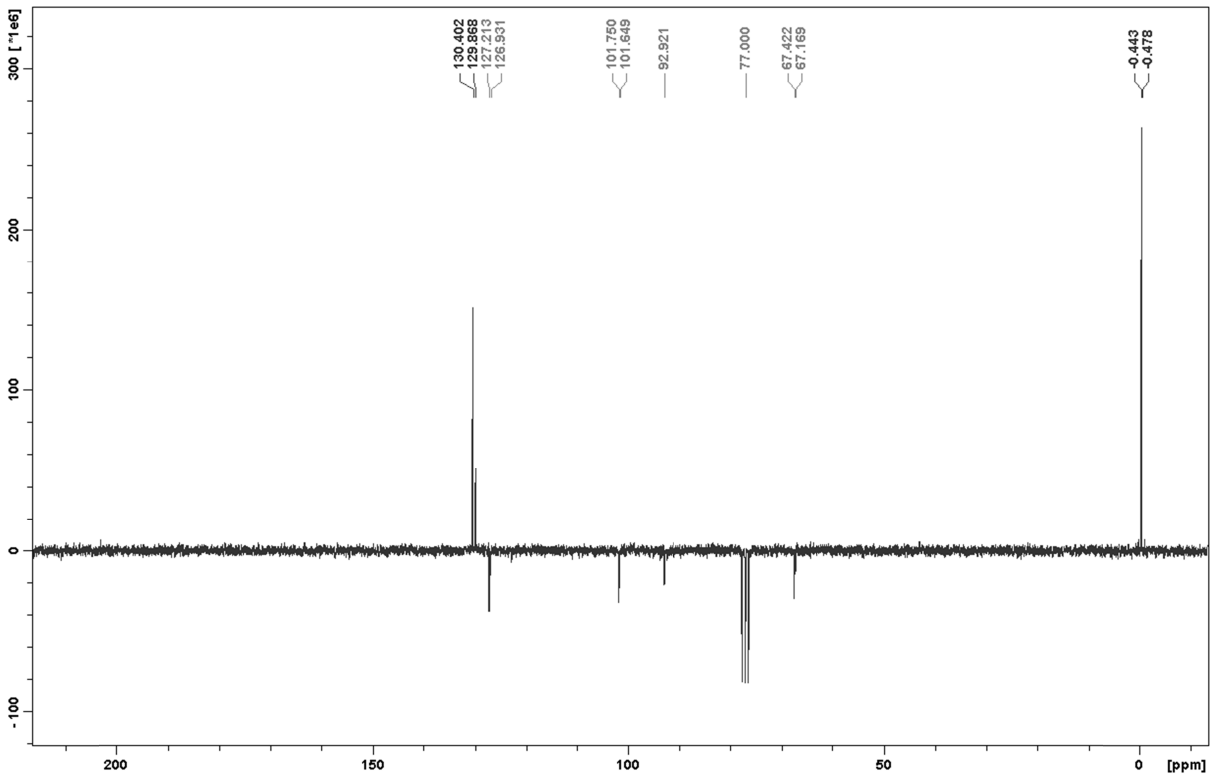


Figure S2: ^{13}C NMR (50 MHz, $CDCl_3$) of compounds 4a and 4b (mixture of isomers)

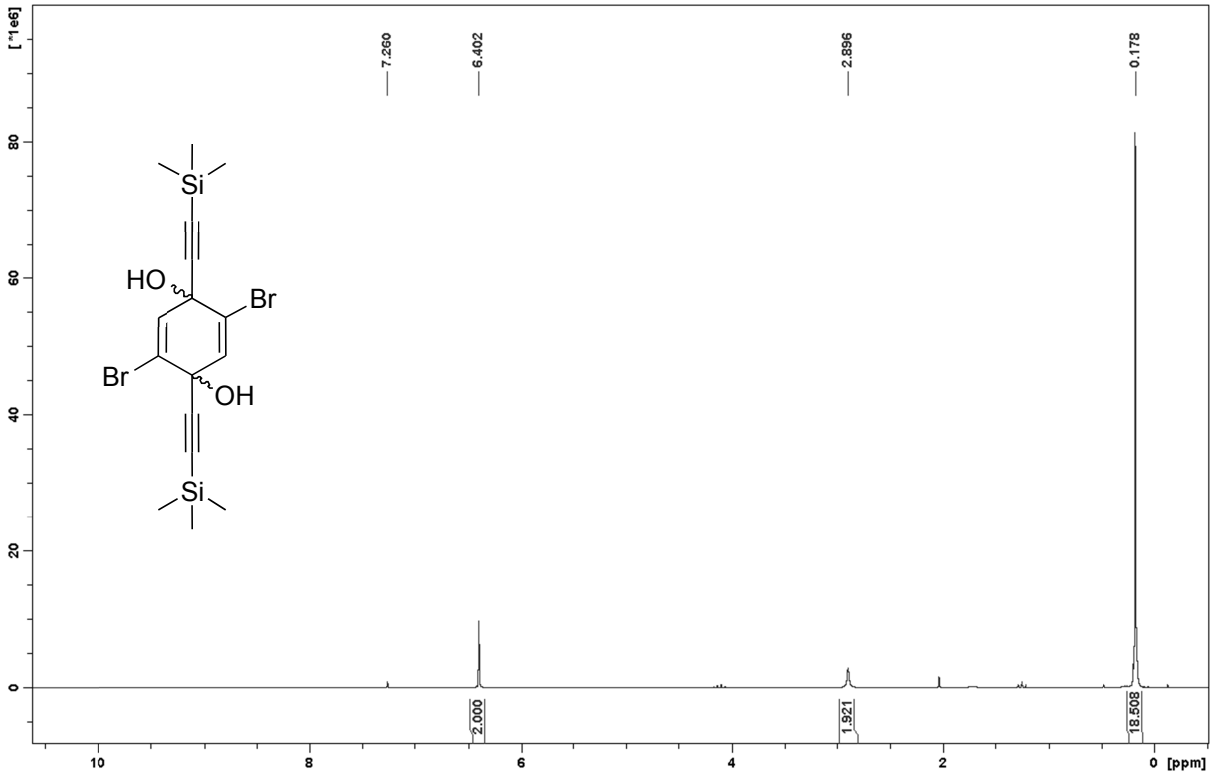


Figure S3: ^{1}H NMR (200 MHz, $CDCl_3$) of compound 4a

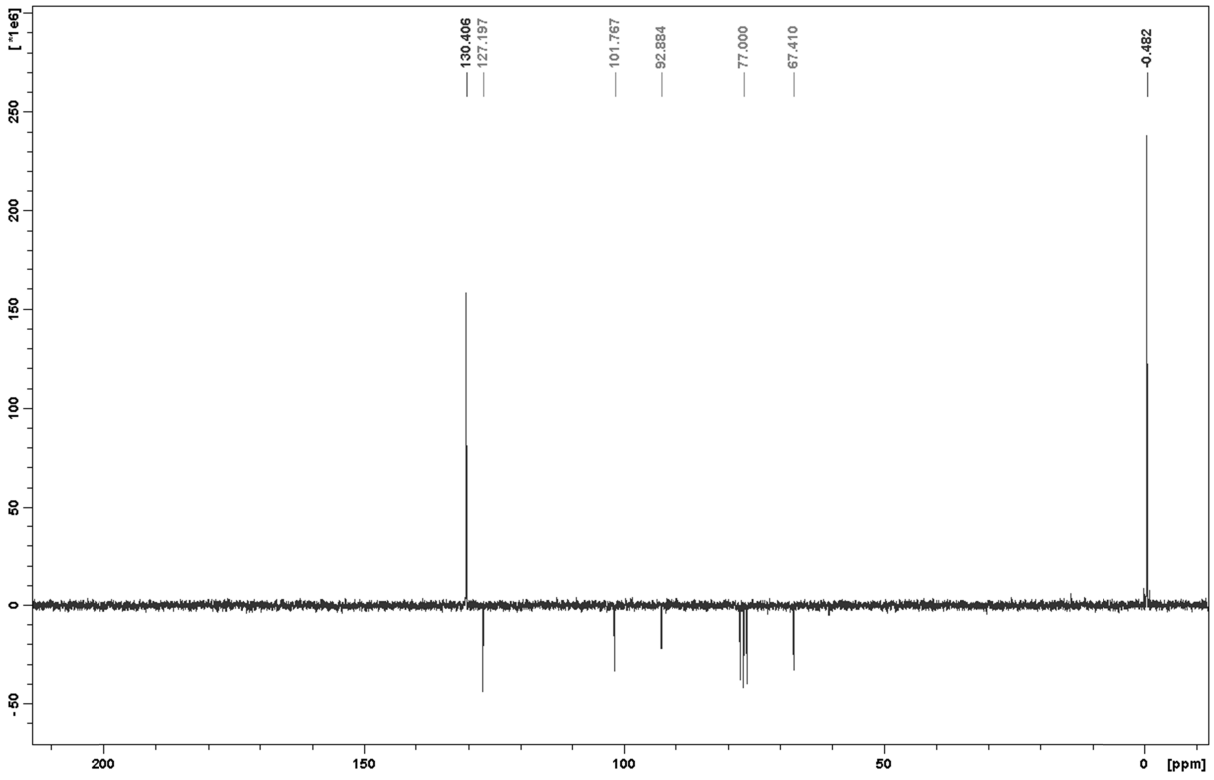


Figure S4: ^{13}C NMR (50 MHz, $CDCl_3$) of compound 4a

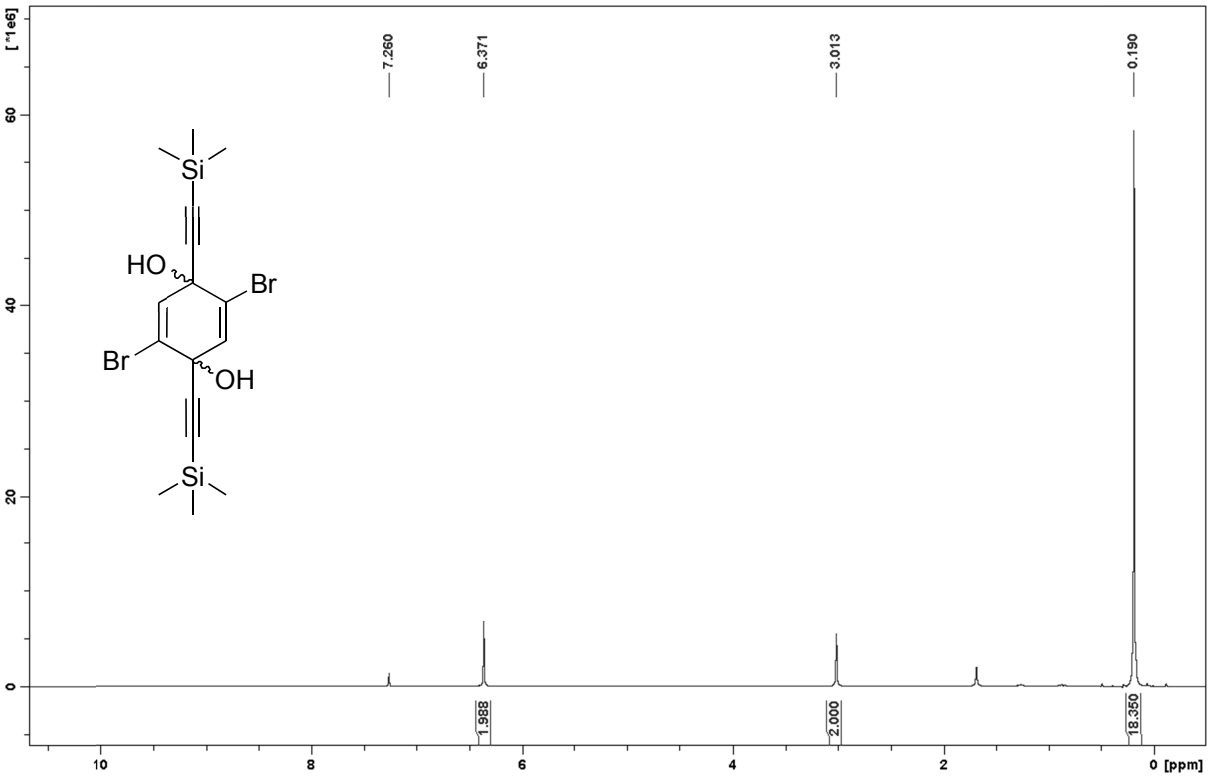


Figure S5: ^{1}H NMR (200 MHz, $CDCl_3$) of compound 4b

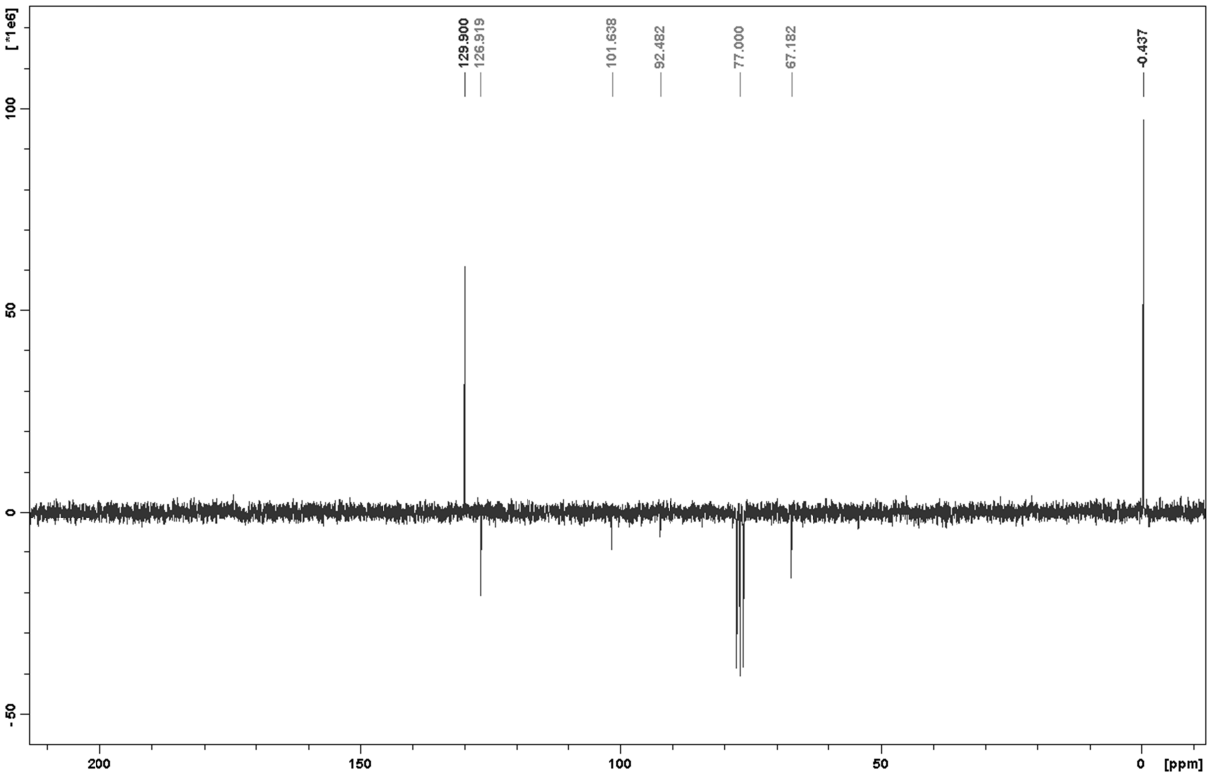


Figure S6: ^{13}C NMR (50 MHz, $CDCl_3$) of compound 4b

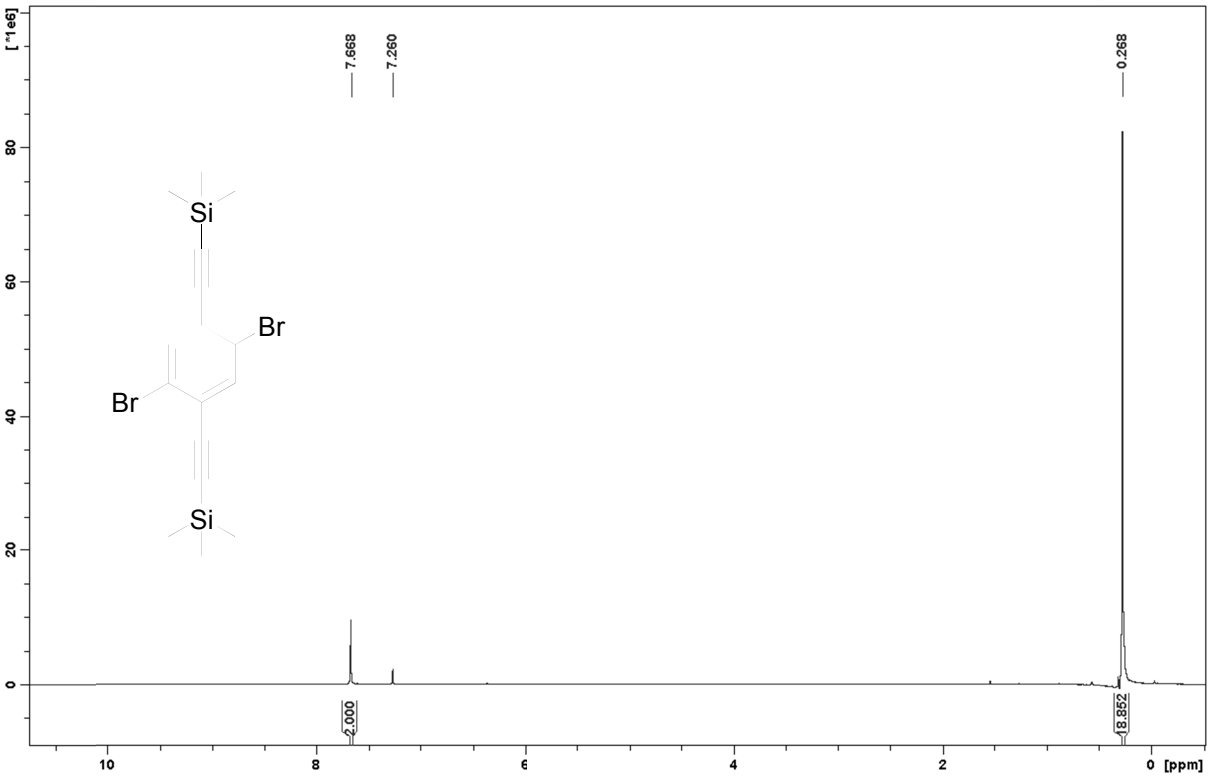


Figure S7: ^{1}H NMR (200 MHz, $CDCl_3$) of compound 5

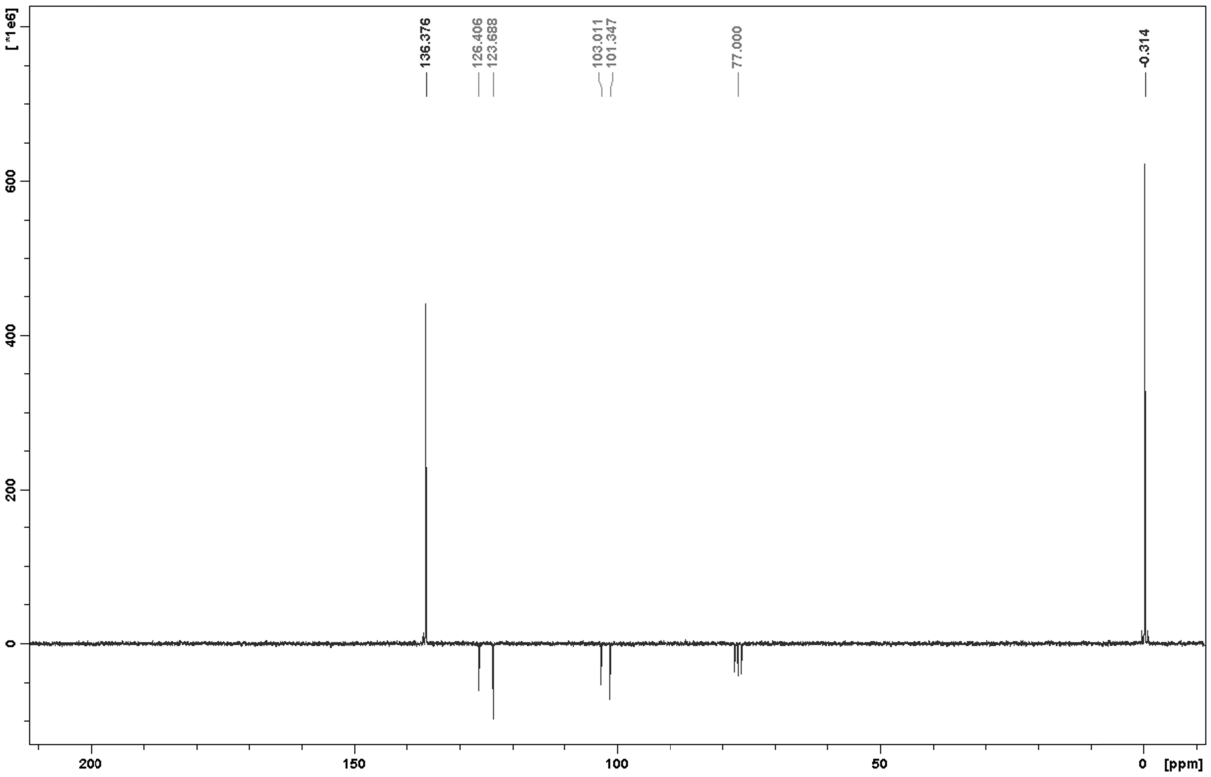


Figure S8: ^{13}C NMR (50 MHz, $CDCl_3$) of compound 5

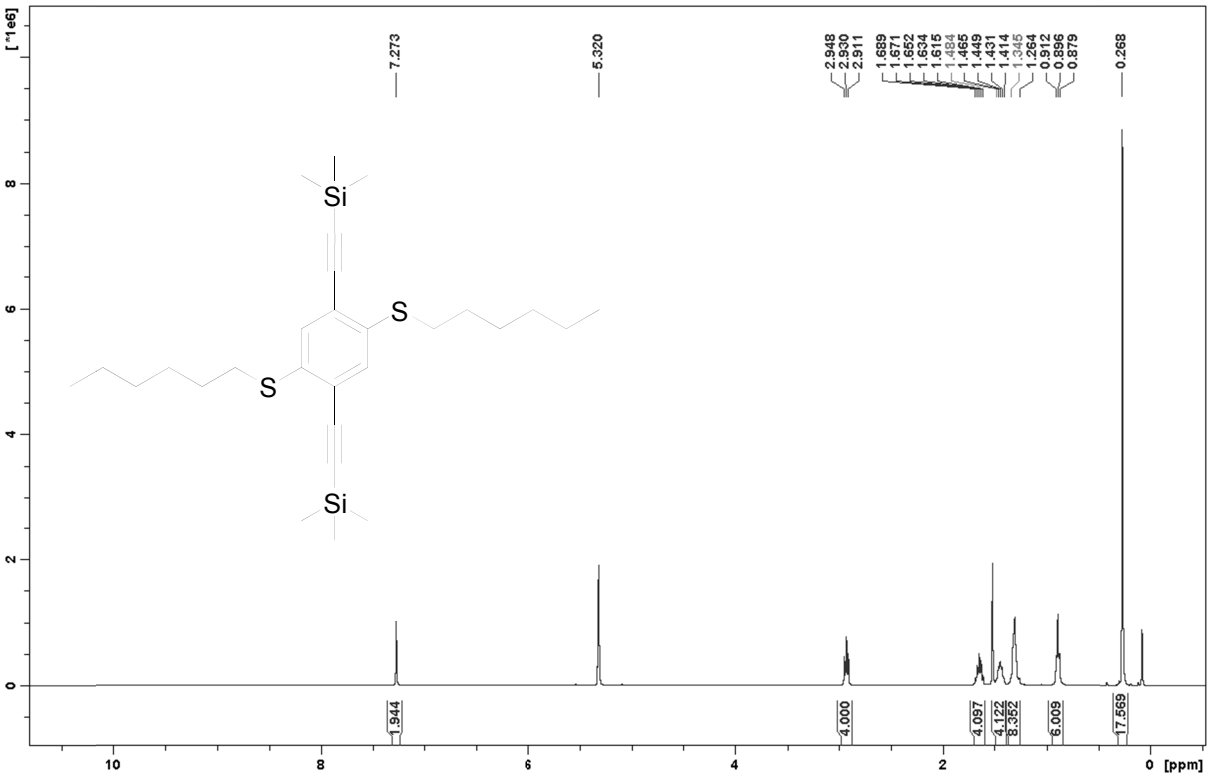


Figure S9: ^{1}H NMR (400 MHz, CD_2Cl_2) of compound 6a

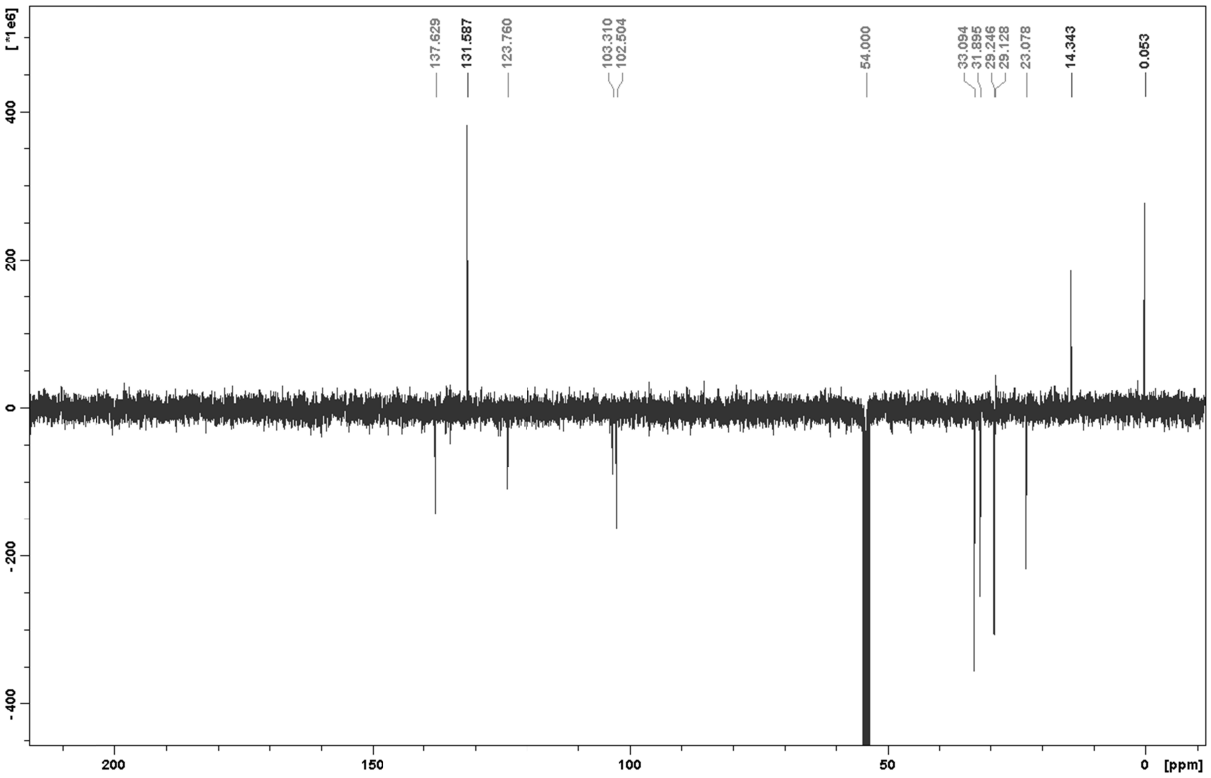


Figure S10: ^{13}C NMR (100 MHz, CD_2Cl_2) of compound 6a

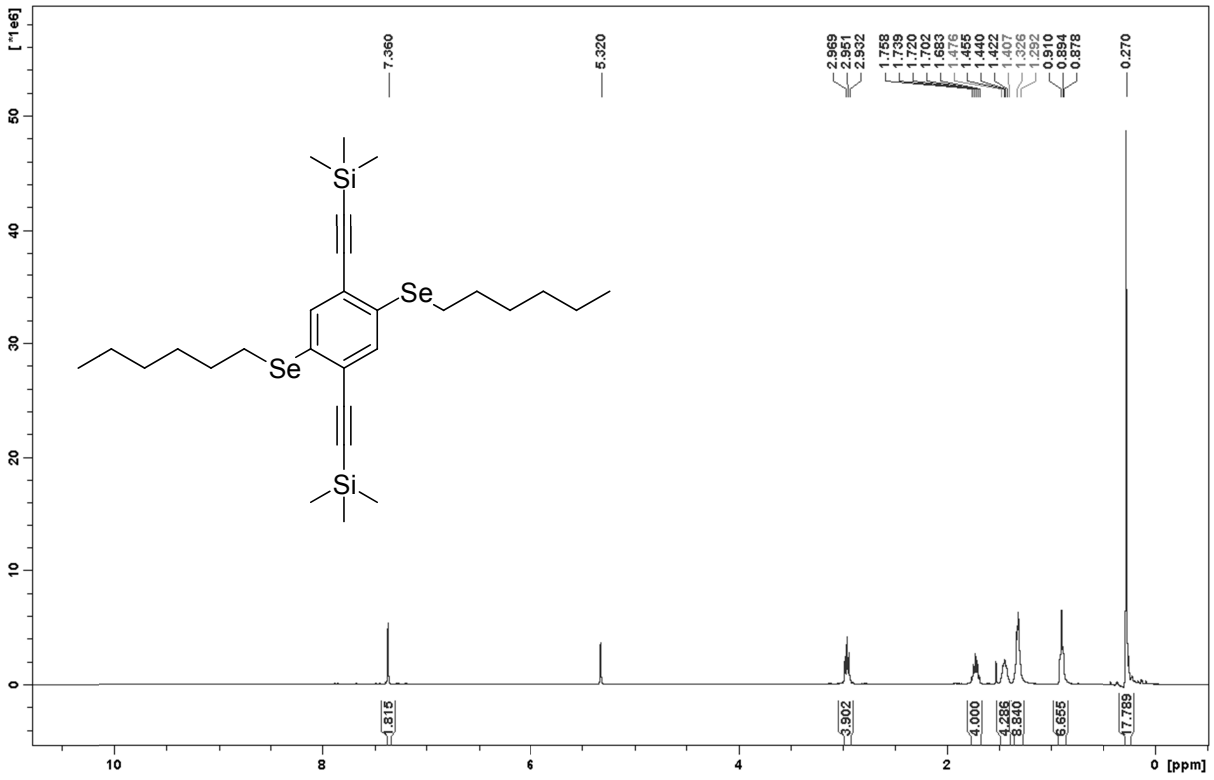


Figure S11: ^{1}H NMR (400 MHz, CD_2Cl_2) of compound 6b

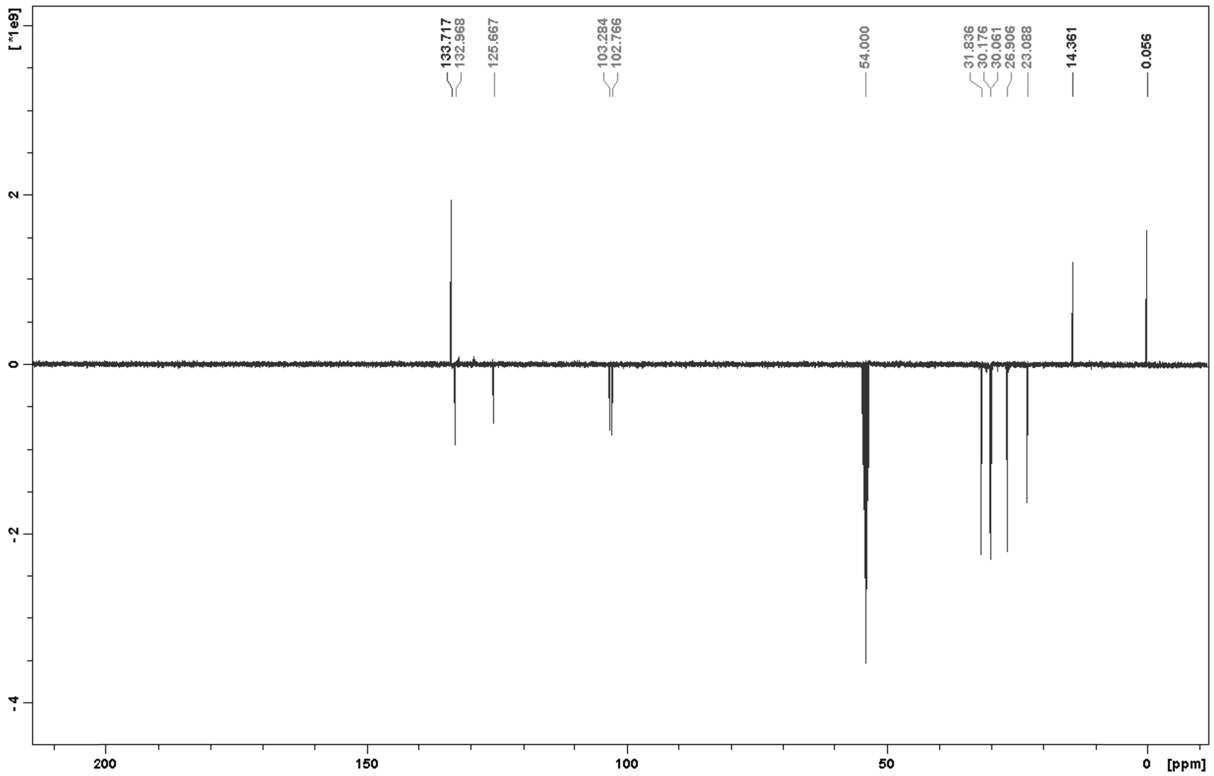


Figure S12: ^{13}C NMR (100 MHz, CD_2Cl_2) of compound 6b

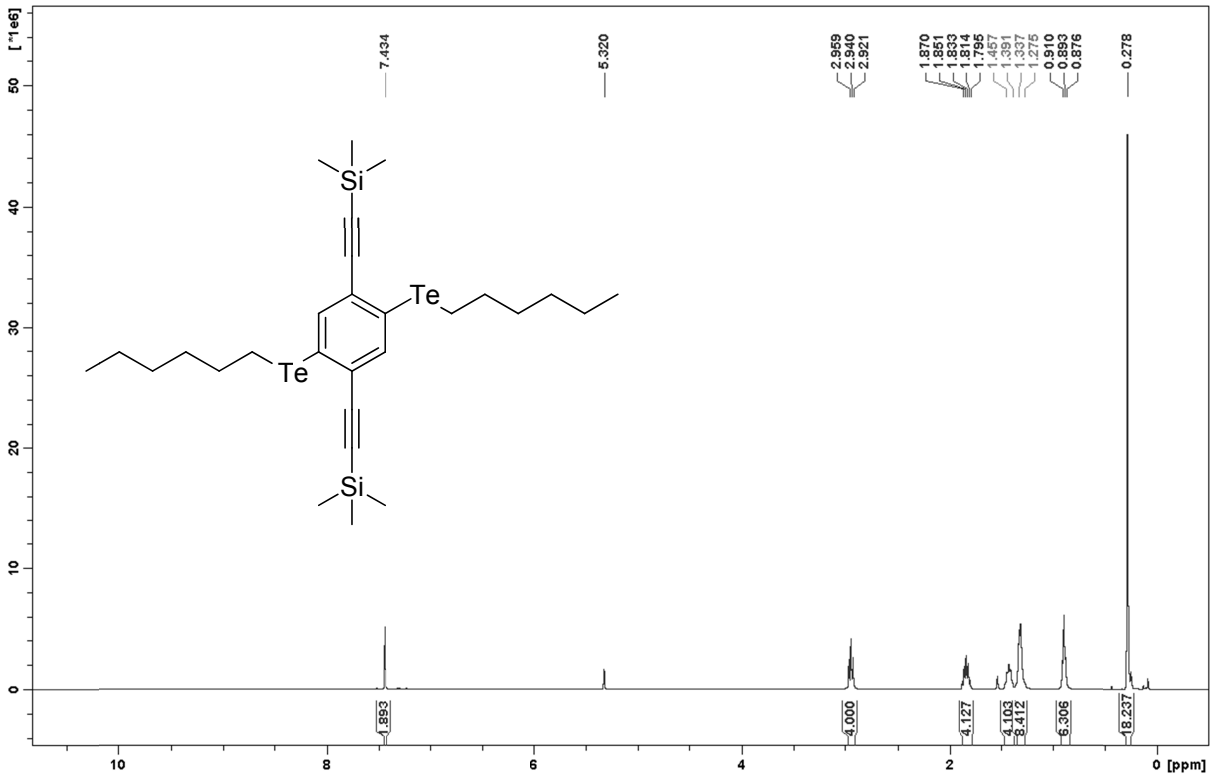


Figure S13: ^{1}H NMR (400 MHz, CD_2Cl_2) of compound 6c

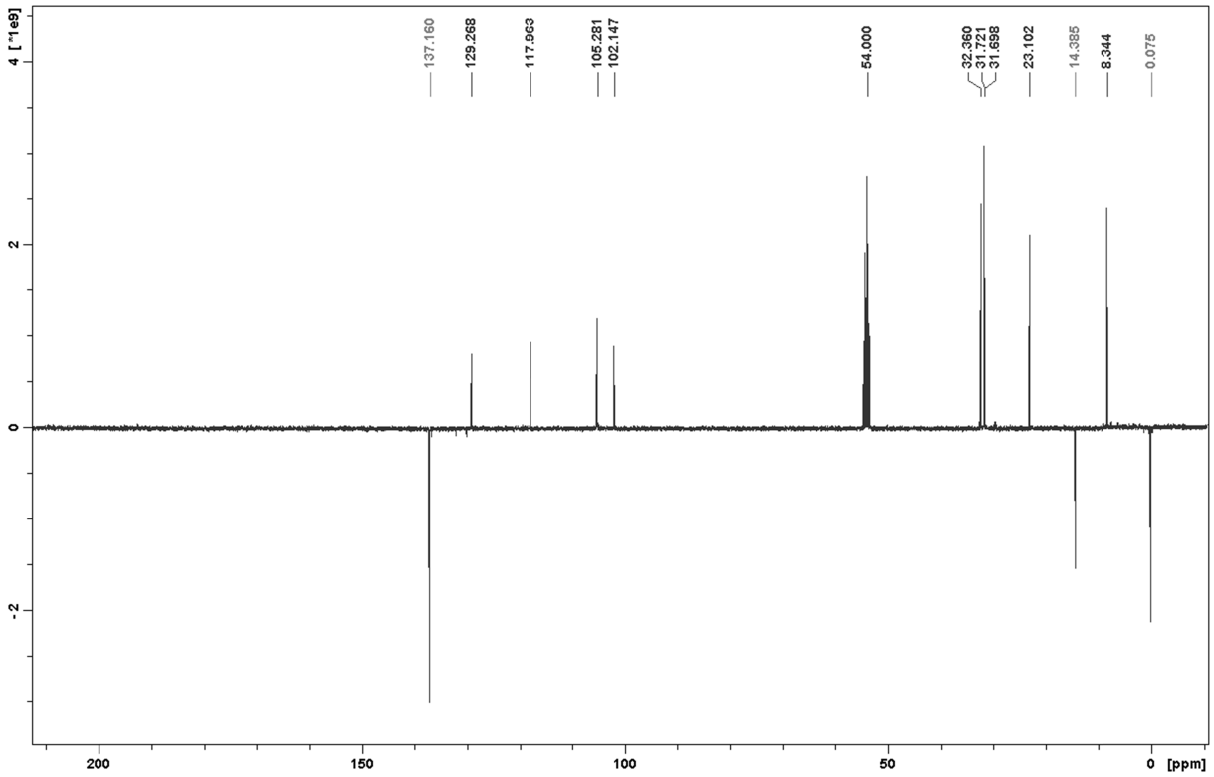


Figure S14: ^{13}C NMR (100 MHz, CD_2Cl_2) of compound 6c

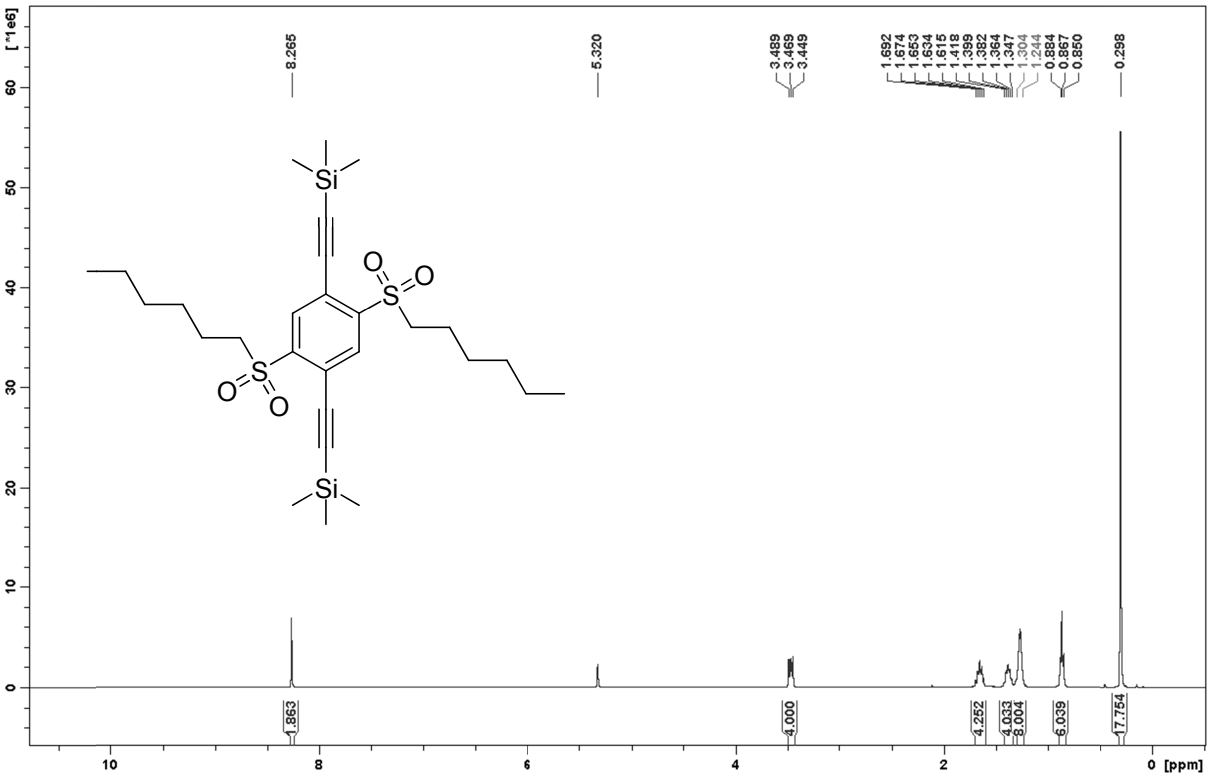


Figure S15: ^{1}H NMR (400 MHz, CD_2Cl_2) of compound 6d

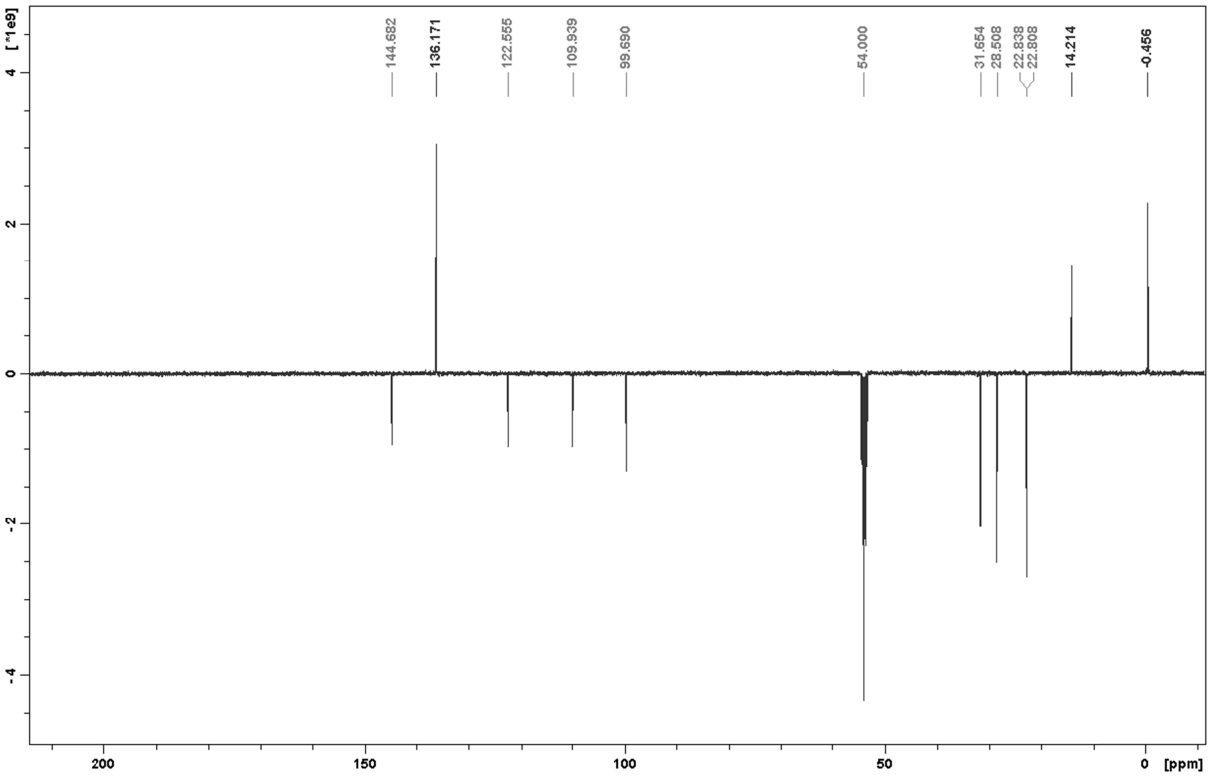


Figure S16: ^{13}C NMR (100 MHz, CD_2Cl_2) of compound 6d

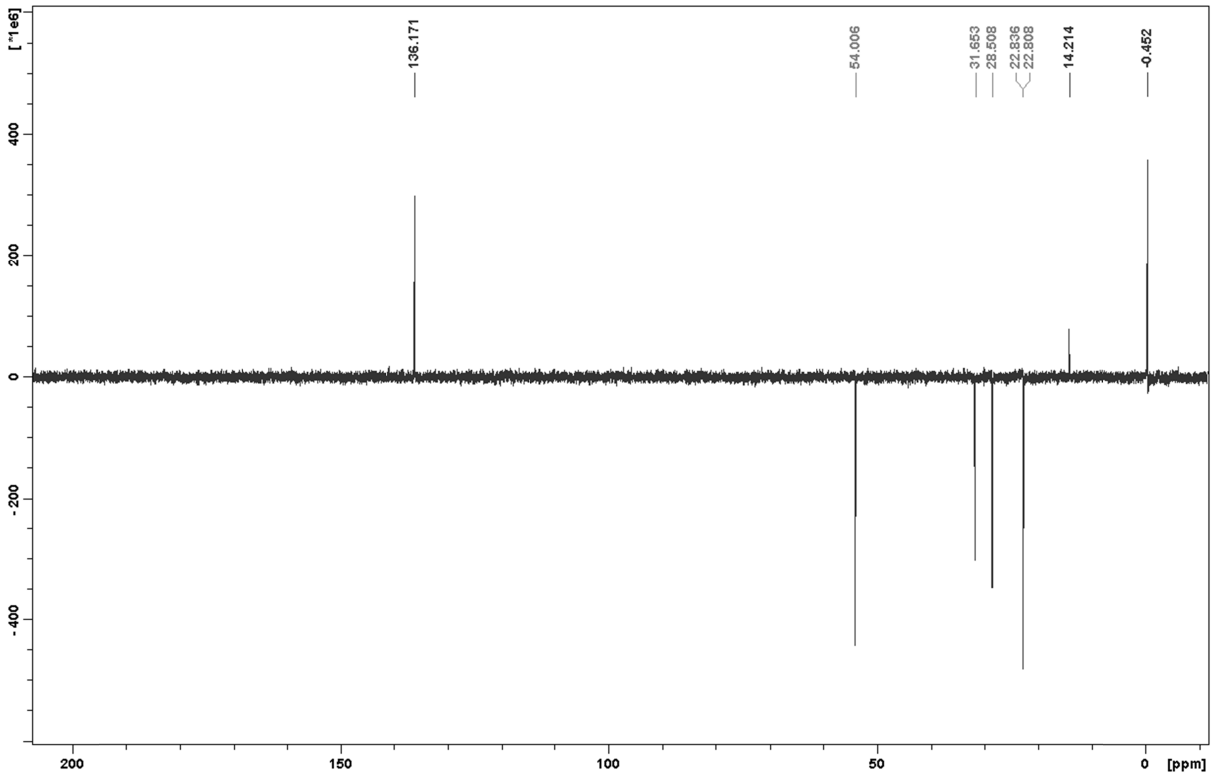


Figure S17: ^{13}C NMR (DEPT, 100 MHz, CD_2Cl_2) of compound 6d

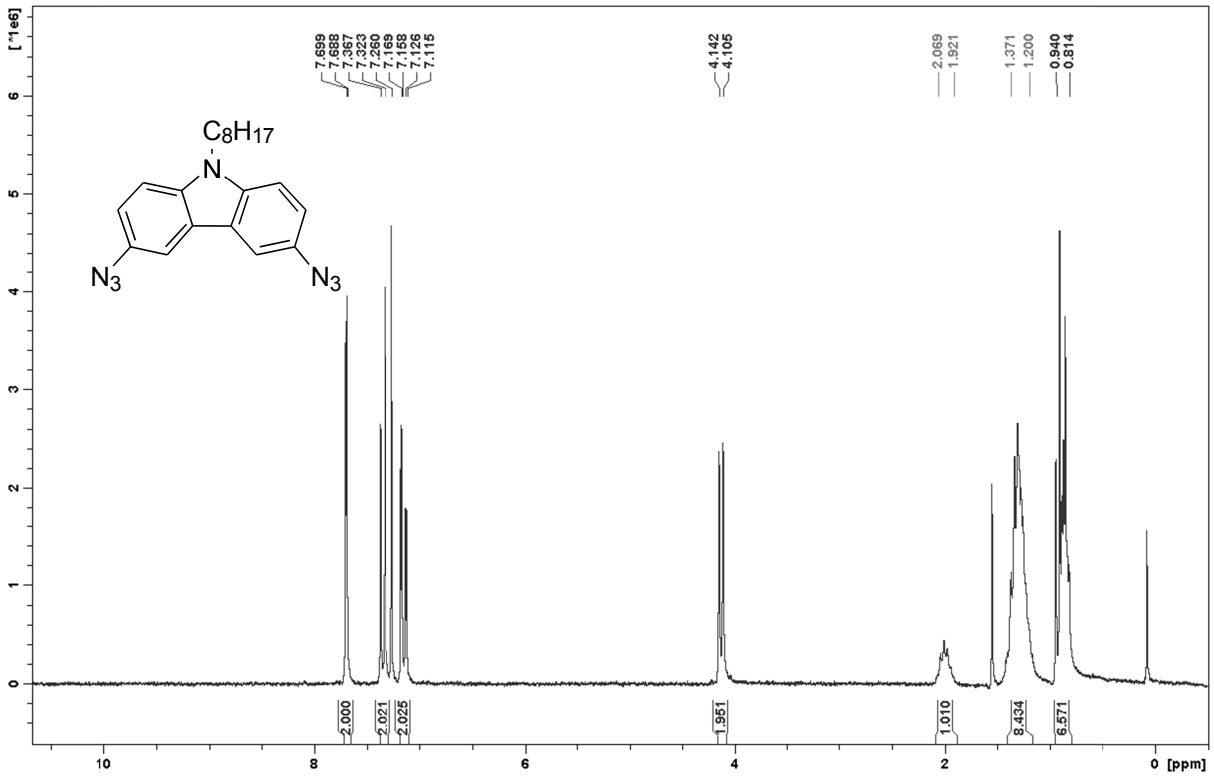


Figure S18: ^{1}H NMR (200 MHz, $CDCl_3$) of compound 7

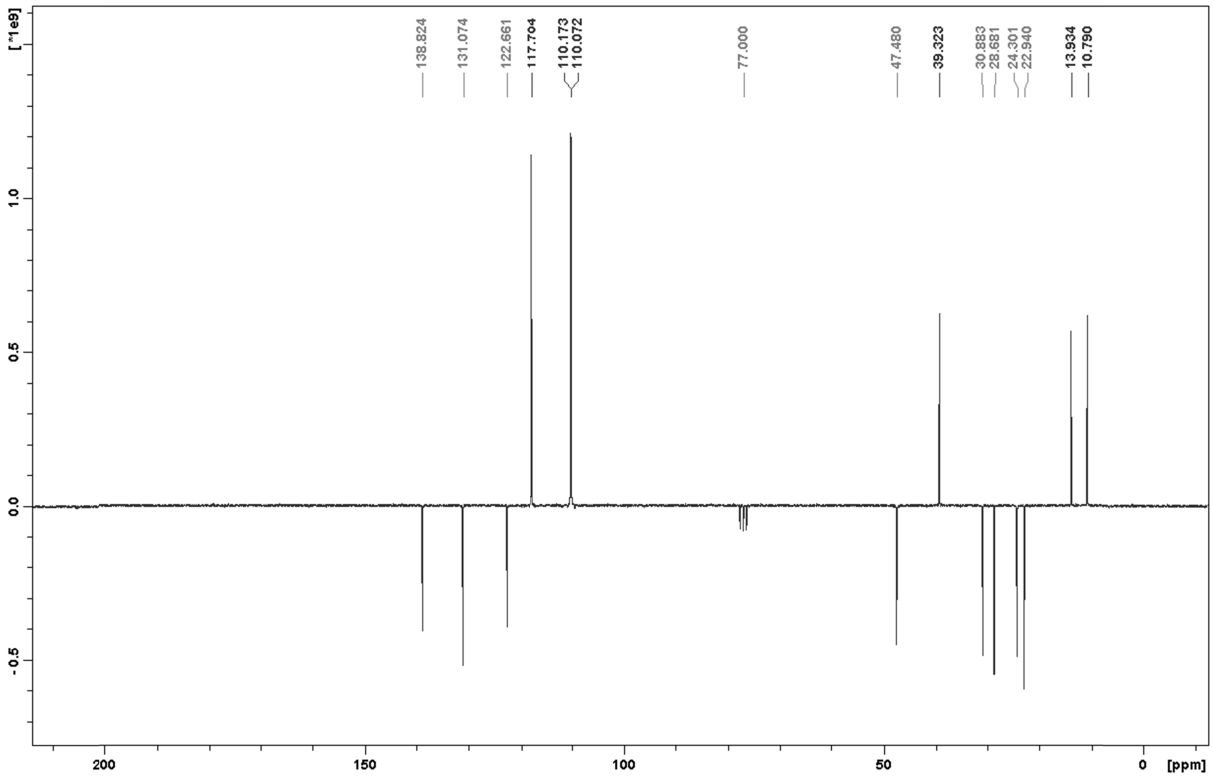


Figure S19: ^{13}C NMR (50 MHz, $CDCl_3$) of compound 7

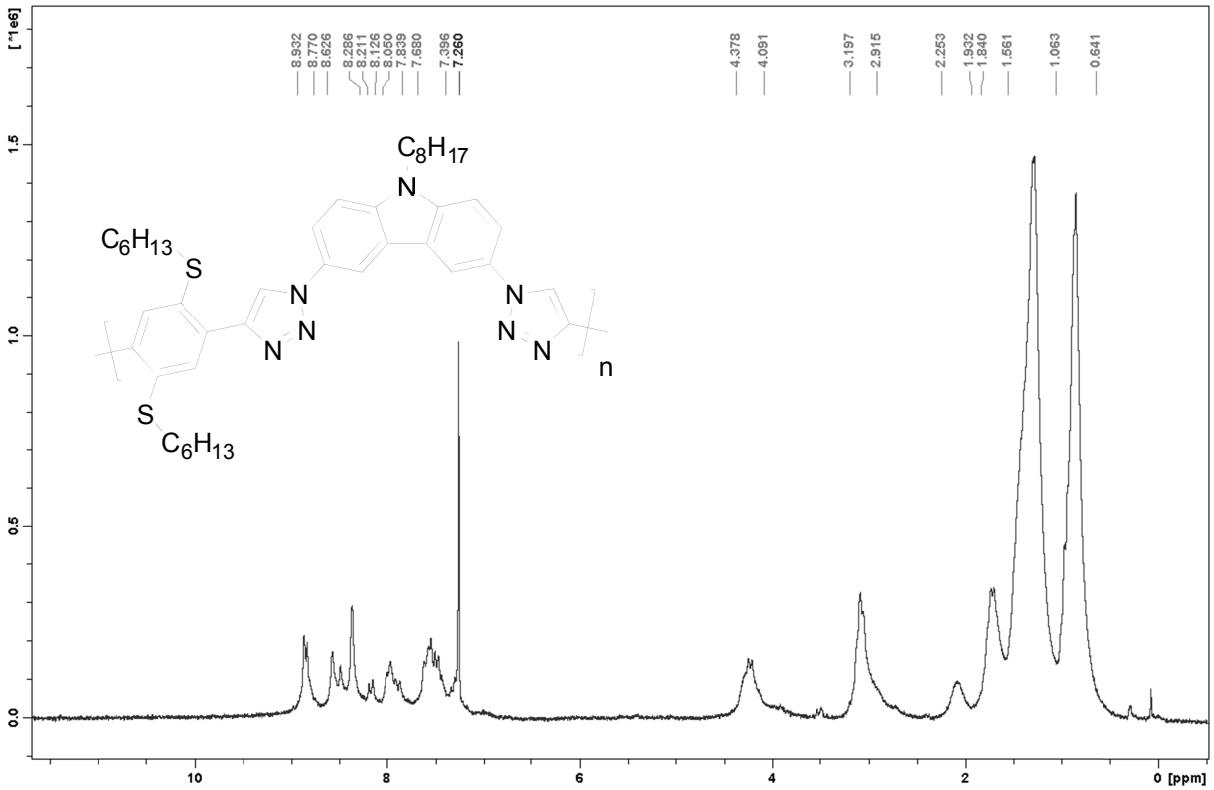


Figure S20: ^{1}H NMR (200 MHz, $CDCl_3$) of polymer 8

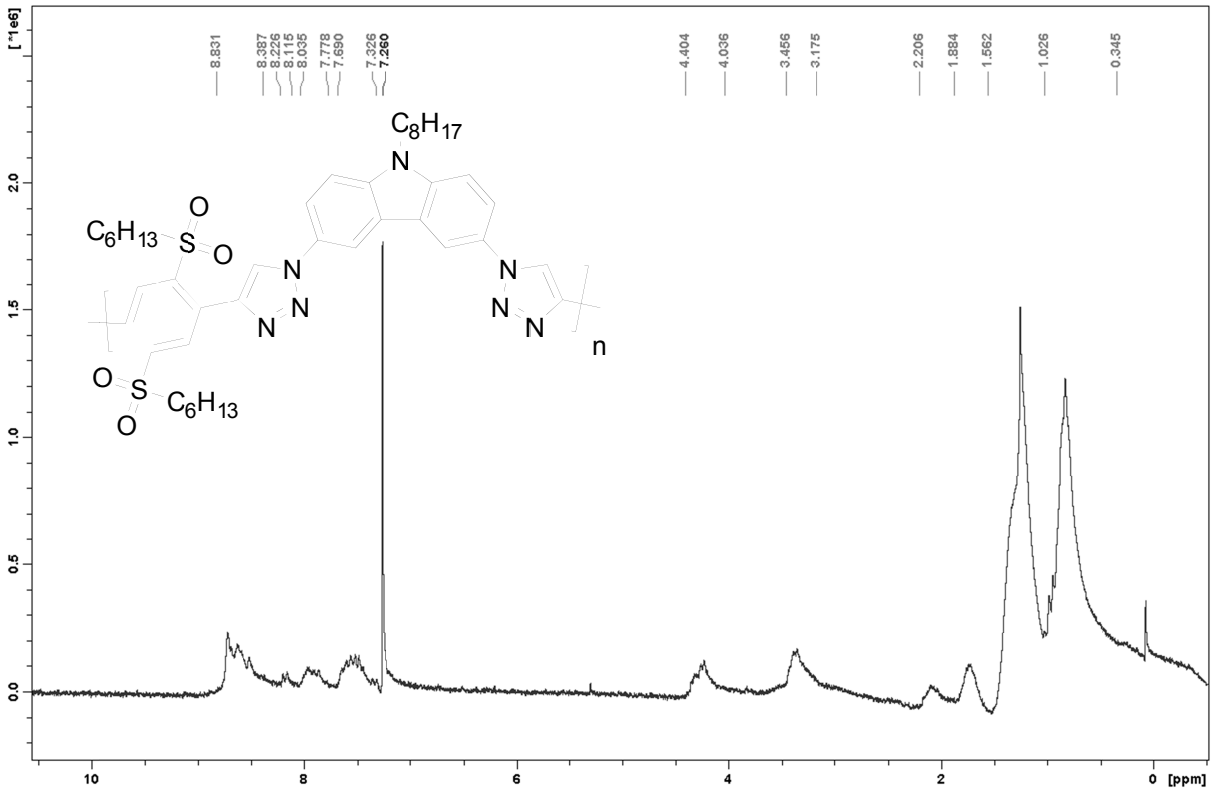


Figure S21: ^{1}H NMR (200 MHz, $CDCl_3$) of compound 9

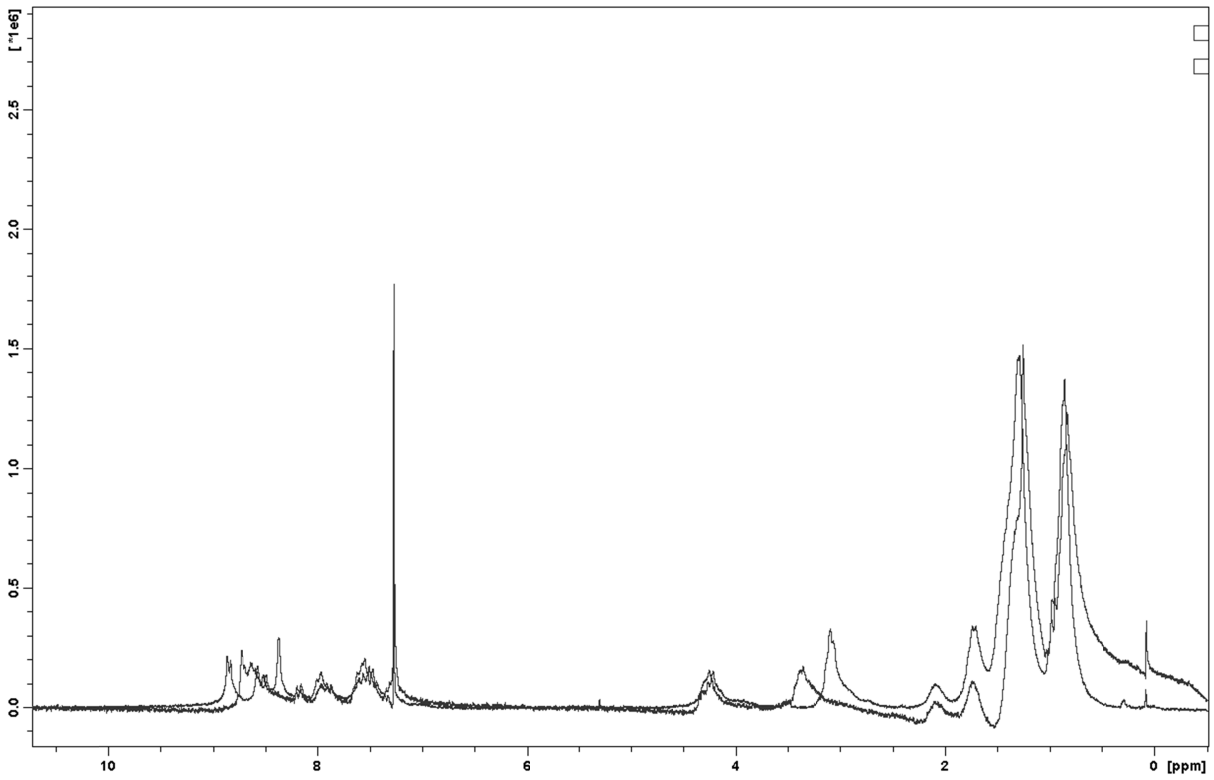


Figure S22: ^{1}H NMR (200 MHz, $CDCl_3$) overlay of compounds 8 and 9

1.3.2 IR spectra

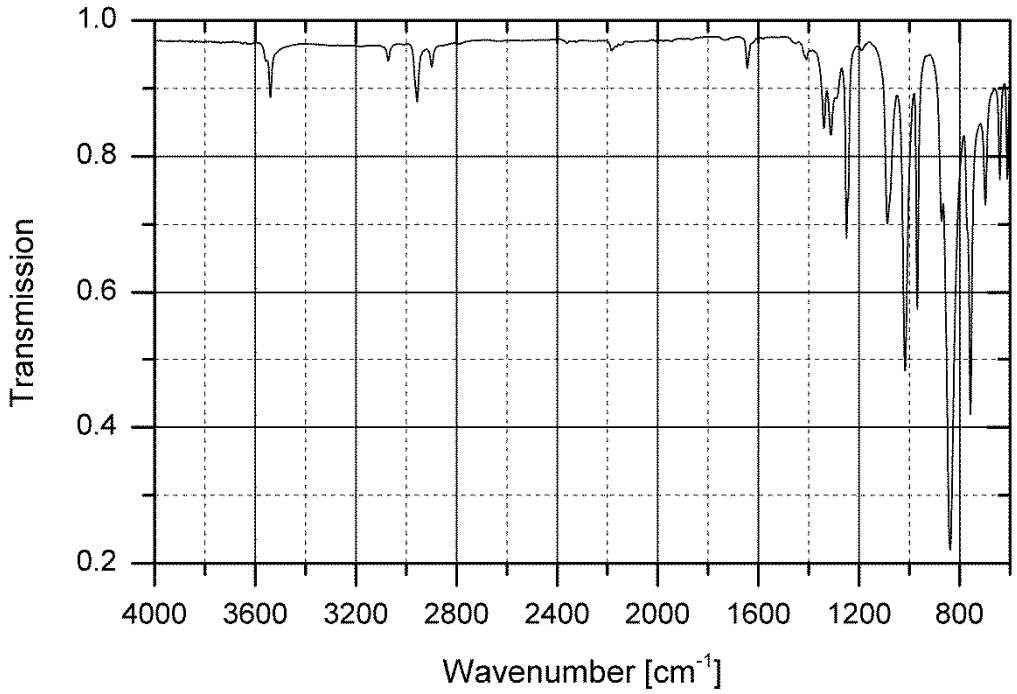


Figure S23: ATR-IR spectrum of 4a

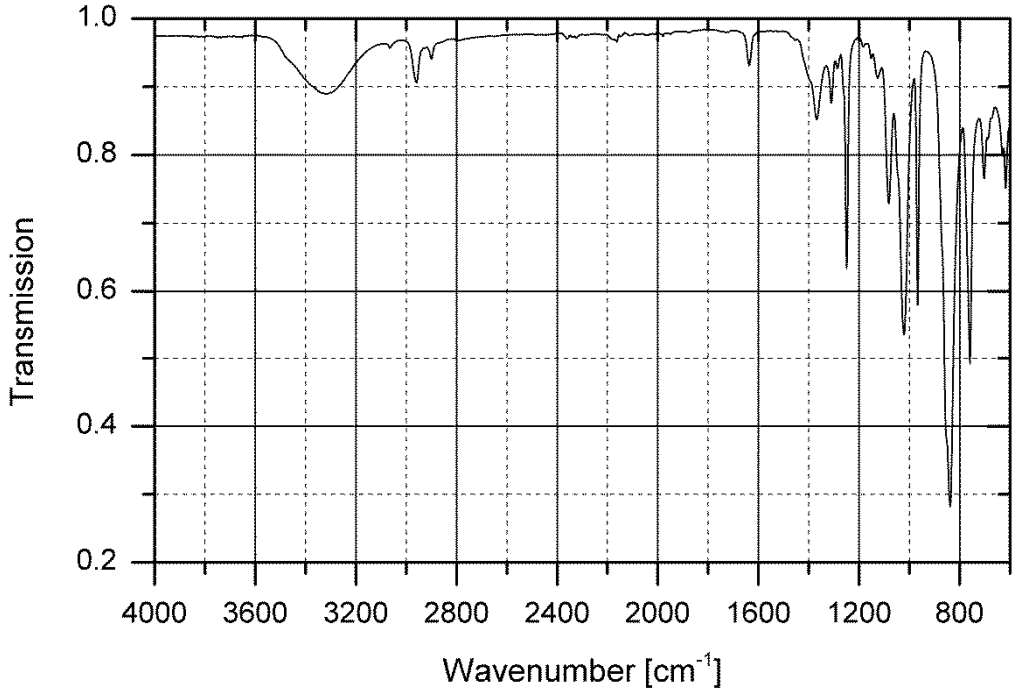


Figure S24: ATR-IR spectrum of 4b

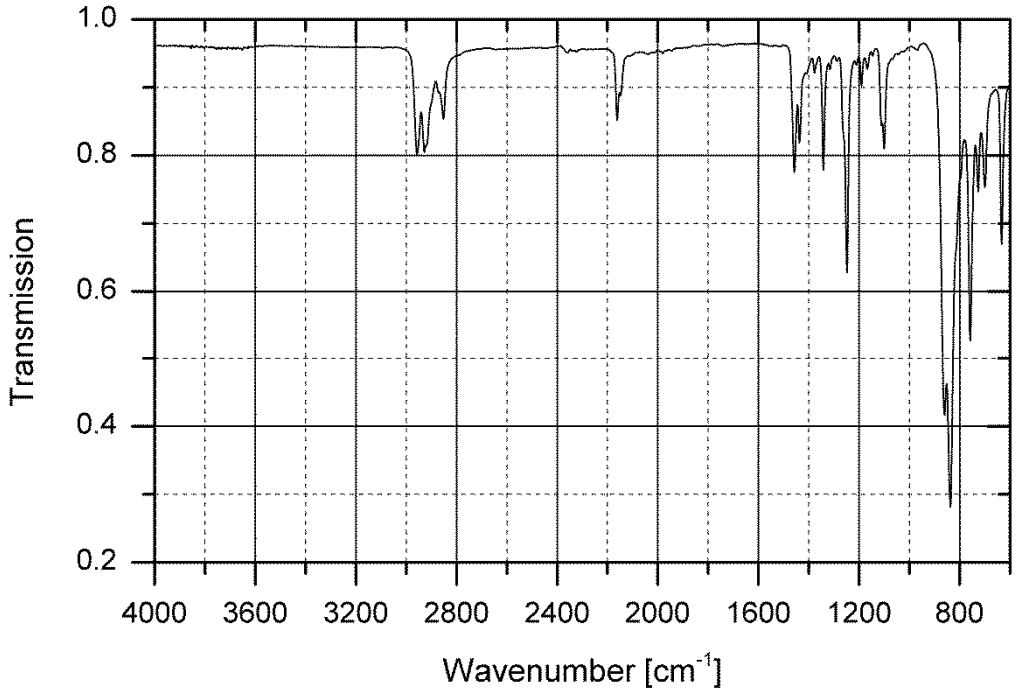


Figure S25: ATR-IR spectrum of 6a

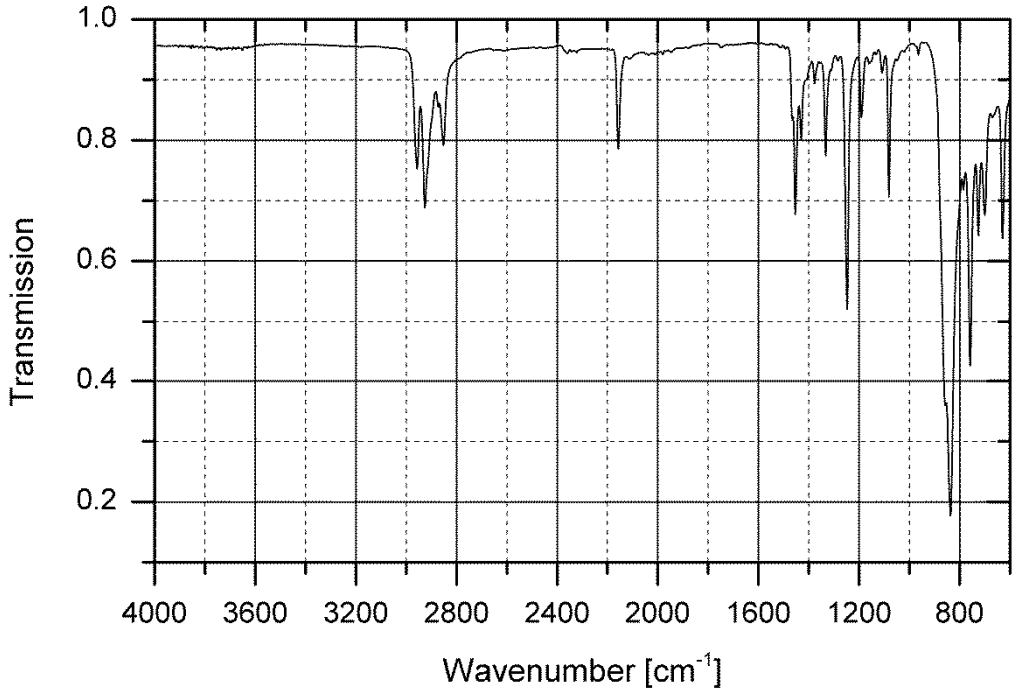


Figure S26: ATR-IR spectrum of 6b

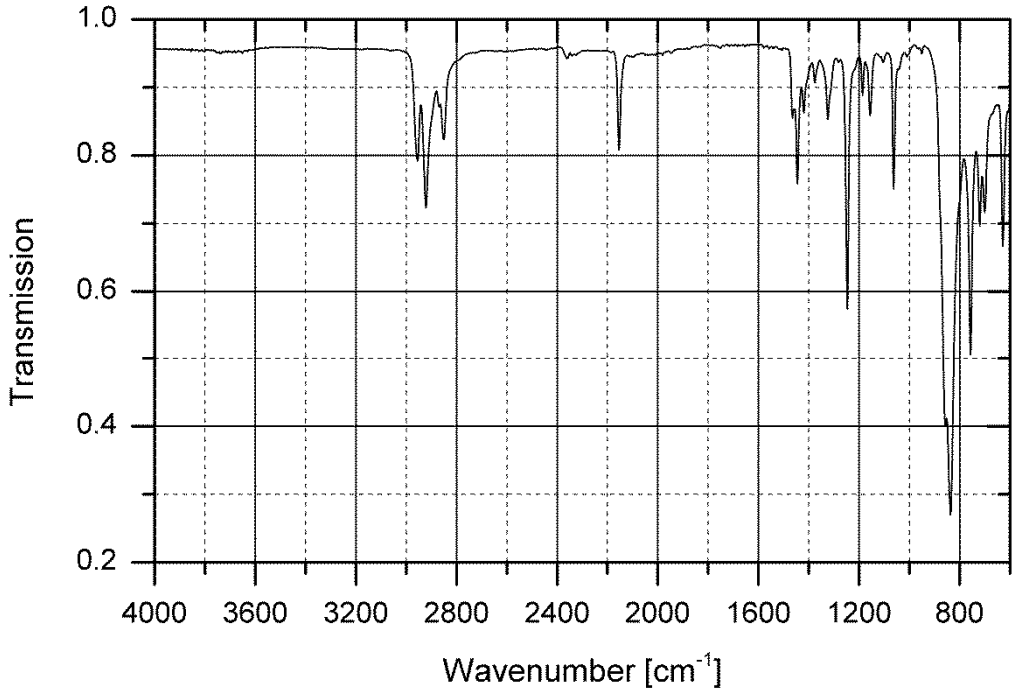


Figure S27: ATR-IR spectrum of 6c

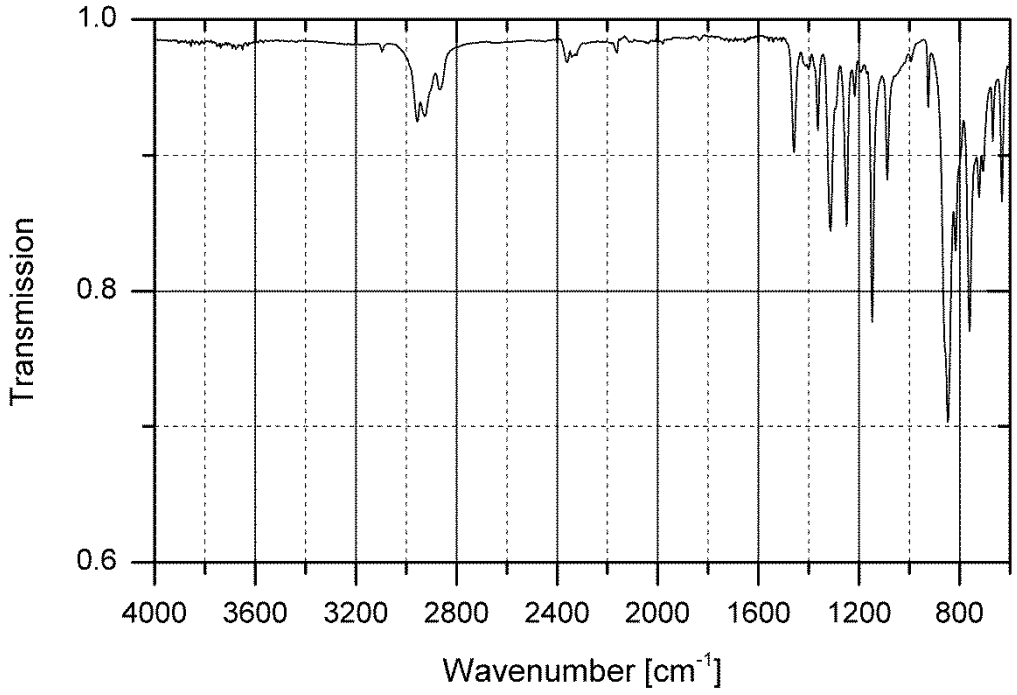


Figure S28: ATR-IR spectrum of 6d

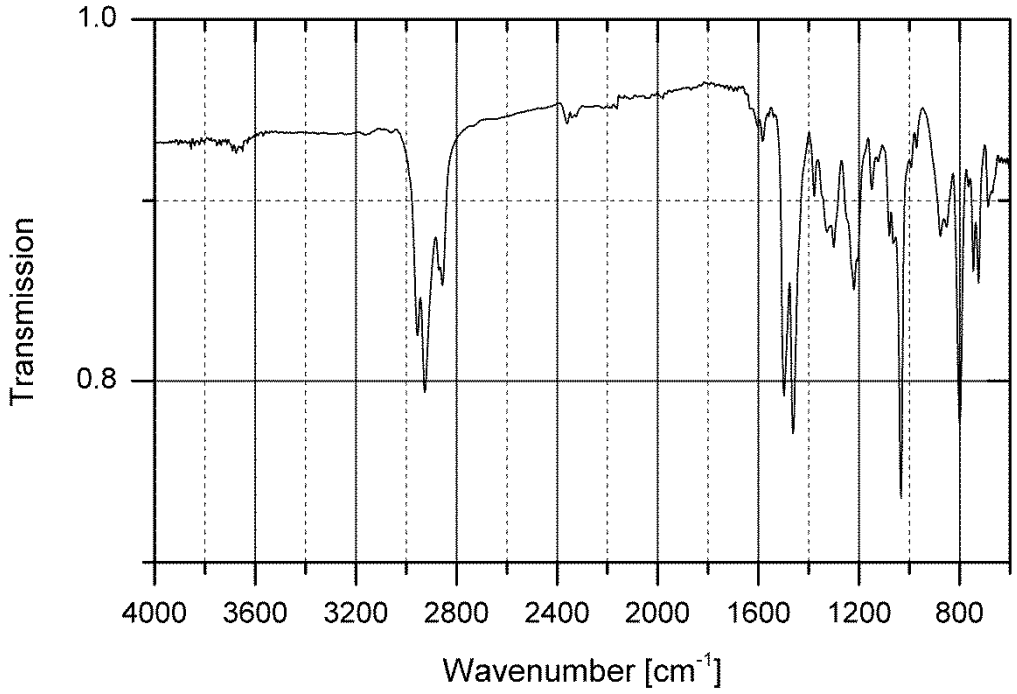


Figure S29: ATR-IR spectrum of 8

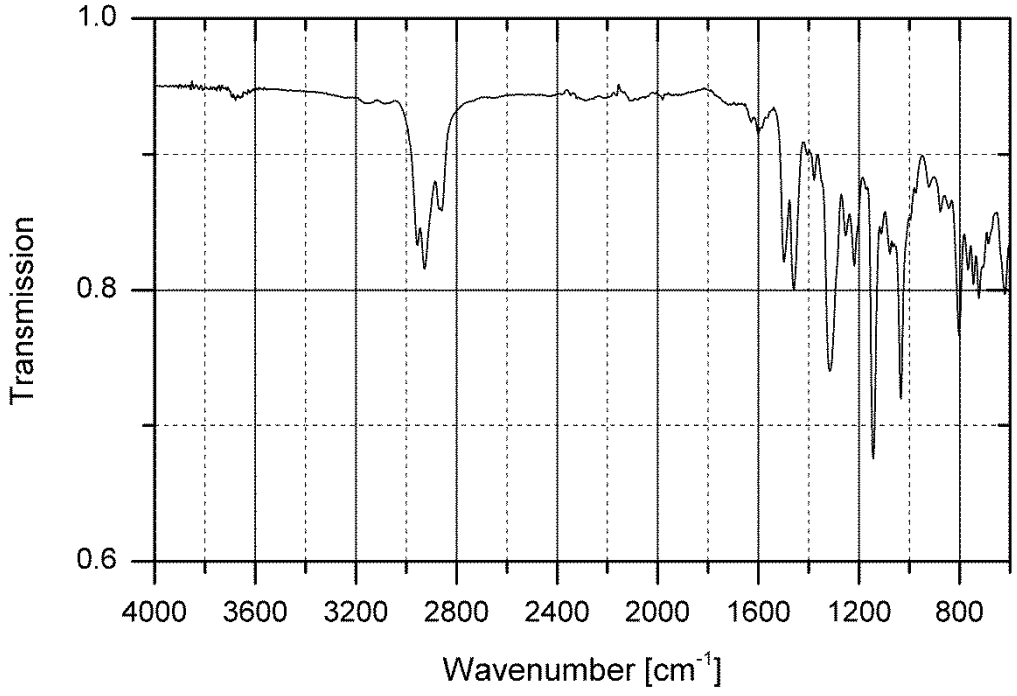


Figure S30: ATR-IR spectrum of 9

2. Crystallographic Part

Crystals of **6a**, **6b** and **6d** suitable for single-crystal diffraction were selected under a polarizing microscope. They were embedded in perfluorinated oil and attached to Kapton® micro-mounts. Intensity data were collected on a Bruker KAPPA APEX II diffractometer equipped with a CCD detector using MoKα radiation (λ=0.71072 Å). Data were reduced with SAINT-Plus [12] and an absorption correction was applied using the multi-scan approach implemented in SADABS [12]. All non-H atoms were located in the electron-density maps obtained by charge-flipping implemented in SUPERFLIP [13]. The structures were refined against F values using JANA2006 [14]. The two terminal C atoms of the hexyl chains in **6d** were refined as disordered over two positions. The site occupation factors of the connected atoms were restrained to the same value. Although the atoms still feature excessive anisotropic displacement parameters, further splitting of the atomic positions did not lead to an improved model. H atoms were placed at computed positions and refined as riding on the parent C atoms.

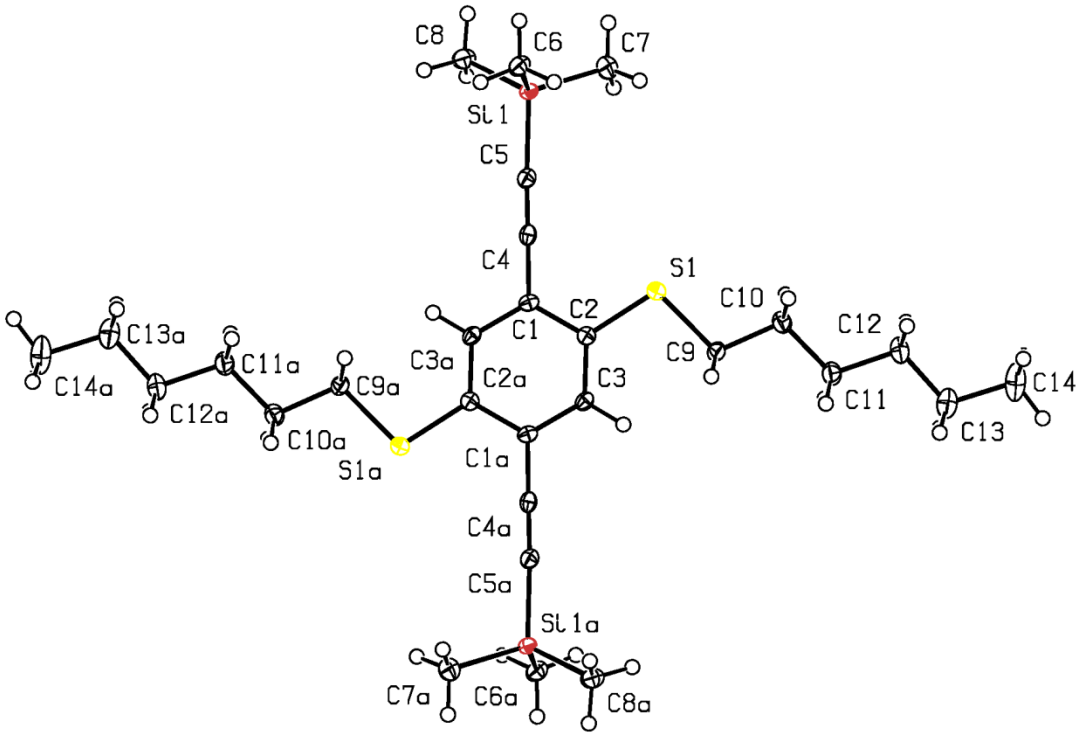


Figure S31: Crystal structure of compound 6a; symmetry codes: a: 3/2-*x*, -1/2-*y*, -*z*; ellipsoids were drawn at the 75% probability levels

$C_{28}H_{46}S_2Si_2$, M_r = 503.0, monoclinic, *C*2/*c*, *a* = 26.9821(16) Å, *b* = 6.2025(3) Å, *c* = 18.9375(11) Å, β = 103.184(2) °, *V* = 3085.8(3) Å^3, *Z* = 4, *μ* = 0.264 mm^{-1}, *T* = 100 K, 41 622 measured, 3 589 independent and 2 773 observed [*I* > 3σ(*I*)] reflections, 145 parameters, *wR* (all data) = 0.038, *R* [*I* > 3σ(*I*)] = 0.034; CCDC reference number 955488.

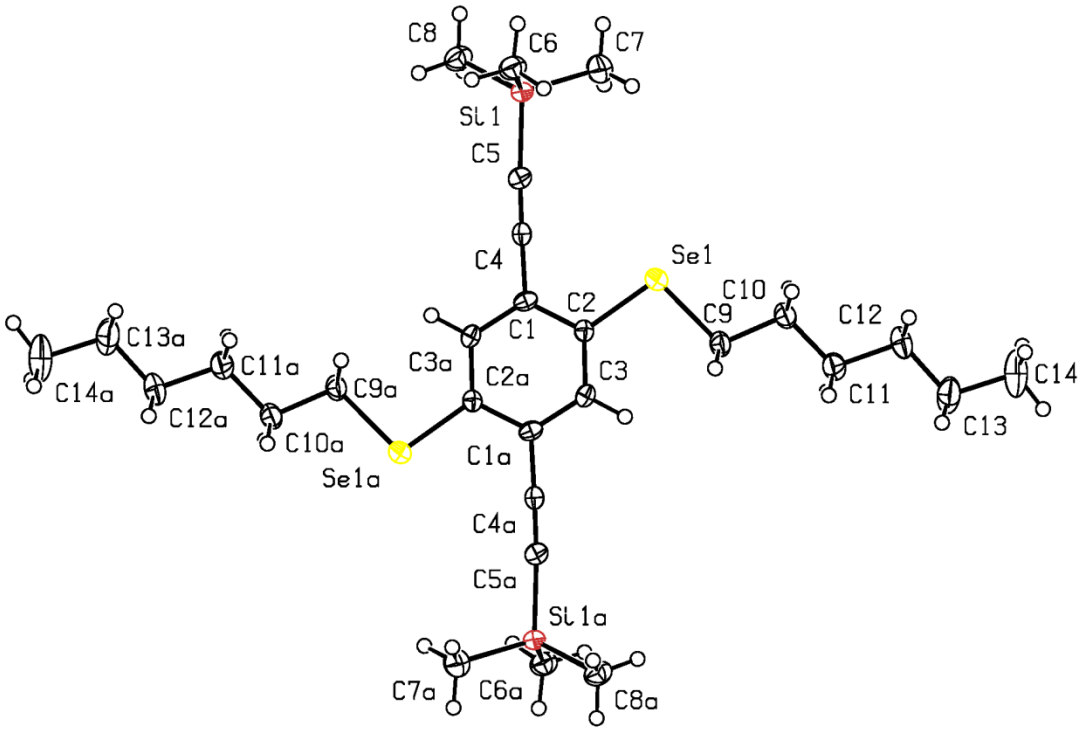


Figure S32: Crystal structure of compound 6b; symmetry codes: a: 3/2-*x*, -1/2-*y*, -*z*; ellipsoids were drawn at the 75% probability levels

$C_{28}H_{46}Se_2Si_2$, M_r = 596.8, monoclinic, *C*2/*c*, *a* = 27.0042(5) Å, *b* = 6.2978(16) Å, *c* = 19.0383(12) Å, β = 102.1861(14) °, *V* = 33164.8(8) Å^3, *Z* = 4, *μ* = 2.429 mm^{-1}, *T* = 100 K, 29 806 measured, 3 595 independent and 2 452 observed [*I* > 3σ(*I*)] reflections, 145 parameters, *wR* (all data) = 0.044, *R* [*I* > 3σ(*I*)] = 0.040; CCDC reference number 955489.

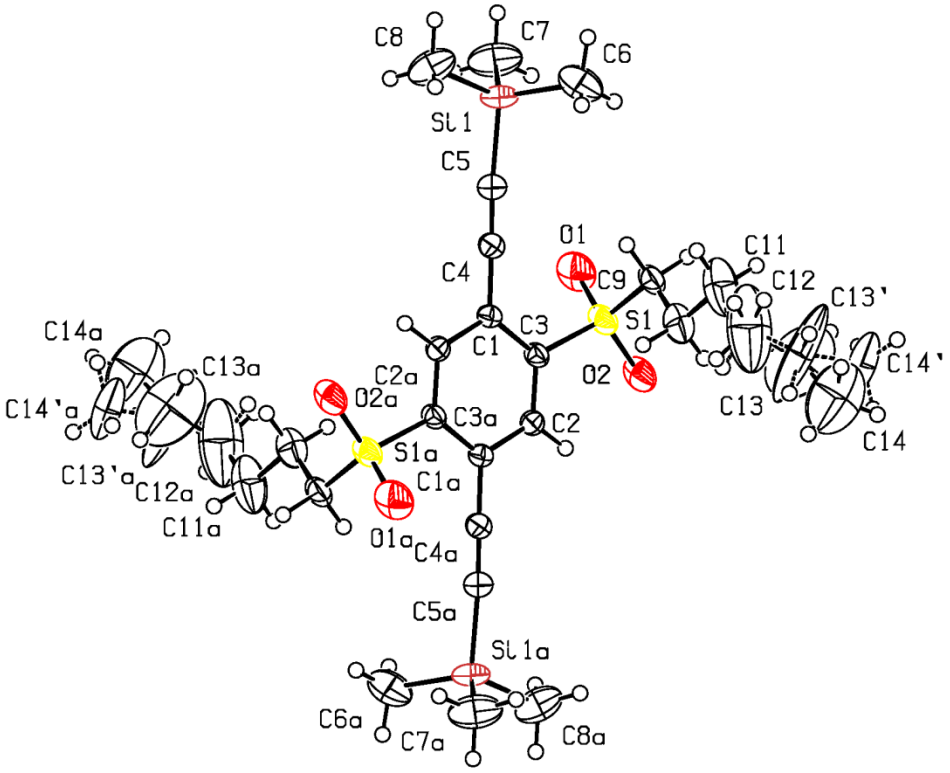


Figure S33: Crystal structure of compound 6d; symmetry codes: a: 1-*x*, -*y*, -*z*; ellipsoids were drawn at the 75% probability levels

$C_{28}H_{46}O_4S_2Si_2$, M_r = 567.0, monoclinic, $P2_1/c$, a = 10.4283(8) Å, b = 10.1568(9) Å, c = 16.2540(14) Å, β = 100.454(3)°, V = 1693.0(2) Å^3, Z = 2, μ = 0.256 mm^{-1}, T = 100 K, 66 626 measured, 4 979 independent and 3 845 observed [$I > 3\sigma(I)$] reflections, 145 parameters, wR (all data) = 0.072, R [$I > 3\sigma(I)$] = 0.054; CCDC reference number 955490.

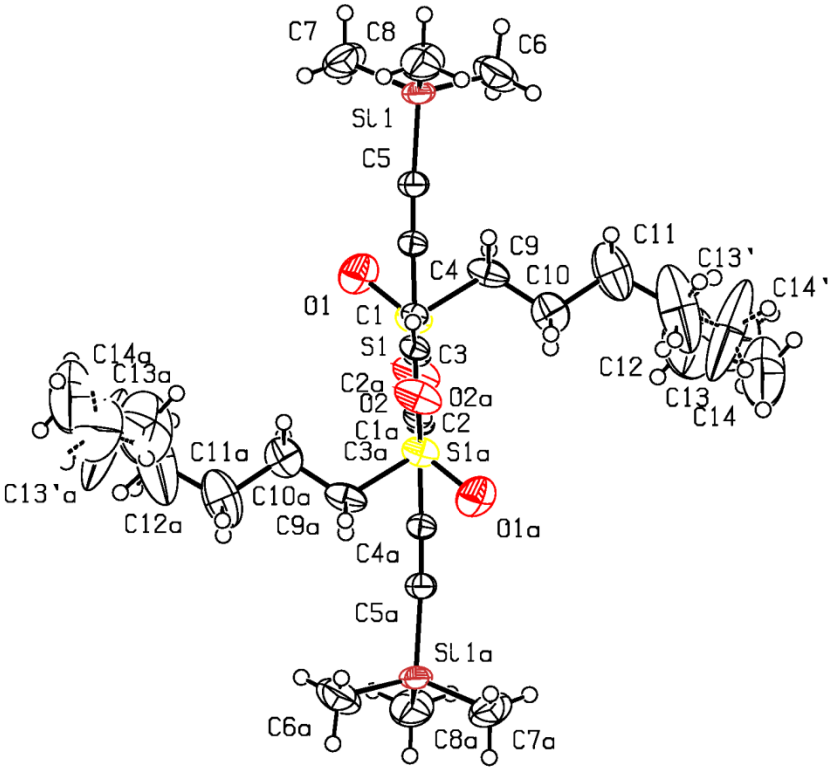


Figure S34: Crystal structure of compound 6d (side); symmetry codes: a: 1-*x*, -*y*, -*z*; ellipsoids were drawn at the 75% probability levels

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