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Electron-transporting phenazinothiadiazoles with engineered microstructure

- Supporting Information -

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CONTENTS

1. General methods

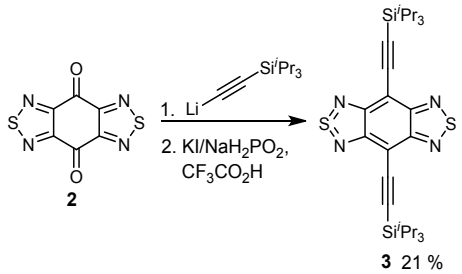
All reagents and solvents were obtained from Fisher Scientific, ABCR, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification. All of the other absolute solvents were dried by a MB SPS-800 using drying columns. Preparation of air- and moisture-sensitive materials was carried out in oven dried flasks under an atmosphere of argon using Schlenk-techniques. For thin layer chromatography Polygram Sil G/UV 254 plates from Macherey, Nagel & Co. KG, Düren (Germany) were used and examined under UV-light irradiation (254 nm and 365 nm). Flash column chromatography was performed on silica gel from Macherey, Nagel & Co. KG, Düren (Germany) (particle size: 0.04-0.063 mm). Melting points were determined with a Melting Point Apparatus MEL-TEMP (Electrothermal, Rochford, UK) and are uncorrected.

^{1}H NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded at room temperature on Bruker Avance DRX 300 (300 MHz), Bruker Avance III 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) and Bruker Avance III 600 (600 MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to residual undeuterated solvent peak.[1] The following abbreviations are used to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). All NMR spectra were integrated and processed using MestReC 4.7. MS spectra were recorded on a Vakuum Generators ZAB-2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometer. Crystal structure analysis was accomplished on Bruker Smart CCD or Bruker APEX diffractometers. Infrared (IR) spectra were recorded on a Jasco FT/IR-4100 spectrometer. Absorption spectra were recorded on a Jasco UV-VIS V-670. Emission spectra were recorded on a Jasco FP-6500. Elemental Analysis was performed by the Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario EL machine. Computational studies were carried out using DFT calculations on Spartan ´10. Geometry optimization was found by B3LYP functional and 6-311+G** basis set. Using this geometry the absolute energy and FMO energies were assigned on frequency analysis by employing B3LYP/6-311+G**. Cyclic voltammetry was performed with a VERSASTAT3-200 potentiostat (Princeton Applied Research) using a gold working electrode, a 0.1 mol/l NBu_4PF_6 solution in THF as solvent and ferrocene/ferrocenium as reference redox system and internal standard. Nomenclature of all new compounds described in the supporting information was determined with the program ACD/ChemScetch 2012 of Advanced Chemistry Development Inc.

[1] H. E. Gottlieb, V. Kotylar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512-7515.

2. Synthesis and analytical data

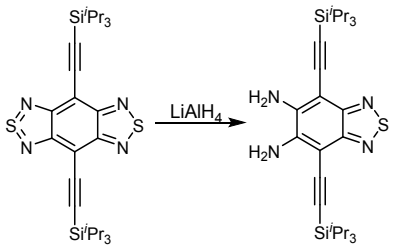
benzo[1,2-c:4,5-c']-4,8-bis((triisopropylsilyl)ethynyl)bis([1,2,5]thiadiazole) (3)



To an oven dried Schlenk tube cooled under nitrogen was added THF (50 mL) and was freeze, pump, thawed three times.Then the Schlenk tube was purged with nitrogen for 5 min and sealed with a rubber septum. The solution was brought to 0 °C on an ice bath and TIPS-acetylene (4.88 g, 2.7 x 10^{-2} mol, 3.0 eq.) was added. Then *n*-butyllithium (10.0 mL of 2.5 M solution, 2.5 x 10^{-2} mol, 2.8 eq.) was added and the solution was stirred for 30 min at 0 °C, the ice bath was removed and the solution was allowed to stir for 30 min at ambient temperature. Compound **2** (2.0 g, 8.9 x 10^{-3} mol) was added to the solution, and the reaction mixture was purged with nitrogen for 5 min. The reaction was then sealed again and allowed to stir for 12 h. The reaction was quenched in wet ethyl ether and the solvent removed *in vacuo*. The intermediate diol was collected by column chromatography over silica gel using pure ethyl acetate (4.26 g, 81%). Without further characterization, the residue was suspended in trifluoroacetic acid and the salts KI (8.4 g, 5 x 10^{-2} mol, 7 eq.) and NaH_2PO_2 (4.45 g, 5 x 10^{-2} mol, 7 eq.) were added to the solution. After stirring for 90 min, the reaction was quenched in water (100 mL) and extracted with dichloromethane (4 x 100 mL). The organic layer was washed with copious amounts of water to remove the acid, chemically dried with anhydrous sodium sulfate, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel using hexanes/dichloromethane (10:3 *v/v*). Compound **3** was collected as a purple solid (1.05 g, 21% yield).

M.p. = 175 °C (decomposition); ^{1}H NMR (400 MHz, δ in $CDCl_3$) 1.23 (m, broad, 42 H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.50, 111.12, 106.32, 101.13, 18.94, 11.62; IR (KBr, cm^{-1}) 3838, 3166, 2943, 2893, 1862, 2758, 2723, 2553, 2241, 2221, 2129, 1944, 1901, 1774, 1465, 1384, 1357, 1288, 1234, 1068, 1010; accurate mass for $C_{28}H_{42}N_4S_2Si_2$: *m/z* = 554.23688 [M+], calc. *m/z* = 554.23895.

4,7-bis((triisopropylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole-5,6-diamine (4)

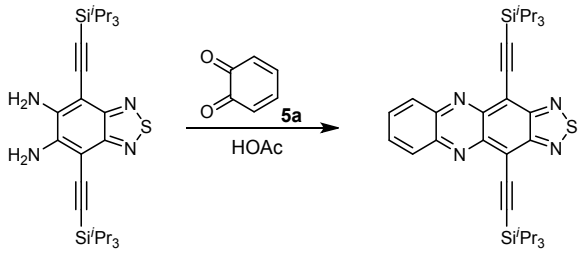


3 **4** 70 %

To an oven dried Schlenk flask, cooled under nitrogen, was added compound **3** (1.80 g, 3.2 x 10^{-3} mol) and freshly distilled THF (75 mL). The solution was purged with nitrogen for 5 min and placed on an ice bath. Then lithium aluminum hydride (1.23 g, 3.2 x 10^{-2}, 10 eq.) was slowly added over thirty minutes and the reaction mixture was sealed with a bubbler and stirred for 12 h while the ice bath came to ambient temperature. After 12 h, the reaction was placed back on an ice bath and very slowly quenched with saturated aqueous ammonium chloride (100 mL) and extracted with ethyl ether (3 x 150 mL) and the solvent was removed i*n vacuo*. The residue was resuspended in dichloromethane, dried with anhydrous sodium sulfate, and the solvent removed *in vacuo*. The crude reaction mixture was separated by column chromatography on silica gel using hexanes/dichloromethane (2:1 *v/v*). The product was recrystallized from hot hexanes. Compound **4** was obtained as a bright yellow solid (1.280 g, 70 %).

M.p. = 206-208 °C; ^{1}H NMR (400 MHz, δ in $CDCl_3$) 4.64 (s, 4H), 1.17 (m, broad, 42H); ^{13}C NMR (100 MHz, δ in $CDCl_3$) 150.59, 143.57, 103.44, 99.79, 97.26, 18.95, 11.49; IR (KBr, cm^{-1}) 3455, 3370, 3275, 3247, 3225, 3162, 3045, 2956, 2943, 2937, 2926, 2887, 2863, 2770, 2753, 2721, 2622, 2358, 2145, 2129, 1650, 1646, 1618, 1529, 1497, 1462, 1455, 1446, 1385, 1265, 1359, 1316, 1250, 1126, 1074, 1016; accurate mass for $C_{28}H_{46}N_4SSi_2$: *m/z* = 526.29419 [M+], calc. *m/z* = 526.29818.

4,11-bis((triisopropylsilyl)ethynyl)-[1,2,5]thiadiazolo[3,4-*b*]phenazine (1a)



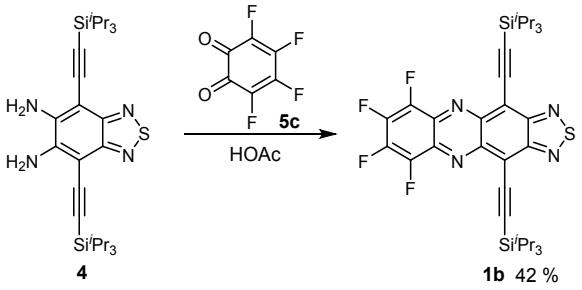
4 **1a** 31 %

In a 50 mL round bottom flask was added compound **4** (0.086 g, 1.6 x 10^{-4} mol) and placed in an oil bath at 50 °C, whereupon compound **5a** (0.053 g, 4.9 x 10^{-3} mol, 3 eq., dissolved in 25 mL dichloromethane) was added slowly over two hours. The reaction mixture was allowed to stir for an additional hour at 50 °C. The reaction mixture was quenched in water and extracted with dichloromethane (3 x 25 mL). The organic layer was dried with anhydrous sodium sulfate and the solvent removed *in vacuo*. The crude reaction mixture was purified by column chromatography on

silica gel using hexane/dichloromethane (2:1 *v/v*) to yield compound **1a** as dark blue-purple crystals (0.030 g, 31% yield).

M.p. = 184-185 °C; ^{1}H NMR (400 MHz, δ in $CDCl_3$) 8.10 (AA' of AA'BB', 2H), 7.77 (BB' of AA'BB', 2H), 1.30 (m, broad, 42H); ^{13}C NMR (100 MHz, δ in $CDCl_3$) 11.74, 19.04, 102.23, 111.92, 114.61, 130.56, 132.33, 142.83, 145.70, 154.73; IR (KBr, cm^{-1}) 3066, 2938, 2923, 2918, 2889, 2862, 2752, 2723, 2132, 1824, 1696, 1522, 1485, 1381, 1022; accurate mass for $C_{34}H_{46}N_4SSi_2$: *m/z* = 598.2963 [M+], calc. *m/z* = 598.2982.

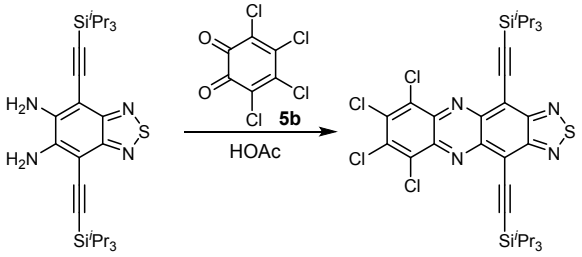
6,7,8,9-tetrafluoro-4,11-bis((triisopropylsilyl)ethynyl)-[1,2,5]thiadiazolo[3,4-*b*]phenazine (1b)



In a round bottom flask covered with aluminum foil **4** (190 mg, 190 µmol) was diluted in methylene chloride (30 mL) with HOAc (5 mL). The freshly prepared *o*-fluoranil (103 mg, 569 µmol) was diluted in methylene chloride and slowly added to the starting material *via* an aluminum foil covered syringe. After stirring at room temperature for 2 h the mixture was diluted with water and extracted three times with methylene chloride. The combined organic layers were dried over Na_2SO_4 and evaporated. The crude product was purified by flash column chromatography (silica gel, petroleum ether/methylene chloride 15:1, 102 mg, 42 %) to obtain **1b** as a crystalline blue solid.

M.p. 218 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27-1.36 (m, 42H); ^{19}F NMR (282 MHz, $CDCl_3$): δ = -149.81--149.70 (m, 2F), -147.80--147.69 (m, 2F); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 11.69, 18.93, 101.39, 114.31, 115.30, 133.58, 141.63, 155.47; IR: υ = 2940, 2889, 2863, 1559, 1446, 1365, 1351, 1180, 1036, 880, 718, 679, 658, 572, 457; UV-VIS λ_{max} (hexane): 667 nm; HR-ESI: *m/z* $[M + H]^+$ calcd. for $C_{34}H_{43}F_4N_4Si_2^+$: 671.26776, found: 671.26831; elemental analysis: calcd. for $C_{34}H_{42}F_4N_4Si_2$: C 60.86, H 6.31, N 8.35, S 4.78, found: C 60.60, H 6.28, N 8.20, S 4.93.

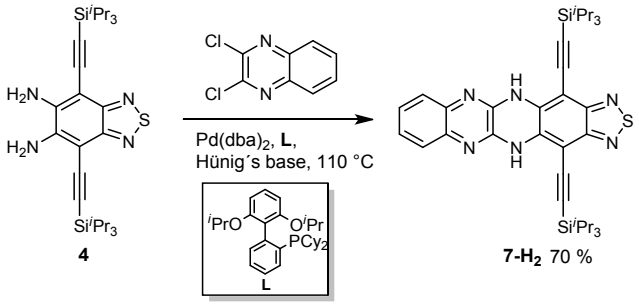
6,7,8,9-tetrachloro-4,11-bis((triisopropylsilyl)ethynyl)-[1,2,5]thiadiazolo[3,4-*b*]phenazine (1c)



Compound **4** (0.166 g, 3.2 x 10^{-4} mol) and **5b** (0.077 g, 3.2 x 10^{-4} mol, 1 eq.) were dissolved in ethanol (7 mL) and acetic acid (2 mL), heated to 85 °C and stirred for 12 h. The crude reaction was extracted with dichloromethane (3 x 25 mL). The organic layer was dried with anhydrous sodium sulfate and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel using hexanes/dichloromethane (2:1, *v/v*) to yield compound **1c** as dark blue-purple crystals (0.050 g, 21% yield).

M.p. = 284-286 °C; ^{1}H NMR (400 MHz δ in $CDCl_3$) 1.26 (m, broad, 42H); ^{13}C NMR (100 MHz δ in $CDCl_3$) 11.66, 18.99, 101.47, 113.93, 115.33, 132.41, 135.92, 140.20, 141.84, 155.83; IR (KBr, cm^{-1}) 2957, 2939, 2920, 2889, 2863, 2756, 2723, 1558, 1457, 1447, 1419, 1366, 1351, 1180, 1134, 1070, 1053, 1036, 1018; accurate mass for $C_{34}H_{42}Cl_4N_4SSi_2$: *m/z* = 734.1418, calc. *m/z* = 734.1425.

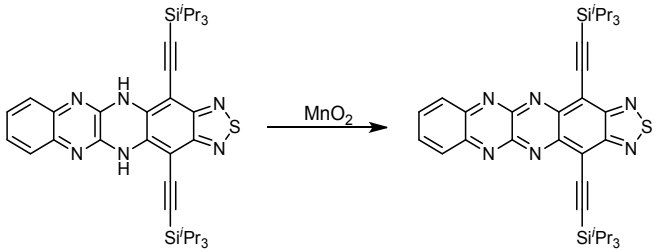
4,13-bis((triisopropylsilyl)ethynyl)-5,12-dihydroquinoxalino[2,3-b][1,2,5]thiadiazolo[3,4-g] quinoxaline (7-H_2)



Hünig´s base (1 mL) was placed under argon atmosphere in a dried Schlenk tube that contained diamine **4** (50.2 mg, 95.3 µmol) and 2,3-dichloro-quinoxaline (28.4 mg, 143 µmol), in addition to the ligand **L** (2.2 mg, 5 mol-%) and $Pd(dba)_2$ (2.7 mg, 5 mol-%). The tube was sealed and the reaction mixture was stirred for 20 h at 110 °C. The reaction mixture was diluted with methylene chloride and saturated aqueous NH_4Cl solution. After extraction of the aqueous phase with methylene chloride the organic phases were collected, dried over Na_2SO_4 and filtered through a pad of silica gel. After evaporation of the solvent the crude product was purified by flash column chromatography to furnish the dihydroacene **7-H_2** as an orange-red solid (silica gel, petroleum ether → petroleum ether/ethyl acetate 100:3, 264 mg, 70 %).

M.p. 246 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.17-1.35 (m, 42H), 7.36-7.41 (m, 2H), 7.54-7.59 (m, 2H), 7.87 (brs, 2H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ = 11.45, 18.98, 96.22, 97.19, 107.01, 126.56, 127.48, 135.94, 139.04, 139.45, 151.41; IR: υ = 3368, 2941, 2889, 2863, 2136, 1583, 1562, 1522, 1455, 1379, 1236, 1141, 880, 819, 739, 559; UV-VIS λ_{max} (hexane): 480 nm; HR-ESI: *m/z* $[M + H]^+$ calcd. for $C_{36}H_{49}N_6SSi_2^+$: 653.32725, found: 653.32752.

4,13-bis((triisopropylsilyl)ethynyl)quinoxalino[2,3-b][1,2,5]thiadiazolo[3,4-g]quinoxaline (7)



7-H$_2$ **7** 34 %

The Dihydroacene **7-H$_2$** (100 mg, 153 µmol) was dissolved in methylene chloride (35 mL) and stirred at rt. After adding an excess of activated manganese dioxide the reaction mixture was stirred for 10 min. After evaporation of the solvent the crude product was purified by flash column chromatography to obtain **7** as a green-brown unstable solid (silica gel, petroleum ether/methylene chloride 20:1 → petroleum ether/methylene chloride 2:1, 34.0 mg, 34 %; reisolated starting material: 41 mg, 41 %).

Decomp. >190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29-1.44 (m, 42H), 7.85-7.91 (m, 2H), 8.25-8.31 (m, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 11.76, 19.08, 102.62, 115.28, 115.48, 131.11, 134.23, 144.52, 144.91, 150.52, 156.34; IR: υ = 2941, 2863, 1733, 1523, 1453, 1439, 1378, 1342, 1258, 1089, 1028, 880, 738, 607, 495; UV-VIS λ_{max} (hexane): 795 nm; HR-ESI: *m/z* $[M + H]^+$ calcd. for $C_{36}H_{47}N_6SSi_2^+$: 651.31160, found: 651.31315.

3. UV-Vis spectra

Figure 1: Acenothiadiazoles in methylene chlorid (from left to right: **1a**, **6**, **1b**, **1c**); ***left:*** under day light; ***right:*** under a hand held black light at an illumination of 365 nm.

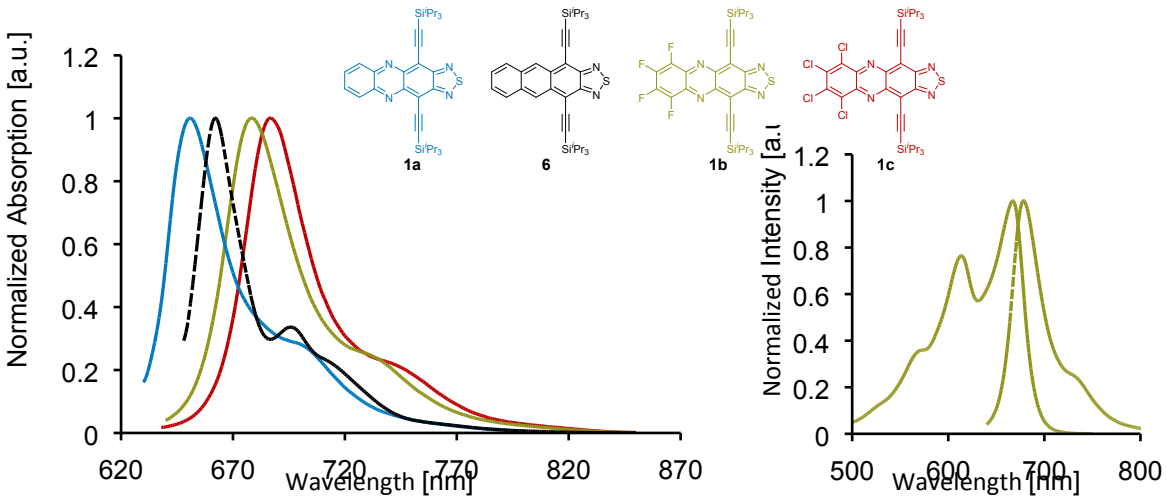


Figure 2: ***left:*** Normalized emission spectra of phenazinothiadiazoles **1a-c** compared to the anthracenothiadiazole **6** in *n*-Hexan; ***right:*** Visualized Stokes shift of **1b** in *n*-Hexan.

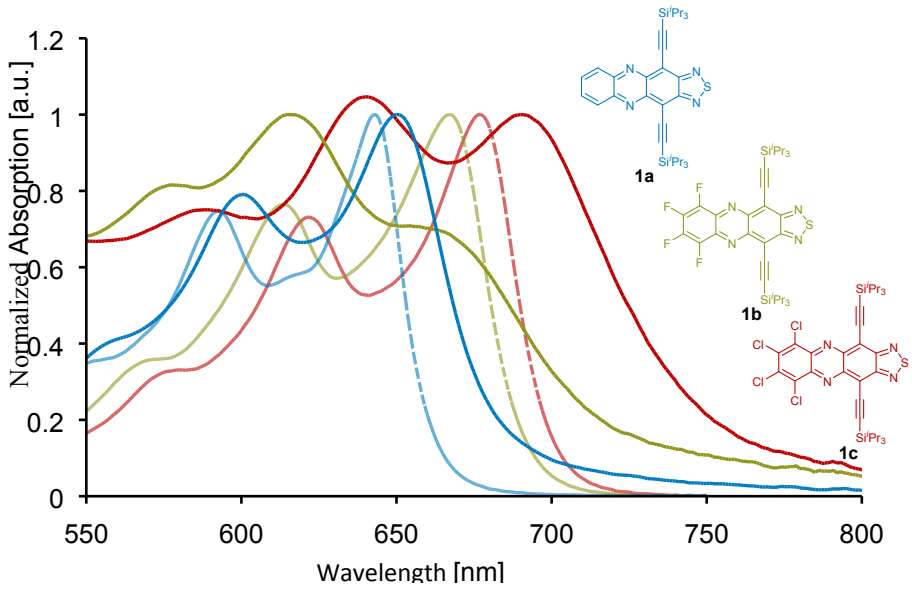


Figure 3: absorption spectra of phenazinothiadiazoles **1a-c** in thin film (solid lines) and in *n*-Hexan (dashed lines).

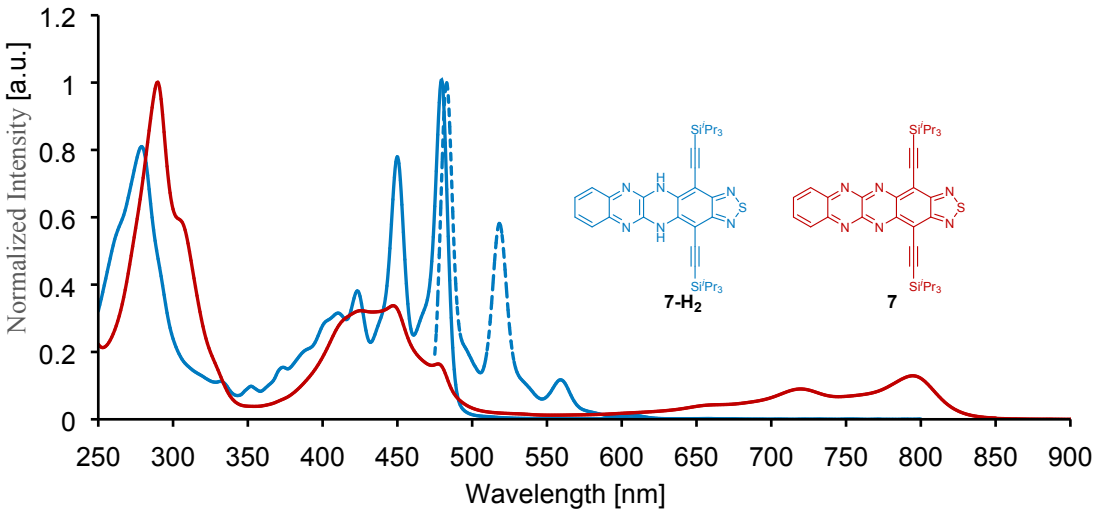


Figure 4: Normalized absorption- (solid line) and emission spectra (dashed lines) of **7-H$_2$** in *n*-hexanes (blue) compared to the absorption spectrum of the oxidised product **7** in *n*-hexanes (red).

4. Computational studies

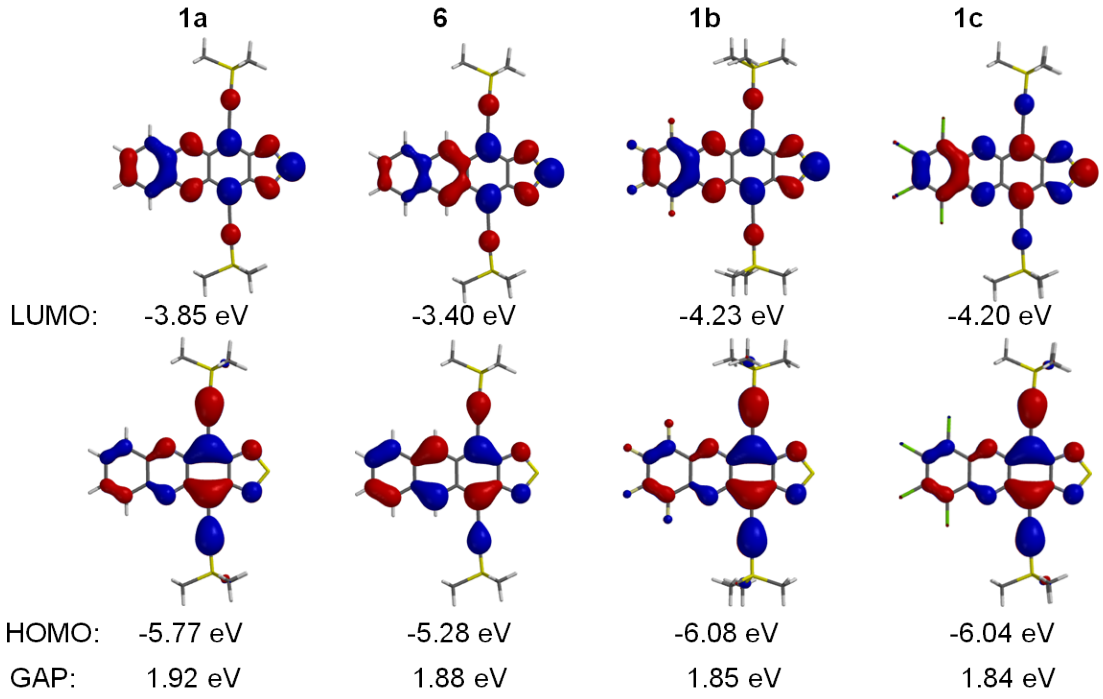
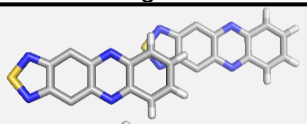
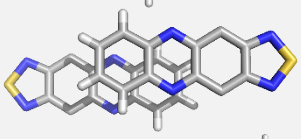
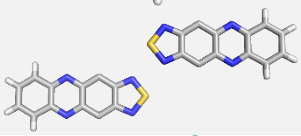
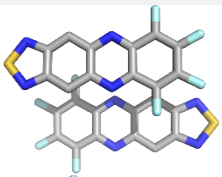
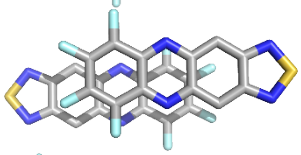
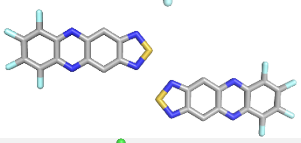
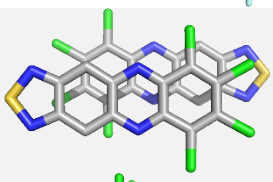
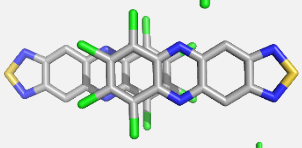
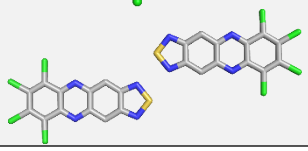


Figure 5: Quantum chemical calculations (Spartan ´10, B3LYP; 6-311+G**) of acenothiadiazoles **1a-c** and **6** (TMS instead of TIPS).

Table 1: transfer integrals of acenothiadiazoles **1a-c**.

compound	arrangement	HOMO [meV] projective method	HOMO [meV] orbital split. method	LUMO [meV] projective method	LUMO [meV] orbital split. method
1a		9.91	67.6	55.1	74.3
		35.5	35.0	63.0	53.9
		9.27	4.30	13.6	6.13
1b		64.9	60.0	74.3	63.3
		22.4	3.35	128	60.7
		5.90	7.20	43.8	36.9
1c		33.7	28.7	56.0	48.8
		30.3	28.1	51.8	45.6
		8.29	9.28	49.2	41.9

5. Crystal Structures

Table 2: crystal structures of acenothiadiazoles **1a-c**, **6**, **7-H$_2$** and **7**.

compound	space group	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]
6	$P\bar{1}$	8.200	13.15	17.19	78.04	81.53	80.55
1a	$P\bar{1}$	8.899	12.51	16.60	71.33	82.10	80.70

1b	$P\bar{1}$	8.128	14.27	17.09	66.85	78.53	80.64
1c	$P\bar{1}$	7.825	14.28	17.16	83.19	80.73	81.49
7-H_2	$P\bar{1}$	7.609	15.03	18.54	113.0	99.44	91.82
7	$P\bar{1}$	7.618	14.39	17.39	98.35	94.93	103.7

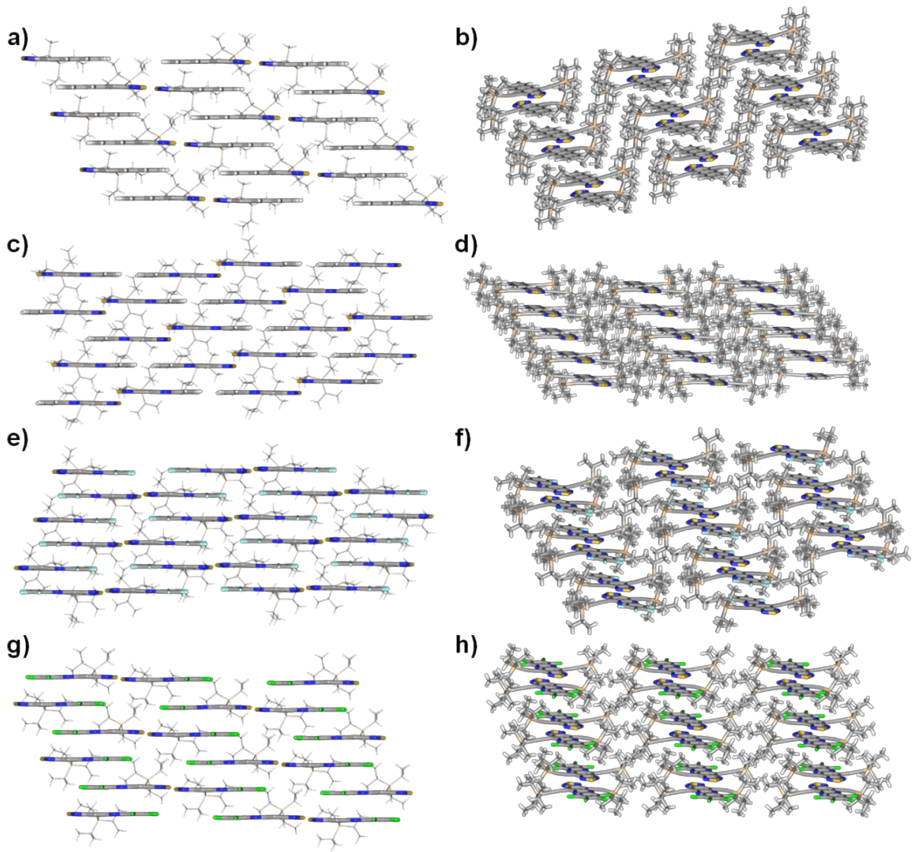


Figure 6: molecular packing of acenothiadiazoles (from top to bottom: **6, 1a, 1b, 1c**); ***left:*** sideview of the brick-wall motif; ***right:*** front view of the packing.

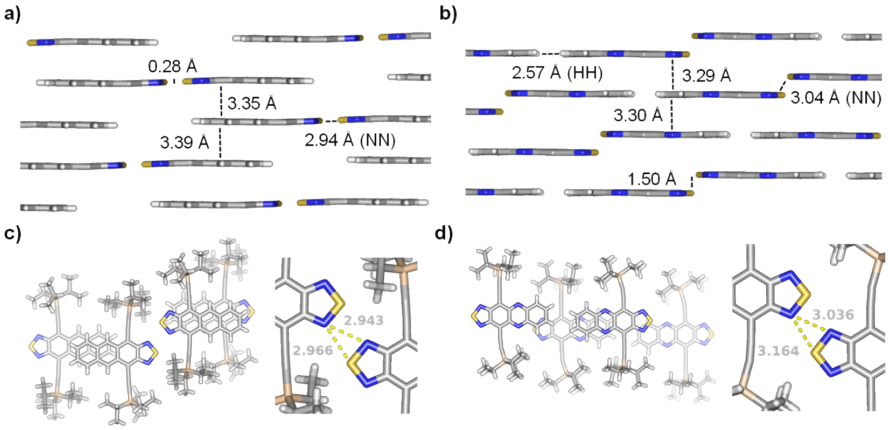


Figure 7: molecular packing of acenothiadiazoles **6** (left) and **1a** (right); ***top:*** sideview of the brickwall motif; ***bottom:*** topview.

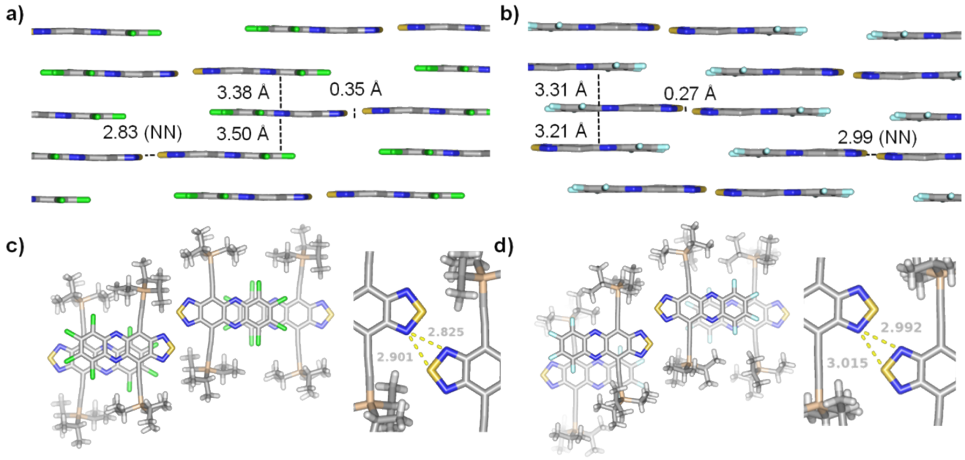


Figure 8: molecular packing of acenothiadiazoles **1c** (left) and **1b** (right); ***top:*** sideview of the brickwall motif; ***bottom:*** topview.

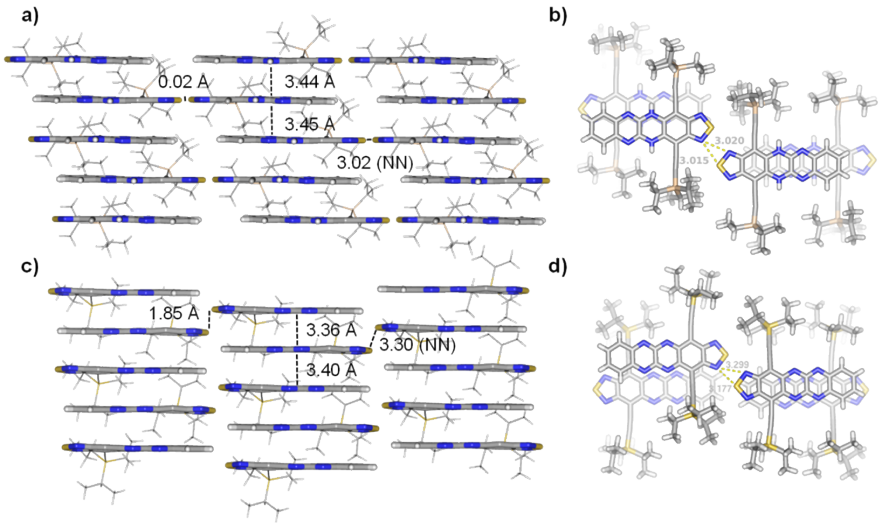


Figure 9: molecular packing of (dihydro-)acenothiadiazoles **7-H_2** (top) and **7** (bottom); ***left:*** sideview of the brickwall motif; ***bottom:*** topview.

6. OFET Fabrication

Thin film transistors have been fabricated on glass slides coated with polyamide (HD MicroSystems). Bottom Au contacts (W=1000 µm) were structured by a standard photolithography and lift-off process and used without further surface modification. The molecules were spin-casted from a chlorobenzene solution and annealed at 80 °C for 10 minutes to remove residual solvent inside a nitrogen purged glovebox. Cytop polymer (AGC Asahi glass) was used as dielectric layer followed by an thermally evaporated gate. The transistors were characterized under a nitrogen atmosphere using a Keithley 4200-SCS.

Electron mobility values μ_e (cm^2/Vs) were extracted from a linear fit of the transfer characteristics in the saturation regime using the following equation:

$$\mu = \left(\frac{\partial \left(I_D\right)^{1/2}}{\partial V_G}\right)^2 \frac{2L}{WC_{ox}}$$

where I_D is the source-drain current [A], V_G the gate voltage [V], W and L are the channel width and length [m], respectively, and C_{ox} [F/m^2] is the dielectric layer capacitance per area unit. The intercept of the linear fit with the gate voltage axis gave V_{th}.

The characteristic device parameters were averaged from several batches of similarly performing devices with varying channel lengths and dielectric thicknesses.

Layer thicknesses were determined by a stylus profiler (DektakXT, Bruker).

Polarized microscopy images were recorded using a Nikon Eclipse LV100Pol microscope under cross polarizes.

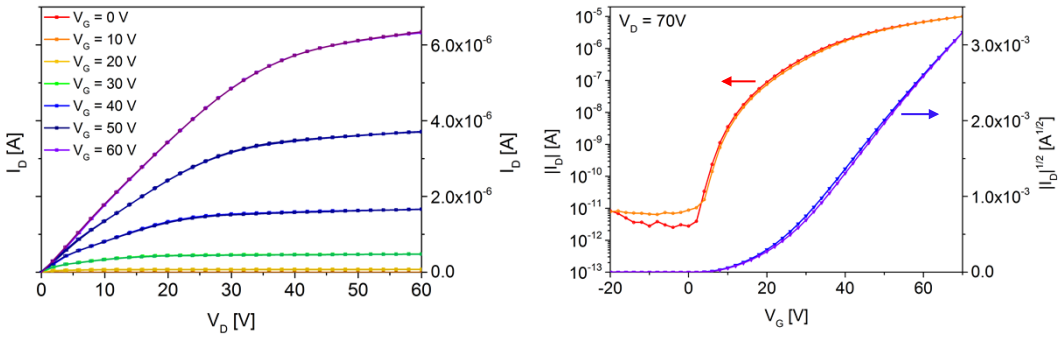


Figure 10: Transfer and output characteristic of a representative thin film transistor with chlorinated phenazinothiodiazol **1c** as active layer at V_D = 70V and W / L = 1000 µm / 50 µm.

7. ^{1}H- ^{19}F- and ^{13}C-NMR spectra

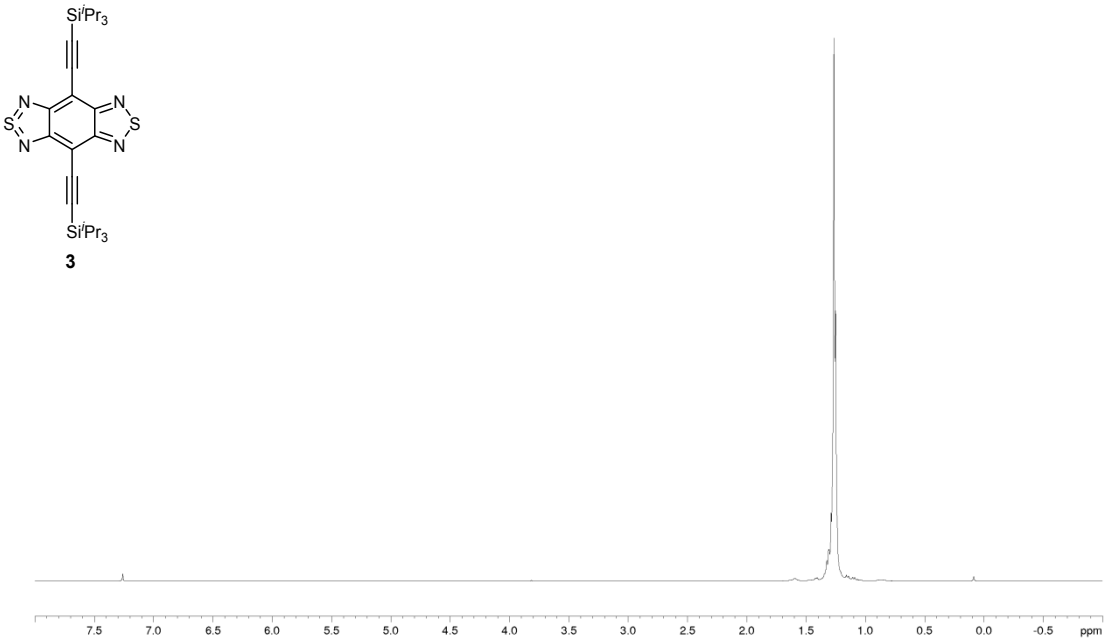


Figure 10: ^{1}H-NMR spectrum of **3**.

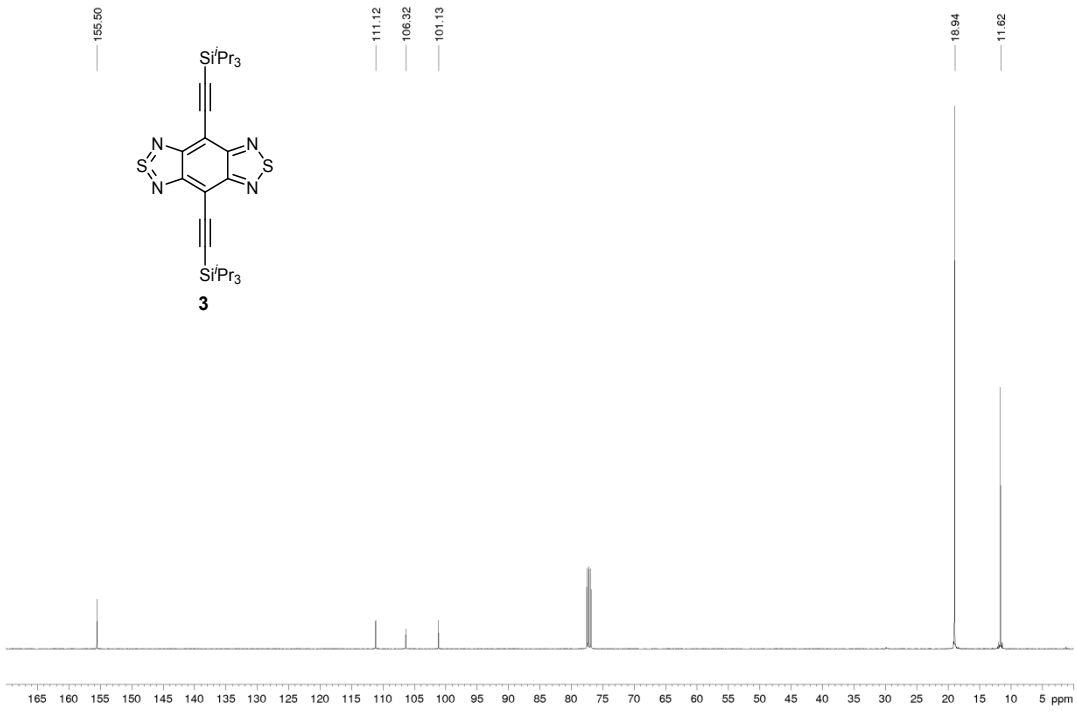


Figure 11: ^{13}C-NMR spectrum of **3**.

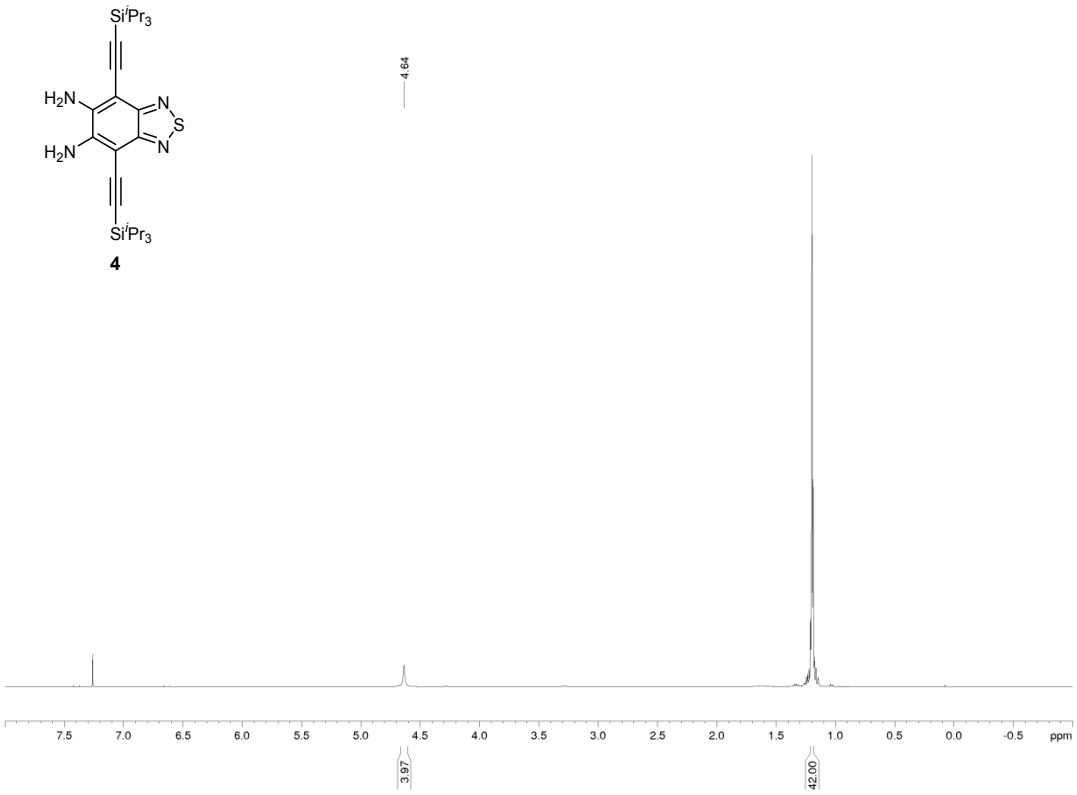


Figure 12: ^{1}H-NMR spectrum of **4**.

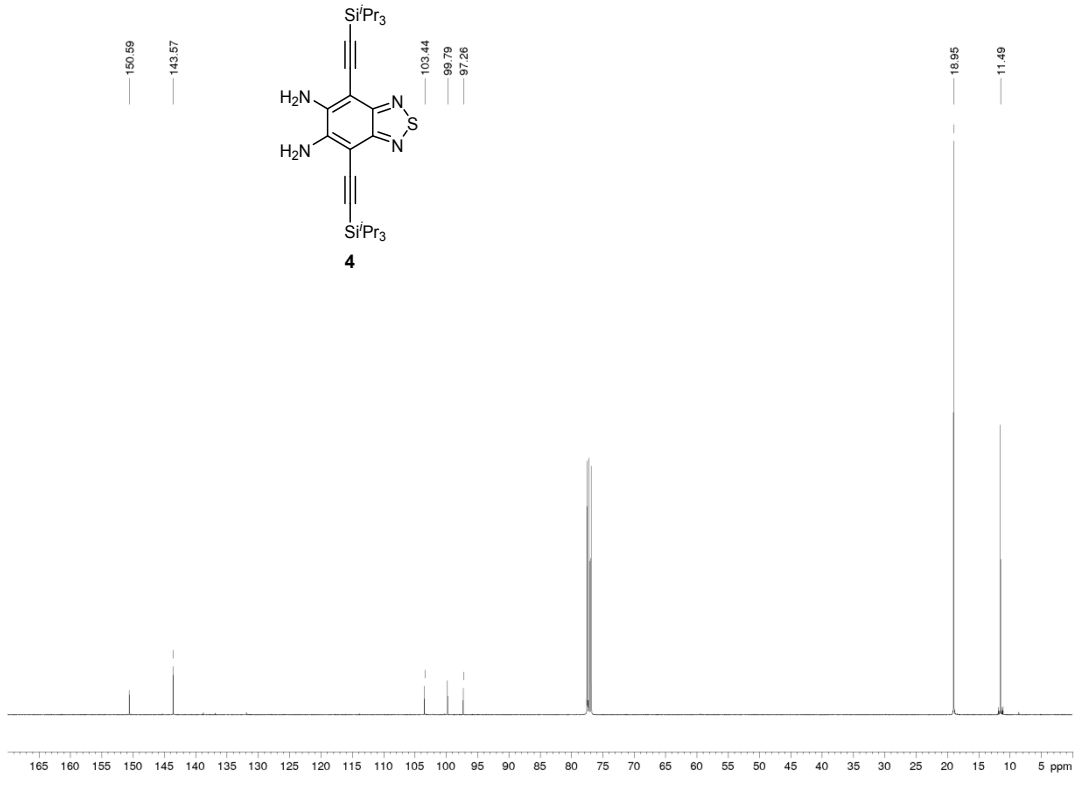


Figure 13: ^{13}C-NMR spectrum of **4**.

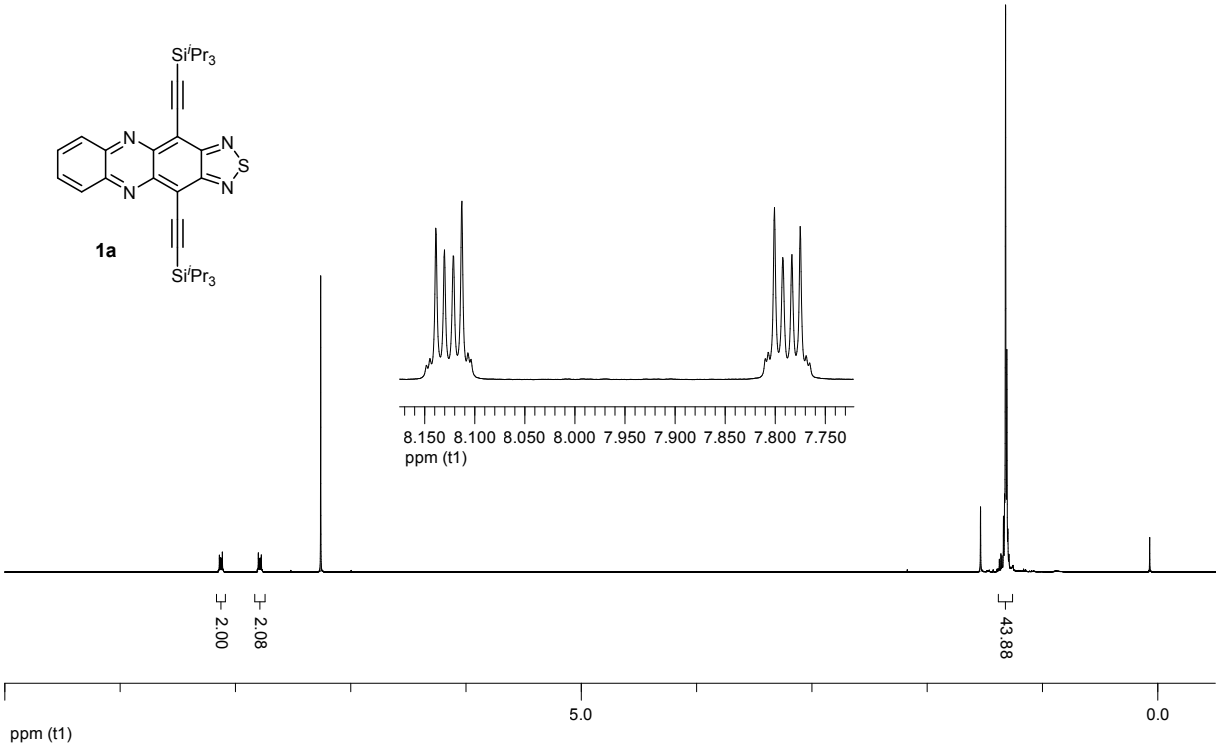


Figure 14: ^{1}H-NMR spectrum of **1a**.

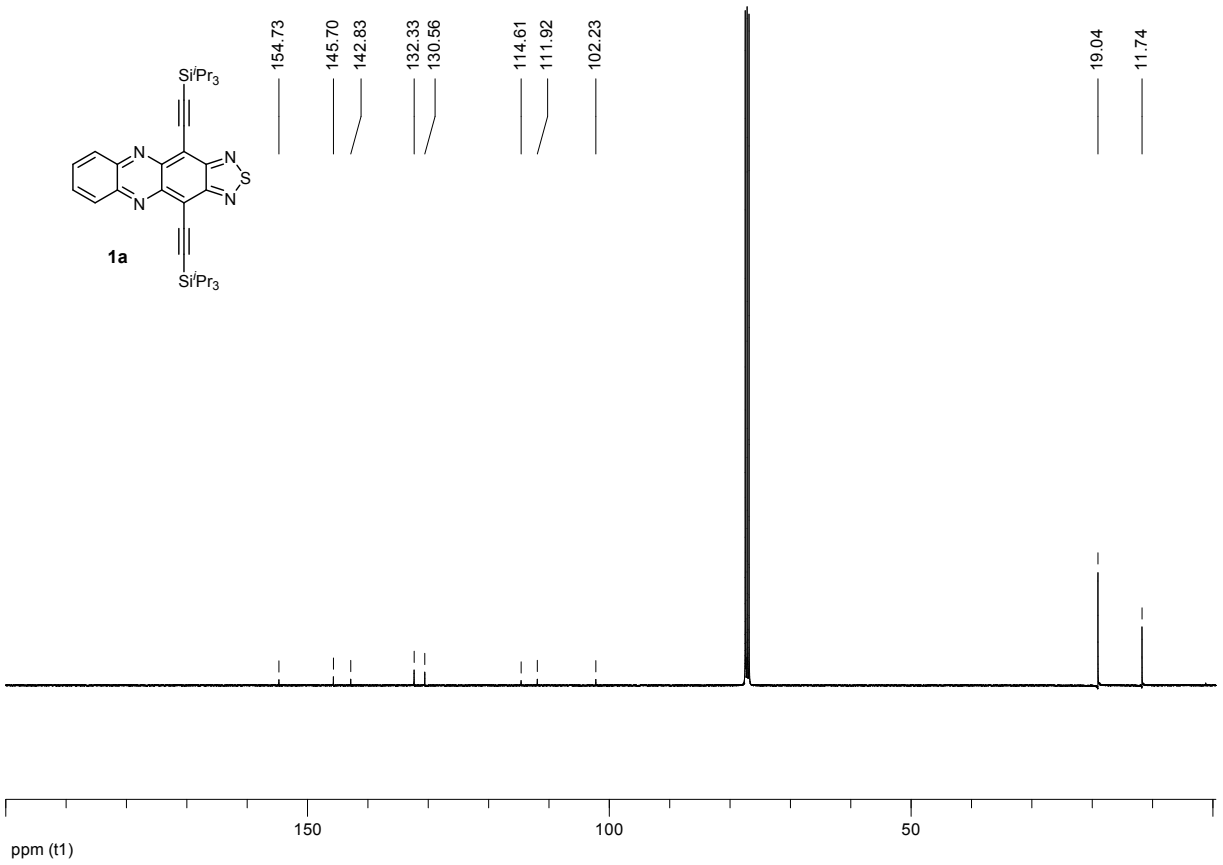


Figure 15: ^{13}C-NMR spectrum of **1a**.

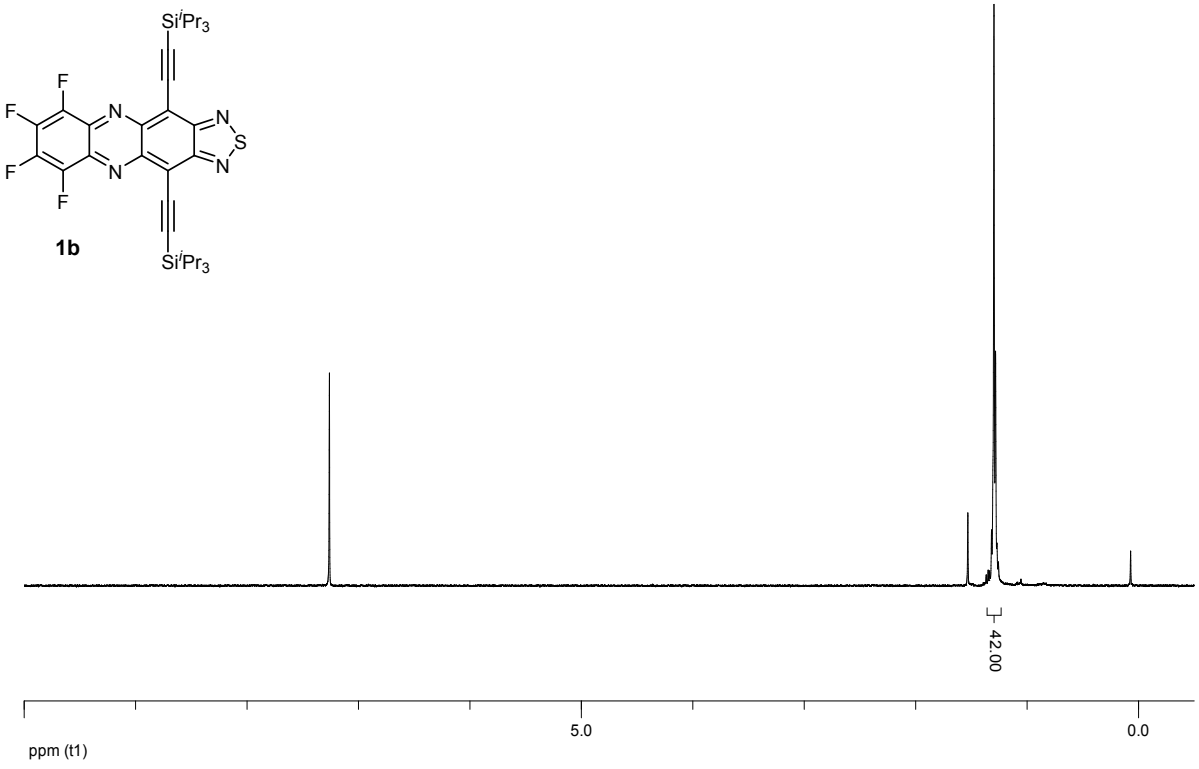


Figure 16: ^{1}H-NMR spectrum of **1b**.

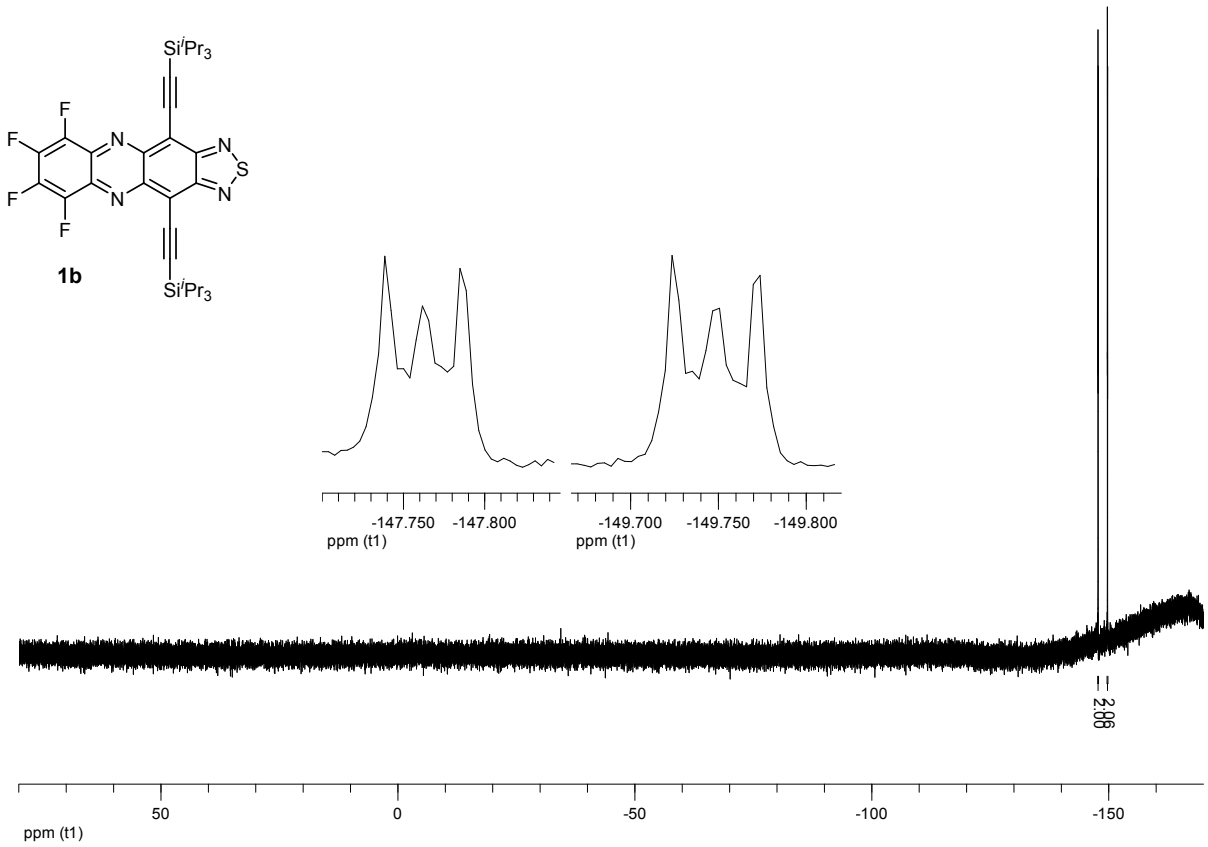


Figure 17: ^{19}F-NMR spectrum of **1b**.

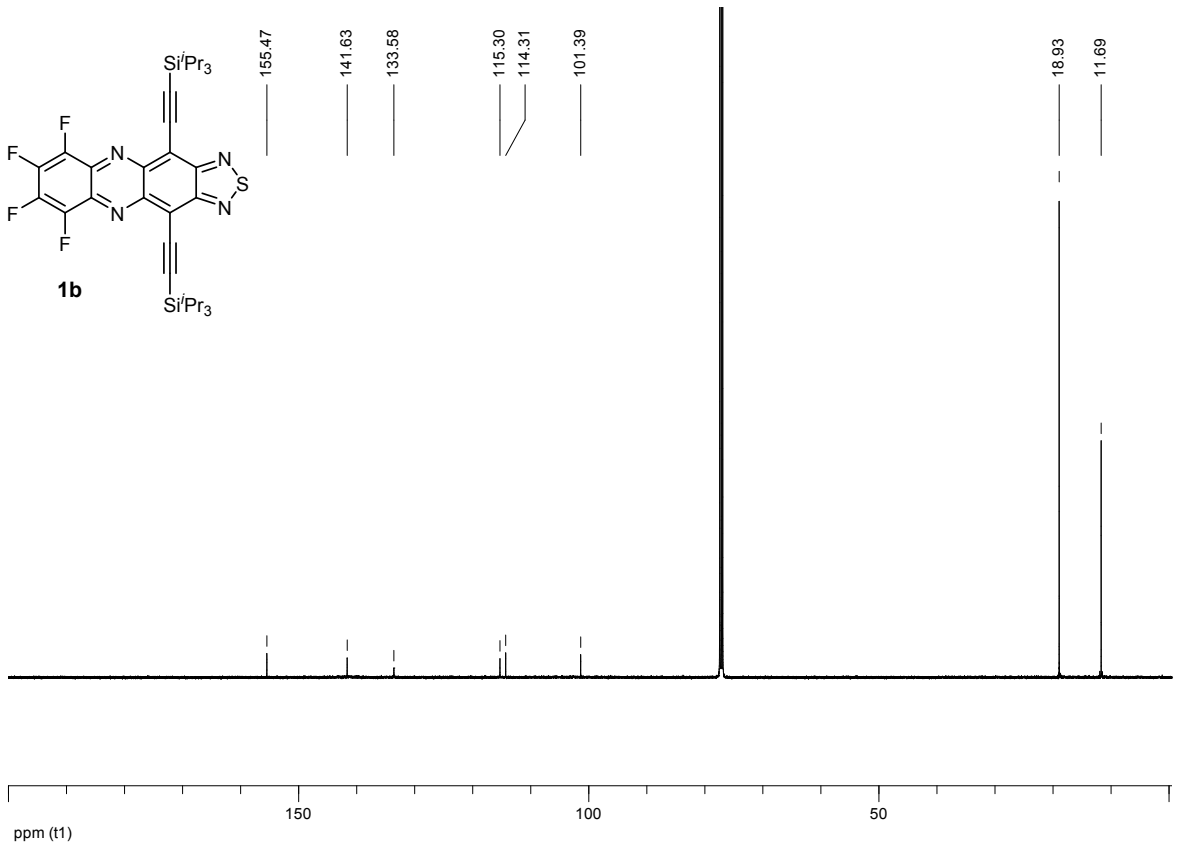


Figure 18: ^{13}C-NMR spectrum of **1b**.

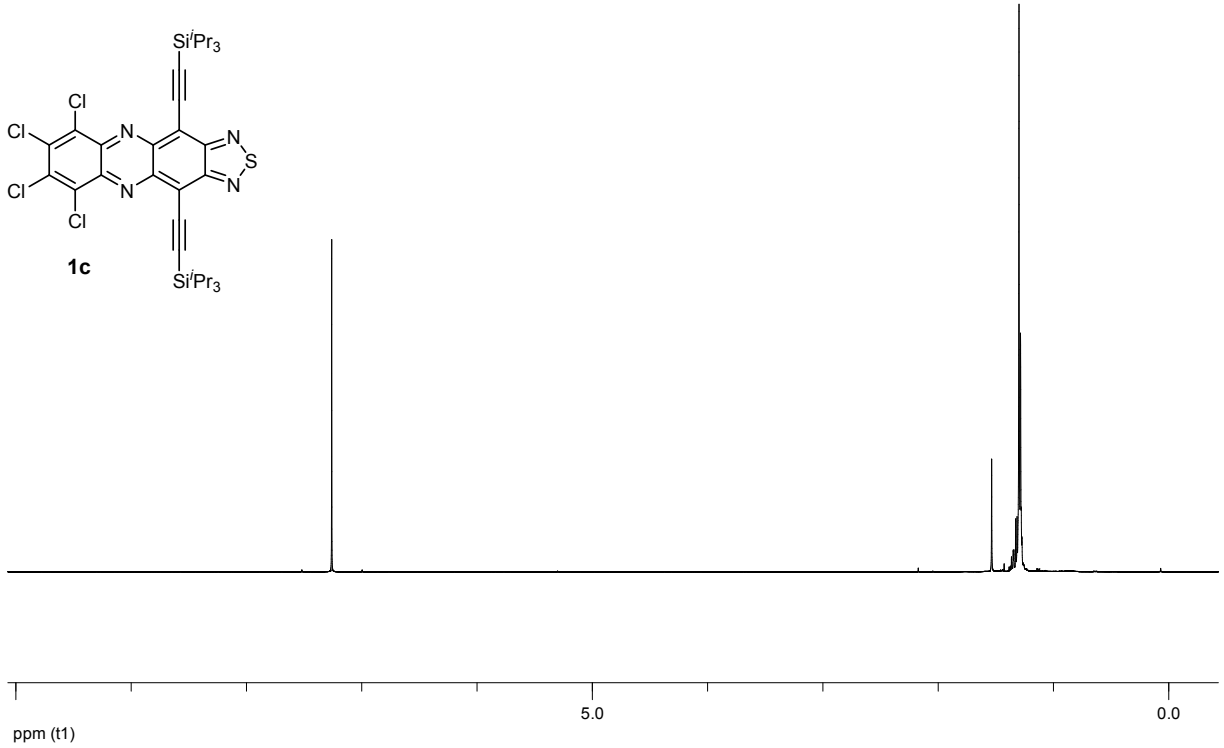


Figure 19: ^{1}H-NMR spectrum of **1c**.

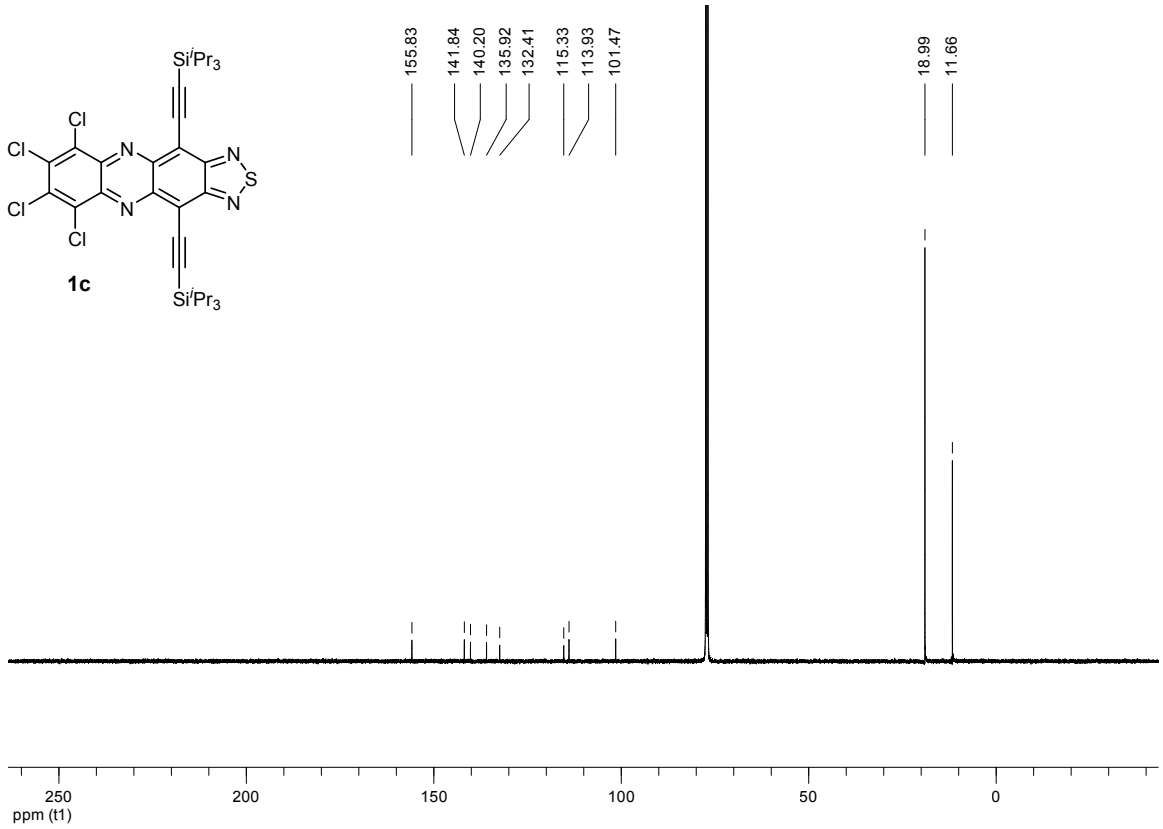


Figure 20: ^{13}C-NMR spectrum of **1c**.

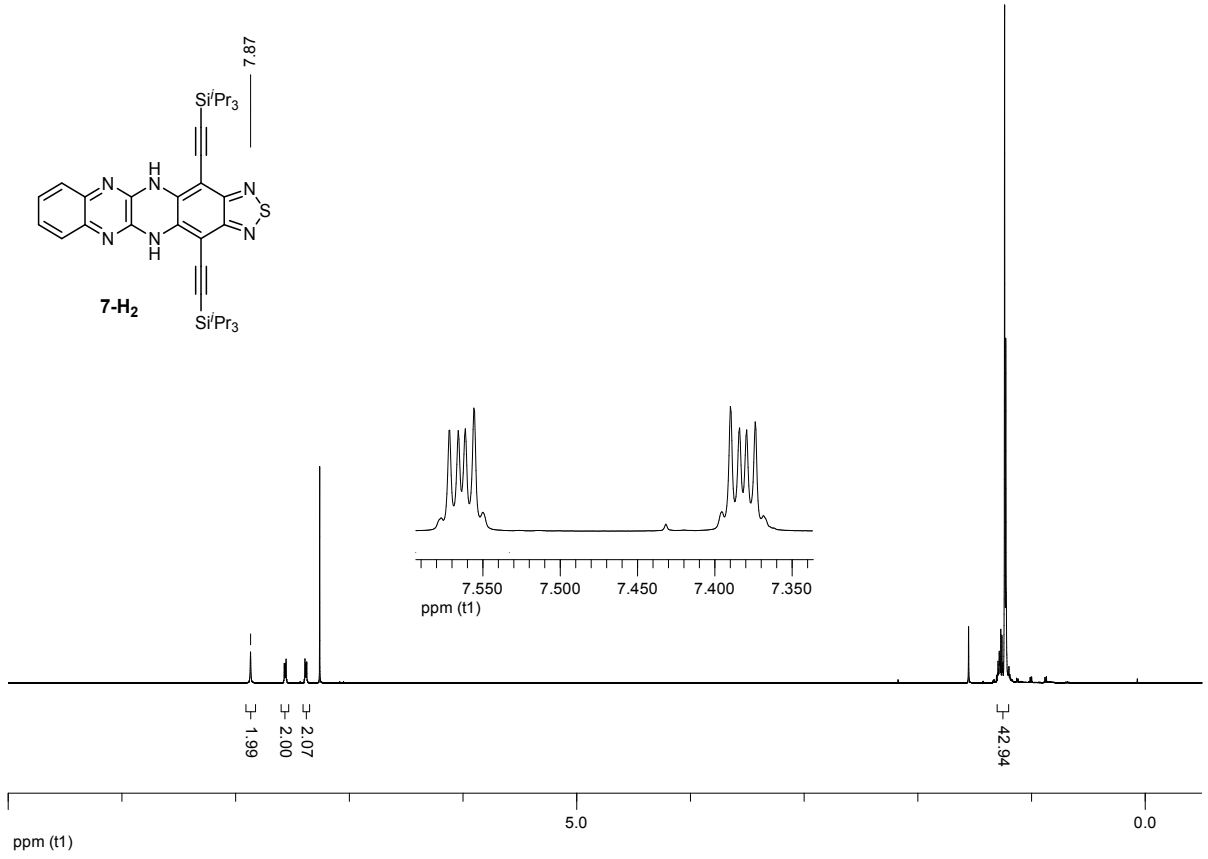


Figure 21: ^{1}H-NMR spectrum of **7-H$_2$**.

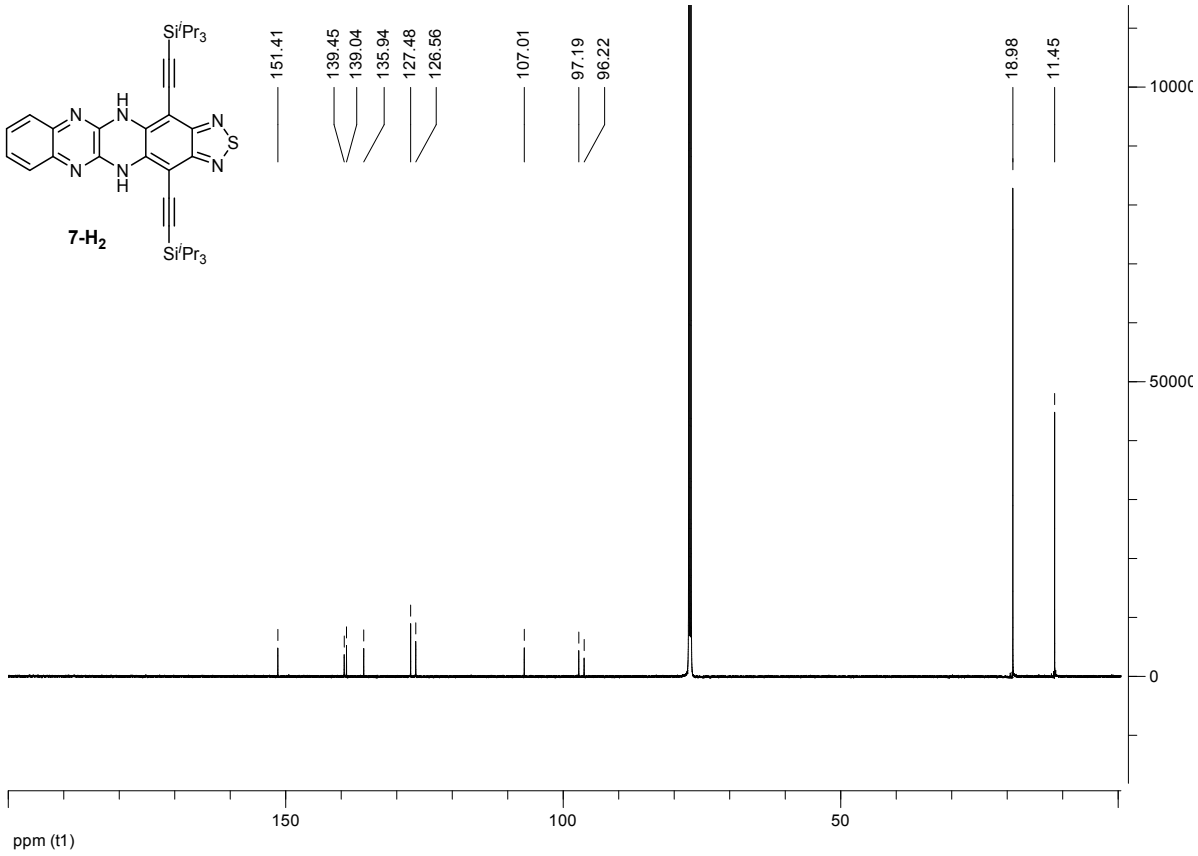


Figure 22: ^{13}C-NMR spectrum of **7-H$_2$**.

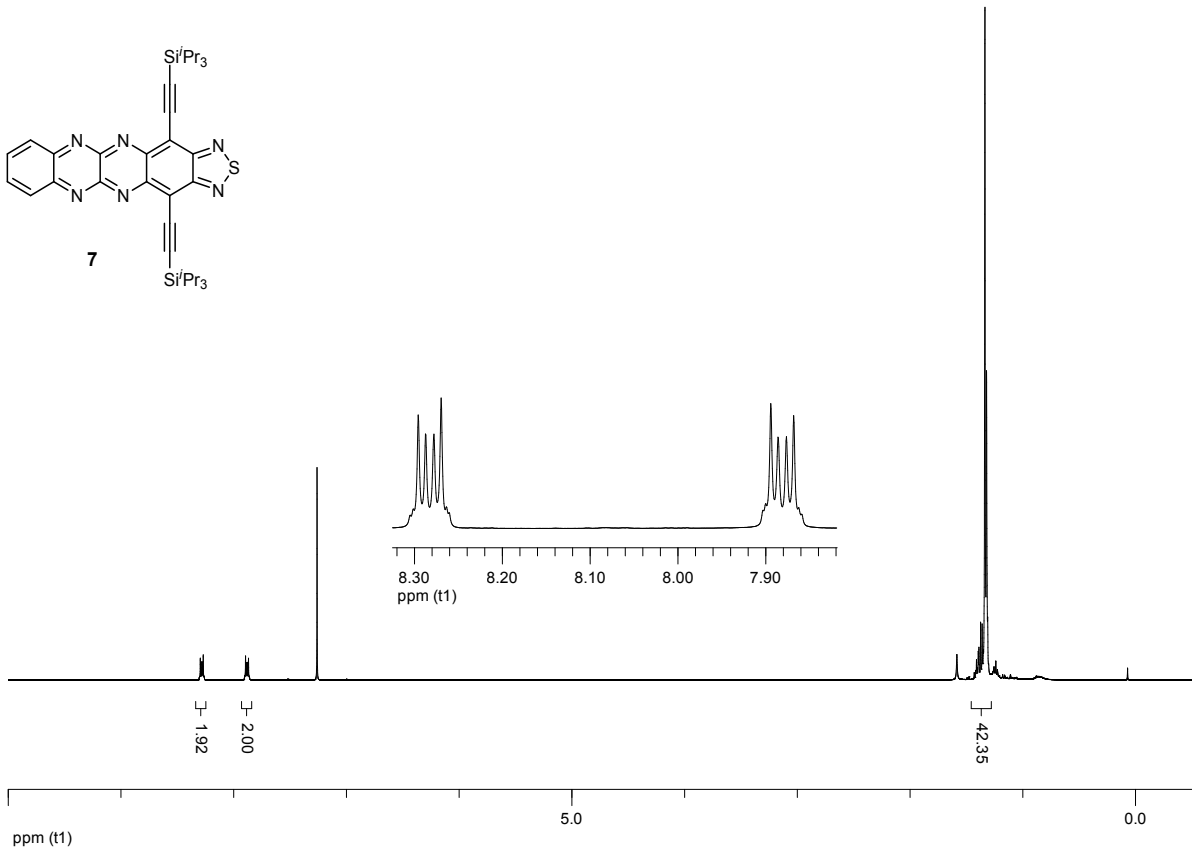


Figure 23: ^{1}H-NMR spectrum of **7**.

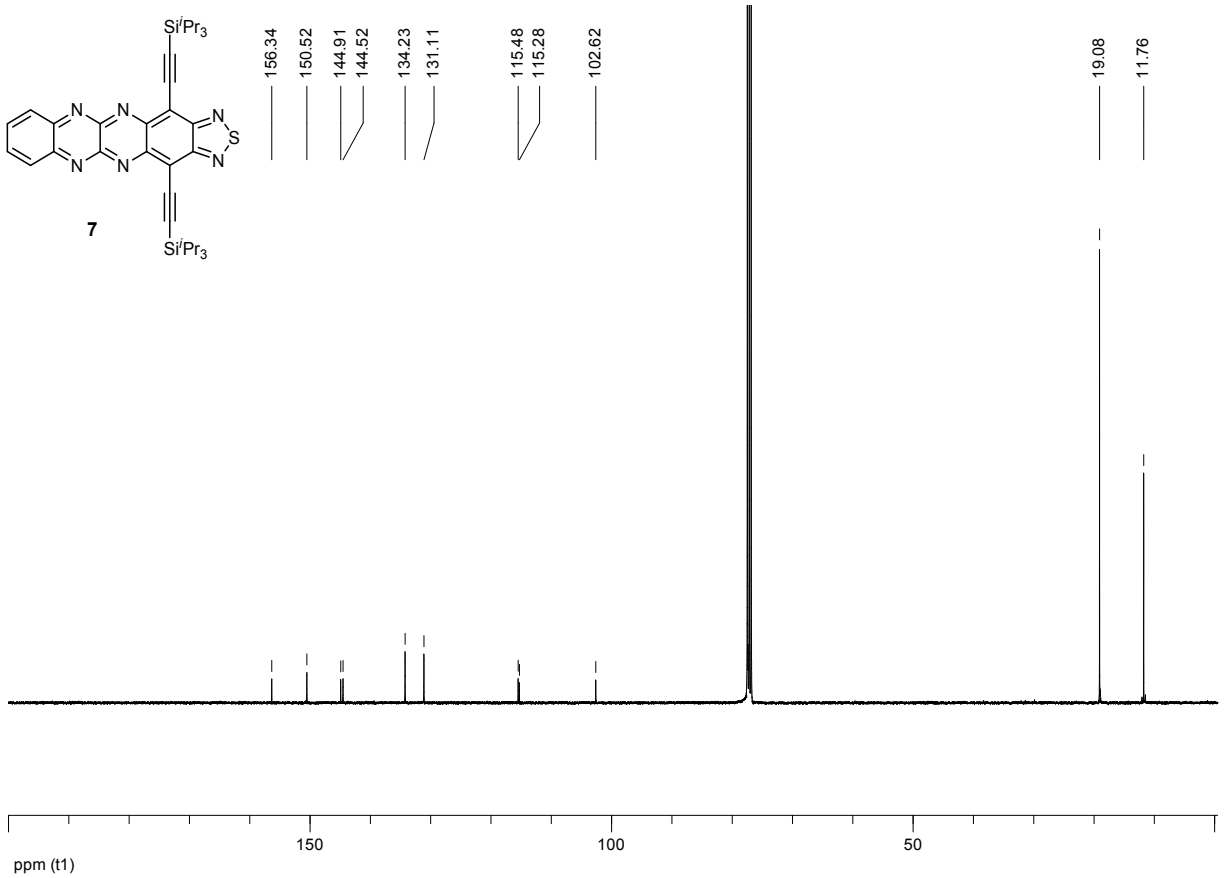


Figure 24: ^{13}C-NMR spectrum of **7**.