

## ELECTRONIC SUPPORTING INFORMATION

### In search of efficient solubilizing groups for liquid and luminescent oligo(phenylene-thiophene) chromophores

Yuriy N. Luponosov<sup>1\*</sup>, Dmitry O. Balakirev<sup>1</sup>, Ivan V. Dyadishchev,<sup>1</sup> Alexander N. Solodukhin<sup>1</sup>,  
Marina A. Obrezkova<sup>1</sup>, Evgeniya A. Svidchenko<sup>1</sup>, Nikolay M. Surin,<sup>1</sup> Sergei A. Ponomarenko<sup>1</sup>

<sup>1</sup>Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences,  
Profsoyuznaya st. 70, Moscow 117393, Russia

\*Corresponding author e-mail: luponosov@ispm.ru (Yu. Luponosov)

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## 1. Experimental part

### 1.1. Materials

1-Bromohexane, 1-bromo-3,5,5-trimethylhexane, 1-bromo-2-butyloctane, 1-bromododecane, trichlorosilane, thiophene, 4,4'-dibromobiphenyl, 1,1,1,3,5,5,5-heptamethylsiloxane, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, *n*-butyllithium (2.5 M solution in hexane) *n*-BuLi, magnesium turnings, palladium chloride (II) PdCl<sub>2</sub>, *tetrakis*(triphenylphosphine)palladium (0) Pd(PPh<sub>3</sub>)<sub>4</sub>, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karsted's catalyst; Pt-cat) were obtained from Sigma-Aldrich Co. and used without further purification. Carbon tetrachloride, THF, toluene, ethanol were dried and purified according to the known techniques and then used as solvents. 1,1,3,3,5,5,7,7-Octamethyltetrasiloxan-1-ol (**4**) was obtained as described in reference [1]. 1-chloro-1,1,3,3,3-pentamethyldisiloxane (**5**) was obtained as described in reference [2]. 2-hexylthiophene (**7a**) was obtained as described in reference [3]. 2-(trimethylsilyl)thiophene (**7d**) was obtained as described in reference [4]. 2-(5-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8a**) was obtained as described in reference [5]. Trimethyl[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl]silane (**8d**) was obtained as described in reference [6]. 2-But-3-en-1-ylthiophene (**9**) was obtained as described in reference [7]. All reactions, unless stated otherwise, were carried out under an inert atmosphere.

### 1.2. Characterization

<sup>1</sup>H NMR spectra were recorded at a "Bruker WP-250 SY" spectrometer, working at a frequency of 250.13 MHz and utilising CDCl<sub>3</sub> signal (7.25 ppm) as the internal standard. <sup>13</sup>C and <sup>29</sup>Si NMR spectra were recorded using a "Bruker Avance II 300" spectrometer at 75 MHz and 60 MHz, respectively. In the case of <sup>1</sup>H NMR spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in CDCl<sub>3</sub>. In the case of <sup>13</sup>C or <sup>29</sup>Si NMR spectroscopy, the compounds to be analyzed were taken in the form of 5% solutions in CDCl<sub>3</sub>. The spectra were then processed on the computer using the ACD Labs software.

Elemental analysis of C, N and H elements was carried out using CHN automatic analyzer CE 1106 (Italy). The settling titration using BaCl<sub>2</sub> was applied to analyze sulfur. Spectrophotometry technique was used for the Si analysis.

In the case of column chromatography, silica gel 60 ("Merck") was taken.

The absorption spectra were recorded on a Shimadzu UV-2501PC (Japan) spectrophotometer in the standard 10 mm photometric quartz cuvette using THF solutions with the concentrations of 10<sup>-5</sup> M. All measurements were carried out at room temperature. A scanning spectrofluorimeter ALS01 M (Russia) with registration in single photon counting mode at successive time intervals

and automatic adjustment of the intensity of the measured emission was used for the registration of photoluminescence spectra (PL). Measurements were carried out for several optical densities in the range from 0.06 to 0.12 absorbance units (correspond to diluted solutions in THF:  $10^{-5}$  –  $10^{-6}$  M) in 10 mm cuvette, measurement geometry –  $90^\circ$ . The PL quantum yield of solutions in THF was determined by comparing with the known quantum yield of the standard - a solution of 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) in cyclohexane (PLQY = 1), using the fluorescence measurement method for optically diluted solutions [8]. To measure the fluorescence spectra of neat liquid luminophores, they were placed between two quartz plates, tightly connected to each other. The thickness of the films varied depending on the required optical density of a given sample. Measurements of the PLQY of neat thin films were carried out in the integrating sphere [9].

Thermogravimetric analysis was carried out in dynamic mode in  $50 \div 700$  °C interval using Mettler Toledo TG50 system equipped with M3 microbalance allowing measuring the weight of samples in 0–150 mg range with 1 µg precision. Heating/cooling rate 10 °C/min was used. Every compound was studied twice: in air and in nitrogen flow of 200 mL/min. DSC scans were obtained with Mettler Toledo DSC30 system with 20 °C/min heating rate in temperature range of -150–280 °C for all compounds. Nitrogen flow of 50 mL/min was used.

The rheological characteristics of the obtained liquid phosphors **TPPT-Si-Hex** and **TPPT-Si-BuOct** in the temperature range from 20 to 100 °C were measured on an MCR-302 rheometer (Anton Paar) in the constant shear strain mode (measuring node cone-plane). Based on the viscosity temperature dependences the activation energy of the viscous flow ( $E_a$ ) was calculated according to the Arrhenius equation:  $\eta = Ae^{E_a/RT}$ , where  $\eta$  - the viscosity, R - the universal gas constant, and T - the temperature expressed in Kelvins.

### 1.3. Synthetic procedures

**Trihexylsilane (2a).** A solution of 1-bromohexane (40.00 g, 242.3 mmol) in 400 mL of anhydrous THF was added dropwise to the suspension of magnesium turnings (5.95 g, 244.9 mmol) in 20 mL of anhydrous THF. The Grignard reagent was refluxed for 1 h and then cooled to 0°C. Afterwards freshly distilled trichlorosilane (7.29 g, 53.8 mmol) was added dropwise to the solution at 0°C. The temperature was then allowed to rise to r.t. and afterwards the reaction was refluxed for other 2 h. Then the reaction mixture was filtered off on a glass filter and washed with petroleum ether. The organic phase was evaporated by distillation and the crude product was purified by a column chromatography on silica gel (eluent: petroleum ether) to give pure product **2a** (14.95 g, 97 %) as a colorless oil.  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.46-0.69 (overlapping peaks, 6H); 0.87 (t,

9H,  $J = 6.71$  Hz); 1.22-1.35 (overlapping peaks, 24H); 3.65 (m,  $M = 7$ , 1H,  $J = 3.36$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 11.35; 14.12; 22.61; 24.67; 31.60; 33.07.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) -6.45.

**Tris(3,5,5-trimethylhexyl)silane (2b)** was obtained as described for compound **2a** using 27.94 g (134.9 mmol) of 1-bromo-3,5,5-trimethylhexane, 170 mL of anhydrous THF, 3.31 g (136.2 mmol) of magnesium and 4.06 g (30.0 mmol) of trichlorosilane to give pure product **2b** (12.20 g, 99%) as a colorless oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.48-0.62 (overlapping peaks, 6H); 0.80-1.41 (overlapping peaks, 51H); 3.63 (m,  $M = 7$ , 1H,  $J = 3.36$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 8.31; 22.15; 30.10; 31.05; 32.11; 34.13; 50.83.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) -4.69.

**Tris(2-butyloctyl)silane (2c)** was obtained as described for compound **2a** using 20.08 g (80.6 mmol) of 1-bromo-2-butyloctane, 120 mL of anhydrous THF, 1.97 g (81.4 mmol) of magnesium and 1.82 g (17.9 mmol) of trichlorosilane to give pure product **2c** (8.74 g, 91%) as a colorless oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.56 (dd, 6H,  $J_1 = 6.71$  Hz,  $J_2 = 3.36$  Hz); 0.84-0.91 (overlapped peaks, 18H); 1.19-1.31 (overlapping peaks, 48H); 1.38-1.48 (overlapping peaks, 3H); 3.85 (m,  $M = 5$ , 1H,  $J = 3.36$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 14.11; 14.18; 18.05; 22.72; 23.09; 26.63; 28.93; 29.74; 31.99; 34.52; 36.16; 36.45.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) -12,94.

**Chloro(trihexyl)silane (3a).** **2a** (14.55 g, 51.1 mmol) was added dropwise to a slurry of  $\text{PdCl}_2$  (0.64 g, 3.6 mmol) in 190 mL of anhydrous carbon tetrachloride. The mixture was refluxed for 2 h and then filtered off under argon stream. Then the solvent was removed by distillation and the residue was dried in vacuum to give pure product **3a** (16.23 g, 99%) as a brown oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.73-0.83 (overlapping peaks, 6H); 0.87 (t, 9H,  $J = 6.70$  Hz); 1.23-1.41 (overlapping peaks, 24H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 14.09; 16.19; 22.54; 22.93; 31.43; 32.84.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) 32.97.

**Chloro[tris(3,5,5-trimethylhexyl)]silane (3b)** was obtained as described for compound **3a** using 12.00 g (29.2 mmol) of compound **2b**, 150 mL of anhydrous carbon tetrachloride and  $\text{PdCl}_2$  (0.36 g, 2.0 mmol) to give pure product **3b** (12.82 g, 98%) as a brown oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm); 0.60-1.07 (overlapping peaks, 45H); 1.11-1.44 (overlapping peaks, 12H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 13.18; 22.05; 30.04; 31.03; 31.84; 32.21; 50.63.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) 34.31.

**Chloro[tris(2-butyloctyl)]silane (3c)** was obtained as described for compound **3a** using 7.00 g (13.0 mmol) of compound **2c**, 91 mL of anhydrous carbon tetrachloride and  $\text{PdCl}_2$  (0.16 g, 0.9 mmol) of to give pure product **3c** (7.11 g, 95%) as a brown oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0,78-0,93 (overlapping peaks, 24H); 1.15-1.33 (overlapping peaks, 48H); 1.60 (overlapping peaks,

3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 14.11; 14.18; 22.70; 23.04; 23.18; 26.42; 28.70; 29.69; 31.96; 36.01; 36.31; 37.72.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) 32.79.

**1,1,1,3,3,5,5,7,7,9,9,11,11-Tridecamethylhexasiloxane (6).** A 40% solution of 1-hydroxynonamethyltetrasiloxane (10 g, 0.055 mol) in dry THF with 6.22 g (0.055 mol) of dry pyridine was added dropwise to a 40% solution of 1-chloro-7-hydroctamethyltetrasiloxane in THF (16 g, 0.055 mol). The reaction mixture was stirred for 6 hours at room temperature. Afterwards the reaction mixture was filtered and the solvent was evaporated by distillation. The residue was purified by vacuum distillation to give **6** (13.5 g, 55%) as a colorless liquid.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.04 (s, 6H); 0.06-0.07 (overlapping peaks, 18H); 0.08 (s, 9H); 0.18 (d, 6H,  $J=2.8$  Hz) 4.74-4.69 (m, 1H,  $M=5$ ,  $J=2.7$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 0.69; 0.85; 1.02; 1.04; 1.14; 1.78.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) 7.29 ( $\underline{\text{Si}}(\text{CH}_3)_3$ ); -6.87 ( $\underline{\text{Si}}(\text{CH}_3)_2\text{H}$ ); -19.82 ( $\underline{\text{Si}}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{H}$ ); -21.33 ( $\underline{\text{Si}}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{H}$ ), -21.80 ( $\underline{\text{Si}}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$ ); -21.97 ( $\underline{\text{Si}}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$ ).

**2-Hexylthiophene (7a)** was obtained as described in reference [3].

**2-Dodecylthiophene (7b).** 2.5 M solution of *n*-butyllithium (76.1 mL, 190.2 mmol) in hexane was added dropwise to solution of thiophene (16.00 g, 190.2 mmol) in 400 mL of anhydrous THF at  $0^\circ\text{C}$ . Afterwards the reaction mixture was stirred for 60 min at r.t. Then 1-bromododecane (47.41 g, 190.2 mmol) was added dropwise to a solution at  $-60^\circ\text{C}$ . The reaction mixture was stirred for 30 min at  $-60^\circ\text{C}$ , then the cooling bath was removed, and the stirring was continued for another 30 min with raising the temperature to r.t. The reaction mixture was poured into distilled water (250 mL) and neutralized with 1 M HCl (190 mL), and then extracted with freshly distilled diethyl ether (600 mL) twice. The combined organic phases were dried over sodium sulfate and filtered. The solvent was evaporated and the crude product was purified by a column chromatography on silica gel (eluent: petroleum ether) to give pure product **7b** (59.31 g, 59%) as a colorless oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.86 (t, 3H,  $J=6.42$  Hz); 1.22-1.35 (overlapped peaks, 18H); 1.66 (m, 2H,  $M=5$ ,  $J=7.63$  Hz); 2.81 (t, 2H,  $J=7.52$  Hz); 6.77 (d, 1H,  $J=3.49$  Hz); 6.90 (dd, 1H,  $J_1=3.35$  Hz,  $J_2=5.18$  Hz); 7.09 (dd, 1H,  $J_1=1.10$  Hz,  $J_2=5.13$  Hz).

**2-(2-Butyloctyl)thiophene (7c)** was obtained as described for compound **7b** using 1.50 g (17.8 mmol) of thiophene, 7.1 mL (17.8 mmol) 2.5 M solution of *n*-butyllithium in hexane, 4.68 g (17.8 mmol) of 1-bromo-2-butyloctane and 38 mL of anhydrous THF to give pure product **7c** (1.53 g, 34%) as a colorless oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.87 (t, 6H,  $J=6.41$  Hz); 1.19-1.37 (overlapping peaks, 16H); 1.56-1.66 (overlapping peaks, 1H); 2.75 (d, 2H,  $J=6.79$  Hz); 6.74 (dd, 1H,  $J_1=1.10$  Hz,  $J_2=3.48$  Hz); 6.90 (dd, 1H,  $J_1=3.48$  Hz,  $J_2=5.13$  Hz); 7.10 (dd, 1H,  $J_1=1.10$

Hz,  $J_2 = 5.14$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 14.10; 14.11; 22.67; 23.00; 26.56; 28.82; 29.64; 31.88; 32.85; 33.18; 34.22; 39.99; 122.88; 124.94; 126.50; 144.31.

**2-(Trimethylsilyl)thiophene (7d)** was obtained as described in reference [4].

**Trihexyl(2-thienyl)silane (7e).** 2.5 M solution of *n*-butyllithium (9.8 mL, 24.6 mmol) in hexane was added dropwise to the solution of thiophene (2.00 g, 24.6 mmol) in 42 mL of anhydrous THF at 0°C. Afterwards the reaction mixture was stirred for 60 min at r.t. Then **3a** (7.85 g, 24.6 mmol) was added dropwise to a solution at -78°C. The reaction mixture was stirred for 30 min at -60°C, then the cooling bath was removed, and the stirring was continued for another 30 min with raising the temperature to r.t. The reaction mixture was poured into distilled water (150 mL) and neutralized with 1 M HCl (25 mL), and then extracted with freshly distilled diethyl ether (200 mL) twice. The combined organic phases were dried over sodium sulfate and filtered. The solvent was evaporated and the crude product was purified by a column chromatography on silica gel (eluent: petroleum ether) to give pure product **7e** (6.99 g, 77%) as a colorless oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.71-0.92 (overlapping peaks, 15H); 1.17-1.40 (overlapping peaks, 24H); 7.16-7.24 (overlapping peaks, 2H); 7.58 (dd, 1H,  $J_1 = 0.91$  Hz,  $J_2 = 4.58$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 13.54; 14.11; 22.61; 23.72; 31.48; 33.37; 127.90; 130.23; 134.45; 137.39.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) -3.90.

**2-thienyl[tris(3,5,5-trimethylhexyl)]silane (7f)** was obtained as described for compound **7e** using 0.9 g (10.7 mmol) of thiophene, 4.3 mL (10.7 mmol) 2.5 M solution of *n*-butyllithium in hexane, 5.01 g (10.7 mmol) of compound **3b** and 23 mL of anhydrous THF to give product **7f** (4.53 g, 86%) as a colorless oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.66-1.47 (overlapping peaks, 57H); 7.17-7.25 (overlapping peaks, 2H); 7.58 (dd, 1H,  $J_1 = 0.91$  Hz,  $J_2 = 4.58$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 10.44; 10.46; 22.11; 30.06; 31.03; 32.24; 33.07; 50.72; 127.88; 130.27; 134.47; 137.21.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) -2.60.

**Tris(2-butyloctyl)(2-thienyl)silane (7g)** was obtained as described for compound **7e** using 2.28 g (27.1 mmol) of thiophene, 10.8 mL (27.1 mmol) 2.5 M solution of *n*-butyllithium in hexane, 15.50 g (27.1 mmol) of compound **3c** and 68 mL of anhydrous THF to give product **7g** (14.37 g, 86%) as a colorless oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.79-0.92 (overlapping peaks, 24H); 1.11-1.33 (overlapping peaks, 48H); 1.47-1.56 (overlapping peaks, 3H); 7.14 (dd, 1H,  $J_1 = 3.05$  Hz,  $J_2 = 4.58$  Hz); 7.23 (dd, 1H,  $J_1 = 0.92$  Hz,  $J_2 = 3.36$  Hz); 7.55 (dd, 1H,  $J_1 = 0.92$  Hz,  $J_2 = 4.58$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 14.12; 14.16; 20.55; 22.72; 23.09; 26.47; 28.77; 29.73; 31.97; 33.89; 36.23; 36.50; 127.73; 130.11; 134.48; 139.15.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) -5.16.

**2-(5-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8a)** was obtained as described in reference [5].

**2-(5-Dodecyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8b)**. 2.5 M solution of *n*-butyllithium (14.48 mL, 36.2 mmol) in hexane was added dropwise to a solution of compound **7b** (9.10 g, 36.2 mmol) in 230 mL of dry THF at -78°C. Afterwards the reaction mixture was stirred for 60 min at -78°C and then isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.70 g, 36.2 mmol) was added in one portion. The reaction mixture was stirred for 30 min at -78 °C, then the cooling bath was removed, and the stirring was continued for another 30 min with raising the temperature to r.t. The reaction mixture was poured into distilled water (100 mL) and neutralized with 1 M HCl (36 mL), and then extracted with freshly distilled diethyl ether (100 mL) twice. The combined organic phases were dried over sodium sulfate and filtered. The solvent was evaporated to give product **8b** (11.70 g, 86%) as a yellowish oil. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 0.87 (t, 3H, *J* = 7.02 Hz); 1.21-1.35 (overlapping peaks, 30H); 1.65 (q, 2H, *J* = 7.63 Hz); 2.82 (m, M = 5, 2H, *J* = 7.63 Hz); 6.85 (d, 1H, *J* = 3.66 Hz); 7.46 (d, 1H, *J* = 3.36 Hz).

**2-[5-(2-butyloctyl)-2-thienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8c)** was obtained as described for compound **8b** using 1.41 g (5.5 mmol) of compound **7c**, 2.2 mL (5.5 mmol) 2.5 M solution of *n*-butyllithium in hexane, 1.09 g (5.5 mmol) of isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 35 mL of anhydrous THF to give product **8c** (14.37 g, 86%) as an yellowish oil. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 0.87 (t, 6H, *J* = 6.97 Hz); 1.21-1.29 (overlapping peaks, 16H); 1.33 (s, 12H); 1.56-1.69 (overlapping peaks, 1H); 2.78 (d, 2H, *J* = 6.61 Hz); 6.82 (d, 1H, *J* = 3.49 Hz); 7.46 (d, 1H, *J* = 3.30 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): (ppm) 14.09; 14.12; 22.66; 22.96; 24.74; 26.56; 28.83; 29.58; 31.87; 32.84; 33.15; 34.42; 39.99; 83.82; 126.82; 137.22; 152.29.

**Trimethyl[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl]silane (8d)** was obtained as described in reference [6].

**Trihexyl[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl]silane (8e)** was obtained as described for compound **8b** using 2.46 g (6.7 mmol) of compound **7e**, 2.7 mL (6.7 mmol) 2.5 M solution of *n*-butyllithium in hexane, 1.25 g (6.7 mmol) of isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 62 mL of anhydrous THF to give product **8e** (2.87 g, 87%) as an yellowish oil. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 0.72-0.90 (overlapping peaks, 15H); 1.19-1.32 (overlapping peaks, 24H); 1.34 (s, 12H); 7.29 (d, 1H, *J* = 3.35 Hz); 7.69 (d, 1H, *J* = 3.36 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): (ppm) 13.47; 14.10; 22.60; 23.66; 24.76; 31.44; 33.37; 83.98; 135.54; 137.77; 145.99. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): (ppm) -3.75.

**[5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl][tris(3,5,5-trimethylhexyl)silane (8f)** was obtained as described for compound **8b** using 3.74 g (7.6 mmol) of compound **7f**, 3.0 mL (7.6 mmol) 2.5 M solution of *n*-butyllithium in hexane, 1.41 g (7.6 mmol) of isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 94 mL of anhydrous THF to give product **8f** (4.37 g, 93%) as a yellowish oil. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 0.64-0.91 (overlapping peaks, 42H); 0.93-1.43 (overlapping peaks, 15H); 1.34 (s, 12H); 7.29 (d, 1H, *J* = 3.31 Hz); 7.69 (d, 1H, *J* = 3.30 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): (ppm) 10.30; 10.35; 10.40; 22.08; 24.77; 30.05; 31.00; 32.23; 32.98; 50.64; 83.99; 135.53; 137.76; 145.83. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): (ppm) -2.43.

**Tris(2-butyloctyl)[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl)silane (8g)** was obtained as described for compound **8b** using 7.25 g (11.7 mmol) of compound **7g**, 4.7 mL (11.7 mmol) 2.5 M solution of *n*-butyllithium in hexane, 2.18 g (11.7 mmol) of isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 217 mL of anhydrous THF to give product **8g** (8.47 g, 97%) as a yellowish oil. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 0.78-0.94 (overlapping peaks, 24H); 1.10-1.32 (overlapping peaks, 48H); 1.34 (s, 12H); 1.46-1.55 (overlapping peaks, 3H); 7.29 (d, 1H, *J* = 3.49 Hz); 7.65 (d, 1H, *J* = 3.30 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): (ppm) 14.12; 14.16; 20.51; 22.71; 23.08; 24.74; 26.42; 28.73; 29.71; 31.96; 33.86; 36.22; 36.46; 83.90; 135.52; 137.68; 148.00. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): (ppm) -4.98.

**2-(5-but-3-en-1-yl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)** was obtained as described for compound **8b** using 8.00 g (58 mmol) of compound **9**, 23.2 mL (58 mmol) 2.5 M solution of *n*-butyllithium in hexane, 10.79 g (58 mmol) of isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 120 mL of anhydrous THF to give product **10** (13.90 g, 91%) as a yellowish oil. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 1.32 (s, 12H); 2.39-2.48 (overlapping peaks, 2H); 2.92-3.00 (overlapping peaks, 2H); 4.97-5.10 (overlapping peaks, 2H); 5.77-5.93 (overlapping peaks, 2H); 6.87 (d, 1H, *J* = 3.40 Hz); 7.46 (d, 1H, *J* = 3.40 Hz).

**2,2'-Biphenyl-4,4'-diylbis(5-but-3-en-1-ylthiophene) (11)**. Degassed solutions of compound **10** (8.45 g, 31.9 mmol) and 4,4'-dibromobiphenyl (3.99 g, 12.8 mmol) in toluene/ethanol mixture (425/63 mL) and 2 M solution of aq. Na<sub>2</sub>CO<sub>3</sub> (64 mL) were added to Pd(PPh<sub>3</sub>)<sub>4</sub> (555 mg, 0.5 mmol). The reaction mixture was stirred at reflux for 12 h. After completion of the reaction, 500 mL of freshly distilled toluene and 250 mL of distilled water were added to the reaction mixture. The organic phase was separated and washed with water. The solvent was evaporated under vacuum, and the crude product was purified by column chromatography on silica gel using toluene as eluent followed by recrystallization from toluene affording compound **10** (3.92 g, 72% yield) as a pale yellow solid. M.p. = 265 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 2.47 (dd, 4H, *J*<sub>1</sub> = 7.32 Hz, *J*<sub>2</sub> = 14.34 Hz); 2.94 (t, 4H, *J* = 7.02 Hz); 4.98-5.17 (overlapping peaks, 4H); 5.89 (ddt, 2H, *J*<sub>1</sub>



= 6.41 Hz,  $J_2 = 10.07$  Hz,  $J_3 = 16.48$  Hz); 6.78 (d, 2H,  $J = 3.66$  Hz); 7.16 (d, 2H,  $J = 3.66$  Hz); 7.61 (s, 8H). Calcd (%) for  $C_{28}H_{26}S_2$ : C, 78.83%; H, 6.14%; S, 15.03%. Found: C, 78.94%; H, 6.01%; S, 15.06%. MALDI-MS: found  $m/z$  426.2; calculated for  $[M]^+$  426.1.

**2,2'-Biphenyl-4,4'-diylbis(5-hexylthiophene) (TPPT-Hex)**. Degassed solutions of compound **8a** (2.70 g, 9.2 mmol) and 4,4'-dibromobiphenyl (1.10 g, 3.5 mmol) in toluene/ethanol mixture (35/8 mL) and 2 M solution of aq.  $Na_2CO_3$  (9 mL) were added to  $Pd(PPh_3)_4$  (265 mg, 0.2 mmol). The reaction mixture was stirred at reflux for 12 h. After completion of the reaction, 50 mL of freshly distilled toluene and 100 mL of distilled water were added to the reaction mixture. The organic phase was separated and washed with water. The solvent was evaporated under vacuum, and the crude product was purified by column chromatography on silica gel using toluene as eluent followed by recrystallization from toluene affording **TPPT-Hex** (1.26 g, 73% yield) as a white solid. M.p. = 260 °C.  $^1H$  NMR (250 MHz,  $CDCl_3$ ): (ppm) 0.83-0.94 (t, 6H,  $J = 6.72$  Hz); 1.26-1.46 (overlapping peaks, 12H); 1.71 (m, M = 5, 4H,  $J = 7.63$  Hz); 2.82 (t, 4H,  $J = 7.63$  Hz); 6.75 (d, 2H,  $J = 3.66$  Hz); 7.16 (d, 2H,  $J = 3.66$  Hz); 7.61 (dd, 8H,  $J_1 = 8.85$  Hz,  $J_2 = 10.38$  Hz). Calcd (%) for  $C_{33}H_{40}S_2$ : C, 79.14%; H, 8.05%; S, 12.80%. Found: C, 79.29%; H, 8.15%; S, 12.61%. MALDI-MS: found  $m/z$  486.1; calculated for  $[M]^+$  486.2.

**2,2'-Biphenyl-4,4'-diylbis(5-dodecylthiophene) (TPPT-Dodec)** was obtained as described for **TPPT-Hex** using compound **8b** (5.00 g, 13.2 mmol), 4,4'-dibromobiphenyl (1.65 g, 5.3 mmol),  $Pd(PPh_3)_4$  (229 mg, 0.2 mmol), toluene/ethanol mixture (125/19 mL) and 2M solution of aq.  $Na_2CO_3$  (13 mL). The crude product was purified by column chromatography on silica gel using toluene as eluent with further recrystallization from toluene affording **TPPT-Dodec** (2.80 g, 81% yield) as a white solid. M.p. = 228 °C.  $^1H$  NMR (250 MHz,  $CDCl_3$ ): (ppm) 0.87 (t, 6H,  $J = 7.02$  Hz); 1.18-1.43 (overlapping peaks, 36H); 1.70 (m, M = 5, 4H,  $J = 7.36$  Hz); 2.82 (t, 4H,  $J = 7.02$  Hz); 6.75 (d, 2H,  $J = 3.36$  Hz); 7.15 (d, 2H,  $J = 3.66$  Hz); 7.56-7.65 (overlapping peaks, 8H). Calcd (%) for  $C_{44}H_{62}S_2$ : C, 80.67%; H, 9.54%; S, 9.79%. Found: C, 80.71%; H, 9.38%; S, 9.65%. MALDI-MS: found  $m/z$  654.4; calculated for  $[M]^+$  654.4.

**2,2'-Biphenyl-4,4'-diylbis[5-(2-butyloctyl)thiophene] (TPPT-BuOct)** was obtained as described for **TPPT-Hex** using compound **8c** (1.90 g, 5.0 mmol), 4,4'-dibromobiphenyl (0.63 g, 2.0 mmol),  $Pd(PPh_3)_4$  (87 mg, 0.1 mmol), toluene/ethanol mixture (48/7 mL) and 2M solution of aq.  $Na_2CO_3$  (5 mL). The crude product was purified by column chromatography on silica gel using hexane as eluent to give **TPPT-BuOct** (0.36 g, 31% yield) as a white solid. M.p. = 41 °C.  $^1H$  NMR (250 MHz,  $CDCl_3$ ): (ppm) 0.86-0.98 (overlapping peaks, 12H); 1.24-1.42 (overlapping peaks, 32H); 1.62-1.75 (overlapping peaks, 2H); 2.79 (d, 4H,  $J = 6.61$  Hz); 6.75 (d, 2H,  $J = 3.48$  Hz); 7.18 (d, 2H,  $J = 3.48$  Hz); 7.63 (dd, 8H,  $J_1 = 8.80$  Hz,  $J_2 = 12.65$  Hz).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):

(ppm) 14.12; 14.15; 22.69; 23.02; 26.60; 28.86; 29.65; 31.90; 32.89; 33.21; 34.65; 39.95; 122.63; 125.75; 126.17; 127.07; 133.80; 138.92; 141.37; 144.40. Calcd (%) for C<sub>44</sub>H<sub>62</sub>S<sub>2</sub>: C, 80.67%; H, 9.54%; S, 9.79%. Found: C, 80.73%; H, 9.42%; S, 9.68%. MALDI-MS: found m/z 654.5; calculated for [M]<sup>+</sup> 654.4.

**[Biphenyl-4,4'-diylbis(thiene-5,2-diyl)]bis(trimethylsilane) (TPPT-Si-Me)** was obtained as described for **TPPT-Hex** using compound **8d** (1.98 g, 7.0 mmol), 4,4'-dibromobiphenyl (0.91 g, 2.9 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (203 mg, 0.2 mmol), toluene/ethanol mixture (36/8 mL) and 2M solution of aq. Na<sub>2</sub>CO<sub>3</sub> (10 mL). The crude product was purified by column chromatography on silica gel using chloroform as eluent with further recrystallization from toluene/ethanol mixture affording **TPPT-Si-Me** (0.78 g, 58% yield) as a white solid. M.p. = 240°C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): 0.35 (s, 18H); 7.23 (d, 2H, *J* = 3.35 Hz); 7.41 (d, 2H, *J* = 3.66 Hz); 7.66 (dd, 8H, *J*<sub>1</sub> = 8.85 Hz, *J*<sub>2</sub> = 18.62 Hz). Calcd (%) for C<sub>26</sub>H<sub>30</sub>S<sub>2</sub>Si<sub>2</sub>: C, 67.47%; H, 6.53%; S, 13.86%; Si, 12.14%. Found: C, 67.61%; H, 6.45%; S, 13.65%; Si, 12.06%. MALDI-MS: found m/z 462.1; calculated for [M]<sup>+</sup> 462.1.

**[Biphenyl-4,4'-diylbis(thiene-5,2-diyl)]bis(trihexylsilane) (TPPT-Si-Hex)** was obtained as described for **TPPT-Hex** using compound **8e** (3.59 g, 7.3 mmol), 4,4'-dibromobiphenyl (0.91 g, 2.9 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (126 mg, 0.1 mmol), toluene/ethanol mixture (89/13 mL) and 2M solution of aq. Na<sub>2</sub>CO<sub>3</sub> (7 mL). The crude product was purified by column chromatography on silica gel using hexane as eluent to give **TPPT-Si-Hex** (2.27 g, 88% yield) as a colorless liquid. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 0.77-0.98 (overlapping peaks, 30H); 1.24-1.48 (overlapping peaks, 48H); 7.20 (d, 2H, *J* = 3.36 Hz); 7.41 (d, 2H, *J* = 3.36 Hz); 7.66 (dd, 8H, *J*<sub>1</sub> = 8.54 Hz, *J*<sub>2</sub> = 20.44 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): (ppm) 13.47; 14.13; 22.63; 23.75; 31.49; 33.40; 124.30; 126.34; 127.16; 133.57; 135.62; 137.72; 139.32; 149.03. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): (ppm) -3.86. Calcd (%) for C<sub>56</sub>H<sub>90</sub>S<sub>2</sub>Si<sub>2</sub>: C, 76.12%; H, 10.27%; S, 7.26%; Si, 6.36%. Found: C, 76.25%; H, 10.31%; S, 7.18%; Si, 6.32%. MALDI-MS: found m/z 882.6; calculated for [M]<sup>+</sup> 882.6.

**[Biphenyl-4,4'-diylbis(thiene-5,2-diyl)]bis[tris(3,5,5-trimethylhexyl)silane] (TPPT-Si-MeHex)** was obtained as described for **TPPT-Hex** using compound **8f** (2.00 g, 3.2 mmol), 4,4'-dibromobiphenyl (0.40 g, 1.3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (56 mg, 0.1 mmol), toluene/ethanol mixture (50/7 mL) and 2M solution of aq. Na<sub>2</sub>CO<sub>3</sub> (3 mL). The crude product was purified by column chromatography on silica gel using hexane as eluent to give **TPPT-Si-MeHex** (1.28 g, 87% yield) as a white solid. M.p. = 53°C <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 0.72-1.06 (overlapping peaks, 88H); 1.10-1.48 (overlapping peaks, 26H); 7.19 (d, 2H, *J* = 3.66 Hz); 7.41 (d, 2H, *J* = 3.36 Hz); 7.66 (dd, 8H, *J*<sub>1</sub> = 8.54 Hz, *J*<sub>2</sub> = 19.53 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): (ppm) 10.40; 22.13; 30.08; 31.05; 32.27; 33.09; 50.74; 124.31; 126.36; 127.18; 133.60; 135.65; 137.56; 139.35;

149.05. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): (ppm) -2.55. Calcd (%) for C<sub>74</sub>H<sub>126</sub>S<sub>2</sub>Si<sub>6</sub>: C, 78.23%; H, 11.18%; S, 5.64%; Si, 4.94%. Found: C, 78.39%; H, 11.06%; S, 5.58%; Si, 4.91%. MALDI-MS: found m/z 1135.0; calculated for [M]<sup>+</sup> 1134.9.

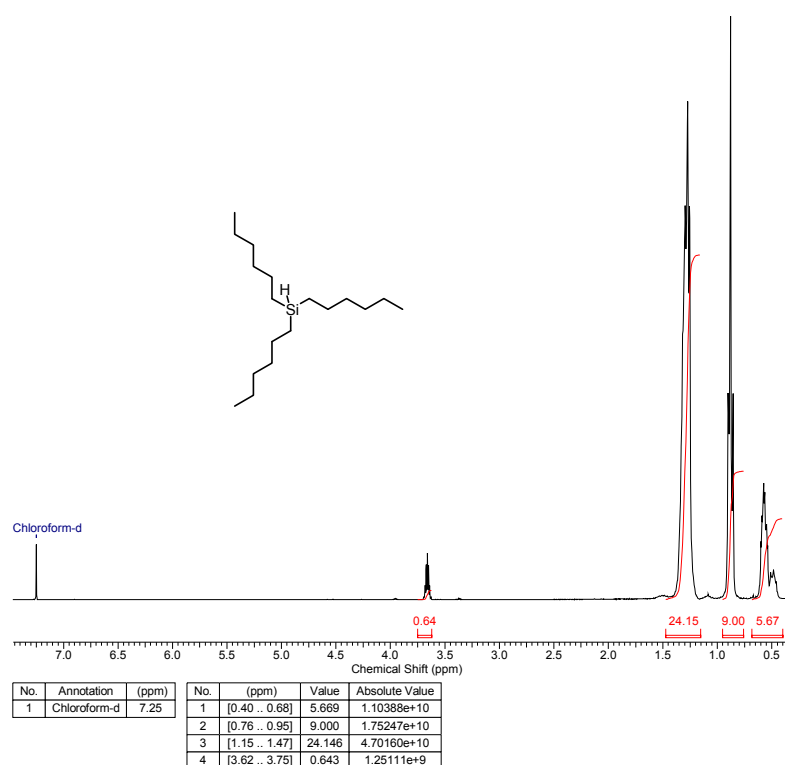
**[Biphenyl-4,4'-diylbis(thiene-5,2-diyl)]bis[tris(2-butyloctyl)silane] (TPPT-Si-BuOct)** was obtained as described for TPPT-Hex using compound **8g** (3.00 g, 4.0 mmol), 4,4'-dibromobiphenyl (0.50 g, 1.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (140 mg, 0.1 mmol), toluene/ethanol mixture (75/11 mL) and 2M solution of aq. Na<sub>2</sub>CO<sub>3</sub> (4 mL). The crude product was purified by column chromatography on silica gel using hexane as eluent to give TPPT-Si-BuOct (1.81 g, 81% yield) as a colorless liquid. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 0.80-0.94 (overlapping peaks, 48H); 1.14-1.33 (overlapping peaks, 96H); 1.53-1.67 (overlapping peaks, 6H); 7.22 (d, 2H, *J* = 3.49 Hz); 7.40 (d, 2H, *J* = 3.48 Hz); 7.67 (dd, 8H, *J*<sub>1</sub> = 8.44 Hz, *J*<sub>2</sub> = 23.84 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): (ppm) 14.12; 14.19; 20.46; 22.73; 23.10; 26.50; 28.80; 29.76; 32.00; 33.93; 36.28; 36.53; 124.16; 126.28; 127.14; 133.72; 135.65; 139.31; 139.62; 148.90. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): (ppm) -5.13. Calcd (%) for C<sub>92</sub>H<sub>162</sub>S<sub>2</sub>Si<sub>6</sub>: C, 79.58%; H, 11.76%; S, 4.62%; Si, 4.05%. Found: C, 79.69%; H, 11.63%; S, 4.51%; Si, 3.94%. MALDI-MS: found m/z 1387.2; calculated for [M]<sup>+</sup> 1387.2.

**trimethyl-[methyl-[4-[5-[4-[4-[5-[4-[methyl-bis(trimethylsilyloxy)silyl]butyl]-2-thienyl]phenyl]phenyl]-2-thienyl]butyl]-trimethylsilyloxy-silyl]oxy-silane (TPPT-Bu-3SiO).** Karstedt's catalyst (27 μL) was added to a solution of 1,1,1,3,5,5,5-heptamethylsiloxane (2.23 g, 10.0 mmol) and compound **11** (1.05 g, 2.5 mmol) in dry toluene (27 mL) at room temperature. The reaction mixture was stirred overnight. The reaction mixture was passed through a thin layer of silica gel after the reaction completion. The solvent was evaporated under vacuum, and the crude product was purified by column chromatography on silica gel using cyclohexane as eluent affording TPPT-Bu-3SiO (0.69 g, 32% yield) as a pale yellow solid. M.p. = 95°C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): (ppm) 0.03 (s, 6H); 0.11 (s, 36H); 0.48-0.59 (overlapping peaks, 4H); 1.39-1.51 (overlapping peaks, 4H); 1.69-1.80 (overlapping peaks, 4H); 2.84 (t, 4H, *J* = 7.50 Hz); 6.76 (d, 2H, *J* = 3.1 Hz); 7.14 (d, 2H, *J* = 3.3 Hz); 7.57-7.67 (overlapping peaks, 8H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): (ppm) -0.23; 1.87; 17.33; 22.63; 29.99; 35.04; 122.73; 125.10; 125.81; 127.09; 133.82; 138.93; 141.18; 145.77. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>): (ppm) -4.98; 7.11. Calcd (%) for C<sub>42</sub>H<sub>70</sub>O<sub>4</sub>S<sub>2</sub>Si<sub>6</sub>: C, 57.87%; H, 8.09%; O, 7.34%; S, 7.36%; Si, 19.33%. Found: C, 57.99%; H, 7.99%; S, 7.25%; Si, 19.21%. MALDI-MS: found m/z 870.3; calculated for [M]<sup>+</sup> 870.4.

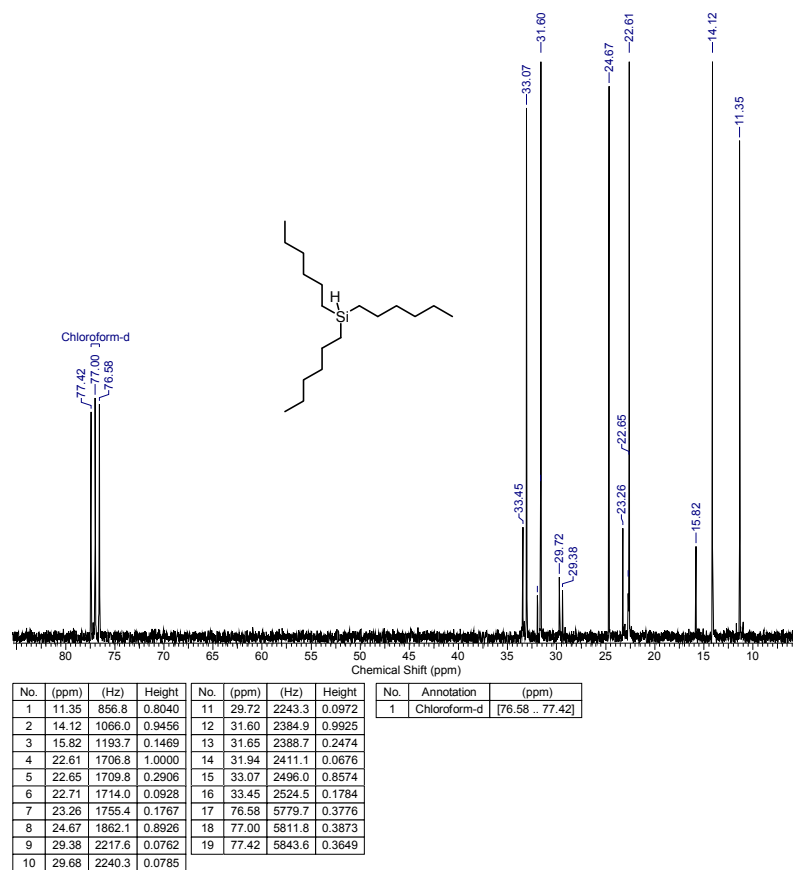
**1,1'-[biphenyl-4,4'-diylbis(thiene-5,2-diylbutane-4,1-diyl)]bis(1,1,3,3,5,5,7,9,9,11,11,11-dodecamethylhexasiloxane) (TPPT-Bu-6SiO)** was obtained as described for compound TPPT-Bu-3SiO using 0.55 g (1.3 mmol) of compound **11**, 1.56 g (3.0 mmol) of compound **6**, dry toluene (14 mL) and Karstedt's catalyst (14 μL). The reaction mixture was stirred for 90 min at 80°C. The

crude product was purified by column chromatography on silica gel using cyclohexane as eluent affording **TPPT-Bu-6SiO** (0.94 g, 45% yield) as a pale yellow solid. M.p. = 85°C.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ): (ppm) 0.07 (s, 24H); 0.10 (s, 24H); 0.10 (s, 12H); 0.11 (s, 18H); 0.58-0.66 (overlapping peaks, 4H); 1.41-1.52 (overlapping peaks, 4H); 1.70-1.81 (overlapping peaks, 4H); 2.84 (t, 4H,  $J = 7.50$  Hz); 6.76 (d, 2H,  $J = 3.5$  Hz); 7.17 (d, 2H,  $J = 3.5$  Hz); 7.58-7.66 (overlapping peaks, 8H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): (ppm) 0.22; 1.09; 1.17; 1.80; 17.96; 22.80; 29.99; 35.29; 122.73; 125.07; 125.80; 127.09; 133.80; 138.95; 141.18; 145.78.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ ): (ppm) -22.00; -21.97; -21.40; -21.27; 7.35; 7.48. Calcd (%) for  $\text{C}_{54}\text{H}_{106}\text{O}_{10}\text{S}_2\text{Si}_{12}$ : C, 49.26%; H, 8.12%; O, 12.15%; S, 4.87%; Si, 25.60%. Found: C, 49.38%; H, 8.22%; S, 4.79%; Si, 25.49%. MALDI-MS: found  $m/z$  1314.4; calculated for  $[\text{M}]^+$  1314.5.

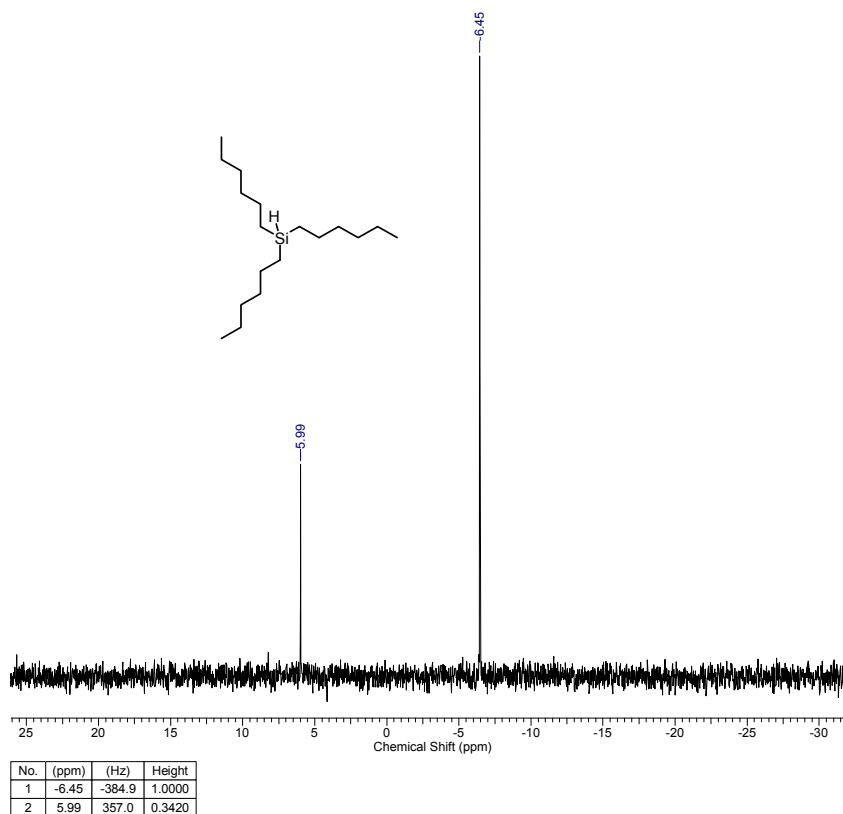
## 2. $^1\text{H}$ , $^{13}\text{C}$ and $^{29}\text{Si}$ NMR spectra



**Figure S1.**  $^1\text{H}$  NMR spectrum of **2a** in  $\text{CDCl}_3$



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of **2a** in  $\text{CDCl}_3$



**Figure S3.**  $^{29}\text{Si}$  NMR spectrum of **2a** in  $\text{CDCl}_3$

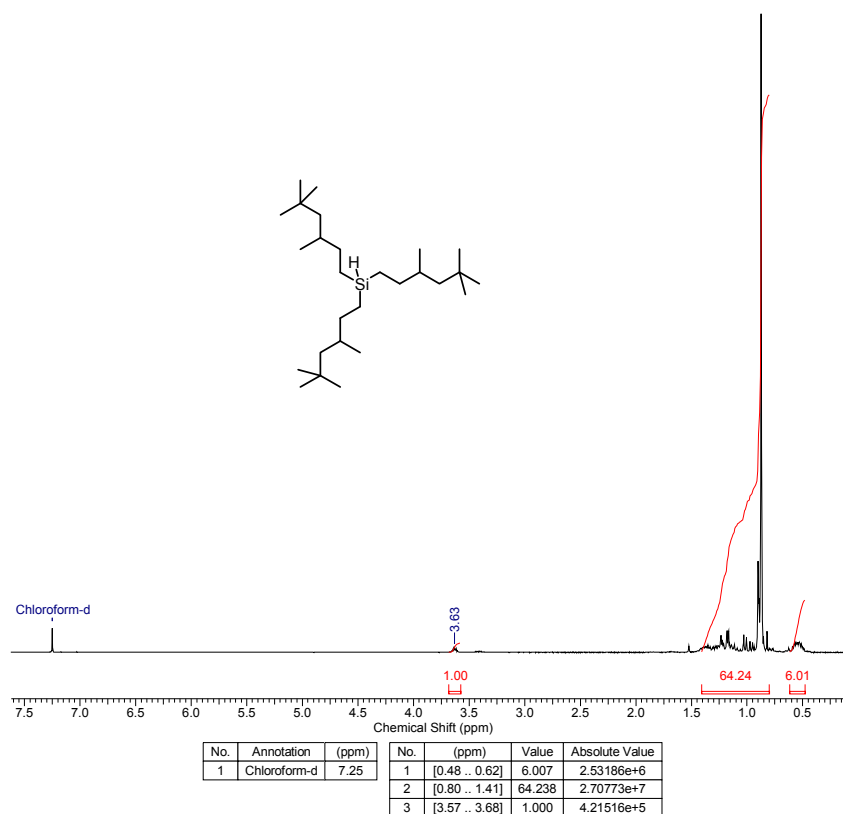


Figure S4.  $^1\text{H}$  NMR spectrum of **2b** in  $\text{CDCl}_3$

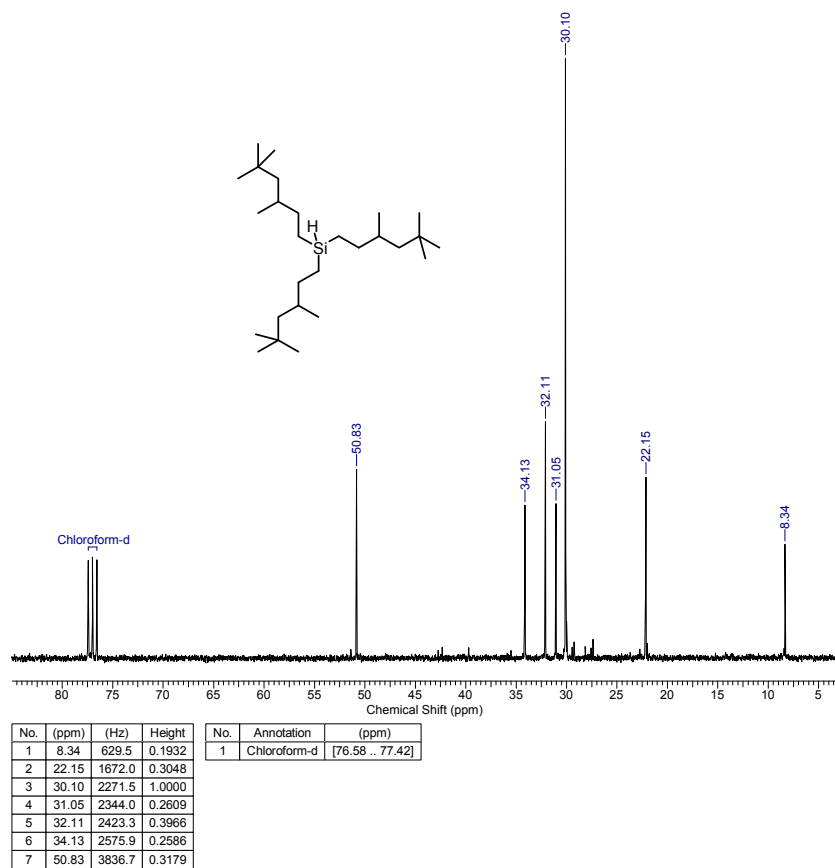


Figure S5.  $^{13}\text{C}$  NMR spectrum of **2b** in  $\text{CDCl}_3$

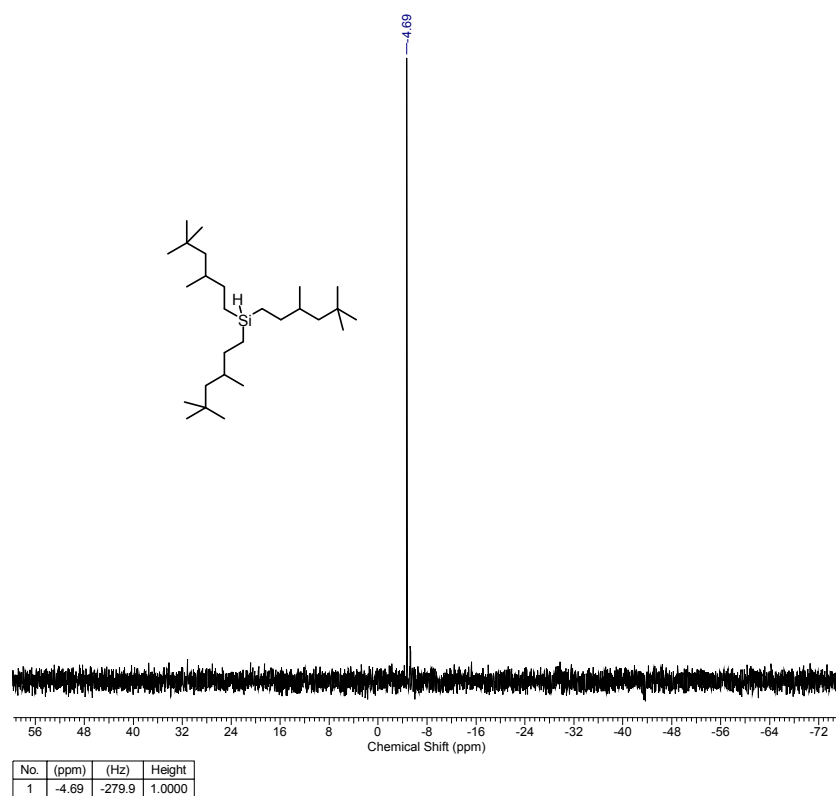


Figure S6.  $^{29}\text{Si}$  NMR spectrum of **2b** in  $\text{CDCl}_3$

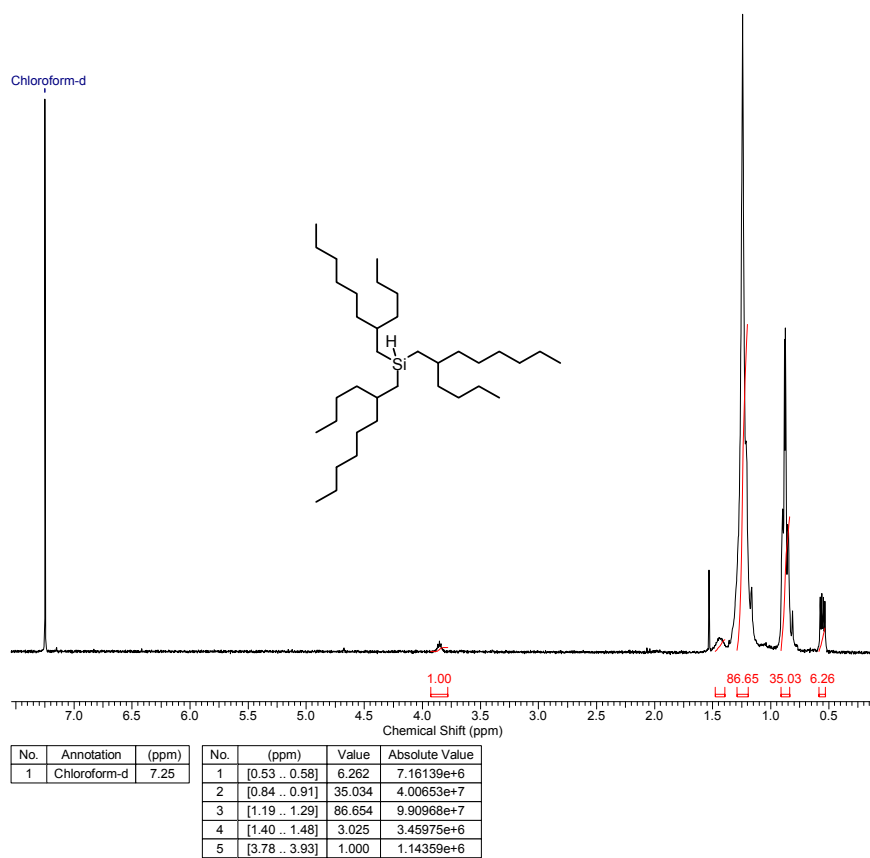
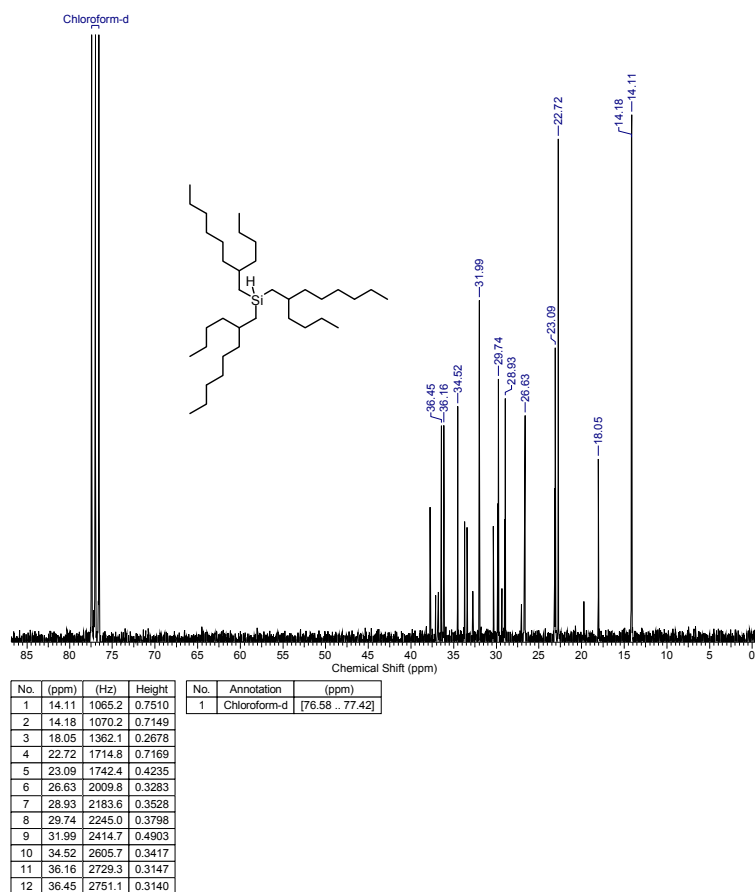
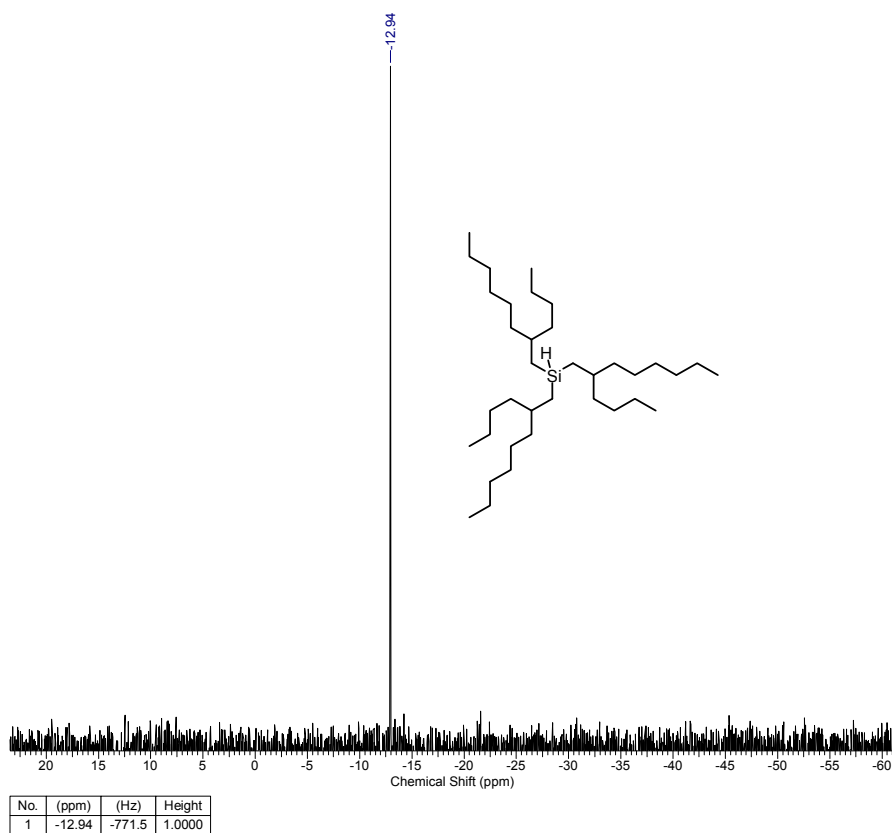


Figure S7.  $^1\text{H}$  NMR spectrum of **2c** in  $\text{CDCl}_3$



**Figure S8.**  $^{13}\text{C}$  NMR spectrum of **2c** in  $\text{CDCl}_3$



**Figure S9.**  $^{29}\text{Si}$  NMR spectrum of **2c** in  $\text{CDCl}_3$



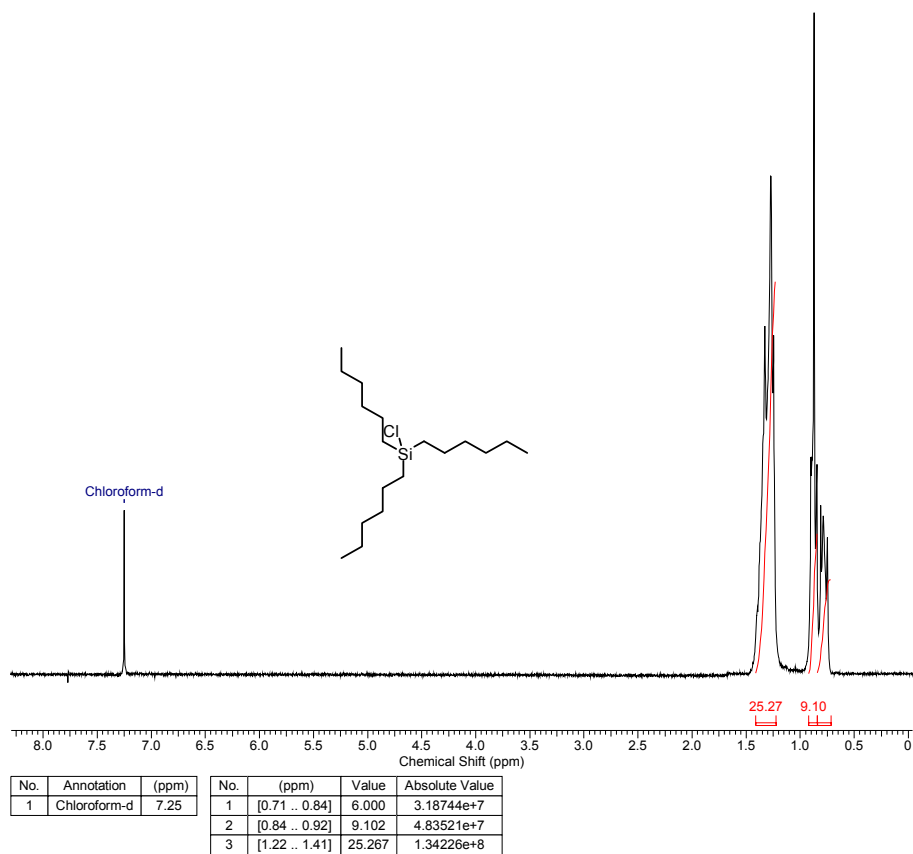


Figure S10. <sup>1</sup>H NMR spectrum of **3a** in CDCl<sub>3</sub>

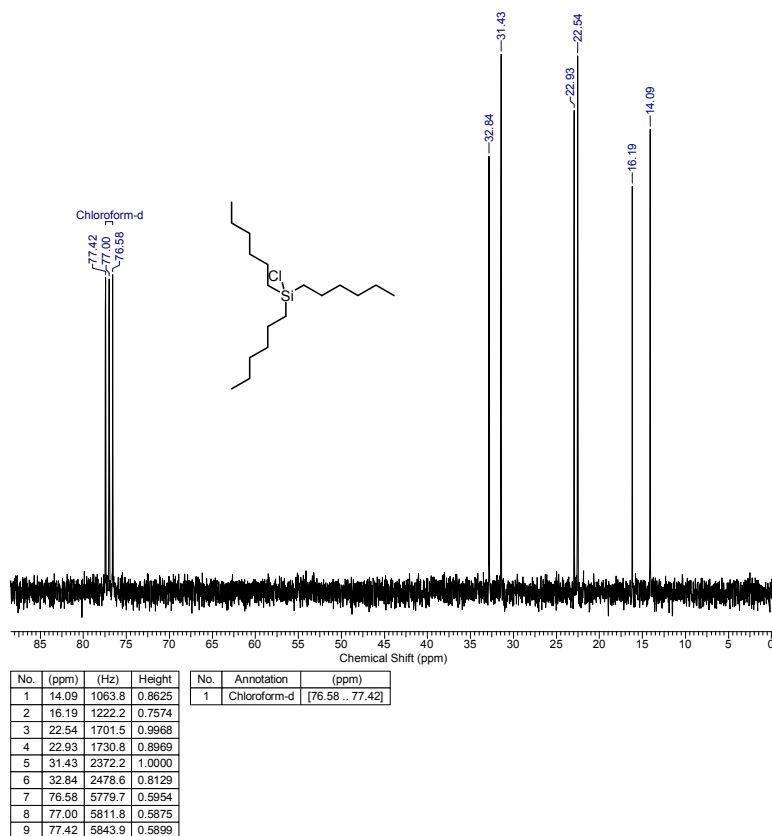


Figure S11. <sup>13</sup>C NMR spectrum of **3a** in CDCl<sub>3</sub>

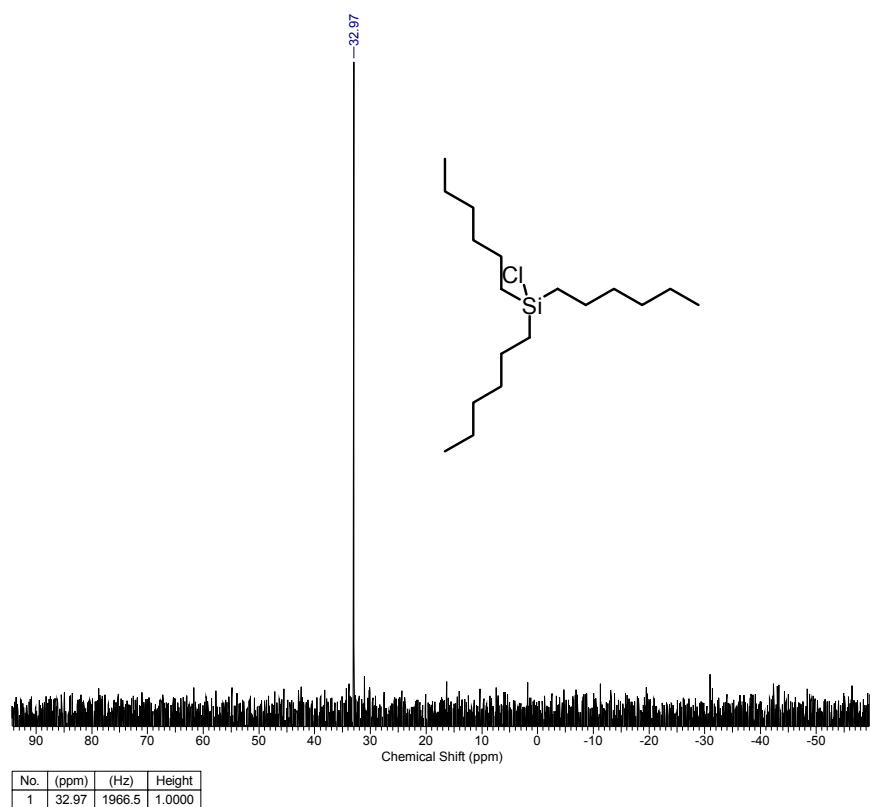


Figure S12.  $^{29}\text{Si}$  NMR spectrum of **3a** in  $\text{CDCl}_3$

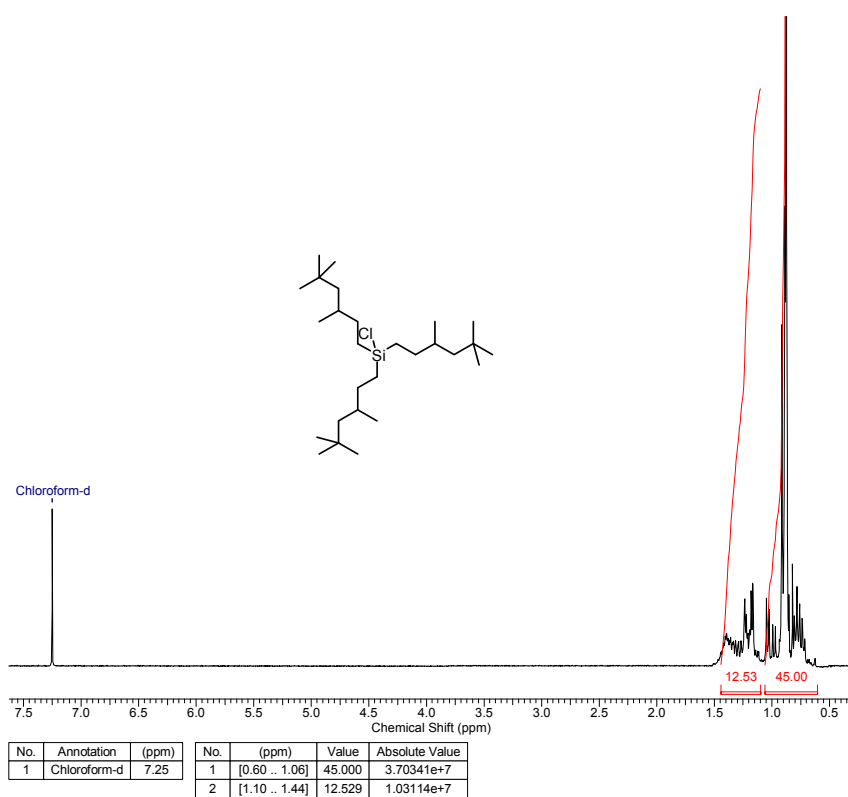


Figure S13.  $^1\text{H}$  NMR spectrum of **3b** in  $\text{CDCl}_3$

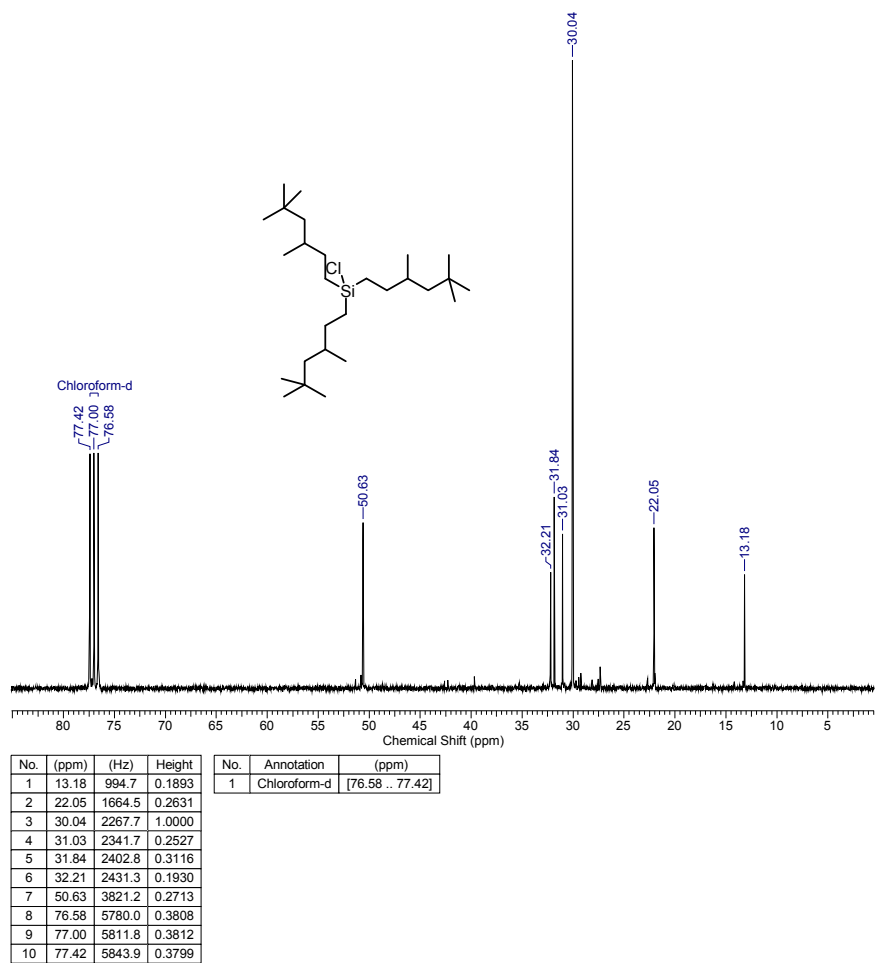


Figure S14.  $^{13}\text{C}$  NMR spectrum of **3b** in  $\text{CDCl}_3$

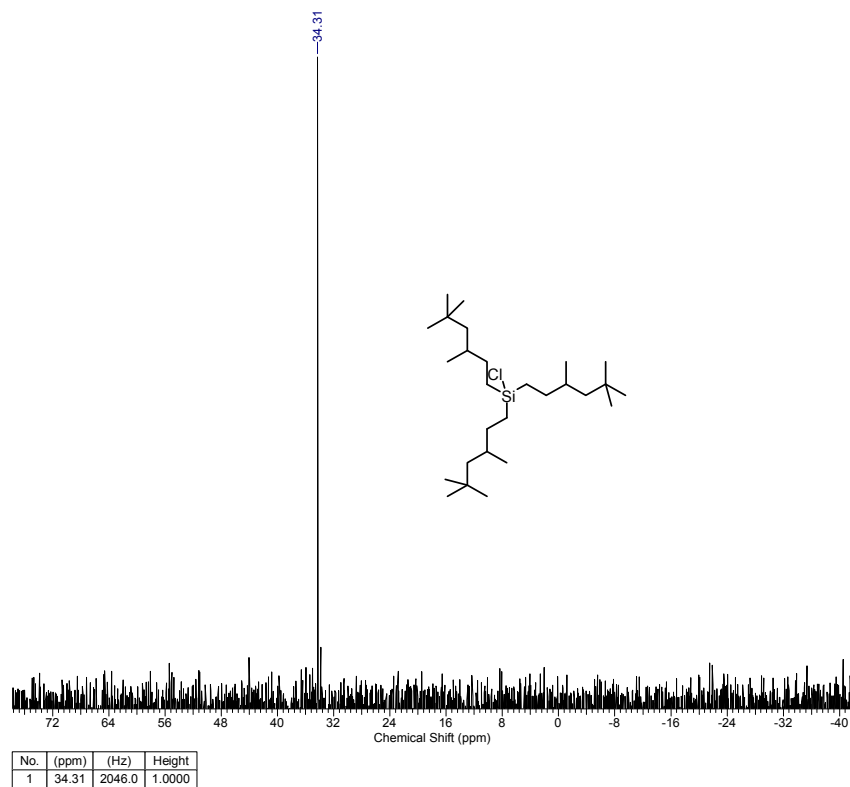


Figure S15.  $^{29}\text{Si}$  NMR spectrum of **3b** in  $\text{CDCl}_3$

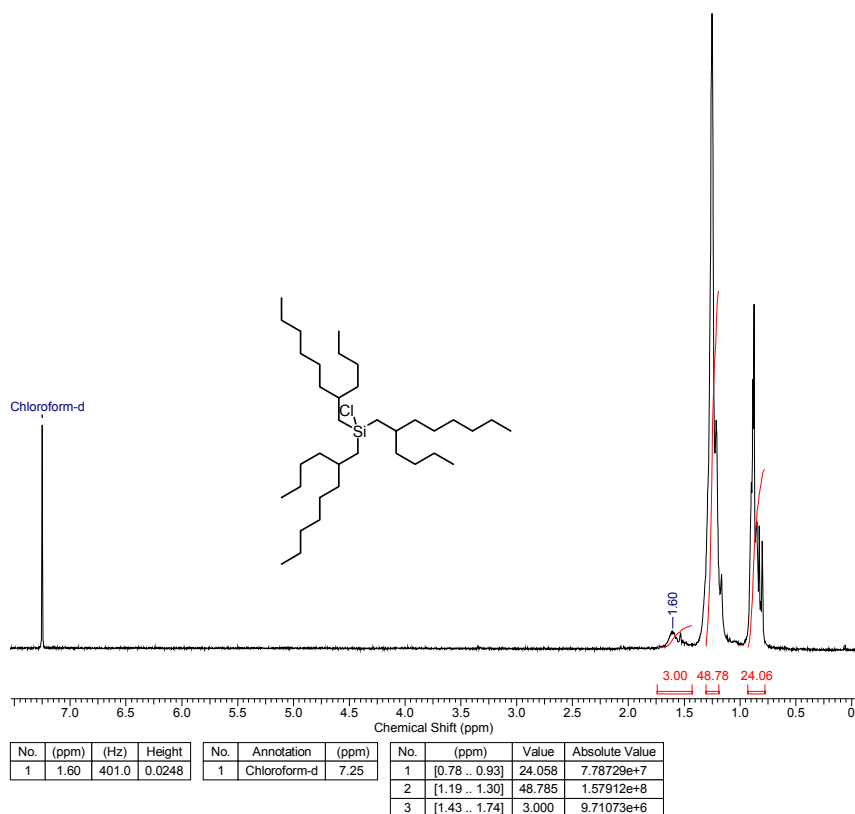


Figure S16.  $^1\text{H}$  NMR spectrum of **3c** in  $\text{CDCl}_3$

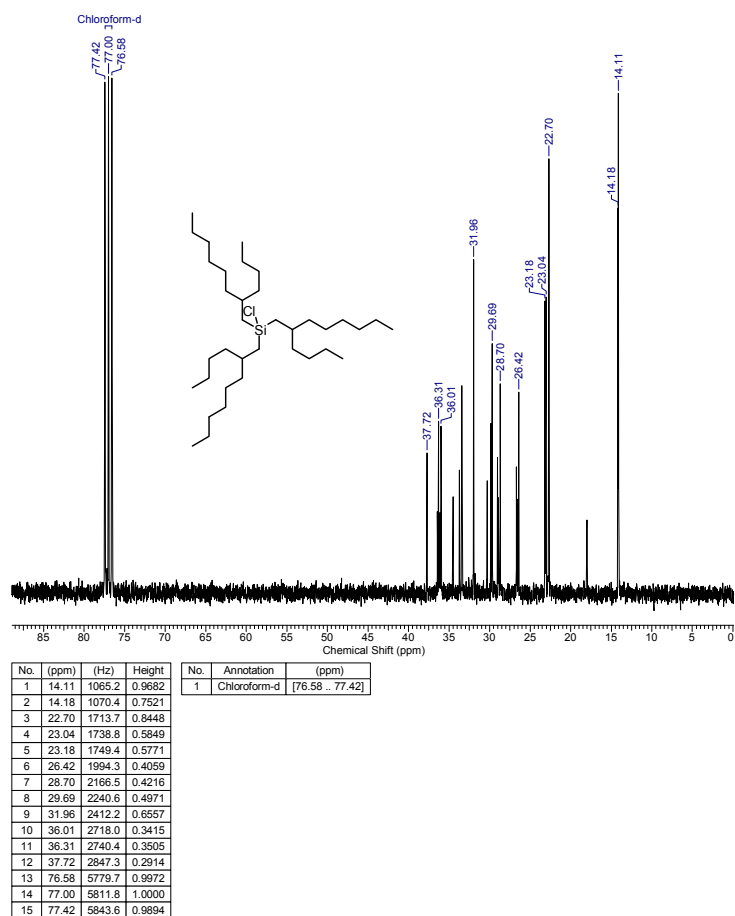


Figure S17.  $^{13}\text{C}$  NMR spectrum of **3c** in  $\text{CDCl}_3$

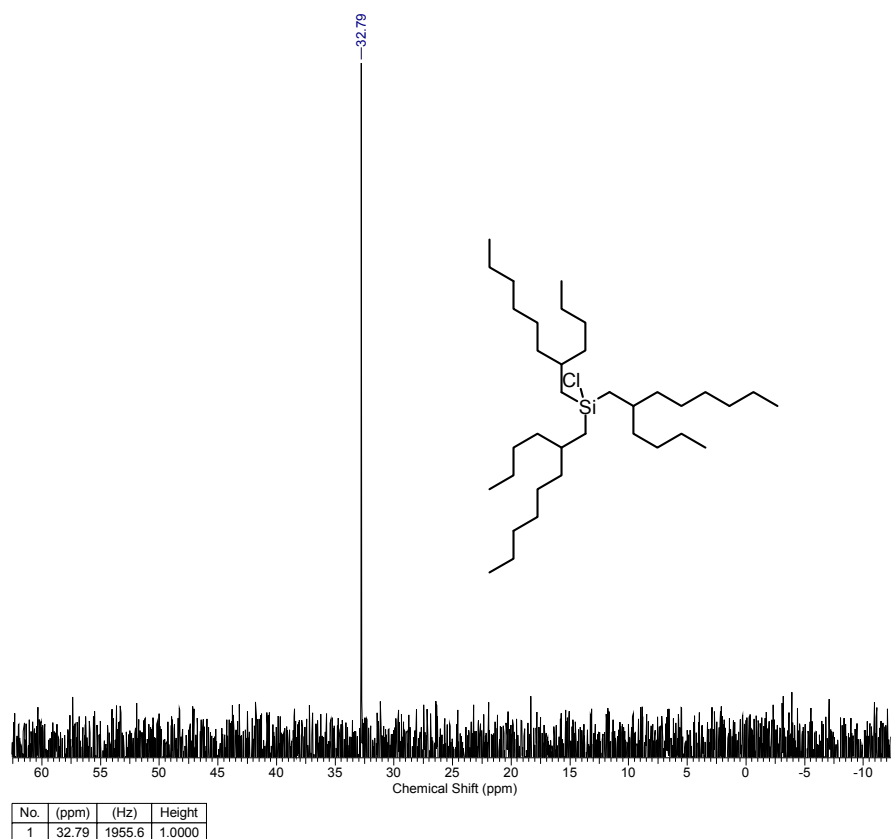


Figure S18.  $^{29}\text{Si}$  NMR spectrum of **3c** in  $\text{CDCl}_3$

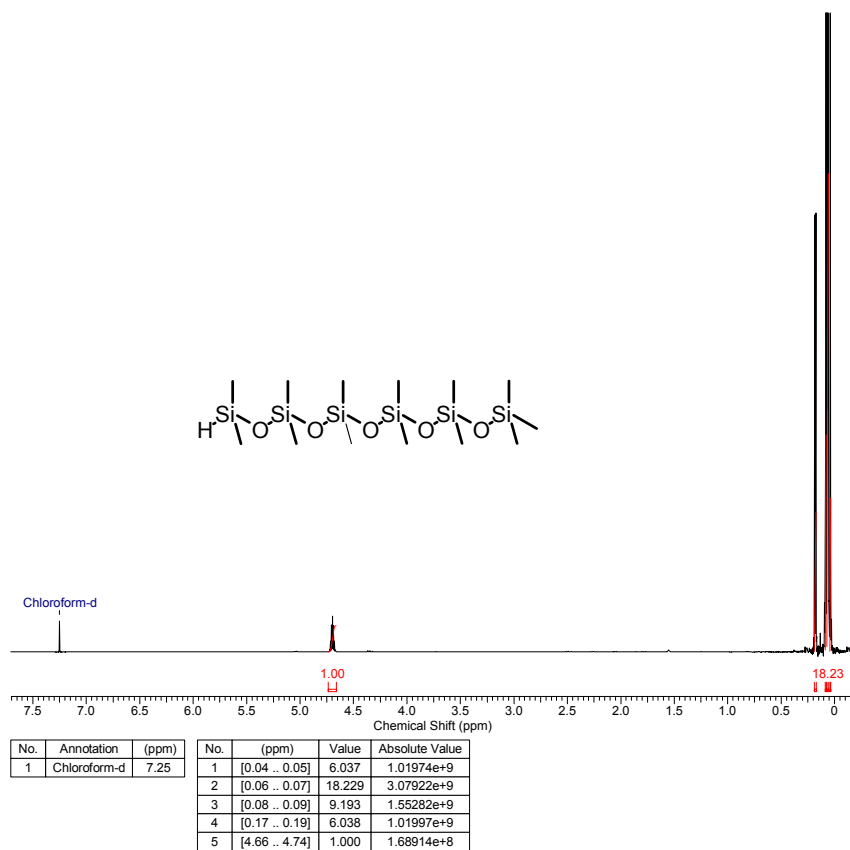


Figure S19.  $^1\text{H}$  NMR spectrum of **6** in  $\text{CDCl}_3$

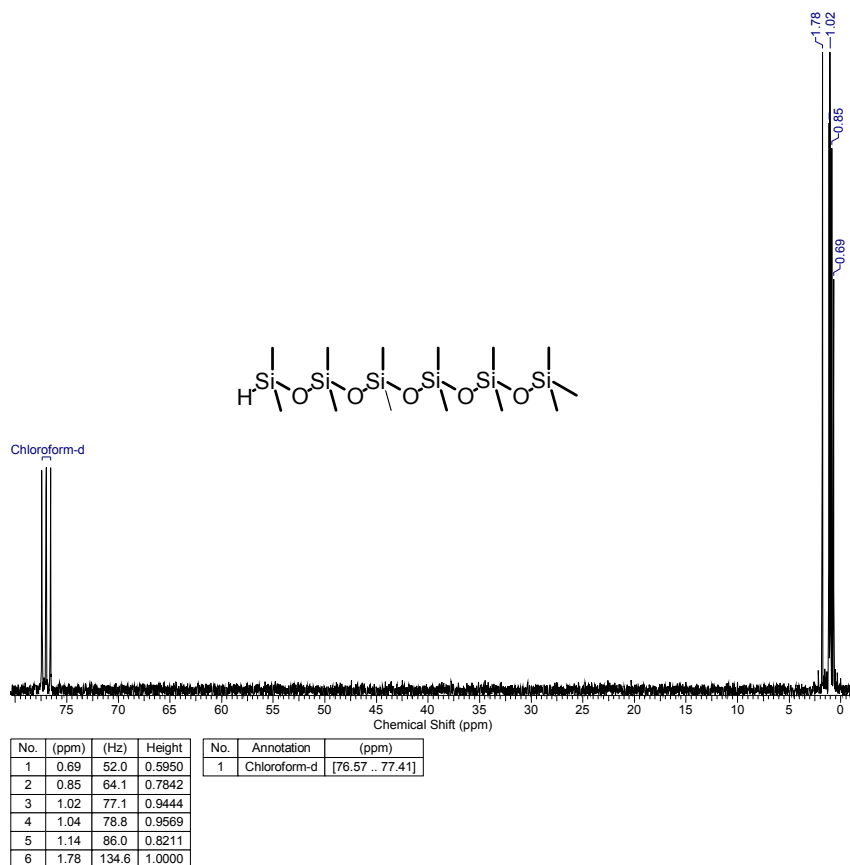


Figure S20.  $^{13}\text{C}$  NMR spectrum of 6 in  $\text{CDCl}_3$

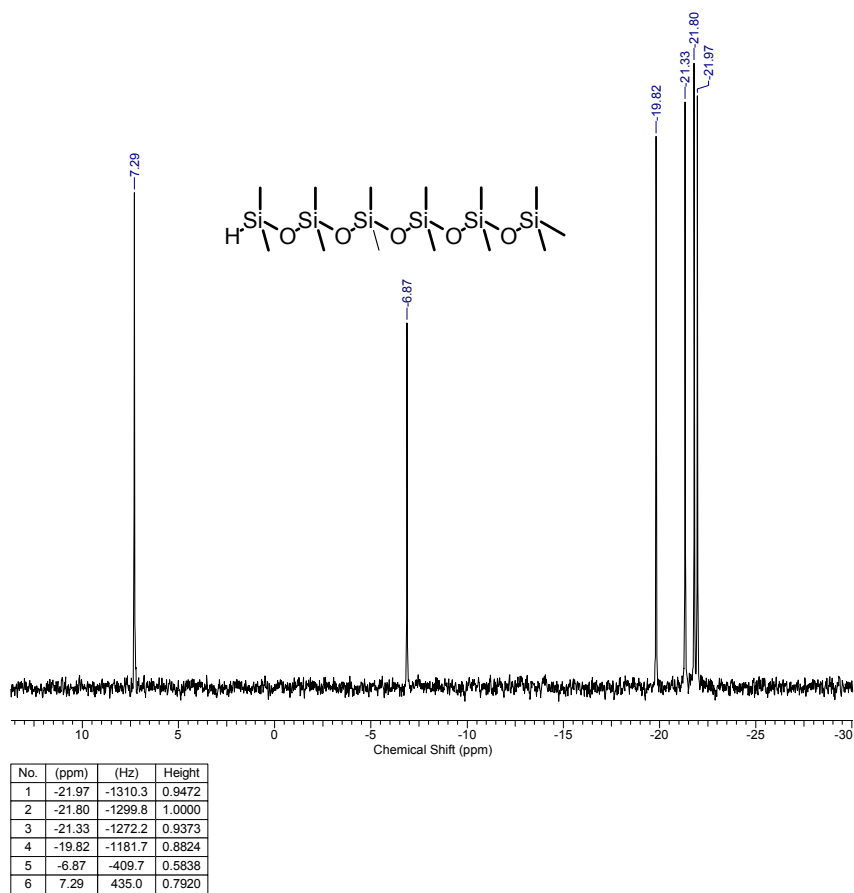


Figure S21.  $^{29}\text{Si}$  NMR spectrum of 6 in  $\text{CDCl}_3$

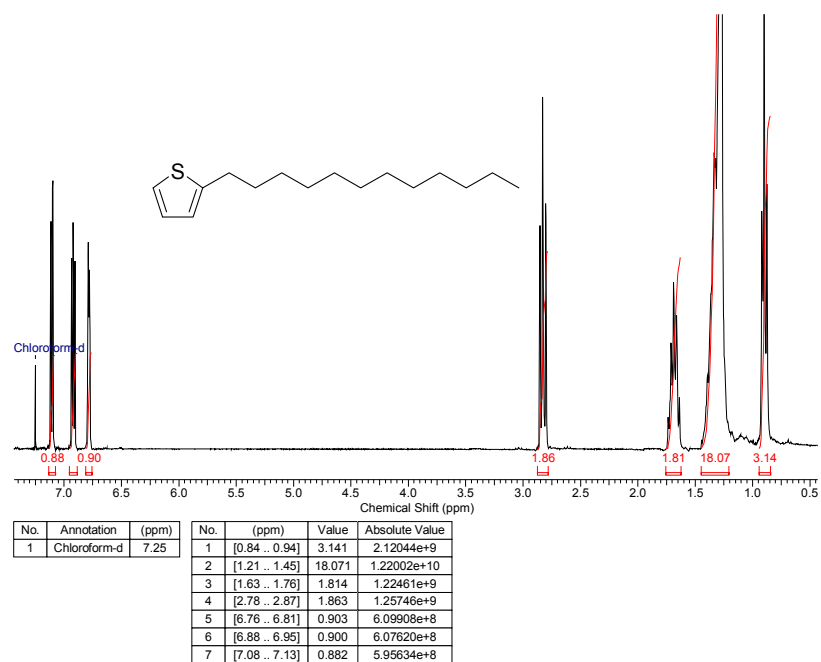


Figure S22.  $^1\text{H}$  NMR spectrum of **7b** in  $\text{CDCl}_3$

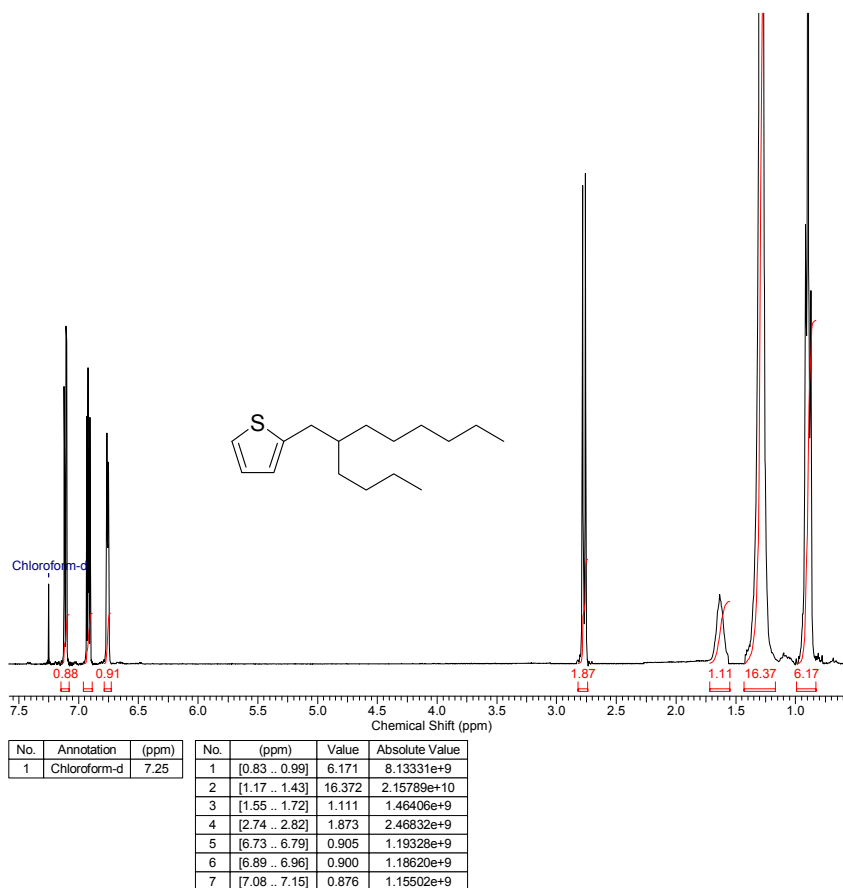


Figure S23.  $^1\text{H}$  NMR spectrum of **7c** in  $\text{CDCl}_3$

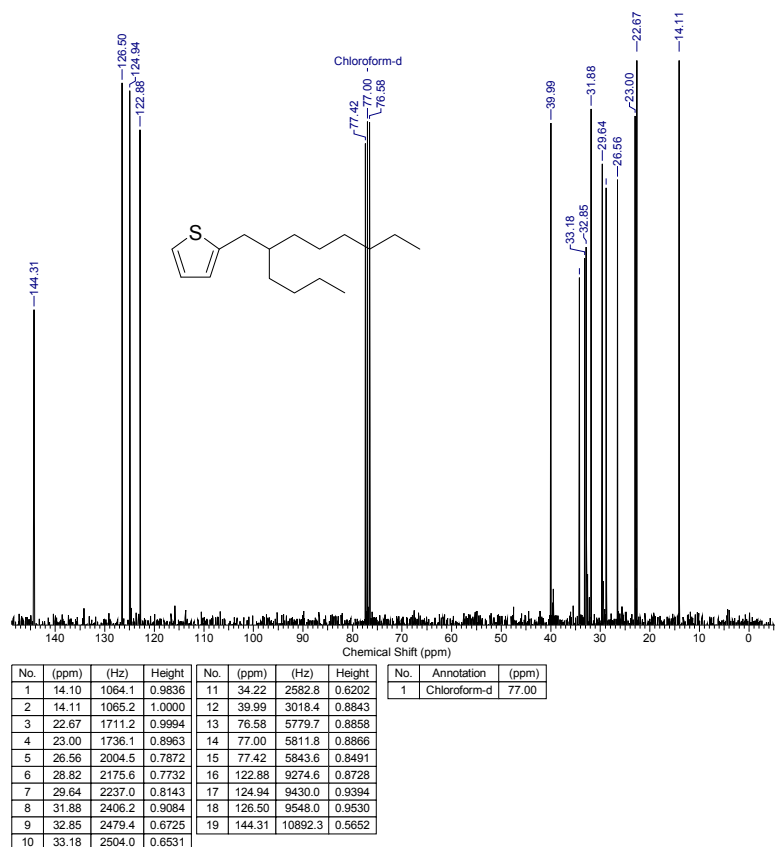


Figure S24.  $^{13}\text{C}$  NMR spectrum of 7c in  $\text{CDCl}_3$

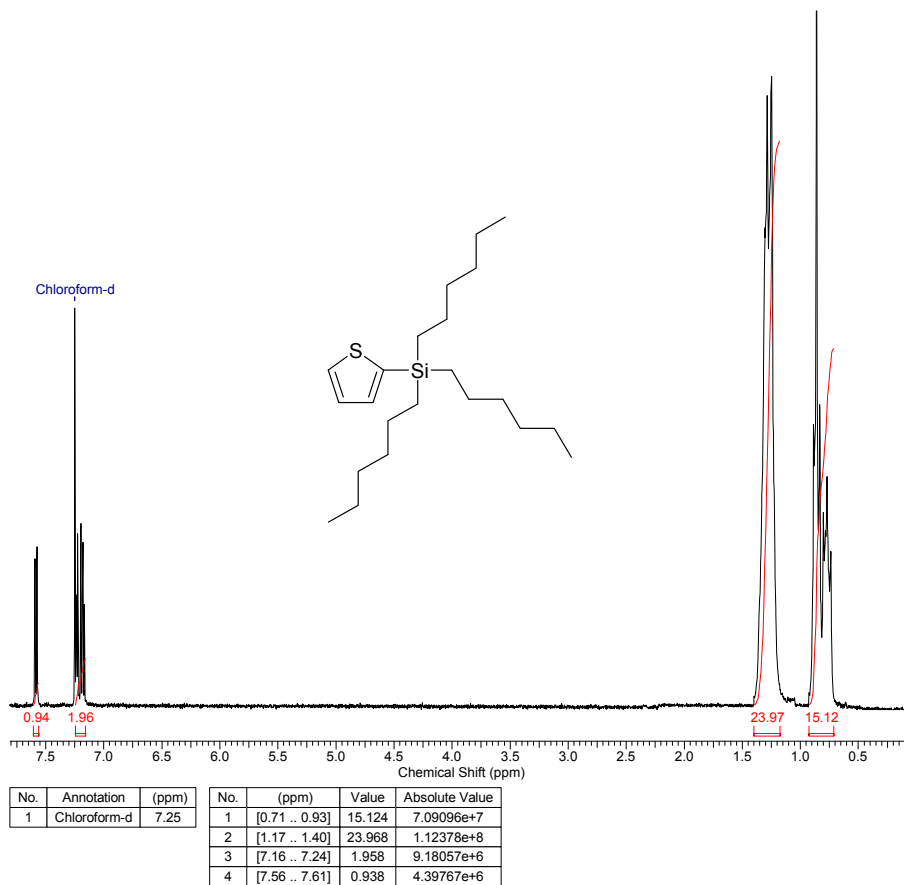


Figure S25.  $^1\text{H}$  NMR spectrum of 7e in  $\text{CDCl}_3$



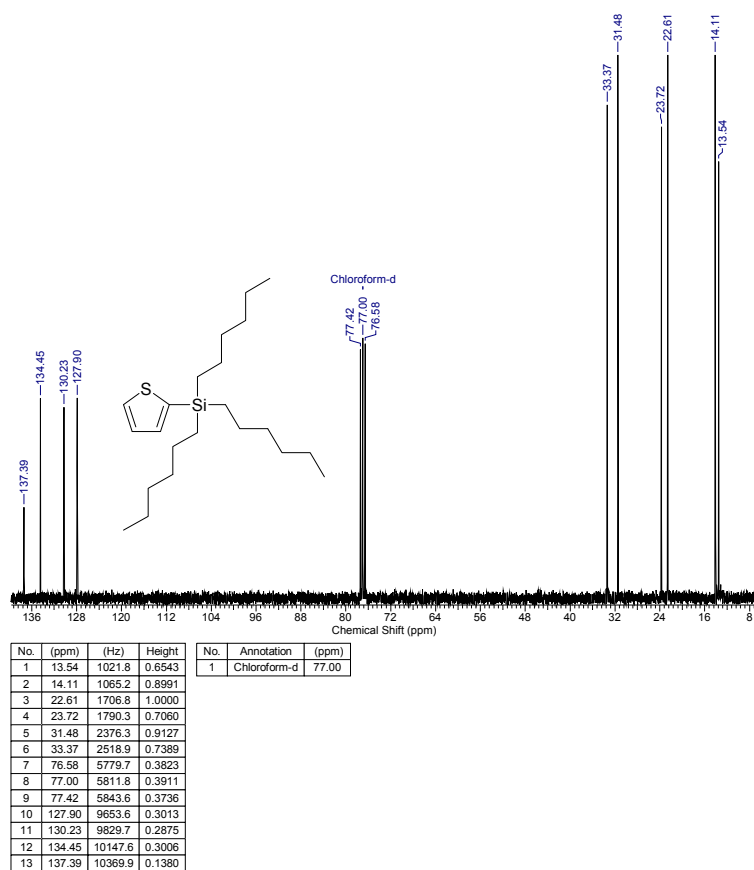


Figure S26.  $^{13}\text{C}$  NMR spectrum of **7e** in  $\text{CDCl}_3$

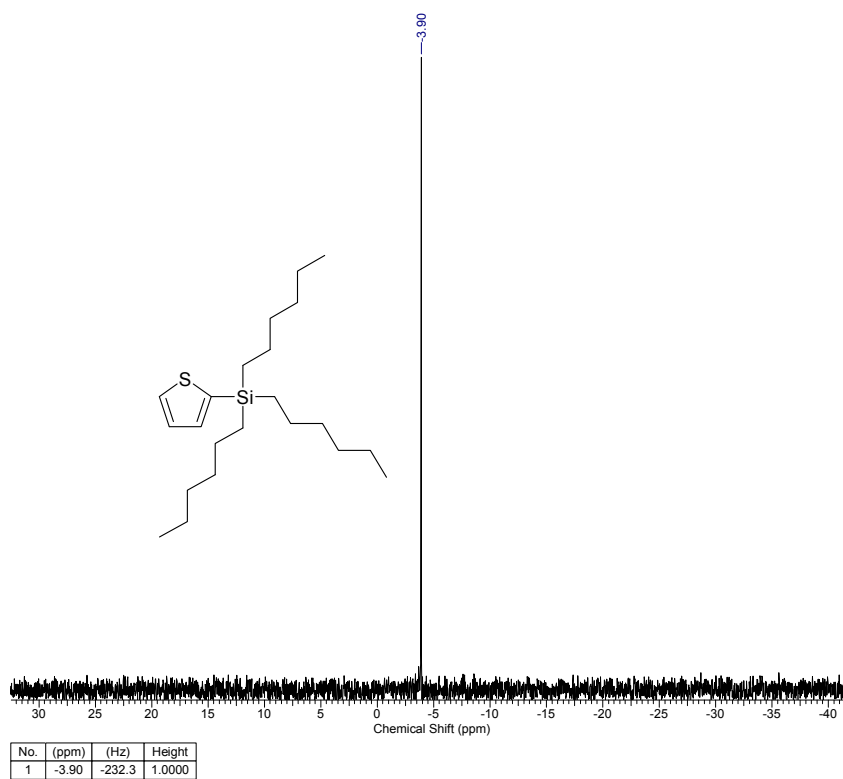


Figure S27.  $^{29}\text{Si}$  NMR spectrum of **7e** in  $\text{CDCl}_3$

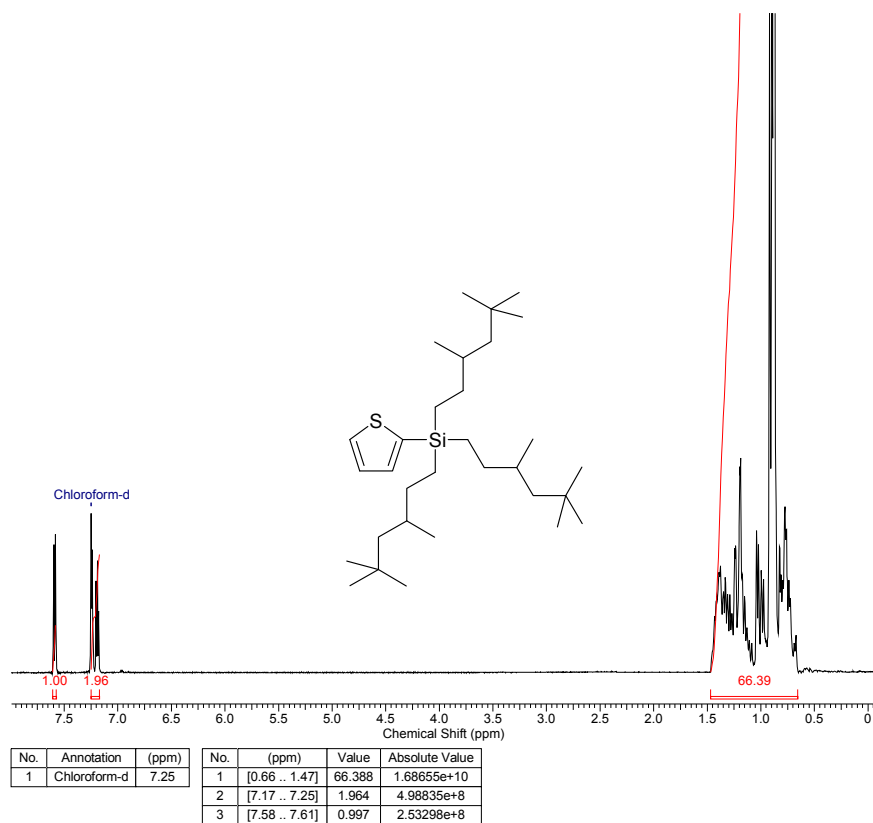


Figure S28.  $^1\text{H}$  NMR spectrum of **7f** in  $\text{CDCl}_3$

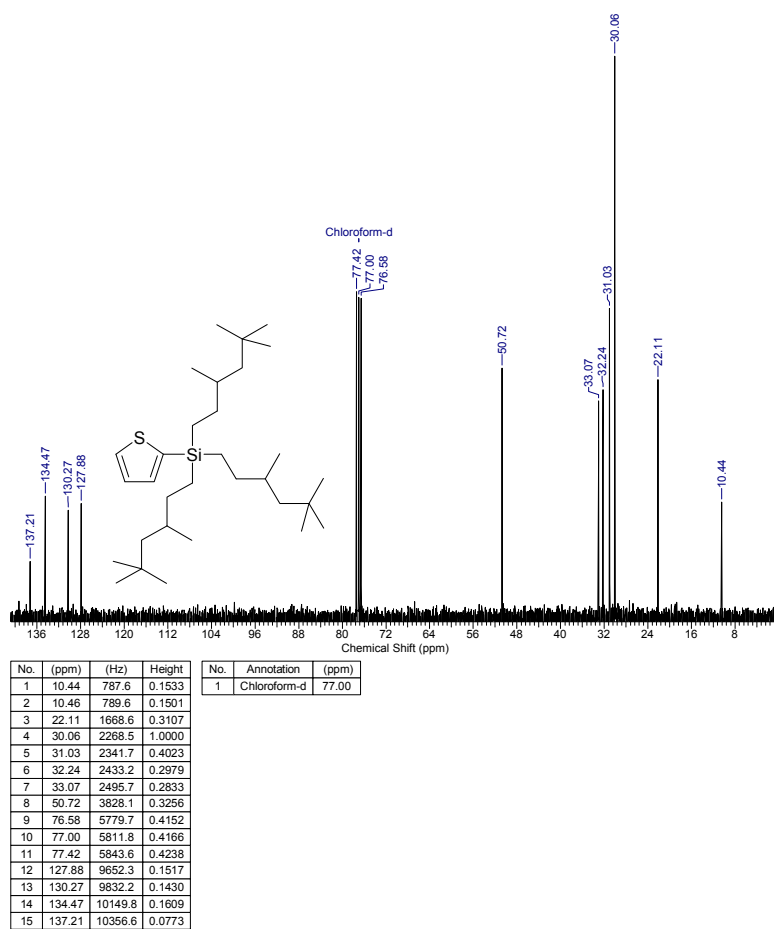


Figure S29.  $^{13}\text{C}$  NMR spectrum of **7f** in  $\text{CDCl}_3$

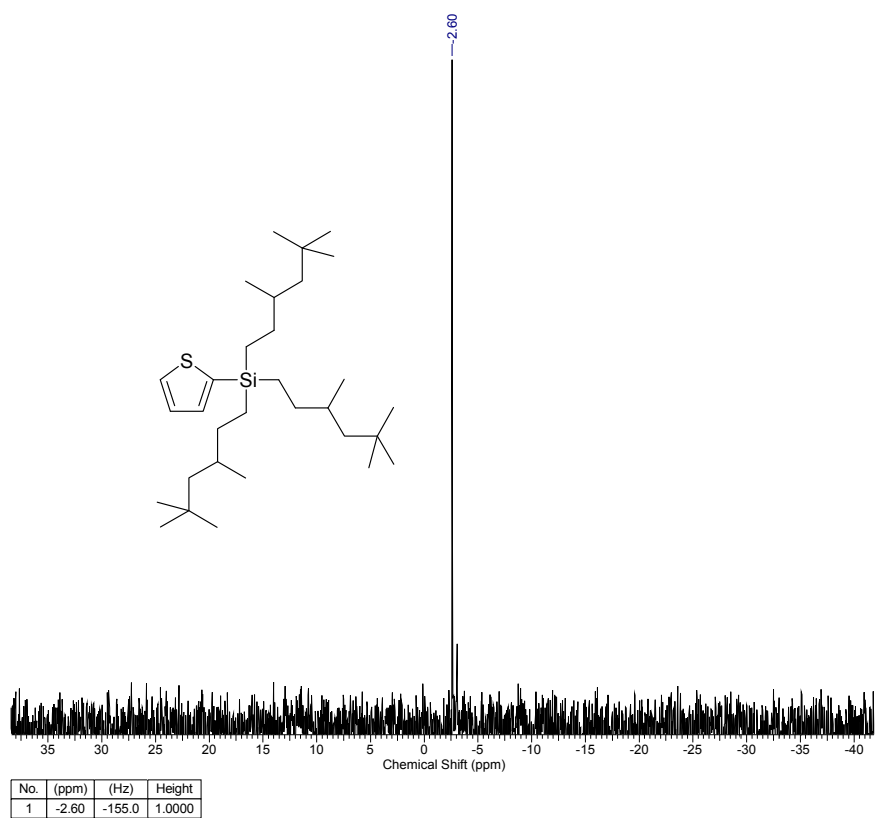


Figure S30.  $^{29}\text{Si}$  NMR spectrum of **7f** in  $\text{CDCl}_3$

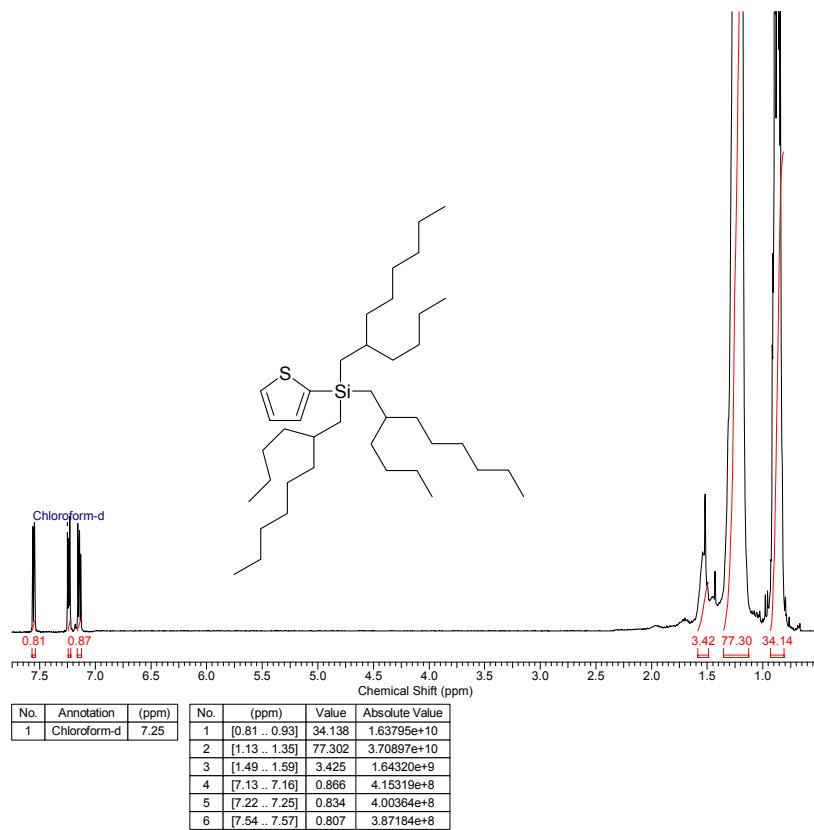


Figure S31.  $^1\text{H}$  NMR spectrum of **7g** in  $\text{CDCl}_3$

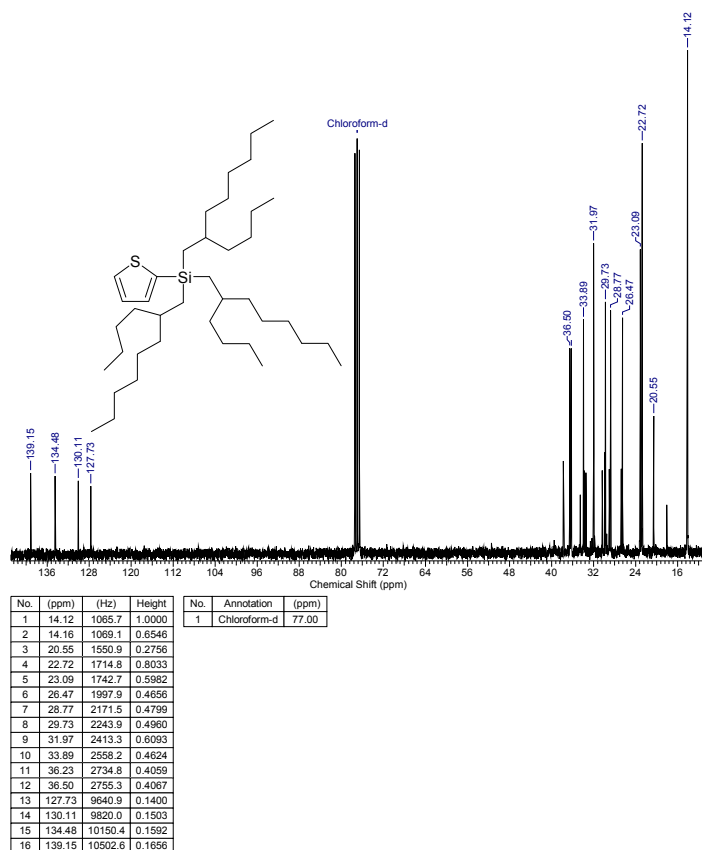


Figure S32.  $^{13}\text{C}$  NMR spectrum of **7g** in  $\text{CDCl}_3$

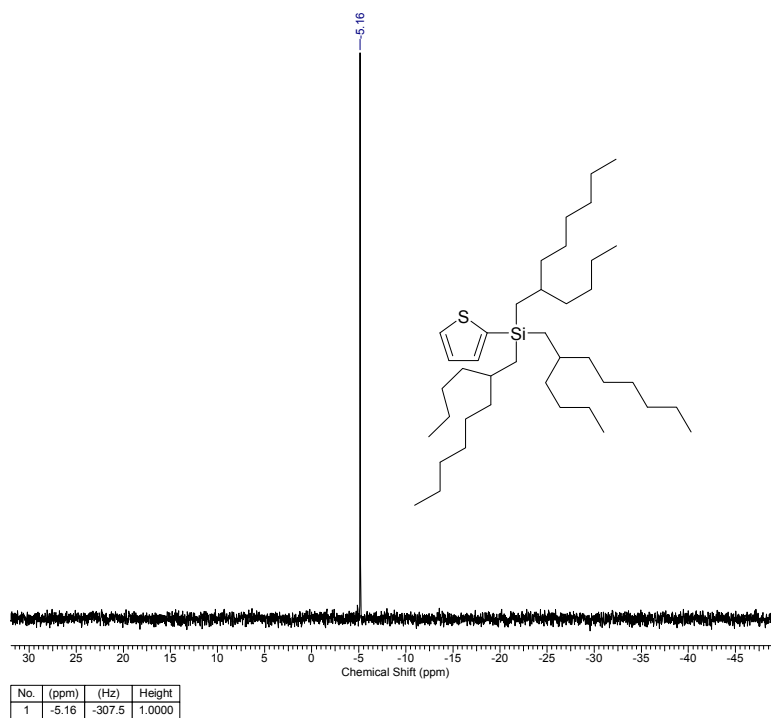


Figure S33.  $^{29}\text{Si}$  NMR spectrum of **7g** in  $\text{CDCl}_3$

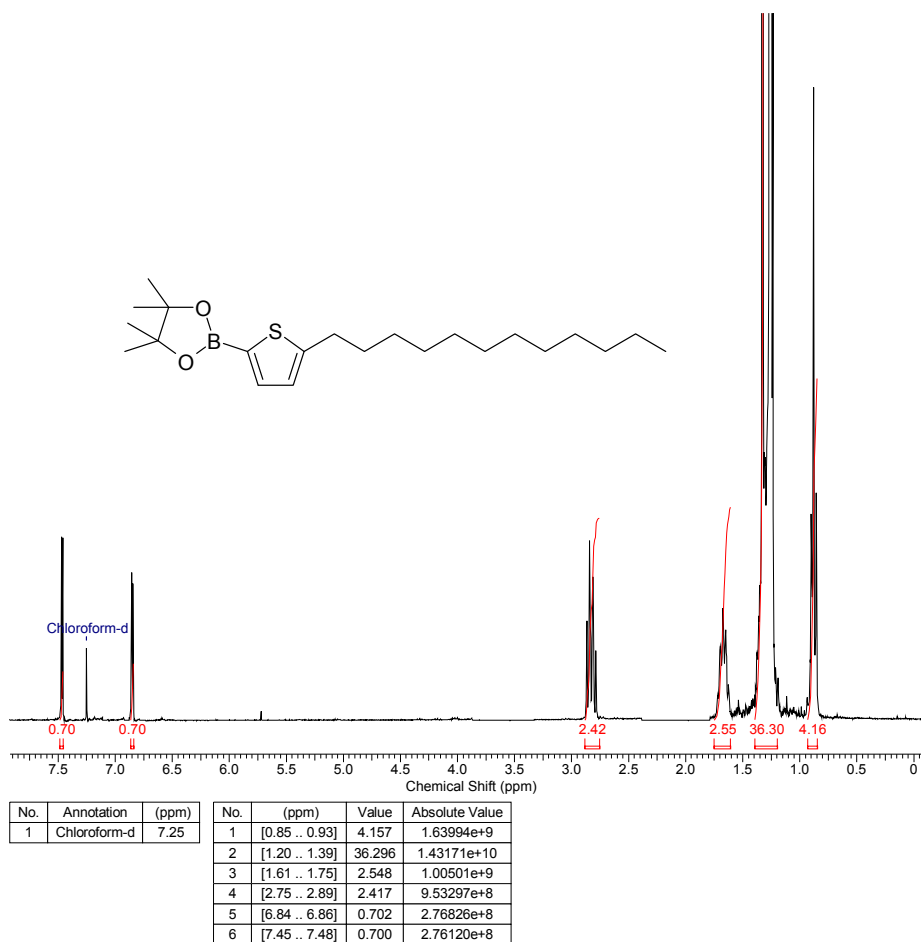


Figure S34. <sup>1</sup>H NMR spectrum of **8b** in CDCl<sub>3</sub>

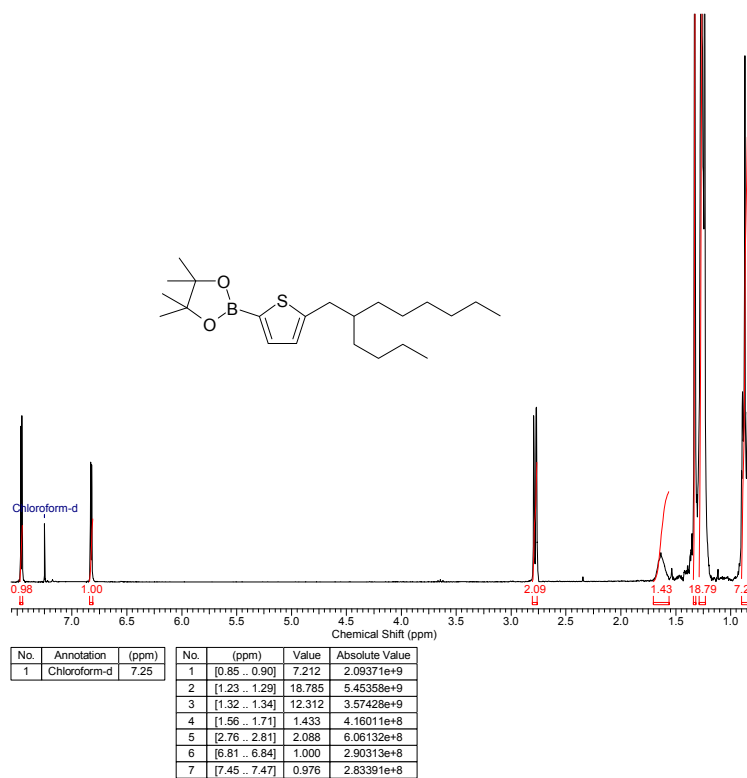


Figure S35. <sup>1</sup>H NMR spectrum of **8c** in CDCl<sub>3</sub>

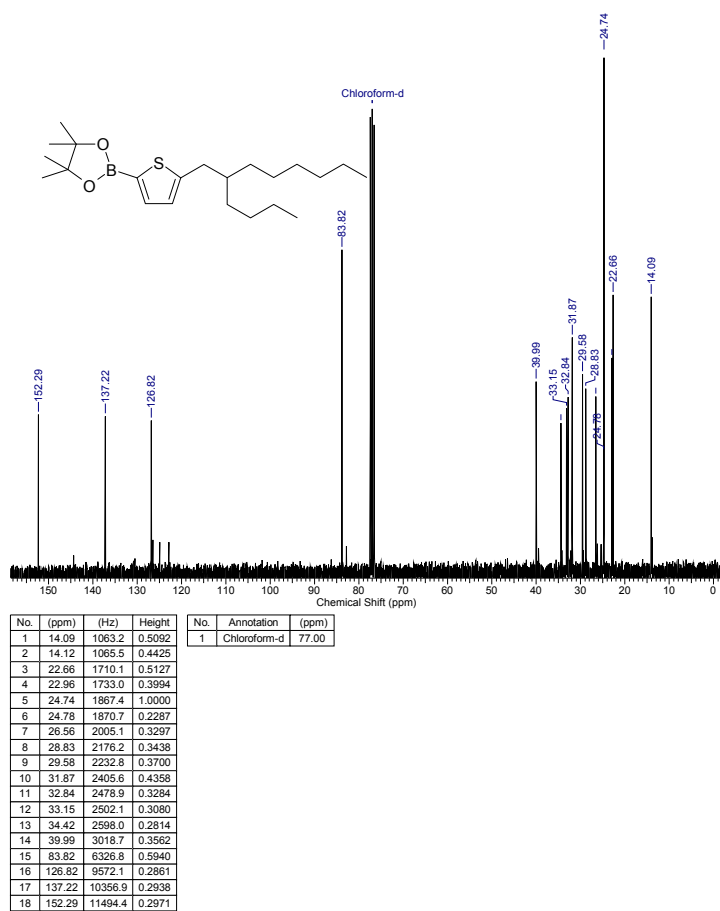


Figure S36.  $^{13}\text{C}$  NMR spectrum of **8c** in  $\text{CDCl}_3$

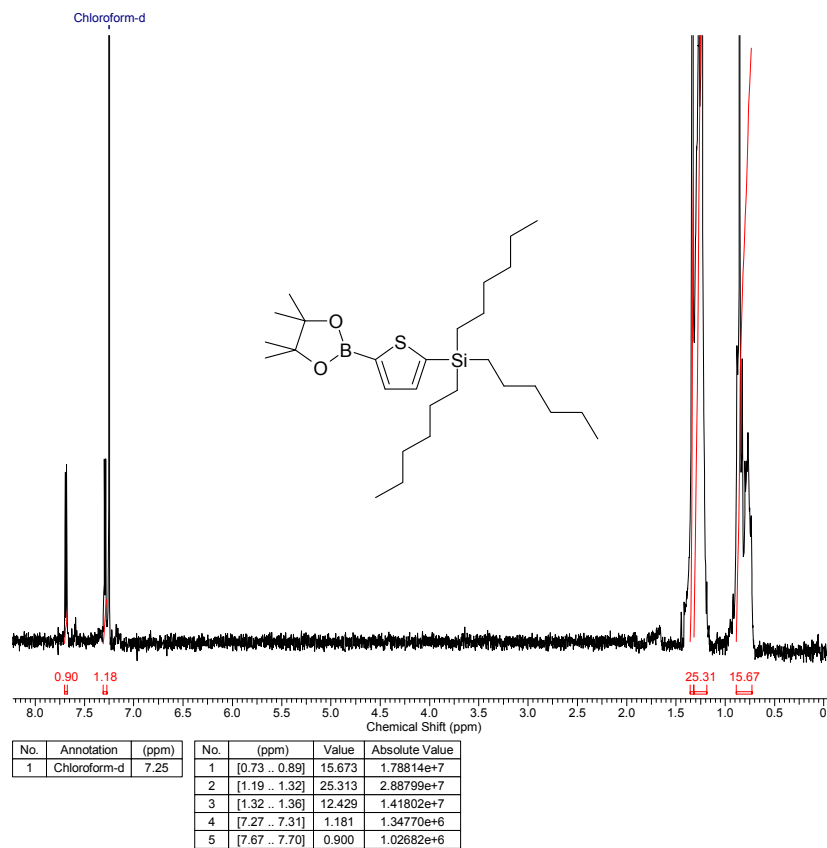


Figure S37.  $^1\text{H}$  NMR spectrum of **8e** in  $\text{CDCl}_3$

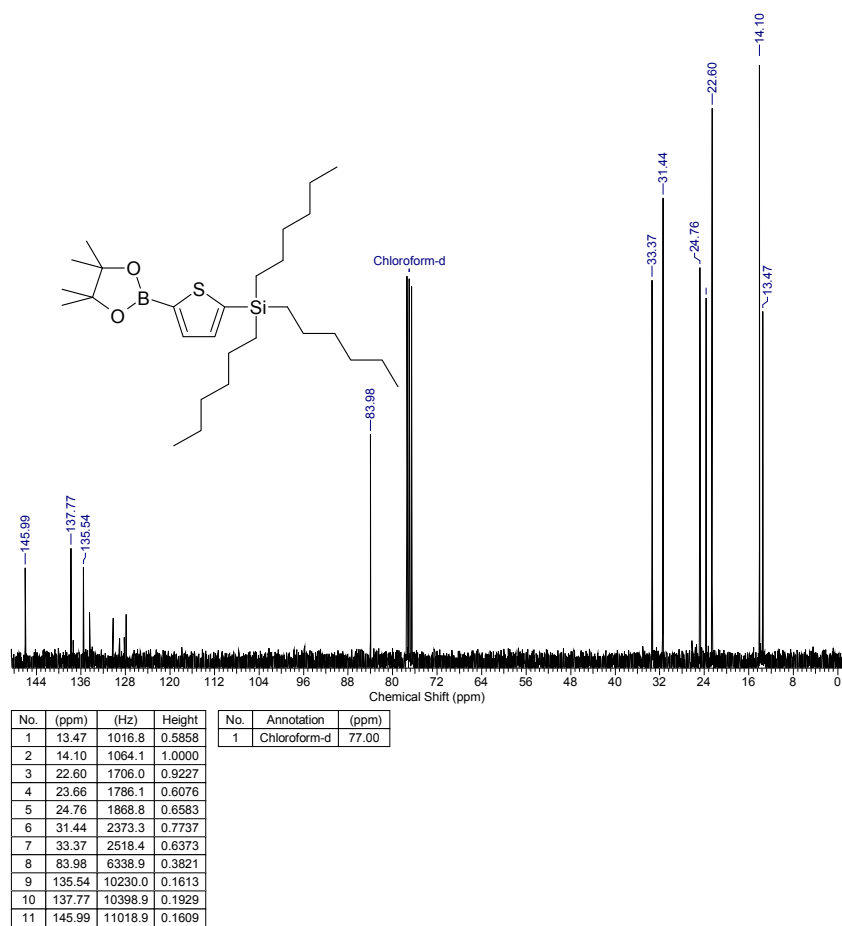


Figure S38.  $^{13}\text{C}$  NMR spectrum of **8e** in  $\text{CDCl}_3$

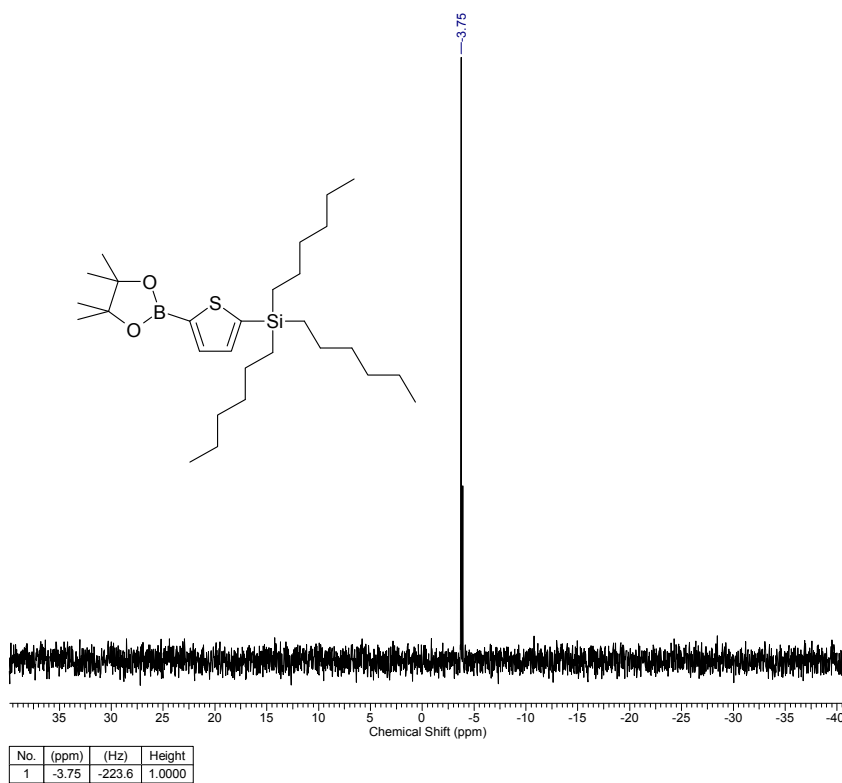


Figure S39.  $^{29}\text{Si}$  NMR spectrum of **8e** in  $\text{CDCl}_3$

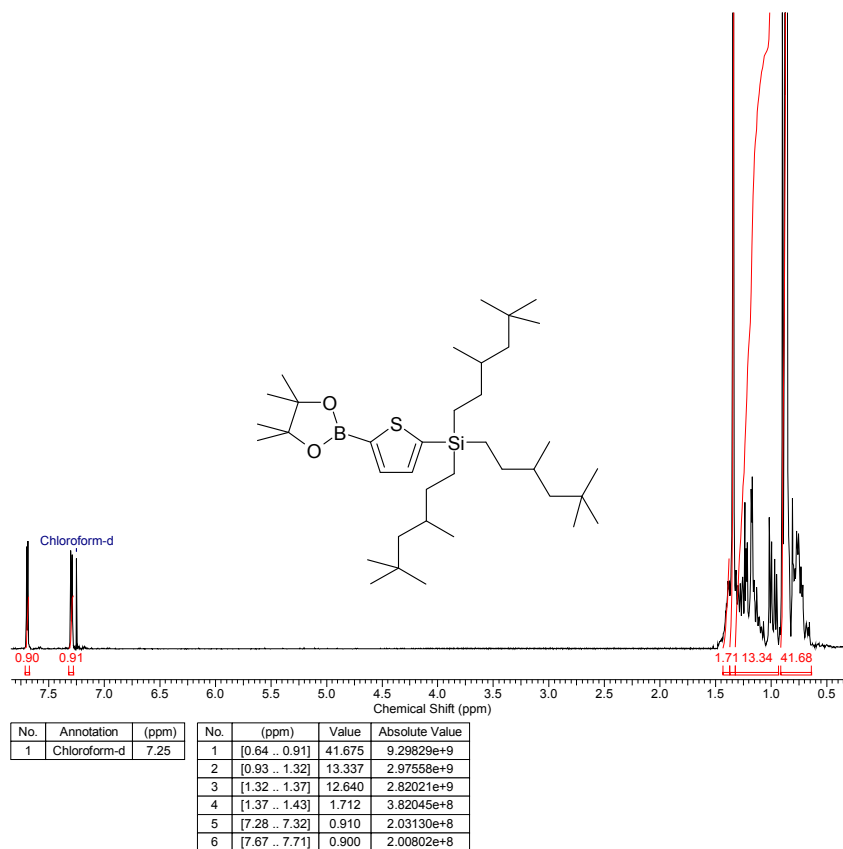


Figure S40.  $^1\text{H}$  NMR spectrum of **8f** in  $\text{CDCl}_3$

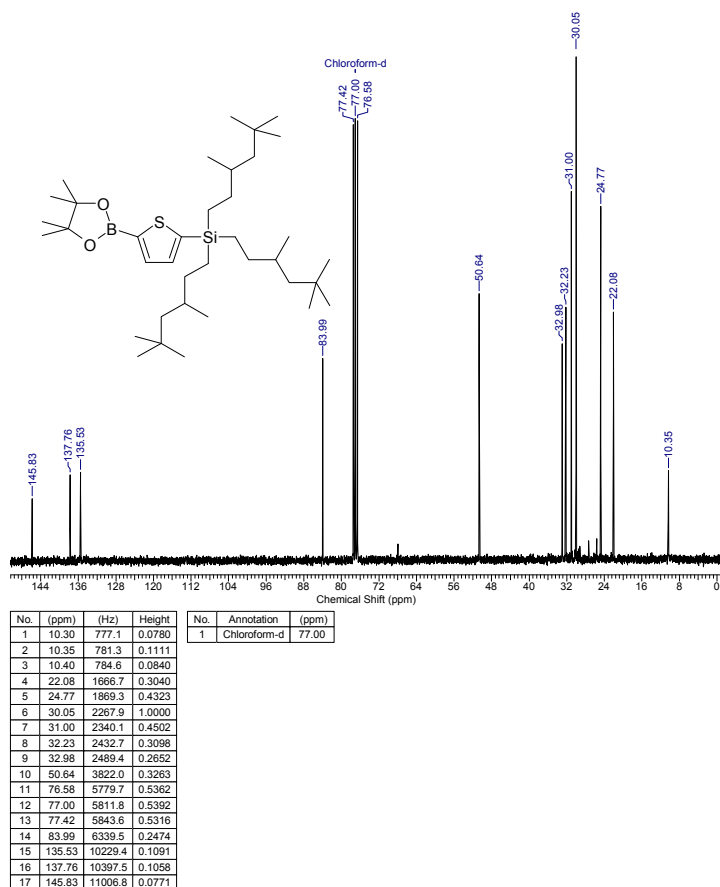


Figure S41.  $^{13}\text{C}$  NMR spectrum of **8f** in  $\text{CDCl}_3$



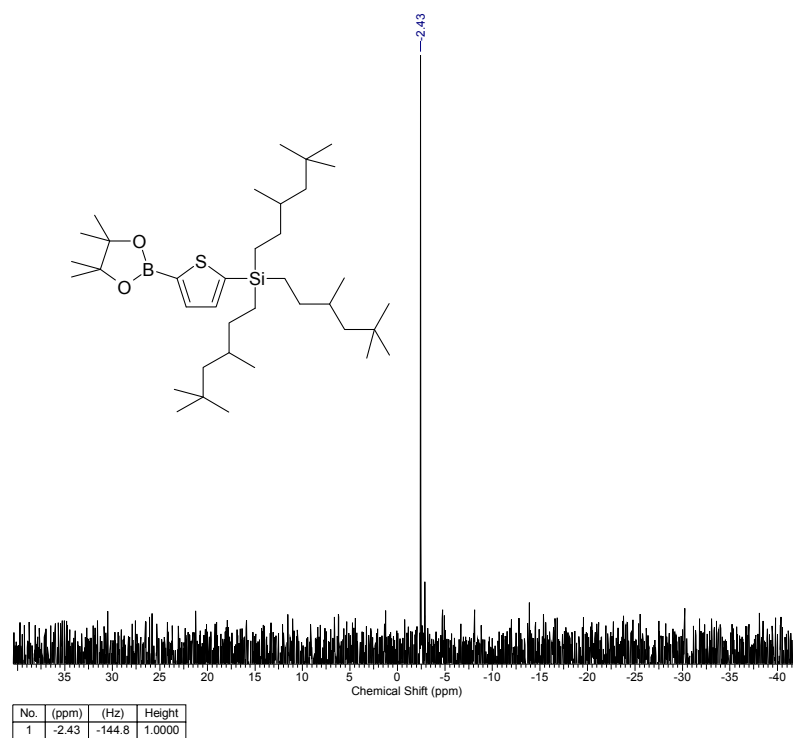


Figure S42.  $^{29}\text{Si}$  NMR spectrum of **8f** in  $\text{CDCl}_3$

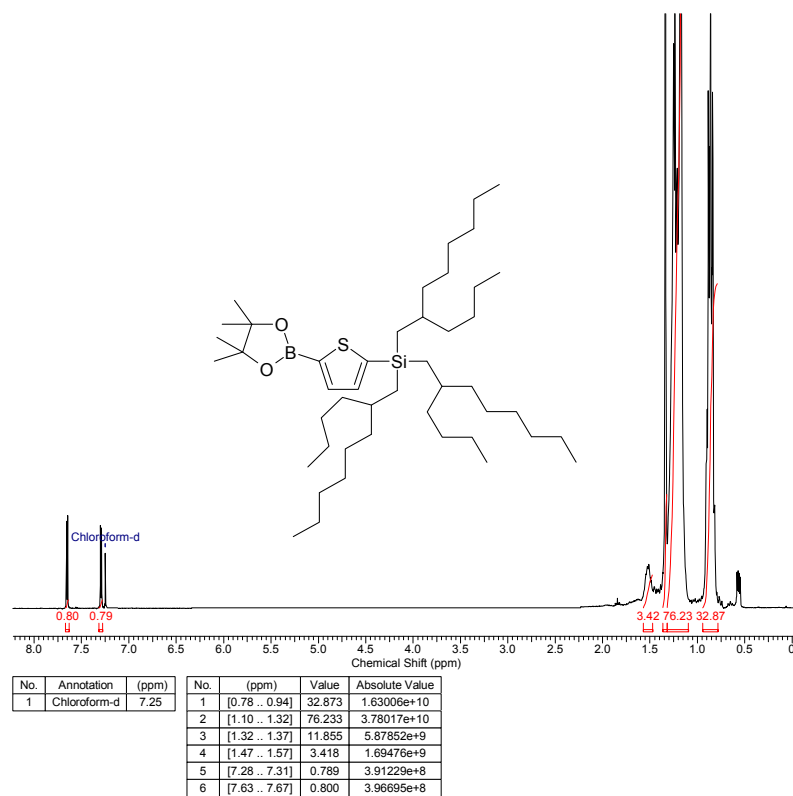


Figure S43.  $^1\text{H}$  NMR spectrum of **8g** in  $\text{CDCl}_3$

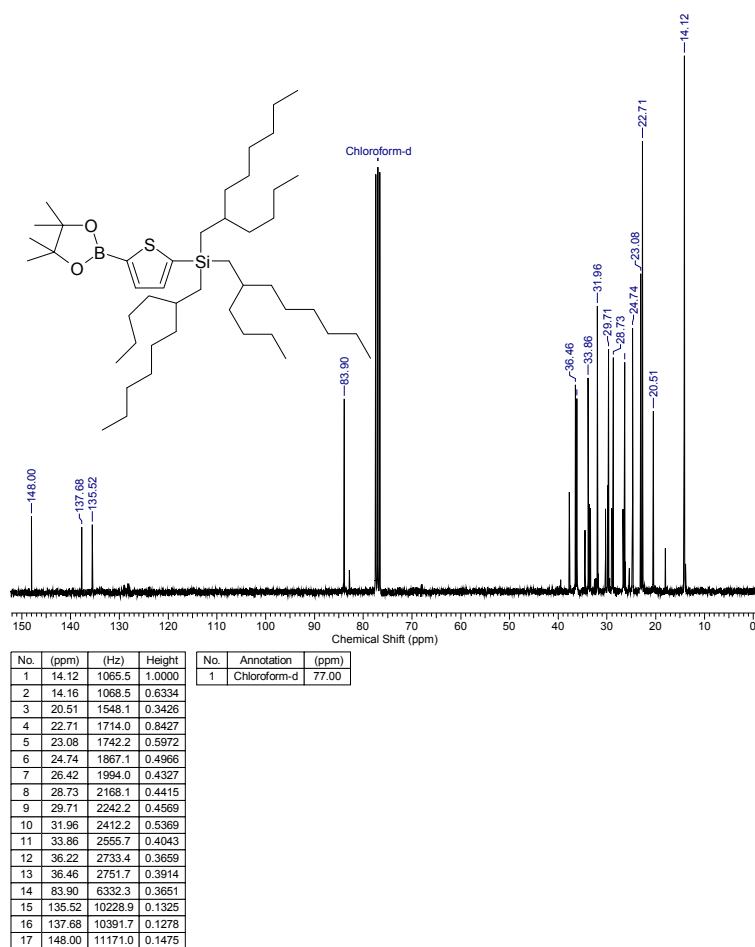


Figure S44.  $^{13}\text{C}$  NMR spectrum of **8g** in  $\text{CDCl}_3$

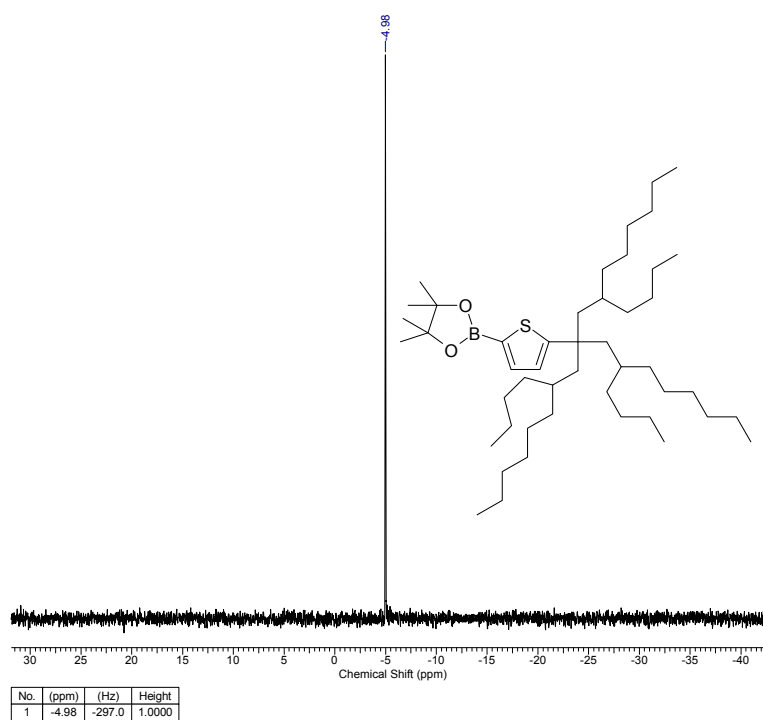


Figure S45.  $^{29}\text{Si}$  NMR spectrum of **8g** in  $\text{CDCl}_3$

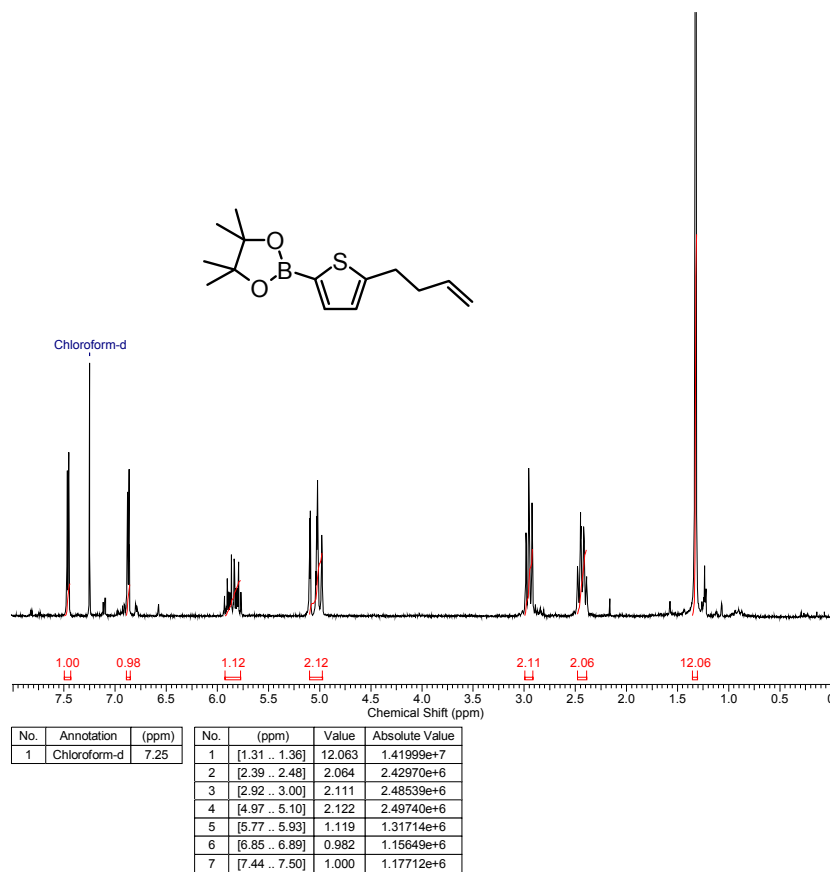


Figure S46.  $^1\text{H}$  NMR spectrum of **10** in  $\text{CDCl}_3$

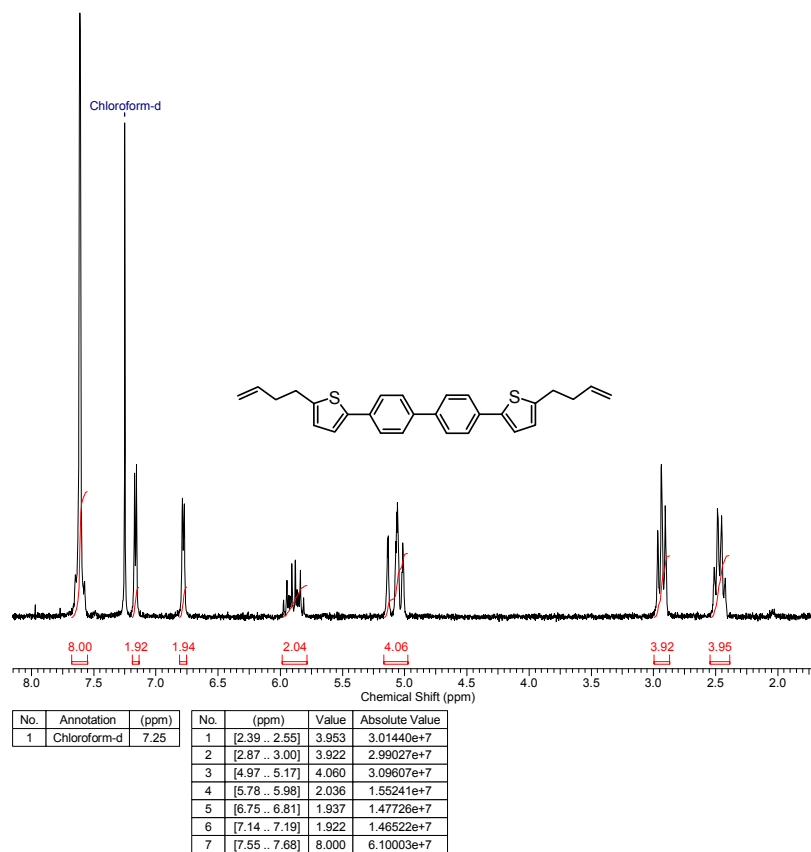


Figure S47.  $^1\text{H}$  NMR spectrum of **11** in  $\text{CDCl}_3$

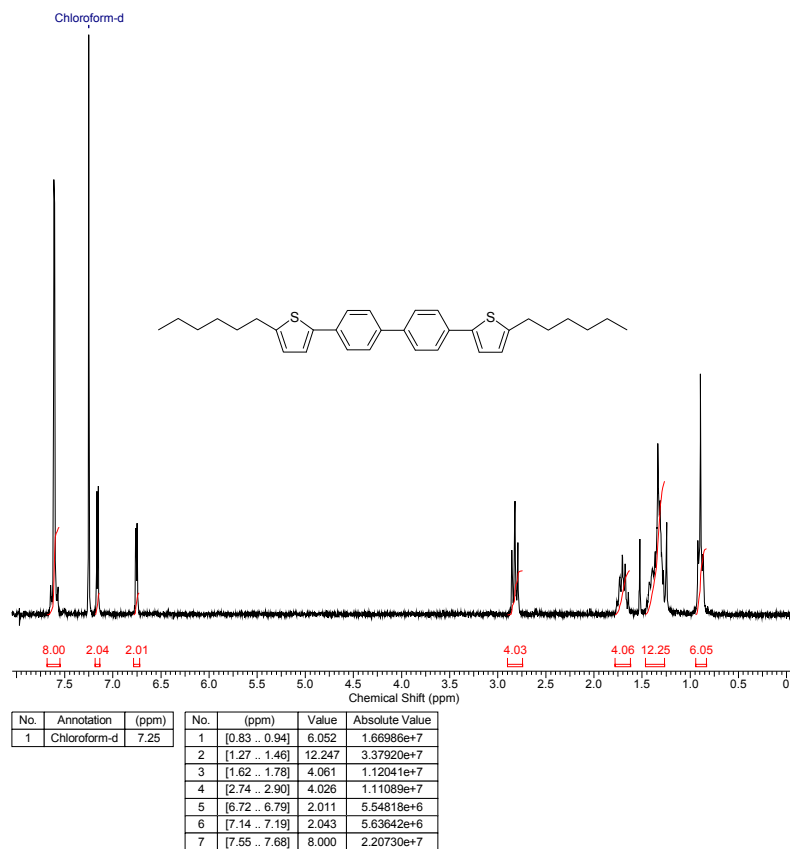


Figure S48. <sup>1</sup>H NMR spectrum of TPPT-Hex in CDCl<sub>3</sub>

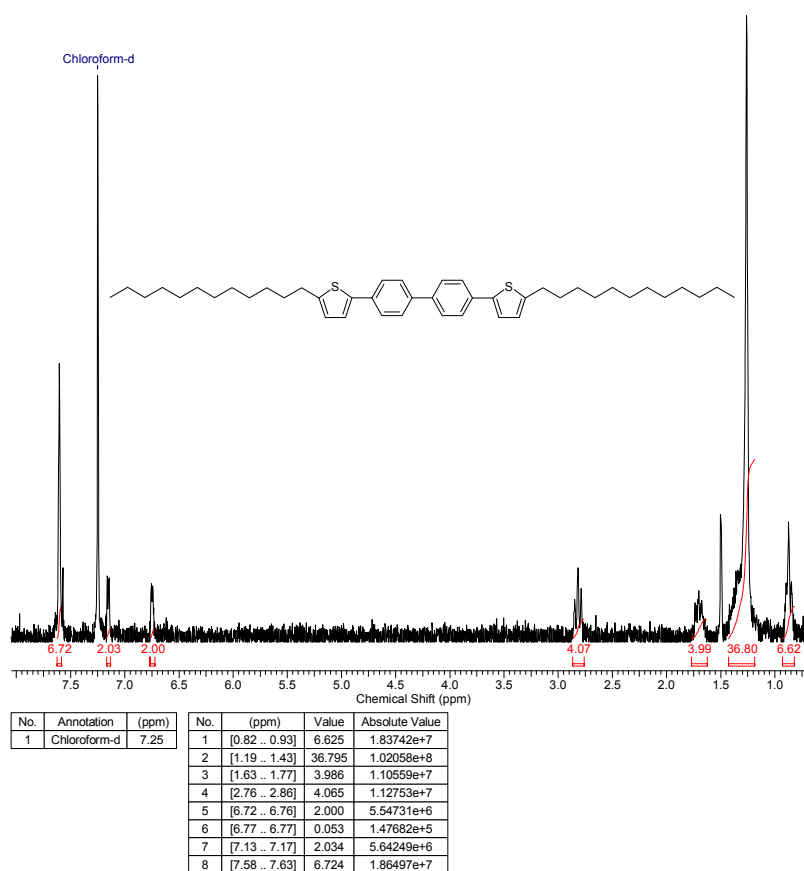


Figure S49. <sup>1</sup>H NMR spectrum of TPPT-Dodec in CDCl<sub>3</sub>

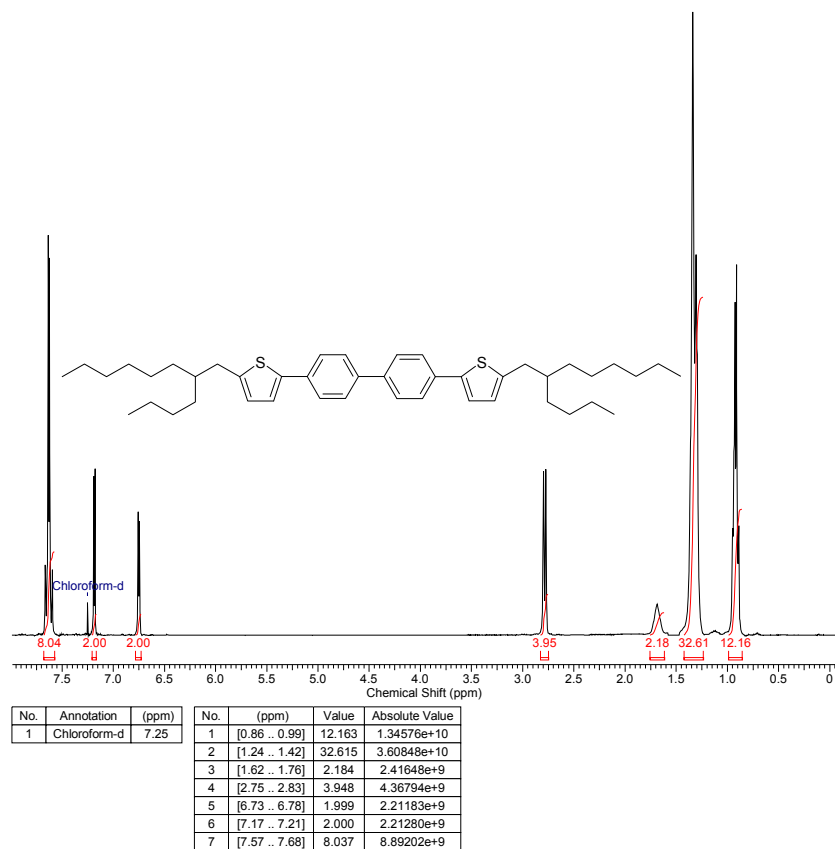


Figure S50.  $^1\text{H}$  NMR spectrum of TPPT-BuOct in  $\text{CDCl}_3$

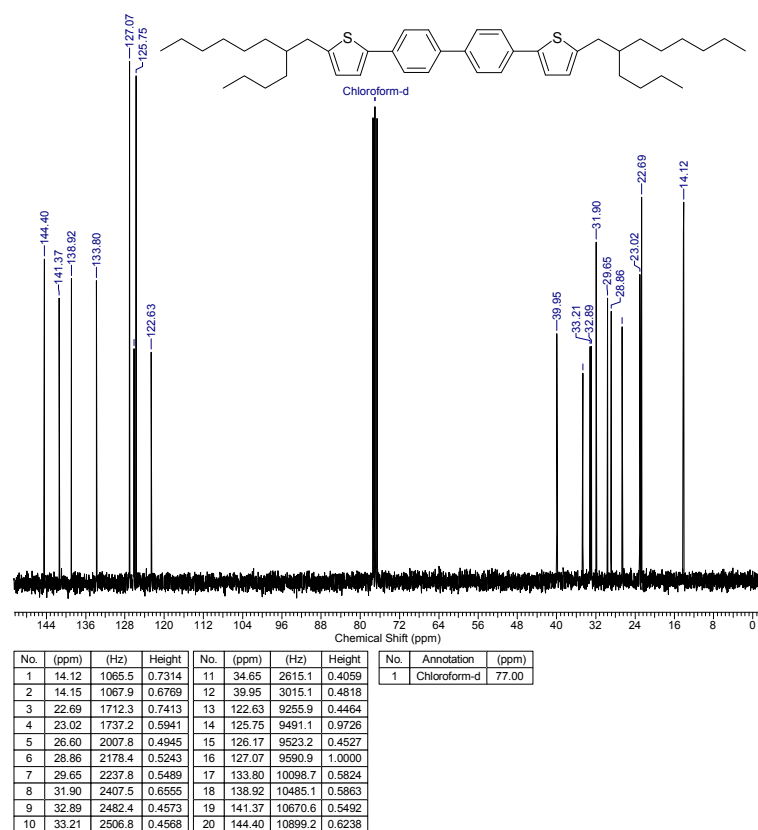


Figure S51.  $^{13}\text{C}$  NMR spectrum of TPPT-BuOct in  $\text{CDCl}_3$

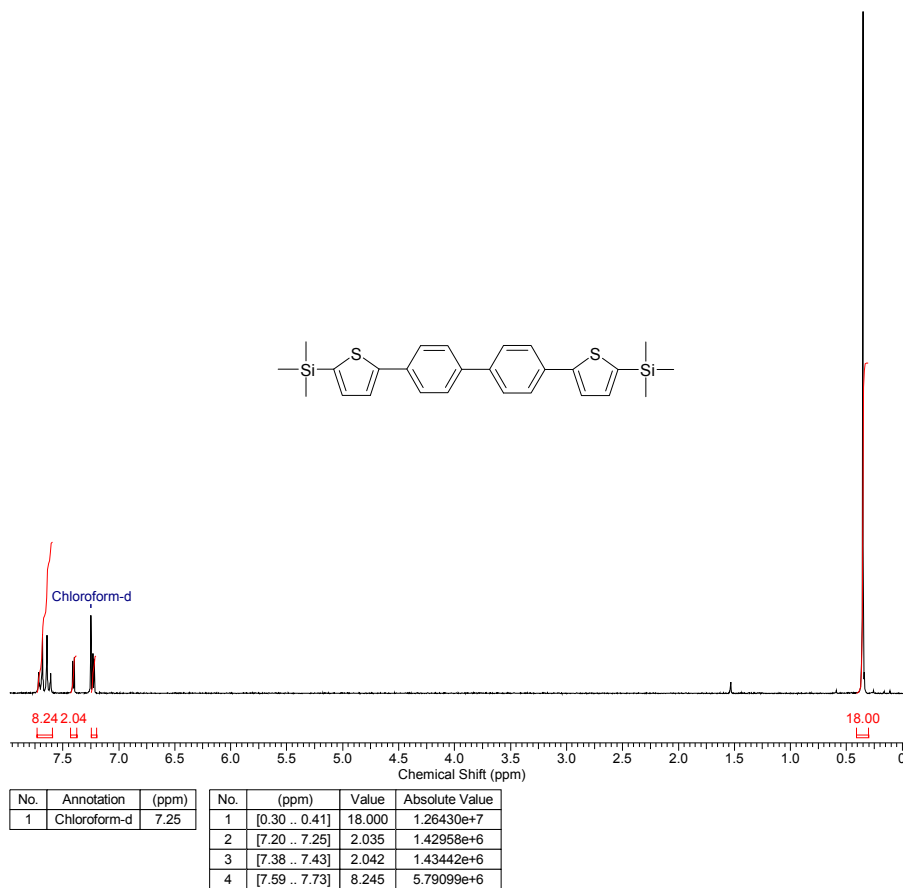


Figure S52.  $^1\text{H}$  NMR spectrum of TPPT-Si-Me in  $\text{CDCl}_3$

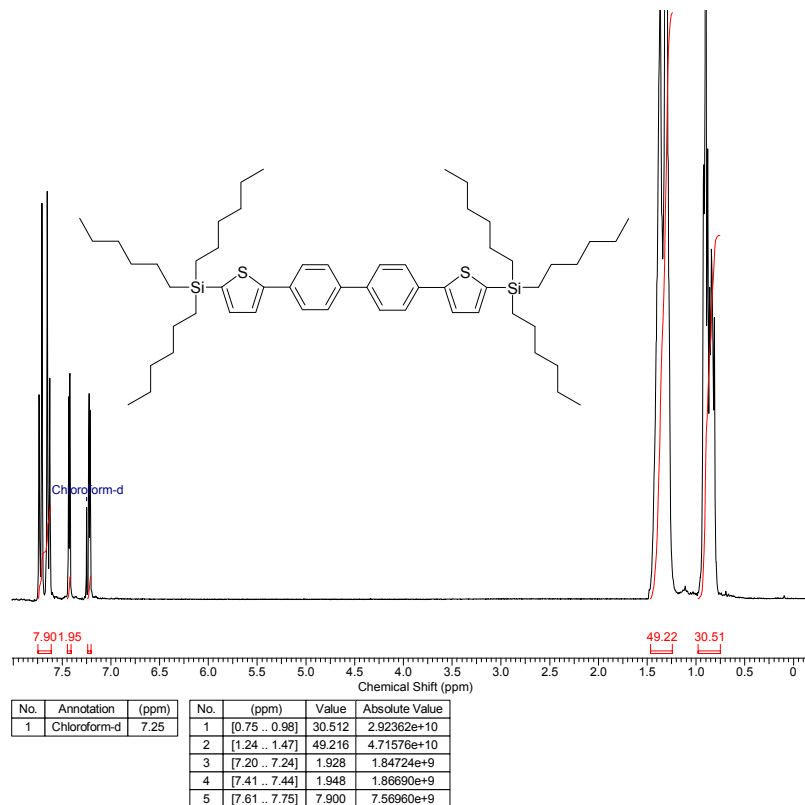
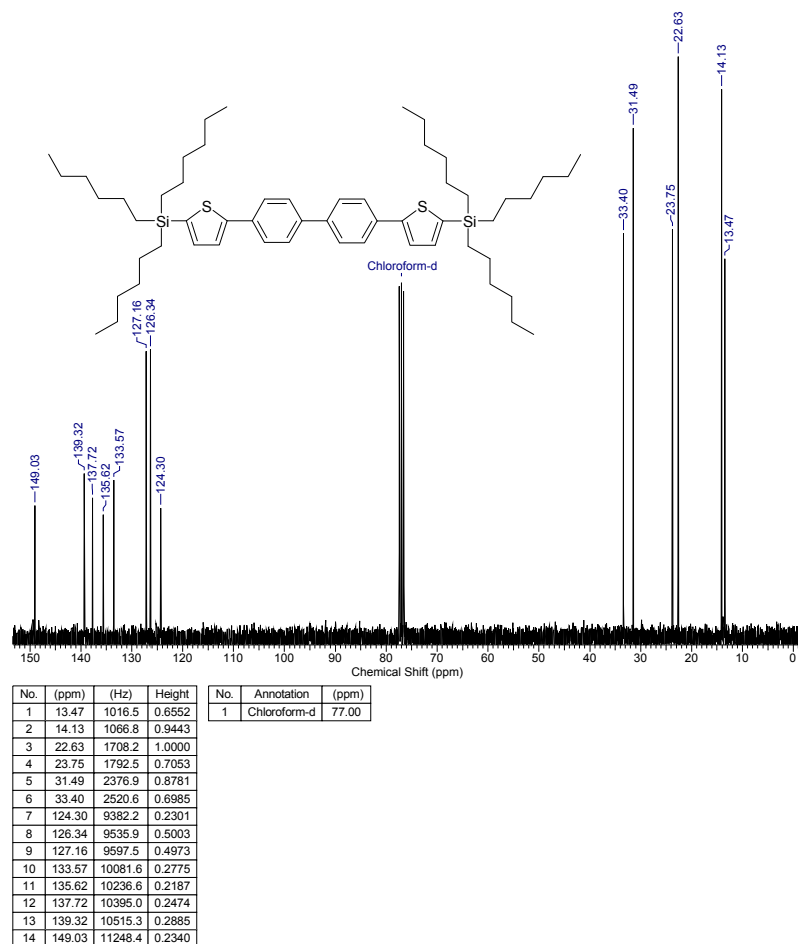
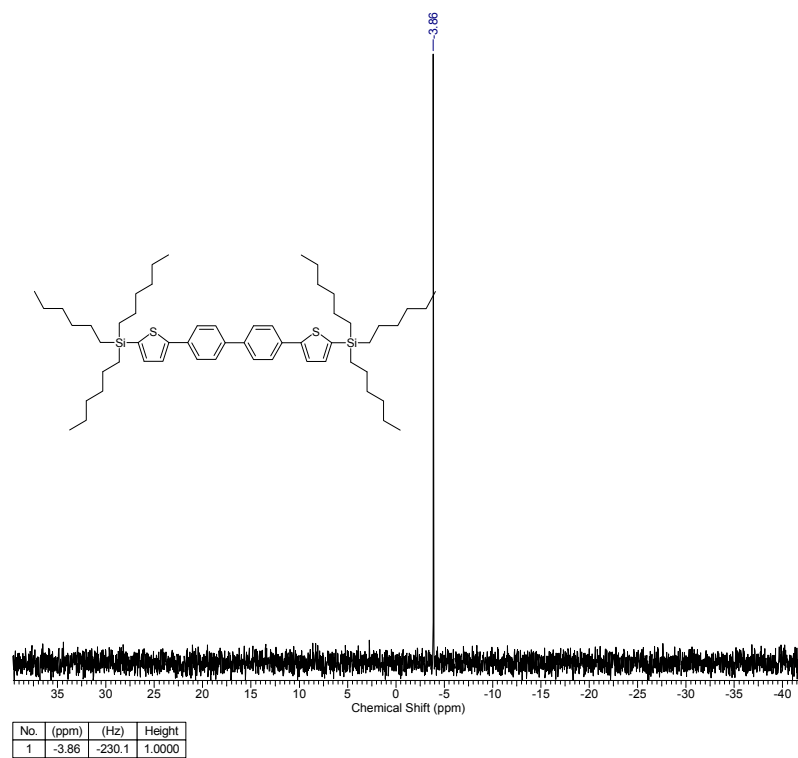


Figure S53.  $^1\text{H}$  NMR spectrum of TPPT-Si-Hex in  $\text{CDCl}_3$



**Figure S54.**  $^{13}\text{C}$  NMR spectrum of TPPT-Si-Hex in  $\text{CDCl}_3$



**Figure S55.**  $^{29}\text{Si}$  NMR spectrum of TPPT-Si-Hex in  $\text{CDCl}_3$

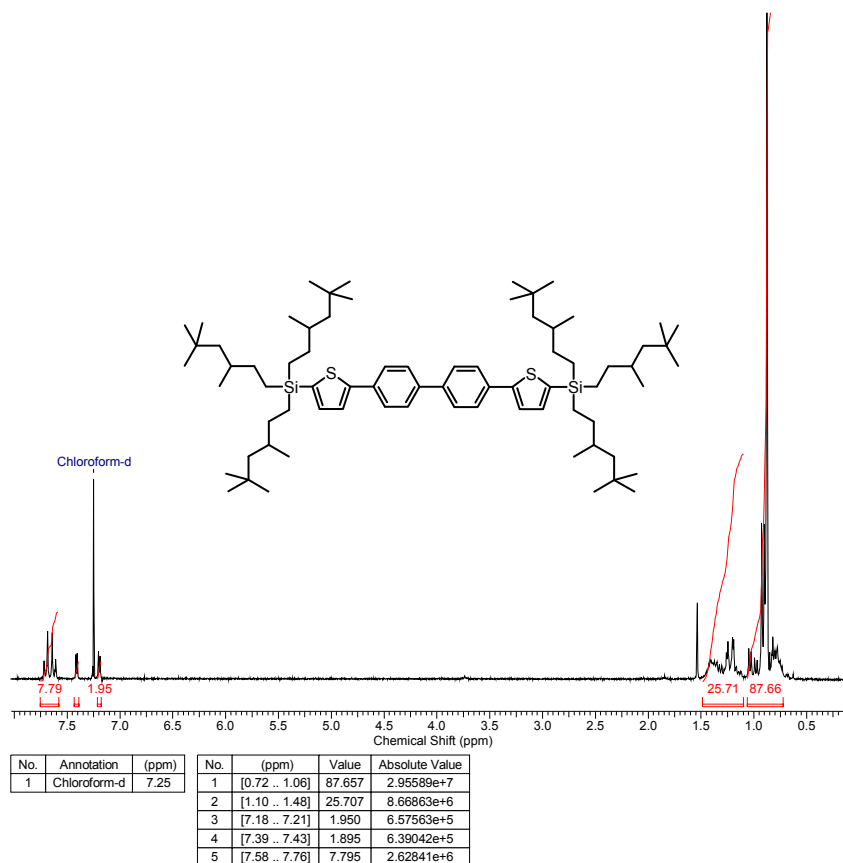


Figure S56.  $^1\text{H}$  NMR spectrum of TPPT-Si-MeHex in  $\text{CDCl}_3$

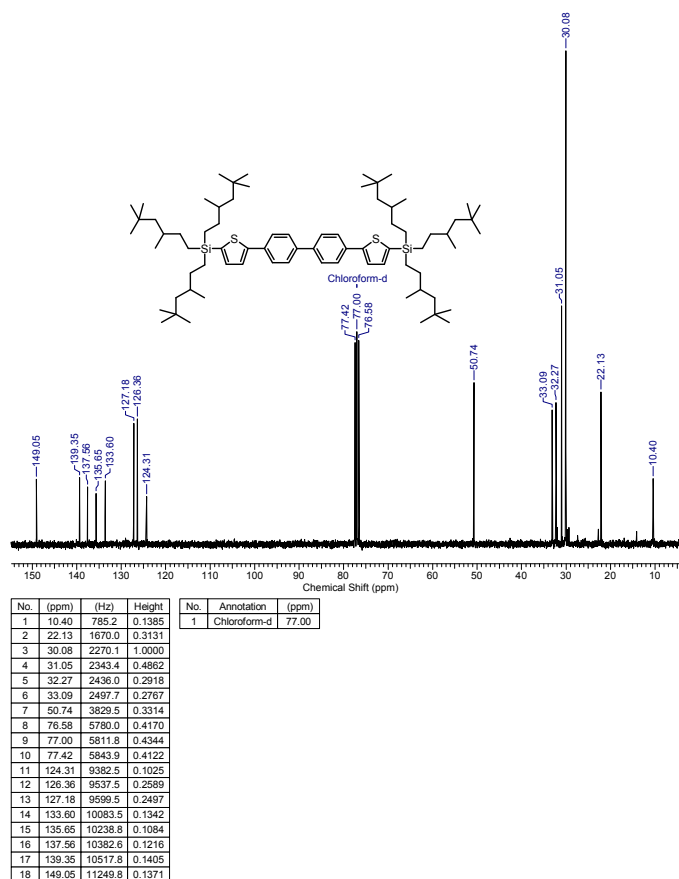


Figure S57.  $^{13}\text{C}$  NMR spectrum of TPPT-Si-MeHex in  $\text{CDCl}_3$



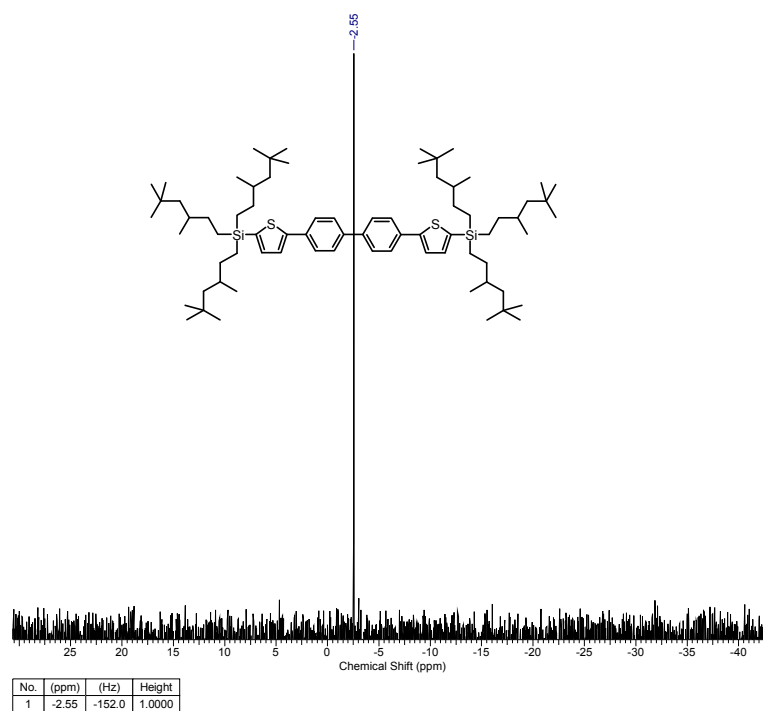


Figure S58.  $^{29}\text{Si}$  NMR spectrum of TPPT-Si-MeHex in  $\text{CDCl}_3$

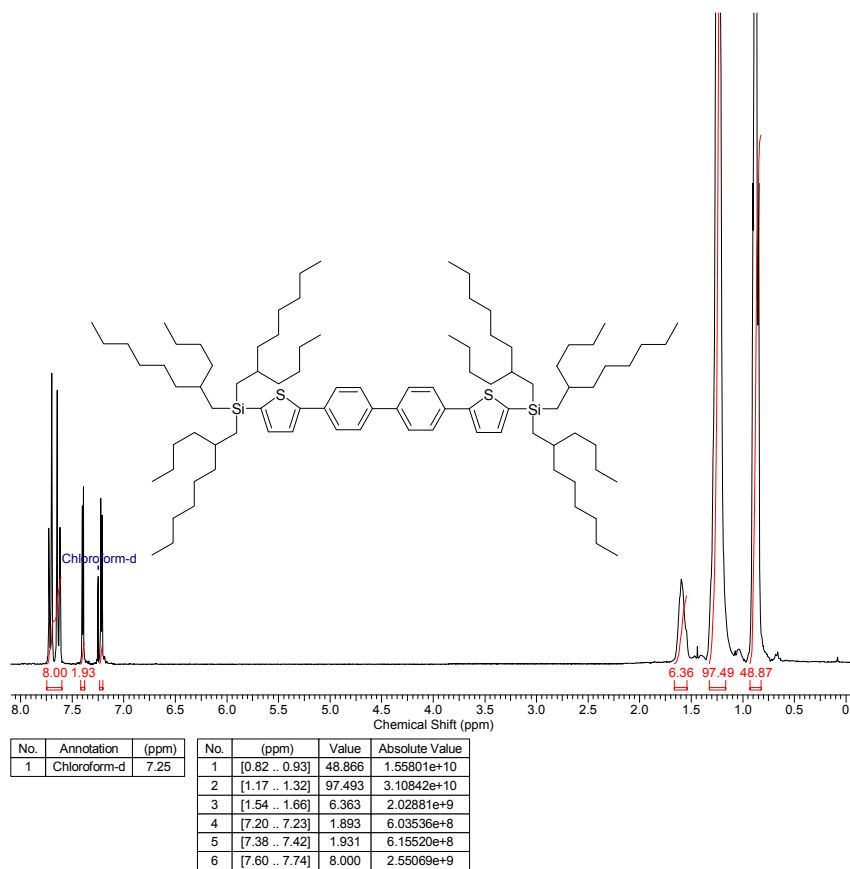
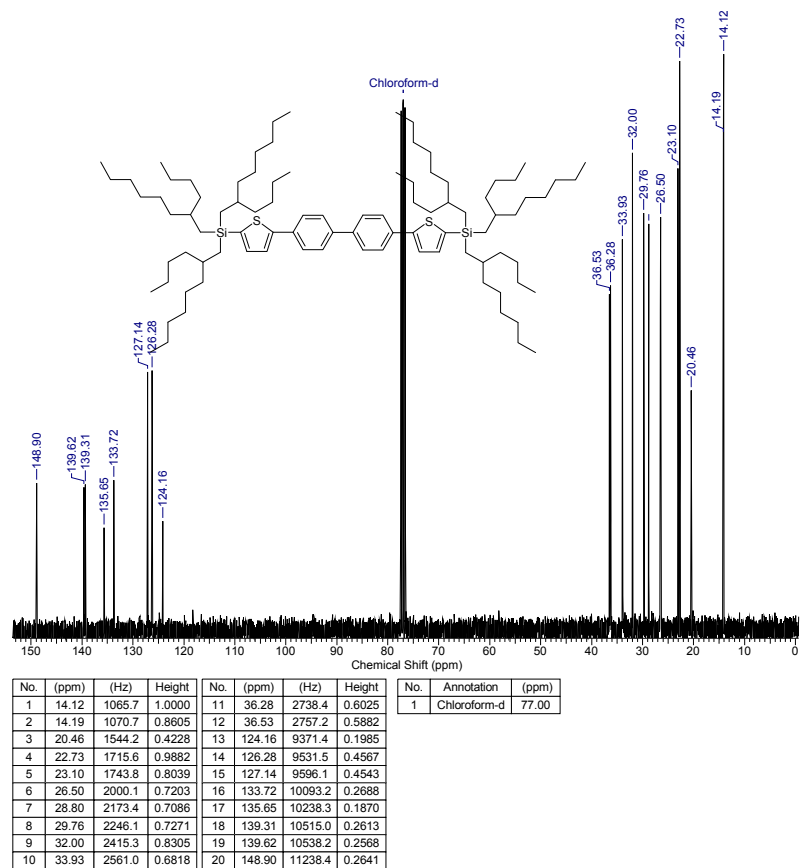
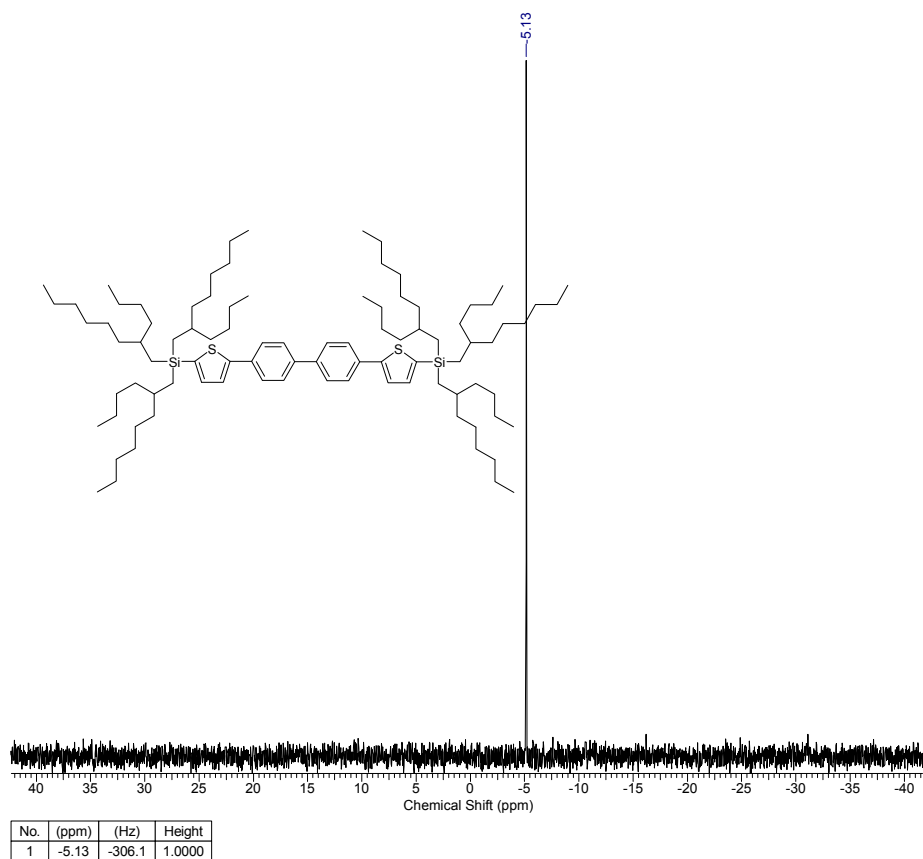


Figure S59.  $^1\text{H}$  NMR spectrum of TPPT-Si-BuOct in  $\text{CDCl}_3$



**Figure S60.**  $^{13}\text{C}$  NMR spectrum of TPPT-Si-BuOct in  $\text{CDCl}_3$



**Figure S61.**  $^{29}\text{Si}$  NMR spectrum of TPPT-Si-BuOct in  $\text{CDCl}_3$

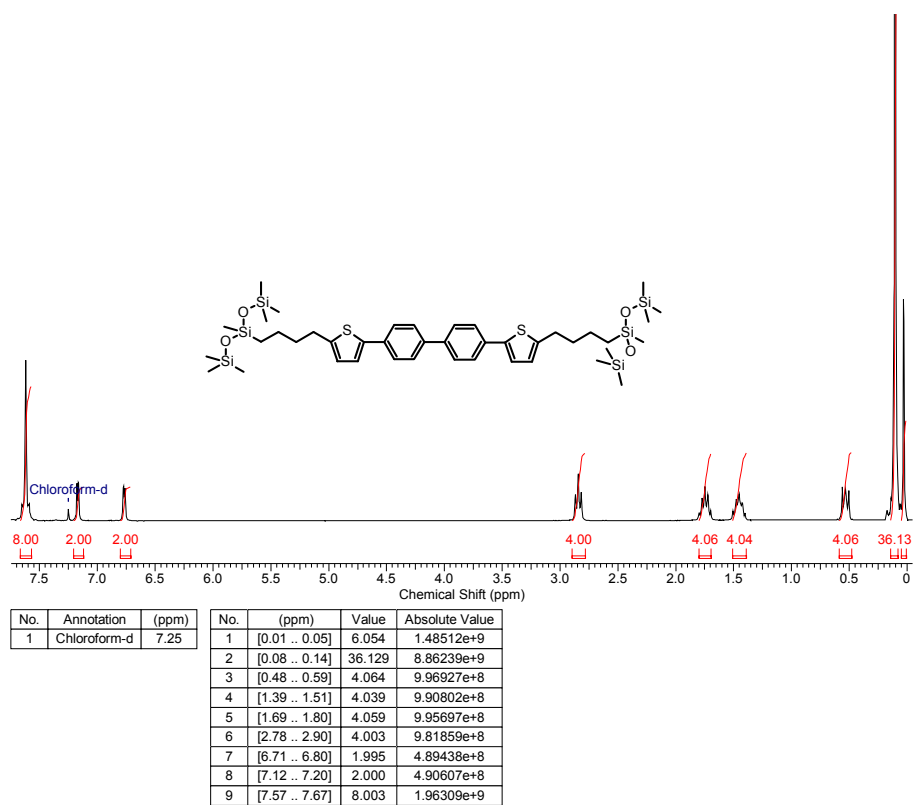


Figure S62. <sup>1</sup>H NMR spectrum of TPPT-Bu-3SiO in CDCl<sub>3</sub>.

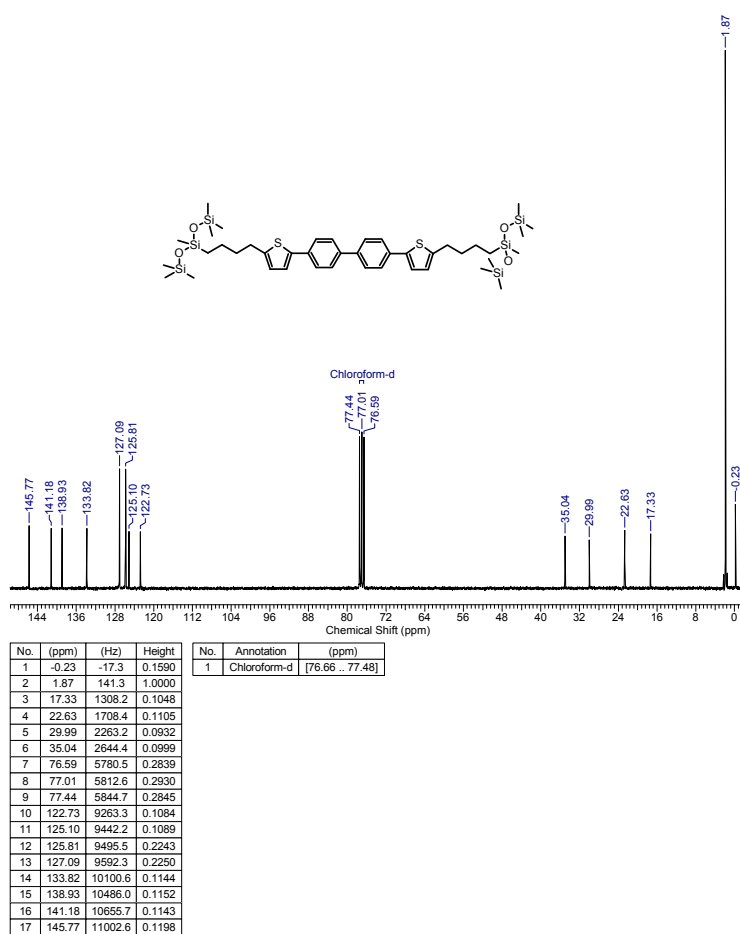
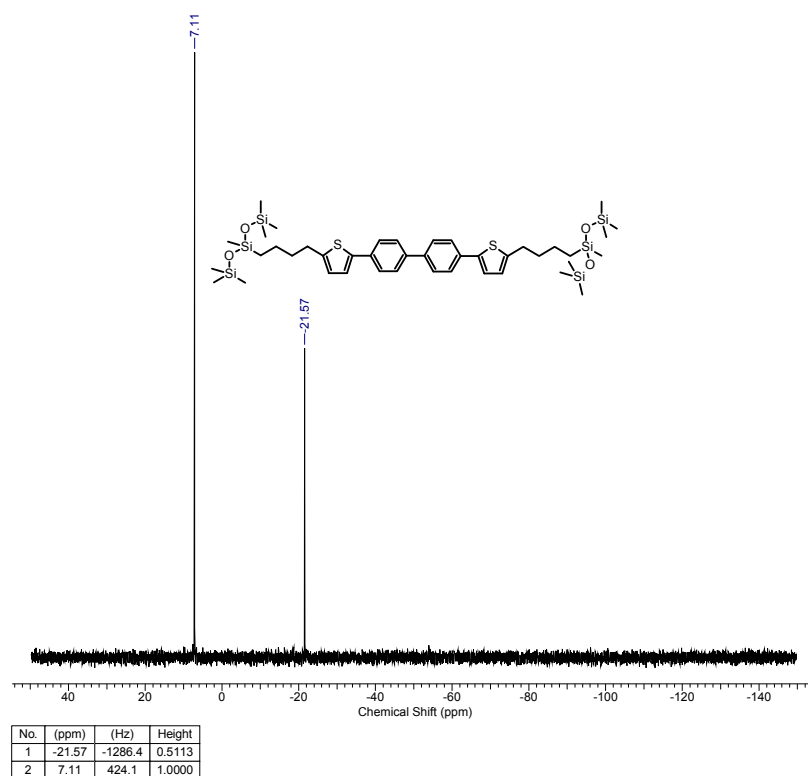
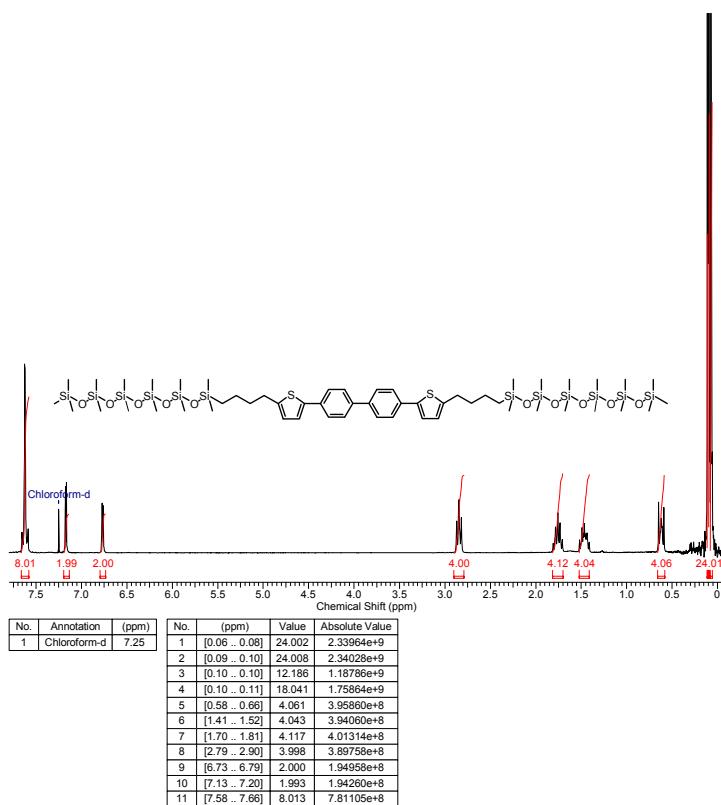


Figure S63. <sup>13</sup>C NMR spectrum of TPPT-Bu-3SiO in CDCl<sub>3</sub>.



**Figure S64.**  $^{29}\text{Si}$  NMR spectrum of TPPT-Bu-3SiO in  $\text{CDCl}_3$ .



**Figure S65.**  $^1\text{H}$  NMR spectrum of TPPT-Bu-6SiO in  $\text{CDCl}_3$ .

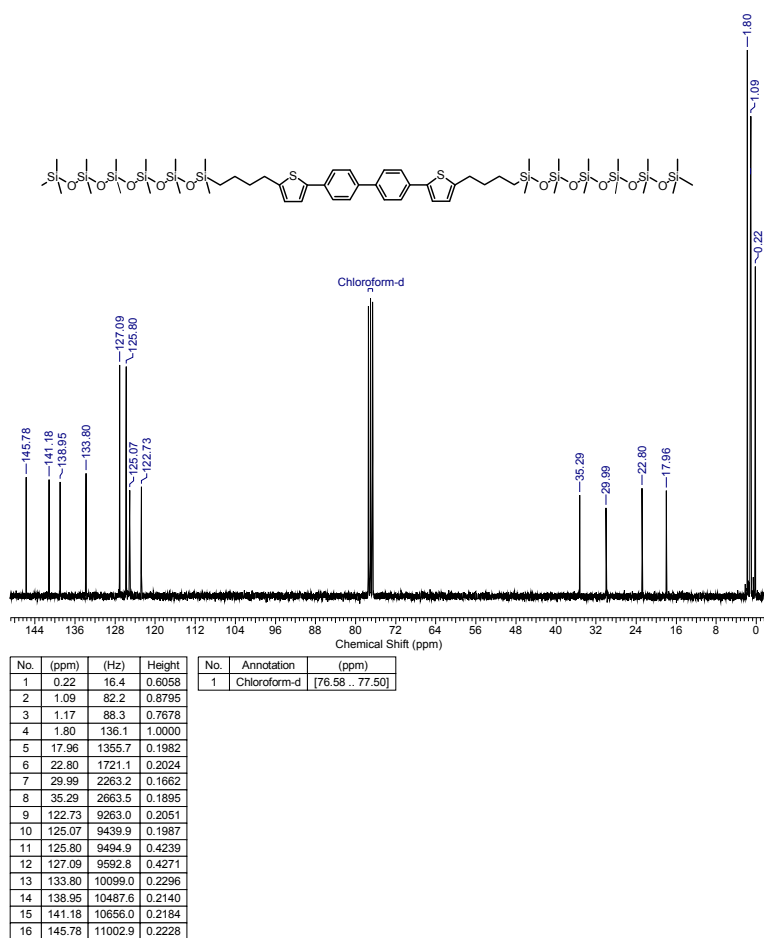


Figure S66.  $^{13}\text{C}$  NMR spectrum of TPPT-Bu-6SiO in  $\text{CDCl}_3$ .

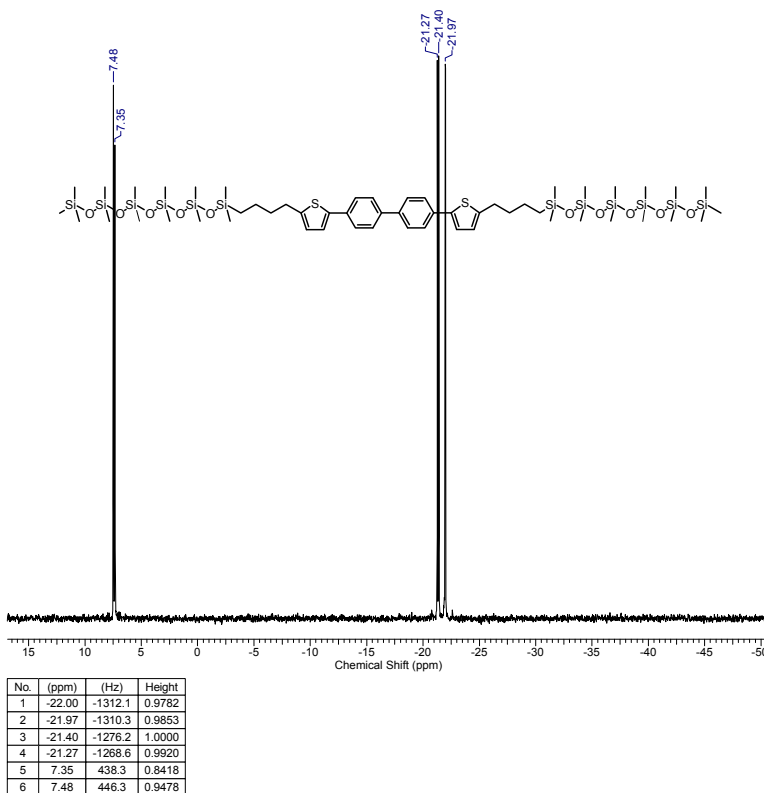
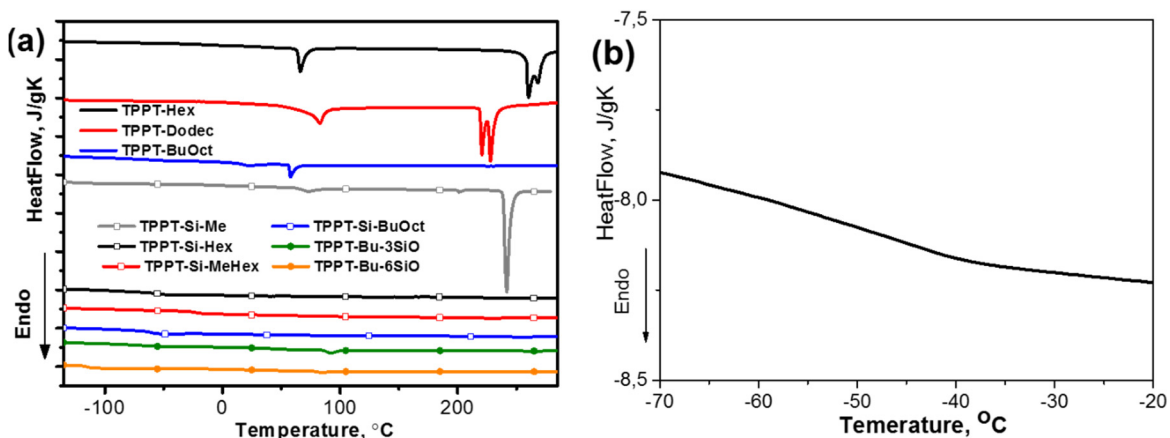
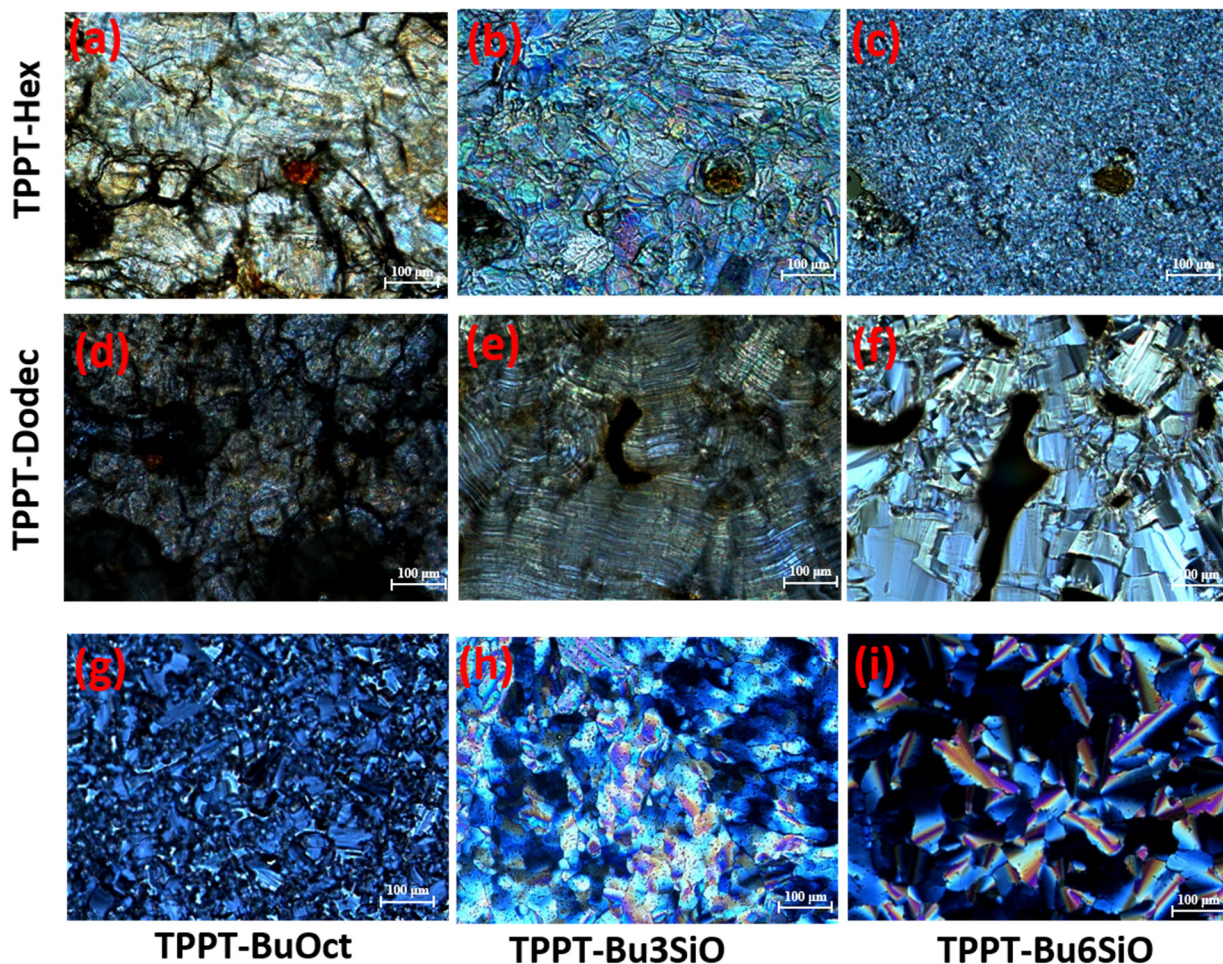


Figure S67.  $^{29}\text{Si}$  NMR spectrum of TPPT-Bu-6SiO in  $\text{CDCl}_3$ .

### 3. Thermal properties and polarizing optical microscopy



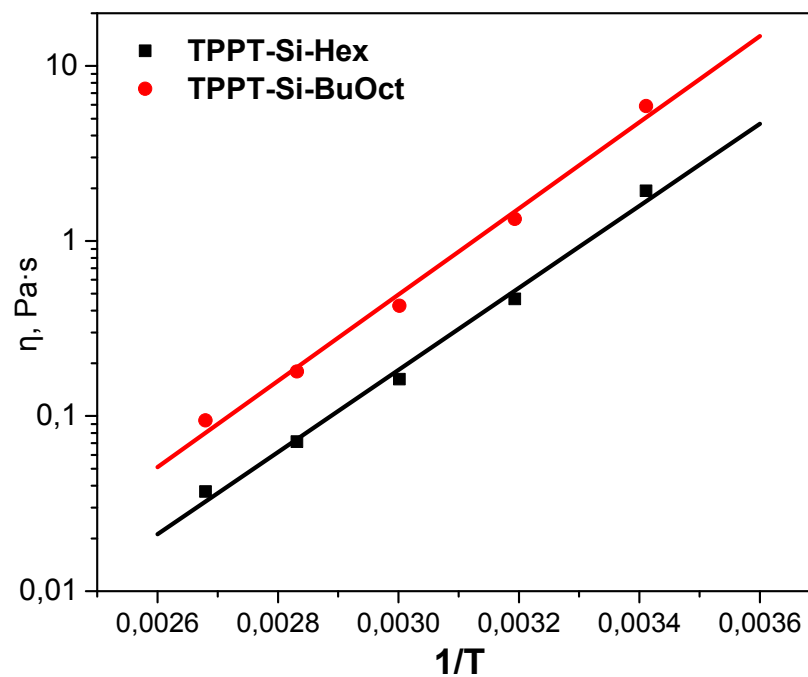
**Figure S68.** (a) The second heating DSC scans of TPPT-based oligomers. (b) The multiplied region of DSC for TPPT-BuOct at the first heating demonstrating the glass transition.



**Figure S69.** Optical polarizing microscopy of TPPT-based oligomers with liquid-crystalline phases. **TPPT-Hex:** (a) crystal phase; (b) smectic phase with a large-grained texture (c) smectic phase with a small-grained texture; **TPPT-Dodec:** (d) crystal phase; (e) smectic phase with a fan-shaped texture (f) smectic phase with a broken fan-shaped texture; **TPPT-BuOct:** (g) smectic phase with a broken fan-shaped texture; **TPPT-Bu3SiO:** (h) hexagonal columnar mesophase texture [10,11, 12]; **TPPT-Bu6SiO:** (i) hexagonal columnar mesophase texture [10,11,12]; The

exact type of the liquid-crystalline phase definition requires comprehensive X-Ray investigation, which will be in the focus of our next manuscript.

#### 4. Rheology



**Figure S70.** Temperature dependences of the viscosity of **TPPT-Si-Hex** (1) and **TPPT-Si-BuOct** (2) in the coordinates of the Arrhenius equation

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