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Supporting Information

Synthesis of organosilicon derivatives of [1]benzothieno[3,2-b][1]-benzothiophene enabling efficient monolayer Langmuir-Blodgett organic field effect transistors

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Contents:

1. General

Bromine, 10-Undecenoyl chloride, heptanoyl chloride, aluminum chloride ($AlCl_3$), sodium borohydride ($NaBH_4$), Zn powder, 1,1,3,3-tetramethyldisiloxane (TMDS) were obtained from Sigma–Aldrich Co. and used without further purification. Chloro(dimethyl)silane (DMCS) was distilled before use. Anhydrous toluene and THF were distilled over CaH_2 under nitrogen atmosphere before using. Dichloromethane was distilled over P_2O_5 before use. [1]Benzothieno[3,2-b][1]benzothiophene (BTBT) was obtained using the procedures described elsewhere.[1] All reactions, unless stated otherwise, were carried out under an inert atmosphere using anhydrous solvents. The solvents were removed in vacuum below 1 Torr at 40 ºC.

^1H NMR spectra were recorded in a "Bruker WP-250" SY spectrometer, working at a frequency of 250.13 MHz and utilizing $CDCl_3$ signal (7.25 ppm) as the internal standard. ^{13}C and ^{29}Si NMR spectra were recorded using a "Bruker Avance II 300" spectrometer at 75 and 60 MHz, respectively. In the case of ^1H NMR spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in $CDCl_3$. In the case of ^{13}C and ^{29}Si NMR spectroscopy, the compounds to be analyzed were taken in the form of 5% solutions in $CDCl_3$. The spectra were then processed on the computer using the ACD Labs software.

GPC analysis was performed by means of a Shimadzu LC10AVP series chromatograph (Japan) equipped with an RID-10AVP refractometer and SPD-M10AVP diode matrix as detectors and a Phenomenex column (USA) with a size of 7.8×300 mm^2 filled with the Phenogel sorbent with a pour size of 500 Å; THF was used as the eluent. For thin layer chromatography (TLC), "Sorbfil" (Russia) TLC plates were used. In the case of column chromatography, silica gel 60 ("Merck") was taken.

Elemental analysis of C, H elements was carried out using CHN automatic analyzer CE1106 (Italy). Experimental error is 0.30−0.50%. Analysis of Br element was carried by visual titration technique using $Hg(NO_3)_2$ and diphenylcarbazone as indicator. The burning was done in the Sheninger flask using alkaline solution of hydrogen peroxide as an absorbent. Experimental error is 0.30−0.50%. The settling titration using $BaCl_2$ was applied to analyze sulfur. Spectrophotometry technique was used for the Si analysis.

Thermogravimetric analysis was carried out in dynamic mode in 30–900 °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 rate was 10 °C/min. Every compound was studied twice: in air and in nitrogen flow of 200 mL/min. DSC scans were obtained with

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[1] Kosata, B.; Kozmic, V.; Svoboda, J.; Novotna, V.; Vanek, P.; Glogarova, M. *Liquid Crystals*, **2003**, *30*, 603–610

Mettler Toledo DSC30 system with 10 °C/min heating/cooling rate in temperature range of +20–250 °C. Nitrogen flow of 50 mL/min was used.

Microwave synthesis was conducting in a microwave synthesizer "Discovery", (CEM corporation, USA), using a standard method with the open vessel option, 50 W.

2. Synthetic procedures

10,11-Dibromoundecanoyl chloride (1)

Bromine (16.00 g, 98.7 mmol) was slowly added to a solution of 10-Undecenoyl chloride (20.00 g, 98.7 mmol) in of dry dichloromethane (50 mL) at 0°C. The mixture was stirred 1 h at 0°C and 1 h at room temperature. After evaporation of the solvent by rotary evaporator, the product was purified by distillation under vacuum (1 mbar, 170 °C) to give pure 10,11-dibromoundecanoyl chloride (28.62 g, 80%) as a colorless liquid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.17 (m, 1H), 3.86 (dd, J = 10.1, 4.3 Hz, 1H), 3.63 (t, J = 10.1 Hz, 1H), 2.90 (t, J = 7.3 Hz, 2H), 2.15 (m, 1H), 1.29-1.88 (overlapping peaks, 13H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.76, 52.99, 47.04, 36.27, 35.93, 29.00, 28.88, 28.60, 28.31, 26.62, 24.98. Anal. calcd. for $C_{11}H_{19}Br_2ClO$: C, 36.44; H, 5.28; Br, 44.08, Cl, 9.78. Found: C, 36.70; H, 5.43; Br, 44.00; Cl, 9.68.

1-([1]Benzothieno[3,2-b][1]benzothiophen-2-yl)-10,11-dibromoundecan-1-one (2)

A solution of [1]Benzothieno[3,2-*b*][1]benzothiophene (BTBT, 1.0 g, 4.2 mmol) in dry dichloromethane (180 ml) was cooled to -5°C and aluminum chloride (1.0 g, 7.5 mmol) was added in one portion. The mixture was stirred for 1 h at the given temperature and then cooled to -70°C. Thereafter, compound **1** (2.71 g, 7.5 mmol) was added dropwise. After 2 h at -70 °C, the reaction mixture was added to water (200 mL) and dichloromethane (300 mL). The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated in vacuum and the product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **2** (2.13 g, 90 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.55 (dd, J = 1.5, 0.6 Hz, 1H), 8.06 (dd, J = 8.2, 1.5 Hz, 1H), 7.94 (m, 3H), 7.49 (m, 2H), 4.17 (m, 1H), 3.86 (dd, J = 10.1, 4.3 Hz, 1H), 3.64 (t, J = 10.1 Hz, 1H), 3.08 (t, J = 7.3 Hz, 2H), 2.15 (m, 1H), 1.73-1.88 (overlapping peaks, 3H), 1.29-1.51 (overlapping peaks, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.48, 142.79, 142.22, 136.92, 136.23, 133.59, 132.95, 132.73, 125.82, 125.12, 124.68, 124.51, 124.13, 122.05, 121.36, 53.11, 38.74, 36.35, 36.00, 29.33, 29.30, 29.20, 28.73, 26.70, 24.45. Anal. calcd. for $C_{25}H_{26}Br_2OS_2$: C, 53.01; H, 4.63; Br, 28.21; S, 11.32. Found: C, 52.92; H, 4.46; Br, 28.53; S, 11.00.

2-(10,11-Dibromoundecyl)-[1]benzothieno[3,2-*b*][1]benzothiophene (3)

To a stirred solution of compound **2** (1.00 g, 1.8 mmol) in dry THF (25 mL), sodium borohydride (0.34 g, 8.9 mmol) and of aluminum chloride (0.59 g, 4.4 mmol) were added successively. After the exothermic reaction had subsided, the mixture was stirred under reflux for

5 h. Thereafter, water (10 mL) was added dropwise. Then the reaction mixture was added to water (100 mL) and dichloromethane (150 mL). The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated in vacuum and the product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **3** (0.81 g, 83 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.9 (dd, *J* = 11.3, 7.6 Hz, 2H),. 7.80 (d, *J* = 8.2 Hz, 1H), 7.73 (s, 1H), 7.43 (m, 2H), 7.30 (dd, *J* = 7.9, 0.9 Hz, 1H), 4.17 (m, 1H), 3.86 (dd, *J* = 10.1, 4.3 Hz, 1H), 3.64 (t, *J* = 10.1 Hz, 1H), 2.78 (t, *J* = 7.3 Hz, 2H), 2.15 (m, 1H), 1.66-1.86 (overlapping peaks, 3H), 1.26-1.51 (overlapping peaks, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.57, 142.06, 140.31, 133.37, 133.25, 132.58, 131.02, 125.89, 124.79, 124.70, 123.98, 123.35, 121.39, 121.25, 53.14, 36.36, 36.10, 36.01, 31.63, 29.41, 29.39, 29.32, 29.21, 28.76, 26.72. Anal. calcd. for $C_{25}H_{28}Br_2S_2$: C, 54.35; H, 5.11; Br, 28.93; S, 11.61. Found: C, 54.24; H, 5.13; Br, 28.69; S, 11.47.

2-(Undec-10-en-1-yl)[1]benzothieno[3,2-b][1]benzothiophene (4)

A mixture of compound **3** (0.25 g, 0.45 mmol) and Zn powder (0.25 g, 3.6 mmol) was added to AcOH (20 ml). The reaction mixture was heated with microwaves for 1–2 min without any stirring. The reaction mixture was then removed from the microwave heater and cooled to room temperature. Water (100 mL) and dichloromethane (100 mL) were added to the reaction mixture and the organic layer was separated. The organic layer was washed with water, dried over sodium sulfate. Evaporation of the solvent give pure compound **4** (0.164 g, 92 %). ^{1}H NMR (250 MHz, $CDCl_3$) *δ* 7.90 (dd, *J* = 14.0, 7.5 Hz, 2H), 7.80 (d, *J* = 8.1, 1H), 7.73 (s, 1H), 7.43 (m, 2H), 7.29 (dd, *J* = 8.1, 1.2, 1H), 5.83 (m, 1H), 4.97 (m, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.05 (dd, *J* = 14.1, 6.8 Hz, 2H), 1.71 (m, 2H), 1.26-1.47 (overlapping peaks, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 142.58, 142.08, 140.36, 139.23, 133.38, 133.27, 132.58, 131.02, 125.89, 124.79, 124.69, 123.98, 123.34, 121.39, 121.24, 114.09, 36.12, 33.80, 31.66, 29.51, 29.49, 29.47, 29.28, 29.12, 28.92. Anal. calcd. ($C_{25}H_{28}S_2$): C, 76.48; H, 7.19; S, 16.33. Found: C, 76.59; H, 6.98; S, 16.11.

Chloro{11-([1]benzothieno[3,2-b][1]benzothien-2-yl)undecyl}dimethylsilane (Cl-Si-Und-BTBT)

Compound **4** (0.15 g, 0.4 mmol) was placed in a 50 mL flask and flooded with argon. Then 10 mL of anhydrous toluene, chloro(dimethyl)silane (0.85 mL, 8 mmol), and Carsted catalyst (10 µL, 0.001 mmol) were added, and the flask was closed by a stopper. The mixture was heated to 90 °C and stirred for 5 h. Then the solvent was removed to give **Ci-Si-Und-BTBT** (0.17 g, 91%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.87 (dd, J = 14.0, 7.5 Hz, 2H), 7.77 (d, J = 8.2, 1H), 7.71 (s, 1H), 7.40 (m, 2H), 7.27 (dd, J = 8.1, 1.3, 2H), 2.75 (t, J = 7.5 Hz, 2H), 1.69 (m, 2H), 1.23-1.43 (overlapping peaks, 16H), 0.80 (m, 2H), 0.39 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 142.56, 142.06, 140.38, 133.37, 133.25, 132.57, 131.00, 125.90, 124.80, 124.70, 123.99, 123.35, 121.39, 121.25, 36.12, 32.96, 31.68, 29.63, 29.54, 29.49, 29.28, 29.23, 22.96 18.97, 1.66. ^{29}Si NMR (60 MHz, $CDCl_3$) δ 32.07.

1-{11-([1]Benzothieno[3,2-b][1]benzothien-2-yl)undecyl}-1,1,3,3-tetramethyl-disiloxane (5)

Compound **4** (0.33 g, 0.7 mmol) was dissolved in toluene (10 mL) and of 1,1,3,3-tetramethyldisiloxane (5 ml) under argon, after which 25 μL of Karstedt's catalyst was added. The reaction was complete after 3 h of stirring at 60 °C. Evaporation of the solvent give pure compound **5** (0.42 g, 98 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 14.0, 7.5 Hz, 2H), 7.80 (d, *J* = 8.1, 1H), 7.73 (s, 1H), 7.43 (m, 2H), 7.29 (dd, *J* = 8.1, 1.2, 1H), 4.70(m, 1H), 2.77 (t, *J* = 7.5 Hz, 2H), 1.72 (m, 2H), 1.26-1.47 (overlapping peaks, 16H), 0.55 (t, *J* = 7.5 Hz, 2H), 0.18 (d, *J* = 2.8, 6H), 0.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.58, 142.08, 140.39, 133.39, 133.28, 132.58, 131.02, 125.90, 124.80, 124.69, 123.98, 123.35, 121.39, 121.25, 36.14, 33.44, 33.39, 31.69, 29.69, 29.59, 29.58, 29.53, 29.41, 29.37, 29.32, 23.18, 18.14, 0.91, 0.05. ^{29}Si NMR (60 MHz, $CDCl_3$) δ 10.00, −6.93. Anal. calcd. ($C_{29}H_{42}OS_2Si_2$): C, 66.10; H, 8.03; S, 12.17; Si, 10.66. Found: C, 65.88; H, 8.18; S, 11.90; Si, 10,88.

1,3-*Bis*{11-([1]benzothieno[3,2-b][1]benzothien-2-yl)undecyl}-1,1,3,3-tetramethyl-disiloxane O(Si-Und-BTBT)$_2$

Compound **4** (0.32 g, 0.8 mmol) and compound **5** (0.35 g, 0.6 mmol) were dissolved in anhydrous toluene (20 mL) under argon, and 25 μL of Karstedt's catalyst was then added. The reaction was complete after the solution was stirred at 65 °C for 6 h. The reaction yield according to GPC analysis was 75%. The crude product was purified by column chromatography on silica gel (eluent mixture toluene : hexane 1:5) to give pure **O(Si-Und-BTBT)$_2$** (0.54 g, 73 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 14.0, 7.5 Hz, 4H), 7.79 (d, *J* = 8.2, 2H), 7.72 (s, 2H), 7.43 (m, 4H), 7.29 (dd, *J* = 8.1, 1.3, 2H), 2.76 (t, *J* = 7.5 Hz, 4H), 1.71 (m, 4H), 1.23-1.43 (overlapping peaks, 32H), 0.51 (t, *J* = 7.5 Hz, 4H), 0.05 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.54, 142.04, 140.36, 133.35, 133.23, 132.55, 130.98, 125.87, 124.77, 124.67, 123.96, 123.32, 121.37, 121.22, 36.12, 33.45, 31.70, 29.71, 29.61, 29.54, 29.41, 29.33, 23.28, 18.41, 0.40. ^{29}Si NMR (60 MHz, $CDCl_3$) δ 7.33. Anal. calcd. ($C_{54}H_{70}OS_4Si_2$): C, 70.53; H, 7.67; S, 13.95; Si, 6.11. Found: C, 70.68; H, 7.64; S, 13.92; Si, 6.11.

1-[7-(10,11-dibromoundecyl)[1]benzothieno[3,2-b][1]benzothien-2-yl]hexan-1-one (6)

A solution compound **3** (0.5 g, 0.9 mmol) in dry dichloromethane (40 mL) was cooled to -5°C and aluminum chloride (0.22 g, 1.6 mmol) was added in one portion. The mixture was stirred for 1 h at the given temperature. Thereafter, the reaction mixture was cooled to -70°C and *n*-hexanoyl chloride (0.2 g, 1.6 mmol) was added dropwise. After 1 h at -70 °C and 8 h at room temperature, the reaction mixture was added to water (200 mL) and dichloromethane (300 mL).

The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated in vacuum and the product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **6** (0.12 g, 20 %). ^{1}H NMR (250 MHz, CDCl$_3$) δ 8.53 (d, J = 0.9 Hz, 1H), 8.05 (dd, J = 8.1, 1.3 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.74 (s, 1H), 7.31 (dd, J = 8.1, 1.2 Hz, 1H,), 4.17 (m, 1H), 3.86 (dd, J= 10.1, 4.3 Hz, 1H), 3.64 (t, J = 10.1 Hz, 1H), 3.06 (t, J = 7.3 Hz, 2H), 2.78 (t, J = 7.5 Hz, 2H), 1.52-1.87 (overlapping peaks, 7H), 2.13 (m, 1H), 1.26-1.51 (overlapping peaks, 14H), 0.94 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 199.54, 143.16, 142.03, 141.29, 136.94, 136.41, 133.37, 132.16, 130.69, 126.16, 124.64, 124.48, 123.42, 121.72, 121.12, 53.12, 38.73, 36.34, 36.14, 36.00, 31.59, 31.56, 29.40, 29.38, 29.31, 29.20, 28.75, 26.70, 24.23, 22.55, 13.97. Anal. calcd. for $C_{31}H_{38}Br_2OS_2$: C, 57.23; H, 5.89; Br, 24.56; S, 9.86. Found: C, 57.30; H, 5.90; Br, 24.55; S, 9.73.

([1]benzothieno[3,2-*b*][1]benzothien-2-yl)-hexan-1-one (8)

A solution of [1]Benzothieno[3,2-*b*][1]benzothiophene (BTBT, 1.0 g, 4.2 mmol) in dry dichloromethane (160 mL) was cooled to -5°C and aluminum chloride (1.0 g, 7.5 mmol) was added in one portion. The mixture was stirred for 1 h at the given temperature. Thereafter, *n*-hexanoyl chloride (1.0 g, 7.5 mmol) was added dropwise. After 1 h at -5 °C, the reaction mixture was added to water (200 mL) and dichloromethane (300 mL). The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated in vacuum and the product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **8** (1.214 g, 86 %). ^{1}H NMR (250 MHz, CDCl$_3$) δ 8.55 (dd, J = 1.5, 0.6 Hz, 1H), 8.06 (dd, J = 8.5, 1.5 Hz, 1H), 7.94 (m, 3H), 7.48 (m, 2H), 3.07 (t, J = 7.3 Hz, 2H), 1.81 (m, 2H), 1.42 (m, 4H), 0.94 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 199.47, 142.78, 142.20, 136.88, 136.18, 133.60, 132.93, 132.72, 125.78, 125.08, 124.64, 124.45, 124.10, 122.01, 121.30, 38.73, 31.58, 24.19, 22.55, 13.96. Anal. calcd. for $C_{20}H_{18}OS_2$: C, 70.97; H, 5.36; S, 18.95. Found: C, 71.08; H, 5.60; S, 18.63.

2-Hexyl-[1]benzothieno[3,2-*b*][1]benzothiophene (9)

To a stirred solution of compound **8** (0.60 g, 1.8 mmol) in dry THF (30 mL) sodium borohydride (0.34 g, 8.9 mmol) and aluminum chloride (0.59 g, 4.4 mmol) were added successively. After the exothermic reaction had subsided, the mixture was stirred under reflux for 4 h. Thereafter, water (10 mL) was added dropwise. Then the reaction mixture was added to water (100 mL) and dichloromethane (150 mL). The organic layer was washed with water, dried over sodium sulfate. The solvent was evaporated in vacuum and the product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **9** (0.44 g, 77 %). ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.90 (dd, J = 14.1, 7.5 Hz, 2H), 7.80 (d, J = 8.2, 1H), 7.73 (s, 1H), 7.44 (m, 2H), 7.30 (dd, J = 8.1, 1.3, 1H), 2.78 (t, J = 7.5 Hz, 2H), 1.72 (m, 2H), 1.36 (m, 6H), 0.92 (t, J = 6.9 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 199.57, 142.07, 140.07, 133.88, 133.26, 132.57, 131.01, 125.88, 124.78, 124.68, 123.97, 123.33, 121.38, 121.23, 36.12, 31.72, 31.64, 28.97, 22.60, 14.09. Anal. calcd. for $C_{20}H_{20}S_2$: C, 74.03; H, 6.21; S, 19.76. Found: C, 74.18; H, 6.44; S, 19.88.

10,11-dibromo-1-(7-hexyl[1]benzothieno[3,2-b][1]benzothien-2-yl)undecan-1-one (10)

A solution of compound **9** (1.0 g, 3.1 mmol) in dry dichloromethane (60 mL) was cooled to -10°C and aluminum chloride (1.23 g, 9.2 mmol) was added in one portion. The mixture was stirred for 1 h at the given temperature. Thereafter, the reaction mixture was cooled to -70°C and compound **1** (5.0 g, 13.9 mmol) was added dropwise. After 2 h at -70 °C, the reaction mixture was added to water (200 mL) and dichloromethane (300 mL). The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated in vacuum and the product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **10** (1.62 g, 81 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.53 (d, J = 0.9 Hz, 1H), 8.05 (dd, J = 8.4, 1.5 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.74 (s, 1H), 7.31 (dd, J = 8.2, J_2 = 1.3 Hz, 1H), 4.18 (m, 1H), 3.86 (dd, J = 10.3, 4.5 Hz, 1H), 3.64 (t, J = 10.0 Hz, 1H), 3.06 (t, J = 7.5 Hz, 2H), 2.78 (t, J = 7.5 Hz, 2H), 2.14 (m, 1H), 1.52-1.87 (overlapping peaks, 7H), 1.26-1.51 (overlapping peaks, 14H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.48, 143.16, 142.03, 141.37, 136.97, 136.44, 133.34, 132.14, 130.67, 126.17, 124.65, 124.49, 123.41, 121.71, 121.13, 53.11, 38.72, 36.35, 36.16, 36.00, 31.70, 31.57, 29.33, 29.31, 29.21, 28.96, 28.73, 26.71, 24.47, 22.59, 14.08. Anal. calcd. for $C_{31}H_{38}Br_2OS_2$: C, 57.23; H, 5.89; Br, 24.56; S, 9.86. Found: C, 56.92; H, 5.65; Br, 24.76; S, 9.64.

2-(10,11-dibromoundecyl)-7-hexyl[1]benzothieno[3,2-b][1]benzothiophene (11)

To a stirred solution of compound **10** (0.3 g, 0.5 mmol) in dry THF (40 mL), sodium borohydride (0.09 g, 2.3 mmol) and aluminum chloride (0.16 g, 1.2 mmol) were added successively. After the exothermic reaction had subsided, the mixture was stirred under reflux for 4 h. Thereafter, water (10 mL) was added dropwise. Then the reaction mixture was added to water (100 mL) and dichloromethane (150 mL). The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated in vacuum and the product was purified by column chromatography on silica gel (eluent toluene) to give pure compound **11** (0.22 g, 75 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H,), 7.72 (s, 2H), 7.28 (dd, J = 8.2, J_2 = 1.3 Hz, 2H), 4.17 (m, 1H), 3.86 (dd, J = 10.3, 4.4 Hz, 1H), 3.63 (t, J = 10.0 Hz, 1H), 2.77(t, J = 7.5 Hz, 4H), 2.14 (m, 1H), 1.52-1.87 (overlapping peaks, 7H), 1.26-1.51 (overlapping peaks, 16H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.41, 140.06, 139.97, 132.55, 132.53, 131.21, 131.19, 125.81, 123.31, 121.05, 53.13, 36.35, 36.11, 36.09, 36.04, 31.73, 31.64, 31.62, 29.41, 29.40, 29.32, 29.22, 28.98, 28.77, 26.73, 22.60, 14.08. Anal. calcd. for $C_{31}H_{40}Br_2S_2$: C, 58.49; H, 6.33; Br, 25.10; S, 10.07. Found: C, 58.30; H, 6.31; Br, 25.32; S, 9.98.

2-Hexyl-7-(undec-10-en-1-yl)[1]benzothieno[3,2-b][1]benzothiophene (12)

A mixture of compound **11** (0.93 g, 1.5 mmol) and Zn powder (0.48 g, 7.3 mmol) were added to AcOH (20 mL). The reaction mixture was heated with microwaves for 1–2 min without any stirring. The reaction mixture was then removed from the microwave heater and cooled to room temperature. Water (100 mL) and dichloromethane (100 mL) were added to the reaction mixture and the organic layer was separated. The organic layer was washed with water and dried over sodium sulfate. Evaporation of the solvent give pure compound **12** (0.64 g, 92 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H,), 7.71 (s, 2H), 7.28 (dd, J = 8.2, J_2 = 1.3 Hz, 2H), 5.82 (m, 1H), 4.97 (m, 2H), 2.77(t, J = 7.5 Hz, 4H), 2.05 (dd, J = 14.2, J_2 = 6.8 Hz, 2H,), 1.72 (m, 4H), 1.25-1.47 (overlapping peaks, 18H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.44, 140.06, 140.04, 139.22 132.57, 131.23, 131.19, 125.82, 123.31, 121.05, 114.09, 36.12, 33.80, 31.74, 31.65, 29.52, 29.50, 29.48, 29.30, 29.13, 28.99, 28.94, 22.60, 14.07. Anal. calcd. for $C_{31}H_{40}S_2$: C, 78.09; H, 8.46; S, 13.45. Found: C, 78.21; H, 8.52; S, 13.42.

1-{11-(7-Hexyl[1]benzothieno[3,2-b][1]benzothien-2-yl)undecyl}-1,1,3,3-tetramethyl-disiloxane (13)

0.33 g (0.7 mmol) compound **12** was dissolved in toluene (10 mL) and 1,1,3,3-tetramethyldisiloxane (1.86 mL) under argon, after which 25 µl of Karstedt’s catalyst was added. The reaction was complete after 3 h of stirring at 50-60 °C. Evaporation of the solvent give pure compound **13** (0.42 g, 98 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H,), 7.70 (s, 2H), 7.26 (dd, J = 8.2, J_2 = 1.3 Hz, 2H), 4.69 (m, 1H), 2.75(t, J = 7.5 Hz, 4H), 1.70 (m, 4H), 1.25-1.47 (overlapping peaks, 20H), 0.90 (t, J = 7.0 Hz, 3H), 0.53 (t, J = 7.5 Hz, 2H), 0.16 (d, J = 2.8, 6H), 0.06 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.42, 140.05, 132.55, 131.21, 125.81, 123.31, 121.05, 36.13, 33.39, 31.74, 31.70, 31.65, 29.69, 29.60, 29.54, 29.37, 29.33, 28.99, 23.21, 23.19, 22.61, 18.15, 14.08, 0.91, 0.21, 0.05. ^{29}Si NMR (60 MHz, $CDCl_3$) δ 10.00, − 6.93. Anal. calcd. for $C_{35}H_{54}S_2Si_2$: C, 68.79; H, 8.91; S, 10.49; Si, 9.19. Found: C, 68.72; H, 9.07; S, 10.44; Si, 9.10.

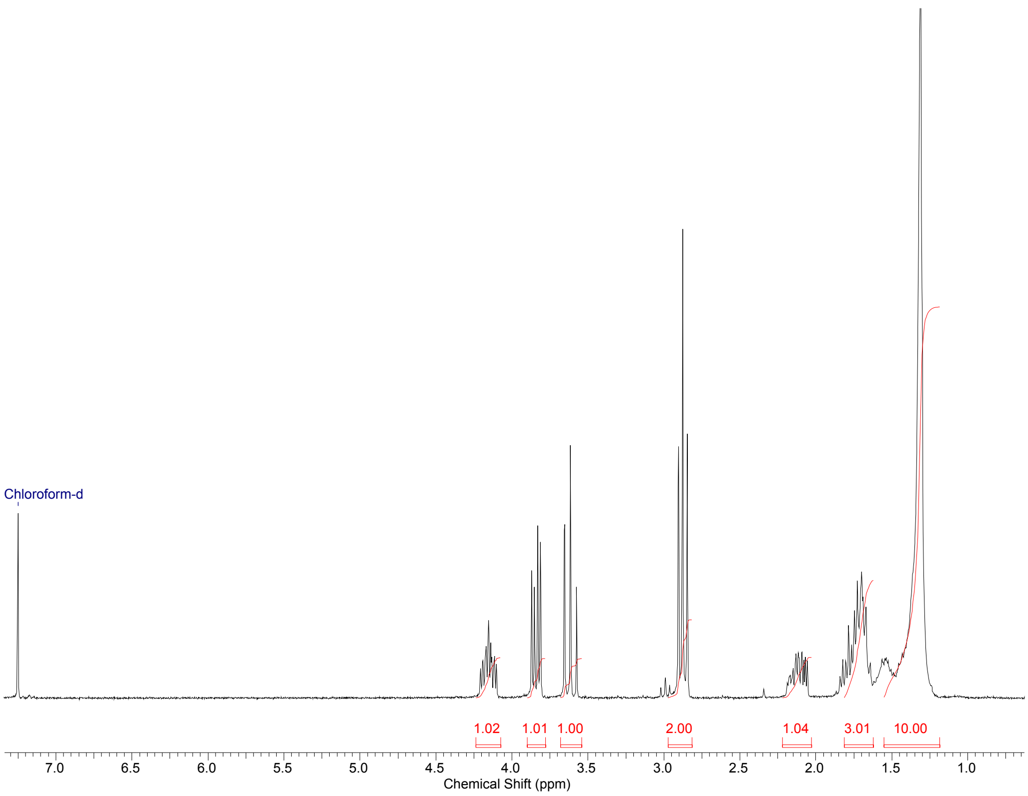
1,3-*Bis*{11-(7-hexyl[1]benzothieno[3,2-b][1]benzothien-2-yl)undecyl}-1,1,3,3-tetramethyldisiloxane O(Si-Und-BTBT-Hex)$_2$

0.27 g (0.6 mmol) compound **12** and 0.35 g (0.6 mmol) compound **13** were dissolved in anhydrous toluene (15 mL) under argon, and 25 µl of Karstedt’s catalyst was then added. The reaction was complete after the solution was stirred at 55 °C for 5 h. The reaction yield according to GPC analysis was 75%. The crude product was purified by column chromatography on silica gel (eluent mixture toluene : hexane 1:10) to give pure **O(Si-Und-BTBT-Hex)$_2$** (0.38 g, 61 %). ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 0.05 (s, 12 H), 0.52 (t, 4 H, J = 7.4 Hz), 0.91 (t, 6 H, J = 7.0 Hz), 1.22-1.47 (overlapping peaks, 48H), 1.71 (m, 8H), 2.76 (t, 4H, J = 7.5 Hz), 7.26 (d, 4H, *J* = 8.1 Hz), 7.70 (s, 4H), 7.76 (d, 2H, *J* = 8.1 Hz). ^{13}C NMR (75 MHz, CDCl$_3$): δ [ppm] 0.40, 14.11, 18.41, 22.61, 23.29, 28.99, 29.35, 29.42, 29.55, 29.62, 29.72, 31.68, 31.73, 33.45, 36.11, 121.03, 123.28, 125.78, 131.15, 132.50, 140.02, 142.37. ^{29}Si (75 MHz, CDCl$_3$): δ [ppm] 7.33. Anal. calcd. for $C_{66}H_{94}OS_4Si_2$: C, 72.87; H, 8.71; S, 11.79; Si, 5.16. Found: C, 72.94; H, 8.81; S, 11.59; Si, 5.26.

Chloro{11-(7-hexyl[1]benzothieno[3,2-b][1]benzothien-2-yl)undecyl}dimethylsilane (Cl-Si-Und-BTBT-Hex)

Compound **12** (0.1 g, 0.2 mmol) was placed in a 50 mL flask and flooded with argon. Then 5 mL of anhydrous toluene, chloro(dimethyl)silane (0.5 mL, 4 mmol), and Carsted catalyst (10 µL, 0.001 mmol) were added, and the flask was closed by a stopper. The mixture was heated to 60 °C and stirred for 5 h. Then the solvent was removed to give **Ci-Si-Und-BTBT-Hex** (0.108 g, 90 %). ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H,), 7.69 (s, 2H), 7.26 (dd, *J* = 8.1, J_2 = 1.3 Hz, 2H), 4.69 (m, 1H), 2.75(t, *J* = 7.5 Hz, 4H), 1.69 (m, 4H), 1.25-1.47 (overlapping peaks, 20H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 2H), 0.39 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 142.37, 140.05, 140.03, 132.51, 131.17, 125.81, 123.31, 121.04, 36.11, 32.96, 31.73, 31.70, 31.68, 29.63, 29.55, 29.49, 29.29, 29.23, 28.98, 22.96, 22.61, 18.97, 14.10, 1.66. ^{29}Si NMR (60 MHz, CDCl$_3$) δ 32.06.

3. ^{1}H, ^{13}C and ^{29}Si NMR spectra



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[1.18 .. 1.55]	10.002	8.89094e+7
2	[1.62 .. 1.81]	3.008	2.67398e+7
3	[2.03 .. 2.22]	1.041	9.25070e+6
4	[2.81 .. 2.97]	1.996	1.77458e+7
5	[3.54 .. 3.68]	1.000	8.89319e+6
6	[3.78 .. 3.90]	1.009	8.97060e+6
7	[4.07 .. 4.24]	1.024	9.10600e+6

Figure S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$

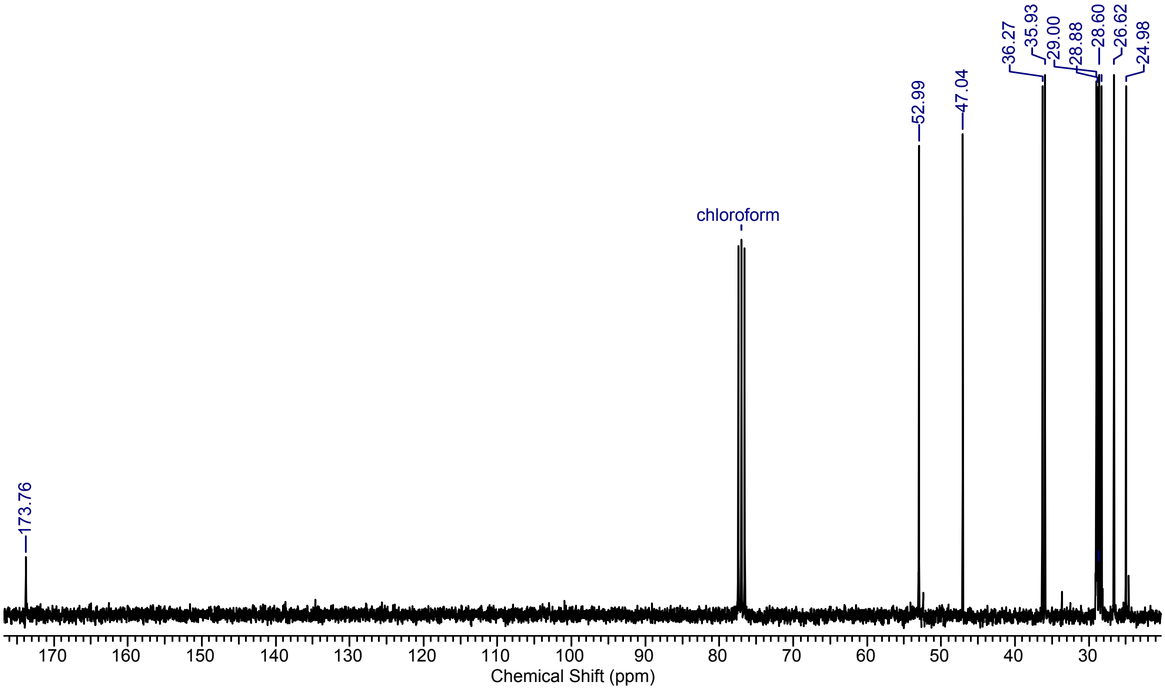
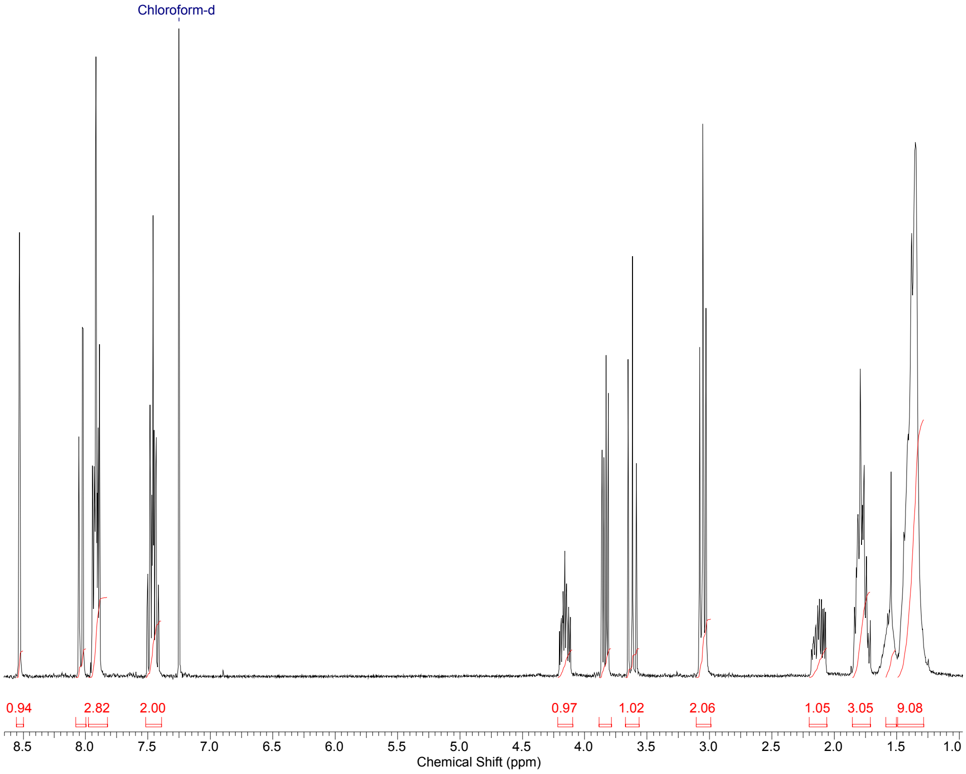


Figure S2. ^{13}C NMR spectrum of compound **1** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[1.28 .. 1.49]	9.081	4.44918e+10
2	[1.50 .. 1.59]	1.008	4.94099e+9
3	[1.71 .. 1.86]	3.050	1.49445e+10
4	[2.06 .. 2.20]	1.047	5.13202e+9
5	[2.99 .. 3.11]	2.057	1.00809e+10
6	[3.57 .. 3.68]	1.020	4.99793e+9
7	[3.79 .. 3.88]	1.016	4.97590e+9
8	[4.10 .. 4.22]	0.973	4.76820e+9
9	[7.39 .. 7.52]	2.000	9.79742e+9
10	[7.82 .. 7.98]	2.821	1.38240e+10
11	[8.00 .. 8.08]	1.010	4.94951e+9
12	[8.50 .. 8.56]	0.939	4.60173e+9

Figure S3. ^{1}H NMR spectrum of compound **2** in $CDCl_3$

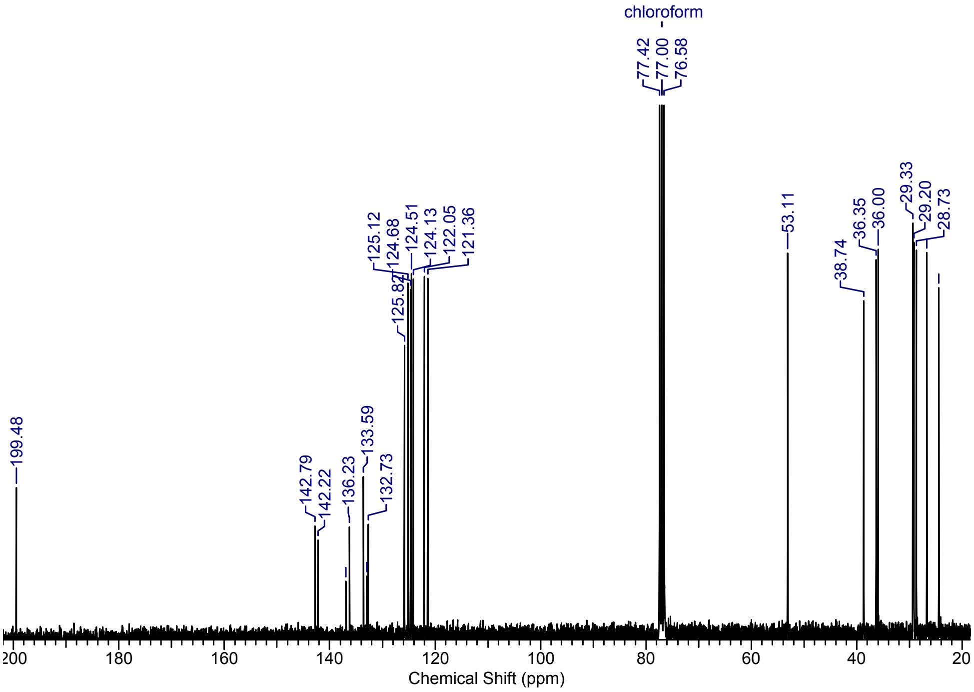
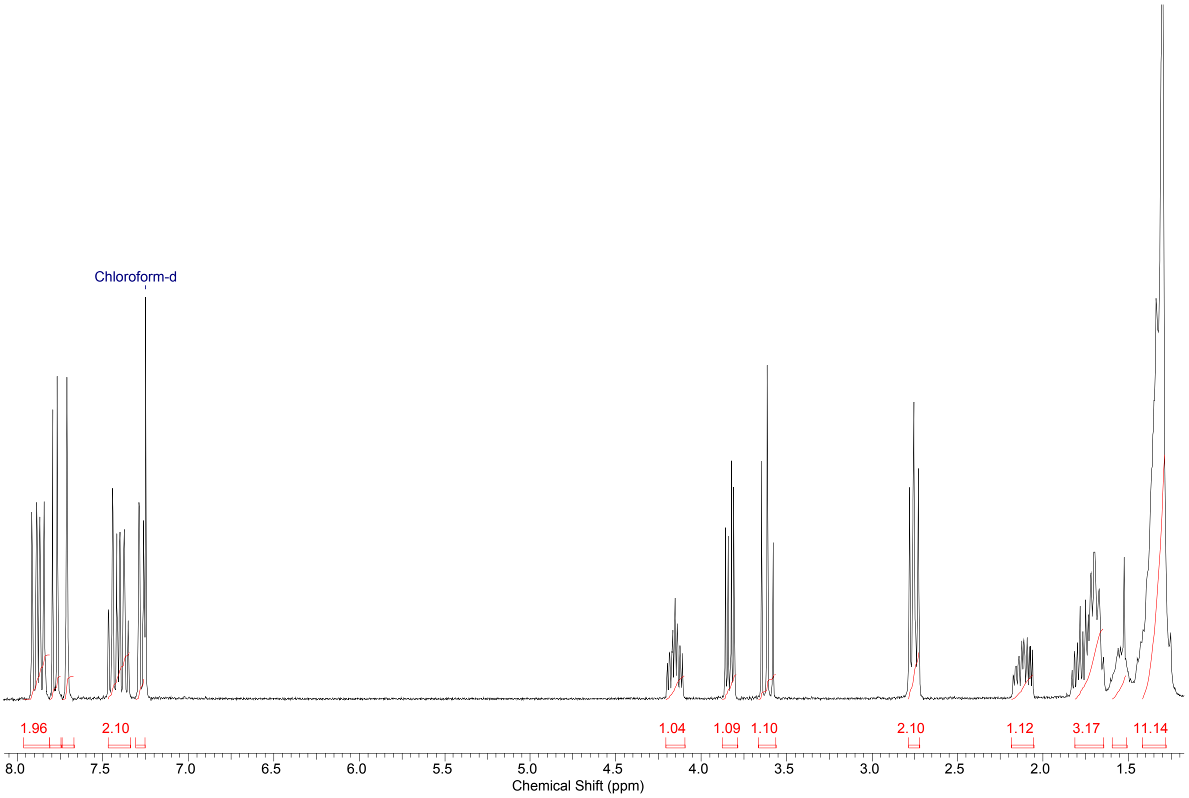


Figure S4. ^{13}C NMR spectrum of compound **2** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[1.28 .. 1.42]	11.136	3.59267e+10
2	[1.51 .. 1.60]	1.101	3.55073e+9
3	[1.65 .. 1.81]	3.173	1.02371e+10
4	[2.06 .. 2.18]	1.117	3.60465e+9
5	[2.72 .. 2.79]	2.103	6.78345e+9
6	[3.56 .. 3.67]	1.099	3.54518e+9
7	[3.79 .. 3.88]	1.090	3.51766e+9
8	[4.09 .. 4.21]	1.040	3.35529e+9
9	[7.25 .. 7.31]	1.074	3.46525e+9
10	[7.34 .. 7.47]	2.098	6.76765e+9
11	[7.67 .. 7.74]	1.010	3.25765e+9
12	[7.75 .. 7.81]	1.020	3.28968e+9
13	[7.81 .. 7.96]	1.961	6.32539e+9

Figure S5. ^{1}H NMR spectrum of compound **3** in $CDCl_3$

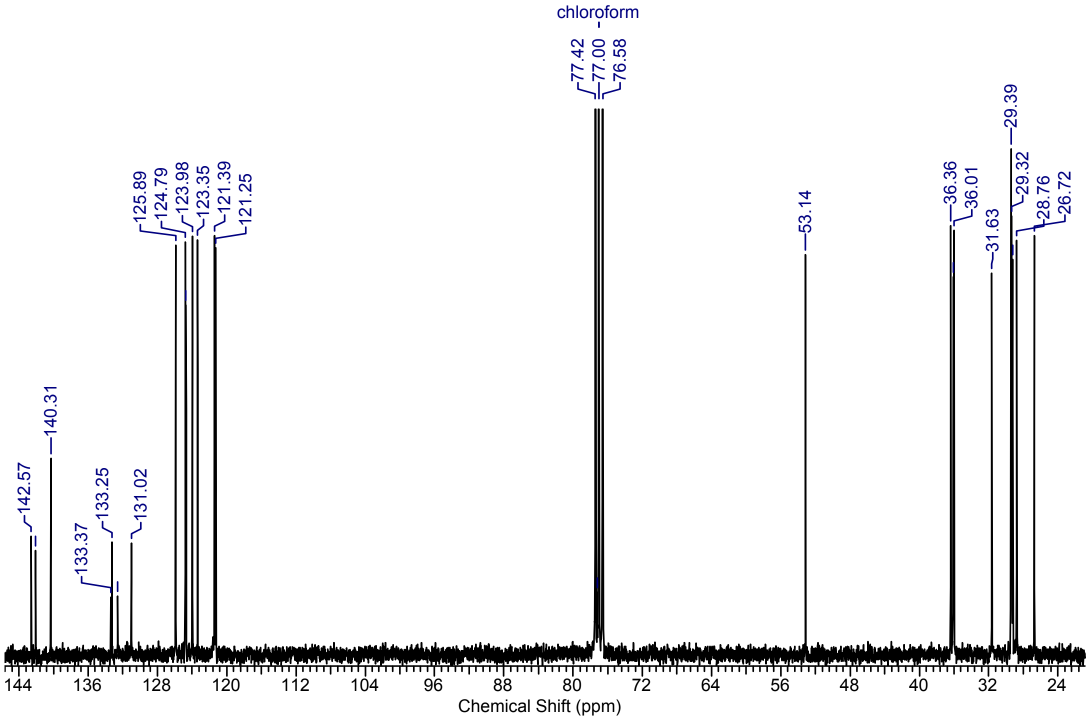
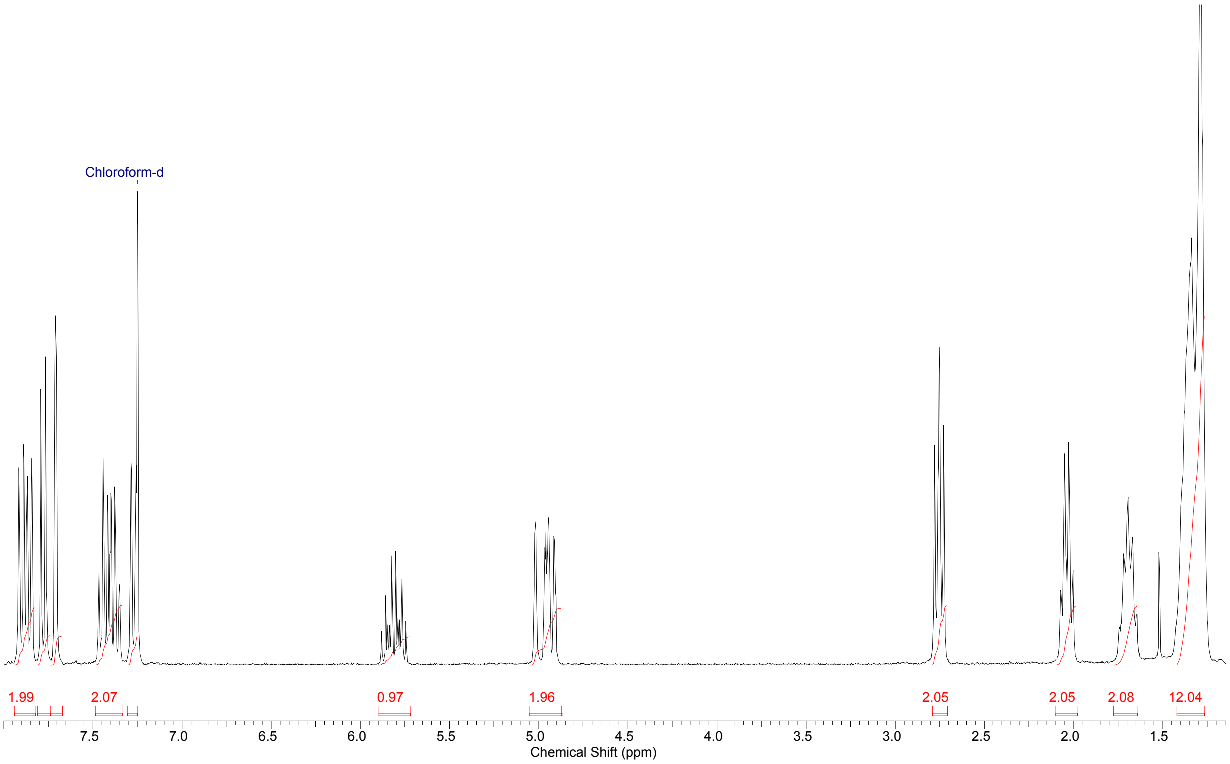


Figure S6. ^{13}C NMR spectrum of compound **3** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[1.27 .. 1.42]	12.044	6.75903e+10
2	[1.64 .. 1.78]	2.075	1.16468e+10
3	[1.98 .. 2.10]	2.048	1.14916e+10
4	[2.71 .. 2.79]	2.052	1.15140e+10
5	[4.87 .. 5.05]	1.957	1.09857e+10
6	[5.72 .. 5.90]	0.973	5.46195e+9
7	[7.25 .. 7.30]	1.057	5.93127e+9
8	[7.34 .. 7.48]	2.072	1.16293e+10
9	[7.67 .. 7.74]	1.000	5.61193e+9
10	[7.74 .. 7.81]	1.017	5.71002e+9
11	[7.82 .. 7.94]	1.986	1.11460e+10

Figure S7. ^{1}H NMR spectrum of compound **4** in $CDCl_3$

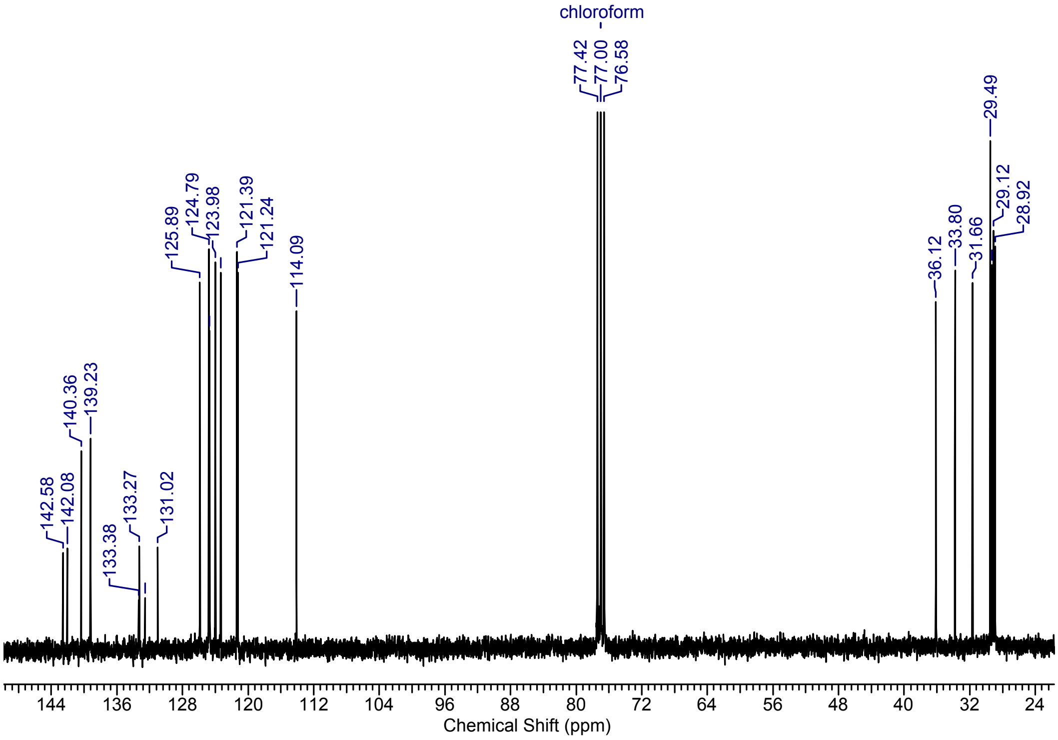
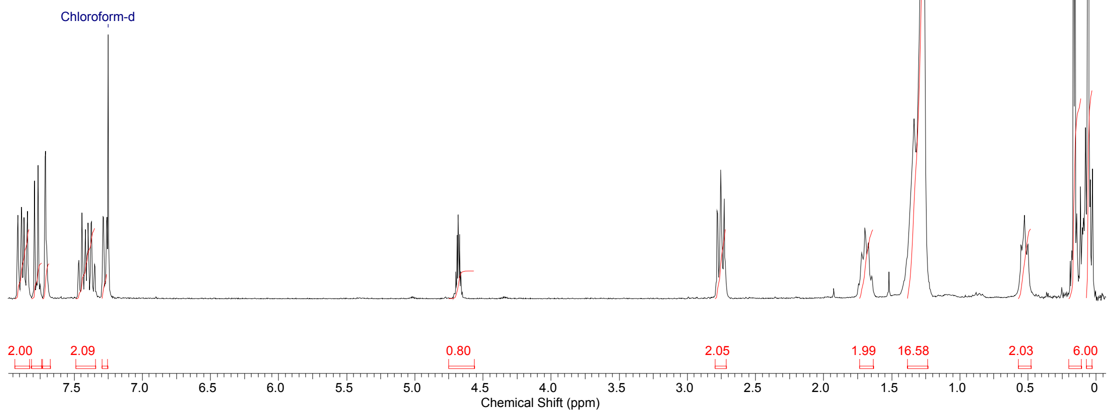


Figure S8. ^{13}C NMR spectrum of compound **4** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.03 .. 0.07]	6.002	7.02911e+9
2	[0.11 .. 0.20]	5.871	6.87576e+9
3	[0.48 .. 0.57]	2.032	2.37964e+9
4	[1.24 .. 1.38]	16.581	1.94190e+10
5	[1.63 .. 1.73]	1.994	2.33563e+9
6	[2.72 .. 2.79]	2.045	2.39508e+9
7	[4.56 .. 4.75]	0.796	9.32247e+8
8	[7.25 .. 7.29]	0.964	1.12860e+9
9	[7.34 .. 7.49]	2.090	2.44724e+9
10	[7.68 .. 7.73]	1.018	1.19189e+9
11	[7.74 .. 7.81]	1.027	1.20300e+9
12	[7.83 .. 7.93]	1.999	2.34165e+9

Figure S9. ^{1}H NMR spectrum of compound **5** in $CDCl_3$

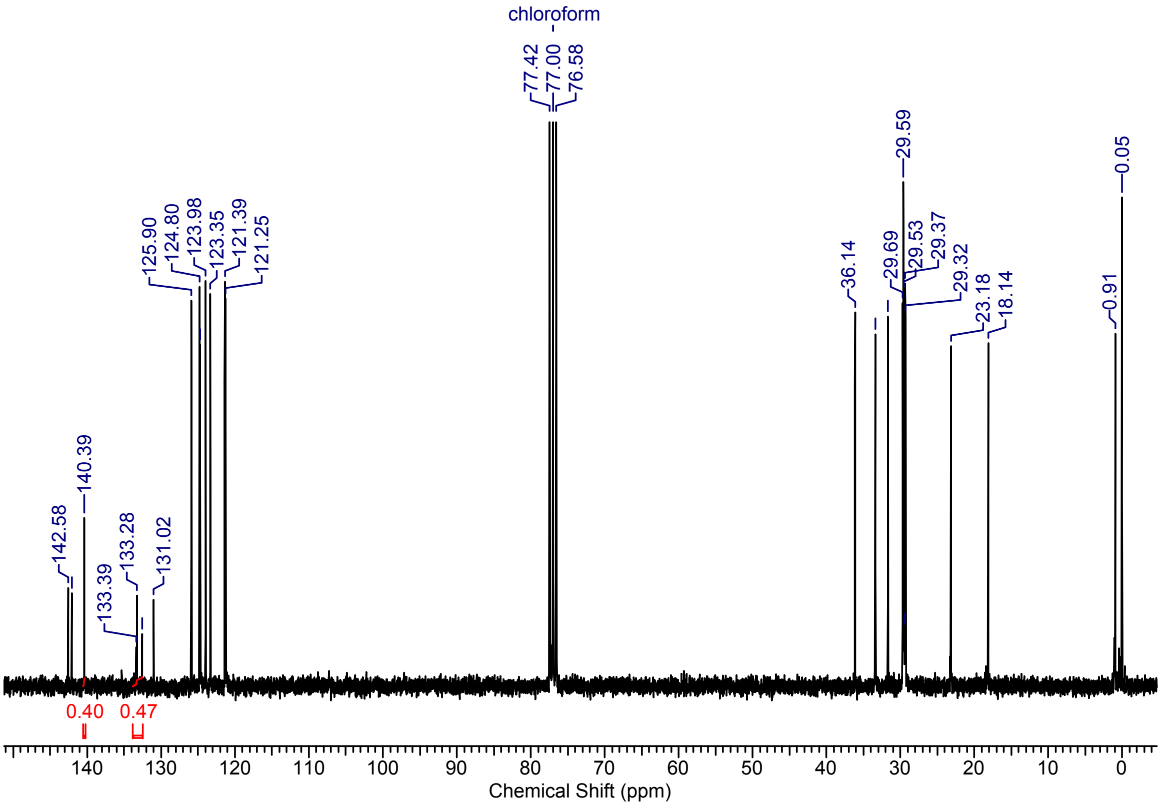


Figure S10. ^{13}C NMR spectrum of compound **5** in $CDCl_3$

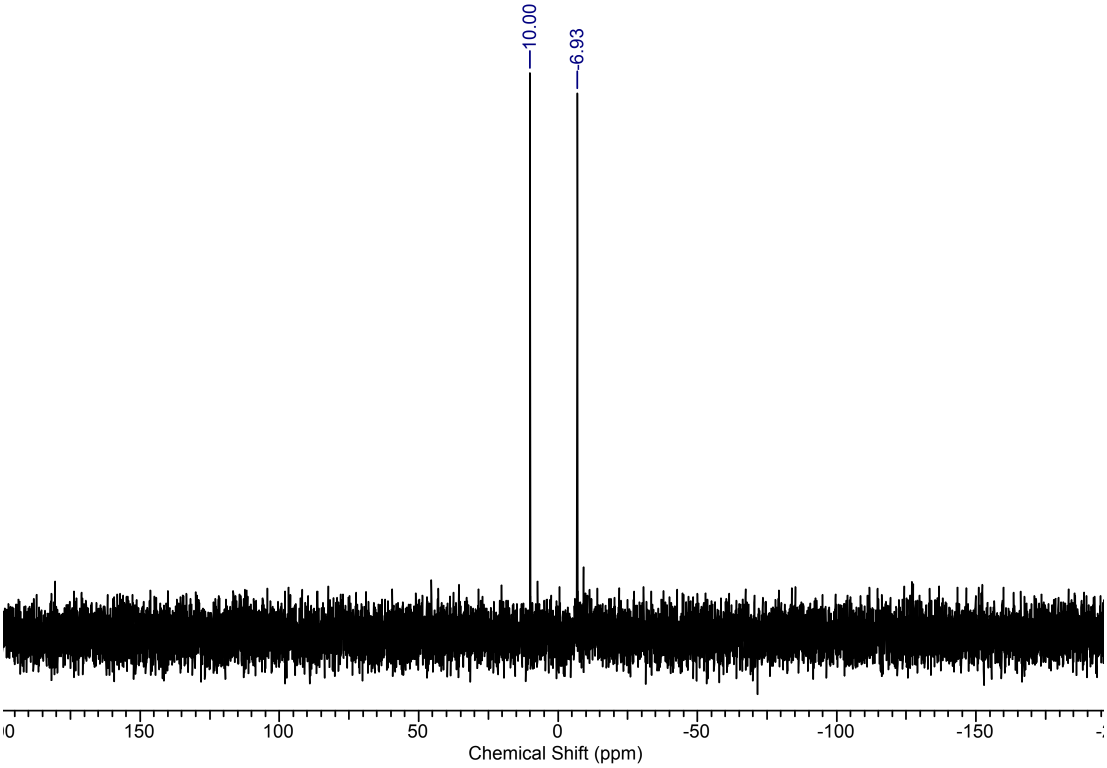
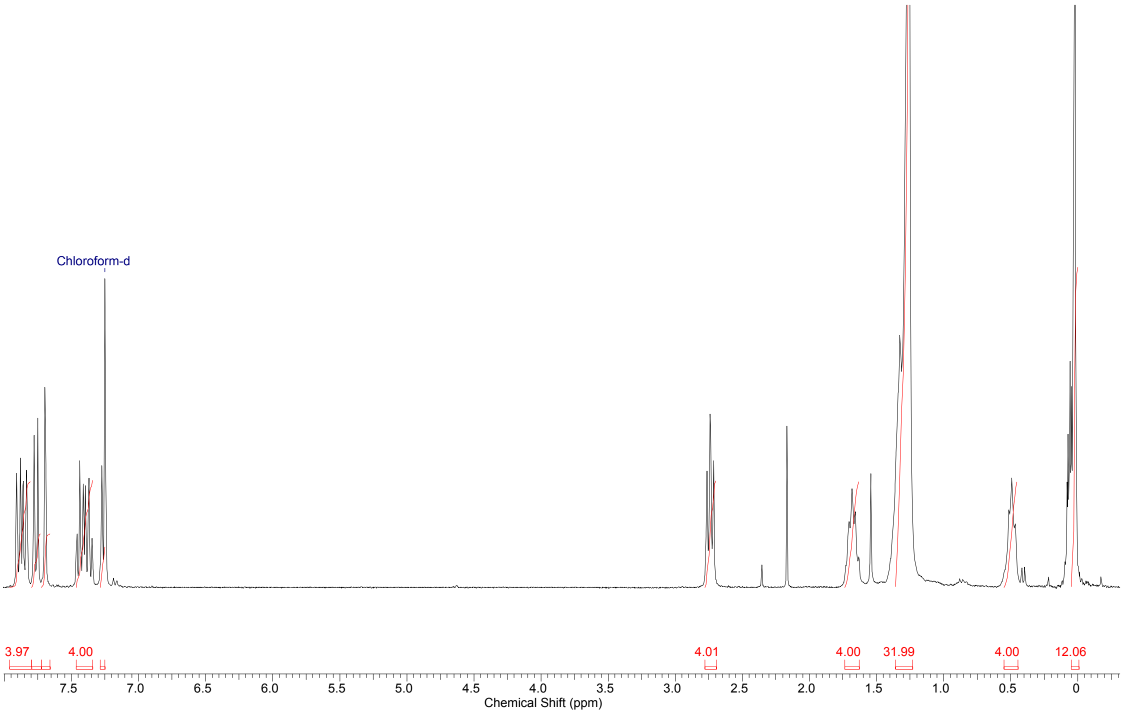


Figure S11. ^{29}Si NMR spectrum of compound **5** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[-0.01 .. 0.05]	12.057	7.94851e+9
2	[0.45 .. 0.55]	3.999	2.63605e+9
3	[1.23 .. 1.36]	31.985	2.10854e+10
4	[1.63 .. 1.74]	3.997	2.63487e+9
5	[2.69 .. 2.78]	4.008	2.64240e+9
6	[7.25 .. 7.28]	2.005	1.32146e+9
7	[7.34 .. 7.46]	3.996	2.63421e+9
8	[7.66 .. 7.73]	1.999	1.31791e+9
9	[7.73 .. 7.80]	2.026	1.33554e+9
10	[7.80 .. 7.96]	3.973	2.61903e+9

Figure S12. ^{1}H NMR spectrum of **O(Si-Und-BTBT)$_2$** in $CDCl_3$

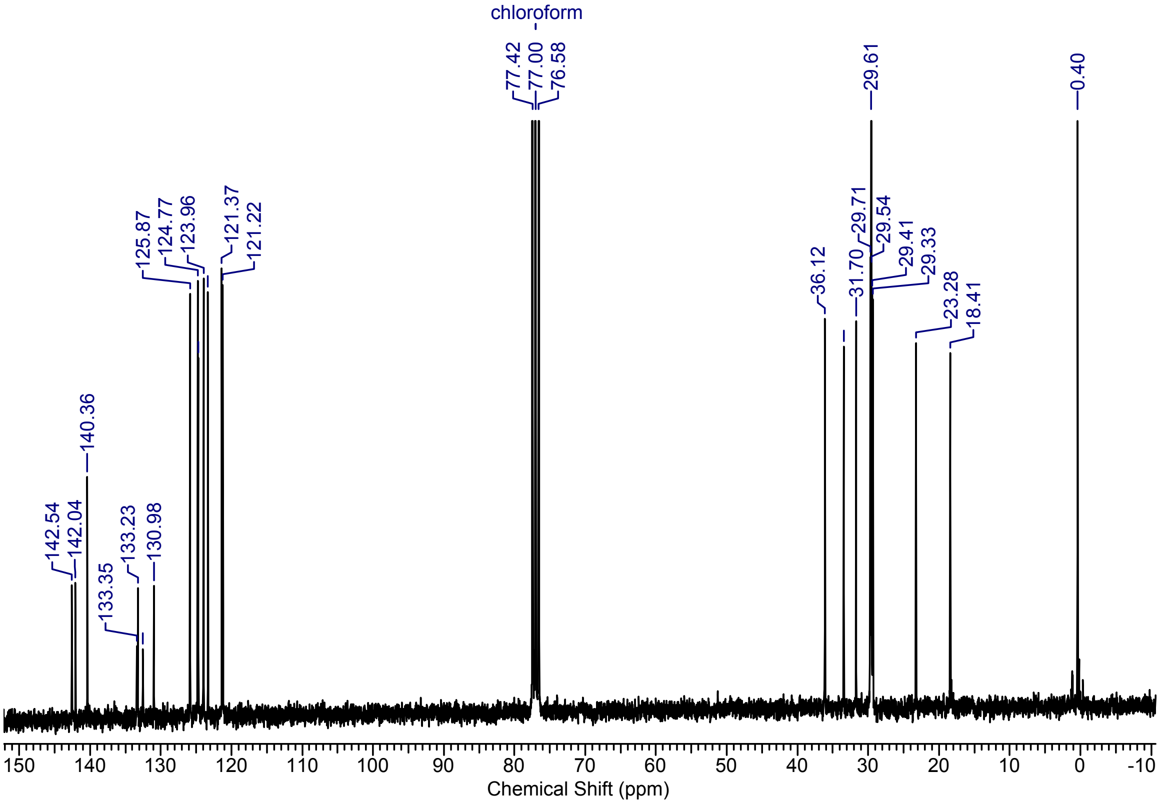


Figure S13. ^{13}C NMR spectrum of **O(Si-Und-BTBT)$_2$** in CDCl$_3$

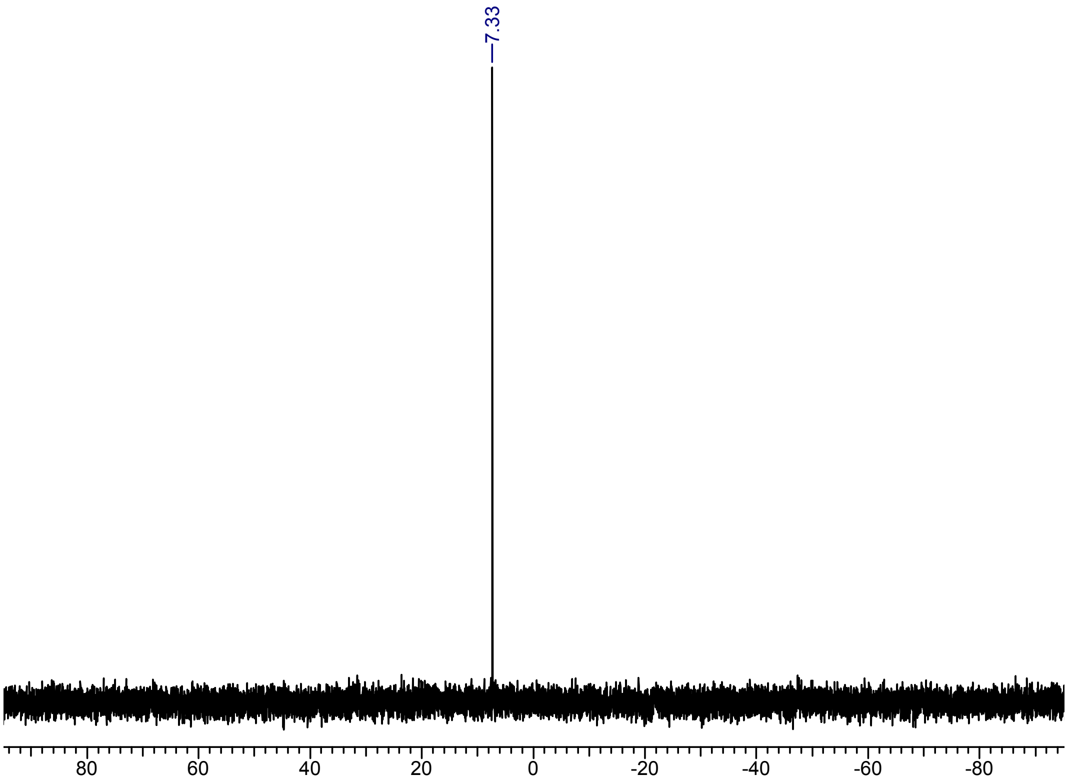
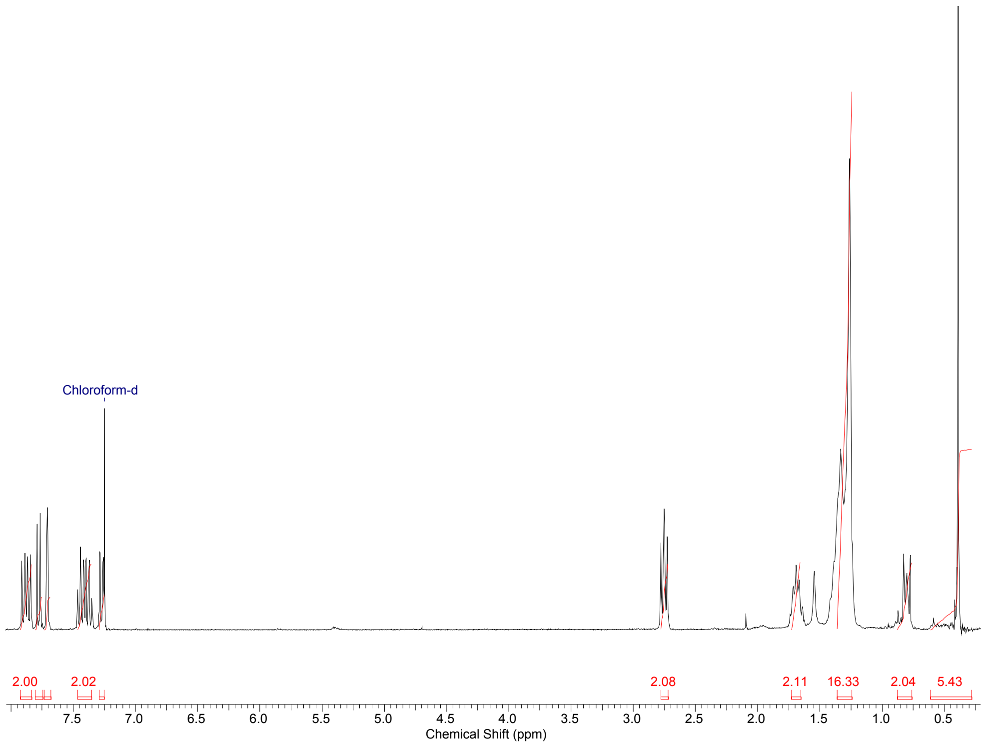


Figure S14. ^{29}Si NMR spectrum of **O(Si-Und-BTBT)$_2$** in CDCl$_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.28 .. 0.61]	5.432	3.74222e+9
2	[0.76 .. 0.88]	2.039	1.40454e+9
3	[1.24 .. 1.36]	16.327	1.12479e+10
4	[1.65 .. 1.73]	2.108	1.45205e+9
5	[2.72 .. 2.78]	2.082	1.43431e+9
6	[7.25 .. 7.29]	1.059	7.29561e+8
7	[7.35 .. 7.46]	2.019	1.39085e+9
8	[7.68 .. 7.73]	1.000	6.88891e+8
9	[7.75 .. 7.81]	1.021	7.03698e+8
10	[7.83 .. 7.92]	1.996	1.37499e+9

Figure S15. ^{1}H NMR spectrum of **Cl-Si-Und-BTBT** in $CDCl_3$

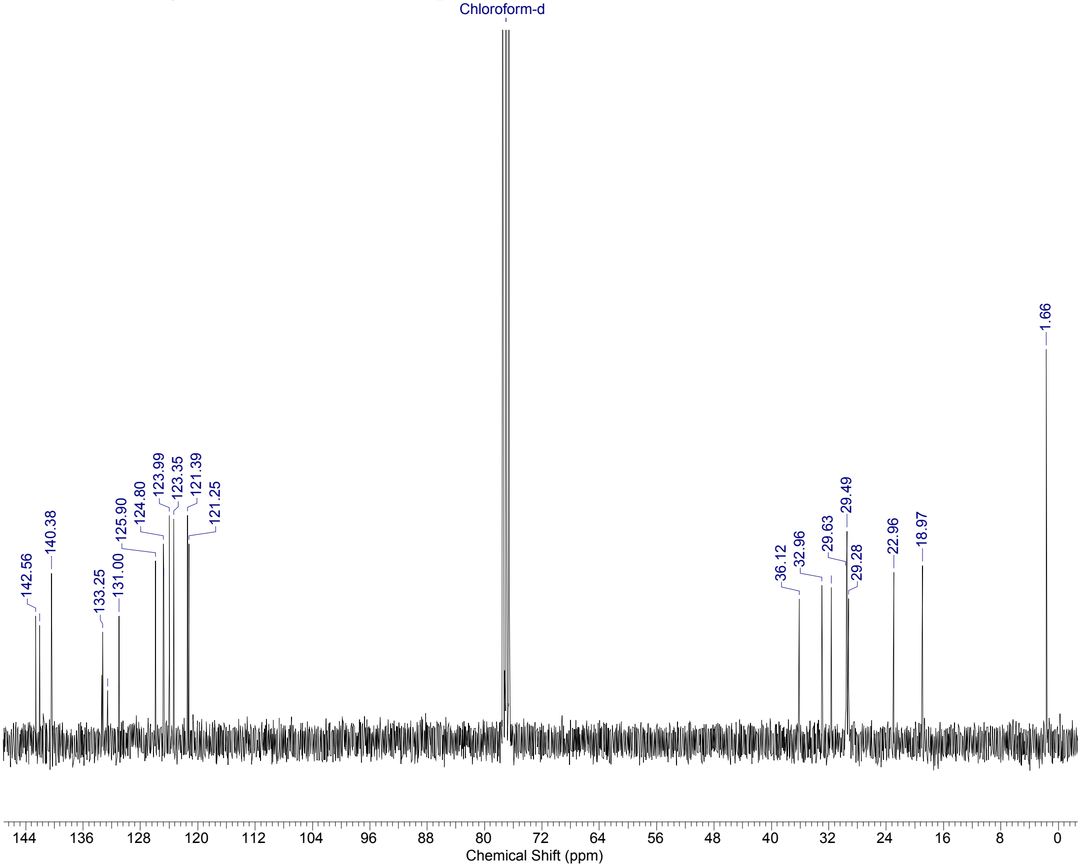


Figure S16. ^{13}C NMR spectrum of **Cl-Si-Und-BTBT** in $CDCl_3$

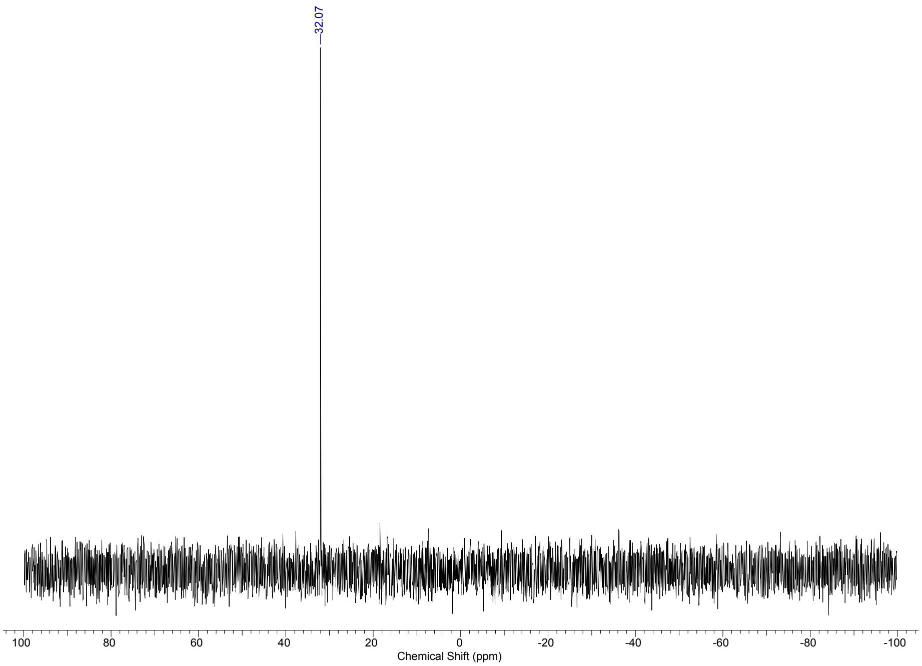
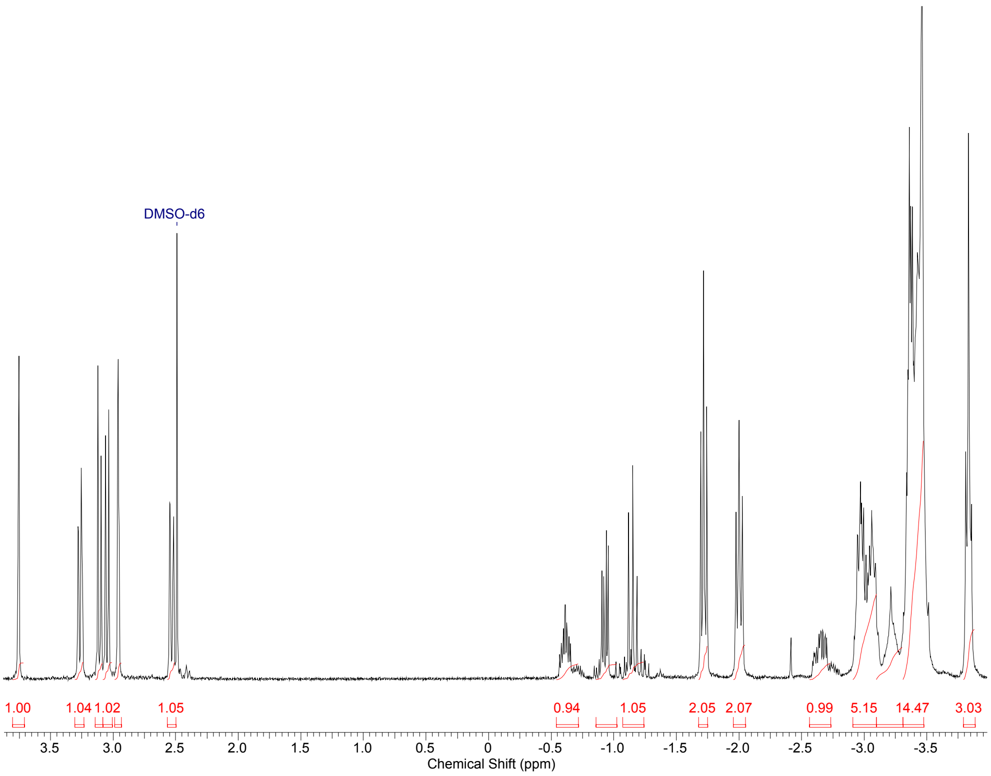


Figure S17. ^{29}Si NMR spectrum of **Cl-Si-Und-BTBT** in CDCl$_3$



No.	Annotation	(ppm)
1	DMSO-d6	2.49

No.	(ppm)	Value	Absolute Value
1	[-3.89 .. -3.79]	3.029	1.62783e+10
2	[-3.47 .. -3.31]	14.466	7.77543e+10
3	[-3.31 .. -3.10]	1.995	1.07225e+10
4	[-3.10 .. -2.91]	5.151	2.76863e+10
5	[-2.73 .. -2.56]	0.989	5.31517e+9
6	[-2.05 .. -1.96]	2.068	1.11176e+10
7	[-1.75 .. -1.68]	2.054	1.10389e+10
8	[-1.24 .. -1.07]	1.052	5.65299e+9
9	[-1.02 .. -0.86]	0.931	5.00527e+9
10	[-0.72 .. -0.54]	0.944	5.07607e+9
11	[2.50 .. 2.57]	1.050	5.64242e+9
12	[2.93 .. 2.99]	0.988	5.30848e+9
13	[3.01 .. 3.08]	1.023	5.49876e+9
14	[3.08 .. 3.14]	1.007	5.41380e+9
15	[3.23 .. 3.31]	1.043	5.60615e+9
16	[3.71 .. 3.80]	1.001	5.37920e+9

Figure S18. ^{1}H NMR spectrum of compound **6** in CDCl$_3$

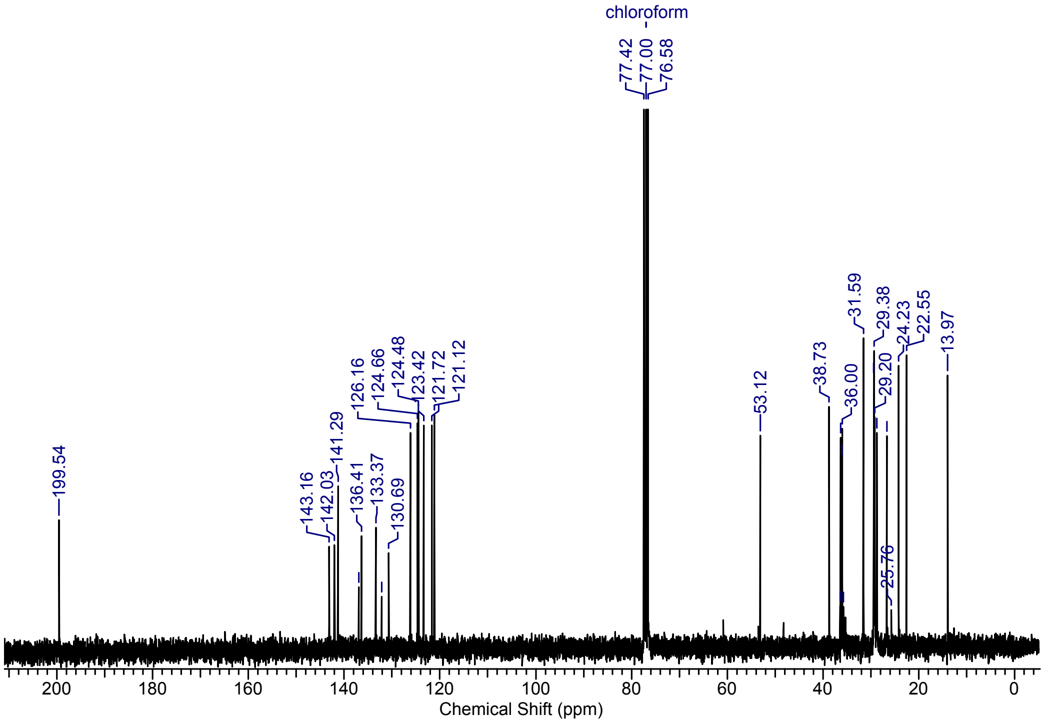
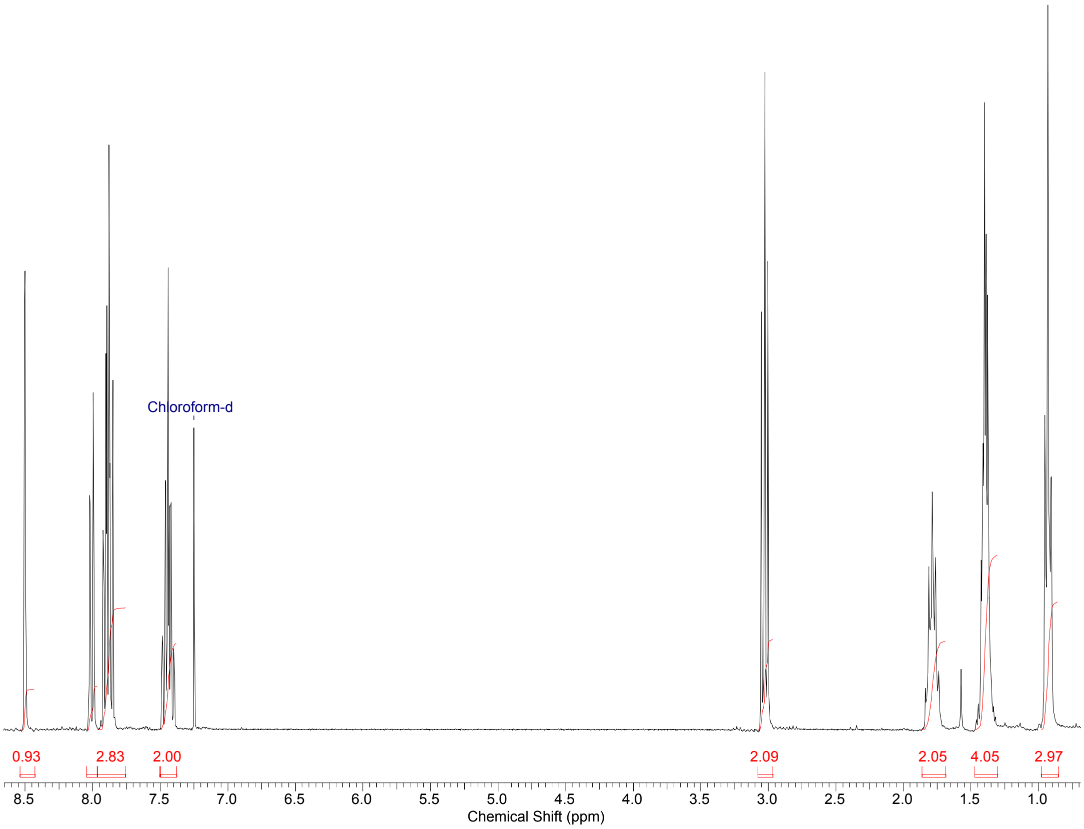


Figure S19. ^{13}C NMR spectrum of compound **6** in CDCl$_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.86 .. 0.98]	2.968	1.72272e+10
2	[1.30 .. 1.47]	4.049	2.35030e+10
3	[1.69 .. 1.87]	2.049	1.18932e+10
4	[2.97 .. 3.08]	2.089	1.21263e+10
5	[7.38 .. 7.50]	2.000	1.16091e+10
6	[7.50 .. 7.50]	0.000	2.69501e+6
7	[7.76 .. 7.96]	2.825	1.63990e+10
8	[7.97 .. 8.04]	1.006	5.84115e+9
9	[8.43 .. 8.54]	0.931	5.40291e+9

Figure S20. ^{1}H NMR spectrum of compound **8** in CDCl$_3$

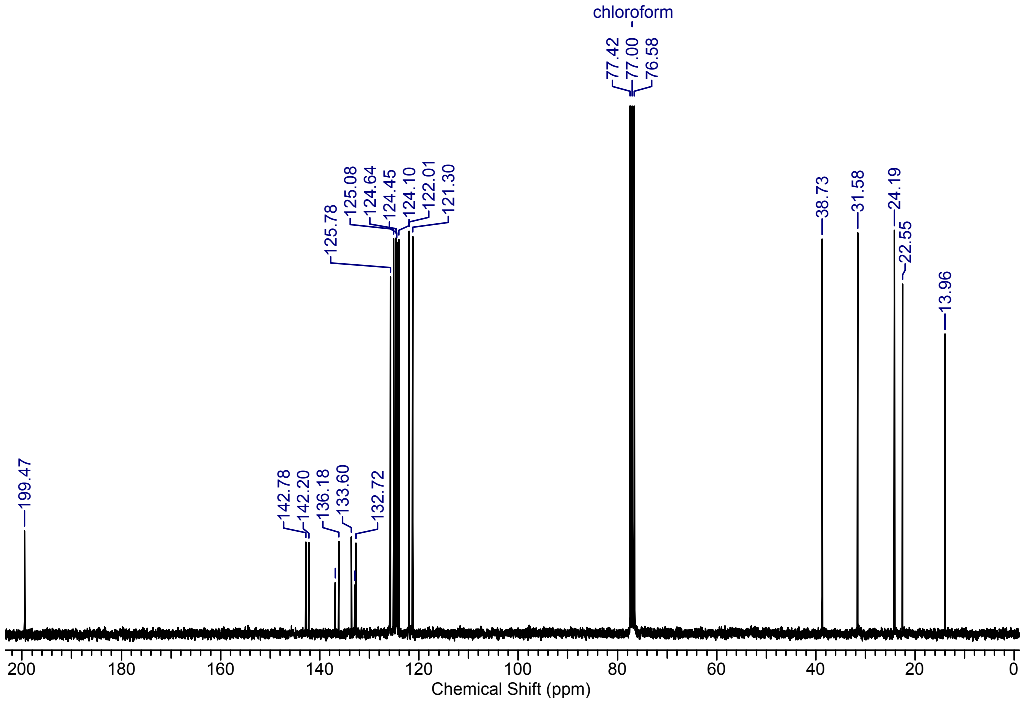
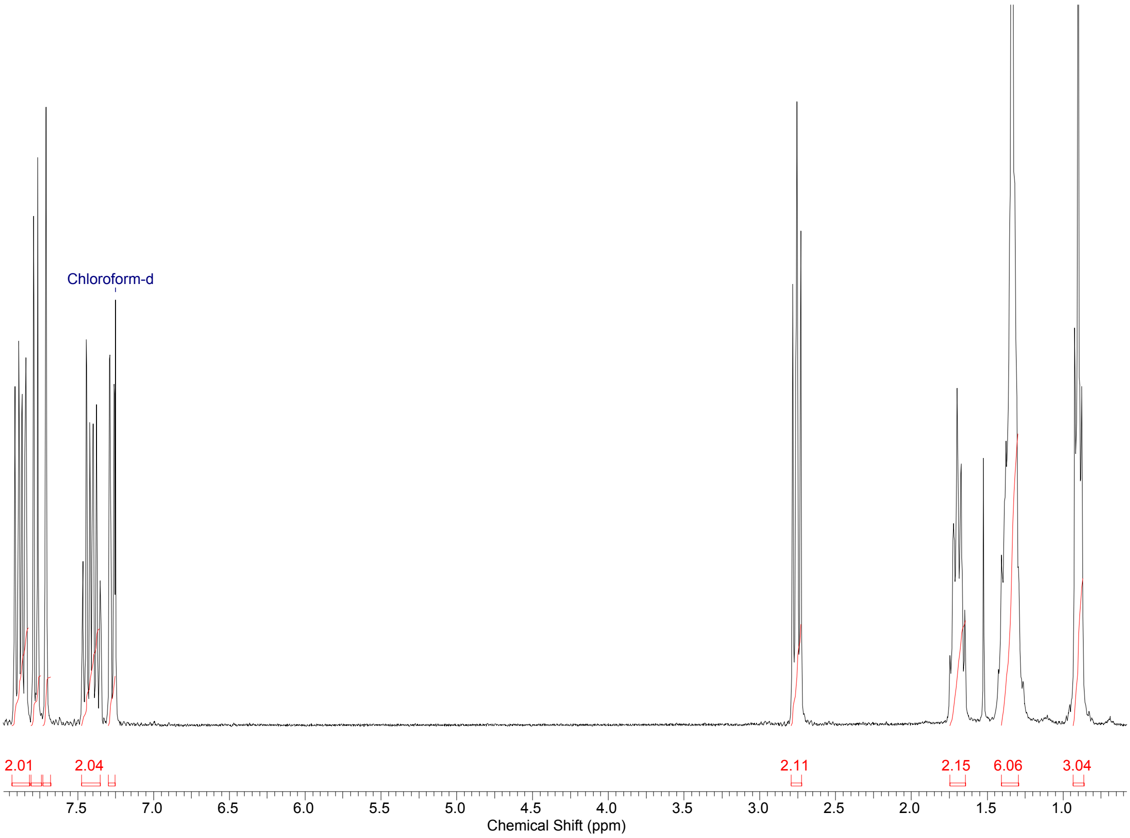


Figure S21. ^{13}C NMR spectrum of compound **8** in CDCl$_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.86 .. 0.93]	3.045	1.68535e+10
2	[1.29 .. 1.41]	6.061	3.35457e+10
3	[1.65 .. 1.75]	2.147	1.18845e+10
4	[2.73 .. 2.79]	2.107	1.16606e+10
5	[7.25 .. 7.30]	1.030	5.69870e+9
6	[7.35 .. 7.48]	2.042	1.13032e+10
7	[7.68 .. 7.73]	0.994	5.50124e+9
8	[7.74 .. 7.81]	1.030	5.70013e+9
9	[7.82 .. 7.94]	2.005	1.10978e+10

Figure S22. ^{1}H NMR spectrum of compound **9** in CDCl$_3$

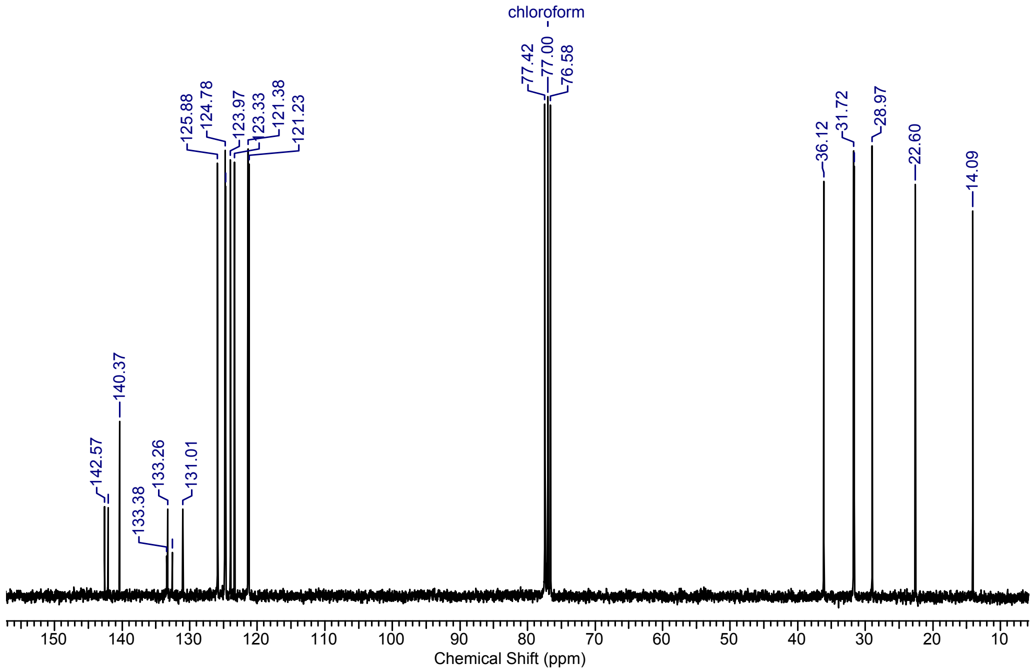
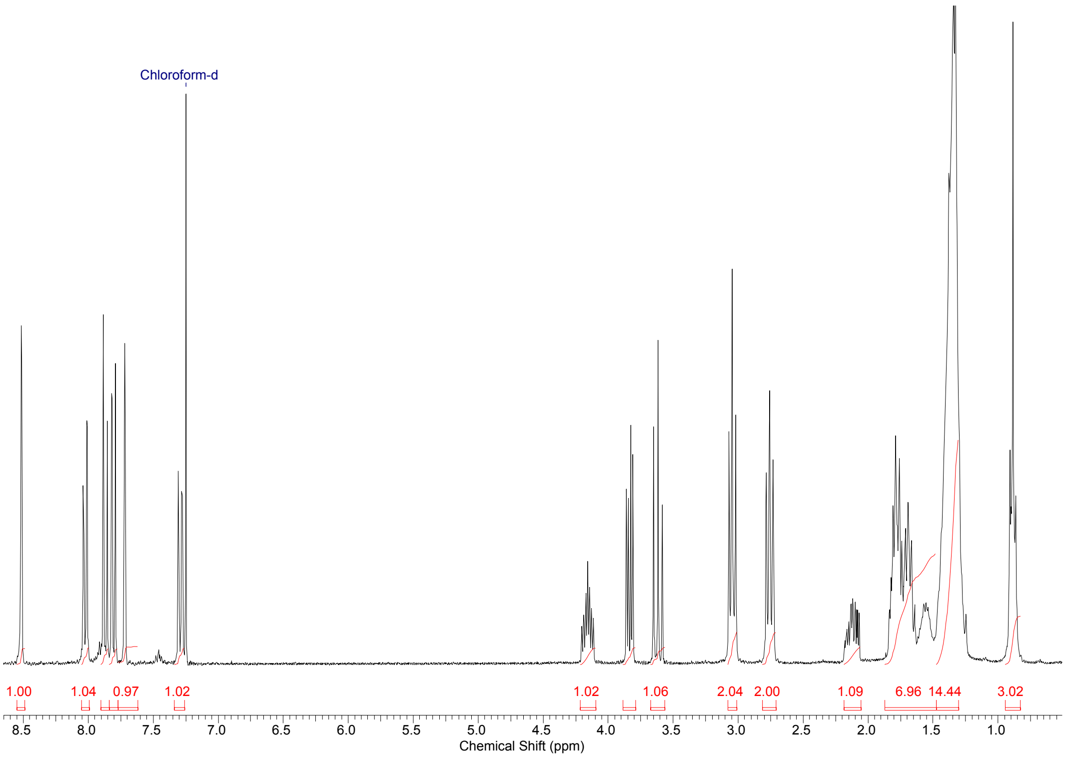


Figure S22. ^{13}C NMR spectrum of compound **9** in CDCl$_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.83 .. 0.95]	3.021	1.67477e+10
2	[1.30 .. 1.47]	14.436	8.00317e+10
3	[1.48 .. 1.87]	6.957	3.85683e+10
4	[2.06 .. 2.19]	1.088	6.02966e+9
5	[2.71 .. 2.81]	2.001	1.10938e+10
6	[3.01 .. 3.08]	2.042	1.13199e+10
7	[3.57 .. 3.67]	1.061	5.88135e+9
8	[3.79 .. 3.88]	1.057	5.85781e+9
9	[4.10 .. 4.22]	1.023	5.67169e+9
10	[7.26 .. 7.34]	1.020	5.65733e+9
11	[7.62 .. 7.77]	0.971	5.38287e+9
12	[7.77 .. 7.84]	0.975	5.40312e+9
13	[7.84 .. 7.90]	1.016	5.63383e+9
14	[7.99 .. 8.05]	1.045	5.79099e+9
15	[8.49 .. 8.55]	1.001	5.54688e+9

Figure S23. ^{1}H NMR spectrum of compound **10** in CDCl$_3$

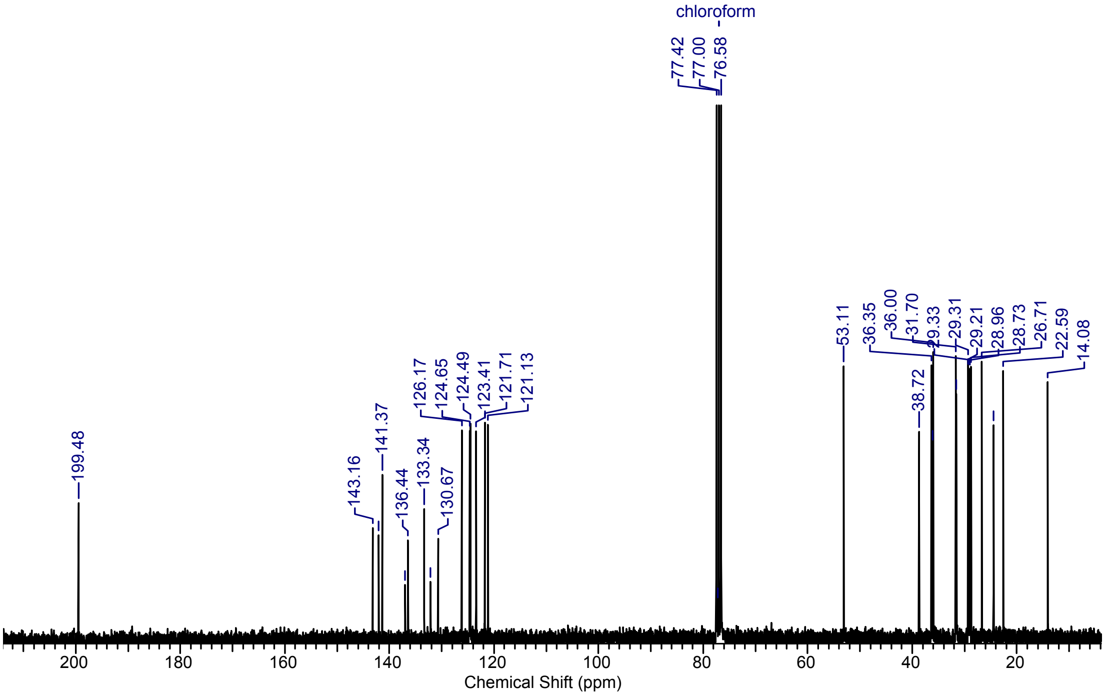
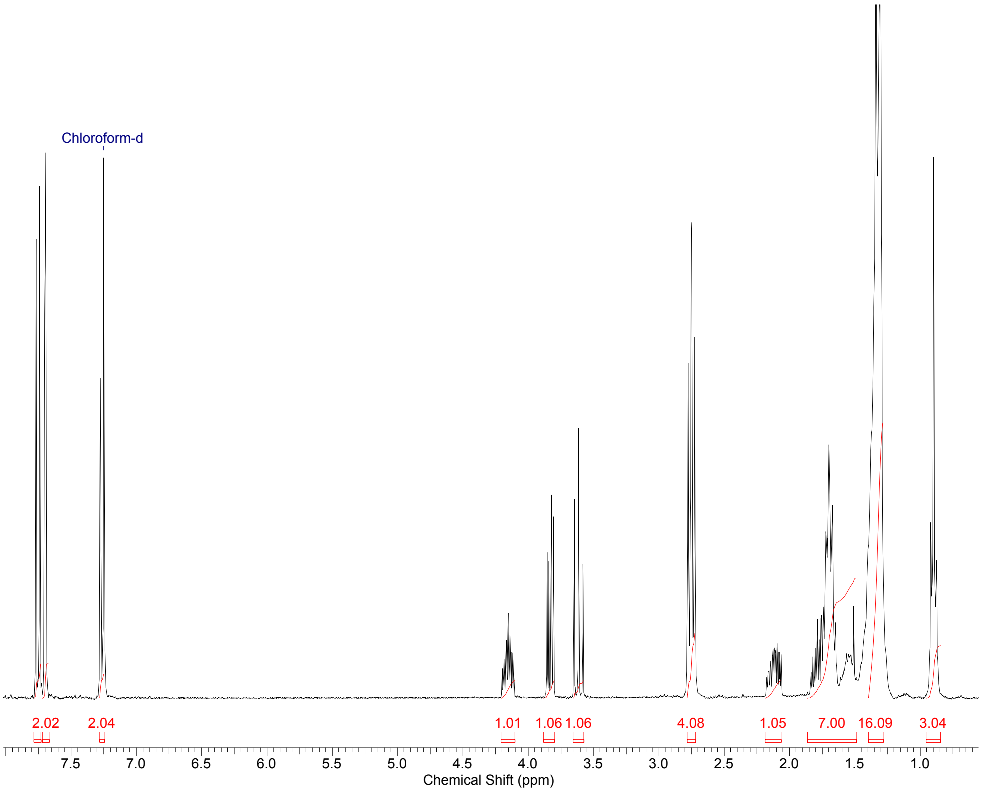


Figure S24. ^{13}C NMR spectrum of compound **10** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.84 .. 0.96]	3.042	1.26789e+10
2	[1.29 .. 1.40]	16.089	6.70476e+10
3	[1.49 .. 1.86]	6.998	2.91620e+10
4	[2.07 .. 2.19]	1.052	4.38426e+9
5	[2.72 .. 2.78]	4.076	1.69873e+10
6	[3.58 .. 3.66]	1.061	4.42128e+9
7	[3.80 .. 3.88]	1.062	4.42622e+9
8	[4.10 .. 4.21]	1.014	4.22610e+9
9	[7.25 .. 7.28]	2.044	8.51781e+9
10	[7.67 .. 7.72]	2.015	8.39920e+9
11	[7.73 .. 7.78]	2.014	8.39488e+9

Figure S25. ^{1}H NMR spectrum of compound **11** in $CDCl_3$

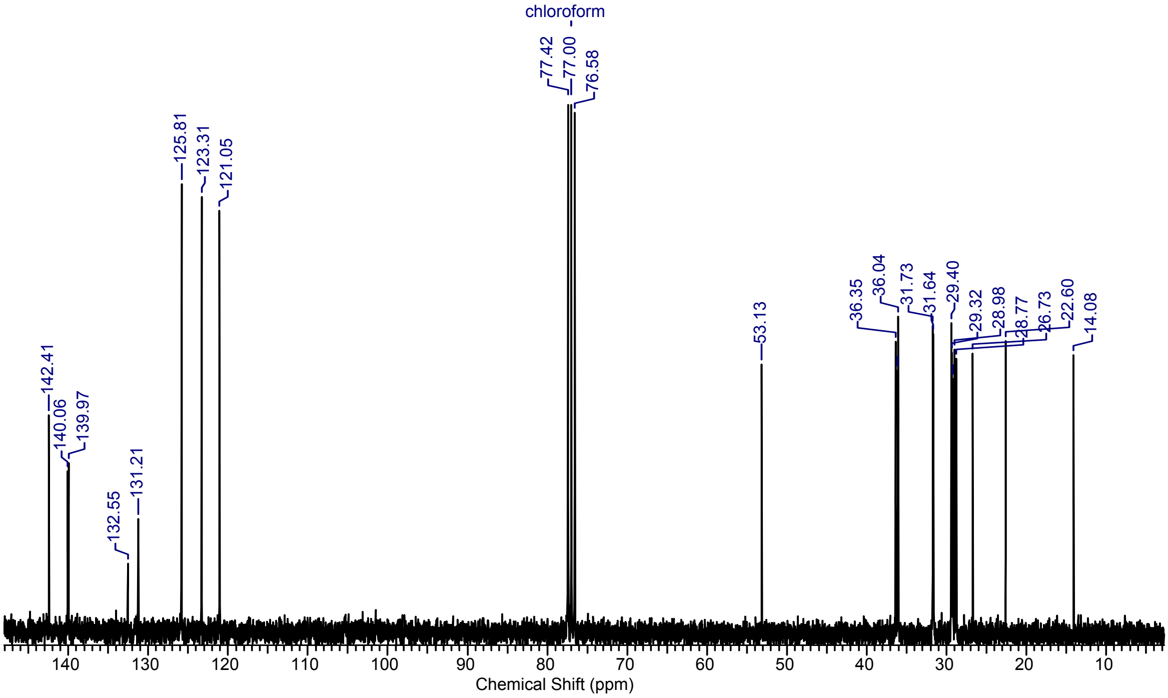
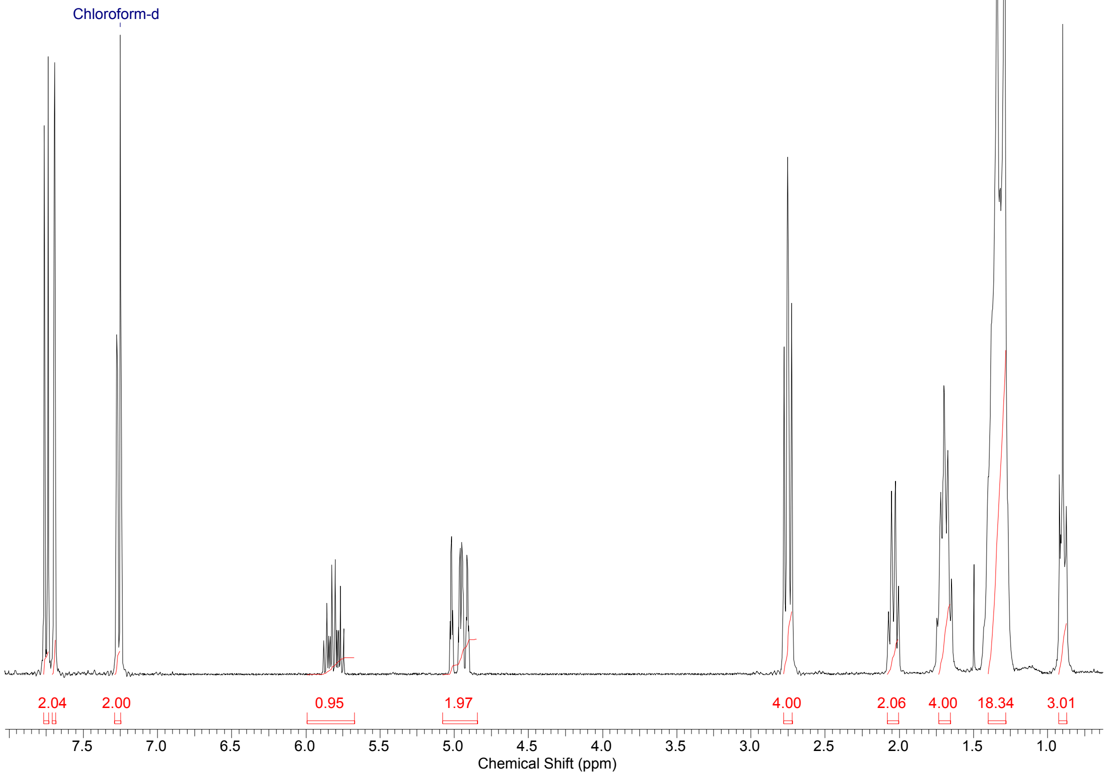


Figure S26. ^{13}C NMR spectrum of compound **11** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.87 .. 0.93]	3.009	7.68942e+9
2	[1.28 .. 1.40]	18.335	4.68519e+10
3	[1.66 .. 1.73]	3.998	1.02163e+10
4	[2.00 .. 2.08]	2.060	5.26450e+9
5	[2.72 .. 2.78]	4.001	1.02235e+10
6	[4.85 .. 5.08]	1.970	5.03353e+9
7	[5.67 .. 5.99]	0.953	2.43557e+9
8	[7.25 .. 7.29]	1.998	5.10470e+9
9	[7.69 .. 7.71]	2.045	5.22544e+9
10	[7.73 .. 7.77]	2.009	5.13379e+9

Figure S27. ^{1}H NMR spectrum of compound **12** in $CDCl_3$

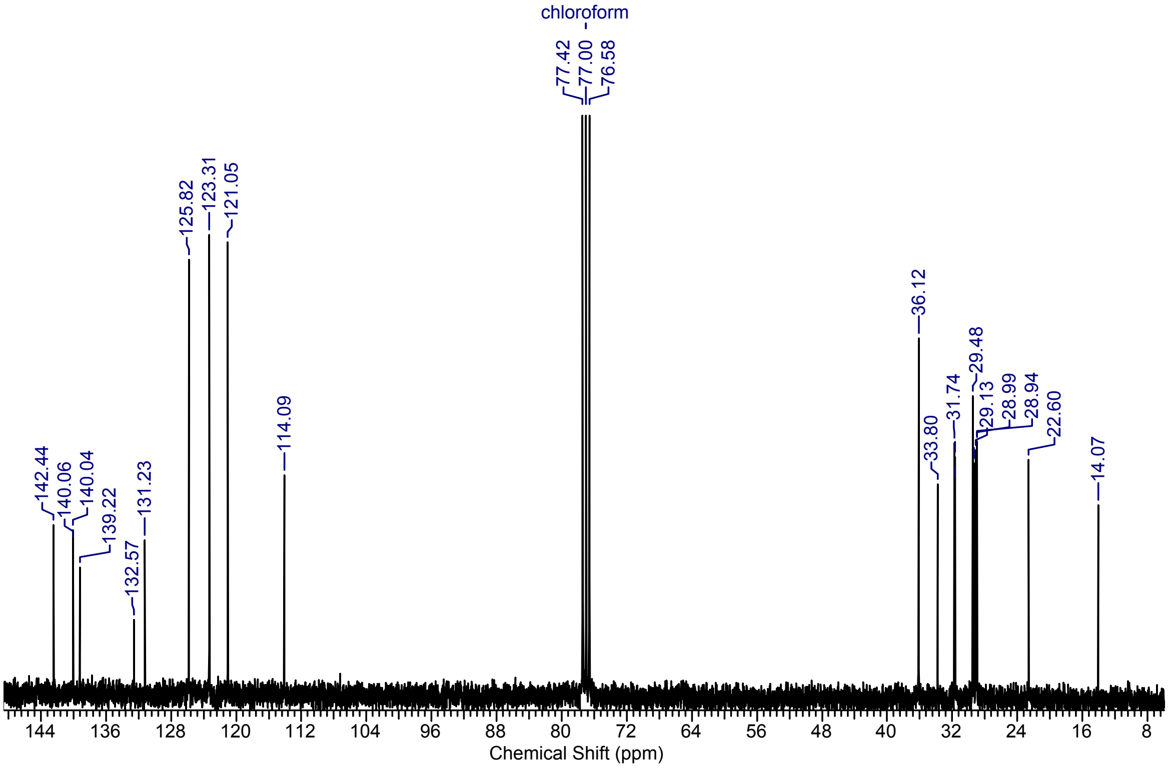
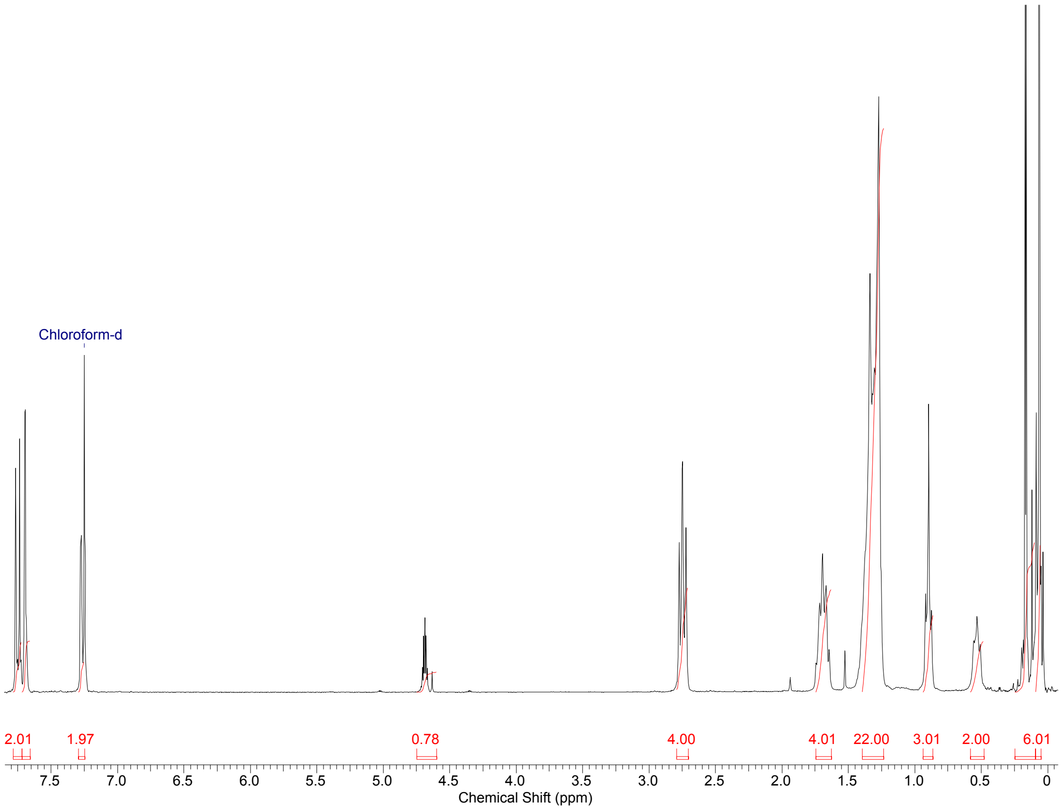


Figure S28. ^{13}C NMR spectrum of compound **12** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.05 .. 0.09]	6.014	7.05347e+9
2	[0.09 .. 0.24]	6.002	7.03889e+9
3	[0.48 .. 0.58]	1.997	2.34249e+9
4	[0.86 .. 0.94]	3.006	3.52516e+9
5	[1.23 .. 1.40]	21.997	2.57976e+10
6	[1.63 .. 1.74]	4.006	4.69822e+9
7	[2.71 .. 2.79]	3.997	4.68740e+9
8	[4.60 .. 4.75]	0.778	9.12987e+8
9	[7.25 .. 7.29]	1.967	2.30680e+9
10	[7.66 .. 7.72]	2.002	2.34785e+9
11	[7.72 .. 7.78]	2.011	2.35802e+9

Figure S29. ^{1}H NMR spectrum of compound **13** in $CDCl_3$

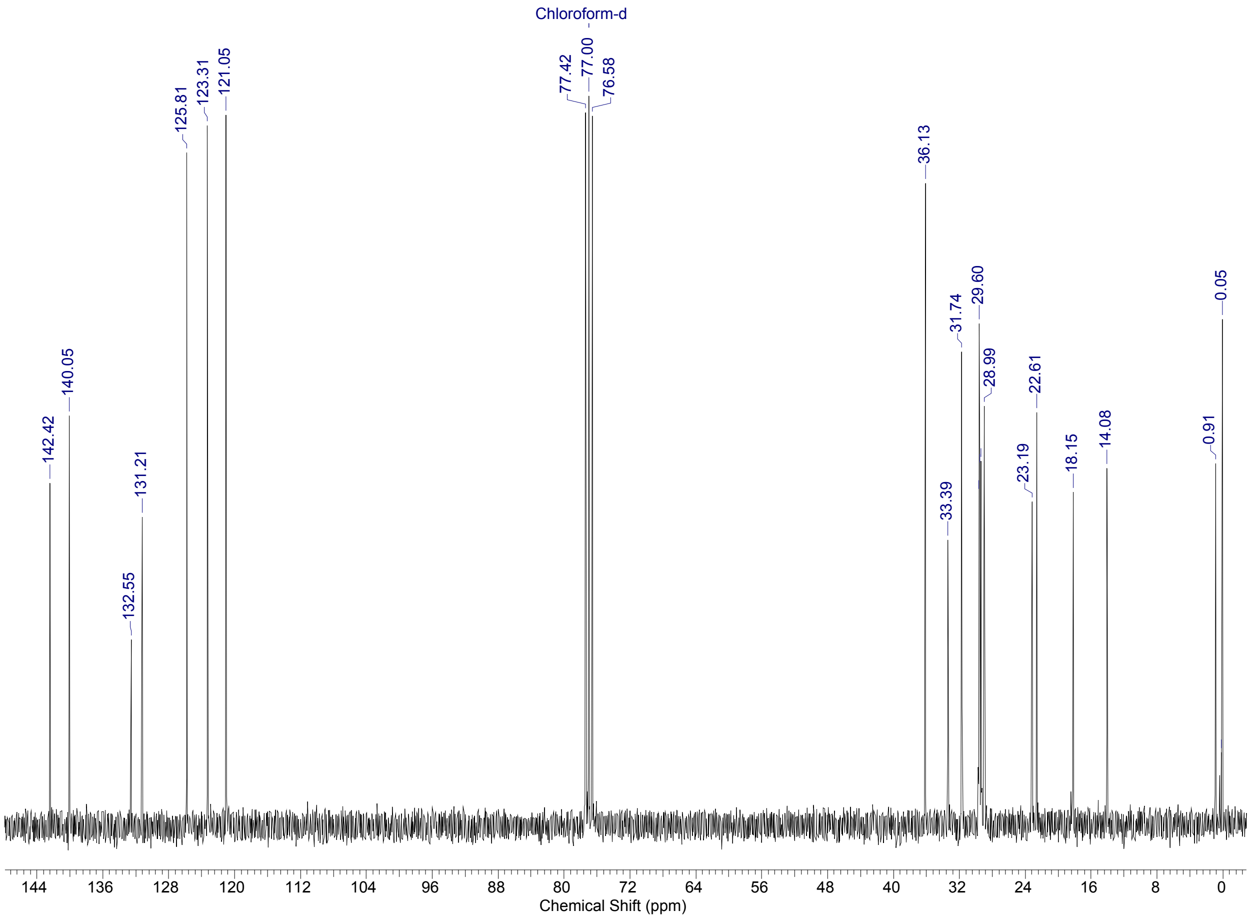


Figure S30. ^{13}C NMR spectrum of compound **13** in $CDCl_3$

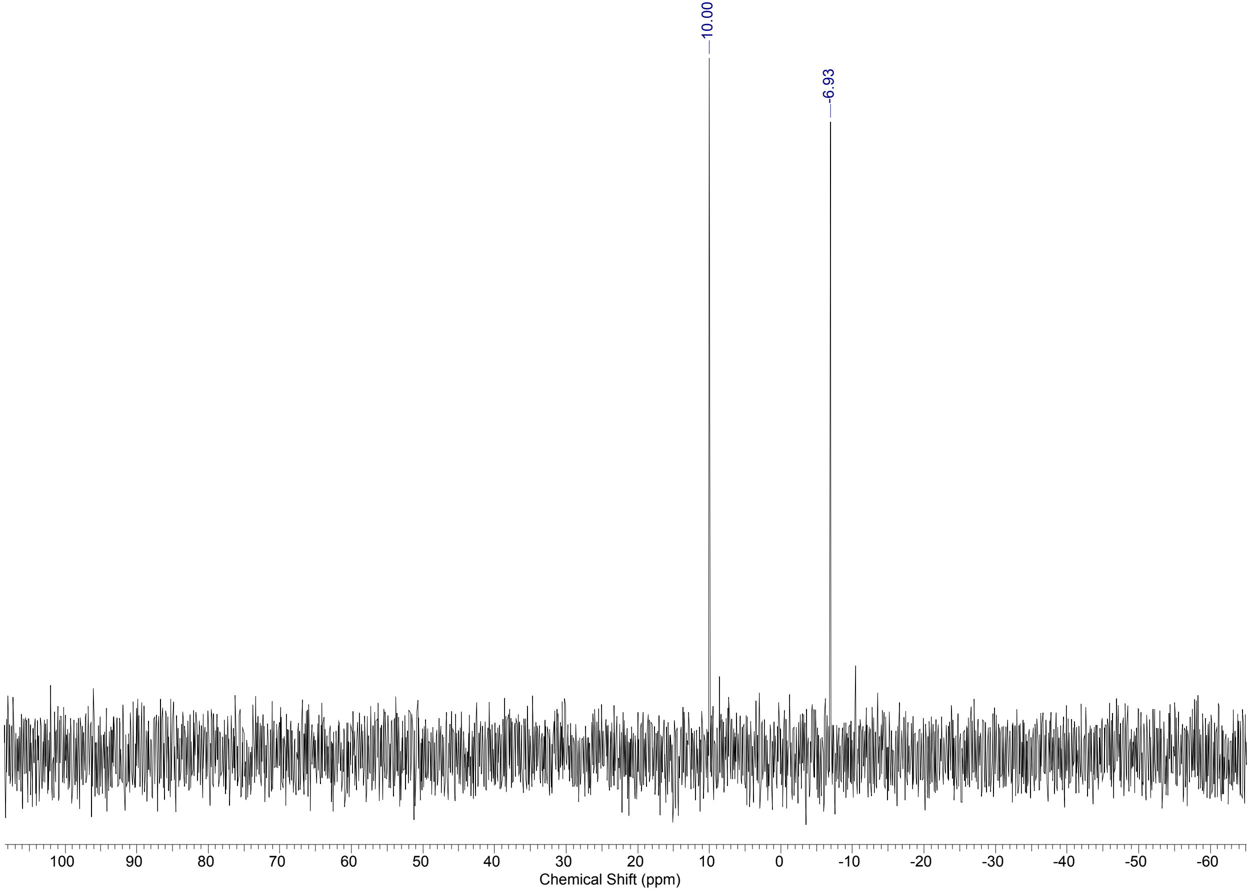
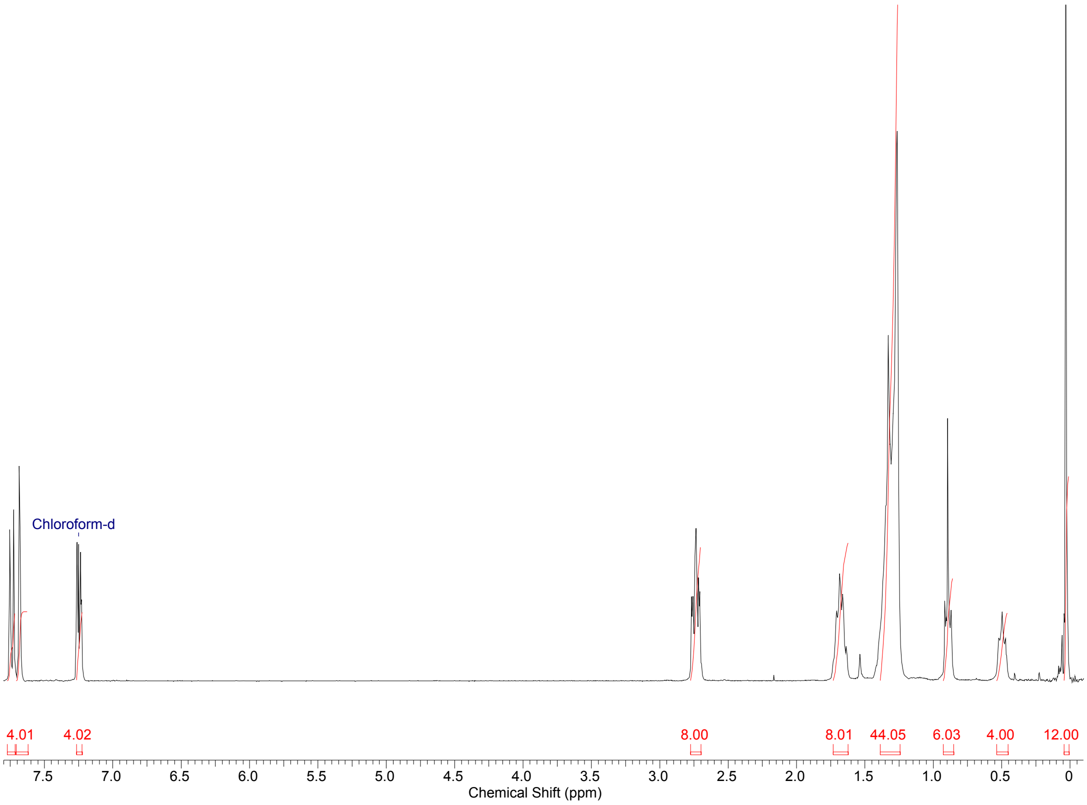


Figure S31. ^{29}Si NMR spectrum of compound **13** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.01 .. 0.04]	11.997	4.18969e+9
2	[0.45 .. 0.54]	4.000	1.39709e+9
3	[0.85 .. 0.93]	6.032	2.10646e+9
4	[1.24 .. 1.39]	44.047	1.53827e+10
5	[1.62 .. 1.73]	8.014	2.79879e+9
6	[2.70 .. 2.77]	8.002	2.79451e+9
7	[7.23 .. 7.27]	4.017	1.40279e+9
8	[7.62 .. 7.71]	4.005	1.39873e+9
9	[7.71 .. 7.77]	4.001	1.39744e+9

Figure S32. ^{1}H NMR spectrum of **O(Si-Und-BTBT-Hex)$_2$** in CDCl$_3$

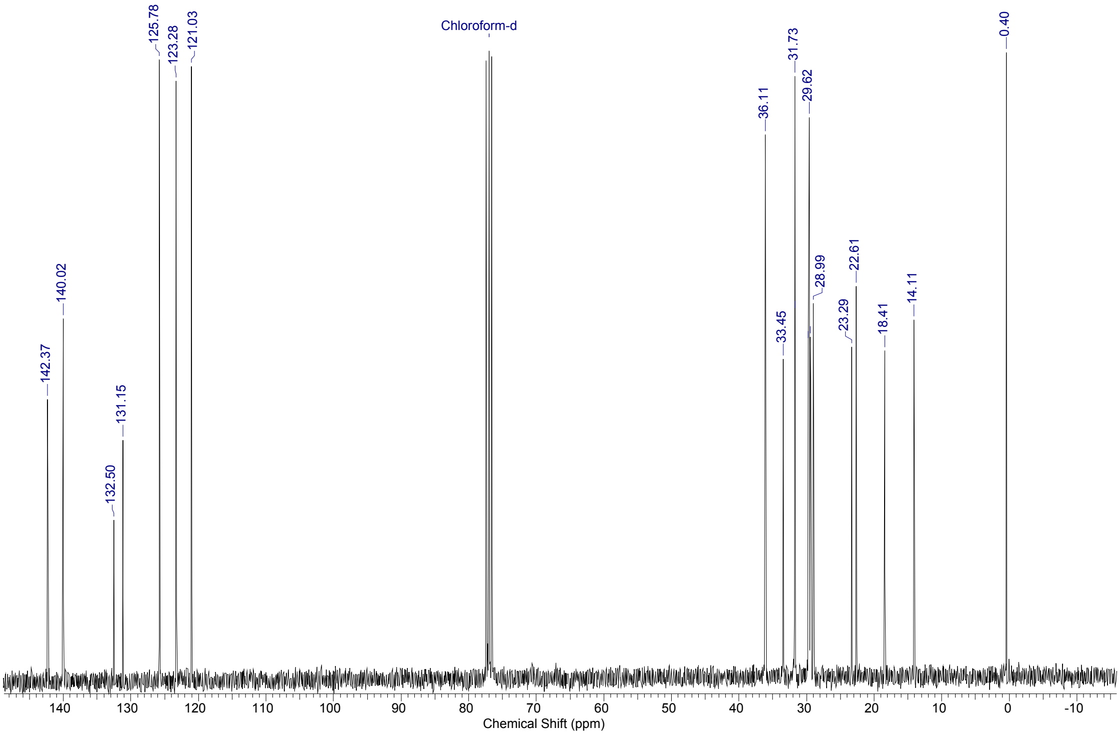


Figure S33. ^{13}C NMR spectrum of **O(Si-Und-BTBT-Hex)$_2$** in CDCl$_3$

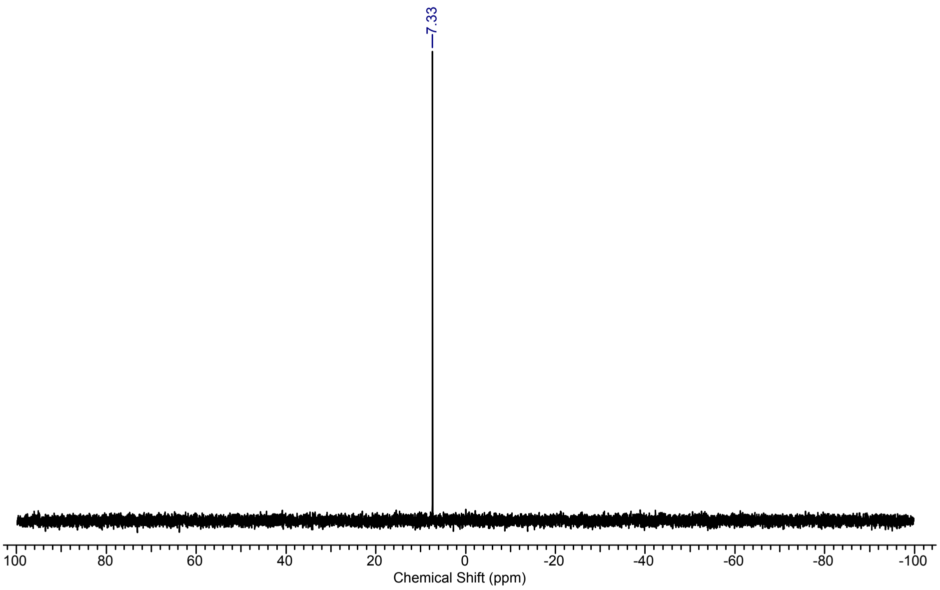
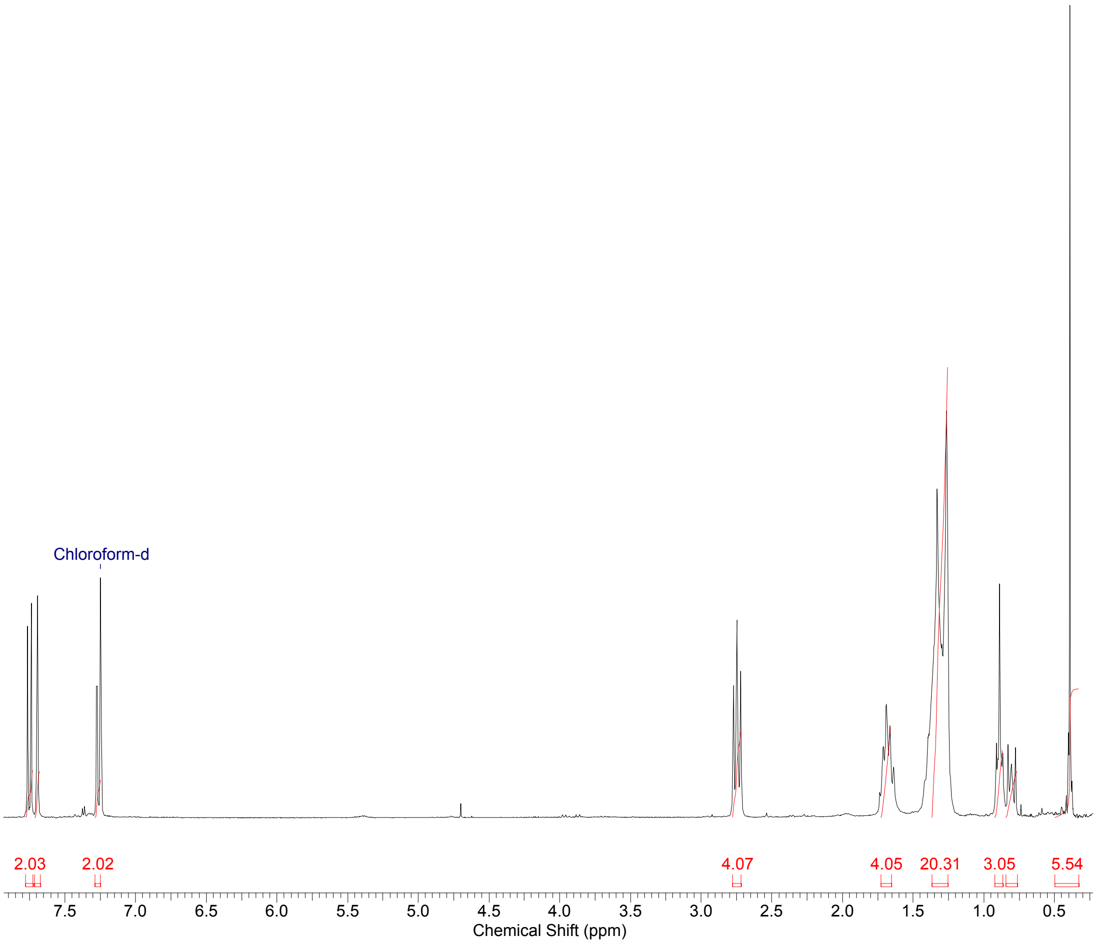


Figure S34. ^{29}Si NMR spectrum of **O(Si-Und-BTBT-Hex)$_2$** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.33 .. 0.50]	5.541	4.89659e+9
2	[0.76 .. 0.85]	1.996	1.76419e+9
3	[0.86 .. 0.92]	3.050	2.69552e+9
4	[1.25 .. 1.37]	20.308	1.79470e+10
5	[1.65 .. 1.73]	4.046	3.57558e+9
6	[2.72 .. 2.78]	4.066	3.59343e+9
7	[7.25 .. 7.29]	2.022	1.78681e+9
8	[7.67 .. 7.72]	2.000	1.76752e+9
9	[7.72 .. 7.78]	2.031	1.79508e+9

Figure S35. ^{1}H NMR spectrum of **Cl-Si-Und-BTBT-Hex** in $CDCl_3$

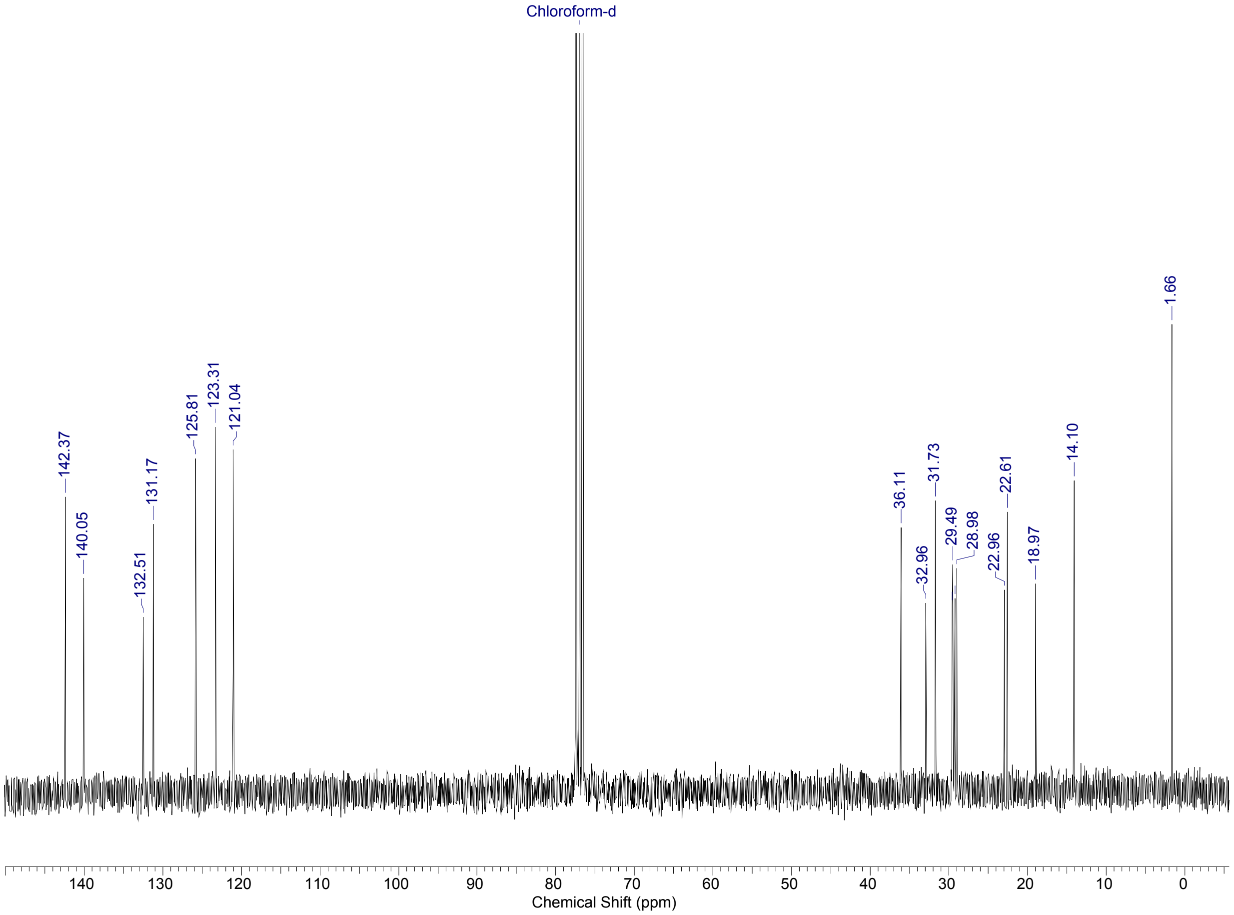


Figure S36. ^{13}C NMR spectrum of **Cl-Si-Und-BTBT-Hex** in $CDCl_3$

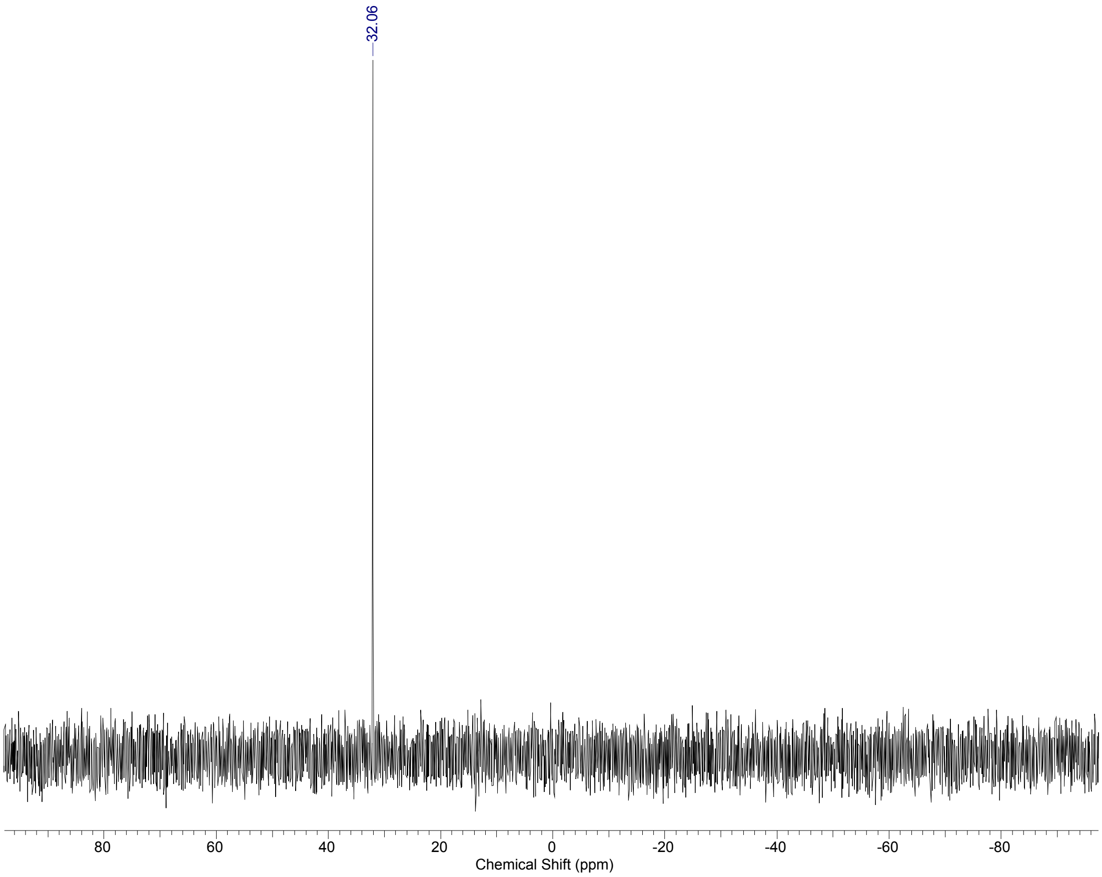


Figure S37. ^{29}Si NMR spectrum of **Cl-Si-Und-BTBT-Hex** in $CDCl_3$

4. Thermal properties

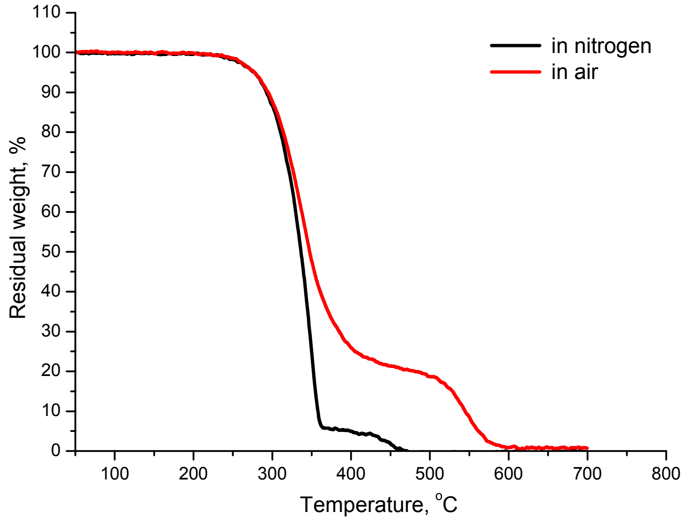


Figure S38. TGA curve of compound **4** at 10 °C/min.

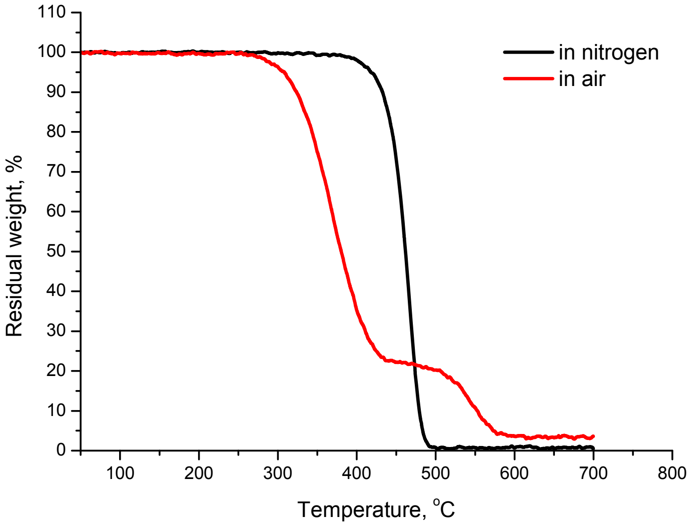


Figure S39. TGA curve of **O(Si-Und-BTBT)$_2$** at 10 °C/min.

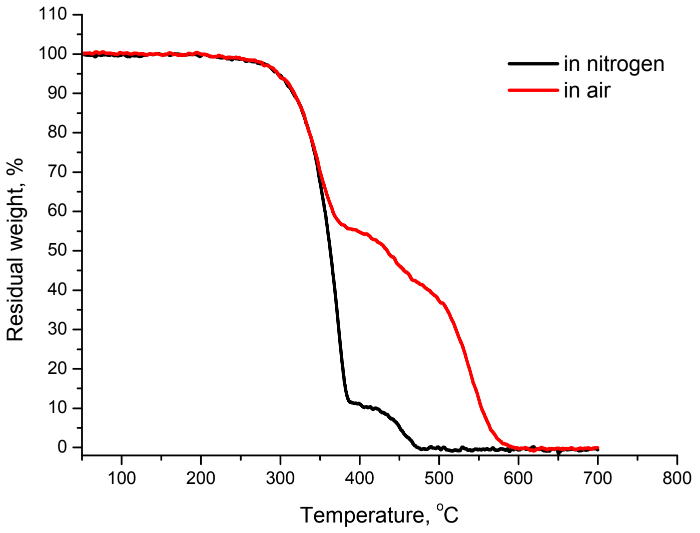


Figure S40. TGA curve of compound **12** at 10 °C/min.

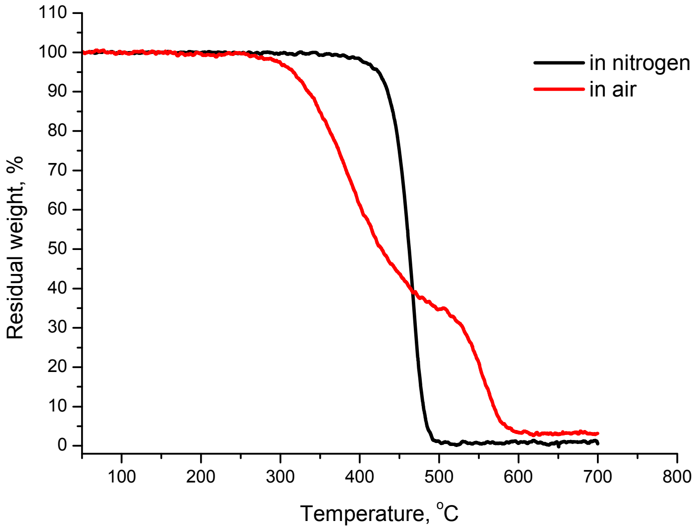


Figure S41. TGA curve of **O(Si-Und-BTBT-Hex)$_2$** at 10 °C/min.

Table S1. Summary of TGA results.

Compound	Temperature of 5% weight loss, °C	
	in air	in nitrogen
4, Undec-BTBT	277	278
O(Si-Und-BTBT)$_2$	308	418
12, Undec-BTBT-Hex	296	297
O(Si-Und-BTBT-Hex)$_2$	316	423

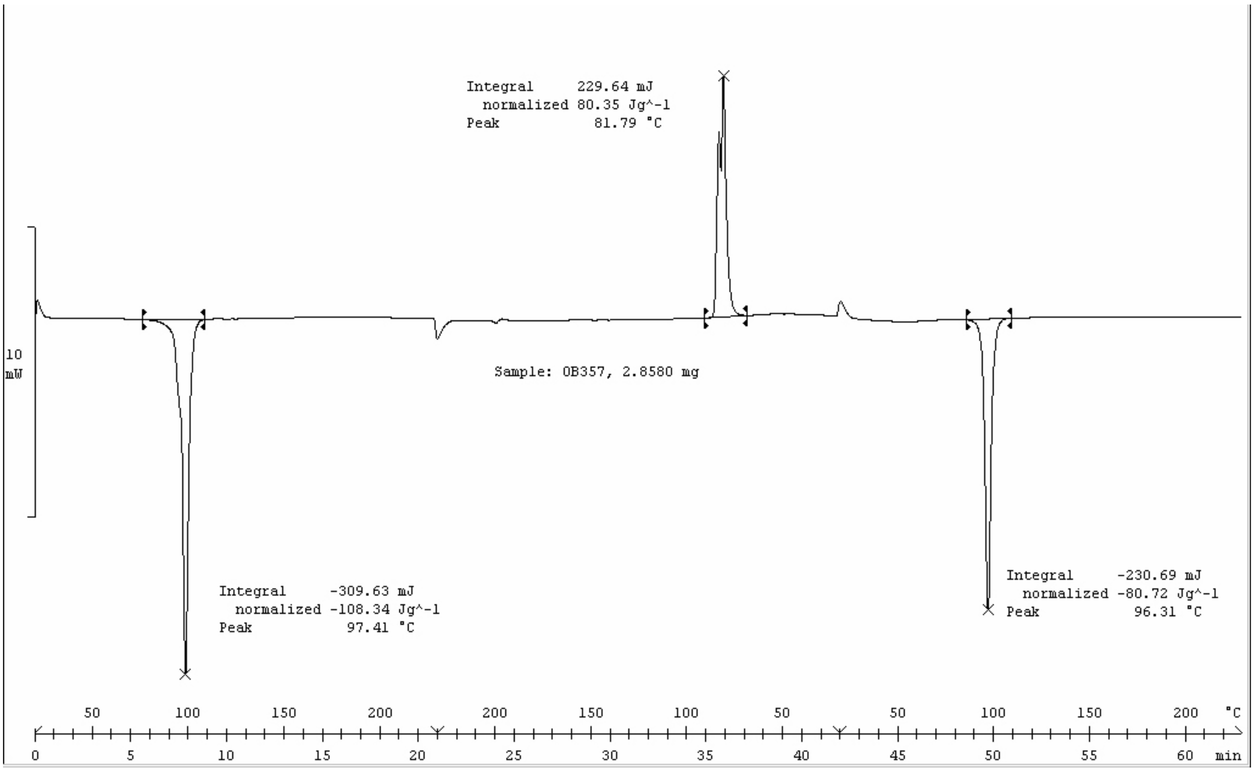


Figure S42. DSC curve (1st heating, 1st cooling and 2nd heating) of compound **4.**

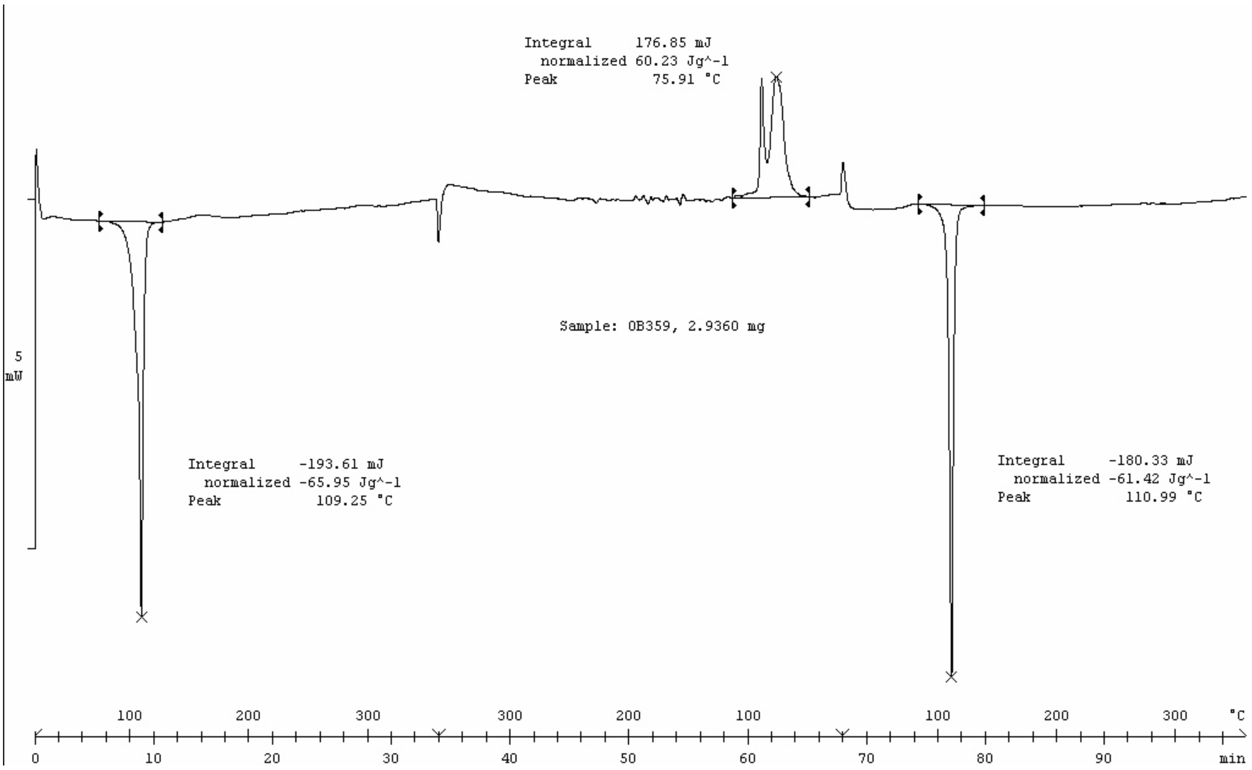


Figure S43. DSC curve (1st heating, 1st cooling and 2nd heating) of **O(Si-Und-BTBT)$_2$.**

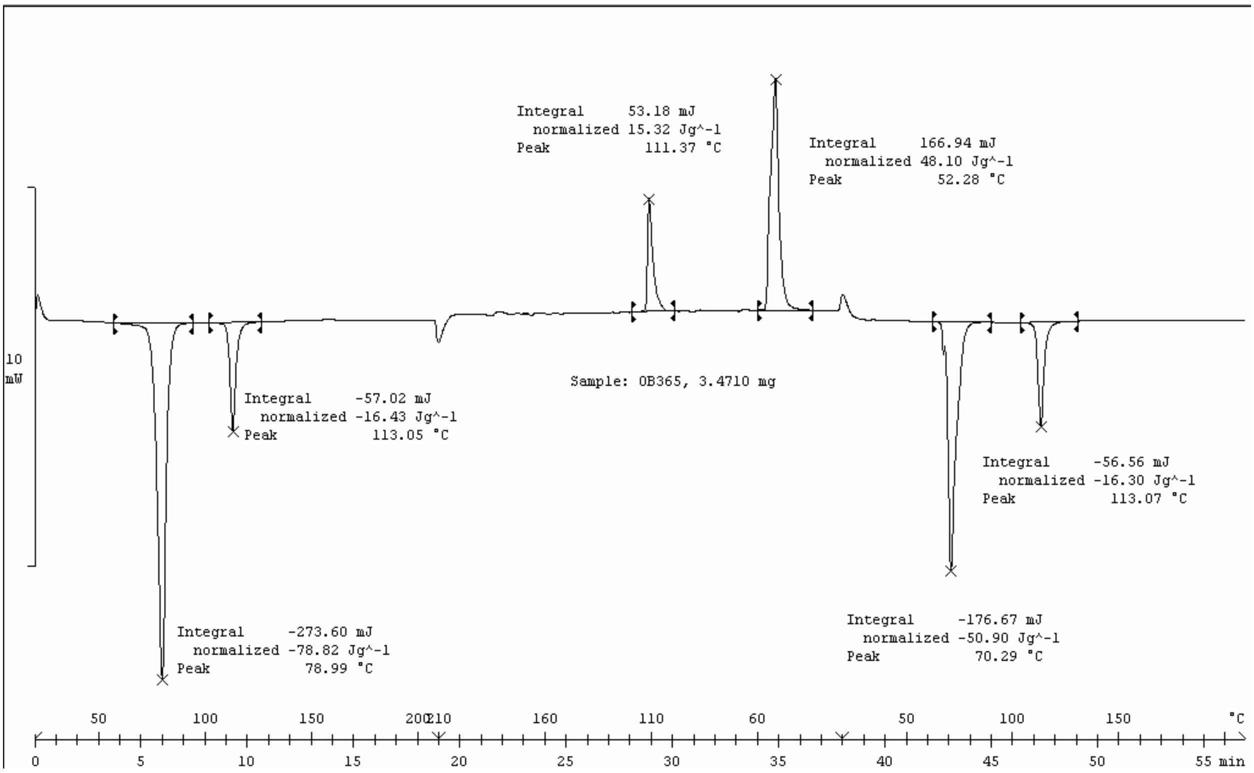


Figure S44. DSC curve (1st heating, 1st cooling and 2nd heating) of compound **12.**

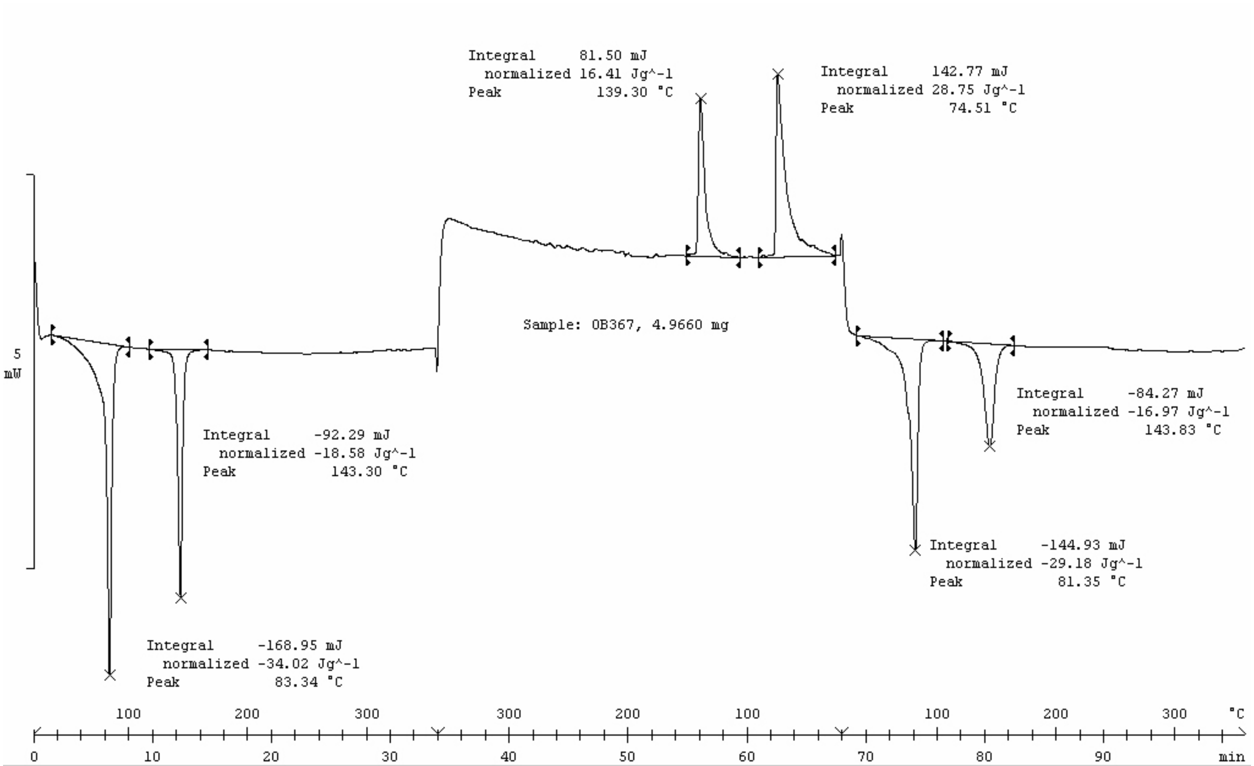


Figure S45. DSC curve (1st heating, 1st cooling and 2nd heating) of **O(Si-Und-BTBT-Hex)$_2$.**

Table S2. Phase behavior of the organosilicon derivatives of BTBT by DSC and polarizing optical microscopy data (Cr – crystal, N – nematic phase, Sm – smectic phase, I – isotropic state).

Compound	Phase transition temperatures, °C and enthalpies, J/g (in parentheses)	
	heating	cooling
O(Si-Und-BTBT)$_2$	Cr 110 (61) I	I 96 (13.4) N 88 (43) Cr
O(Si-Und-BTBT-Hex)$_2$	Cr 83(35) Sm 144(18) I	I 141 (17) Sm 76 (32) Cr

5. Langmuir isotherms

Self-assembly of the materials synthesized on the air-water interface was investigated by Langmuir technique. The spreading solution was prepared by dissolving the materials in toluene at the concentration of 0.33 g/L. The solution was spread on the water surface with a microsyringe, and the film was then left for 5 min to equilibrate before the compression started. Data were collected with a Nima 712BAM system using a Teflon trough and barriers at room temperature. The monolayers were compressed with the speed equal to 100 mm/min. LB films were obtained by transfer on silicon substrates with gold contacts. The vertical (LB) or horisontal (LS) dipping methods with a dipping speed of 8 mm/min were used to obtain monolayer films. Film transfers were performed at different surface pressures close but before to the collapse point.

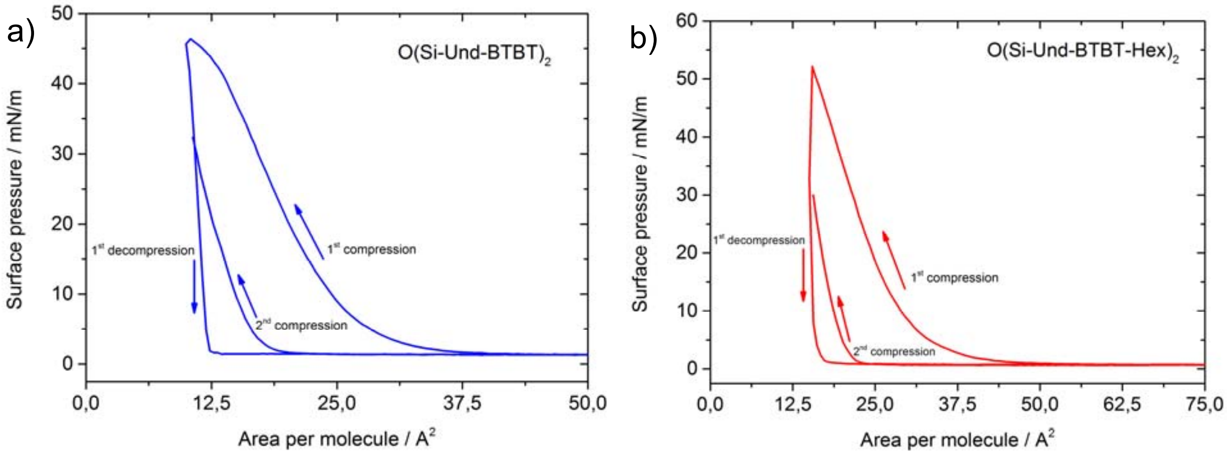


Figure S46. Langmuir isotherms of **O(Si-Und-BTBT)$_2$** (a)**, O(Si-Und-BTBT-Hex)$_2$** (b) (compression-decompression-compression cycle).

6. AFM images of LB films

AFM studies were performed with NT-MDT Solver NEXT (Russia) instrument in a semicontact mode under ambient environment. Commercially available silicon probes Brücker FESPA with resonance frequency 70 kHz were used.

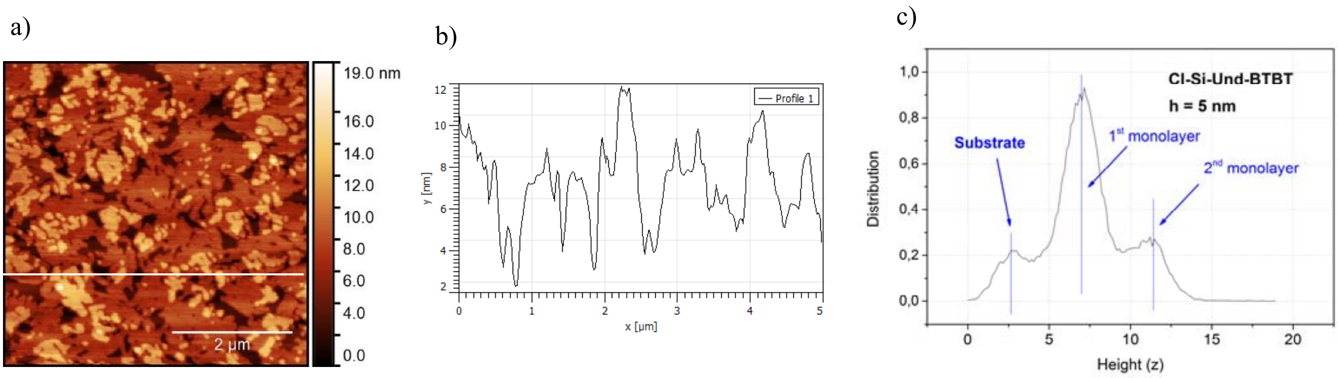


Figure S47. Morphology (a), cross-section (b) and height distribution (c) of **Cl-Si-Und-BTBT** LB film

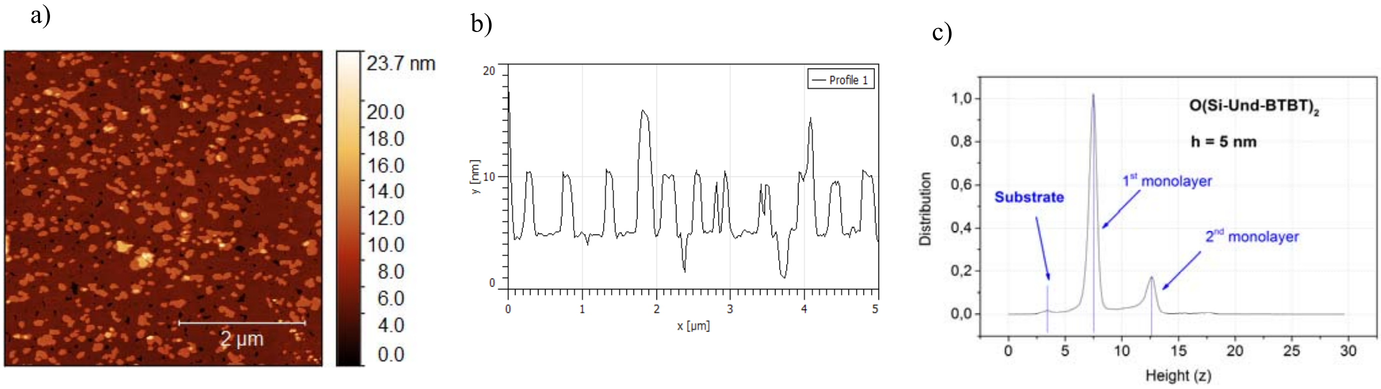


Figure S48. Morphology (a), cross-section (b) and height distribution (c) of **O(Si-Und-BTBT)$_2$** LB film

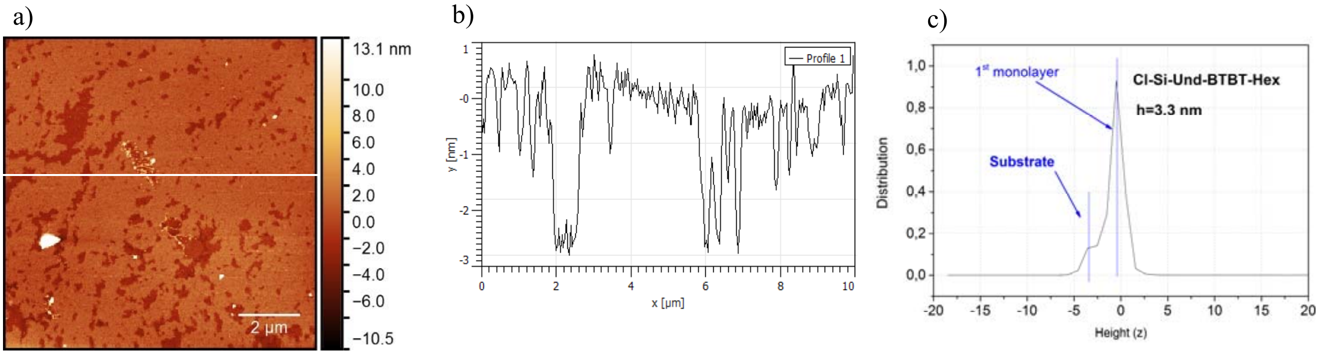


Figure S49. Morphology (a), cross-section (b) and height distribution (c) of **Cl-Si-Und-BTBT-Hex** LB film.

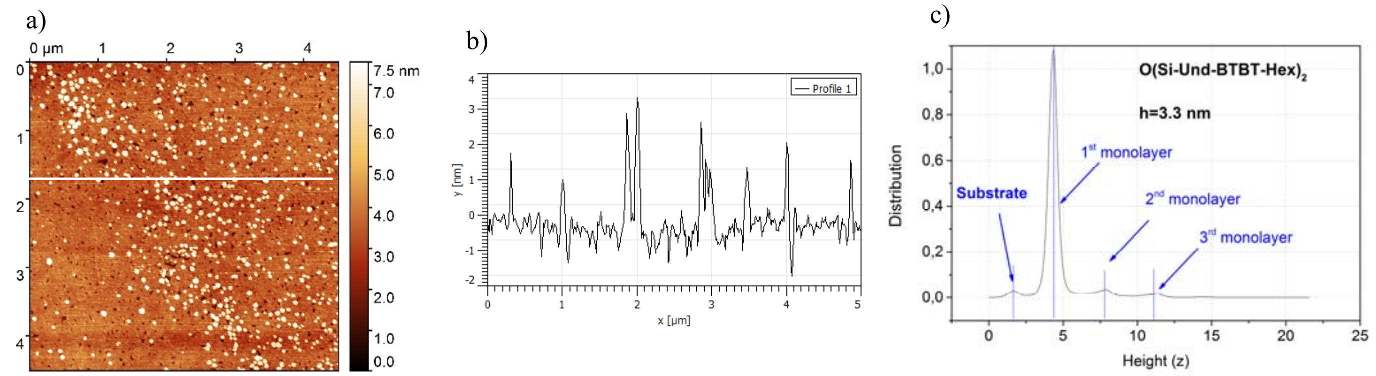


Figure S50. Morphology (a), cross-section (b) and height distribution (c) of **O-(Si-Und-BTBT-Hex)$_2$** LB film.

7. OFET devices preparation

OFETs based on the LB films were prepared on heavily doped silicon substrates with thermally grown oxide as shipped from Ossila. The dielectric thickness was 300 nm, and the measured capacitance was 13 nF/cm^2. Before electrodes deposition the factory photoresist was washed-off using the manufacturer's recommended procedure. Gold source and drain electrodes were thermally evaporated through the shadow mask. The resulting bottom gate bottom contact OFET configuration had fixed channel size of W = 1000 µm and L = 30 µm. Before the semiconductor reposition no additional dielectric pre-treatment has been applied. The LB films of oligomers has been prepared according to the procedure described before [E. V. Agina, A. S. Sizov, D. S. Anisimov, A. A. Trul, O. V. Borshchev, D. Yu. Paraschuk, M. A. Shcherbina, S.N. Chvalun, S.A. Ponomarenko, *Proc. SPIE*, 2015, **9568**, 95680Z].

8. OFET devices characterization

Electrical measurements were performed with Keithley 2636A source-meter in air at room temperature. Saturated field-effect mobilities were extracted from the transfer characteristics using Shockley's gradual-channel model according to the equation:

$$\mu_{sat} = (\frac{2L}{WC})\left(\frac{\partial\sqrt{I_d}}{\partial V_g}|_{V_d}\right)^2$$

For each compound, at least 15 devices with the same device dimensions (W, L, C) were investigated. For BTBT derivatives without hexyl end groups the OFET electrical performance was rather poor: in the case of **Cl-Si-Und-BTBT** the device yield was 0% (0 of 15 tested OFETs showed semiconducting properties), while for **O(Si-Und-BTBT)$_2$** the device yield was 13% (only 2 of 15 devices exhibit charge carrier mobility above 1E-6 cm^2/Vs). For BTBT derivatives with hexyl end groups the mobilities and device yields were much higher: for **Cl-Si-Und-BTBT-Hex** the device yield was about 70 % (15 of 21 devices worked), with the maximum mobility of 1.4E-2 cm^2/Vs and an average mobility of 8E-4 cm^2/Vs. For **O(Si-Und-BTBT-Hex)$_2$** the device yield was about 96% (25 of 26 devices worked), with the maximum mobility of 3E-3 cm^2/Vs and an average mobility of 3E-4 cm^2/Vs.

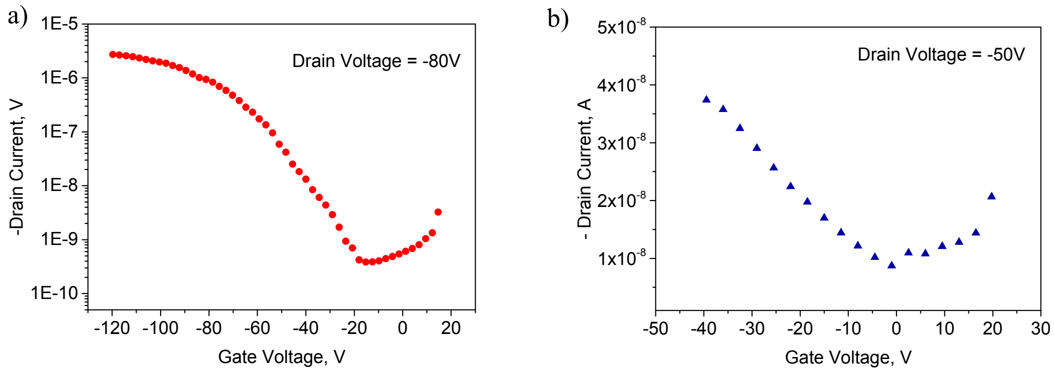


Figure S51. Transfer curves of field-effect transistors based on LB films of **Cl-Si-Und-BTBT-Hex** (a) and **O(Si-Und-BTBT)$_2$** (b).

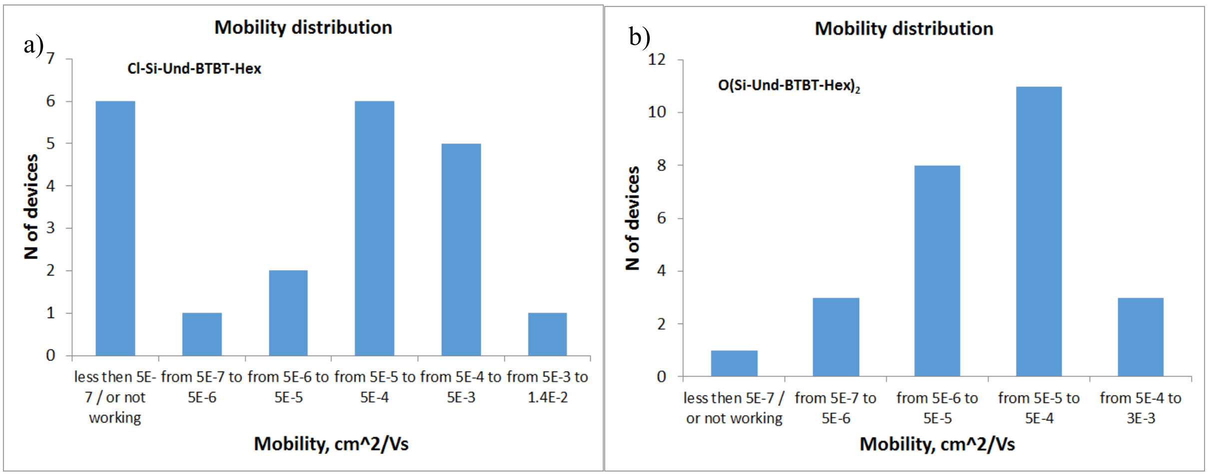


Figure S52. Mobility distribution for OFETS based on LB films of **Cl-Si-Und-BTBT-Hex** (a) and **O(Si-Und-BTBT-Hex)$_2$** (b).