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Supporting Information

Pd-catalyzed disilylation: An efficient way to 2,2'-bis(trimethylsilyl)-biphenyls *via* trapping the transient dibenzopalladacyclopentadienes with hexamethyldisilane

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1) General Information

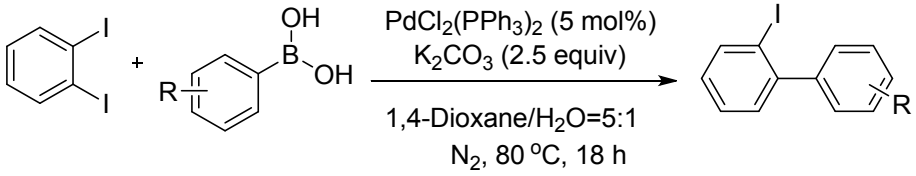
^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX500 spectrometer (FT, 500 MHz for ^{1}H; 126 MHz for ^{13}C) at room temperature, unless otherwise noted. ^{1}H NMR spectra were recorded in $CDCl_3$ and referenced to residual $CHCl_3$ at 7.26 ppm and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC systemcoupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Unless otherwise noted, all starting materials were commercially available and were used without further purification.

2) Synthetic Methods of Starting Materials

a) The ideal catalyst $PdCl_2(PPh_3)_2$ was prepared following a modified literature procedure.[1] A solution of $PdCl_2$ (0.886 g, 5.0 mmol), triphenylphosphine (2.885 g, 11 mmol) was prepared in acetone (50 mL) and the mixture was stirred under air atmosphere for 120 h at room temperature. Then the solvent was removed under reduced pressure, and used directly without further purified.

b) 2-Iodobiphenyl derivatives were prepared according the literature method. [2-4]

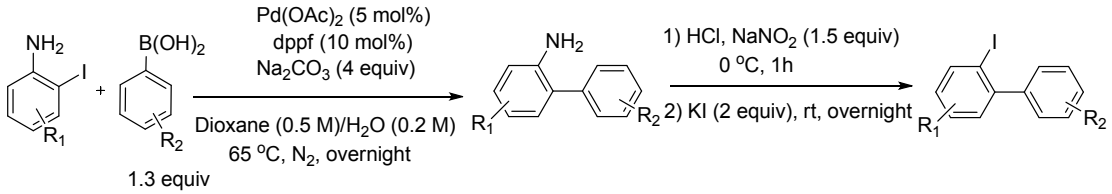
Substrates **2 – 14, 16** were prepared by **Method A**:[2-3]



(A)

A mixture of benzeneboronic acid derivatives (1.2 mmol), 1,2-diiodobenzene (1.0

mmol) were dissolved in dioxane (15 mL) and water (3.0 mL) under nitrogen atmosphere. Then the solution was degassed before tetrakis(triphenyl-phosphine) pdlladium(0) (0.05 mmol) was added followed by potassium carbonate (2.5 mmol) and the eaction was stirred at 80 ^{o}C for 18 hours. After cooling to room temperature, the reaction mixture was diluted in ethyl acetate, and washed with water. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by silica gel column chromatography to afford the title compound. Substrates **17 – 30** were prepared by **Method B**:[4]



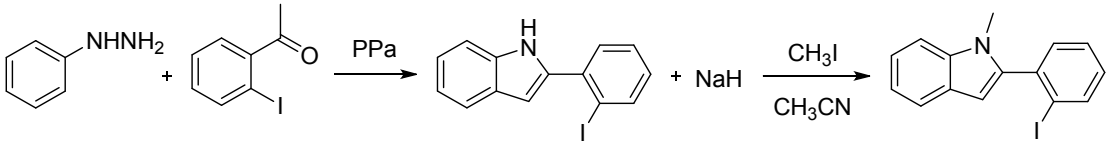
(B)

A 100 mL schlenk tube was charged with substituted 2-iodoaniline (3.0 mmol), substituted phenylboronic acid (3.9 mmol), $Pd(OAc)_2$ (0.15 mmol), dppf (0.3 mmol), Na_2CO_3 (12.0 mmol), 1,4-dioxane (15.0 mL) and water (6.0 mL). The mixture was heated in an oil bath at 65 ^{o}C overnight. After the completion of the reaction, it was allowed to attain to room temperature, then the reaction mixture was filtered and the filtrate diluted in ethyl acetate, and washed with water. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc) to give the corresponding substituted 2-aminobiphenyls.

A solution of concn HCl (36-38%; 1.0 mL, 2.7 mmol) in water (4 mL) was added slowly to the prepared 2-aminobiphenyl (2.0 mmol) at 0 ^{o}C in portions. After stirring for 1 h at 0 ^{o}C, the aqueous solution of $NaNO_2$ (3.0 mmol) was added to the reaction mixture below 5 °C within 10 min and stirred for 1 h. Then an aqueous solution of KI (4.0 mmol) in water (4.0 mL) was added and the reaction mixture was stirred at room temperature overnight. After the completion of the reaction, saturated aqueous $NaHCO_3$ was added to neutralize the acid and adjust the solution to pH > 7. Then the residue was extracted into ethyl acetate (3×5 mL). The combined organic phases were dried over

anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether unless otherwise noted) to give the desired 2-iodobiphenyls.

c) Synthesis of substrates 2-(2-iodophenyl)-1-methyl-1H-indole

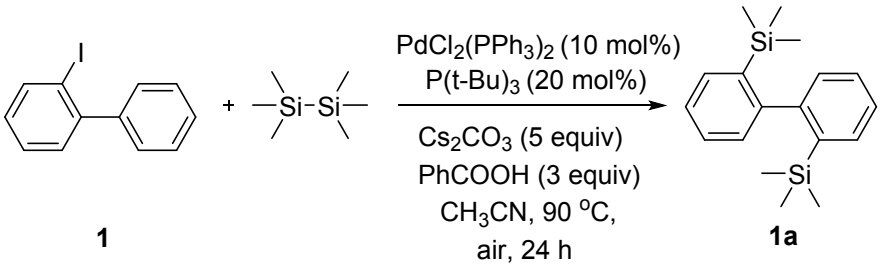


A mixture of 2-iodoacetophenone (5.0 mmol), pheny hydrazine (6.0 mmol) and 25 g polyphosphoric acid (PPa) was added to an Schlenk tube equipped with a stir-bar and stirred at 110 ^oC for 5 h. After the completion of the reaction, the residue was quenched with ice water and extracted into ethyl acetate. The organic phases were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc) to give the corresponding substituted 2-(2-iodophenyl)-1H-indole.

NaH (2.0 equiv) was added to a solution of the above product in CH_3CN (5.0 ml) at 0 ^oC in portions. After stirring for 20 min at 0 ^oC, CH_3I (2.0 equiv) was added dropwise and the reaction mixture was allowed to room temperature and stirred for another 2 h. After completion of the reaction (monitored by TLC), the residue was quenched with water and extracted into ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and the solution was evaporated to dryness. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 10:1) to provide the corresponding substituted 2-(2-iodophenyl)-1-methyl-1H- indole.

3) Typical Experimental Procedures

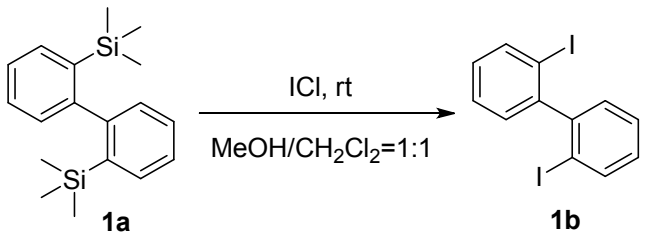
Synthesis of 2,2'-bis(trimethylsilyl)-1,1'-biphenyl **(1a)**



The stirred mixture of 2-iodo-1,1'-biphenyl **1** (0.2 mmol), hexamethyldisilane (3.0 equiv), $PdCl_2(PPh_3)_2$ (10 mol%), $P(t\text{-}Bu)_3$ (20 mol%), Cs_2CO_3 (5.0 equiv) and PhCOOH (3.0 equiv) in CH_3CN (2 mL) at 90 °C for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether unless otherwise noted) to provide the desired products **1a** as a colorless oil.

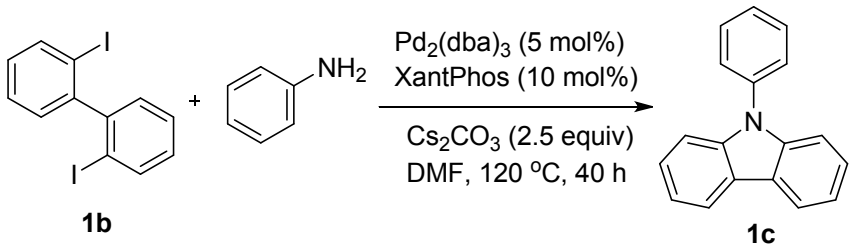
4) Procedure for Application Experiment

Synthesis of substrates 2,2'-diiodo-1,1'-biphenyl **(1b)**



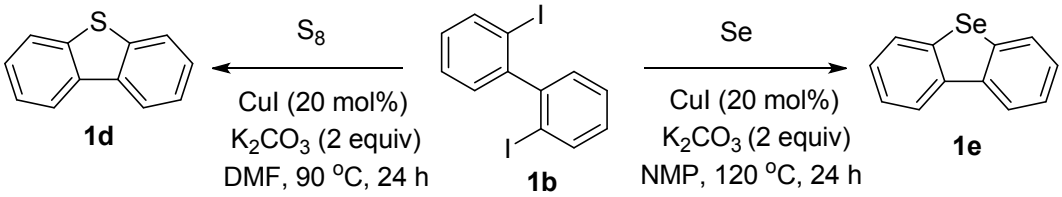
The 25 mL Schlenk tube was charged with 2,2'-bis(trimethylsilyl)- 1,1'-biphenyl **1a** (1.0 mmol), ICl (4.0 mmol), MeOH (1.0 mL) and CH_2Cl_2 (1.0 mL). The mixture was stirred at room temperature for 12 hours. After the completion of the reaction (monitored by TLC), the mixture was quenched with water and extracted with dichloromethane. The organic phases were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether) to give the corresponding 2,2'-diiodo-1,1'-biphenyl **1b** as a white solid.

Synthesis of 9-phenyl-9H-carbazole **(1c)** [5]



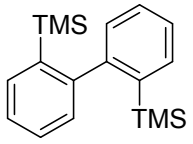
The stirred mixture of 2,2'-diiodo-1,1'-biphenyl **1b** (0.2 mmol), aniline (2.0 equiv), $Pd_2(dba)_3$ (5 mol%), XantPhos (10 mol%) and Cs_2CO_3 (2.5 equiv) in DMF (2 mL) at 120 °C for 40 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether) to provide the desired products **1c** as a white solid.

Synthesis of dibenzo[b,d]thiophene **(1d)** or dibenzo[b,d]selenophene **(1e)** [6-7]

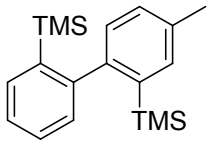


The stirred mixture of 2,2'-diiodo-1,1'-biphenyl **1b** (0.2 mmol), Sulfur powder (or Selenium Powder) (2.0 equiv), CuI (20 mol%) and K_2CO_3 (2.5 equiv) in DMF (or NMP) (2.0 mL) at 90 °C (or 120 °C) for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum) to provide the desired products **1d** (or **1e**) as a white solid.

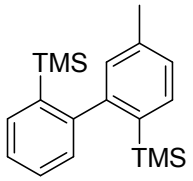
5) Characterization Data



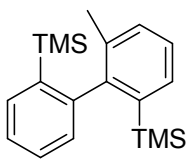
2,2'-bis(trimethylsilyl)-1,1'-biphenyl (1a)[8]: Colorless oil, isolated yield 89% (53 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.63 (m, 2H), 7.39-7.38 (m, 4H), 7.23-7.21 (m, 2H), -0.01 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.94, 138.86, 134.31, 129.92, 127.70, 126.41, 0.35.



(4-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (2a) [8]: White solid, isolated yield 88% (55 mg), mp: 31.7-33.3 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.59 (m, 1H), 7.40 (s, 1H), 7.34-7.33 (m, 2H), 7.16 (d, J = 6.4 Hz, 2H), 7.08 (d, J = 7.35 Hz, 1H), 2.43 (s, 3H), -0.04-0.05 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.97, 147.07, 138.99, 138.56, 135.59, 134.95, 134.26, 130.13, 129.88, 128.40, 127.69, 126.27, 21.34, 0.41, 0.39.

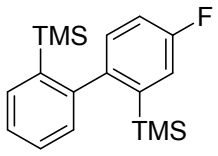


(5-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (3a)[8]: Colorless oil, isolated yield 71% (44 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.57 (m, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.34-7.32 (m, 2H), 7.16 (d, J = 6.5 Hz, 2H), 7.0 (s, 1H), 2.35, -0.08 (d, J = 7.6 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.08, 149.83, 138.75, 137.38, 135.17, 134.40, 134.30, 131.00, 129.74, 127.69, 127.11, 126.29, 21.16, 0.38, 0.33.

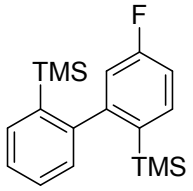


(6-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (4a)[8]: Colorless oil, isolated

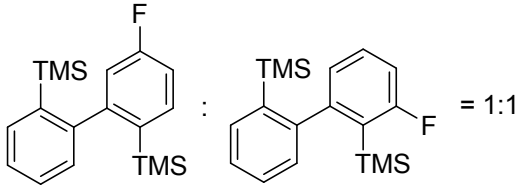
yield 64% (40 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 6.7 Hz, 1.35 Hz, 1H), 7.46 (d, *J* = 7.15 Hz, 1H), 7.40-7.34 (m, 2H), 7.28 (t, *J* = 7.45 Hz, 1H), 7.24 (d, *J* = 7.15 Hz, 1H), 7.11-7.09 (m, 1H), 1.98 (s, 3H), -0.07 (d, *J* = 6.8 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.00, 148.27, 139.26, 139.12, 135.72, 134.68, 131.67, 130.21, 129.64, 128.26, 126.69, 126.26, 21.08, 0.48, 0.17.



(4-fluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (5a)[8]: Colorless oil, isolated yield 80% (49 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 5.8 Hz, 1H), 7.33 (s, 2H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.13-7.11 (m, 2H), 7.01-6.98 (m, 1H), -0.06 (d, *J* = 7.0 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.74, 160.77, 148.87, 145.79, 142.06, 139.17, 134.41, 131.54 (d, *J* = 6.99 Hz), 130.14, 127.22 (d, *J* = 148.29 Hz), 120.48 (d, *J* = 18.61 Hz), 114.36 (d, *J* = 21.02 Hz), 0.40, 0.09. HRMS (ESI) m/z calcd for $C_{18}H_{26}FSi_2^+$ $(M+H)^+$ 317.15516, found 317.15491.

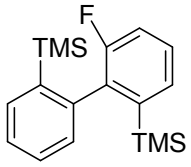


(5-fluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (6a): Colorless oil, isolated yield 92% (56 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.58 (m, 1H), 7.56-7.53 (m, 1H), 7.37-7.33 (m, 2H), 7.15-7.14 (m, 1H), 7.05 (td, *J* = 8.65 Hz, 2.35 Hz, 1H), 6.89 (dd, *J* = 9.95 Hz, 2.3 Hz, 1H), -0.06 (d, *J* = 19.85 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.35, 161.37, 152.28 (d, *J* = 7.08 Hz), 148.57, 138.72, 136.23 (d, *J* = 7.61 Hz), 134.51 (d, *J* = 17.22 Hz), 129.60, 127.80, 126.78, 117.05 (d, *J* = 19.28 Hz), 113.31 (d, *J* = 18.99 Hz), 0.36, 0.32.

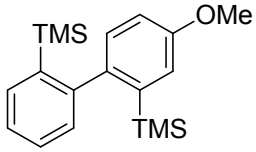


(5-fluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (6a) and (3-fluoro-[1,1'-

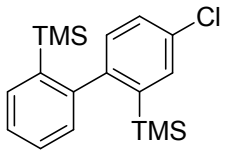
biphen yl]-2,2'-diyl)bis(trimethylsilane) (6a'): Colorless oil, isolated yield 66% (40 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.55-7.54 (m, 1H), 7.35-7.29 (m, 5H), 7.15 (d, *J* = 6.2 Hz, 1H), 7.08-7.04 (m, 2H), 7.00 (t, *J* = 8.9 Hz, 1H), 6.95 (d, *J* = 7.35 Hz, 1H), 6.90 (d, *J* = 9.8 Hz, 1H), 0.01(s, 9H), -0.03 (s, 9H), -0.05 (s, 9H), -0.07 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.59 (d, *J* = 241.19 Hz), 162.37 (d, *J* = 249.38 Hz), 152.29 (d, *J* = 6.82 Hz), 151.61 (d, *J* = 10.41 Hz), 149.14, 148.58, 138.73, 138.27, 136.23 (d, *J* = 7.84 Hz), 134.60 (d, *J* = 3.58 Hz), 134.45, 134.35, 129.99, 129.62, 129.42, 129.34, 127.81, 126.79, 126.57 (d, *J* = 5.52 Hz), 125.21 (d, *J* = 27.38 Hz), 117.07 (d, *J* = 19.53 Hz), 113.68, 113.43 (d, *J* = 9.02 Hz), 113.24, 0.50 (d, *J* = 3.26 Hz), 0.44, 0.36, 0.33.



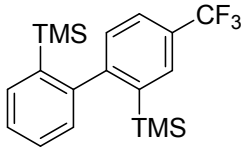
(6-fluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (7a): Colorless oil, isolated yield 66% (40 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.61 (m, 1H), 7.39-7.31 (m, 4H), 7.15 (d, *J* = 5.2 Hz, 1H), 7.10-7.06 (m, 1H), -0.04 (s, 9H), -0.07 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.71, 158.77, 142.51 (d, *J* = 97.46 Hz), 140.17, 136.53 (d, *J* = 15.37 Hz), 134.35, 130.30, 129.72 (d, *J* = 3.65 Hz), 128.50 (d, *J* = 7.27 Hz), 128.16, 127.10, 115.66 (d, *J* = 23.47 Hz), 0.26, - 0.13. HRMS (ESI) m/z calcd for $C_{18}H_{26}FSi_2^+$ $(M+H)^+$ 317.15516, found 317.15540.



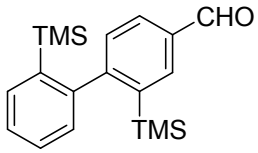
(4-methoxy-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (8a)[8]: Colorless oil, isolated yield 93% (61 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.57(m, 1H), 7.35-7.31 (m, 2H), 7.17-7.15 (m, 1H), 7.14 (d, *J* = 2.65 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.87 (dd, *J* = 8.35 Hz, 2.7 Hz, 1H), 3.87 (s, 3H), -0.05 (d, *J* = 11.2 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.95, 149.61, 142.46, 140.49, 139.28, 134.28, 131.01, 130.38, 127.71, 126.2, 120.27, 112.09, 55.14, 0.42, 0.24. HRMS (ESI) m/z calcd for C19H29OSi2$^+$ $(M+H)^+$ 329.17515, found 329.17523.



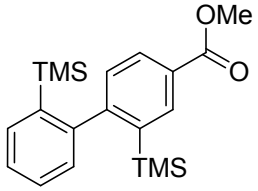
(4-chloro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (9a)[8]: Colorless oil, isolated yield 78% (52 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.52 (s, 1H), 7.31 (t, *J* = 14.6 Hz, 3H), 7.10 (d, *J* = 7.25 Hz 2H), -0.06 (d, *J* = 9.1 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.62, 148.21, 141.72, 138.91, 134.44, 133.93, 132.87, 131.35, 129.88, 127.82, 127.63, 126.71, 0.43, 0.13.



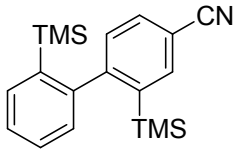
(4-(trifluoromethyl)-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (10a)[8]: White solid, isolated yield 75% (50 mg), mp: 61.6-63 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.61-7.58 (m, 2H), 7.39-7.34 (m, 2H), 7.28 (d, *J* = 7.85 Hz , 1H), 7.12-7.11 (m, 1H), -0.05 (d, *J* = 14.9 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.53, 148.50, 140.37, 138.65, 134.53, 130.78 (q, *J* = 3.36 Hz), 130.07, 129.54, 128.64 (q, *J* = 31.93 Hz), 127.87, 126.95, 124.53 (q, *J* = 272.97 Hz), 124.49 (d, *J* = 3.52 Hz), 0.38, 0.13.



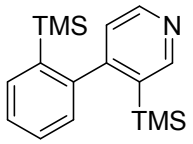
2,2'-bis(trimethylsilyl)-[1,1'-biphenyl]-4-carbaldehyde (11a)[8]: White solid, isolated yield 73% (48 mg), mp: 54.6-57.4 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.10 (d, *J* = 1.4 Hz, 1H), 7.85 (dd, *J* = 7.75 Hz, 1.55 Hz, 1H), 7.62-7.61 (m, 1H), 7.38-7.34 (m, 3H), 7.13-7.11 (m, 1H), -0.04 (d, *J* = 21.9 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.53, 156.46, 148.64, 140.53, 138.41, 136.23, 134.57, 134.33, 130.69, 129.23, 128.86, 127.87, 127.00, 0.41, 0.18. HRMS (ESI) m/z calcd for $C_{19}H_{27}Si_2O^+$ $(M+H)^+$ 327.15949, found 327.15967.



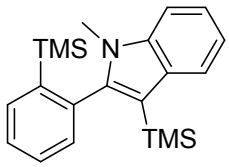
methyl 2,2'-bis(trimethylsilyl)-[1,1'-biphenyl]-4-carboxylate (12a)[8]: Colorless oil, isolated yield 86% (61 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 6.1 Hz 1H), 7.37 (d, *J* = 4.1 Hz, 2H), 7.28 (d, *J* = 4.3 Hz, 1H), 7.14-7.13 (m, 1H), 3.97 (s, 3H), -0.03 (d, *J* = 15.4 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.37, 154.76, 148.97, 139.62, 138.52, 135.58, 134.48, 130.06, 129.40, 128.89, 128.04, 127.81, 126.81, 52.08, 0.41, 0.22. HRMS (ESI) m/z calcd for C20H29O2Si2$^+$ $(M+H)^+$ 357.17006, found 357.17081.



2,2'-bis(trimethylsilyl)-[1,1'-biphenyl]-4-carbonitrile (13a)[8]: White solid, isolated yield 72% (47 mg), mp: 84.1-85.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.61 (s, 2H), 7.37 (s, 2H), 7.28 (s, 1H), 7.09 (d, *J* = 5.7 Hz, 1H), -0.05 (d, *J* = 11.2 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.47, 147.96, 141.24, 138.37, 138.04, 134.60, 131.03, 130.38, 129.17, 127.91, 127.17, 119.29, 110.67, 0.37, 0.00. HRMS (ESI) m/z calcd for $C_{19}H_{26}NSi_2^+$ $(M+H)^+$ 324.15983, found 324.15945.

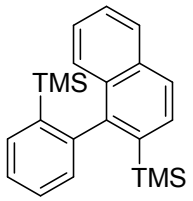


3-(trimethylsilyl)-4-(2-(trimethylsilyl)phenyl)pyridine (14a): Colorless oil, isolated yield 76% (46 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.55 (d, *J* = 4.9 Hz, 1H), 7.61-7.59 (m, 1H), 7.39-7.33 (m, 2H), 7.10 (d, *J* = 4.9 Hz, 1H), 7.09-7.06 (m, 1H), -0.03 (d, *J* = 7.55 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.87, 154.68, 148.78, 147.10, 138.06, 134.63, 133.67, 128.99, 127.93, 127.15, 124.87, 0.47, 0.07. HRMS (ESI) m/z calcd for $C_{17}H_{26}NSi_2^+$ $(M+H)^+$ 300.15983, found 300.15954.

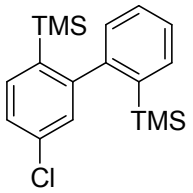


1-methyl-3-(trimethylsilyl)-2-(2-(trimethylsilyl)phenyl)-1H-indole (15a)[8]: Colorless oil, isolated yield 45% (32 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.25 Hz, 1H), 7.44 - 7.41 (m, 1H), 7.36 (td, *J* = 7.45 Hz,

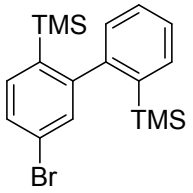
1.05Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 7.65 Hz, 1H), 7.19 (d, J = 7.45 Hz, 1H), 7.16 (t, J = 7.25 Hz, 1H), 3.36 (s, 3H), 0.03 (s, 9H), -0.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.74, 141.28, 139.56, 137.81, 134.51, 132.84, 131.58, 128.05, 127.85, 121.60, 121.25, 119.51, 109.37, 107.63, 30.53, 0.44, -0.23.



trimethyl(2-(2-(trimethylsilyl)naphthalen-1-yl)phenyl)silane (16a): Colorless oil, isolated yield 49% (33 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 6.15 Hz, 2H), 7.67 (d, J = 8.35 Hz, 2H), 7.43 (d, J = 3.1 Hz, 3H), 7.31-7.28 (m, 2H), 7.21 (d, J = 4.15 Hz, 1H), -0.03 (s, 9H), -0.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.90, 146.97, 140.77, 136.13, 134.42, 133.28, 133.20, 130.65, 130.29, 128.13, 127.53, 127.48, 126.67, 126.37, 126.02, 125.38, 0.32, 0.05. HRMS (ESI) m/z calcd for $C_{22}H_{29}Si_2^+$ $(M+H)^+$ 349.18023, found 349.17960.

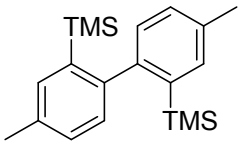


(5-chloro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (22a)[8]: White solid, isolated yield 90% (60 mg), mp: 63-64.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 6.45 Hz, 1H), 7.51 (d, J = 8.05 Hz, 1H), 7.37-7.32 (m, 3H), 7.18 (s, 1H), 7.15-7.14 (m, 1H), -0.05 (d, J = 19.4 Hz, 18H).^{13}C NMR (126 MHz, $CDCl_3$) δ 151.55, 148.50, 138.78, 137.31, 135.70, 134.49, 133.90, 130.01, 129.61, 127.84, 126.82, 126.44, 0.34, 0.24.

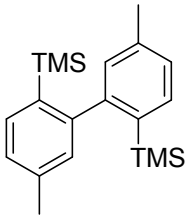


(5-bromo-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (23a): White solid, isolated yield 63% (47 mg), mp: 58.8-59.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 6.4 Hz, 1H), 7.48 (d, J = 8.05 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.35-7.34 (m, 3H), 7.14-7.13 (m, 1H), -0.06 (d, J = 21.2 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.74,

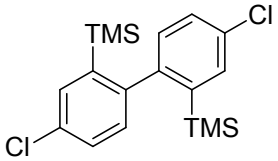
148.41, 138.78, 137.78, 135.88, 134.49, 132.87, 129.60, 129.35, 127.84, 126.83, 122.35, 0.34, 0.20.



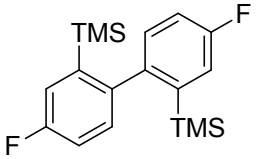
(4,4'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (25a)[8]: White solid, isolated yield 87% (57 mg), mp: 78.6-80.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.16 (d, *J* = 7.1 Hz, 2H), 7.08 (d, *J* = 7.25 Hz, 2H), 2.43 (s, 6H), -0.03 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.08, 138.69, 135.44, 134.93, 130.10, 128.40, 21.34, 0.45.



(5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (26a): Colorless oil, isolated yield 67% (44 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.03 (s, 2H), 2.38 (s, 6H), -0.05 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.02, 137.37, 135.07, 134.43, 130.87, 127.03, 21.18, 0.41.

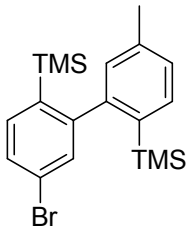


(4,4'-dichloro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (27a) [8]: Colorless oil, isolated yield 75% (55 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 2H), 7.31-7.30 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), -0.04 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.91, 141.78, 134.11, 133.25, 131.34, 127.79, 0.24.

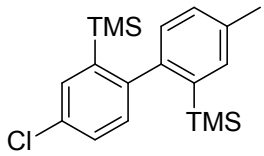


(4,4'-difluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (28a)[8]: White solid, isolated yield 85% (53 mg), mp: 67.6-68.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 5.3 Hz, 2H), 7.05 (d, *J* = 8.05 Hz, 2H), -0.00 (s, 18H). ^{13}C

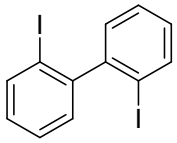
NMR (126 MHz, $CDCl_3$) δ 162.82, 160.85, 144.66, 142.37, 131.77 (d, J = 6.75 Hz), 120.61 (d, J = 18.85 Hz), 114.48 (d, J = 20.99 Hz), 0.13.



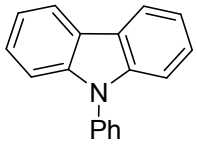
(5-bromo-5'-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (29a): Colorless oil, isolated yield 53% (41 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 7.65 Hz, 1H), 7.34 (s, 1H), 7.18 (d, J = 7.15 Hz, 1H), 6.97 (s, 1H), 2.36 (s, 3H), -0.06 (d, J = 12.35 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.95, 148.36, 137.69, 137.58, 135.88, 135.12, 134.60, 132.76, 130.68, 129.25, 127.54, 122.36, 21.16, 0.40, 0.21.



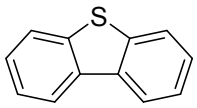
(4-chloro-4'-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (30a)[8]: White solid, isolated yield 85% (59 mg), mp: 75.4-77 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.39 (s, 1H), 7.30 (d, J = 7.85 Hz, 1H), 7.16 (d, J = 7.25 Hz, 1H), 7.10 (d, J = 7.9 Hz, 1H), 7.02 (d, J = 7.45 Hz, 1H), 2.42 (s, 3H), -0.04 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.27, 145.74, 141.83, 138.61, 135.98, 135.10, 133.89, 132.74, 131.57, 129.85, 128.52, 127.62, 21.34, 0.49, 0.21.



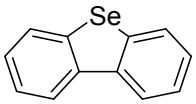
2,2'-diiodo-1,1'-biphenyl (1b)[9]: White solid, isolated yield 97% (79mg), mp: 201-204 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.9 Hz, 0.8 Hz, 2H), 7.44 (td, J = 7.5 Hz, 1.05 Hz, 2H), 7.21 (dd, J = 7.55 Hz, 1.5 Hz, 2H), 7.11 (td, J = 7.75 Hz, 1.55 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.83, 138.80, 129.84, 129.32, 127.98, 99.60.



9-phenyl-9H-carbazole (1c) [5]: White solid, isolated yield 75% (36 mg), mp: 95-97 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.4 Hz, 2H), 7.64-7.61 (m, 4H), 7.51-7.46 (m, 5H), 7.33 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.82, 137.64, 129.83, 127.40, 127.09, 125.88, 123.28, 120.27, 119.85,109.72.



dibenzo[b,d]thiophene (1d)[6]: White solid, isolated yield 86% (36 mg), mp: 97-100 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 5.15 Hz, 2.9 Hz, 2H), 7.88 (dd, *J* = 5.1 Hz, 2.9 Hz, 2H), 7.48 (dd, *J* = 5.5 Hz, 3.0 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.37, 135.49, 126.65, 124.30, 122.76, 121.53.



dibenzo[b,d]selenophene (1e)[7]: White solid, isolated yield 73% (34 mg), mp: 76-78 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 2H), 7.90 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.24, 138.22, 126.83, 126.05, 124.81, 122.82.

6) References

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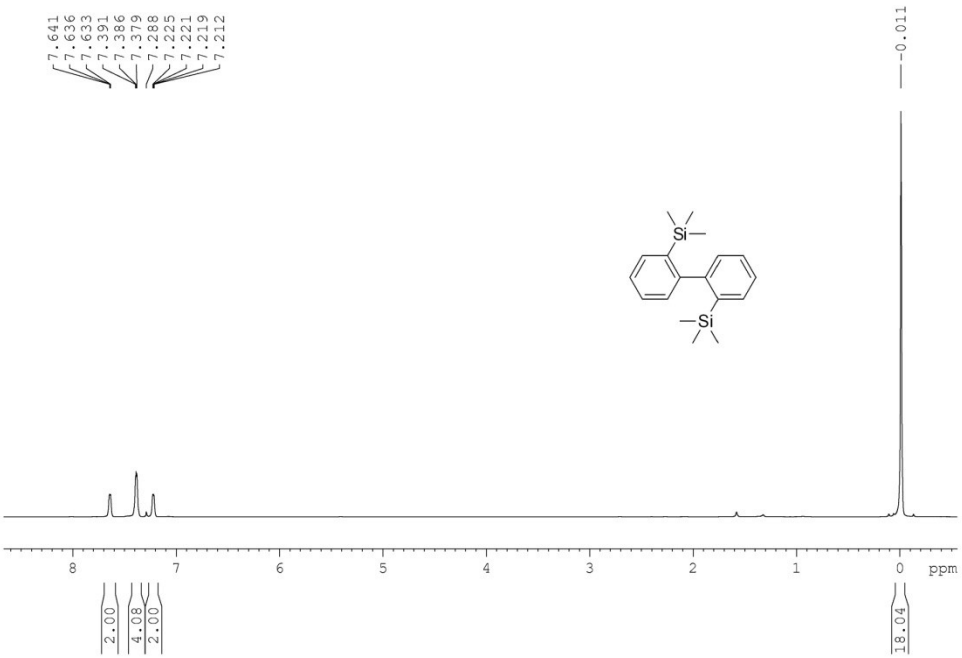
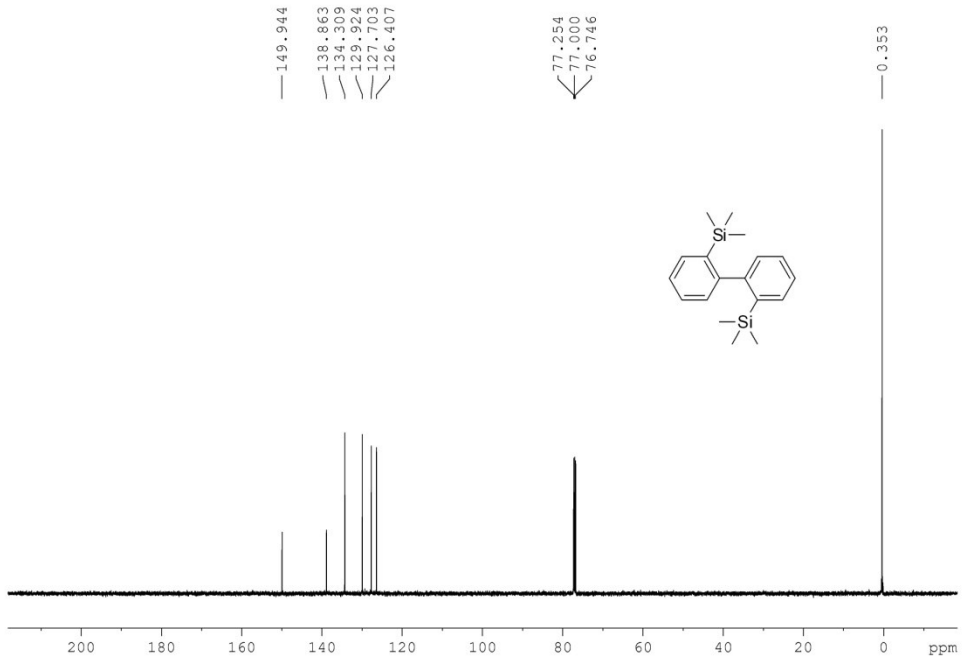
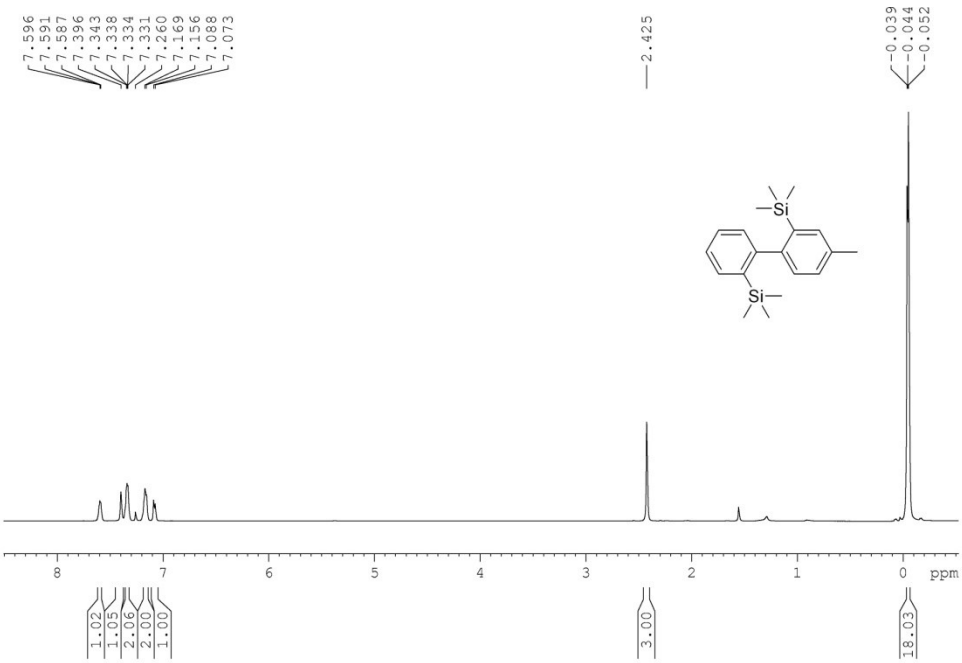
7) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All New Compounds.

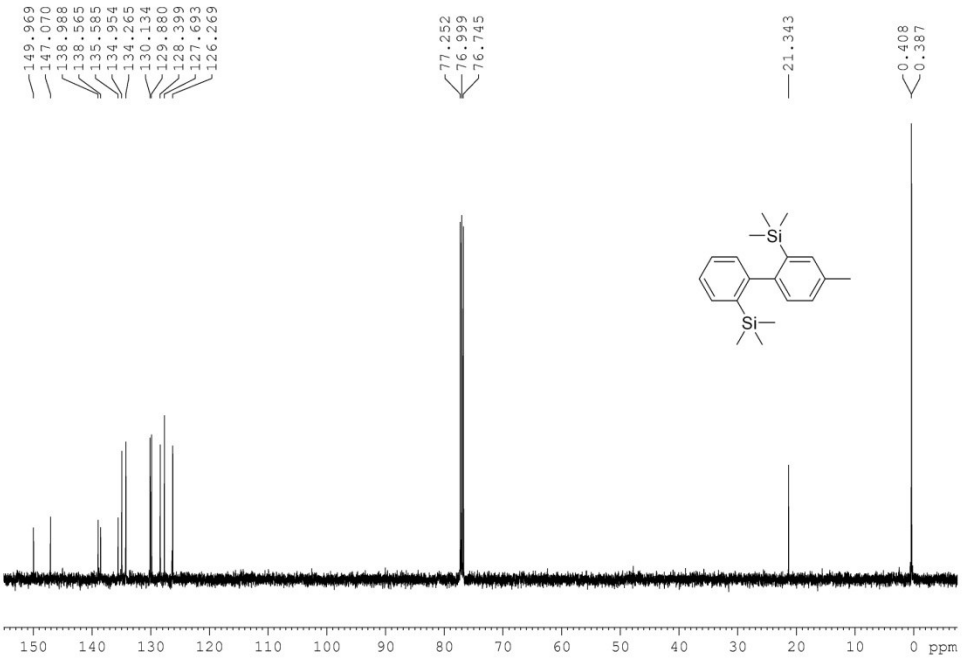
2,2'-bis(trimethylsilyl)-1,1'-biphenyl (1a)



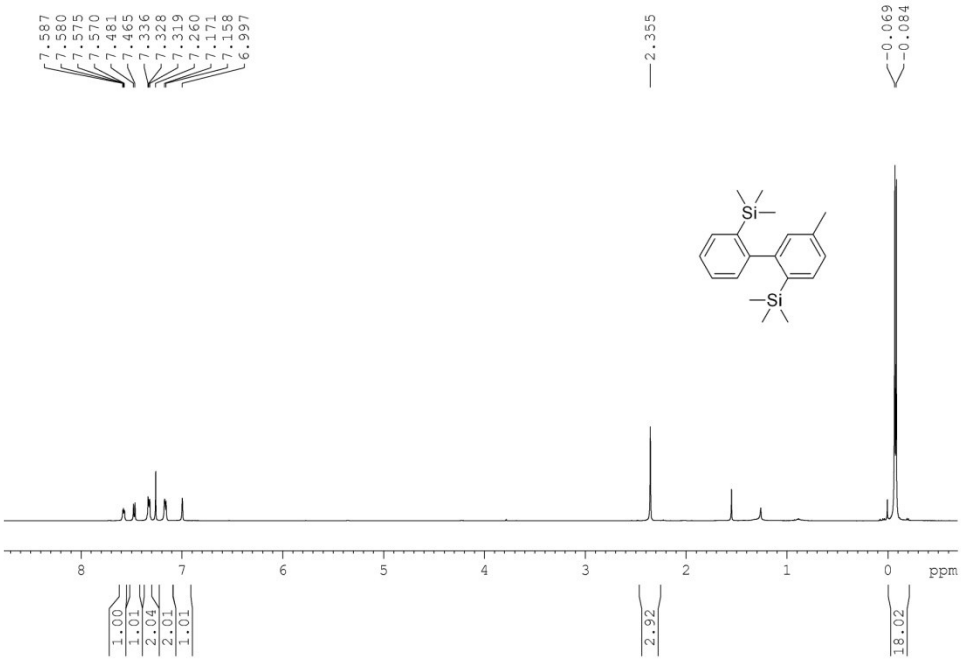


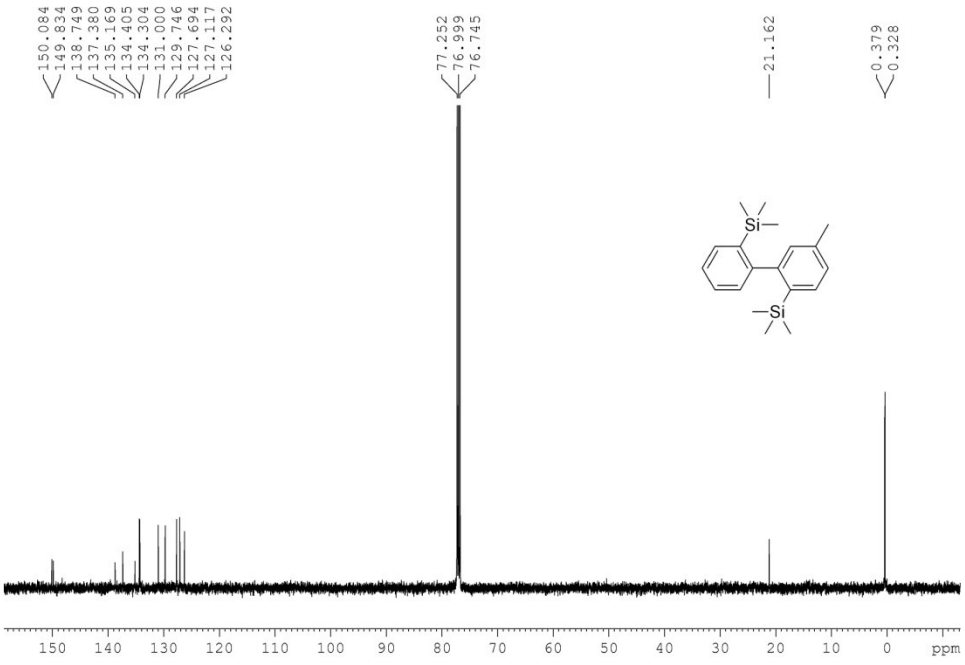
(4-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (2a)



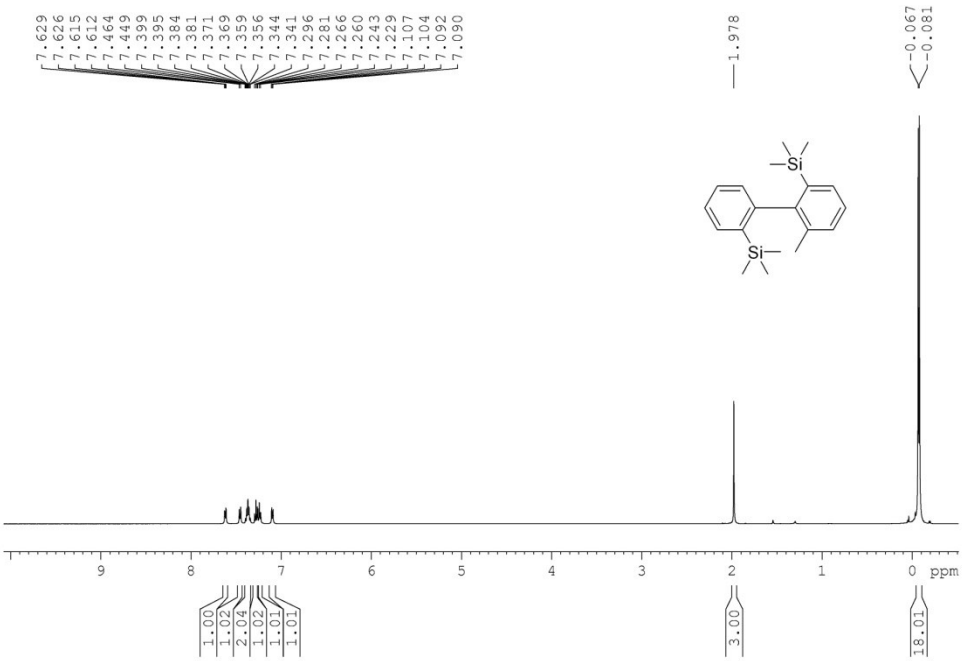


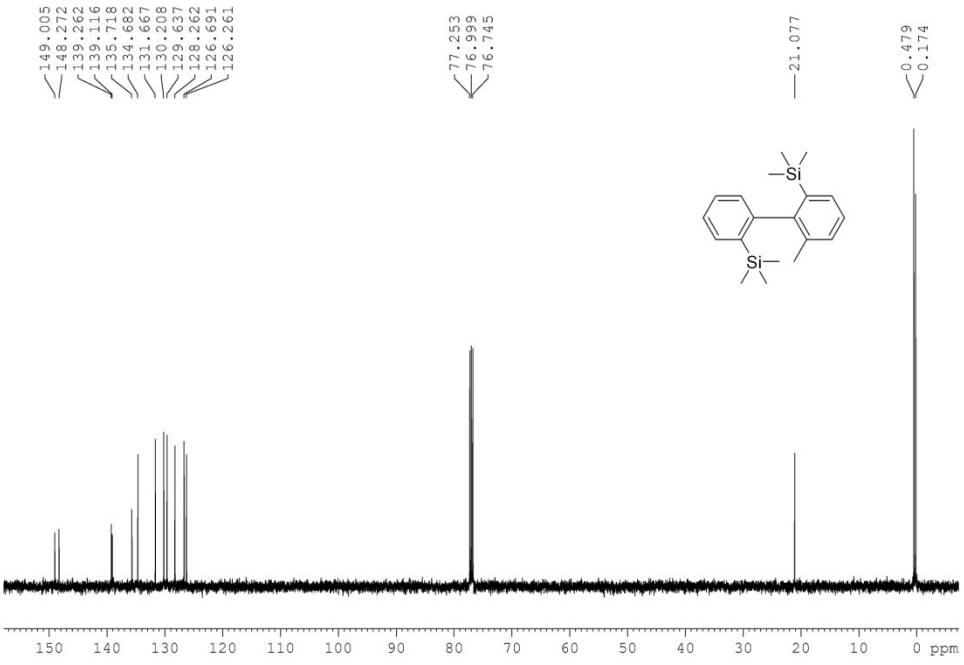
(5-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (3a)



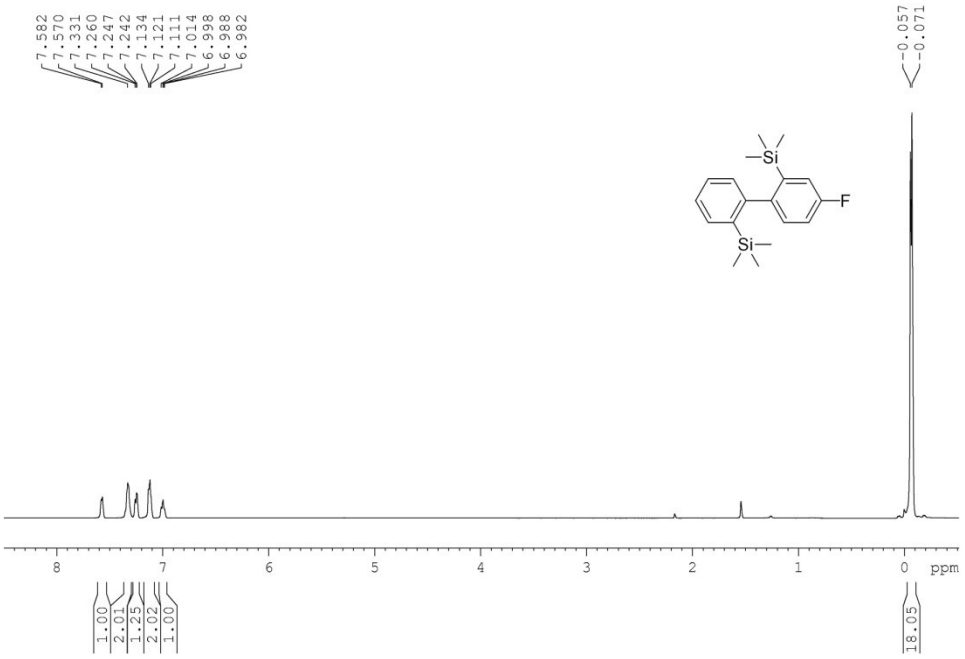


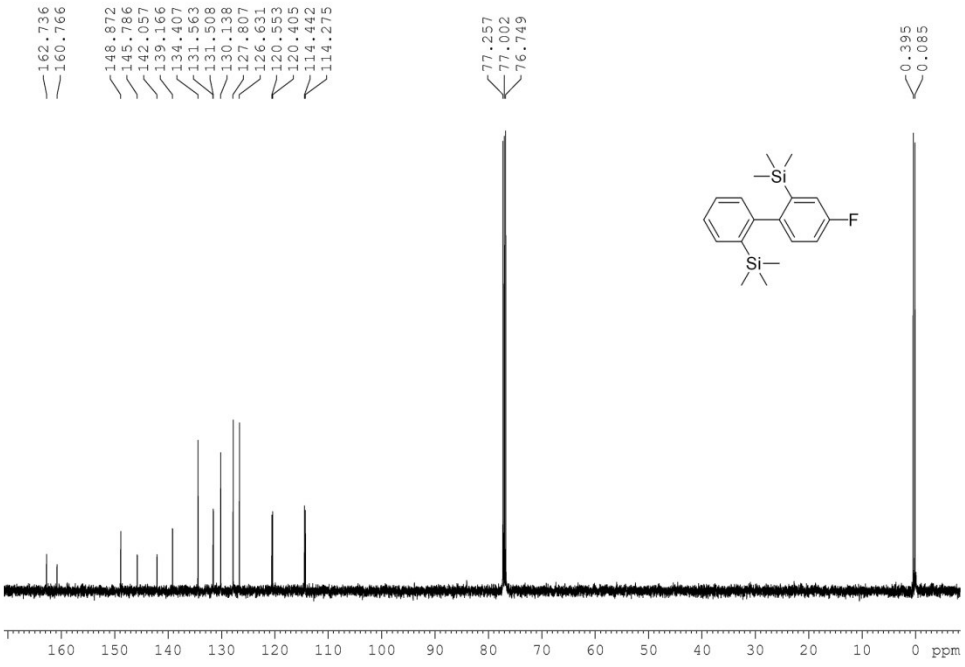
(6-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (4a)



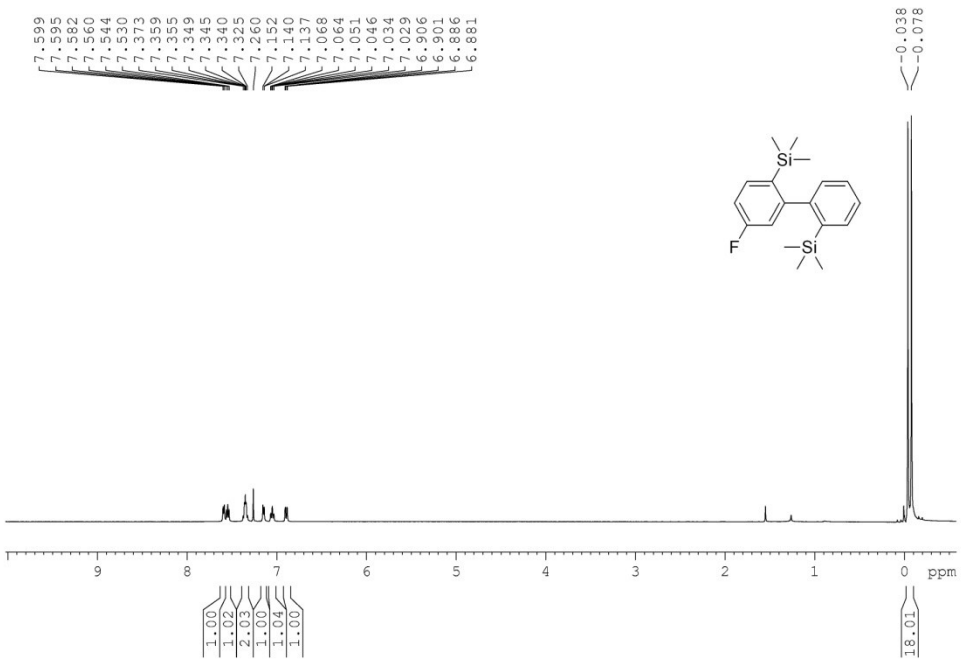


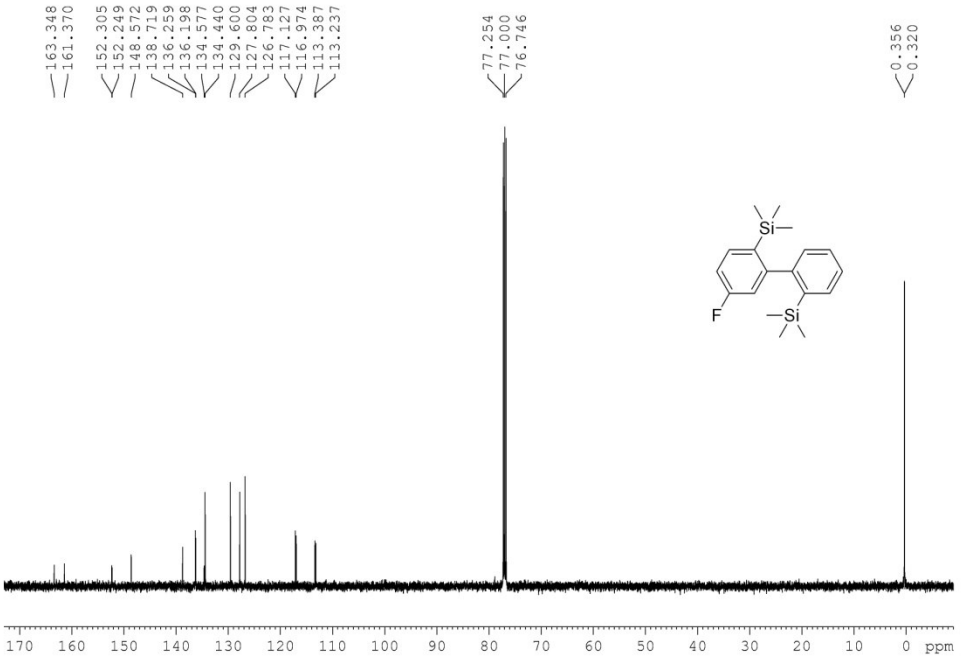
(4-fluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (5a)





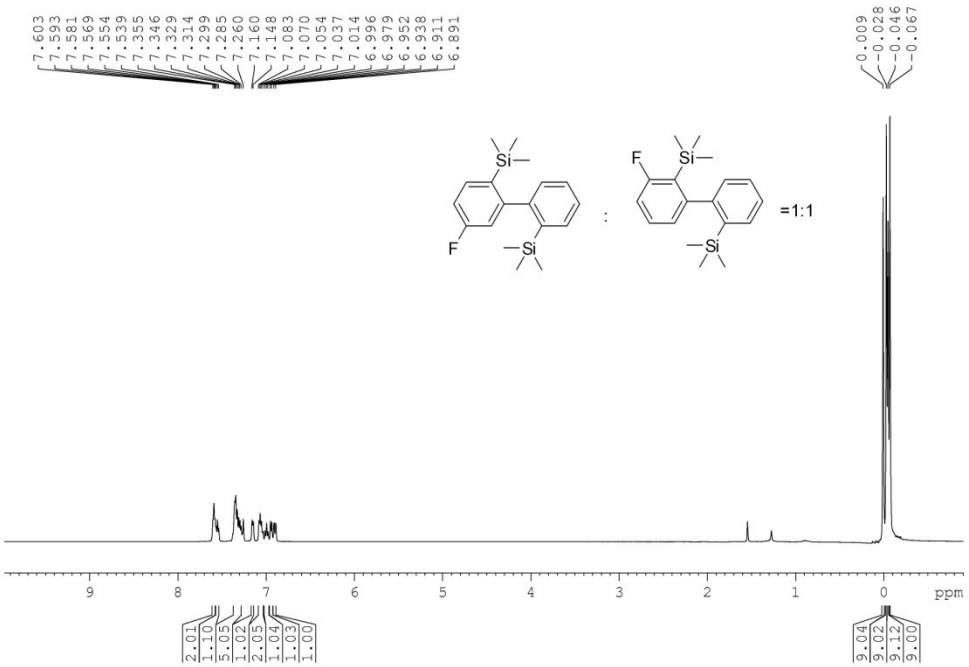
(5-fluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (6a)

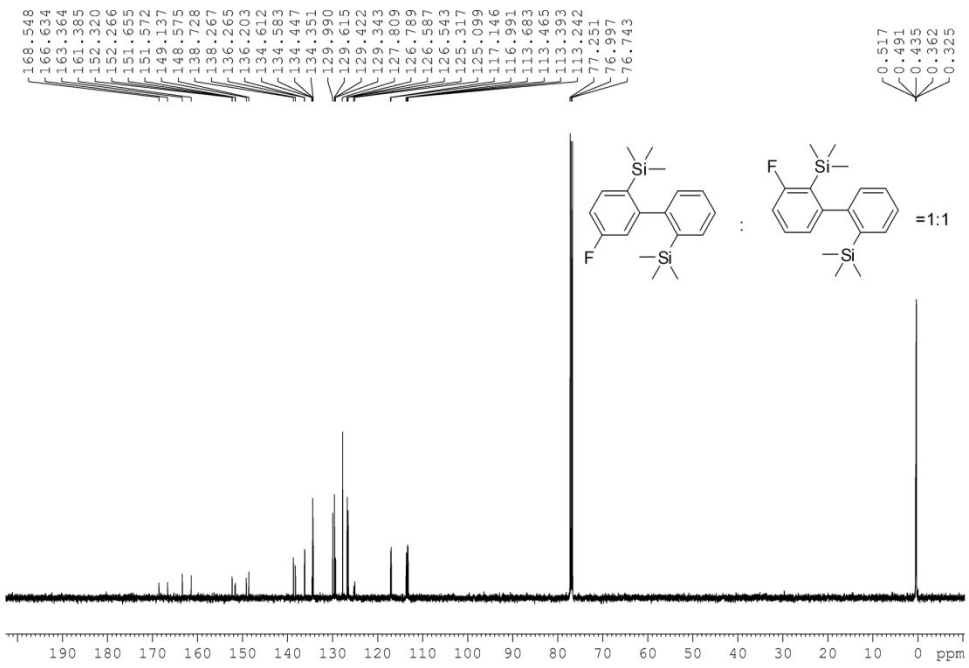




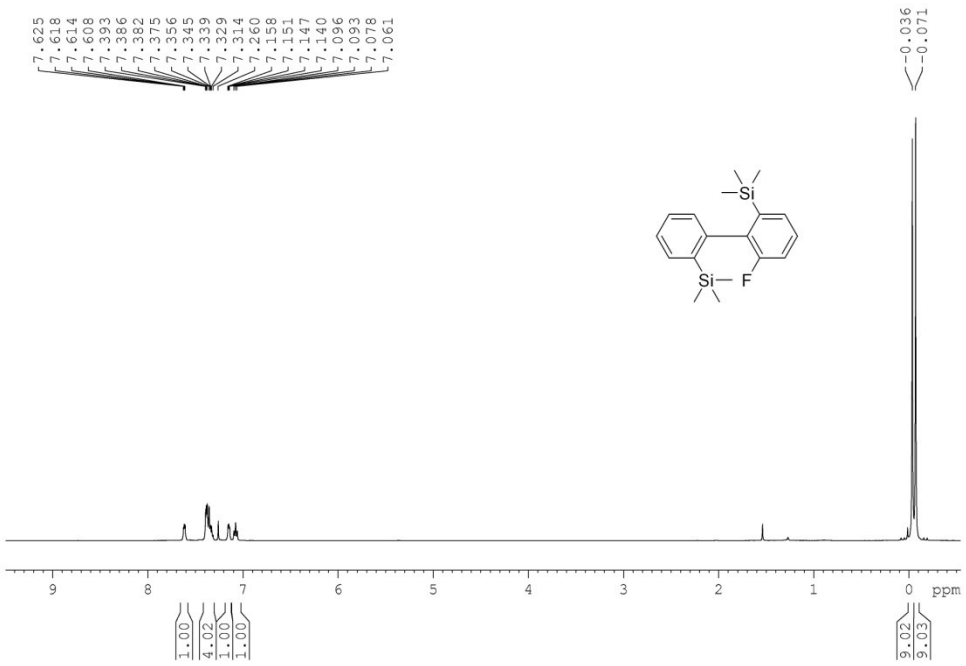
(5-fluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (6a) and (3-fluoro-[1,1'-

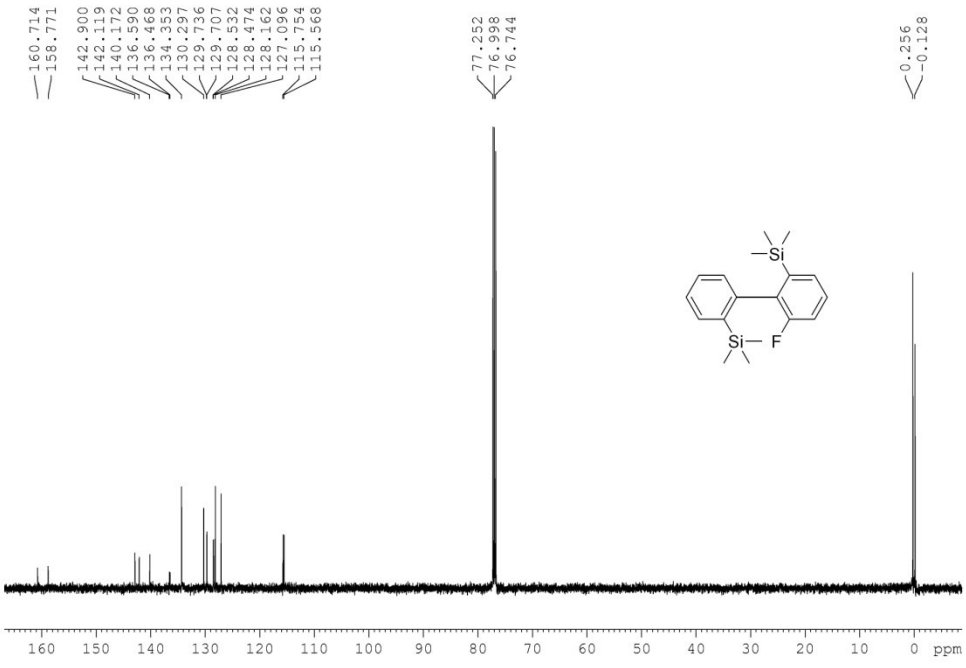
biphen yl]-2,2'-diyl)bis(trimethylsilane) (6a')



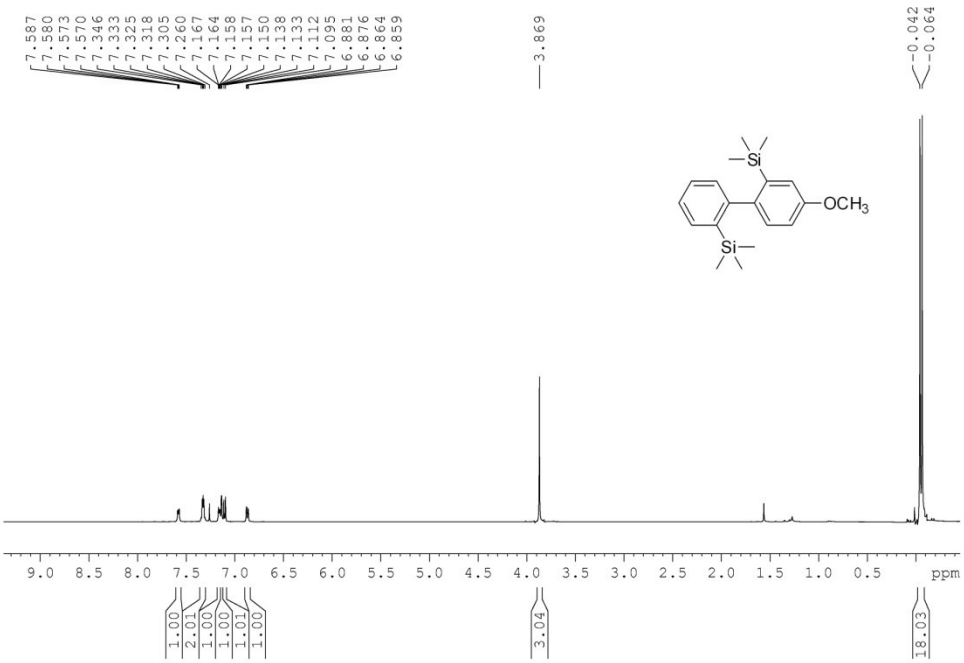


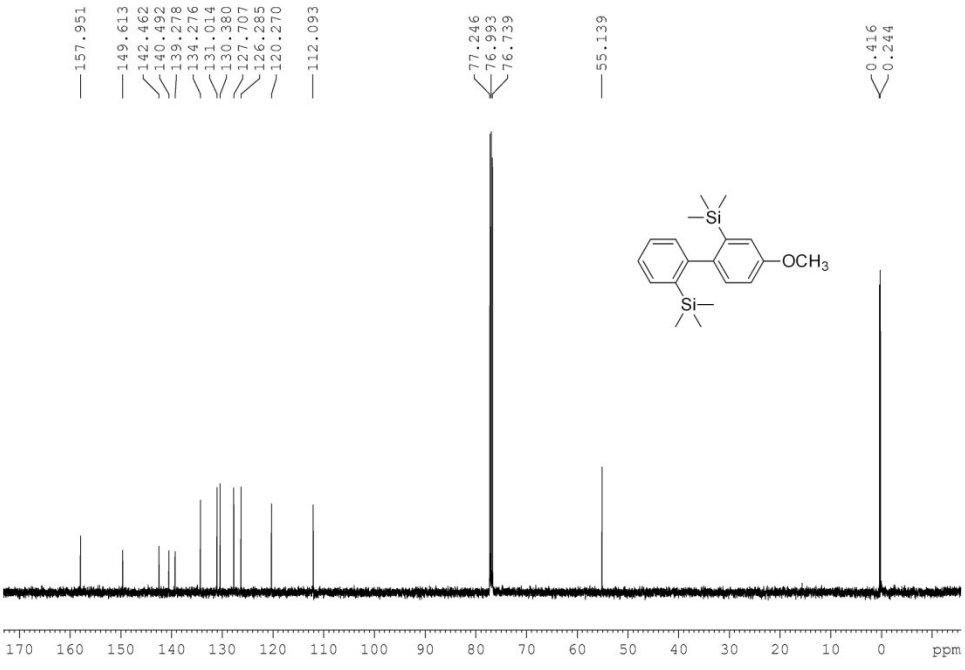
(6-fluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (7a)



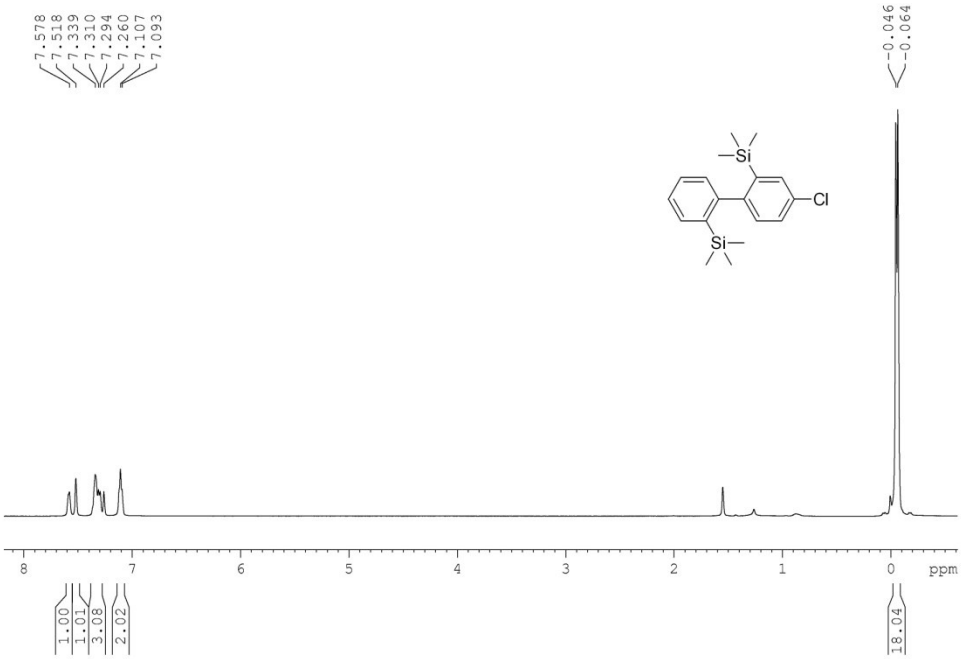


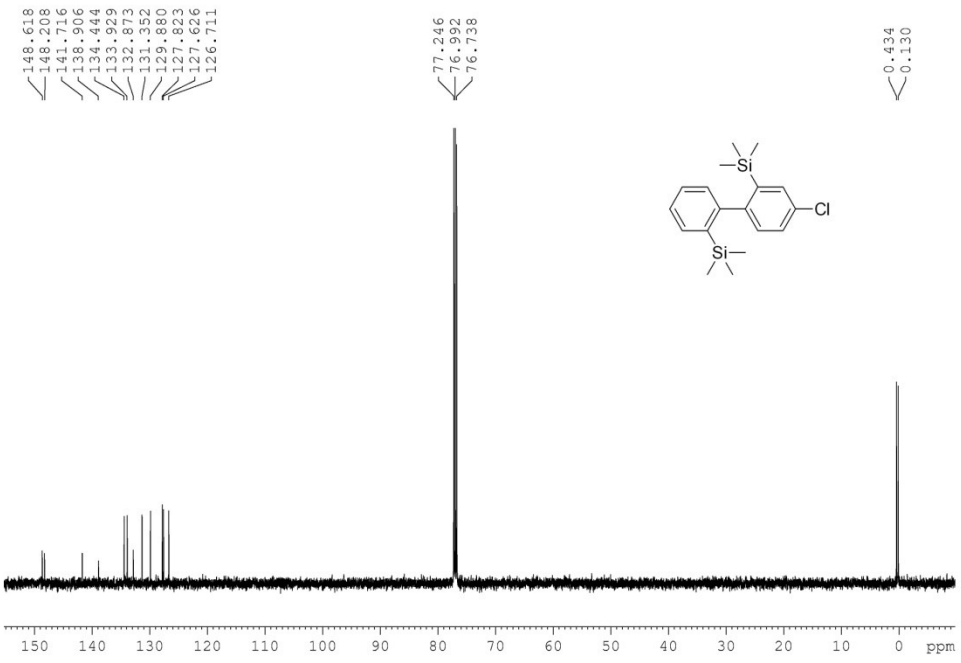
(4-methoxy-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (8a)



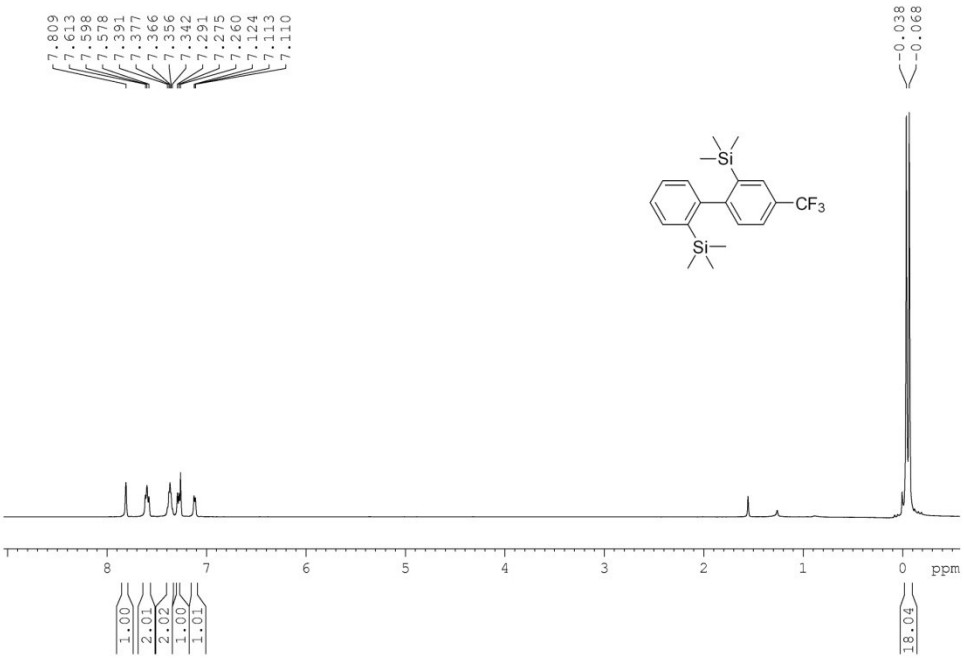


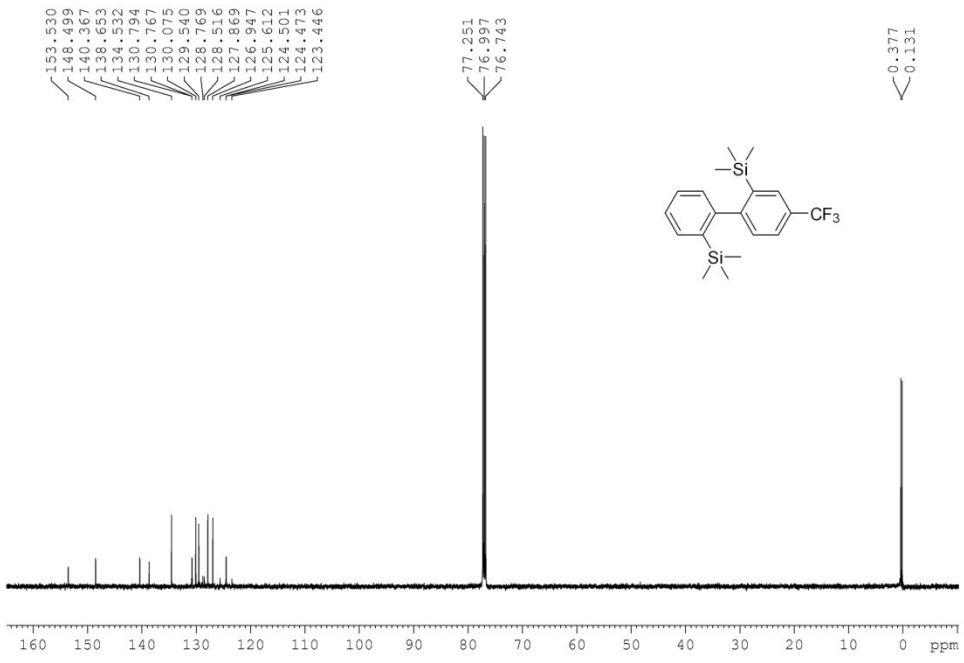
(4-chloro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (9a)



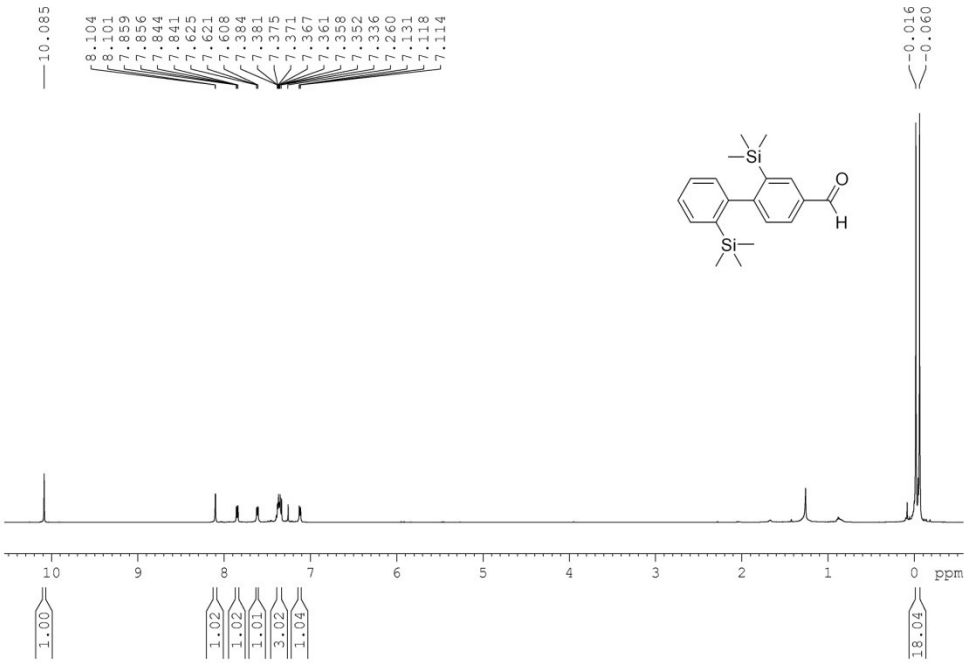


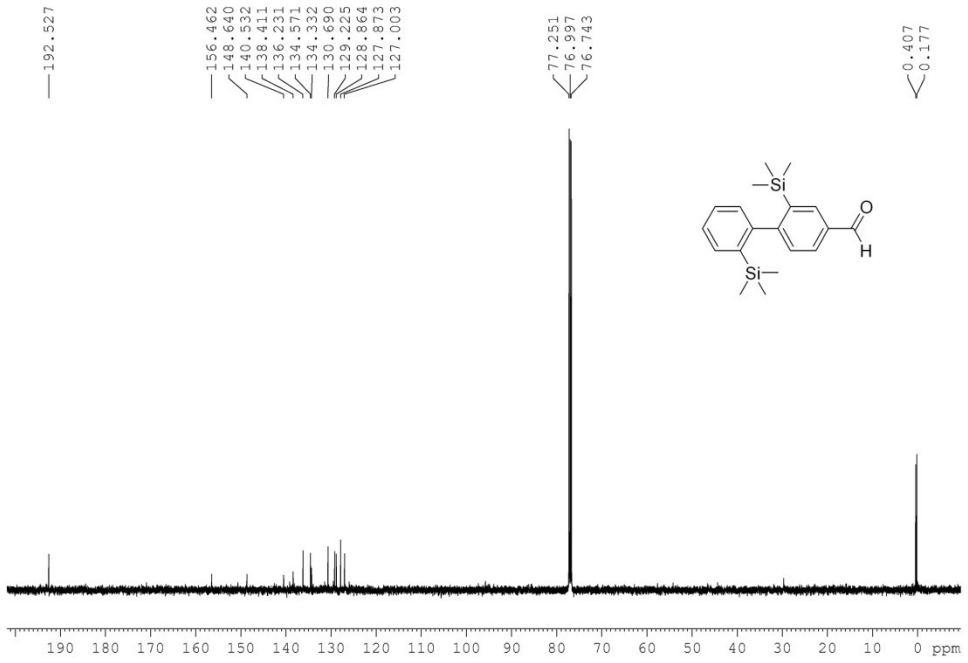
(4-(trifluoromethyl)-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (10a)



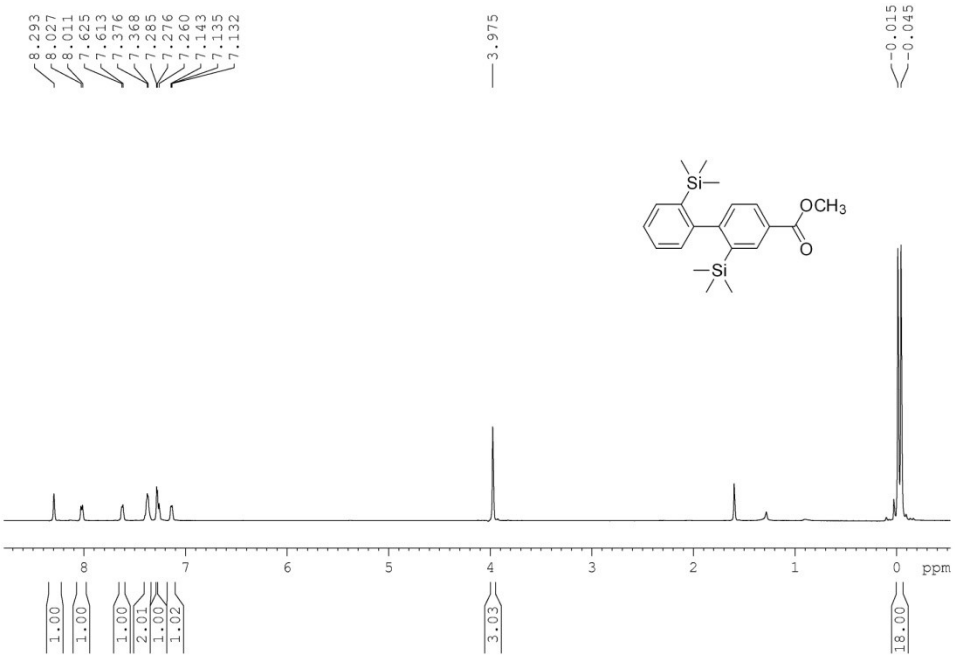


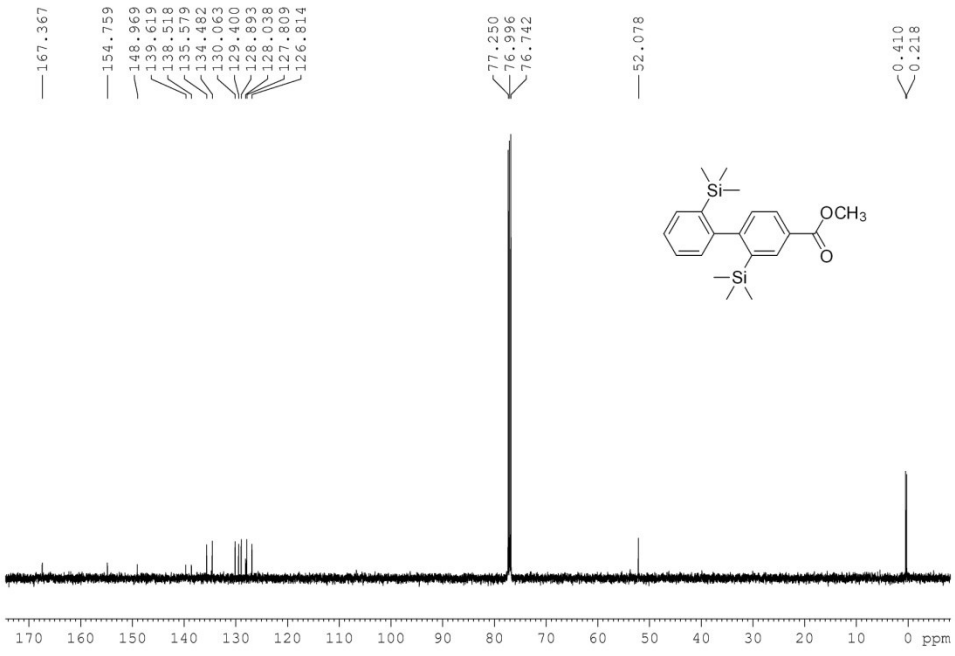
2,2'-bis(trimethylsilyl)-[1,1'-biphenyl]-4-carbaldehyde (11a)



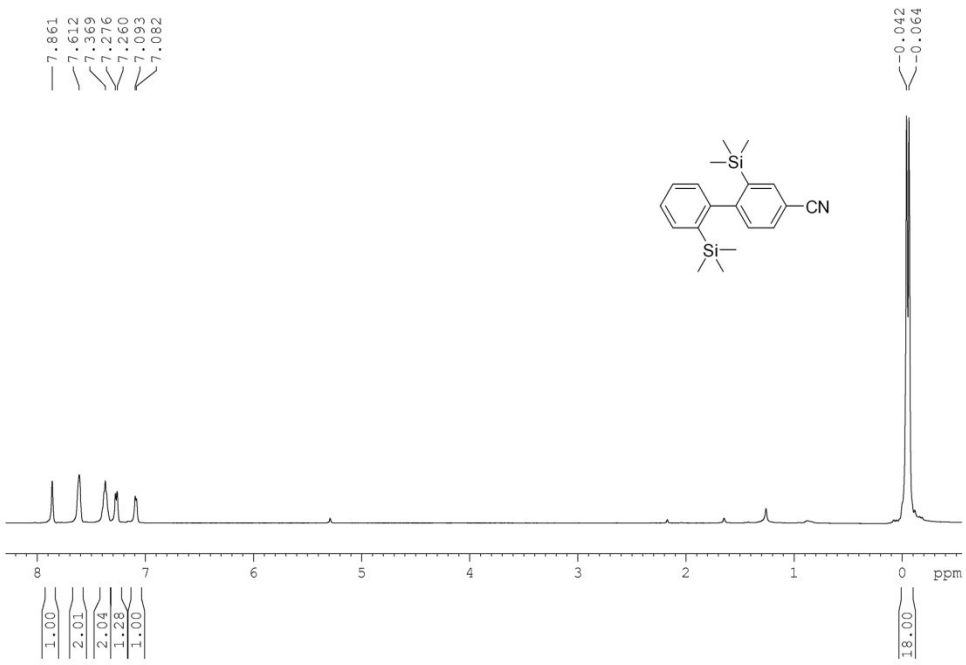


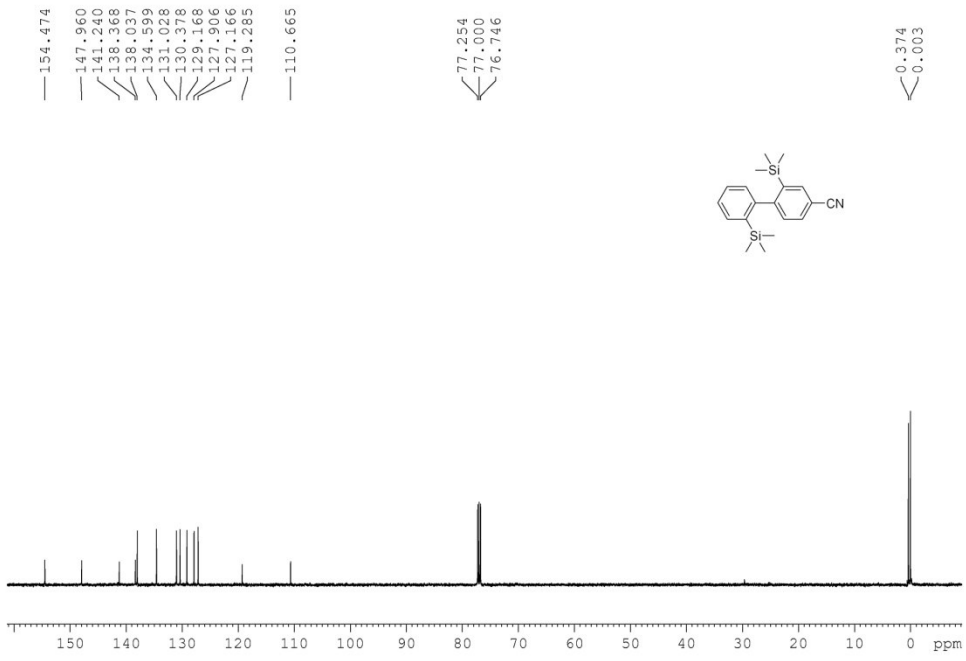
methyl 2,2'-bis(trimethylsilyl)-[1,1'-biphenyl]-4-carboxylate (12a)



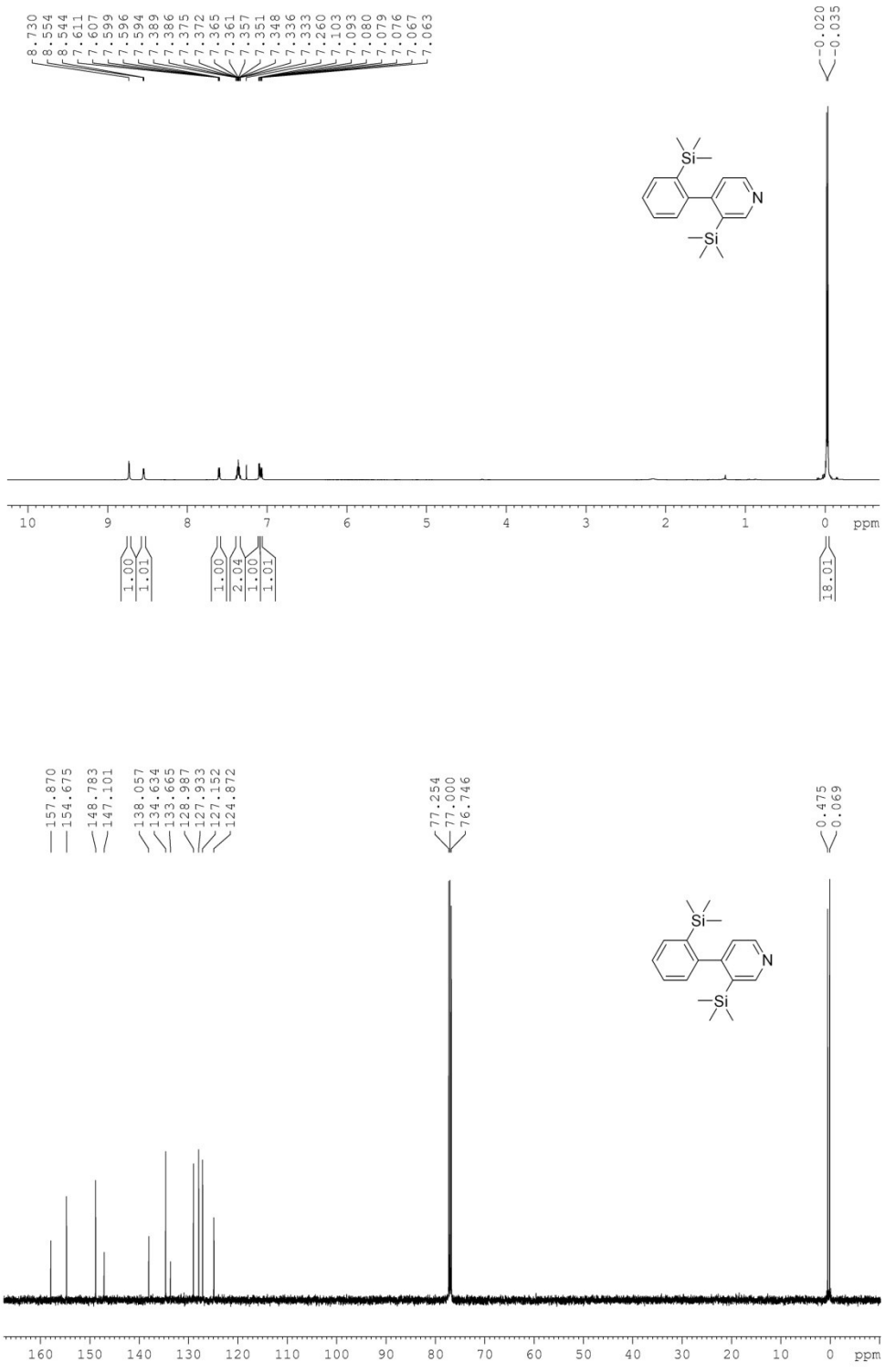


2,2'-bis(trimethylsilyl)-[1,1'-biphenyl]-4-carbonitrile (13a)

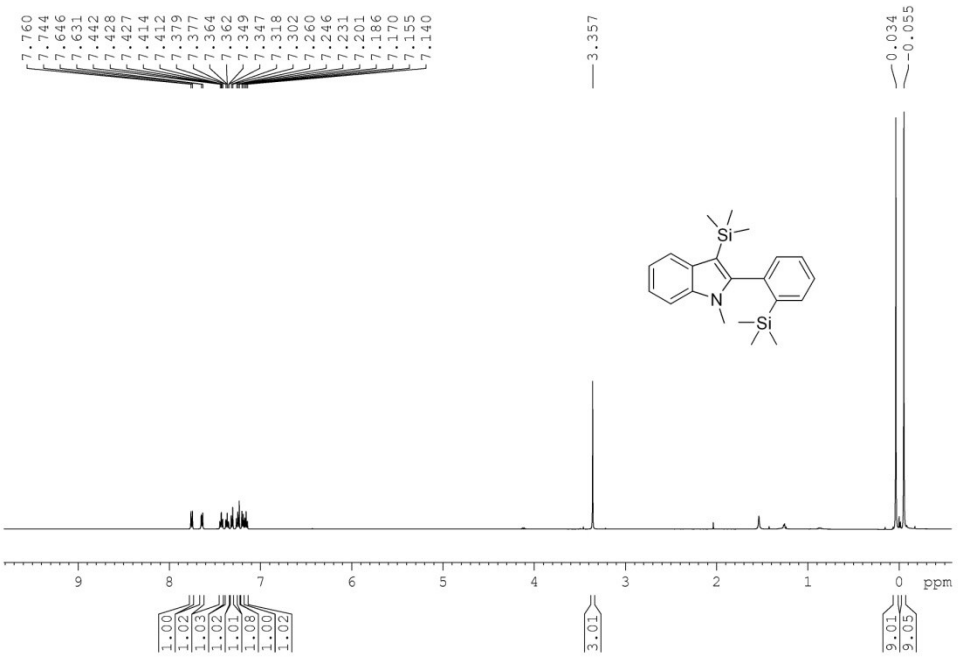


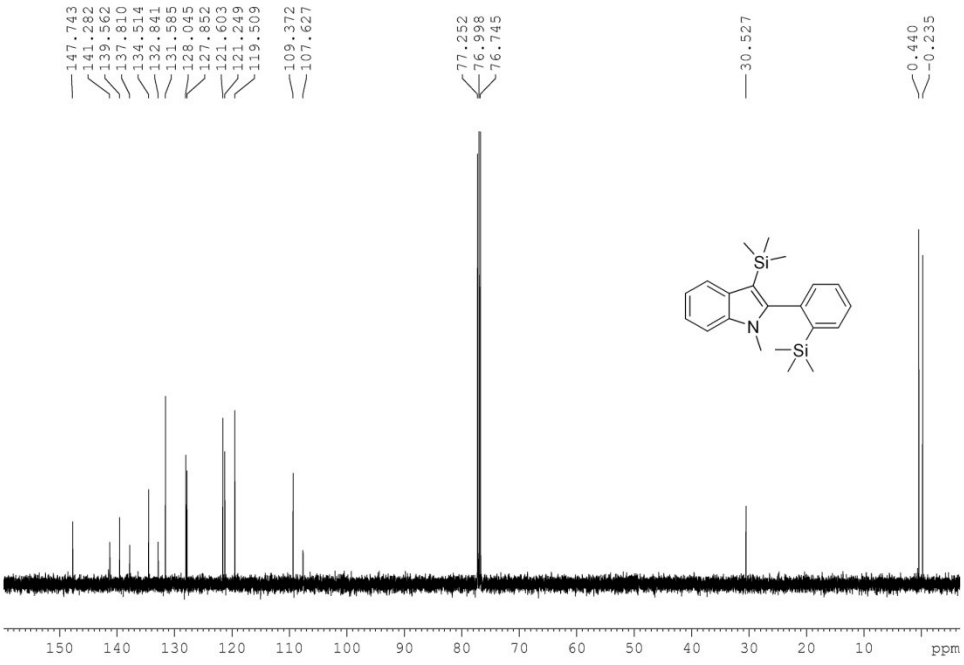


3-(trimethylsilyl)-4-(2-(trimethylsilyl)phenyl)pyridine (14a)

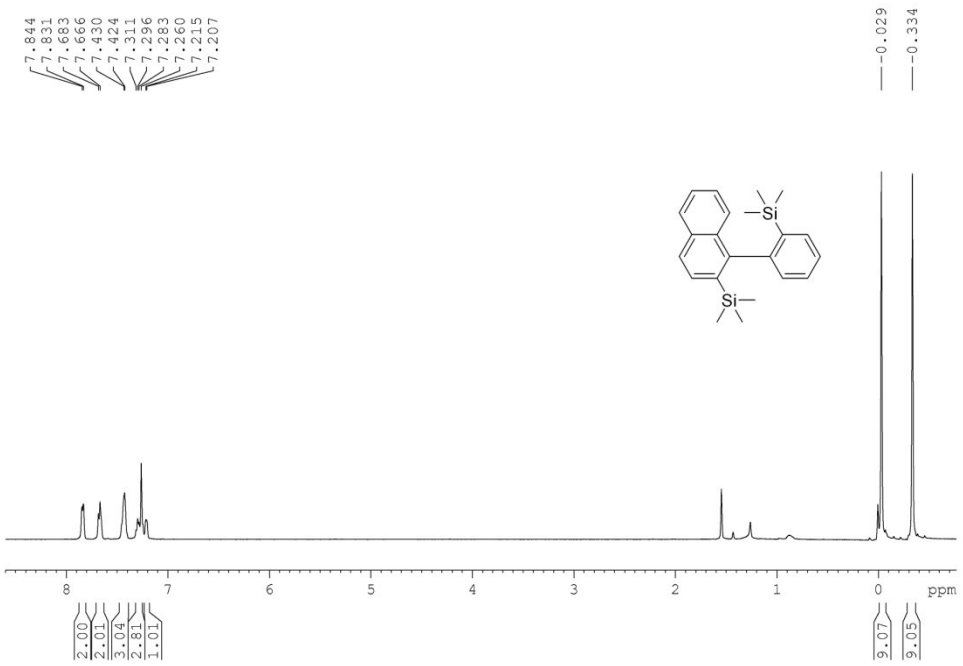


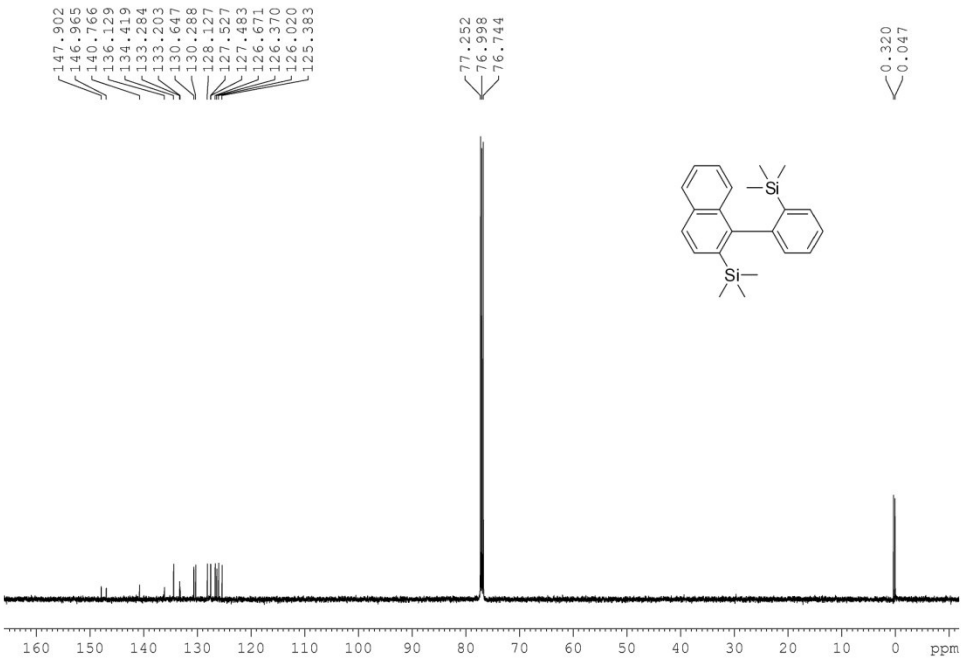
1-methyl-3-(trimethylsilyl)-2-(2-(trimethylsilyl)phenyl)-1H-indole (15a)



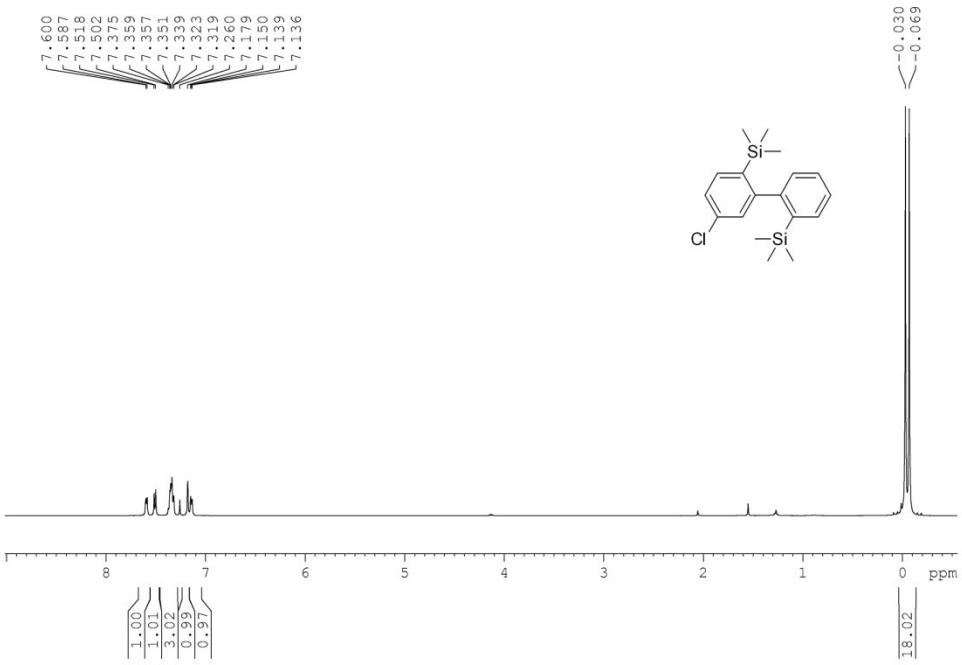


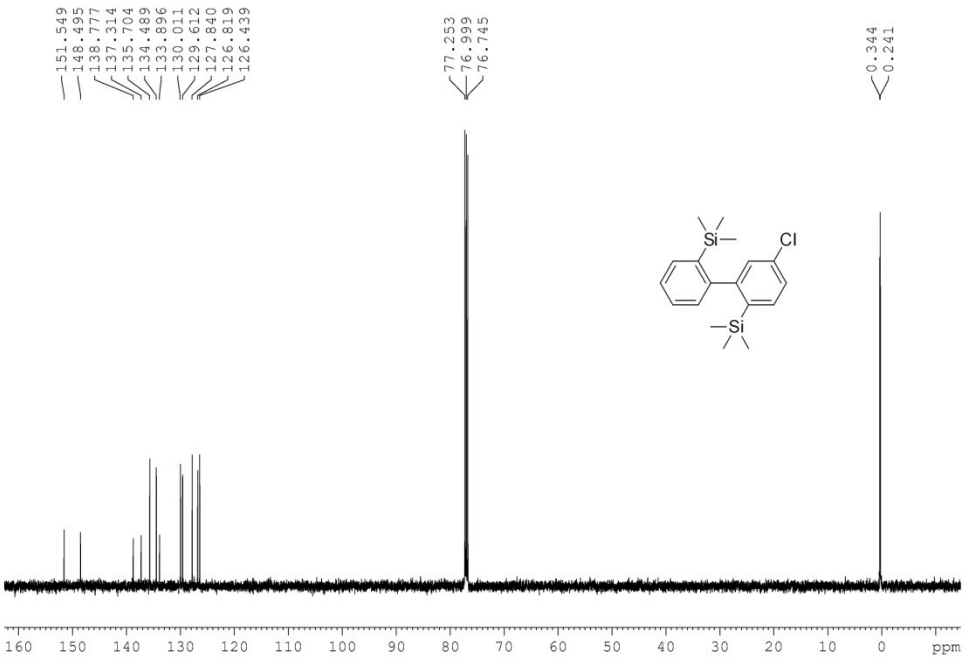
trimethyl(2-(2-(trimethylsilyl)naphthalen-1-yl)phenyl)silane (16a)



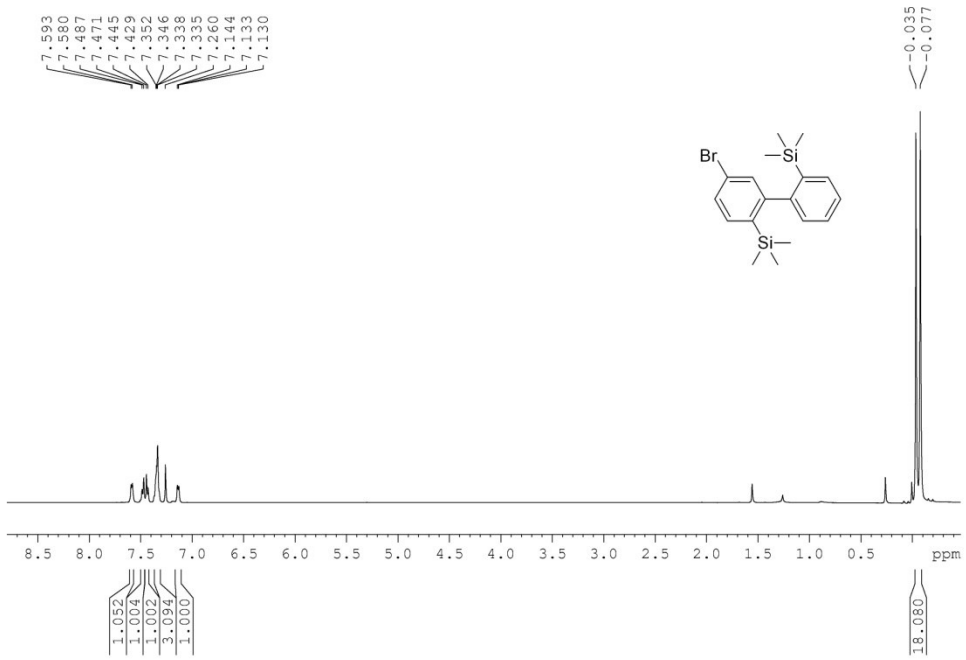


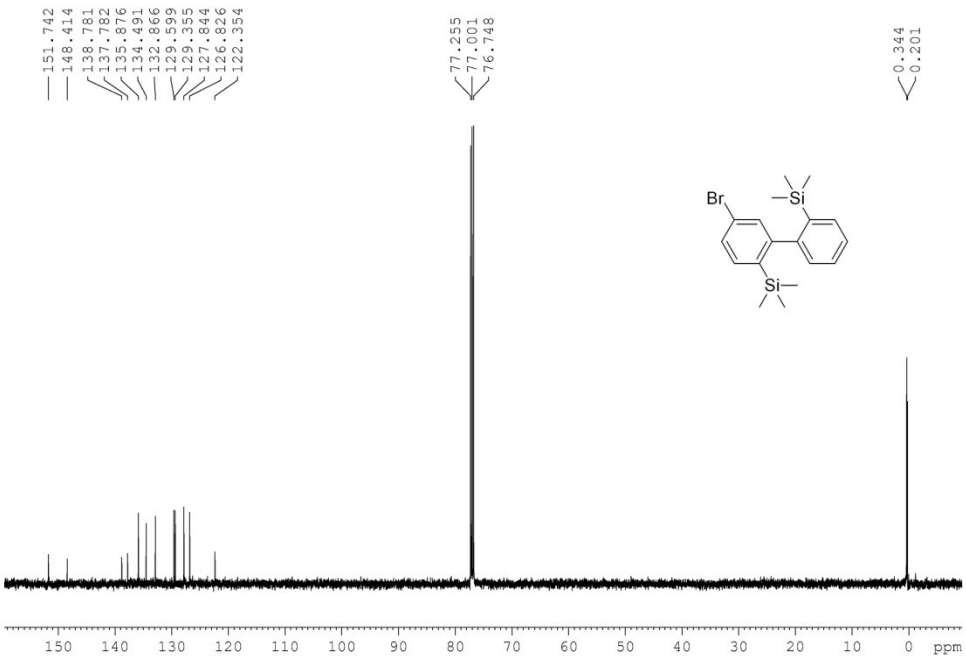
(5-chloro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (22a)



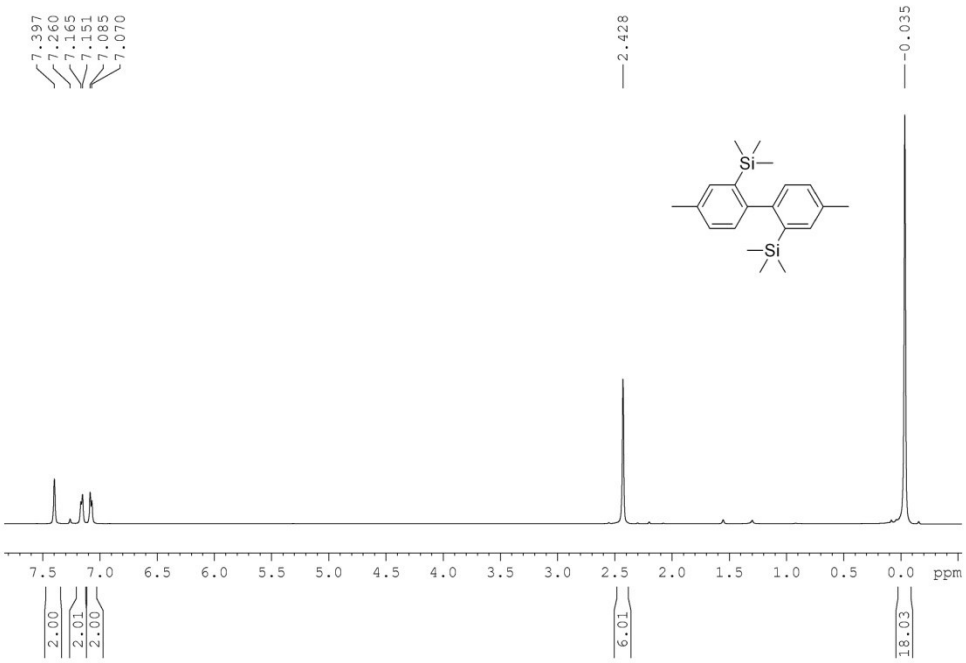


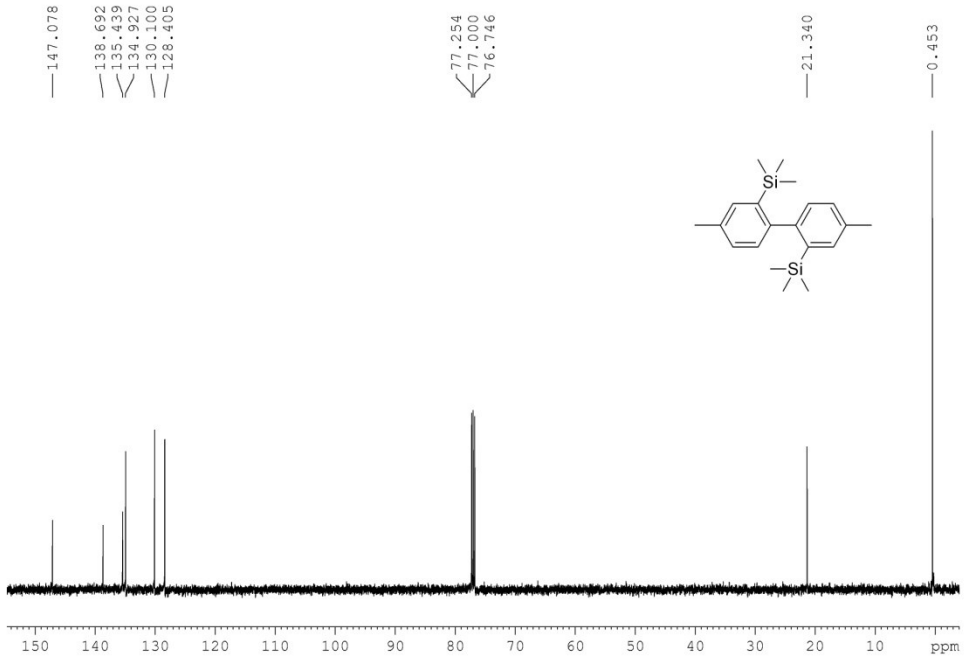
(5-bromo-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (23a)



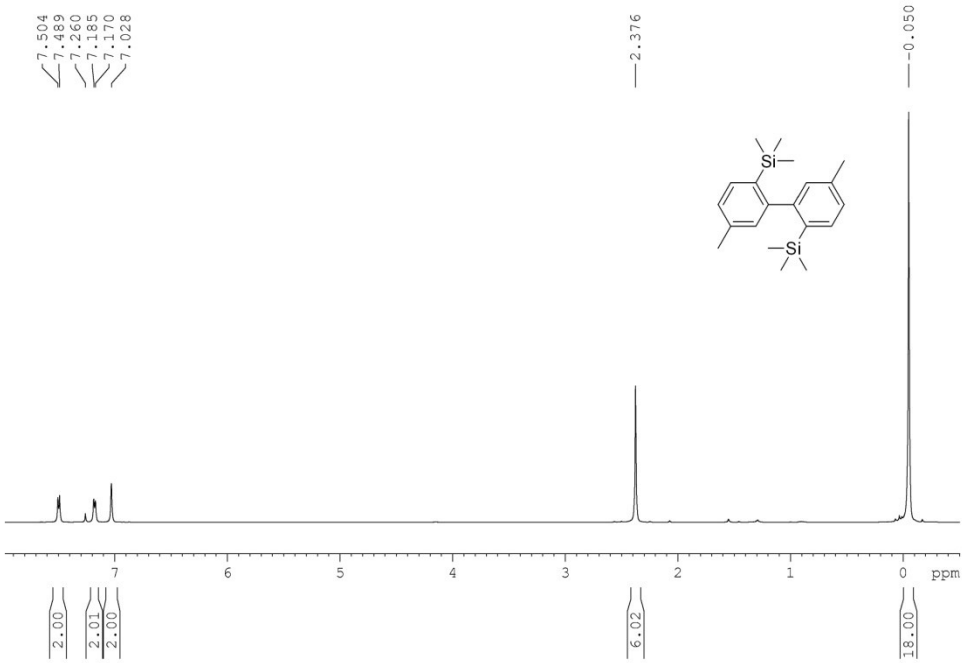


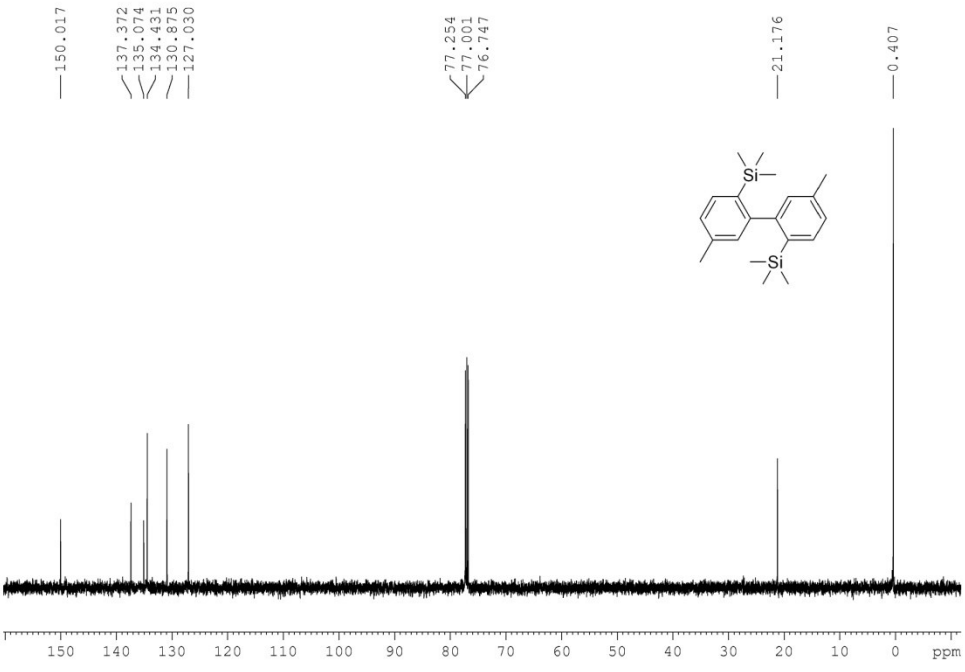
(4,4'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (25a)



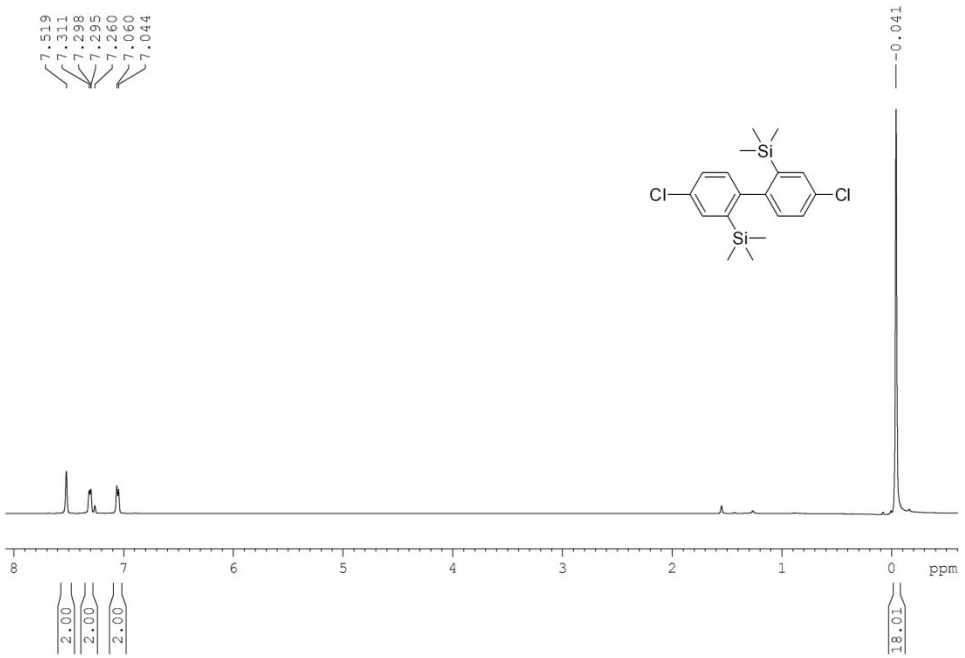


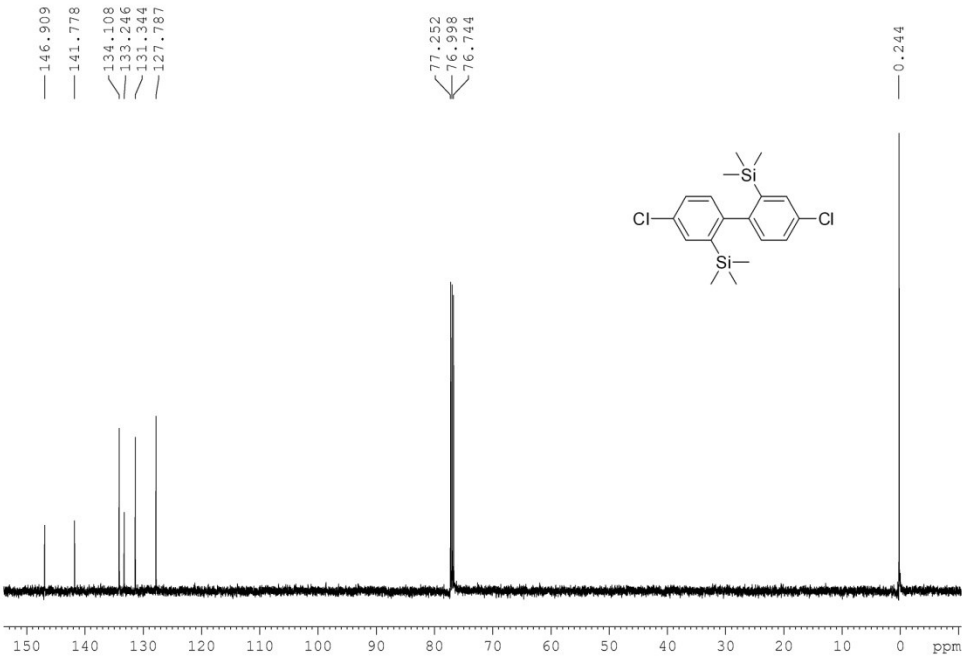
(5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (26a)



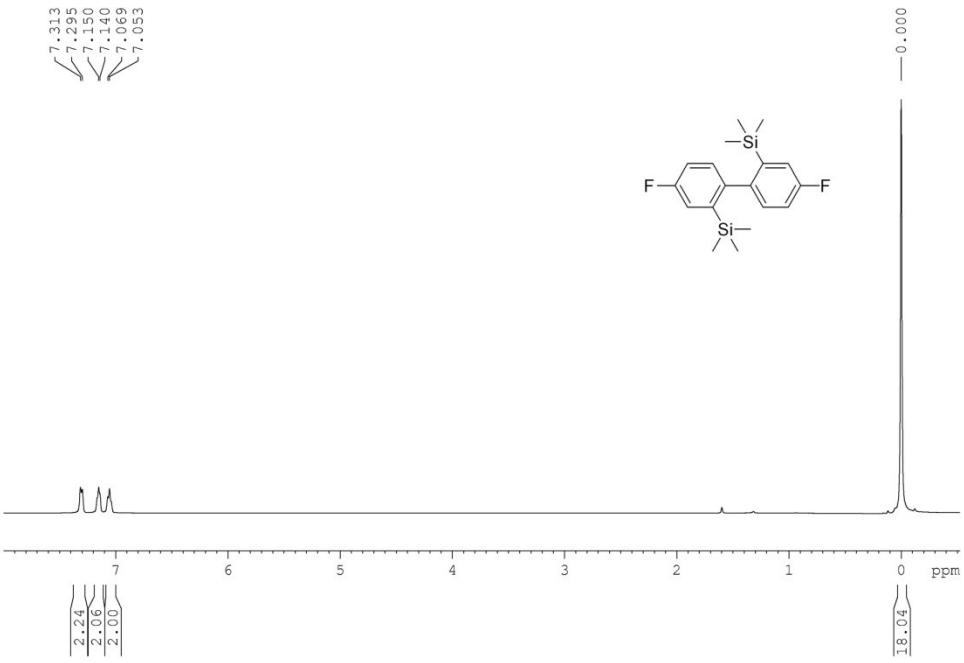


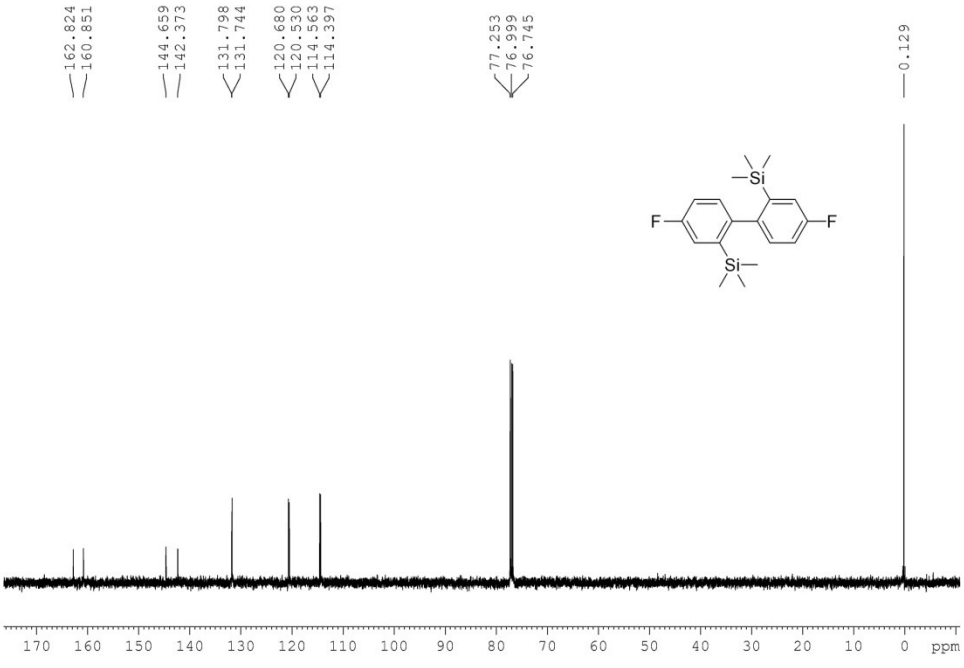
(4,4'-dichloro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (27a)



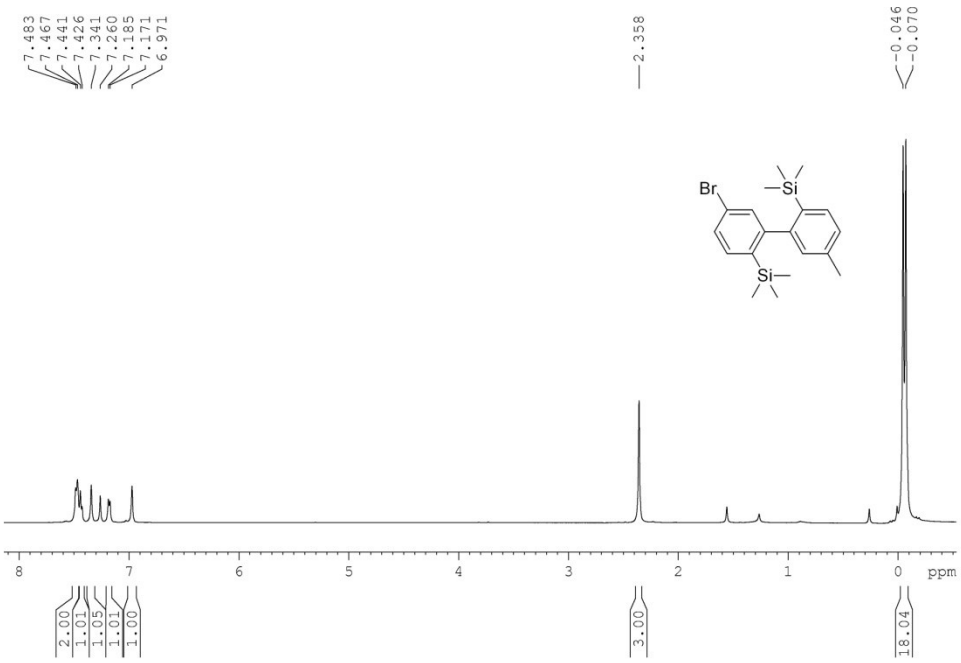


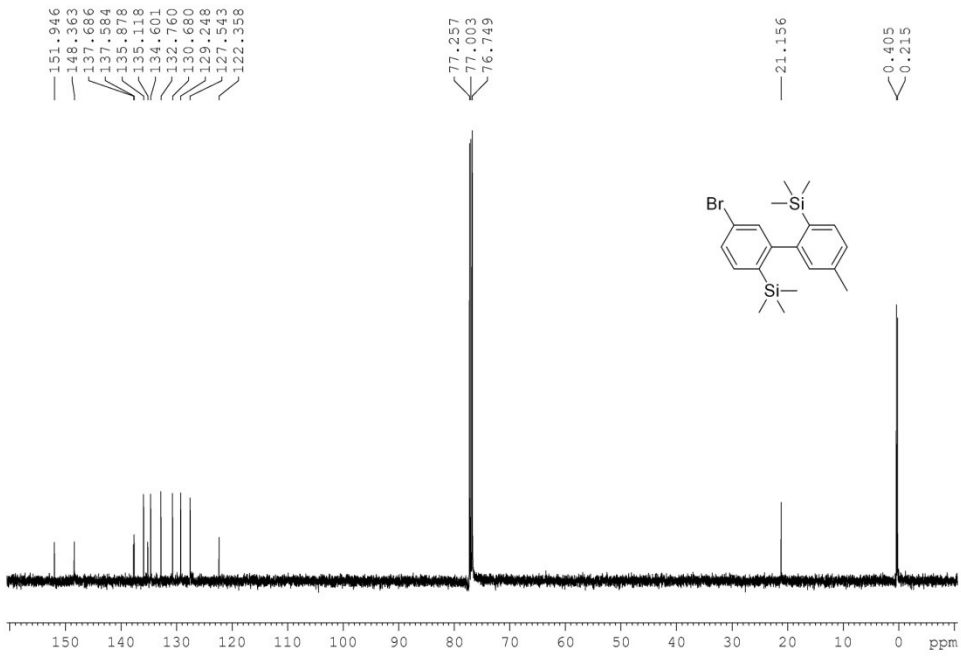
(4,4'-difluoro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (28a)



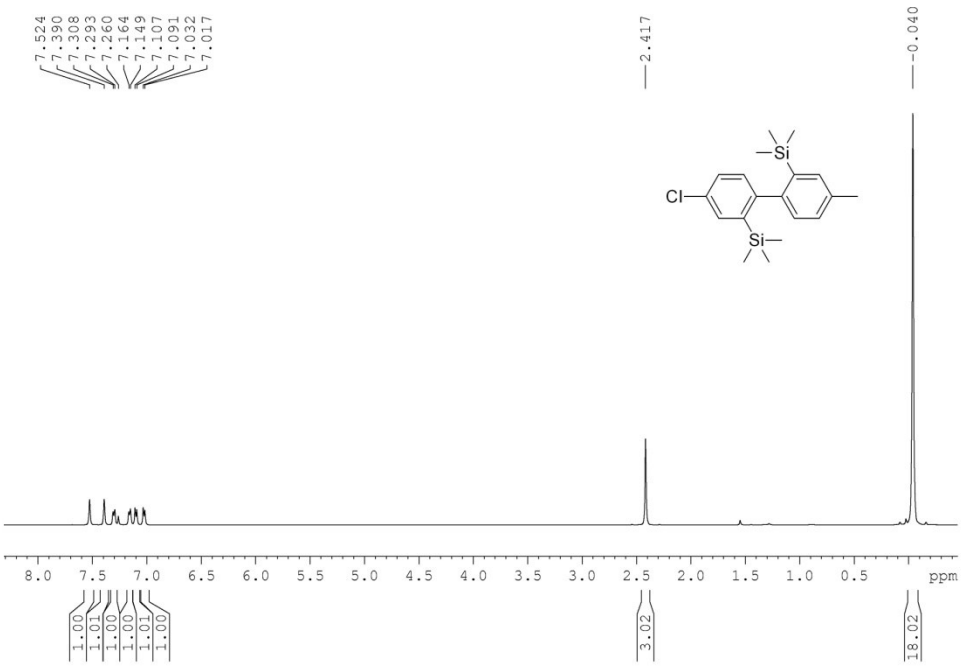


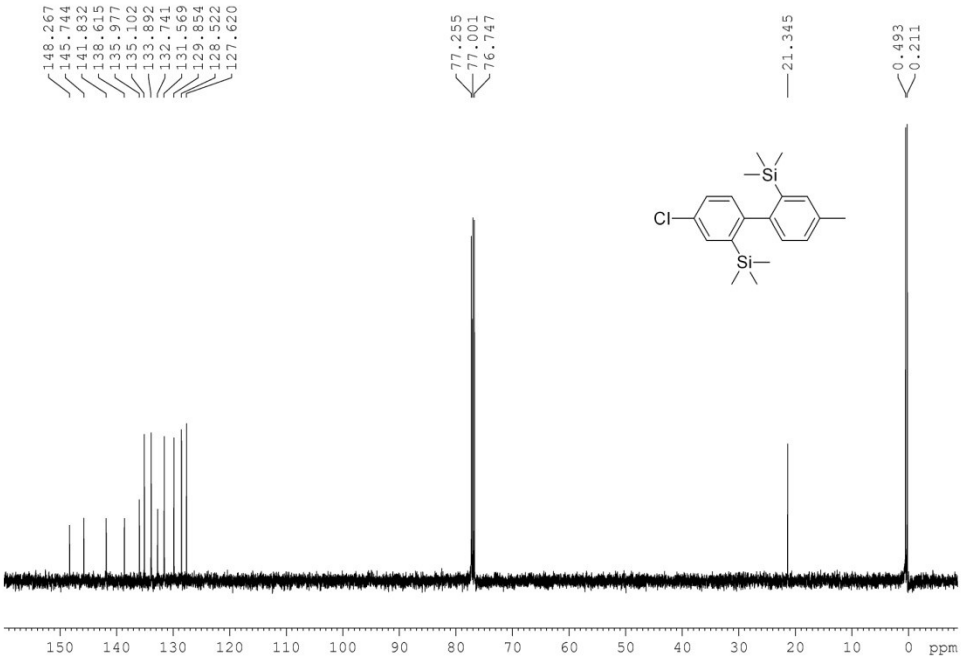
(5-bromo-5'-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (29a)



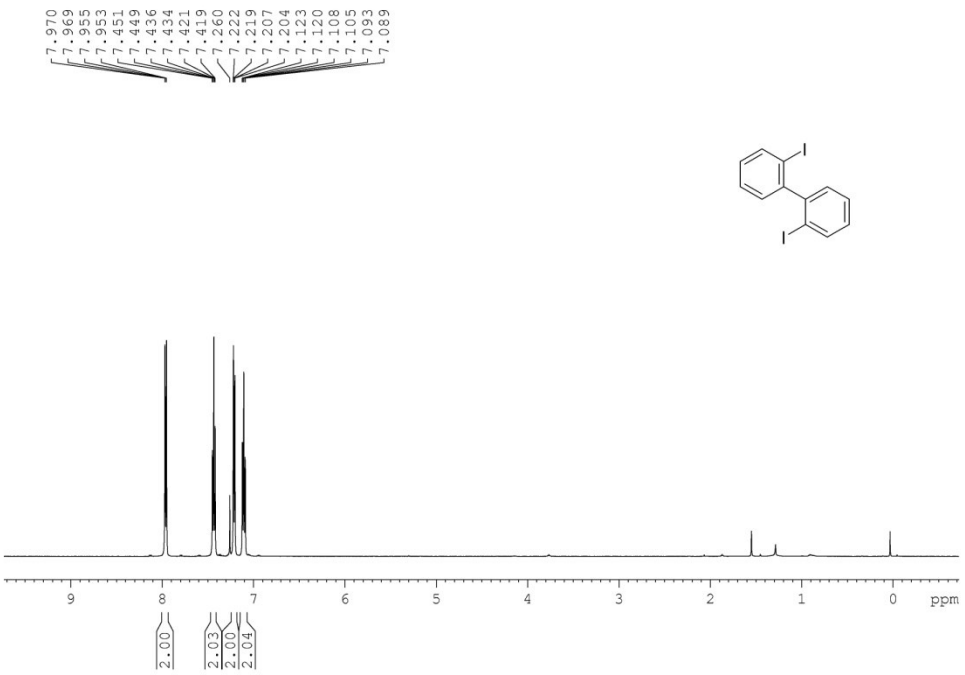


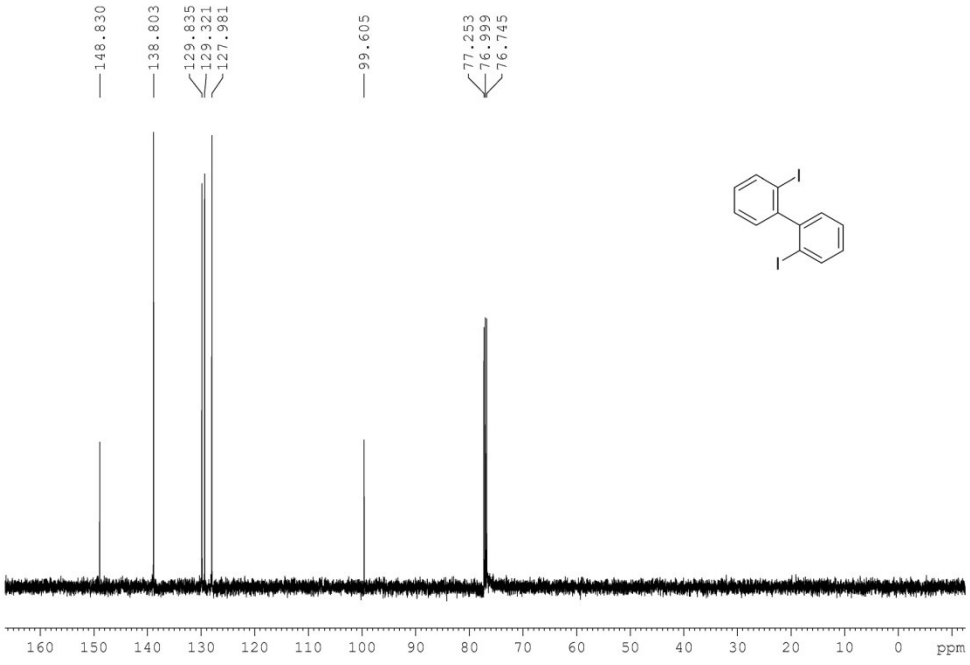
(4-chloro-4'-methyl-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (30a)



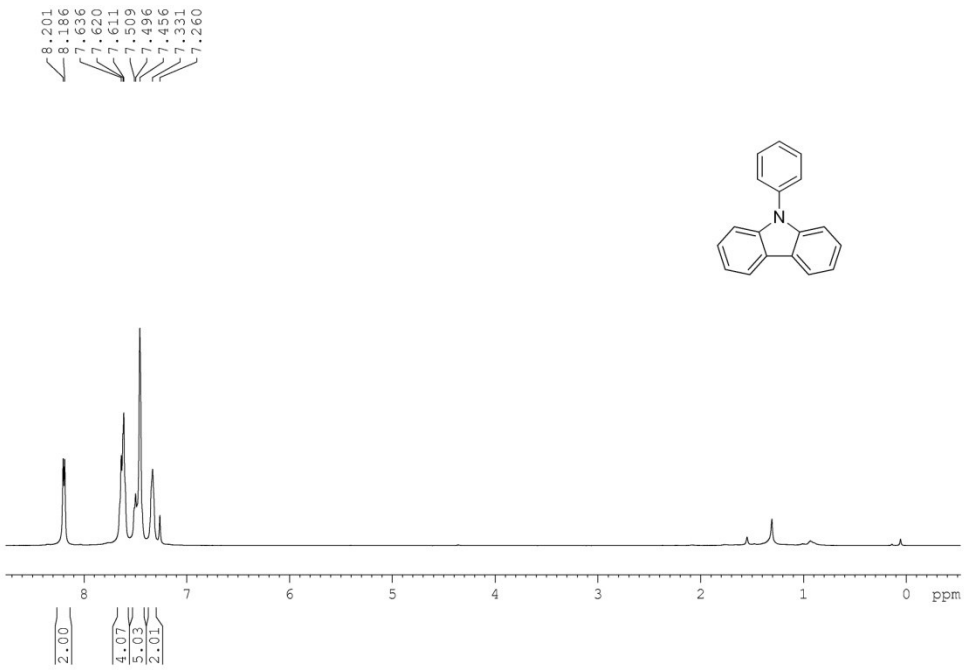


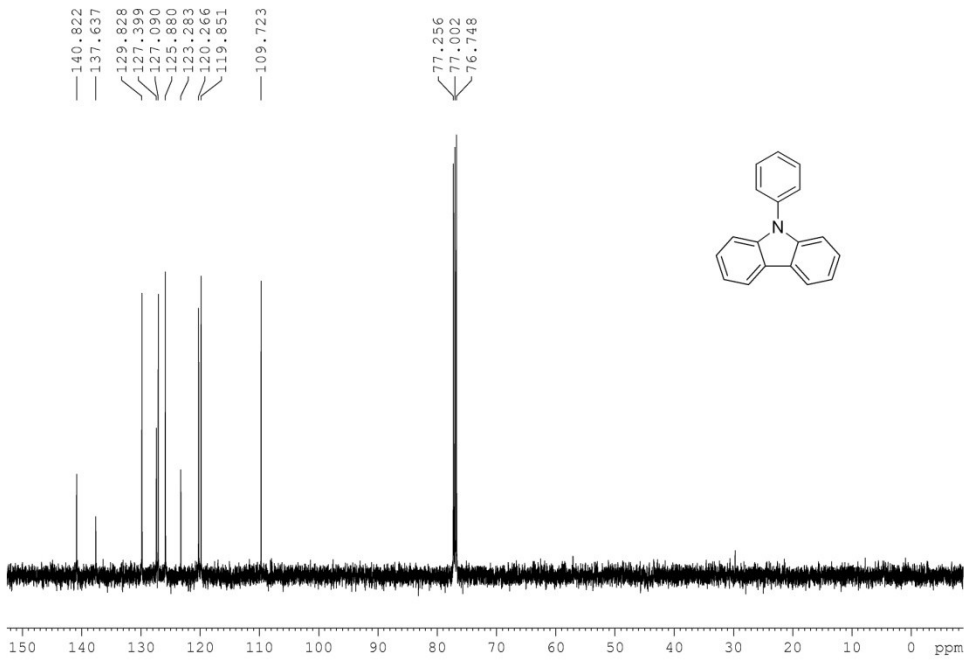
2,2'-diiodo-1,1'-biphenyl (1b)



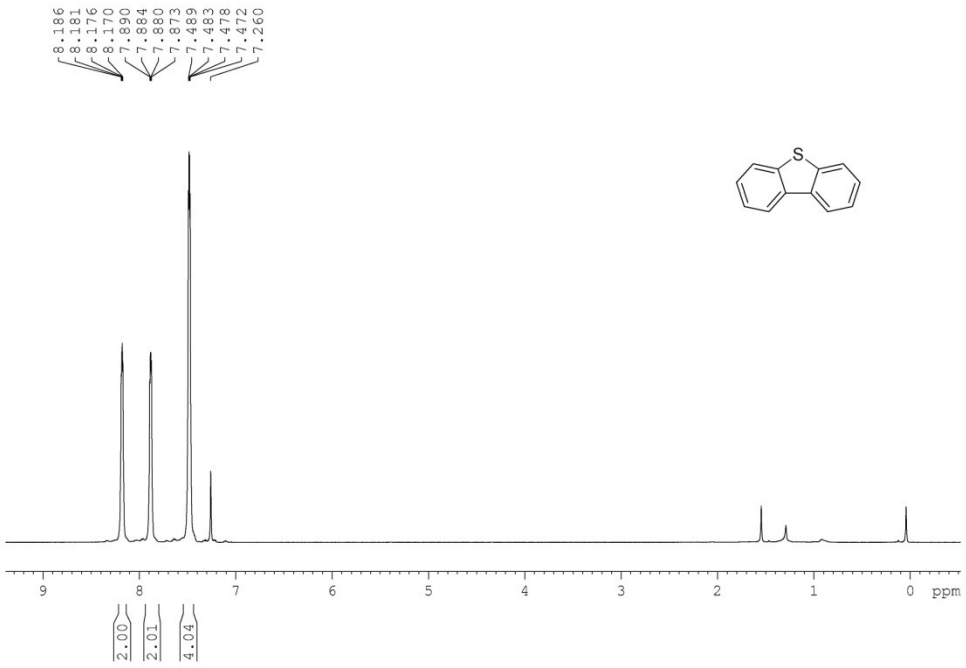


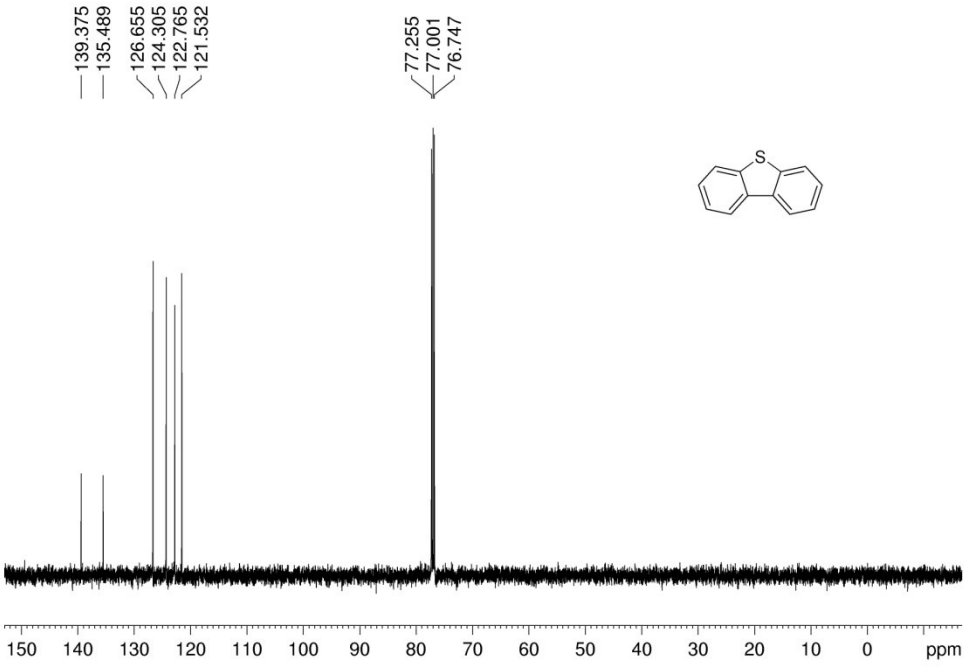
9-phenyl-9H-carbazole (1c)



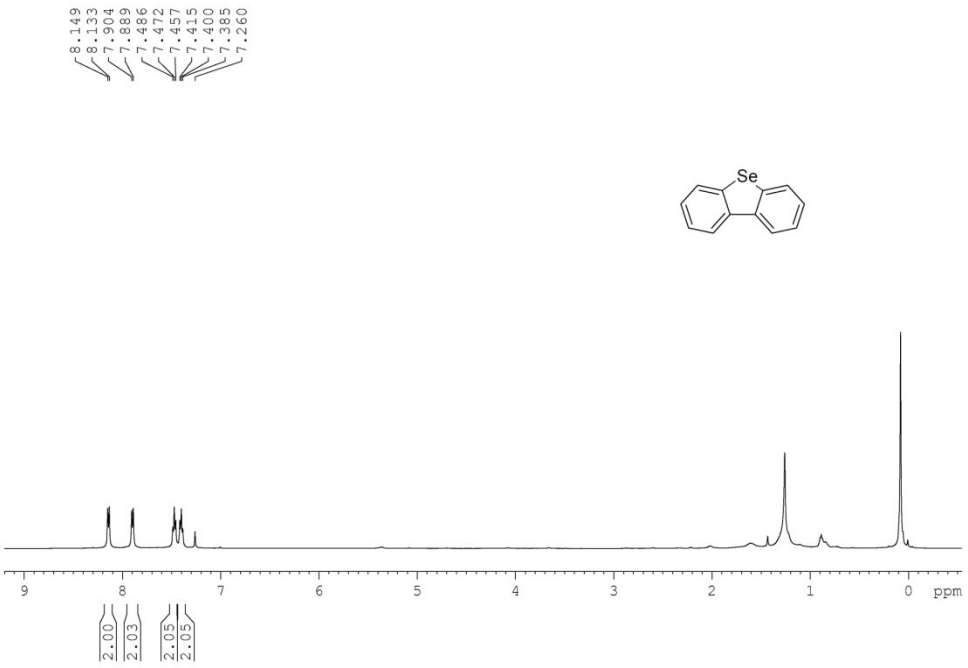


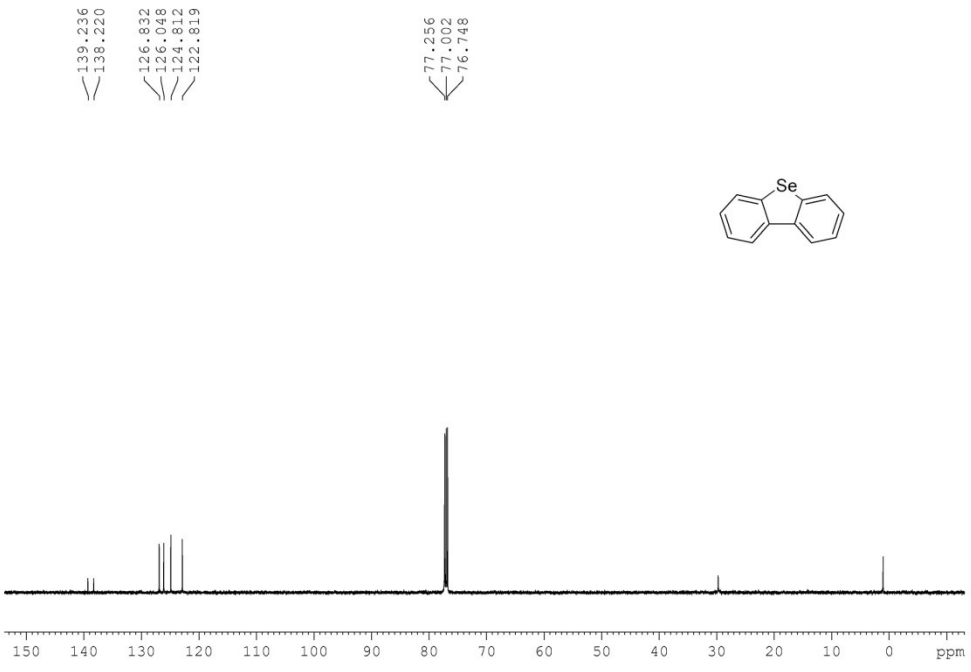
dibenzo[b,d]thiophene (1d)





dibenzo[b,d]selenophene (1e)


8.149
8.133
7.904
7.889
7.486
7.472
7.457
7.415
7.400
7.385
7.260
Se
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.03
2.05
2.05


139.236
138.220
126.832
126.048
124.812
122.819
77.256
77.002
76.748
Se
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

8) The X-ray single-crystal diffraction analysis of 30a (CCDC: 1824773)

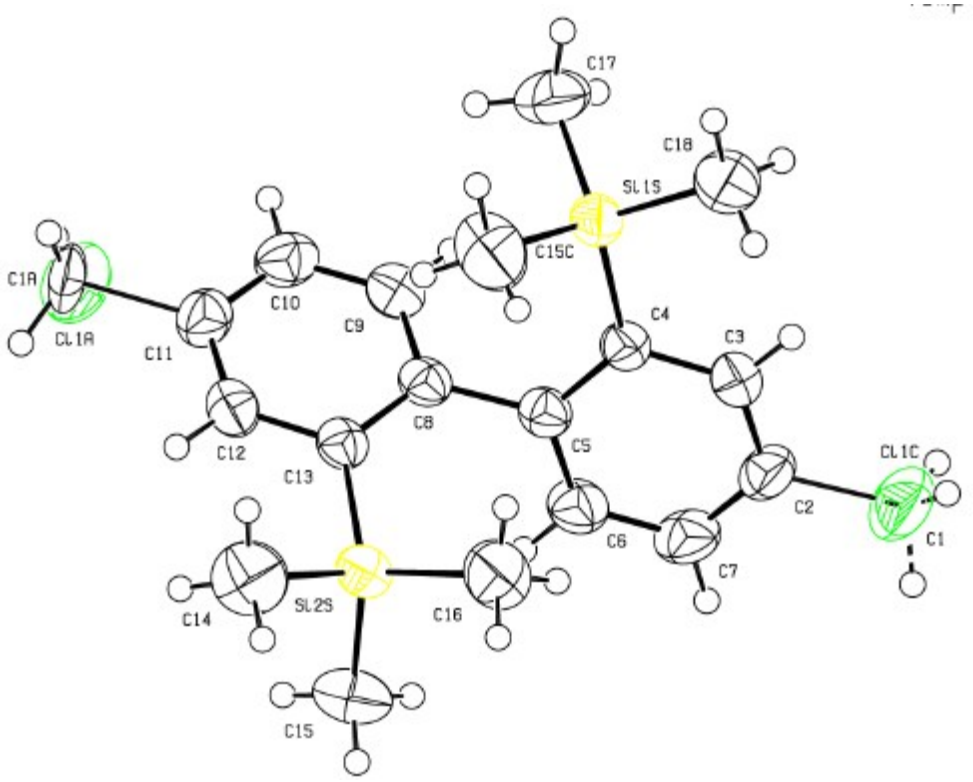


Table 2 Crystal data and structure refinement for exp_319.

Bond precision: C-C = 0.0030 A		Wavelength=0.71073
Cell: a=9.9960(5)	b=13.4663(7)	c=15.1960(8)
alpha=90	beta=96.428(5)	gamma=90
Temperature: 293 K		
Calculated		Reported
Volume	2032.66 (18)	2032.67 (17)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C_{19} H_{27} Cl Si_2	C_{19} H_{27} Cl Si_2
Sum formula	C_{19} H_{27} Cl Si_2	C_{19} H_{27} Cl Si_2
Mr	347.04	347.03
Dx,g cm^{-3}	1.134	1.134
Z	4	4
Mu (mm^{-1})	0.302	0.302
F000	744.0	744.0
F000’	745.42	
h,k,lmax	12,16,18	12,16,18

Nref	4010	3996
Tmin,Tmax	0.913,0.913	0.610,1.000
Tmin’	0.913	

Correction method= # Reported T Limits: Tmin= 0.610 Tmax= 1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 26.022

R(reflections)= 0.0452(3186) wR2(reflections)= 0.1206(3996)

S = 1.034 Npar= 226