Supporting Information

for

Synthesis and Properties of Chromophore-Functionalized Monovinylsilsesquioxane Derivatives

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1. General methods and reagents

The chemicals were purchased from the following sources: dichloromethane (DCM), tetrahydrofuran (THF), n-hexane, chloroform-d, chloroform, ethanol, methanol, acetone, toluene, ethyl acetate, calcium hydride, potassium carbonate (K_2CO_3), 4-bromobenzotrifluoride, 4-bromostyrene (97%), iodobenzene, 4-vinylphenylboronic acid (95%), 5-bromo-2-thienylboronic acid (95%) 4-bromo-1-naphthaleneboronic acid (95%), (98%), trichlorovinylsilane (97%), tetrakis(triphenylphosphine)palladium(0), triethylamine, 9,10-dibromoantracene, molecular sieves type 4Å, silica gel 60 Å and Celite® from Aldrich, pyrene-1-boronic acid (95%), 9-phenanthracenylboronic acid (95%) from Fluorochem, Grubbs 1st Gen Catalyst from Apeiron Synthesis, trisilanolisobutyl POSS® from Hybrid Plastics. Monovinylsubstituted silsesquioxane ($iBu_7Si_8O_8Vi$) was prepared according to the literature procedure.[1]

All reactions were carried out under argon atmosphere using standard Schlenk-line and vacuum techniques. THF was dried with sodium benzophenone ketyl and freshly distilled before use. Trichlorovinylsilane and triethylamine were purified by trap-to-trap distillation. Toluene and hexane were purified by a mBraun MB SPS 800 purification system Ethanol and DCM were dried prior to use over CaH_2. Dichloromethane was additionally passed through a column with alumina and after that, it was degassed by repeated freeze-pump-thaw cycles. DCM, toluene, and ethanol were stored under argon over molecular sieves type 4Å.

2. Instruments and measurement

Nuclear magnetic resonance (NMR) spectroscopy: ^{1}H NMR (300 MHz and 400 MHz), ^{13}C NMR (75 MHz and 100 MHz) and ^{29}Si NMR (79 MHz) spectra were recorded at 25˚C on Brucker Ultra Shield 600, 400 and 300 MHz spectrometers in $CDCl_3$ solution. Chemical shifts are reported in ppm with reference to the residual solvent ($CDCl_3$) peaks for ^{1}H and ^{13}C NMR and to TMS for ^{29}Si NMR.

Thin-layer chromatography (TLC): TLC was conducted on plates coated with 250 mm thick silica gel and column chromatography was performed on silica gel 60 (70-230 mesh) using a mixture of *n*-hexane/DCM.

Matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS): Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF-MS) mass spectra were recorded on an UltrafleXtreme mass spectrometer (Bruker Daltonics), equipped with a SmartBeam II laser (355 nm) in 500-4000 m/z range. 2,5-Dihydroxybenzoic acid (DHB, Bruker Daltonics, Bremen, Germany) served as matrix and was prepared in TA30 solvent (30:70 v/v acetonitrile: 0.1% TFA in water) at 20 mg/mL concentration. Studied samples were dissolved in dichloromethane (2 mg/mL) and then mixed in a ratio 1:1 v/v with a matrix solution. Matrix/sample mixtures (1 µL) were spotted onto the MALDI target and air-dried. Mass spectra were measured in reflection mode. The data were analyzed using the software provided with the Ultraflex instrument - FlexAnalysis (version 3.4). Mass calibration (cubic calibration based on five to seven points) was performed using external standards (Peptide Calibration Standard).

Photophysical properties: Absorption spectra were measured at room temperature using a Cary 100 UV-vis spectrophotometer. Fluorescence spectra of oxygen-free samples were recorded at room temperature using a Perkin-Elmer LS 50B spectrofluorometer. The fluorescence lifetimes of argon-saturated samples were measured at room temperature on a

Fluorescence Lifetime Spectrometer FluoTime 300 from PicoQuant with a time-correlated single-photon counting detection system (TCSPC) using 255 nm and 300 nm diodes as excitation sources.

Thermogravimetric Analyses (TGA) were performed using a TGA/DSC 1 Mettler-Toledo thermal gravimetric analyzer. The measurements were conducted in a nitrogen atmosphere (flow of 60 mL/min), from ambient temperature to 1000°C at the heating rate of 10°C/min. The temperature of initial degradation ($T_{5\%}$) was taken as the onset temperature at which 5 wt% of mass loss occurs.

Elemental analyses were performed using a Vario EL III instrument.

3. General procedure for synthesis of olefins by Suzuki-Miyaura coupling

Iodoarene with bromoarylboronic acid (for **B 4 and B 5**), arylboronic acid with bromostyrene (for **OL 1 and OL 2**) and bromoarene/dibromoarene with 4-vinylphenylboronic (for **OL 3, OL 4, OL 5 and OL 6**) were placed under argon in a Schlenk reactor equipped with a magnetic stirring bar. Then toluene, ethanol, THF (for **B 4 and B 5**) $Pd(PPh_3)_4$ and K_2CO_3 were added. The reaction mixture was stirred and heated in an oil bath at 85 °C for 3-6 hours. The reaction progress was monitored by TLC and GCMS analysis. After the reaction, the crude reaction mixture was extracted with water and ethyl acetate. The organic phase mixture was left over magnesium sulfate for a few hours. After that the final products were filtered off very quickly by a flash column system (glass filter G4, silica gel, Celite®) connected to a membrane pump. The solvent was evaporated and then the product was purified by precipitation in *n*-hexane and dried under a high vacuum.

1-(4-vinylphenyl)pyrene – OL 1

Briefly, 400 mg (1.63 mmol) of pyrene-1-boronic acid and 0.214 ml (1.63 mmol) of 4-bromostyrene were placed in a Schlenk reactor equipped with a magnetic stirring bar. The substrates were evacuated and then toluene (10 ml), ethanol (3 ml), $Pd(PPh_3)_4$ (18.8 mg, 0.0163 mmol) and K_2CO_3 (4.8 ml of 2M solution) were added. Reaction time was 4 h. The product was isolated as described above. Finally, 455 mg (92%) of product was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.25 – 8.16 (m, 4H, C*H*), 8.10 (s, 2H, C*H*), 8.06 – 7.97 (m, 3H, C*H*), 7.63 (s, 4H, C*H*), 6.88 (dd, 1H, J_{HH} = 17.6, 10.9 Hz, =C*H*-), 5.90 (dd, 1H, J_{HH} = 17.6, 0.9 Hz, CH_2), 5.37 (dd, 1H, J_{HH} = 10.9, 0.9 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 140.86, 137.50, 136.70, 131.63, 131.12, 130.94, 130.76, 128.61, 127.90, 127.64, 127.59, 126.39, 126.17, 125.38, 125.27, 125.13, 125.05, 124.99, 124.81, 114.30.

9-(4-vinylphenyl)phenanthrene – OL 2

Briefly, 600 mg (2.7 mmol) of 9-phenanthracenylboronic acid and 0.353 ml (2.7 mmol) of 4-bromostyrene were placed in a Schlenk reactor equipped with a magnetic stirring bar. The substrates were evacuated and then toluene (16 ml), ethanol (5 ml), $Pd(PPh_3)_4$ (31.15 mg, 0.027 mmol) and K_2CO_3 (8 ml of 2M solution) were added. Reaction time was 3 h. The product was isolated as described above. Finally, 710 mg (90%) of product was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.81 – 8.71 (m, 2H, C*H*), 7.98 – 7.89 (m, 2H, C*H*), 7.72 – 7.51 (m, 9H, C*H*), 6.86 (dd, 1H, J_{HH} = 17.6, 10.9 Hz, =C*H*-), 5.88 (d, 1H, J_{HH} = 17.6 Hz, CH_2), 5.35 (d, 1H, J_{HH} = 10.8 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 140.46, 138.56,

136.84, 136.68, 131.68, 131.18, 130.78, 130.40, 130.10, 128.81, 127.58, 127.00, 126.75, 126.66, 126.62, 126.30, 123.06, 122.67, 114.21.

4-(trifluoromethyl)-4'-vinyl-1,1'-biphenyl – OL 3

Briefly, 760 mg (3.38 mmol) of 4-bromobenzotrifluoride and 500 mg (3.38 mmol) of 4-vinylphenylboronic acid were placed in a Schlenk reactor equipped with a magnetic stirring bar. The substrates were evacuated and then toluene (20.3 ml), ethanol (6.8 ml), $Pd(PPh_3)_4$ (39 mg, 0.0338 mmol) and K_2CO_3 (10 ml of 2M solution) were added. Reaction time was 3 h. The product was isolated as described above. Finally, 755 mg (90%) of product was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.70 (s, 4H, C*H*), 7.63 – 7.47 (m, 4H, C*H*), 6.77 (dd, J_{HH} = 17.6, 10.9 Hz, =C*H*-), 5.82 (dd, 1H, J_{HH} = 17.6, 0.9 Hz, CH_2), 5.32 (dd, 1H, J_{HH} = 10.9, 0.9 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.38, 139.16, 137.68, 136.30, 127.53, 127.34, 126.98, 125.91, 125.86, 122.64, 114.74.

2-bromo-5-phenylthiophene - B 4

Briefly, 500 mg (2.45 mmol) of iodobenzene and 532 mg (2.45 mmol) of 5-bromo-2-thienylboronic acid were placed in a Schlenk reactor equipped with a magnetic stirring bar. The substrates were evacuated and then toluene (14.7 ml), ethanol (4.9 ml), $Pd(PPh_3)_4$ (28 mg, 0.0245 mmol) and K_2CO_3 (7.35 ml of 2M solution) were added. Reaction time was 4 h. The product was isolated as described above. Finally, 540 mg (92%) of product was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.52 (d, 2H, J_{HH} = 7.2 Hz, C*H*), 7.38 (t, 2H, J_{HH} = 7.3 Hz, C*H*), 7.31 (m, 1H, C*H*), 7.04 (q, 2H, J_{HH} = 3.9 Hz, C*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 146.02, 133.79, 130.97, 129.16, 128.03, 125.76, 123.37, 111.53

2-phenyl-5-(4-vinylphenyl)thiophene – OL 4

Briefly, 350 mg (1.46 mmol) of 2-bromo-5-phenylthiophene and 227 mg (1.46 mmol) of 4-vinylphenylboronic acid were placed in a Schlenk reactor equipped with a magnetic stirring bar. The substrates were evacuated and then toluene 8.8 (ml), ethanol (2.9 ml), THF (4.4 ml), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) and K_2CO_3 (4.4 ml of 2M solution) were added. Reaction time was 4 h. The product was isolated as described above. Finally, 364 mg (95%) of product was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.71 – 7.52 (m, 5H, C*H*), 7.49 – 7.35 (m, 4H, C*H*), 7.31 (s, 2H, C*H*), 6.73 (dd, 1H, J_{HH} = 17.5, 10.8 Hz, =C*H*-), 5.78 (d, 1H, J_{HH} = 17.6 Hz, CH_2), 5.27 (d, 1H, J_{HH} = 10.9 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 143.44, 136.92, 136.40, 134.42, 133.86, 132.32, 129.07, 128.60, 127.68, 126.90, 125.79, 124.20, 124.13, 114.07.

1-bromo-4-phenylnaphthalene – B 5

Briefly, 500 mg (2.45 mmol) of iodobenzene and 627 mg (2.5 mmol) of 4-bromo-1-naphthaleneboronic acid were placed in a Schlenk reactor equipped with a magnetic stirring bar. The substrates were evacuated and then toluene (14.7 ml), ethanol (4.9 ml), $Pd(PPh_3)_4$ (28 mg, 0.0245 mmol) and K_2CO_3 (7.35 ml of 2M solution) were added. Reaction time was 3 h. The product was isolated as described above. Finally, 650 mg (92%) of product was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.31 (dd, 1H, J_{HH} = 8.6, 1.3 Hz, C*H*), 7.90 – 7.79 (m, 2H, C*H*), 7.62 – 7.55 (m, 1H, C*H*), 7.50 – 7.41 (m, 6H, C*H*), 7.25 – 7.21 (m, 1H, C*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 140.54, 140.08, 133.05, 132.22, 130.13, 129.61, 129.18, 128.50, 128.37, 127.69, 127.60, 127.34, 126.91, 126.81, 122.44.

1-phenyl-4-(4-vinylphenyl)naphthalene – OL 5

Briefly, 400 mg (1.4 mmol) of 1-bromo-4-phenylnaphthalene and 215 mg (1.45 mmol) of 4-vinylphenylboronic acid were placed in a Schlenk reactor equipped with a magnetic stirring bar. The substrates were evacuated and then toluene (8.5 ml), ethanol (2.8 ml), THF (5 ml), $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) and K_2CO_3 (4,2 ml of 2M solution) were added. Reaction time was 3 h. The product was isolated as described above. Finally, 410 mg (95%) of product was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.19 – 7.93 (m, 2H, C*H*), 7.63 – 7.49 (m, 8H, C*H*), 7.51 – 7.41 (m, 5H, C*H*), 6.85 (dd, 1H, J_{HH} = 17.6, 10.9 Hz, =C*H*-), 5.88 (d, 1H, J_{HH} = 17.7 Hz, CH_2), 5.35 (d, 1H, J_{HH} = 10.9 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 140.94, 140.48, 140.04, 139.60, 136.75, 136.67, 132.09, 132.00, 130.49, 130.28, 129.18, 128.44, 128.37, 127.43, 126.61, 126.57, 126.52, 126.48, 126.31, 126.02, 125.44, 114.20.

9, 10-bis(4-vinylphenyl)anthracene – OL 6

Briefly, 342.7 mg (1.02 mmol) of 9,10-dibromoantracene and 302 mg (2.03 mmol) of 4-vinylphenylboronic acid were placed in a Schlenk reactor equipped with a magnetic stirring bar. The substrates were evacuated and then toluene (12.5 ml), ethanol (4.1 ml), $Pd(PPh_3)_4$ (23 mg, 0.0203 mmol) and K_2CO_3 (7.4 ml of 2M solution) were added. Reaction time was 6 h. The product was isolated as described above. Finally, 374mg (96%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 (dd, 4H, J_{HH} = 6.8, 3.3 Hz, C*H*), 7.67 (d, 4H, J_{HH} = 8.1 Hz, C*H*), 7.45 (d, 4H, J_{HH} = 8.1 Hz, C*H*), 7.34 (dd, 4H, J_{HH} = 6.9, 3.3 Hz, C*H*), 6.91 (dd, 2H, J_{HH} = 17.6, 10.9 Hz, C*H*=CH_2), 5.93 (d, 2H, J_{HH} = 17.6 Hz, CH=CH_2), 5.39 (d, 2H, J_{HH} = 10.9 Hz, CH=CH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 138.74, 136.97, 136.89, 136.76, 131.69, 129.98, 127.07, 126.41 125.06, 114.33.

4. General procedure for synthesis of functionalized silsesquioxanes

Chromophore and monovinylsilsesquioxane were placed under argon in a 5 ml reactor connected to vacuum line and equipped with a magnetic stirring bar. 3 ml of dry dichloromethane was added to the reactor and the mixture was placed in an oil-bath in 45 °C. After heating the mixture, first generation Grubbs catalyst was added and the reaction was stirred under reflux for 24 hours. After this time, solvent was evaporated and 3 ml of methanol was added to remains. Precipitate was filtered, dissolved in minimum amount of dichloromethane and purified by column chromatography (Silica Gel, hexane/DCM 9:1). Evaporation of solvent gave analytically pure product which was characterized by ^{1}H, ^{13}C, ^{29}Si NMR and mass spectrometry.

Heptaisobutyl{2-[4-{1-pyrene}phenyl]ethenyl}octasilsesquioxane – P 1

Briefly, 54.8 mg (0.18 mmol) of 1-(4-vinylphenyl)pyrene, 150 mg (0.18 mmol) of monovinylsilsesquioxane and 3 ml of dichloromethane were placed in 5 ml reactor and heated to 45 °C. 1.5 mg (0.0018 mmol) of Grubbs catalyst was added. After 24 hours the reaction was cooled down and the product was purified as described above. 190 mg (94% yield) of analytically pure product was obtained as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.26 – 8.15 (m, 4H, C*H*), 8.11 (s, 2H, C*H*), 8.06 – 7.96 (m, 3H, C*H*), 7.64 (s, 4H, C*H*), 7.32 (d, 1H, J_{HH} = 19.1 Hz, =C*H*), 6.28 (d, 1H, J_{HH} = 19.1 Hz, =C*H*Si), 2.01 – 1.81 (m, 7H, C*H*$(CH_3)_2$), 1.00 (t, 42H, J_{HH} = 6.8 Hz, CH(C*H*$_3)_2$), 0.67 (dd, 14H, J_{HH} = 16.00, 7.0 Hz, C*H*$_2$CH); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 137.37, 136.80, 131.64, 130.98, 130.83, 128.61, 127.71, 127.65, 127.62, 127.56, 126.97, 126.92, 126.20, 125.32, 125.13, 125.05, 125.03, 124.82, 119.15, 25.91, 25.89, 25.87, 24.08, 24.04, 22.70, 22.65; ^{29}Si NMR (119 MHz, $CDCl_3$) δ (ppm): -67.37, -67.80, -79.88 (=CH*Si*);

MALDI-ToF MS: Calcd. for $C_{52}H_{81}O_{12}Si_8$: m/z 1121.3877 [M + H^+]. Found: 1121.4083;

EA: Anal. calcd for $C_{52}H_{81}O_{12}Si_8$ (%):C, 55.77, H, 7.02; found: C, 55.79, H, 7.03.

Heptaisobutyl{2-[4-{9-phenanthrene}phenyl]ethenyl}octasilsesquioxane – P2

Briefly, 50.5 mg (0.18 mmol) of 9-(4-vinylphenyl)phenanthrene, 150 mg (0.18 mmol) of monovinylsilsesquioxane and 3 ml of dichloromethane were placed in 5 ml reactor and heated to 45 °C. 1.5 mg (0.0018 mmol) of Grubbs catalyst was added. After 24 hours the reaction was cooled down and the product was purified as described above. 191 mg (97% yield) of analytically pure product was obtained as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.02 – 7.93 (m, 2H, C*H*), 7.62 – 7.52 (m, 7H, C*H*), 7.49 – 7.42 (m, 5H, C*H* + =C*H*), 6.24 (d, 1H, J_{HH} = 19.1 Hz, =C*H*Si), 1.99 – 1.81 (m, 7H, C*H*$(CH_3)_2$), 0.99 (t, 42H, J_{HH} = 6.4 Hz, CH(C*H*$_3)_2$), 0.66 (dd, 14H, J_{HH} = 14.5, 7.0 Hz, C*H*$_2$CH); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 147.78, 141.38, 140.92, 140.15, 139.50, 136.86, 132.10, 131.97, 130.53, 130.28, 128.46, 127.46, 126.90, 126.62, 126.54, 126.44, 126.08, 126.06, 119.05, 25.91, 25.89, 25.87, 24.08, 24.04, 22.70, 22.65; ^{29}Si NMR (119 MHz, $CDCl_3$) δ (ppm): -67.38, -67.81, -79.88 (=CH*Si*);

MALDI-ToF MS: Calcd. for $C_{50}H_{78}Na^+O_{12}Si_8$: m/z 1117.3540 [M + Na^+]. Found: 1117.3915;

EA: Anal. calcd for $C_{50}H_{78}O_{12}Si_8$ (%):C, 54.80, H, 7.17; found: C, 54.83, H, 7.19.

Heptaisobutyl{2-[4-(trifluoromethyl)-1,1'-bipheny]ethenyl}octasilsesquioxane – P3

Briefly, 44.1 mg (0.18 mmol) of 4-(trifluoromethyl)-4'-vinyl-1,1'-biphenyl, 150 mg (0.18 mmol) of monovinylsilsesquioxane and 3 ml of dichloromethane were placed in 5 ml reactor and heated to 45 °C. 1.5 mg (0.0018 mmol) of Grubbs catalyst was added. After 24 hours reaction was cooled down and the product was purified as described above. 176 mg (92% yield) of analytically pure product was obtained as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.70 (s, 4H, C*H*), 7.57 (q, 4H, J_{HH} = 8.3 Hz, C*H*), 7.19 (s, 1H, =C*H*), 6.21 (d, 1H, J_{HH} = 19.2 Hz, =C*HSi*), 1.95 – 1.81 (m, 7H, C*H*$(CH_3)_2$), 0.98 (dd, 42H, J_{HH} = 6.6, 3.5 Hz, CH(C*H*$_3)_2$), 0.65 (dd, 14H, J_{HH} = 12.8, 7.0 Hz, C*H*$_2$CH); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 147.31, 144.26, 139.97, 137.73, 127.57, 127.54, 127.40, 125.92, 125.89, 119.75, 25.88, 25.86, 24.05, 24.02, 22.67; ^{29}Si NMR (119 MHz, $CDCl_3$) δ (ppm): -67.38, -67.81, 80.09 (=CH*Si*);

MALDI-ToF MS: Calcd. for $C_{43}H_{73}F_3Na^+O_{12}Si_8$: m/z 1085.3100 [M + Na^+]. Found: 1085.3452;

EA: Anal. calcd for $C_{43}H_{73}F_3O_{12}Si_8$ (%):C,48.55, H, 6.92; found: C, 48.57, H, 6.93.

Heptaisobutyl{2-[4-{5-phenylthiophene}phenyl]ethenyl}octasilsesquioxane – P4
Briefly, 47.2 mg (0.18 mmol) of 2-phenyl-5-(4-vinylphenyl)thiophene, 150 mg (0.18 mmol) of monovinylsilsesquioxane and 3 ml of dichloromethane were placed in 5 ml reactor and heated to 45 °C. 1.5 mg (0.0018 mmol) of Grubbs catalyst was added. After 24 hours reaction was cooled down and the product was purified as described above. 176 mg (91% yield) of analytically pure product was obtained as yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.65 -7.58 (m, 4H, C*H*), 7.53 – 7.27 (m, 7H, C*H*), 7.18 (d, 1H, J_{HH} = 19.1 Hz, =C*H*), 6.16 (d, 1H, J_{HH} = 19.1 Hz, =C*H*Si), 1.98 – 1.82 (m, 7H, C*H*$(CH_3)_2$), 0.98 (dd, 42H, J_{HH} = 6.6, 3.7 Hz, CH(C*H*$_3)_2$), 0.65 (dd, 14H, J_{HH} = 12.9, 7.0 Hz, C*H*$_2$CH); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 147.44, 144.05, 143.29, 136.95, 134.66, 134.38, 129.08, 127.74, 127.51, 125.79, 125.77, 124.36, 124.24, 118.82, 25.88, 25.86, 24.05, 24.02, 22.68, 22.62; ^{29}Si NMR (119 MHz, $CDCl_3$) δ (ppm): -67.39, 67.82, -79.91 (=CH*Si*);
MALDI-ToF MS: Calcd. for $C_{46}H_{76}Na^{+}O_{12}SSi_8$: m/z 1099.3104 [M + Na^{+}]. Found: 1099.3544;
EA: Anal. calcd for $C_{46}H_{76}O_{12}S\,Si_8$ (%):C, 51.26, H, 7.11; found: C, 52.28, H, 7.13.

Heptaisobutyl{2-[4-{4-phenylnaphthalene}phenyl]ethenyl}octasilsesquioxane – P5
Briefly, 55.2 mg (0.18 mmol) of 1-phenyl-4-(4-vinylphenyl)naphtalene, 150 mg (0.18 mmol) of monovinylsilsesquioxane and 3 ml of dichloromethane were placed in 5 ml reactor and heated to 45 °C. 1.5 mg (0.0018 mmol) of Grubbs catalyst was added. After 24 hours reaction was cooled down and the product was purified as described above. 196 mg (97% yield) of analytically pure product was obtained as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.01 – 7.94 (m, 2H, C*H*), 7.63 – 7.43 (m, 14H, C*H* + =C*H*), 6.25 (d, 1H, J_{HH} = 19.1 Hz, =C*H*Si), 2.00 – 1.82 (m, 7H, C*H*$(CH_3)_2$), 1.00 (t, 42H, J_{HH} = 6.4, CH(C*H*$_3)_2$), 0.67 (dd, 14H, J_{HH} = 14.5, 7.0 Hz, C*H*$_2$CH); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 147.77, 141.37, 140.91, 140.14, 139.49, 136.86, 132.10, 131.96, 130.53, 130.28, 128.46, 127.45, 126.89, 126.61, 126.54, 126.43, 126.07, 126.05, 119.04, 25.91, 25.89, 25.87, 24.08, 24.04, 22.70, 22.65; ^{29}Si NMR (119 MHz, $CDCl_3$) δ (ppm): -67.38, -67.81, -79.88 (=CH*Si*);
MALDI-ToF MS: Calcd. for $C_{52}H_{80}Na^{+}O_{12}Si_8$: m/z 1143.3696 [M + Na^{+}]. Found: 1143.3927;
EA: Anal. calcd for $C_{52}H_{80}O_{12}Si_8$ (%):C, 55.67, H, 7.19; found: C, 55.68, H, 7.20.

9,10-bis{4-[2-ethenyl(heptaisobutyloctasilsesquioxane)]phenyl}anthracene – P6
Briefly, 68.9 mg (0.18 mmol) of 9,10-bis(4-vinylphenyl)anthracene, 300 mg (0.36 mmol) of monovinylsilsesquioxane and 3 ml of dichloromethane were placed in 5 ml reactor and heated to 45 °C. 1.5 mg (0.0018 mmol) of Grubbs catalyst was added. After 24 hours reaction was cooled down and the product was purified as described above. 326 mg (90% yield) of analytically pure product was obtained as pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 – 7.67 (m, 8H, C*H*), 7.47 (d, 4H, J_{HH} = 8.2 Hz, C*H*), 7.38 (s, 1H, C*H*), 7.36 – 7.32 (m, 5H, C*H* + =C*H*), 6.31 (d, 2H, J_{HH} = 19.1 Hz, =C*H*Si), 2.00 – 1.85 (m, 14H, C*H*$(CH_3)_2$), 1.08 – 0.92 (m, 84H, CH(C*H*$_3)_2$), 0.73 – 0.62 (m, 28H, C*H*$_2$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 147.83, 147.43, 140.16, 137.71, 136.90, 133.36, 131.75, 129.93, 127.88, 127.01, 126.85, 125.28, 123.62, 119.99, 119.18, 84.26, 25.92, 25.89, 24.08, 24.05, 22.67, 22.63; ^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm): -67.35, -67.79, -80.08 (=CHSi);
MALDI-ToF MS: Calcd. for $C_{86}H_{146}O_{24}Si_{16}$: m/z 2013.34330. Found: 2013.6602;
EA: Anal. calcd for $C_{86}H_{146}O_{24}Si_{16}$ (%):C, 51.30, H, 7.31; found: C, 51.32, H, 7.32.

5. NMR spectra of isolated compounds

5.1. NMR spectra of olefins

1-(4-vinylphenyl)pyrene (OL 1)

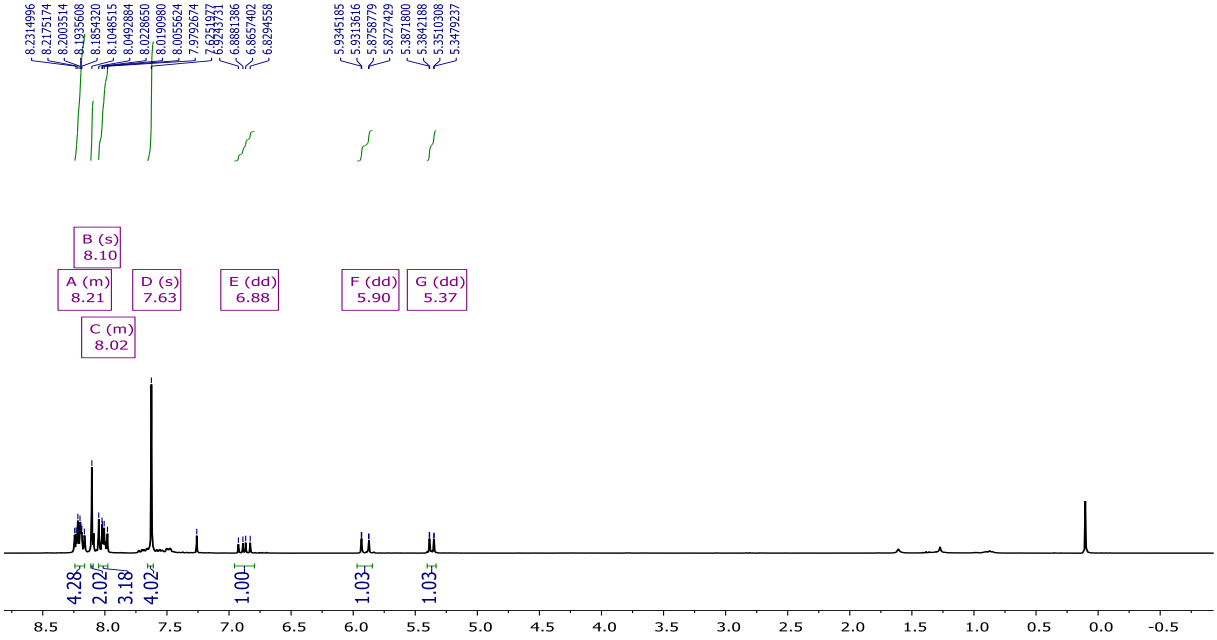

Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **OL 1**

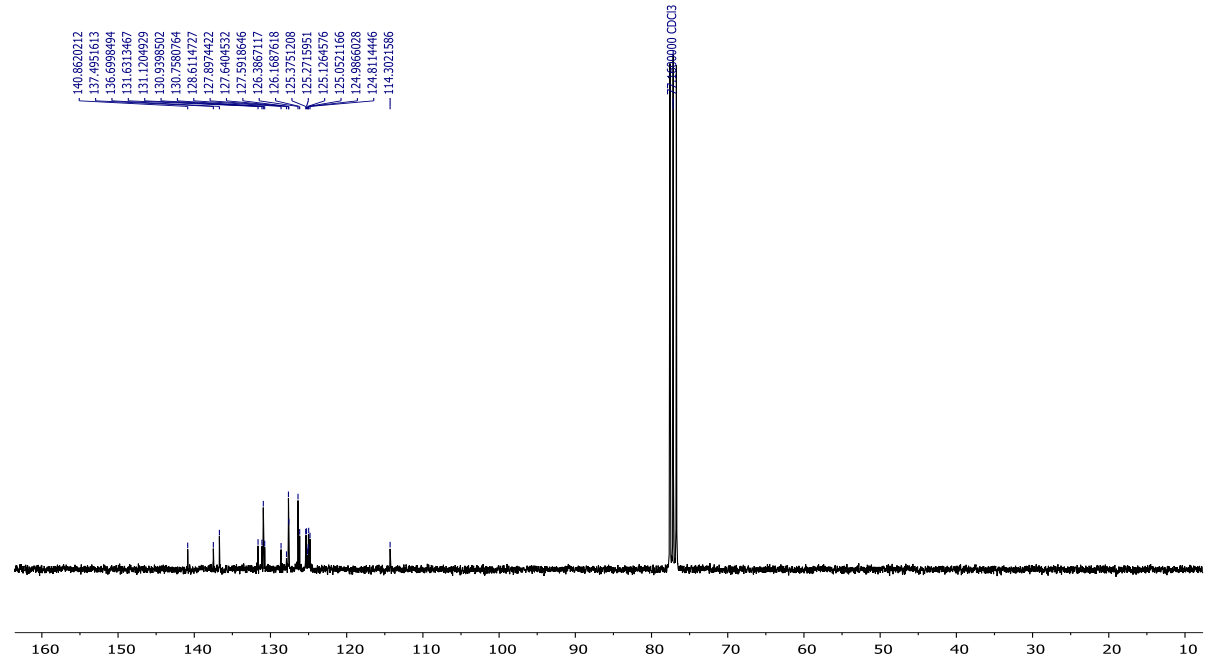

Figure S2. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **OL 1**

9-(4-vinylphenyl)phenanthrene (OL 2)

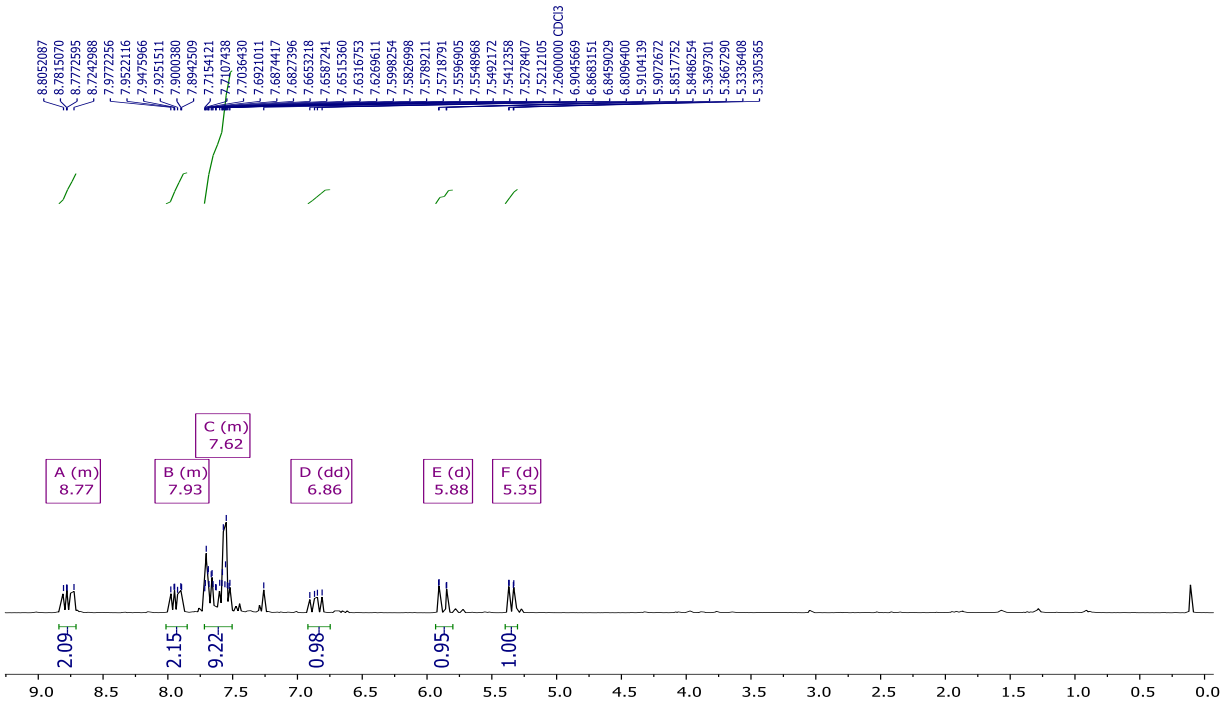

Figure S3. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **OL 2**

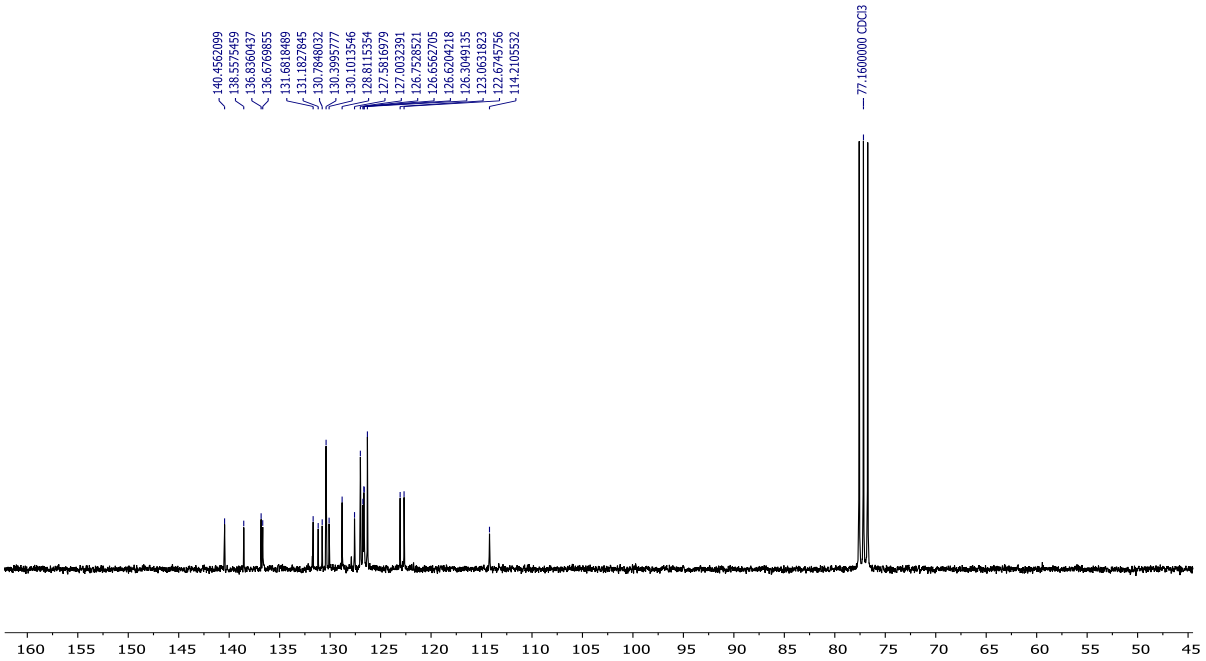

Figure S4. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **OL 2**

4-(trifluoromethyl)-4'-vinyl-1,1'-biphenyl (OL 3)

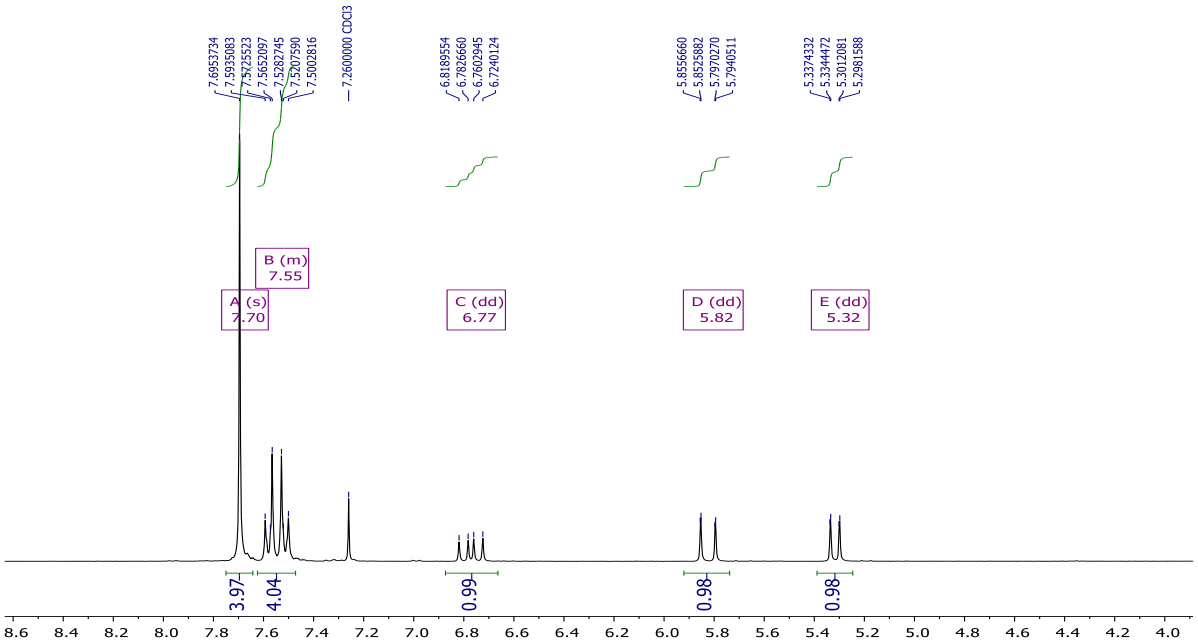

Figure S5. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **OL 3**

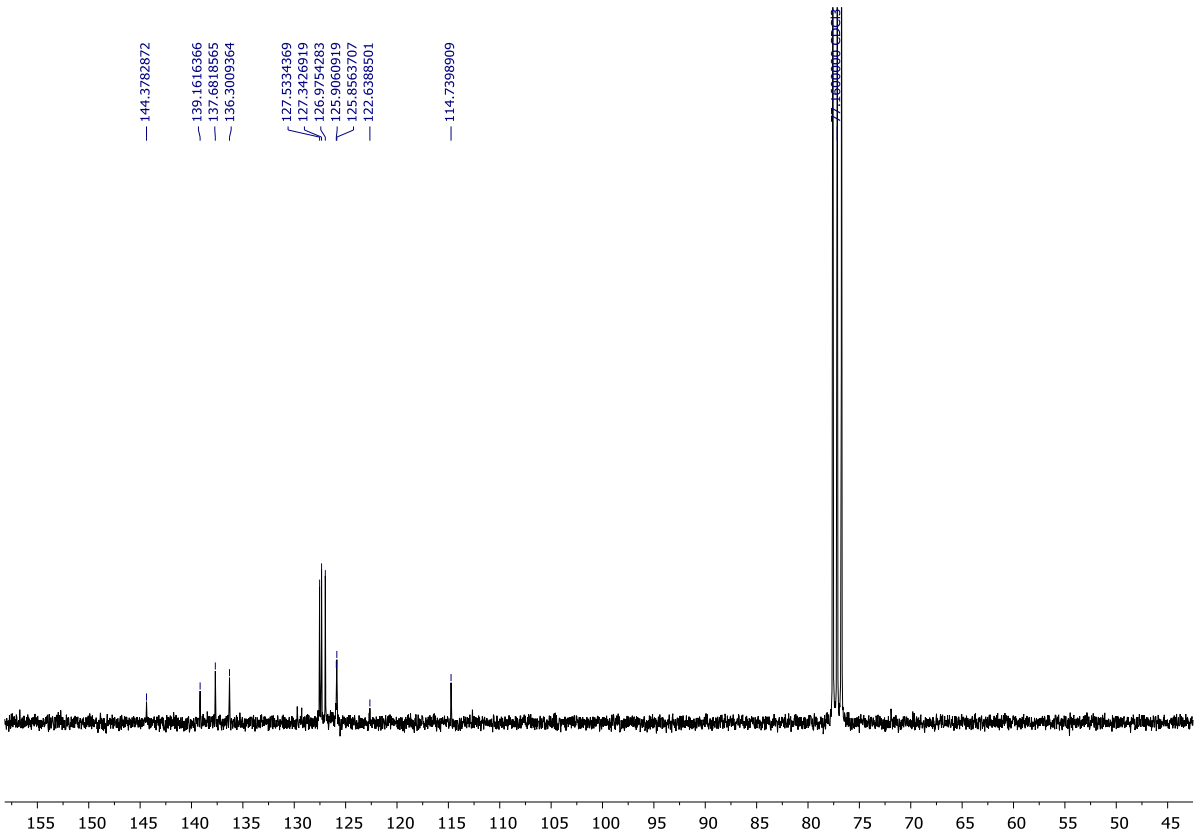

Figure S6. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **OL 3**

2-bromo-5-phenylthiophene (B 4)

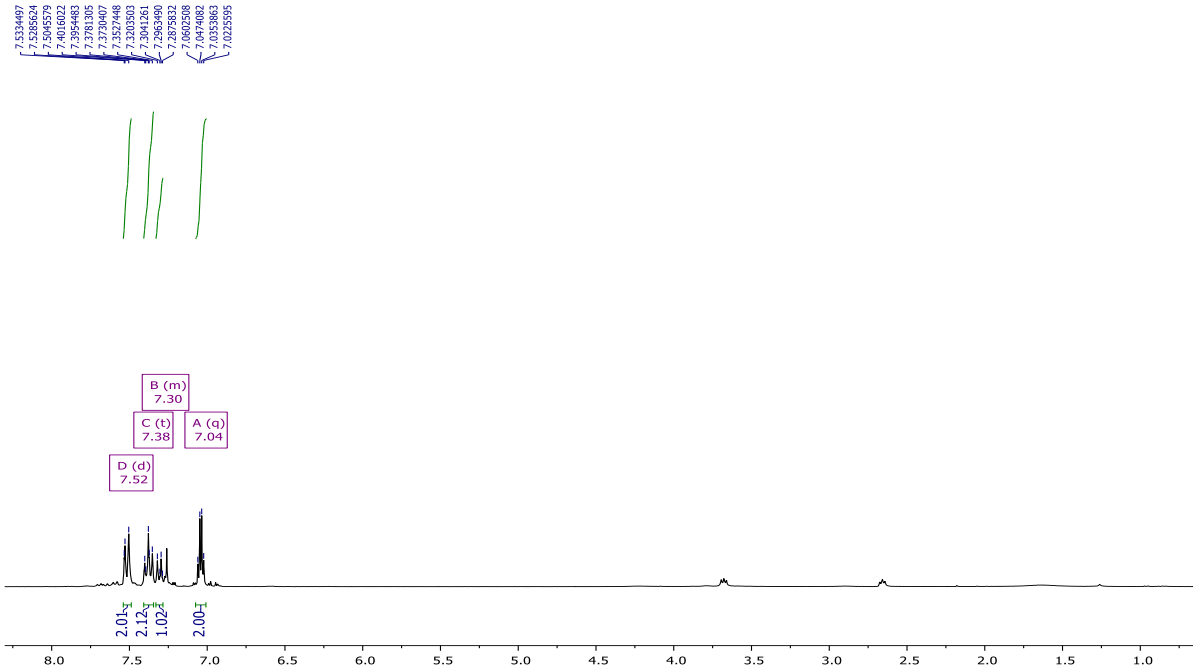

Figure S7. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **B 4**

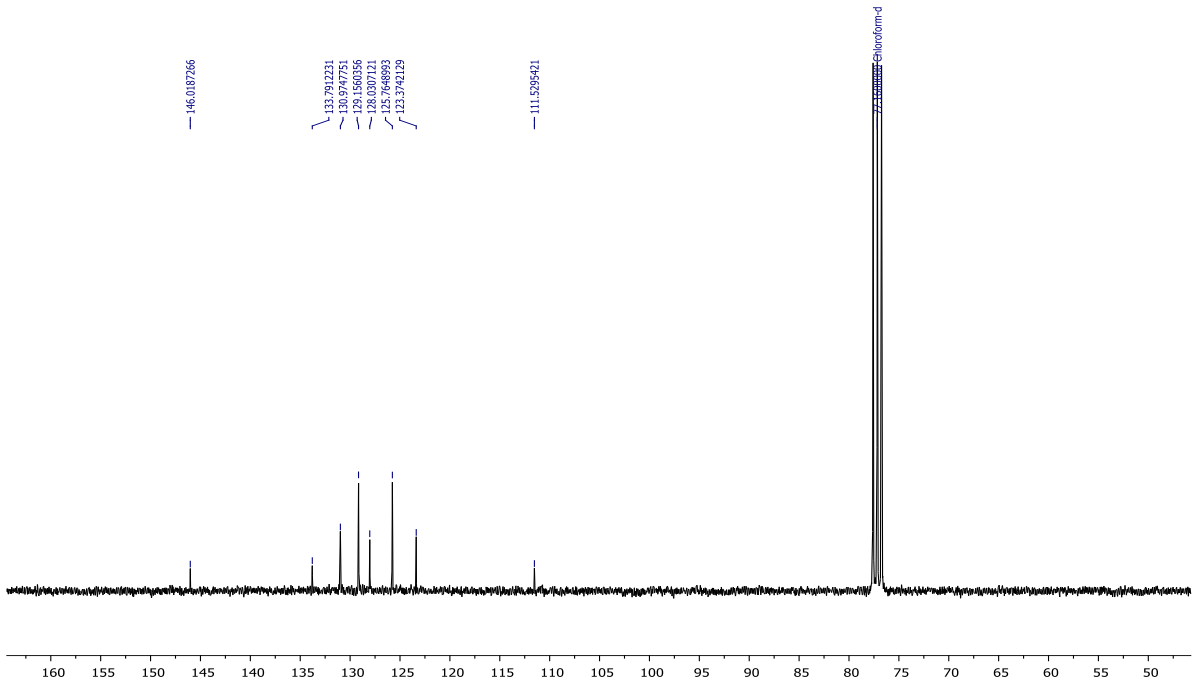

Figure S8. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **B 4**

2-phenyl-5-(4-vinylphenyl)thiophene (OL 4)

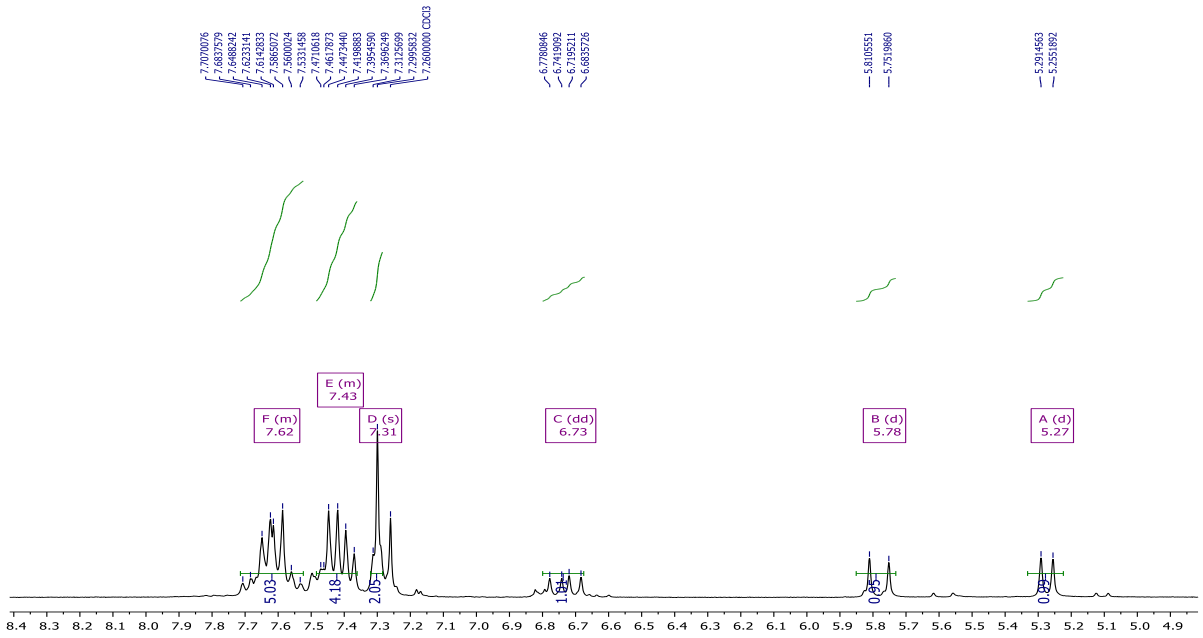

Figure S9. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **OL 4**

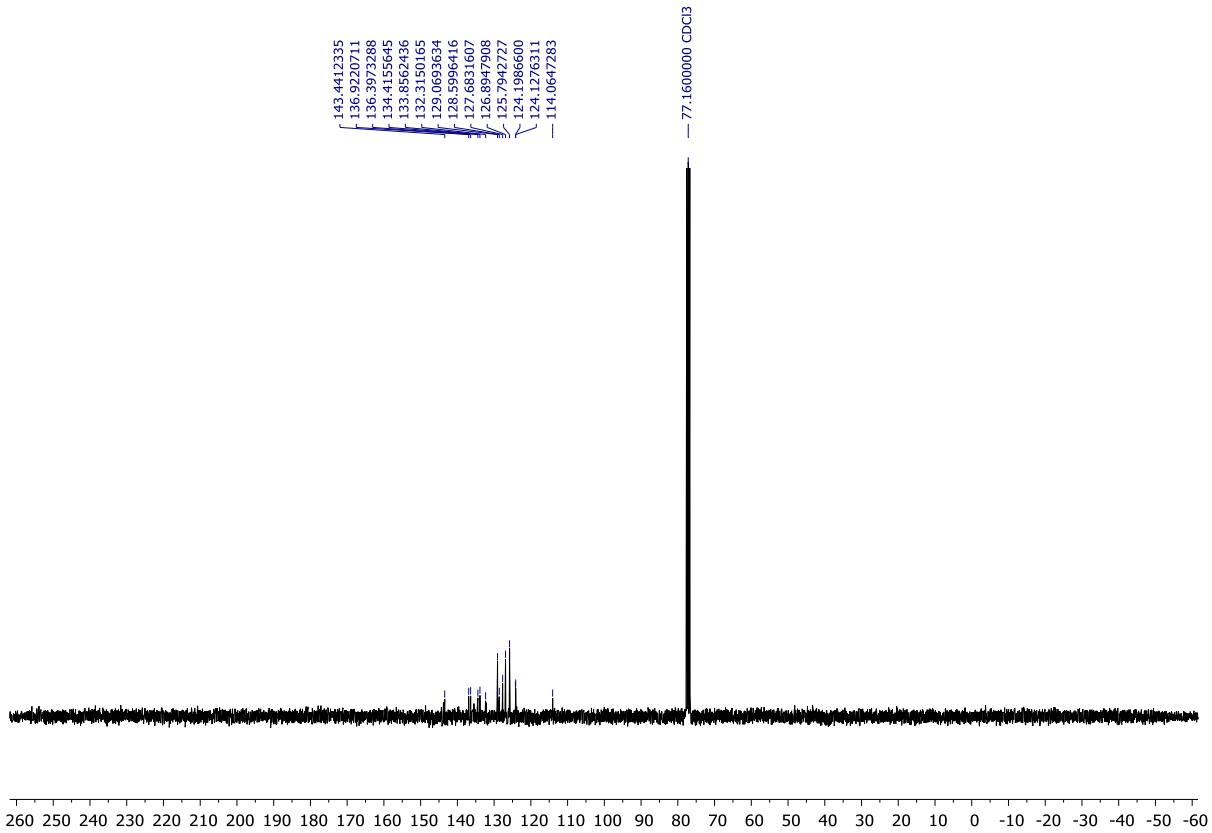

Figure S10. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **OL 4**

1-bromo-4-phenylnaphthalene (B 5)

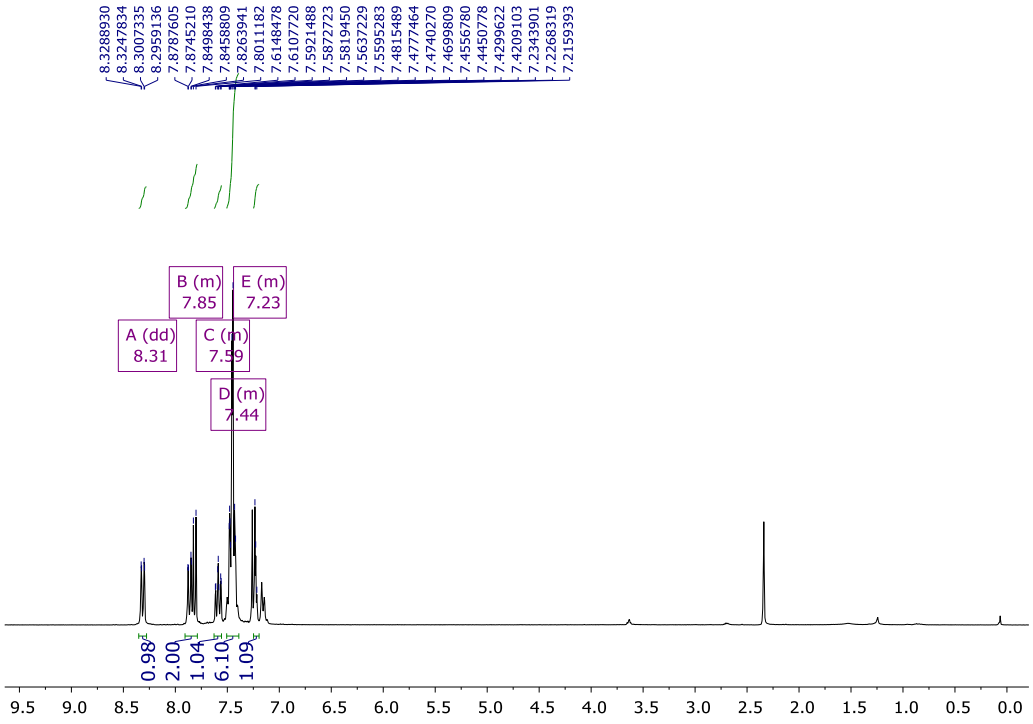

Figure S11. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **B 5**

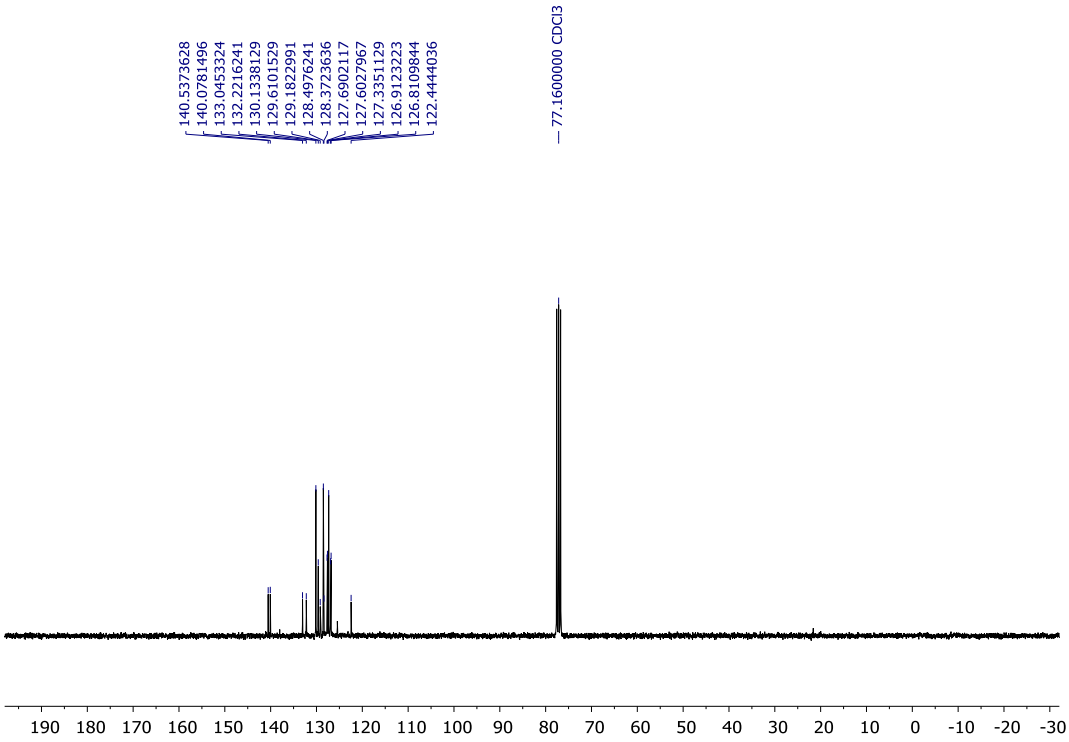

Figure S12. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **B 5**

1-phenyl-4-(4-vinylphenyl)naphthalene (OL 5)

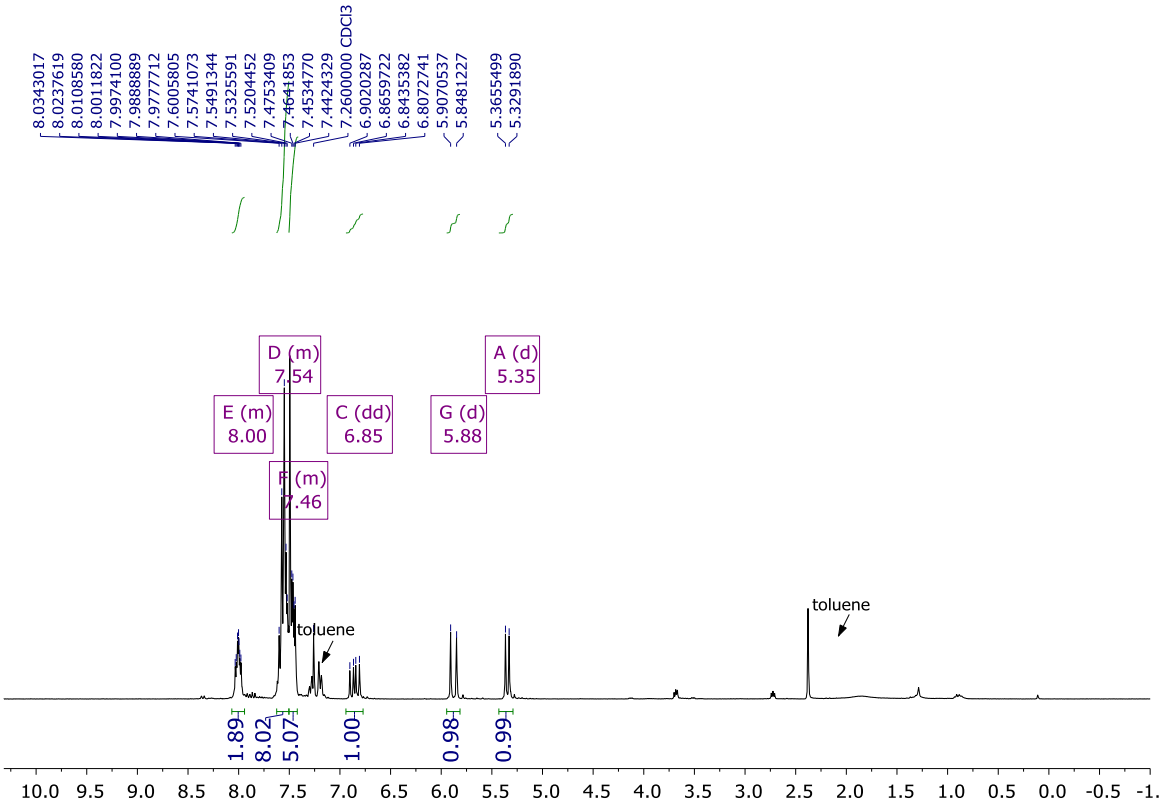

Figure S13. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **OL 5**

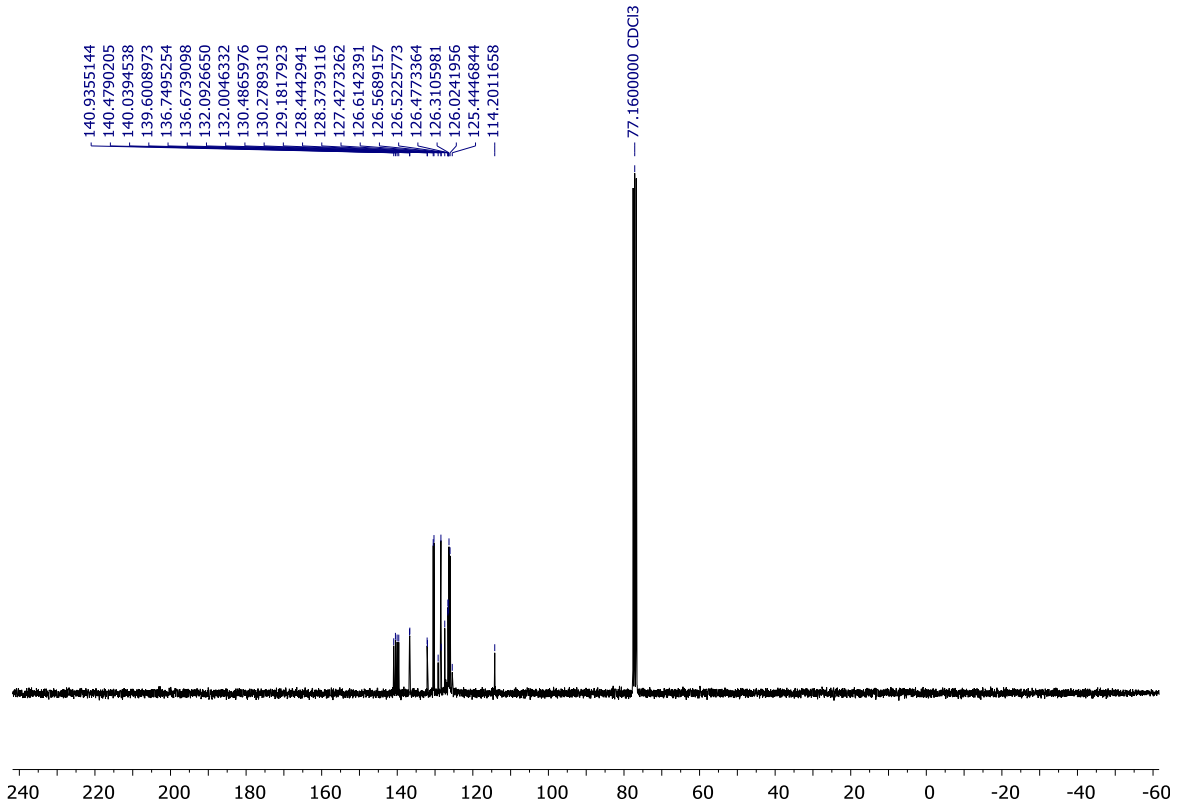

Figure S14. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **OL 5**

9,10-bis(4-vinylphenyl)anthracene (OL 6)

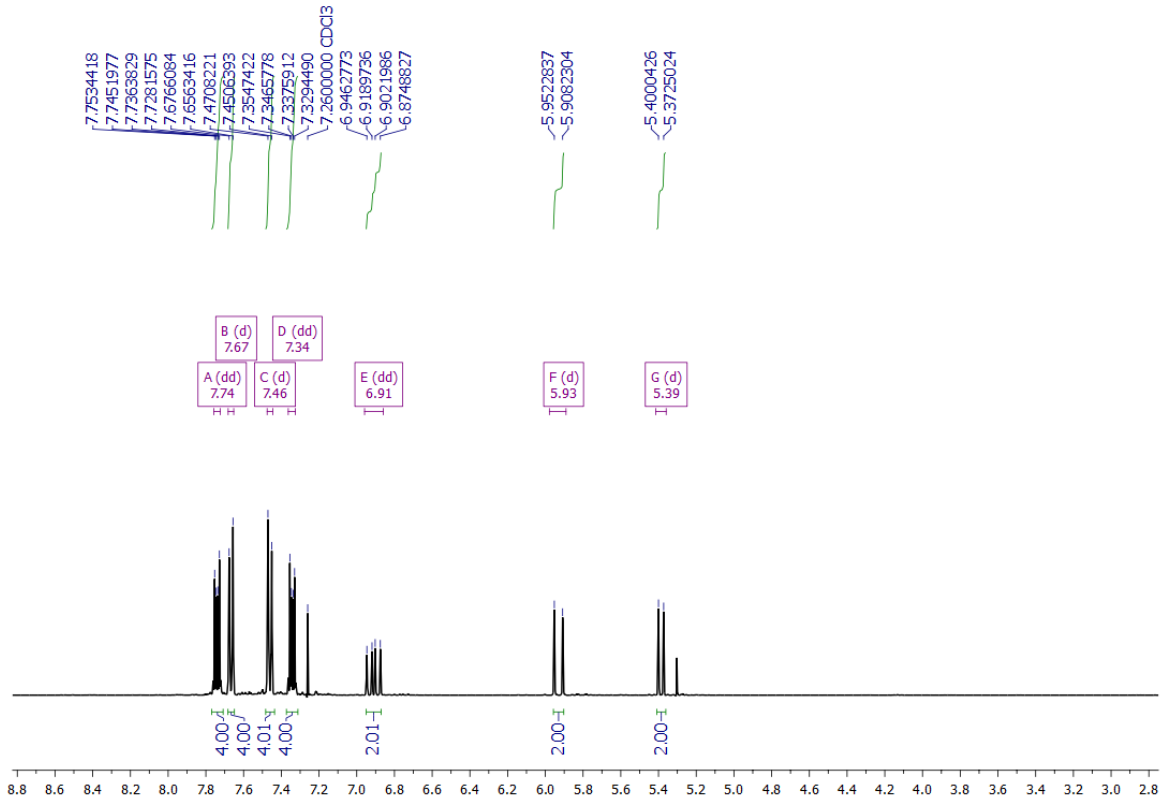

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **OL 6**

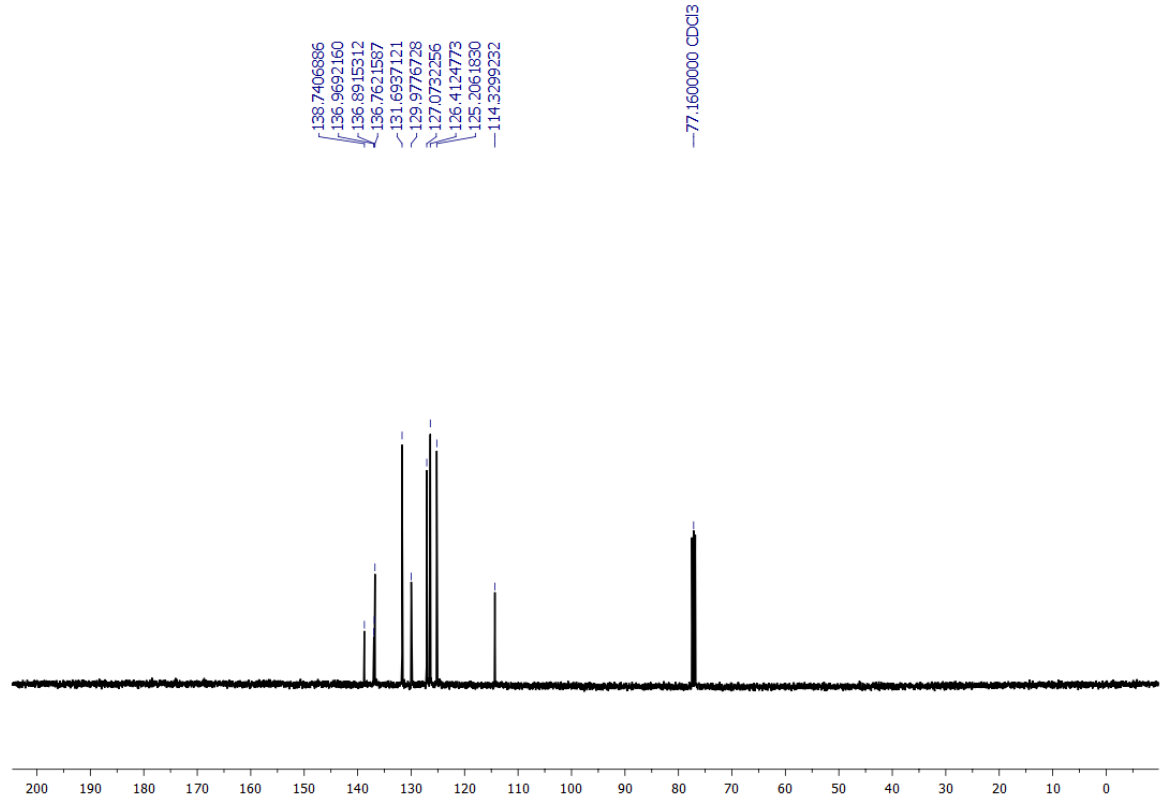

Figure S16. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **OL 6**

5.2. NMR spectra of functionalized silsesquioxanes

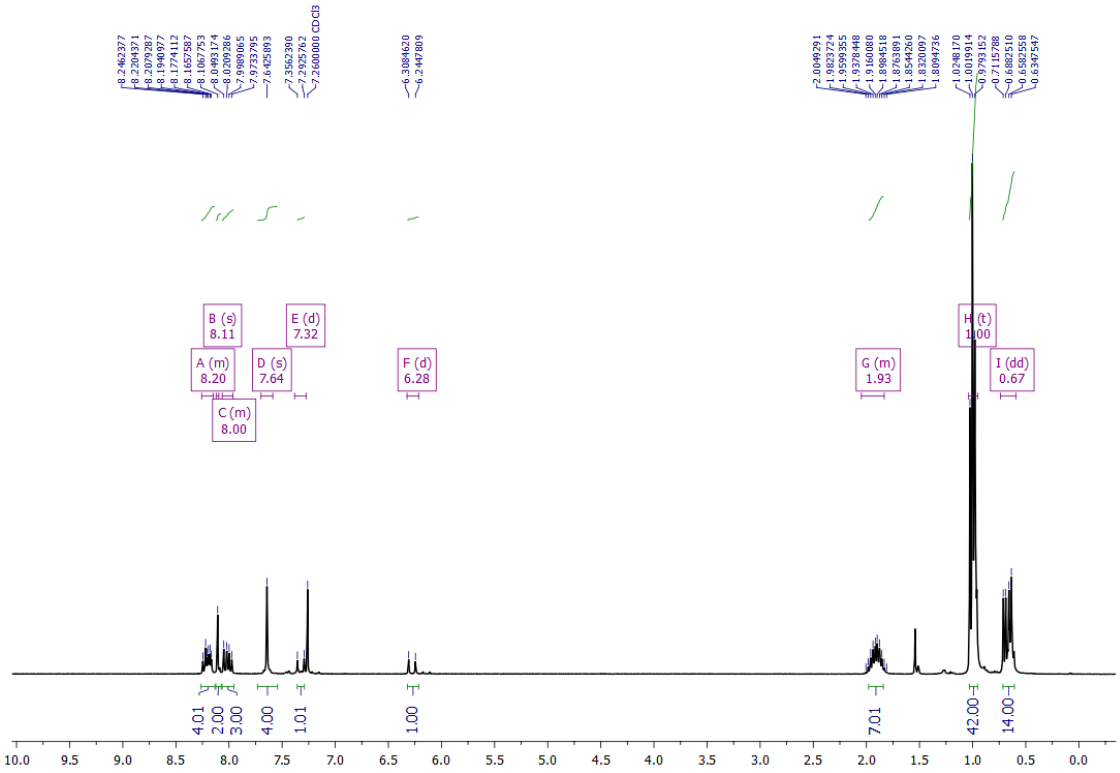

Figure S17. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **P 1**

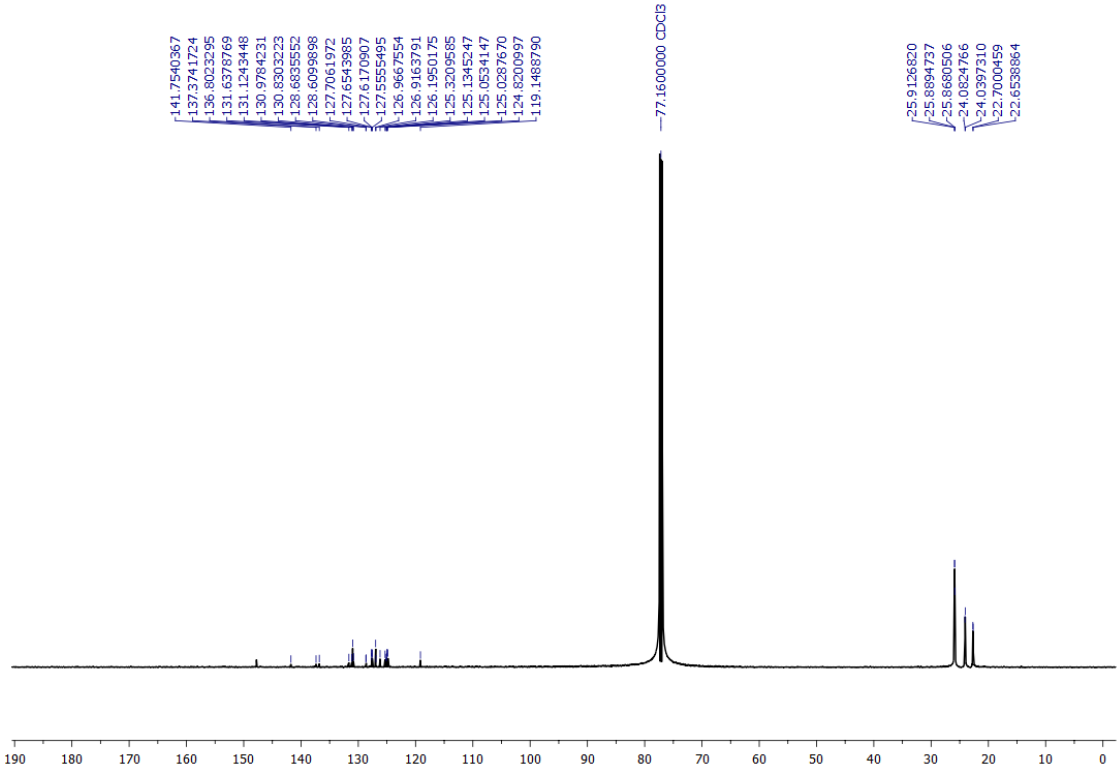

Figure S18. ^{13}C NMR (150 MHz, $CDCl_3$) of compound **P 1**

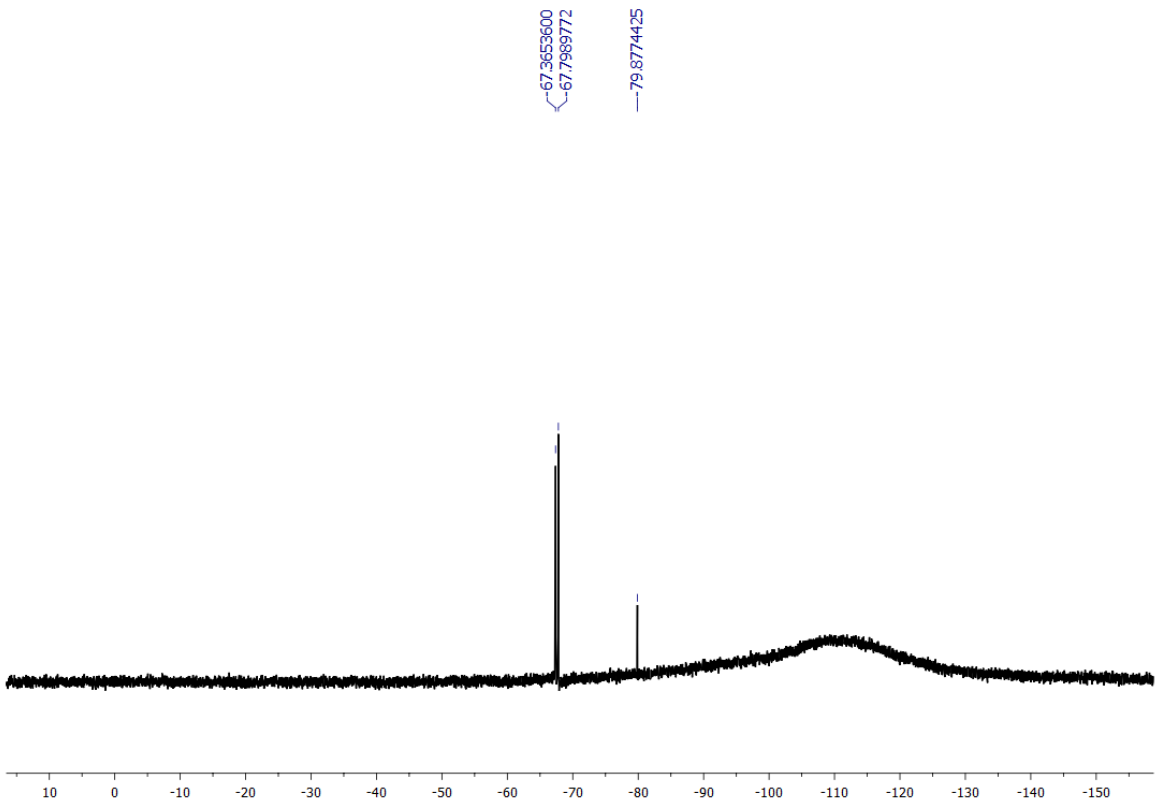

Figure S19. ^{29}Si NMR (119 MHz, $CDCl_3$) of compound **P 1**

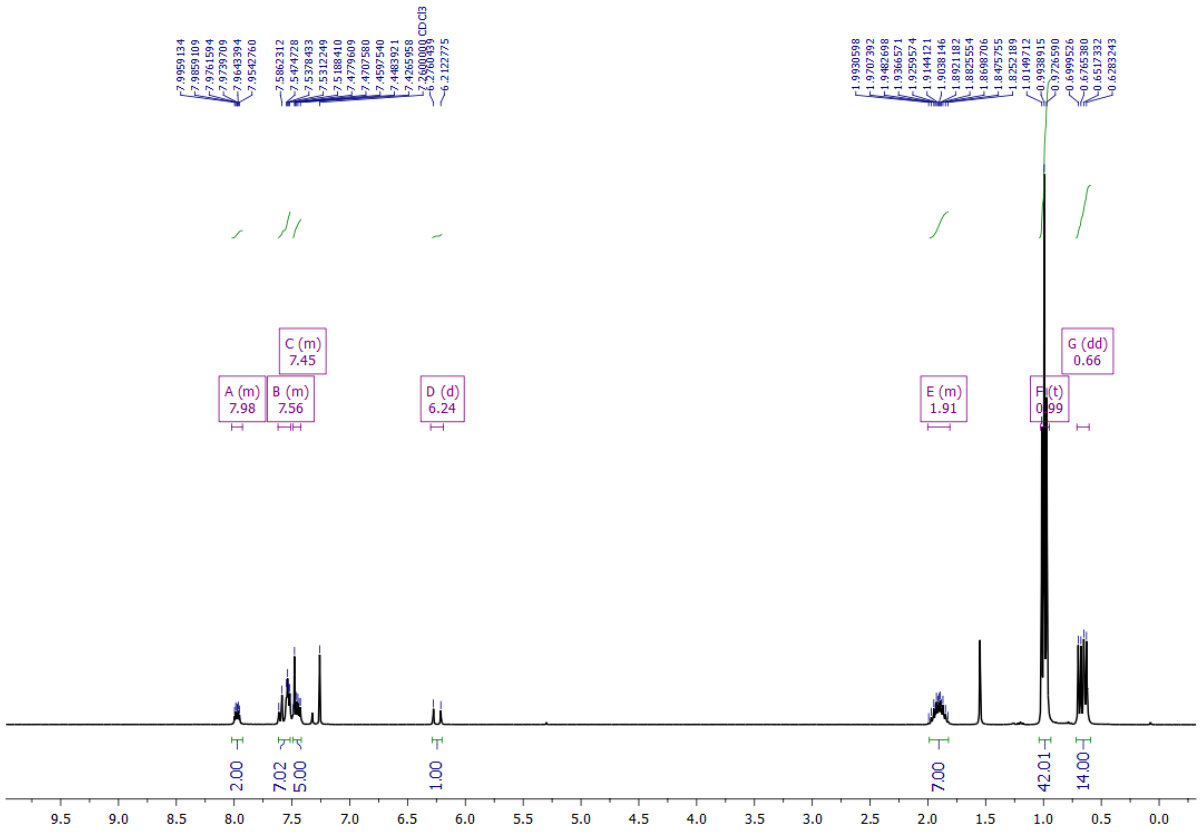

Figure S20. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **P 2**

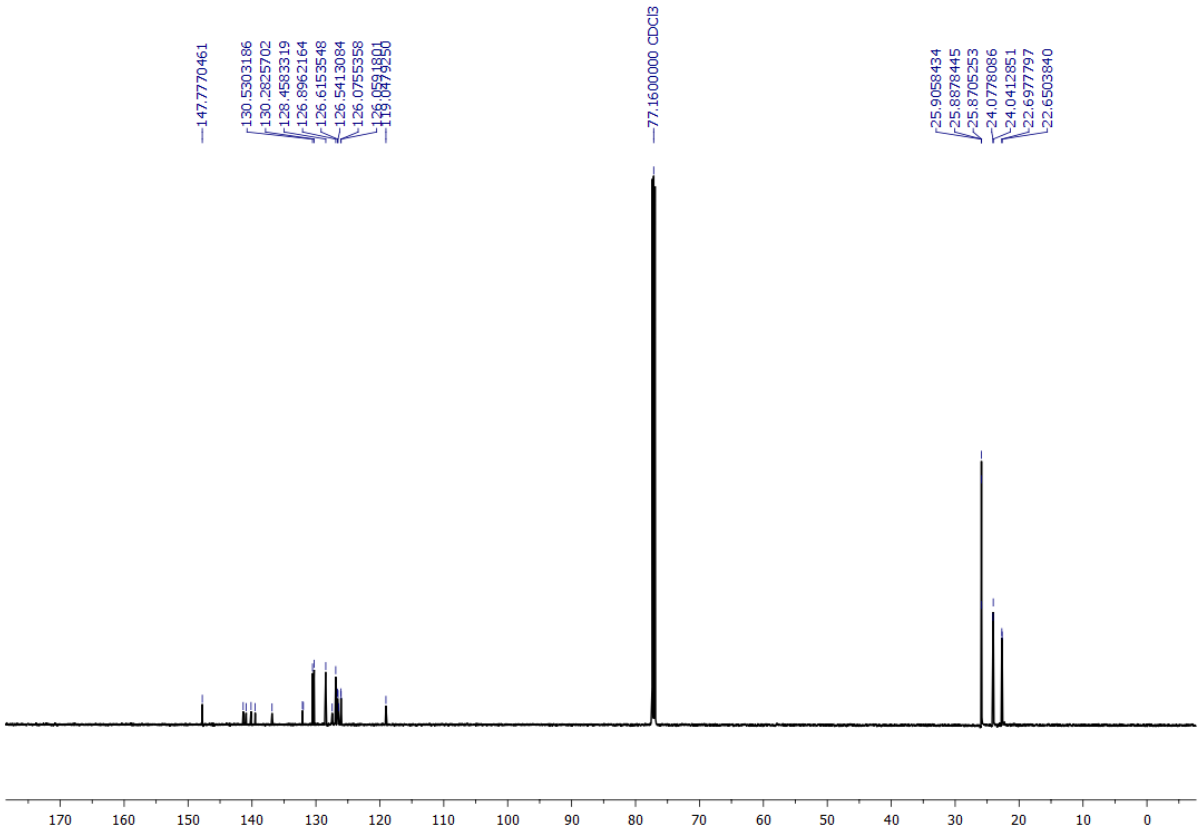

Figure S21. ^{13}C NMR (150 MHz, $CDCl_3$) of compound **P 2**

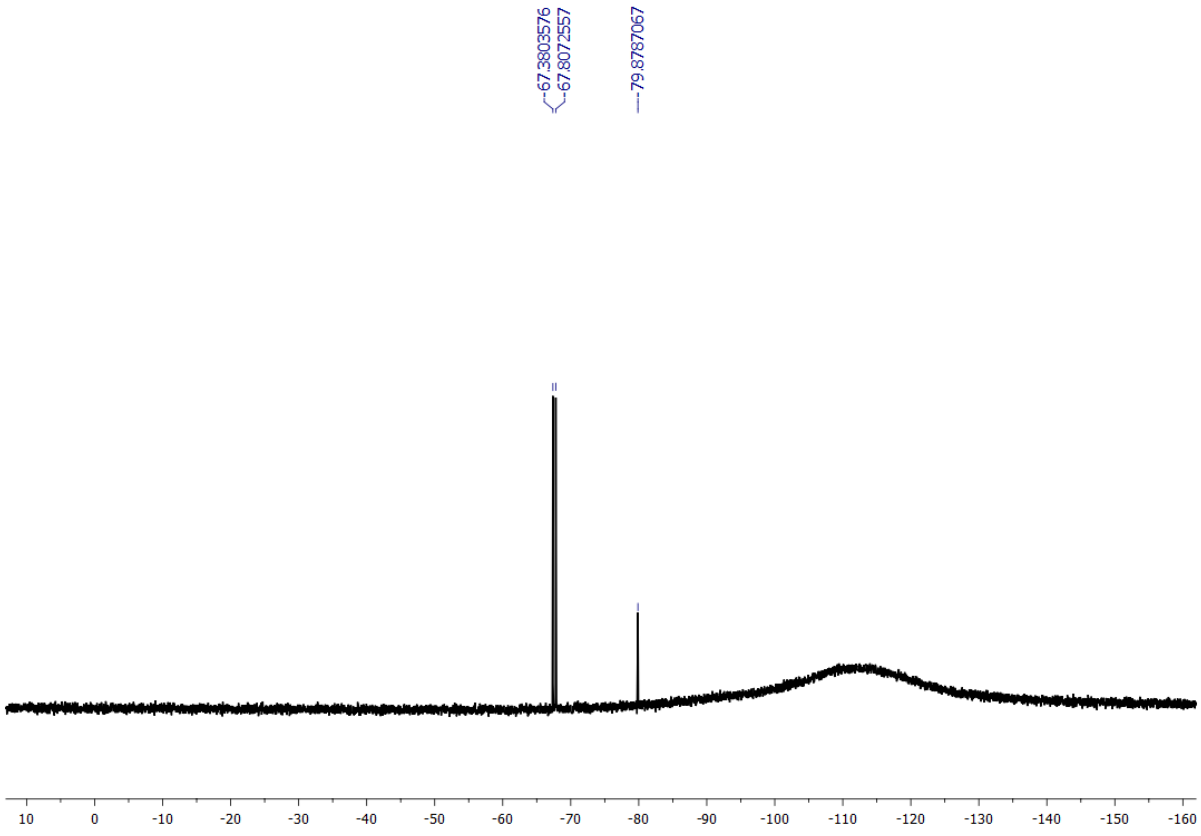

Figure S22. ^{29}Si NMR (119 MHz, $CDCl_3$) of compound **P 2**

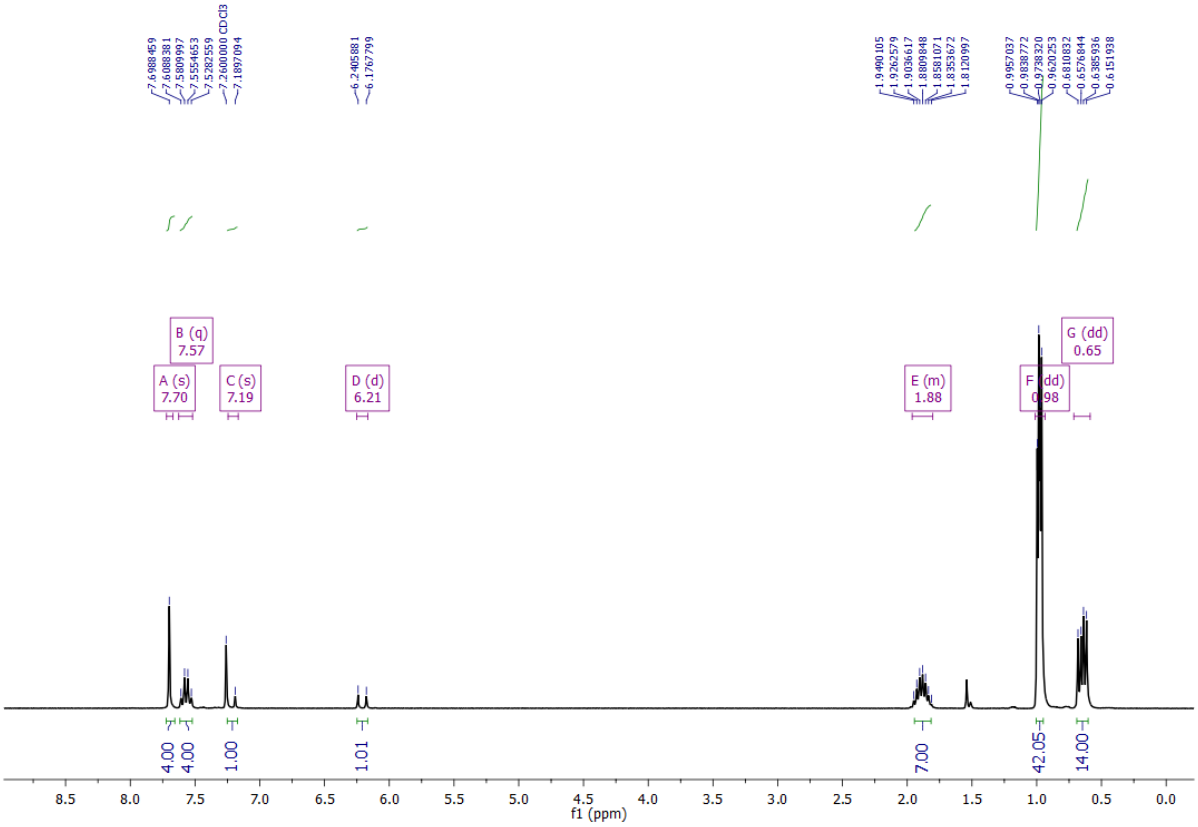

Figure S23. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **P 3**

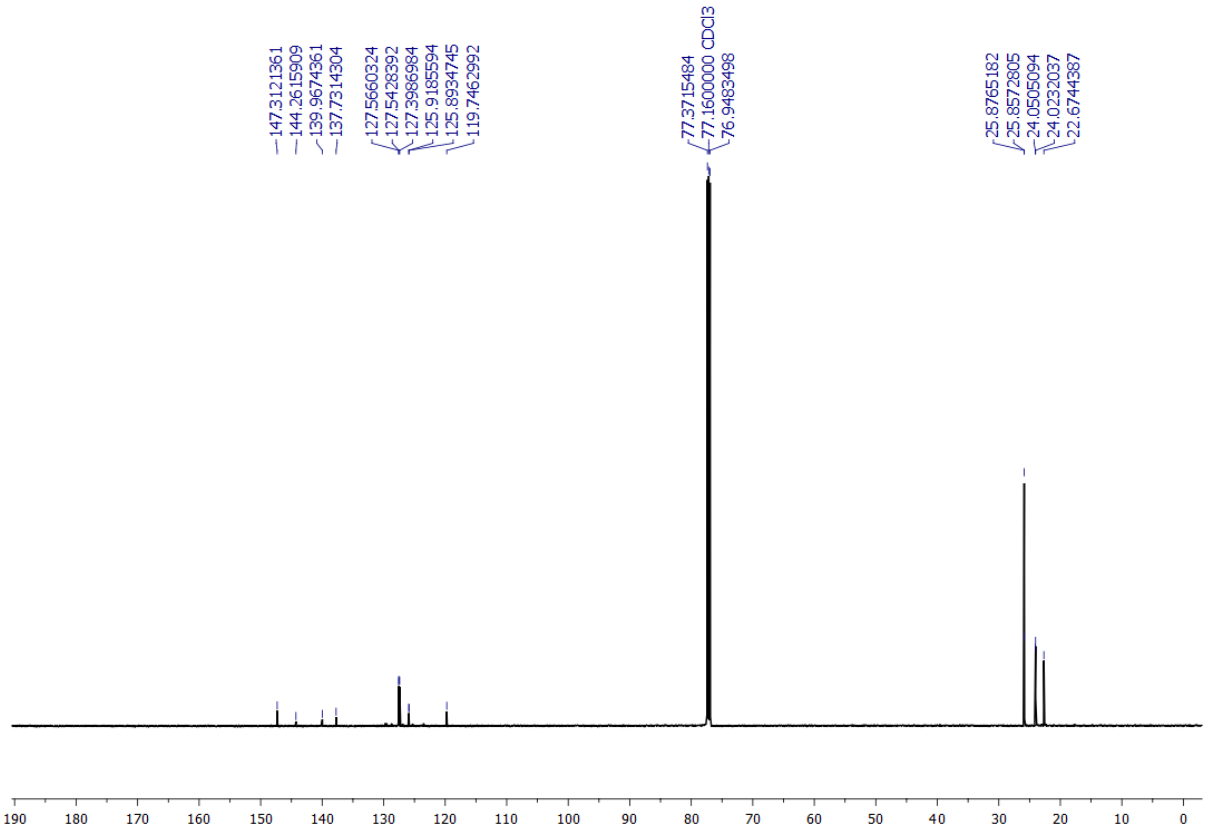

Figure S24. ^{13}C NMR (150 MHz, $CDCl_3$) of compound **P 3**

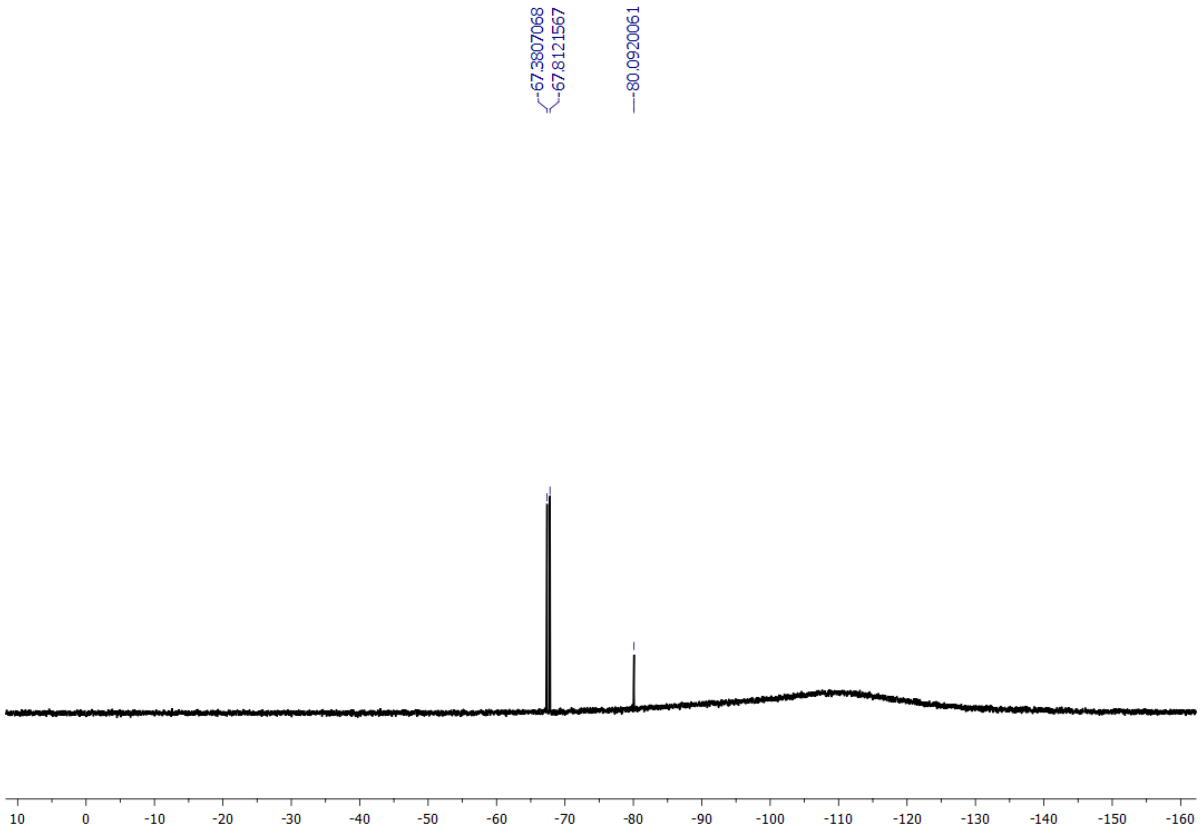

Figure S25. ^{29}Si NMR (119 MHz, $CDCl_3$) of compound **P 3**

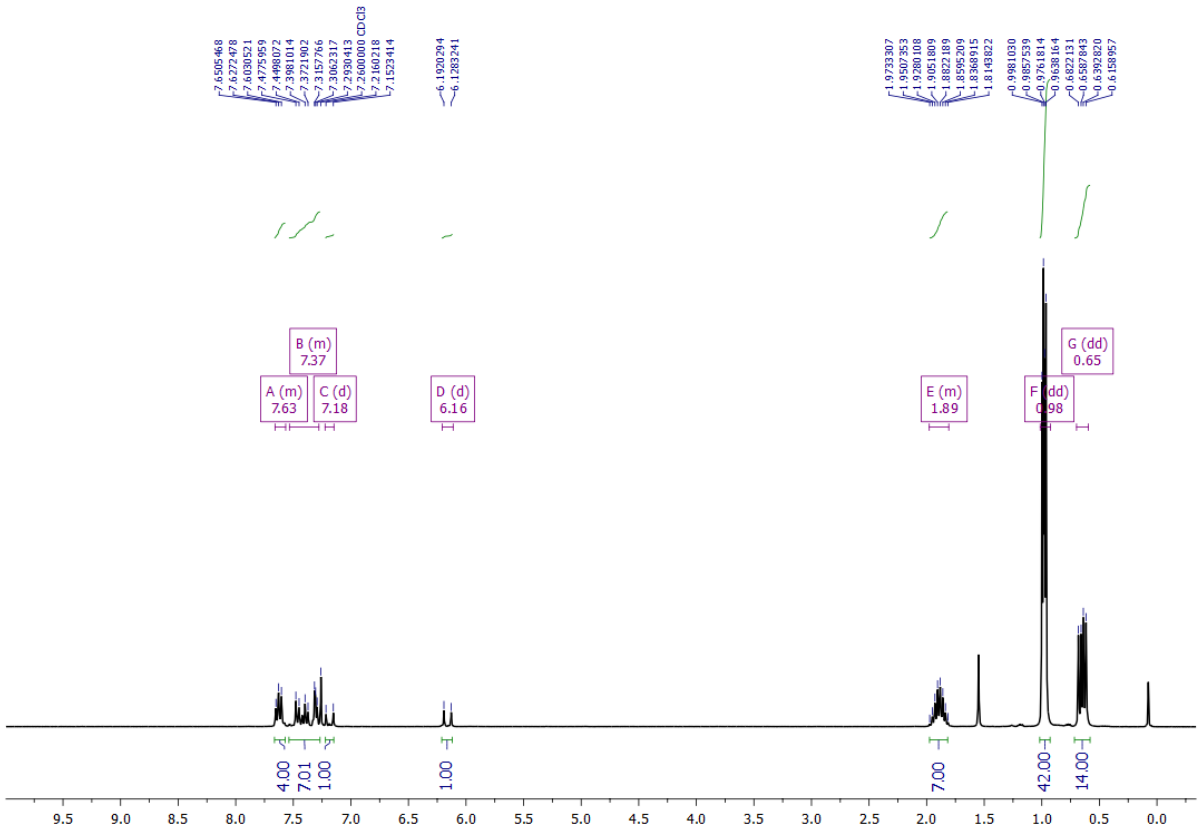

Figure S26. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **P 4**

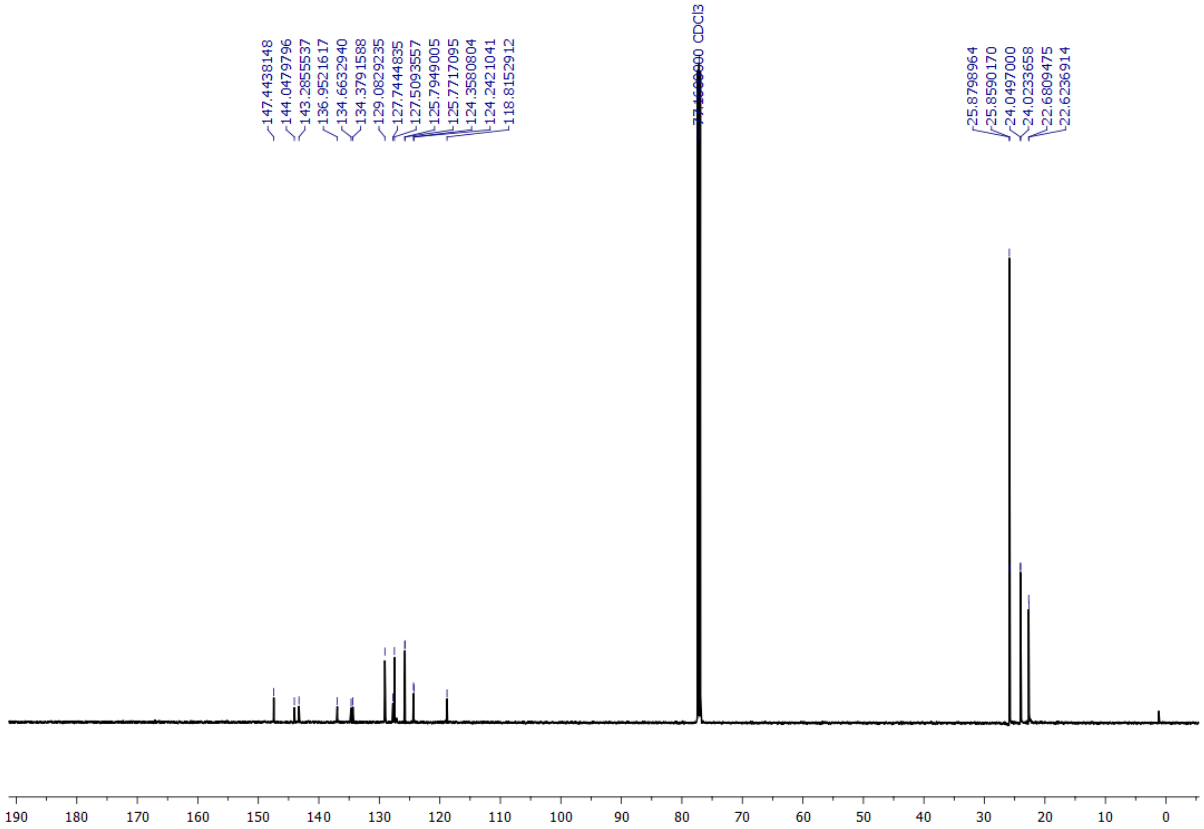

Figure S27. ^{13}C NMR (150 MHz, $CDCl_3$) of compound **P 4**

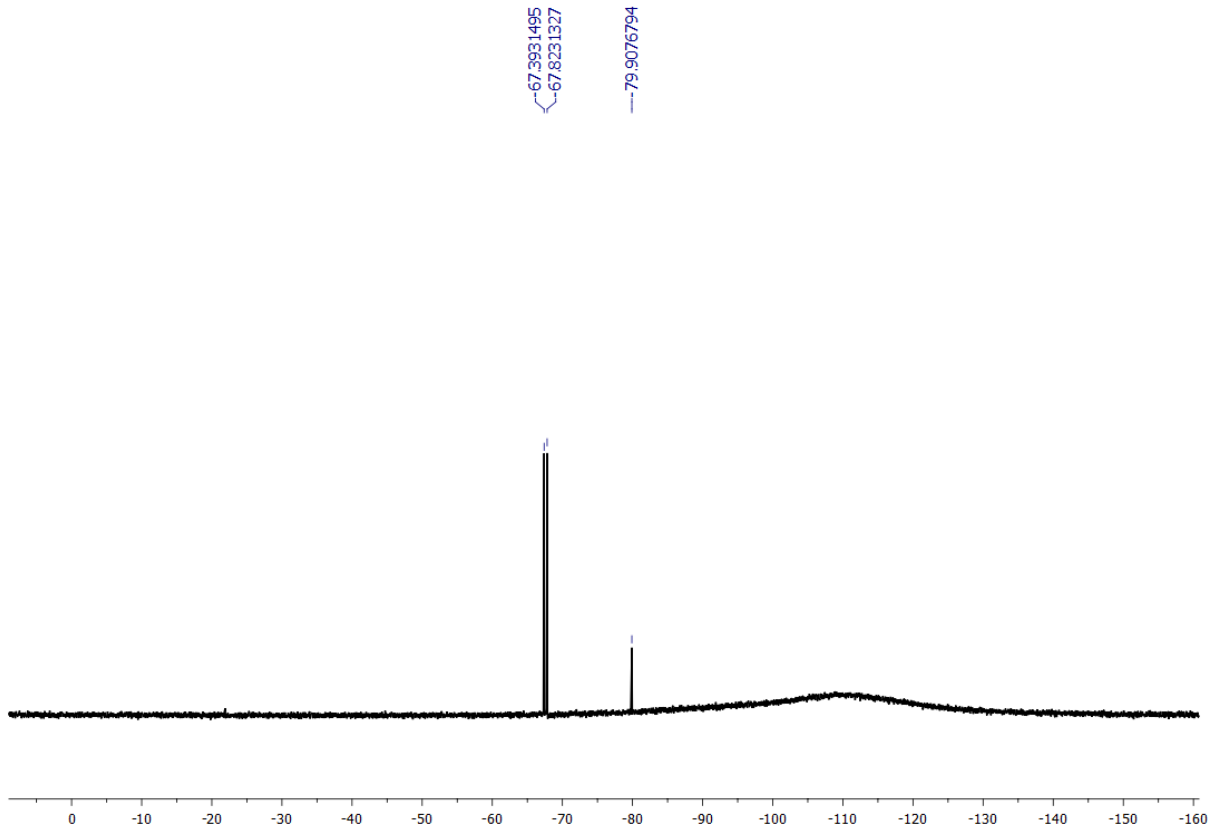

Figure S28. ^{29}Si NMR (119 MHz, $CDCl_3$) of compound **P 4**

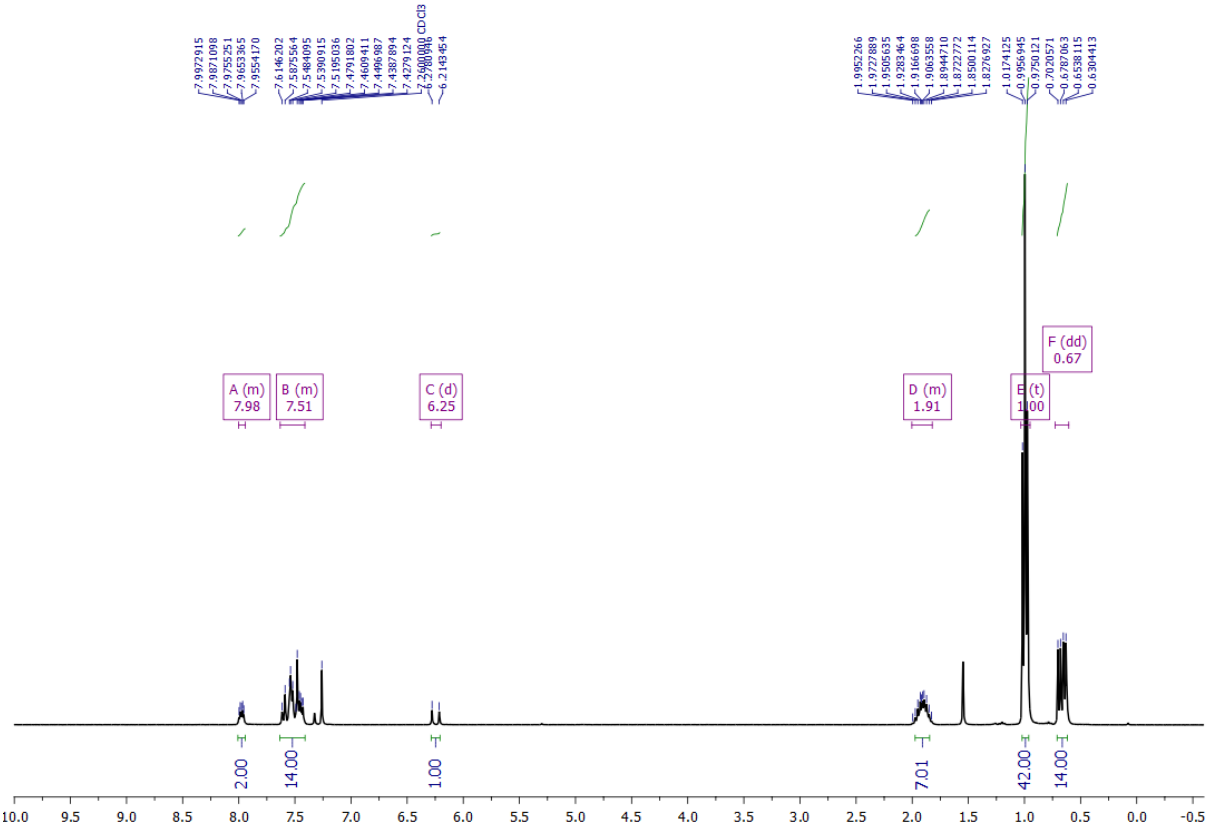

Figure S29. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **P 5**

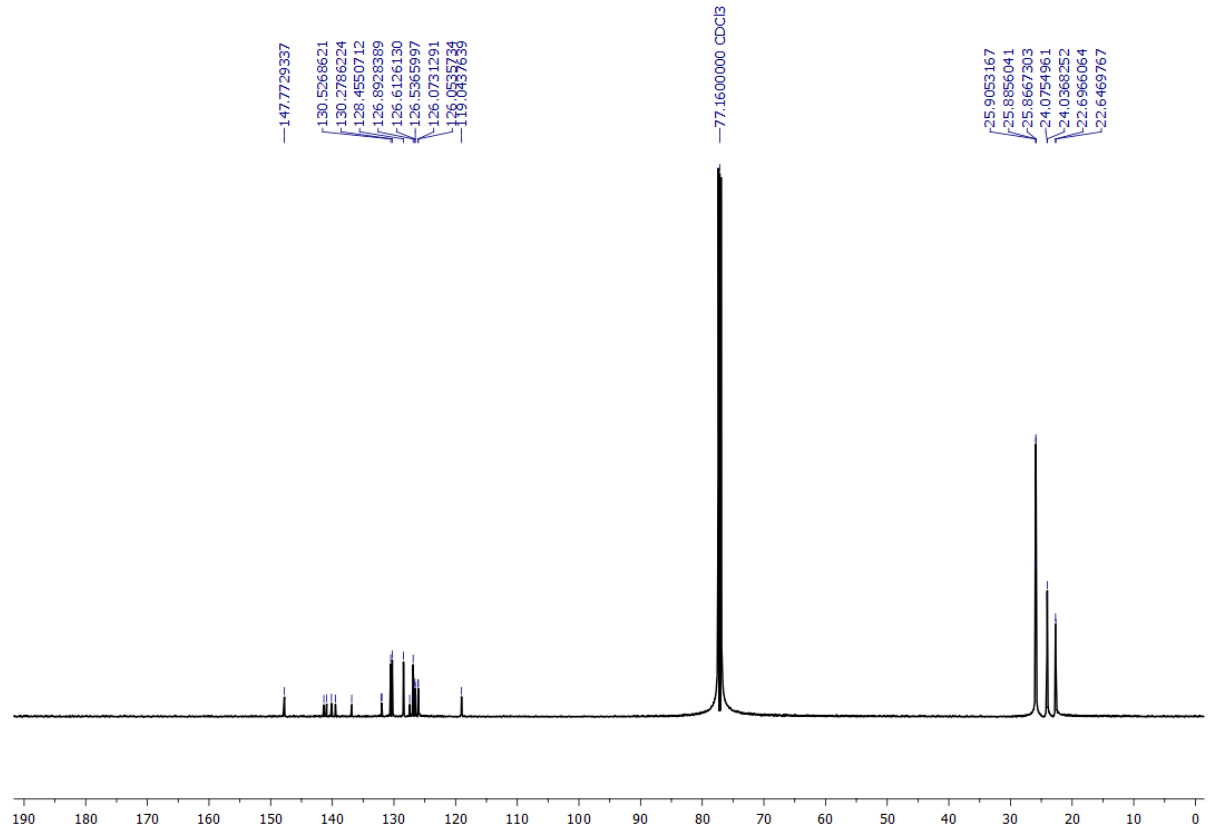

Figure S30. ^{13}C NMR (150 MHz, $CDCl_3$) of compound **P 5**

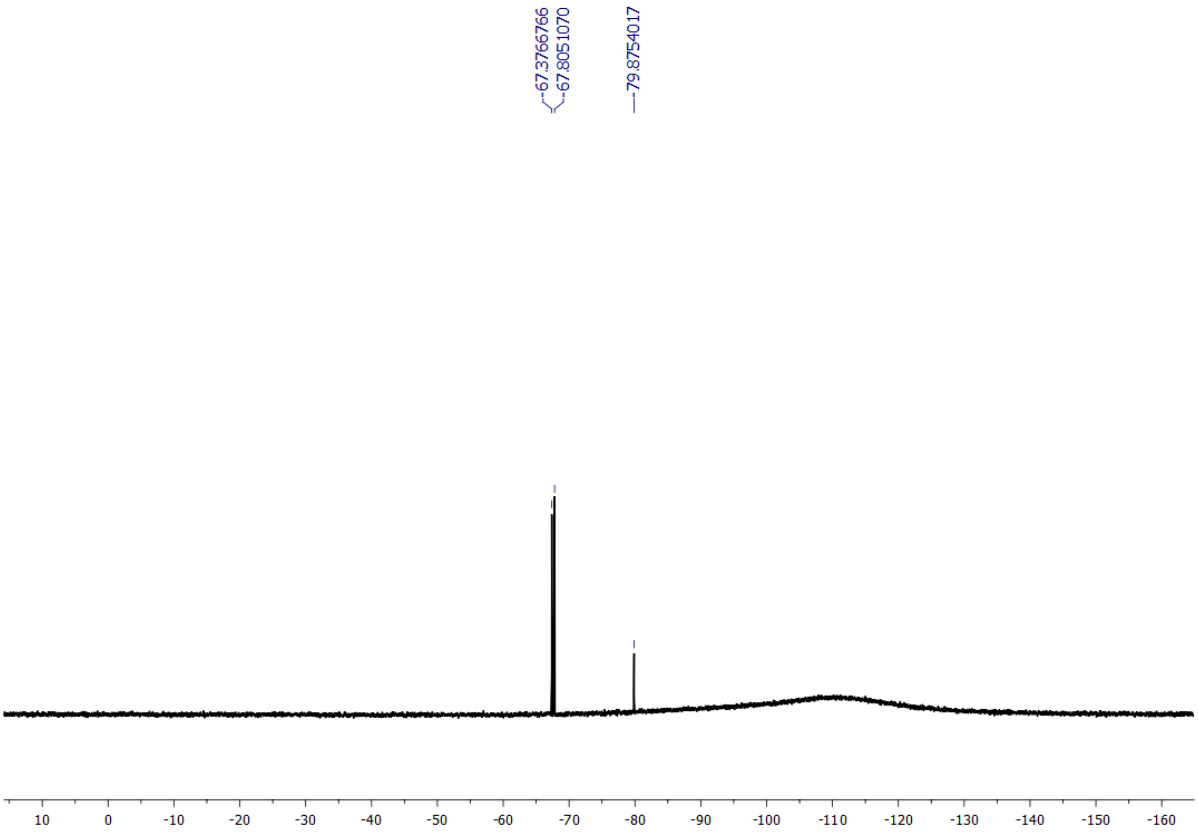

Figure S31. ^{29}Si NMR (119 MHz, $CDCl_3$) of compound **P 5**

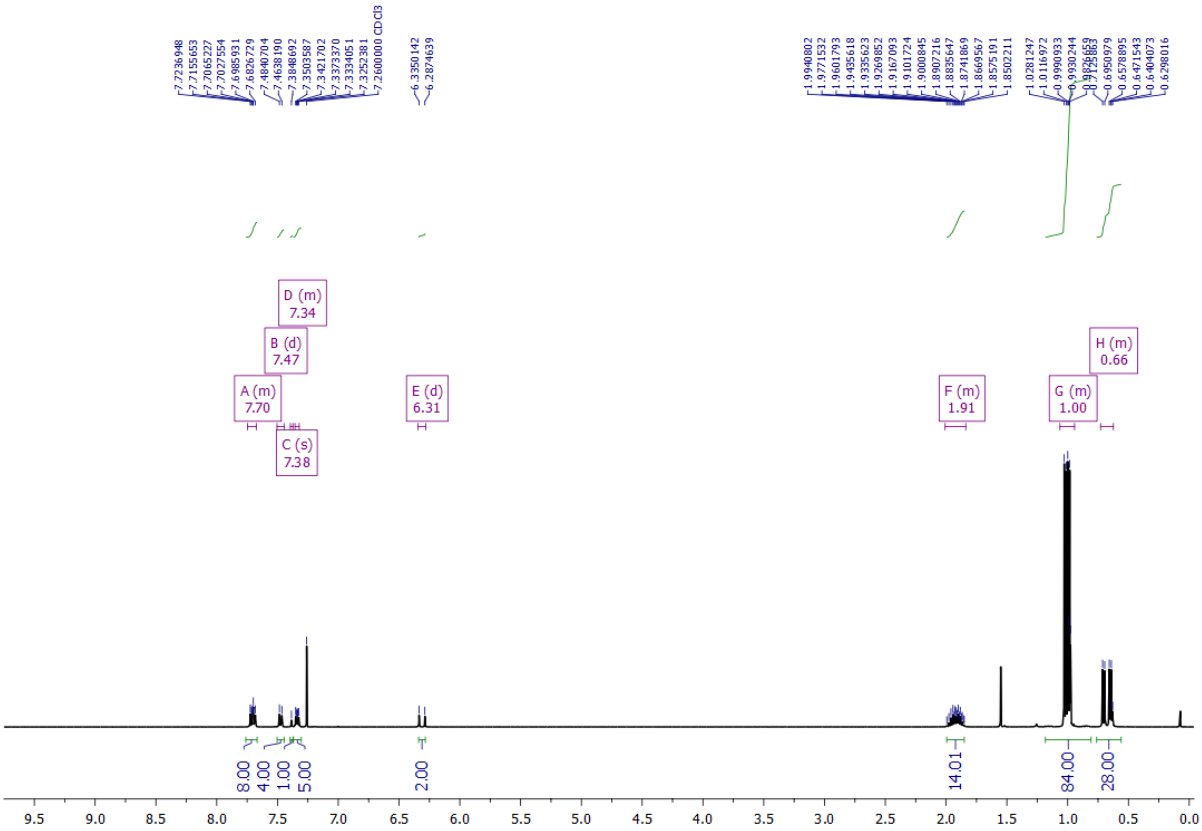

Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **P 6**

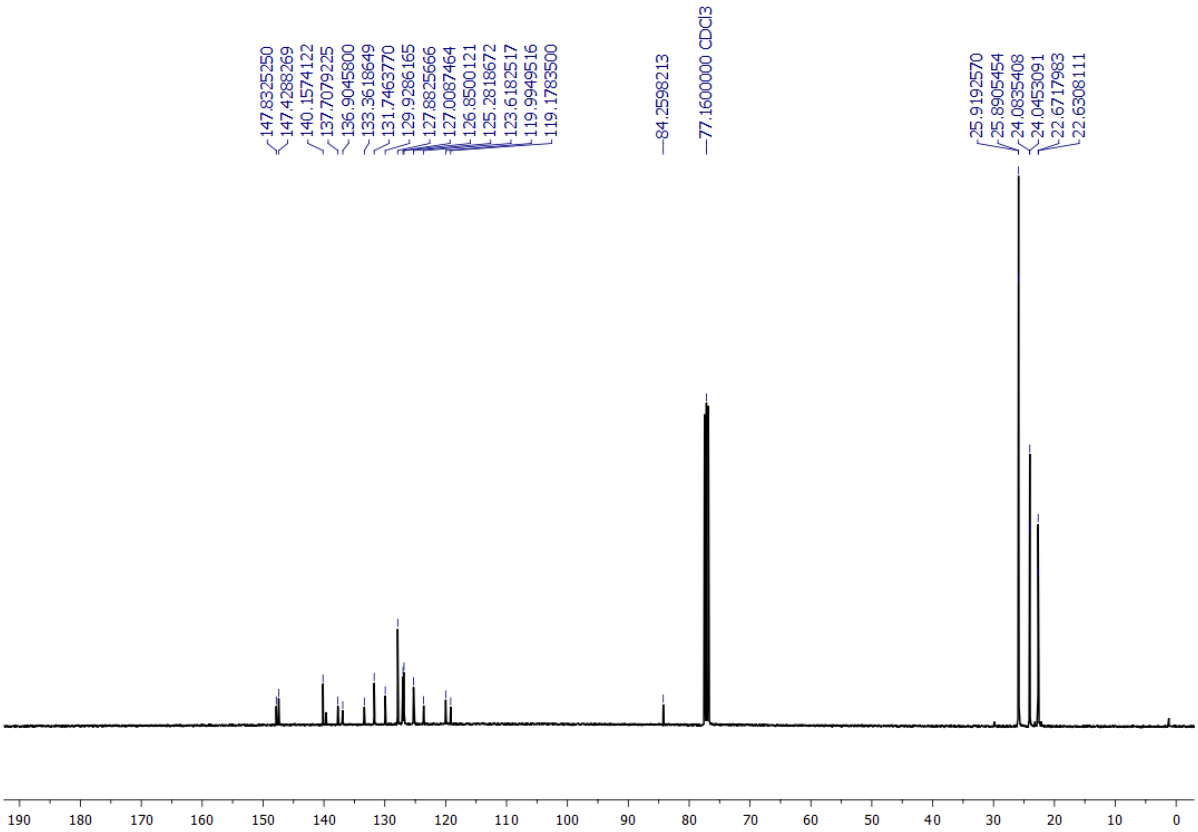

Figure S33. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **P 6**

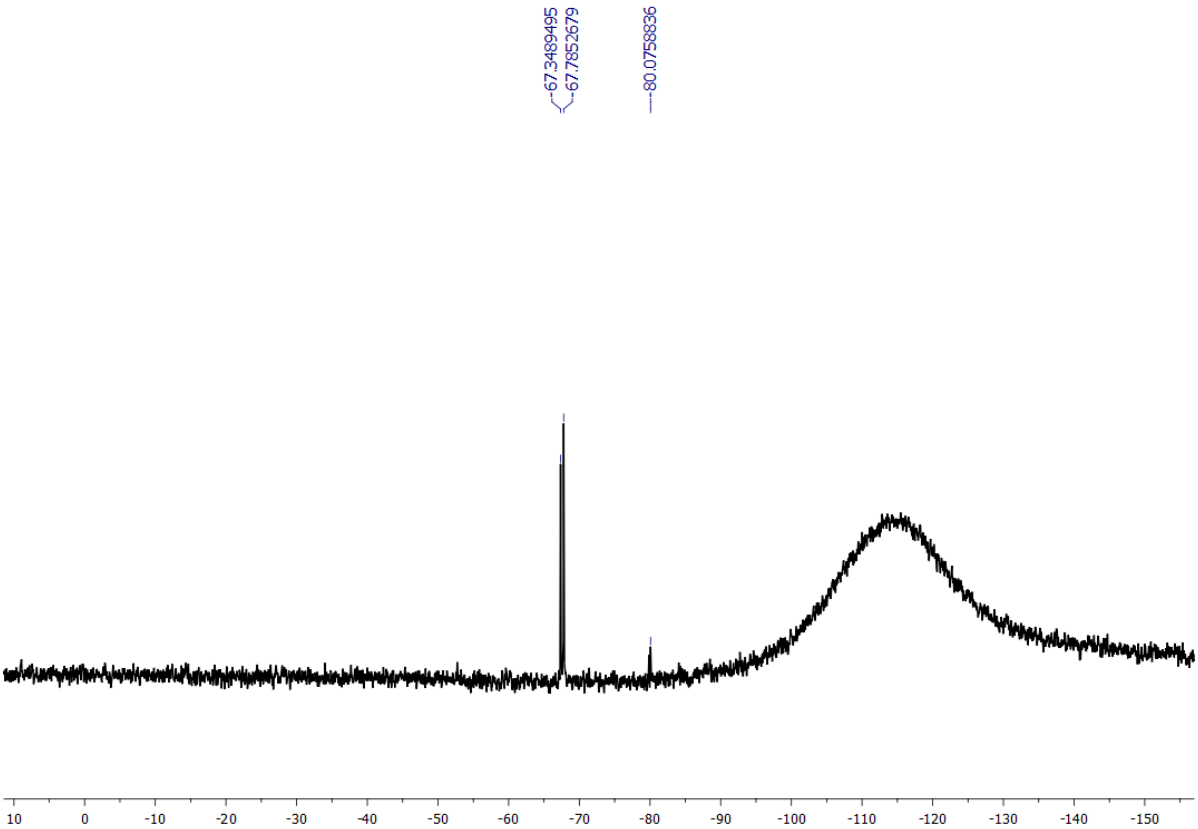

Figure S34. ^{29}Si NMR (79 MHz, $CDCl_3$) of compound **P 6**

6. References

[1] P. Żak, C. Pietraszuk, B. Marciniec, B. Spólnik and W. Danikiewicz, *Adv. Synth. Catal.*, 2009, **351**, 2675–2682.