Supporting Information

Multifunctional imine-POSS as uncommon 3D nanobuilding blocks for supramolecular hybrid materials: Synthesis, structural characterization, and properties

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Experimental Section

General procedures and chemicals: Solvents: dichloromethane, chloroform, hexane, and methanol (HPLC grade) were used as received. (3-Aminopropyl)triethoxysilane (99%, Aldrich), HCl (36–38%, Avantor Performance Materials Poland S.A.), $MgSO_4$, $NaHCO_3$, (Avantor Performance Materials Poland S.A.), $Na(CH_3COO)_3BH$ (97%, Aldrich), and triethylamine (99.5%, Aldrich) were used without further purification. Aldehydes: 2-hydroxy-1-naphthaldehyde, 4-bromobenzaldehyde, 4-nitrobenzaldehyde, benzaldehyde, and salicylaldehyde were of reagent-grade quality and were purchased from Sigma-Aldrich. Chromium(III) acetylacetonate was prepared following the described procedure;[1] octa(3-aminopropyl)silsesquioxane hydrochloride, and octa(3-aminopropyl)silsesquioxane trifluoromethanesulfonate were prepared with a method based on a previously reported procedure.[2]

Methods: ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 500 or a Bruker Avance III 600 spectrometer equipped with broadband inverse gradient probe heads. ^1H NMR spectra were collected at 500.13 MHz using a relaxation delay of 1.0 s and a pulse width of 7°. Spectra were referred to the residual solvent signals (DMSO-d_6, 2.50; $CDCl_3$, 7.26; HOD, 4.79 for D_2O ppm) or TMS (0.00 ppm) as an internal reference. ^{13}C NMR spectra were collected at 125.8 MHz using a relaxation delay of 2.0 s and a pulse width of 15° and referred to the solvent signals (($^{13}CH_3)_2SO$ 39.52, $^{13}CDCl_3$ 77.16 ppm). ^{29}Si NMR spectra were recorded on a Bruker AMX-300 spectrometer using Wildmad PTFE-FEP 5 mm tube liners and were collected at 59.6 MHz using a relaxation delay of 10.0 s and a pulse width of 13°. $Cr(acac)_3$ was added at a concentration of ~10^{-2} mol/L as a shiftless relaxation agent. Chemical shifts were referenced to tetramethylsilane (TMS) ($\delta = 0.00$ ppm). For proton and carbon assignments, COSY, HMBC, and HMQC experiments were performed on the Bruker Avance 500 spectrometer. Two-dimensional NMR spectra were recorded with a 1.0 s recovery delay and with gradient selection. Fourier-Transform Infrared Spectra (FTIR) were recorded on a Bruker Vertex 70 FTIR spectrometer in the transmission mode. The FTIR sample chamber was flushed continuously with N_2 prior to data acquisition in the range 4000−400 cm^{-1} with a precision of ± 1 cm^{-1}. Sample spectra were recorded as Nujol mulls sandwiched between CsI plates or as KBr pellets, optical grade; random cuttings of KBr ground with 1.0 wt % of the sample to be analyzed pressed. High resolution and accurate mass spectra were carried out on a Bruker microTOF-Q spectrometer equipped with an ESI source. Samples were dissolved in chloroform or methanol. The experimental parameters were as follows: scan range: 200–2500 m/z; drying gas: nitrogen; temperature: 200 °C; ion source voltage: 4500 V; in-source collision energy: 10 eV. The instrument operated in the positive ion mode and was calibrated externally with the Tunemix mixture (Bruker Daltonics). The analyzed solutions were introduced at a flow rate of 4.0 L/min. The Compass Data Analysis software was used to determine the formulae of the compounds. The distance between the isotopic peaks allowed the calculation of the charge of the analyzed ions. Elemental analyses (C, H, and N) were performed using a Vario EL III element analyzer. Quantitative analysis of Br was carried out using Mikro-K-Elemental by means of Schoeniger's method. UV-Vis absorption spectra were recorded at room temperature in the wavelength range of 230–800 nm at intervals of 0.5 nm by a Cary 500 SCAN UV-VIS-NIR spectrophotometer. Measurements were performed on a 3.5 mL sample in a quartz cell with a path length of 10 mm, a bandwidth of 1.0 nm, and a scan speed of 250 nm/min. The concentration of the samples was ca. 10^{-5} $mol{\cdot}dm^{-3}$ to give absorption maximum for absorption studies to about 50% for a 1 cm path length. Thermogravimetry and differential thermal analyses (simultaneous TG-DTA) were recorded with a Setaram SETSYS 16/18 instrument. The calibrations of temperature and weight were performed following the procedure reported in the instruction manual of the equipment using indium (NIST SRM 2232) as the standard material for temperature and a set of exactly weighed samples supplied by Shimadzu for weight. Samples for thermogravimetric characterization were placed in open alumina crucibles in synthetic air (60% N_2, 40% O_2) or nitrogen dynamic atmosphere (flow rate: $1{\cdot}dm^3{\cdot}h^{-1}$). A heating rate of 10 $°C{\cdot}min^{-1}$ was applied, and all samples were studied between 30 and 1000 °C. For the compounds in which solvent molecules were found in the crystal lattice (**3** and **5**), additionally TG was conducted in the air atmosphere. Based on the weight losses, the amount of the solvent was calculated. The decomposition onset temperature was determined as the temperature at the maximum rate of weight loss (T_m) for the first weight loss. The purity of all novel compounds was determined by combustion analysis, which confirmed that they were at least 99% pure. Differential Scanning Calorimetry (DSC) traces were obtained using a Perkin Elmer model 8500. Temperature and enthalpy calibrations were performed using high purity standards (n-heptane and indium). The samples (2–5 mg, obtained *via* crystallization) were placed in sealed Al-pans at a heating rate of 10 $°C\cdot min^{-1}$ and a helium flow of 20.0 $mL\cdot min^{-1}$. The images were obtained using an FEI Tecnai G2 F20 X-TWIN Transmission Electron Microscope equipped with a Penta FET EDX detector at an acceleration voltage of 200 kV. The colloidal suspension of the sample with a concentration of about 5 $mg\cdot mL^{-1}$ in methanol was drop-cast on a 3 mm holey carbon copper grid and dried under an IR lamp for 15 min. The progress of the reaction was monitored by thin layer chromatography (TLC). TLC was performed on Merck silica gel 60 F254 plates. Chromatograms were visualized using UV light (254 nm). For the detection of unreacted amine, the chromatograms were first dipped in a 5% (w/v) solution of ninhydrin in 95% aqueous ethanol, and finally charred on a hot plate. Preparative separations were performed on a Sepacore® chromatography system (Büchi Labortechnik) consisting of two C-605 pump modules, a C-620 control unit, a C-640 UV-VIS detector, and a C-660 fraction collector. The system was controlled by the SepacoreControl 1.3 software. Flash chromatography separations were performed on pre-packed silica gel (40–63 μm) or silica HP (15–40 μm) polypropylene cartridges (21.0 × 129 mm, Büchi) at a flow rate of 25 $mL\cdot min^{-1}$. X-ray crystallography: the obtained crystals were immersed in perfluoropolyalkylether, a single crystal was selected, mounted on a glass fiber, and placed in a low-temperature N_2 stream. The crystallographic data collections for X-ray structure determinations of compounds **1**–**5** were performed on a Xcalibur PX four-circle diffractometer with a Ruby CCD detector with graphite monochromatized MoKa (λ = 0.71073 Å) radiation. The data were collected at 100(2) K (for compound **1**), 80(2) K (for compounds **2**–**3** and **5**), and 110(2) K (for compound **4**) using an Oxford Cryosystems cooler. Data collection, cell refinement, data reduction and analysis were carried out with the Xcalibur PX software, CrysAlis PRO (Agilent, 2012). The crystal structures of all compounds were solved by the direct methods with SHELXS-2013[3] and refined by a full-matrix least squares technique on F^2 using SHELXL-2014[4] with anisotropic thermal parameters for the non-H-atoms, except for the low-occupied positions of disordered atoms. The crystal data and the details of the data collection and the structure refinement are given in Tables S1, S4, S7, S10, and S12. CCDC 1456557 (**1**), 146559 (**2**), 146561 (**3**) 1456558 (**4**), and 1456560 (**5**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre. For compounds **1**–**5,** powder XRD studies were also performed. Such measurements were carried out to reveal if the resulting powders confirmed the same compositions as single crystals. Powder X-ray diffraction (PXRD) patterns of the dried powders were recorded on Bruker D8 ADVANCE diffractometer equipped with a copper lamp ($\lambda_{CuK\alpha}$ = 1.5406 Å) at 30 kV and 40 mA with a slit of 0.1°. Standard measurements were done for 2θ = 5°–50° with a 2θ step of 0.008° and a counting time of 0.5 s.

Syntheses:

General procedure A – Synthesis of imine-functionalized POSS: An aldehyde (3.41 mmol, 8 equiv) was added dropwise to a solution of octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and $MgSO_4$ (0.100 g) in the mixture of methanol (20 mL) and chloroform (5 mL). The resulting solution was stirred for 5 h at room temperature or until the reaction was completed, which was confirmed by TLC. After that time, the solvent was evaporated. The crude product was washed with water (3 × 20 mL). Workup by recrystallization or flash column chromatography gave the product, which was dried *in vacuo* (25 °C, 0.5 mbar), affording spectroscopically pure product.

General procedure B – Preparation of amines by a reduction reaction using $Na(CH_3COO)_3BH$: A mixture of the appropriate imine-POSS (1.0 equiv) and sodium triacetoxyborohydride (28 equiv) in the mixture of dichloromethane (20 mL) and methanol (1 mL) was stirred at room temperature for 2 h. The reaction mixture was neutralized with saturated $NaHCO_3$ and extracted with $CHCl_3$ (3 × 50 mL). The combined extracts were washed with brine, dried under $MgSO_4$, filtered, and evaporated *in vacuo* to give the final product.

Synthesis of 1. Benzaldehyde (0.347 mL, 0.362 g, 3.41 mmol, 8 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and methanol (20 mL) reacted according to General Procedure A for 2 h. Workup (recrystallization from chloroform) gave the product as a white solid in 92% yield (0.621 g, 0.391 mmol). Crystals suitable for single-crystal X-ray diffraction studies were obtained by recrystallization from a methanol solution. After 24 h, colorless, transparent needle-like crystals were obtained (size: 0.19 × 0.04 × 0.02 mm^3). mp (obtained from DSC, He): 133 °C; fp (obtained from DSC, He): 75 °C; mp (obtained from DTA, N_2): 137 °C; mp (obtained from DTA, air): 137 °C; ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.24 (s, 8H, C*H*N), 7.69 (t, $^3J_{HH}$ = 6.3 Hz, 16H, *o*-Ar), 7.38–7.33 (m, 24H, *m*-Ar and *p*-Ar), 3.59 (t, $^3J_{HH}$ = 6.6 Hz, 16H, CH_2N), 1.86–1.80 (m, 16H, CH_2), 0.69 (t, $^3J_{HH}$ = 8.3 Hz, 16H, $SiCH_2$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 161.1 (s, *C*=N), 136.4 (s, *i*-Ar), 130.5 (s, *p*-Ar), 128.6 (s, *m*-Ar), 128.2 (s, *o*-Ar), 64.1 (s, CH_2N), 24.4 (s, CH_2), 9.8 (s, $SiCH_2$); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$, 20 °C): δ = -66.54 (s); HR-MS (ESI+, TOF/$CHCl_3$), *m/z*: 1585.5372 $[M + H]^+$ (calcd 1585.5375), 793.2718 $[M + 2H]^{2+}$ (calcd 793.2724), 529.1877 $[M + 3H]^{3+}$ (calcd 529.1840); elemental analysis calcd (%) for $C_{80}H_{96}N_8O_{12}Si_8$ (1586.35): C 60.57, H 6.10, N 7.06; found: C 60.51, H 6.19, N 7.01; FTIR (nujol, KBr): $\tilde{\nu}$ = 1647(s, $\nu_{C=N}$) and 1580 (w, $\nu_{C=N}$), 1112 (s, $\nu_{\text{ring-asym Si-O-Si}}$), 754 (m, Ar), 693(m, Ar); UV−vis (dichloromethane, 293 K) λ [nm] (log ε in M^{-1} cm^{-1}): 247 (5.10), 278 (3.96), 287 (3.78); decomposition onset temperature (DTG, 10 °C·min^{-1}): 352 °C (air), 343 °C (N_2); temperature of decomposition to SiO_2 (determined by TGA measurement, air, 10 °C·min^{-1}), residue yield: 638 °C, 30.50% (calcd 30.30%).

Synthesis of 2. 4-Bromobenzaldehyde (0.643 g, 3.41 mmol, 8 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and methanol (20 mL) reacted according to General Procedure A for 2 h. Workup (recrystallization from chloroform) gave the product as a white solid in 83% yield (0.788 g, 0.355 mmol). Single crystals were grown from methanol solution by slow evaporation at room temperature. After a month, colorless, transparent needle-like crystals were obtained (size: 0.51 × 0.46 × 0.37 mm^3). mp (obtained from DSC, He): 169 °C; fp (obtained from DSC, He): 128 °C; mp (obtained from DTA, N_2): 180 °C; mp (obtained from DTA, air): 180 °C; ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.16 (s, 8H, C*H*N), 7.53 (d, $^3J_{HH}$= 8.5 Hz, 16H, *o*-Ar), 7.48 (d, $^3J_{HH}$= 8.4 Hz, 16H, *m*-Ar), 3.55 (t, $^3J_{HH}$ = 6.6 Hz, 16H, CH_2N), 1.82–1.76 (m, 16H, CH_2), 0.66 (t, $^3J_{HH}$ = 8.4 Hz, 16H, $SiCH_2$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 159.9 (s, *C*=N), 135.2 (s, *i*-Ph), 132.0 (s, *m*-Ph), 129.6 (s, *o*-Ph), 125.1 (s, *p*-Ph), 64.1 (s, CH_2N), 24.4 (s, CH_2), 9.8 (s, $SiCH_2$); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$, 300 K): δ = -66.7 (s); FTIR (nujol, KBr): $\tilde{\nu}$ = 1644 (s, $\nu_{C=N}$), 1588 (w, $\nu_{C=N}$), 1158 (s, $\nu_{\text{ring-asym Si-O-Si}}$), 816 (w, ν_{C-Br}); HRMS (ESI+, TOF/$CHCl_3$), *m/z*: 2212.8174 $[M + H]^+$ (calcd 2212.8187), 1106.4249 $[M + 2H]^{2+}$ (calcd 1106.4145), 738.2822 $[M + 3H]^{3+}$ (calcd 738.2777); elemental analysis calcd (%) for $C_{80}H_{88}Br_8N_8O_{12}Si_8$ (2217.52): C 43.33, H 4.00, N 5.05;

found: C 43.38, H 4.09, N 5.01; UV−vis (dichloromethane, 293 K) λ [nm] (log ε in M^{-1} cm^{-1}): 256 (3.89), 283 (3.03), 292 (2.80); decomposition onset temperature (DTG, 10 °C·min^{-1}): 300 °C (air), 303 °C (N_2); temperature of decomposition to SiO_2 (determined by TGA measurement, air, 10 °C·min^{-1}), residue yield: 625 °C, 25.82% (calcd 21.68%).

Synthesis of 3. 4-Nitrobenzaldehyde (0.543 g, 3.41 mmol, 8.0 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and the mixture of methanol (20 mL) and chloroform (5 mL) reacted according to General Procedure A for 2 h. Workup (flash column chromatography, eluent: hexane/CH_2Cl_2, 1:1 v/v) gave the product as a yellowish solid in 65% yield (0.543 g, 0.279 mmol). Single crystals were grown from chloroform by slow evaporation at room temperature. After a week, yellow, transparent needle-like crystals were obtained (size: 0.35 × 0.1 × 0.1 mm^3). mp (obtained from DSC, He): 206 °C; fp (obtained from DSC, He): 146 °C; mp (obtained from DTA, N_2): 204 °C; mp (obtained from DTA, air): 204 °C; ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.32 (s, 8H, C*H*N), 8.19 (d, $^3J_{HH}$ = 8.8 Hz, 16H, Ar), 7.83 (d, $^3J_{HH}$ = 8.8 Hz, 16H, Ar), 3.63 (t, $^3J_{HH}$ = 6.5 Hz, 16H, $C\mathit{H}_2N$), 1.89–1.79 (m, 16H, $C\mathit{H}_2$), 0.72 (t, $^3J_{HH}$ = 8.1 Hz, 16H, $SiC\mathit{H}_2$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 158.9 (s, *C*=N), 149.1, 141.7, 128.7, 124.0, (s, 6C, Ar), 64.3 (s, $\mathit{C}H_2N$), 24.4 (s, $\mathit{C}H_2$), 9.9 (s, $Si\mathit{C}H_2$); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$, 300 K): δ = -66.7 (s); FTIR (nujol, KBr): $\tilde{\nu}$ = 1645 (m, $\nu_{C=N}$), 1601 (m, ν_{NO2}), 1523 (m, $\nu_{asym\ NO2}$) 1343 (m, $\nu_{sym\ NO2}$) 1189 (m, $\nu_{C\text{-}N}$), 1108 (s, $\nu_{ring\text{-}asym\ Si\text{-}O\text{-}Si}$); HRMS (ESI+, TOF/$CHCl_3$), *m/z*: 1945.4211 $[M + H]^+$ (calcd 1945.4181), 973.2254 $[M + 2H]^{2+}$ (calcd 973.2127); elemental analysis calcd (%) for $C_{80}H_{88}N_{16}O_{28}Si_8$ (1946.33): C 49.37, H 4.56, N 11.51; found: C 49.42, H 4.51, N 11.57; UV−vis (dichloromethane, 293 K) λ [nm] (log ε in M^{-1} cm^{-1}): 285 (5.33); decomposition onset temperature (DTG, 10 °C·min^{-1}): 272 °C (air), 278 °C (N_2); temperature of decomposition to SiO_2 (determined by TGA measurement, air, 10 °C·min^{-1}), residue yield: 662 °C, 24.40% (calcd 24.70%).

Synthesis of 4. Salicylaldehyde (0.366 mL, 0.416 g, 3.41 mmol, 8.0 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and the mixture of methanol (20 mL) and chloroform (5 mL) reacted according to General Procedure A for 2 h. Workup (recrystallization from chloroform) gave the product as a yellow solid in 98% yield (0.716 g, 0.418 mmol). Single crystals were grown from methanol solution by slow evaporation at -8°C. After one month, yellow, transparent block crystals were obtained (size: 0.14 × 0.13 × 0.05 mm^3). mp (obtained from DSC, He): 124 °C; fp (obtained from DSC, He): 58 °C; mp (obtained from DTA, N_2): 124 °C; mp (obtained from DTA, air): 124 °C; ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ =13.61 (s, 8H, OH), 8.27 (s, 8H, C*H*N), 7.27 (t, $^3J_{HH}$ = 7.2 Hz, 8H, 4-Ph), 7.17 (d, $^3J_{HH}$= 7.7 Hz, 8H, 6-Ph), 6.90 (d, $^3J_{HH}$= 8.0 Hz, 8H, 3-Ph), 6.82 (t, $^3J_{HH}$ = 7.5 Hz, 8H, 5-Ph), 3.55 (t, $^3J_{HH}$ = 6.6 Hz, 16H, $C\mathit{H}_2N$), 1.82–1.76 (m, 16H, $C\mathit{H}_2$), 0.72 (t, $^3J_{HH}$ = 8.3 Hz, 16H, $SiC\mathit{H}_2$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 165.0 (s, *C*=N), 161.5 (s, Ph-OH), 132.2, 131.3 (s, 4,6-Ph), 118.9 (s, 5-Ph), 118.5 (s, 1-Ph), 117.1 (s, 3-Ph), 64.7 (s, $\mathit{C}H_2N$), 24.5 (s, $\mathit{C}H_2$), 9.6 (s, $Si\mathit{C}H_2$); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$, 300 K): δ = -66.7 (s); FTIR (nujol, KBr): $\tilde{\nu}$ = 2659 (m, $\nu_{O\text{-}H}$), 1631(s, $\nu_{C=N}$), 1581 (w, $\nu_{C=N}$), 1477 (m, $\nu_{C\text{-}O}$), 1280 (s, $\nu_{C\text{-}O}$), 1188 (m, $\nu_{C\text{-}N}$), 1099 (s, $\nu_{ring\text{-}asym\ Si\text{-}O\text{-}Si}$), 788 (w, $\nu_{N\text{-}C}$), 756 (m, $\nu_{keto\text{-}formN\text{-}H}$); HRMS (ESI+, TOF/$CHCl_3$), *m/z*: 1713.4968 $[M + H]^+$ (calcd 1713.5371), 857.2574 $[M + 2H]^{2+}$ (calcd 857.2520), 571.8456 $[M + 3H]^{3+}$ (calcd 571.8371); elemental analysis calcd (%) for $C_{80}H_{96}N_8O_{20}Si_8$ (1714.34): C 56.05, H 5.64, N 6.54; found: C 56.10, H 5.61, N 6.52; UV−vis (dichloromethane, 293 K) λ [nm] (log ε in M^{-1} cm^{-1}): 253 (4.96), 316 (4.60), 416 (3.08); decomposition onset temperature (DTG, 10 °C·min^{-1}): 343 °C (air), 344 °C (N_2); temperature of decomposition to SiO_2 (determined by TGA measurement, air, 10 °C·min^{-1}), residue yield: 631 °C, 27.87% (calcd 28.04%).

Synthesis of 5. 2-Hydroxy-1-naphthaldehyde (0.587 g, 3.41 mmol, 8.00 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and methanol (20 mL) reacted according to General Procedure A for 2 h. Workup gave the product as a yellow solid of imine in 84% yield (0.755 g, 0.357 mmol). Crystals suitable for single-crystal X-ray diffraction studies were obtained by dissolving this compound (0.01 g) in methanol (20 mL), heating it up to melting, and slow cooling to -8 °C; after a few months, **5** crystallized as yellow needles (size: 0.23 × 0.2 × 0.04 mm^3). mp (obtained from DSC, He): 89 °C; fp (obtained from DSC, He): 73 °C; mp (obtained from DTA, N_2, recrystallized from methanol): 94 °C; mp (obtained from DTA, air, recrystallized from methanol): 95 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ =14.45 (s, 8H, NH), 8.64 (s, 8H, C*H*N), 7.75 (d, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz, 8H, Nph), 7.61 (d, $^{3}J_{\mathrm{HH}}$ = 9.3 Hz, 8H, Nph), 7.54 (d, $^{3}J_{\mathrm{HH}}$ = 8.7 Hz, 8H, Nph), 7.30 (t, $^{3}J_{\mathrm{HH}}$ = 8.3 Hz, 8H, Nph), 7.16 (t, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, 8H, Nph), 6.85 (d, $^{3}J_{\mathrm{HH}}$ = 8.0 Hz, 8H, Nph), 3.54 (t, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, 16H, CH_2N), 1.79–1.85 (m, 16H, CH_2), 0.78 (t, $^{3}J_{\mathrm{HH}}$ = 8.5 Hz, 16H, SiCH_2); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 177.1 (s, *C*=N), 158.0 (s, Ph-OH), 137.4, 133.9, 129.2, 128.0, 126.1, 125.2, 122.7, 117.9, 106.6 (s, Nph), 54.9 (s, *C*H_2N), 24.6 (s, *C*H_2), 9.1 (s, Si*C*H_2); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$, 300 K): δ = -67.0 (s); FTIR (nujol, KBr): $\tilde{\nu}$ = 3348 (m, $\nu_{\mathrm{N\text{-}H}}$), 1633(s, $\nu_{\mathrm{C=N}}$), 1546 (w, $\nu_{\mathrm{C=N}}$), 1267 (s, $\nu_{\mathrm{C=O}}$), 1192 (m, $\nu_{\mathrm{C\text{-}N}}$), 1114 (s, $\nu_{\text{ring-asym Si-O-Si}}$), 749 (m, $\delta_{\mathrm{N\text{-}H}}$); HRMS (ESI+, TOF/$CHCl_3$), *m/z*: 2113.6986 [M + H]$^+$ (calcd 2113.6220), 1057.3229 [M + 2H]$^{2+}$ (calcd 1057.3146), 705.2191 [M + 3H]$^{3+}$ (calcd 705.2122); elemental analysis calcd (%) for $C_{112}H_{112}N_8O_{20}Si_8$ (2114.81): C 63.61, H 5.34, N 5.30; found: C 63.68, H 5.39, N 5.33; UV−vis (dichloromethane, 293 K) λ [nm] (log ε in M^{-1} cm^{-1}): 308 (3.47), 402 (3.34), 422 (3.35); decomposition onset temperature (DTG, 10 °C·min^{-1}): 331 °C (air), 330 °C (N_2); temperature of decomposition to SiO_2 (determined by TGA measurement, air, 10 °C·min^{-1}), residue yield: 652 °C, 22.86% (calcd 22.73%).

Synthesis of 6. This compound was prepared by General Procedure B. Compound **1** (0.100 g, 0.0630 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.374 g, 1.77 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave **6** as a colorless liquid in 95% yield (0.096 g, 0.0598 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.29–7.31 (m, 40H, Ph), 3.77 (s, 16H, NCH_2Ph), 2.65 (t, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, 16H, CH_2N), 1.59–1.65 (m, 16H, CH_2), 0.65 (t, $^{3}J_{\mathrm{HH}}$ = 8.5 Hz, 16H, SiCH_2); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 140.5, 128.4, 128.1, 126.9 (s, 6C, Ph), 53.9 (s, N*C*H_2Ph), 52.0 (s, *C*H_2N), 23.3 (s, *C*H_2), 9.6 (s, Si*C*H_2); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$, 300 K): δ = -66.7 (s); HRMS (ESI+, TOF/$CHCl_3$), *m/z*: 1601.6829 [M + H]$^+$ (calcd 1601.6768), 801.3403 [M + 2H]$^{2+}$ (calcd 801.3350), 534.5599 [M + 3H]$^{3+}$ (calcd 534.5591); elemental analysis calcd (%) for $C_{80}H_{112}N_8O_{12}Si_8$ (1602,48): C 59.96, H 7.04, N 6.99; found: 59.92, H 7.08, N 6.92.

Synthesis of 7. This compound was prepared by General Procedure B. Compound **2** (0.100 g, 0.0451 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.268 g, 1.26 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave **7** as a colorless solid in 91% yield (0.092 g, 0.0412 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.37 (d, $^{3}J_{\mathrm{HH}}$= 8.3 Hz, 16H, *o*-Ar), 7.13 (d, $^{3}J_{\mathrm{HH}}$= 8.3 Hz, 16H, *m*-Ar), 3.67 (s, 16H, NCH_2Ph), 2.57 (t, $^{3}J_{\mathrm{HH}}$ = 6.2 Hz, 16H, CH_2N), 1.63–1.48 (m, 16H, CH_2), 0.60 (t, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, 16H, SiCH_2); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 139.4 (s, *i*-Ph), 131.3 (s, *m*-Ph), 129.7 (s, *o*-Ph), 120.5 (s, *p*-Ph), 53.1 (s, N*C*H_2Ph), 51.7 (s, *C*H_2N), 23.2 (s, *C*H_2), 9.4 (s, Si*C*H_2); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$, 300 K): δ = -66.7 (s); HRMS (ESI+, TOF/$CHCl_3$), *m/z*: 2228.9452 [M + H]$^+$ (calcd 2228.9439), 1116.9735 [M + 2H]$^{2+}$ (calcd 1116.9742), 745.6529 [M + 3H]$^{3+}$ (calcd 745.6515); elemental analysis calcd (%) for $C_{80}H_{104}Br_8N_8O_{12}Si_8$ (2233.64): C 42.73, H 4.68, N 5.05, Br 28.79; found: C 42.68, H 4.70, N 5.11, Br 28.72.

Synthesis of 8. This compound was prepared by General Procedure B. Compound **3** (0.100 g, 0.0514 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.305 g, 1.44 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave **8** as a beige solid in 90% yield (0.089 g, 0.046 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.09 (d, $^{3}J_{\mathrm{HH}}$ = 8.5 Hz, 16H, *m*-Ar), 7.49 (d, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz, 16H, *o*-Ar), 3.84 (s, 16H, NCH_2Ph), 2.56 (t, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, 16H, CH_2N), 1.60–1.50 (m, 16H, CH_2), 0.58 (t, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 16H, SiCH_2); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 146.9, 130.7, 128.5, 123.6, (s, 6C, Ar), 53.1 (s, N*C*H_2Ph), 51.9 (s, *C*H_2N), 23.4 (s, *C*H_2), 9.4 (s, Si*C*H_2); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$, 300 K): δ = -66.7 (s); HRMS (ESI+, TOF/$CHCl_3$), *m/z*: 1945.4175 [M + H]$^+$ (calcd 1945.4181), 973.7125 [M + 2H]$^{2+}$ (calcd 973.7137), 649.4775 [M + 3H]$^{3+}$ (calcd 649.4782); elemental analysis calcd (%) for $C_{80}H_{88}N_{16}O_{28}Si_8$ (1946.33): C 49.37, H 4.56, N 11.51; found C 49.42, H 4.51, N 11.40. UV−vis (dichloromethane, 293 K) λ [nm] (log ε in M^{-1} cm^{-1}): 277 (4.52);

Synthesis of 9. This compound was prepared by General Procedure B. Compound **4** (0.100 g, 0.0583 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.346 g, 1.63 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave **9** as a white solid in 97% yield (0.098 g, 0.0566 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.12 (td, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.6 Hz, 8H, Ph), 6.95 (d, $^3J_{HH}$ = 7.5 Hz, 8H, Ph), 6.75 – 6.75 (m, 8H, Ph), 6.74 – 6.72 (m, 16H, Ph), 3.97 (s, 16H, NCH_2Ph), 2.67 (t, $^3J_{HH}$ = 7.1 Hz, 16H, CH_2N), 1.59–1.66 (m, 16H, CH_2), 0.64 (t, $^3J_{HH}$ = 8.5 Hz, 16H, SiCH_2); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 159.2 (s, Ph-OH), 151.4, 150.5, 142.9, 122.2, 121.9 (s, 5xPh), 64.1 (s, CH_2N), 45.9 (s, NCH2Ph), 24.2 (s, CH_2), 9.8 (s, SiCH_2); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$, 300 K): δ = -66.6 (s); FTIR (nujol, KBr): $\tilde{\nu}$ = 3311 (m, $\nu_{N\text{-}H}$), 2723 (m, $\nu_{O\text{-}H}$), 1739, 1589 (m, $\delta_{N\text{-}H}$), 1260 (s, $\nu_{C\text{-}O}$), 1097 (s, $\nu_{\text{ring-asym Si-O-Si}}$), 800 (w, $\nu_{N\text{-}C}$), 751 (m, $\delta_{O\text{-}H}$); HRMS (ESI+, TOF/$CHCl_3$), *m/z*: 1729.6275 $[M + H]^+$ (calcd 1729.6220), 865.3137 $[M + 2H]^{2+}$ (calcd 865.3146); elemental analysis calcd (%) for $C_{80}H_{112}N_8O_{20}Si_8$ (1730.47): C 55.53, H 6.52, N 6.48. found: C 55.50, H 6.58, N 6.41; UV−vis (dichloromethane, 293 K) λ [nm] (log ε in M^{-1} cm^{-1}): 232 (4.32), 278 (4.20);

Synthesis of 10. This compound was prepared by General Procedure B. Compound **5** (0.100 g, 0.0473 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.281 g, 1.32 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave **10** as a yellowish solid in 86% yield (0.087 g, 0.0408 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.72 (d, $^3J_{HH}$ = 8.4 Hz, 8H, Nph), 7.59 (d, $^3J_{HH}$ = 9.3 Hz, 8H, Nph), 7.37 (d, $^3J_{HH}$ = 8.7 Hz, 8H, Nph), 7.26 (t, $^3J_{HH}$ = 8.3 Hz, 8H, Nph), 7.24 (t, $^3J_{HH}$ = 7.8 Hz, 8H, Nph), 7.00 (d, $^3J_{HH}$ = 8.0 Hz, 8H, Nph), 4.38 (s, 16H, NCH_2Ph), 2.68 (t, $^3J_{HH}$ = 6.5 Hz, 16H, CH_2N), 1.60–1.71 (m, 16H, CH_2), 0.64 (t, $^3J_{HH}$ = 8.5 Hz, 16H, SiCH_2); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 157.0 (s, Ph-OH), 132.5, 129.1, 128.9, 128.5, 126.4, 122.5, 121.0, 119.5, 111.9. (s, Nph), 51.4 (s, CH_2N), 47.8 (s, NCH2Ph), 23.1 (s, CH_2), 9.4 (s, SiCH_2); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$, 300 K): δ = -66.3 (s); HRMS (ESI+, TOF/MeOH), m/z: 2129.7472 $[M + H]^+$ (calcd 2129.7472); elemental analysis calcd (%) for $C_{112}H_{129}N_8O_{20}Si_8$ (2130.94): C 63.21, H 6.14, N 5.19. found: C 63.13, H 6.05, N 5.26; UV−vis (dichloromethane, 293 K) λ [nm] (log ε in M^{-1} cm^{-1}): 237 (4.39), 279 (8.87), 290 (3.77), 320 (3.47), 332 (3.55);

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Table S1. Crystal data and structure refinement for **1**.

Identification code	mj661
Empirical formula	$C_{80}H_{96}N_8O_{12}Si_8$
Formula weight	1586.36
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	9.982(3)
b/Å	13.141(4)
c/Å	16.763(5)
α/°	82.27(3)
β/°	82.12(3)
γ/°	77.37(3)
Volume/Å^3	2112.9(11)
Z	1
ρ_{calc}g/cm^3	1.247
μ/mm^{-1}	0.19
F(000)	840
Crystal size/mm^3	0.19 × 0.04 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.6 to 61.6
Index ranges	$-14 \leq h \leq 13$, $-18 \leq k \leq 12$, $-23 \leq l \leq 23$
Reflections collected	15995
Independent reflections	11237 [R_{int} = 0.0384, R_{sigma} = 0.1040]
Data/restraints/parameters	11237/0/487
Goodness-of-fit on F^2	1.006
Final R indexes [I>=2σ (I)]	R_1 = 0.0628, wR_2 = 0.1128
Final R indexes [all data]	R_1 = 0.1169, wR_2 = 0.1337
Largest diff. peak/hole / e Å^{-3}	0.51/-0.42

Table S2. Selected bond distances (Å) and bond angles (°) of **1**.

Atom	Atom	Length	Atom	Atom	Atom	Angle
	Si-O			**O-Si-O**		
Si1	O1	1.6267(18)	O5	Si1	O2	108.97(9)
Si1	O2	1.6220(18)	O5	Si1	O1	109.31(9)
Si1	O5	1.6215(18)	O2	Si1	O1	108.84(9)
Si2	O2	1.6213(18)	O3	Si2	O2	109.34(10)
Si2	O3	1.6185(18)	O3	Si2	O6^1	108.94(9)
Si2	O6^1	1.6212(19)	O6^1	Si2	O2	108.96(9)
Si3	O1^1	1.6237(19)	O3	Si3	O1^1	109.40(9)
Si3	O3	1.6226(17)	O4	Si3	O3	108.46(9)
Si3	O4	1.6180(18)	O4	Si3	O1^1	109.01(9)
Si4	O4	1.6271(18)	O5	Si4	O4	108.98(9)
Si4	O5	1.6256(17)	O6	Si4	O5	109.16(9)
Si4	O6	1.6253(18)	O6	Si4	O4	108.99(9)
	Si-C			**Si-O-Si**		
Si1	C1A	1.839(2)	Si1	O5	Si4	149.60(11)
Si2	C1B	1.839(2)	Si2	O3	Si3	150.07(11)
Si3	C1C	1.846(2)	Si2	O2	Si1	147.75(11)
Si4	C1D	1.840(3)	Si2^1	O6	Si4	145.71(11)
	C=N		Si3	O4	Si4	148.16(12)
N1A	C4A	1.263(3)	Si3^1	O1	Si1	145.48(11)
N1B	C4B	1.269(3)				
N1C	C4C	1.268(3)				
N1D	C4D	1.263(3)				
	C-N					
N1A	C3A	1.464(3)				
N1B	C3B	1.458(3)				
N1C	C3C	1.466(3)				
N1D	C3D	1.460(3)				

Symmetry code: ^{1}2-X,1-Y,1-Z

Table S3. Geometry of hydrogen bonds and close contacts for **1**.

D*—H···*A	**d(D—H)/Å**	**d(H···*A*)/Å**	**d(*D*···*A*)/Å**	***D*—H···*A* /°**
		Intermolecular, weak		
C2B—H2BB···N1A^2	0.99	2.53	3.391(4)	146

Symmetry code: ^{2}1+X,+Y,+Z

Table S4. Crystal data and structure refinement for **2**.

Identification code	mj488a	
Empirical formula	$C_{80}H_{88}Br_8N_8O_{12}Si_8$	
Formula weight	2217.58	
Temperature/K	80	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions:		
	a = 11.895(3) Å	α = 66.17(5)°
	b = 14.061(4) Å	β = 85.35(5)°
	c = 15.763(4) Å	γ = 68.70(5)°
Volume/Å^3	2240.3(15)	
Z	1	
ρ_{calc}g/cm^3	1.644	
μ/mm^{-1}	3.75	
F(000)	1112	
Crystal size/mm^3	0.51 × 0.46 × 0.37	
Radiation	MoKα (λ = 0.71073)	
2Θ range for data collection/°	5.5 to 56.1	
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-20 \leq l \leq 20$	
Reflections collected	20253	
Independent reflections	10851 [R_{int} = 0.0347, R_{sigma} = 0.0735]	
Data/restraints/parameters	10851/16/598	
Goodness-of-fit on F^2	1.06	
Final R indexes [I>=2σ (I)]	R_1 = 0.0497, wR_2 = 0.0954	
Final R indexes [all data]	R_1 = 0.0720, wR_2 = 0.1104	
Largest diff. peak/hole / e Å^{-3}	1.06/-1.24	
Absorption correction	Analytical	
Max. and min. transmission	0.366 to 0.260	
Refinement method	Full-matrix least-squares on F^2	

Table S5. Selected bond distances (Å) and bond angles (°) of **2**.

Atom	Atom	Length	Atom	Atom	Atom	Angle
	Si-O			**O-Si-O**		
O1	Si3^{1}	1.619(3)	O1	Si1	O2	108.78(14)
O1	Si1	1.620(3)	O1^{1}	Si3	O4	109.79(14)
O2	Si1	1.622(3)	O1^{1}	Si3	O3	108.87(14)
O2	Si2	1.623(2)	O3	Si2	O2	108.68(14)
O3	Si2	1.617(2)	O4	Si3	O3	108.95(13)
O3	Si3	1.626(2)	O5	Si1	O1	109.68(14)
O4	Si3	1.620(2)	O5	Si1	O2	109.24(13)
O4	Si4	1.624(2)	O5	Si4	O4	108.20(13)
O5	Si1	1.616(3)	O6	Si4	O5	109.35(13)
O5	Si4	1.624(2)	O6	Si4	O4	108.14(13)
O6	Si2^{1}	1.612(3)	O6^{1}	Si2	O3	109.48(13)
O6	Si4	1.614(3)	O6^{1}	Si2	O2	108.83(14)
	Si-C			**Si-O-Si**		
Si1	C1A	1.845(3)	Si1	O2	Si2	151.76(16)
Si2	C1B	1.839(4)	Si1	O5	Si4	143.18(16)
Si3	C1C	1.837(3)	Si2	O3	Si3	143.04(16)
Si4	C1D	1.835(4)	Si2^{1}	O6	Si4	152.45(17)
	C-N		Si3	O4	Si4	152.03(17)
C4A	N1A	1.254(5)	Si3^{1}	O1	Si1	150.86(15)
C4B	N1B	1.266(4)				
C4C	N1C	1.266(5)				
C4D	N1D	1.251(12)				
C4E	N1E	1.256(11)				
	C-N					
C3A	N1A	1.461(5)				
C3B	N1B	1.447(5)				
C3C	N1C	1.442(5)				
C3D	N1D	1.439(18)				
C3E	N1E	1.47(2)				
	C-Br					
Br1	C8A	1.903(4)				
Br2	C8B	1.881(4)				
Br3	C8C	1.898(5)				
Br4	C8D	1.776(11)				

Symmetry code: ^{1}2-X,-Y,-Z

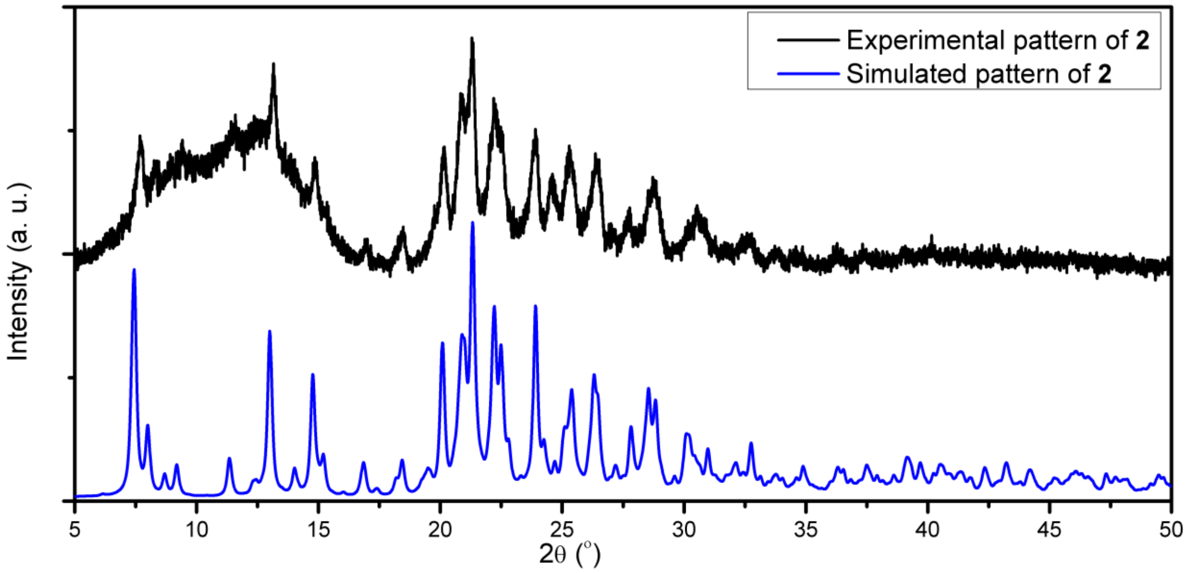

Figure S1. The simulated XRD patterns from the single crystal data and the experimental powder XRD patterns of compound **2**.

Table S6. Crystal data and structure refinement for **3**.

Identification code	MJ517a
Empirical formula	$C_{80}H_{86}N_{16}O_{28}Si_8\cdot4(CHCl_3)$
Formula weight	2421.83
Temperature/K	80
Crystal system	triclinic
Space group	P-1
a/Å	9.578(4)
b/Å	16.150(7)
c/Å	18.867(7)
α/°	108.08(4)
β/°	98.79(3)
γ/°	92.53(3)
Volume/Å^3	2729(2)
Z	1
ρ_{calc}g/cm^3	1.474
μ/mm^{-1}	0.47
F(000)	1246
Crystal size/mm^3	0.35 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.7 to 61.6
Index ranges	$-13 \leq h \leq 12$, $-22 \leq k \leq 21$, $-25 \leq l \leq 24$
Reflections collected	22452
Independent reflections	14558 [$R_{int} = 0.024$, $R_{sigma} = 0.052$]
Data/restraints/parameters	14558/9/817
Goodness-of-fit on F^2	1.02
Final R indexes [I>=2σ (I)]	$R_1 = 0.067$, $wR_2 = 0.170$
Final R indexes [all data]	$R_1 = 0.096$, $wR_2 = 0.189$
Largest diff. peak/hole / e Å^{-3}	1.00/-0.54

Table S7. Selected bond distances (Å) and bond angles (°) of **3**.

Atom	Atom	Length	Atom	Atom	Atom	Angle
	Si-O			**O-Si-O**		
Si1	O1	1.628(2)	O4	Si1	O1	108.78(10)
Si1	O4	1.626(2)	O5	Si1	O1	109.06(10)
Si1	O5	1.618(2)	O2	Si2	O1	109.31(10)
Si2	O1	1.6241(19)	O6^{1}	Si2	O1	108.79(10)
Si2	O2	1.617(2)	O3	Si3	O2	108.99(10)
Si2	O6^{1}	1.624(2)	O5^{1}	Si3	O2	108.28(11)
Si3	O2	1.624(2)	O5^{1}	Si3	O3	108.62(11)
Si3	O3	1.623(2)	O6	Si4	O3	109.15(10)
Si3	O5^{1}	1.623(2)	O5	Si1	O4	109.26(11)
Si4	O3	1.6251(19)	O3	Si4	O4	108.68(10)
Si4	O4	1.626(2)	O6	Si4	O4	109.32(11)
Si4	O6	1.625(2)	O2	Si2	O6^{1}	109.45(10)
	Si-C			**Si-O-Si**		
Si1	C1A	1.836(2)	Si1	O5	Si3^{1}	148.60(12)
Si2	C1B	1.837(3)	Si2	O1	Si1	144.77(12)
Si3	C1C	1.886(10)	Si2	O2	Si3	152.96(13)
Si3	C1E	1.72(2)	Si2^{1}	O6	Si4	147.36(12)
Si4	C1D	1.837(3)	Si3	O3	Si4	145.41(13)
	C=N		Si4	O4	Si1	152.17(13)
N1A	C4A	1.270(4)				
N1B	C4B	1.262(4)				
N1C	C4C	1.254(7)				
N1D	C4D	1.265(4)				
N1E	C4E	1.408(18)				
	C-N					
C3A	N1A	1.458(4)				
C3B	N1B	1.474(4)				
C3C	N1C	1.589(8)				
C3D	N1D	1.456(4)				
C3E	N1E	1.76(3)				

Symmetry code: ^{1}2-X,-Y,-Z;

Table S8. Geometry of hydrogen bonds and close contacts for **3**.

D—H···*A*	d(D—H)/Å	d(H···*A*)/Å	d(*D*···*A*)/Å	*D*—H···*A* /°
Intermolecular, moderate				
C4B—H4B···O1A[3]	0.95	2.48	3.365(4)	154
Intramolecular, moderate				
C3A—H3A···Cl19[2]	0.99	2.73	3.68(2)	161
C7B—H7B···Cl18[2]	0.95	2.88	3.541(13)	128

Symmetry codes: [2]1-X,2-Y,-Z; [3]2-X,2-Y,1-Z

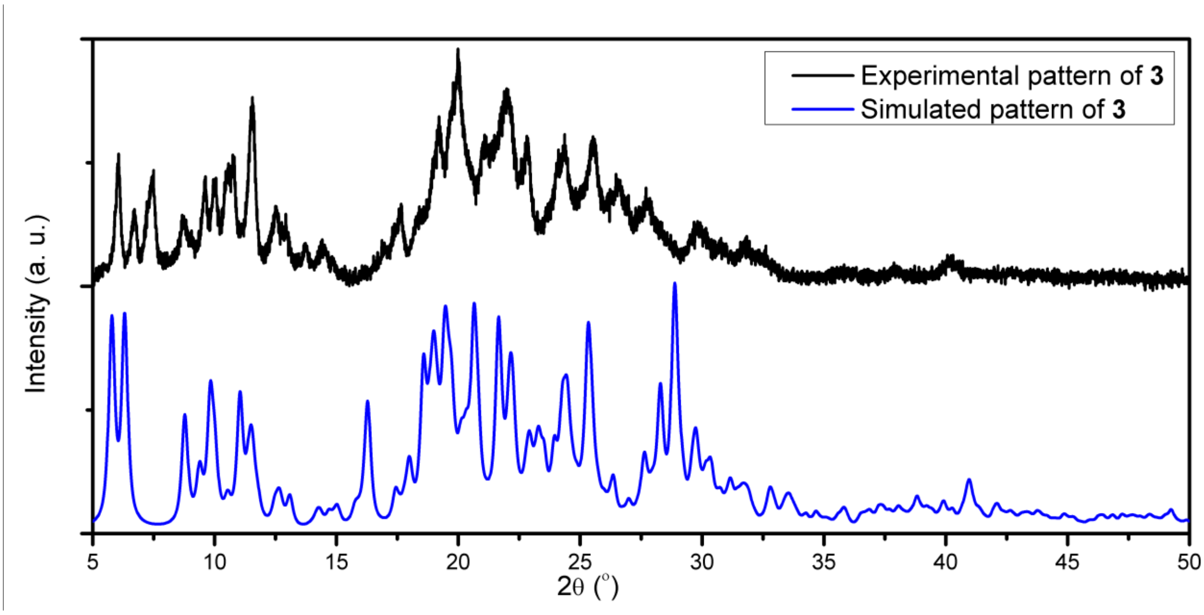

Figure S2. The simulated XRD patterns from the single crystal data and the experimental powder XRD patterns of compound **3** after remove of solvent.

Table S9. Crystal data and structure refinement for **4**.

Identification code	MJ487
Empirical formula	$C_{80}H_{96}N_8O_{20}Si_8$
Formula weight	1714.36
Temperature/K	110
Crystal system	triclinic
Space group	P-1
a/Å	9.381(3)
b/Å	14.034(4)
c/Å	16.112(5)
α/°	91.48(3)
β/°	94.07(3)
γ/°	90.06(3)
Volume/Å^3	2115.1(11)
Z	1
ρ_{calc}g/cm^3	1.346
μ/mm^{-1}	0.20
F(000)	904
Crystal size/mm^3	0.14 × 0.13 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.7 to 61.3
Index ranges	$-12 \leq h \leq 13$, $-20 \leq k \leq 11$, $-20 \leq l \leq 22$
Reflections collected	19597
Independent reflections	11718 [R_{int} = 0.0244, R_{sigma} = 0.0529]
Data/restraints/parameters	11718/0/527
Goodness-of-fit on F^2	1.01
Final R indexes [I>=2σ (I)]	R_1 = 0.0475, wR_2 = 0.1042
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1163
Largest diff. peak/hole / e Å^{-3}	0.41/-0.26

Table S10. Selected bond distances (Å) and bond angles (°) of **4**.

Atom	Atom	Length	Atom	Atom	Atom	Angle
	Si-O				**O-Si-O**	
Si1	O1	1.6302(14)	O5	Si1	O2	109.20(7)
Si1	O2	1.6265(13)	O5	Si1	O1	109.76(7)
Si1	O5	1.6206(14)	O2	Si1	O1	108.86(7)
Si2	O2	1.6234(14)	O3	Si2	O6^{1}	109.13(7)
Si2	O3	1.6206(14)	O3	Si2	O2	109.74(7)
Si2	O6^{1}	1.6233(13)	O6^{1}	Si2	O2	108.95(7)
Si3	O1^{1}	1.6314(14)	O3	Si3	O4	109.50(7)
Si3	O3	1.6232(14)	O3	Si3	O1^{1}	108.60(7)
Si3	O4	1.6255(13)	O4	Si3	O1^{1}	108.86(7)
Si4	O4	1.6265(13)	O5	Si4	O6	108.82(7)
Si4	O5	1.6231(14)	O5	Si4	O4	109.43(7)
Si4	O6	1.6245(14)	O6	Si4	O4	108.39(7)
	Si-C				**Si-O-Si**	
Si1	C1A	1.8444(19)	Si1	O1	Si3^{1}	144.98(8)
Si2	C1B	1.8381(18)	Si1	O5	Si4	152.16(9)
Si3	C1C	1.8486(18)	Si2	O2	Si1	143.90(9)
Si4	C1D	1.8425(18)	Si2	O3	Si3	152.46(9)
	C=N		Si2^{1}	O6	Si4	145.93(8)
N1A	C4A	1.281(2)	Si3	O4	Si4	144.30(8)
N1B	C4B	1.281(2)				
N1C	C4C	1.275(2)				
N1D	C4D	1.285(2)				
	C-N					
N1A	C3A	1.461(2)				
N1B	C3B	1.460(2)				
N1C	C3C	1.465(3)				
N1D	C3D	1.465(2)				
	C-O					
O1A	C6A	1.354(2)				
O1B	C6B	1.349(2)				
O1C	C6C	1.347(2)				
O1D	C6D	1.353(2)				

Symmetry code: ^{1}2-X,-Y,-Z

Table S11. Geometry of hydrogen bonds and close contacts for **4**.

D—H···*A*	d(D—H)/Å	d(H···*A*)/Å	d(*D*···*A*)/Å	*D*—H···*A* /°
		Intramolecular, strong		
O1B—H1B···N1B	0.84	1.83	2.575(2)	148
O1D—H1D···N1D	0.84	1.85	2.596(2)	148
O1C—H1C···N1C	0.84	1.86	2.596(2)	146
O1A—H1A···N1A	0.84	1.90	2.641(2)	147
		Intermolecular, weak		
C2A—H2AB···O1B^{2}	0.99	2.39	3.150(2)	134

Symmetry code: ^{2}-1+X,+Y,+Z

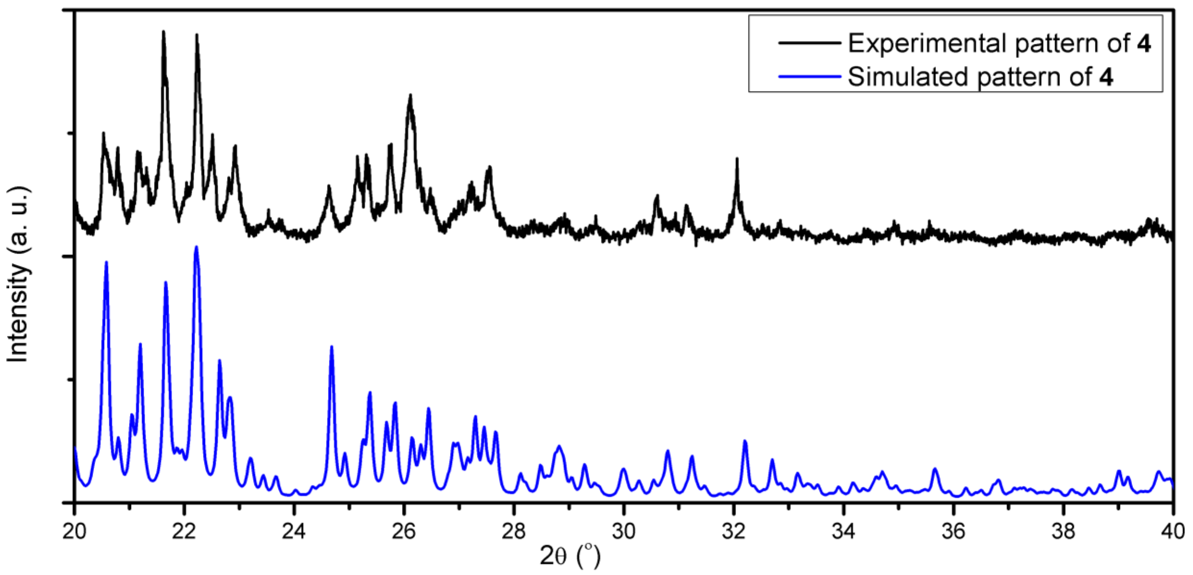

Figure S3. The simulated XRD patterns from the single crystal data and the experimental powder XRD patterns of compound **4**.

Table S12. Crystal data and structure refinement for **5**.

Identification code	MJ491b	
Moiety formula	$C_{112}H_{112}N_8O_{20}Si_8 \cdot 6.1(CH_3OH)$	
Formula weight	2310.26	
Temperature/K	80	
Radiation	MoKα (λ = 0.71073)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.292(6) Å	α = 97.14(4)°
	b = 14.663(7) Å	β = 97.17(4)°
	c = 15.109(7) Å	γ = 110.39(4)°
Volume/Å^3	2896(2)	
Z	1	
ρ_{calc}g/cm^3 (calculated)	1.325	
Absorption coefficient μ/mm^{-1}	0.17	
F(000)	1222	
Crystal size/mm^3	0.23 × 0.2 × 0.04	
2Θ range for data collection/°	5.5 to 51.0	
Index ranges	$-17 \le h \le 17$, $-16 \le k \le 17$, $-12 \le l \le 18$	
Reflections collected	18913	
Independent reflections	10761 [R_{int} = 0.0562, R_{sigma} = 0.1430]	
Data/restraints/parameters	10761/7/772	
Goodness-of-fit on F^2	1.01	
Final R indexes [I>=2σ (I)]	R_1 = 0.0721, wR_2 = 0.1426	
Final R indexes [all data]	R_1 = 0.1485, wR_2 = 0.1770	
Largest diff. peak/hole / e Å^{-3}	0.46/-0.42	
Absorption correction	none	
Refinement method	Full-matrix least-squares on F^2	

Table S13. Selected bond distances (Å) and bond angles (°) of **5**.

Atom	Atom	Length	Atom	Atom	Atom	Angle
	Si-O			**O-Si-O**		
O1	Si1	1.623(3)	O1	Si4	O4	109.39(16)
O1	Si4	1.619(3)	O2	Si1	O5	109.76(16)
O2	Si1	1.622(3)	O2	Si1	O1	108.79(16)
O2	Si2	1.625(3)	O2	Si2	O6	109.01(16)
O3	Si2	1.628(3)	O2	Si2	O3	109.42(16)
O3	Si3	1.618(3)	O3	Si3	O5^{1}	109.48(16)
O4	Si3	1.625(3)	O3	Si3	O4	109.64(16)
O4	Si4	1.625(3)	O5	Si1	O1	108.56(16)
O5	Si1	1.623(3)	O5^{1}	Si3	O4	109.15(16)
O5	Si3^{1}	1.619(3)	O6	Si2	O3	109.20(16)
O6	Si2	1.627(3)	O6^{1}	Si4	O1	109.11(15)
O6	Si4^{1}	1.615(3)	O6^{1}	Si4	O4	109.26(16)
	Si-C			**Si-O-Si**		
Si1	C1A	1.844(4)	Si1	O2	Si2	149.0(2)
Si2	C1B	1.837(4)	Si3	O3	Si2	148.82(19)
Si3	C1C	1.841(4)	Si3	O4	Si4	148.52(19)
Si4	C1D	1.842(4)	Si3^{1}	O5	Si1	148.37(19)
	C-N		Si4	O1	Si1	150.1(2)
C4A	N1A	1.304(6)	Si4^{1}	O6	Si2	148.5(2)
C4B	N1B	1.306(5)				
C4C	N1C	1.303(5)				
C4D	N1D	1.307(5)				
	C-N					
C3A	N1A	1.463(6)				
C3B	N1B	1.458(5)				
C3C	N1C	1.454(5)				
C3D	N1D	1.466(5)				
	C=O					
C6A	O1A	1.305(6)				
C6B	O1B	1.273(5)				
C6C	O1C	1.270(5)				
C6D	O1D	1.289(5)				

Symmetry code: ^{1}1-X,-Y,1-Z

Table S14. Geometry of hydrogen bonds and close contacts for **5**.

D*—H···*A	**d(D—H)/Å**	**d(H···*A*)/Å**	**d(*D*···*A*)/Å**	***D*—H···*A* /°**
Intramolecular, strong				
N1D—H1D···O1D	0.88	1.80	2.519(5)	138
N1A—H1A···O1A	0.88	1.85	2.545(6)	134
N1C—H1C···O1C	0.88	1.92	2.595(5)	132
N1B—H1B···O1B	0.88	1.92	2.606(5)	133
Intramolecular, moderate				
N1C—H1C···O1B^{6}	0.88	2.23	2.842(5)	127
N1B—H1B···O1C^{4}	0.88	2.38	3.066(5)	135
Intermolecular, moderate				
O1M—H1M···O1D	0.84	1.84	2.679(5)	174
O4M—H4M···O1A	0.84	1.96	2.715(9)	148
O2M—H2M···O1C	0.85	1.92	2.766(9)	179
O3M—H3M···O1C	0.84	2.24	2.816(12)	126
O5M—H5M···O1	0.84	2.52	3.32(2)	159
Intermolecular, weak				
C4A—H4A···O6M^{2}	0.95	2.25	3.16(4)	160
C4B—H4B···O1M^{3}	0.95	2.40	3.299(6)	157
C2A—H2AA···O8M^{7}	0.99	2.45	3.35(2)	150
C3C—H3CB···O1M^{5}	0.99	2.53	3.446(6)	153

Symmetry codes: ^{2}1+X,+Y,+Z; ^{3}1-X,-Y,1-Z; ^{4}+X,+Y,-1+Z; ^{5}-1+X,+Y,+Z; ^{6}+X,+Y,1+Z; ^{7}1-X,1-Y,1-Z;

Table S15. Thermal properties of **1-5** based on TG-DTA studies.

Comp.	Atm.	Melting temperature [°C]	Calculated residue yield [%]	Residue yield [%]	Δ	$T_{5\%}$	T_1	T_2	T_3
1	Air	137	30.30	30.50	0.20	292	352	638	
1	N_2	137	30.30	34.44	4.14	304	343	666	
2	Air	180	21.68	25.82	4.14	293	300	443	625
2	N_2	180	21.68	30.34	8.66	302	303	419	649
3	Air	204	24.70	24.40	-0.30	270	272	662	
3	N_2	204	24.70	38.32	13.62	271	278	661	
4	Air	124	28.04	27.87	-0.17	306	343	631	
4	N_2	124	28.04	45.16	17.12	322	344	631	
5	Air	78	22.73	22.86	0.13	298	330	652	
5	N_2	78	22.73	29.63	6.90	299	326	665	

Calculated residue yield [%] calculated based on the decomposition to silicon dioxide SiO_2. Δ = The difference between the determined and calculated values. $T_{5\%}$ refers to the temperature at which a 5% loss in weight is observed. The T_1, T_2, T_3, T_4 temperatures correspond to the maximum rate of decomposition for each stage evaluated from the peaks of the DTG curves.

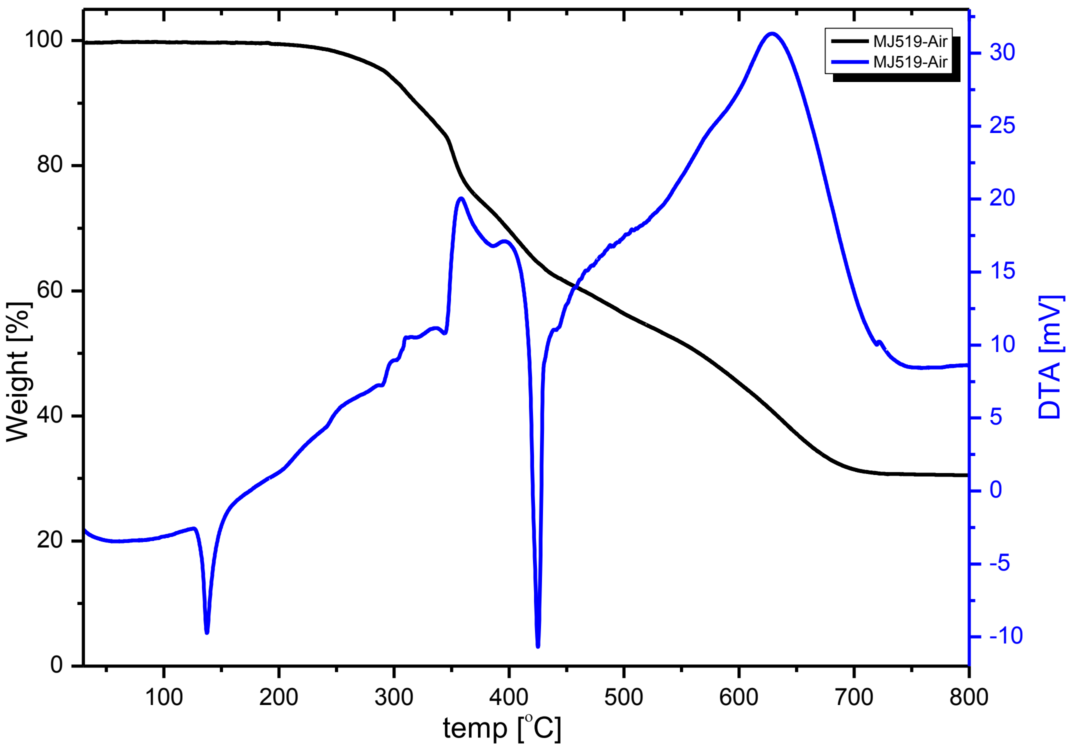

Figure S4. TG (black line), and DTA (blue line) thermogram of **1** at a heating rate of 10 °C/min. Left graph in the air atmosphere (60% N_2, 40% O_2).

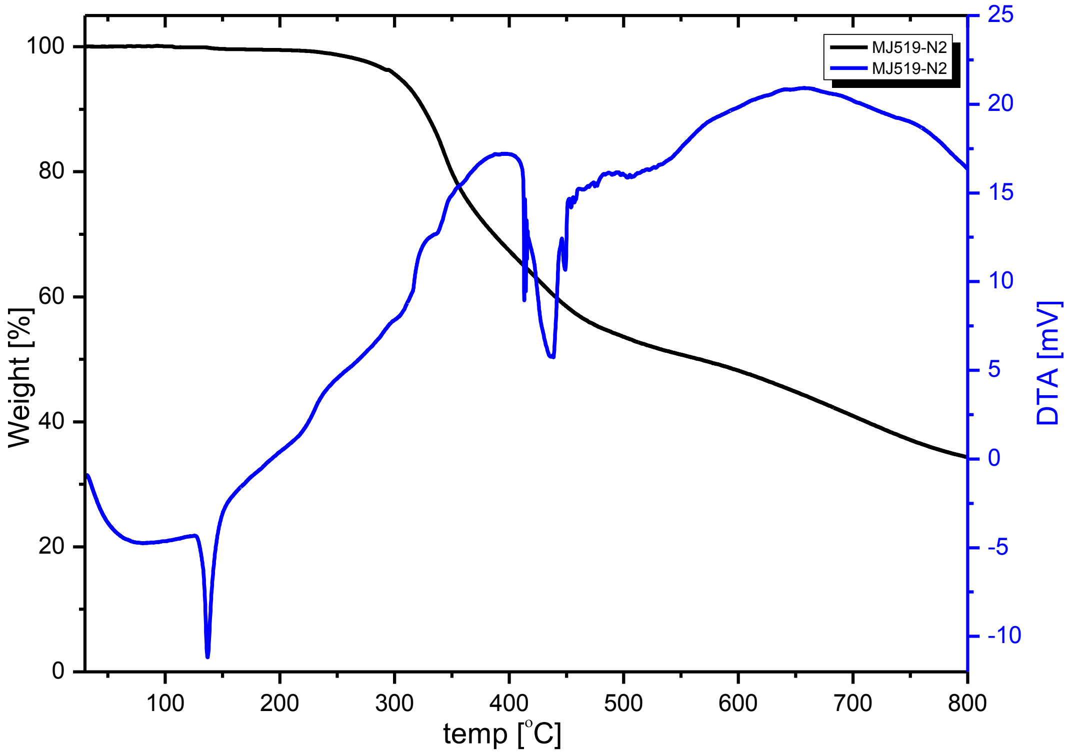

Figure S5. TG (black line), and DTA (blue line) thermogram of **1** at a heating rate of 10 °C/min. In nitrogen.

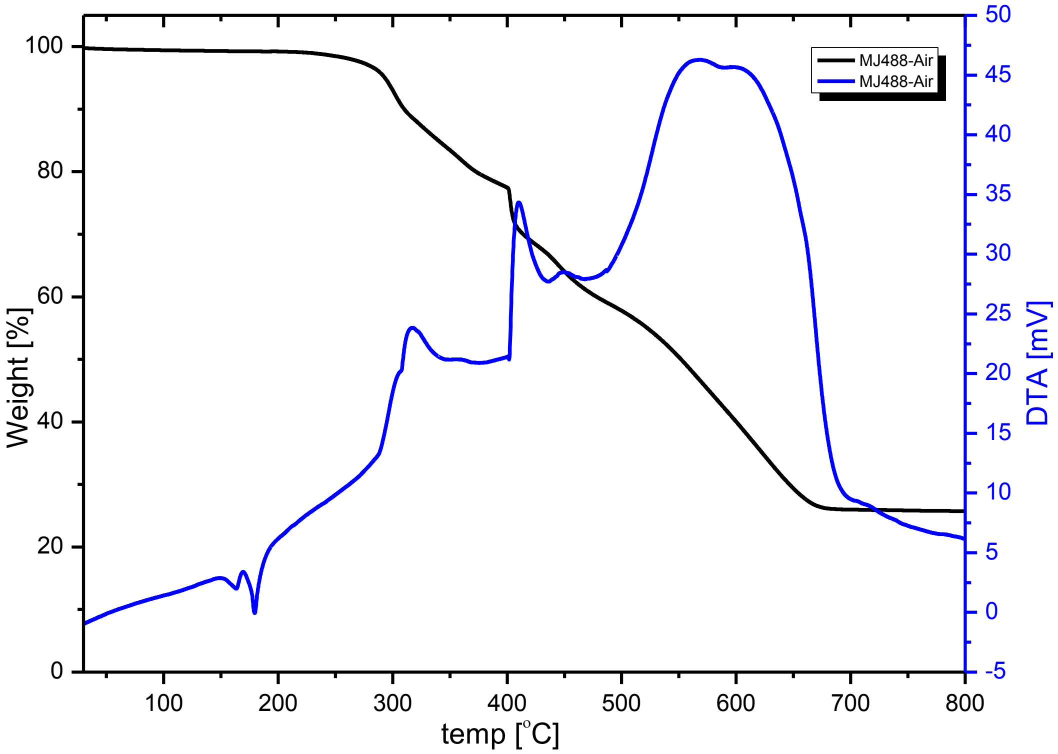

Figure S6. TG (black line), and DTA (blue line) thermogram of **2** at a heating rate of 10 °C/min. Left graph in the air atmosphere(60% N_2, 40% O_2).

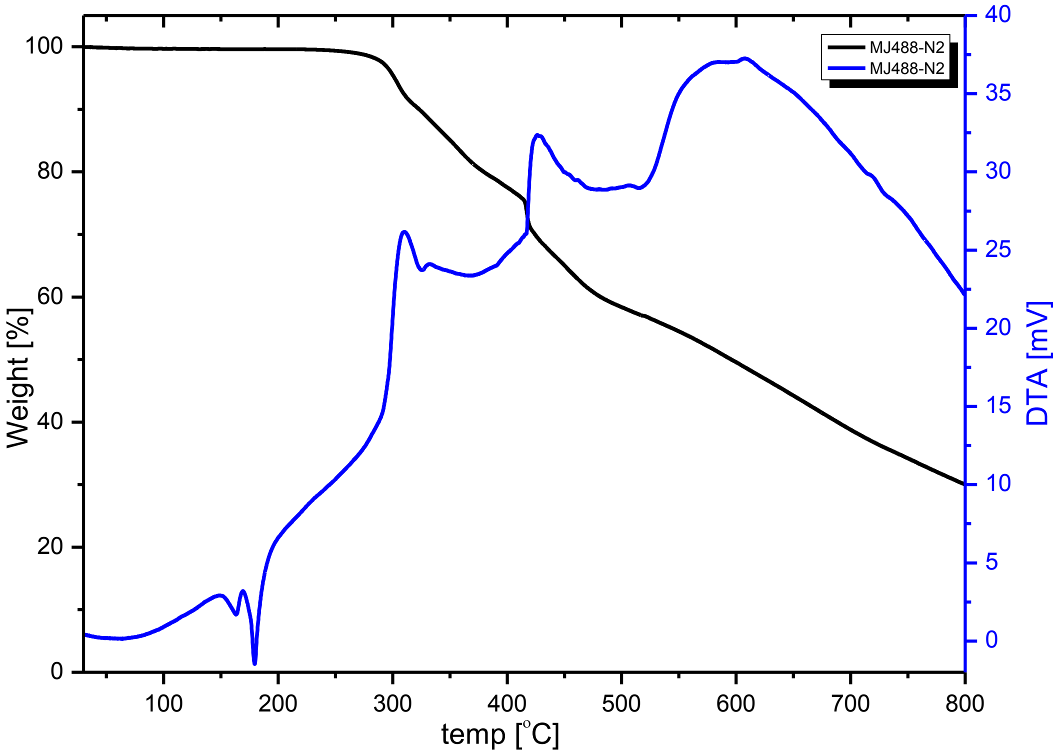

Figure S7. TG (black line), and DTA (blue line) thermogram of **2** at a heating rate of 10 °C/min. In nitrogen.

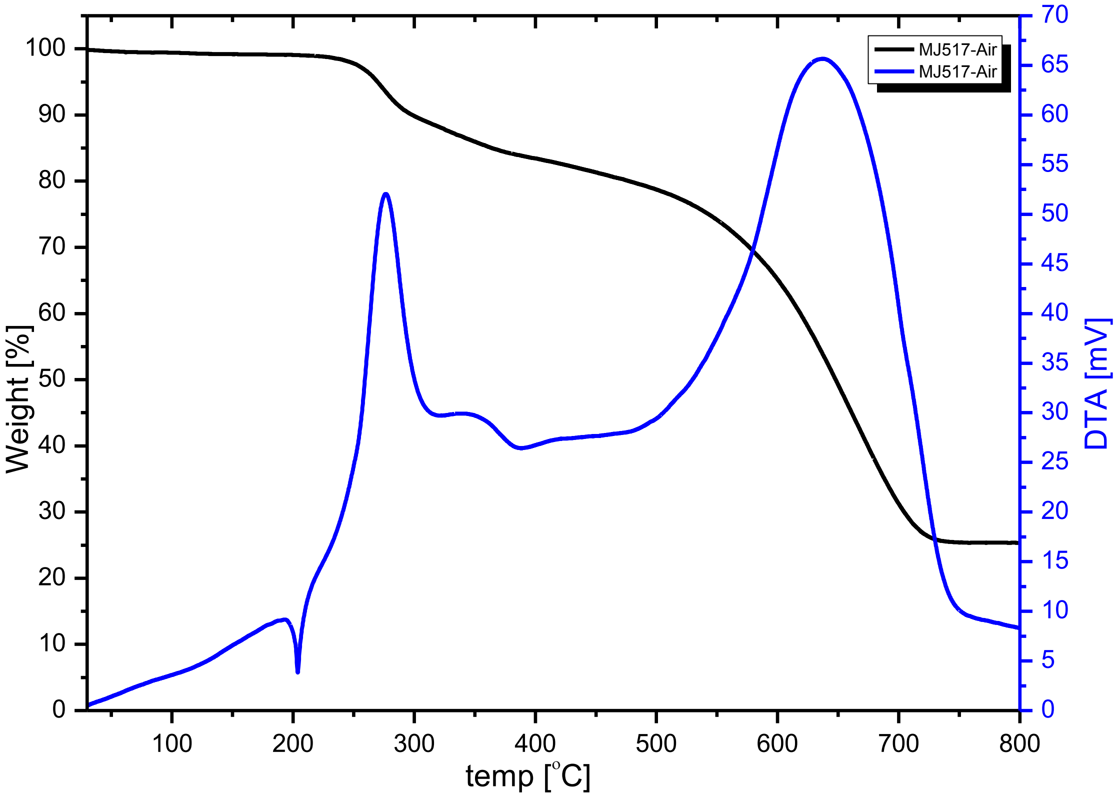

Figure S8. TG (black line), and DTA (blue line) thermogram of **3** at a heating rate of 10 °C/min. Left graph in the air atmosphere(60% N_2, 40% O_2).

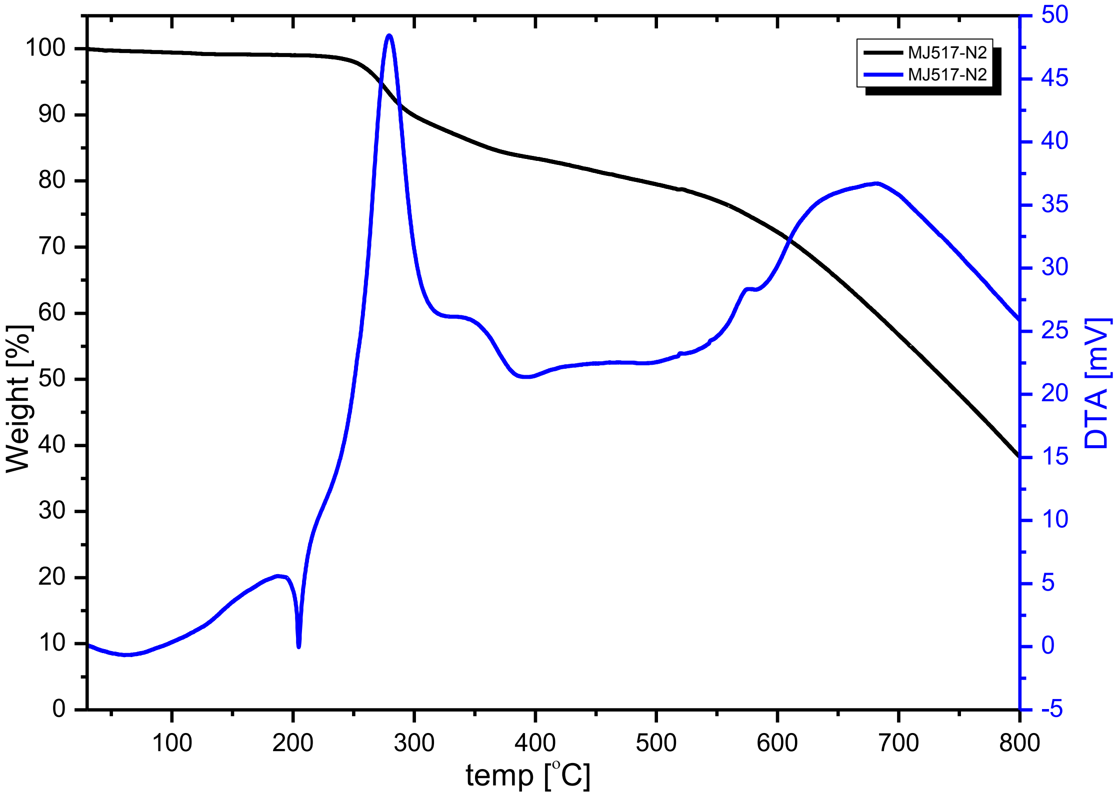

Figure S9. TG (black line), and DTA (blue line) thermogram of **3** at a heating rate of 10 °C/min. In nitrogen.

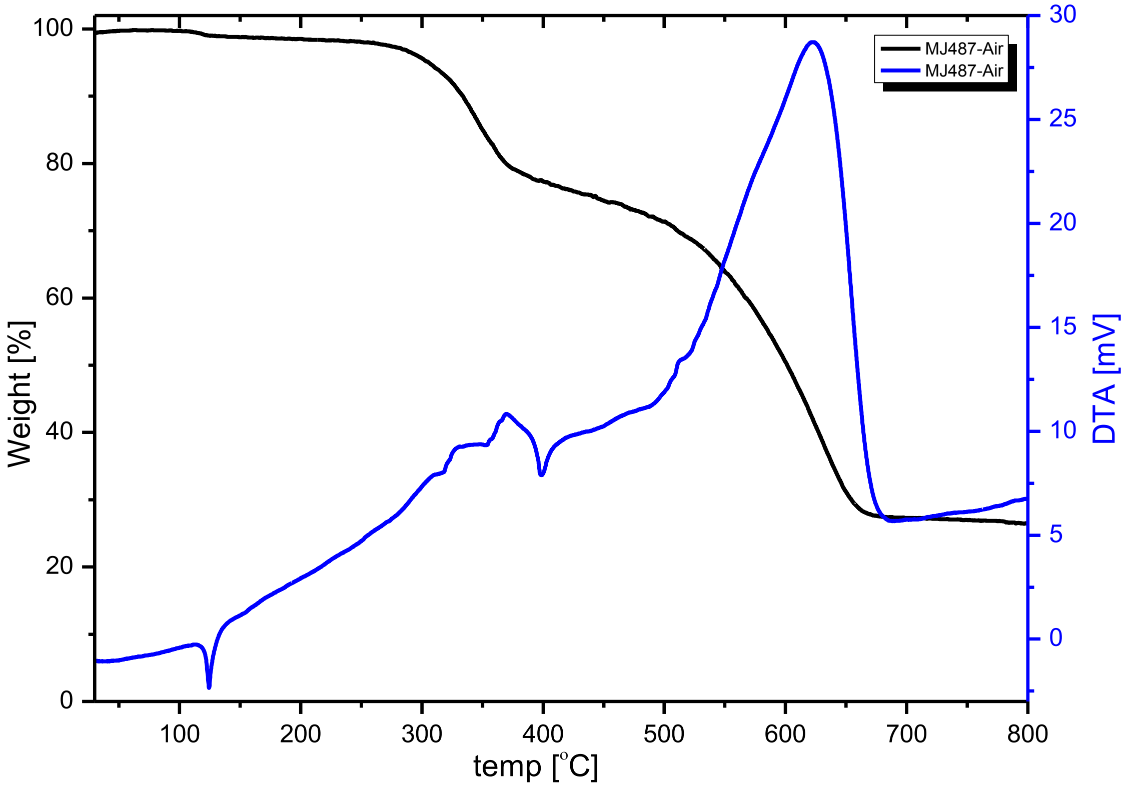

Figure S10. TG (black line), and DTA (blue line) thermogram of **4** at a heating rate of 10 °C/min. Inthe air atmosphere(60% N_2, 40% O_2).

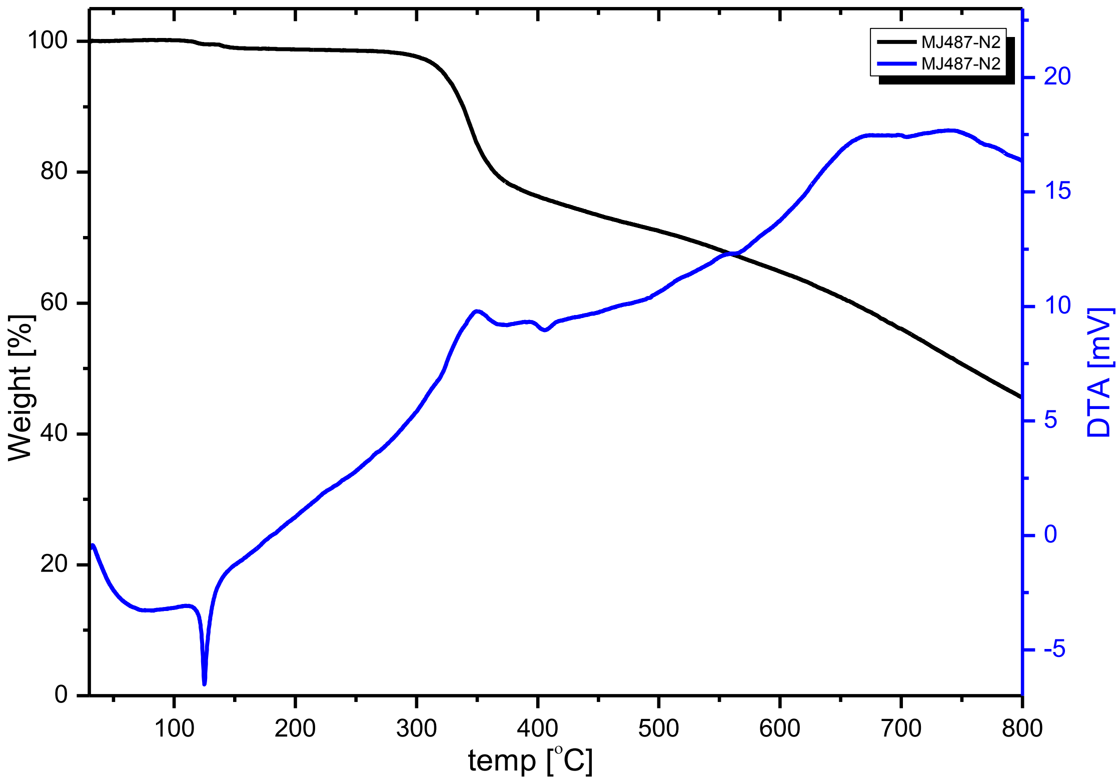

Figure S11. TG (black line), and DTA (blue line) thermogram of **4** at a heating rate of 10 °C/min. In the in nitrogen.

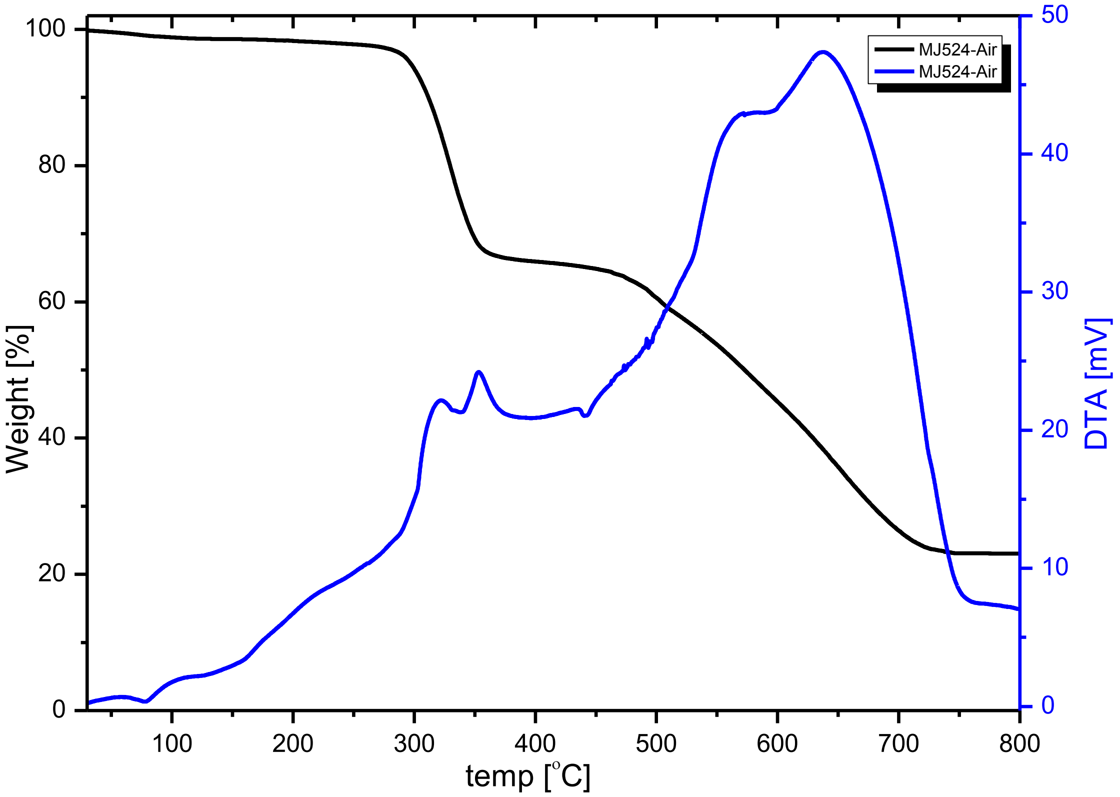

Figure S12. TG (black line), and DTA (blue line) thermogram of **5** at a heating rate of 10 °C/min. In the air atmosphere (60% N_2, 40% O_2).

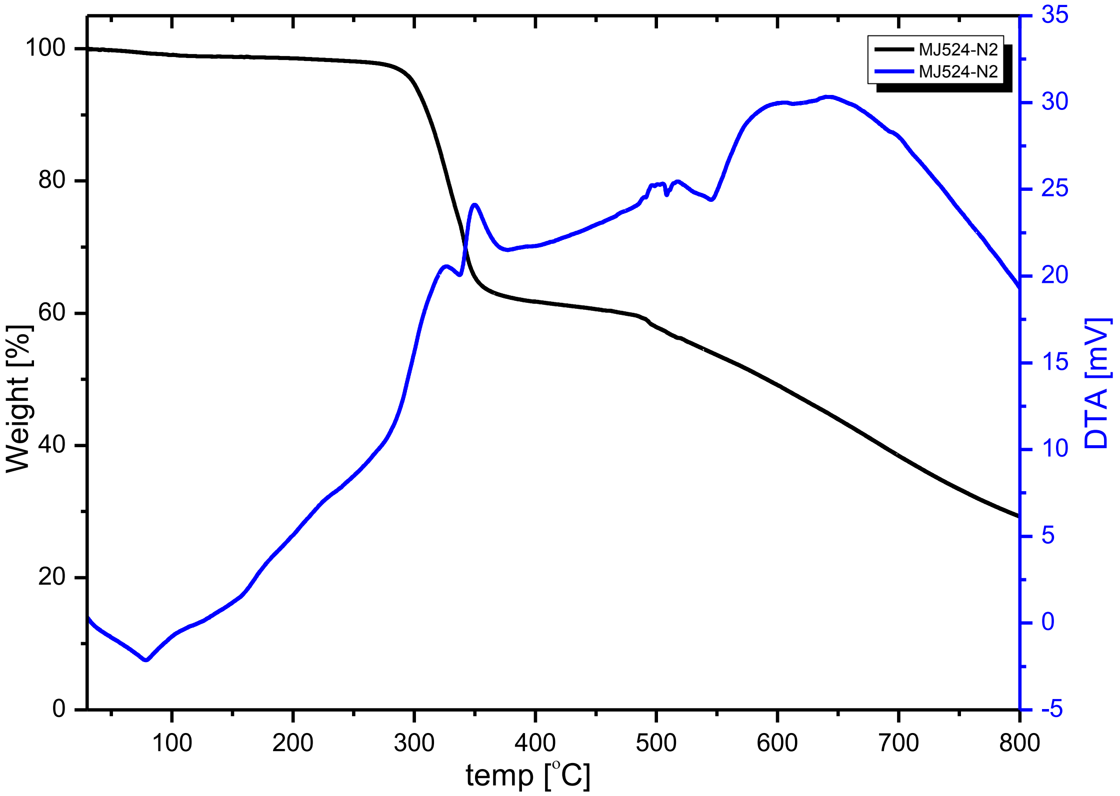

Figure S13. TG (black line), and DTA (blue line) thermogram of **5** at a heating rate of 10 °C/min. In nitrogen.

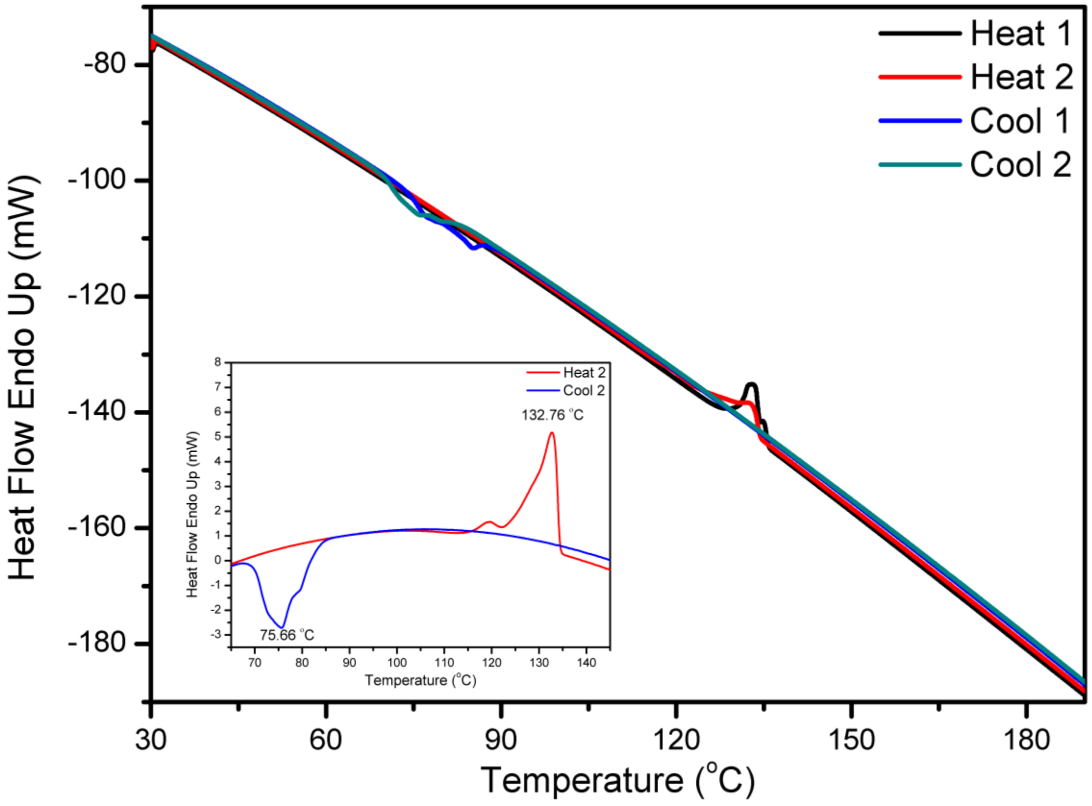

Figure S14. DSC of **1**, 1st and 2nd heat & cooling cycle (10 °C/min in the helium atmosphere).

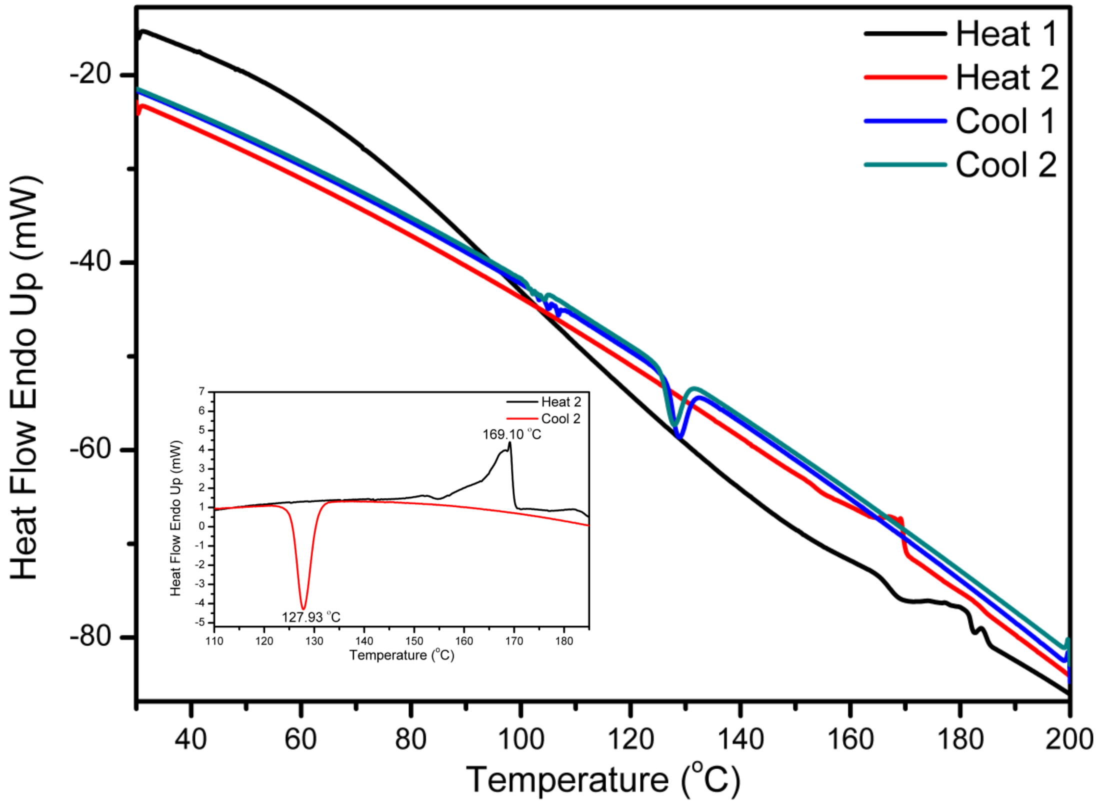

Figure S15. DSC of **2**, 1st and 2nd heat & cooling cycle (10 °C/min in the helium atmosphere).

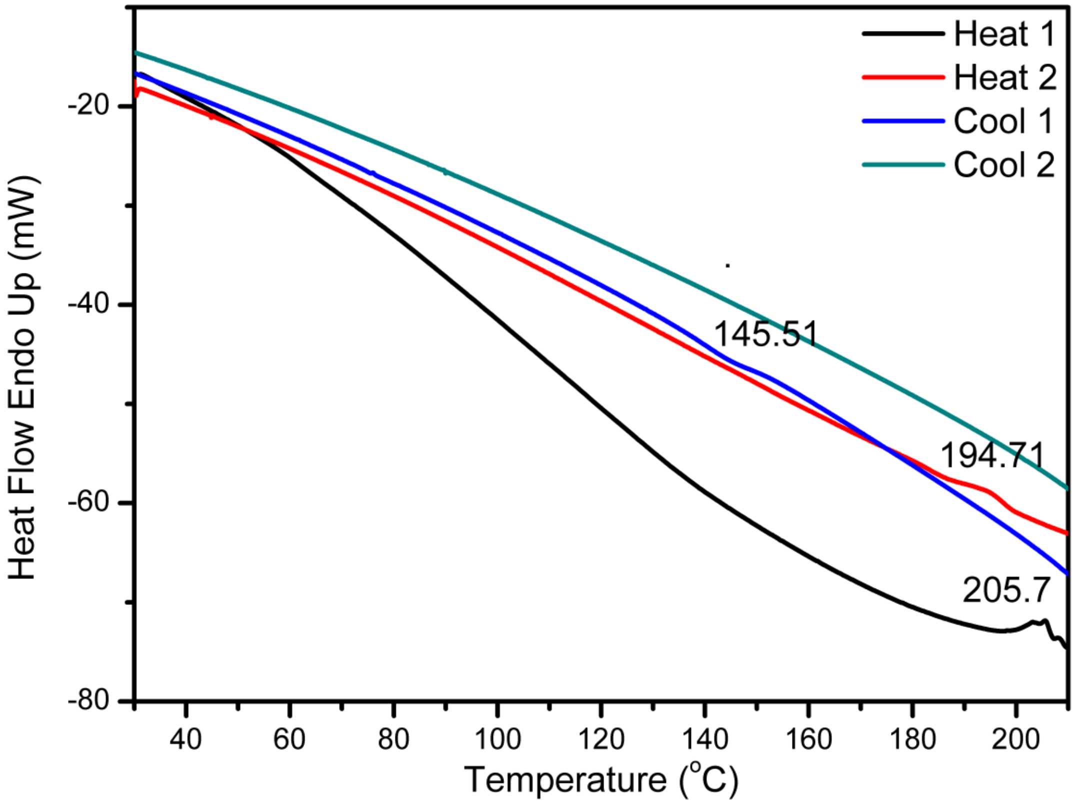

Figure S16. DSC of **3**, 1st and 2nd heat & cooling cycle (10 °C/min in the helium atmosphere).

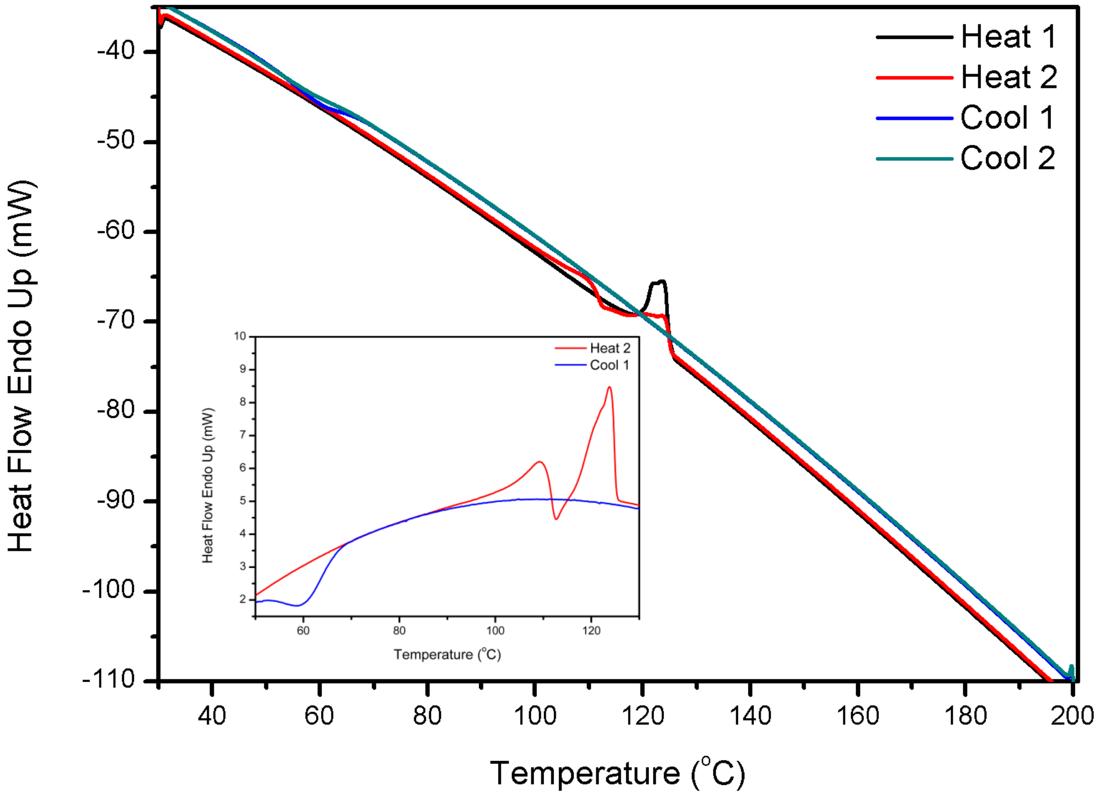

Figure S17. DSC of **4**, 1st and 2nd heat & cooling cycle (10 °C/min in the helium atmosphere).

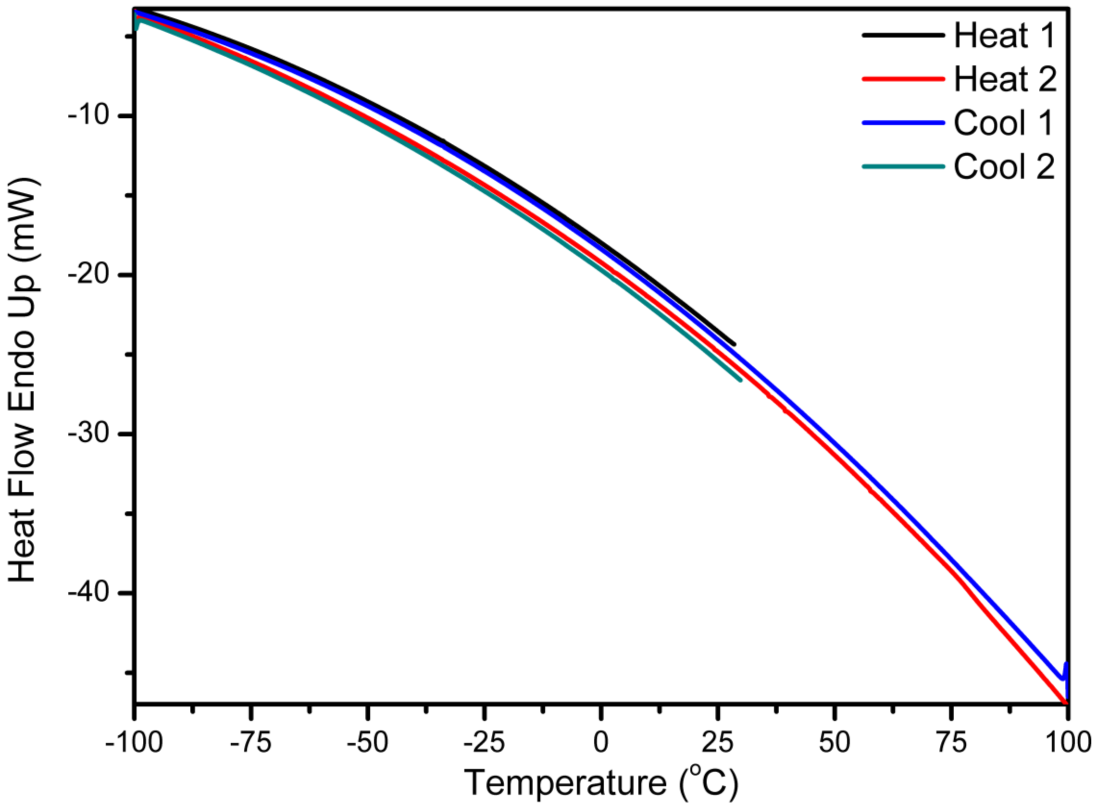

Figure S18. DSC of **5** (recrystallized from chloroform), 1st and 2nd heat & cooling cycle (10 °C/min in the helium atmosphere).

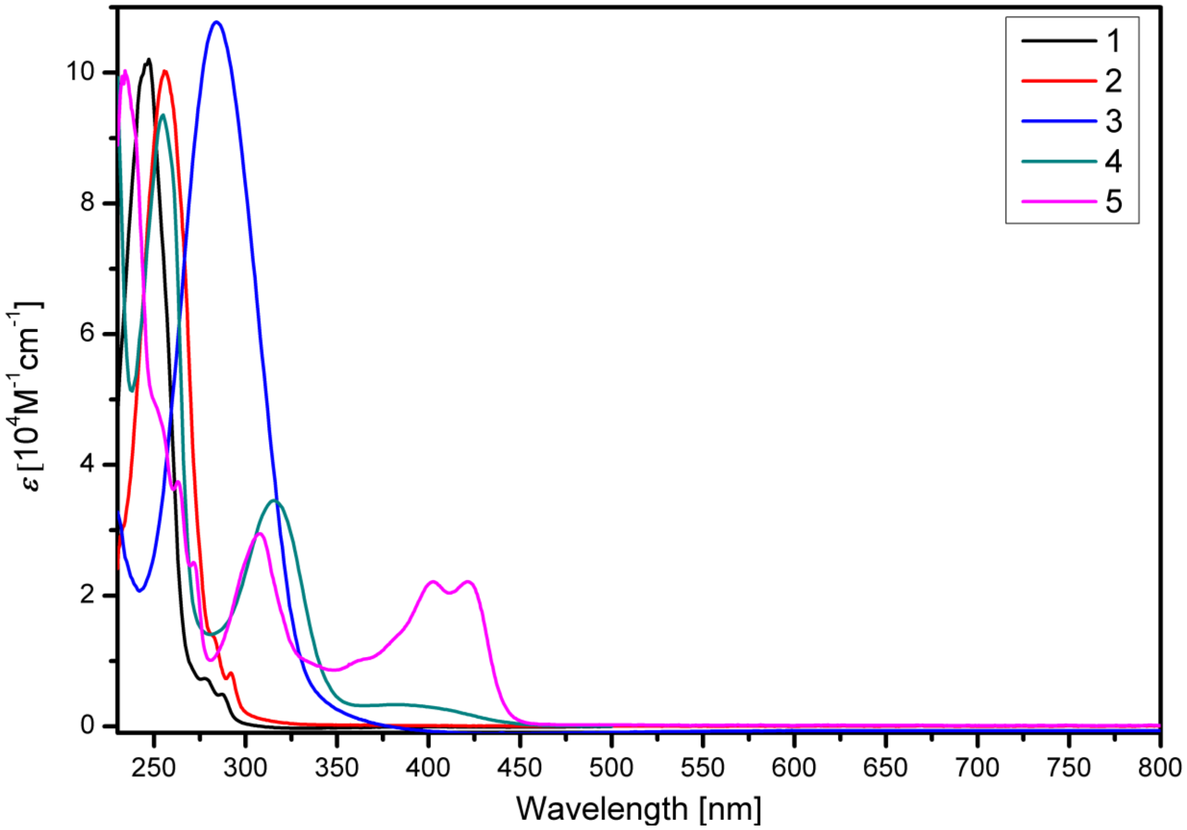

Figure S19. The electronic absorption spectra of **1**-**5** (dichloromethane, 298K).

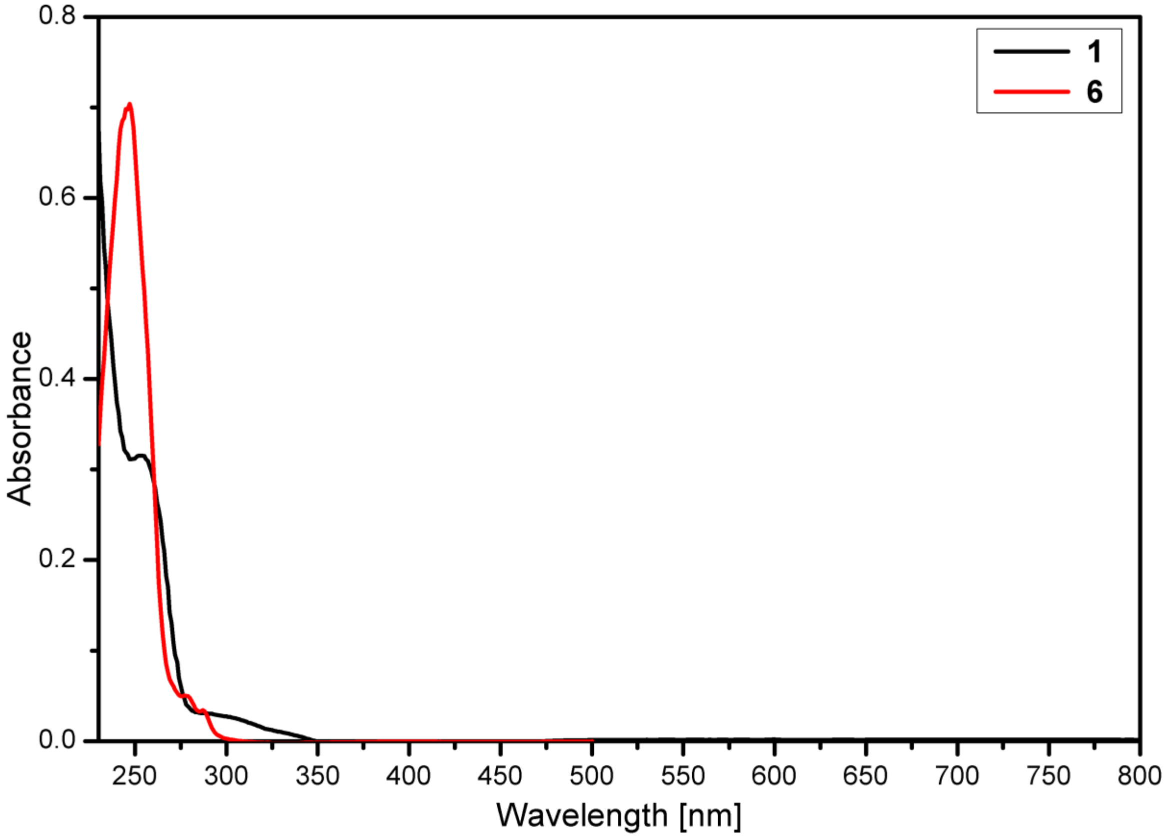

Figure S20. The electronic absorption spectra (dichloromethane, 298K) of **6** (red) and **1** (black).

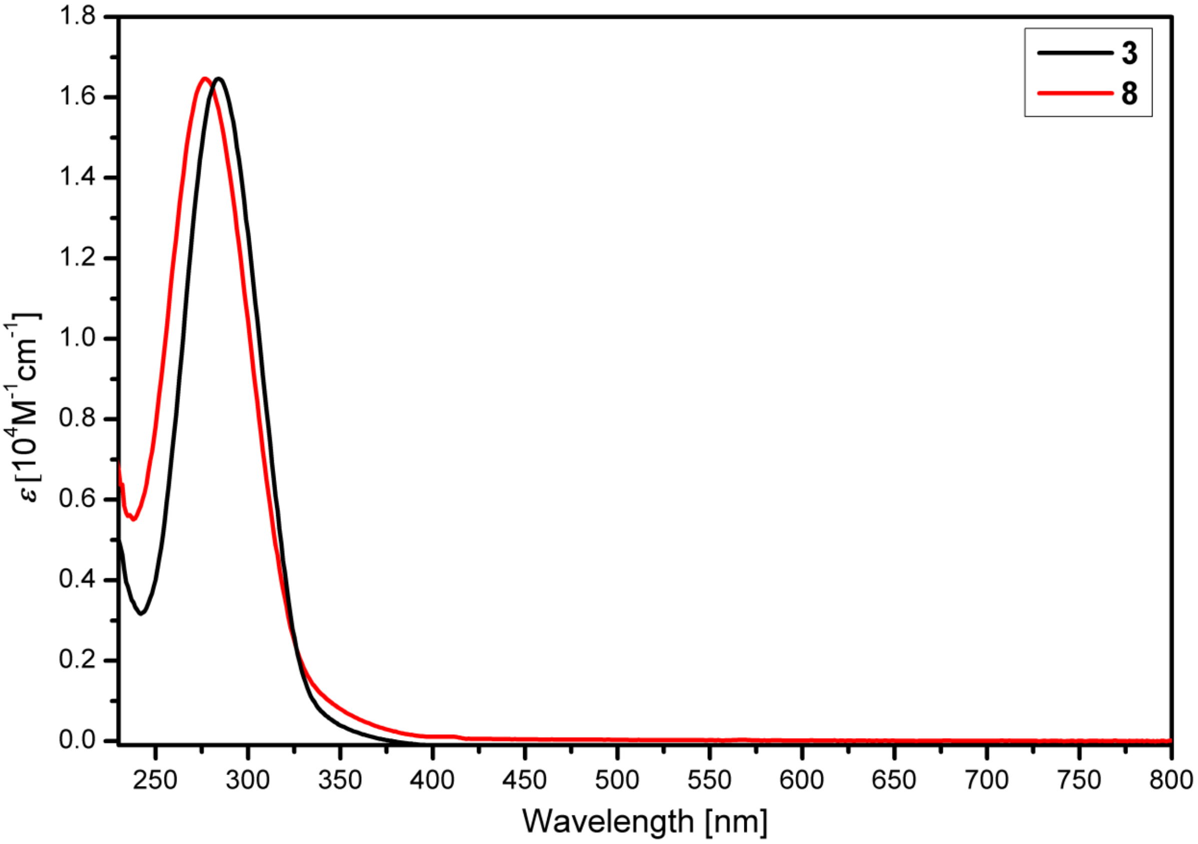

Figure S21. The electronic absorption spectra (dichloromethane, 298K) of **8** (red) and **3** (black).

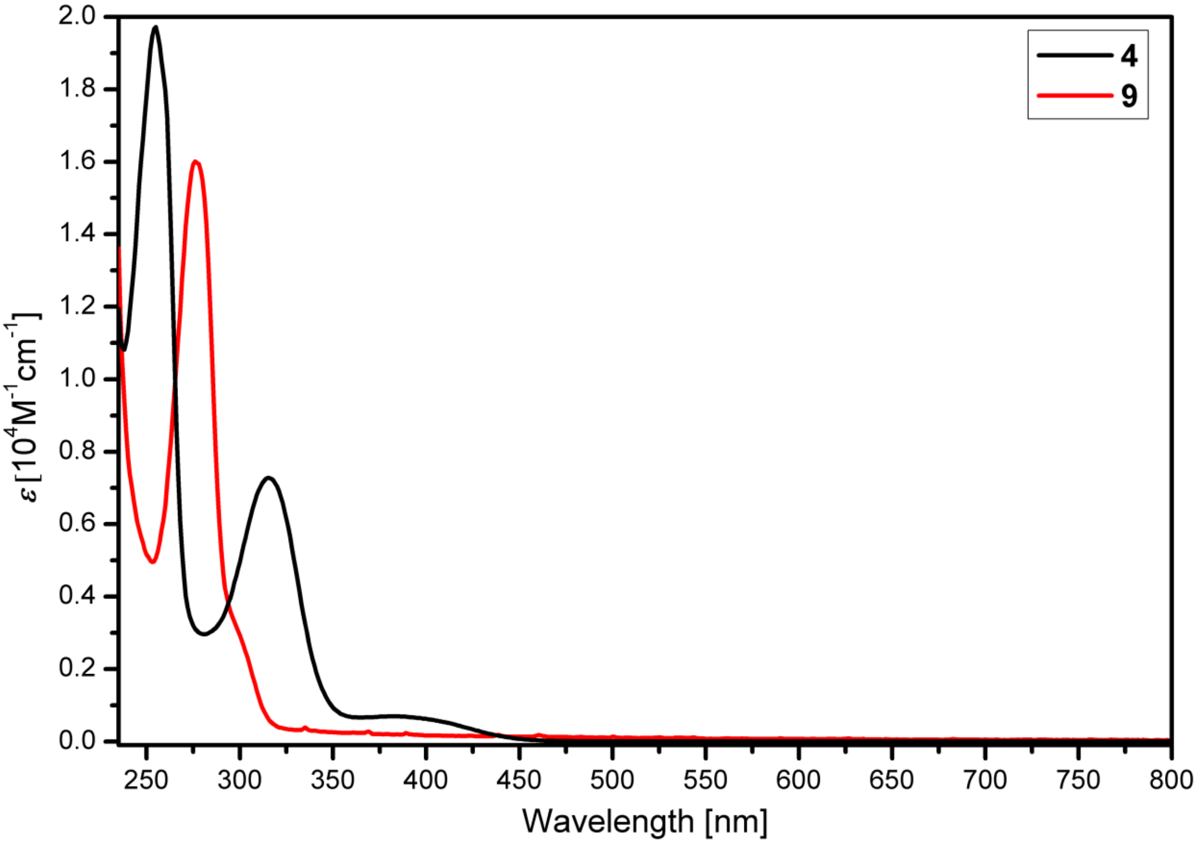

Figure S22. The electronic absorption spectra (dichloromethane, 298K) of **9** (red) and **4** (black).

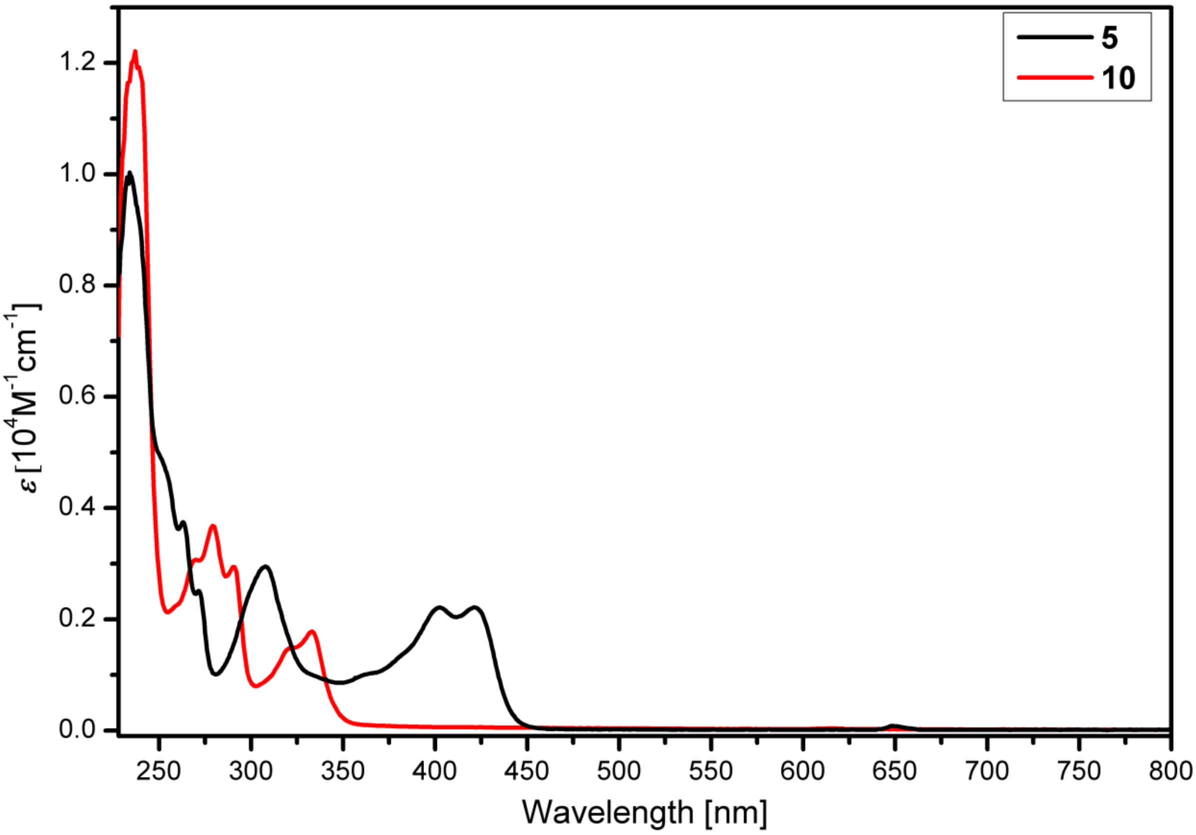

Figure S23. The electronic absorption spectra (dichloromethane, 298K) of **10** (red) and **5** (black).

Table S16. Selected NMR and FT-IR data.

Compound	^{1}H NMR[a] N=CH	^{13}C NMR[a] C=N	^{29}Si NMR[a]	FT-IR[b] N=CH; Si-O-Si
1	8.27	165.0	-66.7	1631; 1099
2	8.22	164.8	-66.6	1634; 1116
3	8.27	164.7	-66.7	1632; 1115
4	8.27	160.8	-67.0	1624; 1113
5	8.33	166.0	-66.6	1634; 1099
6	10.40	160.5	-66.7	1632; 1089
7	8.64	158.1	-67.0	1633[c]; 1114
8	8.24	161.1	-66.5	1647; 1112
9	8.16	159.9	-66.7	1644; 1158
10	8.26	159.3	-67.2	1646; 1094
11	8.32	158.9	-66.7	1645; 1108
12	7.00	158.9	-66.7	1645; 1108
13	8.11	160.9	-67.1	1639; 1121
14	8.34	162.0	-66.6	1648; 1113
15	8.20	159.3	-66.7	1647; 1098
16	7.94	153.5	-67.3	1675; 1098
17	8.33	154.4	-66.7	1634; 1107
18	8.01	153.1	-66.3	1637; 1095
19	8.83	155.5	-66.5	1645; 1113

[a] Measured in CDCl$_3$. [b] Powder measured in Nujol mull. [c] C=C-NH moiety.

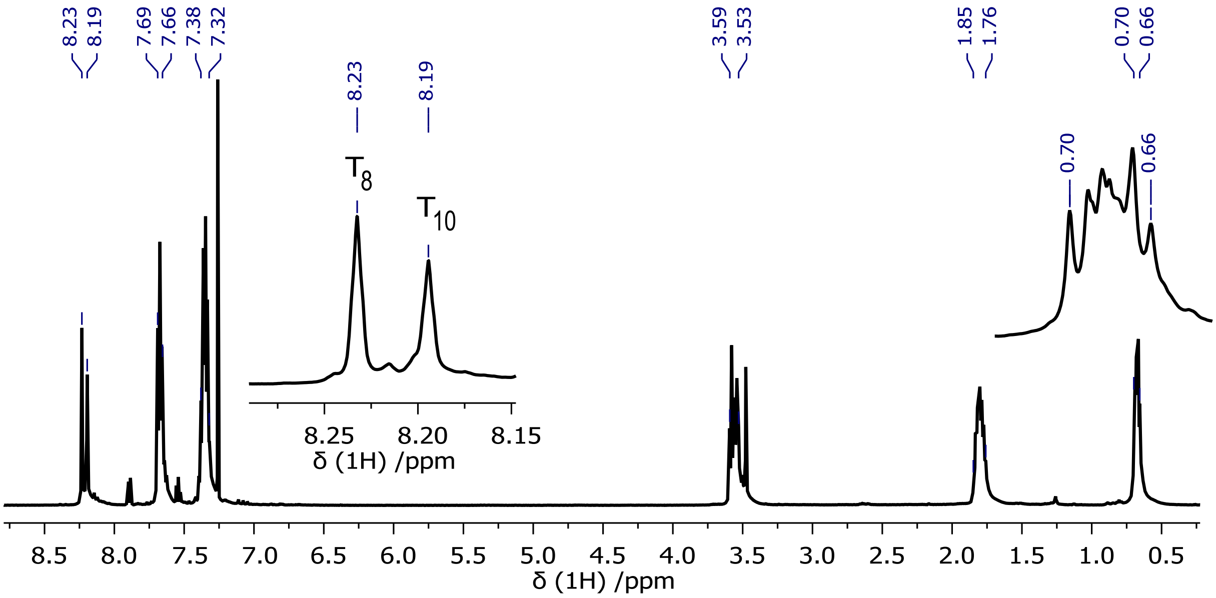

Figure S24. ^{1}H (500 MHz, CDCl$_3$) spectrum of the crude product of reaction of OAS-POSS-CF$_3$SO$_3$ with benzoic aldehyde.

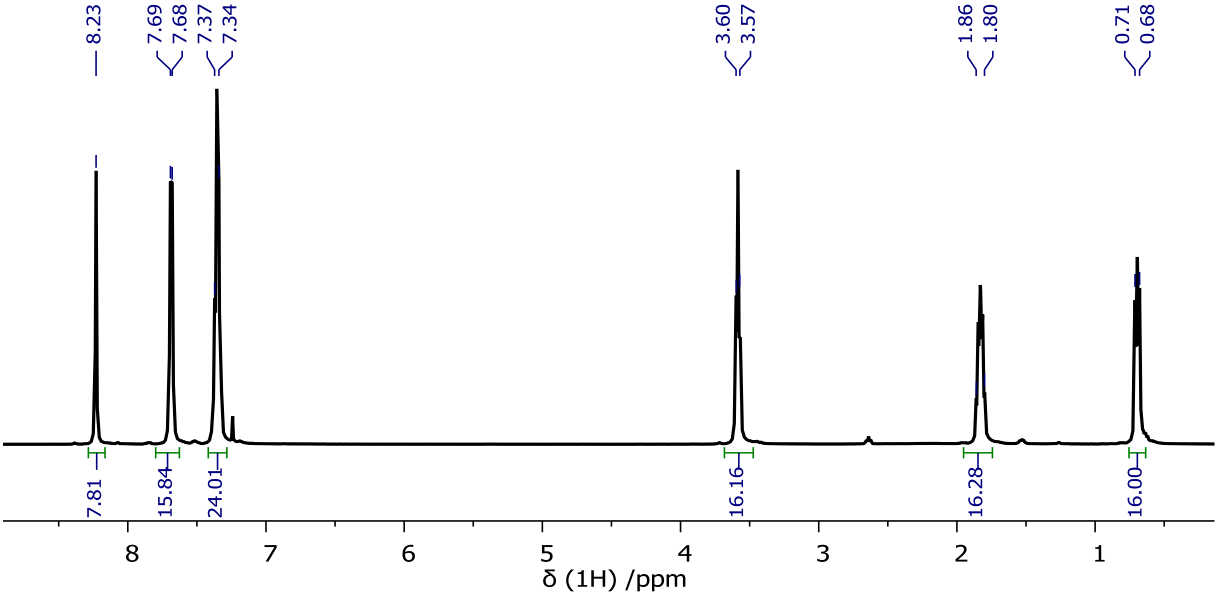

Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **1**.

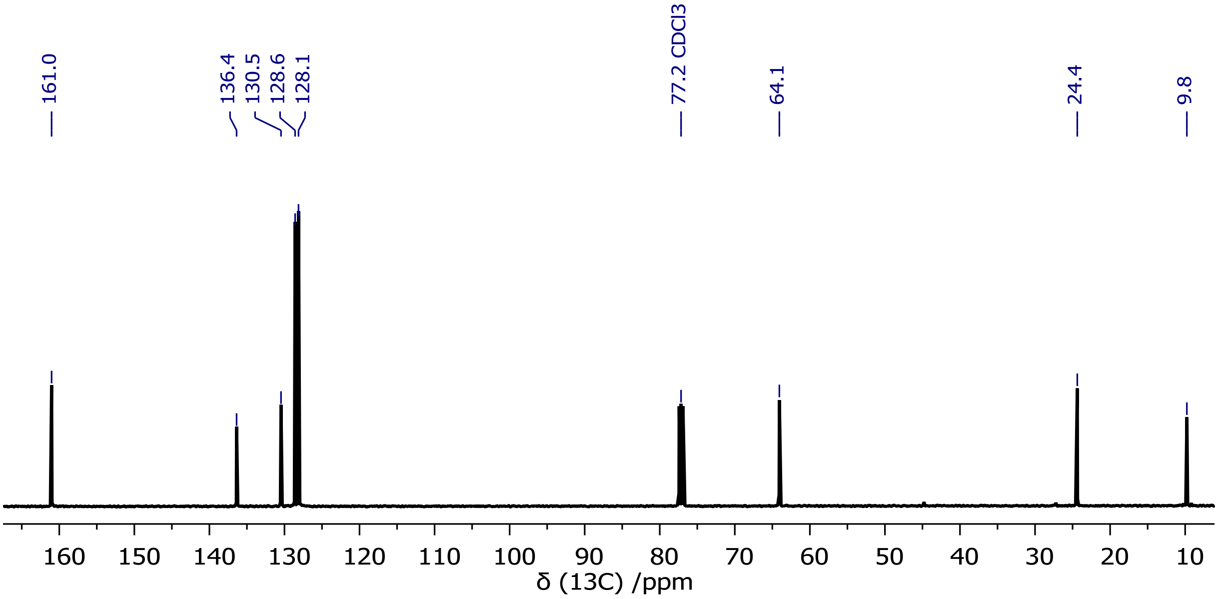

Figure S6. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **1**.

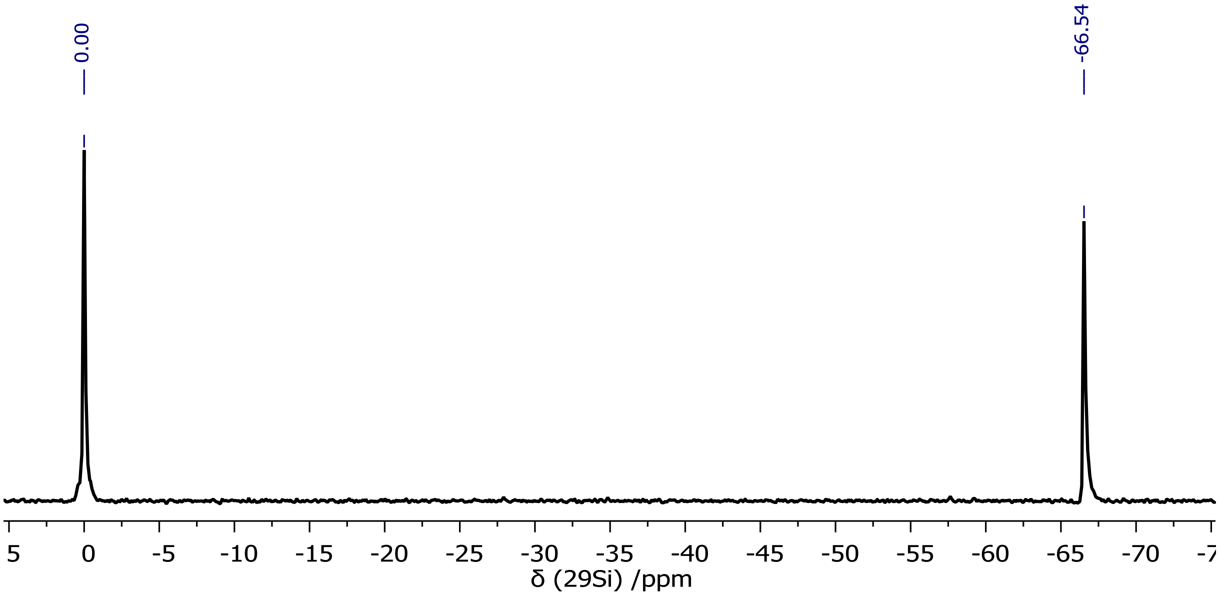

Figure S27. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **1**.

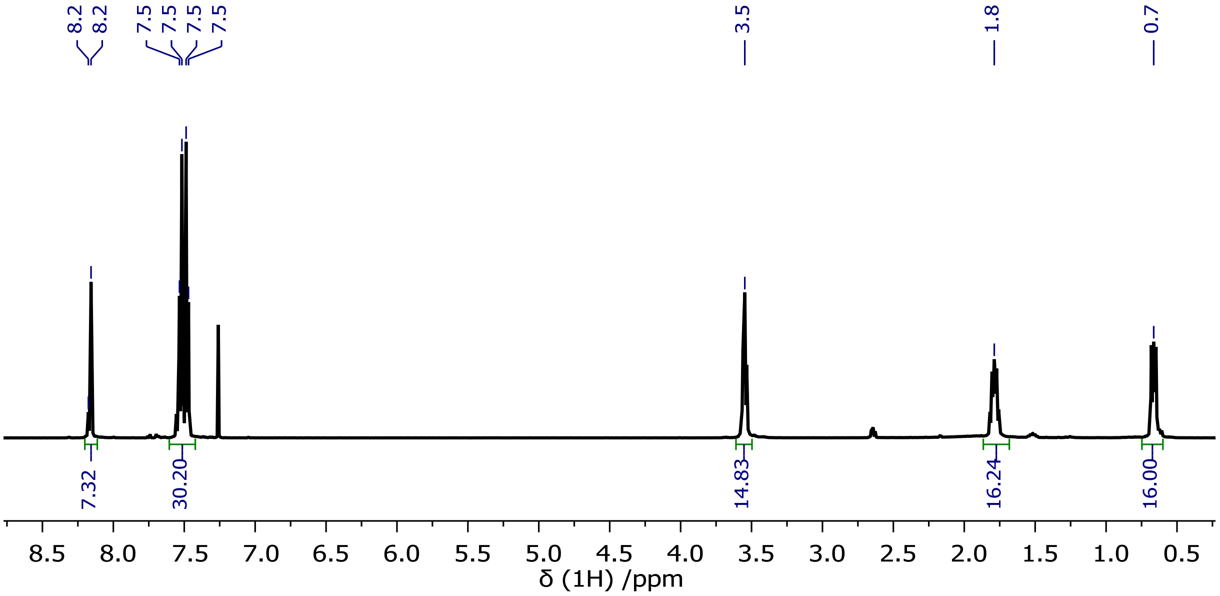

Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **2**.

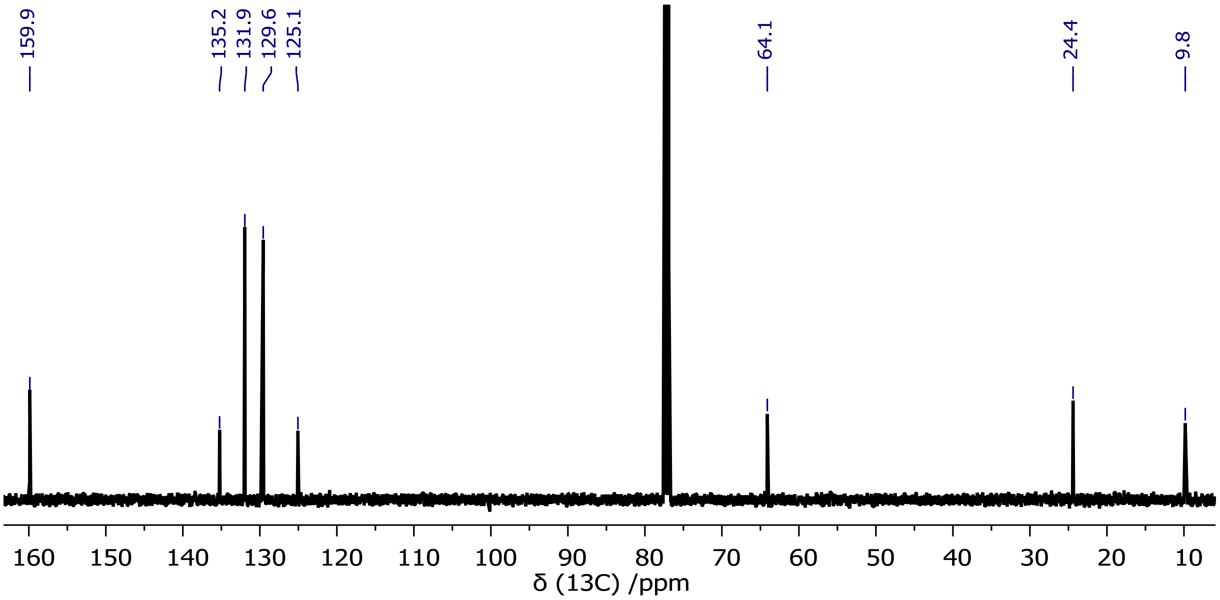

Figure S29. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **2**.

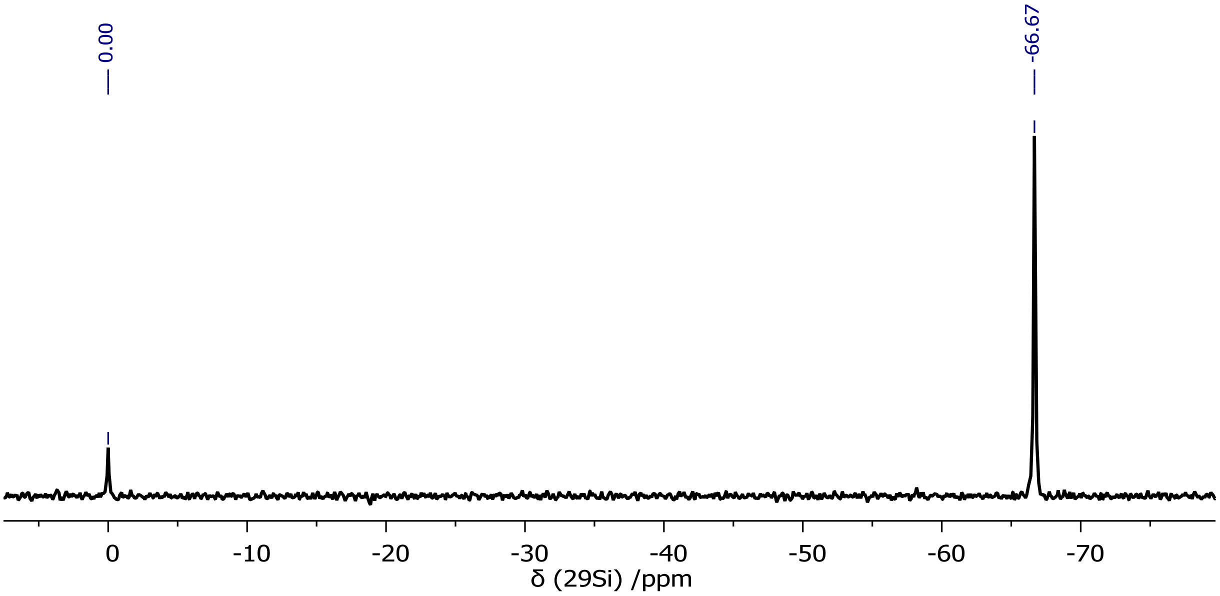

Figure S30. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **2**.

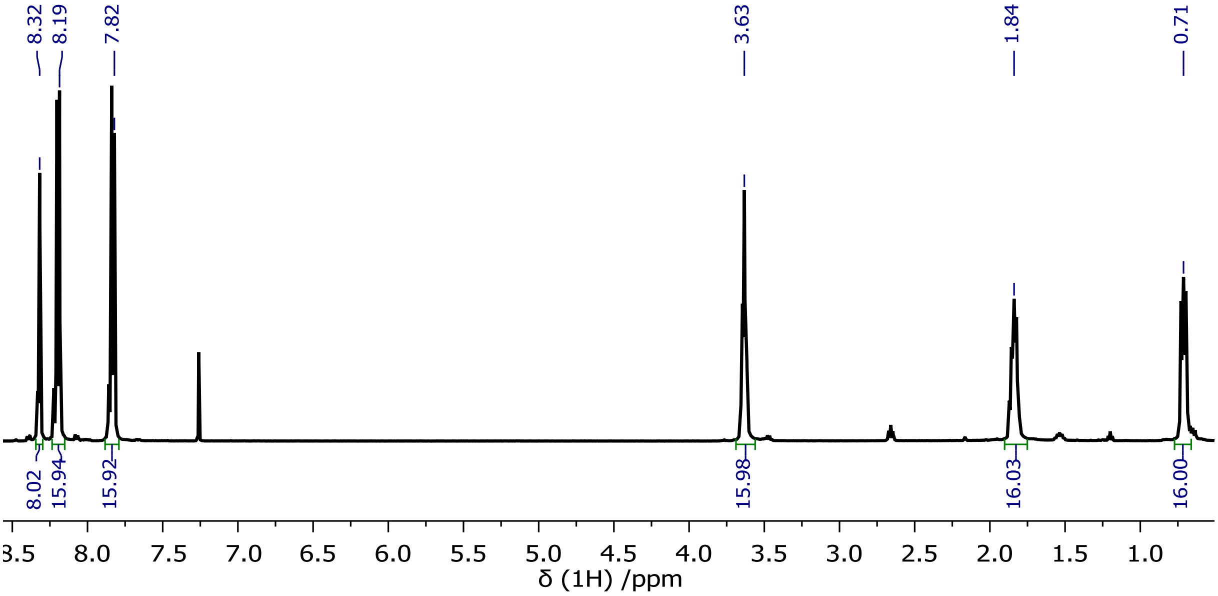

Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **3**.

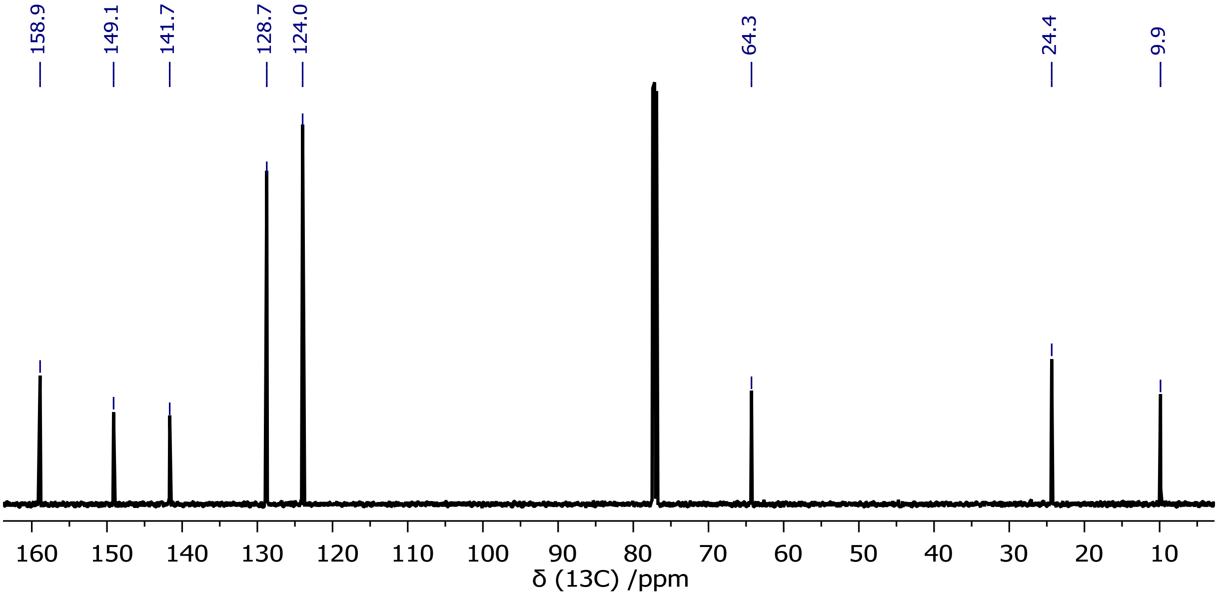

Figure S32. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **3**.

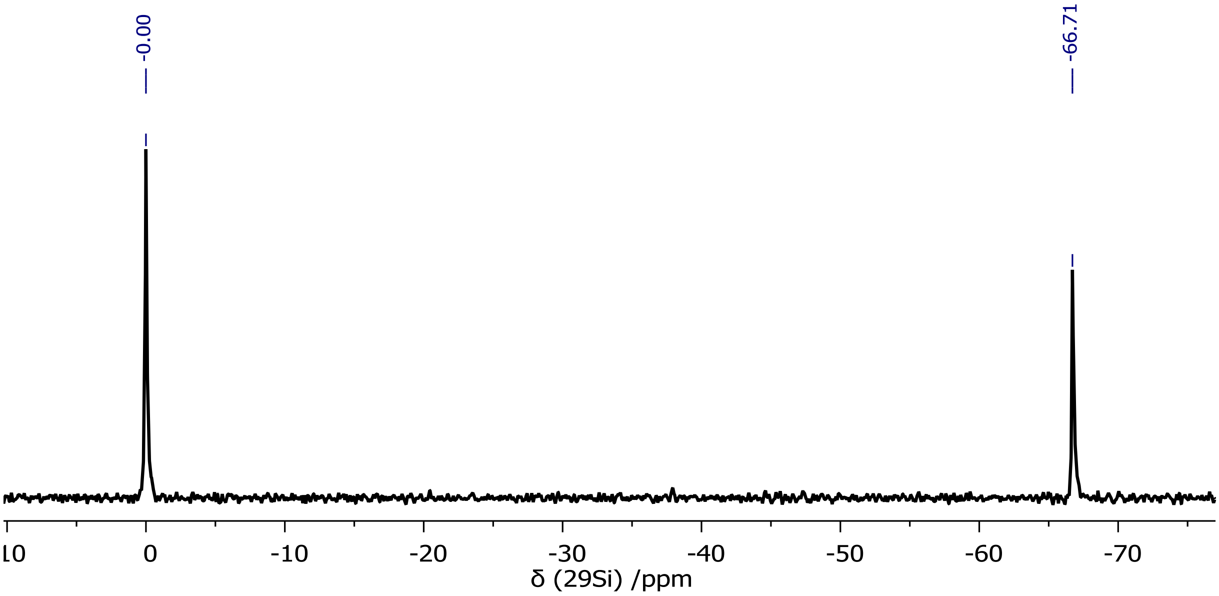

Figure S33. ^{29}Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of **3**.

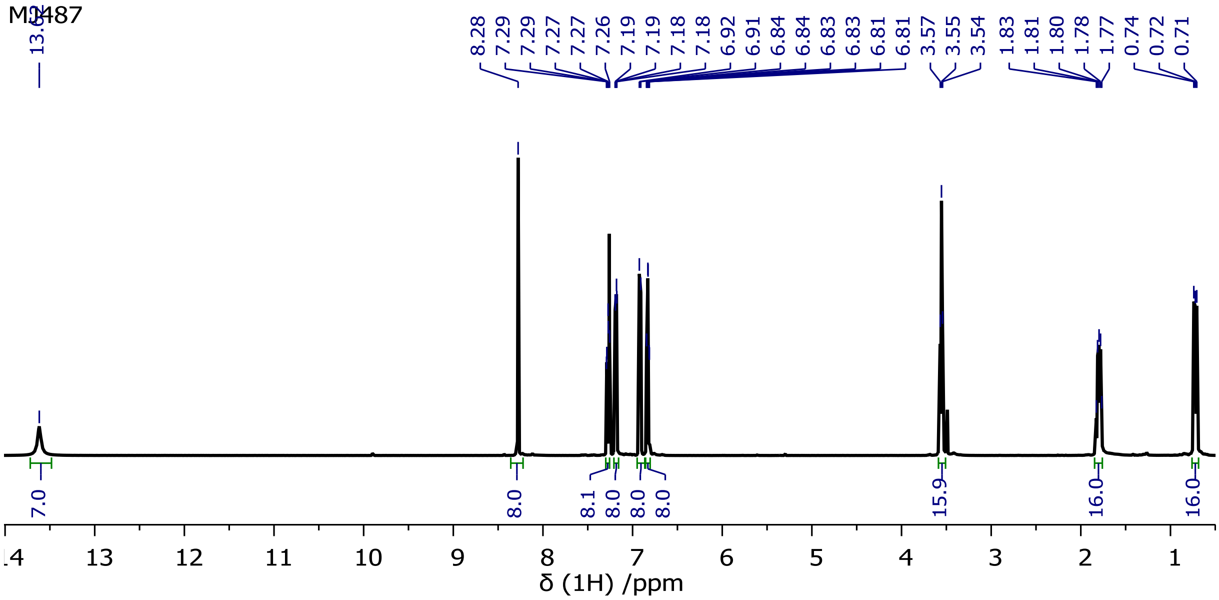

Figure S34. ^{1}H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of **4**.

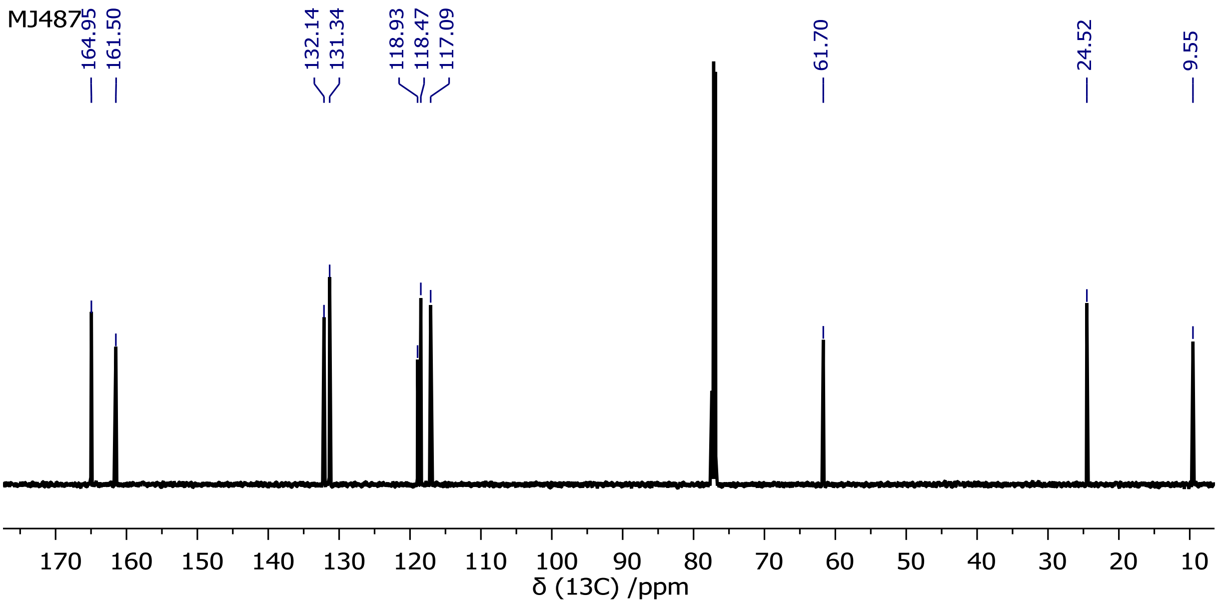

Figure S35. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **4**.

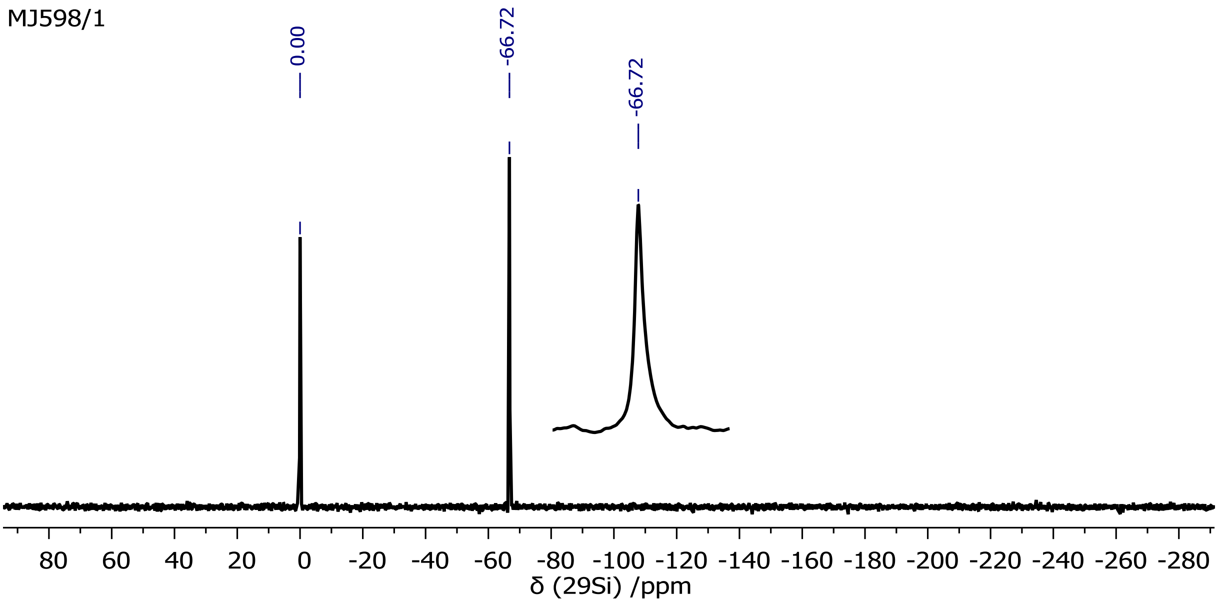

Figure S36. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **4**.

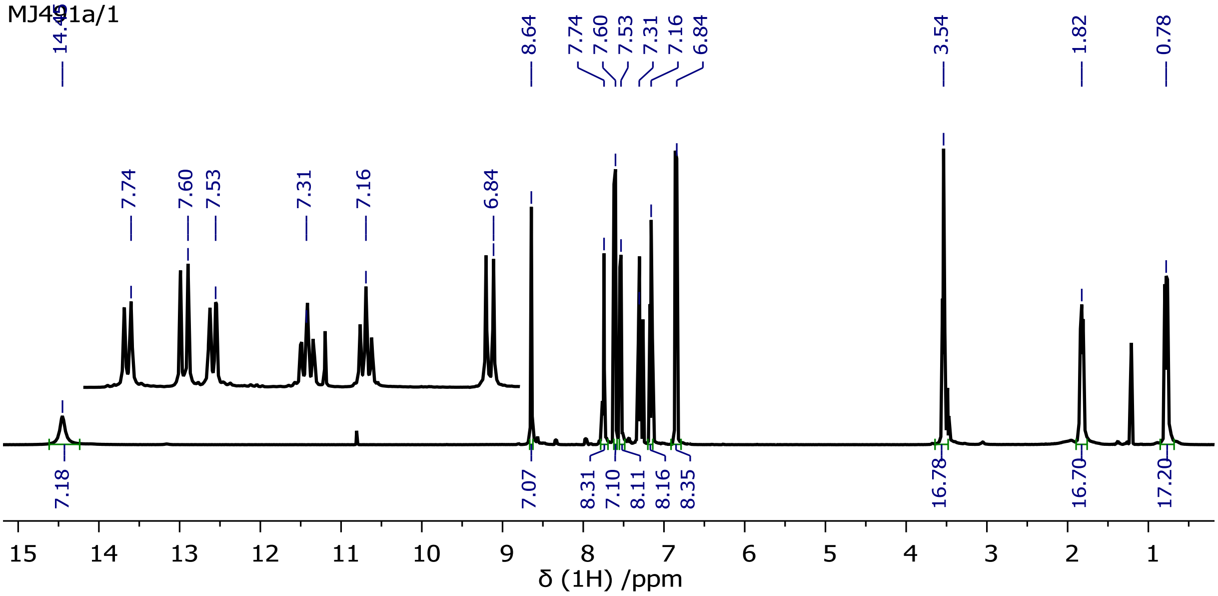

Figure S37. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **5**.

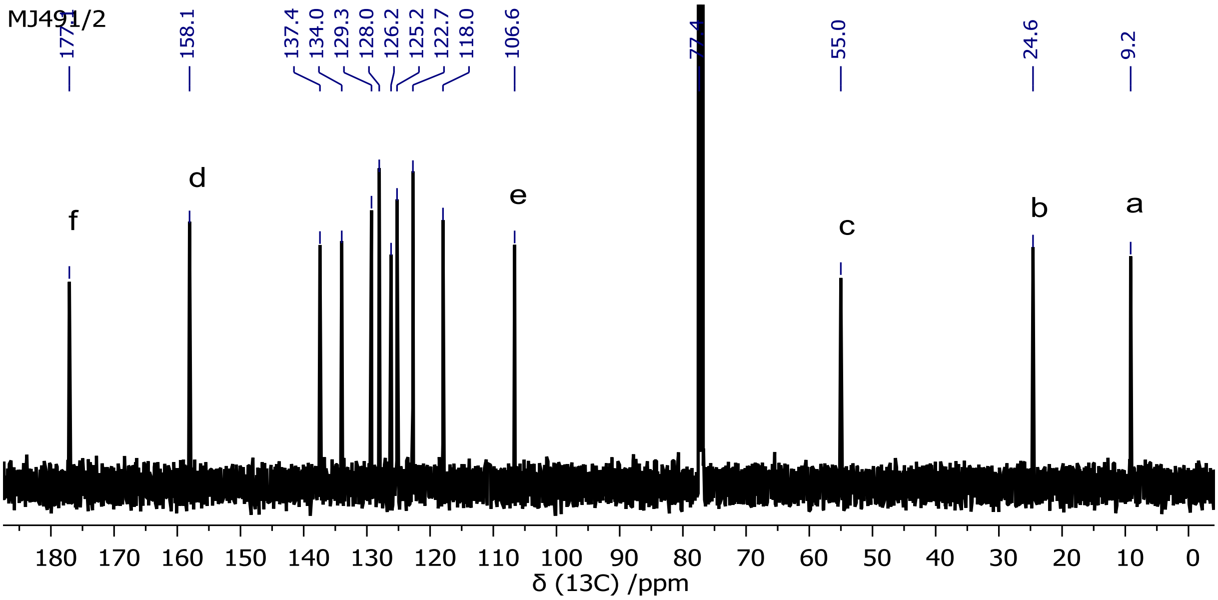

Figure S38. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **5**.

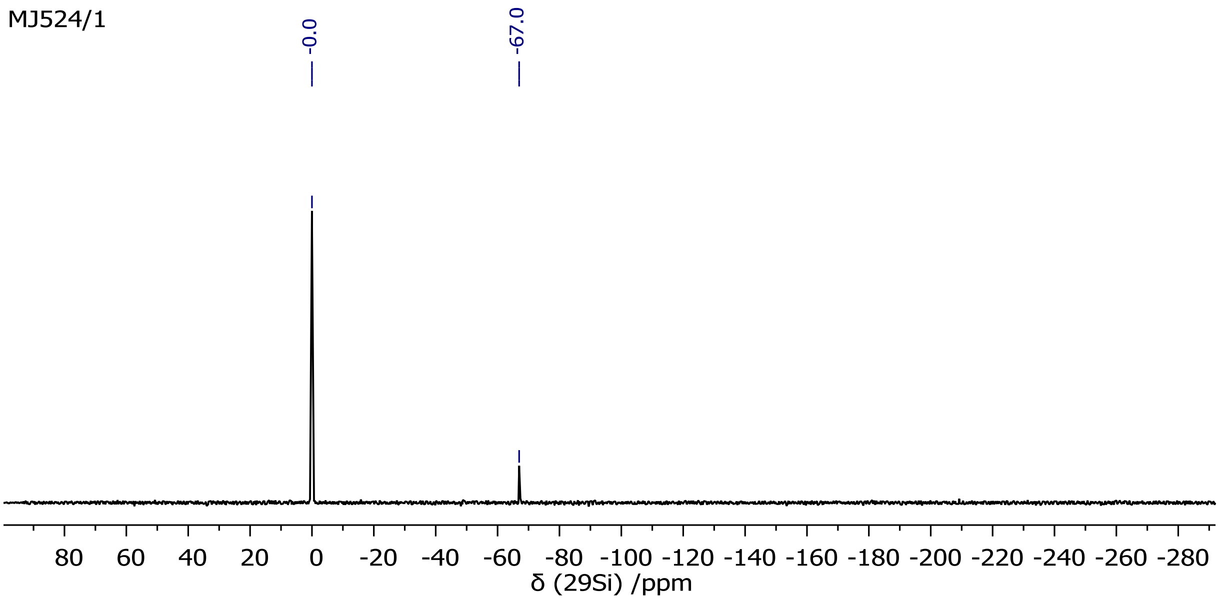

Figure S39. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **5**.

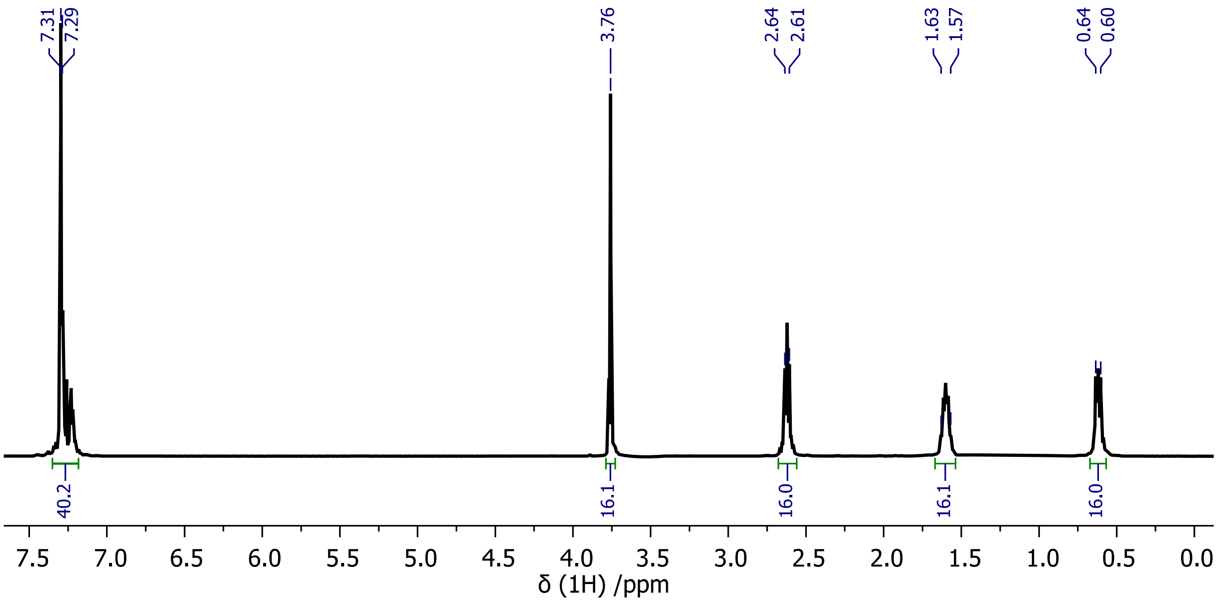

Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **6**.

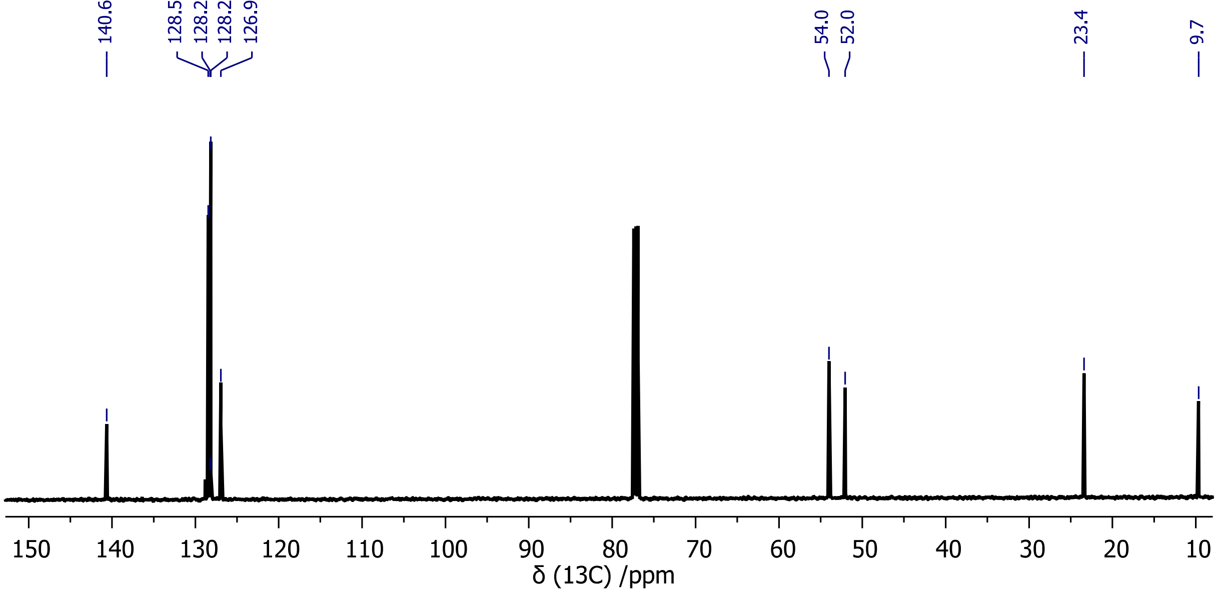

Figure S41. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **6**.

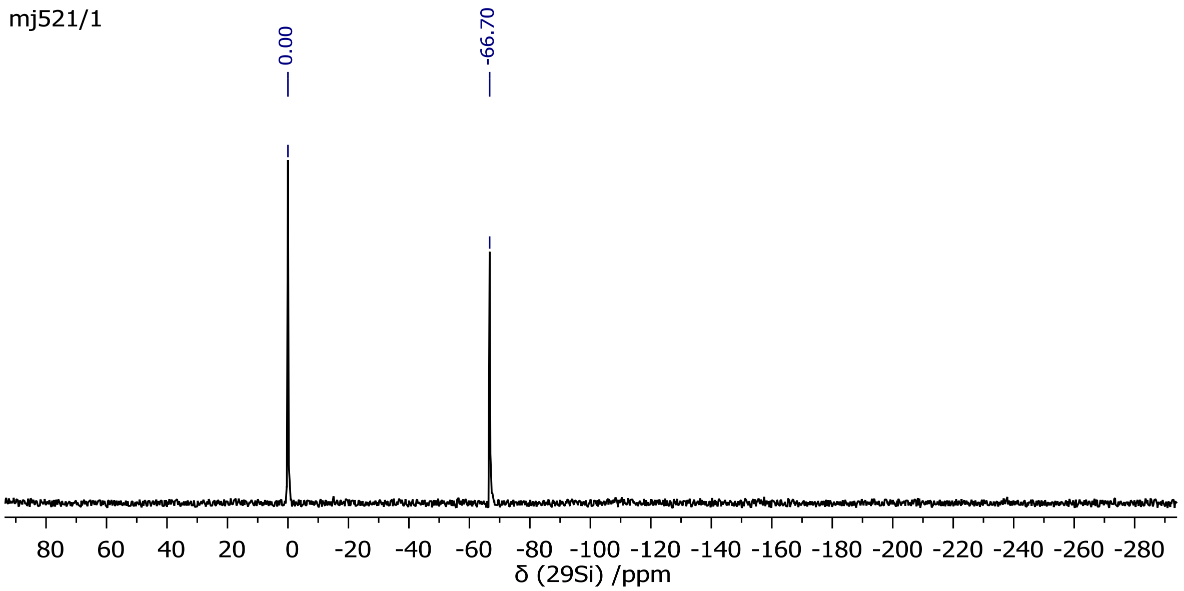

Figure S42. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **6**.

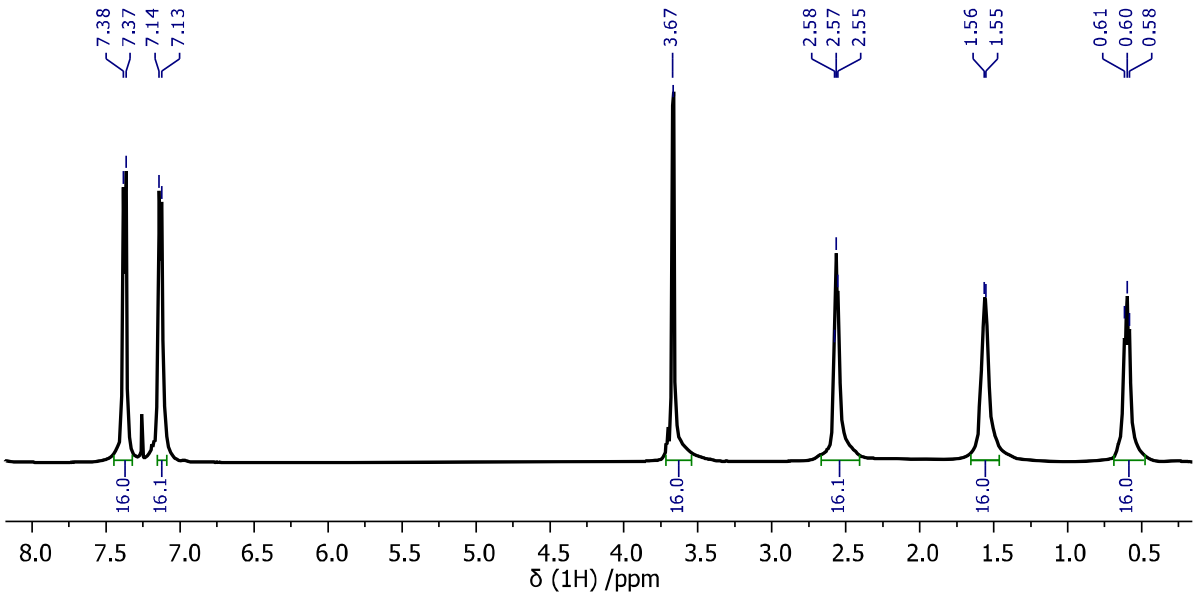

Figure S43. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **7**.

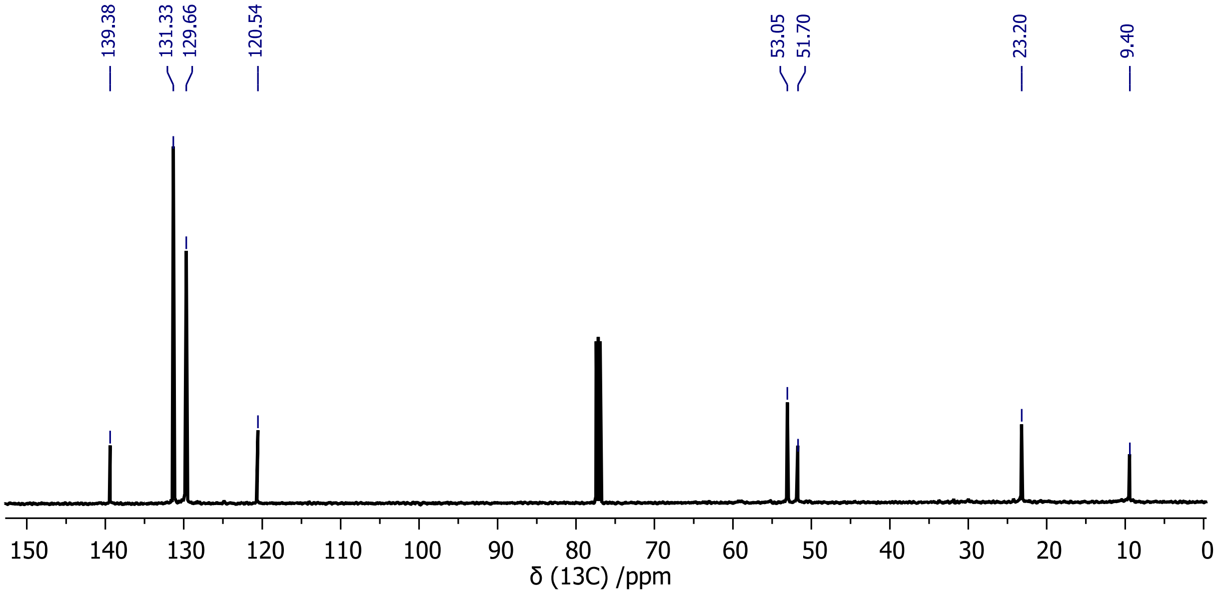

Figure S44. ^{13}C NMR (126 MHz, CDCl$_3$, 300 K) spectrum of **7**.

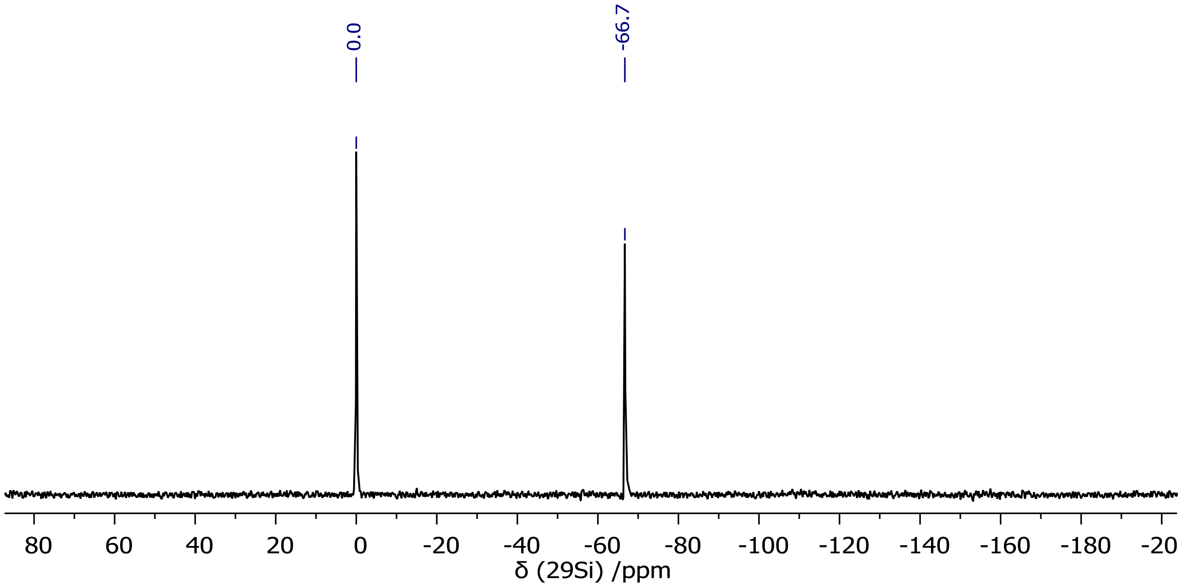

Figure S45. ^{29}Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of **7**.

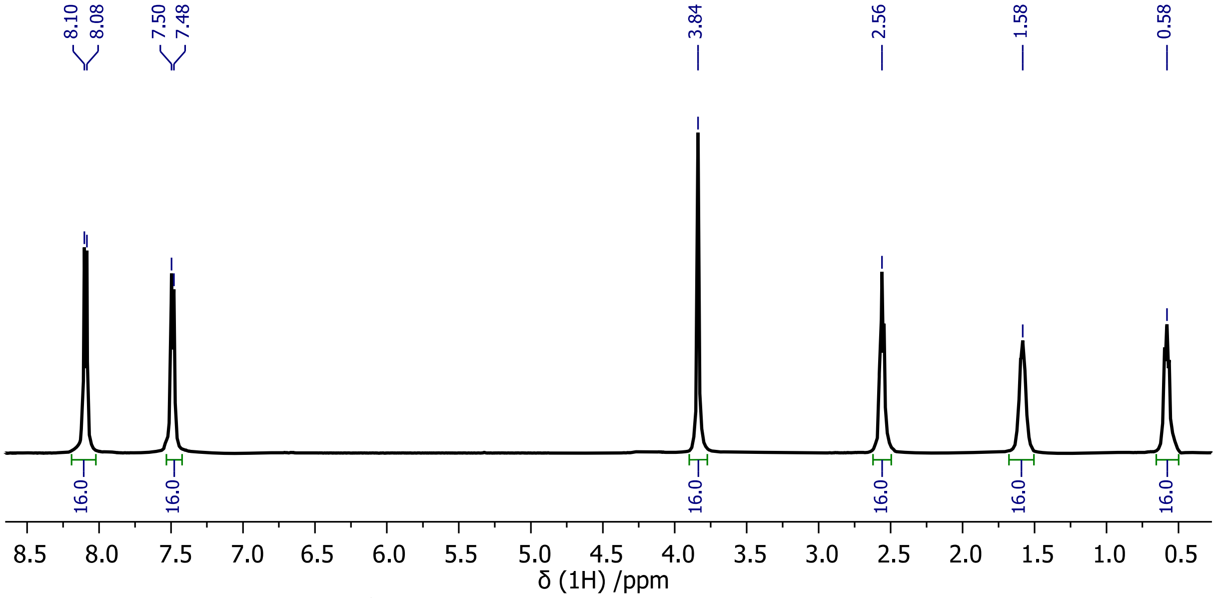

Figure S46. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K)spectrum of **8**.

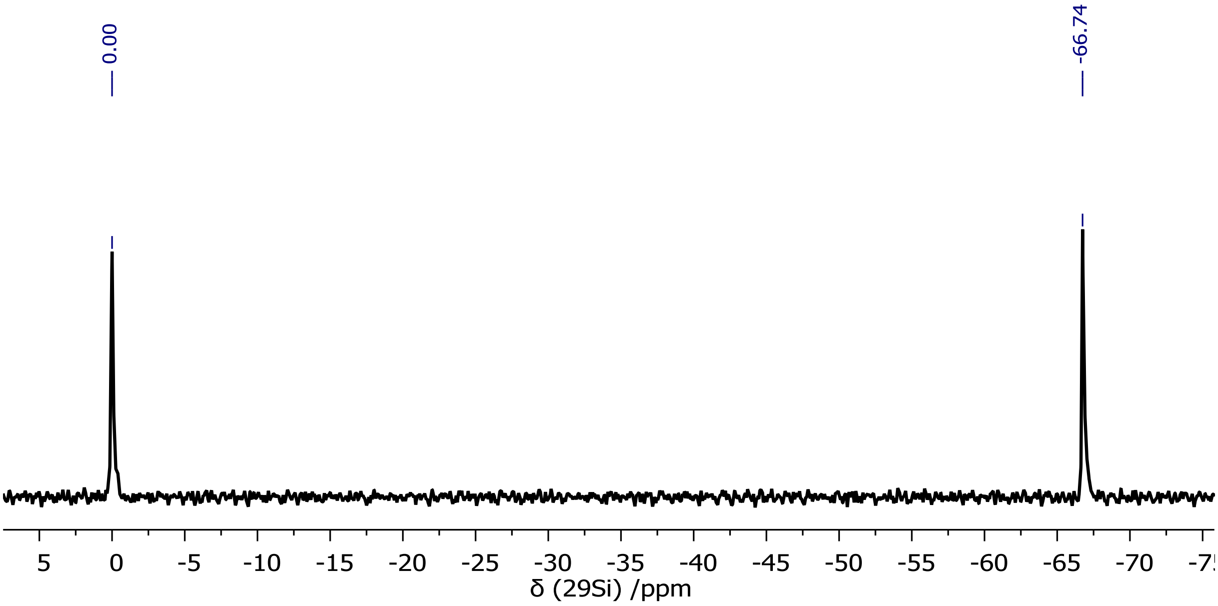

Figure S47. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **8**.

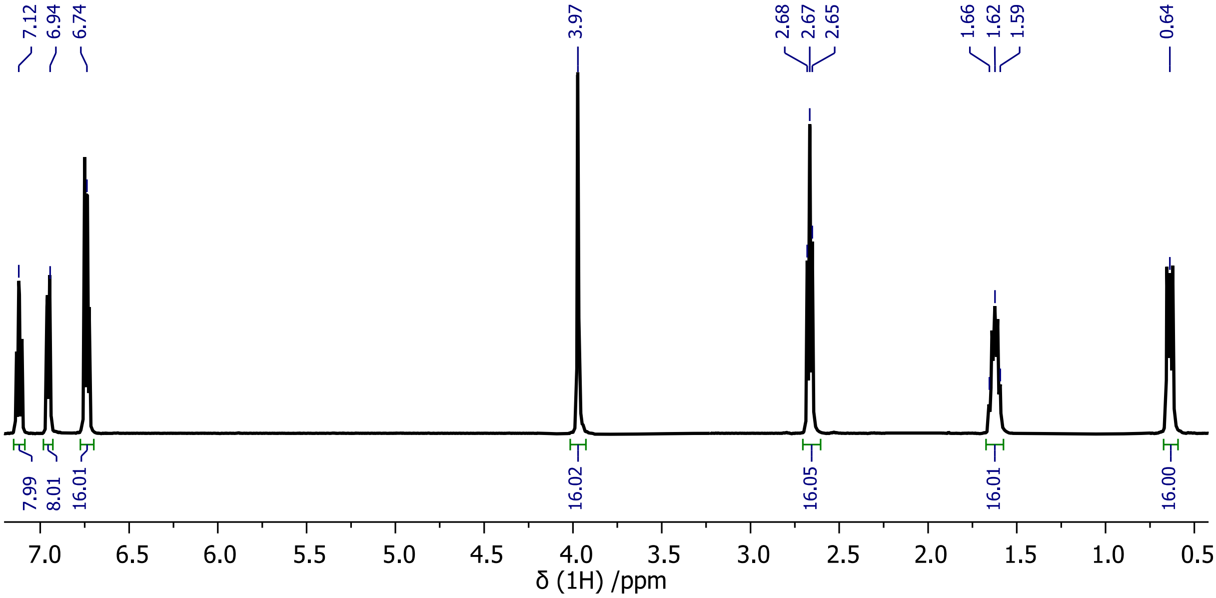

Figure S48. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **9**.

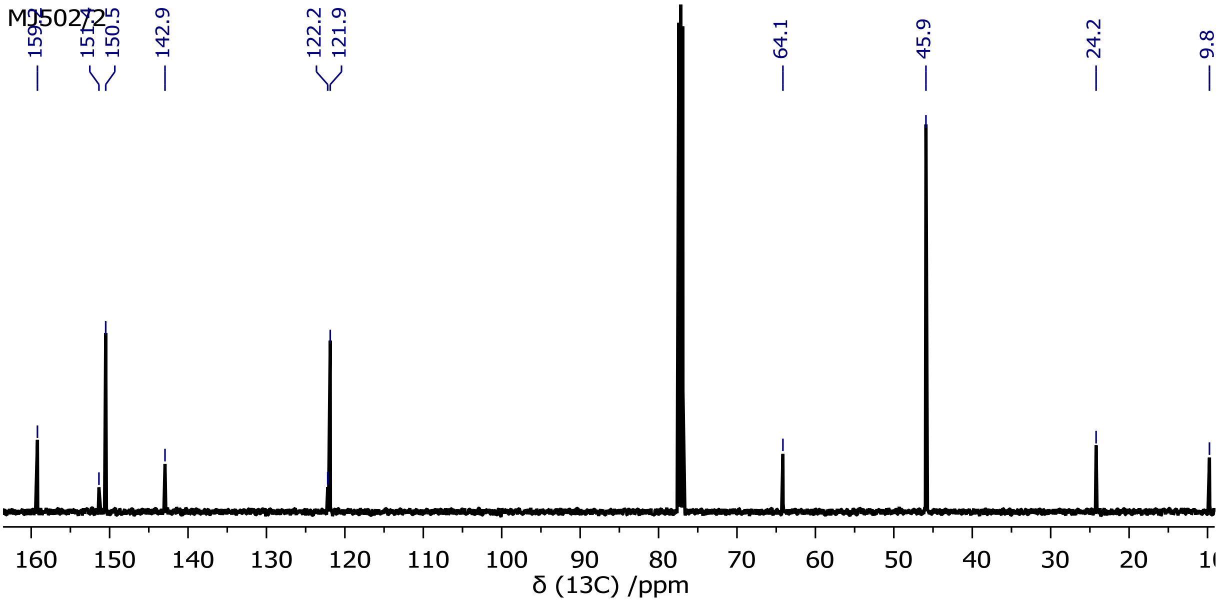

Figure S49. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **9**.

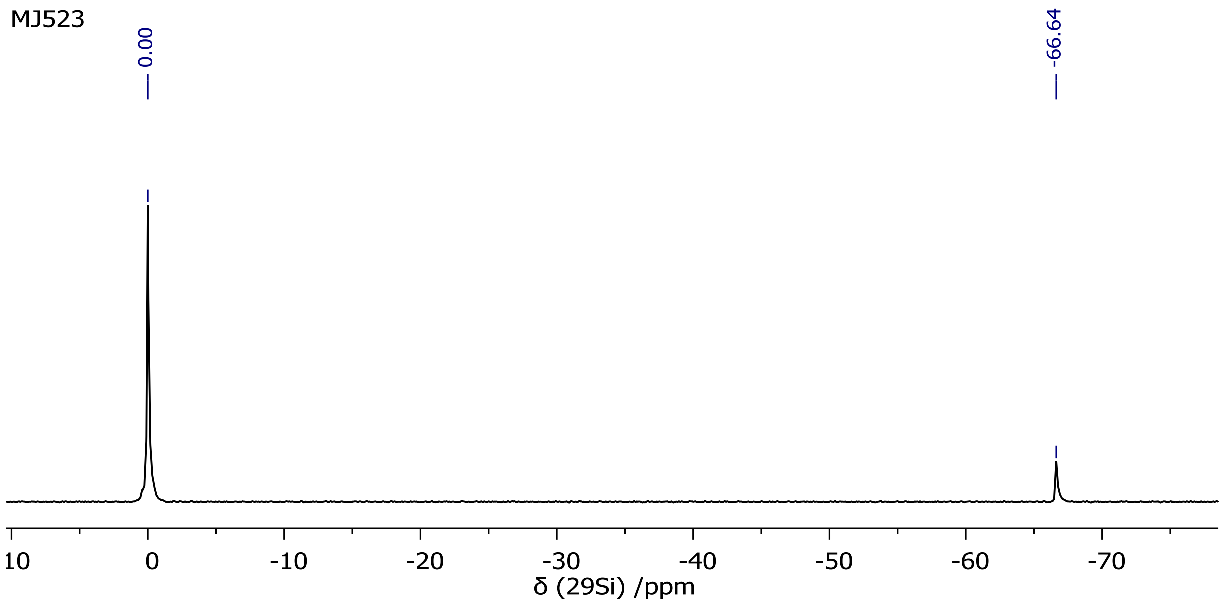

Figure S50. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **9**.

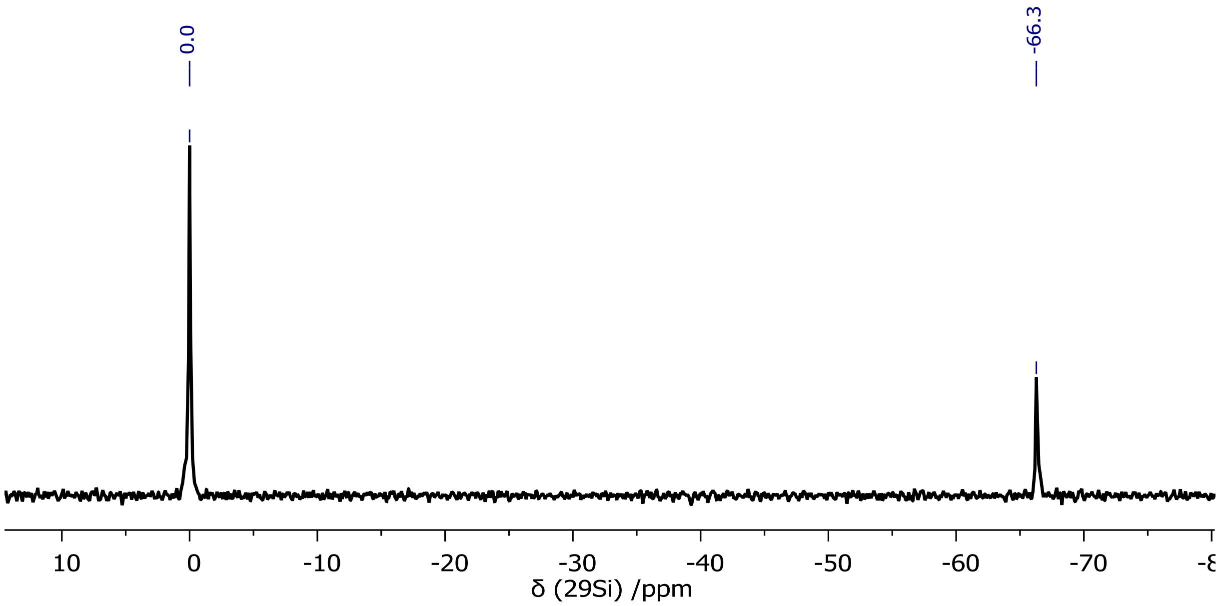

Figure S51. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **10**.

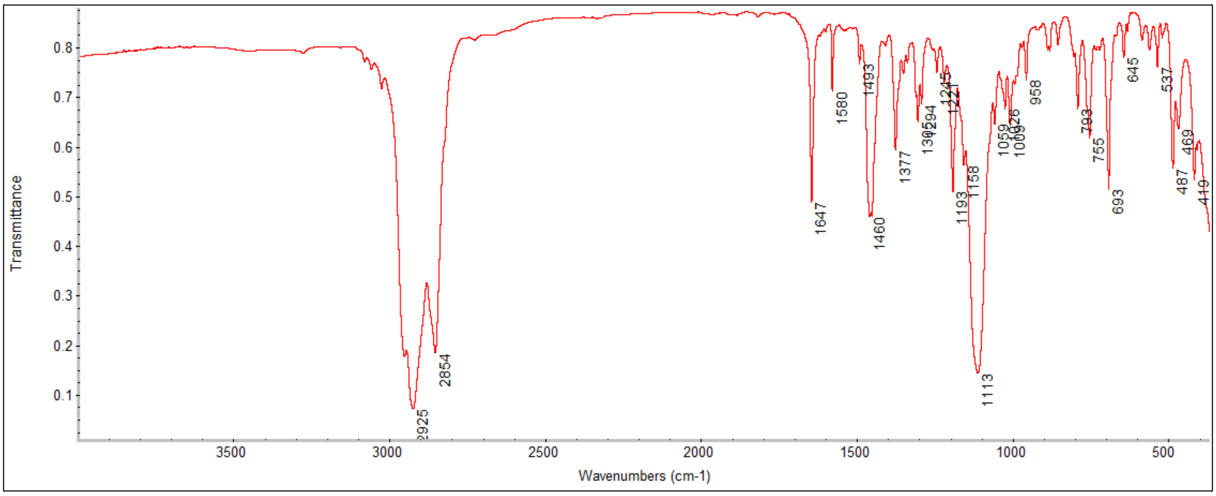

Figure S51. FT-IR (nujol) spectrum of **1**.

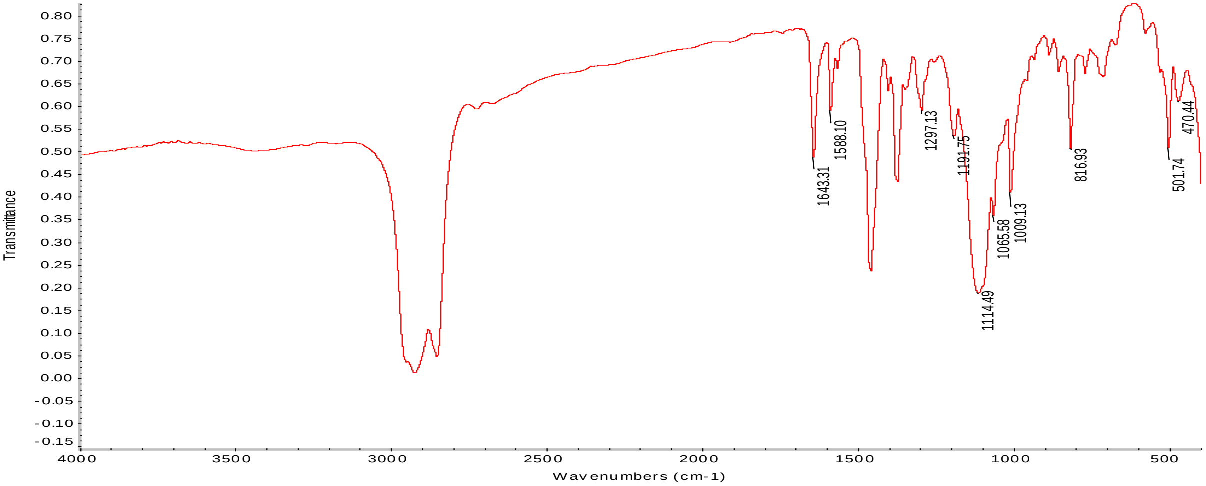

Figure S52. FT-IR (nujol) spectrum of **2**.

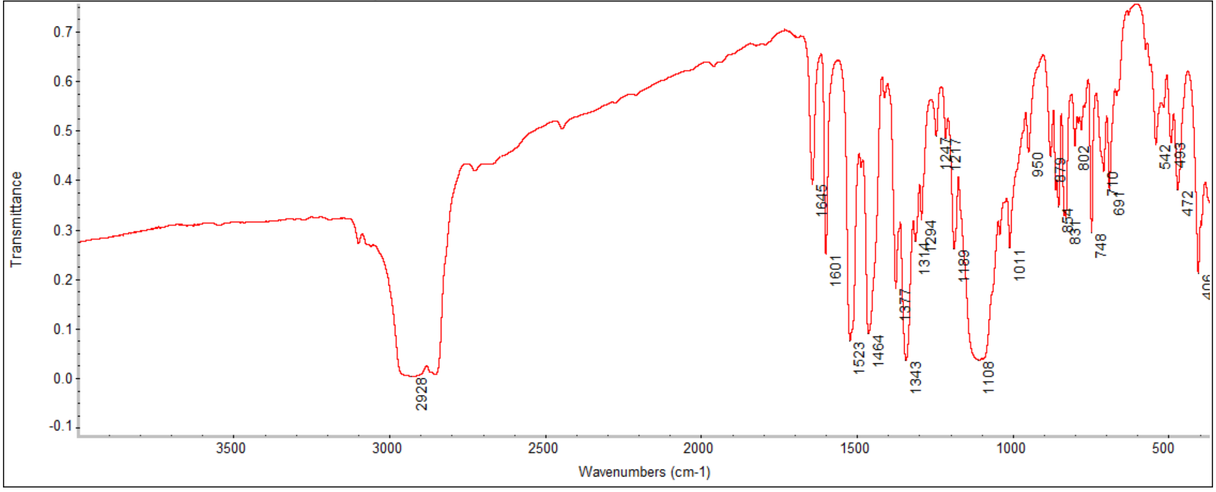

Figure S53. FT-IR (nujol) spectrum of **3**.

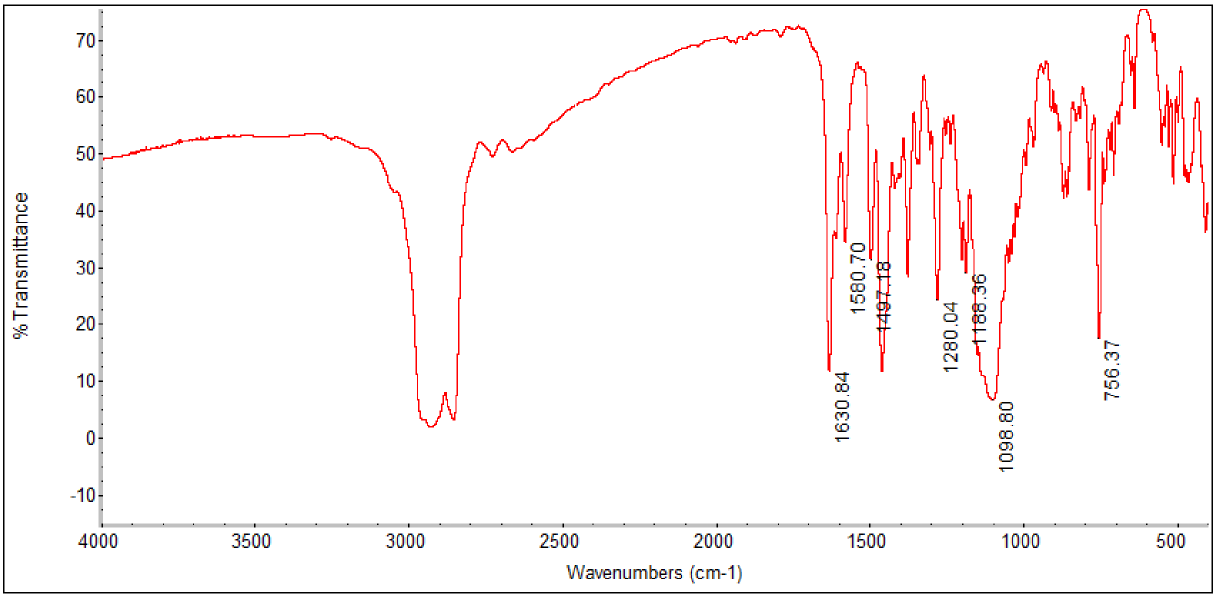

Figure S54. FT-IR (nujol) spectrum of **4**.

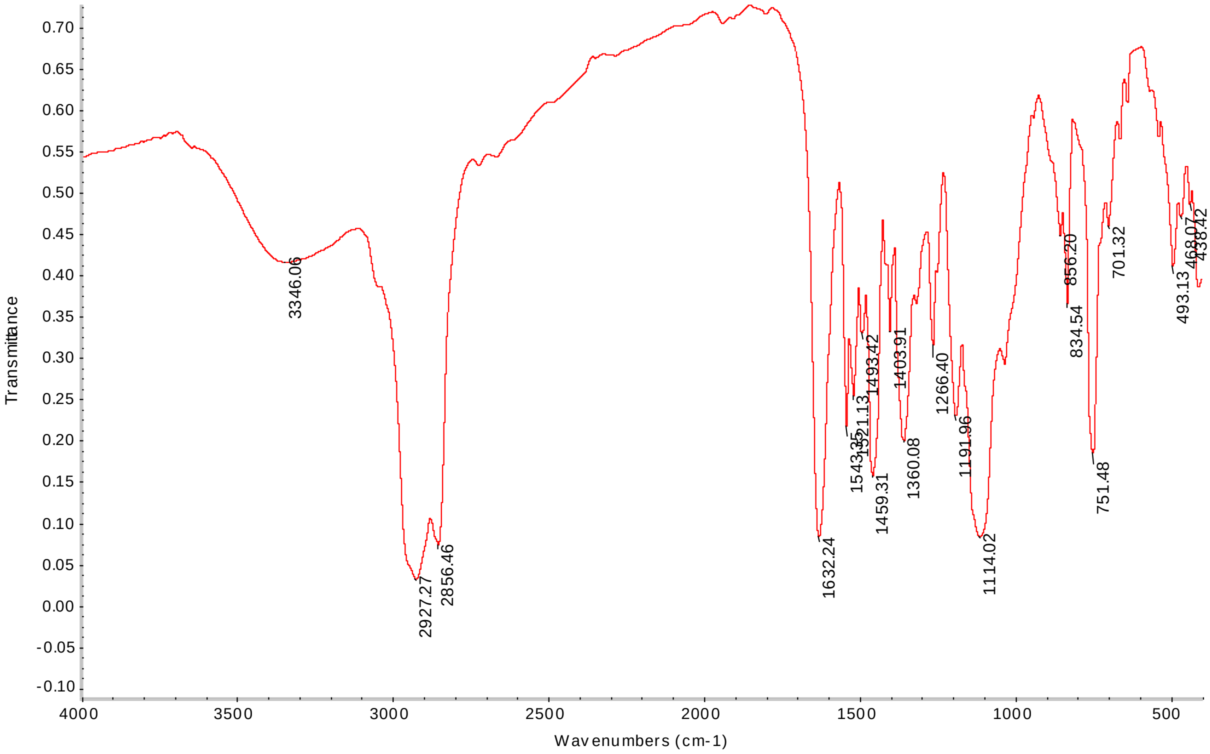

Figure S55. FT-IR (nujol) spectrum of **5**.

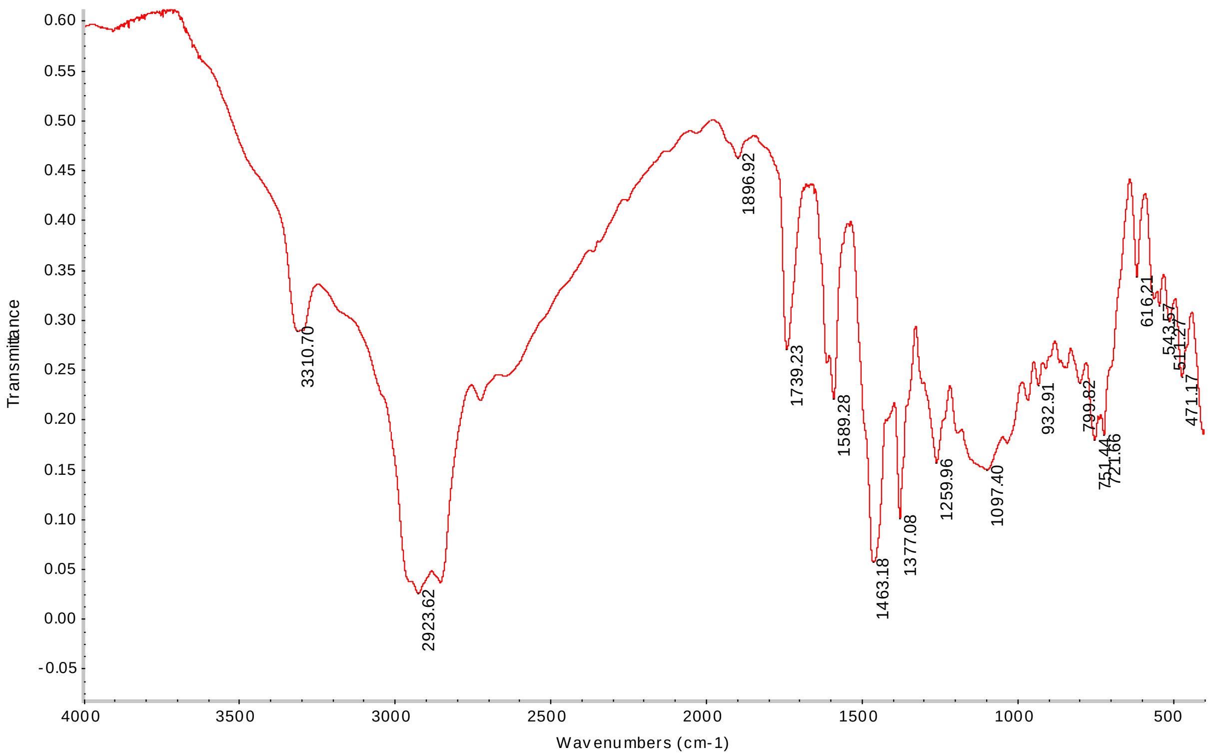

Figure S56. FT-IR (KBr pellets) spectrum of **9**.

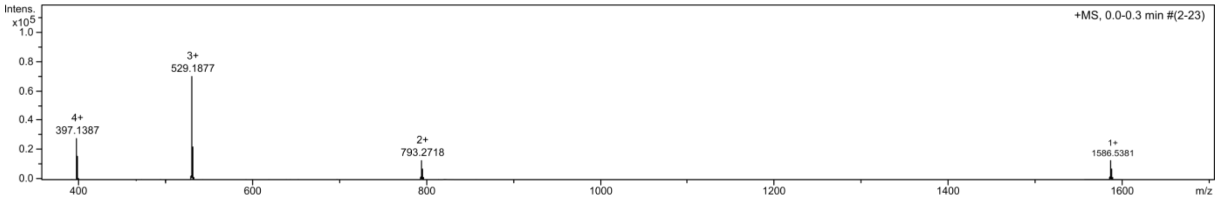

Figure S57. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **1**.

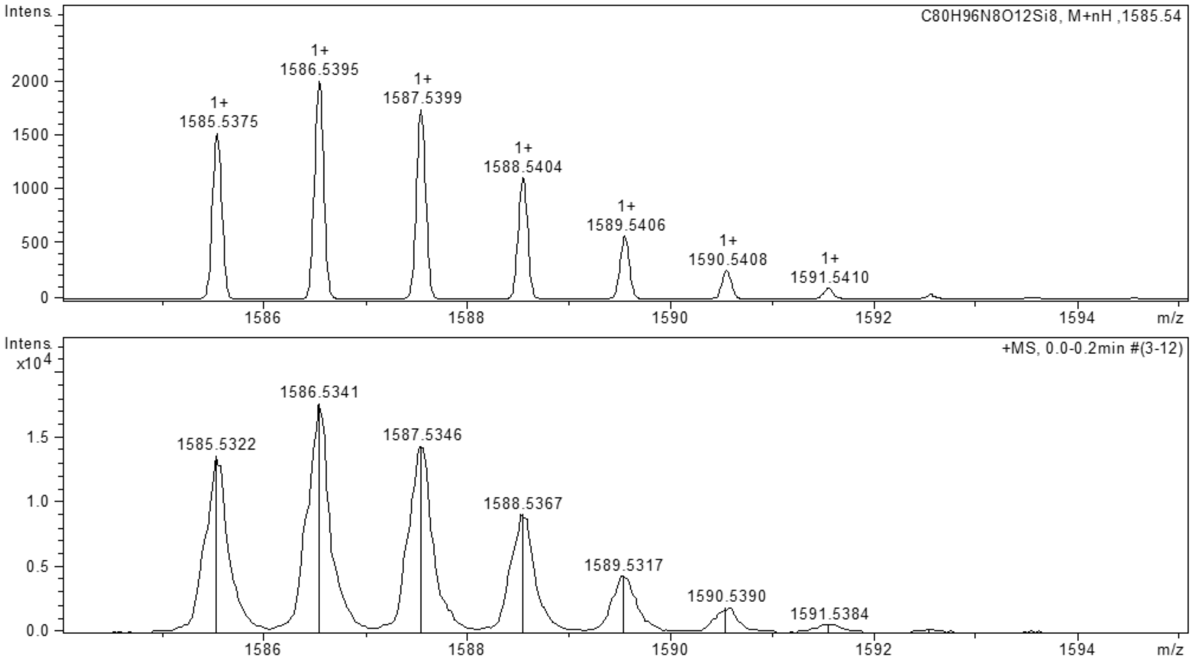

Figure S58. Simulated (top) and measured (bottom) MS (ESI+, TOF, $CHCl_3$) spectra of **1**.

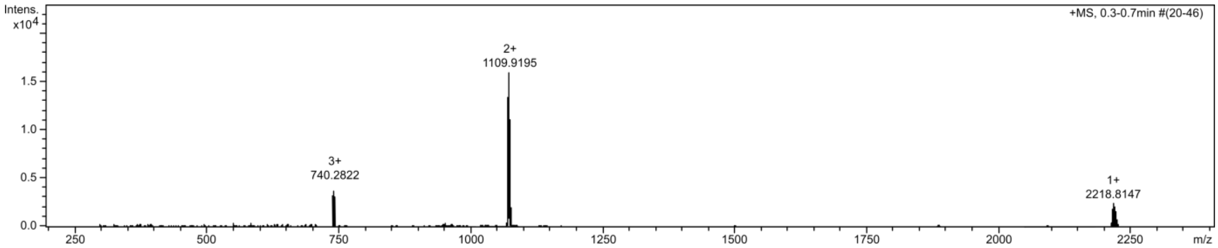

Figure S59. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **2**.

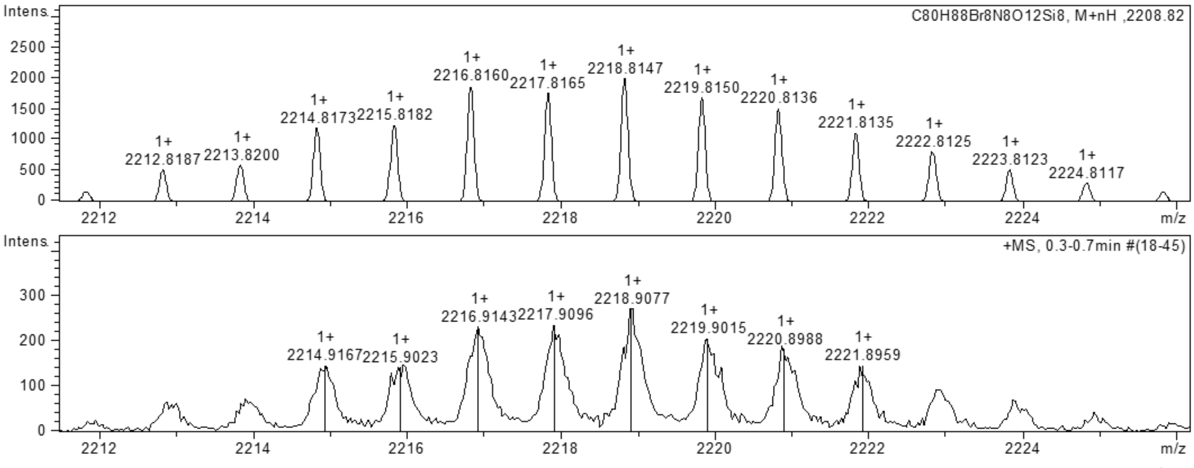

Figure S60. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, $CHCl_3$) spectra of **2**.

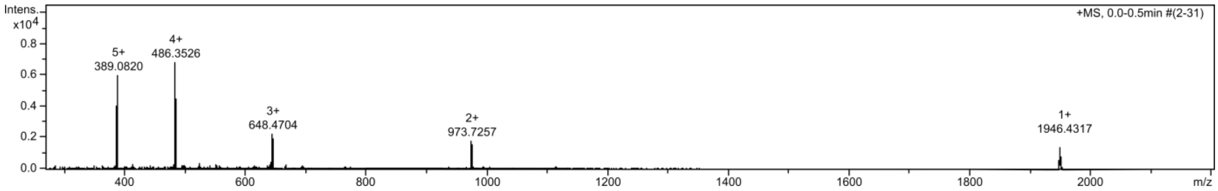

Figure S61 HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **3**.

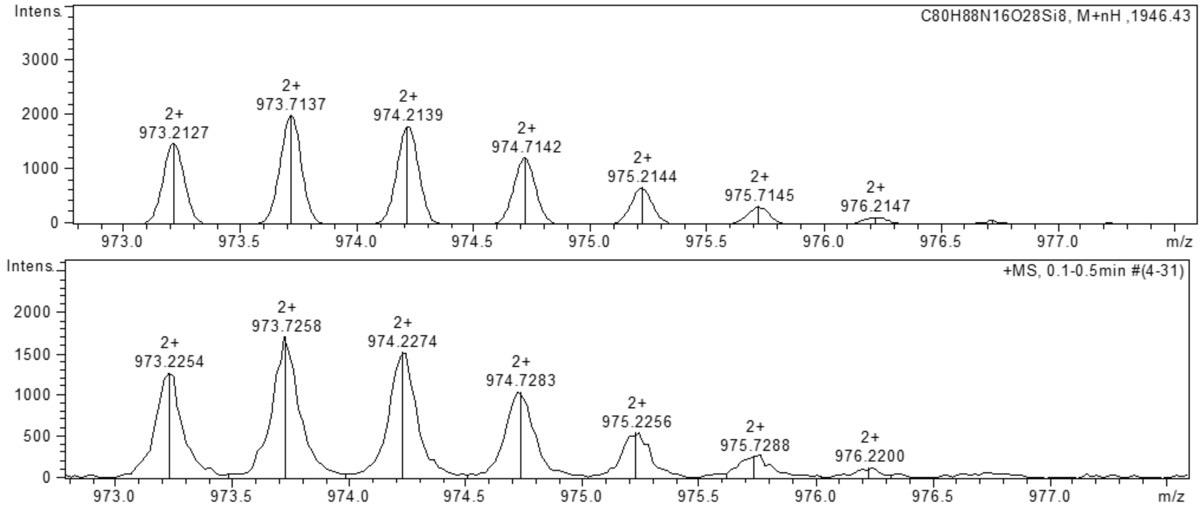

Figure S62. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, $CHCl_3$) spectra of **3**.

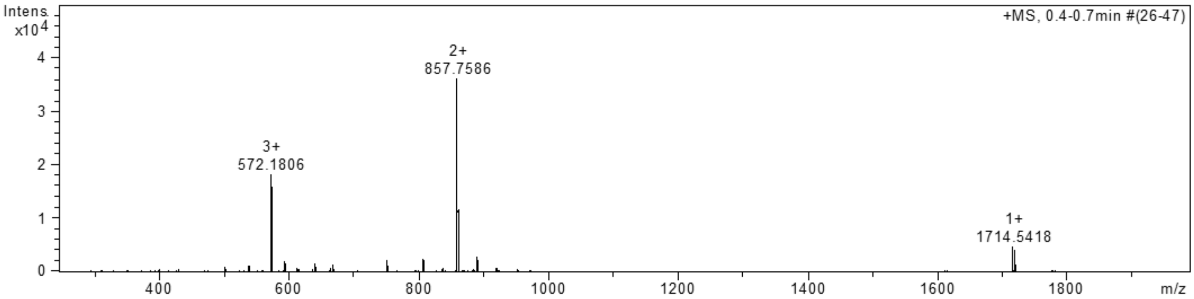

Figure S63. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **4**.

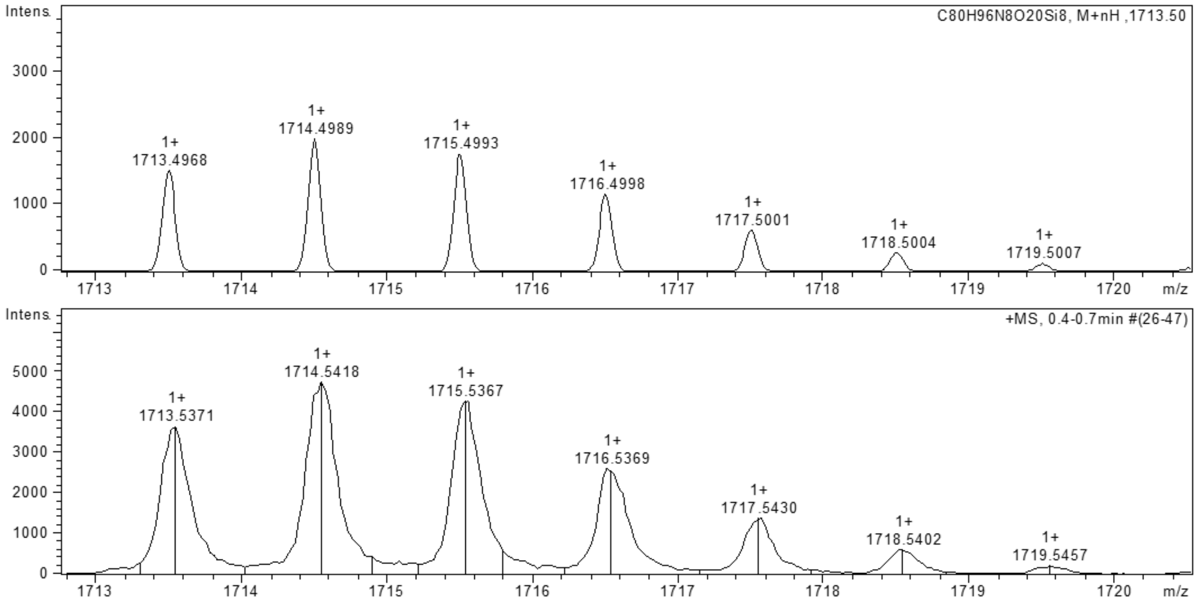

Figure S64. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, $CHCl_3$) spectra of **4**.

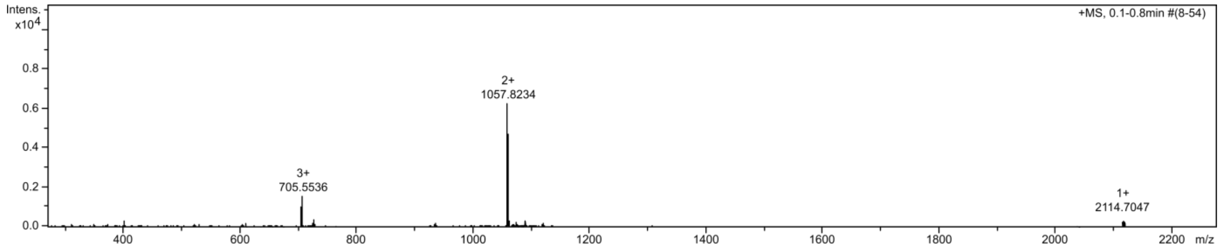

Figure S65. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **5**.

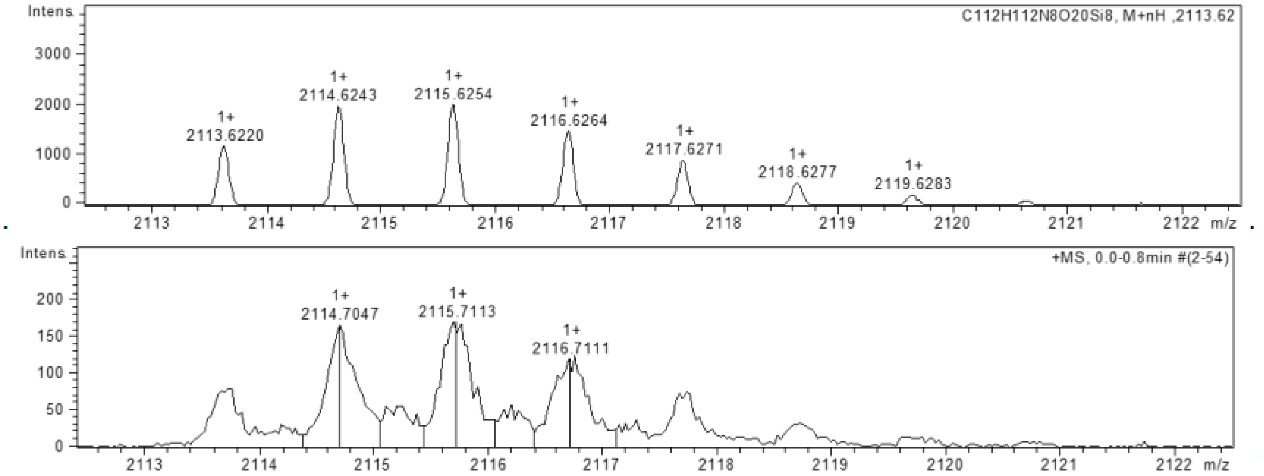

Figure S66. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, $CHCl_3$) spectra of **5**.

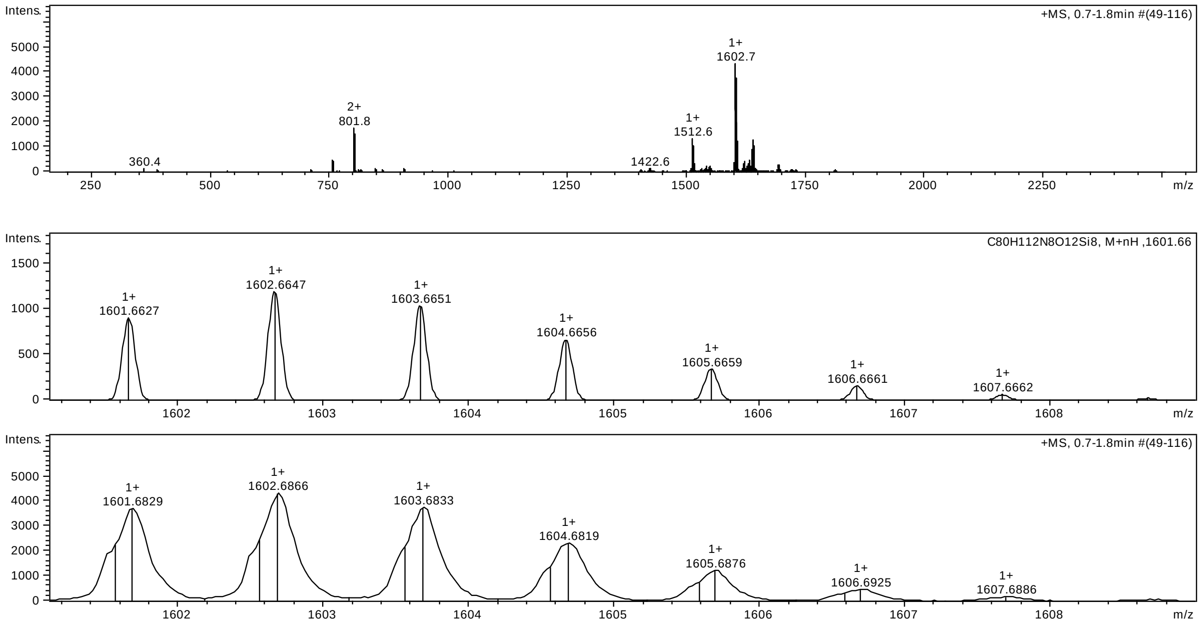

Figure S67. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, $CHCl_3$) spectra of **6**.

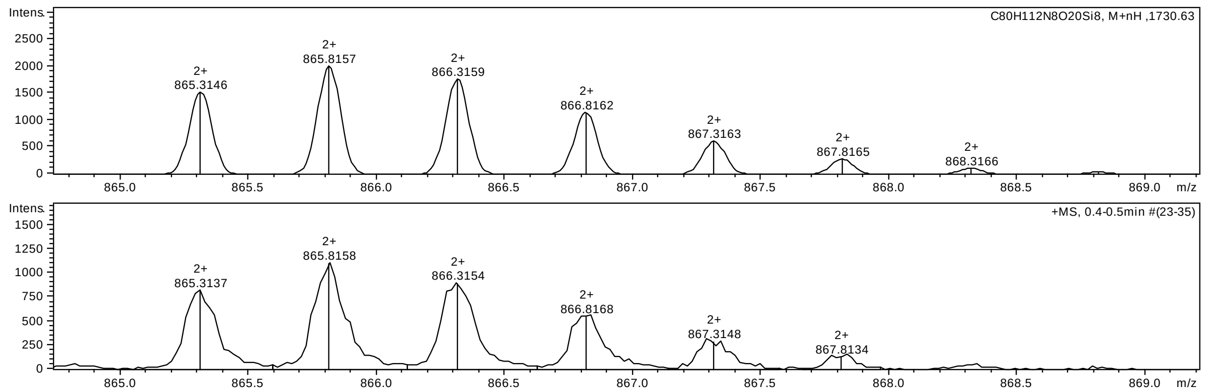

Figure S68. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, $CHCl_3$) spectra of **9**.

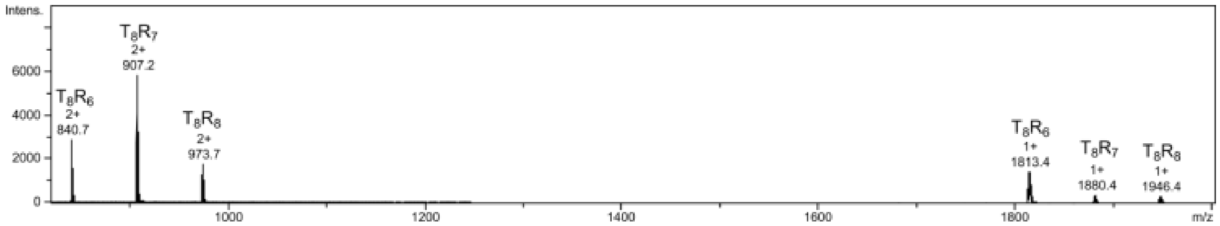

Figure S69. MS spectrum of **3** showing hexa-T_8R_6 and hepta-T_8R_7 derivatives. Spectrum was measured for crude product after the reaction of OAS-POSS-Cl with 4-nitrobenzoic aldehyde.

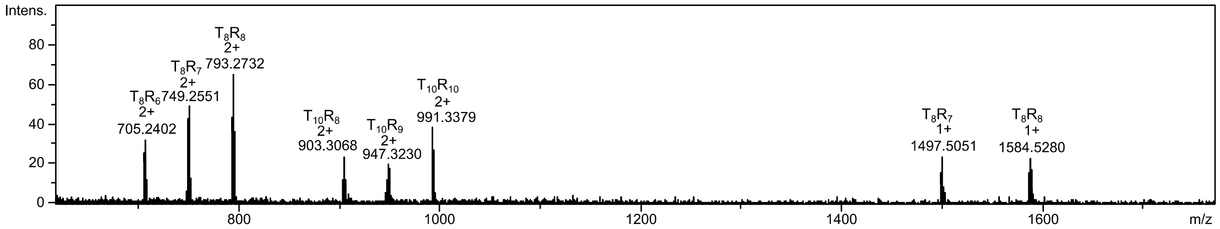

Figure S70. HR-MS spectra of the crude product of reaction of OAS-POSS-CF_3SO_3 with benzoic aldehyde.

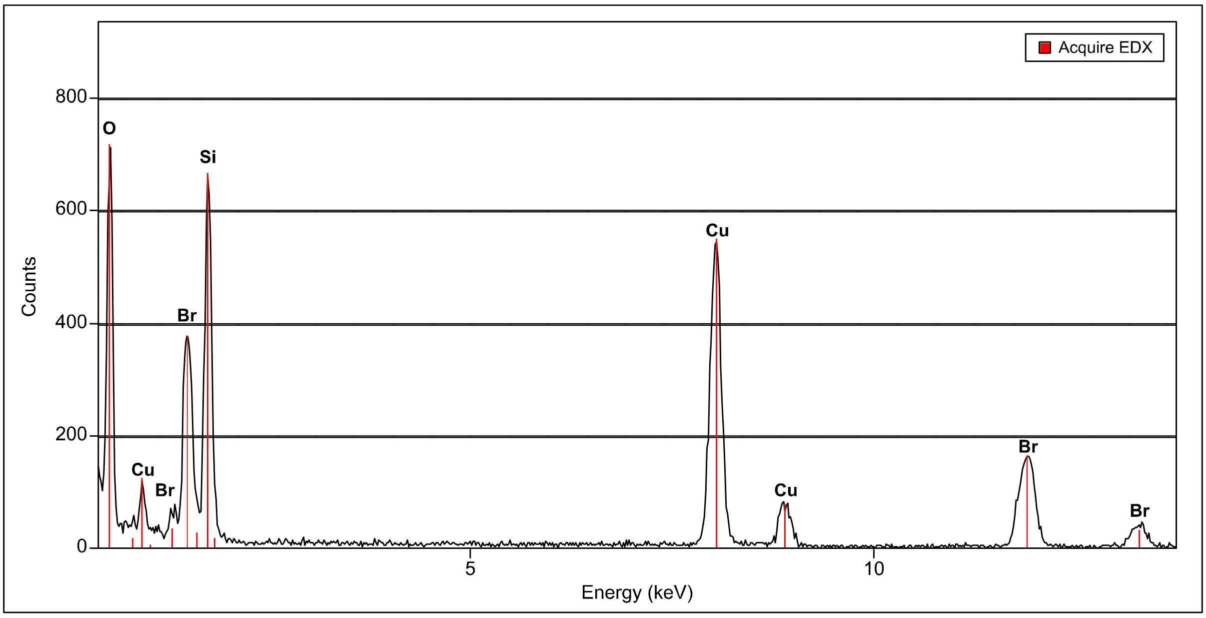

Figure S71. EDS spectrum of **2** after heating to the decomposition temperature (copper content is derived from the high-purity conducting Cu grid).