Supporting Information

for

N-Heterocyclic carbene-based ruthenium–hydride catalysts for the synthesis of unsymmetrically functionalized double-decker silsesquioxanes

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CONTENTS:

1. Materials and methods

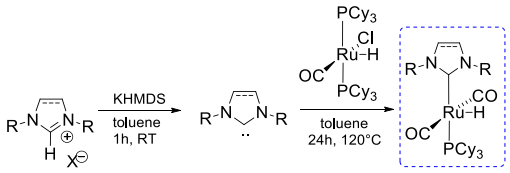
All the syntheses and catalytic tests were carried out under a dry argon atmosphere using standard Schlenk-line and vacuum techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 300 spectrometer operating at 300 and 100.63 MHz, respectively. ^{31}P NMR spectra were recorded on a Mercury 300 spectrometer operating at 121.5 MHz. ^{29}Si NMR spectra were recorded on a Bruker Ascend 400 Nanobay spectrometer operating at 79.50 MHz. High-resolution mass spectroscopy was performed using a Waters Synapt G2-S HDMS mass spectrometer equipped with an electrospray ion source and a quadrupole-time-of-flight mass analyzer with the resolving power FWHM 38000 using methanol as the solvent. The capillary voltage was set to 4.5 kV, the sampling was set at 40 and the source temperature was 120 °C. In the ESI-MS spectra, the sodiated ion was observed as the most abundant ion. Additionally, protonated ions and cluster ions with methanol were present in all the spectra with various intensities. GC analyses were carried out on a Varian CP-3800 instrument equipped with a Rtx-5 column (30 m length, 0.53 mm internal diameter) and a thermal conductivity detector (TCD). GC/MS analyses were performed on a Varian Saturn 2100T instrument equipped with a DB-5 capillary column (30 m length) and an ion trap detector. Fourier-transform infrared spectra were recorded on a Bruker Tensor 27 spectrophotometer equipped with a SPECAC Golden Gate, diamond ATR unit. In all cases, 16 scans at a resolution of 2 cm^{-1} were recorded. Thin layer chromatography was performed on plates coated with 250 mm thick silica gel. Column chromatography was performed on silica gel 60 (70–230 mesh) using *n*-hexane/dichloromethane as eluent.

Dichloromethane, acetone, tetrahydrofuran, ethanol, methanol, propanol, chloroform-*d*, benzene-d_6, styrene, 4-chlorostyrene, 4-bromostyrene, 4-methoxystyrene, 4-(trifluoromethyl)styrene, 4-methylstyrene, potassium bis(trimethylsilyl)amide (KHMDS), tricyclohexylphosphine, calcium hydride, 1,5-cyclooctadiene, decane, dodecane, ethyl vinyl ether, vinyloxytrimethylsilane, 2,6-diisopropylaniline, paraformaldehyde, 2,4,6-trimethylaniline, glyoxal (40 wt. % solution in water), ethyl acetate, zinc chloride, sodium chloride, hydrochloric acid, sodium tetrafluoroborate, formic acid, triethyl orthoformate, chlorotrimethylsilane, anhydrous magnesium sulfate, copper(I) chloride and 4Å molecular sieves were purchased from Aldrich. Triethylamine and silica gel 60 were obtained from Fluka. Vinylmethyldichlorosilane was purchased from ABCR. Tetrasilanol POSS (DDSQ-4OH) was obtained from Hybrid Plastics. *n*-Hexane and toluene were purchased from Chempur. The Grubbs first generation benzylidene catalyst was supplied by Apeiron Synthesis. Ruthenium(III) chloride hydrate came from Lancaster. 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride (IMes•HCl), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IDip•HCl), 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (SIMes•HCl), and 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (SIDip•HCl) were prepared according to published procedures.[1–3] The [RuHCl(CO)(PCy_3)$_2$] complex[4] and divinyl-substituted double-decker silsesquioxanes (DDSQ-2Vi) **1A**–**C**[5] were synthesized according to literature. All the

solvents (except tetrahydrofuran) were dried over CaH_2 prior to use and stored under argon over 4Å molecular sieves. Dichloromethane (DCM) was additionally passed through a column filled with alumina and after that it was degassed by repeated freeze-pump-thaw cycles. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and freshly distilled prior to use.

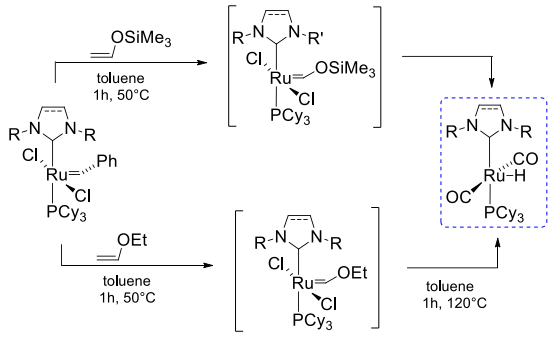
2. Synthesis and characterization of ruthenium–hydride complexes I-IV

2.1. Method A: from [RuHCl(CO)(PCy_3)$_2$]

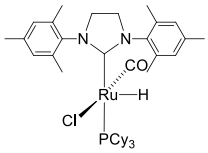
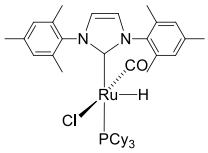
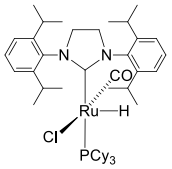
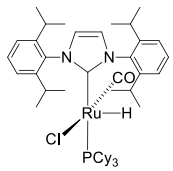


A 25 mL high-pressure Schlenk vessel equipped with a magnetic stirring bar and connected to gas and vacuum lines was charged with an imidazol(in)ium salt (5.84×10^{-4} mol, 1 equiv.), potassium bis(trimethylsilyl)amide (128 mg, 6.43×10^{-4} mol, 1.1 equiv.) and dry toluene (5 mL). The reaction mixture was stirred at room temperature for 1 h. The [RuHCl(CO)(PCy_3)$_2$] complex (424 mg, 5.84×10^{-4} mol, 1 equiv.) was then added and the reaction mixture was stirred for 24 h at 120 °C. After this time, the reaction mixture was filtered on a pad of Celite and the pad was rinsed with toluene. The solvent was evaporated under vacuum. Cold ethanol was added to the residue to afford a yellow-orange precipitate. The precipitate was filtered off and dried under vacuum.

2.2. Method B: from [$RuCl_2$(=CHPh)(NHC)(PCy_3)]



A 25 mL high-pressure Schlenk vessel equipped with a magnetic stirring bar and connected to gas and vacuum lines was charged with [$RuCl_2$(=CHPh)(NHC)(PCy_3)] (1.77×10^{-4} mol, 1 equiv.), ethyl vinyl ether or vinyloxytrimethylsilane (1.77×10^{-2} mol, 100 equiv.) and dry toluene (5 mL). The reaction mixture was stirred at 50 °C for 1 h and at 120 °C for an additional hour when ethyl vinyl ether was used. After this time, the solvent was evaporated under vacuum. Cold ethanol was added to the residue to afford a yellow-orange precipitate. The precipitate was filtered off and dried under vacuum.

 **Complex I**	Yellow-orange solid (85% isolated yield); ^{1}H NMR (C_6D_6, δ, ppm): –24.90 (d, 1H, J_{HH} = 21.3 Hz, Ru-*H*), 2.13 (s, 6H, *p*-CH_3), 1.09 – 1.89, 2.20 – 2.22 (m, 33H, Cy), 2.55 – 2.67 (br s, 12H, *o*-CH_3), 3.25 (s, 4H, NCH_2), 6.81 (s, 2H, *m*-C*H*), 6.85 (s, 2H, *m*-C*H*); ^{13}C NMR (C_6D_6, δ, ppm): 19.3, 21.1, 26.9, 28.0, 28.1, 29.9, 30.8, 34.3 (d, *J* = 17.7 Hz), 50.9 (d, *J* = 3.8 Hz), 126.9, 128.5, 128.9, 129.5, 137.5, 202.0 (d, *J* = 13.0 Hz), 217.9 (d, *J* = 89.0 Hz); ^{31}P NMR (C_6D_6, δ, ppm): 46.80 (s, *P*Cy_3). These spectroscopic data matched those reported in the literature.[6]
 **Complex II**	Yellow-orange solid (78% isolated yield); ^{1}H NMR (C_6D_6, δ, ppm): –24.82 (d, 1H, J_{HH} = 21.3 Hz, Ru-*H*), 2.12 (s, 6H, *p*-CH_3), 1.14 – 2.21 (m, 33H, Cy), 2.38 (s, 6H, *o*-CH_3), 2.49 (s, 6H, *o*-CH_3), 6.22 (s, 2H, NC*H*=C*H*N), 6.79 (s, 2H, *m*-C*H*), 6.83 (s, 2H, *m*-C*H*); ^{31}P NMR (C_6D_6, δ, ppm): 47.80 (s, *P*Cy_3). These spectroscopic data matched those reported in the literature.[6]
 **Complex III**	Yellow-orange solid (75% isolated yield); ^{1}H NMR (CD_2Cl_2, δ, ppm): –24.35 (d, 1H, J_{HH} = 21 Hz, Ru-*H*), 1.03-1.68 (m, 33H, PCy_3), 1.26 (d, 6H, J_{HH} = 7.0 Hz, CH(CH_3)$_2$), 1.29 (d, 6H, J_{HH} = 7.0 Hz, CH(CH_3)$_2$), 1.38 (d, 6H, J_{HH} = 6.5 Hz, CH(CH_3)$_2$), 1.44 (d, 6H, J_{HH} = 6.5 Hz, CH(CH_3)$_2$), 1.95 – 2.02 (m, 4H, NCH_2), 3.58 (sept, 2H, J_{HH} = 6.5 Hz, C*H*(CH_3)$_2$), 3.70 (sept, 2H, J_{HH} = 6.5 Hz, C*H*(CH_3)$_2$), 7.24 – 7.27 (m, 4H, *m*-C*H* ^{Im}), 7.36 (t, 2H, J_{HH} = 7.0 Hz, *p*-C*H* ^{Im}); ^{13}C NMR (CD_2Cl_2, δ, ppm): 23.28, 23.36, 26.69, 26.82, 26.85, 27.85, 27.87, 27.94, 28.82, 28.85, 29.61, 30.33, 34.20, 34.35, 124.07, 128.93, 136.04, 148.33, 210.2 (d, *J* = 14.3 Hz, Ru-*C*O), 212.4 (d, *J* = 82.3 Hz; Ru-*C*N_2); ^{31}P NMR (CD_2Cl_2, δ, ppm): 47.04 (s, *P*Cy_3). These spectroscopic data matched those reported in the literature.[6]
 **Complex IV**	Yellow-orange solid (88% isolated yield); ^{1}H NMR (C_6D_6, δ, ppm): –24.74 (d, 1H, J_{HH} = 21 Hz, Ru-*H*), 1.05-1.69 (m, 33H, PCy_3), 1.28 (d, 6H, J_{HH} = 7.0 Hz, CH(CH_3)$_2$), 1.30 (d, 6H, J_{HH} = 7.0 Hz, CH(CH_3)$_2$), 1.37 (d, 6H, J_{HH} = 6.5 Hz, CH(CH_3)$_2$), 1.46 (d, 6H, J_{HH} = 6.5 Hz, CH(CH_3)$_2$), 3.59 (sept, 2H, J_{HH} = 6.5 Hz, C*H*(CH_3)$_2$), 3.72 (sept, 2H, J_{HH} = 6.5 Hz, C*H*(CH_3)$_2$), 6.24 (s, 2H, NC*H*=C*H*N), 7.23 – 7.27 (m, 4H, *m*-C*H* ^{Im}), 7.38 (t, 2H, J_{HH} = 7.0 Hz, *p*-C*H* ^{Im}); ^{31}P NMR (C_6D_6, δ, ppm): 47.71 (s, *P*Cy_3). These spectroscopic data matched those reported in the literature.[6]

3. General procedures for the catalytic tests

3.1. Silylative coupling of ViSi(OSiMe$_3$)$_3$ with styrene

An oven-dried 5 mL glass reactor equipped with a reflux condenser and a magnetic stirring bar was charged under argon with CH_2Cl_2 (2 mL), tris(trimethylsiloxy)silane (30 µL, 8.62×10^{-5} mol), dodecane (20 µL) and styrene (10 µL, 8.62×10^{-5} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 °C). Then a ruthenium–hydride complex (**I-IV**) (8.62×10^{-7} mol) was added to the mixture under argon. After 5 min, copper(I) chloride (0.0004 g, 4.31×10^{-6} mol) was added. The reaction mixture was heated under reflux for 24 h. Conversion of the substrates was monitored by gas chromatography. Reaction yields and selectivities were calculated on the basis of the ^{1}H NMR spectra of the reaction mixture.

3.2. Silylative coupling of DDSQ-2ViSiMe (1A) with 4-chlorostyrene (2d)

A 5 mL glass reactor equipped with a reflux condenser and connected to gas and vacuum lines was charged under argon with CH_2Cl_2 (2 mL), DDSQ-2ViSiMe (**1A**) (0.1 g, 8.29×10^{-5} mol), dodecane (20 μL) and 4-chlorostyrene (10 μL, 8.29×10^{-5} mol). The mixture was warmed up to 45 °C in an oil bath and ruthenium–hydride complex **III** (0.0007 g, 8.29×10^{-7} mol) was added to the mixture under argon. After 5 min, copper(I) chloride (0.0004 g, 4.14×10^{-6} mol) was added. The reaction mixture was heated under reflux until full conversion of 4-chlorostyrene was detected by TLC (8 h). Reaction yield and selectivity were calculated on the basis of the ^{1}H NMR spectra of the reaction mixture.

3.3. Silylative coupling of DDSQ-2ViSi (1A-C) with styrenes

A 5 mL glass reactor equipped with a reflux condenser and connected to gas and vacuum lines was charged under argon with CH_2Cl_2 (2 mL), DDSQ-2ViSi (**1A-C**) (8.29×10^{-5} mol), an internal standard (decane or dodecane, 20 μL) and styrene (**2a-e**) (8.29×10^{-5} mol). The mixture was warmed up to 45 °C in an oil bath and ruthenium–hydride complex **III** (0.0007 g, 8.29×10^{-7} mol) was added to the mixture under argon. After 5 min, copper(I) chloride (0.0004 g, 4.14×10^{-6} mol) was added. The reaction mixture was heated under reflux until full conversion of styrene (**2a-e**) was detected by TLC. Then the second type of styrene (**3a-e**) (8.29×10^{-5} mol) was added and the reaction was resumed. Conversion of the styrene (**3a-e**) was monitored by TLC. Reaction yields and selectivities were calculated on the basis of the ^{1}H NMR spectra of the reaction mixture.

4. Synthesis of symmetrically functionalized divinylsilsesquioxanes (4A-a-a and 4A-e-e)

A 5 mL glass reactor equipped with a reflux condenser and connected to gas and vacuum lines was charged under argon with CH_2Cl_2 (3 mL), DDSQ-2ViSi (**1A**) (1.24×10^{-4} mol) and styrene (**2a**) or 4-methoxystyrene (**2e**) (2.48×10^{-4} mol). The mixture was warmed to 45 °C in an oil bath and ruthenium–hydride complex **III** (0.0010 g, 1.24×10^{-6} mol) was added to the mixture under argon. After 5 min, copper(I) chloride (0.0006 g, 6.2×10^{-6} mol) was added. The reaction mixture was heated under reflux for 8 h. Then the solvent was evaporated under vacuum and cold *n*-hexane (5 mL) was added to the residue to form a colorless precipitate. The precipitate was filtered off and purified by column chromatography (silica gel 60, *n*-hexane/CH_2Cl_2 = 1/5) to remove ruthenium complexes. Evaporation of the solvent gave an analytically pure sample (white powder).

5. General procedure for the synthesis of unsymmetrically functionalized divinyl-silsesquioxanes

A 25 mL two-necked glass reactor equipped with a reflux condenser and connected to gas and vacuum lines was charged under argon with DDSQ-2ViSi (**1A-C**) (2.9×10^{-4} mol) and styrene (**2a-e**) (2.9×10^{-4} mol) and CH_2Cl_2 (6 mL). The mixture was warmed up to 45 °C in an

oil bath and ruthenium–hydride complex **III** (0.0024 g, 2.9×10^{-6} mol) was added to the mixture under argon. After 5 min, copper(I) chloride (0.0014 g, 1.45×10^{-5} mol) was added. The reaction mixture was heated under reflux until full conversion of styrene (**2a-e**) was detected by TLC. Then the second type of styrene (**3a-e**) (2.9×10^{-4} mol) was added and the catalytic system was left for night. Then the solvent was evaporated under vacuum and cold *n*-hexane (2 mL) was added to the residue to form a colorless precipitate. The precipitate was filtered off and purified by column chromatography (silica gel 60, *n*-hexane/CH_2Cl_2 = 1/5) to remove the ruthenium impurities. Evaporation of the solvent gave an analytically pure sample (white powder).

6. Analytical data of isolated products

9-(E)-4-Chlorostyrylmethyl-19-(E)-vinylmethyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane

^{1}H NMR ($CDCl_3$, δ, ppm): 0.38 (s, 3H, CH_3), 0.44 (s, 3H, CH_3), 5.78 – 6.33 (m, 3H, H_2C=C*H*-Si), 6.45 (d, 2H, J_{HH} = 19.3 Hz, =C*H*-Si), 6.89-7.23 and 7.29-7.63 (m, 45H, =C*H*-C_6H_4-Cl and C_6H_5)

Di[9,19-(E)-styrylmethyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]-decasiloxane (4A-a-a)

^{1}H NMR ($CDCl_3$, δ, ppm): 0.439-0.445 (overlapping s, 6H, CH_3), 6.44 (d, 2H, J_{HH} = 19.3 Hz, =C*H*-Si), 7.12 (d, 2, J_{HH} = 19.3 Hz, =C*H*-C_6H_5), 6.89-7.6 (m, 50H, C_6H_5-); ^{13}C NMR ($CDCl_3$, δ, ppm): -0.79 (*C*H_3), 123.94, 126.78, 127.52 (t, *J* = 7.9 Hz), 127.77, 128.38 (d, *J* = 1.7 Hz), 130.11, 130.21, 130.3, 130.34, 130.54, 130.79, 131.93, 133.94, 134.08, 137.50, 146.59; ^{29}Si NMR ($CDCl_3$, δ, ppm): -30.17, -78.30, -79.15, -79.51, -79.84; MS (FD): m/z (%): 1379.16 (79), 1380.16 (100), 1381.16 (89), 1382.16 (52), 1383.16 (28); HRMS (FD): calcd. for $C_{66}H_{60}O_{14}Si_{10}Na$: 1379.1574; found: 1379.1569.

Di[9,19-(E)-4-methoxystyrylmethyl]-1,3,5,7,11,13,15,17-octaphenylpentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4A-e-e)

^{1}H NMR ($CDCl_3$, δ, ppm): 0.43 (s, 6H, CH_3), 3.81 (s, 6H, OCH_3), 6.27 (d, 2H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.68 – 6.80 (m, 4H, -C_6H_4-OCH_3), 6.90 – 7.25 (m, 18H, =C*H*-C_6H_4-OCH_3 and C_6H_5-), 7.27 – 7.72 (m, 28H, C_6H_5-); ^{13}C NMR ($CDCl_3$, δ, ppm): -0.71 (*C*H_3), 55.33 (O*C*H_3), 113.78, 121.27, 127.55 (t, *J* = 7.0 Hz), 127.79, 128.15, 130.12, 130.22, 130.33, 130.61, 130.73, 130.94, 131.14, 132.07, 134.01, 134.12, 134.15, 146.09, 159.88; ^{29}Si NMR ($CDCl_3$, δ, ppm): -29.82, -78.36, -79.25, -79.57, -79.88.

9-(E)-4-Bromostyrylmethyl-19-(E)-styrylmethyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4A-a-c)

^{1}H NMR ($CDCl_3$, δ, ppm): 0.45 (s, 6H, CH_3), 6.42 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.46 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.89 – 7.65 (m, 51H, =C*H*-C_6H_5, =C*H*-C_6H_4-Br and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): -0.80 (*C*H_3), -0.74 (*C*H_3), 122.28, 122.31, 122.32, 122.33, 123.97, 124.02, 125.02, 125.06, 126.84, 127.50, 127.53, 127.58, 127.59, 127.62, 127.63, 127.66, 127.72, 127.83, 127.86, 127.90, 128.29, 128.42, 128.44, 129.76, 130.26, 130.29, 130.39, 130.41, 130.45, 130.47, 130.59, 130.62, 130.79 (d, *J* = 3.6 Hz), 130.85 (d, *J* = 3.6 Hz), 131.04, 131.10, 131.49, 131.51, 131.85, 131.91, 131.95, 132.00, 133.98 (d, *J* = 1.5 Hz), 134.00 (d, *J* = 1.5 Hz), 134.08, 134.11, 134.14, 134.22, 134.23, 136.50 (d, *J* =2.3 Hz), 137.58 (d, *J* = 2.3 Hz), 145.26, 145.27, 146.67, 165.42, 165.46; ^{29}Si NMR ($CDCl_3$, δ, ppm): -29.80, -30.19, -78.31, -78.35, -79.52, -79.56; MS (FD): m/z(%): 1456.11 (11), 1457.06 (47), 1458.07 (62), 1459.07 (100), 1460.07 (91), 1461.07 (68), 1462.07 (40), 1463.07 (29), 1464.07 (11); HRMS (FD): calcd. for $C_{66}H_{59}BrO_{14}NaSi_{10}$: 1457.0679; found: 1457.0704.

9-(E)-4-Methoxystyrylmethyl-19-(E)-styrylmethyl-1,3,5,7,11,13,15,17-octaphenylpenta-cyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4A-a-e)

^{1}H NMR ($CDCl_3$, δ, ppm): 0.42 – 0.47 (overlapping s, 6H, CH_3), 3.83 (s, 3H, OCH_3), 6.28 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.46 (d, 1H, J_{HH} = 19.3 Hz, =C*H*-Si), 6.76 (d, 2H, J_{HH} = 8.5 Hz, -C_6H_4-OCH_3), 6.71 – 7.79 (m, 49H, =C*H*-C_6H_5, =C*H*-C_6H_4-OCH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): -0.75 (*C*H_3), -0.71 (*C*H_3), -55.33 (O*C*H_3), 113.79, 121.26, 124.02, 126.84, 127.50, 127.57, 127.64, 127.80, 127.82, 128.16, 128.44, 130.14, 130.24, 130.35, 130.38, 130.62, 130.68, 130.74, 130.88 (d, *J* = 2.4 Hz), 130.94 (d, *J* = 2.4 Hz), 131.13, 132.01 (d, *J* = 1.7 Hz), 132.08 (d, *J* = 1.7 Hz), 134.02, 134.14, 134.16, 137.59, 146.10, 146.66, 159.90; ^{29}Si NMR ($CDCl_3$, δ, ppm): -30.12, -30.18, -30.47, -30.52, -78.28, -78.30, -79.48, -79.51, -79.55, -79.58; MS (FD): m/z (%): 1409.17 (82), 1410.16 (100), 1411.17 (99), 1412.17 (62), 1413.17 (33), 1414.16 (18), 1415.16 (11), 1417.19 (13); HRMS (FD): calcd. for $C_{67}H_{62}O_{16}NaSi_{10}$: 1409.1679; found: 1409.1667.

9-(E)-4-Methylstyrylmethyl-19-(E)-4-methoxystyrylmethyl-1,3,5,7,11,13,15,17-octaphenyl-pentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4A-b-e)

^{1}H NMR ($CDCl_3$, δ, ppm): 0.45 (s, 6H, CH_3), 2.36 (s, 3H, -C_6H_4-CH_3), 3.83 (s, 3H, OCH_3), 6.29 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.39 (d, 1H, J_{HH} = 19.1 Hz, =C*H*-Si), 6.76 (d, 2H, J_{HH} = 8.4 Hz, -C_6H_4-), 6.77 (d, 2H, J_{HH} = 8.6 Hz, -C_6H_4-), 6.91 – 7.82 (m, 46H, =C*H*-C_6H_4-OCH_3, =C*H*-C_6H_4-CH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): -0.71 (br s, *C*H_3), 21.30 (-C_6H_4-*C*H_3), 55.34 (O*C*H_3), 113.79, 121.28, 122.69, 126.79, 127.50, 127.57, 127.65, 127.68, 127.81, 128.17, 129.13, 130.14, 130.24, 130.35, 130.63, 130.93, 130.96, 131.16, 132.06, 132.09, 134.03, 134.07, 134.95, 138.38, 146.11, 146.60, 159.91; ^{29}Si NMR ($CDCl_3$, δ, ppm): -29.80, -29.95, -78.33 (br s), -79.54 (br s); MS (FD): m/z(%): 1423.18 (81), 1424.17 (100), 1425.18 (89), 1426.18 (62), 1427.18

(31), 1428.18 (18), 1429.17 (10); HRMS (FD): calcd. for $C_{68}H_{64}O_{15}NaSi_{10}$: 1423.1711; found: 1423.1782.

9-(E)-4-Bromostyrylmethyl-19-(E)-4-methoxystyrylmethyl-1,3,5,7,11,13,15,17-octaphenyl-pentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4A-c-e)

^{1}H NMR ($CDCl_3$, δ, ppm): 0.44 – 0.48 (overlapping s, 6H, C*H*$_3$), 3.84 (s, 3H, OC*H*$_3$), 6.30 (d, 1H, J_{HH} = 19.3 Hz, =C*H*-Si), 6.47 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.78 (d, 2H, J_{HH} = 8.7 Hz, -C$_6$*H*$_4$-), 6.92 (m, 48H, =C*H*-C$_6$*H*$_4$-OCH$_3$, =C*H*-C$_6$*H*$_4$-Br and C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$, δ, ppm): -0.74 (*C*H$_3$), -0.72 (*C*H$_3$), -55.34 (O*C*H$_3$), 113.79, 121.27, 124.03, 126.84, 127.57 (d, *J* = 7.4 Hz), 127.64, 127.80, 127.82, 128.16, 128.44, 130.14, 130.24, 130.35, 130.38, 130.62, 130.88 (d, *J* = 2.5 Hz), 130.94 (d, *J* = 2.3 Hz), 132.01 (d, *J* = 1.9 Hz), 132.08 (d, *J* = 1.8 Hz), 134.02 (br s), 134.15 (d, *J* = 1.9 Hz), 137.59, 146.11, 146.66, 159.89, 159.90; ^{29}Si NMR ($CDCl_3$, δ, ppm): -29.81, -30.20, -78.31, -78.35, -79.20, -79.24, -79.63, -79.56, -79.86; MS (FD): m/z(%): 1487.08 (52), 1488.08 (65), 1489.08 (99), 1490.08 (100), 1491.08 (78), 1492.08 (45), 1493.08 (29), 1494.07 (13); HRMS (FD): calcd. for $C_{67}H_{61}BrO_{15}NaSi_{10}$: 1487.0804; found: 1487.0801.

9-(E)-4-Chlorostyrylmethyl-19-(E)-4-methoxystyrylmethyl-1,3,5,7,11,13,15,17-octaphenyl-pentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4A-d-e)

^{1}H NMR ($CDCl_3$, δ, ppm): 0.45 (s, 6H, C*H*$_3$), 3.83 (s, 3H, OC*H*$_3$), 6.29 (d, 1H, J_{HH} = 19.5 Hz, =C*H*-Si), 6.40 (d, 1H, J_{HH} = 19.4 Hz, =C*H*-Si), 6.77 (d, 2H, J_{HH} = 8.6 Hz, -C$_6$*H*$_4$-), 6.92 – 7.82 (m, 48H, =C*H*-C$_6$*H*$_4$-OCH$_3$, =C*H*-C$_6$*H*$_4$-Cl and C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$, δ, ppm): -0.80, -0.72, 55.33, 113.77, 121.20, 121.26, 124.83, 124.88, 127.55, 127.57, 127.58, 127.59, 127.78, 127.79, 127.83, 127.84, 127.98, 128.15, 128.54, 129.74, 130.21, 130.25, 130.33, 130.36, 130.42, 130.45, 130.58, 130.60, 130.86, 130.93, 131.85, 131.92, 132.00, 132.07, 133.97, 134.00, 134.10, 134.14, 136.07, 145.18, 145.20, 146.09, 146.11, 159.89, 159.93, 165.40, 165.44; ^{29}Si NMR ($CDCl_3$, δ, ppm): -29.75, -29.82, -30.46, -30.53, -78.29, -78.36, -79.53, -79.57, -79.69; MS (FD): m/z(%): 1439.18 (71), 1440.18 (85), 1441.19 (70), 1442.18 (51), 1443.13 (90), 1444.13 (100), 1445.13 (98), 1446.13 (89), 1447.14 (59), 1448.13 (38), 1449.09 (30), 1450.08 (22), 1451.08 (23), 1452.07 (19).

9-(E)-Styrylphenyl-19-(E)-4-methylstyrylphenyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4B-a-b)

^{1}H NMR ($CDCl_3$, δ, ppm): 2.35 (s, 3H, C*H*$_3$), 6.51 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.58 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 7.00 – 7.84 and 8.07 – 8.29 (m, 61H, =C*H*-C$_6$*H*$_5$, =C*H*-C$_6$*H*$_4$-OCH$_3$ and C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$, δ, ppm): 21.29 (*C*H$_3$), 120.96, 122.35, 126.90, 126.95, 127.41, 127.48, 127.56, 127.84 (br s), 128.42, 128.56, 129.11, 129.75, 130.09, 130.16, 130.20, 130.42, 130.44, 130.60, 130.64, 130.65, 130.80, 137.74 (d, *J* = 1.6 Hz), 131.78 (d, *J* = 1.6 Hz), 134.07, 134.16, 134.62, 134.63, 134.77, 134.82, 137.46, 138.54, 148.14, 148.18, 165.46; ^{29}Si NMR ($CDCl_3$, δ, ppm): -44.28, -44.55, -77.99, -78.03, -79.38, -79.39, -79.50; MS (FD): m/z (%):

1517.20 (42), 1518.21 (52), 1519.20 (60), 1520.16 (100), 1521.16 (98), 1522.17 (71), 1523.17 (40), 1524.17 (20), 1525.17 (10); HRMS (FD): calcd. for $C_{77}H_{66}O_{14}NaSi_{10}$: 1517.2043; found: 1517.2041.

*9-(*E*)-Styrylphenyl-19-(*E*)-4-methoxystyrylphenyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4B-a-e)*

^{1}H NMR ($CDCl_3$, δ, ppm): 3.82 (s, 3H, OCH_3), 6.43 (d, 1H, J_{HH} = 19.0 Hz, =C*H*-Si), 6.57 (d, 1H, J_{HH} = 19.0 Hz, =C*H*-Si), 6.75 (d, 2H, J_{HH} = 8.5 Hz, -C_6H_4-OCH_3), 6.95 – 7.80 (m, 58H, =C*H*-C_6H_5, =C*H*-C_6H_4-OCH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 55.32 (O*C*H_3), 113.77, 119.52, 122.36, 126.95, 127.40, 127.47, 127.48, 127.56, 127.63, 127.71, 127.81, 127.83, 127.85, 127.89, 128.30, 128.41, 128.55, 130.06, 130.15, 130.18, 130.20, 130.40, 130.43, 130.51, 130.60, 130.62, 130.68, 130.74, 130.79, 131.74 (d, *J* = 2.9 Hz), 131.81 (d, *J* = 2.9 Hz), 134.06, 134.07, 134.12, 134.15, 134.17, 134.19, 134.21, 134.62, 134.63, 134.85, 134.86, 137.46, 147.60, 148.13, 160.01 (br s); ^{29}Si NMR ($CDCl_3$, δ, ppm): -43.60, -43.87, -78.09, -78.13, -79.47, -79.50, -79.56; MS (FD): m/z (%): 1533.20 (75), 1534.20 (99), 1435.20 (100), 1536.21(69), 1537.20 (39), 1538.19 (16), 1539.21 (10); HRMS (FD): calcd. for $C_{77}H_{66}O_{15}NaSi_{10}$: 1533.1992; found: 1533.2014.

*9-(*E*)-4-Bromostyrylphenyl-19-(*E*)-4-methoxystyrylphenyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4B-c-e)*

^{1}H NMR ($CDCl_3$, δ, ppm): 3.82 (s, 3H, OCH_3), 6.40 (d, 1H, J_{HH} = 19.6 Hz, =C*H*-Si), 6.52 (d, 1H, J_{HH} = 19.7 Hz, =C*H*-Si), 6.75 (d, 2H, J_{HH} = 7.7 Hz, -C_6H_4-), 6.97 – 7.80 (m, 58H, =C*H*-C_6H_4-Br, =C*H*-C_6H_4-OCH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 55.33 (O*C*H_3), 113.77, 119.46, 119.52, 122.47, 122.49, 123.45, 123.51, 127.40, 127.42, 127.44, 127.49, 127.51, 127.52, 127.55, 127.60, 127.64, 127.66, 127.83, 127.88, 127.89, 127.92, 128.11, 128.31, 128.40, 130.08, 130.09, 130.21, 130.24, 130.28, 130.32, 130.36, 130.41, 130.44, 130.51, 130.54, 130.60, 130.50, 131.52, 131.59, 131.66, 131.74, 131.82, 134.05, 134.07, 134.08, 134.12, 134.13, 134.17, 134.22, 134.83, 134.87, 136.38, 146.66, 147.62, 160.01, 160.04; ^{29}Si NMR ($CDCl_3$, δ, ppm): -44.05, -44.11, -44.84, -44.90, -77.94, -78.04, -79.39, -79.40 -79.45, -79.48; MS (FD): m/z (%): 1611.10 (49), 1612.10 (60), 1613.11 (99), 1614.10 (100), 1615.10 (77), 1616.11 (48), 1617.11 (25), 1618.12 (12); HRMS (FD): calcd. for $C_{77}H_{65}BrO_{15}NaSi_{10}$: 1611.1097; found: 1611.1062.

*9-(*E*)-4-Chlorostyrylphenyl-19-(*E*)-4-methoxystyrylphenyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4B-d-e)*

^{1}H NMR ($CDCl_3$, δ, ppm): 3.82 (s, 3H, OCH_3), 6.40 (d, 1H, J_{HH} = 19.6 Hz, =C*H*-Si), 6.52 (d, 1H, J_{HH} = 19.7 Hz, =C*H*-Si), 6.75 (d, 2H, J_{HH} = 7.7 Hz, -C_6H_4-), 6.95 – 7.80 (m, 58H, =C*H*-C_6H_4-Cl, =C*H*-C_6H_4-OCH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 55.30 (O*C*H_3), 113.77, 119.46, 119.52, 123.25, 123.32, 127.40, 127.42, 127.44, 127.48, 127.51, 127.52, 127.54, 127.56, 127.59,

127.63, 127.64, 127.66, 127.72, 127.76, 127.82, 127.83, 127.87, 127.89, 127.91, 128.11, 128.31, 128.54, 128.56, 129.76, 130.07, 130.09, 130.20, 130.21, 130.24, 130.27, 130.31, 130.33, 130.36, 130.41, 130.44, 130.50, 130.54, 130.60, 130.66, 130.68, 130.74, 130.75, 130.79, 130.80, 131.59, 131.67, 131.74, 131.81, 134.04, 134.05, 134.07, 134.08, 134.12, 134.13, 134.16, 134.17, 134.22, 134.36, 134.82, 134.86, 135.95, 146.61, 147.60, 147.61, 160.00, 160.03; ^{29}Si NMR ($CDCl_3$, δ, ppm): -44.06, -44.89, -77.94, -78.05, -79.37, -79.39, -79.42; MS (FD): m/z (%): 1563.21 (46), 1564.21 (59), 1565.20 (65), 1567.16 (71), 1568.16 (90), 1569.16 (100), 1570.16 (89), 1571.16 (59), 1572.16 (40), 1573.12 (45), 1574.11 (34), 1575.12 (30), 1575.12 (19).

9-(E)-4-Methylstyryl-4-methoxyphenyl-19-(E)-styryl-4-methoxyphenyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4C-a-b)

^{1}H NMR ($CDCl_3$, δ, ppm): 2.35 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.51 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.58 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.46 – 6.53 and 6.97 – 7.71 (m, 59H, =C*H*-C_6H_4-OCH_3, =C*H*-C_6H_4-CH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 21.27 (*C*H_3), 54.96 (O*C*H_3), 54.97 (O*C*H_3), 113.55, 113.85, 121.37, 121.38, 122.75, 122.77, 125.77, 125.78, 125.92, 125.93, 126.88, 126.93, 127.34, 127.35, 127.44 (br s), 127.54 (br s), 127.81, 127.83, 128.40, 128.49, 129.09, 129.75, 130.18, 130.20, 130.37, 130.40, 130.69, 130.70, 130.73, 131.84, 131.86, 131.88, 131.89, 134.07, 134.19, 134.91, 135.83, 137.55, 138.44, 147.86, 147.90, 161.22, 161.27; ^{29}Si NMR ($CDCl_3$, δ, ppm): -43.60, -43.87, -78.09, -78.13, -79.47, -79.50, -79.56; MS (FD): m/z(%): 1577.23 (71), 1578.22 (100), 1579.22 (98), 1580.19 (90), 1581.19 (78), 1582.18 (60), 1583.18 (40), 1584.19 (20), 1585.18 (10); HRMS (FD): calcd. for $C_{79}H_{70}O_{16}NaSi_{10}$: 1577.2254; found: 1577.222.

9-(E)-4-Bromostyryl-4-methoxyphenyl-19-(E)-styryl-4-methoxyphenyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4C-a-c)

^{1}H NMR ($CDCl_3$, δ, ppm): 3.79 (s, 6H, OCH_3), 6.53 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.57 (d, 1H, J_{HH} = 19.2 Hz, =C*H*-Si), 6.82 (d, 4H, J_{HH} = 8.1 Hz, -C_6H_4-), 6.96 – 7.70 (m, 55H, =C*H*-C_6H_4-Br, =C*H*-C_6H_5, -C_6H_4-OCH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 55.33 (O*C*H_3), 113.77, 113.78, 119.46, 119.52, 123.25, 123.32, 127.40, 127.42, 127.44, 127.48, 127.51, 127.52, 127.54, 127.56, 127.59, 127.63, 127.64, 127.66, 127.72, 127.76, 127.82, 127.83, 127.87, 127.89, 127.91, 128.11, 128.31, 128.54, 128.56, 129.76, 130.07, 130.09, 130.20, 130.21, 130.24, 130.27, 130.31, 130.33, 130.36, 130.41, 130.44, 130.50, 130.54, 130.60, 130.66, 130.68, 130.74, 130.75, 130.79, 130.80, 131.59, 131.67, 131.74, 131.81, 134.04, 134.05, 134.07, 134.08, 134.10, 134.12, 134.13, 134.16, 134.17, 134.22, 134.82, 134.86, 135.95, 135.96, 146.61, 146.62, 147.60, 147.61, 160.00, 160.03; ^{29}Si NMR ($CDCl_3$, δ, ppm): -43.79, -43.86, -44.15, -44.20, -78.02, -78.07, -79.43, -79.46, -79.49, -79.52; MS (FD): m/z (%): 16.41 (49), 1642.12 (62), 1643.12 (100), 1644.12 (99), 1645.13 (72), 1646.12 (48), 1647.12 (25), 1648.11 (13); HRMS (FD): calcd. for $C_{78}H_{67}BrO_{16}NaSi_{10}$: 1641.1203; found: 1641.1255.

9-(E)-4-Chlorostyryl-4-methoxyphenyl-19-(E)-styryl-4-methoxyphenyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4C-a-d)

^{1}H NMR ($CDCl_3$, δ, ppm): 3.79 (s, 6H, OCH_3), 3.82 (s, 3H, OCH_3), 6.39 (d, 1H, J_{HH} = 19.3 Hz, =C*H*-Si), 6.57 (d, 1H, J_{HH} = 19.3 Hz, =C*H*-Si), 6.45 – 6.59 and 6.94 – 7.68 (m, 59H, =C*H*-C_6H_5, =C*H*-C_6H_4-OCH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 54.98 (O*C*H_3), 54.99 (O*C*H_3), 113.56 (d, *J* = 3.8 Hz), 113.76, 122.70, 122.74, 123.66, 123.71, 125.73, 125.75, 127.37, 127.45, 127.46, 127.48, 127.55, 127.57, 127.60, 127.63, 127.84, 127.86, 128.09, 128.40, 128.53, 128.54, 130.21, 130.23, 130.30, 130.36, 130.41, 130.43, 130.47, 130.49, 130.62, 130.67, 131.71, 131.75, 131.78, 131.83, 134.04, 134.06, 134.17, 134.18, 135.79, 135.82, 137.53, 137.54, 146.32, 146.42, 147.90, 161.27, 161.34; ^{29}Si NMR ($CDCl_3$, δ, ppm): -43.82, -43.87, -78.04, -78.09, -79.48, -79.51; MS (FD): m/z (%): 1597.17 (65), 1598.17 (88), 1599.17 (100), 1600.18 (72), 1601.17 (52), 1602.18 (38), 1603.17 (18), 1604.16 (11); HRMS (FD): calcd. for $C_{78}H_{67}ClO_{16}NaSi_{10}$: 1597.1708; found: 1597.1708.

9-(E)-4-Methoxystyryl-4-methoxyphenyl-19-(E)-styryl-4-methoxyphenyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4C-a-e)

^{1}H NMR ($CDCl_3$, δ, ppm): 3.79 (s, 6H, OCH_3), 3.82 (s, 3H, OCH_3), 6.39 (d, 1H, J_{HH} = 19.3 Hz, =C*H*-Si), 6.57 (d, 1H, J_{HH} = 19.3 Hz, =C*H*-Si), 6.70 – 6.81 (m, 6H, -C_6H_4-), 6.94 – 7.68 (m, 53H, =C*H*-C_6H_5, =C*H*-C_6H_4-OCH_3, -C_6H_4-OCH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 54.97 (O*C*H_3), 55.32 (O*C*H_3), 113.56 (d, *J* = 3.8 Hz), 113.76, 119.93, 122.76, 125.76, 125.77, 126.93, 127.35, 127.45, 127.55, 127.82 (d, *J* = 1.9 Hz), 128.27, 128.41, 128.50, 130.19, 130.39 (d, *J* = 2.9 Hz), 130.58, 130.69 (d, *J* = 2.3 Hz), 130.75 (d, *J* = 2.0 Hz), 131.84 (d, *J* = 1.9 Hz), 131.91 (d, *J* = 1.8 Hz), 134. 08 (d, *J* = 1.0 Hz), 134.20 (d, *J* = 1.5 Hz), 135.83, 147.37, 147.89, 159.96, 161.20, 161.26; ^{29}Si NMR ($CDCl_3$, δ, ppm): -43.44, -43.87, -78.09, -78.14, -79.48, -79.52, -79.58; MS (FD): m/z (%): 1593.22 (72), 1594.22 (100), 1595.22 (91), 1596.22 (68), 1597.22 (37), 1598.21 (20), 1599.21 (12); HRMS (FD): calcd. for $C_{79}H_{70}O_{17}NaSi_{10}$: 1593.2203; found: 1593.2178

9-(E)-4-Bromostyryl-4-methoxyphenyl-19-(E)-4-methylstyryl-4-methoxyphenyl-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (4C-b-c)

^{1}H NMR ($CDCl_3$, δ, ppm): 2.32 (s, 3H, CH_3), 3.77 (s, 6H, OCH_3), 6.47 (d, 1H, J_{HH} = 18.9 Hz, =C*H*-Si), 6.50 (d, 1H, J_{HH} = 18.9 Hz, =C*H*-Si), 6.72 – 6.84 (m, 4H, -C_6H_4-CH_3 i -C_6H_4-Br), 6.93 – 7.68 (m, 54H, =C*H*-C_6H_4-Br, =C*H*-C_6H_4-CH_3, -C_6H_4-OCH_3 and C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 21.31 (*C*H_3), 55.01 (O*C*H_3), 113.57, 113.66, 121.33, 121.39, 122.40, 122.42, 123.87, 123.93, 125.43, 125.46, 125.89, 125.94, 126.89, 127.38, 127.39, 127.45, 127.47, 127.49, 127.52, 127.55, 127.59, 127.63, 127.84, 127.89, 128.40, 129.12, 130.23, 130.32, 130.39, 130.42, 130.49, 130.52, 130.61, 130.65, 130.68, 130.71, 130.75, 131.50, 131.71, 131.78, 131.83, 131.91, 134.06, 134.09, 134.19, 134.92, 135.81, 135.85, 136.48, 138.48, 138.52, 146.45, 147.89, 161.24, 161.37; ^{29}Si NMR ($CDCl_3$, δ, ppm): -43.53, -43.59, -44.15, -44.21, -78.02, -78.11, -79.48 (br s); MS (FD): m/z (%):1655.13 (47), 1656.13 (65), 1657.16 (99), 1658.16

(100), 1659.13 (81), 1660.14 (49), 1661.14 (29), 1662.13 (18), 1663.11 (10); HRMS (FD): calcd. for $C_{79}H_{69}BrO_{16}NaSi_{10}$: 1655.1359; found: 1655.1377.

7. References

[1] A. J. Arduengo III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. N. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron*, **1999**, *55*, 14523-14534.

[2] L. Delaude, M. Szypa, A. Demonceau, A. F. Noels, *Adv. Synth. Catal.,* **2002**, *344*, 749-756.

[3] M. Hans, J. Lorkowski, A. Demonceau, L. Delaude, *Beilstein J. Org. Chem.* **2015**, *11*, 2318-2325.

[4] J. Levison, S. D. Robinson, *J. Chem. Soc. A*., **1970**, 2947-2954.

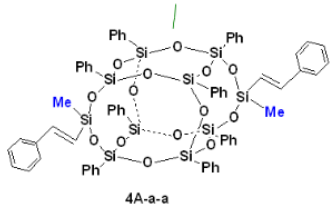
[5] P. Żak, B. Dudziec, M. Kubicki, B. Marciniec, *Chem. Eur. J.*, **2014**, *20*, 9387 – 9393.

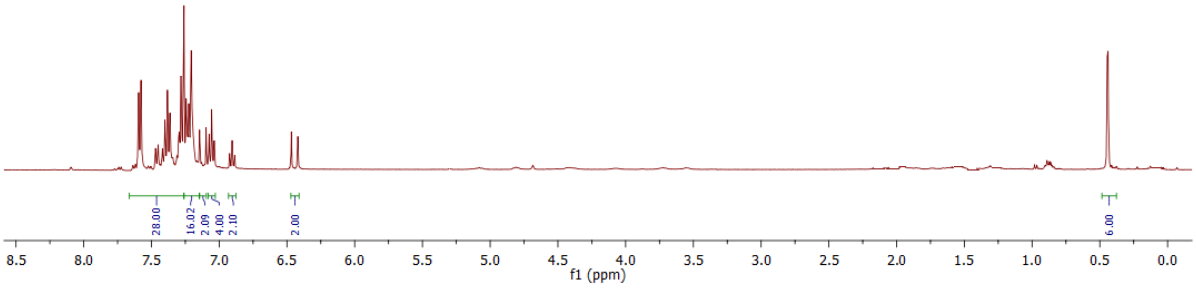
[6] Y. Mutoh, Y. Mohara, S. Saito, *Org. Lett*., **2017**, *19*, 5204–5207.

8. NMR spectra of isolated products

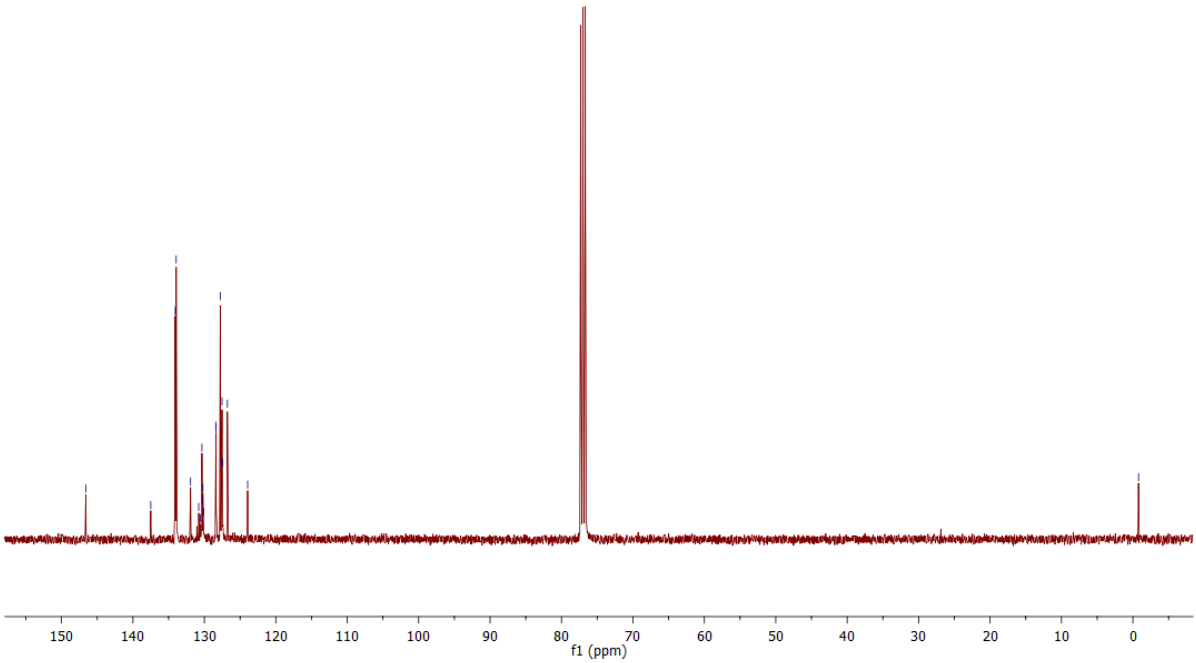
8.1. Symmetrically functionalized divinylsilsesquioxanes

^{1}H NMR ($CDCl_3$, δ, ppm)

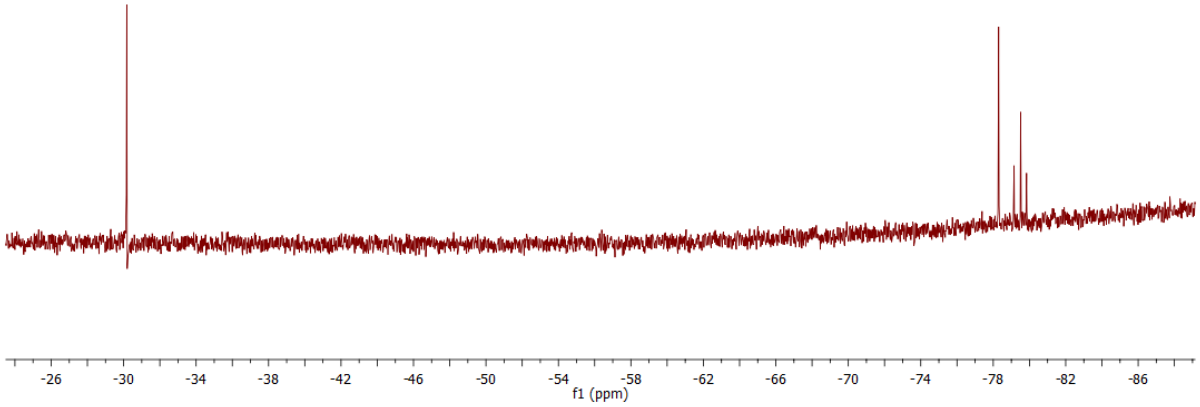




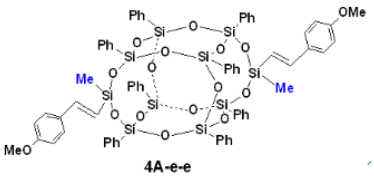
^{13}C NMR ($CDCl_3$, δ, ppm)



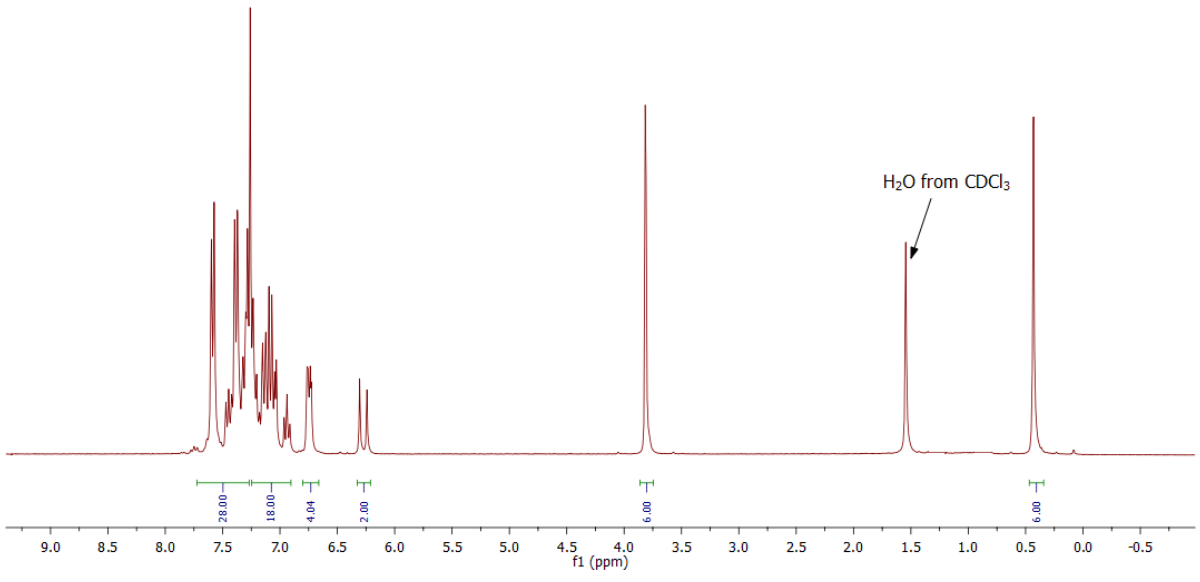
^{29}Si NMR ($CDCl_3$, δ, ppm)



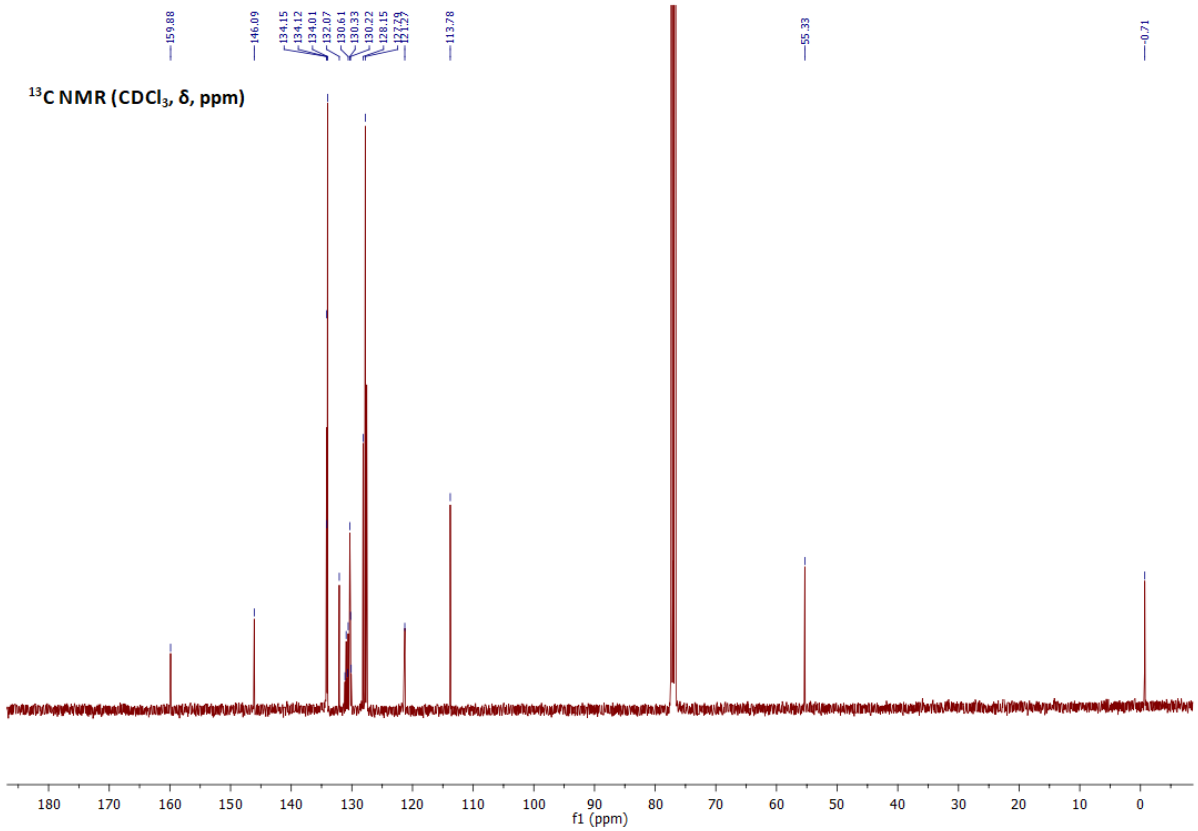
^{1}H NMR ($CDCl_3$, δ, ppm)



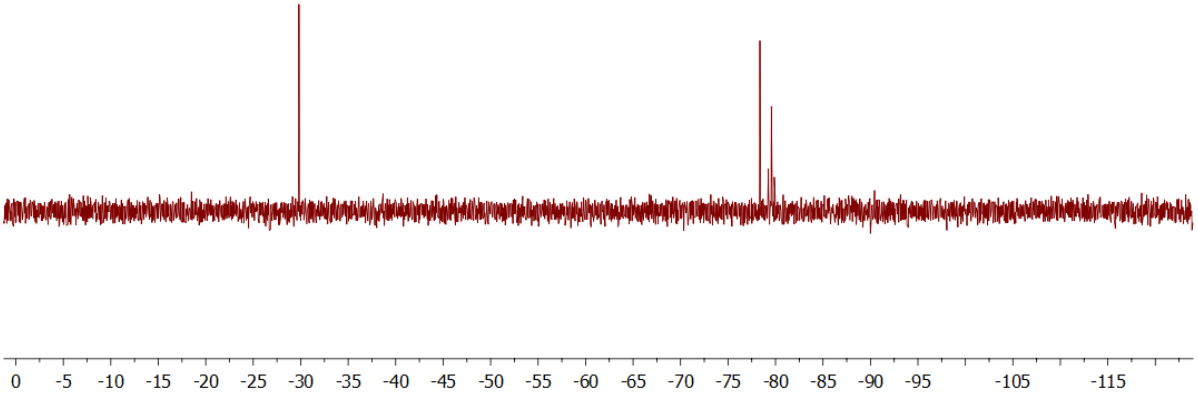
4A-e-e



^{13}C NMR ($CDCl_3$, δ, ppm)

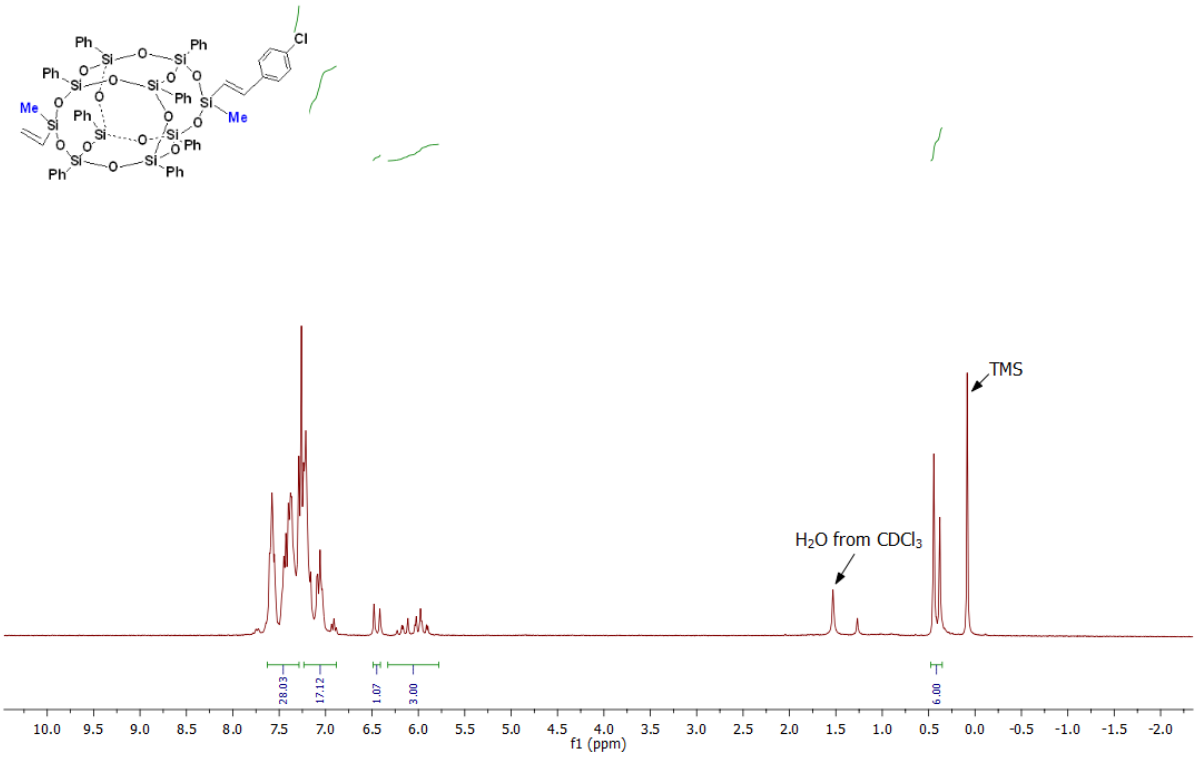


^{29}Si NMR ($CDCl_3$, δ, ppm)

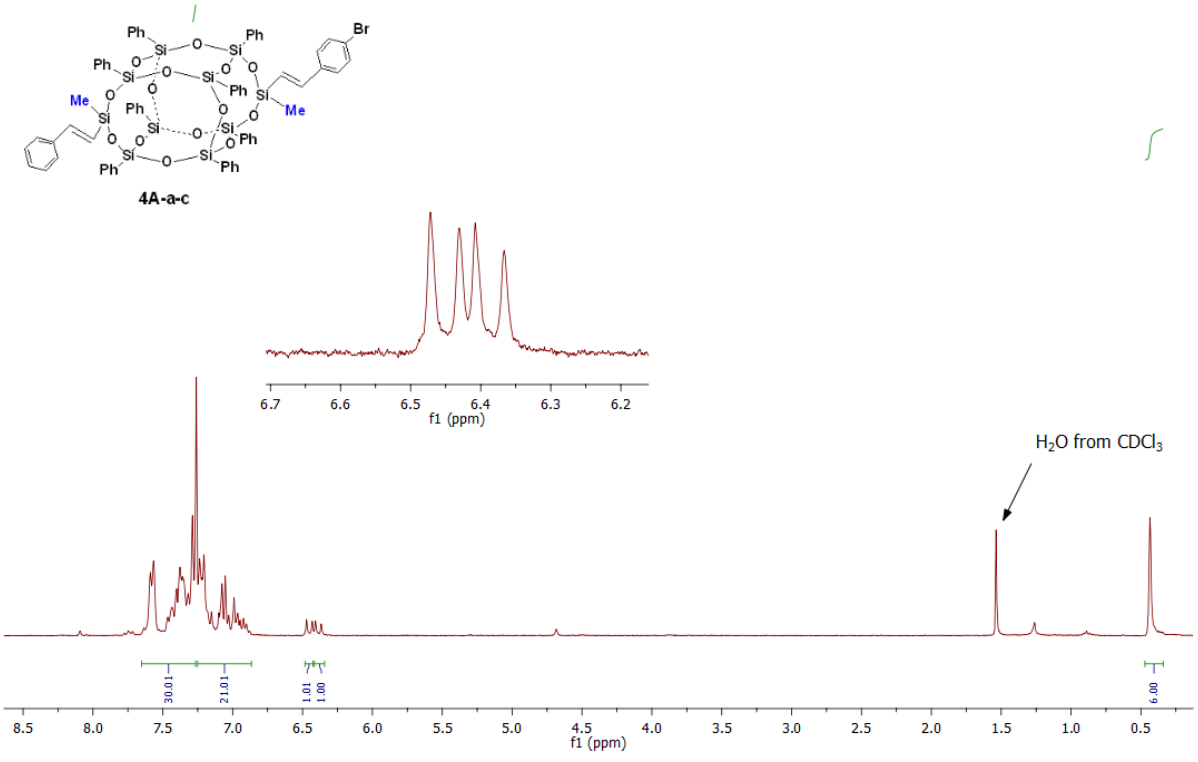


8.2. Unsymmetrically functionalized divinylsilsesquioxanes

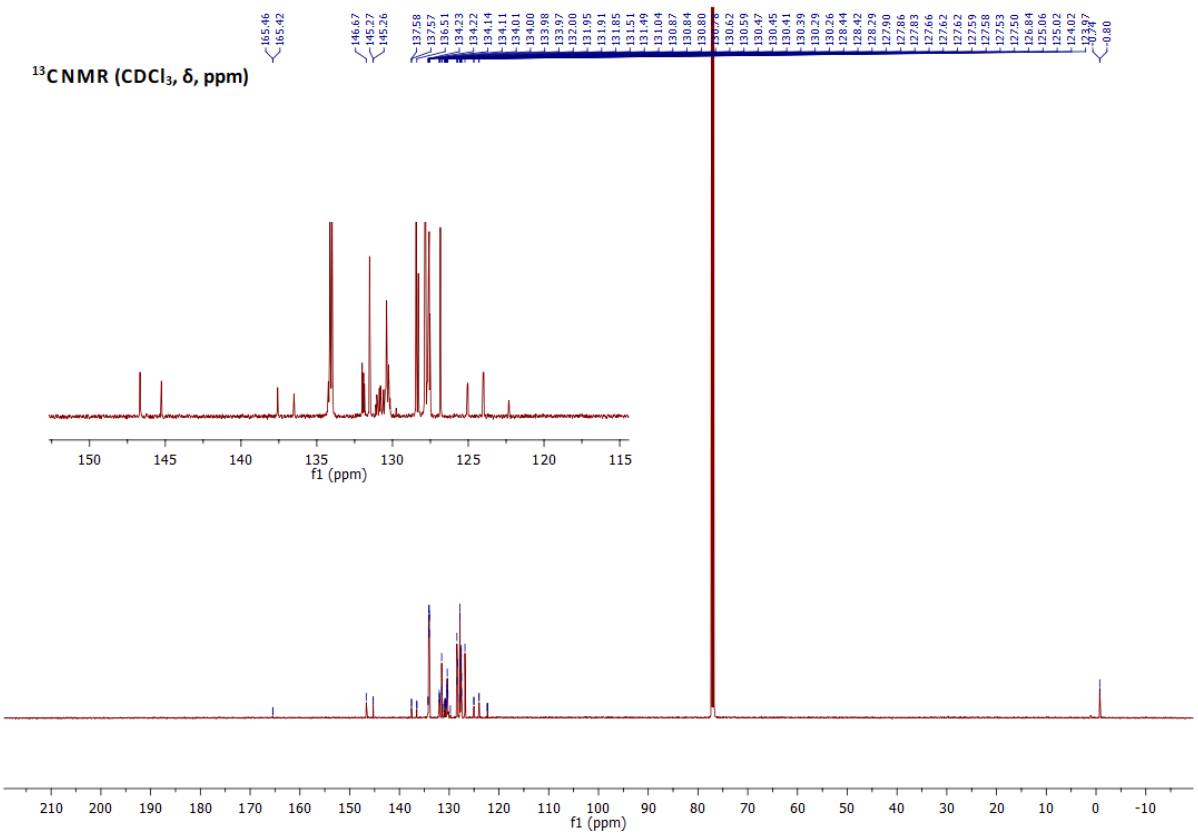
^{1}H NMR ($CDCl_3$, δ, ppm)



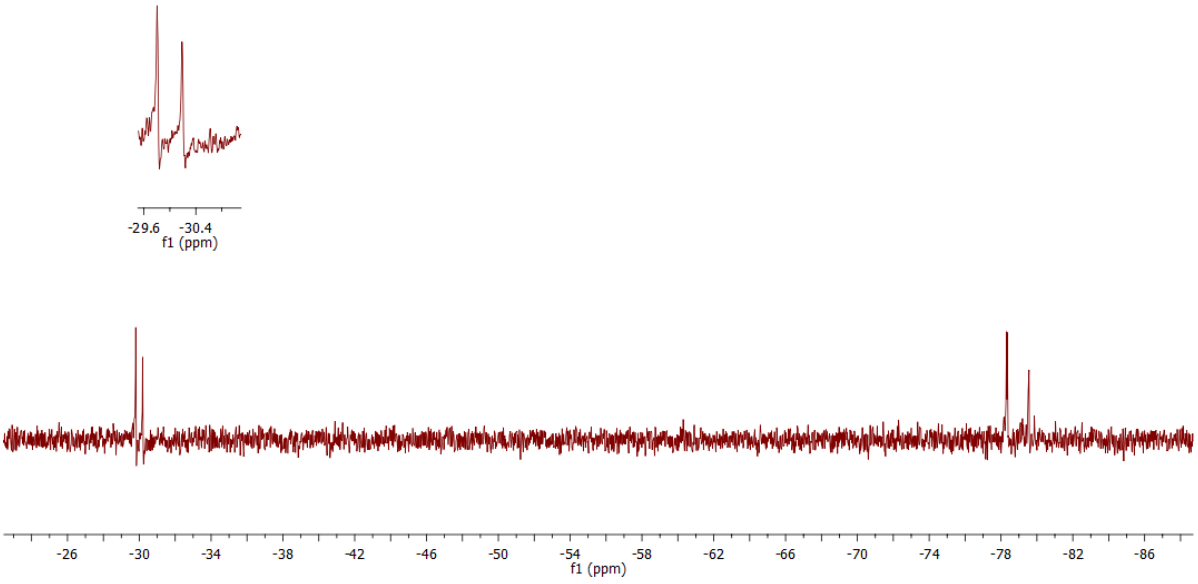
^{1}H NMR ($CDCl_3$, δ, ppm)



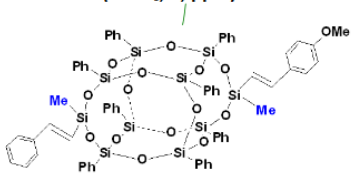
^{13}C NMR ($CDCl_3$, δ, ppm)



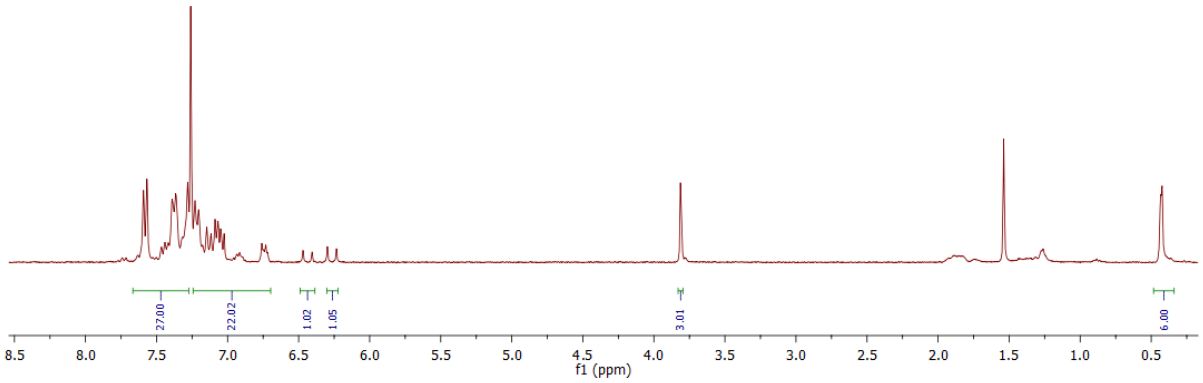
^{29}Si NMR ($CDCl_3$, δ, ppm)



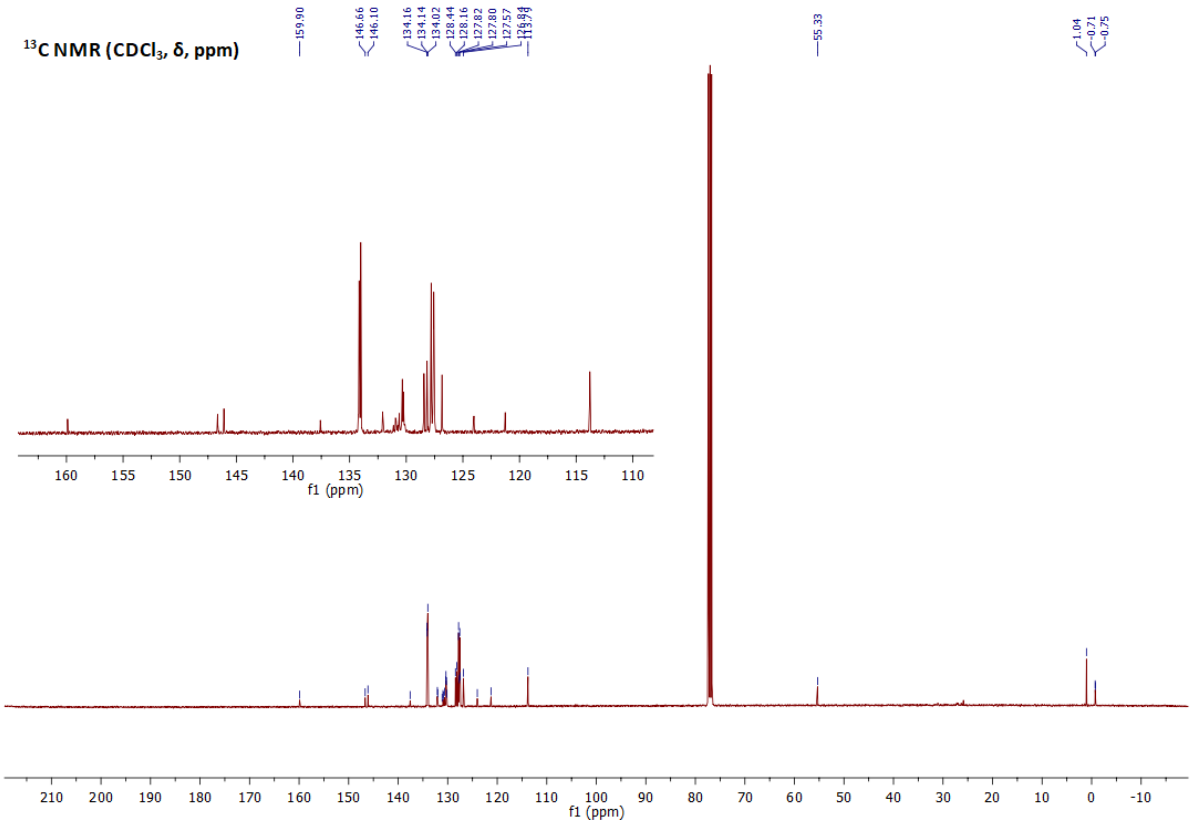
^{1}H NMR ($CDCl_3$, δ, ppm)



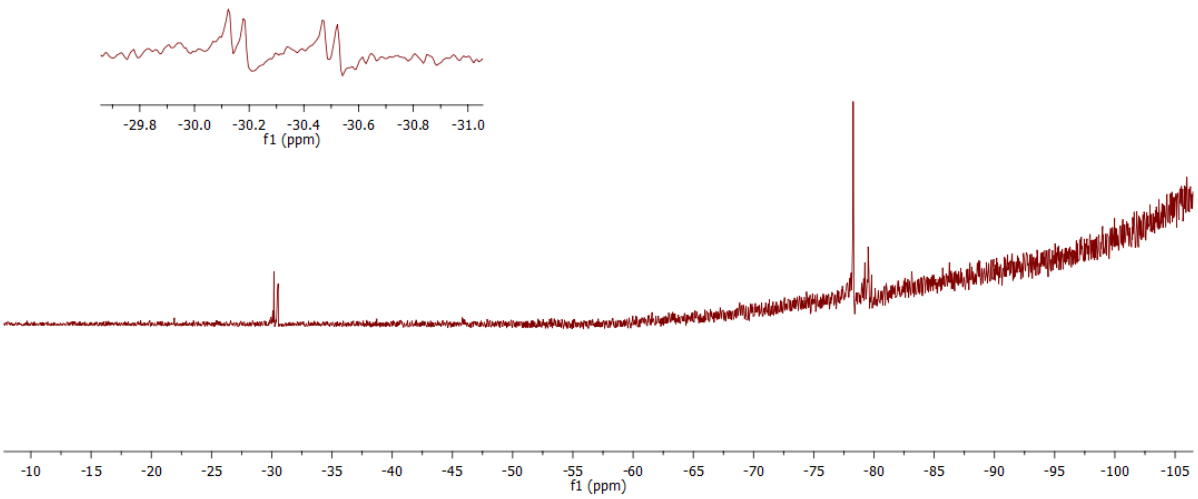
4A-a-e



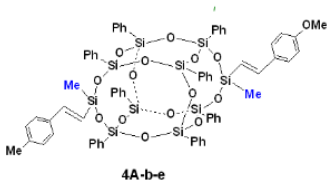
^{13}C NMR ($CDCl_3$, δ, ppm)



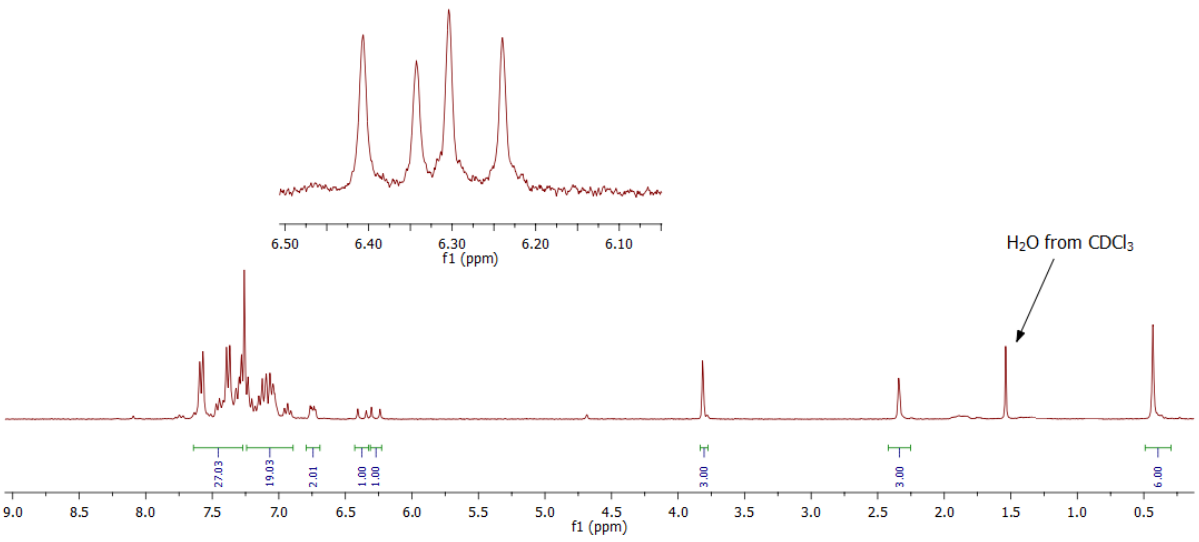
^{29}Si NMR ($CDCl_3$, δ, ppm)



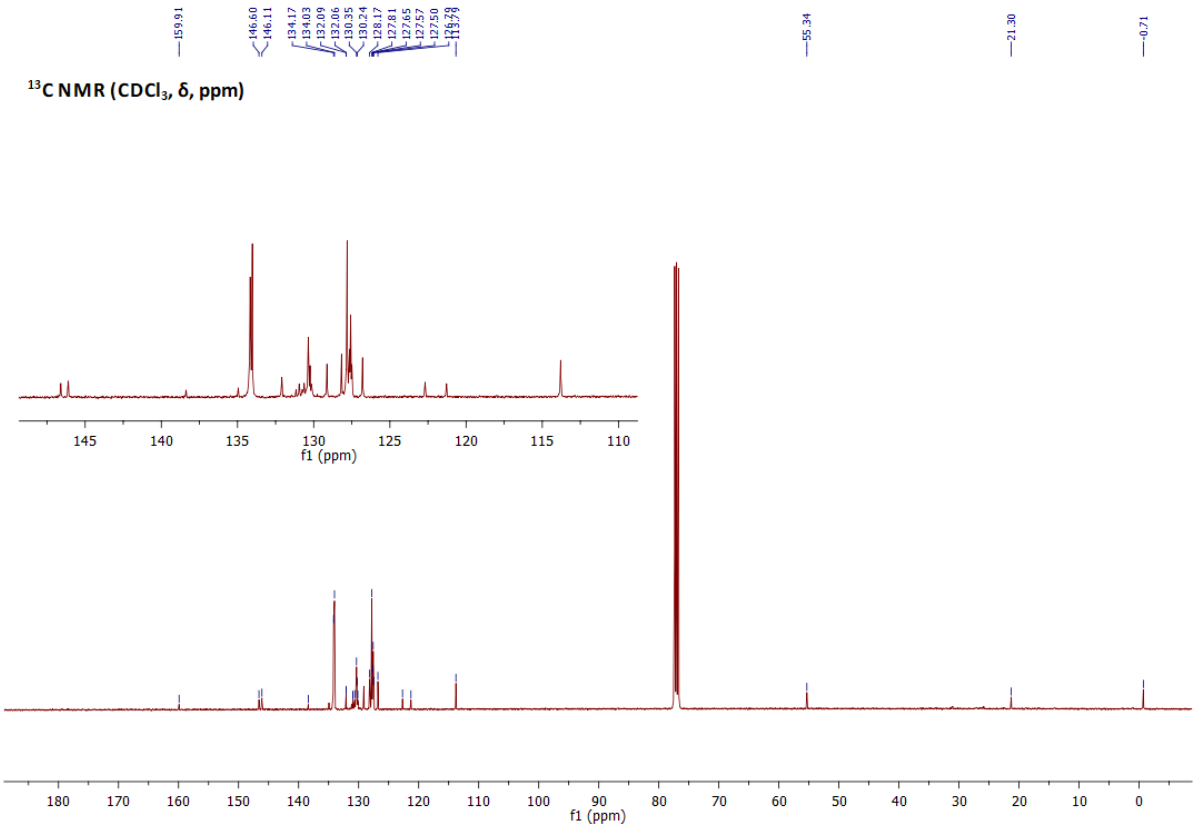
^{1}H NMR ($CDCl_3$, δ, ppm)



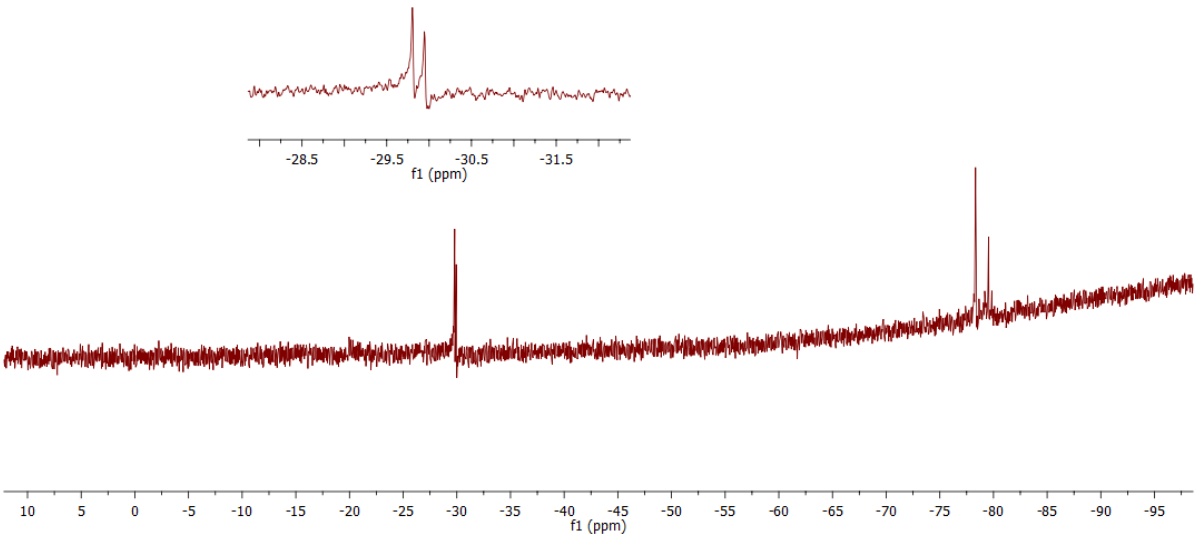
4A-b-e



^{13}C NMR ($CDCl_3$, δ, ppm)



^{29}Si NMR ($CDCl_3$, δ, ppm)



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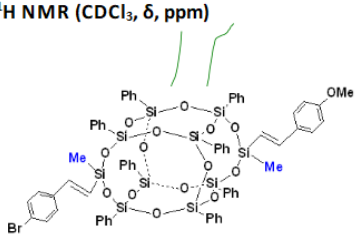
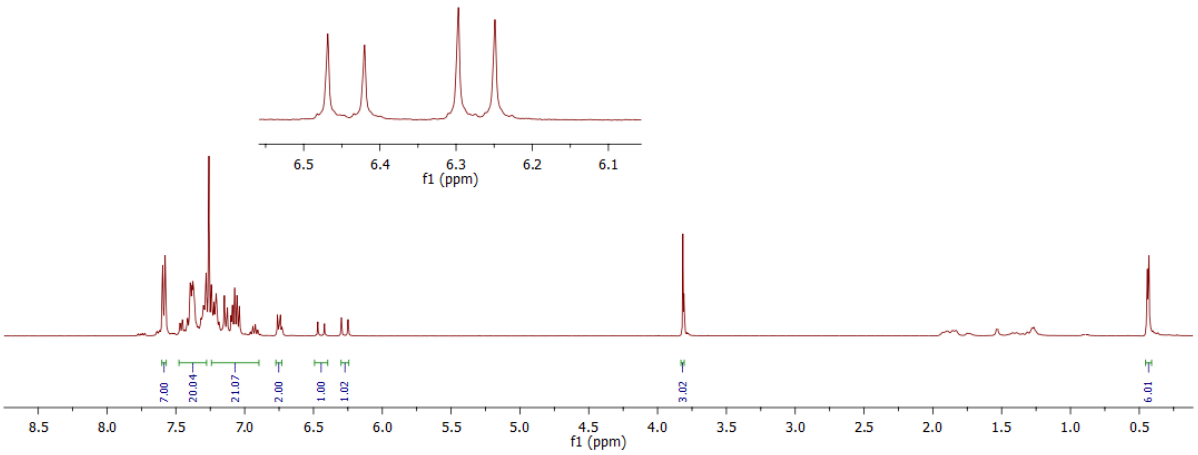
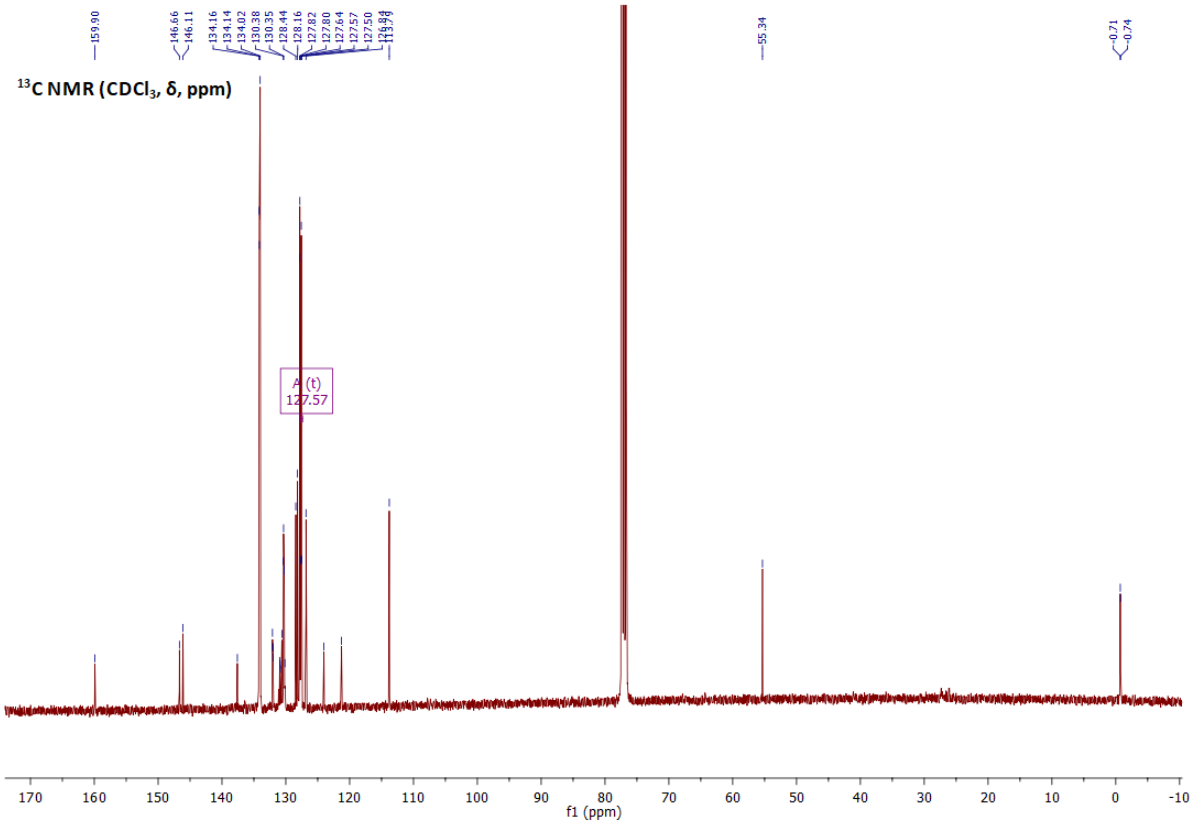


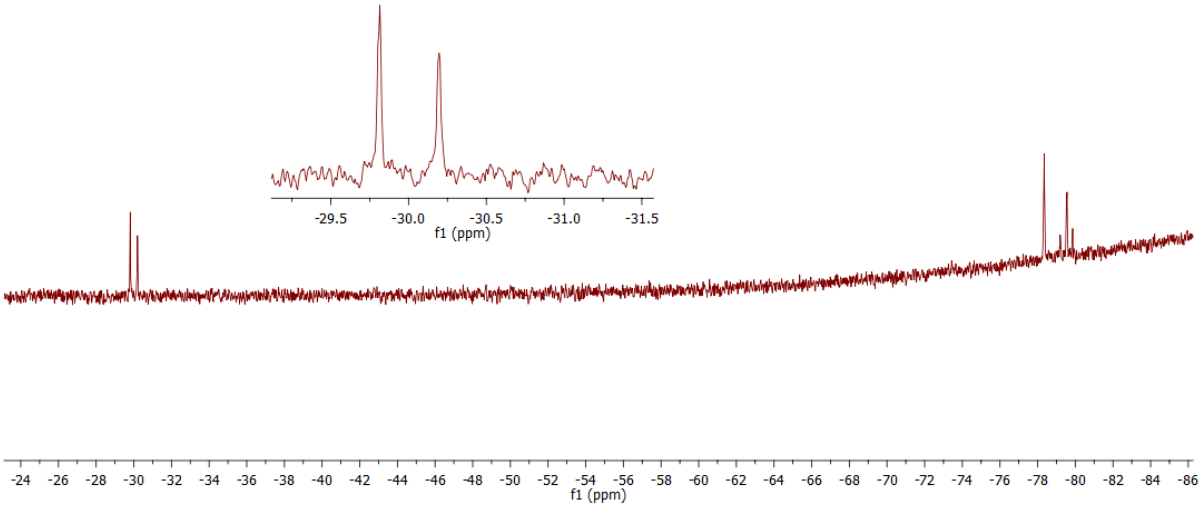
4A-c-e



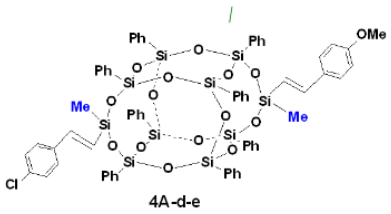
^{13}C NMR ($CDCl_3$, δ, ppm)



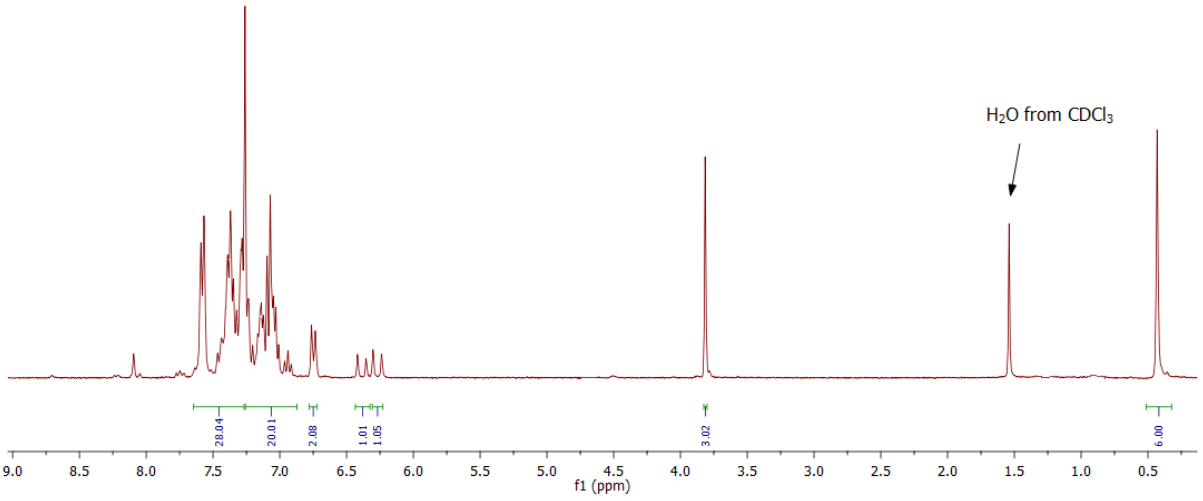
^{29}Si NMR ($CDCl_3$, δ, ppm)



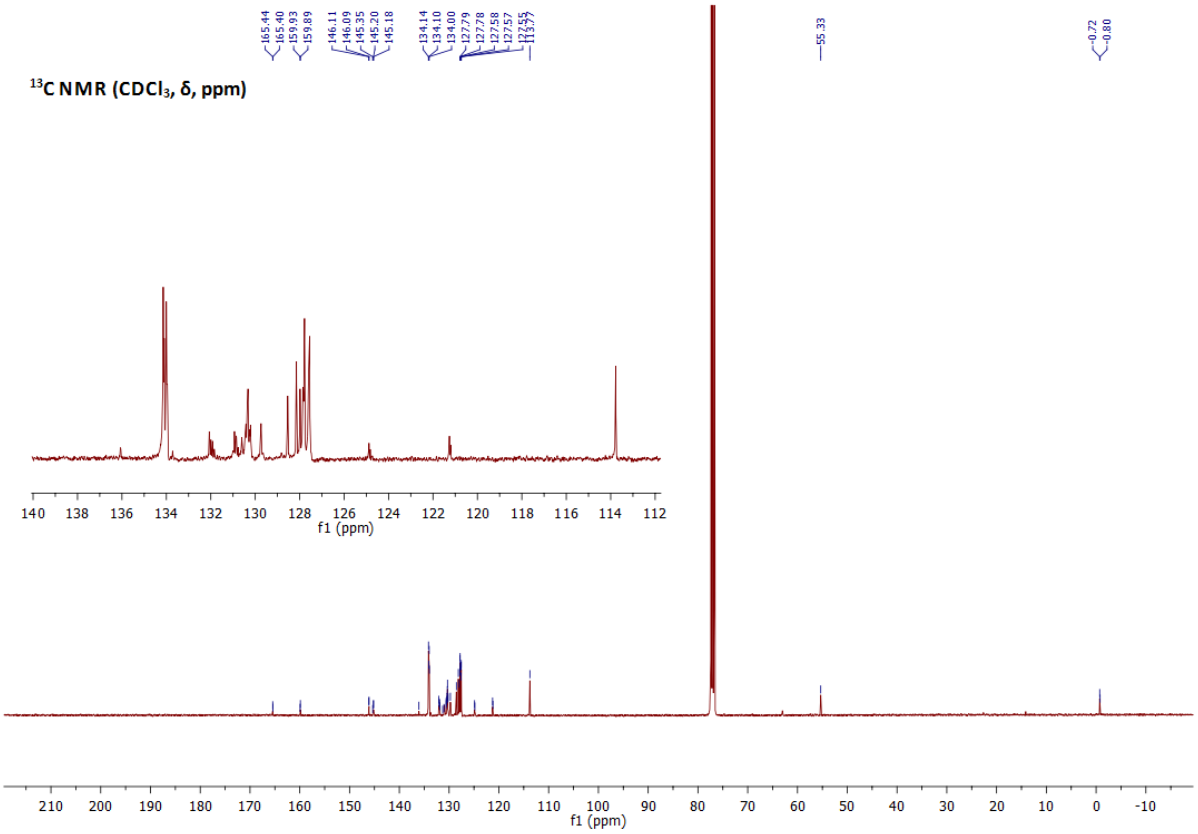
^{1}H NMR ($CDCl_3$, δ, ppm)



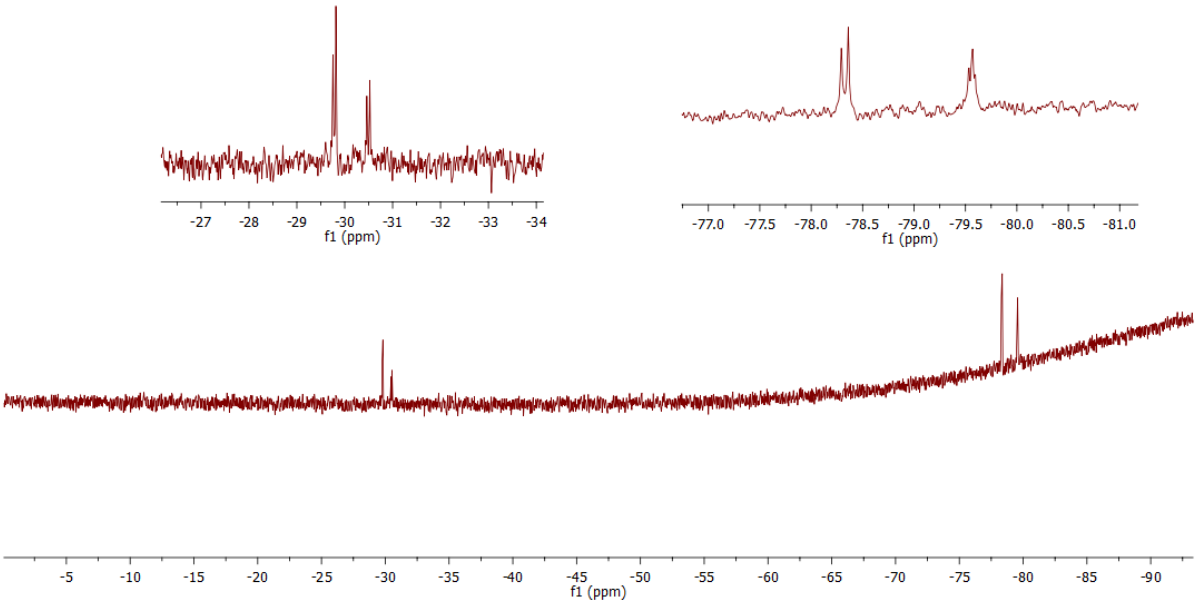
4A-d-e



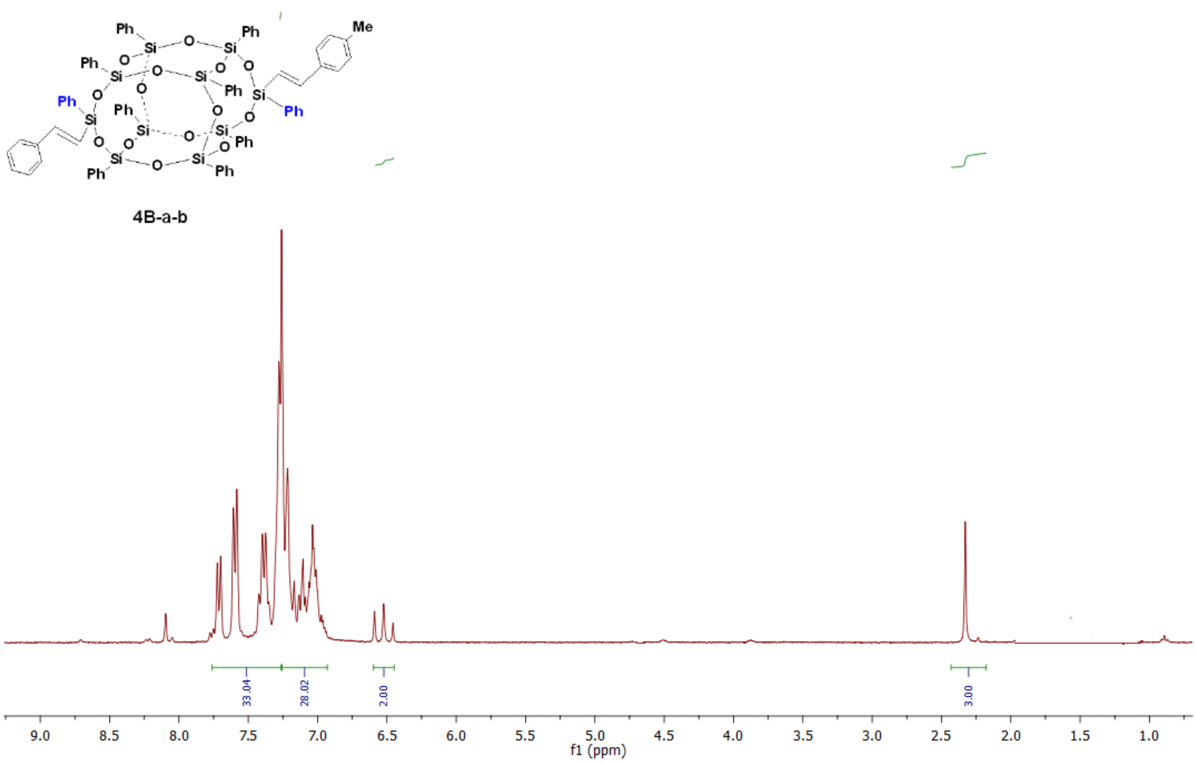
^{13}C NMR ($CDCl_3$, δ, ppm)



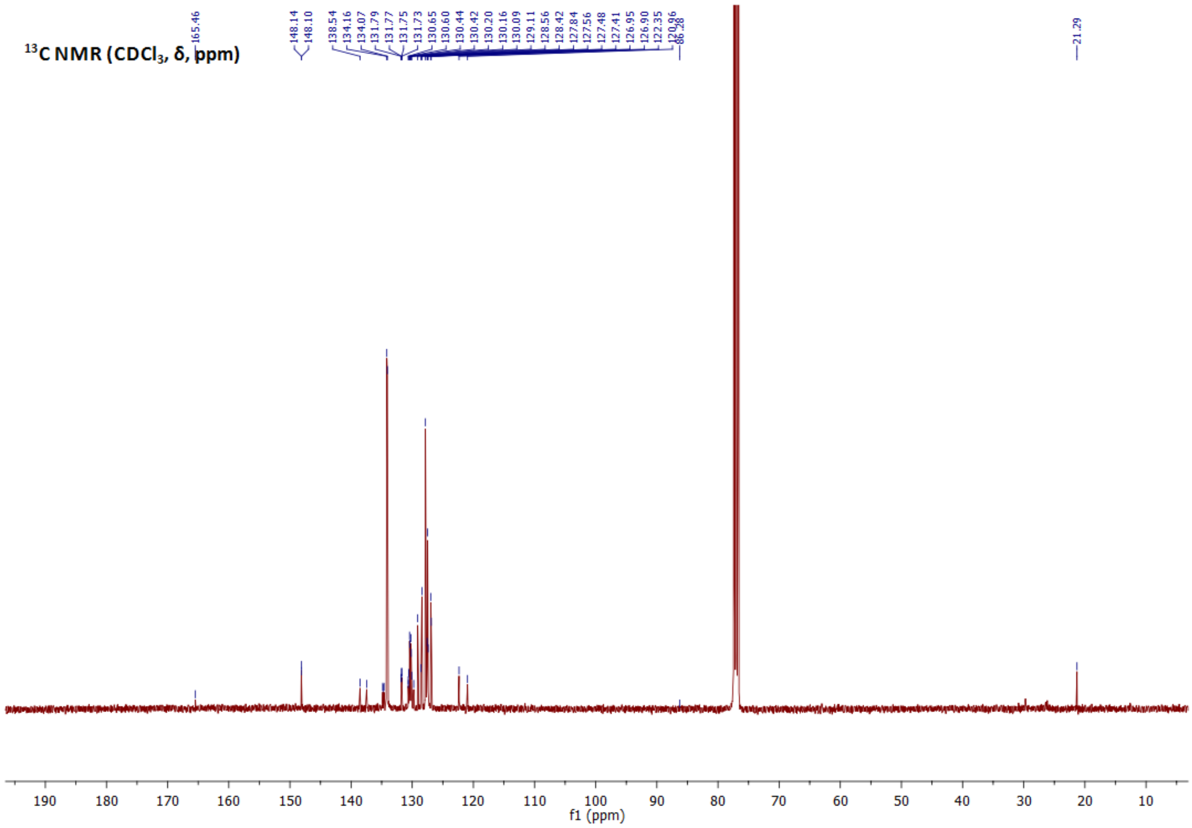
^{29}Si NMR ($CDCl_3$, δ, ppm)



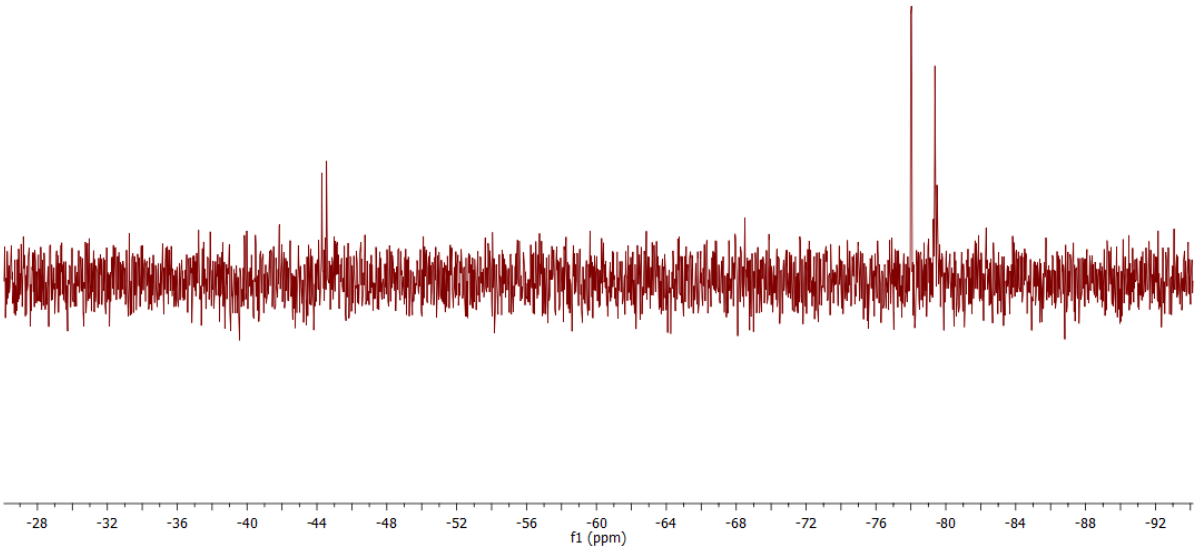
[1]H NMR ($CDCl_3$, δ, ppm)



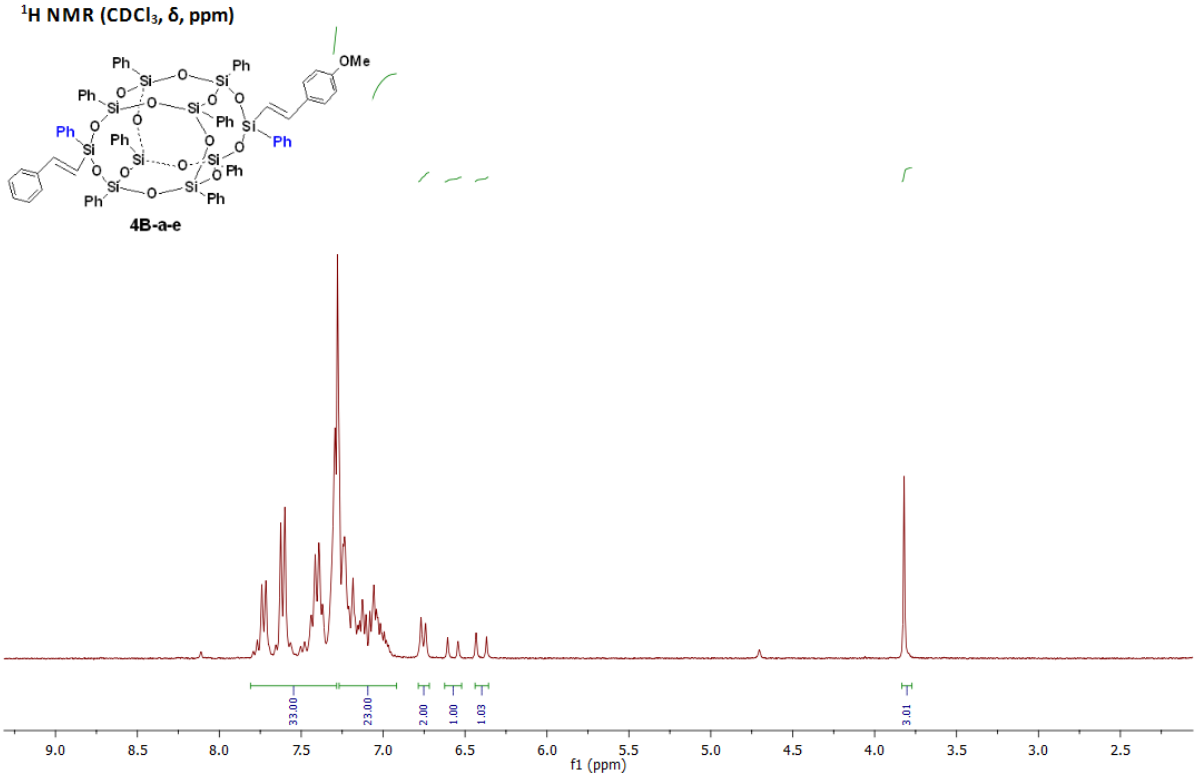
[13]C NMR ($CDCl_3$, δ, ppm)



^{29}Si NMR ($CDCl_3$, δ, ppm)

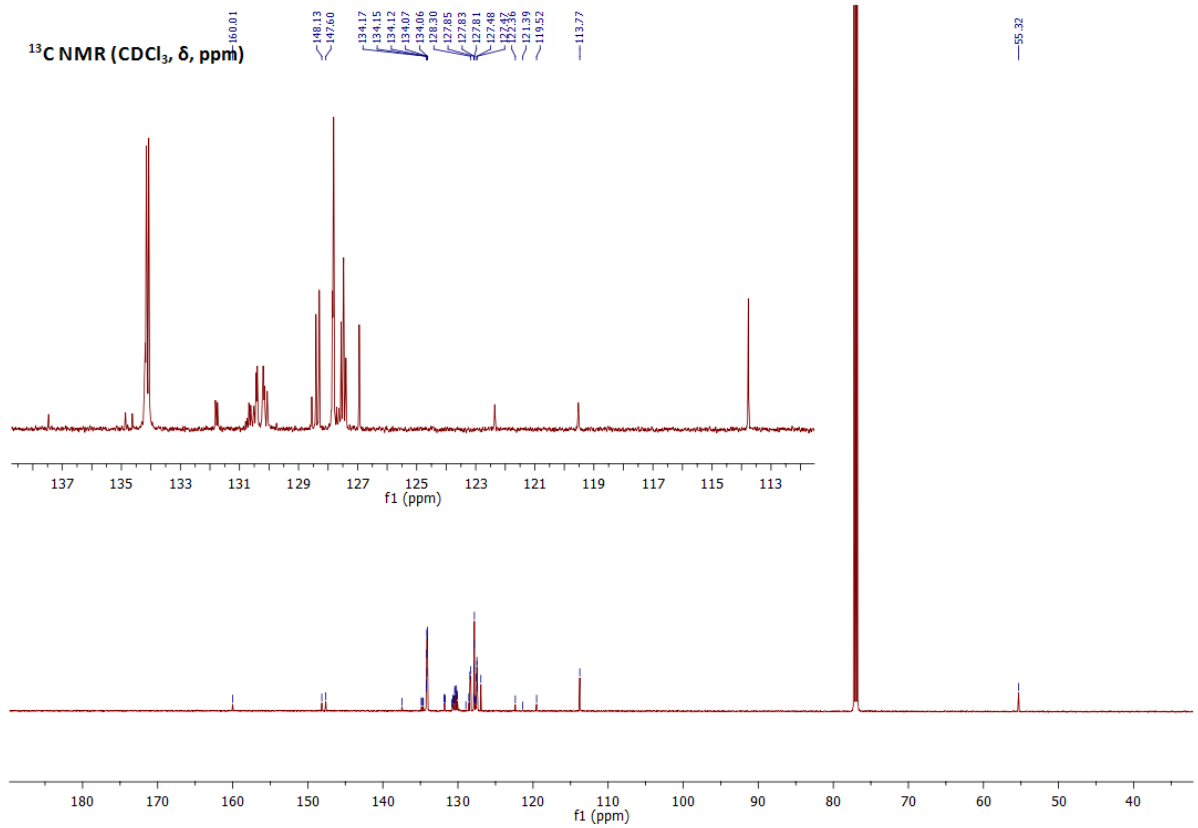


^{1}H NMR ($CDCl_3$, δ, ppm)



4B-a-e

^{13}C NMR ($CDCl_3$, δ, ppm)



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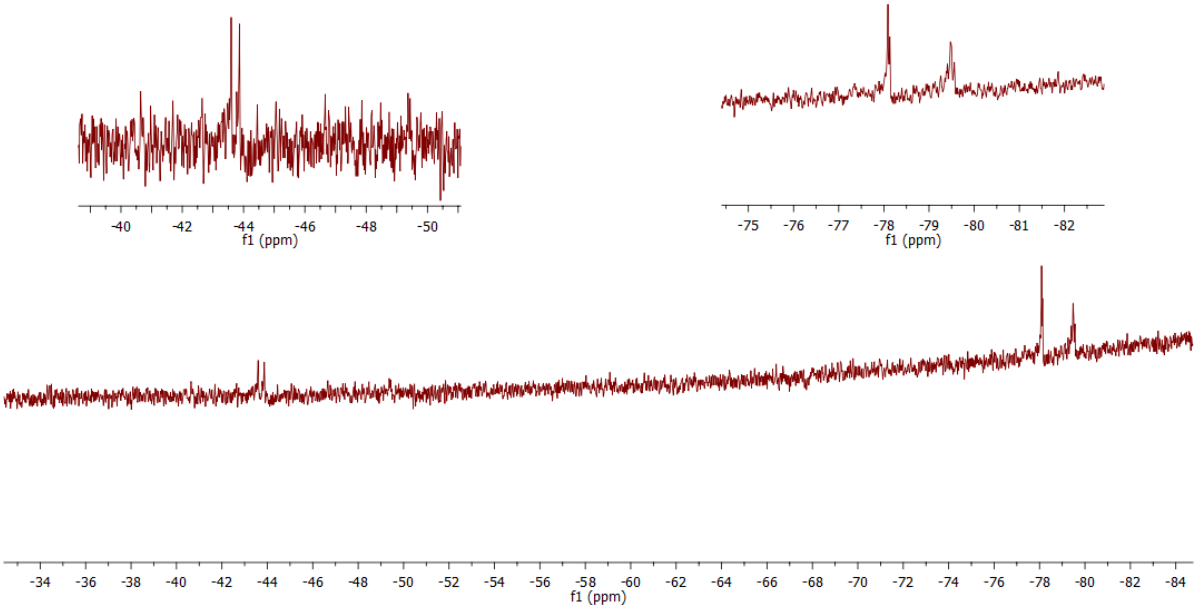
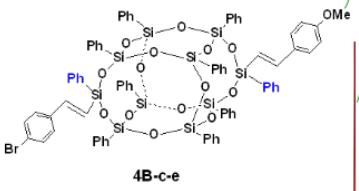
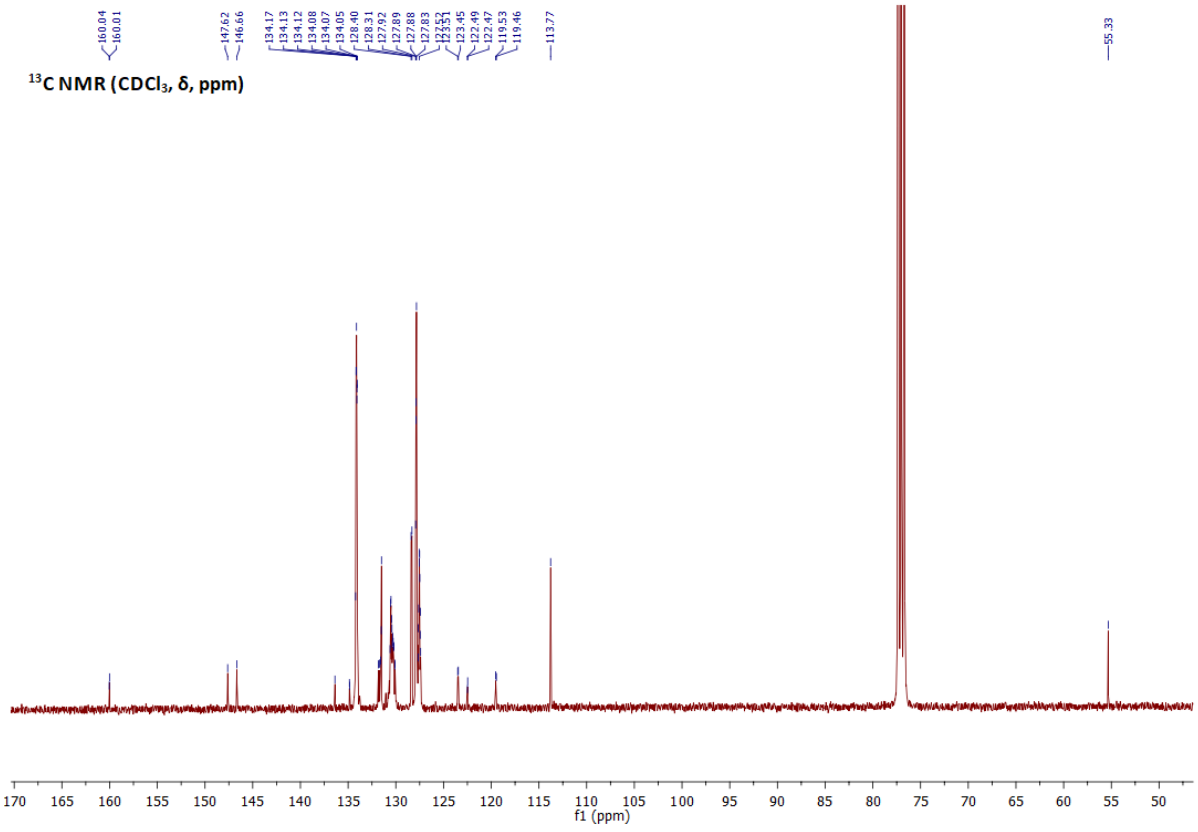


^{1}H NMR ($CDCl_3$, δ, ppm)

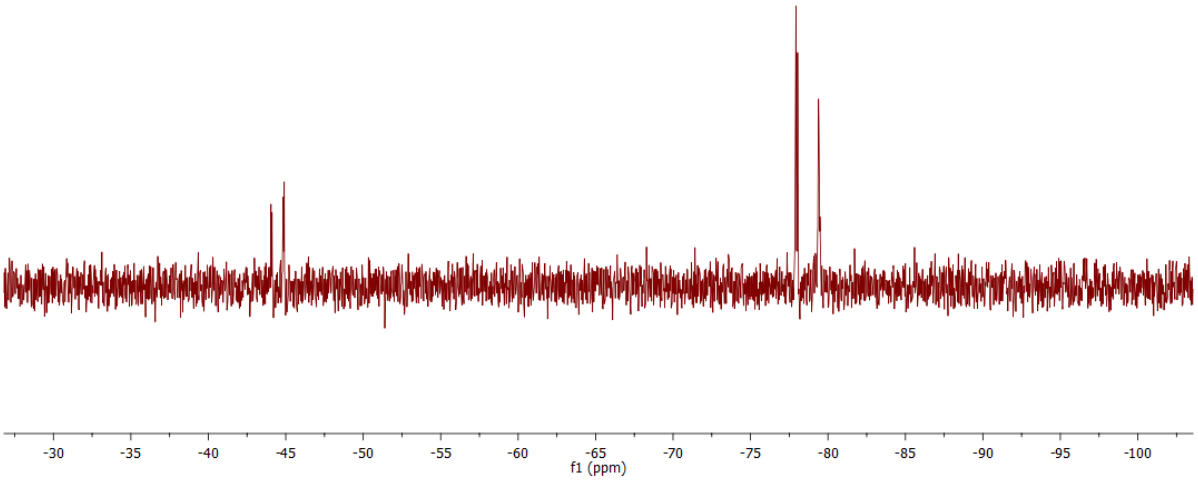


4B-c-e

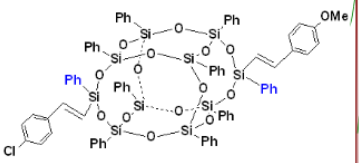
^{13}C NMR ($CDCl_3$, δ, ppm)



^{29}Si NMR ($CDCl_3$, δ, ppm)

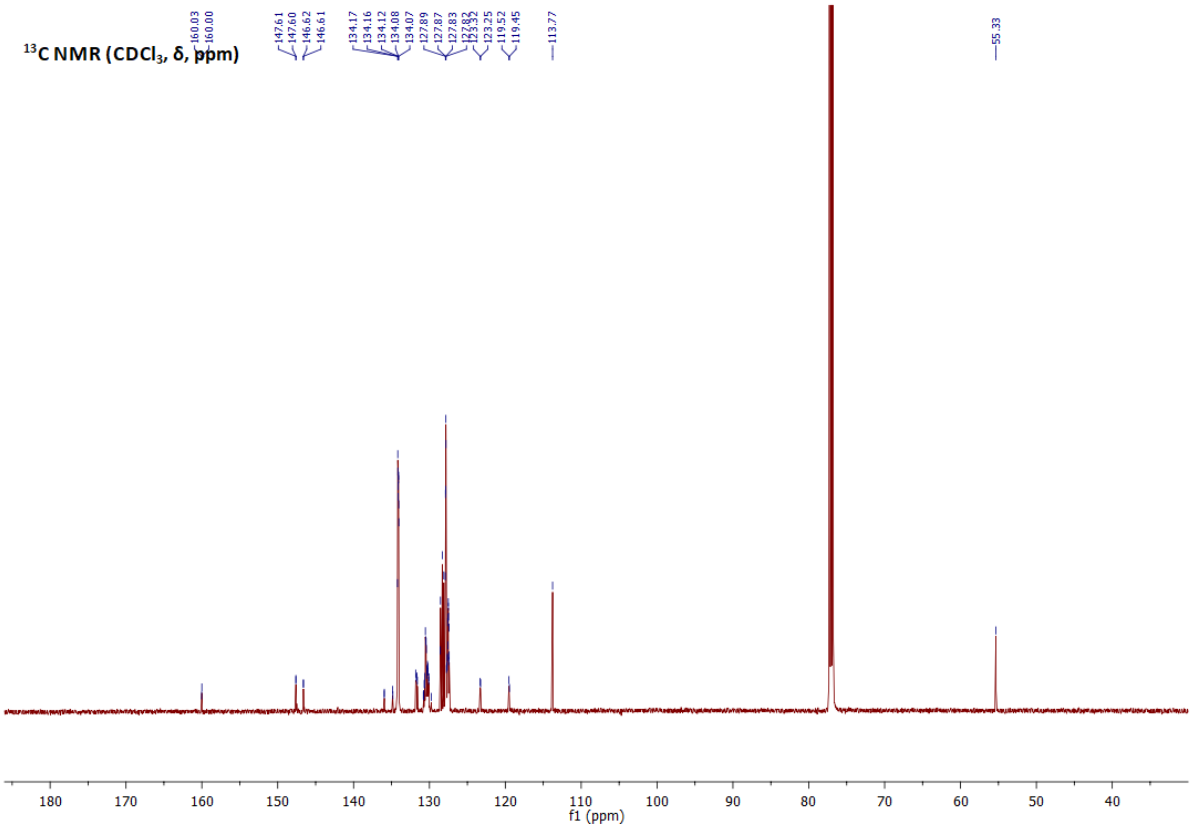


^{1}H NMR ($CDCl_3$, δ, ppm)

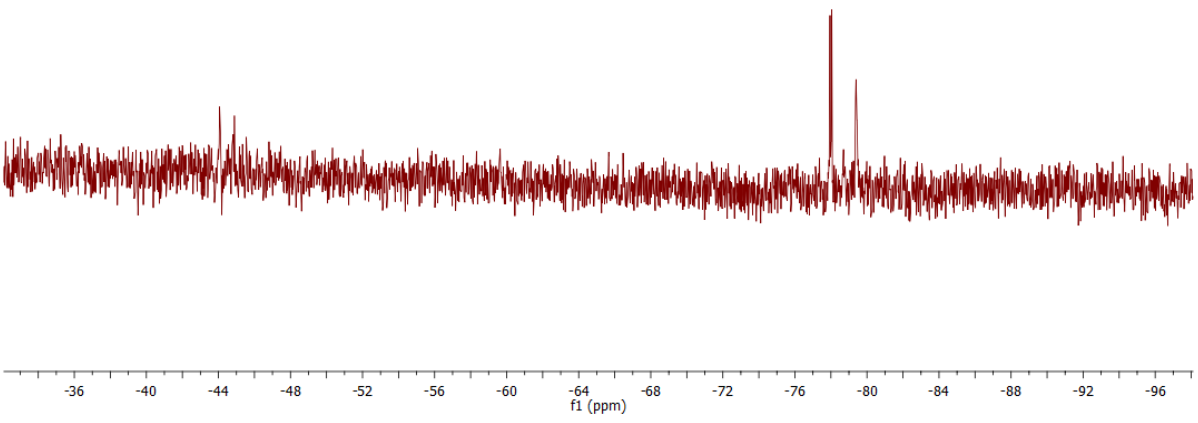


4B-d-e

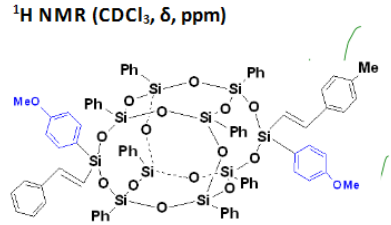
^{13}C NMR ($CDCl_3$, δ, ppm)



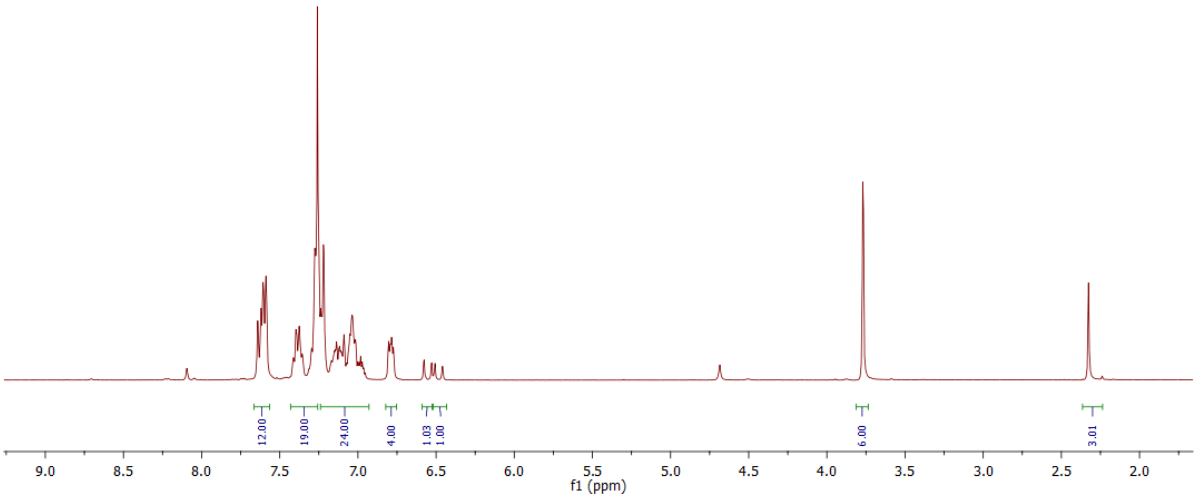
^{29}Si NMR ($CDCl_3$, δ, ppm)



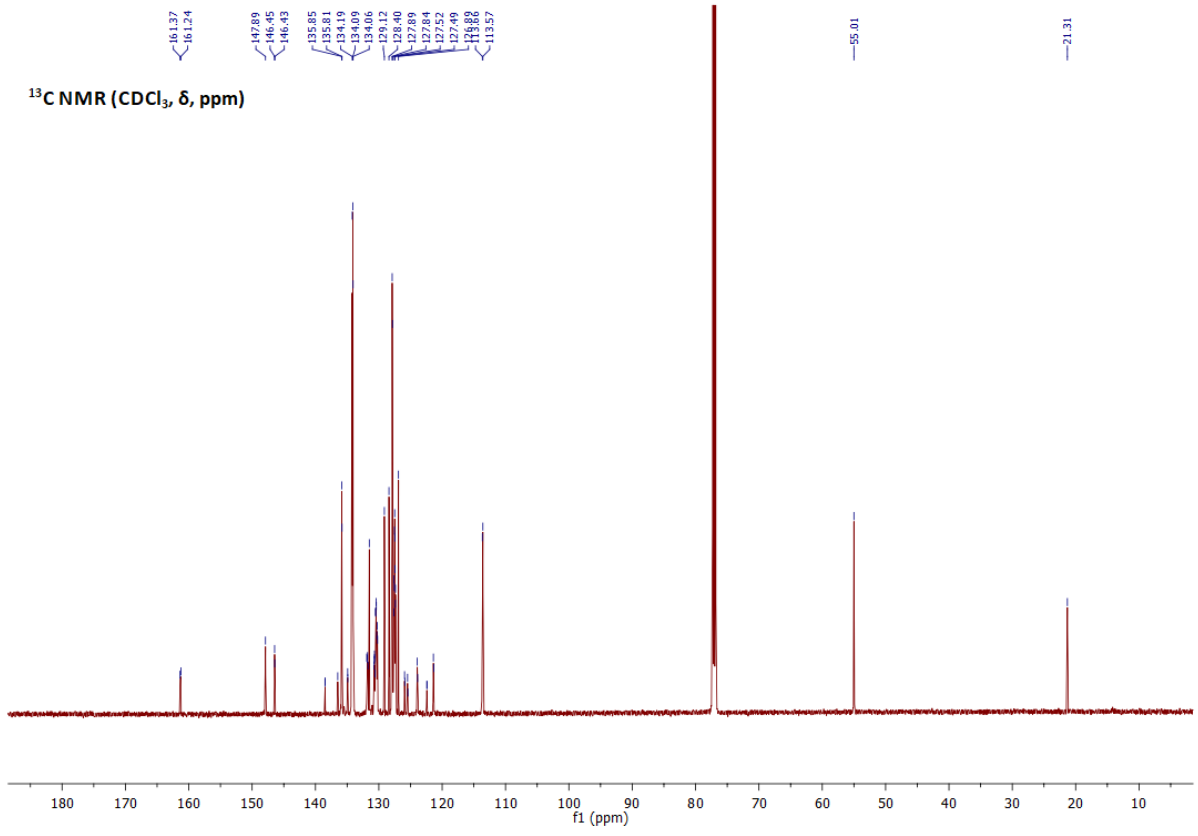
^{1}H NMR ($CDCl_3$, δ, ppm)



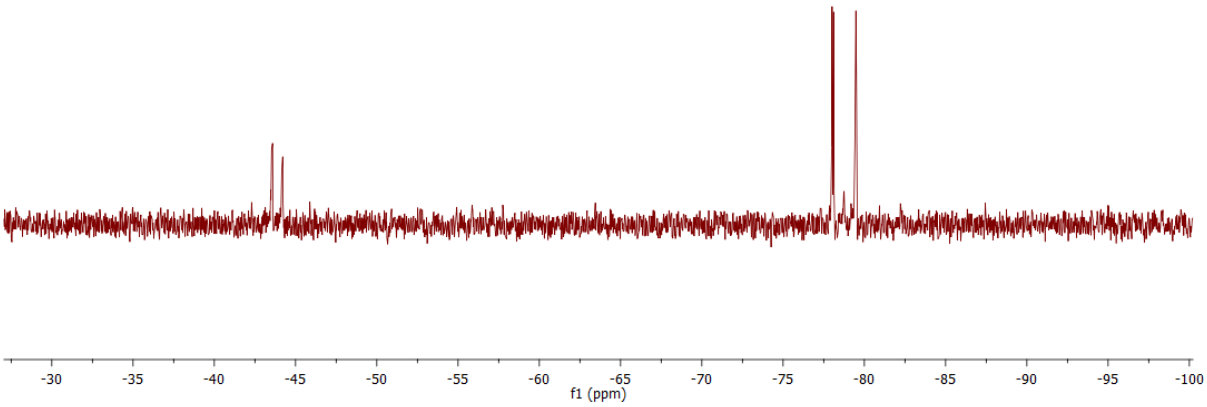
4C-a-b



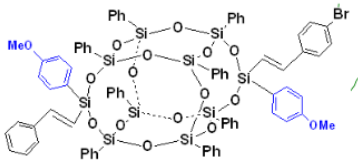
^{13}C NMR ($CDCl_3$, δ, ppm)



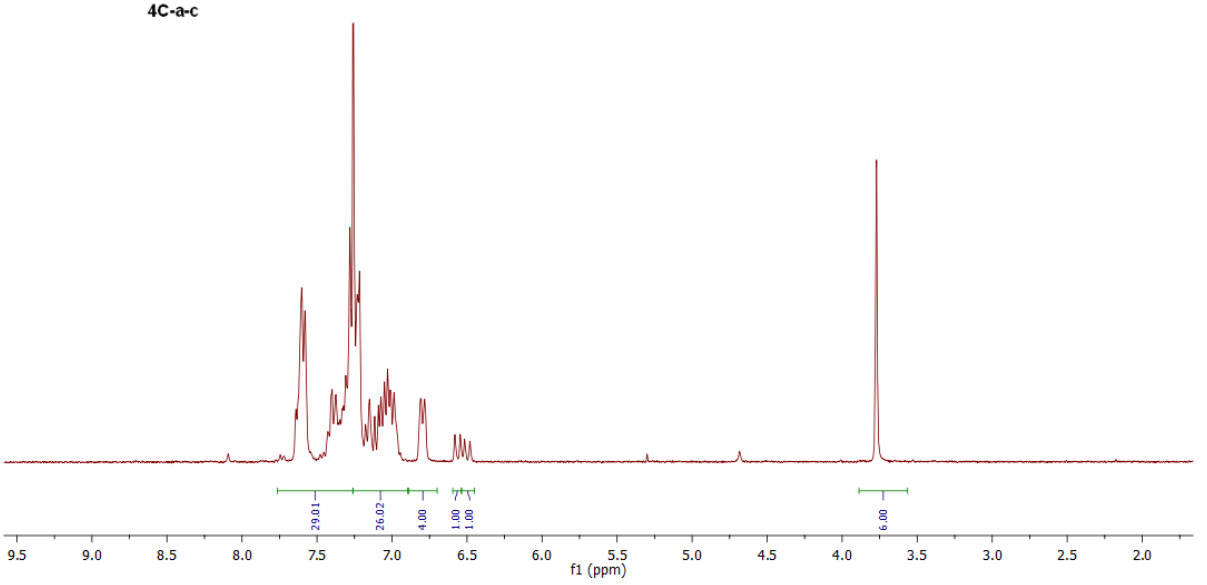
^{29}Si NMR ($CDCl_3$, δ, ppm)



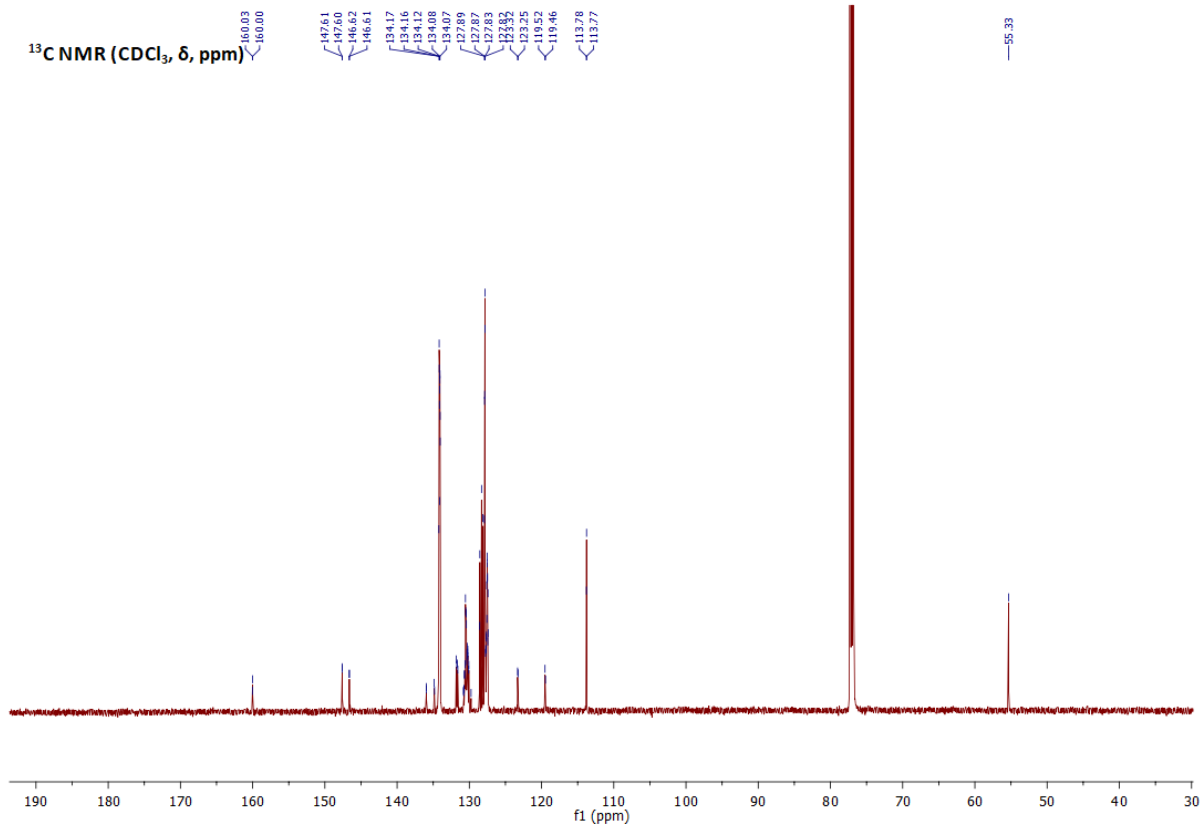
^{1}H NMR ($CDCl_3$, δ, ppm)



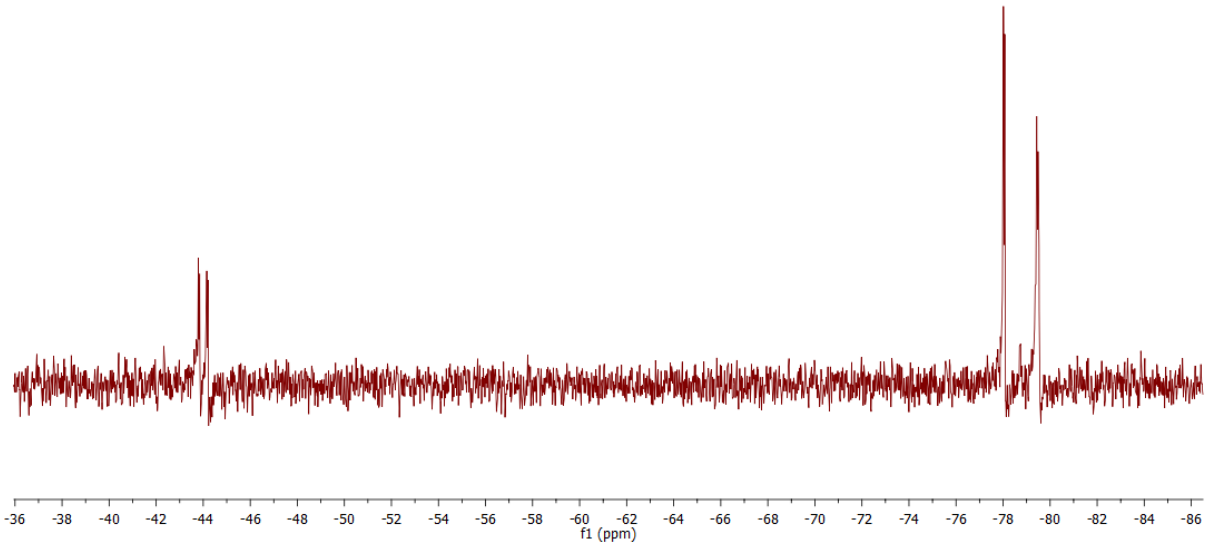
4C-a-c

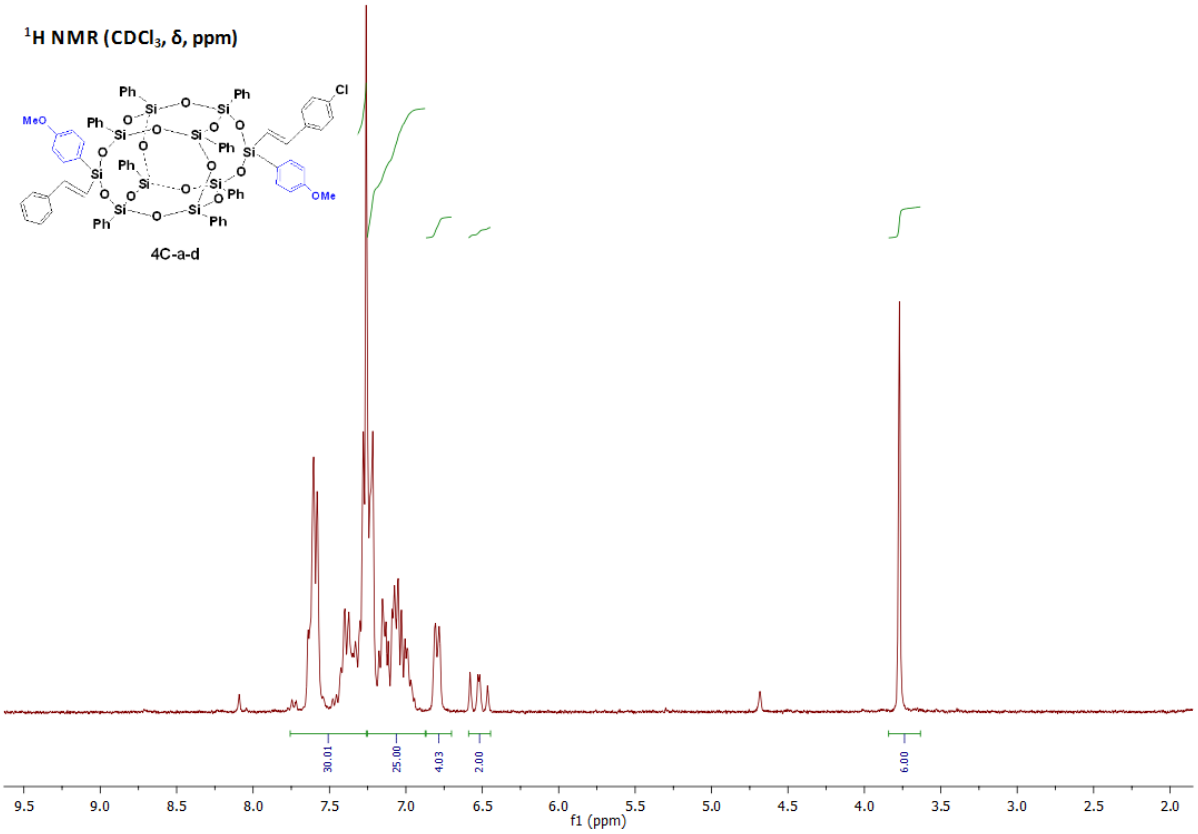


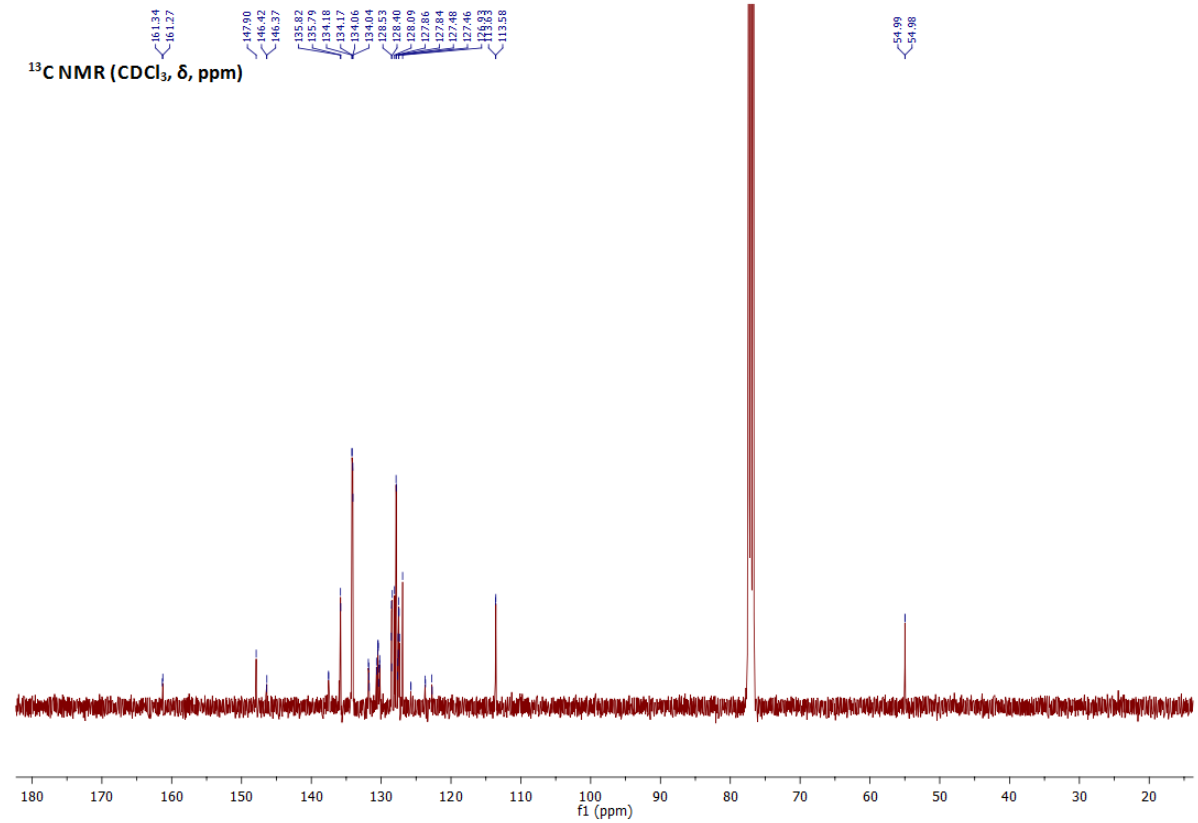
^{13}C NMR ($CDCl_3$, δ, ppm)



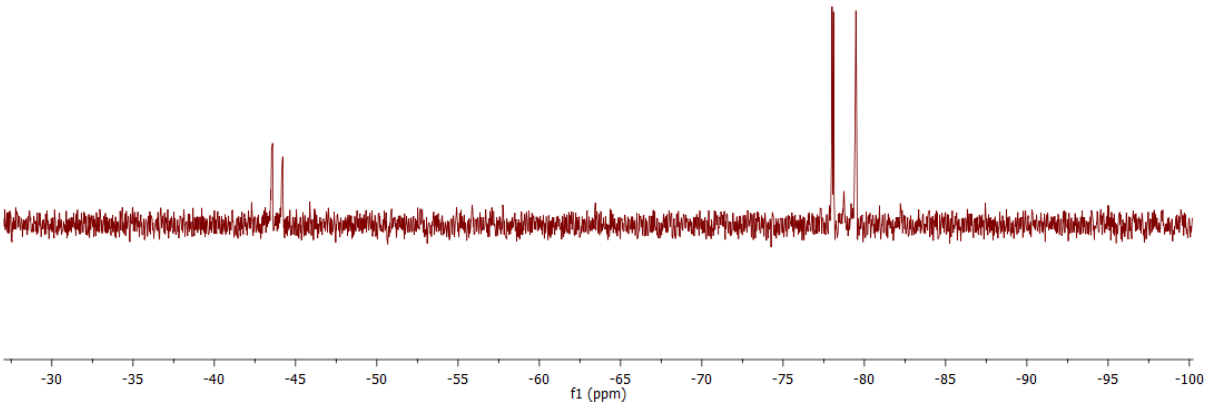
^{29}Si NMR ($CDCl_3$, δ, ppm)



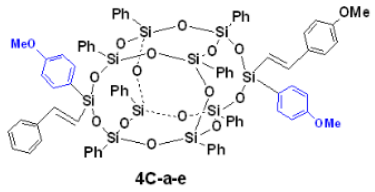

^{1}H NMR ($CDCl_3$, δ, ppm)
MeO
Cl
OMe
Ph
Si
O
4C-a-d
30.01
25.00
4.03
2.00
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


^{13}C NMR ($CDCl_3$, δ, ppm)
161.34
161.27
147.90
146.42
146.37
135.82
135.79
134.18
134.17
134.06
134.04
129.53
128.40
128.09
127.86
127.84
127.48
127.46
113.58
54.99
54.98
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

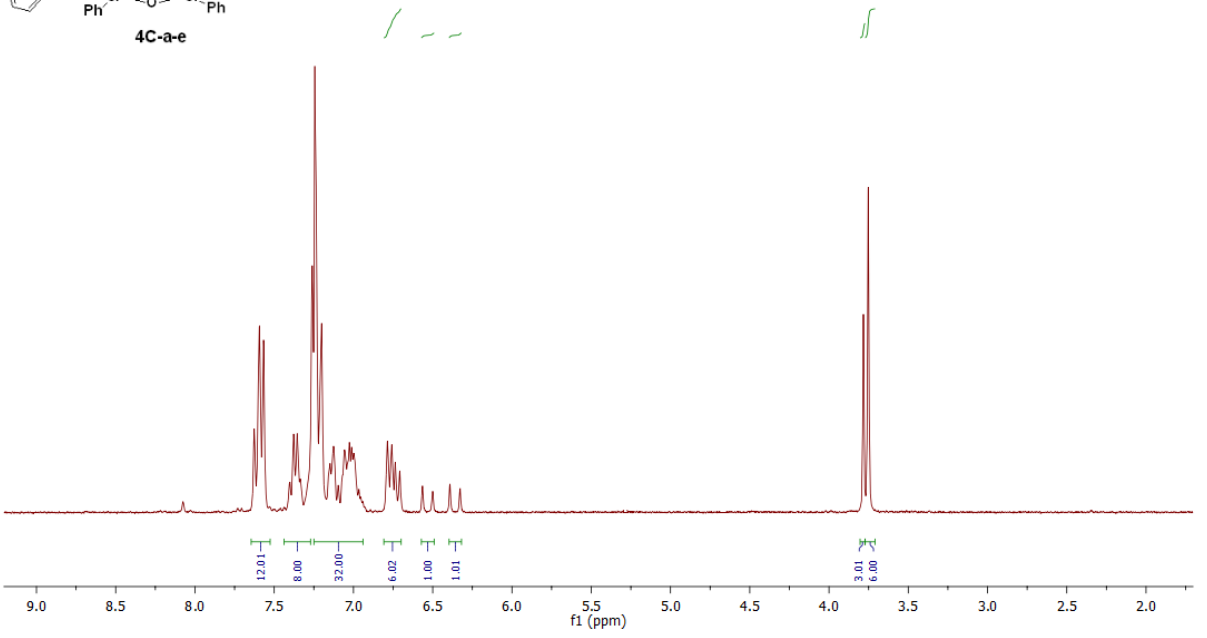
^{29}Si NMR ($CDCl_3$, δ, ppm)



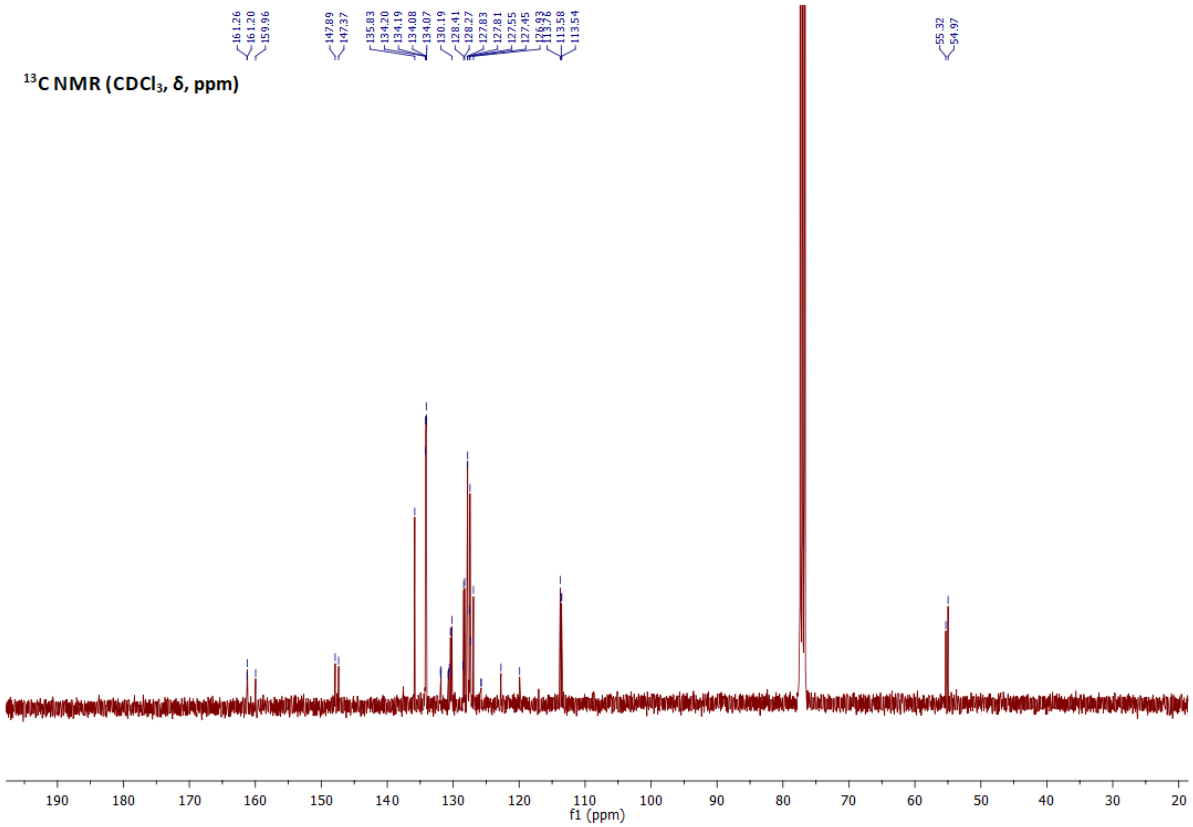
^{1}H NMR ($CDCl_3$, δ, ppm)



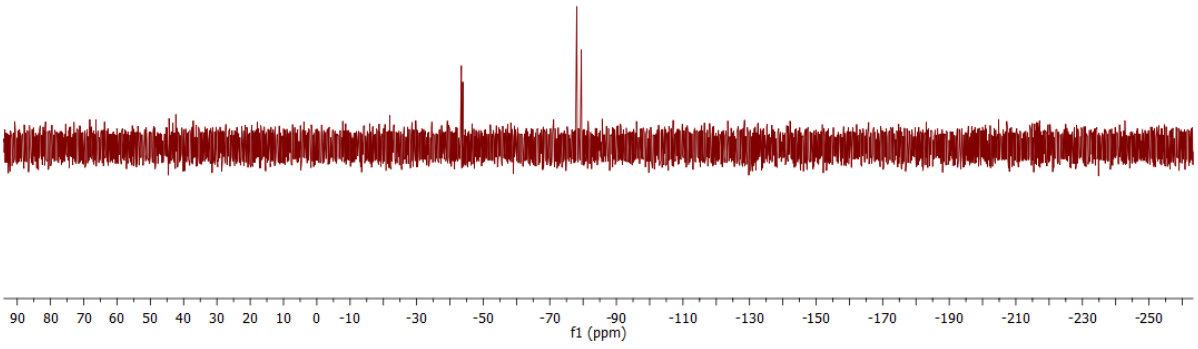
4C-a-e



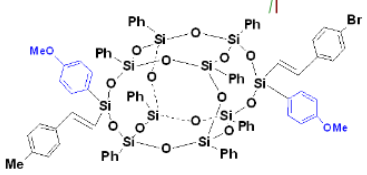
^{13}C NMR ($CDCl_3$, δ, ppm)



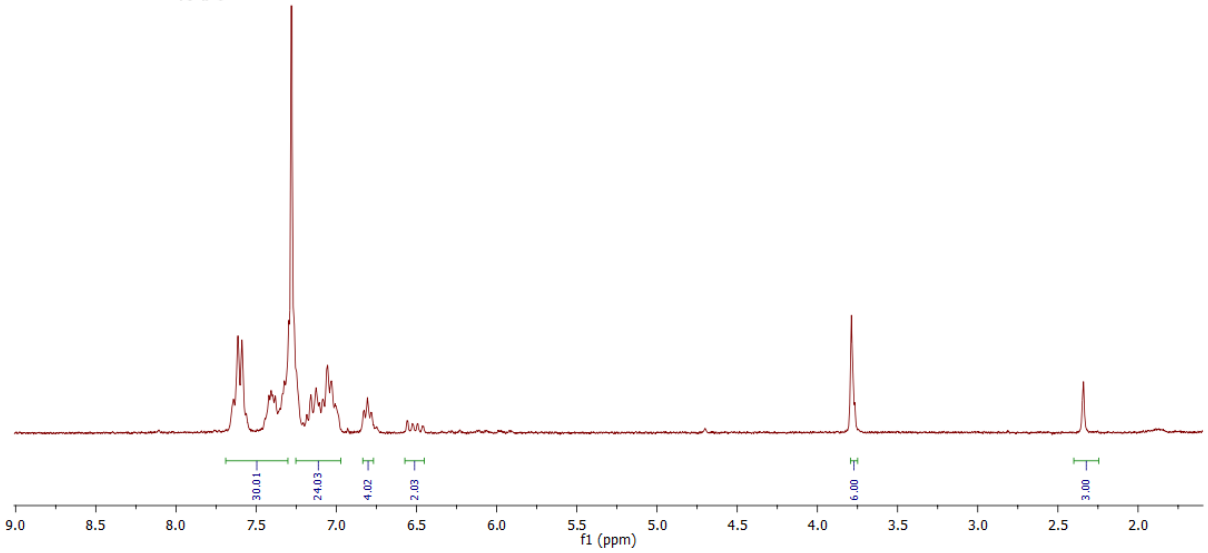
^{29}Si NMR ($CDCl_3$, δ, ppm)



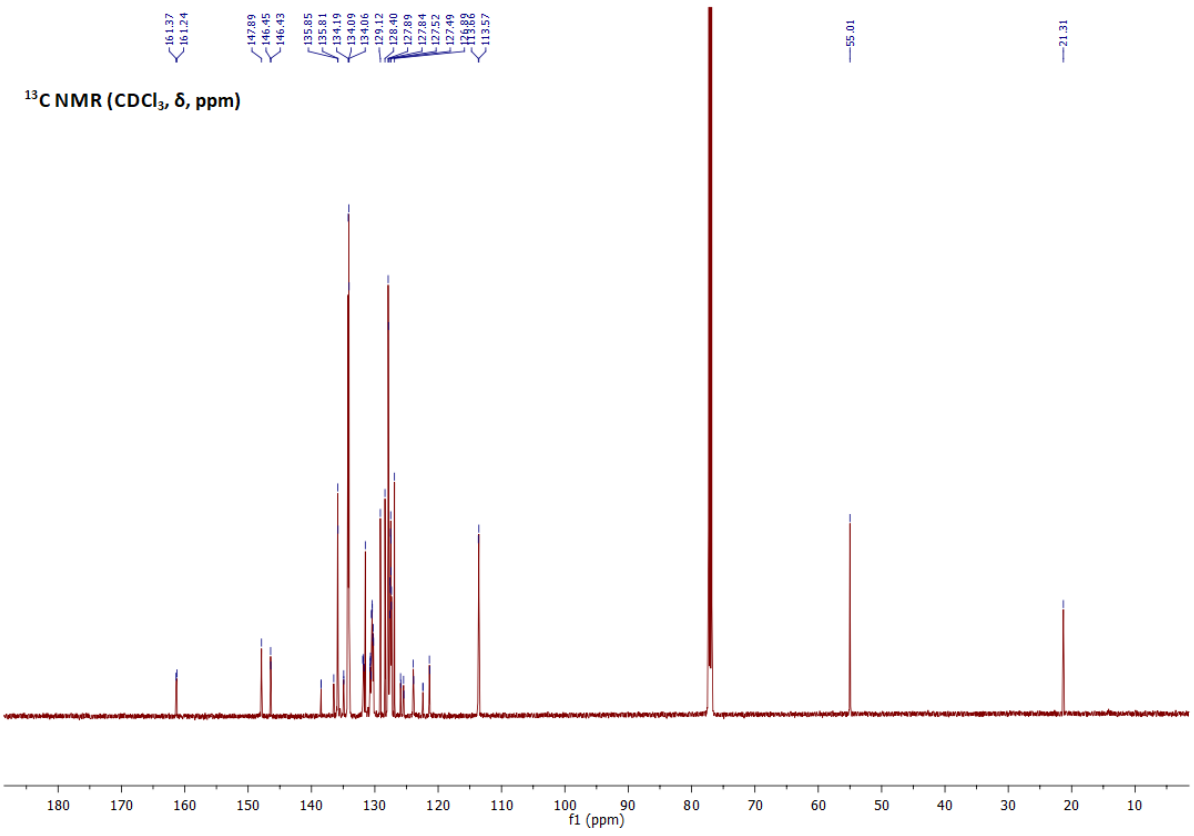
^{1}H NMR ($CDCl_3$, δ, ppm)



4C-b-c



^{13}C NMR ($CDCl_3$, δ, ppm)



^{29}Si NMR ($CDCl_3$, δ, ppm)