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Supporting Information for

The unusual *cis*- and *trans*- architecture of dihydrofunctional double-decker shaped silsesquioxane and synthesis of its ethyl bridged π-conjugated arene derivatives

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1. General Considerations

The chemicals were obtained from the following sources: toluene, dichloromethane, tetrahydrofuran, potassium carbonate and trimethylamine were purchased from Fluka. Methanol and ethanol were purchased from POCH. DDSQ-4OH (TetraSilanolPhenyl POSS) was purchased from Hybrid Plastics. Methyldichlorosilane, 4-vinylplenylboronic acid, 1-bromo-naphtalene, bromopentafluorobenzene, bromobenzene, 9-bromoanthracene, 1,4-dibromobenzene, 1,4-dibromotetra-fluorobenzene, 9,10-dibromoanthracene, 1,4-dibromo-naphtalene and Celite®, Karstedt's catalyst (platinum(0)-1,3- divinyl-1,1,3,3-tetramethyldisiloxane complex [Pt(dvs)], solution in xylene with 2% of Pt), tetrkis(triphenyl-phosphine) palladium(0) ($[Pd(PPh_3)_4]$) were purchased from Sigma-Aldrich Chemical Company (A Part of a Merck Group). The above mentioned solvents were stored over molecular sieves type 4Å. All liquid substrates were also dried and degassed by bulb-to-bulb distillation.

2. Measurements

Nuclear magnetic resonance spectroscopy (NMR)

^{1}H and ^{13}C NMR measurements were conducted using a spectrometer (Bruker Ultrashield 300 MHz), ^{29}Si NMR spectra were recorded using spectrometer (BruckerAscend^{TM} 400 MHz Nanobay) in $CDCl_3$.

FT-IR spectroscopy

Fourier Transform-Infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 Fourier transform spectrophotometer that was equipped with a SPECAC Golden Gate, diamond ATR unit with a resolution of 2cm^{-1}.

Real-time FT-IR spectroscopy

Real-timeFT-IR measurements were performed on a Mettler Toledo ReactIR 15 equipped with a DS 6.3mm AgXDiComp Fiber Probe with a diamond sensor, and a Mercury Cadmium Telluride detector. For all the spectra 256 scans were recorded with the resolution of 1cm^{-1} in 1,2,5 and 10 min intervals.

UV-vis spectroscopy

The UV-visible spectra were recorded on NICOLET EVOLUTION 220 PC spectrophotometer, and baseline corrections and normalizations were carried out using INSIGHT software. HPLC pure grade $CHCl_3$ was used as a solvent.

Gel Permeation Chromatography (GPC)

GPC analyses were performed using a Waters Alliance 2695 system equipped with Waters 2414 RI detector and a set of three serially connected Waters HR columns (Waters Styragel HR1, HR2 and HR4). The measurements were carried out with THF as a mobile phase in a flow rate of 0.60 mL/min; column oven temperature was 35°C and detector temperature 40°C. All molecular weight (M_n, M_w) and polydispersity index (PDI) values were calculated based on calibration curve using polystyrene standards (Shodex) in a range from 1.31×103 to 3.64×106 Da.

Thermogravimetric Analysis (TGA)

TGA analyses were performed using a TA Instruments TGA Q50 thermal gravimetric analyzer. The measurements were conducted in nitrogen atmosphere (flow of 60 mL/min), from ambient temperature to 800°C at the heating rate of 10°C/min. The temperature of initial degradation (T_d) was taken as the onset temperature at which 5 wt% of mass loss occurs.

Matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS)

MALDI-TOF mass spectra were recorded on a UltrafleXtreme mass spectrometer (Bruker Daltonics), equipped with a SmartBeam II laser (355 nm) in 500-4000 m/z range. 2,5-Dihydroxybenzoic acid (DHB, Bruker Daltonics, Bremen, Germany) served as matrix and was prepared in TA30 solvent (30:70 v/v acetonitrile: 0.1% TFA in water) at a concentration of 20 mg/mL. Studied samples were dissolved in dichloromethane (2 mg/mL) and then mixed in a ratio 1:1 v/v with matrix solution.

Matrix/sample mixtures (1 µL) were spotted onto the MALDI target and dried in air. Mass spectra were measured in reflection mode. The data were analyzed using the software provided with the Ultraflex instrument - FlexAnalysis (version 3.4). Mass calibration (cubic calibration based on five to seven points) was performed using external standards (Peptide Calibration Standard).

X-ray crystallography

Diffraction data were collected at 130(1) K by the ω-scan technique on Agilent Technologies four-circle Xcalibur diffractometer with Eos CCD detector and graphite-monochromated Mo K_{α}radiation (λ=0.71069 Å). The data were corrected for Lorentz-polarization as well as for absorption effects.[1] Precise unit-cell parameters were determined by a least-squares fit of 6786 reflections of the highest intensity, chosen from the whole experiment. The structure was solved with SIR92[2] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-2013.[3] The scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times U_{eq} of appropriate carrier atoms. There are two symmetry-independent halves of C_i-symmetrical molecules of 1 in the asymmetric part of the unit cell. Interestingly, in both these molecules the Si-CH$_3$ fragments are disordered. In molecule A the Si atom has been found in two alternative positions (s.o.f.'s refined at 69.7(5)% and 30.3(5)%), while in the molecule B the methyl groups are disordered over two positions with s.o.f.'s of 58.1% and 41.9%. Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-1481315. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

3. Synthetic Procedures

3.1.1 Synthesis of 9,19-di(hydro)octaphenyl double-decker silsesqiuoxane (DDSQ-2SiH) (1)

DDSQ-2SiH(1) was synthesized *via* well-known hydrolytic condensation of tetrasilanol form of silsesquioxane with methyldichlorosilane.[4] Typically, DDSQ-4OH (10 g, 9.35 mmol) and Et$_3$N (5.52 mL, 39.60 mmol) were added into two-neck round-bottom flask equipped with a magnetic stirrer, anhydrous THF (450 mL) was added with vigorous stirring. The reaction mixture was placed in ice-water bath and purged with highly pure argon. Then methyldichlorosilane (1.96 mL, 18.87 mmol) was added. Reaction was carried out for 24 hours at room temperature. Then insoluble solid of triethylammonium chloride was removed by filtration on a glass frit, volatiles and THF were eliminated *via* rotary evaporation. Crude product was dissolved in DCM and extracted three times with water. After solvent removal, the solid was dried *in vacuo* for 4 hours the product (8.2 g) was obtained with yield of 76 %.

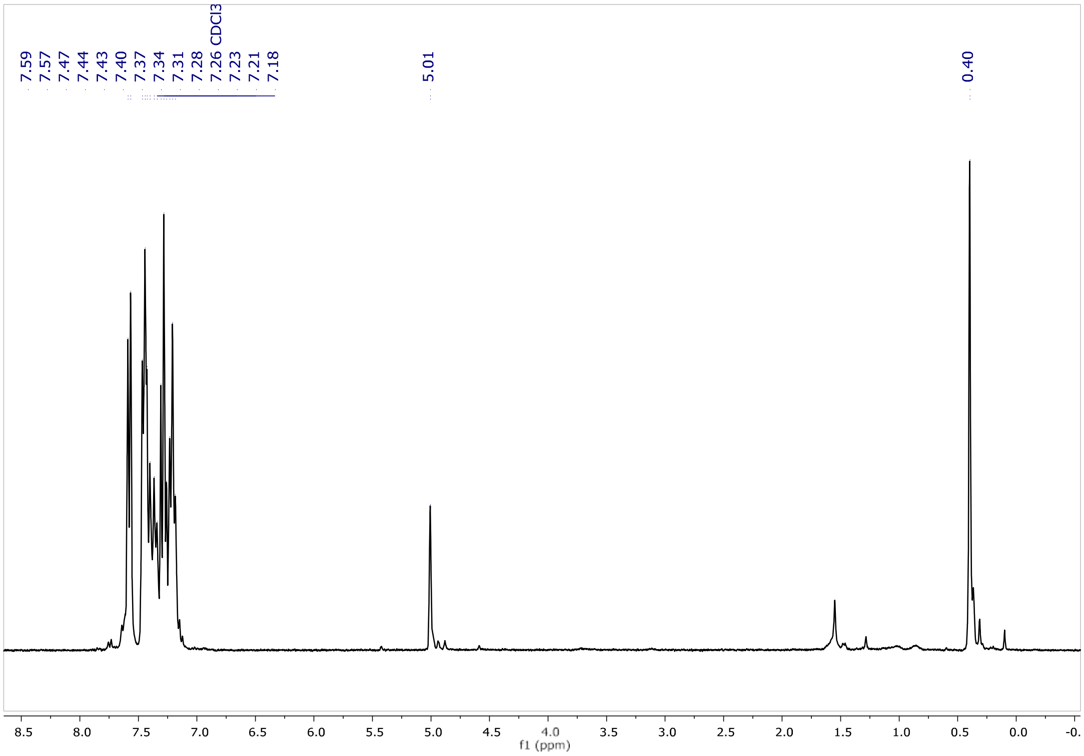
M.p. = 273°C. FT-IR (cm^{-1}) 3073, 3051 (C-H$_{phenyl}$); 2960 (Si-CH$_3$), 2190 (Si-H), 1594 (C=C$_{phenyl}$), 1258 (Si-CH$_3$), 1050, 1030 (Si-O), 997 (C-H$_{phenyl}$), 900, (Si-H). ^{1}H NMR (ppm, CDCl$_3$) 0.39 (d, 6H, J_{HH} = 1.5 Hz, Si-C$\underline{H_3}$), 5.01(qu, 2H, J_{HH} = 1.5 Hz, Si-$\underline{H}$), 7.08-7.78 (m, 40H, C$_{Ar}$-H). ^{13}C NMR (ppm, CDCl$_3$) 0.63 (-CH$_3$), 127.60; 130.40; 130.48; 131.57; 133.90 (C$_{Ar}$). ^{29}Si NMR (ppm, CDCl$_3$) -32.77 , -77.80, -79.09, -79.28, -79.49

Crystal data:

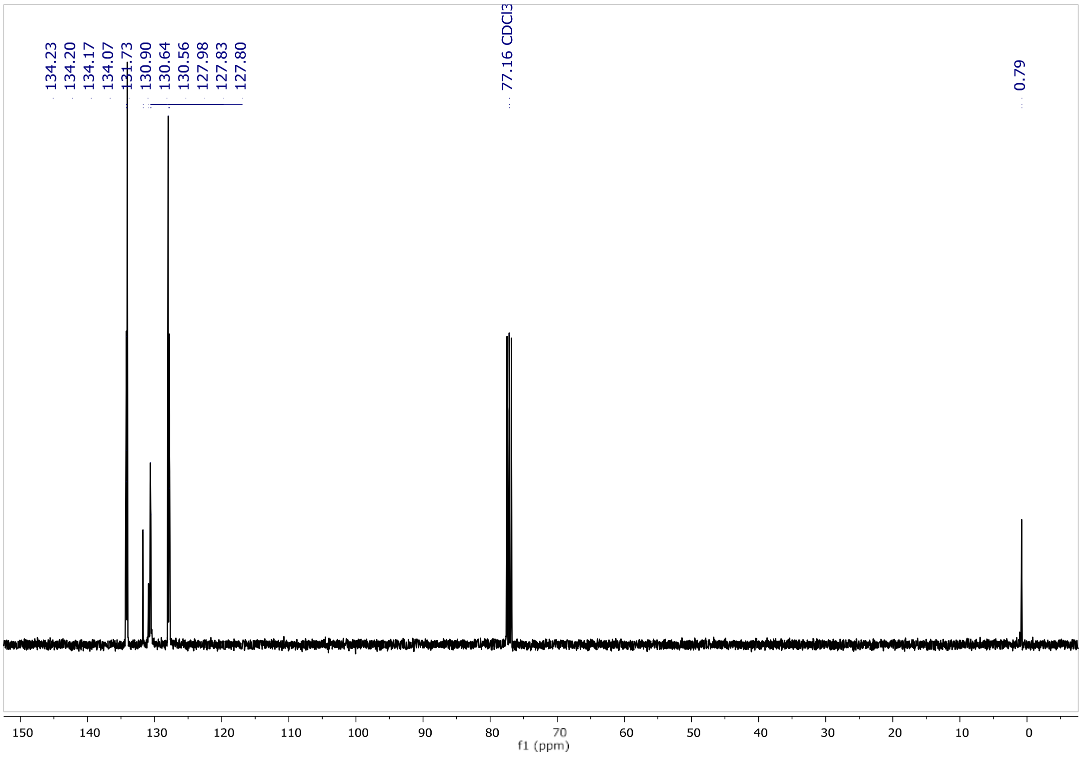
1: $C_{50}H_{46}O_{14}Si_{10}$, M_r = 1151.77, triclinic, P-1 ,a = 10.5118(5) Å, b = 13.8528(8) Å, c = 19.5175(6) Å, α = 98.402(4)°, β = 90.407(3)°, γ = 90.950(4)°, V= 2811.1(2) Å^3, Z=2, d_x=1.36 g·cm^{-3}, F(000)=1196, μ=0.296 mm^{-1}, 19356 reflections collected, of which 9894 unique (R_{int}=0.032), 7282 with $I>2\sigma(I)$, $R(F)[I>2\sigma(I)]$ = 0.047, $wR(F^2)(I>2\sigma(I))$=0.125, R(F)[all data]=0.073, $wR(F^2)$[all data]=0.136, S=1.06, max/min $\Delta\rho$ in the final ΔF map: 0.90/-0.53 e·Å^{-3}.

Specta of a mixture of *cis*- and *trans*- di[9,19- hydro-methyl]-1,3,5,7,11,13,15,17-octa(phenyl)pentacyclo[11.7.1.$1^{3,11}$.$1^{5,17}$.$1^{7,15}$]decasiloxane (1)

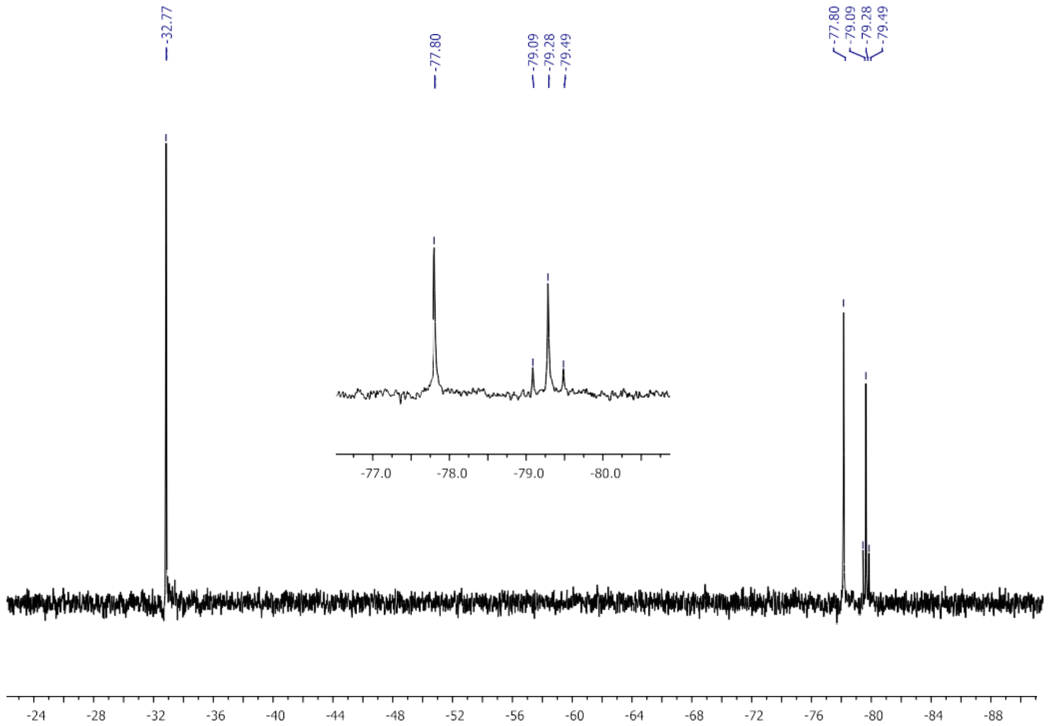
^{1}H NMR ($CDCl_3$, 400MHz):



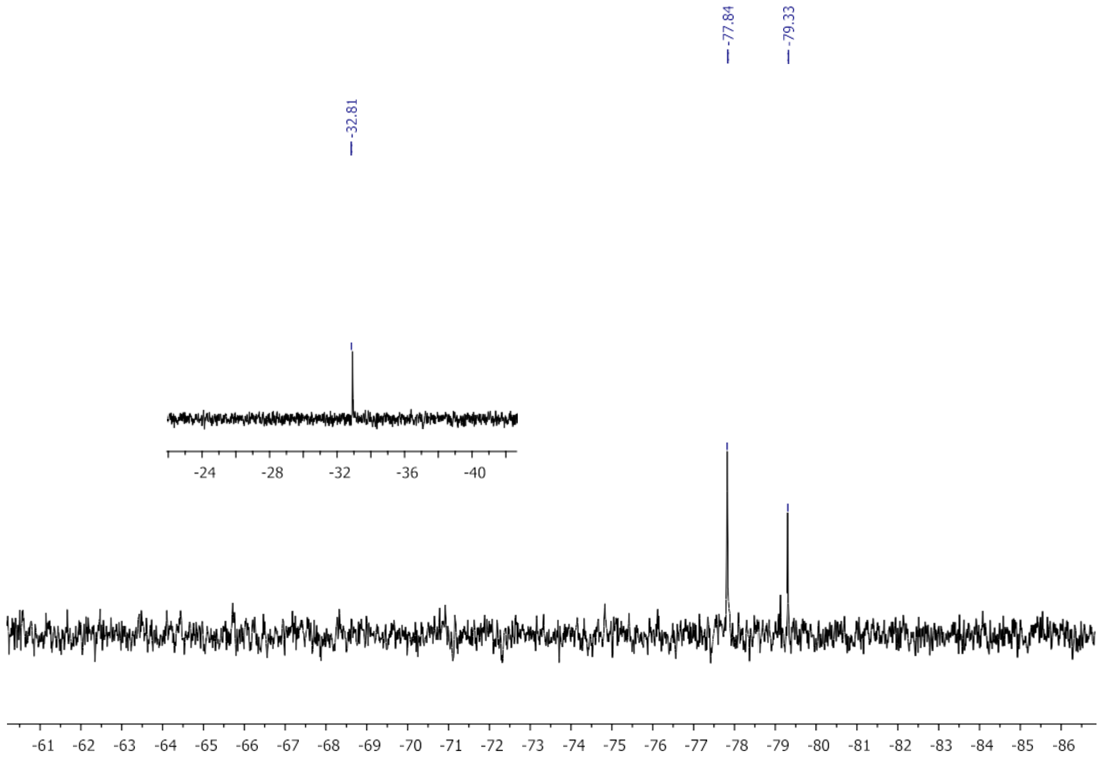
***^{13}C NMR** ($CDCl_3$, 125 MHz):*



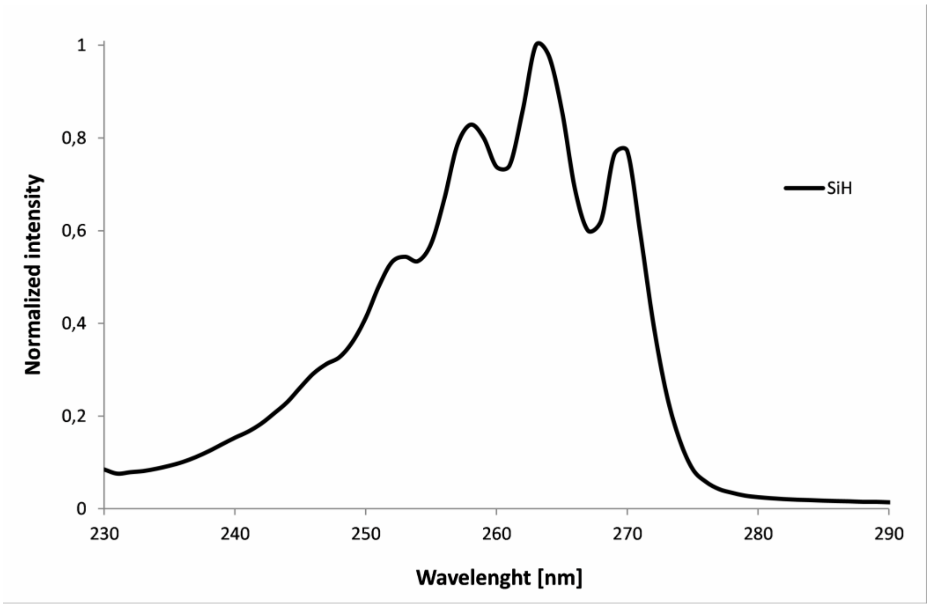
***^{29}Si NMR** (CDCl$_3$, 99 MHz):*



Fragment of ^{29}Si NMR spectrum of *trans*- di[9,19- hydro-methyl]-1,3,5,7,11,13,15,17-octa(phenyl)pentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (1)



UV-visible absorption spectra of **1** in $CHCl_3$ solution:



3.2 Synthesis of styryl- and bis(styryl)arenes

Styryl- and bis(styryl)arenes (**2a-d** and **4a-d**) were obtained according to the literature.[5] Typically, a mixture of aryl bromine and 4-vinylplenylboronic acid were placed in a two-necked round-bottom flask equipped with magnetic stirrer and condenser. Then, anhydrous toluene and ethanol (3:1) were added. The suspension was heated in oil bath at 60-90°C and catalyst ($[Pd(PPh_3)_4]$, 1 mol%) and the solution of K_2CO_3 (2M) was added. After the reaction was completed (monitored by GCMS analysis) obtained mixture was filtered off by flash chromatography (silica gel 40, Celite®, DCM) to remove impurities from catalyst. Next DCM and other solvents were eliminated via rotary evaporation. Crude product was dissolved in DCM and extracted with water three times. After solvent removal, the solid was dried *in vacuo* for 4 hours, products (**2a-d** and **4a-d**) were obtained with yield of 73-95 %.

3.3 General Procedure for FT-IR *in situ* monitored hydrosilylation reaction

A mixture containing 0.2g (0.173mmol) of DDSQ and equimolar amount of bis(styryl)arene or 0.346 mmol of styrylarene and 2mL of toluene was placed in a glass reactor set (10mL) (described below) and heated at 90°C, then, the catalyst was added. Reaction mixture was stirred at 90°C and monitored by *in-situ* FT-IR spectroscopy to designate the endpoint of process. For quantitative description of DDSQ-2SiH conversion band at $907cm^1$ derived from Si-H bond was analyzed.

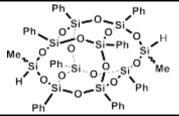
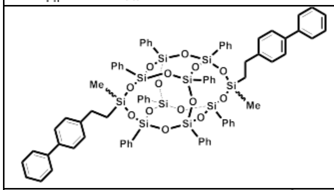
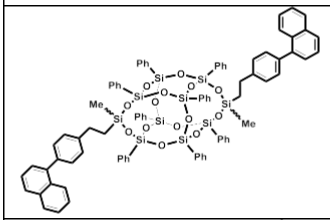
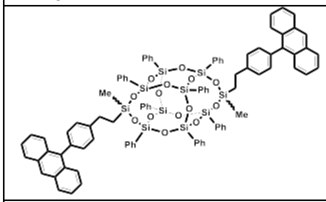
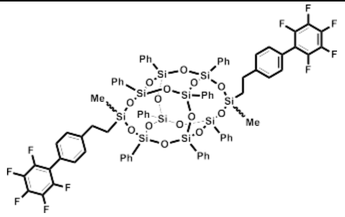
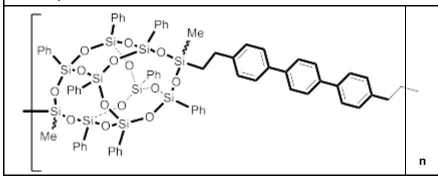
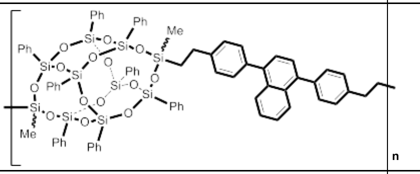
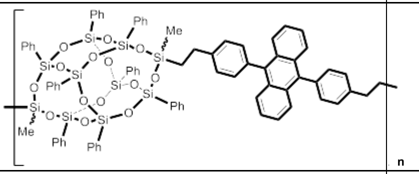
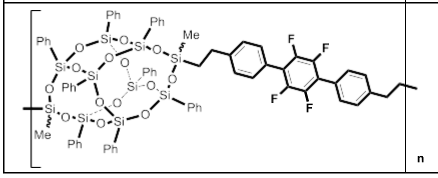
3.4 General procedure for the synthesis of 9, 19-bis(ethyl-aryl)-octaphenyl double-decker shaped silsesquioxanes - molecular systems (3a-d)

To a two-neck round-bottom flask equipped with a magnetic stirrer, condenser and IR *in-situ* probe, **DDSQ-2SiH** (0.2 g, 0.173 mmol), an anhydrous toluene (2 mL) and stoichiometric amount of olefin (2 a-d) were added. The reaction mixture was heated up to 90°C and 2% solution of Karstedt's catalyst in xylene (Pt(dvs) 5×10^{-4} – 10^{-4} mol per 1 mol of **1** was added. Reactions were carried out until the conversionof 1 was near to 100%, that was precisely specified due to IR *in-situ* spectroscopy. After that reaction mixture was filtered off by flash chromatography (silica gel 40, Celite®, DCM) to remove impurities from catalyst. If necessary (present of the unreacted olefin), product was purified by precipitationin methanol/DCM to afford 3(a-d) (76-82% yield).

3.5 General procedure for the synthesis of co-oligomeric aryl-ethyl- double-decker shaped silsesquioxanes - macromolecular systems (5a-d)

A two-neck round-bottom flask equipped with a magnetic stirrer and IR *in-situ* probe was charged with **1** (0.2 g, 0.173 mmol), anhydrous toluene (2 mL) and stoichiometric amount of bis(styryl)arene (4 a-d). After heated up to 90°C, 2% solution of Karstedt catalyst was added. Reactions were controlled by IR *in-situ* spectroscopy, that provided define substrate conversion and its real reaction time consequently. Polymeric products were obtained by precipitation in methanol/DCM. Obtained solids (**5a-d**) were isolated by decantation and dried under reduced pressure. The prepared polymers were characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy as well as GPC and TGA analyses were performed.

4. Table of isolated compounds:

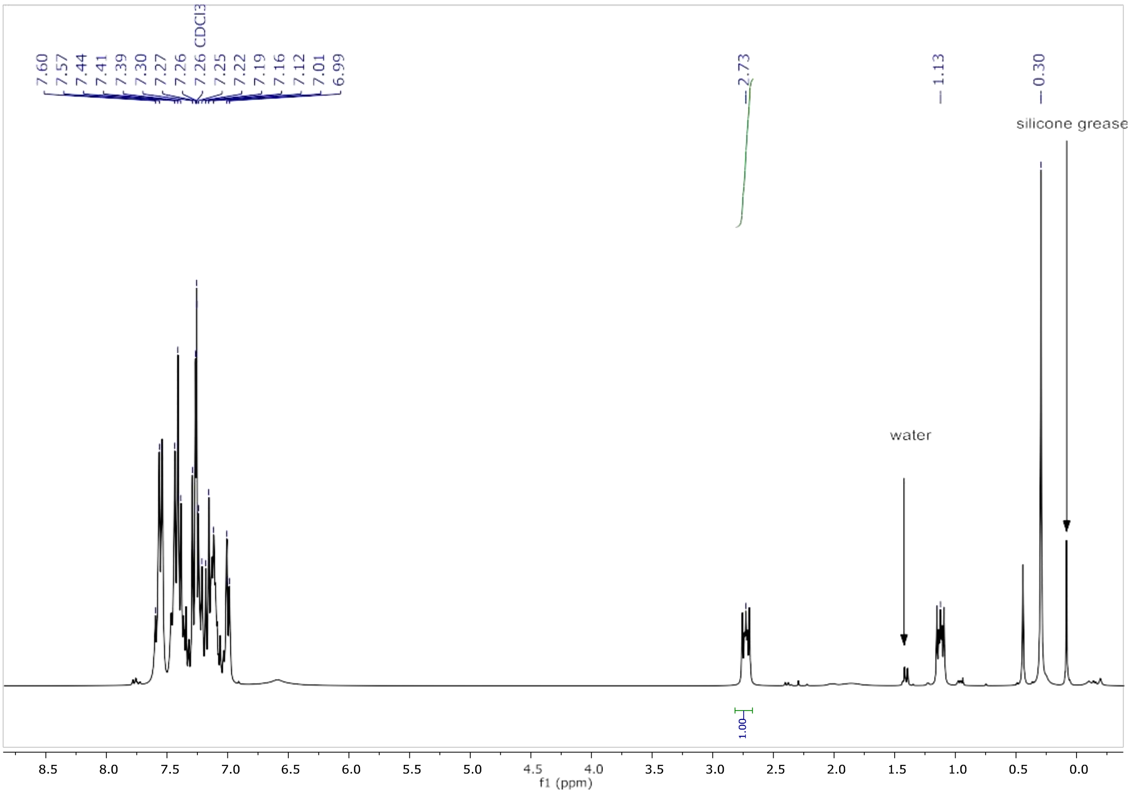
Structure	Compound #	NMR spectra page:	UV-Vis spectrum page:
	**1**	S -4-	S -6-
	**3a**	S -9-	S -11-
	**3b**	S -12-	S -14-
	**3c**	S -15-	S -17-
	**3d**	S -18-	S -20-
	**5a**	S -21-	S -23-
	**5b**	S -24-	S -26-
	**5c**	S -27-	S -29-
	**5d**	S -30-	S -32-

5. Spectroscopic analysis of obtained molecular (3a-d) products:

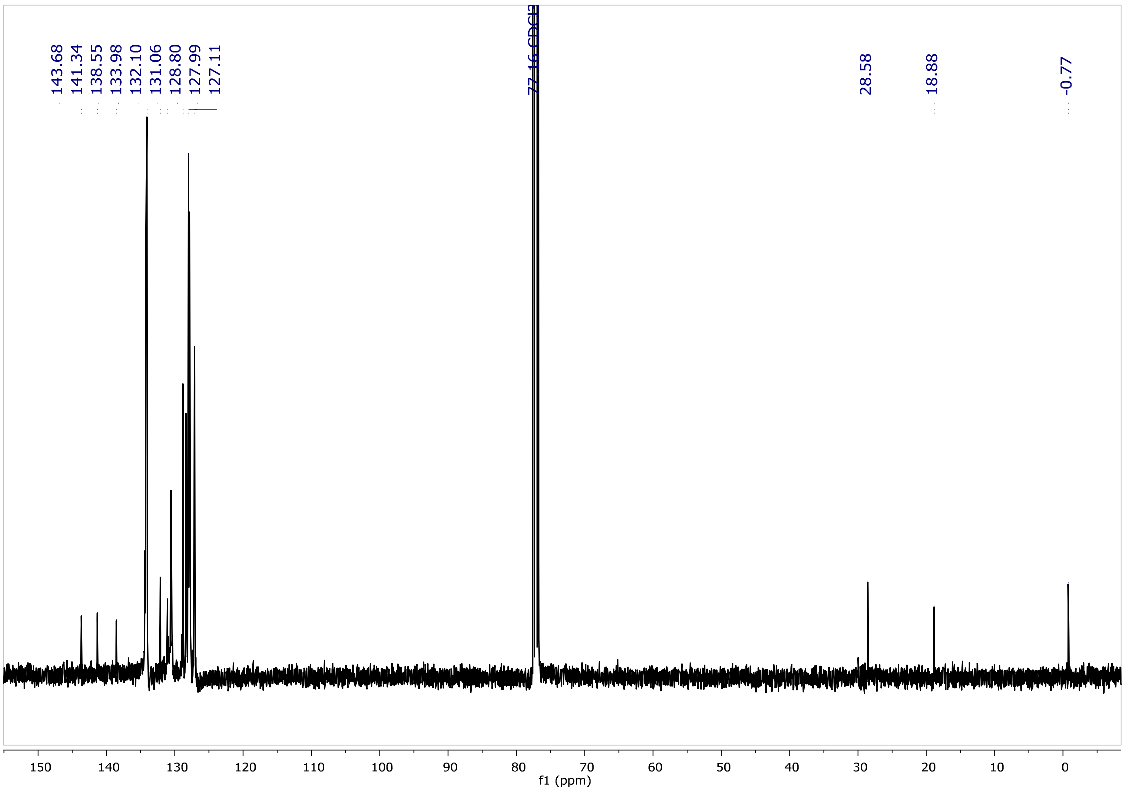
***trans*-di[9,19-(4-phenylethylbenzene)]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]-decasiloxane (3a)**.

M.p. = 203°C. FT-IR (cm^{-1}): 3073, 3052, 3027 (C-H$_{phenyl}$), 1594, 1430 (C=C$_{phenyl}$), 1261 (Si-CH$_3$), 1050, 1027 (Si-O), 997 (C-H$_{phenyl}$), 804, 773 (Si-CH$_2$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.30 (s, 6H, Si-C$\underline{H_3}$), 1.13 (t, 2H, J_{HH} = 6 Hz, Si-C$\underline{H_2}$-), 2.73 (t, 2H, J_{HH} = 6 Hz, C$_{Ar}$ -C$\underline{H_2}$-), 6.99-7.60 (m, 58 H, C$_{Ar}$-H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 0.77 (-CH$_3$), 18.88 (-CH$_2$-), 28.58 (-CH$_2$-), 127.11; 127.99; 128.80; 131.06; 132.10; 133.98; 138.55; 141.34; 143.68 (C$_{Ar}$). ^{29}Si NMR (CDCl$_3$, 99 MHz): δ -18.20, -78.51, -79,49. MALDI-ToF MS (m/z): 1536.2 ([M + Na + H]$^+$, calcd. for C$_{78}$H$_{73}$NaO$_{14}$Si$_{10}$: 1536.2)

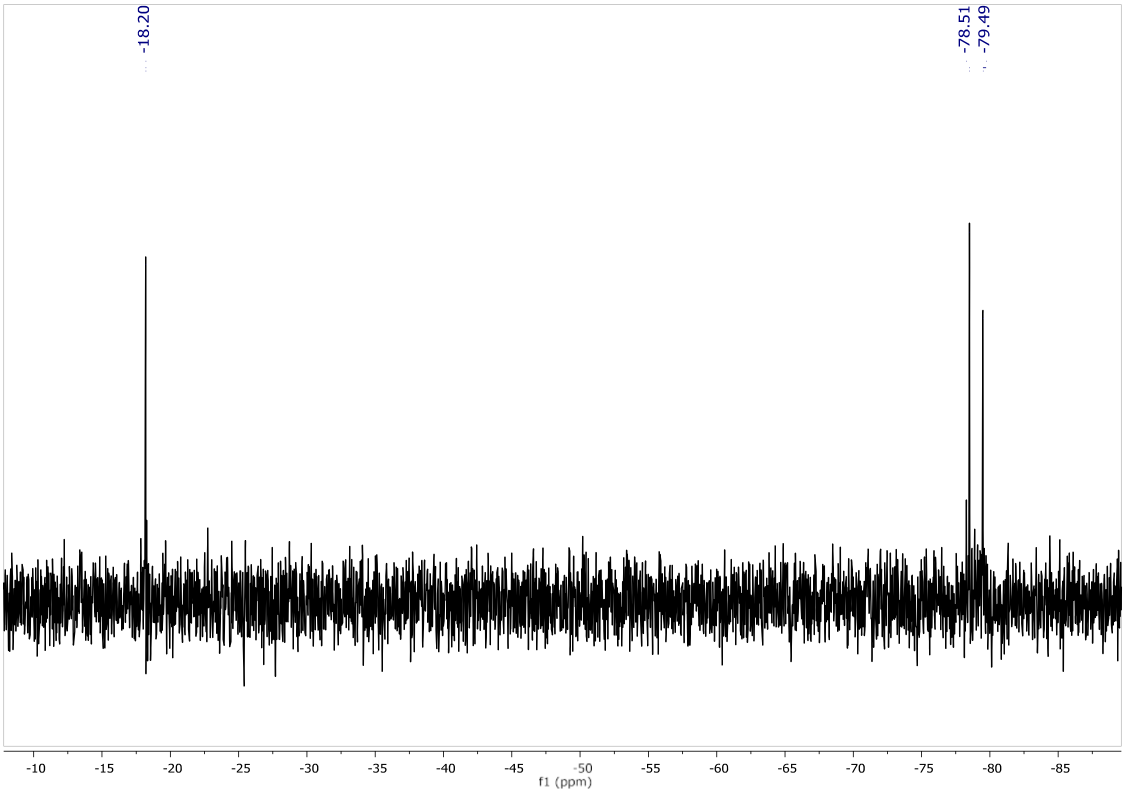
^{1}H NMR (CDCl$_3$, 400MHz):



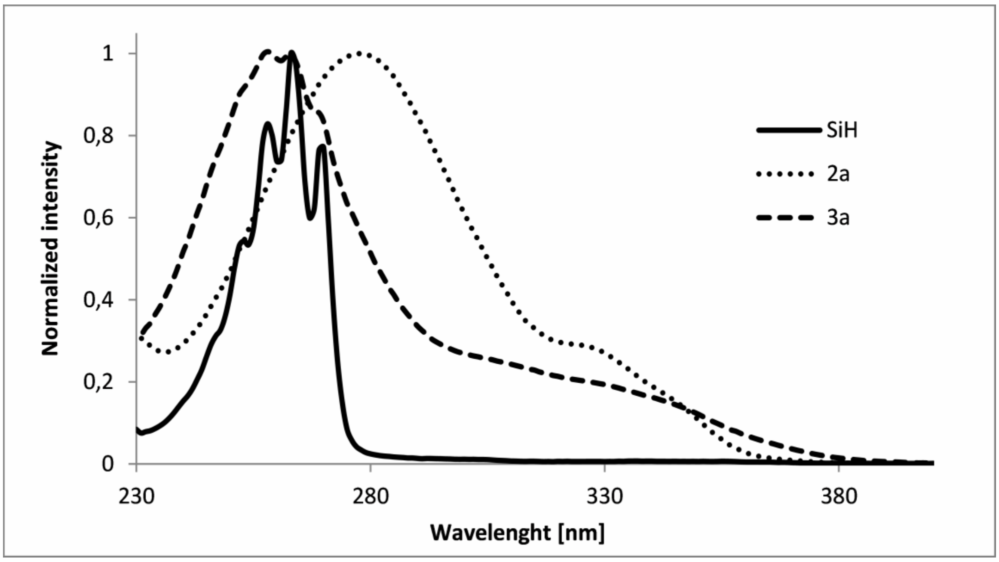
^{13}**C NMR** *($CDCl_3$, 125 MHz):*



^{29}**Si NMR** *($CDCl_3$, 99 MHz):*



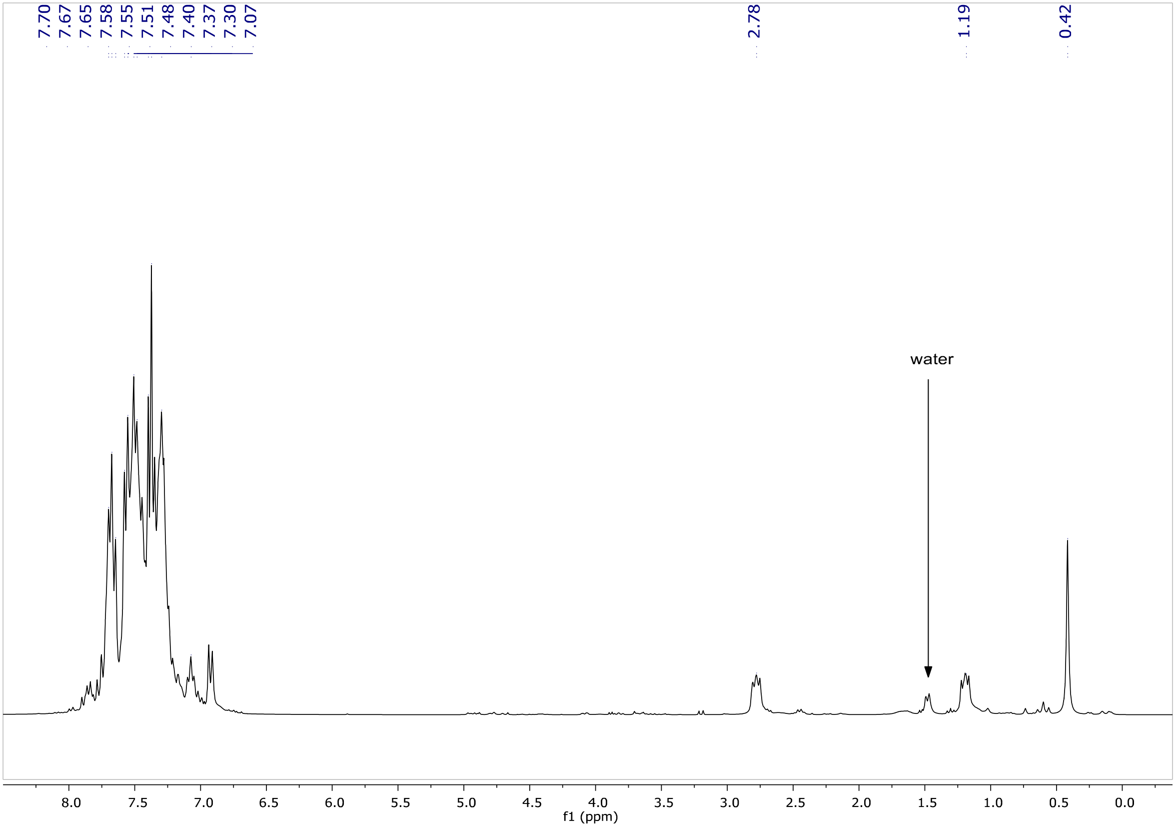
UV-visible absorption spectra of **1**, **2a** and **3a** product in $CHCl_3$ solution:



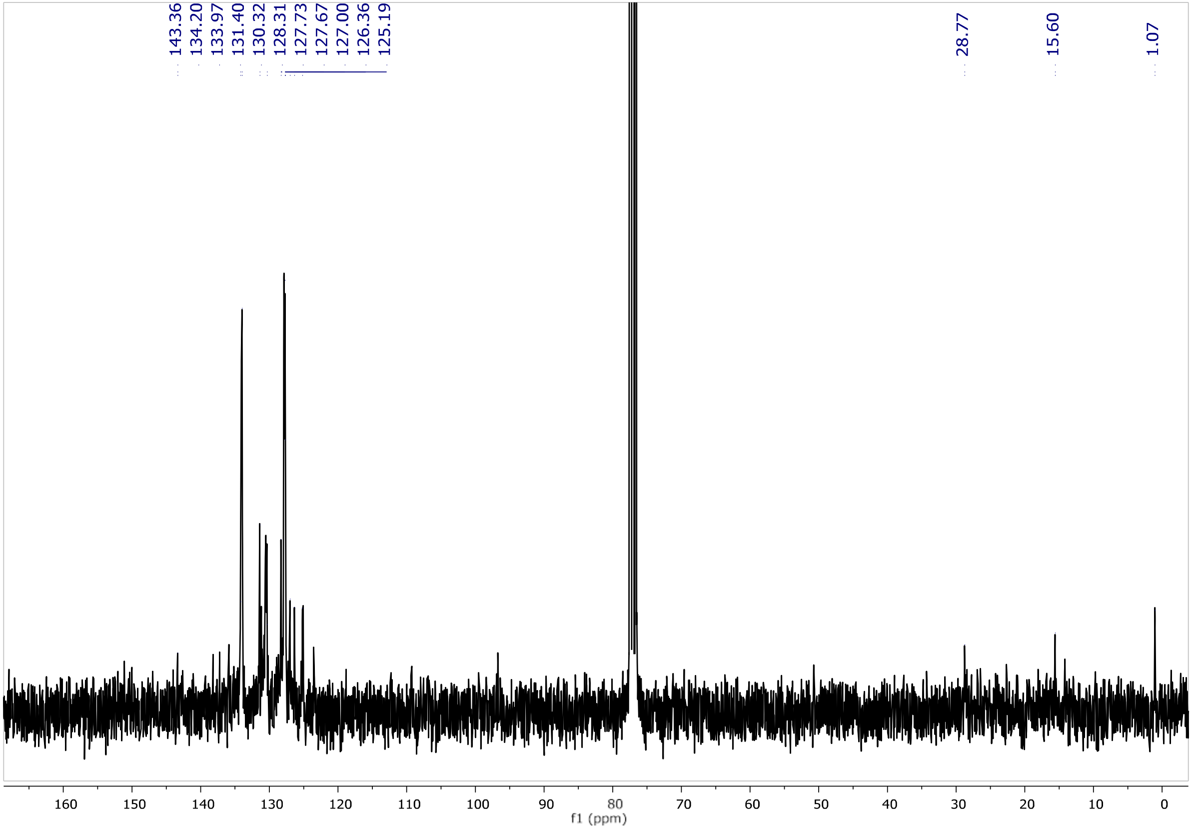
***trans*- di[9,19-(4-(1-naphthyl)ethylbenzene)]-1,3,5,7,11,13,-15,17-octaphenylpentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (3b)**.

M.p. = 137°C. FT-IR (cm^{-1}): 3072, 3048 (Si-P); 2961, 2924 (Si-CH$_3$), 1593, 1430 (C=C$_{phenyl}$), 1260 (Si-CH$_3$), 1078, 1027 (Si-O), 997 (C-H$_{phenyl}$), 799, 777 (Si-CH$_2$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.42 (s, 6H, Si-C$\underline{H_3}$), 1.19 (t, 2H, J_{HH} = 15 Hz, Si-C$\underline{H_2}$-)2.78(t, 2H, J_{HH} = 48 Hz, C$_{Ar}$ -C$\underline{H_2}$-), 7.07-7.70 (m, 62 H,,C$_{Ar}$-H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 1.07 (-CH$_3$), 15.60 (-CH$_2$-), 28.77 (-CH$_2$-), 125.19; 126.36; 127.00; 127.67; 127.73; 128.31; 130.32; 131.40; 133.97; 134.20 (C$_{Ar}$). ^{29}Si NMR (CDCl$_3$, 99 MHz): δ -18.38, -78.50, -79.51. MALDI-ToF MS (m/z): 1652.2 [M + K + H]$^+$, calcd. for C$_{86}$H$_{77}$KO$_{14}$Si$_{10}$: 1652.2

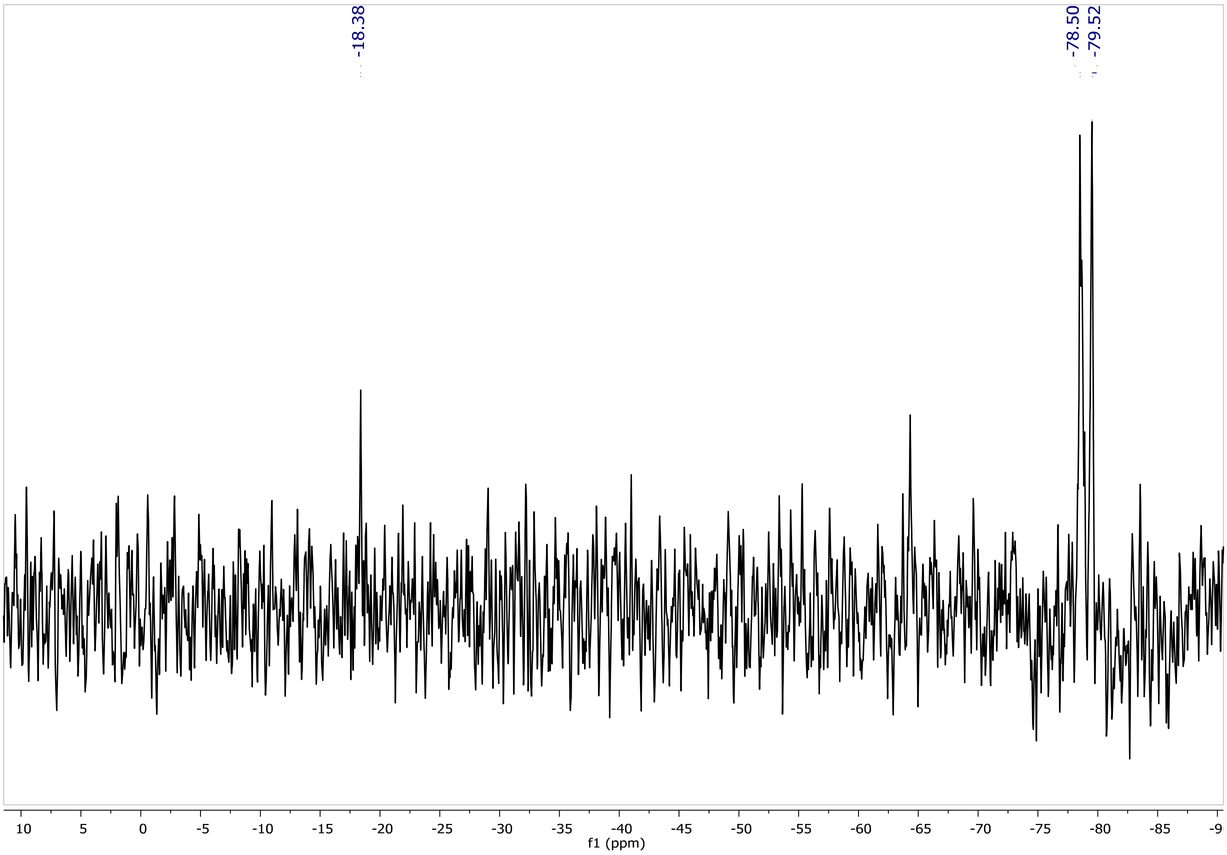
^{1}H NMR (CDCl$_3$, 400MHz):



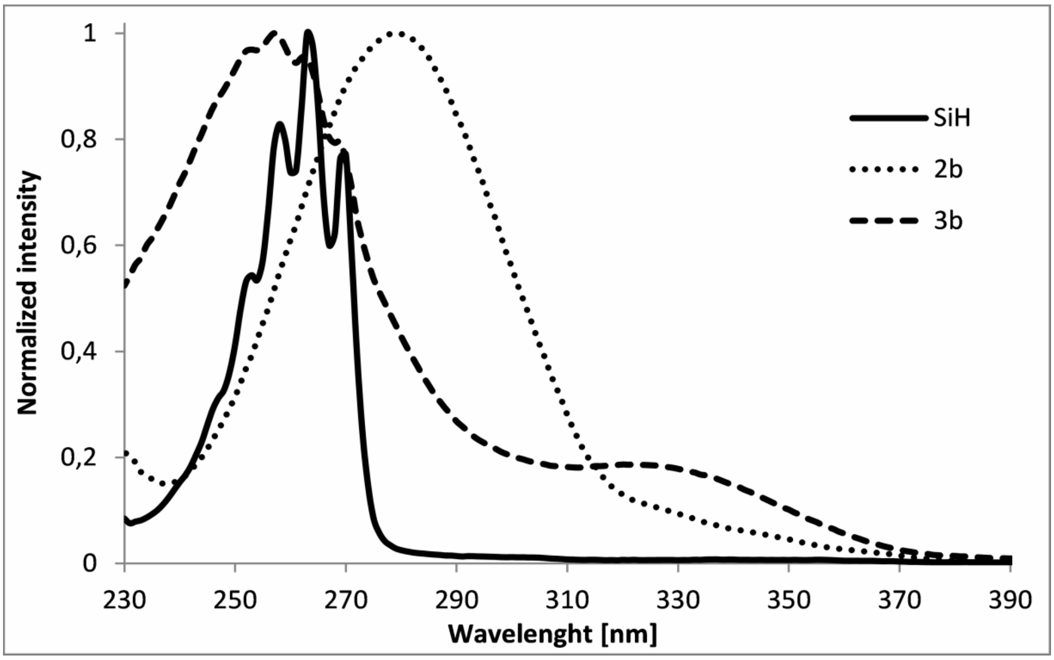
^{13}C NMR *(CDCl$_3$, 125 MHz):*



^{29}Si NMR *(CDCl$_3$, 99 MHz):*

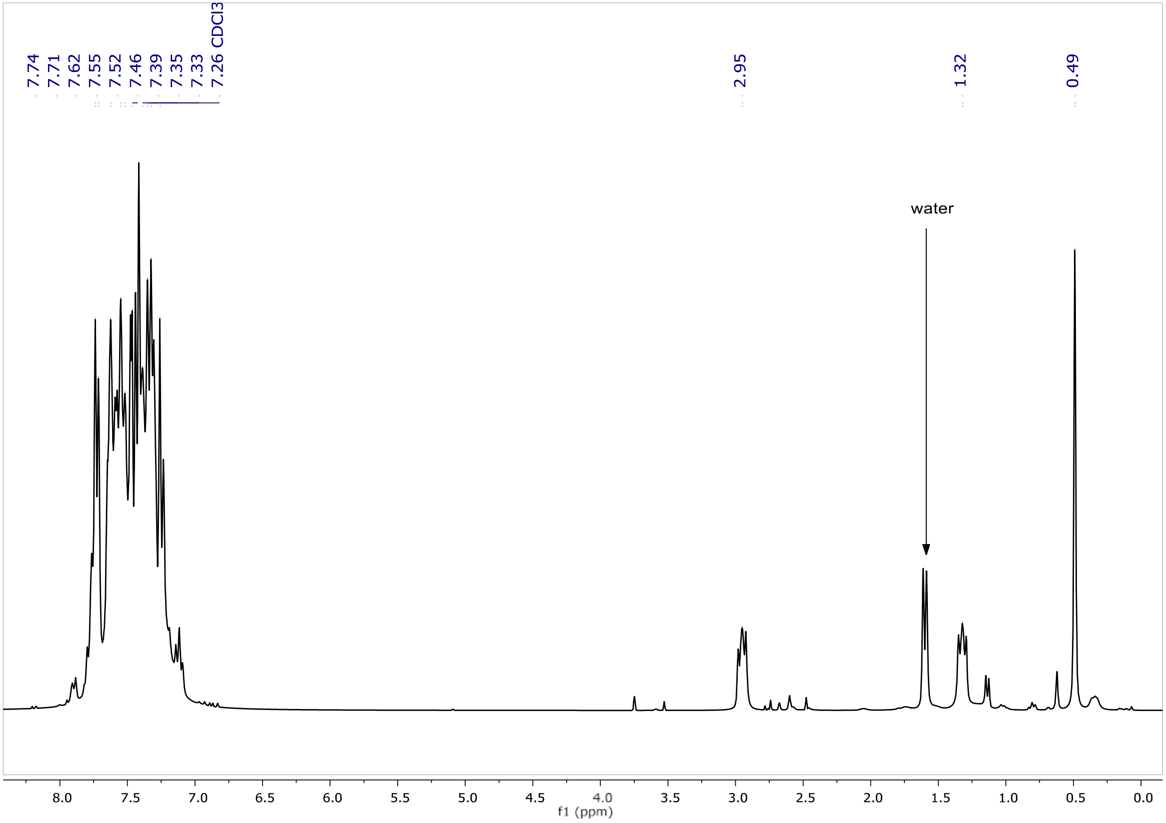


UV-visible absorption spectra of **1**, **2b** and **3b** product in $CHCl_3$ solution:

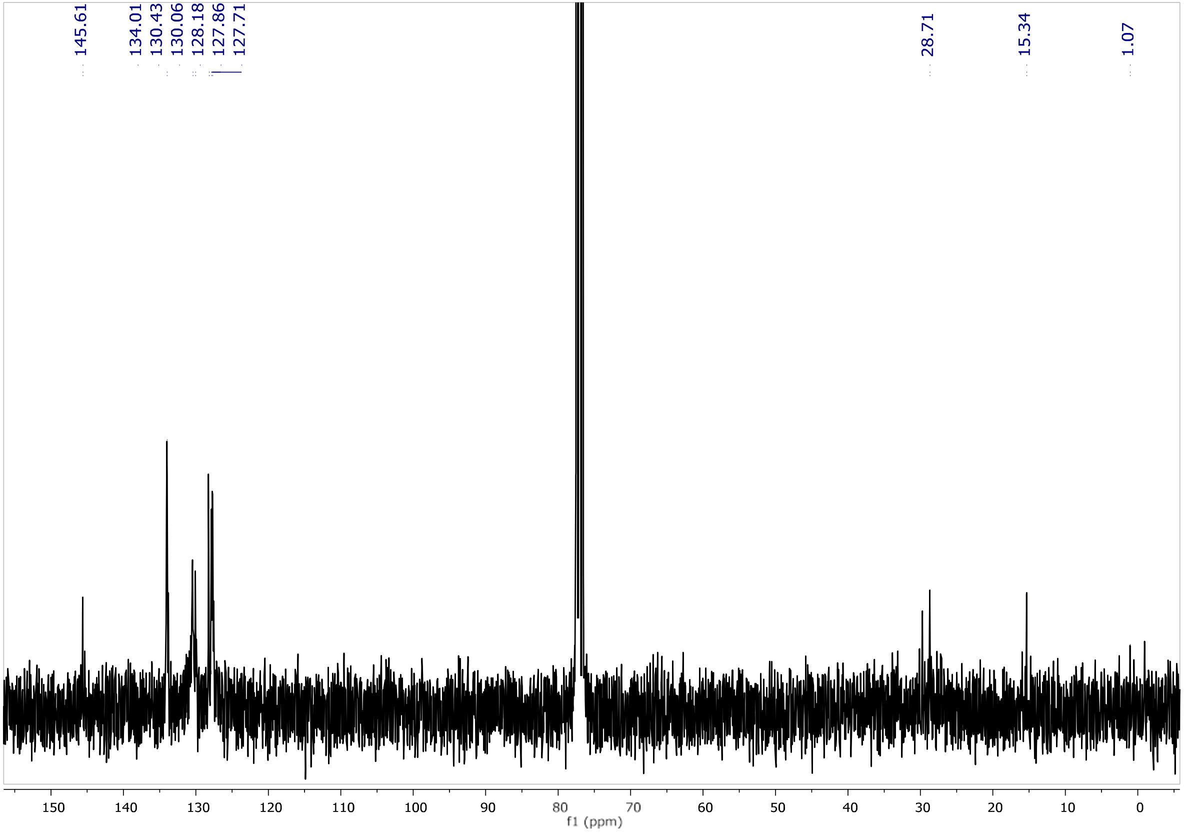


***cis*- and *trans*- mixture of di[9,19-(4-(9-anthracenyl)ethylbenzene)]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (3c)**.
M.p. = 211°C. FT-IR (cm^{-1}): 3074 (C-H$_{phenyl}$), 2962, 2927 (Si-CH$_3$), 2851; 1595, 1430 (C=C$_{phenyl}$), 1080, 1027 (Si-O), (Si-CH$_3$), 998 (C-H$_{phenyl}$), 798, 738 (Si-CH$_2$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.49 (s, 6H, Si-C$\underline{H_3}$), 1.32 (t, 2H, J_{HH} = 21 Hz, Si-C$\underline{H_2}$-), 2.95 (t, 2H, J_{HH} = 15 Hz, C$_{Ar}$ -C$\underline{H_2}$-), 6.99-8.00 (m, 66H, C$_{Ar}$-H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 1.07 (-CH$_3$), 15.34 (-CH$_2$-), 28.71 (-CH$_2$-), 127.71; 127.86; 128.18; 130.06; 130.43; 134.01; 145.61 (C$_{Ar}$). ^{29}Si NMR (CDCl$_3$, 99 MHz): δ -18.03, -78.52, -79.39, -79.48, -79.58. MALDI-ToF MS (m/z): 1751.2 [M + K]$^+$, calcd. for $C_{94}H_{80}KO_{14}Si_{10}$: 1751.2

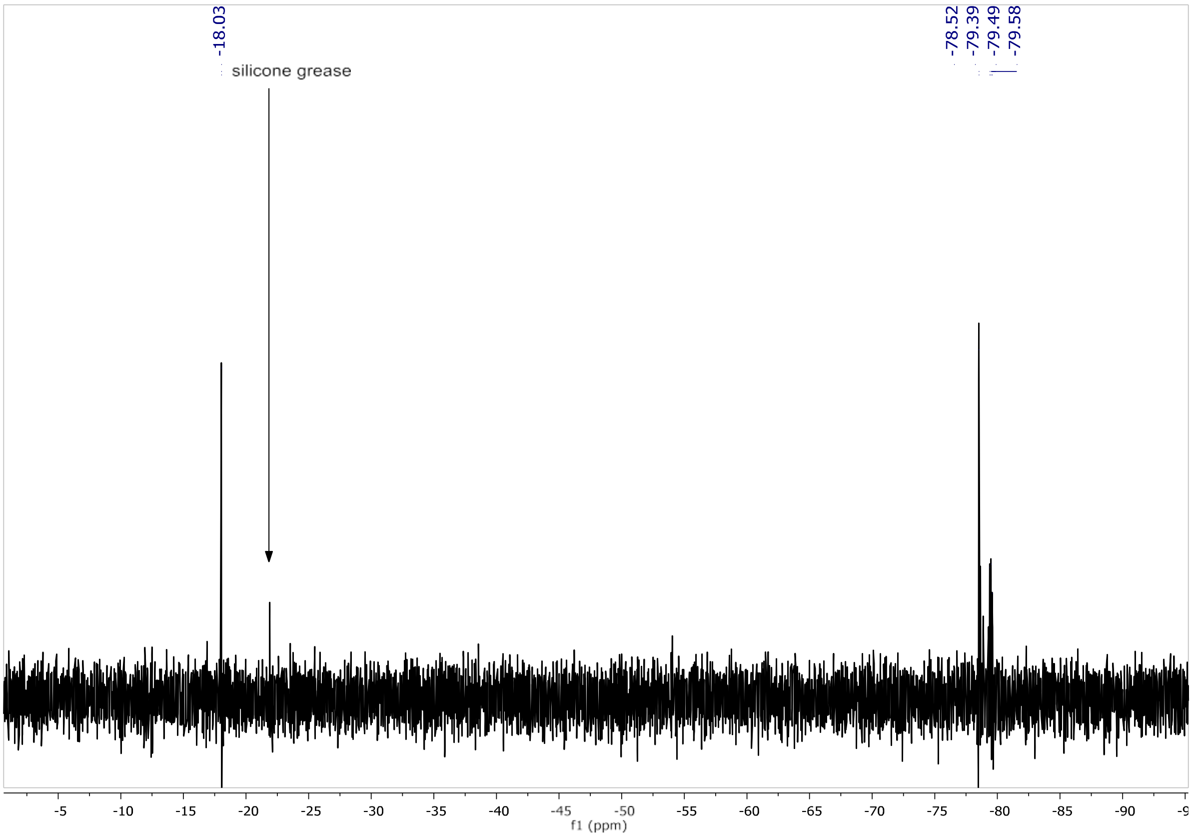
^{1}H NMR (CDCl$_3$, 400MHz):



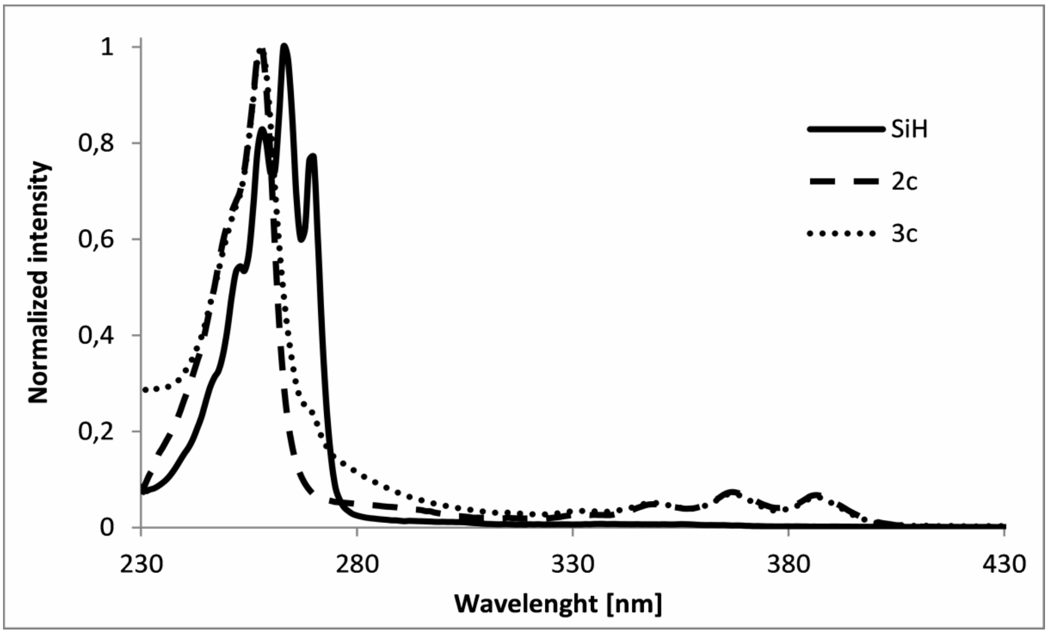
***^{13}C NMR** (CDCl$_3$, 125 MHz):*



***^{29}Si NMR** (CDCl$_3$, 99 MHz):*



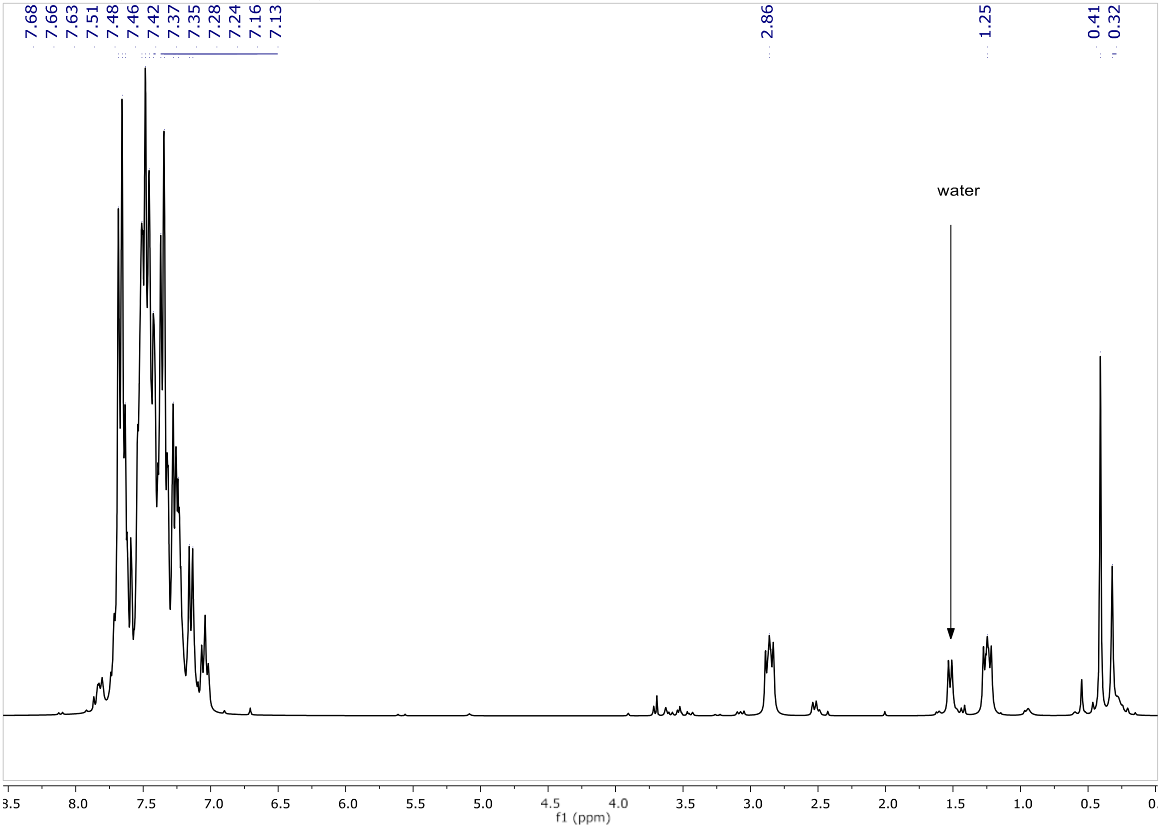
UV-visible absorption spectra of **1**, **2c** and **3c** product in CHCl$_3$ solution:


Normalized intensity
1
0,8
0,6
0,4
0,2
0
230
280
330
380
430
Wavelenght [nm]
SiH
2c
3c

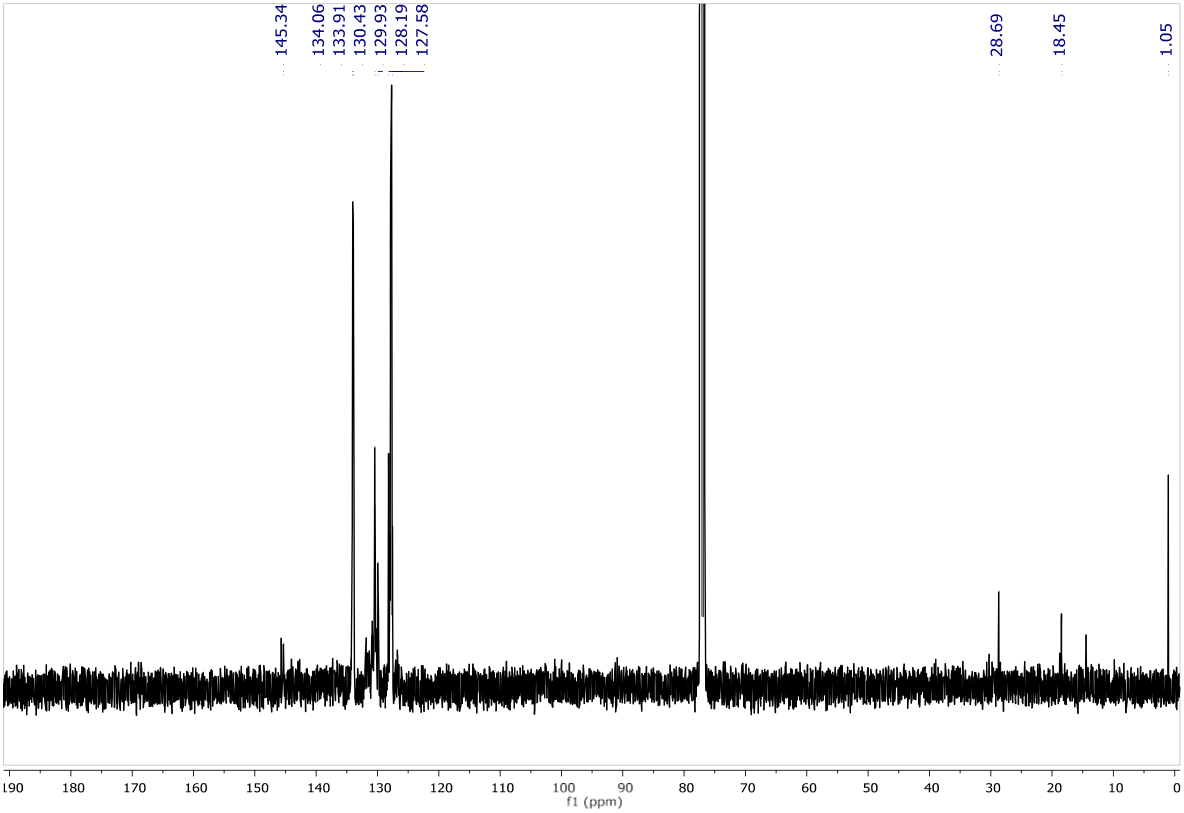
cis- and _trans_- mixture of di[9,19-(4-(2,3,4,5,6-penta-fluorophenyl)ethylbenzene)]-1,3,5,7,11,13,15,17-octaphenyl-penta-cyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane (3d).

M.p. = 203°C. FT-IR (cm^{-1}): 3073, 3051 (C-H$_{phenyl}$), 2960 (Si-CH$_3$), 1594, 1430 (C=C$_{phenyl}$), 1258 (Si-CH$_3$), 1050, 1030 (Si-O), 997 (C-H$_{phenyl}$) 795, (Si-CH$_2$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ0.32, 0.41 (s, 6H, Si-C$\underline{H_3}$), 1.25 (t, 2H, J_{HH} = 15 Hz, Si-C$\underline{H_2}$-), 2.86 (t, 2H, J_{HH} = 18 Hz, C$_{Ar}$ -C$\underline{H_2}$-), 7.13-7.68 (m, 48H, C$_{Ar}$-H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 1.05 (-CH$_3$), 18.47 (-CH$_2$-), 28.69 (-CH$_2$-), 127.58; 128.19; 129.93; 130.43; 133.91; 134.06; 145.34 (C$_{Ar}$). ^{29}Si NMR (CDCl$_3$, 99 MHz): δ -18.03, -78.52, -79.36, -79.44, -79.63. MALDI-ToF MS (m/z): 1716.1 [M + Na]$^+$, calcd. for $C_{78}H_{63}F_{10}NaO_{14}Si_{10}$: 1716.1

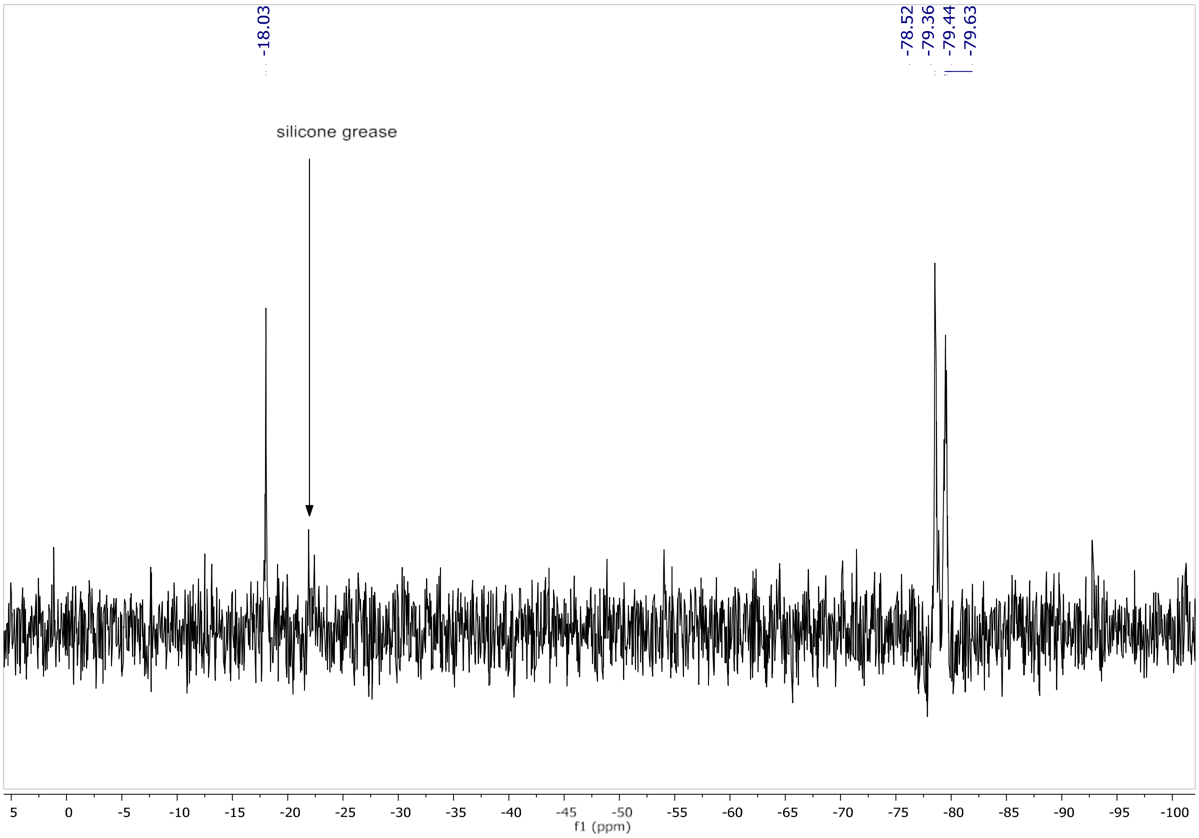
^{1}H NMR (CDCl$_3$, 400MHz):



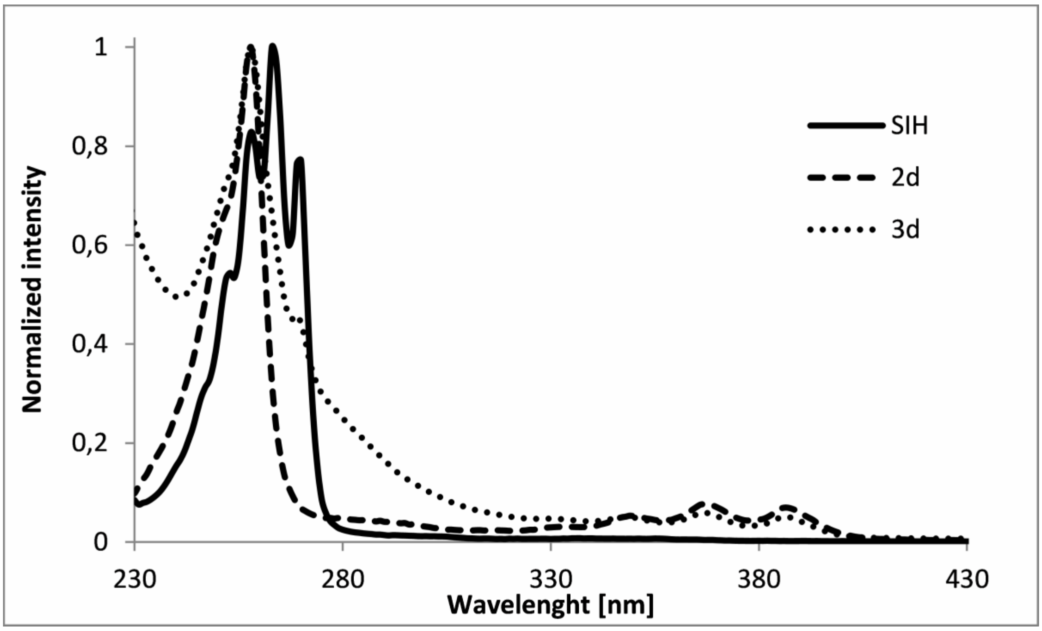
^{13}C NMR ($CDCl_3$, 125 MHz):



^{29}***Si NMR*** *($CDCl_3$, 99 MHz):*



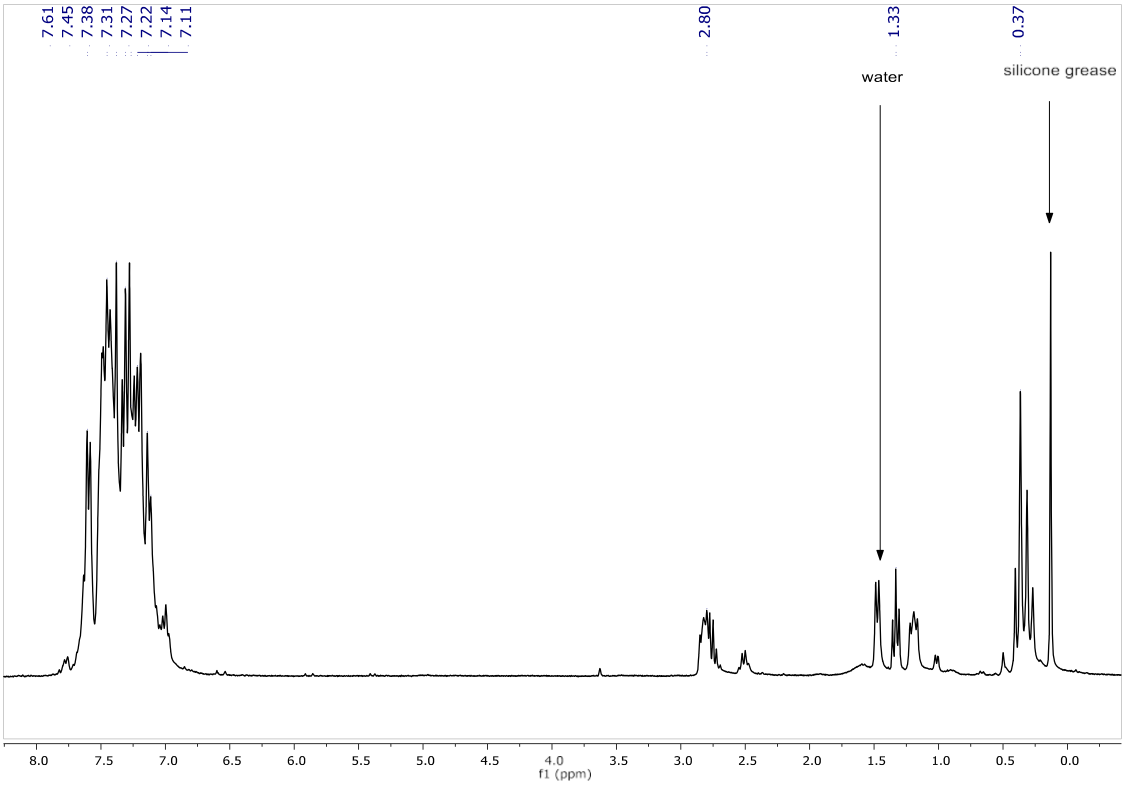
UV-visible absorption spectra of **1**, **2d** and **3d** product in $CHCl_3$ solution:



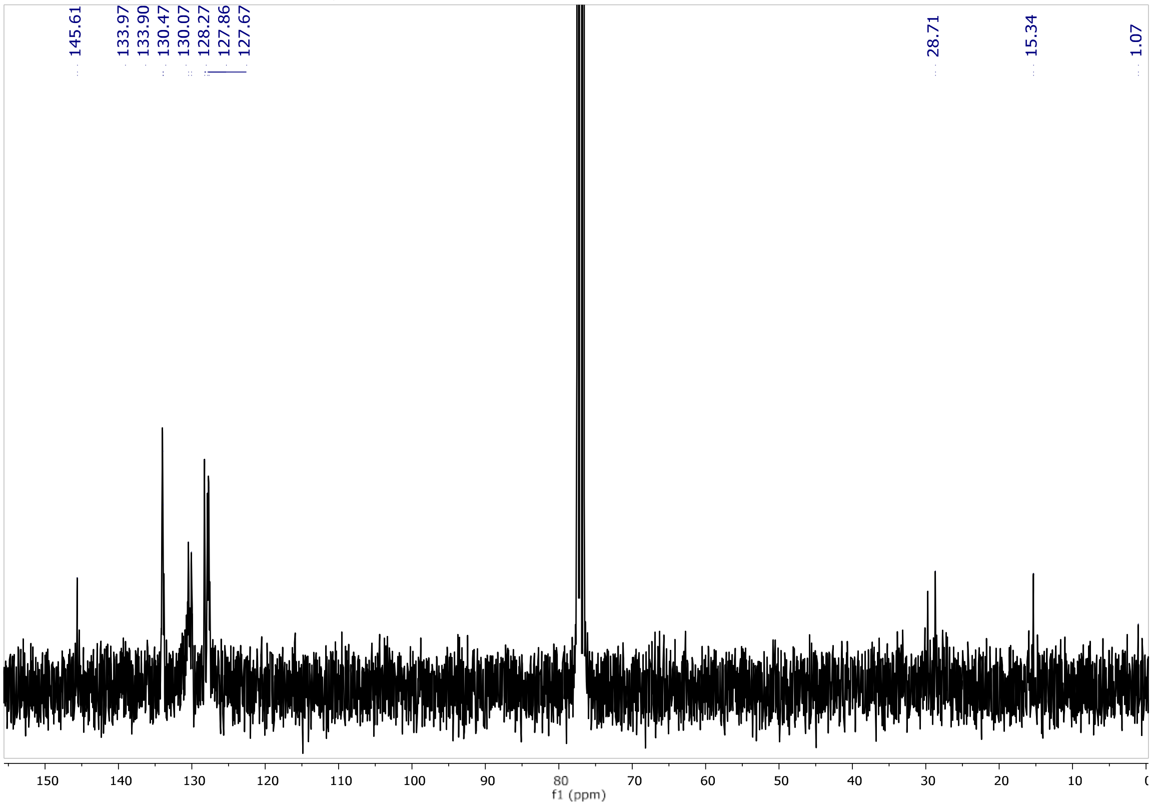
6. Spectroscopic analysis of obtained macromolecular (5a-d) products

oligo{[9,19-(4-phenylethylbenzene)]-1,3,5,7,11,13,15,17-octaphenylpentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane}s (5a).
M.p. = 247 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ0.27, 0.32. 0.37, 0.40 (s, Si-C$\underline{H}_3$), 1.19 (m, Si-C$\underline{H}_2$-), 2.82 (m, C$_{Ar}$ -C$\underline{H}_2$-), 7.11-7.61 (m, C$_{Ar}$-H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 1.07 (-CH$_3$), 15.34 (-CH$_2$), 28.71 (-CH$_2$-), 127.67, 127.86, 128.27, 130.07, 130.47, 133.90, 133.97, 145.61, (C$_{Ar}$). ^{29}Si NMR (CDCl$_3$, 99 MHz): δ -18.39, -78.50, -79.54

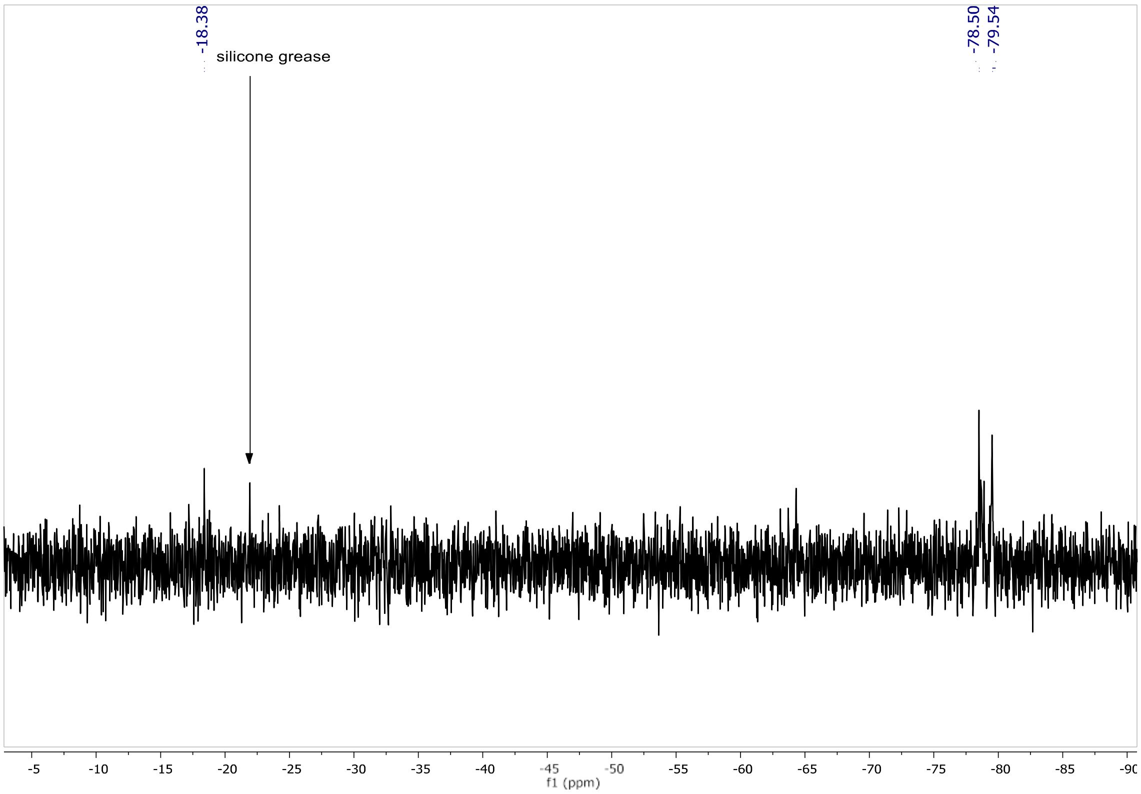
^{1}H NMR (CDCl$_3$, 400MHz):



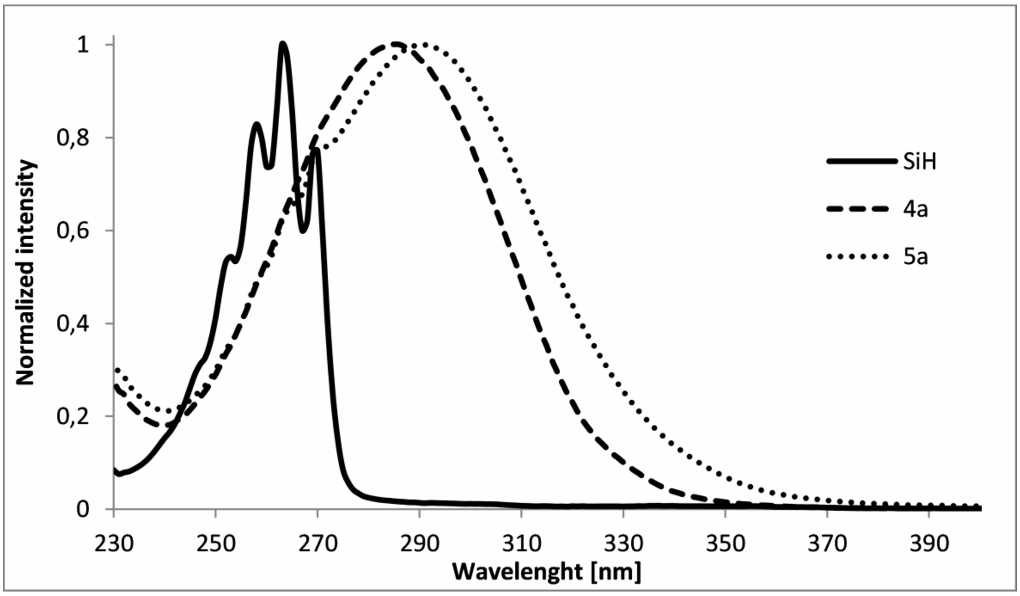
^{13}C NMR (CDCl$_3$, 125 MHz):



^{29}Si NMR (CDCl$_3$, 99 MHz):



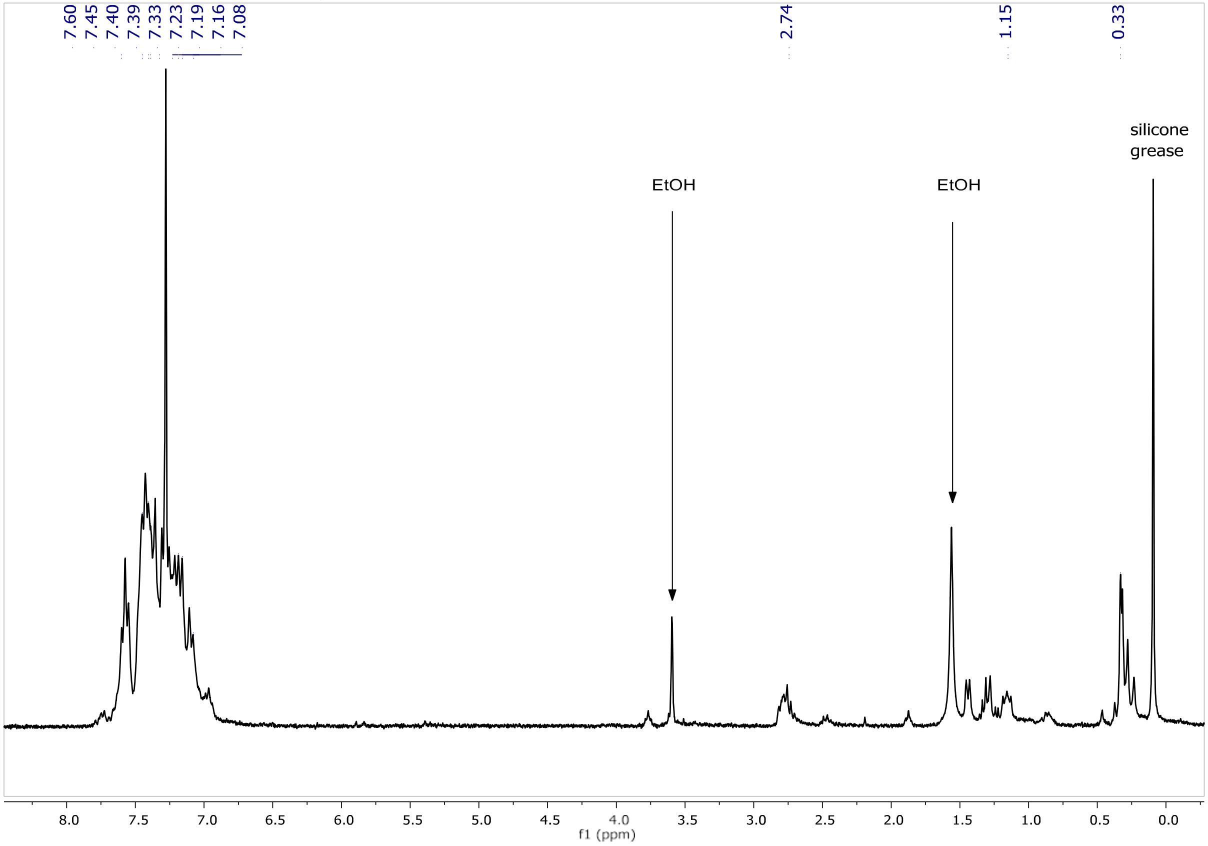
UV-visible absorption spectra of **1**, **4a** and **5a** product in $CHCl_3$ solution:



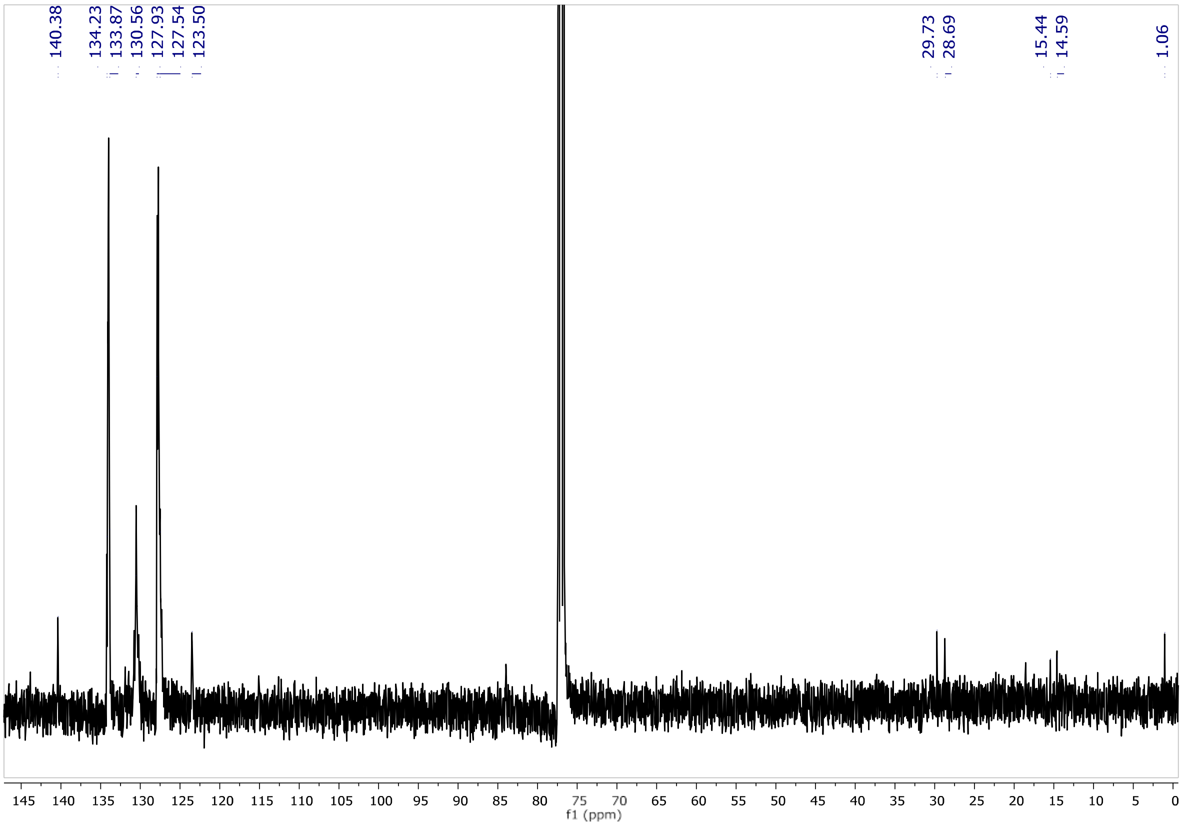
oligo{[9,19-(4-(1-naphthyl)ethylbenzene)]-1,3,5,7,11,13,15,17-octaphenylpentacyclo[11.7.1.$1^{3,11}$.$1^{5,17}$.$1^{7,15}$]decasiloxane}s (5b).

M.p. = 254 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ0.23, 0.28 (s, Si-C$\underline{H_3}$), 1.15 (m, Si-C$\underline{H_2}$-), 2.76 (m, C$_{Ar}$ -C$\underline{H_2}$-), 7.08-7.60 (m, C$_{Ar}$-H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 1.06 (-CH$_3$), 14.59, 15.44 (-CH$_2$-), 28.69, 29.73 (-CH$_2$-), 123.50, 127.54, 127.93, 130.56, 133.87, 134.23, 140.38, (C$_{Ar}$). ^{29}Si NMR (CDCl$_3$, 99 MHz): δ -18.12, -78.47, -79.46

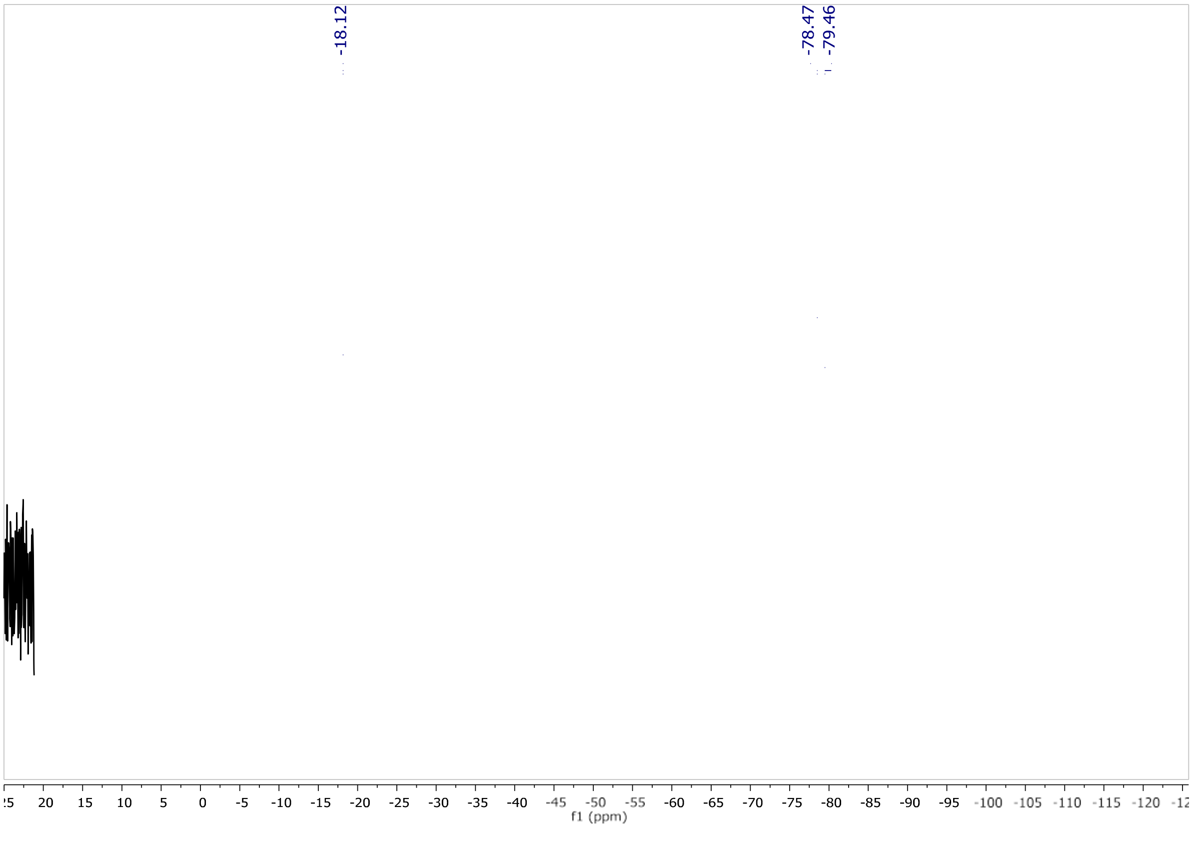
^{1}H NMR (CDCl$_3$, 400MHz):



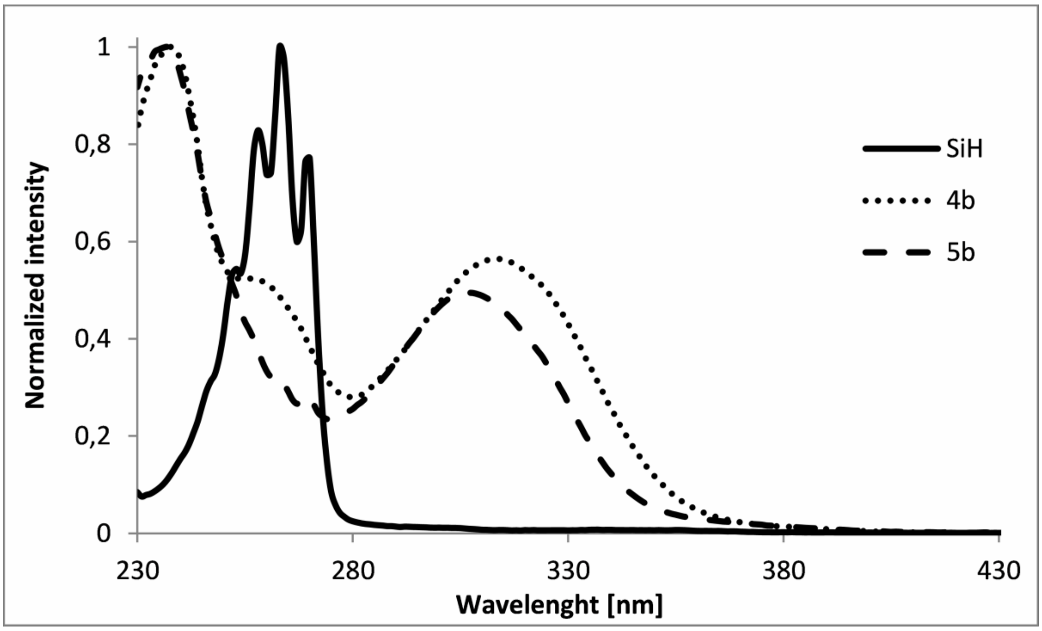
^{13}C NMR ($CDCl_3$, 125 MHz):



^{29}Si NMR ($CDCl_3$, 99 MHz):



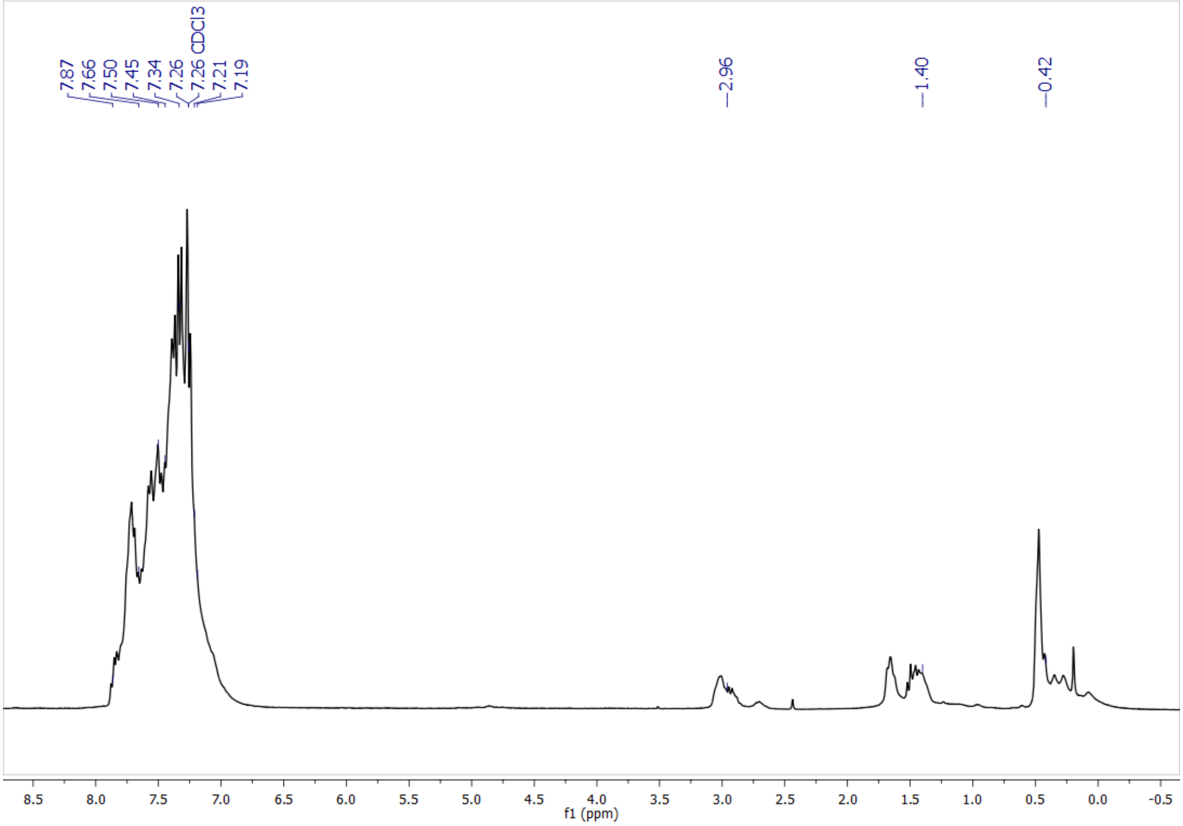
UV-visible absorption spectra of **1**, **4b** and **5b** product in $CHCl_3$ solution:



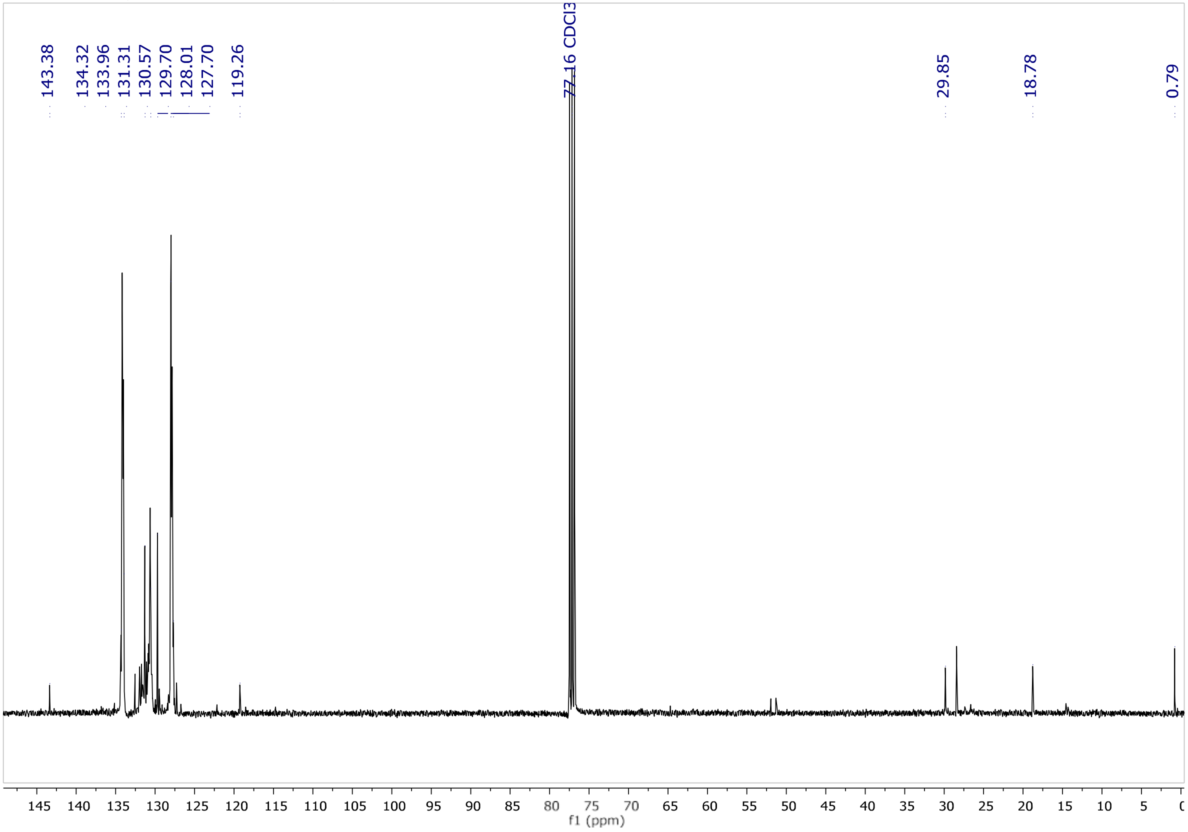
oligo{[9,19-(4-(9-anthracenyl)ethylbenzene)]-1,3,5,7,11,13,-15,17-octaphenylpentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]-decasiloxane}s (5c).

M.p. = 340 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.07, 0.32. 0.37, 0.40 (s, Si-C$\underline{H}_3$), 1.19 (m, Si-C$\underline{H}_2$-), 2.82 (m, C$_{Ar}$ -C$\underline{H}_2$-), 7.11-7.61 (m, C$_{Ar}$-H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 0.79 (-CH$_3$), 18.78 (-CH$_2$), 29.85 (-CH$_2$-), 123.49, 127.73, 127.87, 130.19, 130.50, 130.81, 133.98, 140.39 (C$_{Ar}$). ^{29}Si NMR (CDCl$_3$, 99 MHz): δ -18.32, -78.47, -79.39.

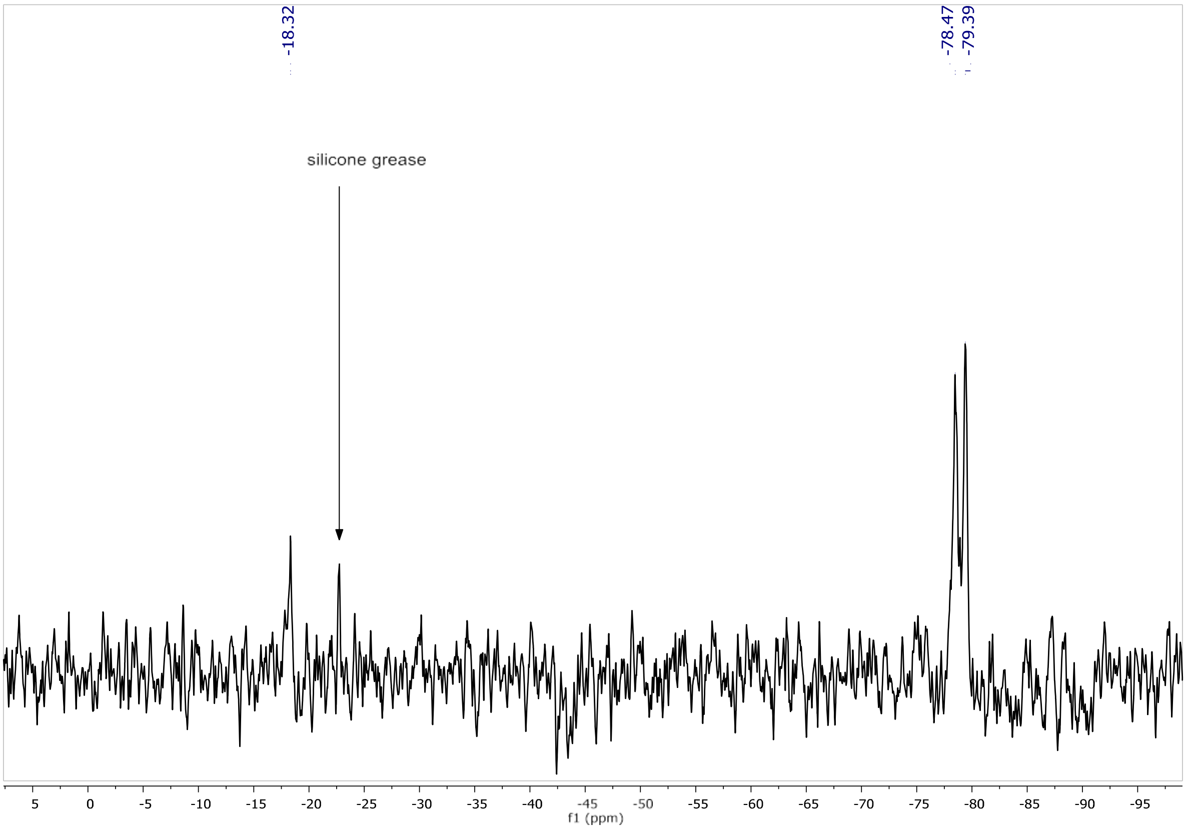
^{1}H NMR (CDCl$_3$, 400MHz):



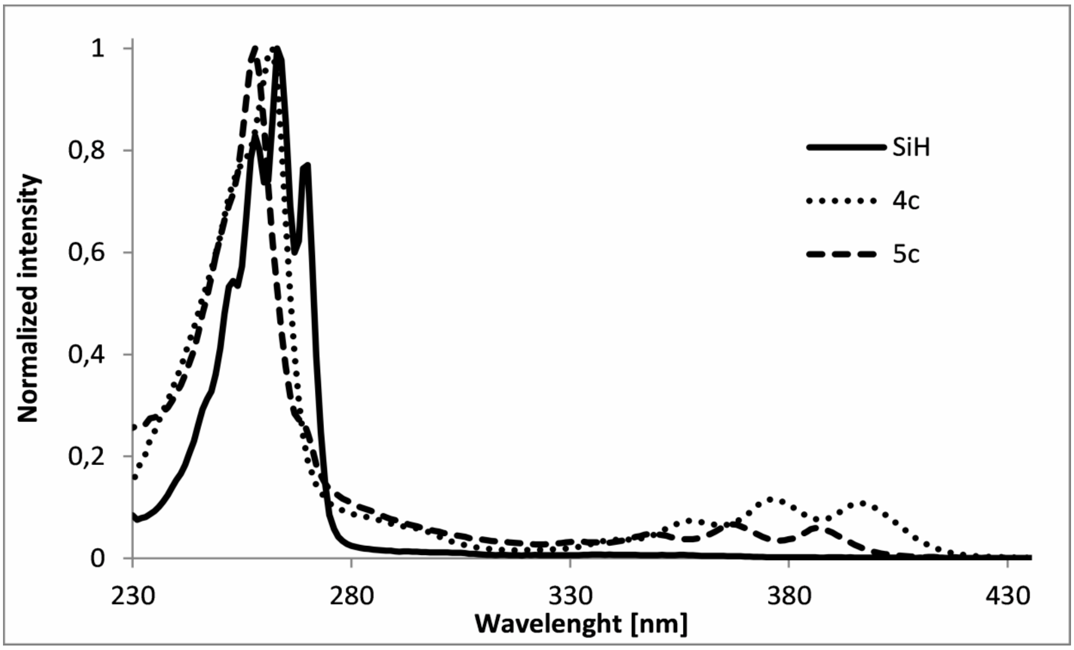
^{13}***C NMR (CDCl$_3$, 125 MHz):***



^{29}***Si NMR (CDCl$_3$, 99 MHz):***



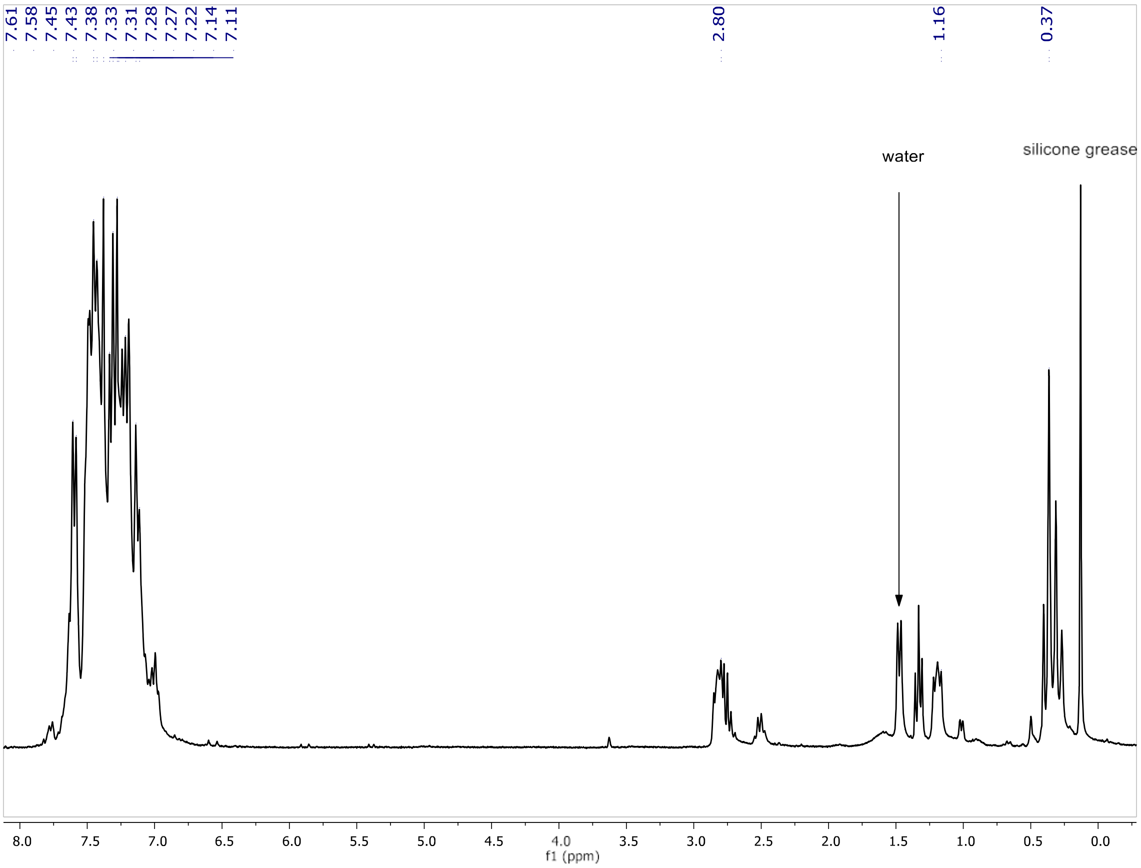
UV-visible absorption spectra of **1**, **4c** and **5c** product in $CHCl_3$ solution:



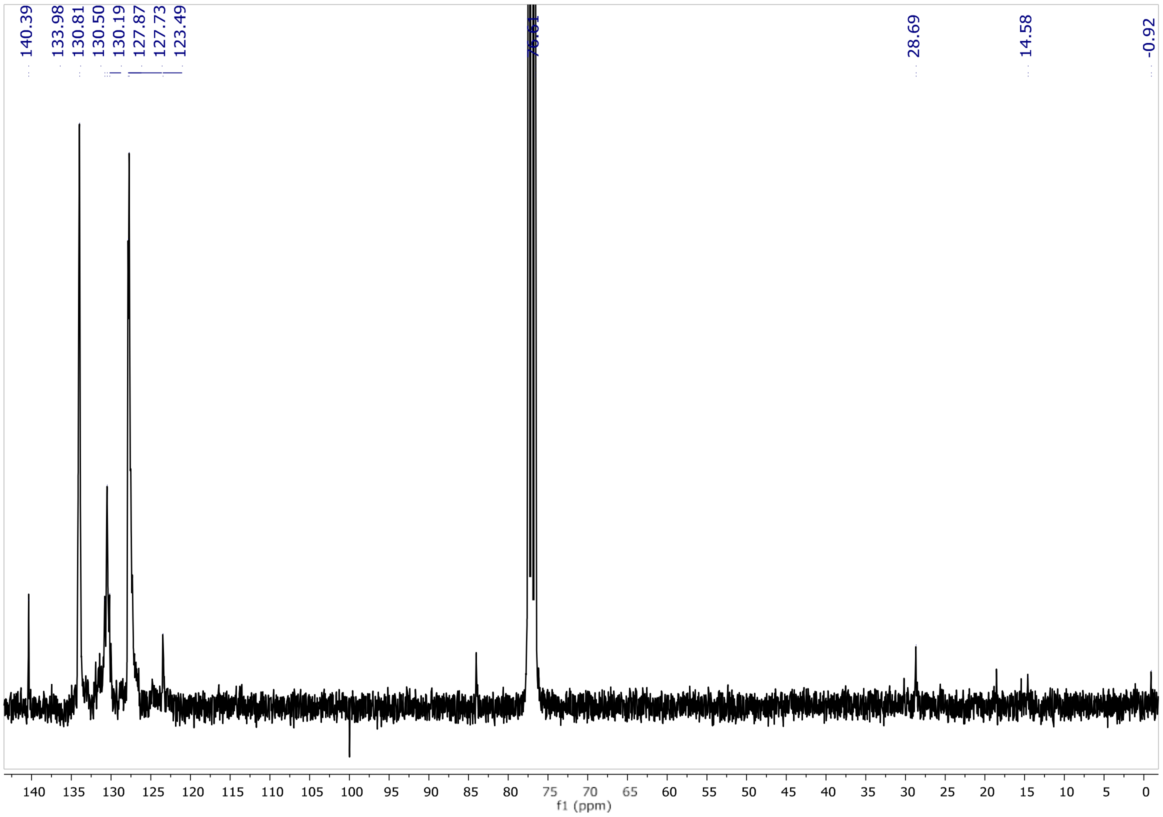
poly{[9,19-(4-(2,3,4,5,6-penta-fluorophenyl)ethylbenzene)]-1,3,5,7,11,13,15,17-octaphenylpentacyclo-[11.7.1.1^{3,11}.1^{5,17}.1^{7,15}]decasiloxane}s (5d).

M.p. = 254 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.27, 0.31. 0.37, 0.40 (s, Si-C$\underline{H}_3$), 1.19 (m, Si-C$\underline{H}_2$-), 2.82 (m, C$_{Ar}$ -C$\underline{H}_2$-), 6.90-7.79 (m, C$_{Ar}$-H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 0.92 (-CH$_3$), 14.58 (-CH$_2$-), 28.69 (-CH$_2$-), 123.49, 127.73, 127.87, 130.19, 130.50, 130.81, 133.98, 140.39, (C$_{Ar}$). ^{29}Si NMR (CDCl$_3$, 99 MHz): δ -18.32, -78.45, -79.46

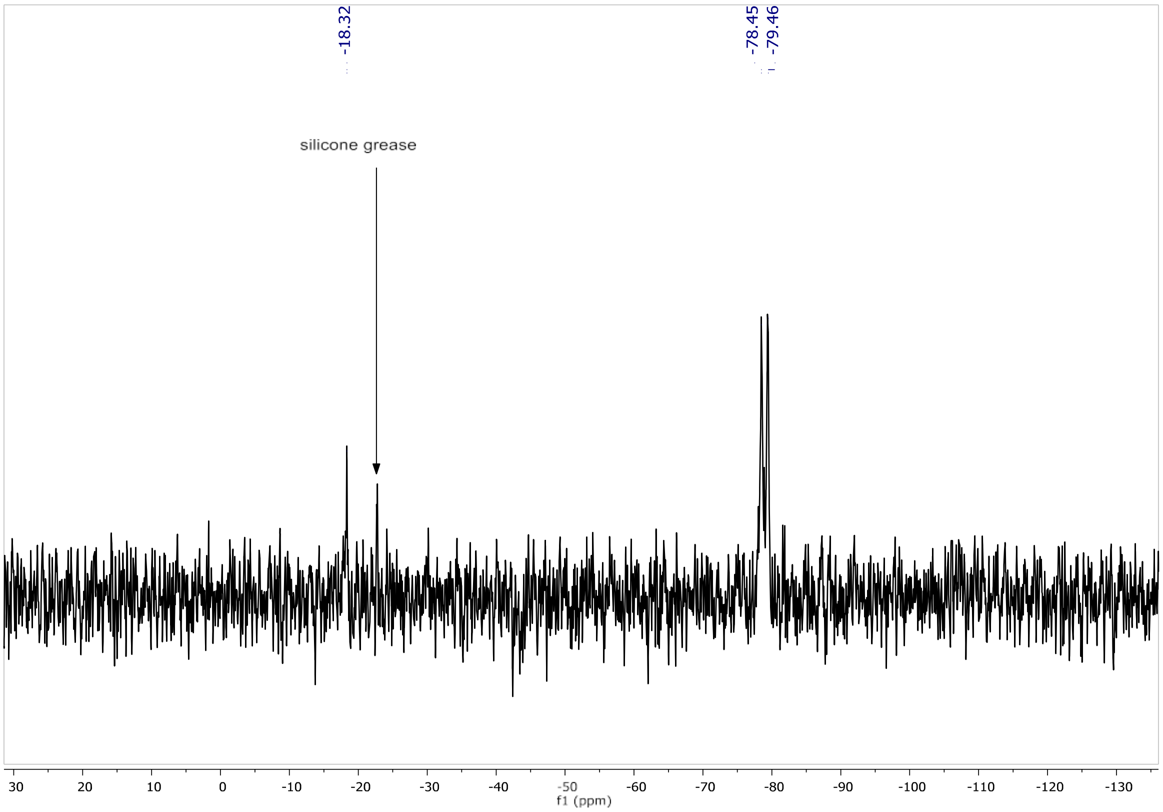
^{1}H NMR (CDCl$_3$, 400MHz):



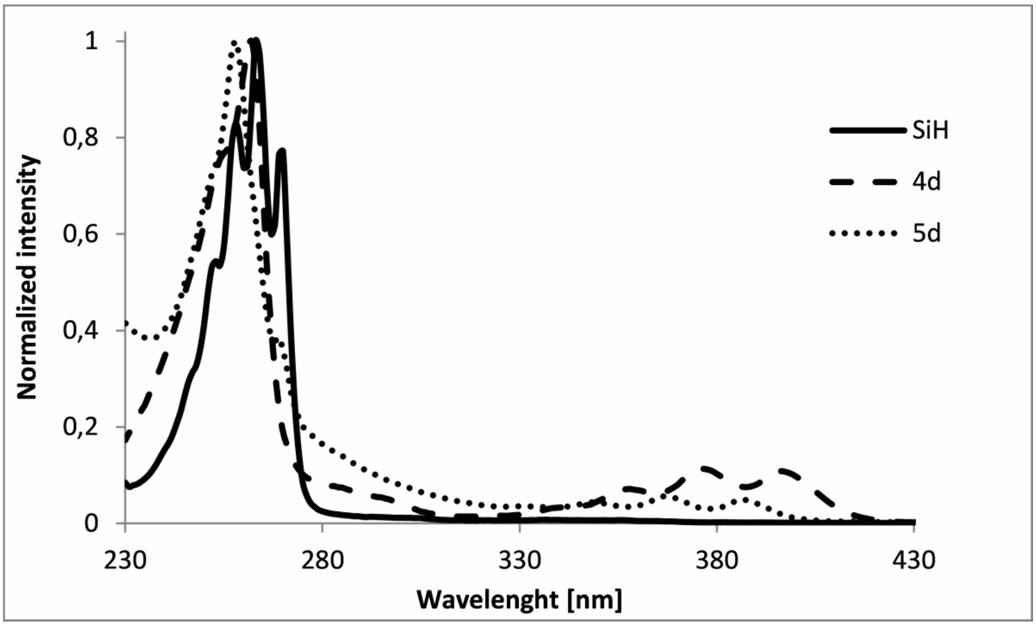
^{13}C NMR (CDCl$_3$, 125 MHz):



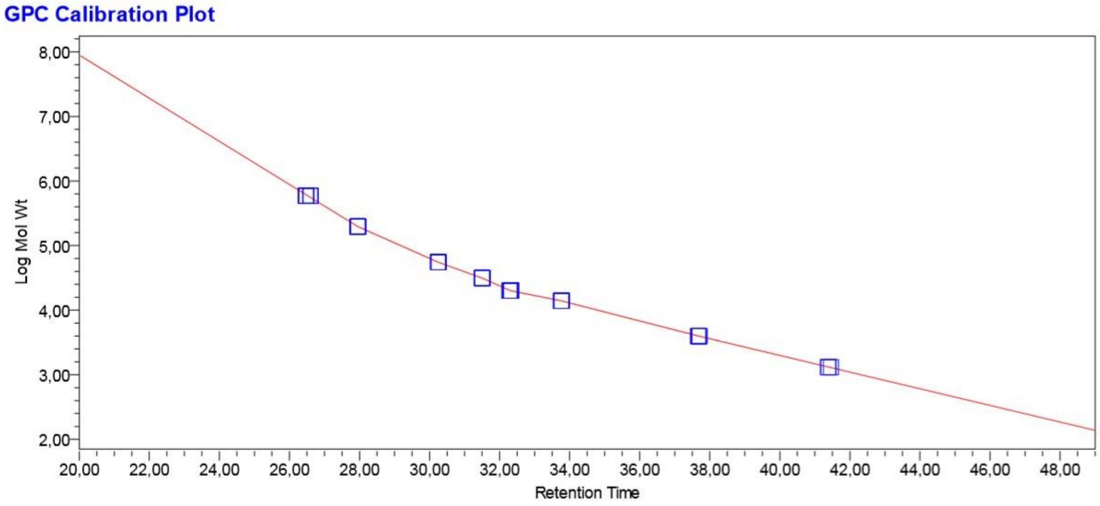
^{29}Si NMR (CDCl$_3$, 99 MHz):



UV-visible absorption spectra of **1**, **4d** and **5d** product in $CHCl_3$ solution:



7. GPC Calibration Curve



8. References

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