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Synthesis and optical properties of highly luminescent phenyloxazole silane polymer

Maxim S. Skorotetcky, Nikolay M. Surin, Oleg V. Borshchev and Sergei A. Ponomarenko

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1. Synthesis of polymer 8 and its precursors

1.1. Materials

Hexane solutions of 2.5 and 1.6 *M n*-butyllithium, 1,4-dibromobenzene and 2,2-dimethyl-1,3-propanediol were obtained from Acros organics; tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$, *p*-toluenesulfonic acid monohydrate (TsOH), lithium *tert*-butoxide, *p*-tolylsulfonylmethyl isocyanide (TosMIC), and THF (spectroscopic grade) were obtained from Sigma–Aldrich and used as received. Solvents THF, DMF, 1,4-dioxane and benzene were dried and purified according to the standard procedures. The solvents were removed under vacuum (1 mbar) at 40 °C. All reactions, unless otherwise stated, were carried out in an inert atmosphere using anhydrous solvents.

1.2. Characterization techniques

The ^1H NMR spectra were recorded on a Bruker WP250 SY spectrometer (250.13 MHz) using the residual signal of $CDCl_3$ (δ 7.27 ppm) as the internal standard. The ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker Avance II 300 spectrometer at working frequencies 75 MHz and 60 MHz, respectively. In the case of ^1H NMR spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in $CDCl_3$. In the case of ^{13}C or ^{29}Si NMR spectroscopy, the compounds to be analyzed were taken in the form of 3-5% solutions in $CDCl_3$. The spectra were then processed on the computer using the ACD Labs v.10.04 software.

Elemental analysis of C, H, N elements was carried out using CHN automatic analyzer CE1106 (Italy). Experimental error is 0.30−0.50 %. The burning was done in the Sheninger flask using alkaline solution of hydrogen peroxide as an absorbent. Spectrophotometry technique was used for the Si analysis as described elsewhere (ISO 6382:1981) [1].

GPC analysis was performed on a Shimadzu instrument with a $RID10A^{VP}$ refractometer and a $SPD\text{-}M10A^{VP}$ diode matrix as detectors using $7.8 \times 300\ mm^2$ Phenomenex columns (USA) filled with the Phenogel sorbent with pore size of 500 Å and THF as the eluent. In the case of column chromatography, silica gel 60 (“Merck”) was taken. For thin layer chromatography, “Sorbfil” (Russia) plates were used.

Light scattering experiments were performed on Shimadzu HPLC System, equipped with $DGU20A_3$ degasser unit, LC-20AD pump, CTO-20A column oven with a Phenomenex column (USA) with a size of $7.8\times300\ mm^2$ filled with the Phenogel sorbent with a pour size of 10^5 Å, RID-10A refractometer, Viscotek 270 Dual detector (RALS and LALS) and Omnisec 4.5 Software. The sample loop was 100 μL, angle RALS was 90°, angle LALS was 7°. The system was calibrated using polystyrene standards with $M_w = 1.0\times10^4$ and $M_w = 1.27\times10^5$, dn/dc = 0.185 (Polymer Laboratories). The molar weights of the standards were chosen in the range of

M_w of the samples under investigation for better accuracy of the measurements. Using the exact concentrations of the samples, close to 5.00 mg/mL, the values of dn/dc were determined from RI data. Then this value was used by Omnisec 4.5 software to calculate the M_w from the light scattering (RALS and LALS) data.

Thermogravimetric analysis was carried out in dynamic mode in 30 ÷ 900°C interval using Mettler Toledo TG50 system equipped with M3 microbalance allowing measuring the weight of samples in 1 - 150 mg range with 1 μg precision. Heating/cooling rate was chosen to be 10 deg min^{-1}. Every compound was studied twice: in air and in nitrogen flow of 200 ml min^{-1}. DSC scans were obtained with Mettler Toledo DSC30 system with 20 deg min^{-1} heating/cooling rate in temperature range of 20 - 290 °C. Nitrogen flow of 50 ml min^{-1} was used.

The absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer in the standard 10 mm photometric quartz cuvette using THF solution with concentrations of 10^{-5} M. A scanning spectrofluorimeter ALS01M with registration in single photon counting mode at successive time intervals and automatic adjustment of the intensity of measured emission was used for the measurements of luminescence spectra. Spectral correction of the fluorescence and excitation spectra were performed automatically. The source of light was a high-pressure arc xenon lamp. The spectral width of the slit of the excitatory monochromator was 3 nm, the luminescence detection monochromator was 3 nm. The fluorescence quantum yield was measured by comparing the intensity of dilute (10^{-6} *M*) solutions of luminophores in THF with the fluorescence intensity of POPOP dye in cyclohexane [2]. Thin films of the polymer fractions were prepared by spin coating technique from THF solution (10 g L^{-1}).

1.3. Synthesis of phenyloxazoles

Tetrakis(4-bromophenyl)silane (1). This compound was obtained by the method described previously [3] using 1,4-dibromobenzene (36.18 g, 153.4 mmol, 4 equiv.), 2,5 *M* solution of *n*-butyllithium in hexane (60 ml, 150 mmol, 3.92 equiv.) and teterachlorosilane (4.3 ml, 37.6 mmol, 0.98 equiv.). The yield of compound **1** was 90 % (22.51 g). Purity was estimated as 97% according to GPC analysis. The product was used in the subsequent synthesis without further purification. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.36 (d, 8 H, J =8.6 Hz), 7.54 (d, 8 H, J =8.6 Hz).

4,4'-[Bis(4-bromphenyl)silanediyl]dibenzaldehyde (2). A solution of *n*-butyllithium in hexane (1.6 *M*, 33 ml, 52.5 mmol, 2.1 equiv.) was added dropwise to a solution of compound **1** (16.30 g, 25.0 mmol, 1 equiv.) in THF (350 mL) cooled to -78 °C. The reaction mixture was stirred for 60 min at -78 °C, and then *N*,*N*-dimethylformamide (3 mL) was added in one portion. The mixture was stirred for additional 15 min at -78 °C and then the cooling bath was removed. After completion of the reaction, 1 *M* HCl was added to the reaction mixture (until acidic pH value) followed by the addition of diethyl ether (500mL) and water (500 mL). The organic phase was separated, washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure (10 mbar). The crude product was purified by column chromatography on silica gel using toluene as the eluent. Yield: 58% (7.96 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.38 (d, 4 H, J =8.2 Hz), 7.56 (d, 4 H, J =8.6 Hz), 7.67 (d, 4 H, J =8.2 Hz), 7.89 (d, 4 H, J =8.2 Hz), 10.07 (s, 2 H).

Bis(4-bromophenyl){bis[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]}silane (3). A solution of compound **2** (5 g, 9.1 mmol, 1 equiv.), 2,2-dimethyl-1,3-propanediol (7.54 g, 72.7 mmol, 8 equiv.) and *p*-toluenesulfonic acid (0.34 g, 1.8 mmol, 0.2 equiv) in benzene (150 mL) was stirred at reflux with Dean–Stark trap. After completion of the reaction, trimethylamine (1 mL), diethyl ether (250 mL) and water (200 mL) were added. The organic phase was separated, washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure (10 mbar) to leave the crude product as a colorless solid. It was used in the subsequent reactions without further purification. Yield: 98 % (6.42 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.82 (s, 6 H), 1.31 (s, 6 H), 3.67 (d, 4 H, J= 11.29 Hz), 3.79 (d, 4 H, J= 11.29 Hz), 5.42 (s, 2 H), 7.35 (d, 4 H, J =7.9 Hz), 7.47-7.55 (overlapping peaks, 11 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.85; 23.01; 30.23; 77.68; 101.51; 124.96; 125.80; 131.15; 132.45; 133.67; 136.31; 137.77; 140.14. ^{29}Si NMR (60 MHz, $CDCl_3$): δ = -14.04. Found for **3** (%): C, 60.18; H, 5.44; Br, 21.73; Si, 3.64; calcd (%) for $C_{36}H_{38}Br_2O_4Si$: C, 59.84; H, 5.30; Br, 22.12; Si, 3.89.

5-[4-(2-Ethylhexyl)phenyl]-1,3-oxazole (4). *Step 1.* 4-(2-Ethylhexyl)-benzaldehyde was obtained by the method described above for compound **2** from 1-bromo-4-(2-ethylhexyl)benzene (25.50 g, 94.7 mmol, 1 equiv.), 2.5 *M* solution of *n*-butyllithium in hexane (40 ml, 99.5 mmol, 1.05 equiv.) and *N*,*N*-dimethylformamide (9 mL, 0.12 mol, 1.23 equiv). The crude product was distilled in vacuum, yield: 15.28 g (74%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (m, 6 H), 1.27 (m, 8 H), 1.62 (m, 1 H), 2.62 (d, 2 H, J =7.3 Hz), 7.32 (d, 2 H, J =8.2 Hz), 7.80 (d, 2 H, J =7.9 Hz), 9.98 (s, 1 H).

Step 2. A solution of the above aldehyde (20.5 g, 94.0 mmol, 1 equiv.), *p*-tolylsulfonylmethyl isocyanide (19.27 g, 98.7 mmol, 1.05 equiv.) and anhydrous potassium carbonate (25.99 g, 0.188 mmol, 2 equiv.) in methanol (250 mL) was stirred at reflux for 1.5 hours. After completion of the reaction, diethyl ether (400 mL) and water (350 mL) were added. The organic phase was separated, washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure (10 mbar). The product was purified by column chromatography on silica gel (eluent toluene) to give the pure compound **4** as a colorless solid (19.03 g, 79.7%). ^{1}H NMR (250 MHz, $CDCl_3$): δ =0.89 (t, 6 H, J =7.3 Hz), 1.28 (m, 8 H), 1.61 (m, 1 H), 2.56 (d, 2 H, J=7.0 Hz), 7.22 (d, 2 H, J =8.6 Hz), 7.32 (s, 1 H), 7.57 (d, 2 H, J =8.2 Hz), 7.91 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.74, 14.10, 22.98, 25.36, 28.77, 32.25, 39.89, 41.02, 120.80, 124.17, 125.13, 129.69, 142.75, 150.10, 151.75. Found for **4** (%): C, 79.51; H, 9.15; N, 5.29; calcd (%) for $C_{17}H_{23}NO$: C, 79.33; H, 9.01; N, 5.44; O, 6.22.

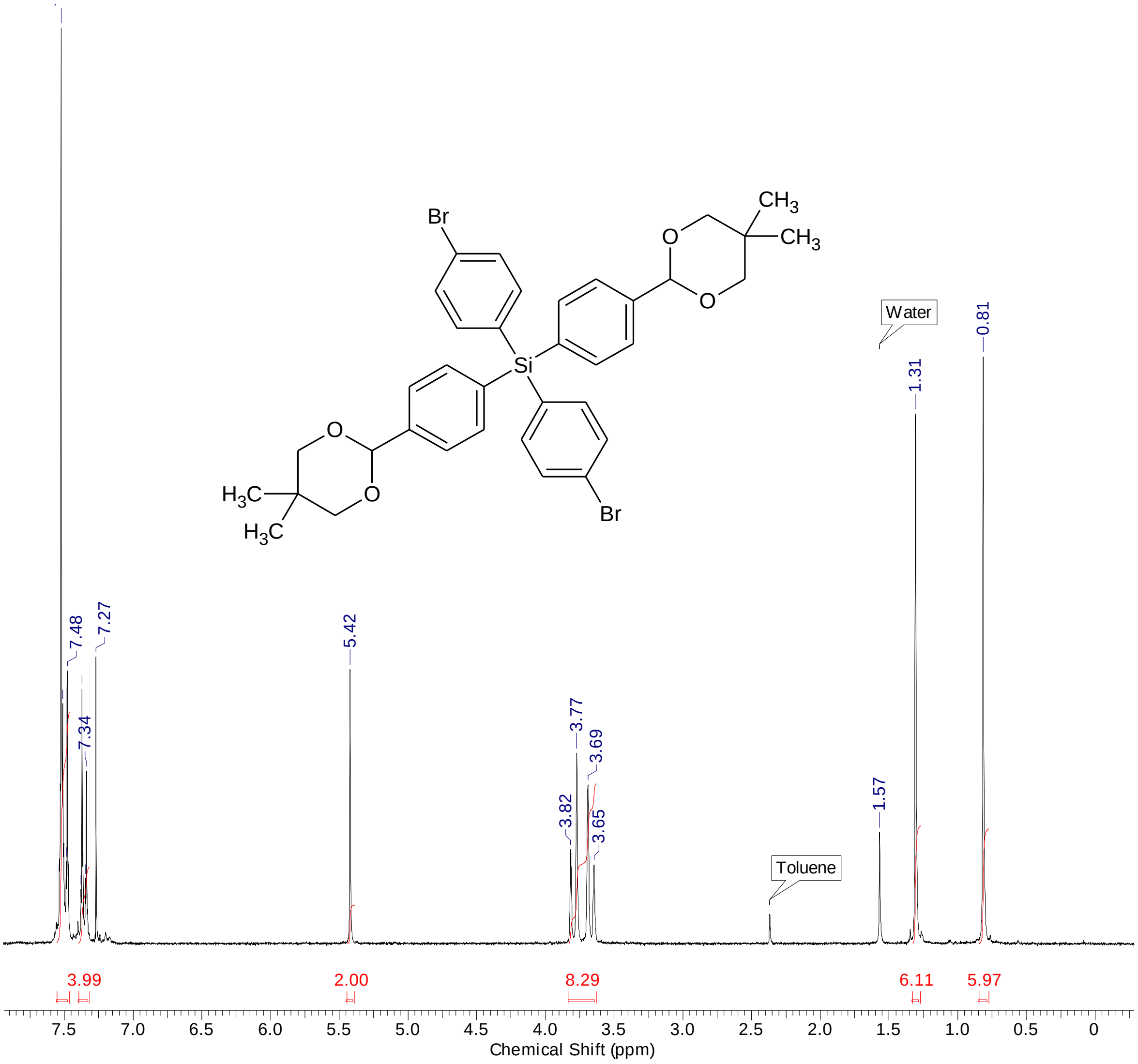
2,2'-({Bis[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]silanediyl}dibenzene-4,1-diyl)bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole} (5). A solution of reactants **3** (3.46 g, 4.7 mmol, 1 equiv) and **4** (2.95 g, 11.49 mmol, 2.5 equiv.), lithium *tert*-butoxide (2.29 g, 28.7 mmol, 6.25 equiv.) and $Pd(PPh_3)_4$ (130 mg, 0.11 mmol, 1 %) in 1.4-dioxane (80 mL) was stirred at reflux for 2 hours. After completion of the reaction, diethyl ether (200 mL) and water (20 mL) were added. The organic phase was separated, washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure (10 mbar). The product was purified by column chromatography on silica gel (eluent toluene: ethyl acetate – 10:1) to give the pure compound **5** (3.18 g, 55%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.82 (s, 6 H), 0.89 (t, 12 H, J =7.3 Hz), 1.28 (m, 22 H), 1.60 (s, 2 H), 2.57 (d, 4 H, J=7.0 Hz), 3.68 (d, 4 H, J= 11.3 Hz), 3.80 (d, 4 H, J= 11.3 Hz), 5.44 (s, 2 H), 7.24 (d, 4 H, J =8.2 Hz), 7.43 (s, 2 H), 7.54-7.70 (overlapping peaks, 16 H), 8.10 (d, 4 H, J =8.2 Hz). ^{13}C MNR (75 MHz, $CDCl_3$): δ =10.76; 14.10; 21.86; 22.99; 23.03; 25.40; 28.80; 30.25; 32.29; 39.96; 41.05; 77.69; 101.57; 122.97; 124.08; 125.31; 125.41; 125.81; 128.57; 129.73; 133.91; 136.37; 136.48; 136.73; 140.07; 142.67; 151.72; 160.63. ^{29}Si NMR (60 MHz, $CDCl_3$): δ = -14.36. Found for **5** (%): C, 78.37; H, 7.64; N, 2.58; Si, 2.53; calcd (%) for $C_{70}H_{82}N_2O_6Si$: C, 78.17; H, 7.68; N, 2.60; Si, 2.61.

4,4'-[Bis(4-{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazol-2-yl}phenyl)silanediyl] dibenzaldehyde (6). A solution of compound **5** (3.38 g, 2.78 mmol) in acetone (70 mL) and 1 *M* solution of HCl (10 mL) was stirred at reflux. After completion of the reaction, diethyl ether and water (200 mL each) were added. The organic phase was separated, washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure (10 mbar). The product was purified by column chromatography on silica gel (eluent toluene: ethyl acetate – 3:1) to give the pure compound **6** (2.79 g, 90%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, 12 H, J =7.3 Hz), 1.28 (m, 16 H), 1.61 (m, 2 H), 2.57 (d, 4 H, J=7.0 Hz), 7.25 (d, 4 H, J =8.2 Hz), 7.46 (s, 2 H), 7.61-7.83 (overlapping peaks, 14 H), 7.93-7.98 (overlapping peaks, 2 H), 8.18 (d, 4 H, J =8.55 Hz), 10.11 (s, 2 H). Found for **6** (%): C, 80.15; H, 6.73; N, 3.44; Si, 3.08; calcd (%) for $C_{60}H_{62}N_2O_4Si$: C, 79.78; H, 6.92; N, 3.10; Si, 3.11.

2,2'-({Bis[4-(1,3-oxazol-5-yl)phenyl]silanediyl}dibenzene-4,1-diyl)bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole} (7). Anhydrous potassium carbonate (704 mg, 5.09 mmol, 2 equiv.) was added to a solution of compound **6** (2.3 g, 2.55 mmol, 1 equiv.) and *p*-tolylsulfonylmethyl isocyanide (522 mg, 2.67 mmol, 1.05 equiv.) in a mixture of methanol (50 mL) and THF (10 mL). The reaction mixture was stirred at reflux for 2 hours. After completion of the reaction, diethyl ether and water (200 mL each) were added. The organic phase was separated, washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure (10 mbar). The product was purified by column chromatography on silica gel (eluent toluene: ethyl acetate – 3:1) to give the pure compound **7** (1.67 g, 72 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, 12 H, J =7.0 Hz), 1.28 (m, 16 H), 1.61 (m, 2 H), 2.57 (d, 4 H, J=7.0 Hz), 7.24 (d, 4 H, J =8.2 Hz), 7.45 (s, 4 H), 7.61-7.77 (overlapping peaks, 16 H), 7.97 (s, 2 H), 8.16 (d, 4 H, J =7.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ =10.76; 14.10; 22.98; 25.39; 28.79; 32.28; 39.95; 41.05; 122.40; 123.02; 123.91; 124.07; 125.22; 125.63; 128.89; 129.19; 129.76; 133.73; 135.61; 136.67; 136.85; 142.81; 150.79; 151.20; 151.86; 160.44. ^{29}Si NMR (60 MHz, $CDCl_3$): δ = -14.42. Found for **7** (%): C, 78.01; H, 6.66; N, 5.56; Si, 2.73; calcd (%) for $C_{64}H_{64}N_4O_4Si$: C, 78.33; H, 6.57; N, 5.71; Si, 2.86.

Poly(2,2'-{benzene-1,4-diyl[(4-{2-[4-(5-phenyl-1,3-oxazol-2-yl)phenyl]-1,3-oxazol-5-yl}phenyl)silanediyl]dibenzene-4,1-diyl}bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole}) (8). A degassed solution of compound **7** (1.57 g, 1.6 mmol, 1 equiv.), lithium *tert*-butoxide (320 mg, 4.0 mmol, 2.5 equiv.), $Pd(PPh_3)_4$ (27 mg, 0.024 mmol, 1.5%) and 1,4-dibromobenzene (377 mg, 1.6 mmol, 1 equiv.) in dioxane (60 mL) was stirred at reflux for 24 h. After completion the reaction, compound **4** (50 mg, 19.4 mmol) and bromobenzene (61 mg, 38.85 mmol) were added successively with an interval of a few hours for blocking the end groups. After refluxing for additional 4 hours, water (200 mL) was added. The resulting precipitate was filtered off and washed with water and acetone. Fractional precipitation, using THF as the solvent and hexane as the precipitating agent, was carried out. Further purification was made by chelation with sodium diethyl dithiocarbamate and extraction with acetone and chloroform. As a result, 0.45 g (26%) of pure polymer **8** was isolated. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (t, 12 H, J =6.4 Hz), 1.27 (m, 16 H), 1.65 (m, 2 H), 2.58 (d, 4 H, J=7.0 Hz), 7.23 (d, 4 H, J =7.6 Hz), 7.44 (s, 2 H), 7.59 (s, 2 H), 7.59-7.86 (overlapping peaks, 18 H), 8.17 (d, 4 H, J =7.3 Hz), 8.24 (s, 2 H). Found for **8** (%): C, 79.36; H, 6.38; N, 5.27; Si, 2.68; calcd (%) for $(C_{70}H_{66}N_4O_4Si)_n$: C, 79.66; H, 6.30; N, 5.31; Si, 2.66.

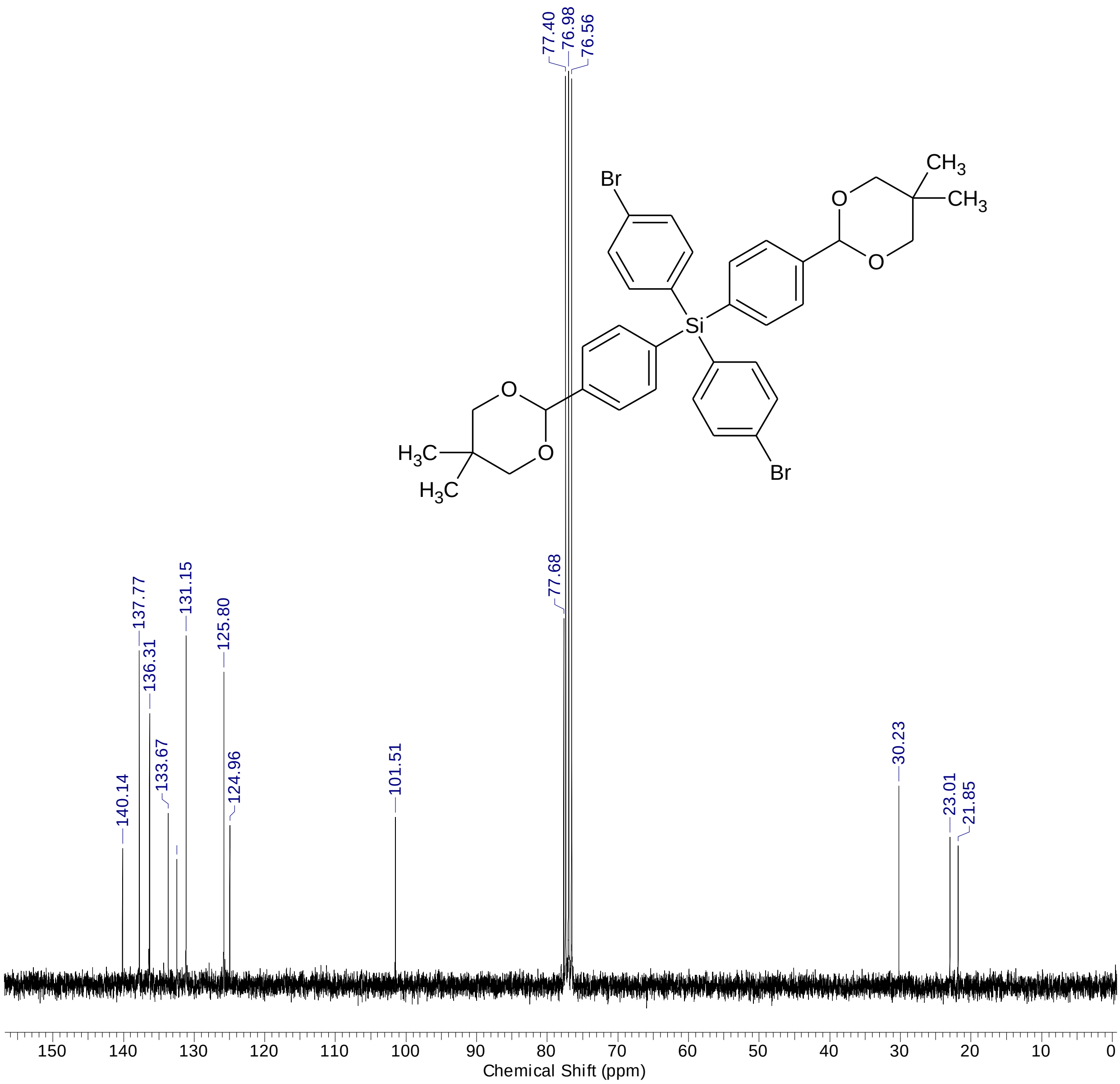
2. ^{1}H, ^{13}C and ^{29}Si NMR spectra



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.7713 .. 0.8434]	5.96528339	1.95893520e+7	5.96528339
2	[1.2714 .. 1.3276]	6.10936689	2.00625080e+7	6.10936689
3	[3.6305 .. 3.8303]	8.28914547	2.72206660e+7	8.28914547
4	[5.3865 .. 5.4434]	2.00220871	6.57503950e+6	2.00220871
5	[7.3174 .. 7.3955]	3.98590875	1.30892980e+7	3.98590875
6	[7.4616 .. 7.5542]	12.01175022	3.94453040e+7	12.01175022

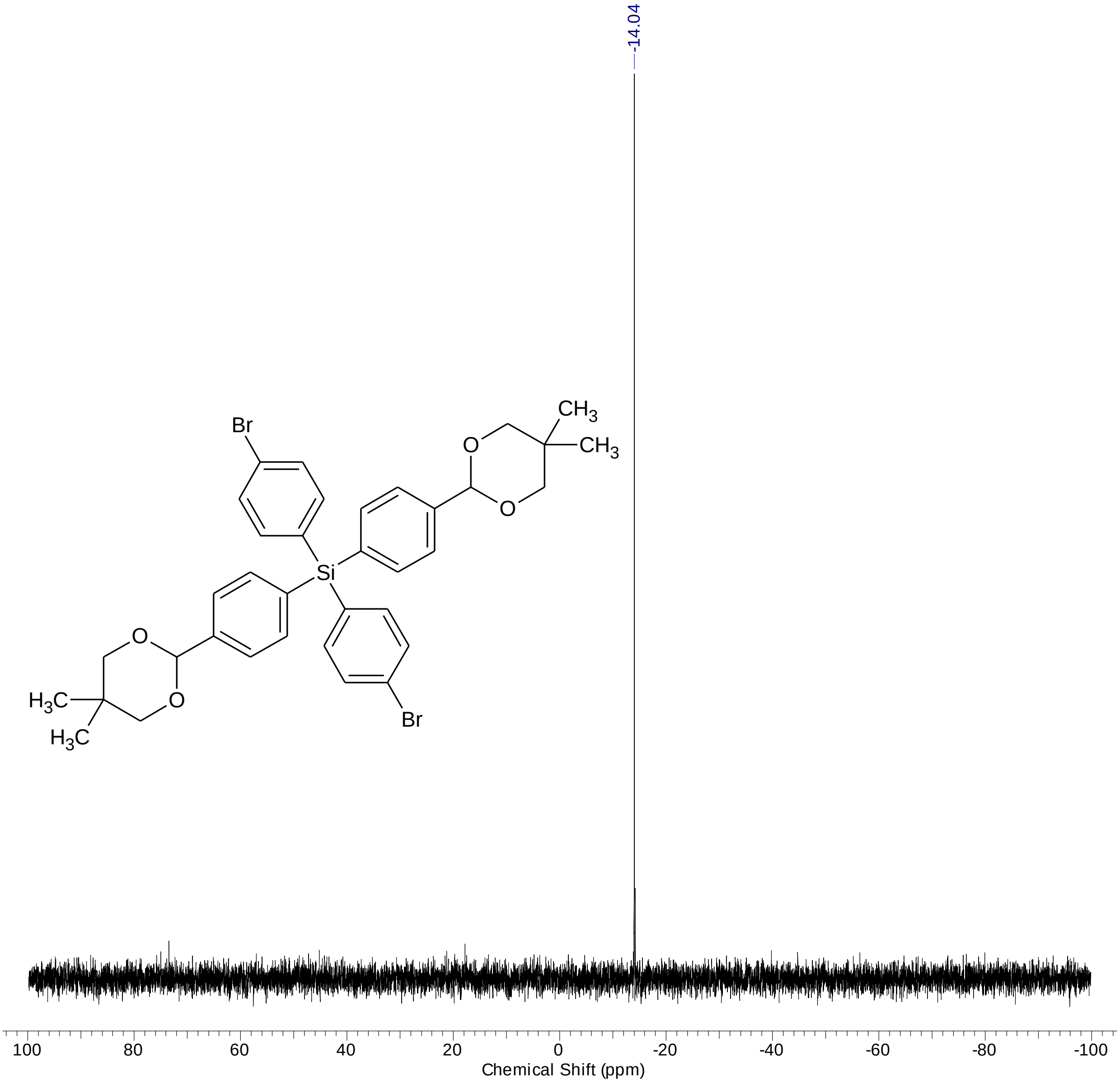
No.	(ppm)	Height
1	0.81	0.6406
2	1.31	0.5787
3	1.57	0.1214
4	3.65	0.0861
5	3.69	0.1735
6	3.77	0.2081
7	3.82	0.1029
8	5.42	0.2994
9	7.27	0.3133
10	7.34	0.1885
11	7.35	0.0714
12	7.37	0.2782
13	7.38	0.0592
14	7.48	0.2981
15	7.49	0.0897
16	7.51	0.2621
17	7.52	1.0000

Figure S1 ^{1}H NMR spectrum of bis(4-bromophenyl){*bis*[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]}silane (**3**).



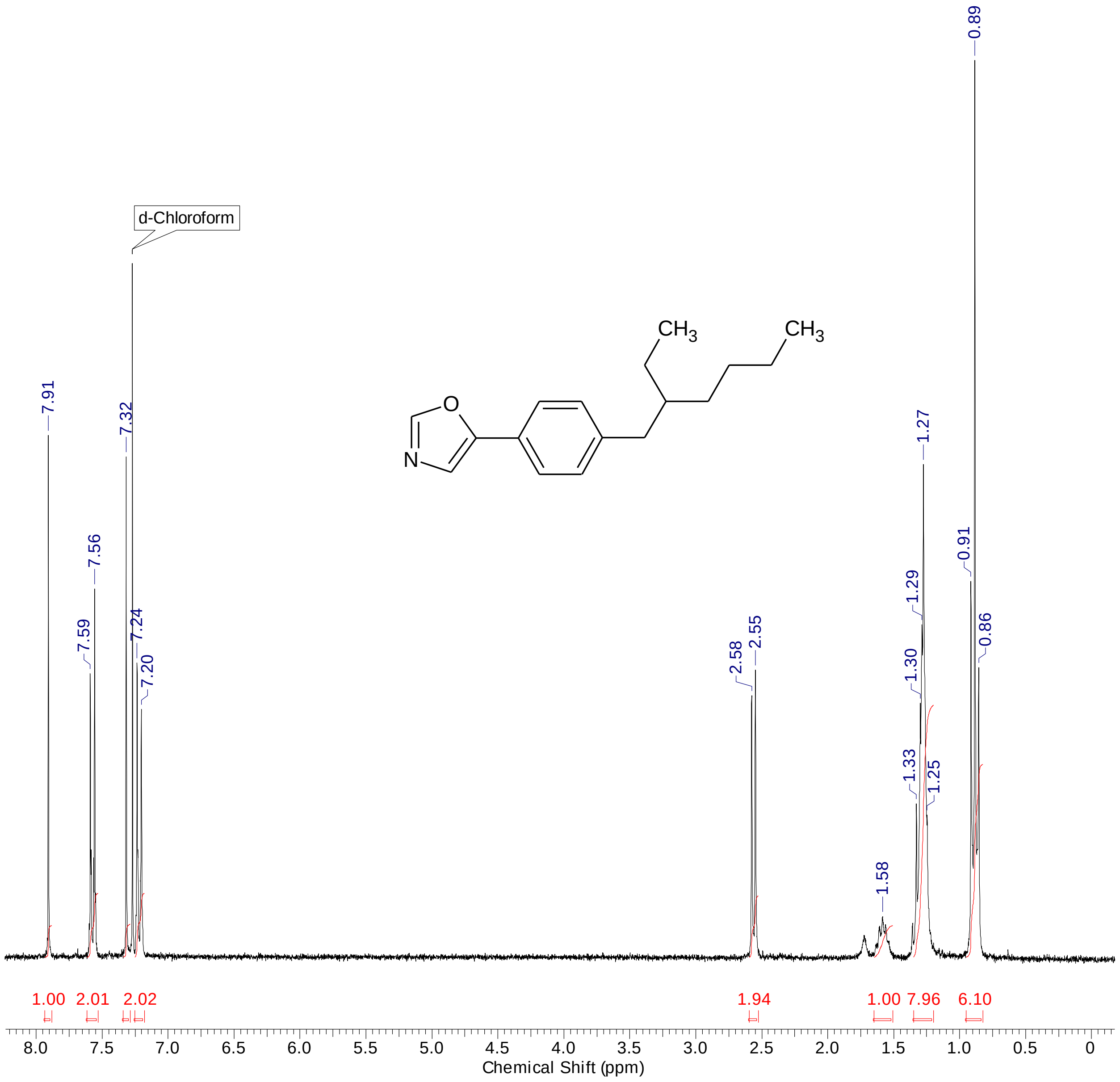
No.	(ppm)	Height
1	21.85	0.1585
2	23.01	0.1679
3	30.23	0.2234
4	76.56	0.9916
5	76.98	1.0000
6	77.40	0.9946
7	77.68	0.4056
8	101.51	0.1898
9	124.96	0.1809
10	125.80	0.3474
11	131.15	0.3864
12	132.45	0.1443
13	133.67	0.1939
14	136.31	0.3022
15	137.77	0.3706
16	140.14	0.1554

Figure S2 ^{13}C NMR spectrum of bis(4-bromophenyl){bis[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]}silane (**3**).



No.	(ppm)	Height
1	-14.04	1.0000

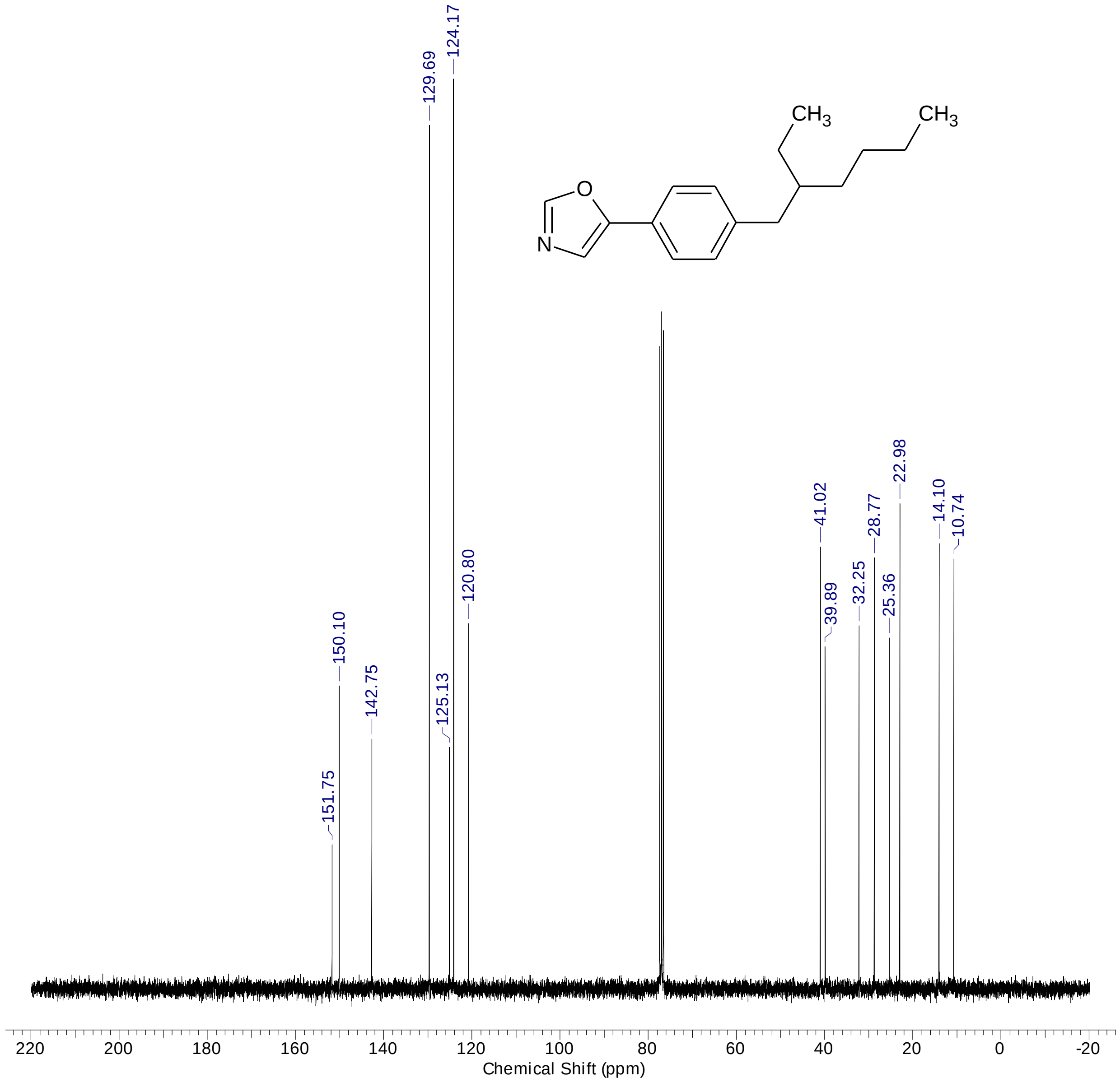
Figure S3 ^{29}Si NMR spectrum of bis(4-bromophenyl){bis[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]}silane (**3**).



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.8218 .. 0.9515]	6.09969234	4.76513800e+7	6.09969234
2	[1.1997 .. 1.3499]	7.96423054	6.22173280e+7	7.96423054
3	[1.5070 .. 1.6481]	1.00376213	7.84148600e+6	1.00376213
4	[2.5267 .. 2.5950]	1.94035470	1.51582360e+7	1.94035470
5	[7.1785 .. 7.2513]	2.01846075	1.57684090e+7	2.01846075
6	[7.2877 .. 7.3401]	1.04643917	8.17488300e+6	1.04643917
7	[7.5313 .. 7.6133]	2.01403570	1.57338390e+7	2.01403570
8	[7.8819 .. 7.9365]	1.00251734	7.83176150e+6	1.00251734

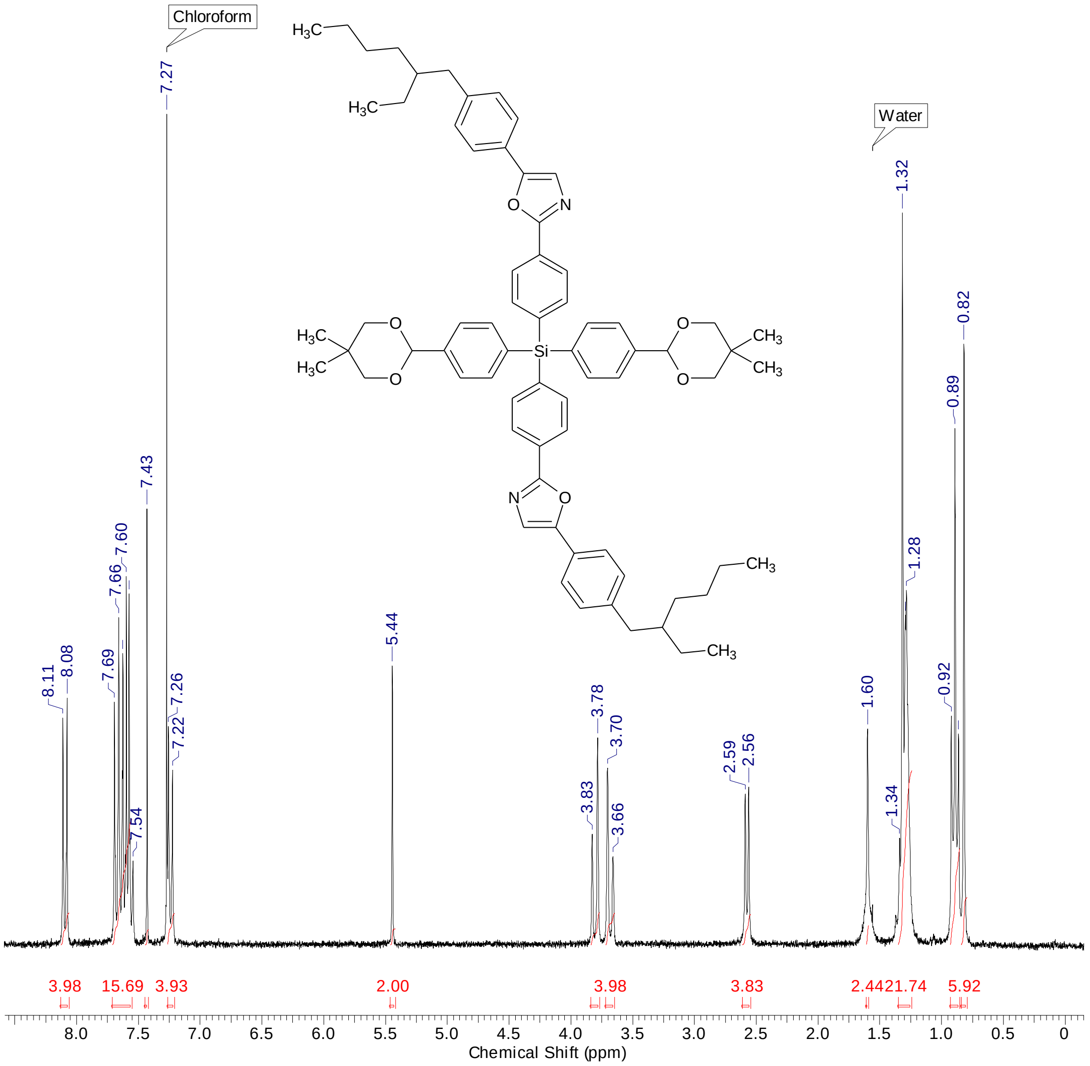
No.	(ppm)	Height
1	0.86	0.3230
2	0.89	1.0000
3	0.91	0.4191
4	1.25	0.1585
5	1.27	0.5499
6	1.29	0.3710
7	1.30	0.2833
8	1.33	0.1714
9	1.58	0.0453
10	2.55	0.3204
11	2.58	0.2921
12	7.20	0.2765
13	7.24	0.3281
14	7.32	0.5582
15	7.56	0.4107
16	7.59	0.3164
17	7.91	0.5820

Figure S4 ^{1} H NMR spectrum of 5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole (**4**).



No.	(ppm)	Height
1	10.74	0.4726
2	14.10	0.4897
3	22.98	0.5331
4	25.36	0.3857
5	28.77	0.4741
6	32.25	0.3994
7	39.89	0.3764
8	41.02	0.4856
9	120.80	0.4016
10	124.17	1.0000
11	125.13	0.2655
12	129.69	0.9490
13	142.75	0.2746
14	150.10	0.3329
15	151.75	0.1585

Figure S5 ^{13}C NMR spectrum of 5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole (**4**).

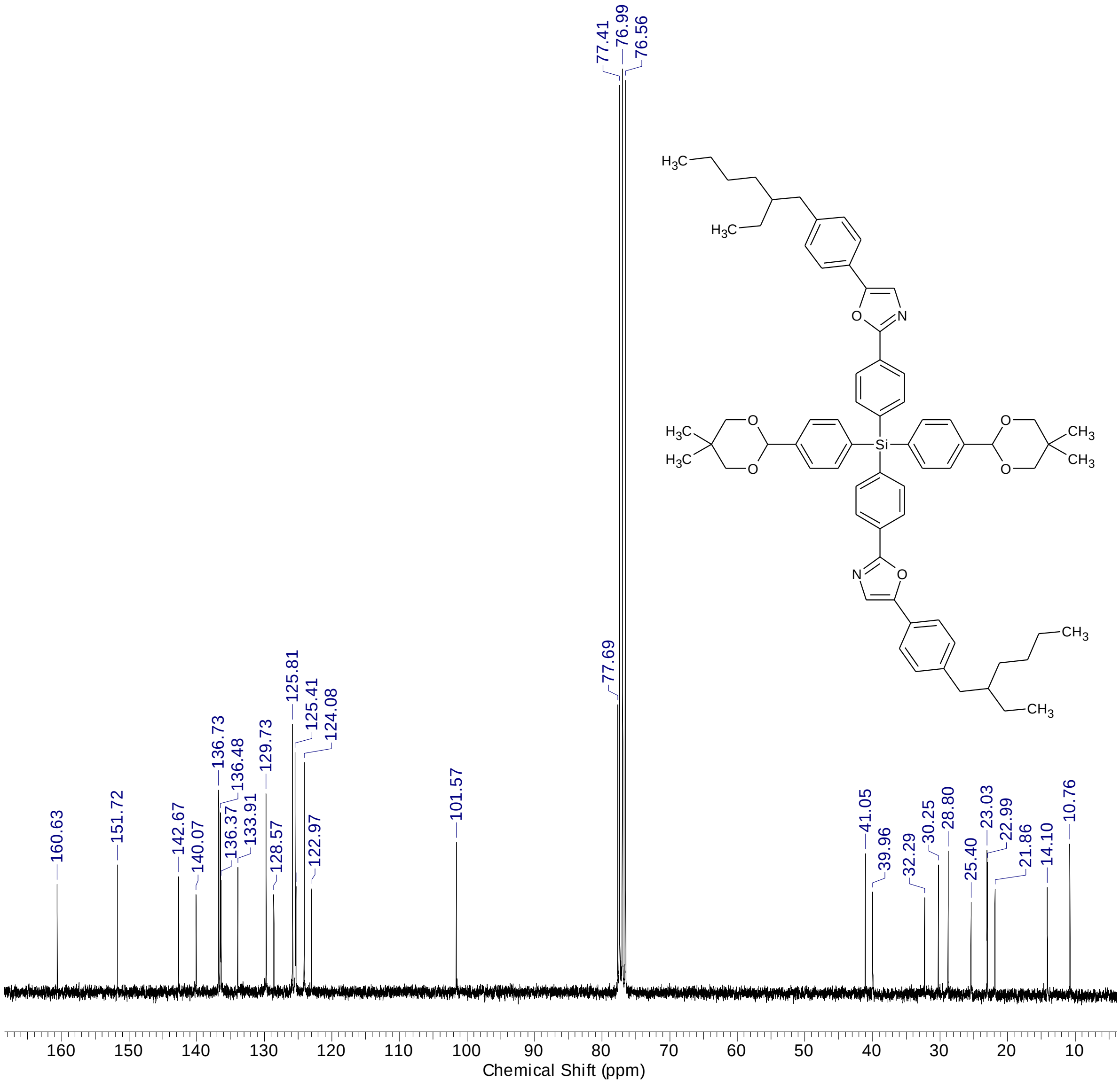


No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.7938 .. 0.8401]	5.91865730	1.56884780e+7	5.91865730
2	[0.8518 .. 0.9296]	12.01857376	3.18574160e+7	12.01857376
3	[1.2401 .. 1.3496]	21.74423218	5.76370440e+7	21.74423218
4	[1.5917 .. 1.6083]	2.44242811	6.47410000e+6	2.44242811
5	[2.5436 .. 2.6111]	3.82791853	1.01465950e+7	3.82791853
6	[3.6454 .. 3.7170]	3.97525048	1.05371250e+7	3.97525048
7	[3.7679 .. 3.8381]	4.02337694	1.06646930e+7	4.02337694
8	[5.4201 .. 5.4636]	2.00000000	5.30136400e+6	2.00000000
9	[7.2079 .. 7.2636]	3.92787981	1.04115600e+7	3.92787981
10	[7.4165 .. 7.4447]	1.91721559	5.08192900e+6	1.91721559
11	[7.5508 .. 7.7120]	15.68921852	4.15871280e+7	15.68921852
12	[8.0606 .. 8.1281]	3.97617507	1.05395760e+7	3.97617507

No.	(ppm)	Height
1	0.82	0.7237
2	0.86	0.2543
3	0.89	0.6218
4	0.92	0.2758
5	1.28	0.4273
6	1.29	0.3970
7	1.32	0.8813
8	1.34	0.1289
9	1.60	0.2604
10	2.56	0.1905
11	2.59	0.1819
12	3.66	0.1069
13	3.70	0.2128
14	3.78	0.2497
15	3.83	0.1333
16	5.44	0.3363
17	7.22	0.2106
18	7.26	0.2631

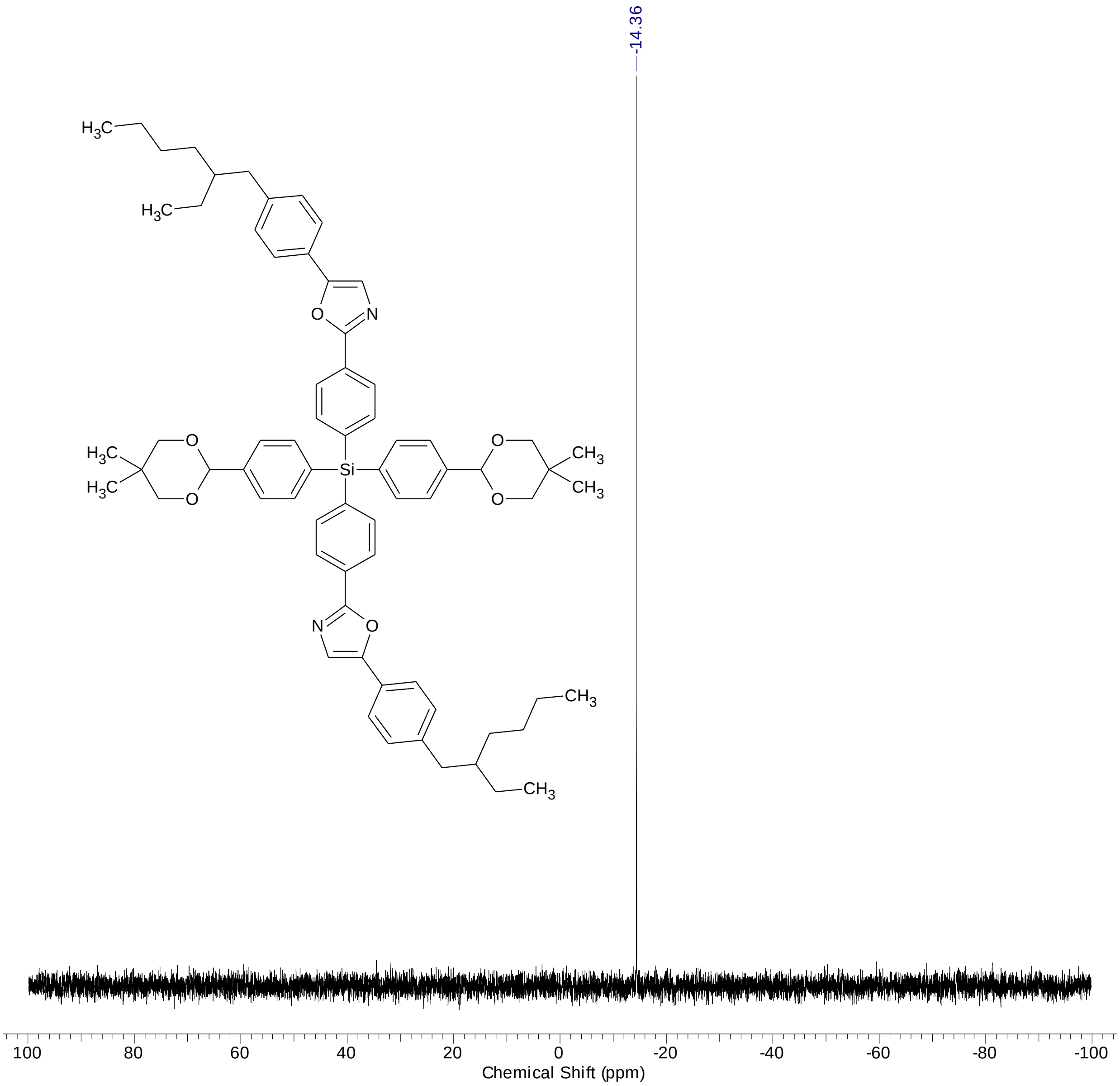
No.	(ppm)	Height
19	7.27	1.0000
20	7.43	0.5249
21	7.54	0.1012
22	7.58	0.4230
23	7.60	0.4439
24	7.63	0.3508
25	7.66	0.3942
26	7.69	0.2925
27	8.08	0.2971
28	8.11	0.2732

Figure S6 ^{1}H NMR spectrum of 2,2'-({bis[4-(5,5-dimethyl-1,3-dioxane-2-yl)phenyl]silanediyl}dibenzene-4,1-diyl)bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole} (**5**).



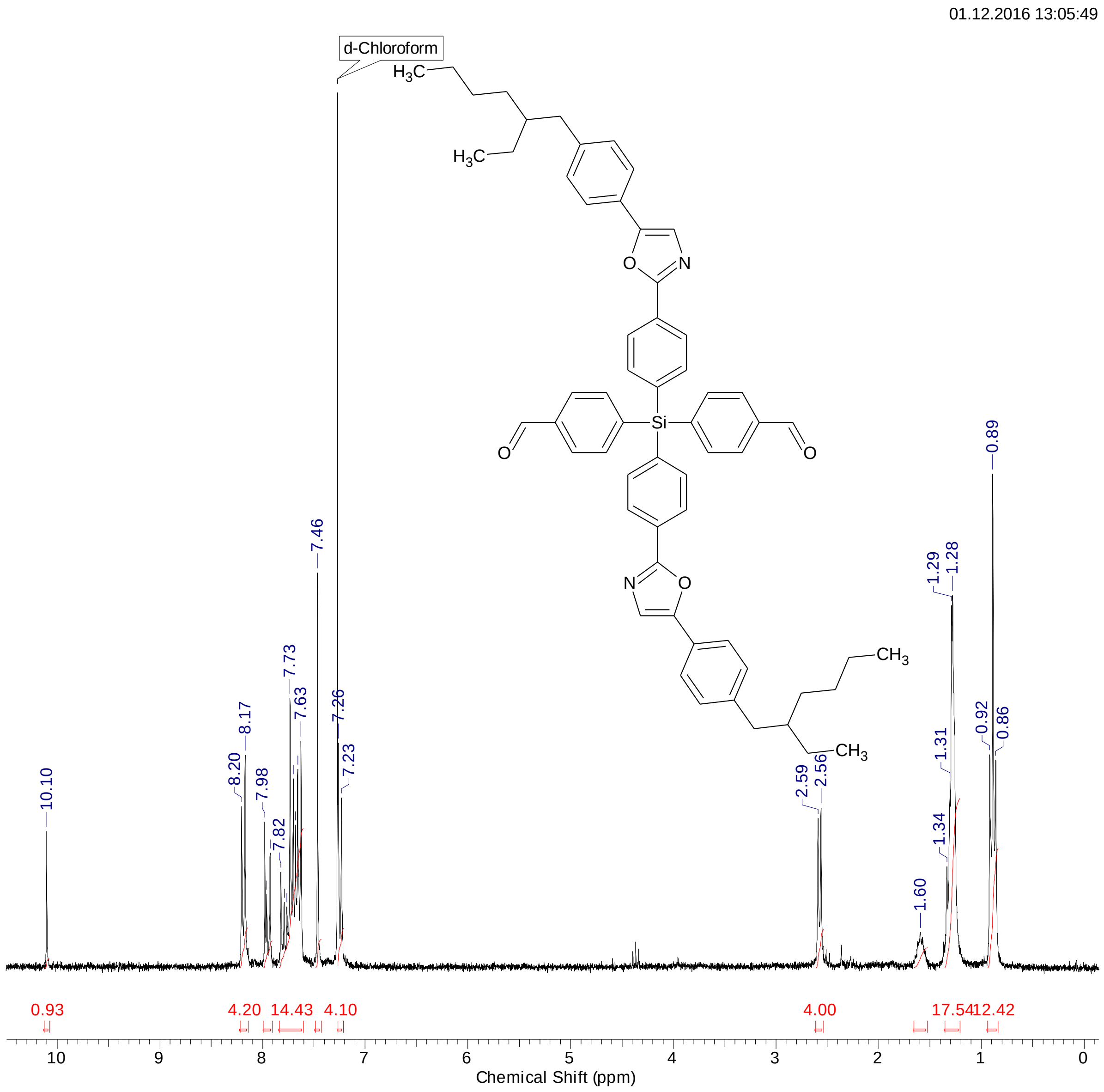
No.	(ppm)	Height
1	10.76	0.1715
2	14.10	0.1248
3	21.86	0.1230
4	22.99	0.1518
5	23.03	0.1648
6	25.40	0.1090
7	28.80	0.1639
8	30.25	0.1490
9	32.29	0.1140
10	39.96	0.1198
11	41.05	0.1608
12	76.56	0.9880
13	76.99	1.0000
14	77.41	0.9822
15	77.69	0.3201
16	101.57	0.1732
17	122.97	0.1236
18	124.08	0.2583
19	125.31	0.1262
20	125.41	0.2696
21	125.81	0.2995
22	128.57	0.1171
23	129.73	0.2250
24	133.91	0.1460
25	136.37	0.1328
26	136.48	0.2045
27	136.73	0.2290
28	140.07	0.1174
29	142.67	0.1366
30	151.72	0.1490
31	160.63	0.1283

Figure S7 ^{13}C NMR spectrum of 2,2'-({bis[4-(5,5-dimethyl-1,3-dioxane-2-yl)phenyl]silanediyl}dibenzene-4,1-diyl)bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole} (**5**).



No.	(ppm)	Height
1	-14.36	1.0000

Figure S8 ^{29}Si NMR spectrum of 2,2'-({bis[4-(5,5-dimethyl-1,3-dioxane-2-yl)phenyl]silanediyl}dibenzene-4,1-diyl)bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole} (**5**).

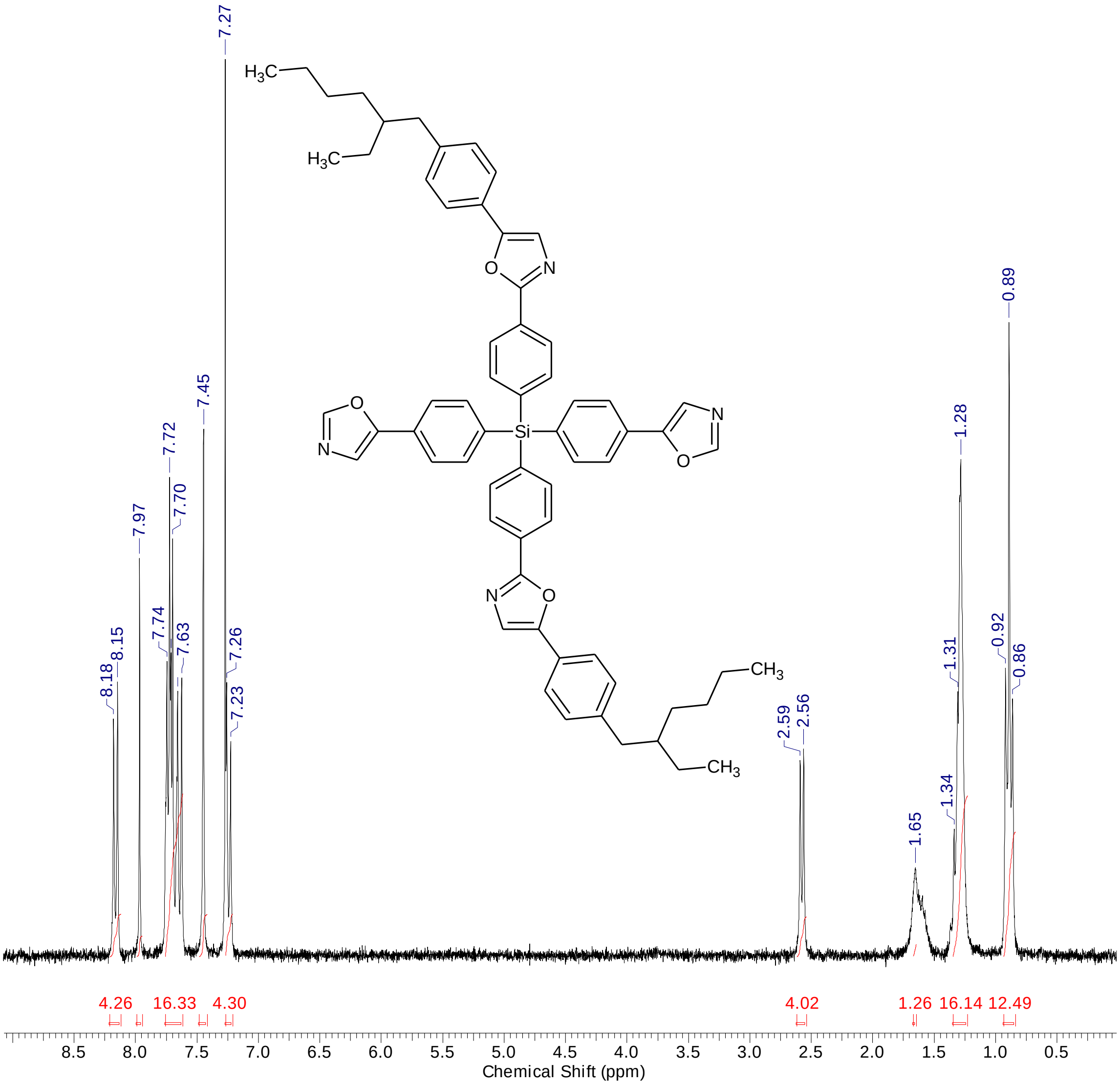


No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.8361 .. 0.9394]	12.42061424	2.80858200e+7	12.42061424
2	[1.2097 .. 1.3558]	17.54260254	3.96677960e+7	17.54260254
3	[1.5275 .. 1.6565]	2.12038755	4.79467650e+6	2.12038755
4	[2.5354 .. 2.6129]	3.99545407	9.03462600e+6	3.99545407
5	[7.2114 .. 7.2675]	4.09517288	9.26011300e+6	4.09517288
6	[7.4270 .. 7.4860]	2.97902608	6.73625250e+6	2.97902608
7	[7.6029 .. 7.8391]	14.43148232	3.26328480e+7	14.43148232
8	[7.9054 .. 7.9896]	2.80662847	6.34642250e+6	2.80662847
9	[8.1416 .. 8.2199]	4.20197153	9.50160900e+6	4.20197153
10	[10.0713 .. 10.1260]	0.92988974	2.10269125e+6	0.92988974

No.	(ppm)	Height
1	0.86	0.2373
2	0.89	0.5646
3	0.92	0.2440
4	1.28	0.4259
5	1.29	0.4140
6	1.31	0.2129
7	1.34	0.1162
8	1.60	0.0408
9	2.56	0.1830
10	2.59	0.1709
11	7.23	0.1948
12	7.26	0.2572
13	7.46	0.4517
14	7.63	0.2592
15	7.66	0.2273
16	7.68	0.1632
17	7.70	0.2161
18	7.73	0.3082

No.	(ppm)	Height
19	7.76	0.0699
20	7.79	0.0749
21	7.82	0.1095
22	7.93	0.1312
23	7.96	0.0843
24	7.98	0.1668
25	8.17	0.2433
26	8.20	0.1849
27	10.10	0.1558

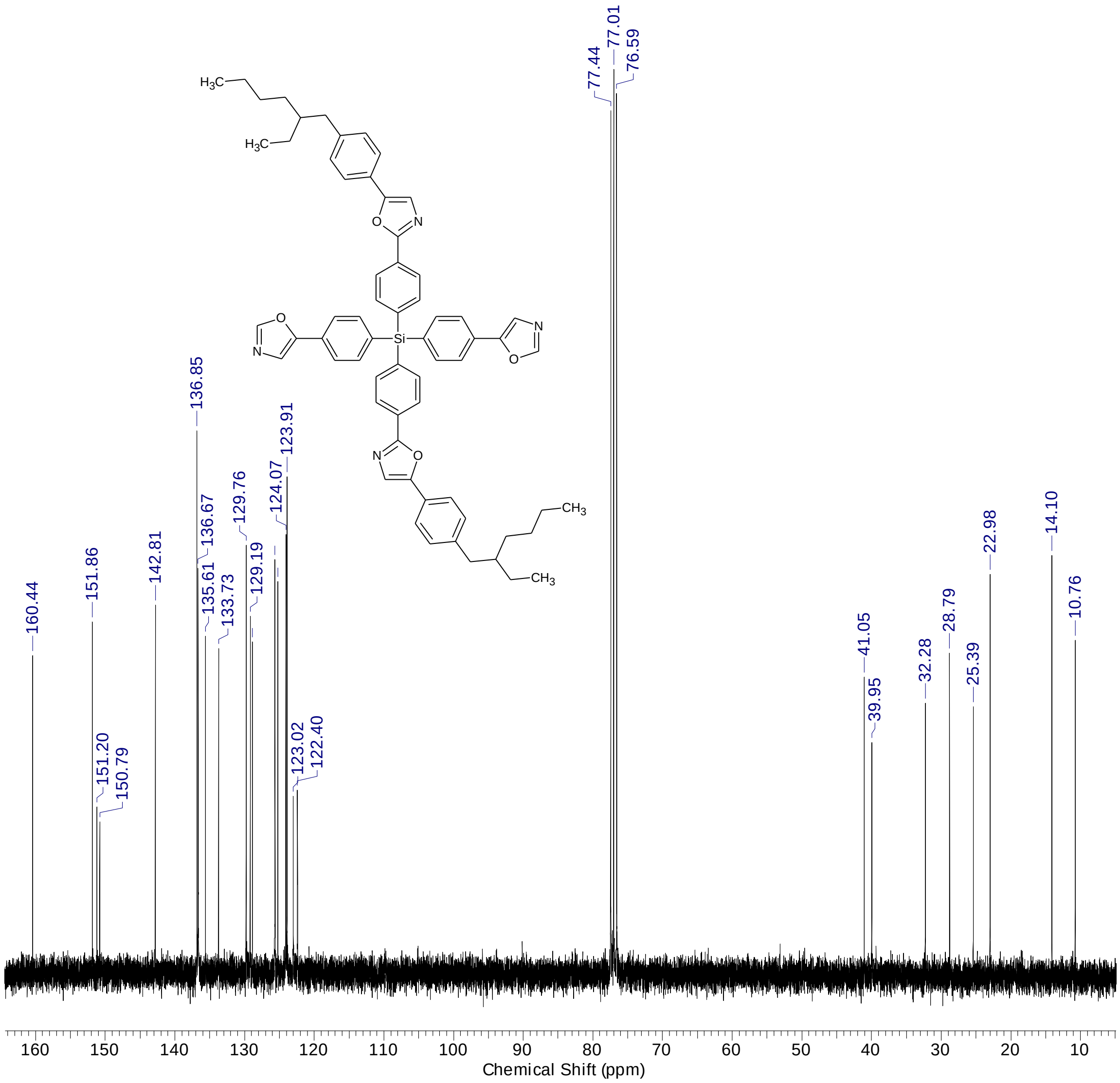
Figure S9 ^{1} H NMR spectrum of 4,4'-[bis(4-{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazol-2-yl}phenyl)silanediyl]dibenzaldehyde (**6**).



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1[0.	8381 .. 0.93	12.48719597	4.43248040e+7	12.48719597
2[1.	2270 .. 1.34	16.14131737	5.72955480e+7	16.14131737
3[1.	6450 .. 1.66	1.26046371	4.47416750e+6	1.26046371
4[2.	5363 .. 2.61	4.02002096	1.42695480e+7	4.02002096
5[7.	2093 .. 7.26	4.29718399	1.52533710e+7	4.29718399
6[7.	4161 .. 7.48	4.24602270	1.50717680e+7	4.24602270
7[7.	6157 .. 7.75	16.33393097	5.79792520e+7	16.33393097
8[7.	9448 .. 7.98	2.08561134	7.40312850e+6	2.08561134
9[8.	1181 .. 8.21	4.26079130	1.51241920e+7	4.26079130

No.	(ppm)	Height
1	0.86	0.2877
2	0.89	0.7069
3	0.92	0.3218
4	1.28	0.5546
5	1.31	0.2958
6	1.34	0.1426
7	1.65	0.0996
8	2.56	0.2315
9	2.59	0.2190
10	7.23	0.2400
11	7.26	0.3060
12	7.27	1.0000
13	7.45	0.5882
14	7.63	0.3109
15	7.66	0.2959
16	7.70	0.4657
17	7.71	0.3388
18	7.72	0.5347
19	7.74	0.3293
20	7.97	0.4442
21	8.15	0.3067
22	8.18	0.2655

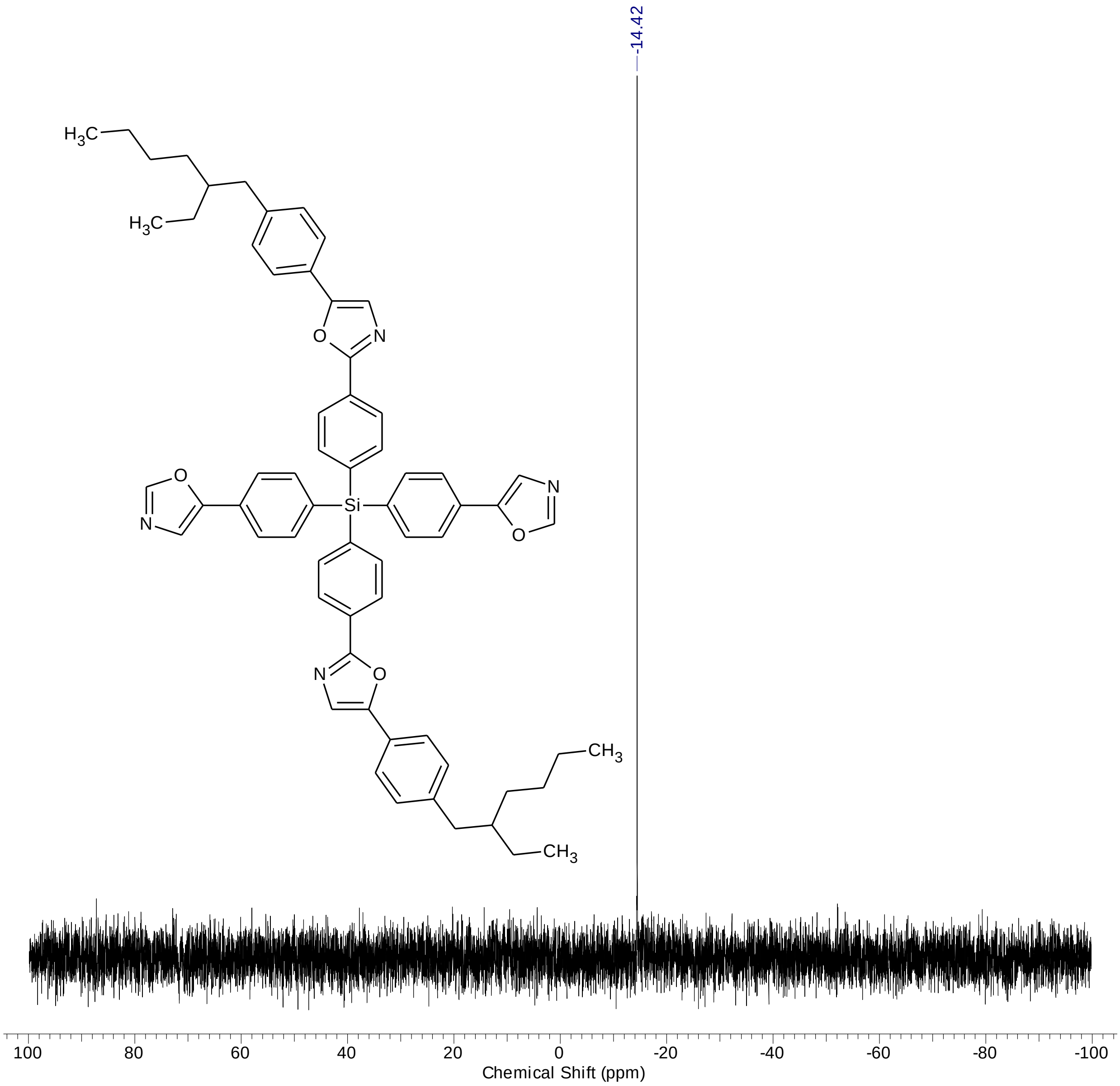
Figure S10 ^{1}H NMR spectrum of 2,2'-({bis[4-(1,3-oxazol-5-yl)phenyl]silanediyl} dibenzene-4,1-diyl)bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole} (**7**).



No.	(ppm)	Height
1	10.76	0.3779
2	14.10	0.4706
3	22.98	0.4498
4	25.39	0.3060
5	28.79	0.3644
6	32.28	0.3099
7	39.95	0.2668
8	41.05	0.3381

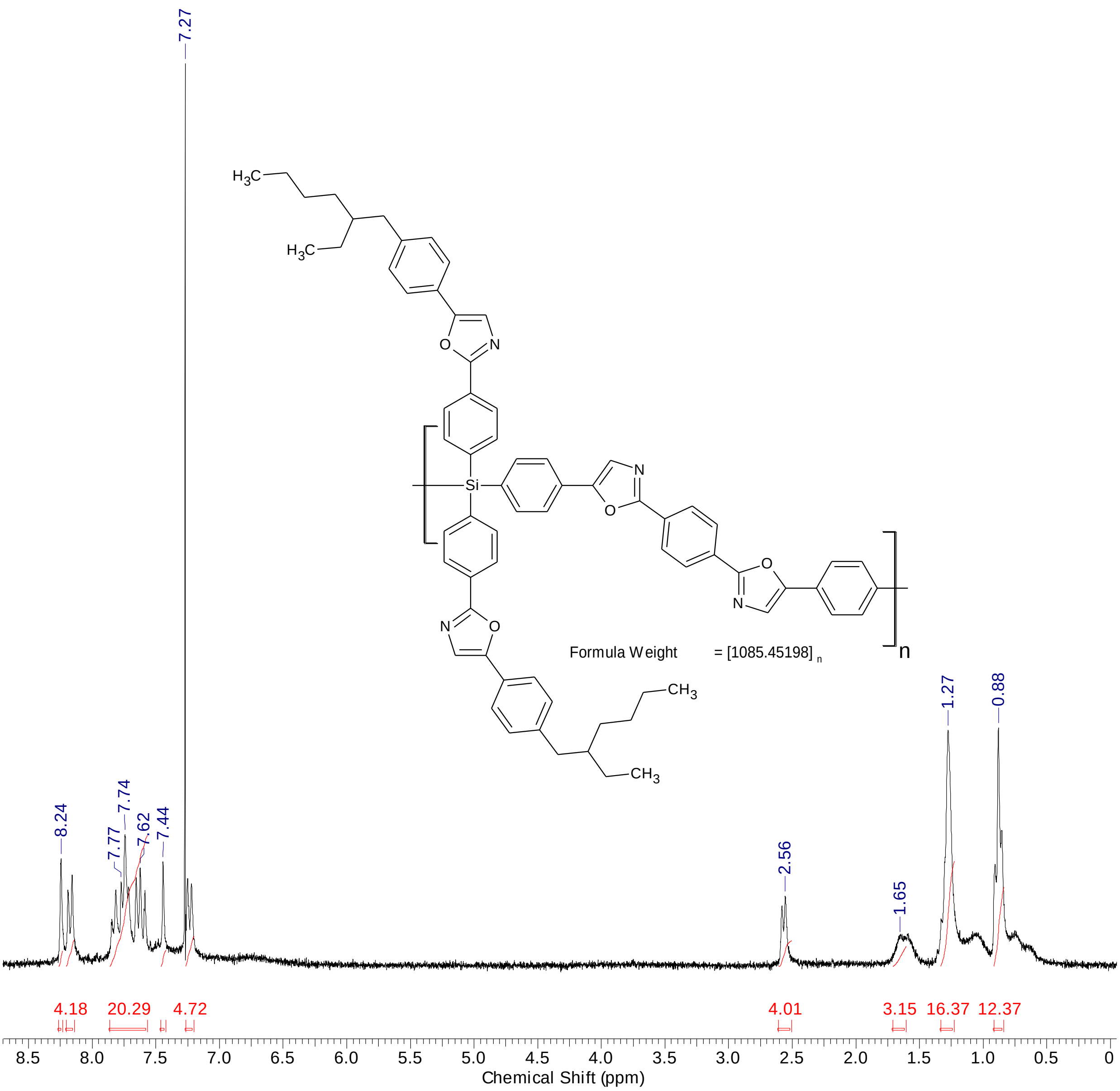
No.	(ppm)	Height
9	76.59	0.9736
10	77.01	1.0000
11	77.44	0.9547
12	122.40	0.2148
13	123.02	0.2086
14	123.91	0.5564
15	124.07	0.4935
16	125.22	0.4424
17	125.63	0.4663
18	128.89	0.3766
19	129.19	0.4046
20	129.76	0.4818
21	133.73	0.3691
22	135.61	0.3828
23	136.67	0.4569
24	136.85	0.6062
25	142.81	0.4166
26	150.79	0.1809
27	151.20	0.1968
28	151.86	0.3983
29	160.44	0.3613

Figure S11 ^{13}C NMR spectrum of 2,2'-({bis[4-(1,3-oxazol-5-yl)phenyl] silanediyl}dibenzene-4,1-diyl)bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole} (**7**).



No.	(ppm)	Height
1	-14.42	1.0000

Figure S12 ^{29}Si NMR spectrum of 2,2'-({bis[4-(1,3-oxazol-5-yl)phenyl] silanediyl}dibenzene-4,1-diyl)bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole} (**7**).



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.8366 .. 0.91	12.37006664	3.68670080e+7	12.37006664
2	[1.2262 .. 1.33	16.37380028	4.87994960e+7	16.37380028
3	[1.6048 .. 1.70	3.14680386	9.37854600e+6	3.14680386
4	[2.5046 .. 2.60	4.01016903	1.19516680e+7	4.01016903
5	[7.1995 .. 7.26	4.71999168	1.40671810e+7	4.71999168
6	[7.4208 .. 7.46	2.55163932	7.60475300e+6	2.55163932
7	[7.5670 .. 7.86	20.29347992	6.04814720e+7	20.29347992
8	[8.1400 .. 8.20	4.18459272	1.24715100e+7	4.18459272
9	[8.2318 .. 8.26	2.44956517	7.30053750e+6	2.44956517

No.	(ppm)	Height
1	0.88	0.2645
2	1.27	0.2617
3	1.65	0.0334
4	2.56	0.0784
5	7.27	1.0000
6	7.44	0.1163
7	7.62	0.1095
8	7.74	0.1464
9	7.77	0.0938
10	8.24	0.1195

Figure S13 ^{1}H NMR spectrum poly(2,2'-{benzene-1,4-diyl[(4-{2-[4-(5-phenyl-1,3-oxazol-2-yl)phenyl]-1,3-oxazol-5-yl}phenyl)silanediyl]dibenzene-4,1-diyl}bis{5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole}) **(8)**.

3. Thermogravimetric analysis and differential scanning calorimetry data

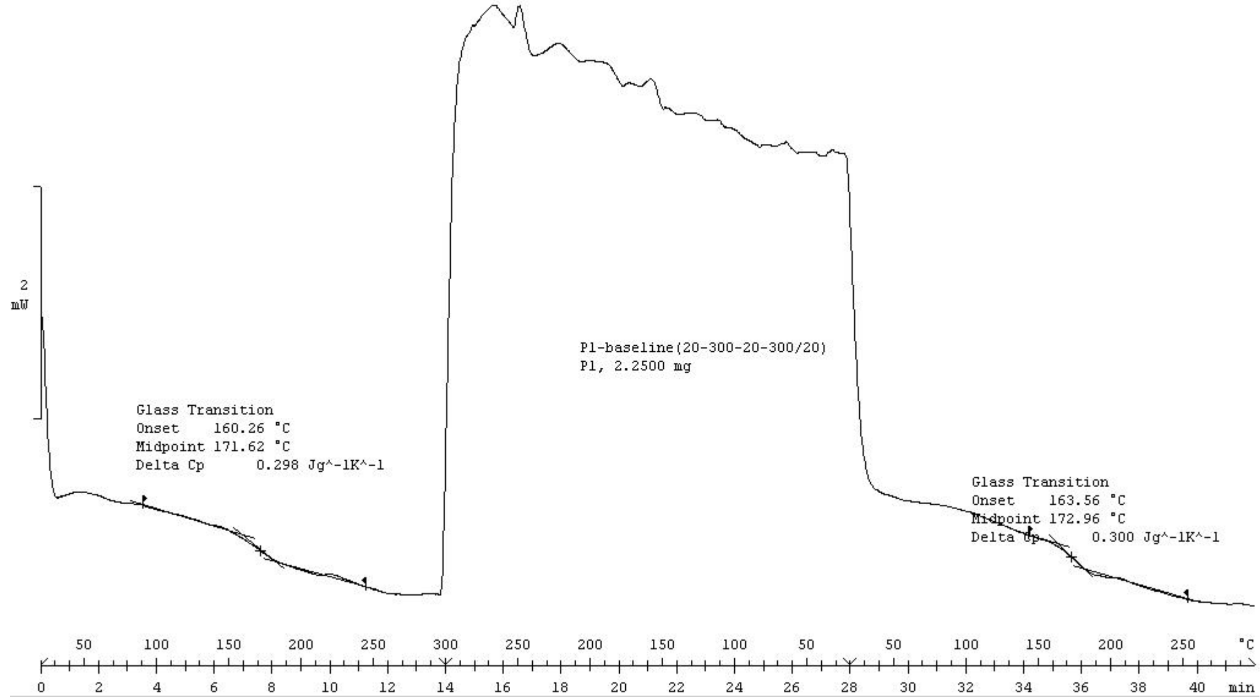


Figure S14 DSC thermograms of P1.

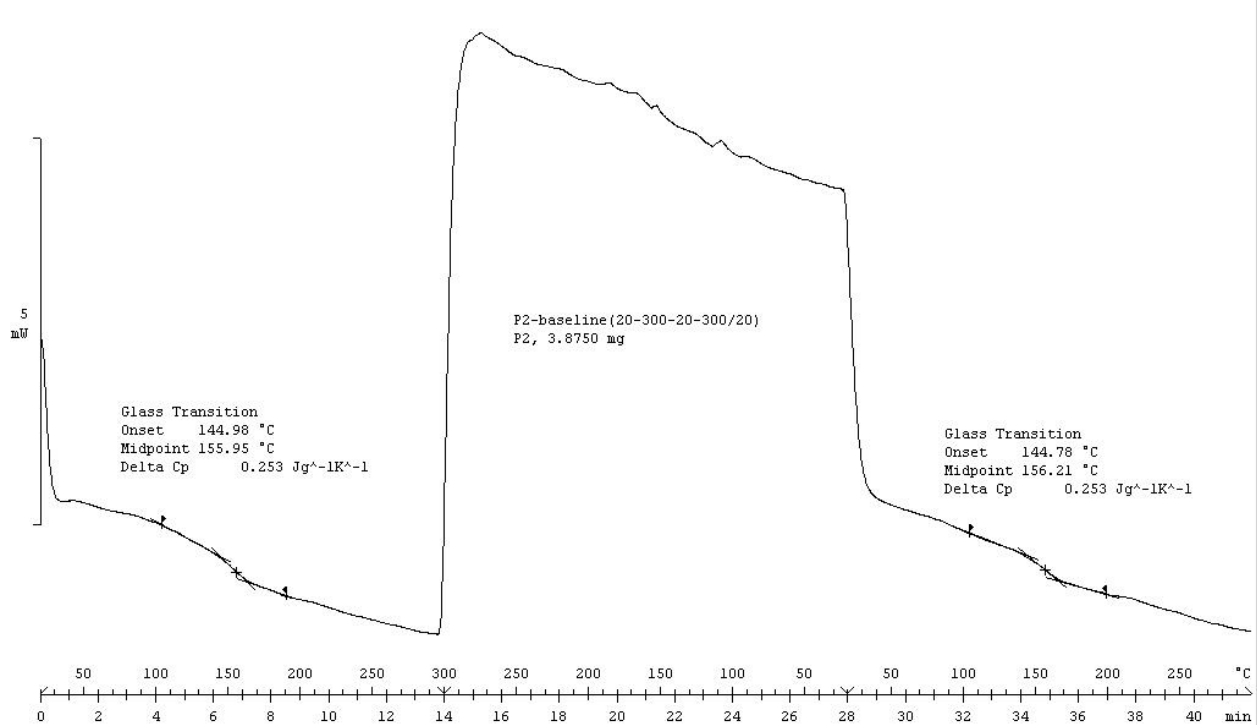


Figure S15 DSC thermograms of P2.

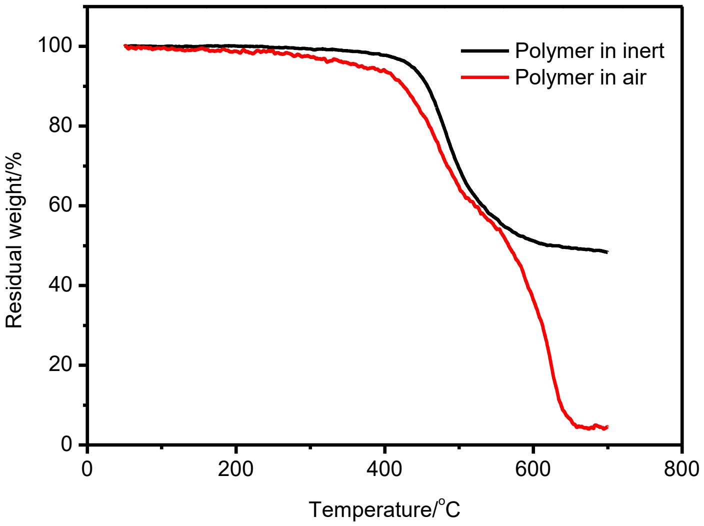
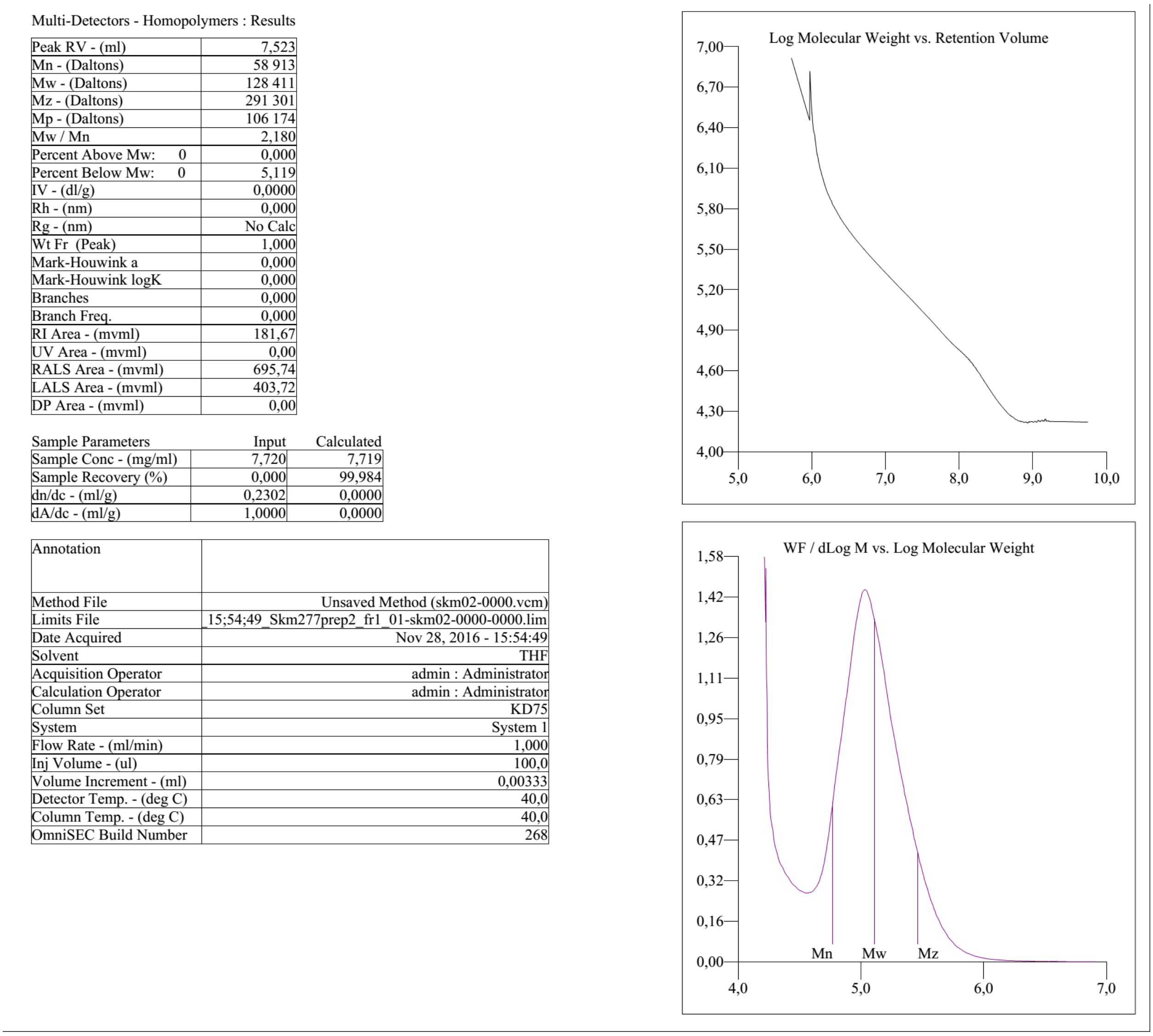


Figure S16 TGA curves of polymer **8** before fractionation.

4. Light scattering data



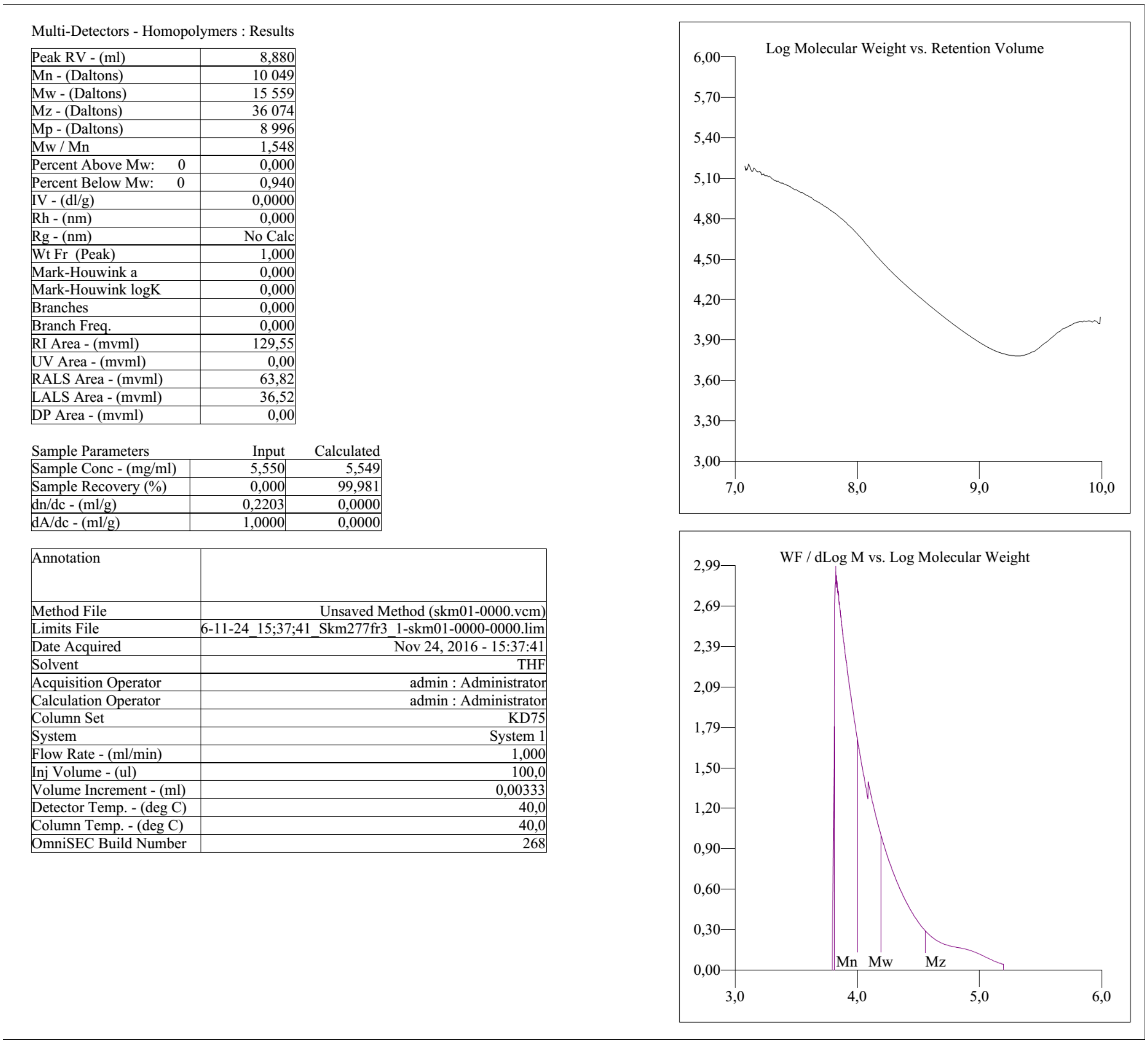
Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	7,523
Mn - (Daltons)	58 913
Mw - (Daltons)	128 411
Mz - (Daltons)	291 301
Mp - (Daltons)	106 174
Mw / Mn	2,180
Percent Above Mw: 0	0,000
Percent Below Mw: 0	5,119
IV - (dl/g)	0,0000
Rh - (nm)	0,000
Rg - (nm)	No Calc
Wt Fr (Peak)	1,000
Mark-Houwink a	0,000
Mark-Houwink logK	0,000
Branches	0,000
Branch Freq.	0,000
RI Area - (mvml)	181,67
UV Area - (mvml)	0,00
RALS Area - (mvml)	695,74
LALS Area - (mvml)	403,72
DP Area - (mvml)	0,00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	7,720	7,719
Sample Recovery (%)	0,000	99,984
dn/dc - (ml/g)	0,2302	0,0000
dA/dc - (ml/g)	1,0000	0,0000

Annotation	
Method File	Unsaved Method (skm02-0000.vcm)
Limits File	15;54;49_Skm277prep2_fr1_01-skm02-0000-0000.lim
Date Acquired	Nov 28, 2016 - 15:54:49
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	KD75
System	System 1
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	100,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	40,0
Column Temp. - (deg C)	40,0
OmniSEC Build Number	268

Figure S17 Light scattering data for P1.



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	8,880
Mn - (Daltons)	10 049
Mw - (Daltons)	15 559
Mz - (Daltons)	36 074
Mp - (Daltons)	8 996
Mw / Mn	1,548
Percent Above Mw: 0	0,000
Percent Below Mw: 0	0,940
IV - (dl/g)	0,0000
Rh - (nm)	0,000
Rg - (nm)	No Calc
Wt Fr (Peak)	1,000
Mark-Houwink a	0,000
Mark-Houwink logK	0,000
Branches	0,000
Branch Freq.	0,000
RI Area - (mvml)	129,55
UV Area - (mvml)	0,00
RALS Area - (mvml)	63,82
LALS Area - (mvml)	36,52
DP Area - (mvml)	0,00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	5,550	5,549
Sample Recovery (%)	0,000	99,981
dn/dc - (ml/g)	0,2203	0,0000
dA/dc - (ml/g)	1,0000	0,0000

Annotation	
Method File	Unsaved Method (skm01-0000.vcm)
Limits File	6-11-24_15;37;41_Skm277fr3_1-skm01-0000-0000.lim
Date Acquired	Nov 24, 2016 - 15:37:41
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	KD75
System	System 1
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	100,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	40,0
Column Temp. - (deg C)	40,0
OmniSEC Build Number	268

Figure S18 Light scattering data for P2.

Table S1 Molecular Characteristics of P1 and P2 fractions of polymer 8.

Polymer	PS		LS		$M_w(LS)/M_w(PS)$	n	m
	$M_w \times 10^{-3}$	PDI	$M_w \times 10^{-3}$	PDI			
P1	102.8	1.8	128.4	2.18	1.25	236	118
P2	8.8	1.13	15.5	1.15	1.76	28	14

[a]Notes: PS – molecular weight characteristics obtained using calibration according to the polystyrene standards, LS – molecular weight characteristics obtained using the dual light scattering detectors, n = average number of **PPO** repeating units in the macromolecule, m = average number of **POPOP** fragments in the macromolecule

References

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[1] N. E. Gelman, E. A. Terenteva, T. M. Shanina and L. M. Kiparenko, *Metody kolichestvennogo elementnogo mikroanaliza*, Khimiya, Moscow, 1987 (in Russian).

[2] I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 1971.

[3] H. Yu, C. Shen, M. Tian, J. Qu and Z. Wang, *Macromolecules*, 2012, **45**, 5140.