Supporting Information

Copper-Driven Formation of Siloxanes via Dehydrocoupling Between Hydrosilanes and Silanols

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CONTENT

GENERAL INFORMATION

An orange solid, commonly known as Stryker's reagent ($[(PPh_3)CuH]_6$) was purchased from Acros Organics and stored in the glovebox to prevent the influence of air and moisture on the exact structure of the catalyst, similarly to the other reagents (silanols and hydrosilanes). Therefore, each reaction was also set up in a glovebox to minimize the impact of conditions on the process. However, as described later in the manuscript, the reaction can also proceed in an air atmosphere, and it is faster in this case.

Solvents used for all experiments were purchased from Honeywell, dried over calcium hydride (CaH_2), and purified by distillation. Silanols were purchased from Ambeed. Commercially available hydrosilanes were purchased from Sigma Aldrich (Merck), Angene or Ambeed, and used as received. Di-(p-tolyl)silane was synthesized *via* well-known procedure from the corresponding dichlorosilane through subsequent reduction over $LiAlH_4$.[1] (4-bromophenyl)dimethylsilane was synthesized via well-known procedure from 1,4-dibromobenzene.[2] The progress of reactions (conversion of silanols or hydrosilanes) was monitored by GC chromatography using Bruker Scion 460-GC and Agilent 5977B GC/MSD with Agilent 8860 GC System. The structures of products were determined by NMR spectroscopy, IR spectroscopy, and MS (mass spectrometry). The ^1H NMR (400 or 600 MHz), and ^{13}C NMR (101 or 151 MHz) spectra were recorded on Bruker Avance III HD NanoBay spectrometer, using chloroform-d ($CDCl_3$) as the solvent. Deuterated solvents were purchased from Sigma Aldrich (Merck) ($CDCl_3$ 99.8 atom% D) and used as received. FT- IR spectra were taken on a Nicolet™ iS50 FTIR Spectrometer. In the case of IR spectroscopy in real-time, the measurements were made using a ReactIR 15 Mettler Toledo spectrophotometer, equipped with a 9-reflection probe with a diamond window of 9.5 mm AgX DiComp Mettler Toledo and an MCT detector cooled with nitrogen.

STRUCTURES OF SUBSTRATES AND THEIR NUMBERING

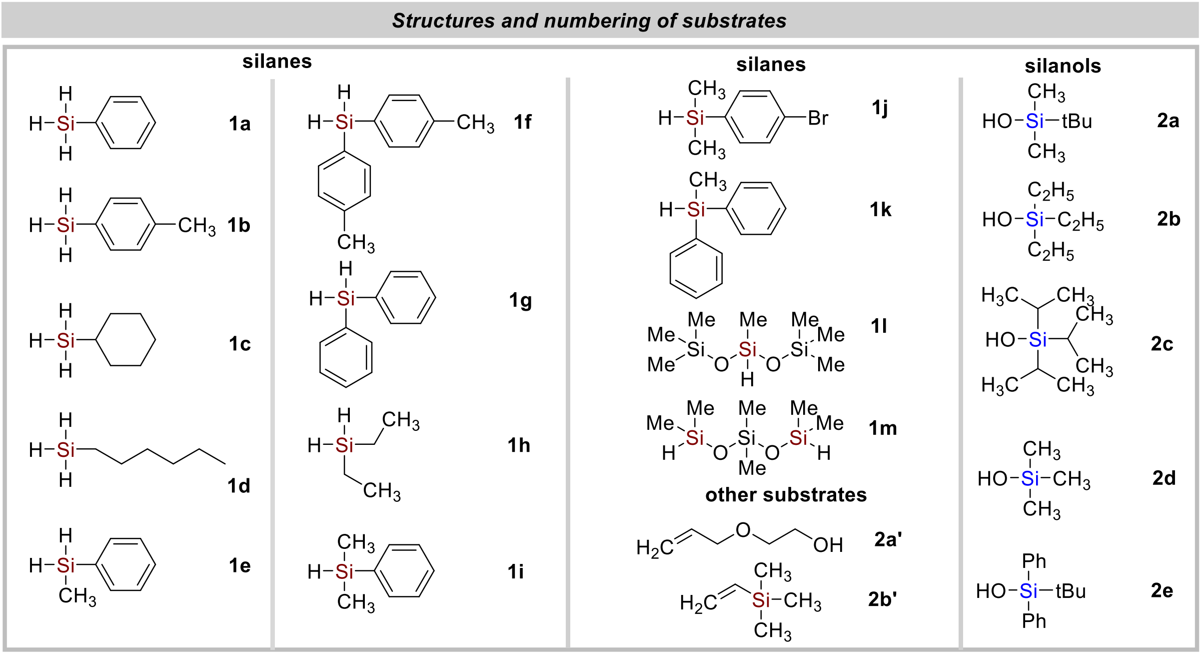
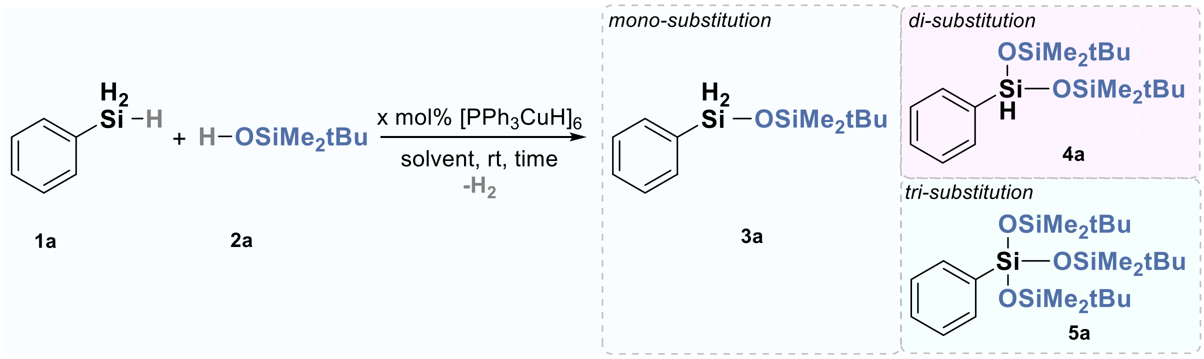


Figure S1. Structures and numbering of substrates used in the synthesis of siloxanes.

OPTIMIZATION OF REACTION CONDITIONS

Table S1. Optimization studies for a copper-catalyzed dehydrogenative silylation of phenylsilane with tert-butyldimethylsilanol.[a]



Entry	Variation of conditions	Catalyst loading (mol%)	Molar ratio [**1a**]:[**2a**]	Conversion of **1a** or **2a** [%][i]; {isolated yield};	Selectivity [%][j] [**3a**]:[**4a**]:[**5a**]
1	no catalyst[a]	-	1:1	0	-
2	no catalyst[b]	-	1:1	0	-
3	in toluene[c]	0.25	1:1	99 (**2a**)	91:9:0
4	in toluene[d]	0.25	1:1	99 (**2a**)	60:40:0
5	in toluene[c]	0.125	1:1	99 (**2a**); {**3a**, 80%}	90:10:0
6	in toluene[d]	0.125	1:1	99 (**2a**); {**3a**, 79%}	92:8:0
7	in toluene[d]	0.125	1.5:1	99 (**2a**); {**3a**, 82%}	98:2:0
8	in hexane[e]	0.125	1.5:1	99 (**2a**); {**3a**, 81%}	97:3:0
9	in toluene[d]	0.125	2:1	99 (**2a**); {**3a**, 87%}	99:1:0
10	in hexane[e]	0.125	2:1	99 (**2a**); {**3a**, 84%}	99:1:0
11	in acetonitrile[f]	0.125	2:1	99 (**2a**); {**3a**, 86%}	95:5:0
12	in 2-methyltetrahydrofuran[g]	0.125	2:1	65 (**2a**)	97:3:0
13	in toluene[d]	0.25	1:2	99 (**1a**); {**4a**, 92%}	0:100:0
14	in toluene[e]	0.25	1:3	99 (**1a**)	0:100:0
15	CuCl$_2$ instead of [PPh$_3$CuH]$_6$[h]	2	1:2	3 (**1a**)	0:100:0
16	Cu(OAc)$_2$ instead of [PPh$_3$CuH]$_6$[h]	2	1:2	2 (**1a**)	0:100:0

[a]All reaction conditions: **1a** (1 eq.), **2a** (1 eq.), toluene (0.25 mL), rt, under argon atmosphere, 20 h. [b]All reaction conditions: **1a** (1 eq.), **2a** (1 eq.), toluene, rt, under air atmosphere, 20 h. [c]Under argon atmosphere, 20 h. [d]Under air atmosphere, 30 min. [e]Under air atmosphere, 1 h. [f]Under air atmosphere, 3 h. [g]Under air atmosphere, 6 h. [h]Under air atmosphere, in toluene, 20 h. [i]Conversion of **1a** or **2a** determined by GC. [j]Selectivity of [mono-sub]:[di-sub]:[tri-sub] products determined by GC

GENERAL SYNTHETIC PROCEDURES

Synthesis of compounds 3a, 3e and 3f

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.125 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.5 mL), primary hydrosilane **1** (2 eq., 2 mmol), and the corresponding silanol **2** (1 eq., 1 mmol) were added.

Then the sealed vial with the reagents was removed from the glove box. At this point, the synthesis can be consistently conducted by stirring the contents of the sealed vial for 20 hours (this is the averaged time for all substrates to maintain a high level of conversion). Alternatively, the vial can be opened for 15 seconds, then closed, and the mixture stirred for 30 minutes (this is the averaged time for all substrates to maintain a high level of conversion).

After this time, regardless of the chosen method, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 ml) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure products were identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Synthesis of compounds 3b and 3c

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.125 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.5 mL), phenylsilane **1a** (3.0 eq., 3.0 mmol, 377 µL), and the corresponding silanol **2** (1.0 eq., 1.0 mmol) were added.

Then the sealed vial with the reagents was removed from the glove box. At this point, the synthesis can be consistently conducted by stirring the contents of the sealed vial for 20 hours (this is the averaged time for all substrates to maintain a high level of conversion). Alternatively, the vial can be opened for 15 seconds, then closed, and the mixture stirred for 30 minutes (this is the averaged time for all substrates to maintain a high level of conversion).

After this time, regardless of the chosen method, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure products **3b** and **3c** were identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Synthesis of compound 3d

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.125 mol%, 0.00125 g, 0.000637 mmol). Next, toluene (0.5 mL), phenylsilane **1a** (10.0 eq., 5.0 mmol, 608.7 µL), and trimethylsilanol **2d** (1.0 eq., 0.5 mmol, 11 µL) were added.

Then the sealed vial with the reagents was removed from the glove box. Next, the vial was opened for 15 seconds, then closed, and the mixture stirred for 30 minutes.

After this time, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure product **3d** was identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Synthesis of compounds 3g-3k

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.5 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.5 mL), secondary hydrosilane **1** (1 eq., 0.25 mmol), and the corresponding silanol **2** (1 eq., 0.25 mmol) were added.

Then the sealed vial with the reagents was removed from the glove box. At this point, the synthesis can be consistently conducted by stirring the contents of the sealed vial for 20 hours (this is the averaged time for all substrates to maintain a high level of conversion). Alternatively, the vial can be opened for 15 seconds, then closed, and the mixture stirred for 30 minutes (this is the averaged time for all substrates to maintain a high level of conversion).

After this time, regardless of the chosen method, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure products **3g**-**3k** were identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Synthesis of compound 3l-3o

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.125 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.25 mL), tertiary hydrosilane **1i-1l** (1.0 eq., 1.0 mmol, 153 µL), and trimethylsilanol **2d** (1.5 eq., 1.5 mmol, 165 µL) were added.

Then the sealed vial with the reagents was removed from the glove box. Next, the vial was opened for 15 seconds in ambient atmosphere, then closed, and the mixture stirred for 30 minutes.

After this time, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure products **3l-3o** were identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Synthesis of compound 3p

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.250 mol%, 0.0050 g, 0.00254 mmol). Next, toluene (0.25 mL), 1,1,3,3,5,5-hexamethyltrisiloxane **1m** (1.0 eq., 1.0 mmol, 0.208 g), and trimethylsilanol **2d** (3.0 eq., 2.0 mmol, 170 μL) were added.

Then the sealed vial with the reagents was removed from the glove box. Next, the vial was opened for 15 seconds in ambient atmosphere, then closed, and the mixture stirred for 30 minutes.

After this time, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure products **3p** was identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Synthesis of compounds 4a-4i

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.25 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.25 mL), primary hydrosilane **1** (1.0 eq., 0.5 mmol), and the corresponding silanol **2** (2.0 eq., 1.0 mmol) were added.

Then the sealed vial with the reagents was removed from the glove box. At this point, the synthesis can be consistently conducted by stirring the contents of the sealed vial for 20 hours (this is the averaged time for all substrates to maintain a high level of conversion). Alternatively, the vial can be opened for 15 seconds, then closed, and the mixture stirred for 30 minutes (this is the averaged time for all substrates to maintain a high level of conversion).

After this time, regardless of the chosen method, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure products **4a**-**4i** were identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Synthesis of compounds 4j and 4k

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.25 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.25 mL), secondary hydrosilane **1** (1.0 eq., 0.5 mmol), and trimethylsilanol **2** (2.0 eq., 1.0 mmol, 112.8 μL) were added.

Then the sealed vial with the reagents was removed from the glove box. Next, the vial was opened for 15 seconds, then closed, and the mixture stirred for 30 minutes (this is the averaged time for all substrates to maintain a high level of conversion).

After this time, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure products **4j** and **4k** were identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Synthesis of compounds 5a and 5b

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.5 mol%, 0.0050 g, 0.00254 mmol). Next, toluene (0.25 mL), primary hydrosilane **1** (1.0 eq., 0.5 mmol), and trimethylsilanol **2** (1.5 eq., 0.75 mmol, 84.6 μL) were added.

Then the sealed vial with the reagents was removed from the glove box. Next, the vial was opened for 15 seconds, then closed, and the mixture stirred for 30 minutes.

After this time, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure products **5a** and **5b** were identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Alcoholysis of mono-hydrosiloxane 4a with 2-allyloxyethanol (2a')

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (1 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.25 mL), hydrosiloxane **4a** (1.0 eq., 0.127 mmol, 0.036 g), and 2-allyloxyethanol (**2a'**) (2.0 eq., 0.254 mmol, 0.026 g) were added.

Then the sealed vial with the reagents was removed from the glove box. Then, the vial was opened for 15 seconds in ambient atmosphere, then closed, and the mixture stirred for 30 minutes.

After this time, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure product **6a** was identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, and mass spectrometry.

Hydrosilylation of vinyltrimethylsilane (2b') with 4e

To a 5 mL vial equipped with a magnetic stirring bar, [Pt_2(dvdms)$_3$] was added (0.2 mol%). Next, toluene (0.5 mL), hydrosiloxane **4e** (1.0 eq., 0.1 mmol, 0.029 g), and vinyltrimethylsilane (**2b'**) (1.2 eq., 0.12 mmol, 0.012 g) were added. The vial was stirred for 4 hours at 60°C. After this time, toluene and low-boiling residue of the reagents were evaporated. Then, the crude product was separated from the residues *via* bulb-to-bulb distillation under reduced pressure. The pure product **6b** was identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Scaled-up synthesis of 4c

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 5 mL vial equipped with a magnetic stirring bar, [(PPh_3)CuH]$_6$ was added (0.25 mol%, 0.0196 g, 0.01 mmol). Next, toluene (0.25 mL), phenylsilane **1a** (1.0 eq., 4.0 mmol, 492.5 µL), and tert-butyldimethylsilanol **2a** (2.0 eq., 8.0 mmol, 1.26 mL) were added.

Then the sealed vial with the reagents was removed from the glove box. Next, the vial was opened for 15 seconds in ambient atmosphere, then closed, and the mixture stirred for 30 minutes.

After this time, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (10 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure product **4c** was obtained in 90% yield (1.32 g).

Synthesis of compound 4c in the presence of TEMPO

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To two 5 mL vials equipped with a magnetic stirring bar, [(PPh_3)CuH]$_6$ was added (0.25 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.25 mL), phenylsilane **1a** (1.0 eq., 0.5 mmol), *tert*-butyldimethylsilanol **2a** (2.0 eq., 1.0 mmol), and TEMPO (1.0 eq.) were added.

To another two 5 mL vials equipped with a magnetic stirring bar, [(PPh_3)CuH]$_6$ was added (0.25 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.25 mL), phenylsilane **1a** (1.0 eq., 0.5 mmol), *tert*-butyldimethylsilanol **2a** (2.0 eq., 1.0 mmol), and TEMPO (2.0 eq.) were added.

Then the sealed vials with the reagents were removed from the glove box. At this point, the synthesis in the presence of TEMPO was conducted by stirring the contents of the sealed vial for 24 hours (reaction under argon atmosphere) or alternatively, the vial was opened for 15 seconds, then closed, and the mixture stirred for 30 minutes. Such a procedure was repeated for both scenarios – with 1.0 eq. and 2.0 eq. of TEMPO.

After this time, regardless of the chosen method, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the vial were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure product **4c** was identified by mass spectrometry and its yield was calculated.

Synthesis of compound 4c in the presence of mercury drops

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To two 25 mL Schlenk tube equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.25 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.25 mL), phenylsilane **1a** (1.0 eq., 0.5 mmol), and *tert*-butyldimethylsilanol **2a** (2.0 eq., 1.0 mmol) were added.

Then the sealed Schlenk tubes with the reagents were removed from the glove box. At this point, few drops of mercury were added to Schlenk tubes under an argon atmosphere using Schlenk line. Subsequently, the synthesis in the presence of Hg was conducted by stirring the content of the sealed tube for 24 hours (reaction under argon atmosphere) or alternatively, the tube was opened for 15 seconds, then closed, and the mixture stirred for 30 minutes.

After this time, regardless of the chosen method, toluene and low-boiling residue of the reagents were evaporated. Subsequently, the remaining substances in the tubes were washed with pentane (2 mL) and filtered through a celite-packed Pasteur pipette. Then, using rotavap, pentane was removed, and the remaining product was separated from all low-boiling residues under reduced pressure. The pure product **4c** was identified by mass spectrometry and its yield was calculated.

Use of real-time FT-IR spectroscopy during the synthesis of compound 4c

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

To a 25 mL Schlenk tube equipped with a magnetic stirring bar, $[(PPh_3)CuH]_6$ was added (0.25 mol%, 0.0025 g, 0.00127 mmol). Next, toluene (0.25 mL), phenylsilane **1a** (1.0 eq., 0.5 mmol), and *tert*-butyldimethylsilanol **2a** (2.0 eq., 1.0 mmol) were added.

Then the sealed Schlenk tube with the reagents was removed from the glove box. Next, the test tube was opened, and the IR probe was immediately inserted.

In-situ FT-IR analysis showed that after approximately 5 minutes, full conversion of the substrates to product **4c** was already observed.

Use of NMR spectroscopy during mechanistic studies

Attention! The entire procedure of taking and weighing individual reagents was carried out in a glove box.

Conditions 1: $[(PPh_3)CuH]_6$ (10 mg) in 0.6 mL of C_6D_6

Conditions 2: $tBuMe_2SiOH$ (20 μL) in 0.6 mL of C_6D_6

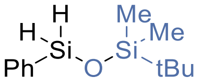
Conditions 3: $PhSiH_3$ (20 μL) in 0.6 mL of C_6D

Conditions 4: $[(PPh_3)CuH]_6$ (10 mg) and $PhSiH_3$ (6.3 μL) in 0.5 mL of C_6D_6

Conditions 5: $[(PPh_3)CuH]_6$ (10 mg) and $tBuMe_2SiOH$ (8 μL) in 0.5 mL of C_6D_6

CHARACTERIZATION DATA FOR ALL PRODUCTS

1-(*tert*-Butyl)-1,1-dimethyl-3-phenyldisiloxane (3a)



1-(*tert*-Butyl)-1,1-dimethyl-3-phenyldisiloxane was obtained in 87% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[3]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 2H), 7.40 – 7.28 (m, 3H), 5.03 (s, 2H), 0.82 (s, 9H), -0.00 (s, 6H).

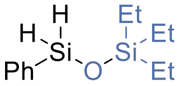
^{13}C NMR: (101 MHz, $CDCl_3$) δ 135.2, 134.1, 130.3, 128.1, 25.8, 18.5, -3.3.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 15.5, -30.2.

EI-MS m/z (rel. int.): 195 ($[M-C_3H_7]^+$, 1%), 181 (100), 165 (15), 57 (30).

IR: (neat) vmax cm^{-1}: 2954, 2929, 2857, 2138, 1254, 1122, 1056, 900.

1,1,1-Triethyl-3-phenyldisiloxane (3b)



1,1,1-Triethyl-3-phenyldisiloxane was obtained in 90% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[3]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56 – 7.44 (m, 2H), 7.36 – 7.21 (m, 3H), 5.01 (s, 2H), 0.82 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 8.5, Hz, 6H).

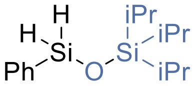
^{13}C NMR: (101 MHz, $CDCl_3$) δ 135.4, 134.0, 130.3, 128.1, 6.8, 6.1.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 15.1, -30.0.

EI-MS m/z (rel. int.): 209 ($[M-C_2H_5]^+$, 100%), 181 (40), 153 (40), 78 (30).

IR: (neat) vmax cm^{-1}: 2955, 2876, 2138, 1238, 1122, 1059, 951.

1,1,1-Triisopropyl-3-phenyldisiloxane (3c)



1,1,1-Triisopropyl-3-phenyldisiloxane was obtained in 76% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[3]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.74 – 7.47 (m, 2H), 7.41 – 7.25 (m, 3H), 5.12 (s, 2H), 1.05 – 0.57 (m, 21H).

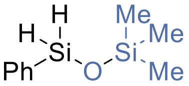
^{13}C NMR: (101 MHz, $CDCl_3$) δ 135.5, 134.1, 130.3, 128.1, 17.9, 12.8.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 11.0, -30.0.

EI-MS m/z (rel. int.): 237 ($[M-C_3H_7]^+$, 100%), 209 (30), 181 (35), 167 (40).

IR: (neat) vmax cm^{-1}: 3071, 2942, 2865, 2141, 1592, 1247, 1054, 839.

1,1,1-Trimethyl-3-phenyldisiloxane (3d)



1,1,1-Trimethyl-3-phenyldisiloxane was obtained in 88% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[3]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 2H), 7.34 – 7.23 (m, 3H), 4.94 (s, 2H), -0.00 (s, 9H).

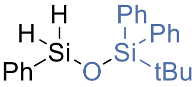
^{13}C NMR: (101 MHz, $CDCl_3$) δ 136.0, 134.1, 130.3, 128.2, 1.5.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 13.2, -30.5.

EI-MS m/z (rel. int.): 196 ($[M]^+$, 5%), 181 (100), 165 (5), 78 (30).

IR: (neat) vmax cm^{-1}: 3070, 2958, 2139, 1429, 1253, 1122, 1053, 905.

1-(*tert*-Butyl)-1,1,3-triphenyldisiloxane (3e)



1-(*tert*-Butyl)-1,1,3-triphenyldisiloxane was obtained in 99% yield as a colorless oil. The title compound is a new compound.

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.76 – 7.52 (m, 5H), 7.42 – 7.17 (m, 10H), 5.24 (s, 2H), 0.97 (s, 9H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 135.1, 135.0, 134.6, 134.3, 130.5, 129.7, 128.2, 127.8, 26.7, 19.7.

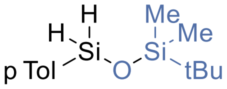
^{29}Si NMR: (80 MHz, $CDCl_3$) δ -2.0, -32.9.

EI-MS m/z (rel. int.): 305 ($[M-C_4H_9]^+$, 100%), 227 (40), 181 (25), 57 (10).

IR: (neat) vmax cm^{-1}: 3071, 2930, 2857, 2160, 1591, 1428, 1048, 833.

EA: $C_{22}H_{26}OSi_2$ (362.152): calcd. C 72.87, H 7.23; found C 73.03, H 7.28.

1-(*tert*-Butyl)-1,1-dimethyl-3-(p-tolyl)disiloxane (3f)



1-(*tert*-Butyl)-1,1-dimethyl-3-(*p*-tolyl)disiloxane was obtained in 95% yield as a colorless oil. The title compound is a new compound.

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56 – 7.36 (m, 2H), 7.17 – 7.06 (m, 2H), 5.02 (s, 2H), 2.31 (s, 3H), 0.82 (s, 9H), -0.00 (s, 6H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 134.2, 133.5, 133.4, 128.9, 128.7, 128.7, 25.8, 21.8, -2.9, -3.3.

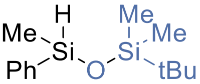
^{29}Si NMR: (80 MHz, $CDCl_3$) δ 15.3, -30.0.

EI-MS m/z (rel. int.): 237 ($[M-CH_3]^+$, 1%), 195 (100), 179 (10), 91 (10).

IR: (neat) vmax cm^{-1}: 2954, 2857, 2142, 1604, 1253, 1117, 954, 645.

EA: $C_{13}H_{24}OSi_2$ (252.137): calcd. C 61.84, H 9.58; found C 61.99, H 9.62.

1-(*tert*-Butyl)-1,1,3-trimethyl-3-phenyldisiloxane (3g)



1-(*tert*-Butyl)-1,1,3-trimethyl-3-phenyldisiloxane was obtained in 99% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[4]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.61 – 7.48 (m, 2H), 7.37 – 7.29 (m, 3H), 5.13 (q,

J = 2.8 Hz, 1H), 0.83 (s, 9H), 0.36 (d, *J* = 2.8 Hz, 3H), -0.00 (s, 6H).

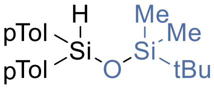
^{13}C NMR: (101 MHz, $CDCl_3$) δ 138.1, 133.5, 129.8, 128.0, 77.5, 77.2, 76.8, 25.8, 18.4, -0.0, -3.0.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 13.5, -14.9.

EI-MS m/z (rel. int.): 237 ($[M-CH_3]^+$, 5%), 195 (100), 179 (20), 135 (10).

IR: (neat) vmax cm^{-1}: 3070, 2928, 2857, 2122, 1592, 1120, 1005, 893.

1-(*tert*-Butyl)-1,1-dimethyl-3,3-di-p-tolyldisiloxane (3h)



1-(*tert*-Butyl)-1,1-dimethyl-3,3-di-p-tolyldisiloxane was obtained in 80% yield as a colorless oil. The title compound is a new compound.

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.52 – 7.37 (m, 4H), 7.20 – 7.02 (m, 4H), 5.42 (s, 1H), 2.31 (s, 6H), 0.83 (s, 9H), -0.00 (s, 6H).

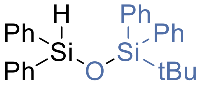
^{13}C NMR: (101 MHz, $CDCl_3$) δ 140.0, 134.4, 132.9, 128.8, 25.9, 21.7, 18.5, -3.0.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 14.4, -22.4.

EI-MS m/z (rel. int.): 285 ($[M-C_4H_9]^+$, 100%), 193 (40), 149 (10), 91 (10).

IR: (neat) vmax cm^{-1}: 3012, 2856, 2119, 1603, 1471, 1253, 1020, 831.

1-(*tert*-Butyl)-1,1,3,3-tetraphenyldisiloxane (3i)



1-(*tert*-Butyl)-1,1,3,3-tetraphenyldisiloxane was obtained in 99% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[5]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.57 – 7.43 (m, 8H), 7.37 – 7.16 (m, 12H), 5.63 (s, 1H), 0.94 (s, 9H).

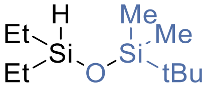
^{13}C NMR: (101 MHz, $CDCl_3$) δ 135.6, 135.2, 134.6, 130.2, 129.6, 128.0, 127.9, 127.7, 26.9, 19.7.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ -9.1, -20.6.

EI-MS m/z (rel. int.): 381 ($[M-C_4H_9]^+$, 100%), 303 (50), 181 (25), 78 (20).

IR: (neat) vmax cm^{-1}: 3069, 2857, 2127, 1428, 1262, 1111, 1026, 732.

1-(*tert*-Butyl)-3,3-diethyl-1,1-dimethyldisiloxane (3j)



1-(*tert*-Butyl)-3,3-diethyl-1,1-dimethyldisiloxane was obtained in 88% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[4]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.51 (t, J = 2.3 Hz, 1H), 0.99 (t, J = 7.9 Hz, 6H), 0.90 (s, 9H), 0.62 (qd, J = 7.9, 2.2 Hz, 4H), 0.06 (s, 6H).

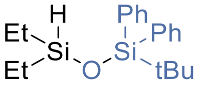
^{13}C NMR: (101 MHz, $CDCl_3$) δ 25.8, 18.4, 7.2, 6.7, -3.1.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 11.8, -0.7.

EI-MS m/z (rel. int.): 175 ($[M-C_3H_7]^+$, 1%), 161 (100), 133 (80), 105 (85).

IR: (neat) vmax cm^{-1}: 2955, 2878, 2106, 1471, 1252, 1054, 1003, 967.

1-(*tert*-Butyl)-3,3-diethyl-1,1-diphenyldisiloxane (3k)



1-(*tert*-Butyl)-3,3-diethyl-1,1-diphenyldisiloxane was obtained in 98% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[6]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.80 – 7.47 (m, 4H), 7.37 – 7.18 (m, 6H), 5.20 – 4.40 (m, 1H), 0.97 (s, 9H), 0.86 (t, J = 7.9 Hz, 6H), 0.67 – 0.54 (m, 4H).

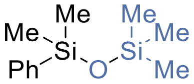
^{13}C NMR: (101 MHz, $CDCl_3$) δ 135.8, 135.1, 129.5, 127.7, 26.8, 19.6, 7.2, 6.7.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 1.6, -11.6.

EI-MS m/z (rel. int.): 285 ($[M-C_4H_9]^+$, 100%), 183 (20), 151 (20), 57 (30).

IR: (neat) vmax cm^{-1}: 3071, 2956, 2857, 2107, 1427, 1235, 1109, 1069.

1,1,1,3,3-Pentamethyl-3-phenyldisiloxane (3l)



1,1,1,3,3-Pentamethyl-3-phenyldisiloxane was obtained in 90% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[7]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.99 – 7.37 (m, 2H), 7.36 – 7.15 (m, 3H), 0.23 (s, 6H), -0.00 (s, 9H).

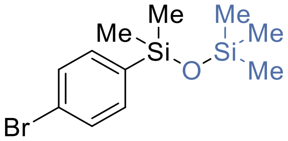
^{13}C NMR: (101 MHz, $CDCl_3$) δ 140.6, 133.4, 129.6, 128.1, 2.4, 1.3.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 8.7, -2.6.

EI-MS m/z (rel. int.): 224 ($[M]^+$, 1%), 209 (100), 193 (30), 91 (10).

IR: (neat) vmax cm^{-1}: 3071, 2959, 1429, 1254, 1121, 1059, 840.

1-(4-Bromophenyl)-1,1,3,3,3-pentamethyldisiloxane (3m)



1-(4-Bromophenyl)-1,1,3,3,3-pentamethyldisiloxane was obtained in 80% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[8]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.27 – 7.23 (m, 2H), 0.16 (s, 6H), -0.06 (s, 9H).

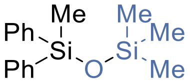
^{13}C NMR: (101 MHz, $CDCl_3$) δ 139.1, 134.7, 131.0, 124.1, 2.1, 1.0.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 9.2, -2.5.

EI-MS m/z (rel. int.): 304 ($[M]^+$, 2%), 289 (30), 207 (100), 91 (15).

IR: (neat) vmax cm^{-1}: 2956, 1575, 1480, 1376, 1253, 1048, 837, 722.

1,1,1,3-Tetramethyl-3,3-diphenyldisiloxane (3n)



1,1,1,3-Tetramethyl-3,3-diphenyldisiloxane was obtained in 83% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[9]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 – 7.52 (m, 4H), 7.43 – 7.30 (m, 6H), 0.62 (s, 3H), 0.12 (s, 9H).

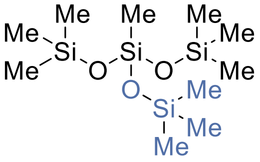
^{13}C NMR: (101 MHz, $CDCl_3$) δ 138.1, 133.7, 129.3, 127.5, 1.8, -0.7.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 9.9, -12.4.

EI-MS m/z (rel. int.): 286 ($[M]^+$, 5%), 271 (100), 193 (70), 135 (10).

IR: (neat) vmax cm^{-1}: 3069, 2956, 1428, 1253, 1113, 1046, 837, 695.

1,1,1,3,5,5,5-Heptamethyl-3-((trimethylsilyl)oxy)trisiloxane (3o)



1,1,1,3,5,5,5-Heptamethyl-3-((trimethylsilyl)oxy)trisiloxane was obtained in 84% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[9]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 0.10 (s, 27H), -0.00 (s, 3H).

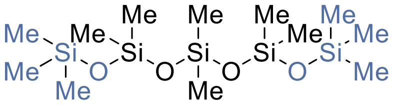
^{13}C NMR: (101 MHz, $CDCl_3$) δ 1.8, -2.0.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 7.4, -64.3.

EI-MS m/z (rel. int.): 295 ($[M-CH_3]^+$, 20%), 279 (10), 207 (100), 73 (70).

IR: (neat) vmax cm^{-1}: 2959, 1251, 1045, 873, 837, 792, 756, 689.

1,1,1,3,3,5,5,7,7,9,9,9-Dodecamethylpentasiloxane (3p)



1,1,1,3,3,5,5,7,7,9,9,9-Dodecamethylpentasiloxane was obtained in 97% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[10]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 0.00 (s, 18H), -0.02 (s, 6H), -0.04 (s, 12H).

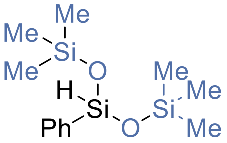
^{13}C NMR: (101 MHz, $CDCl_3$) δ 1.9, 1.3.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 7.3, -21.4, -22.2.

EI-MS m/z (rel. int.): 369 ($[M-CH_3]^+$, 20%), 281 (100), 147 (100), 73 (90).

IR: (neat) vmax cm^{-1}: 3055, 2960, 1589, 1435, 1258, 1192, 1118, 720.

1,1,1,5,5,5-Hexamethyl-3-phenyltrisiloxane (4a)



1,1,1,5,5,5-Hexamethyl-3-phenyltrisiloxane was obtained in 92% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[4]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.31 – 7.17 (m, 3H), 4.84 (s, 1H), 0.00 (s, 18H).

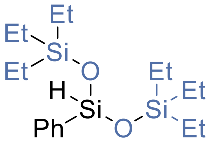
^{13}C NMR: (101 MHz, $CDCl_3$) δ 137.2, 133.3, 130.2, 127.9, 1.9.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 10.7, -49.4.

EI-MS m/z (rel. int.): 283 ($[M]^+$, 10%), 269 (100), 135 (70), 121 (30).

IR: (neat) vmax cm^{-1}: 2958, 2152, 1430, 1252, 1125, 1047, 823, 753.

1,1,1,5,5,5-Hexaethyl-3-phenyltrisiloxane (4b)



1,1,1,5,5,5-Hexaethyl-3-phenyltrisiloxane was obtained in 94% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[11]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.57 – 7.32 (m, 2H), 7.27 – 7.09 (m, 3H), 4.88 (s, 1H), 0.90 – 0.73 (m, 18H), 0.51 – 0.35 (m, 12H).

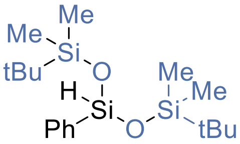
^{13}C NMR: (101 MHz, $CDCl_3$) δ 137.6, 133.2, 130.1, 127.8, 6.8, 6.3.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 13.0, -49.6.

EI-MS m/z (rel. int.): 283 (25%), 269 (100), 135 (40), 121 (15).

IR: (neat) vmax cm^{-1}: 2954, 2876, 2147, 1458, 1238, 1124, 1002, 851.

1,5-Di-*tert*-butyl-1,1,5,5-tetramethyl-3-phenyltrisiloxane (4c)



1,5-Di-*tert*-butyl-1,1,5,5-tetramethyl-3-phenyltrisiloxane obtained in 92% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[12]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.35 – 7.26 (m, 3H), 4.97 (s, 1H), 0.89 – 0.71 (m, 18H), 0.03 – -0.04 (m, 12H).

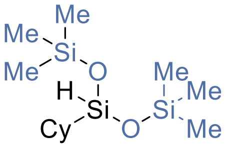
^{13}C NMR: (101 MHz, $CDCl_3$) δ 137.3, 133.2, 130.1, 127.9, 25.8, 18.3, -2.9.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 13.2, -49.4.

EI-MS m/z (rel. int.): 353 ($[M-CH_3]^+$, 1%), 311 (100), 269 (50), 57 (50).

IR: (neat) vmax cm^{-1}: 2955, 2929, 2857, 2147, 1471, 1253, 1124, 1049.

3-Cyclohexyl-1,1,1,5,5,5-hexamethyltrisiloxane (4d)



3-Cyclohexyl-1,1,1,5,5,5-hexamethyltrisiloxane obtained in 99% yield as a colorless oil. The title compound is a new compound.

^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.26 (s, 1H), 1.66 – 1.50 (m, 5H), 1.17 – 0.94 (m, 5H), 0.56 – 0.37 (m, 1H), -0.00 (s, 18H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 27.6, 27.1, 26.7, 25.8, 1.9.

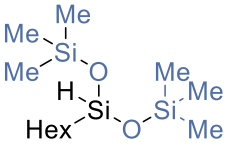
^{29}Si NMR: (80 MHz, $CDCl_3$) δ 9.0, -37.0.

EI-MS m/z (rel. int.): 290 ($[M]^+$, 1%), 207 (100), 193 (40), 73 (40).

IR: (neat) vmax cm^{-1}: 2958, 2849, 2130, 1448, 1251, 1189, 1049, 996.

EA: $C_{12}H_{30}O_2Si_3$ (290.155): calcd. C 49.59, H 10.41; found C 49.48, H 10.42.

3-Hexyl-1,1,1,5,5,5-hexamethyltrisiloxane (4e)



3-Hexyl-1,1,1,5,5,5-hexamethyltrisiloxane obtained in 87% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[4]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.44 (s, 1H), 1.28 – 1.10 (m, 8H), 0.85 – 0.70 (m, 3H), 0.59 – 0.31 (m, 2H), -0.00 (s, 18H).

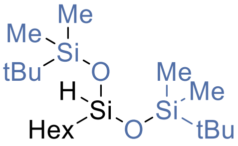
^{13}C NMR: (101 MHz, $CDCl_3$) δ 32.7, 31.8, 22.7, 22.2, 17.4, 14.3, 1.8.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 9.1, -36.0.

EI-MS m/z (rel. int.): 291 ($[M]^+$, 5%), 277 (50), 207 (100), 193 (60).

IR: (neat) vmax cm^{-1}: 2957, 2858, 2138, 1457, 1251, 1044, 889, 825.

1,5-Di-*tert*-butyl-3-hexyl-1,1,5,5-tetramethyltrisiloxane (4f)



1,5-Di-*tert*-butyl-3-hexyl-1,1,5,5-tetramethyltrisiloxane obtained in 95% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[4]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.55 (s, 1H), 1.37 – 1.17 (m, 8H), 0.85 – 0.80 (m, 21H), 0.58 – 0.35 (m, 2H), -0.00 (s, 12H).

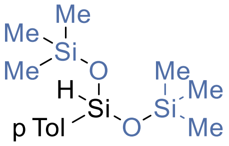
^{13}C NMR: (101 MHz, $CDCl_3$) δ 32.8, 31.8, 25.8, 22.7, 22.2, 18.3, 17.6, 14.3, -3.0.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 11.1, -36.6.

EI-MS m/z (rel. int.): 361 ($[M-CH_3]^+$, 1%), 319 (100), 235 (60), 57 (65).

IR: (neat) vmax cm^{-1}: 2955, 2857, 2133, 1471, 1362, 1253, 1004, 880.

1,1,1,5,5,5-Hexamethyl-3-(p-tolyl)trisiloxane (4g)



1,1,1,5,5,5-Hexamethyl-3-(p-tolyl)trisiloxane obtained in 98% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[4]

^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.48 – 7.24 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 4.83 (s, 1H), 2.22 (s, 3H), -0.00 (s, 18H).

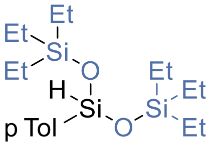
^{13}C NMR: (101 MHz, CDCl$_3$) δ 140.1, 133.8, 133.3, 128.7, 21.7, 1.9.

^{29}Si NMR: (80 MHz, CDCl$_3$) δ 10.5, -48.9.

EI-MS m/z (rel. int.): 297 ([M]$^+$, 20%), 283 (100), 149 (60), 91 (30).

IR: (neat) vmax cm^{-1}: 2958, 2151, 1606, 1393, 1251, 1119, 876, 824.

1,1,1,5,5,5-Hexaethyl-3-(*p*-tolyl)trisiloxane (4h)



1,1,1,5,5,5-Hexaethyl-3-(*p*-tolyl)trisiloxane obtained in 81% yield as a colorless oil. The title compound is a new compound.

^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 4.91 (s, 1H), 2.24 (s, 3H), 1.03 – 0.68 (m, 18H), 0.46 (q, *J* = 7.9 Hz, 12H).

^{13}C NMR: (101 MHz, CDCl$_3$) δ 140.2, 134.5, 133.6, 129.0, 22.1, 7.1, 6.6.

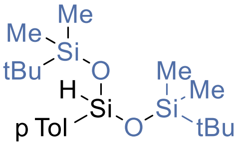
^{29}Si NMR: (80 MHz, CDCl$_3$) δ 12.8, -49.2.

EI-MS m/z (rel. int.): 353 ([M-C_2H_5]$^+$, 100%), 323 (10), 121 (20), 91 (15).

IR: (neat) vmax cm^{-1}: 2954, 2876, 2145, 1606, 1414, 1119, 1002, 853.

EA: $C_{19}H_{38}O_2Si_3$ (382.218): calcd. C 59.62, H 10.01; found C 59.45, H 9.57.

1,5-Di-*tert*-butyl-1,1,5,5-tetramethyl-3-(p-tolyl)trisiloxane (4i)



1,5-Di-*tert*-butyl-1,1,5,5-tetramethyl-3-(p-tolyl)trisiloxane obtained in 87% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[4]

^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.57 – 7.46 (m, 2H), 7.39 – 7.24 (m, 3H), 5.03 – 4.84 (m, 1H), 0.86 – 0.72 (m, 18H), 0.09 – -0.05 (m, 12H).

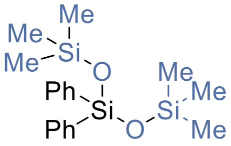
^{13}C NMR: (101 MHz, CDCl$_3$) δ 137.3, 133.2, 130.1, 127.9, 25.8, 18.3, -2.9.

^{29}Si NMR: (80 MHz, CDCl$_3$) δ 13.3, -49.4.

EI-MS m/z (rel. int.): 353 ([M-CH_3]$^+$, 1%), 311 (100), 269 (50), 57 (50).

IR: (neat) vmax cm^{-1}: 2955, 2929, 2147, 1471, 1253, 1124, 1049, 1004.

1,1,1,5,5,5-Hexamethyl-3,3-diphenyltrisiloxane (4j)



1,1,1,5,5,5-Hexamethyl-3,3-diphenyltrisiloxane obtained in 82% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[13]

^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.50 – 7.43 (m, 4H), 7.29 – 7.19 (m, 6H), -0.00 (s, 18H).

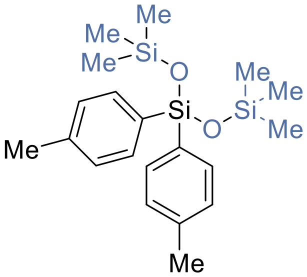
^{13}C NMR: (101 MHz, CDCl$_3$) δ 136.8, 134.3, 129.8, 127.7, 2.0.

^{29}Si NMR: (80 MHz, CDCl$_3$) δ 9.7, -47.5.

EI-MS m/z (rel. int.): 360 ([M]$^+$, 1%), 345 (100), 267 (30), 135 (45).

IR: (neat) vmax cm^{-1}: 3070, 2957, 1592, 1429, 1251, 998, 835, 716.

1,1,1,5,5,5-hexamethyl-3,3-di-*p*-tolyltrisiloxane (4k)



1,1,1,5,5,5-hexamethyl-3,3-di-*p*-tolyltrisiloxane obtained in 86% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[14]

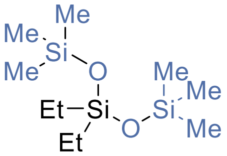
^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.36 (d, J = 7.9 Hz, 2H), 7.06 – 7.03 (m, 2H), 2.24 (s, 6H), 0.00 (s, 18H).

^{13}C NMR: (101 MHz, CDCl$_3$) δ 139.9, 134.7, 133.8, 128.8, 22.0, 2.4.

^{29}Si NMR: (80 MHz, CDCl$_3$) δ 9.3, -46.5.

EI-MS m/z (rel. int.): 388 ([M]$^+$, 10%), 373 (100), 281 (90), 149 (90).

3,3-Diethyl-1,1,1,5,5,5-hexamethyltrisiloxane (4l)



3,3-Diethyl-1,1,1,5,5,5-hexamethyltrisiloxane obtained in 96% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[15]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.9 Hz, 6H), 0.35 (q, *J* = 8.0 Hz, 4H), -0.00 (s, 18H).

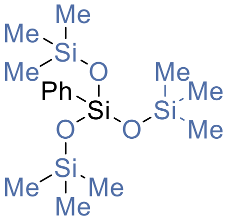
^{13}C NMR: (101 MHz, $CDCl_3$) δ 7.3, 6.4, 1.7.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 6.5, -20.8.

EI-MS m/z (rel. int.): 249 ($[M-CH_3]^+$, 30%), 235 (100), 73 (30), 59 (25).

IR: (neat) vmax cm^{-1}: 2957, 2879, 1459, 1414, 1251, 1044, 1010, 834.

1,1,1,5,5,5-Hexamethyl-3-phenyl-3-((trimethylsilyl)oxy)trisiloxane (5a)



1,1,1,5,5,5-Hexamethyl-3-phenyl-3-((trimethylsilyl)oxy)trisiloxane obtained in 95% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[9]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.32 – 7.18 (m, 3H), -0.00 (s, 27H).

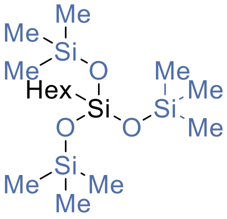
^{13}C NMR: (101 MHz, $CDCl_3$) δ 135.7, 134.0, 129.6, 127.7, 1.9.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 8.8, -77.9.

EI-MS m/z (rel. int.): 357 ($[M-CH_3]^+$, 50%), 253 (55), 207 (70), 135 (100).

IR: (neat) vmax cm^{-1}: 2958, 1430, 1250, 1129, 1044, 833, 753, 716.

3-Hexyl-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (5b)



3-Hexyl-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane obtained in 95% yield as a colorless oil. The title compound was known in the literature, and all spectroscopic data are in agreement.[16]

^{1}H NMR: (400 MHz, $CDCl_3$) δ 1.26 – 1.11 (m, 8H), 0.89 – 0.71 (m, 3H), 0.40 – 0.29 (m, 2H), -0.00 (s, 27H).

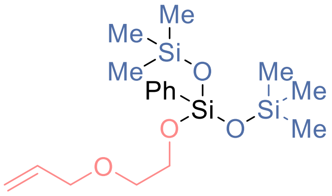
^{13}C NMR: (101 MHz, $CDCl_3$) δ 33.0, 31.8, 23.5, 22.8, 14.6, 14.3, 1.9.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 7.0, -65.2.

EI-MS m/z (rel. int.): 365 ($[M-CH_3]^+$, 10%), 207 (80), 193 (60), 73 (100).

IR: (neat) vmax cm^{-1}: 2958, 2925, 1456, 1190, 1042, 834, 753, 710.

3-(2-(Allyloxy)ethoxy)-1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane (6a)



3-(2-(Allyloxy)ethoxy)-1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane obtained in 82% yield as a colorless oil. The title compound is a new compound.

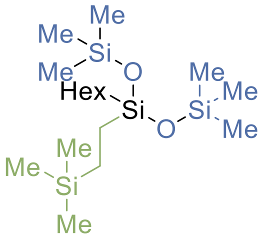
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 2H), 7.30 – 7.13 (m, 3H), 5.83 – 5.67 (m, 1H), 5.24 – 4.94 (m, 2H), 3.87 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.73 (t, *J* = 5.6 Hz, 2H), 3.42 (t, *J* = 5.6 Hz, 2H), -0.00 (s, 18H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 135.1, 134.4, 134.1, 130.0, 127.8, 116.9, 72.3, 71.2, 62.0, 1.9.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 13.1, -78.1.

EA: $C_{17}H_{32}O_4Si_3$ (384.161): calcd. C 53.08, H 8.38; found C 53.27, H 8.43.

3-Hexyl-1,1,1,5,5,5-hexamethyl-3-(2-(trimethylsilyl)ethyl)trisiloxane (6b)



3-Hexyl-1,1,1,5,5,5-hexamethyl-3-(2-(trimethylsilyl)ethyl)trisiloxane obtained in 85% yield as a colorless oil. The title compound is a new compound.

^{1}H NMR: (400 MHz, $CDCl_3$) δ 1.26 – 1.15 (m, 8H), 0.86 – 0.76 (m, 3H), 0.44 – 0.35 (m, 2H), 0.34 – 0.20 (m, 4H), -0.00 (s, 18H), -0.12 (s, 6H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 33.2, 31.8, 23.2, 22.8, 15.7, 14.3, 8.4, 8.0, 2.1, -2.1.

^{29}Si NMR: (80 MHz, $CDCl_3$) δ 6.3, 3.1, -21.8.

EI-MS m/z (rel. int.): 377 ($[M-CH_3]^+$, 10%), 307 (15), 291 (100), 275 (5).

EA: $C_{17}H_{44}O_2Si_4$ (392.242): calcd. C 51.97, H 11.29; found C 52.17, H 11.32.

SPECTRA FOR ALL PRODUCTS

1-(tert-Butyl)-1,1-dimethyl-3-phenyldisiloxane (3a)

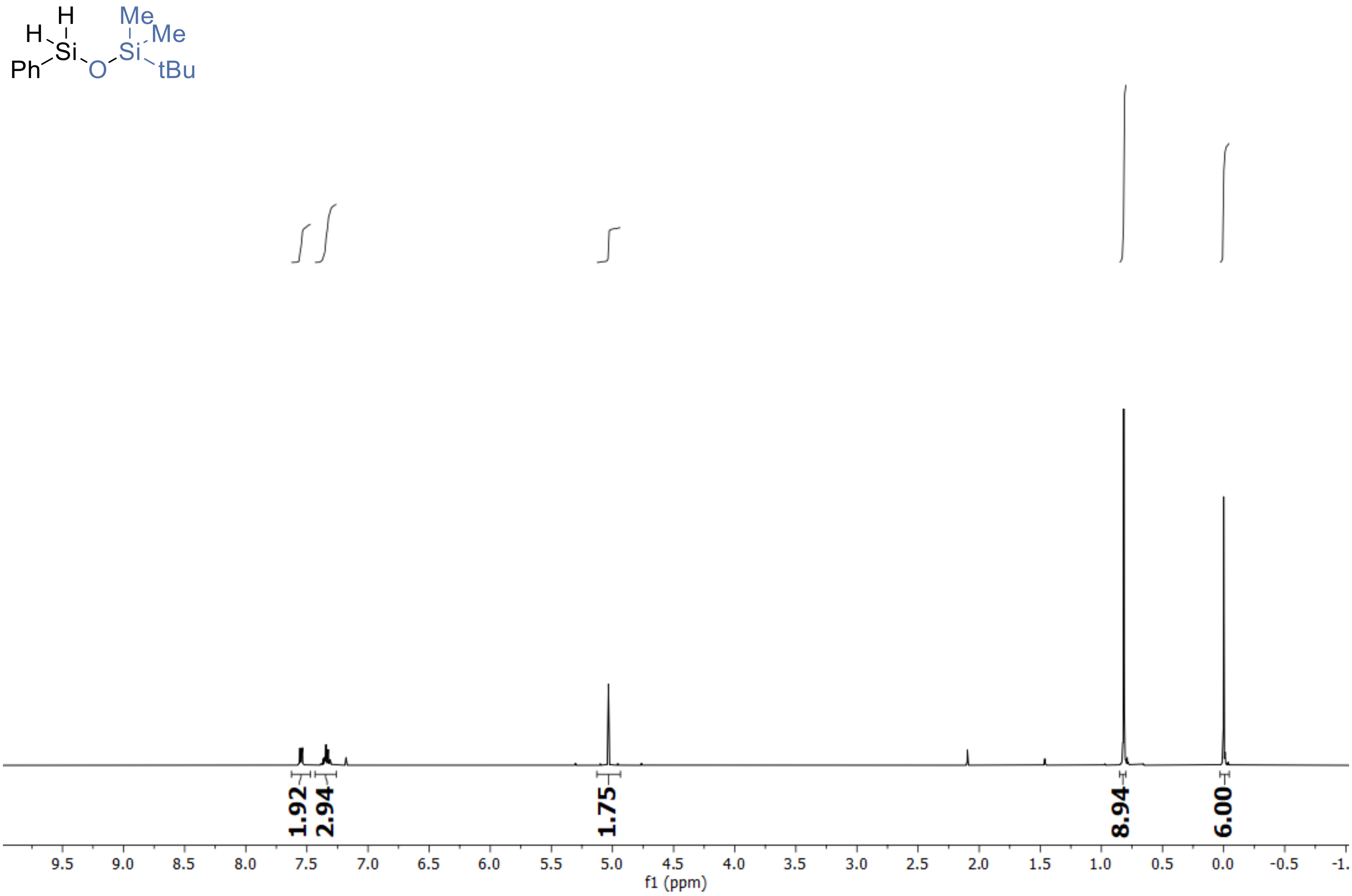


Figure S2. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1-(tert-Butyl)-1,1-dimethyl-3-phenyldisiloxane (**3a**).

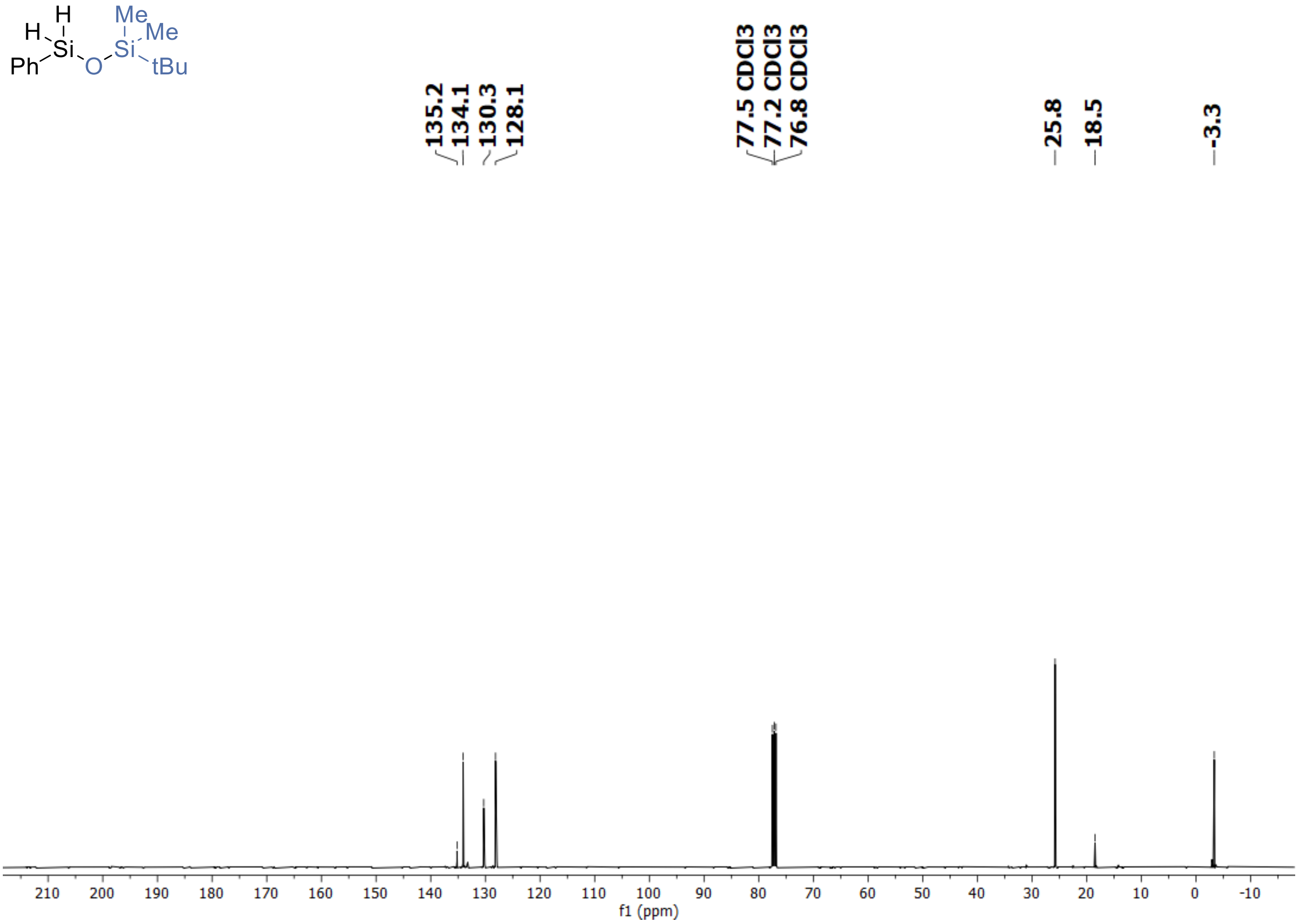


Figure S3. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1-(tert-Butyl)-1,1-dimethyl-3-phenyldisiloxane (**3a**).

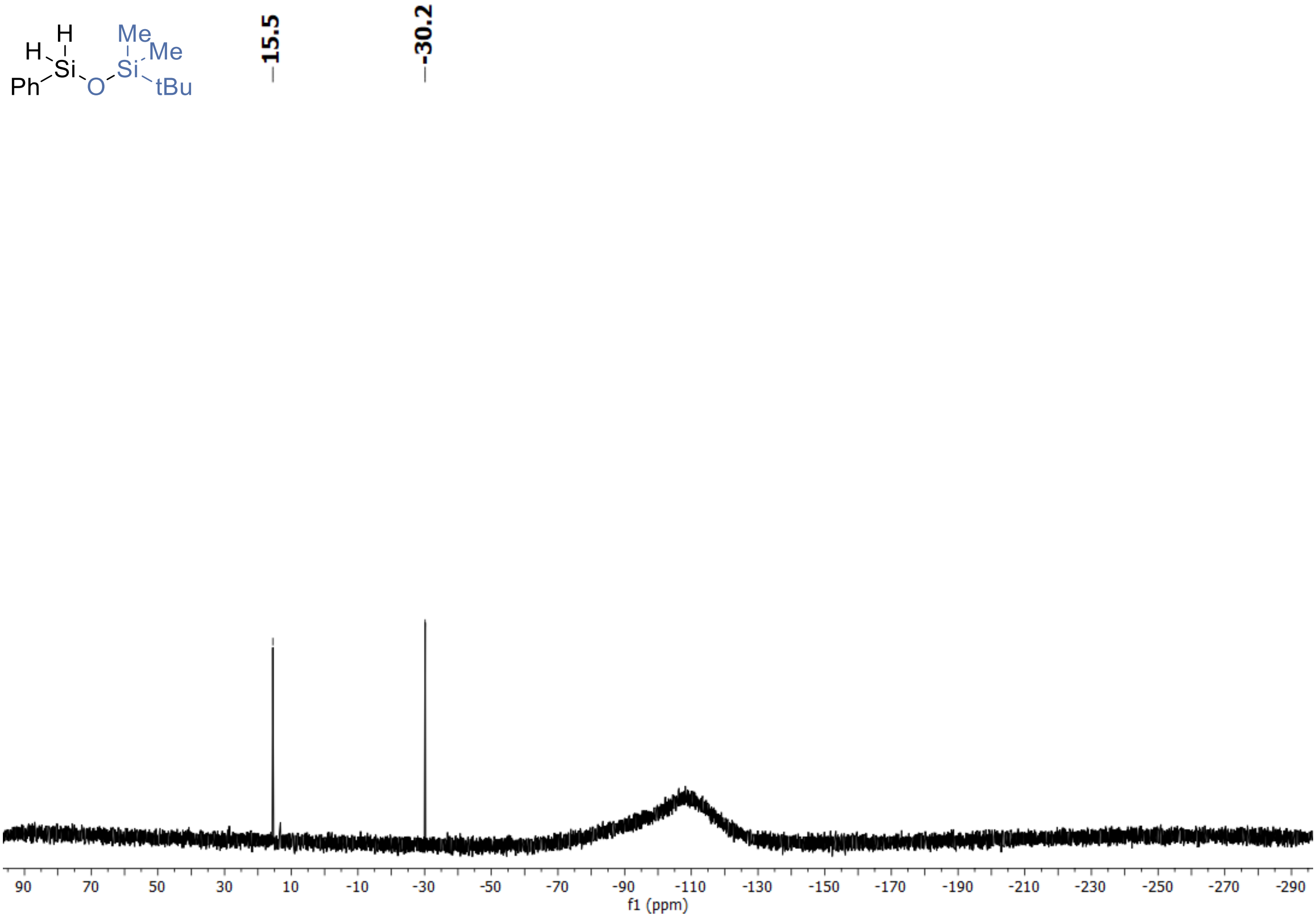


Figure S4. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1-(tert-Butyl)-1,1-dimethyl-3-phenyldisiloxane (3a).

1,1,1-Triethyl-3-phenyldisiloxane (3b)

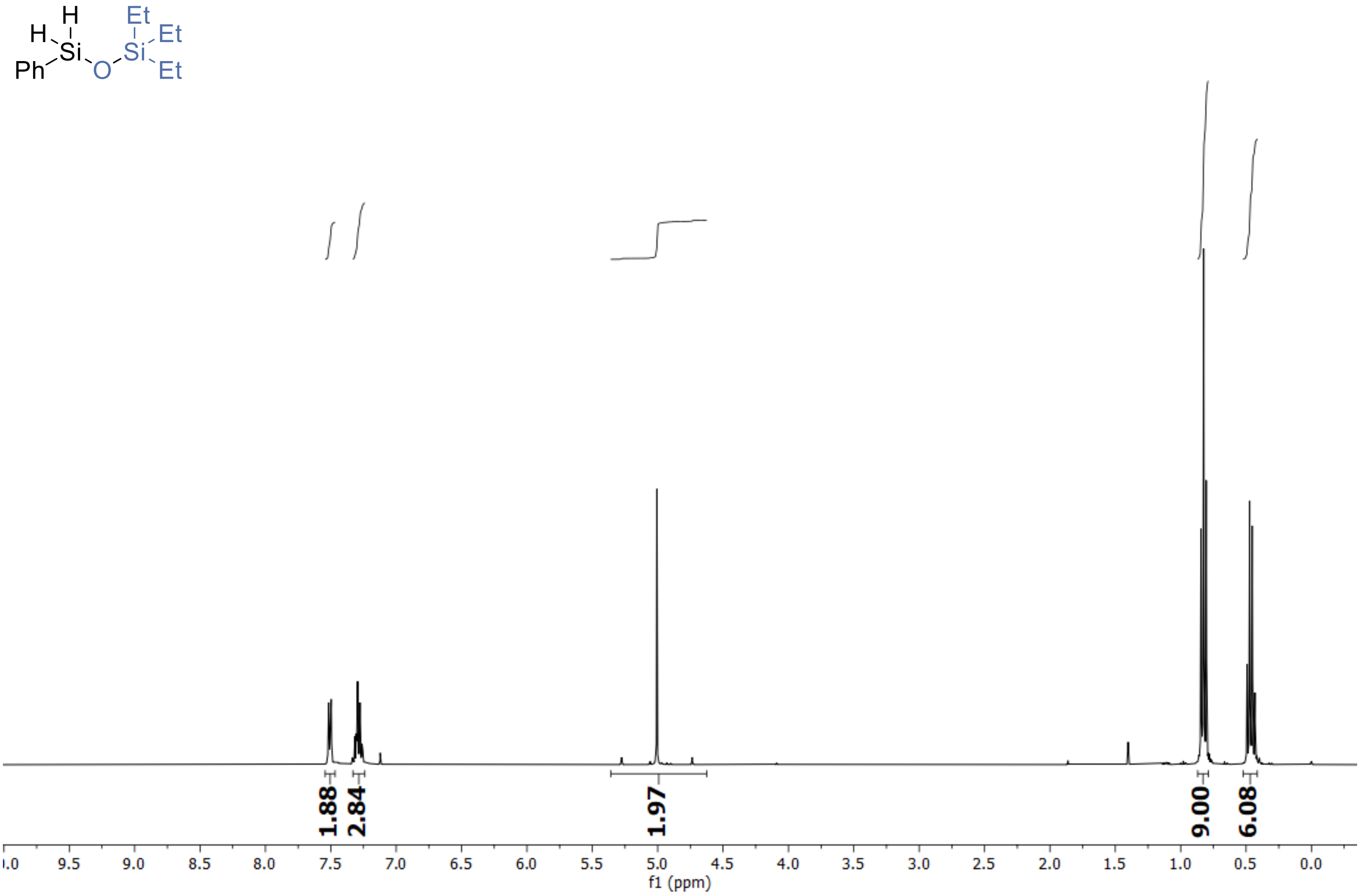


Figure S5. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1-triethyl-3-phenyldisiloxane (**3b**).

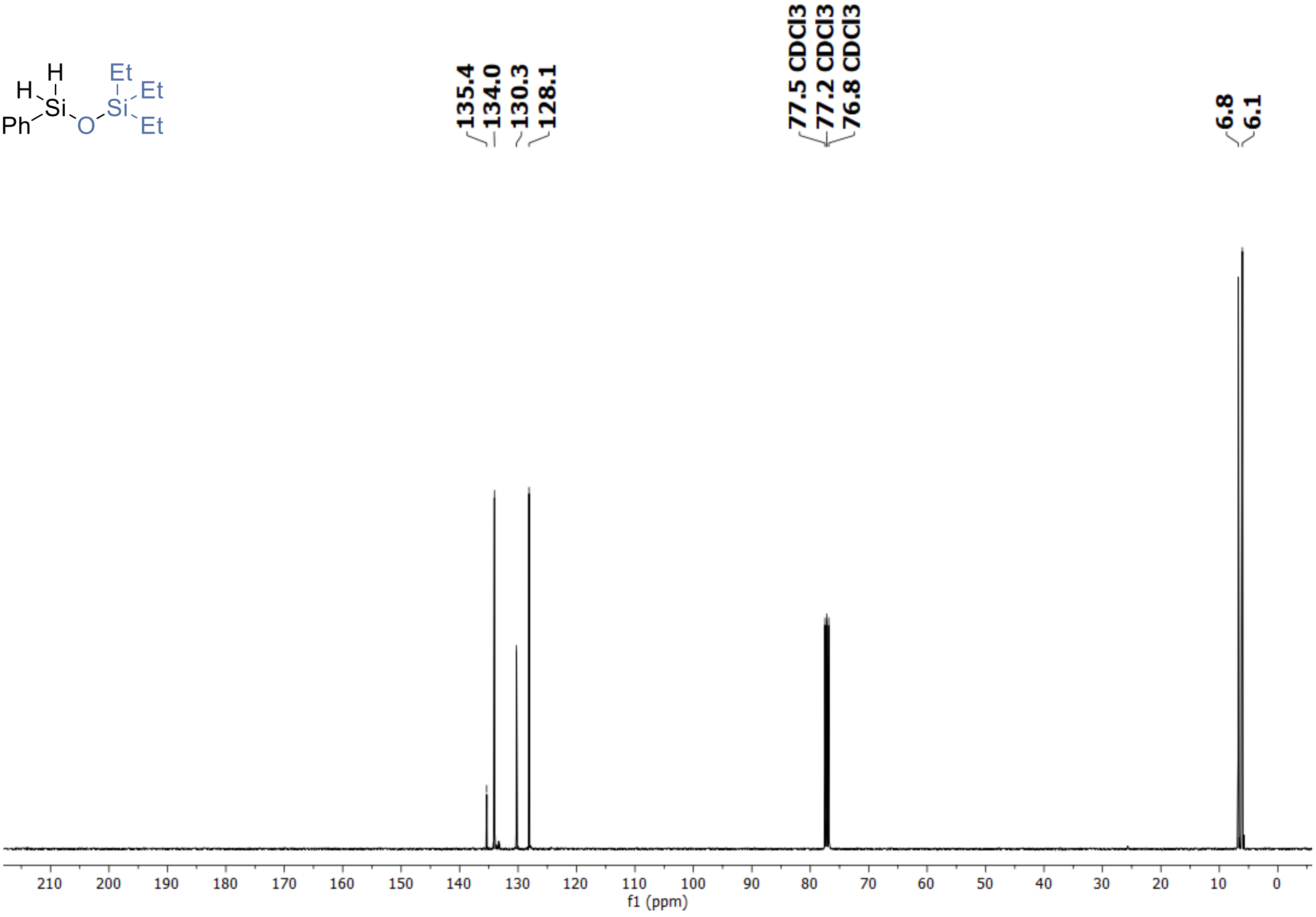


Figure S6. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1-triethyl-3-phenyldisiloxane (**3b**).

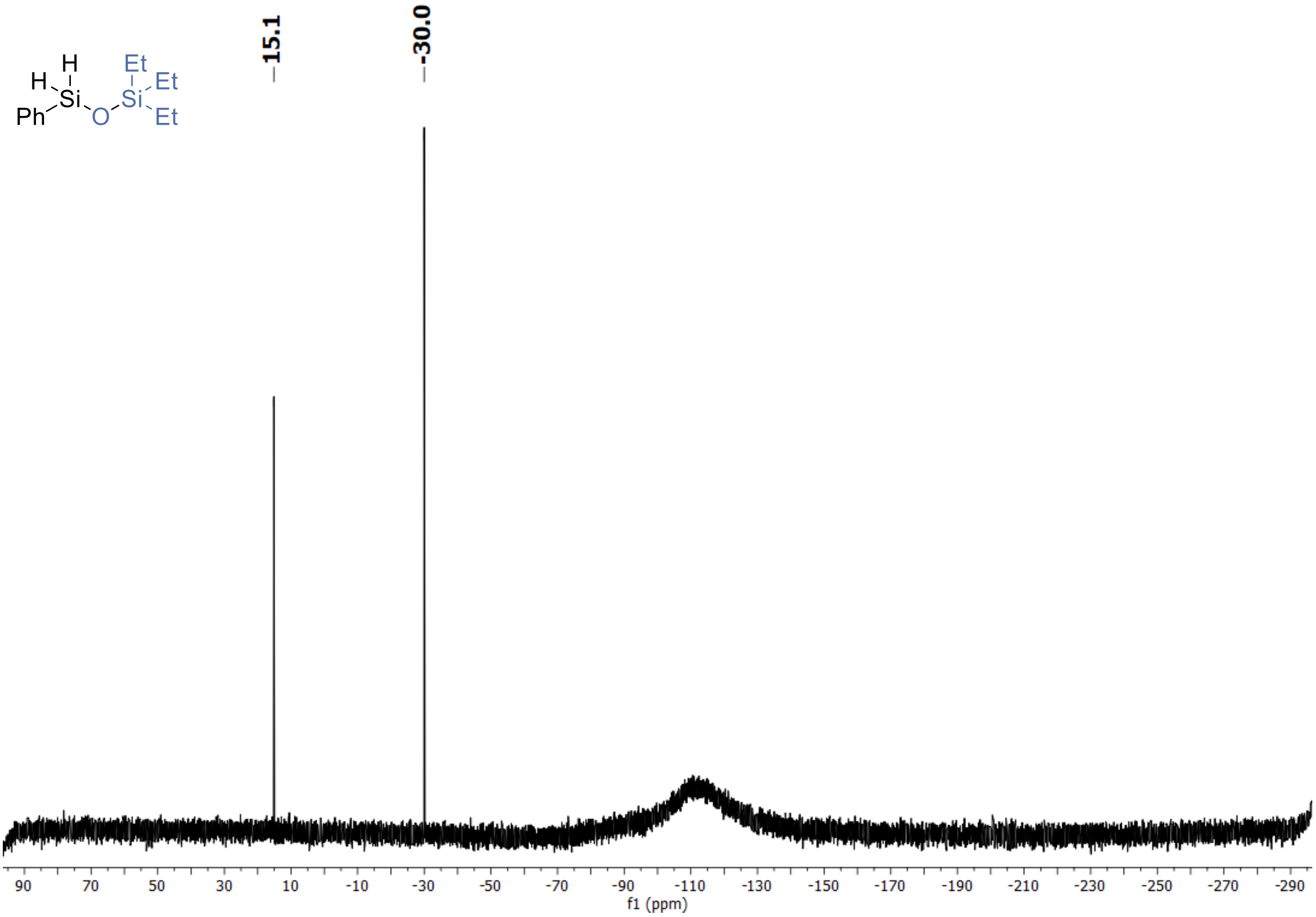


Figure S7. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1-triethyl-3-phenyldisiloxane (**3b**).

1,1,1-Triisopropyl-3-phenyldisiloxane (3c)

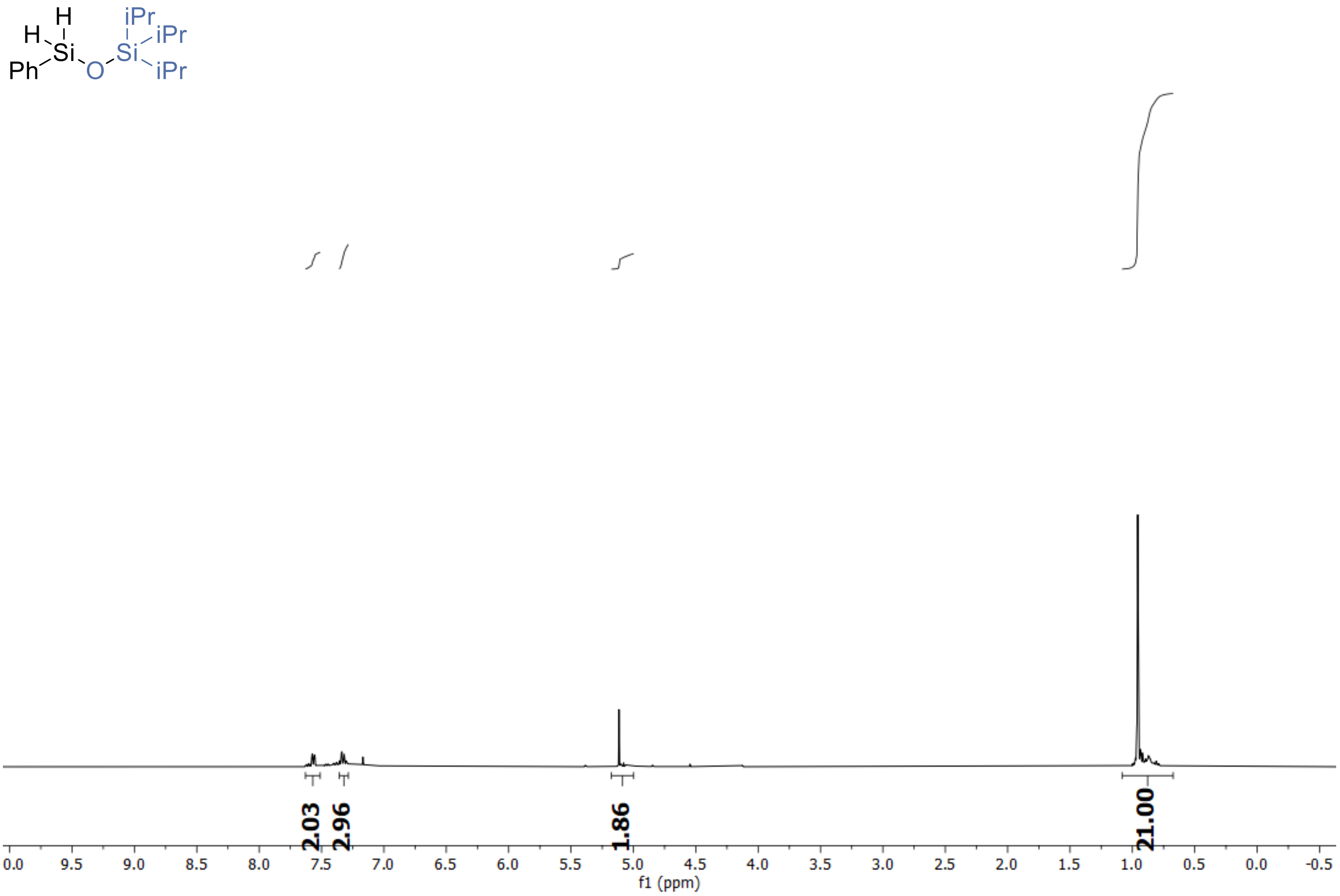


Figure S8. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1-triisopropyl-3-phenyldisiloxane (**3c**).

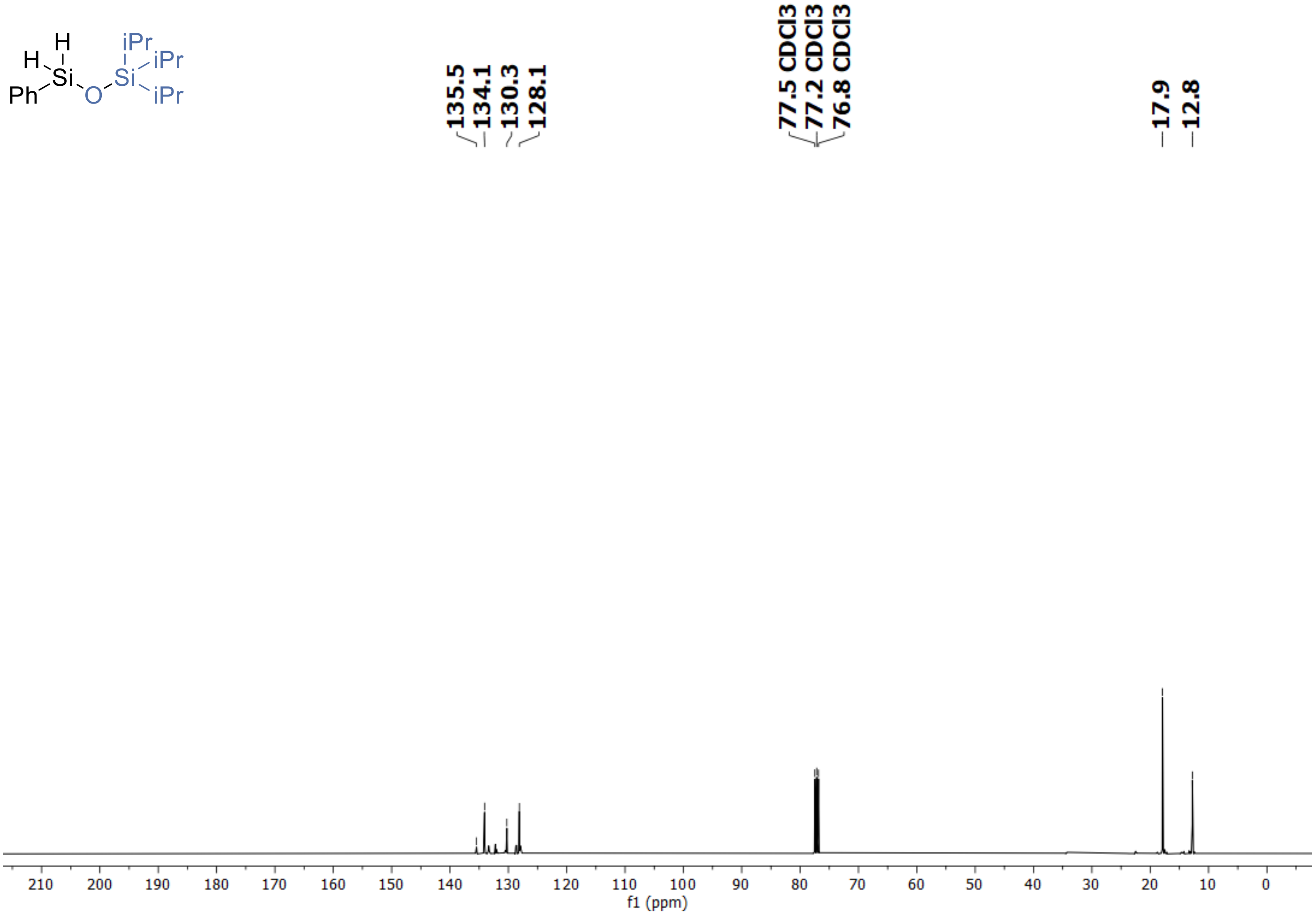


Figure S9. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1-triisopropyl-3-phenyldisiloxane (**3c**).

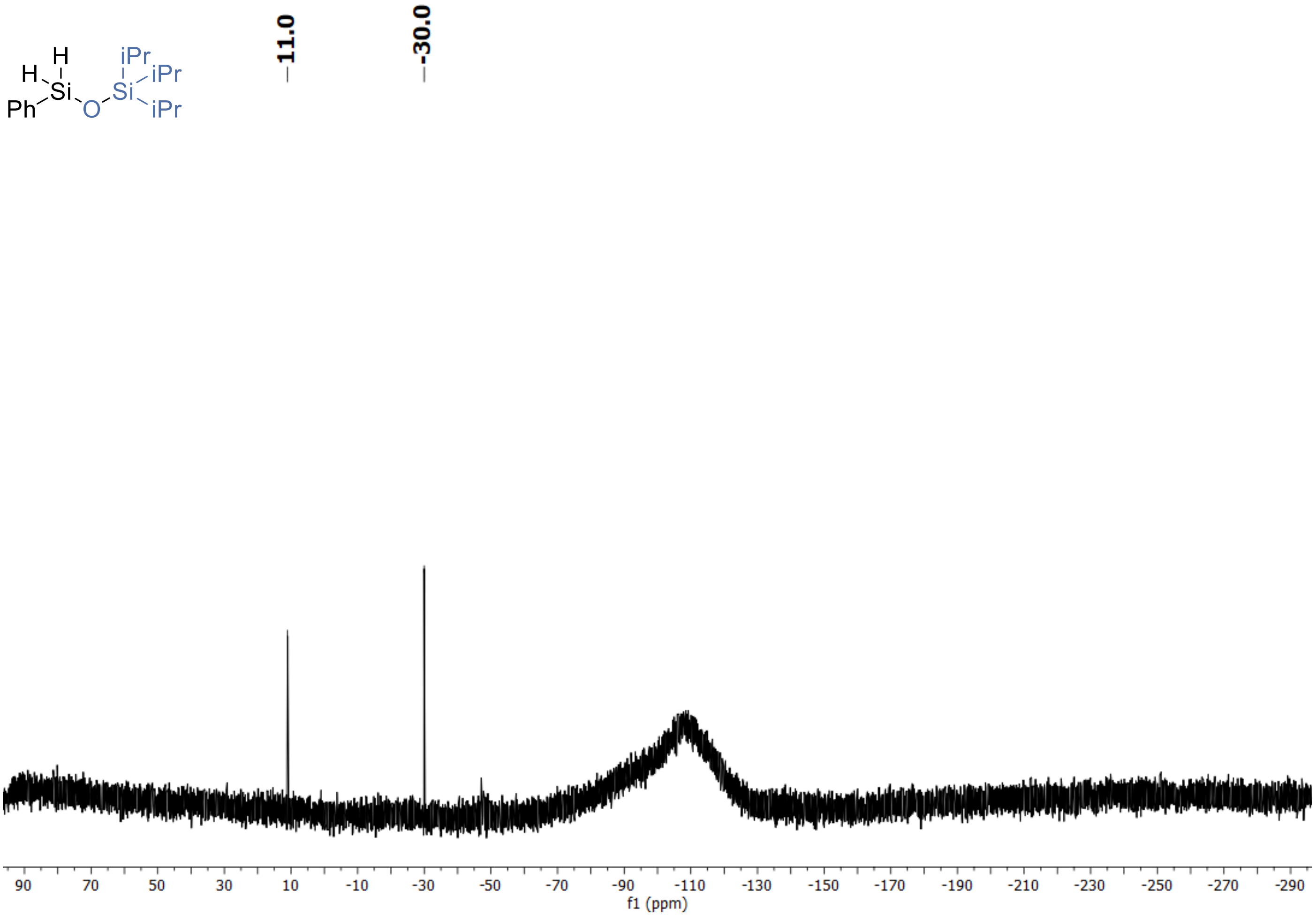
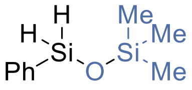


Figure S10. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1-triisopropyl-3-phenyldisiloxane (**3c**).

1,1,1-Trimethyl-3-phenyldisiloxane (3d)



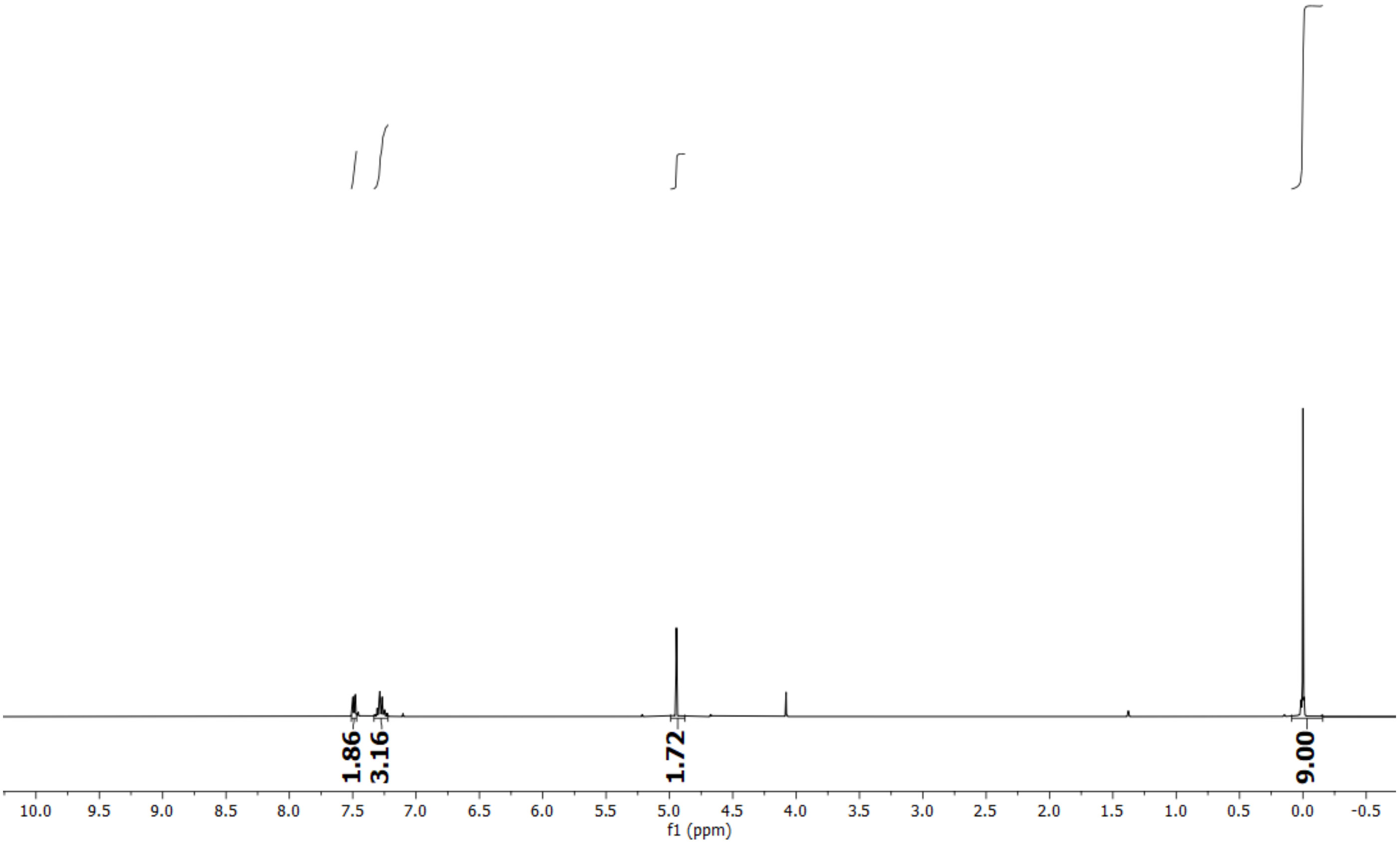


Figure S11. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1-trimethyl-3-phenyldisiloxane (**3d**).

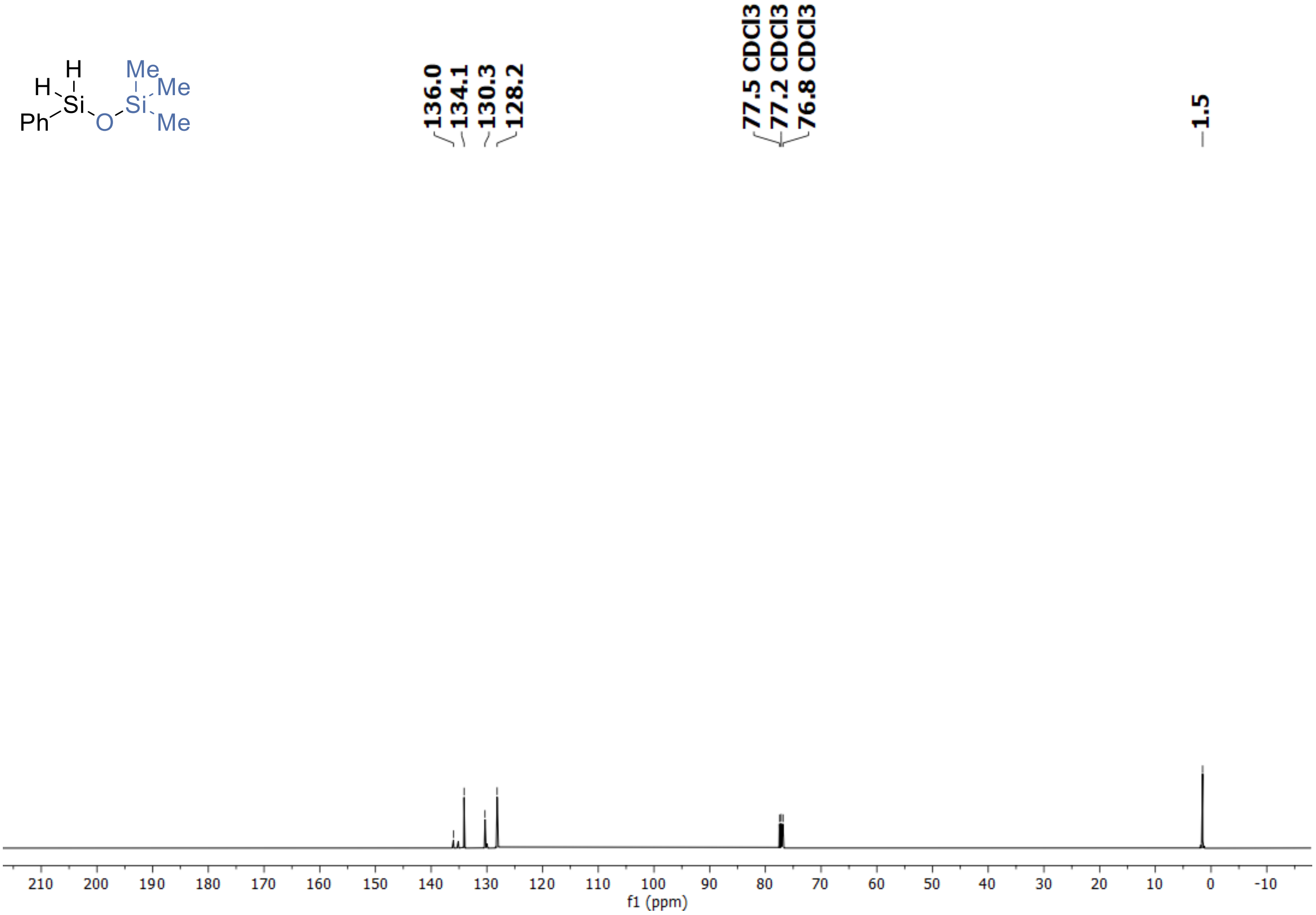


Figure S12. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1-trimethyl-3-phenyldisiloxane (**3d**).

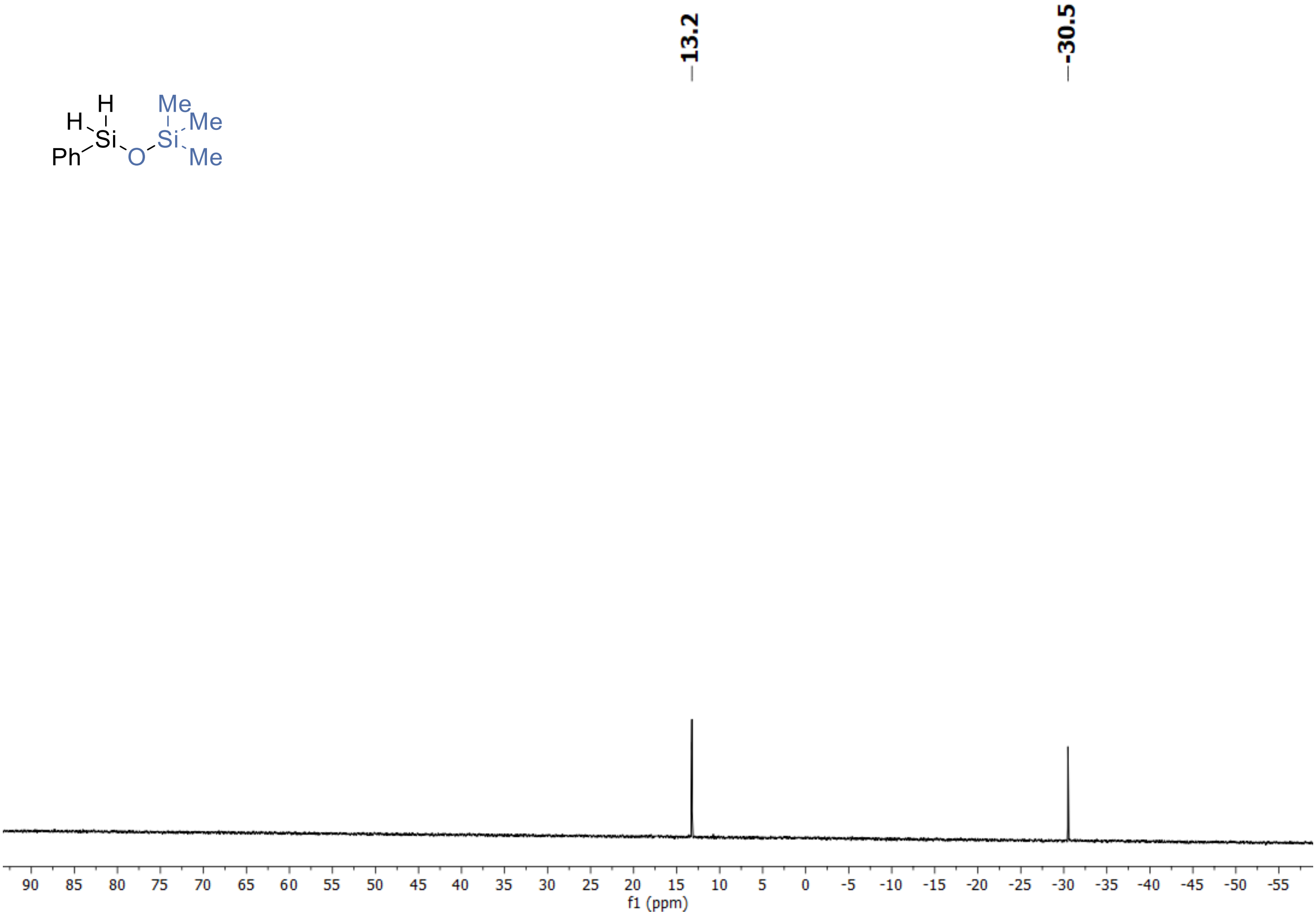


Figure S13. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1-trimethyl-3-phenyldisiloxane (**3d**).

1-(*tert*-Butyl)-1,1,3-triphenyldisiloxane (3e)

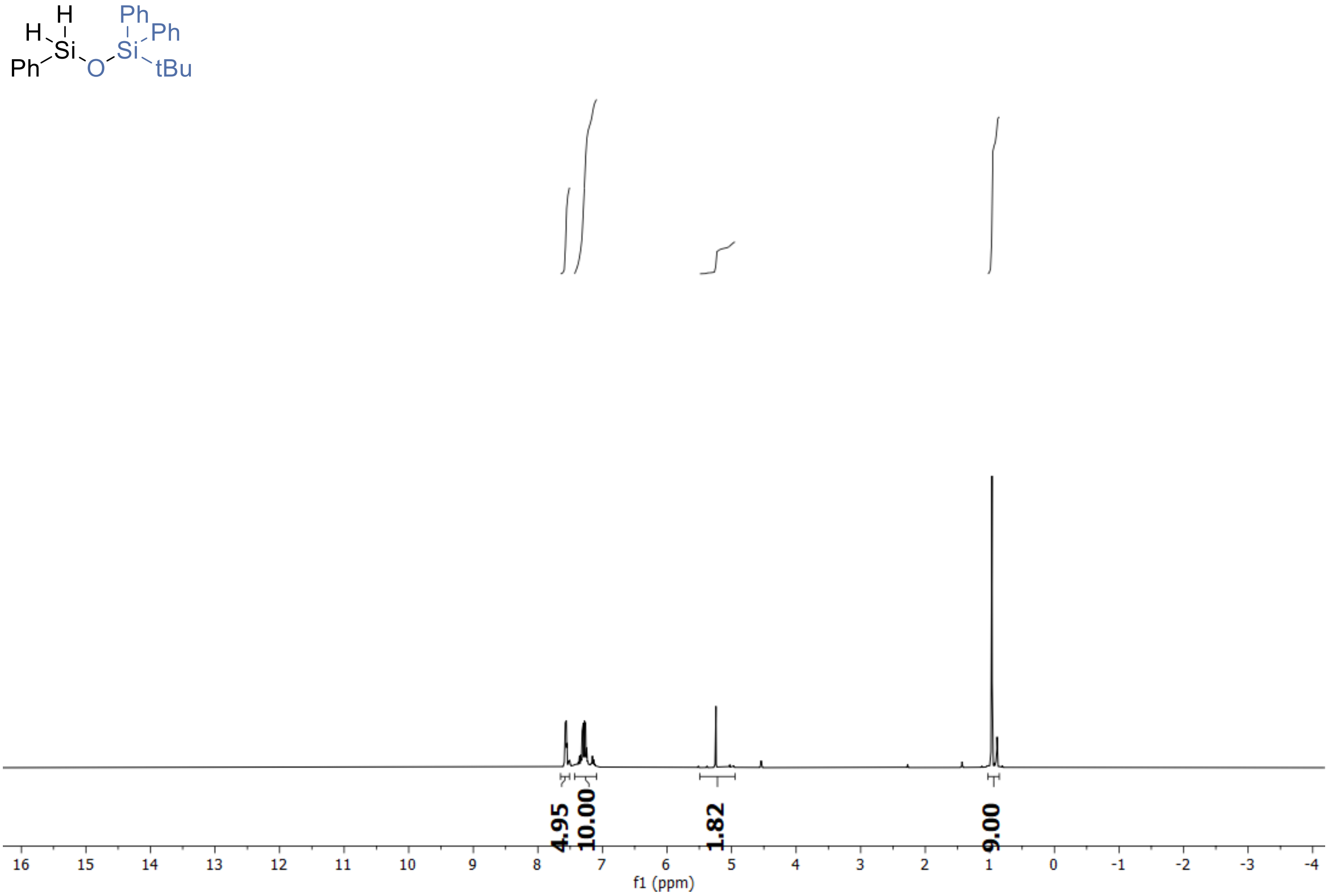


Figure S14. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1-(tert-butyl)-1,1,3-triphenyldisiloxane (**3e**).

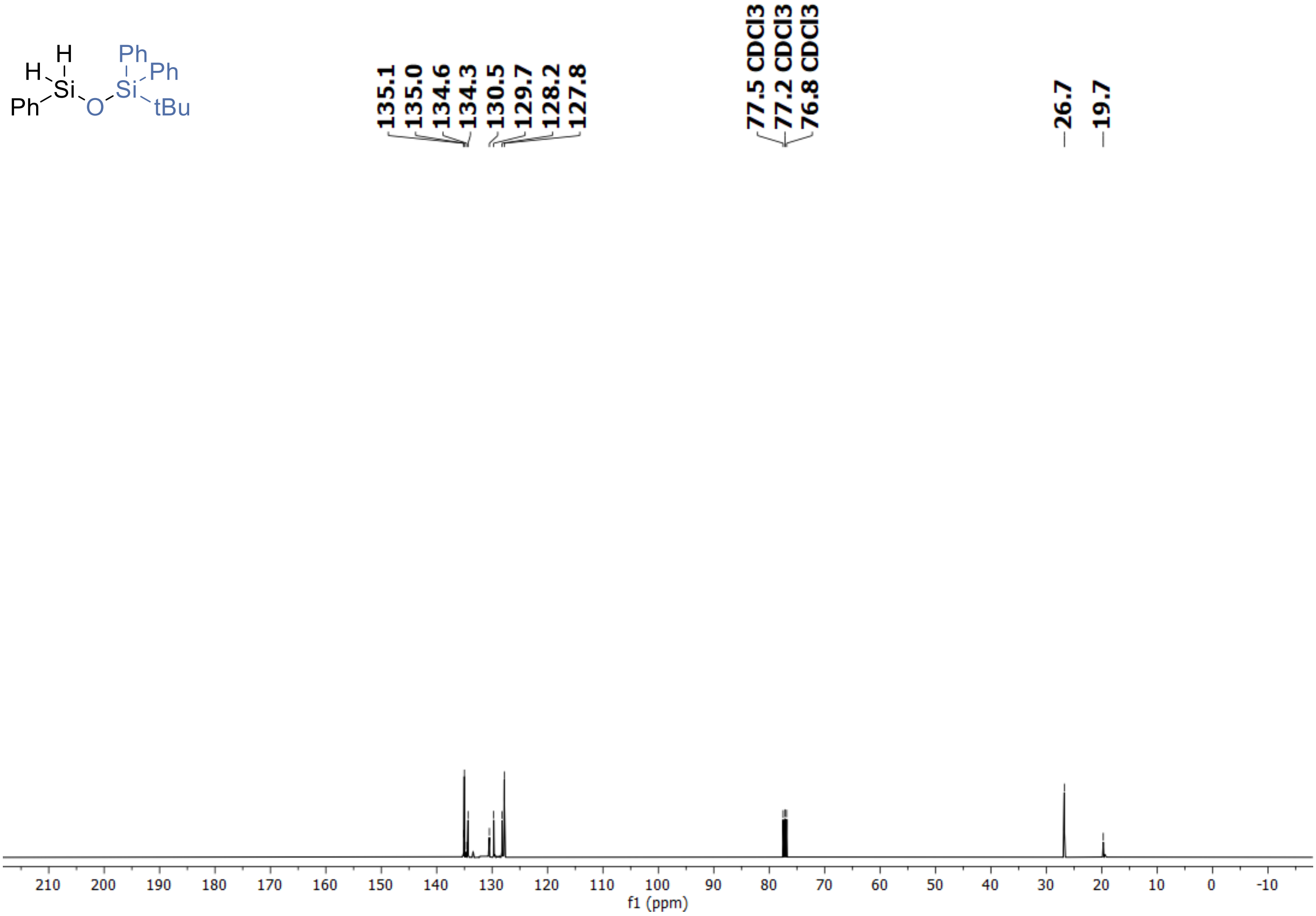


Figure S15. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1-(tert-butyl)-1,1,3-triphenyldisiloxane (**3e**).

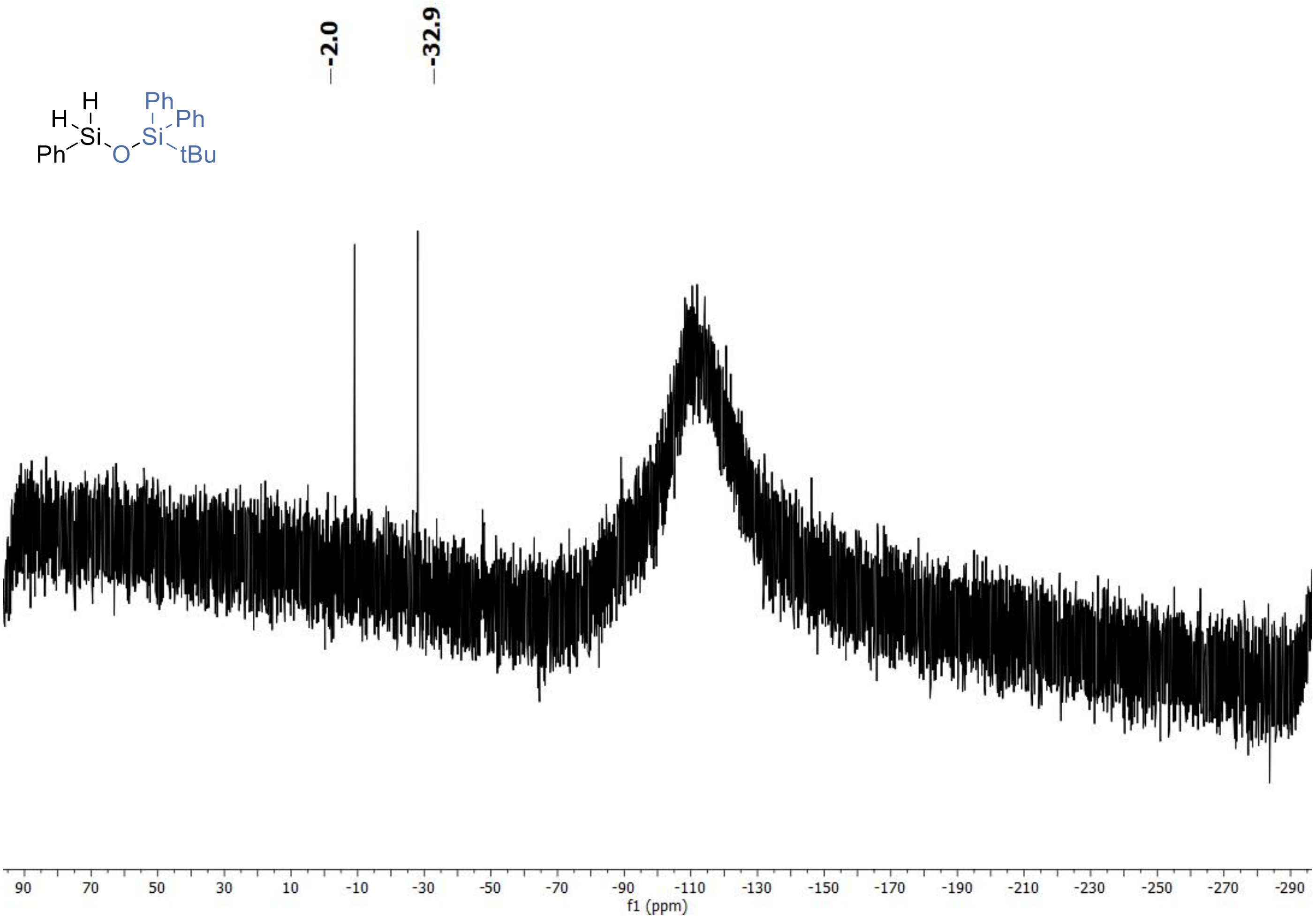


Figure S16. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1-(tert-butyl)-1,1,3-triphenyldisiloxane (**3e**).

1-(*tert*-Butyl)-1,1-dimethyl-3-(p-tolyl)disiloxane (3f)

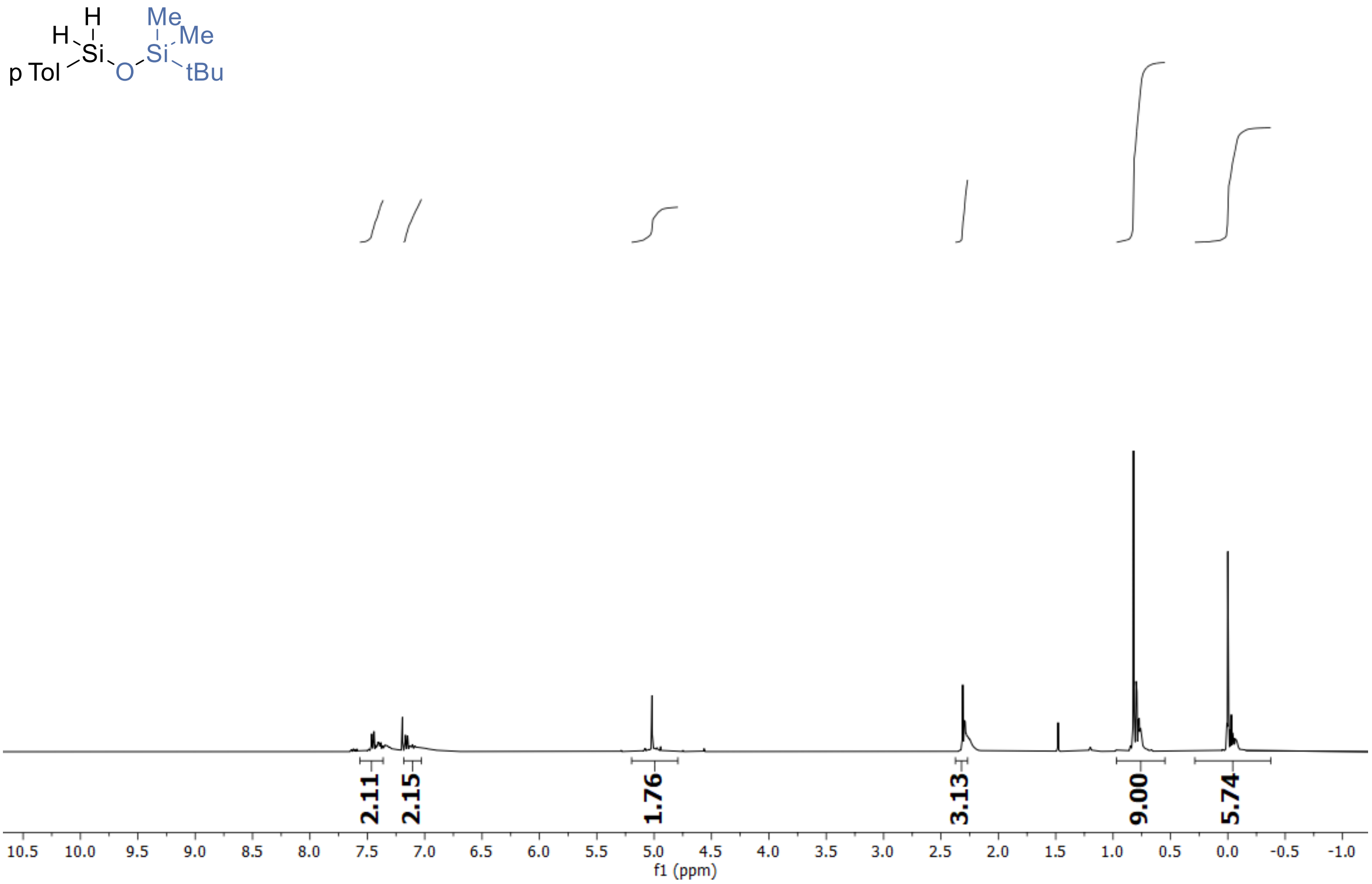


Figure S17. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1-dimethyl-3-(p-tolyl)disiloxane (**3f**)

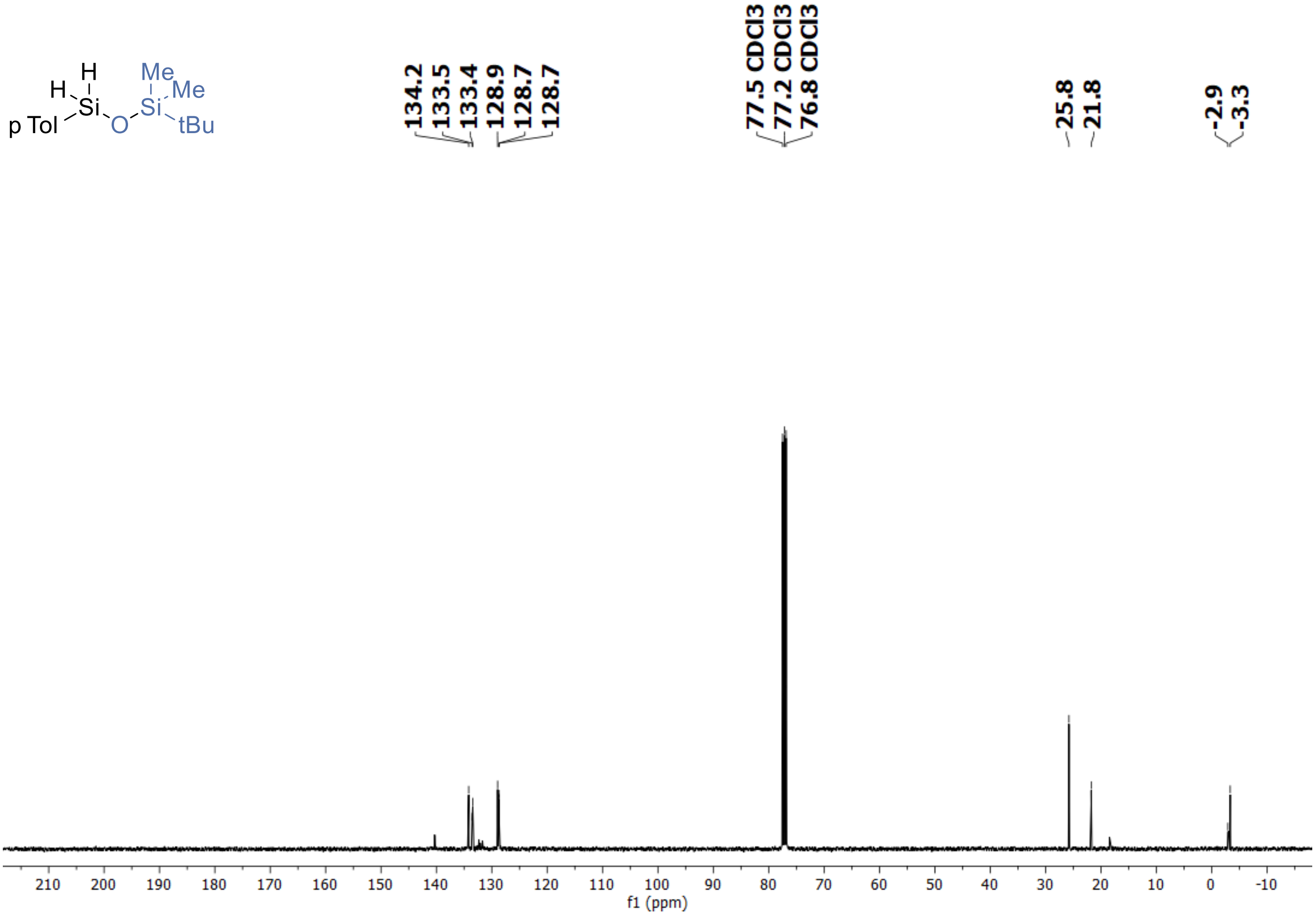


Figure S18. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1-dimethyl-3-(p-tolyl)disiloxane (**3f**)

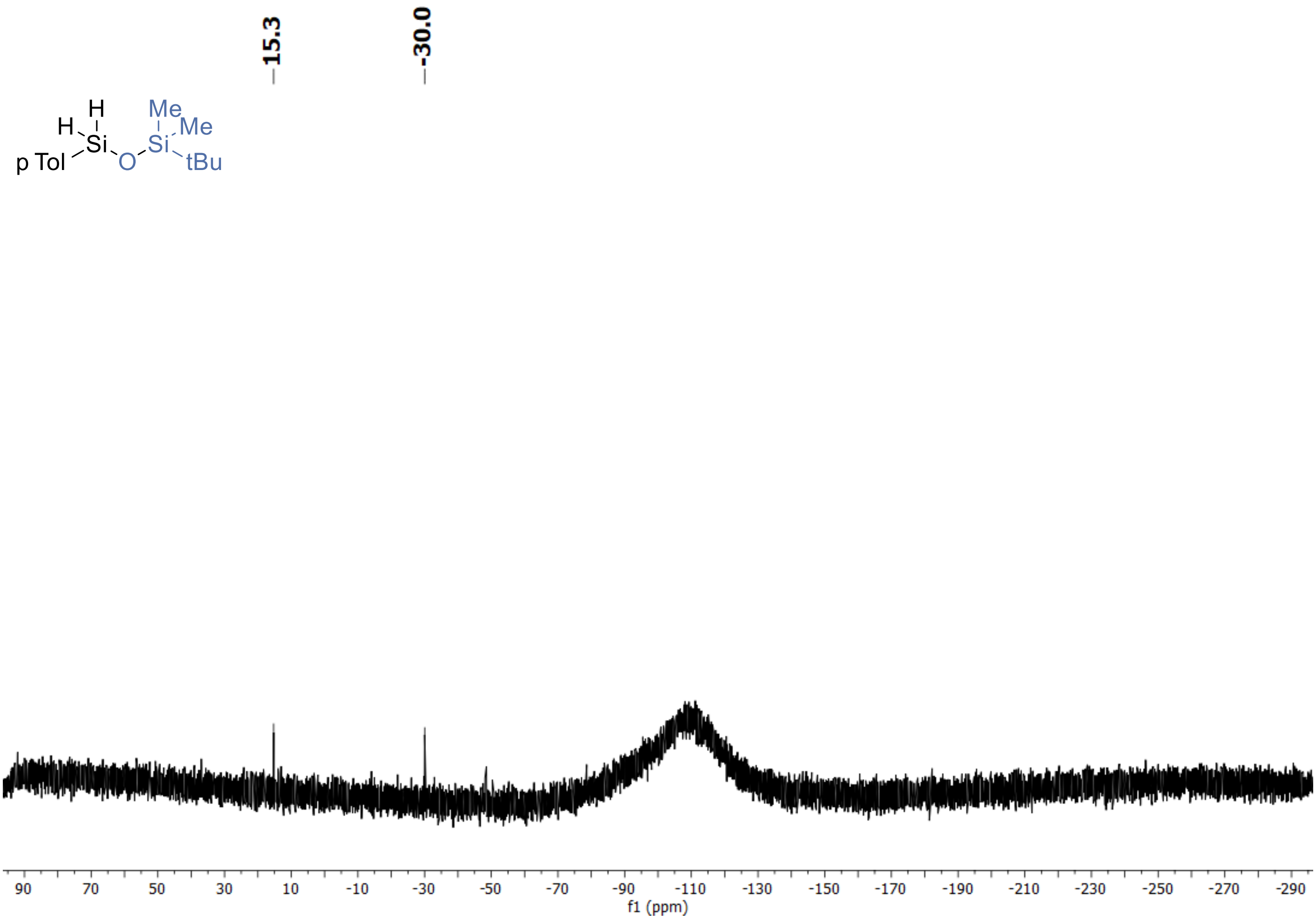


Figure S19. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1-dimethyl-3-(p-tolyl)disiloxane (**3f**)

1-(*tert*-Butyl)-1,1,3-trimethyl-3-phenyldisiloxane (3g)

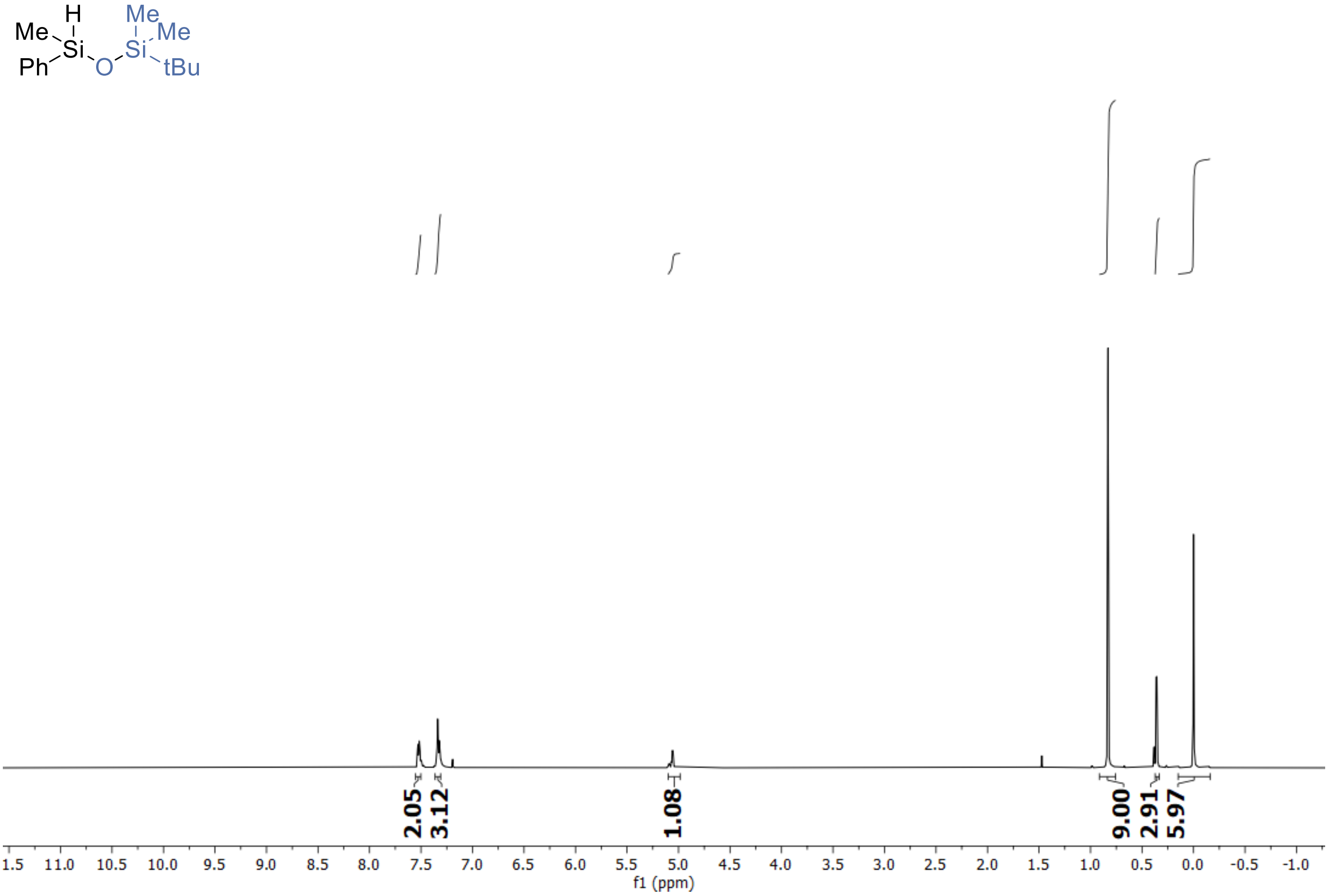


Figure S20. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1,3-trimethyl-3-phenyldisiloxane (**3g**).

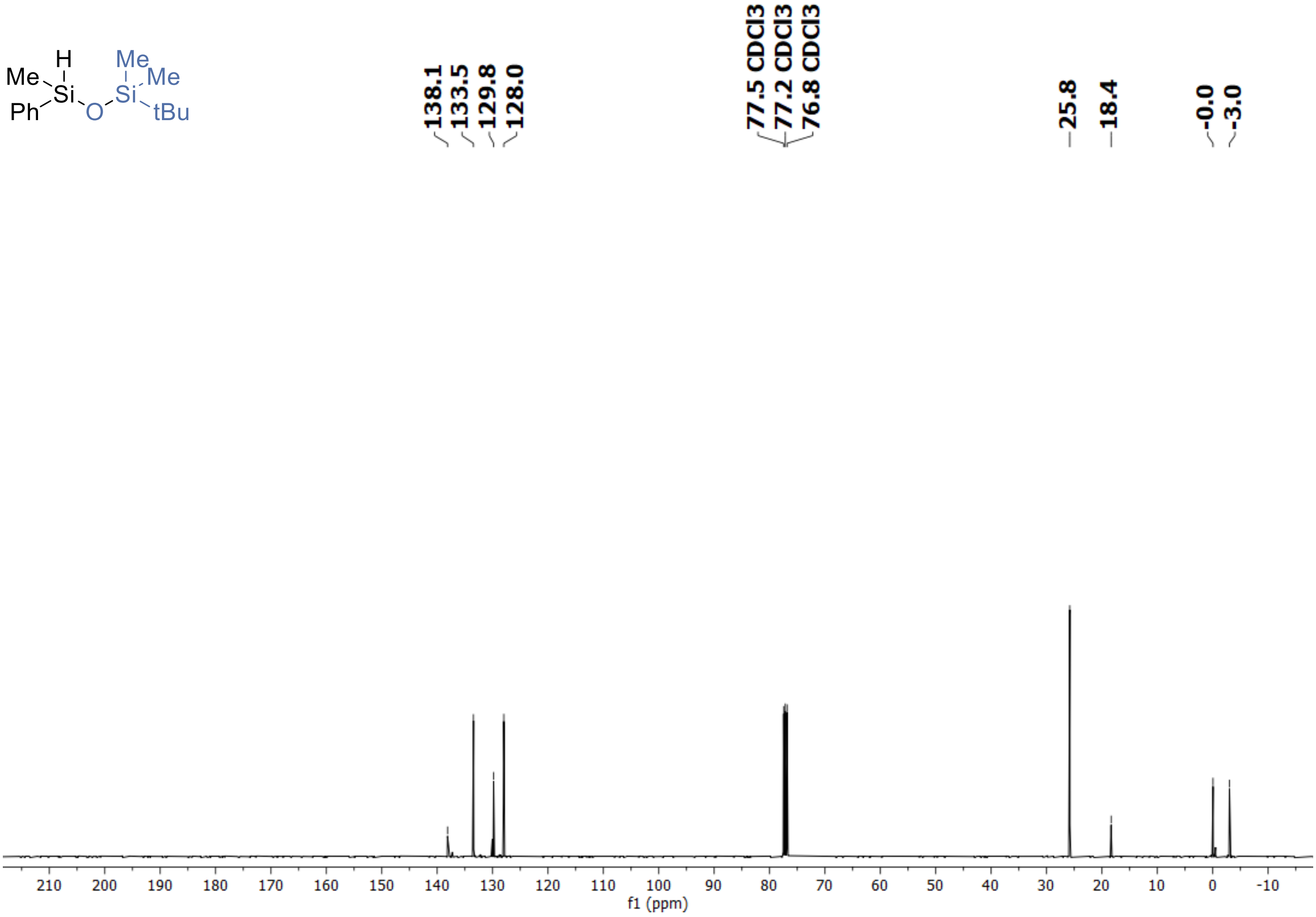


Figure S21. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1,3-trimethyl-3-phenyldisiloxane (**3g**).

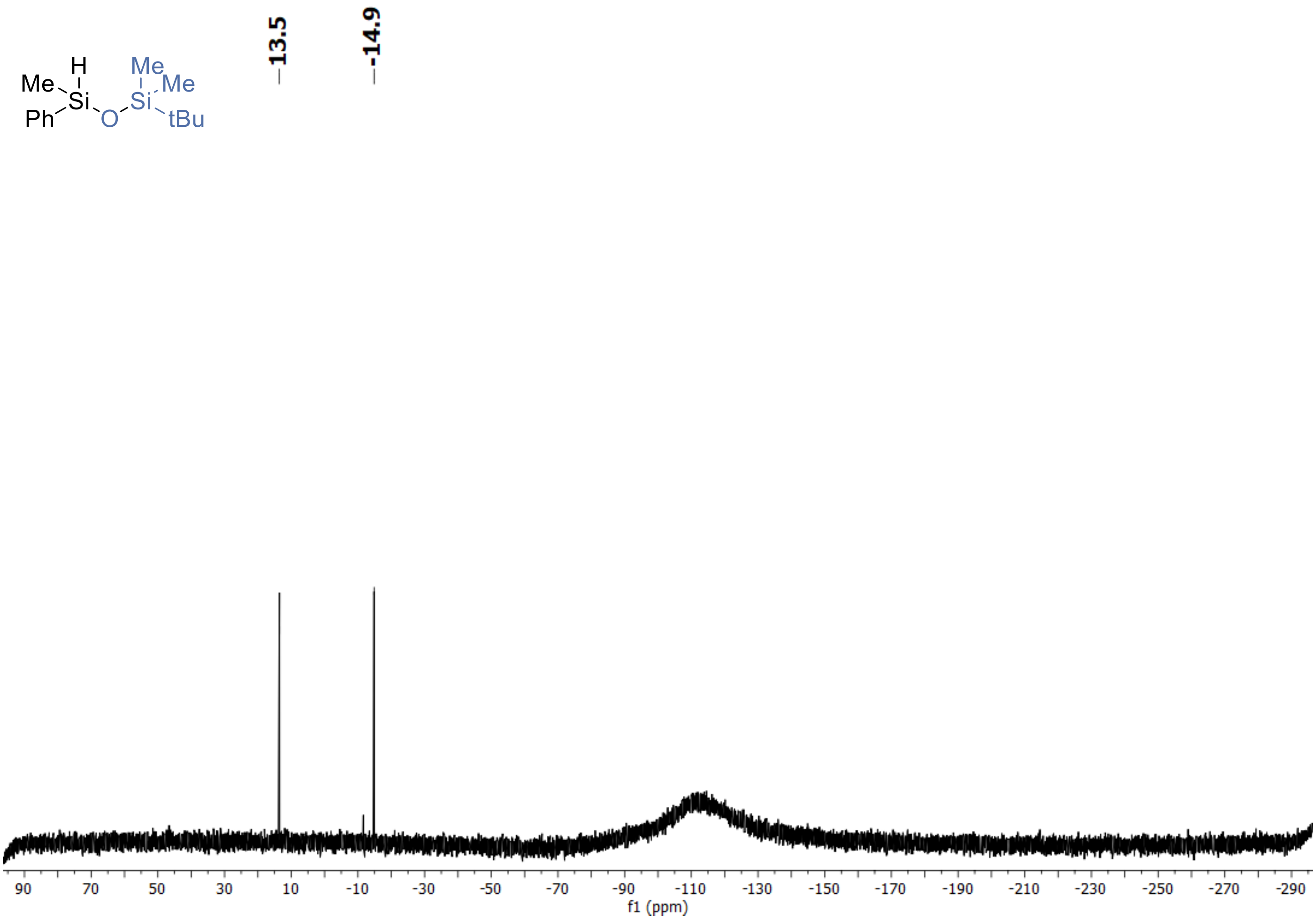


Figure S22. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1,3-trimethyl-3-phenyldisiloxane (**3g**).

1-(*tert*-Butyl)-1,1-dimethyl-3,3-di-*p*-tolyldisiloxane (3h)

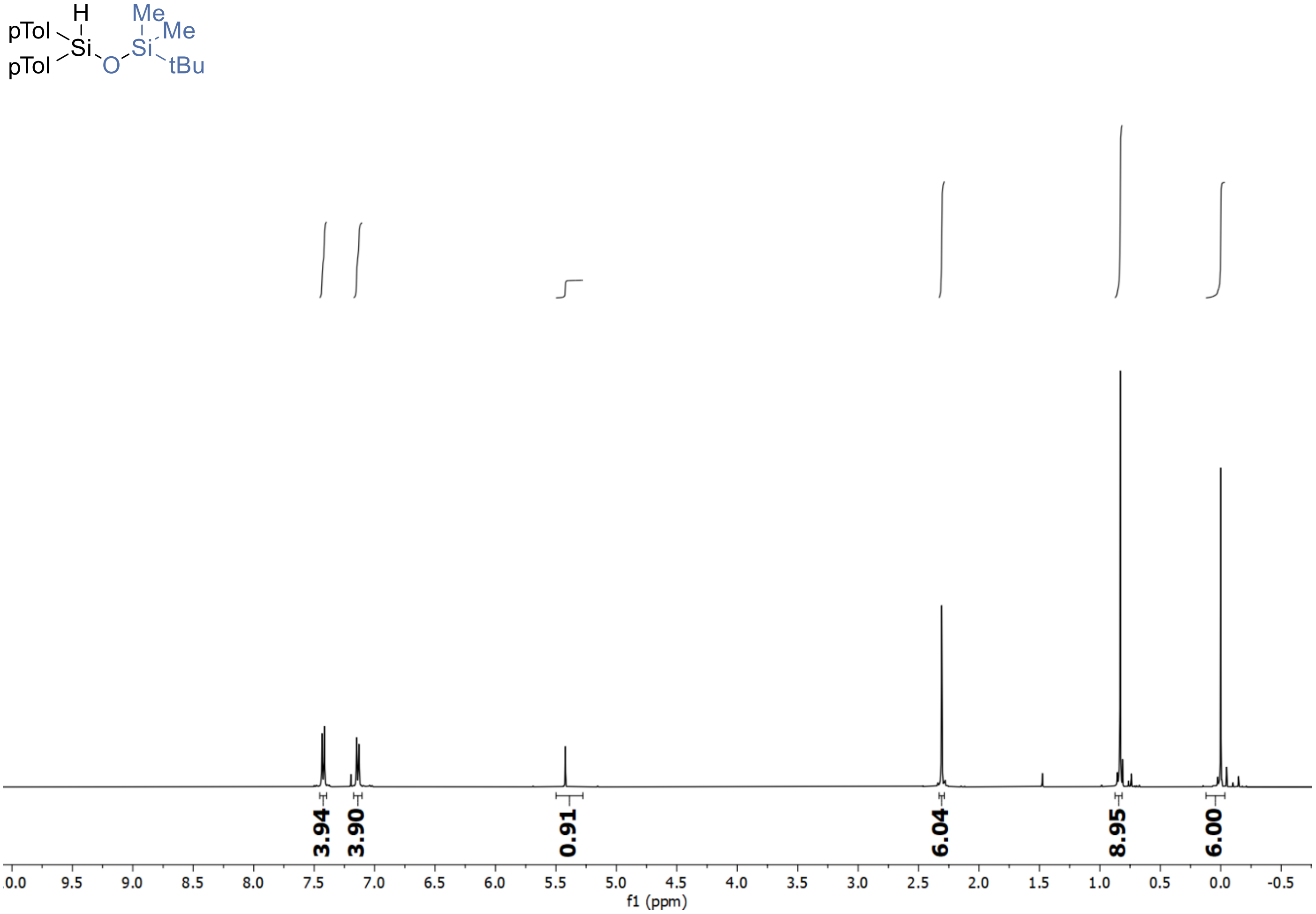


Figure S23. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1-dimethyl-3,3-di-*p*-tolyldisiloxane (**3h**).

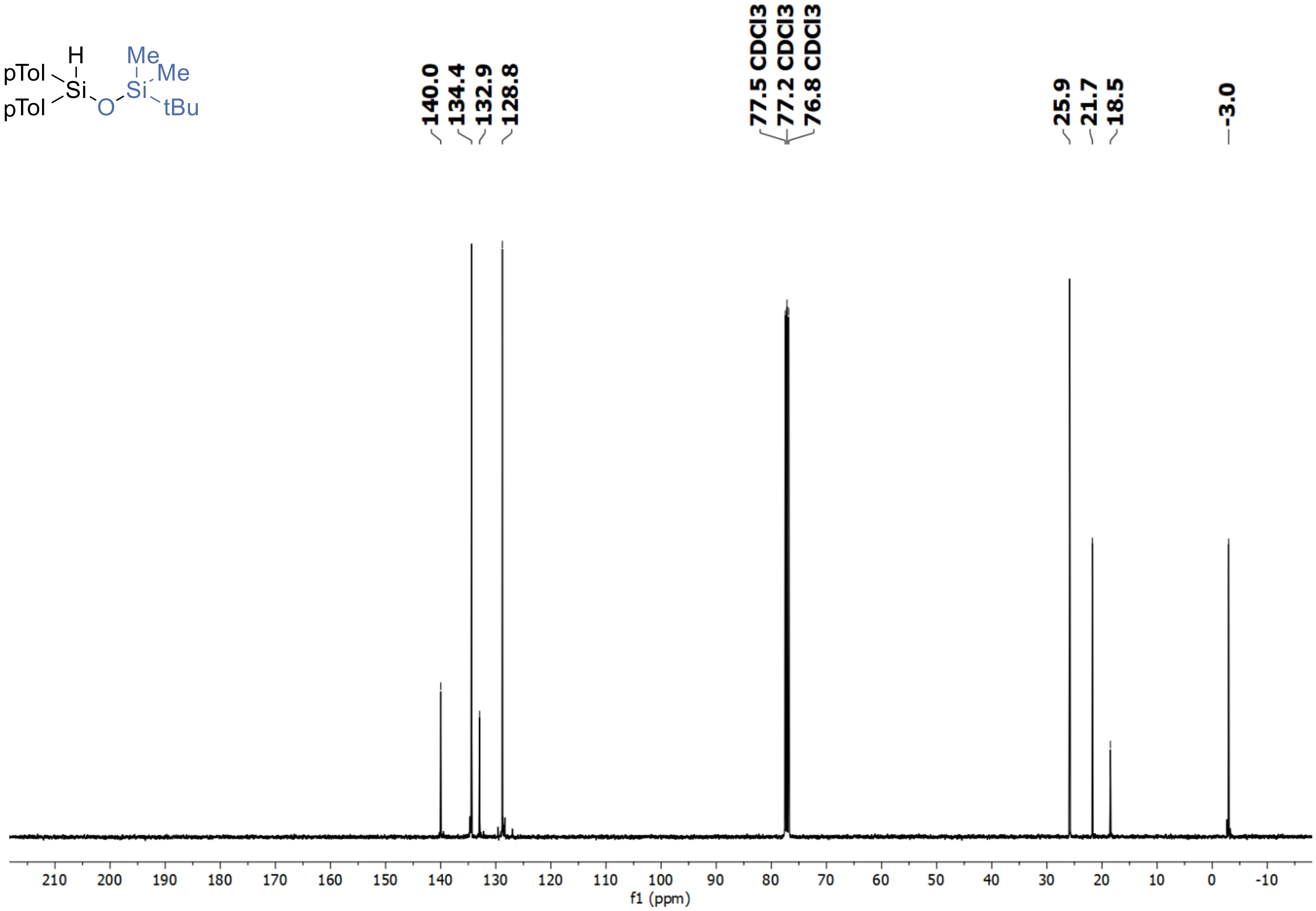


Figure S24. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1-dimethyl-3,3-di-*p*-tolyldisiloxane (**3h**).

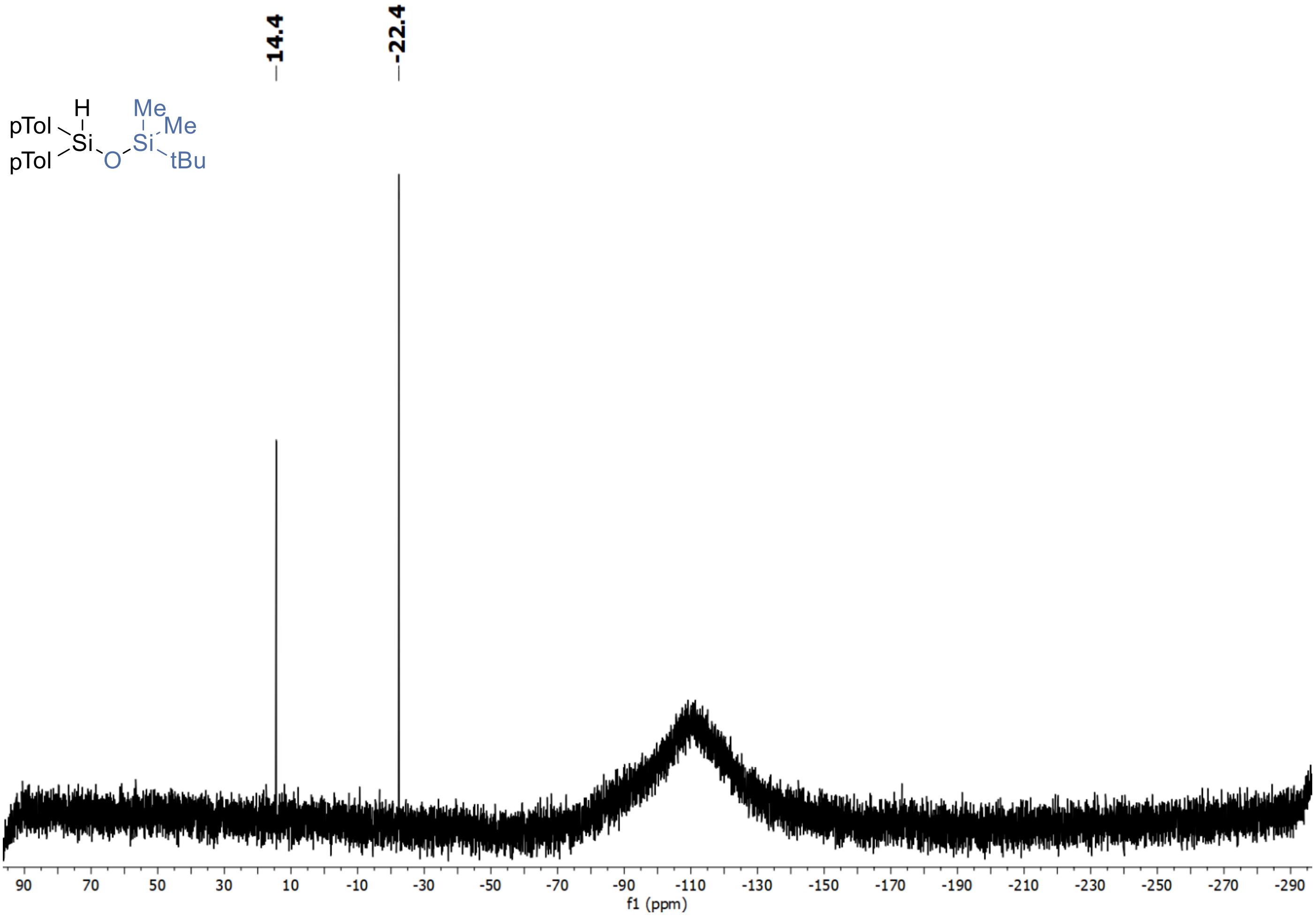


Figure S25. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1-dimethyl-3,3-di-*p*-tolyldisiloxane (**3h**).

1-(*tert*-Butyl)-1,1,3,3-tetraphenyldisiloxane (3i)

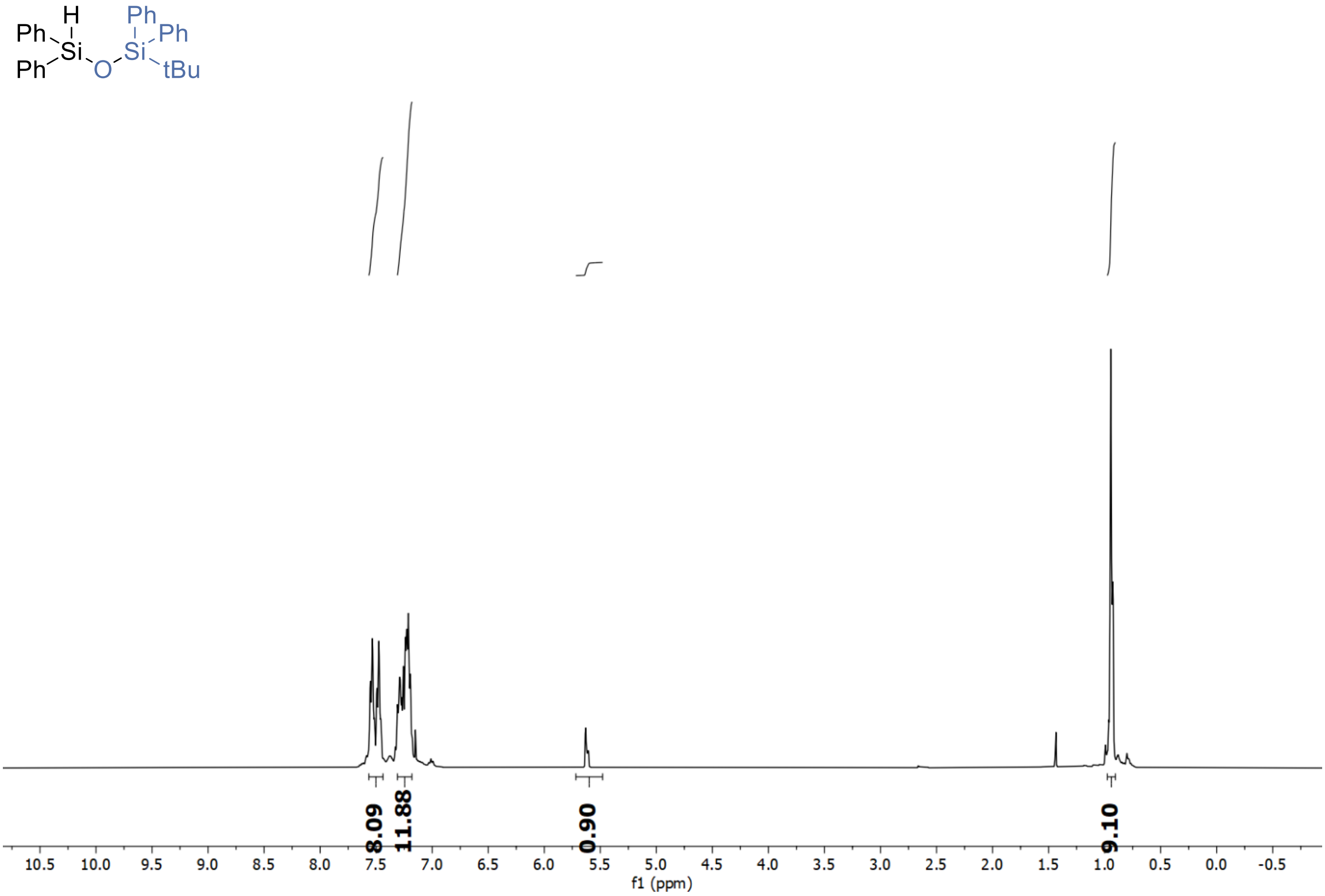


Figure S26. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1,3,3-tetraphenyldisiloxane (**3i**).

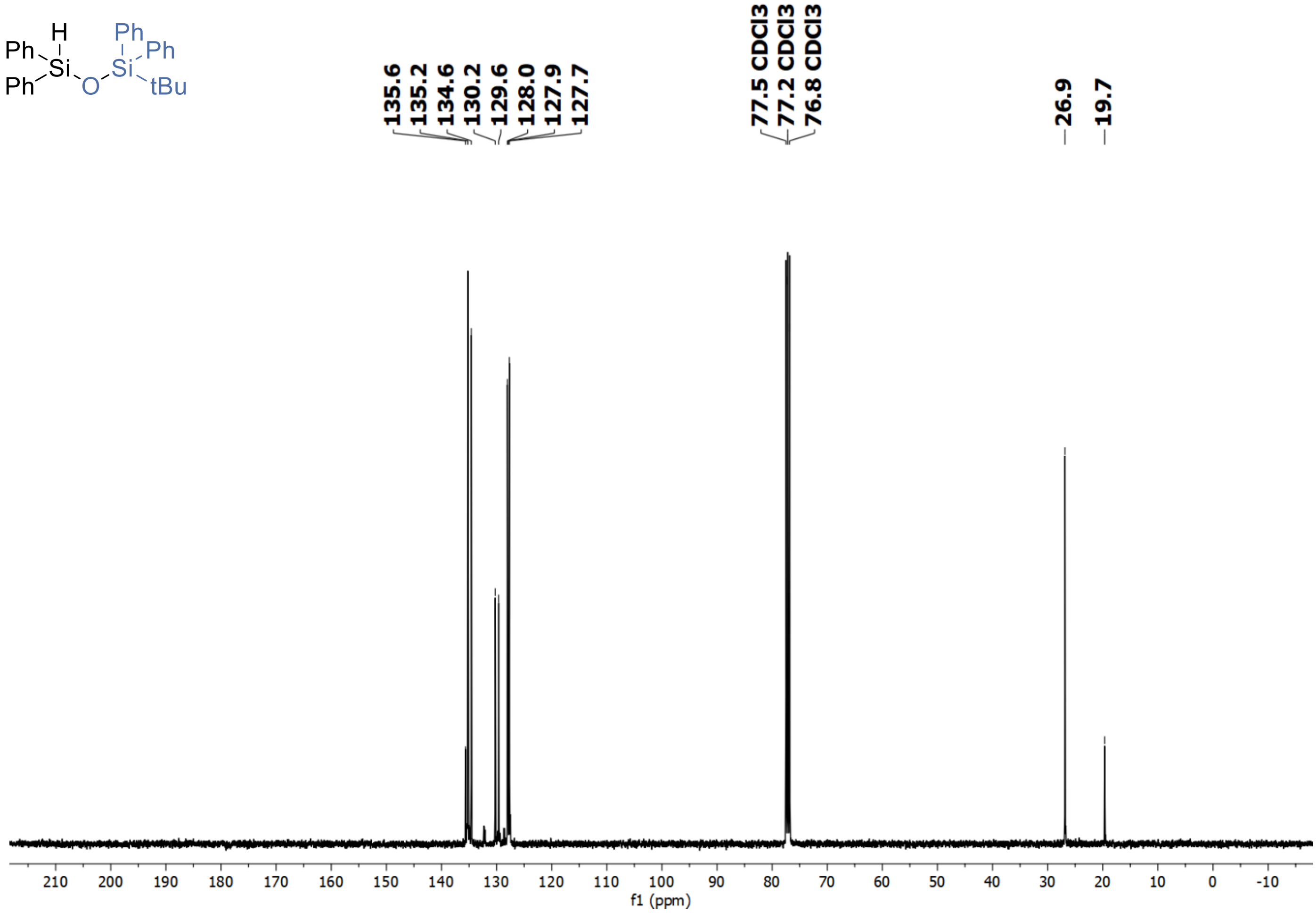


Figure S27. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1,3,3-tetraphenyldisiloxane (**3i**).

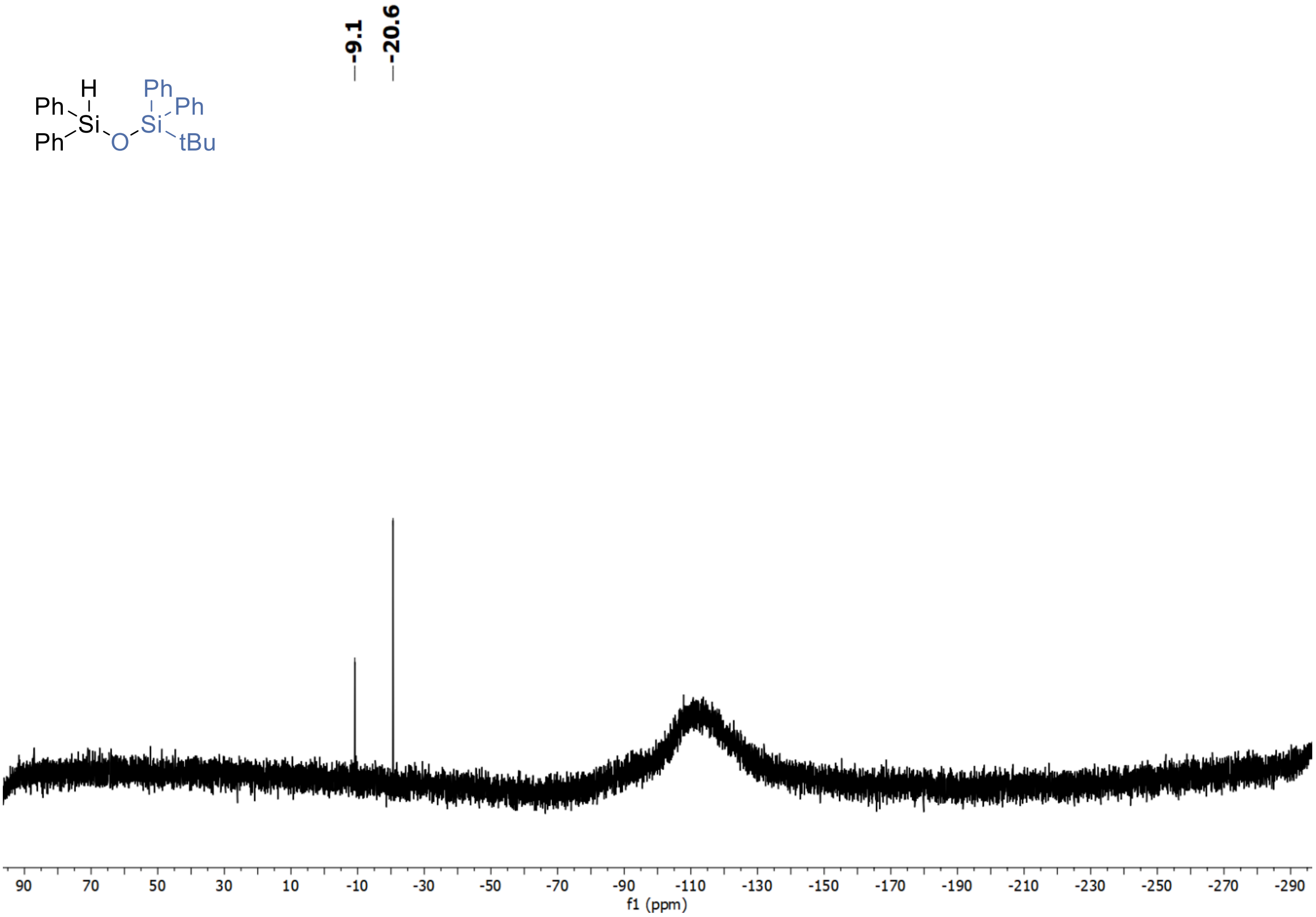


Figure S28. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-1,1,3,3-tetraphenyldisiloxane (**3i**).

1-(*tert*-Butyl)-3,3-diethyl-1,1-dimethyldisiloxane (3j)

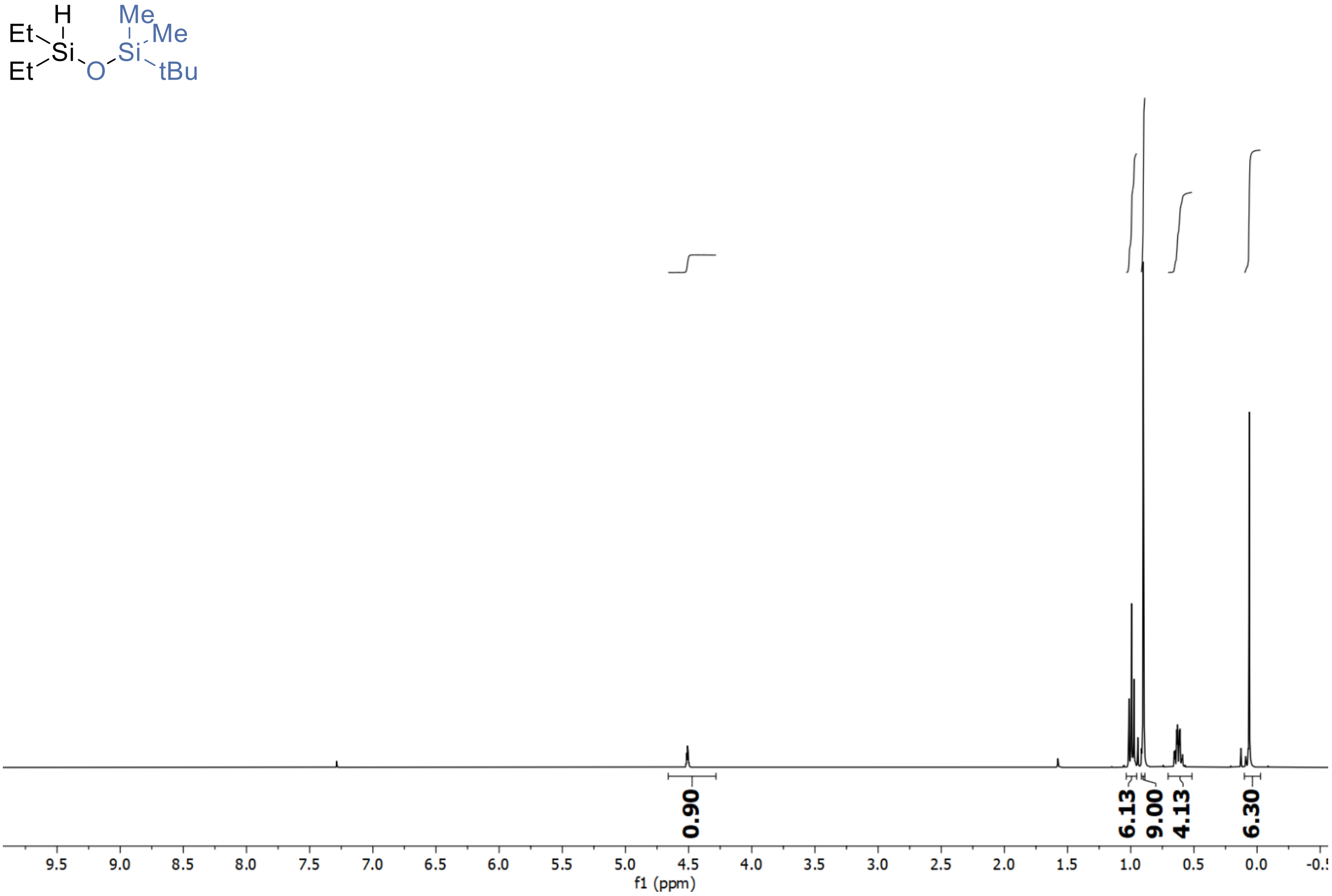


Figure S29. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-3,3-diethyl-1,1-dimethyldisiloxane (**3j**).

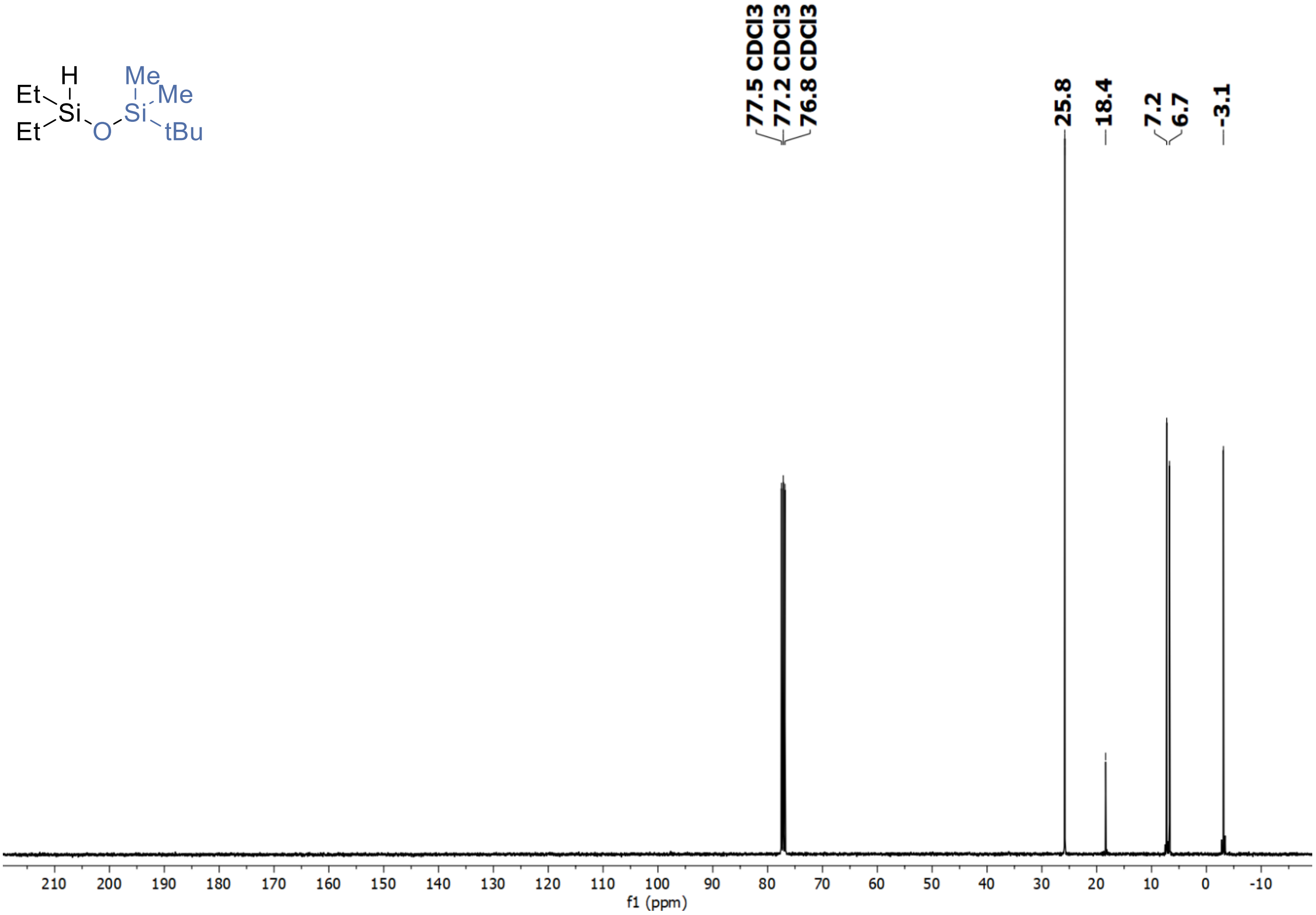


Figure S30. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-3,3-diethyl-1,1-dimethyldisiloxane (**3j**).

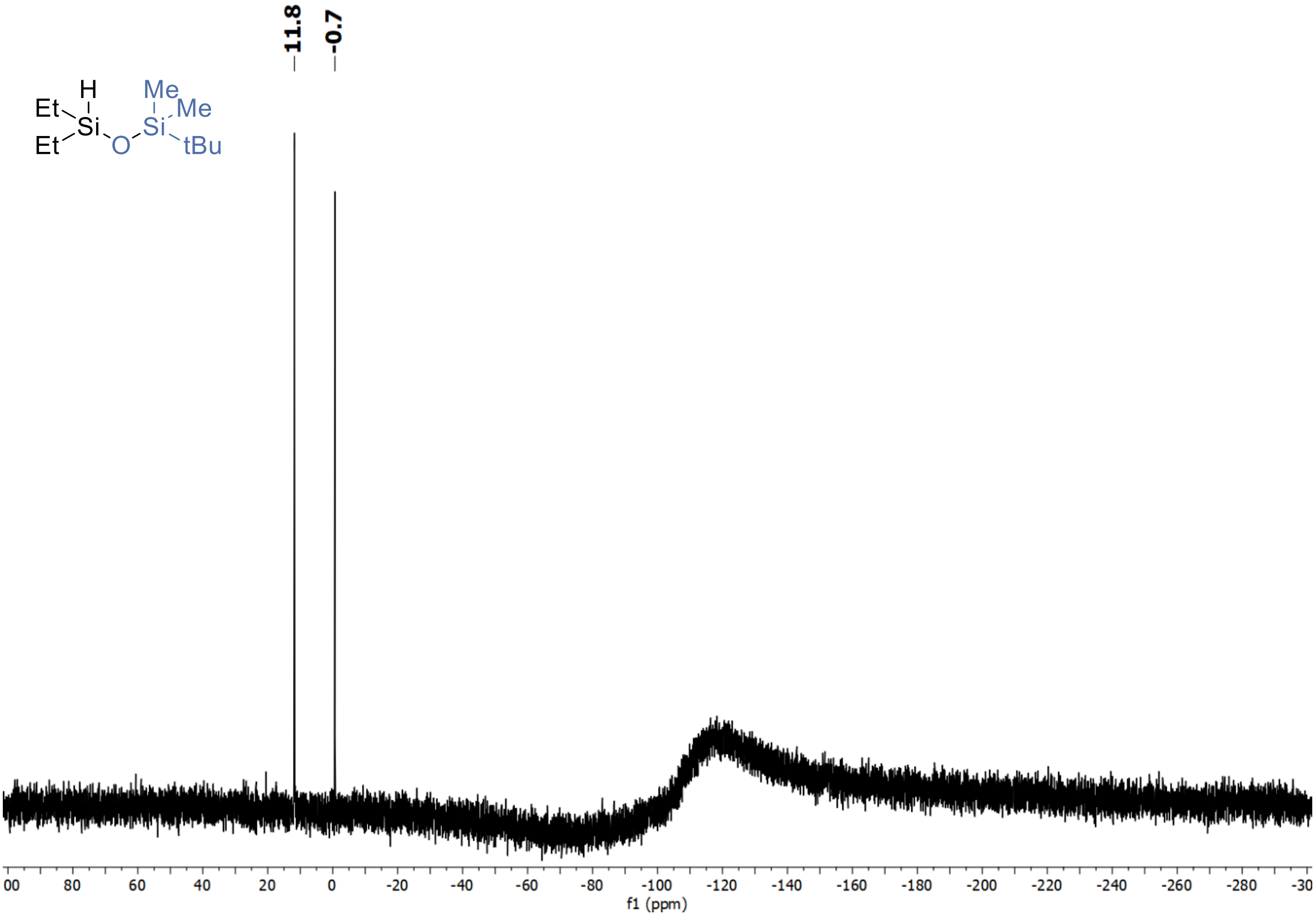


Figure S31. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-3,3-diethyl-1,1-dimethyldisiloxane (**3j**).

1-(*tert*-Butyl)-3,3-diethyl-1,1-diphenyldisiloxane (3k)

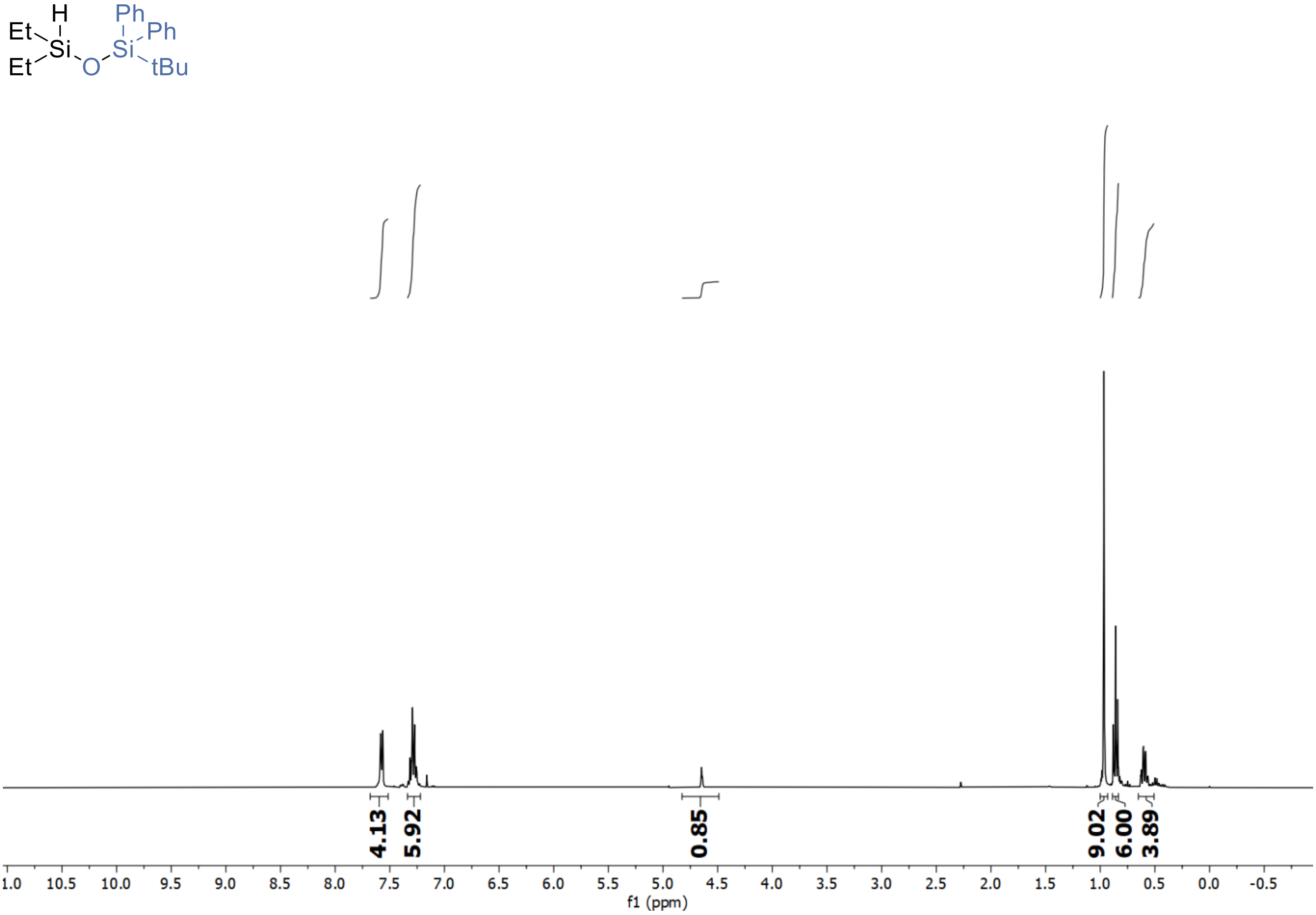


Figure S32. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-3,3-diethyl-1,1-dimethyldisiloxane (**3k**).

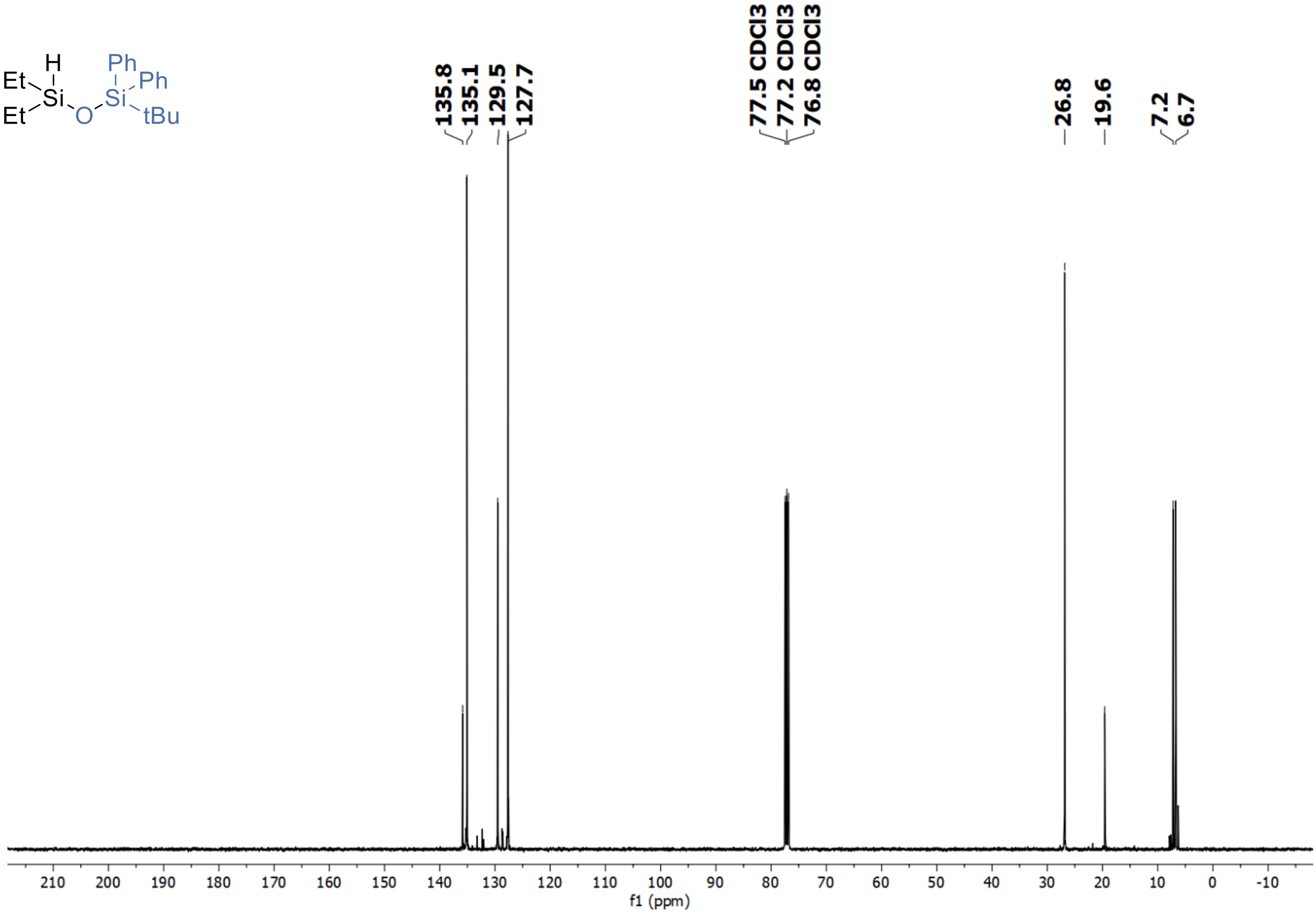


Figure S33. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-3,3-diethyl-1,1-dimethyldisiloxane (**3k**).

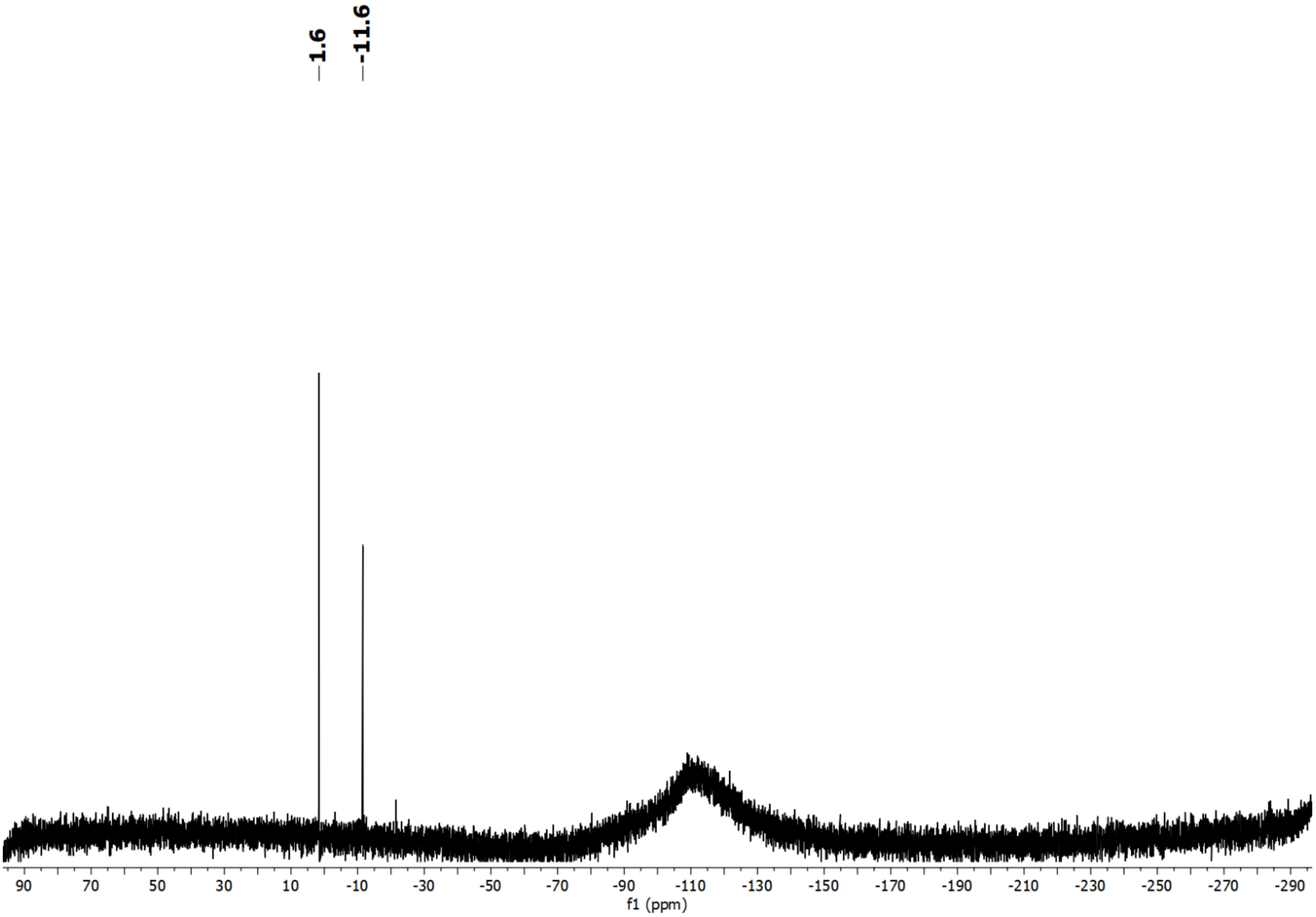


Figure S34. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1-(*tert*-butyl)-3,3-diethyl-1,1-dimethyldisiloxane (**3k).**

1,1,1,3,3-Pentamethyl-3-phenyldisiloxane (3l)

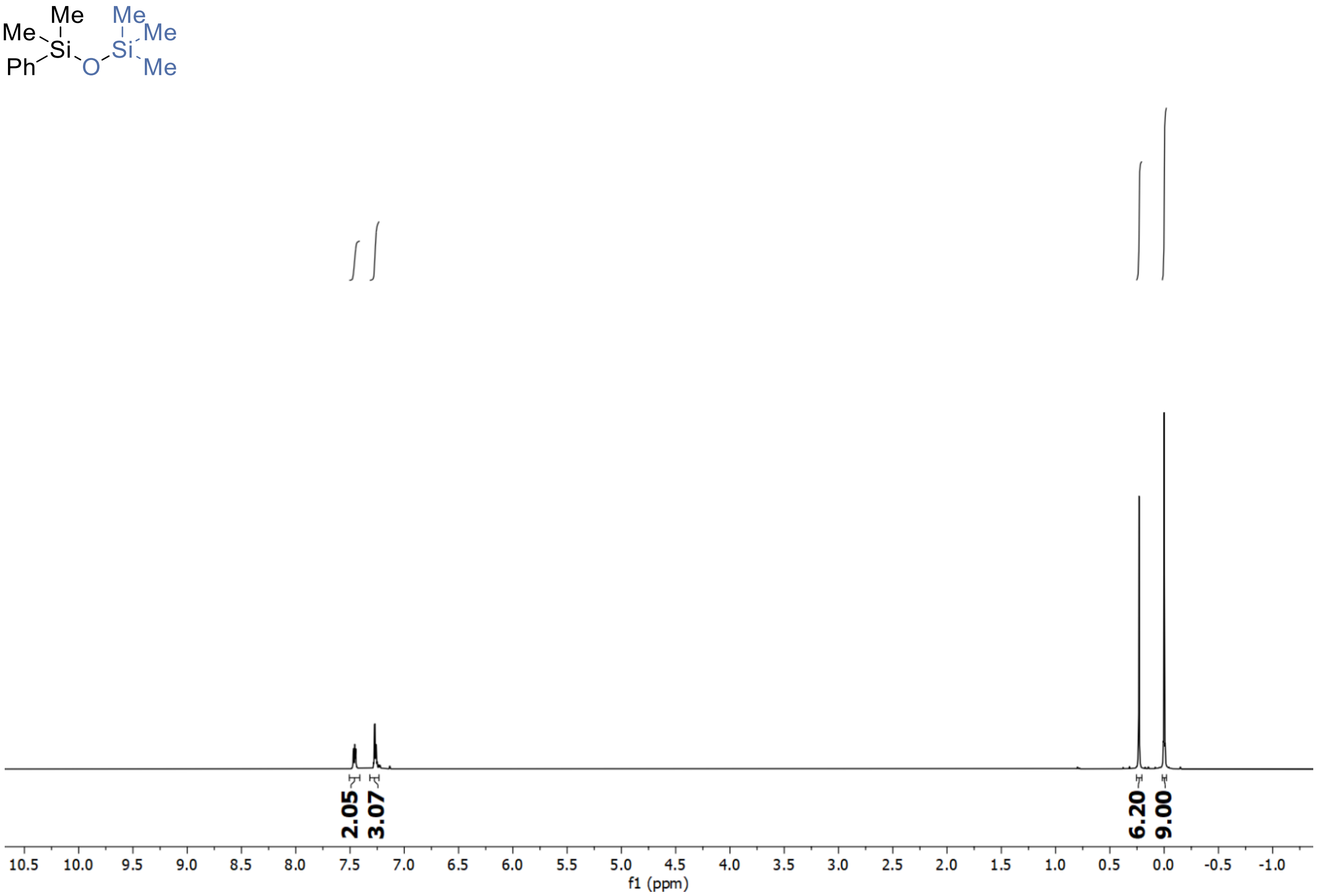


Figure S35. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,3,3-pentamethyl-3-phenyldisiloxane (**3l**).

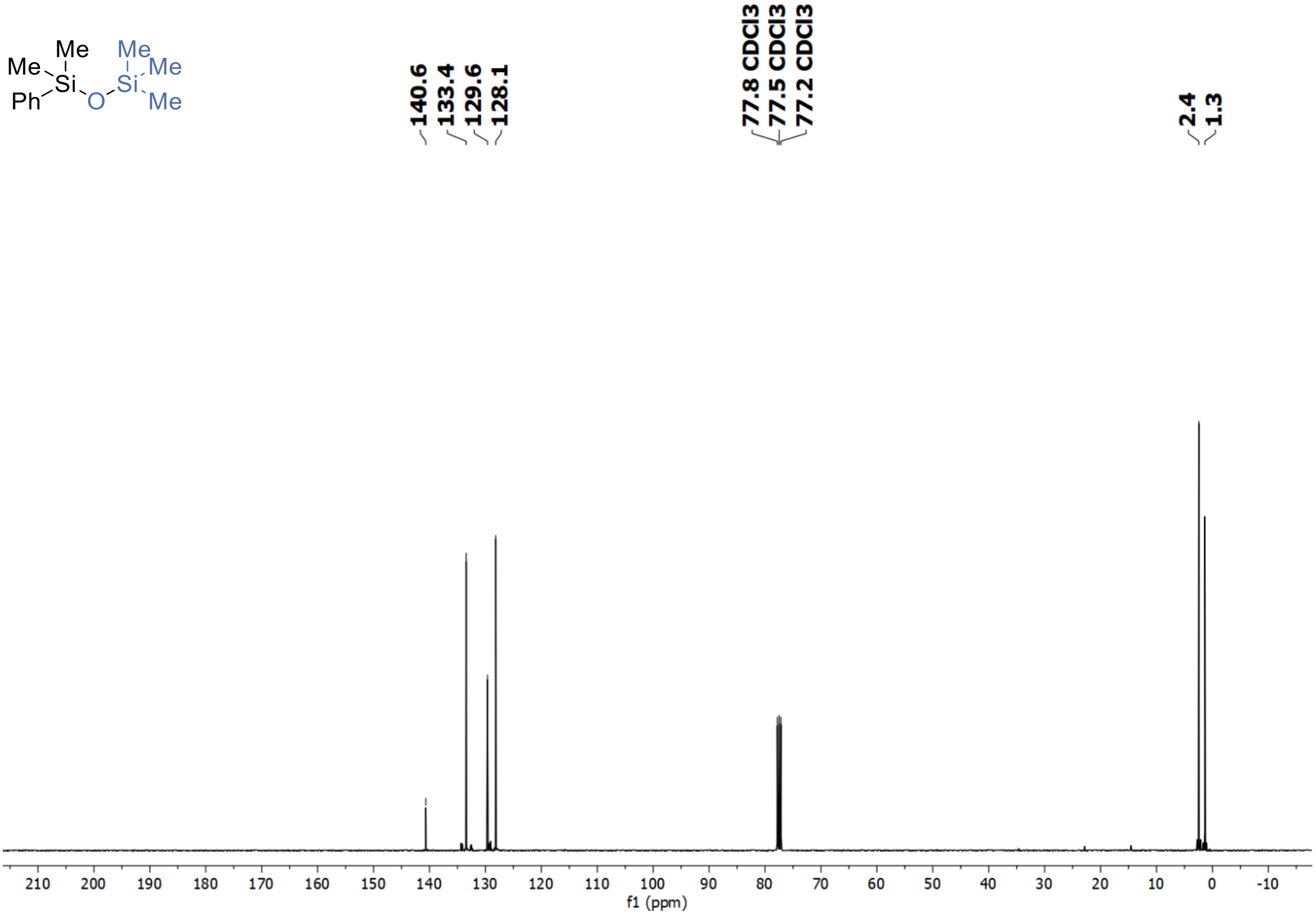


Figure S36. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,3,3-pentamethyl-3-phenyldisiloxane (**3l**).

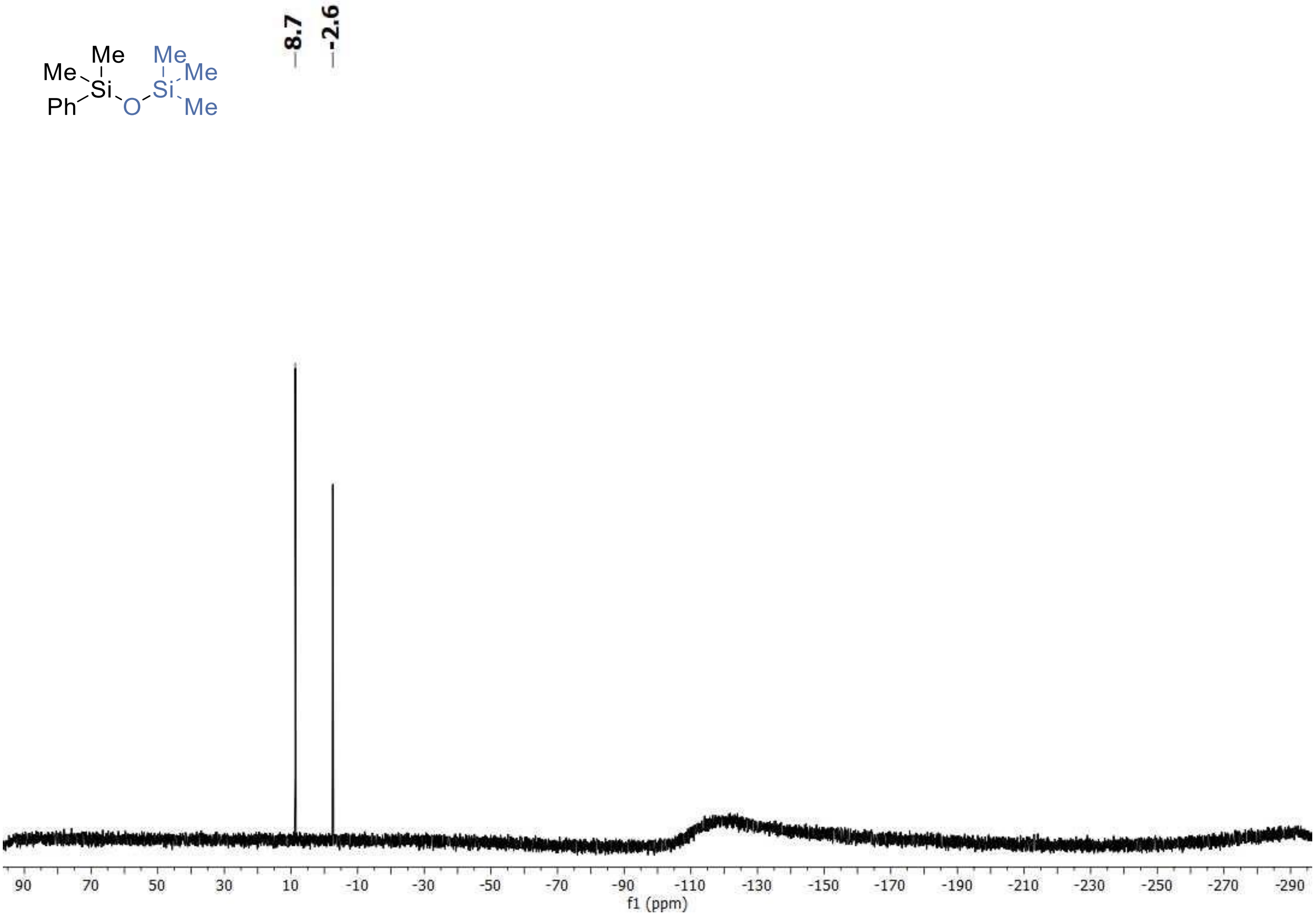


Figure S37. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,3,3-pentamethyl-3-phenyldisiloxane (**3l**).

1-(4-Bromophenyl)-1,1,3,3,3-pentamethyldisiloxane (3m)

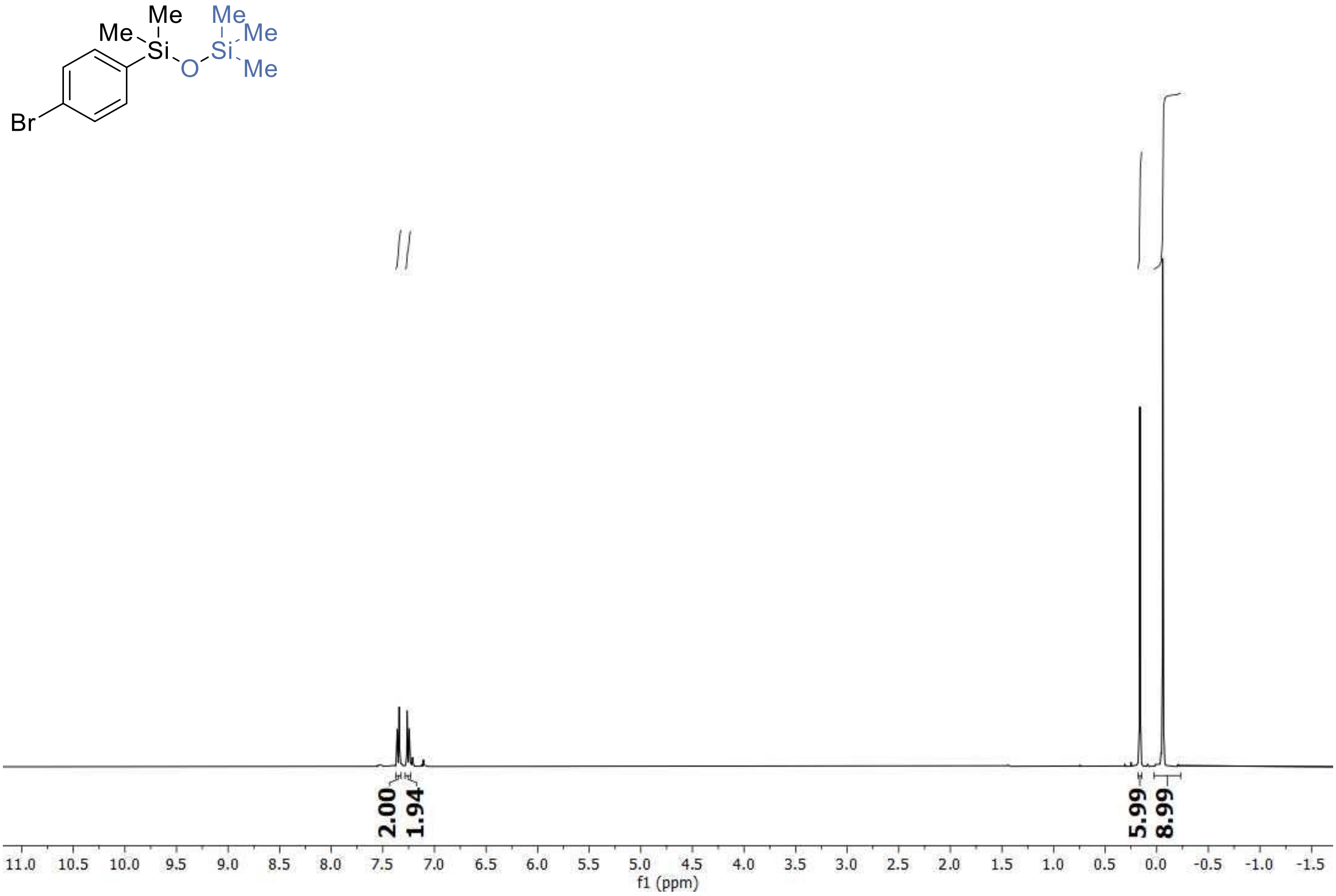


Figure S38. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1-(4-bromophenyl)-1,1,3,3,3-pentamethyldisiloxane (**3m**).

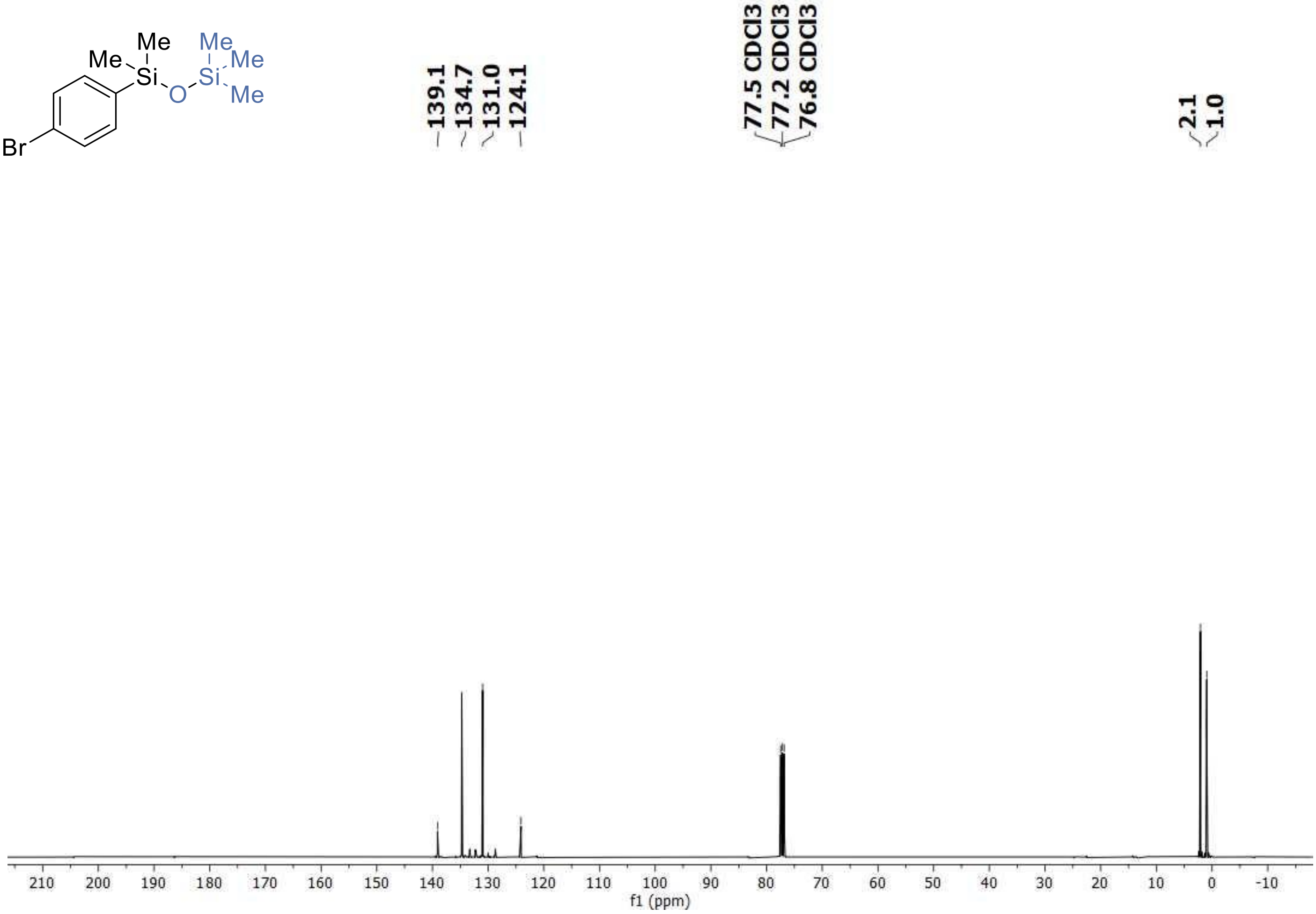


Figure S39. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1-(4-bromophenyl)-1,1,3,3,3-pentamethyldisiloxane (**3m**).

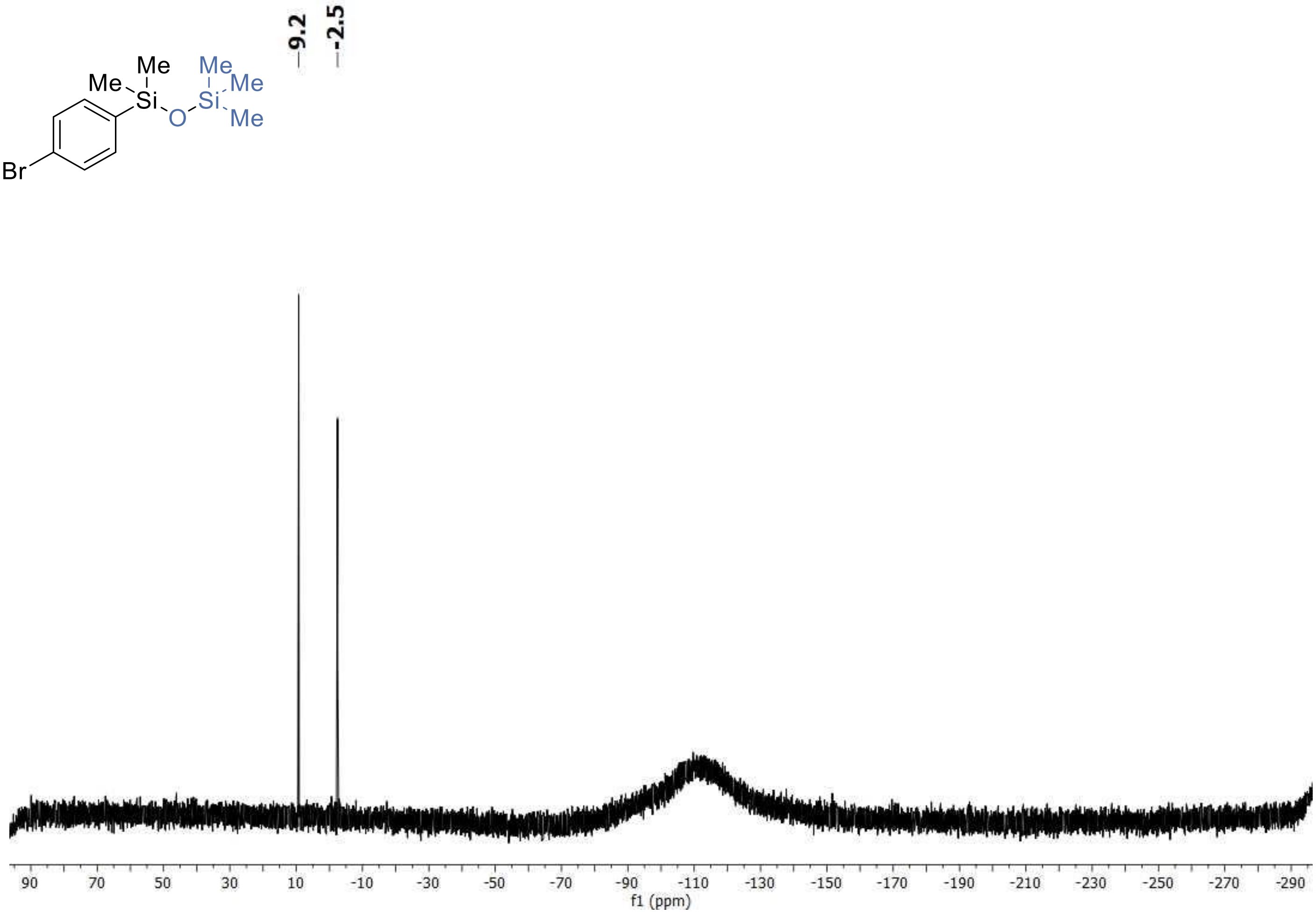


Figure S40. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1-(4-bromophenyl)-1,1,3,3,3-pentamethyldisiloxane (**3m**).

1,1,1,3-Tetramethyl-3,3-diphenyldisiloxane (3n)

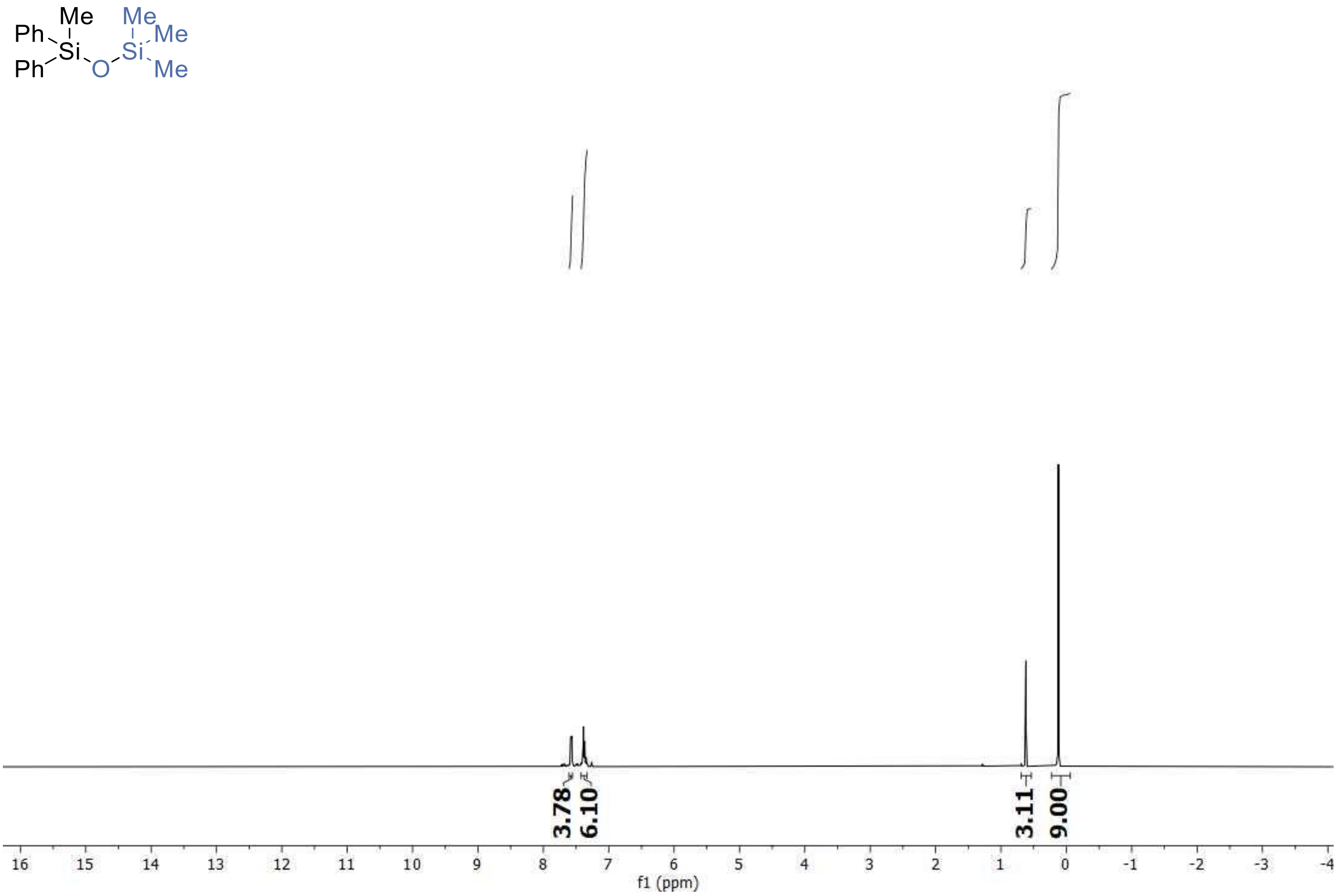


Figure S41. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,3-tetramethyl-3,3-diphenyldisiloxane (**3n**).

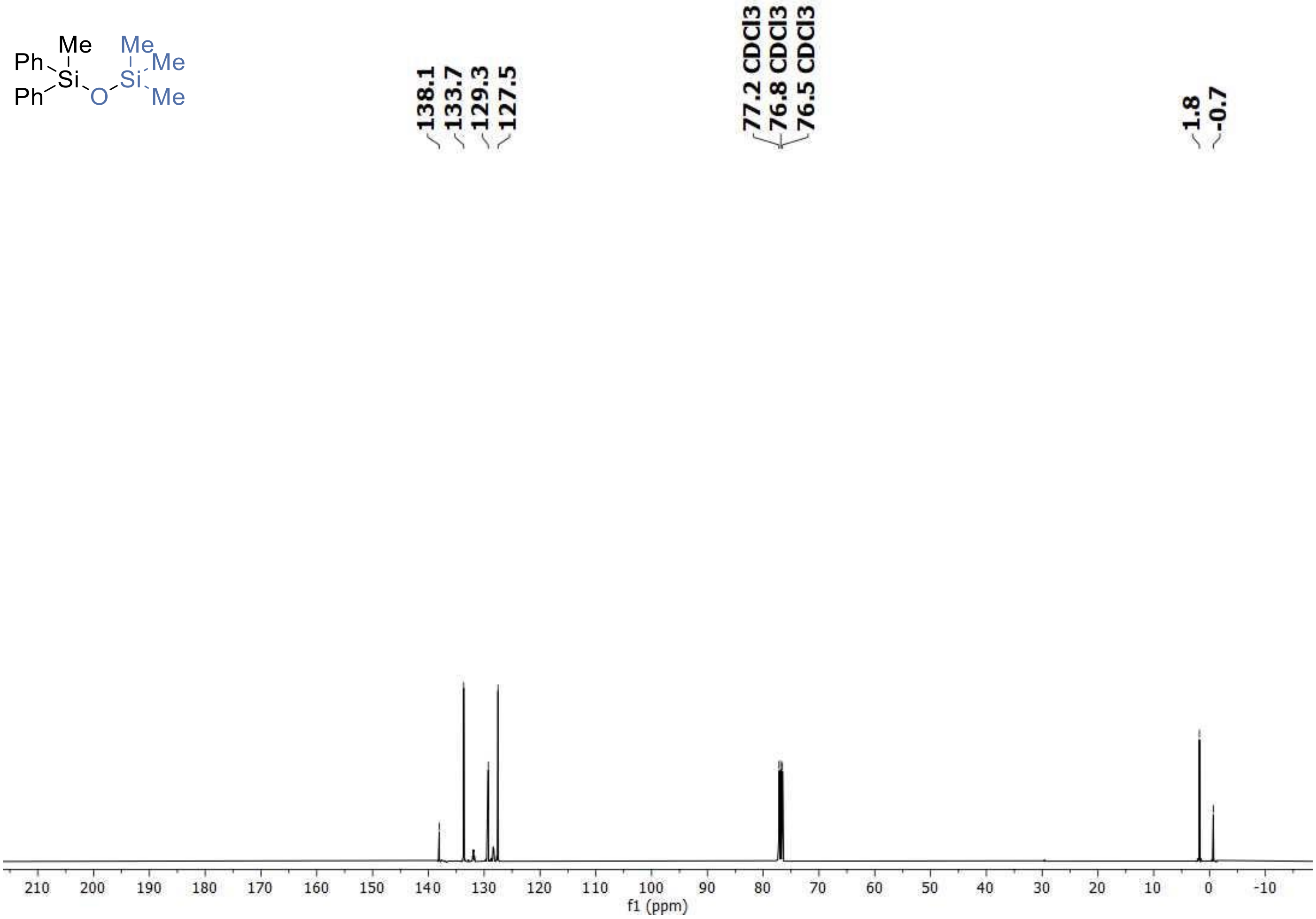


Figure S42. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,3-tetramethyl-3,3-diphenyldisiloxane (**3n**).

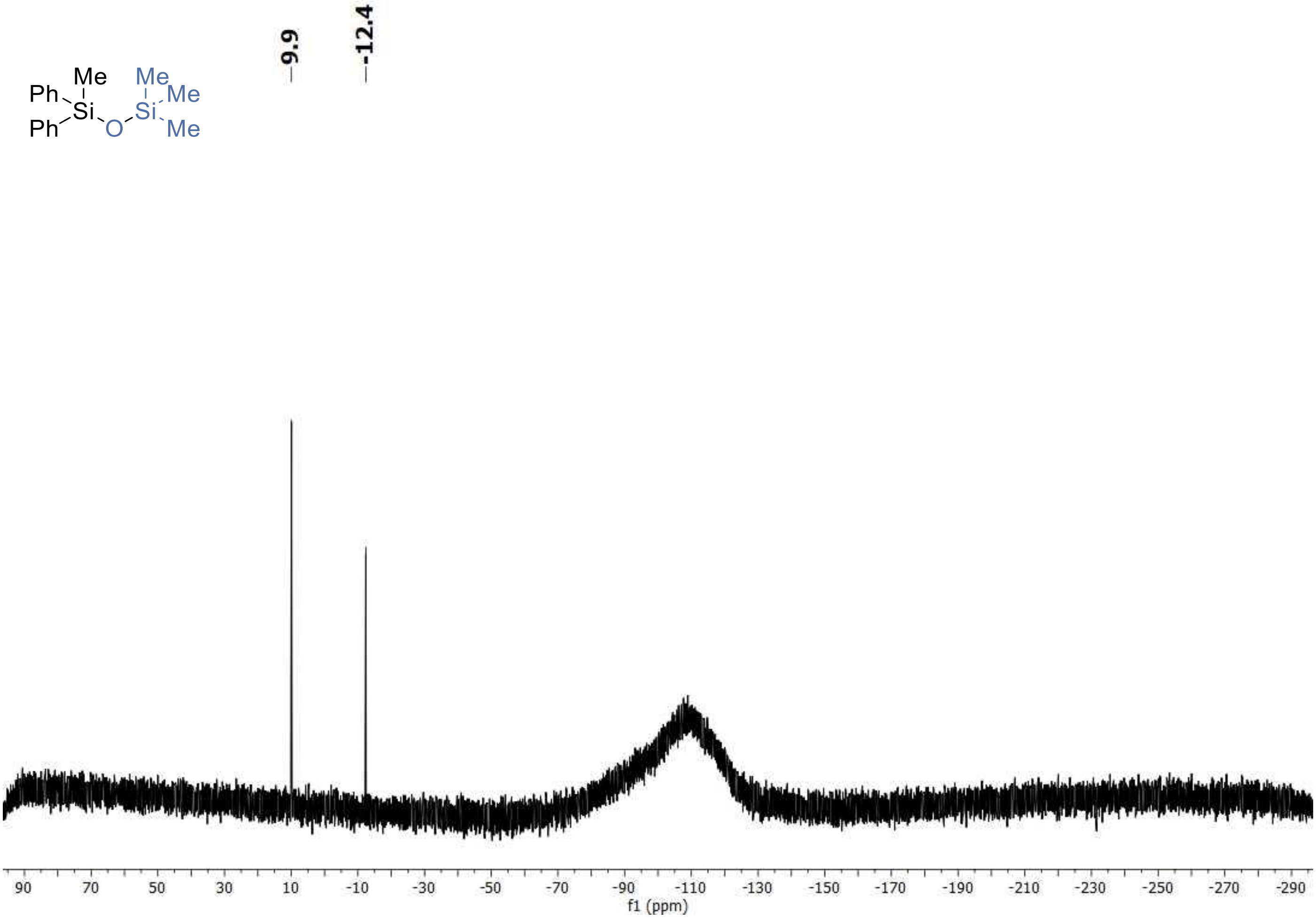


Figure S43. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,3-tetramethyl-3,3-diphenyldisiloxane (**3n**).

1,1,1,3,5,5,5-Heptamethyl-3-((trimethylsilyl)oxy)trisiloxane (3o)

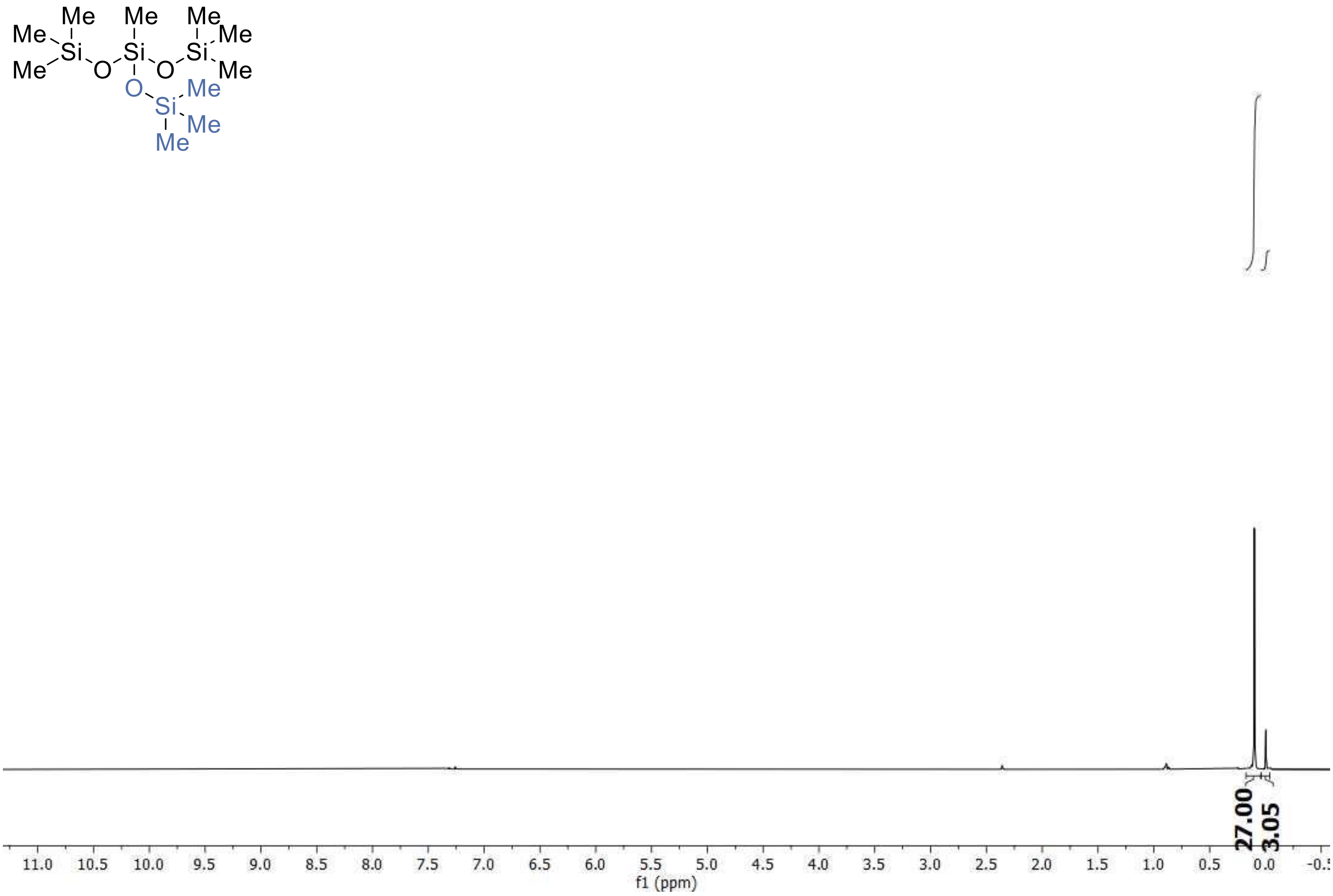


Figure S44. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,3,5,5,5-heptamethyl-3-((trimethylsilyl)oxy) (**3o**).

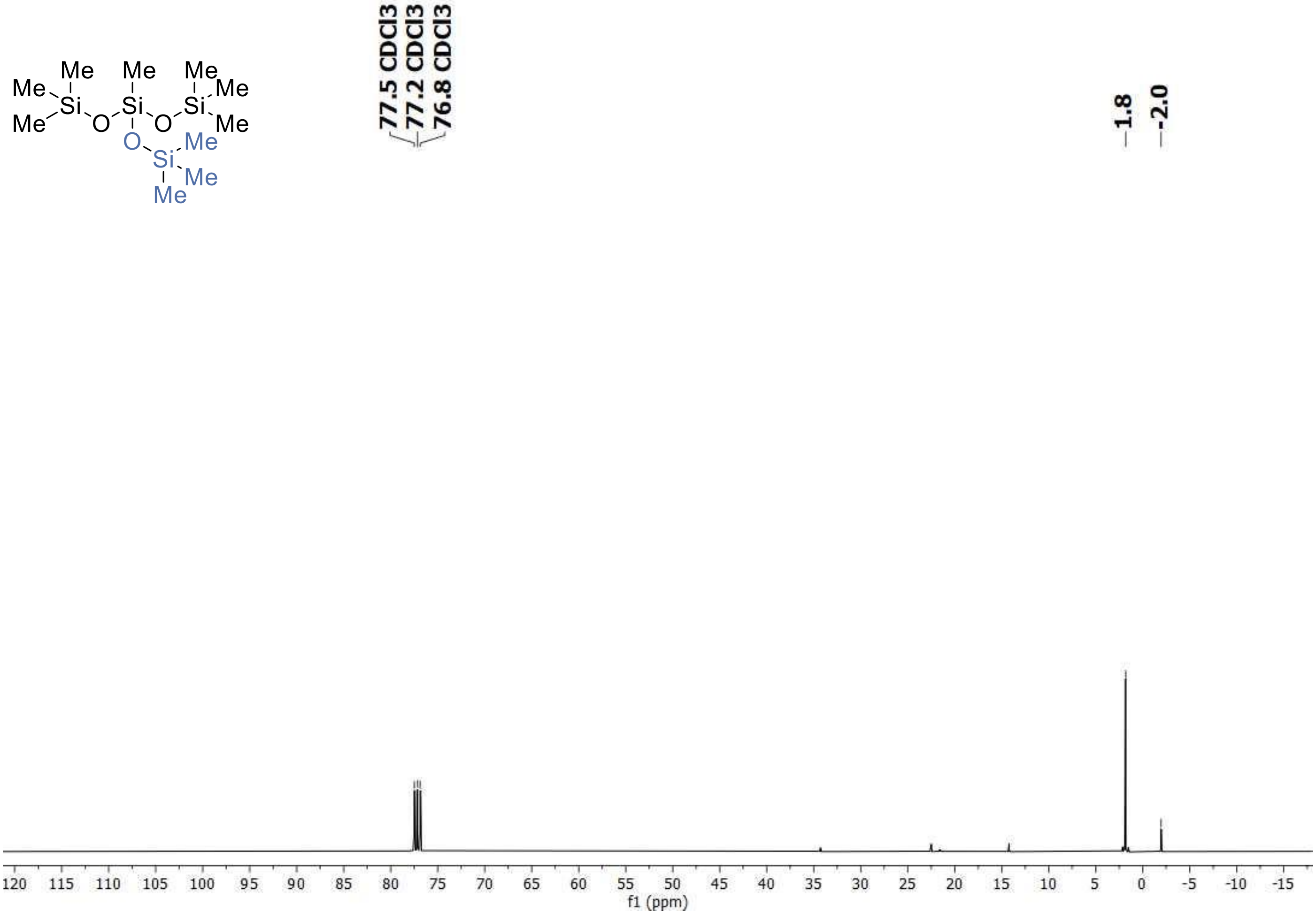


Figure S45. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,3,5,5,5-heptamethyl-3-((trimethylsilyl)oxy) (**3o**).

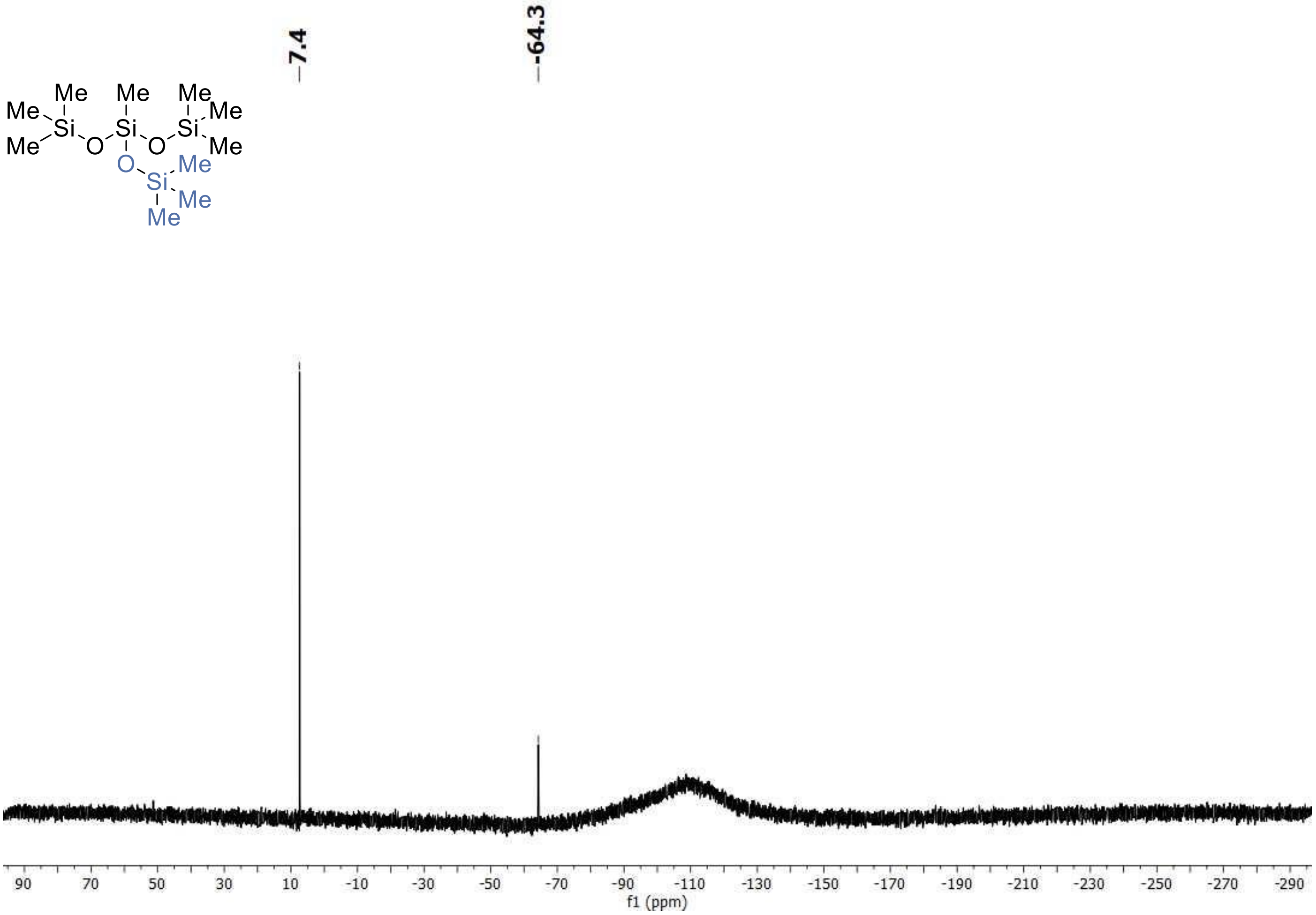


Figure S46. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,3,5,5,5-heptamethyl-3-((trimethylsilyl)oxy) (**3o**).

1,1,1,3,3,5,5,7,7,9,9,9-Dodecamethylpentasiloxane (3p)

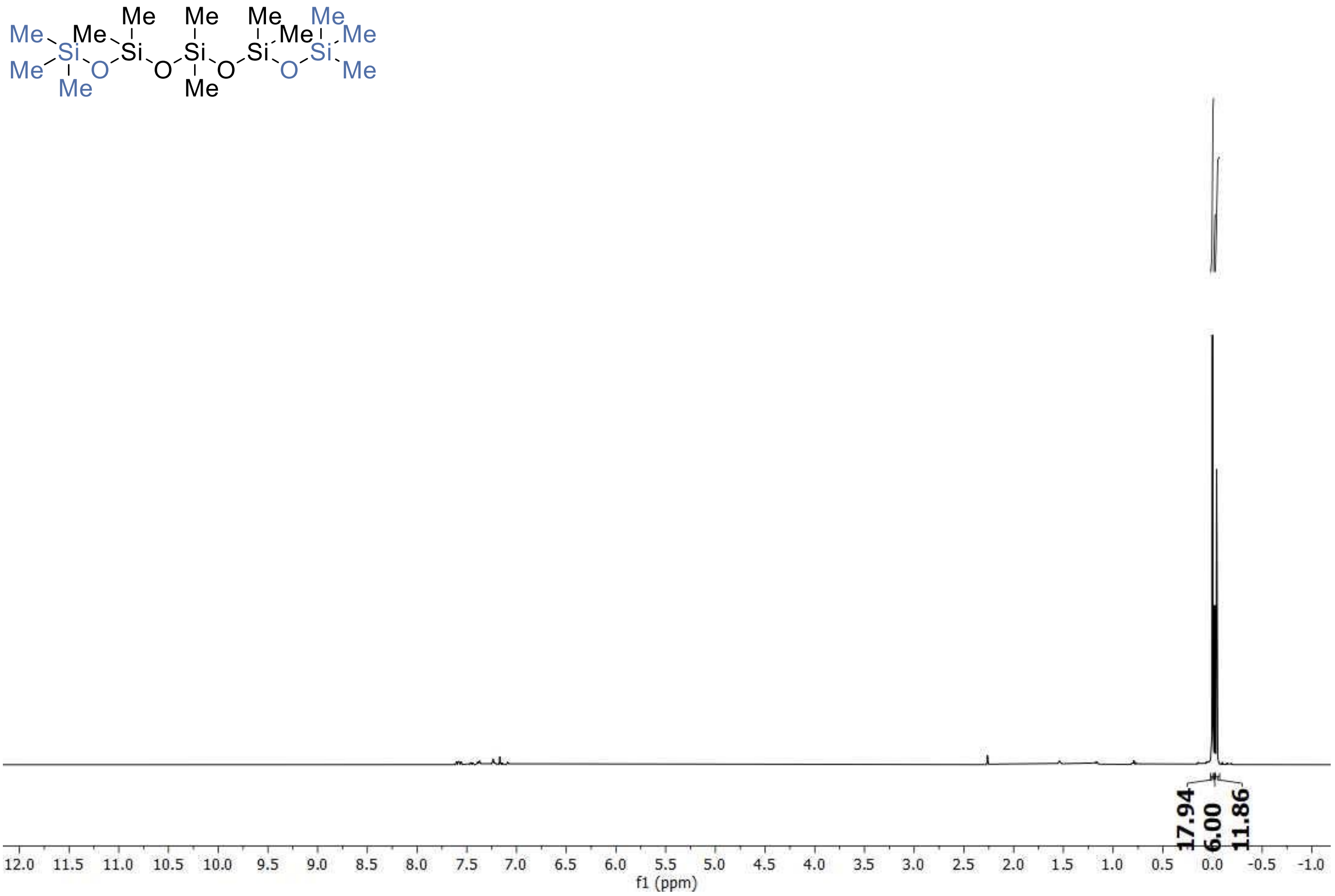


Figure S47. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,3,3,5,5,7,7,9,9,9-dodecamethylpentasiloxane (**3p**).

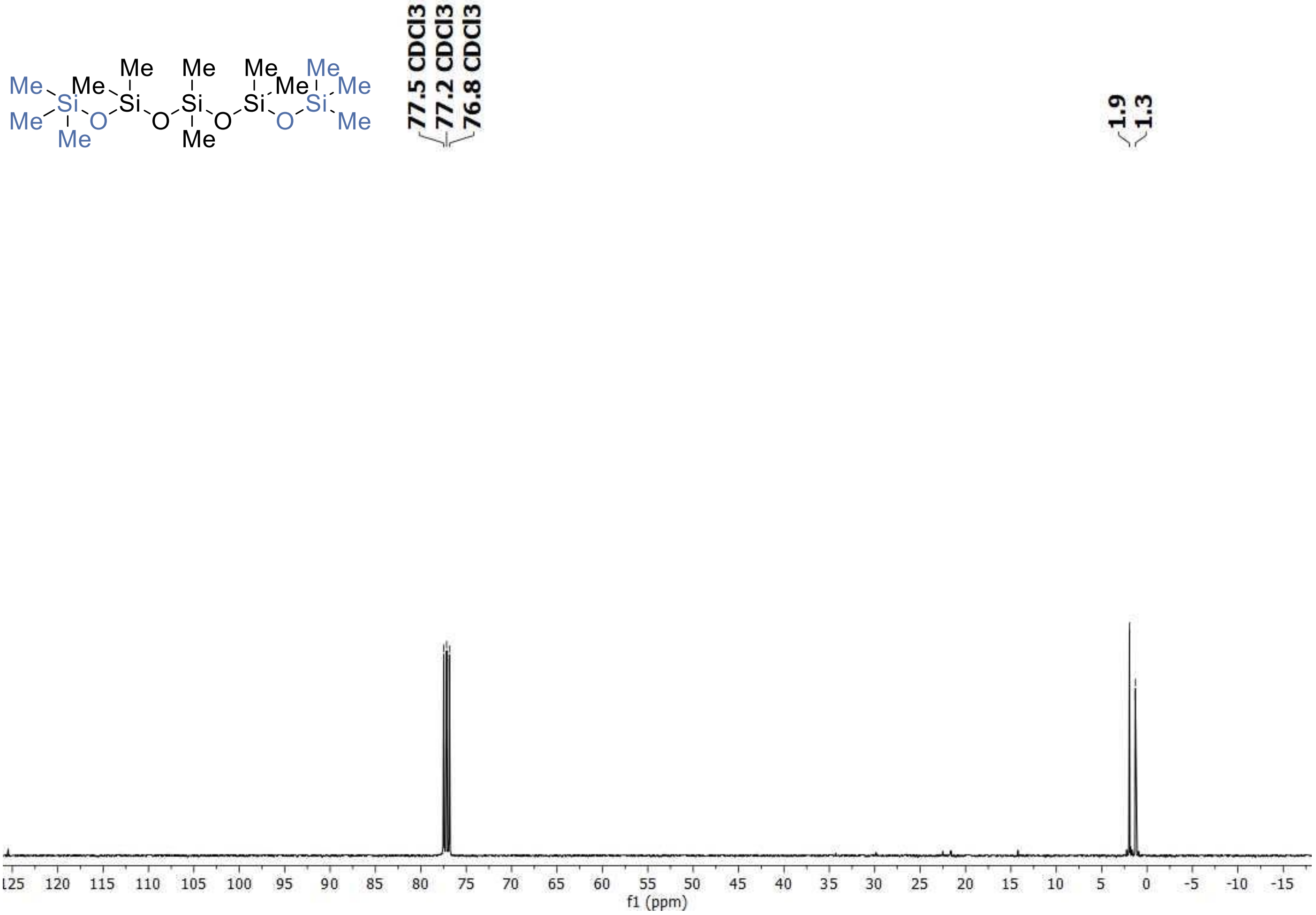


Figure S48. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,3,3,5,5,7,7,9,9,9-dodecamethylpentasiloxane (**3p**).

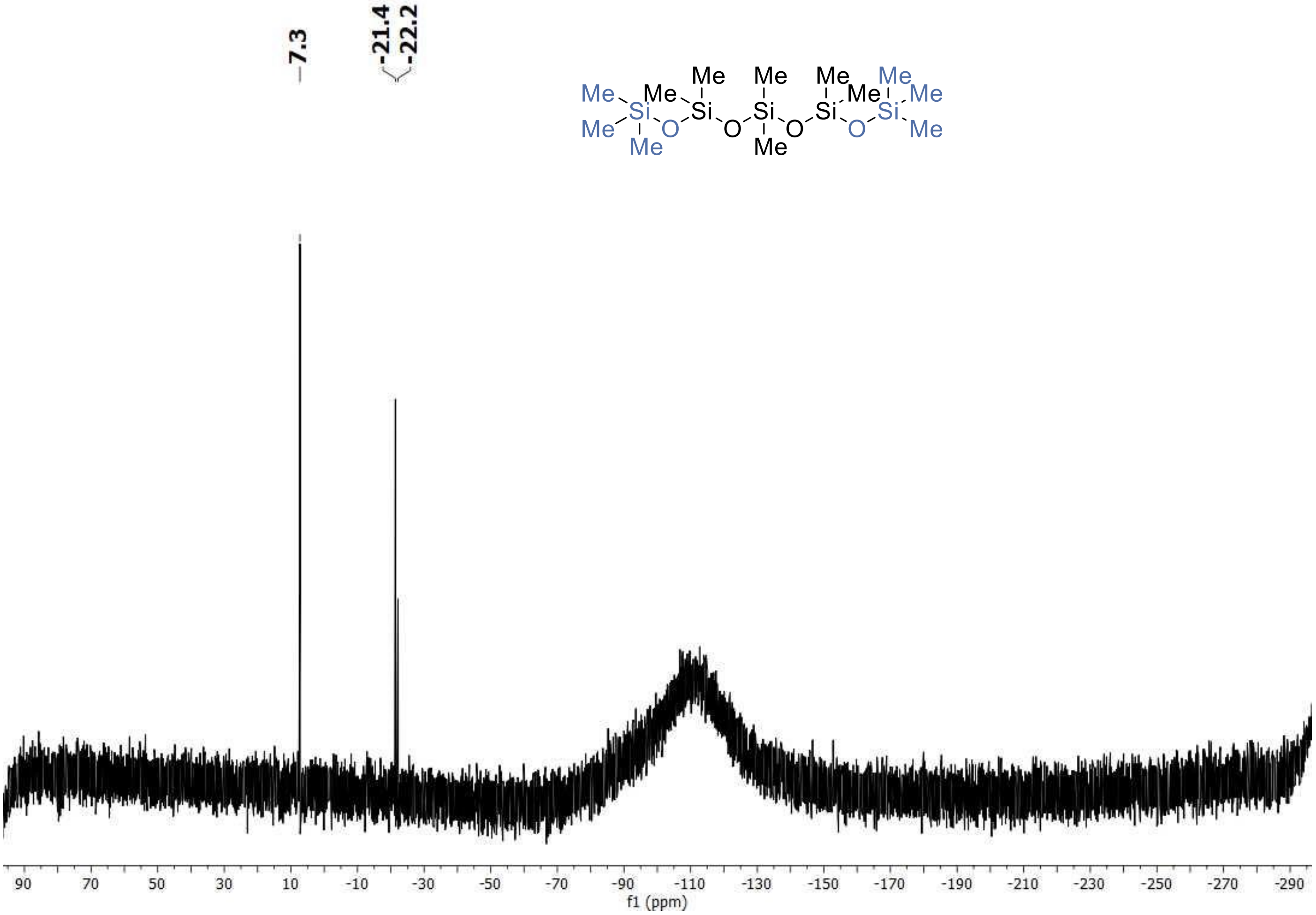
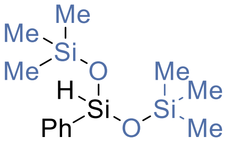


Figure S49. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,3,3,5,5,7,7,9,9,9-dodecamethylpentasiloxane (**3p**).

1,1,1,5,5,5-Hexamethyl-3-phenyltrisiloxane (4a)



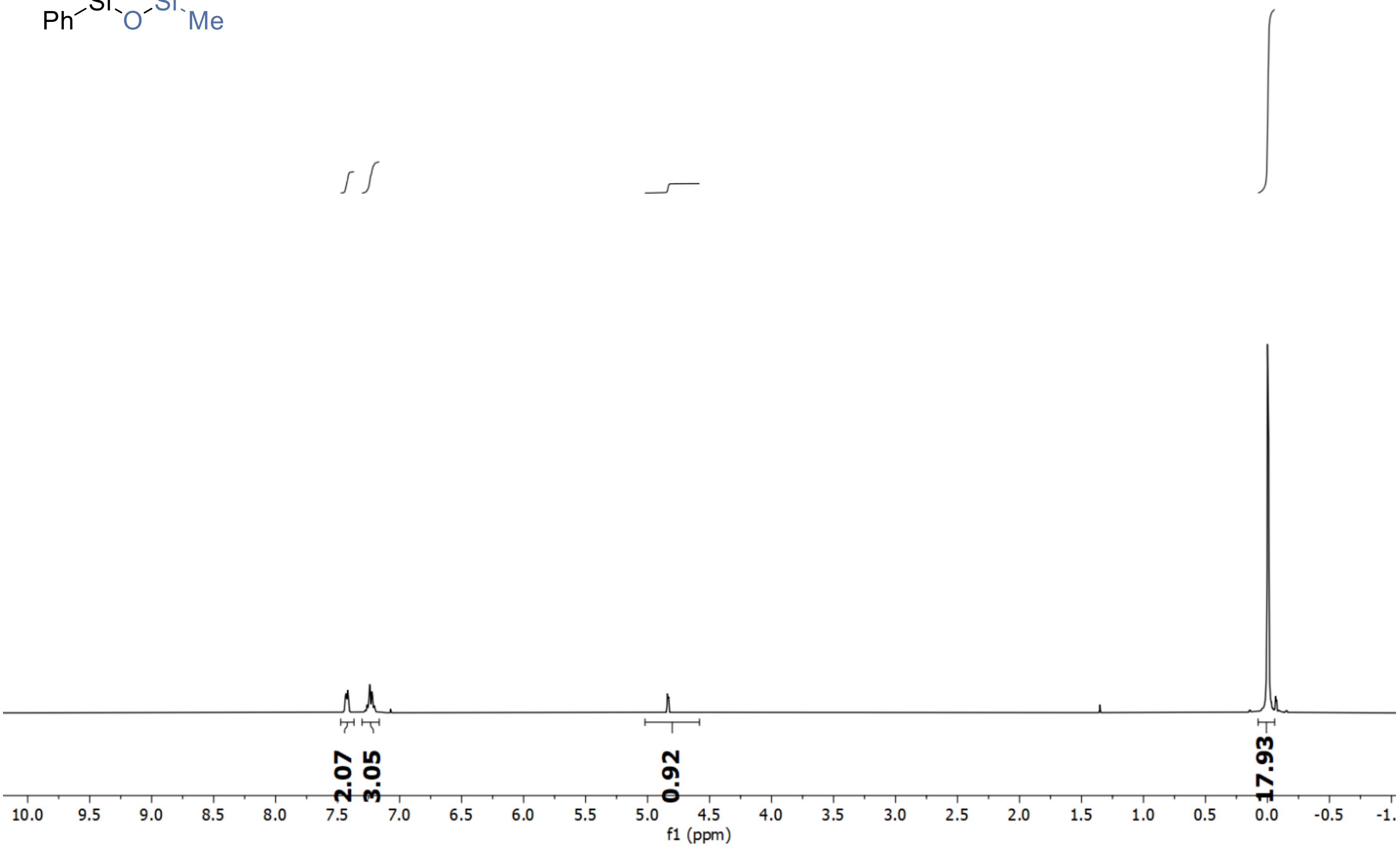


Figure S50. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane (**4a**).

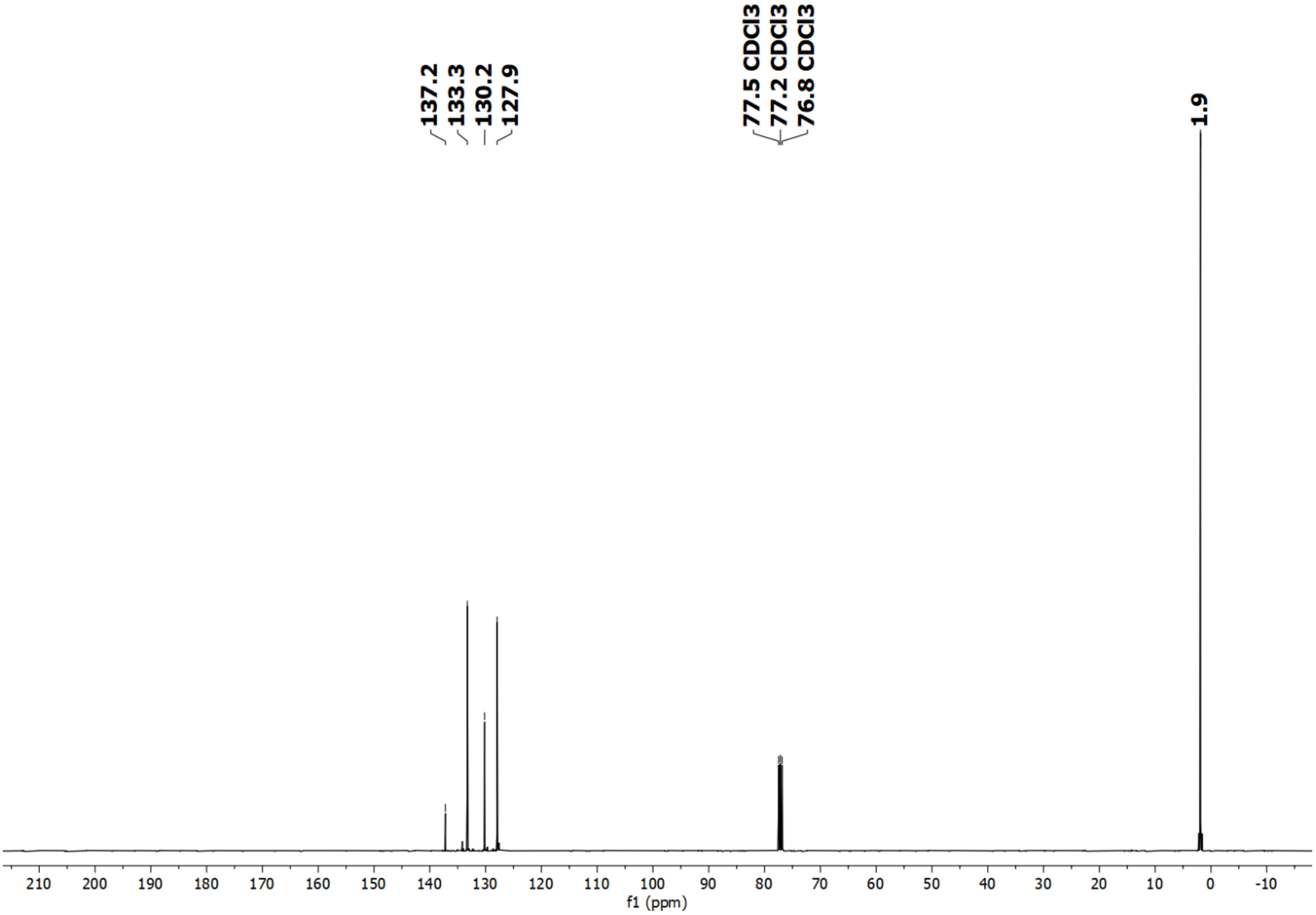


Figure S51. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane (**4a**).

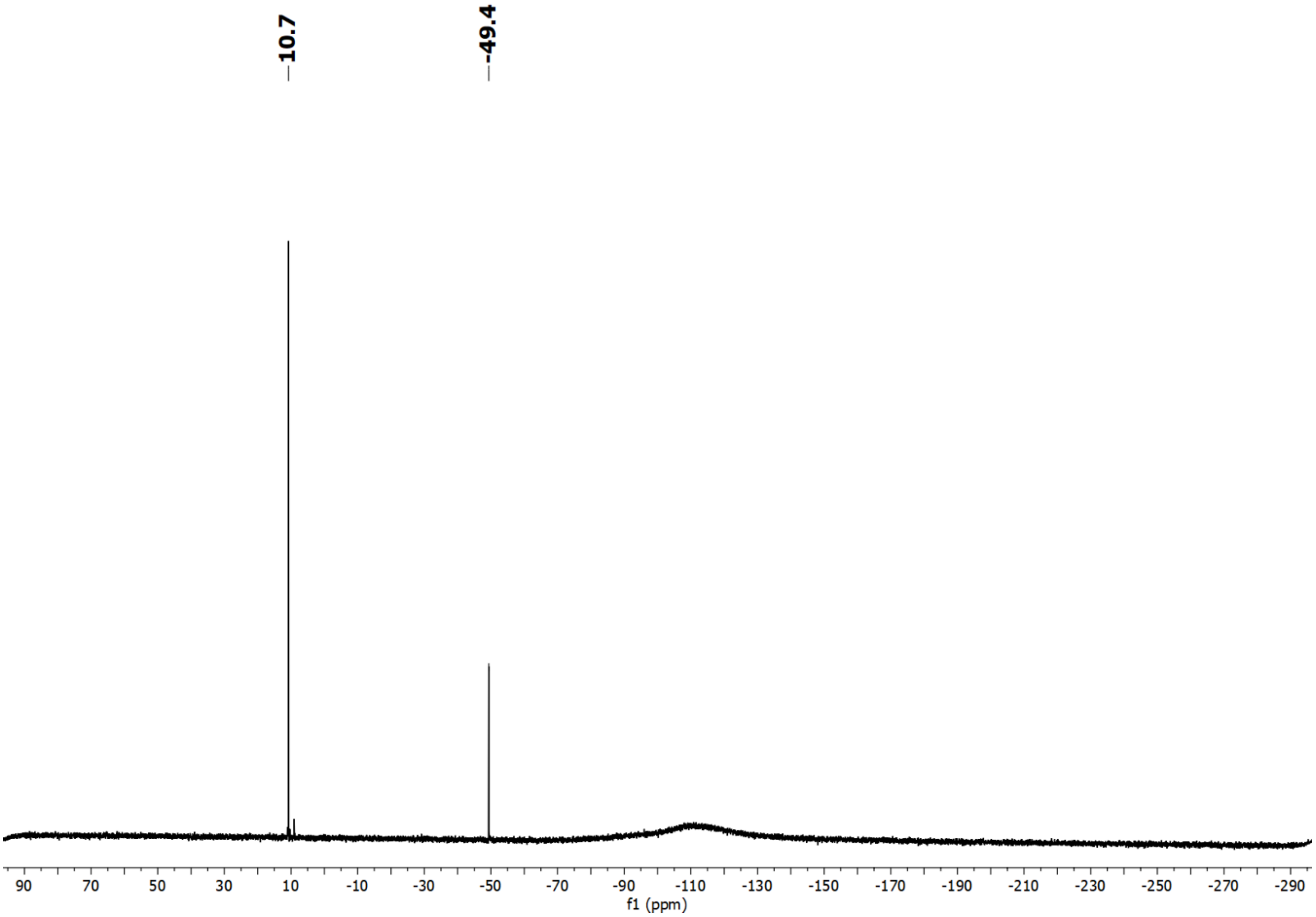


Figure S52. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane (**4a**).

1,1,1,5,5,5-Hexaethyl-3-phenyltrisiloxane (4b)

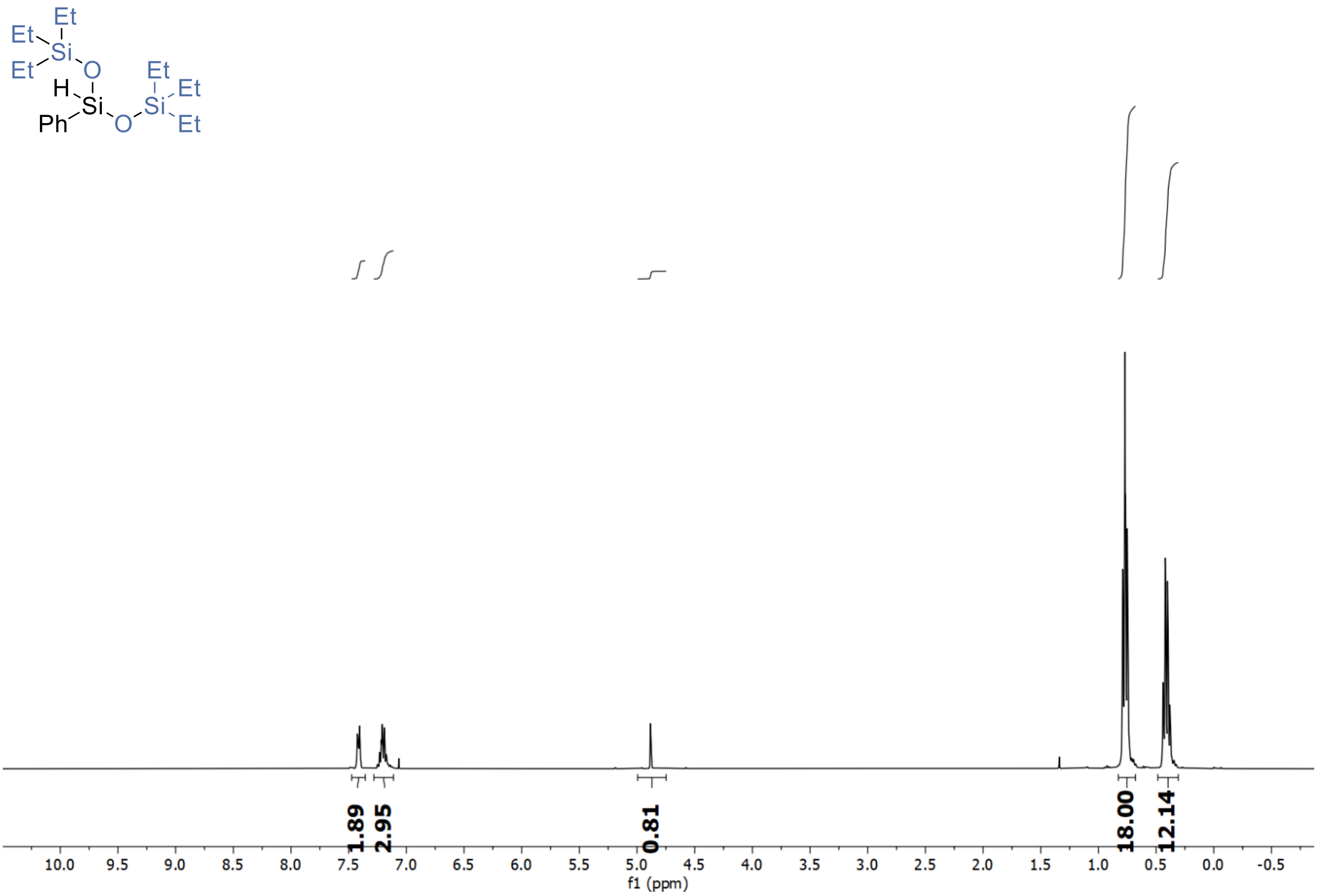


Figure S53. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexaethyl-3-phenyltrisiloxane (**4b**).

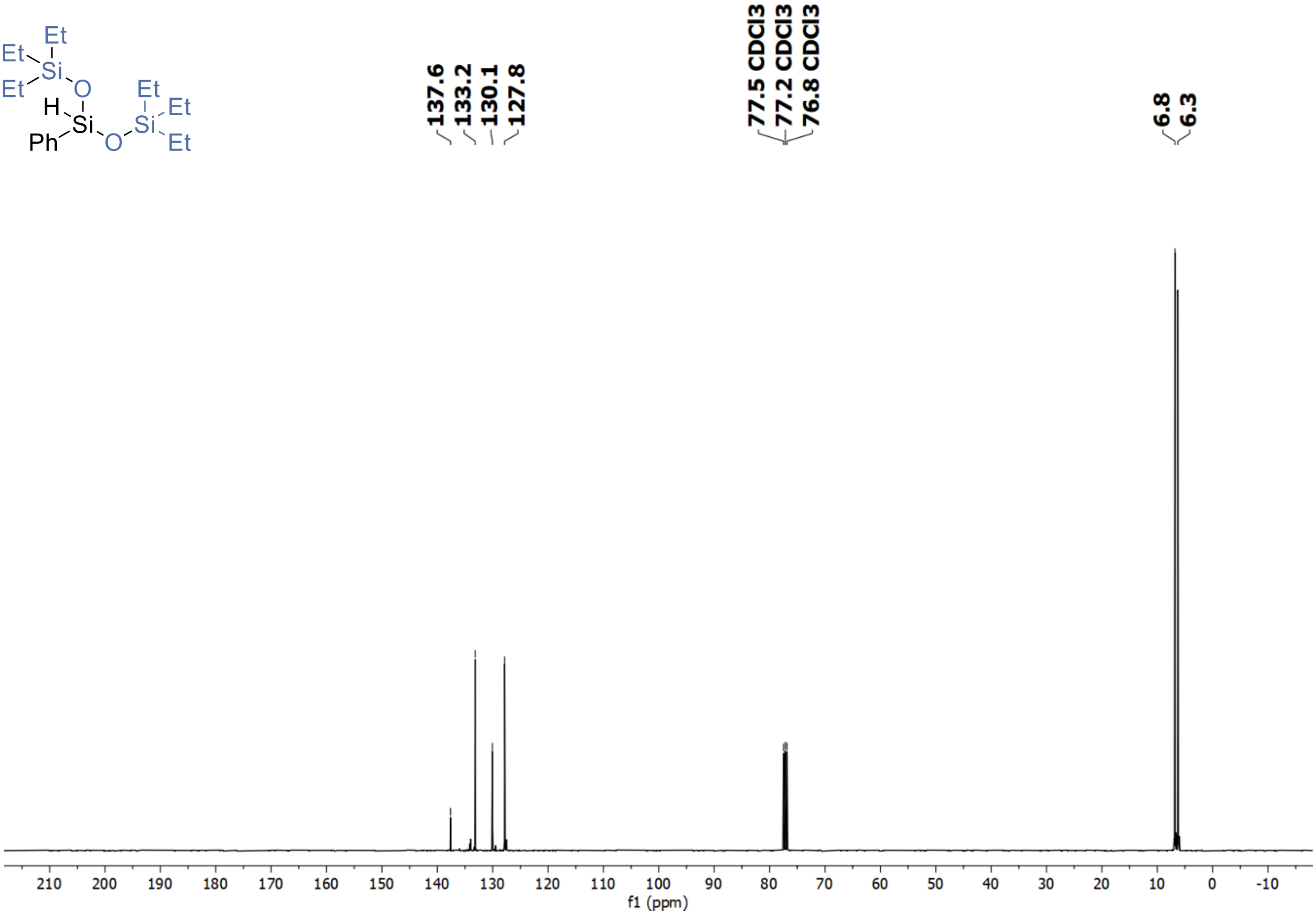


Figure S54. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexaethyl-3-phenyltrisiloxane (**4b**).

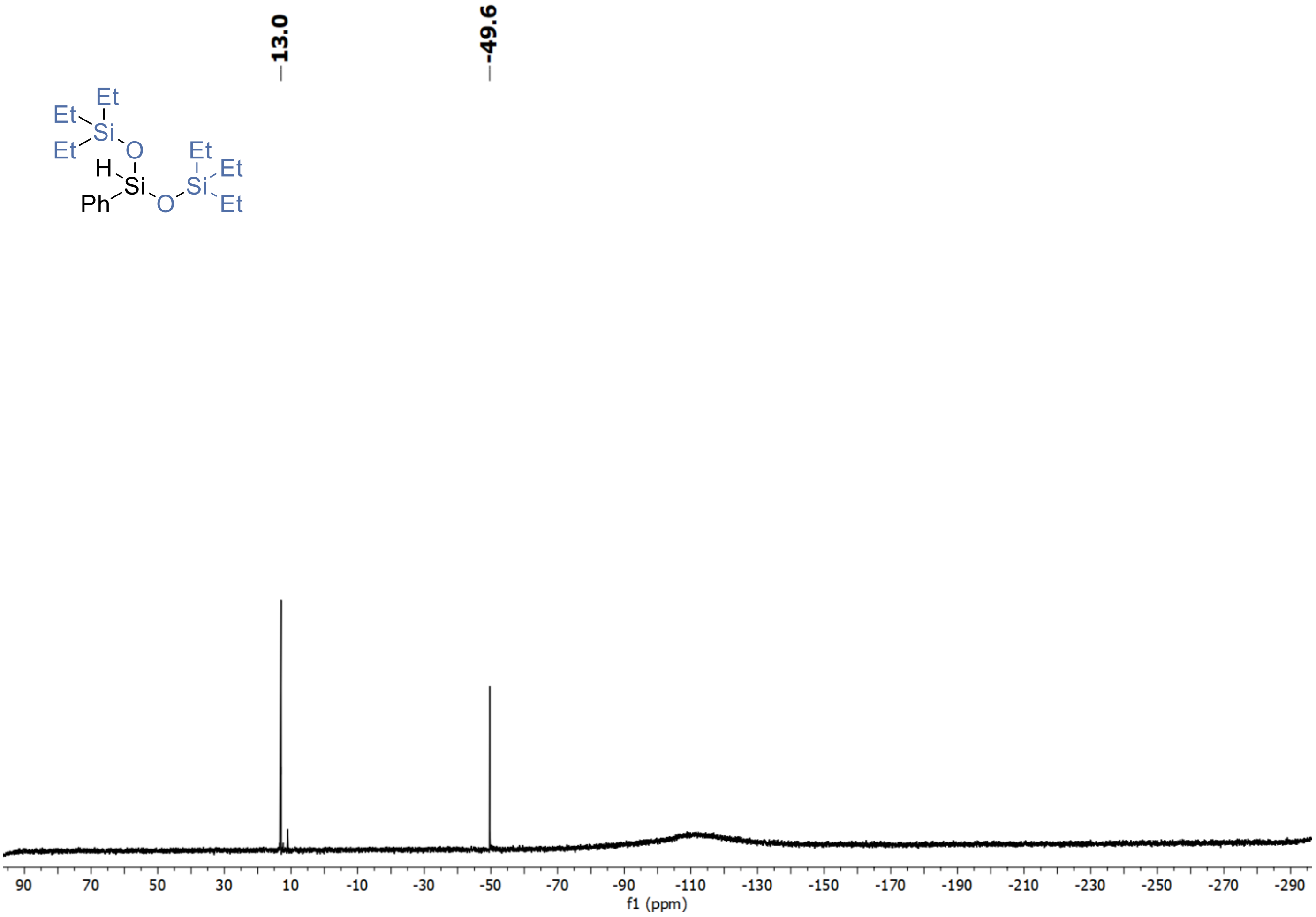


Figure S55. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexaethyl-3-phenyltrisiloxane (**4b**).

1,5-Di-*tert*-butyl-1,1,5,5-tetramethyl-3-phenyltrisiloxane (4c)

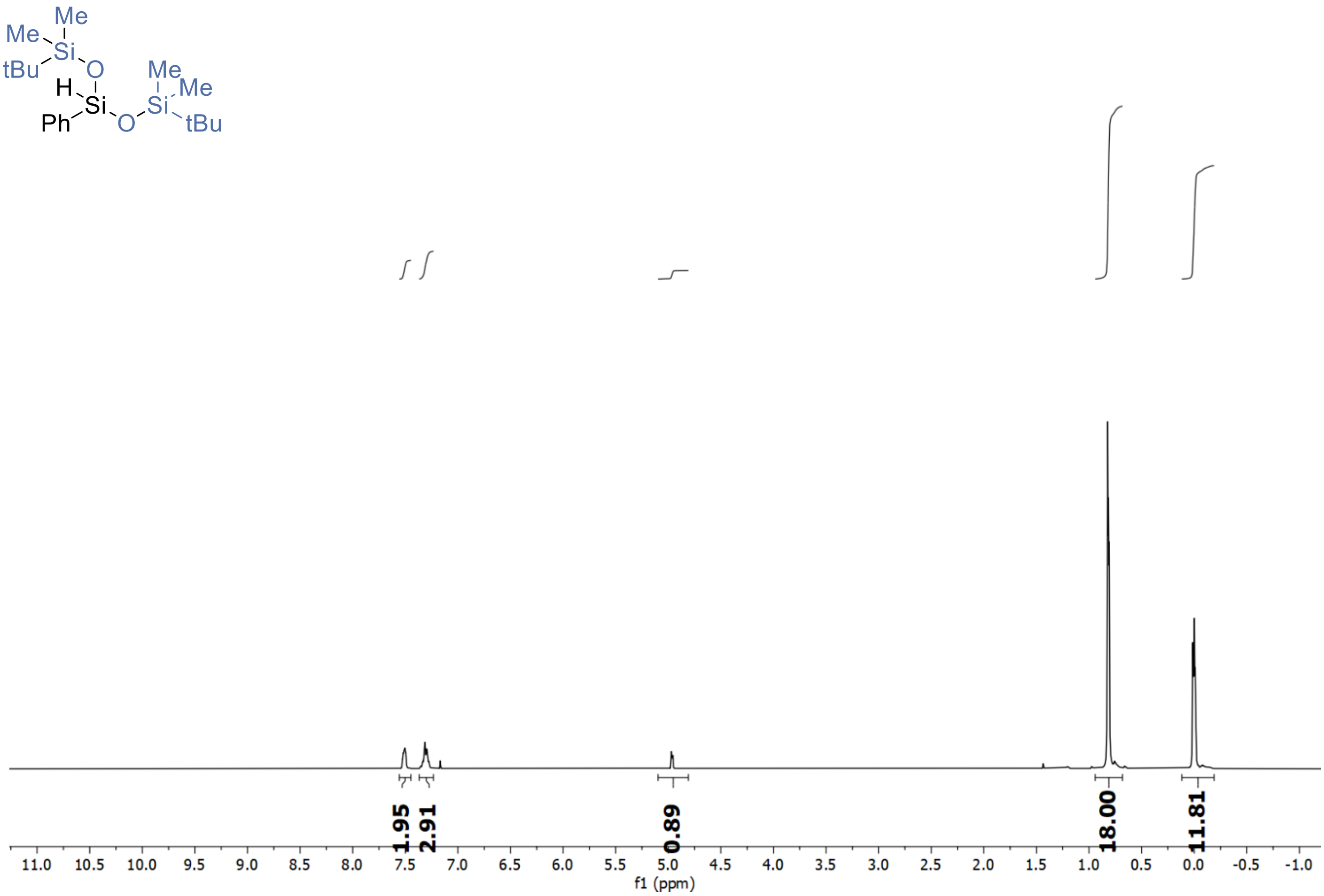


Figure S56. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,5-di-*tert*-butyl-1,1,5,5-tetramethyl-3-phenyltrisiloxane (**4c**).

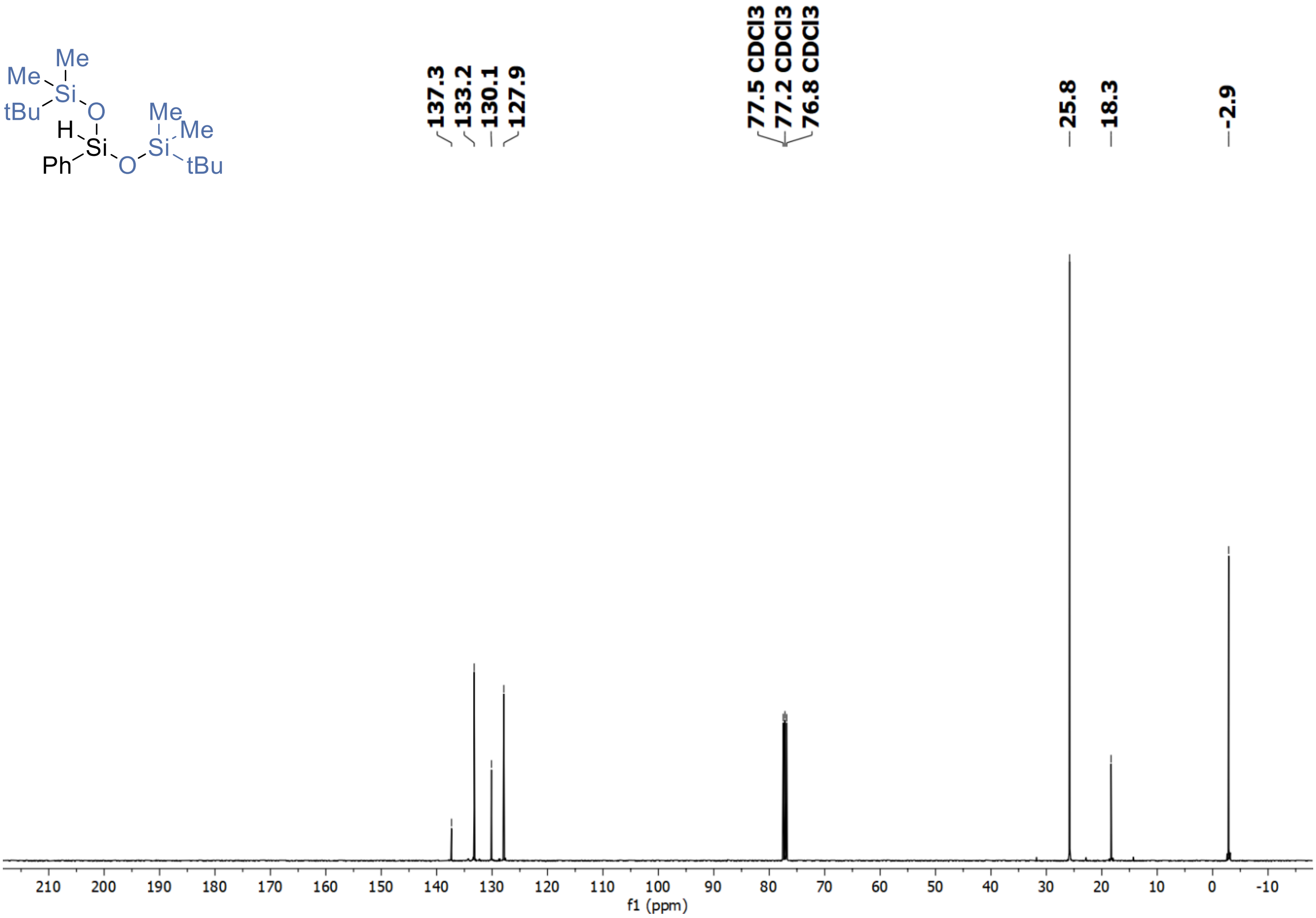


Figure S57. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,5-di-*tert*-butyl-1,1,5,5-tetramethyl-3-phenyltrisiloxane (**4c**).

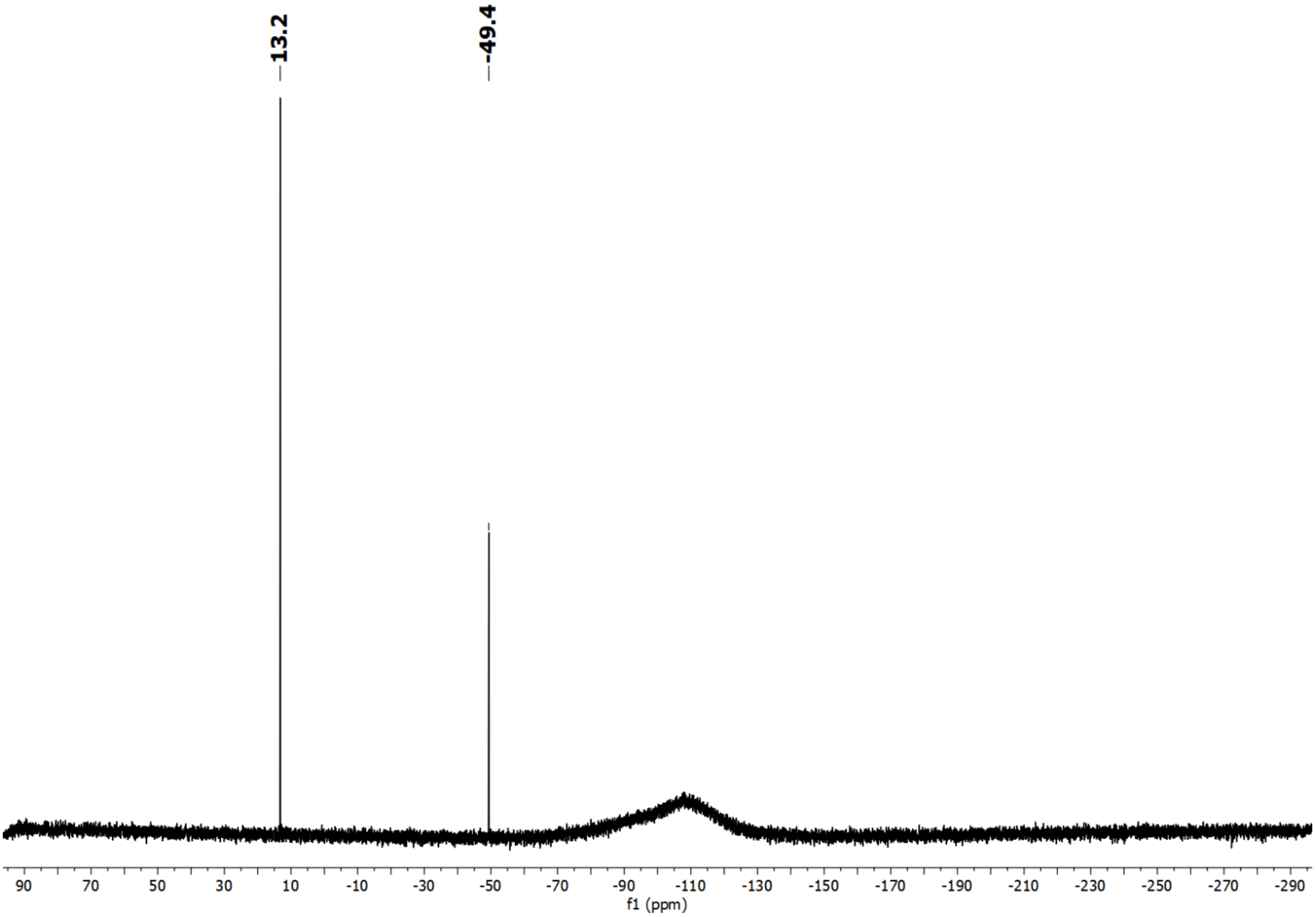


Figure S58. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,5-di-*tert*-butyl-1,1,5,5-tetramethyl-3-phenyltrisiloxane (**4c**).

3-Cyclohexyl-1,1,1,5,5,5-hexamethyltrisiloxane (4d)

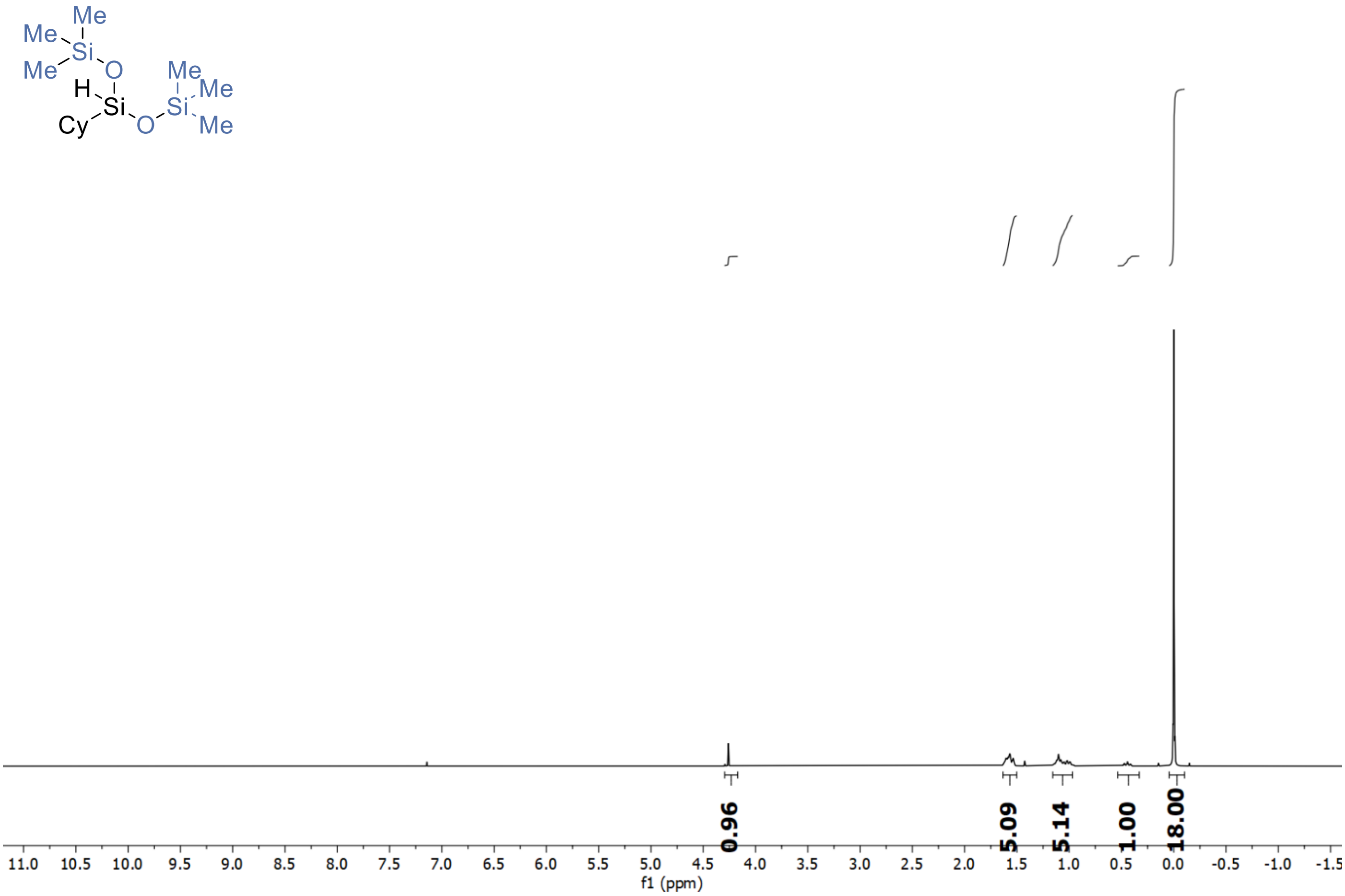


Figure S59. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 3-cyclohexyl-1,1,1,5,5,5-hexamethyltrisiloxane (**4d**).

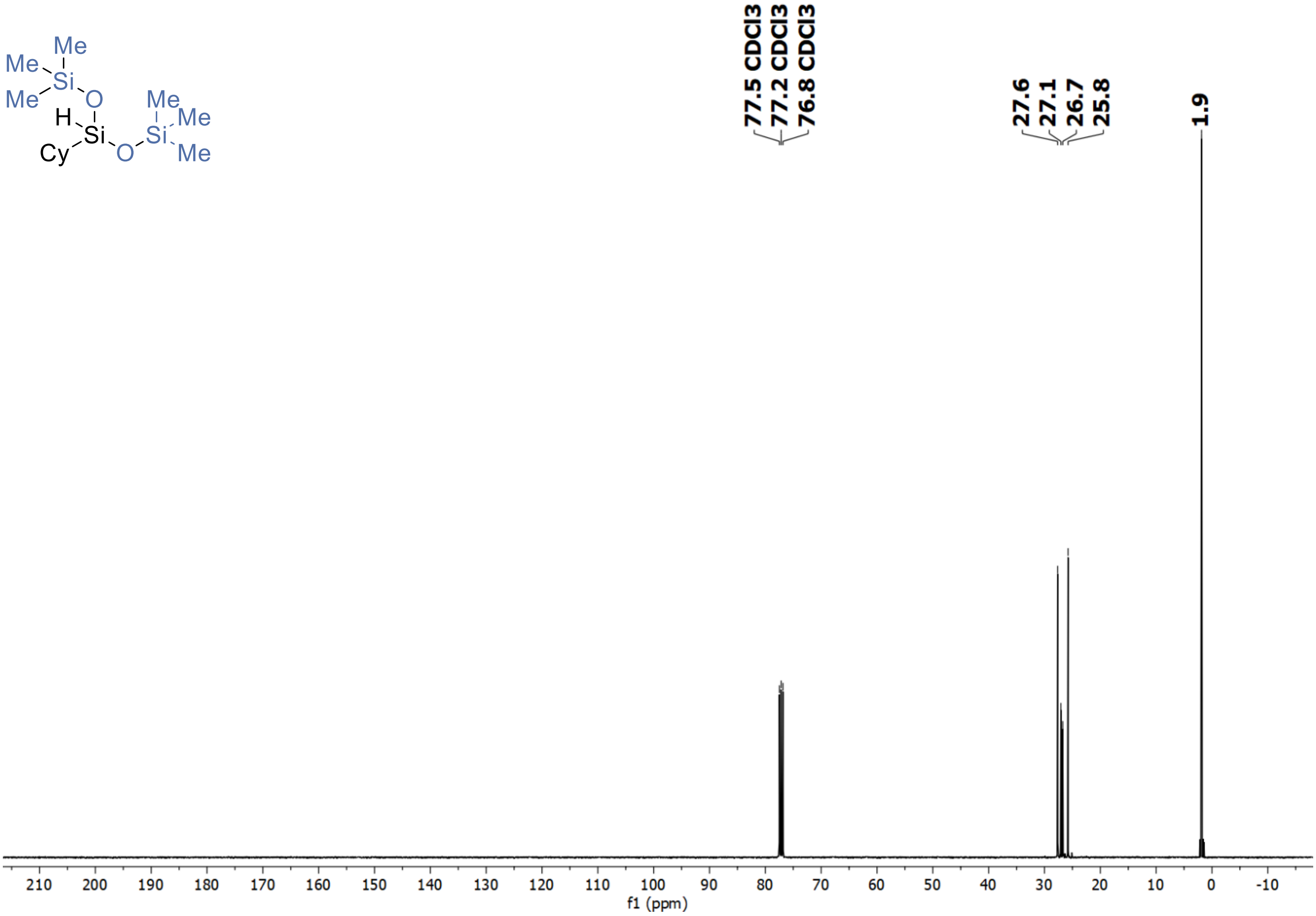


Figure S60. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 3-cyclohexyl-1,1,1,5,5,5-hexamethyltrisiloxane (**4d**).

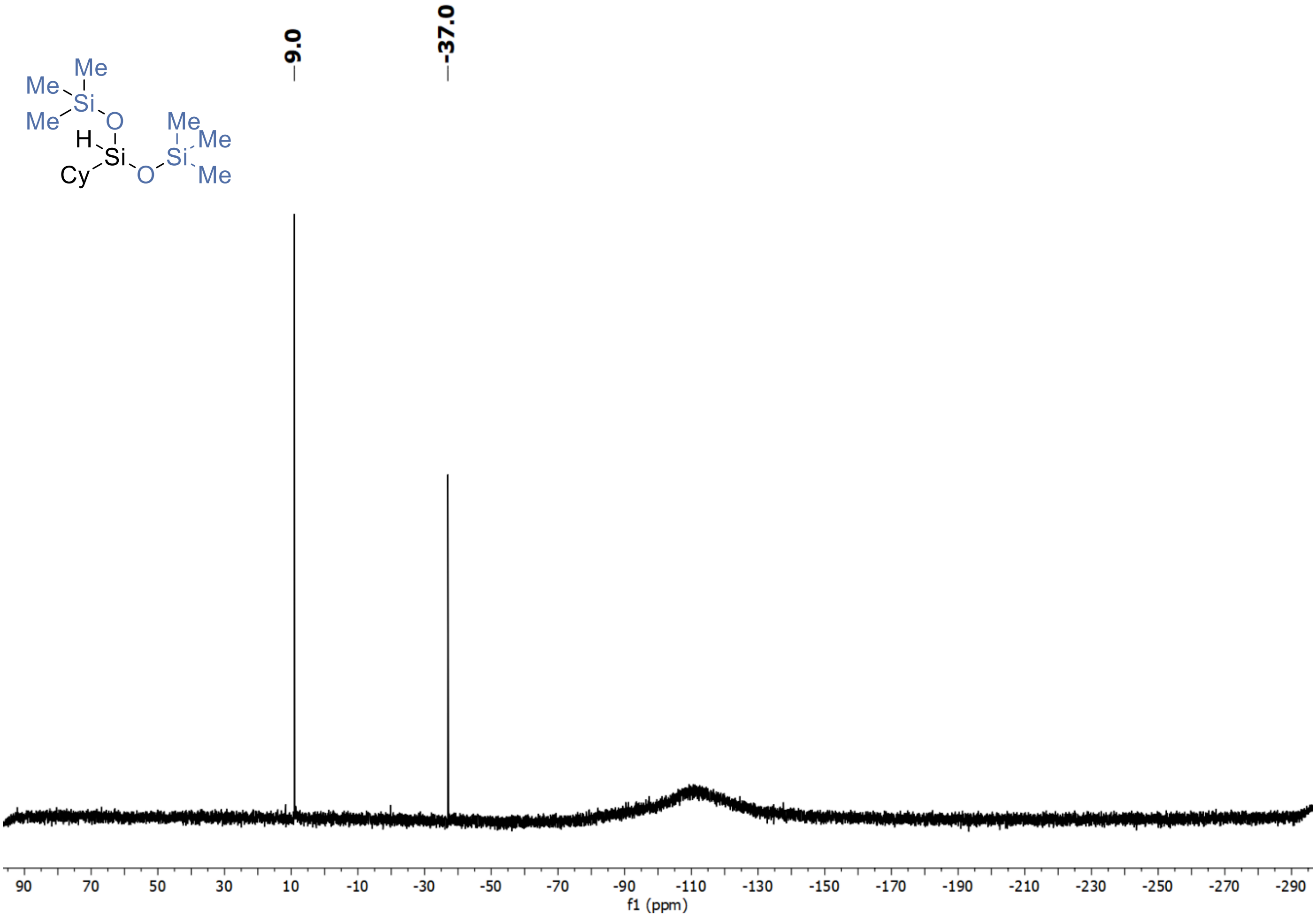


Figure S61. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 3-cyclohexyl-1,1,1,5,5,5-hexamethyltrisiloxane (**4d**).

3-Hexyl-1,1,1,5,5,5-hexamethyltrisiloxane (4e)

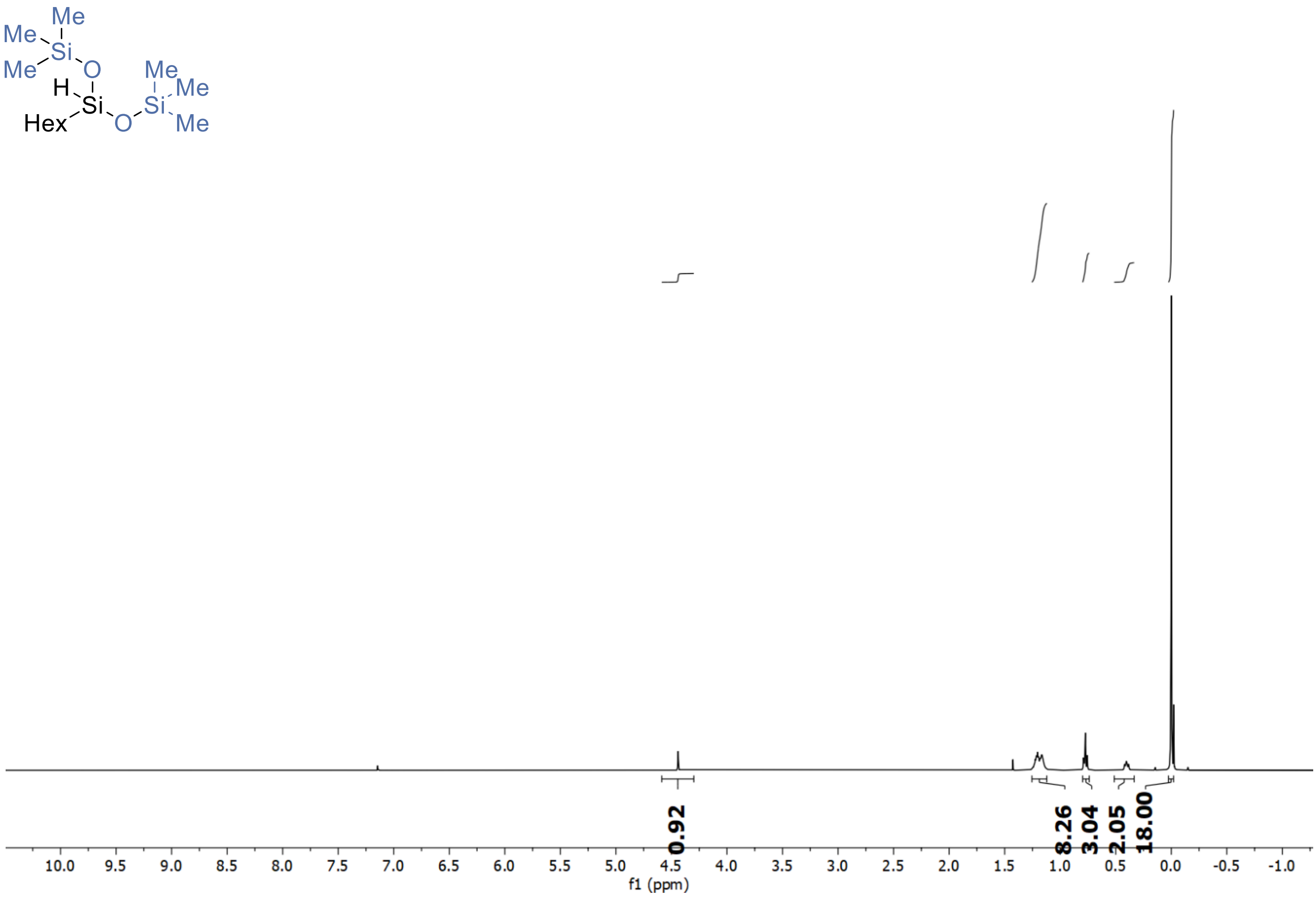


Figure S62. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 3-hexyl-1,1,1,5,5,5-hexamethyltrisiloxane (**4e**).

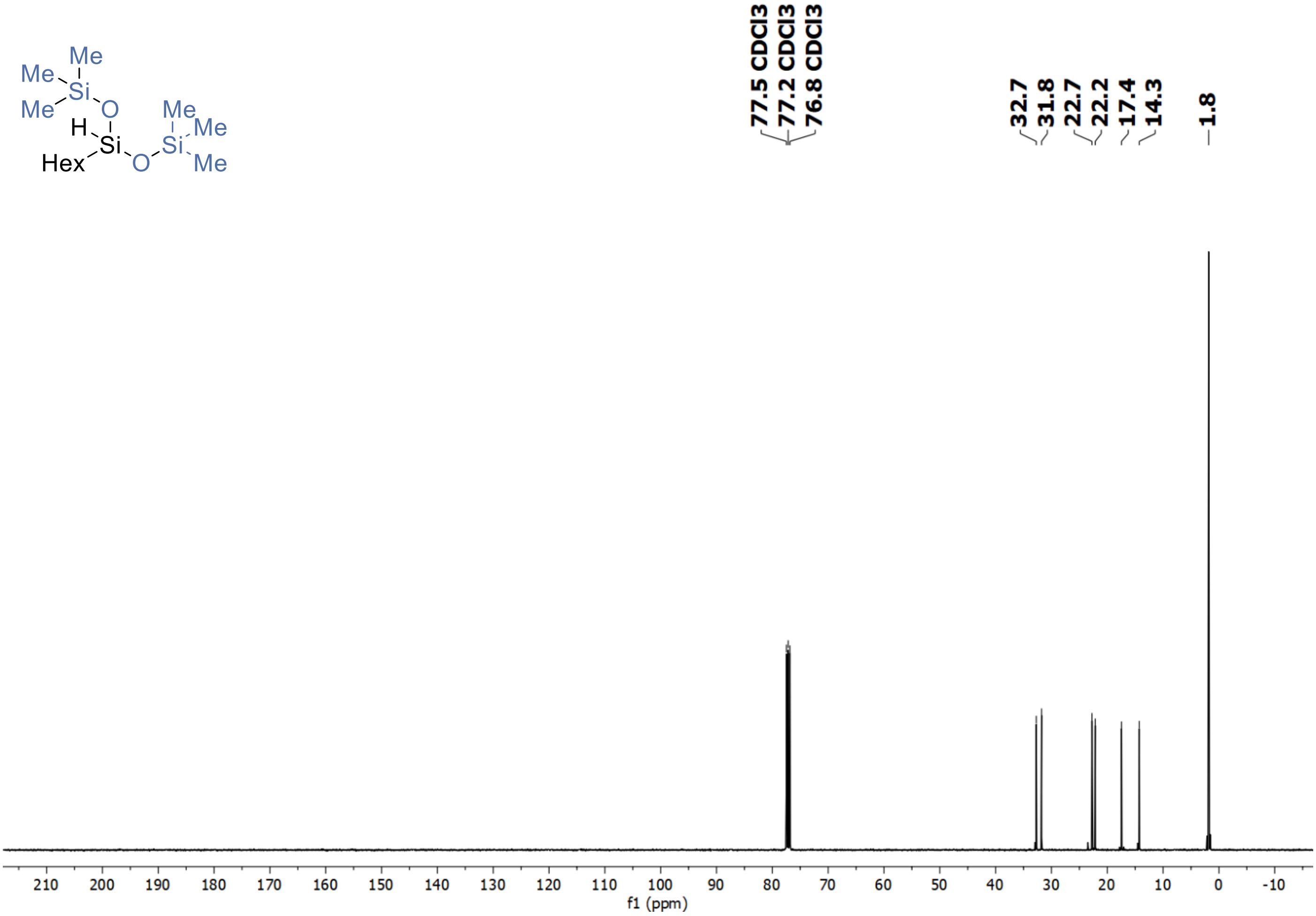


Figure S63. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 3-hexyl-1,1,1,5,5,5-hexamethyltrisiloxane (**4e**).

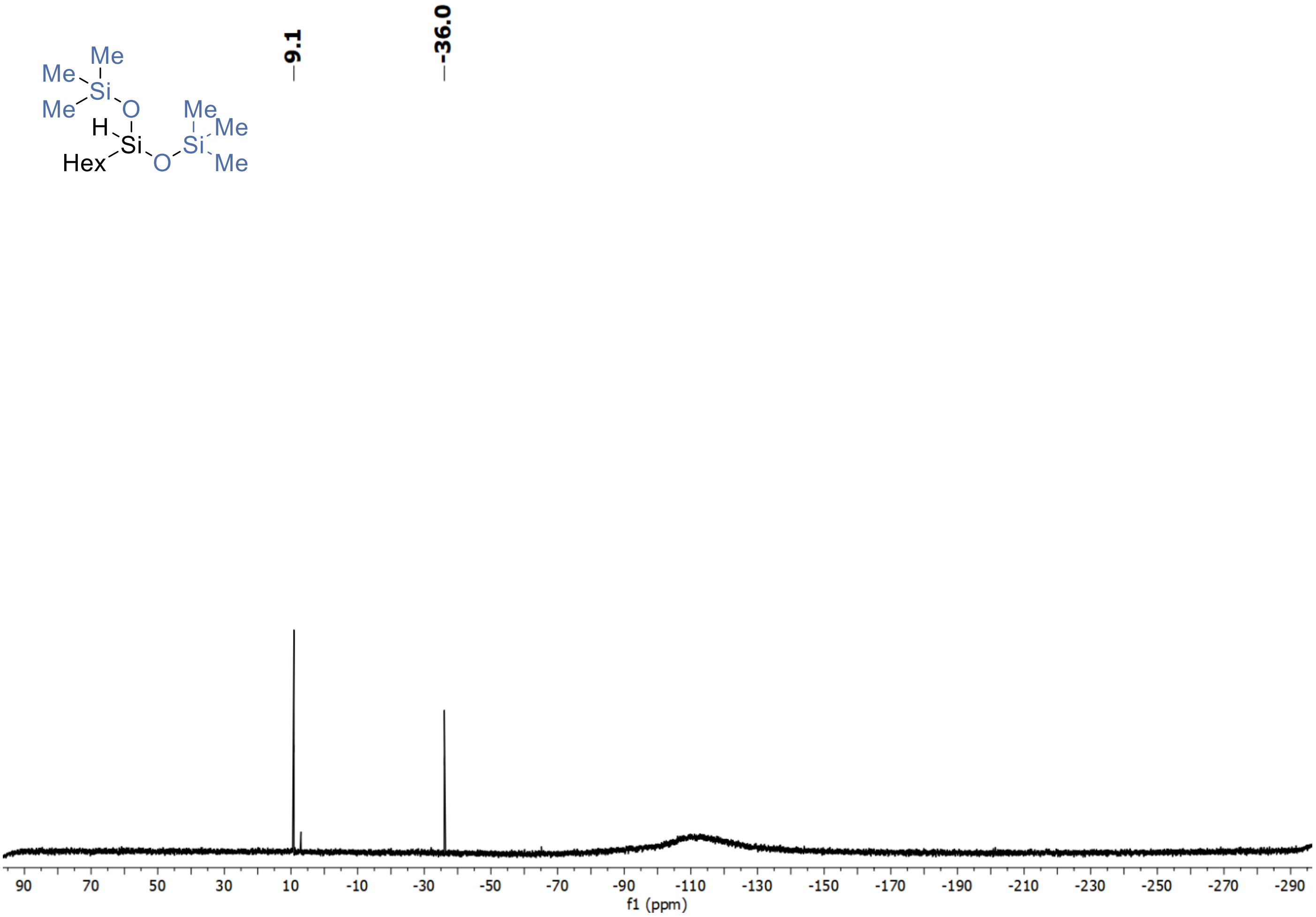


Figure S64. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 3-hexyl-1,1,1,5,5,5-hexamethyltrisiloxane (**4e**).

1,5-Di-*tert*-butyl-3-hexyl-1,1,5,5-tetramethyltrisiloxane (4f)

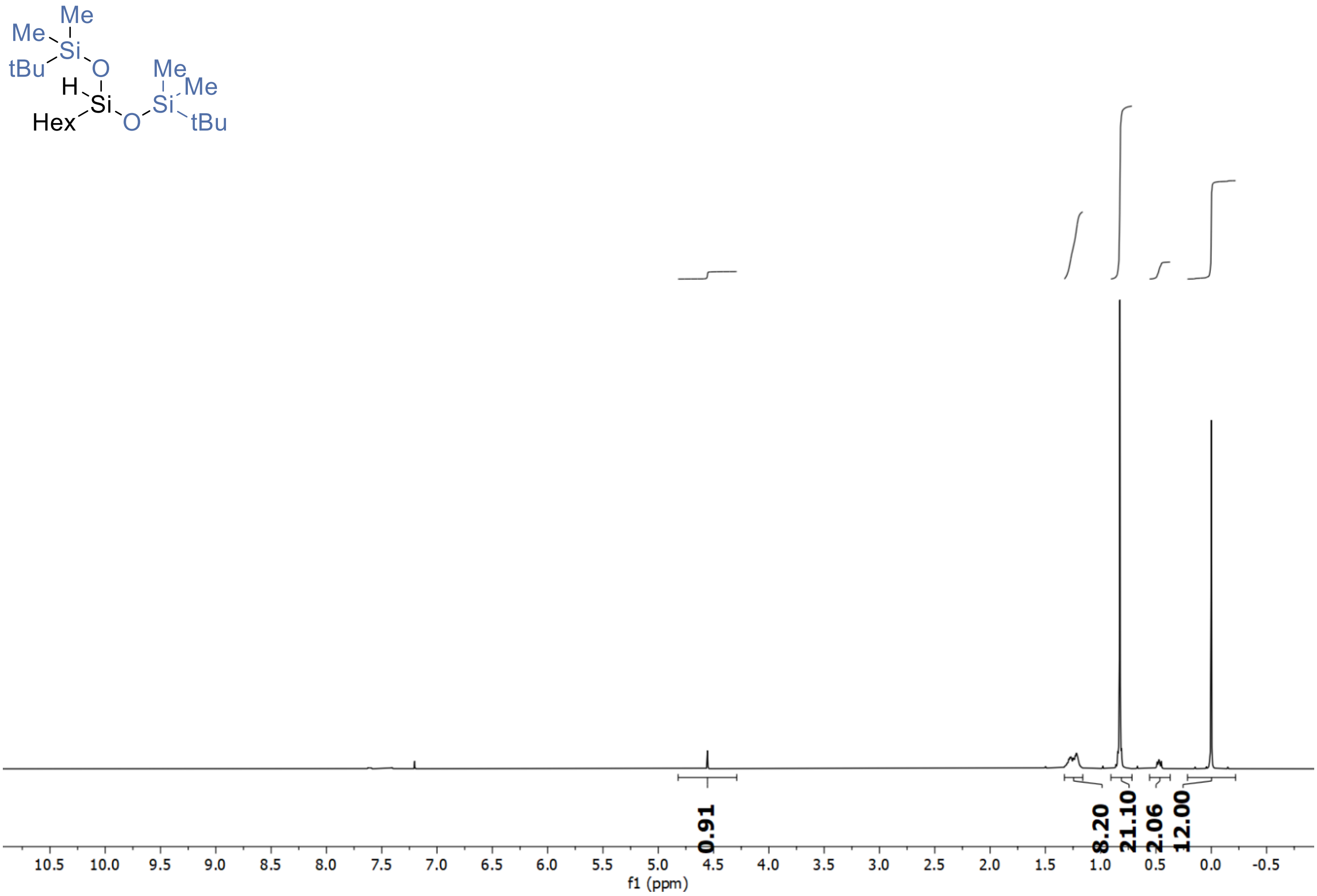


Figure S65. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,5-di-*tert*-butyl-3-hexyl-1,1,5,5-tetramethyltrisiloxane (**4f**).

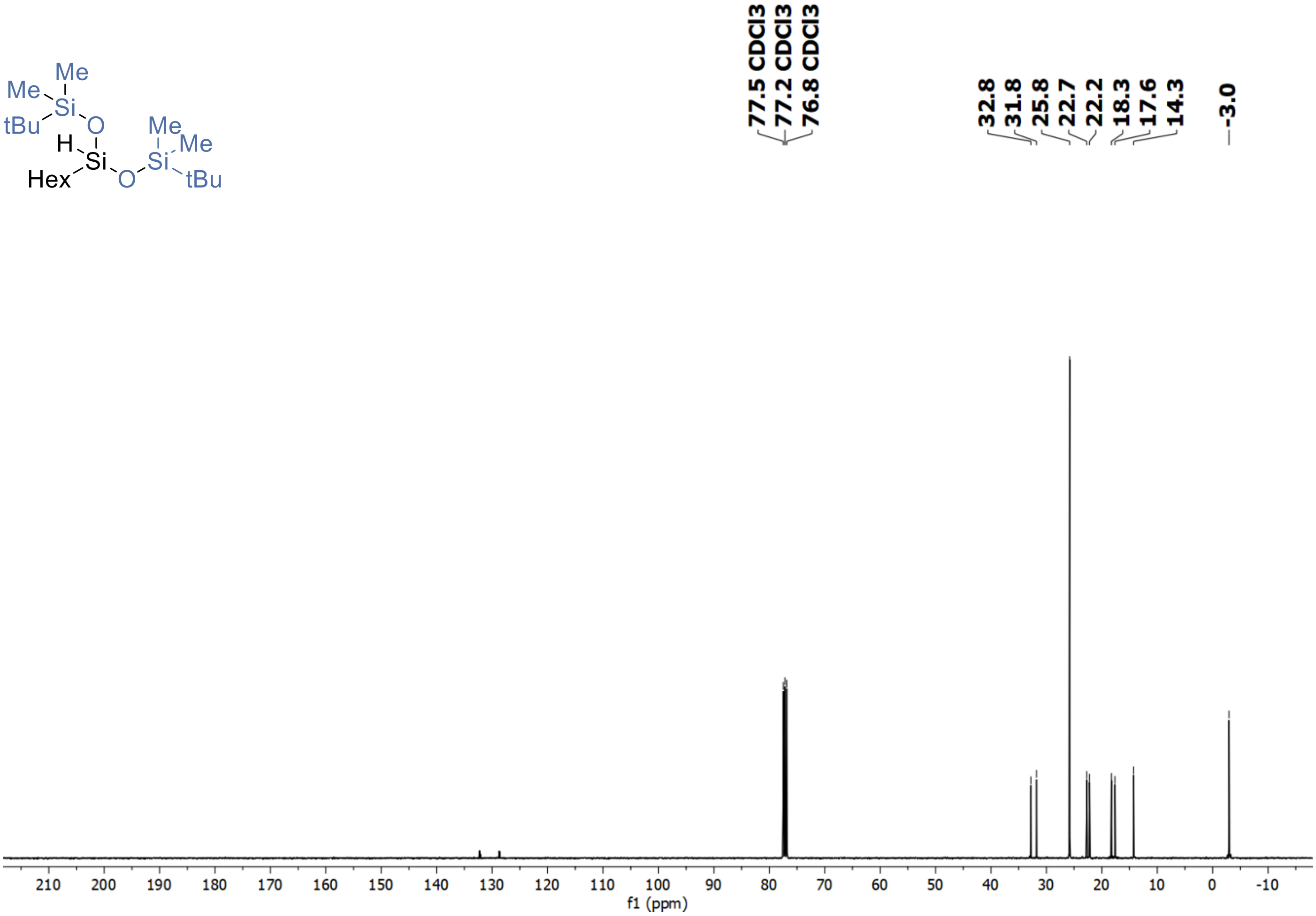


Figure S66. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,5-di-*tert*-butyl-3-hexyl-1,1,5,5-tetramethyltrisiloxane (**4f**).

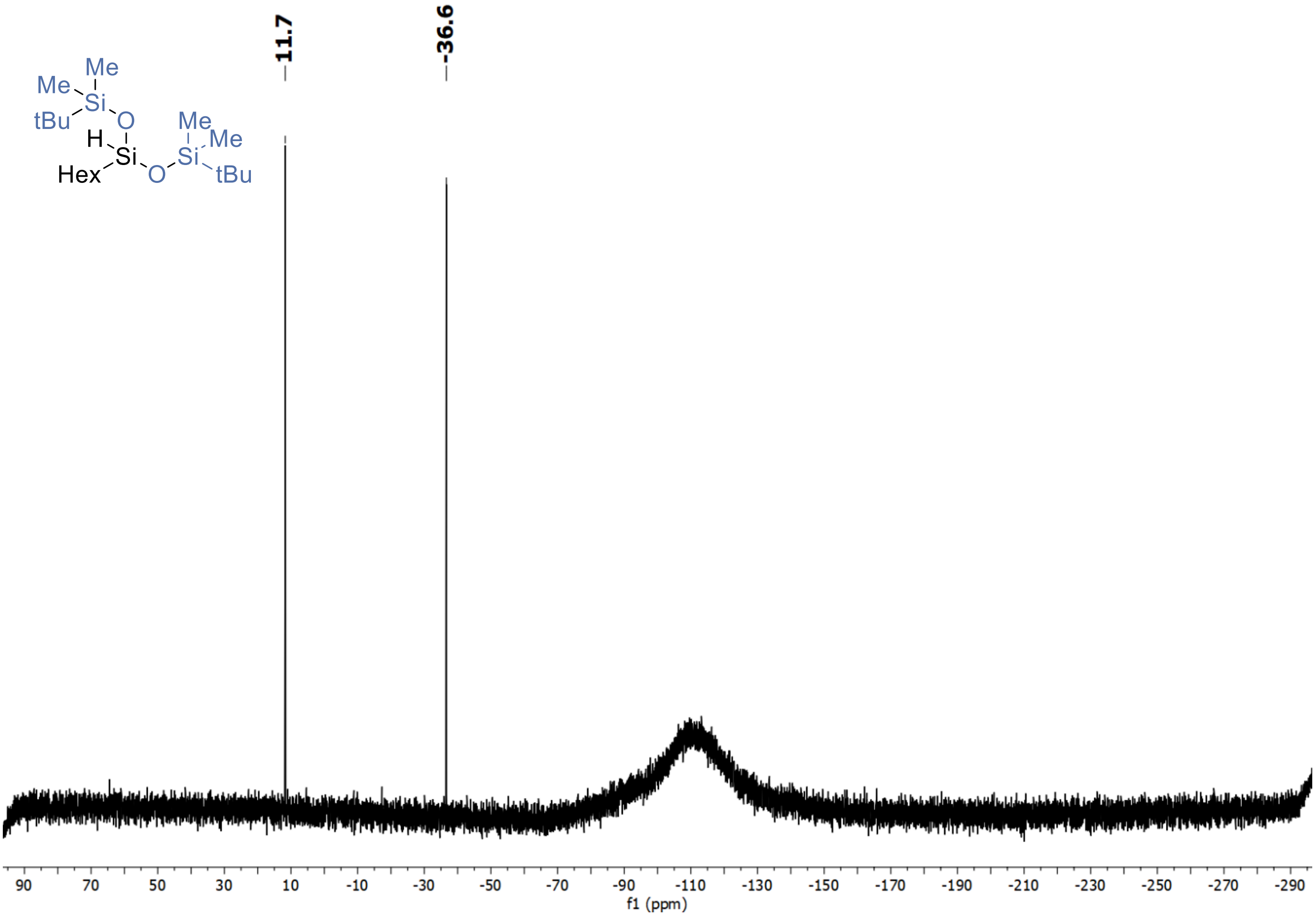


Figure S67. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,5-di-*tert*-butyl-3-hexyl-1,1,5,5-tetramethyltrisiloxane (**4f**).

1,1,1,5,5,5-Hexamethyl-3-(p-tolyl)trisiloxane (4g)

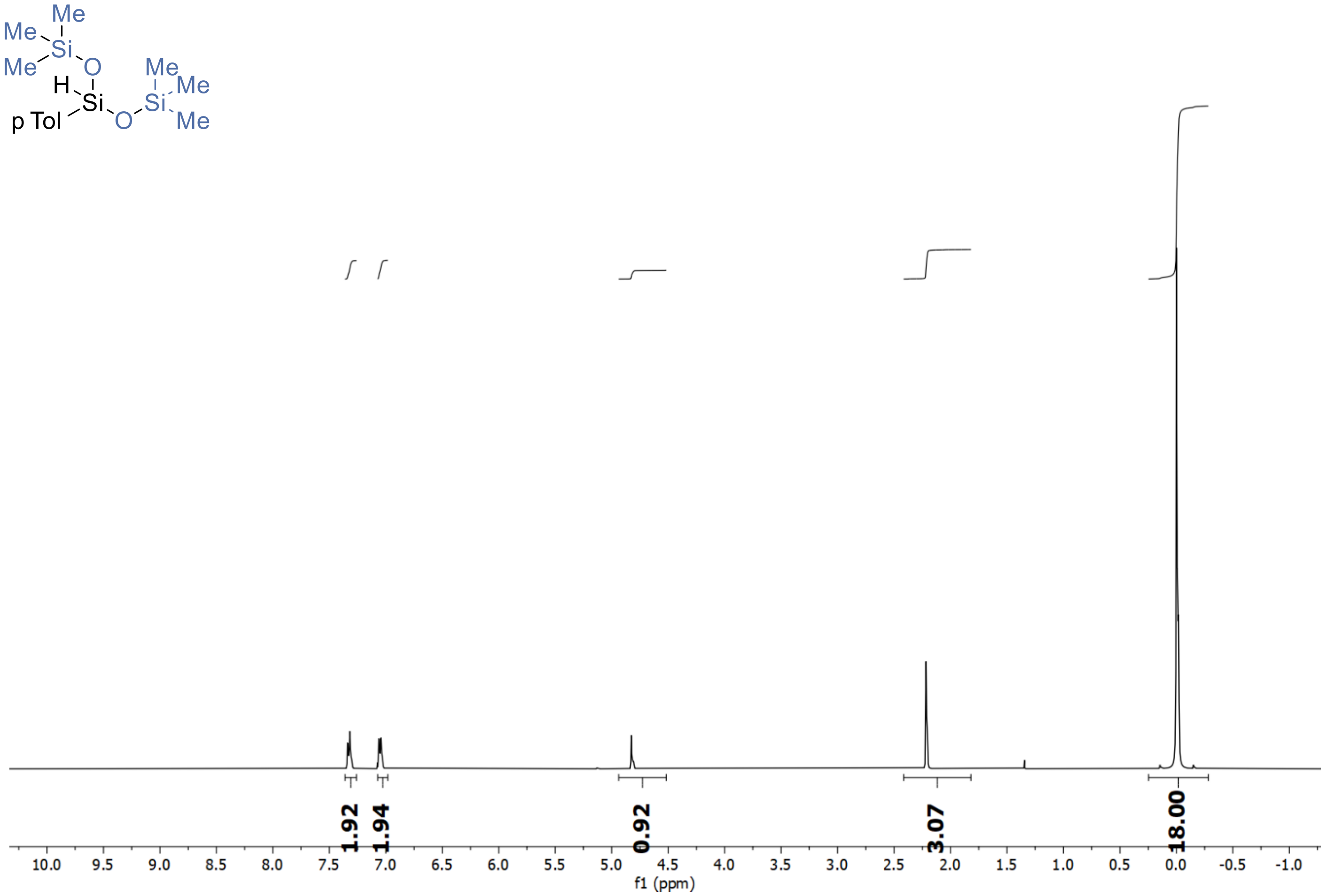


Figure S68. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3-(p-tolyl)trisiloxane (**4g**).

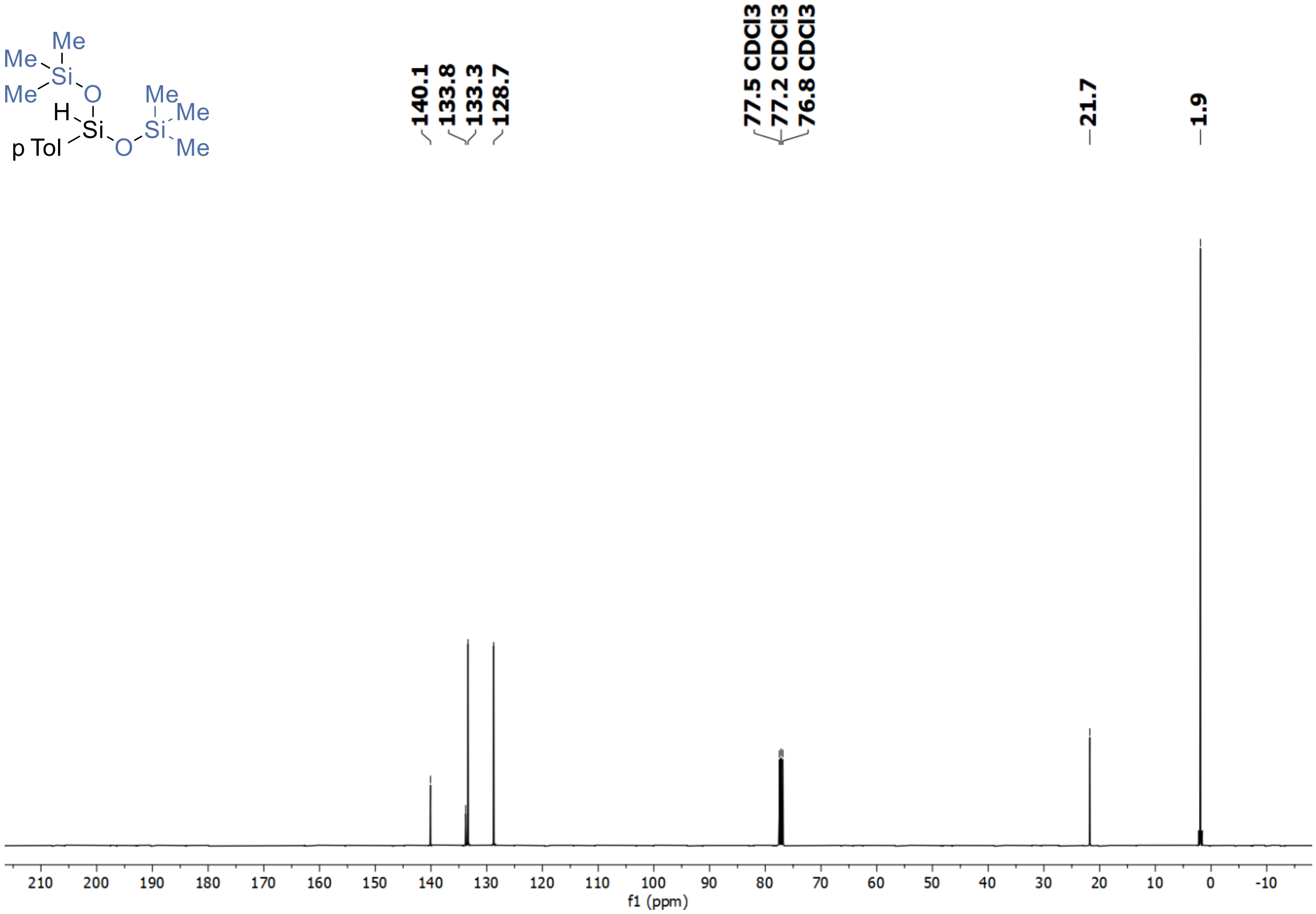


Figure S69. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3-(p-tolyl)trisiloxane (**4g**).

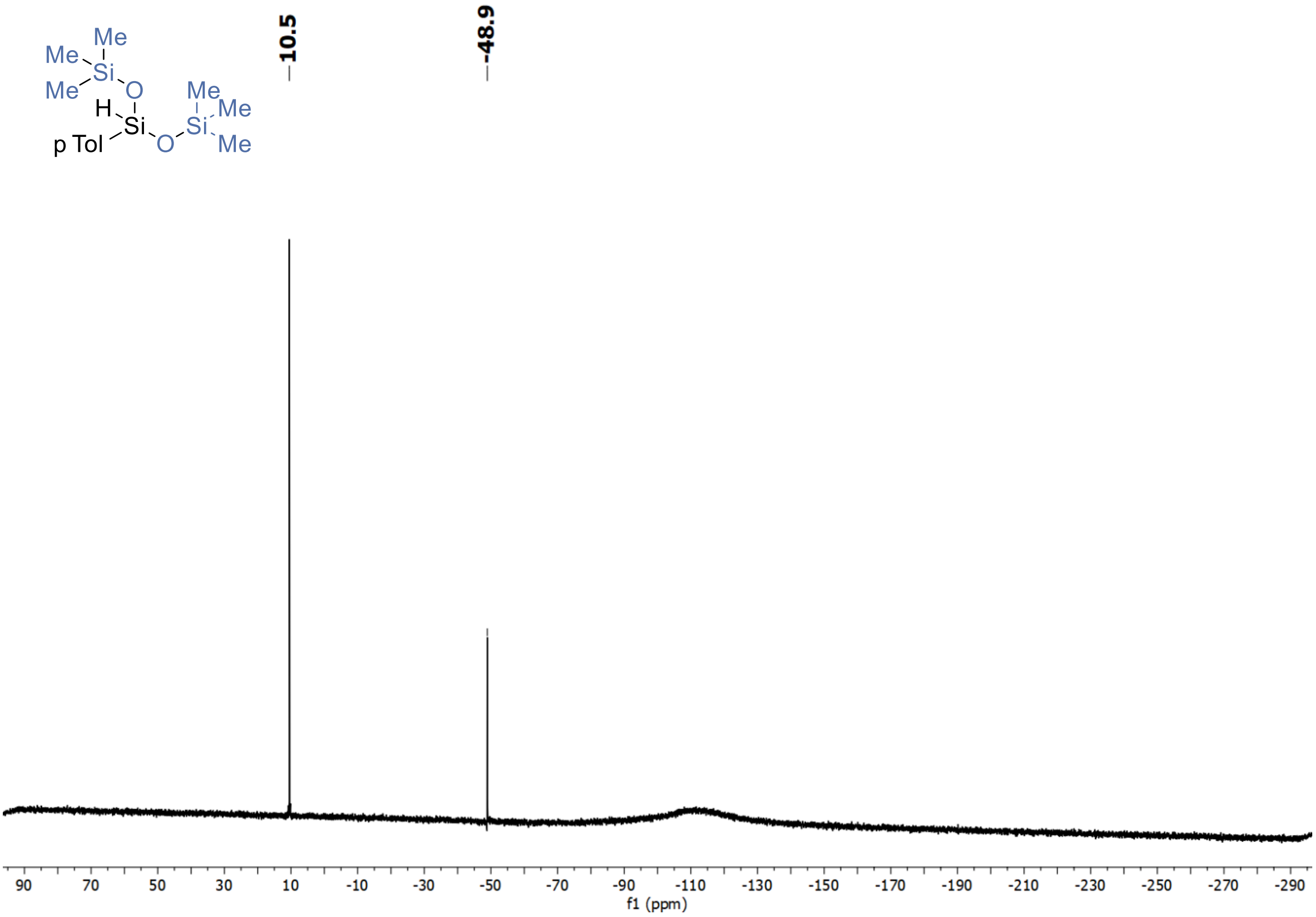
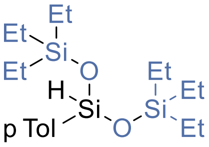


Figure S70. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3-(p-tolyl)trisiloxane (**4g**).

1,1,1,5,5,5-Hexaethyl-3-(*p*-tolyl)trisiloxane (4h)



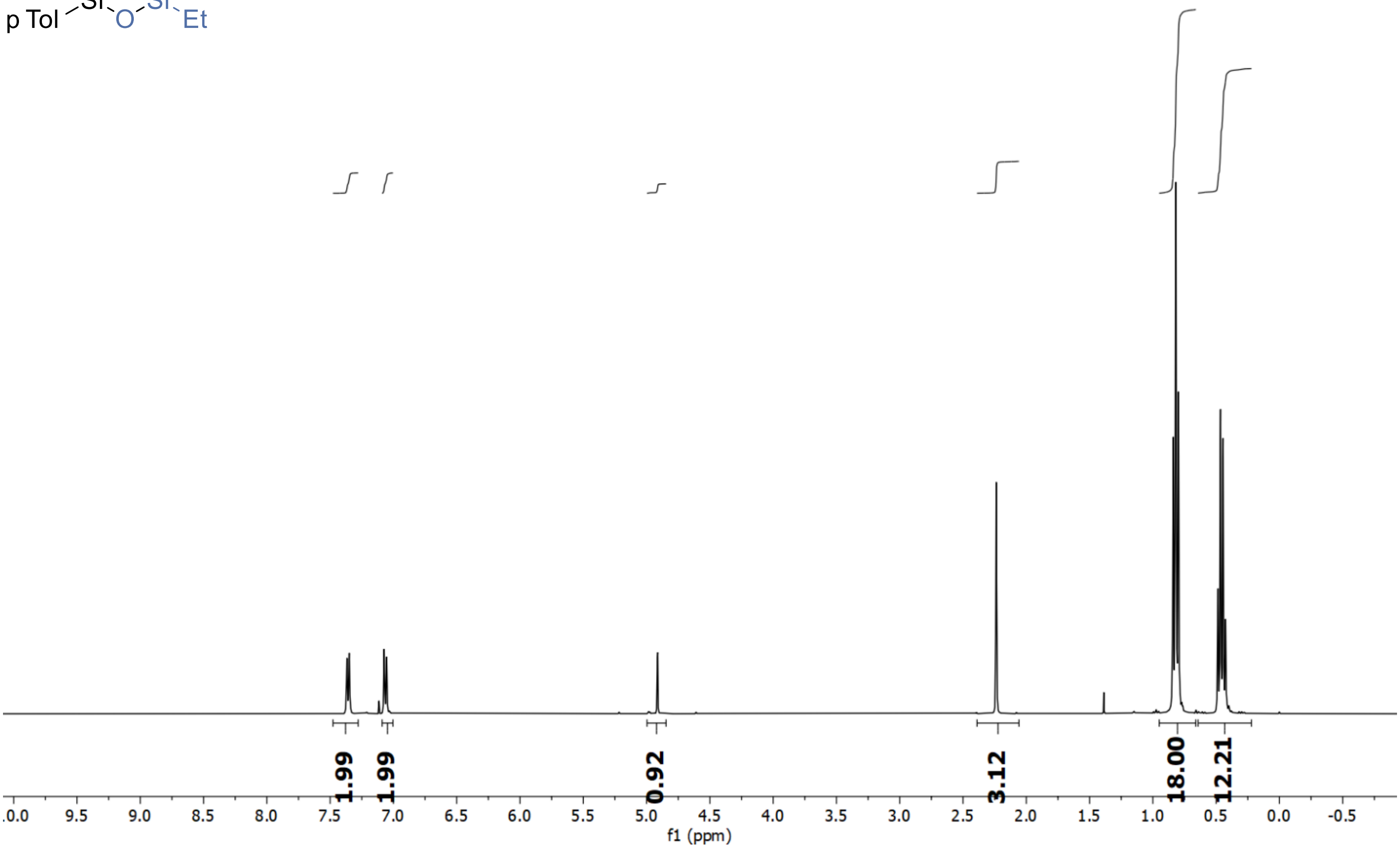


Figure S71. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexaethyl-3-(*p*-tolyl)trisiloxane (**4h**).

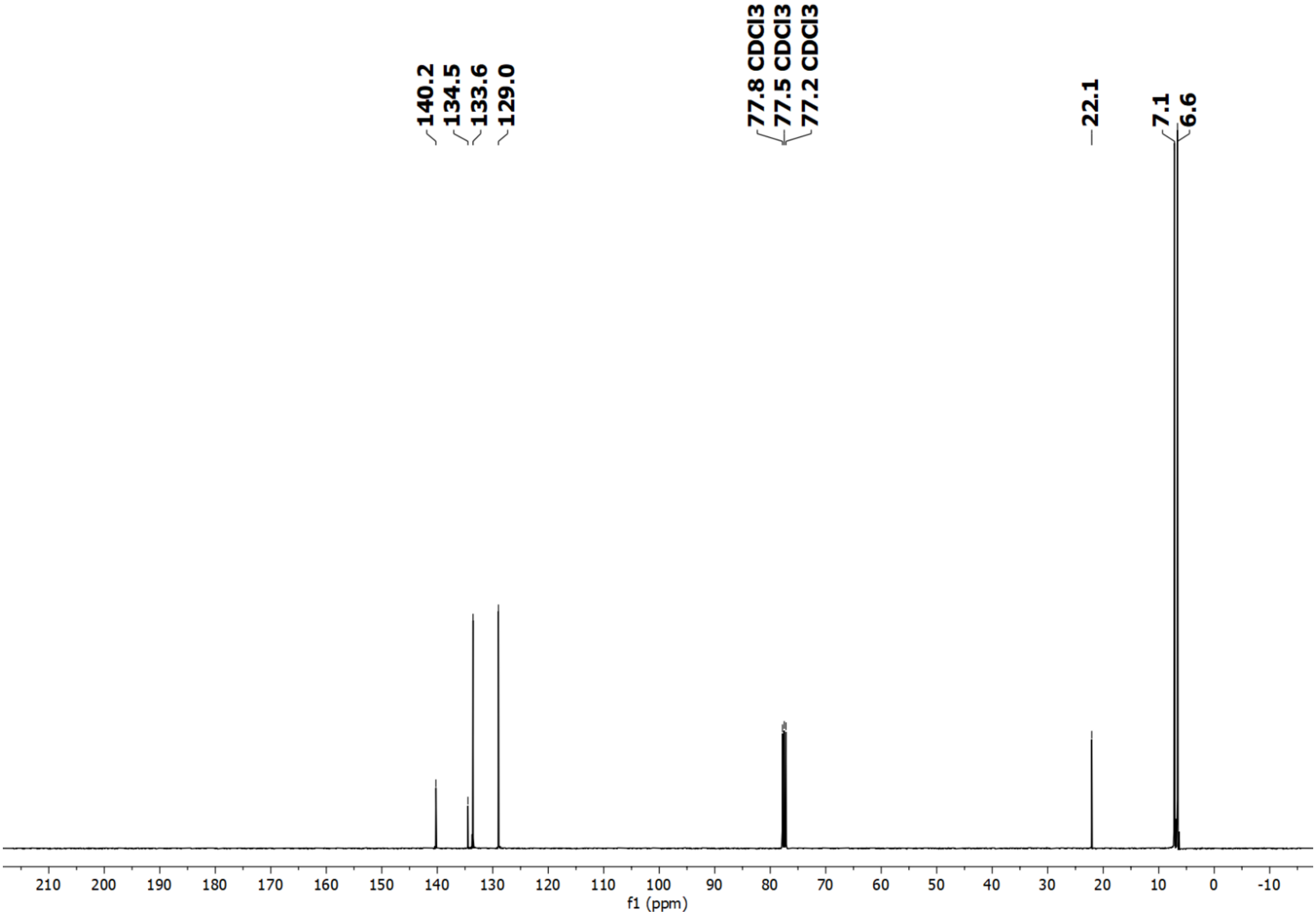


Figure S72. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexaethyl-3-(*p*-tolyl)trisiloxane (**4h**).

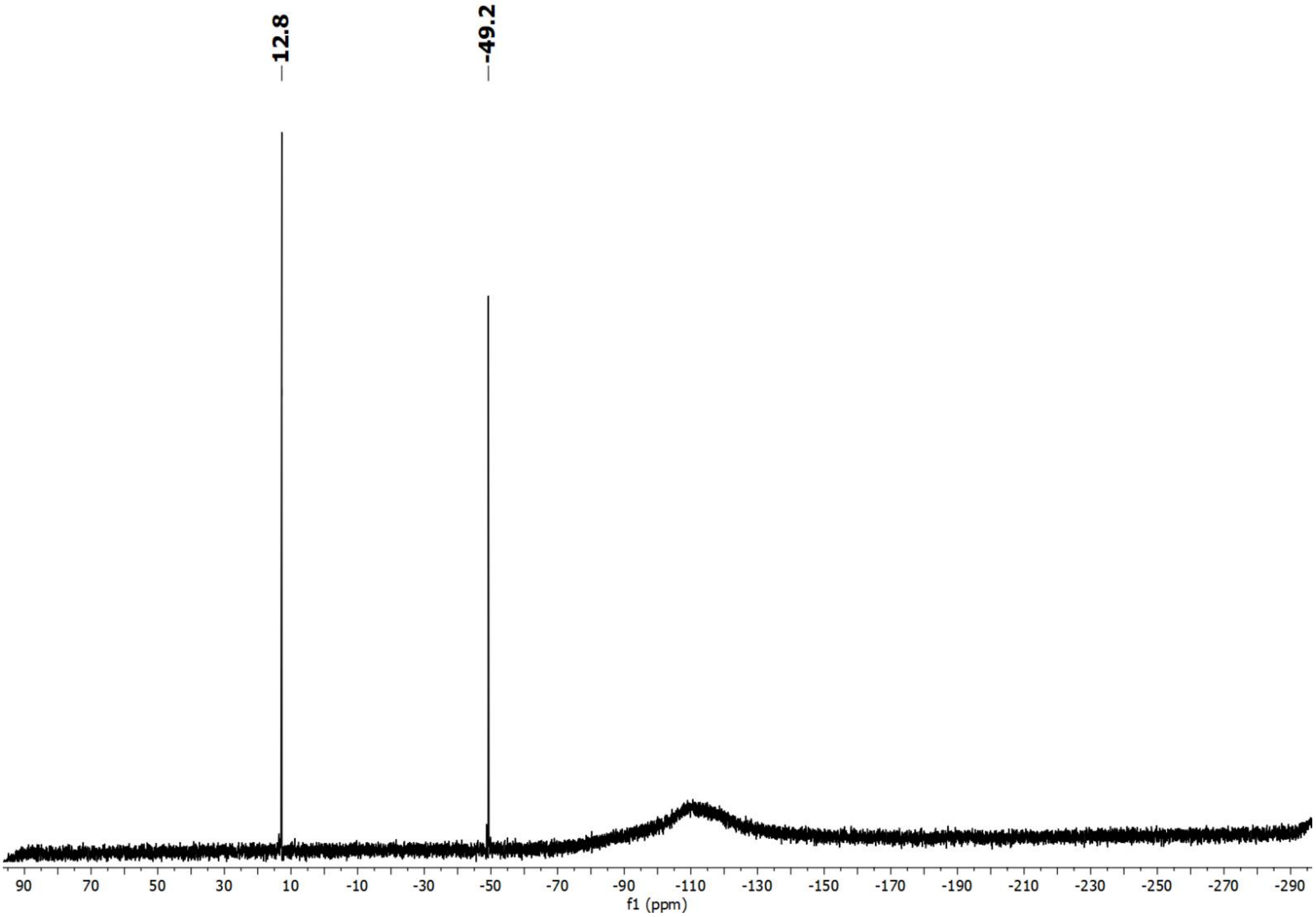


Figure S73. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexaethyl-3-(*p*-tolyl)trisiloxane (**4h**).

1,5-Di-*tert*-butyl-1,1,5,5-tetramethyl-3-(p-tolyl)trisiloxane (4i)

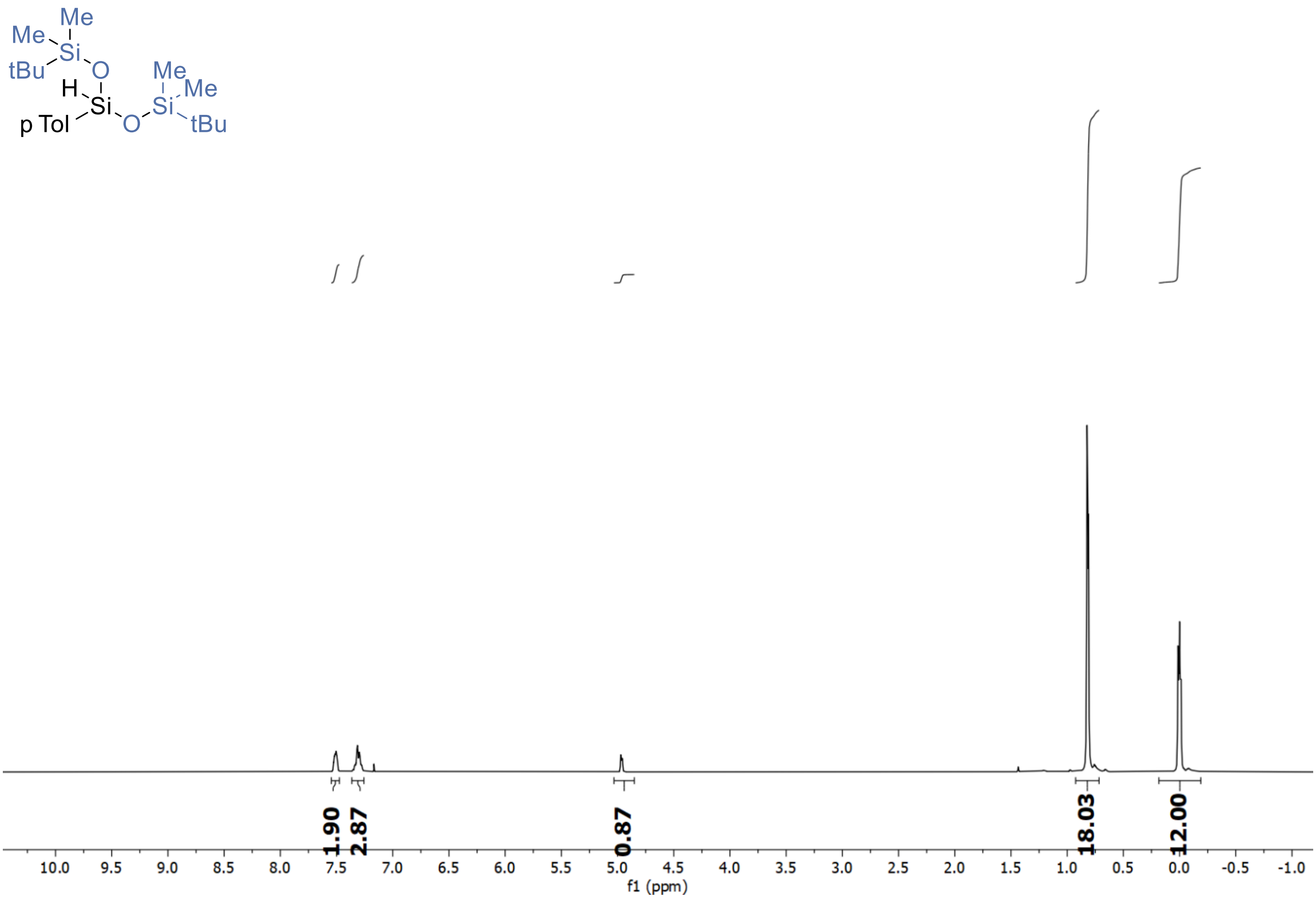


Figure S74. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,5-di-*tert*-butyl-1,1,5,5-tetramethyl-3-(*p*-tolyl)trisiloxane (**4i**).

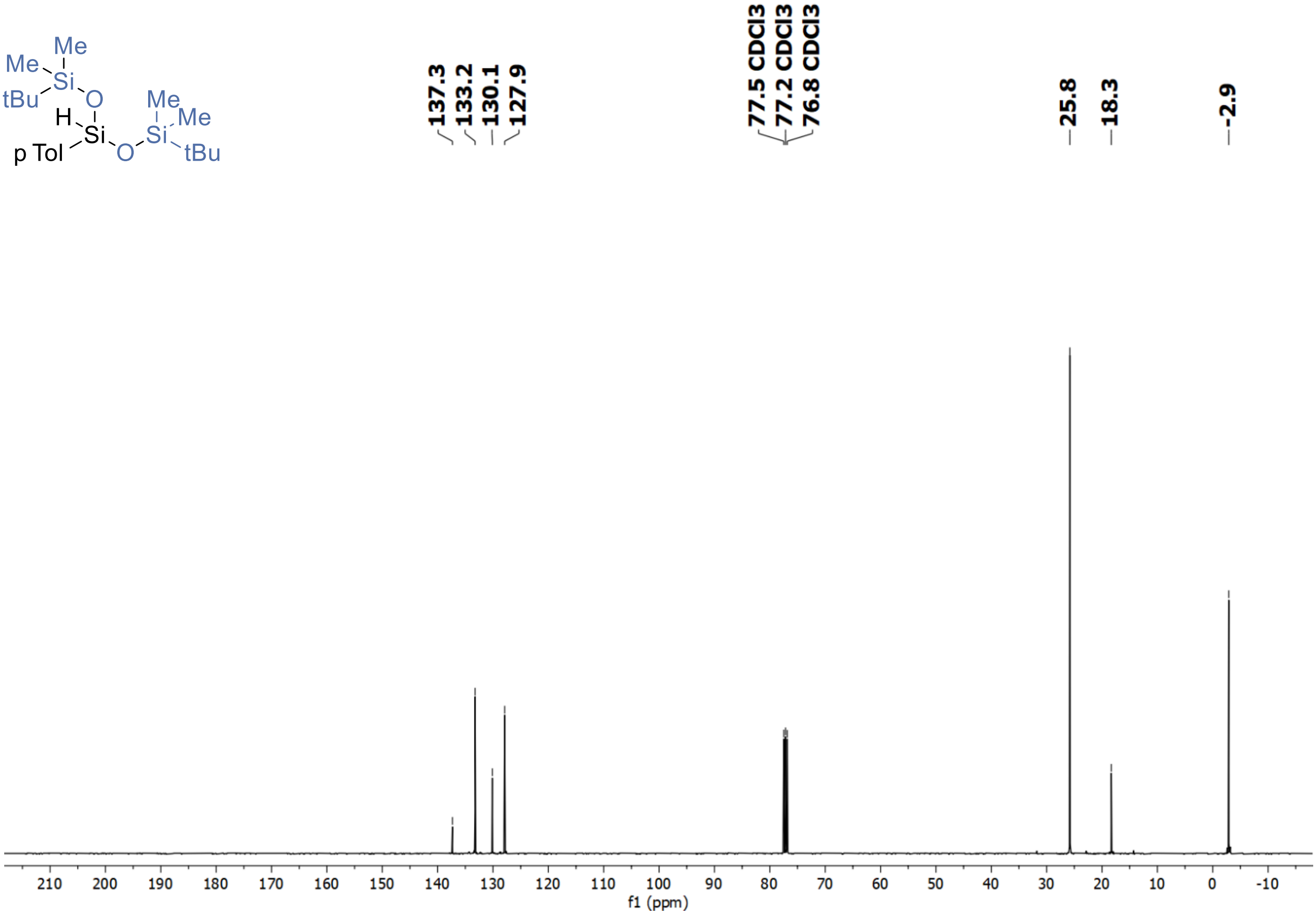


Figure S75. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,5-di-*tert*-butyl-1,1,5,5-tetramethyl-3-(*p*-tolyl)trisiloxane (**4i**).

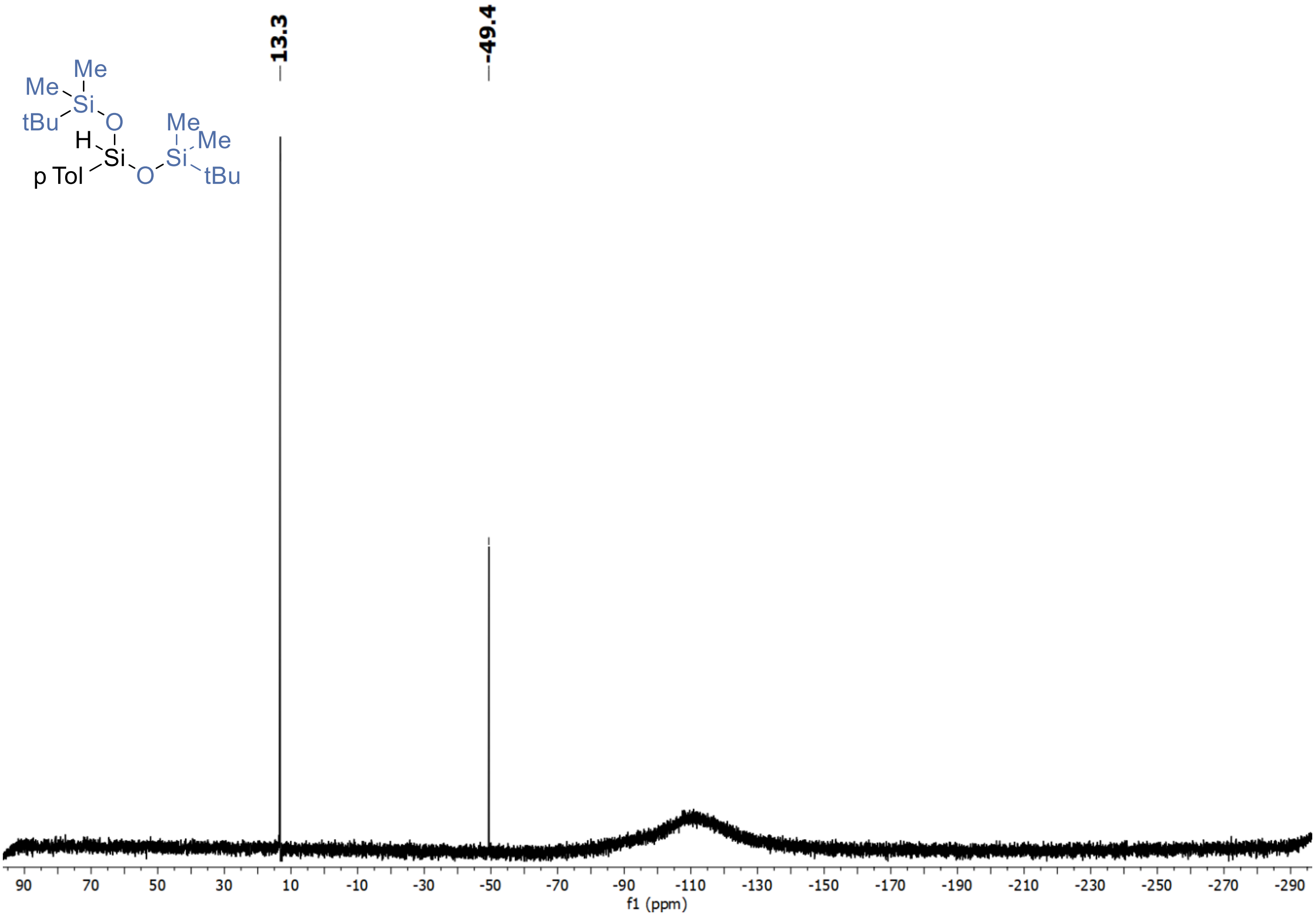


Figure S76. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,5-di-*tert*-butyl-1,1,5,5-tetramethyl-3-(*p*-tolyl)trisiloxane (**4i**).

1,1,1,5,5,5-Hexamethyl-3,3-diphenyltrisiloxane (4j)

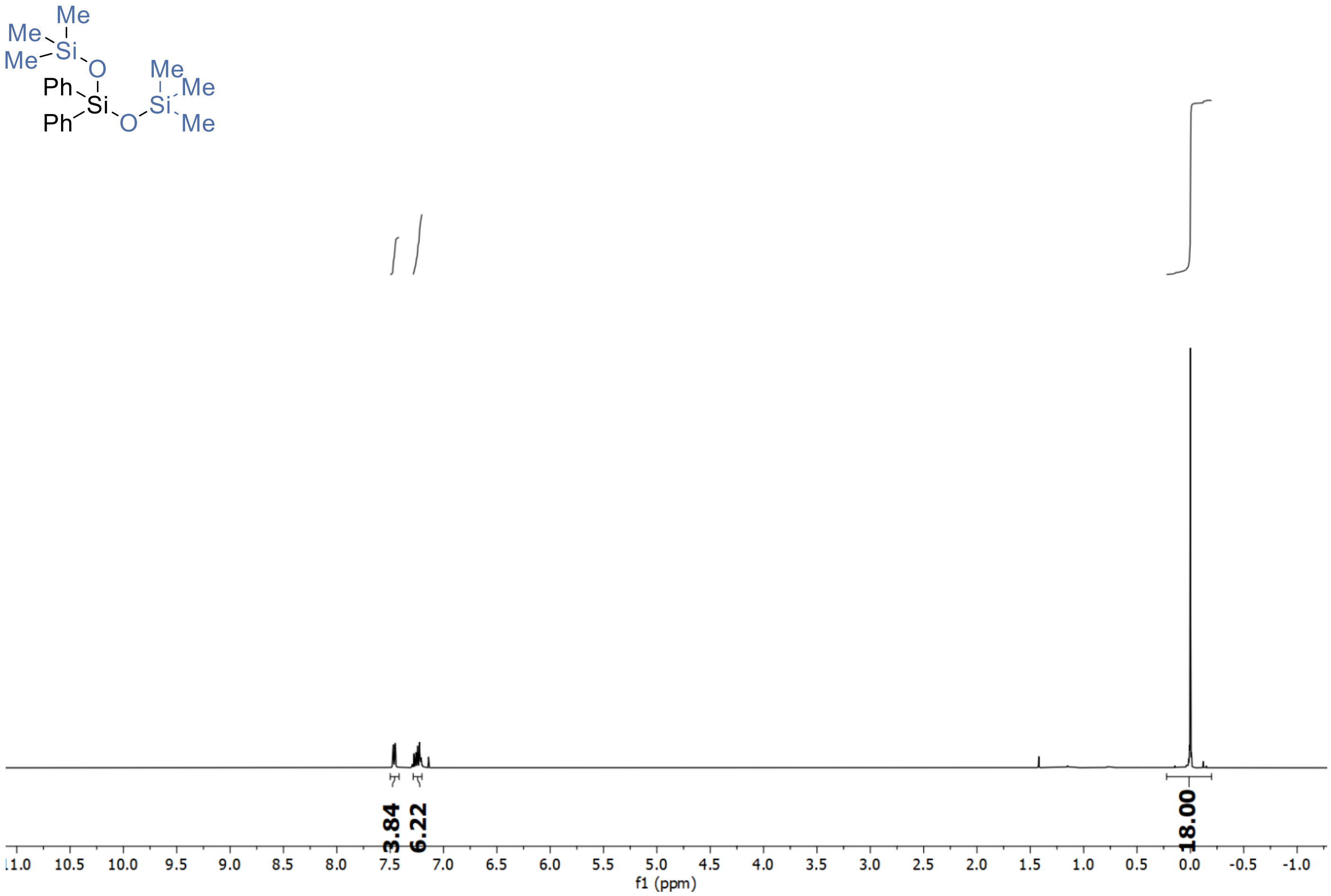


Figure S77. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-Hexamethyl-3,3-diphenyltrisiloxane (**4j**).

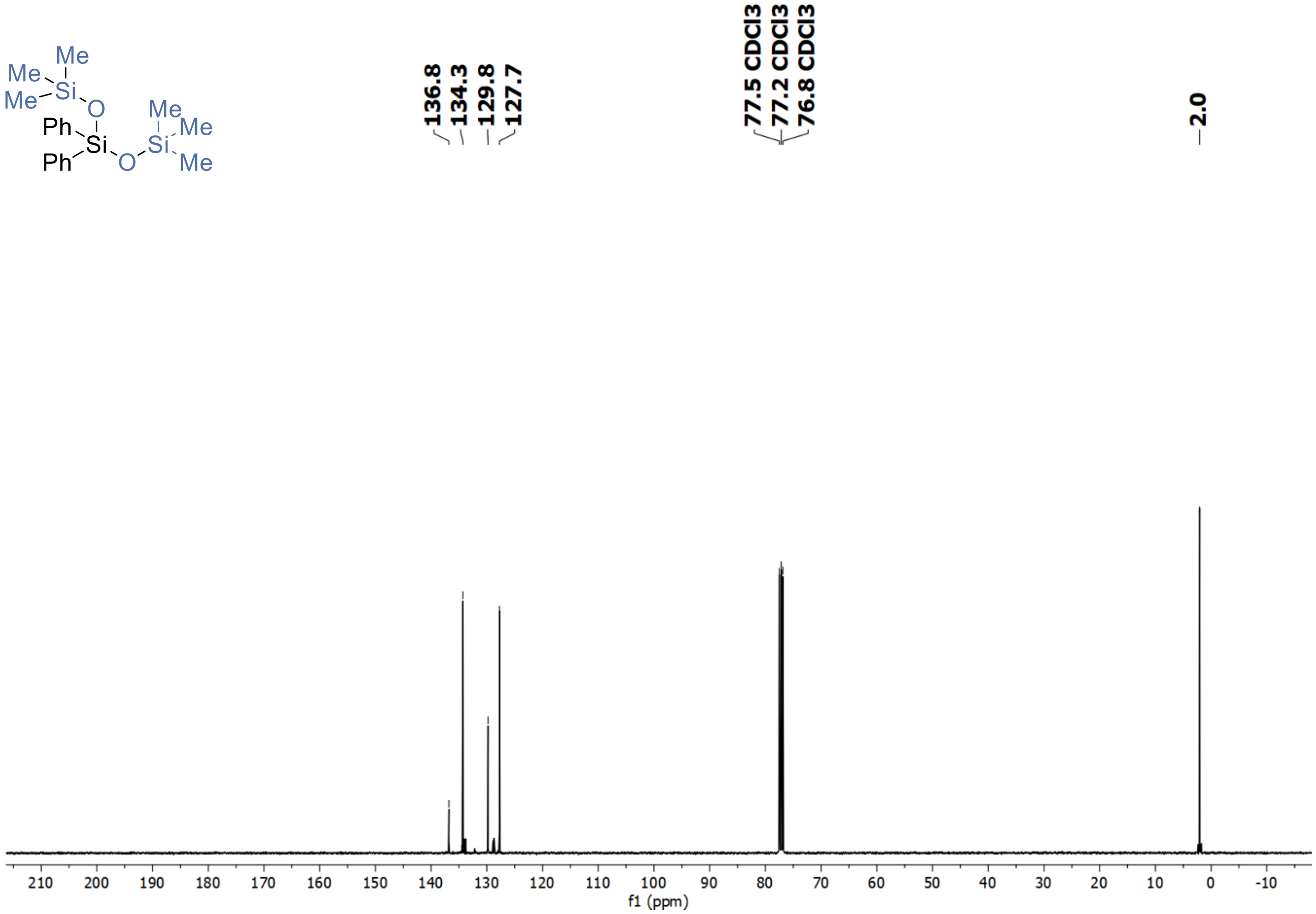


Figure S78. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-Hexamethyl-3,3-diphenyltrisiloxane (**4j**).

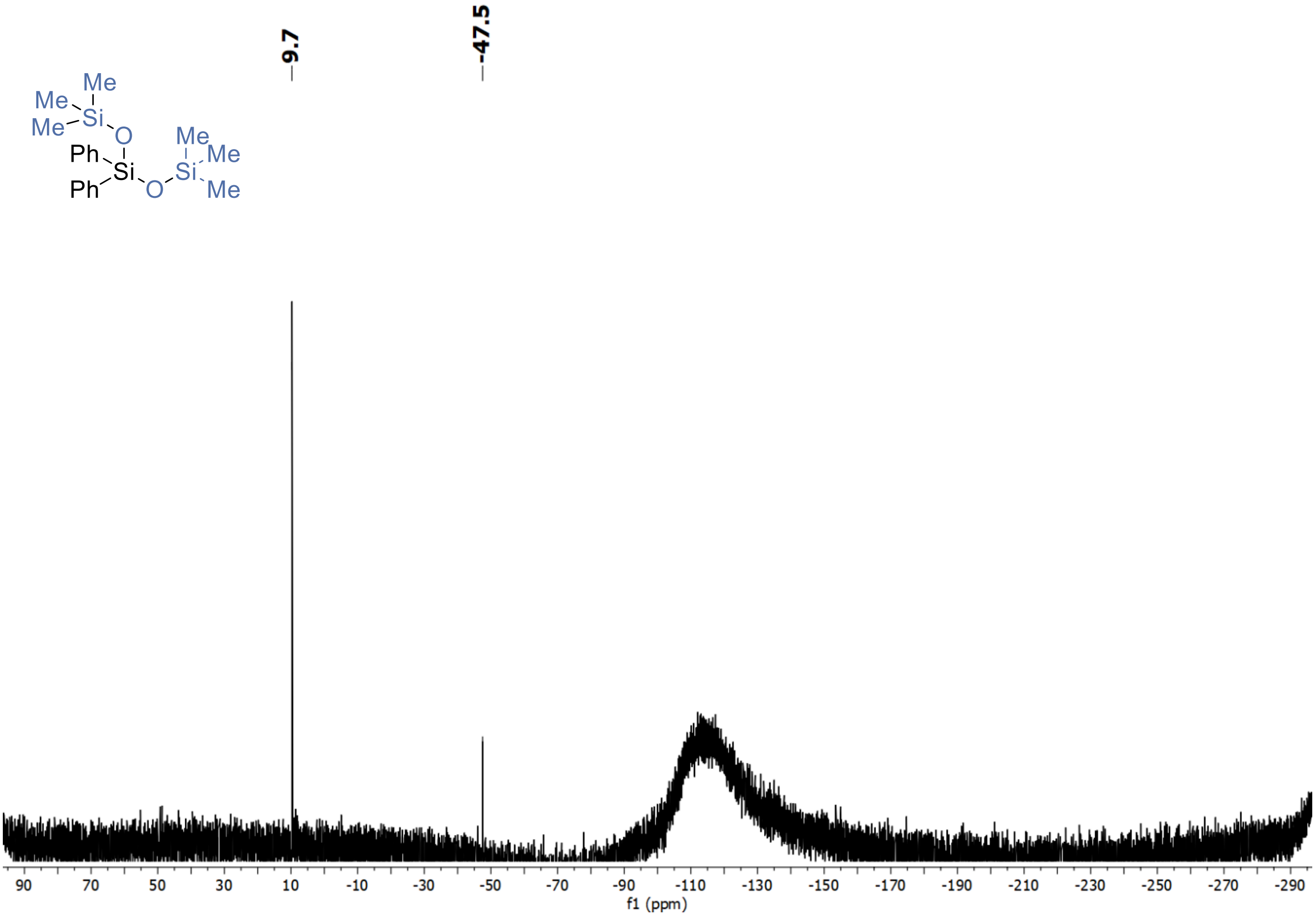


Figure S79. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-Hexamethyl-3,3-diphenyltrisiloxane (**4j**).

1,1,1,5,5,5-Hexamethyl-3,3-di-*p*-tolyltrisiloxane (4k)

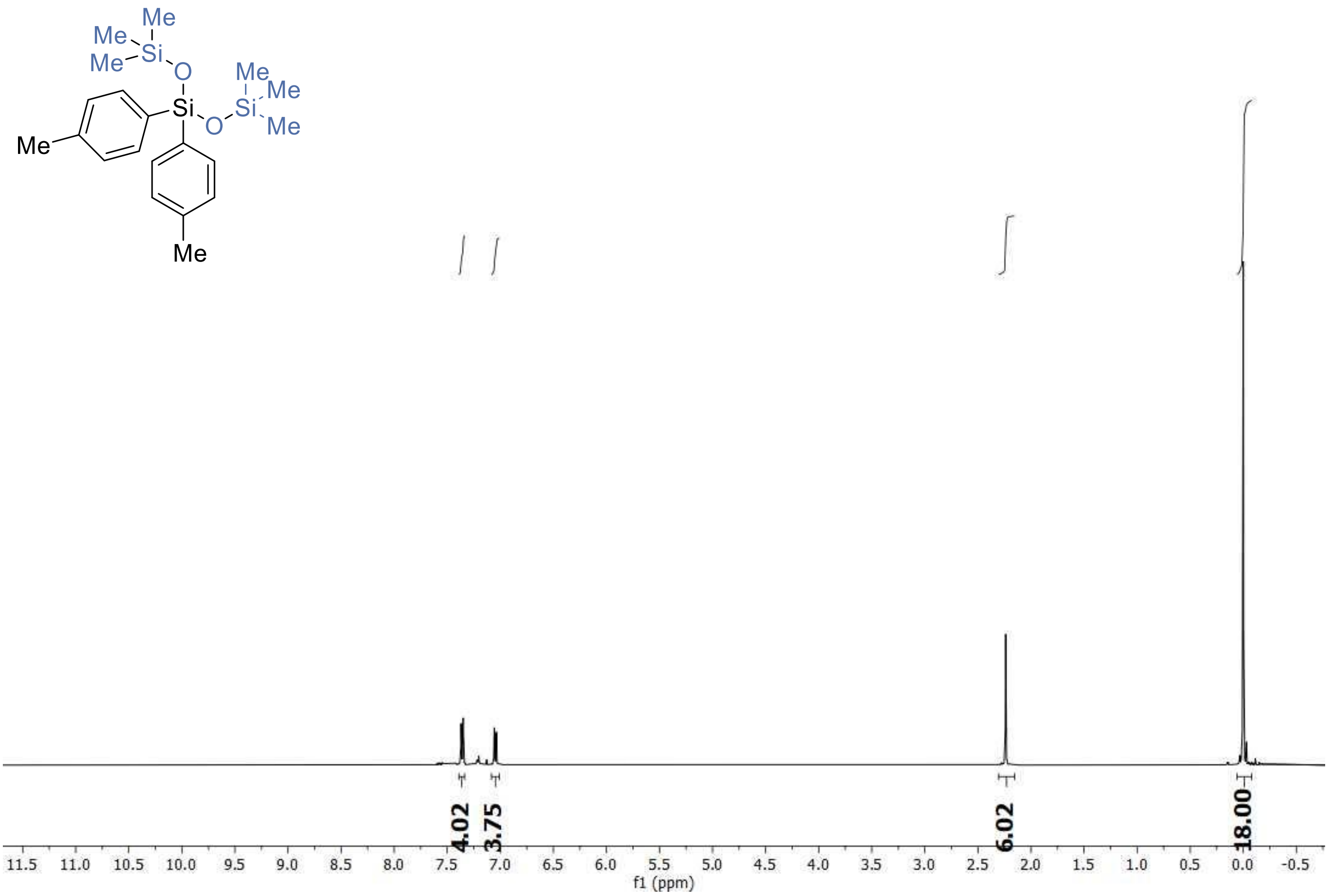


Figure S80. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3,3-di-p-tolyltrisiloxane (**4k**).

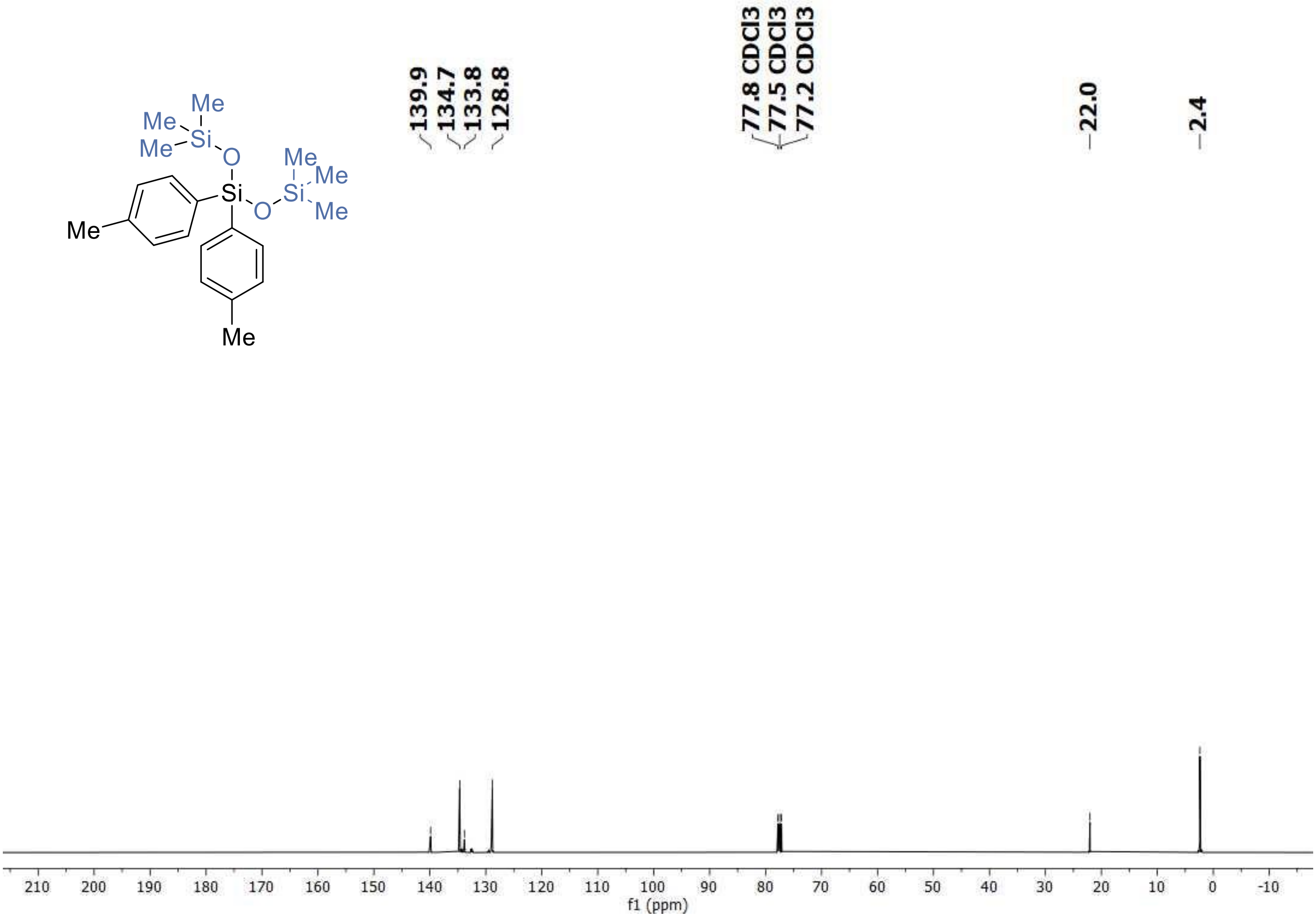


Figure S81. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3,3-di-p-tolyltrisiloxane (**4k**).

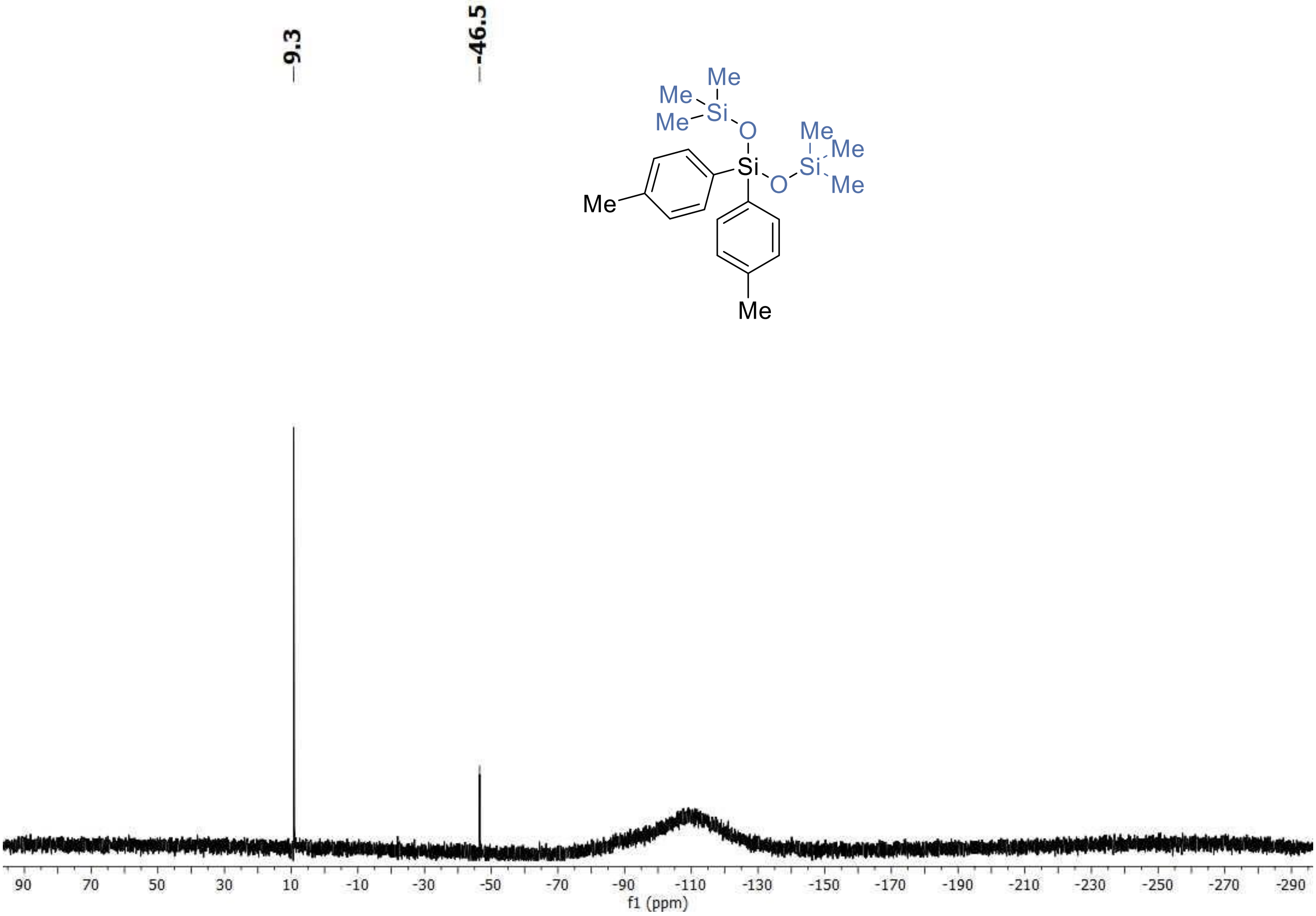


Figure S82. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3,3-di-p-tolyltrisiloxane (**4k**).

3,3-Diethyl-1,1,1,5,5,5-hexamethyltrisiloxane (4l)

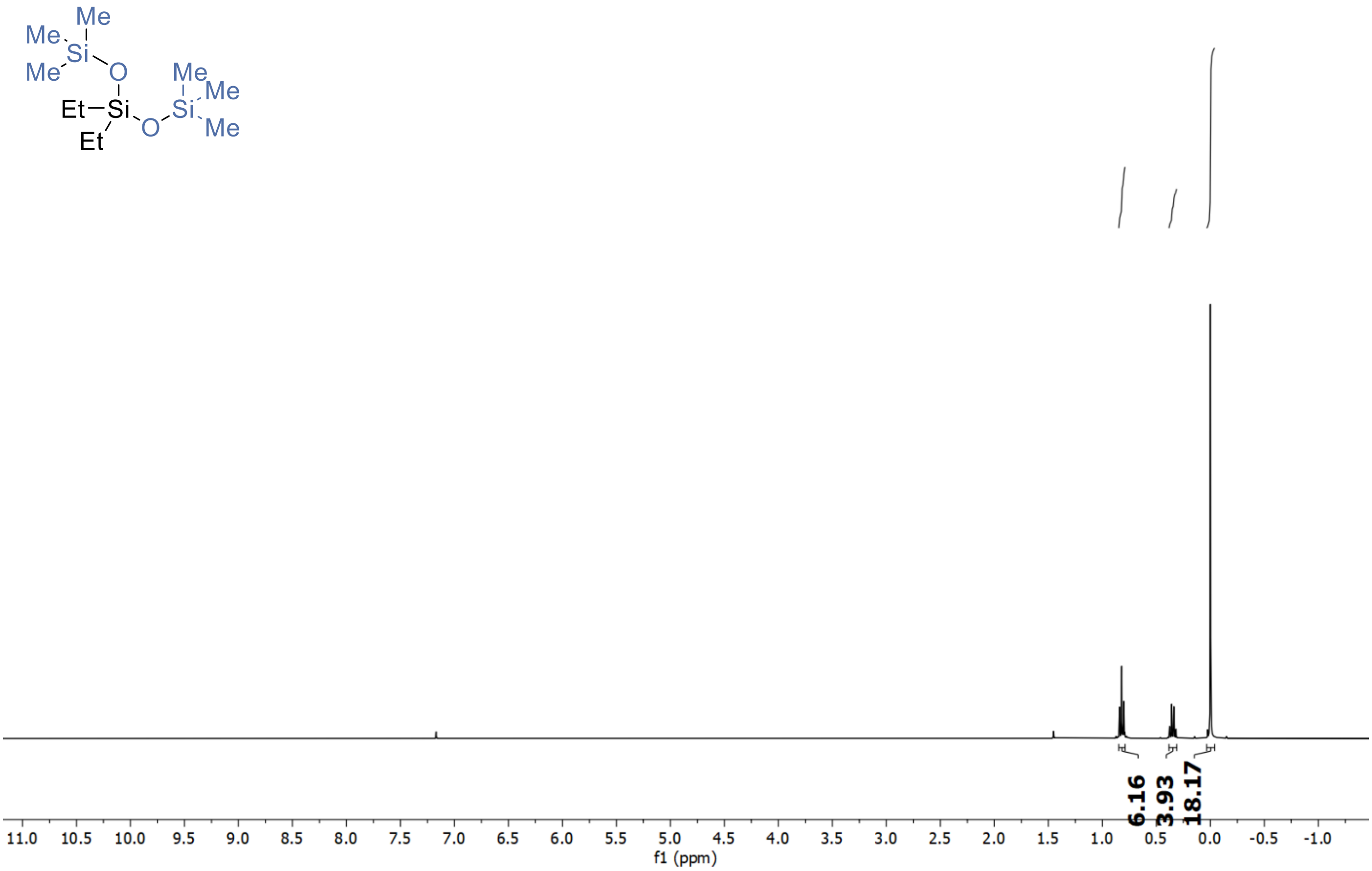


Figure S83. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 3,3-diethyl-1,1,1,5,5,5-hexamethyltrisiloxane (**4l**).

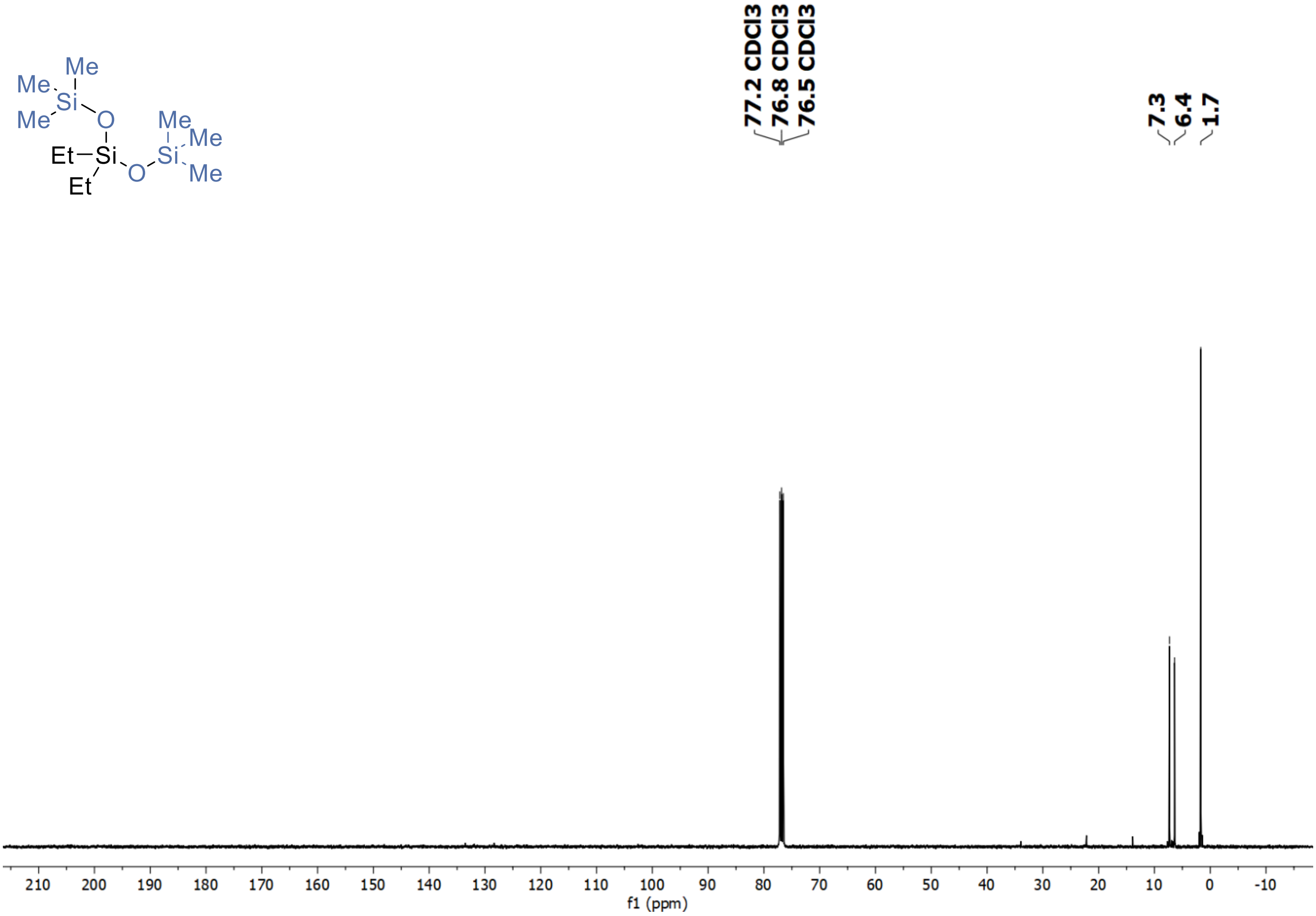


Figure S84. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 3,3-diethyl-1,1,1,5,5,5-hexamethyltrisiloxane (**4l**).

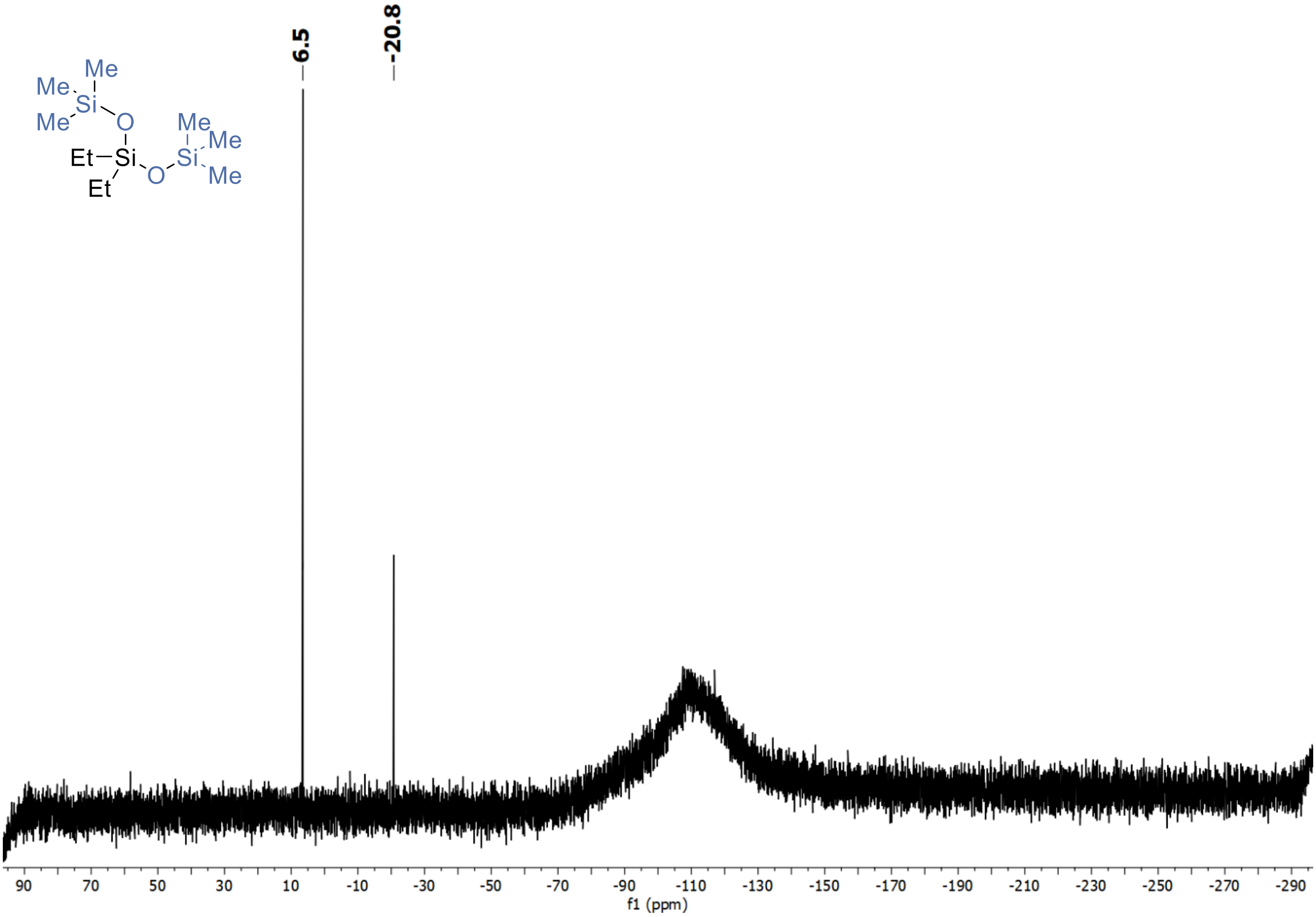


Figure S85. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 3,3-diethyl-1,1,1,5,5,5-hexamethyltrisiloxane (**4l**).

1,1,1,5,5,5-Hexamethyl-3-phenyl-3-((trimethylsilyl)oxy)trisiloxane (5a)

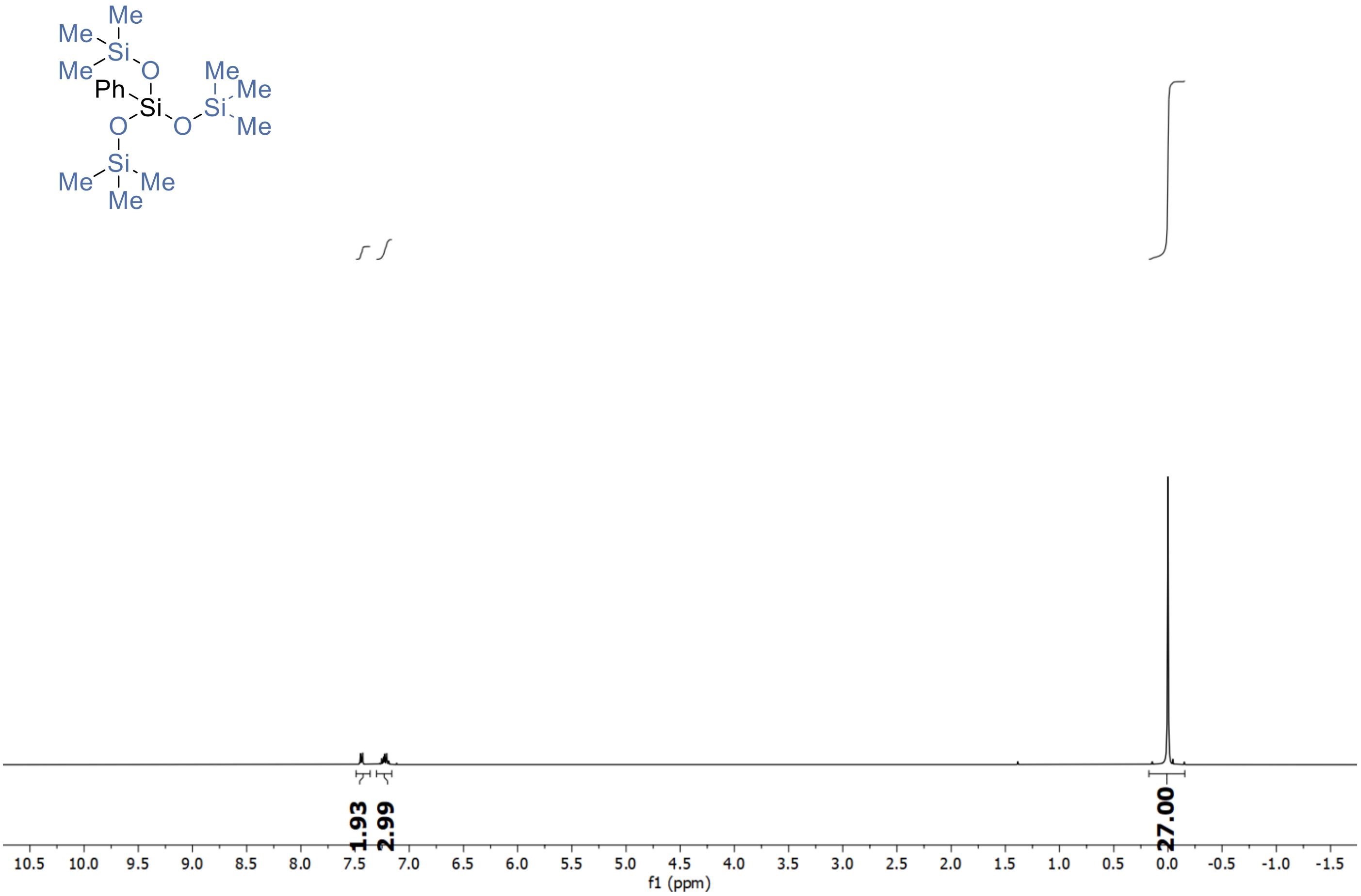


Figure S86. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3-phenyl-3-((trimethylsilyl)oxy)trisiloxane (**5a**).

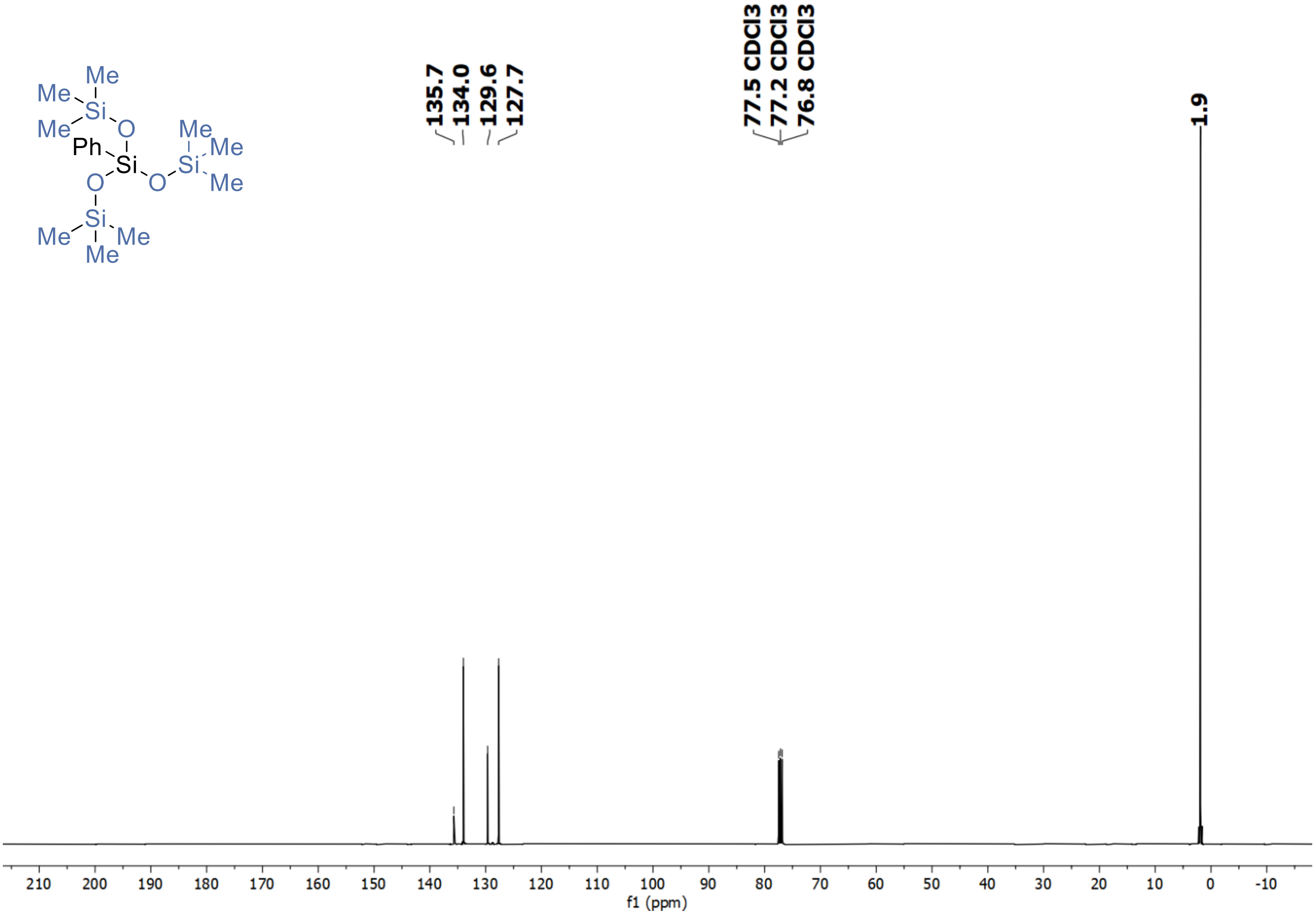


Figure S87. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3-phenyl-3-((trimethylsilyl)oxy)trisiloxane (**5a**).

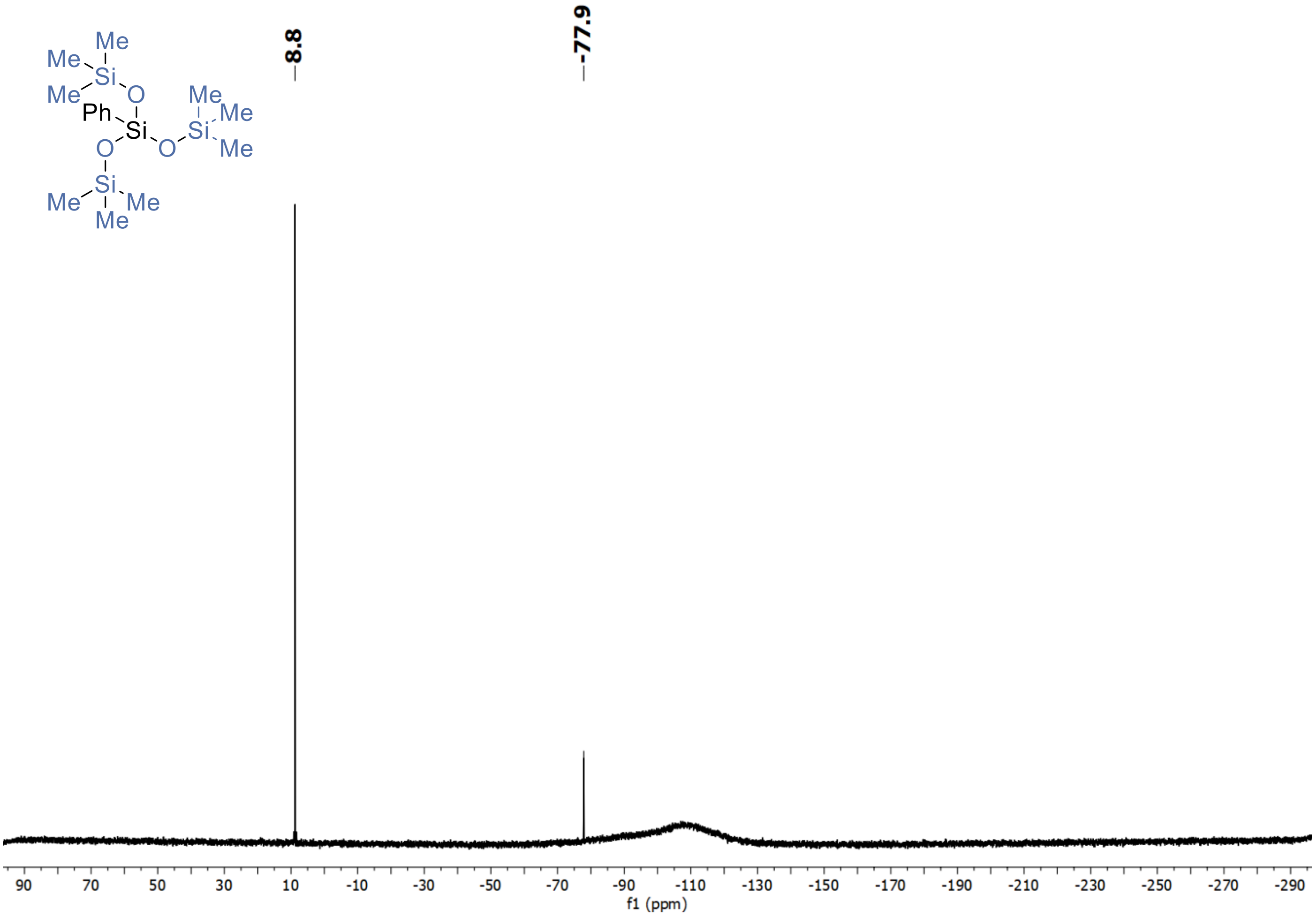


Figure S88. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 1,1,1,5,5,5-hexamethyl-3-phenyl-3-((trimethylsilyl)oxy)trisiloxane (**5a**).

3-Hexyl-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (5b)

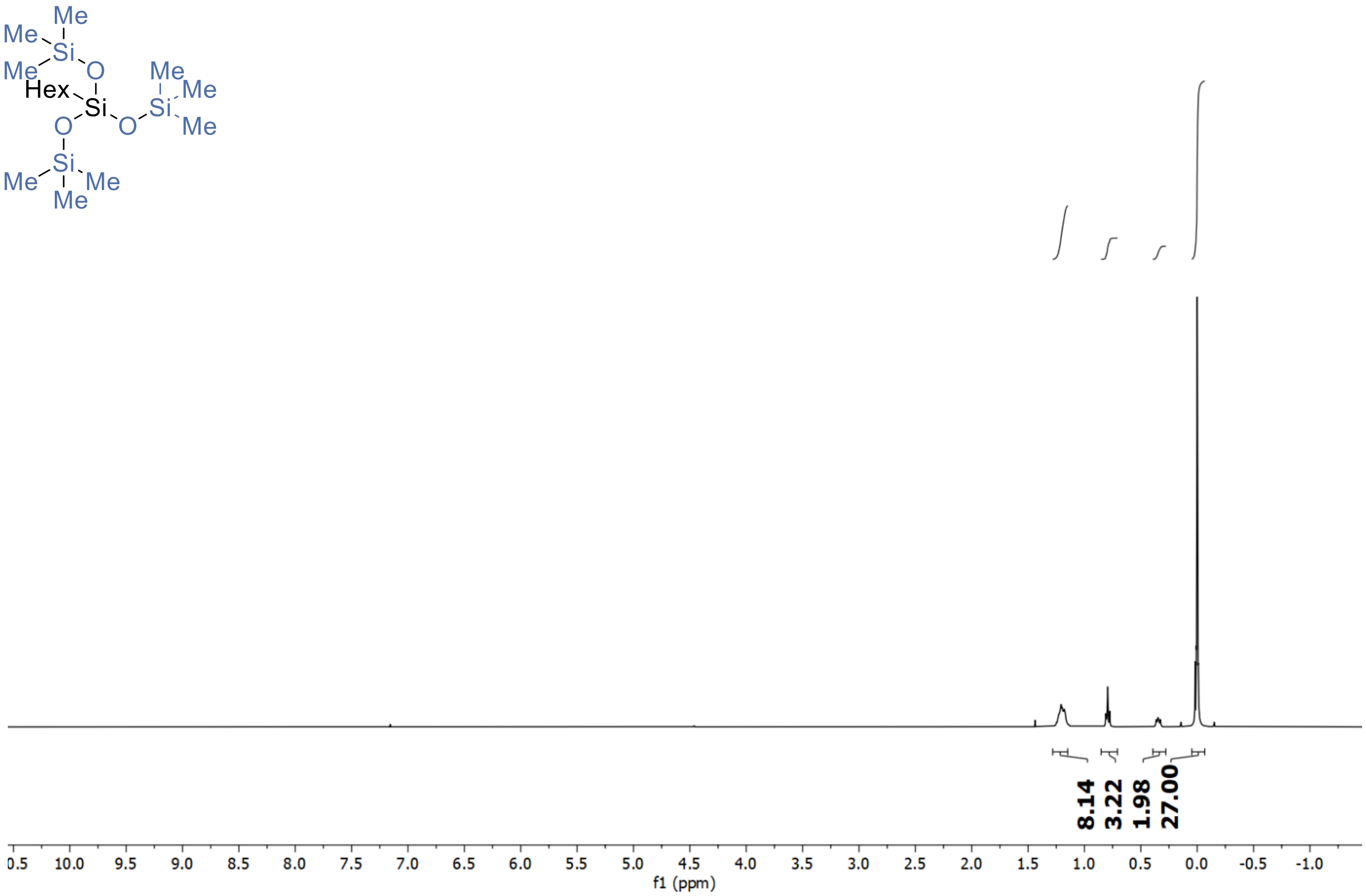


Figure S89. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 3-hexyl-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (**5b**).

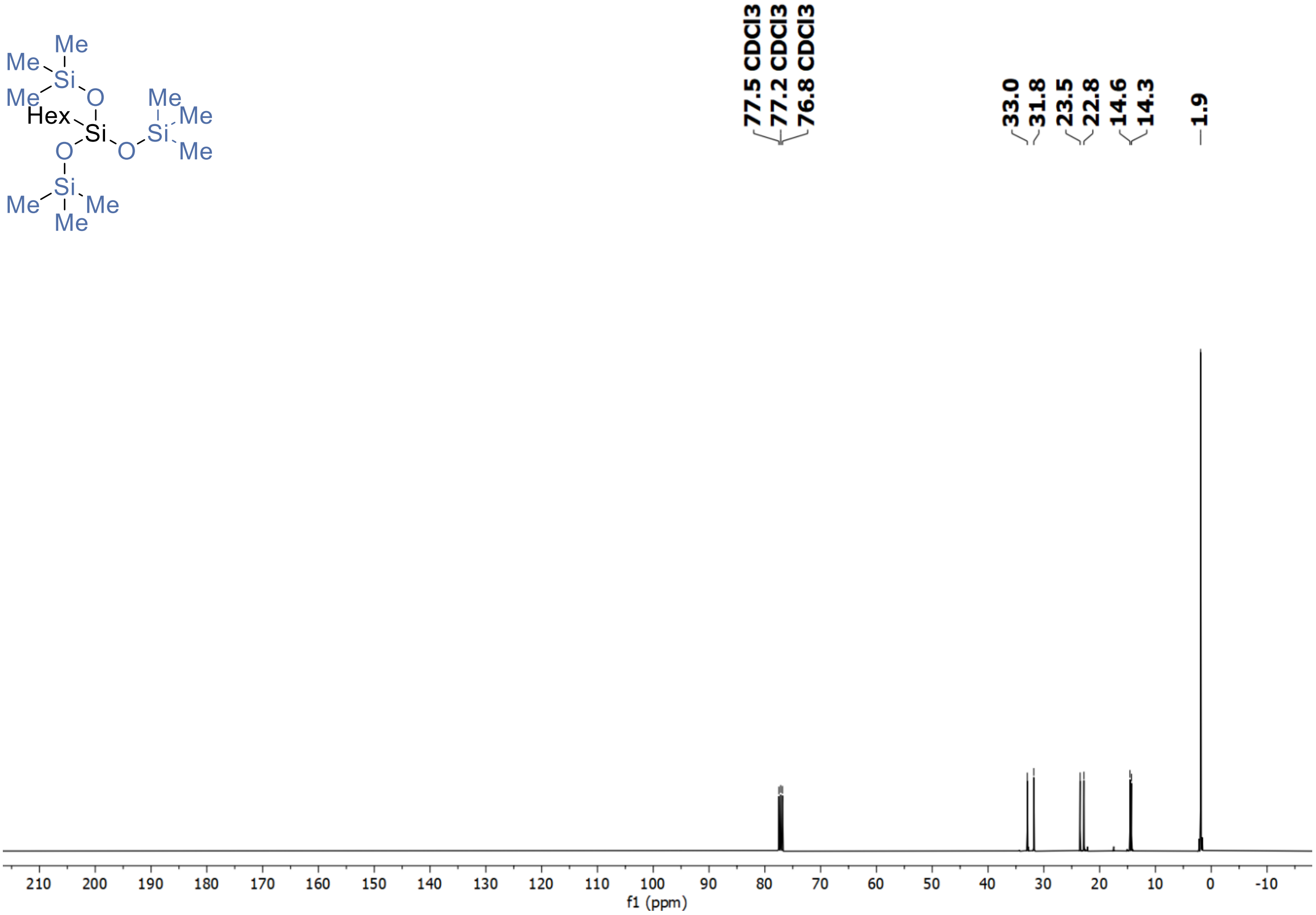


Figure S90. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 3-hexyl-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (**5b**).

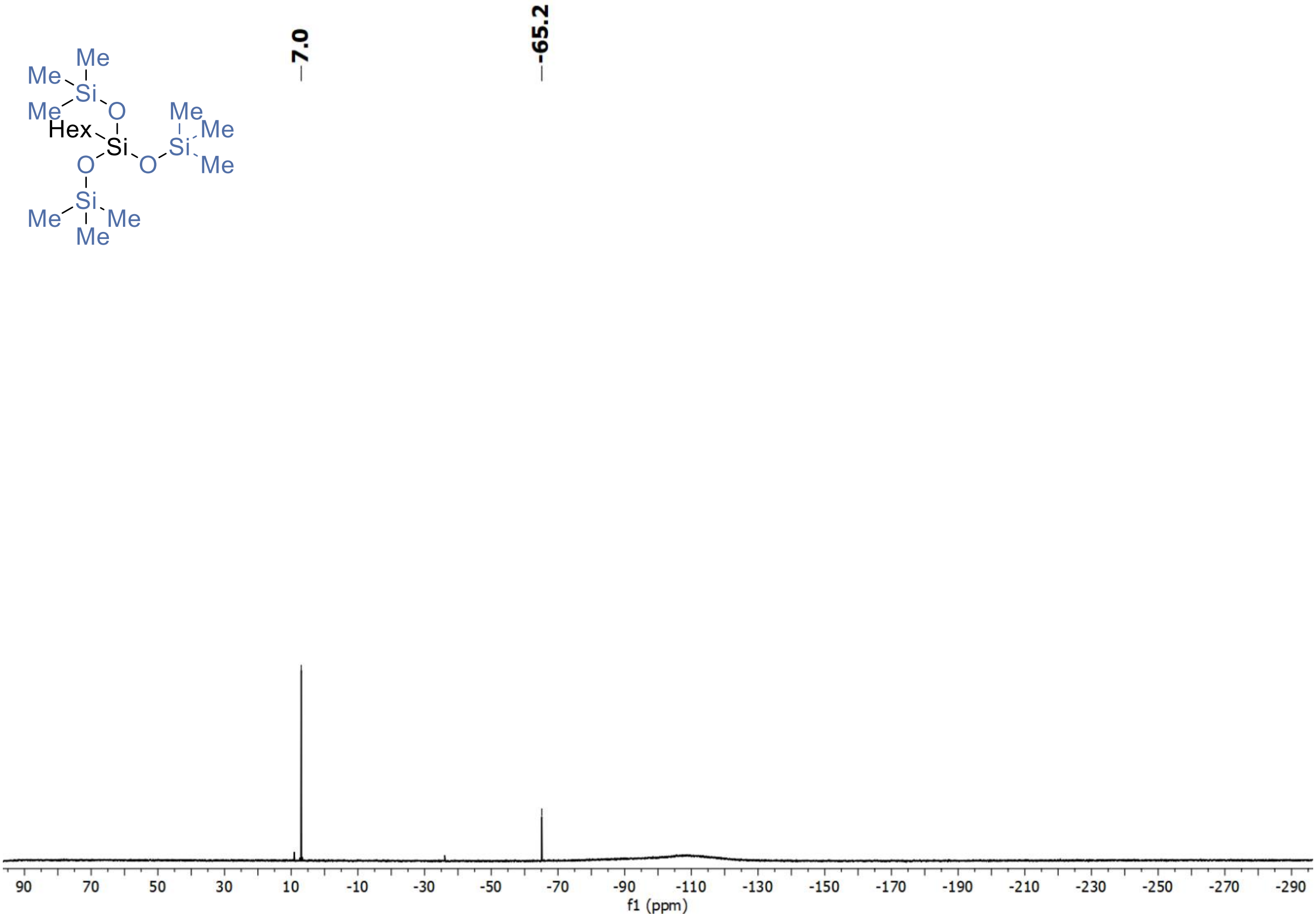


Figure S91. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 3-hexyl-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (**5b**).

3-(2-(Allyloxy)ethoxy)-1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane (6a)

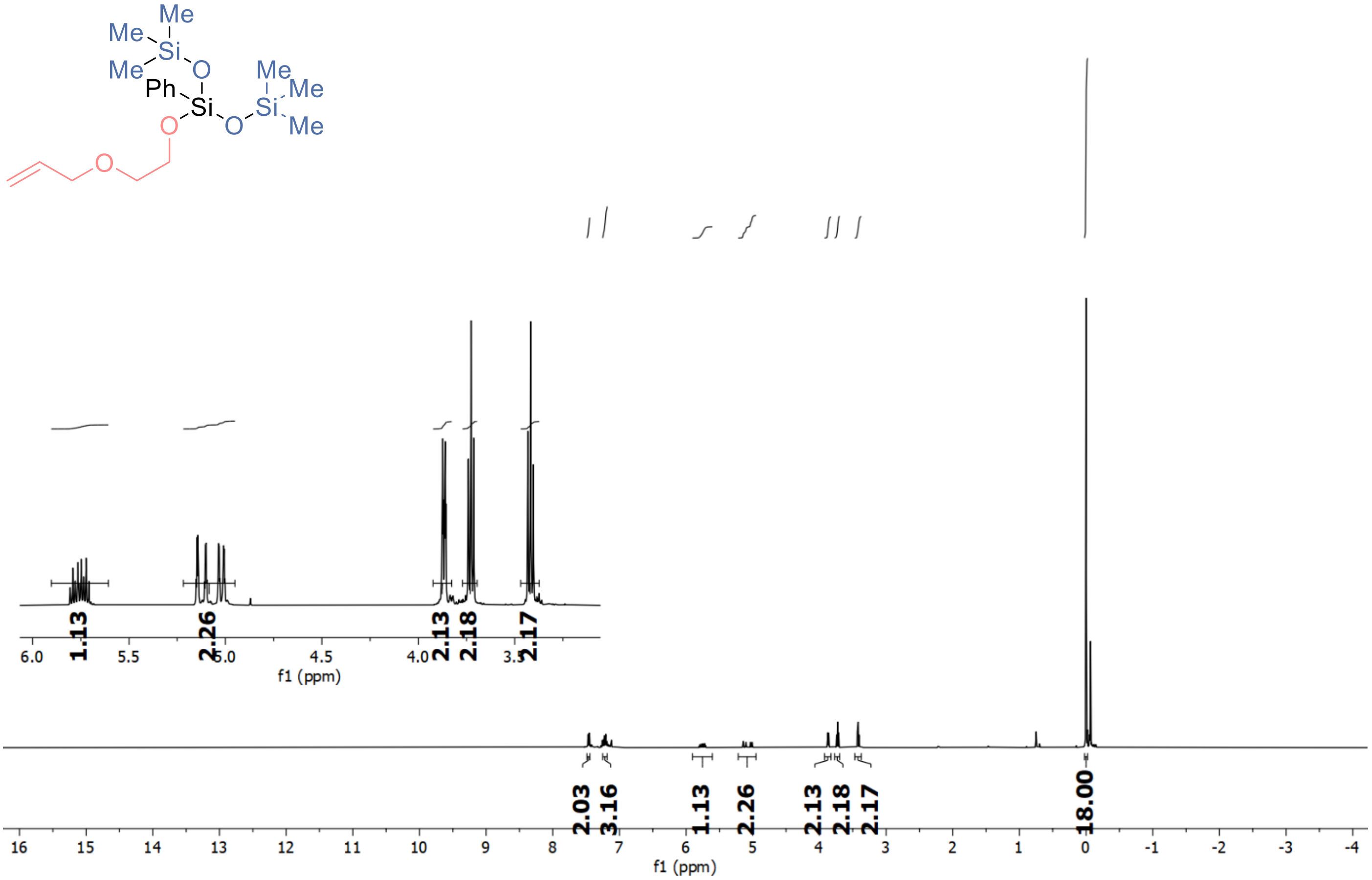


Figure S92. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 3-(2-(allyloxy)ethoxy)-1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane (**6a**).

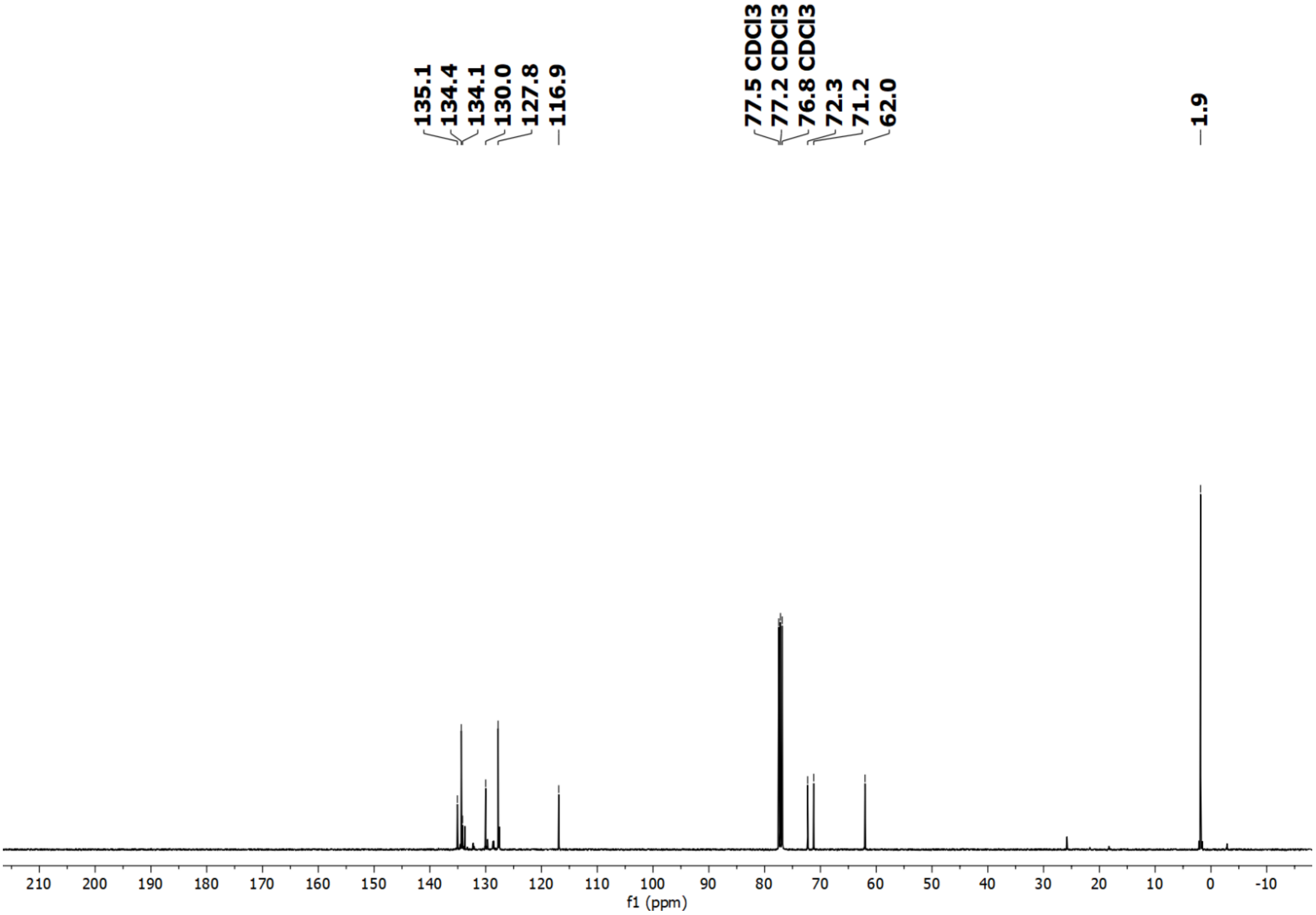


Figure S93. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 3-(2-(allyloxy)ethoxy)-1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane (**6a**).

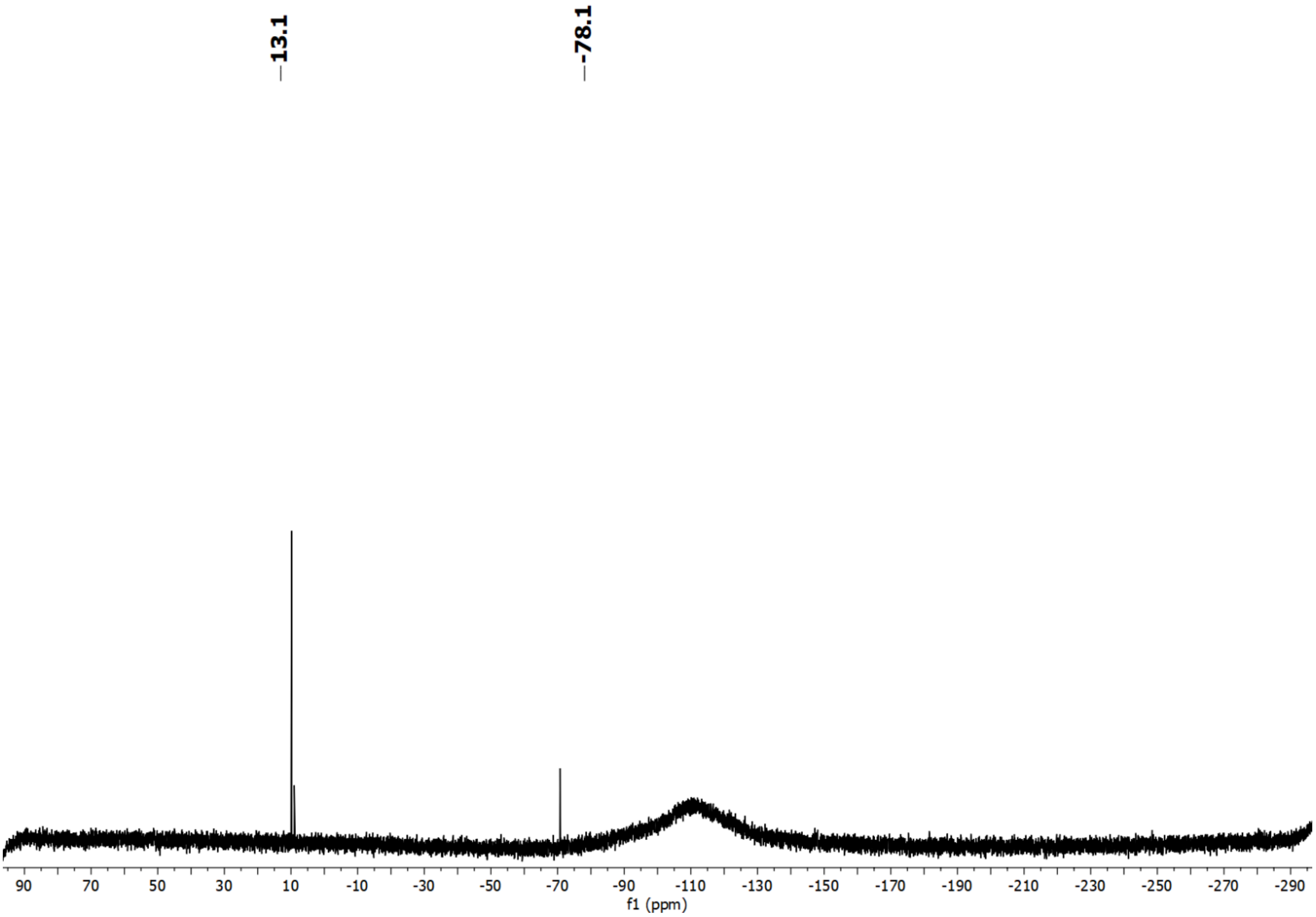
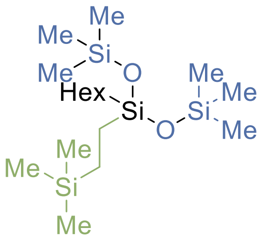


Figure S94. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 3-(2-(allyloxy)ethoxy)-1,1,1,5,5,5-hexamethyl-3-phenyltrisiloxane (**6a**).

3-Hexyl-1,1,1,5,5,5-hexamethyl-3-(2-(trimethylsilyl)ethyl)trisiloxane (6b)



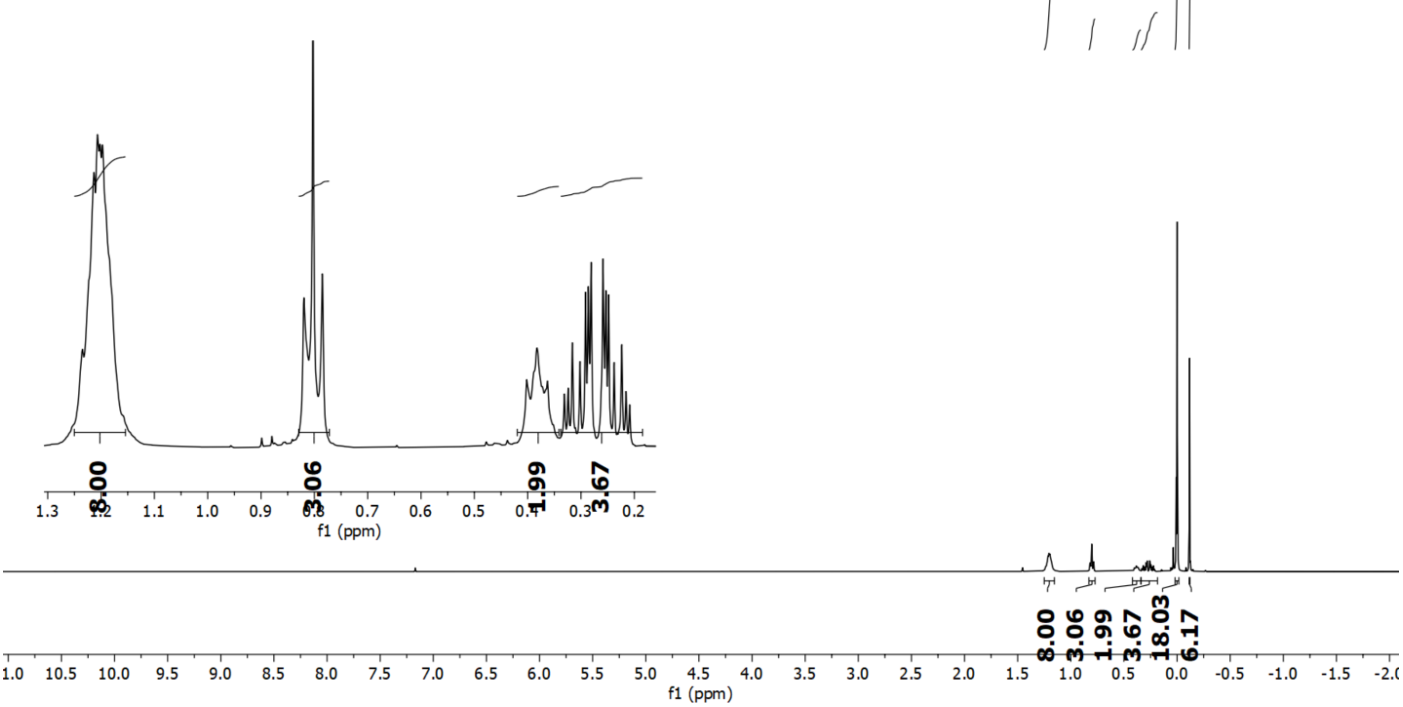


Figure S95. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 3-hexyl-1,1,1,5,5,5-hexamethyl-3-(2-(trimethylsilyl)ethyl)trisiloxane (**6b**).

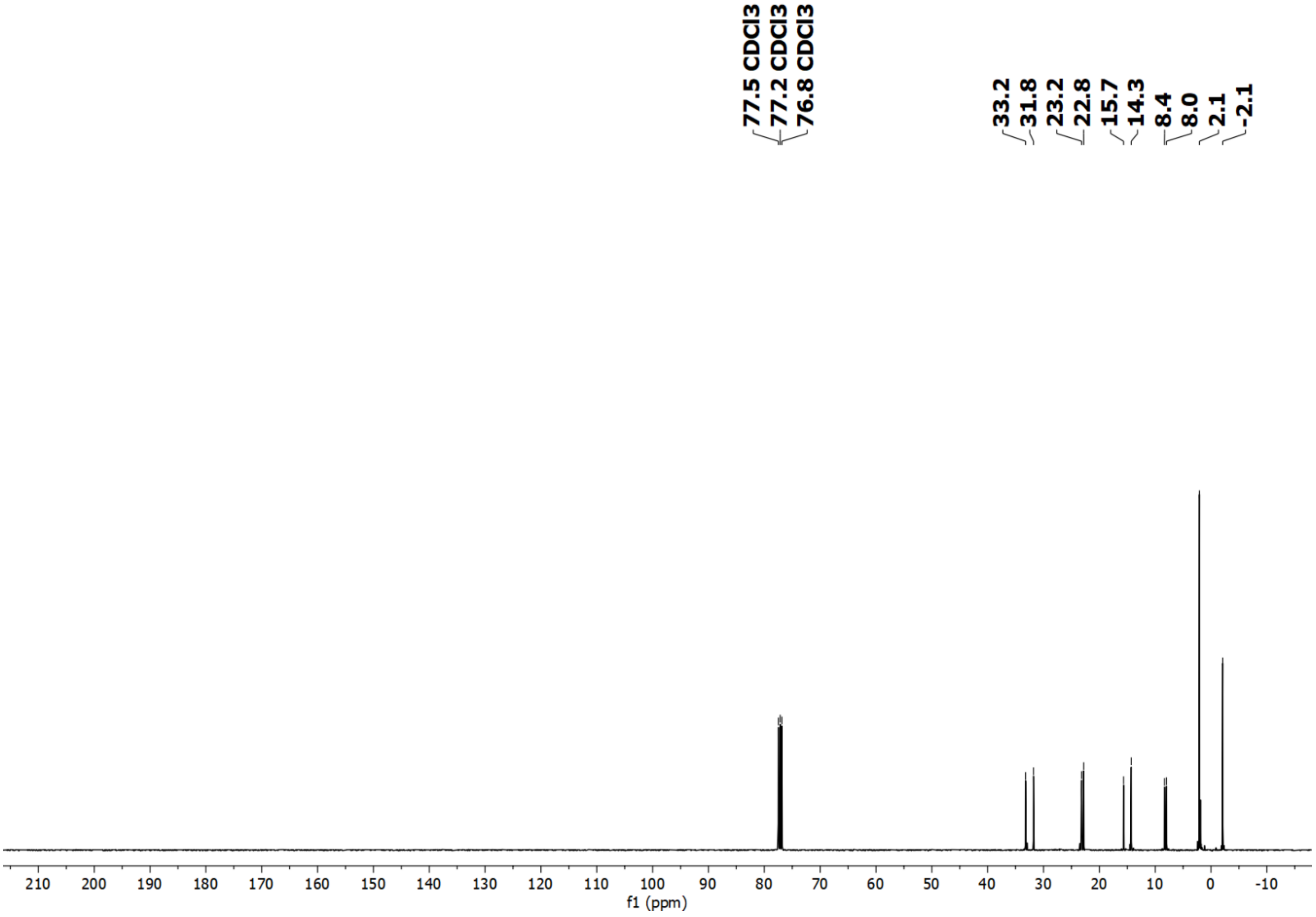


Figure S96. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 3-hexyl-1,1,1,5,5,5-hexamethyl-3-(2-(trimethylsilyl)ethyl)trisiloxane (**6b**).

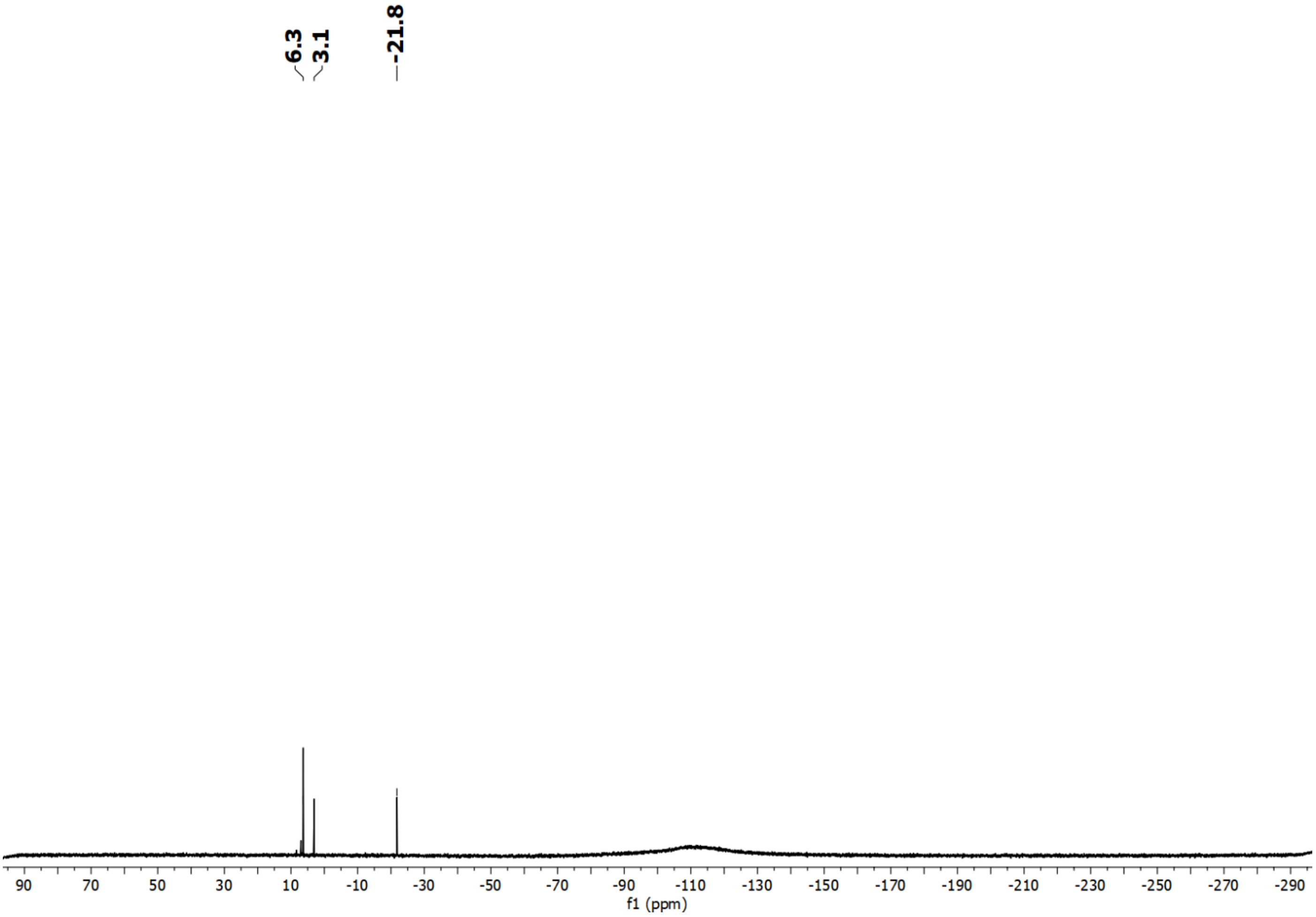


Figure S97. ^{29}Si NMR (80 MHz, Chloroform-d, 25°C) of 3-hexyl-1,1,1,5,5,5-hexamethyl-3-(2-(trimethylsilyl)ethyl)trisiloxane (**6b**).

MECHANISTIC STUDIES

Supplement 1

^{1}H NMR spectra of [(PPh$_3$)CuH]$_6$
^{1}H NMR: (400 MHz, Benzene-*d*$_6$) δ 7.72 – 7.61 (m, 6H), 6.95 (t, *J* = 7.4 Hz, 4H), 6.74 (t, *J* = 7.5 Hz, 6H), 3.52 (t, *J* = 5.6 Hz, 1H).

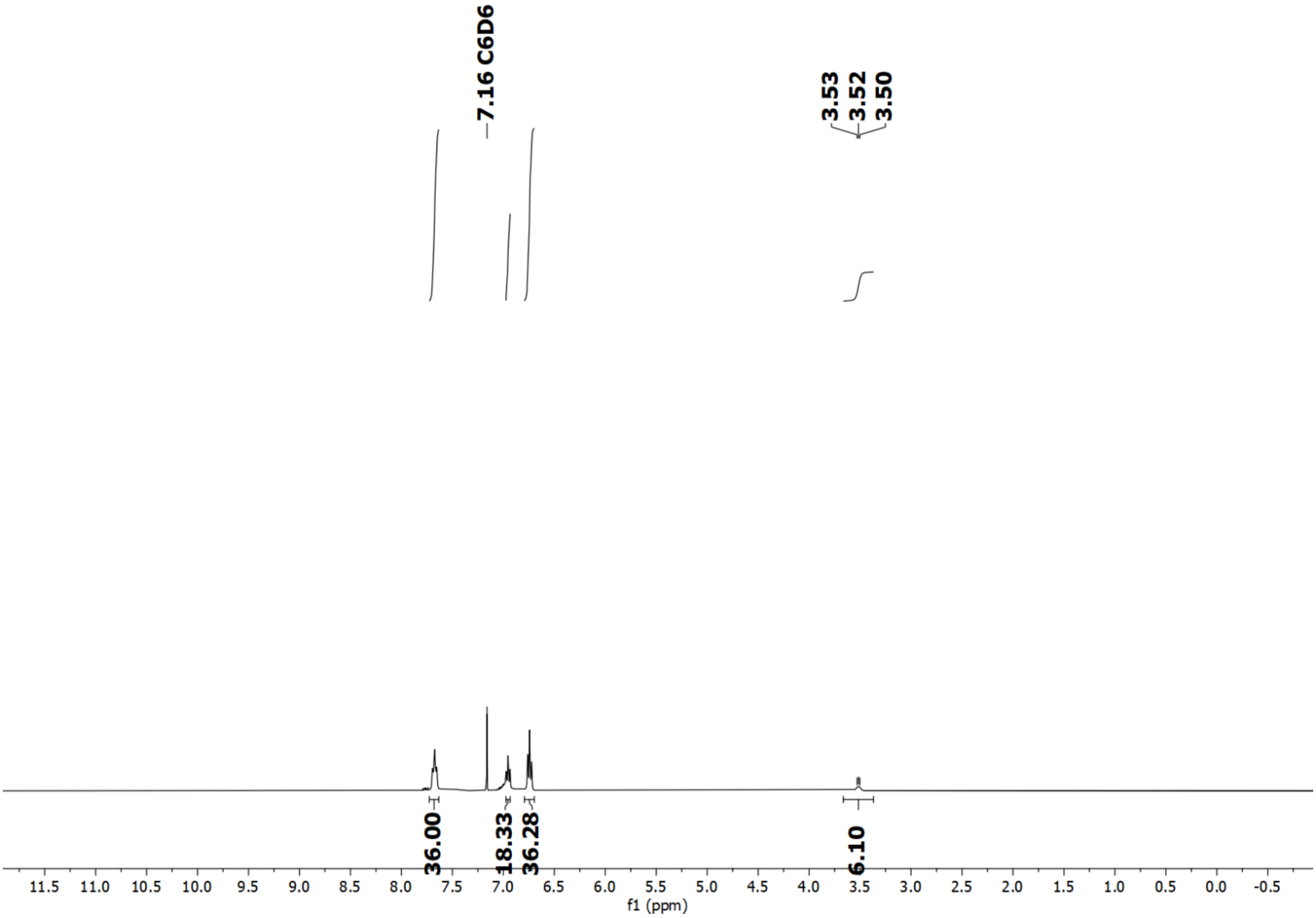


Figure S98. ^{1}H NMR (400 MHz, benzene-d$_6$, 25°C) of Stryker's reagent.

Supplement 2

^{1}H NMR spectra of mixture of [(PPh$_3$)CuH]$_6$ and silanol – Dihydrogen evolution

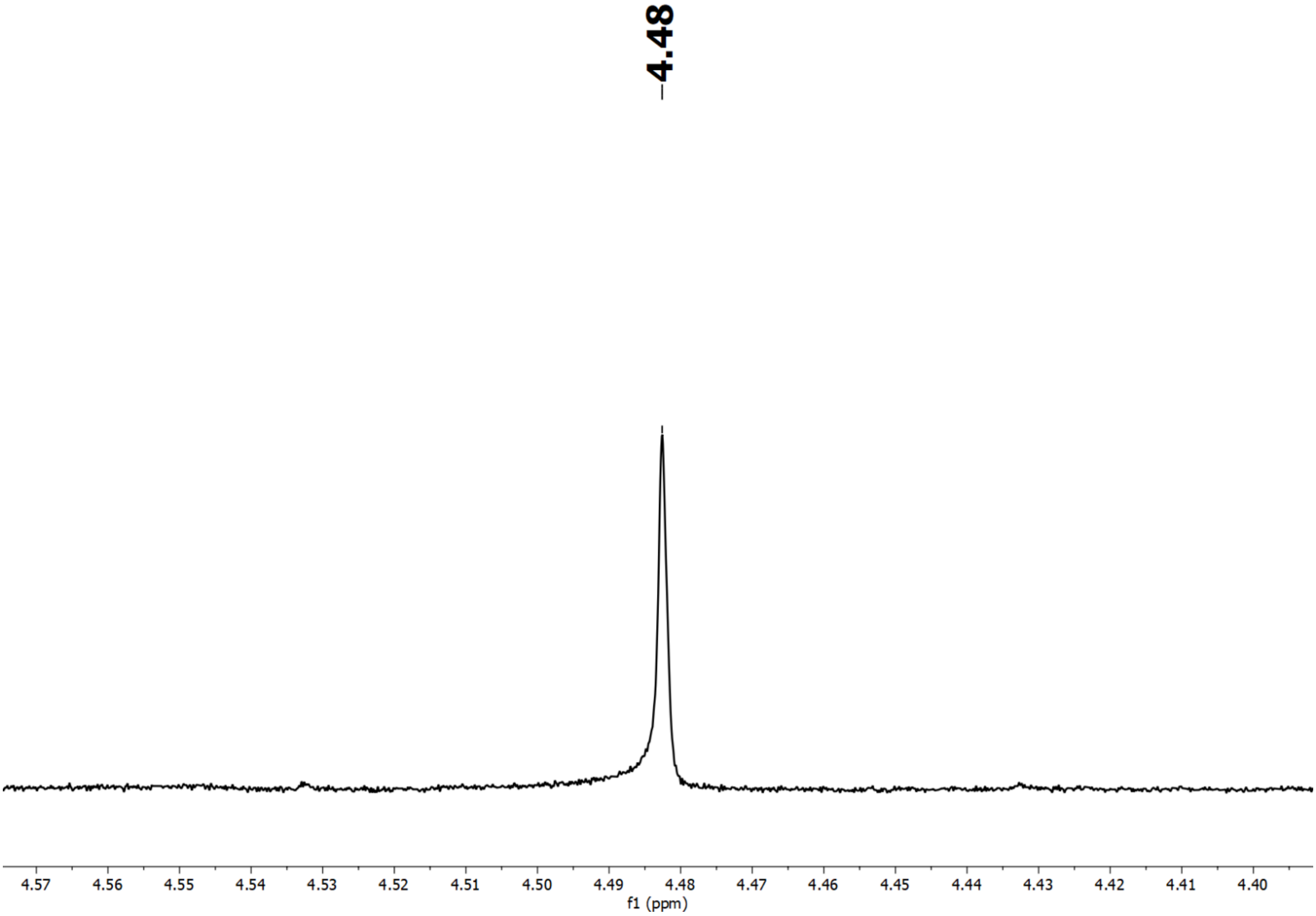


Figure S99. ^{1}H NMR (400 MHz, chloroform-d, 25°C) of the mixture of Stryker's reagent and *tert*-butyldimethylsilanol.

Supplement 3

^{29}Si NMR spectra of: sole tert-butyldimethylsilanol (part a), mixture of [(PPh$_3$)CuH]$_6$ and silanol (part b), 1,5-di-tert-butyl-1,1,5,5-tetramethyl-3-phenyltrisiloxane (part c), and the typical reaction between tert-butyldimethylsilanol and phenylsilane in the presence of [(PPh$_3$)CuH]$_6$ (part d).

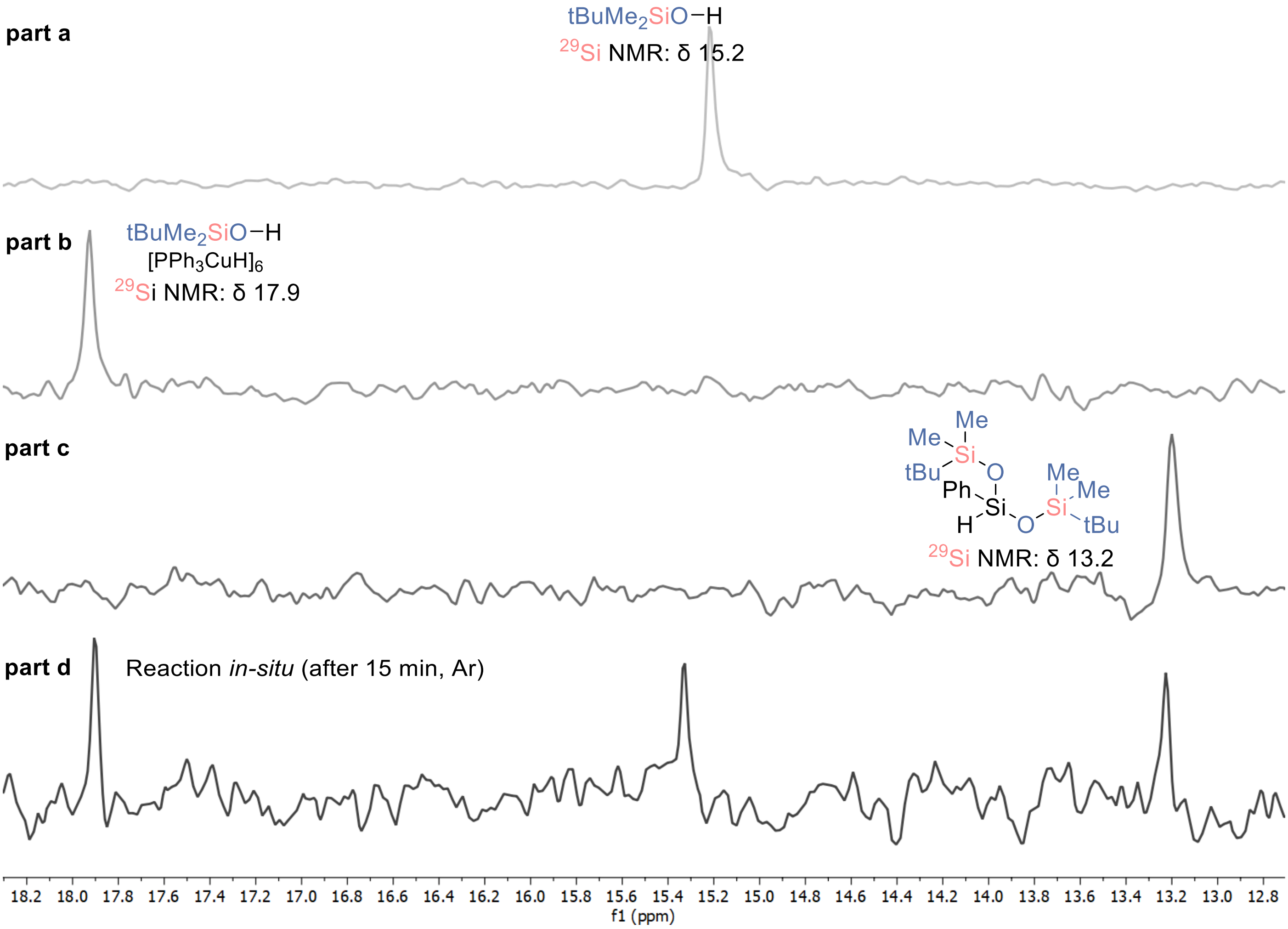


Figure S100. ^{29}Si NMR (80 MHz, chloroform-d, 25°C) of the mixture of Stryker's reagent and *tert*-butyldimethylsilanol.

REFERENCES

1 P. D. Prince, M. J. Bearpark, G. S. McGrady and J. W. Steed, Hypervalent hydridosilicates: synthesis, structure and hydride bridging, *Dalton Trans.*, 2007, **2**, 271–282.

2 Z. Li, J.-G. Liu, W.-P. Zhang and M.-H. Xu, Enantioselective Si–H Insertion of Arylvinyldiazoesters Promoted by Rhodium(I)/Diene Complexes, *Adv. Synth. Catal.*, 2024, in press, DOI:10.1002/adsc.202400241.

3 Y. Satoh, M. Igarashi, K. Sato and S. Shimada, Highly Selective Synthesis of Hydrosiloxanes by Au-Catalyzed Dehydrogenative Cross-Coupling Reaction of Silanols with Hydrosilanes, *ACS Catal.*, 2017, **7**, 1836–1840.

4 E. Szafoni, K. Kuciński and G. Hreczycho, Cobalt-catalyzed dehydrogenative cross-coupling reaction: Selective access to dihydrosiloxanes, hydrosiloxanes and functionalized silsesquioxanes, J. Catal., 2023, **423**, 1–9.

5 H. Zhang and D. Zhao, Synthesis of Silicon-Stereogenic Silanols Involving Iridium-Catalyzed Enantioselective C–H Silylation Leading to a New Ligand Scaffold, ACS Catal., 2021, 11, 10748–10753.

6 Y. Lin, K.-Z. Jiang, J. Cao, Z.-J. Zheng, Z. Xu, Y.-M. Cui and L.-W. Xu, Adv. Synth. Catal., 2017, **359**, 2247–2252.

7 . Hirabayashi, J. Ando, J. Kawashima, Y. Nishihara, A. Mori and T. Hiyama, Novel Carbon-Carbon Bond Formation through Mizoroki-Heck Type Reaction of Silanols and Organotin Compounds, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1409–1417.

8 T. Aoki, J. Watanabe, Y. Ishimoto, E. Oikawa, Y. Hayakawa and M. Nishida, Synthesis and polymerization of p-pentamethyldisiloxanyl-α,β,β-trifluorostyrene and the oxygen permeability of the polymer, *J. Fluor. Chem.*, 1992, **59**, 285–288.

9 M. Igarashi, K. Kubo, T. Matsumoto, K. Sato, W. Ando and S. Shimada, Pd/C-catalyzed cross-coupling reaction of benzyloxysilanes with halosilanes for selective synthesis of unsymmetrical siloxanes, *RSC Adv.*, 2014, **4**, 19099–19102.

10 G. Engelhardt, H. Jancke, M. Mägi, T. Pehk, E. Lippmaa, Über die 1H-, 13C- und 29Si-NMR chemischen Verschiebungen einiger linearer, verzweigter und cyclischer Methylsiloxan-Verbindungen, *J. Organomet. Chem.*, 1971, **28**, 293–300.

11 S. Pattanaik and C. Gunanathan, Cobalt-Catalyzed Selective Synthesis of Disiloxanes and Hydrodisiloxanes, *ACS Catal*., 2019, **9**, 5552–5561.

12 31 K. Kuciński, H. Stachowiak and G. Hreczycho, Silylation of silanols with hydrosilanes via main-group catalysis: the synthesis of unsymmetrical siloxanes and hydrosiloxanes, *Inorg. Chem. Front.*, 2020, **7**, 4190–4196.

13 K. Kuciński and G. Hreczycho, O-Metalation of silanols and POSS silanols over Amberlyst-15 catalyst: A facile route to unsymmetrical siloxanes, borasiloxanes and germasiloxanes, *Inorganica Chim. Acta*, 2019, **490**, 261–266.

14 J. Ohshita, D. Hamamoto, K. Kimura, A. Kunai, Anodic polymerization of dithienosilole and electroluminescent properties of the resulting polymer, *J. Organomet. Chem.*, 2005, **690**, 3027–3032.

15 P. A. Di. Giorgio, L. H. Sommer and F. C. Whitmore, Di-t-butyl-di-aminoalkyl Silicates, *J. Am. Chem. Soc.*, 1949, **7**1, 3254–3256.

16 G. Calzaferri, R. Imhof and K. W. Törnroos, Structural and vibrational properties of the octanuclear silasesquioxane $C_6H_{13}(H_7Si_8O_{12})$, *J. Chem. Soc. Dalton Trans.*, 1994, 3123–3128