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Supporting Information

An Easily Accessed Nickel Nanoparticle Catalyst for Alkene Hydrosilylation with Tertiary Silanes

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Supporting information

Content	Page
1. Chemicals and Reagents 2. Physical methods	S2
3.Preparation and characterization of Ni precatalysts	S3
4. General procedures for the hydrosilylation reactions	S10
5. Optimization of hydrosilylation reaction conditions	S11
6. Evaluation of the activity of Ni catalyst	S12
7. Experiments for the investigation of nature of catalyst’s species	S12
8. TEM examination of Ni catalysts	S13
9. UV-Vis spectra of active Ni nanoparticles and precatalysts	S16
10. Detailed descriptions of the products	S19
11. References	S29
12. NMR spectra	S30

1. Chemicals and Reagents

All manipulations were carried out under an inert N_2(g) atmosphere using standard Schlenk or glovebox techniques. Solvents were purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glove box without exposure to air. Deuterated solvents were purchased from ARMAR AG and were degassed and stored over activated 3 Å molecular sieves. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. Liquid compounds were degassed by standard freeze-pump-thaw procedures prior to use. The following chemicals were prepared according to procedures in the literature:

substrates tert-butyl(hex-5-enyloxy)dimethylsilane [1], 2,2-dimethyl-4-pentenal ethylene acetal (**3l**)[2]; (E)-((but-2-en-1-yloxy)methyl)benzene[3], (E)-pent-1-en-1-ylcyclohexane[4], (Z)-2-(hex-3-en-1-yl)-1,3-dioxolane[5], (Z)-tert-butyldimethyl(octadec-9-en-1-yloxy)silane (analogously to tert-butyl(hex-5-enyloxy)dimethylsilane) [1].

2. Physical methods

The ^{1}H and ^{13}C NMR spectra were recorded at 293 K or 373 K on Bruker Avance 400 spectrometers. ^{1}H NMR chemical shifts were referenced to residual solvent as determined relative to Me_4Si ($\delta = 0$ ppm). The $^{13}C\{^1H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.16 ppm). IR spectra were recorded on solid samples on a Varian 800 FT-IR spectrometer using ATR sampling techniques. UV-Vis spectra were recordered on Varian Cary 50 Bio spectrometer. GC measurement was conducted on a Perkin-Elmer Clarus 400 GC with a FID detector. GC-MS measurements were conducted on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. HRMS (ESI, APCI and APPI) measurements were conducted at the EPFL ISIC Mass Spectrometry Service with a Micro Mass QTOF. Elemental analyses were performed on a Carlo Erba EA 1110 CHN instrument and ICP emission spectrometer Shimadzu ICPE-9000. PXRD measurements were carried out on X'Pert Philips diffractometer in Bragg-Brentano geometry with monochromatic $CuK_{\alpha1,2}$ radiation and a fast Si-PIN multi-strip detector (0.1540 nm). Microstructure was examined by a FEI Tecnai Osiris transmission electron microscopy (TEM) equipped with high brightness XFEG gun. Energy-dispersive X-ray spectroscopy (EDX) mapping images was taken under a scanning TEM (STEM) modal. The nanocrystals size distribution was measured directly from the typical TEM images.

3. Preparation and characterization of Ni precatalysts

Summary: IR analysis indicated the absence of hydroxyl ligands in all samples (Fig. S1-S3). Power X-ray diffraction measurements indicated that Ni(O^{t}Bu)$_2$ in all samples were amorphous, and the samples prepared using NaO^{t}Bu and KO^{t}Bu contained additionally crystalline NaCl and KCl, respectively (Fig. S4-S6). These two samples are labelled Ni(O^{t}Bu)$_2$•xNaCl and Ni(O^{t}Bu)$_2$•xKCl. Elemental analysis showed that the samples prepared using LiO^{t}Bu was Ni(O^{t}Bu)$_2$ with nearly no LiCl. On the other hand, the samples prepared using NaO^{t}Bu and KO^{t}Bu contained significant amounts of NaCl (about 1.6 equiv) and KCl (about 1.4 equiv), respectively, in addition to Ni(O^{t}Bu)$_2$.

Preparation of Ni(O^{t}Bu)$_2$

In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with Ni(TMEDA)Cl$_2$ (1.228 g, 5.0 mmol), LiO^{t}Bu (0.80 g, 10.0 mmol) and 15 mL of dry ^{t}BuOH. Resulting mixture was stirred for 48 hours at 60°C. After cooling down to room temperature, blue solid was filtered off (the solution must be colorless) and washed 3 times with small portions of THF and 1 time with pentane. After drying under reduced pressure, 0.85 g (4.9 mmol, 98%) of Ni(O^{t}Bu)$_2$ was obtained.

Elemental analysis: Anal. Calcd for $C_8H_{18}NiO_2$: C, 46.89.14; H, 8.85; Ni, 28.7. Found: C, 46.70; H, 8.90; Ni, 29.0.

IR: ν (cm^{-1}) 2970, 1358, 1186, 926, 763, 621.

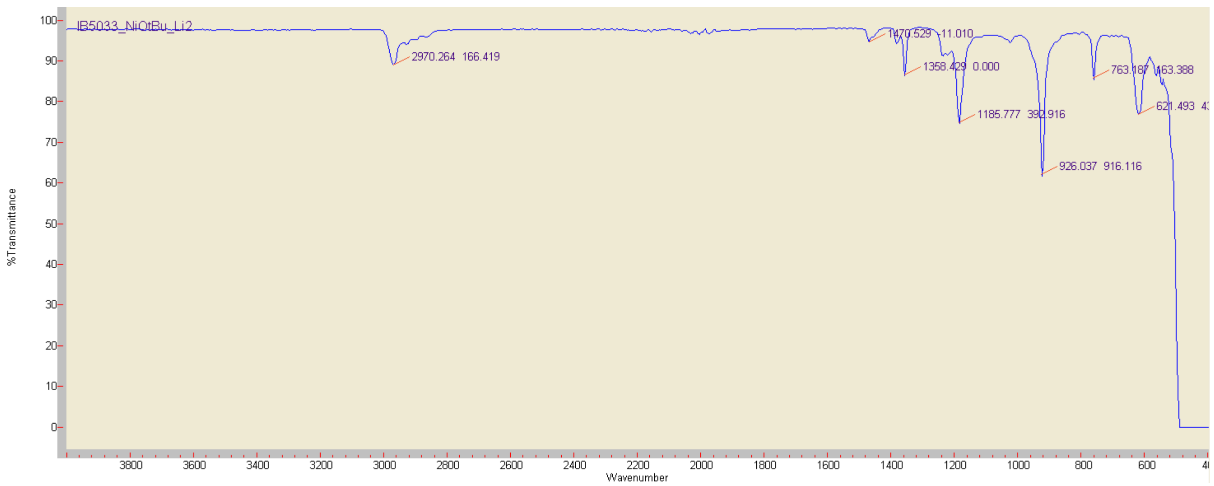


Figure S1. IR spectrum of Ni(O^{t}Bu)$_2$

Preparation of $Ni(O^tBu)_2$•xKCl

In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with $Ni(TMEDA)Cl_2$ (1.228 g, 5.0 mmol), KO^tBu (1.122 g, 10.0 mmol) and 20 mL of dry THF. Resulting mixture was stirred for 24 hours at 60°C. After cooling down to room temperature, blue solid was filtered off (the solution must be colorless) and washed 3 times with small portions of THF. After drying under reduced pressure, 1.61 g of precatalyst $Ni(O^tBu)_2$•xKCl was obtained.

Note : Centrifugation can be used instead of filtration. $Ni(O^tBu)_2$•xKCl is moisture sensitive and should be stored under N_2.

CHN elemental analysis of one batch: found: C, 27.09; H, 5.10; N, 0.00.

The observed C:H ratio (5.312) and the absence of N suggest that the organic part of the precatalyst should be O^tBu (calculated C:H ratio is 5.296).

ICP-AES elemental analysis of this batch: found: K, 19.0; Ni, 19.5.

The K:Ni ratio is approximately 1.5.

CHN elemental analysis of another batch: found: C, 30.00; H, 5.47; N, 0.00.

ICP-AES elemental analysis of this other batch: found: K, 15.62; Ni, 18.55.

The K:Ni ratio is roughly 1.3.

Thus, the x values of $Ni(O^tBu)_2$•xKCl vary slightly from sample to sample in the range of about 1.4. However, the catalytic activity of many different batches of samples is identical within the uncertainty of analysis. Thus, a general formula of $Ni(O^tBu)_2$•xKCl is used.

IR: ν (cm^{-1}) 2973, 1358, 1187, 928, 764, 621.

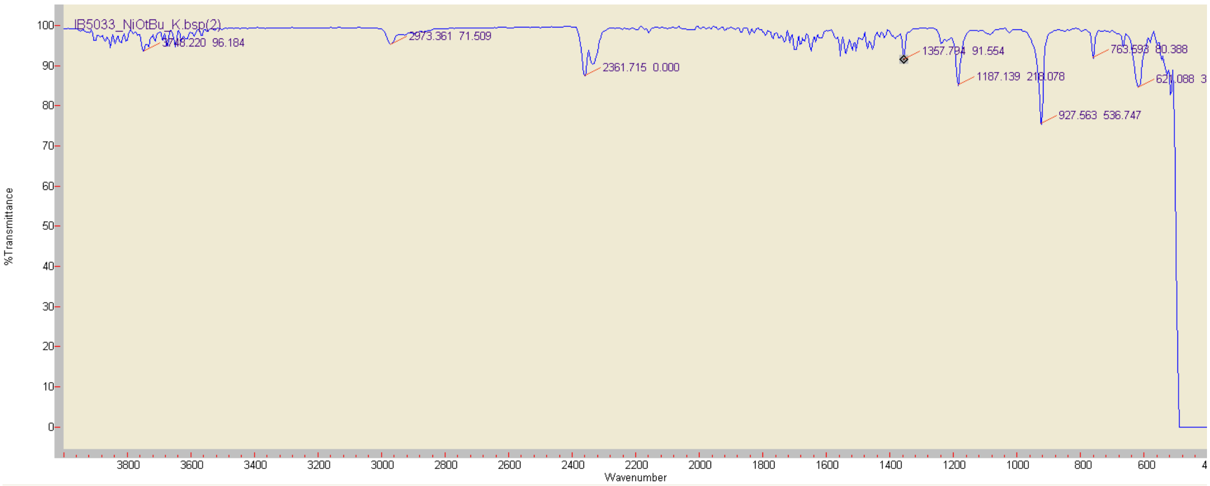


Figure S2. IR spectrum of $Ni(O^tBu)_2$•xKCl

Preparation of Ni(O^{t}Bu)$_2$•xNaCl

Prepared by the procedure described above from Ni(TMEDA)Cl$_2$ (614 mg, 2.5 mmol) and NaO^{t}Bu (480 mg, 5.0 mmol). 722 mg of precatalyst isolated.

CHN elemental analysis: Found: C, 30.31; H, 5.64; N, 0.00.

The observed C:H ratio (5.374) and the absence of N suggest that the organic part of the precatalyst should be O^{t}Bu (calculated C:H ratio is 5.296).

ICP-AES elemental analysis: found: Na, 10.96; Ni, 17.90.

The K:Ni ratio is roughly 1.6.

IR: ν (cm^{-1}) 2969, 1358, 1188, 930, 763, 619.

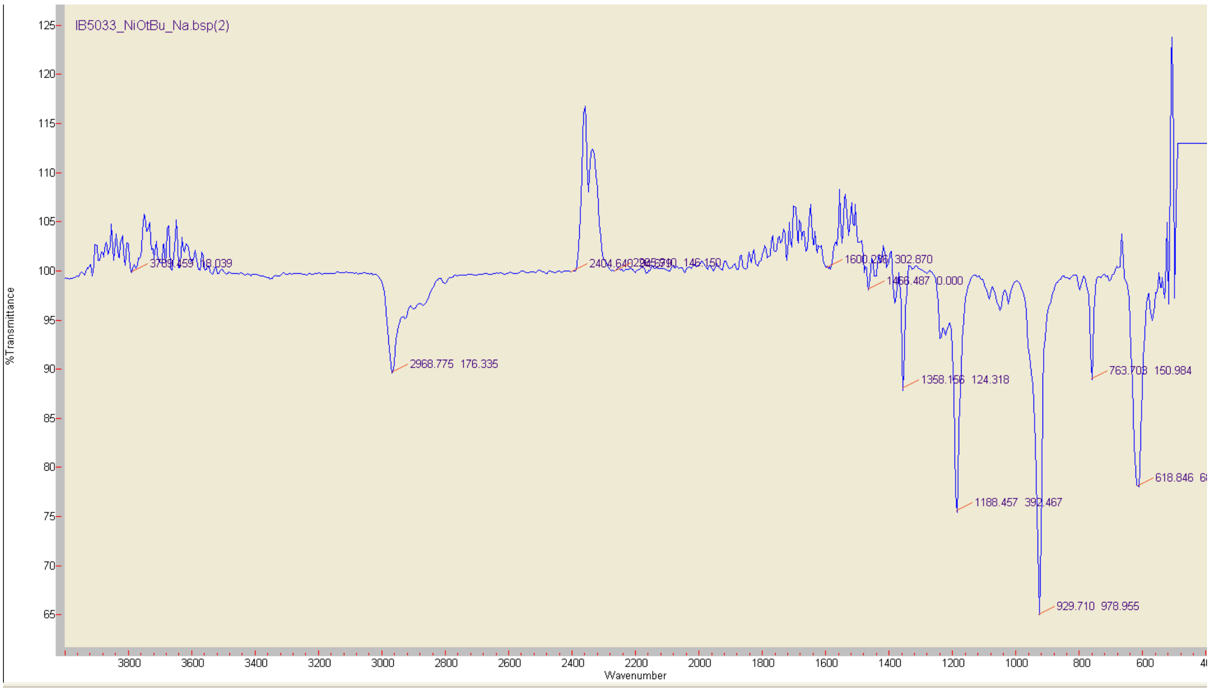


Figure S3. IR spectrum of Ni(O^{t}Bu)$_2$•xNaCl

PXRD spectra of Ni precatalysts

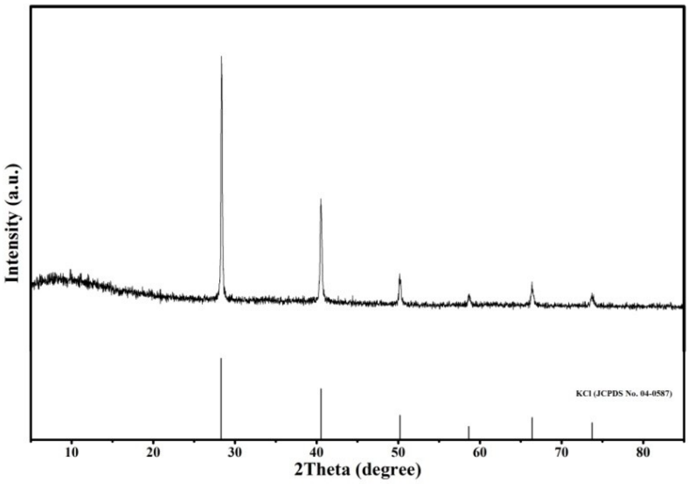


Figure S4. PXRD spectrum of Ni(O^{t}Bu)$_2$•xKCl (corresponds to sylvite (KCl))

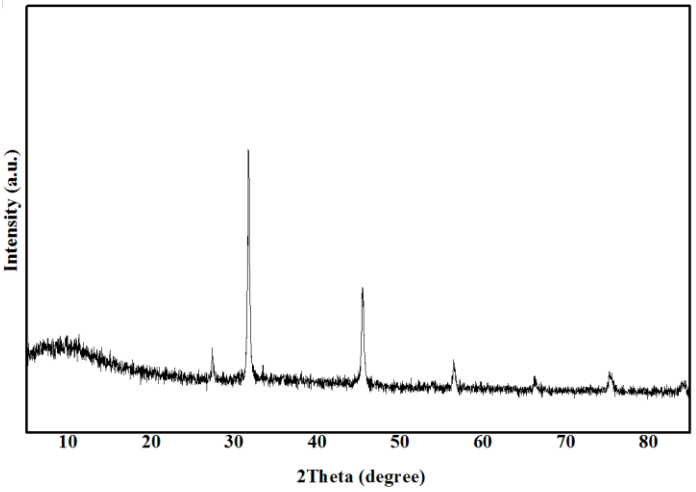


Figure S5. PXRD spectrum of Ni(O^{t}Bu)$_2$•xNaCl (corresponds to halite (NaCl))

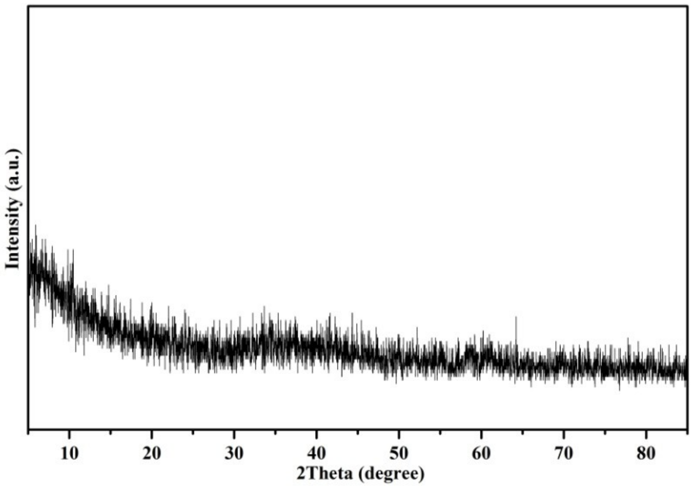
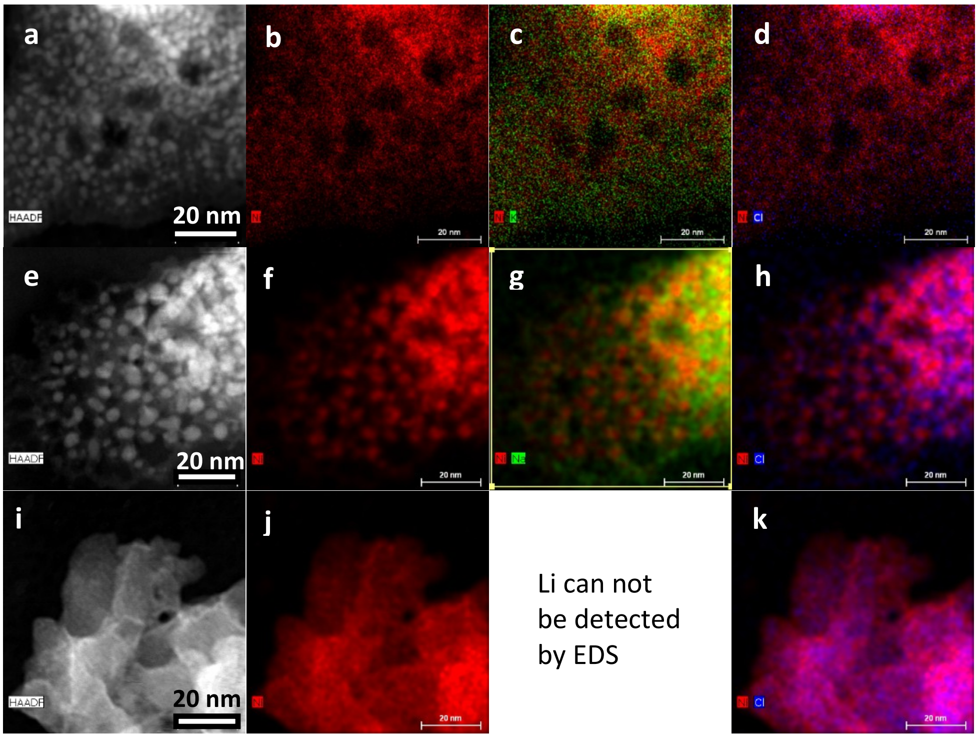


Figure S6. PXRD spectrum of Ni(O^{t}Bu)$_2$

Elemental mapping images of precatalysts

Summary: Elemental mapping analysis (based on Energy-dispersive X-ray spectroscopy-EDS) suggested that besides NaCl and KCl crystals, some Na^+/K^+ and Cl^- ions were absorbed on the $Ni(O^tBu)_2$ in both $Ni(O^tBu)_2$•xNaCl and $Ni(O^tBu)_2$•xKCl (Fig. S7).



Ni : K : Cl =
1.0 : 0.23 : 0.02

Ni : Na : Cl =
1.0 : 0.19 : 0.03

Li can not
be detected
by EDS

Ni : Li : Cl =
1.0 : / : 0.09

Figure S7. (a) HAADF image of $Ni(O^tBu)_2$•xKCl; (b) the elemental mapping image corresponding to $Ni(O^tBu)_2$•xKCl based on Ni signal; (c) combined Ni and K signals in $Ni(O^tBu)_2$•xKCl; (d) combined Ni and Cl signals in $Ni(O^tBu)_2$•xKCl; (e) HAADF image of $Ni(O^tBu)_2$•xNaCl; (f) the elemental mapping image corresponding to $Ni(O^tBu)_2$•xNaCl based on Ni signal; (g) combined Ni and Na signals in $Ni(O^tBu)_2$•xNaCl; (h) combined Ni and Cl signals in $Ni(O^tBu)_2$•xNaCl; (i) HAADF image of $Ni(O^tBu)_2$; (j) the elemental mapping image corresponding to $Ni(O^tBu)_2$ based on Ni signal; (k) combined Ni and Cl signals in $Ni(O^tBu)_2$.

TEM images of precatalysts

Summary: Transmission electron microscopy (TEM) images revealed a significant difference between the morphology of the pure $Ni(O^tBu)_2$ and the composites $Ni(O^tBu)_2$•xNaCl and $Ni(O^tBu)_2$•xKCl (Fig. S8). $Ni(O^tBu)_2$•xNaCl and $Ni(O^tBu)_2$•xKCl have a porous structure possibly due to the hard templating effect of in situ formed NaCl and KCl.[6] On the other hand, pure $Ni(O^tBu)_2$ is made of nanosheets. Interestingly, under the high-energy electron beams (accelerated voltage: 200 kV) for only less than 1 minute, well dispersed Ni nanoparticles were formed from $Ni(O^tBu)_2$•xNaCl and $Ni(O^tBu)_2$•xKCl, but not from pure $Ni(O^tBu)_2$ which stayed intact. This observation is consistent with the easier tendency of $Ni(O^tBu)_2$•xNaCl and $Ni(O^tBu)_2$•xKCl than pure $Ni(O^tBu)_2$ to form Ni nanoparticles (see main text).

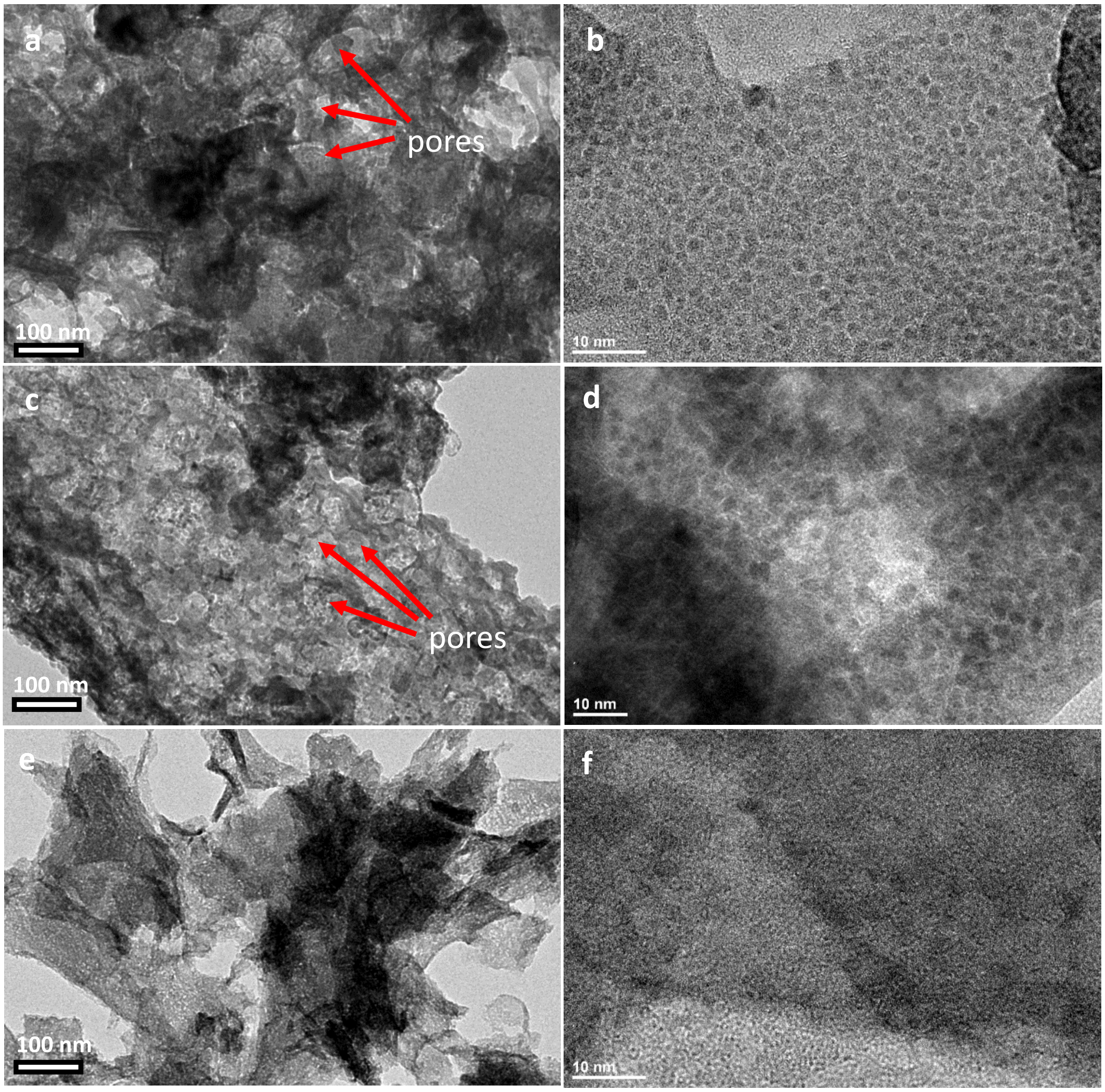


Figure S8. (a) Bright field TEM image of Ni(O^{t}Bu)$_2$•xNaCl; (b) TEM image of Ni(O^{t}Bu)$_2$•xNaCl after 30 seconds under the electron beam indicating the formation of nickel nanoparticles. (c) Bright field TEM image of Ni(O^{t}Bu)$_2$•xKCl; (d) TEM image of Ni(O^{t}Bu)$_2$•xKCl after 30 seconds under the electron beam indicating the formation of nickel nanoparticles. (e) Bright field TEM image of Ni(O^{t}Bu)$_2$. (f) TEM image of Ni(O^{t}Bu)$_2$ after 30 seconds under the electron beam indicating no formation of nickel nanoparticles.

4. General procedures for hydrosilylation reactions

Safety note: $(MeO)_3SiH$ and $(EtO)_3SiH$ may form pyrophoric gaseous SiH_4 during the storage or reaction. Although during catalysis SiH_4 was not observed, we urge the users of these procedures to be alert to the possibility of SiH_4 formation and possible exotherms and to take suitable precautions.

General procedure for the Ni-catalyzed hydrosilylation of 1-decene with various silanes (General Procedure I, Table S1)

In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with $Ni(O^tBu)_2{\bullet}xKCl$ (3.5 mg, corresponding to 1% of Ni) and 2 mL of dry THF. The suspension of precatalyst was stirred for 5 minutes. 1-Decene (140 mg, 1.0 mmol), silane (1.2 mmol) and dodecane (30 μL) were added. After 4 hours the solution was subjected to GCMS analysis. THF was removed under reduced pressure. Crude products were dissolved in hexane and filtered through a pad of silica.

General procedure for the Ni-catalyzed hydrosilylation of terminal alkenes with $(MeO)_3SiH$ (General Procedure II, Table 1)

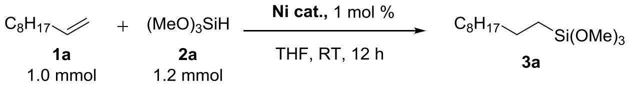
In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with $Ni(O^tBu)_2{\bullet}xKCl$ (3.5 mg, corresponding to 1% of Ni) and 2 mL of dry THF. The suspension of precatalyst was stirred for 5 minutes. Alkene (1.0 mmol) and trimethoxysilane (146 mg, 1.2 mmol) were added at room temperature. After 4 hours THF was removed under reduced pressure. The residue was purified by flash chromatography to afford the desired product.

General procedure for the Ni-catalyzed isomerizing hydrosilylation of internal alkenes with $(MeO)_3SiH$ (General Procedure III, Table 2)

In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with $Ni(O^tBu)_2{\bullet}xKCl$ (2 or 5% of Ni) and 3 mL of dry THF. The suspension of precatalyst was stirred for 5 minutes. Internal alkene (1.0 mmol) and trimethoxysilane (1.2 mmol) were added at room temperature. After 12 hours THF was removed under reduced pressure. The residue was purified by flash chromatography to afford the desired product.

5. Optimization of hydrosilylation reaction conditions

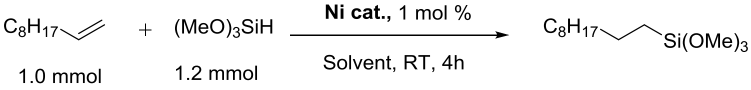
Table S1. Nickel precatalysts for 1-decene hydrosilylation with trimethoxysilane[a]



Entry	Catalyst	Yield, %[b]
1	$Ni(O^tBu)_2$•xKCl	88
2	$Ni(O^tBu)_2$•xNaCl	79
3	$Ni(O^tBu)_2$	28
4	$Ni(OMe)_2$•xKCl	65
5	$Ni(OAc)_2$	<2
6	$Ni(OTf)_2$	<1
7	$Ni(acac)_2$	23
8	$Ni(OH)_2$	0
9	$Ni(COD)_2$	5

[a] Conditions : 1-decene (1 mmol), $(MeO)_3SiH$ (1.2 mmol.), Ni cat. (1 mol %), THF (2 mL), 12 hours, RT. [b] Determined by GC-MS using dodecane as an internal standard.

Table S2. The optimization of the solvent for Ni-catalysed 1-decene hydrosilylation with $(MeO)_3SiH$[a]



Entry	Solvent	Yield, %[b]
1	THF	85
2	DMA	69
3	Dioxane	81
4	Toluene	11
5	MeCN	<5

[a] Conditions : 1-decene (1 mmol), silane (1.2 mmol.), Ni precat. (1 mol %), THF (2 mL), 4 hours, RT. [b] Determined by GC-MS using dodecane as an internal standard.

1,4-Dioxane and THF were the best solvents.

6. Evaluation of the activity of Ni(O^{t}Bu)$_2$·xKCl

In a nitrogen filled glovebox a 30 mL vial with a screw cap was charged with 1-decene (1.4 g, 10 mmol) and 3.1 mg of Ni precatalyst (0.1 mol %). The mixture was stirred for 5 minutes and (MeO)$_3$SiH (1.28 g, 10.5 mmol) was added (Caution: exotermic reaction!). The reaction was stirred at room temperature and aliquots for GCMS analysis were taken every 5 minutes (CDCl$_3$ was used as a solvent). After 30 min the GCMS yield of **3a** was 85% (TON > 850; TOF = 1700 h^{-1}).

7. Experiments for the investigation of nature of catalyst's species

Hg-test experiment

The reaction conditions were the same as in entry 1, Table 1, except that 200 equiv. Hg relative to Ni catalyst was added in the beginning of the reaction.

The use of prepared Ni nanoparticles colloid for 1-decene hydrosilylation

In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with Ni(O^{t}Bu)$_2$•xKCl (3.5 mg, corresponding to 1% of Ni) and 1 mL of dry THF. The suspension of precatalyst was stirred for 5 minutes. Trimethoxysilane (5 mg, 0.04 mmol) was added to activate the precatalyst and the mixture was allowed to stir for 10 minutes. In a separate vial 1-decene (140 mg, 1 mmol), triethoxysilane (197 mg, 1.2 mmol), dodecane (30 μL) and 1 mL of THF were placed. The solution containing the active catalyst was added to the reagents. After 4 hours 74 % of hydrosilylation product **3b** was obtained according to GC-MS.

Filtration test

The conditions of General Procedure I were reproduced using (MeO)$_3$SiH. A vial was charged with Ni(O^{t}Bu)$_2$•xKCl (3.5 mg, corresponding to 1% of Ni) and 2 mL of dry THF. 1-Decene (140 mg, 1.0 mmol), trimethoxysilane (1.2 mmol) and dodecane (30 μL) were added. After 4 minutes the conversion reached 13%, and the mixture was filtered through a pad of celite, giving a colorless solution. This solution was left stirring overnight. GCMS analysis carried out on the next day showed the same 13% of conversion.

8. TEM examination of Ni catalysts

Preparation of the samples

In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with $Ni(O^tBu)_2$•xKCl (18 mg) and 2 mL of dry THF. The suspension of precatalyst was stirred for 5 minutes. 1-Hexene (84 mg, 1.0 mmol) and trimethoxysilane (146 mg, 1.2 mmol) were added. After 10 minutes of stirring at room temperature, reaction mixture was filtered through a 0.22 μm PTFE membrane. The samples for TEM analysis were prepared by placing two drops of filtered solution on the TEM grid and drying in nitrogen-filled glovebox for 1 hour.

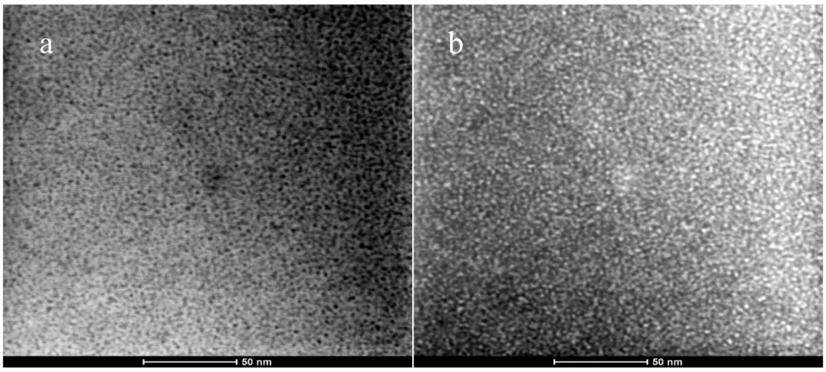


Figure S9. (a) Bright field TEM image and (b) the corresponding HAADF image of nickel nanocrystals in large area. The black dots in bright field TEM image and white dots in HAADF image are nickel nanocrystals.

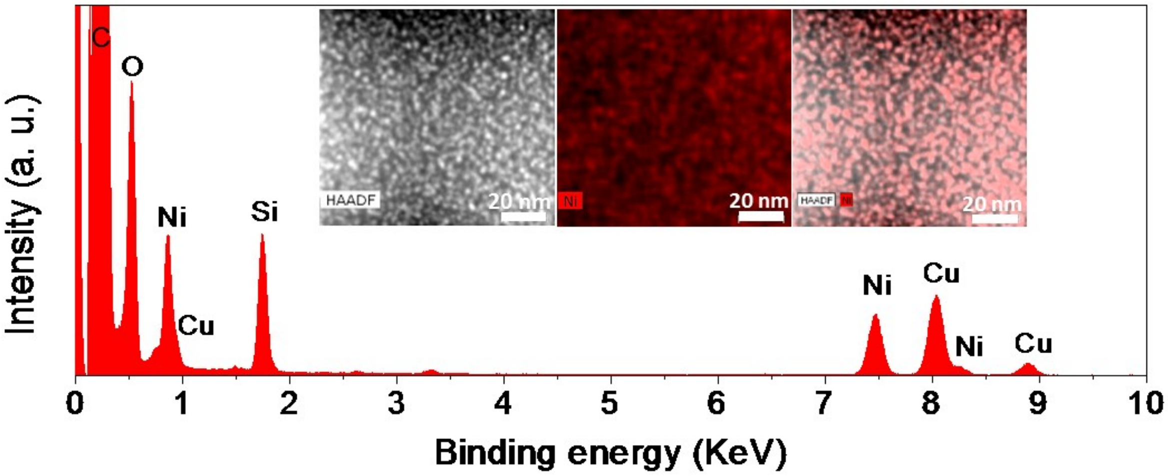


Figure S10. Elemental mapping analysis on nickel nanocrystals. The insets in the energy dispersive X-ray spectra show the HAADF image of the analyzed region, the corresponding elemental mapping image based on nickel signal, and combined HAADF and elemental mapping image based on nickel signal. The Carbon (C) and Copper (Cu) signals are from sample support (the carbon-coated copper grid) for TEM observation. The Si and O are due to $(MeO)_3SiH$ and $(MeO)_3SiO^tBu$.

Comparison of the activation of $Ni(O^tBu)_2$•xKCl and $Ni(O^tBu)_2$ under standard reaction conditions

Preparation of the samples

In a nitrogen filled glovebox, two oven-dried 30 mL re-sealable screw-cap vials equipped with Teflon coated magnetic stirring bars were charged with $Ni(O^tBu)_2$•xKCl (9 mg) and $Ni(O^tBu)_2$ (5 mg, 0.025 mmol). In each vial 1 mL of dry THF was added. The suspensions of precatalysts were stirred for 5 minutes. In each vial 1-hexene (42 mg, 0.5 mmol) and trimethoxysilane (73 mg, 0.6 mmol) were added. After 15 minutes, the first two samples for TEM were prepared. The samples for TEM analysis were prepared by placing a drop of solution on the TEM grid and drying in nitrogen-filled glovebox for 10 minutes. After 6 hours, a second pair of samples was prepared.

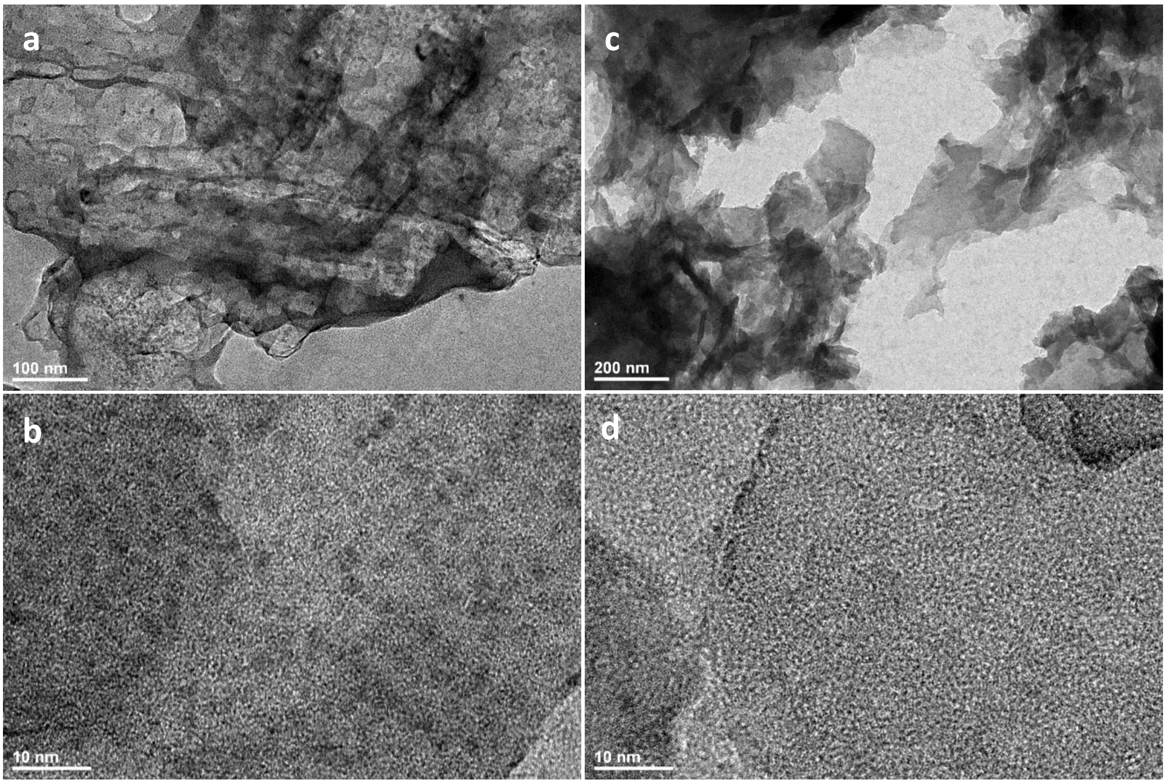


Figure S11. Comparison of bright field TEM images of reaction mixtures after 15 minutes. (a) Low-magnification image of the reaction mixture from $Ni(O^tBu)_2$•xKCl; the particles of $Ni(O^tBu)_2$•xKCl (Fig. S8c) have disappeared and the oily product is seen in the image. Small nickel particles can be found inside this oily product. (b) High-magnification images showing the presence of Ni nanoparticles formed from $Ni(O^tBu)_2$•xKCl in reaction conditions; (c) Low-magnification image of the reaction mixture from $Ni(O^tBu)_2$; the particles of $Ni(O^tBu)_2$ (Fig. S8e) remain. (d) High-magnification TEM image showing no Ni NP formed from $Ni(O^tBu)_2$.

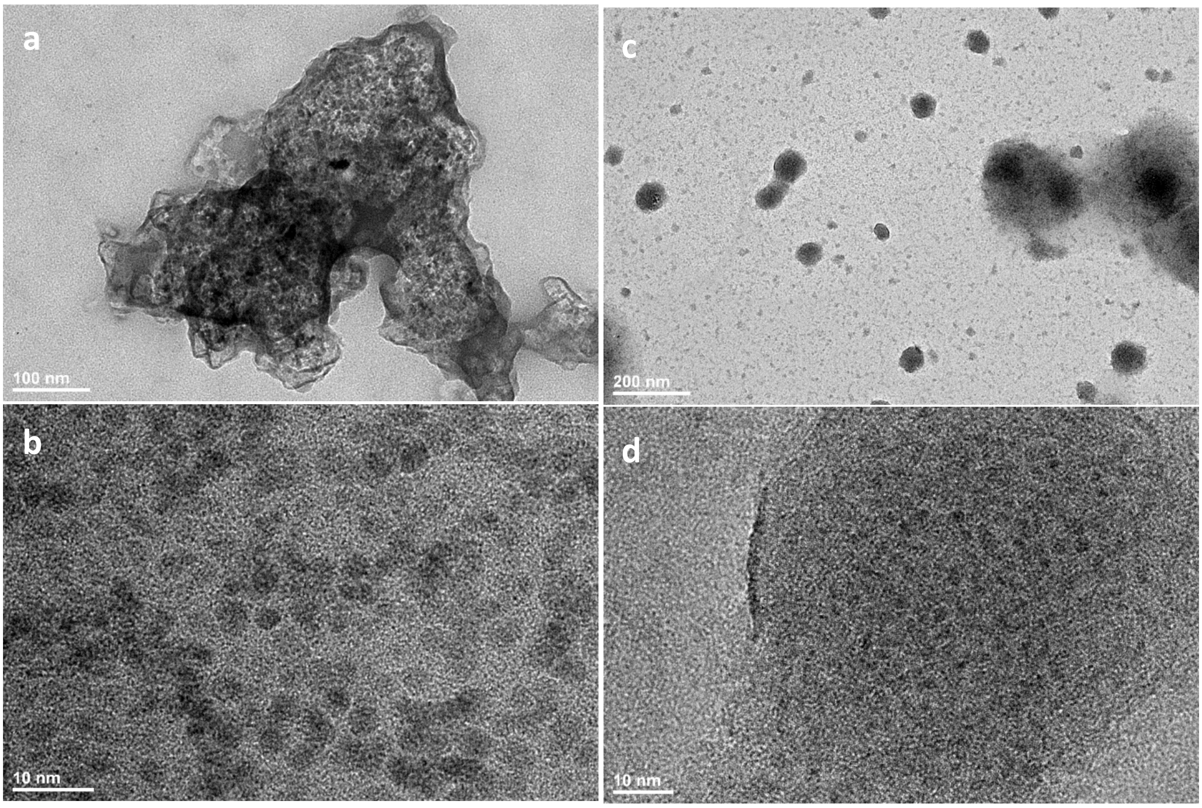


Figure S12. (a),(b) Bright field TEM images of nickel nanocrystals in large area after 6 hours of reaction with $Ni(O^tBu)_2$•xKCl precatalyst; (c), (d) Bright field TEM images of nickel particles after 6 hours of reaction with $Ni(O^tBu)_2$ precatalyst.

9. UV-Vis spectra of active Ni nanoparticles and precatalysts

The UV-Vis spectrum of a colloidal solution containing the nickel nanoparticles is similar to the spectra of other reported colloidal nickel particles (Fig. S13), [7] suggesting that no soluble nickel alkoxide species were in the solution. The catalyst solution was generated by reaction of $Ni(O^tBu)_2$•xKCl with $(MeO)_3SiH$. The UV-Vis spectra of $Ni(O^tBu)_2$•xKCl (Fig.S14) and $Ni(TMEDA)Cl_2$ (Fig. S15) were recorded. The overlay of UV-Vis spectra of solutions containing colloidal Ni and the precatalyst (Fig. S16) show that no complex is present in the colloidal solution.

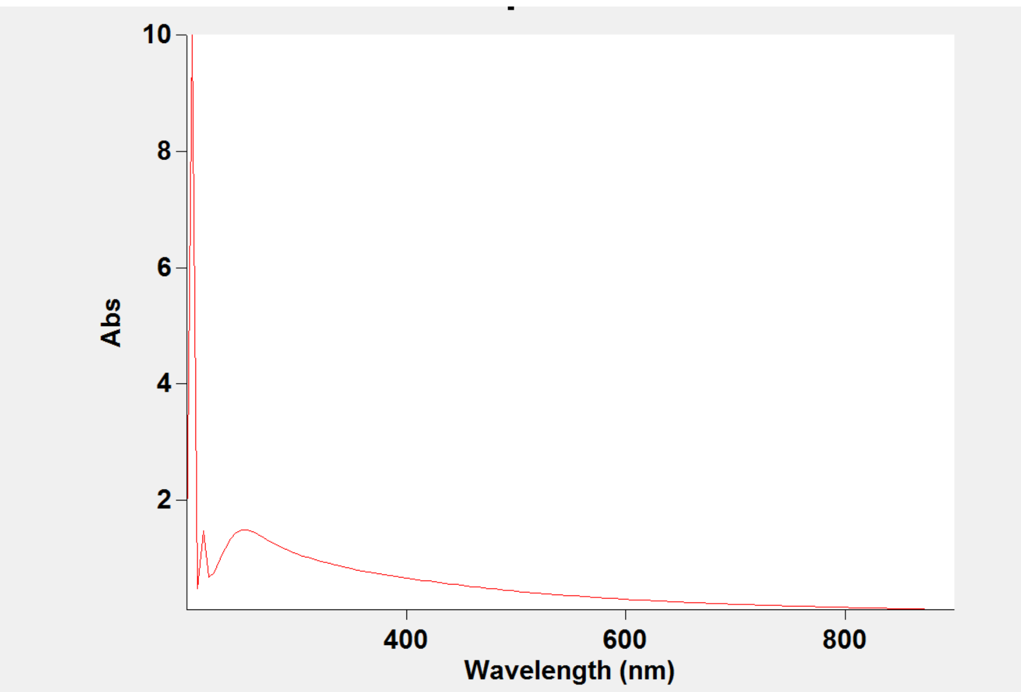


Figure S13. UV-Vis spectrum of the reaction solution mixture containing Ni nanoparticles (the same solution used for Fig.S4). The sample was diluted with THF. The spectrum is similar to the spectra of Ni colloids.[7]

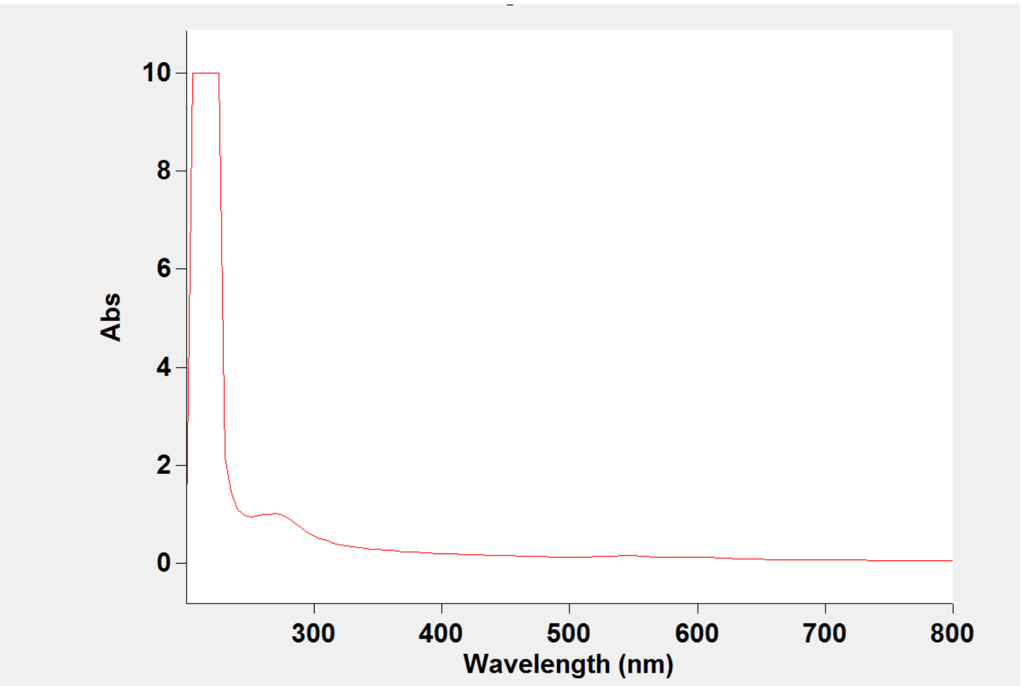


Figure S14. UV-Vis spectrum of the solution containing starting precatalyst Ni(O^{t}Bu)$_2$•xKCl.

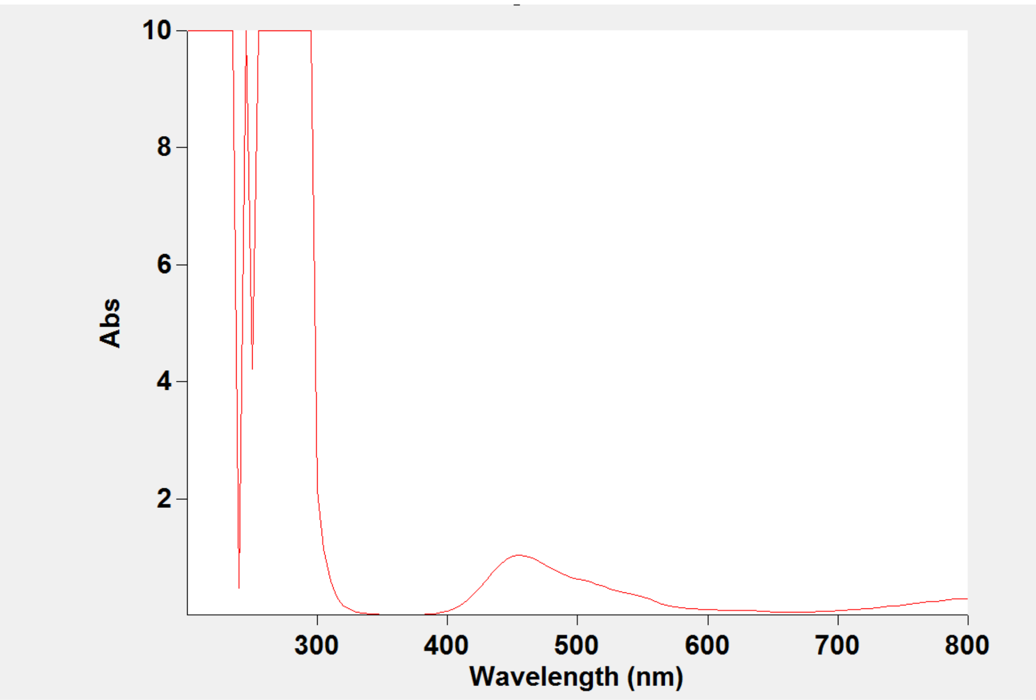


Figure S15. UV-Vis spectrum of the solution of Ni(TMEDA)Cl$_2$.

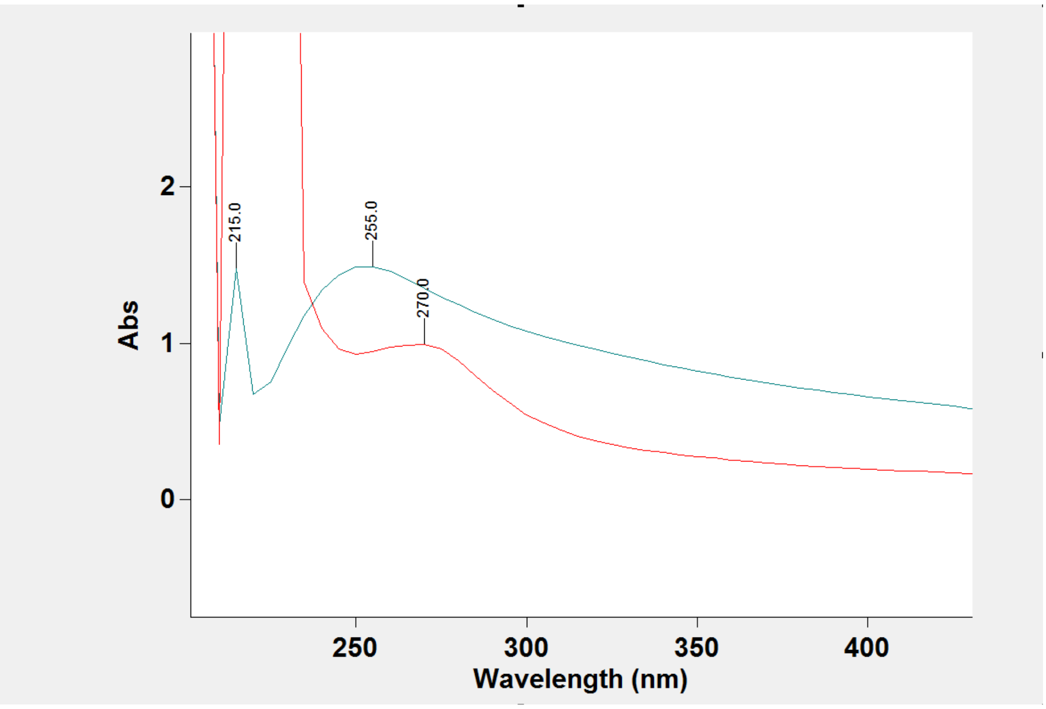


Figure S16. Overlay of UV-Vis spectra of the solutions containing Ni nanoparticles (blue) and starting precatalyst Ni(O^{t}Bu)$_2$•xKCl (red).

10. Detailed descriptions of the products

^{n}DecylSi(OMe)$_3$ (3a)

Following the general procedure I the title compound was obtained as colorless oil (225 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 9H), 1.43-1.21 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H), 0.67-0.62 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 50.6, 33.3, 32.1, 29.8, 29.7, 29.5 29.4, 22.8, 22.7, 14.3, 9.3.

HRMS (ESI): calculated for ($C_{13}H_{31}O_3Si$, M+H), 263.2043; found 263.2048.

The spectroscopic data is in agreement with previously reported.[8]

^{n}DecylSi(OEt)$_3$ (3b)

Following the general procedure I the title compound was obtained as colorless oil (267 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (q, *J* = 7.0 Hz, 6H), 1.43-1.21 (m, 25H), 0.88 (t, *J* = 6.4 Hz, 3H), 0.65-0.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 58.4, 33.3, 32.1, 29.8, 29.7, 29.5, 29.4, 22.9, 22.8, 18.4, 14.2, 10.5.

The spectroscopic data is in agreement with previously reported.[9]

^{n}DecylSi(OMe)Me$_2$ (3c)

Following the general procedure I the title compound was obtained as colorless oil (190 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) 3.42 (s, 3H), 1.37-1.22 (m, 16H), 0.88 (t, *J* = 6.2 Hz, 3H), 0.61-0.58 (m, 2H), 0.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ, 50.4, 33.6, 32.1, 29.9, 29.8, 29.5, 23.3, 22.9, 16.1, 14.3, -2.5.

Elemental analysis: Anal. Calcd for $C_{13}H_{30}OSi$: C, 67.75; H, 13.12; found : C, 67.82 ; H, 12.99.

^{n}DecylSi(OEt)$_2$Me (3d)

Following the general procedure I the title compound was obtained as colorless oil (211 mg, 77 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (q, *J* = 7.0 Hz, 4H), 1.38-1.19 (m, 22H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.63-0.59 (m, 2H), 0.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 58.1, 33.5, 32.1 29.8, 29.7, 29.5, 29.5, 23.0, 22.8, 18.5, 14.2, 14.0, -4.8.

Elemental analysis: Anal. Calcd for $C_{15}H_{34}O_2Si$: C, 65.63; H, 12.48; found : C, 65.73 ; H, 12.41.

^{n}Decyl-Si(Me)$_2$-OSiMe$_3$ (3e)

In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with Ni(O^{t}Bu)$_2$•xKCl (18 mg) and 1-decene (700 mg, 5 mmol). The suspension of precatalyst was stirred for 5 minutes. PMDS (890 mg, 6 mmol) and $(MeO)_3SiH$ (12 mg for activation of Ni catalyst) were added and mixture was stirred for 2 hours at 60°C. After filtration in hexane through a pad of silica the title compound was obtained as colorless oil (750 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32-1.23 (m, 16H), 0.88 (t, J = 7.0 Hz, 3H), 0.52-0.48 (m, 2H), 0.06 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 33.6, 32.1, 29.9, 29.8, 29.6, 29.5, 23.5, 22.9, 18.6, 14.3, 2.14, 0.5.

HRMS (ESI): calculated for ($C_{15}H_{34}O_3SiAg$, M+Ag), 393.1199; found 393.1196.

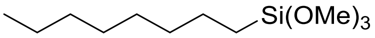
^{n}DecylSiPh$_3$ (3h)

Following the general procedure I the title compound was obtained as a white solid (176 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 6H), 7.37-7.33 (m, 9H), 1.50-1.42 (m, 2H), 1.37-1.18 (m,16H), 0.87 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 135.6, 129.4, 128.0, 34.0, 32.1, 29.8, 29.7, 29.5, 29.3, 24.1, 22.8, 14.3, 13.4.

Elemental analysis: Anal. Calcd for $C_{28}H_{36}Si$: C, 83.93; H, 9.06; found : C, 89.98 ; H, 8.99.



Trimethoxy(octyl)silane (4a)

Following the general procedure II the title compound was obtained as colorless oil (208 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (s, 9H), 1.45-1.37 (m, 2H), 1.34-1.26 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H), 0.66-0.63 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 50.5, 33.3, 32.0, 29.4, 29.3, 22.8, 22.7, 14.2, 9.3.

Spectroscopic data is in agreement with published[10]

$^{n}C_{18}H_{37}\text{-}Si(OMe)_3$

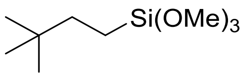
Trimethoxy(octadecyl)silane (4b)

Following the general procedure II the title compound was obtained as colorless oil (315 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (s, 9H), 1.45-1.20 (m, 32H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.66-0.62 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 50.9, 33.6, 32.4, 30.2, 30.0, 29.9, 29.8, 23.2, 23.1, 14.6, 9.6.

HRMS (ESI): calculated for ($C_{21}H_{47}O_3Si$, M+H), 375.3294; found 375.3294.



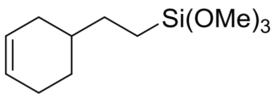
(3,3-Dimethylbutyl)trimethoxysilane (4c)

Following the general procedure II the title compound was obtained as colorless oil (160 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (s, 9H), 1.32-1.26 (m, 2H). 0.86 (s, 9H), 0.62-0.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 50.6, 36.4, 31.0, 28.6, 3.6.

HRMS (ESI): calculated for ($C_9H_{22}O_3SiNa$, M+Na), 229.1236; found 229.1242.



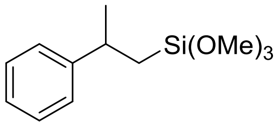
(2-(Cyclohex-3-en-1-yl)ethyl)trimethoxysilane (4d)

Following the general procedure II the title compound was obtained as colorless oil (145 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (m, 2H), 3.56 (s, 9H), 2.13-2.02 (m, 3H), 1.76-1.71 (m, 1H), 1.64-1.58 (m, 1H), 1.50-1.33 (m, 3H), 1.21-1.12 (m, 1H), 0.68-0.64 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 127.1, 126.6, 50.6, 36.3, 31.6, 29.3, 28.5, 25.4, 6.4.

HRMS (APCI): calculated for ($C_{11}H_{23}O_3Si$, M+H), 231.1416; found 231.1413.



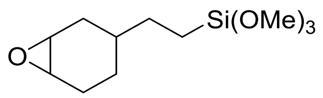
Trimethoxy(2-phenylpropyl)silane (4e)

Following the general procedure II the title compound was obtained as colorless oil (133 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.14 (m, 5H), 3.47 (s, 9H), 3.03-2.97 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.10-0.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 128.4, 126.6, 126.0, 50.5, 34.9, 25.2, 19.5.

HRMS (ESI): calculated for ($C_{12}H_{20}O_3SiNa$, M+Na), 263.1079; found 263.1083.



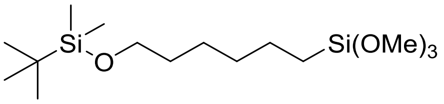
(2-(7-Oxabicyclo[4.1.0]heptan-3-yl)ethyl)trimethoxysilane (mixture of 2 diastereomers) (4f)

Following the general procedure II using $(MeO)_3SiH$ (183 mg, 1.5 mmol) the title compound was obtained as colorless oil (182 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 9H), 3.20-3.13 (m, 2H), 2.22-2.14 (m, 1H), 2.11-1.97 (m, 1H), 1.87-1.67 (m, 1H), 1.55-1.06 (m, 5H), 0.94-0.84 (m, 1H), 0.64-0.59 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 53.4, 52.9, 52.1, 52.0, 50.7, 35.4, 32.4, 31.5, 30.4, 29.5, 29.0, 26.9, 25.5, 24.0, 23.7, 6.4, 6.3.

HRMS (ESI): calculated for ($C_{11}H_{22}O_4SiNa$, M+Na), 269.1185; found 269.1188.



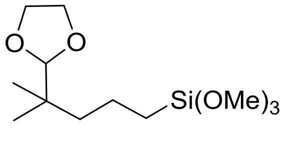
O-tert-butyldimethylsilyl 6-(trimethoxysilyl)hexan-1-ol (4g)

Following the general procedure II the title compound was obtained as a colorless oil (310 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61-3.56 (m, 11H), 1.52-1.47 (m, 2H), 1.44-1.30 (m, 6H), 0.89 (s, 9H), 0.67-0.63 (m, 2H), 0.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 63.4, 50.6, 33.0, 32.9, 25.6, 22.7, 18.5, 9.2, -5.2.

HRMS (ESI): calculated for ($C_{15}H_{37}O_4Si$, M+H), 337.2230; found 337.2223.



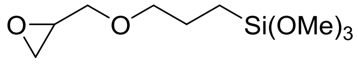
(4-(1,3-Dioxolan-2-yl)-4-methylpentyl)trimethoxysilane (4h)

Following the general procedure II the title compound was obtained as a colorless oil (263 mg, 95%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 4.53 (s, 1H), 3.94-3.82 (m, 4H), 3.57 (s, 9H), 1.43-1.32 (m, 4H), 0.88 (s, 6H), 0.64-0.60 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 110.1, 65.3, 50.6, 41.7, 37.3, 21.5, 16.9, 10.3.

HRMS (ESI): calculated for ($C_{12}H_{27}O_5Si$, M+H), 279.1628 found 279.1622.



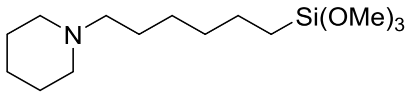
Trimethoxy(3-(oxiran-2-ylmethoxy)propyl)silane (4i)

Following the general procedure II the title compound was obtained as a colorless oil (145 mg, 61%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.71 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.61-3.59 (m, 1H), 3.57(s, 9H), 3.50-3.46 (m, 2H), 3.42-3.37 (m, 1H), 2.80-2.78 (m, 1H), 2.62-2.60 (m, 1H), 1.74-1.67 (m, 2H), 0.70-0.66 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 73.6, 71.5, 50.9, 50.6, 44.4, 22.9, 5.3.

HRMS (ESI): calculated for ($C_{19}H_{20}O_5SiNa$, M+Na), 259.0978 found 259.0984.



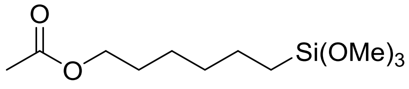
1-(6-(Trimethoxysilyl)hexyl)piperidine (4j)

Following the general procedure II the title compound was obtained as a yellow oil (260 mg, 90%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.57 (s, 9H), 2.40-2.31 (br, 4H), 2.28-2.24 (m, 2H), 1.61-1.55 (m, 4H), 1.50-1.28 (m, 10H), 0.66-0.62 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 59.8, 54.8, 50.5, 33.2, 27.5, 27.0, 26.1, 24.6, 22.6, 9.2.

HRMS (ESI): calculated for ($C_{14}H_{32}NO_3Si$, M+H), 290.2151; found 290.2150.



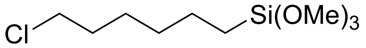
6-(Trimethoxysilyl)hexyl acetate (4k)

Following the general procedure II the title compound was obtained as a colorless oil (176 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.8 Hz, 2H), 3.57 (s, 9H), 2.04 (s, 3H), 1.65-1.60 (m, 2H), 1.45-1.34 (m, 6H), 0.67-0.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 64.7, 50.6, 32.8, 28.6, 25.7, 22.6, 21.1, 9.2.

HRMS (ESI): calculated for ($C_{11}H_{24}O_5SiNa$, M+Na), 287.1291; found 287.1297.



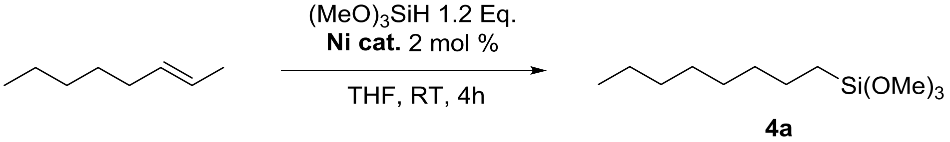
(6-Chlorohexyl)trimethoxysilane (4l)

Following the general procedure II using $(MeO)_3SiH$ (183 mg, 1.5 mmol) the title compound was obtained as a colorless oil (140 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (s, 9H), 3.53 (t, *J* = 6.7 Hz, 2H), 1.80-1.74 (m, 2H), 1.48-1.33 (m, 6H), 0.67-0.63 (m, 2H).

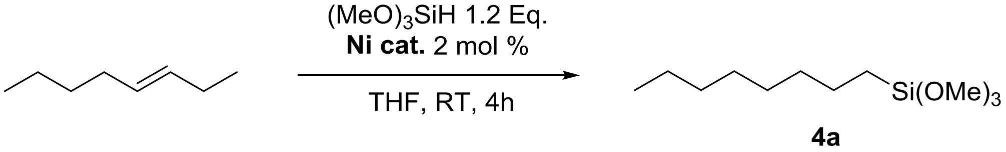
^{13}C NMR (101 MHz, $CDCl_3$) δ 50.6, 45.2, 32.6, 32.4, 26.6, 22.6, 9.2.

HRMS (ESI): calculated for ($C_9H_{22}ClO_3Si$, M+H), 241.1027; found 241.1023.



Trimethoxy(octyl)silane (4a) obtained from trans-2-octene

Following the general procedure III, the title compound was prepared using trans-2-octene (112 mg), trimethoxysilane (146 mg) and $Ni(O^tBu)_2$•xKCl (7 mg). The crude product was filtered through a pad of silica to afford the title compound as colorless oil (223 mg, 95%). Spectroscopic data were identical to those reported for the same compound above.

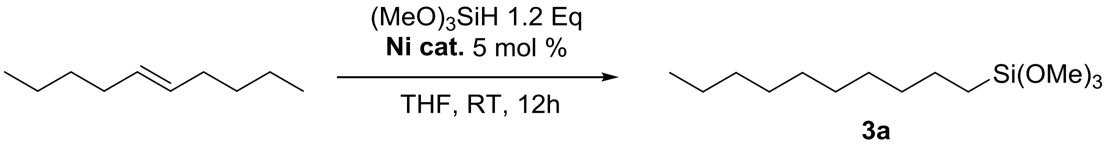


Trimethoxy(octyl)silane (4a) obtained from trans-3-octene

Following the general procedure III, the title compound was prepared using trans-3-octene (112 mg), trimethoxysilane (146 mg) and $Ni(O^tBu)_2$•xKCl (7 mg). The crude product was filtered through a pad of silica to afford the title compound as colorless oil (226 mg, 97%). Spectroscopic data were identical to those reported for the same compound above.

Trimethoxy(octyl)silane (4a) obtained from trans-4-octene

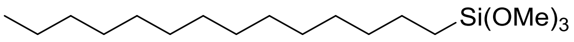
Following the general procedure III, the title compound was prepared using trans-4-octene (112 mg), trimethoxysilane (146 mg) and Ni(O^{t}Bu)$_2$•xKCl (18 mg). The crude product was filtered through a pad of silica to afford the title compound as colorless oil (207 mg, 89%). Spectroscopic data were identical to those reported for the same compound above.



3a

Decyltrimethoxysilane (3a) obtained from trans-5-decene

Following the general procedure III, the title compound was prepared using trans-5-decene (140 mg), trimethoxysilane (146 mg) and Ni(O^{t}Bu)$_2$•xKCl (18 mg). The crude product was filtered through a pad of silica to afford the title compound as colorless oil (218 mg, 83%). Spectroscopic data were identical to those reported for the same compound above.



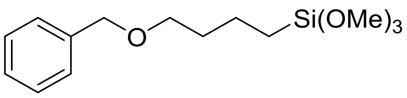
Trimethoxy(tetradecyl)silane (5a)

Following the general procedure III, the title compound was prepared using trans-7-tetradecene (196 mg), trimetoxysilane (146 mg) and Ni(O^{t}Bu)$_2$•xKCl (18 mg). The crude product was purified by flash column chromatography using hexane as an eluent to afford the title compound as colorless oil (225 mg, 71%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.57 (s, 9H), 1.45-1.37 (m, 2H), 1.34-1.22 (m, 22H), 0.88 (t, *J* = 6.7 Hz, 3H), 0.67-0.63 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 50.6, 33.3, 32.1, 29.9, 29.8, 29.7, 29.5, 29.4, 22.8, 22.7, 14.3, 9.3.

HRMS (ESI): calculated for ($C_{17}H_{39}O_3Si$, M+H), 319.2668; found 319.2661.



(4-(Benzyloxy)butyl)trimethoxysilane (5b)

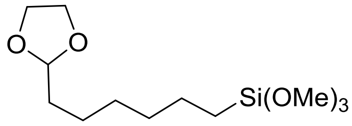
Following the general procedure III, the title compound was prepared using (E)-((but-2-en-1-yloxy)methyl)benzene (162 mg), trimethoxysilane (146 mg) and Ni(O^{t}Bu)$_2$•xKCl (7 mg).

The crude product was purified by flash column chromatography using hexane as an eluent to afford the title compound as colorless oil (210 mg, 74%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35-7.23 (m, 5H), 4.49 (s, 2H), 3.56 (s, 9H), 3.47 (t, *J* = 7.8 Hz, 2H), 1.70-1.63 (m, 2H), 1.54-1.45 (m, 2H), 0.68-0.64 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 138.8, 128.5, 127.7, 127.6, 73.0, 70.1, 50.6, 33.1, 19.5, 9.1.

HRMS (ESI): calculated for ($C_{14}H_{24}O_4SiNa$, M+Na), 307.1342; found 307.1343.



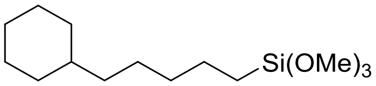
(6-(1,3-Dioxolan-2-yl)hexyl)trimethoxysilane (5c)

Following the general procedure III, the title compound was prepared using (Z)-2-(hex-3-en-1-yl)-1,3-dioxolane (156 mg), trimethoxysilane (146 mg) and Ni(O^{t}Bu)$_2$•xKCl (18 mg). The crude product was purified by flash column chromatography using mixture hexane/EtOAc (20:1) as an eluent to afford the title compound as colorless oil (220 mg, 79%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 4.84 (t, *J* = 4.8 Hz, 1H), 3.96-3.94 (m, 2H), 3.86-3.84 (m, 2H), 3.56 (s, 9H), 1.67-1.62 (m, 2H), 1.43-1.31 (m, 8H), 0.66-0.62 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 104.7, 64.9, 50.5, 34.0, 33.1, 29.3, 24.0, 22.6, 9.2.

HRMS (ESI): calculated for ($C_{12}H_{26}O_5SiNa$, M+Na), 301.1447; found 301.1448.



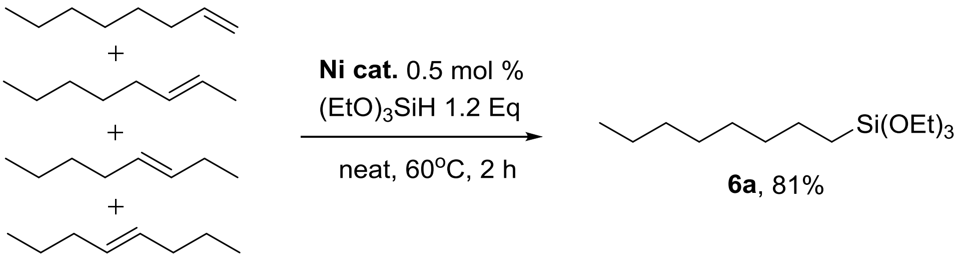
(5-Cyclohexylpentyl)trimethoxysilane (5d)

Following the general procedure III, the title compound was prepared using (E)-pent-1-en-1-ylcyclohexane (152 mg), trimethoxysilane (146 mg) and Ni(O^{t}Bu)$_2$•xKCl (18 mg). The crude product was purified by flash column chromatography using hexane as an eluent to afford the title compound as colorless oil (190 mg, 69%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.57 (s, 9H), 1.72-1.62 (m, 2H), 1.43-1.11 (m, 12H), 0.90-0.81 (m, 2H), 0.66-0.62 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 50.6, 37.8, 37.5, 33.6 (2C), 26.9, 26.6 (2C), 22.8, 9.3.

HRMS (ESI): calculated for ($C_{14}H_{31}O_3Si$, M+H), 275.2043; found 275.2041.



6a, 81%

Triethoxy(octyl)silane (6a)

Mixture of octenes was prepared from 1-octene (112 mg, 1 mmol), 2-octene (112 mg, 1 mmol), 3-octene (112 mg, 1 mmol), and 4-octene (112 mg, 1 mmol). In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with Ni precatalyst $Ni(O^tBu)_2$•xKCl (7 mg, corresponding to approx. 0.5 % of Ni) and mixture of octenes (448 mg). The suspension of precatalyst was stirred for 5 minutes. Triethoxysilane (787 mg, 4.8 mmol) was added and reaction mixture was allowed to stir for 2 hours at 60˚C. Then THF was removed under reduced pressure. The residue was filtered through silica pad to afford the desired product (892 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (q, *J* = 7.0 Hz, 6H), 1.42-1.21 (m, 21H), 0.88 (t, *J*= 6.9 Hz, 3H), 0.65-0.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 58.4, 33.4, 32.1, 29.4, 22.9, 22.8, 18.5, 14.3, 10.5.

These spectroscopic data is in agreement with previously reported[11].

HS:DHS ratio and terminal selectivity were determined by GC-MS analysis.

23,23-diethoxy-2,2,3,3-tetramethyl-4,24-dioxa-3,23-disilahexacosane (6b)

In a nitrogen filled glovebox, an oven-dried 30 mL re-sealable screw-cap vial equipped with a Teflon coated magnetic stirring bar was charged with Ni precatalyst $Ni(O^tBu)_2$•xKCl (18 mg, corresponding to 10 % of Ni) and 2 mL of dry THF. The suspension of precatalyst was stirred for 5 minutes. TBS-protected oleyl alcohol (obtained from 85% pure oleyl alcohol, 369314 Aldrich) (192 mg, 0.5 mmol) and triethoxysilane (164 mg, 1.0 mmol) were added and reaction mixture was allowed to stir for 24 hours at 0˚C. Then THF was removed under reduced pressure. The residue was purified by flash chromatography to afford the desired product as a colorless oil (123 mg, 45%). HS:DHS ratio and terminal selectivity were determined by GC-MS analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (q, *J* = 7.0 Hz, 6H), 3.60 (t, *J* = 6.6 Hz, 2H), 1.54-1.47 (m, 2H), 1.43-1.37 (m, 2H), 1.31-1.20 (m, 37H), 0.89 (s, 9H), 0.65-0.61 (m, 2H), 0.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 63.5, 58.4, 33.4, 33.1, 29.9, 29.81, 29.78, 29.7, 29.6, 29.4, 26.1, 26.0, 22.9, 18.5, 10.5, -5.1.

HRMS (ESI): calculated for ($C_{30}H_{67}O_4Si_2$, M+H), 547.4578; found 547.4587.

11. References

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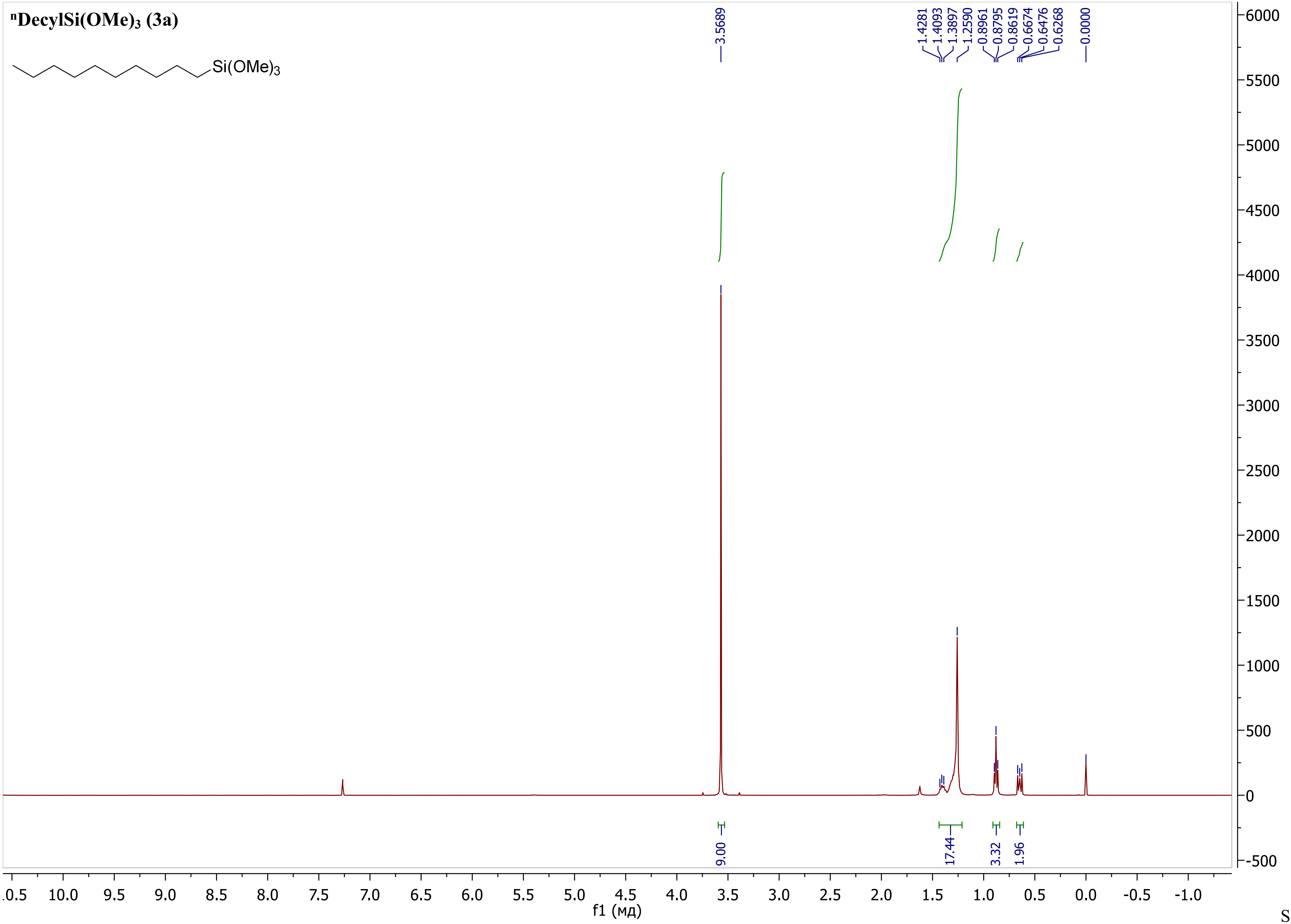
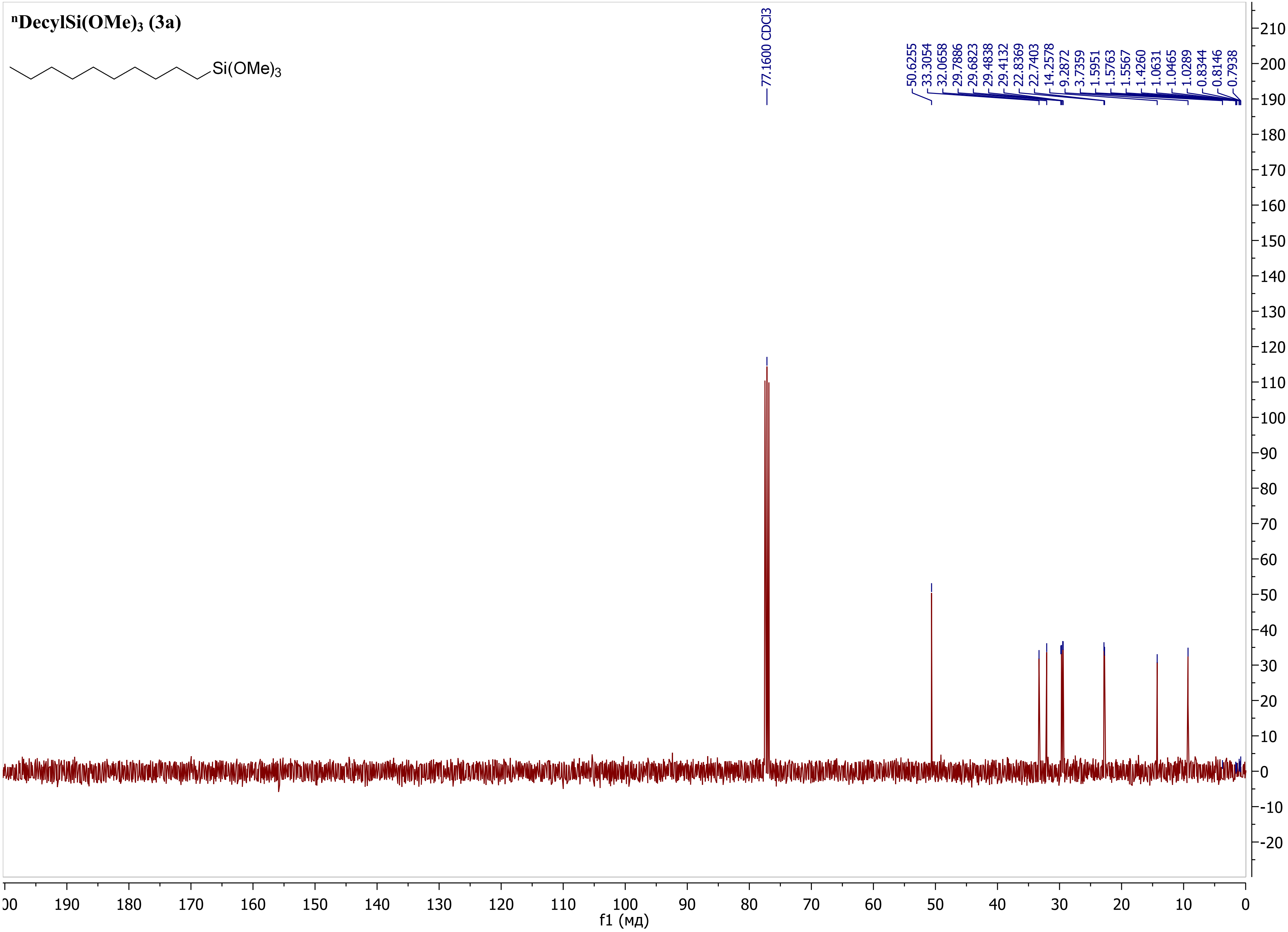
^{n}DecylSi(OMe)$_3$ (3a)



ⁿDecylSi(OMe)₃ (3a)



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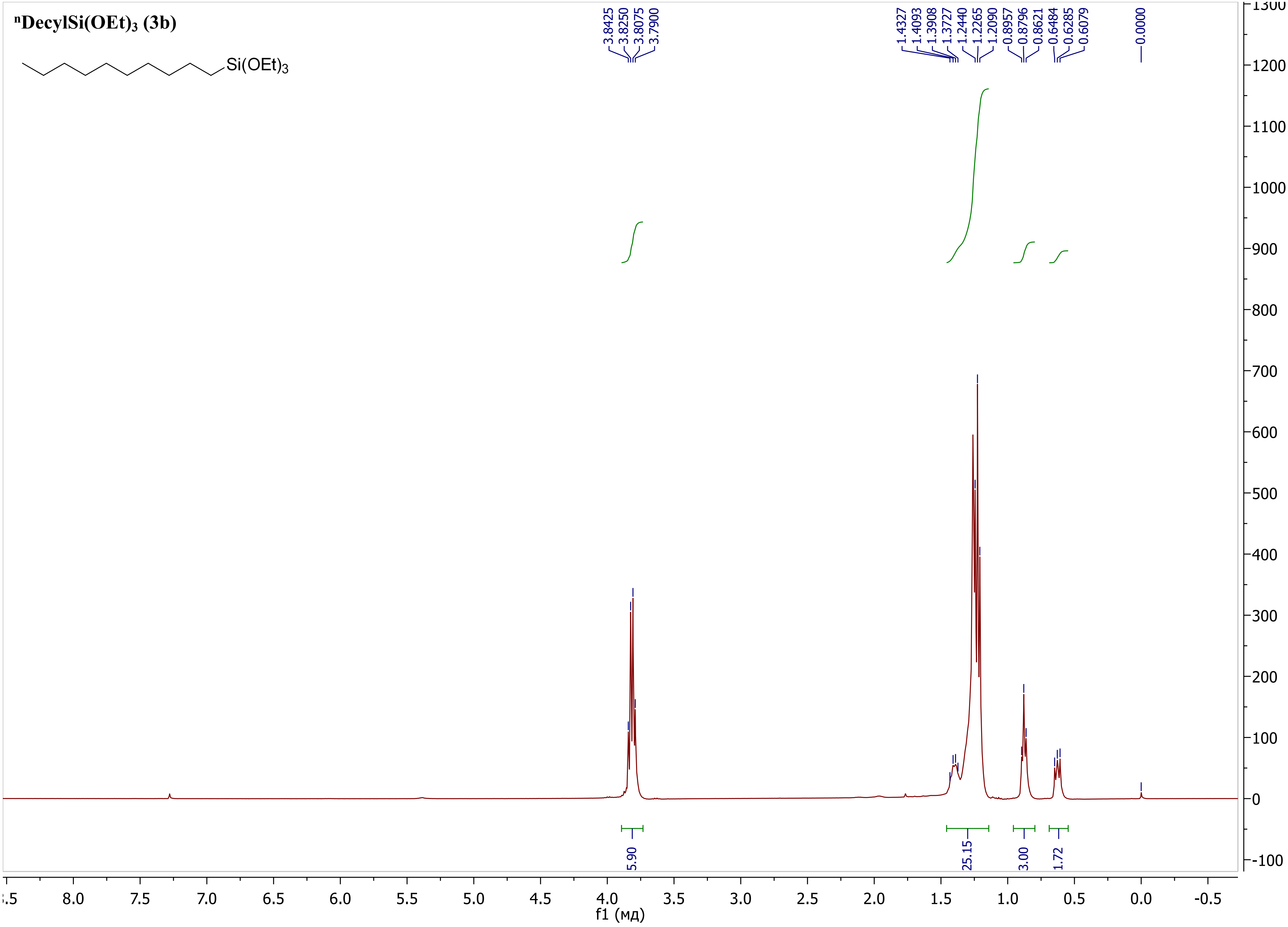

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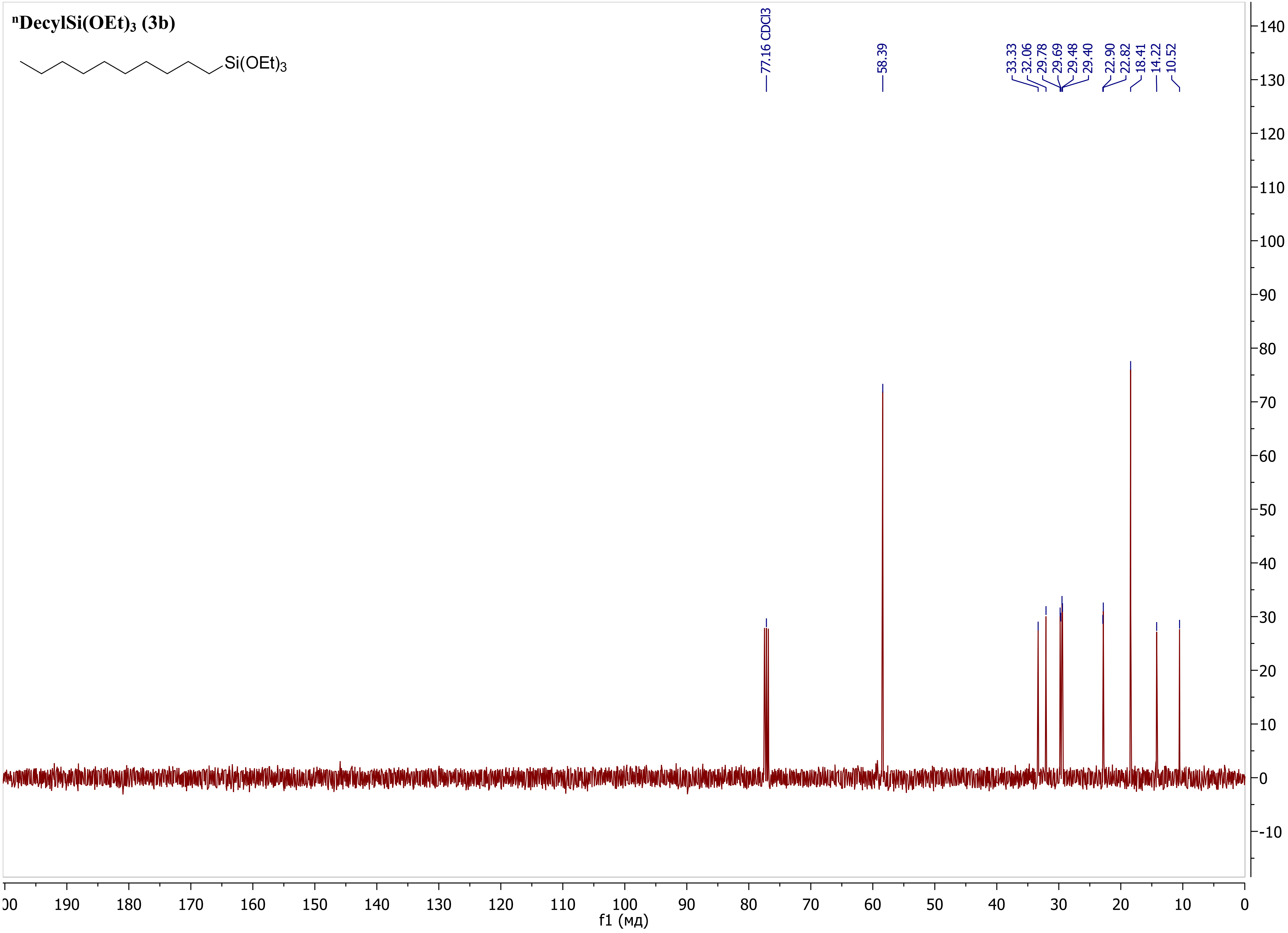
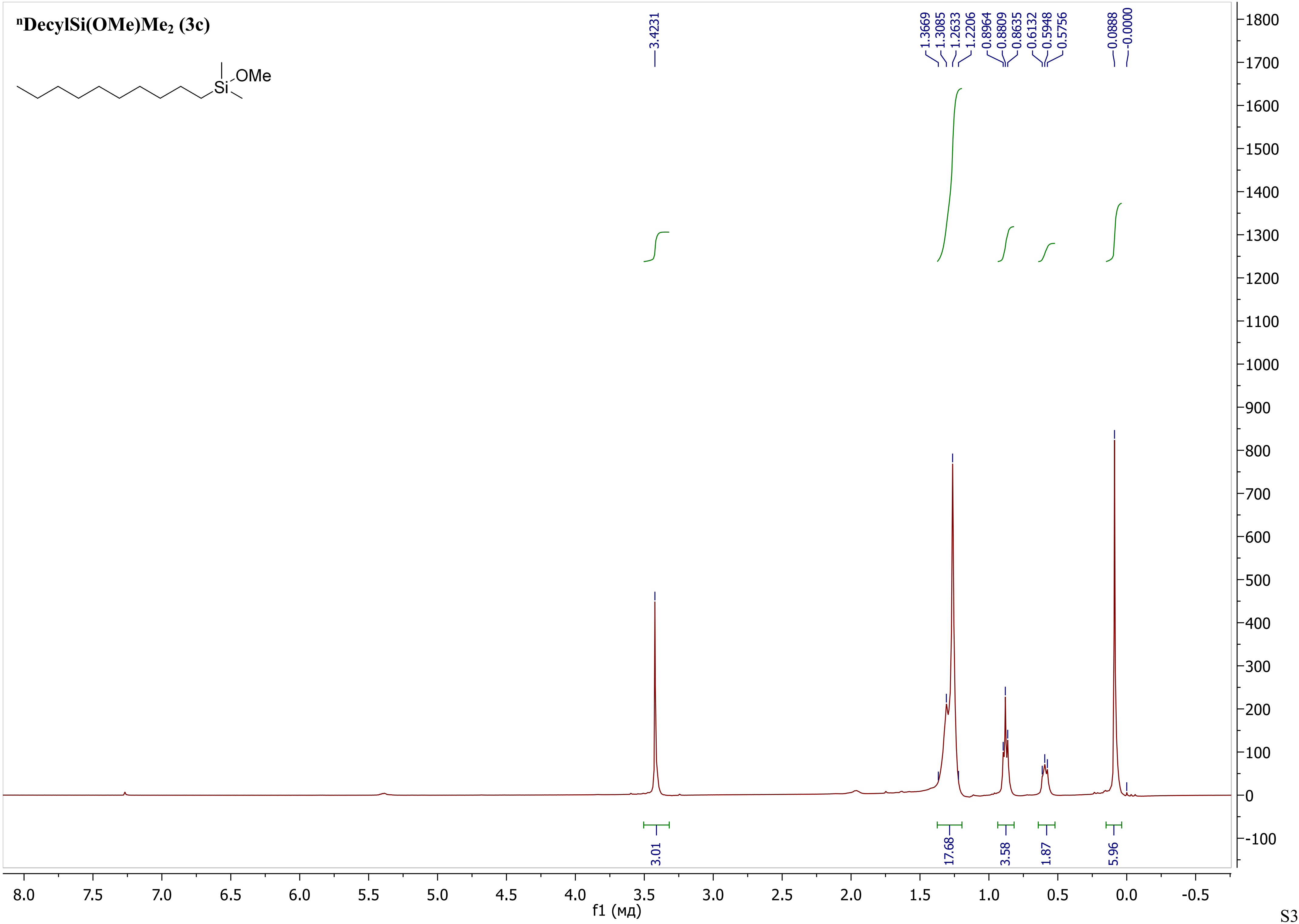


^{n}DecylSi(OMe)Me$_2$ (3c)



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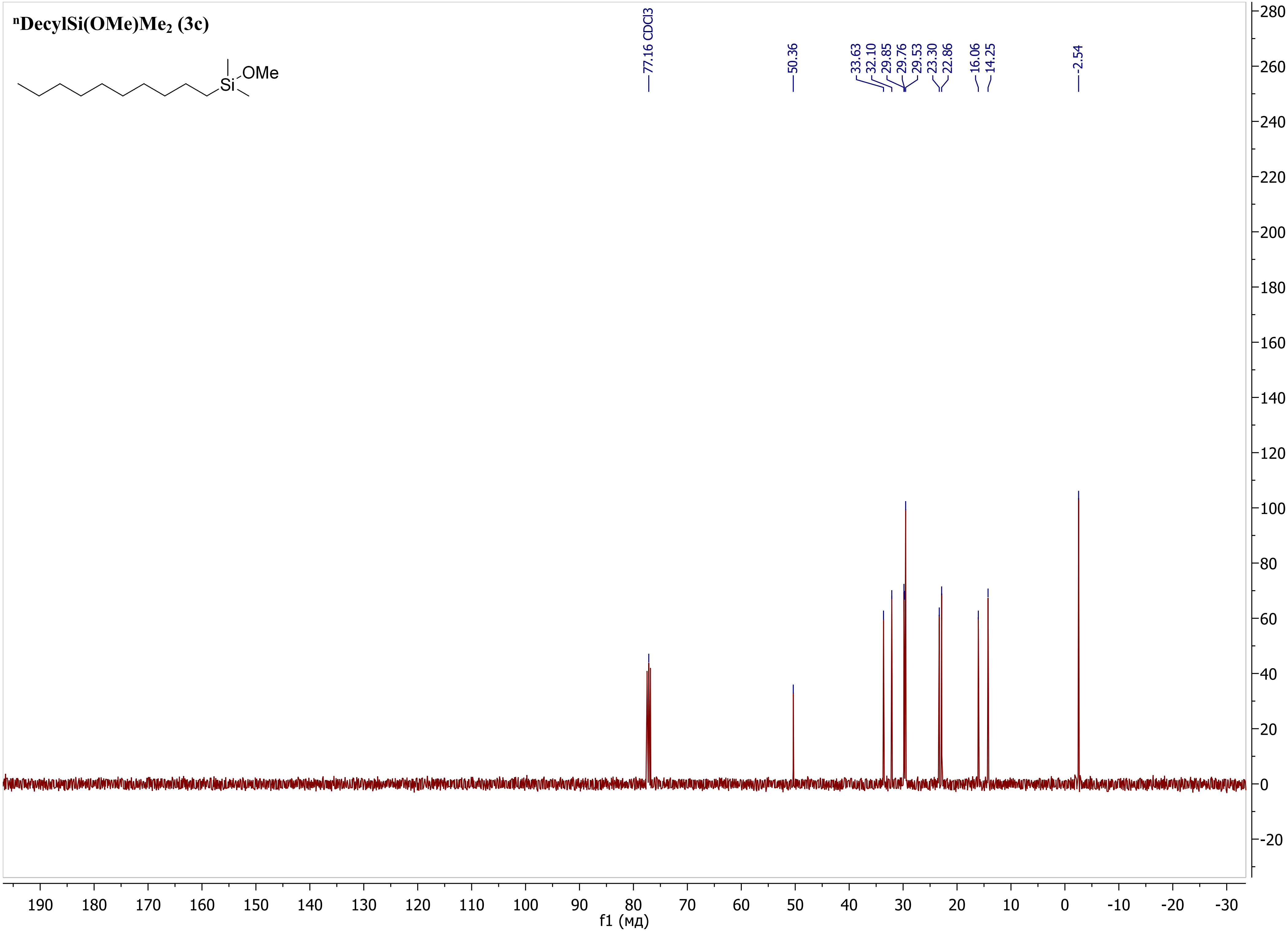

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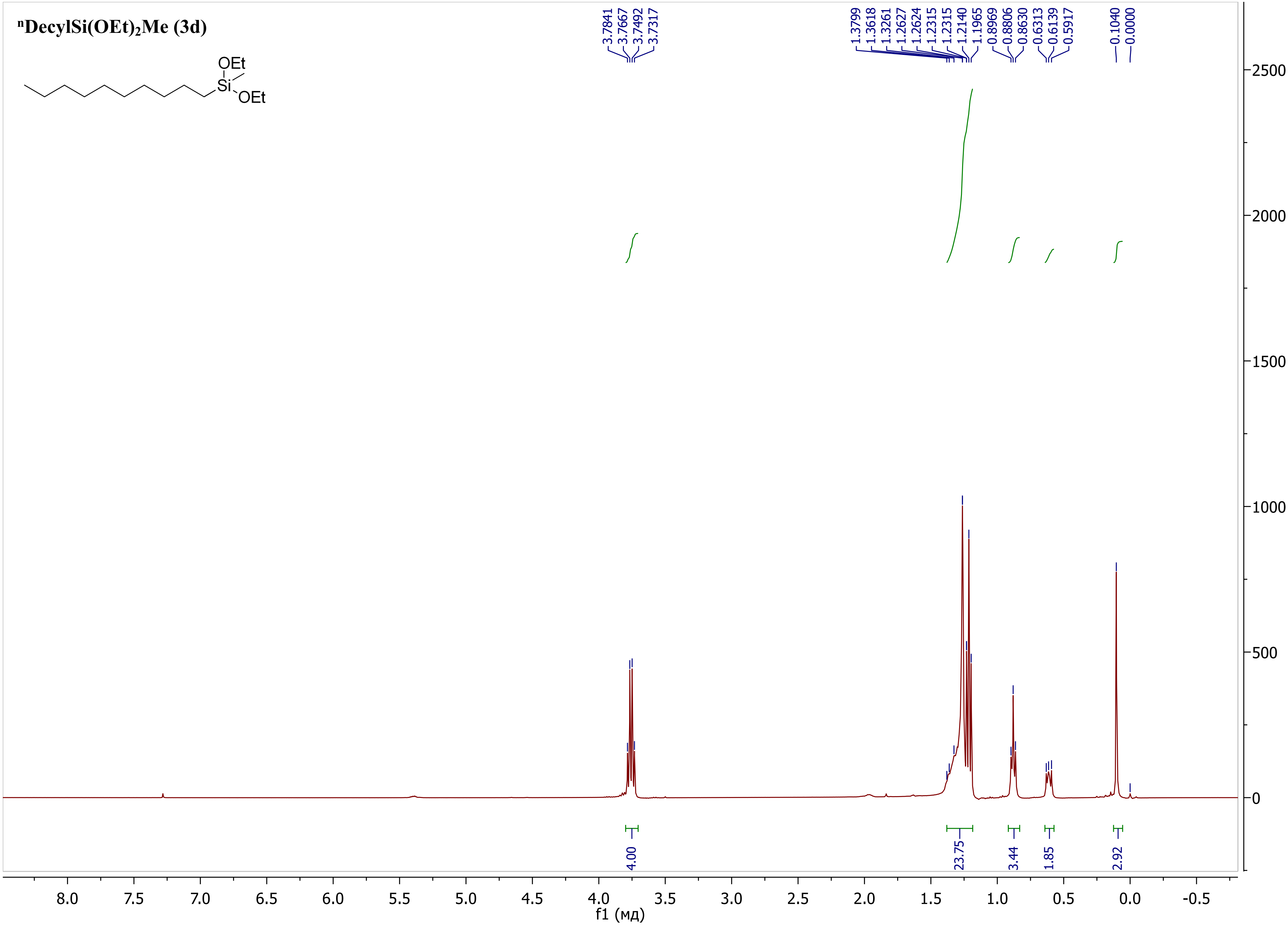

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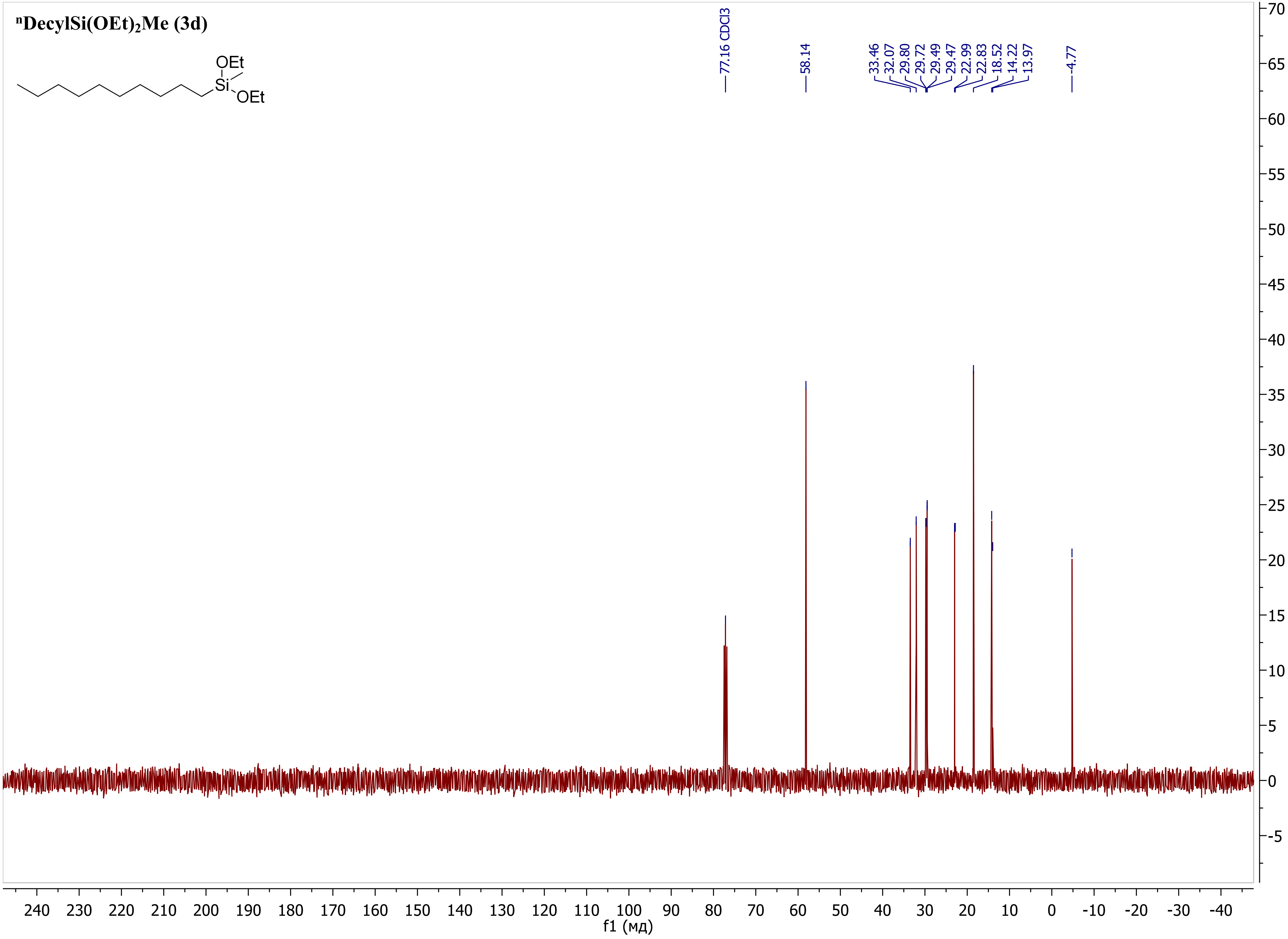

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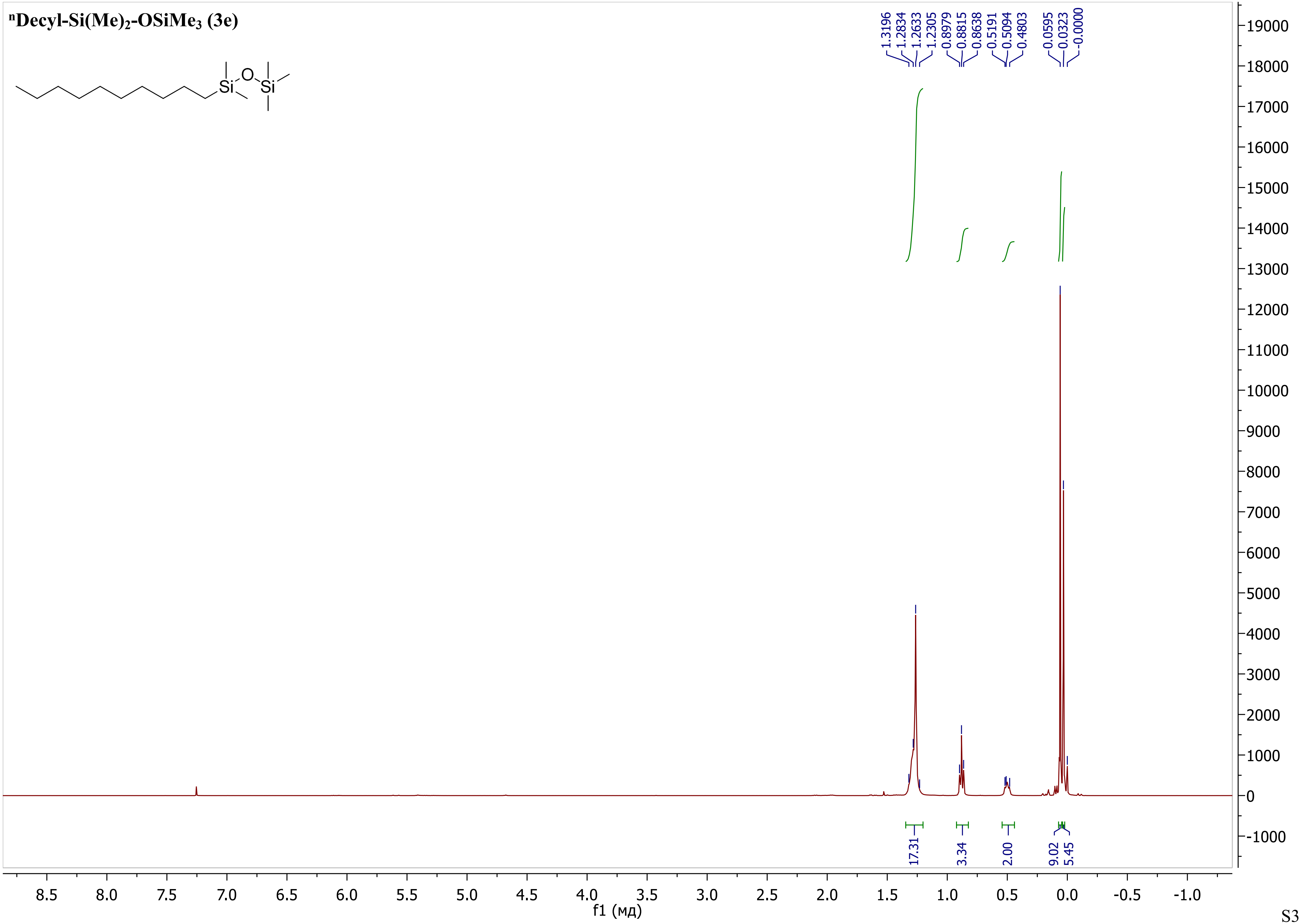

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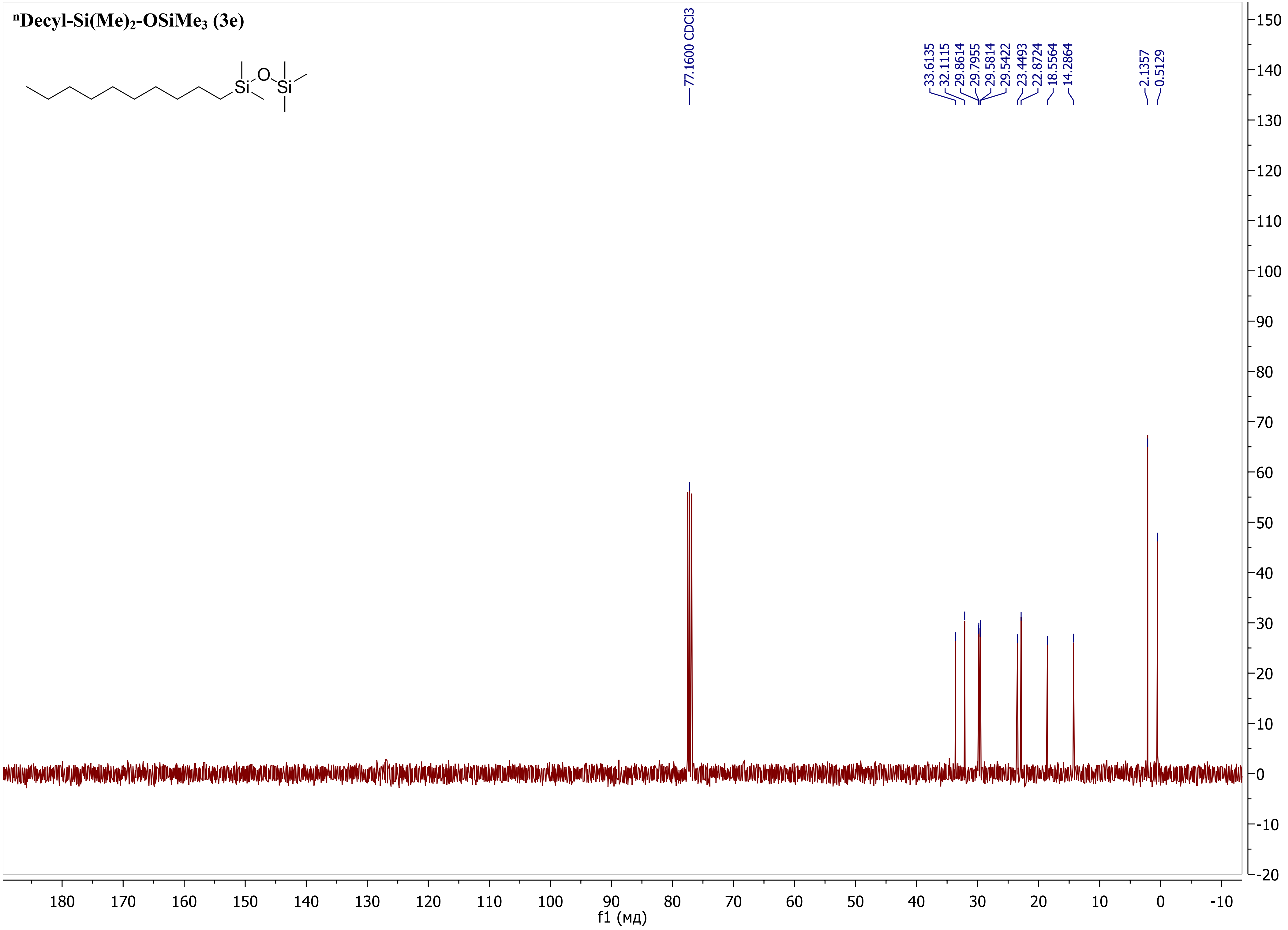

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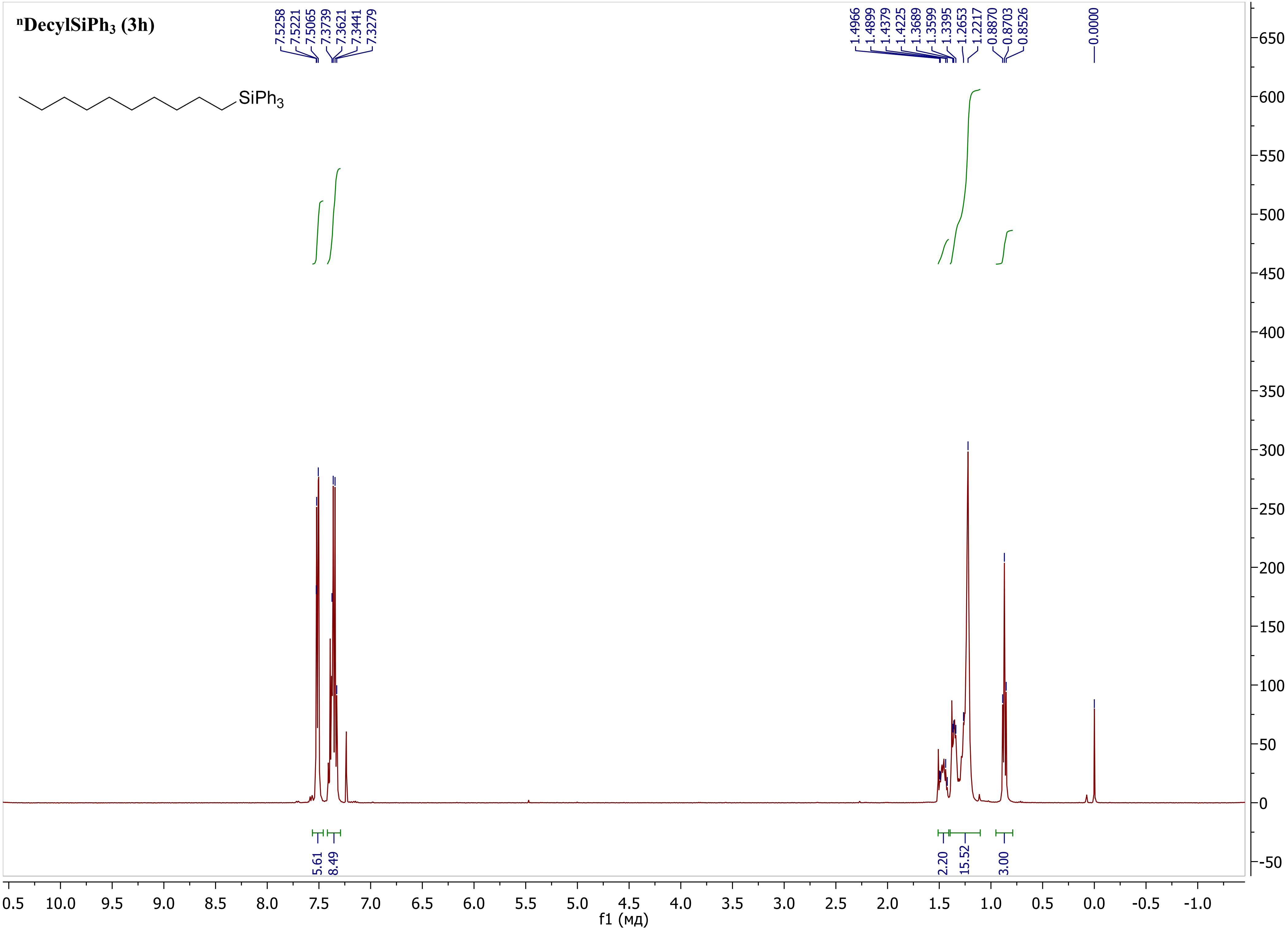

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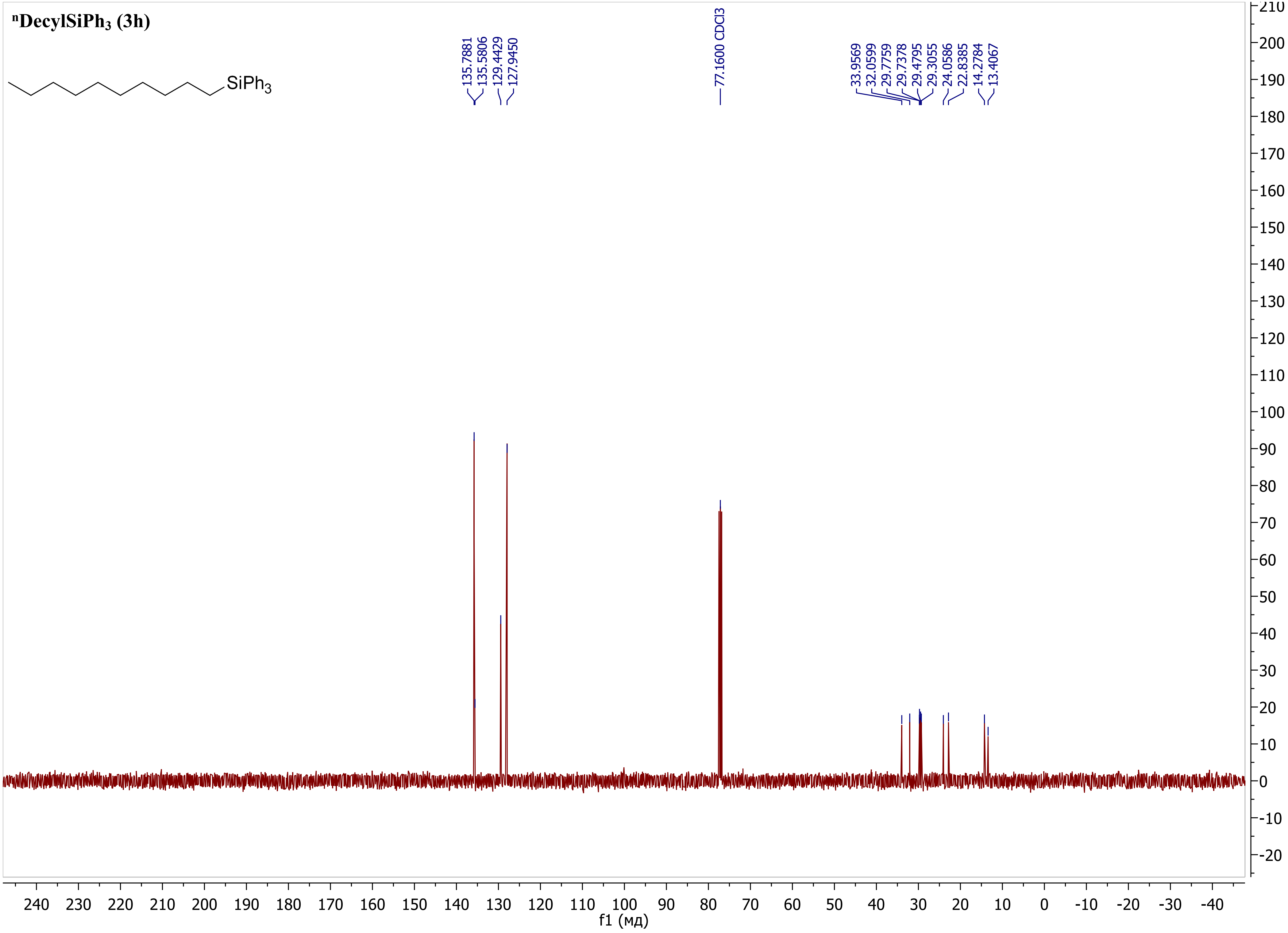
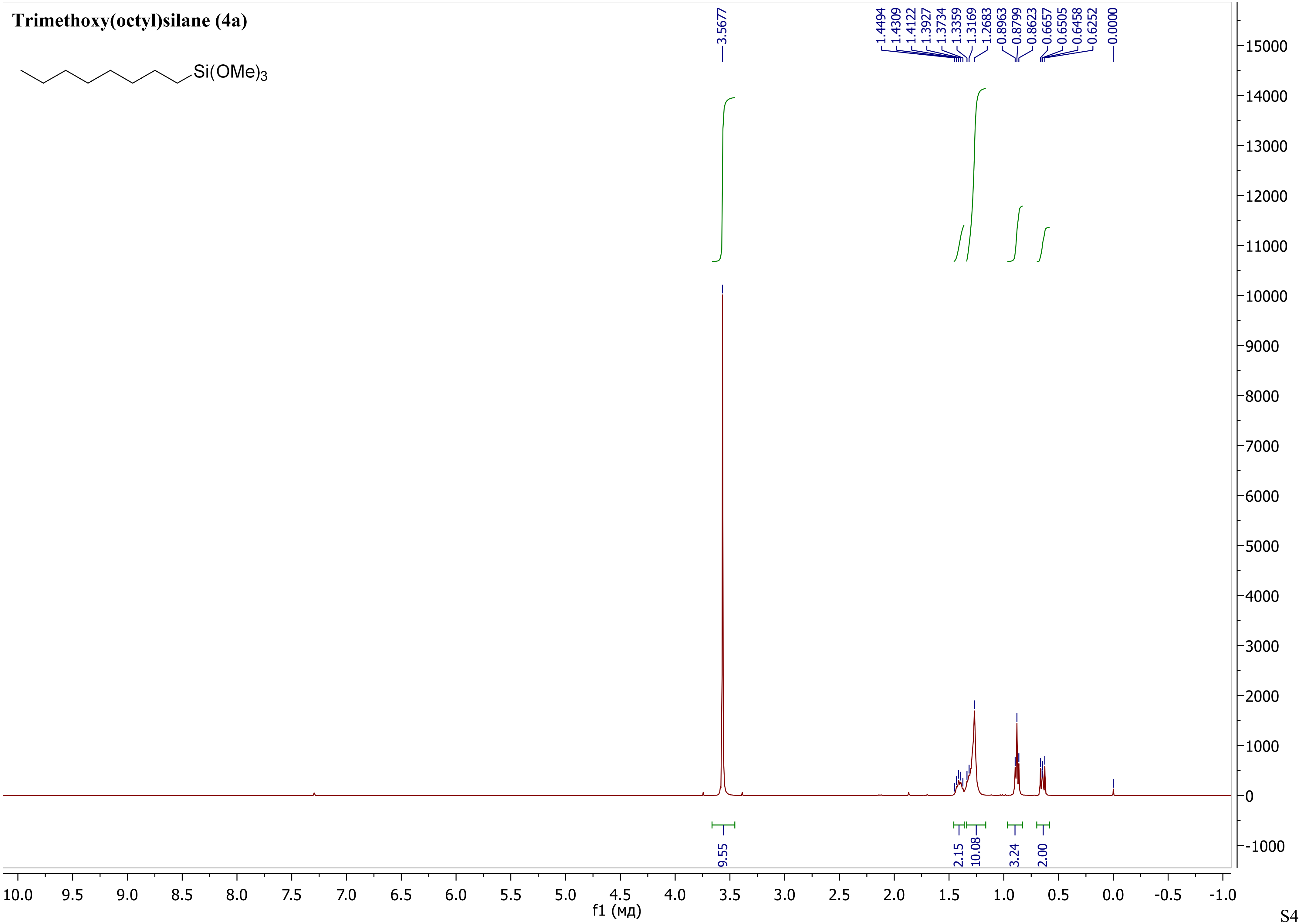
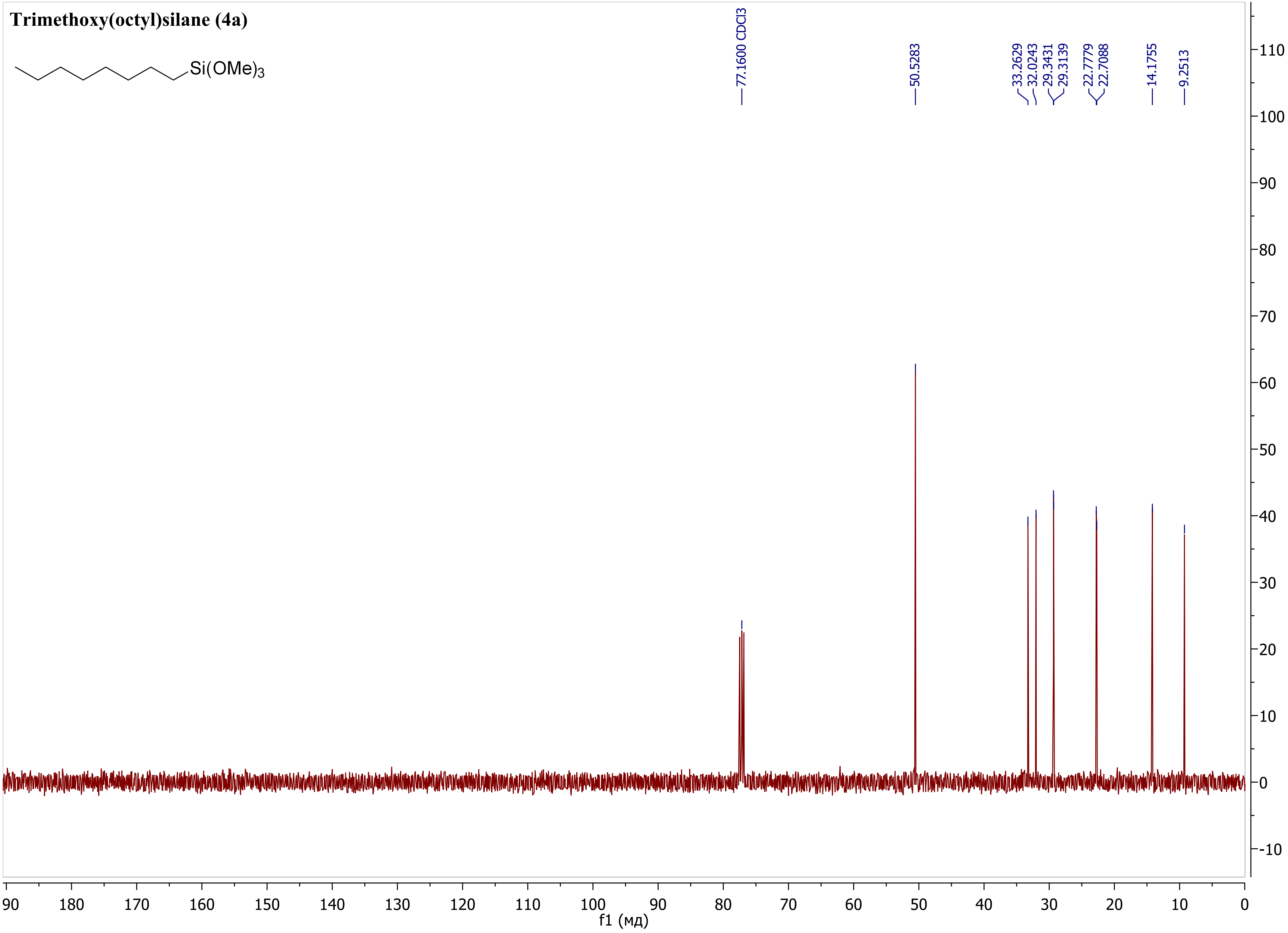


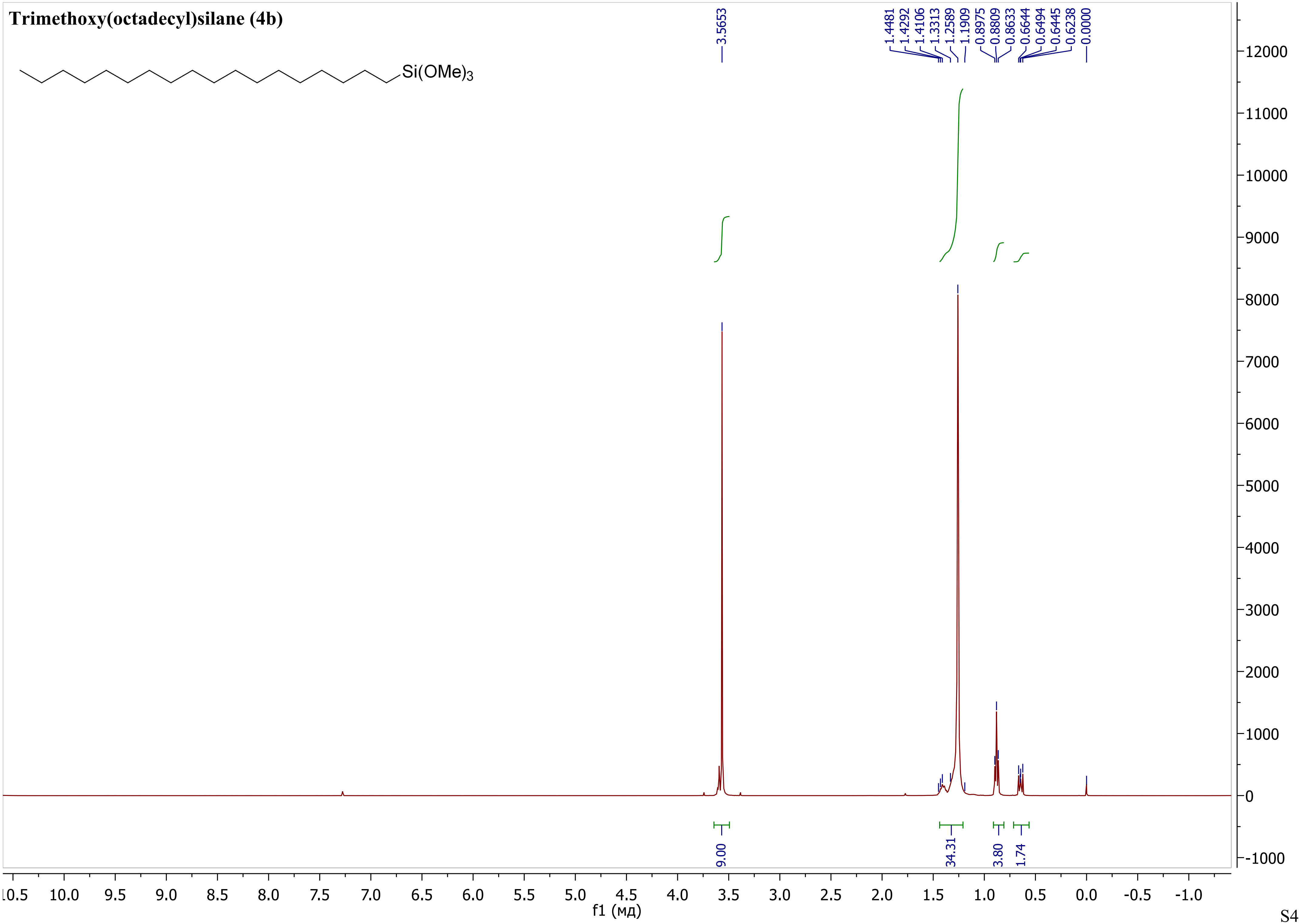
Trimethoxy(octyl)silane (4a)



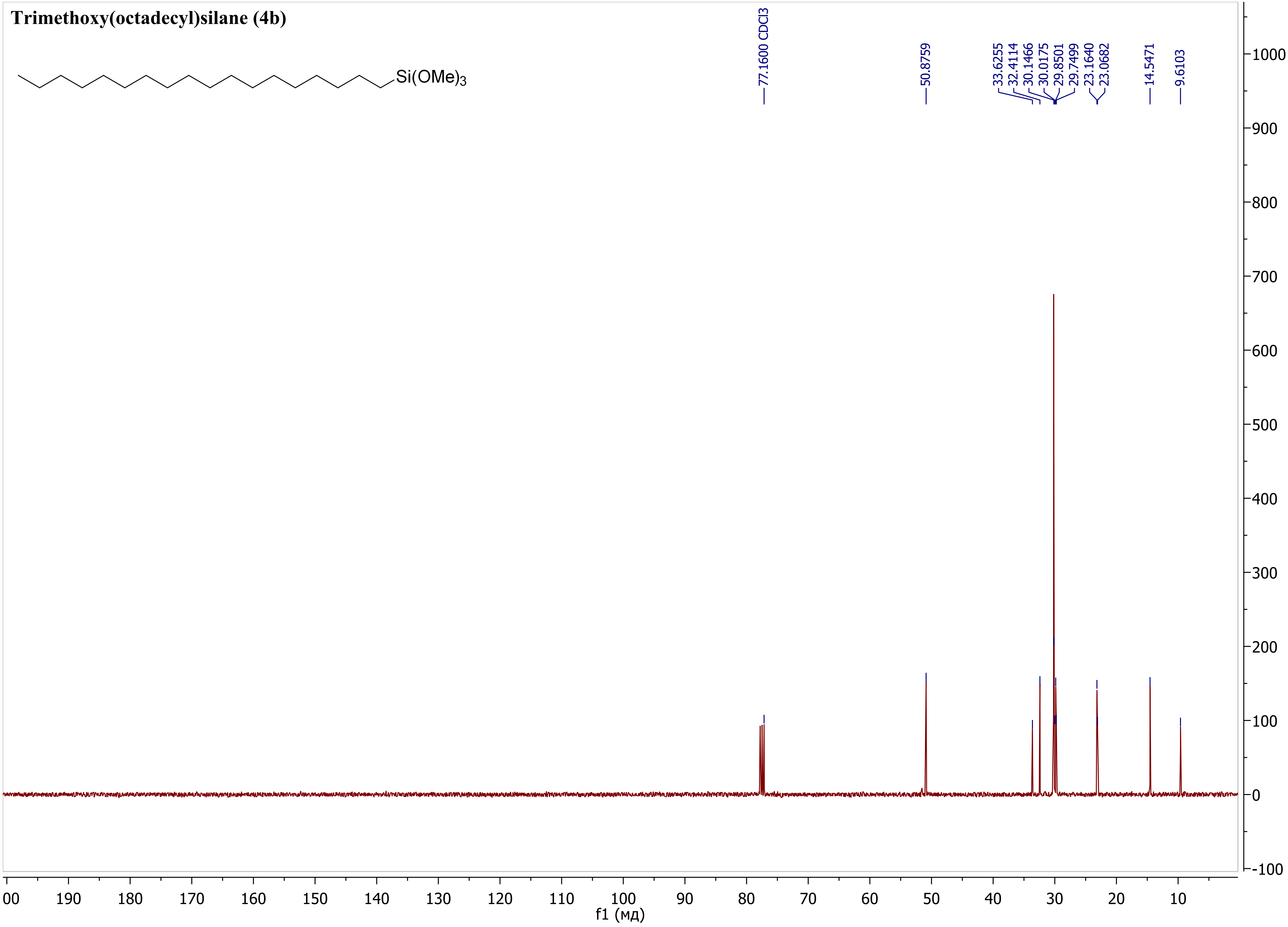
Trimethoxy(octyl)silane (4a)



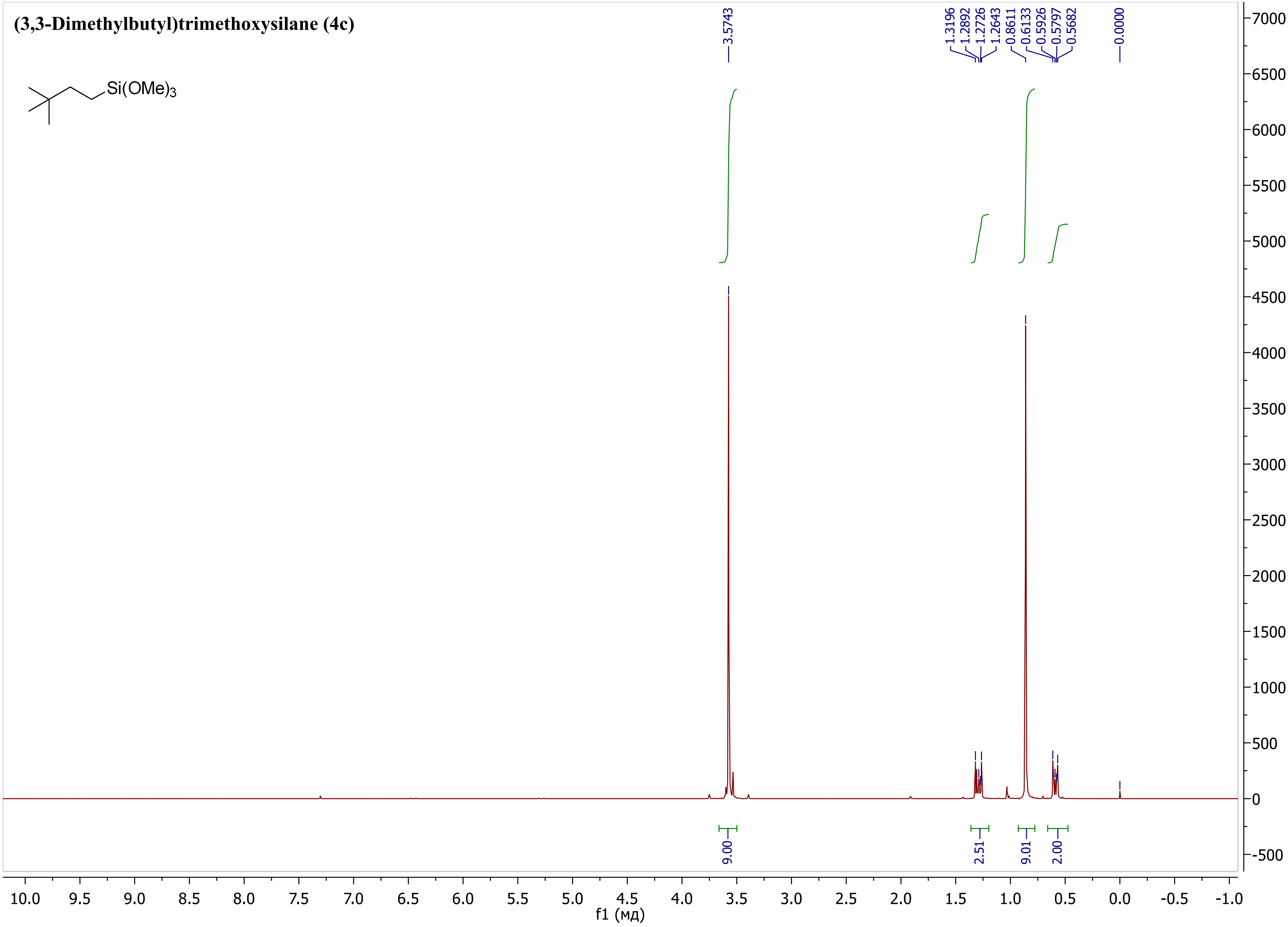
Trimethoxy(octadecyl)silane (4b)



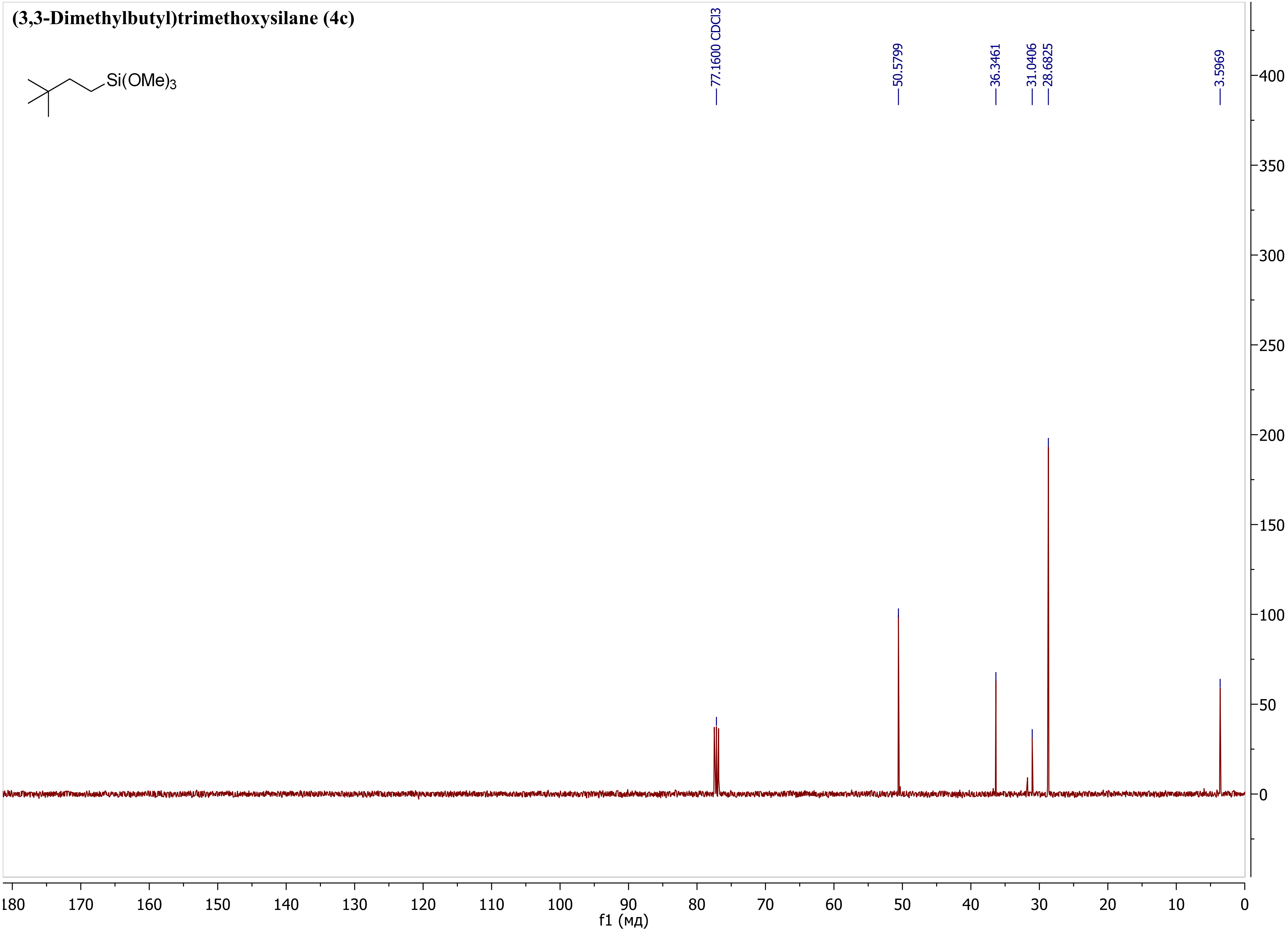
Trimethoxy(octadecyl)silane (4b)



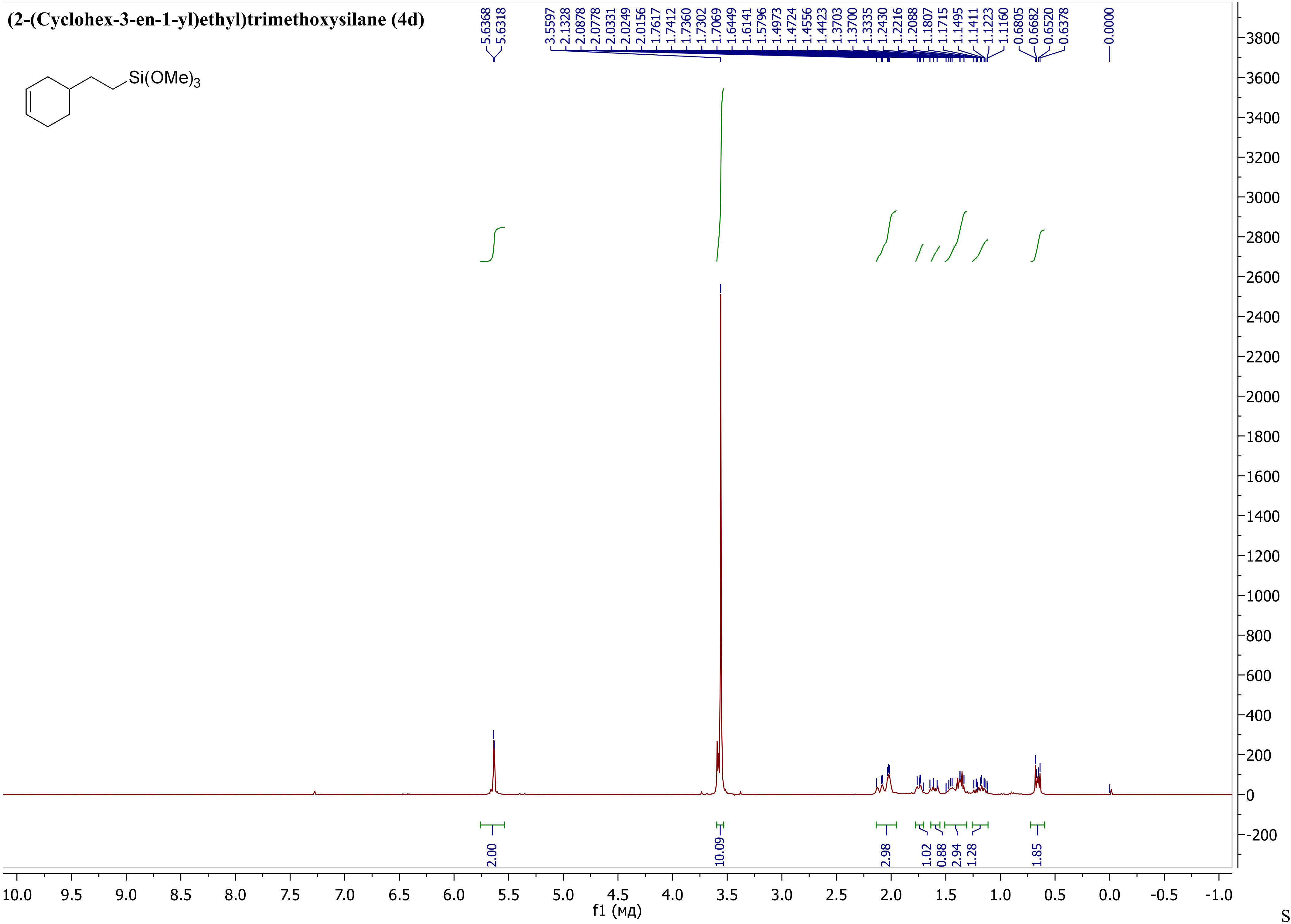
(3,3-Dimethylbutyl)trimethoxysilane (4c)



(3,3-Dimethylbutyl)trimethoxysilane (4c)



(2-(Cyclohex-3-en-1-yl)ethyl)trimethoxysilane (4d)



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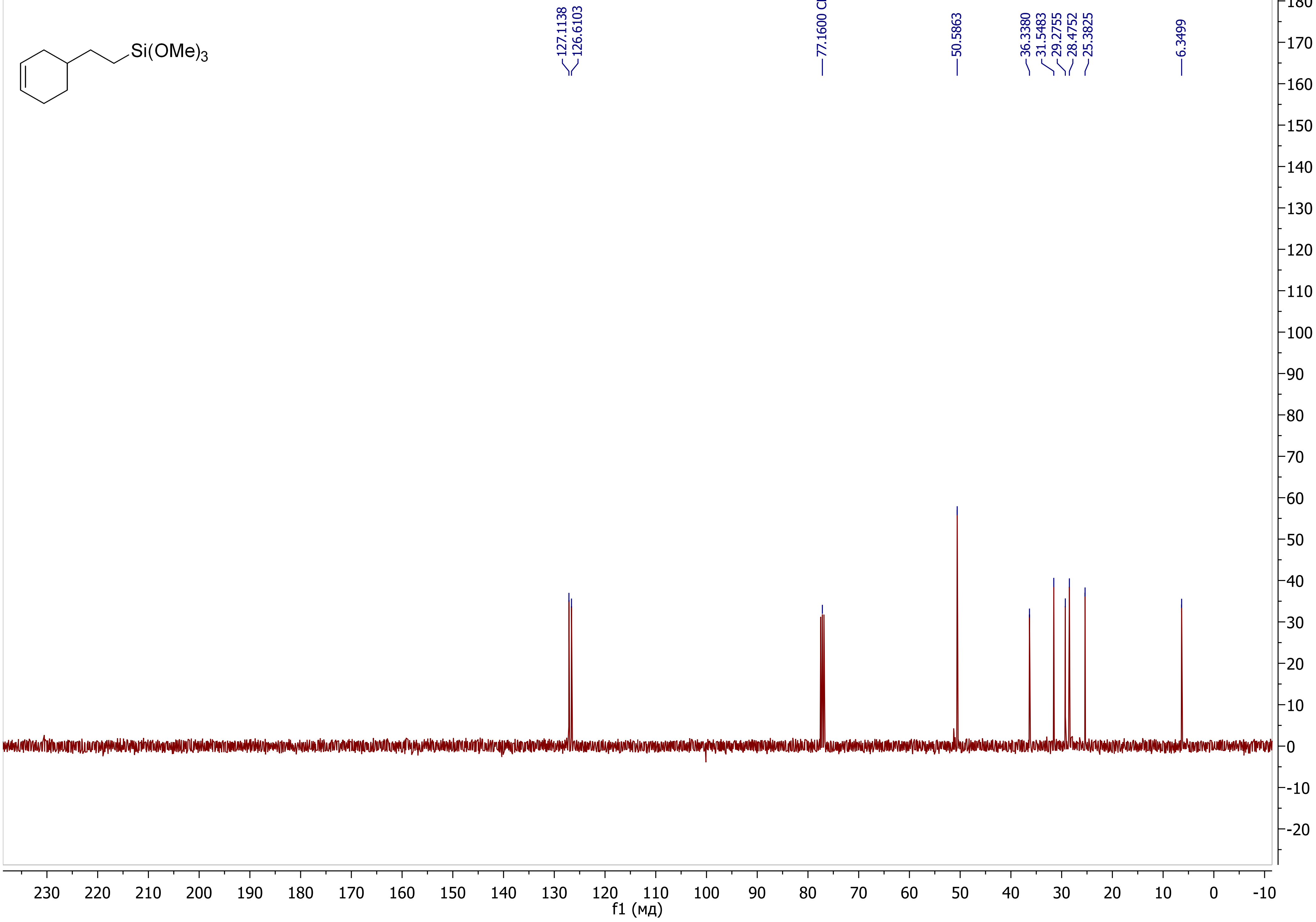
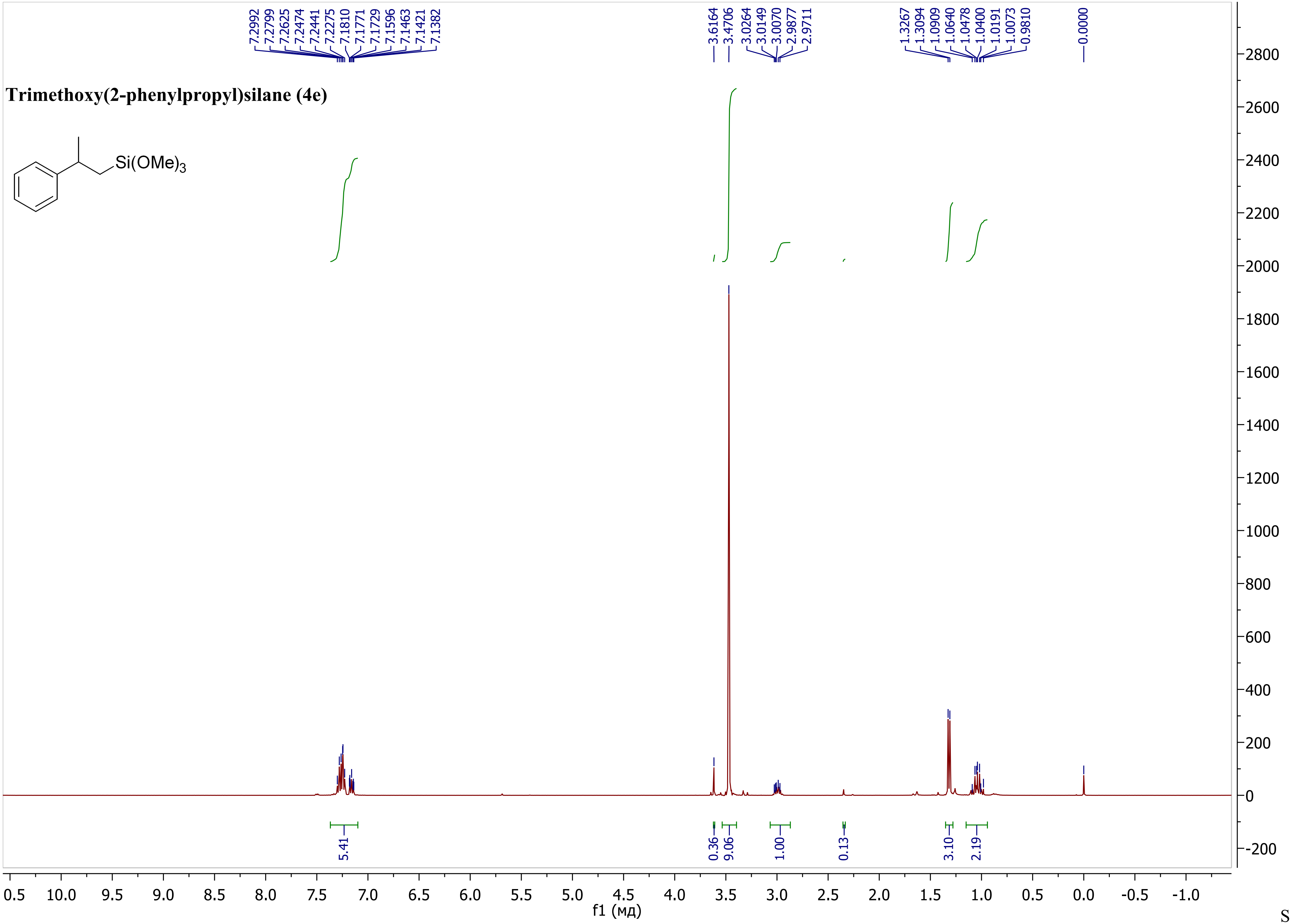
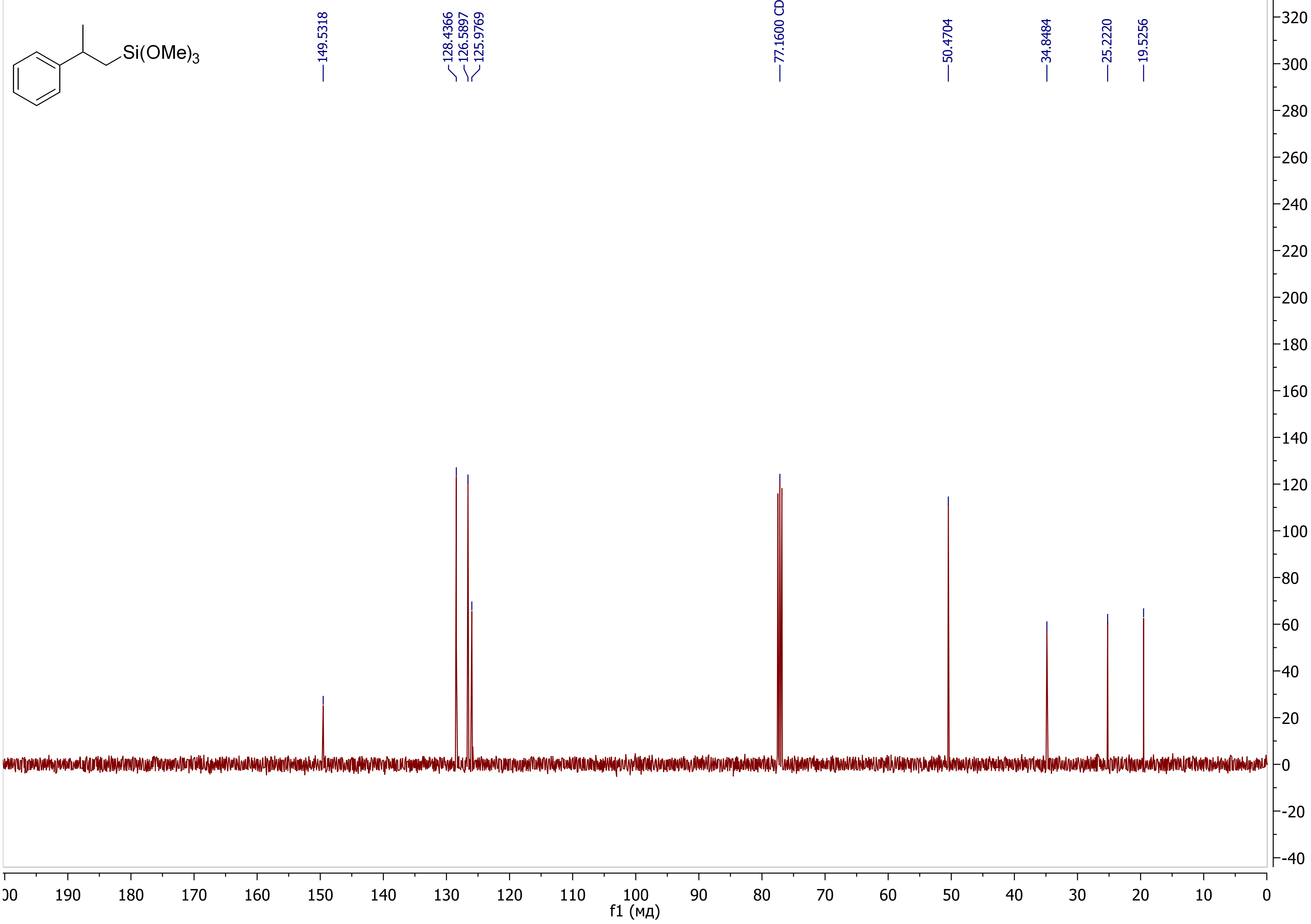


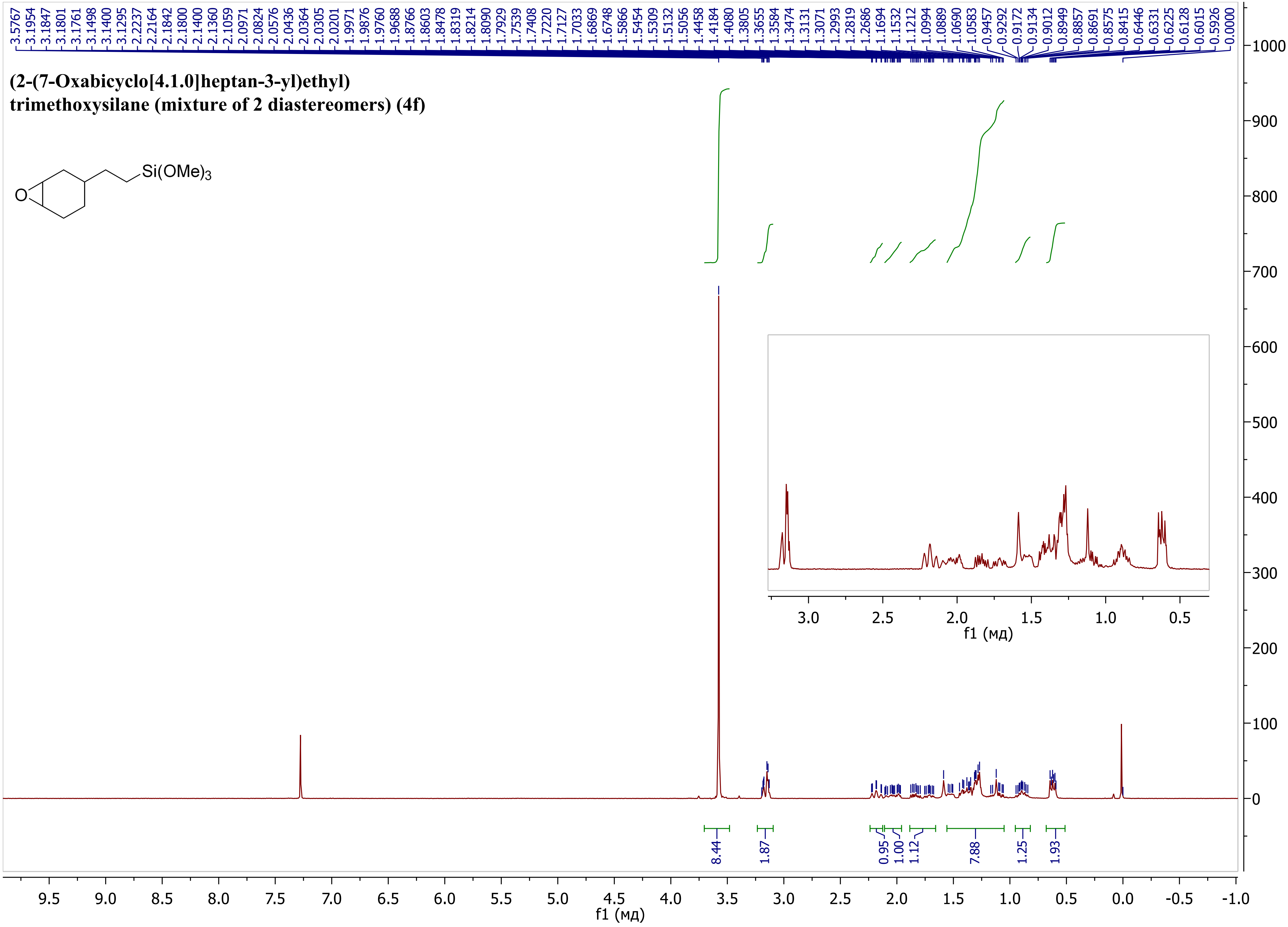
Trimethoxy(2-phenylpropyl)silane (4e)



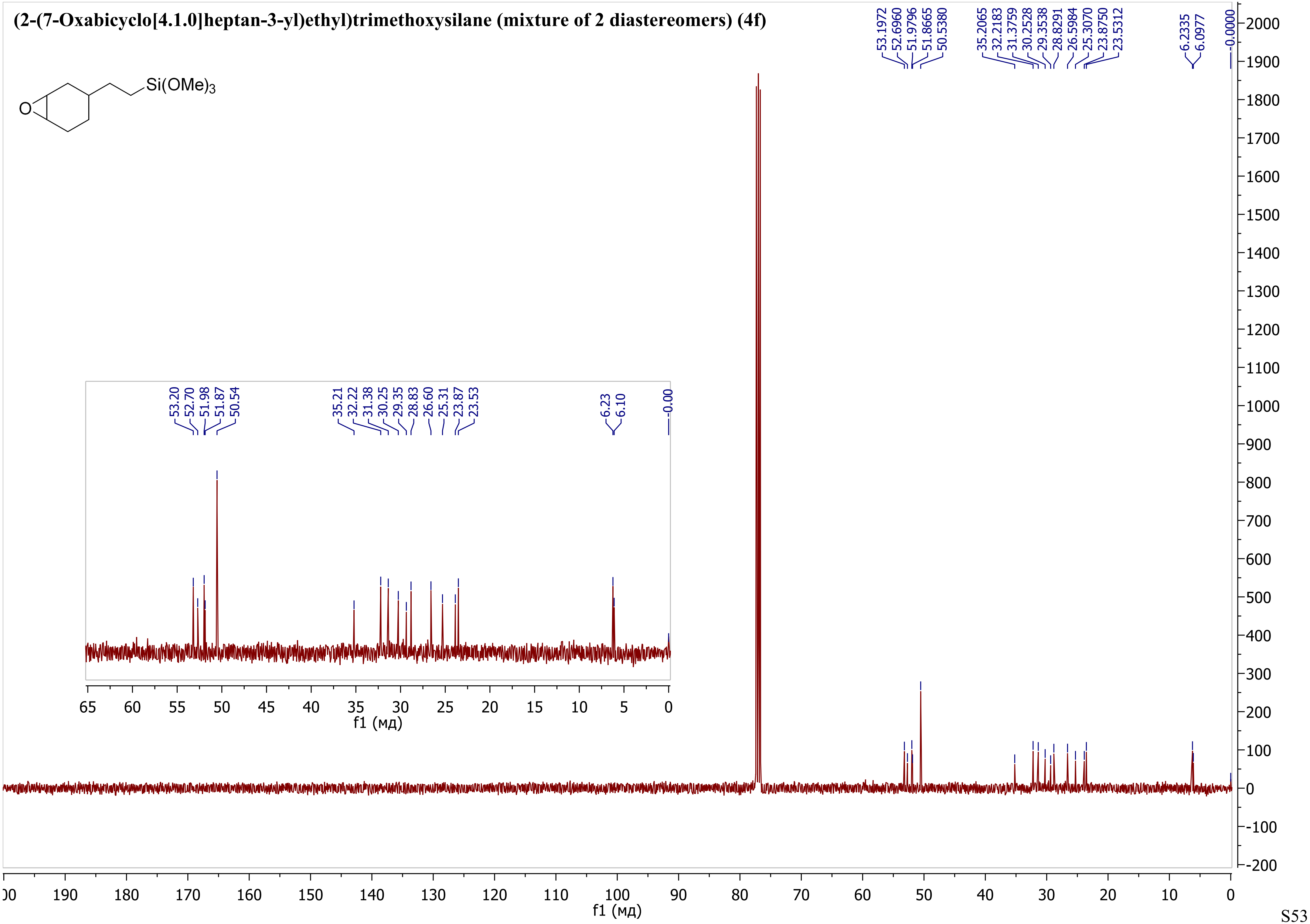
Trimethoxy(2-phenylpropyl)silane (4e)



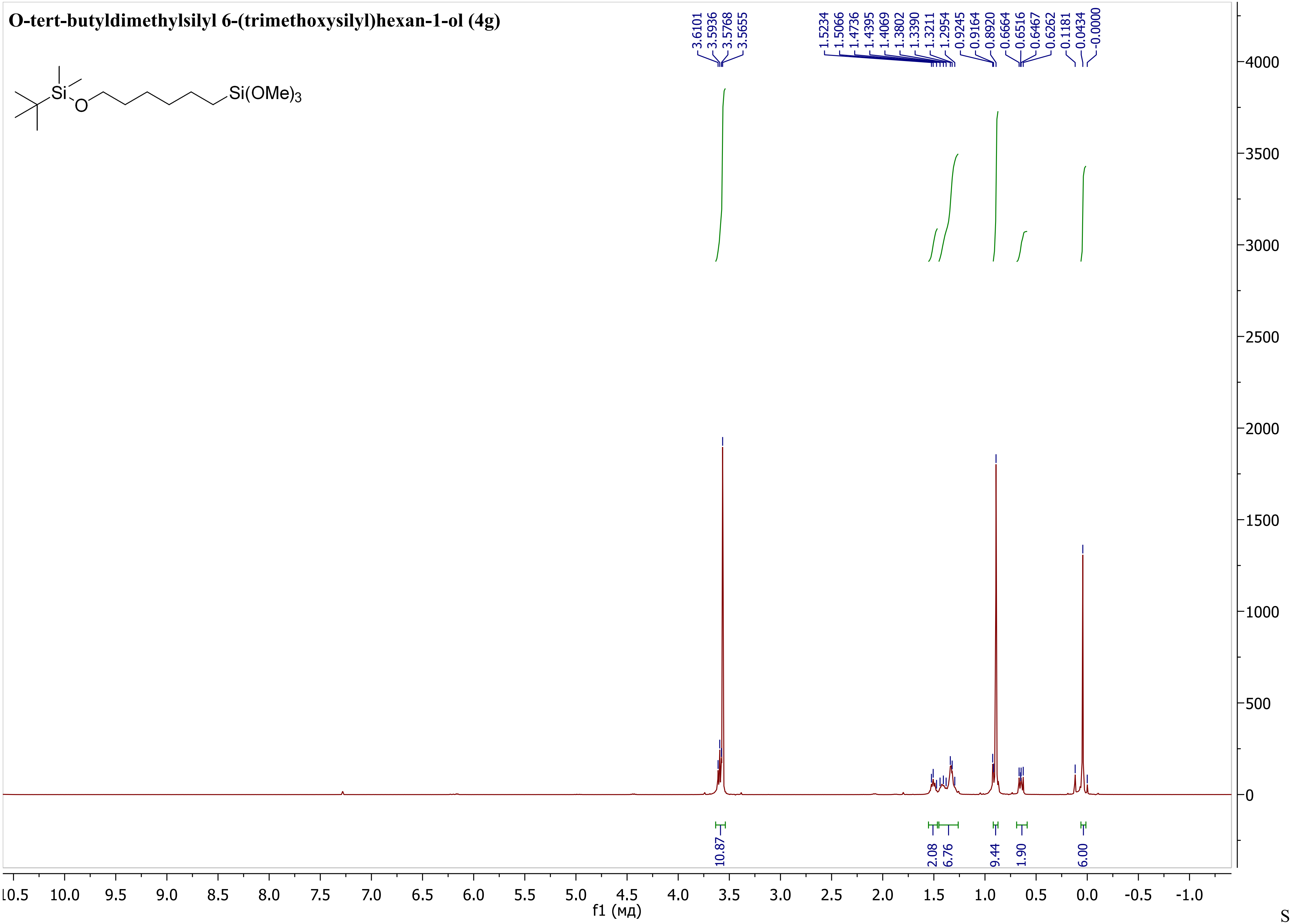
(2-(7-Oxabicyclo[4.1.0]heptan-3-yl)ethyl) trimethoxysilane (mixture of 2 diastereomers) (4f)



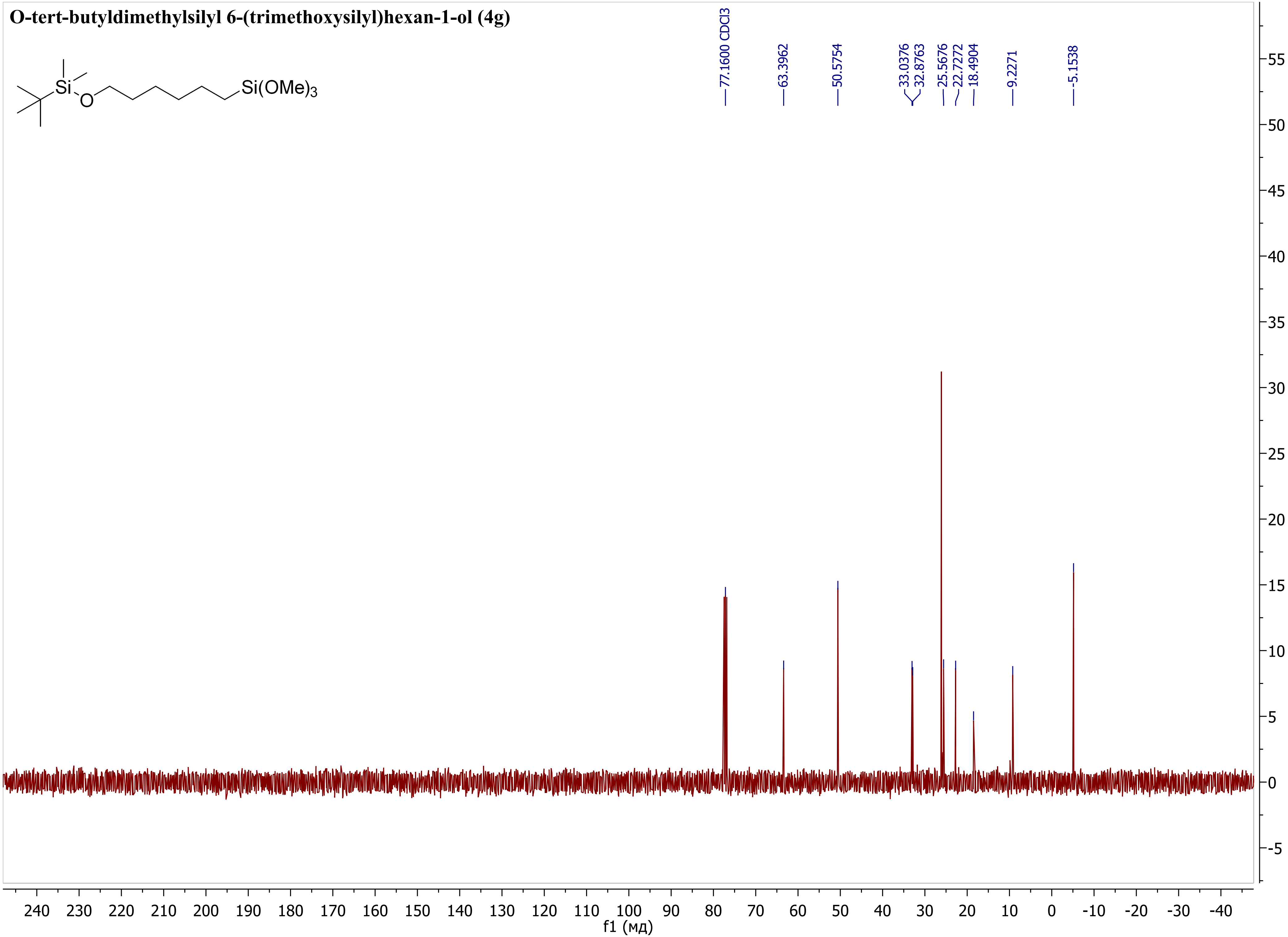
(2-(7-Oxabicyclo[4.1.0]heptan-3-yl)ethyl)trimethoxysilane (mixture of 2 diastereomers) (4f)



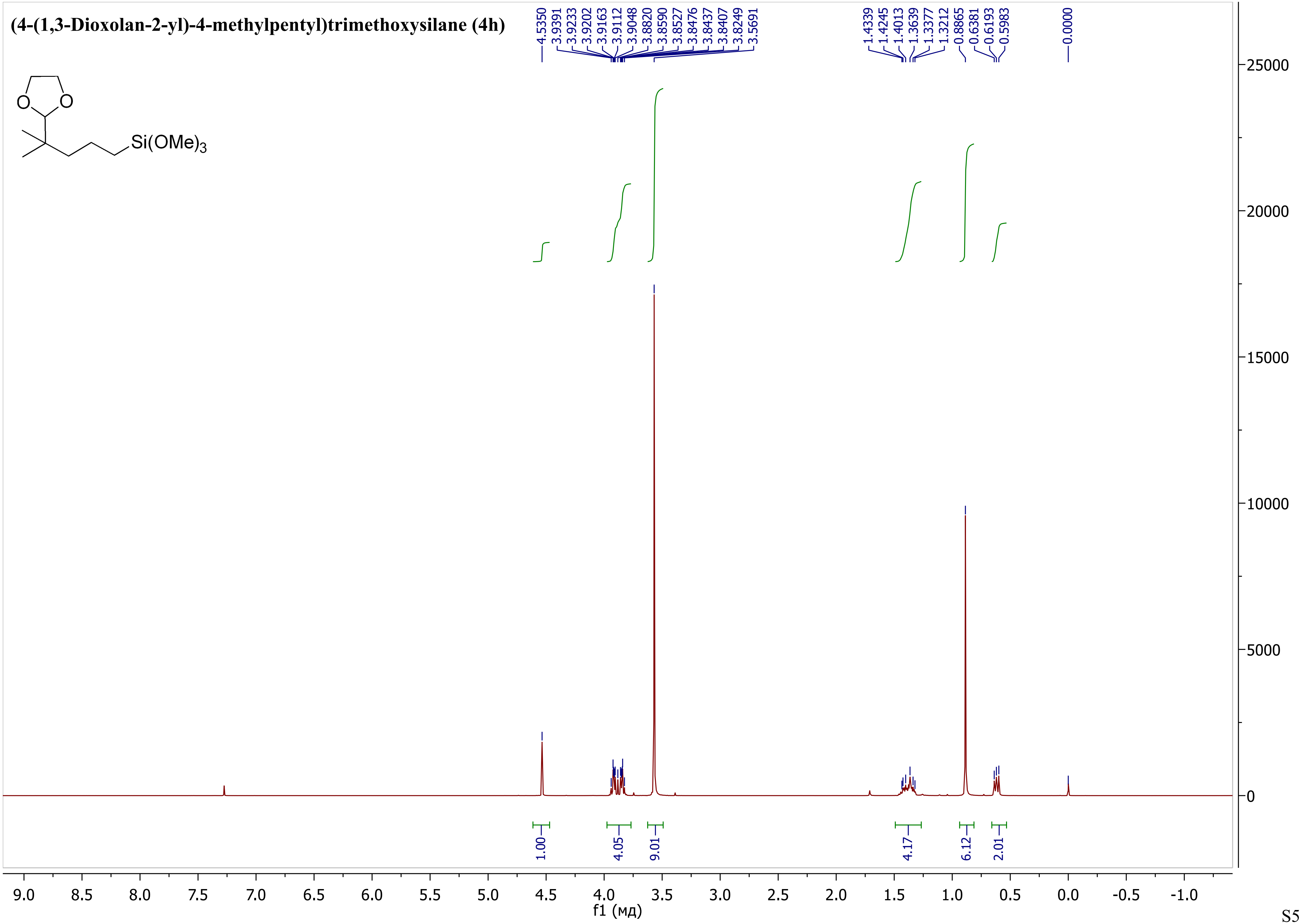
O-tert-butyldimethylsilyl 6-(trimethoxysilyl)hexan-1-ol (4g)



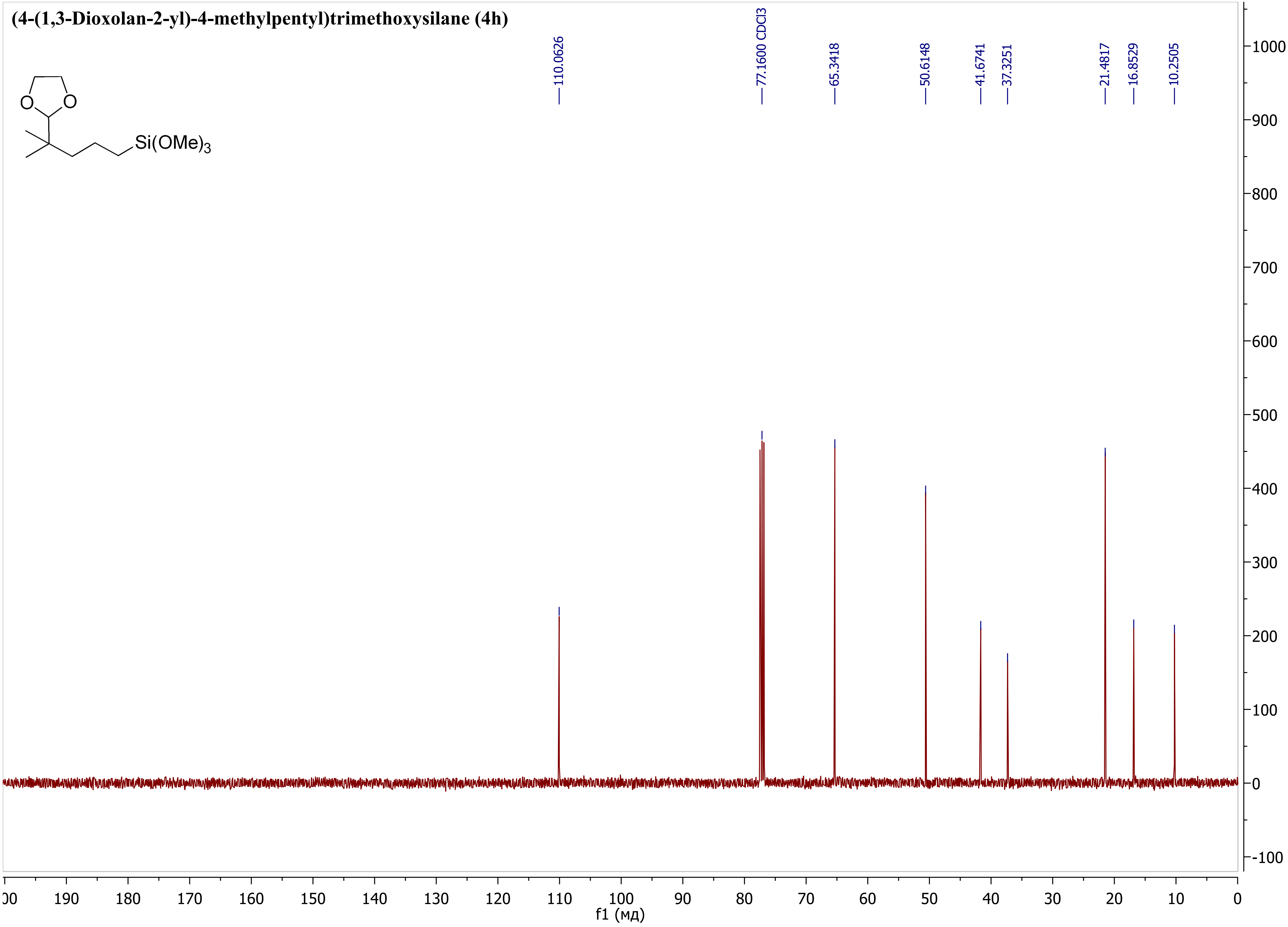
O-tert-butyldimethylsilyl 6-(trimethoxysilyl)hexan-1-ol (4g)



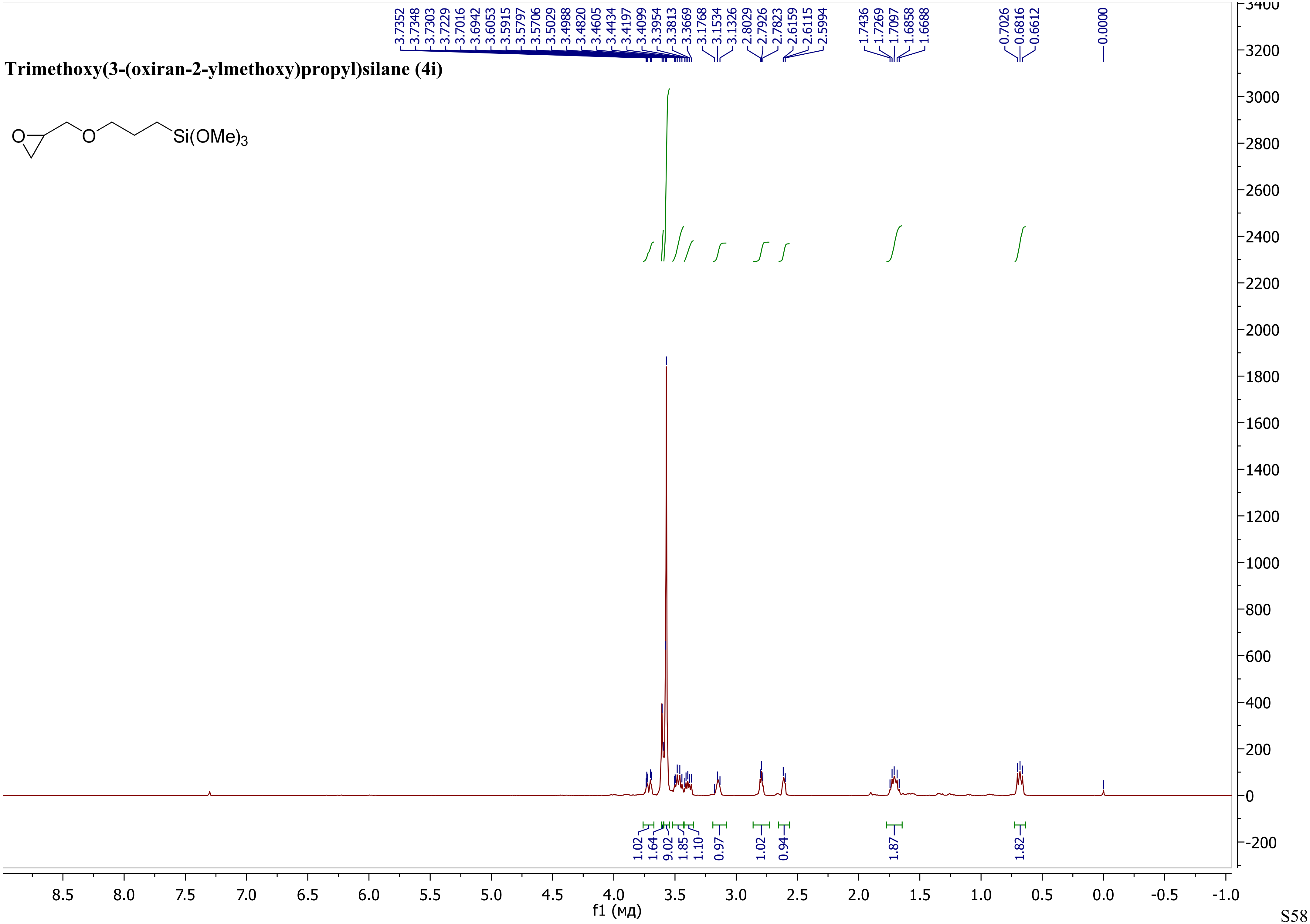
(4-(1,3-Dioxolan-2-yl)-4-methylpentyl)trimethoxysilane (4h)



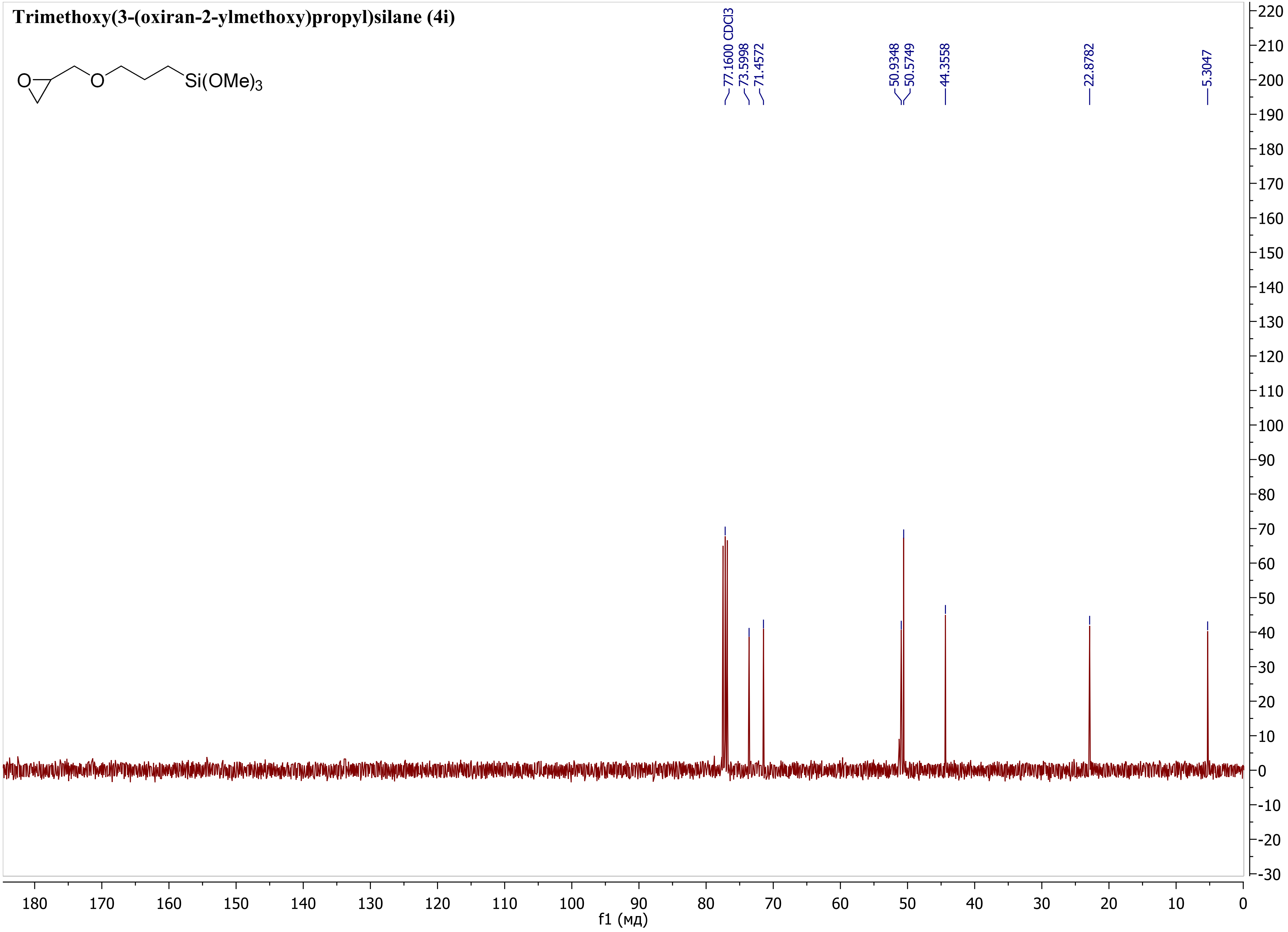
(4-(1,3-Dioxolan-2-yl)-4-methylpentyl)trimethoxysilane (4h)



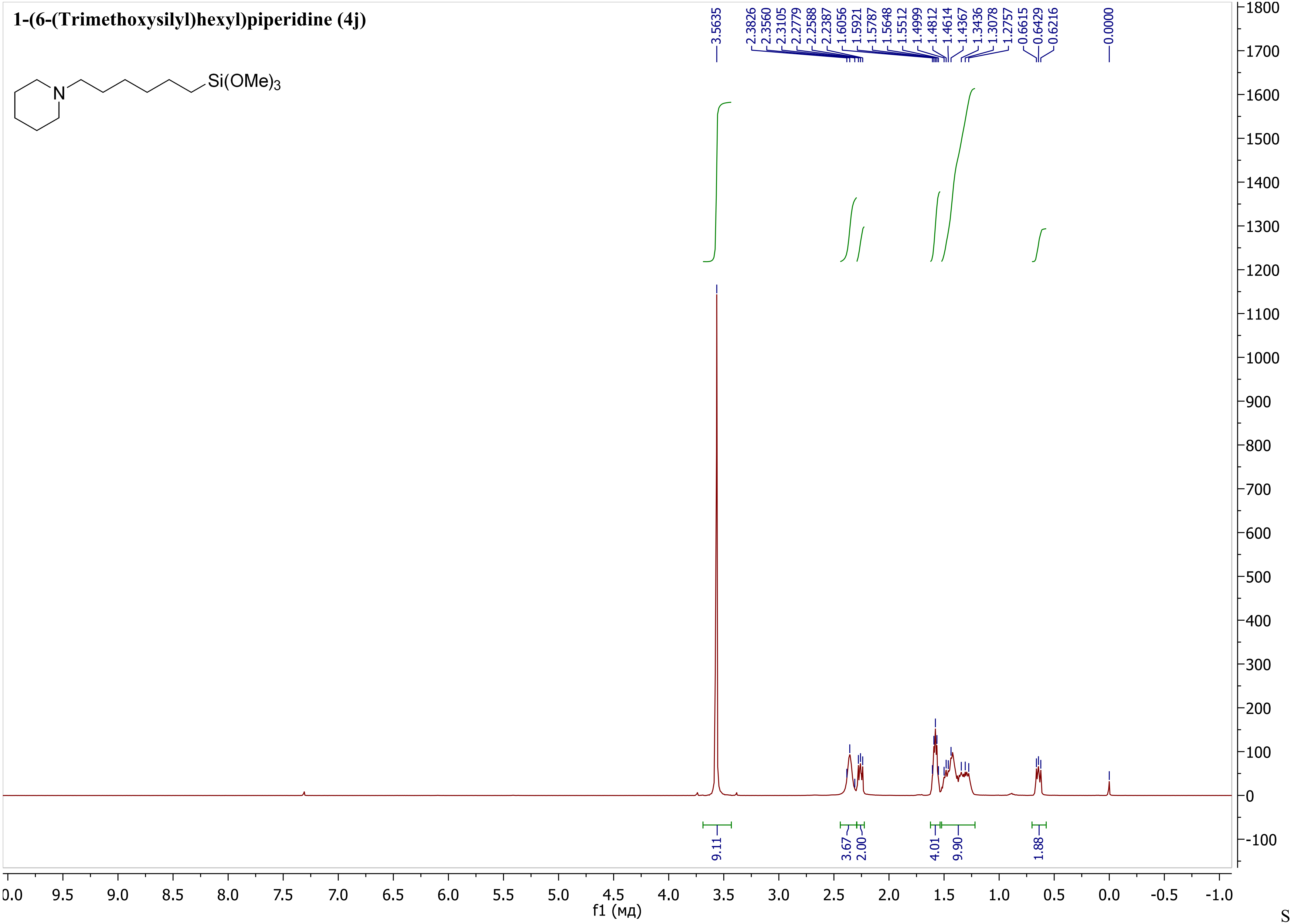
Trimethoxy(3-(oxiran-2-ylmethoxy)propyl)silane (4i)



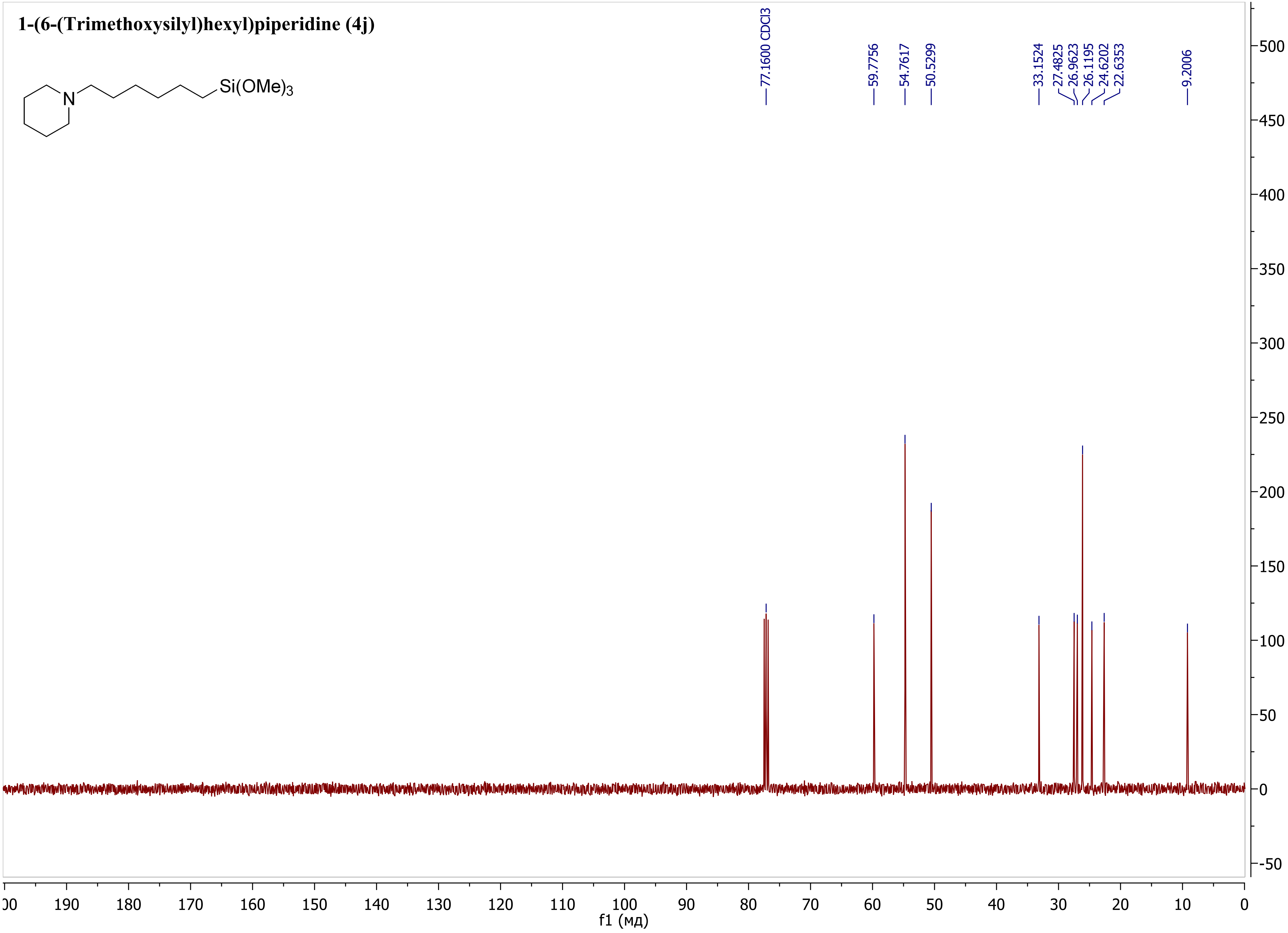
Trimethoxy(3-(oxiran-2-ylmethoxy)propyl)silane (4i)



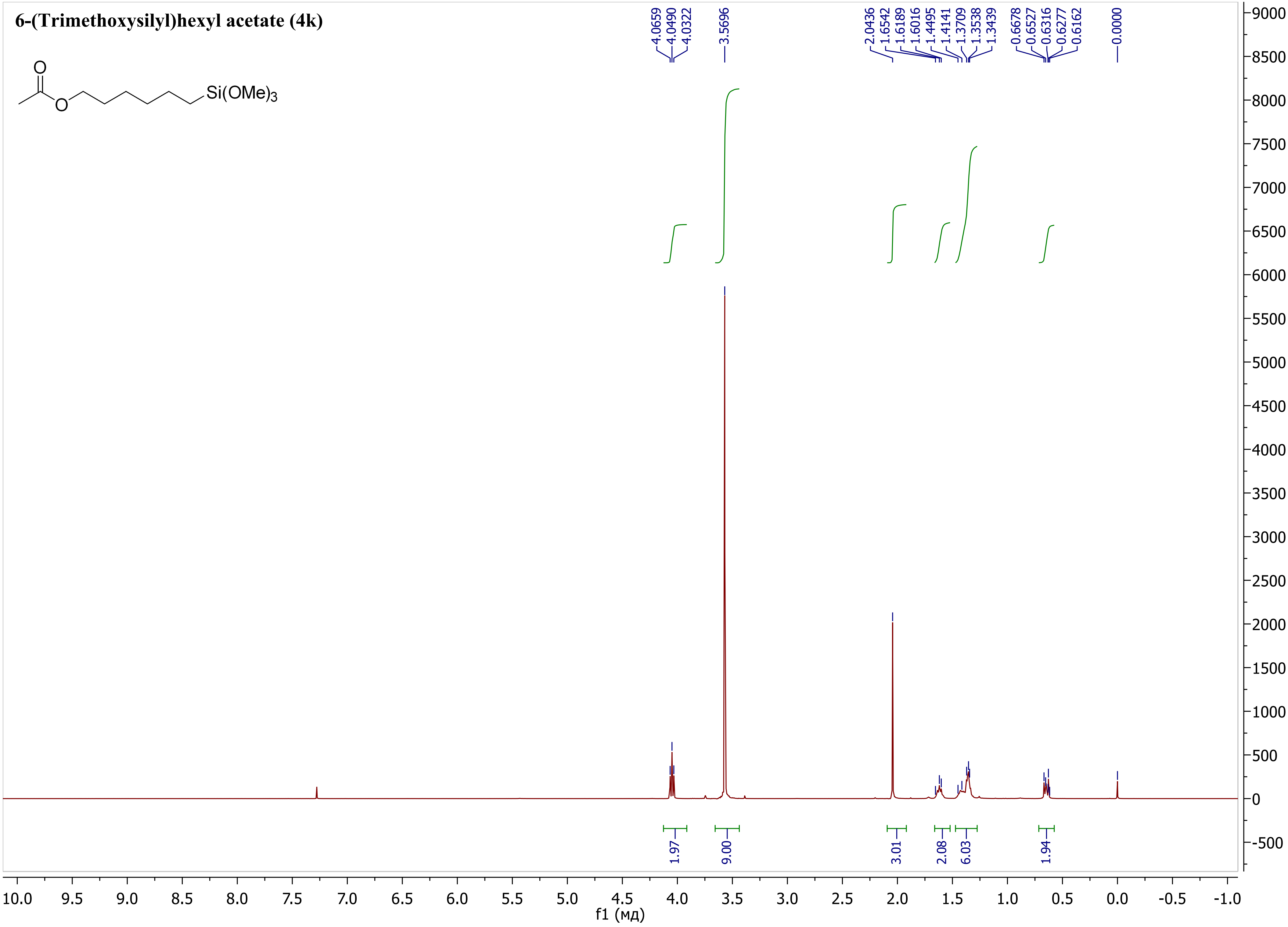
1-(6-(Trimethoxysilyl)hexyl)piperidine (4j)



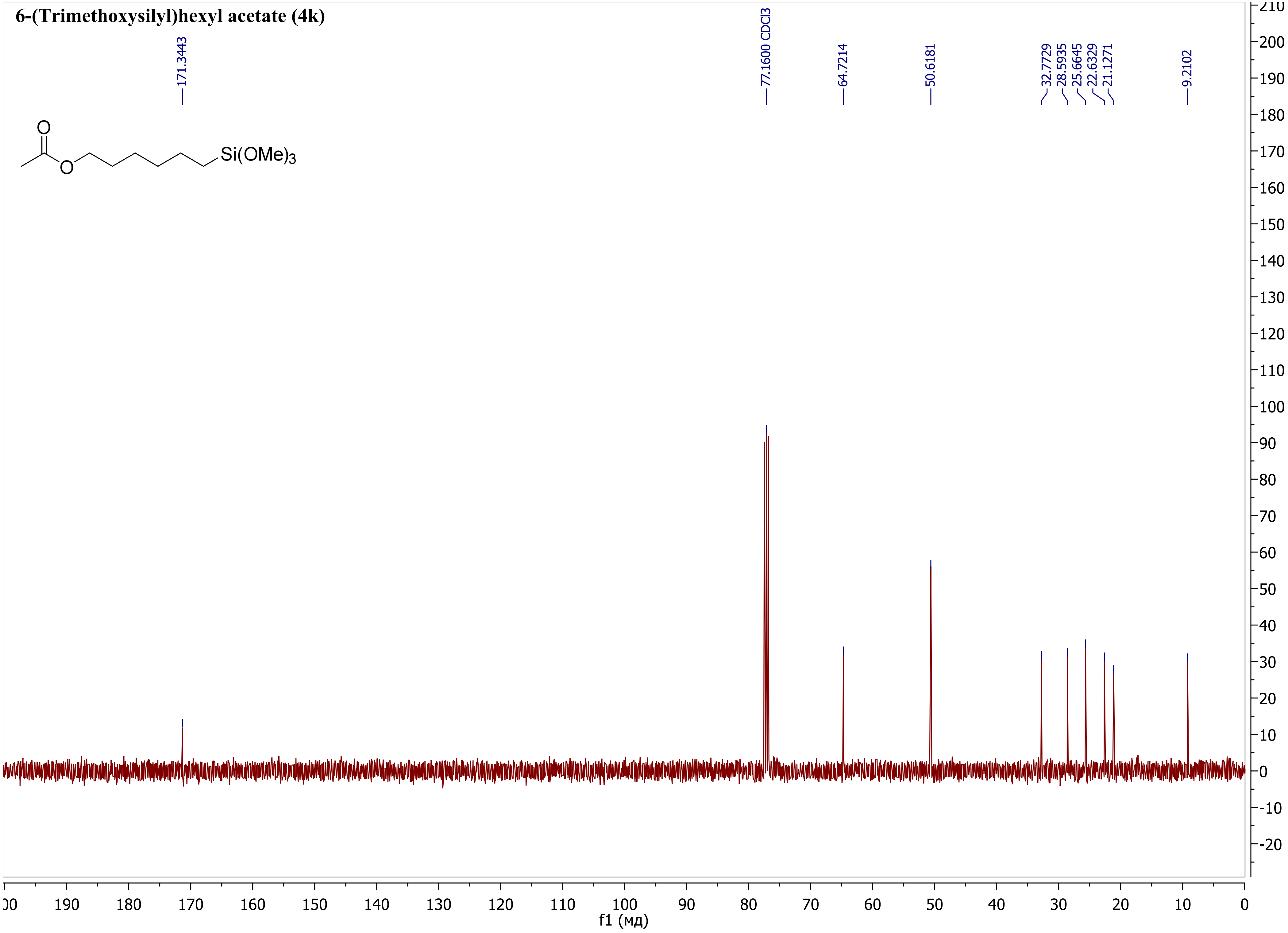
1-(6-(Trimethoxysilyl)hexyl)piperidine (4j)



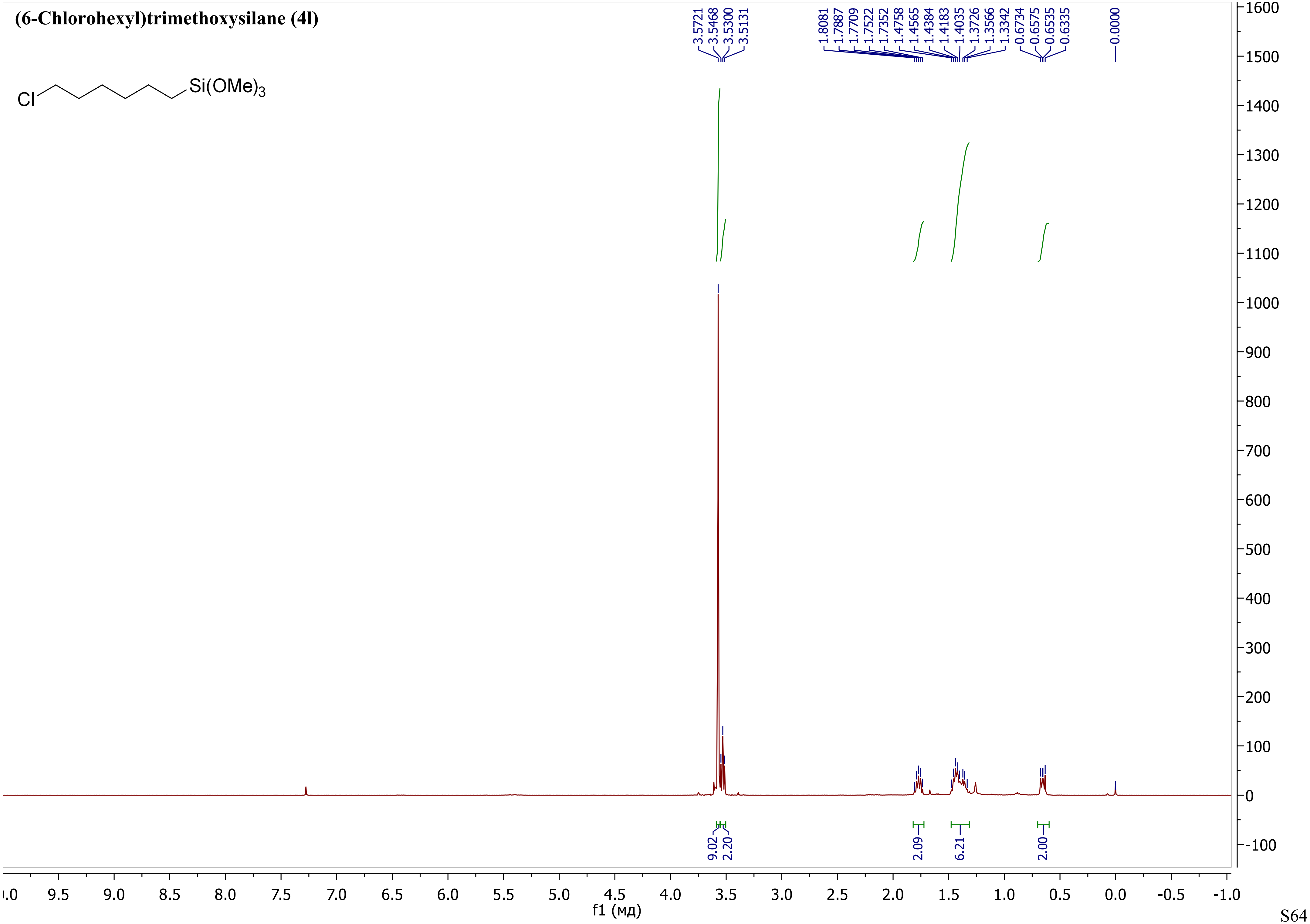
6-(Trimethoxysilyl)hexyl acetate (4k)



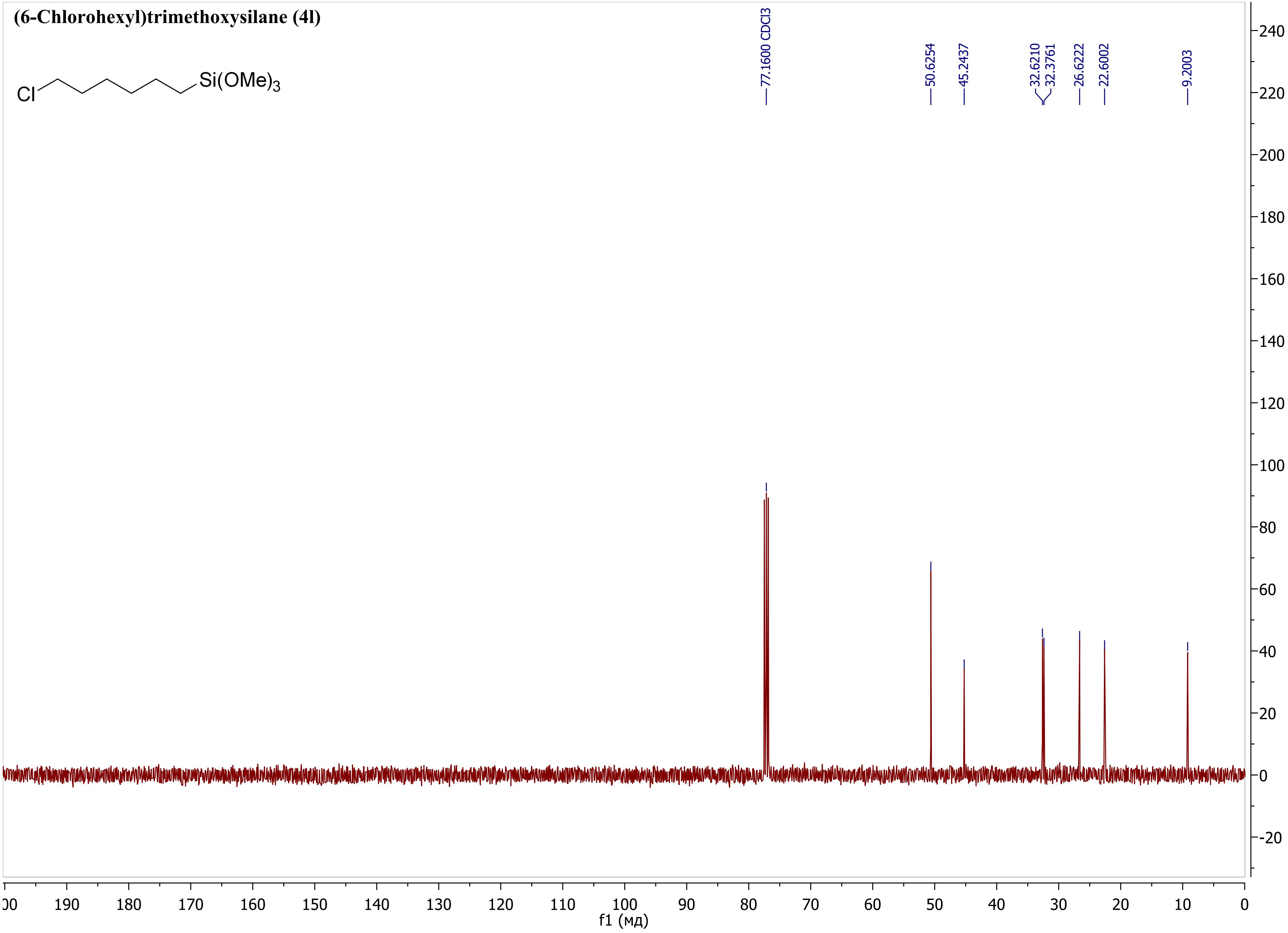
6-(Trimethoxysilyl)hexyl acetate (4k)



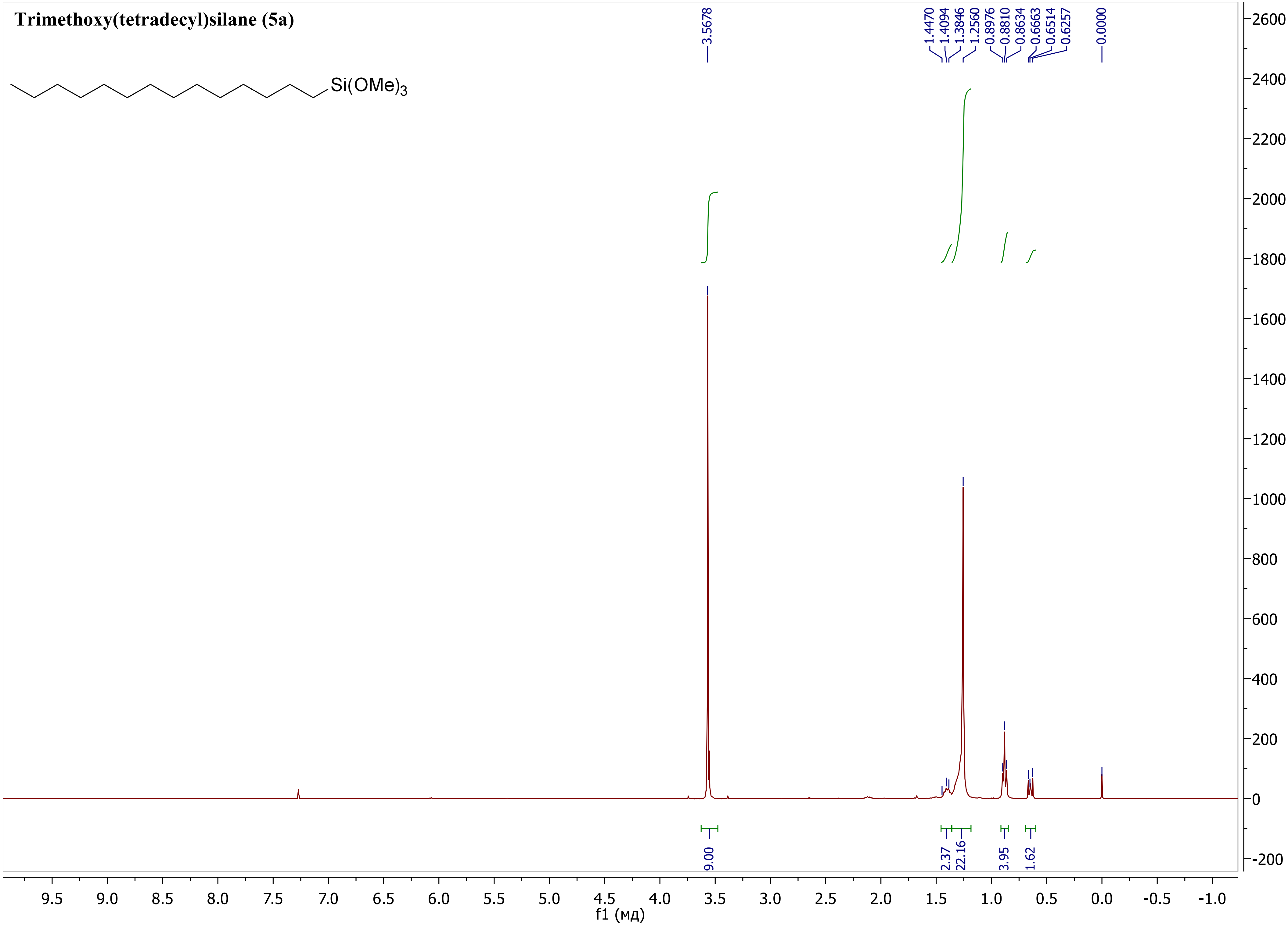
(6-Chlorohexyl)trimethoxysilane (4l)



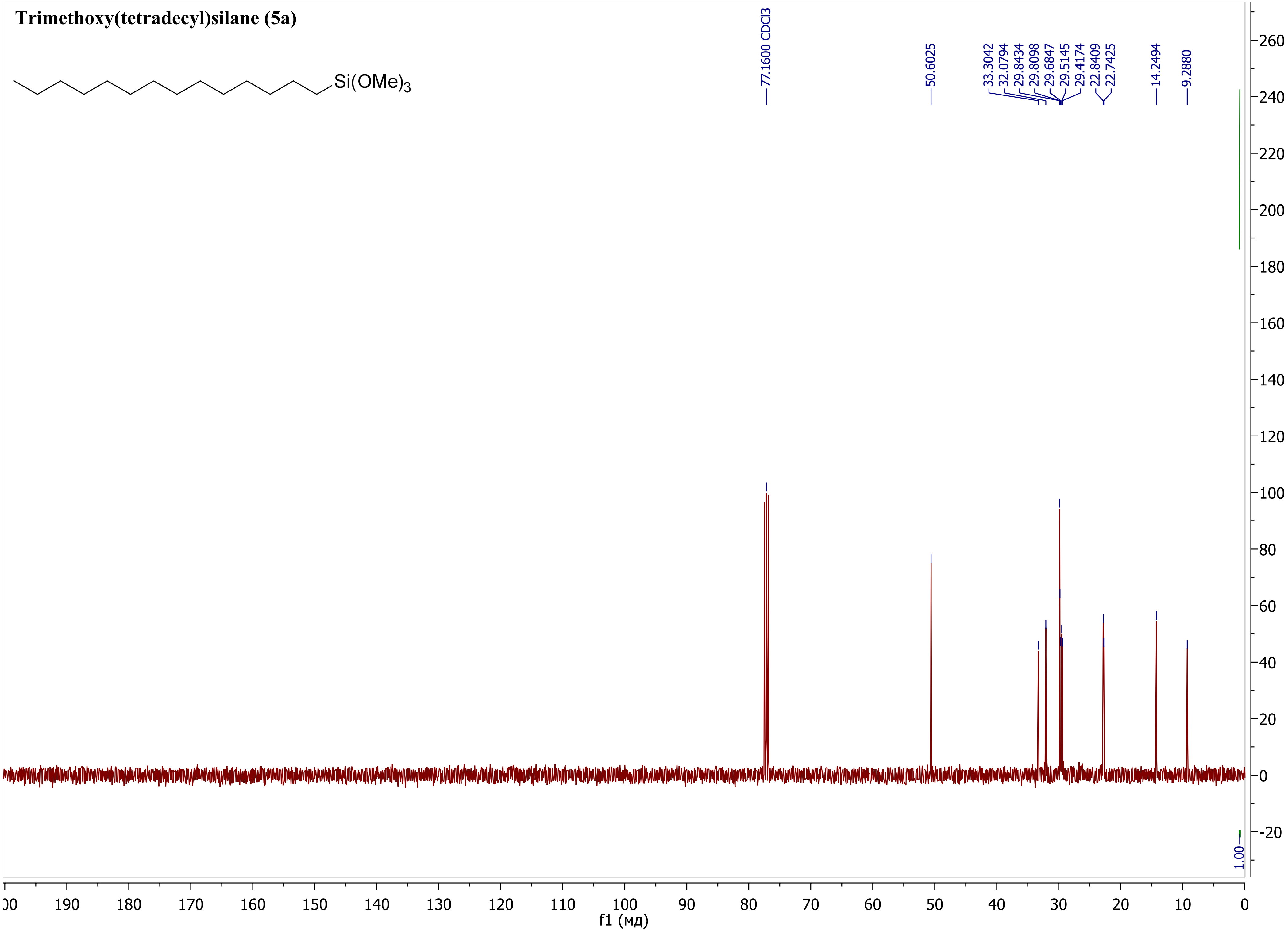
(6-Chlorohexyl)trimethoxysilane (4l)



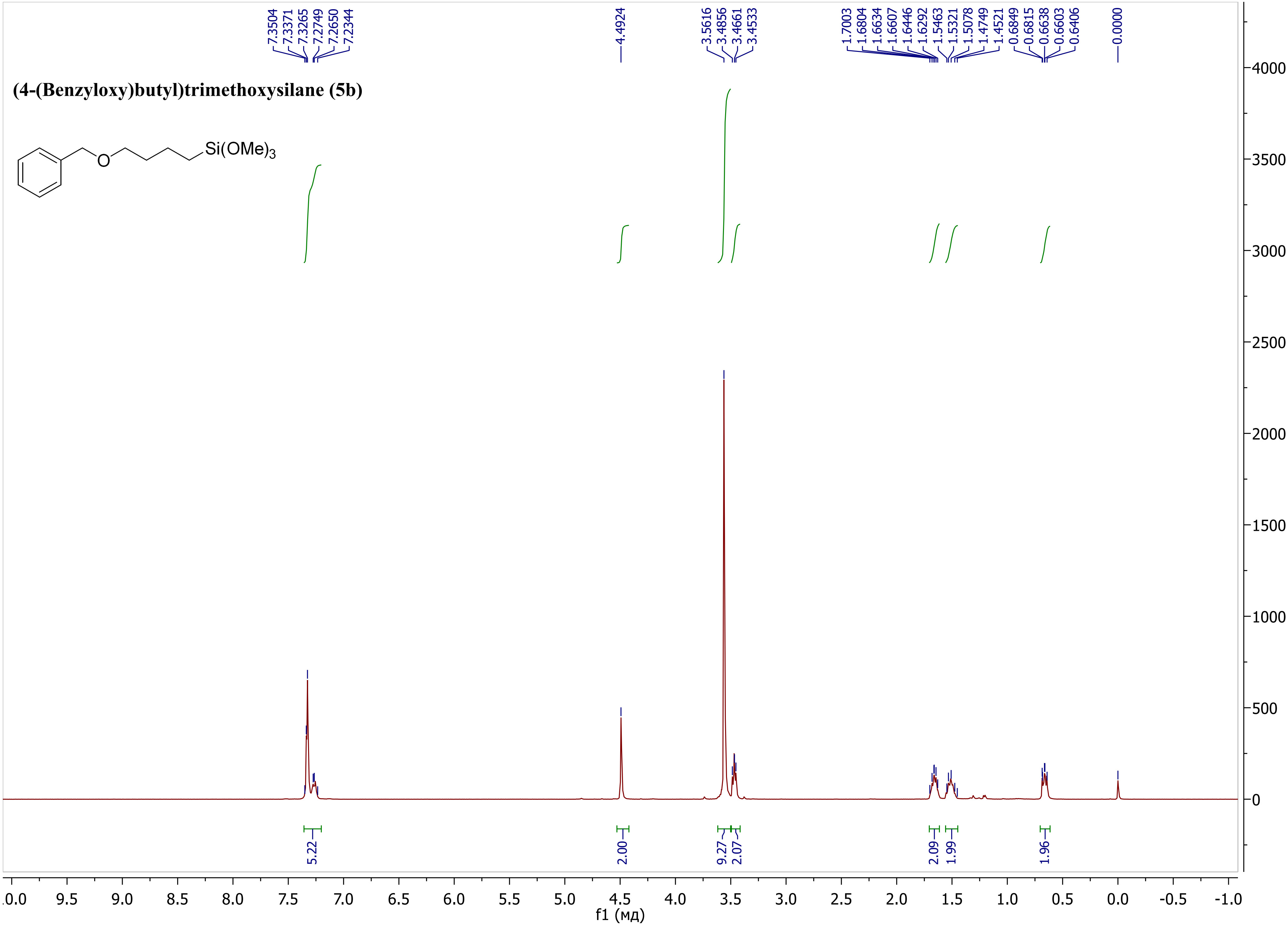
Trimethoxy(tetradecyl)silane (5a)



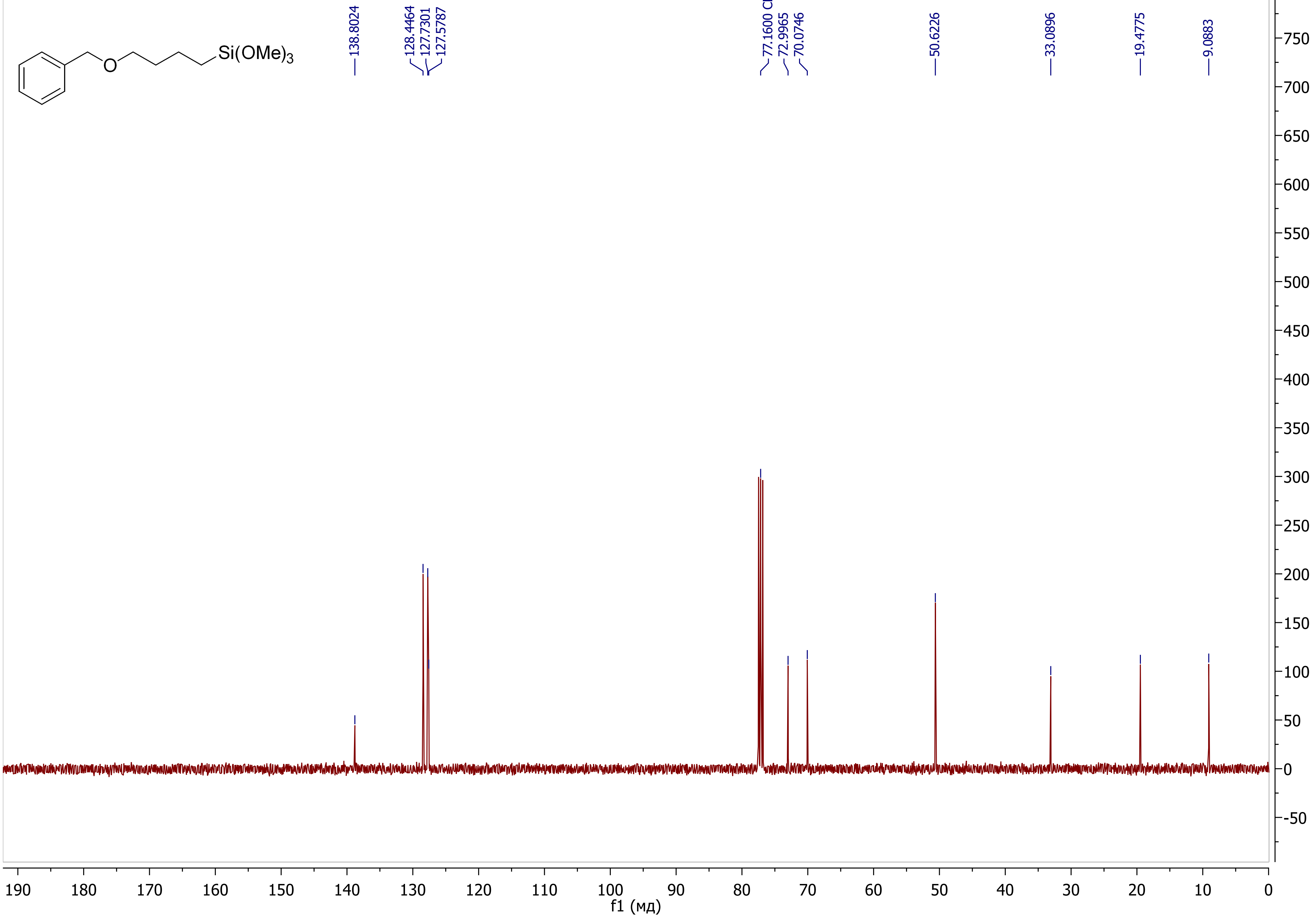
Trimethoxy(tetradecyl)silane (5a)



(4-(Benzyloxy)butyl)trimethoxysilane (5b)



(4-(Benzyloxy)butyl)trimethoxysilane (5b)



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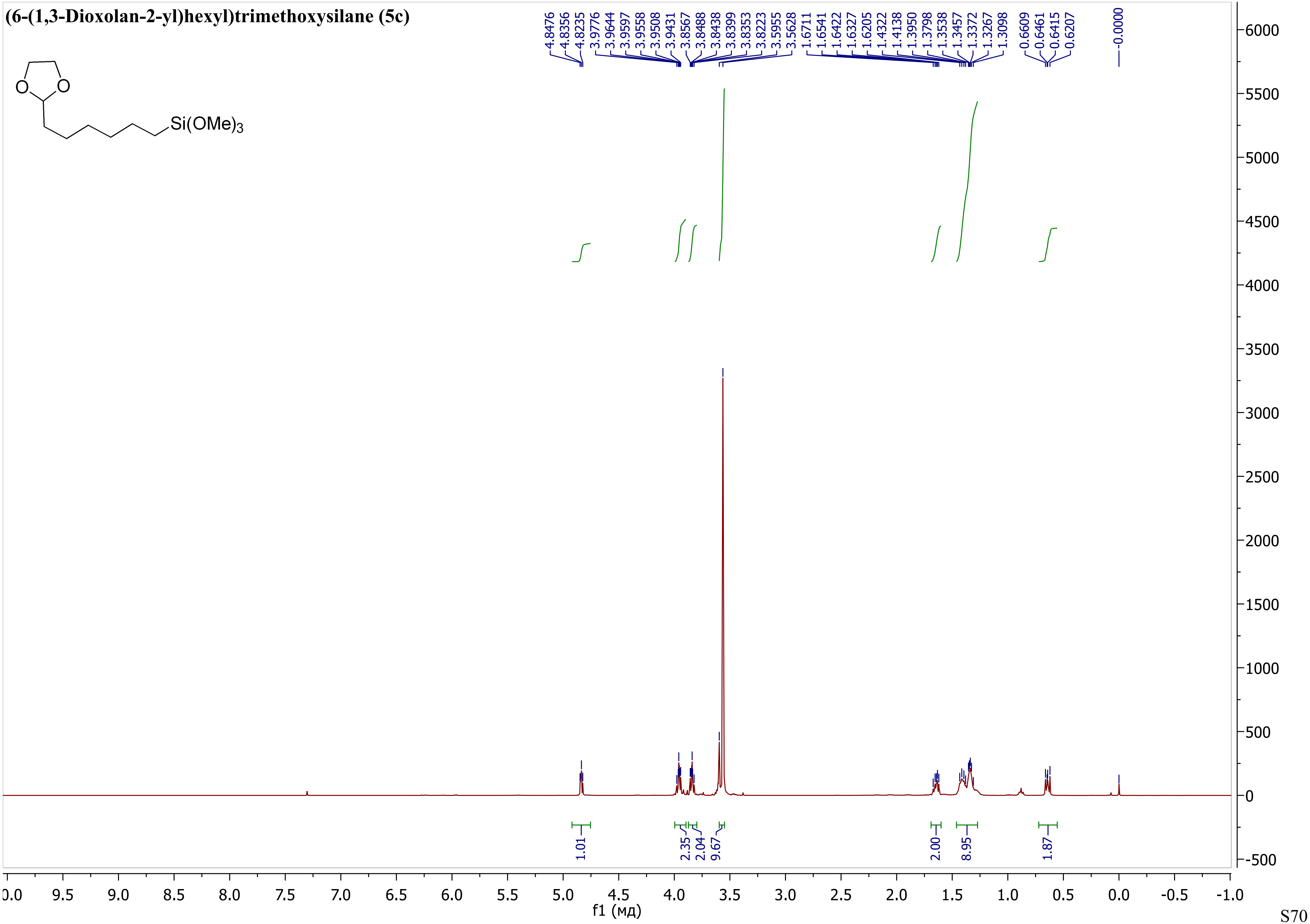

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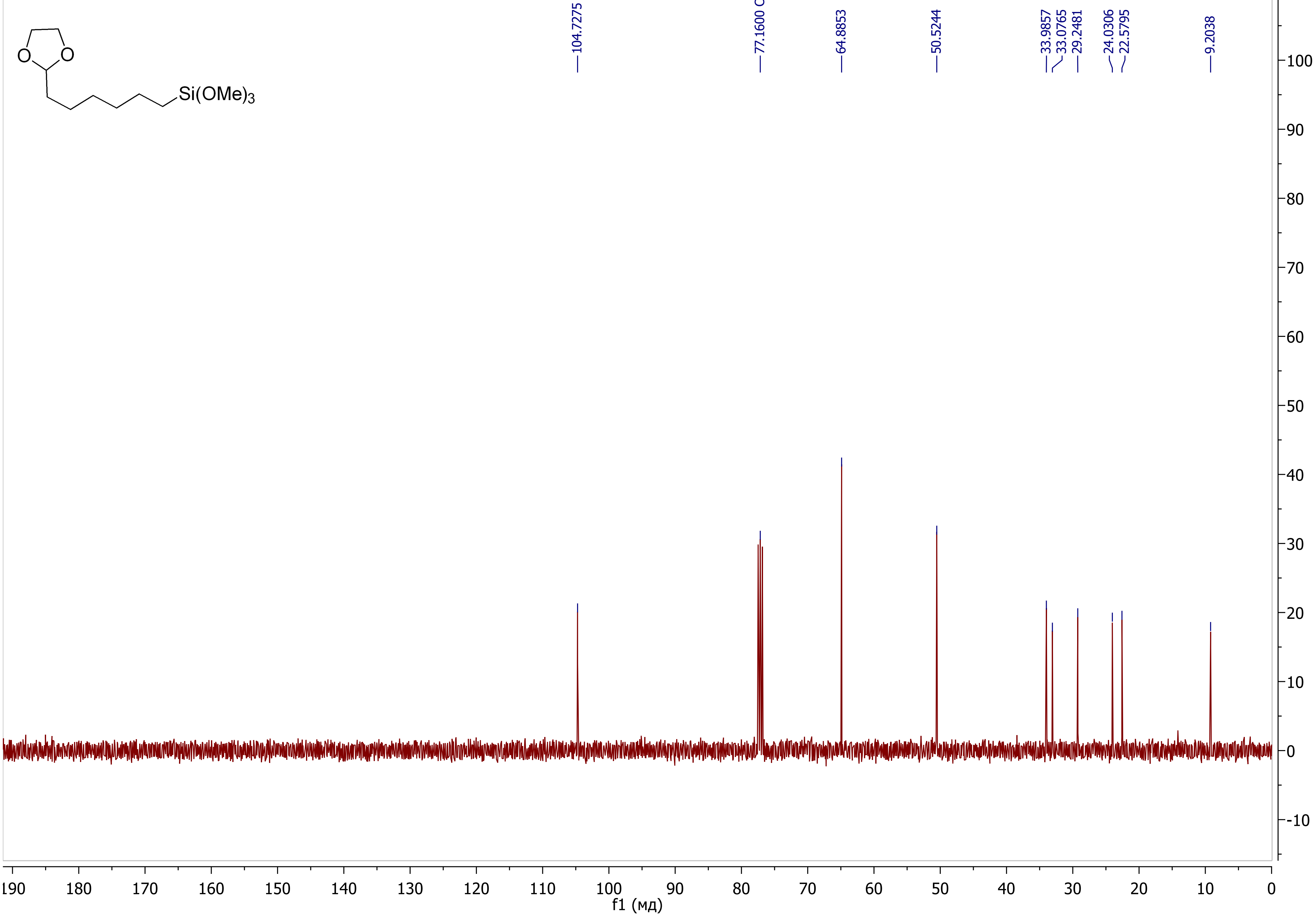
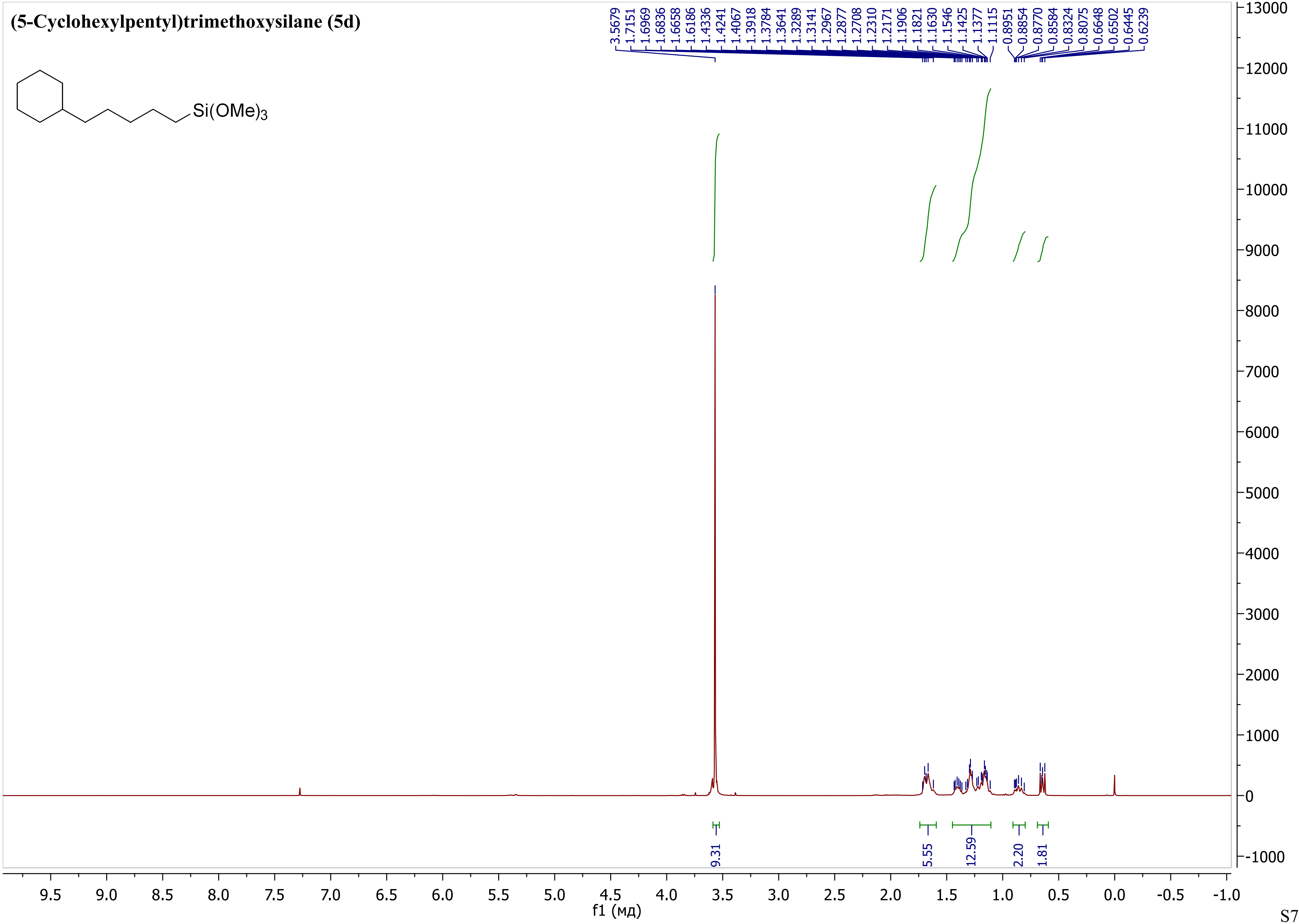
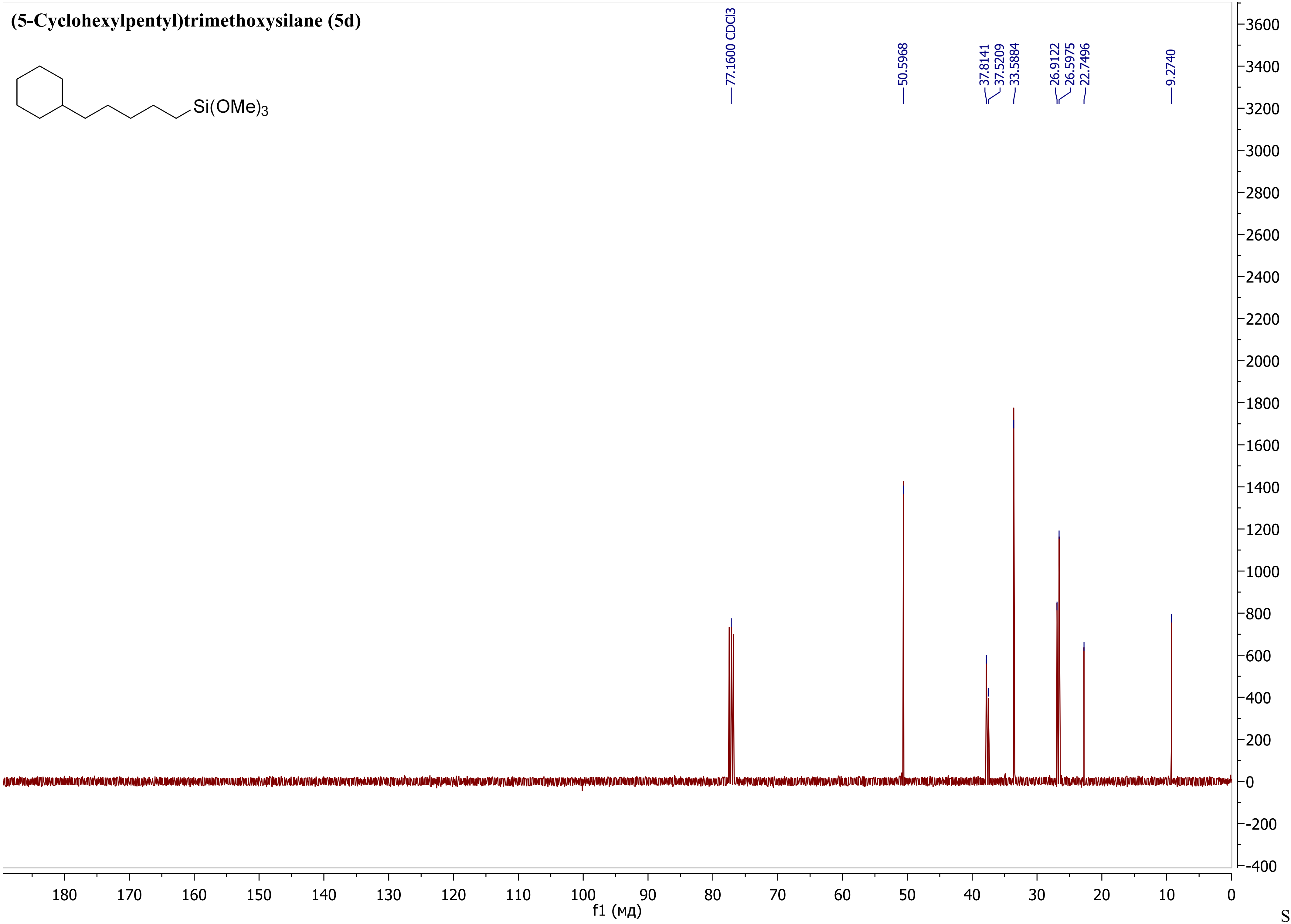


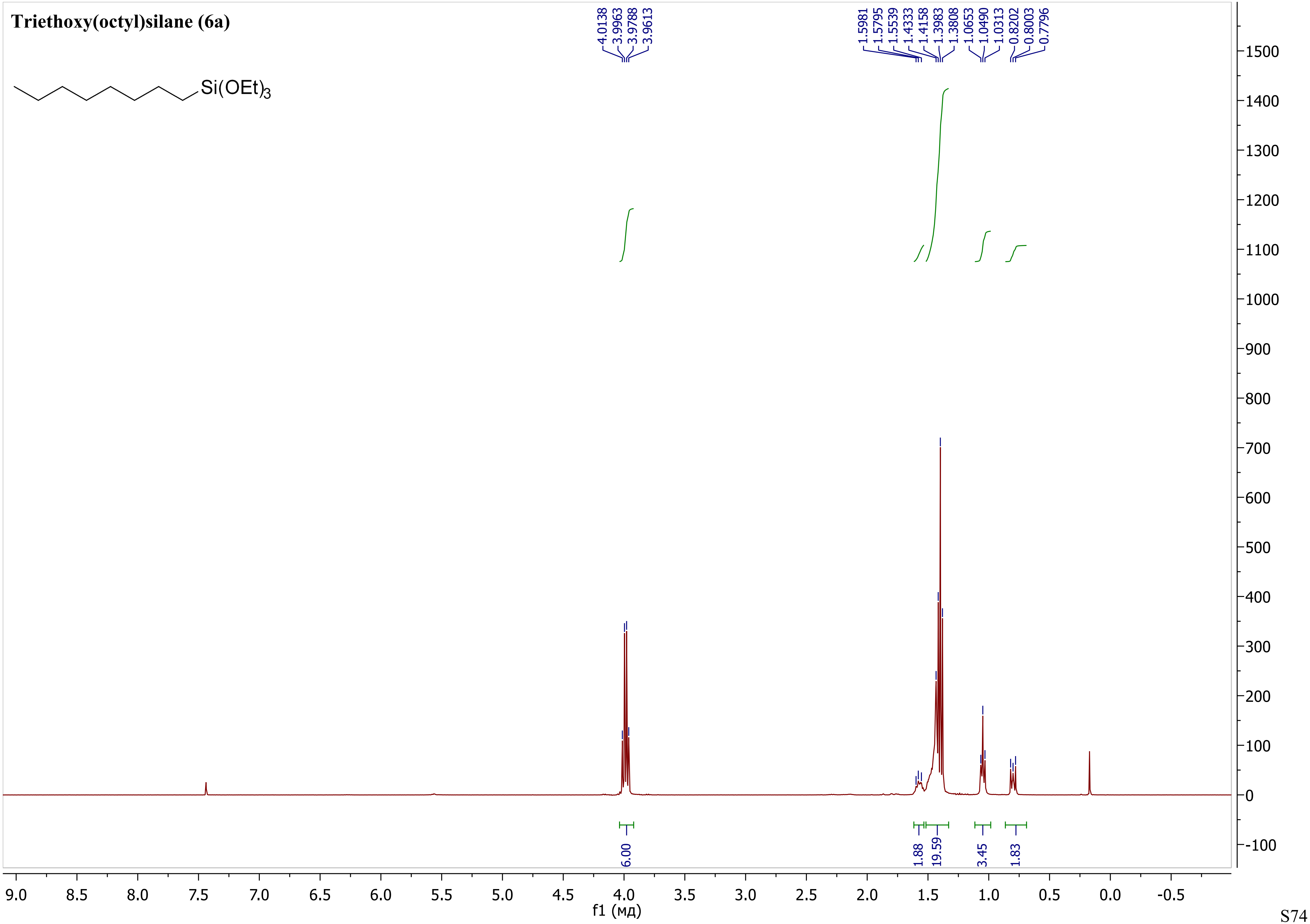
(5-Cyclohexylpentyl)trimethoxysilane (5d)



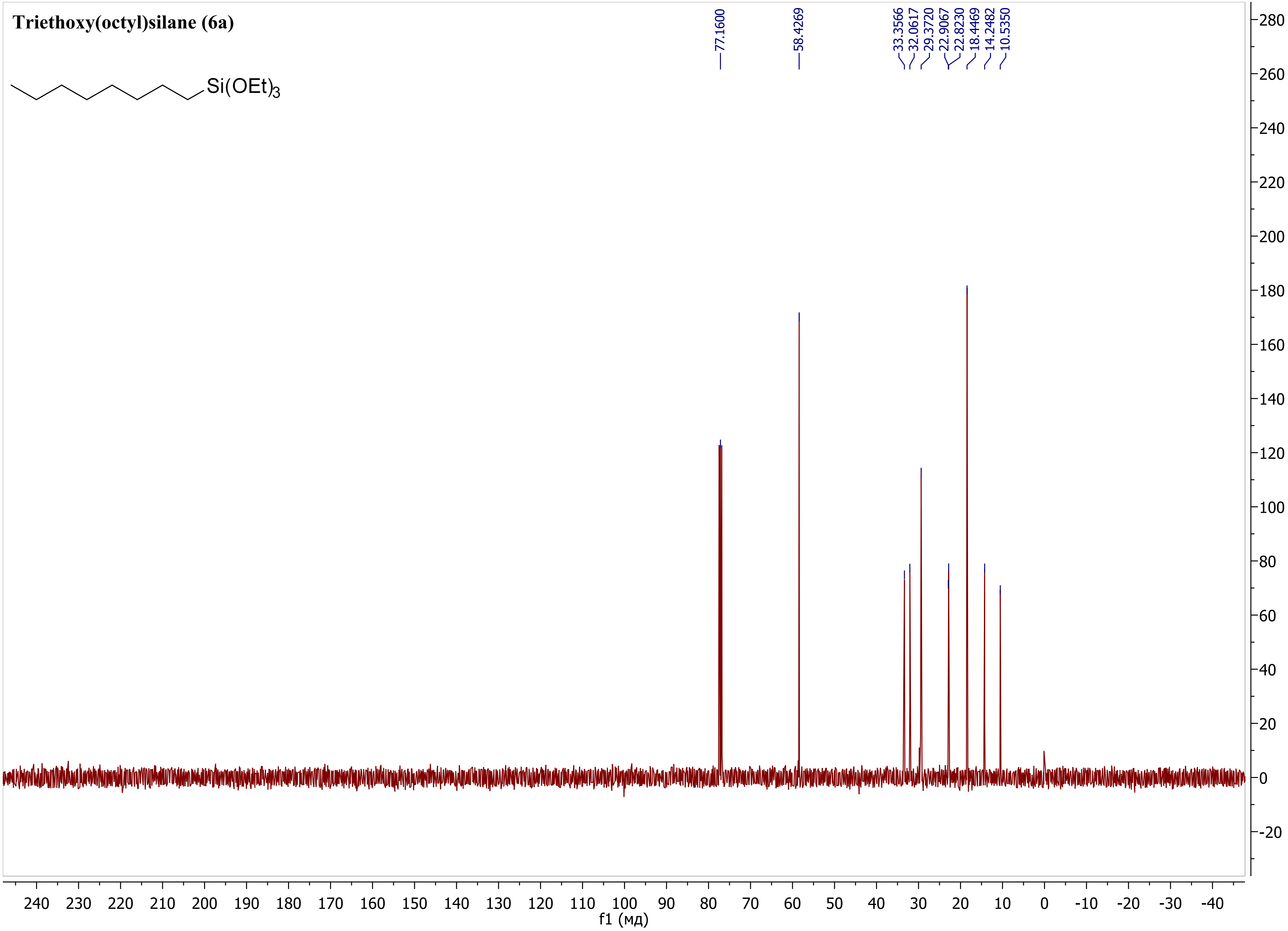
(5-Cyclohexylpentyl)trimethoxysilane (5d)



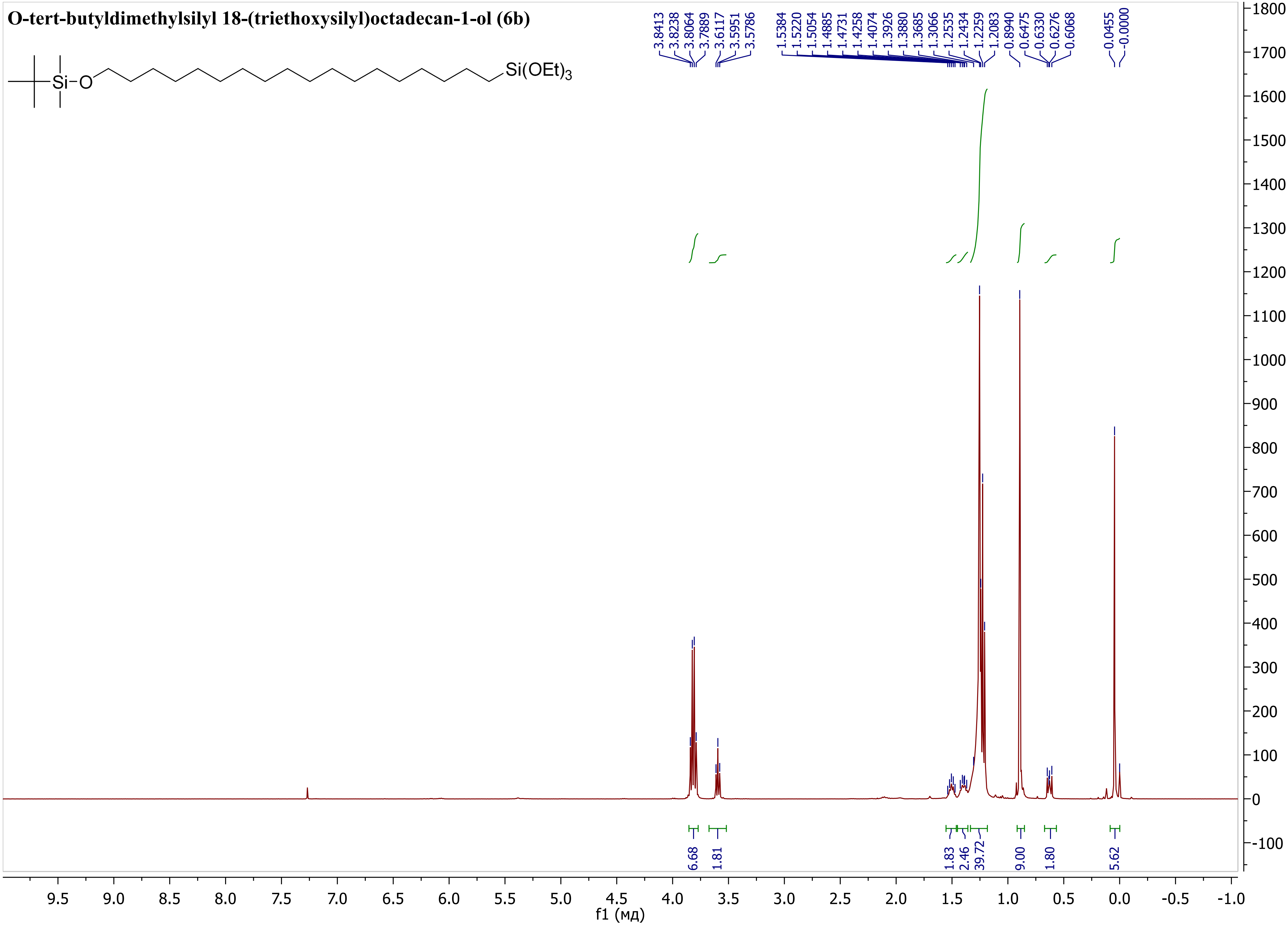
Triethoxy(octyl)silane (6a)



Triethoxy(octyl)silane (6a)



O-tert-butyldimethylsilyl 18-(triethoxysilyl)octadecan-1-ol (6b)



O-tert-butyldimethylsilyl 18-(triethoxysilyl)octadecan-1-ol (6b)