Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Information

Sequential hydrothiolation-hydrosilylation: a route to the creation of new organosilicon compounds with preset structures

Ilya Krizhanovskiy[a], Maxim Temnikov [a], Fedor Drozdov[b], Alexander Peregudov [a], Anton Anisimov [a*]**

[a] A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS) Russia, Moscow, Vavilova St. 28,

[b] Enikolopov Institute of Synthetic Polymeric Materials Russian Academy of Sciences (ISPM RAS), Russia, Moscow

*anisimov@ineos.ac.ru

**temnikov88@gmail.com

Contents

Common information

All the solvents were purified before use as described earlier[1].

Vinyldimethylsilane was synthesized using a known procedure[2].

Cis-tetra[vinyl(dimethylsiloxy)]tetrasiloxane was synthesized according to the published technique[3].

3-(trimethoxysilyl)propane-1-thiol, thioacetic acid, benzenethiol, 4-chlorobenzenethiol, decane-1-thiol, mercaptosuccinic acid and mercaptoacetic acid were purchased from Acros. Vinyldimethylchlorosilane, trichlorosilane, methyltrichlorosilane, methyldichlorosilane were purchased from Sigma-Aldrich.

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AvanceTM 500 spectrometer (Germany) (at 500.13, 125.47, and 99.36 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively). The ^{1}H chemical shifts were measured relative to TMS using residual signal of solvent $CDCl_3$ (7.26 ppm). The ^{13}C chemical shifts were measured relative to TMS using signal of solvent $CDCl_3$ (77.16 ppm). The ^{29}Si chemical shifts were measured relative to TMS used as the external standard.

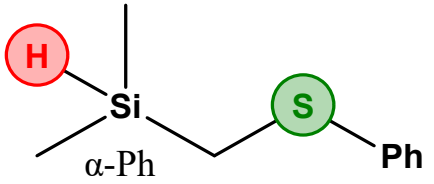
IR spectra were recorded on an IR spectrometer with a Fourier transformer Shimadzu IRTracer-100. KBr pellets and thin layers on KBr windows were used as samples.

High-resolution mass spectra (HRMS) of compounds were measured using a Bruker micrOTOF II instrument with electrospray ionization (ESI).

GPC analysis was performed on the "Shimadzu" (Japan, Germany), the detector - refractometer RID - 20 Å, the column – Phenogel 5u 500Å (Size (300 x 7,8 mm)); standart – polystyrene, eluent – toluene, THF; temperature - 40°C; speed of flow 1ml/sec.

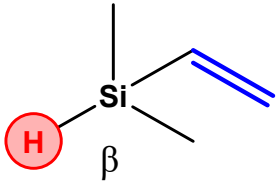
Thiol-ene radical addition

Synthesis of dimethyl(vinyl)silane (compound α-Ph): Synthesis and spectra were described in [4].

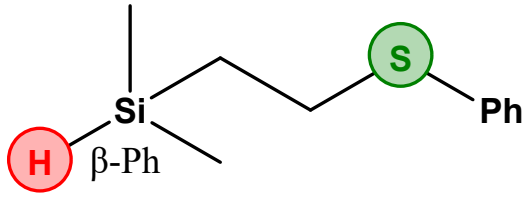


^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 7.35 – 7.27 (m, 4H), 7.18 – 7.11 (m, 1H), 4.14 – 4.07 (m, 1H), 2.29 (d, J = 3.0 Hz, 2H), 0.27 (d, J = 3.7 Hz, 6H).

Synthesis of dimethyl(vinyl)silane (compound β): Synthesis and spectra were described in [2].



Synthesis of dimethyl(2-(phenylthio)ethyl)silane (compound β-Ph): A mixture of benzenethiol (0.3 g, 2.7 mmol) and **compound β** (0.47 g, 5.4 mmol) in dry hexane (2 ml) was irradiated by UV lamp for 4 hours under stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.52 g) was 98%.



^{1}H NMR (500 MHz, C_6D_6, δ/ppm, J/Hz): δ 7.28 (d, J = 7.5 Hz, 2H), 7.03 (t, J = 7.7 Hz, 2H), 6.93 (t, J = 7.4 Hz, 1H), 4.00 – 3.95 (m, 1H), 2.83 – 2.78 (m, 2H), 0.90 – 0.85 (m, 2H), -0.10 (d, J = 3.7 Hz, 6H).

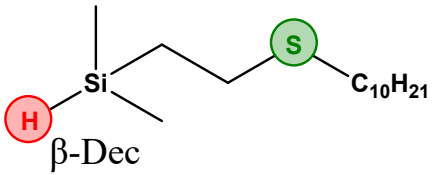
^{13}C NMR (126 MHz, C_6D_6, δ/ppm, jmod): 137.49, 129.04, 128.77, 125.53, 29.56, 14.27, -4.96.

^{29}Si NMR (99 MHz, C_6D_6, δ/ppm): -13.76.

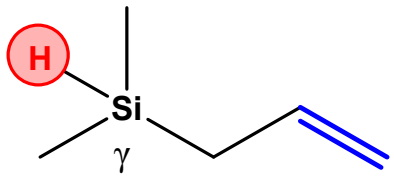
IR: 3075, 3060, 2958, 2920, 2857, 2115, 1585, 1481, 1439, 1262, 1250, 1164, 1092, 1069, 1026, 1012, 906, 886, 837, 738, 691 cm^{-1}.

CHN: Calc. (%) for $C_6H_{16}OSi_2$, MM: 196.38, C, 61.16; H, 8.21; S, 16.33; Si, 14.30. Found: (%) C, 61.14; H, 8.23; S, 16.32; Si, 14.31 %.

Synthesis of dimethyl(2-(decylthio)ethyl)silane (compound β-Dec): Synthesis and spectra were described in [5].

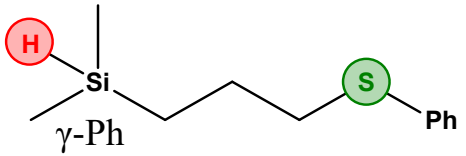


Synthesis of allyldimethylsilane (compound γ): The solution of 30.5 g (0.4 mol, 1 eq) of 3-chloroprop-1-ene in 160 ml of THF was added slowly to 12.2 g (0.5 mol, 1.25 eq) of Mg under argon atmosphere at room temperature. Then the 37.8 g (0.4 mol, 1 eq) of chlorodimethylsilane was added also dropwise and after the end of the dropping the reaction mixture was stirred continually for 12 h. Then the saturated NH4Cl solution was added to the reaction mixture. The solution was filtered from the resulting precipitate and the decane was added to the resulting solution. THF was washed from this solution with distilled water. The organic solution was dried overnight with anhydrous sodium sulfate. The target product was obtained as colorless oil by distillation (BP = 60 °C, atm) and a yield 72% (28.8 g) were obtained.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 5.88 – 5.76 (m, 1H), 4.95 – 4.84 (m, 2H), 3.93 – 3.84 (m, 1H), 1.62 (d, J = 7.8 Hz, 2H), 0.11 (d, J = 3.6 Hz, 6H).

Synthesis of dimethyl(3-(phenylthio)propyl)silane (compound γ-Ph): A mixture of benzenethiol (0.3 g, 2.7 mmol) and **compound γ** (0.541 g, 5.4 mmol) in hexane (2 ml) was irradiated by UV lamp for 4 hours under



stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.55 g) was 97%.

^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm, J/Hz): 7.41 – 7.31 (m, 4H), 7.25 – 7.19 (m, 1H), 3.91 (dp, J = 7.1, 3.6 Hz, 1H), 3.00 (t, J = 7.4 Hz, 2H), 1.81 – 1.69 (m, 2H), 0.83 – 0.75 (m, 2H), 0.12 (d, J = 3.7 Hz, 6H).

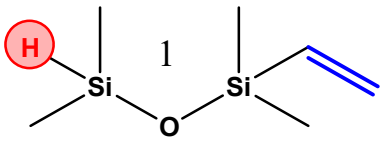
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm, jmod): 136.77 (s), 128.96 (s), 128.76 (s), 125.66 (s), 36.79 (s), 24.30 (s), 13.70 (s), -4.58 (s).

^{29}Si NMR (99 MHz, C_6D_6, δ/ppm): 13.20.

IR: 2955, 2922, 2111, 1585, 1481, 1439, 1250, 886, 837, 737, 690 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{11}H_{18}SSi + H]^+$ 209.0815, found 209.0836.

Synthesis of 1,1,3,3-tetramethyl-1-vinyldisiloxane (compound 1): A round-bottom single-neck flask, equipped with a reflux condenser was charged with 1,1,3,3-tetramethyldisiloxane (43.26 g, 0.322 mol), 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (20 g, 0.107 mol) and sulfonic resin (3.15 g). A mixture was heated at 70 °C for 2 hours. After that, the solution was separated from sulfonic resin by filtration and the target product (17.28 g, yield 61% and GC purity 99%) was purified by distillation at the atmospheric pressure.



^{1}H NMR (600 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.14-0.16 (s, 6H); 0.17-0.23 (d, 6H, J = 2.8 Hz); 4.62-4.76 (septet, 1H, J = 2.8 Hz); 5.66-6.19 (m, 3H).

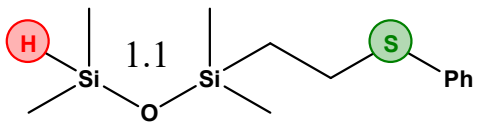
^{13}C NMR (151 MHz, $CDCl_3$, δ/ppm): 0.10; 0.86; 131.91; 139.11.

^{29}Si NMR (119 MHz, $CDCl_3$, δ/ppm): -5.77; 1.79.

IR: 3046, 2961, 2904, 2125, 1407, 1255, 1061, 1009, 956, 910, 838, 817, 785, 706 cm^{-1}.

CHN: Calc. (%) for $C_6H_{16}OSi_2$, MM: 160,36, C, 44.94; H, 10.06; O, 9.98; Si, 35.03. Found: (%) C, 44.98; H, 10.03; O, 9.92; Si, 35.07.

Synthesis of 1,1,3,3-tetramethyl-1-(2-(phenylthio)ethyl)disiloxane (compound 1.1): A mixture of benzenethiol (0.081 g, 0.7 mmol) and **compound 1** (0.237 g, 1.4 mmol) in dry hexane (1 ml) was irradiated by UV lamp for 4 hours under stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.19 g) was 97%.



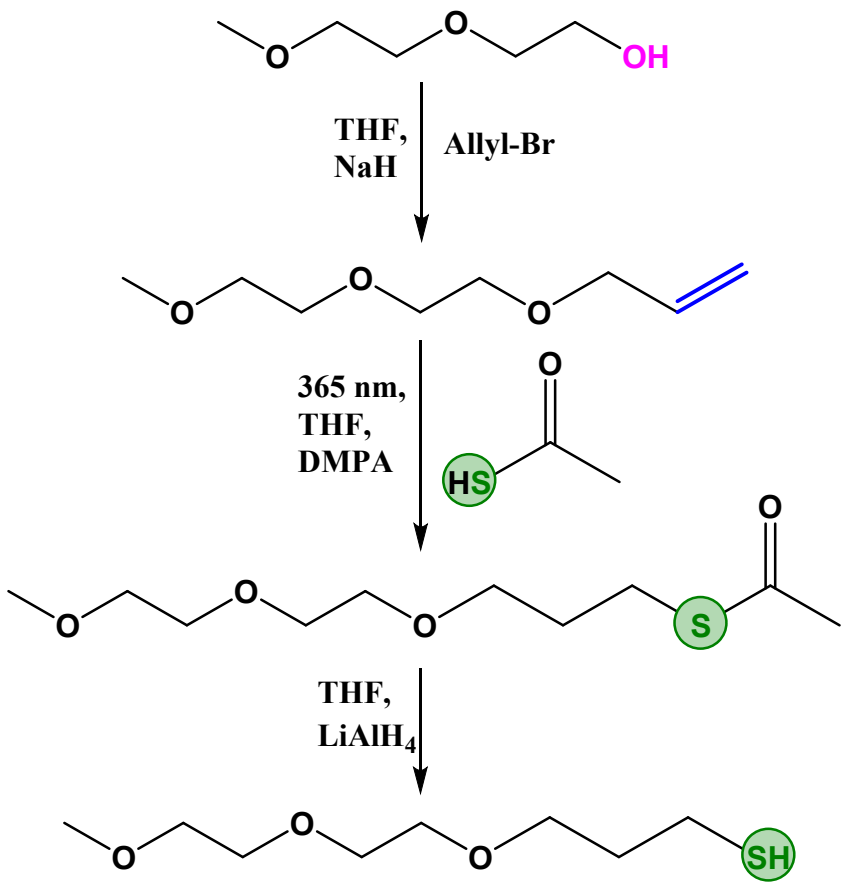
^{1}H NMR (600 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.13-0.15 (s, 6H); 0.19-0.21 (d, 6H, J = 2.0 Hz); 0.96-1.02 (m, 2H); 2.99-3.03 (m, 2H); 4.69-4.73 (m, 1H); 7.17-7.37 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$, δ/ppm): 137.12, 128.97,128.84, 125.71, 28.71, 18.41, 0.88, 0.11.

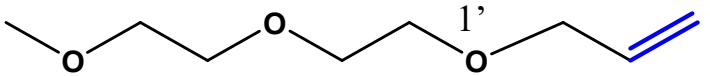
^{29}Si NMR (119 MHz, $CDCl_3$, δ/ppm): 8.14, -5.85.

IR: 2957, 2121, 1255, 1062, 909, 838, 817, 786 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$calcd for $[C_{12}H_{22}OSSi_2 + H]^+$ 269.0846, found 269.0851; $[M+NH_4]^+$ calcd for $[C_{12}H_{22}OSSi_2 + NH_4]^+$ 287.1190, found 287.0944; $[M+Na]^+$ calcd for $[C_{12}H_{22}OSSi_2 + Na]^+$ 293.0822, found 293.1253;



Methods of synthesis for derivatives of 1,1,3,3-tetramethyl-1-vinyldisiloxane and 1,1-diethoxy-3,3-dimethyl-1-vinyldisiloxane (compounds 13-14, 16) through thiol-ene reaction.

Synthesis of 3-[2-(2-methoxyethoxy)-ethoxy]-prop-1-ene (compound 1'): All synthetic 

operations were carried out under argon atmosphere. A solution of 2-(2-methoxyethoxy)ethanol (10.0 g, 0.0833 mol) in dry THF (120 mL) was added

in drops to a suspension of sodium hydride (2.2 g, 0.0916 mol) in dry THF (30 mL) under stirring. After 2 h a solution of allyl bromide (12.1 g, 0.1000 mol) in dry THF (20 mL) was added after which the mixture was boiled for 5 hours and left to stir overnight at room temperature. Next, after filtation, the solvent was evaporated off. The target product (12.42 g, yield 93%) was purified by distillation.

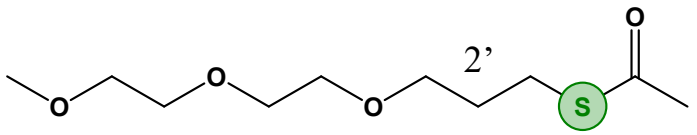
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.34 (s, 3H); 3.47-3.67 (m, 8H); 3.92-4.08 (d, 2H, J = 5.6 Hz); 5.07-5.30 (m, 1H); 5.79-5.94 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 58.97; 69.36; 70.51; 70.60; 71.88; 72.17; 117.01; 134.70.

IR: 926 cm^{-1}, 1110, 1457, 1649, 2873, 3080 cm^{-1}.

HRMS (ESI) m/z $[M + H]^+$: calcd for $[C_8H_{16}O_3 + H]^+$, 161.1172; found, 161.1171; $[M + NH_4]^+$: calcd for $[C_8H_{16}O_3 + NH_4]^+$, 178.1438; found, 178.1438; $[M + Na]^+$: calcd for $[C_8H_{16}O_3 + Na]^+$, 183.0992; found, 183.0992.

Synthesis of 3-[2-(2-(2-methoxy)-ethoxy)-ethoxy]-propyl thioacetate (compound 2'): A mixture of **compound 1'** (4.00 g, 0.0250 mol), thioacetic acid (2.09 g, 0.0275 mol), DMPA (0.1218 g, 0.4752 mmol) in THF (60 ml) was irradiated by UV lamp for 4 hours under stirring at room temperature. After that irradiated mixture was filtered through the silica gel and evaporated under 1 Torr till the constant weight. The product was pale yellow oil (5.78 g, yield 98% and GC purity 96%).

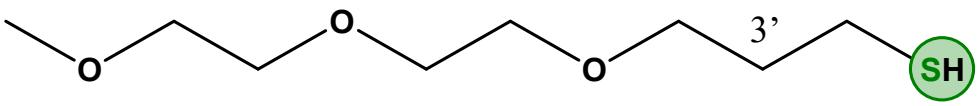


^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 1.77-1.89 (quint, 2H, J = 6.8 Hz); 2.30 (s, 3H); 2.86-2.97 (t, 2H, J = 7.2 Hz); 3.36 (s, 3H); 3.44-3.68 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 25.90; 29.48; 30.52; 58.93; 69.47; 70.11; 70.46; 71.85; 195.71.

IR: 628, 1111, 1692, 2873 cm^{-1}.

HRMS (ESI) m/z $[M + H]^+$: calcd for $[C_{10}H_{20}O_4S + H]^+$, 237.1159; found, 237.1155; $[M + NH_4]^+$: calcd for $[C_{10}H_{20}O_4S + NH_4]^+$, 254.1425; found, 254.1421; $[M + Na]^+$: calcd for $[C_{10}H_{20}O_4S + Na]^+$, 259.0978; found, 259.0975.



Synthesis of 3-[2-(2-methoxyethoxy)-ethoxy]-1-propanethiol (compound 3'): All synthetic operations were carried out under argon atmosphere. A solution of **compound 2'** (5.78 g, 0.0245 mol) in dry ether (20 mL) was added in drops to a suspension of lithium aluminium hydride (1.39 g, 0.0367 mol) in dry THF (10 mL) under stirring at 0°C. The mixture was then stirred for 5 hours at room temperature. Further, the excess of LAH was decomposed and the precipitate was coagulated by slowly (dropwise) adding of a saturated aqueous solution of NH_4Cl (50 mL) to the mixture with stirring (under argon and at 0-5°C temperature). The solution was separated from the precipitate by filtration, the precipitate was washed with 3x25 mL of hexane. Extracts were connected to the solution, dried over Na_2SO_4 and evaporated under 1 Torr. The product (3.71 g, yield 74%) was further purified by Kugelrohr distillation (160°C, 1 Torr) to get the target compound.

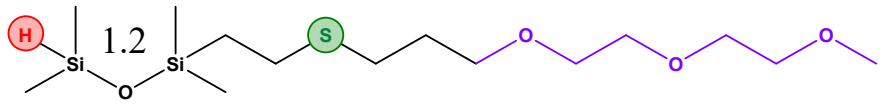
^1H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 1.30-1.41 (t, 1H, J = 8.0 Hz); 1.79-1.90 (quint, 2H, J = 6.4 Hz); 2.54-2.65 (q, 2H, J = 3.2 Hz); 3.35 (s, 3H); 3.48-3.74 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 21.41; 33.71; 59.02; 69.06; 70.18; 70.58; 71.91.

IR: 528, 851, 1112, 1456, 2557, 2868, 2921 cm^{-1}.

HRMS (ESI) m/z $[M + H]^+$: calcd for $[C_8H_{18}O_3S + H]^+$, 195.1049; found, 195.1055; $[M + NH_4]^+$: calcd for $[C_8H_{18}O_3S + NH_4]^+$, 212.1315; found, 212.1322; $[M + Na]^+$: calcd for $[C\ C_8H_{18}O_3S + Na]^+$, 217.0889; found, 217.0877.

Synthesis of 1,1,3,3-tetramethyl-1-[2-(3-[2-(2-methoxyethoxy)ethoxy]propylthio)ethyl] disiloxane (compound 1.2): A



1.2

mixture of **compound 3'** (2.00 g, 0.0103 mol) and **compound 1** (3.30 g, 0.0206 mmol) in THF (30 ml) was irradiated by UV lamp for 4 hours under stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight. The product was pale colorless oil (3.65 g, yield 99% and GC purity 95%).

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.07 (s, 6H); 0.11-0.18 (d, 6H, J = 2.1 Hz); 0.82-0.91 (m, 2H); 1.77-1.89 (quint, 2H, J = 7.2 Hz); 2.46-2.65 (m, 4H); 3.35 (s, 3H); 3.46-3.68 (m, 10H); 4.57-4.71 (m, 1H).

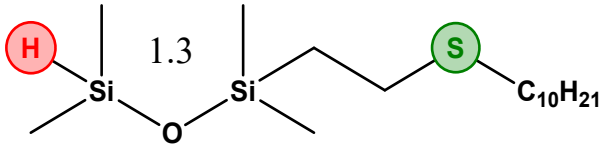
^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 0.02; 0.83; 18.76; 26.72; 28.44; 29.51; 58.99; 69.83; 70.15; 70.51; 71.89.

^{29}Si NMR (100 MHz, $CDCl_3$, δ/ppm): -8.14 ($\underline{Si}(CH_3)_2CH_2CH_2S$); 6.12 ($\underline{Si}(CH_3)_2H$).

IR: 841, 911, 1060, 1113, 1256, 1455, 2120, 2873, 2954 cm^{-1}.

HRMS (ESI) m/z $[M + Na]^+$: calcd for $[C_{14}H_{34}O_4SSi_2 + Na]^+$, 377.1609; found, 377.1599.

Synthesis of 1-(2-(decylthio)ethyl)-1,1,3,3-tetramethyldisiloxane (compound 1.3): A mixture of decane-1-thiol (0.052 g, 0.3 mmol) and **compound 1** (0.143 g, 0.9 mmol) in dry hexane (0.5 ml) was irradiated by UV lamp for 4 hours under stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight. The product was pale colorless oil (0.98 g, yield 98% and GC purity 100%).



1.3

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 4.72 – 4.68 (m, 1H), 2.61 – 2.56 (m, 2H), 2.53 (t, J = 7,5 2H), 1.62 – 1.56 (m, 2H), 1.43 – 1.36 (m, 2H), 1.34 – 1.26 (m, 14H), 0.94 – 0.87 (m, 5H combined signal from Si-CH_2 and CH_3 in tiodecyl part), 0.18 (d, J = 2.8 Hz, 6H), 0.12 (s, 6H).

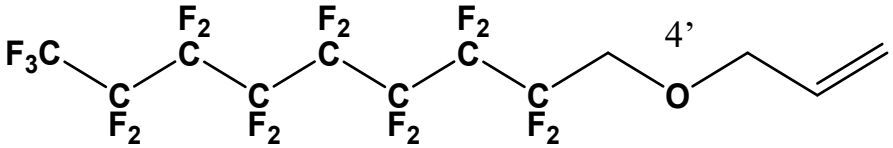
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm, jmod): 31.90 (s), 31.88 (s), 29.60 (s), 29.57 (s), 29.55 (s), 29.32 (s), 29.28 (s), 29.00 (s), 26.74 (s), 22.68 (s), 18.90 (s), 14.10 (s), 0.85 (s), 0.04 (s).

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): δ 8.19 (s), -6.16 (s).

IR: 2957, 2926, 2855, 2122, 1254, 1063, 908, 840, 817 cm^{-1}.

HRMS (ESI) m/z $[M + H]^+$: calcd for $[C_{16}H_{38}OSSi_2 + H]^+$, 333.2098; found, 333.2091.

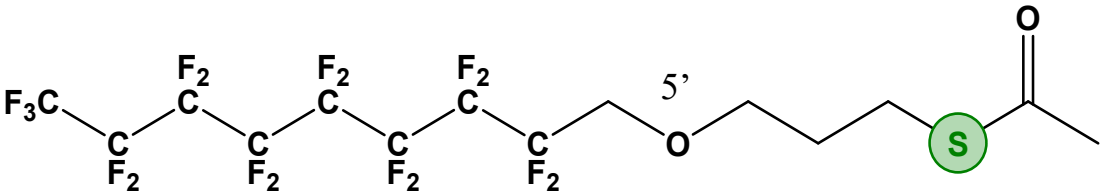
Synthesis of allyloxy-1H,1H-heptadecafluorononane (compound 4'): was proceed according (and describe here [DOI: 10.1134/S1070363214110139] and here [DOI: 10.1021/ja992794r]). 100.04 g (0.22 mol) of 1H,1H-heptadecafluoro-1-nonanol was dissolved in 500 ml of dry dioxane under argon. 9.8 g (0.24 mol) of NaOH was added portionwise and the reaction mixture was stirred at 65 °C for 3 h. Then, 34.9 g (0.29 mol) of allyl bromide was added to the reaction mixture dropwise and stirred under heating for 18 hours. After the reaction was completed, the mixture was extracted with methyl tert-butyl ether (2x500 ml) and washed with water 3 times. The organic layer was dried over sodium sulfate. The solvent was distilled off under reduced pressure. The pure product was obtained by fractional distillation under a vacuum of 75-80 mbar. Collected the fraction with b.p. = 140 - 143 °C. The product yield was 96 g (89%).



^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 5.97 – 5.80 (m, 1H), 5.38 – 5.24 (m, 2H), 4.14 (d, J = 5.7 Hz, 2H), 3.93 (t, J = 14.0 Hz, 2H).

Full description can be found here [6].

Synthesis of thioacetoxypropyl-1H,1H-heptadecafluorononane (compound 5'): 19.11 g (0.039 mol) of **compound 4'** were dissolved in 100 ml of dry methyl tert-butyl ether and 4.45 g (0.058 mol) of thioacetic acid were added. Traces



DMPA was added and the mixture was bubbled with argon for 10 min. Then the mixture was irradiated with UV light (365 nm) for 16 h. After the reaction was completed, the mixture was washed with sodium carbonate solution and water. Dried over sodium sulfate. The solvent was distilled off under reduced pressure. The product was dried under reduced pressure (0.1 mbar) and used further without purification. The product yield was 20.1 g (88% of theory).

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.92 (t, J = 13.9 Hz, 2H), 3.64 (t, J = 6.0 Hz, 2H), 2.94 (t, J = 7.1 Hz, 2H), 2.32 (s, 3H), 1.95 – 1.81 (m, 2H).

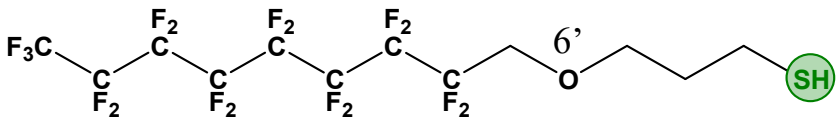
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm): 195.74 (s), 122.85 (t, J = 33.0 Hz), 119.73 – 118.30 (m), 116.12 – 114.91 (m), 114.83 – 113.42 (m), 112.96 – 111.51 (m), 111.49 – 110.15 (m), 109.31 – 107.45 (m), 107.37 – 103.86 (m), 71.31 (s), 67.87 (t, J = 25.6 Hz), 30.50 (s), 29.56 (s), 25.52 (s).

^{19}F NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): -81.01 (t, J = 10.0 Hz), -119.73 (s), -122.12 (s), -122.88 (s), -123.51 (s), -126.30 (s).

IR: 2931, 2884, 1696, 1357, 1333, 1243, 1206, 1148, 1135, 1007, 958 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{14}H_{11}F_{17}O_2S+ nH]^+$ 567.0281, found 567.0290; $[M+NH_4]^+$ calcd for $[C_{14}H_{11}F_{17}O_2S + NH_4]^+$ 584.0547, found 584.0560; $[M+NH_4]^+$ calcd for $[C_{14}H_{11}F_{17}O_2S + Na]^+$ 589.0101, found 589.0103; $[M+K]^+$ calcd for $[C_{14}H_{11}F_{17}O_2S + K]^+$ 604.9840, found 604.9850;

Synthesis of 3-((2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)oxy)propane-1-thiol (compound 6'): 0.04 g (1.8 mmol) of metallic sodium was dissolved in 20 ml of dry ethylene glycol. The mixture was



stirred until sodium was dissolved totally. Next, 20.1 g (0.035 mol) of **compound 5'** were added dropwise and the mixture was refluxed for 2 hours. The reaction mixture was extracted with diethyl ether, washed with 1N hydrochloric acid and water. The organic layer was dried over sodium sulfate. The solvent was distilled off under reduced pressure. The pure product was obtained by fractional distillation under vacuum of 0.5 mbar. Collected the fraction with b.p. = 73 - 75 °C. The product yield was 13.4 g (75%).

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.96 (t, J = 13.8 Hz, 2H), 3.74 (t, J = 5.9 Hz, 2H), 2.66 (q, J = 15.1, 7.0 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.37 (t, J = 8.1 Hz, 1H).

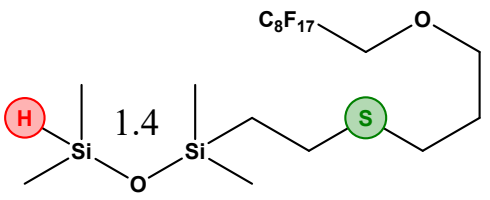
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm): 118.27 (t, J = 32.9 Hz), 117.60 (t, J = 30.6 Hz), 115.98 (t, J = 33.1 Hz), 115.55 (t, J = 30.8 Hz), 114.00 – 112.50 (m), 111.49 – 110.73 (m), 110.77 – 110.14 (m), 109.06 – 108.11 (m), 70.81 (s), 67.95 (t, J = 25.6 Hz), 33.54 (s), 20.91 (s).

^{19}F NMR (282 MHz, $CDCl_3$, δ/ppm, J/Hz): -80.87 (t, J = 10.0 Hz, 3H), -119.67 (s, 2H), -122.07 (s, 6H), -122.81 (s, 2H), -123.45 (s, 2H), -126.22 (s, 2H).

IR: 662, 706, 1149, 1204, 1241, 1333, 2885, 2944 cm^{-1}.

HRMS (ESI) m/z: $[M+NH_4]^+$ calcd for $[C12H9F17OS+ NH_4]^+$ 542.0441, found 542.0435.

Synthesis of 1,1,3,3-tetramethyl-1-(2-(3-((2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)oxy)propane-1-thio)ethyl)disiloxane (compound 1.4): A mixture of **compound 6'** (0.038 g, 0.073 mmol) and **compound 1** (0.035 g, 0.022 mmol) was irradiated by UV lamp for 4 hours under stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.048 g) was 96%, GPC purity 99%.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): δ 4.73 – 4.68 (m, 1H), 3.96 (t, J = 13.8 Hz, 2H), 3.73 (t, J = 6.1 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 2.61 – 2.57 (m, 2H), 1.95 – 1.86 (m, 2H), 0.97 – 0.88 (m, 2H), 0.19 (d, J = 2.8 Hz, 6H), 0.12 (s, 6H).;

^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm): δ 118.27 (t, J = 32.9 Hz), 117.62 (t, J = 30.6 Hz), 115.98 (t, J = 32.7 Hz), 115.57 (t, J = 30.6 Hz), 113.92 – 112.78 (m), 111.42 – 110.84 (m), 110.92 – 110.06 (m), 109.03 – 108.03 (m), 71.54 (s), 67.94 (t, J = 25.6 Hz), 29.40 (s), 28.00 (s), 26.81 (s), 18.79 (s), 0.77 (s), -0.05 (s).

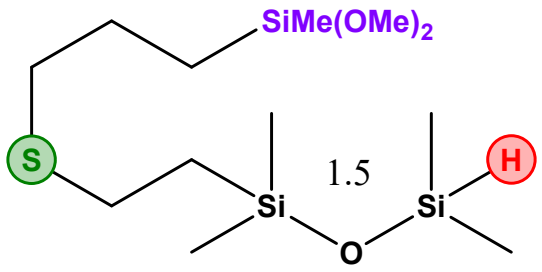
^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): δ -5.99, 8.15;

^{19}F NMR (282 MHz, $CDCl_3$, δ/ppm, J/Hz): δ -80.84 (t, J = 9.0 Hz, 3H), -119.64 (s, 2H), -122.06 (s, 6H), -122.80 (s, 2H), -123.42 (s, 2H), -126.20 (s, 2H).

IR: 2960, 2918, 2886, 2123, 1242, 1212, 1153, 1064, 909, 840 cm^{-1}.

HRMS (ESI) m/z $[M+Na]^+$ calcd for $[C_{18}H_{25}F_{17}O_2SSi_2+ Na]^+$ 707.0735, found 707.0723; $[M+K]^+$ calcd for $[C_{18}H_{25}F_{17}O_2SSi_2+ K]^+$ 723.0474, found 723.0638; $[M+H]^+$calcd fo $[C_{18}H_{25}F_{17}O_2SSi_2+ H]^+$ 683.0759, found 683.0752.

Synthesis of 1-(2-(3-(methyl-dimethoxysilyl-)propylthio)ethyl)-1,1,3,3-tetramethyldisiloxane (compound 1.5): A mixture of (3-mercaptopropyl)-methyl-dimethoxysilane (0.264 g, 1.47 mmol) and **compound 1** (0.706 g, 4.2 mmol) in dry toluene (1 ml) was irradiated by UV lamp for 4 hours under stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight. The product was pale colorless oil (0.48 g, yield 96% and GC purity 100%).



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 4.72 – 4.68 (m, 1H), 3.53 (s, 6H), 2.60 – 2.54 (m, 4H), 1.72 – 1.64 (m, 2H), 0.91 (ddd, J = 9.2, 6.4, 3.6 Hz, 2H), 0.79 – 0.73 (m, 2H), 0.21 – 0.17 (m, 6H), 0.14 (s, J = 3.4 Hz, 3H), 0.12 (s, 6H).

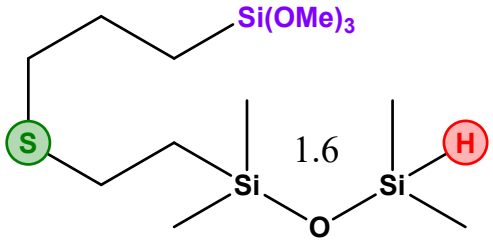
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm, jmod): 50.20, 35.07, 26.64, 23.05, 18.94, 12.69, 0.86, 0.05, -5.77.

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): 8.18, -1.72, -6.09.

IR: 2958, 2939, 2916, 2835, 2121, 1414, 1256, 1190, 1166, 1087, 909, 876, 838, 817, 784, 769 cm^{-1}.

HRMS (ESI) m/z $[M + H]^+$: calcd for $[C_{12}H_{32}O_3SSi_3 + H]^+$, 341.1453; found, 341.1448; $[M + Na]^+$: calcd for $[C_{12}H_{32}O_3SSi_3 + Na]^+$ 363.1272; found, 363.1263.

Synthesis of 1-(2-(3-(trimethoxysilyl-)propylthio)ethyl)-1,1,3,3-tetramethyldisiloxane (compound 1.6): A mixture of (3-mercaptopropyl)-trimethoxysilane (0.275 g, 1.4 mmol) and **compound 1** (0.675 g, 4.2 mmol) in dry toluene (1 ml) was irradiated by UV lamp for 4 hours under stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight. The product was pale colorless oil (0.49 g, yield 98% and GC purity 100%).



1.6

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 4.71 – 4.67 (m, 1H), 3.58 (s, 9H), 2.60 – 2.53 (m, 4H), 1.77 – 1.67 (m, 2H), 0.96 – 0.87 (m, 2H), 0.82 – 0.74 (m, 2H), 0.18 (d, J = 2.8 Hz, 6H), 0.12 (s, 6H).

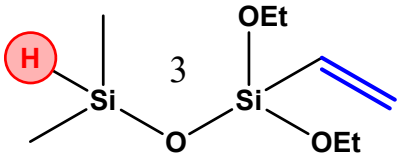
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm, jmod): 50.52 (s), 34.81 (s), 26.58 (s), 22.88 (s), 18.92 (s), 8.63 (s), 0.85 (s), 0.04 (s).

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): 8.19 (s), -6.10 (s), -42.27 (s).

IR: 2956, 2944, 2916, 2840, 2121, 1255, 1192, 1089, 909, 839, 817, 769 cm^{-1}

HRMS (ESI) m/z $[M + H]^+$: calcd for $[C_{12}H_{32}O_4SSi_3 + H]^+$, 357.1402; found, 357.1393; $[M + Na]^+$: calcd for $[C_{12}H_{32}O_4SSi_3 + Na]^+$ 379.1221; found, 379.1213; $[M + K]^+$: calcd for $[C_{12}H_{32}O_4SSi_3 + K]^+$ 395.0953; found, 395.0961.

Synthesis of 1,1-diethoxy-3,3-dimethyl-1-vinyldisiloxane (compound 3): A 500 mL two-neck round-bottom flask equipped with a magnetic stirbar, reflax condenser and gas inlet was charged with vinyltriethoxysilane (100.84 g, 0.530 mol) and dry toluene (100 ml). An equivalent amount of NaOH (21.19 g, 0.530 mol) was added to the flask and the mixture was boiled until NaOH completely reacted. Then, toluene and ethanol were evaporated off and obtained salt was dissolved in hexane (200 ml). A solution of chlorodimethylsilane (52.93 g, 0.557 mol) in hexane (50 ml) was added to a solution of salt, which was beforehand cooled to -30 °C. The obtained mixture was stirred overnight. Then, the solution was separated from NaBr by filtration, solvent was evaporated off and the target product (78.12 g, yield 67% and GC purity 99%) was purified by vacuum distillation (T_B=63°C at 20 Torr pressure).



^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.17-0.23 (d, 6H, J = 3.6 Hz), 1.11-1.23 (t, 6H, J = 5.2 Hz), 3.67-3.94 (q, 4H, J = 5.2 Hz), 4.64-4.83 (m, 1H), 5.73-6.17 (m, 3H).

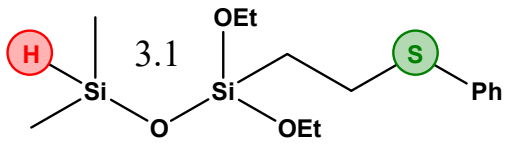
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm): 0.33, 18.02, 58.16, 130.36, 135.88.

^{29}Si NMR (60 MHz, $CDCl_3$, δ/ppm): -64.54, -4.34.

IR: 2975, 2928, 2885, 2132, 1256, 1168, 1103, 1080, 1010, 962, 905, 837, 771 cm^{-1}

HRMS (ESI) m/z $[M - H]^+$ calcd for $[C_8H_{20}O_3Si_2 - H]^+$ 219.0867, found 219.0863.

Synthesis of 1,1-diethoxy-3,3-dimethyl-1-(2-(phenylthiol-)ethyl-)disiloxane (compound 3.1): A mixture of benzenethiol (0.45 g, 4.1 mmol) and **compound 3** (0.30 g, 0.51 mmol) in pentane (8 ml) was irradiated by



UV lamp for 4 hours under stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.51 g) was 97%.

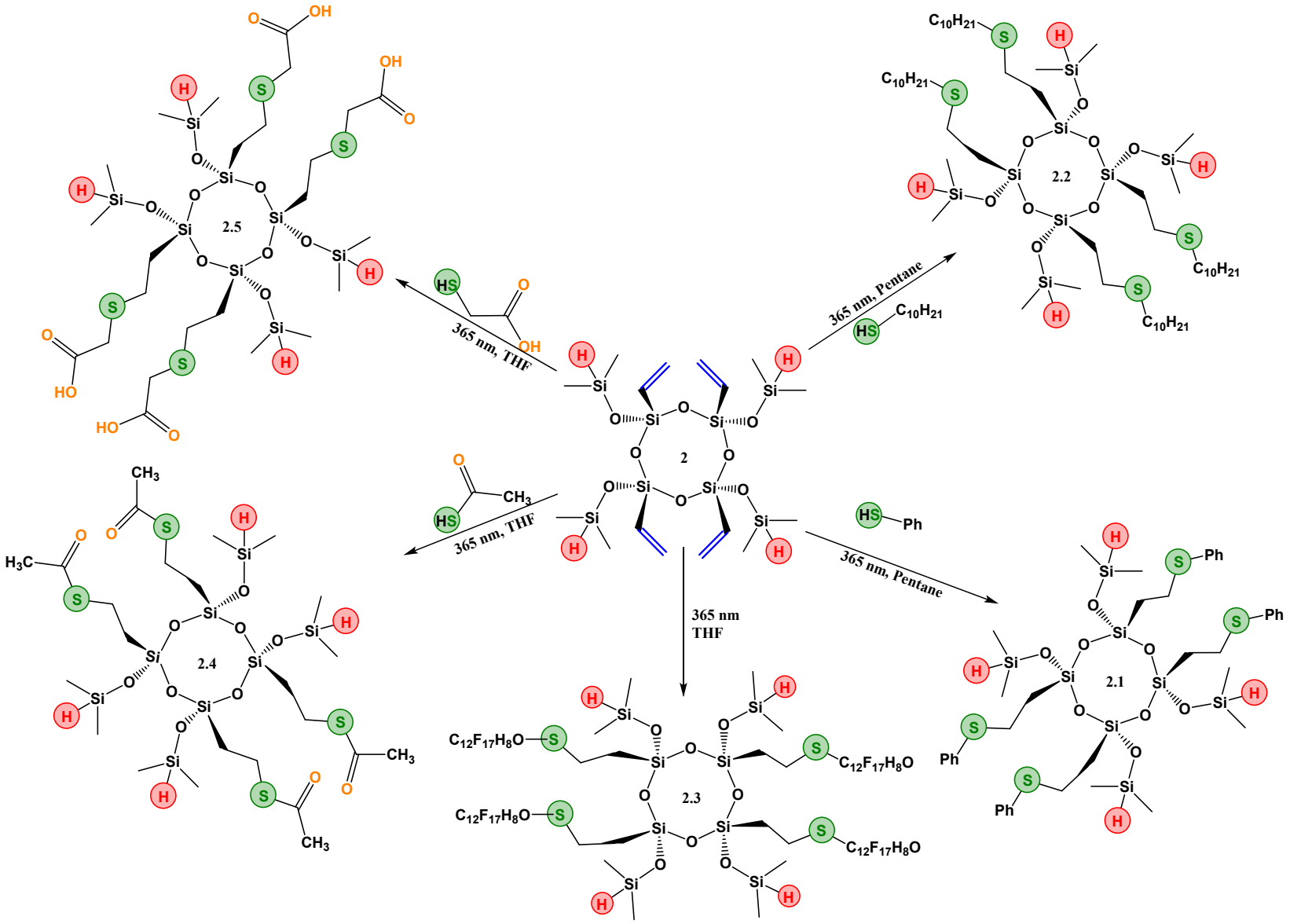
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.21-0.28 (d, 6H, J = 1.6 Hz); 0.99-1.07 (m, 2H); 1.19-1.28 (t, 6H, J = 4.8 Hz); 3.00-3.06 (m, 2H); 3.76-3.86 (quartet, 4H, J = 4.4 Hz); 4.74-4.80 (m, 1H); 7.15-7.36 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 136. 80, 129.09, 128.83, 125.76, 58.37, 28.26, 18.27, 12.49, 0.58.

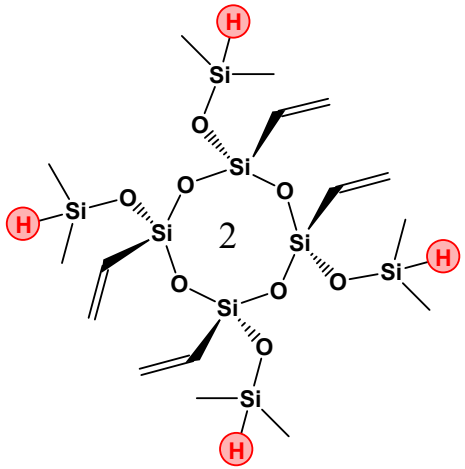
^{29}Si NMR (80 MHz, $CDCl_3$, δ/ppm): -4.24, -54.38.

IR: 2973, 2925, 2890, 2130, 1255, 1171, 1079, 959, 906, 772, 739 cm^{-1}.

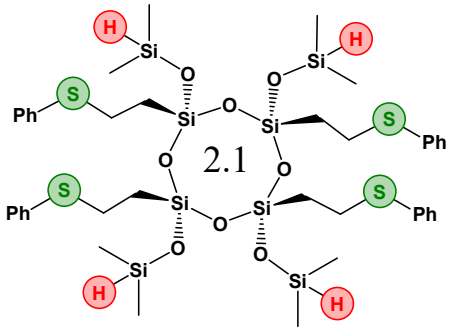
HRMS (ESI) m/z $[M+Na]^+$ calcd for $[C_{14}H_{26}O_3SSi_2+Na]^+$ 353.1033, found 353.1034.


2.5
2.2
2
2.4
2.1
2.3
365 nm, THF
365 nm, Pentane
365 nm, THF
365 nm, Pentane
365 nm
THF

Synthesis of (2s,4s,6s,8s)-2,4,6,8-tetrakis((dimethylsilyl)oxy)-2,4,6,8-tetrakisvinyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane (compound 2): Synthesis was described here [3].



Synthesis of (2s,4s,6s,8s)-2,4,6,8-tetrakis((dimethylsilyl)oxy)-2,4,6,8-tetrakis(2-(phenylthio)ethyl)-1,3,5,7,2,4,6,8-tetraoxatetrasilocane (compound 2.1): A mixture of benzenethiol (0.45 g, 4.1 mmol) and **compound 2** (0.30 g, 0.51 mmol) in pentane (8 ml) was irradiated by UV lamp for 4 hours under stirring at room temperature. After that, irradiated mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.56 g) was 99%.



^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.23-0.26 (d, 24H, J = 1.6 Hz); 0.93-1.01 (m, 8H); 2.91-2.98 (m, 8H); 4.75-4.78 (m, 4H); 7.21-7.33 (m, 20H).

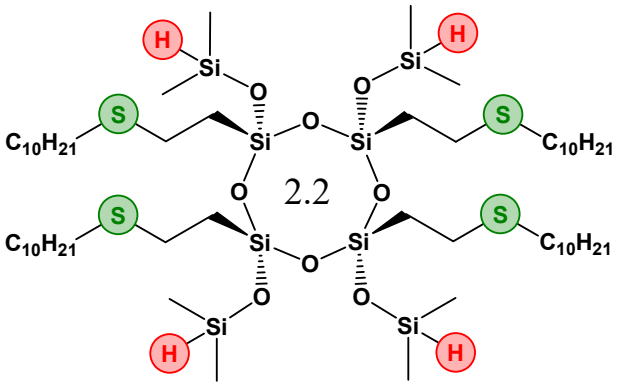
^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 136.47, 129.25, 129.00, 126.04, 28.39, 14.16, 0.56.

^{29}Si NMR (80 MHz, $CDCl_3$, δ/ppm): -4, -69.

IR: 3075, 3059, 2959, 2923, 2900, 2135, 1584, 1481, 1439, 1421, 1277, 1253, 1177, 1123, 1069, 1009, 904, 836, 771, 736, 690, 630 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $[C_{40}H_{64}O_8S_4Si_8 + NH_4]^+$ 1042.1976, found 1042.1967; $[M+Na]^+$ calcd for $[C_{40}H_{64}O_8S_4Si_8 + Na]^+$ 1047.1530, found 1047.1937; $[M+K]^+$ calcd for $[C_{40}H_{64}O_8S_4Si_8 + K]^+$ 1063.1270, found 1063.1291; $[M+H]^+$calcd fo $[C_{40}H_{64}O_8S_4Si_8 + H]^+$ 1025.1711, found 1025.1681.

Synthesis of (2s,4s,6s,8s)-2,4,6,8-tetrakis(2-(decylthio)ethyl)-2,4,6,8-tetrakis((dimethylsilyl)oxy)-1,3,5,7,2,4,6,8-tetraoxatetrasilocane (compound 2.2): A mixture of decane-1-thiol (0.18 g, 1.02 mmol), **compound 2** (0.10 g, 0.17 mmol) and benzophenone (4 mg) was irradiated by UV lamp for 4 hours under stirring at room temperature. Then the product was separated by chromatography. Yield of the target product (0.17 g) was 88%.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 4.75 – 4.77 (m, 4H), 2.59 – 2.56 (m, 8H), 2.53 (t, J = 7.4 Hz, 8H), 1.63 – 1.56 (m, 8H), 1.42 – 1.37 (m, 8H), 1.32 – 1.27 (m, 48H), 0.96 – 0.92 (m, 8H), 0.90 (t, J = 7.0 Hz, 12H), 0.25 (d, J = 2.7 Hz, 24H).

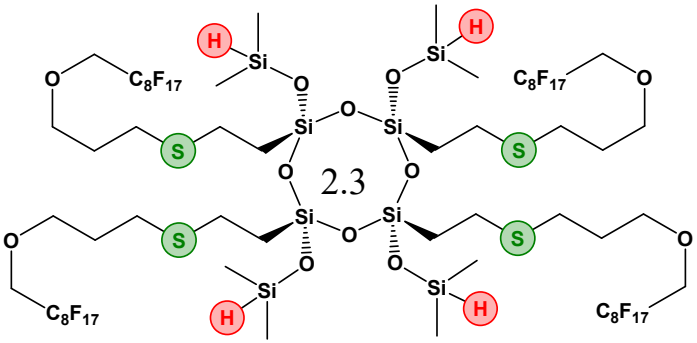
^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm, DEPT-135): 32.07, 31.93, 29.64, 29.61, 29.37, 29.09, 26.43, 22.70, 14.65, 14.12, 0.54.

^{29}Si NMR (80 MHz, $CDCl_3$, δ/ppm): -4.35, -69.75.

IR: 2924, 2853, 2137, 1466, 1253, 1176, 1116, 1065, 907, 836, 771 cm^{-1}.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $[C_{56}H_{128}O_8S_4Si_8 + H]^+$ 1281.6719, found 1281.6674; $[M + NH_4]^+$ calcd for $[C_{56}H_{128}O_8S_4Si_8 + NH_4]^+$ 1298.6984, found 1298.6937; $[M + Na]^+$ calcd for $[C_{56}H_{128}O_8S_4Si_8 + Na]^+$ 1303.6538, found 1303.6566.

Synthesis of (2s,4s,6s,8s)-2,4,6,8-tetrakis((dimethylsilyl)oxy)-2,4,6,8-tetrakis(2-(3-((2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)oxy)propane-1-thio)ethyl)-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane (compound 2.3): A mixture of **compound 6'** (0.205 g, 0.39 mmol), **compound 2** (0.044 g, 0.075 mmol) and benzophenone (4 mg) was irradiated by UV lamp for 4 hours under stirring at room temperature. Then the product was separated by chromatography. Yield of the target product (0.17 g) was 85%.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 4.78 – 4.74 (m, 4H), 3.95 (t, J = 14.0 Hz, 8H), 3.72 (t, J = 6.1 Hz, 8H), 2.62 (t, J = 7.2 Hz, 8H), 2.59 – 2.55 (m, 8H), 1.93 – 1.86 (m, 8H), 0.96 – 0.90 (m, 8H), 0.25 (d, J = 2.7 Hz, 24H).

^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm): 118.26 (t, J = 33.1 Hz), 117.68 (t, J = 30.9 Hz), 115.97 (t, J = 33.0 Hz), 115.63 (t, J = 30.8 Hz), 114.02 – 113.45 (m), 113.35 – 112.57 (m), 111.43 – 110.17 (m), 109.02 – 108.01 (m), 71.51 (s), 67.85 (t, J = 25.2 Hz), 29.35 (s), 28.36 – 28.01 (m), 26.36 (s), 14.50 (s), 0.40 (s).

^{19}F NMR (282 MHz, $CDCl_3$, δ/ppm): -80.88 (t, J = 9.5 Hz), -119.81 (s), -122.10 (s), -122.85 (s), -123.52 (s), -126.25 (s).

^{29}Si NMR (119 MHz, C_6D_6, δ/ppm): -4.0, -69.4.

IR: 2961, 2920, 2137, 1203, 1148, 1064, 903, 771, 667 cm^{-1}.

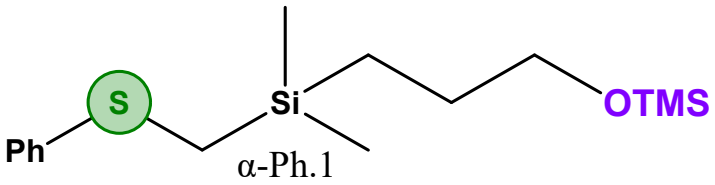
HRMS (ESI) m/z: $[M + H]^+$ calcd for $[C_{56}H_{128}O_8S_4Si_8 + H]^+$ 2682.1259, found 2682.1255.

Hydrosilylation

Methods of synthesis for compounds 24-29 (the hydrosilylation reaction).

General procedure for the synthesis of silane and siloxanes derivatives through the hydrosilylation reaction: A vacuum reaction tube was charged with disiloxane, allyl or vinyl modificator, solvent (toluene or THF) and Karsted's catalyst. Then, the mixture was stirred for 24 hours at 60 °C (in some cases at 80 or 100 °C). After that, the obtained solution was evaporated under 1 Torr till the constant weight.

Synthesis of (3-(dimethyl((phenylthio)methyl)silyl)propoxy)trimethylsilane (compound α-Ph.1): A mixture of **compound α-Ph (**0.051 g, 0.28 mmol), (allyloxy)(trimethyl)silane (0.11 g, 0.84 mmol), Karsted's catalyst (0,001% mol) in toluene (0.5 ml) was stirred for 48 hours at 60 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.087 g) was 99%.



α-Ph.1

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 7.34 – 7.28 (m, 4H), 7.14 (tt, J = 7.0, 1.7 Hz, 1H), 3.59 (t, J = 7.0 Hz, 2H), 2.23 (s, 2H), 1.68 – 1.59 (m, 2H), 0.71 – 0.64 (m, 2H), 0.20 (s, 6H), 0.16 (s, 9H).

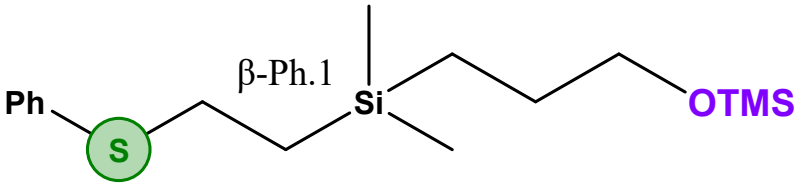
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm, jmod): 140.34, 128.69, 126.05, 124.66, 65.37, 26.94, 16.96, 10.81, -0.40, -3.29.

^{29}Si NMR (79 MHz, $CDCl_3$, δ/ppm): 17.22, 3.33.

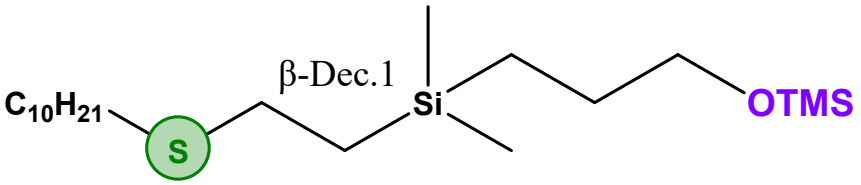
IR: 3075, 3060, 2956, 2930, 2886, 2724, 1583, 1480, 1439, 1410, 1391, 1296, 1250, 1189, 1159, 1095, 1052, 1026, 1007, 922, 879, 842 , 737, 697, 689 cm^{-1}.

HRMS (ESI) m/z $[M + H]^+$ calcd for $[C_{15}H_{28}OSSi_2 + H]^+$ 313.1472, found 313.1475; $[M + NH_4]^+$ calcd for $[C_{15}H_{28}OSSi_2 + NH_4]^+$ 330.1738, found 330.1732; $[M + Na]^+$ calcd for $[C_{15}H_{28}OSSi_2 + Na]^+$ 335.1292, found 335.1293.

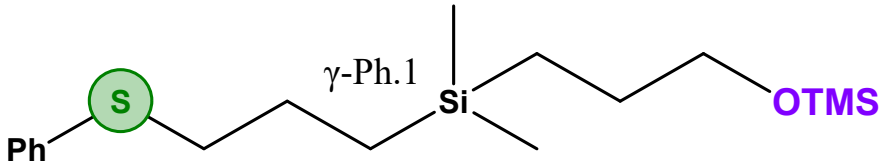
Synthesis of (3-(dimethyl((phenylthio)ethyl)silyl)propoxy)trimethylsilane (compound β-Ph.1): A mixture of **compound β-Ph** (0.051 g, 0.26 mmol), (allyloxy)(trimethyl)silane (0.102 g, 0.78 mmol), Karsted's catalyst (in different runs were used amounts about 0.1, 0.3, 1 and 3% mol) in toluene (0.5 ml) was stirred for 72 hours at 60, 80 or 100 °C. Investigating of resulted mixture with ^{1}H NMR shows total absence of expected product. We add some **α-Ph** (0.051 g, 0.28 mmol) to check the catalyst activity. Investigating of second mixture with ^{1}H NMR also shows total absence of **α-Ph.1**.



Synthesis of (3-(dimethyl((decylthio)ethyl)silyl)propoxy)trimethylsilane (compound β-Dec.1): A mixture of **compound β-Dec** (0.051 g, 0.2 mmol), (allyloxy)(trimethyl)silane (0.078 g, 0.6 mmol), Karsted's catalyst (in different runs were used amounts about 0.1, 0.3, 1 and 3% mol) in toluene (0.5 ml) was stirred for 72 hours at 60, 80 or 100 °C. Investigation of resulted mixture with ^{1}H NMR shows total absence of expected product.



Synthesis of (3-(dimethyl((phenylthio)propyl)silyl)propoxy)trimethylsilane (compound γ-Ph.1): A mixture of **compound γ-Ph** (0.051 g, 0.24 mmol), (allyloxy)(trimethyl)silane (0.094 g, 0.72 mmol), Karsted's catalyst (in different runs

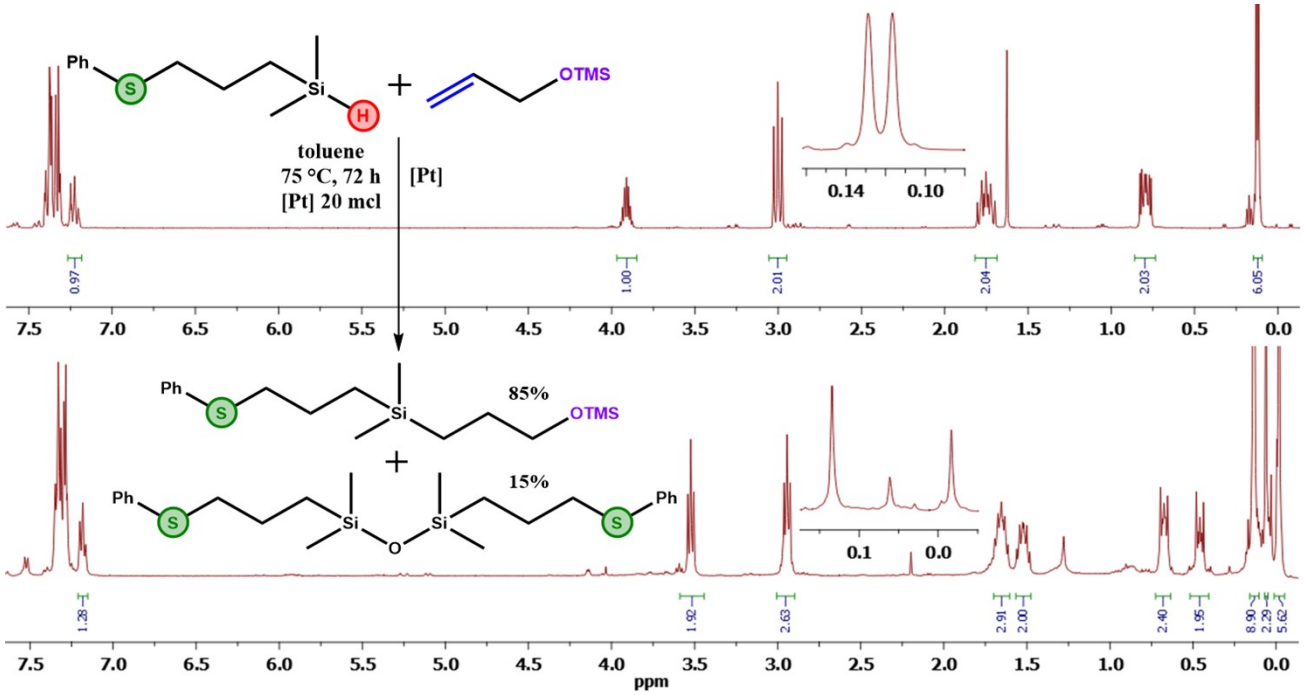


were used amounts about 0.1, 0.3, 1 and 3% mol) in toluene (0.5 ml) was stirred for 72 hours at 60, 80 or 100 °C. Investigation of resulted mixture with ^{1}H NMR shows slow and incomplete formation of hydrosilylation product.

An approximate calculation of hydrosilylation reaction of the γ-Ph compound selectivity:

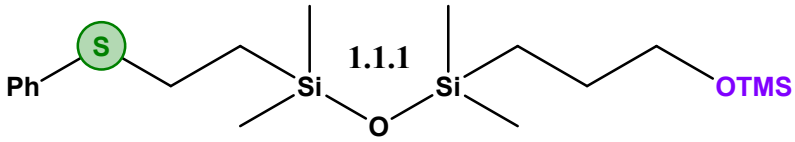
$$S = \frac{N_{aim}}{N_{aim} + N_{by}} = \frac{1}{1 + 0{,}15} = 87\%$$

The amount of the by-product was taken as 15%, since the intensity of the signals from the dimerization product is two times higher than from the



hydrosilylation products, and the excess intensity is approximately equal to 0.3.

Synthesis of 1,1,3,3-tetramethyl-1-(2-(phenylthio)ethyl)-3-(3-((trimethylsilyl)oxy)propyl)disiloxane (compound 1.1.1): A mixture of **compound 1.1** (0.18 g, 0.67 mmol), (allyloxy)(trimethyl)silane (0.17 g, 1.33 mmol), Karsted's catalyst (0.5% mol) in toluene (0.68 ml) was stirred for 24 hours at 60 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.24 g) was 91%.



^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.07-0.09 (s, 6H); 0.11-0.13 (s, 6H); 0.13-0.14 (s, 9H); 0.47-0.52 (m, 2H); 0.94-0.99 (m, 2H); 1.52-1.59 (m, 2H); 2.96-3.02 (m, 2H); 3.52-3.56 (t, 2H, J = 4.8 Hz); 7.16-7.35 (m, 5H).

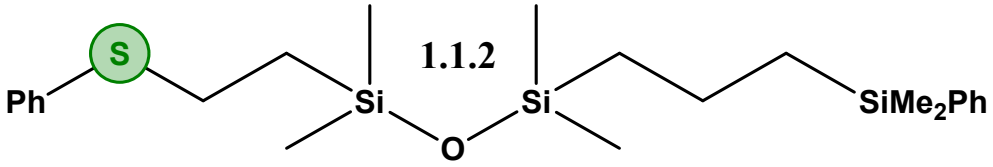
^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.17, 128.91, 128.83, 125.66, 65.46, 28.79, 26.56, 18.58, 14.05, 0.44, 0.29, - 0.39.

^{29}Si NMR (80 MHz, $CDCl_3$, δ/ppm): 17.02, 8.72, 5.93.

IR: 2956, 1252, 1092, 1060, 840, 796, 737, 691 cm^{-1}.

HRMS (ESI) m/z $[M + Na]^+$ calcd for $[C_{18}H_{36}O_2SSi_3 + Na]^+$ 423.1636, found 423.1621.

Synthesis of 1-(3-(dimethyl(phenyl)silyl)propyl)-1,1,3,3-tetramethyl-3-(2-(phenylthio)ethyl)disiloxane (compound 1.1.2): A mixture of **compound 1.1** (0.2 g, 0.74 mmol), allyl(dimethyl)phenylsilane (0.26 g, 1.48 mmol), Karsted's catalyst (1% mol) in toluene (0.6 ml) was stirred for 24 hours at 80 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.26 g) was 79%.



^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.06-0.08 (s, 6H); 0.11-0.12 (s, 6H); 0.30-0.32 (s, 6H); 0.61-0.66 (m, 2H); 0.84-0.89 (m, 2H); 0.95-1.00 (m, 2H); 1.40-1.47 (m, 2H); 2.99-3.03 (m, 2H); 7.19-7.57(m, 10H).

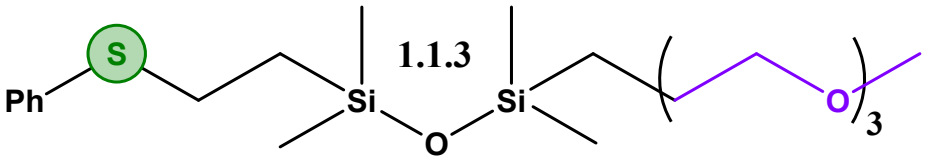
^{13}C NMR (80 MHz, $CDCl_3$, δ/ppm): 139.67, 137.23, 133.59, 128.87, 128.80, 127.76, 125.67, 28.78, 22.92, 20.14, 18.59, 17.87, 0.54, 0.46, -2.90.

^{29}Si NMR (80 MHz, $CDCl_3$, δ/ppm): 7.96, 5.65, -3.73.

IR: 3075, 3059, 2953, 2924, 2877, 1585, 1480, 1439, 1253, 1059, 841, 796, 737, 690 cm^{-1}.

CHN: Calc. (%) for $C_{23}H_{38}OSSi_3$, MM: 446.87, C, 61.82; H, 8.57; O, 3.58; S, 7.18; Si, 18.85. Found: (%) C, 61.75; H, 8.51; O, 3.57; S, 7.22; Si, 18.95.

Synthesis of 12,12,14,14-tetramethyl-16-(phenylthio)-2,5,8,13-tetraoxa-12,14-disilahexadecane (compound 1.1.3): A mixture of **compound 1.1** (0.2 g, 0.74 mmol), 3-[2-(2-methoxyethoxy)ethoxy]-prop-1-ene (0.28 g, 1.48 mmol), Karsted's catalyst (1% mol) in toluene (0.6 ml) was stirred for 24 hours at 80 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.24 g) was 91%.



^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.06-0.08 (s, 6H); 0.10-0.12 (s, 6H); 0.49-0.54 (m, 2H); 0.93-0.98 (m, 2H); 1.58-1.64 (m, 2H); 2.96-3.01 (m, 2H); 3.39-3.41 (s, 3H); 3.41-3.45 (t, 2H, J = 4.4 Hz); 3.56-3.59 (m, 2H); 3.61-3.63 (m, 2H); 3.65-3.69 (m, 4H); 7.19-7.34 (m, 5H).

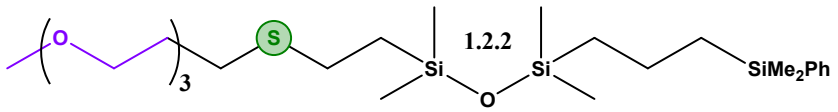
^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.15, 128.89, 128.82, 125.66, 74.16, 71.97, 70.67, 70.56, 70.04, 59.05, 28.78, 23.41, 18.56, 14.21, 0.43, 0.28.

^{29}Si NMR (80 MHz, $CDCl_3$, δ/ppm): 8.62, 5.96.

IR: 2953, 2924, 2873, 1584, 1481, 1254, 1109, 1057, 840, 796, 738, 691 cm^{-1}.

HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $[C_{20}H_{38}O_4SSi_2 + NH_4]^+$ 448.2368, found 448.2358; $[M + Na]^+$ calcd for $[C_{20}H_{38}O_4SSi_2 + Na]^+$ 453.1922, found 453.1915; $[M + K]^+$ calcd for $[C_{20}H_{38}O_4SSi_2 + K]^+$ 469.1661, found 469.1709.

Synthesis of 15,15,17,17,21-pentamethyl-21-phenyl-2,5,8,16-tetraoxa-12-thia-15,17,21-trisiladocosane (compound 1.2.2): A mixture of **compound 1.2** (0.30 g, 0.85 mmol), allyl(dimethyl)phenylsilane (0.30 g, 1.69 mmol), Karsted's catalyst (1% mol) in THF (1.4 ml) was stirred for 24 hours at 85 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the target product (0.30 g, 65% yield) was isolated by flash chromatography (stationary phase – Silica C18, eluent – acetonitrile).



1.2.2

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): -0.018 (s, 6H); 0.014 (s, 6H); 0.20 (s, 6H); 0.46-0.64 (m, 2H); 0.74-0.86 (m, 4H); 1.27-1.42 (m, 2H); 1.76-1.88 (quintet, 2H, J = 7.2 H), 2.43-2.61 (m, 4H); 3.35 (s, 3H); 3.49-3.66 (m, 10H); 7.27-7.53 (m, 5H).

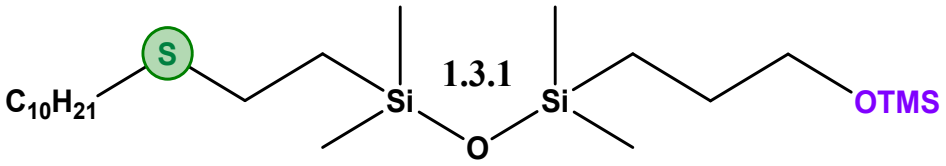
^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): -2.94; 0.36; 0.48; 17.79; 19.03; 20.04; 22.84; 26.86; 28.46; 29.53; 59.02; 69.87; 70.18; 70.51; 71.92; 127.67; 128.71; 133.48; 139.56.

^{29}Si NMR (80 MHz, $CDCl_3$, δ/ppm, HMBC ^{1}H-^{29}Si): -3.81, 5.64, 7.65.

IR: 703; 798; 838; 1061; 1113; 1254; 1426; 2874; 2914; 2954; 3068 cm^{-1}.

MS (ESI) m/z $[M + H]^+$: calcd for $[C_{25}H_{50}O_4SSi_3 + H]^+$, 531.2810; found, 531.2801; $[M + NH_4]^+$: calcd for $[C_{25}H_{50}O_4SSi_3 + NH_4]^+$, 548.3076; found, 548.3042; $[M + Na]^+$: calcd for $[C_{25}H_{50}O_4SSi_3 + Na]^+$, 553.3630; found, 553.2626; $[M + K]^+$: $[C_{25}H_{50}O_4SSi_3 + K]^+$, 569.2369; found, 569.2379.

Synthesis of 1-(2-(decylthio)ethyl)-1,1,3,3-tetramethyldisiloxane (compound 1.3.1):



1.3.1

A mixture of **compound 1.3** (0.2 g, 0.6 mmol), (allyloxy)(trimethyl)silane (0.110 g, 1,2 mmol), Karsted's catalyst (0.2% mol) in dioxane (0.5 ml) was stirred for 24 hours at room temperature. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.24 g) was 96%.

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.54 (t, J = 7.1 Hz, 2H), 2.59 – 2.55 (m, 2H), 2.55 – 2.51 (t, J = 7.34 Hz, 2H), 1.62 – 1.52 (m, 4H), 1.43 – 1.36 (m, 2H), 1.34 – 1.27 (m, 12H), 0.92 – 0.87 (m, 5H), 0.52 – 0.48 (m, 2H), 0.13 (s, 9H), 0.10 (s, 6H), 0.08 (s, 6H).

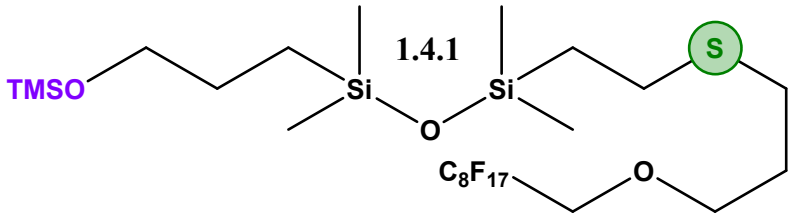
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm): 65.46 (s), 31.90 (s), 29.62 (s), 29.58 (s), 29.56 (s), 29.32 (s), 29.29 (s), 29.01 (s), 26.88 (s), 26.56 (s), 22.68 (s), 19.15 (s), 14.11 (s), 14.04 (s), 0.37 (s), 0.27 (s), -0.42 (s).

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): 16.97 (s), 8.40 (s), 5.97 (s).

IR: 2950, 2926, 2855, 1467, 1458, 1437, 1412, 1379, 1252, 1189, 1162, 1094, 1060, 1008, 922, 880, 840, 797 cm^{-1}.

HRMS (ESI) m/z $[M + NH_4]^+$: calcd for $[C_{22}H_{52}O_2SSi_3 + NH_4]^+$, 482.3334; found, 482.3324; $[M + Na]^+$: calcd for $[C_{22}H_{52}O_2SSi_3 + Na]^+$, 487.2888; found, 487.2880; $[M + K]^+$: calcd for $[C_{22}H_{52}O_2SSi_3 + K]^+$, 503.2619; found, 503.2627.

Synthesis of 1,1,3,3-tetramethyl-1-(2-(3-((2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)oxy)propane-1-thio)ethyl)-3-(3-((trimethylsilyl)oxy)propyl)disiloxane (compound 1.4.1): A mixture of **compound 1.4** (0.2 g, 0.29 mmol), (allyloxy)(trimethyl)silane (0.08 g, 0.6 mmol), Karsted's catalyst (0,1% mol) in dioxane (0.5 ml) was stirred for 24 hours at 60 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.23 g) was 95%.



^{1}H NMR (600 MHz, $CDCl_3$, δ/ppm, J/Hz): δ 3.96 (t, J = 13.8 Hz, 2H), 3.72 (d, J = 12.1 Hz, 2H), 3.54 (t, J = 7.1 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 2.58 – 2.55 (m, 2H), 1.93 – 1.86 (m, 2H), 1.58 – 1.51 (m, 2H), 0.92 – 0.86 (m, 2H), 0.52 – 0.46 (m, 2H), 0.13 (s, 9H), 0.09 (s, 6H), 0.07 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, δ/ppm): δ 121.10 – 106.87 (m), 71.55 (s), 67.94 (t, J = 25.5 Hz), 65.44 (s), 29.40 (s), 28.00 (s), 26.91 (s), 26.54 (s), 19.02 (s), 14.00 (s), 0.29 (s), 0.20 (s), -0.48 (s).

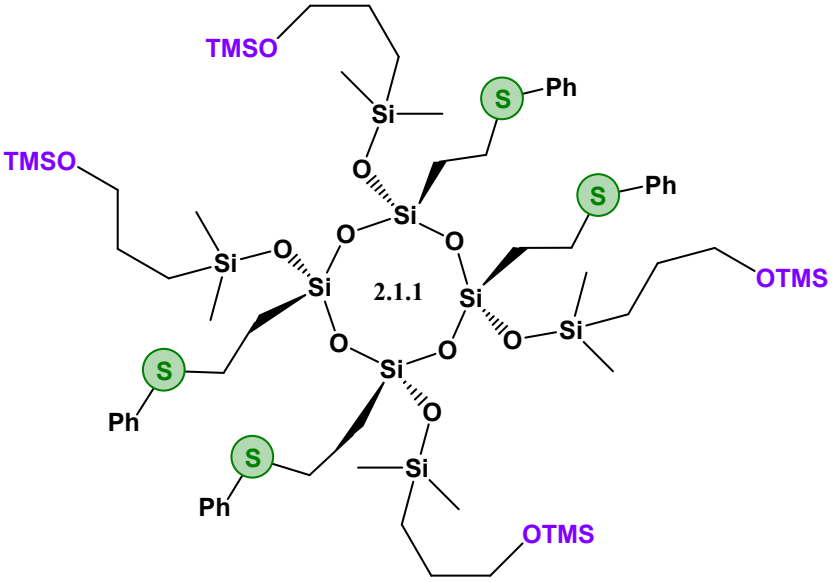
^{29}Si NMR (99 MHz C_6D_6, δ/ppm): δ 6.00, 8.45, 15.44.

^{19}F NMR (471 MHz, C_6D_6, δ/ppm): δ -81.08, -119.30, -121.82, -121.95, -122.76, -123.14.

IR: 2957, 1251, 1213, 1153, 1064, 841, 796 cm^{-1}.

HRMS (ESI) m/z $[M + NH_4]^+$: calcd for $[C_{24}H_{39}F_{17}O_3SSi_3 + NH_4]^+$, 832.1995; found, 832.1983; $[M + Na]^+$: calcd for $[C_{24}H_{39}F_{17}O_3SSi_3 + Na]^+$, 837.1548; found, 837.1556;

Synthesis of (2s,4s,6s,8s)-2,4,6,8-tetrakis((dimethyl(3-((trimethylsilyl)oxy)propyl)silyl)oxy)-2,4,6,8-tetrakis(2-(phenylthio)ethyl)-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane (compound 2.1.1): A mixture of **compound 2.1 (**0.1 g, 0.1 mmol), (allyloxy)(trimethyl)silane (0.09 g, 0,8 mmol), Karsted's catalyst (0,2% mol) in dry toluene (0.5 ml) was stirred for 48 hours at room temperature. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.15 g) was 98%.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 7.31 – 7.24 (m, 16H), 7.19 – 7.15 (m, 4H), 3.51 (t, J = 7.0 Hz, 8H), 2.93 – 2.88 (m, 8H), 1.57 – 1.50 (m, 8H), 0.93 – 0.88 (m, 8H), 0.57 – 0.52 (m, 24H), 0.13 (s, 5H), 0.12 (s, 36H).

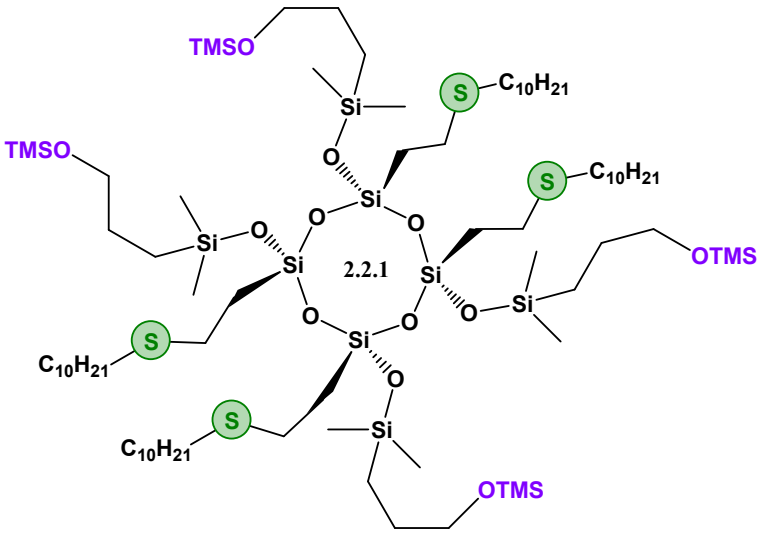
^{13}C NMR (151 MHz, $CDCl_3$, δ/ppm): 129,44; 129,11; 127,94; 127,78; 127,62; 126,01; 66,07; 28,77; 26,72; 14,86; 14,05; 0,17; - 0,50.

^{29}Si NMR (119 MHz, $CDCl_3$, δ/ppm): 16, 11, -71;

IR: 3060, 2956, 2929, 1585, 1481, 1439, 1252, 1177, 1110, 1060, 922, 841, 789, 737, 690 cm^{-1}.

CHN: Calc. (%) for $C_{64}H_{120}O_{12}S_4Si_{12}$, MM: 1546.91, C, 49.69; H, 7.82; O, 12.41; S, 8.29; Si, 21.79. Found: (%) C, 49.65; H, 7.80; O, 12.40; S, 8.33; Si, 21.82.

Synthesis of (2s,4s,6s,8s)-2,4,6,8-tetrakis(2-(decylthio)ethyl)-2,4,6,8-tetrakis((dimethyl(3-((trimethylsilyl)oxy)propyl)silyl)oxy)-1,3,5,7,2,4,6,8-tetraoxatetrasilocane (compound 2.2.1): A mixture of compound **2.2** (0.15 g, 0.12 mmol), (allyloxy)(trimethyl)silane (0.25 g, 1,44 mmol) and Karsted's catalyst (0.2% mol) in dry dioxane (or toluene) (0.5 ml) was stirred for 24 hours at 60 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.2 g) was 94%.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.53 (t, J = 7.0 Hz, 8H), 2.58 – 2.50 (m, 16H), 1.62 – 1.51 (m, 16H), 1.44 – 1.36 (m, 8H), 1.28 (s, J = 16.5 Hz, 36H), 0.90 (t, J = 6.9 Hz, 20H), 0.59 – 0.53 (m, 8H), 0.14 (s, 24H), 0.13 (s, 36H).

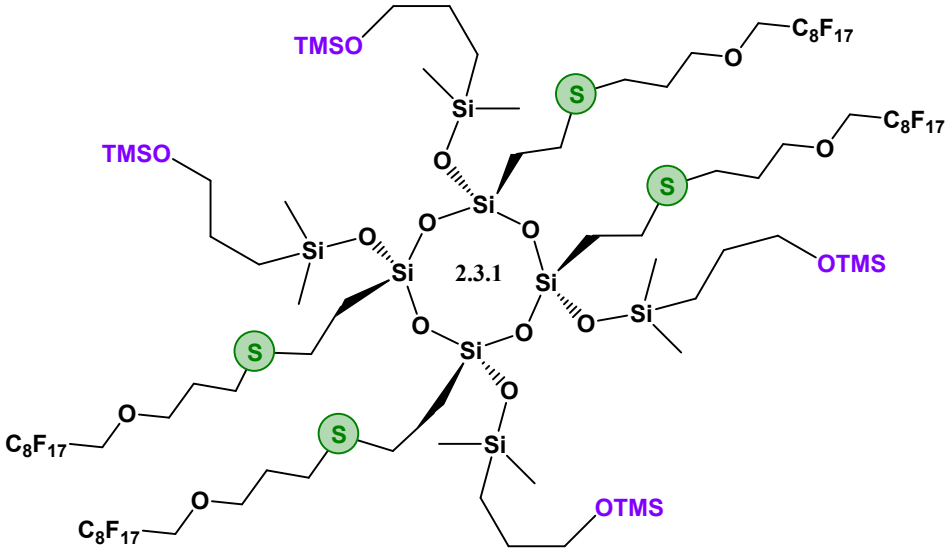
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm, jmod): 65.30, 32.16, 31.93, 29.66, 29.64, 29.40, 29.38, 29.12, 26.66, 26.42, 22.70, 15.23, 14.12, 13.77, 0.13, -0.43.

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): 16.91, 10.48, -71.25.

IR: 2956, 2925, 2855, 1251, 1176, 1098, 1064, 1008, 922, 879, 841, 789 cm^{-1}.

HRMS (ESI) m/z $[M + NH_4]^+$: calcd for $[C_{80}H_{184}O_{12}S_4Si_{12} + NH_4]^+$, 1821.0218; found, 1821.0185; $[M + Na]^+$: calcd for $[C_{80}H_{184}O_{12}S_4Si_{12} + Na]^+$, 1823.9794; found, 1824.0050.

Synthesis of (2s,4s,6s,8s)-2,4,6,8-tetrakis((dimethyl(3-((trimethylsilyl)oxy)propyl)silyl)oxy)-2,4,6,8-tetrakis(2-(3-((2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)oxy)propane-1-thio)ethyl)-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane (compound 2.3.1): A mixture of compound **2.3** (0.1 g, 0.037 mmol), (allyloxy)(trimethyl)silane (0.19 g, 1,48 mmol) and Karsted's catalyst (0.6% mol) in dry dioxane (or toluene) (0.5 ml) was stirred for 24 hours at 60 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.11 g) was 90%.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.95 (t, J = 14.0 Hz, 8H), 3.72 (t, J = 6.1 Hz, 8H), 3.53 (t, J = 6.9 Hz, 8H), 2.62 (t, J = 7.1 Hz, 8H), 2.58 – 2.53 (m, 8H), 1.90 (dt, J = 13.0, 6.4 Hz, 8H), 1.59 – 1.51 (m, 8H), 0.93 – 0.87 (m, 8H), 0.59 – 0.54 (m, 8H), 0.15 (s, 24H), 0.12 (s, 36H).

^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm, J/Hz, jmod): 118.25 (t, J = 33.3 Hz), 117.70 (t, J = 30.5 Hz), 115.96 (t, J = 33.3 Hz), 115.64 (t, J = 31.0 Hz), 113.90 – 113.29 (m), 113.23 – 112.54 (m), 111.28 – 110.26 (m), 108.96 – 107.98 (m), 71.51 (s), 67.82 (t, J = 25.1 Hz), 65.24 (s), 29.35 (s), 28.24 (s), 26.53 (s), 26.39 (s), 15.10 (s), 13.74 (s), 0.06 (s), -0.54 (s).

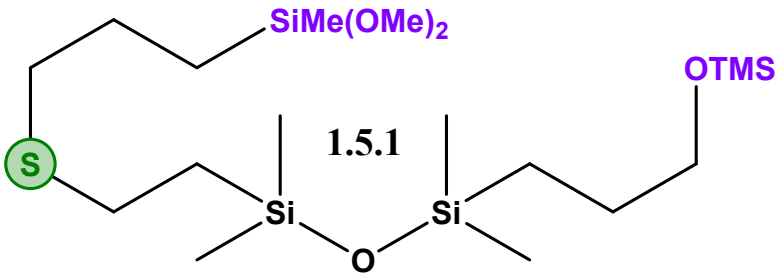
^{19}F NMR (282 MHz, $CDCl_3$, δ/ppm, J/Hz): -80.93 (t, J = 10.3 Hz, 12H), -119.86 (s, 8H), -122.13 (s, 24H), -122.89 (s, 8H), -123.55 (s, 8H), -126.29 (s, 8H).

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): 16.98, 10.76, -71.48.

IR: 2958, 2929, 2881, 1246, 1206, 1154, 1135, 1098, 1061, 1009, 922, 879, 843, 791, 707 cm^{-1}.

HRMS (ESI) m/z calcd for $[C_{88}H_{132}F_{68}O_{16}S_4Si_{12}+ NH_4]^+$, 3220.4896; found, 3220.4808.

Synthesis of 1-(2-(3-(methyl-dimethoxysilyl)-propylthio)-ethyl)-3-((trimethylsilyl)-oxy)-propy-1,1,3,3-tetramethyldisiloxane (compound 1.5.1): A mixture of **compound 1.5 (**0.15 g, 0.44 mmol), (allyloxy)(trimethyl)silane (0.11 g, 0.8 mmol) and Karsted's catalyst (0.1% mol) in dry toluene (0.5 ml) was stirred for 24 hours at 60 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.2 g) was 96%.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.55 – 3.52 (t, J = 7.1 Hz, 2H), 3.53 (s, 6H), 2.58 – 2.53 (m, 4H), 1.71 – 1.63 (m, 2H), 1.58 – 1.51 (m, 2H), 0.91 – 0.86 (m, 2H), 0.78 – 0.73 (m, 2H), 0.52 – 0.46 (m, 2H), 0.13 (s, 3H), 0.13 (s, 9H), 0.09 (s, 6H), 0.07 (s, 6H).

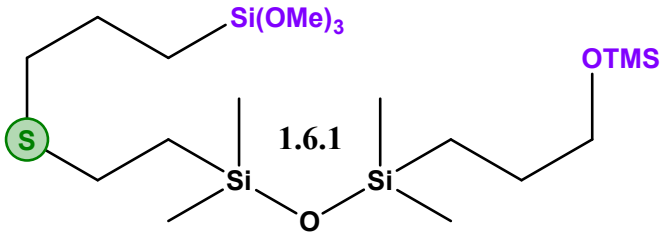
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm, jmod): 65.45 (s), 50.18 (s), 35.08 (s), 26.77 (s), 26.55 (s), 23.06 (s), 19.17 (s), 14.02 (s), 12.69 (s), 0.36 (s), 0.26 (s), -0.43 (s), -5.77 (s).

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): 16.96 (s), 8.43 (s), 5.94 (s), -1.74 (s).

IR: 2956, 2938, 2835, 1412, 1252, 1190, 1162, 1091, 1009, 922, 880, 840, 797 cm^{-1}.

HRMS (ESI) m/z $[M + NH_4]^+$: calcd for $[C_{18}H_{46}O_4SSi_4 + NH_4]^+$ 488.2532, found 488.2522; $[M + Na]^+$: calcd for $[C_{18}H_{46}O_4SSi_4 + Na]^+$ 493.2086, found 493.2079; $[M + K]^+$: calcd for $[C_{18}H_{46}O_4SSi_4 + K]^+$ 509.1825, found 509.1819.

Synthesis of 1-(2-(3-(trimethoxysilyl)-propylthio)-ethyl)-3-((trimethylsilyl)-oxy)-propy-1,1,3,3-tetramethyldisiloxane (compound 1.6.1): A mixture of **compound 1.6** (0.15 g, 0.42 mmol), (allyloxy)(trimethyl)silane (0.11 g, 0.84 mmol) and Karsted's catalyst (0.1% mol) in dry toluene (0.5 ml) was stirred for 24 hours at 60 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.2 g) was 97%.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.58 (s, 9H), 3.53 (t, J = 7.1 Hz, 2H), 2.56 (t, J = 8.7 Hz, 2H), 1.75 – 1.67 (m, 2H), 1.58 – 1.51 (m, 2H), 0.91 – 0.86 (m, 2H), 0.80 – 0.76 (m, 2H), 0.51 – 0.46 (m, 2H), 0.13 (s, 9H), 0.09 (s, 6H), 0.07 (s, 6H).

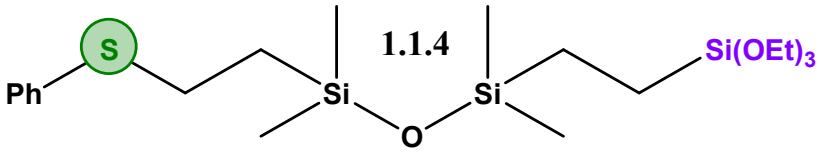
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm, jmod): 65.45 (s), 50.52 (s), 34.82 (s), 26.72 (s), 26.55 (s), 22.88 (s), 19.15 (s), 14.02 (s), 8.63 (s), 0.36 (s), 0.25 (s), -0.43 (s).

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): 16.96 (s), 8.43 (s), 5.95 (s), -42.28 (s).

IR: 2955, 2915, 2840, 1412, 1252, 1191, 1161, 1090, 1009, 922, 880, 840, 799 cm^{-1}.

HRMS (ESI) m/z $[M + NH_4]^+$: calcd for $[C_{18}H_{46}O_5SSi_4 + NH_4]^+$ 504.2481, found 504.2469; $[M + Na]^+$: calcd for $[C_{18}H_{46}O_5SSi_4 + Na]^+$ 509.2035; found 509.2024; $[M + K]^+$: calcd for $[C_{18}H_{46}O_5SSi_4 + K]^+$ 525.1775, found 525.1762.

Synthesis of 1,1,3,3-tetramethyl-1-(2-(phenylthio)ethyl)-3-(2-(triethoxysilyl)ethyl)disiloxane (compound 1.1.4): A mixture of **compound 1.1** (0.2 g, 0.74 mmol), triethoxy(vinyl)silane (0.28 g, 1.48 mmol), Karsted's catalyst (0,1% mol) in toluene (0.6 ml) was stirred for 24 hours at 80 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.3 g) was 89%.



^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.06-0.08 (s, 6H); 0.11-0.13 (s, 6H); 0.55-0.58 (m, 4H); 0.93-0.98 (m, 2H); 1.23-1.27 (t, 9H, J = 4.8 Hz); 2.97-3.01 (m, 2H); 3.82-3.86 (q, 6H, J = 4.8 Hz); 7.19-7.34 (m, 5H).

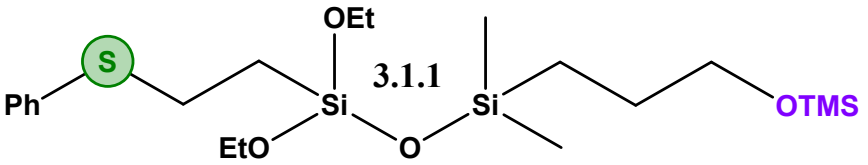
^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.16, 128.83, 128.81, 125.63, 58.43, 28.73, 18.53, 18.35, 9.19, 1.83, 0.43, 0.39.

^{29}Si NMR (80 MHz, $CDCl_3$, δ/ppm): 9.17, 5.90, -44.55.

IR: 2973, 2924, 2887, 1254, 1166, 1104, 1079, 957, 841, 786 cm^{-1}.

HRMS (ESI) m/z $[M + Na]^+$ calcd for $[C_{20}H_{40}O_4SSi_3 + Na]^+$ 483.1847, found 483.1837.

Synthesis of 9-ethoxy-2,2,7,7-tetramethyl-9-(2-(phenylthio)ethyl)-3,8,10-trioxa-2,7,9-trisiladodecane (compound 3.1.1): A mixture of **compound 3.1** (0.18 g, 0.67 mmol), (allyloxy)(trimethyl)silane (0.17 g, 1.33 mmol), (0.8% mol)



Karsted's catalyst in toluene (0.68 ml) was stirred for 24 hours at 100 °C. After that, the obtained solution was evaporated under 1 Torr till the constant weight and the yield of the target product (0.24 g) was 91%.

^{1}H NMR (600 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.13-0.14 (s, 9H); 0.14-0.15 (s, 6H); 0.54-0.60 (m, 2H); 0.98-1.02 (m, 2H); 1.20-1.25 (t, 6H, J = 4.8 Hz); 1.55-1.61 (m, 2H); 2.99-3.04 (m, 2H); 3.52-3.57 (t, 2H, J = 4.4 Hz); 3.76-3.81 (t, 4H, J = 4.8 Hz); 7.16-7.35 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$, δ/ppm): 136.82, 129.01, 128.84, 125.73, 65.37, 58.27, 28.33, 26.39, 18.32, 13.83, 12.66, 0.00, -0.42.

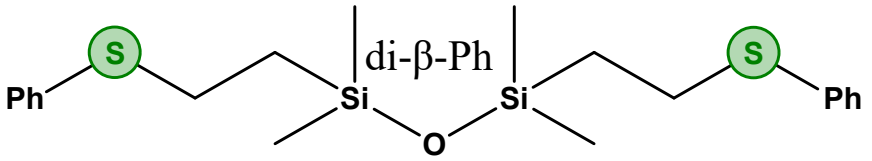
^{29}Si NMR (119 MHz, $CDCl_3$, δ/ppm): 17.15, 10.20, -55.19.

IR: 2955, 2928, 2897, 2876, 1584, 1481, 1439, 1257, 1253, 1175, 1065, 1011, 841, 797, 779 cm^{-1}.

CHN: Calc. (%) for $C_{20}H_{40}O_4SSi_3$, MM: 460.85, C, 52.13; H, 8.75; O, 13.89; S, 6.95; Si, 18.28. Found: (%) C, 52.10; H, 8.71; O, 13.90; S, 6.97; Si, 18.32.

Dehydrocondensation of si-h with water on tris(pentafluorophenyl)borane

Synthesis of 1,1,3,3-tetramethyl-1,3-bis(2-(phenylthio)ethyl)disiloxane (compound di-β-Ph):



A mixture of **compound β-Ph (**0.05 g, 0.25 mmol), water (10 mg) and Tris(pentafluorophenyl)borane (1 mg) in toluene (0.5 ml) was stirred for 30 minutes at room temperature. Then the mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.051 g) was 99%.

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 7.29 – 7.22 (m, 8H), 7.15 – 7.11 (m, 2H), 2.98 – 2.89 (m, 4H), 0.96 – 0.87 (m, 4H), 0.08 (s, 12H).

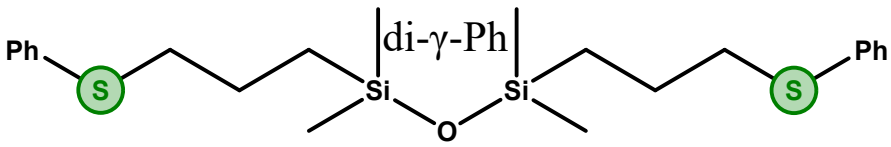
^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm): 137.06 (s), 129.03 (s), 128.89 (s), 125.78 (s), 28.83 (s), 18.54 (s), 0.47 (s).

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): 6.86 (s).

IR: 3075, 3059, 2954, 2919, 1585, 1573, 1517, 1481, 1471, 1439, 1414, 1254, 1164, 1062, 1026, 1009, 840, 789, 737, 690 cm^{-1}.

HRMS (ESI) m/z $[M + Na]^+$: calcd for $[C_{20}H_{30}OS_2Si_2 + Na]^+$ 429.1173; found, 429.1169.

Synthesis of 1,1,3,3-tetramethyl-1,3-bis(3-(phenylthio)propyl)disiloxane (compound di-γ-Ph): A mixture of **compound γ-Ph** (0.05 g, 0.24 mmol), water (10 mg) and tris(pentafluorophenyl)borane (1 mg) in toluene (0.5 ml) was stirred for 30 minutes at room temperature. Then the mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.051 g) was 99%.



^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm, J/Hz): 7.34 (dd, J = 8.3, 1.1 Hz, 4H), 7.29 (t, J = 6.6 Hz, 4H), 7.18 (t, J = 7.3 Hz, 2H), 2.95 – 2.92 (t, J = 7,4 Hz, 4H), 1.70 – 1.61 (m, 4H), 0.69 – 0.62 (m, 4H), 0.04 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm): 136.89 (s), 129.02 (s), 128.84 (s), 125.70 (s), 37.01 (s), 23.32 (s), 17.91 (s), 0.32 (s).

^{29}Si NMR (99 MHz, $CDCl_3$, δ/ppm): 7.31 (s).

IR: 3075, 3059, 2954, 2924, 1585, 1481, 1439, 1253, 1059, 1026, 841, 796, 737, 690 cm^{-1}.

HRMS (ESI) m/z $[M + H]^+$: calcd for $[C_{22}H_{34}OS_2Si_2 + H]^+$, 435.1662; found, 435.1654; $[M + NH_4]^+$: calcd for $[C_{22}H_{34}OS_2Si_2 + NH_4]^+$ 452.1928; found, 452.1899; $[M + Na]^+$: calcd for $[C_{22}H_{34}OS_2Si_2 + Na]^+$ 457.1482; found, 457.1470.

Spectra

Hydrotiolation

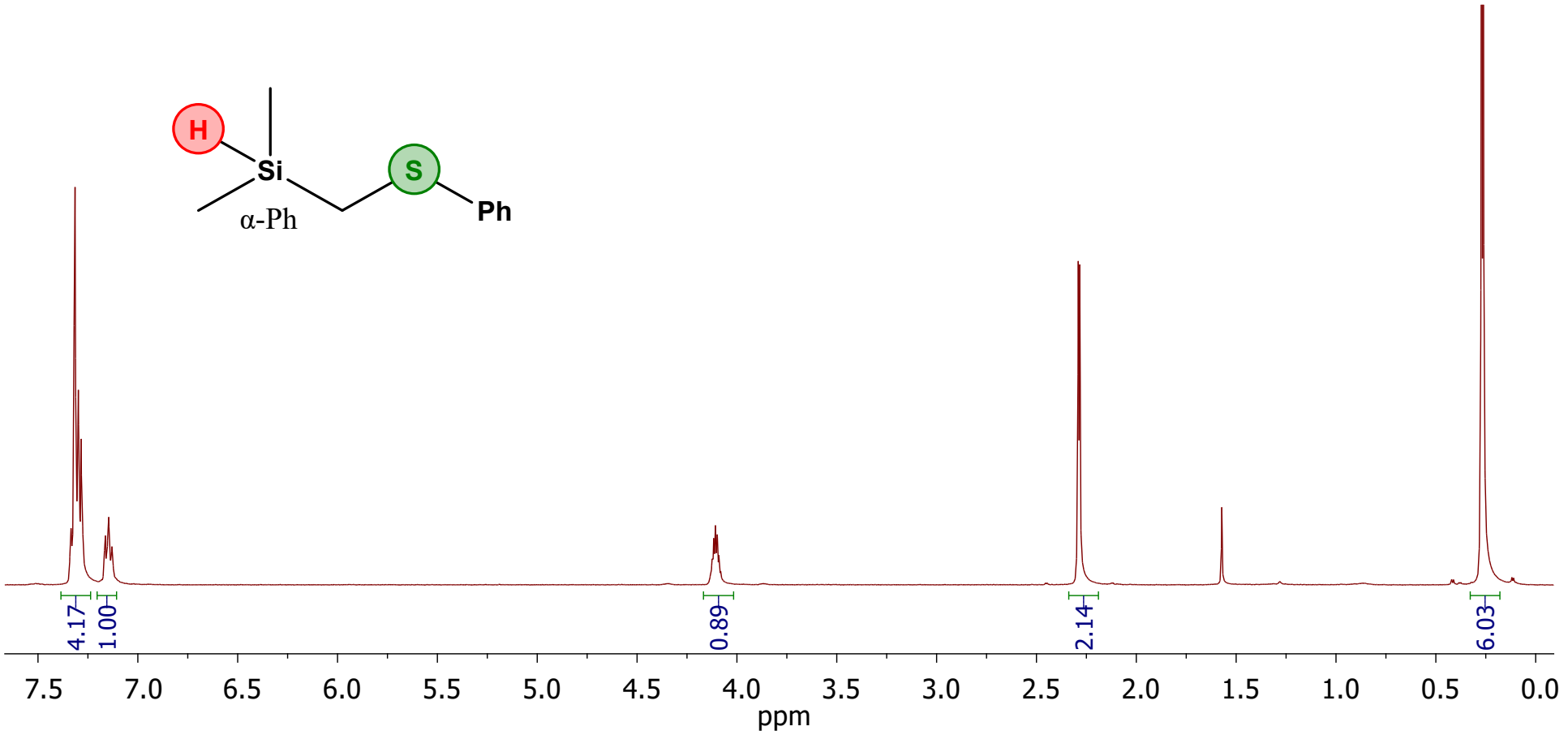


Figure 1s. ^{1}H NMR spectrum of compound **α-Ph** (500 MHz, solvent – $CDCl_3$).

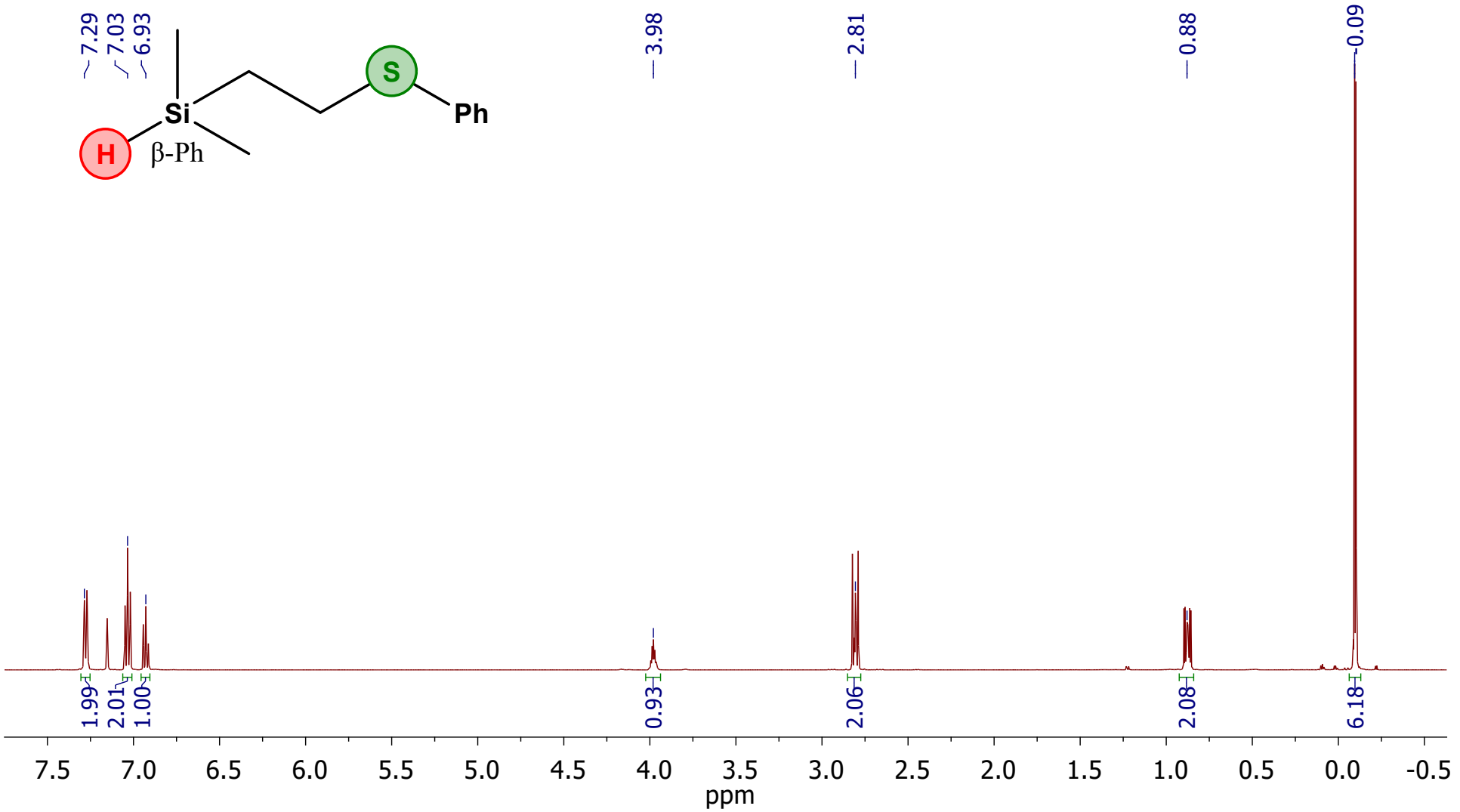


Figure 2s. ^{1}H NMR spectrum of compound **β-Ph** (500 MHz, solvent – C_6D_6).

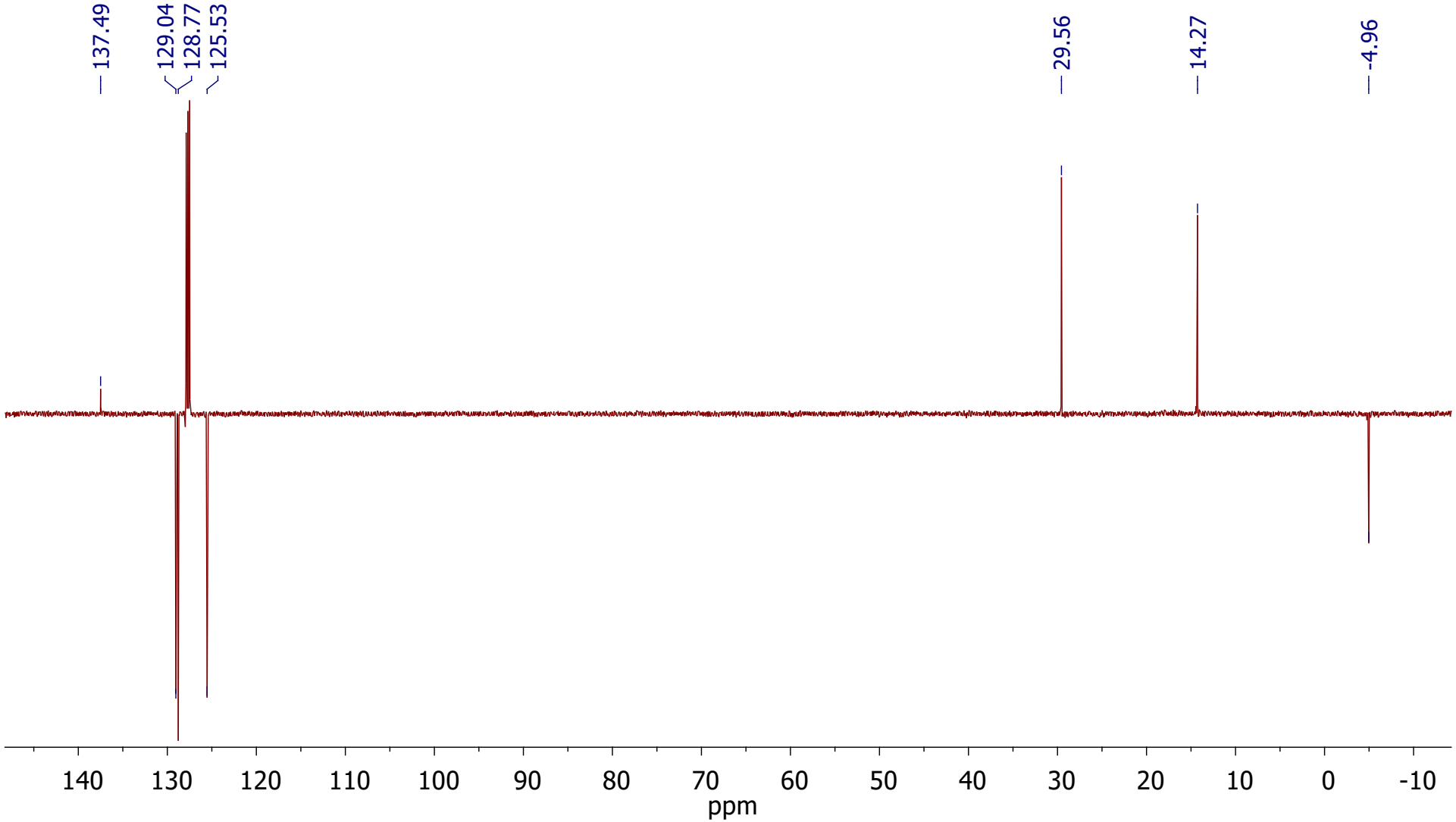


Figure 3s. ^{13}C NMR spectrum of compound **β-Ph** (500 MHz, solvent – C_6D_6, jmod).

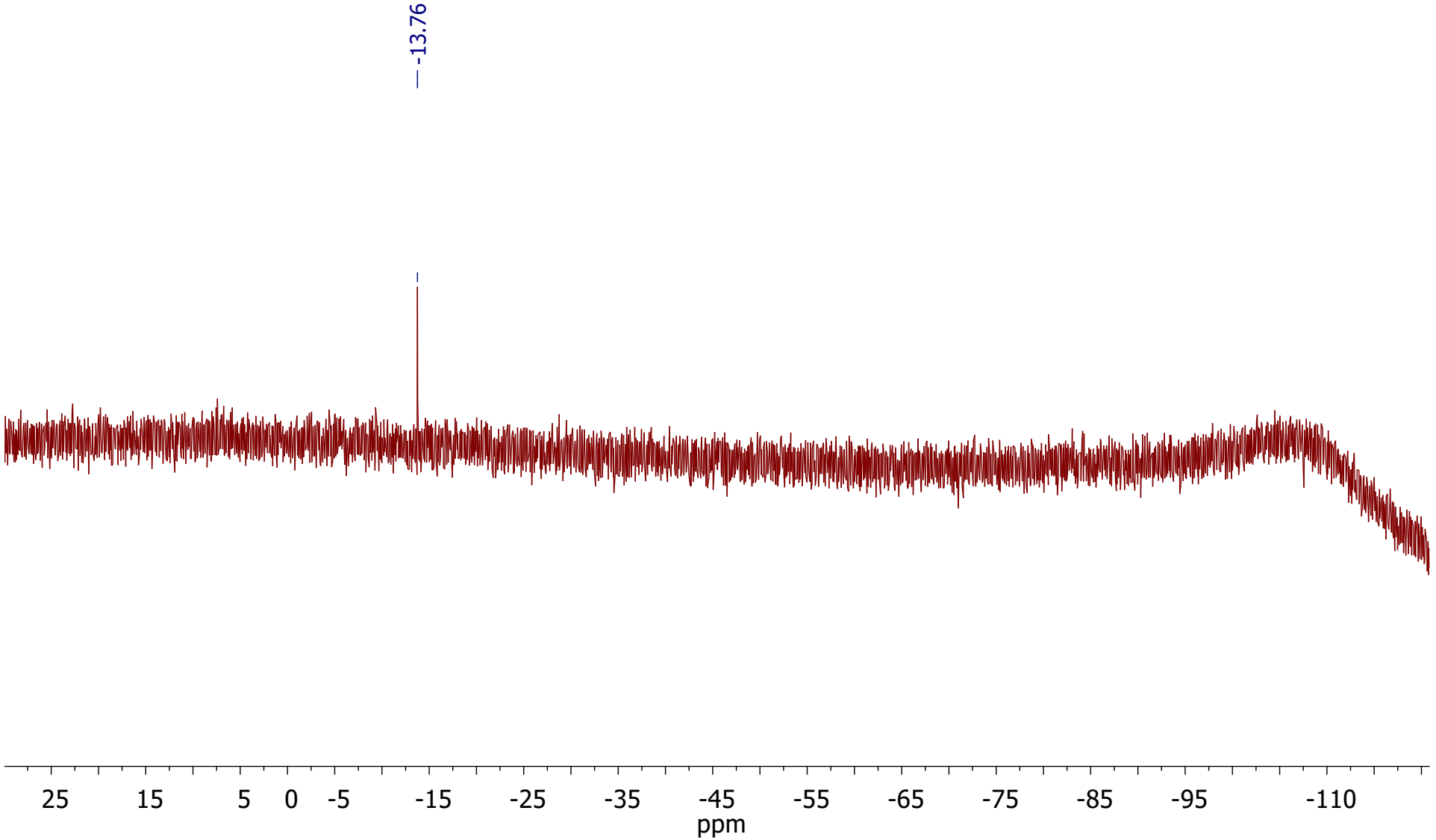


Figure 4s. ^{29}Si NMR spectrum of compound **β-Ph** (500 MHz, solvent – C_6D_6).

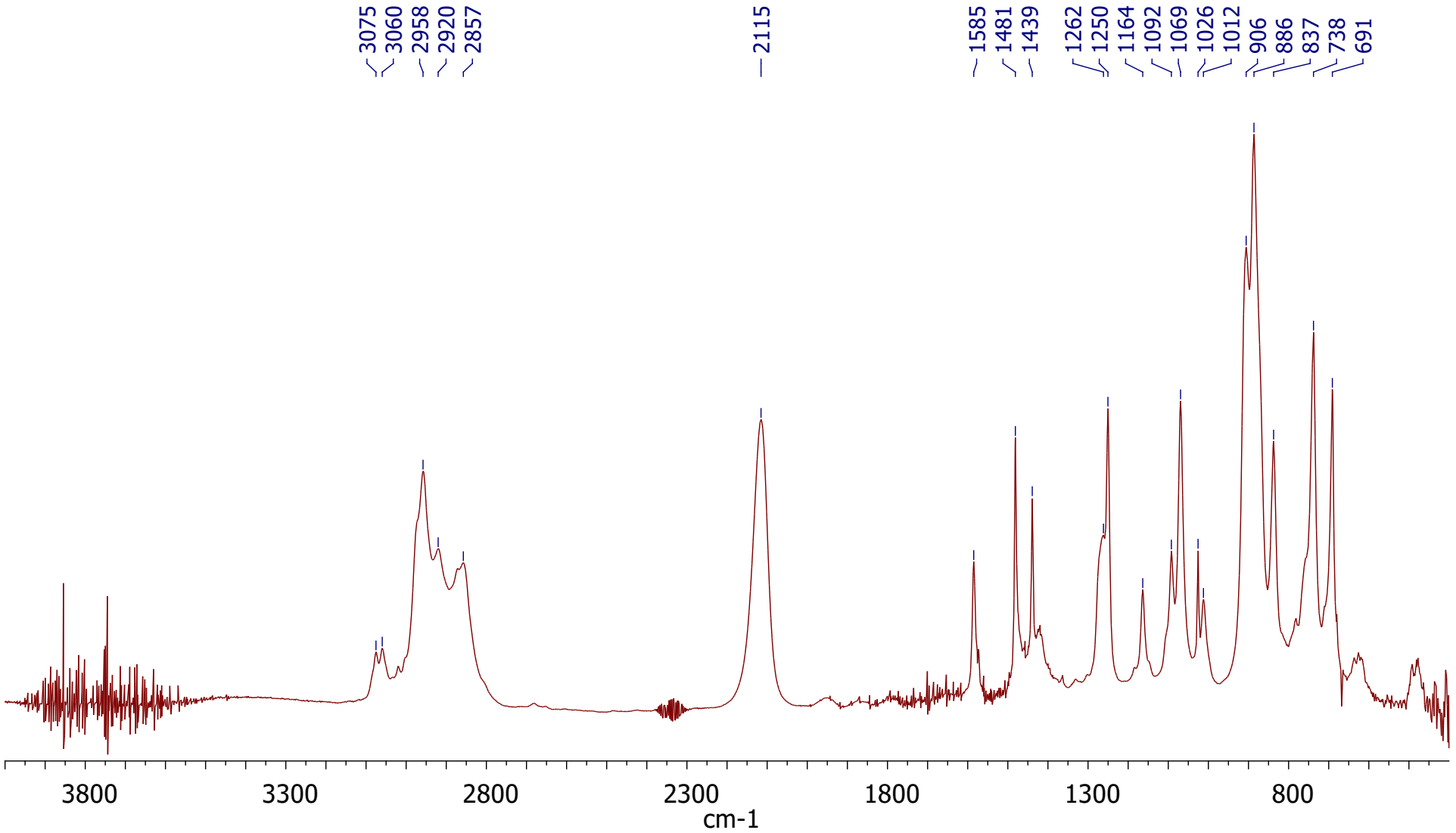


Figure 5s. IR-spectrum of compound **β-Ph.**

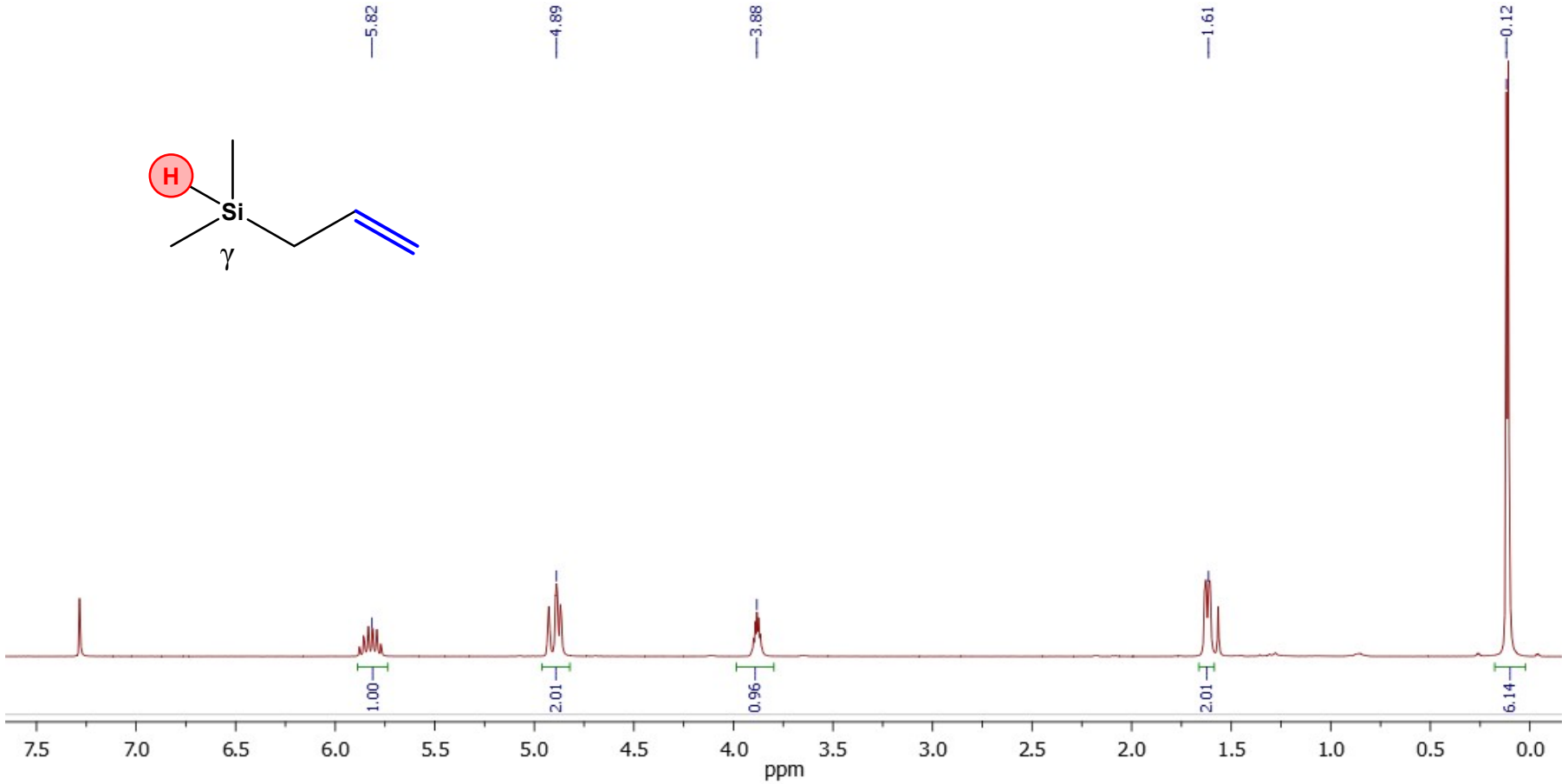


Figure 6s. ^{1}H NMR spectrum of compound **γ** (500 MHz, solvent – $CDCl_3$).

γ

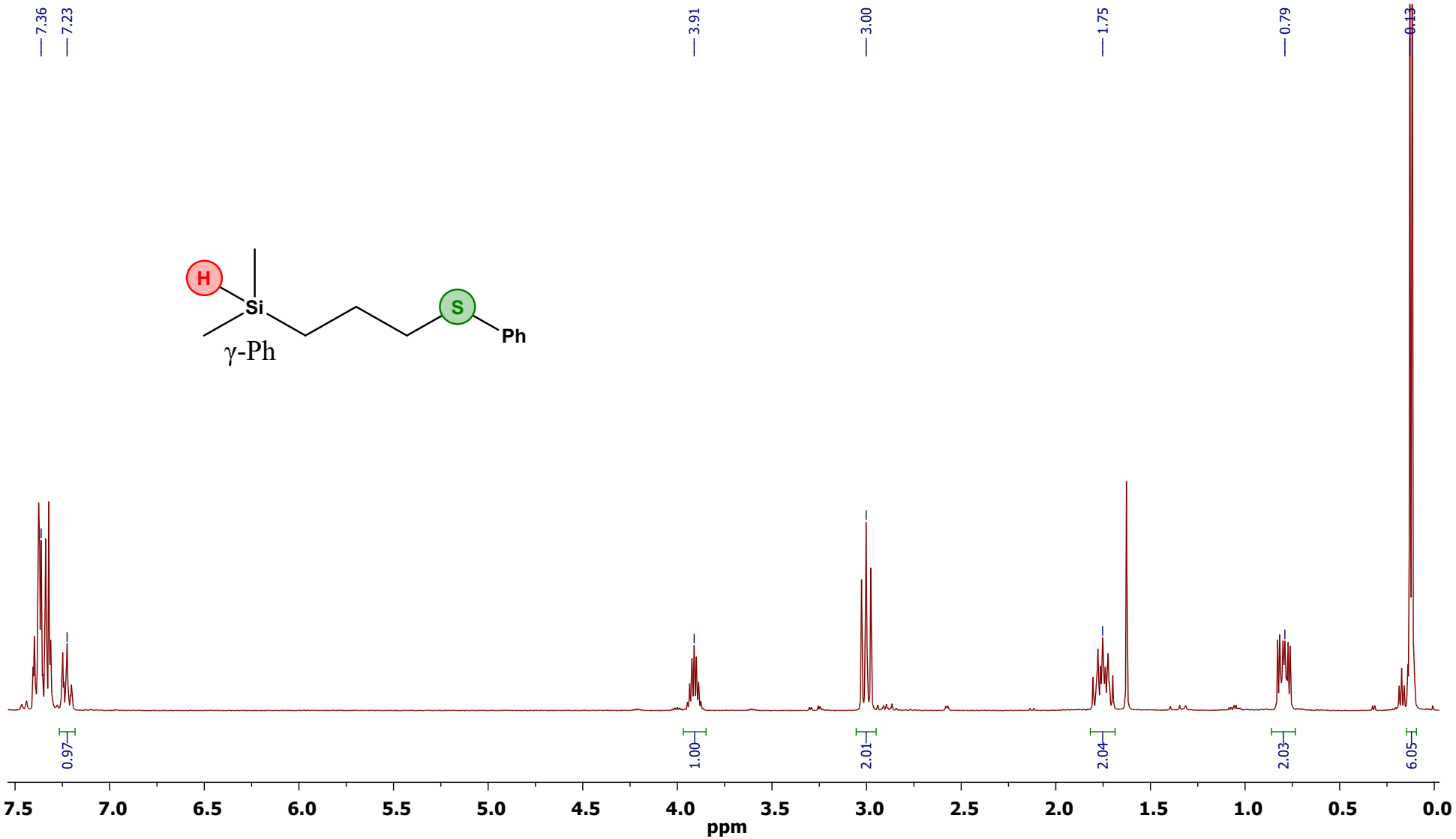


Figure 7s. ^{1}H NMR spectrum of compound **γ-Ph** (500 MHz, solvent – $CDCl_3$).

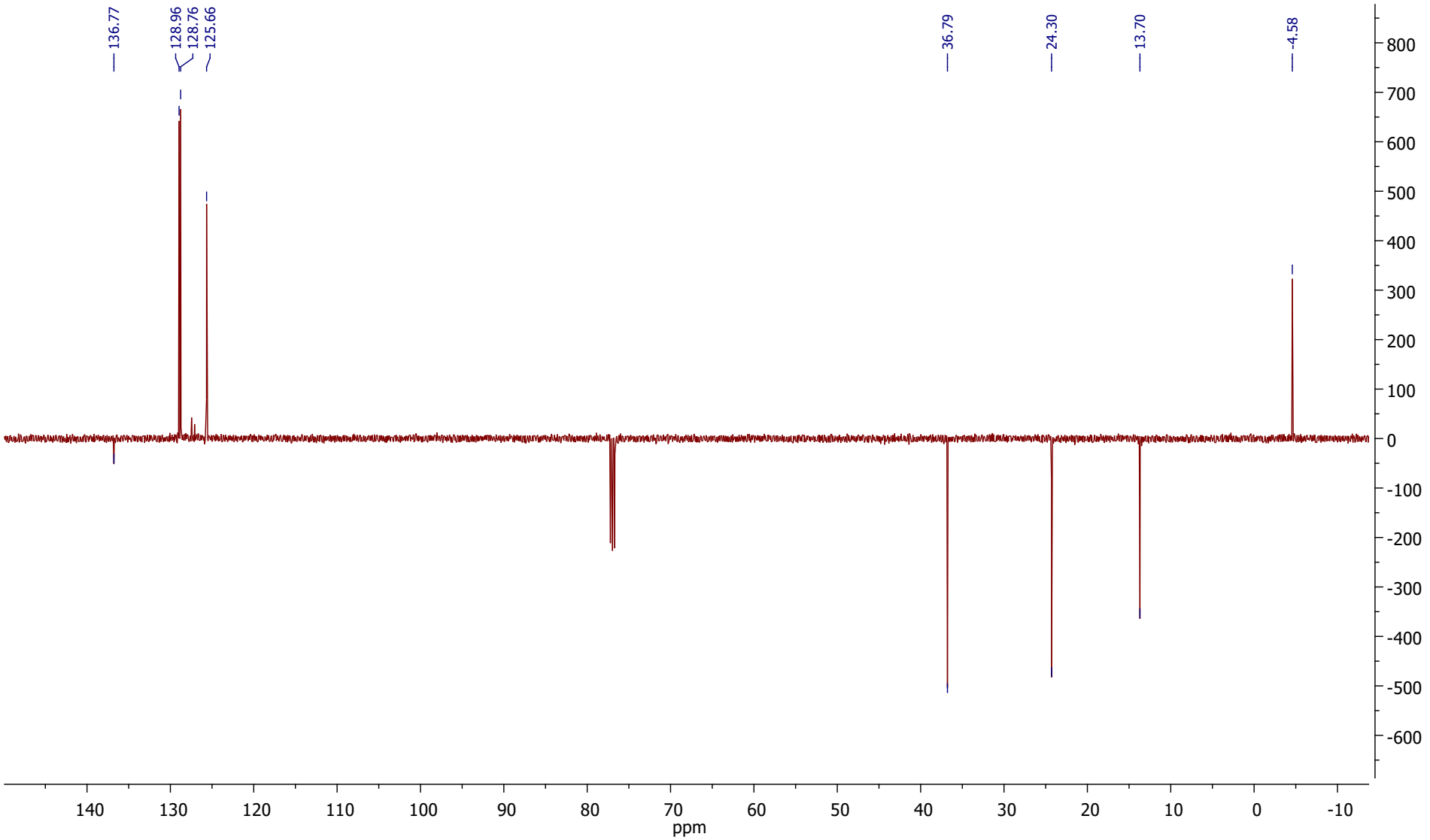


Figure 8s. ^{13}C NMR spectrum of compound **γ-Ph** (500 MHz, solvent – $CDCl_3$, jmod).

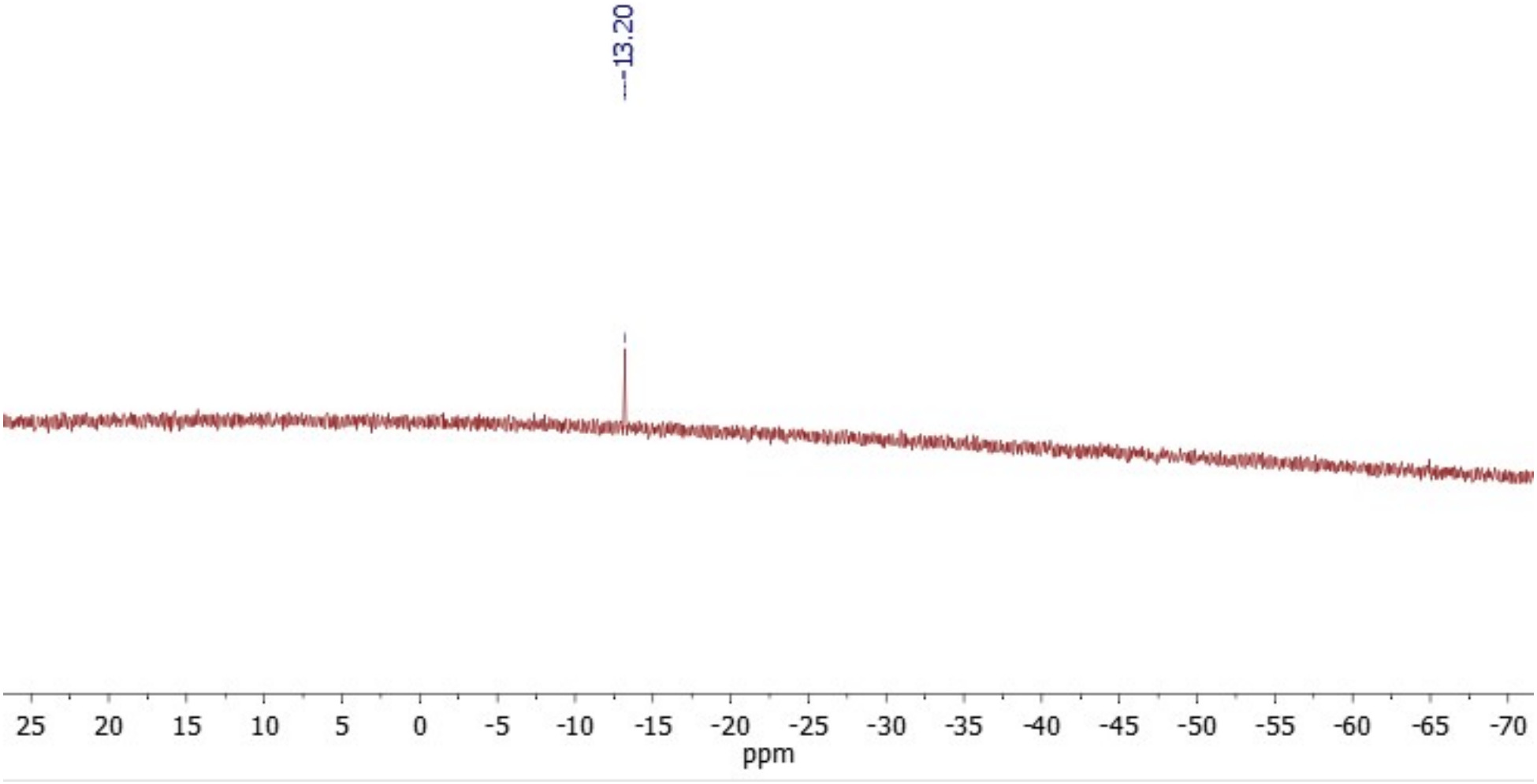


Figure 9s. ^{29}Si NMR spectrum of compound **γ-Ph** (500 MHz, solvent – $CDCl_3$).

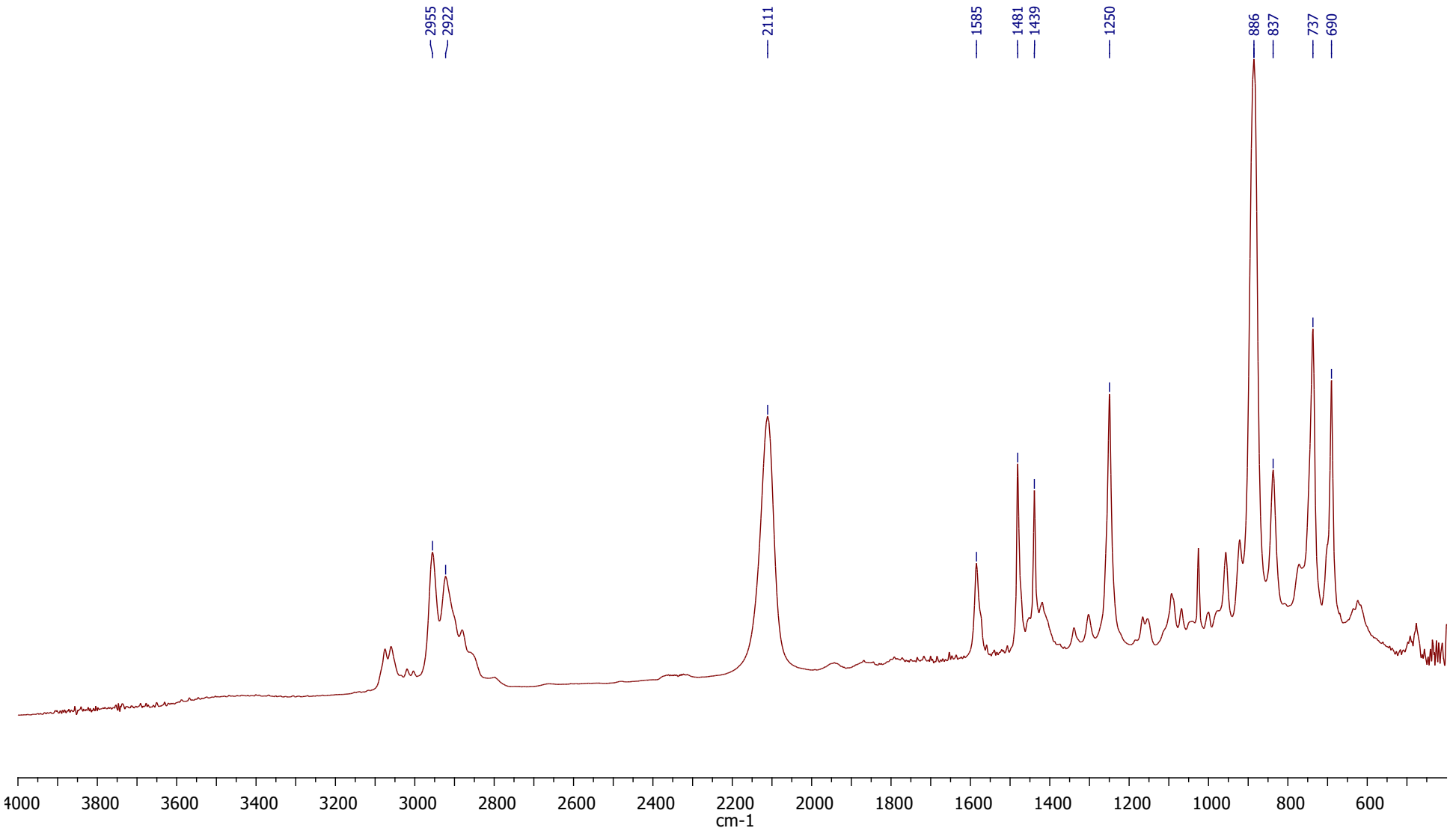


Figure 10s. IR-spectrum of compound **γ-Ph.**

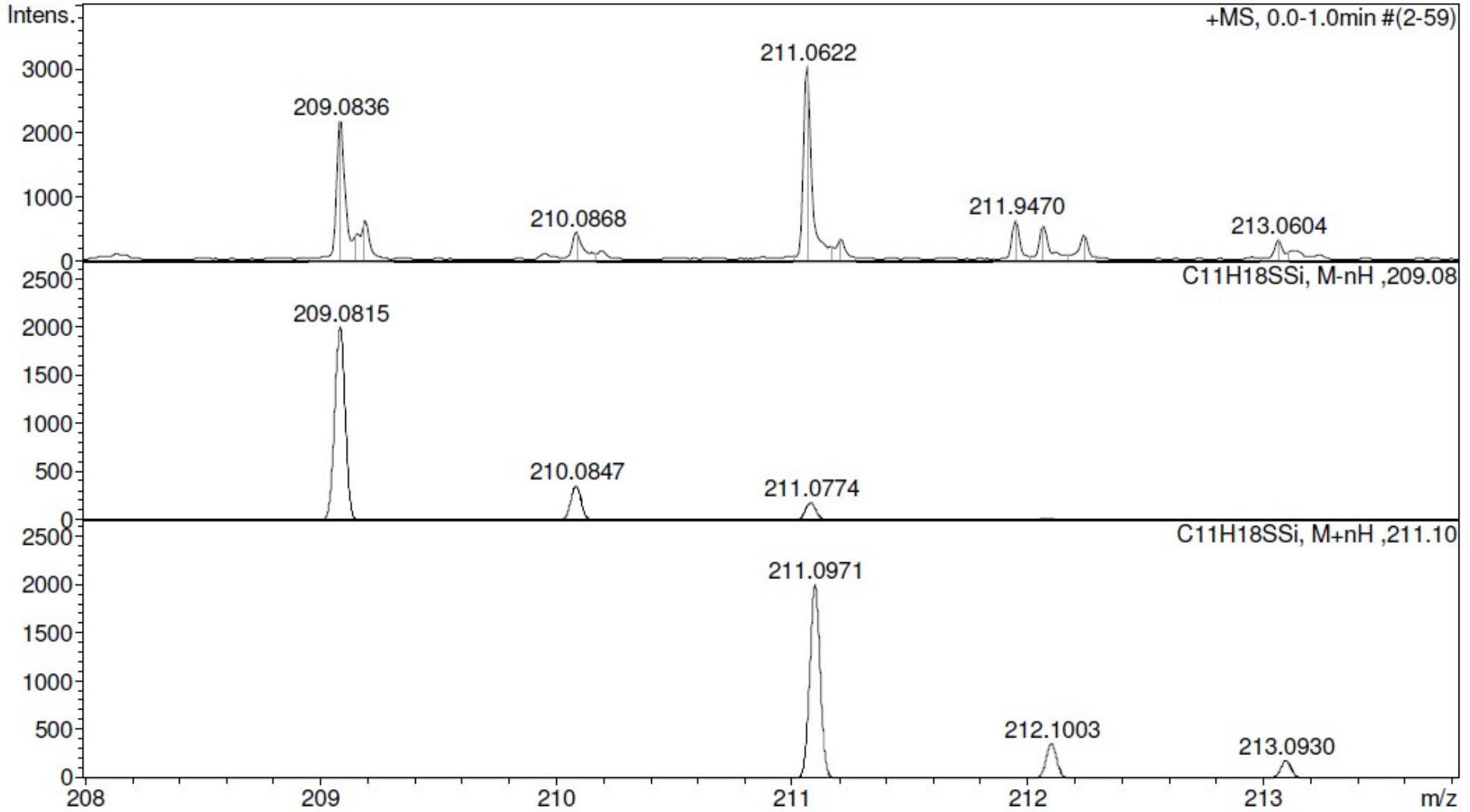


Figure 11s. HRMS (ESI) for compound **γ-Ph.**

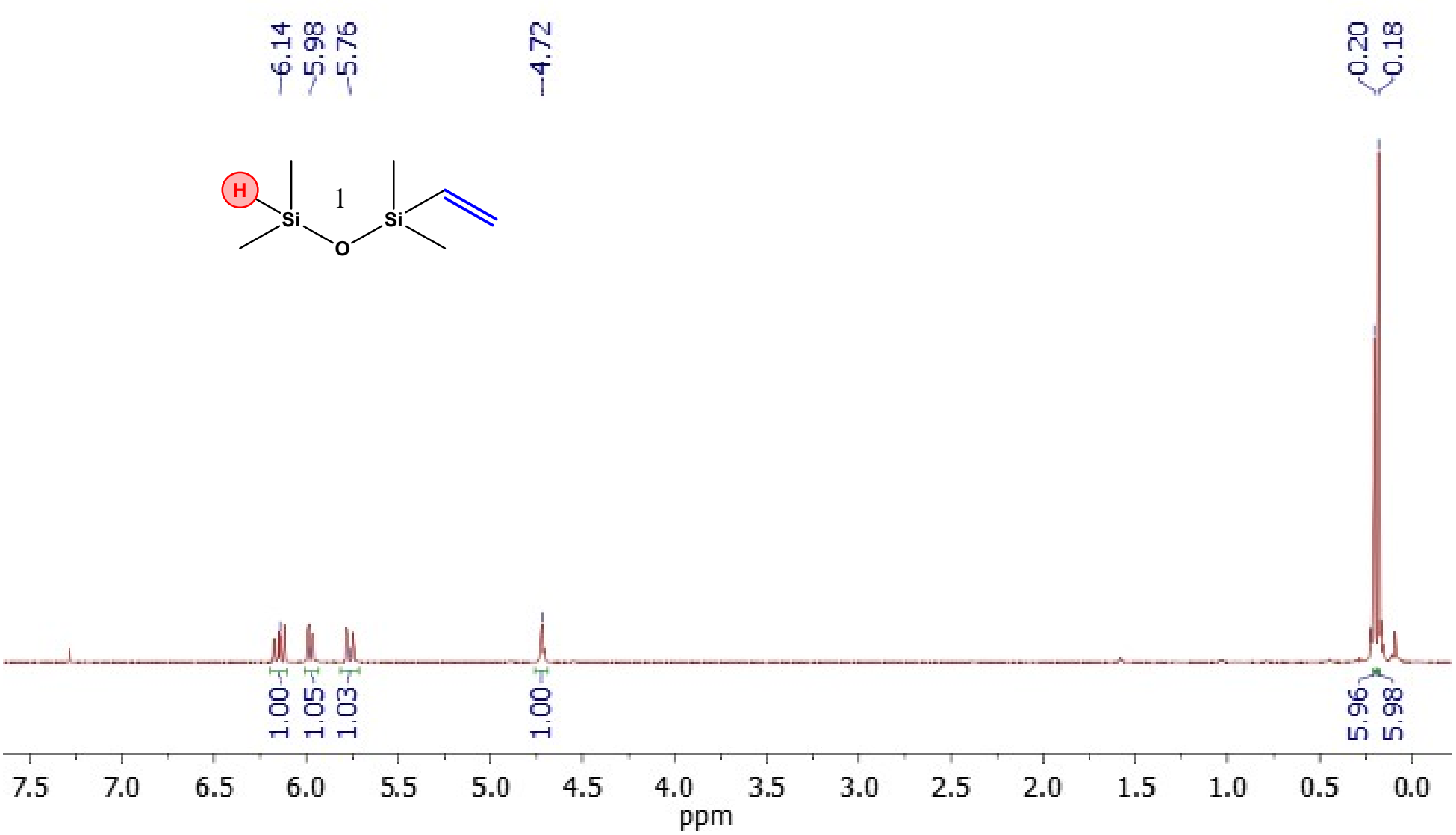


Figure 12s. ^{1}H NMR spectrum of compound **1** (500 MHz, solvent – $CDCl_3$).

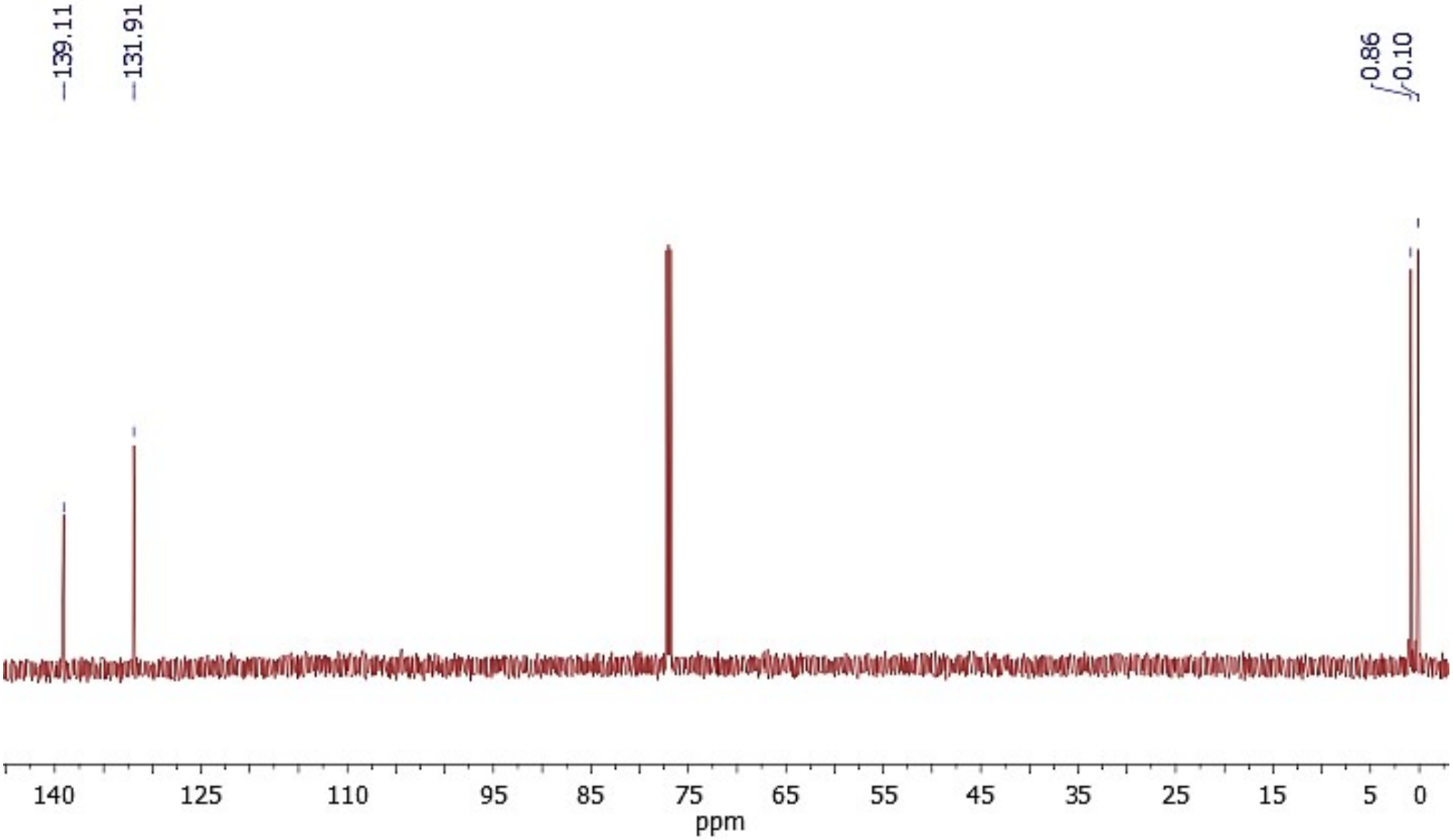


Figure 13s. ^{13}C NMR spectrum of compound **1** (500 MHz, solvent – $CDCl_3$).

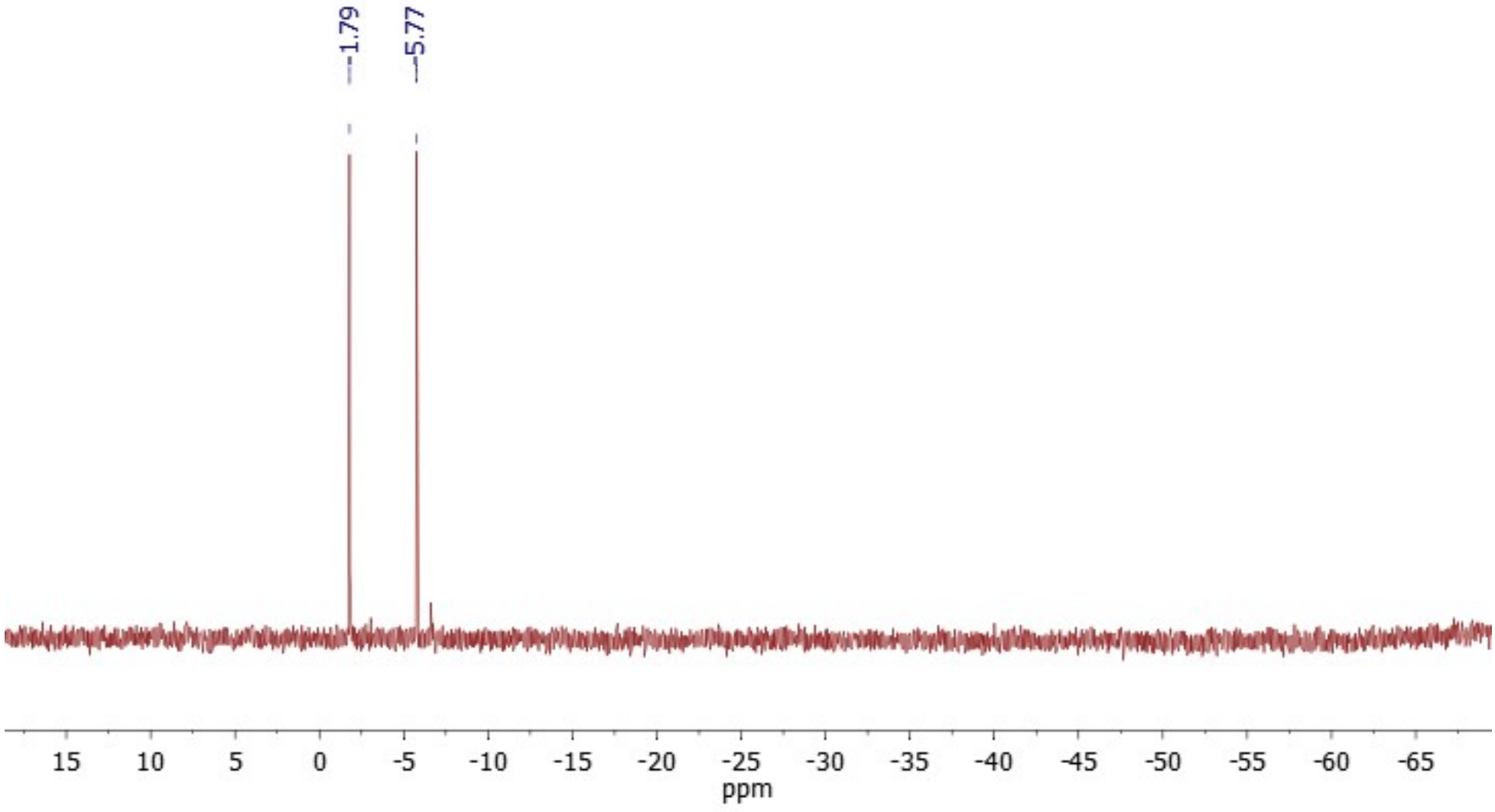


Figure 14s. ^{29}Si NMR spectrum of compound **1** (500 MHz, solvent – $CDCl_3$).

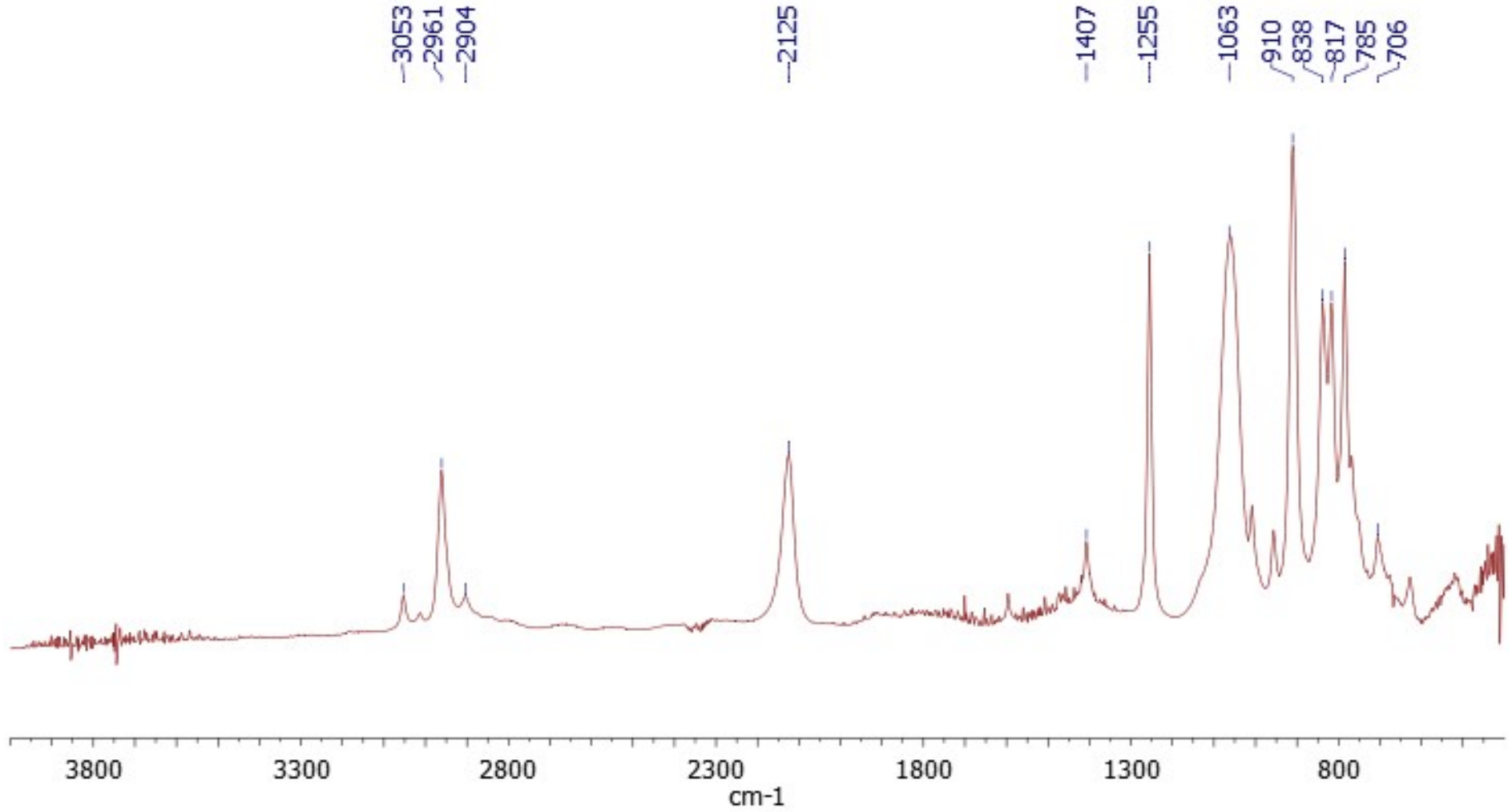


Figure 15s. IR-spectrum of compound **1.**

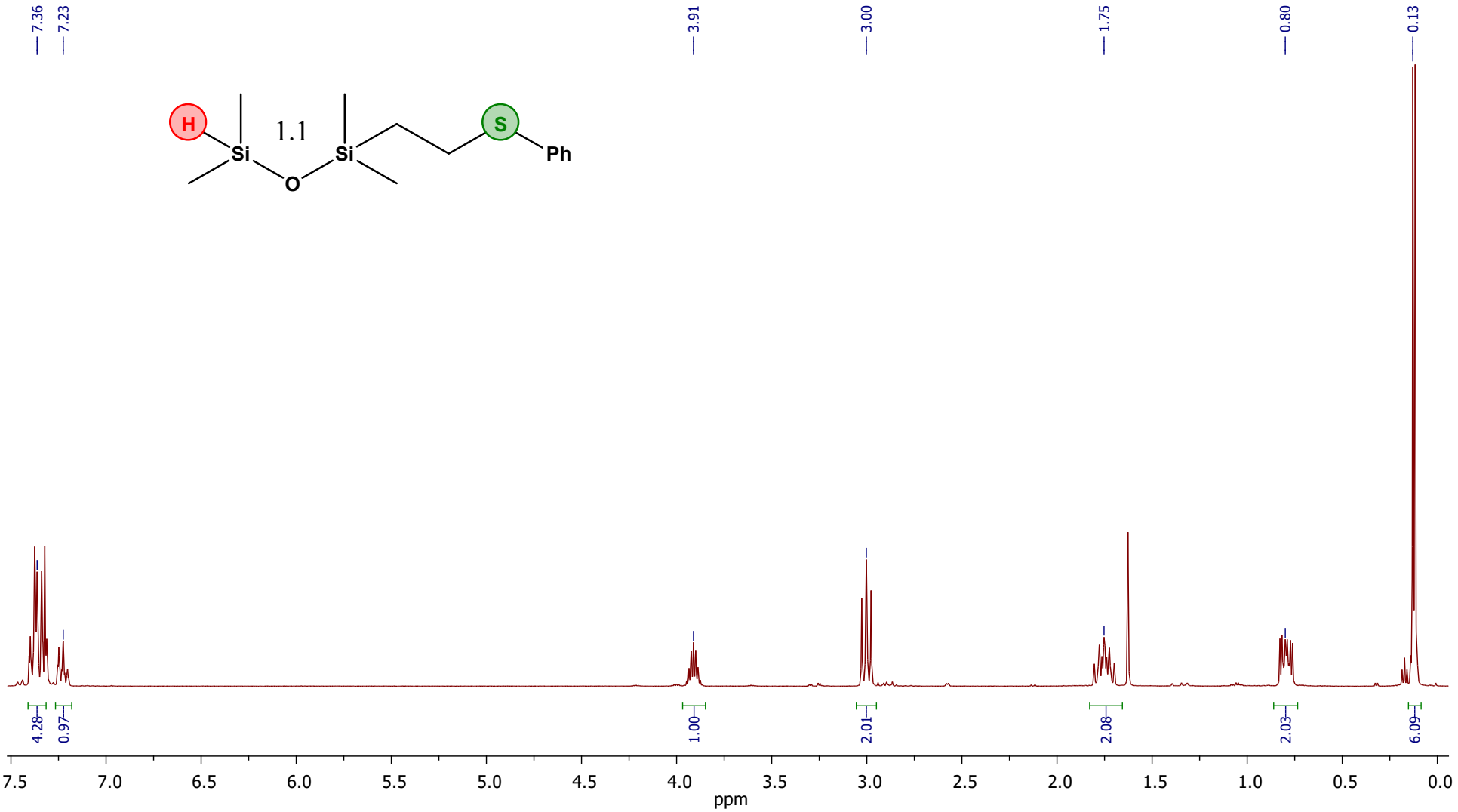


Figure 16s. ^{1}H NMR spectrum of compound **1.1** (400 MHz, solvent – $CDCl_3$).

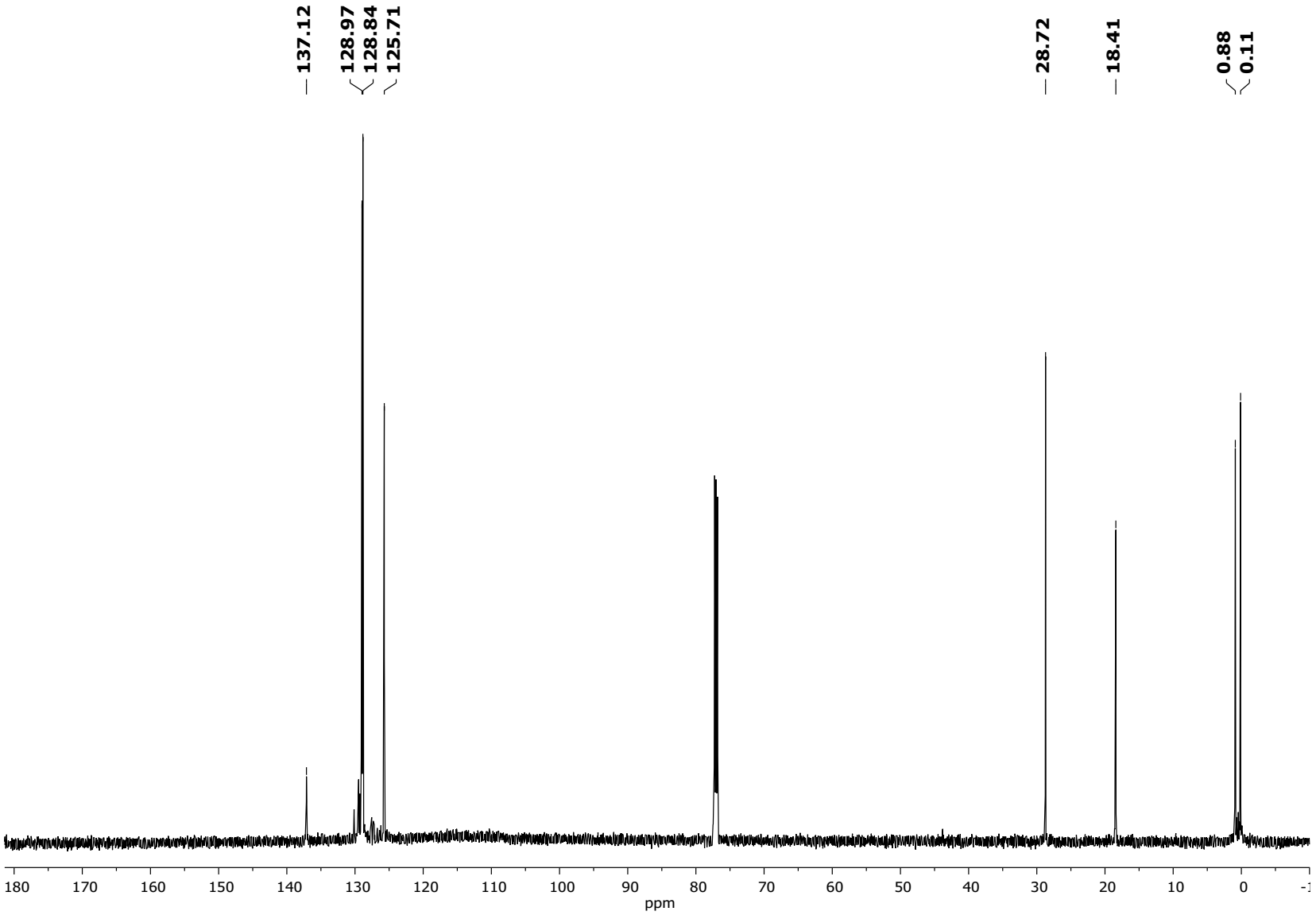


Figure 17s. ^{13}C NMR spectrum of compound **1.1** (400 MHz, solvent – $CDCl_3$).

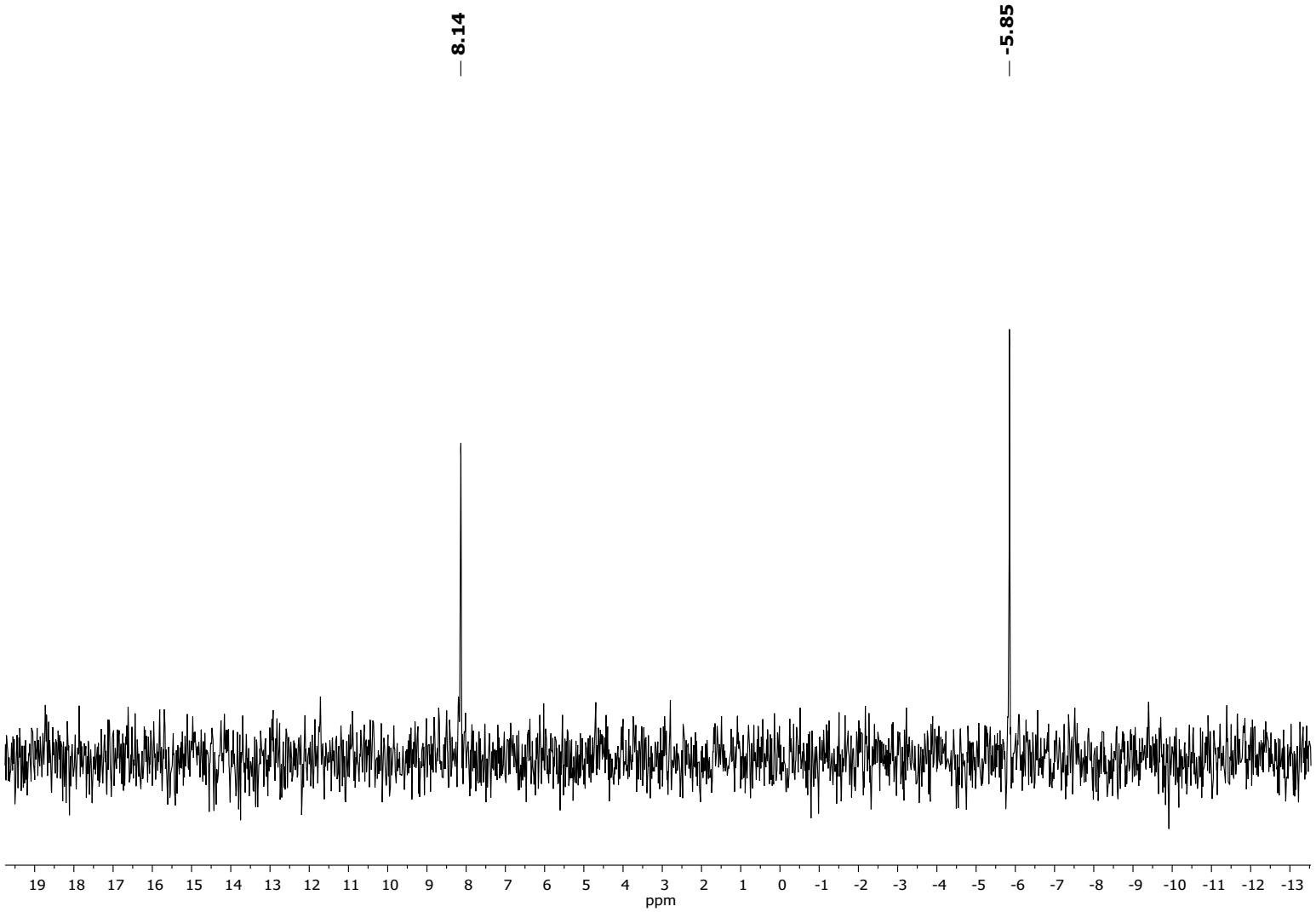


Figure 18s. ^{29}Si NMR spectrum of compound **1.1** (400 MHz, solvent – $CDCl_3$).

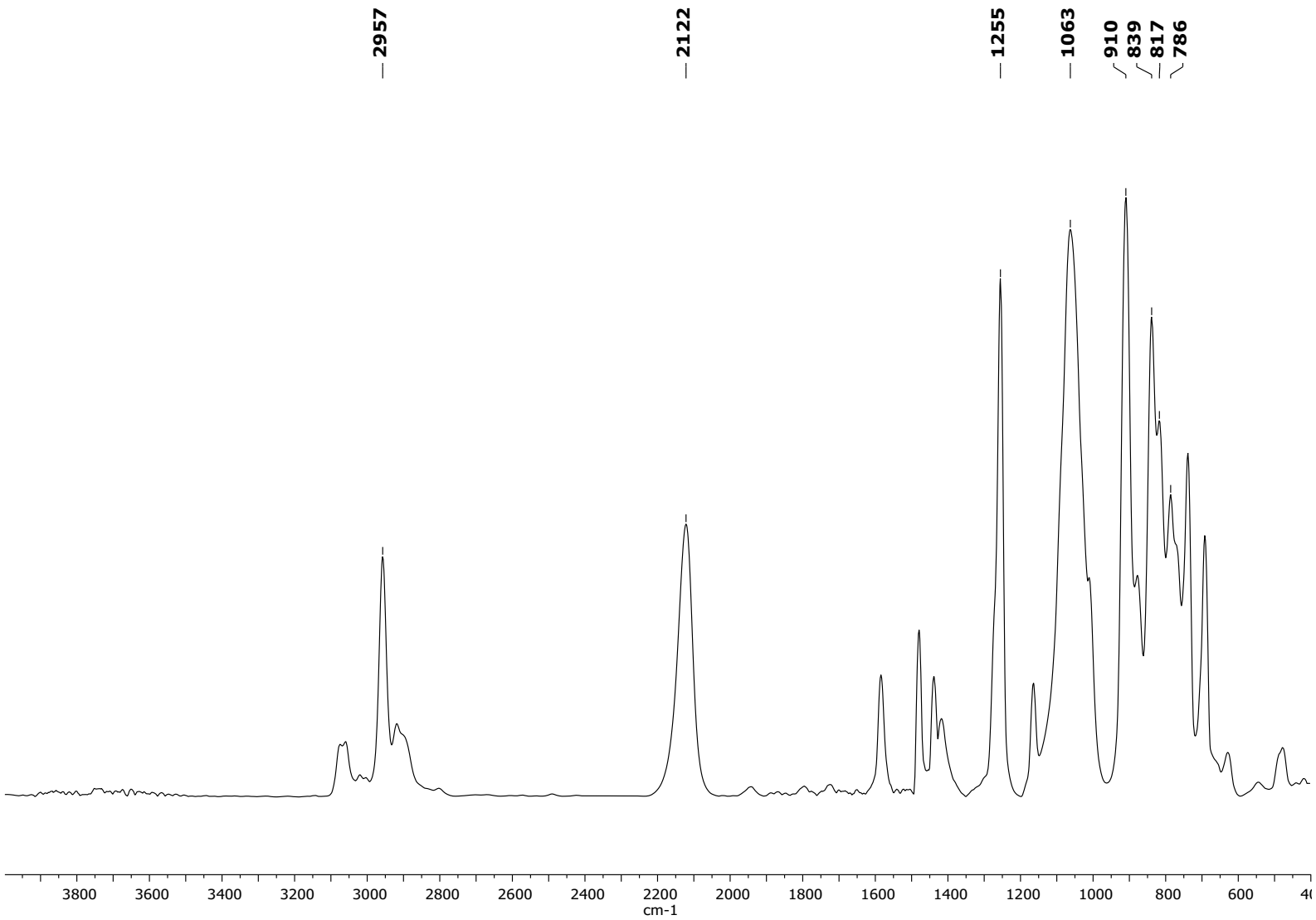


Figure 19s. IR-spectrum of compound **1.1.**

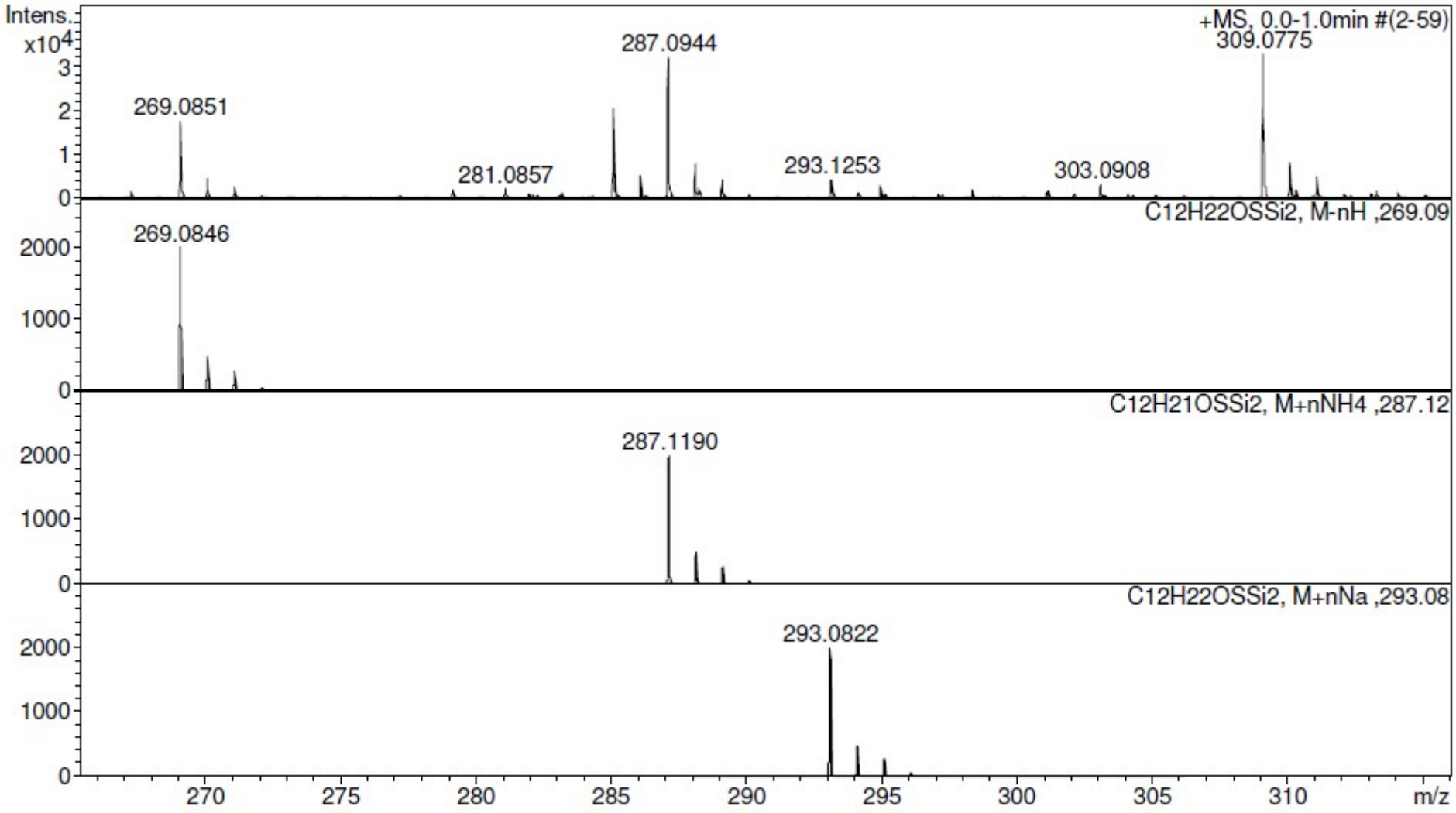


Figure 20s. HRMS (ESI) for compound **1.1.**

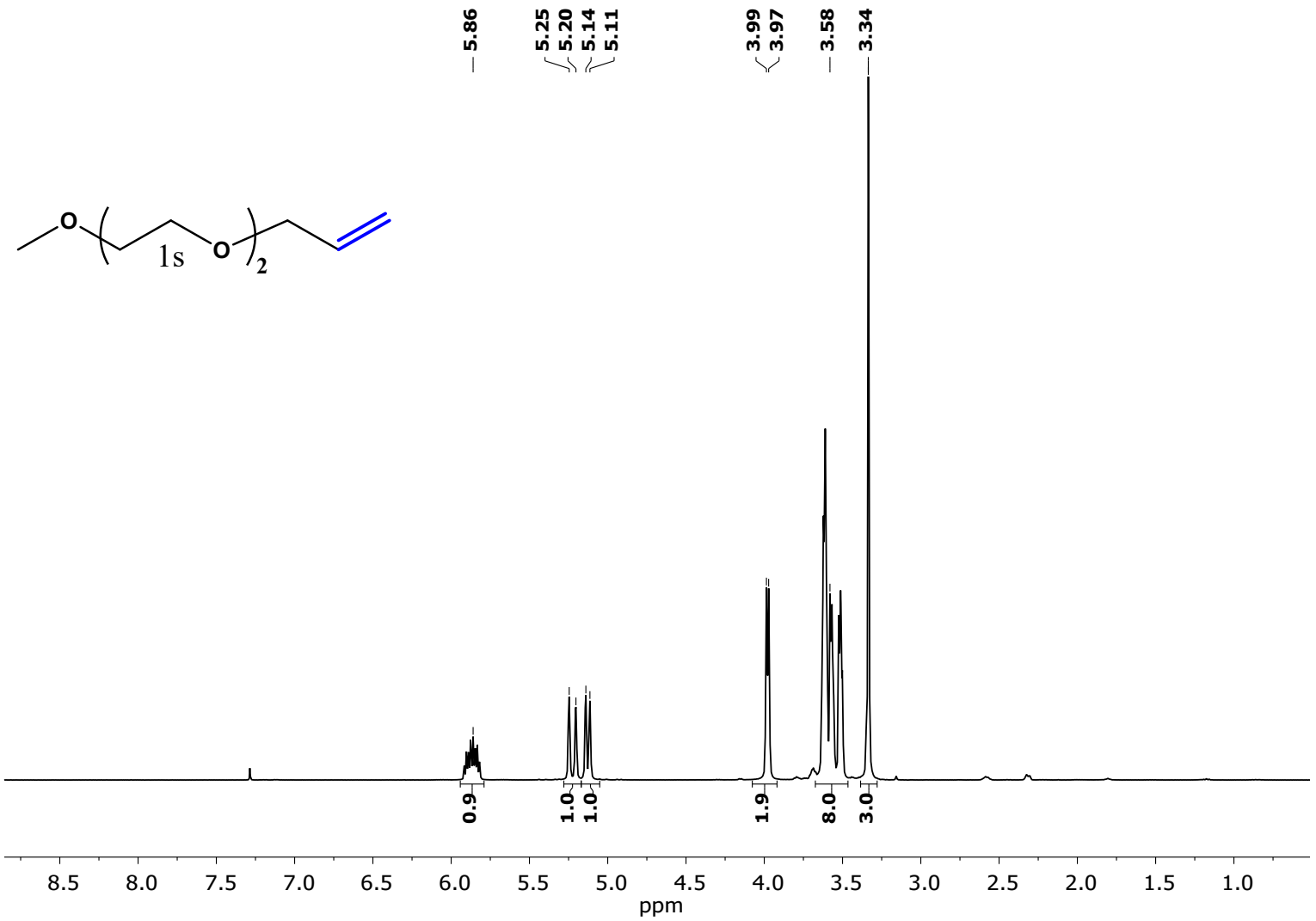


Figure 21s. ^{1}H NMR spectrum of compound **1'** (400 MHz, solvent – $CDCl_3$).

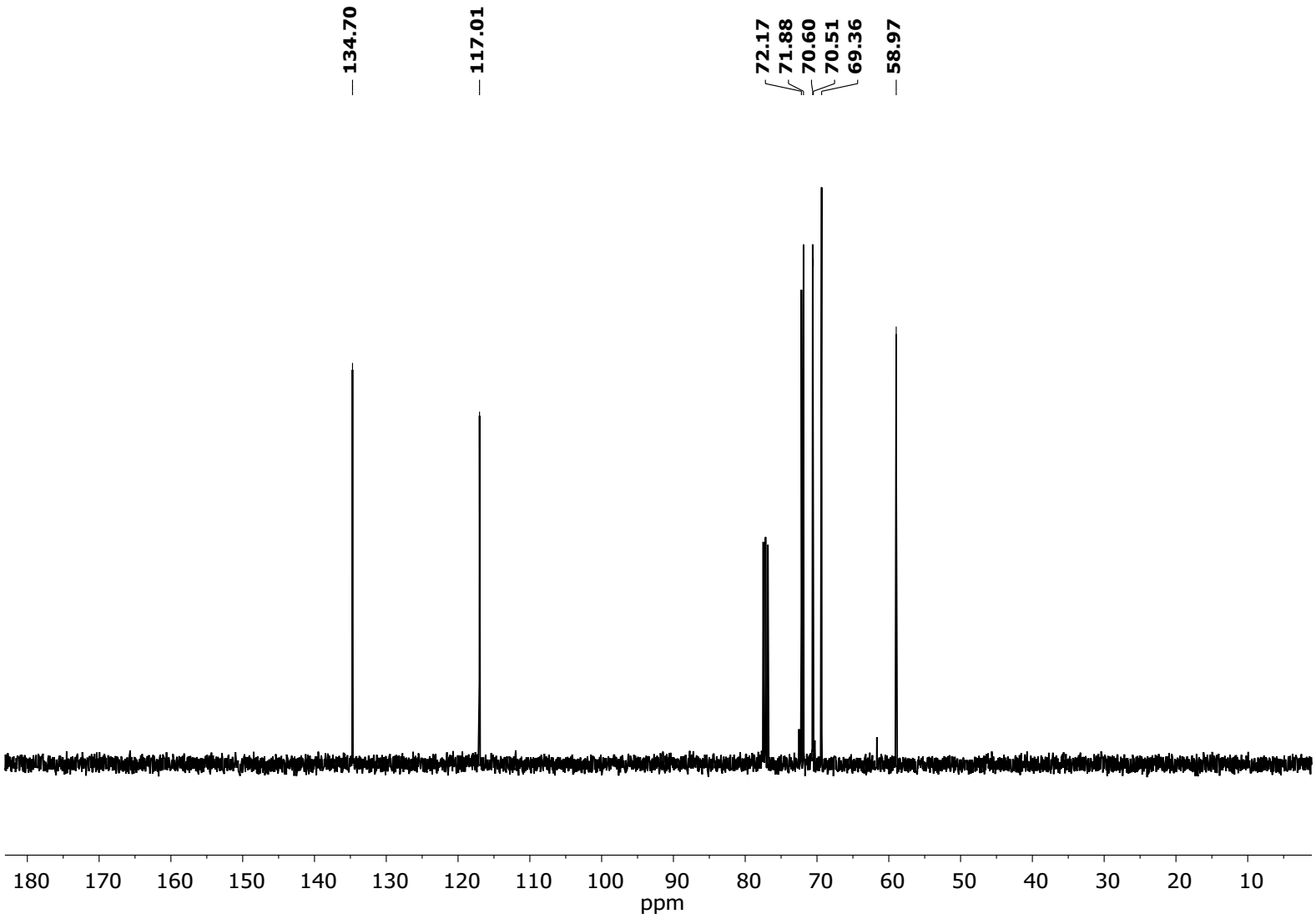


Figure 22s. ^{13}C NMR spectrum of compound **1'** (100 MHz, solvent – $CDCl_3$).

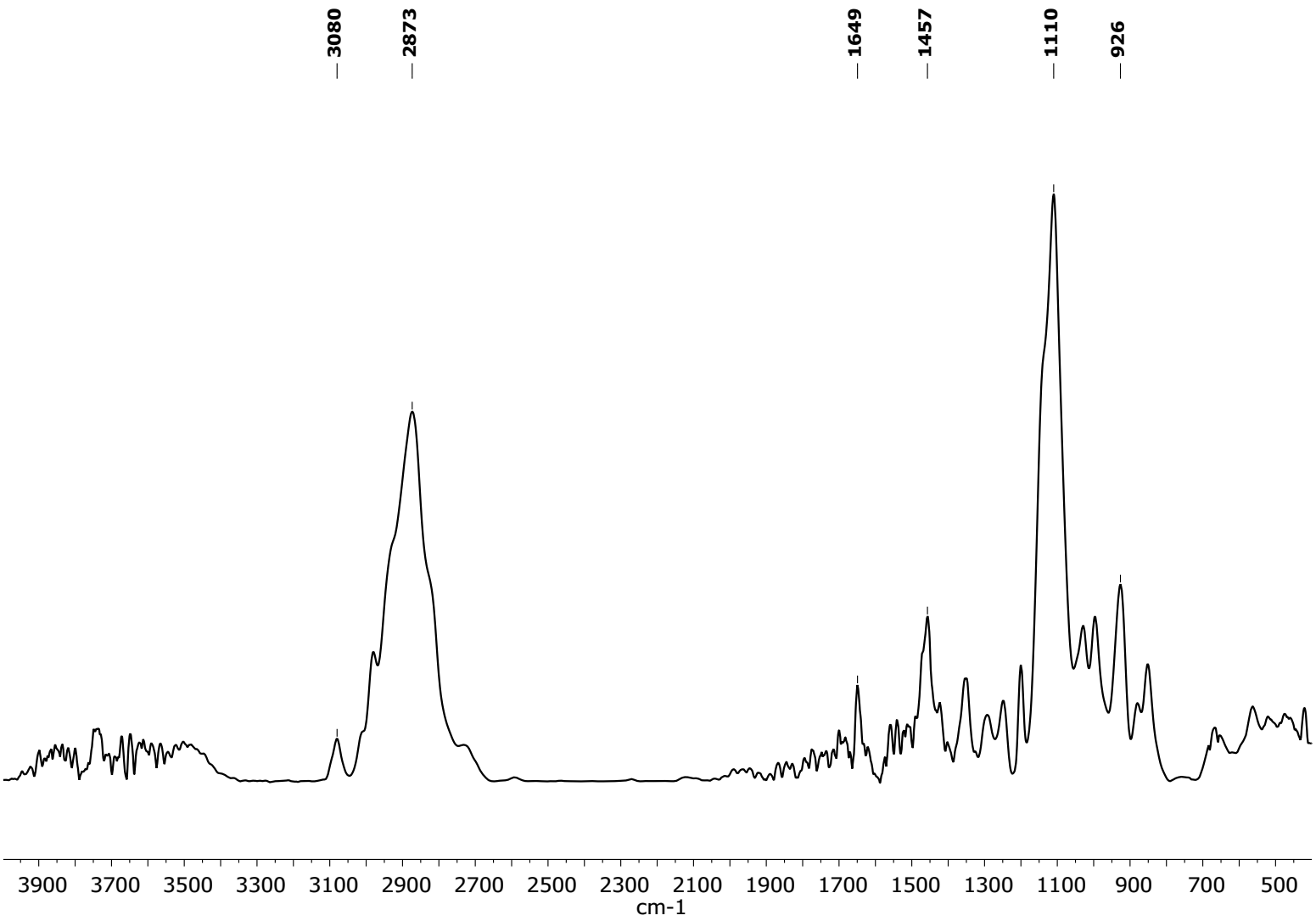


Figure 23s. IR-spectrum of compound **1'.**

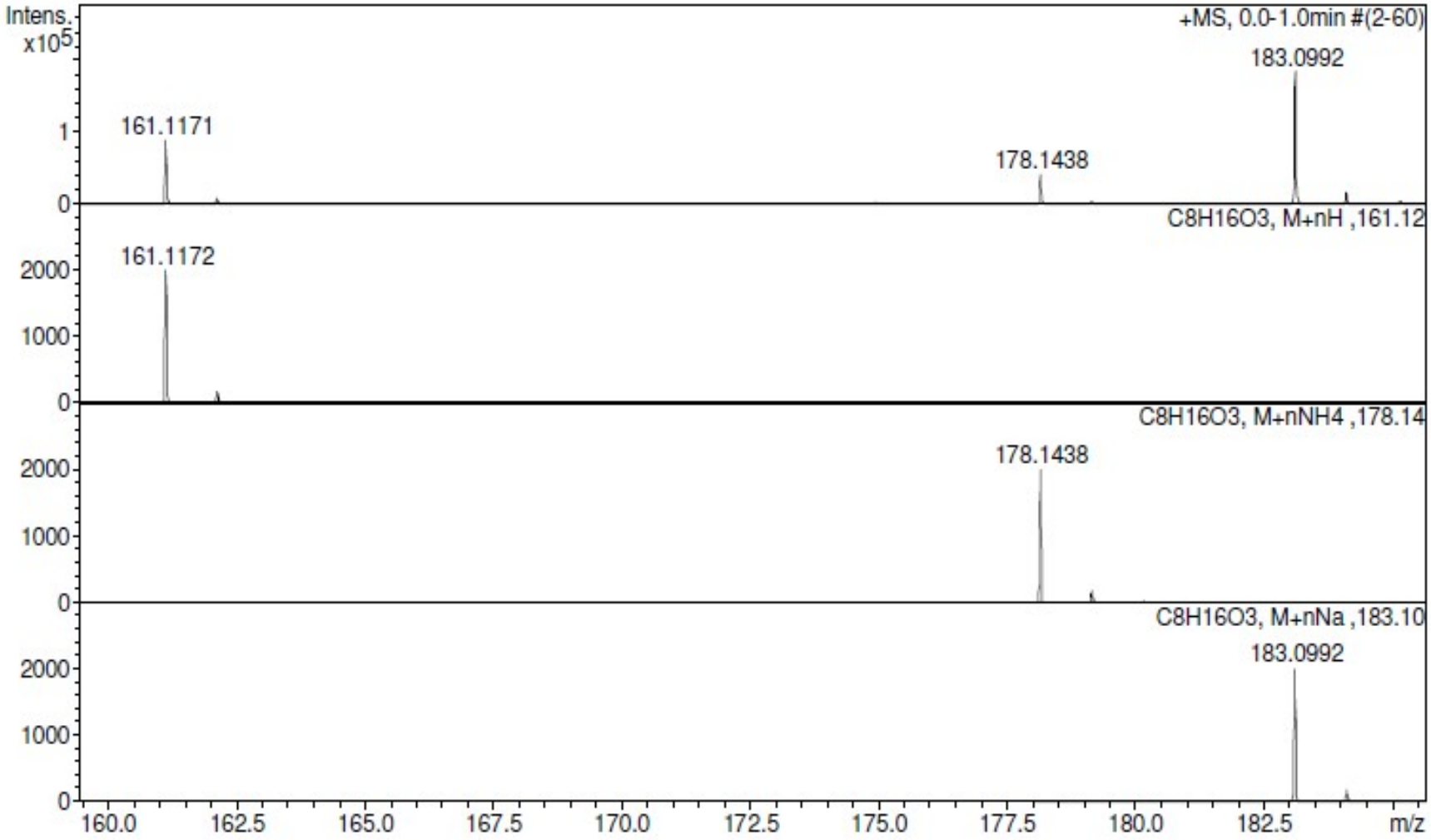


Figure 24s. HRMS (ESI) for compound **1'**.

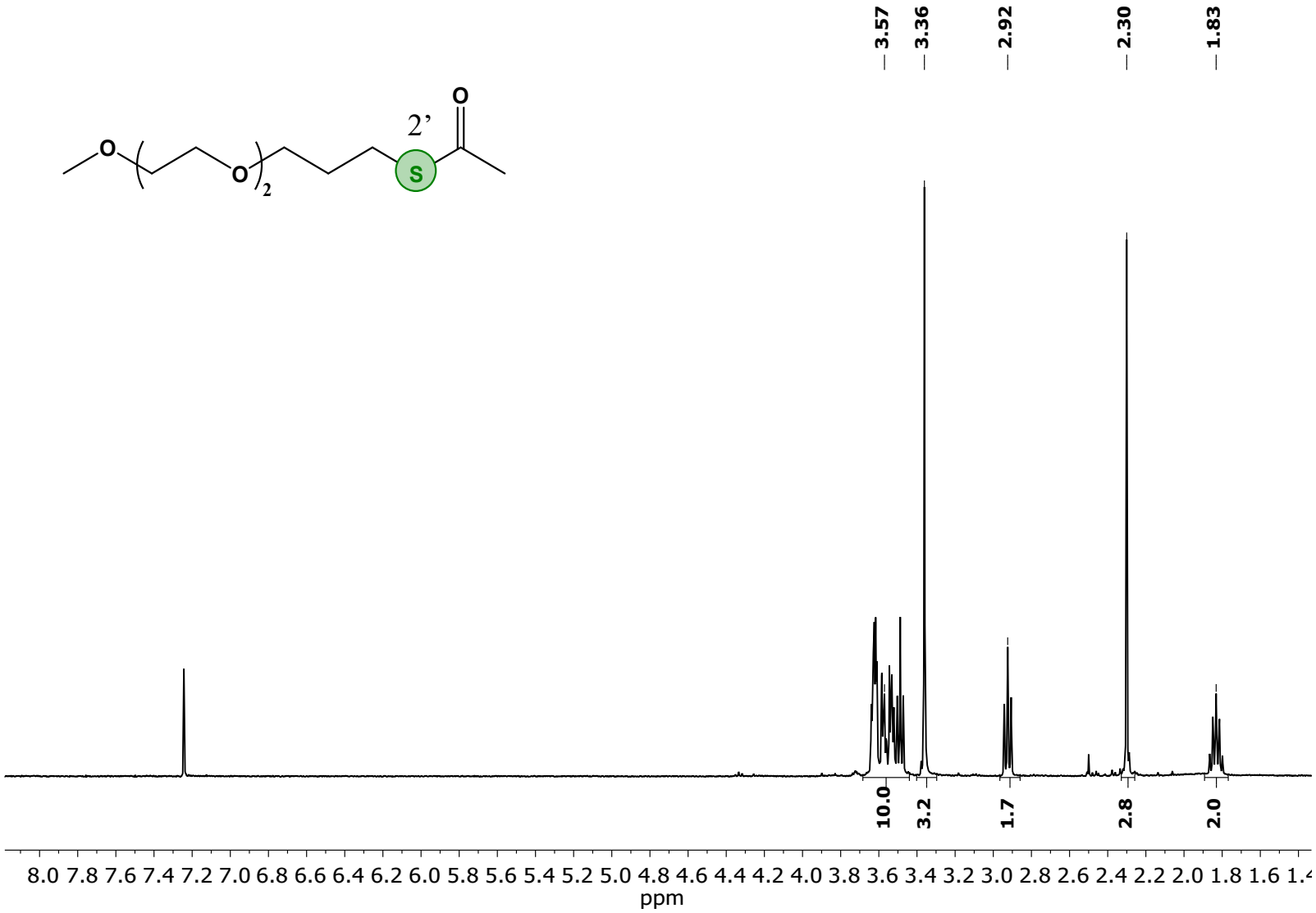


Figure 25s. ^{1}H NMR spectrum of compound **2'** (400 MHz, solvent – $CDCl_3$).

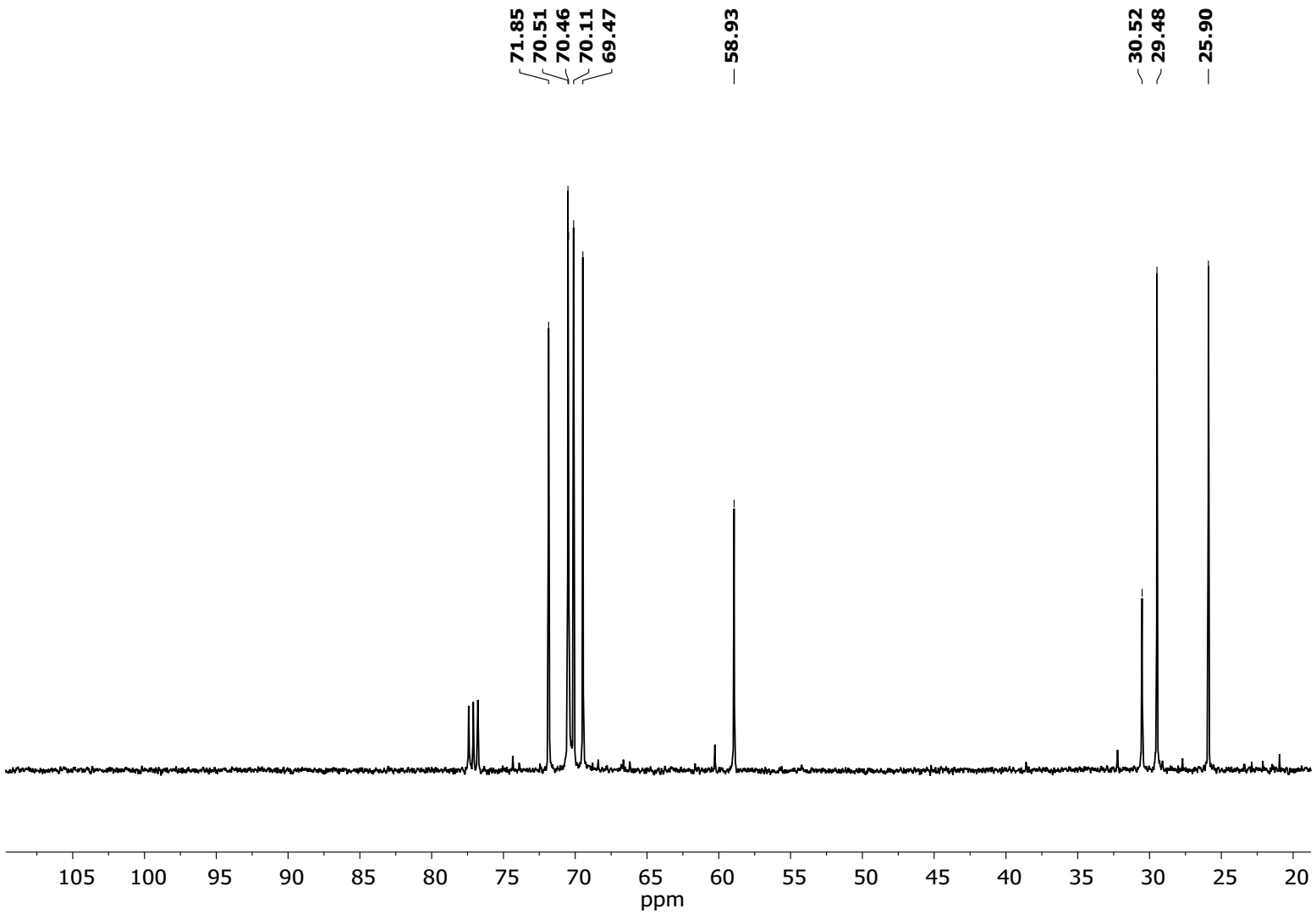


Figure 26s. ^{13}C NMR spectrum of compound **2'** (100 MHz, solvent – $CDCl_3$).

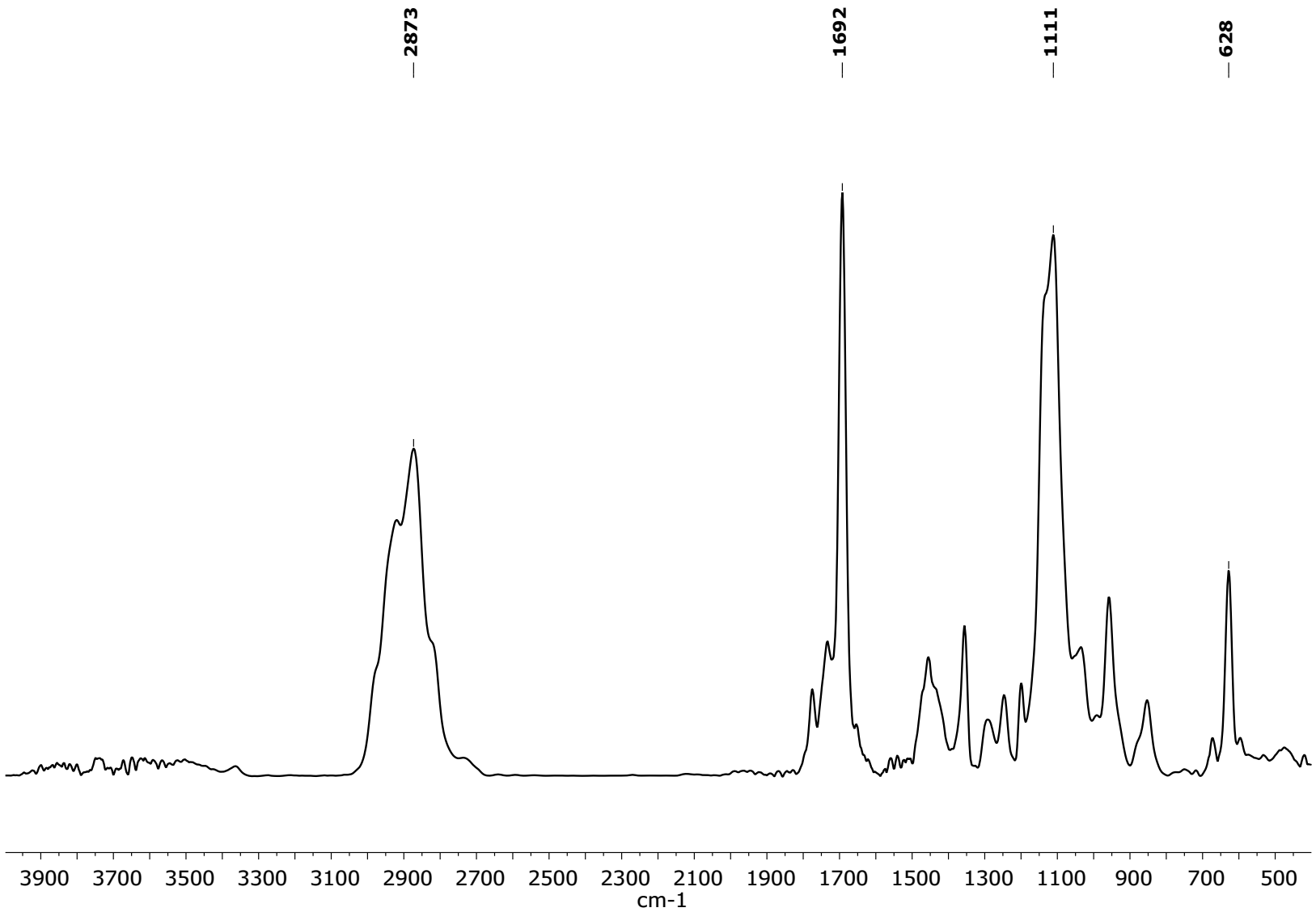


Figure 27s. IR-spectrum of compound **2'.**

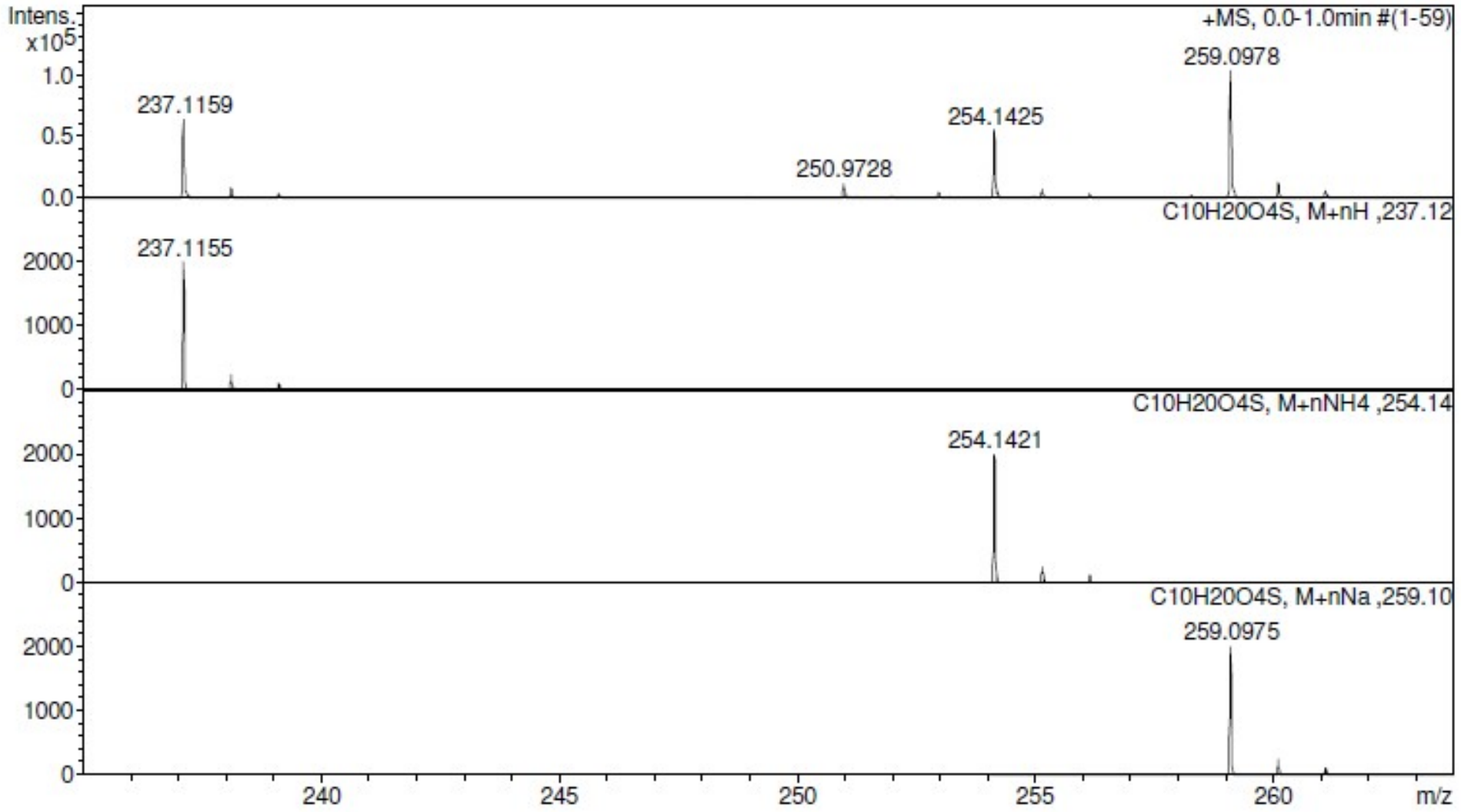


Figure 28s. HRMS (ESI) for compound **2'**.

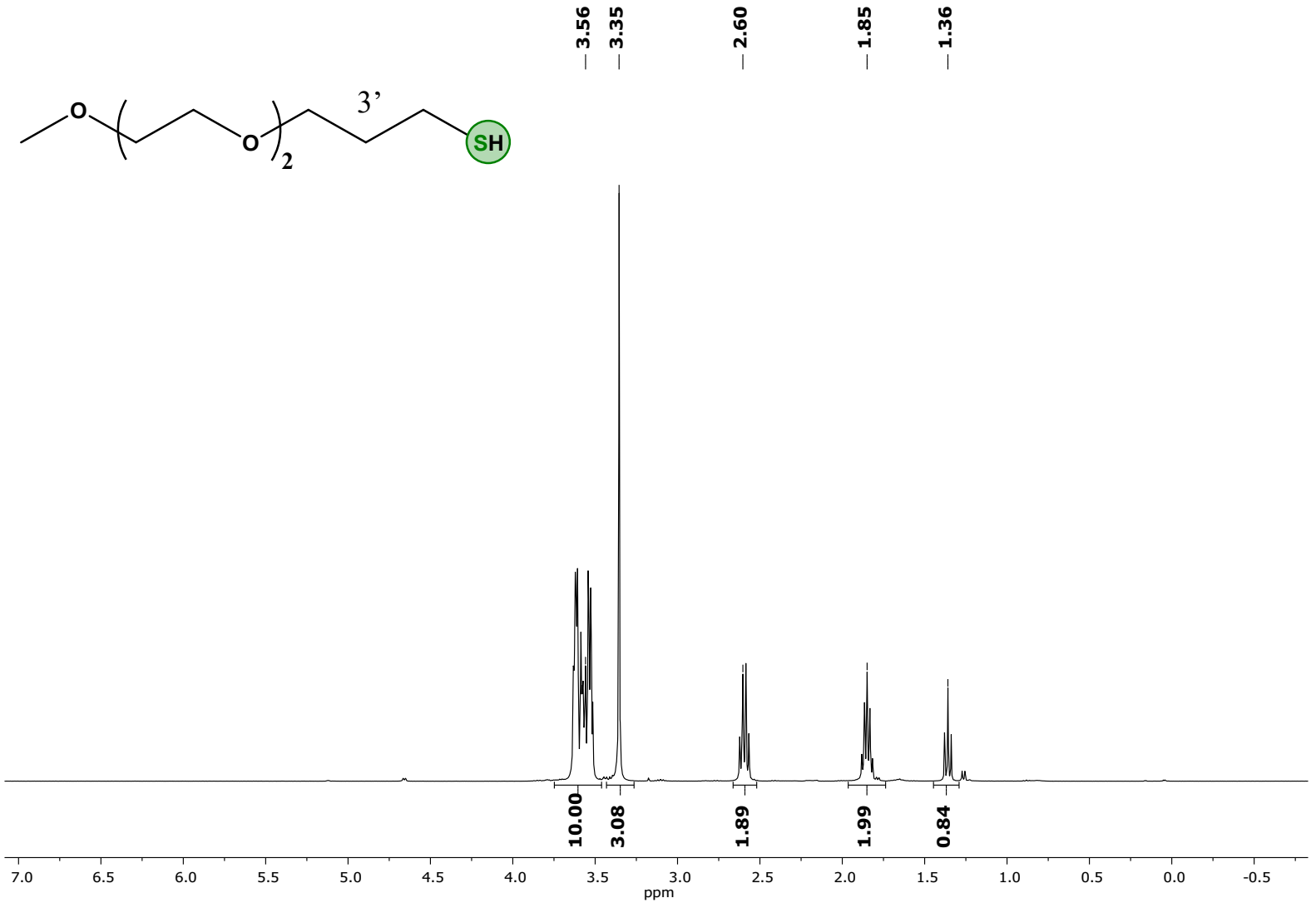


Figure 29s. ^{1}H NMR spectrum of compound **3'** (400 MHz, solvent – $CDCl_3$).

2'

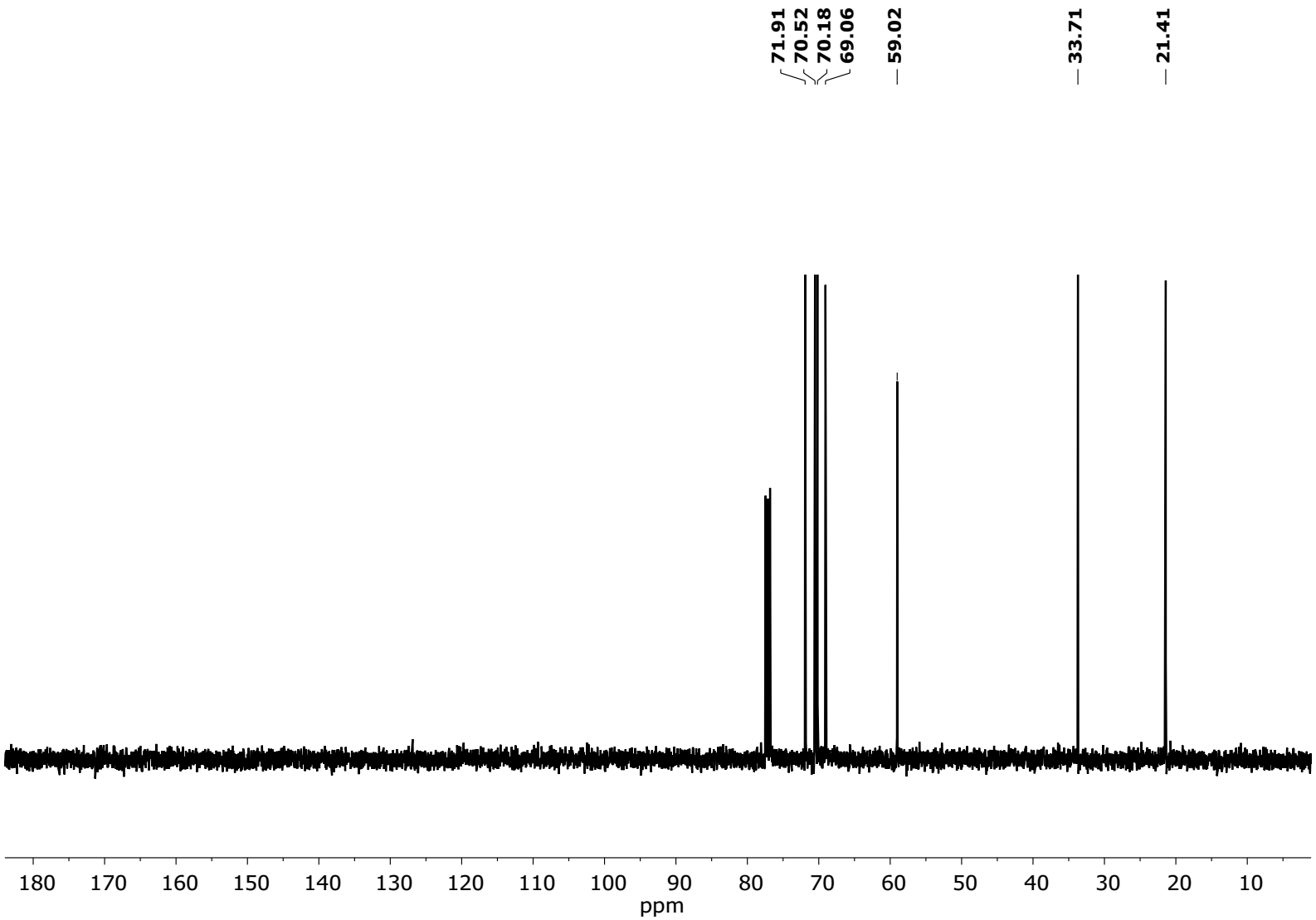


Figure 30s. ^{13}C NMR spectrum of compound **3'** (100 MHz, solvent – $CDCl_3$).

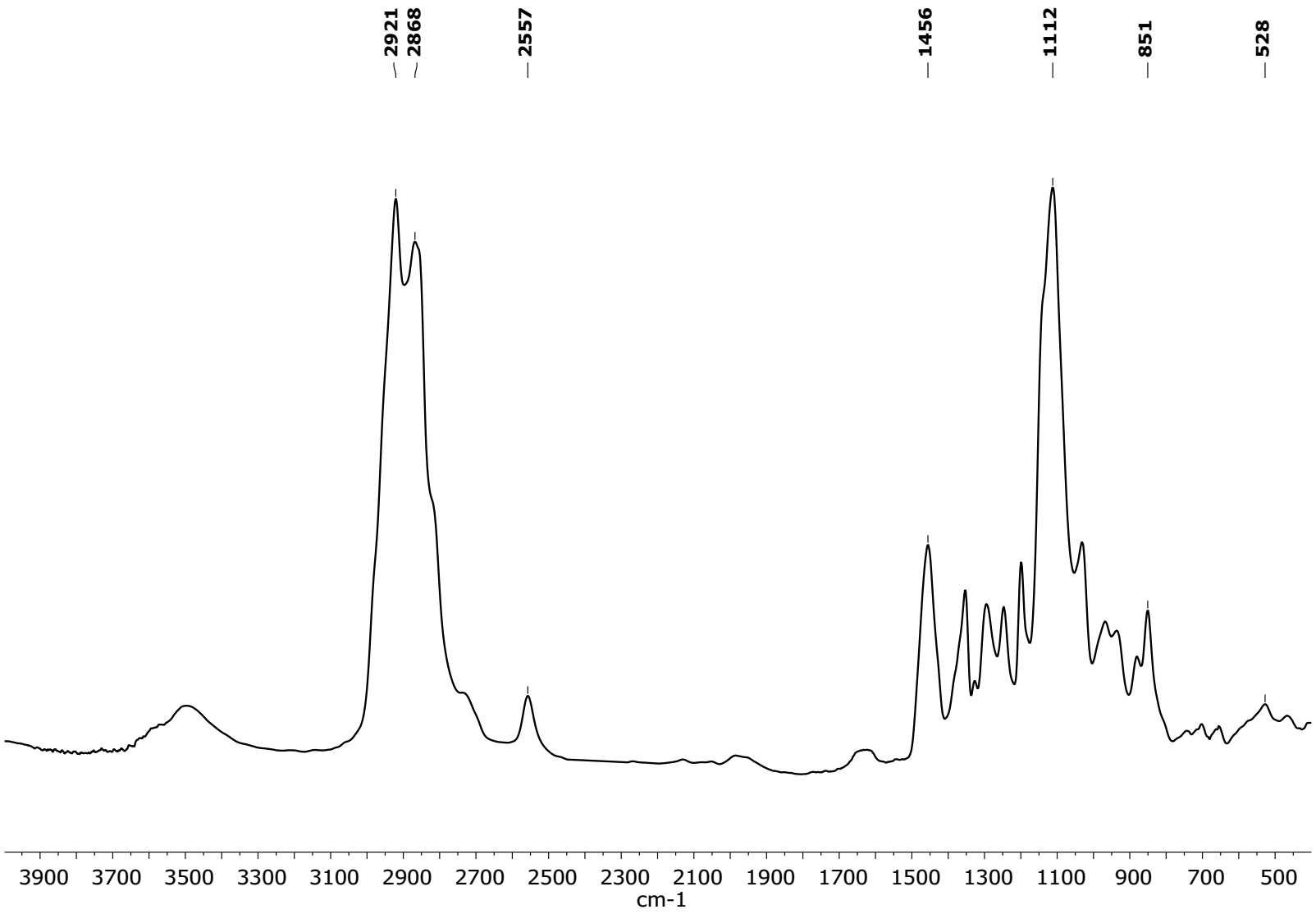


Figure 31s. IR-spectrum of compound **3'.**

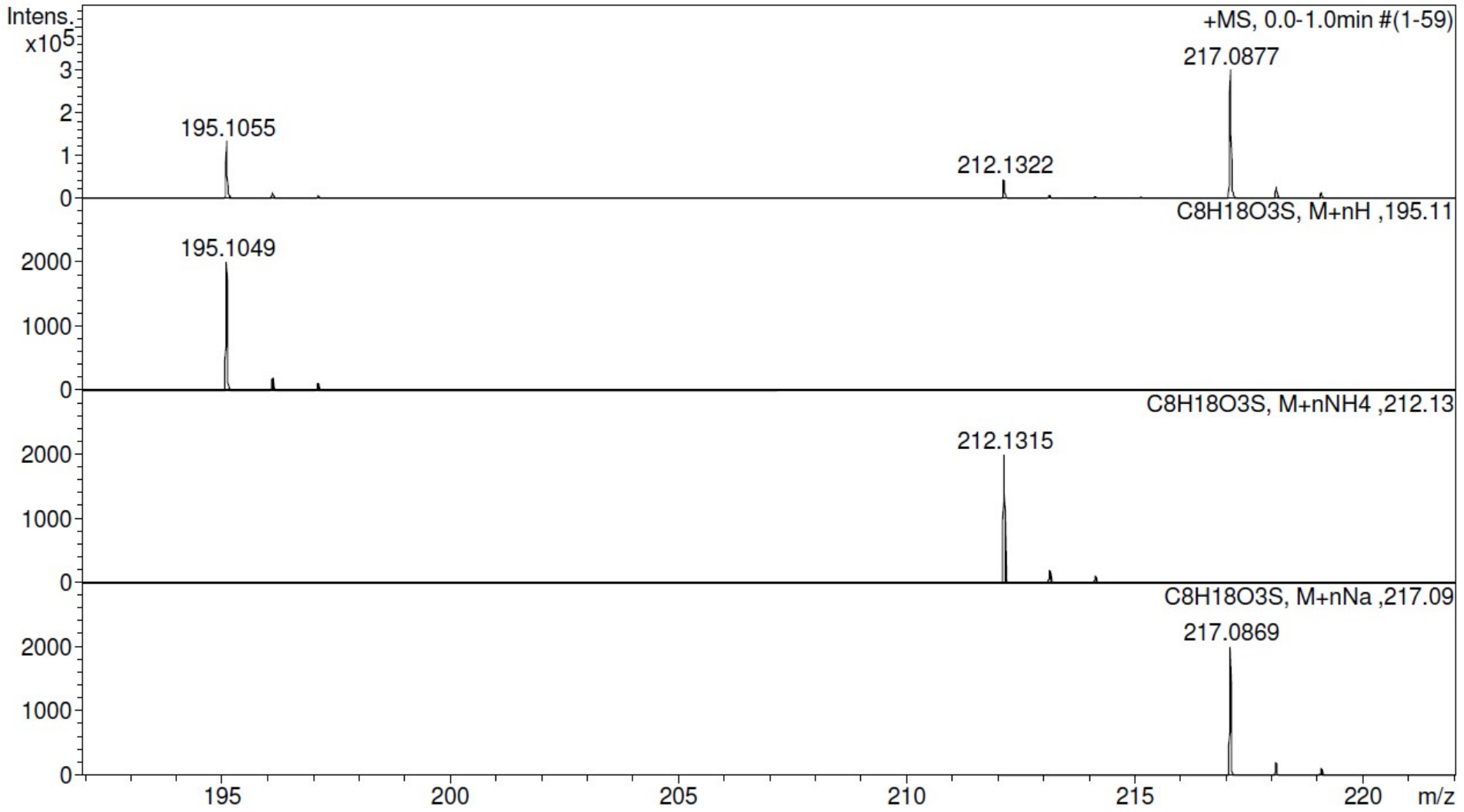


Figure 32s. HRMS (ESI) for compound **3'**.

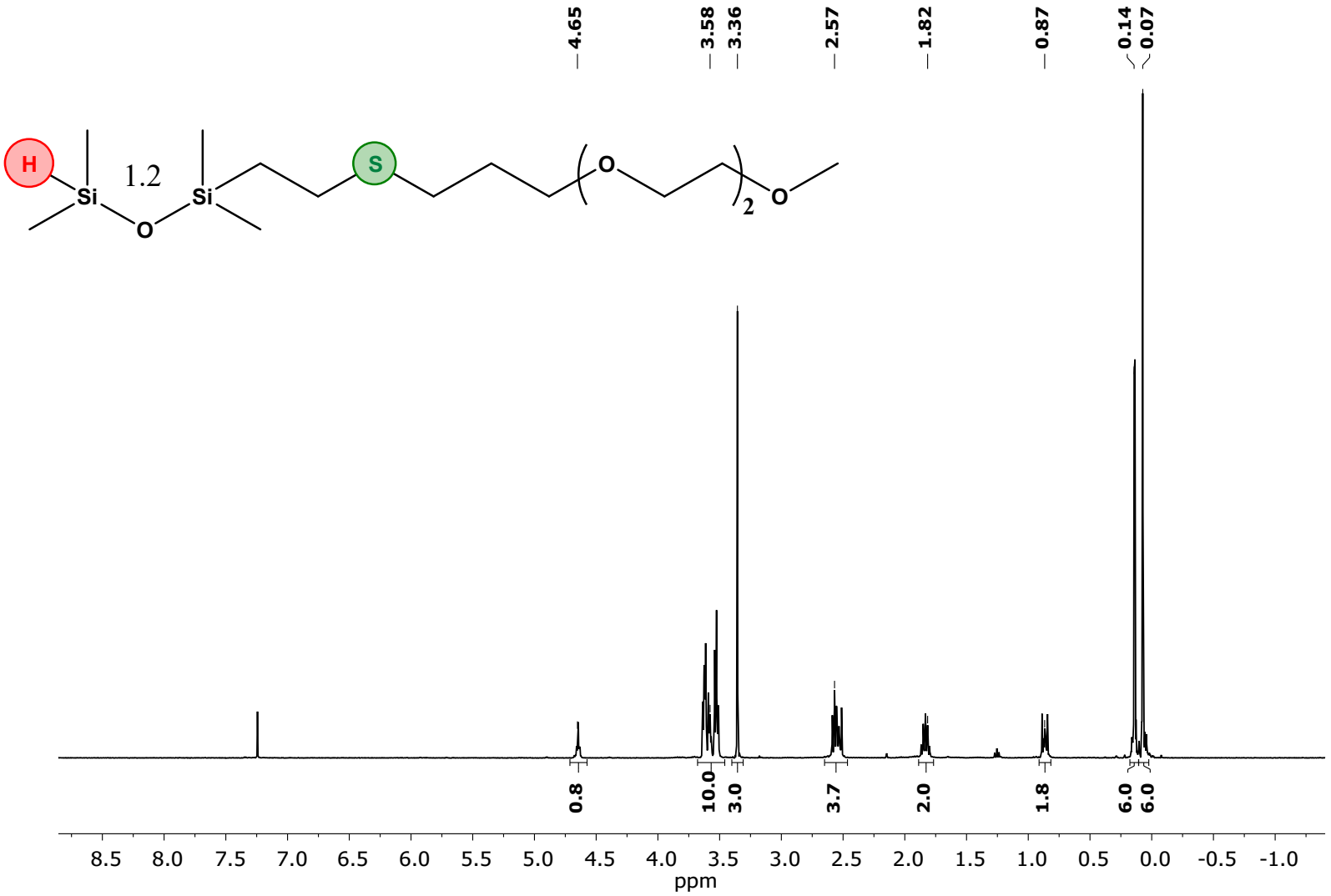


Figure 33s. ^{1}H NMR spectrum of compound **1.2** (400 MHz, solvent – $CDCl_3$).

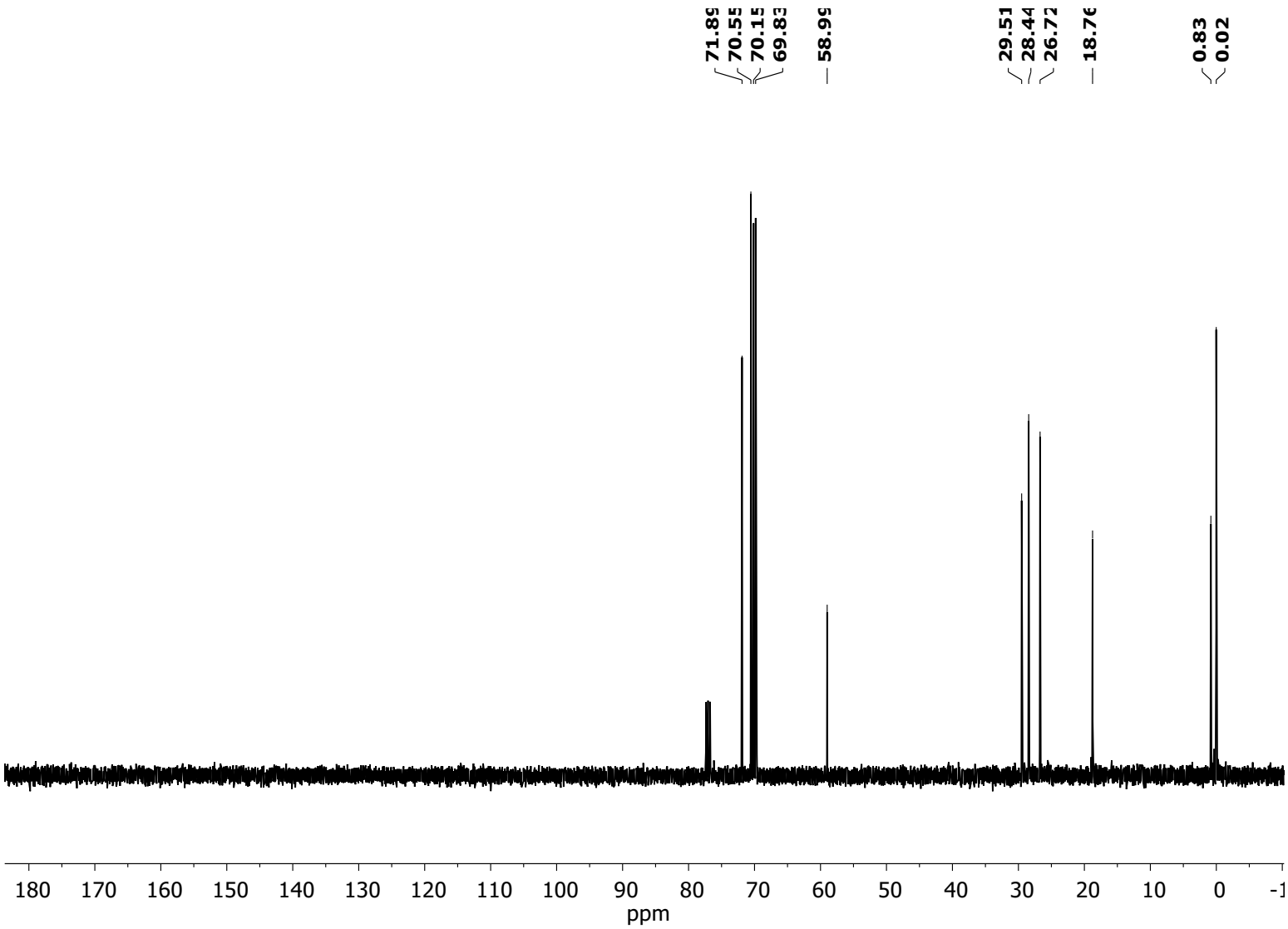


Figure 34s. ^{13}C NMR spectrum of compound **1.2** (100 MHz, solvent – $CDCl_3$).

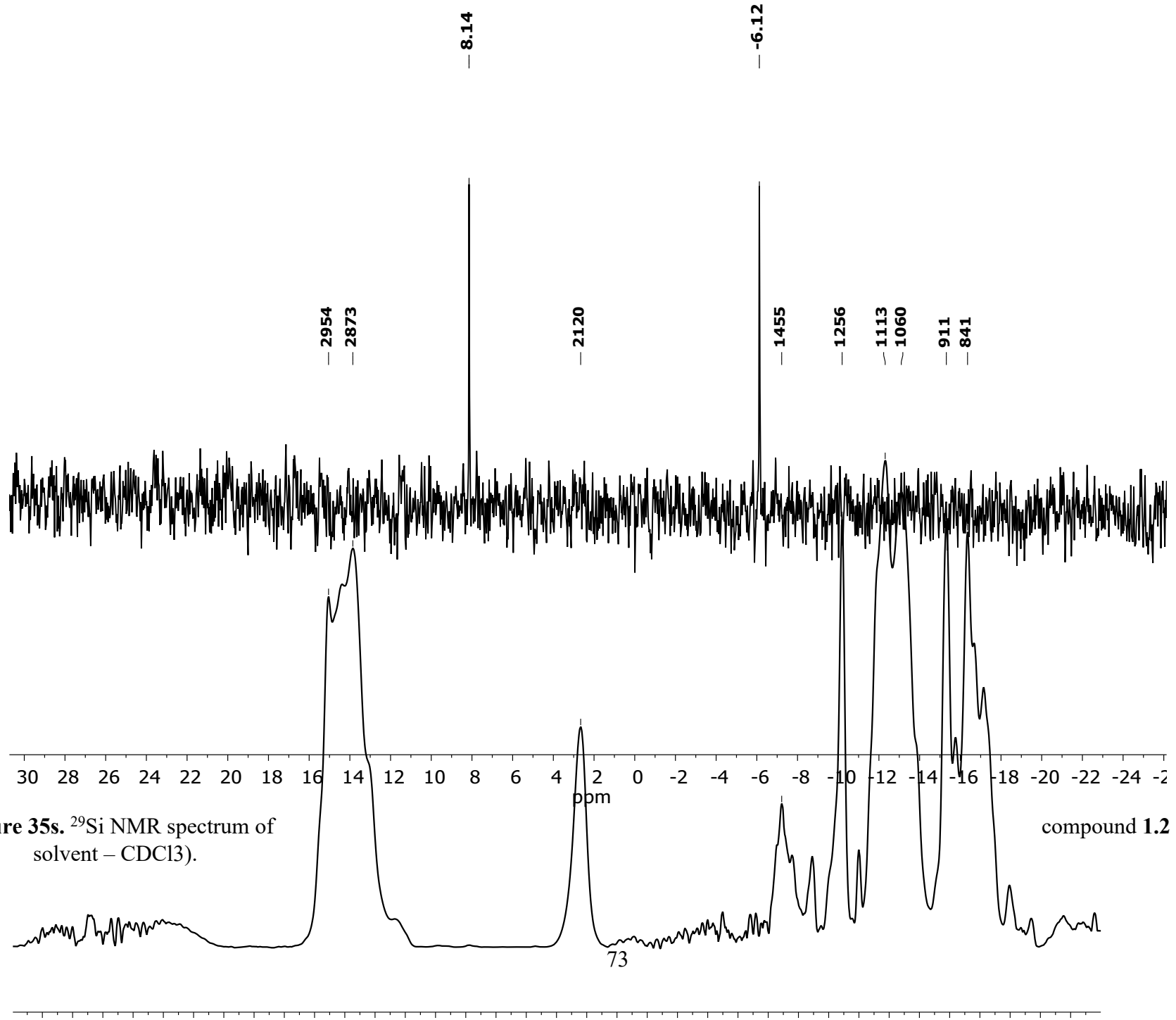


Figure 35s. ^{29}Si NMR spectrum of compound **1.2** (100 MHz, solvent – CDCl3).

Figure 36s. IR-spectrum of compound **1.2**.

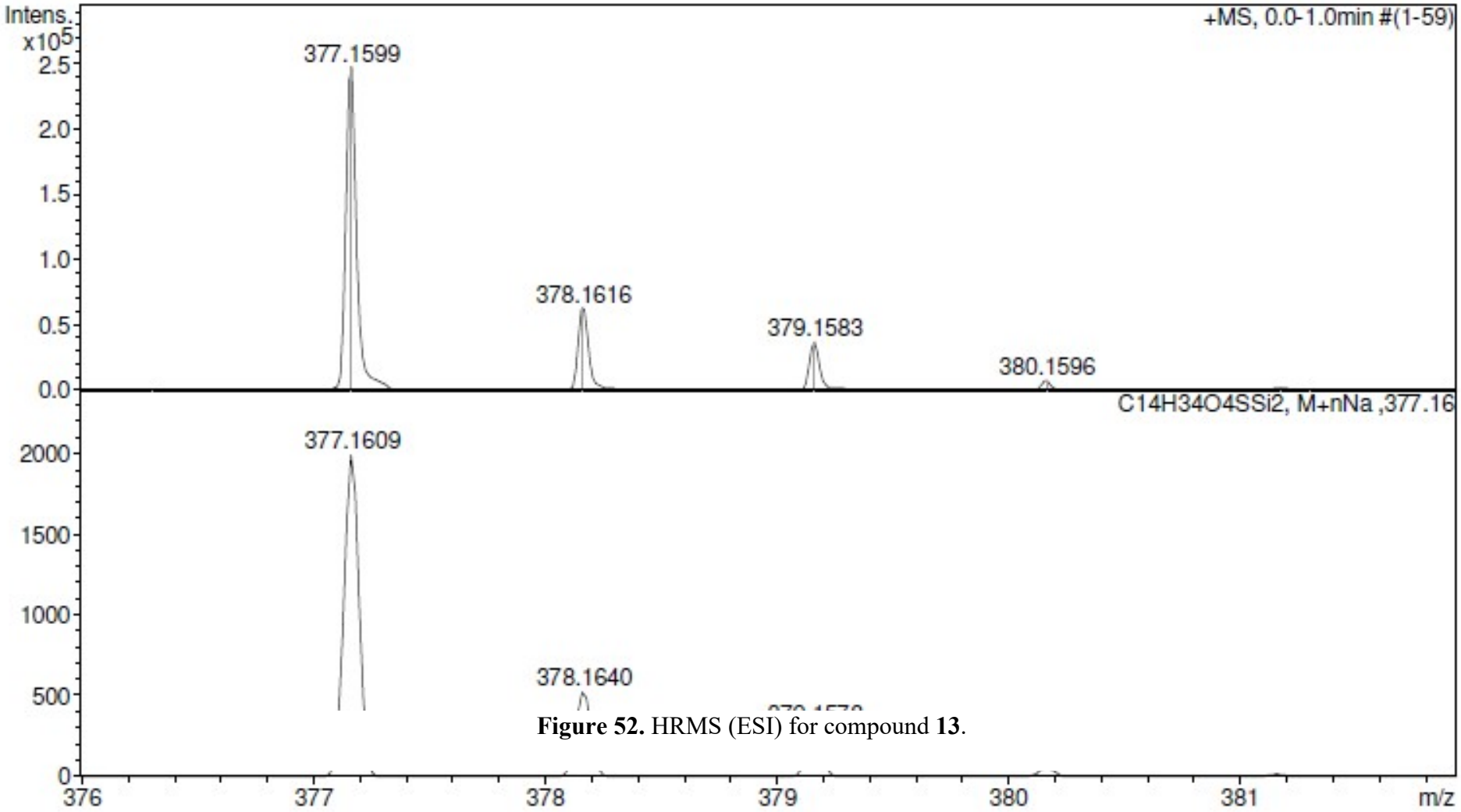


Figure 52. HRMS (ESI) for compound **13**.

Figure 37s. HRMS (ESI) for compound **1.2**.

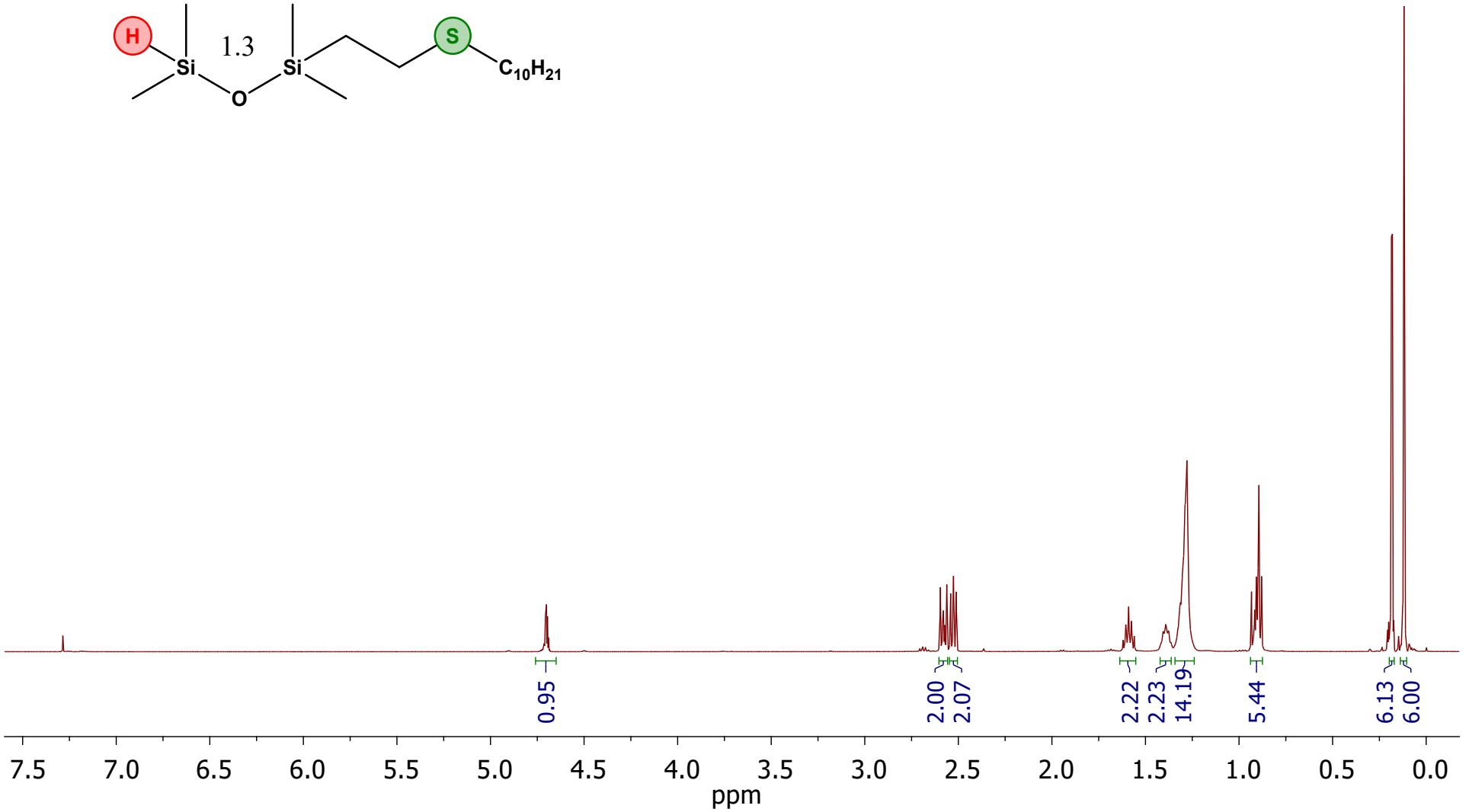


Figure 38s. ^{1}H NMR spectrum of compound **1.3** (500 MHz, solvent – $CDCl_3$).

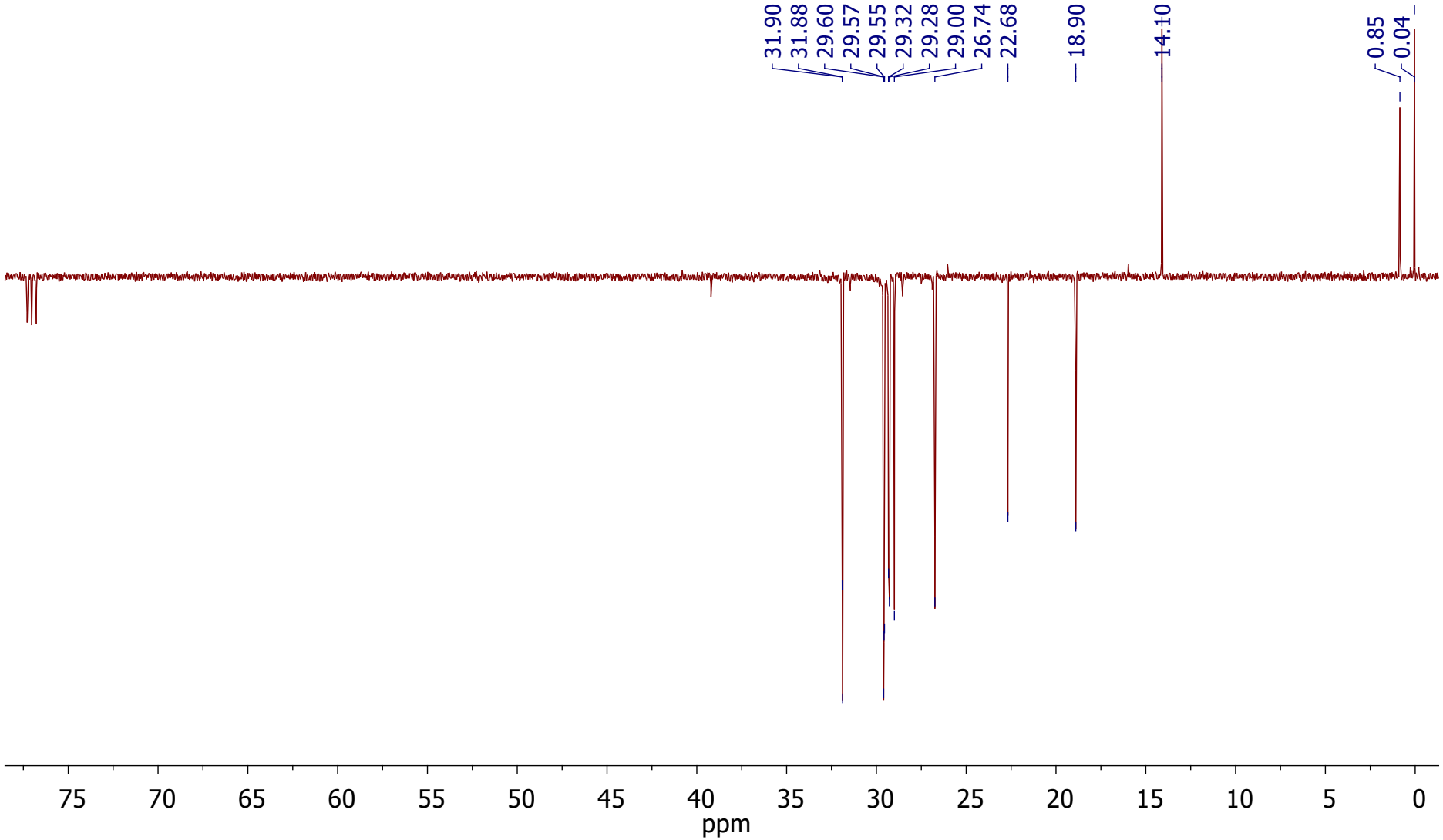


Figure 39s. ^{13}C NMR spectrum of compound **1.3** (500 MHz, solvent – $CDCl_3$, jmod).

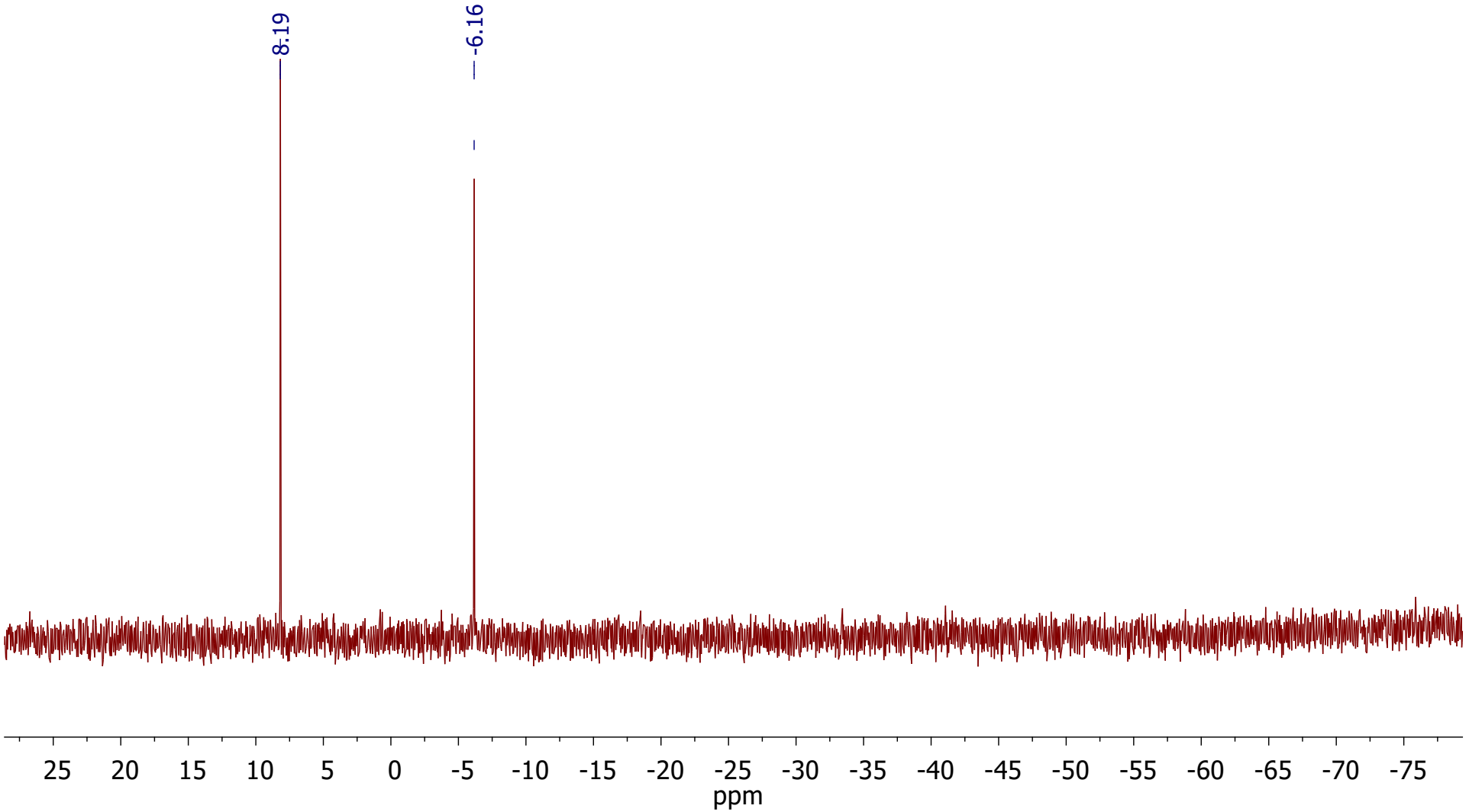


Figure 40s. ^{29}Si NMR spectrum of compound **1.3** (500 MHz, solvent – $CDCl_3$).

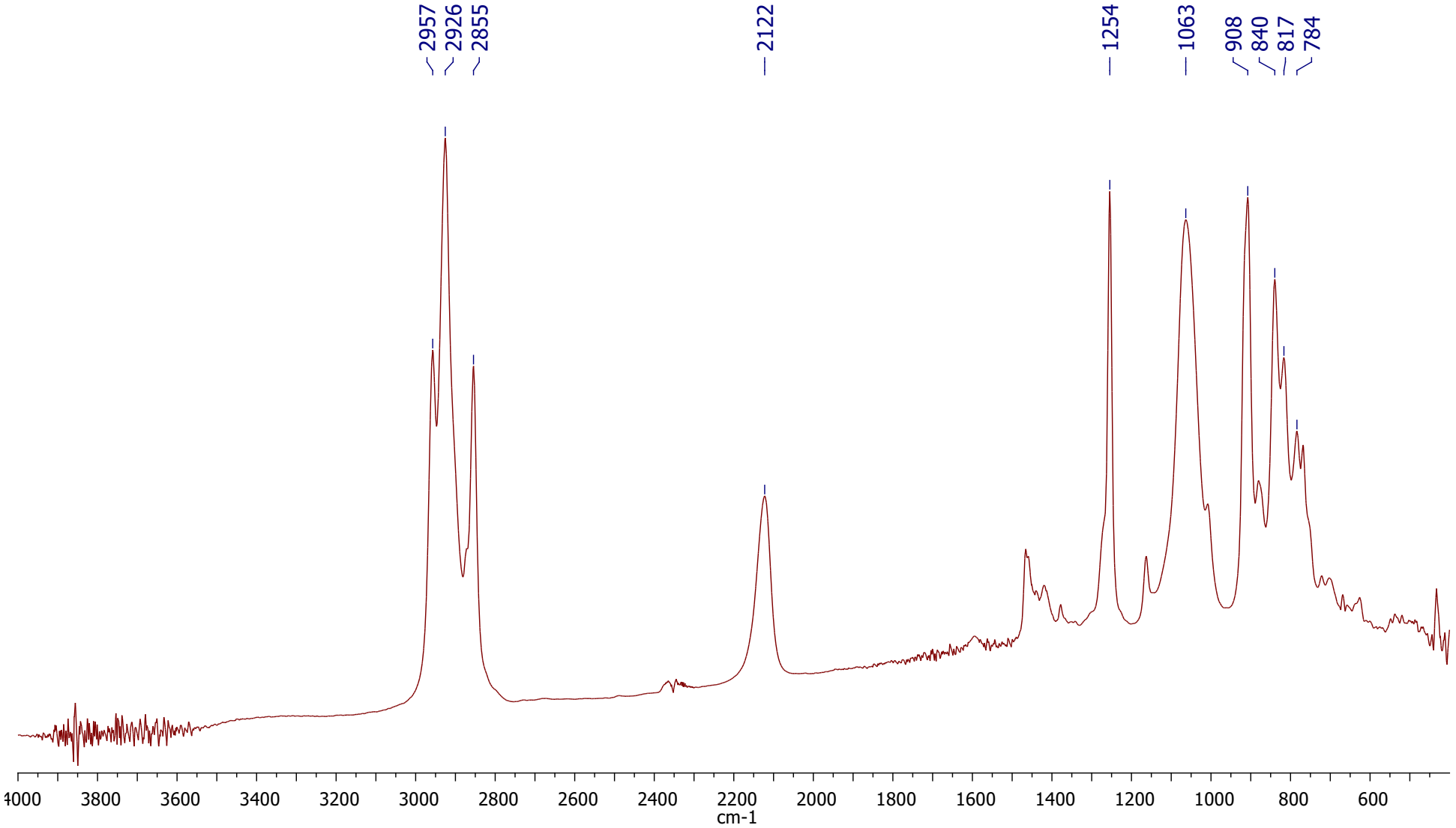


Figure 41s. IR-spectrum of compound **1.3**.

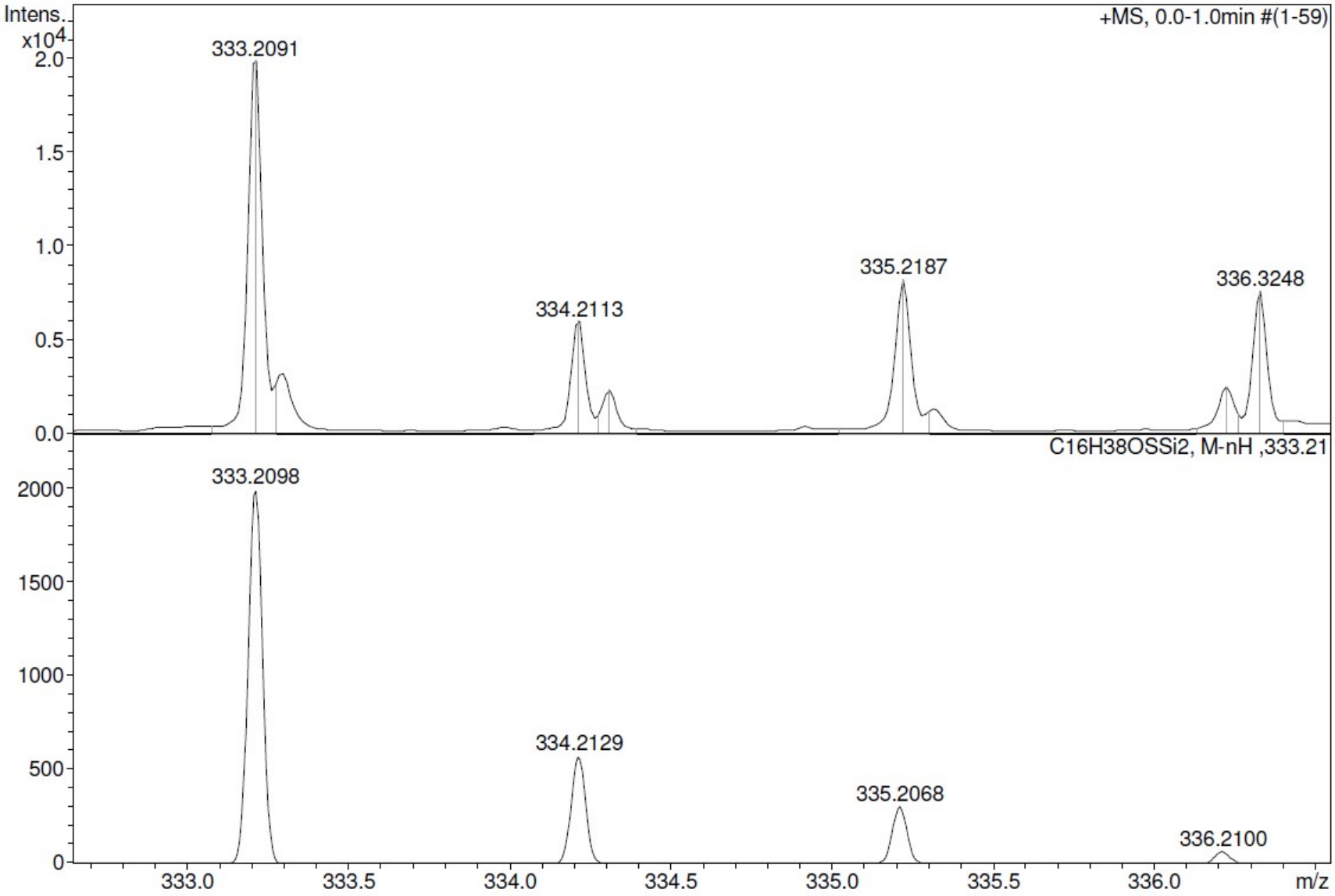


Figure 42s. HRMS (ESI) for compound **1.3**.

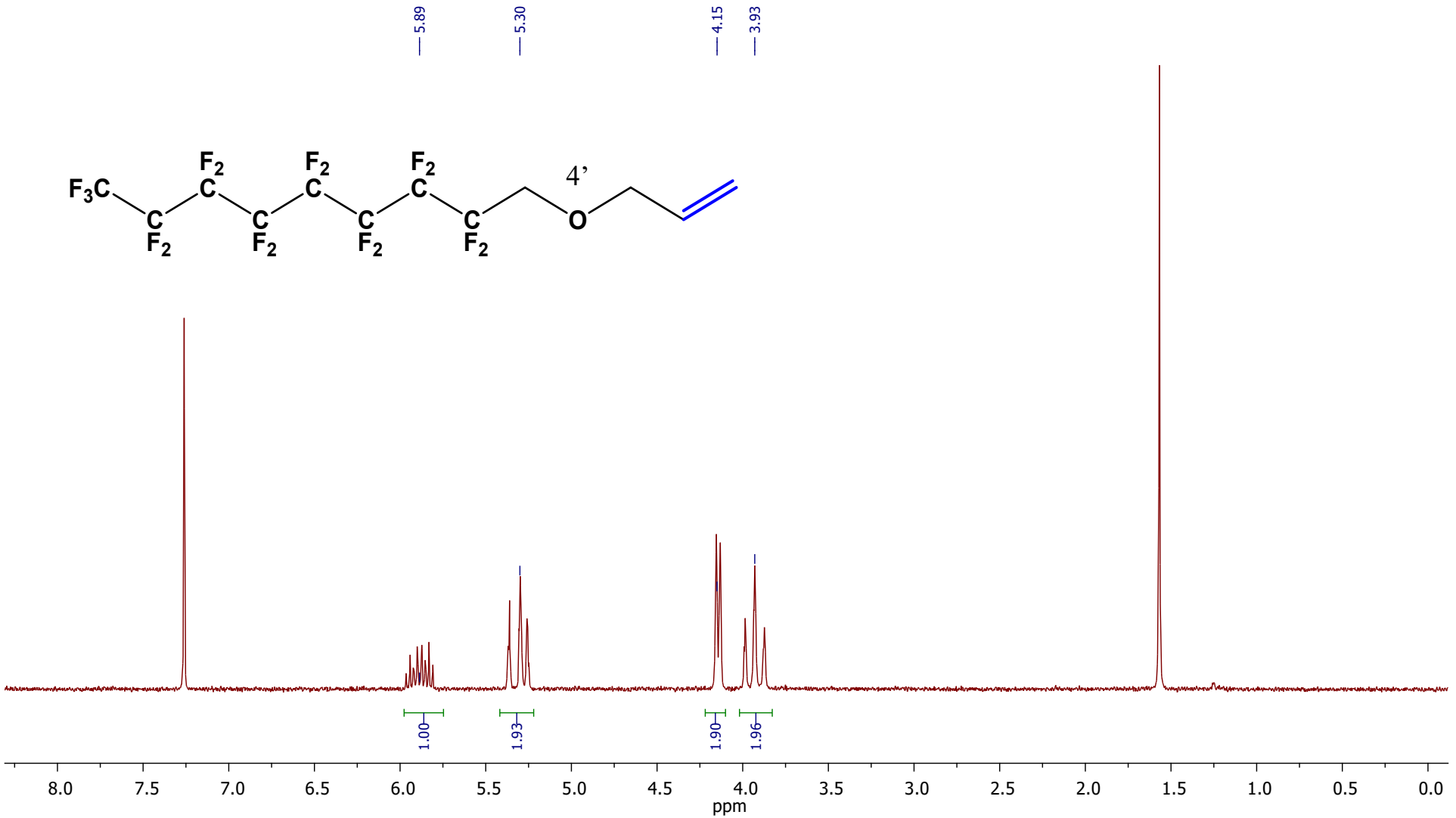


Figure 43s. ^{1}H NMR spectrum of compound **4'** (400 MHz, solvent – $CDCl_3$).

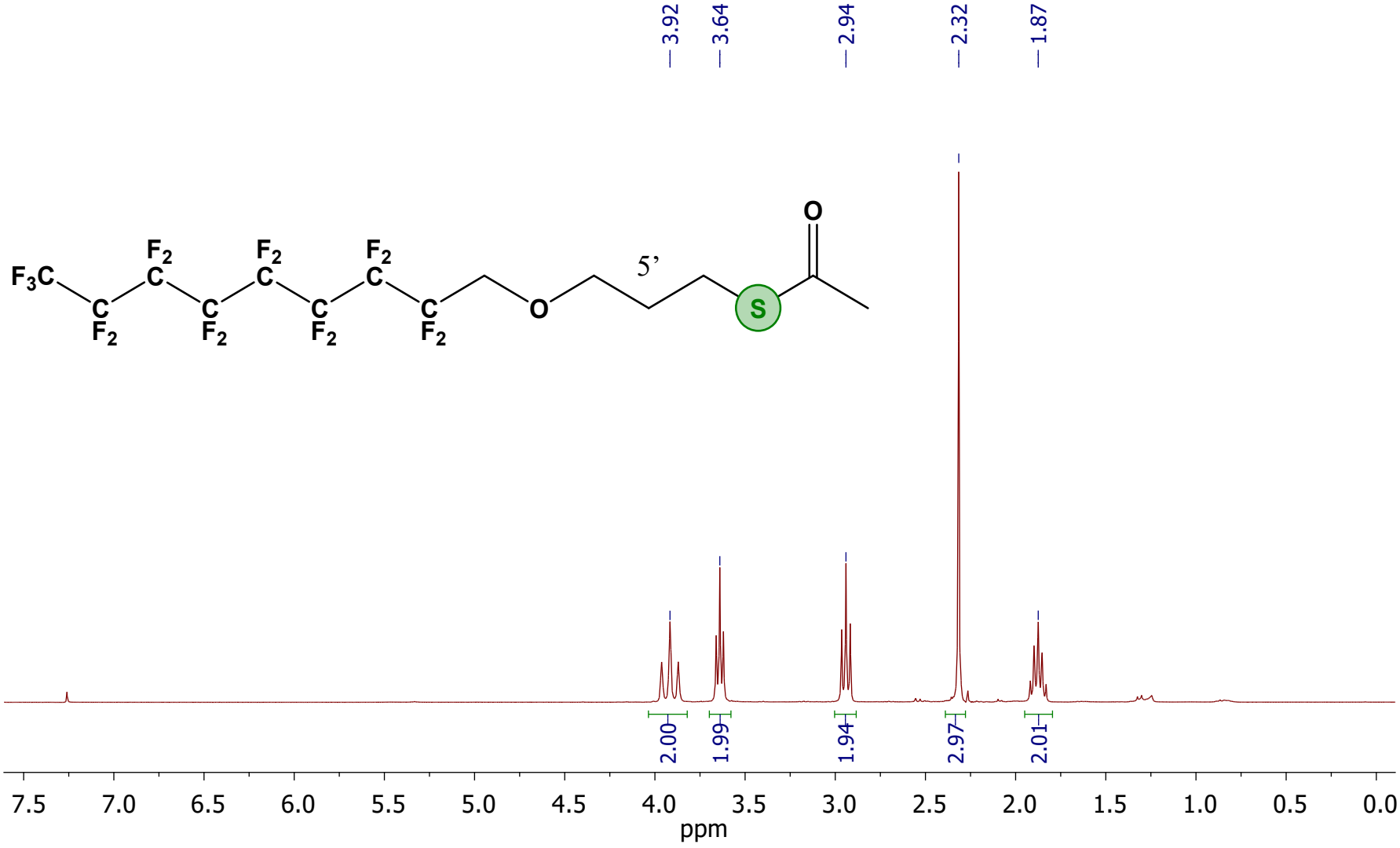


Figure 44s. ^{1}H NMR spectrum of compound **5’** (400 MHz, solvent – $CDCl_3$).

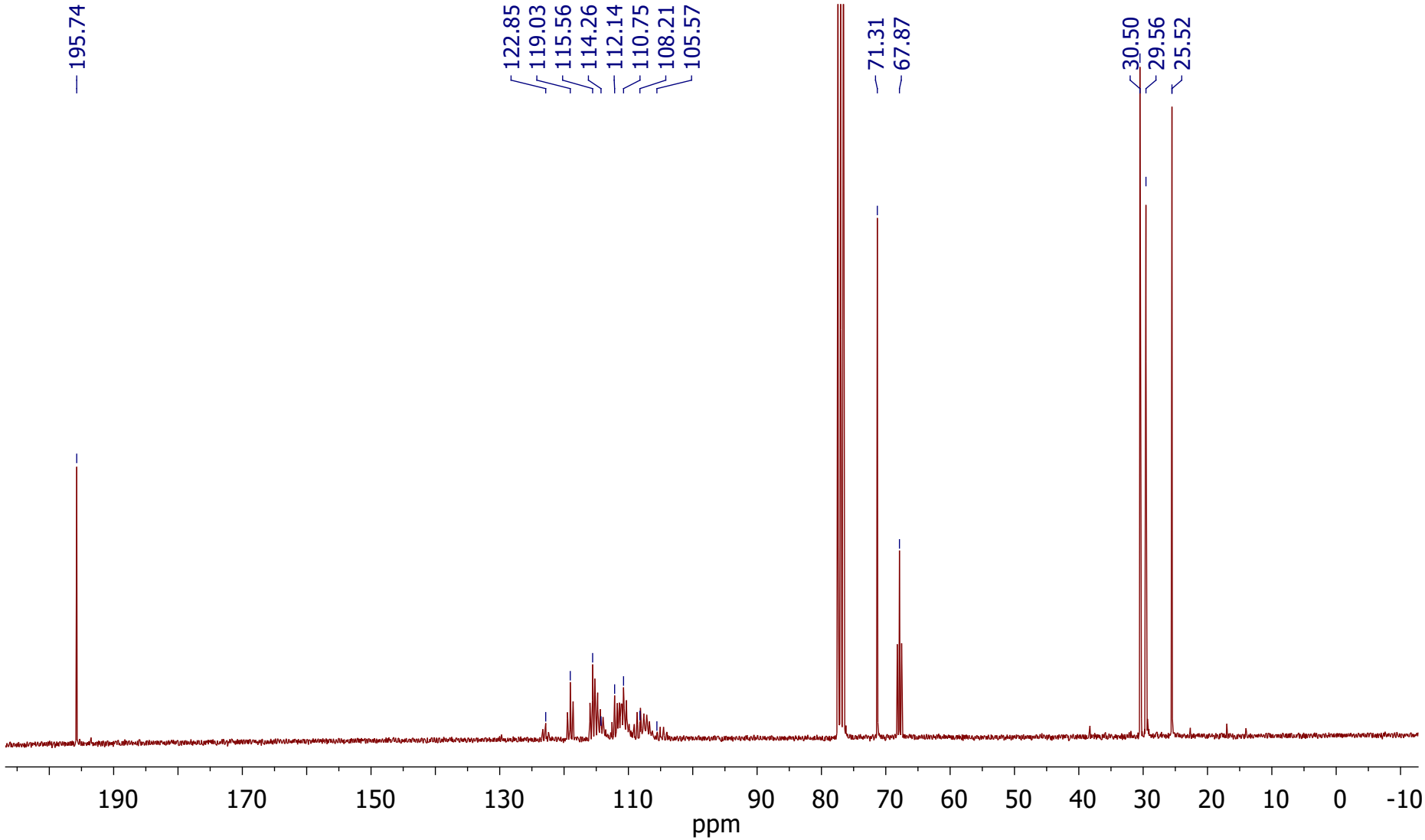


Figure 45s. ^{13}C NMR spectrum of compound **5'** (500 MHz, solvent – $CDCl_3$).

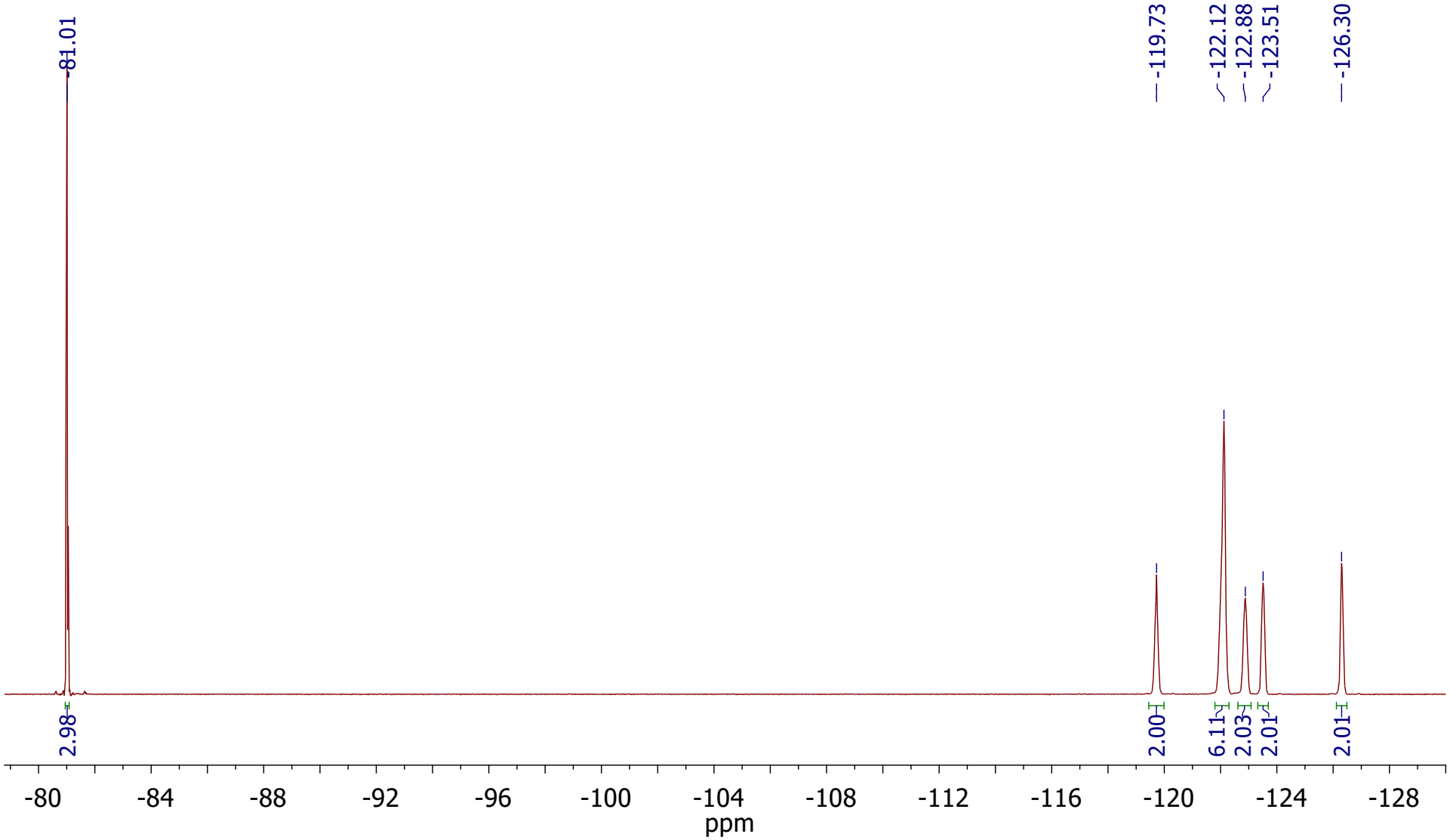


Figure 46s. ^{29}F NMR spectrum of compound **5'** (400 MHz, solvent – $CDCl_3$).

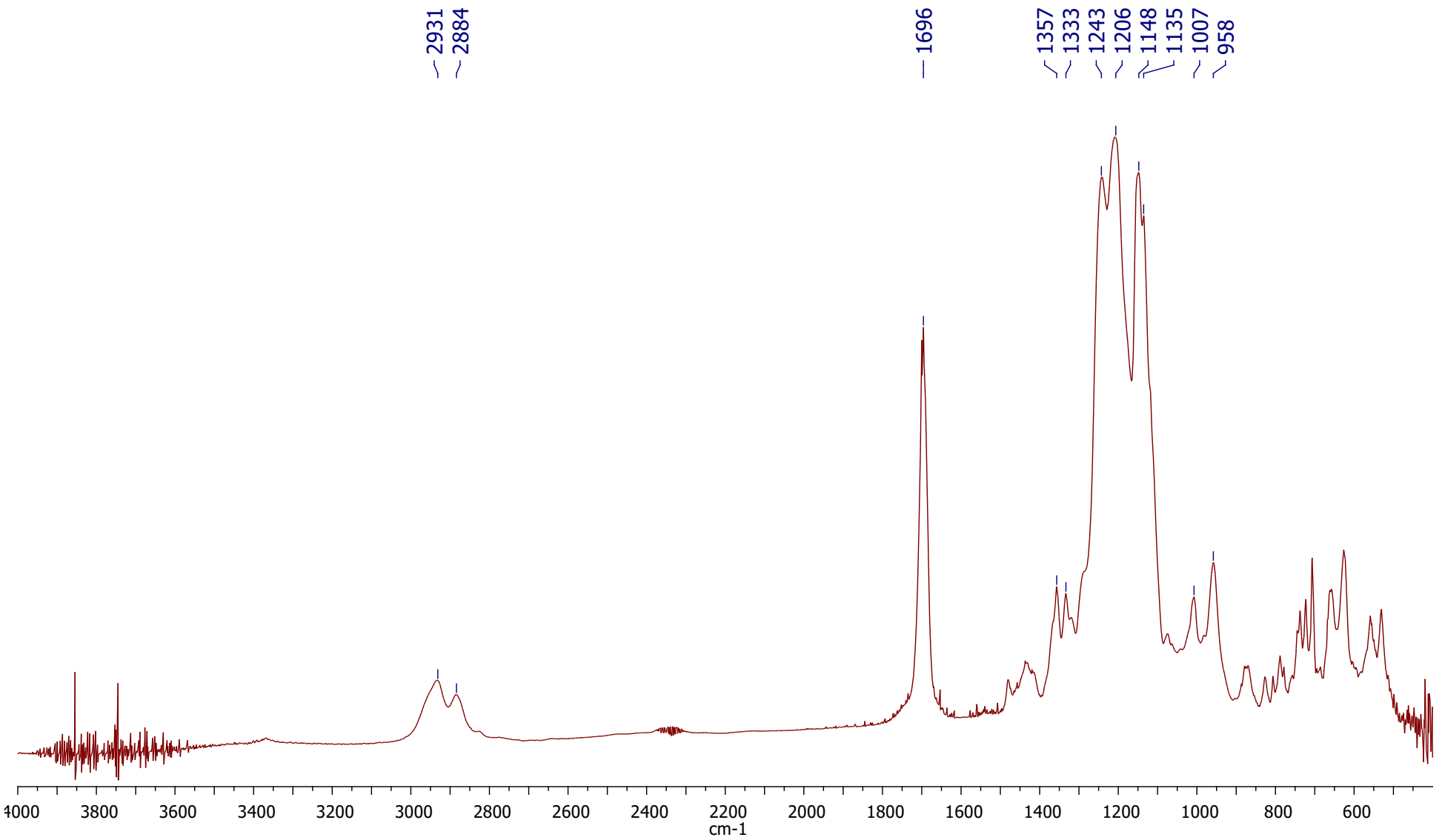


Figure 47s. IR-spectrum of compound **5'**.

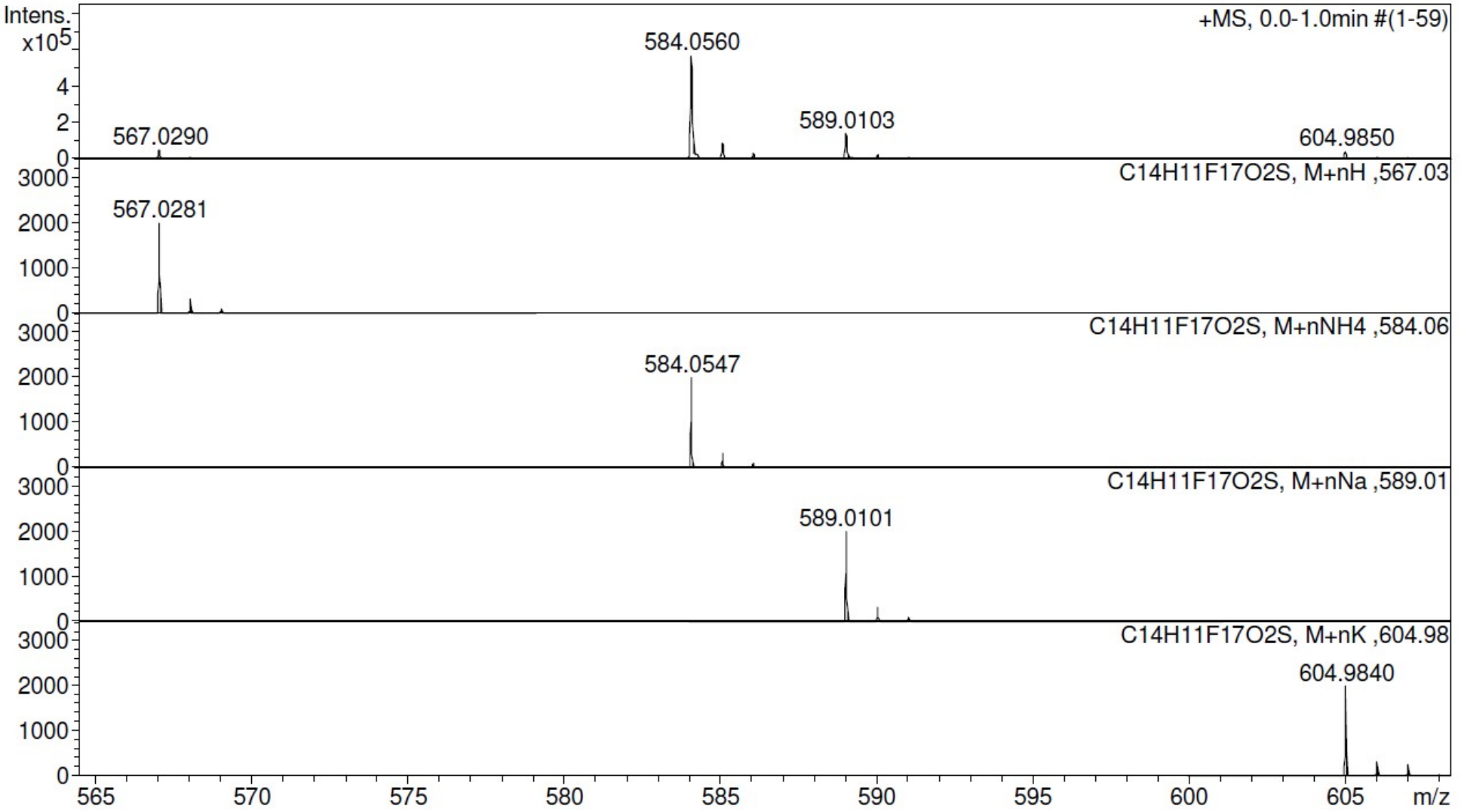


Figure 48s. HRMS (ESI) for compound **5'**.

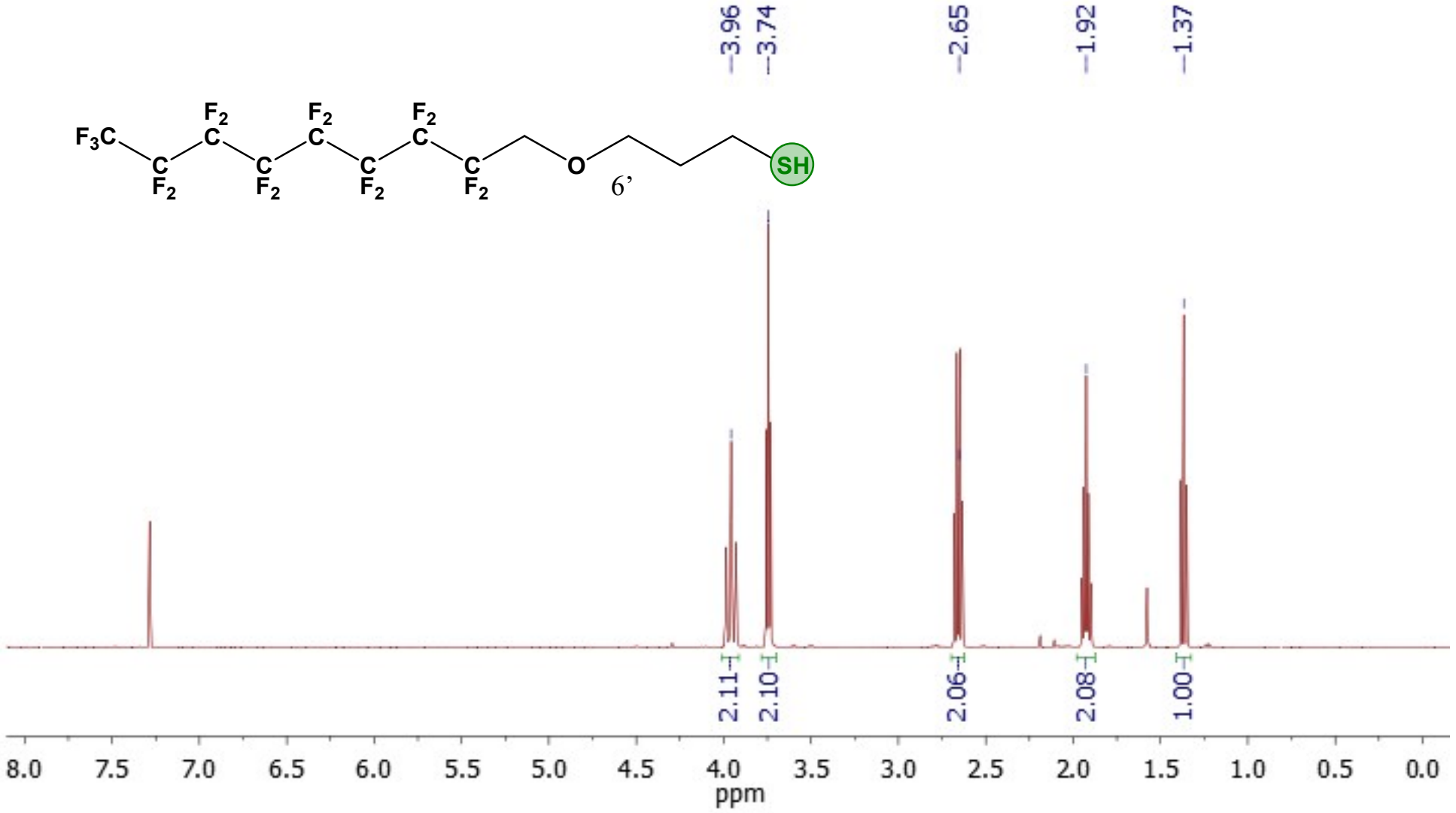


Figure 49s. ^{1}H NMR spectrum of compound **6’** (500 MHz, solvent – $CDCl_3$).

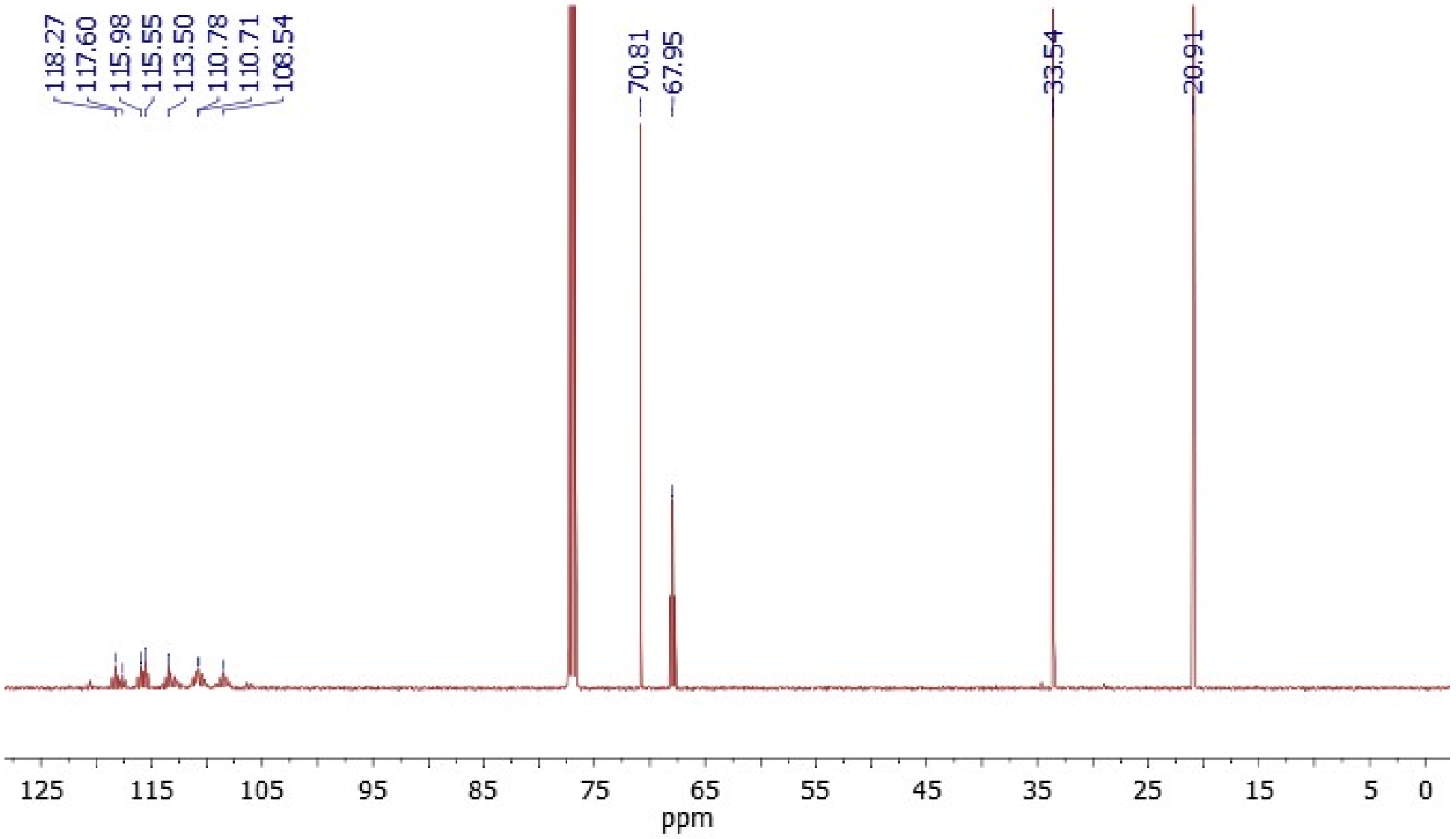


Figure 50s. ^{13}C NMR spectrum of compound **6'** (500 MHz, solvent – $CDCl_3$).

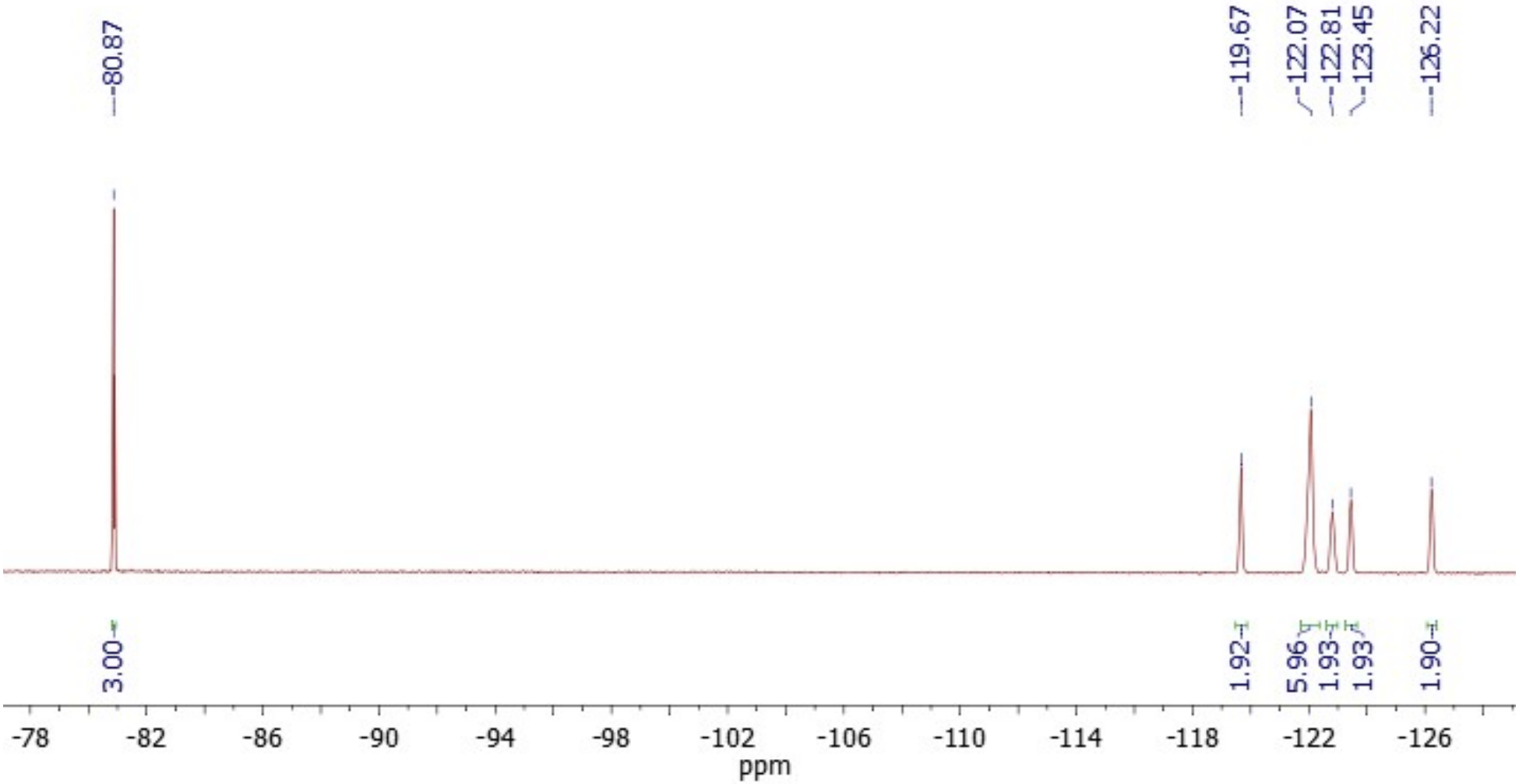


Figure 51s. ^{29}F NMR spectrum of compound **6'** (400 MHz, solvent – $CDCl_3$).

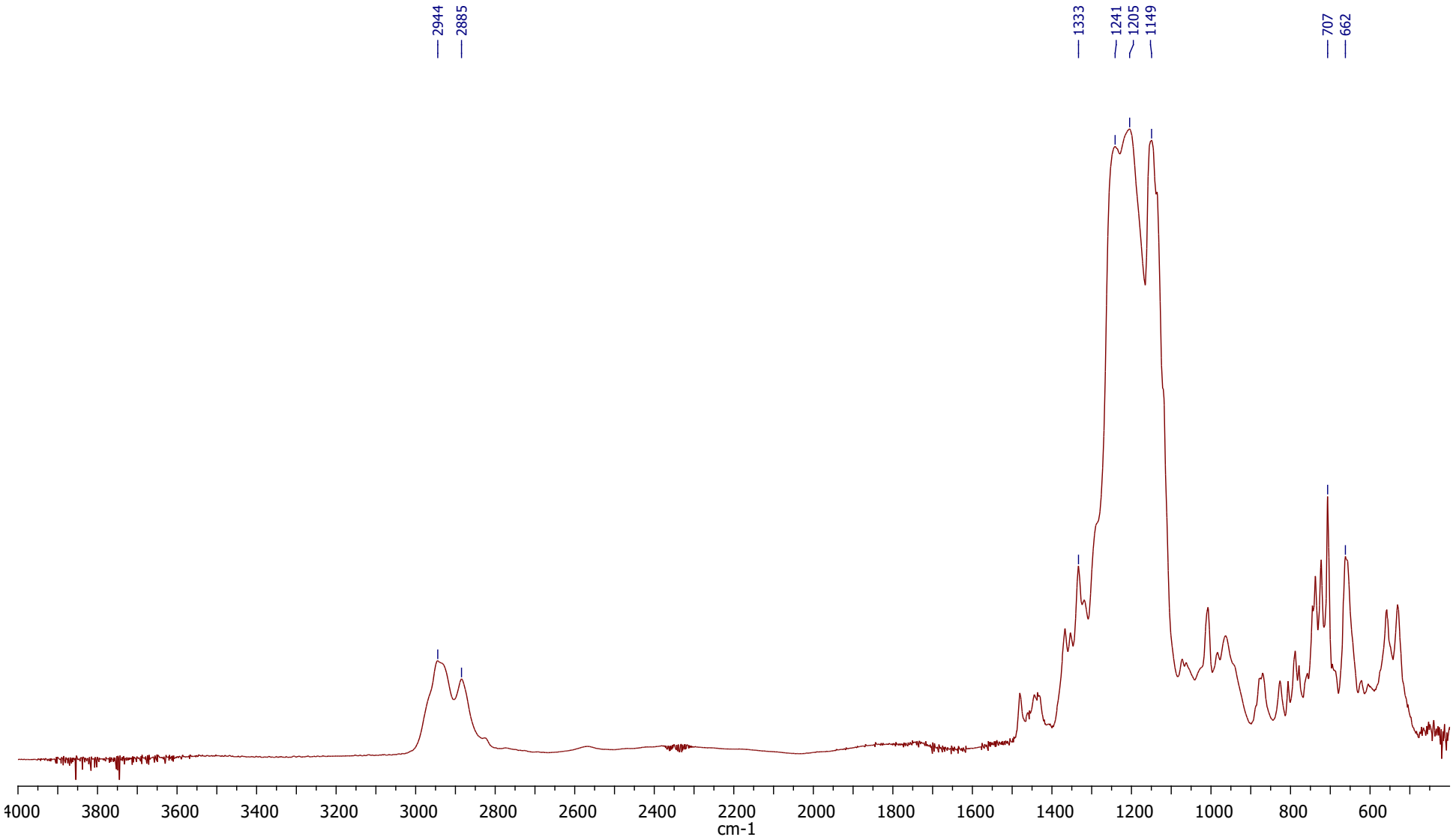


Figure 52s. IR-spectrum of compound **6'**.

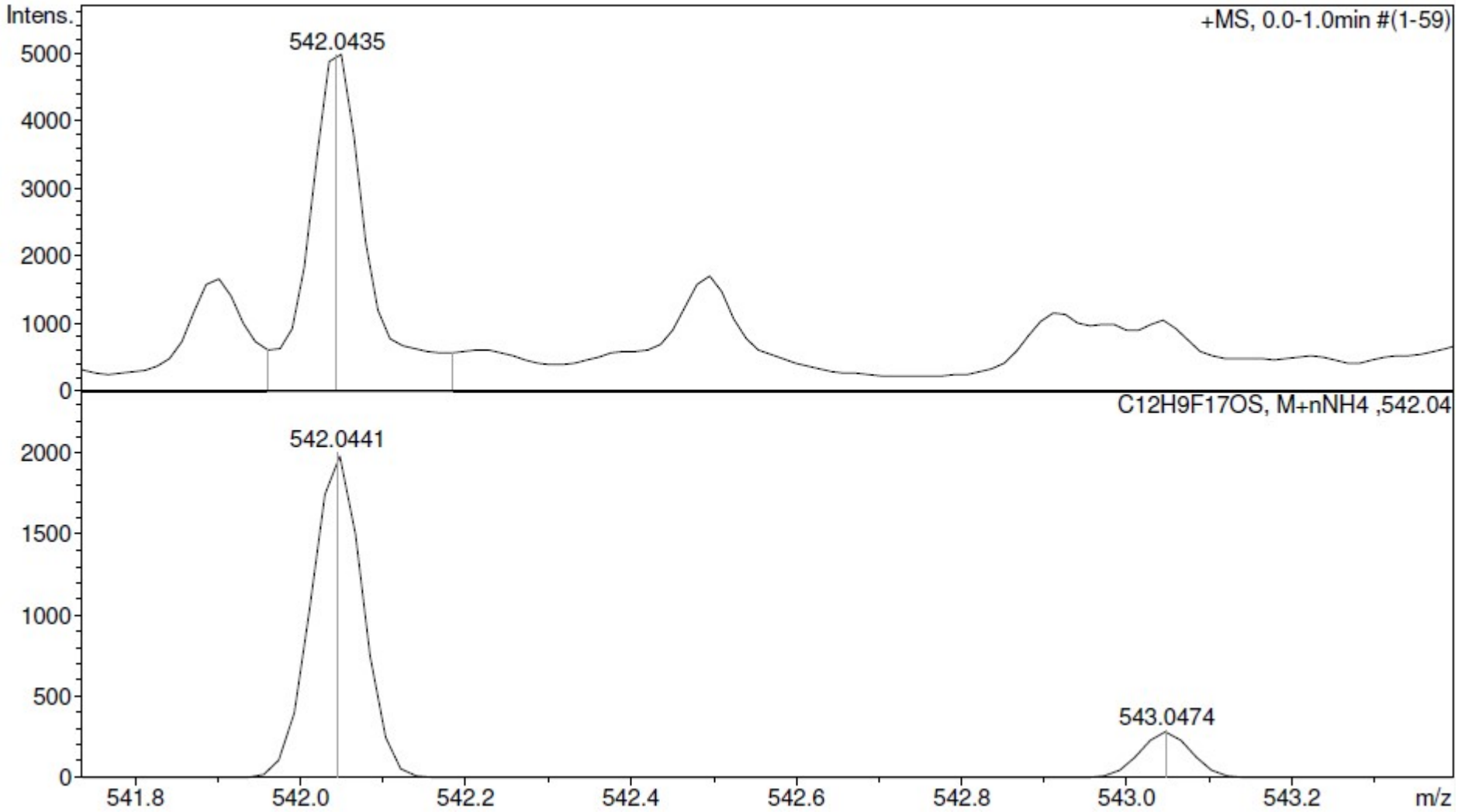


Figure 53s. HRMS (ESI) for compound **6'**.

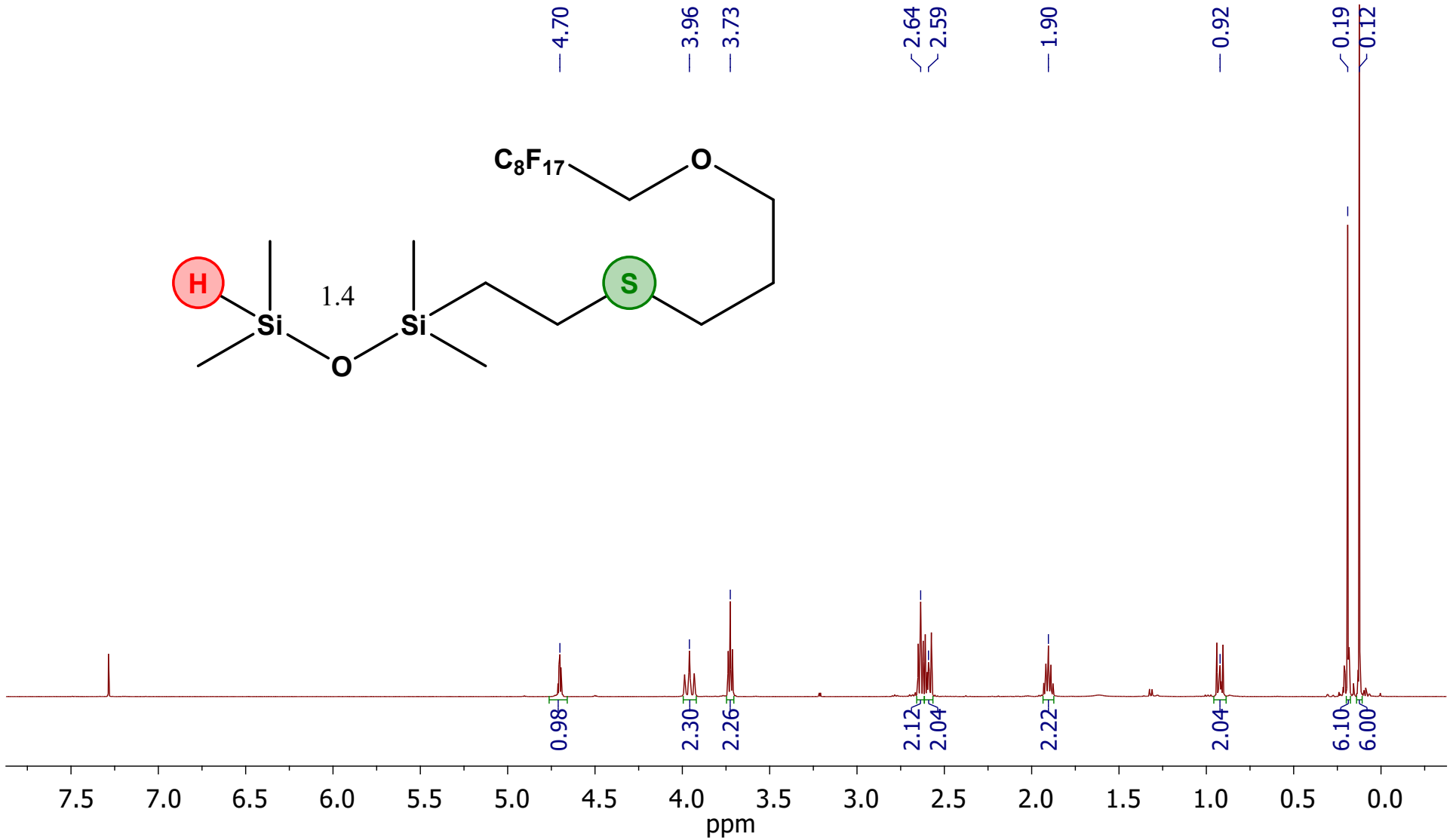


Figure 54s. ^{1}H NMR spectrum of compound **1.4** (500 MHz, solvent – $CDCl_3$).

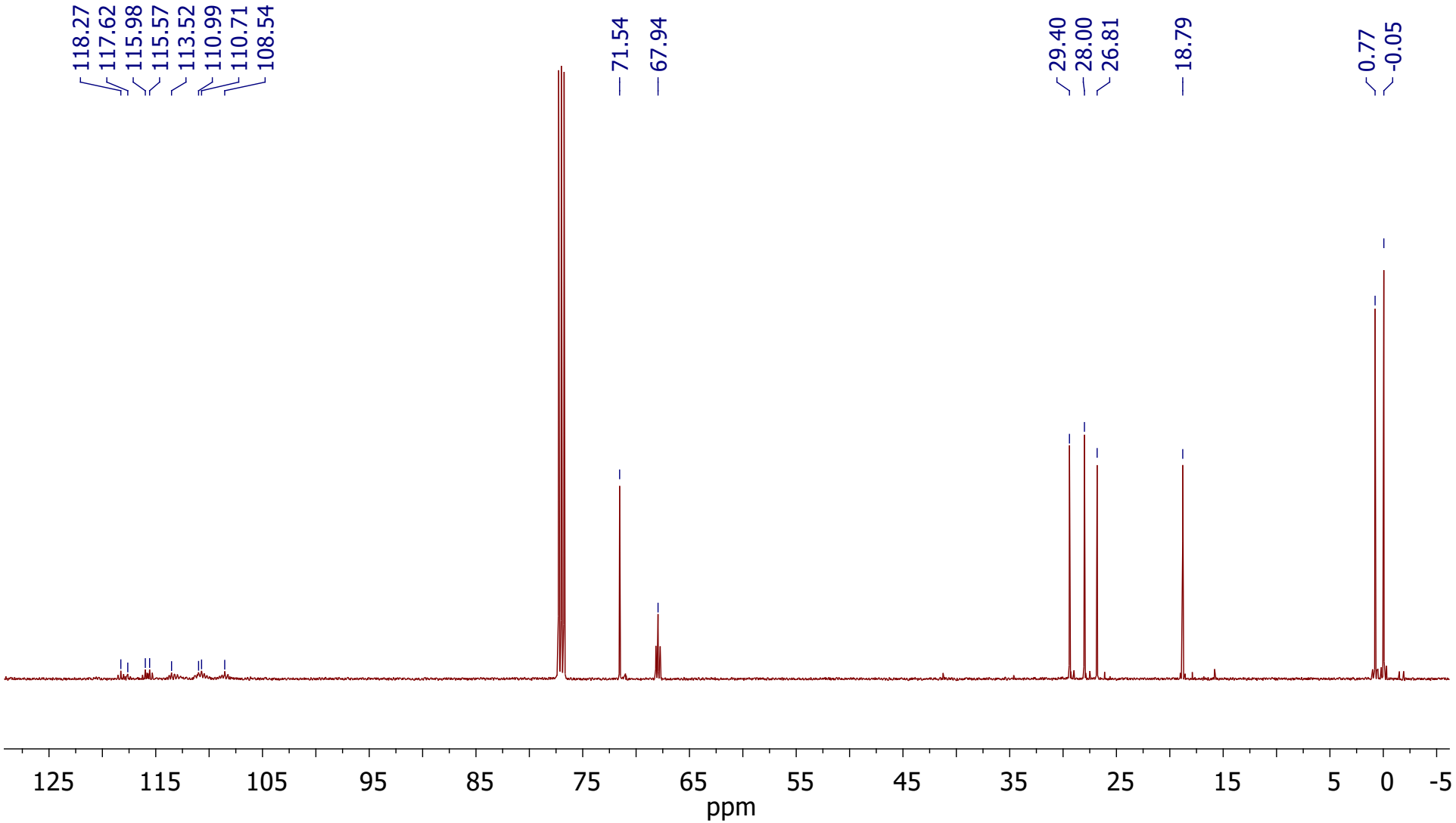


Figure 55s. ^{13}C NMR spectrum of compound **1.4** (400 MHz, solvent – $CDCl_3$).

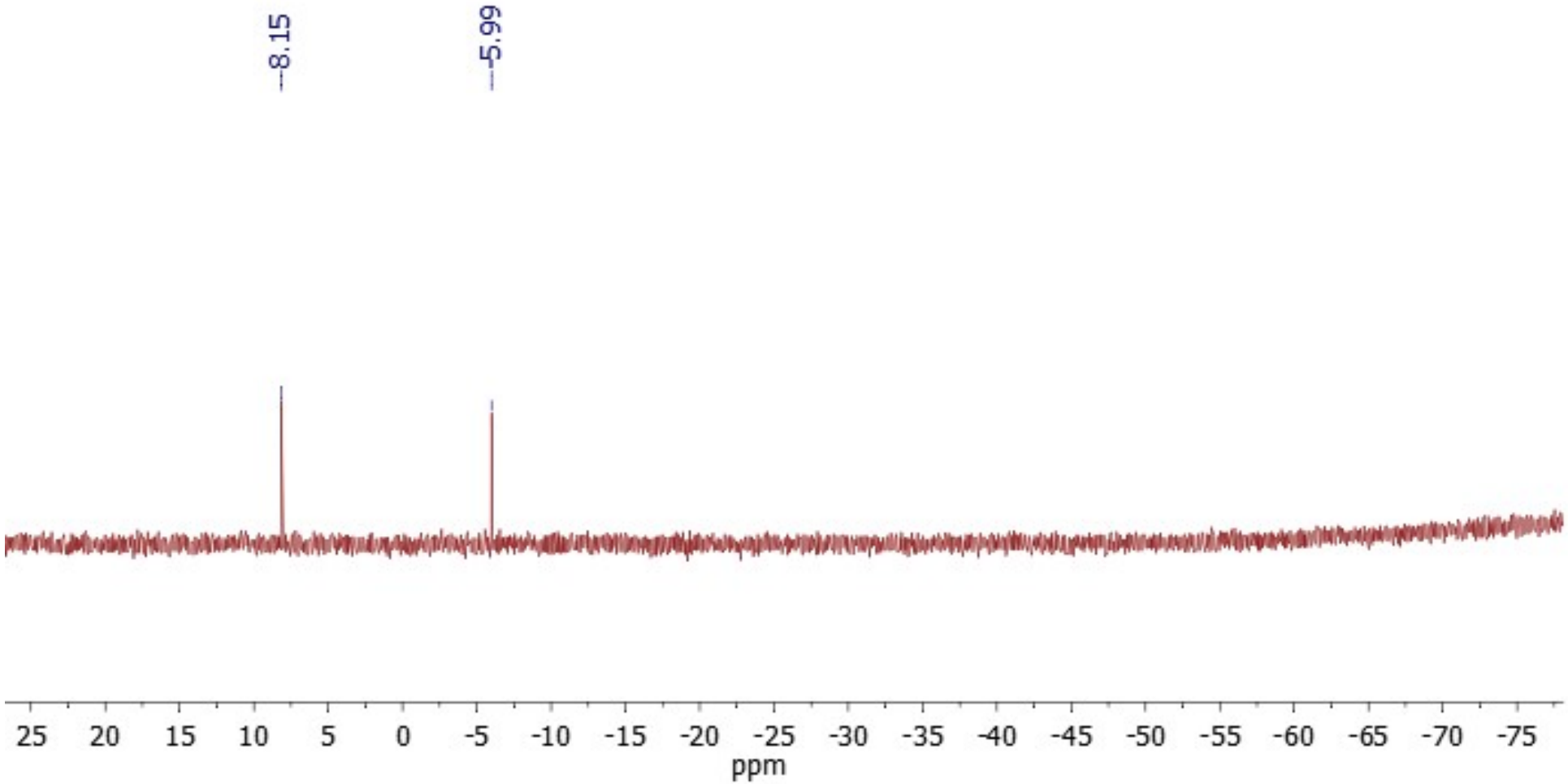


Figure 56s. ^{29}Si NMR spectrum of compound **1.4** (500 MHz, solvent – $CDCl_3$).

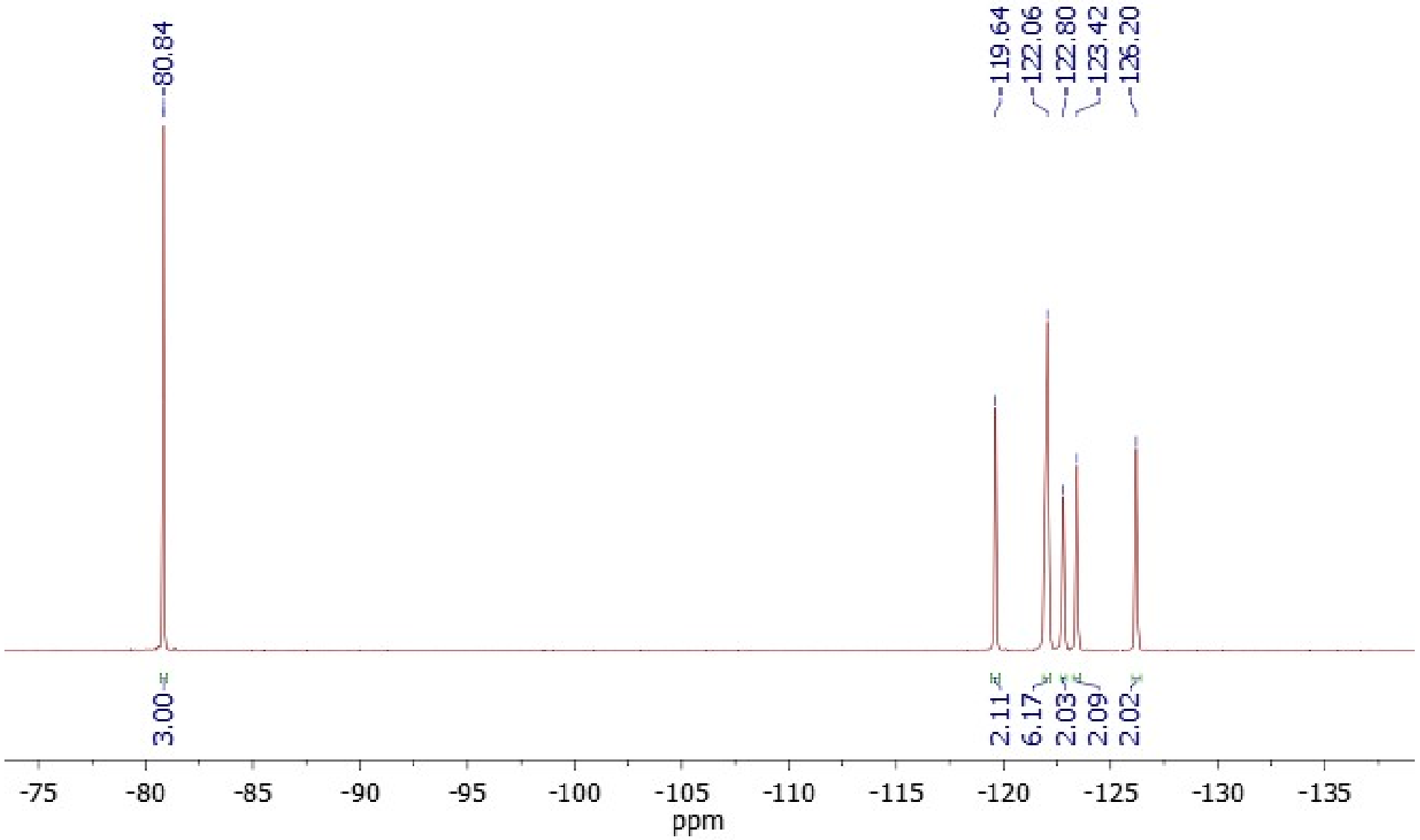


Figure 57s. ^{19}F NMR spectrum of compound **1.4** (300 MHz, solvent – $CDCl_3$).

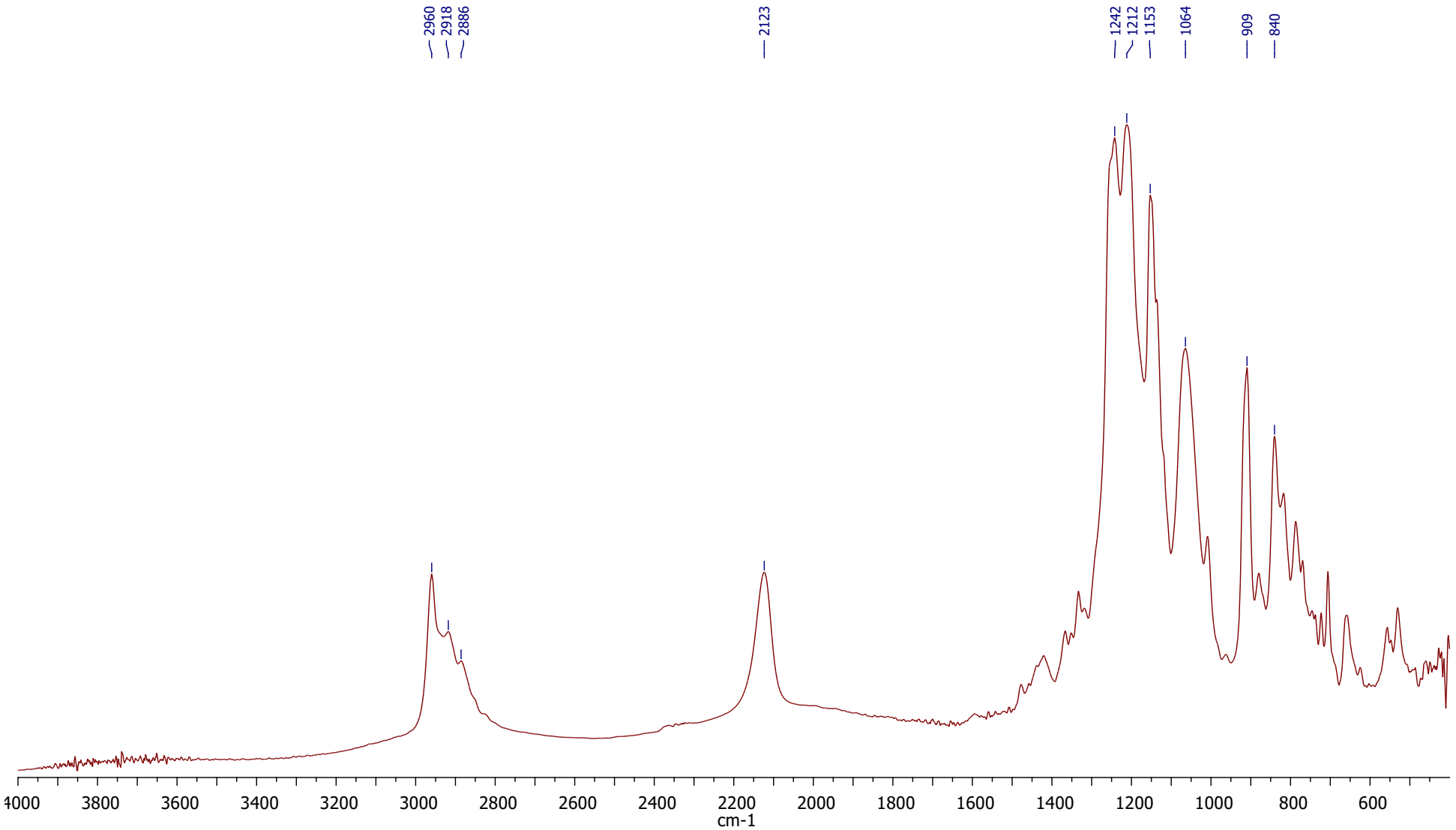


Figure 58s. IR-spectrum of compound **1.4**.

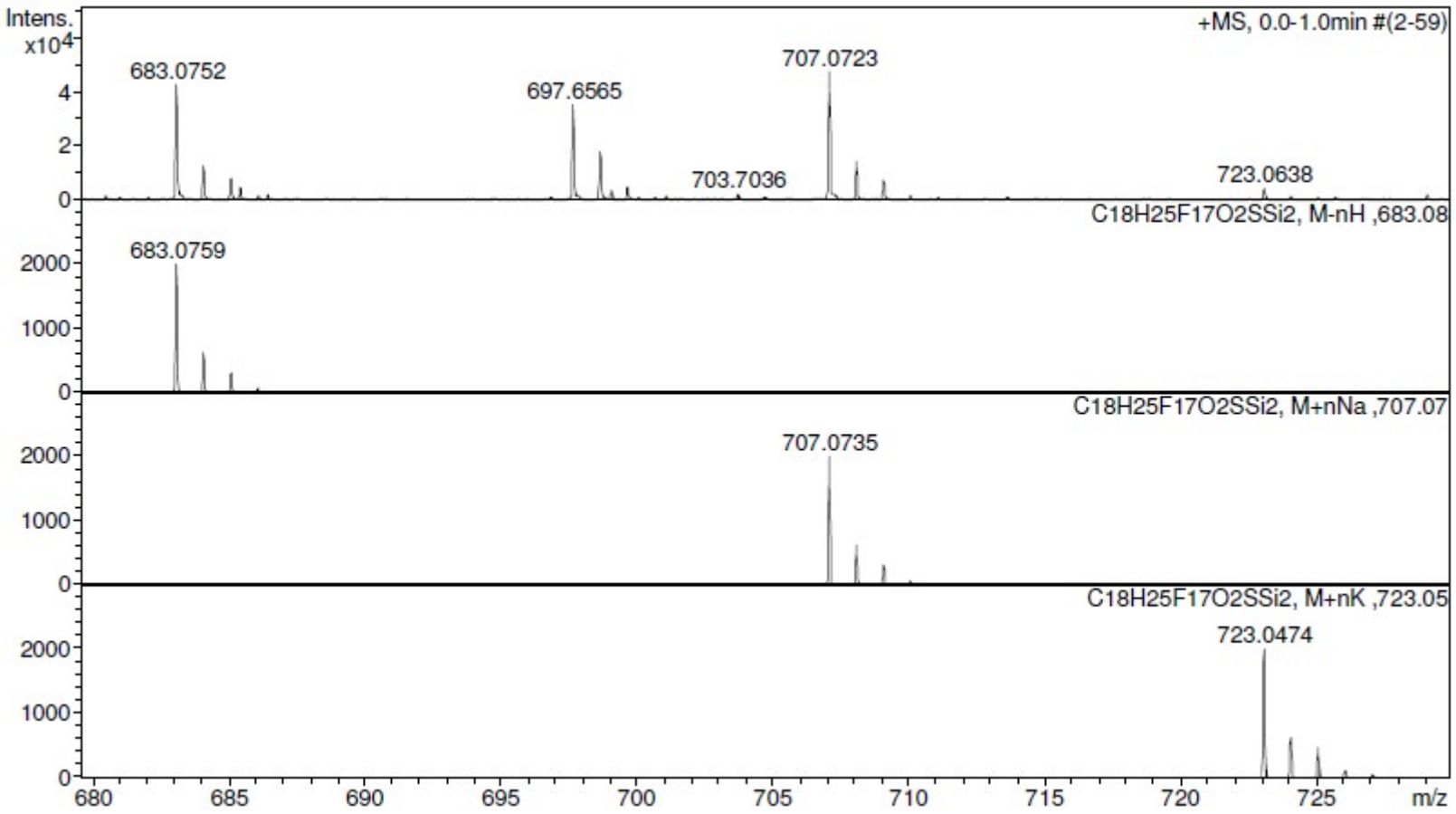


Figure 59s. HRMS (ESI) for compound **1.4**

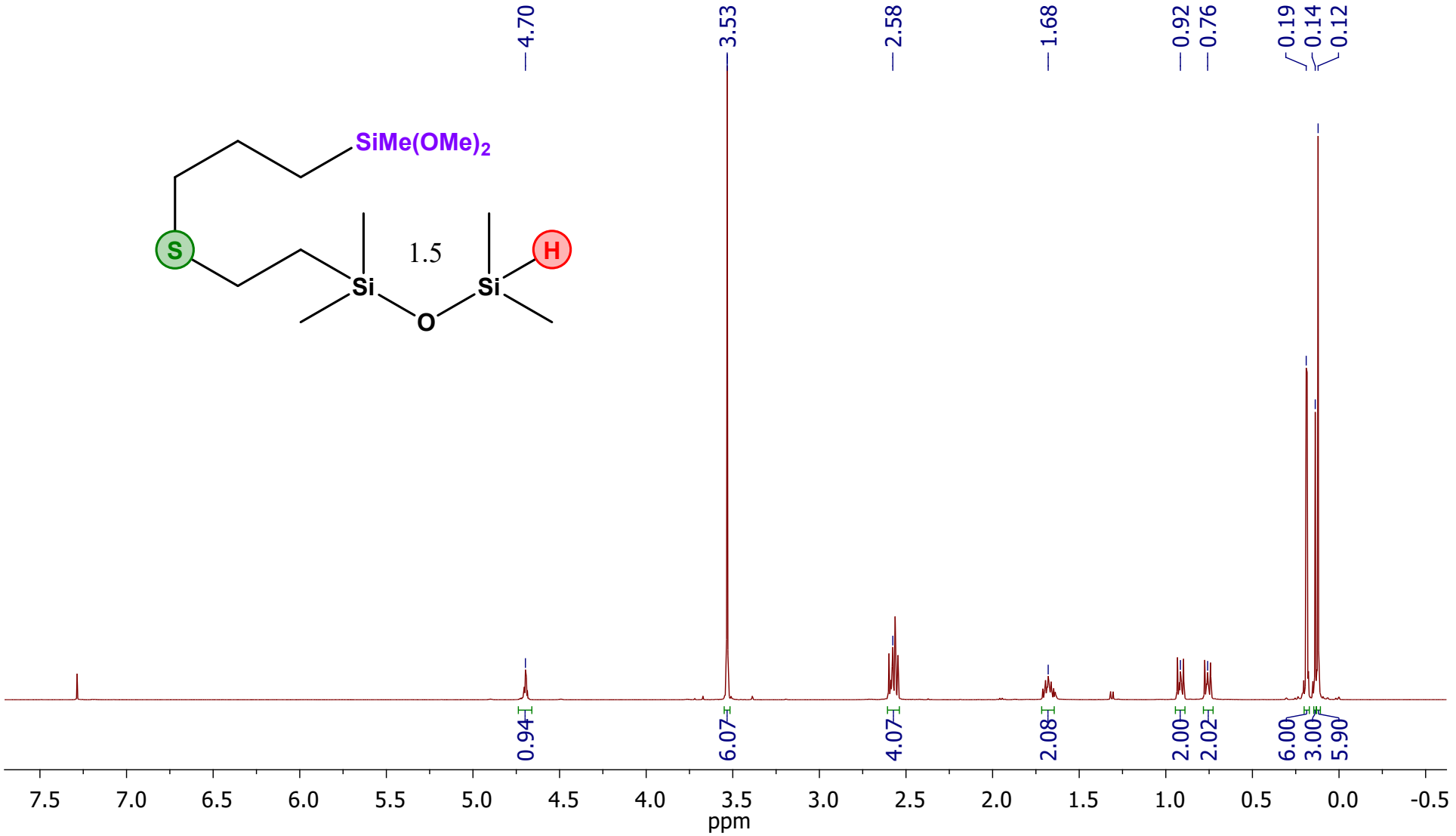


Figure 60s. ^{1}H NMR spectrum of compound **1.5** (500 MHz, solvent – $CDCl_3$).

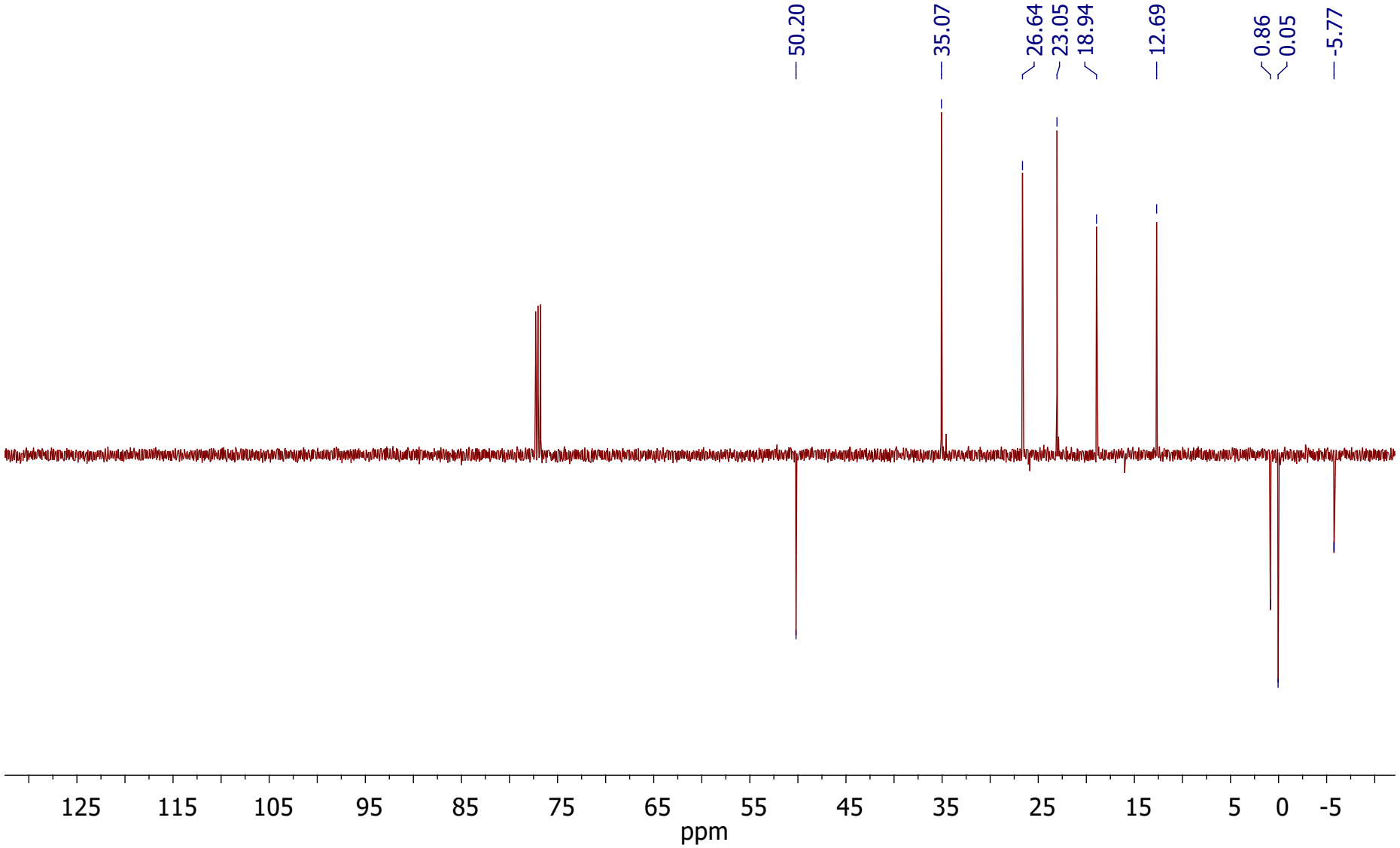


Figure 61s. ^{13}C NMR spectrum of compound **1.5** (400 MHz, solvent – $CDCl_3$, jmod).

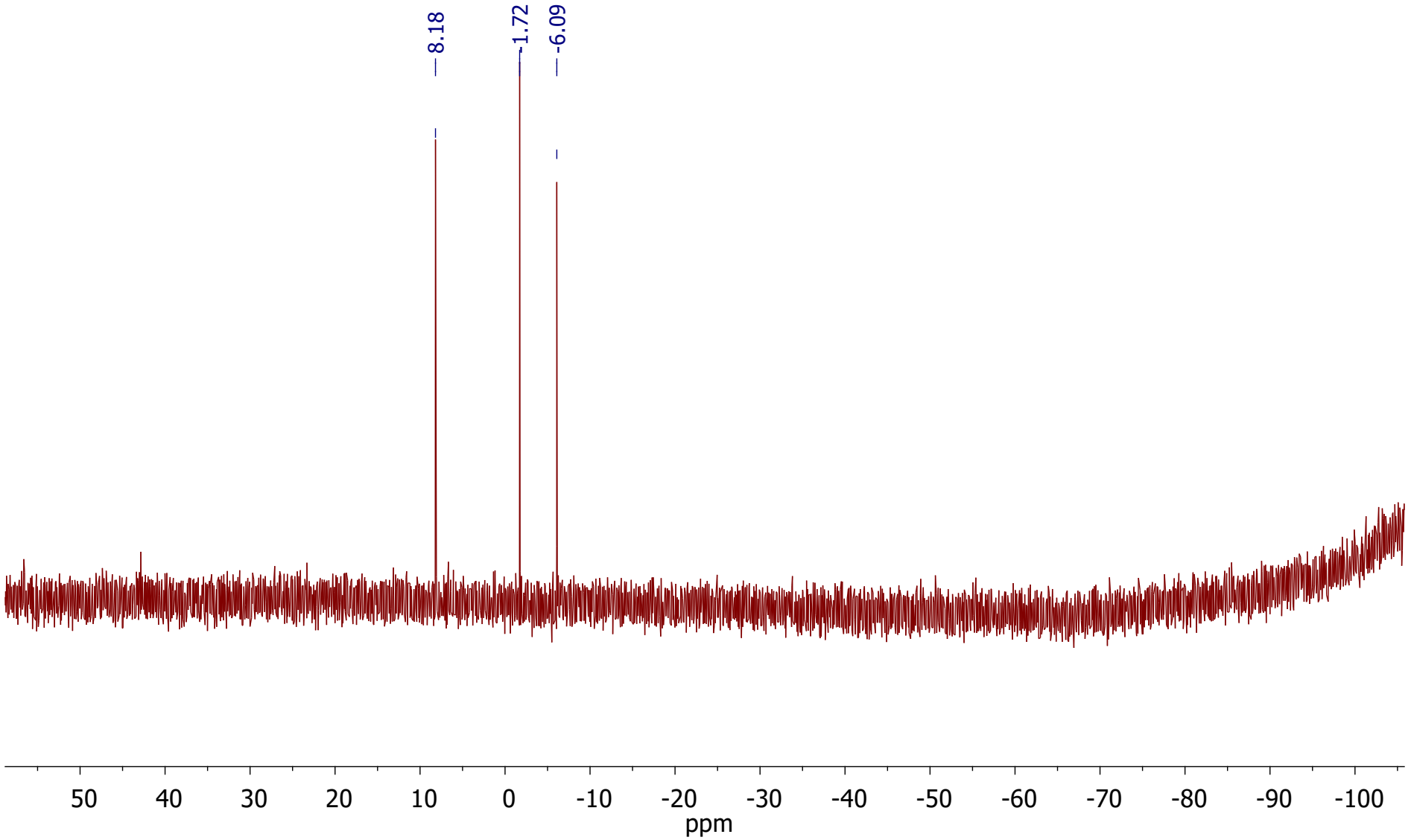


Figure 62s. ^{29}Si NMR spectrum of compound **1.5** (400 MHz, solvent – $CDCl_3$).

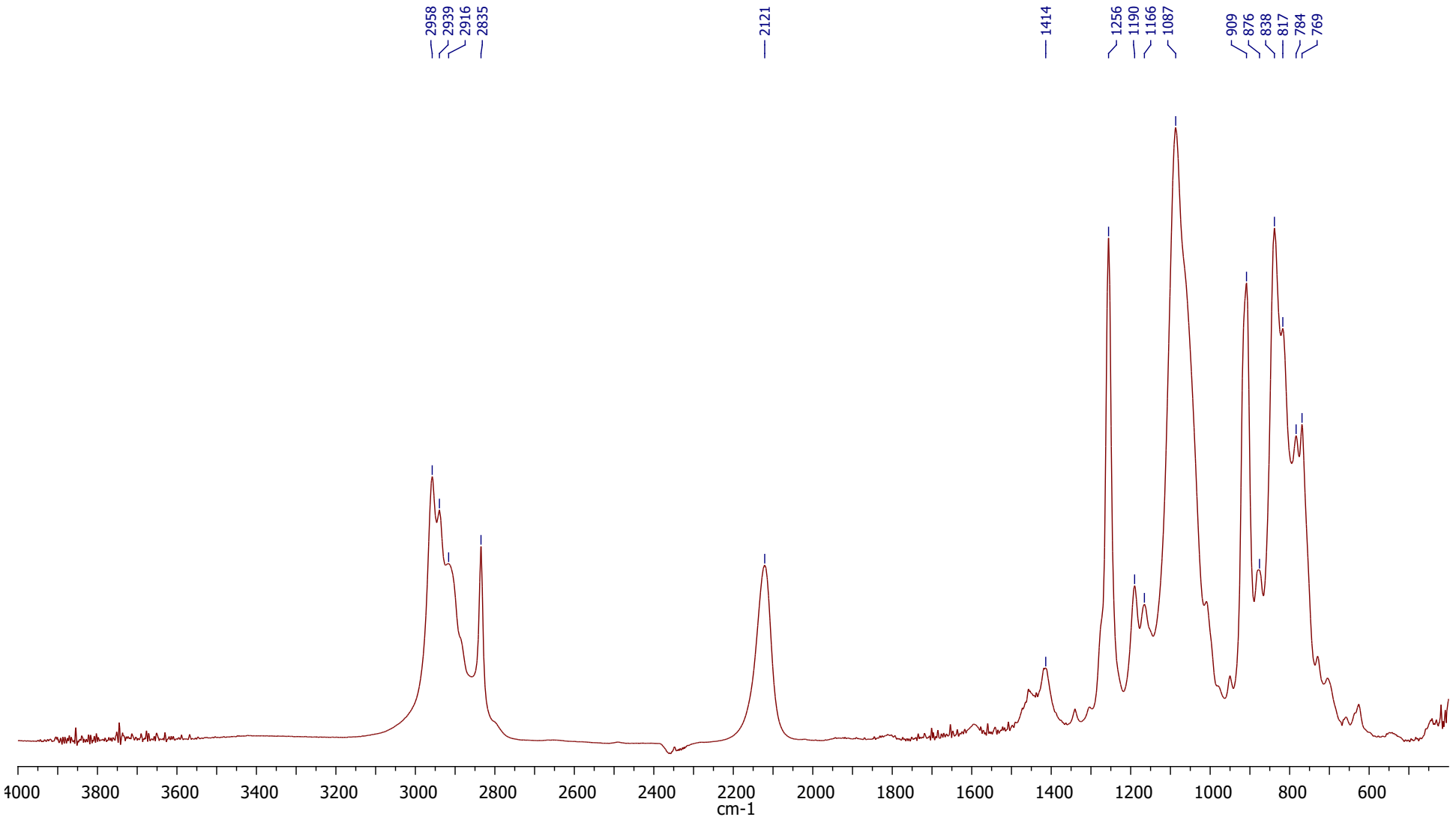


Figure 63s. IR-spectrum of compound **1.5**.

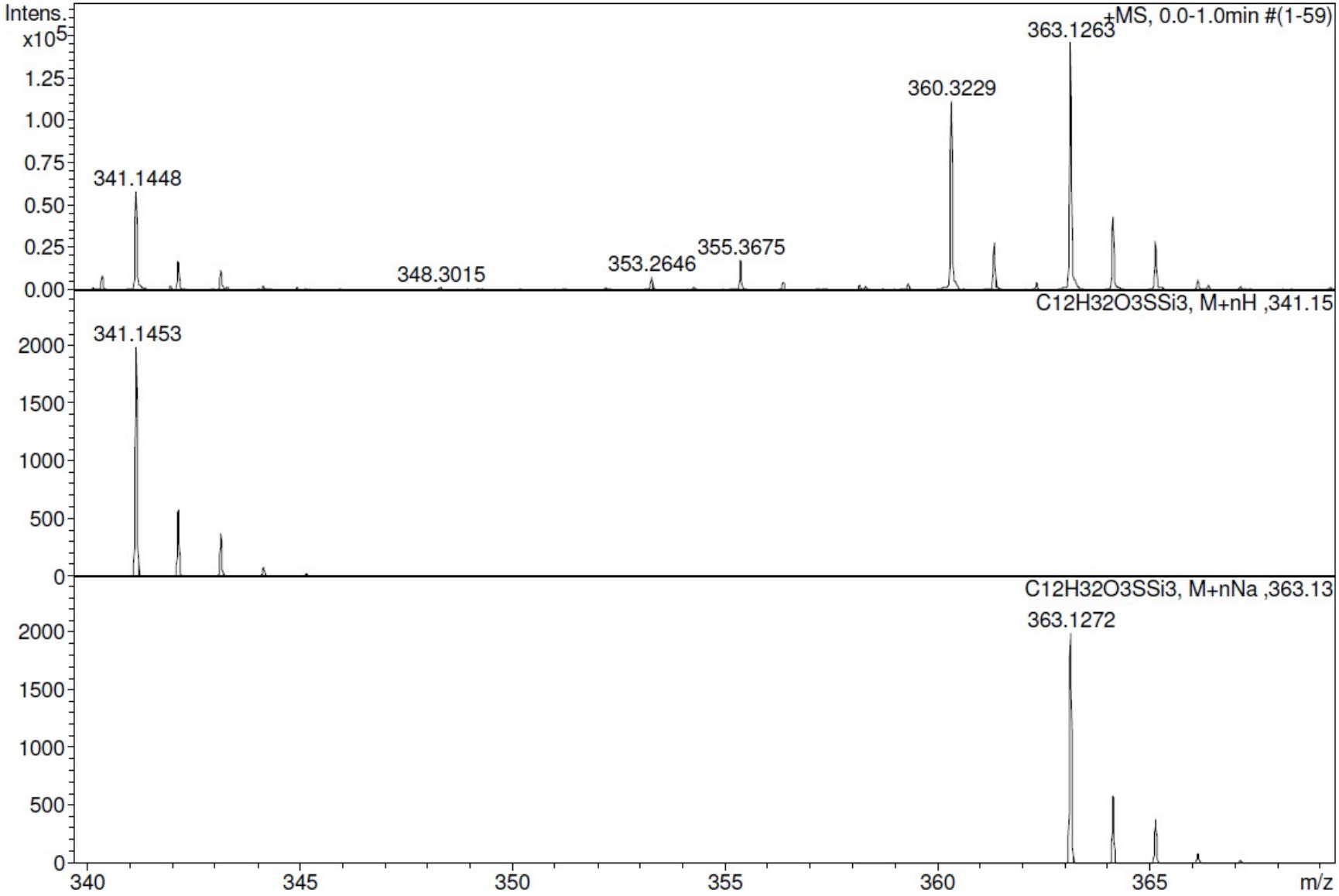


Figure 64s. HRMS (ESI) for compound **1.5**.

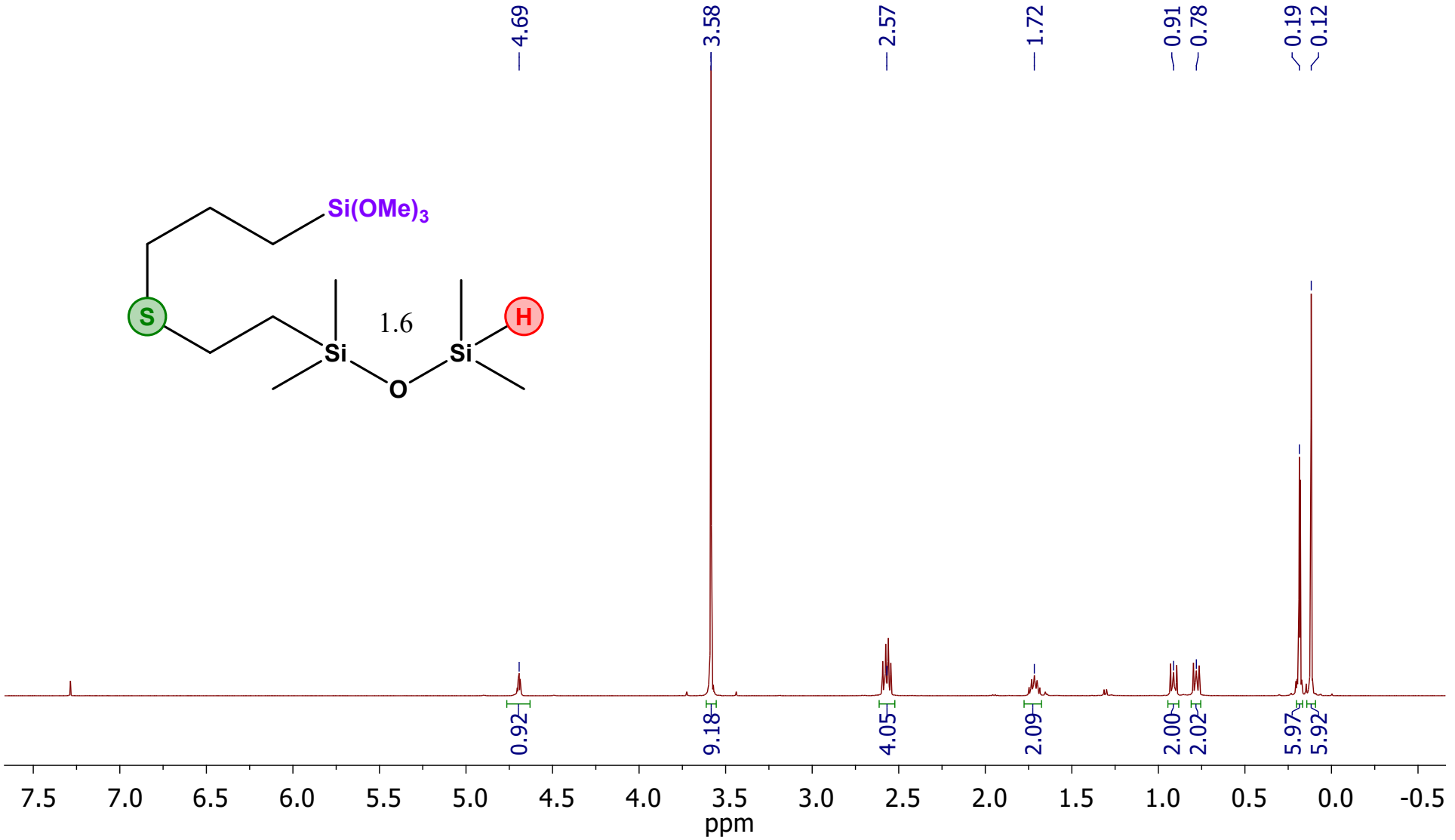


Figure 65s. ^{1}H NMR spectrum of compound **1.6** (500 MHz, solvent – $CDCl_3$).

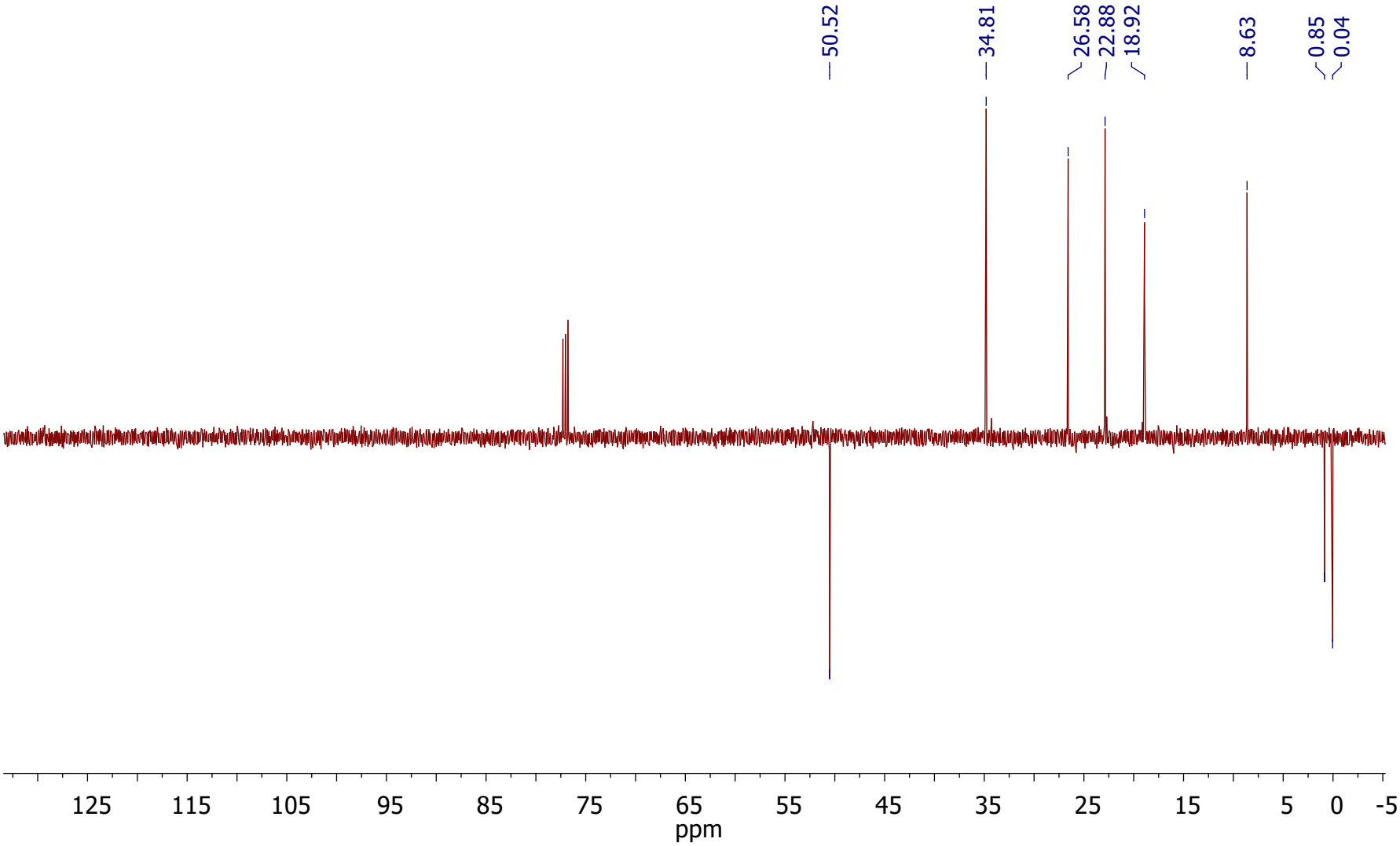


Figure 66s. ^{13}C NMR spectrum of compound **1.6** (400 MHz, solvent – $CDCl_3$, jmod).

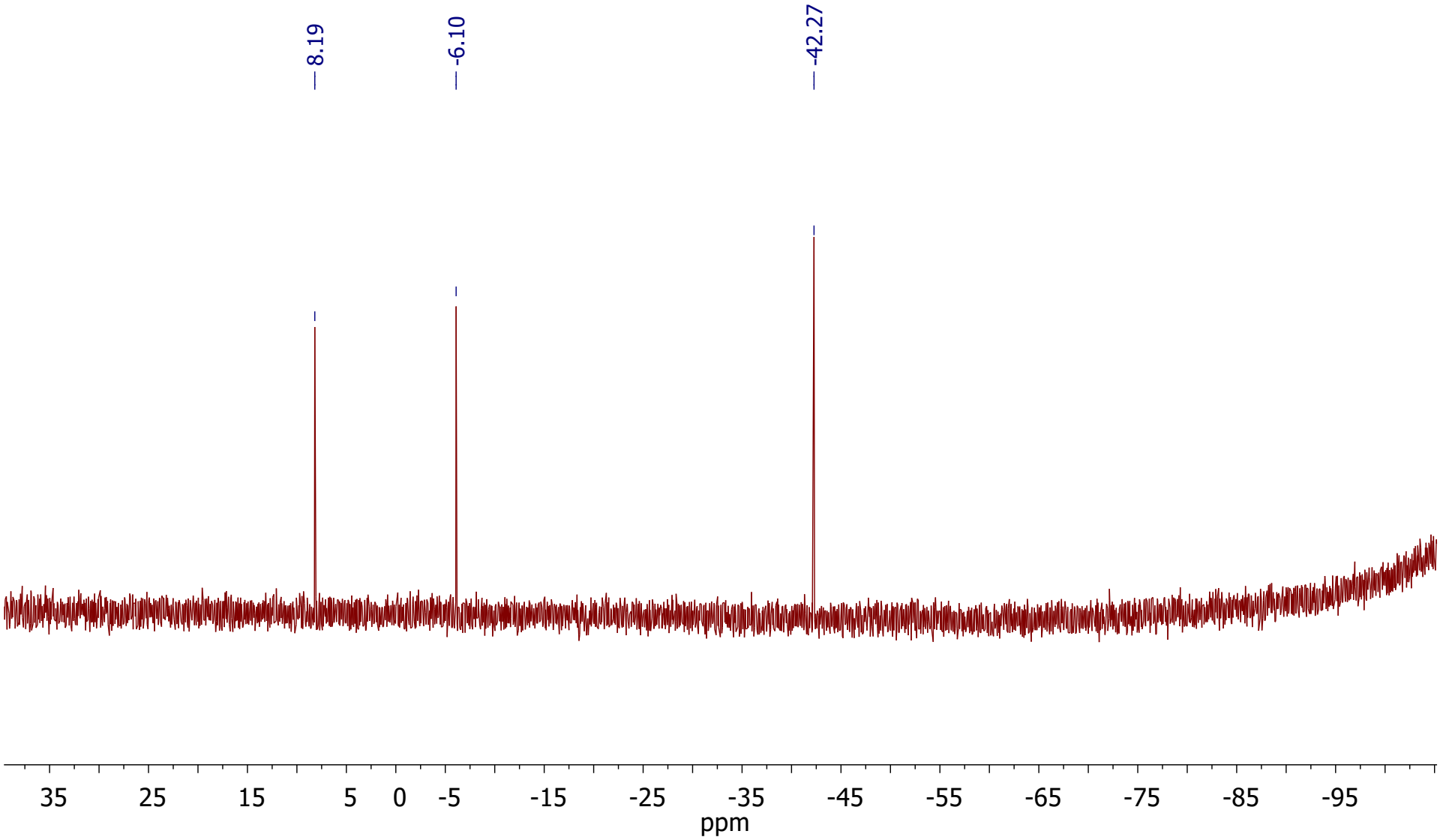


Figure 67s. ^{29}Si NMR spectrum of compound **1.6** (400 MHz, solvent – $CDCl_3$).

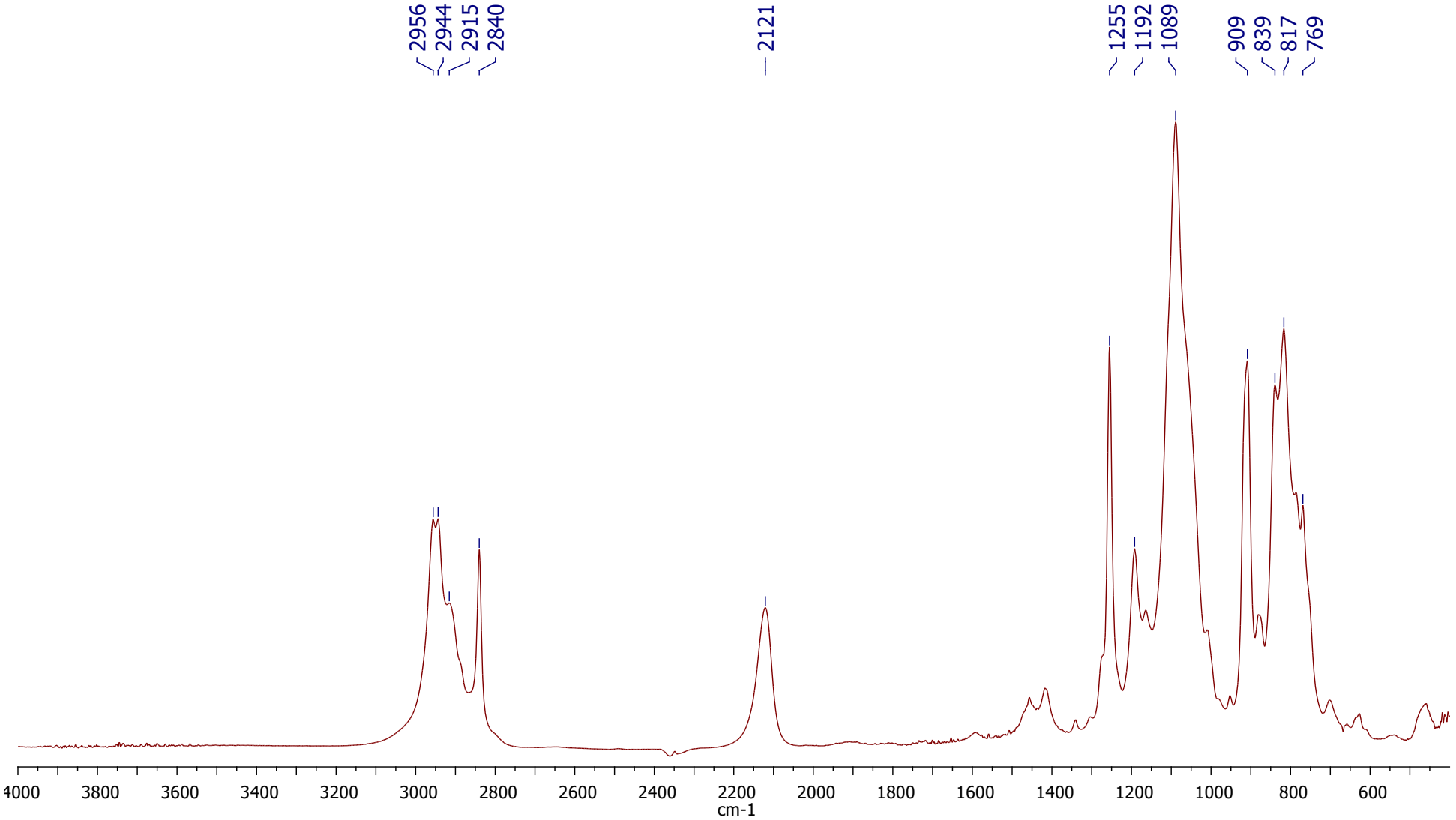


Figure 68s. IR-spectrum of compound **1.6**.

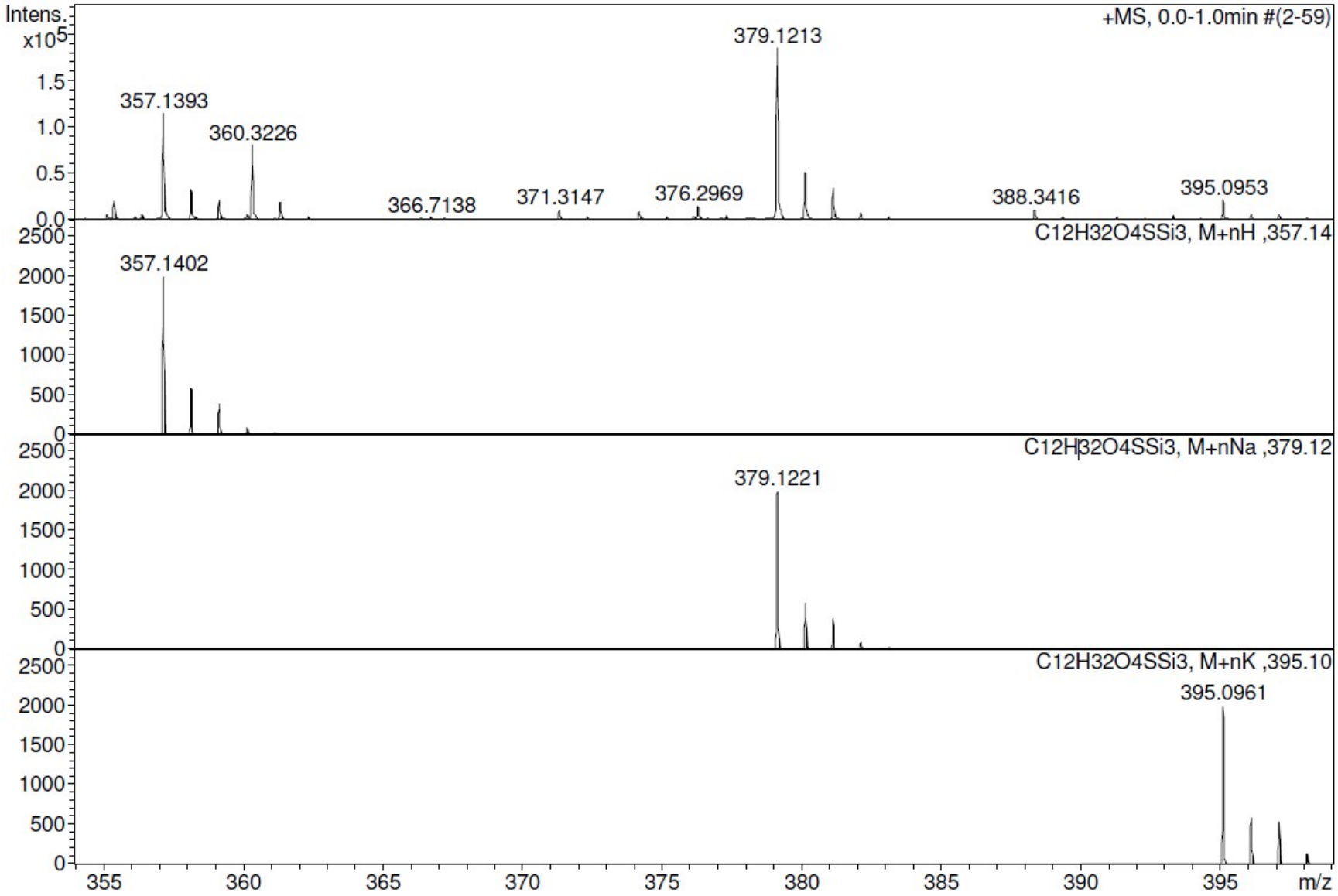


Figure 69s. HRMS (ESI) for compound **1.6**.

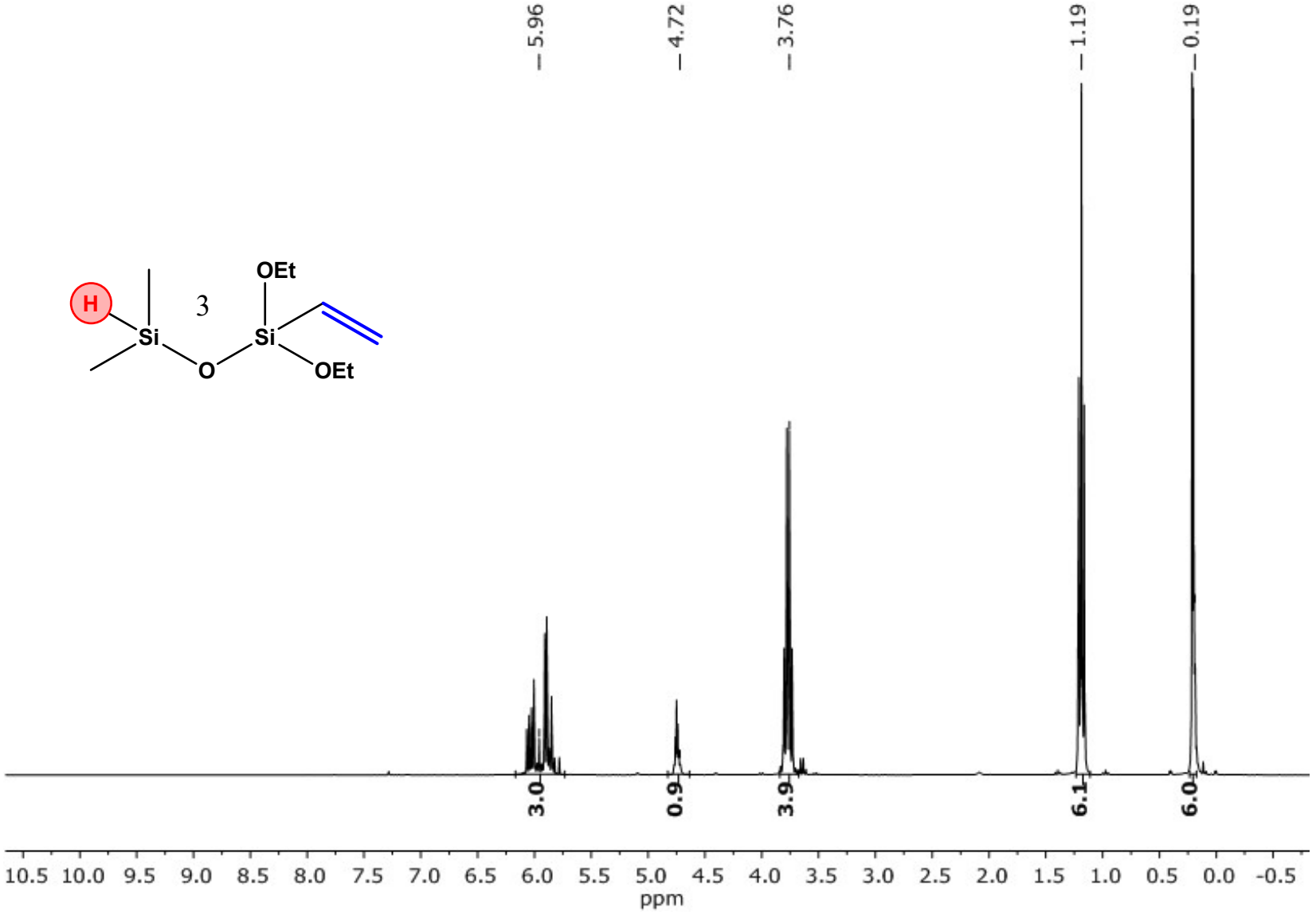


Figure 70s. ^{1}H NMR spectrum of compound **3** (400 MHz, solvent – $CDCl_3$).

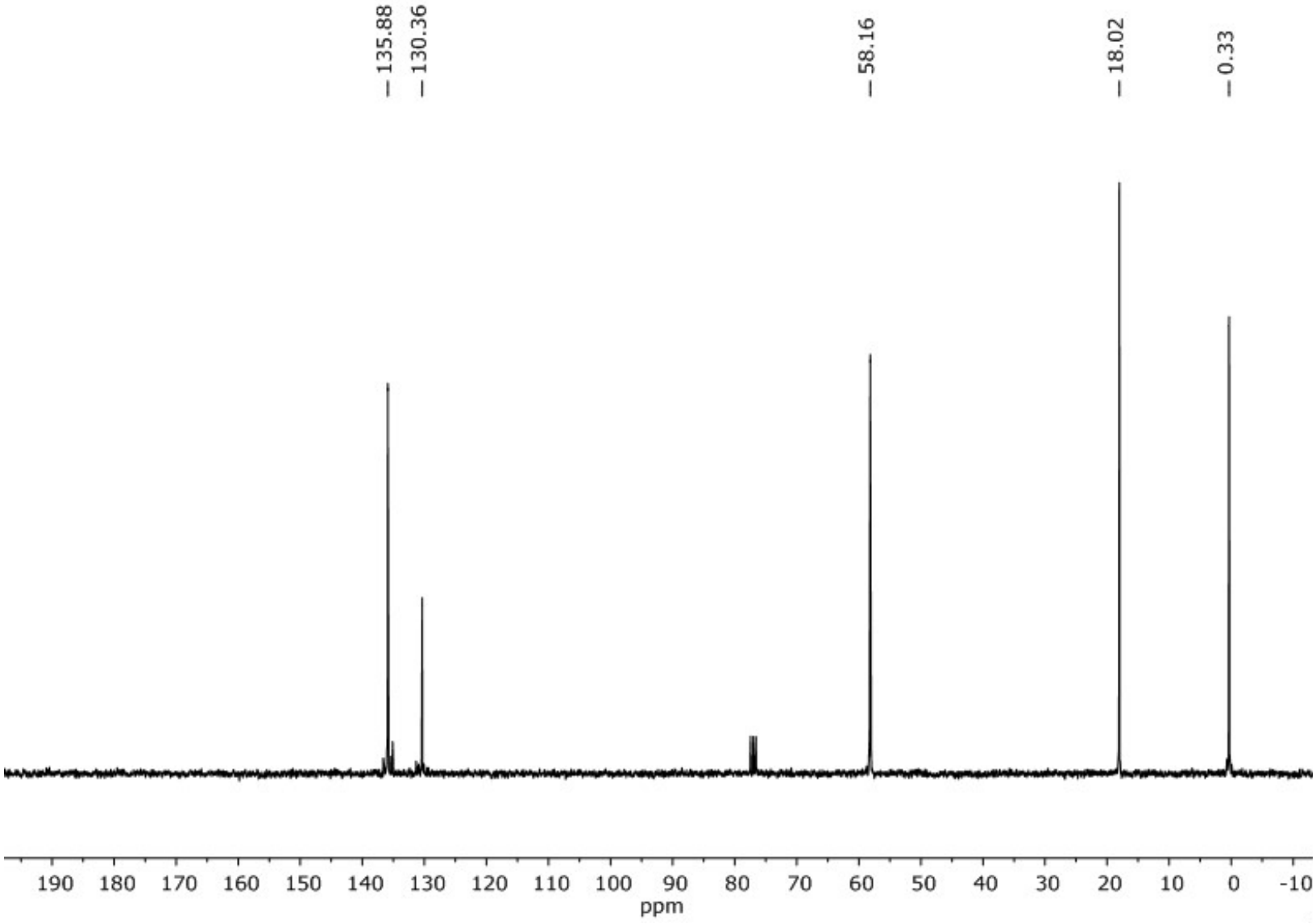


Figure 71s. ^{13}C NMR spectrum of compound **3** (400 MHz, solvent – $CDCl_3$).

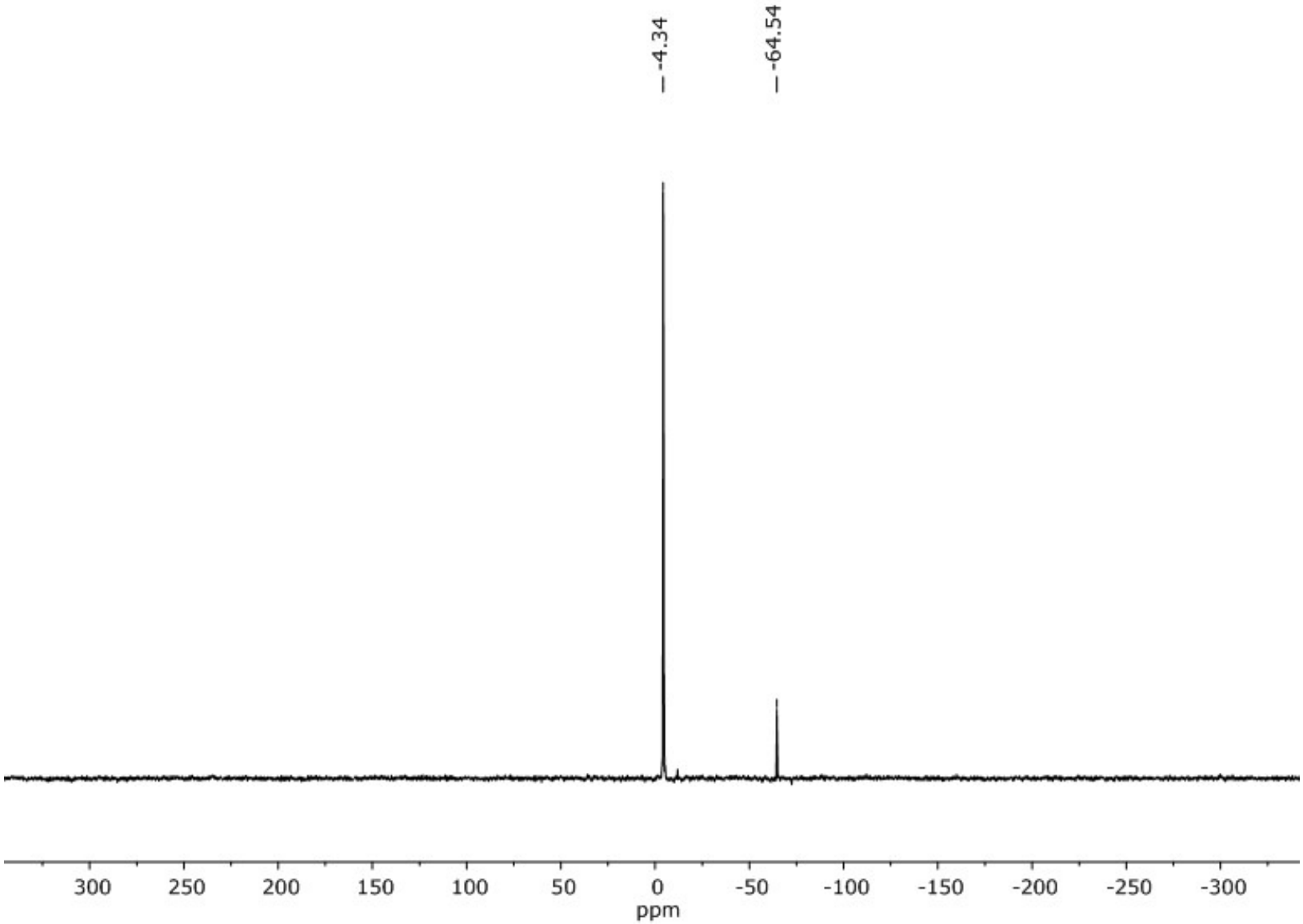


Figure 72s. ^{29}Si NMR spectrum of compound **3** (400 MHz, solvent – CDCl3).

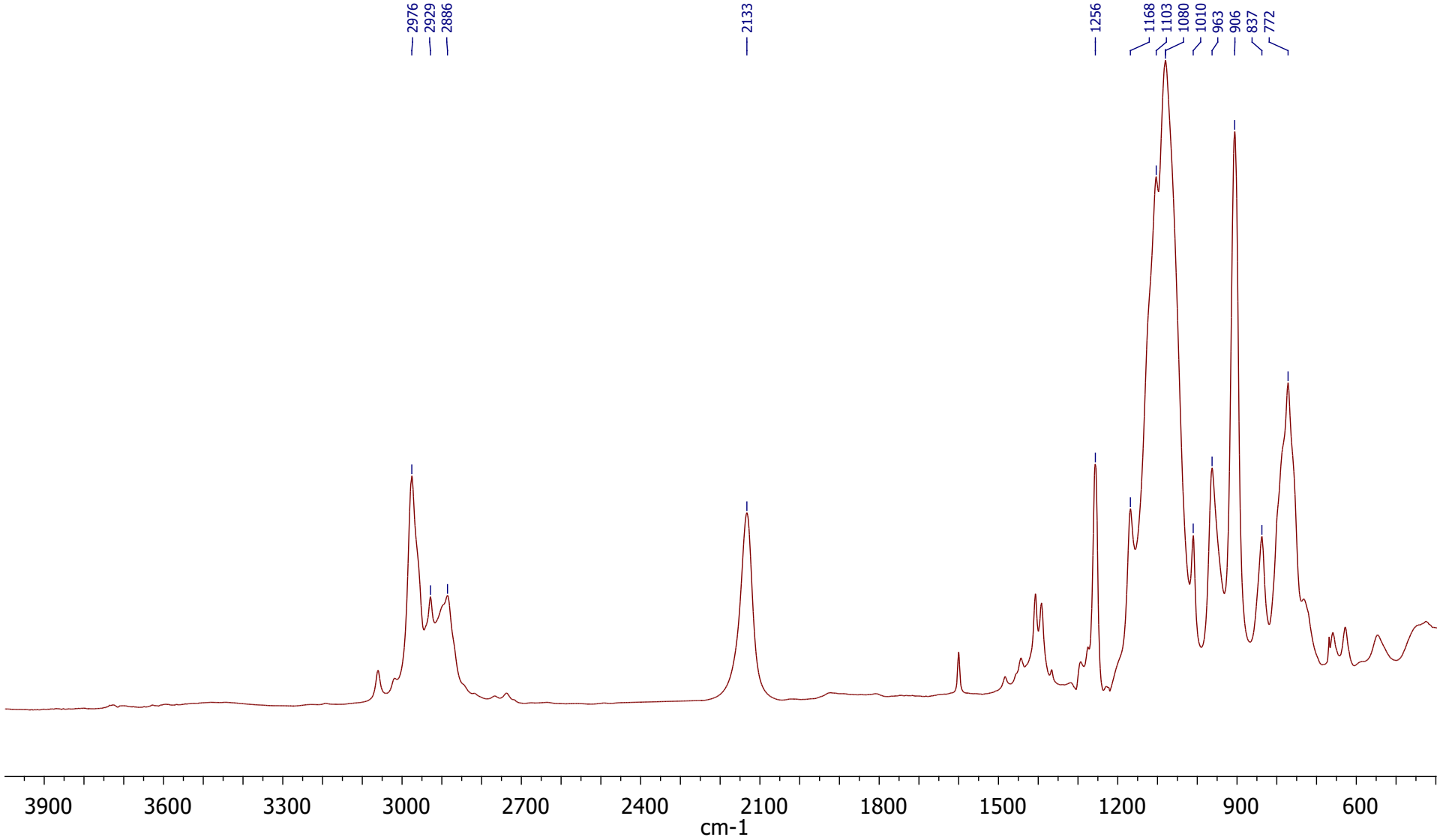


Figure 73s. IR-spectrum of compound **3**.

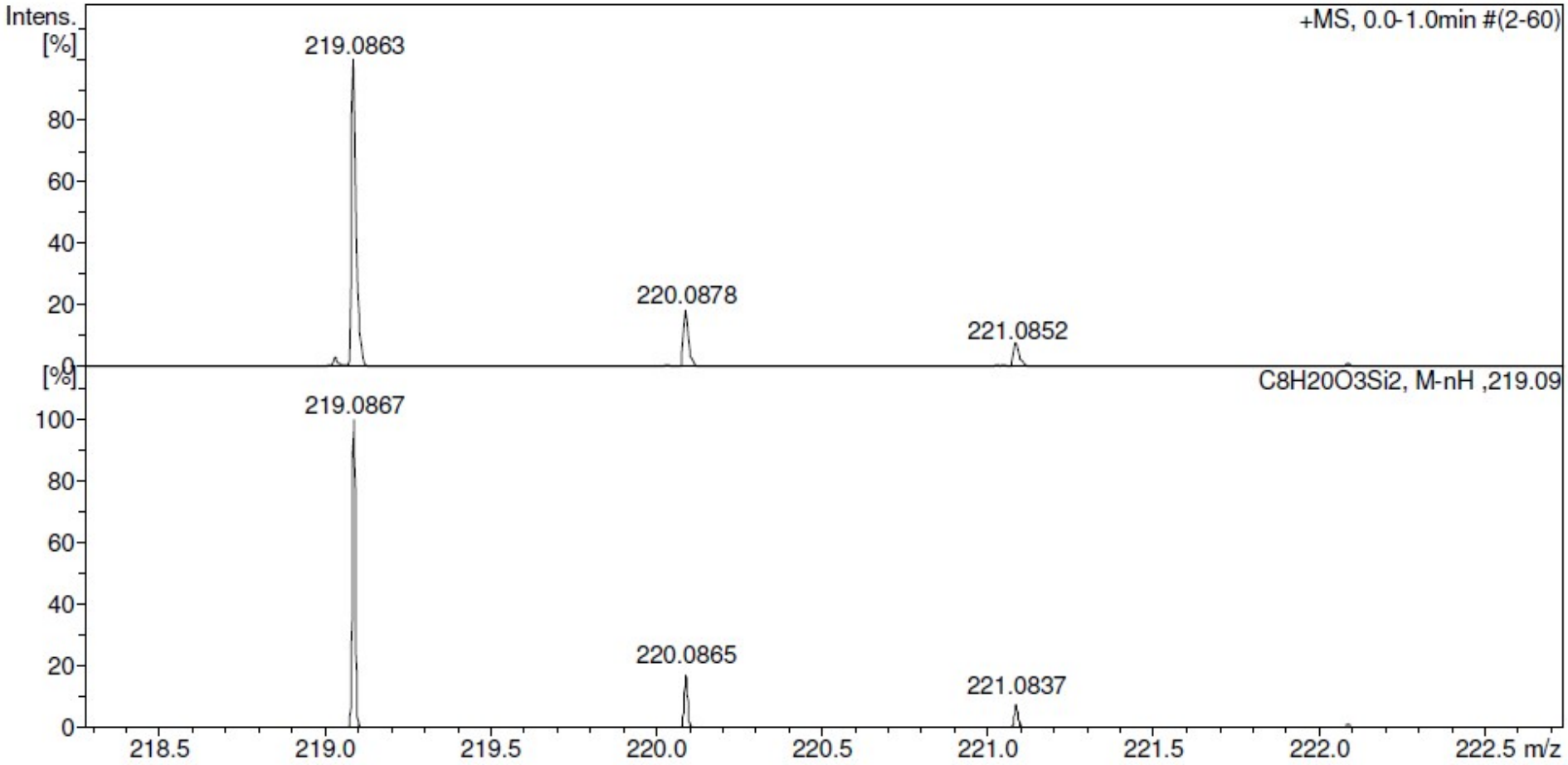


Figure 74s. HRMS (ESI) for compound **3**.

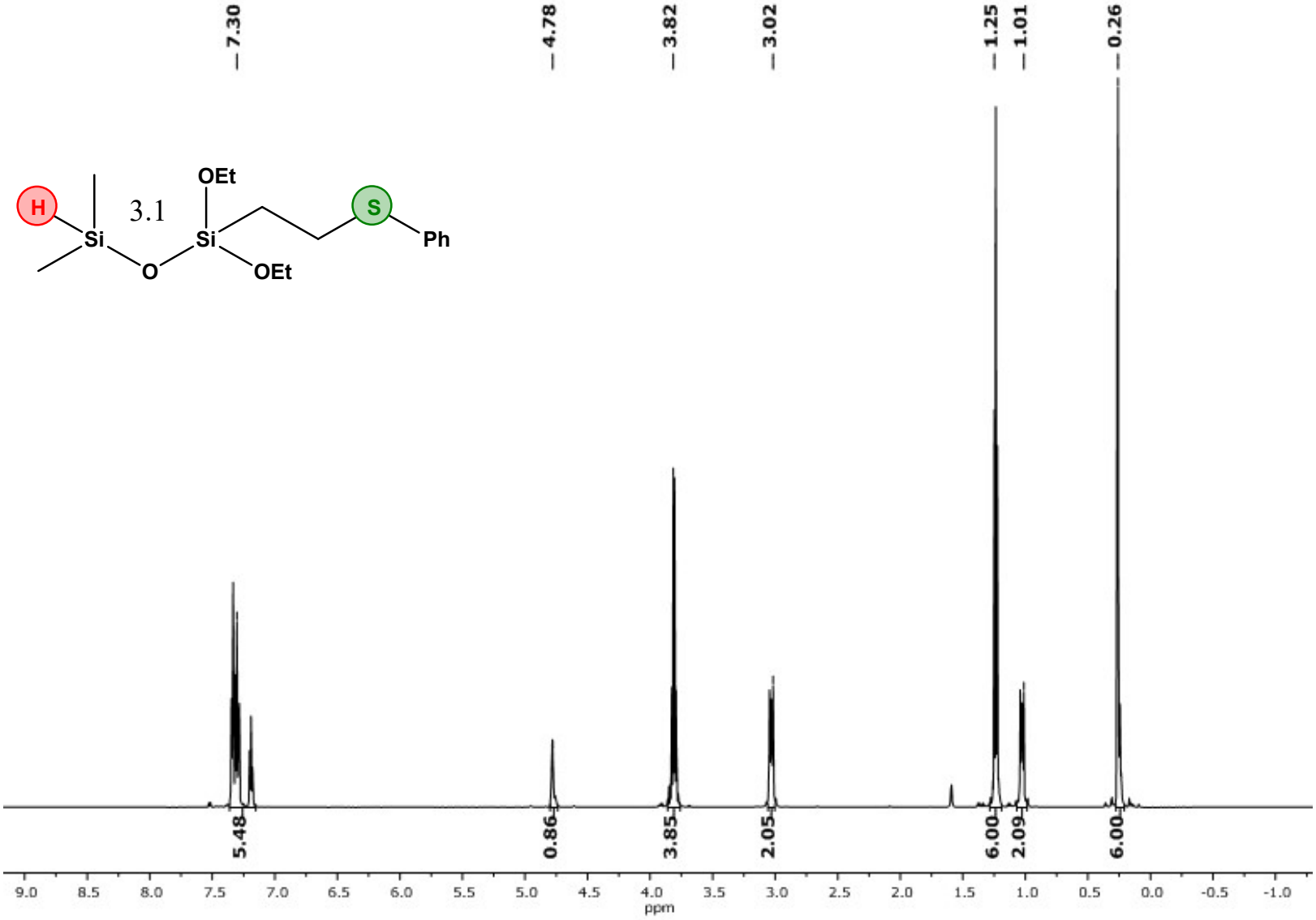


Figure 75s. ^{1}H NMR spectrum of compound **3.1** (400 MHz, solvent – $CDCl_3$).

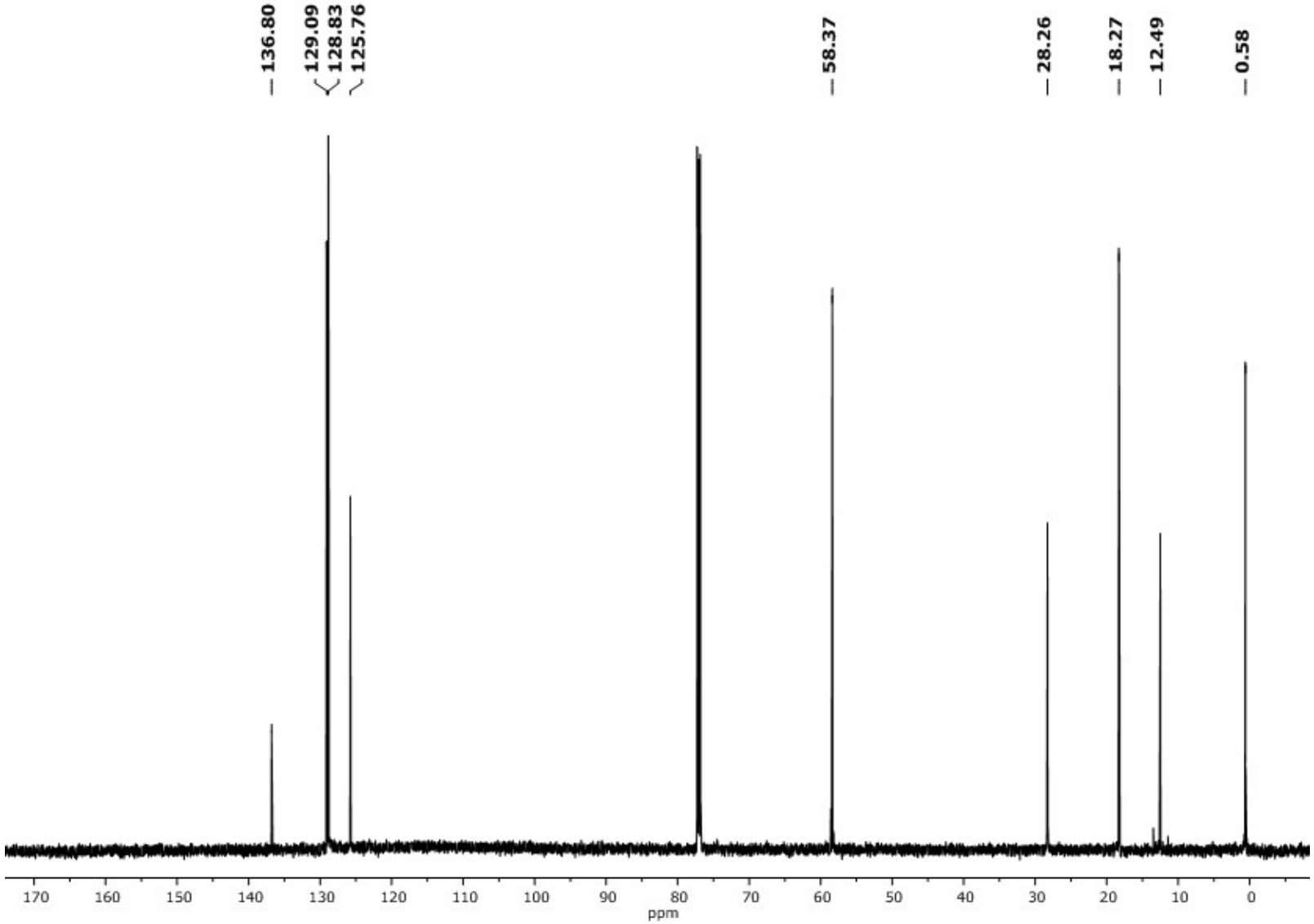


Figure 76s. ^{13}C NMR spectrum of compound **3.1** (100 MHz, solvent – $CDCl_3$).

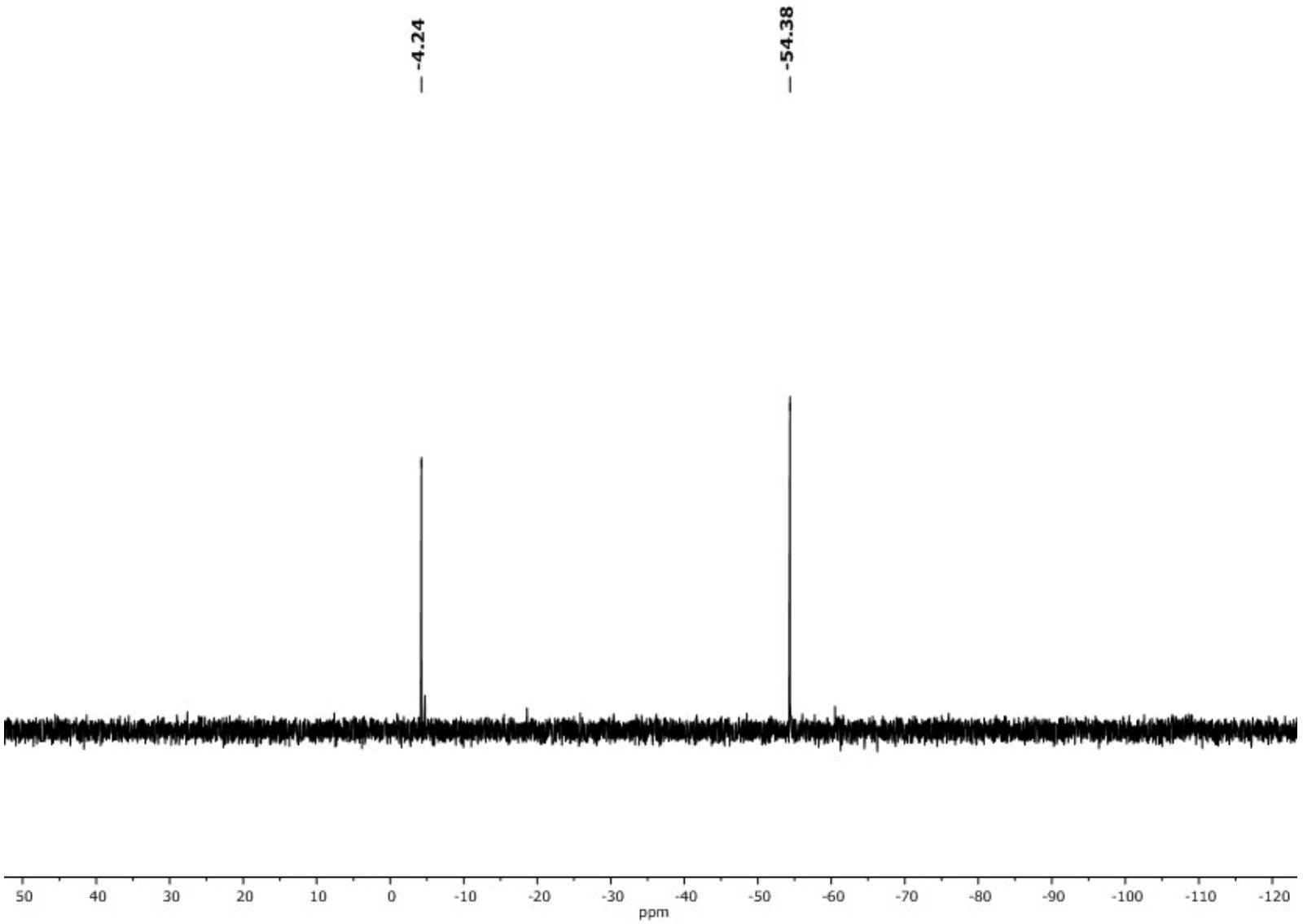


Figure 77s. ^{29}Si NMR spectrum of compound **3.1** (80 MHz, solvent – $CDCl_3$).

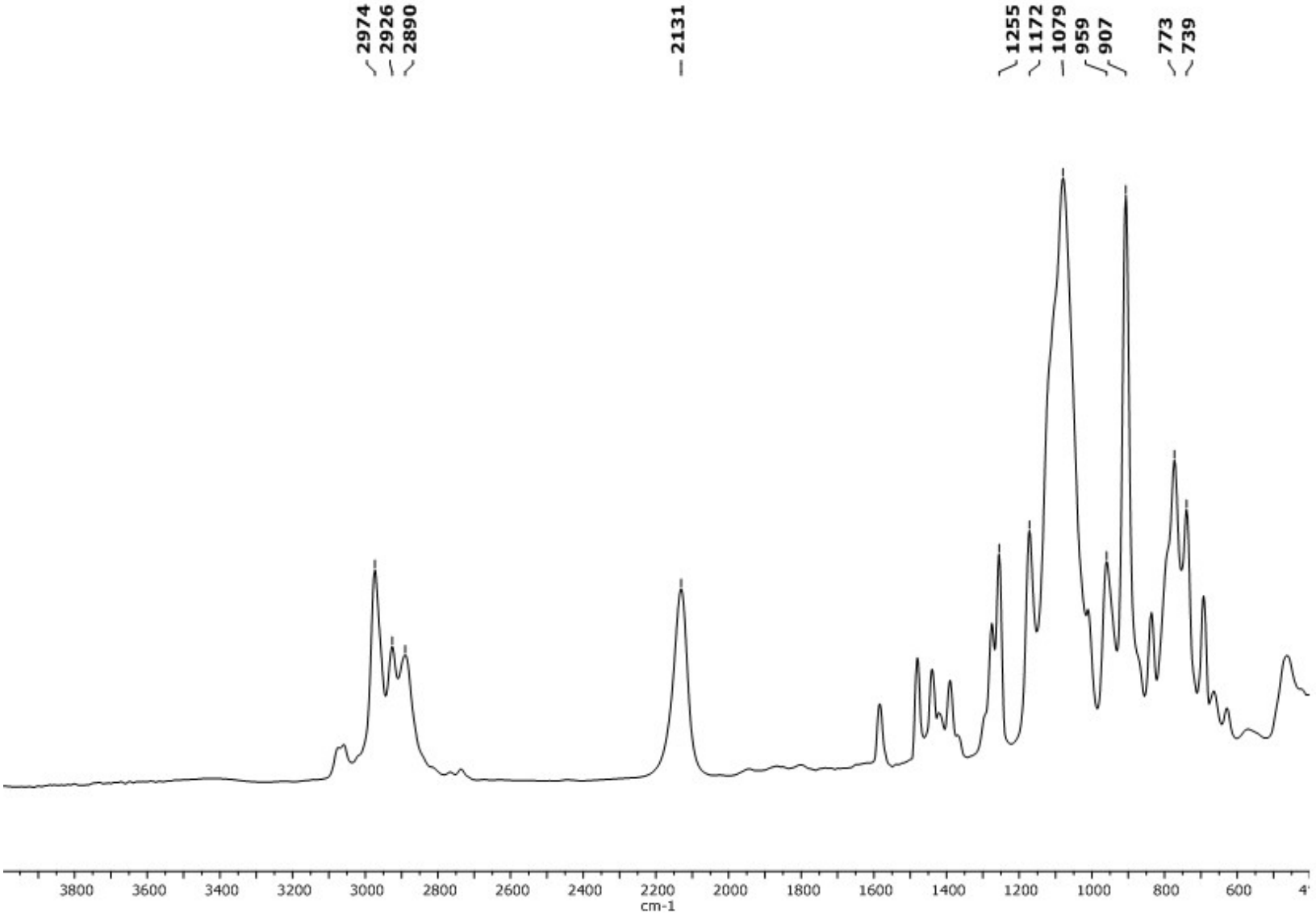


Figure 78s. IR-spectrum of compound **3.1**.

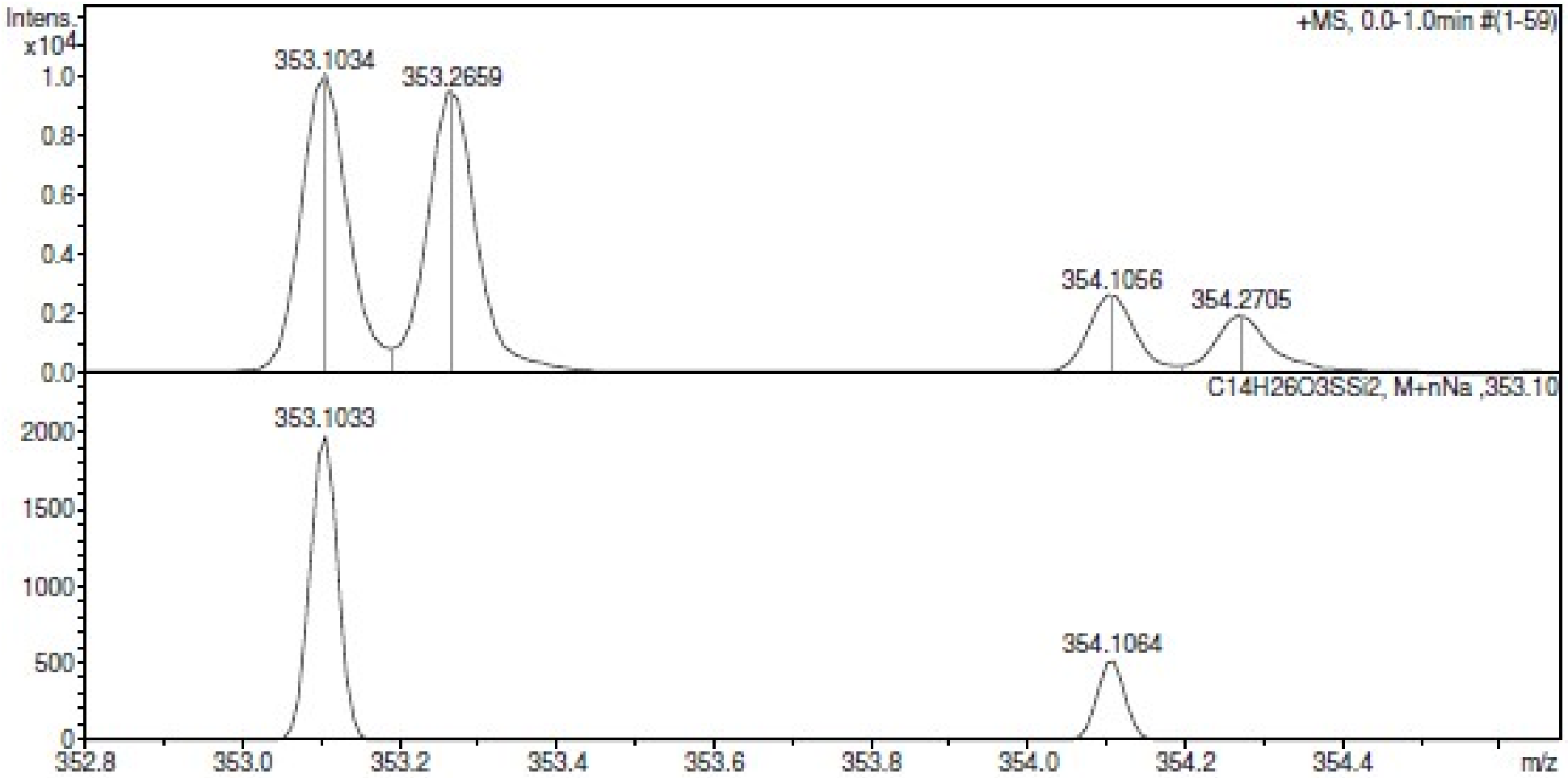


Figure 79s. HRMS (ESI) for compound **3.1**.

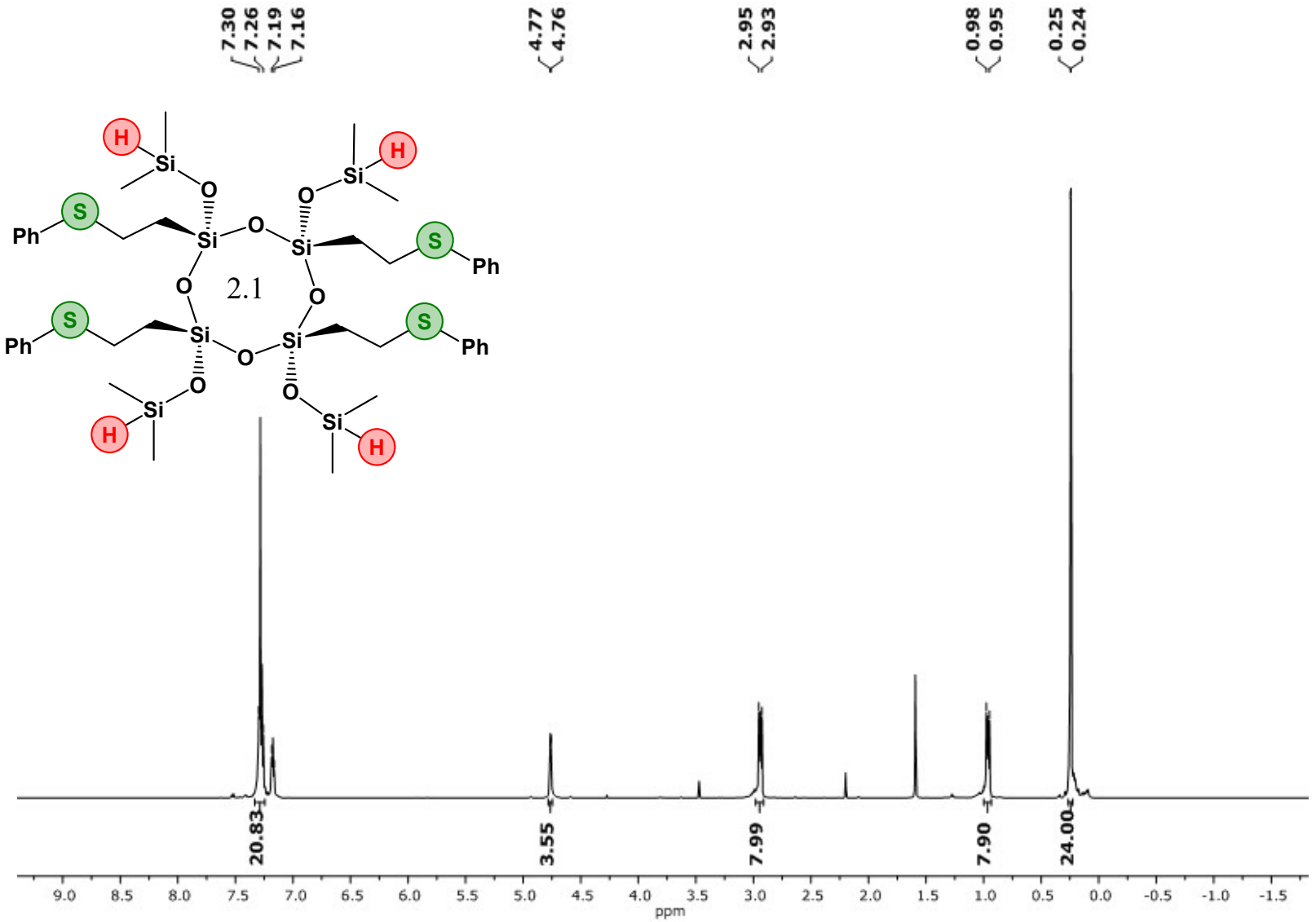


Figure 80. ^{1}H NMR spectrum of compound **2.1** (400 MHz, solvent – $CDCl_3$).

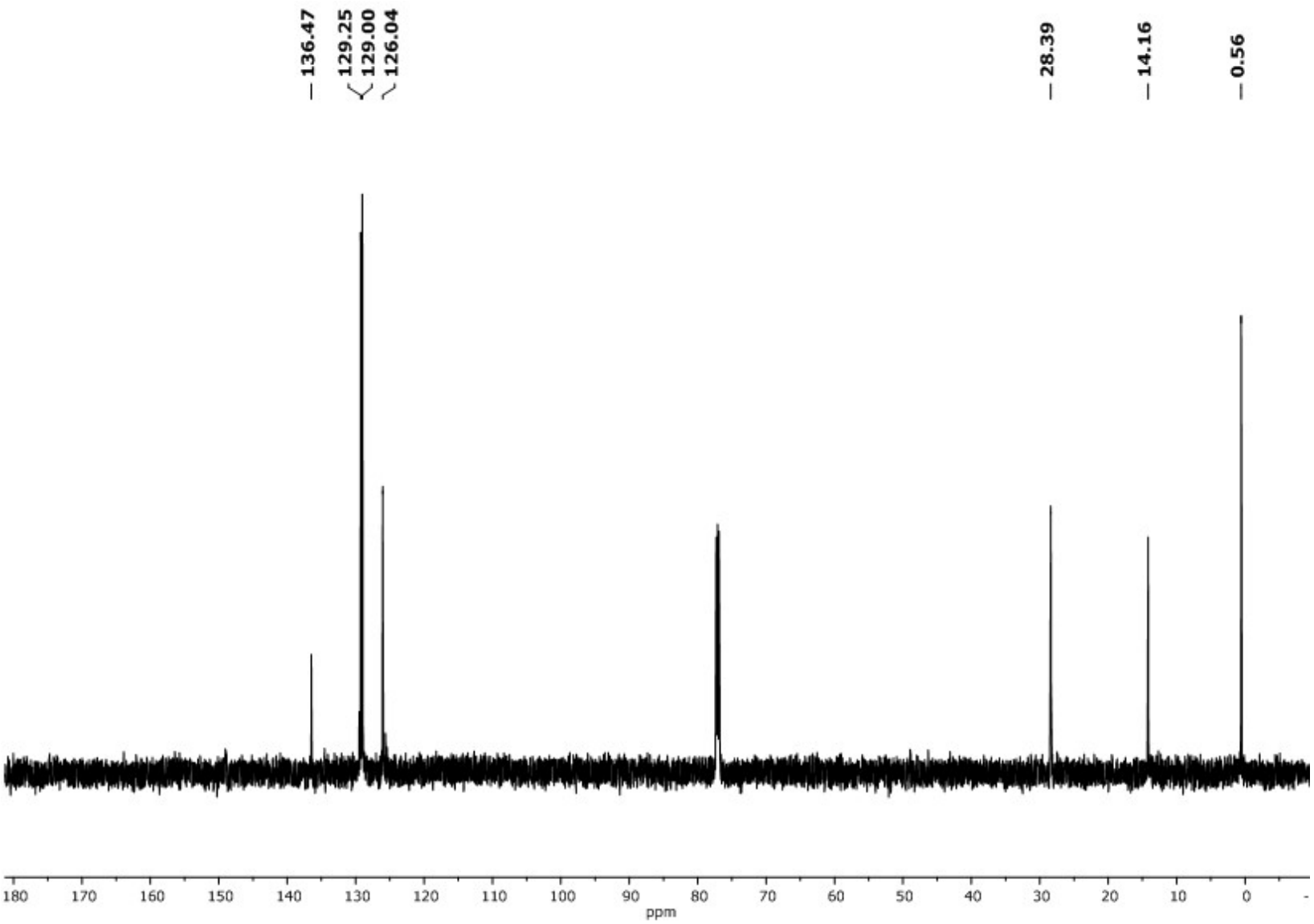


Figure 81s. ^{13}C NMR spectrum of compound **2.1** (100 MHz, solvent – $CDCl_3$).

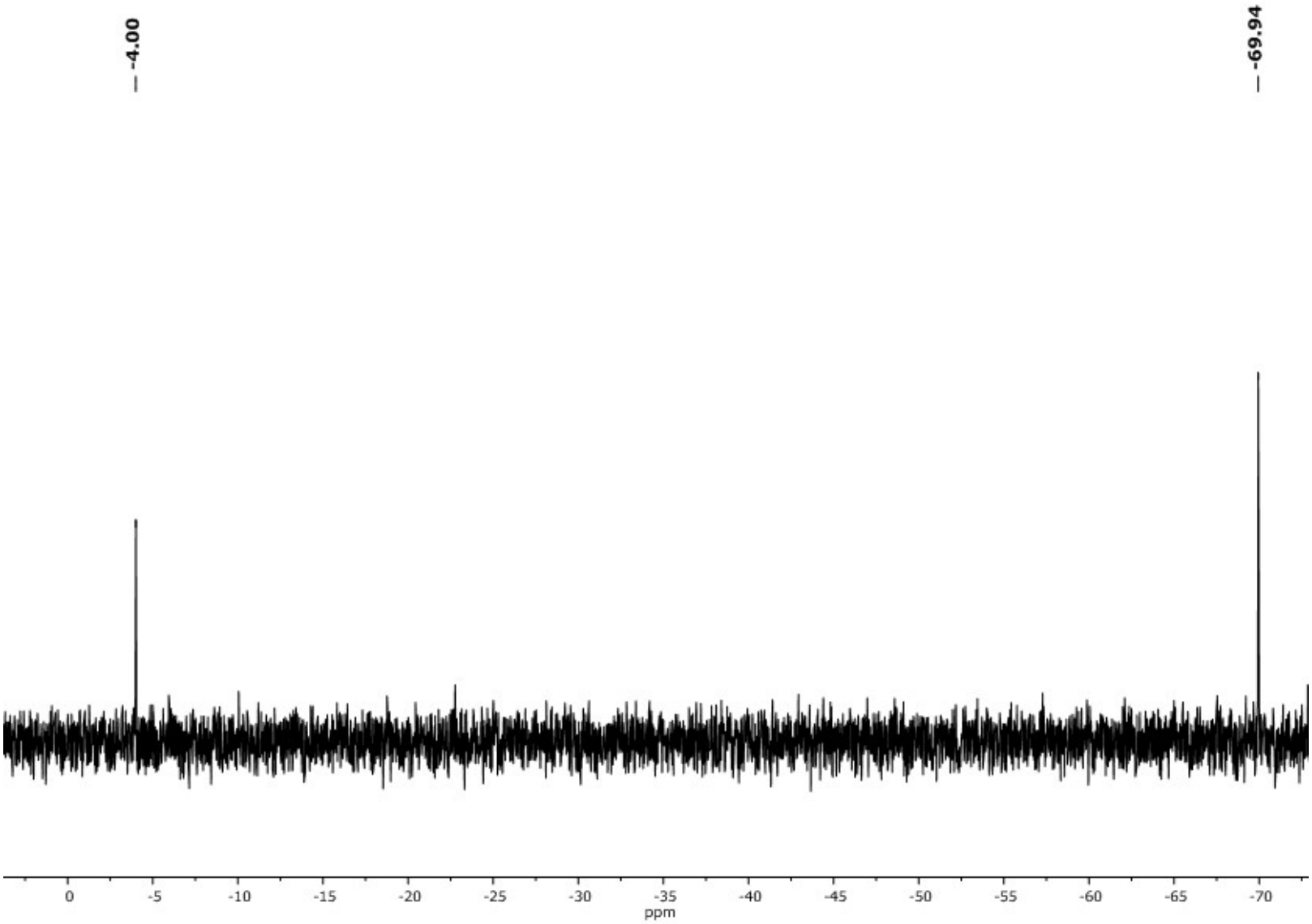


Figure 82s. ^{29}Si NMR spectrum of compound **2.1** (80 MHz, solvent – $CDCl_3$).

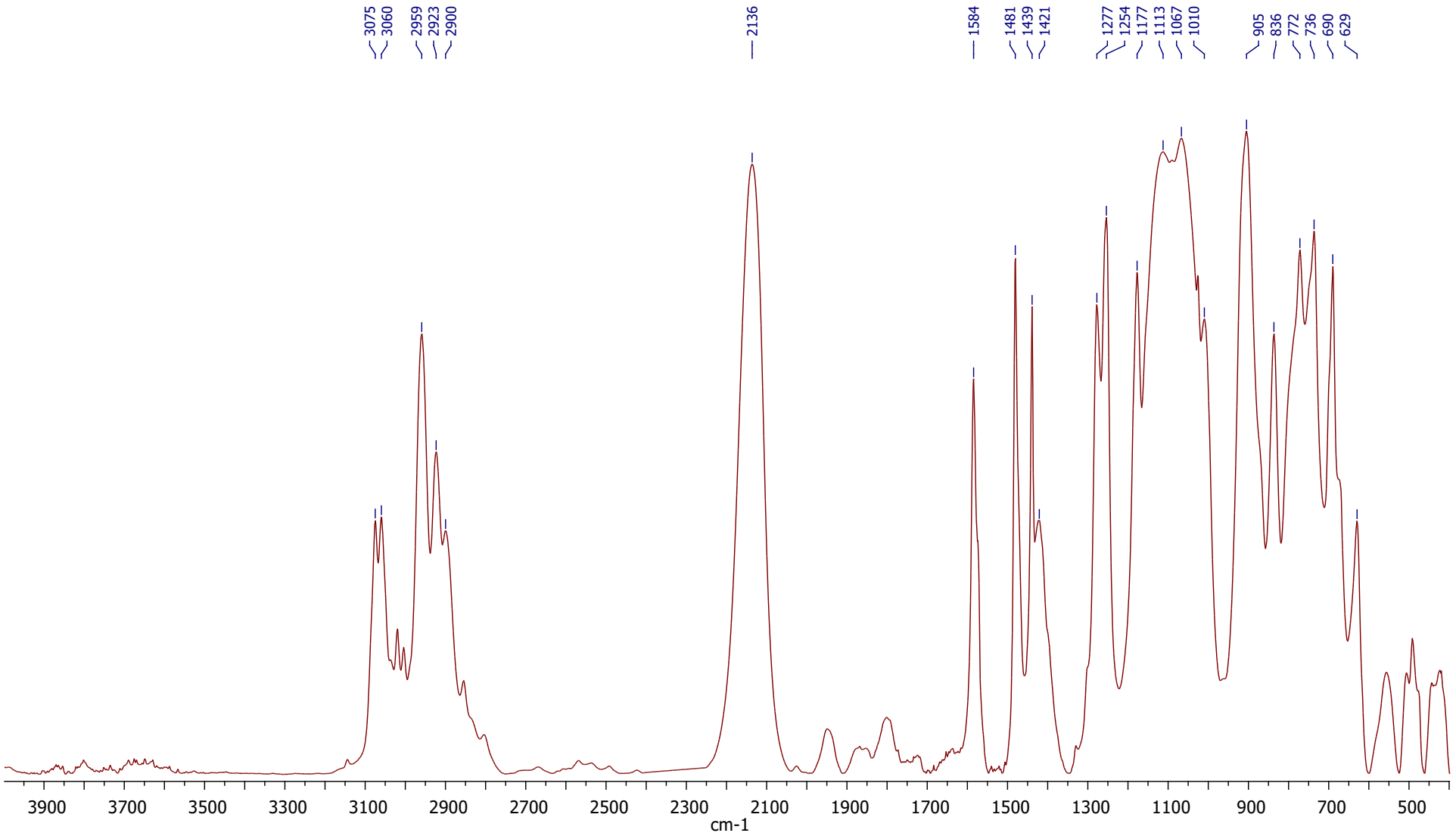


Figure 83s. IR-spectrum of compound **2.1**.

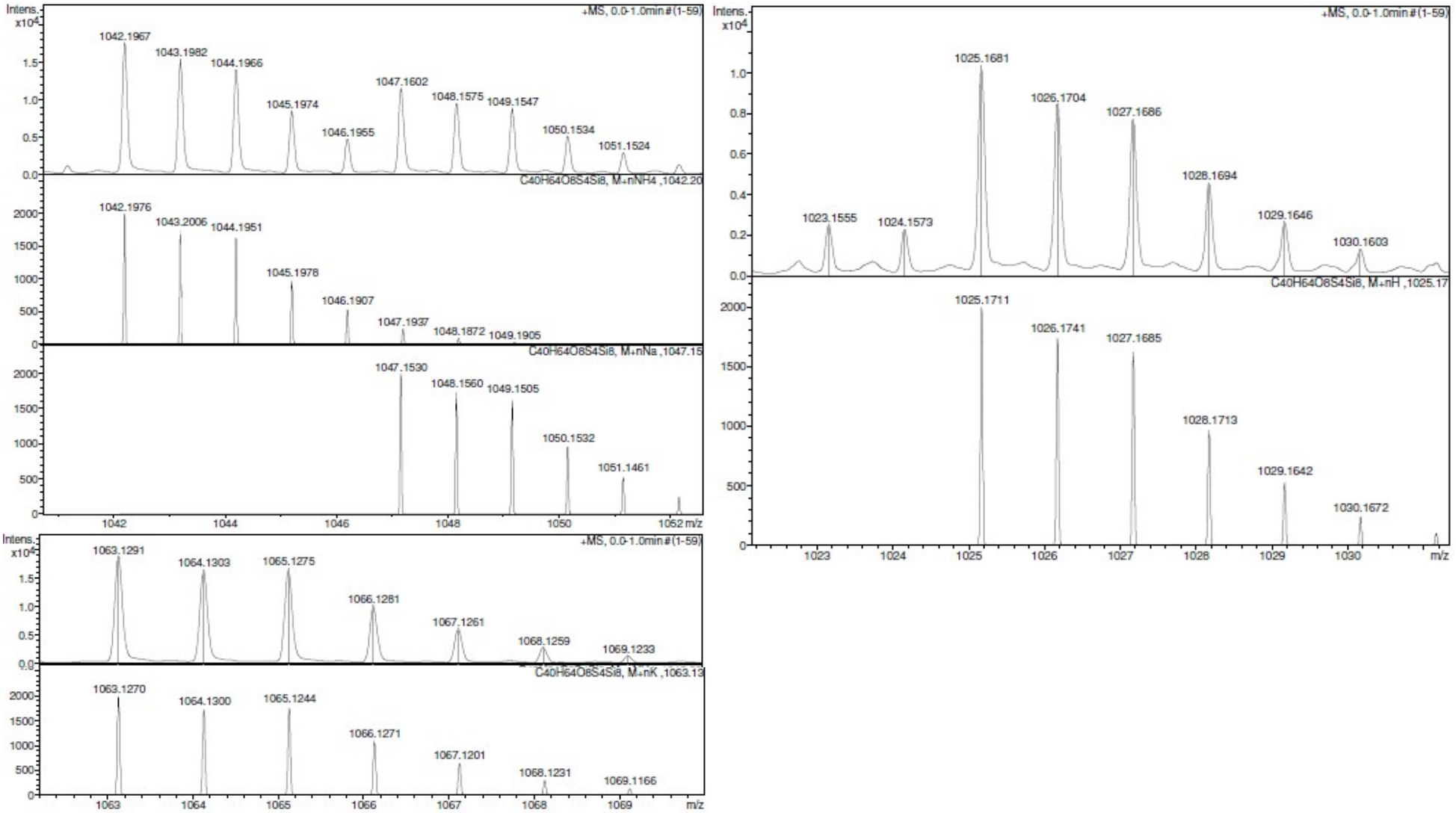


Figure 84s. HRMS (ESI) for compound **2.1**.

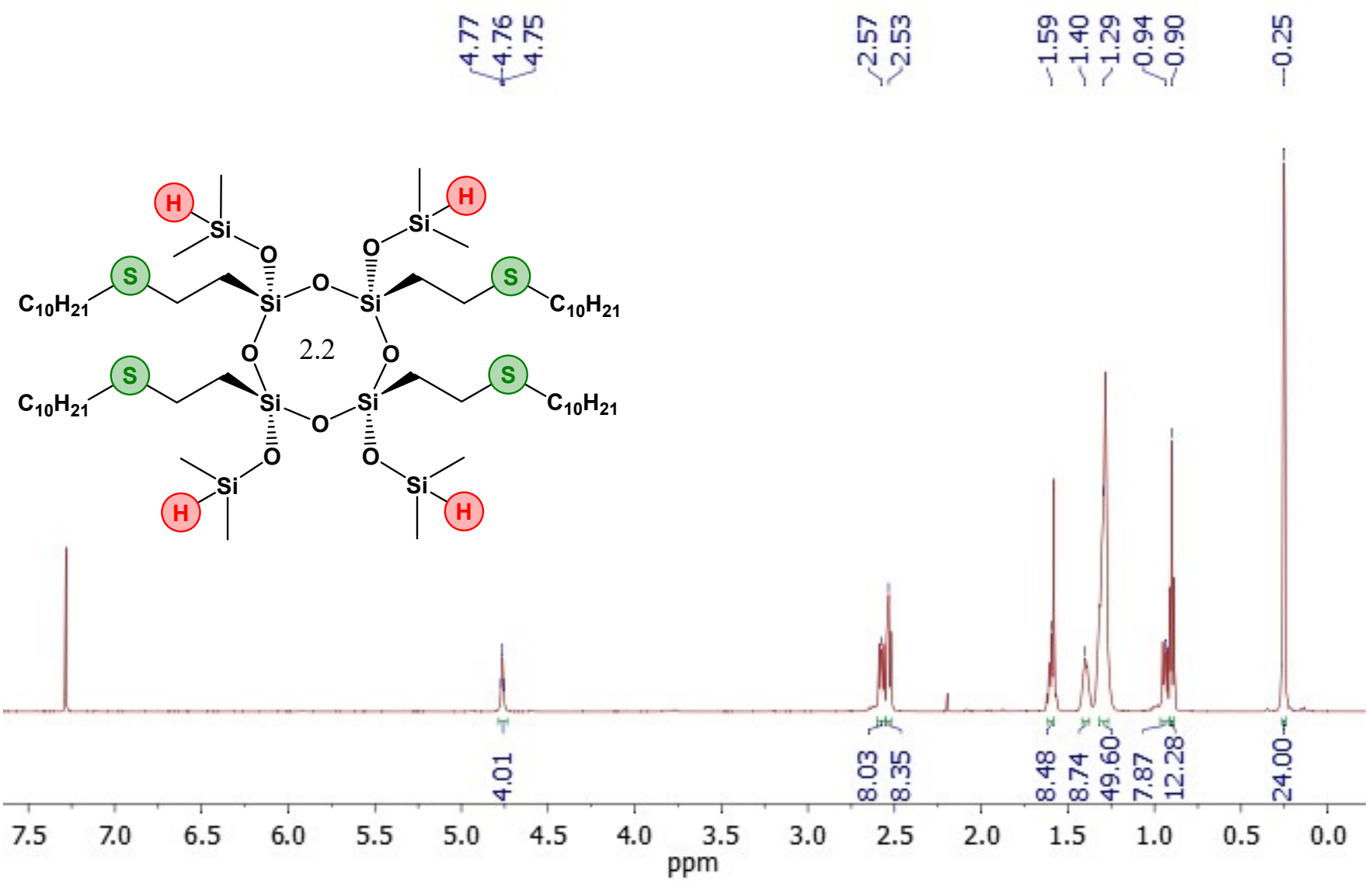


Figure 85s. ^{1}H NMR spectrum of compound **2.2** (500 MHz, solvent – $CDCl_3$).

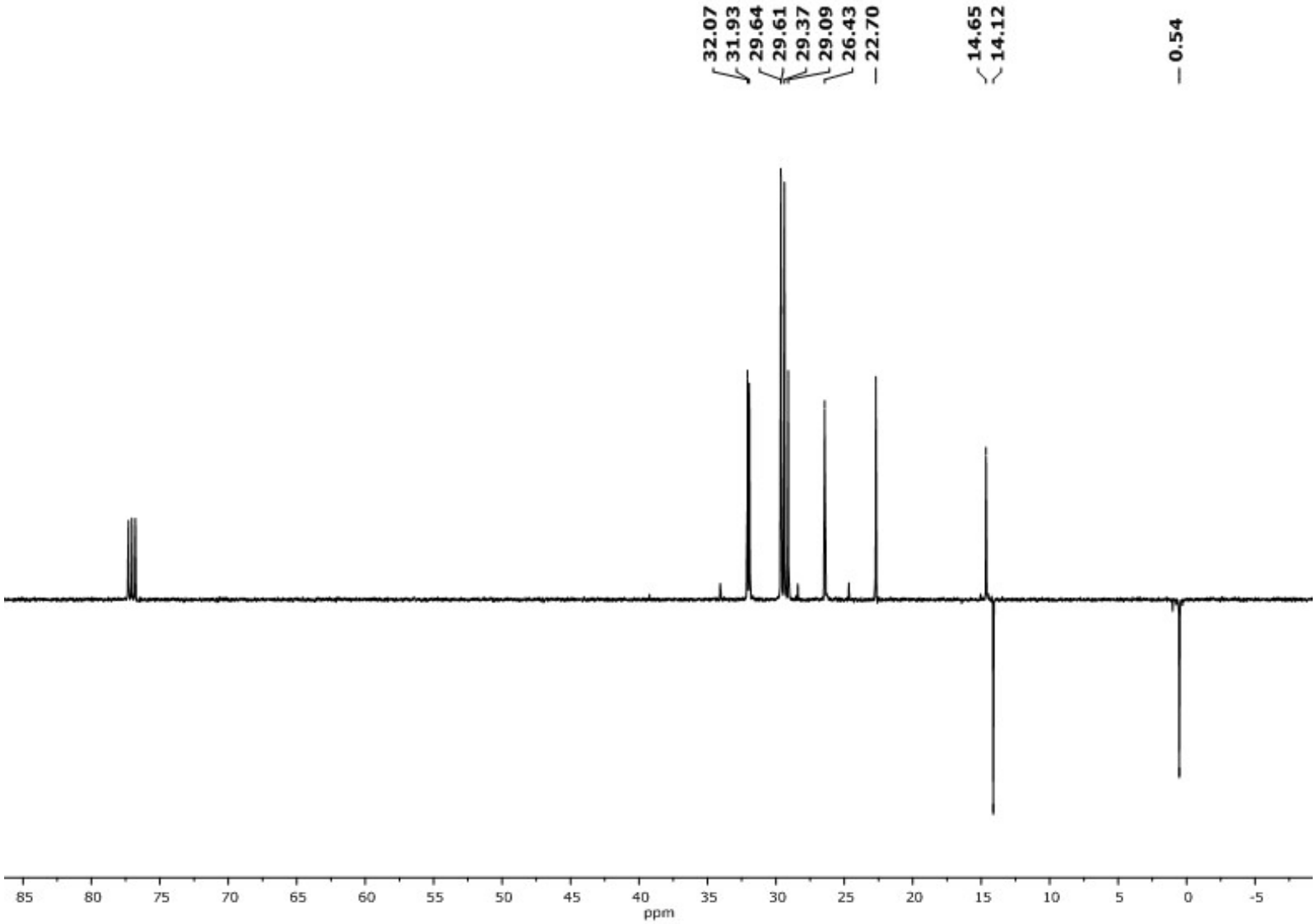


Figure 86s. ^{13}C NMR spectrum of compound **2.2** (DEPT-135, 100 MHz, solvent – $CDCl_3$, jmod).

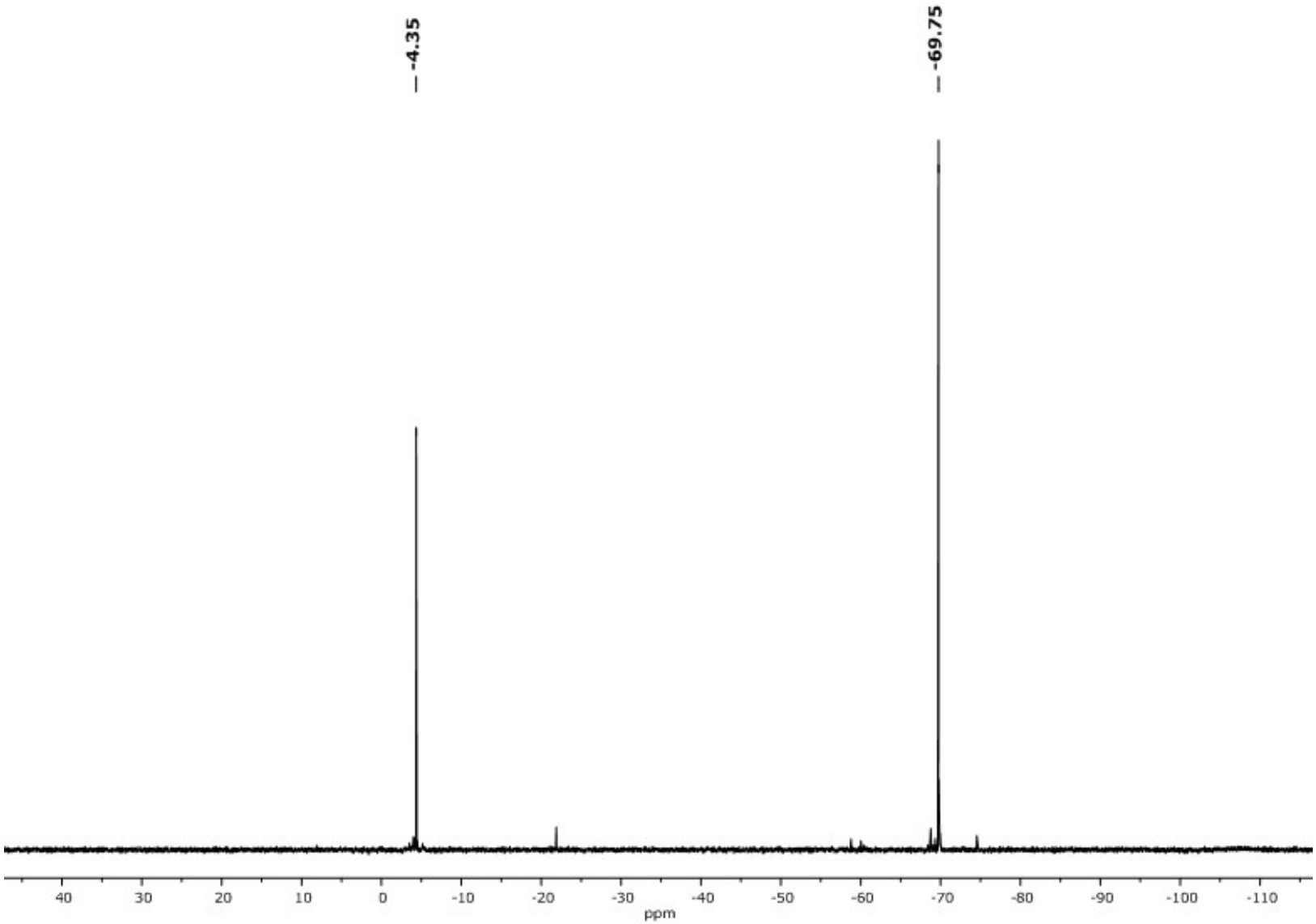


Figure 87s. ^{29}Si NMR spectrum of compound **2.2** (80 MHz, solvent – $CDCl_3$).

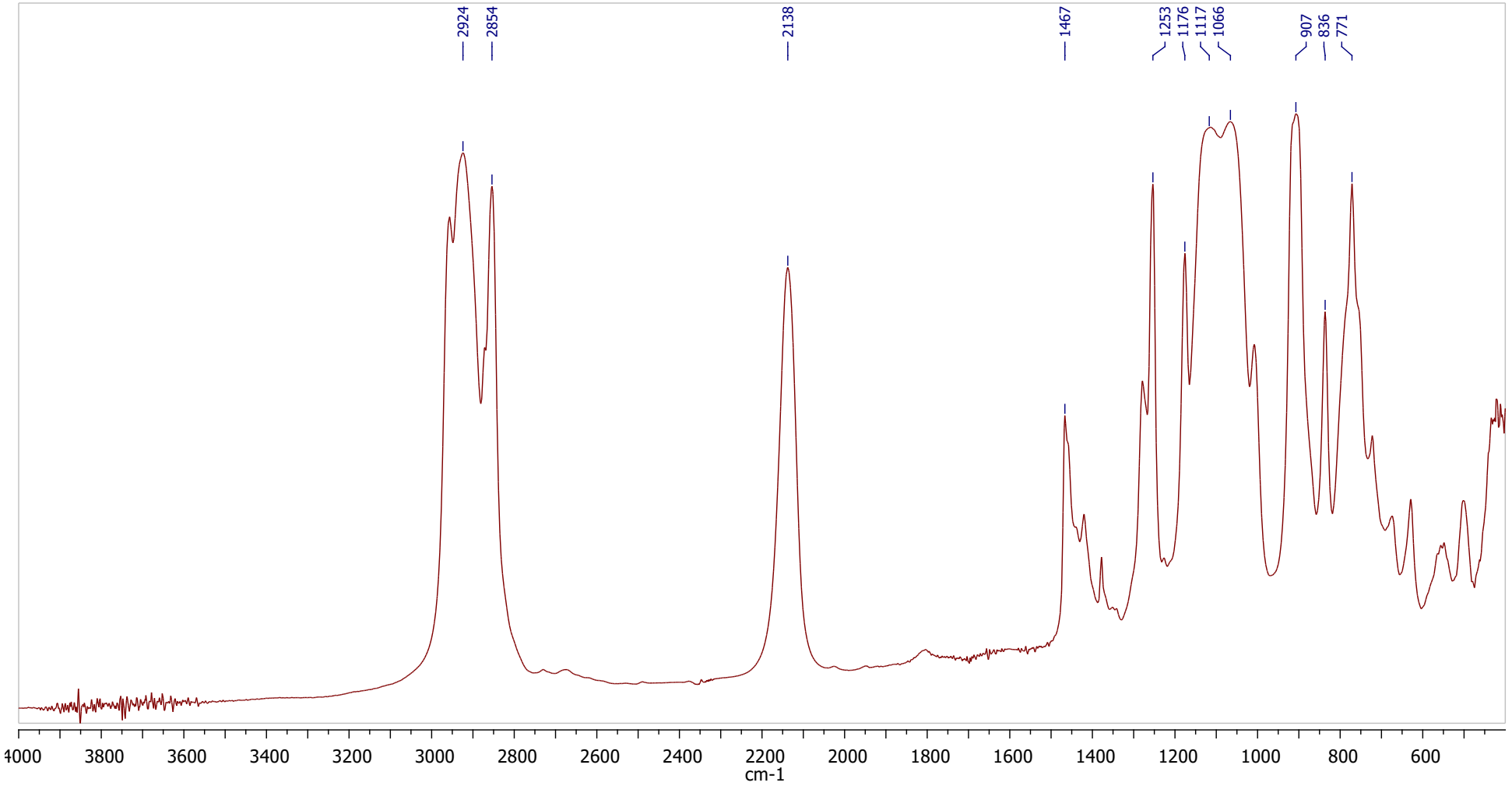


Figure 88s. IR-spectrum for compound **2.2**.

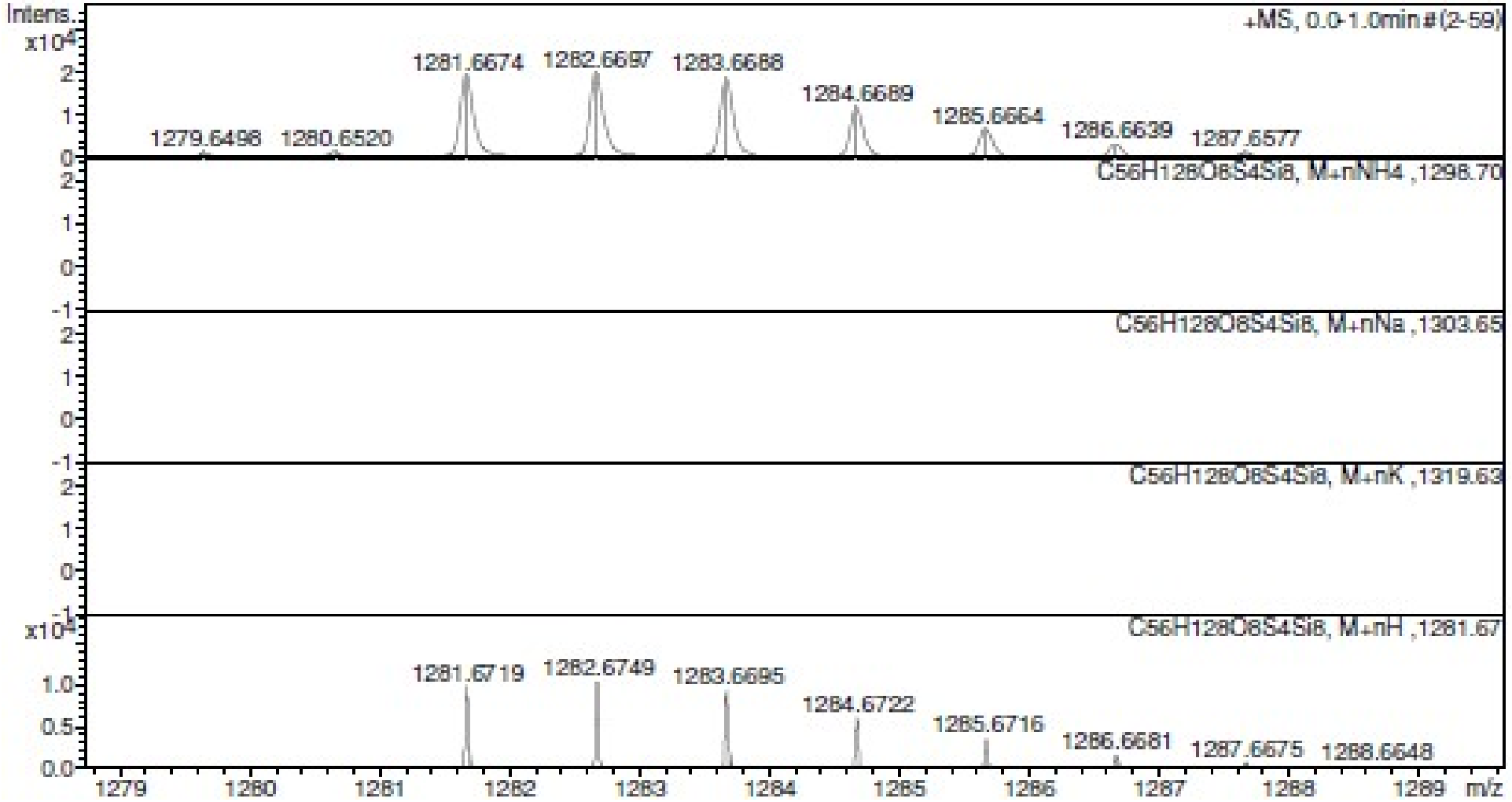


Figure 89s. HRMS (ESI) for compound **2.2**.

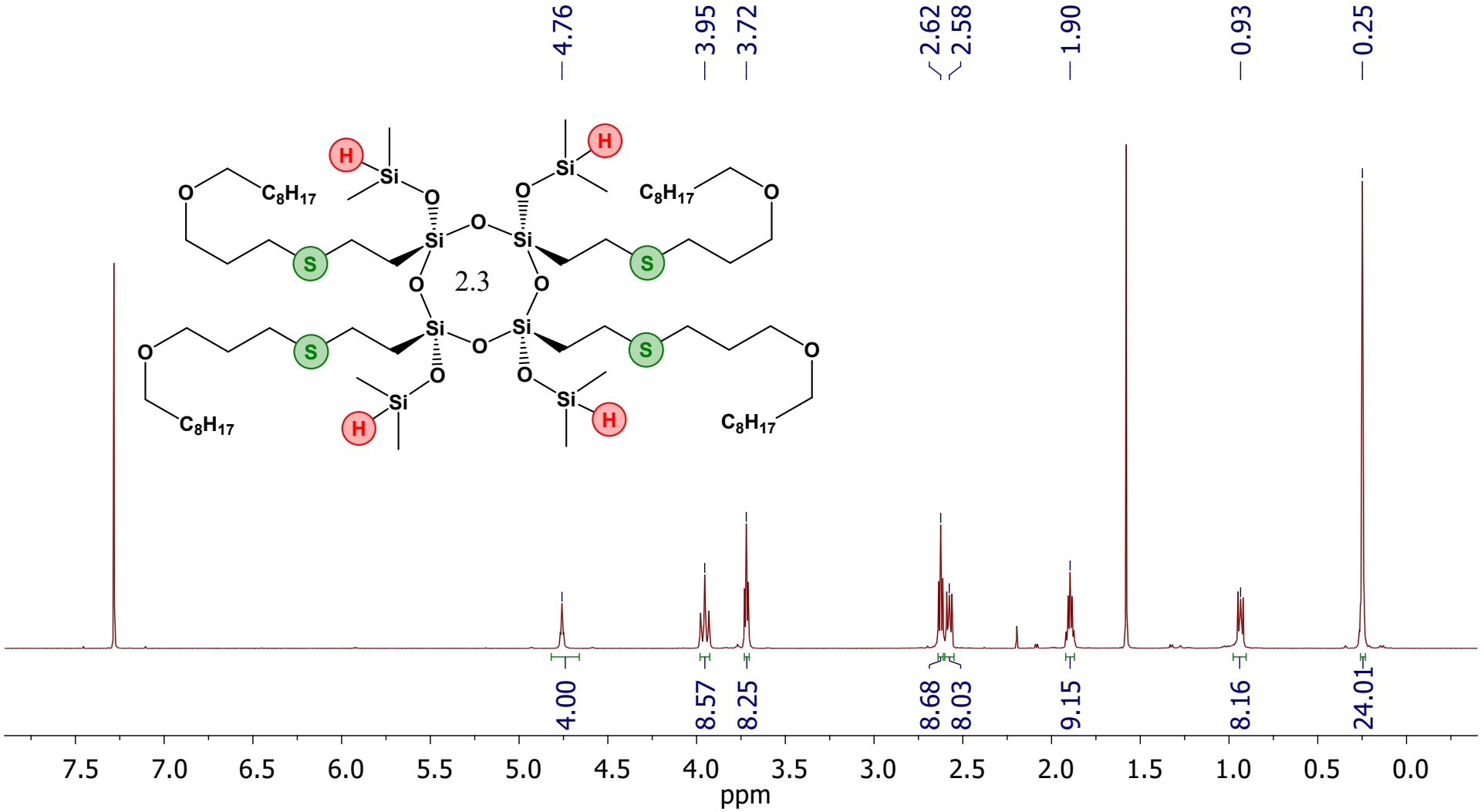


Figure 90s. ^{1}H NMR spectrum of compound **2.3** (500 MHz, solvent – $CDCl_3$).

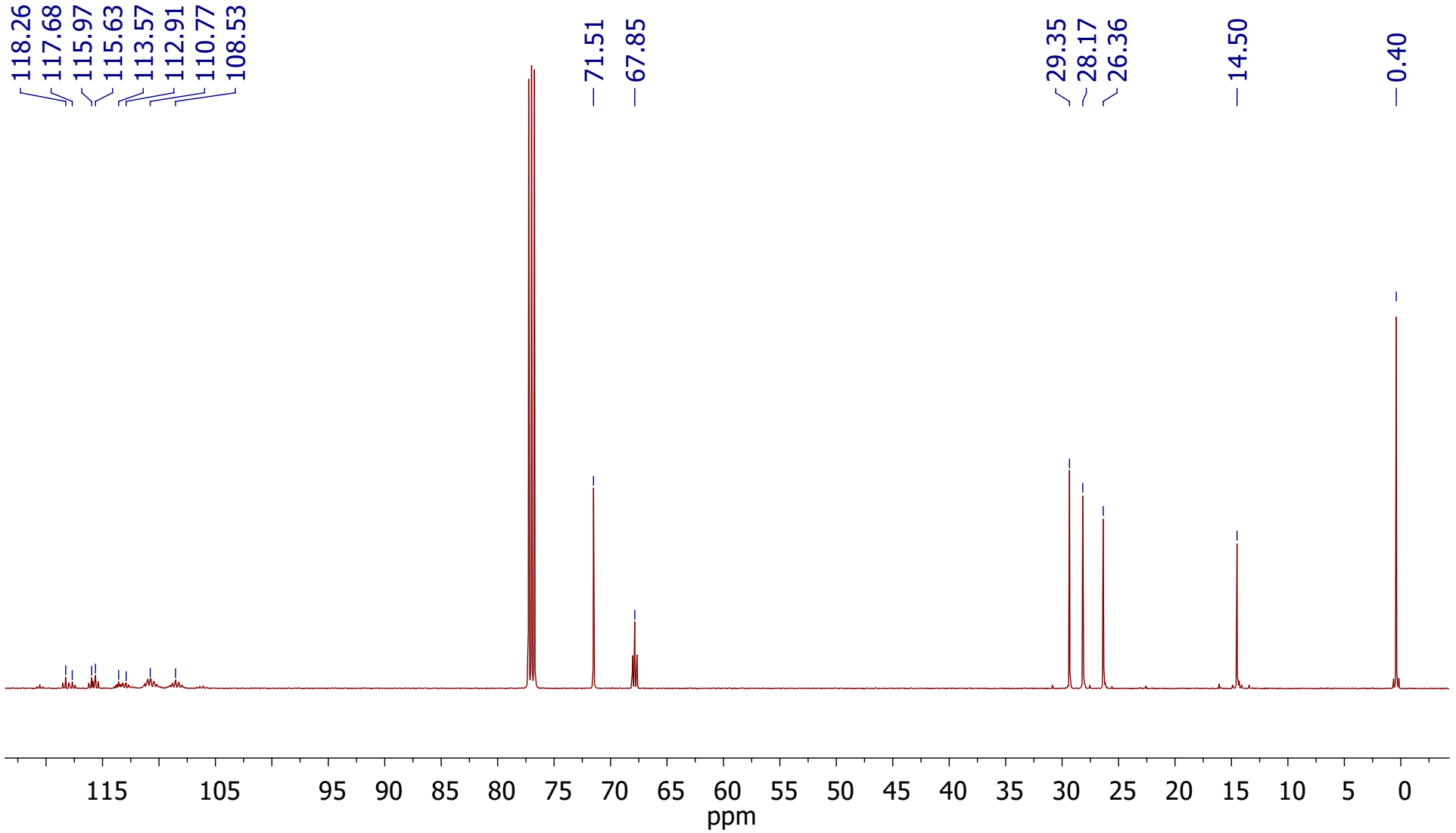


Figure 91s. ^{13}C NMR spectrum of compound **2.3** (500 MHz, solvent – $CDCl_3$).

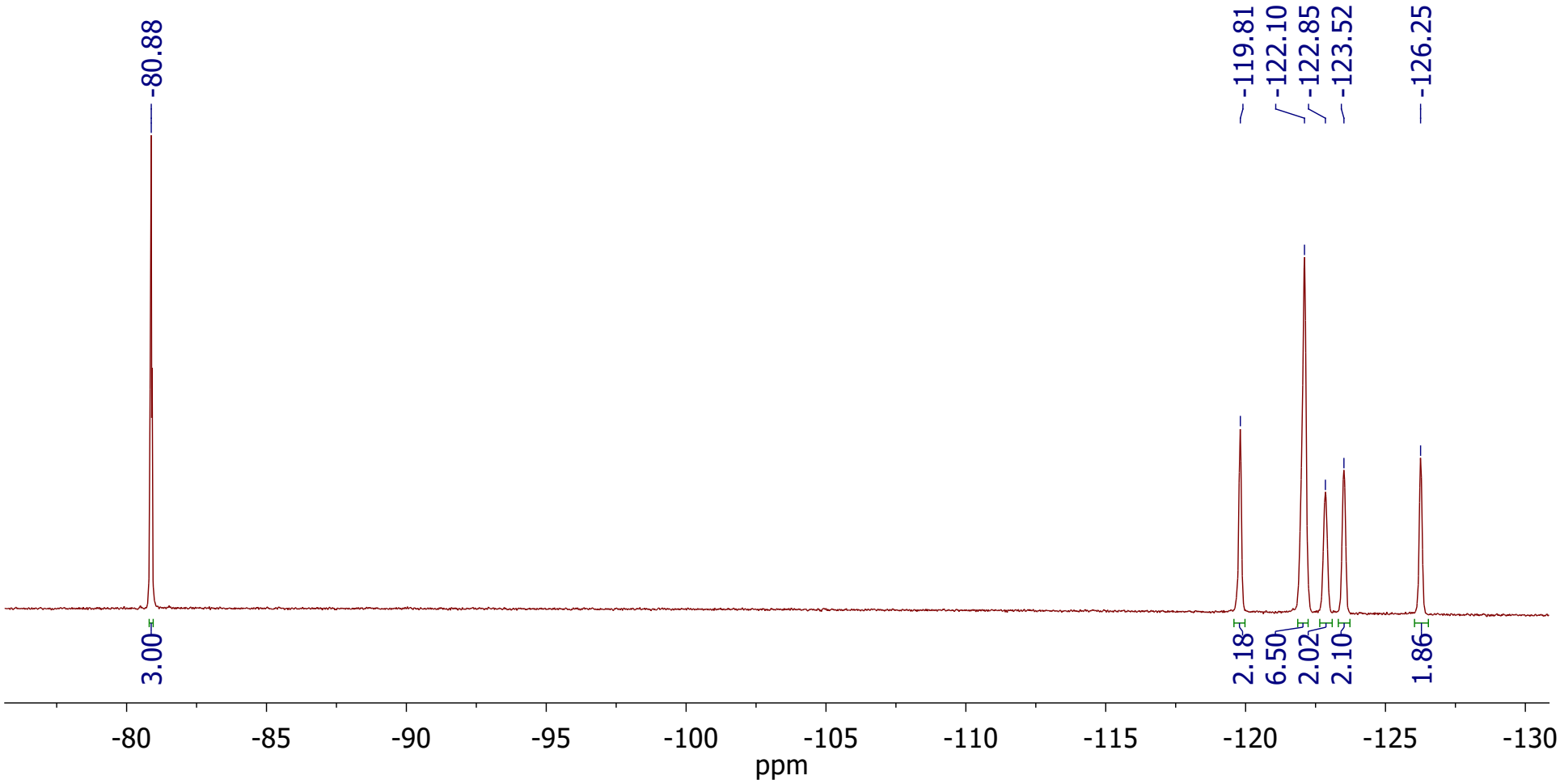


Figure 92s. ^{19}F NMR spectrum of compound **2.3** (300 MHz, solvent – $CDCl_3$).

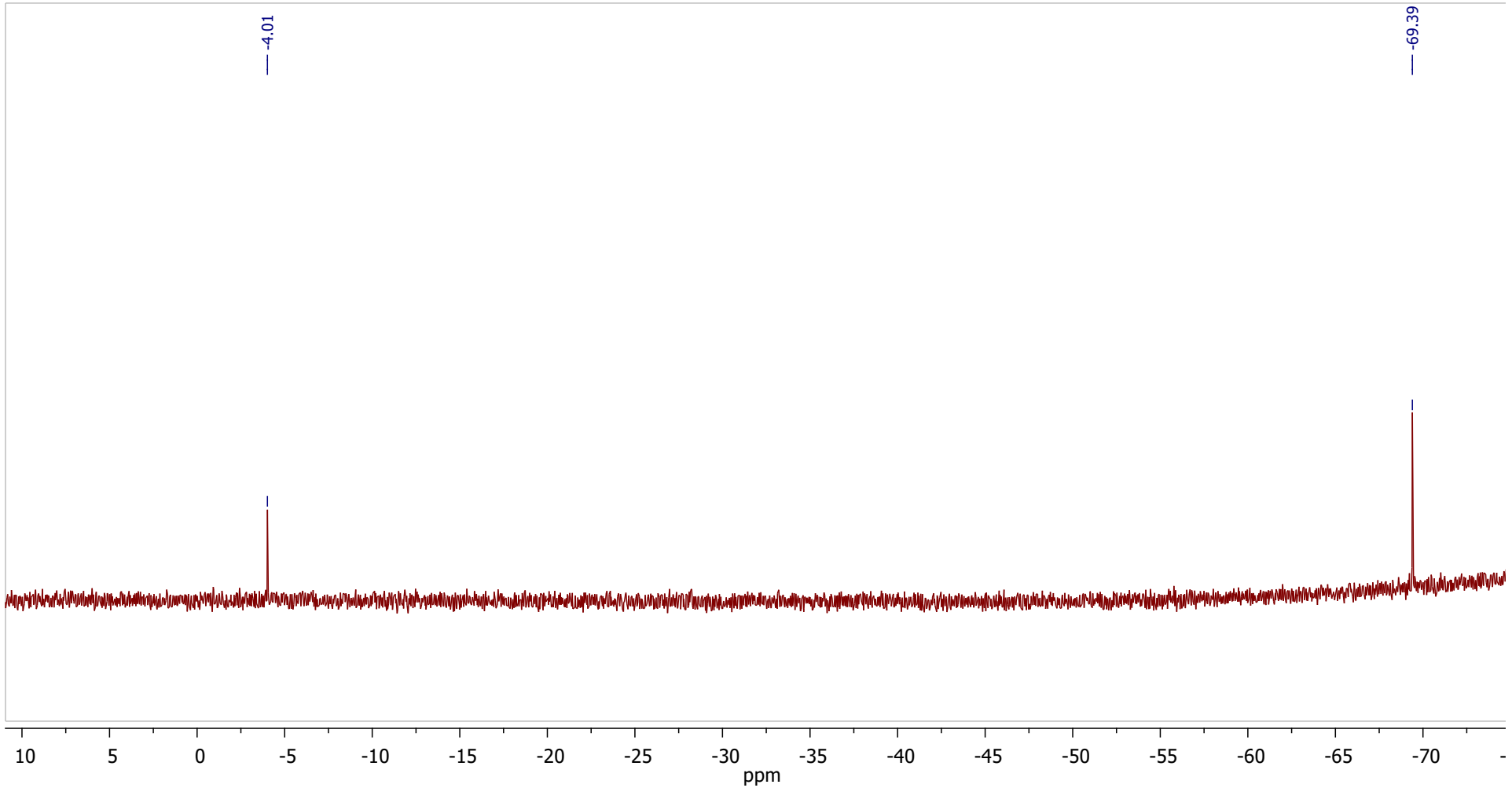


Figure 93s. ^{29}Si NMR spectrum of compound **2.3** (500 MHz, solvent – $CDCl_3$).

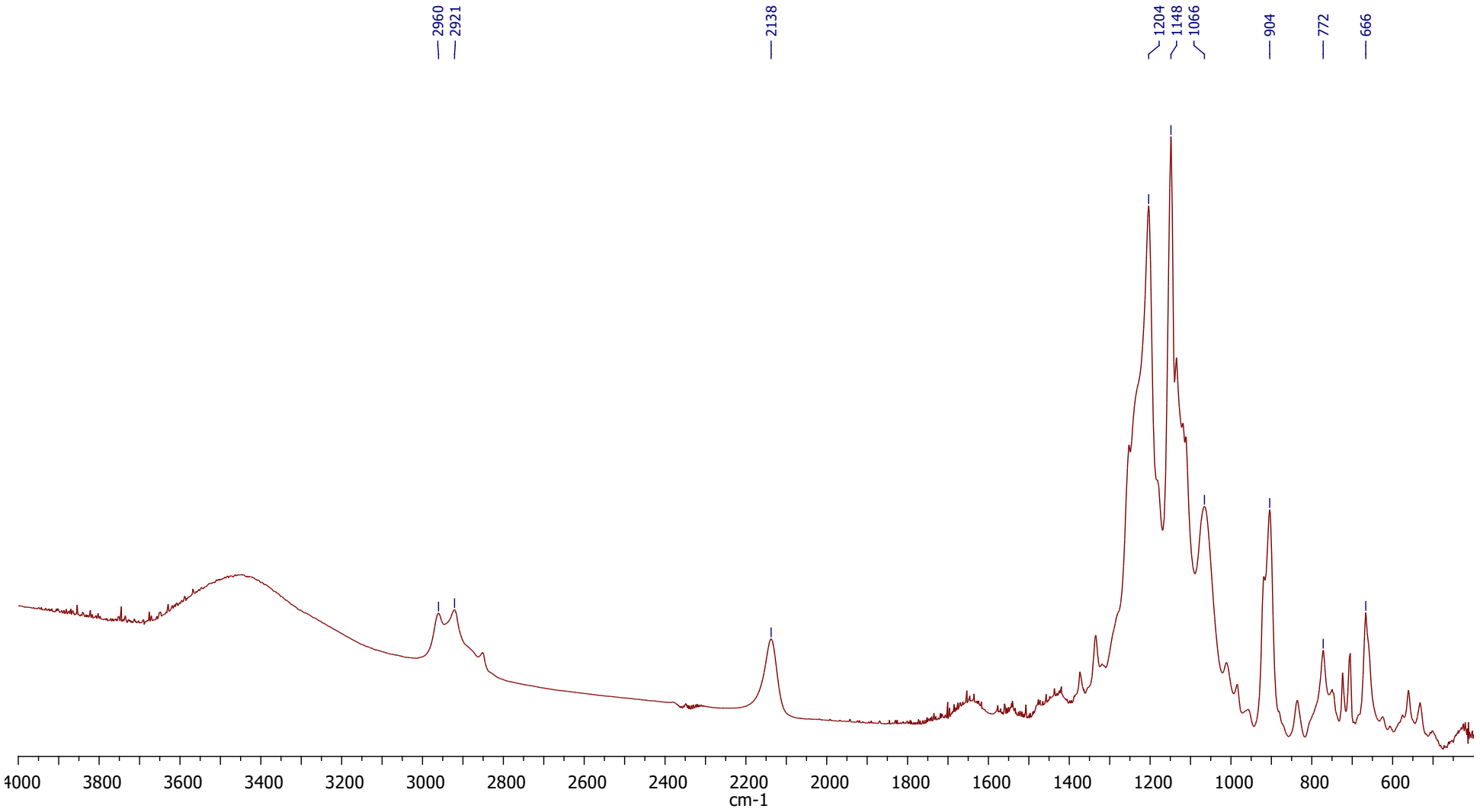


Figure 94s. IR-spectrum of compound **2.3**.

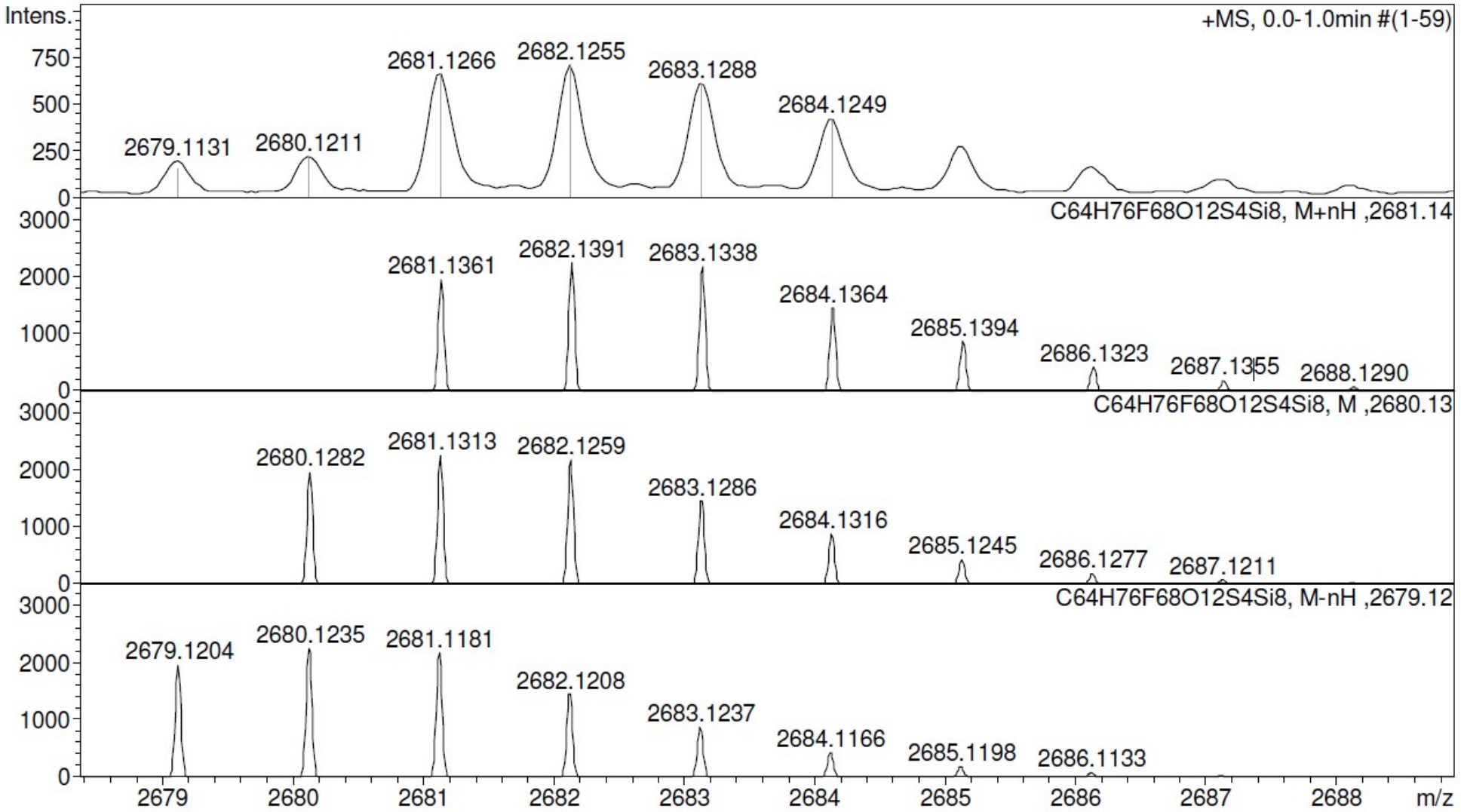


Figure 95s. HRMS (ESI) for compound **2.3**.

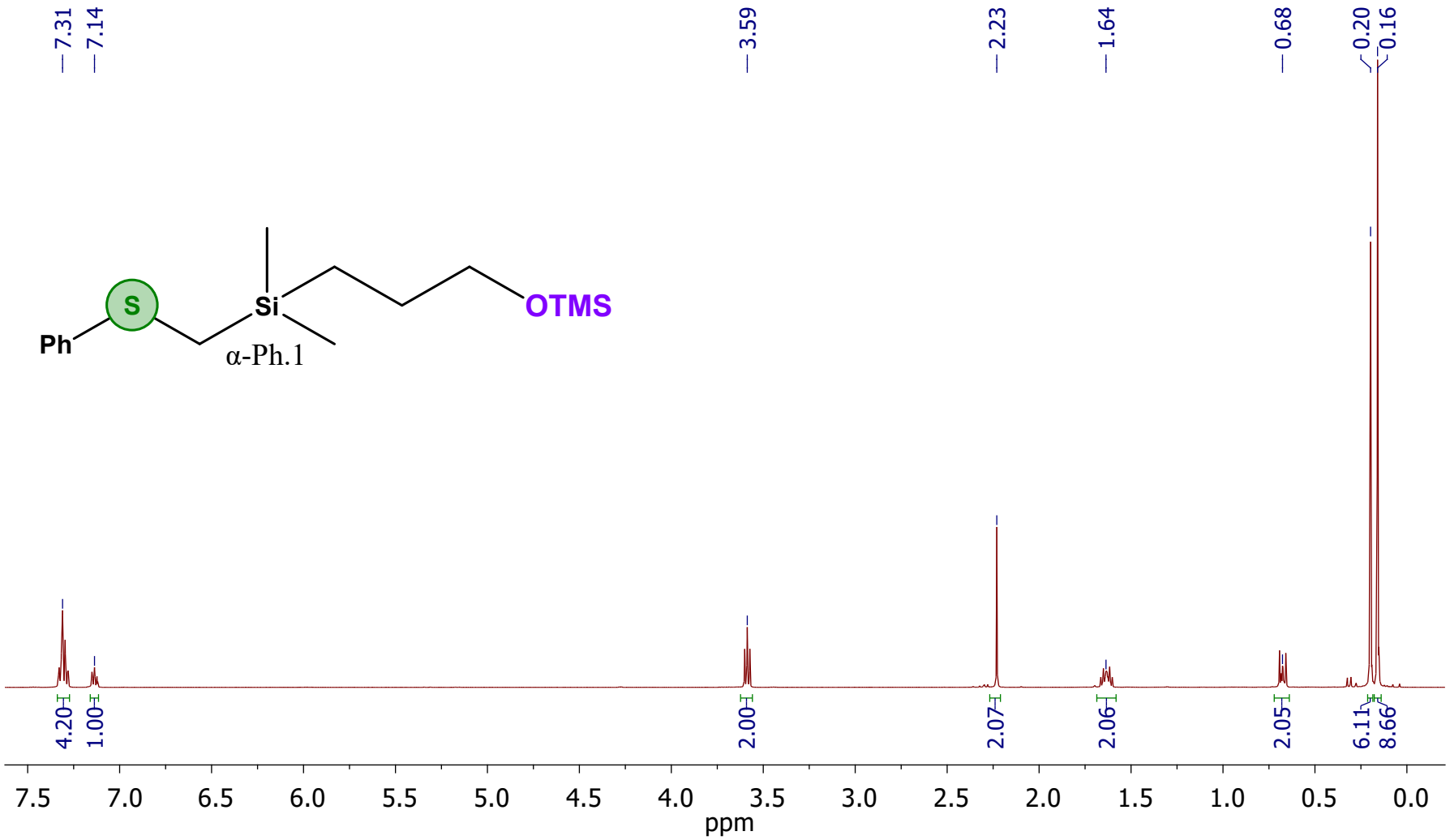


Figure 96s. ^{1}H NMR spectrum of compound **α-Ph.1** (600 MHz, solvent – $CDCl_3$).

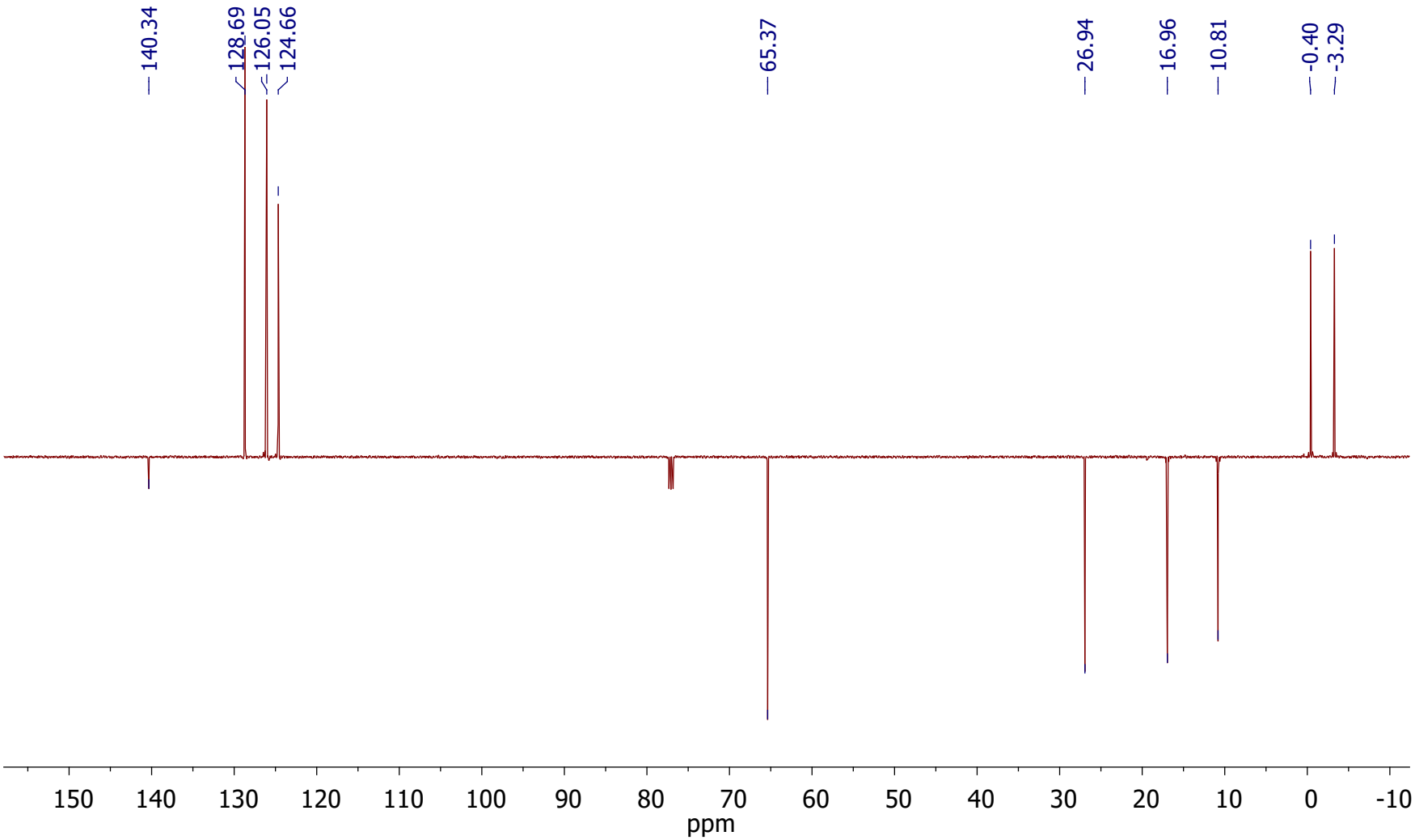


Figure 97s. ^{13}C NMR spectrum of compound **α-Ph.1** (400 MHz, solvent – $CDCl_3$, jmod).

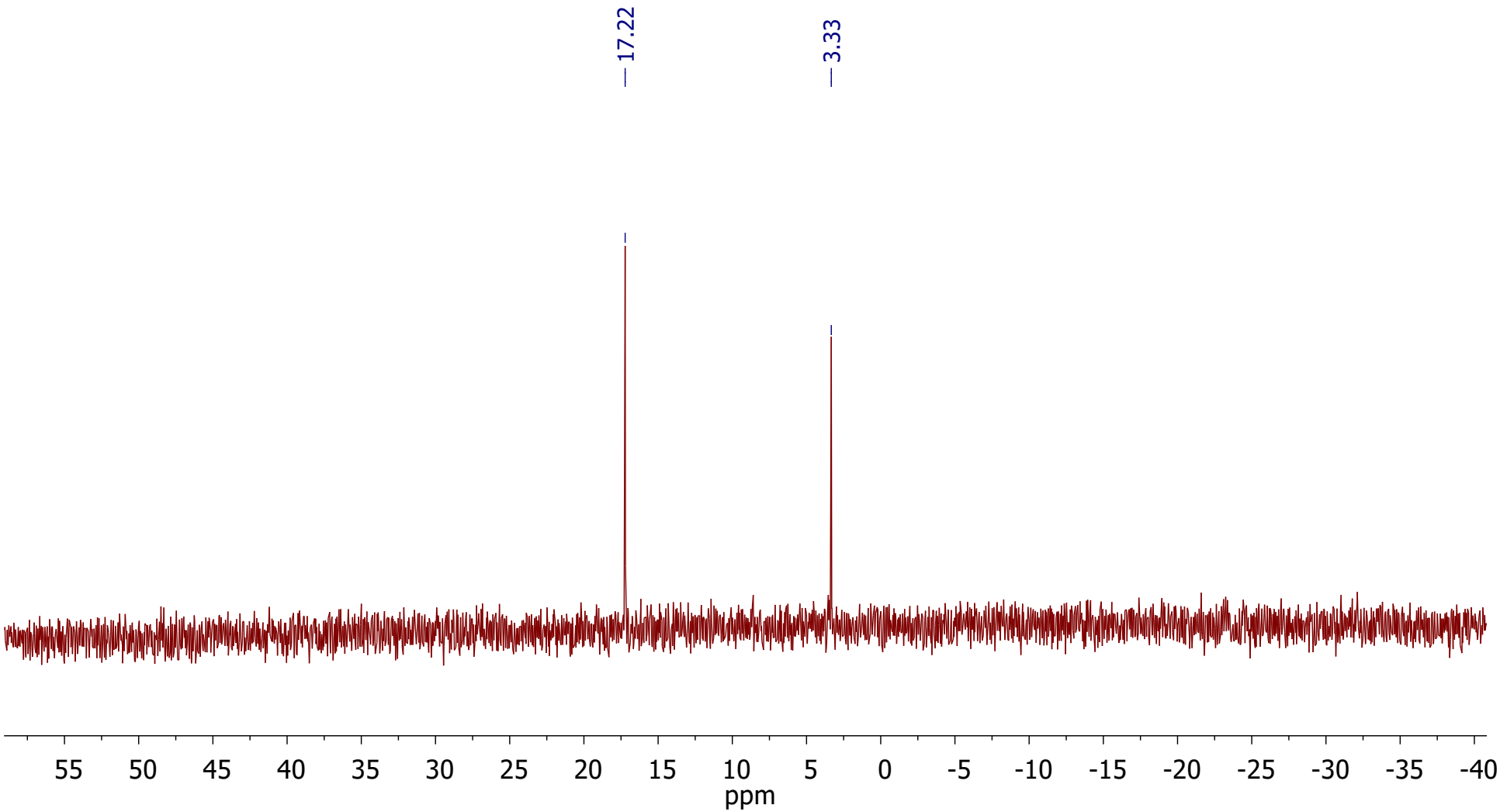


Figure 98s. ^{29}Si NMR spectrum of compound **α-Ph.1** (400 MHz, solvent – $CDCl_3$).

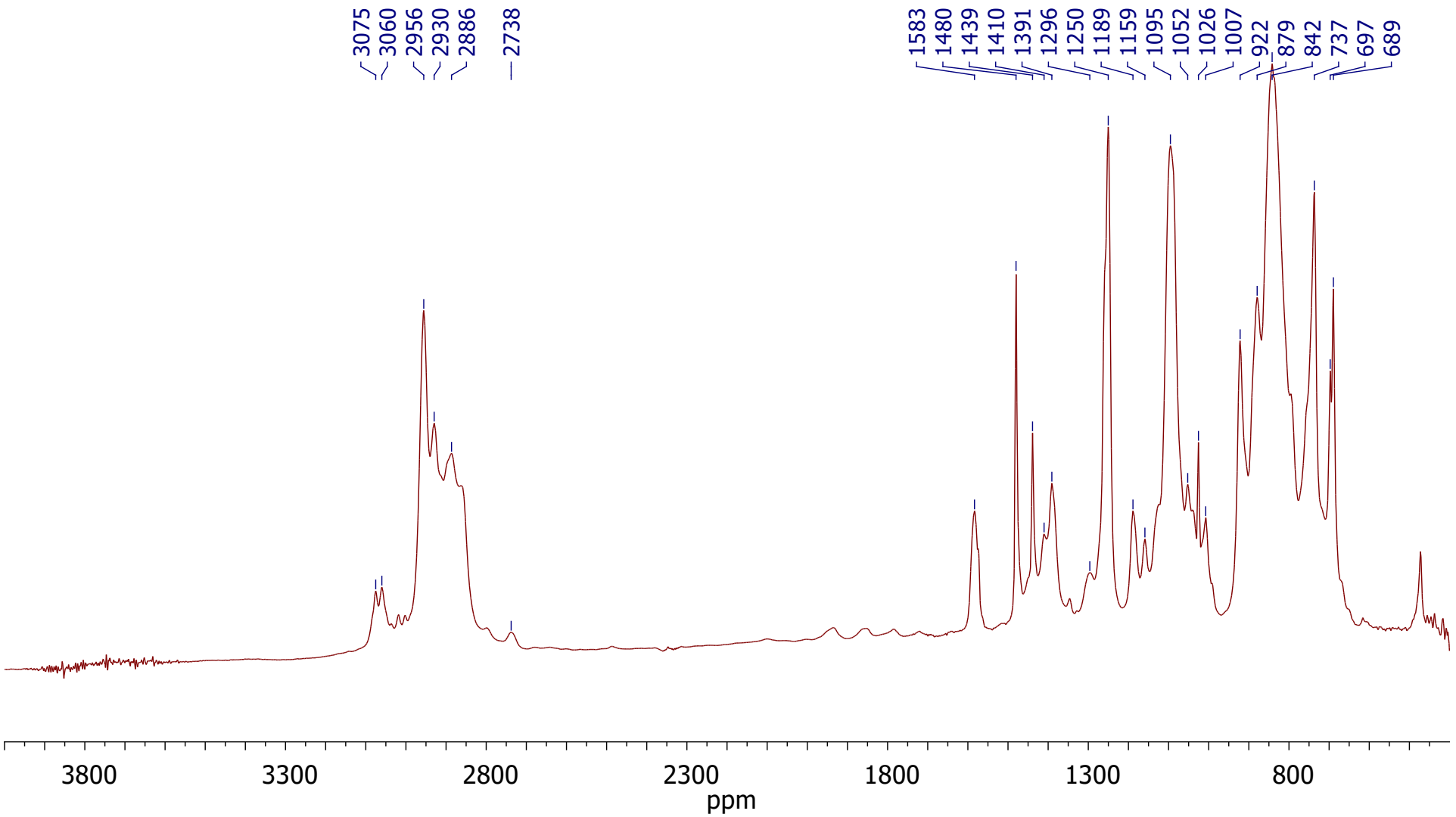


Figure 99s. IR-spectrum of compound **α-Ph.1**.

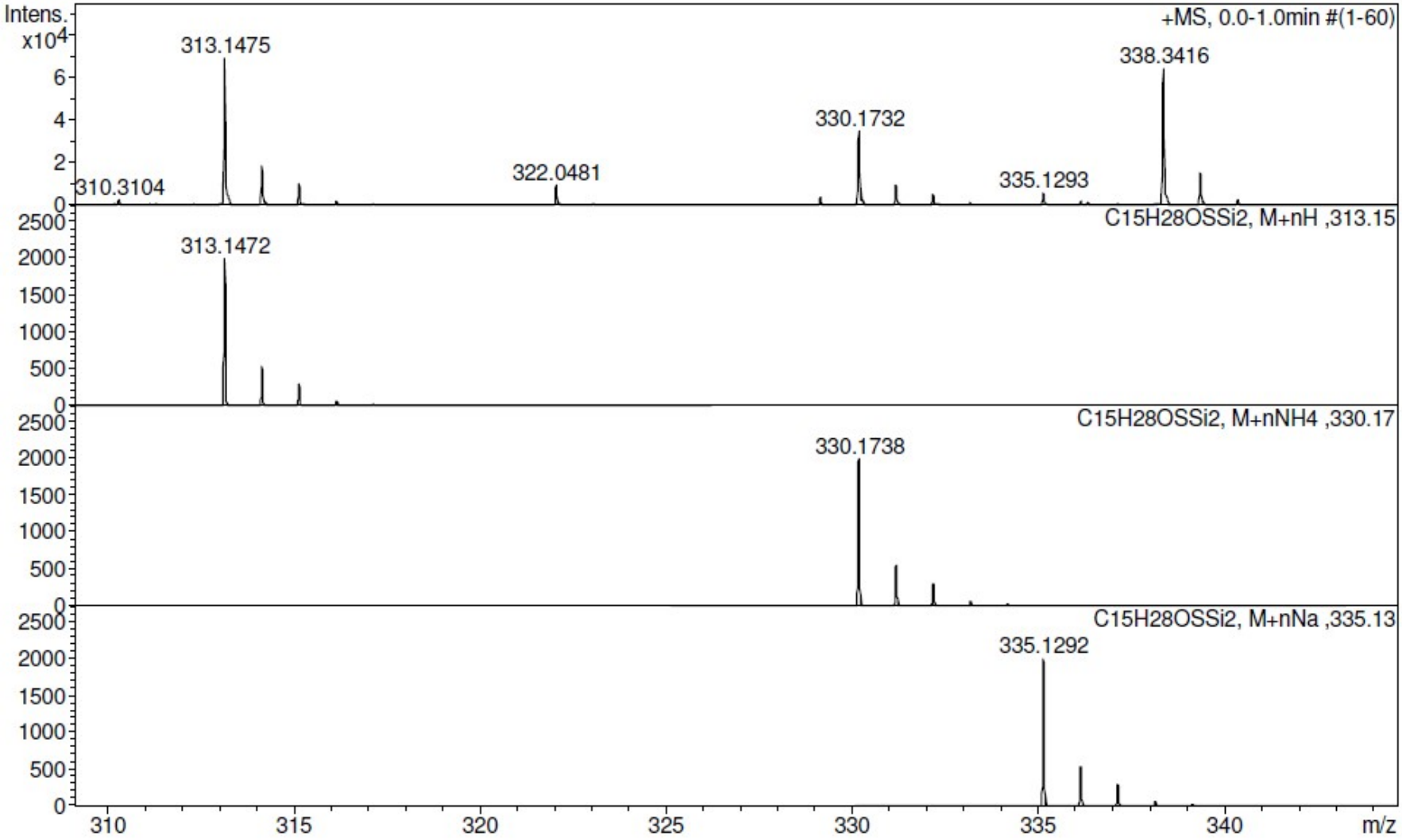


Figure 100s. HRMS (ESI) for compound **α-Ph.1**.

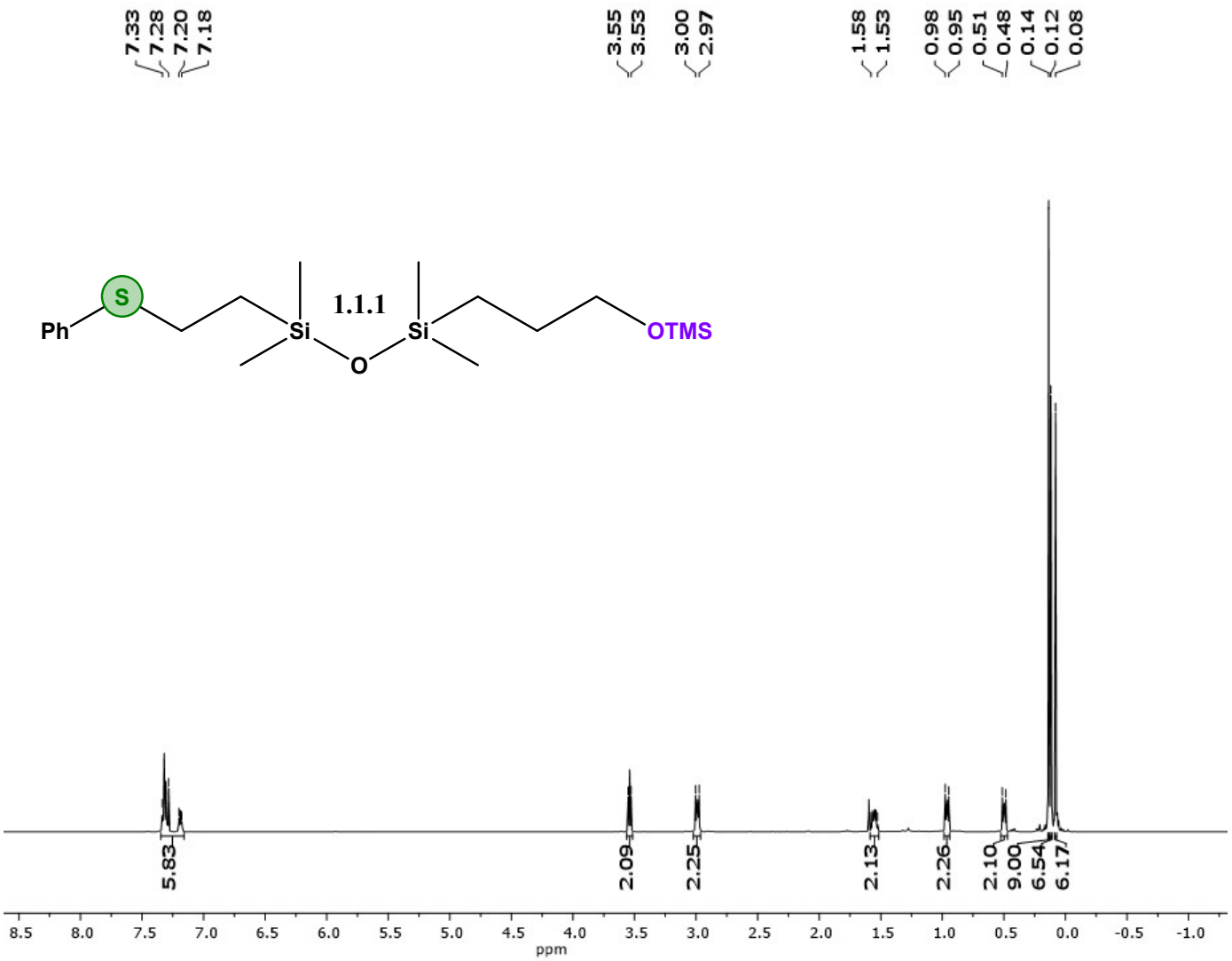


Figure 101s. ^{1}H NMR spectrum of compound **1.1.1** (400 MHz, solvent – $CDCl_3$).

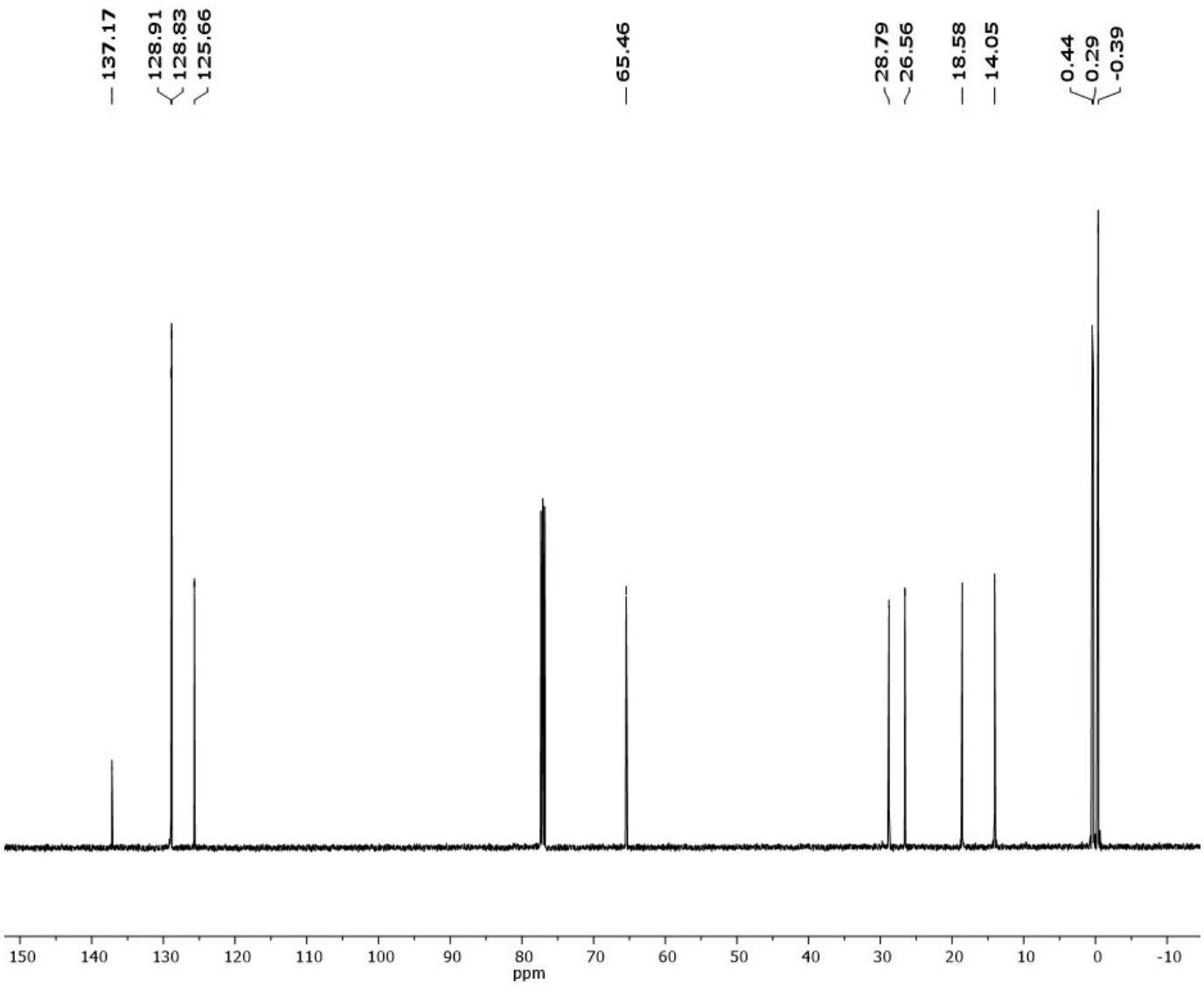


Figure 102s. ^{13}C NMR spectrum of compound **1.1.1** (100 MHz, solvent – $CDCl_3$).

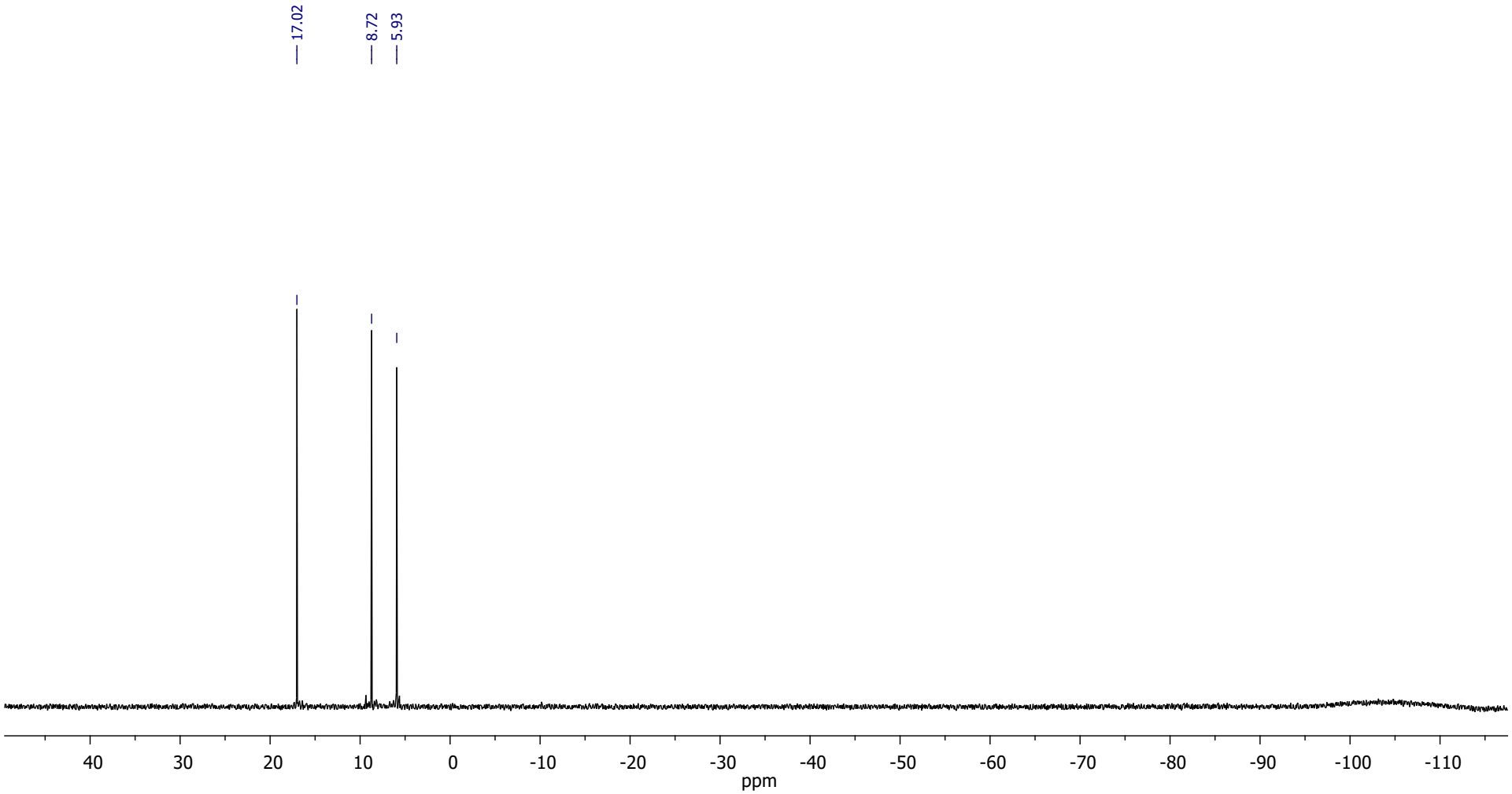


Figure 103s. ^{29}Si NMR spectrum of compound **1.1.1** (80 MHz, solvent – $CDCl_3$).

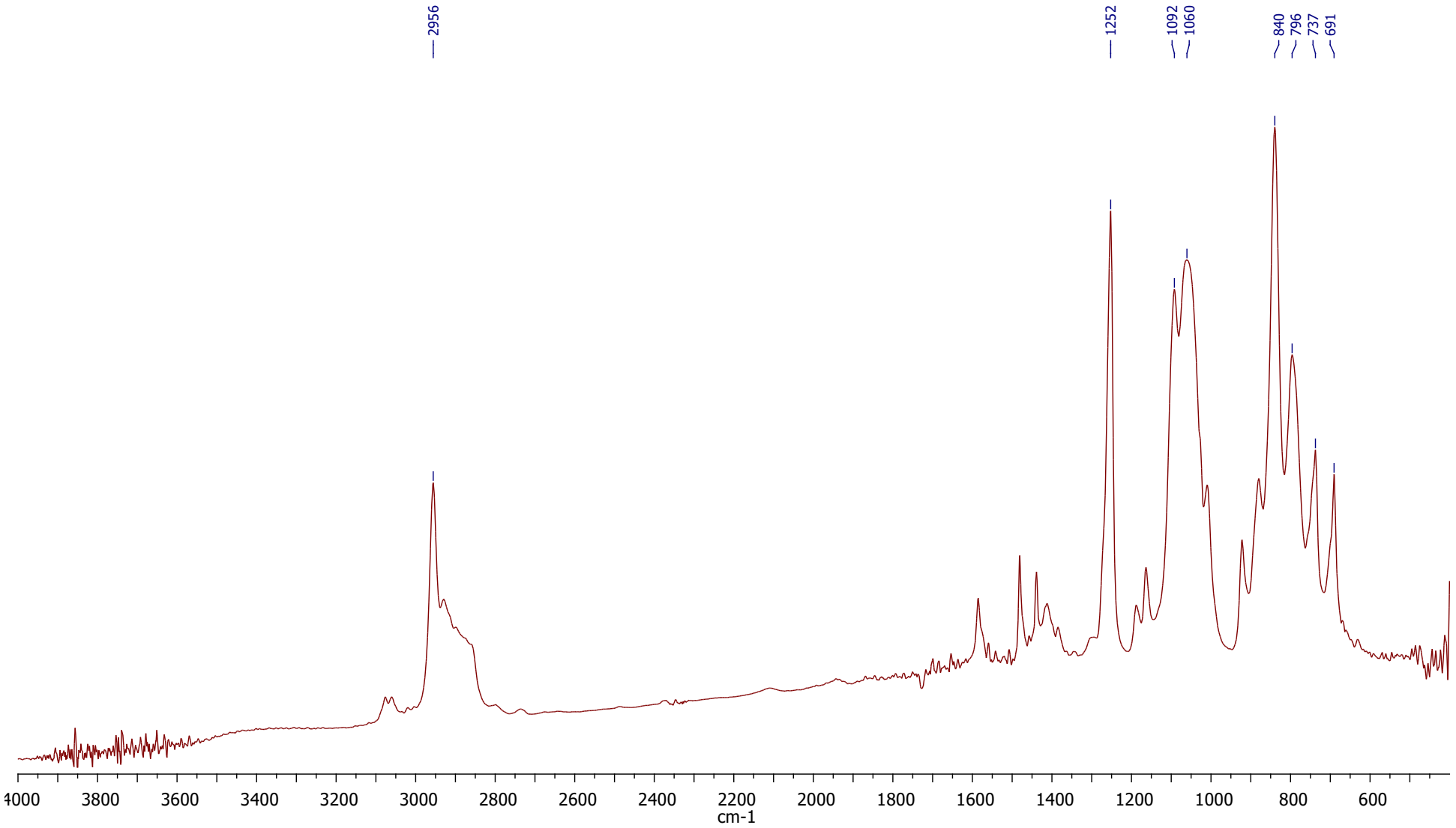


Figure 104s. IR-spectrum of compound **1.1.1**.

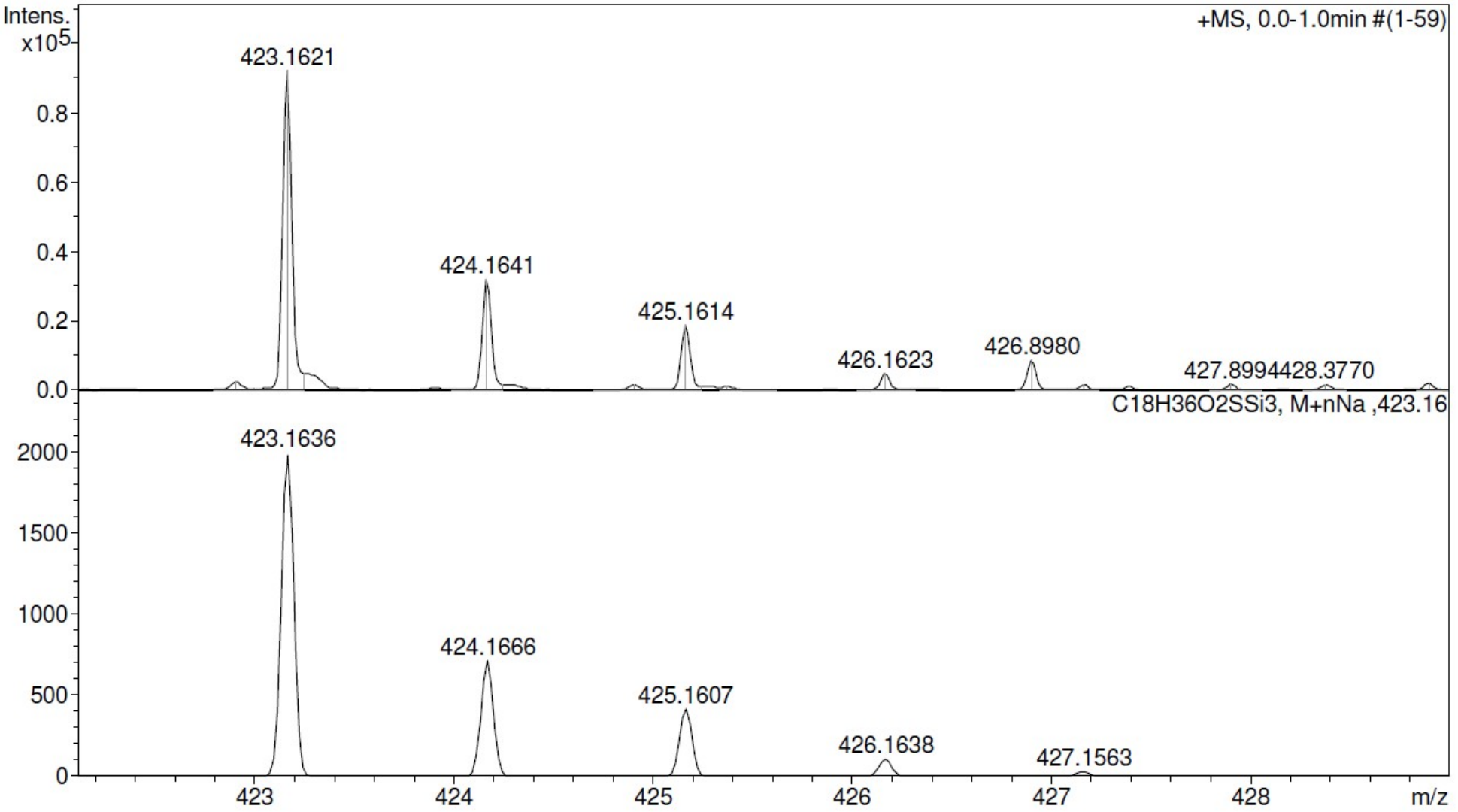


Figure 105s. HRMS (ESI) for compound **1.1.1**.

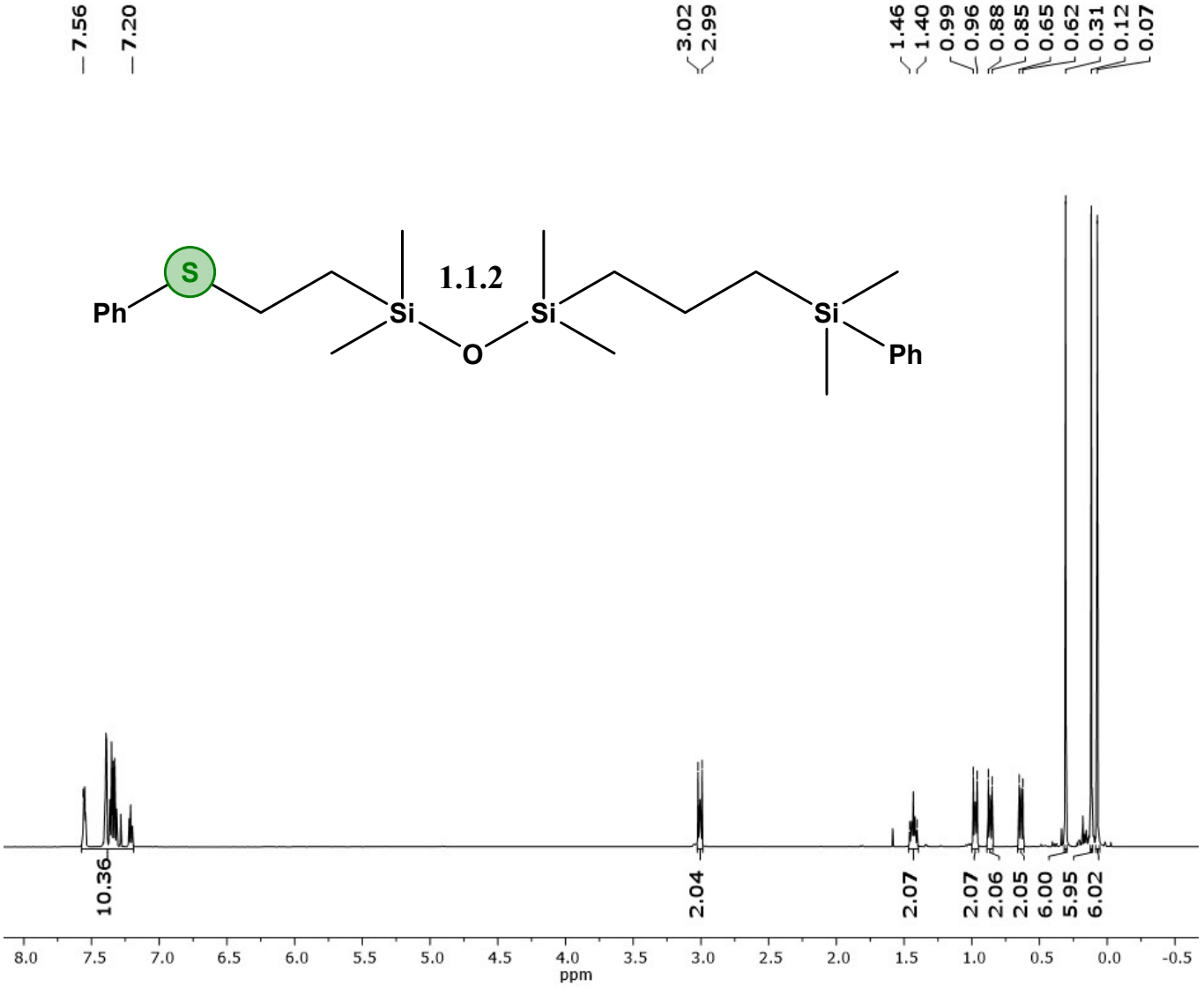


Figure 106s. ^{1}H NMR spectrum of compound **1.1.2** (400 MHz, solvent – $CDCl_3$).

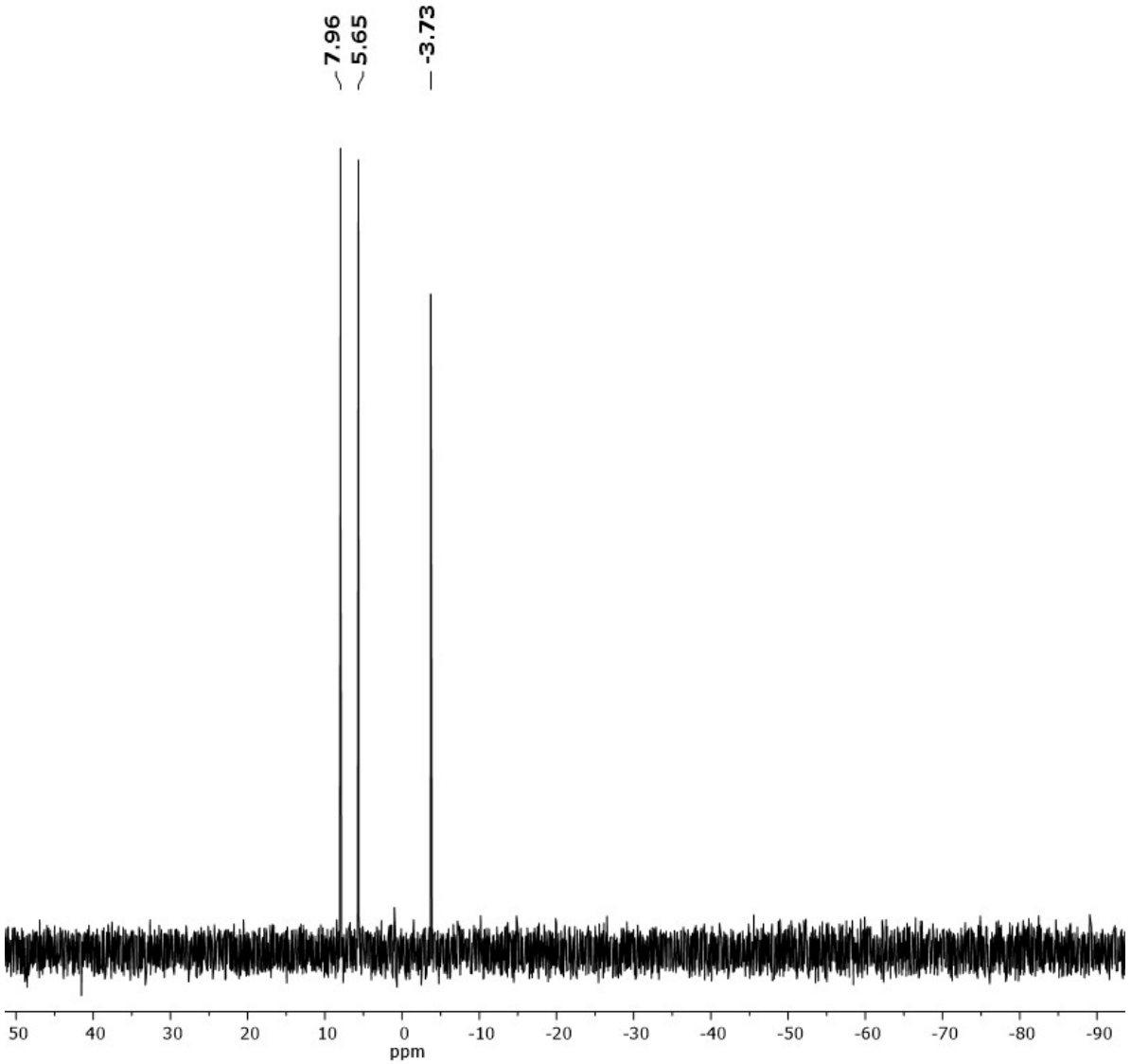


Figure 107s. ^{29}Si NMR spectrum of compound **1.1.2** (80 MHz, solvent – $CDCl_3$).

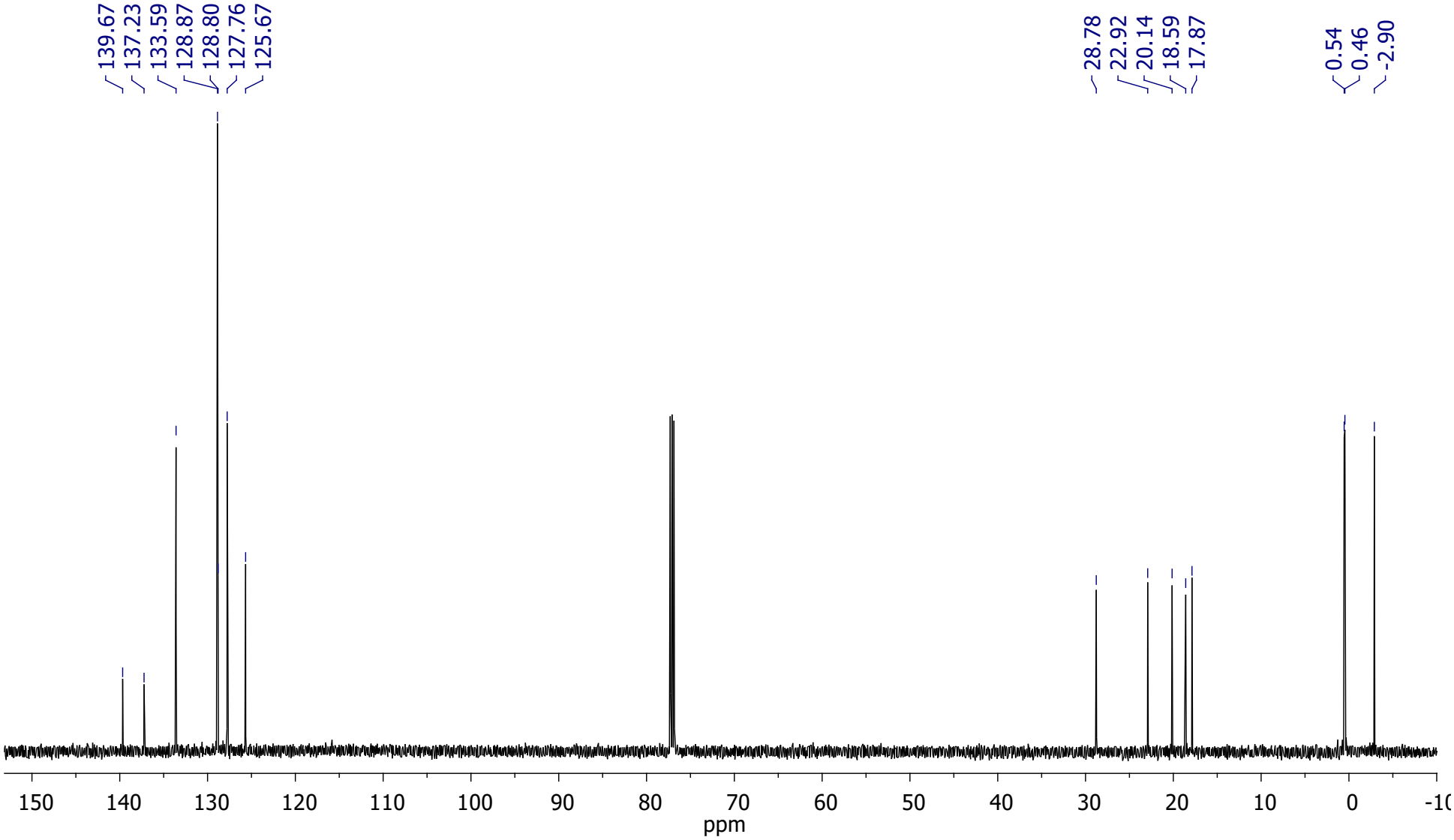


Figure 108s. ^{13}C NMR spectrum of compound **1.1.2** (80 MHz, solvent – $CDCl_3$).

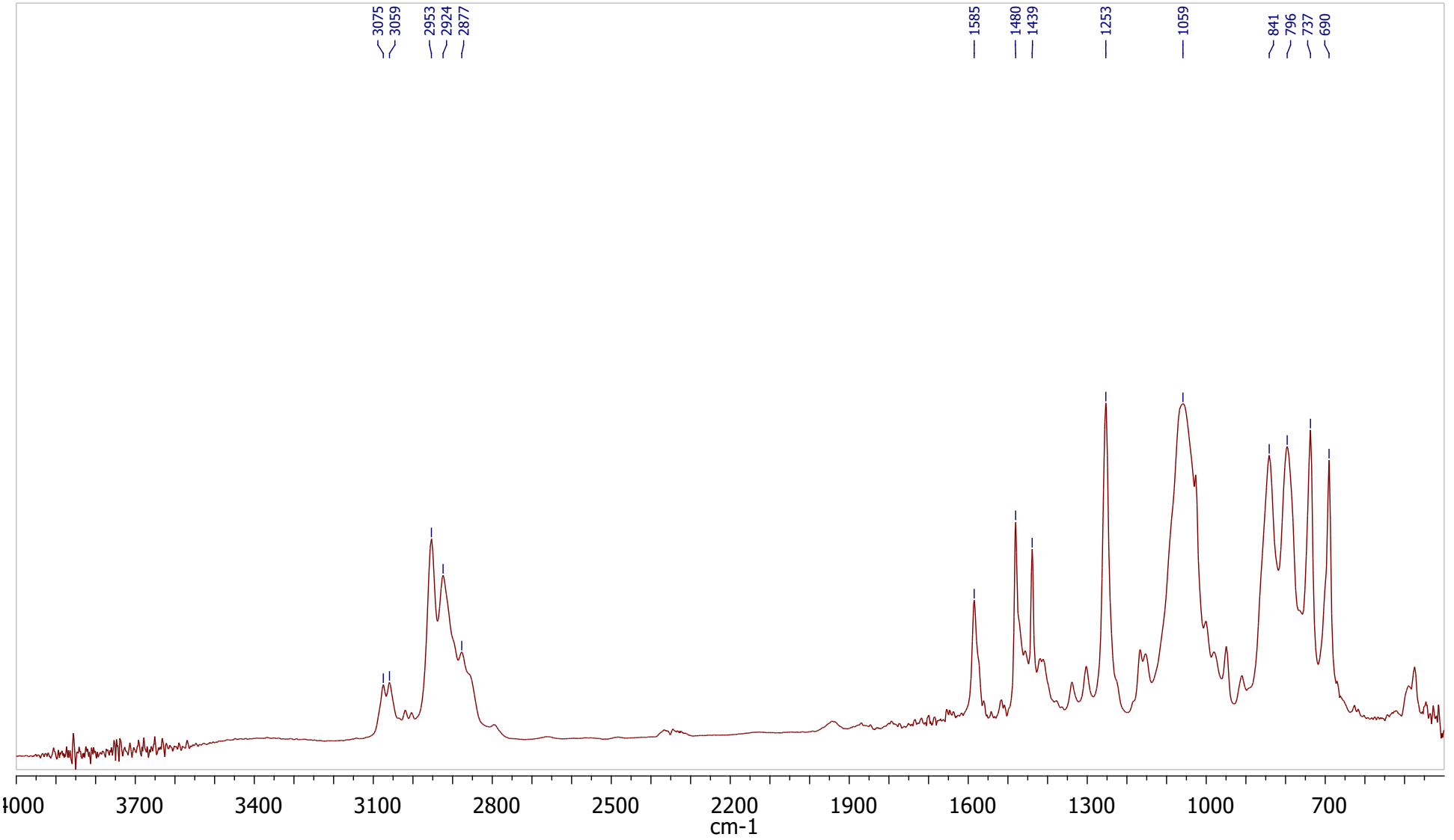


Figure 109s. IR-spectrum of compound **1.1.2**.

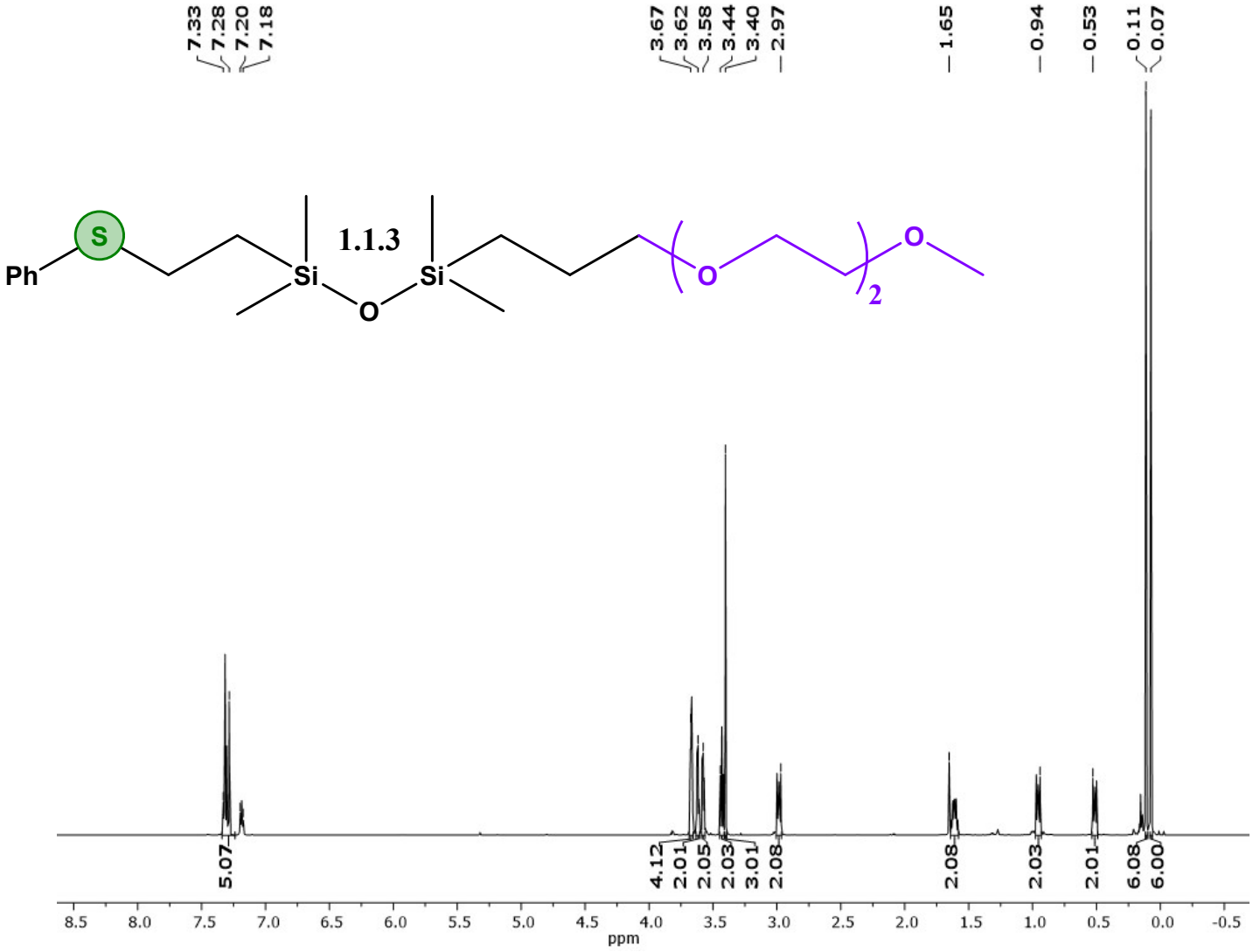


Figure 110s. ^{1}H NMR spectrum of compound **1.1.3** (400 MHz, solvent – $CDCl_3$).

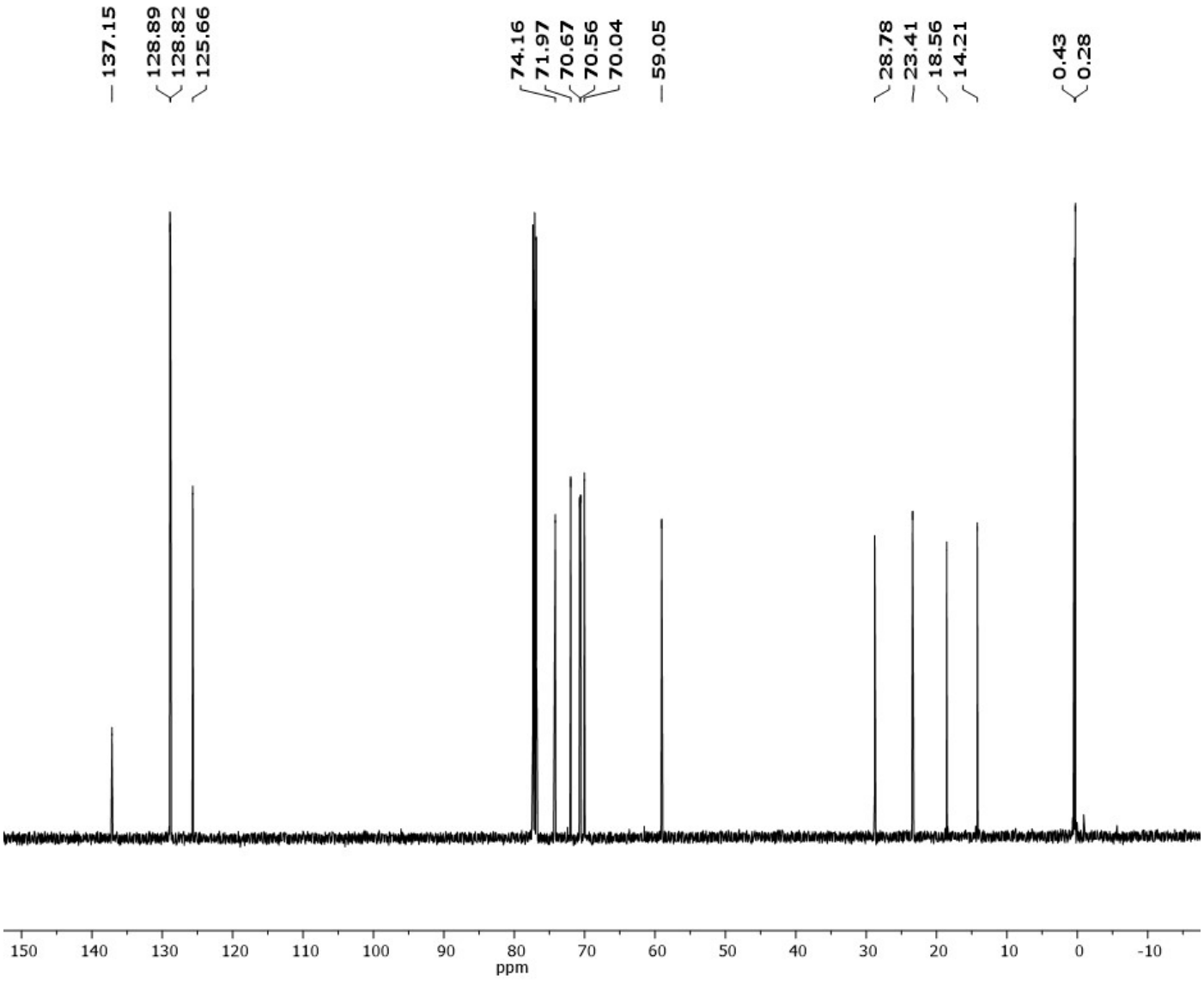


Figure 111s. ^{13}C NMR spectrum of compound **1.1.3** (100 MHz, solvent – $CDCl_3$).

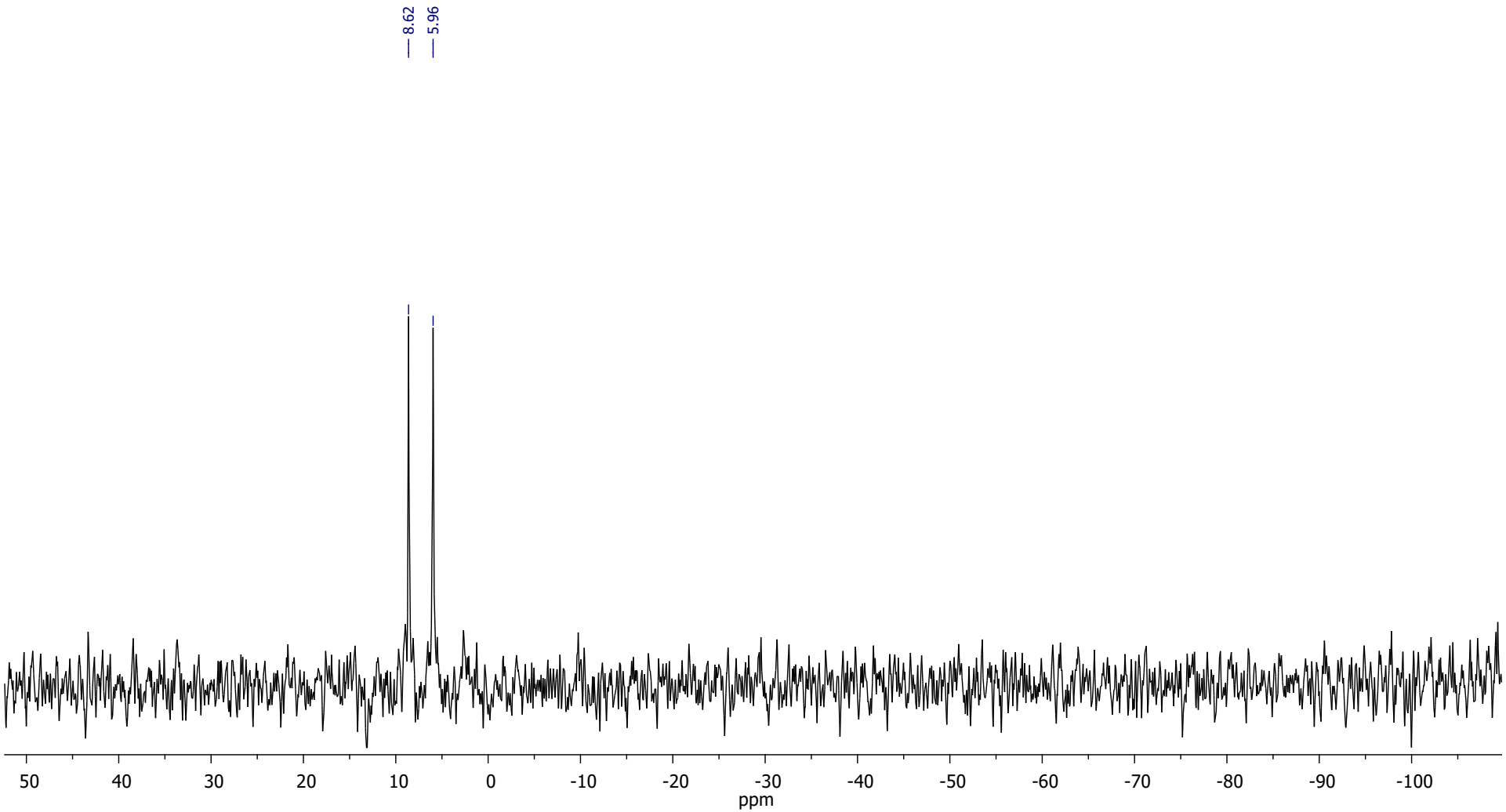


Figure 112s. ^{29}Si NMR spectrum of compound **1.1.3** (80 MHz, solvent – $CDCl_3$).

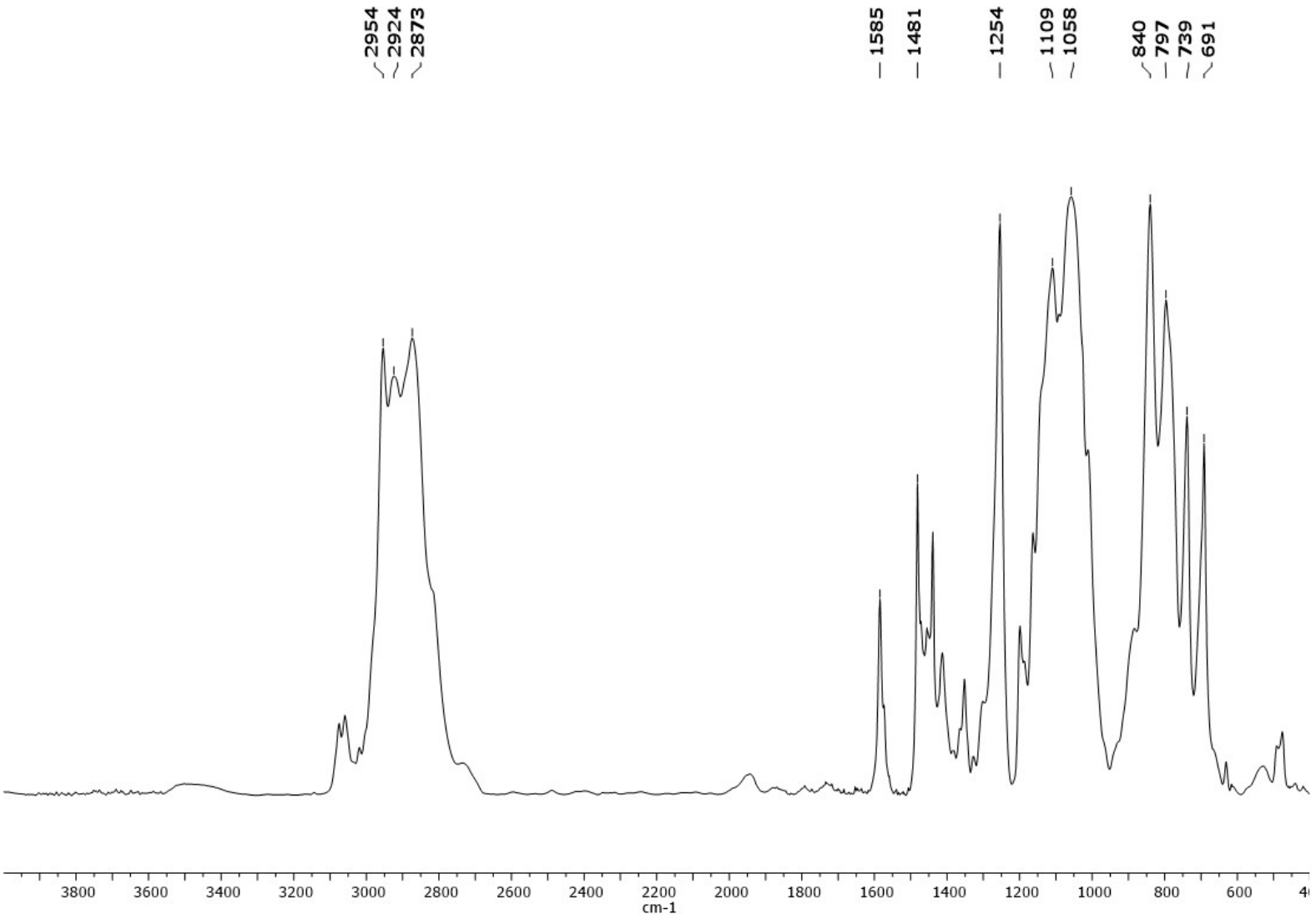


Figure 113s. IR-spectrum of compound **1.1.3**.

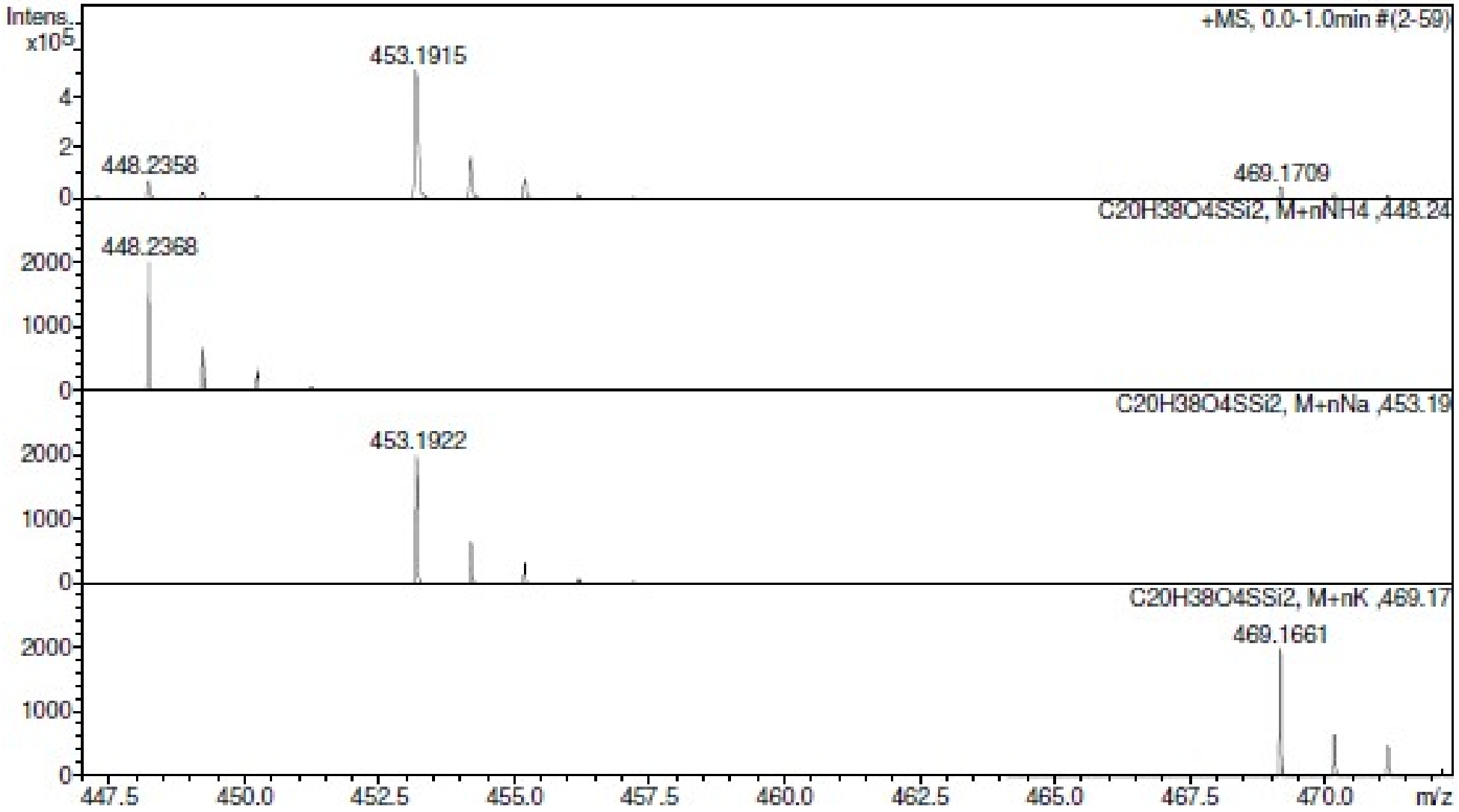


Figure 114s. HRMS (ESI) for compound **1.1.3**.

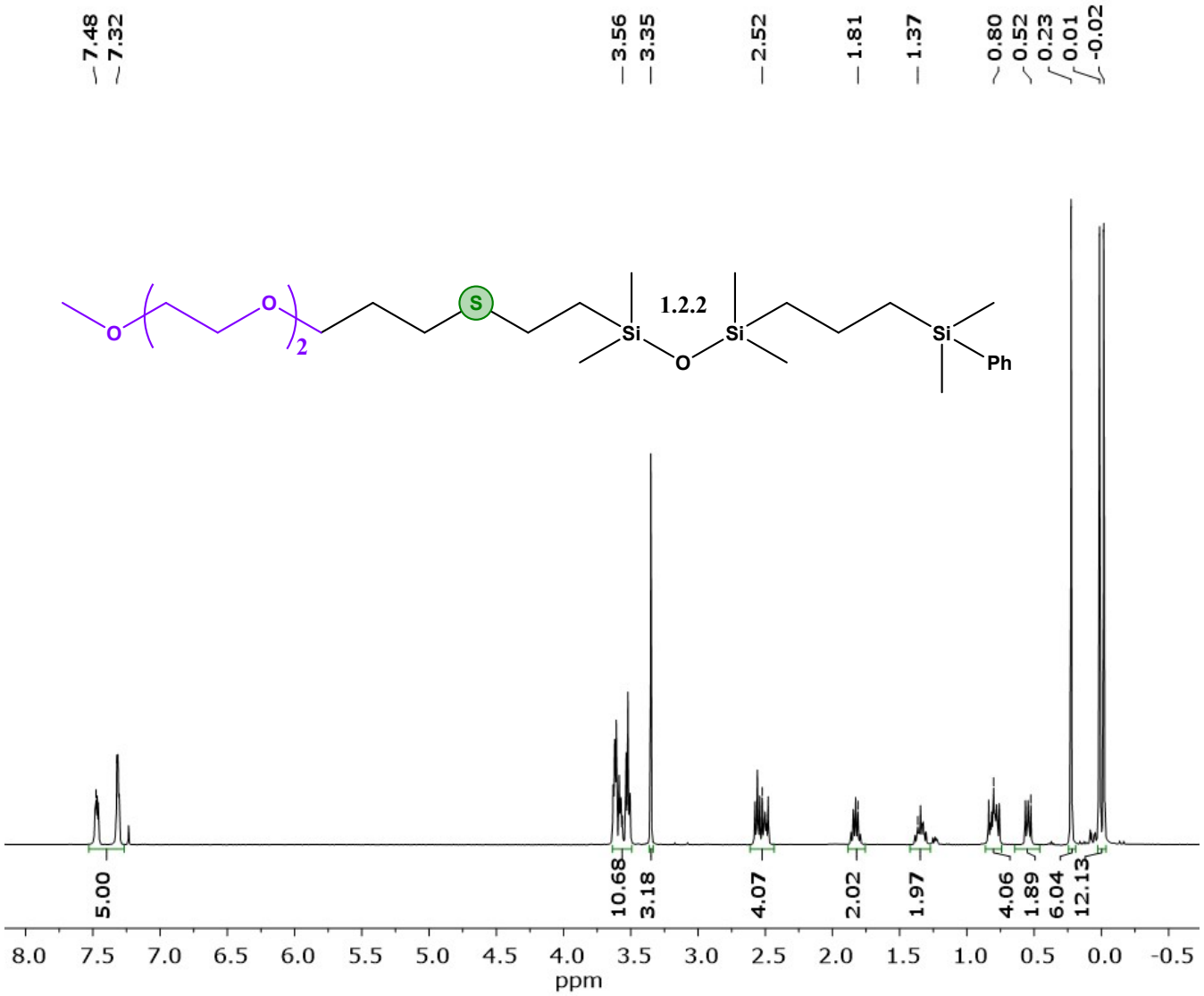


Figure 115s. ^{1}H NMR spectrum of compound **1.2.2** (400 MHz, solvent – $CDCl_3$).

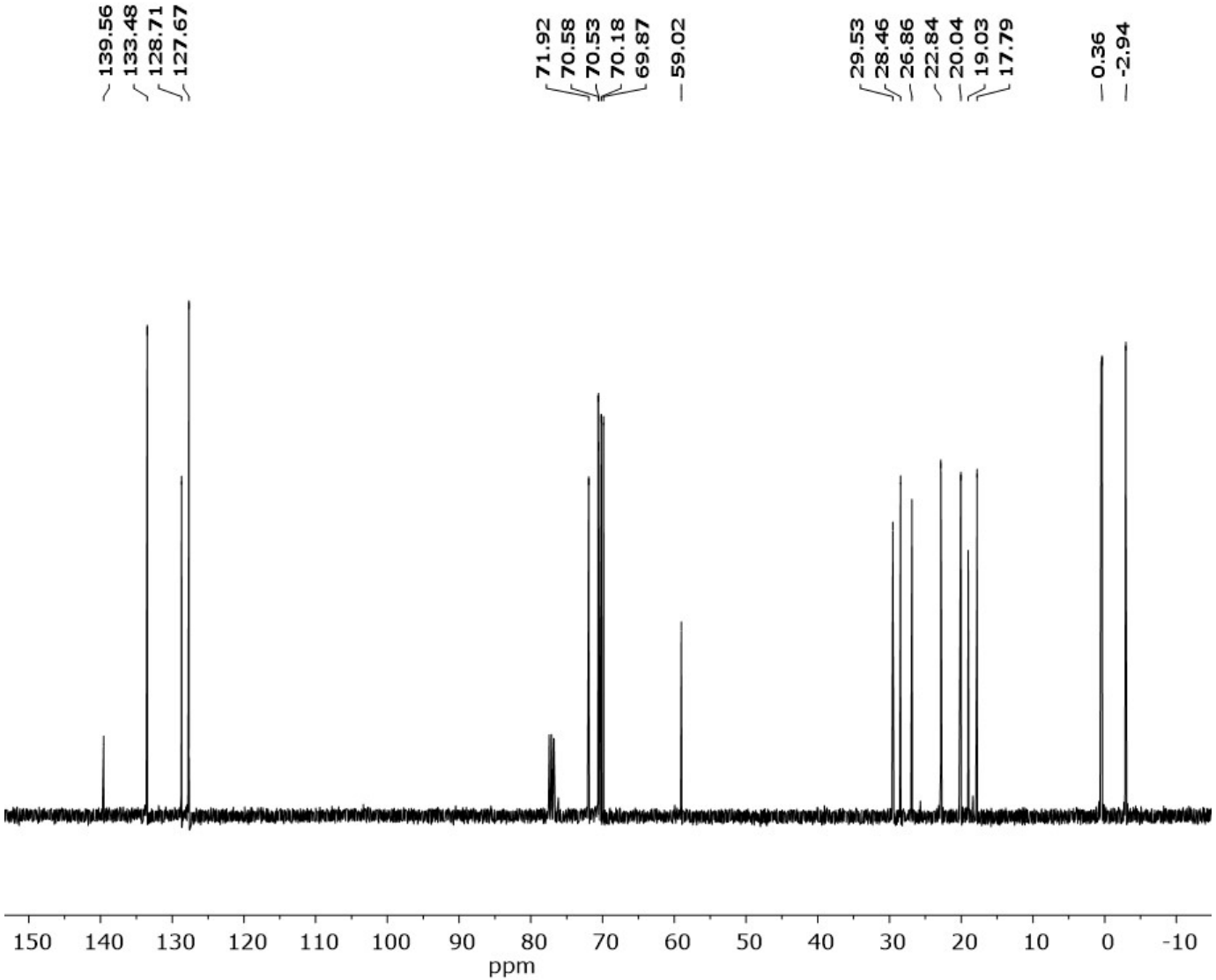


Figure 116s. ^{13}C NMR spectrum of compound **1.2.2** (100 MHz, solvent – $CDCl_3$).

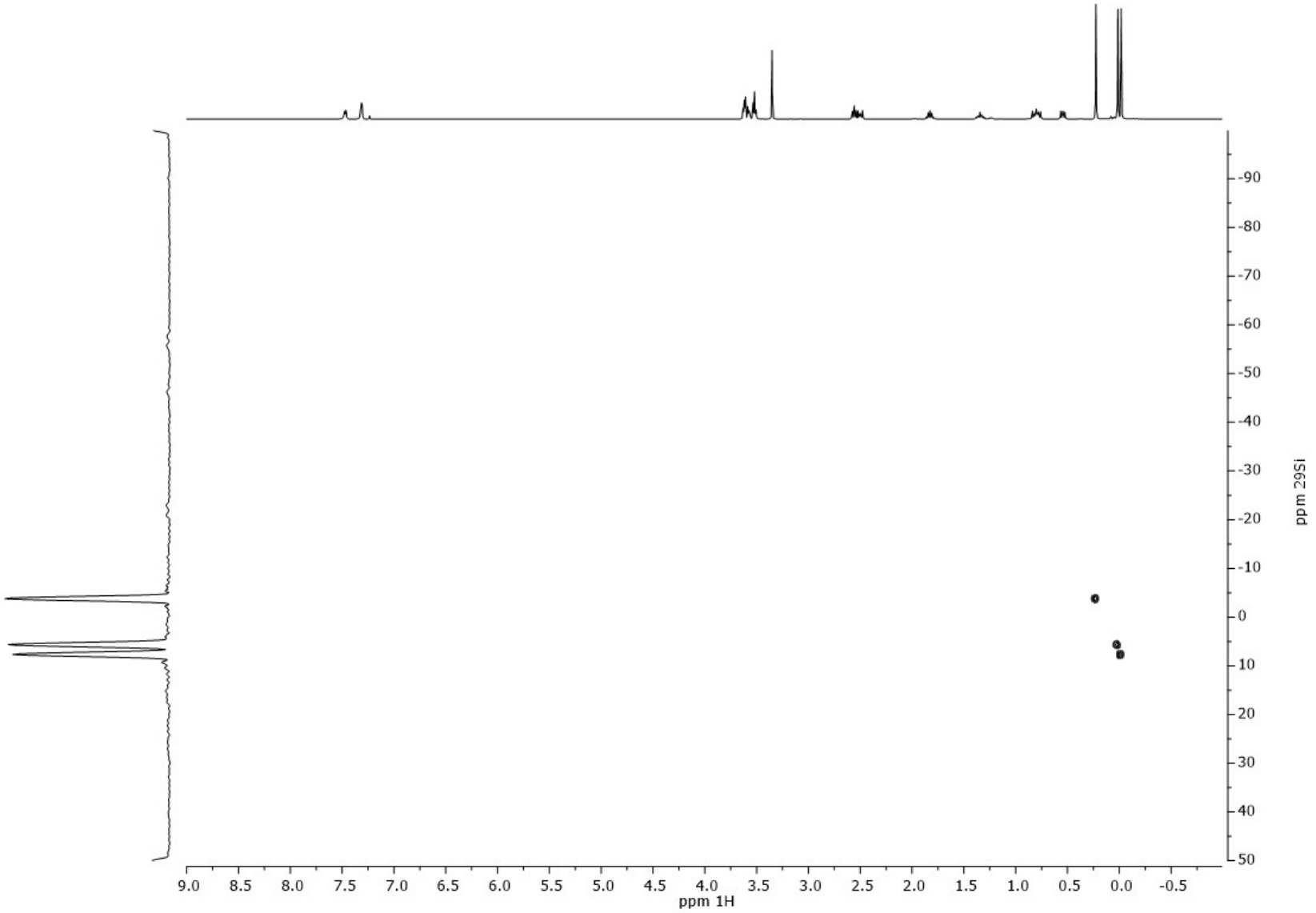


Figure 117s. HMBC ^{1}H-^{29}Si NMR spectrum of compound **1.2.2** (solvent – $CDCl_3$).

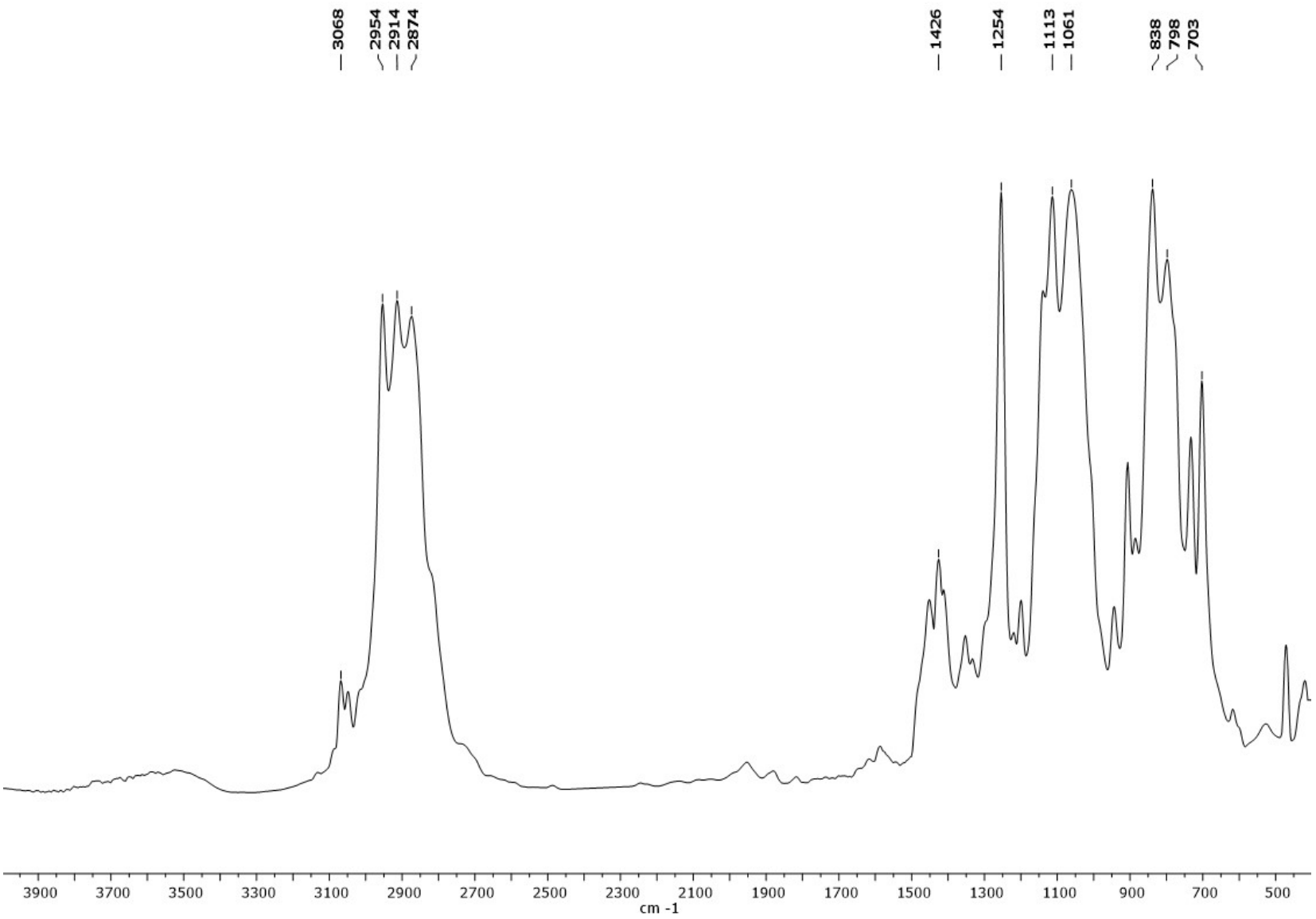


Figure 118s. IR-spectrum of compound **1.2.2**.

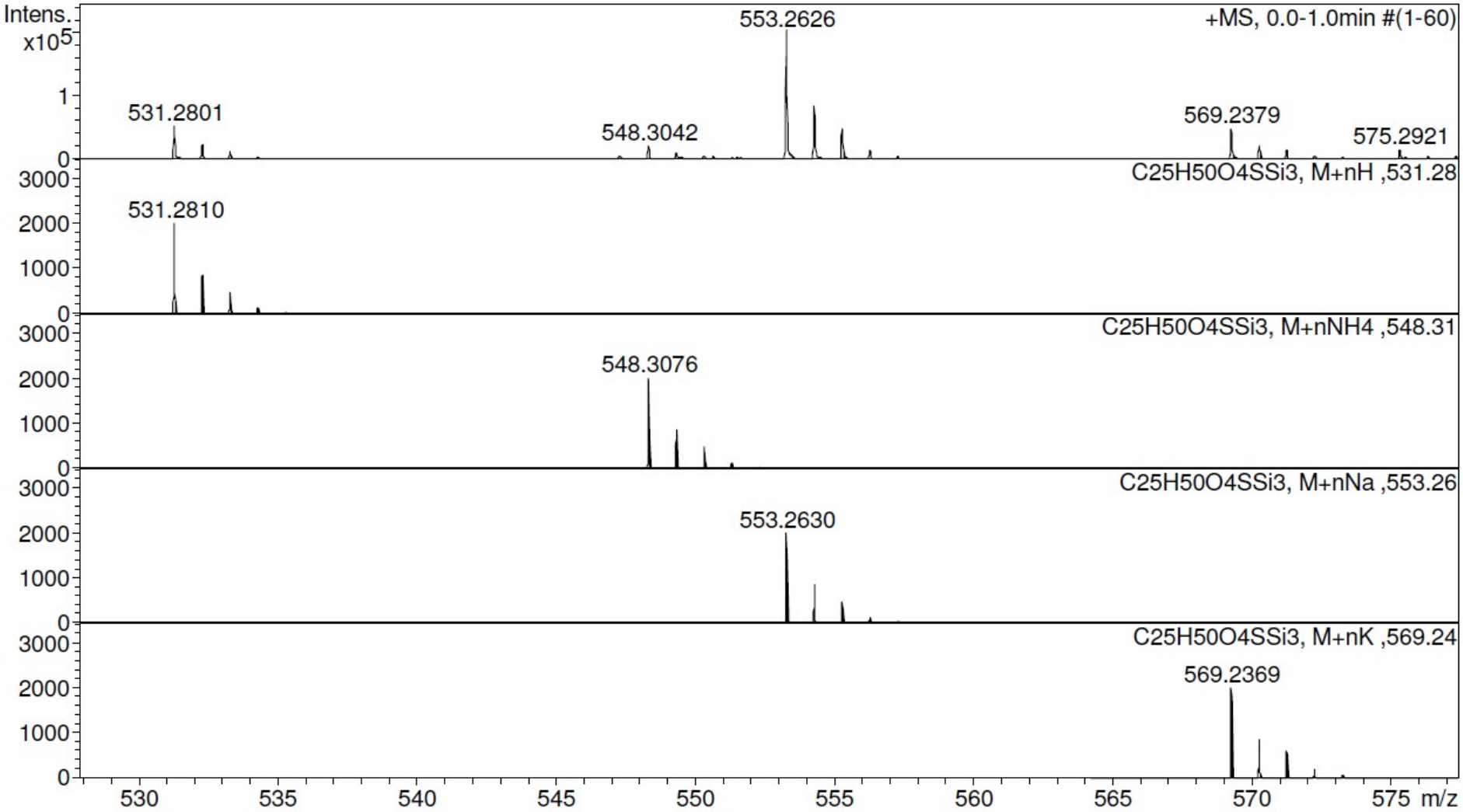


Figure 119s. HRMS (ESI) for compound **1.2.2**.

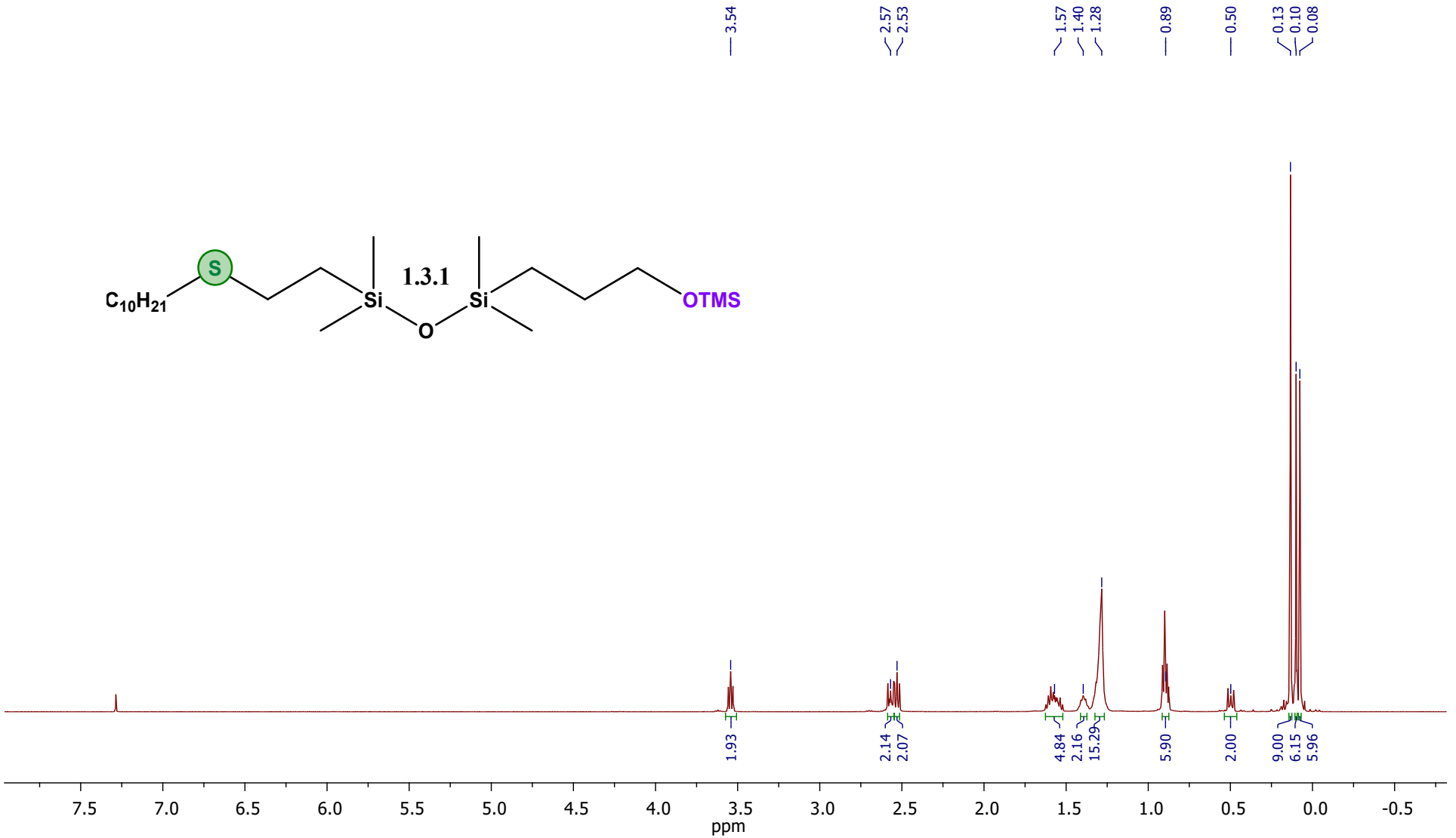


Figure 120s. ^{1}H NMR spectrum of compound **1.3.1** (500 MHz, solvent – $CDCl_3$).

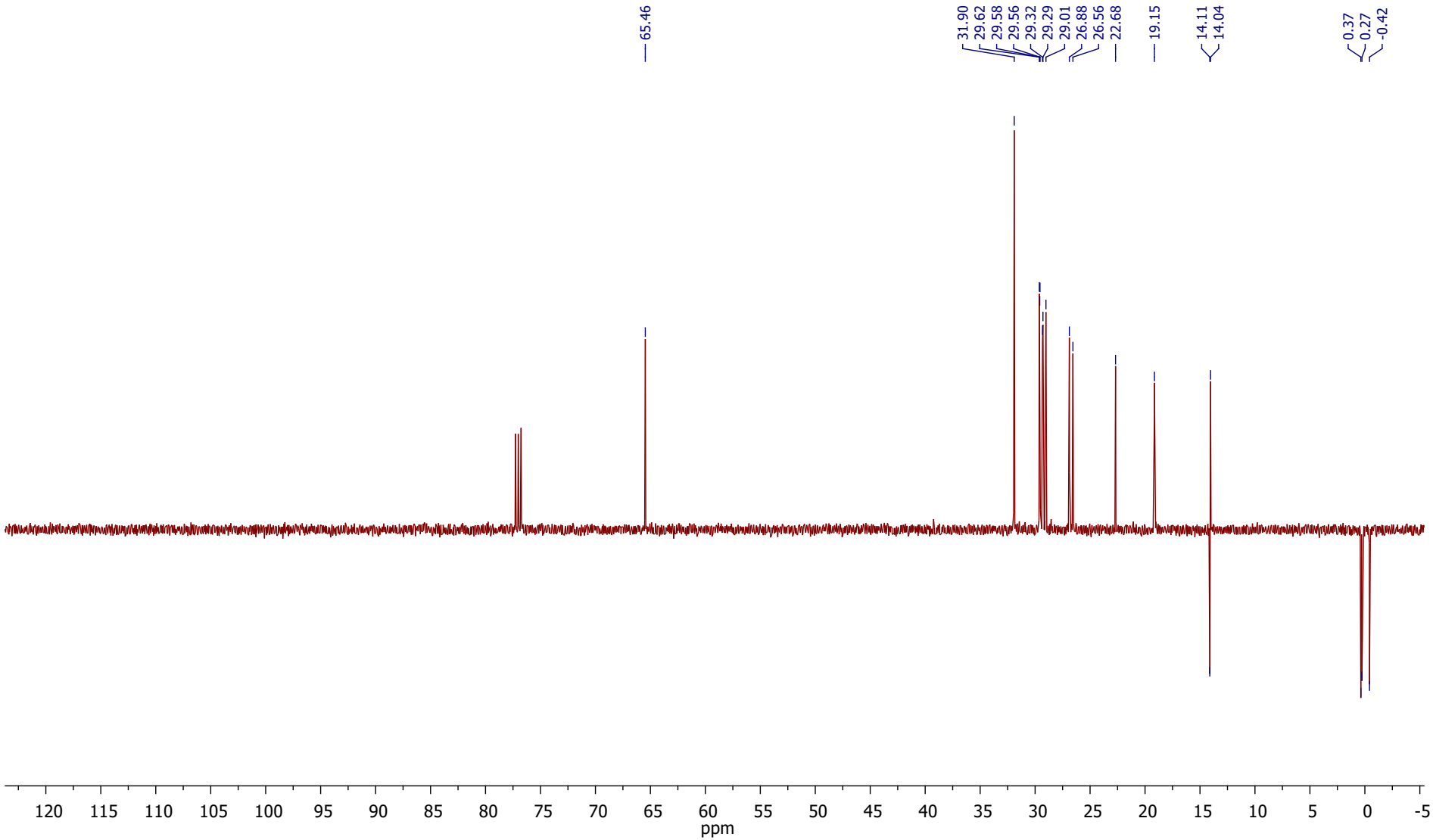


Figure 121s. ^{13}C NMR spectrum of compound **1.3.1** (500 MHz, solvent – $CDCl_3$, jmod).

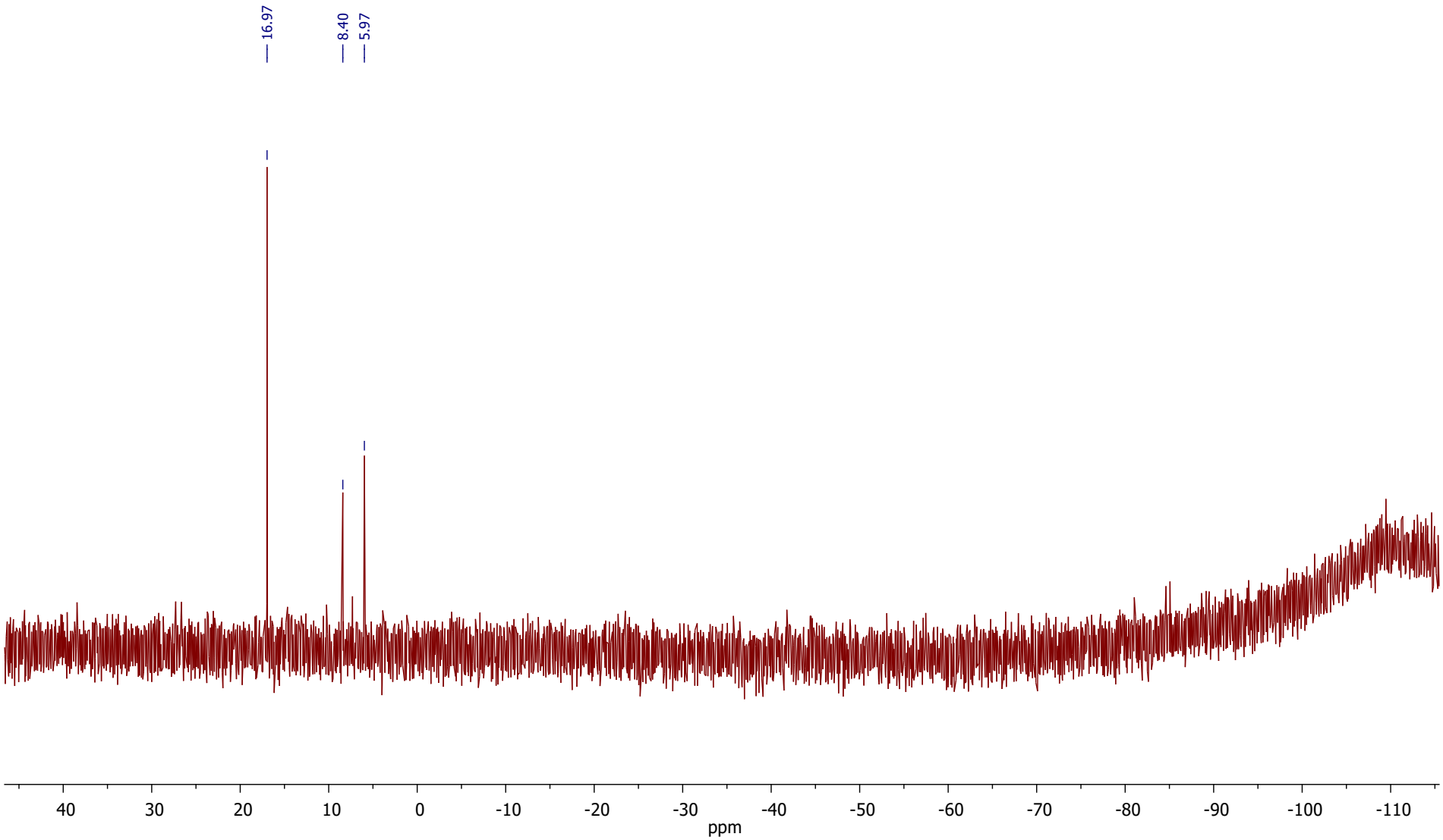


Figure 122s. ^{29}Si NMR spectrum of compound **1.3.1** (500 MHz, solvent – $CDCl_3$).

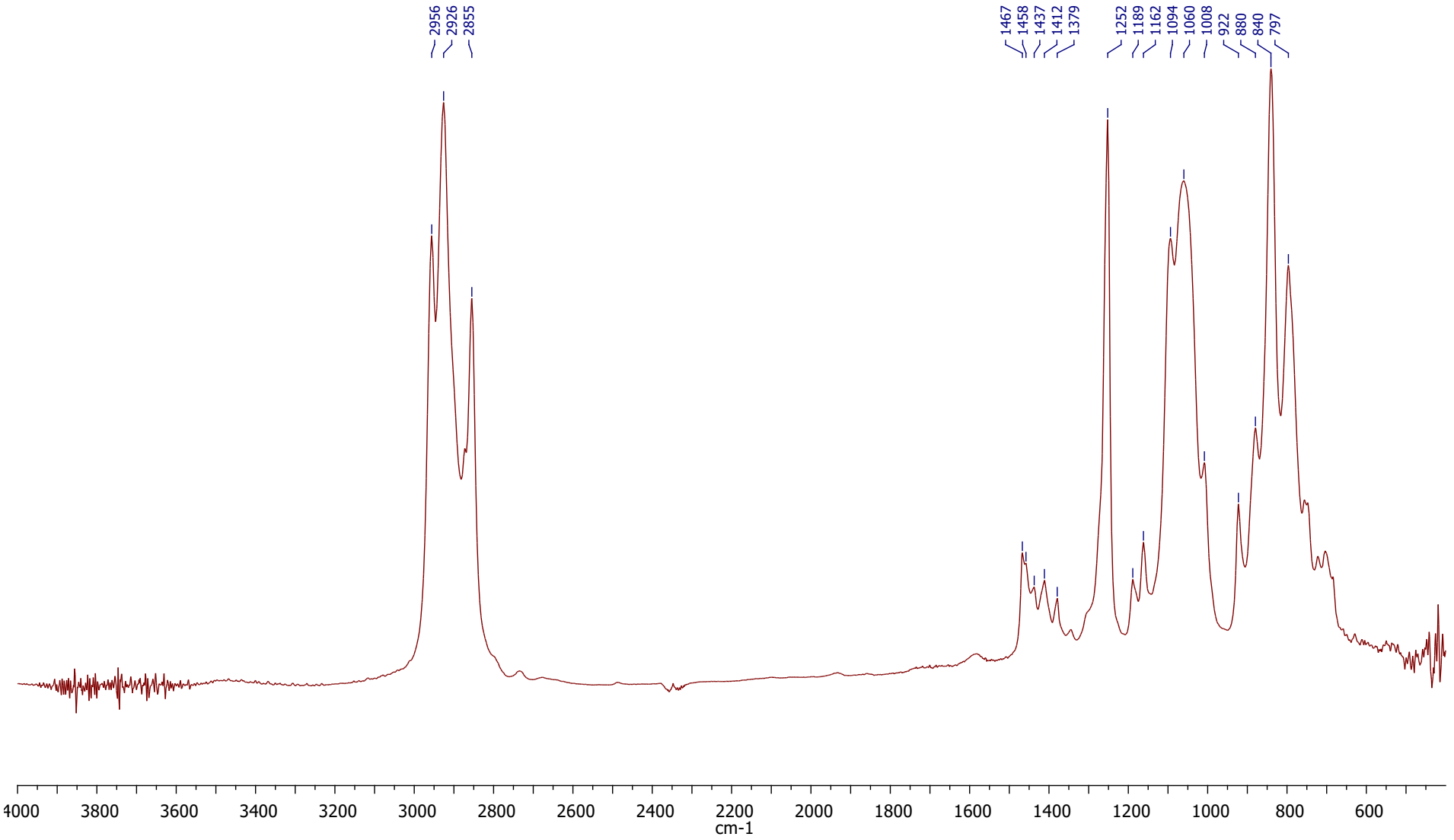


Figure 123s. IR-spectrum of compound **1.3.1**.

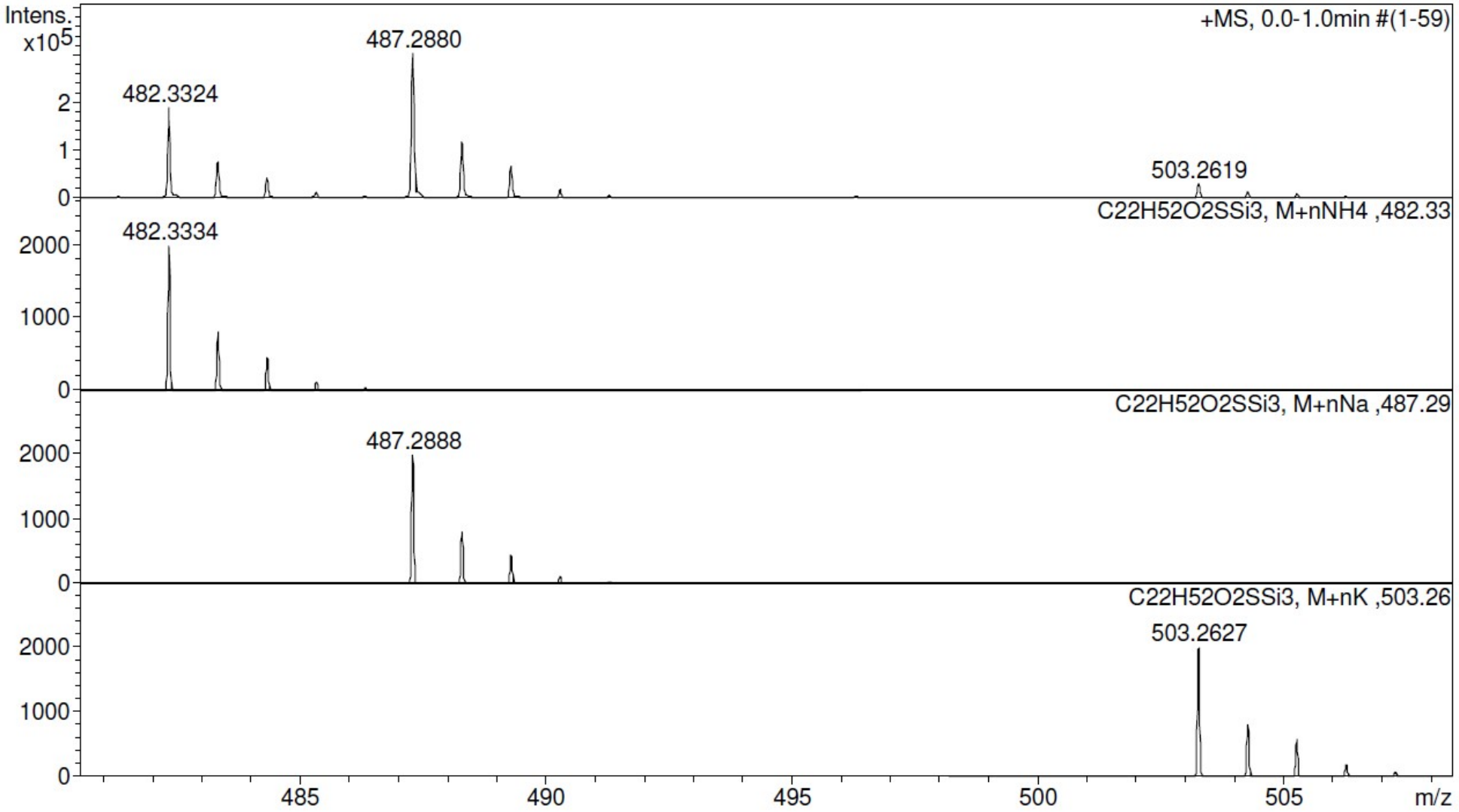


Figure 124s. HRMS (ESI) for compound **1.3.1**.

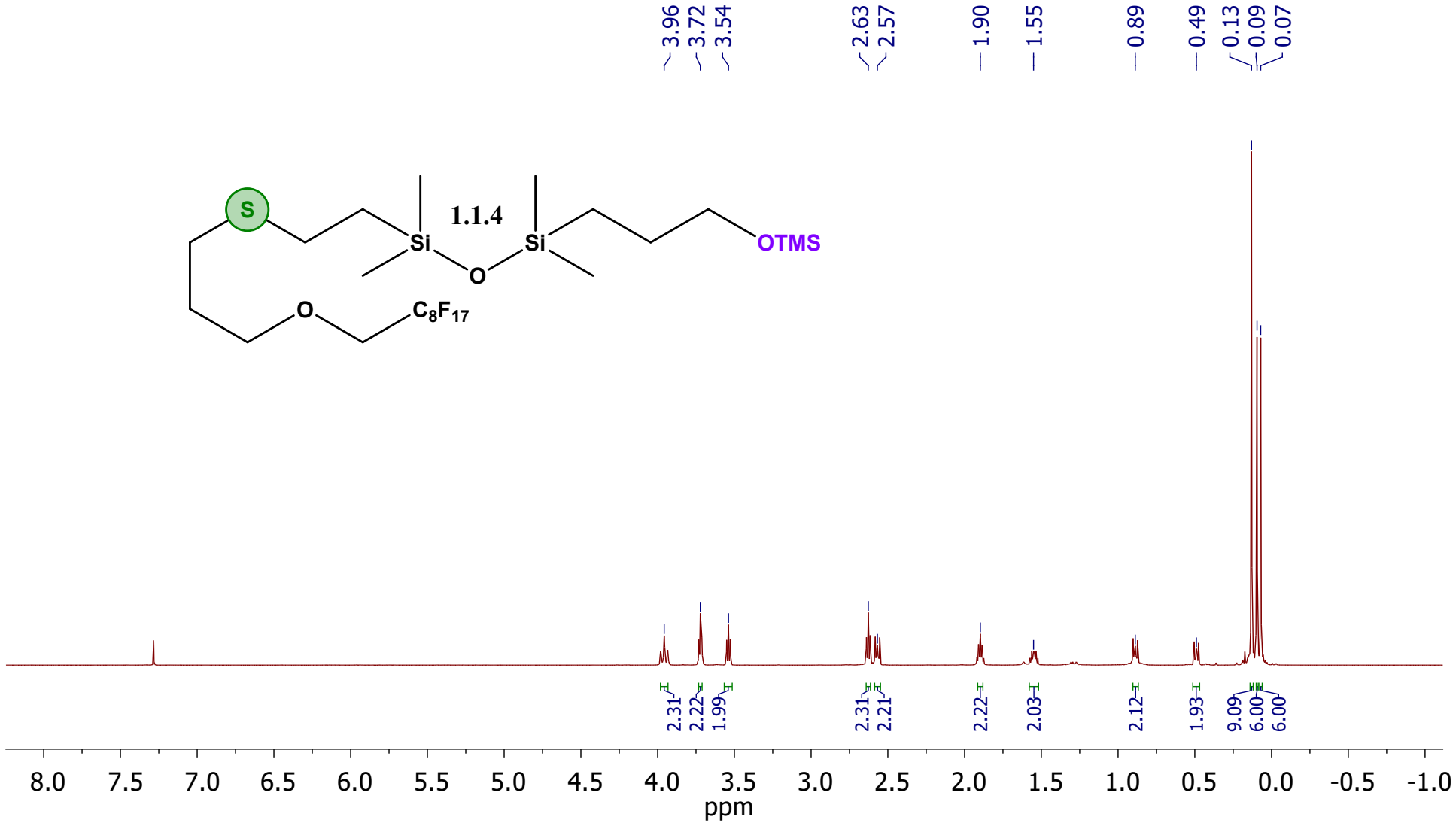


Figure 125s. ^{1}H NMR spectrum of compound **1.4.1** (500 MHz, solvent – $CDCl_3$).

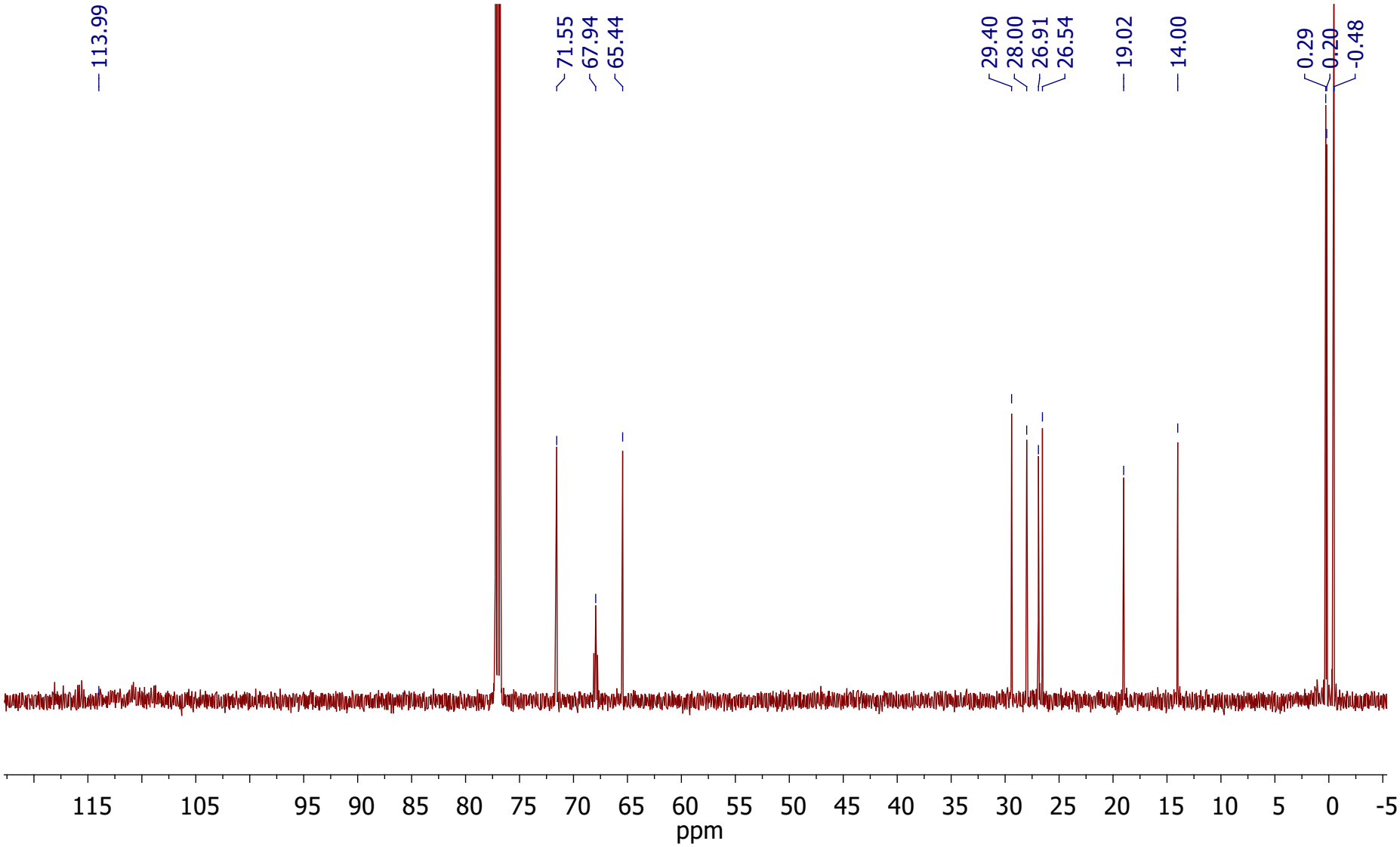


Figure 126s. ^{13}C NMR spectrum of compound **1.4.1** (500 MHz, solvent – $CDCl_3$).

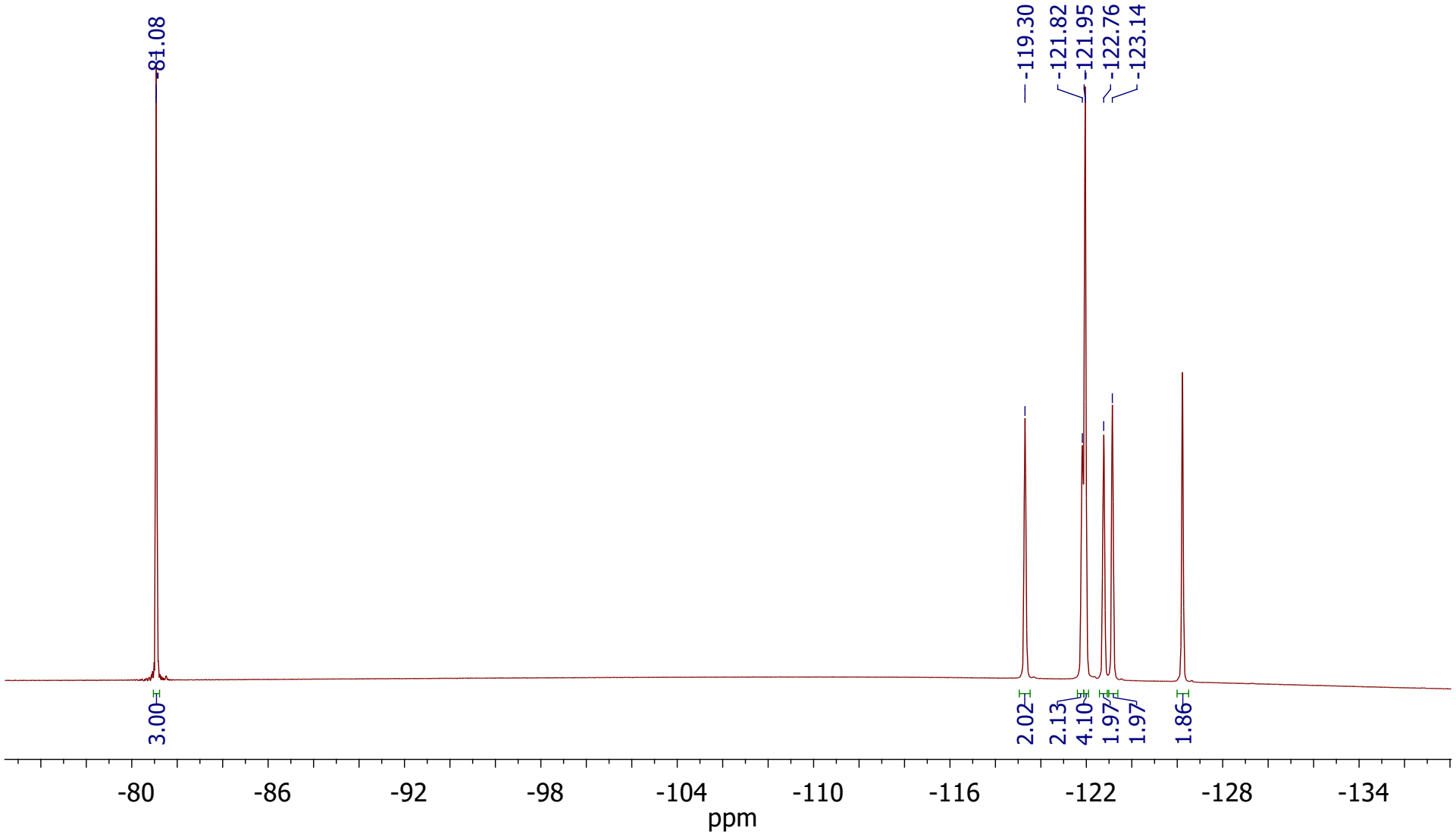


Figure 127s. ^{19}F NMR spectrum of compound **1.4.1** (300 MHz, solvent – $CDCl_3$).

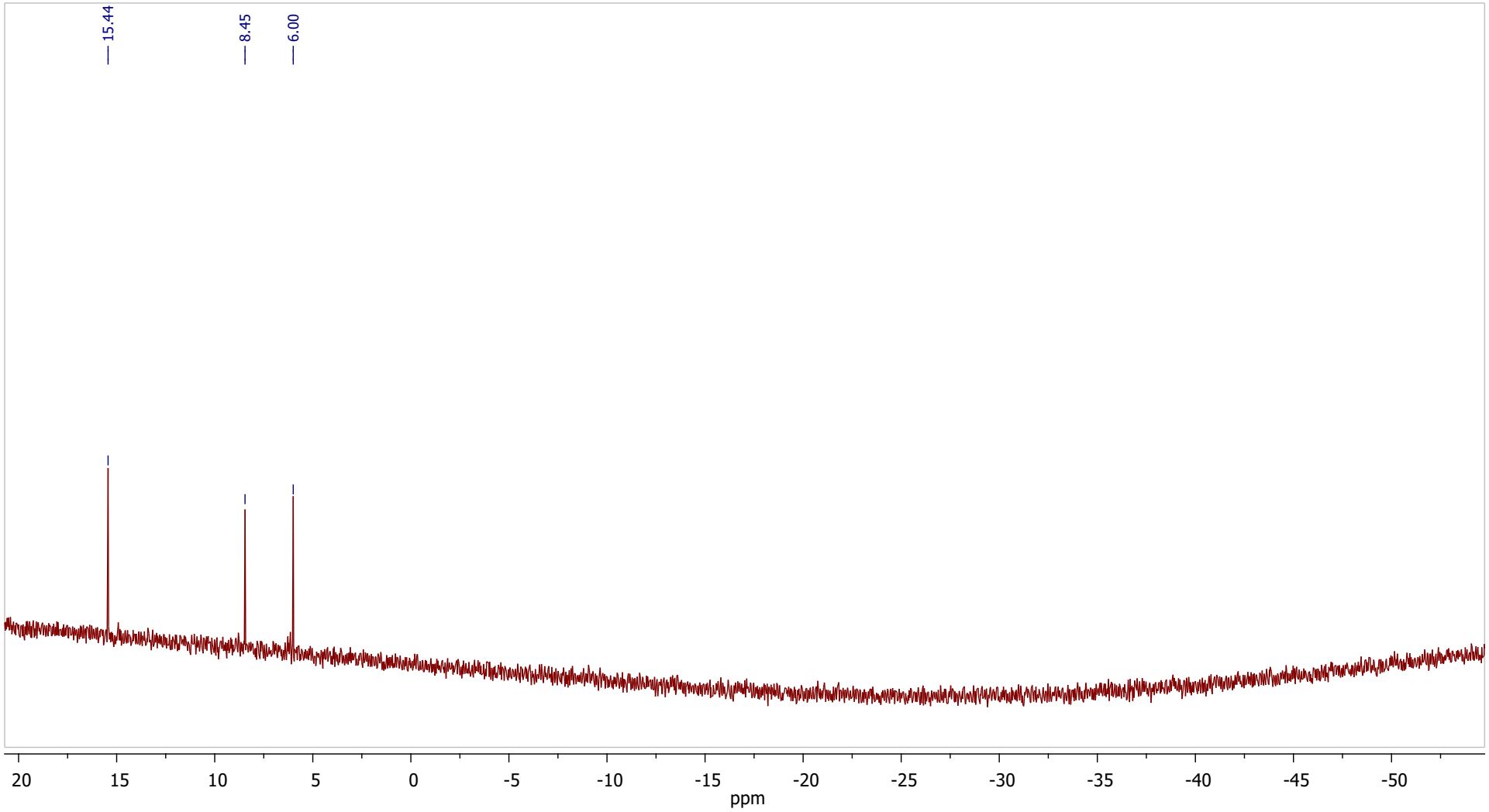


Figure 128s. ^{29}Si NMR spectrum of compound **1.4.1** (500 MHz, solvent – $CDCl_3$).

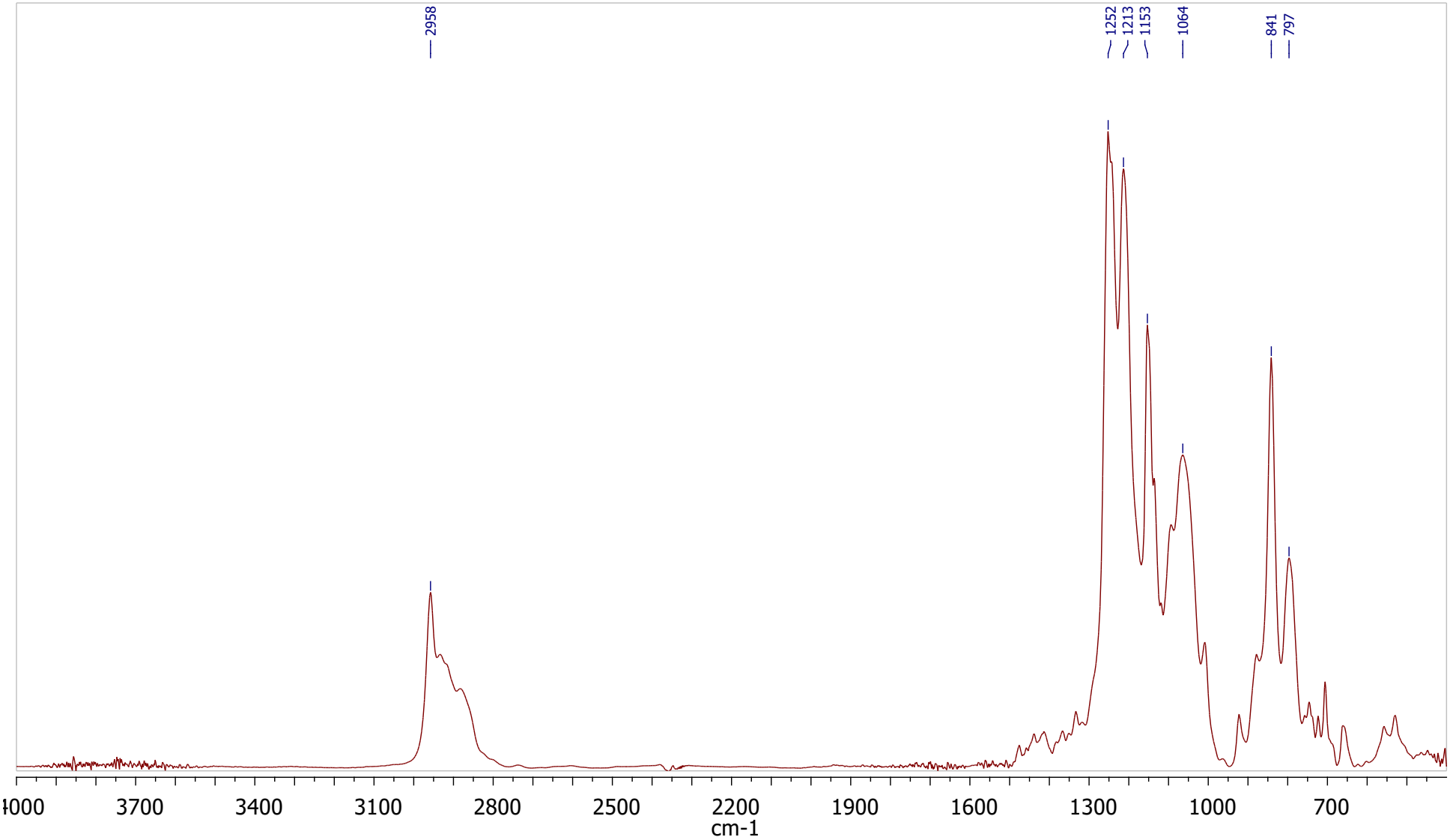


Figure 129s. IR-spectrum of compound **1.4.1**.

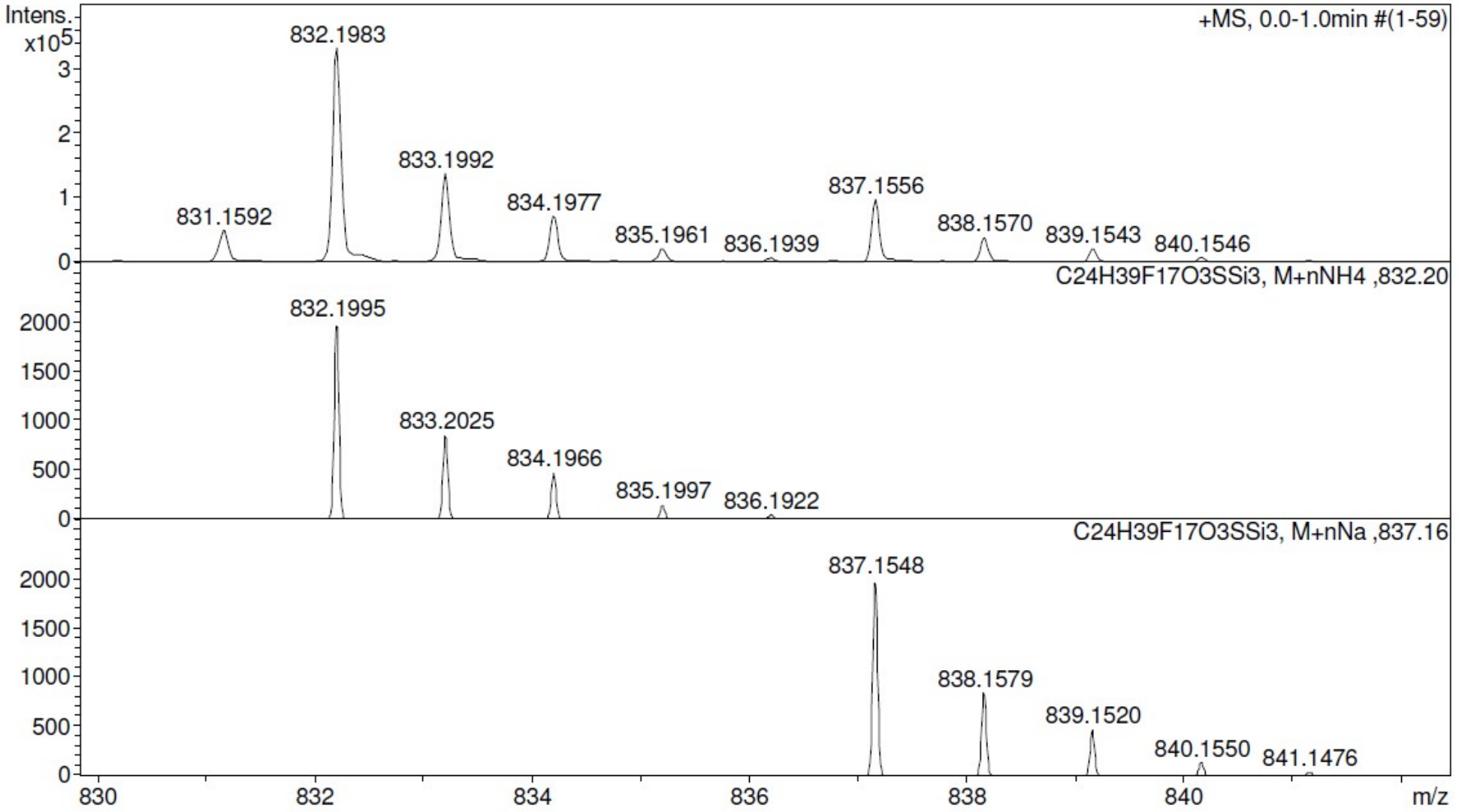


Figure 130s. HRMS (ESI) for compound **1.4.1**.

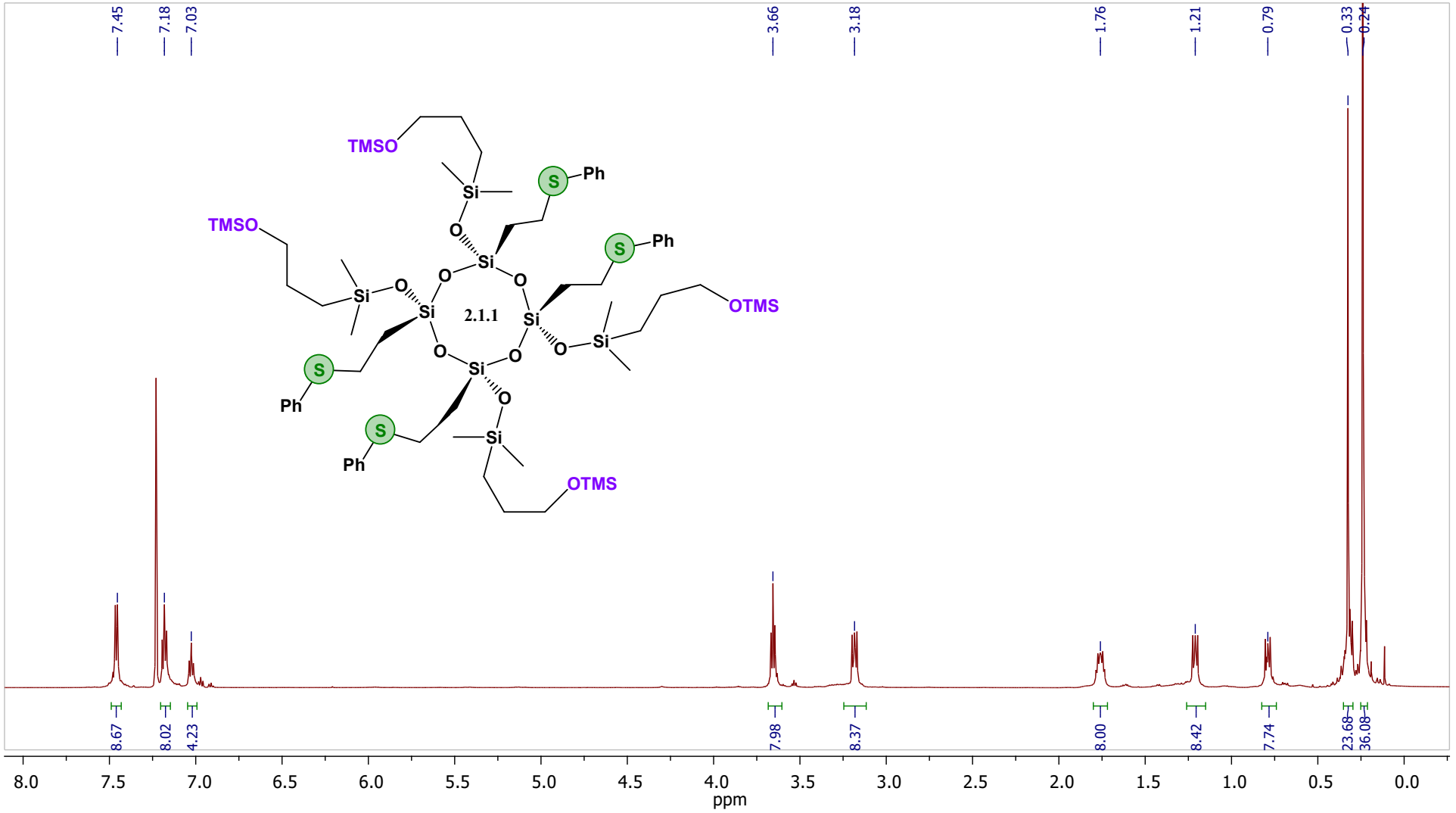


Figure 131s. ^{1}H NMR spectrum of compound **2.1.1** (500 MHz, solvent – $CDCl_3$).

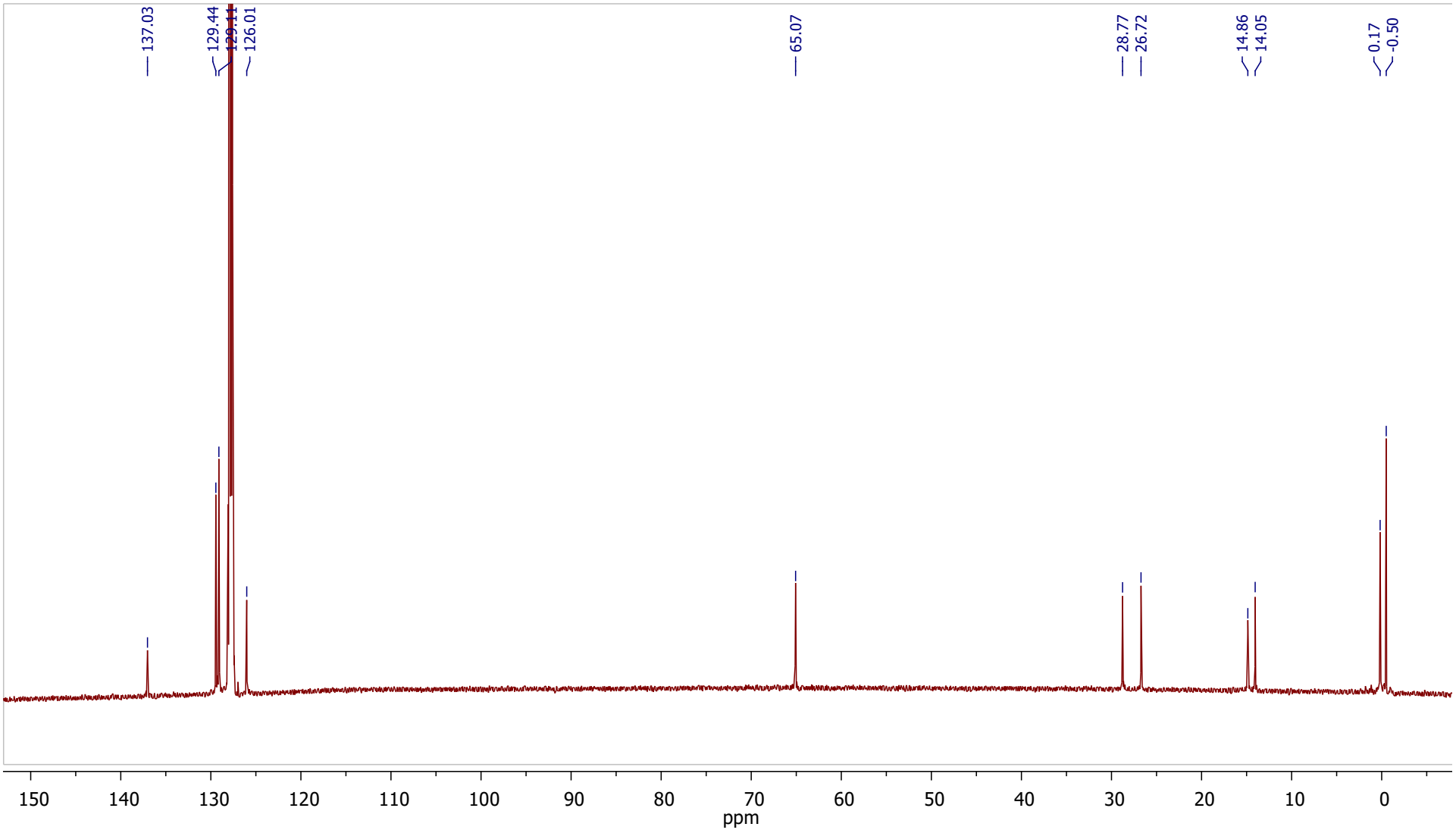


Figure 132s. ^{13}C NMR spectrum of compound **2.1.1** (500 MHz, solvent – $CDCl_3$).

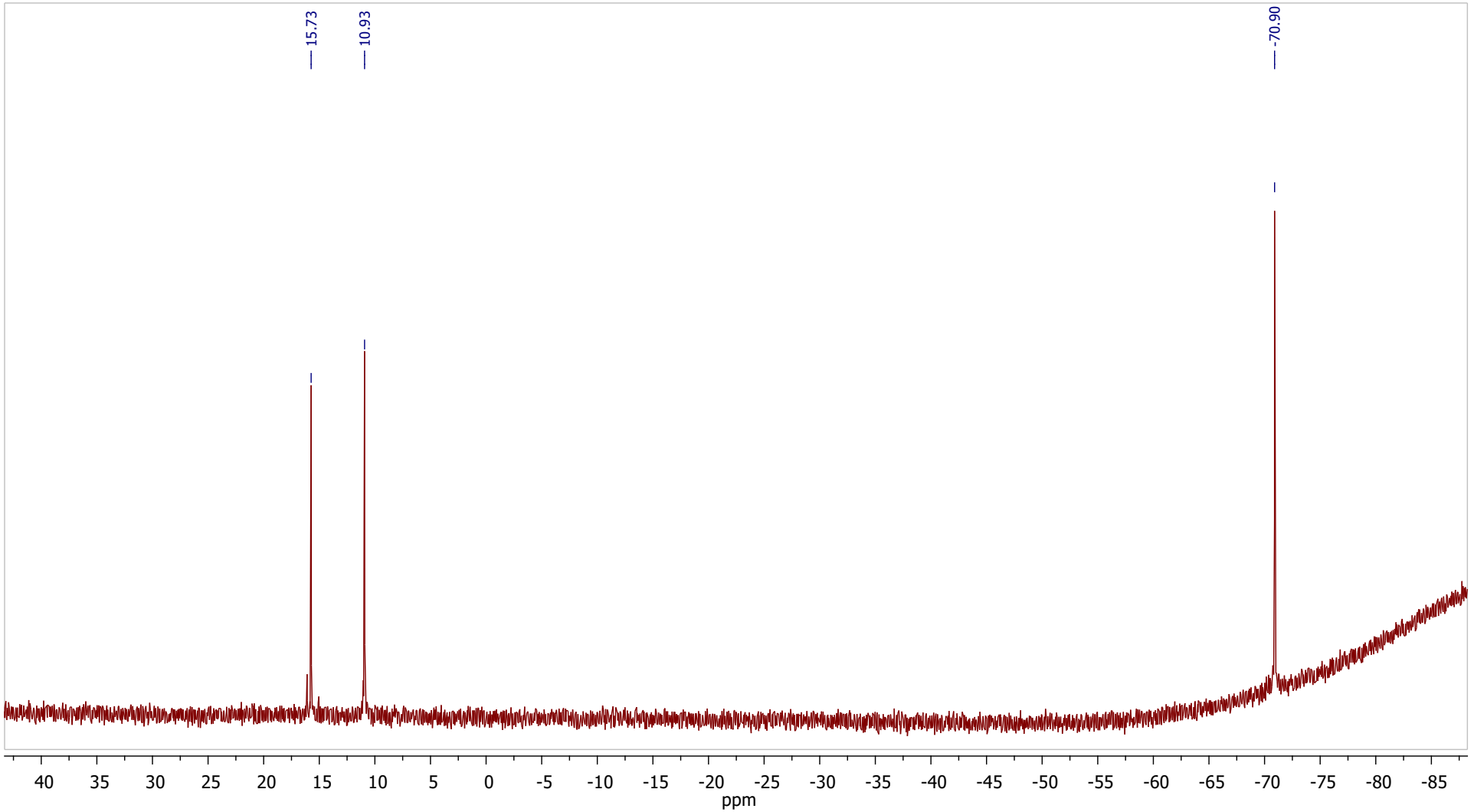


Figure 133s. ^{29}Si NMR spectrum of compound **2.1.1** (500 MHz, solvent – $CDCl_3$).

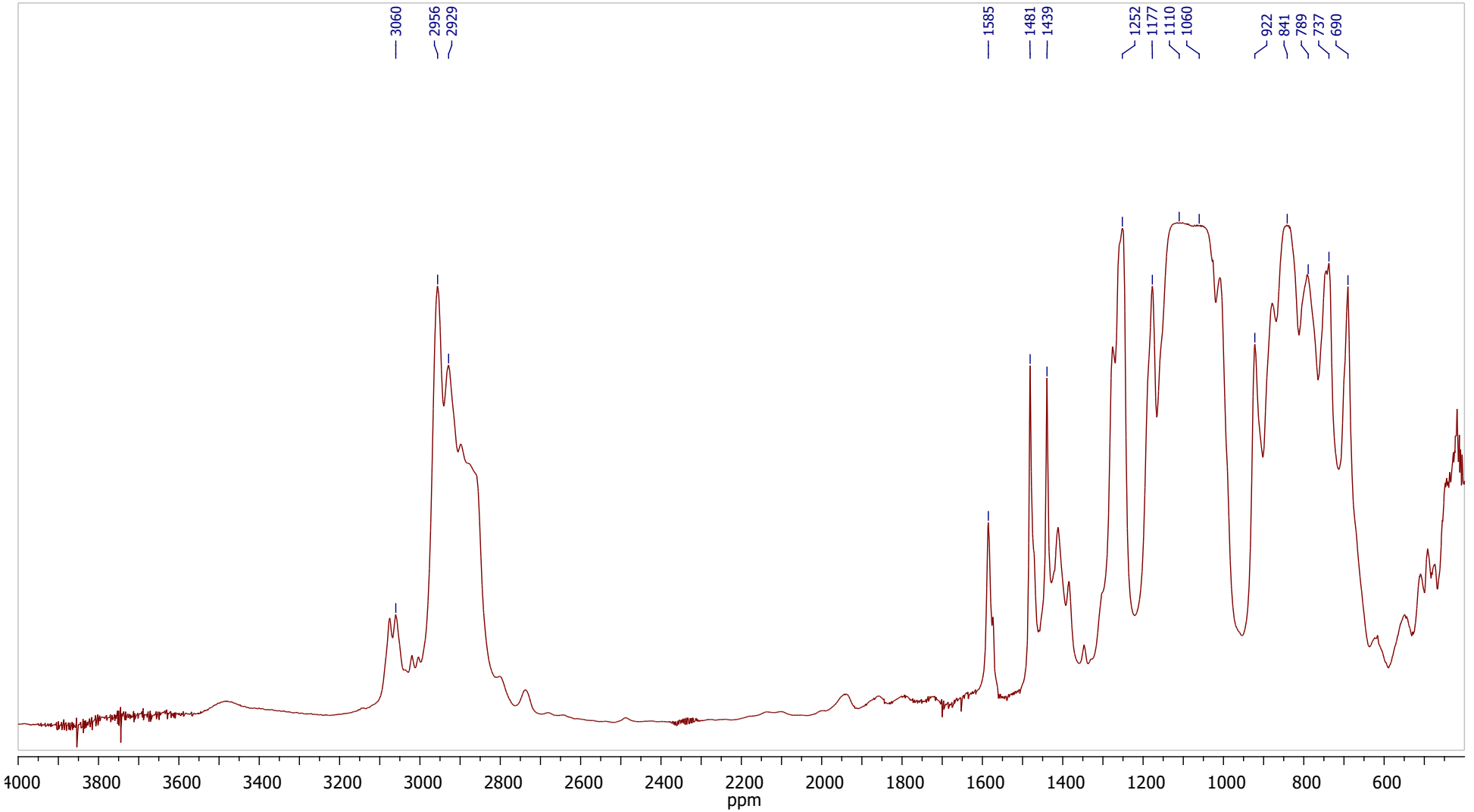


Figure 134s. IR-spectrum of compound **2.1.1**.

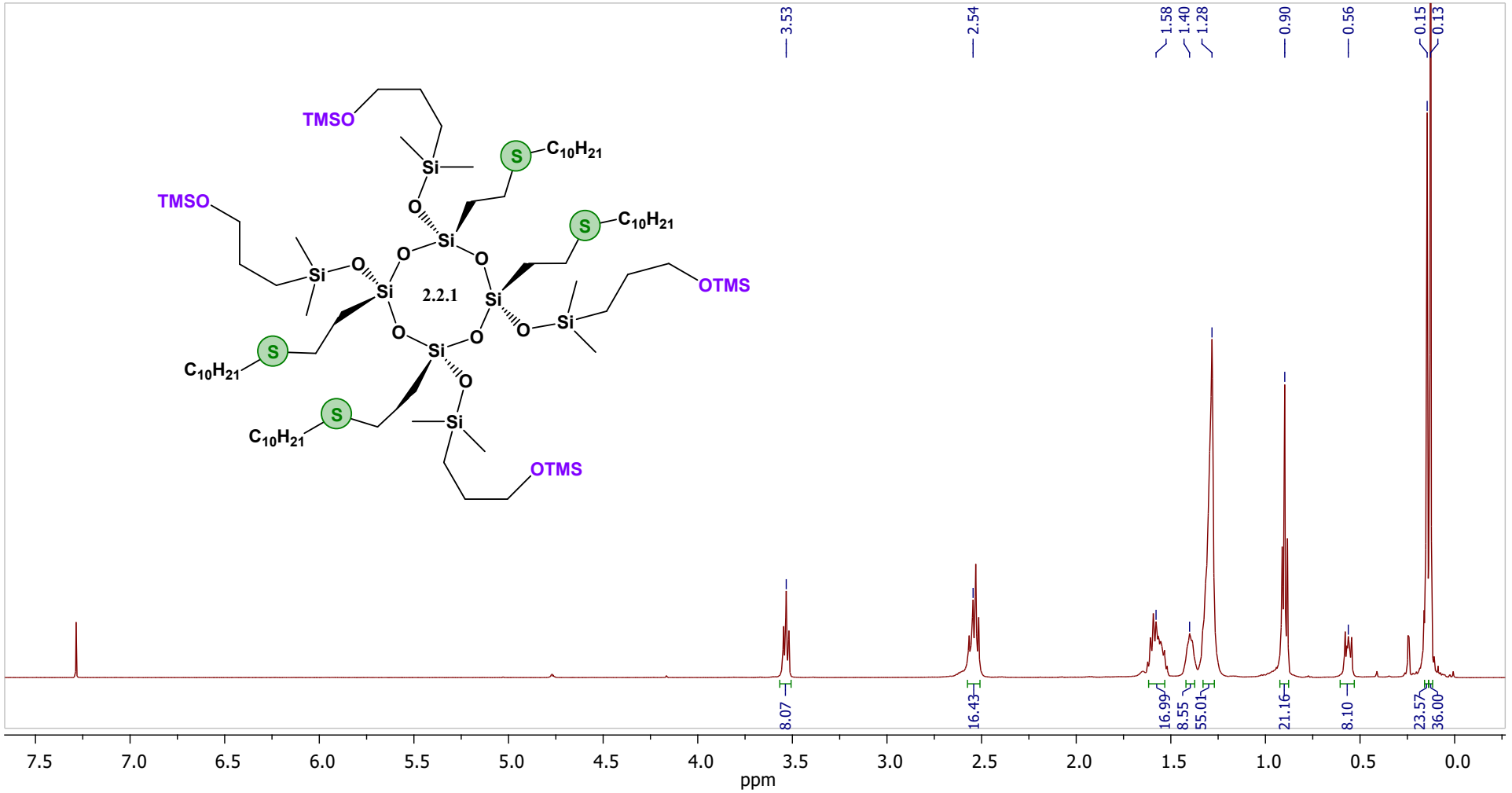


Figure 135s. ^{1}H NMR spectrum of compound **2.2.1** (500 MHz, solvent – $CDCl_3$).

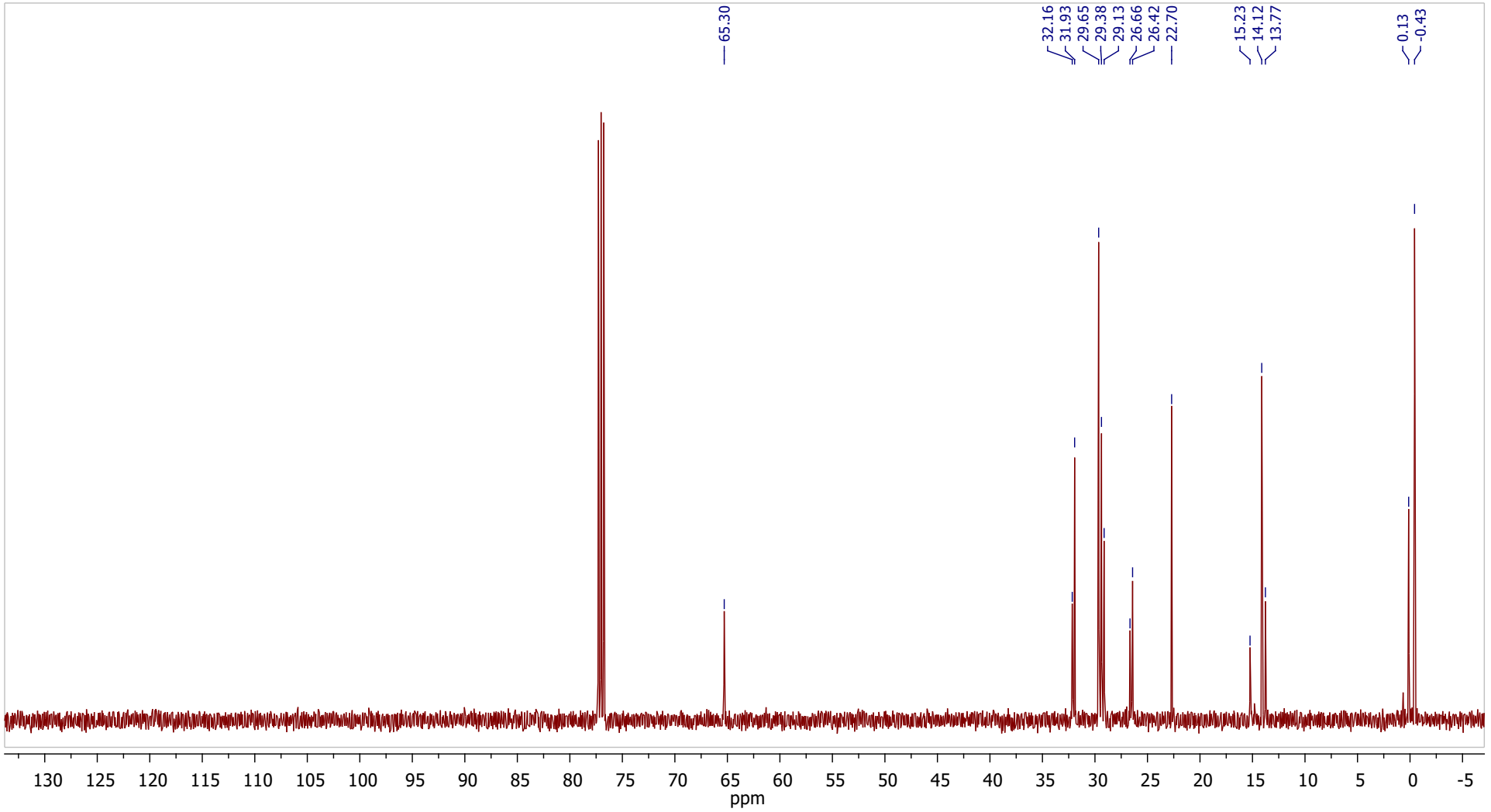


Figure 136s. ^{13}C NMR spectrum of compound **2.2.1** (500 MHz, solvent – $CDCl_3$).

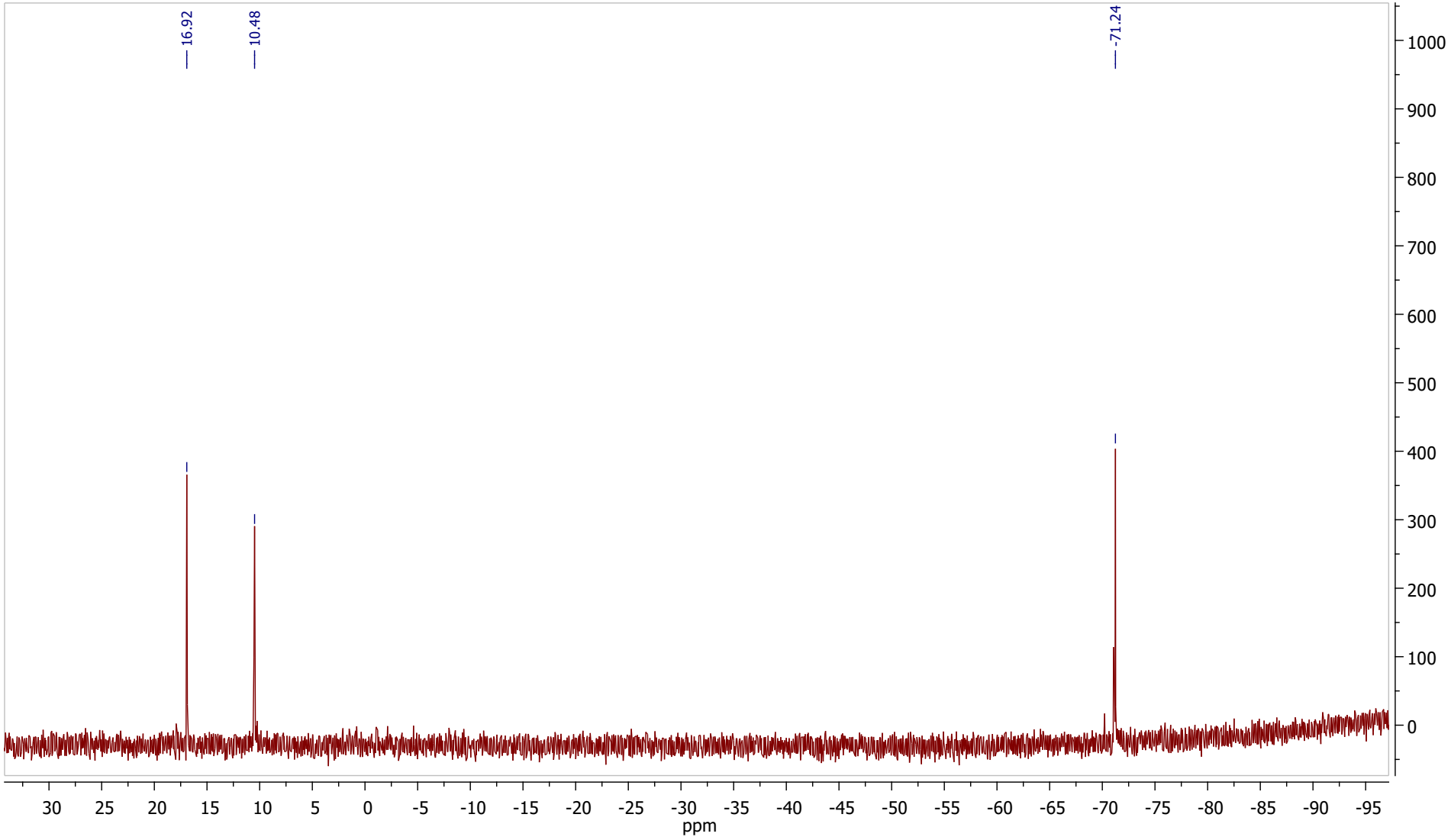


Figure 137s. ^{29}Si NMR spectrum of compound **2.2.1** (500 MHz, solvent – $CDCl_3$).

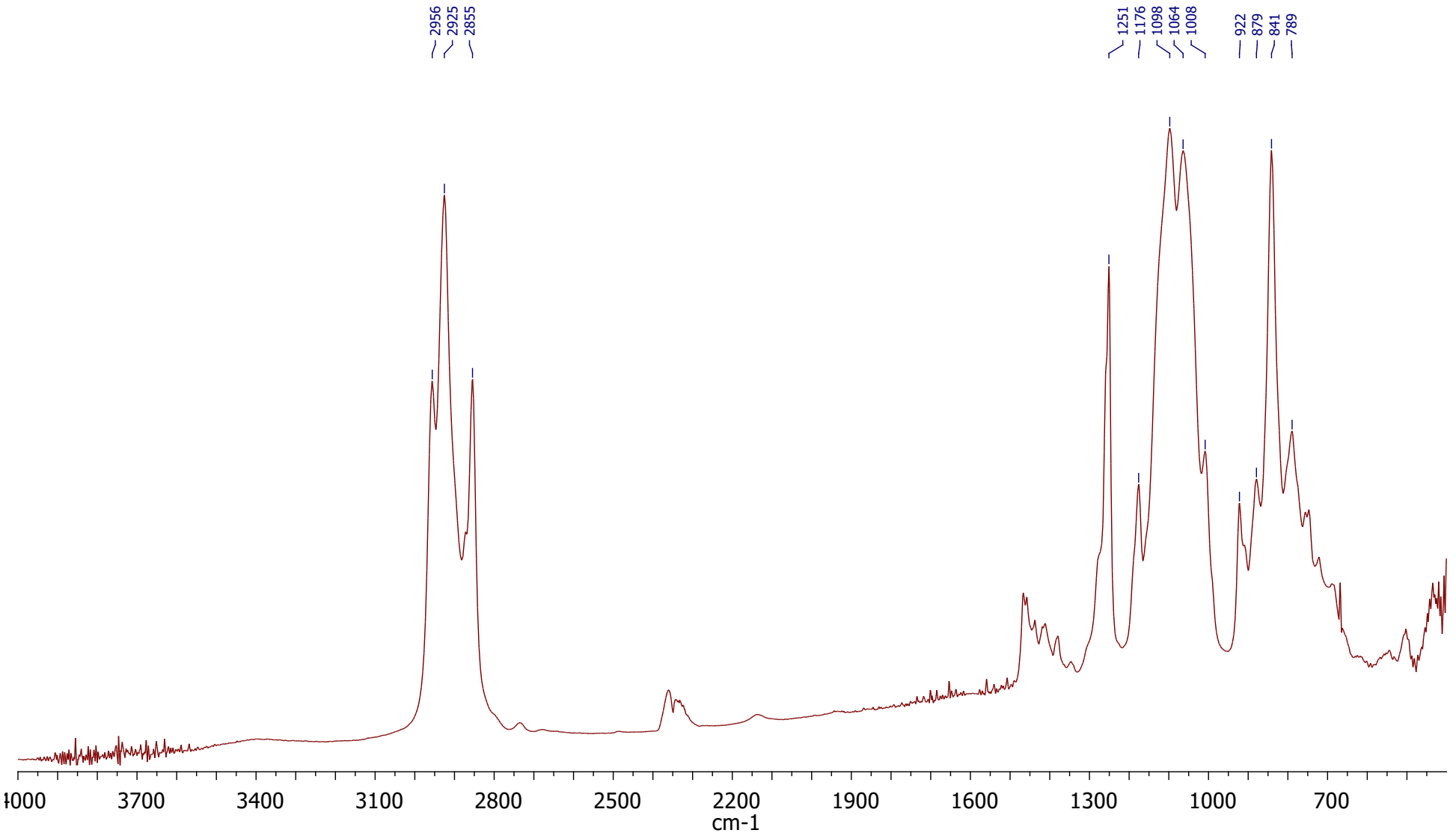


Figure 138s. IR-spectrum of compound **2.2.1**.

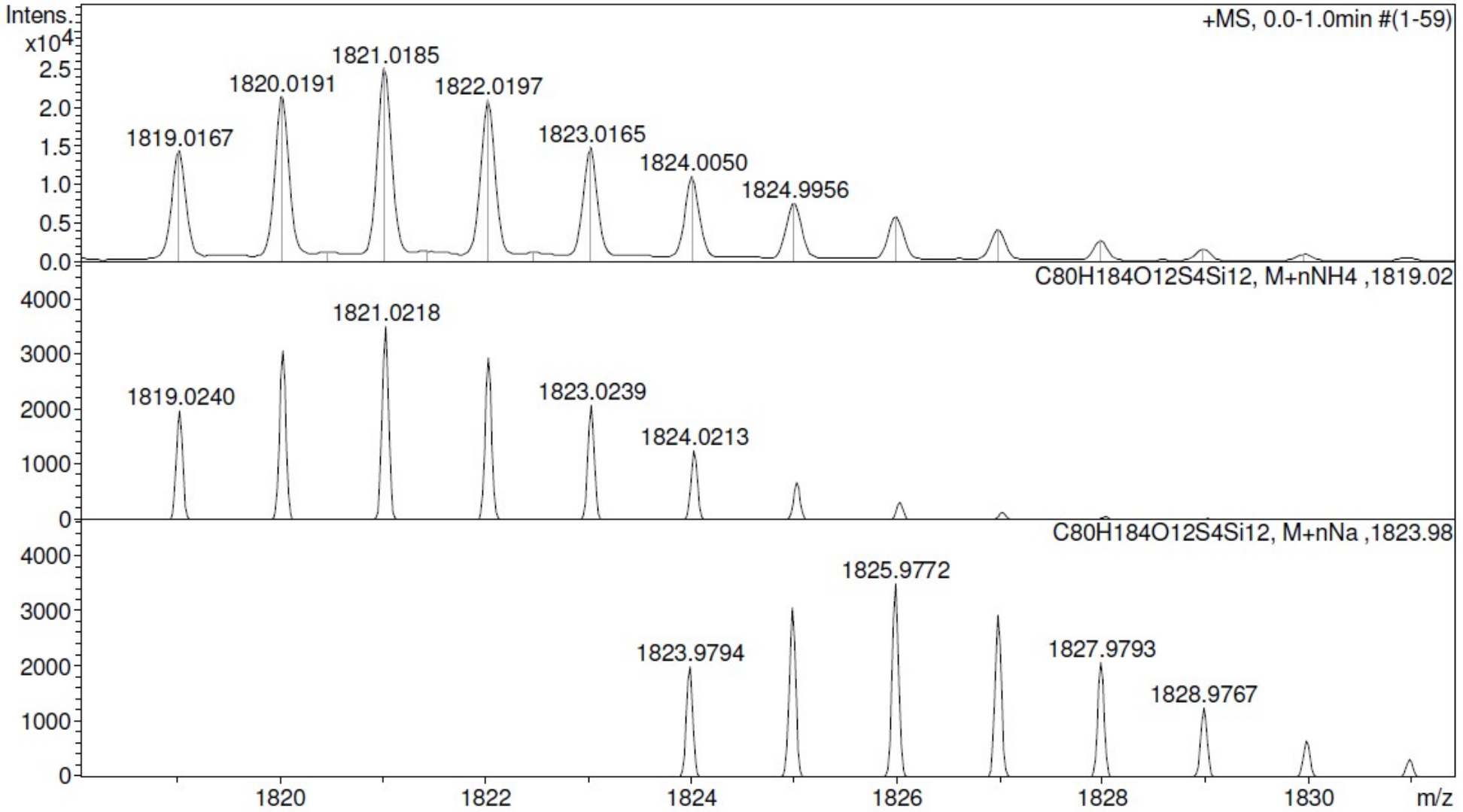


Figure 139s. HRMS (ESI) for compound **2.2.1**.

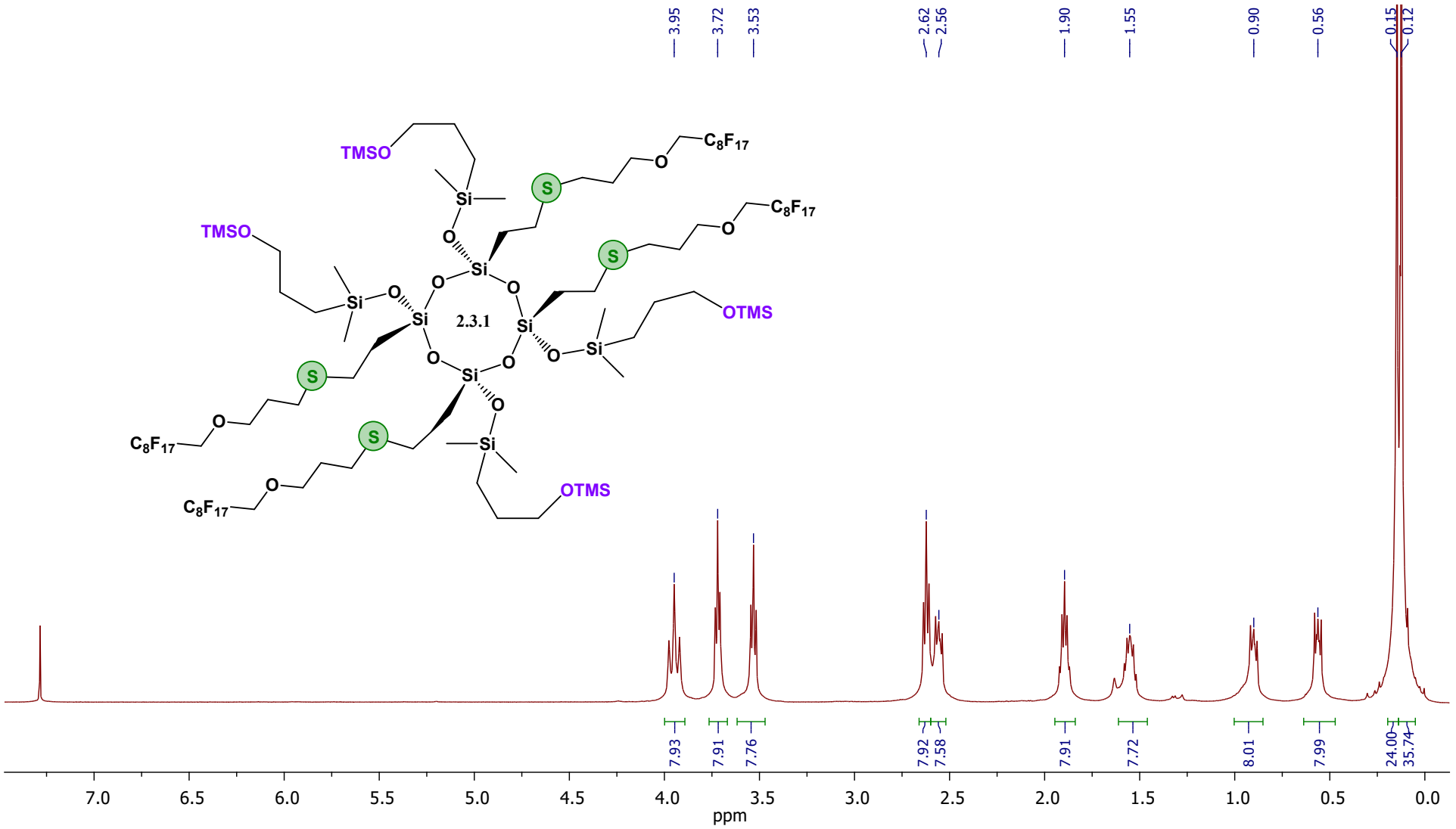


Figure 140s. ^{1}H NMR spectrum of compound **2.3.1** (500 MHz, solvent – $CDCl_3$).

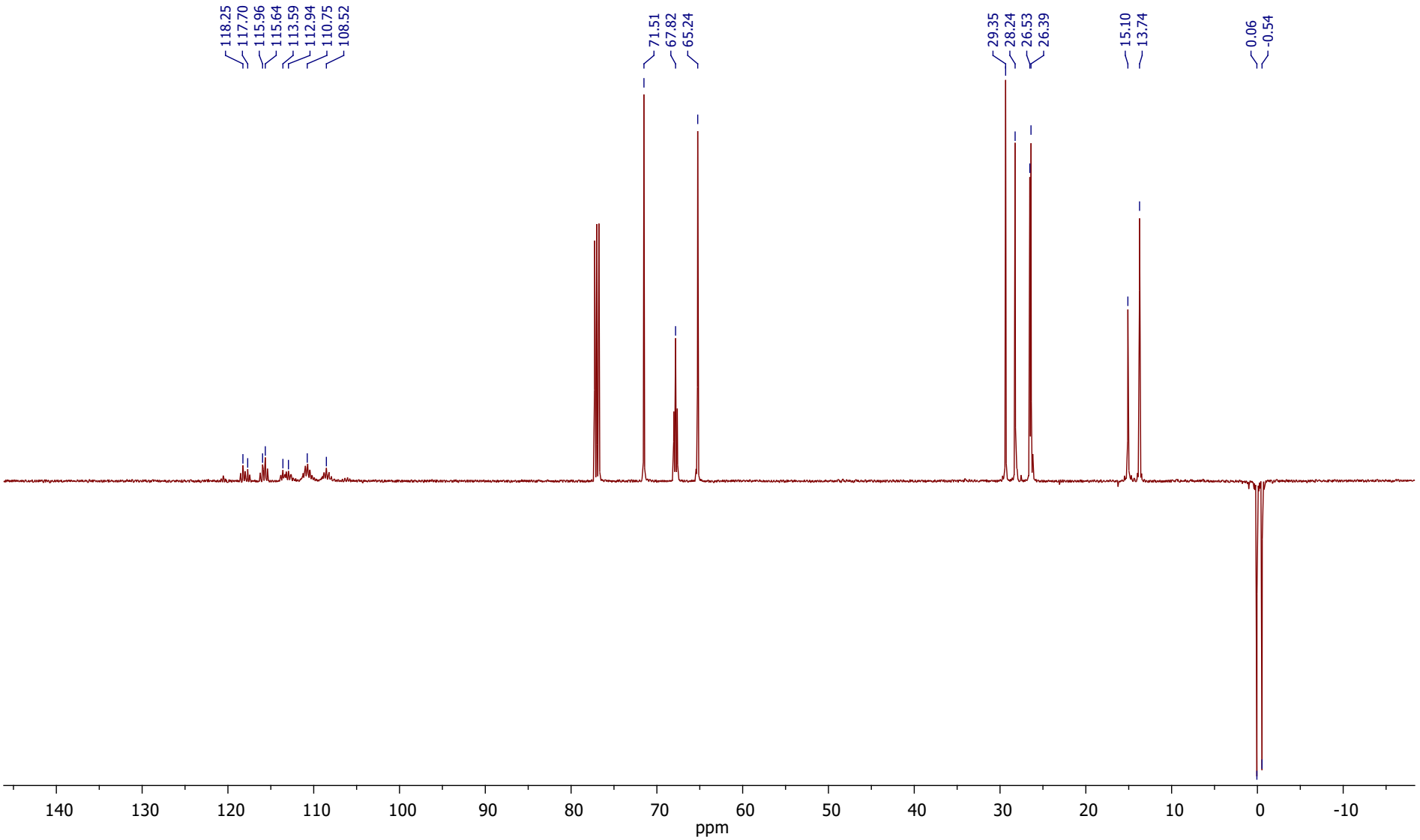


Figure 141s. ^{13}C NMR spectrum of compound **2.3.1** (500 MHz, solvent – $CDCl_3$, jmod).

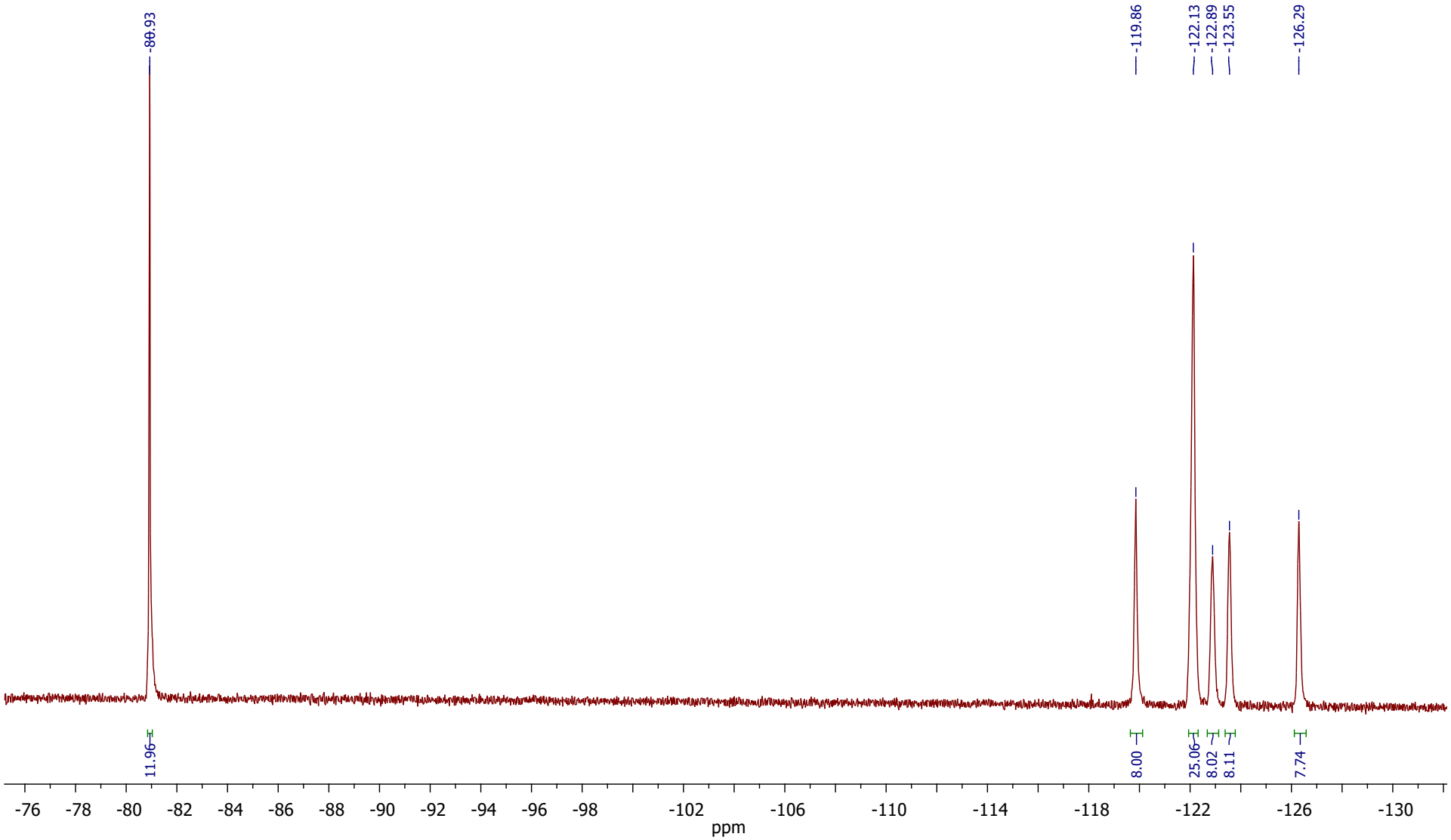


Figure 142s. ^{19}F NMR spectrum of compound **2.3.1** (300 MHz, solvent – $CDCl_3$).

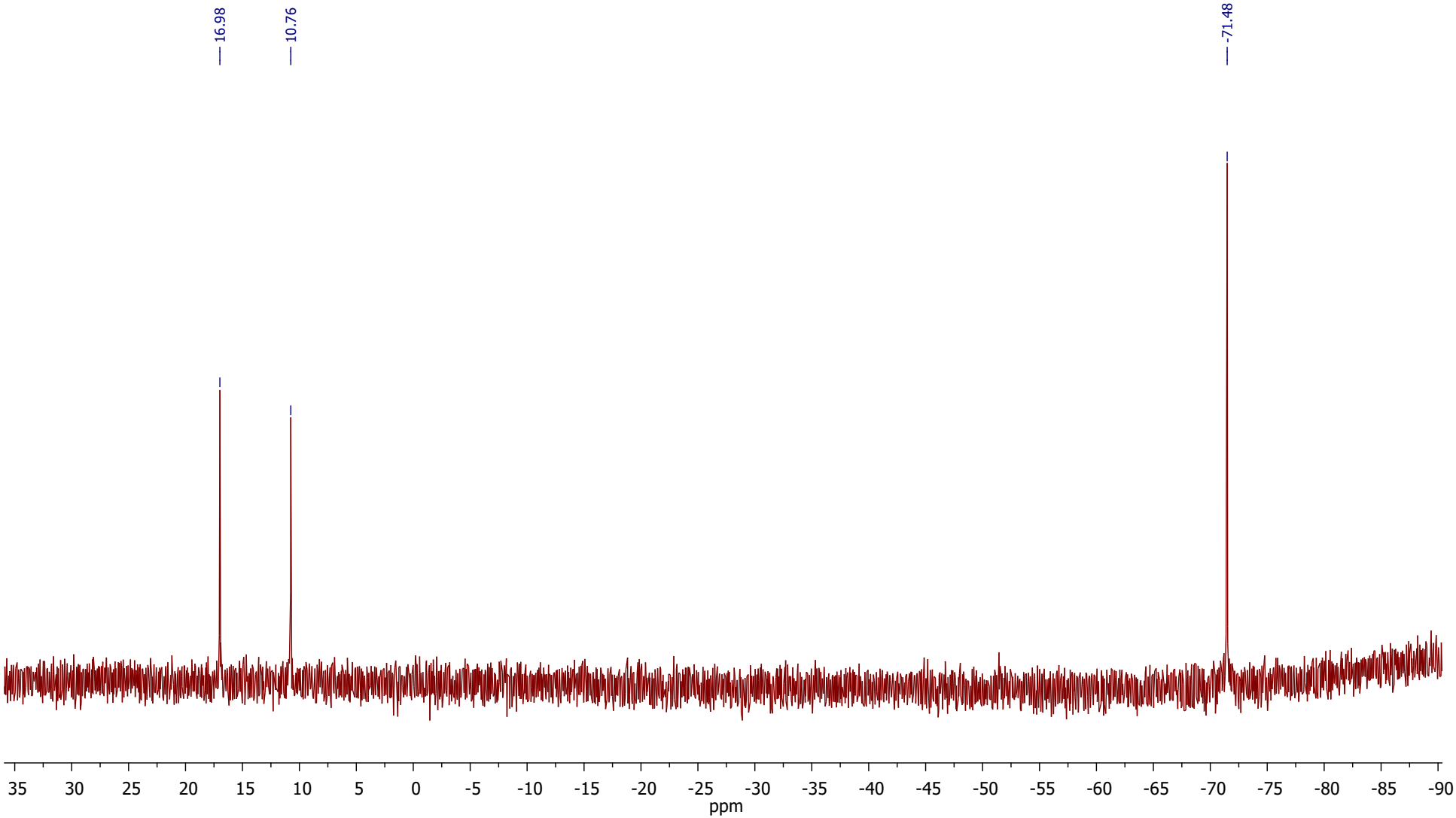


Figure 143s. ^{29}Si NMR spectrum of compound **2.3.1** (500 MHz, solvent – $CDCl_3$).

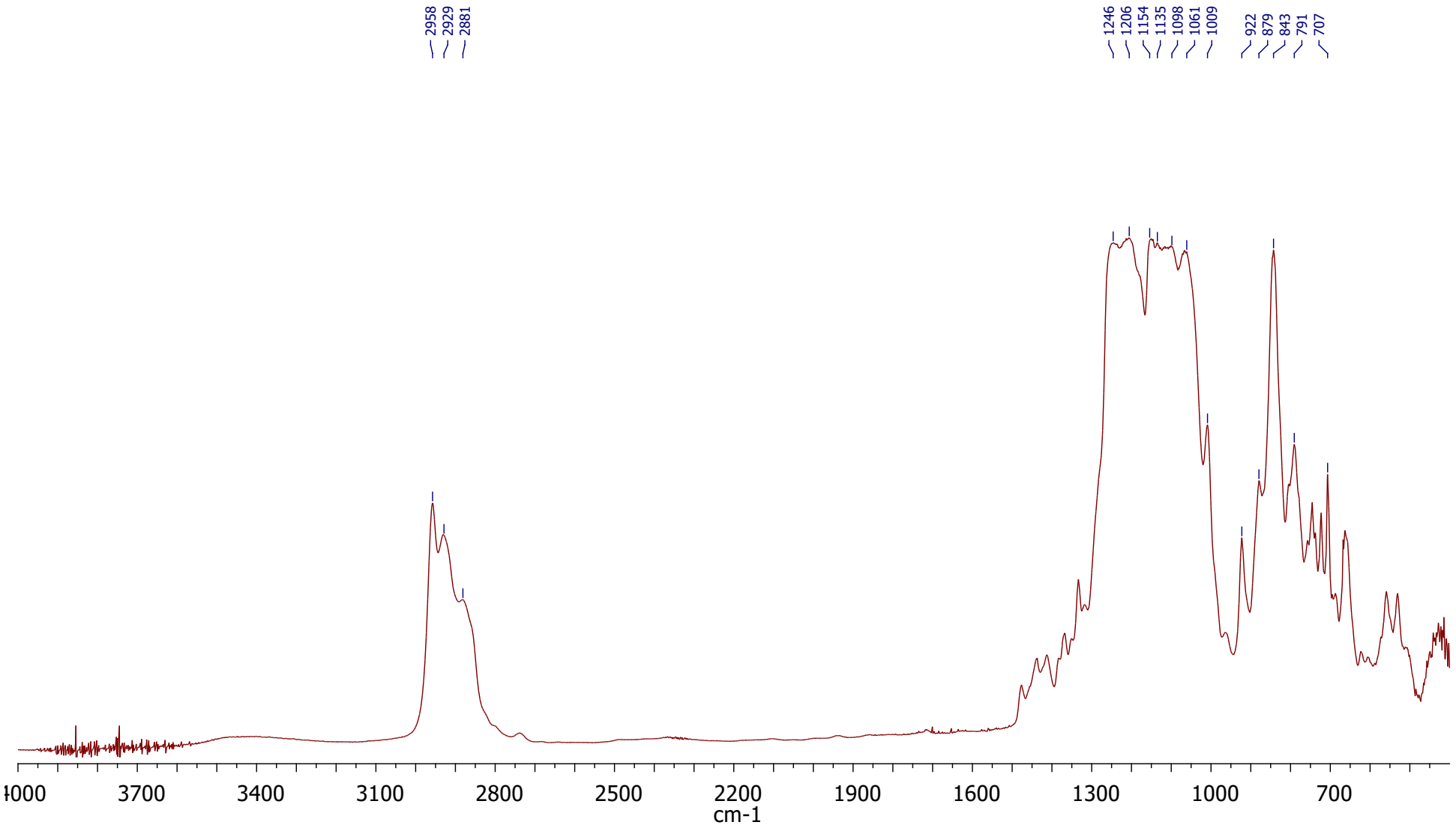


Figure 144s. IR-spectrum of compound **2.3.1**.

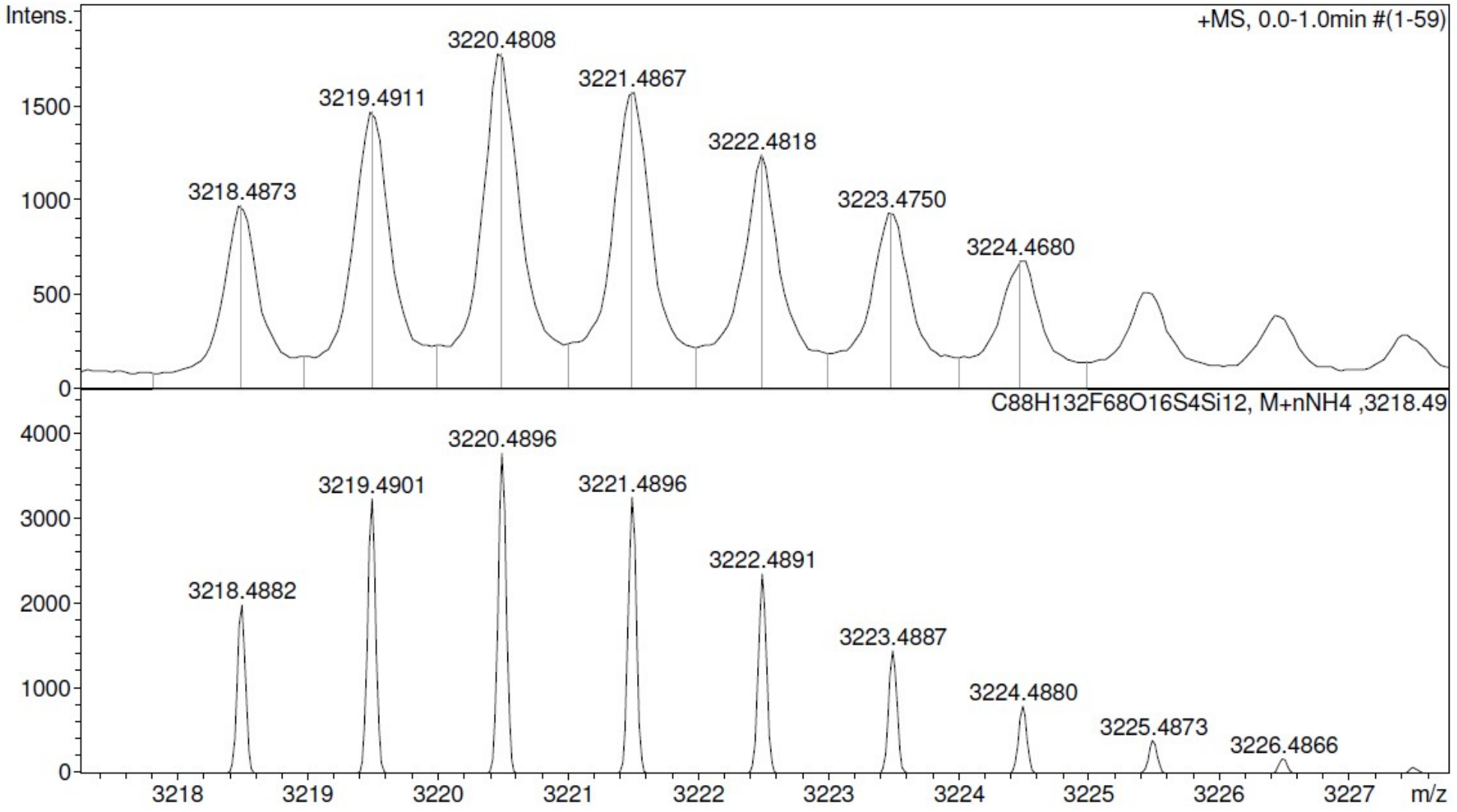


Figure 145s. HRMS (ESI) for compound **2.3.1**.

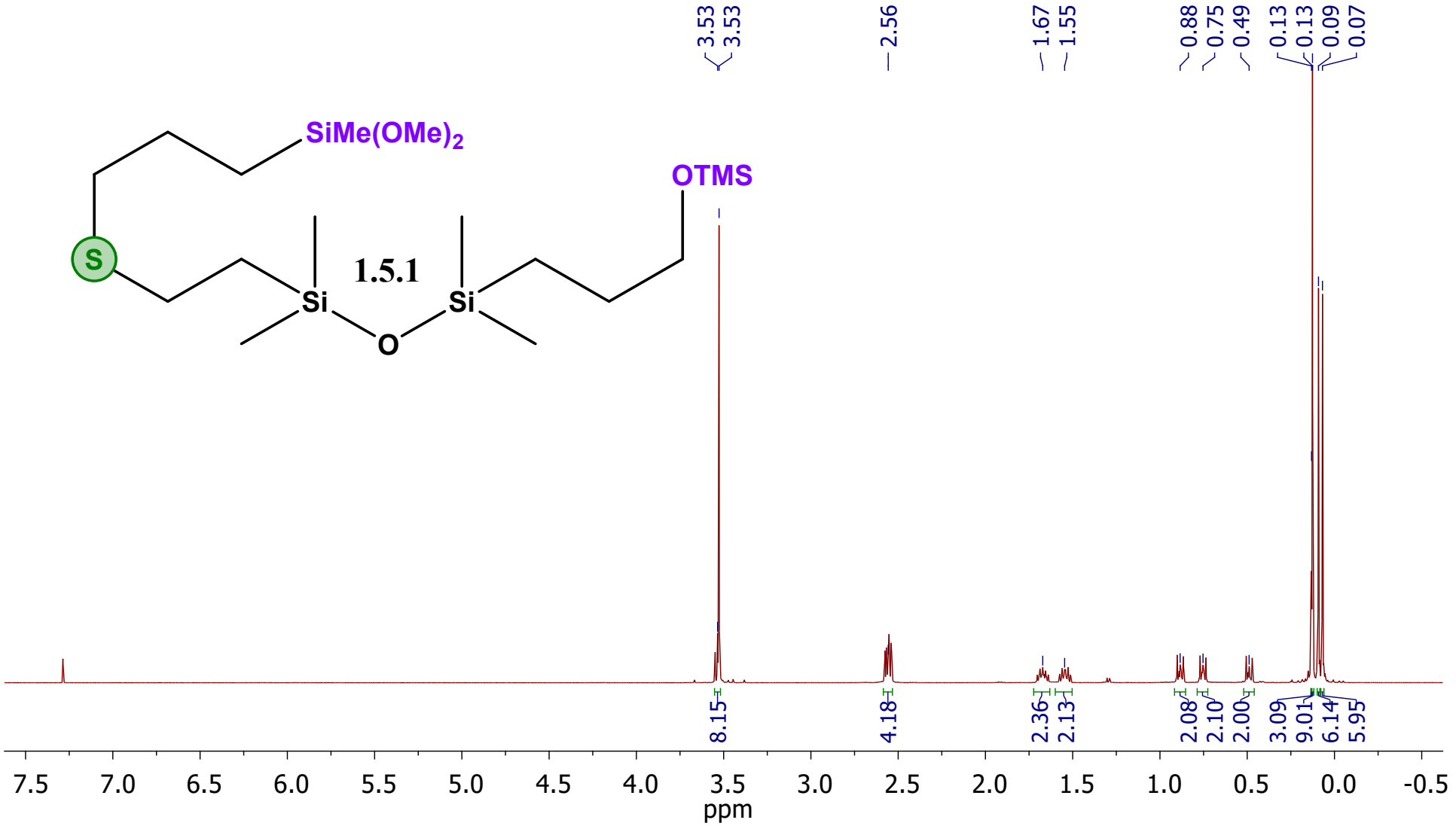


Figure 146s. ^{1}H NMR spectrum of compound **1.5.1** (500 MHz, solvent – $CDCl_3$).

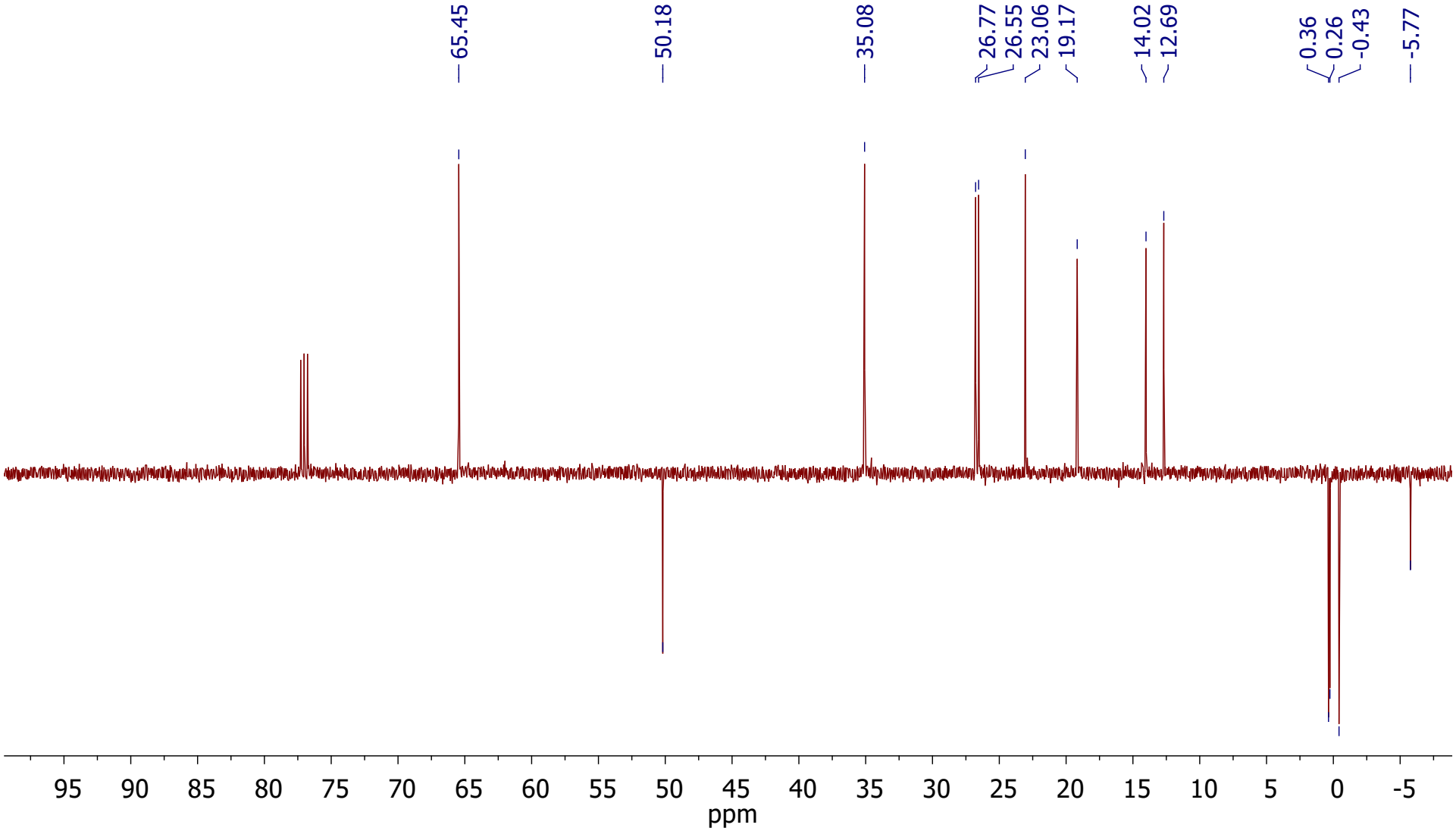


Figure 147s. ^{13}C NMR spectrum of compound **1.5.1** (500 MHz, solvent – $CDCl_3$, jmod).

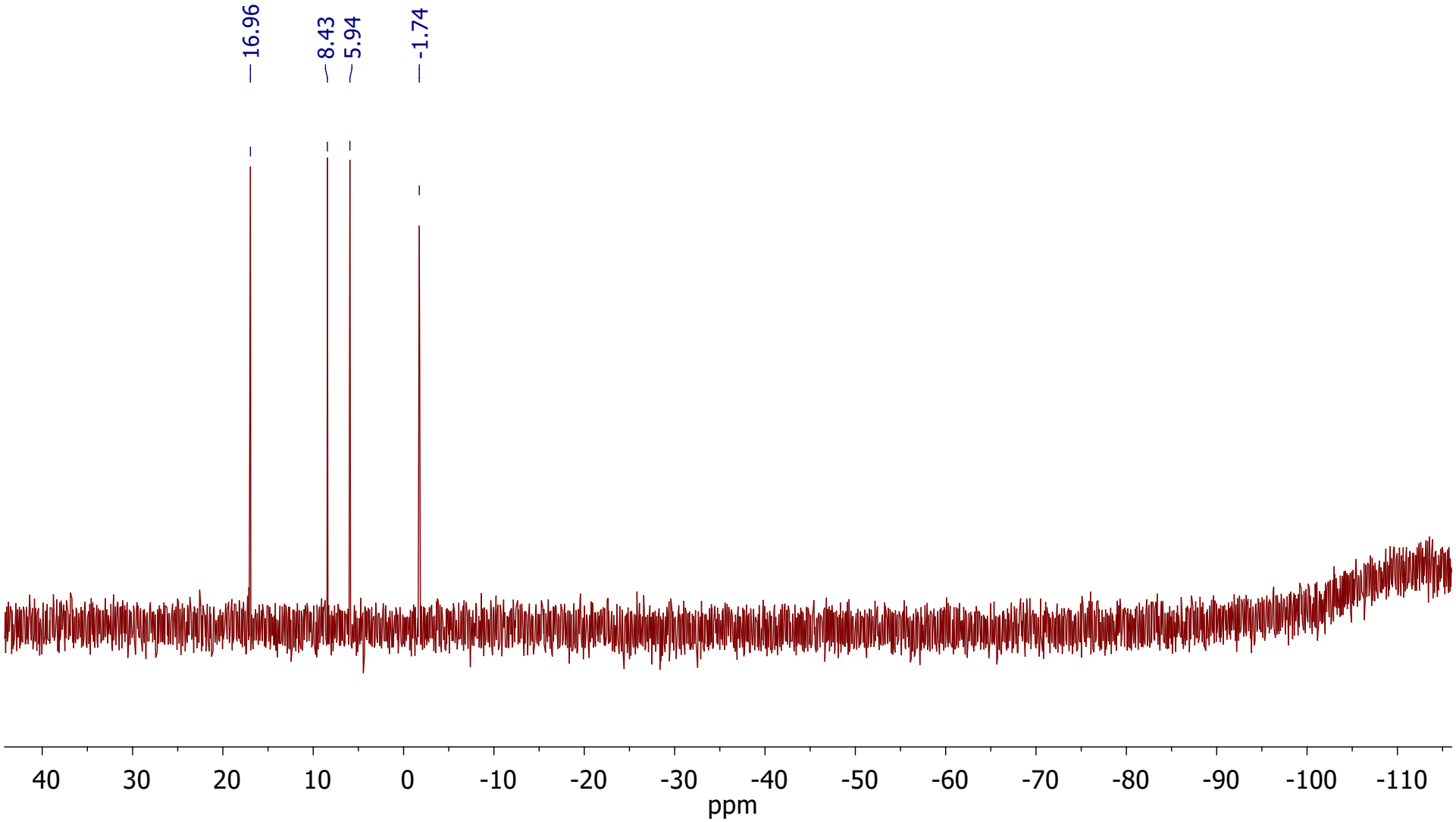


Figure 148s. ^{29}Si NMR spectrum of compound **1.5.1** (500 MHz, solvent – $CDCl_3$).

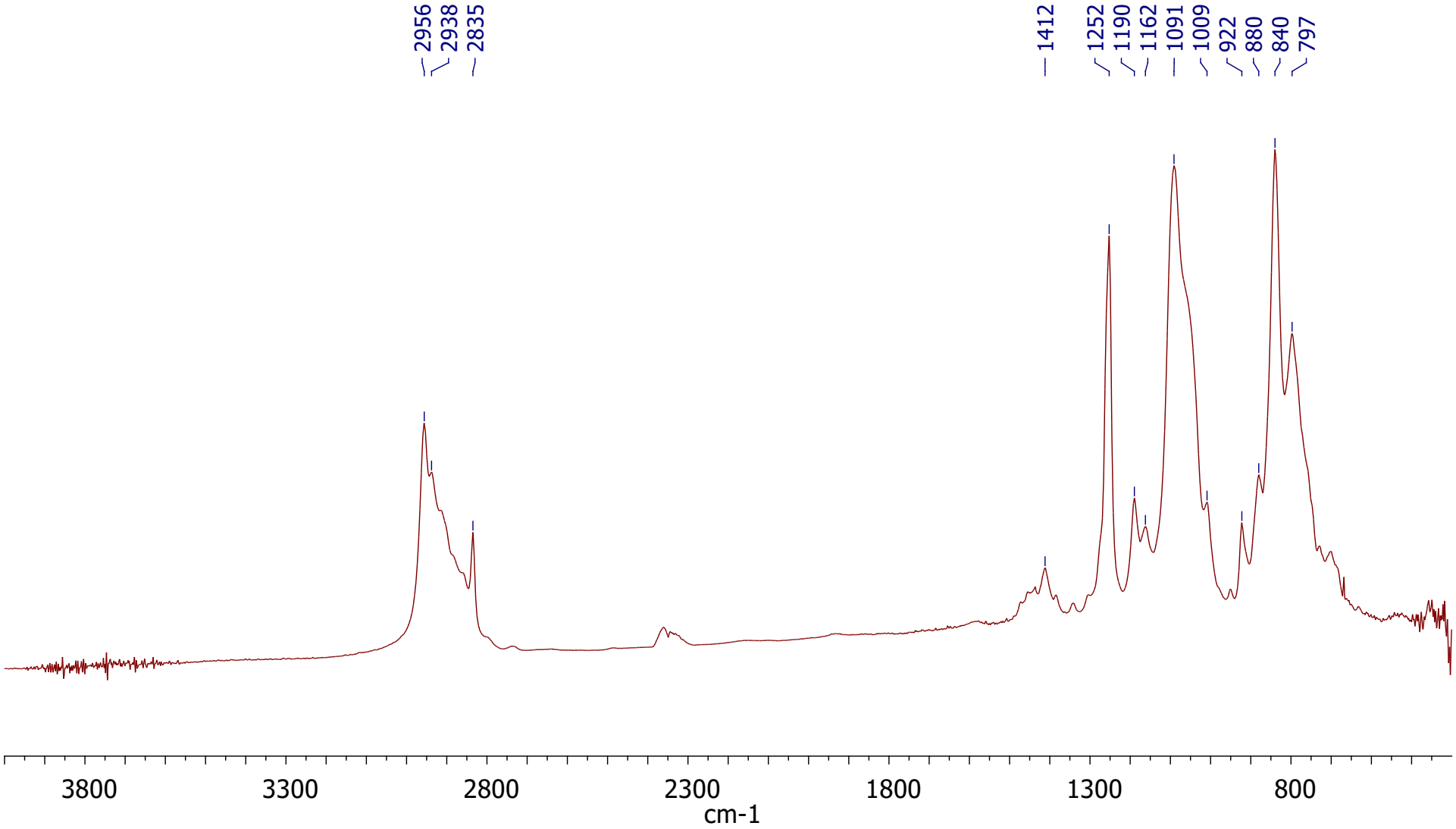


Figure 149s. IR-spectrum of compound **1.5.1**.

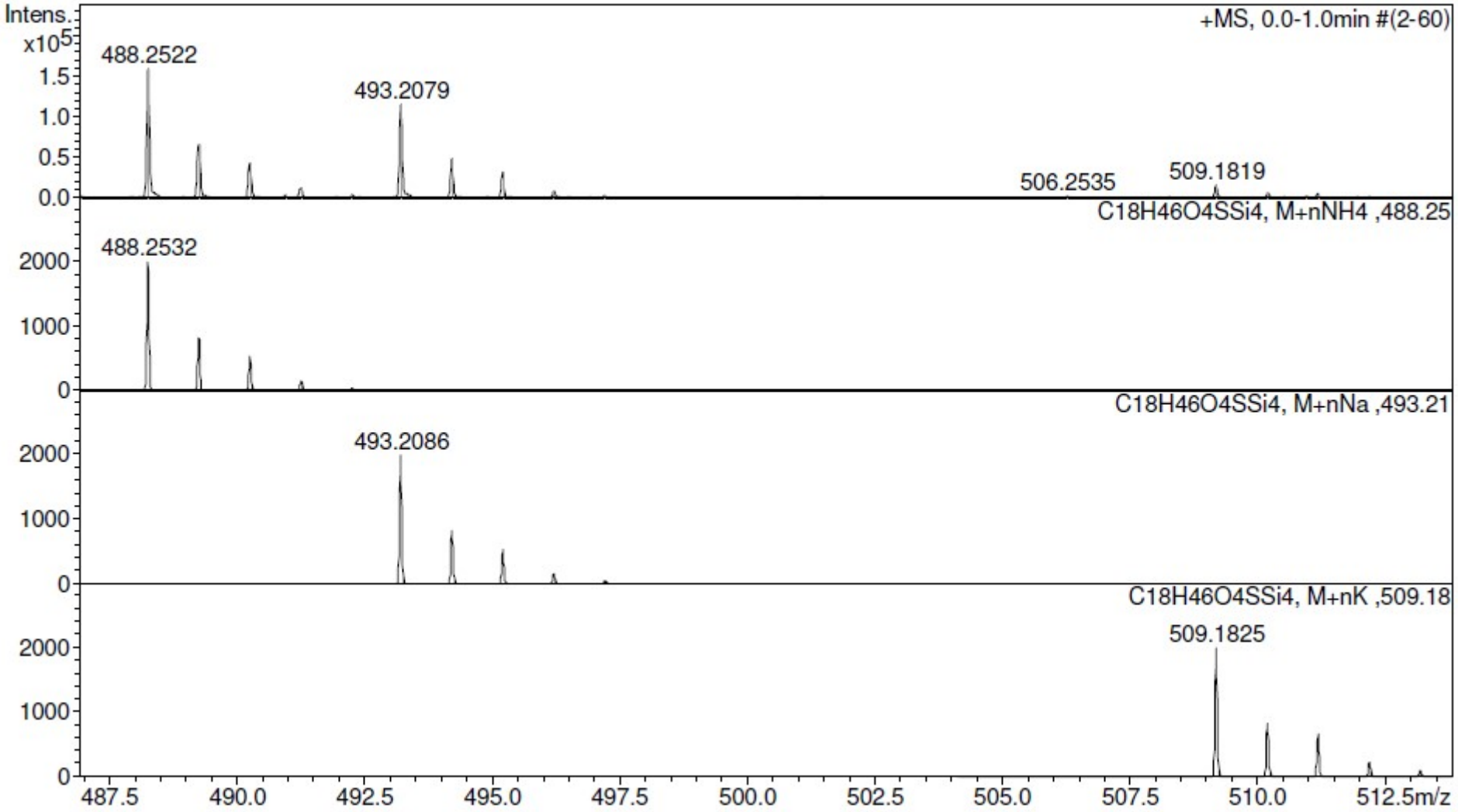


Figure 150s. HRMS (ESI) for compound **1.5.1**.

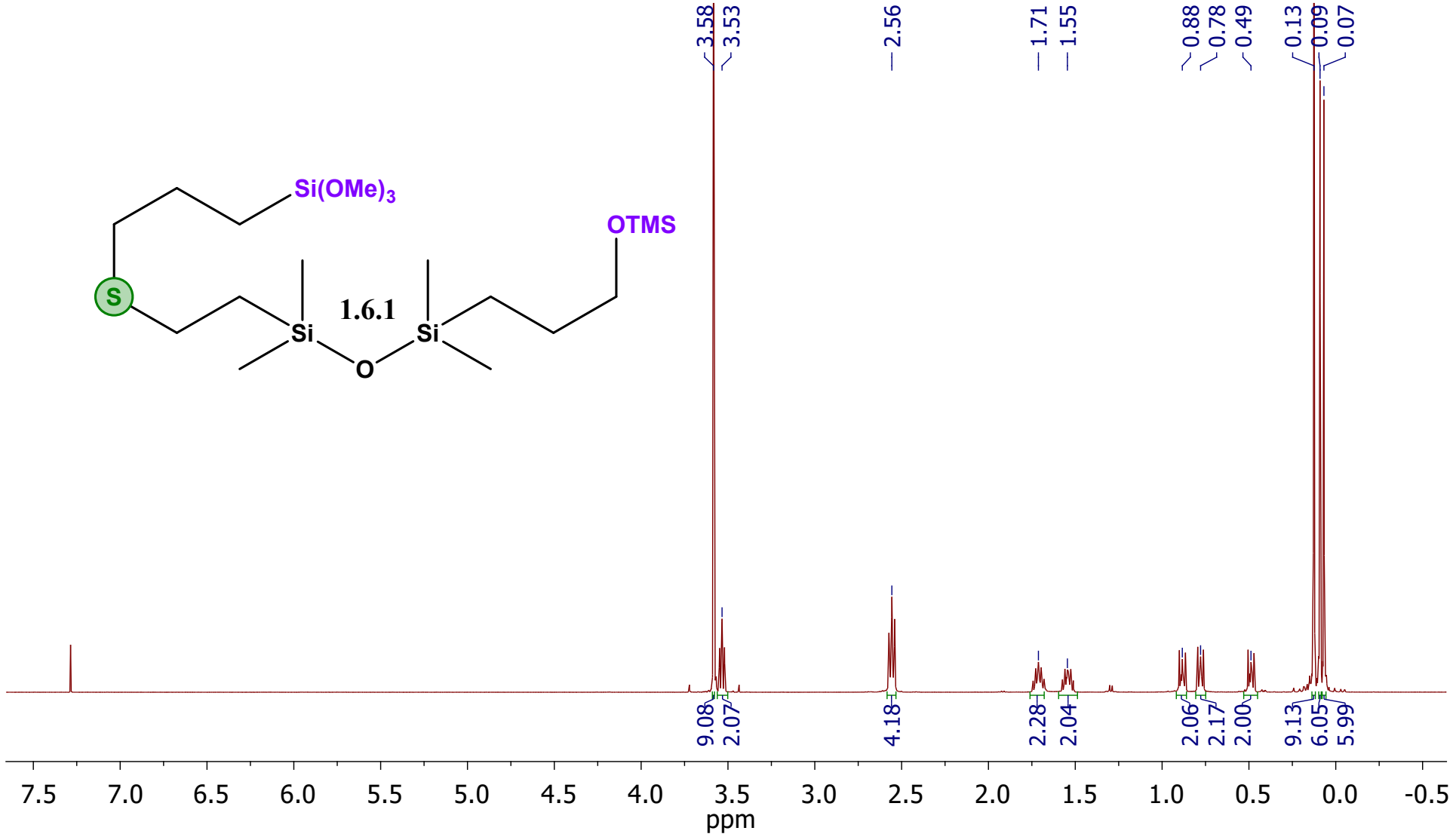


Figure 151s. ^{1}H NMR spectrum of compound **1.6.1** (500 MHz, solvent – $CDCl_3$).

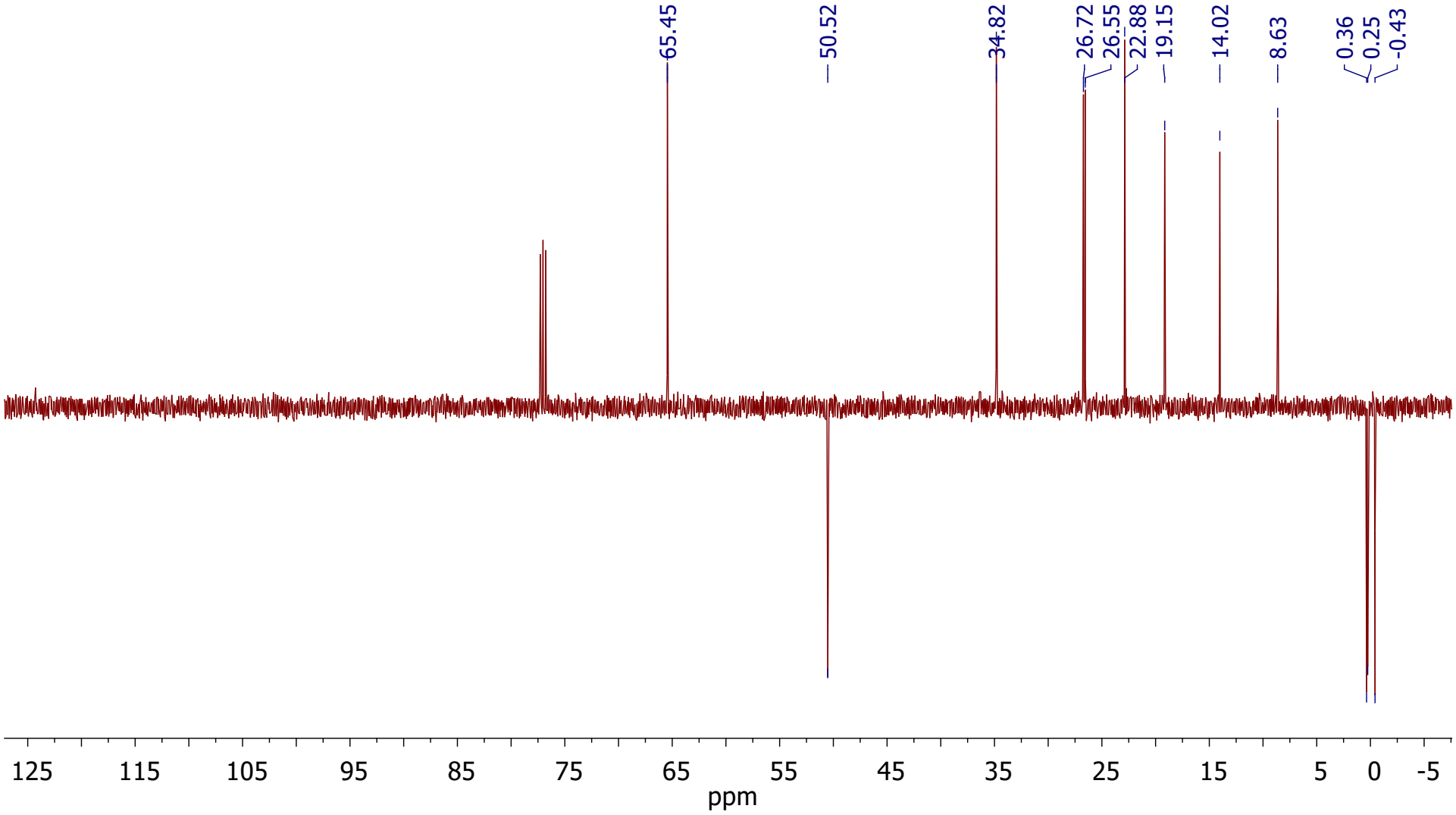


Figure 152s. ^{13}C NMR spectrum of compound **1.6.1** (500 MHz, solvent – $CDCl_3$, jmod).

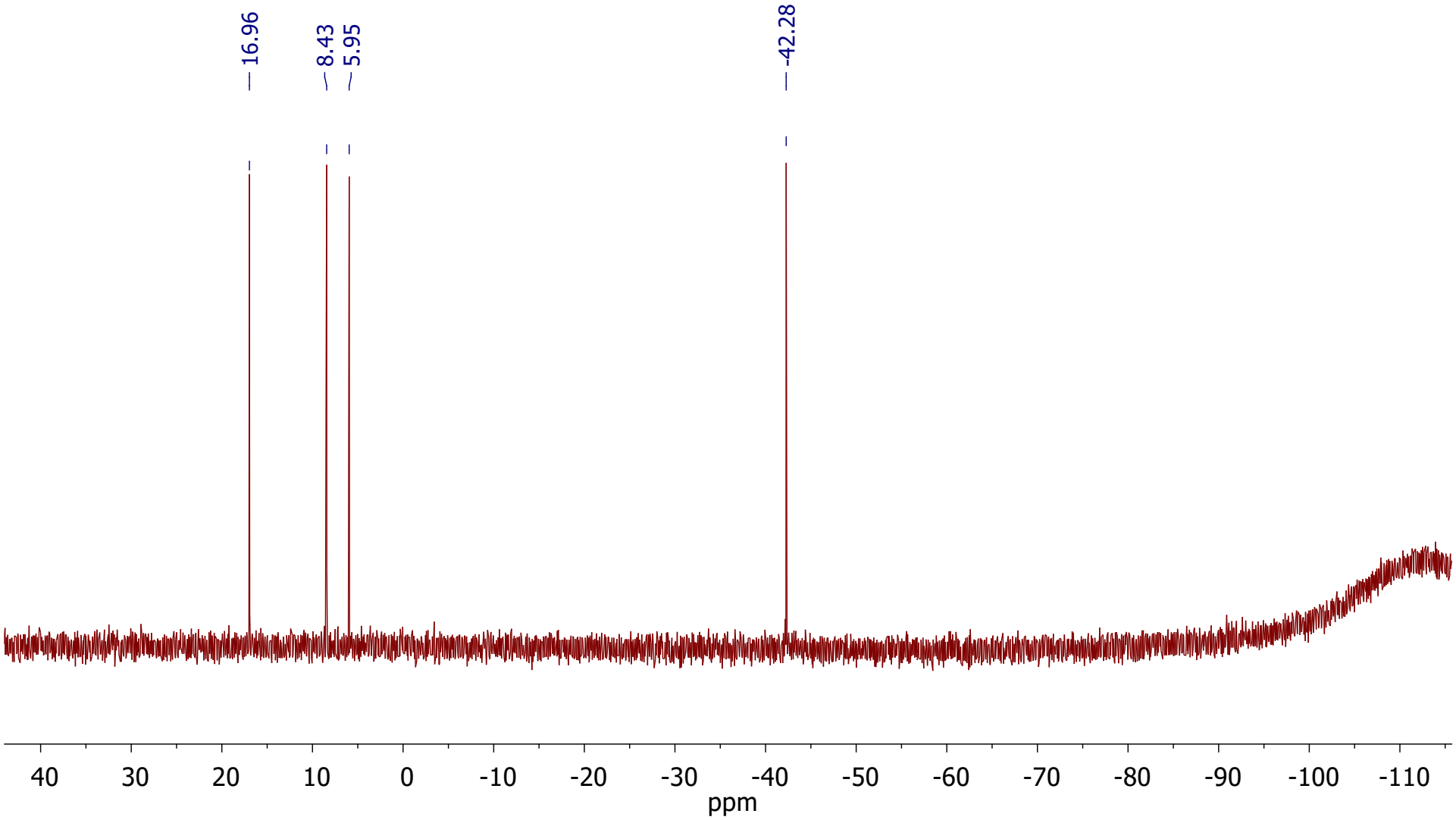


Figure 153s. ^{29}Si NMR spectrum of compound **1.6.1** (500 MHz, solvent – $CDCl_3$).

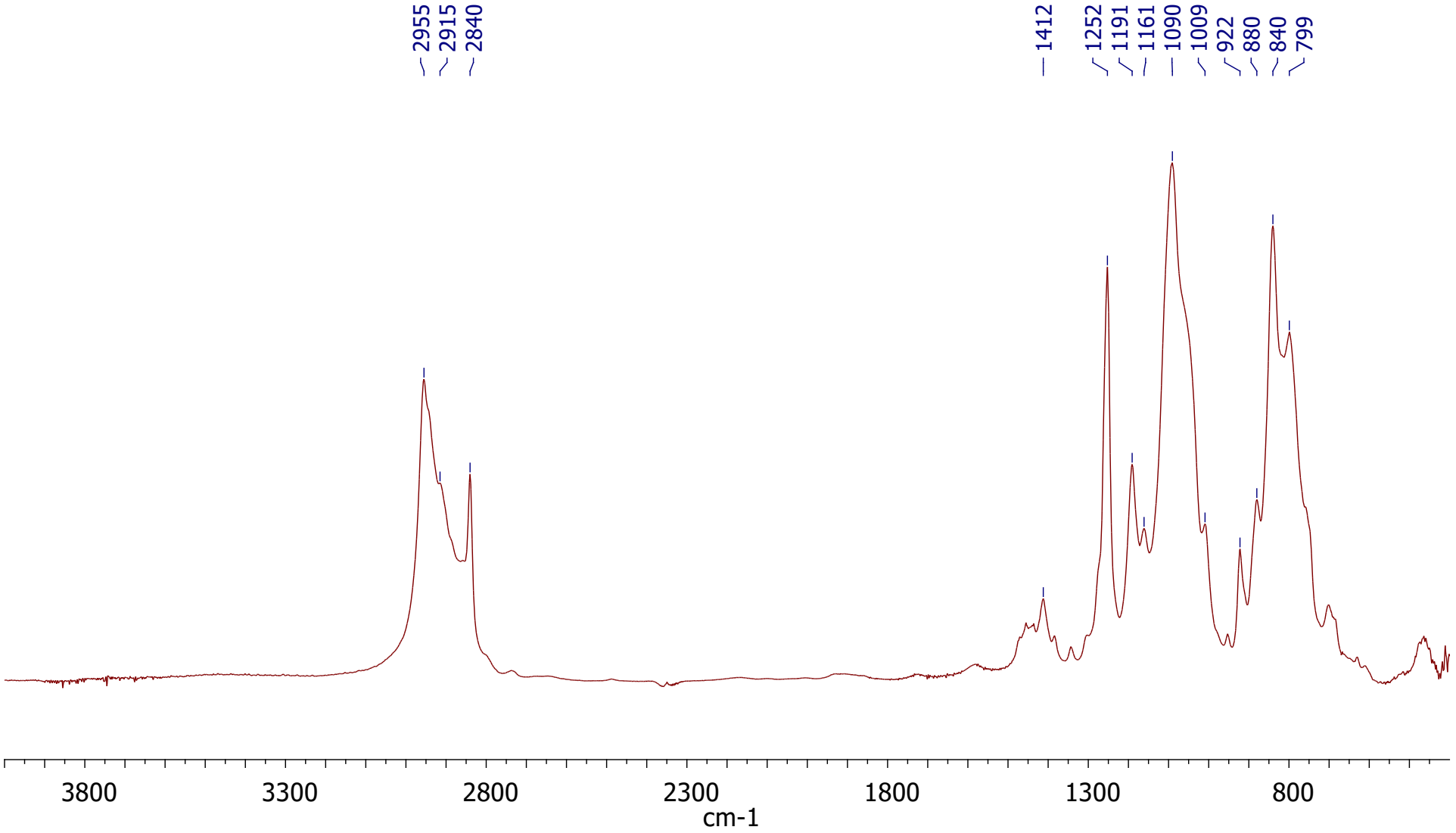


Figure 154s. IR-spectrum of compound **1.6.1**.

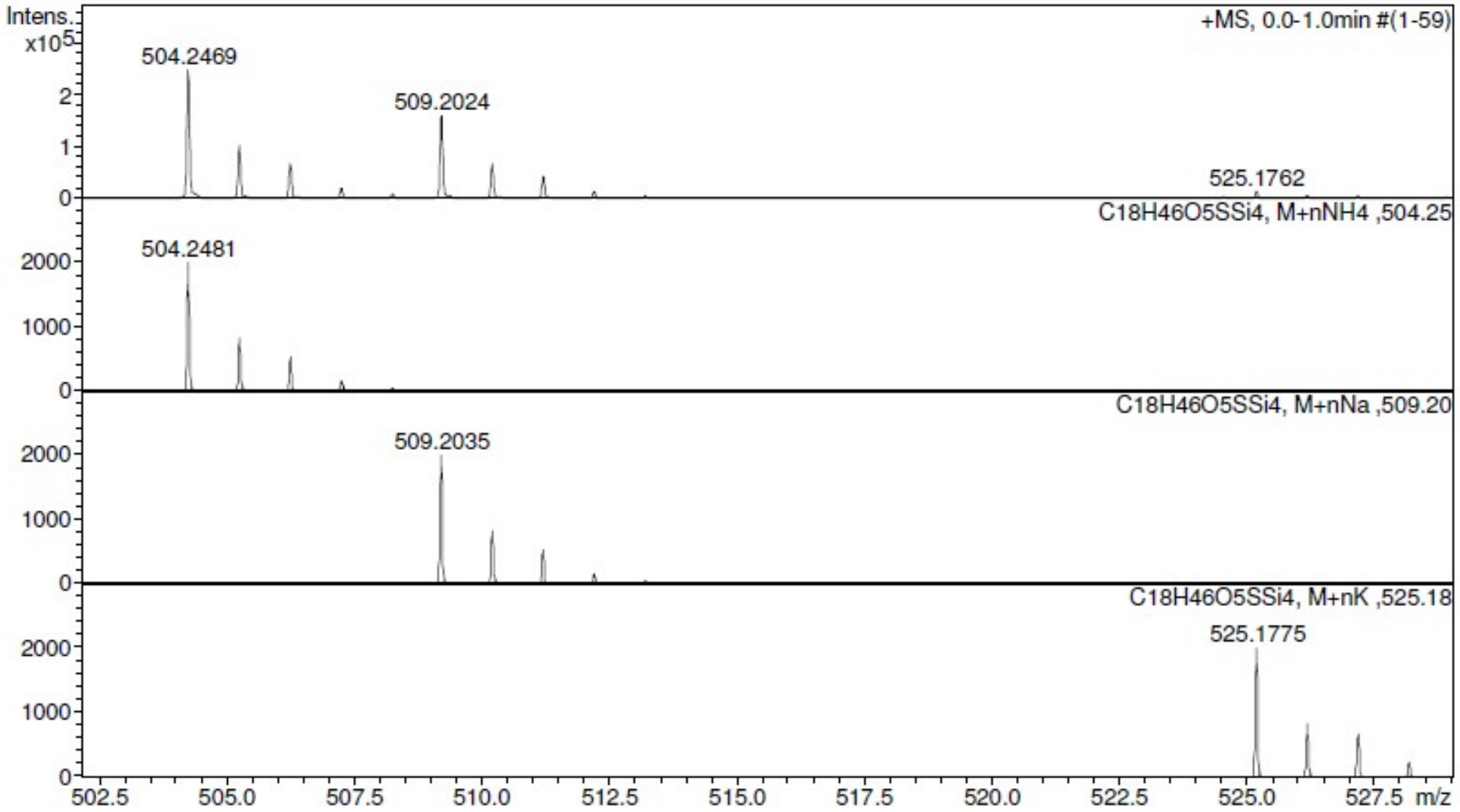


Figure 155s. HRMS (ESI) for compound **1.6.1**.

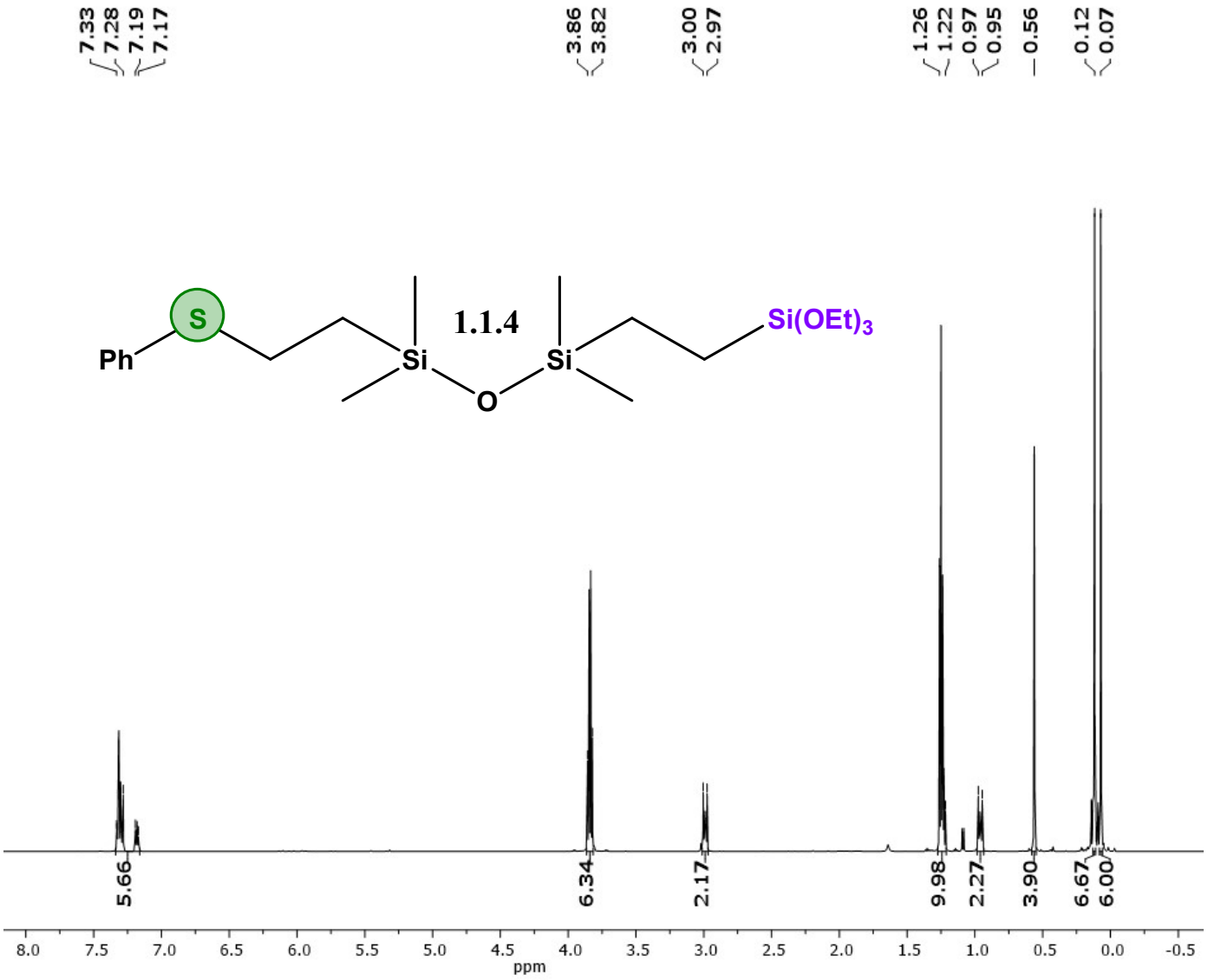


Figure 156s. ^{1}H NMR spectrum of compound **1.1.4** (400 MHz, solvent – $CDCl_3$).

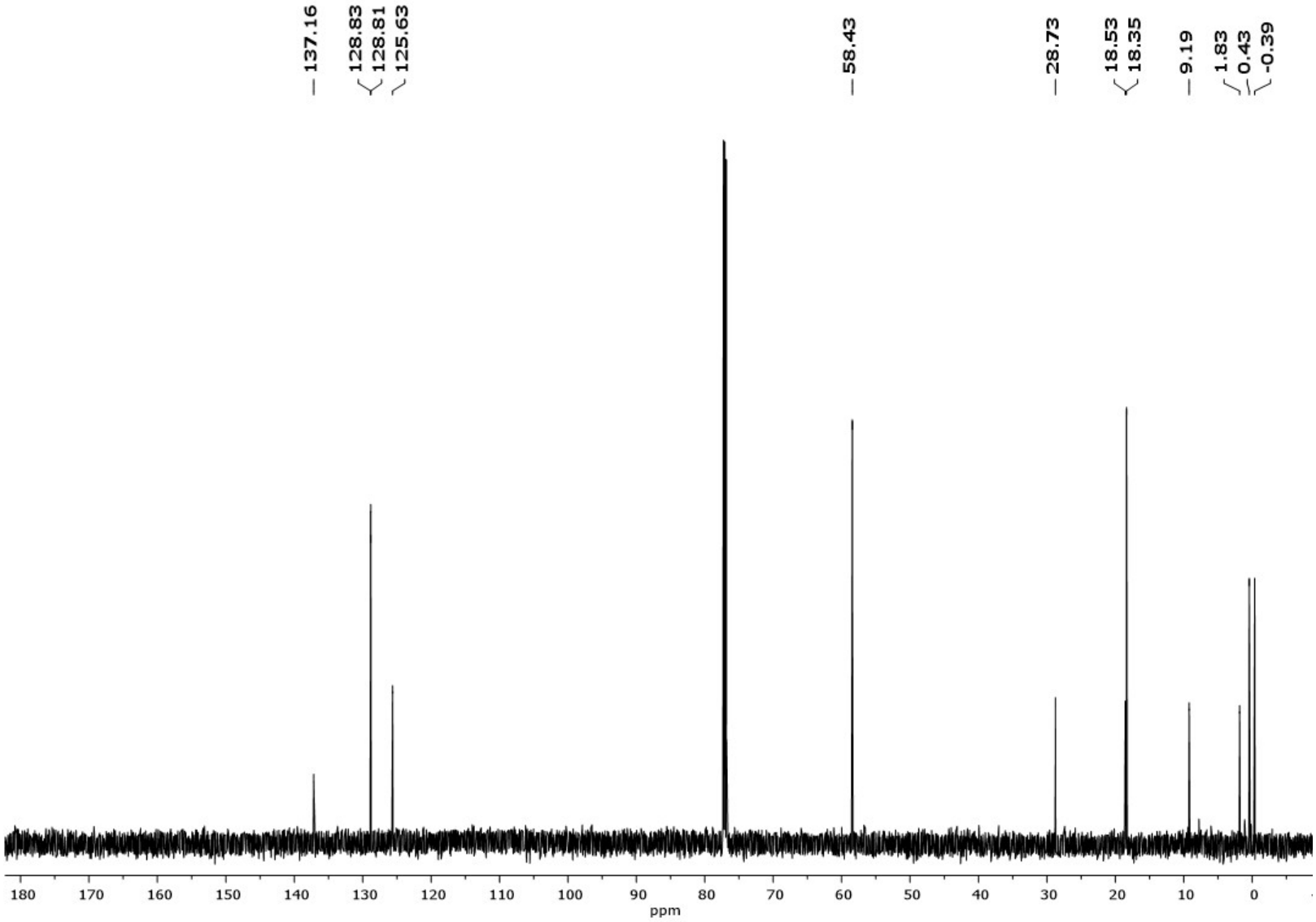


Figure 157s. ^{13}C NMR spectrum of compound **1.1.4** (100 MHz, solvent – $CDCl_3$).

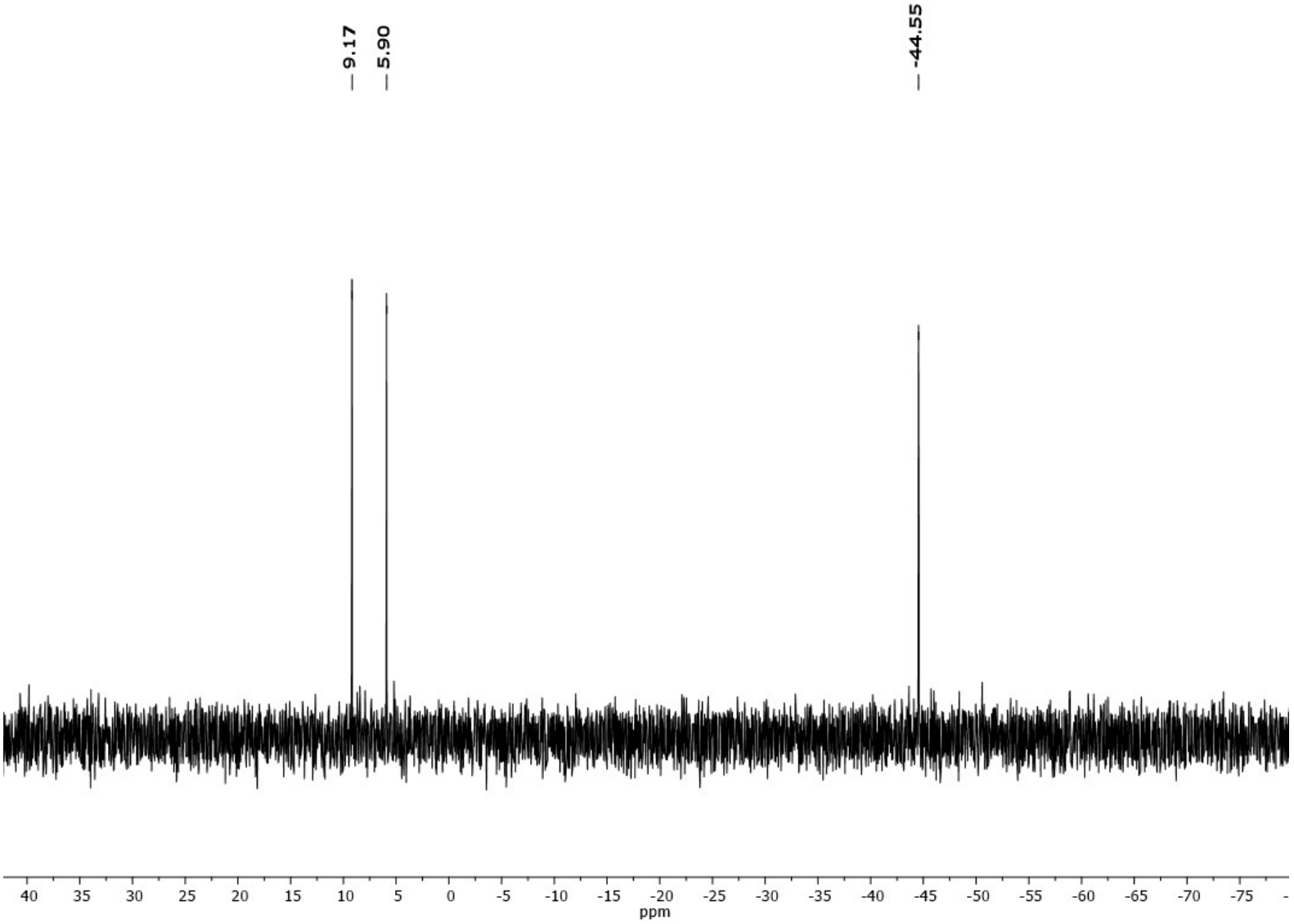


Figure 158s. ^{29}Si NMR spectrum of compound **1.1.4** (80 MHz, solvent – $CDCl_3$).

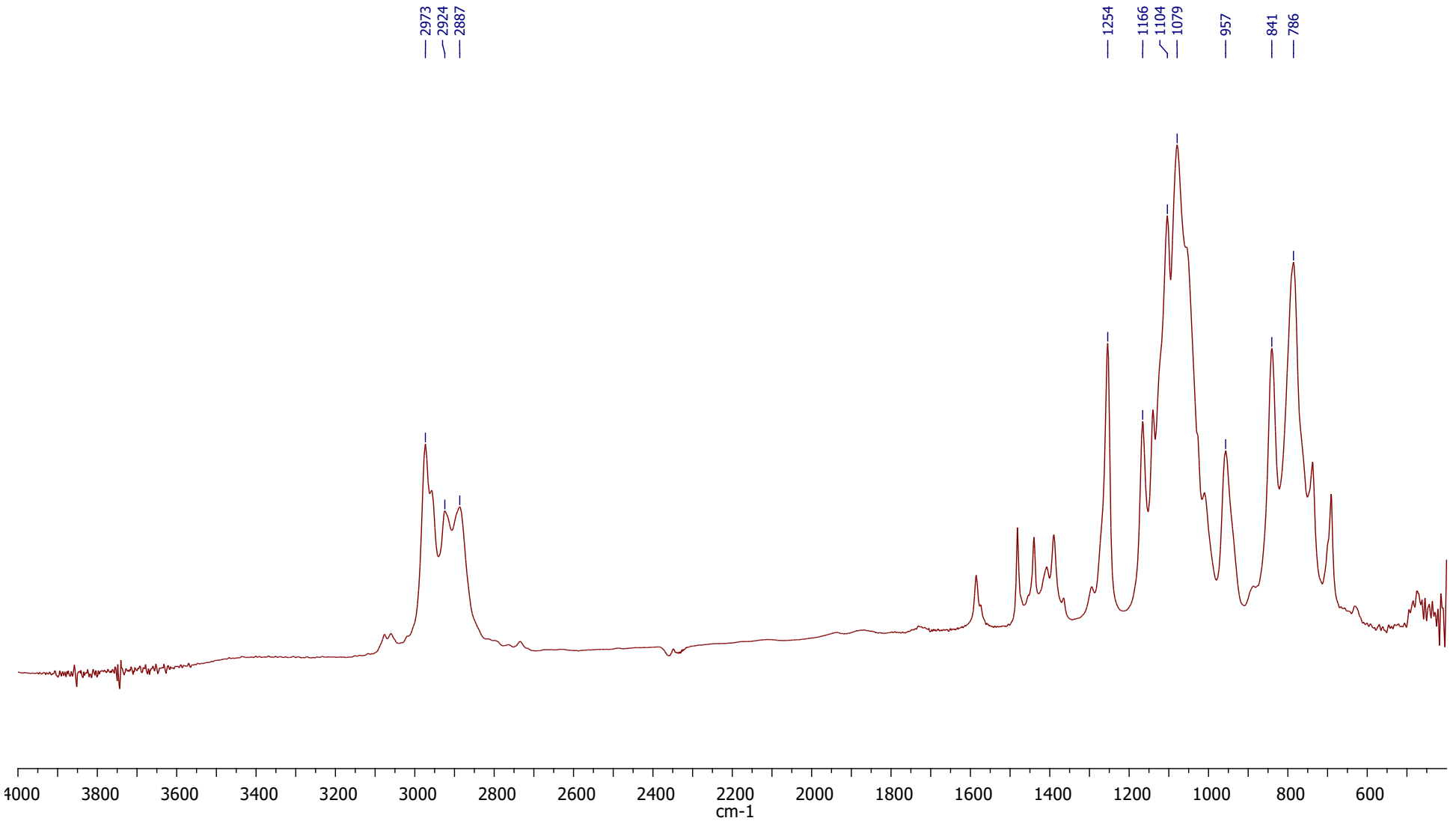


Figure 159s. IR-spectrum of compound **1.1.4**.

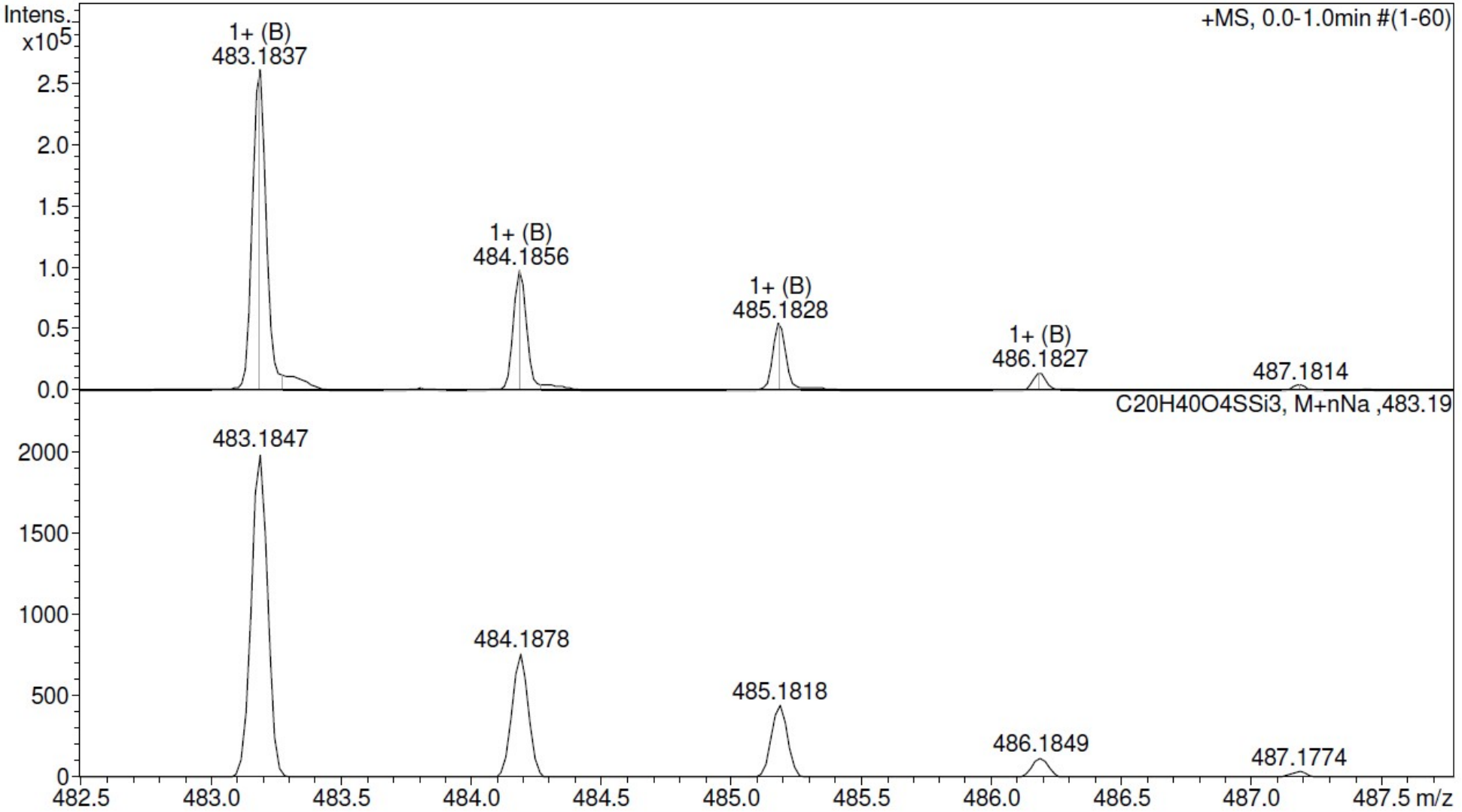


Figure 160s. HRMS (ESI) for compound **1.1.6**.

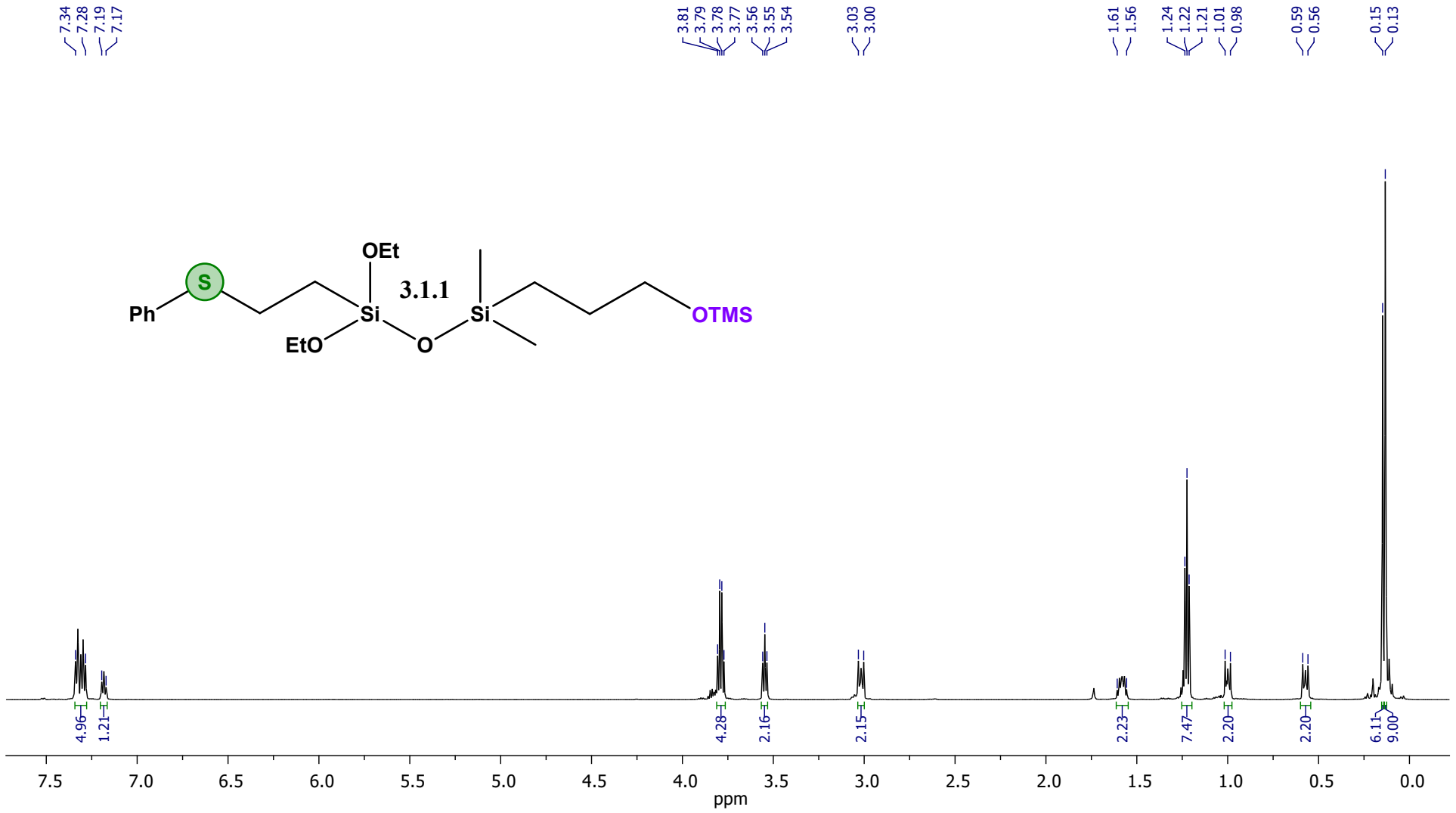


Figure 161s. ^{1}H NMR spectrum of compound **3.1.1** (400 MHz, solvent – $CDCl_3$).

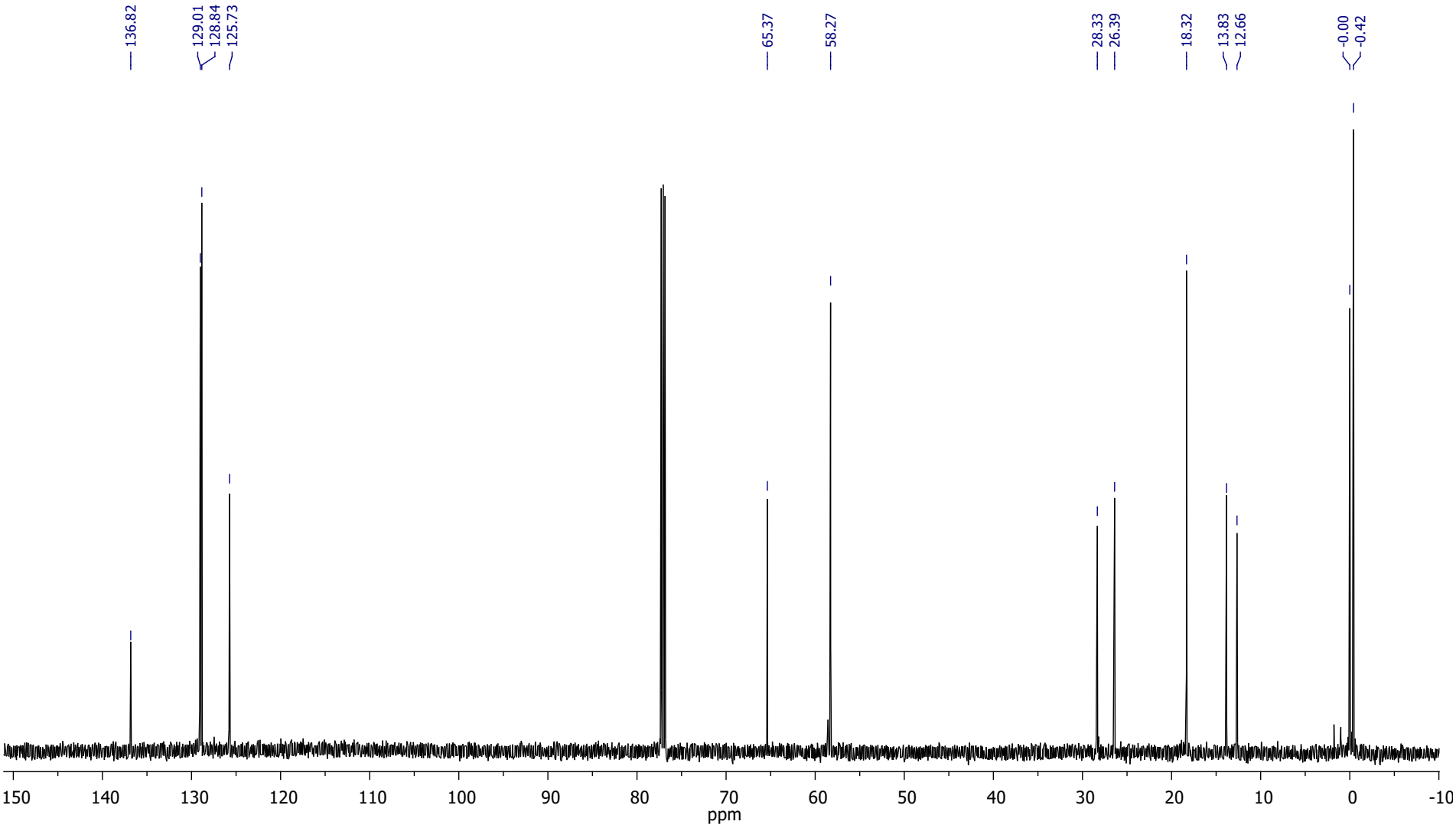
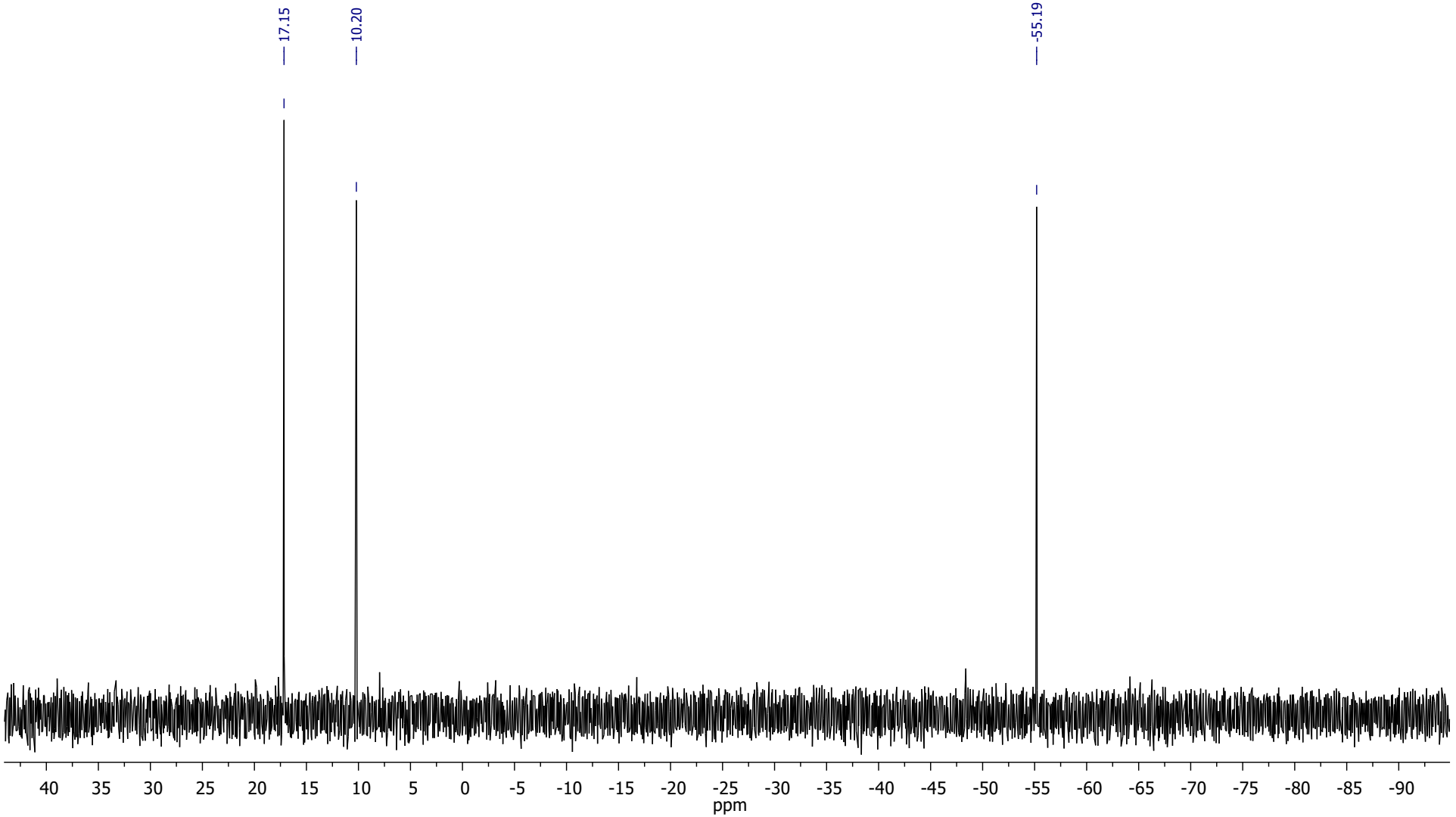


Figure 162s. ^{13}C NMR spectrum of compound **3.1.1** (400 MHz, solvent – $CDCl_3$).

Figure 163s. ^{29}Si NMR spectrum of compound **3.1.1** (400 MHz, solvent – $CDCl_3$).



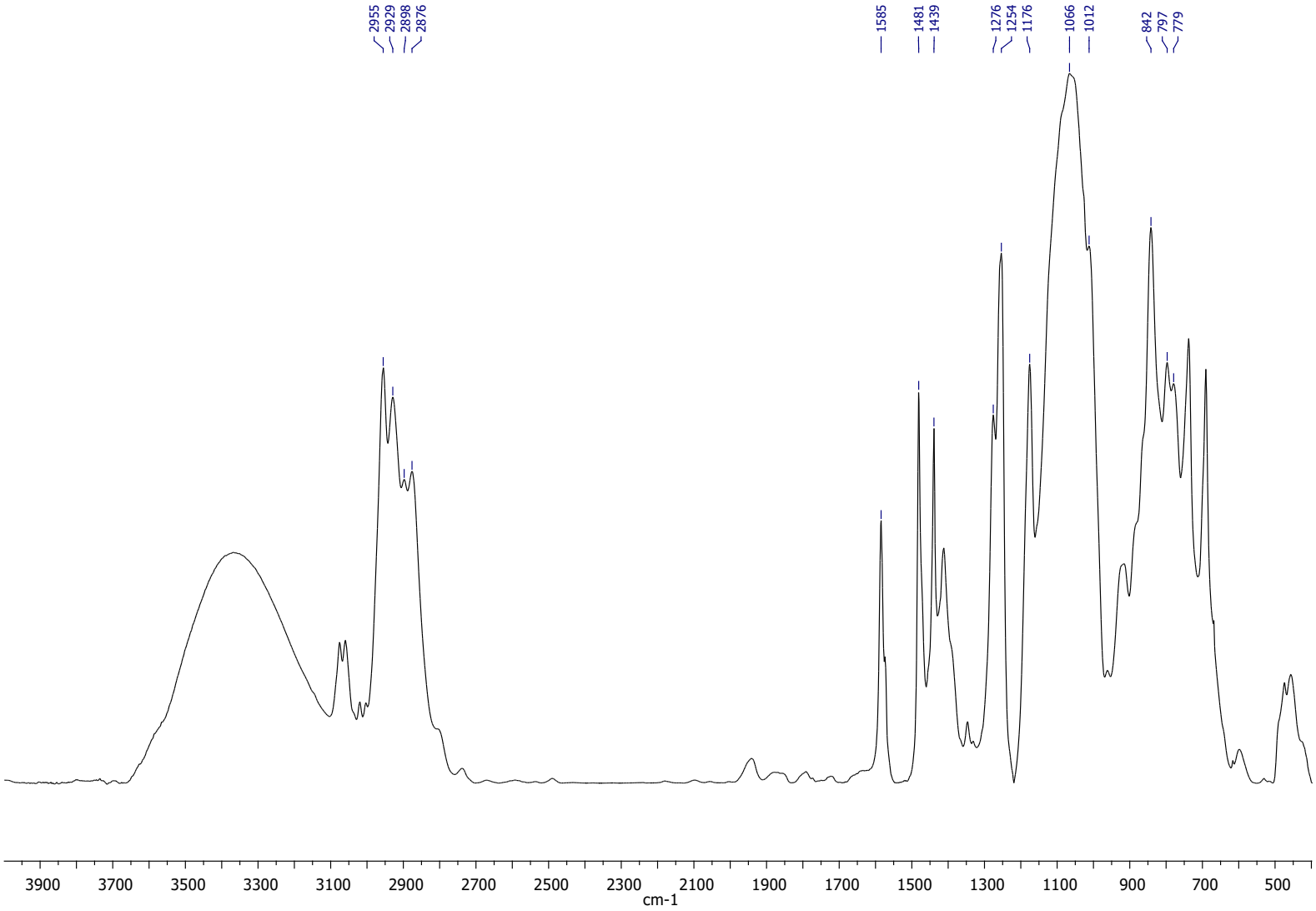


Figure 164s. IR-spectrum of compound **3.1.1**. (the presence of an OH group is associated with the presence of moisture in potassium bromine, which leads to the partial hydrolysis during the analysis)

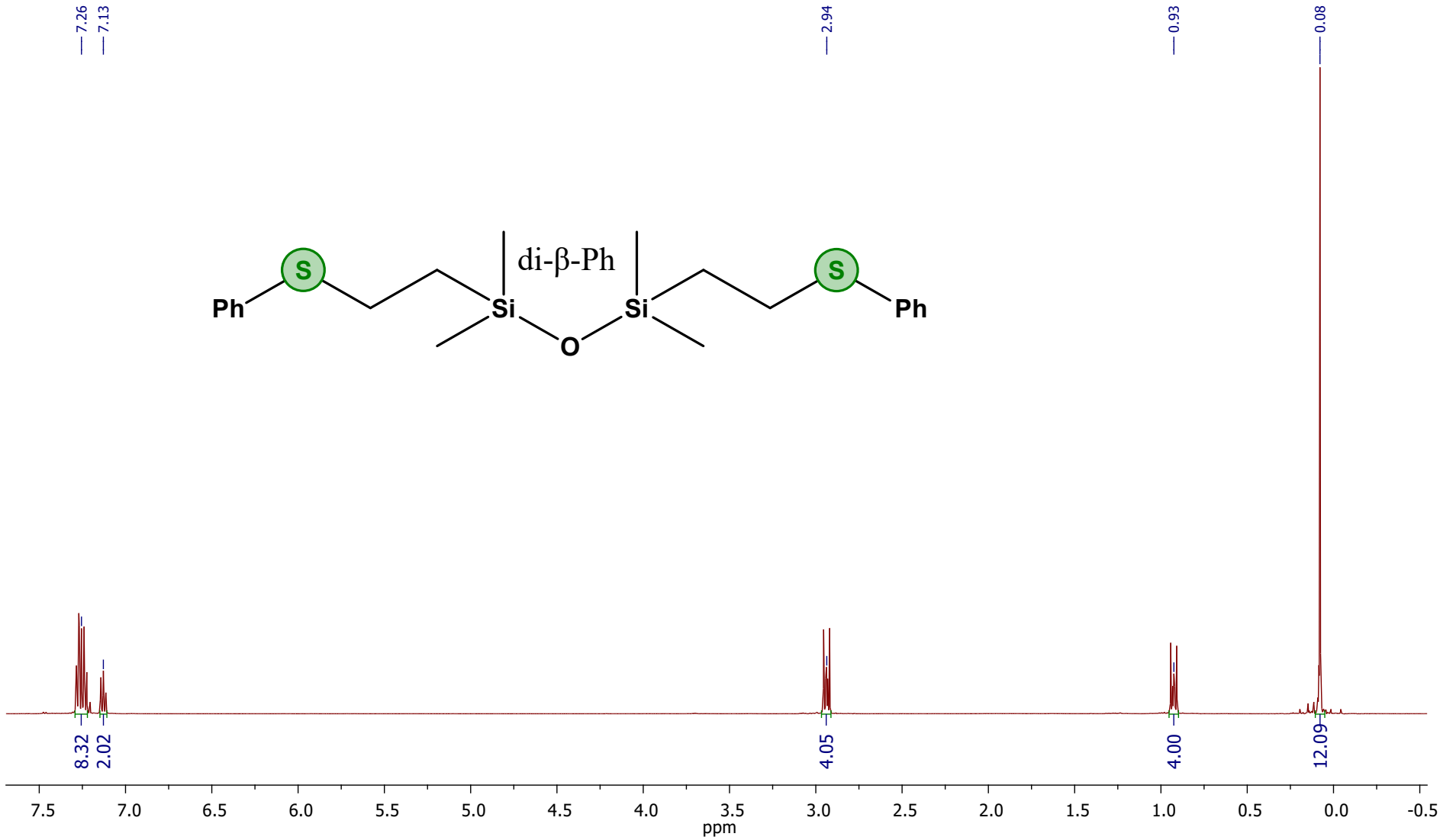


Figure 165s. ^{1}H NMR spectrum of compound **di-β-Ph** (500 MHz, solvent – $CDCl_3$).

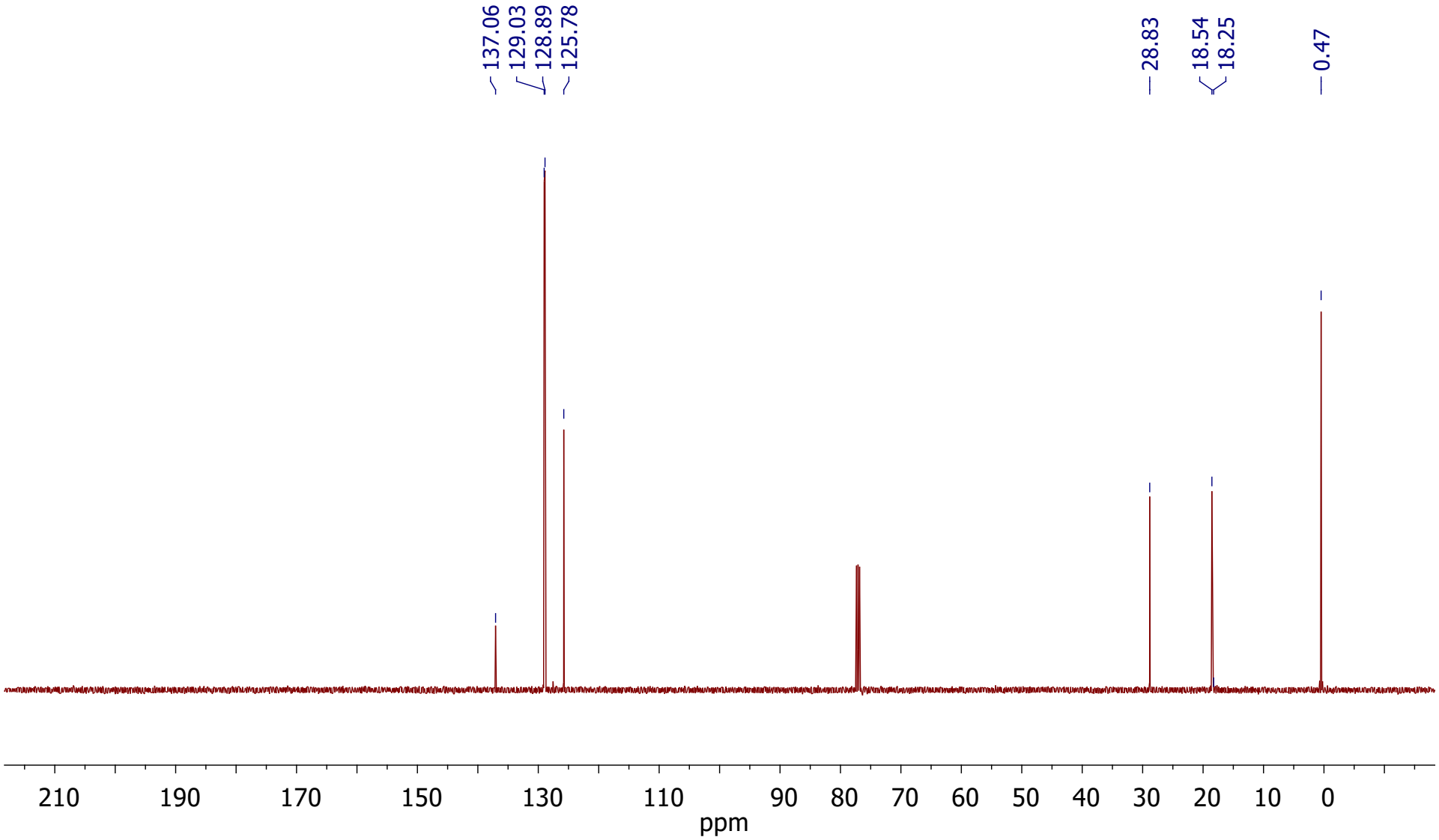


Figure 166s. ^{13}C NMR spectrum of compound **di-β-Ph** (500 MHz, solvent – $CDCl_3$).

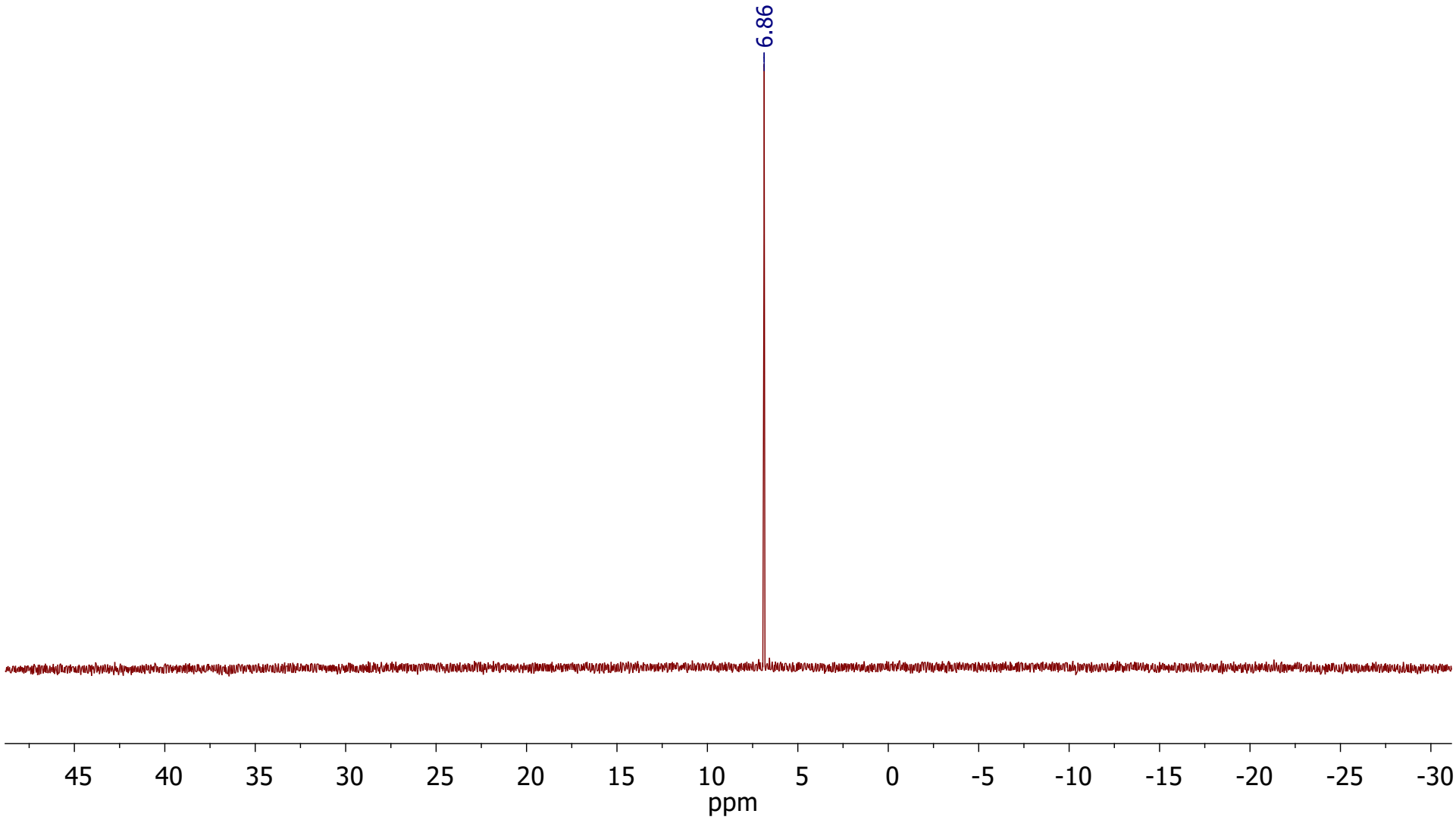


Figure 167s. ^{29}Si NMR spectrum of compound **di-β-Ph** (500 MHz, solvent – $CDCl_3$).

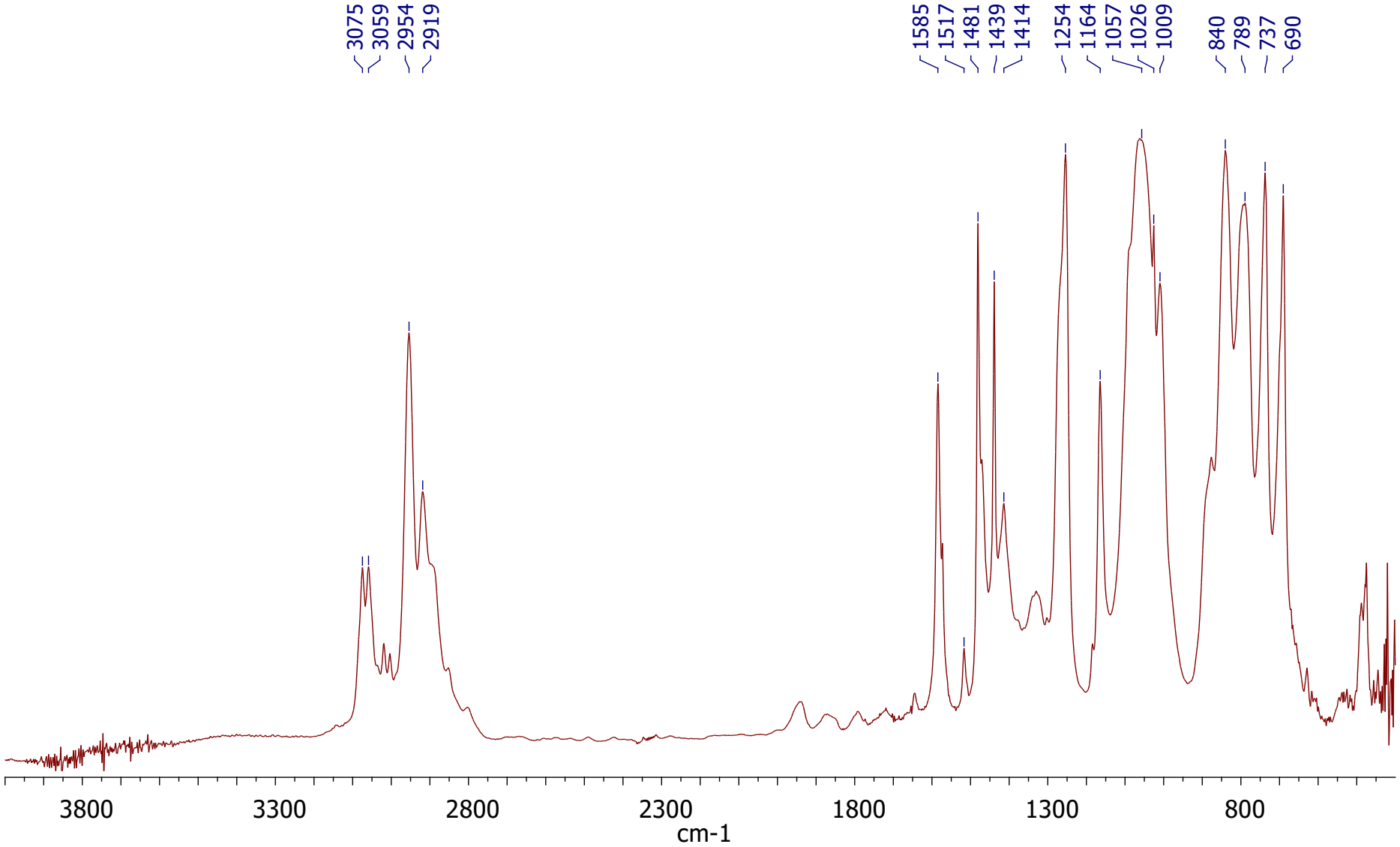


Figure 168s. IR-spectrum of compound **di-β-Ph**.

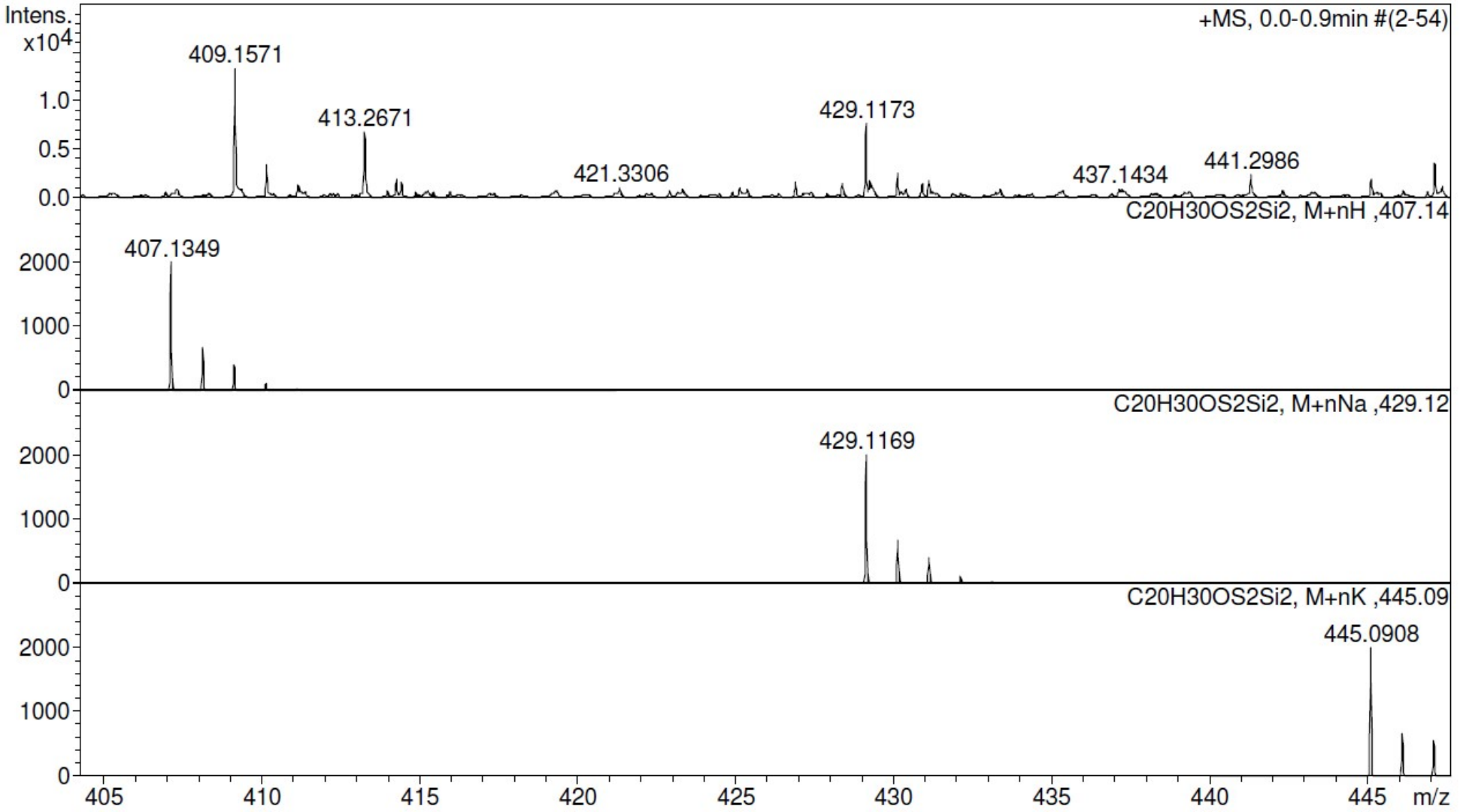


Figure 169s. HRMS (ESI) for compound **di-β-Ph**.

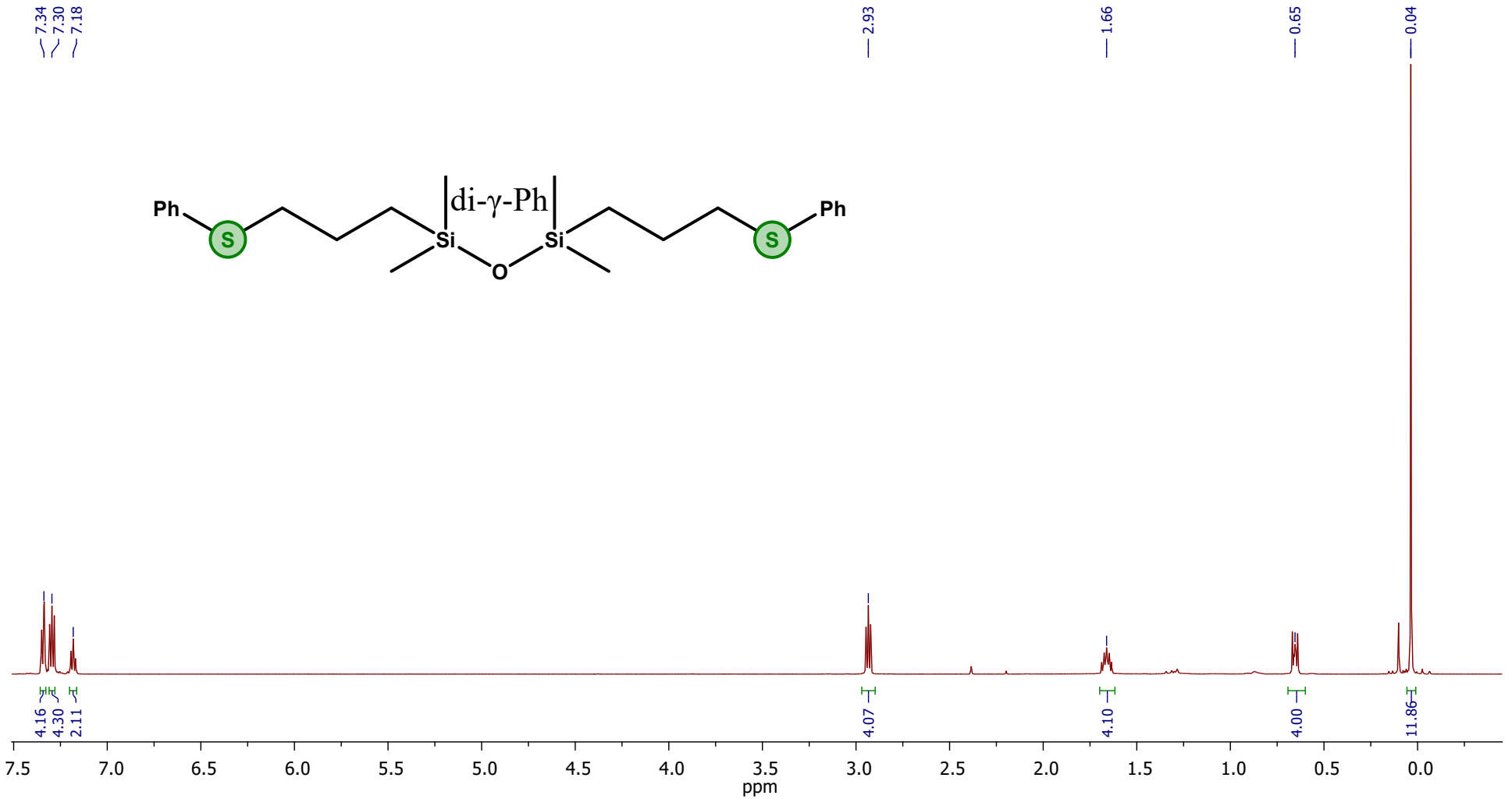


Figure 170s. ^{1}H NMR spectrum of compound **di-γ-Ph** (500 MHz, solvent – $CDCl_3$).

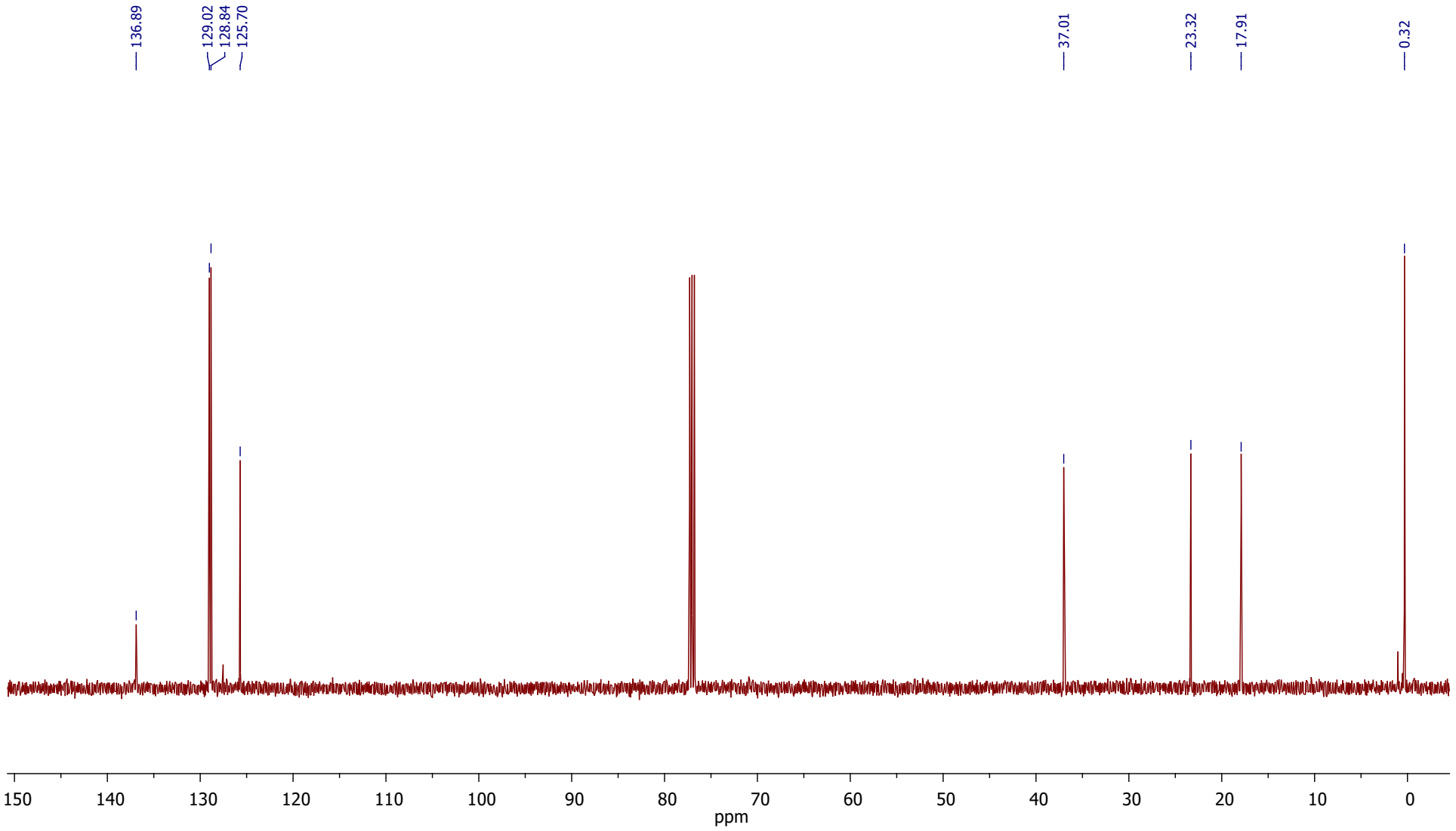


Figure 171s. ^{13}C NMR spectrum of compound **di-γ-Ph** (400 MHz, solvent – $CDCl_3$).

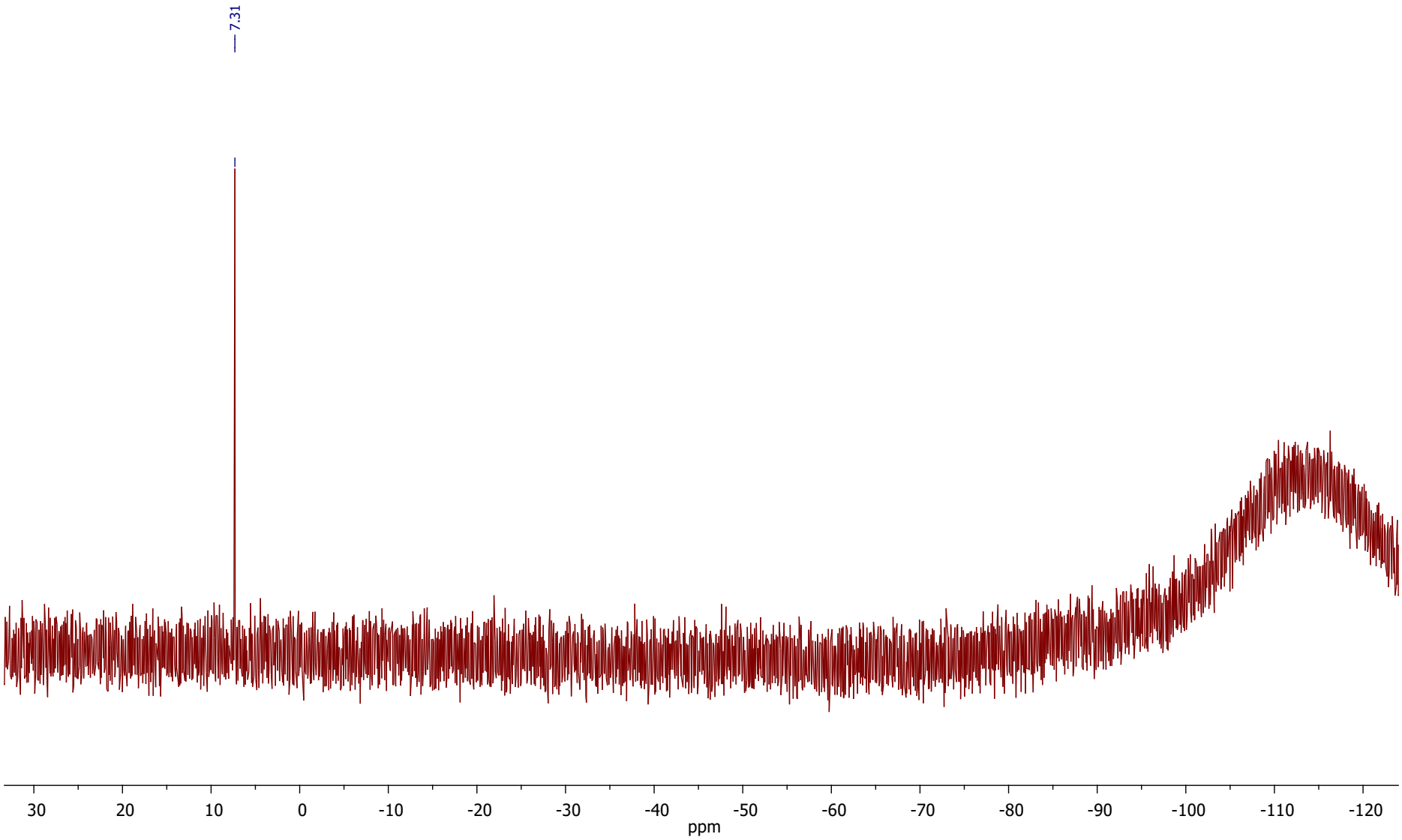


Figure 172s. ^{29}Si NMR spectrum of compound **di-γ-Ph** (400 MHz, solvent – $CDCl_3$).

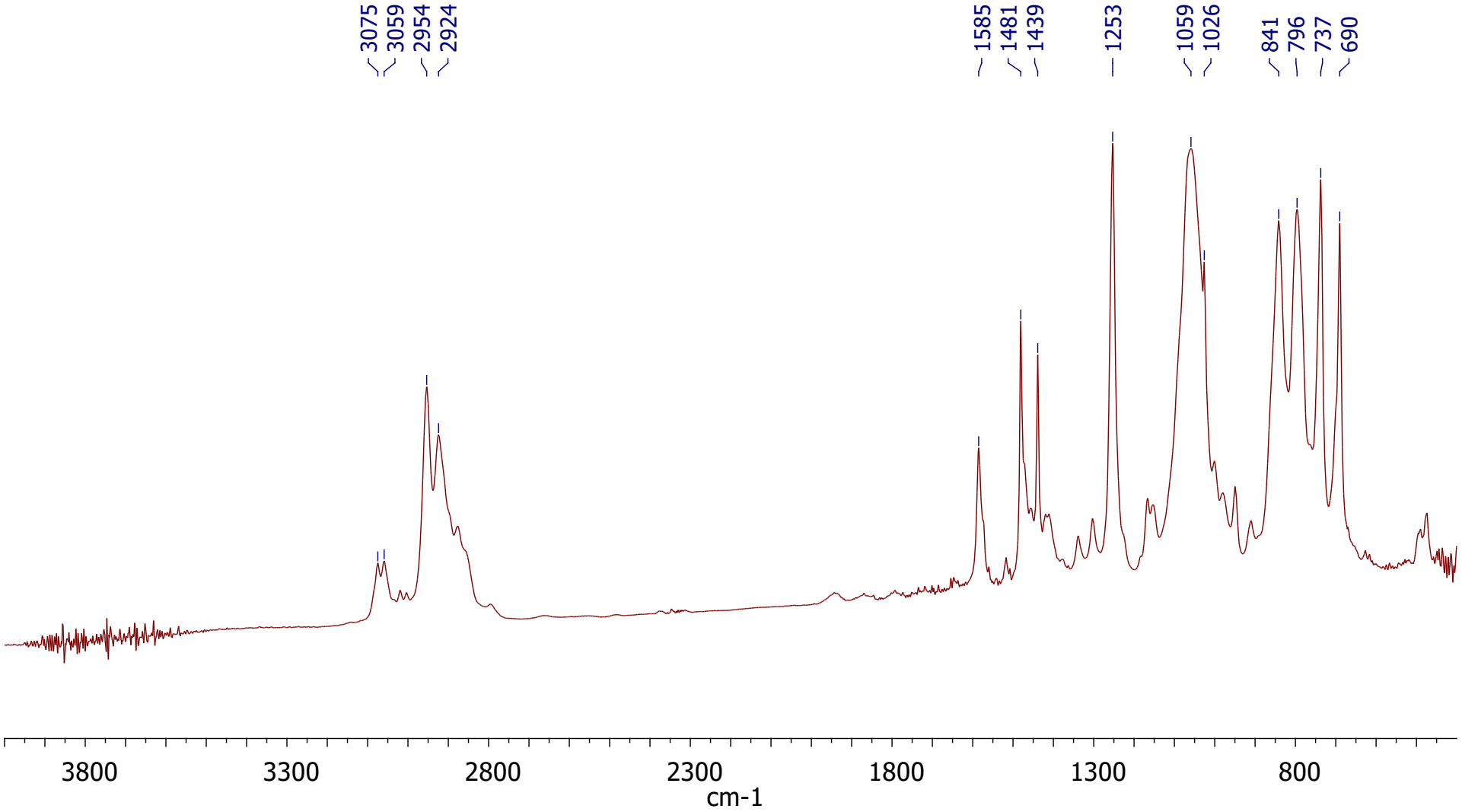


Figure 173s. IR-spectrum of compound **di-γ-Ph**.

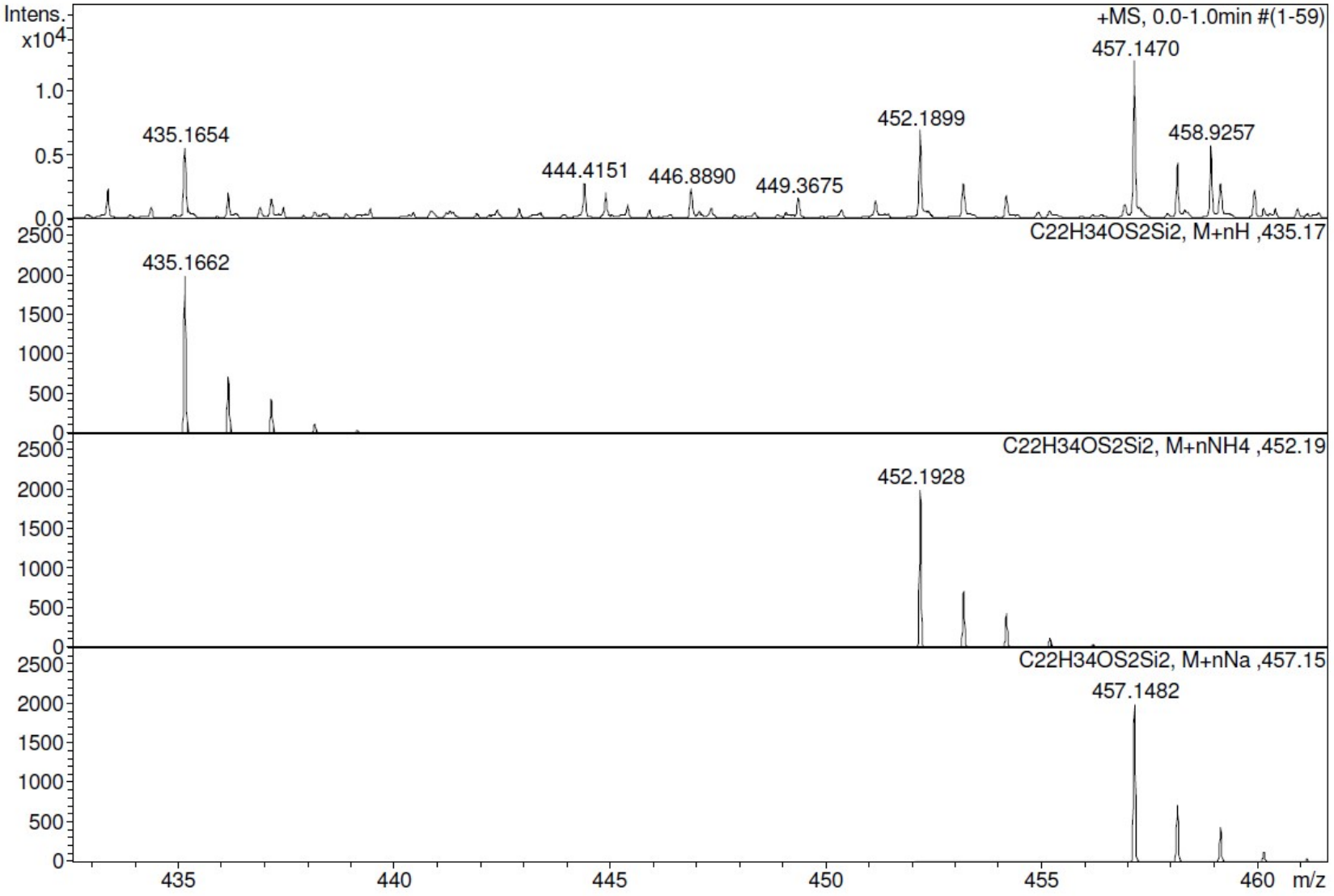


Figure 174s. HRMS (ESI) for compound **di-γ-Ph**.

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