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SUPPORTING INFORMATION

Interaction of organodialkoxysilanolates with carbon dioxide

M. N. Temnikov[1], N. V. Cherkun[1], K. L. Boldyrev[1,2], S. N. Zimovets[1], E. G. Kononova[1], I. V. Elmanovich[1,3], Marat Gallyamov[1,3] and A. M. Muzafarov[1,2]

[1]A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences Vavilova St. 28, 119991, GSP-1, Moscow, Russia

[2]N.S. Enikolopov Institute of Synthetic Polymeric Materials, a foundation of the Russian Academy of Sciences

[3]Faculty of Physics, Lomonosov Moscow State University, 119991 Leninskie gory 1-2, Moscow, Russian Federation

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1. Experimental

2. GC, GPC, IR, NMR,

3. References

1. Experimental

1.1 General Considerations

Solvents were prepared according to earlier [1] described procedures. All solvents were purified before use. Ethoxyethane was distilled from sodium under argon. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon atmosphere.

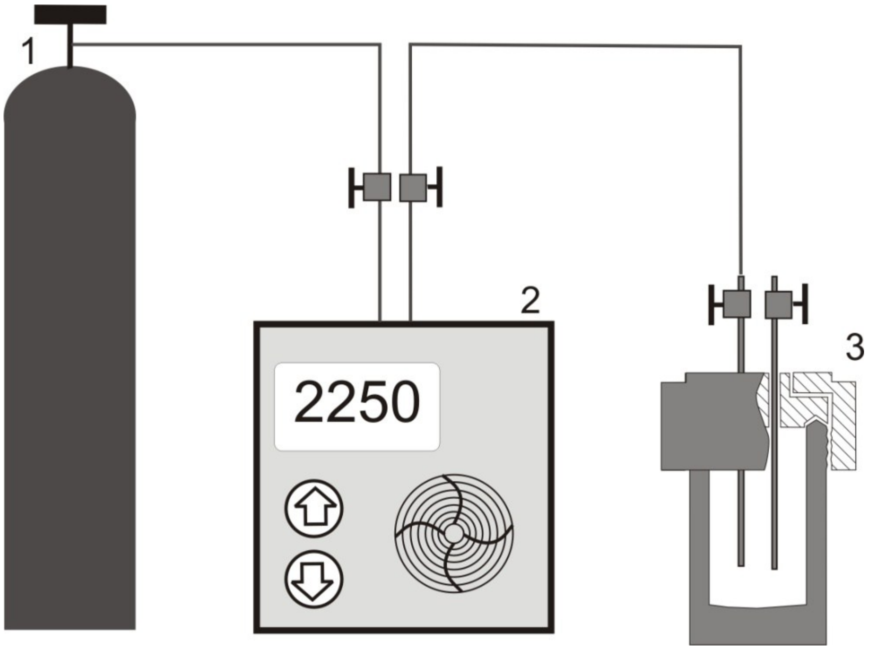
NMR spectra were recorded Bruker Avance-III HD 400 spectrometer (Germany) operating at 400, 101 and 79 MHz for ^{1}H, ^{13}C and ^{29}Si respectively. Spectra were recorded a spectrometer using chloroform-d, hexadeuterobenzene and deuteroxide as solvent. Spectra was processed a Mestrenova.

IR spectra were obtained using an IR spectrometer with a Fourier transformer Bruker "Tensor 37" (Germany). The samples were prepared by pressing KBr pellets.

GPC analysis was performed on the "Shimadzu" (Japan, Germany), the detector - refractometer RID - 20A, the column - Phenogel 50A (Size (300 x 7,8 mm)); eluent - toluene.

GC analysis was performed on a chromatograph (Crystallux 4000, Russia) at 50—280 °C,

20°/min; detector – katharometer, columns (2 mm × 2 m) with 5 % SE-30 stationary phase deposited onto Chromaton-N-AW-HMDS, helium as a carrier gas (60mL/min). Data were detected and processed using the «NetChrom 2.0 » program packages (Crystallux, Russia).



Scheme 1: General scheme of high pressure equipment setup used for synthesis in autoclave.

The high pressure equipment setup consists of CO_2 tank (MGPZ, Russia), CO_2 pump (SCF-24, Scientific systems Inc., USA) and a stainless still autoclave (20 ml). At first the compounds are placed inside autoclave. Then the desired pressure and flow rate are set on the operating module of SCF-24 and the pump fills the autoclave using the CO_2 from the tank. After that the autoclave is sealed and placed in a thermostat.

1.2. Synthesis

1.2.1 Synthesis of dimethyl(tetraethoxy)disiloxane

a) Reaction of $MeSi(OEt)_2ONa$ with CO_2: 46,80 g (0,2625 mol) of $MeSi(OEt)_3$ were added to 3,50 g (0,0875 mol) of NaOH. After that the solution was stirred intensively until full homogenization was achieved at 25 ºC. Then the alcohol formed during the reaction was removed from the reaction mixture under the remaining pressure of 12 mbar. The reaction mixture was then cooled to 0 ºC and bubbled with CO_2 from a CO_2 tank (MGPZ, Russia) with flow rate of 0,2 ml/min for 1 hour with intensive stirring. After white precipitate was formed, the temperature of the reaction mixture was risen to ambient and 50 ml of dry diethyl ether was added to the mixture. The soluble part of the mixture was separated by centrifugation under 9000 rpm. The procedure was repeated 3 timed. Afterwards the solvent was evaporated. The mixture was analyzed by GPC and GC (Fig. 1 and 3) The main reaction product was dimethyl(tetraethoxy)disiloxane with the 70% reaction yield according to GC and GPC. Non-soluble precipitate was analyzed with ^{13}C NMR in deuterated water and with elemental analysis. Silicon and hydrogen impurity and a lack of sodium are due to the presence of remaining organosilicon oligomers.

b) Reaction of $MeSi(OEt)_2ONa$ with CO_2 in the autoclave: 2,58 g (0,015 mol) of Sodium methyl(diethoxy)silanolates were placed in the autoclave. Then the autoclave was filled with CO_2 (as described in Scheme 1) under a flow rate of 20 ml/min to a pressure of 150 bar. Stirring was performed under ambient temperature for 5 minutes and then the autoclave was decompressed and opened. The heterogenic mixture formed in the autoclave was treated as described in the paragraph above. According to GC and GPC (Fig. 2 and 3) the main reaction product was dimethyl(tetraethoxy)disiloxane with 57% yield.

Purity of the obtained disiloxane were 99,8%.

CHN: Calc. (%) for Na_2CO_3, MM: 105.99, C, 11.33; H, 0.0; Na, 43.38; O, 45.29; Si, 0.0. Found: (%) C, 11.45; H, 0.62; Na, 38.40; O, 48.81; Si, 0.72.

^{13}C NMR (101MHz, D_2O, ppm) δ 166.02.

CHN: Calc. (%) for $C_{10}H_{26}O_5Si_2$, MM: 282.48, C, 42.52; H, 9.28; O, 28.32; Si, 19.88. Found: (%) C, 42.38; H, 9.25; O, 28.34 Si, 20.03.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.71(q, $^3J_{(H,H)}$ = 7.0Hz, 8H, $Si\text{-}O\underline{\mathbf{CH_2}}CH_3$), 1.11(t, $^3J_{(H,H)}$ = 7.0Hz, 12H, $Si\text{-}OCH_2\underline{\mathbf{CH_3}}$), 0,03(s, 6H, $Si\text{-}\underline{\mathbf{CH_3}}$).

^{13}C NMR (101MHz, $CDCl_3$, ppm) 57.87 ($Si\text{-}O\underline{C}H_2CH_3$), 17.95 ($Si\text{-}O\text{-}CH_2\underline{C}H_3$), -5.95 ($Si\text{-}\underline{C}H_3$).

^{29}Si NMR (79 MHz, $CDCl_3$, ppm) -50.89.

1.2.2 Synthesis of compound tetramethyl(diethoxy)disiloxane

a) Reaction of $Me_2Si(OEt)ONa$ with CO_2: method is analaquos to 1.2.1 (a) experiment, with 4 g of NaOH (0,1 mol); 44,4 g of $Me_2Si(Oet)_2$ (0,3 mol); yield 61%.

b) Reaction of $Me_2Si(OEt)ONa$ with CO_2 in the autoclave: method is analaquos to 1.2.1 (b) experiment, with 2,13 g of $Me_2Si(OEt)ONa$ (0,015 mol); yield 75%,

Purity of the obtained disiloxane were 96,9%.

CHN: Calc. (%) for $C_8H_{22}O_3Si_2$, MM: 222.43, C, 43.20; H, 9.97; O, 21.58; Si, 25.25. Found: (%) C, 43.11; H, 9.77; O, 21.92 Si, 25.20.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.61(q, $^3J_{(H,H)}$ = 7.0Hz, 4H, $Si\text{-}O\underline{\mathbf{CH_2}}CH_3$), 1.14(t, $^3J_{(H,H)}$ = 7.0Hz, 6H, $Si\text{-}OCH_2\underline{\mathbf{CH_3}}$), 0.04(s, 12H, $Si\text{-}\underline{\mathbf{CH_3}}$).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) 57.61 ($Si\text{-}O\underline{C}H_2CH_3$), 18.18 ($Si\text{-}OCH_2\underline{C}H_3$), -1.32 ($Si\text{-}\underline{C}H_3$).

^{29}Si NMR (79 MHz, $CDCl_3$, ppm) -12.94.

1.2.3 Synthesis of compound divinyl(tetraethoxy)disiloxane

a) Reaction of $ViSi(OEt)_2ONa$ with CO_2: method is analaquos to 1.2.1 (a) experiment, with 4 g of NaOH (0,1 mol); 54,4 g of $ViSi(OEt)_3$ (0,3 mol); yield 85%.

b) Reaction of $ViSi(OEt)_2ONa$ with CO_2 in the autoclave: method is analaquos to 1.2.1 (b) experiment, with 2,73 g of $ViSi(OEt)_2ONa$ (0,015 mol); yield 74%.

Purity of the obtained disiloxane were 98,3%.

CHN: Calc. (%) for $C_{12}H_{26}O_5Si_2$, MM: 306.50, C, 47.02; H, 8.55; O, 26.10; Si, 18.33. Found: (%) C, 46.16; H, 8.26; O, 27.7; Si, 17.88.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.15–5.78 (m, 6H, Si-$\underline{\mathbf{CH{=}CH_2}}$), 3.80 (q, $^3J_{(H,H)}$ = 7.0Hz, 8H, Si-O$\underline{\mathbf{CH_2}}$$CH_3$), 1.18 (t, $^3J_{(H,H)}$ = 7.0Hz, 12H, Si-O- $CH_2\underline{\mathbf{CH_3}}$).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 136.31 (Si-CH=$\underline{\mathrm{C}}H_2$), 129.90 (Si-$\underline{\mathrm{C}}$H=$CH_2$), 58.30(Si-O-$\underline{\mathrm{C}}H_2CH_3$), 18.00 (Si-O-$CH_2\underline{\mathrm{C}}H_3$).

^{29}Si NMR (79 MHz, $CDCl_3$, ppm) δ -66.19.

1.2.4 Synthesis of compound diphenyl(tetraethoxy)disiloxane

a) Reaction of $PhSi(OEt)_2ONa$ with CO_2: method is analaquos to 1.2.1 (a) experiment, with 4 g of NaOH (0,1 mol); 72,1g of $PhSi(OEt)_3$ (0,3 mol); yield 95%.

b) Reaction of $PhSi(OEt)_2ONa$ c CO_2 in the autoclave: method is analaquos to 1.2.1 (b) experiment, with 3,51 g of $PhSi(OEt)_2ONa$ (0,015 mol); yield 94%.

Purity of the obtained disiloxane were 98,9%.

CHN: Calc. (%) for $C_{20}H_{30}O_5Si_2$, MM: 306.62, C, 59.08; H, 7.44; O, 19.67; Si, 13.81. Found: (%) C, 59.19; H, 7.58; O, 19.46 Si, 13.77.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81 (dd, $^3J_{(H,H)}$ = 7,0Hz,1.5, 4H, Si-C_6H_5), 7.57 – 7.34 (m, 6H, Si-C_6H_5), 3.99 (q, $^3J_{(H,H)}$ = 7.0Hz, 8H, Si-O$\underline{\mathbf{CH_2}}$$CH_3$), 1.32 (t, 12H, Si-$OCH_2\underline{\mathbf{CH_3}}$).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 134,66-127,86 (Si-$\underline{\mathrm{C}}_6H_5$), 58.80 (Si-O$\underline{\mathrm{C}}H_2CH_3$), 18.20 (Si-$OCH_2\underline{\mathrm{C}}H_3$).

^{29}Si NMR (79 MHz, $CDCl_3$, ppm) δ -65.11.

1.2.5 Reaction of Sodium phenyl(diethoxy)silanolates with CO_2 (dry ice):

3,3 g (0,014 mol) of Sodium phenyl(diethoxy)silanolates solution in 33 ml of THF was quickly dropped in a three-neck flask equipped with mechanical stirrer and containing 24 g of dry ice. The reaction mixture was stirred for 1 hour under -60–(-40) ^{o}C. After that the transparent solution was heated to ambient temperature. A sample was selected and analyzed by means of IR spectroscopy (Fig. 22) Then 1,519 g (0,014 mol) of trimethylchlorosilane solution in 10 ml of THF was dropped to the mixture. After stirring for 3 hours white precipitate was formed. The non-soluble part was separated as described for previous experiments. The soluble part was analyzed by means of GC (Fig 21), the yield was 50 %.

IR (cm^{-1}): 3073, 3052, 2976-2891, 1626, 1431, 1343, 1136, 1078

2. GC, GPC, IR, NMR

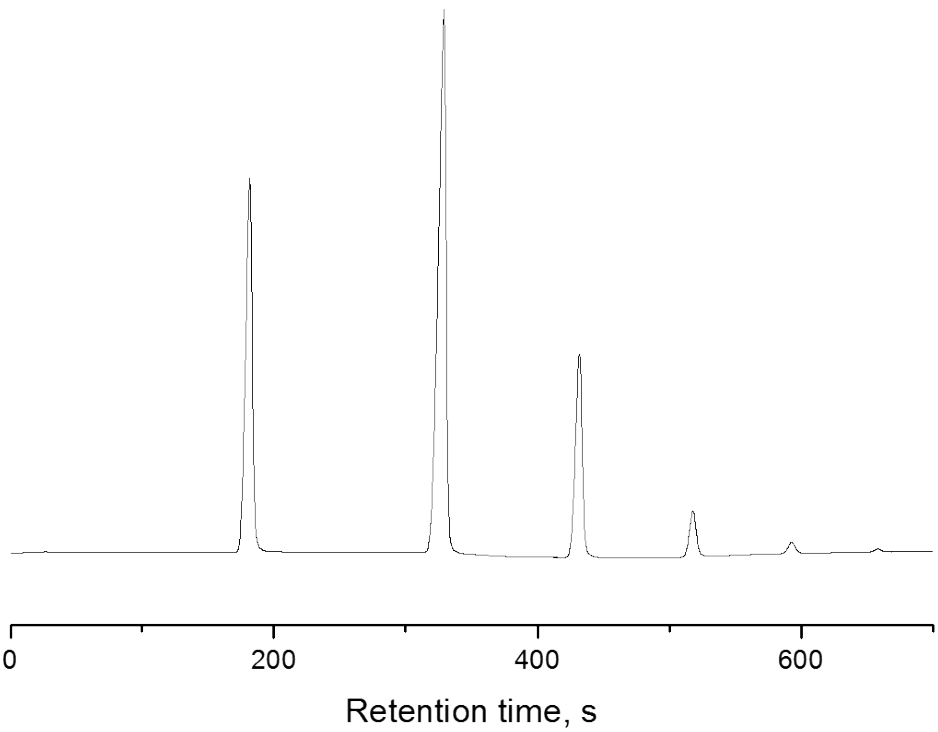


Figure 1: GC - curves of reaction mixture for reaction of Sodium methyl(diethoxy)silanolates with CO_2

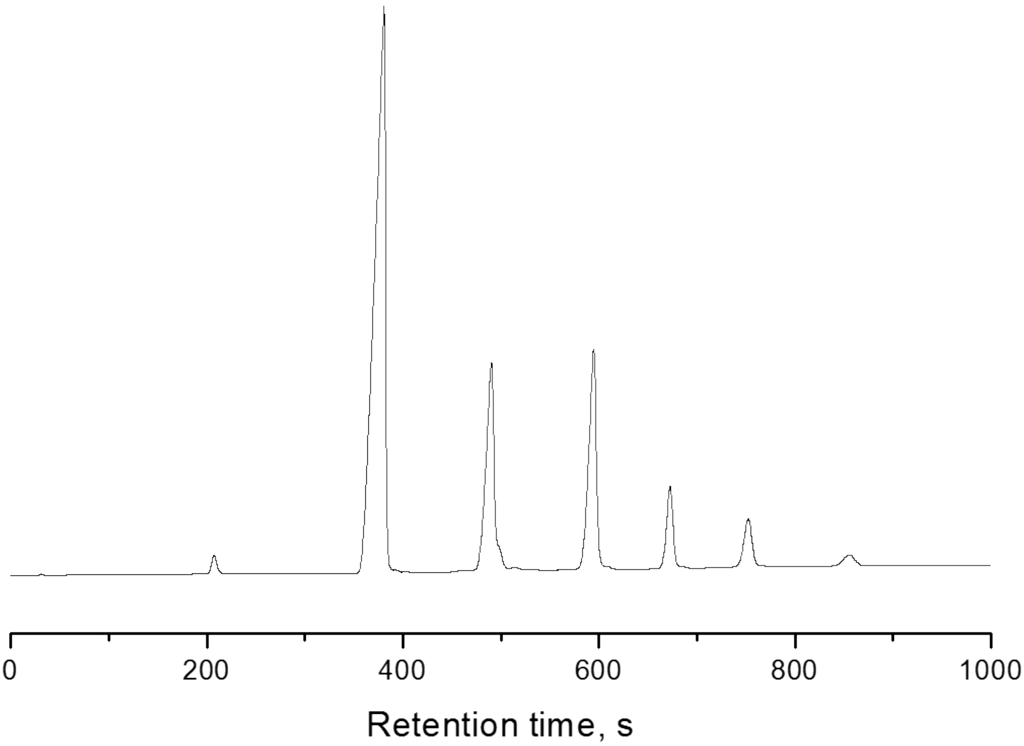


Figure 2: GC - curves of reaction mixture for reaction of Sodium methyl(diethoxy)silanolates with CO_2 in autoclave

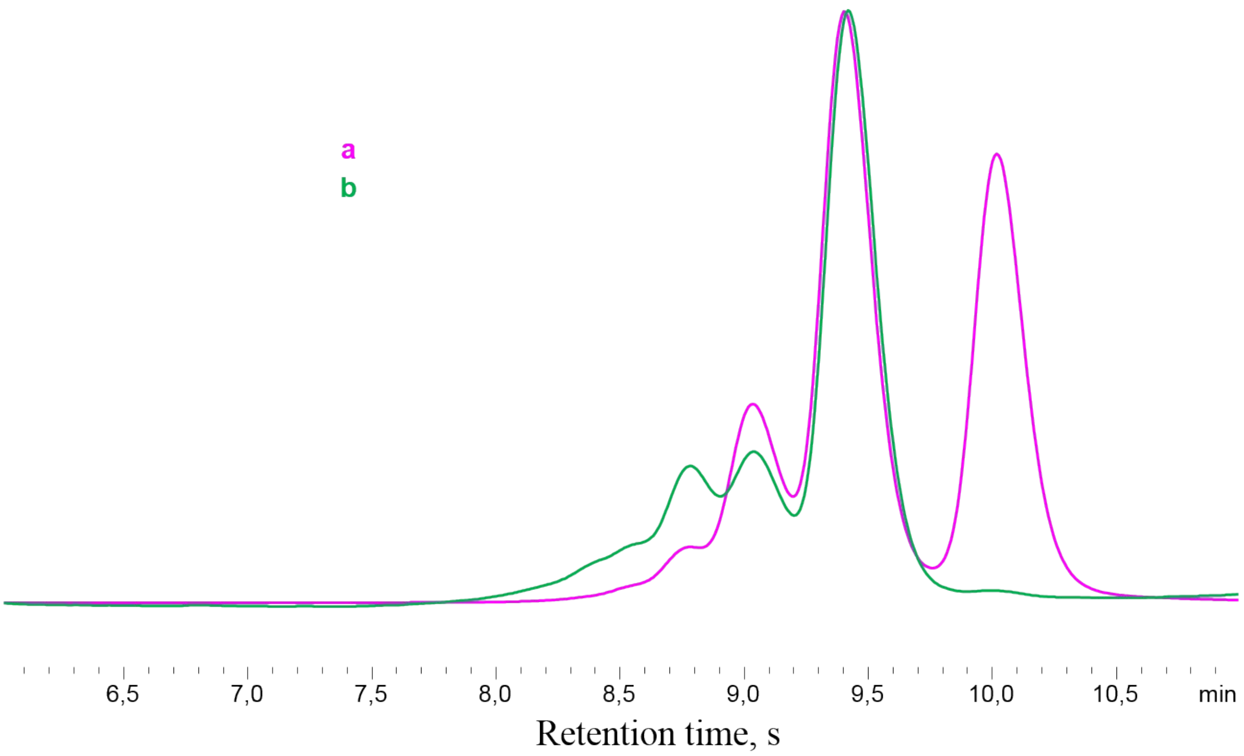


Figure 3: GPC - curves of reaction mixture for reaction of Sodium methyl(diethoxy)silanolates with carbon dioxide in autoclave (b) and with bubbling CO_2 (a)

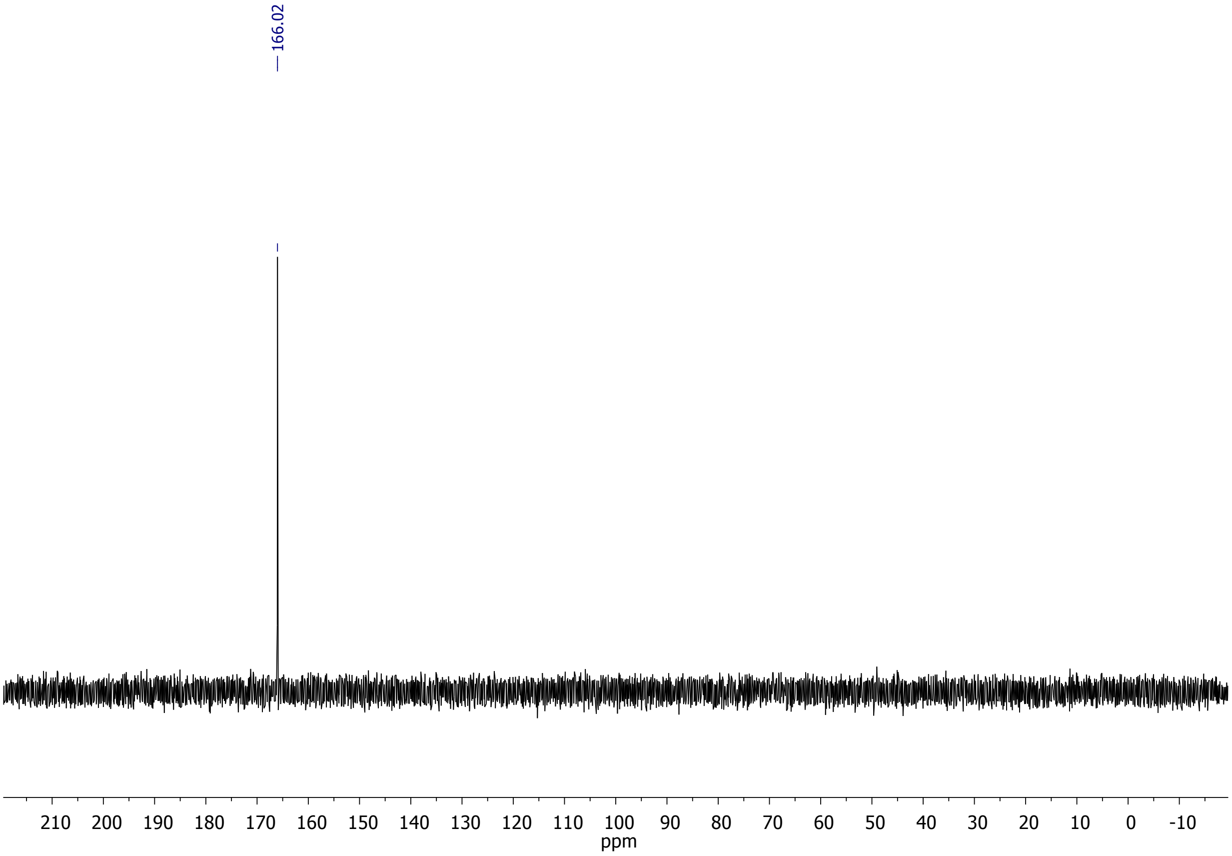


Figure 4: ^{13}C NMR spectrum (101 MHz, D_2O) of insoluble residue (Na_2CO_3)

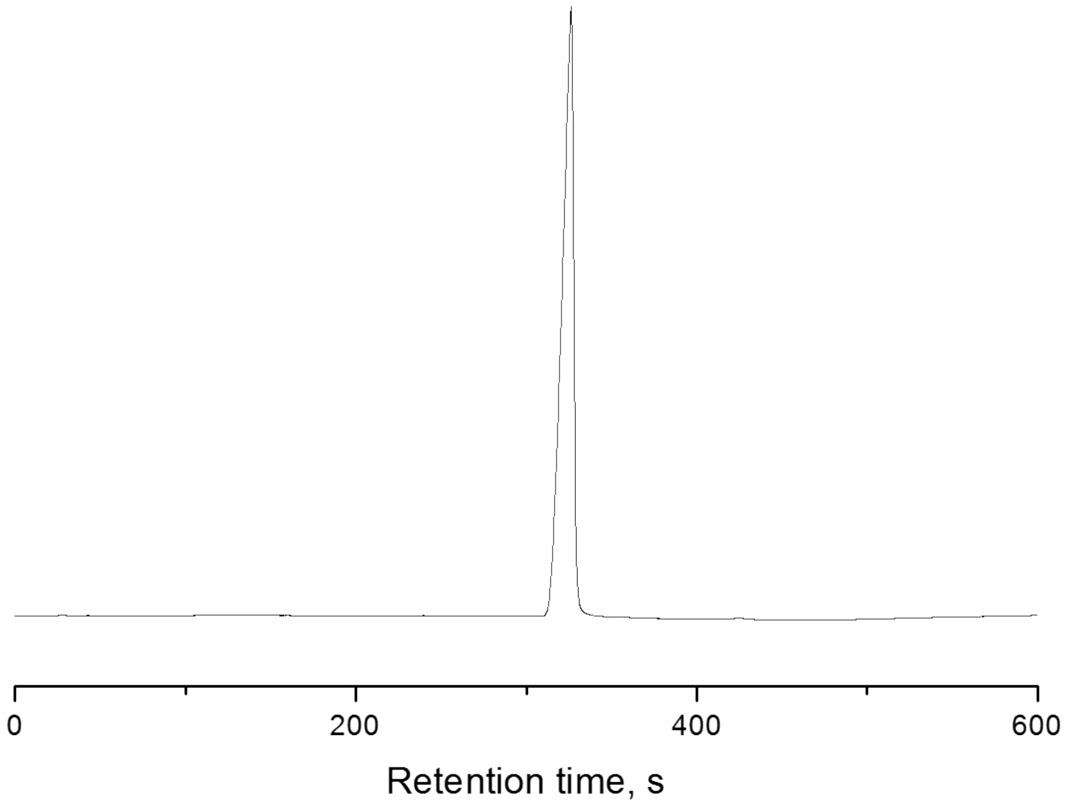


Figure 5: GC - curve of dimethyl(tetraethoxy)disiloxane

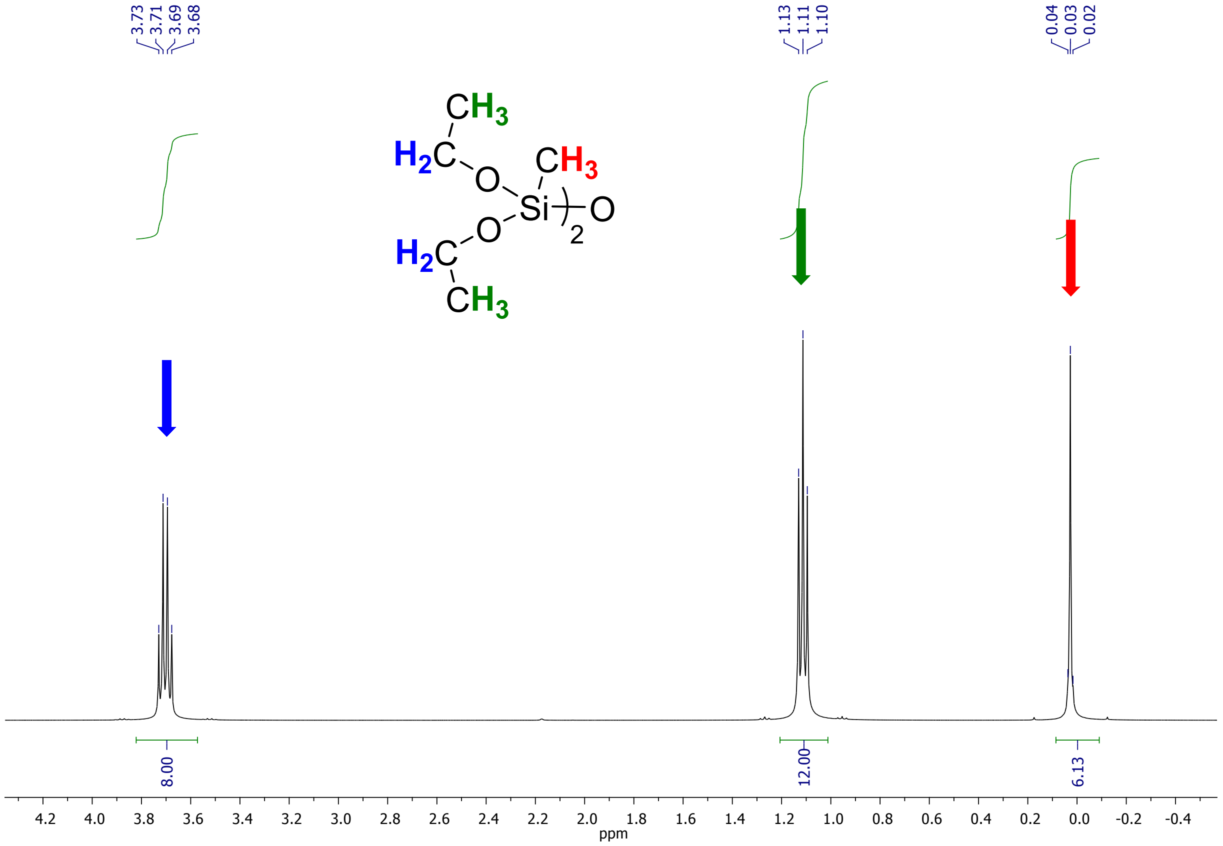


Figure 6: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of dimethyl(tetraethoxy)disiloxane

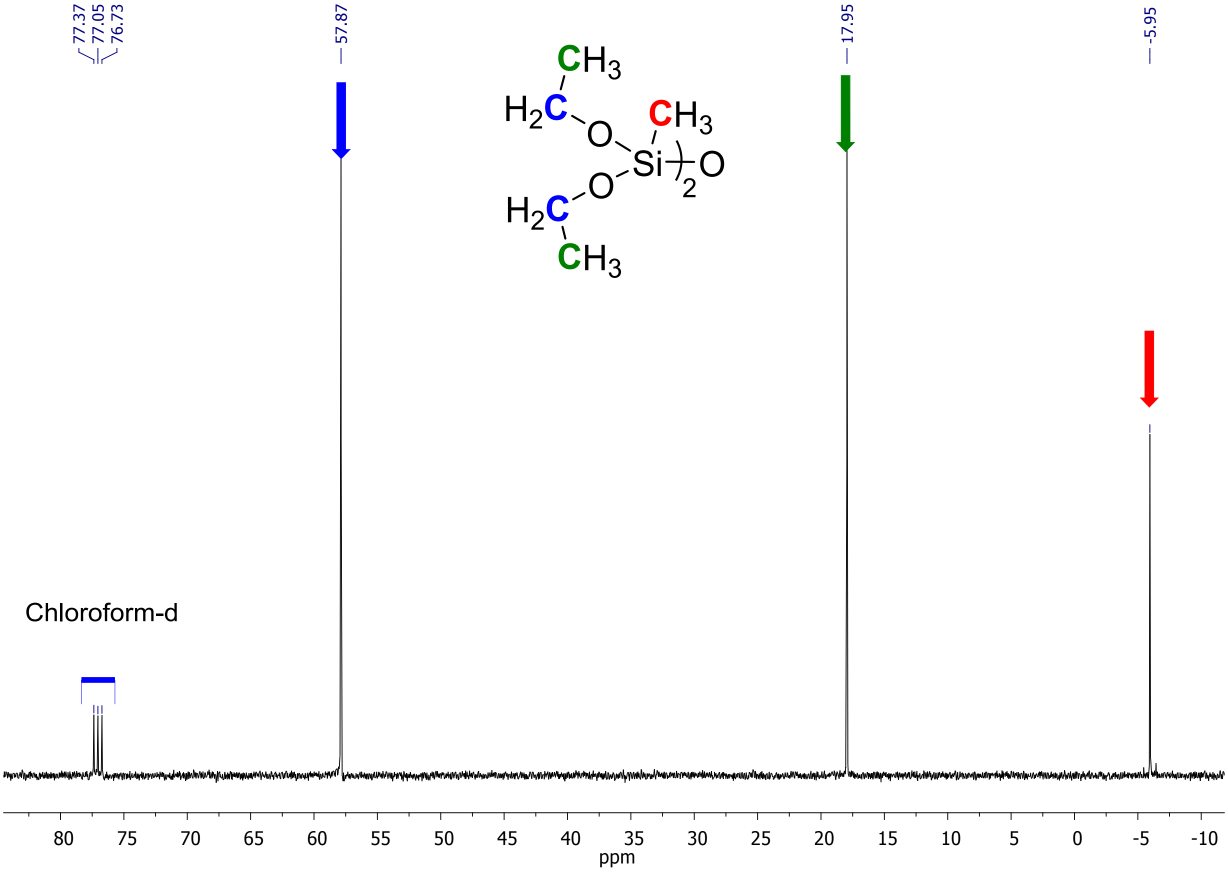


Figure 7: ^{13}C NMR spectrum (101 MHz, CDCl$_3$) of dimethyl(tetraethoxy)disiloxane

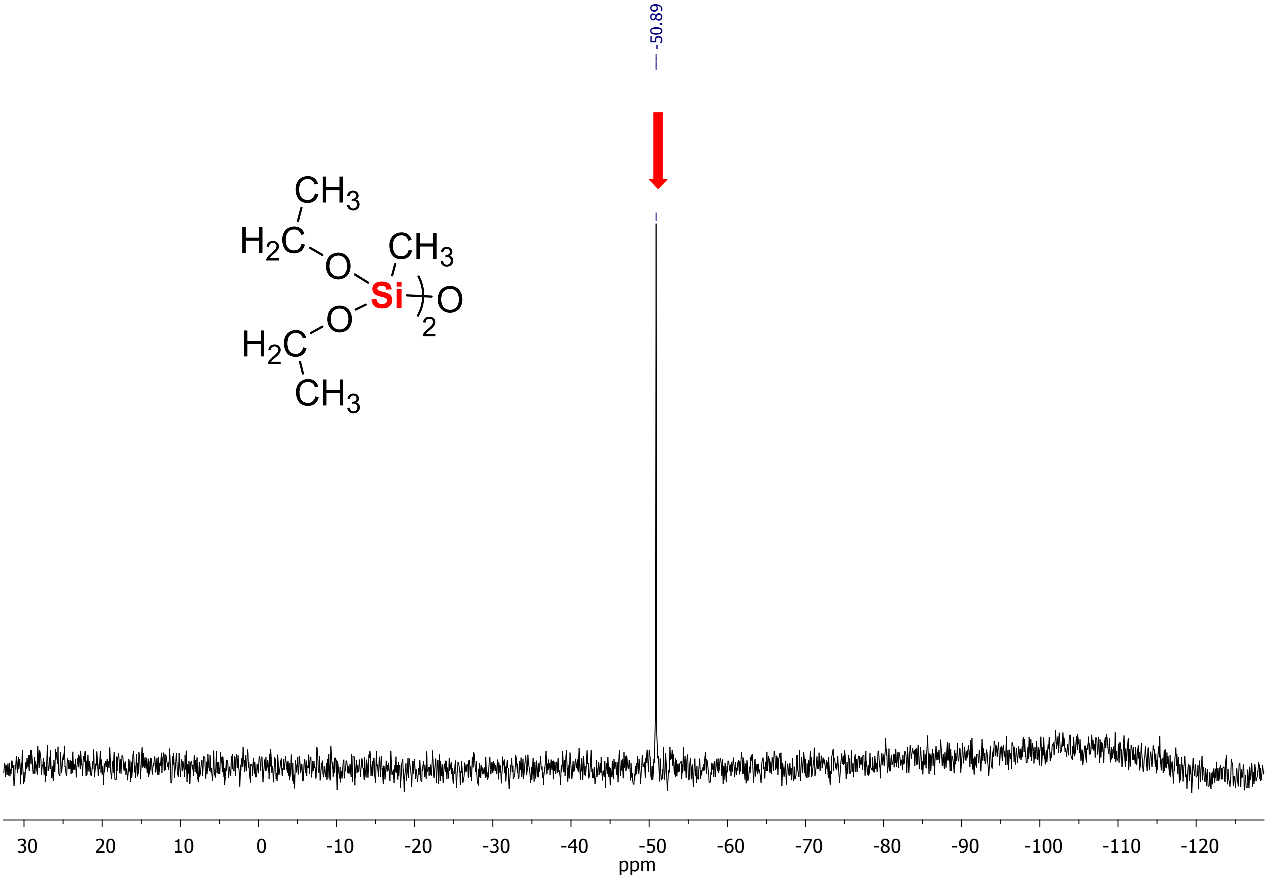


Figure 8: ^{29}Si NMR spectrum (79 MHz, $CDCl_3$) of dimethyl(tetraethoxy)disiloxane

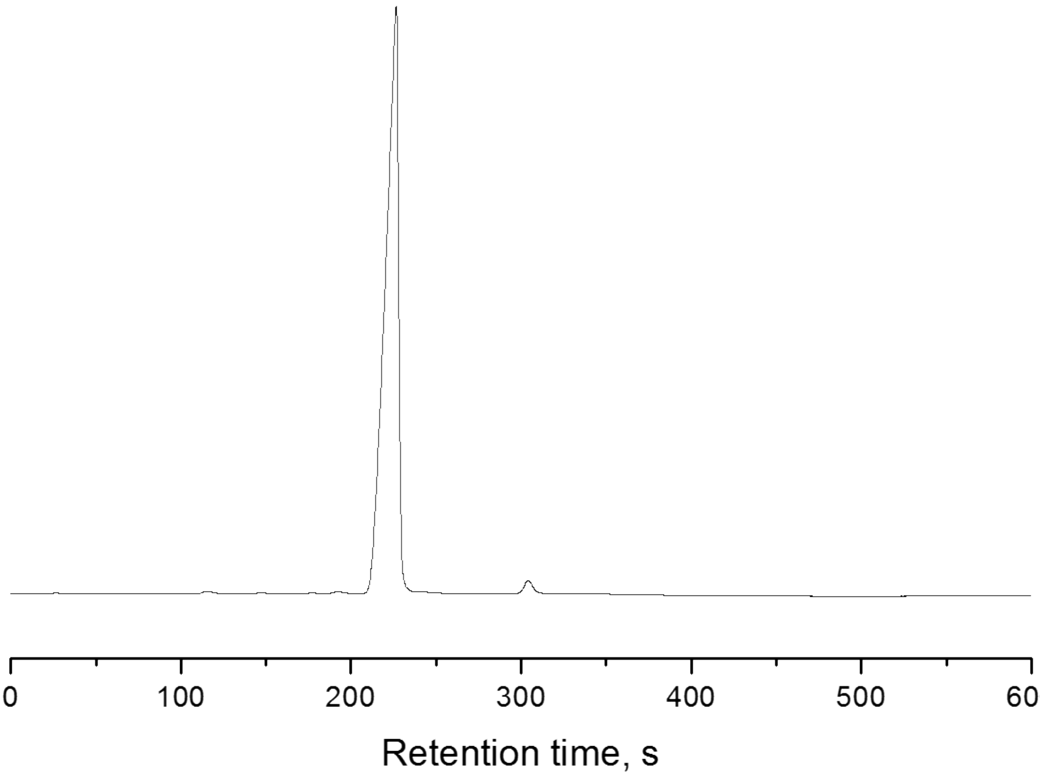


Figure 9: GC - curve of tetramethyl(diethoxy)disiloxane

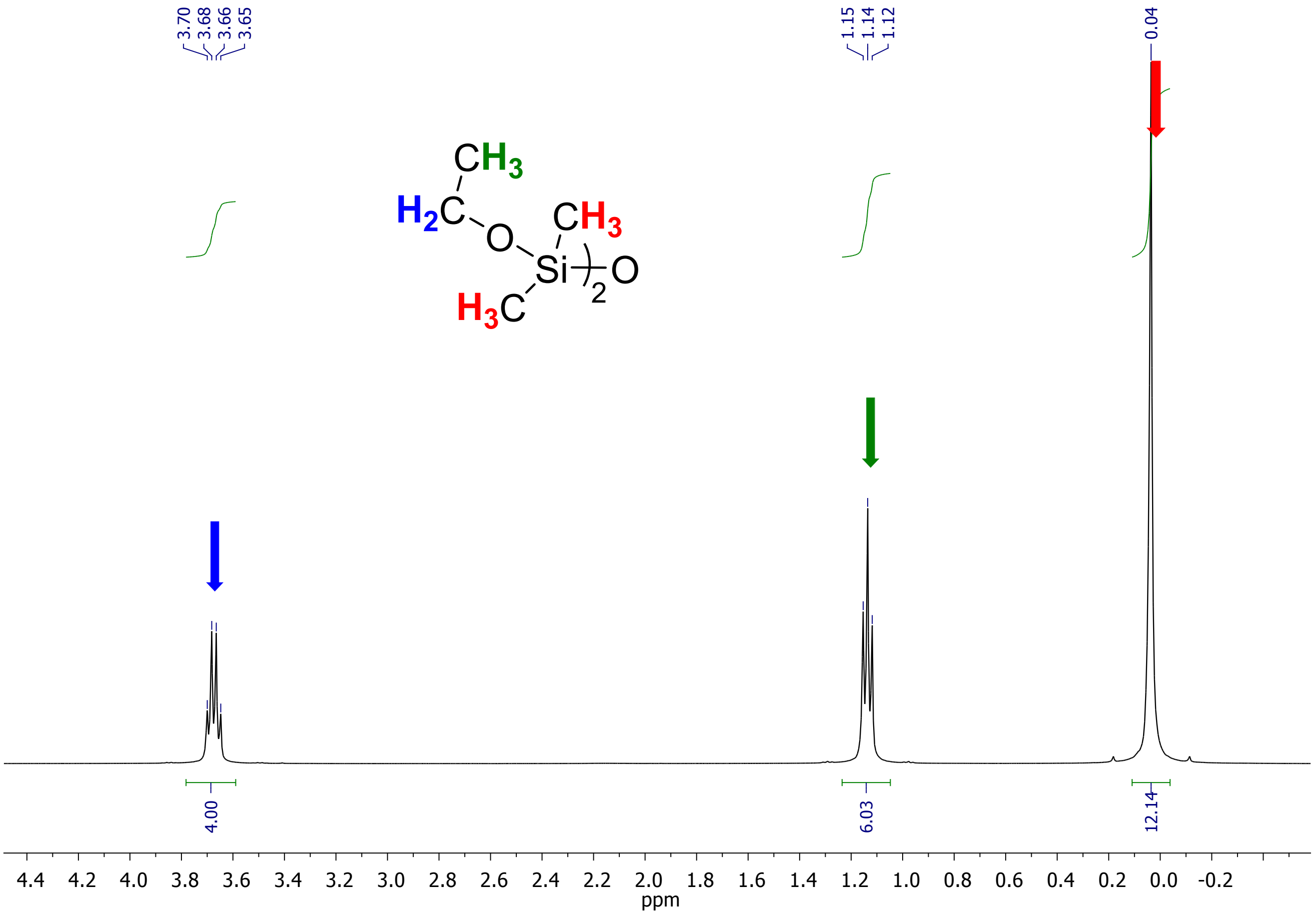


Figure 10: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of tetramethyl(diethoxy)disiloxane

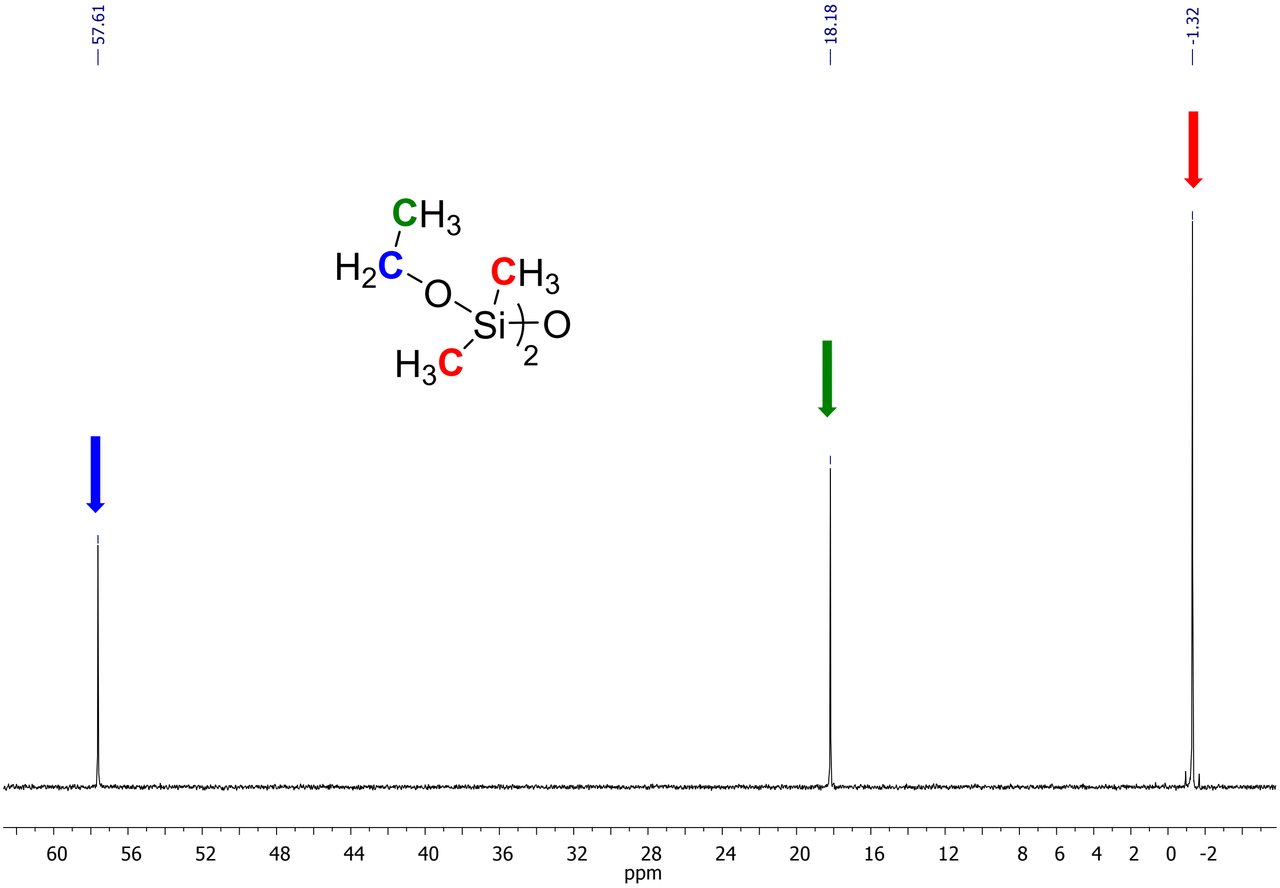


Figure 11: ^{13}C NMR spectrum (101 MHz, CDCl$_3$) of tetramethyl(diethoxy)disiloxane

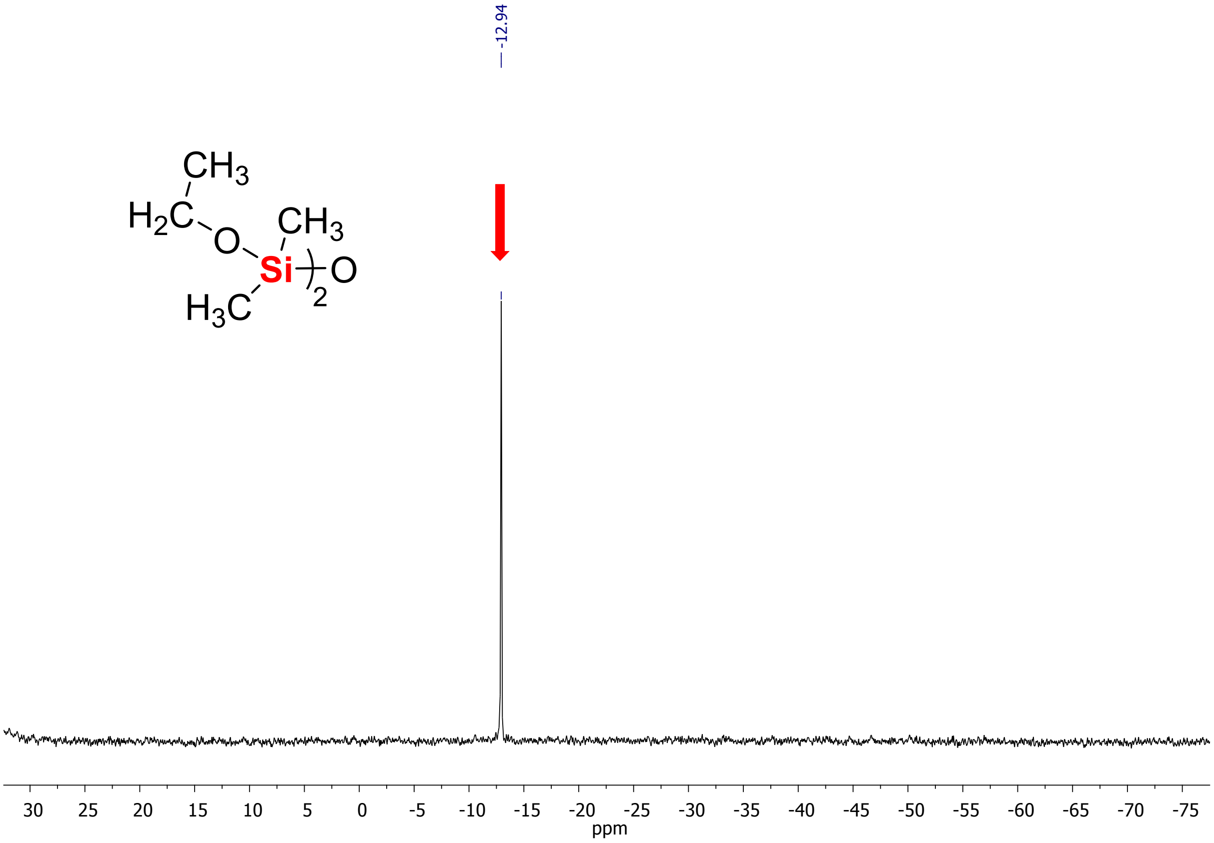


Figure 12: ^{29}Si NMR spectrum (79 MHz, $CDCl_3$) of tetramethyl(diethoxy)disiloxane

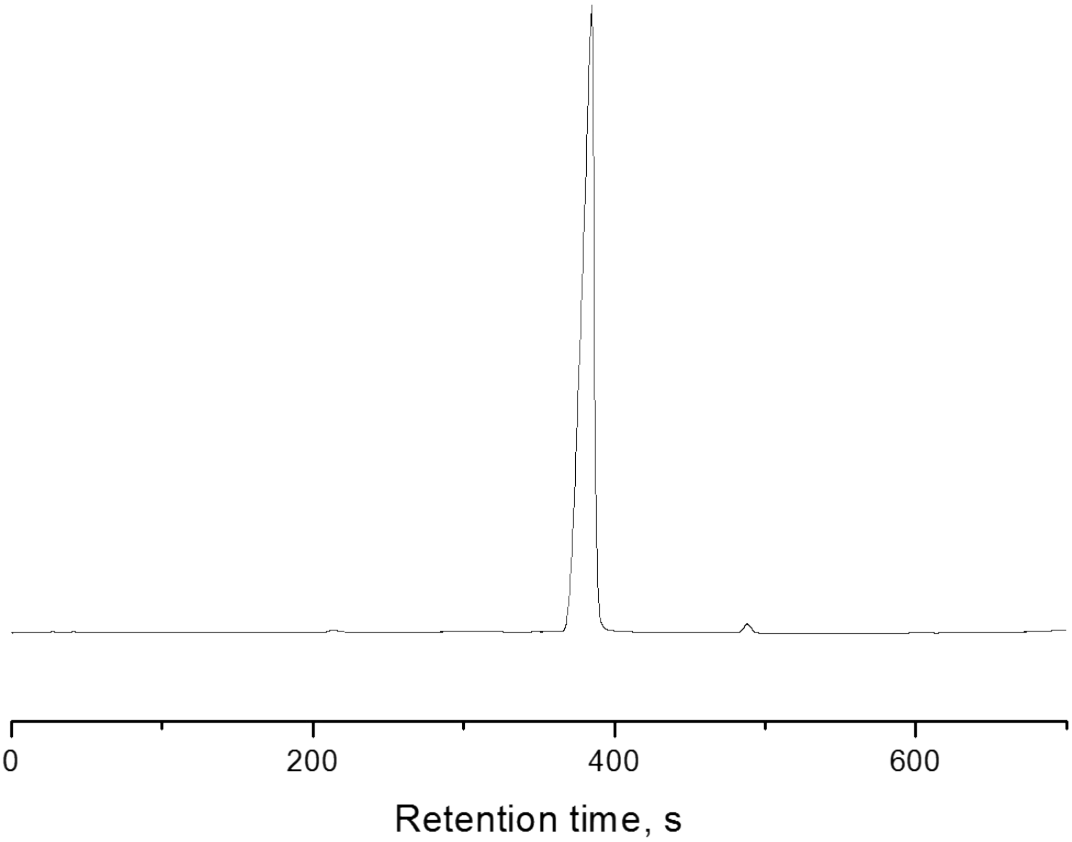


Figure 13: GC - curve of divinyl(tetraethoxy)disiloxane

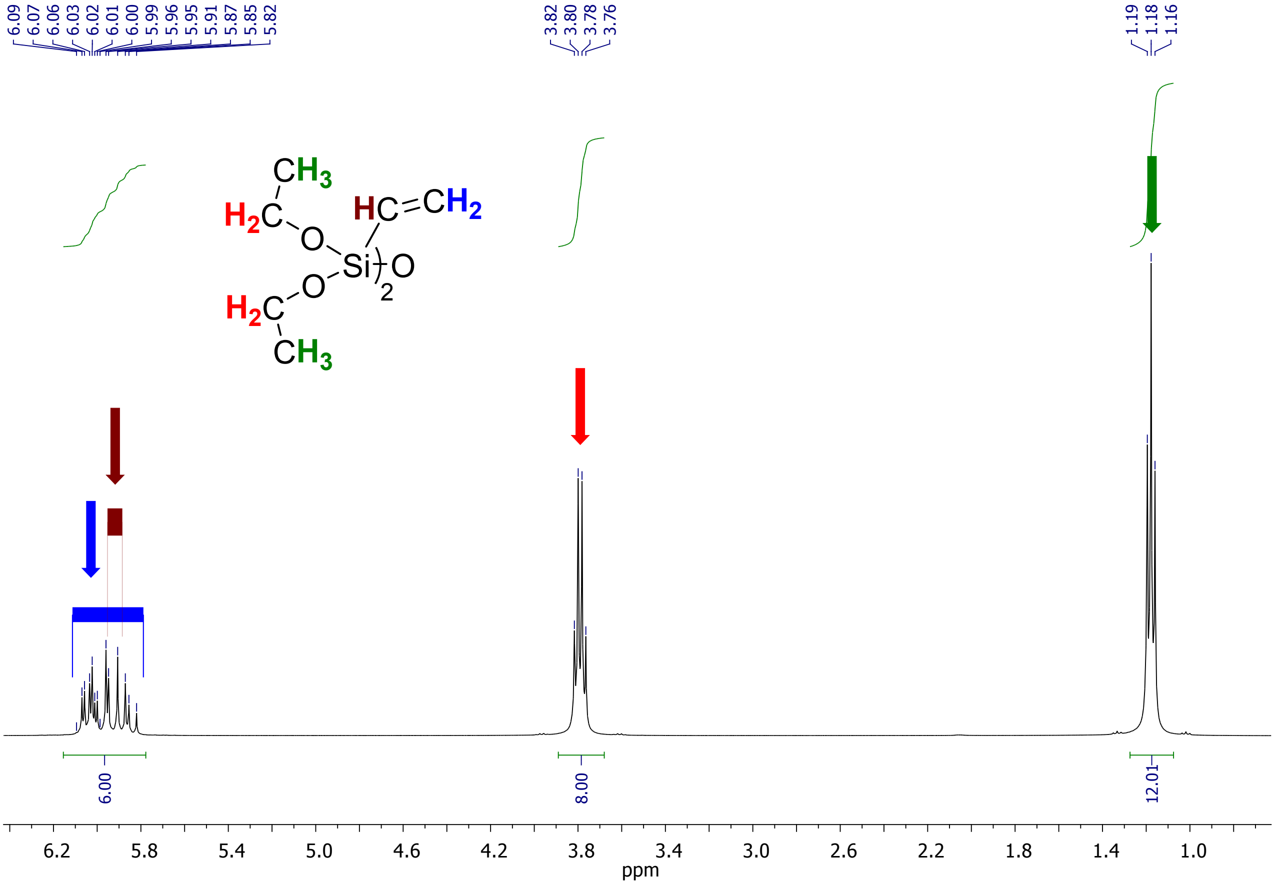


Figure 14: ^1H NMR spectrum (400 MHz, $CDCl_3$) of divinyl(tetraethoxy)disiloxane

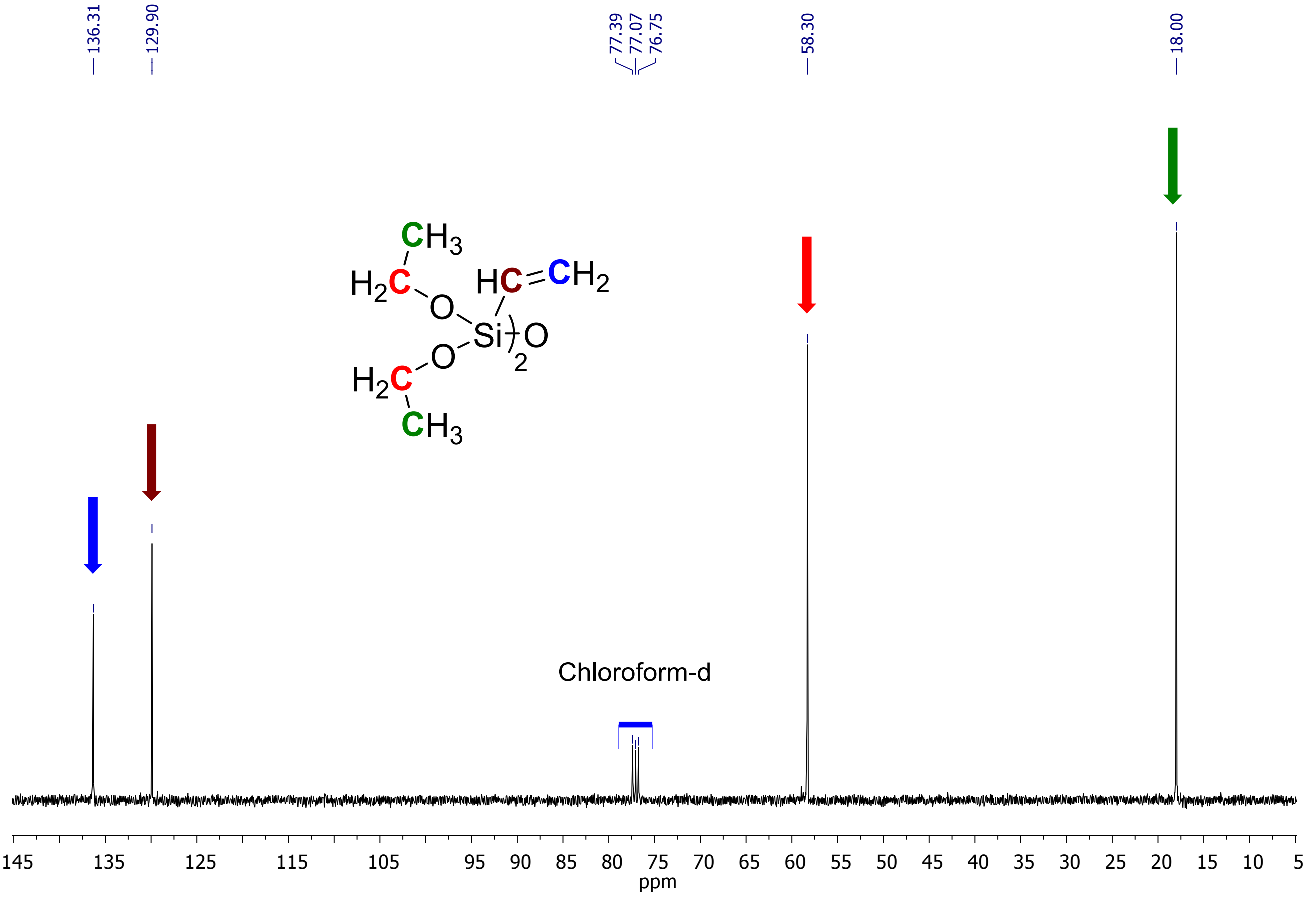


Figure 15: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of divinyl(tetraethoxy)disiloxane

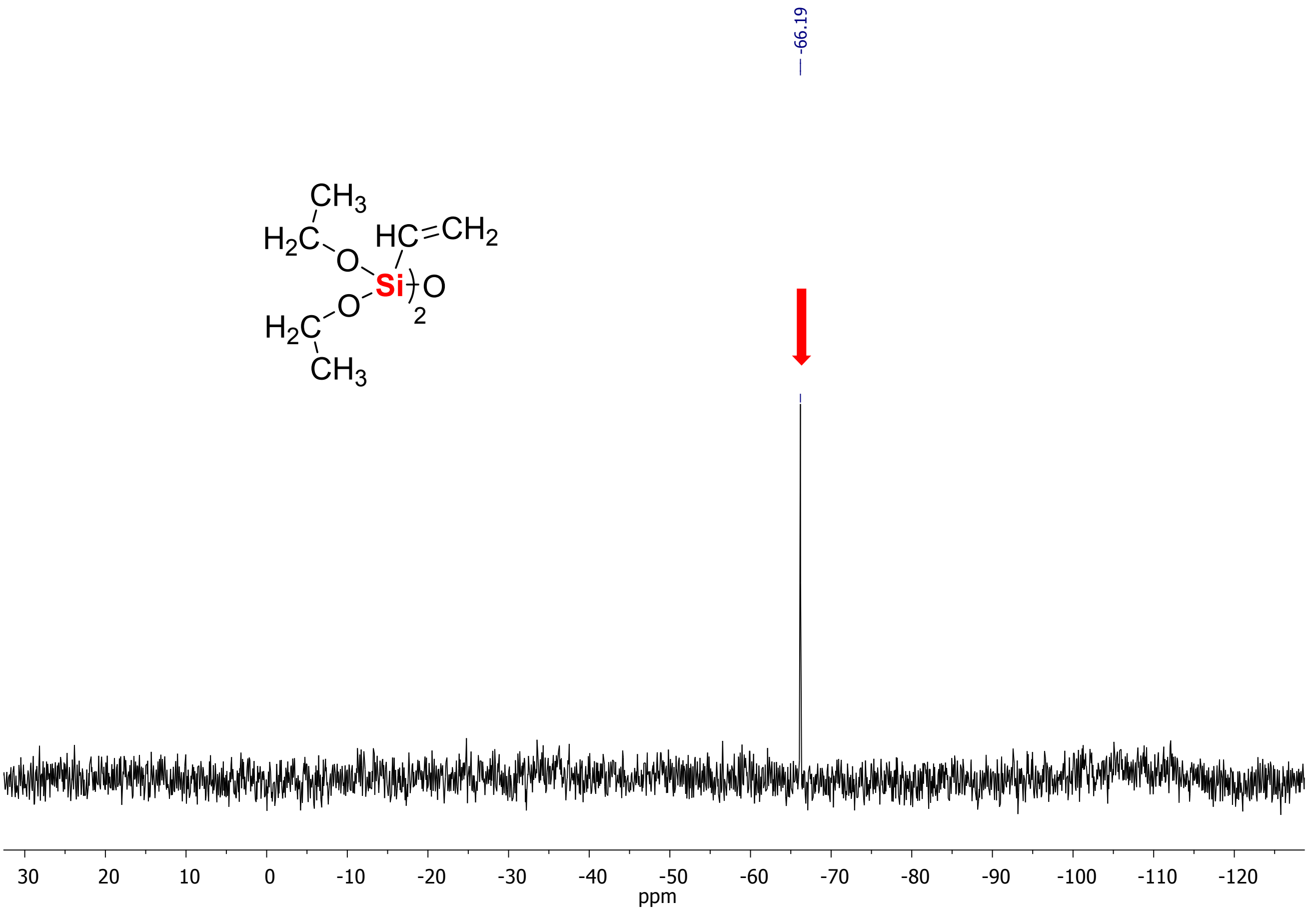


Figure 16: ^{29}Si NMR spectrum (79 MHz, CDCl$_3$) of divinyl(tetraethoxy)disiloxane

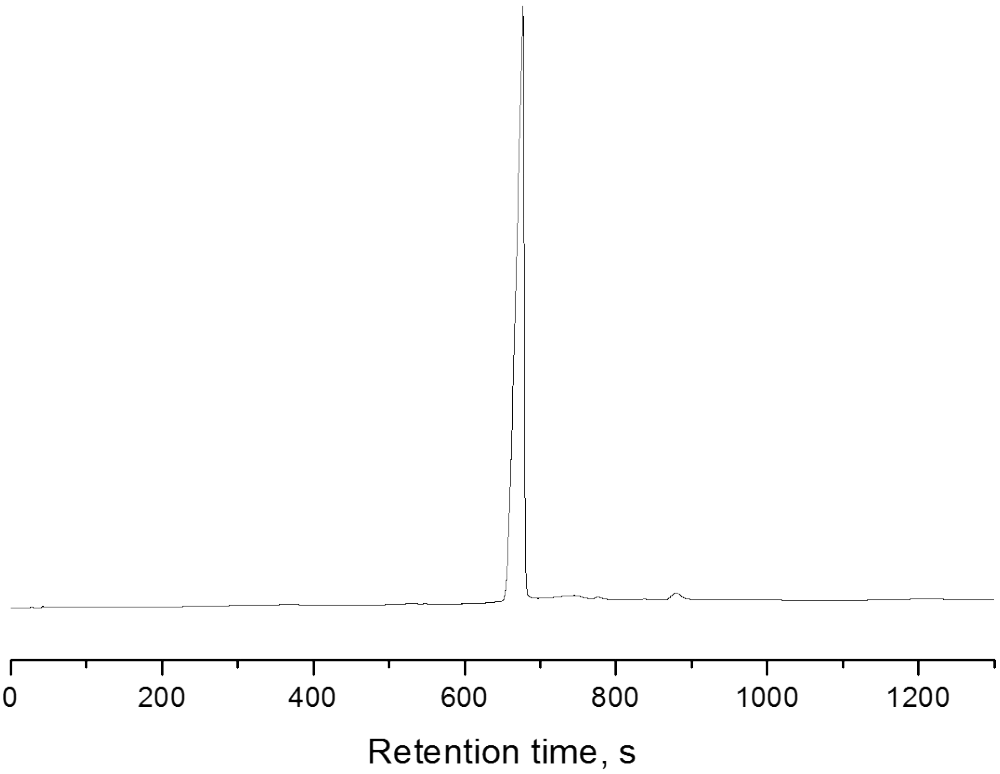


Figure 17: GC - curve of diphenyl(tetraethoxy)disiloxane

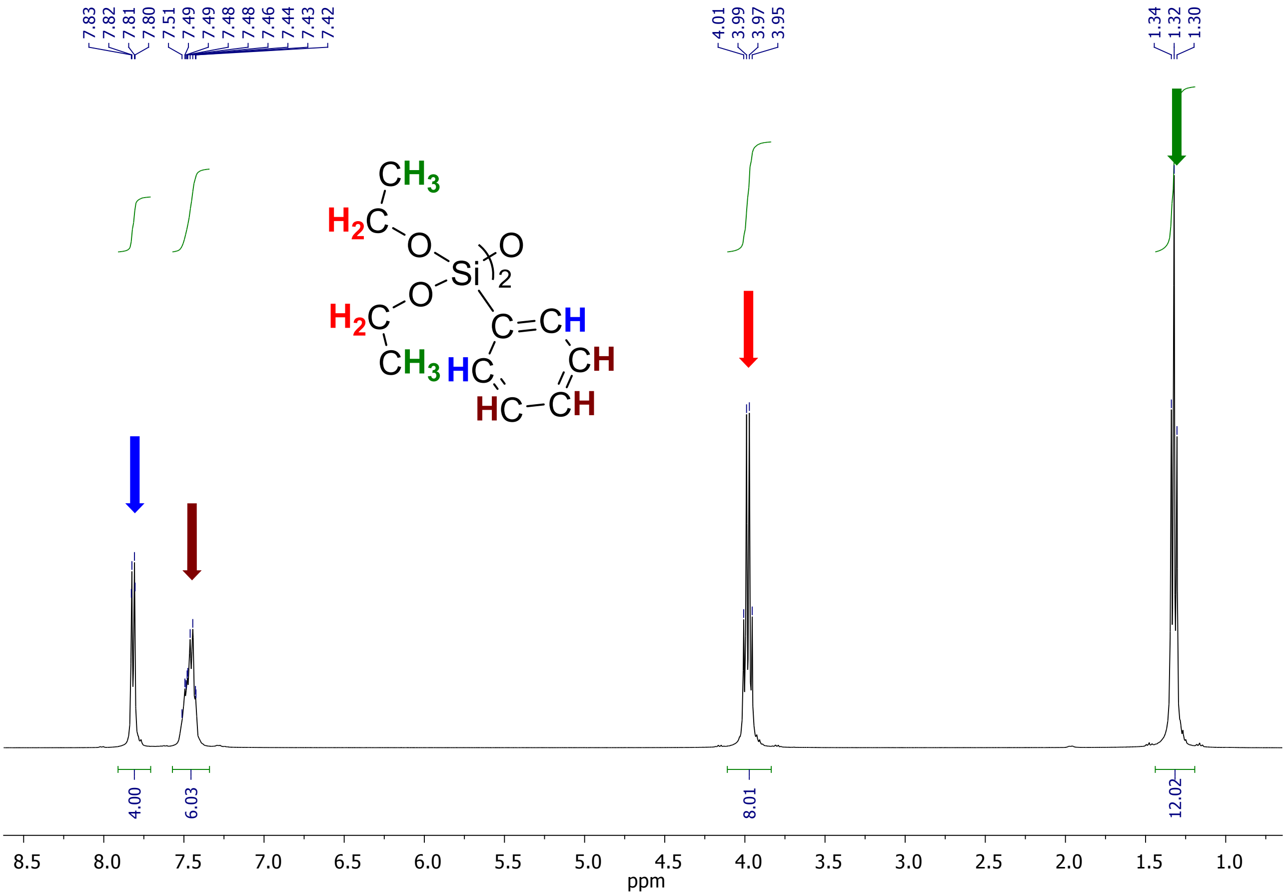


Figure 18: ^1H NMR spectrum (400 MHz, $CDCl_3$) of diphenyl(tetraethoxy)disiloxane

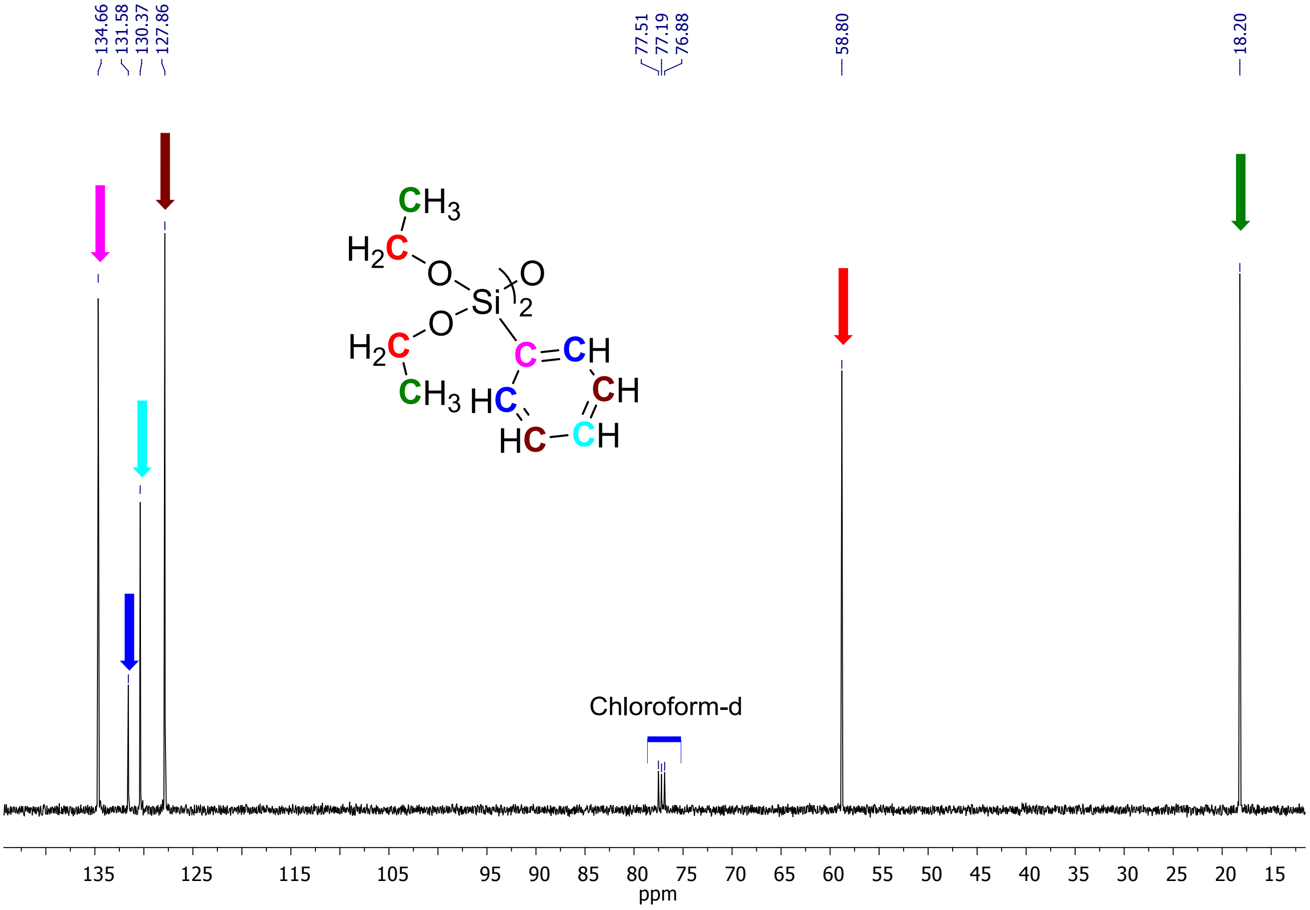


Figure 19: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of diphenyl(tetraethoxy)disiloxane

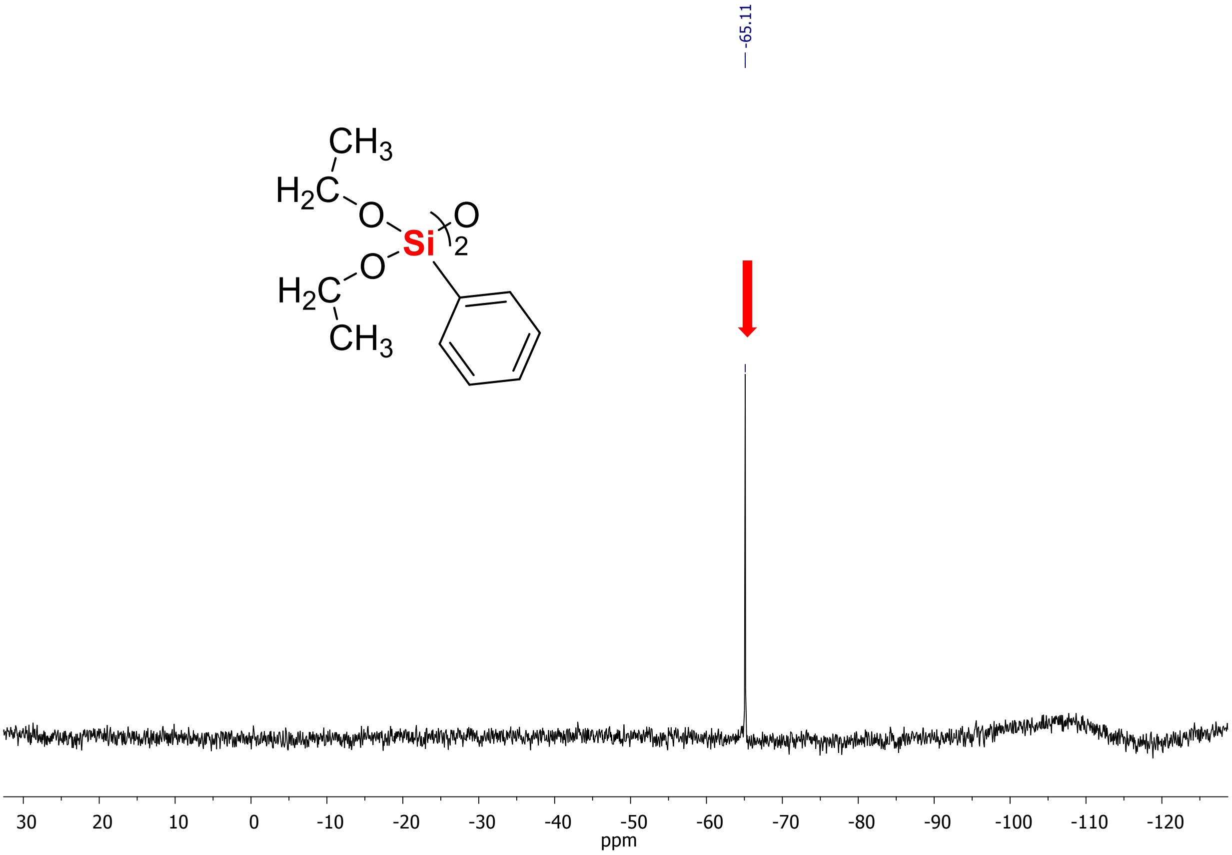


Figure 20: ^{29}Si NMR spectrum (79 MHz, $CDCl_3$) of diphenyl(tetraethoxy)disiloxane

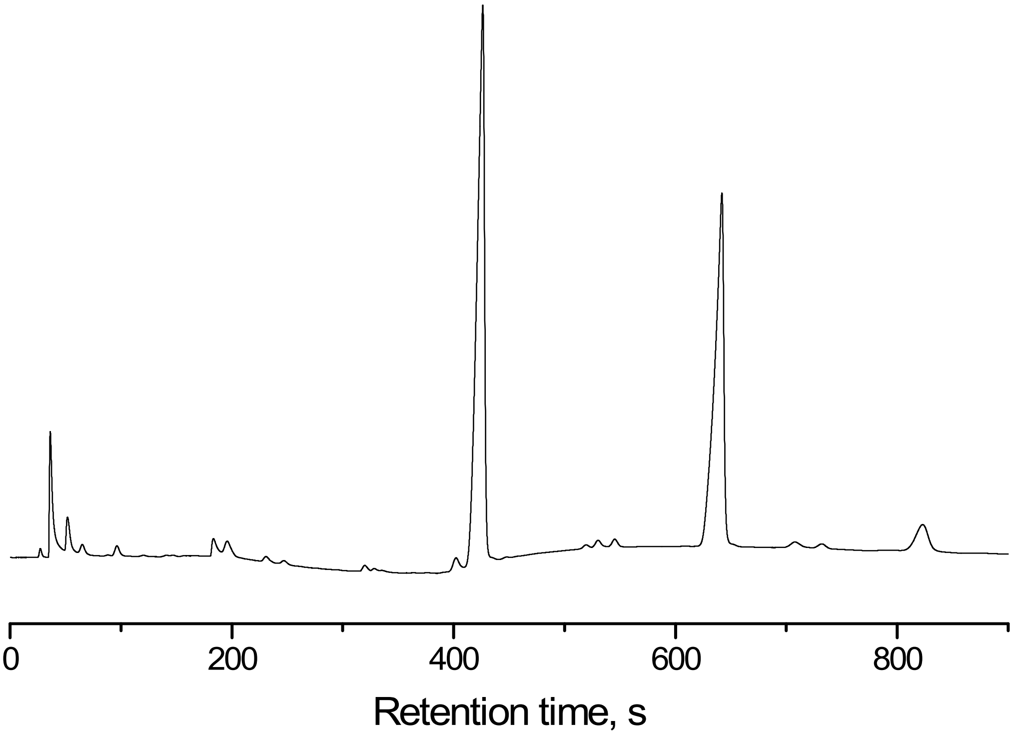


Figure 1: ***GC - curves of reaction mixture for reaction of 1.2.5***

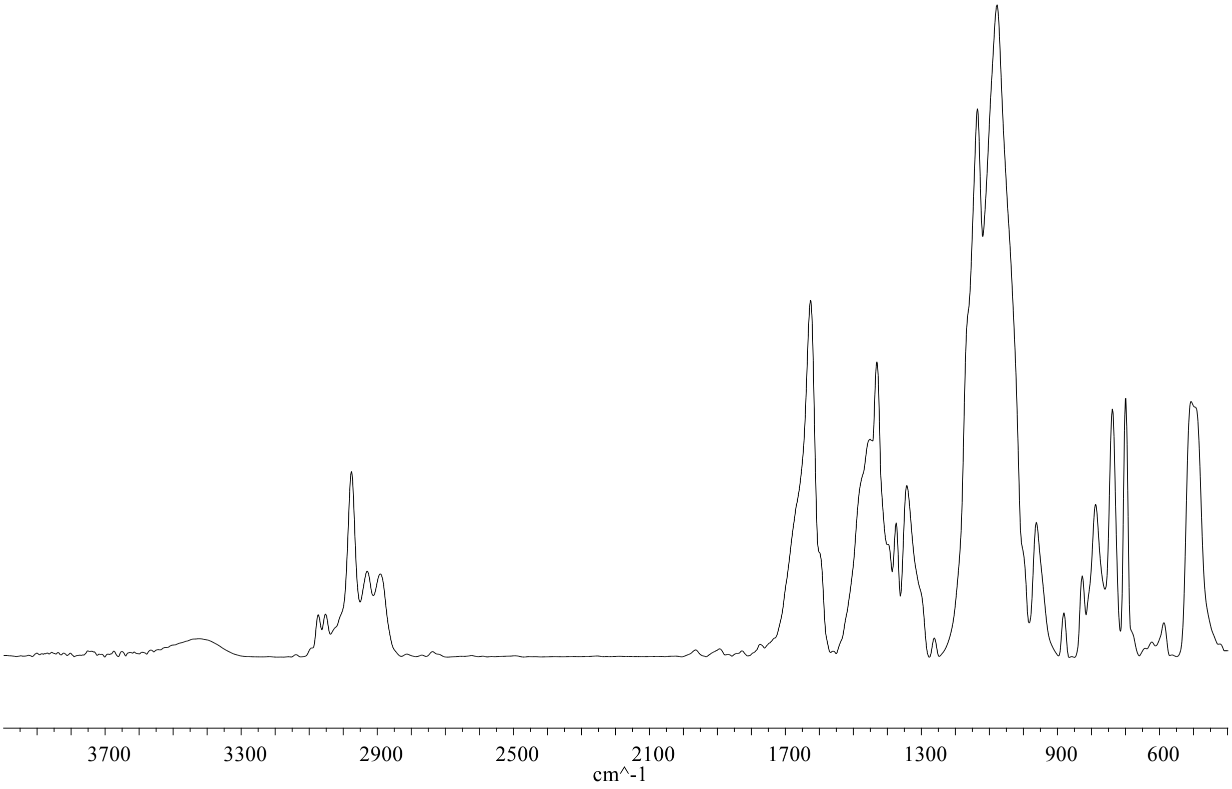


Figure 22: IR spectrum of sample of reaction 1.2.5

5. References

1. Gordon, A.J., Ford, R.A. The Chemist´s Companion; Wiley-Intersci.: Publ.: New York—London—Sydney—Toronto, 1972.