Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Application of Multifunctional Silylenes and Siliranes as Universal Crosslinkers for Metal-Free Curing of Silicones

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1. General Methods and Instrumentation

All manipulations (except for polymerizations with **16** and OH-terminated PDMS) and were carried out under argon or nitrogen atmosphere using standard Schlenk or glovebox techniques. Glassware was heat-dried under vacuum prior to use. Unless otherwise stated, all chemicals were purchased from *Sigma-Aldrich*, *ABCR* or *TCI Chemicals* and used as received. Compounds for screening reactions were carefully dried and purified prior to use. PDMS-compounds were received from *WACKER Chemie AG* or purchased from *ABCR*. All siloxanes for crosslinking experiments were degassed and dried to avoid problems with oxygen and water. For vinyl- and hydrosiloxanes we applied high vacuum and heat for several days. Carbinol and silanol terminated siloxanes were additionally flashed over dry neutral alumina and 3 Å molecular sieve. *Cis*-2-Butene (2.0) and *Trans*-2-butene (2.0) were purchased from *Linde AG* and used as received. A Li/Na alloy was prepared by melting elemental Li (*Sigma-Aldrich*, 99 %, trace metal basis) and Na (*Sigma-Aldrich*, 99.8 %, sodium basis) in a Ni crucible to 200 °C under argon in a glove-box. After mixing and subsequent cooldown the alloy was cut into small pieces for reductions. Al_2O_3 (neutral) and carbon black were dried for 72 h at 150 °C in high vacuum. n-Hexane, n-Pentane, THF, Et_2O, Benzene and toluene were refluxed over sodium/benzophenone or CaH_2, distilled and deoxygenated prior to use. All solvents were analysed for remaining H_2O by Karl-Fischer titration prior to use. Deuterated benzene (C_6D_6) and toluene (C_7D_8) were obtained from *Deutero Deutschland GmbH* and were dried and stored over 3 Å molecular sieves. All NMR samples were prepared under argon in *J. Young* PTFE tubes.

NMR-Spectroscopy

NMR spectra were recorded on *Bruker* AV-500C, AV-500 or DRX-400 spectrometers at ambient temperature (300 K). ^{1}H, ^{13}C and ^{29}Si NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane. $\delta(^{1}H)$ and $\delta(^{13}C)$ were referenced internally to the relevant residual solvent resonances. $\delta(^{29}Si)$ was referenced to the signal of tetramethylsilane (TMS) ($\delta = 0$ ppm) as external standard.

Mass Spectrometry

Mass spectra (MS-CI) were recorded on a double focusing *Finnigan* MAT 90 mass spectrometer (isobutene, 150 eV) or TOF LCT 700 from *Waters* equipped with an ion source from *Linden CMS GmbH*. For LIFDI-MS the substances were dissolved in dry solvents and filtrated (syringe-filter, 0.45 µm) before measuring.

UV-Vis Measurements

For UV-Vis measurements a *Varian* Cary 50 Scan photometer was used in combination with custom-made UV-cuvettes with attached vacuum connection. n-Pentane and n-hexane were used as solvents.

Rheologic Measurements

Rheologic measurements were conducted with an *Anton Paar* MCR 302 with an additional hood for inert gas and custom-made plates. The transfer of compound mixtures into the rheometer was conducted under protective gas. Measuring frequency $f = 1$ Hz, gradually decreasing amplitude (starting at 10 %, automatic decrease of 1/10 when moment $M > 1$ mNm). $\tan(\delta)$ values of fully crosslinked (steady viscosity) elastomers are calculated as mean values of the last 100 data points. This is necessary due to high fluctuations when measuring solid elastomers with deformations as low as 0.01 %.

Shore Measurements

Shore A and Shore A0 measurements were conducted with a *Sauter* HBA 100-0 or *Zwick/Roell* 3130 tool. The measuring duration was 3 seconds. All given values are average values from 5 measurements. The thickness of measured elastomers was at least 6 mm, some specimens were cut and stacked to reach the required height.

Elemental Analysis

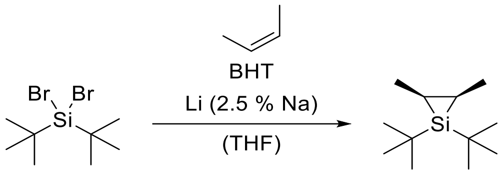
Elemental analyses (EA) were conducted with a EURO EA (*HEKA tech*) instrument equipped with a CHNS combustion analyser.

2. Synthesis and Characterization of New Compounds

Precursors of silirane **1** tBu_2SiHCl, tBu_2SiH_2 and tBu_2SiBr_2 were synthesized according to literature.[1-4] tBu_2SiBr_2 was additionally purified by crystallisation from dry MeCN at -30 °C. Highly pure tBu_2SiBr_2 is a colourless waxy solid.

Siliranes *cis*-1,1-di-*tert*-butyl-2,3-dimethylsilirane and *trans*-1,1-di-*tert*-butyl-2,3-dimethyl-silirane were synthesized *via* modified procedures described in literature.[4-6]

2.1.1. Synthesis of *cis*-1,1-di-*tert*-butyl-2,3-dimethylsilirane/*trans*-1,1-di-*tert*-butyl-2,3-dimethylsilirane **1**



A 500 mL high-pressure Schlenk-tube with a PTFE sealed screw cap was equipped with a PTFE-coated stir bar and was loaded with 30.0 g (99.3 mmol, 1.00 eq.) of tBu_2SiBr_2, 100 mg (0.45 mmol, 0.005 eq.) 3,5-Di-*tert*-butyl-4-hydroxytoluene (BHT) and 17.5 g (198.6 mmol, 2 eq.) tetrahydrofuran. The reaction tube was cooled down to -78 °C with a dry ice/isopropanol mixture. Present argon atmosphere was removed *in vacuo* and 111.4 g (1.9 mol, 20.0 eq.) *cis*-2-butene was condensed into the cooled reaction mixture by pressurizing it with 1.80 bar of the respective gas. After re-pressurizing with argon, 5.51 g (2.5 % Na, 794.4 mmol, 8.0 eq.) Li/Na alloy chunks were added to the reaction mixture, followed by vigorous stirring at room temperature for 16 h. After full conversion (^{29}Si-NMR verification) *cis*-2-butene gas was released and remaining solvent was removed under vacuum. The crude slurry was extracted 5 times with each 50 mL n-pentane to precipitate and separate the generated LiBr by filtration. After filtration (syringe-filter) n-pentane was removed again and the remaining oil purified by bulb-to-bulb distillation (40 °C, 10^{-2} mbar, N_2 cooled trap). 14.4 g (72.6 mmol, 73 %) *cis*-1,1-di-*tert*-butyl-2,3-dimethylsilirane is received as a colourless clear oil.

cis-$tBu_2Si(CHMe)_2$: **^{1}H-NMR:** (300 K, 500 MHz, C_6D_6) δ = 1.06 (s, 9H, *t*Bu), 1.04–1.10 (m, 2H, -Si-C*H*-), 1.17 (s, 9H, *t*Bu), 1.40–1.41 (m, 6H, -CH-*Me*). **^{13}C-NMR:** (300 K, 125 MHz, C_6D_6) δ = 10.0 (Si-*C*H-), 10.3 (Si-*C*H-), 18.6 (-CH-*Me*), 20.9 (-CH-*Me*), 30.0 (*t*Bu-Me), 31.6 (*t*Bu-Me). **^{29}Si-NMR:** (300 K, 100 MHz, C_6D_6) δ = -53.2. **CI-MS**: 197.3 $[M-H]^+$.

The *trans*-species of **1** is synthesised analogously with *trans*-2-butene. For subsequent silylene transfer reaction both stereoisomers were equally suitable and yielded identical products.

trans-$tBu_2Si(CHMe)_2$: **^{1}H-NMR:** (297 K, 300 MHz, C_6D_6) δ = 1.06 (s, 2H, -Si-C*H*-), 1.09 (s, 18H, *t*Bu), 1.54–1.47 (m, 6H, -CH *Me*). **^{29}Si-NMR:** (300 K, 100 MHz, C_6D_6) δ = -43.9. **CI-MS**: 197.3 $[M-H]^+$.

2.2. Multifunctional Silirane Crosslinkers 5–10

2.2.1. General Procedure for Multifunctional Silirane Crosslinkers **5**–**10**

2.80 mmol (1.00 eq.) of the respective vinyl-functionalized reagent and x•1.20 eq. silirane **1** were mixed with 5 mL toluene in a 20 mL Schlenk-tube (x = number of vinyl-moieties at the reagent). While stirring 1 mg (4.01 µmol, 0.0014 eq.) AgOTf was added to the reaction. The mixture was heated up to 60 °C and stirred for 16 h. Emerging butene gas was released over a relief valve. Full conversion was verified by ^{1}H-NMR (absence of vinyl-H). The solvent and remaining **1** were removed by high vacuum (60 °C, 10^{-5} mbar) from the product. Separation of the catalyst was carried out by diluting the crude product in 5 mL pentane and subsequent filtration over an appropriate amount of aluminium oxide (Al_2O_3). The aluminium oxide was further washed with 2 mL pentane. At last the solvent was removed in vacuo to obtain the silirane crosslinkers as colourless viscous fluids. The yield strongly depends on the filtration step. Raw yield is always 100 %, workup loss can be up to 50 %.

2.2.2. 1,3-Bis(1,1-di-*tert*-butylsilirane-2-yl)-1,1,3,3-tetramethyldisiloxane **5**

^{1}H-NMR: (500 MHz, C_6D_6) δ = -0.26–-0.19 (m, 2H, tBu$_2$SiC*H*), 0.33–0.38 (m, 12H, Si-*Me*), 0.6–.78 (m, 4H, tBu$_2$SiC*H$_2$*), 1.05–1.07 (m, 18H, *t*Bu), 1.16–1.18 (m, 18H, *t*Bu). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 5.47, -48.42, -48.45, -48.57, -48.73.[1]

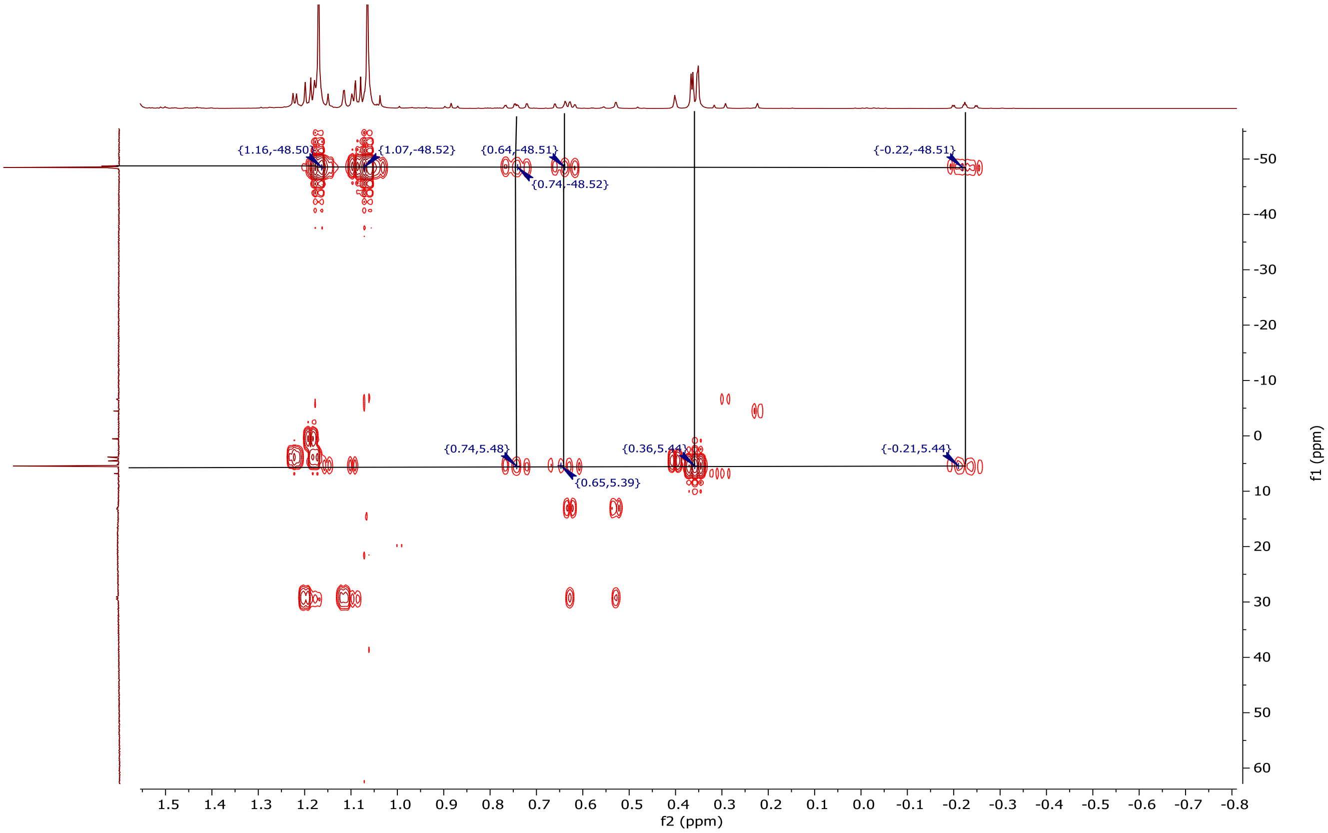


Figure 1: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **5**. Raw product contains monosubstituted species and sideproducts derived from ^{t}Bu$_2$SiMe$_2$-silirane **1.**

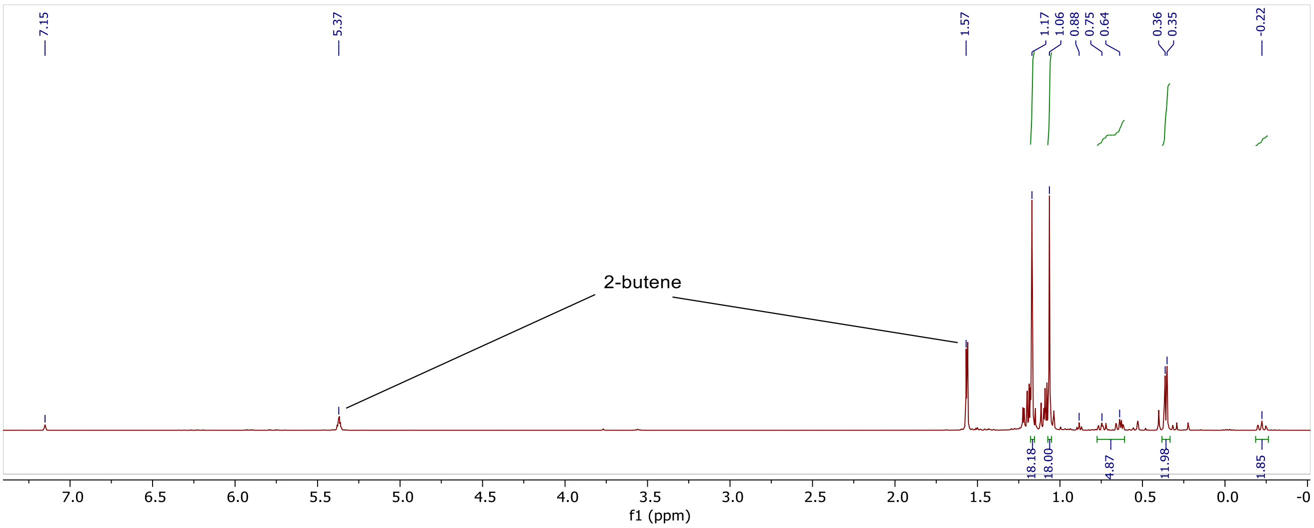


Figure 2: ^{1}H-NMR (500 MHz, C_6D_6) of compound **5**. Raw product contains monosubstituted species and sideproducts derived from ^{t}Bu$_2$SiMe$_2$-silirane **1**.

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[1] Compound **5** is a mixture of various stereoisomers, which results in multiple signals for e.g. silirane-Si.

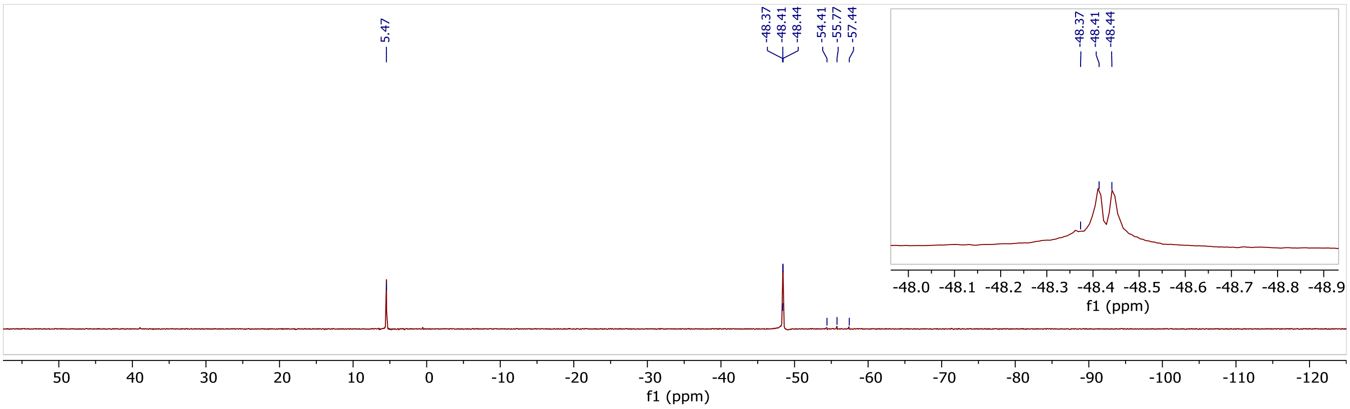

Figure 3: ^{29}Si-ig-NMR (100 MHz, C_6D_6) of compound **5**. Raw product contains monosubstituted species and sideproducts derived from ^{t}Bu$_2$SiMe$_2$-silirane **1**.

2.2.3. Tetrakis(1,1-di-*tert*-butylsilirane-2-yl)silane **6**

Yield: 91 %. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = 0.10–0.29 (m, 4H, -C*H*-), 0.62–0.88 (m, 8H, -C*H*$_2$-), 1.18–1.22 (m, 36H, *t*Bu), 1.31–1.34 (m, 36H, *t*Bu). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = -46.5–(-43.9) (-*Si*-*t*Bu$_2$), 5.0–5.2 (*Si*-(CH)$_4$-). **CI-MS:** 704.2 [M$^+$].

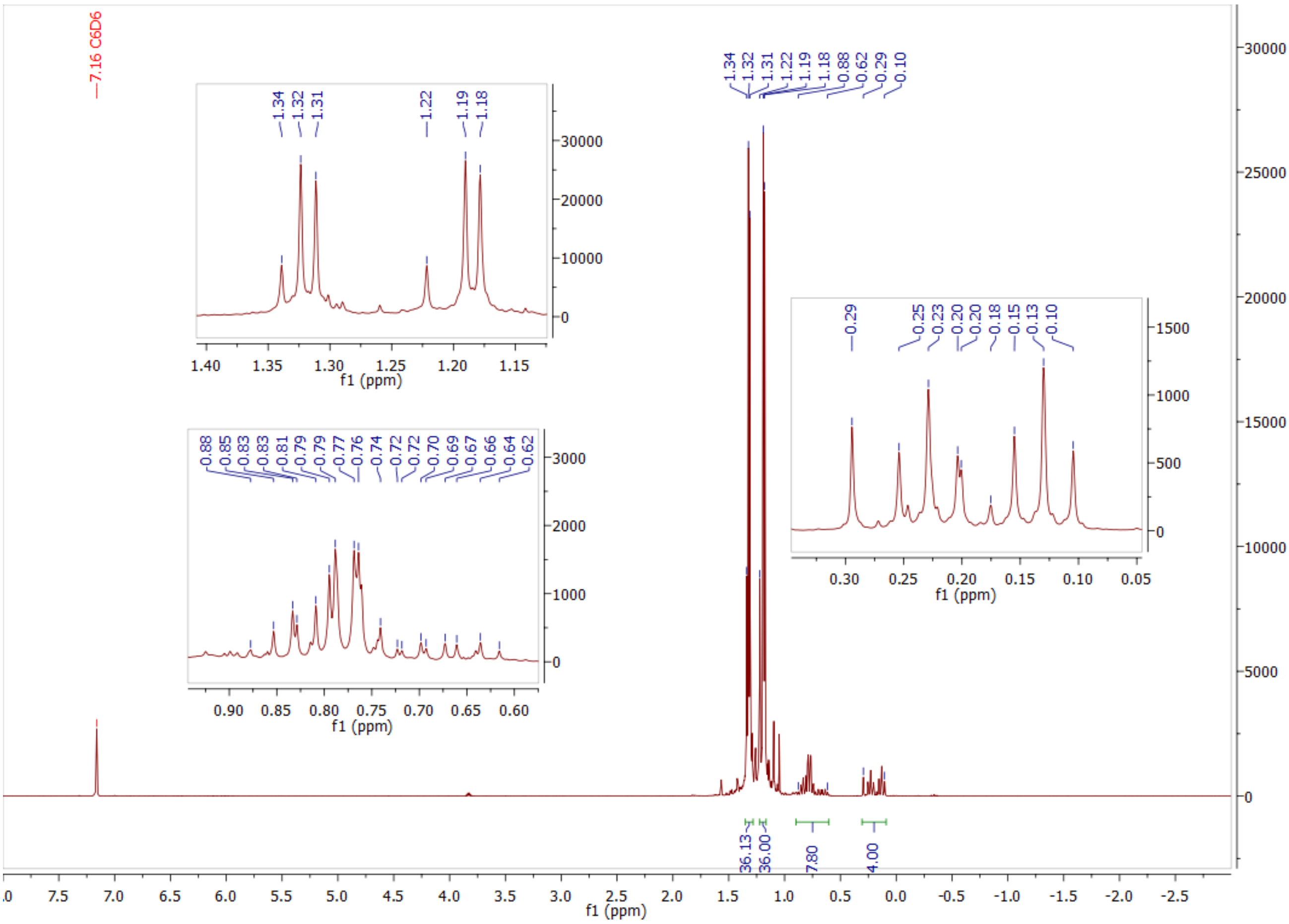

Figure 4: ^{1}H-NMR (500 MHz, C_6D_6) of compound **6.** Contains diastereomers and ^{t}Bu$_2$SiMe$_2$ silirane. When integrated over entire signal-areas the integrals relate to the molecular structure.

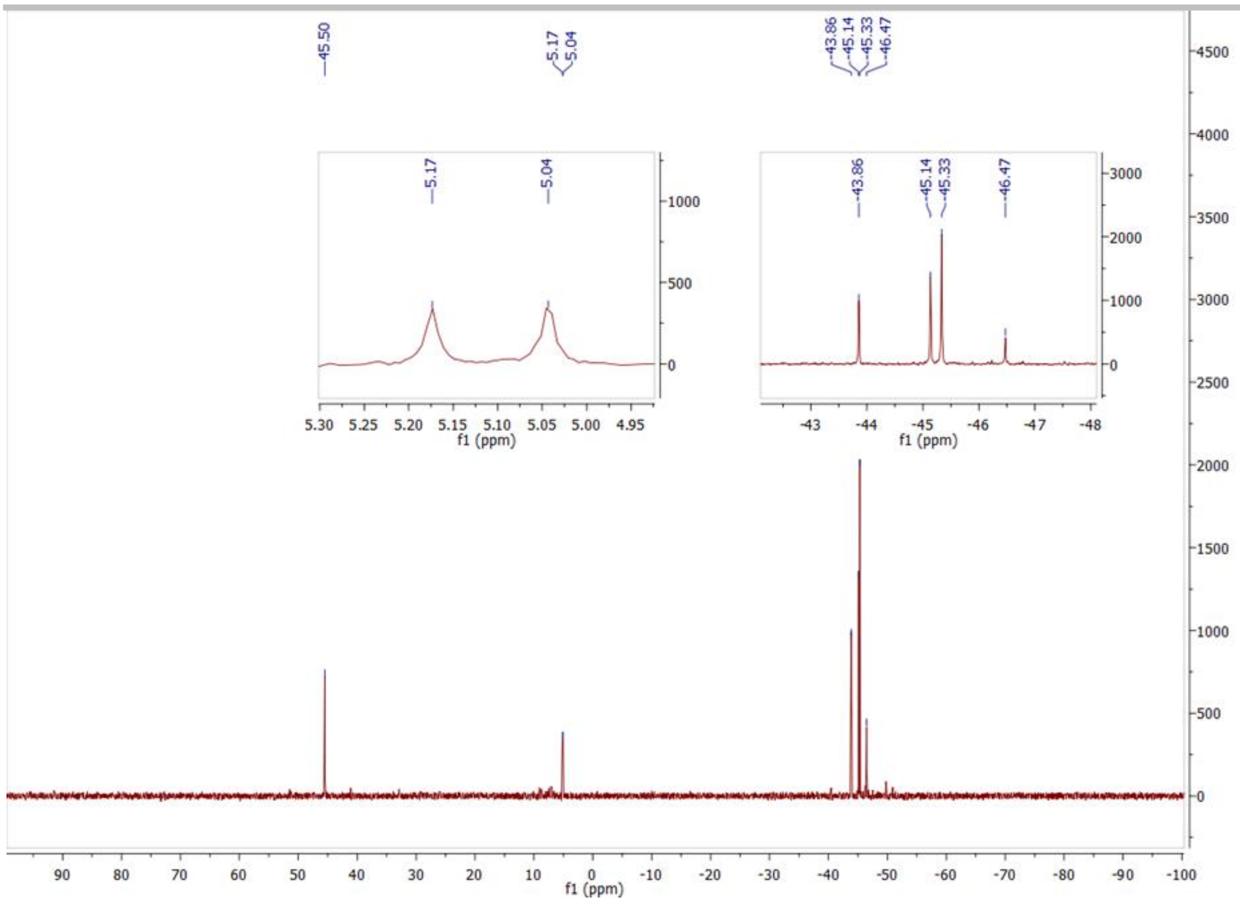

Figure 5: ^{29}Si-ig-NMR (100 MHz, C_6D_6) of compound **6**. Contains diastereomers and ^{t}Bu$_2$SiMe$_2$ silirane.

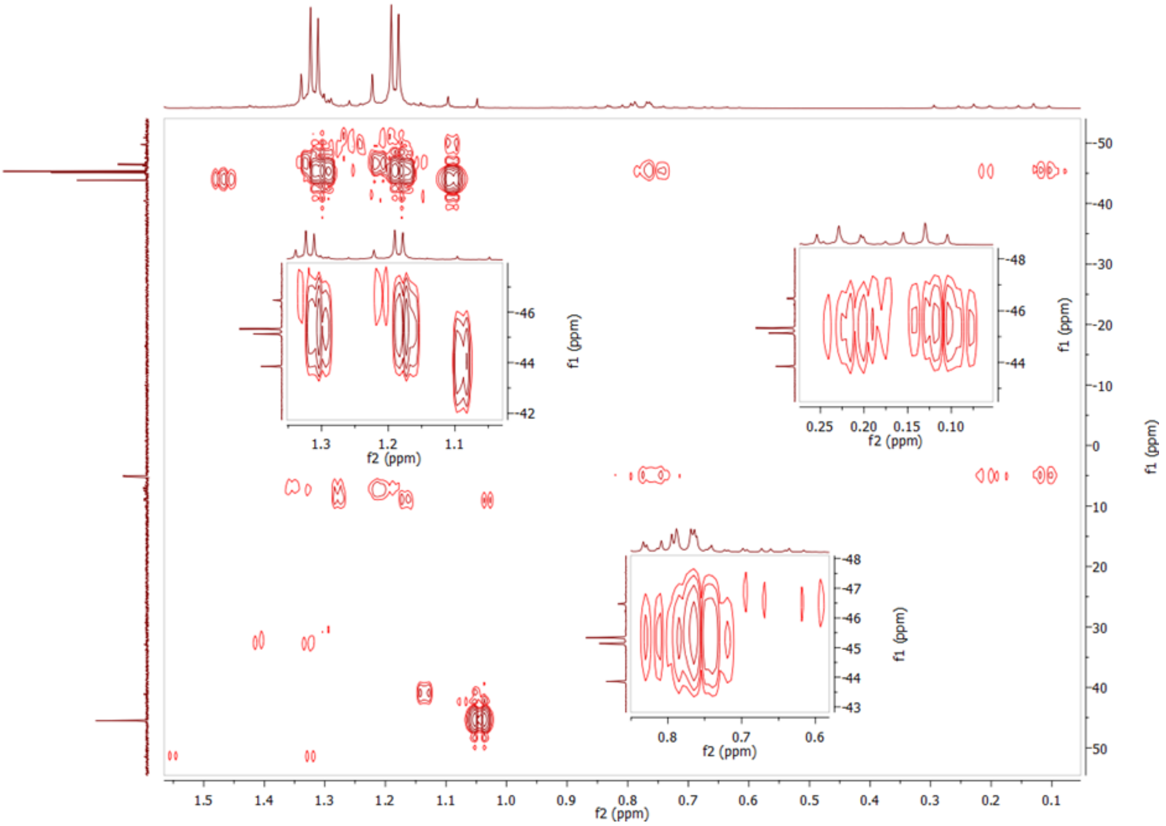

Figure 6: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **6.**

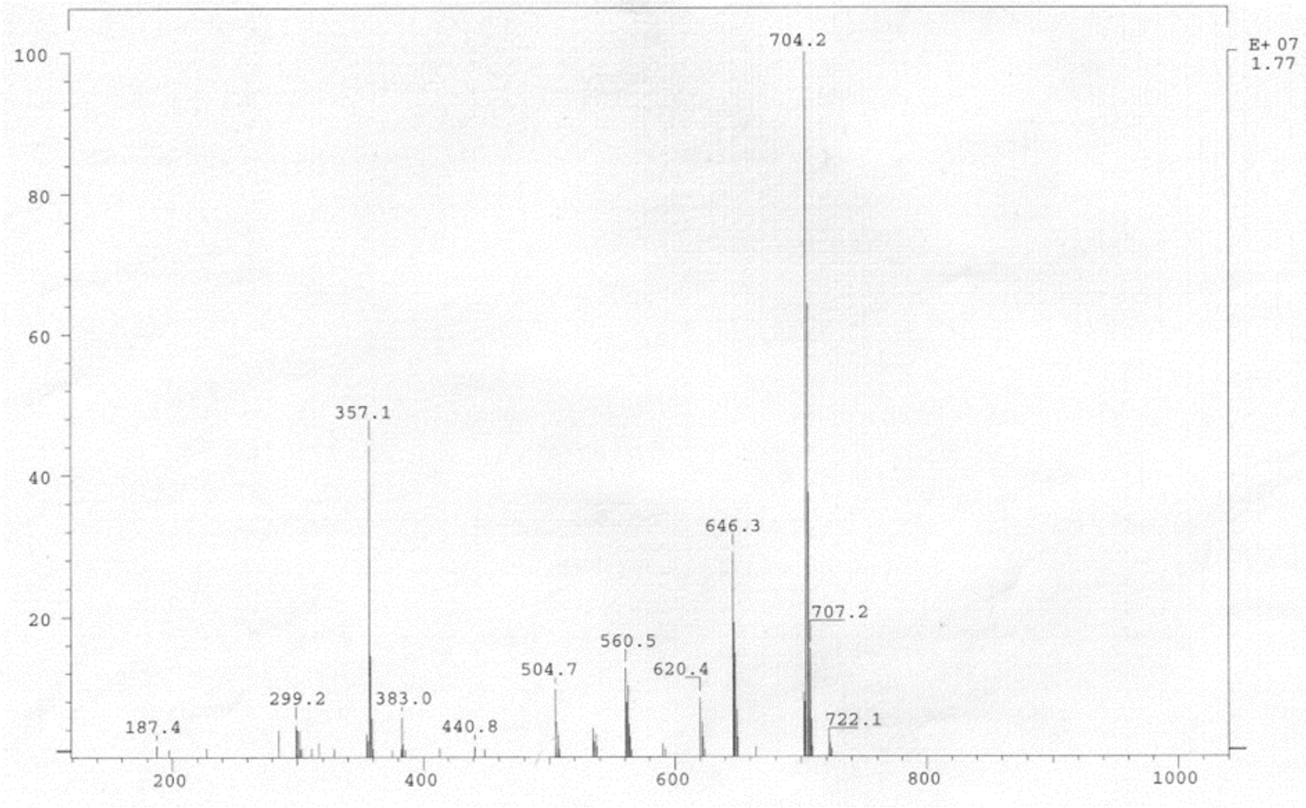

Figure 7: CI-MS spectrum of compound **6**.

2.2.4. 2,4,6,8-Tetrakis(1,1-di-*tert*-butylsilirane-2-yl)-2,4,6,8-tetramethyl-cyclotetrasiloxane **7**

Yield: 85 %. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = -0.16–0.02 (m, 4H, -C*H*-), 0.46–0.66 (m, 12H, Si-*Me*), 0.77–0.88 (m, 8H, -C*H*$_2$-), 1.04–1.13 (m, 36H, *t*Bu), 1.24–1.31 (m, 36H, *t*Bu). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = -49.8–(-49.0) (-*Si*-*t*Bu$_2$), -23.8–(-21.9) (-*Si*-O-). **CI-MS**: 911.4[M]$^+$, 769.8 [M-Si*t*Bu$_2$]$^+$, 628.1 [M-2Si*t*Bu$_2$]$^+$.

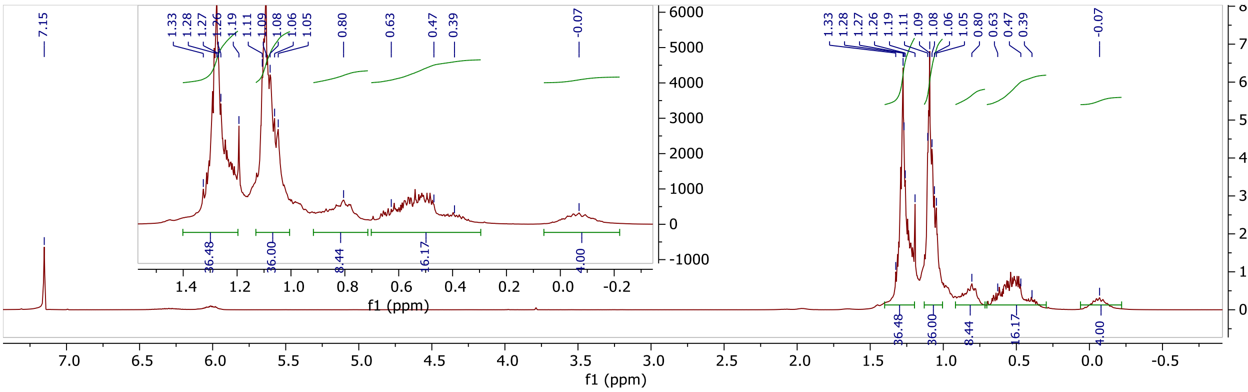

Figure 8: ^{1}H-NMR (500 MHz, C_6D_6) of compound **7.** Contains diastereomers. When integrated over entire signal-areas the integrals relate to the molecular structure.

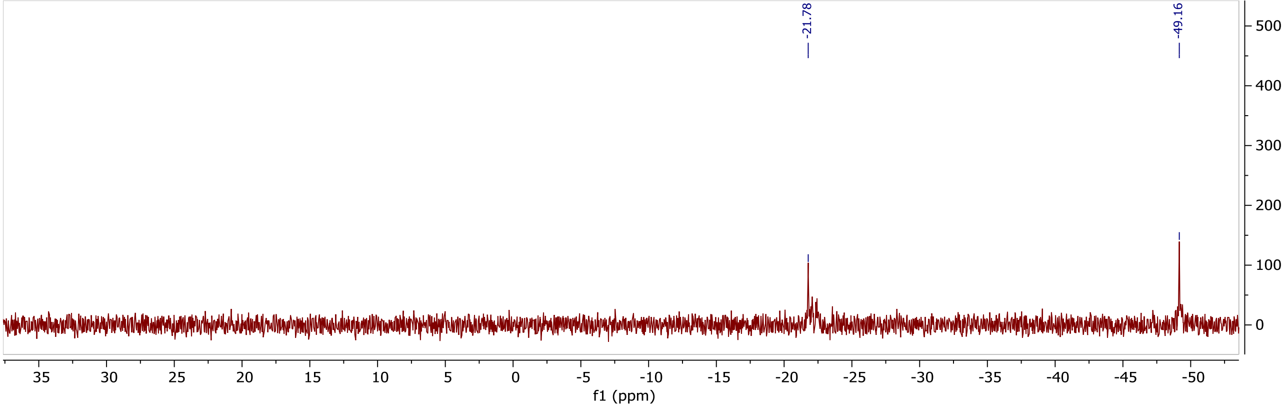

Figure 9: ^{29}Si-ig-NMR (100 MHz, C_6D_6) of compound **7**. Contains diastereomers.

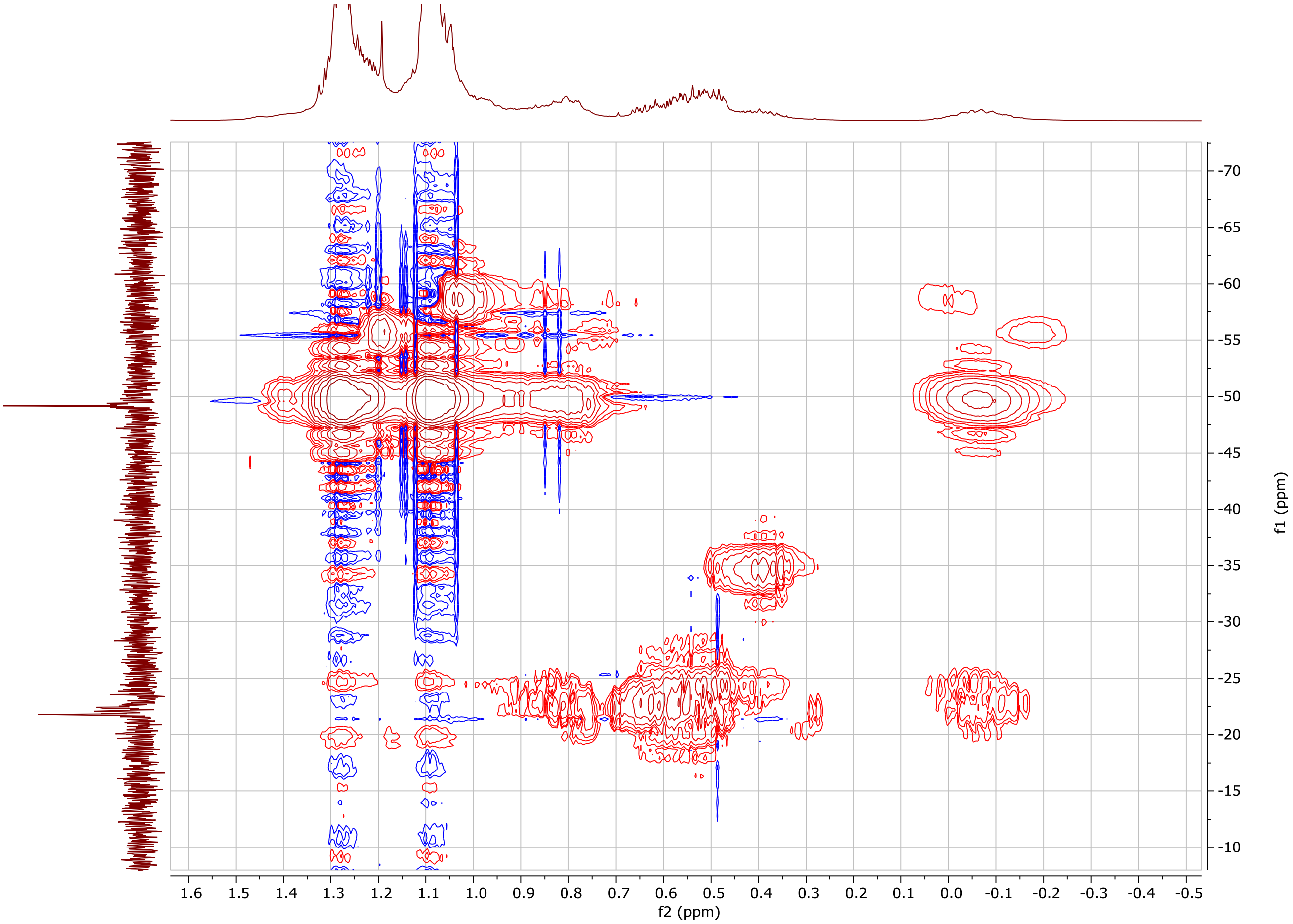

Figure 10: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **7.**

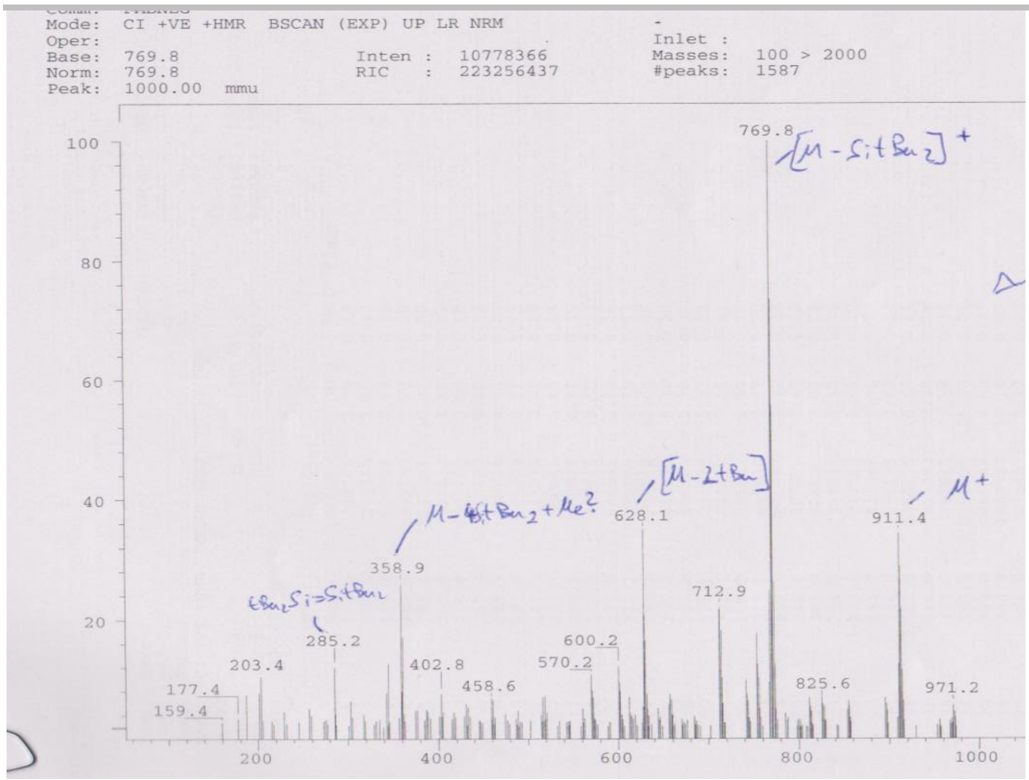

Figure 11: CI-MS spectrum of compound **7**.

2.2.5. Tetrakis((1,1-di-*tert*-butylsilirane-2-yl)methyl)silane **8**

Yield: 82 %. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = 0.39–0.44 (m, 4H, tBu$_2$SiC*H*), 1.10–1.11 (m, 36H, *t*Bu), 1.19–1.22 (m, 8H, Si(CH_2)$_4$), 1.25–1.26 (m, 36H, *t*Bu), 1.40–1.47 (m, 4H, tBu$_2$SiCH_2), 1.60–1.66 (m, 4H, tBu$_2$SiCH_2). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 5.0 (*Si*-(CH$_2$)$_4$-), -49.5 (-*Si*-tBu$_2$). **CI-MS**: 760.0[M]$^+$, 285.2 [Si$_2t$Bu$_4$]$^+$.

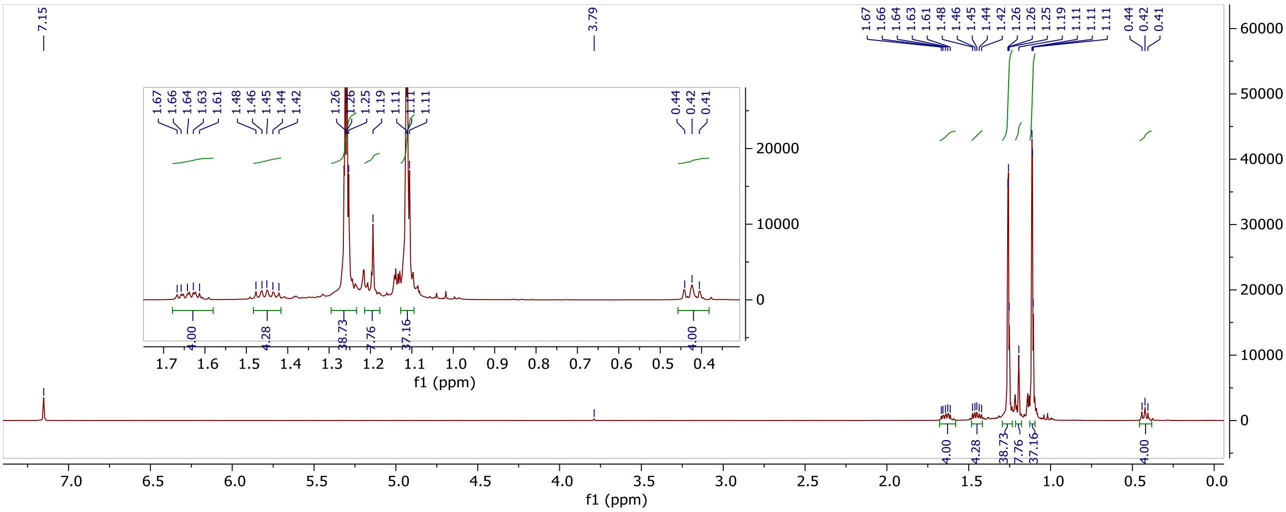

Figure 12: ^{1}H-NMR (500 MHz, C_6D_6) of compound **8.** Contains diastereomers.

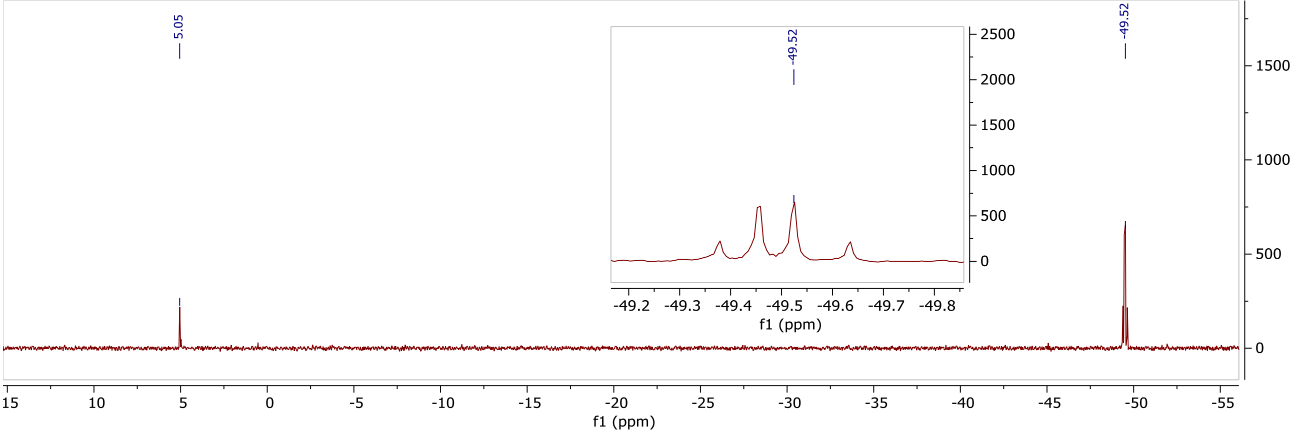

Figure 13: ^{29}Si-ig-NMR (100 MHz, C_6D_6) of compound **8**. Contains diastereomers.

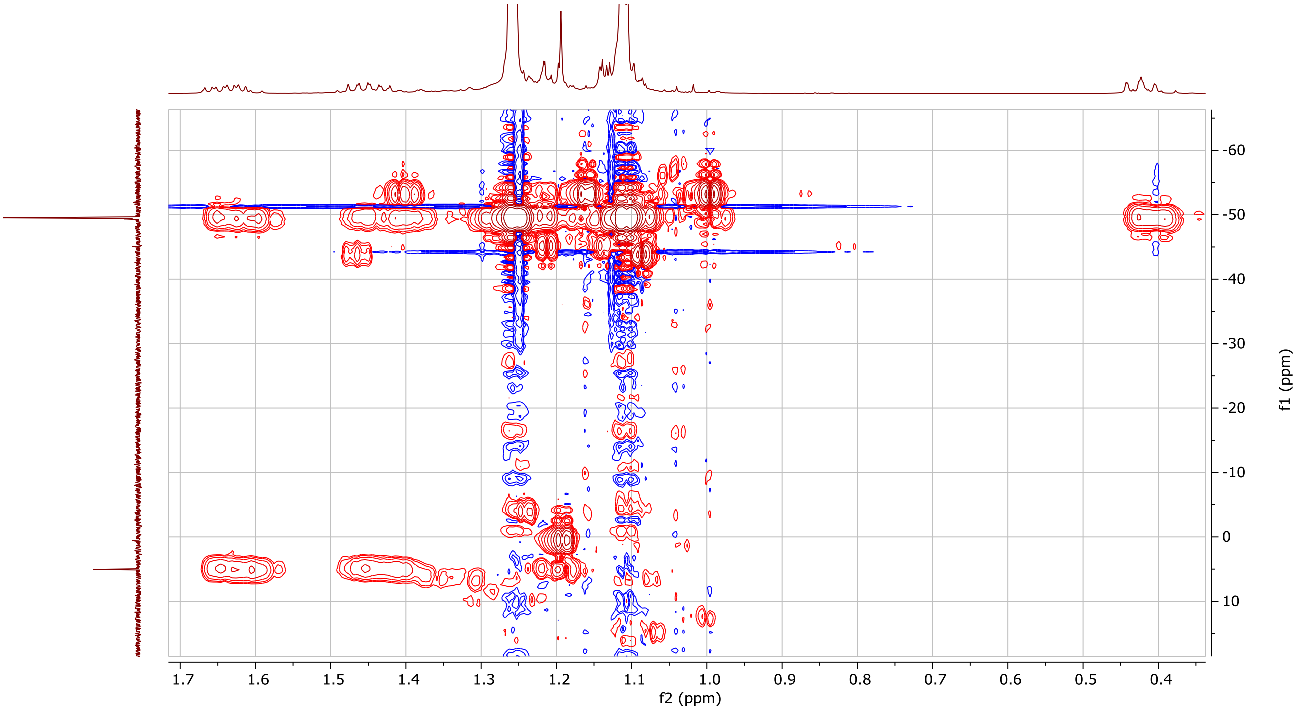

Figure 14: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **8.**

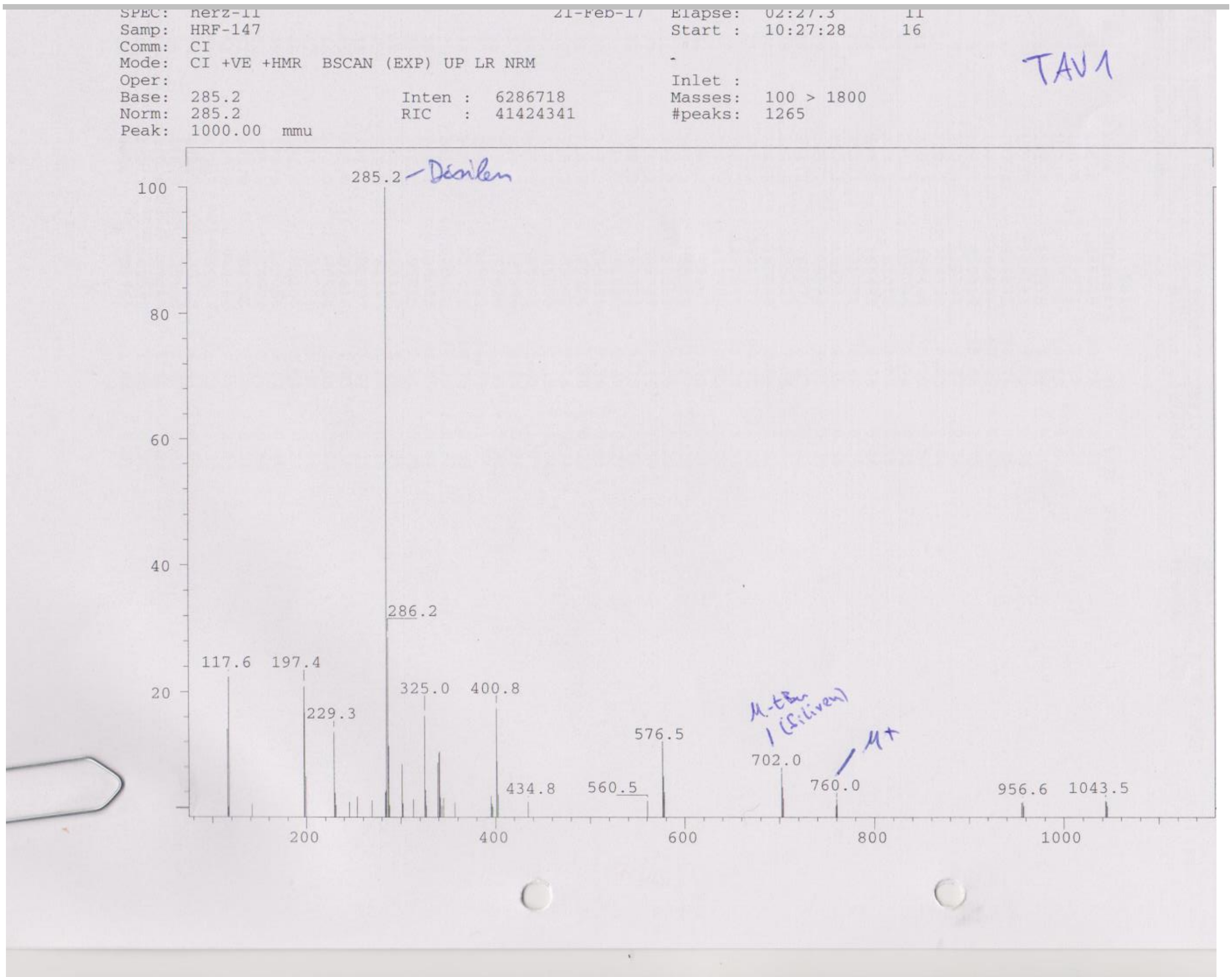

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Figure 15: CI-MS spectrum of compound **8**.

2.2.6. Poly(((1,1-di-*tert*-butylsilirane-2-yl)methylsiloxane)-co-dimethylsiloxane) Copolymer **9**

Yield: 85 %. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = -0.18 (m, 5H, tBu$_2$SiC*H*), 0.17–0.56 (m, 159H, Si-*Me*), 0.70–0.87 (m, 10H, tBu$_2$SiC*H$_2$*), 1.06–1.17 (m, 45H, *t*Bu), 1.21–1.34 (m, 45H, *t*Bu). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = -21.3–(-22.7) (-*Si*Me$_2$-O-), -23.66 (-*Si*MeR-O-), -49.17 (-*Si*-*t*Bu$_2$).[2]

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[2] Only a single analysis method was conducted (NMR). MS was not possible due to high M_w and lability of siliranes. EA not meaningful, since compound **9** and **10** are a mixture of polymers of different length with a statistical distribution. NMR can be regarded as structural proof and proof of purity due to complete disappearance of vinyl protons in ^{1}H-NMR and correlations between silirane-Si and PDMS-backbone. Furthermore, the structure is confirmed by successful polymerizations with these compounds.

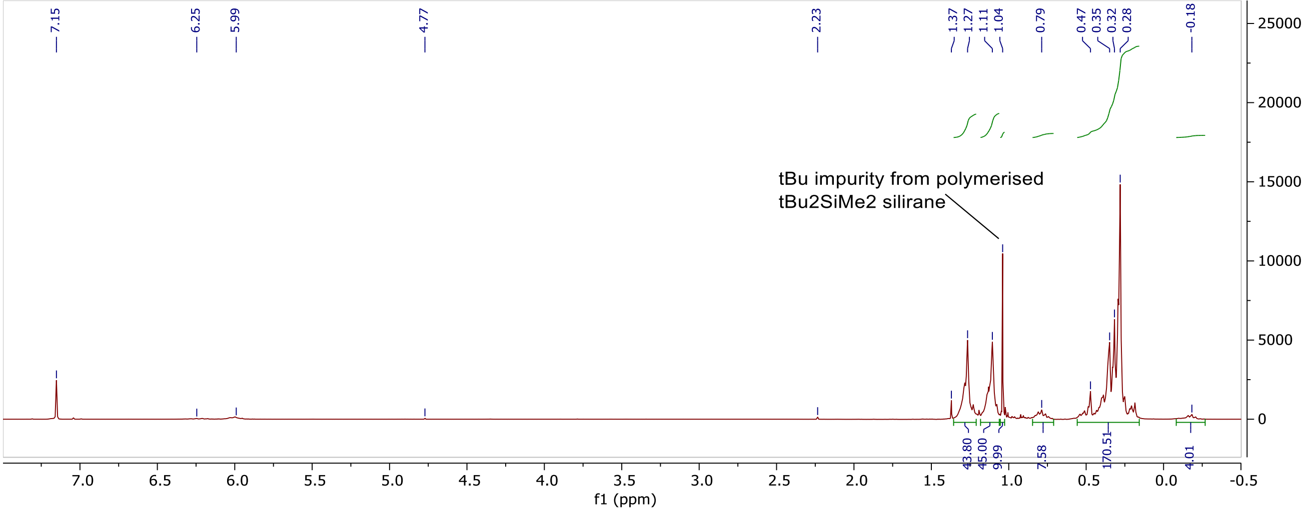

Figure 16: ^{1}H-NMR (500 MHz, C_6D_6) of compound **9.**

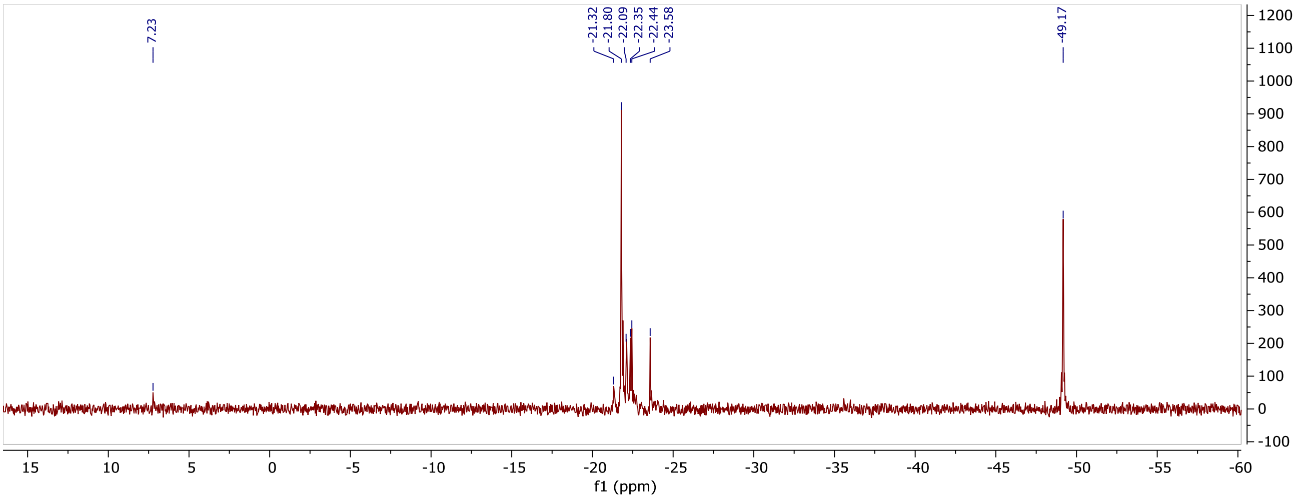

Figure 17: ^{29}Si-ig-NMR (100 MHz, C_6D_6) of compound **9.**

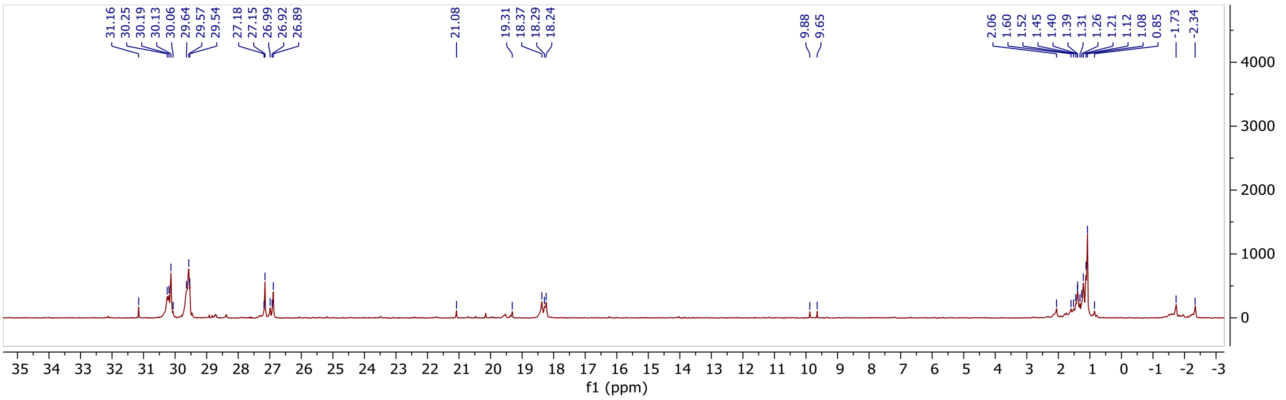

Figure 18: ^{13}C-NMR (125 MHz, C_6D_6) of compound **9**.

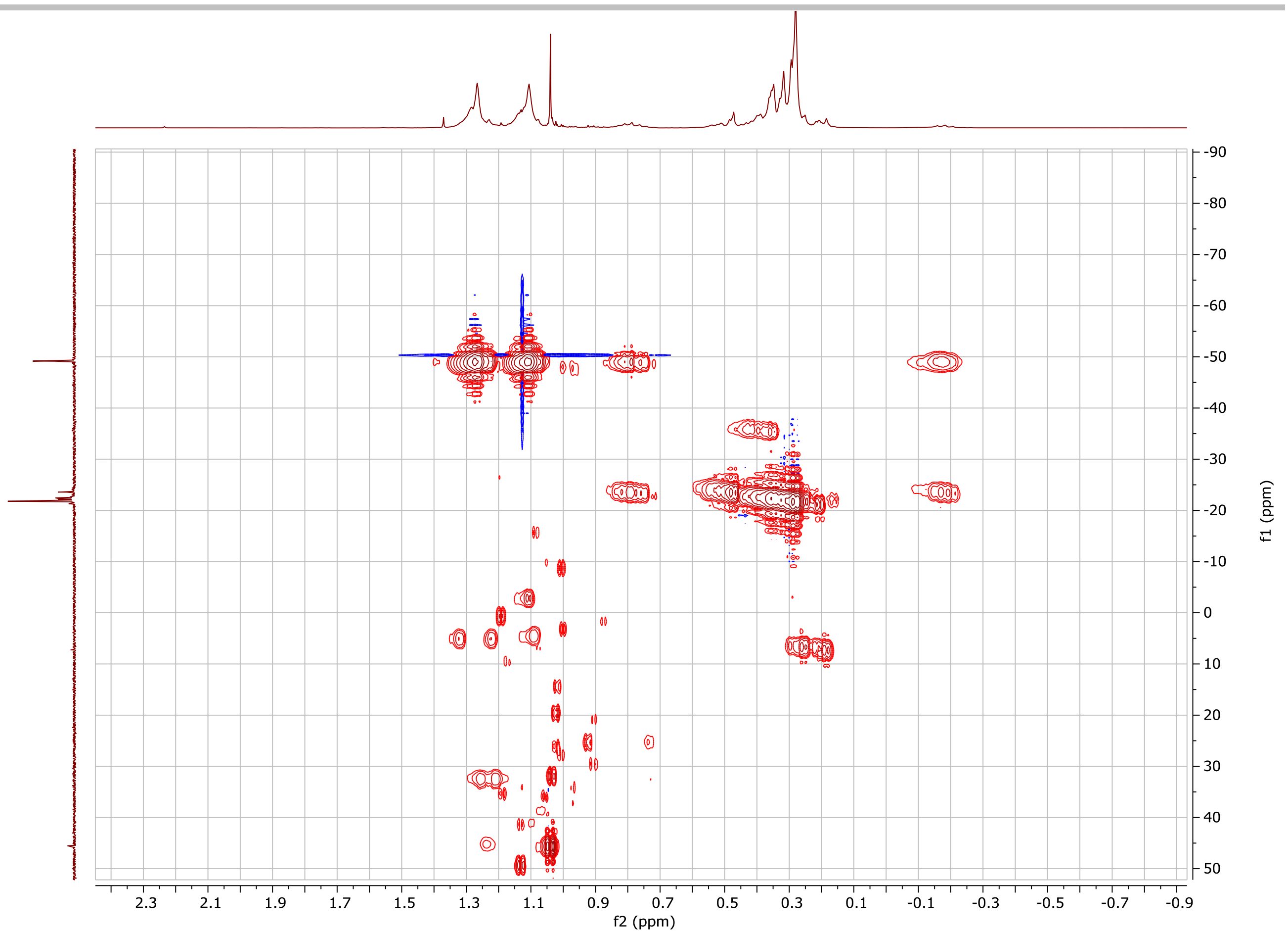

Figure 19: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **9.**

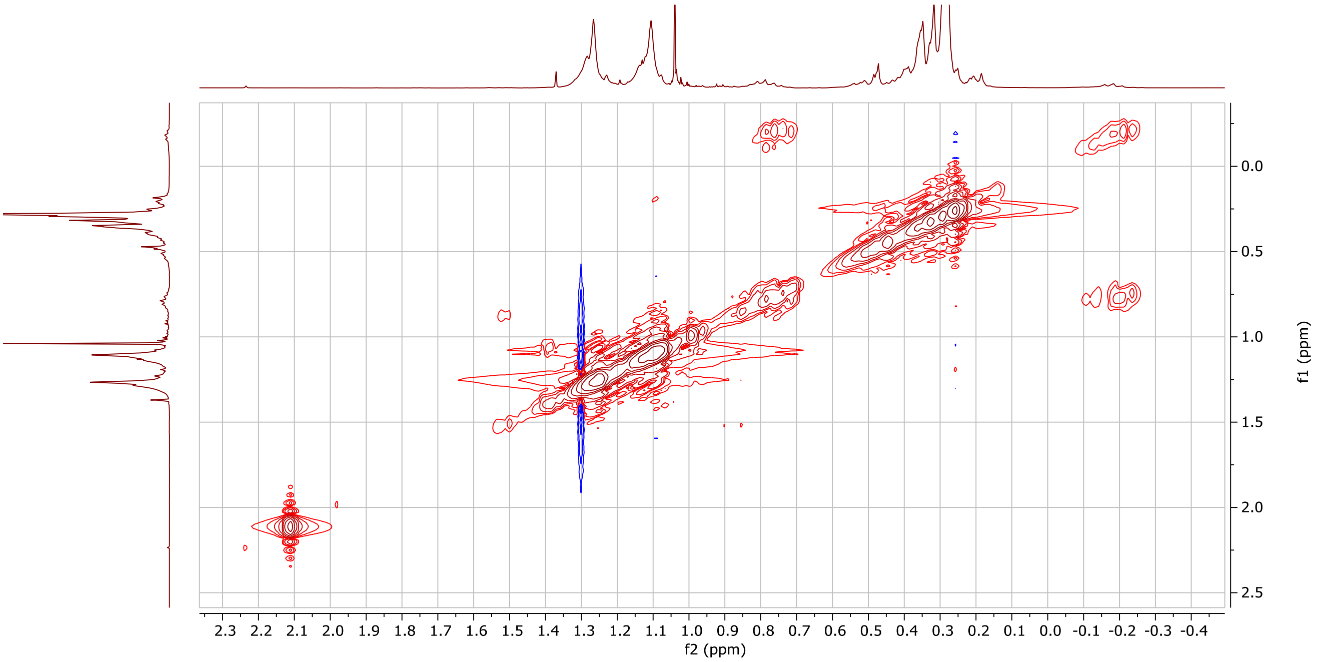

Figure 20: ^{1}H-COSY (100 MHz, C_6D_6) of compound **9**. Correlation of silirane protons.

2.2.7. Poly(((1,1-di-*tert*-butylsilirane-2-yl)methylsiloxane)-*co*-dimethylsiloxane) Copolymer **10**

Yield: 85 %. **^{1}H-NMR:** (500 MHz, C_6D_6) *δ* = -0.20 (m, *t*Bu$_2$SiC*H*), 0.17–0.56 (m, Si-*Me*), 0.73–0.90 (m, *t*Bu$_2$SiC*H$_2$*), 1.06–1.19 (m, *t*Bu), 1.21–1.34 (m, *t*Bu). **^{29}Si-NMR:** (100 MHz, C_6D_6) *δ* = -21.3–(-21.3) (-*Si*Me$_2$-O-), -23.66 (-*Si*MeR-O-), -49.17 (-*Si*-*t*Bu$_2$).[3]

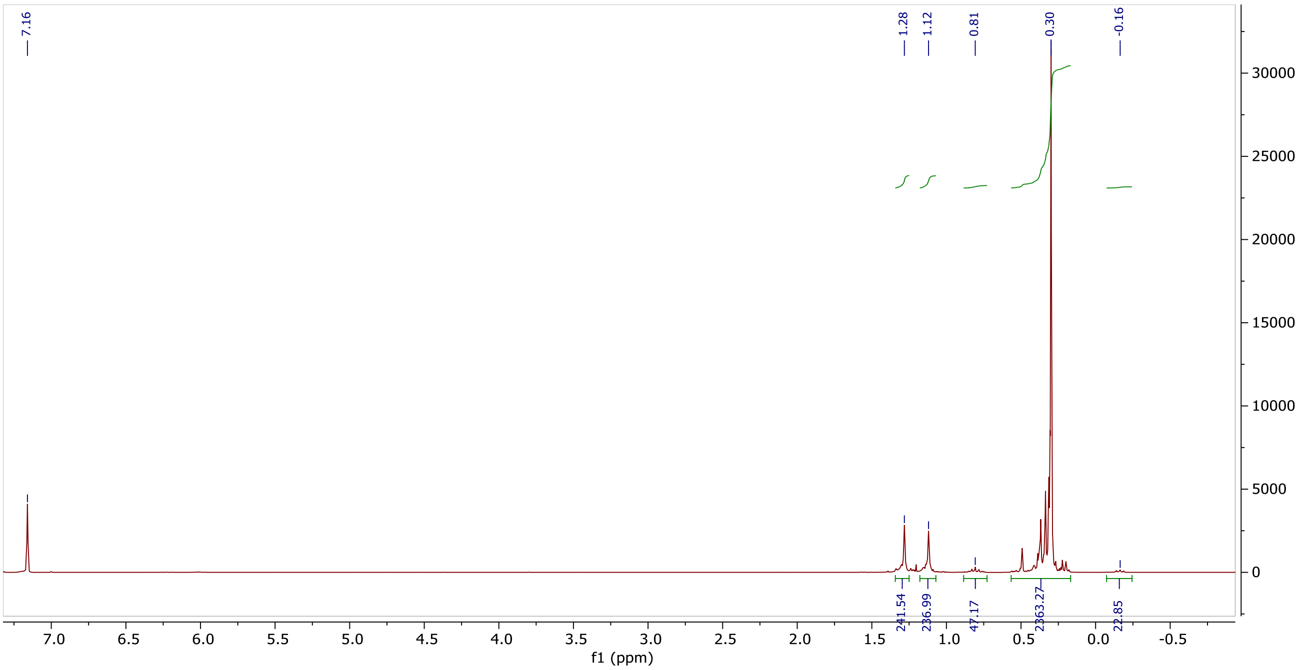

Figure 21: ^{1}H-NMR (500 MHz, C_6D_6) of compound **10.**

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[3],[2] Only a single analysis method was conducted (NMR). MS was not possible due to high M_w and lability of siliranes. EA not meaningful, since compound **9** and **10** are a mixture of polymers of different length with a statistical distribution. NMR can be regarded as structural proof and proof of purity due to complete disappearance of vinyl protons in ^{1}H-NMR and correlations between silirane-Si and PDMS-backbone. Furthermore, the structure is confirmed by successful polymerizations with these compounds.

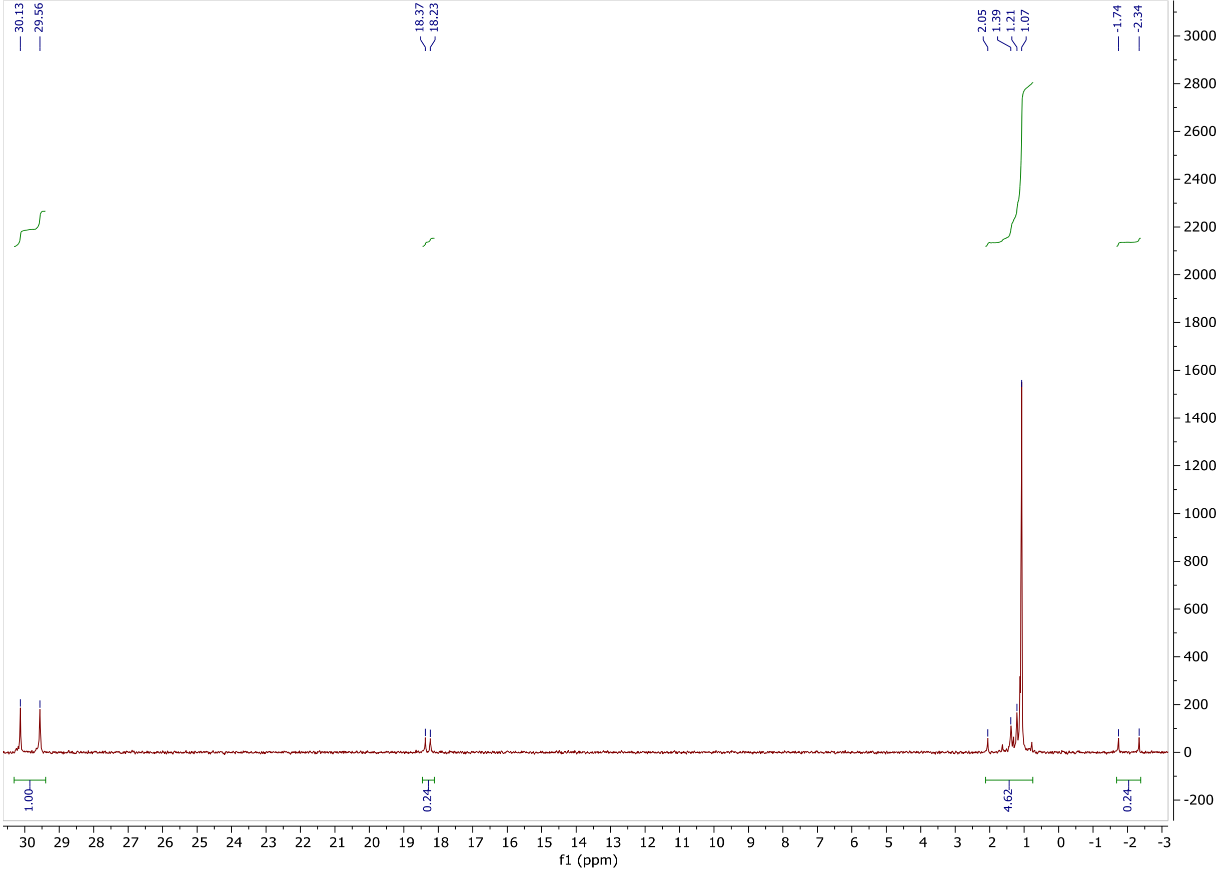


Figure 22: ^{13}C-NMR (100 MHz, C_6D_6) of compound **10**.

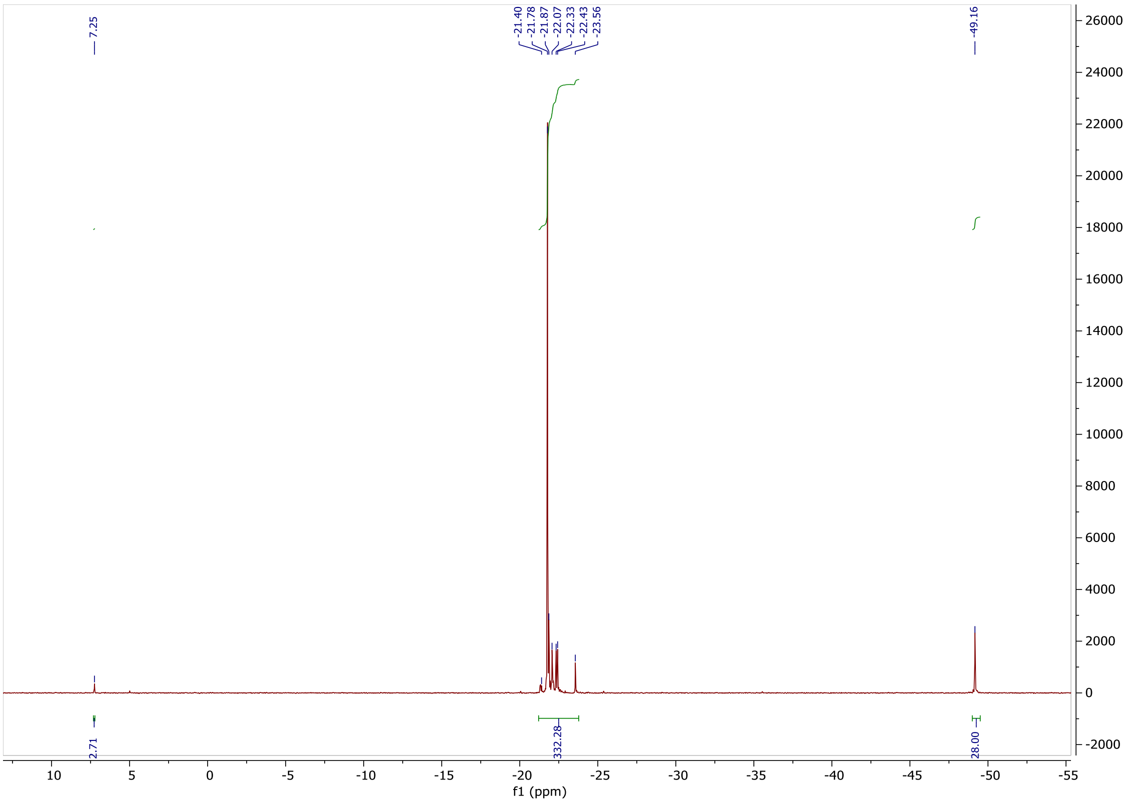


Figure 23: ^{29}Si-inept-NMR (100 MHz, C_6D_6) of compound **10**.

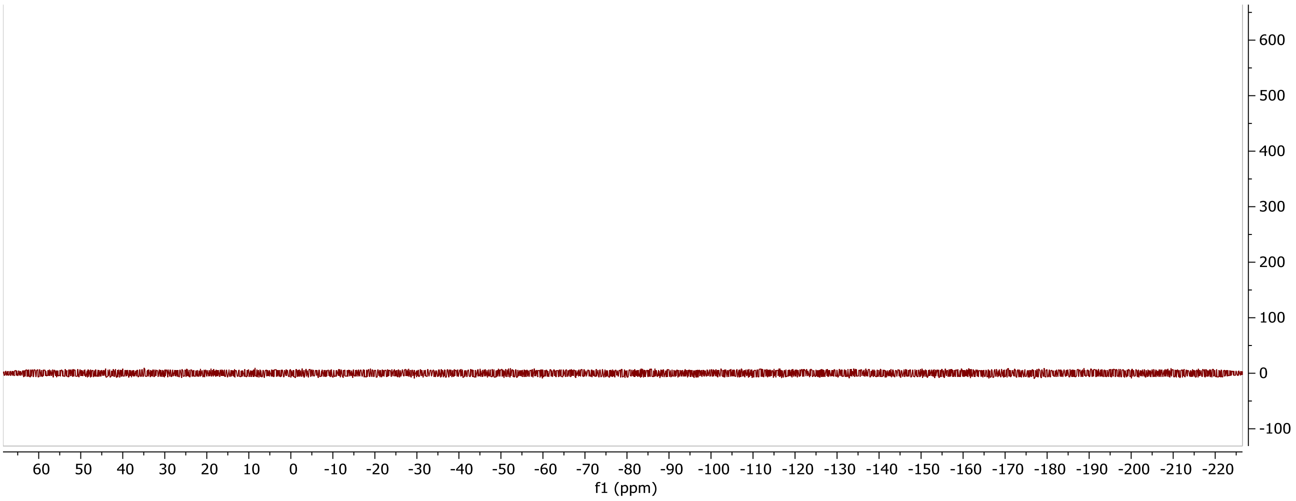


Figure 24: ^{19}F-NMR (470 MHz, C_6D_6) of compound **10** to demonstrate complete AgOTf removal.

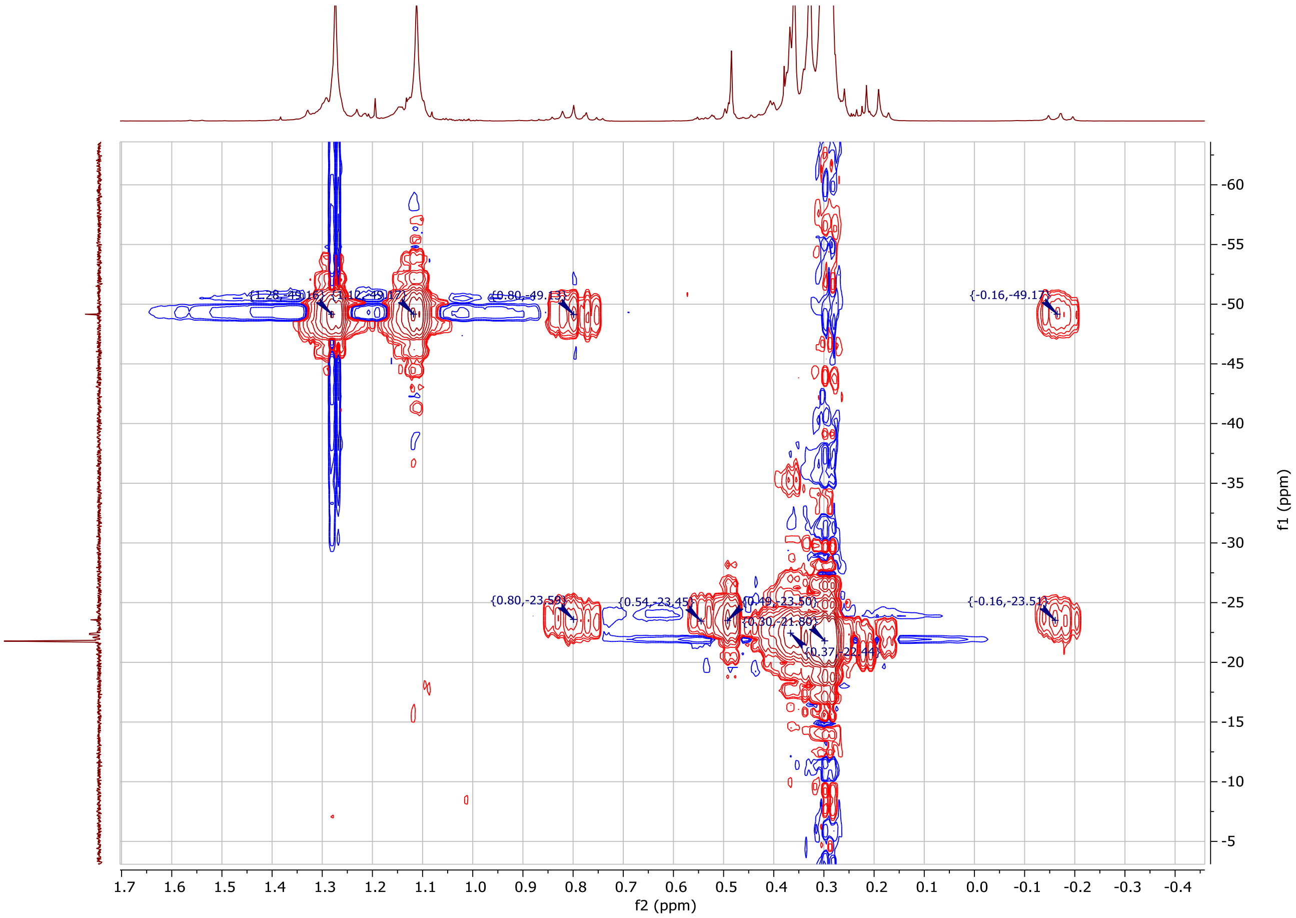


Figure 25: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **10**.

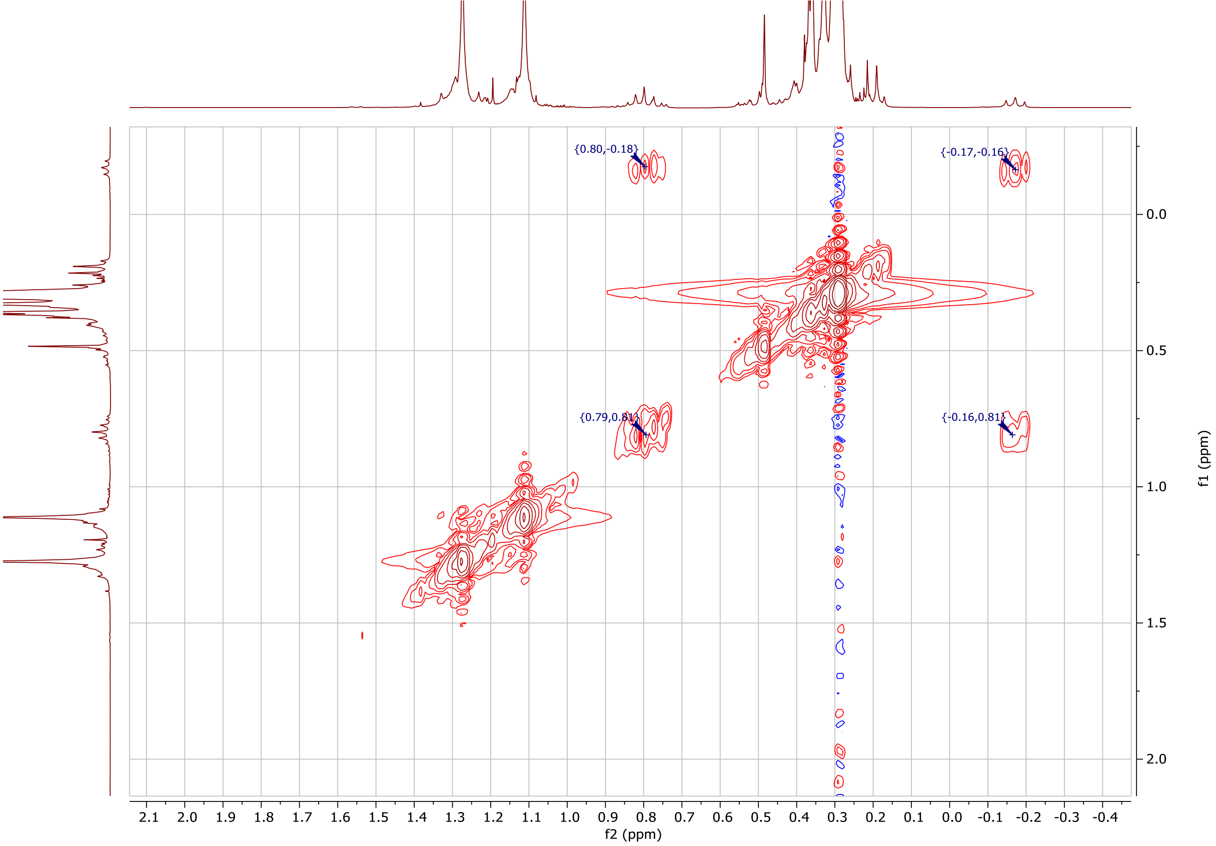
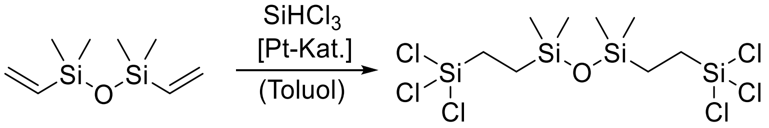


Figure 26: ^{1}H-COSY (100 MHz, C_6D_6) of compound **10**. Correlation of silirane protons.

2.3. Difunctional Silirane Crosslinkers 15-16

2.3.1. 1,1,3,3-Tetramethyl-1,3-bis(2-(trichloro-silyl)ethyl)disiloxane **12**



A 250 mL Schenk-flask with a PTFE-coated stir bar was loaded with 100 g (740 mmol, 4.00 eq.) trichlorosilane and 30 mL toluene. 34.4 g (180 mmol, 1.00 eq.) divinyltetramehtyldisiloxane was added under an inert atmosphere. Subsequently 0.05 mL *Karstedt*-catalyst (2.1 – 2.4 % Pt in xylene) was added to the reaction mixture and stirred for 18 h at room temperature. After removing solvent and excess trichlorosilane under vacuum the clear, yellow liquid was filtered over dry neutral aluminiumoxide to separate remaining Pt-catalyst from the reaction. 81.3 g (177 mmol) of the product was obtained as a clear, colourless liquid.

Yield: 95 %. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = 0.10 (s, 12H), 0.55–0.60 (m, 4H), 1.05–1.10 (m, 4H). **^{13}C-NMR:** (125 MHz, C_6D_6) δ = 0.4, 9.3, 17.3. **^{29}Si-NMR**: (100 MHz, C_6D_6) δ = 8.1, 13.8. **EA:** experimental (calculated) C 20.93 (21.01), H 4.63 (4.41) %.

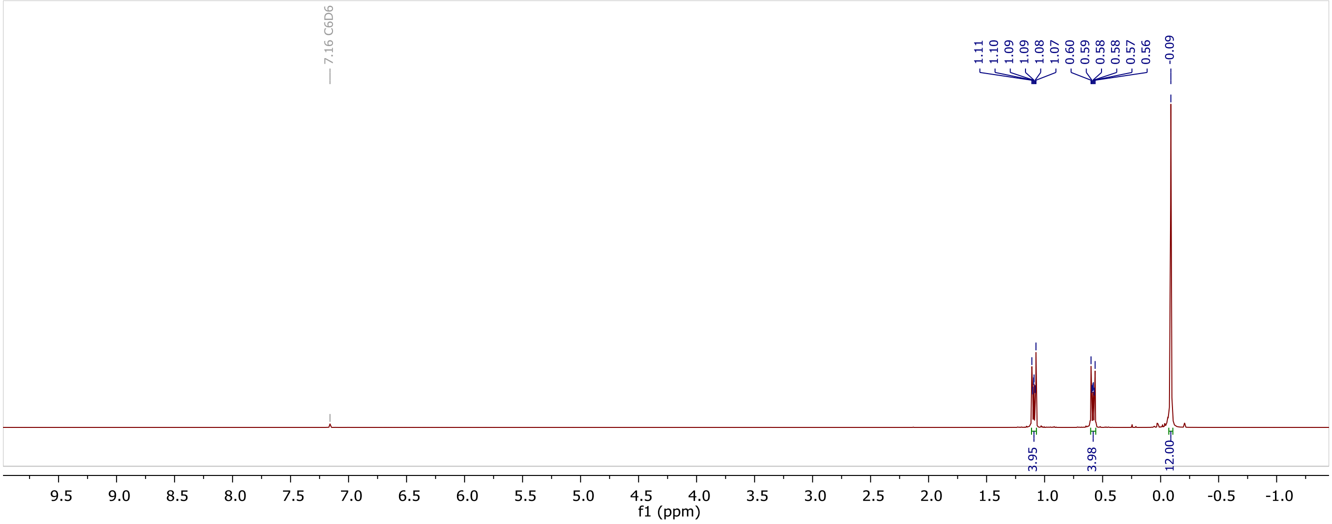


Figure 27: ^{1}H-NMR (500 MHz, C_6D_6) of compound **12.**

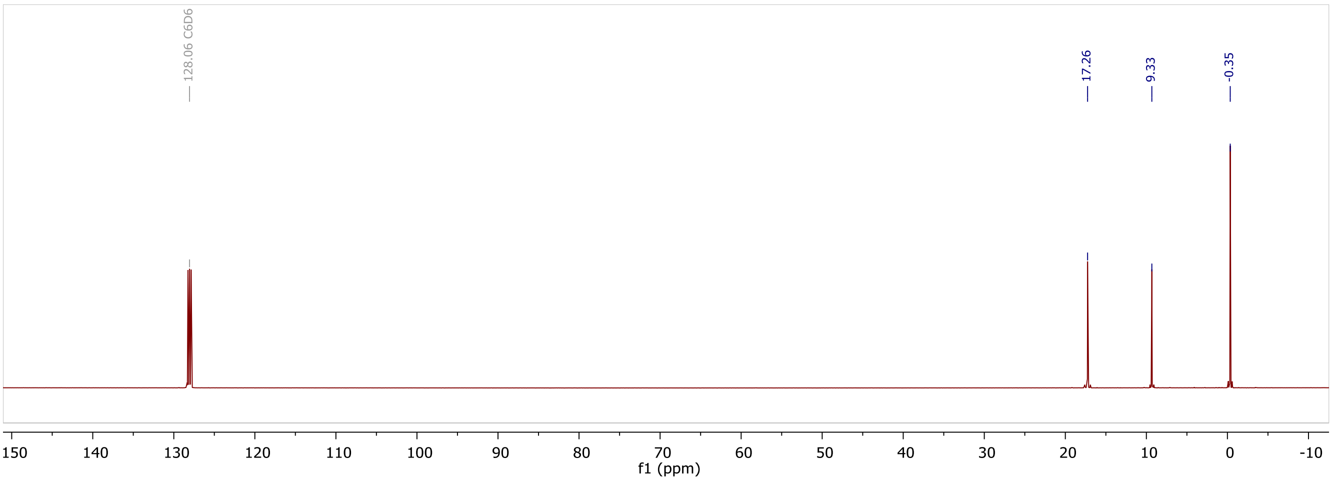


Figure 28: ^{13}C-NMR (125 MHz, C_6D_6) of compound **12**.

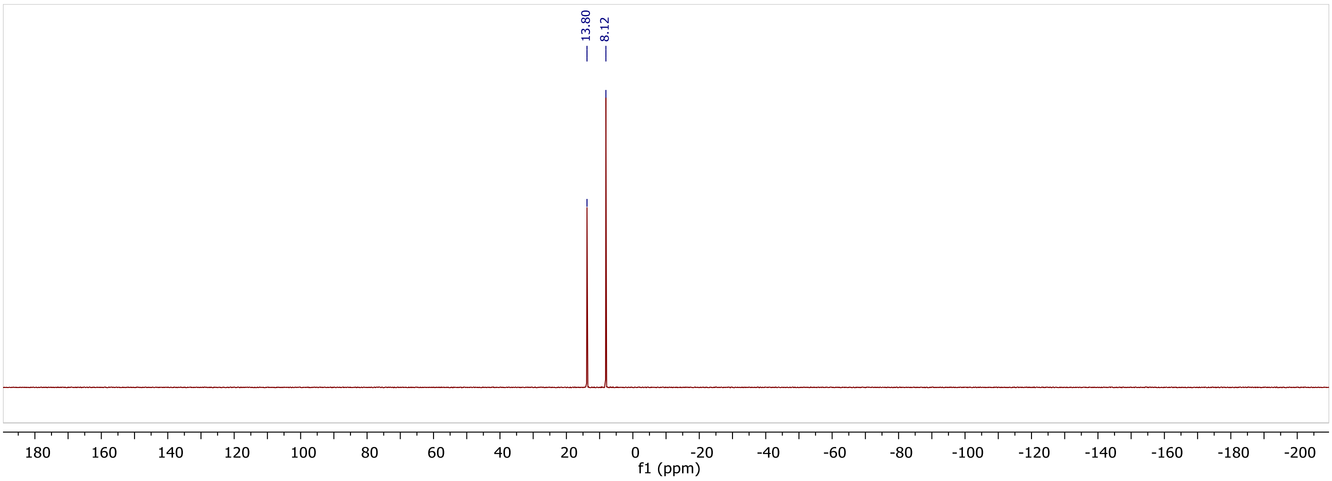


Figure 29: ^{29}Si-ig-NMR (100 MHz, C_6D_6) of compound **12**.

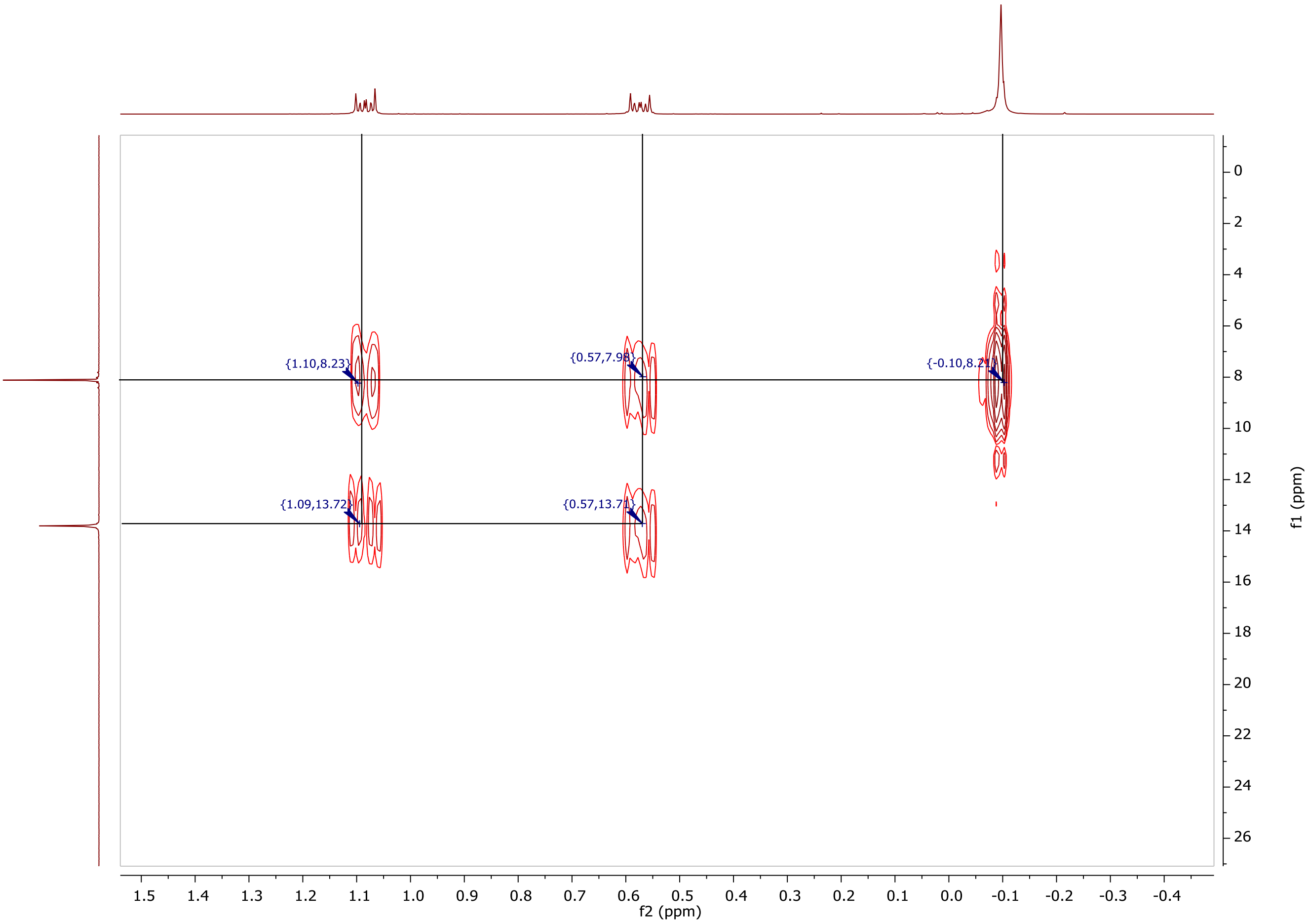
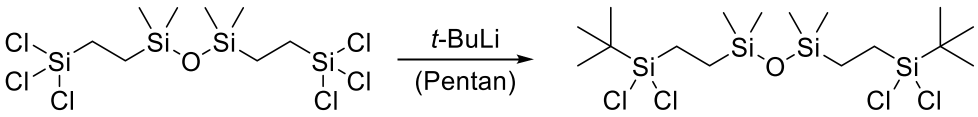


Figure 30: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **12**.

2.3.2. 1,3-Bis(2-(*tert*-butyl-dichlorosilyl)ethyl) 1,1,3,3,-tetramethyldisiloxane **13**



A 250 mL Schenk-round-bottom flask was equipped with a PTFE-coated stir bar and filled with 30.0 g (65.6 mmol, 1.00 eq.) 1,1,3,3-Tetramethyl-1,3-bis(2-(trichloro-silyl)-ethyl)disiloxane **12** and 75 mL pentane. Subsequently the reaction mixture was cooled down to 0 °C, while 8.40 g (131 mmol, 2.00 eq.) *tert*-butyllithium solution (1.7 M) was slowly added through a dropping funnel over the period of 30 min. Then the reaction was stirred vigorously for 8 h at 0 °C before it was allowed to warm up to room temperature again. Emerged lithium chloride was separated from the crude product by filtration. The occurred suspension was separated from generated lithium chloride by filtration and solvent was removed *in vacuo* to give a yellowish solid. The crude product was purified by sublimation in a high vacuum (110 °C, 10^{-5} mbar), giving 22.0 g (43.9 mmol) of **13** as a white solid.

Yield: 67 %. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = 0.05 (s, 12H), 0.78–0.82 (m, 4H), 1.00 (s, 18H), 1.04–1.08 (m, 4H). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 8.2, 38.5. **EA**: experimental (calculated) C 38.25 (38.39), H 7.76 (7.65) %.

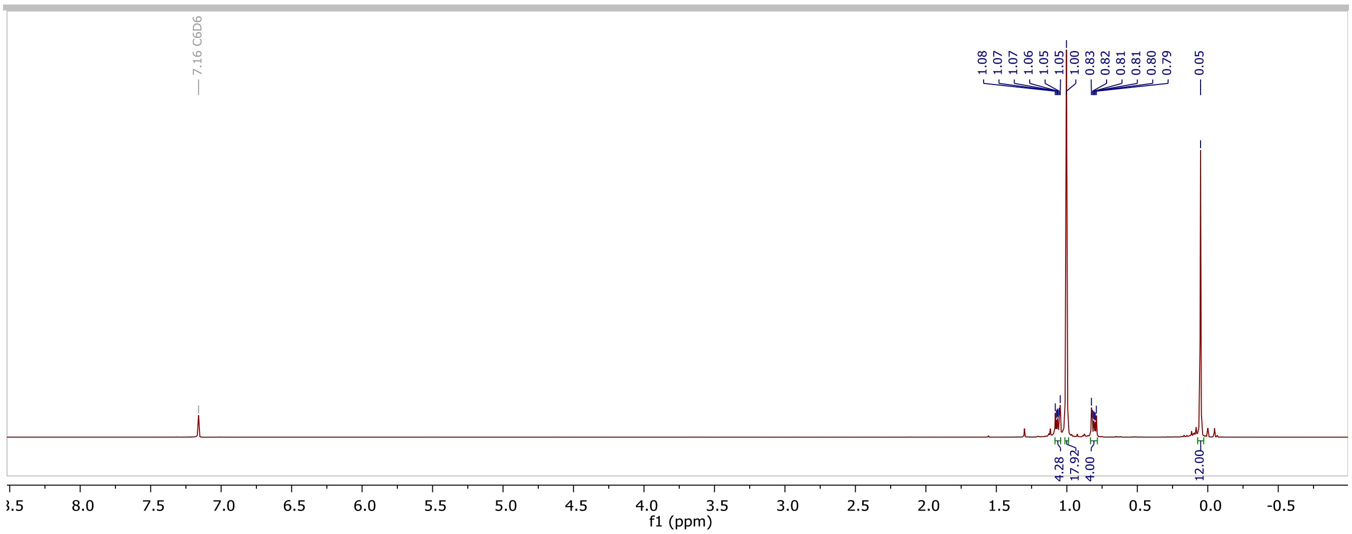


Figure 31: ^{1}H-NMR (500 MHz, C_6D_6) of compound **13**.

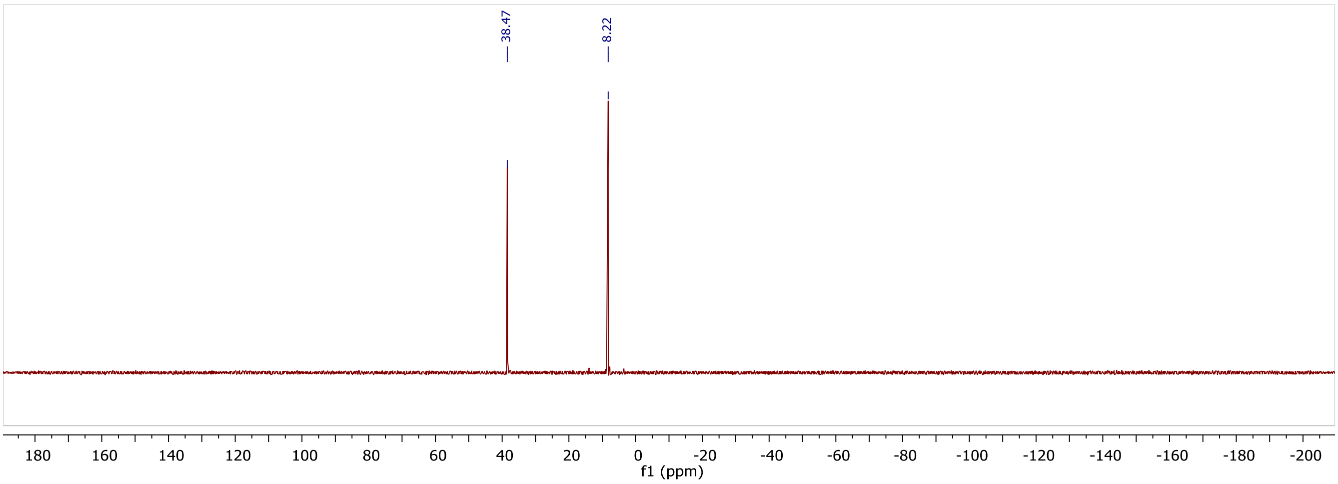
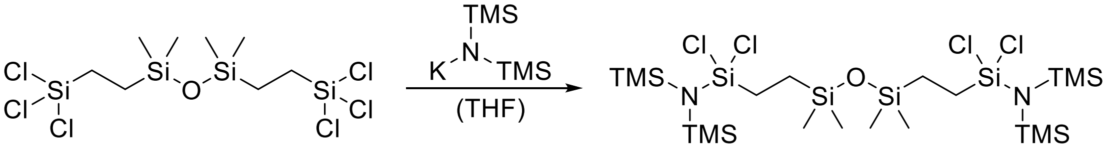


Figure 32: ^{29}Si-ig-NMR (100 MHz, C_6D_6) of compound **13**.

2.3.3. 1,1'-((1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(ethane-2,1-diyl))bis(1,1-dichloro-*N*,*N*-bis(trimethylsilyl)-silanamine) **14**



In a 250 mL Schlenk round-bottom flask 10.0 g (21.9 mmol, 1.00 eq.) 1,1,3,3-Tetramethyl-1,3-bis(2-(tri-chloro-silyl)ethyl)disiloxane **12** was charged with 40 mL THF and cooled to 0 °C. A solution of 8.27 g (43.7 mmol, 2.00 eq.) potassium bis(trimethylsilyl)amide diluted in 30 mL THF was slowly added to the reaction flask through a dropping funnel over 30 minutes. The reaction mixture was stirred at room temperature for 6 h subsequently. Remaining solvent was removed under vacuum, then the crude product was solved in 40 mL pentane again. The so formed suspension was filtered and washed with 10 mL pentane again. Then the solvent was removed *in vacuo* to result in 12.5 g (17.7 mmol) **14** as a clear, light yellow liquid.

Yield: 81 %. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = 0.07 (s, 12H), 0.33 (s, 36H), 0.83–0.87 (m, 4H), 1.25–1.29 (m, 4H). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 2.2, 6.4, 8.5. **EA:** experimental (calculated) C 33.49 (33.97), H 7.96 (7.98), N 3.94 (3.96) %.

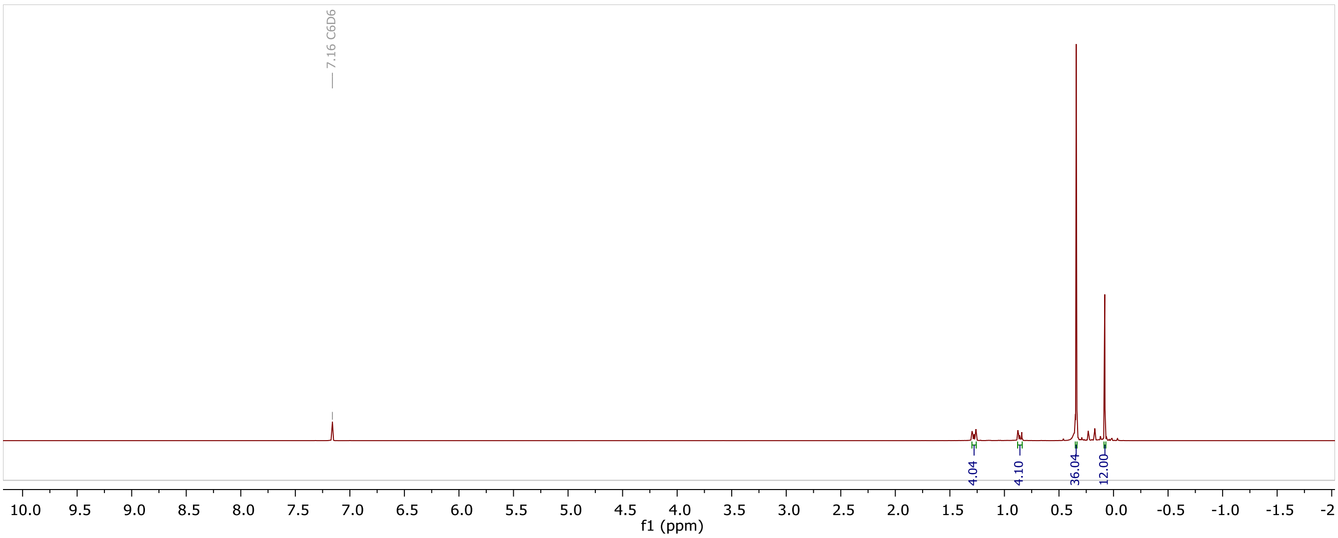


Figure 33: ^{1}H-NMR (500 MHz, C_6D_6) of compound **14.**

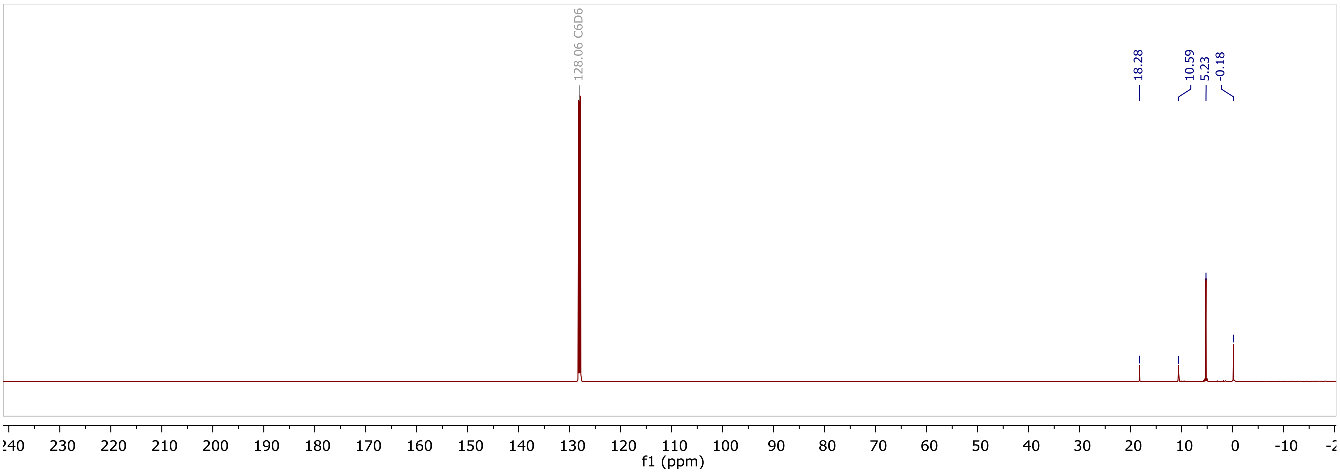


Figure 34: ^{13}C-NMR (125 MHz, C_6D_6) of compound **14**.

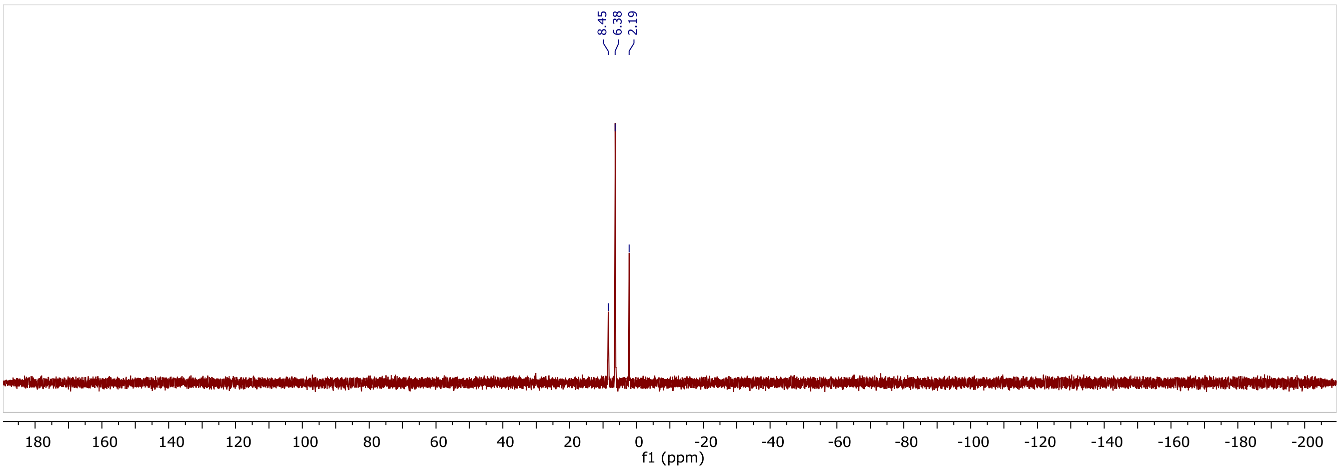


Figure 35: ^{29}Si.ig-NMR (100 MHz, C_6D_6) of compound **14**.

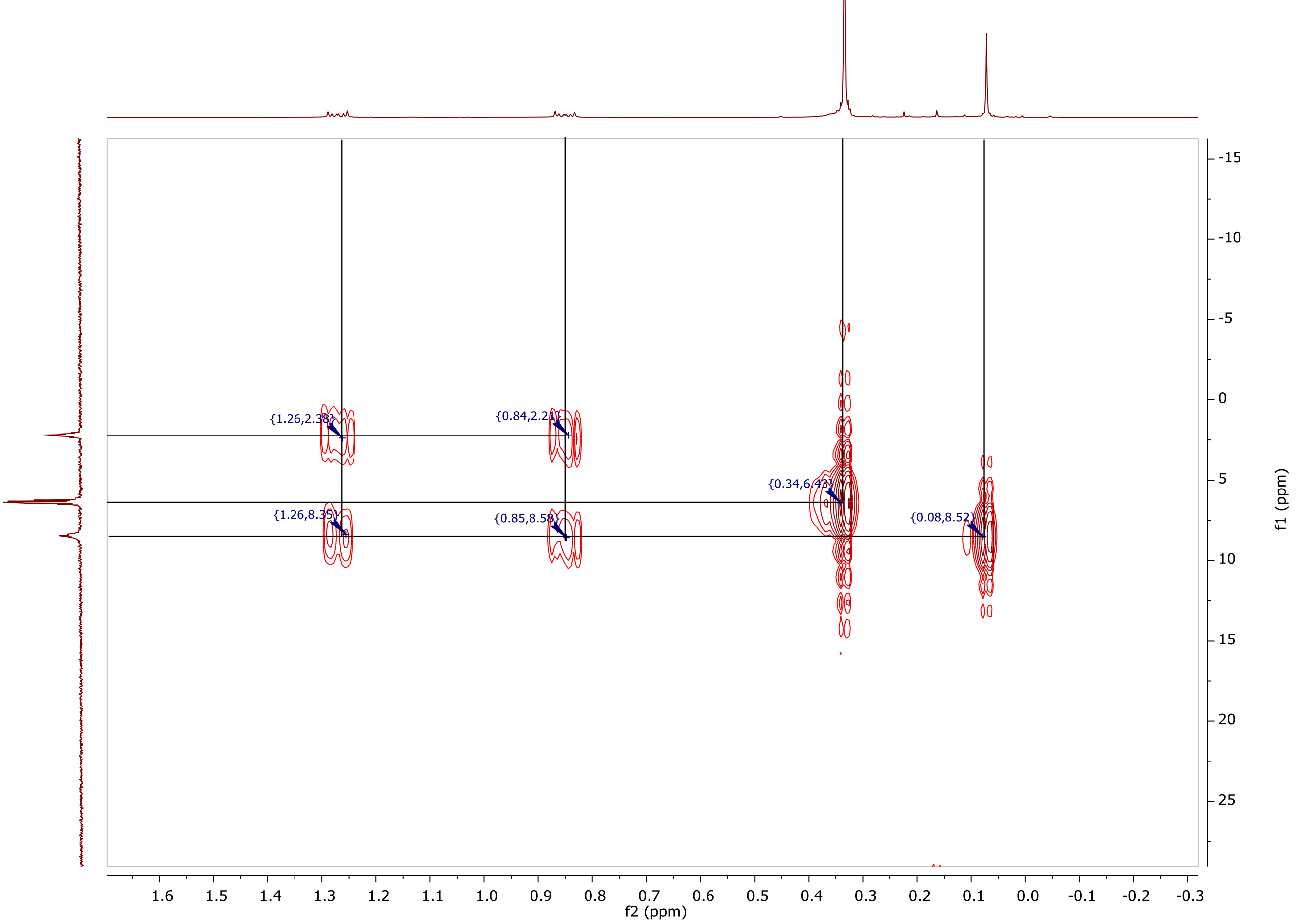
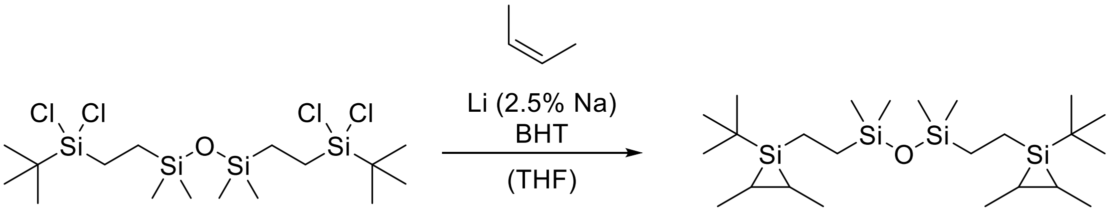


Figure 36: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **14**.

2.3.4. 1,3-bis(2-(1-(*tert*-butyl)-2,3-dimethylsiliran-1-yl)ethyl)-1,1,3,3-tetramethyldisiloxane **15**



A 250 mL Schlenk-tube was equipped with a PTFE-coated stir bar and was loaded with 10.0 g (20.0 mmol, 1.00 eq.) of **13**, 50 mL THF and 20 mg (0.09 mmol, 0.001 eq.) 3,5-Di-*tert*-butyl-4-hydroxytoluene (BHT) to suppress radical side reactions. The reaction tube was cooled down to -78°C with a dry ice/isopropanol mixture. Present argon atmosphere was removed *in vacuo* and 33.6 g (600 mmol, 30.0 eq.) *cis*-2-butene was condensed onto the cooled reaction mixture by pressurizing it with 1.80 bar of the respective gas. After re-pressurizing with argon, 2.10 g (300 mmol, 15.0 eq.) Li/Na alloy chunks (2.5 % Na) were added to the reaction mixture, followed by vigorous stirring at room temperature for 7 days. By the end of the reduction, *cis*-2-butene gas and remaining solvent was removed under vacuum. The slurry crude was diluted in 50 mL pentane to precipitate and separated the generated lithium chloride by filtration. The product was collected by removing the remaining solvent *in vacuo* to afford 7.80 g (16.7 mmol, 86 %) of the silylene-crosslinker **15** as a colourless oil with high viscosity.

The product was a mixture of diastereomeric *cis*- and *trans*-isomers. Small amounts of a constitutional isomer from the respective 1-butene could be found due to the containing impurities of isomers in the used *cis*-2-butene gas. The three different species could be assigned by ^{1}H-^{29}Si-HMBC NMR measurements, but no distinct differentiation of the respective *cis/trans* species could be achieved.

Cis/Trans species: 67 % relative ratio. **^{1}H-NMR:** (500 MHz, C_6D_6) *δ* = 0.15–0.16 (m, 12H), 0.86–0.89 (m, 8H), 1.04 (s, 18H), 1.11–1.12 (m, 4H) 1.36–1.38 (m, 12H). **^{29}Si-NMR**: (100 MHz, C_6D_6) *δ* = -49.7, 7.3. **LIFDI-MS**: 469.95 [M]$^+$, 413.99 [M-C_4H_8]$^+$, 358.03 [M-C_8H_{16}]$^+$.

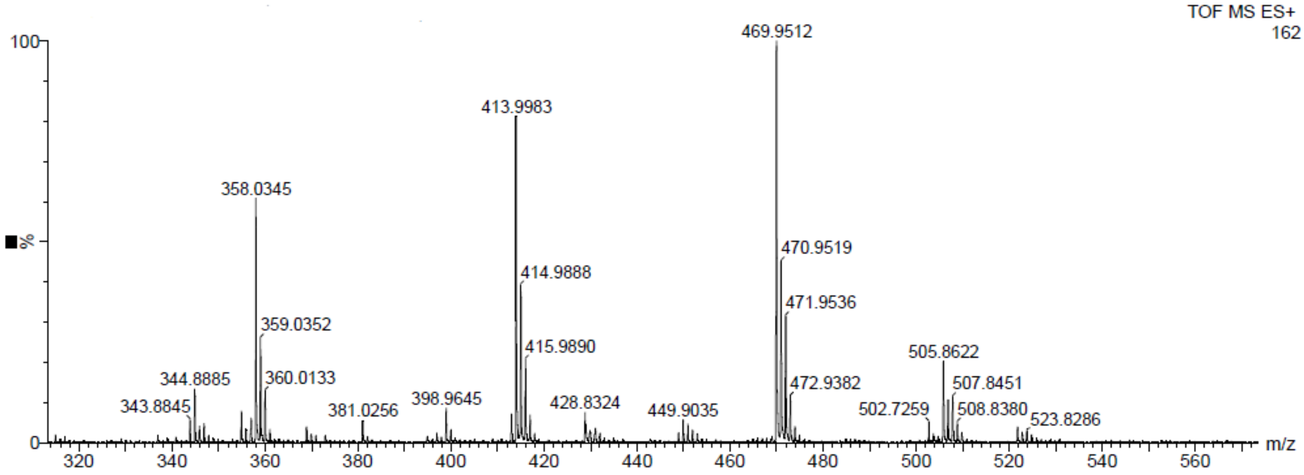


Figure 37: LIFDI-MS spectrum of compounds **15**.

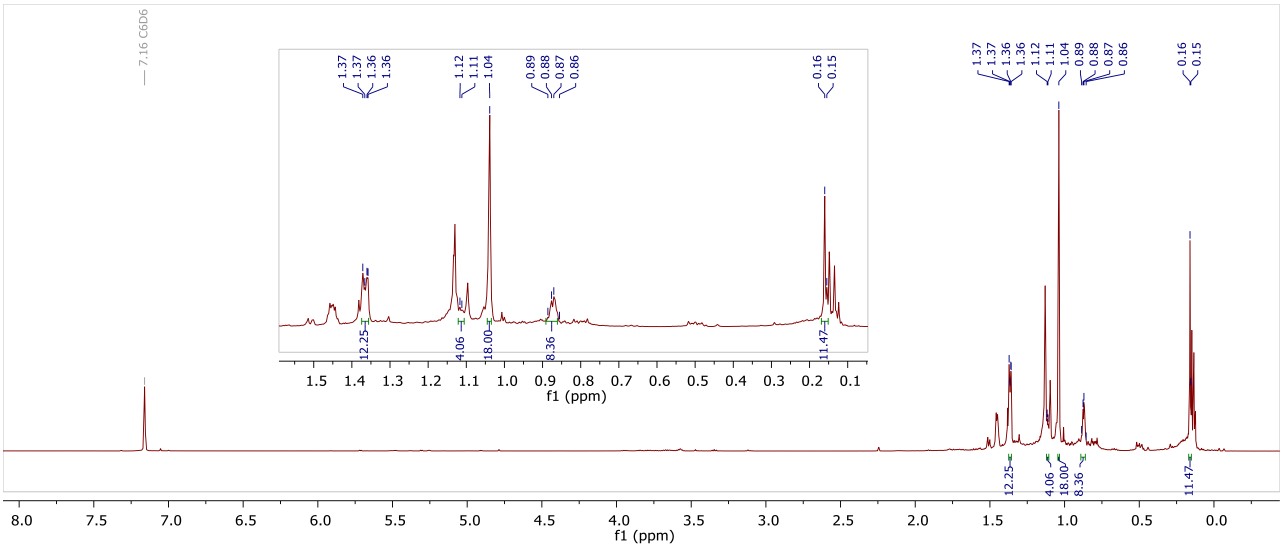


Figure 38: ^{1}H-NMR (500 MHz, C_6D_6) of compound **15** (cis/trans-species).

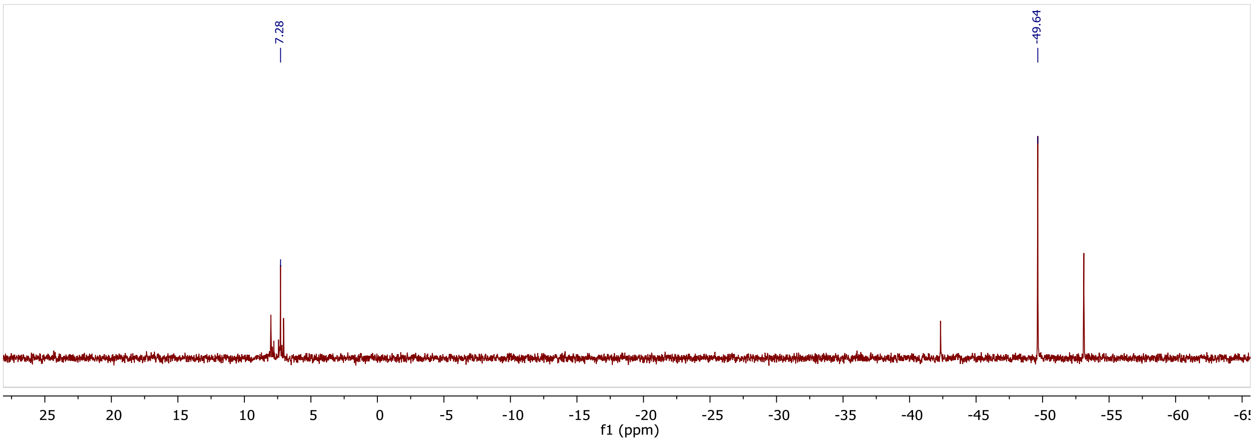


Figure 39: ^{29}Si.ig-NMR (100 MHz, C_6D_6) of compound **15** (cis/trans-species).

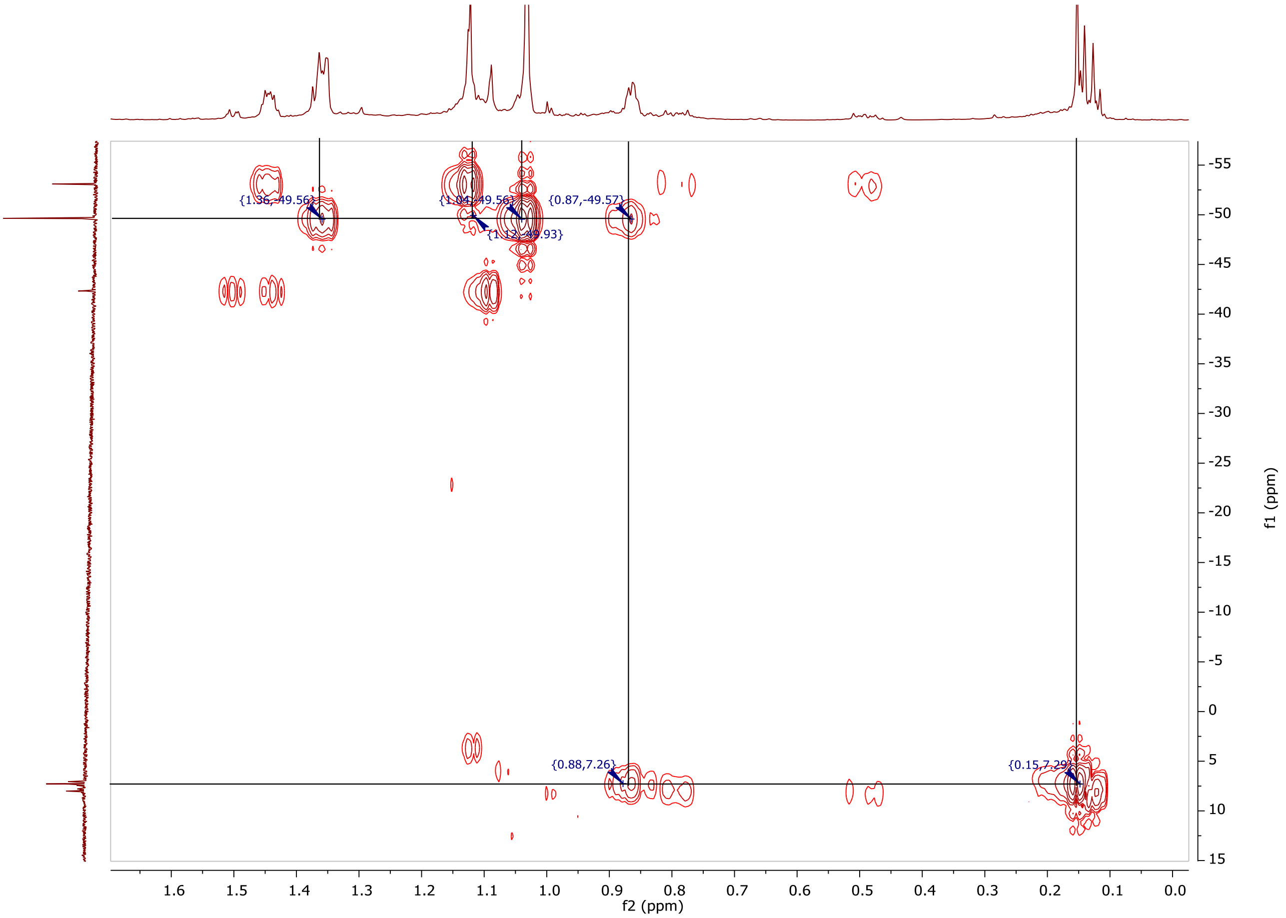


Figure 40: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **15** (cis/trans-species).

Trans/Cis species: 24 % relative ratio. **^{1}H-NMR:** (500 MHz, C_6D_6): δ = 0.12–0.14 (m, 12H), 0.46–0.52 (m, 4H), 0.74–0.78 (m, 4H), 1.12 (s, 18H), (m, 4H), 1.43–1.45 (m, 12H). **^{29}Si-NMR**:(100 MHz, C_6D_6): δ = -53.1, 8.0. **LIFDI-MS**: 469.95 $[M]^+$, 413.99 $[M-C_4H_8]^+$, 358.03 $[M-C_8H_{16}]^+$.

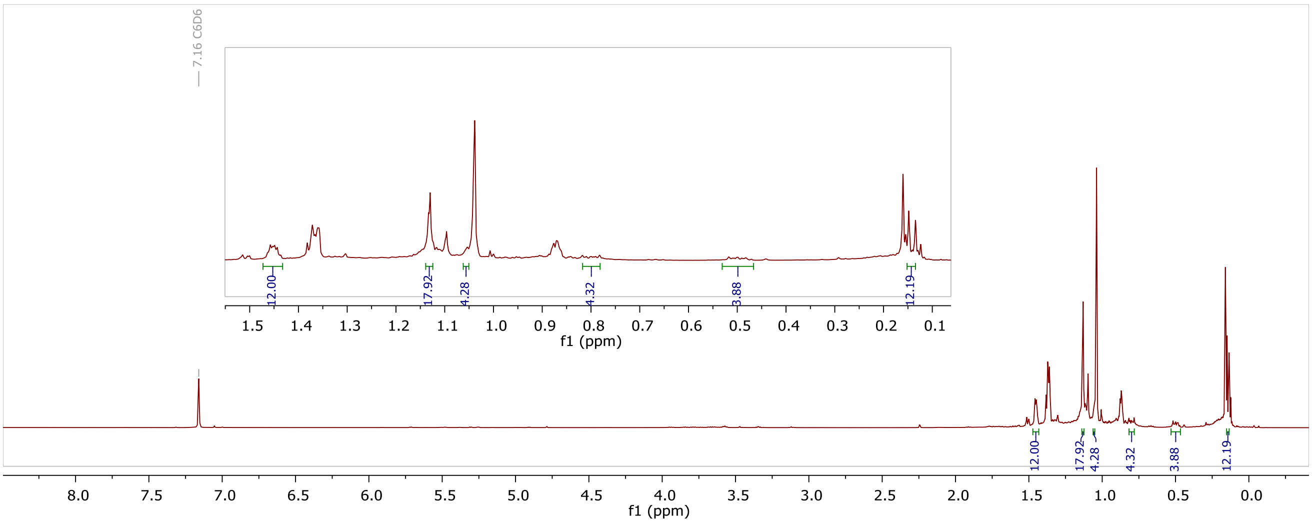


Figure 41: ^{1}H-NMR (500 MHz, C_6D_6) of compound **15** (trans/cis-species).

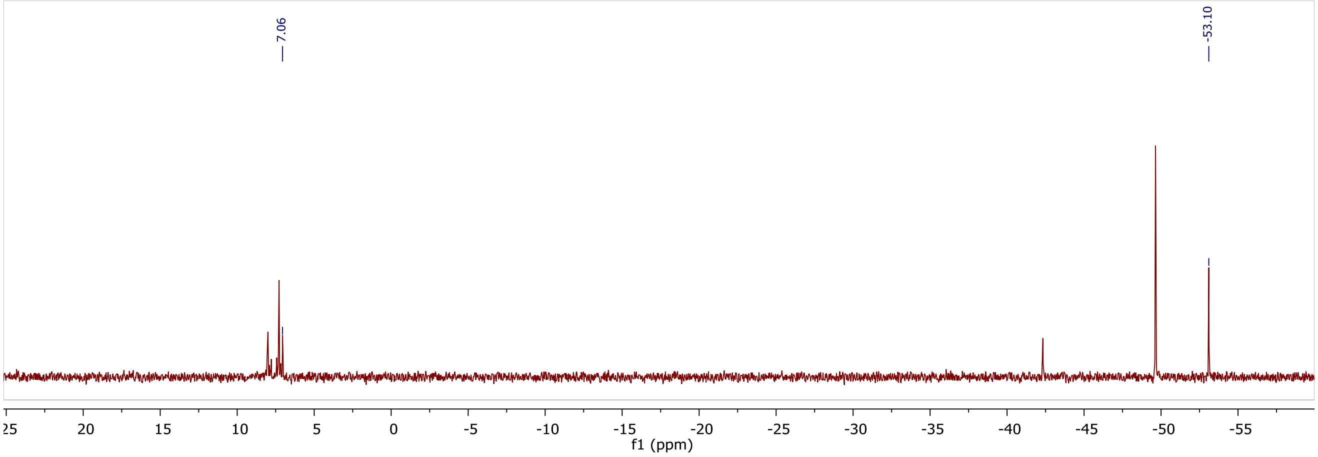


Figure 42: ^{29}Si.ig-NMR (100 MHz, C_6D_6) of compound **15** (trans/cis-species).

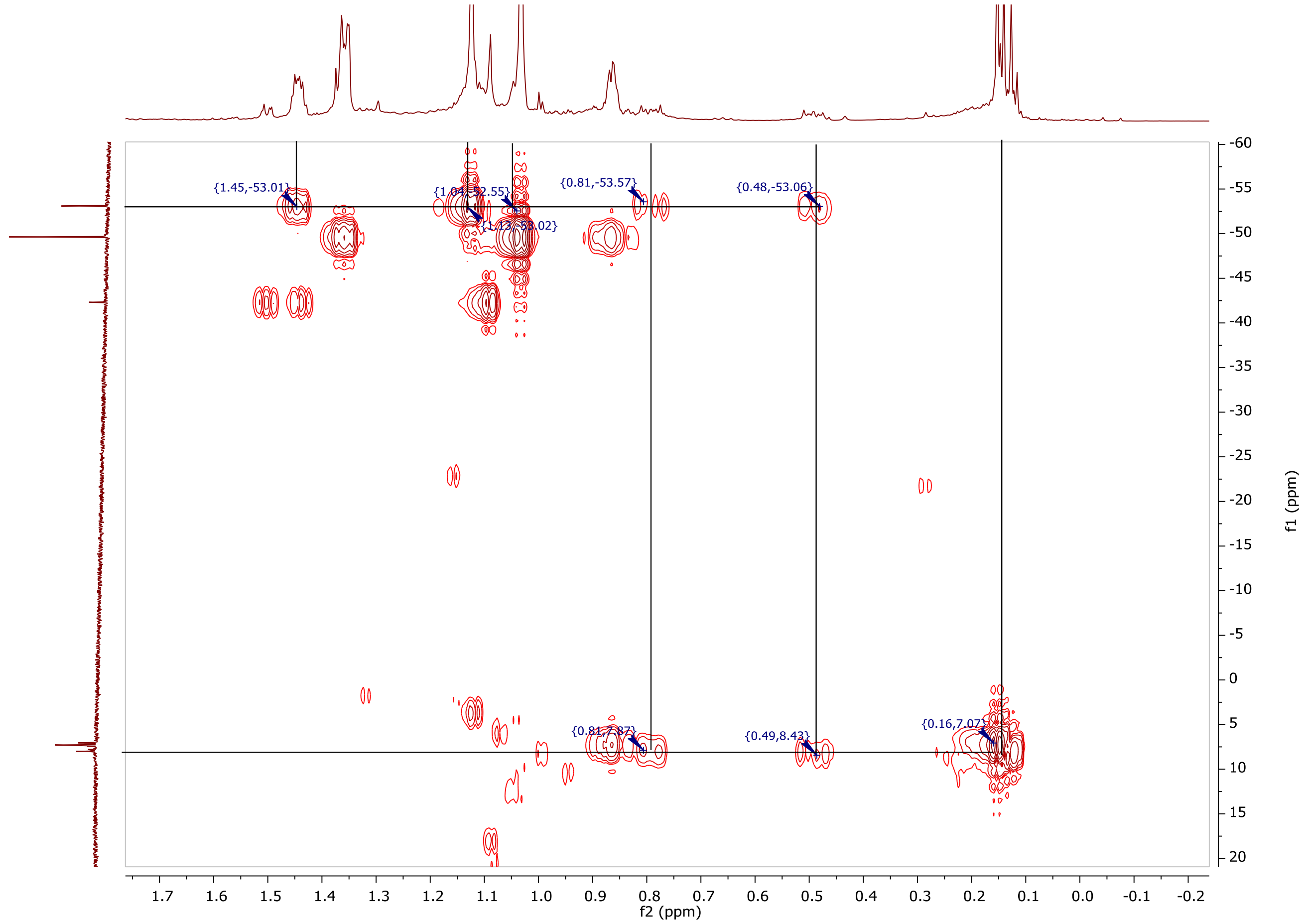


Figure 43: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **15** (trans/cis-species).

1-butene-species: 9 % relative ratio. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = 0.07–0.10 (m, 12H), 0.59–0.68 (m, 4H), 0.79–0.81 (m, 4H), 1.08 (s, 18H), 1.18–1.19 (m, 2H), 1.19–1.20 (m, 4H), 1.39–1.40 (m, 4H), 1.47–1.49 (m, 6H). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = -42.3, 6.9. **LIFDI-MS**: 469.95 $[M]^+$, 413.99 $[M-C_4H_8]^+$, 358.03 $[M-C_8H_{16}]^+$.

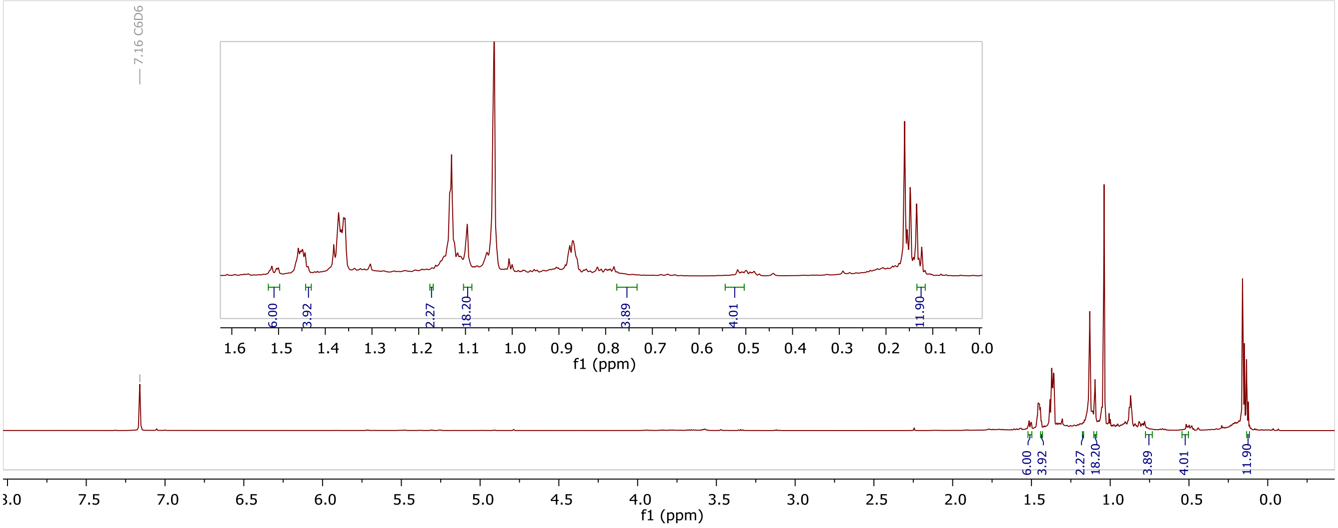


Figure 44: ^{1}H-NMR (500 MHz, C_6D_6) of compound **15** (1-butene species).

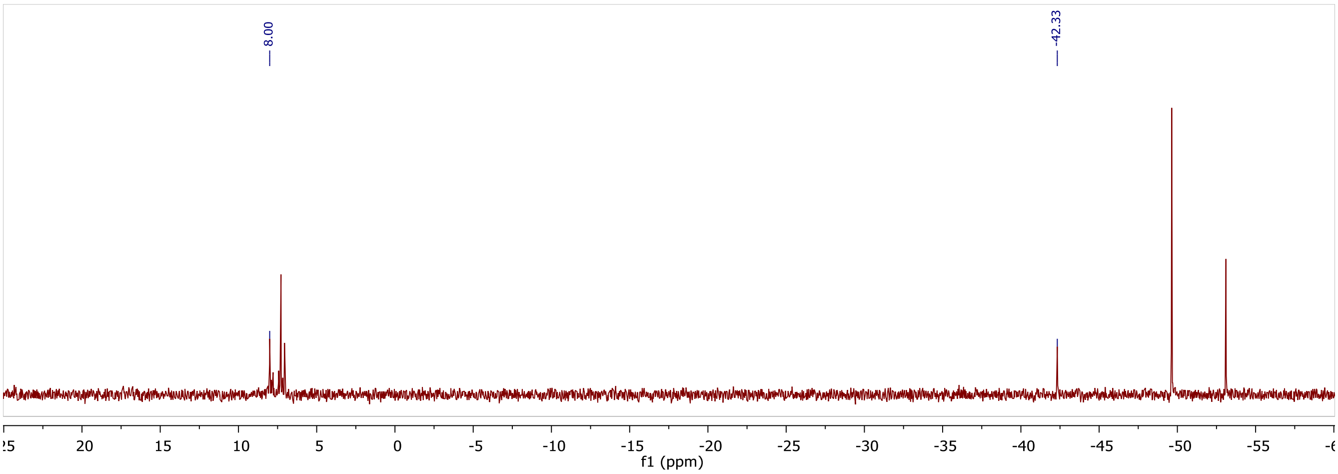


Figure 45: ^{29}Si.ig-NMR (100 MHz, C_6D_6) of compound **15** (1-butene species).

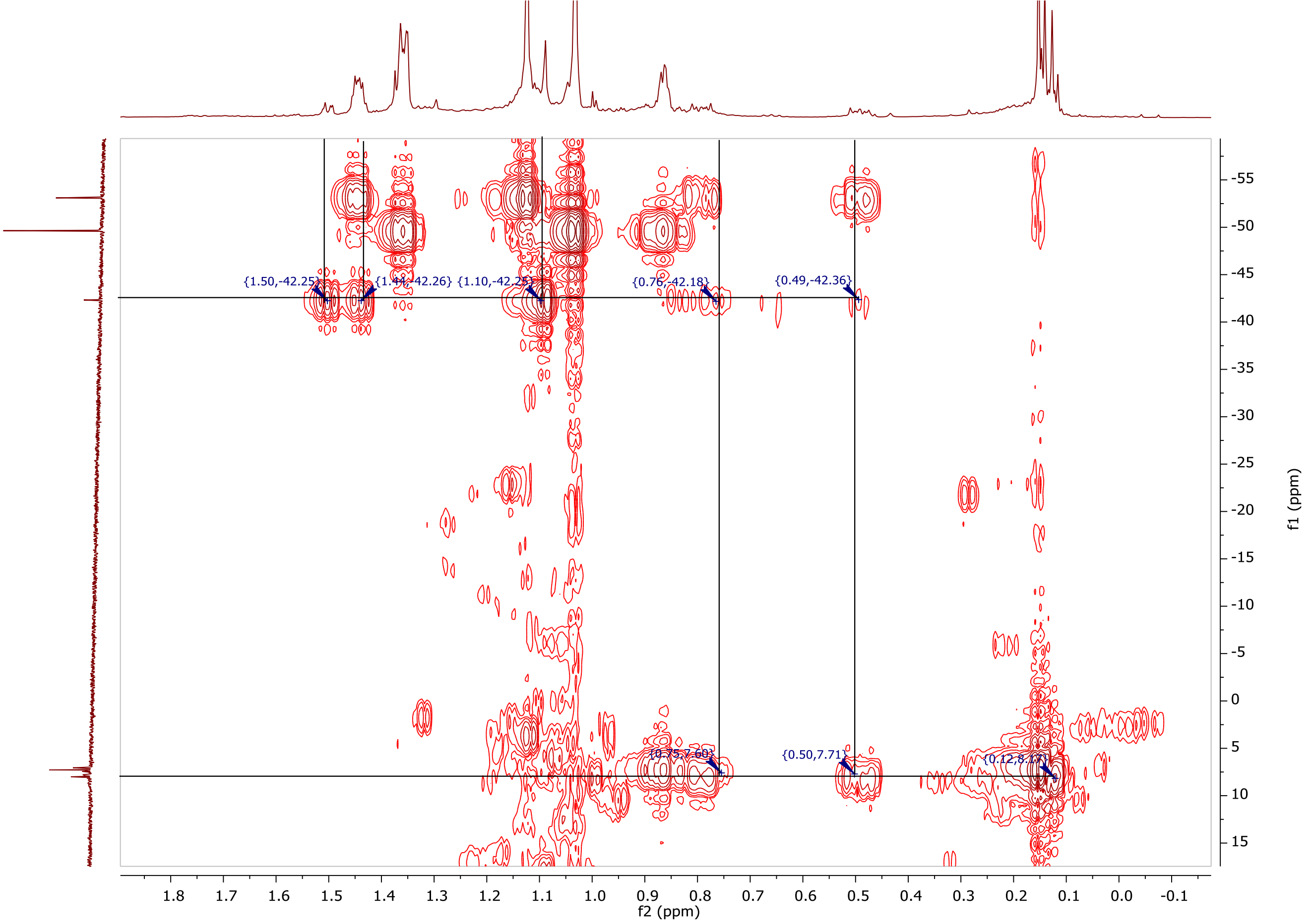
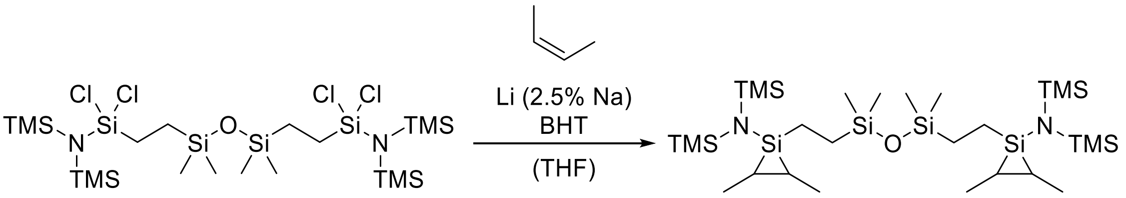


Figure 46: ^1H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **15** (1-butene species).

2.3.5. 1,1'-((1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(ethane-2,1-diyl))bis(2,3-dimethyl-N,N-bis(trimethylsilyl)siliran-1-amine) **16**



A 250 mL Schlenk-tube was equipped with a PTFE-coated stir bar and was loaded with 10.0 g (14.1 mmol, 1.00 eq.) of **14**, 50 mL THF and 20 mg (0.09 mmol, 0.001 eq.) 3,5-Di-*tert*-butyl-4-hydroxytoluene (BHT) to suppress radical side reactions. The reaction tube was cooled down to -78 °C with a dry ice/isopropanol mixture. Present argon atmosphere was removed *in vacuo* and 30.6 g (424.2 mmol, 30.0 eq.) *cis*-2-butene was condensed onto the cooled reaction mixture by pressurizing it with 1.80 bar of the respective gas. After re-pressurizing with argon, 1.47 g (212.1 mmol, 15.0 eq.) Li/Na alloy chunks (2.5 % Na) were added to the reaction mixture, followed by vigorous stirring at room temperature for 7 days. By the end of the reduction, *cis*-2-butene gas and remaining solvent was removed under vacuum. The slurry crude was diluted in 50 mL pentane to precipitate and separated the generated lithium chloride by filtration. The product was collected by removing the remaining solvent *in vacuo* to afford 5.46 g (8.06 mmol, 57 %) of the silylene-crosslinker **16** as a colourless oil.

The product was a mixture of diastereomeric *cis*- and *trans*-isomers. Small amounts of a constitutional isomer from the respective 1-butene could be found due to the containing impurities of isomers in the used *cis*-2-butene gas. The three different species could be assigned by ^1H-^{29}Si-HMBC NMR measurements, but no distinct differentiation of the respective *cis/trans* species could be achieved.

Cis/Trans species: 70 % relative ratio. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = 0.12–0.13 (m, 12H), 0.22 (s, 36H), 0.77–0.80 (m, 8H), 1.12–1.15 (m, 4H), 1.19–1.21 (m, 12H). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = -50.0, 4.7, 7.8. **LIFDI-MS:** 675.61 $[M]^+$, 619.70 $[M-C_4H_8]^+$.

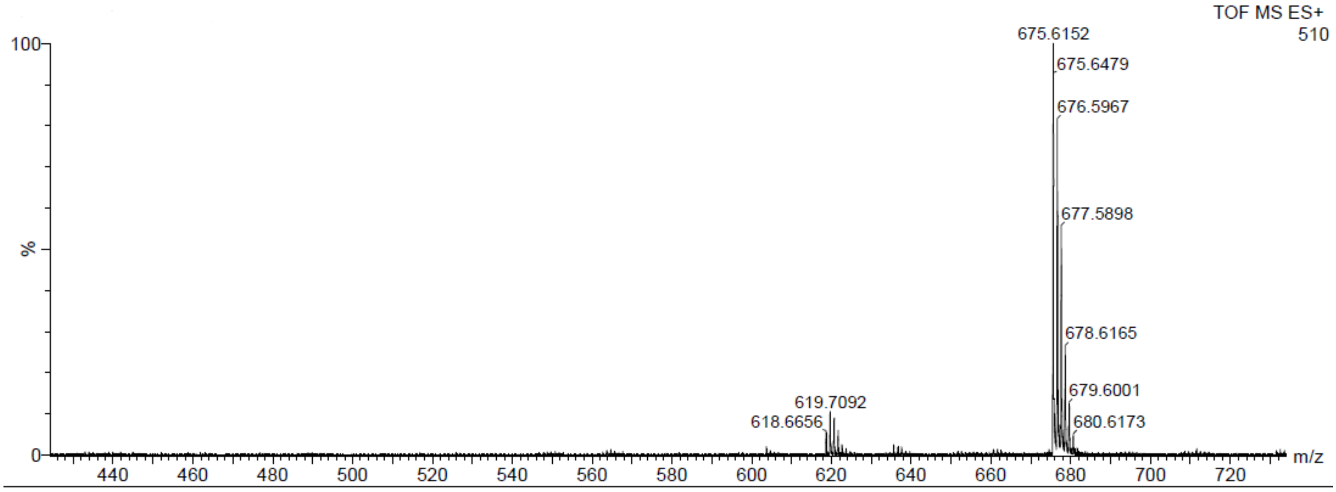


Figure 47: LIFDI-MS spectrum of compounds **16**.

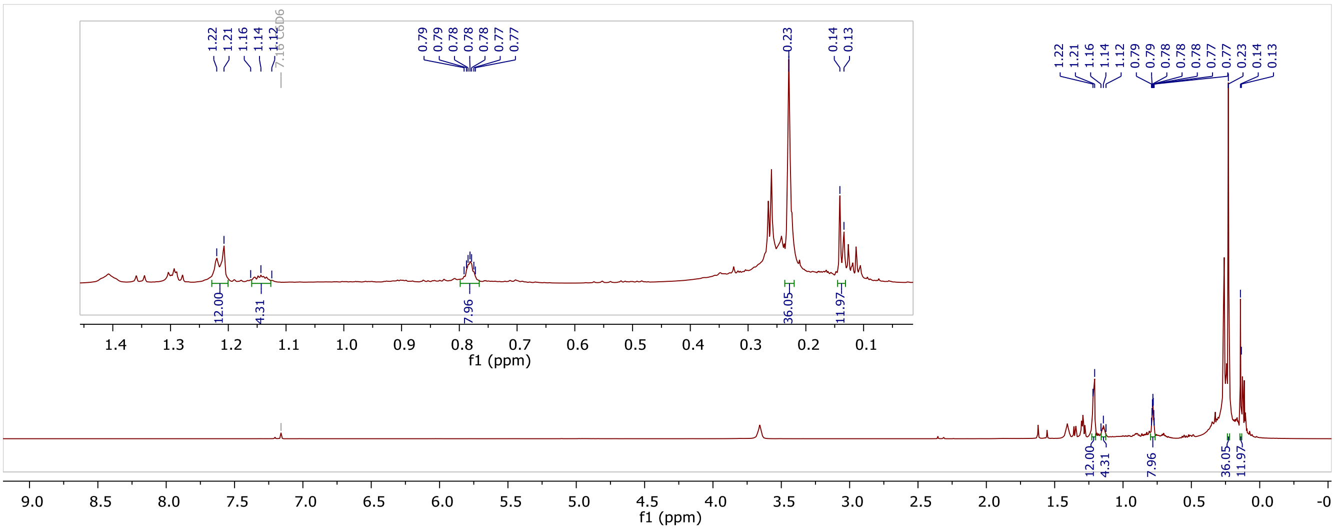


Figure 48: ^{1}H-NMR (500 MHz, C_6D_6) of compound **16** (cis/trans-species).

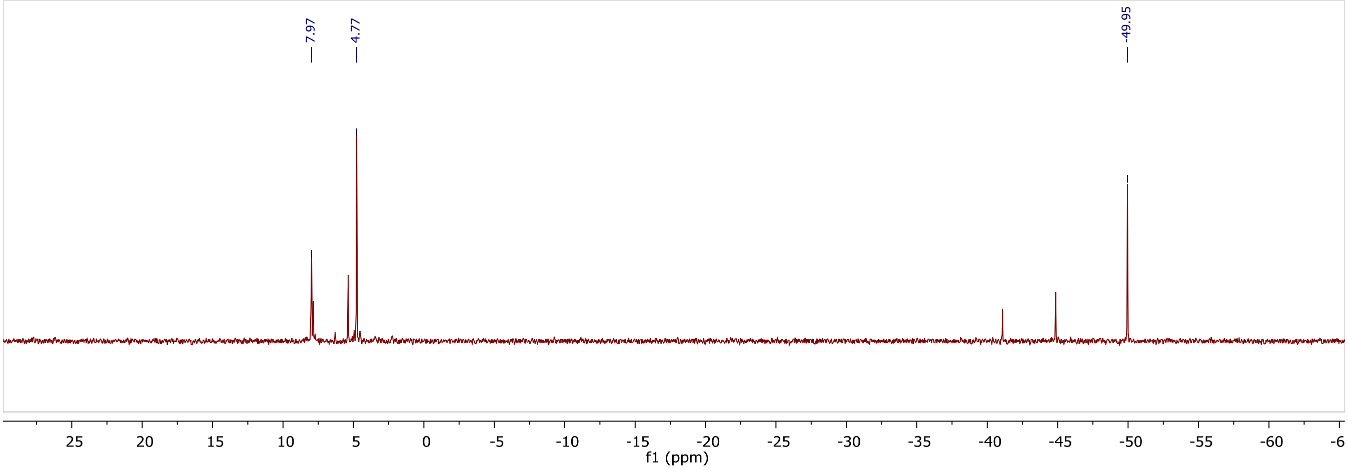


Figure 49: ^{29}Si.ig-NMR (100 MHz, C_6D_6) of compound **16** (cis/trans-species).

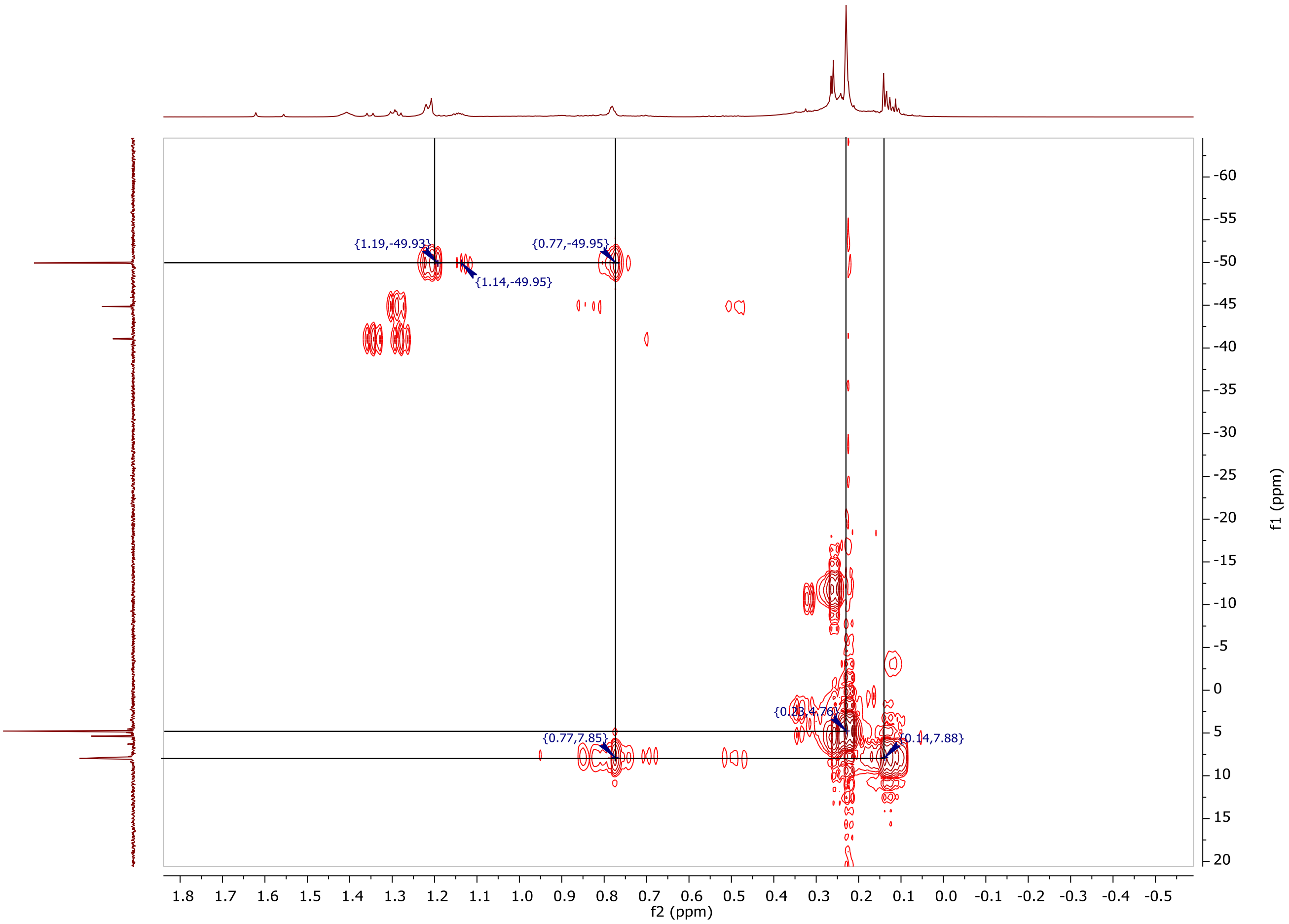


Figure 50: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **16** (cis/trans-species).

Trans/ Cis species: 70 % relative ratio. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = 0.11–0.12 (m, 12H), 0.25–0.26 (m, 36H), 0.47–0.52 (m, 4H), 0.81–0.85 (m, 4H), 1.17–1.18 (m, 4H), 1.27–1.30 (m, 12H). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 44.9, 4.70, 7.68. **LIFDI-MS:** 675.61 [M]$^+$, 619.70 [M-C_4H_8]$^+$.

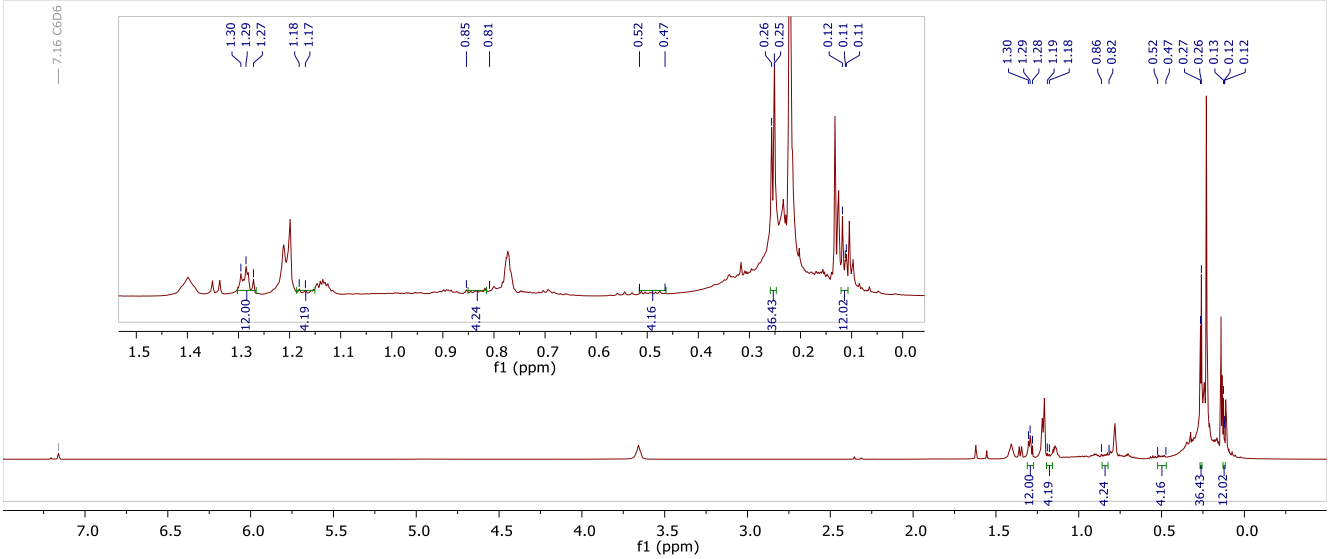


Figure 51: ^{1}H-NMR (500 MHz, C_6D_6) of compound **16** (trans/cis-species).

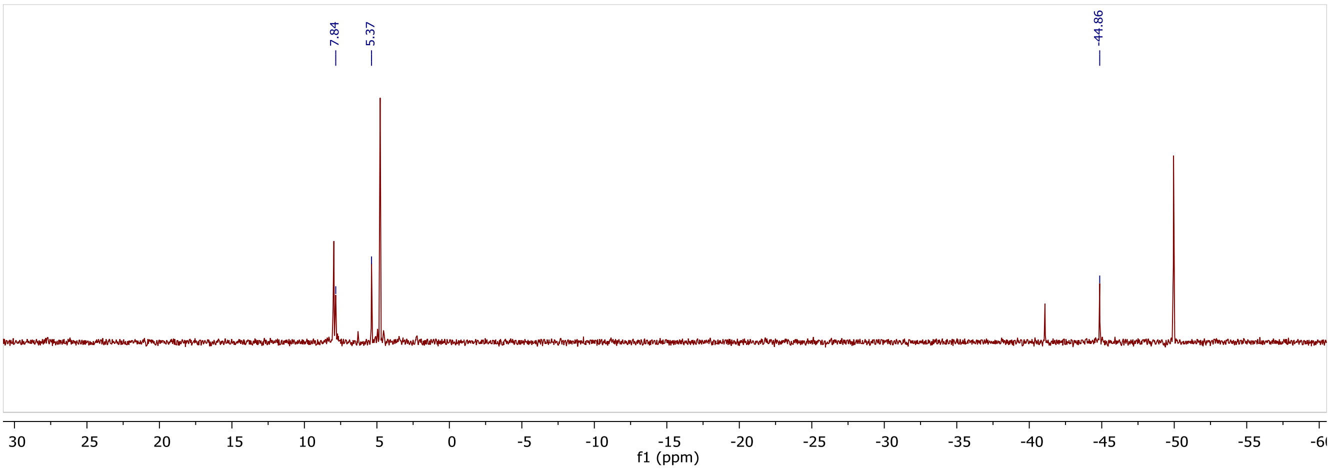


Figure 52: ^{29}Si.ig-NMR (100 MHz, C_6D_6) of compound **16** (trans/cis-species).

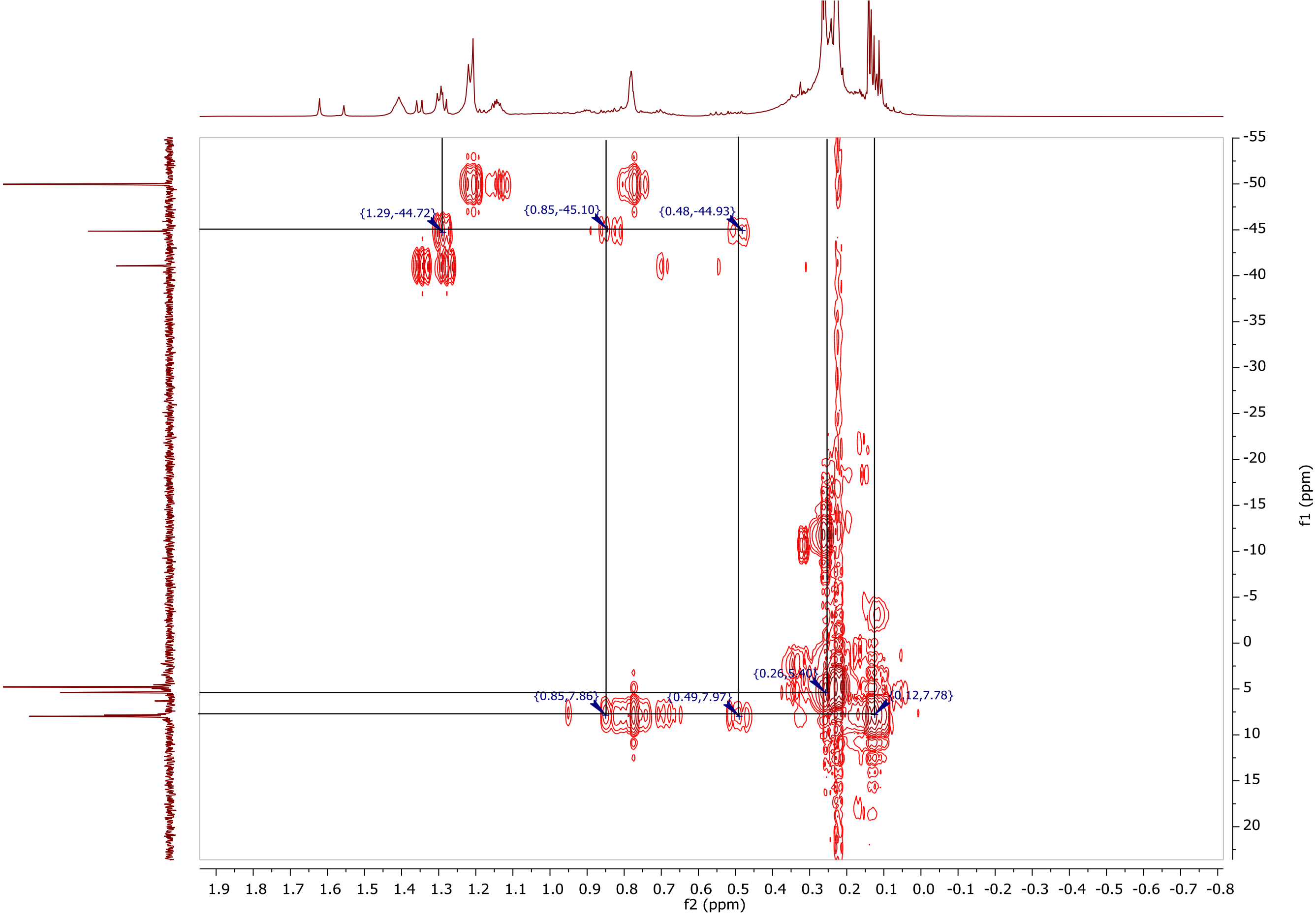


Figure 53: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **16** (trans/cis-species).

1-butene-species: 12 % relative ratio. **^{1}H-NMR:** (500 MHz, C_6D_6) δ = 0.09–0.10 (m, 12H), 0.23–0.24 (m, 36H), 0.52–0.57 (m, 4H), 0.67–0.74 (m, 8H), 0.93–0.99 (m, 4H), 1.27 (m, 2H), 1.34–1.35 (m, 6H). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = -41.1, 5.3, 7.8. **LIFDI-MS:** 675.61 [M]$^{+}$, 619.70 [M-C_4H_8]$^{+}$.

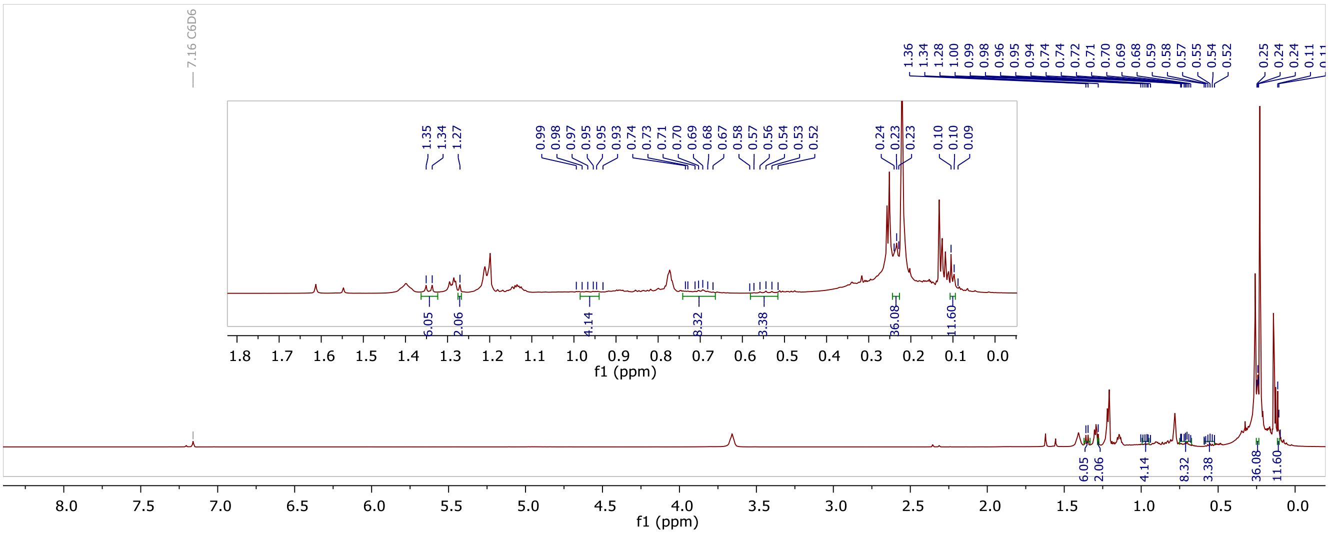


Figure 54: ^{1}H-NMR (500 MHz, C_6D_6) of compound **16** (1-butene species).

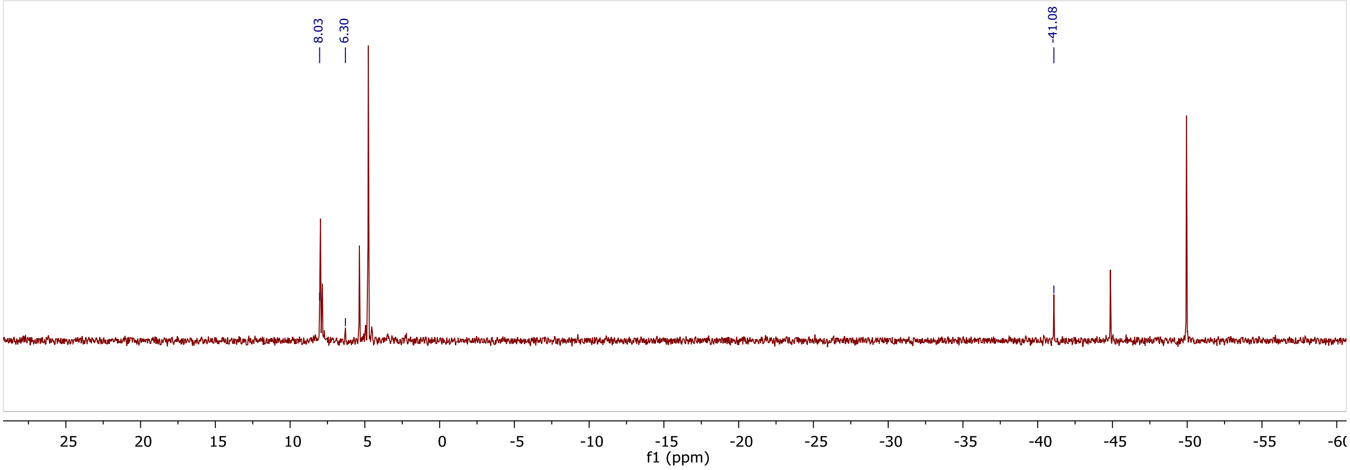


Figure 55: ^{29}Si.ig-NMR (100 MHz, C_6D_6) of compound **16** (1-butene species).

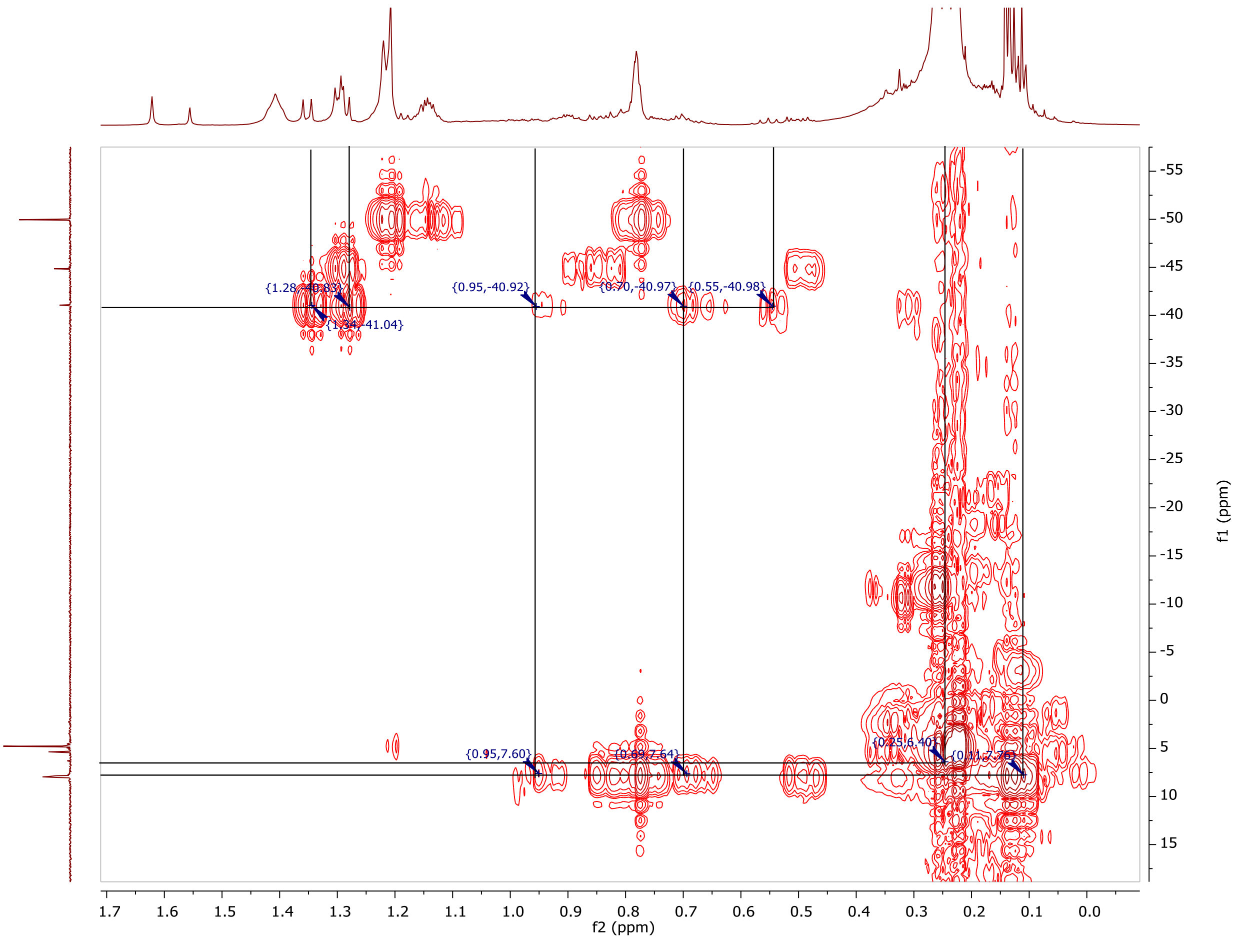


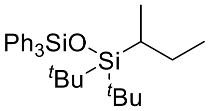
Figure 56: ^{1}H-^{29}Si-HMBC (500 MHz/100 MHz, C_6D_6) of compound **16** (1-butene species).

2.4. Screening Reactions and Screening Products

2.4.1. Ring opening

General Procedure: 30 mg (151.2 µmol, 1.0 eq.) of **1** and 1.0 eq. of the respective silanol or alcohol (dry) are dissolved in 0.6 ml C_6D_6 in a high-pressure J-Young NMR-tube. The tube is capped with a PTFE screw-cap. The mixture is heated to 80 °C in an oil-bath until the reactants are consumed or the reaction reached maximum conversion. The reaction progress can be monitored by ^{1}H-NMR and/or ^{29}Si-NMR. ^{29}Si-ig (inverse gated decoupling) pulse sequence allows quantitative integration of the Si-signals and therefore estimation of reaction progress.

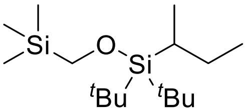
1-(*sec*-Butyl)-1,1-di-*tert*-butyl-3,3,3-triphenyldisiloxane



Substrate: Triphenylsilanol

^{1}H-NMR: (500 MHz, C_6D_6) δ = 0.89 (t, 3 H, CH_2-CH_3), 1.07 (s, 9 H, *t*Bu), 1.09 (s, 9 H, *t*Bu), 1.19 (d, 3 H, CH-CH_3), 2.00 (dq, 1 H, C*H*), 1.24 (m, 2 H, CH_2-CH_3), 7.20 (m, 9 H, Ph), 7.82 (m, 6 H, Ph). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 6.10 (Si*t*Bu_2), -21.23 (*Si*Ph_3).

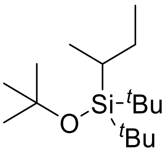
sec-Butyldi-*tert*-butyl((trimethylsilyl)methoxy)silane



Substrate: Trimethylsilylmethanol

^{1}H-NMR: (500 MHz, C_6D_6) δ = 0.05 (s, 9 H, Si*Me*$_3$), 0.98 (t, 3 H, CH_2CH_3), 1.11 (d, 18 H, *t*Bu), 1.14 (s, 3 H, CH-CH_3), 1.24 (m, 1 H, CH_2-CH_3), 1.87 (dqd, 1 H, C*H*-CH_3), 3.41 (s, 2 H, CH_2-SiMe_3) (1 H of CH_2-CH_3 superimposed). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 8.07 (Si*t*Bu_2), -0.75(*Si*Me_3).

tert-Butoxy(*sec*-butyl)di-*tert*-butylsilane



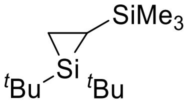
Substrate: *tert*-Butanol

^{1}H-NMR: (500 MHz, C_6D_6) δ = 0.87 (m, 1 H, C$H_2$$CH_3$), 0.96 (t, 3 H, CH_2CH_3), 1.04 (s, 18 H, *t*Bu), 1.11 (d, 3 H, CH-CH_3), 1.21 (m, 1 H, C$H_2$$CH_3$), 1.59 (m, 3 H, O*t*Bu), 1.82 (m, 1 H, C*H*-CH_3). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 9.06 (Si*t*Bu_2).

2.4.2. Silylene Transfer

General Procedure: 2.0 g (10.08 mmol, 1.2 eq.) of **1** and 1.0 eq. of the respective olefin or are dissolved in 5 ml dry toluene in a screw-cap vial with integrated rubber septum. The emerging butene gas must be released over a syringe needle in the septum. The mixture is heated to 80 °C in an oil-bath until the reactants are consumed. The reaction progress can be monitored by ^{1}H-NMR and/or ^{29}Si-NMR. ^{29}Si-ig (inverse gated decoupling) pulse sequence allows quantitative integration of the Si-signals and therefore estimation of reaction progress. Excess **1** is removed in high vacuum. Acceleration of the reaction can be achieved by addition of catalytic amounts AgOTf.[7-10] Products can be refined by high-vacuum (10^{-3}) bulb-to-bulb distillation.

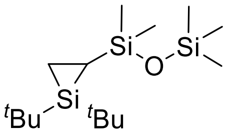
1,1-Di-*tert*-butyl-2-(trimethylsilyl)silirane



Substrate: Vinyltrimethylsilane

^{1}H-NMR: (500 MHz, C_6D_6) δ = -0.31 (dd, 1 H, C*H*), 0.22 (s, 9 H, Si*Me*$_3$), 0.48 (dd, 1 H, CH), 0.73 (dd, 1 H, C*H*), 1.04 (s, 9 H, *t*Bu), 1.10 (s, 9 H, *t*Bu). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 1.01(SiMe$_3$), -48.33 (Si*t*Bu$_2$). **^{13}C-NMR:** (125 MHz, C_6D_6) δ = -2.9, -1.3, 1.1, 29.6, 30.0.

1,1-Di-*tert*-butyl-2-(1,1,3,3,3-pentamethyldisiloxaneyl)silirane



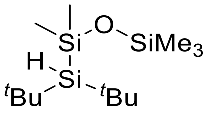
Substrate: Vinylpentamethyldisiloxane

^{1}H-NMR: (500 MHz, C_6D_6) δ = -0.32 (t, 1 H, C*H*), 0.16 (s, 9 H, Si*Me*$_3$), 0.28 (s, 3 H, OSi*Me*), 0.31 (s, 3 H, OSi*Me*), 0.61 (t, 1 H, C*H*), 0.69 (m, 1 H, C*H*), 1.04 (s, 9 H, *t*Bu), 1.16 (s, 9 H. *t*Bu). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 6.43 (*Si*Me$_3$), 5.77 (*Si*Me$_2$), -48.35 (Si*t*Bu$_2$).

2.4.3. Silylene Insertion

General Procedure: 30 mg (151.2 µmol, 1.0 eq.) of **1** or 30 mg (133.7 µmol, 1 eq.) of 7,7-di-*tert*-butyl-7-silabicyclo[4.1.0]heptane and an equivalent amount of screening compound (1.0 eq.) is dissolved in 0.6 ml C_6D_6 in a high-pressure J-Young NMR-tube. The tube is capped with a PTFE screw-cap. The mixture is heated to 140 °C in an oil-bath (High pressure! Use explosion shield or sand bath) until the reactants are consumed or the reaction reached maximum conversion. The reaction progress can be monitored by ^{1}H-NMR and/or ^{29}Si-NMR. ^{29}Si-ig (inverse gated decoupling) pulse sequence allows quantitative integration of the Si-signals and therefore estimation of reaction progress.

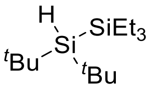
1-(Di-*tert*-butylsilyl)-1,1,3,3,3-pentamethyldisiloxane



Substrate: Pentamethyldisiloxane

^{1}H-NMR: (500 MHz, C_6D_6) δ = 0.12 (s, 9 H, Si*Me*$_3$), 0.39 (s, 6 H, Si*Me*$_2$), 1.17 (s, 18 H, *t*Bu), 3.59 (s, 1 H, Si-H). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 8.32 ($SiMe_3$), 5.48 ($SiMe_2$), -6.58 (SiH*t*Bu$_2$).

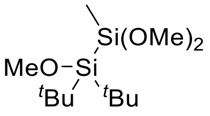
2,2-Di-*tert*-butyl-1,1,1-triethyldisilane



Substrate: Triethylsilane

^{1}H-NMR: (500 MHz, C_6D_6) δ = 0.77 (q, 6 H, C*H*$_2$), 1.05 (t, 9 H, Me), 1.14 (s, 18 H, *t*Bu), 3.69 (s, 1 H, Si-H). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = -6.2 (SiH*t*Bu$_2$), -8.13 ($SiEt_3$).

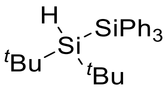
1,1-Di-*tert*-butyl-1,2,2-trimethoxy-2-methyldisilane



Substrate: Trimethoxymethylsilane

^{1}H-NMR: (500 MHz, C_6D_6) δ = 0.30 (s, 3 H, Si*Me*), 1.20 (s, 18 H, *t*Bu$_2$), 3.37 (s, 6 H, SiO*Me*$_2$), 3.63 (s, 3 H, SiO*Me*). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = 12.07 (Si*t*Bu$_2$), -0.83 ($SiMe_2OMe$). **^{13}C-NMR:** (125 MHz, C_6D_6) δ = 0.7, 22.7, 28.5, 50.1, 54.4.

2,2-Di-*tert*-butyl-1,1,1-triphenyldisilane



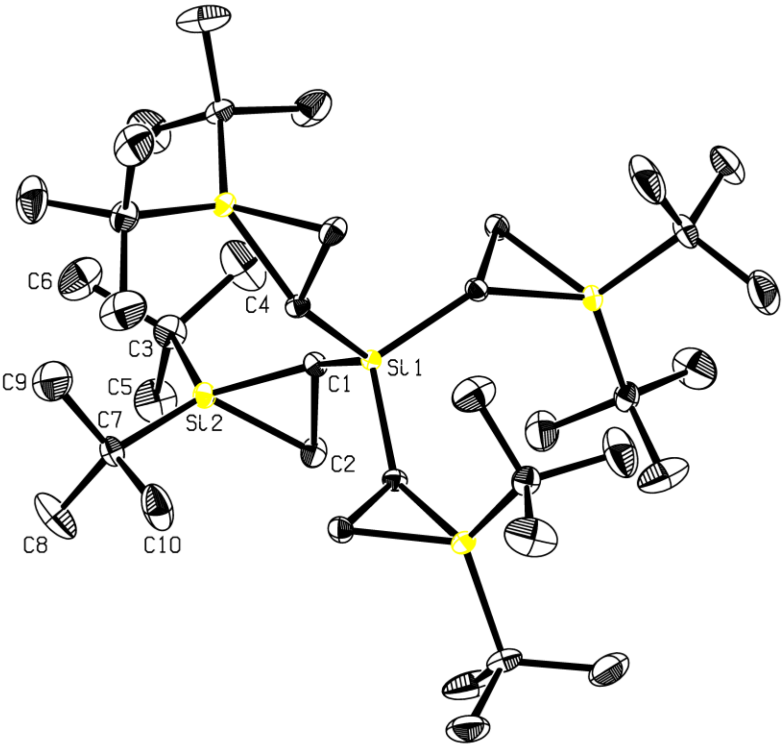
Substrate: Triphenylsilane

^{1}H-NMR: (500 MHz, C_6D_6) δ = 1.07 (s, 18 H, *t*Bu$_2$), 4.37 (s, 1 H, SiH), 7.12 – 7.19 (m, 9 H, Ph), 7.81 – 7.89 (m, 6 H, Ph). **^{29}Si-NMR:** (100 MHz, C_6D_6) δ = -6.0 ($SiPh_3$), -21.7 (SiH*t*Bu$_2$).

UV-Vis Experiments

Based on reports from Boudjouk and Fink on photolytic silirane cleavage we investigated the potential for photochemical curing.[5-6, 11] UV-VIS measurements revealed absorption maxima for siliranes **1**, **6**–**10**, **15** and **16** in the range of 210–230 nm. UV-Photolysis of **1** at 254 nm (in cyclohexane-d_{12}) in presence of screening compounds gave the expected insertion products (analogously to thermolysis). Due to insufficient absorption this reaction required long irradiation. The requirement for highly energetic UV-C radiation, which is not compatible with siloxanes, disqualifies compounds **6**–**10**, **15** and **16** for photocrosslinking.

3. X-ray Crystallographic Data



Tetrakis(1,1-di-tert-butylsilirane-2-yl)silane **6**

CCDC Deposition Number	1953911
Diffractometer operator	Philipp J. Altmann
Formula weight	176.38
Temperature	100(2) K
Bond precision:	C-C = 0.0031 A
Wavelength	0.71073 Å
Crystal size	0.070 x 0.085 x 0.149 mm
Crystal habit	clear colourless fragment
Crystal system	tetragonal
Space group	I 41/a
Unit cell dimensions	a = 16.882(2) Å α = 90°
	b = 16.882(2) Å β = 90°
	c = 16.323(2) Å γ = 90°
Volume	4652.1(13) Å3
Z	16
Density (calculated)	1.007 g/cm3
Absorption coefficient	0.177 mm-1
F(000)	1576
Diffractometer Bruker	D8 Kappa Apex II
Radiation source	fine-focus sealed tube, Mo
Theta range	2.41 to 25.02°
Index ranges	-20<=h<=20, -20<=k<=20, -19<=l<=19
Reflections collected	74129
Independent reflections	2054 [R(int) = 0.0497]
Coverage of independent refl.	100.0%

Absorption correction	Multi-Scan
Max. and min. transmission	0.9880 and 0.9740
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	Σ w(Fo^2 - Fc^2)^2
Data / restraints / parameters	2054 / 0 / 108
Goodness-of-fit on F2	1.035
Δ/σmax	0.001
Final R indices	1813 data; I>2σ(I) R1 = 0.0431, wR2 = 0.1071
	all data R1 = 0.0496, wR2 = 0.1125
Weighting scheme	w=1/[σ2(Fo2)+(0.0468P)2+14.2967P] where P=(Fo2+2Fc2)/3
Largest diff. peak and hole	0.761 and -0.319 eÅ-3
R.M.S. deviation from mean	0.059 eÅ-3

Bond lengths (Å) for **6:**

Si1-C1 1.8895(19)   Si1-C1 1.8895(19)
Si1-C1 1.8895(19)   Si1-C1 1.8895(19)
Si2-C2 1.836(2)   Si2-C1 1.869(2)
Si2-C7 1.900(2)   Si2-C3 1.914(2)
C1-C2 1.584(3)   C1-H1 1.0
C2-H2A 0.99   C2-H2B 0.99
C3-C4 1.517(3)   C3-C5 1.535(3)
C3-C6 1.557(3)   C4-H4A 0.98
C4-H4B 0.98   C4-H4C 0.98
C5-H5A 0.98   C5-H5B 0.98
C5-H5C 0.98   C6-H6A 0.98
C6-H6B 0.98   C6-H6C 0.98
C7-C8 1.528(3)   C7-C9 1.529(3)
C7-C10 1.536(3)   C8-H8A 0.98
C8-H8B 0.98   C8-H8C 0.98
C9-H9A 0.98   C9-H9B 0.98
C9-H9C 0.98   C10-H10A 0.98
C10-H10B 0.98   C10-H10C 0.98

Bond angles (°) for **6**:

C1-Si1-C1 107.81(6)   C1-Si1-C1 107.81(6)
C1-Si1-C1 112.85(12)   C1-Si1-C1 112.85(12)
C1-Si1-C1 107.81(6)   C1-Si1-C1 107.81(6)
C2-Si2-C1 50.63(8)   C2-Si2-C7 118.74(10)
C1-Si2-C7 121.43(9)   C2-Si2-C3 113.16(10)
C1-Si2-C3 116.84(9)   C7-Si2-C3 118.04(10)
C2-C1-Si2 63.60(10)   C2-C1-Si1 123.25(14)
Si2-C1-Si1 139.44(11)   C2-C1-H1 107.3
Si2-C1-H1 107.3   Si1-C1-H1 107.3
C1-C2-Si2 65.77(10)   C1-C2-H2A 117.1
Si2-C2-H2A 117.1   C1-C2-H2B 117.1
Si2-C2-H2B 117.1   H2A-C2-H2B 114.2
C4-C3-C5 109.9(2)   C4-C3-C6 108.3(2)
C5-C3-C6 106.85(19)   C4-C3-Si2 110.20(15)
C5-C3-Si2 108.57(16)   C6-C3-Si2 112.95(16)
C3-C4-H4A 109.5   C3-C4-H4B 109.5
H4A-C4-H4B 109.5   C3-C4-H4C 109.5
H4A-C4-H4C 109.5   H4B-C4-H4C 109.5
C3-C5-H5A 109.5   C3-C5-H5B 109.5
H5A-C5-H5B 109.5   C3-C5-H5C 109.5
H5A-C5-H5C 109.5   H5B-C5-H5C 109.5
C3-C6-H6A 109.5   C3-C6-H6B 109.5
H6A-C6-H6B 109.5   C3-C6-H6C 109.5
H6A-C6-H6C 109.5   H6B-C6-H6C 109.5
C8-C7-C9 110.7(2)   C8-C7-C10 107.5(2)
C9-C7-C10 107.2(2)   C8-C7-Si2 111.78(16)
C9-C7-Si2 111.38(15)   C10-C7-Si2 108.00(14)

C7-C8-H8A 109.5	C7-C8-H8B 109.5
H8A-C8-H8B 109.5	C7-C8-H8C 109.5
H8A-C8-H8C 109.5	H8B-C8-H8C 109.5
C7-C9-H9A 109.5	C7-C9-H9B 109.5
H9A-C9-H9B 109.5	C7-C9-H9C 109.5
H9A-C9-H9C 109.5	H9B-C9-H9C 109.5
C7-C10-H10A 109.5	C7-C10-H10B 109.5
H10A-C10-H10B 109.5	C7-C10-H10C 109.5
H10A-C10-H10C 109.5	H10B-C10-H10C 109.5

4. Rheological Measurements

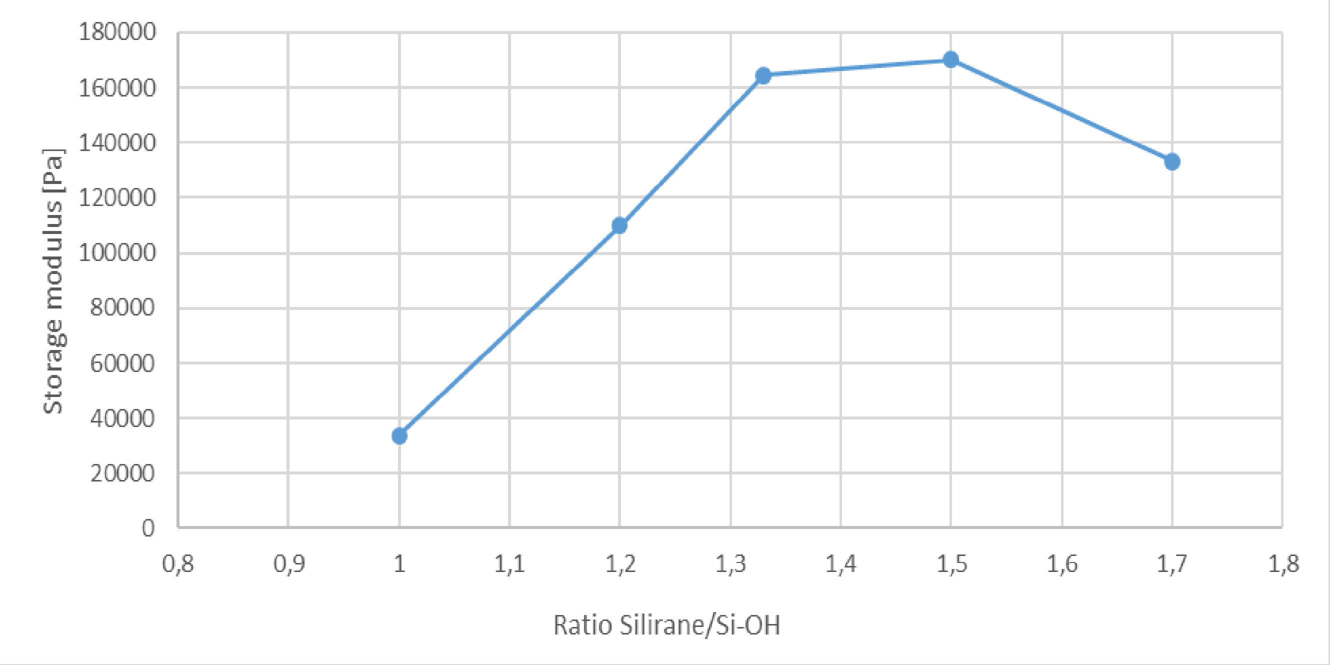


Figure 57: Storage modulus of crosslinked elastomers made from **8** and SiOH-terminated PDMS (n~131). Values are taken after full crosslinking (steady viscosity) at 110 °C.

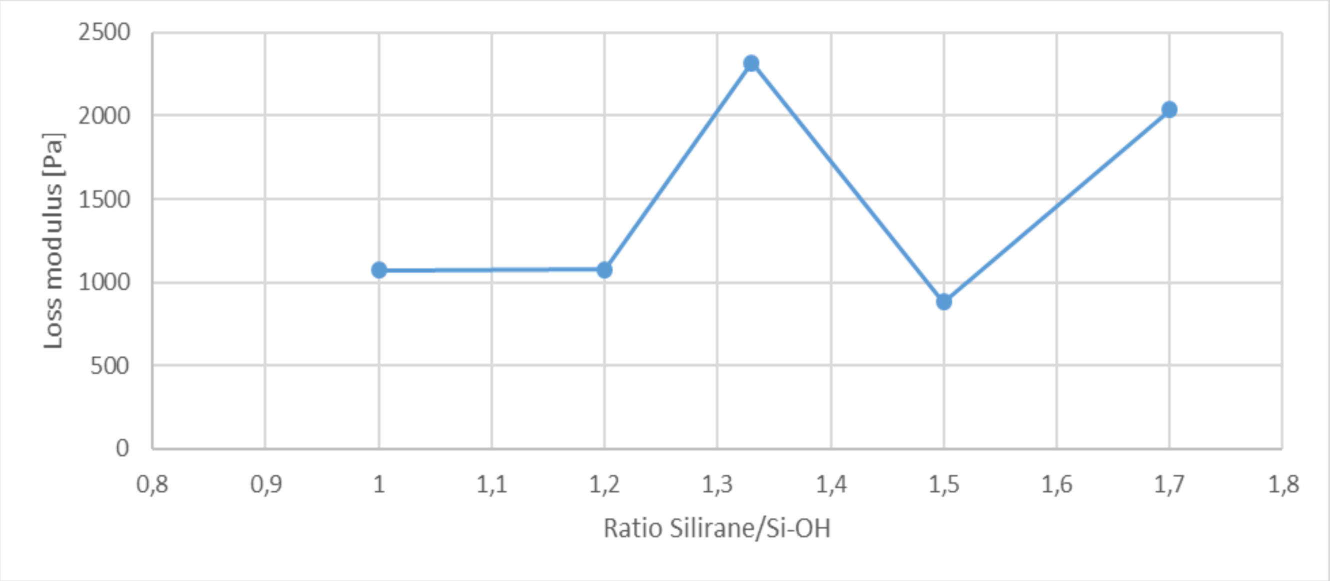


Figure 58: Loss modulus of crosslinked elastomers made from **8** and SiOH-terminated PDMS (n~131). Values are taken after full crosslinking (steady viscosity) at 110 °C.

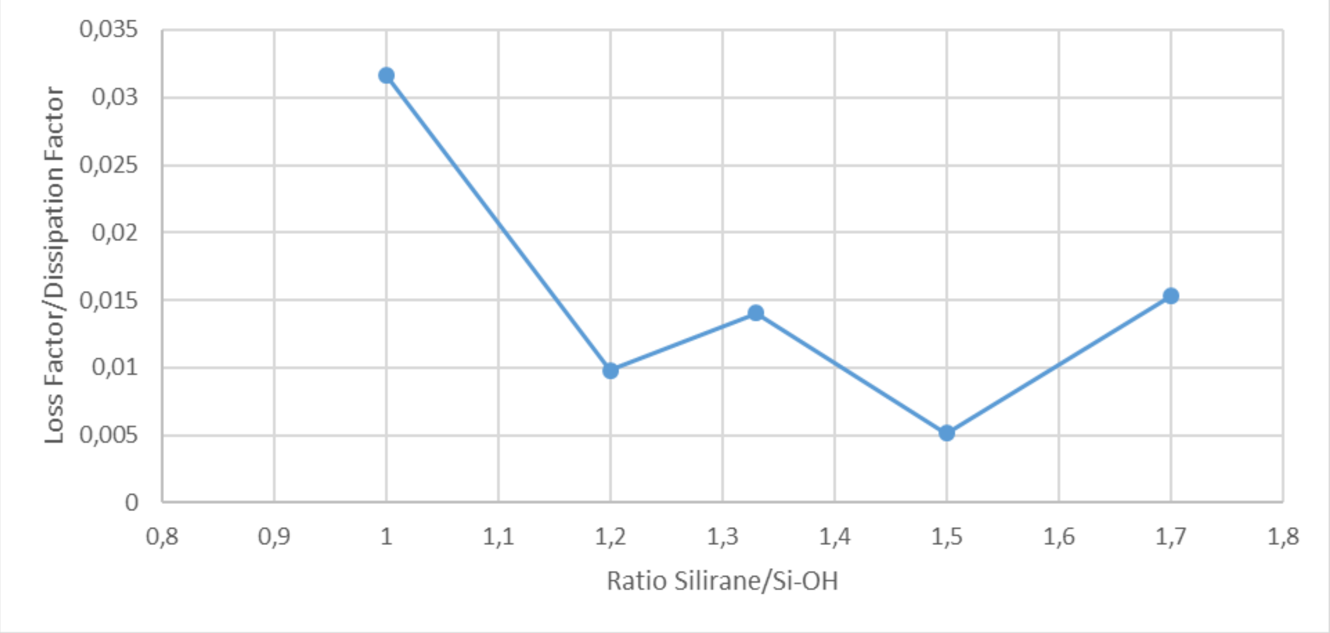


Figure 59: Loss factor tan(δ) of crosslinked elastomers made from **8** and SiOH-terminated PDMS (n~131). Values are taken after full crosslinking (steady viscosity) at 110 °C and are mean values of 100 measuring points.

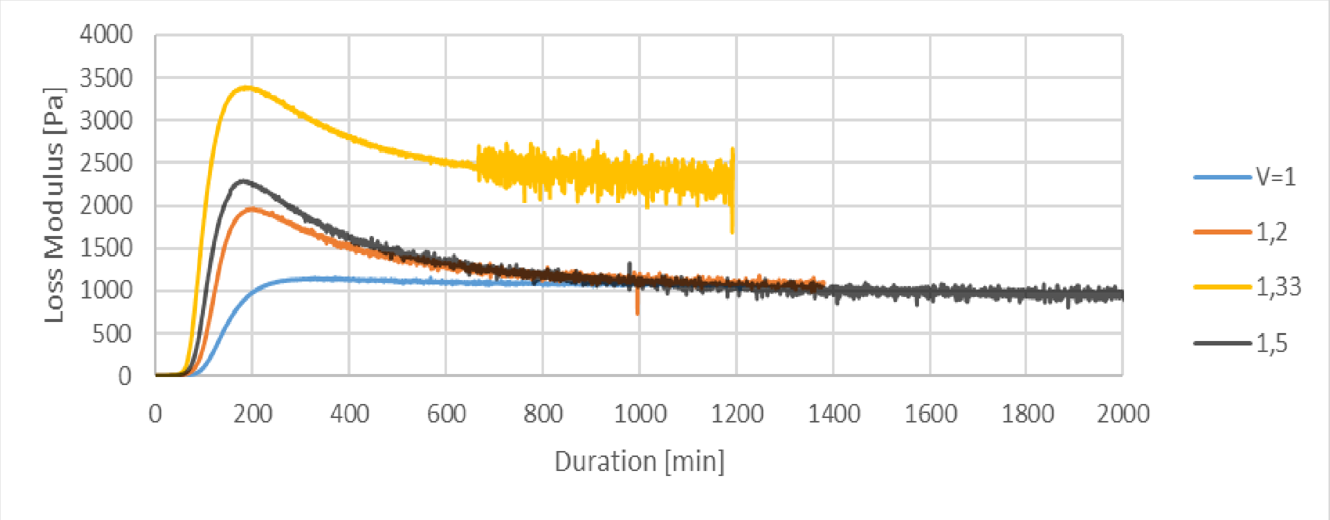


Figure 60: Loss modulus of mixtures made from **8** and SiOH-terminated PDMS (n~131) during crosslinking process at 110 °C. V = Ratio Silirane/Si-OH.

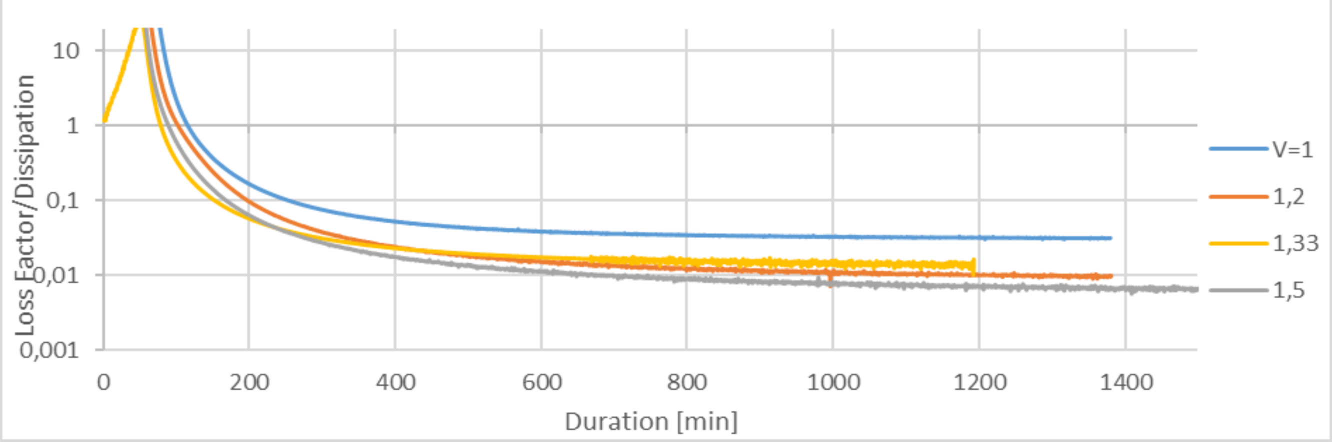


Figure 61: Loss factor tan(δ)of mixtures made from **8** and SiOH-terminated PDMS (n~131) during crosslinking process at 110 °C. V = Ratio Silirane/Si-OH.

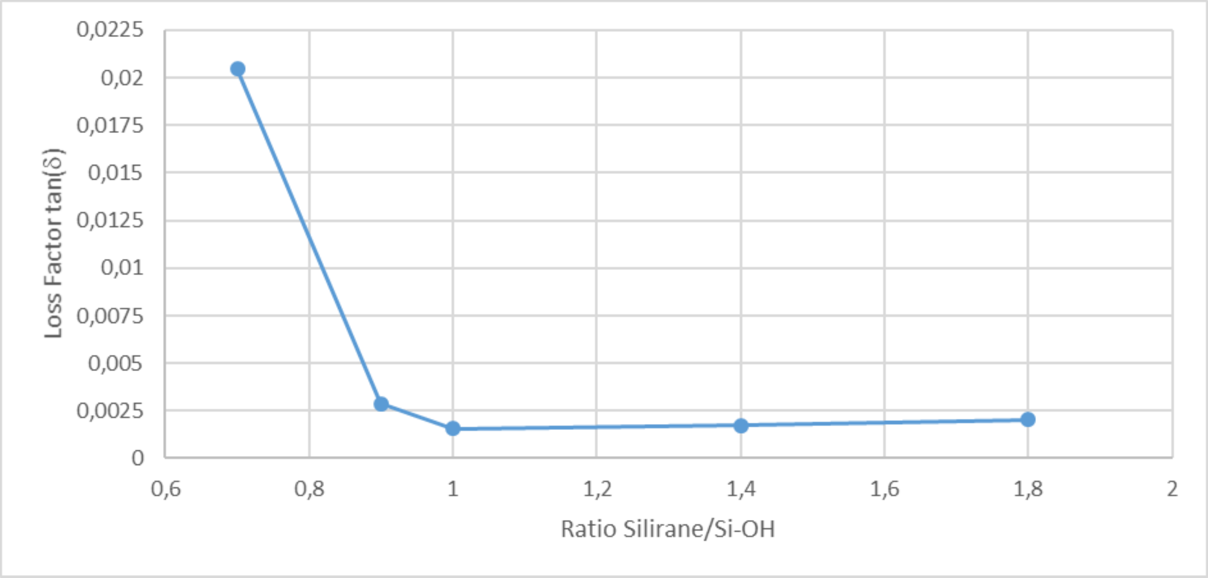


Figure 62: Loss factor tan(δ) of crosslinked elastomers made from **9** and SiOH-terminated PDMS (n~131). Values are taken after full crosslinking (steady viscosity) at 110 °C and are mean values of 100 measuring points.

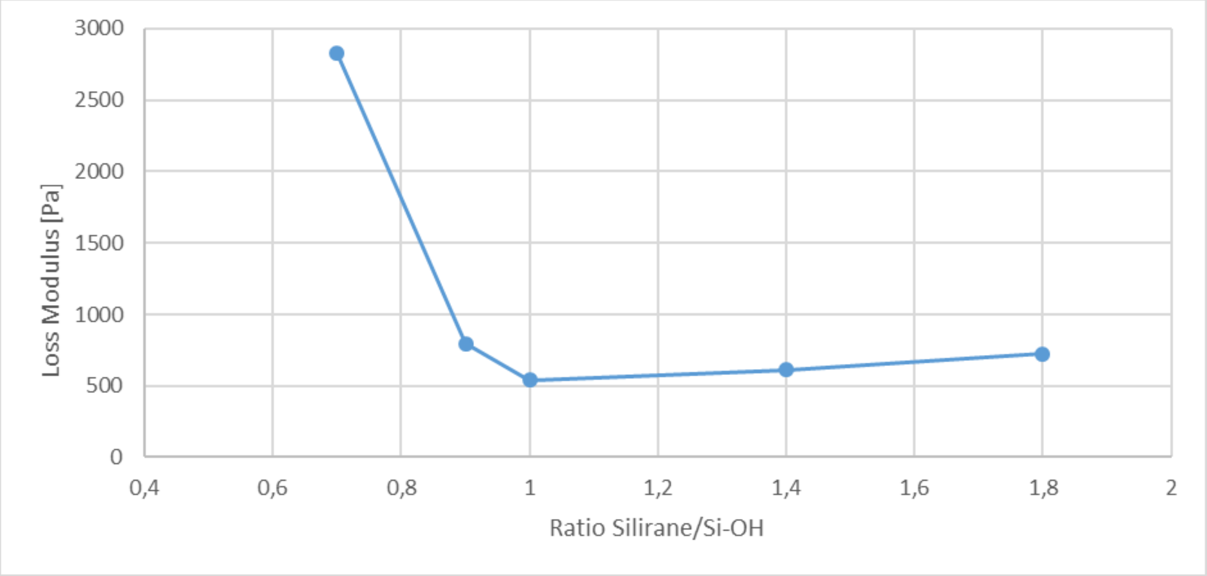


Figure 63: Loss modulus of crosslinked elastomers made from **9** and SiOH-terminated PDMS (n~131). Values are taken after full crosslinking (steady viscosity) at 110 °C.

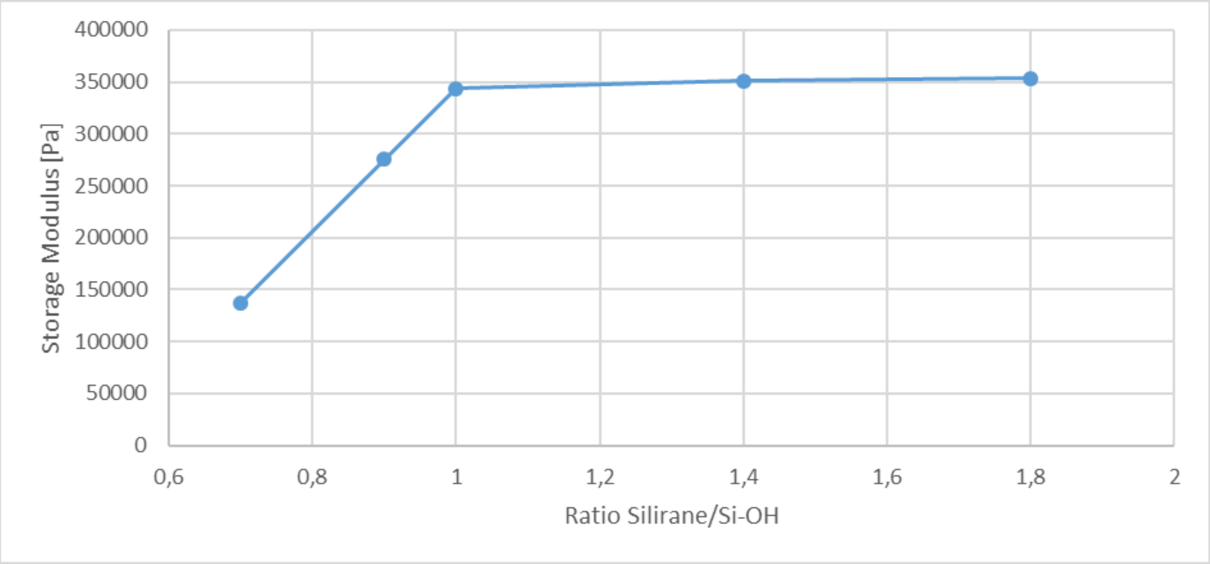


Figure 64: Storage modulus of crosslinked elastomers made from **9** and SiOH-terminated PDMS (n~131). Values are taken after full crosslinking (steady viscosity) at 110 °C.

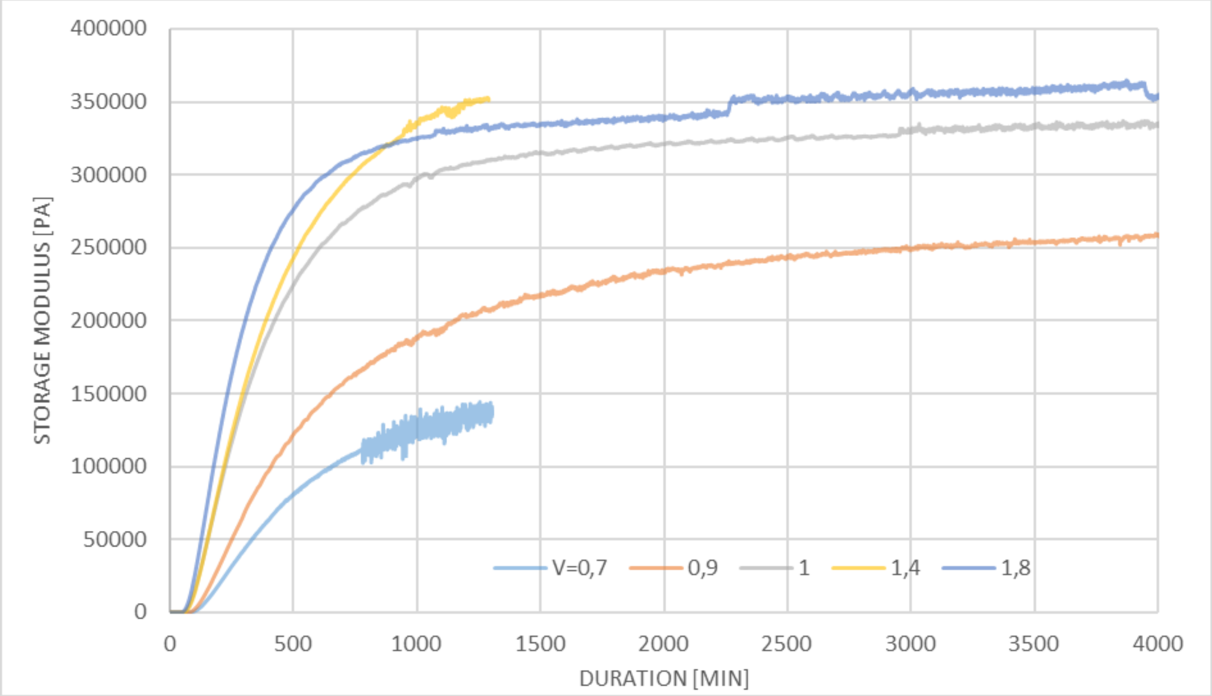


Figure 65: Storage modulus of mixtures made from **9** and SiOH-terminated PDMS (n~131) during crosslinking process at 110 °C. V = Ratio Silirane/Si-OH.

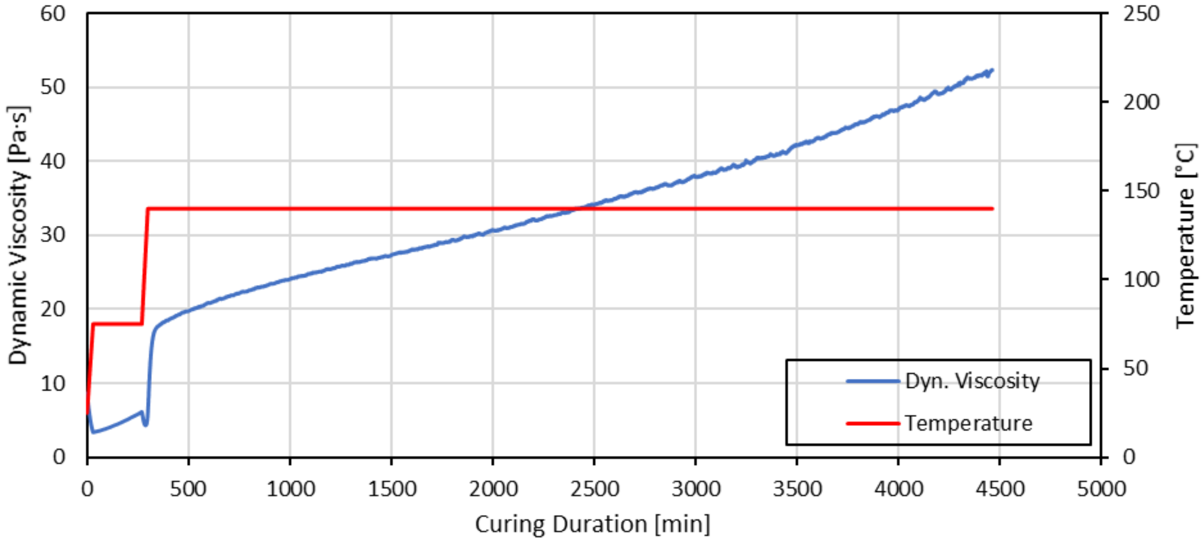


Figure 66: Complex viscosity of crosslinker **15** and Si-OH terminated PDMS (n~131) during curing process at different temperatures in a ratio of 2 (Silirane/Si-OH).

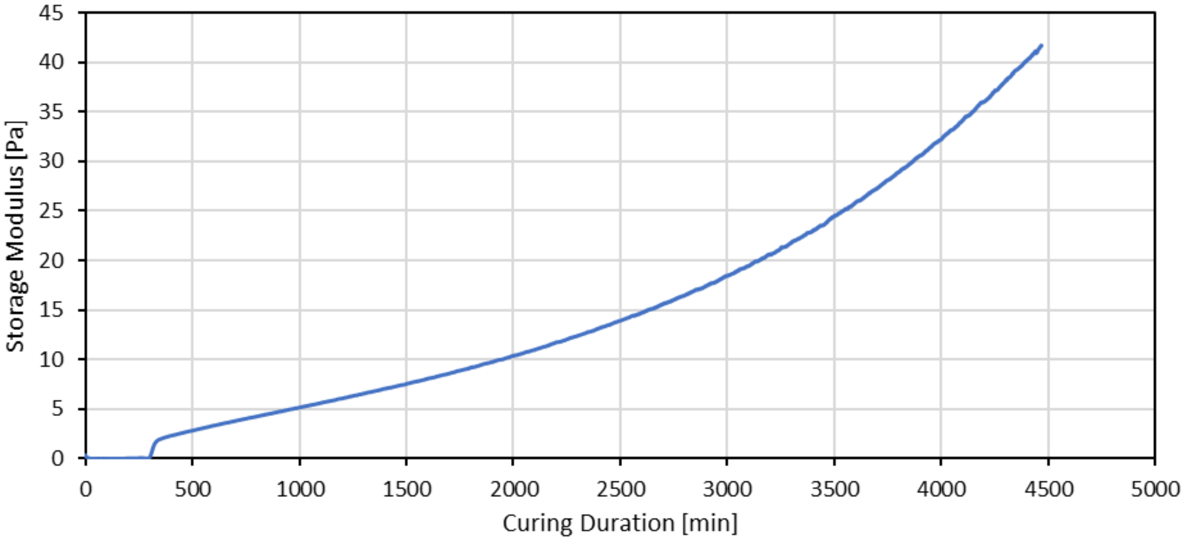


Figure 67: Storage modulus of crosslinker **15** and Si-OH terminated PDMS (n~131) during crosslinking process in Silirane/Si-OH ratio of 2.

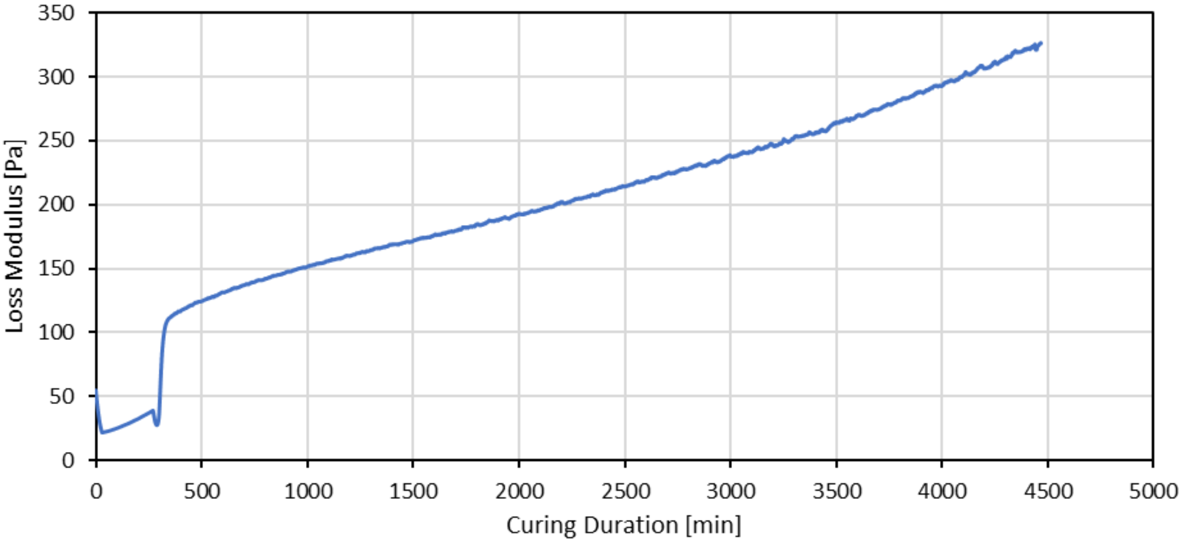


Figure 68: Loss modulus of crosslinker **15** and Si-OH terminated PDMS (n~131) during crosslinking process in Silirane/Si-OH ratio of 2.

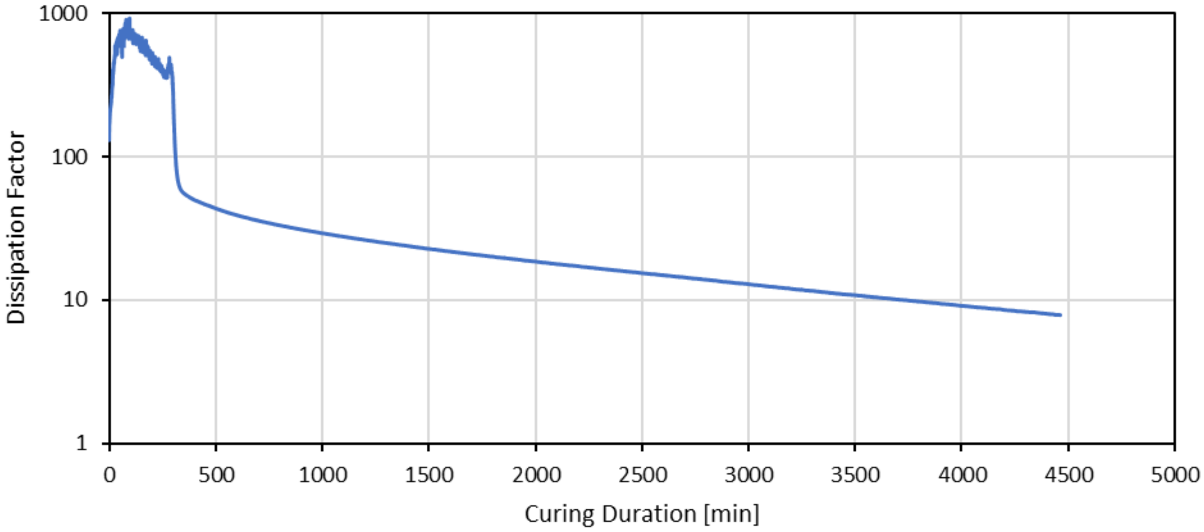


Figure 69: Dissipation factor tan(￿) of crosslinker **15** and Si-OH terminated PDMS (n~131) during crosslinking process in Silirane/Si-OH ratio of 2.

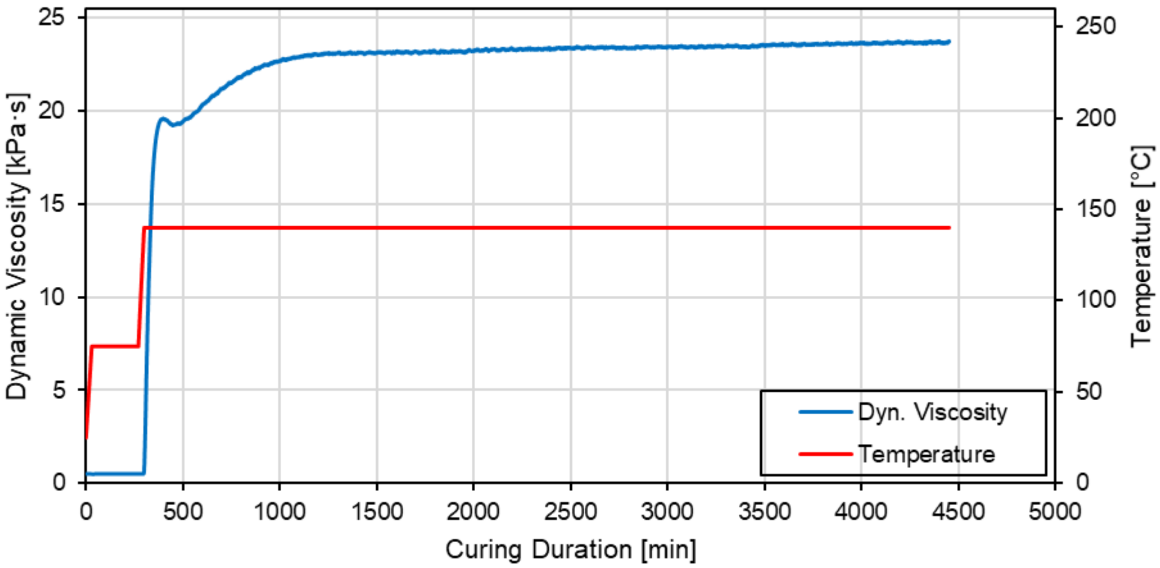


Figure 70: Complex viscosity of crosslinker **16** and Si-OH terminated PDMS (n~131) during curing process at different temperatures in a ratio of 2 (Silirane/Si-OH).

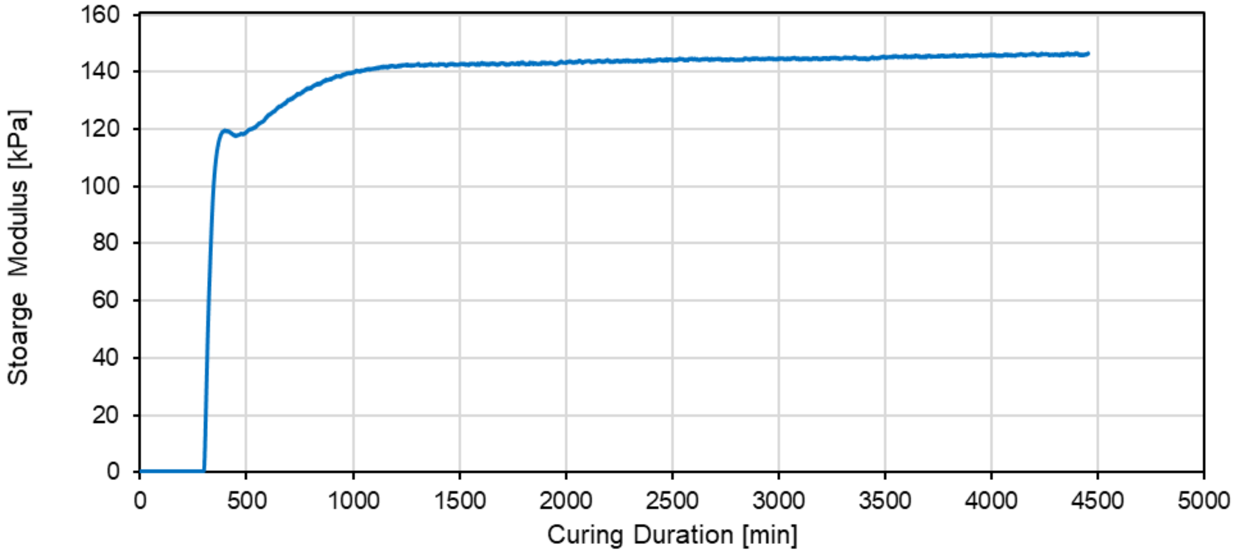


Figure 71: Storage modulus of crosslinker **16** and Si-OH terminated PDMS (n~131) during crosslinking process in Silirane/Si-OH ratio of 2.

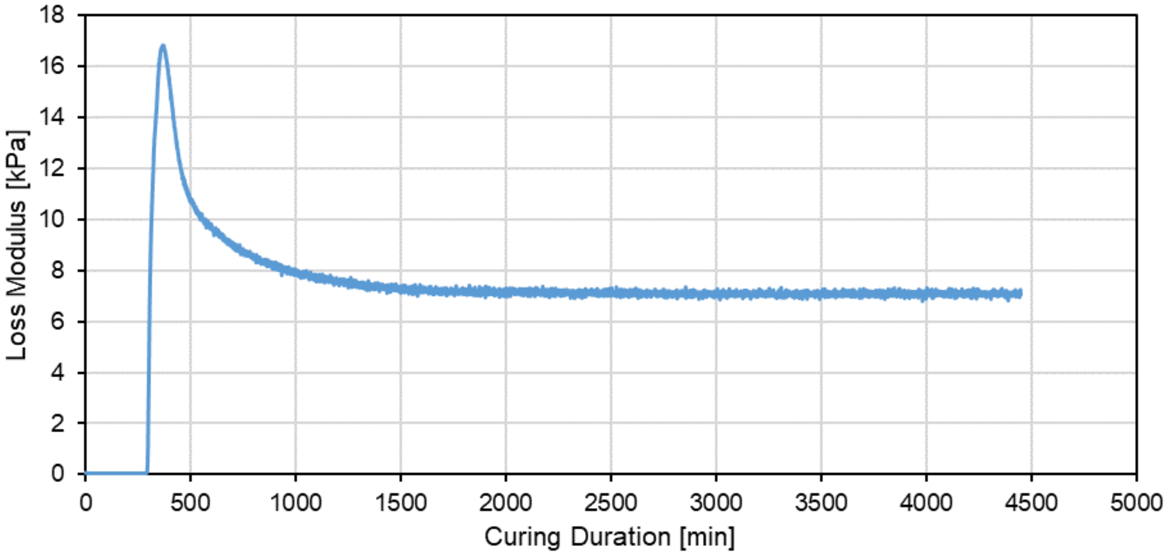


Figure 72: Loss modulus of crosslinker **16** and Si-OH terminated PDMS (n~131) during crosslinking process in Silirane/Si-OH ratio of 2.

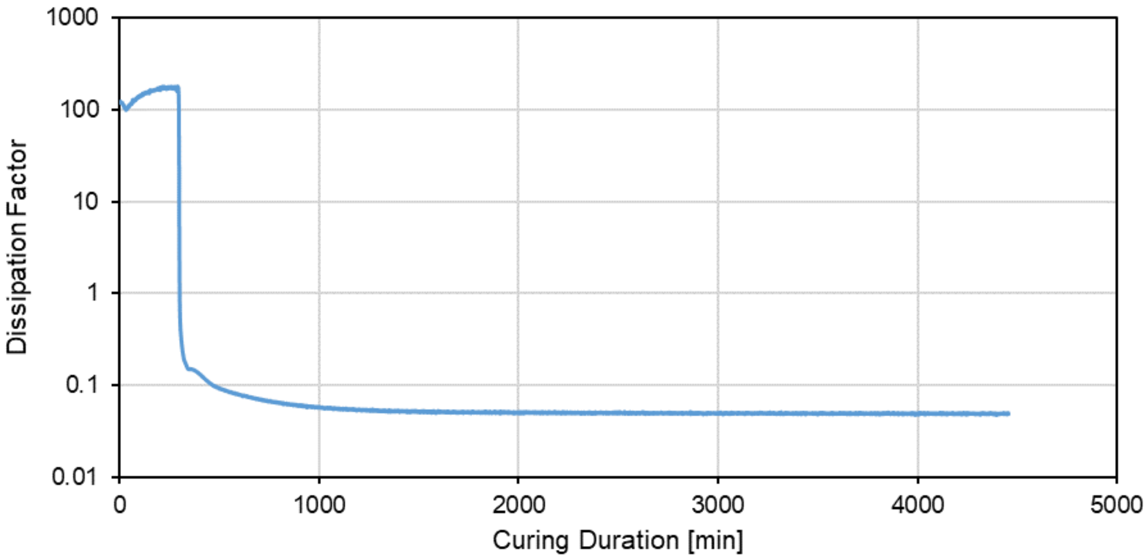


Figure 73: Dissipation factor tan(δ) of crosslinker **16** and Si-OH terminated PDMS (n~131) during crosslinking process in Silirane/Si-OH ratio of 2.

5. IR-Spectroscopy Data

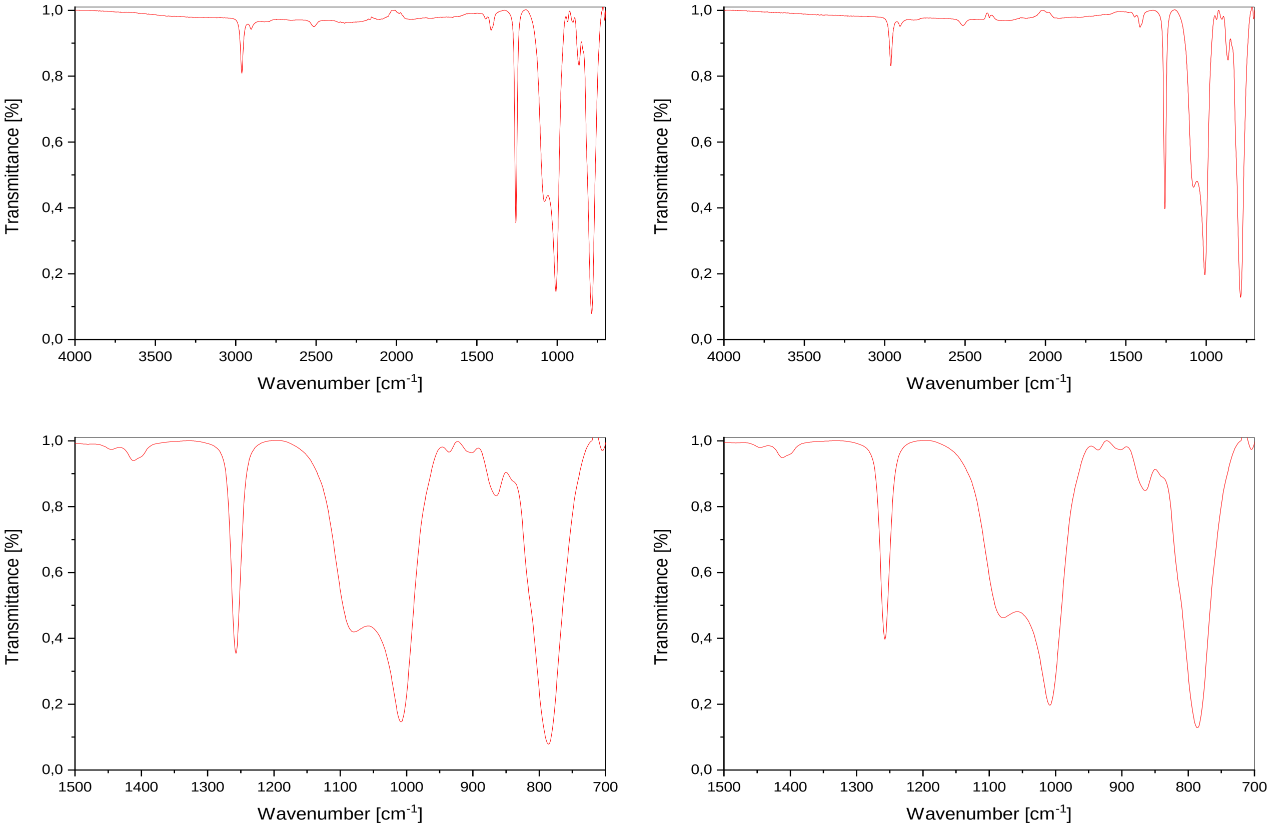


Figure 74: FT-IR-Measurements of elastomer cured with crosslinker **16** and Si-OH terminated PDMS (n~131, Silirane/Si-OH ratio of 2) before (left) and after 2 h treatment in boiling water (right). Characteristic Si-N-Si band of Tris(trimethylsilyl)amine (“NTMS”) at 908 cm^{-1} (lit. value at 915 cm^{-1}).[12]

6. Shore Hardness of Crosslinked Elastomers

Table 1. Shore-A Hardness of various crosslinked elastomers. Mixtures were cured at 110 °C for 72 h in inert atmosphere. Shore Hardness was measured after crosslinking and checked again after 8 weeks to detect aging.

Crosslinker	**PDMS**	**Mixing Ratio (Silirane/ funct. Groups PDMS)**	**Shore-A Hardness**
8	9800 g/mol, Si-OH term.	1.0	16.5
8	9800 g/mol, Si-OH term.	1.1	14.5
8	9800 g/mol, Si-OH term.	1.3	6.2
8	9800 g/mol, Si-OH term.	1.5	1.5
9	9800 g/mol, Si-OH term.	1.0	9.8
9	9800 g/mol, Si-OH term.	1.3	5.1
9	9800 g/mol, Si-OH term.	1.5	0
10	9800 g/mol, Si-OH term.	4.0	4.1
10	36000 g/mol, Si-OH term.	6.0	10.5
10	36000 g/mol, Si-OH term.	9.0	13.5
6	13540 g/mol, Si-CH_2OH term.	1.0	4.1
9	1286 g/mol, Propylamine term.	1.25	27.5
6	9800 g/mol, Si-OH term.	1.0	9.1

Table 2. Shore-A0 Hardness of various crosslinked elastomers. Mixtures were cured at 140 °C for 12 h in inert atmosphere. Shore-A0 hardness was measured after crosslinking. Subsequent swelling tests were conducted in toluene at room temperature.

Crosslinker	**PDMS**	**Mixing Ratio (Silirane/ funct. Groups PDMS)**	**Shore-A0 Hardness**	**Swelling ratio [%]**	**Gel fraktion [%]**
15	**17**, 2400 g/mol, Si-H lateral, term.	0.30	50	729	0.83
15	**17**, 2400 g/mol, Si-H lateral, term.	0.50	55	823	0.85
15	**17**, 2400 g/mol, Si-H lateral, term.	1.00	60	10.54	0.92
15	**18,** 55000 g/mol, Si-H lateral	0.33	2	-	0.42
15	**18,** 55000 g/mol, Si-H lateral	1.00	10	-	0.73
15	**18,** 55000 g/mol, Si-H lateral	5.00	80	1093	0.95

16	**19**, 9800 g/mol, Si-OH term.	0.50	11	1410	0.90
16	**19**, 9800 g/mol, Si-OH term.	1.00	25	690	0.95
16	**19**, 9800 g/mol, Si-OH term.	2.00	33	380	0.96
16	**20**, 36000 g/mol, Si-OH term.	0.50	3	1840	0.91
16	**20**, 36000 g/mol, Si-OH term.	1.00	14	1120	0.95
16	**20**, 36000 g/mol, Si-OH term.	2.00	20	760	97.3

7. References

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