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Hydrothiolation with preservation of the Si-H bond: a new approach for the synthesis of functional organosilicon compounds

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Common information

All the solvents were purified before use as described earlier¹.

Vinyldimethylsilane was synthesized using a known procedure².

Methyldiallylsilane, methyltriallylsilane and triallylsilane were synthesized using a known procedure from dichloromethylsilane, trichloromethylsilane and trichlorosilane respectively³.

Cis-tetra[vinyl(dimethylsiloxy)]tetrasiloxane was synthesized according to the published technique⁴.

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.

¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Bruker AvanceTM 500 spectrometer (Germany) (at 500.13, 125.47, and 99.36 MHz for ¹H, ¹³C, and ²⁹Si, respectively). The ¹H chemical shifts were measured relative to TMS using residual signal of solvent CDCl₃ (7.26 ppm). The ¹³C chemical shifts were measured relative to TMS using signal of solvent CDCl₃ (77.16 ppm). The ²⁹Si 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).

Methods

General procedure for the synthesis of thiol derivatives of silanes and siloxanes through thiol-ene «click» reaction

All synthetic operations were carried out under argon atmosphere. A round-bottom single-neck flask was charged with silane (or siloxane), thiol and solvent (THF or pentane). The mixture was irradiated by UV lamp (365 nm) for 4 hours under stirring at room temperature. After irradiation, the obtained solution was evaporated under 1 Torr till the constant weight.

Methods of synthesis for compounds 1-7

Synthesis of dimethyl(vinyl)silane²

To a suspension of 2,54 g (0,052 mol) of LiAlH₄ in 150 ml of diglyme, 32 g (0,21 mol) of Me₂VinSiCl, in 20 ml of diglyme was added dropwise on stirring at 0°C. After stirring for 4 h at the mixture was added saturated NH₄Cl aqueous solution. After routine treatment and drying over Na₂SO₄, Me₂VinSiH was isolated by distillation. Yield 15.02 g (83%).¹H NMR (CDCl₃, δ , ppm, J/Hz): 0.18 (d, J = 3.6 Hz, 5H), 4.12 – 4.06 (m, 1H), 5.79 (dd, J = 20.1, 3.9 Hz, 1H), 6.02 (dd, J = 14.5, 3.8 Hz, 1H), 6.19 (ddd, J = 20.0, 14.6, 1.9 Hz, 1H).

Synthesis of 2-((2-(dimethylsilyl)ethyl)thio)acetic acid (compound 1)

A mixture of dimethyl(vinyl)silane (0.1 g, 1.16 mmol) and mercaptoacetic acid (0.11 g, 1.2 mmol) in dry THF (4 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 (0.201 g) was 97%.



A mixture of dimethyl(vinyl)silane (0.1 g, 1.15 mmol), mercaptoacetic acid (0.11 g, 1.2 mmol) and AIBN (3 mg) in dry THF (1 ml) was stirred for three hours at 85C°. After that, mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.201 g) was 98%. ¹H NMR ((CD₃)₂CO, δ , ppm, J/Hz): 0.13 (d, J = 3.6 Hz, 6H), 1.02 – 0.97 (m, 2H), 2.77 – 2.74 (t, J = 8.6 Hz, 2H), 3.27 (s, 2H), 3.93 – 3.88 (m, 1H). ¹³C NMR ((CD₃)₂CO, δ , ppm): 170.96, 32.66, 28.01, 13.97, -5.41. ²⁹Si NMR ((CD₃)₂CO, δ , ppm): -13.39.

IR: 2957, 2116, 2709, 1422, 1297, 1251, 885 cm⁻¹.

HRMS (ESI) m/z $[M + Na]^+$ calcd for $[C_6H_{14}O_2SSi + Na]^+$ 201.0376, found 201.0396.

Synthesis of 2-((2-(dimethylsilyl)ethyl)thio)succinic acid (compound 2)

A mixture of dimethyl(vinyl)silane (0.1 g, 1.2 mmol) and mercaptosuccinic acid (0.17 g, 1.13 mmol) in dry THF (4 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 target product (0.256 g) was obtained in 96% yield.



Or

A mixture of dimethyl(vinyl)silane (0.1 g, 1.2 mmol), mercaptosuccinic acid (0.17 g, 1.12 mmol) and AIBN (3 mg) in dry THF (1 ml) was stirred for three hours at 85C°. After that mixture was evaporated under 1 Torr till the constant weight and the target product (0.258 g) was obtained in 97% yield. ¹H NMR ((CD₃)₂CO, δ , ppm, J/Hz): 0.11-0.17 (d, 6H, J = 2.8 Hz); 0.91-1.08 (m, 2H); 2.63-2.70 (m, 1H); 2.78-2.88 (m, 2H); 2.91-2.99 (m, 1H); 3.63-3.70 (m, 1H); 3.89-3.94 (septet, 1H, J = 2.8 Hz).

¹³C NMR ((CD₃)₂CO, δ, ppm): 172.32, 171.40, 41.17, 35.96, 27.19, 14.08, -5.41.

²⁹Si NMR ((CD₃)₂CO, δ, ppm): -13.31.

IR: 2957, 2114, 1691, 1416, 1308, 1291, 1251, 885 cm⁻¹.

HRMS (ESI) m/z [M + Na]⁺ calcd for $[C_8H_{16}O_4SSi + Na]^+ 259.0431$, found 259.0432; [M + Na]⁺ calcd for $[C_8H_{15}NaO_4SSi + Na]^+ 281.0250$, found 281.0249; [M + K]⁺ calcd for $[C_8H_{15}NaO_4SSi + K]^+ 296.9990$, found 296.9985.

Synthesis of (2-(decylthio)ethyl)dimethylsilane (compound 3)

A mixture of dimethyl(vinyl)silane (0.1 g, 1.16 mmol) and decane-1-thiol (0.21 g, 1.2 mmol) in dry pentane (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 and the target product (0.287 g) was obtained in 95% yield.



Or

A mixture of dimethyl(vinyl)silane (0.1 g, 1.15 mmol), decane-1-thiol (0.21 g, 1.2 mmol) and AIBN (3 mg) in dry pentane (1 ml) was stirred for three hours at 85C°. After that, mixture was evaporated under 1 Torr till the constant weight and the target product (0.287 g) was obtained in 96% yield.

¹H NMR (CDCl₃, δ, ppm, J/Hz): 0.08-0.18 (d, 6H, J = 2.8 Hz); 0.85-0.93 (m, 3H); 0.94-1.02 (m, 2H); 1.25-1.42 (m, 14H); 1.52-1.66 (m, 2H); 2.58 (m, 2H); 2.58-2.65 (m, 2H); 3.86-3.95 (septet, 1H, J = 2.8 Hz).

¹³C NMR (CDCl₃, δ, ppm): -4.52; 14.12; 14.97; 22.69; 27.90; 29.01; 29.28; 29.33; 29.56; 29.58; 29.62; 31.91; 31.96.

²⁹Si NMR (CDCl₃, δ, ppm): -13.58.

IR: 2955, 2924, 2853, 2115, 1466, 1249, 905, 886, 836 cm⁻¹.

Synthesis of (2-((4-chlorophenyl)thio)ethyl)dimethylsilane (compound 4)



A mixture of dimethyl(vinyl)silane (0.06 g, 0.71 mmol) and 4-chlorobenzenethiol (0.1 g, 0.69 mmol) in dry pentane (2.2 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 target product (0.153 g) was obtained in 96% yield.

Or

A mixture of dimethyl(vinyl)silane (0.06 g, 0.71 mmol), 4-chlorobenzenethiol (0.1 g, 0.68 mmol) and AIBN (3 mg) in dry pentane (1 ml) was stirred for three hours at 85C°. After that, mixture was evaporated under 1 Torr till the constant weight and the target product (0.153 g) was obtained in 97% yield.

¹H NMR (CDCl₃, δ, ppm, J/Hz): 0.13-0.16 (d, 6H, J = 2.4 Hz); 0.99-1.05 (m, 2H); 2.97-3.01 (m, 2H); 3.91-3.97 (septet, 1H, J = 2.8 Hz); 7.22-7.34 (m, 4H).

¹³C NMR (CDCl₃, δ, ppm): 135.48, 131.75, 130.47, 128.97, 30.20, 14.44, -4.53.

²⁹Si NMR (CDCl₃, δ, ppm): -13.41.

IR: 2956, 2916, 2116, 1475, 1421, 1389, 1252, 1096, 1011, 905, 884, 836, 813 cm⁻¹.

Synthesis of dimethyl(2-(phenylthio)ethyl)silane (compound 5)



A mixture of dimethyl(vinyl)silane (0.1 g, 1.16 mmol) and benzenethiol (0.13 g, 1.2 mmol) in dry pentane (4 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 target product (0.221 g) was obtained in 97% yield.

Or

A mixture of dimethyl(vinyl)silane (0.1 g, 1.15 mmol), benzenethiol (0.13 g, 1.2 mmol) and AIBN (3 mg) in dry pentane (1 ml) was stirred for three hours at 85C°. After that, mixture was evaporated under 1 Torr till the constant weight and the target product (0.221 g) was obtained in 98% yield.

¹H NMR (CDCl₃, δ, ppm, J/Hz): 0.11-0.19 (d, 6H, J = 2.4 Hz); 1.01-1.07 (m, 2H); 2.99-3.05 (m, 2H); 3.90-3.98 (septet, 1H, J = 2.4 Hz); 7.16-7.40 (m, 5H).

¹³C NMR (CDCl₃, δ, ppm): 136.47, 129.25, 129.00, 126.04, 28.39, 14.16, 0.56.
²⁹Si NMR (CDCl₃, δ, ppm): -13,41.
IR: 3074, 3059, 2959, 2923, 2136, 1584, 1480, 1438, 1277, 1253, 1112, 1066, 904, 836, 771, 736, 689 cm⁻¹.

Synthesis of 2-(dimethylsilyl)ethylethanethioate (compound 6)

A mixture of dimethyl(vinyl)silane (0.11 g, 1.28 mmol) and thioacetic acid (0.1 g, 1.3 mmol) in dry THF (3.3 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 target product (0.204 g) was obtained in 98% yield.



Or

A mixture of dimethyl(vinyl)silane (0.11 g, 1.27 mmol), thioacetic acid (0.1 g, 1.3 mmol) and AIBN (3 mg) in dry THF (1 ml) was stirred for three hours at 85C°. After that, mixture was evaporated under 1 Torr till the constant weight and the target product (0.203 g) was obtained in 98% yield. ¹H NMR (C₆D₆, δ , ppm, J/Hz): -0.11-(-0.05) (d, 6H, J = 2.8 Hz); 0.78-0.85 (m, 2H); 1.85-1.91 (s, 3H); 2.83-2.89 (m, 2H); 3.94-4.01 (septet, 1H, J = 2.8 Hz).

¹³C NMR (C₆D₆, δ, ppm): 194.09, 29.84, 25.34, 15.12, -5.10.

²⁹Si NMR (C₆D₆, δ, ppm): -14.06.

IR: 2959, 2925, 2899, 2117, 1691, 1253, 1135, 1109, 902, 887 cm⁻¹.

HRMS (ESI) $m/z [M + H]^+$ calcd for $[C_6H_{14}OSSi + H]^+$ 163.0607, found 163.0427; $[M - H]^-$ calcd for $[C_6H_{14}OSSi - H]^-$ 161.0451, found 161.0452.

Synthesis of 2-(3-(trimethoxysilyl)-propylthio)-ethyl-dimethylsilane (compound 7)

A mixture of dimethyl(vinyl)silane (0.05 g, 0.6 mmol) and 3-(trimethoxysilyl)propane-1-thiol (0.11 g,

0.56 mmol) in dry THF (4 ml) was irradiated by UV lamp for 4 hours under stirring at room temperature.

H Si S Si(OMe)₃

After that, irradiated mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.153 g) was 97%.

Or

A mixture of dimethyl(vinyl)silane (0.05 g, 0.6 mmol), 3-(trimethoxysilyl)propane-1-thiol (0.11 g, 0.55 mmol) and AIBN (3 mg) in dry THF (1 ml) was stirred for three hours at 85C°. After that, mixture was evaporated under 1 Torr till the constant weight and the yield of the target product (0.149 g) was 96%.

¹H NMR (C_6D_6 , δ , ppm, J/Hz): -0.06-(-0.02) (d, 6H, J = 3.2 Hz); 0.74-0.81 (m, 2H); 0.84-0.91 (m, 2H); 1.76-1.84 (m, 2H); 2.43-2.51 (m, 4H); 3.40-3.43 (s, 9H); 4.00-4.05 (septet, 1H, J = 2.8 Hz).

¹³C NMR (C₆D₆, δ, ppm): 49.96, 34.72, 27.49, 23.07, 14.77, 8.76,

²⁹Si NMR (C₆D₆, δ, ppm): -13.83, -42.75.

IR: 2942, 2911, 2705, 2113, 1250, 1190, 1088, 904, 886, 814, 762 cm⁻¹.

HRMS (ESI) m/z $[M + Na]^+$ calcd for $[C_{10}H_{26}O_3SSi_2 + Na]^+$ 305.1033, found 305.1028.

Methods of synthesis for compounds 8-9

Synthesis of allylsilanes³

To 53.5 g (2.20 mol) of magnesium, and 30 mL of dry THF, a solution of 115.0 g (1.00 mol) of methyldichlorosilane and 168.4 g (2.20 mol) of allyl chloride in 700 mL of dry THF was added dropwise so that a modest reflux took place. After 20 h of refluxing, the reaction mixture was cooled to ambient temperature, and about 500 mL of water was added carefully to dissolve the residue. The organic layer was separated, dried by Na2SO4, and distilled. Yield: 77.1 g (61%) of a colorless liquid. Purity: 99% gas chromatography (GC). Triallylsilane was prepared analogously.

Synthesis of tris(3-(phenylthio)propyl)silane (compound 8)

A mixture of benzenethiol (0.23 g, 2.1 mmol) and triallylsilane (0.1 g, 0,66 mmol) in dry pentane (16 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 (0.306 g) was 96%.

¹H NMR (CDCl₃, δ, ppm, J/Hz): 0.71-0.77 (m, 6H); 1.62-1.70 (m, 6H); 2.89-2.94 (t, 6H, J = 4.8 Hz); 3.70-3.75 (m, 1H); 7.14-7.38 (m, 15H).

¹³C NMR (CDCl₃, δ, ppm): 136.64, 129.10, 128.94, 125.86, 36.83, 24.39, 10.59.

²⁹Si NMR (CDCl₃, δ, ppm): -7.41.

IR: 3070, 2919, 2089, 1582, 1477, 1436, 1244, 1091, 965, 843, 764, 724, 689 cm⁻¹.

HRMS (ESI) m/z [M-H]⁻ calcd for [C₂₇H₃₄S₃Si-H]⁻ 481.1508, found 481.1502; [M+Na]⁺ calcd for [C₂₇H₃₄S₃Si+Na]⁺ 505.1484, found 505.1478.

Synthesis of methylbis(3-(phenylthio)propyl)silane (compound 9)

A mixture of benzenethiol (0.19 g, 1.68 mmol) and diallyl(methyl)silane (0.10 g, 0.79 mmol) in dry pentane (10 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 (0.263 g) was 96%.

¹H NMR (CDCl₃, δ, ppm, J/Hz): 0.00-0.04 (δ, 3H, J = 3.6 Hz); 0.66-0.78 (m, 4H); 1.60-1.70 (m, 4H); 2.87-2.93 (t, 4H, J = 7.2 Hz); 3.73-3.79 (m, 1H); 7.19-7.35 (m, 10H).

¹³C NMR (CDCl₃, δ, ppm): 136.75, 129.06, 128.91, 125.81, 36.84, 24.37, 12.18, -6.32.

²⁹Si NMR (CDCl₃, δ, ppm): -10.25.

IR: 3073, 3057, 2949, 2921, 2879, 2106, 1583, 1478, 1438, 1250, 878, 850, 738, 691 cm⁻¹.

HRMS (ESI) m/z [M - H]⁻ calcd for $[C_{19}H_{26}S_2S_1 - H]^-$ 345.1161, found 345.1154.

Methods of synthesis for compounds 10-13

Synthesis of cis-tetra[vinyl(dimethylsiloxy)]tetrasiloxane (compound 10)⁴

Potassium cis-tetravinylcyclotetrasiloxanolate (0.01 mol) was slowly added to solution of chlorodimethylsilane (0.06 mol) and pyridine (0.06 mol) in toluene (50 mL). The mixture was stirred at room temperature for 6 h. The solid precipitate was filtered off and filtrate was washed with water. The organic layer was separated and dried (Na_2SO_4). The solvent was evaporated in vacuo to give a compound **11** as colourless oil.

Synthesis of thiol-containing polysiloxane (compound 11)

Synthesis of thiol-containing polysiloxane was described in our previous work.³ A mixture of 3-mercaptopropyltrimethoxysilane (50 g,0.254 mol), acetic acid (178.33 g, 2.972 mol), hexamethyldisiloxane (23 g, 0.142 mol) and acetyl chloride (0.5 g, 0.0064 mol) was stirred at refluxed for 24 h. Then toluene (200 mL) was added to the re- action mixture. After the washing by water the solution was dried by Na2SO4 and a solvent was removed by rotor evaporator. After drying in vacuo the product in 98% yield was obtained. 1H NMR (400 MHz, CDCl₃, δ, ppm): 0.17-0.07 (m, 9 H, Si-CH3), 0.80-0.53 (m, 2.0 H, Si-CH2-CH2-CH2-SH), 1.39-1.26 (m, 1.0 H, Si-CH2-CH2-CH2-SH), 1.78-1.58 (m, 2 H, Si-CH2-CH2-SH), 2.61-2.47 (m, 2 H, Si-CH2-CH2-SH). GPC data: Mn = 780, Mw = 840, PDI = 1.08.

Synthesis of monolith material (12)

Compounds 11 (1.15 g, 1.97 mmol) and 12 (1.77 g, 7.88 mmol) were mixed in teflon support. The mixture was irradiated with UV (365 nm) for 5 min at room temperature. Product – rigid transparence monolith.

IR: 840, 902, 1049, 1101, 1252, 2137, 2855, 2925, 2158 cm⁻¹.

Synthesis of aerogel (13)

Synthesis of aerogel was described in our previous work.³ The general process of aerogel preparation involves five consecutive steps. In the first step, all the components including vinyl-precursor 11, thiol-precursor 12, AIBN (5 mg) and dry pentane as a co-solvent were charged in a high-pressure steel reactor (20 mL). Then at room temperature the reactor was filled with CO2 up to a pressure of 250 atm using a CO₂ pump (SCF-24, Scientific systems Inc., USA). After this, the reaction mixture was dispergated in an ultrasonic bath at 40 C for 10 min. The latter procedure is required for solubilization of all components in scCO₂. In the next step, the reactor was placed in an air oven and maintained at 85 °C for 1 h. It should be noted that under these conditions the pressure in the reactor increases to 750 atm. Then the reactor was cooled to 40 °C and CO₂ was carefully removed. In the last step, the reactor was opened and aerogel was taken out. Density of aerogel was 0.26 g/ml.

IR: 755, 841, 907, 1059, 1116, 1180, 1257. 1340, 1418, 1451, 1698, 2141, 2858, 2928, 2961 cm⁻¹.

X-ray crystal structure determination

Crystals (C₂₇H₃₄S₃Si, M = 482.81) are hexagonal, space group $P6_3$ /m, at 120(2) K a = 14.6919(5), c = 6.9649(3) Å, V = 1301.97(10) Å³, Z = 2, $d_{calc.} = 1.232$ g/cm³, $\mu = 3.44$ cm⁻¹. Single-crystal X-ray diffraction experiment was carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated MoK α radiation, $\lambda = 0.71073$ Å, ω -scan technique, T = 120(2) K); 1364 independent reflections ($R_{int} = 0.0230$) with $2\theta_{max} = 60.0^{\circ}$ were collected and used in refinement. The structure was solved by direct methods and refined in SHELXL⁵ by the full-matrix least-squares technique against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and included in the structure factors calculation in the riding motion approximation. The refinement converged to $wR_2 = 0.0843$ and GOF = 1.045 for all independent reflections ($R_1 = 0.0324$ was calculated against F for 1332 observed reflections with I > 2 σ (I)). CCDC 2047237 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre http://www.ccdc.cam.ac.uk.



Figure S1. ¹H NMR spectrum of compound 1 (400 MHz, solvent – $(CD_3)_2CO$).





Figure S3. ²⁹Si NMR spectrum of compound 1 (80 MHz, solvent – $(CD_3)_2CO$).



Figure S4. IR-spectrum of compound 1.



Figure S5. HRMS (ESI) for compound 1.



Figure S6. ¹H NMR spectrum of compound **2** (400 MHz, solvent – $(CD_3)_2CO$).



Figure S7. ¹³C NMR spectrum of compound **2** (DEPT-135, 100 MHz, solvent – $(CD_3)_2CO$).





Figure S9. IR-spectrum of compound 2.



Figure S10. HRMS (ESI) for compound 2.



Figure S11. ¹H NMR spectrum of compound **3** (400 MHz, solvent – $CDCl_3$).



Figure S12. ¹³C NMR spectrum of compound **3** (DEPT-135, 100 MHz, solvent – $CDCl_3$).



Figure S13. ²⁹Si NMR spectrum of compound **3** (80 MHz, solvent – $CDCl_3$).



Figure S14. IR-spectrum of compound 3.



Figure S15. ¹H NMR spectrum of compound **4** (400 MHz, solvent – $CDCl_3$).



Figure S16. ¹³C NMR spectrum of compound 4 (100 MHz, solvent – $CDCl_3$).



Figure S17. ²⁹Si NMR spectrum of compound 4 (80 MHz, solvent – $CDCl_3$).



Figure S18. IR-spectrum of compound 4.



Figure S19. ¹H NMR spectrum of compound **5** (400 MHz, solvent – $CDCl_3$).



Figure S20. ¹³C NMR spectrum of compound **5** (100 MHz, solvent – $CDCl_3$).





Figure S22. IR-spectrum of compound 5.



Figure S23. ¹H NMR spectrum of compound **6** (400 MHz, solvent – C_6D_6).



Figure S24. ¹³C NMR spectrum of compound **6** (100 MHz, solvent – C_6D_6).



Figure S25. ²⁹Si NMR spectrum of compound **6** (80 MHz, solvent – C_6D_6).



Figure S26. IR-spectrum of compound 6.



Figure S27. HRMS (ESI) for compound 6.



Figure S28. ¹H NMR spectrum of compound 7 (400 MHz, solvent – C_6D_6).



Figure S29. ¹³C NMR spectrum of compound 7 (DEPT-135, 100 MHz, solvent – C_6D_6).



Figure S30. ²⁹Si NMR spectrum of compound 7 (80 MHz, solvent – C_6D_6).



Figure S31. IR-spectrum of compound 7.



Figure S32. HRMS (ESI) for compound 7.



Figure S33. ¹H NMR spectrum of compound **8** (400 MHz, solvent – $CDCl_3$).



Figure S34. ¹³C NMR spectrum of compound **8** (100 MHz, solvent – $CDCl_3$).





Figure S36. IR-spectrum of compound 8.



Figure S37. HRMS (ESI) for compound 8.



Figure S38. ¹H NMR spectrum of compound **9** (400 MHz, solvent – $CDCl_3$).



Figure S39. ¹³C NMR spectrum of compound **9** (100 MHz, solvent – $CDCl_3$).



Figure S40. ²⁹Si NMR spectrum of compound **9** (80 MHz, solvent – $CDCl_3$).



Figure S41. IR-spectrum of compound 9.



Figure S42. HRMS (ESI) for compound 9.



Figure S43. IR-spectrum of compound 12.



Figure S44. IR-spectrum of compound 13.

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