Thiol−Ene Reaction for the Synthesis of Multifunctional Branched Organosilanes

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Summary: Various commercially available thiols react photochemically with tetravinylsilane to give the corresponding tetrasubstituted thioether compounds. The reactions are conducted in air using typical borosilicate glassware. Yields range from 64 to 100%, and purification steps, if necessary, involve simple precipitation or extraction steps. Thiol addition occurs predominantly to give the anti-Markovnikov product; amounts of Markovnikov addition range from 1 to 5%.

Introduction

Organosilicon dendrimer chemistry has matured rapidly over the past 15 years.[1−3] The most common dendrimers of this type are the carbosilane dendrimers, which are generally prepared via a divergent synthesis consisting of alternating hydrosilylation and Grignard reaction steps. On the basis of our longstanding interest in organosilicon dendrimers,[1,4] we are actively searching for new preparative methods to these materials. We have recently become interested in the thiol−ene reaction (also known as hydrothiolation),[5,6] which is the sulfur version of the hydrosilylation reaction. The thiol−ene reaction has recently seen widespread use for the formation of various polymeric organic materials.[6−8] Among the beneficial features of the thiol−ene reaction are its easy initiation (by heat, light, AIBN, amine catalysis), high yields (often quantitative), high regioselectivity, lack of sensitivity to water and oxygen, and tolerance to a wide variety of solvents and functional groups. Another attractive aspect is the commercial availability of a wide variety of (multi)functionalized thiols that undergo the thiol−ene reaction with various substrates, including vinylsilanes.[9−18] We believe the combined advantages of the thiol−ene reaction make it ideal for the synthesis of new carbosilane−thioether dendrimers.[19]

In this paper, we demonstrate the utility of the thiol−ene reaction by describing the synthesis of a series of multifunctional organosilicon thioethers from tetravinylsilane. The reactions proceed in high yield under photochemical irradiation. In addition to serving as cores for divergent dendrimer growth, these compounds may also be viewed as potential multipodal chelators[20−29] or stabilizers of transition-metal nanoparticles.[30−33]

Results and Discussion

In all cases, the syntheses of the title compounds followed the same general procedure (equation 1). The thiol and tetravi-

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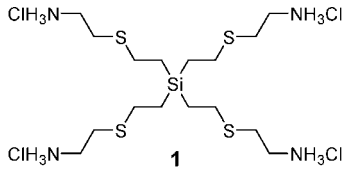
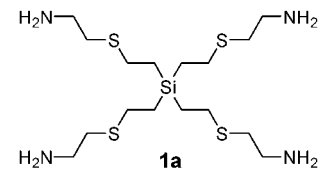
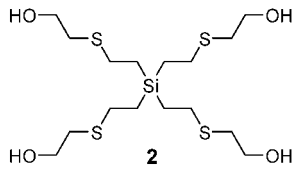
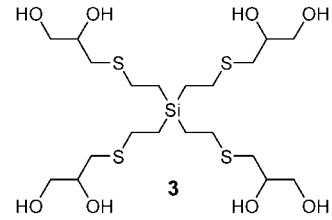
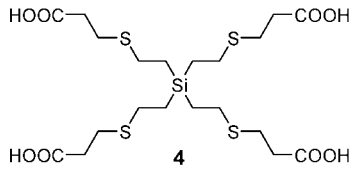
Chart 1

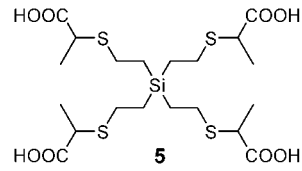


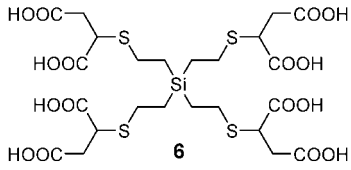


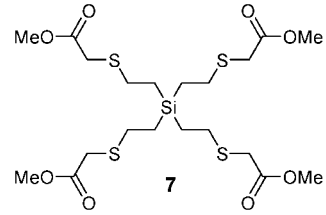


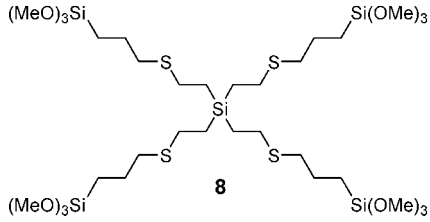


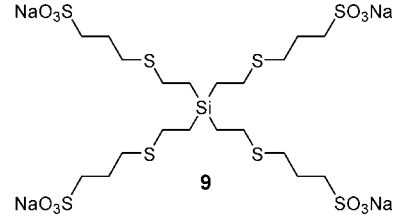


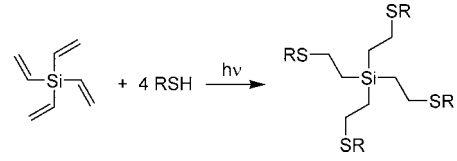












(1)

nylsilane were dissolved in a suitable solvent (typically methanol). In certain cases, it was necessary to add 1 mol % of benzophenone (based on the total moles of reactants) as a photoinitiator. Irradiation was provided by a General Electric 275W sunlamp, a broadband source with a maximum emittance at 365 nm.[34] It should be noted that ordinary borosilicate glassware was used, and no special efforts were made to degas the reaction mixture or exclude atmospheric oxygen during the reaction. In all cases, the reaction was complete in 2−4 h, noted by the complete disappearance of vinyl proton resonances in the ^{1}H NMR spectra. It is noteworthy that, save for the synthesis of **9**, an exact stoichiometric amount of thiol was sufficient to drive the reaction to completion.

Structures of the products prepared are shown in Chart 1, and yields are reported in Table 1. In general, yields were excellent, and the products required little if any purification. In some cases, simple purification steps were performed to remove minor traces of impurity. For example, compound **1** was isolated by simple precipitation into 2-propanol. Carboxyl-terminated compounds **4**−**6** were obtained by extraction into aqueous NaOH and then into ethyl acetate after reacidification. Sulfonate **9** was isolated in pure form by precipitation techniques. Some loss of product occurred during these steps which accounts for the moderately lower yields.

As mentioned above, in certain cases benzophenone was added to the reaction mixture as a photoinitiator. Products freed of the small amounts of added benzophenone were easy to obtain. In some cases (compounds **3** and **7**), the syntheses could be completed without adding benzophenone by simply extending the reaction time to eight hours. For compounds **5** and **6**, the organic extractions of the carboxylate salt solutions effectively removed the benzophenone. Finally, the precipitations used to isolate **1** and **9** also completely removed the benzophenone.

Like hydrosilylation, thiol−ene reactions with alkenes can give either of two possible products corresponding to Markovnikov (α-product) or anti-Markovnikov (β-product) addition

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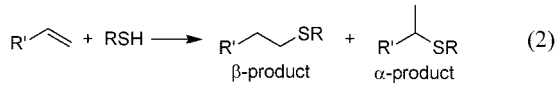
Table 1. Yields and Characterization Data for 1−9

compd	yield (%)	% α-isomer	soluble in[a]
1	74	4.0	H_2O, MeOH
1a[b]	81		H_2O, MeOH, *i*-PrOH, hot CH_2Cl_2
2	95	1.0	H_2O, MeOH, *i*-PrOH, CH_2Cl_2
3	96	1.5	hot H_2O, MeOH, hot *i*-PrOH
4	92	4.3	hot H_2O, MeOH, *i*-PrOH, hot toluene (partially)
5	76	*c*	H_2O (moderately), MeOH, *i*-PrOH, Et_2O, CH_2Cl_2, hot toluene (moderately)
6	68	1.4	hot H_2O (moderately), MeOH, *i*-PrOH, Et_2O
7	100	5.2	MeOH, hot *i*-PrOH, Et_2O, CH_2Cl_2, toluene
8	100	1.5	hot MeOH, *i*-PrOH, Et_2O, hot hexanes, CH_2Cl_2, toluene
9	66	2.7	H_2O (moderately)

[a] Solvents tested were water, methanol, 2-propanol, diethyl ether, hexanes, dichloromethane, and toluene; 40 mg of compound were added to 1 mL of solvent. [b] Obtained by treating **1** with aq KOH. [c] NMR signals of α-isomer were obscured by product signals.

(eq 2). The presence of α-products is indicated in the ^{1}H NMR spectrum by the presence of a doublet around δ 1.2−1.3 ppm. The corresponding quartet is often difficult to locate, as it is usually buried under the signals of other protons in the products. Thiol−ene addition to give *β*-products normally predominates, as was observed in this case. Percentages of α-products were determined by ^{1}H NMR spectroscopy and are given in Table 1. The low percentages of α-addition indicate the majority of the product molecules appear as shown in Chart 1. The highest observed α-product percentage was in compound **7**, with the value of 5.2% indicating that on average only one out of every five molecules possesses one α-addition arm. Although these products are present in small amounts, it is important to understand that they would not lead to *defects* as commonly understood by dendrimer chemists. Defects are unreacted branches in dendrimer structures which lead to incomplete wedges. The presence of α-addition products do not represent defects and will likely have little to no effect on any subsequent growth or dendrimer properties.



(2)

In conclusion, we have demonstrated the facile synthesis of a variety of functionalized organosilicon−thioether compounds. The tremendous versatility and robustness of thiol−ene chemistry make this an attractive approach. We are currently exploring the application of these compounds as cores for carbosilane−thioether dendrimers.

Experimental Section

Materials and Equipment. All thiols, benzophenone, and solvents were purchased from commercial sources and used as received. Tetravinylsilane was prepared from the reaction of vinylmagnesium bromide and tetrachlorosilane in THF.[35] UV radiation was provided by a General Electric (GE) 275W sunlamp bulb. NMR data were obtained on a JEOL ECA-500 NMR spectrometer. Elemental analyses were obtained using a CE Elantech Thermo-Finnigan Flash 1112 elemental analyzer. ESI mass spectrometry was provided by the Washington University Mass Spectrometry Resource with support from the NIH National Center for Research Resources (Grant No. P41RR0954).

General Synthetic Procedure. All reactions were conducted in the presence of air. Tetravinylsilane and the appropriate thiol were added to methanol (5 mL) in a 10-mL round-bottomed flask equipped with a stir bar and condenser. The flask was irradiated for 2−4 h and the reaction monitored by ^{1}H NMR spectroscopy. When the reaction was complete, the reaction mixture was concentrated via rotary evaporation and the product purified as needed.

Synthesis of 1 and 1a. Compound **1** was prepared using the general procedure from tetravinylsilane (305 mg, 2.24 mmol), 2-mercaptoethylamine hydrochloride (1.02 g, 8.96 mmol), and benzophenone (20.4 mg, 0.112 mmol). When the reaction was complete, the mixture was concentrated and poured into 2-propanol to precipitate the product. After filtration, compound **1** was collected as a hygroscopic white powder (981 mg, 74%). No melting point was observed on heating to 275 °C. ^{1}H NMR (500 MHz, D_2O): δ 1.01 (t, ^3J = 8.9 Hz, $-SiCH_2CH_2$, 8H), 2.66 (t, ^3J = 8.6 Hz, $-SiCH_2CH_2$, 8H), 2.83 (t, ^3J = 6.6 Hz, $-SCH_2CH_2NH_3Cl$, 8H), 3.16 (t, ^3J = 6.9 Hz, $-SCH_2CH_2NH_3Cl$, 8H). ^{13}C NMR (125 MHz, D_2O): δ 12.2 ($-SiCH_2CH_2$), 26.3 ($-SiCH_2CH_2$), 28.1 ($-SCH_2CH_2NH_3Cl$), 38.5 ($-SCH_2CH_2NH_2$). ^{29}Si NMR (99 MHz, D_2O): δ 3.03. Anal. Calcd for $C_{16}H_{44}Cl_4N_4S_4Si$: C, 32.53; H, 7.51. Found: C, 32.24; H, 7.61. LRESI: 223.2 $[M - 4HCl + 2H]^{2+}$. Compound **1** (1.32 g, 2.24 mmol) was dissolved in 50% aqueous KOH solution (5 mL). After saturation with $NaCl_{(s)}$, the solution was extracted with dichloromethane (2 × 30 mL). The organic layer was washed once with deionized H_2O and once with saturated $NaCl_{(aq)}$. Drying the organic layer over anhydrous Na_2SO_4 and concentration afforded **1a** as a viscous yellow liquid (818 mg, 81%). ^{1}H NMR (500 MHz, D_2O): δ 1.03 (t, ^3J = 8.9 Hz, $-SiCH_2CH_2$, 8H), 2.61−2.65 (m, $-SiCH_2CH_2$, $-SCH_2CH_2$, 16H), 2.75 (t, ^3J = 6.6 Hz, $-SCH_2CH_2NH_2$, 8H). ^{13}C NMR (125 MHz, D_2O): δ 13.1 ($-SiCH_2CH_2$), 26.7 ($-SiCH_2CH_2$), 34.5 ($-SCH_2CH_2NH_2$), 40.2 ($-SCH_2CH_2NH_2$). ^{29}Si NMR (99 MHz, D_2O): δ 2.96. Anal. Calcd for $C_{16}H_{40}N_4S_4Si$: C, 43.20; H, 9.06. Found: C, 42.84; H, 9.08. LRESI data was not obtained because **1a** slowly hardens/cross-links on standing.

Synthesis of 2. Compound **2** was prepared using the general procedure from tetravinylsilane (309 mg, 2.27 mmol) and 2-mercaptoethanol (0.64 mL, 9.08 mmol). After removal of solvents in vacuo, compound **2** was obtained as a pale yellow oil (971 mg, 95%). ^{1}H NMR (500 MHz, D_2O): δ 1.00 (t, ^3J = 8.6 Hz, $-SiCH_2CH_2$, 8H), 2.60 (t, ^3J = 8.3 Hz, $-SiCH_2CH_2$, 8H), 2.72 (t, ^3J = 5.7 Hz, $-SCH_2CH_2OH$, 8H), 3.73 (t, ^3J = 5.7 Hz, $-SCH_2CH_2OH$, 8H). ^{13}C NMR (125 MHz, D_2O): δ 13.2 ($-SiCH_2CH_2$), 27.1 ($-SiCH_2CH_2$), 35.1 ($-SCH_2CH_2OH$), 60.9 ($-SCH_2CH_2OH$).^{29}Si NMR (99 MHz, D_2O): δ 2.99. Anal. Calcd for $C_{16}H_{36}O_4S_4Si$: C, 42.83; H, 8.09. Found: C, 43.22; H, 8.04. LRESI: 449.1 $[M + H]^+$, 466.1 $[M + NH_4]^+$, 471.2 $[M + Na]^+$, 431.2 $[M - H_2O]^+$.

Synthesis of 3. Compound **3** was prepared using the general procedure from tetravinylsilane (256 mg, 1.88 mmol), 1-thioglycerol (0.65 mL, 7.52 mmol), and benzophenone (17.1 mg, 0.094 mmol). The reaction solution was washed with hexanes and concentrated. Removal of solvents in vacuo at 80 °C afforded **3** as a viscous pale yellow oil (1.03 g, 96%). Compound **3** can also be prepared without benzophenone after 8 h of irradiation. ^{1}H NMR (500 MHz,

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D_2O): δ 0.97 (t, ^3J = 8.6 Hz, $-SiCH_2CH_2$, 8H), 2.59−2.68 (m, $-CH_2SCH_2$, 16H), 3.45−3.58 (m, $-CH_2OH$, 8H), 3.72−3.74 (m, $-CHOH$, 4H). ^{13}C NMR (125 MHz, D_2O): δ 12.7 ($-SiCH_2CH_2$), 27.5 ($-SiCH_2CH_2$), 34.3 ($-SCH_2CH$), 64.5 ($-CH_2OH$), 70.9 ($-CHOH$). ^{29}Si NMR (99 MHz, D_2O): δ 2.85. Anal. Calcd for $C_{20}H_{44}O_8S_4Si$: C, 42.22; H, 7.80. Found: C, 42.34; H, 7.69. LRESI: 569.2 $[M + H]^+$, 586.2 $[M + NH_4]^+$, 591.3 $[M + Na]^+$.

Synthesis of 4. Compound **4** was prepared using the general procedure from tetravinylsilane (243 mg, 1.78 mmol) and 3-mercaptopropionic acid (0.62 mL, 7.12 mmol). After concentration, the crude product was dissolved in 1 M aqueous NaOH solution (20 mL) and the resulting solution extracted with ether (2 × 20 mL). The aqueous phase was then acidified to pH 1 with 1 M aqueous HCl solution. The resulting cloudy solution was extracted with ethyl acetate (3 × 30 mL). The organic layer was washed with deionized water (2 × 10 mL) and saturated $NaCl_{(aq)}$, dried over Na_2SO_4, and concentrated to afford **4** as a hygroscopic white powder (916 mg, 92%). Mp: 105−108 °C. ^1H NMR (500 MHz, acetone-d_6): δ 1.05 (t, ^3J = 8.3 Hz, $-SiCH_2CH_2$, 8H), 2.56 (t, ^3J = 7.3 Hz, $-SCH_2CH_2CO_2H$, 8H), 2.67 (t, ^3J = 8.8 Hz, $-SiCH_2CH_2$, 8H), 2.74 ($-SCH_2CH_2CO_2H$). ^{13}C NMR (125 MHz, acetone-d_6): δ 12.8 ($-SiCH_2CH_2$), 26.4 ($-SiCH_2CH_2$), 26.7 ($-SCH_2CH_2CO_2H$), 34.3 ($-SCH_2CH_2CO_2H$), 172 ($-COOH$). ^{29}Si NMR (99 MHz, acetone-d_6): δ 3.83. Anal. Calcd for $C_{20}H_{36}O_8S_4Si$: C, 42.83; H, 6.47. Found: C, 42.48; H, 6.53. LRESI: 561.2 $[M + H]^+$, 578.3 $[M + NH_4]^+$, 583.3 $[M + Na]^+$.

Synthesis of 5. Compound **5** was prepared using the general procedure from tetravinylsilane (243 mg, 1.78 mmol), thiolactic acid (0.63 mL, 7.12 mmol), and benzophenone (16.2 mg, 0.089 mmol). Compound **5** was purified using the same procedure described for **4**, except the alkaline solution was extracted a total of three times with ether. The product was obtained as a pale yellow gum (678 mg, 68%). ^1H NMR (500 MHz, acetone-d_6): δ 0.95−1.11 (m, $-SiCH_2CH_2$, 8H), 1.35 (d, ^3J = 6.9 Hz, $-SCHCH_3$, 12H), 2.69−2.82 (m, $-SiCH_2CH_2$, 8H), 3.45 (q, ^3J = 7.1 Hz, $-SCH$, 4H). ^{13}C NMR (125 MHz, acetone-d_6): δ 12.6 ($-SiCH_2CH_2$), 16.7 ($-SCHCH_3$), 26.4 ($-SiCH_2CH_2$), 40.2 ($-SCHCH_3$), 174 ($-COOH$). ^{29}Si NMR (99 MHz, acetone-d_6): δ 3.07. Anal. Calcd for $C_{20}H_{36}O_8S_4Si$: C, 42.83; H, 6.47. Found: C, 42.80; H, 6.33. LRESI: 561.1 $[M + H]^+$, 578.2 $[M + NH_4]^+$, 583.3 $[M + Na]^+$.

Synthesis of 6. Compound **6** was prepared using the general procedure from tetravinylsilane (185 mg, 1.36 mmol), mercaptosuccinic acid (817 mg, 5.44 mmol), and benzophenone (12.4 mg, 0.068 mmol). Compound **6** was purified using the same procedure described for **4**. The product was obtained as a hard, transparent solid (684 mg, 68%). ^1H NMR (500 MHz, acetone-d_6): δ 0.97−1.19 (m, $-SiCH_2CH_2$, 8H), 2.63−2.95 (m, $-CH_2SCHCH_2CO_2H$, 16H), 3.66−3.69 (m, $-CHCO_2H$, 4H). ^{13}C NMR (125 MHz, acetone-d_6): δ 12.5 ($-SiCH_2CH_2$), 26.6 ($-SiCH_2CH_2$), 36.0 ($-SCHCH_2$), 41.1 ($-SCHCH_2$), 171 ($-CHCOOH$), 172 ($-CH_2COOH$). ^{29}Si NMR (99 MHz, acetone-d_6): δ 3.30. Anal. Calcd for $C_{24}H_{36}O_{16}S_4Si$: C, 39.12; H, 4.92. Found: C, 39.24; H, 4.93. LRESI: 736.9 $[M + H]^+$, 754.0 $[M + NH_4]^+$, 759.2 $[M + Na]^+$.

Synthesis of 7. Compound **7** was prepared using the general procedure from tetravinylsilane (243 mg, 1.78 mmol), methyl thioglycolate (0.64 mL, 7.12 mmol), and benzophenone (16.2 mg, 0.089 mmol). Removal of solvents in vacuo afforded **7** as a viscous pale yellow oil (1.05 g, 100%). Compound **7** can also be prepared without benzophenone after 8 h of irradiation. ^1H NMR (500 MHz, $CDCl_3$): δ 0.92 (t, ^3J = 8.6 Hz, $-SiCH_2CH_2$, 8H), 2.59 (t, ^3J = 8.6 Hz, $-SiCH_2CH_2$, 8H), 3.16 (s, $-SCH_2$, 8H), 3.62 (s, $-OCH_3$, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.3 ($-SiCH_2CH_2$), 27.6 ($-SiCH_2CH_2$), 33.1 ($-SCH_2CO_2CH_3$), 52.4 ($-OCH_3$), 170 ($-COOCH_3$). ^{29}Si NMR (99 MHz, $CDCl_3$): δ 4.29. Anal. Calcd for $C_{20}H_{36}O_8S_4Si$: C, 42.83; H, 6.47. Found: C, 42.69; H, 6.46. LRESI: 560.9 $[M + H]^+$, 578.2 $[M + NH_4]^+$, 583.3 $[M + Na]^+$.

Synthesis of 8. Compound **8** was prepared using the general procedure from tetravinylsilane (681 mg, 5.00 mmol) and 3-mercaptopropyl(trimethoxy)silane (3.72 mL, 20.0 mmol). After removal of solvents in vacuo, compound **8** was obtained as a pale yellow liquid (4.60 g, 100%). ^1H NMR (500 MHz, $CDCl_3$): δ 0.74 (t, ^3J = 8.3 Hz, $-CH_2Si(CH_3O)_3$, 8H), 0.96 (t, ^3J = 8.6 Hz, $-SiCH_2CH_2$, 8H), 1.68 (quintet, ^3J = 7.7 Hz, $-CH_2CH_2CH_2$, 8H), 2.51−2.54 (m, $-CH_2SCH_2$, 16H), 3.56 (s, $-SiOCH_3$, 36H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 8.66 ($-CH_2Si(CH_3O)_3$), 13.2 ($-SiCH_2CH_2$), 22.9 ($-CH_2CH_2CH_2$), 27.0 ($-SiCH_2CH_2$), 35.0 ($-SCH_2CH_2CH_2$), 50.5 ($-SiOCH_3$). ^{29}Si NMR (99 MHz, $CDCl_3$): δ −42.0 ($-SiOCH_3$), 2.60 ($-SiCH_2CH_2$). Anal. Calcd for $C_{32}H_{76}O_{12}S_4Si_5$: C, 41.70; H, 8.31. Found: C, 41.60; H, 8.36. LRESI: 937.9 $[M + NH_4]^+$, 943.4 $[M + Na]^+$.

Synthesis of 9. Compound **9** was prepared using the general procedure from tetravinylsilane (204 mg, 1.50 mmol), 3-mercaptopropanesulfonate sodium salt (1.18 g, 6.6 mmol), and benzophenone (14.8 mg, 0.081 mmol). In this case, a mixture of methanol (5 mL) and distilled water (2 mL) was used as the solvent. After the reaction was complete, the reaction mixture was cooled in an ice−water bath to increase precipitation of the product. The solid was filtered and washed quickly with methanol. The solid was then suspended in isopropyl alcohol with stirring and then filtered and dried in vacuo. Compound **9** was collected as a hygroscopic white powder (809 mg, 64%). No melting point was observed on heating to 275 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 0.88 (t, ^3J = 8.6 Hz, $SiCH_2CH_2$, 8H), 1.77 (quintet, ^3J = 7.4 Hz, $-CH_2CH_2SO_3Na$, 8H), 2.55−2.46 (m, $-CH_2SCH_2$, $-CH_2SO_3Na$, 24H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 13.1 ($-SiCH_2CH_2$), 25.7 ($-CH_2CH_2SO_3Na$), 26.7 ($-SiCH_2CH_2$), 30.7 ($-SCH_2CH_2CH_2$), 50.7 ($-CH_2SO_3Na$). ^{29}Si NMR (99 MHz, DMSO-d_6): 3.68. Anal. Calcd for $C_{20}H_{40}Na_4O_{12}S_8Si$: C, 28.29; H, 4.75. Found: C, 28.24; H, 4.89. LRESI: 849.1 $[M + H]^+$, 871.1 $[M + Na]^+$, 865.1 $[M + O + H]^+$ or $[M + K - Na]^+$.

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