

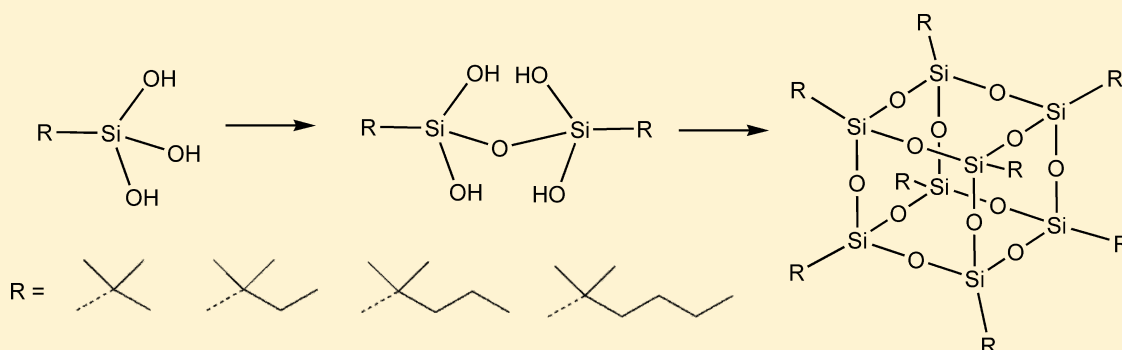
Silanetriols as Powerful Starting Materials for Selective Condensation to Bulky POSS Cages

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S Supporting Information



ABSTRACT: Controlled condensation reactions of tertiary silanetriols $\text{CH}_3(\text{CH}_2)_n(\text{CH}_3)_2\text{CSi}(\text{OH})_3$ (**1b–f**; $n = 1–5$) in the presence of trifluoroacetic acid and the hydrolysis of $\text{CH}_3(\text{CH}_2)_6(\text{CH}_3)_2\text{CSiCl}_3$ (**3**) lead to the selective formation of the corresponding disiloxane tetrols $[\text{CH}_3(\text{CH}_2)_n(\text{CH}_3)_2\text{CSi}(\text{OH})_2]_2\text{O}$ (**2b–g**; $n = 1–6$) in good yields. The TBAF-driven condensation reactions of the silanetriols $\text{CH}_3(\text{CH}_2)_n(\text{CH}_3)_2\text{CSi}(\text{OH})_3$ (**1a–c**; $n = 0–2$) as well as of the disiloxane-1,1,3,3-tetrol **2d** ($n = 3$) yield in the selective formation of the first T_8 cages bearing tertiary carbon substituents, $\text{CH}_3(\text{CH}_2)_n(\text{CH}_3)_2\text{C}$ (**4a–d**; $n = 0–3$), which was not possible via the condensation of their alkoxysilane counterparts so far. The resulting compounds **2b–g** and **4a–d** have been characterized by multinuclear NMR, MS, and single-crystal X-ray diffraction.

INTRODUCTION

Octasilsesquioxanes T_8 ($\text{T} = \text{RSi}(\text{O}-)_3$ with $\text{R} =$ inorganic or organic substituent, H) belong to the class of POSS compounds (POSS = polyhedral oligomeric silsesquioxanes) which have attracted much attention in recent years.^{1,2} As hybrid materials with properties of both SiO_2 and siloxanes,³ they enjoy widespread applications for example in catalysis,⁴ as model systems for silica surfaces,^{5,6} in the design of superoleophobic surfaces,⁷ ionic liquids,⁸ and biocompatible materials,⁹ and in polymer chemistry.² The synthetic approach toward such octasilsesquioxanes is based on the hydrolytic condensation of trifunctional silanes RSiX_3 , where R is a stable organic substituent and X a reactive moiety (i.e. $\text{X} = \text{Cl}$, OMe , etc.) and mostly accompanied by low selectivity, low yields, and long reaction times strongly dependent on many parameters such as the nature of the substituent R , the catalyst, the amount of water, etc.^{2,3} The synthesis of T_8 was revolutionized by Bassindale et al., who treated trialkoxysilanes with tetrabutylammonium fluoride (TBAF) in THF, which in many cases led to the selective formation of T_8 cages in yields of up to 95%.^{10–12} The precise mechanism of POSS formation is complex and is still under investigation. The intermediate formation of the primary hydrolysis products $\text{RSi}(\text{OH})_3$ has been postulated starting from trichlorosilanes.¹³ The synthesis of T_6 cages from their corresponding silanetriol counterparts

has already been described by Unno et al. and in our laboratories using multistep procedures.^{14–16} Therefore, we wanted to investigate whether a one-pot synthesis starting from silanetriols works equally well as the classical TBAF procedure established by Bassindale et al., which starts from alkoxysilanes. In addition, this investigation should also shed light on the question of whether silanetriols really do occur as intermediates in the classical TBAF procedure.

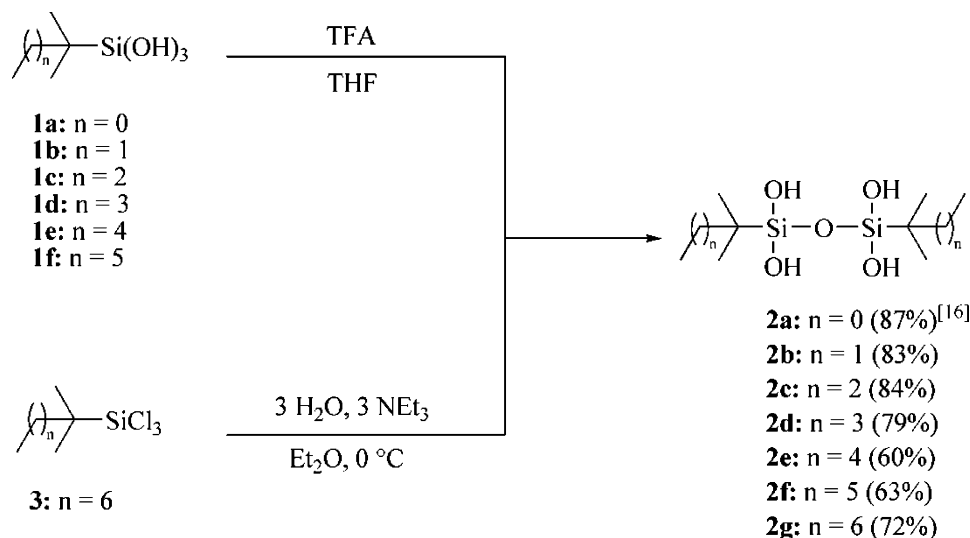
RESULTS AND DISCUSSION

Recently we have established a multistep synthesis toward stable amphiphilic silanetriols bearing tertiary carbon substituents, $\text{H}_3\text{C}(\text{CH}_2)_n(\text{CH}_3)_2\text{CSi}(\text{OH})_3$ (**1b–f**; $n = 1–5$).¹⁷ Owing to their great stability in the solid state as well as in solution these compounds are potential starting materials for controlled condensation reactions toward discrete siloxane species.^{18,19} First we wanted to investigate whether the condensation of such compounds can be stopped at its primary stage: the disiloxane-1,1,3,3-tetrols. Despite their interesting properties and possible applications, e.g. as anion receptors²⁰ or in optically active materials,²¹ examples of such disiloxanetetrols are rather rare. Only a few publications have dealt with the

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Scheme 1. Synthesis of the Disiloxane-1,1,3,3-tetrols 2b–g^a

^aIsolated yields are quoted in parentheses.

targeted synthesis of such compounds via the hydrolysis of the corresponding trichlorosilane precursors.^{22–26} We have already been able to show that treatment of *t*-BuSi(OH)₃ (**1a**) with trifluoroacetic acid (TFA) yielded the exclusive formation of the corresponding primary condensation product [*t*-BuSi(OH)₂]₂O (**2a**) as a crystalline material.¹⁶ Following this protocol, mixing the silanetriols **1b–f** with TFA in THF solution resulted in the formation of the corresponding disiloxane-1,1,3,3-tetrols [H₃C(CH₂)_n(CH₃)₂CSi(OH)₂]₂O (**2b–f**; *n* = 1–5) in pure form and high yields (Scheme 1). In addition to this, the hydrolysis of (1,1-dimethyloctyl)-trichlorosilane, H₃C(CH₂)₆(CH₃)₂CSiCl₃ (**3**), in the presence of NEt₃ gave the disiloxane-1,1,3,3-tetrol **2g** exclusively instead of the corresponding silanetriol (Scheme 1). The ²⁹Si NMR data of compounds **2b–g** are in agreement with the chemical shift of **2a** known in the literature and range between –49.9 and –51.9 ppm.¹⁶

The compounds **2b,d,g** could be obtained as single crystals suitable for X-ray diffraction. The solid-state structures of all compounds show extensive networks of intermolecular hydrogen bonding similar to that for **2a**.^{16,24} One molecule interacts with six adjacent molecules, resulting in sheetlike structures (Figures 1–3). Whereas compounds **2b,g** arrange in parallel sheet structures, compound **2d** shows a herringbone pattern

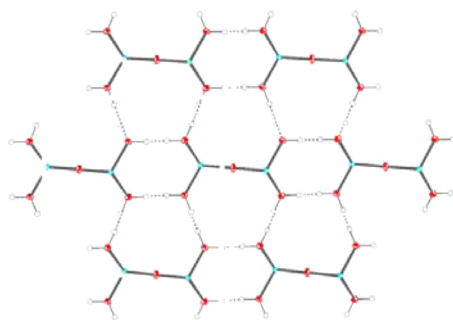


Figure 1. Exemplary H bonding between one molecule and six neighbors in **2b**. The carbon substituents are omitted for clarity. The ellipsoids are drawn at the 30% probability level.

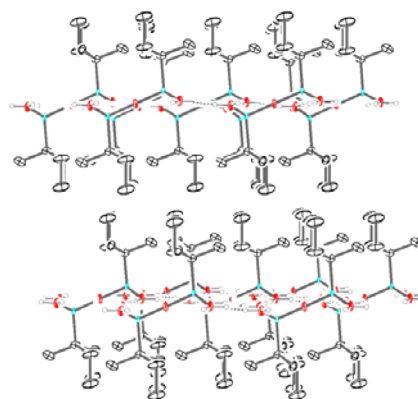


Figure 2. Exemplary layer structure in **2b**. The ellipsoids are drawn at the 30% probability level.

(Figures 2 and 3). The increasing alkyl chains show a near-linear zigzag orientation (Figure 4).

The O...O and H...O distances are comparable to those of the two known modifications of [*t*-BuSi(OH)₂]₂O, **2a** and **2a'** (Table 1).^{16,24} On the basis of their geometric parameters the hydrogen bond interactions can be classified as moderate to strong.²⁷ While the observed Si–O–Si angle of compound **2b** is 180° due to symmetry reasons (monoclinic, C₂/m) and therefore comparable to Lickiss' modification of **2a'**, the angles of compounds **2d,g** are 175.0(4) and 173.8°, respectively, and lie between the different observed Si–O–Si angles (165.6° (**2a**)¹⁶ and 180° (**2a'**)²⁴) of [*t*-BuSi(OH)₂]₂O. These angles, however, are in agreement with the observed strong intermolecular interactions via hydrogen bonding. The Si–O_{siloxane} distances are slightly shortened in comparison to the Si–OH distance (Table 2). The Si–C distances range between 1.8553(19) and 1.881(6) Å. The data found in **2b,d,g** are in good agreement with values known in the literature for other disiloxane-1,1,3,3-tetrols.^{16,24}

Having established a synthetic protocol toward successively CH₂ elongated disiloxane-1,1,3,3-tetrols, we wanted to investigate whether a targeted approach to higher condensed oligomers such as POSS cages is possible starting from these

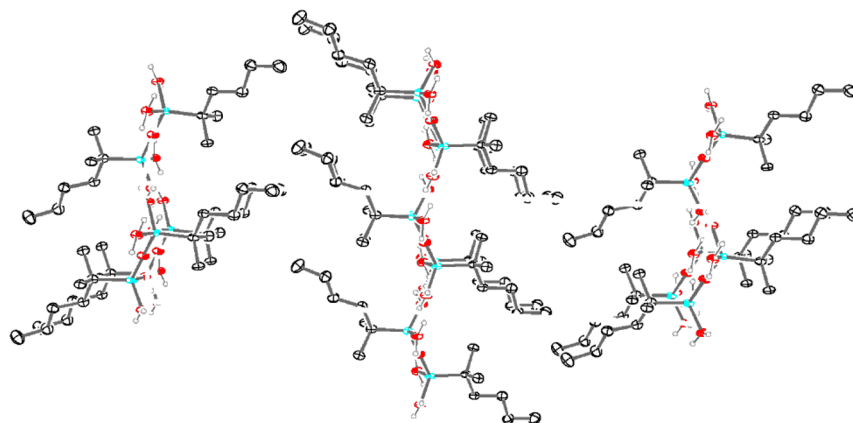


Figure 3. Herringbone pattern of compound 2d. The ellipsoids are drawn at the 30% probability level.

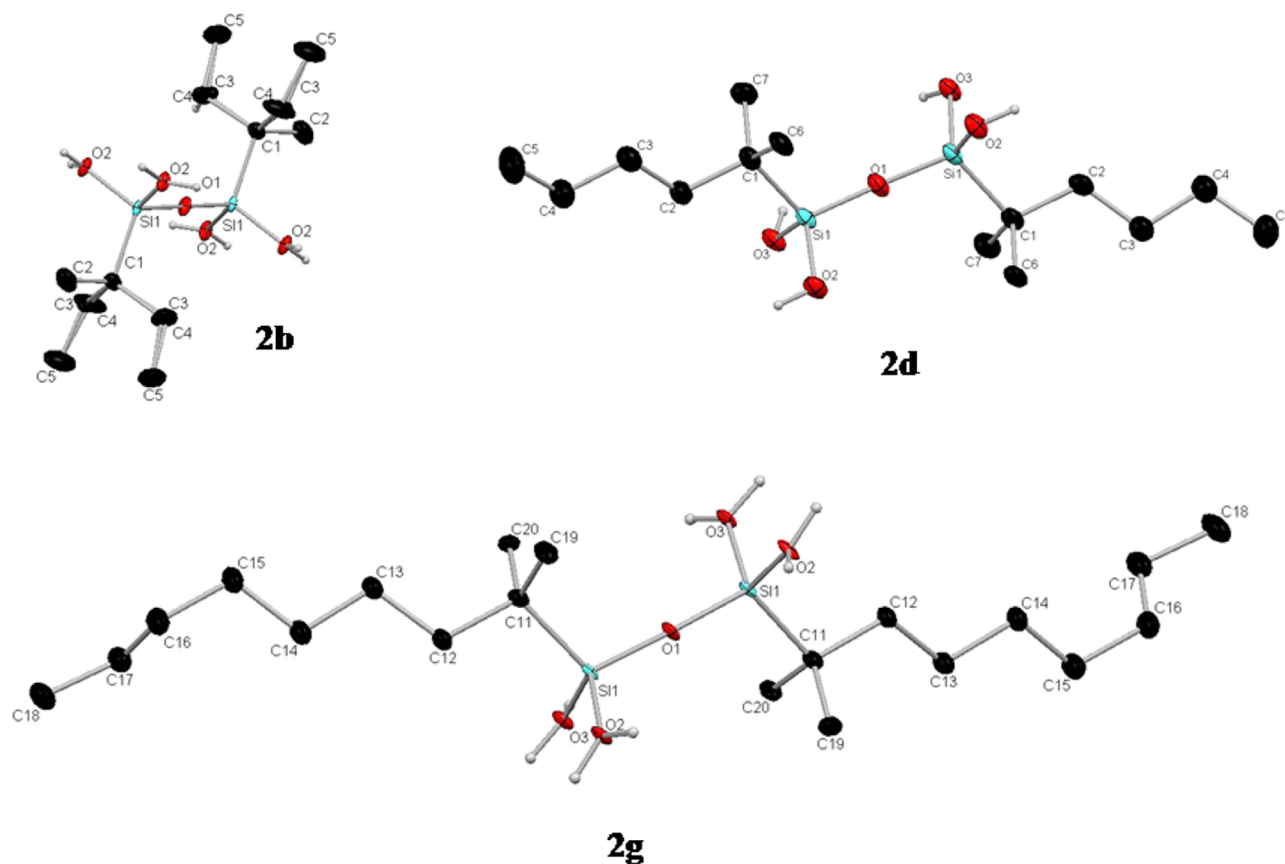


Figure 4. Crystal structures of disiloxanes **2b,d,g**. The hydrogen atoms of the carbon substituents are omitted for clarity. The ellipsoids are drawn at the 30% probability level. In **2b** the carbon atoms of the ethyl group and one methyl group are disordered over two sites. In **2b,g** the H atoms of the OH group are disordered over two sites (occupancy 0.5).

Table 1. Hydrogen Bonds of **2b,d,g**^a

	D—H...A	<i>d</i> (D...A), Å	∠(D—H...A), deg
2a ¹⁶	O—H...O	2.668–2.674	152–176
2a ²⁴	O—H...O	2.678–2.690	N/A
2b	O—H...O ^{iii,ii}	2.658–2.662	176–177
2d	O—H...O ^{iii,iv,v}	2.658–2.706	142–162
2g	O—H...O ^{vi}	2.662–2.695	145–161

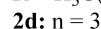
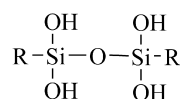
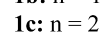
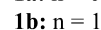
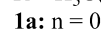
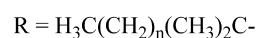
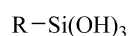
^aSymmetry transformations used to generate equivalent atoms: (i) $x - 1, y, 2 - z$; (ii) $3/2 - x, 3/2 - y, 2 - z$; (iii) $x, -y - 1, -z$; (iv) $x + 1/2, -y - 1/2, -z$; (v) $x - 1/2, -y - 1/2, -z$; (vi) $x - 1, y - 1, z$.

silanetriols. Traditionally POSS cages are prepared by controlled hydrolysis of suitable trichlorosilanes or trialkoxysilanes. A general method has been established by Bassindale and co-workers, employing TBAF as a catalyst to transform alkoxy silanes into T₈-POSS cages in the presence of water.^{10,12} The templating effect of the fluoride ion has been nicely illustrated by its encapsulation into a T₈ cage.¹¹ Despite the great success of this method, the yields can be quite low with certain substituents. For *tert*-butyl for instance, the corresponding T₈ cage could not be obtained.¹⁰ On the other hand, we recently reported the syntheses and crystal structures of *tert*-butyl-substituted POSS cages T₆ and T₇(OH)₃ starting from

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 2b,d,g

	2b	2d	2g
Si–OH	1.6340(8)	1.647(4)	1.6104(8)–1.636(2)
Si–O _{siloxane}	1.6050(4)	1.6234(14)	1.610(8)
Si–C	1.8553(19)	1.881(6)	1.860(3)
Si–O–Si	180.0	175.0(4)	173.8(2)
O(H)–Si–O(H)	105.99(6)	105.7(2)	105.44(11)
O(H)–Si–O _{siloxane}	105.99(6)–108.79(3)	105.7(2)–108.9(2)	109.03(12)–109.07(13)
O(H)–Si–C	111.56(5)	111.3(2)–111.5(2)	111.56(15)–111.94(15)
O _{siloxane} –Si–C	110.03(7)	110.57(19)	109.67(11)
Si–C–C–C	–170.9(5)	171.44(12)	–172.4(3)
C–C–C–C(H ₃)		174.08(17)	–176.5(4)

Scheme 2. Synthesis of the Compounds 4a–d



TBAF

THF

TBAF

THF

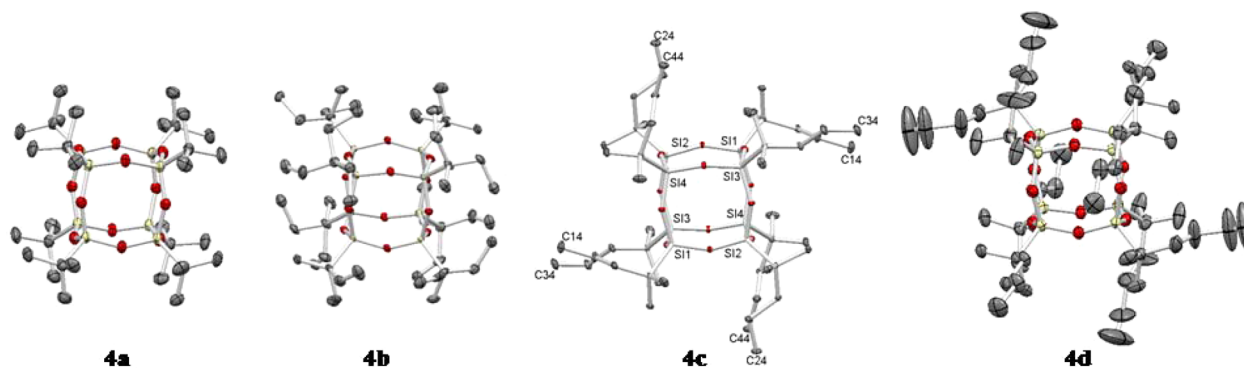
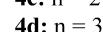
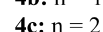
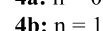
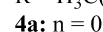
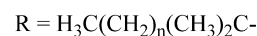
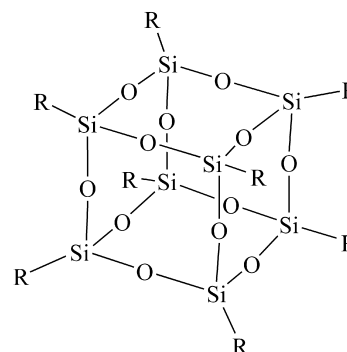


Figure 5. Crystal structures of compounds 4a–d. The hydrogen atoms have been omitted for clarity. The ellipsoids are drawn at the 30% probability level.

the corresponding silanetriol, which confirms that the formation of *tert*-butyl-substituted POSS cages is possible.¹⁶ Therefore, we combined both approaches and explored the formation of POSS cages starting from silanetriols **1a–c** in the presence of TBAF as catalyst. Following this protocol, we obtained several T₈-POSS cages **4a–c**, which were previously unknown (Scheme 2). In addition to the high potential of silanetriols as starting materials in POSS synthesis, also the treatment of its primary condensation product, i.e. disiloxane-1,1,3,3-tetrol **2d**, with TBAF has been explored, which results in the selective formation of the corresponding T₈ **4d** as well. The latter results provide experimental proof in support of the

hypothesis that POSS formation proceeds via the corresponding disiloxanes.

In addition, the *tert*-butyl-substituted T₈ cage **4a** has been obtained by starting from silanetriol **1a**, which was not available starting from the corresponding trialkoxysilane.¹⁰ The identity of compound **4a** could be established on the basis of X-ray crystallography, solid-state NMR, and mass spectrometry. In agreement with Bassindale's report¹⁰ dealing with *t*-BuSi(OR)₃, the treatment of **1a** with TBAF also resulted in a white insoluble powder which can hardly be characterized with solution-based techniques except for proton NMR. We assume that *tert*-butyl-substituted T_n cages have also been formed in

Bassindale's approach but high substituent rigidity resulting in low solubility precluded further characterization. The solubility issue can be overcome by introducing the elongated and more flexible *tert*-butyl derivatives $\text{CH}_3(\text{CH}_2)_n(\text{CH}_3)_2\text{C}-$ ($n = 1-3$). The ^{29}Si chemical shifts of compounds **4a–d** range between -67.1 and -68.4 ppm and are comparable to data known in the literature for T_8 cages.^{10,12} Compounds **4a–d** could be obtained as single crystals suitable for X-ray diffraction. Compound **4a** crystallizes in the triclinic space group $P\bar{1}$ and is the first T_8 cage bearing a tertiary carbon substituent (Figure 5).

Compound **4b** crystallizes in the trigonal space group $R\bar{3}c$. The 1,1-dimethylpropyl groups are disordered over three orientations, and the almost spherical molecules arrange in a slightly distorted cubic closed packing (Figure 6). Compound

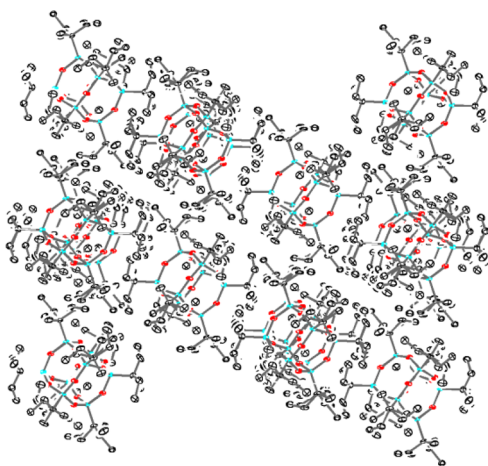


Figure 6. Packing in the crystal structure of compound **4b**. The hydrogen atoms have been omitted for clarity. The ellipsoids are drawn at the 30% probability level.

4c crystallizes in the triclinic space group $P\bar{1}$ (Figure 5). Although the conformations of the four independent 1,1-dimethylbutyl substituents are quite different, the C atoms at the ends of the chains (C14, C24, C34, C44) lie in a plane that is almost coplanar with the best plane through the Si atoms Si1, Si2, Si3, and Si4 (angle of $2.78(1)^\circ$ between the planes). Compound **4d** crystallizes in the monoclinic space group $P2_1/n$ (Figure 5). Due to the unrefinable displacement parameters the probability ellipsoids of the 1,1'-dimethylpentyl moieties are significantly large. Nevertheless, the structure refinements reported here yielded R1 values in the range of 2.64–4.54% for compounds **4a–c**, remarkably low in comparison to those for other reported T_8 solid-state structures. The residual electron densities for all T_8 cages reported here give no

indication for any unallocated atoms. Therefore, these results corroborate that the Si_8O_{12} cages of compounds are empty voids.

In **4a–d** all interatomic distances and angles are quite uniform, indicating a comparable steric situation for this continuous series of tertiary alkyl substituted POSS cages which is not significantly affected by the chain extension (Table 3). Moreover, the observed data fit well with those available from the literature.^{10,12} The internal Si...Si distances reflect the geometry of the Si_8O_{12} cage (Figure 7). Although the data vary only marginally among **4a–d**, the lower limit of the *p*-Si...Si distances decreases constantly with increasing chain length (Table 3).

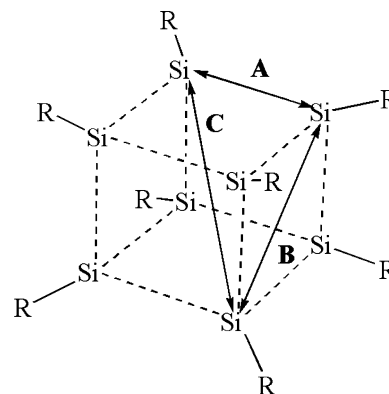


Figure 7. Interatomic Si...Si distances in T_8 POSS cages.¹²

SUMMARY AND CONCLUSION

In summary, we have shown that the treatment of silanetriols $\text{H}_3\text{C}(\text{CH}_2)_n(\text{CH}_3)_2\text{CSi}(\text{OH})_3$ ($n = 1-5$) with trifluoroacetic acid results in the exclusive formation of the corresponding primary condensation products $[\text{H}_3\text{C}(\text{CH}_2)_n(\text{CH}_3)_2\text{CSi}(\text{OH})_2]_2\text{O}$. The range of known disiloxane-1,1,3,3-tetrols could be extended by a series of successively CH_2 elongated alkyl-substituted congeners which may have interesting properties as gemini surfactants, a class of compounds which has attracted much attention in recent years.²⁸ These properties will be investigated in the future. In addition, a synthetic access toward the first T_8 POSS cages bearing tertiary carbon substituents was possible. In a variation of Bassindale's TBAF protocol the corresponding T_8 cages could be isolated in pure form in good yields starting from the aforementioned silanetriols $\text{H}_3\text{C}(\text{CH}_2)_n(\text{CH}_3)_2\text{CSi}(\text{OH})_3$ ($n = 0-2$) and disiloxane-1,1,3,3-tetrol $[\text{H}_3\text{C}(\text{CH}_2)_n(\text{CH}_3)_2\text{CSi}(\text{OH})_2]_2\text{O}$ ($n = 3$). High-quality X-ray diffraction data confirm the presence of an empty void within the Si_8O_{12} cages and therefore

Table 3. Selected Bond Lengths (Å) and Angles (deg) of **4a–d**

	4a	4b	4c	4d
Si–O	1.6217(16)–1.6308(15)	1.617(13)–1.6203(12)	1.6215(6)–1.6269(7)	1.616(3)–1.626(3)
Si–C	1.868(2)–1.872(2)	1.865(4)–1.865(2)	1.8634(8)–1.8727(8)	1.861(4)–1.873(4)
<i>o</i> -Si...Si (A)	3.12–3.16	3.12	3.11–3.14	3.12–3.14
<i>m</i> -Si...Si (B)	4.42–4.45	4.42	4.40–4.43	4.42–4.44
<i>p</i> -Si...Si (C)	5.43–5.44	5.41	5.40–5.44	5.39–5.43
Si–O–Si	146.76(11)–152.81(11)	148.96(8)–149.53(9)	146.06(4)–151.20(4)	147.84(18)–151.62(18)
O–Si–O	108.83(9)–109.75(10)	108.78(7)–109.17(7)	108.25(3)–109.43(3)	108.30(14)–109.47(14)
O–Si–C	109.19(10)–110.83(10)	109.33(8)–110.35(7)	108.14(4)–112.48(4)	108.61(16)–111.37(16)

encourage future investigation of the encapsulation of small molecules and neutral atoms or ions.^{11,29–32} The fact that POSS cages are accessible from silanetriols which are not accessible from the corresponding trialkoxysilanes under comparable conditions indicate that discrete silanetriols may not necessarily occur in protocols based on alkoxy silanes, even at low pH values where hydrolysis is expected to outpace condensation.

EXPERIMENTAL SECTION

All manipulations were carried out under an inert argon atmosphere using standard Schlenk techniques. All solvents were dried and freshly distilled over Na/K alloy (Et₂O, THF, pentane, heptane) or CaH₂ (NEt₃, CH₂Cl₂, CDCl₃). Compound **1a** was prepared according to literature procedures.³³ The preparation of the silanetriols **1b–f** and trichlorosilane **3** has been described elsewhere.¹⁷ TBAF (1 M in THF) and trifluoroacetic acid have been purchased and used without further purification.

¹H and ¹³C NMR data have been recorded on a Bruker Avance III 300 MHz spectrometer (operating at 300 and 75.4 MHz) or a Varian MR-400 MHz spectrometer (operating at 400 and 100.5 MHz). ²⁹Si NMR data have been recorded on a Bruker Avance III 300 MHz spectrometer (operating at 59.6 MHz) or a Varian VNMRs 500 MHz spectrometer (operating at 99.3 MHz). All measurements have been performed at room temperature using TMS as external standard.

Solid-state NMR spectra at 9.4 T (ν_0 = 79.5 MHz (²⁹Si) or 100.6 MHz (¹³C)) were recorded at ambient temperature (296 K) on a Bruker Avance 400 spectrometer equipped with a 4 mm MAS probe. All spectra were acquired using magic angle spinning (MAS) at spinning speeds between 9 and 14 kHz, and high power ¹H decoupling was applied during acquisition.

ESI-mass spectra have been recorded on a Agilent Technologies S975C inert XL MSD with SIS Direct Insertion Probe. ESI and APCI mass spectra have been recorded on a Finnigan LCQ Deca (ThermoQuest). HR-ESI-MS spectra have been recorded using a micrOTOF (Bruker Daltonics) and an Apollo "Ion Funnel" ESI ion source. IR spectra have been recorded using a Bruker Alpha Platinum ATR spectrometer. Elemental analysis data have been recorded on a Euro EA Elementar analysator of HEKAtech. X-ray diffraction measurements were performed on a Stoe IPDS2 or a Bruker-AXS SMART APEX 2 CCD diffractometer using graphite-monochromated Mo K α radiation. The structures were solved using direct methods (SHELXL-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97). Details of the structure determinations and refinement for **2b,d,g** and **4a–d** are summarized in Table S1 (Supporting Information). Supplementary crystallographic data for this paper can be obtained free of charge by quoting CCDC 1031585–1031591 from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of the 1,3-Bis(1,1-dimethyl-*n*-alkyl)disiloxane-1,1,3,3-tetrols **2b–f.** Trifluoroacetic acid (0.15 mL, 0.22 g, 1.9 mmol) was added to a solution of 0.3 mmol of the corresponding tertiary silanetriol **1b–f** in 2 mL of THF at room temperature. After partial evaporation of the volatiles the compounds **2b–f** were obtained as pale crystalline solids which were washed with pentane and dried in vacuo. The yields ranged between 60 and 84%.

1,3-Bis(1,1-dimethylpropyl)disiloxane-1,1,3,3-tetrol (2b). Yield: 83%. ¹H NMR (300 MHz, THF-*d*₈): δ (ppm) 4.87 (b, 4H, –Si–OH), 1.40 (m, 4H, –CH₂–), 0.94 (s, 12H, –C(CH₃)₂–), 0.90 (t, ³J_{HH} = 7.5 Hz, 6H, –CH₃). ¹³C NMR (75.4 MHz, THF-*d*₈): δ (ppm) 32.7 (CH₂), 23.7 (C_q), 21.7 (CH₃), 9.5 (CH₃). ²⁹Si NMR (59.6 MHz, THF-*d*₈): δ (ppm) –49.9. IR: 3126 (b), 2946 (s), 2865 (w), 1463 (w), 1109 (s), 847 (s), 704 (s), 624 (w), 423 (s) cm^{–1}. MS/EI: m/z (%) 282 (5) [M]⁺, 71 (20) [C₅H₁₁]⁺, 57 (100) [C₄H₉]⁺. MSAPCI(+): m/z (%) 586 (100) [2 M + Na]⁺, 868 (37) [3 M + Na]⁺, 305 [M + Na]⁺. HRMS/ESI(+): m/z 305.1222 [M + Na]⁺, calcd for [C₁₀H₂₆O₅Si₂Na]⁺ 305.1216. Anal. Calcd for C₁₀H₂₆O₅Si₂: C, 42.45; H, 9.26. Found: C, 42.34; H, 9.37.

1,3-Bis(1,1-dimethylbutyl)disiloxane-1,1,3,3-tetrol (2c). Yield: 84%. ¹H NMR (300 MHz, THF-*d*₈): δ (ppm) 4.88 (b, 4H, –Si–OH), 1.45–1.28 (m, 8H, –CH₂–CH₂–), 0.96 (s, 12H, –C(CH₃)₂–), 0.86 (m, 6H, –CH₃). ¹³C NMR (75.4 MHz, THF-*d*₈): δ (ppm) 43.5 (CH₂), 24.3 (CH₂), 21.7 (C_q), 18.7 (CH₃), 15.5 (CH₃). ²⁹Si NMR (59.6 MHz, THF-*d*₈): δ (ppm) –51.9. IR: 3103 (b), 2954 (s), 2865 (w), 1463 (w), 1113 (s), 848 (s), 717 (w), 650 (w), 431 (s) cm^{–1}. HRMS/ESI(+): m/z 333.1529 [M + Na]⁺, calcd for [C₁₂H₃₀O₅Si₂Na]⁺ 333.1529. Anal. Calcd for C₁₂H₃₀O₅Si₂: C, 46.41; H, 9.74. Found: C, 46.66; H, 9.63.

1,3-Bis(1,1-dimethylpentyl)disiloxane-1,1,3,3-tetrol (2d). Yield: 79%. ¹H NMR (300 MHz, THF-*d*₈): δ (ppm) 4.89 (b, 4H, –Si–OH), 1.37–1.21 (m, 12H, –CH₂–CH₂–CH₂–), 0.95 (s, 12H, –C(CH₃)₂–), 0.89 (m, 6H, –CH₃). ¹³C NMR (75.4 MHz, THF-*d*₈): δ (ppm) 40.5 (CH₂), 27.6 (CH₂), 24.6 (CH₂), 24.2 (C_q), 21.4 (CH₃), 14.4 (CH₃). ²⁹Si NMR (59.6 MHz, THF-*d*₈): δ (ppm) –51.7. IR: 3125 (b), 2952 (s), 2862 (w), 1463 (w), 1115 (s), 854 (s), 721 (s), 668 (s), 450 (s) cm^{–1}. MS/EI: m/z (%) = 338 (2) [M]⁺, 239 (40) [M – C₇H₁₅]⁺, 155 (100), 99 (5) [C₇H₁₅]⁺, 57 (30) [C₄H₉]⁺. MS/ESI(+): m/z (%) 361 (100) [M + Na]⁺, 699 (2) [2 M + Na]⁺. HRMS/ESI(+): m/z 361.1842 [M + Na]⁺, calcd for [C₁₄H₃₄O₅Si₂Na]⁺ 361.1837. Anal. Calcd for C₁₄H₃₄O₅Si₂: C, 49.66; H, 10.12. Found: C, 49.78; H, 10.09.

1,3-Bis(1,1-dimethylhexyl)disiloxane-1,1,3,3-tetrol (2e). Yield: 60%. ¹H NMR (300 MHz, THF-*d*₈): δ (ppm) 4.88 (b, 4H, –Si–OH), 1.40–1.23 (m, 16H, –CH₂–CH₂–CH₂–CH₂–), 0.96 (s, 12H, –C(CH₃)₂–), 0.88 (m, 6H, –CH₃). ¹³C NMR (75.4 MHz, THF-*d*₈): δ (ppm) 40.7 (CH₂), 34.1 (CH₂), 25.0 (CH₂), 24.2 (CH₂), 23.5 (C_q), 21.5 (CH₃), 14.4 (CH₃). ²⁹Si NMR (59.6 MHz, THF-*d*₈): δ (ppm) –49.9. IR: 3096 (b), 2950 (s), 2860 (w), 1464 (w), 1116 (s), 849 (s), 722 (s), 669 (s), 427 (s) cm^{–1}. MS/EI: m/z (%) 366 (2) [M]⁺, 253 (40) [M – C₈H₁₇]⁺, 155 (100), 113 (5) [C₈H₁₇]⁺, 57 (30) [C₄H₉]⁺. HRMS/ESI(+): m/z 389.2138 [M + Na]⁺, calcd for [C₁₆H₃₈O₅Si₂Na]⁺ 389.2155. Anal. Calcd for C₁₆H₃₈O₅Si₂: C, 52.41; H, 10.45. Found: C, 52.07; H, 10.56.

1,3-Bis(1,1-dimethylheptyl)disiloxane-1,1,3,3-tetrol (2f). Yield: 63%. ¹H NMR (400 MHz, THF-*d*₈): δ (ppm) 5.02 (s, 4H, –Si–OH), 1.40–1.24 (m, 20H, –CH₂–CH₂–CH₂–CH₂–CH₂–), 0.95 (s, 12H, –C(CH₃)₂–), 0.88 (m, 6H, –CH₃). ¹³C NMR (100.5 MHz, THF-*d*₈): δ (ppm) 41.0 (CH₂), 33.0 (CH₂), 31.7 (CH₂), 25.3 (CH₂), 24.4 (CH₂), 23.7 (C_q), 21.6 (CH₃), 14.5 (CH₃). ²⁹Si NMR (99.3 MHz, THF-*d*₈): δ (ppm) –49.9. IR: 3127 (b), 2926 (s), 2857 (s), 1465 (w), 1080 (b), 856 (s), 722 (w), 670 (w), 429 (w) cm^{–1}. MS/ESI(+): m/z (%) 417 (100) [M + Na]⁺. HRMS/ESI(+): m/z 417.2455 [M + Na]⁺, calcd for [C₁₈H₄₂O₅Si₂Na]⁺ 417.2468. Anal. Calcd for C₁₈H₄₂O₅Si₂: C, 54.77; H, 10.73. Found: C, 54.57; H, 10.99.

1,3-Bis(1,1-dimethyloctyl)disiloxane-1,1,3,3-tetrol (2g). A solution of 2.71 g (9.8 mmol; 1 equiv) of (1,1-dimethyloctyl)-trichlorosilane (**3**) in Et₂O was slowly added to a solution of 0.53 g (29.4 mmol; 3 equiv) of H₂O and 2.97 g (29.4 mmol; 3 equiv) of NEt₃ in Et₂O at 0 °C. After the addition was complete, the reaction mixture was slowly warmed to room temperature and stirred for further 3 h. The white precipitate was removed by filtration, and all volatiles were removed in vacuo. The remaining solid was washed with pentane and recrystallized from Et₂O/heptane (1/1). Compound **2g** could be obtained in 72% yield (1.5 g, 3.5 mmol) as a pale crystalline material.

¹H NMR (300 MHz, THF-*d*₈): δ (ppm) 4.89 (s, 3H, –Si–OH), 1.40–1.23 (m, 16H, –CH₂–CH₂–CH₂–CH₂–), 0.96 (s, 12H, –C(CH₃)₂–), 0.88 (m, 6H, –CH₃). ¹³C NMR (75.4 MHz, THF-*d*₈): δ (ppm) 41.0 (CH₂), 33.0 (CH₂), 31.9 (CH₂), 30.7 (CH₂), 30.5 (CH₂), 24.6 (CH₂), 23.6 (C_q), 21.6 (CH₃), 14.5 (CH₃). ²⁹Si NMR (59.6 MHz, THF-*d*₈): δ (ppm) –49.9. IR: 3080 (b), 2925 (s), 2856 (s), 1463 (w), 1119 (s), 857 (s), 722 (s), 670 (s), 433 (s) cm^{–1}. MS/EI: m/z (%) 422 (2) [M]⁺, 281 (70) [M – C₁₀H₂₁]⁺, 219 (10) [M – C₁₀H₂₃O₃Si]⁺, 203 (5) [M – C₁₀H₂₃O₃Si]⁺, 141 (70) [C₁₀H₂₁]⁺, 57 (100) [C₄H₉]⁺. MS/ESI(+): m/z (%) 699 (2) [2 M + Na]⁺, 445 (100) [M + Na]⁺. HRMS/ESI(+): m/z 445.2763 [M + Na]⁺, calcd for [C₂₀H₄₆O₅Si₂Na]⁺ 445.2781. Anal. Calcd for C₂₀H₄₆O₅Si₂: C, 56.82; H, 10.97. Found: C, 57.31; H, 10.99.

Synthesis of the Octakis(1,1-dimethyl-*n*-alkyl)-octasilsesquioxanes **4a–c.** One equivalent of TBAF (1 M in

THF) was added to a solution of 2 equiv of the corresponding tertiary silanetriol **1a–c** in THF at room temperature. After the mixture was stirred for 24 h, all volatiles were removed in vacuo and the yellow oil was mixed with acetone. The white precipitate was filtered off and recrystallized from acetone/dichloromethane. The compounds **4b,c** could be obtained as pale crystalline materials in yields of 40–44%. Compound **4a** was obtained in 60% yield as a pale, poorly soluble powder which was washed several times with acetone and dried in vacuo.

Octakis(tert-butyl)octasilsesquioxane (4a). Yield: 60%. ^1H NMR (250 MHz, acetone- d_6): δ (ppm) 1.04 (s, $-\text{C}(\text{CH}_3)_3$). ^{13}C NMR (CP-MAS): δ (ppm) 55.6 (C_q), 24.2 (CH_3). ^{29}Si NMR (CP-MAS): δ (ppm) -68.4 . IR: 2957 (w), 2935 (w), 2859 (w), 1474 (w), 1234 (w), 1095 (s), 837 (w), 532 (s), 467 (s), 418 (s) cm^{-1} . MS/EI: m/z (%) 872 (10) $[\text{M}]^+$, 815 (100) $[\text{C}_{28}\text{H}_{63}\text{Si}_8\text{O}_{12}]^+$, 57 (45) $[\text{C}_4\text{H}_9]^+$. MS/ESI(+): m/z 895.29 (17) $[\text{M} + \text{Na}]^+$. HRMS/ESI(+): m/z 895.3070 $[\text{M} + \text{Na}]^+$, calcd for $[\text{C}_{32}\text{H}_{72}\text{O}_{12}\text{Si}_8\text{Na}]^+$ 895.3076. Anal. Calcd for $\text{C}_{32}\text{H}_{72}\text{O}_{12}\text{Si}_8$: C, 44.00; H, 8.31. Found: C, 43.98; H, 8.40.

Octakis(1,1-dimethylpropyl)octasilsesquioxane (4b). Yield: 44%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 1.40 (q, $^3J_{\text{HH}} = 7.5$ Hz, 16H, $-\text{CH}_2-$), 0.97 (s, 48H, $-\text{C}(\text{CH}_3)_2$), 0.92 (t, $^3J_{\text{HH}} = 7.5$ Hz, 24H, $-\text{CH}_3$). ^{13}C NMR (100.5 MHz, CDCl_3): δ (ppm) 32.1 (C_q), 23.1 (CH_3), 20.9 (CH_2), 9.5 (CH_3). ^{29}Si NMR (99.3 MHz, CDCl_3): δ (ppm) -67.2 ; IR: 2963 (w), 2860 (w), 1460 (w), 1260 (w), 1083 (s), 836 (w), 798 (s), 548 (s), 482 (s), 416 (s) cm^{-1} . MS/EI: m/z (%) 984 (10) $[\text{M}]^+$, 914 (10) $[\text{C}_{35}\text{H}_{78}\text{O}_{12}\text{Si}_8]^+$, 844 (30) $[\text{C}_{30}\text{H}_{68}\text{O}_{12}\text{Si}_8]^+$, 774 (10) $[\text{C}_{25}\text{H}_{58}\text{O}_{12}\text{Si}_8]^+$, 704 (5) $[\text{C}_{20}\text{H}_{48}\text{O}_{12}\text{Si}_8]^+$, 71 (100) $[\text{C}_5\text{H}_{11}]^+$. HRMS/ESI(+): m/z 1023.4061 $[\text{M} + \text{K}]^+$, calcd for $[\text{C}_{40}\text{H}_{88}\text{O}_{12}\text{Si}_8\text{K}]^+$ 1023.4061. Anal. Calcd for $\text{C}_{40}\text{H}_{88}\text{O}_{12}\text{Si}_8$: C, 48.73; H, 9.00. Found: C, 48.51; H, 8.89.

Octakis(1,1-dimethylbutyl)octasilsesquioxane (4c). Yield: 40%. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 1.45–1.26 (m, 32H, $-\text{CH}_2-$), 0.98 (s, 48H, $-\text{C}(\text{CH}_3)_2$), 0.87 (t, $^3J_{\text{HH}} = 6.8$ Hz, 24H, $-\text{CH}_3$). ^{13}C NMR (75.4 MHz, CDCl_3): δ (ppm) 42.9 (C_q), 23.6 (CH_3), 20.7 (CH_2), 18.8 (CH_2), 15.0 (CH_3). ^{29}Si NMR (59.6 MHz, CDCl_3): δ (ppm) -67.4 . IR: 2956 (w), 2870 (w), 1469 (w), 1259 (w), 1067 (s), 838 (s), 798 (s), 545 (s), 447 (s) cm^{-1} . MS/EI: m/z (%) 1096 (10) $[\text{M}]^+$, 928 (10) $[\text{C}_{36}\text{H}_{80}\text{O}_{12}\text{Si}_8]^+$, 844 (5) $[\text{C}_{30}\text{H}_{68}\text{O}_{12}\text{Si}_8]^+$, 760 (2) $[\text{C}_{24}\text{H}_{56}\text{O}_{12}\text{Si}_8]^+$, 591 (5) $[\text{C}_{12}\text{H}_{32}\text{O}_{12}\text{Si}_8]^+$, 507 (5) $[\text{C}_6\text{H}_{20}\text{O}_{12}\text{Si}_8]^+$, 85 (100) $[\text{C}_6\text{H}_{13}]^+$. HRMS/ESI(+): m/z 1119.5561 $[\text{M} + \text{Na}]^+$, calcd for $[\text{C}_{48}\text{H}_{104}\text{O}_{12}\text{Si}_8\text{Na}]^+$ 1119.5574. Anal. Calcd for $\text{C}_{48}\text{H}_{104}\text{O}_{12}\text{Si}_8$: C, 52.51; H, 9.55. Found: C, 52.73; H, 9.59.

Octakis(1,1-dimethylpentyl)octasilsesquioxane (4d). One equivalent of TBAF (1 M in THF) was added to a solution of 2 equiv of the corresponding disiloxane-1,1,3,3-tetrol **2d** in THF at room temperature. After the mixture was stirred for 24 h, all volatiles were removed in vacuo and the yellow oil was mixed with acetone. The white precipitate was filtered off and recrystallized from acetone/dichloromethane. Compound **4d** could be obtained as a pale crystalline material in 10% yield.

Yield: 10%. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 3.31–3.26 (m, 16H, $-\text{CH}_2-$), 1.63–1.55 (m, 16H, $-\text{CH}_2-$), 1.42–1.33 (m, 16H, $-\text{CH}_2-$), 1.18 (s, 48H, $-\text{C}(\text{CH}_3)_2$), 0.93 (t, $^3J_{\text{HH}} = 7.1$ Hz, 24H, $-\text{CH}_3$). ^{13}C NMR (75.4 MHz, CDCl_3): δ (ppm) 58.8 (CH_2), 31.8 (C_q), 29.3 (CH_3), 24.1 (CH_2), 19.8 (CH_2), 13.7 (CH_3). ^{29}Si NMR (59.6 MHz, CDCl_3): δ (ppm) -66.9 . HRMS/ESI(+): m/z 1231.6850 $[\text{M} + \text{Na}]^+$, calcd for $[\text{C}_{56}\text{H}_{120}\text{O}_{12}\text{Si}_8\text{Na}]^+$ 1231.6826. Anal. Calcd for $2(\text{C}_{56}\text{H}_{120}\text{O}_{12}\text{Si}_8) \cdot \text{C}_{16}\text{H}_{36}\text{FN}$: C, 57.32; H, 10.37. Found: C, 57.69; H, 10.51.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures and CIF files giving crystallographic data for **2b,d,g** and **4a–d** and spectroscopic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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