

**Silicone Dendrons and Dendrimers from Orthogonal SiH
Coupling Reactions**

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Silicone Dendrons and Dendrimers from Orthogonal SiH Coupling Reactions

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There are many potential applications for precise, large molecular weight silicone structures. The available elegant routes to silicone dendrimers are compromised by the use of reactions that involve acid/base formation: either type of catalyst can initiate silicone equilibration, which can lead to the loss of structural integrity of the dendrimers. Platinum-catalyzed hydrosilylation and $B(C_6F_5)_3$ -catalyzed Piers Rubinsztajn reactions were shown to be orthogonal. Sequential utilization of the two reactions can be applied both convergently and divergently to prepare both silicone dendrons and dendrimers. Precise silicone compounds of molecular weights in excess of 13,500 g/mol were prepared in good to excellent yield without the problems of degradative metathesis.

Introduction

The benefits of well-structured dendrimeric structures arising from both convergent¹ and divergent syntheses are now well recognized.²⁻⁶ Poly(amidoamine)s (PAMAMs),⁷ arguably the best explored materials of this type because of their commercial availability, show particular utility for the delivery of bioactive compounds, including small molecule drugs and for in vitro gene transfection.^{8,9} However, many other dendrimeric systems have been developed that utilize a very broad variety of chemistries and which are targeted to diverse applications.¹⁰

A requirement for any dendrimer synthesis is near perfect conversion during bond formation steps as each generation is added.^{11, 12} An additional requirement is that the iterative reaction conditions leading to higher molecular weight (MW) materials must not affect the structure of the lower generation starting materials. The latter requirement has particularly challenged the development of silicone and carbosiloxane dendrimers¹³ because silicones are susceptible to degradation in the presence of both acids and bases.¹⁴

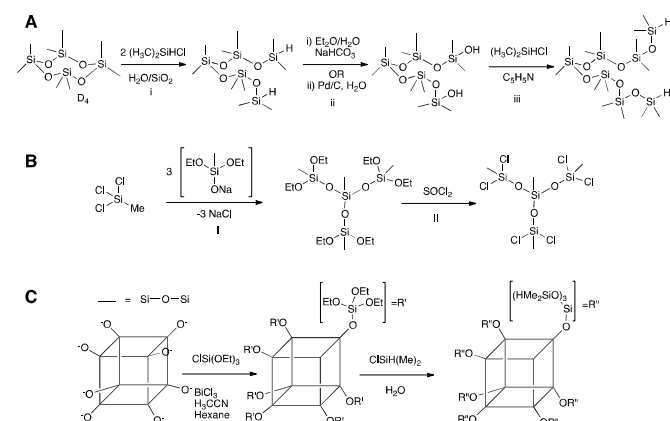
Three beautiful accounts of dendrimeric silicone synthesis have been reported. Although each provides elegant methods leading to larger molecular weight silicones, they utilize reaction conditions that can lead to loss of structural integrity of the dendrimer.

Masamune and co-workers reported a simple three step process to prepare large molecular weight silicone dendrimers of calculated MW of up to 15,073 g/mol.¹⁵ The assembly hinges on the use of chlorosilanes, which undergo to facile hydrolysis with adventitious water. Water leads to both structural defects and an HCl byproduct. The other key reaction uses a basic amine catalyst (Scheme 1A).

Muzafarov and co-workers created one of the most dense dendrimer structures so far reported by taking advantage of sodium oxyorganoalkoxysilanes (Scheme 1B).^{16, 17} Basic

moieties in the monomer and chlorosilane end groups in the evolving dendrimer, are both sensitive to water.¹⁷

Reports from the group of Kuroda focus on routes to silicones of well-defined molecular architecture. In a first report, $BiCl_3$ was used to construct explicit alkoxyxiloxane oligomers with relative ease, avoiding the formation of intermediate silanol groups^{18, 19} (Scheme 1C). In a second report, the use of the use of a two-step silylation process is discussed.^{20, 21} These methods constitute important new methods to prepare well-defined siloxane based macrostructures of precise molecular architecture, but continue to be challenged by the low hydrolytic stability of chlorosilanes.

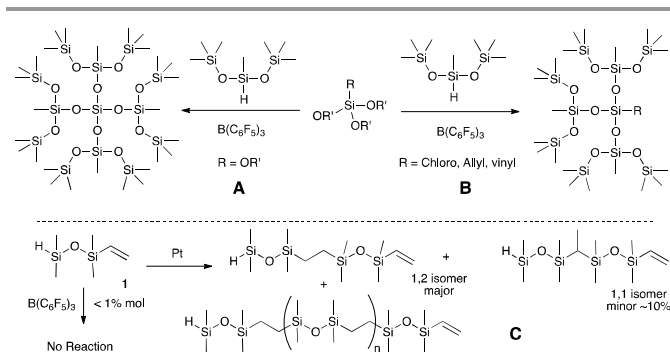


Scheme 1. A: three step process to prepare large MW dendrimers involving: i) ring opening hydrolysis; ii) conversion of Si-H to Si-OH using mild basic conditions on Pd/C; and, iii) coupling to chlorosilanes. B: the use of sodiumoxyorganoalkoxysilanes in the preparation of large MW dendrimers. C: Iterative bismuth-catalyzed condensation of chlorosilanes with silanols, followed by hydrolytic condensation.

The Piers-Rubinsztajn reaction (PR) allows the assembly of small, precise silicone structures,²² including organofunctional silicones, that possess vinyl or allyl groups^{23,24} (Scheme 2A,B), leading to the synthesis of new, well defined surfactants^{25, 26} and a rapid method to prepare siloxane based elastomers^{27, 28} and foams.²⁷ Although the key catalyst $B(C_6F_5)_3$ (BCF) is a strong Lewis acid²⁹ that, with water, forms a Brønsted acid, the conditions of the reaction do not lead to siloxane metathesis.²⁴ The reaction thus fulfills one of the key requirements for dendrimer synthesis.

Controlled dendrimer synthesis also needs at least one additional, orthogonal reaction to allow iterative growth procedures that do not lead to ill-defined hyperbranched polymers. We chose to use platinum-catalyzed hydrosilylation, a highly efficient process (typically >98% yield).³⁰ The only disadvantage of the reaction is that the reaction is highly regioselective but not regiospecific (Scheme 2C).

We reasoned that these two reactions could be combined iteratively to create larger structures. Neither set of reaction conditions affects siloxane bonds, so that any structure that is encoded during synthesis should be able to persist during dendrimer growth. We report on the application of these processes to the generic, high yielding synthesis of silicone dendrons and dendrimers.



Scheme 2. Using the Piers-Rubinsztajn reaction to prepare: A: non-functional; and, B: functional silicone based compounds. C: Platinum-catalyzed hydrosilylation of **1** gives both 1,2- and 1,1-isomers. In the presence of < 1% mol $B(C_6F_5)_3$ hydrosilylation is not observed.

Experimental Section

Materials and Methods

Vinyltetramethyldisiloxane **1**, triethoxysilane, tetraethyl orthosilicate (TEOS), were purchased from Gelest and distilled prior to use. 1,1,1,3,5,5,5-Heptamethyltrisiloxane **3**, pentamethyldisiloxane **4**, phenyldimethylsilane **5** and vinyl(trimethylsiloxy)silane were purchased from Gelest and used as received. Chloropropyltriethoxysilane, chloropropyltrimethoxysilane, chromium (III) acetylacetonate, anhydrous dimethylformamide, sodium azide and tris(pentafluorophenyl)borane (95%) were purchased from Aldrich and used as received. Compound **2** was prepared following literature protocols.²⁵ Commercial solvents: hexane, dichloromethane and toluene were dried over activated alumina prior to use.

¹H NMR, ¹³C NMR and ²⁹Si NMR experiments were recorded at room temperature and performed on Bruker Avance 500 and 600 MHz nuclear magnetic resonance spectrometers. Note: in

the ¹H NMR of compounds formed by hydrosilylation, only data for the major, terminal hydrosilylation isomer (Figure 1) are reported, which comprises >90 % of the product. The minor peaks were only identifiable in low generation molecules. High-resolution mass Spectrometry was performed with a Hi-Res Waters/Micromass Quattro Ultima (Q-TOF mass spectrometer). Gel Permeation Chromatography (GPC) Data was collected on a Viscotek VE 2001 GPC solvent/sample module. MALDI mass spec was collected on a Bruker Autoflex III at McGill University by Dr. Nadim Saade.

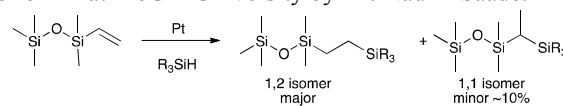


Figure 1: Hydrosilylation produces two isomers

Synthesis of Compound 6

To tetrakis(vinyltetramethyldisiloxane)silane **2** (0.053 g, 0.073 mmol) in an oven dried 25 mL round-bottomed flask were added 1,1,1,3,5,5,5-heptamethyltrisiloxane **3** (0.086g, 0.386 mmol, ~ 5 equiv) and 5 mL of dry hexane. A drop of platinum (0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The homogeneous mixture was then heated to 40 $^{\circ}C$ under a nitrogen atmosphere for ~ 4 h, or until all the vinylic peaks were shown to be consumed via ¹H NMR. The resulting solution was then allowed to stir with activated charcoal (~ 1 g) for 1 h. Once complete, the mixture was gravity filtered and concentrated in vacuo. The concentrate was heated to 170 $^{\circ}C$ under high vacuum for 30 min (1 mmHg) to ensure complete removal of excess volatile starting materials, yielding colourless liquid **6** (isolated yield, 0.075 g, 67%).

¹H-NMR ($CDCl_3$, 600 MHz): δ = 0.42 (m, 8 H, -SiCH₂CH₂Si(CH₃)₂), 0.33 (m, 8 H, SiCH₂CH₂Si(CH₃)₂), 0.08 (M, 72 H, ((Si(CH₃)₃O)₂Si(CH₃)₃), 0.07 (s, 24 H, CH₂Si(CH₃)₂OSi(CH₃)₂O), 0.06 (s, 24 H, CH₂Si(CH₃)₂OSi(CH₃)₂O), -0.02 (m, 12 H, ((Si(CH₃)₃O)₂Si(CH₃)₃) ppm. ¹³C-NMR ($CDCl_3$, 150 MHz): δ = 9.49, 8.99, 1.99, 1.20, -0.4, -1.06 ppm. ²⁹Si-NMR ($CDCl_3$, 119 MHz, 1% w/v Cr(acac)₃): δ = 8.49 (M^{†14}), 6.82 (M), -20.75 (D), -21.34 (D), -109.51 (Q) ppm. HRMS (ES Positive mode): m/z [M+NH₄]⁺ calc. = 1,632.6226; found = 1,634.6277.

Synthesis of Compound 7

To tetrakis(vinyltetramethyldisiloxane)silane **2** (0.054 g, 0.073 mmol) in an oven dried 25 mL round-bottomed flask were added pentamethyldisiloxane **4** (0.054 g, 0.37 mmol, 5 equiv) and 5 mL of dry hexane. A drop of platinum (0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The resulting solution was then heated to 40 $^{\circ}C$ under a nitrogen atmosphere for ~ 4 h, or when all vinylic peaks were shown as consumed via ¹H NMR. The solution was then treated with activated charcoal (~1 g) and allowed to stir for 1 h, gravity filtered and concentrated in vacuo. The remaining solution was then heated to 170 $^{\circ}C$ under high vacuum for 30 min (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **7** (isolated yield, 0.067g, 70%).

¹H-NMR ($CDCl_3$, 600 MHz): δ = 0.39-0.41 (m, 16 H, -OSiCH₂CH₂SiO-), 0.07 (s, 24 H, OSi(CH₃)₂CH₂CH₂), 0.08 (s, 24 H, CH₂OSi(CH₃)₂OSi(CH₃)₃), 0.05 (m, 36 H, OSi(CH₃)₃), 0.03 (s, 24H, OSi(CH₃)₂O Si(CH₃)₂) ppm. ¹³C-NMR ($CDCl_3$, 150 MHz): δ = 9.74, 9.63, 2.13, 1.23, -0.26, -0.36 ppm. ²⁹Si-NMR ($CDCl_3$, 119 MHz, 1% w/v Cr(acac)₃): δ = 8.47 (M),

6.99 (M), -21.36 (D), -109.60 (Q) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1,338.5514; found = 1,338.5526.

Synthesis of Compound 8

To tetrakis(vinyltetramethyldisiloxy)silane **2** (0.076 g, 0.104 mmol) in an oven dried 25 mL round-bottomed flask were added phenyldimethylsilane **5** (0.071 g, 0.521 mmol ~ 5 equiv) and 5 mL of dry hexane. A drop of platinum (0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The solution was then heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or when all vinylic peaks were consumed as shown by 1H NMR. The solution was then treated with activated charcoal (~1 g) and allowed to stir for 1 h, gravity filtered and concentrated in vacuo. The residue was heated at 170 °C under high vacuum for 30 min (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **8** (isolated yield, 0.086 g, 65%).

1H -NMR ($CDCl_3$, 600 MHz): δ = 7.50 (m, 8 H, C_6H_5 , *meta*), 7.34 (m, 12 H, C_6H_5 , *ortho,para*), 0.64 (m, 8 H, $SiCH_2CH_2Si(CH_3)_2$), 0.44 (m, 8 H, $SiCH_2CH_2Si(CH_3)_2$), 0.24 (s, 24 H, $Si(CH_3)_2(C_6H_5)$), 0.05 (s, 24 H $OSi(CH_3)_2OSi(CH_3)_2CH_2$), 0.03 (s, 24 H $OSi(CH_3)_2OSi(CH_3)_2CH_2$) ppm. ^{13}C -NMR ($CDCl_3$, 150 MHz): δ = 139.65, 133.76, 128.88, 127.82, 10.28, 7.20, 1.22, -0.34, -3.46 ppm. ^{29}Si -NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ = 8.31(M), -1.33 (M), -21.27 (D), -109.52 (Q) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1,290.5389; found = 1,290.5430.

Synthesis of Compound 9

To vinyl(trimethylsiloxy)silane (0.313 g, 0.97 mmol) in an oven dried 25 mL round-bottomed flask were added triethoxysilane (0.241 g, 1.47 mmol, 1.5 equiv) and 5 mL of dry toluene. A drop of platinum (0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The homogeneous mixture was then heated to 60 °C under a nitrogen atmosphere and monitored via 1H NMR until all the vinylic peaks were consumed (~ 24 h). Activated charcoal was added to the solution, which was allowed to stir for 1 h, gravity filtered and concentrated in vacuo. The residual oil was heated to 75 °C under high vacuum for 10 min (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **9** (isolated yield, 0.252 g, 59%).

1H -NMR ($CDCl_3$, 500 MHz): δ = 3.84 (q, 6 H, $-SiOCH_2CH_3$, J = 5.85 Hz), 0.09 (t, 9 H, $-SiOCH_2CH_3$, J = 5.85 Hz), 0.55-0.59 (m, 2 H, $-SiCH_2CH_2Si-$), 0.43-0.47 (m, 2 H, $-SiCH_2CH_2Si-$), 0.09 (s, 27 H, $-OSi(CH_3)_3$) ppm. ^{13}C -NMR ($CDCl_3$, 150 MHz): δ = 58.50, 18.45, 5.84, 2.21, 1.88 ppm. ^{29}Si -NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ = 6.35 (M), -44.85 (T), -65.89 (T) ppm. HRMS (ES Positive mode): m/z $[M+H]^+$ calc. = 487.2219; found = 487.2240.

Synthesis of Compound 10

To **9** (0.050 g, 0.115 mmol) in an oven dried 25 mL round-bottomed flask were added pentamethyldisiloxane **4** (0.073 g, 0.49 mmol ~ 4.2 eq) and 5 mL of dry hexane. The solution was then stirred at room temperature for 1 min before the addition of tris(pentafluorophenyl)borane (50 μ l of a solution containing 40 mg dissolved in 1 ml of toluene, 3.9×10^{-3} mmol). After ~ 30 s induction time, moderate evolution of gas and heat from the solution occurred. The solution was then heated to 60 °C for 15 min to ensure complete reaction. The solution was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting mixture was gravity filtered and the liquid phase concentrated under reduced pressure. The residue was then subjected to Kugelrohr distillation under high

vacuum (1 mmHg, 170 °C), to remove excess starting materials, yielding colourless **10** (isolated yield, 0.074 g, 85.6 %).

1H -NMR ($CDCl_3$, 500 MHz): δ = 0.414-0.479 (m, 4 H, $-OSiCH_2CH_2SiO-$), 0.09 (s, 54 H, $OSi(CH_3)_3CH_2CH_2Si(OSi(CH_3)_2OSi(CH_3)_3)_3$), 0.06 (s, 18 H, $OSi(CH_3)_3CH_2CH_2Si(OSi(CH_3)_2OSi(CH_3)_3)_3$) ppm. ^{13}C -NMR ($CDCl_3$, 150 MHz): δ = 6.26, 6.19, 1.97, 1.86, 1.23 ppm. ^{29}Si -NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ = 6.82 (M), 6.86 (M), -22.36 (D), -66.32 (T), -68.49 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 858.3295; found = 858.3320.

Synthesis of Compound 11

To tetrakis(vinyltetramethyldisiloxy)silane **2** (0.250 g, 0.34 mmol) in an oven dried 25 mL round-bottomed flask were added triethoxysilane (0.242 g, 1.47 mmol, 4.3 equiv) and 5 mL of dry hexane. A drop of platinum (0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The homogeneous mixture was heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or until all vinylic peaks were shown to be consumed as determined by 1H NMR. Activated charcoal (~1 g) was added and the mixture was allowed to stir for 1 h, subjected to gravity filtration and the liquid phase was then concentrated in vacuo. The residue was then heated to 100 °C under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **11** (isolated yield, 0.410 g, 86.3 %).

1H -NMR ($CDCl_3$, 500 MHz): δ 3.80 (q, 24 H, $Si(OCH_2CH_3)_3$, J = 10 Hz), 1.21 (t, 2 H, $Si(OCH_2CH_3)_3$, J = 7.5 Hz), 0.54 (s, 16 H, $O_3SiCH_2CH_2Si(OCH_2CH_3)_3$), 0.07 (s, 24 H, $SiOSi(CH_3)_2OSi(CH_3)_2CH_2$), 0.06 (s, 24 H, $SiOSi(CH_3)_2OSi(CH_3)_2CH_2$). ^{13}C -NMR ($CDCl_3$, 125 MHz): δ 58.39, 18.35, 9.11, 1.82, 1.07, -0.52 ppm. ^{29}Si -NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.44 (M), -21.10 (D), -44.49 (T), -109.5 (Q) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1,402.6030; found = 1,402.6062.

Synthesis of Compound 12

To **11** (0.100 g, 0.072 mmol) in an oven dried 25 mL round-bottomed flask were added vinyltetramethyldisiloxane **1** (0.185 g, 1.15 mmol, 16 equiv) and 5 mL of dry hexane. The solution was stirred at room temperature for 1 min before addition of tris(pentafluorophenyl)borane (50 μ l of a solution containing 40 mg dissolved in 1 ml of toluene, 3.9×10^{-3} mmol). After a ~30 s induction time, moderate evolution of gas and heat from the solution occurred. The solution was then heated to 60 °C for 15 min to ensure complete reaction, then allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting mixture was gravity filtered and the liquid fraction concentrated under reduced pressure. The resulting residue was then subject to Kugelrohr distillation under high vacuum (1 mmHg, 170 °C), to remove excess starting materials, yielding colourless **12** (isolated yield, 0.164 g, 77.9 %).

1H NMR ($CDCl_3$, 600 MHz): δ 6.11 (dd, 4 H, $R_3SiCHCHH$, J = 15.0, 20 Hz), 5.91 (dd, 4 H's, $R_3SiCHCHH$, J = 4.0, 15.0 Hz), 5.74 (dd, 4 H, $R_3SiCHCHH$, J = 4.0, 20 Hz), 0.48-0.51 (m, 8 H, $O(H_3C)_2Si(CH_2CH_2SiO(CH_3)_2)$), 0.36-0.39 (m, 8 H $O(H_3C)_2Si(CH_2CH_2SiO(CH_3)_2)$), 0.13 (s, 72 H, $OSi(CH_3)_2CH=CH_2$), 0.04 ppm (s, 120 H, $OSi(CH_3)_2O$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.48 (CH vinyl), 131.77 (CH_2 vinyl), 9.78, 5.87, 1.30, 1.20, 0.45, -0.39 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -8.39 (M), -4.125 (M), -21.33 (D), -67.88 (T), -109.56 ppm (Q). MALDI MS (ES

Positive mode): m/z $[M+Na]^+ = 2,972.956$, $[M+CH_3CN+Na]^+ = 3012.888$.

Synthesis of Compound 13

To **12** (0.025 g, 0.008 mmol) in an oven dried 25 mL round-bottomed flask were added 1,1,1,3,5,5,5-heptamethyltrisiloxysilane **3** (0.034 g, 0.154 mmol ~ 20 equiv) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethylidisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was then heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or until all vinylic peaks were shown to be consumed using 1H NMR. Activated charcoal (~1 g) was then added and the dispersion allowed to stir for 1 h gravity filtered and concentrated in vacuo. The residual material was then heated to 170 °C under high vacuum for 30 min (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **13** (isolated yield, 0.027 g, 86 %).

1H -NMR ($CDCl_3$, 600 MHz): δ 0.32-0.45 (m, 64 H, $[(Si(Osi(CH_3)_3)_2(CH_3)CH_2CH_2Si(CH_3)_2Osi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2Osi(CH_3)_2O)_4]$, 0.08 (s, 216 H, $[(Si(Osi(CH_3)_3)_2(CH_3)CH_2CH_2Si(CH_3)_2Osi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2Osi(CH_3)_2O)_4]$, 0.06 (s, 192 H, $[(Si(Osi(CH_3)_3)_2(CH_3)CH_2CH_2Si(CH_3)_2Osi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2Osi(CH_3)_2O)_4]$, -0.01 (s, 36 H, $[(Si(Osi(CH_3)_3)_2(CH_3)CH_2CH_2Si(CH_3)_2Osi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2Osi(CH_3)_2O)_4]$). ^{13}C -NMR ($CDCl_3$, 150 MHz): δ 10.01, 9.72, 6.04, 2.20, 1.54, -0.18, -0.84 ppm. ^{29}Si -NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.25 (M), 6.76 (M), -20.85 (D), -21.41 (D), -22.20 (D), -67.95 (T), -77.90, -108.9 (Q) ppm. MALDI m/z for $[M+Na]^+ = 5,643.584$.

Synthesis of Compound 14

To **12** (0.020 g, 0.0068 mmol) in an oven dried 25 mL round-bottomed flask were added pentamethylidisiloxane **4** (0.014 g, 0.095 mmol ~ 14 equiv) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethylidisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The solution was heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or when all vinylic peaks had been consumed according to 1H NMR, then treated with activated charcoal (~1 g) with stirring for 1 h. After gravity filtration and concentration in vacuo, the residue was heated to 170 °C under high vacuum for 30 min (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **14** (isolated yield, 0.027 g, 86 %).

1H -NMR ($CDCl_3$, 600 MHz): δ = 0.48-0.52 (m, 8 H, $-OSi(CH_3)_2CH_2CH_2SiO_3^-$), 0.37-0.44 (m, 56 H, $-OSi(CH_3)_2CH_2CH_2SiO_3^-$, $-OSi(CH_3)_2CH_2CH_2Si(CH_3)_2O^-$), 0.01-0.07 ppm (combination of singlets, 372 H, all CH_3 groups). ^{13}C -NMR ($CDCl_3$, 125 MHz): δ = 9.74, 9.64, 5.86, 5.85, 2.12, 1.57, 1.35, 1.17, -0.26, -0.37 ppm. ^{29}Si -NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ = 8.38 (M), 8.26 (M), 7.93 (M), 6.95 (M), -21.38 (D), -22.18 (D), -67.93 (T), -109.56 (Q) ppm. MALDI m/z : for $[M+Na]^+ = 4,758.221$.

Synthesis of Compound 15

To **12** (0.020 g, 0.0068 mmol) in an oven dried 25 mL round-bottomed flask were added phenyldimethylsilane **5** (0.013 g, 0.095 mmol ~ 14 equiv) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethylidisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was then heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or when all vinylic peaks were shown to be consumed via 1H NMR. After cooling, activated charcoal (~1 g) was added and the mixture allowed to stir for 1 h. After gravity filtration and concentration in vacuo the residue

was heated to 170 °C under high vacuum for 30 min (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **15** (isolated yield, 0.025 g, 81 %).

1H -NMR ($CDCl_3$, 600 MHz): δ = 7.47-7.49 (m, 24 H, C_6H_5 , *meta*), 7.31-7.32 (m, 36 H, C_6H_5 , *ortho, para*), 0.62-0.65 (m, 24 H, $-SiCH_2CH_2Si(CH_3)_2C_6H_5$), 0.47-0.51 (m, 8 H, $-OSi(CH_3)_2SiCH_2CH_2SiO_3^-$), 0.40-0.44 (m, 24 H, $-SiCH_2CH_2Si(CH_3)_2C_6H_5$), 0.35-0.39 (m, 8 H, $-OSi(CH_3)_2SiCH_2CH_2SiO_3^-$), 0.24 (s, 72 H, $-SiCH_2CH_2Si(CH_3)_2C_6H_5$), 0.03-0.06 (combination of singlets, 192 H, $Si(Osi(CH_3)_2Osi(CH_3)_2CH_2CH_2Si(Osi(CH_3)_2Osi(CH_3)_2CH_2-)_3)_4$) ppm. ^{13}C -NMR ($CDCl_3$, 150 MHz): δ = 139.58, 133.72, 128.85, 127.80, 10.27, 9.79, 7.18, 5.84, 1.32, -0.36, -3.47 ppm. ^{29}Si -NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ = 8.43 (M), -8.14 (M), -1.37 (M), -21.32 (D), -22.09 (D), -67.93 (T), -109.52 (Q) ppm.

Synthesis of Compound 16

To **12** (0.06 g, 0.02 mmol) in an oven dried 25 mL round-bottomed flask were added triethoxysilane (0.047 g, 0.284 mmol ~ 14 equiv) and 5 mL of dry toluene. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethylidisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The homogeneous mixture was then heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or until all vinylic peaks were shown to be consumed by 1H NMR. Activated charcoal (~1 g) was added and the mixture was allowed to stir for 1 h, gravity filtered and concentrated in vacuo. The residue was then heated to 90 °C under high vacuum for 30 min (1 mmHg) to ensure complete removal of excess triethoxysilane, yielding colourless liquid **16**. (isolated yield, 0.082 g, 82 %).

1H -NMR ($CDCl_3$, 500 MHz): δ 3.81 (q, 72 H, $-OCH_2CH_3$, $J = 10$ Hz) 1.21 (t, 109 H, $-OCH_2CH_3$, $J = 10$ Hz), 0.53 (s, 48 H, 0.01 (s, 36 H, $(CH_3CH_2O)_3SiCH_2CH_2-$), 0.47-0.66 (m, 8 H, $-O_3SiCH_2CH_2Si(CH_3)_2O-$), 0.38-0.41 (m, 8 H, $-O_3SiCH_2CH_2Si(CH_3)_2O-$), 0.06, 0.05, 0.048 ppm (three overlapping singlet's, 192 H, $(-CH_2Si(CH_3)_2Osi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2Osi(CH_3)_2O)_4Si$). ^{13}C -NMR ($CDCl_3$, 150 MHz): δ 58.49, 18.45, 9.80, 9.22, 5.87, 1.94, 1.32, -0.43 ppm. ^{29}Si -NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.36 (M), 8.11 (M), -21.35 (D), -22.02 (D), -44.63 (T), -67.89 (T), -109.37 (Q).

Synthesis of Monohydride Dendron 17

Vinyltris(trimethylsiloxy)silane (2 g, 6.2 mmol) was added to a solution of tetramethylidisiloxane (8.33 g, 62.0 mmol) in 15 mL of dry toluene. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethylidisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was then heated to 40 °C under a nitrogen atmosphere for 3 h, the solvent was removed in vacuo and the remaining liquid was distilled under high vacuum (1 mmHg) at 125 °C yielding pure **17** (2.48 g, 87% yield). Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

1H -NMR ($CDCl_3$, 600 MHz): δ 4.68-4.71 (m, 1 H, $Si(CH_3)_2H$), 0.44-0.47 (m, 2 H, $SiCH_2CH_2Si(CH_3)_2$), 0.33-0.36 (m, 2 H, $SiCH_2CH_2Si(CH_3)_2$), 0.18 (d, $J = 2.72$ Hz, 6 H, $Si(CH_3)_2H$), 0.07 (s, 33 H, $(Si(CH_3)_3O)_3$, $SiCH_2CH_2Si(CH_3)_2$). ^{13}C -NMR ($CDCl_3$, 150 MHz): δ 9.88, 5.91, 1.90, 1.06, -0.77 ppm. ^{29}Si -NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 10.27 (M), 6.77 (M), -7.25 (M), -65.25 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4^+]$ calc. = 474.2199; found = 474.2220.

Synthesis of Monohydride Dendron 18

Vinyltris(pentamethylidisiloxy)silane (1.58 g, 2.81 mmol) was added to a solution of tetramethylidisiloxane (5.36 g, 39.9

mmol) in 15 mL of dry toluene. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was then heated to 40 °C under a nitrogen atmosphere for 3 h. The solvent was then removed in vacuo and the remaining liquid was distilled under high vacuum (1 mmHg) at 160 °C yielding pure **18** (1.08 g, 57% yield).

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ 4.70 (m, 1 H, $\text{Si}(\text{CH}_3)_2\text{H}$), 0.52-0.54 (m, 2 H, $\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$), 0.41-0.44 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}$), 0.16 (d, 6 H, $J = 2.56$ Hz, $\text{Si}(\text{CH}_3)_2\text{H}$), 0.10 (s, 27 H, $[\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.07 (s, 24 H, $[\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O}]_3$). $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ 9.76, 5.91, 1.99, 1.28, 1.07, -0.55 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 99 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ 10.15 (M), 6.80 (M), -7.29 (M), -22.28 (D), -68.38 (T) ppm. HRMS (ES Positive mode): m/z $[\text{M}+\text{Na}^+]$ calc. = 696.2763; found = 696.2782.

Synthesis of Monohydride Dendron 19

Vinyltris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane (1.52 g, 1.98 mmol) was added to a solution of tetramethyldisiloxane (3.53 g, 26.3 mmol) in 15 mL of dry toluene. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The solution was then heated to 40 °C under a nitrogen atmosphere for 3 h, the solvent was removed in vacuo and the remaining liquid was distilled under high vacuum (1 mmHg) at 160 °C yielding pure **19** (1.05g, 60% yield).

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ 4.68-4.72 (m, 1H, $\text{Si}(\text{CH}_3)_2\text{H}$), 0.55-0.57 (m, 2 H, $\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$), 0.43-0.46 (m, 2 H, $\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$), 0.15 (d, $J = 2.86$ Hz, 6 H, $\text{Si}(\text{CH}_3)_2\text{H}$), 0.10 (s, 60 H, $[\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.05 (s, 16 H, $[\text{Si}(\text{CH}_3)_3\text{O}]_2\text{SiCH}_3\text{O}$) + $\text{O}_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$). $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ 7.67, 3.88, 0.05, -0.85, -2.46, -3.82 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 99 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ 10.07 (M), 6.96 (M), -7.43 (M), -66.65 (T), -70.03 (T) ppm. HRMS (ES Positive mode): m/z $[\text{M}+\text{NH}_4^+]$ calc. = 918.3327; found = 918.3304.

Synthesis of Compound 20

To 3-chloropropyltrimethoxysilane (1.00 g, 5.03 mmol) in an oven dried 25 mL round-bottomed flask were added vinyltetramethyldisiloxane **1** (4.04 g, 25.15 mmol \sim 5 eq) and 10 mL of dry hexane. The solution was stirred at room temperature for 1 min before the addition of tris(pentafluorophenyl)borane (50 μ l of a solution containing 40 mg dissolved in 1 ml of toluene, 3.9×10^{-3} mmol). After a \sim 30 s induction time, moderate evolution of gas and heat from the solution occurred. The solution was allowed to cool to room temperature before the addition of neutral alumina (\sim 1.5 g). The resulting mixture was first gravity filtered and then concentrated under reduced pressure. The product was then subjected to Kugelrohr distillation under high vacuum (1 mmHg, 162 °C), to ensure completely pure **20** (isolated yield after distillation, 1.98 g, 62%).

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ 6.12 (dd, 3 H, $J = 14.5$, 20.4 Hz), 5.94 (dd, 3 H, $J = 3.9$, 14.5 Hz), 5.73 (dd, 3 H, $J = 3.6$, 20.4 Hz), 3.50 (t, 2 H, $\text{CH}_2\text{CH}_2\text{Cl}$), 1.82-1.89 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.62-0.65 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2$), 0.16 (s, 18 H, $[\text{CH}_2\text{CHSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.08 (s, 18 H, $[\text{CH}_2\text{CHSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$) ppm. $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ 139.58, 132.11, 47.93, 27.24, 12.28, 1.49, 0.61 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 99 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ -3.84 (M), -20.87 (D), -69.68 (T) ppm. HRMS (ES Positive mode): m/z $[\text{M}+\text{NH}_4^+]$ calc. = 648.2103; found = 648.2109.

Synthesis of Compound 21

To chloropropyltris(vinyltetramethyldisiloxy)silane **20** (0.250 g, 0.395 mmol) in an oven dried 25 mL round-bottomed flask were added 1,1,1,3,5,5,5-heptamethyltrisiloxane **3** (0.396 g, 1.78 mmol, 4.5 equiv) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was heated to 40 °C under a nitrogen atmosphere for \sim 4 h or until all vinylic peaks were consumed, as shown by $^1\text{H NMR}$. The solution was then treated with activated charcoal (\sim 1 g) with stirring for 1 h, the mixture was gravity filtered and the filtrate concentrated in vacuo. The residue was heated to 100 °C under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **21** (isolated yield, 0.483 g, 94%).

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ 3.50 (t, 2 H, $J = 6.93$ Hz, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 1.83-1.88 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.62-0.65 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.33-0.46 (m, 12 H, $[\text{CH}_3((\text{CH}_3)_3\text{SiO})_2\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}-]$), 0.09 (s, 54 H, $[\text{CH}_3((\text{CH}_3)_3\text{SiO})_2\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}-]$), 0.07 (s, 18 H, $[\text{CH}_3((\text{CH}_3)_3\text{SiO})_2\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}-]$), 0.07 (s, 18 H, $[\text{CH}_3((\text{CH}_3)_3\text{SiO})_2\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}-]$), 0.00 (s, 9 H, $[\text{CH}_3((\text{CH}_3)_3\text{SiO})_2\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}-]$). $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ 47.82, 27.31, 12.28, 9.73, 9.23, 2.21, 1.54, -0.19, -0.82 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 99 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ 8.16 (M), 6.43 (M), -21.31 (D), -22.13 (D), -70.19 (T) ppm. HRMS (ES Positive mode): m/z $[\text{M}+\text{NH}_4^+]$ calc. = 1,314.4886; found = 1,314.4889.

Synthesis of Compound 22

To chloropropyltris(vinyltetramethyldisiloxy)silane **20** (0.250 g, 0.395 mmol) in an oven dried 25 mL round-bottomed flask were added pentamethyldisiloxane **4** (0.264 g, 1.78 mmol, 4.5 equiv) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The mixture was then heated to 40 °C under a nitrogen atmosphere for \sim 4 h, or until all vinylic groups were consumed as shown by $^1\text{H NMR}$. The solution was then treated with activated charcoal (\sim 1 g) with stirring for 1 h. Once complete, the mixture was gravity filtered and the filtrate concentrated in vacuo. The residue was then heated to 100 °C under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **22**. (isolated yield, 0.398, 86%). Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ 3.50 (t, 2 H, $J = 6.9$ Hz, $\text{R}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 1.83-1.88 (m, 2 H, $\text{R}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.62-0.65 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.38-0.45 (m, 12 H, $-\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}-$), 0.07 (s, 36 H, $[(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.06 (s, 27 H, $[(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3\text{SiCH}_2-$), 0.04 (s, 18 H, $[(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3\text{SiCH}_2-$). $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ 47.84, 27.33, 12.32, 9.96, 9.86, 2.34, 1.55, -0.04, -0.17 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 99 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ 8.56 (M), 8.35 (M), 7.03 (M), -21.72 (D), -69.71 (T) ppm. HRMS (ES Positive mode): m/z $[\text{M}+\text{NH}_4^+]$ calc. = 1,092.4322; found = 1,092.4318.

Synthesis of Compound 23

To chloropropyltris(vinyltetramethyldisiloxy)silane **20** (0.250 g, 0.395 mmol) in an oven dried 25 mL round-bottomed flask were added phenyldimethylsilane **5** (0.242 g, 1.78 mmol, 4.5 equiv) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μ l of a 2%

by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was heated to 40 °C under a nitrogen atmosphere for ~ 4 h; reaction completion was shown by the absence of vinylic peaks in the ^1H NMR. The solution was treated with activated charcoal (~ 1 g) and the mixture allowed to stir for 1 h. The solution was then gravity filtered and concentrated in vacuo. The residue was then heated to 100 °C under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **23** (isolated yield, 0.29 g, 70%).

^1H -NMR (CDCl_3 , 600 MHz): δ 7.49-7.51 (m, 6 H, $[(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_2]$, *meta*), 7.34-7.35 (m, 9 H, $[(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_2]$, *ortho,para*), 3.42 (t, 2 H, $J = 6.93$ Hz, $\text{O}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 1.78-1.83 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.57-0.60 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.62-0.66 (m, 6 H, $[(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}]$), 0.42-0.45 (m, 6 H, $[(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}]$), 0.25 (s, 18 H, $[(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}]$), 0.05 (s, 18 H, $[(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}]$), 0.04 (s, 18 H, $[(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}]$), 0.04 (s, 18 H, $[(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}]$). ^{13}C -NMR (CDCl_3 , 150 MHz): δ 139.78, 133.97, 129.11, 128.04, 47.82, 27.28, 12.28, 10.51, 7.45, -0.16, -3.26 ppm. ^{29}Si -NMR (CDCl_3 , 99 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ 8.40 (M), -1.33 (M), -21.63 (D), -69.67 (T) ppm. HRMS (ES Positive mode): m/z $[\text{M}+\text{NH}_4]^+$ calc. = 1,056.4228; found = 1,056.4220.

Synthesis of Compound 24

To chloropropyltris(vinyltetramethylsiloxy)-silane **20** (0.110 g, 0.166 mmol) in an oven dried 25 mL round-bottomed flask were added mono Si-H dendron **17** (0.331 g, 0.747 mmol) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethylsiloxy catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was then heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or when all vinylic peaks were consumed, as shown by ^1H NMR. Activated charcoal (~1 g) was added and the mixture allowed to stir for 1 h, gravity filtered and concentrated in vacuo. The residue was then heated to 150 °C under high vacuum (1 mmHg) to ensure complete removal solvent/starting materials, yielding colourless liquid **24** (isolated yield, 0.28 g, 81 %).

^1H -NMR (CDCl_3 , 600 MHz): δ 3.50 (t, 2 H, $J = 6.90$ Hz, $\text{CH}_2\text{CH}_2\text{Cl}$), 1.74-1.77 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.52-0.55 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2$), 0.31-0.37 (m, 18 H, $[(\text{Si}(\text{CH}_3)_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}(\text{Si}(\text{CH}_3)_2\text{O})_3]$), 0.22-0.25 (m, 6 H, $[(\text{Si}(\text{CH}_3)_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}(\text{Si}(\text{CH}_3)_2\text{O})_3]$), -0.01 (s, 81 H, $[(\text{Si}(\text{CH}_3)_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}(\text{Si}(\text{CH}_3)_2\text{O})_3]$), -0.03 (s, 36 H, $[(\text{Si}(\text{CH}_3)_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}(\text{Si}(\text{CH}_3)_2\text{O})_3]$), -0.05 (s, 18 H, $[(\text{Si}(\text{CH}_3)_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}(\text{Si}(\text{CH}_3)_2\text{O})_3]$), -0.05 (s, 18 H, $[(\text{Si}(\text{CH}_3)_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}(\text{Si}(\text{CH}_3)_2\text{O})_3]$), ppm. ^{13}C -NMR (CDCl_3 , 150 MHz): δ 47.63, 27.14, 12.12, 10.09, 9.76, 9.66, 6.00, 1.90, 1.34, -0.23, -0.26, -0.38 ppm. ^{29}Si -NMR (CDCl_3 , 119 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ 8.57 (M), 8.18 (M), 8.13 (M), 7.12 (M), -21.73 (D), -64.62 (T), -69.72 (T) ppm. HRMS (ES Positive mode): m/z $[\text{M}+\text{NH}_4]^+$ calc. = 2,016.7687; found = 2,016.7669.

Synthesis of Compound 25

To chloropropyltris(vinyltetramethylsiloxy)-silane **20** (0.026 g, 0.042 mmol) in an oven dried 25 mL round-bottomed flask were added mono Si-H dendron **18** (0.086 g, 0.126 mmol) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-

tetramethylsiloxy catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or when all vinylic peaks were shown to be consumed by ^1H NMR. Activated charcoal (~1 g) was added and the mixture allowed to stir for 1 h, after which it was gravity filtered and the filtrate concentrated in vacuo. The residue was then heated to 150 °C under high vacuum (1 mmHg) to ensure complete removal solvent/starting materials, yielding colourless liquid **25** (isolated yield, 0.068 g, 61 %).

^1H -NMR (CDCl_3 , 600 MHz): δ 3.49 (t, 2 H, $J = 6.90$ Hz, $\text{CH}_2\text{CH}_2\text{Cl}$), 1.82-1.87 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.61-0.64 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2$), 0.49-0.56 (m, 6 H, $[(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.39-0.46 (m, 18 H, $[(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.09 (s, 81 H, $[(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.07 (s, 36 H, $[(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.06 (s, 54 H, $[(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.04 (s, 18 H, $[(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.03 (s, 18 H, $[(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$). ^{13}C -NMR (CDCl_3 , 150 MHz): δ 47.78, 27.32, 12.31, 10.14, 9.95, 9.86, 6.16, 2.19, 1.53, 1.48, -0.04, -0.18 ppm. ^{29}Si -NMR (CDCl_3 , 99 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ 8.24 (M), 7.72 (M), 7.57 (M), 6.78 (M), -22.16 (D), -22.33 (D), -68.30 (T), -70.15 (T) ppm. HRMS (ES Positive mode): m/z $[\text{M}+\text{NH}_4]^+$ calc. = 2,682.9360; found = 2,682.9324.

Synthesis of Compound 26

To chloropropyltris(vinyltetramethylsiloxy)-silane **20** (0.023 g, 0.037 mmol) in an oven dried 25 mL round-bottomed flask were added mono Si-H dendron **19** (0.100 g, 0.111 mmol) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethylsiloxy catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was then heated to 40 °C under a nitrogen atmosphere for ~ 4 h, at which point all vinylic peaks had been consumed via ^1H NMR. The mixture was treated with activated charcoal (~ 1 g) with stirring for 1 h, gravity filtered and concentrated in vacuo. The residue was then heated to 150 °C under high vacuum (1 mmHg) to ensure complete removal of solvent and starting materials, yielding colourless liquid **26** (isolated yield, 0.076 g, 62%).

^1H -NMR (CDCl_3 , 600 MHz): δ 3.49 (t, 2 H, $J = 6.90$ Hz, $\text{CH}_2\text{CH}_2\text{Cl}$), 1.82-1.87 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 0.61-0.64 (m, 2 H, $\text{O}_3\text{SiCH}_2\text{CH}_2$), 0.54-0.57 (m, 6 H, $[(\text{Si}(\text{OSi}(\text{CH}_3)_3)_2(\text{CH}_3)\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.40-0.46 (m, 18 H, $[(\text{Si}(\text{OSi}(\text{CH}_3)_3)_2(\text{CH}_3)\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.10 (s, 162 H, $[(\text{Si}(\text{OSi}(\text{CH}_3)_3)_2(\text{CH}_3)\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.06 (s, 36 H, $[(\text{Si}(\text{OSi}(\text{CH}_3)_3)_2(\text{CH}_3)\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.05 (s, 27 H, $[(\text{Si}(\text{OSi}(\text{CH}_3)_3)_2(\text{CH}_3)\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.033 (s, 18 H, $[(\text{Si}(\text{OSi}(\text{CH}_3)_3)_2(\text{CH}_3)\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$), 0.028 (s, 18 H, $[(\text{Si}(\text{OSi}(\text{CH}_3)_3)_2(\text{CH}_3)\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}]_3$). ^{13}C -NMR (CDCl_3 , 150 MHz): δ

47.77, 27.33, 12.32, 9.96, 9.88, 6.08, 2.12, 1.53, -0.02, -0.19, -1.69 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 99 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ 8.15 (M), 7.70 (M), 7.66 (M), 6.95 (M), -22.18 (D), -66.66 (T), -67.74 (T), -69.99 (T) ppm. HRMS (ES Positive mode): m/z $[\text{M}+2\text{NH}_4]^{2+}/2$ (doubly charged ion) calc. = 1,686.0691; found = 1,686.0885.

Synthesis of Compound 27

To tetrakis(vinyltetramethyldisiloxy)silane **2** (0.297 g, 0.041 mmol) in an oven dried 25 mL round-bottomed flask were added small monohydride dendron **17** (0.075 g, 0.164 mmol, 4 equiv) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The solution was heated to 40 °C under a nitrogen atmosphere for ~ 4 h: all vinylic peaks in the $^1\text{H NMR}$ had been consumed. Activated charcoal (~ 1 g) was added, and the mixture was allowed to stir for 1 h, gravity filtered and concentrated in vacuo. The residue was heated to 100 °C under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **27** (isolated yield, 0.086g, 82%).

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ = 0.39-0.45 (m, 24 H, $\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$, $\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$), 0.31-0.34 (m, 8 H, $\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O}_3\text{SiCH}_2$), 0.09 (s, 108 H, $(\text{Si}(\text{CH}_3)_3\text{O})_3$), 0.07 (s, 48 H, $\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$), 0.029-0.03 (s, s, 48 H, $\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}$) ppm. $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ = 10.07, 9.74, 9.64, 5.97, 1.88, 1.20, -0.25, -0.28, -0.38 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 119 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ = 8.44 (M), 8.17 (M), 8.11 (M), 7.11 (M), -21.42 (D), -64.61 (T), -109.54 (Q) ppm. HRMS (ES Positive mode): m/z $[\text{M}+\text{NH}_4]^+$ calc. = 2,570.9977; found = 2,571.0056

Synthesis of Compound 28

To tetrakis(vinyltetramethyldisiloxy)silane **2** (0.260 g, 0.036 mmol) in an oven dried 25 mL round-bottomed flask were added linear mono hydride dendron **18** (0.098 g, 0.144 mmol, 4 equiv) and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was heated to 40 °C under a nitrogen atmosphere for ~ 4 h, at which time all vinylic peaks in the $^1\text{H NMR}$ were consumed. The solution was then treated with activated charcoal and the mixture allowed to stir for 1 h, was then gravity filtered and the filtrate concentrated in vacuo. The residue was heated to 100 °C under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **28** (isolated yield, 0.099g, 79%).

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ = 0.49-0.52 (m, 8 H, $(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3\text{SiCH}_2$), 0.39-0.42 (m, 24 H, $\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$, $\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$), 0.08 (s, 108 H, $(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3$), 0.07-0.06 (s,s, 48 H, $\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$), 0.05 (s, 72 H, $(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3$), 0.02 (s, 24 H, $\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{Si}$), 0.02 (s, 24 H, $\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{Si}$) ppm. $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ = 9.93, 9.73, 9.64, 5.94, 1.97, 1.27, 1.19, -1.26, -0.38 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 119 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ = 8.43 (M), 8.19 (M), 8.02 (M), 7.18 (M), -21.43 (D), -21.91 (D), -67.86 (T), -109.55 (Q) ppm. MALDI m/z : for $[\text{M}+\text{Na}]^+$ = 3,470.333.

Synthesis of Compound 29

To tetrakis(vinyltetramethyldisiloxy)silane **2** (0.260 g, 0.036 mmol) in an oven dried 25 mL round-bottomed flask were added monohydride dendron **19** (0.130 g, 0.144 mmol, 4 equiv)

and 5 mL of dry hexane. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was heated to 40 °C under a nitrogen atmosphere for ~ 4 h or when all vinylic peaks in the $^1\text{H NMR}$ were consumed and then activated charcoal (~1 g) was added and the mixture allowed to stir for 1 h, gravity filtered and the filtrate concentrated in vacuo. The resulting residue was then heated to 100 °C under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless liquid **29** (isolated yield, 0.136g, 87%).

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ = 0.54-0.57 (m, 8 H, $(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3\text{SiCH}_2$), 0.40-0.45 (m, 24 H, $\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$, $\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$), 0.10 (s, 216 H, $(\text{Si}(\text{CH}_3)_3\text{OSi}(\text{CH}_3)_2\text{O})_3$), 0.06-0.07 (s,s, 48 H, $\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$), 0.05 (s, 36 H, $((\text{Si}(\text{CH}_3)_3\text{O})_2\text{Si}(\text{CH}_3)_3)$), 0.03 (s, 24 H, $\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{Si}$), 0.02 (s, 24 H, $\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{Si}$) ppm. $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ = 9.75, 9.73, 9.65, 5.86, 1.90, 1.18, -0.25, -0.40, -1.92 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 119 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ = 8.44 (M), 8.19 (M), 8.02 (M), 7.40 (M), -21.42 (D), -66.24 (T), -69.55 (T), -109.53 (Q) ppm. MALDI m/z : for $[\text{M}+\text{Na}]^+$ = 4,359.605.

Synthesis of Compound 30

To **12** (0.018 g, 0.006 mmol) in an oven dried 25 mL round-bottomed flask were added mono Si-H dendron **18** (0.05 g, 0.075 mmol, 12 equiv) and 5 mL of dry toluene. A drop of platinum (0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or when all vinylic peaks were consumed as shown by $^1\text{H NMR}$. Activated charcoal (~ 1 g) was added and the mixture stirred for 1 h, gravity filtered and the filtrate concentrated in vacuo. The resulting residue was then heated to 170 °C under high vacuum for 30 min (1 mmHg) to ensure complete removal of excess starting materials, yielding colourless viscous liquid **30** (isolated yield, 0.058 g, 84 %).

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ 0.41-0.43 (m + m, 32 H, $-\text{CH}_2-$) 0.30-0.33 (m + m, 80 H, CH_2-), -0.10-0.01 (multiple singlet's 876 H $\text{Si}(\text{CH}_3)_2 + \text{Si}(\text{CH}_3)_3$). $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ 9.93, 9.82, 9.73, 9.65, 5.94, 5.86, 1.97, 1.47, 1.32, 1.26, 1.12, -0.27, -0.38, -0.43 ppm. $^{29}\text{Si-NMR}$ (CDCl_3 , 119 MHz, 1% w/v $\text{Cr}(\text{acac})_3$): δ 8.24 (M), 8.15 (M), 8.01 (M), 7.17 (M), 6.72 (M), -22.24 (D), -22.77 (D), -22.99 (D), -67.85 (T), -68.05 (T), -109.58 (Q) ppm. MALDI m/z for $[\text{M}+\text{Na}]^+$ = 11,131.237. GPC PDI = 1.08.

Synthesis of Compound 31

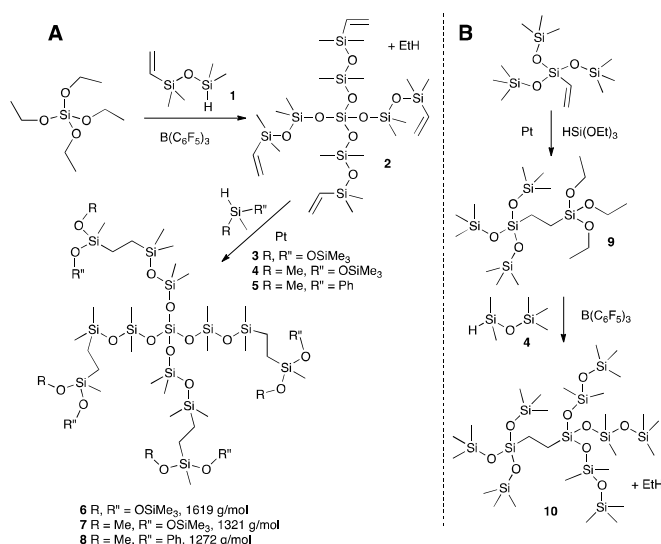
To **12** (0.013 g, 0.004 mmol) in an oven dried 25 mL round-bottomed flask were added mono Si-H dendron **19** (0.046 g, 0.051 mmol, 12 equiv) and 5 mL of dry toluene. A drop of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was added. The solution was heated to 40 °C under a nitrogen atmosphere for ~ 4 h, or when all vinylic peaks were shown to be consumed by $^1\text{H NMR}$. The solution was treated with activated charcoal (~1 g) and the mixture allowed to stir for 1 h, gravity filtered and the filtrate concentrated in vacuo. The residue was then heated to 170 °C under high vacuum for 30 min (1 mmHg) to ensure complete removal of excess starting materials, yielding a colourless viscous liquid **31** (isolated yield, 0.045 g, 76 %).

Results and Discussion

Prior to initiating dendrimer synthesis, it was necessary to ensure that the two reactions involving iterative conversion of alkoxy silanes to hydrosilanes using Piers-Rubinsztajn, and hydrosilanes to vinylsilanes using hydrosilylation, were truly orthogonal. The key monomer used in this process was vinyltetramethyldisiloxane **1**. Compound **1** readily undergoes self-condensation by platinum-catalyzed hydrosilylation (Scheme 2C). $B(C_6F_5)_3$ is also known to induce hydrosilylation, but only at higher catalyst concentrations (>5mol%).³¹ Importantly, no evidence of self-condensation of **1** in our hands was observed if $B(C_6F_5)_3$ concentrations were kept below 1 mol% catalyst (Scheme 2). Model studies, to demonstrate that the iterative PR/hydrosilylation sequence was efficient, started with **1** and $Si(OEt)_4$: subsequent elaboration of the tetravinyl product **2**²⁵ with a series of hydrosilanes **3-5** led cleanly to gram quantities of star shaped silicones of molecular weights from about 1,200-1,600 g/mol in isolated yields of 65-70% after distillation (**6-8**, Scheme 3A): conversions by ¹H NMR exceeded 95%. In order to ensure the process could also be completed in the reverse order (i.e., hydrosilylation first, followed by the PR), $H-Si(OEt)_3$ was hydrosilylated to commercially available vinyltris(trimethyl-siloxy)silane yielding **9**, followed by the direct tethering of **5** using Piers-Rubinsztajn conditions, which led cleanly to **10** (Scheme 3B).

Having demonstrated the Piers-Rubinsztajn and hydrosilylation reactions are orthogonal, attention was turned to the synthesis of dendrons and dendrimers. Compound **2** was subjected first to hydrosilylation with triethoxysilane ($H-Si(OEt)_3$) to generate **11** and then to the Piers-Rubinsztajn with **1** yielding **12**, bearing twelve vinyl groups (Figure 2). It should be noted that the major isomer formed via hydrosilylation was the 1,2-product, which was mixed, however, with small amounts of the 1,1 isomer (~10%), as shown by ¹H NMR: the reaction mixture otherwise showed the absence of other products (Figure 2). The MALDI mass spectrum indicate the presence of single compound exhibiting $[M+Na]^+$ and $[M+CH_2CN+Na]^+$ peaks at 2,972.956 and 3,012.888 g/mol, respectively. There were no other peaks, for example, indicating dimers, other oligomers or dendrimers with defects. The GPC exhibited a small shoulder on the high molecular weight side of the curve that constitutes approx. ~10 % of the desired peak (Supporting Information). We ascribe this to compounds in the mixture containing a higher than average portion of the 1,1-isomers.

G2 dendrimers of MW 4,500-5,600 g/mol could also be prepared using this process. For example, by capping **12** with hydrosilanes **3**, **4** and **5** yields **13**, **14** and **15** (Figure 2, Supporting Information), respectively: yields for the coupling ranged from 81-86%. Efforts to expand this process to larger generation dendrimers by first forming G2-type dendrimers **16** from $H-Si(OEt)_3$ were hampered by lower than expected yields. We ascribe this to the sensitivity of alkoxy groups to traces of moisture, which the available apparatus could not avoid. Although the by-product EtOH is not problematic, as is the case of chlorosilanes (HCl), hydrolysis and condensation led to molecular weight broadening.



Scheme 3. A. Preparation of tetrakis(vinyltetramethyldisiloxy)silane **2** and hydrosilylation using hydrosilanes **3-5**. B. Iterative hydrosilylation, then the PR reaction to give **10**.

Larger molecular weight and functional silicone macrostructures were prepared using a convergent method. The resulting silicone dendrons were designed to be monofunctional for use in larger dendrimers or other syntheses. Examples of monohydrido compounds, **17**, **18** and **19**, prepared in two steps, are shown in Scheme 4A. Monovinyl-silicones were first prepared via Piers-Rubinsztajn conditions starting from vinyltriethoxysilane²⁴ and subsequently modified using hydrosilylation and a large excess of tetramethyldisiloxane (~30 eq of Si-H to vinyl): the resulting compounds were isolated by distillation.

Dendrons bearing organic groups could be similarly prepared: such molecules are starting materials for polymeric surfactants.^{25, 26} For example, the reaction of vinyltetramethyldisiloxane **1** with chloropropyltrimethoxysilane in the presence of $B(C_6F_5)_3$ gave chloropropyltris(vinyltetramethyldisiloxy)silane **20** which was distilled at reduced pressure (at the cost of a lower yield) to ensure complete purity (~1 mmHg, 162 °C). Larger organofunctional dendrons **21**, **22** and **23** were prepared from commercially available starting materials **3-5** (Scheme 4B). The size of these compounds could be further increased by addition of the complex monofunctional SiH-containing dendrons **17**, **18** and **19** (Scheme 4C). Thus, **24**, **25** and **26** with molecular weights ranging from 2,000 to 3,350 g/mol and with various styles of branching could be prepared in two simple steps.

The combination of divergent and convergent routes could be exploited to give larger dendrimeric structures. G1-type carbosiloxane dendrimers resulting from the simple combination of smaller, siloxane based cores, such as **2** with mono Si-H compounds **17**, **18** and **19** led to moderately sized siloxane macrostructures **27**, **28** and **29**. Higher molecular weight polymers were available by combining G2-dendron **12** with compound **18** to yield monodisperse macrostructure **30** with molecular weight 11,131 g/mol in a coupling yield of 84%: G2-dendron **19** was analogously combined with **12** to give **31** (molecular weight 13,773 g/mol; as potassium adduct, 13,813 g/mol, by MALDI with a PDI of 1.08 by GPC, Figure 3B).

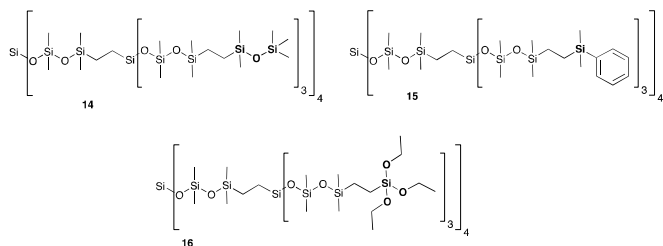
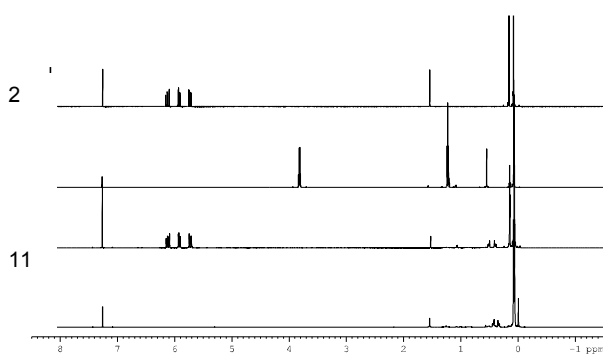
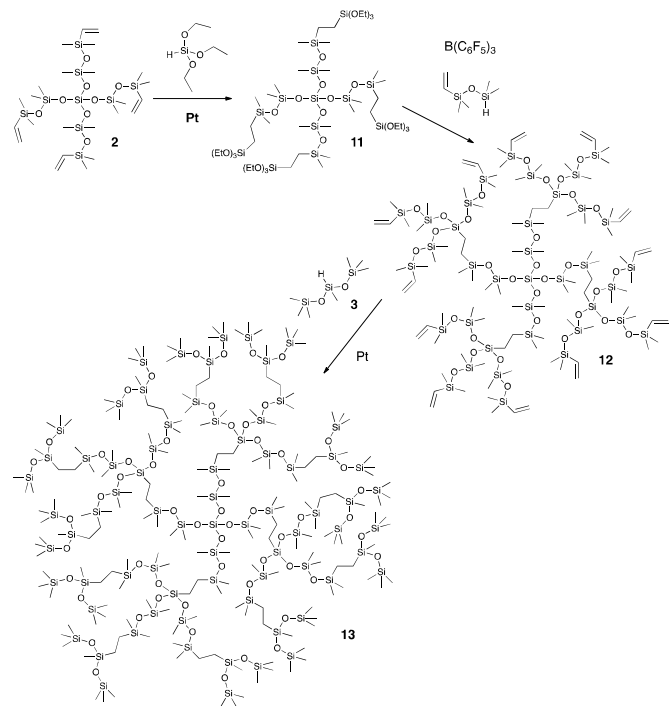
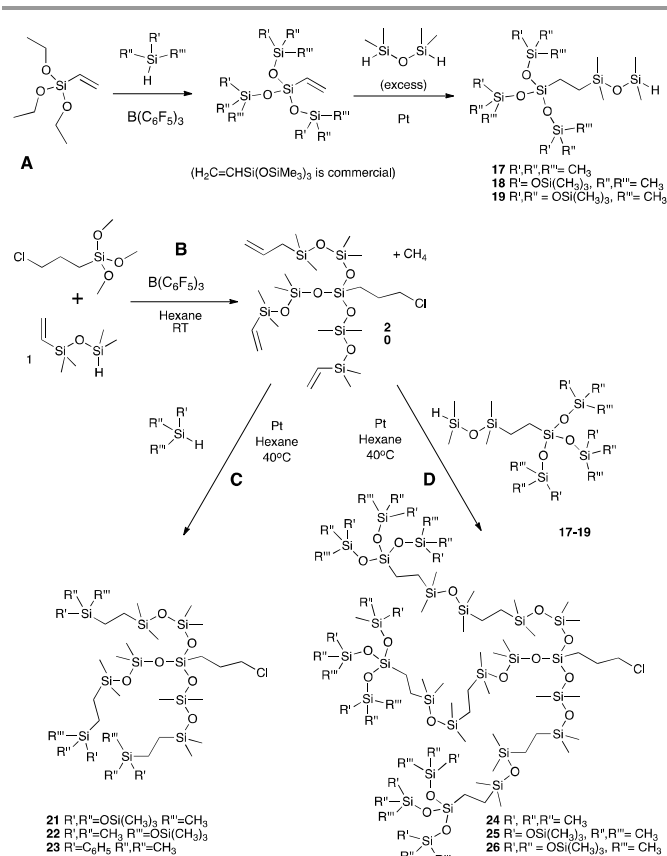
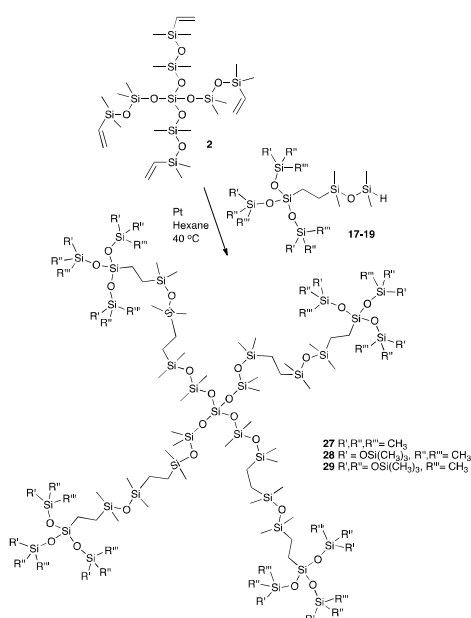


Figure 2. NMR of compounds containing four vinyl groups **2**, **11** containing twelve ethoxy groups, and **12** containing twelve vinyl groups. End capping **12** leads with **3** leads to **13**. Analogous reactions with **12** lead to **14-16** with MW ranging from 4500-5600 g/mol.



Scheme 4. Synthesis of A: monohydride dendrons and B-D: chloropropyl-functional dendrons.

A key challenge in the synthesis of precise, highly branched silicones is avoiding the introduction of acids or bases that can lead to silicone metathesis and loss of structural integrity. The combination of efficient Piers-Rubinsztajn coupling and platinum-catalyzed hydrosilylation provides a simple and efficient strategy to assemble carbosiloxane macrostructures – using neither acidic nor basic conditions, and avoiding chlorosilanes – under conditions that do not elicit silicone metathesis. The alternation of these two processes can be applied in both divergent and convergent strategies: dendrimers currently as large as 13,773 g/mol can be readily prepared in few steps in good to excellent yields: the lowest yielding reaction was 56%, but most were in excess of 80%. The functional tolerance of the Piers-Rubinsztajn reaction permits the synthesis of mono- and multi-functional silicones, which allows the ready preparation of large molecular with precise structures, and which can be combined with other classes of small molecules and polymers.



Scheme 5: By simply tethering prepared dendrons to tetravinyl core **2**, moderately sized carbosiloxane G1 type dendrimers **27**, **28** and **29** can be prepared in few steps.

Conclusions

The Piers-Rubinsztajn condensation and platinum-catalyzed hydrosilylation can be combined convergently or divergently to produce silicones of precise structures with molecule weights up to about 5000 g mol^{-1} . The reactions are perfectly orthogonal, and neither reaction leads to degradation of the silicone structures. Although neither route on its own led to error free dendimeric structures, the formation of intermediate sized dendrons by divergently could be capped by convergently generated dendrons to prepare dendrimers of molecules weights in excess of $13,000 \text{ g mol}^{-1}$.

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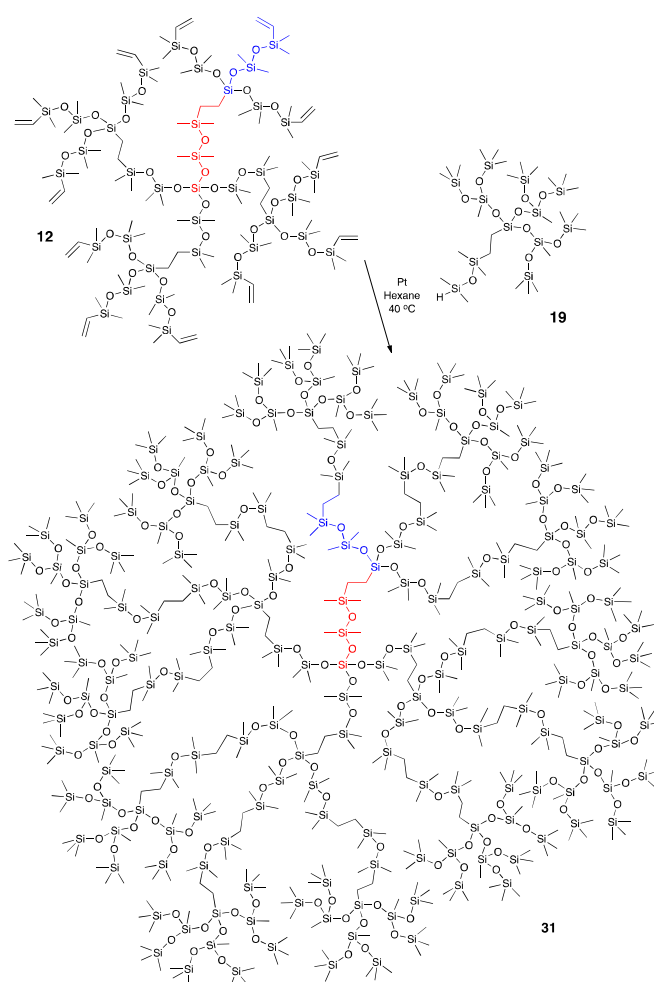


Figure 3. Preparation of A: mono functional Si-H dendrons for use in convergent dendrimer synthesis and B: combining a divergent and convergent approach to give a G2-like carbosiloxane dendrimer **31**.

Notes and references

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† The General Electric nomenclature for silicones, where M = Me_3SiO - (monofunctional), D = $\text{Me}_2\text{SiO}_{2/2}$ (bifunctional), T = $(\text{MeSiO})_{3/2}$ (trifunctional) and Q = $\text{SiO}_{4/2}$ (tetrafunctional).

Electronic Supplementary Information (ESI) available: MALDI MS of **12**, **14**, **29**, **30**, and **31**. See DOI: 10.1039/b000000x/

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