

Facile Synthesis of Dendron Branched Silicone Polymers

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Supporting Information

Experimental

Materials

n-Butyllithium (nominally 2.5 M) was purchased from Sigma Aldrich was shown by titration before use to have a concentration of 1.725 M. Chlorodimethylvinylsilane, triflic acid and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt's catalyst) in xylene (Pt ~2%) were purchased from Sigma Aldrich and used as received. Chromium (III) acetylacetonate was purchased from Sigma Aldrich and was used as received as a relaxation agent for ²⁹Si NMR experiments. Tris(pentafluorophenyl)borane (B(C₆F₅)₃, BCF catalyst) was purchased from Alpha Aesar and used as received. Allyltrimethoxysilane, bis(trimethylsilylsiloxy)methylsilane, pentamethyldisiloxane, octamethylcyclotetrasiloxane (D₄), 1,3,5,7-tetramethylcyclotetrasiloxane (D^H₄), hexamethylcyclotrisiloxane (D₃) and hexamethyldisiloxane, HMS-053 **6** (25,200 g/mol, 5.6% MeHSiO) and HMS-992 **10** (~2,000 g/mol, mole %: 100% MeHSiO) were purchased from Gelest and used as received (Figure S1). Commercial solvents including hexane, toluene and tetrahydrofuran were dried using an activated alumina column prior to use.

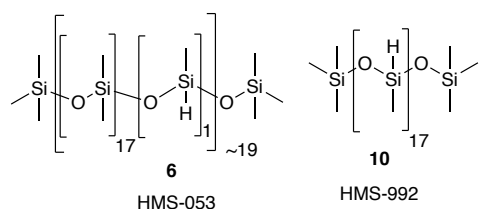


Figure S1: Functional polymers from Gelest. HMS-053 **6** and HMS-992 **10**.

Methods

^1H NMR, ^{13}C NMR and ^{29}Si NMR experiments (at 600, 150 and 119 MHz, respectively) were recorded at room temperature on a Bruker Avance 600MHz nuclear magnetic resonance spectrometer.

GPC data was collected on a Viscotek GPC Max (VE 2001 GPC Solvent/Sample Module) using a Viscotek VE 3580 RI Detector and a Viscotek 270 Dual Detector using a PolyAnalytik Superes PAS-101 (8mmx30cm) column with a single pore, 6nm particle size, a plate count >18,000, and an exclusion limit of 1.5K. The column was packed with hard styrene-divinylbenzene gel. The samples were run in toluene.

FTIR data was collected on a Nicolet 6700 FTIR using Thermo Electron's OMNIC software.

Viscosity measurements were performed on two rheometers. A cone-and-plate Stresstech Rheometer by ATS RheoSystems was used for the majority of the measurements. The stress range was set between 0.1 and 150Pa for a logarithmic sample set, with a 1s delay time between 70 measurements. Select measurements were made on a TA Instruments Discovery HR-3 Hybrid Rheometer with a 40mm steel Peltier plate. The shear rate was set between 0.1 and 500 s^{-1} for a logarithmic sample set with 5 points per decade.

***n*-BuMe₂SiD₈SiMe₂HC=CH₂[†] 1**

D₃ (44.3892 g, 199.538 mmol) was weighed into a 1 L three-neck round-bottomed flask that was then flushed with nitrogen before capping and leaving under a slow nitrogen flow. Dry hexane (120 mL) was added with a syringe and the solution was left to stir for ~15 min, until all of the D₃ had dissolved. *n*-BuLi was added dropwise (18 mL of 1.73 M and 13 mL of 2.2 M in cyclohexanes, 59.7 mmol) over the course of ~30 min. The reaction was left to stir for 2 h at room temperature. Dry THF (16 mL) was added to the reaction, which was left stirring for 48 h. Chlorodimethylvinylsilane in excess (12 mL, 87.0 mmol) was added dropwise. The reaction was left stirring overnight. The reaction was transferred to a clean, one-neck 1 L round-bottomed flask and hexane, THF and

[†] Silicone nomenclature: M = OSiMe₃; D = OSiMe₂.

excess chlorodimethylvinylsilane were removed under reduced pressure. The solution was then filtered through Celite packed with dry hexane and then excess hexane was removed from the filtrate under reduced pressure. Any impurities or excess cyclics were distilled off at 150 °C for 45 min and the final yield of **1** was 36.66 g (75% yield).

¹H NMR (CDCl₃, 600MHz): δ 6.16-6.10 (dd, 1H, *J*=15.15 Hz, *J*=21.6 Hz), 5.95-5.92 (dd, 1H, *J*=4.3 Hz, *J*=15.15 Hz), 5.76-5.72 (dd, 1H, *J*=4.3 Hz, *J*=21.1 Hz), 1.35-1.28 (m, 4.5H), 0.90-0.87 (t, 3H, *J* = 7.0 Hz), 0.54-0.52 (t, 2H, *J* = 9.2 Hz), 0.16 (s, 6H), 0.07 (m, 65H) ppm.

Allyltris(pentamethyldisiloxanyl)silane 2

Allyltrimethoxysilane (5.0328 g, 31.017 mmol) was added to a 250 mL round-bottomed flask. Dry hexanes (~10 mL) were added to the reaction and the flask was capped and flushed with nitrogen. BCF catalyst solution (110 mL, 0.0365 g/mL toluene, 7.84 x 10⁻³ mmol) was added before slowly adding in excess pentamethyldisiloxane (22.7582 g, 153.401 mmol). In between additions of pentamethyldisiloxane, four additional 10 mL amounts of BCF catalyst solution were added. After ~45 min the reaction was shown to be complete by ¹H NMR and ~1.5 g of neutral alumina was added to the flask to remove the BCF. The solution was left to stir for ~1 h before gravity filtering the product and rinsing with hexane. Hexanes were removed under reduced pressure, yielding 14.6443 g of **2** (85% yield).

¹H NMR (CDCl₃, 600 MHz): δ 6.13 (dd, 1H, *J* = 14.8, 20.4 Hz), 5.93 (dd, 1H, *J* = 3.8, 14.8 Hz), 5.74 (dd, 1H, *J* = 3.8, 20.4 Hz), 1.57 (d, 2H, *J* = 7.9 Hz), 0.19-0.05 (m, 46H) ppm. ¹³C NMR (CDCl₃, 150 MHz): δ 133.86-133.73, 114.4, 22.32, 2.04, 1.31 ppm. ²⁹Si NMR (CDCl₃, 119 MHz, Cr(acac)₃): δ 6.99, -20.91 to -21.72, -72.99 to -74.66 ppm. ES+ MS *m/z* for [M + NH₄]⁺ = 576.4 (impurity at 632.4 and 824.4).

Allyltris(bis(trimethylsiloxy)methylsilyl)silane 3

Allyltrimethoxysilane (5.0087 g, 30.868 mmol) was added to a 250 mL round-bottomed flask. Dry hexanes (~10 mL) were added to the reaction and the flask was capped and flushed with nitrogen. BCF catalyst solution (600 μL, 0.0400g/mL toluene, 4.68 x 10⁻² mmol) was added before slowly

adding excess bis(trimethylsiloxy)methylsilane (34.4652 g, 154.900 mmol). In between additions of bis(trimethylsiloxy)methylsilane, four additional 200 mL amounts of BCF catalyst solution were added. The reaction was left under nitrogen overnight. Neutral alumina (~1 g) was added to the flask. The solution was left to stir for ~1 h before gravity filtering the product and rinsing with hexane. Hexanes were removed under reduced pressure. Excess bis(trimethylsiloxy)methylsilane was removed by distillation at 120 °C for ~45 min yielding 19.4302 g of **3** (81% yield).

^1H NMR (CDCl_3 , 600MHz): δ 6.13 (dd, 1H, J = 14.8, 20.4 Hz), 5.93 (dd, 1H, J = 3.8, 14.8 Hz), 5.74 (dd, 1H, J = 3.8, 20.4 Hz), 1.57 (d, 2H, J = 7.9 Hz), 0.20-0.02 (m, 70H) ppm. ^{13}C NMR (CDCl_3 , 150MHz): δ 133.69, 114.51, 22.09, 1.96, -1.88 ppm. ^{29}Si NMR (CDCl_3 , 119MHz, $\text{Cr}(\text{acac})_3$): δ 7.89, -66.28 ppm. ES+ MS m/z for $[\text{M} + \text{NH}_4]^+$ = 798.4 (impurity at 854.5).

$\text{Me}_3\text{SiO}[(\text{Me}_2\text{SiO})_n(\text{MeHSiO})_m]_z\text{SiMe}_3$, $n = 10$, $m = 1$ $z \sim 2.5$ MW = 2200 g/mol **4**
 D_4 (92.15 g, 310.669 mmol), D^{H}_4 (7.47 g, 31.047 mmol), and hexamethyldisiloxane (7.60 g, 46.817 mmol) were weighed into a 1 L round-bottomed flask and stirred for 10 min. Triflic acid (400 mL, 4.52 mmol) was added to the reaction. The reaction was left for 48 h at room temperature. Magnesium oxide (~4 g) was added to quench the acid and this was left to stir overnight. Dry hexane (~75 mL) was added and the reaction was left stirring for ~3 h. The reaction was filtered through Celite packed with hexane before removing hexanes from the filtrate under reduced pressure. This reaction was heated at 160 °C under high vacuum (1 mmHg) in three separate batches to remove excess cyclics and smaller polymers, yielding 91 g of product (85% yield).

^1H NMR (CDCl_3 , 600MHz): δ 4.69 (m, 1H), 0.17-0.08 (m, 70H). ^{13}C NMR (CDCl_3 , 150MHz): δ 2.00, 1.25 ppm. ^{29}Si NMR (CDCl_3 , 119MHz, $\text{Cr}(\text{acac})_3$): δ 7.26, -21.64, -37.57 ppm. GPC Mn: 2270, Mw: 5000, PDI: 2.21.

Note that this reaction was duplicated at a later date to generate a similar polymer that was mostly used in these experiments. ^1H NMR (CDCl_3 , 600MHz): δ 4.68 (s, 1H), 0.17 to -0.01 (m, 70H). Mn (GPC) is ~2200 g/mol.

Me₃SiO[(Me₂SiO)_n(MeHSiO)_m]_zSiMe₃, n = 10, m = 1 z~4.4 MW = 3700 g/mol 5

D₄ (92.2668 g, 311.061 mmol), D^H₄ (7.4142 g, 24.996 mmol), and hexamethyldisiloxane (2.9140 g, 17.9456 mmol) were weighed into a 1 L round-bottomed flask and stirred for 10 min. Triflic acid (400 mL, 4.52 mmol) was added to the reaction. The reaction was left for 48 h at room temperature. Magnesium oxide (~4 g) was added to quench the acid and this was left to stir for ~2 h. Dry hexane (~75 mL) was added and the reaction was left stirring overnight. The reaction was filtered through Celite packed with hexane before removing the hexanes from the filtrate under reduced pressure. This reaction was heated at 180 °C under high vacuum (1 mmHg) in three separate batches to remove excess cyclics and smaller polymers, yielding 86.5818 g of product in the stillpot (84% yield).

¹H NMR (CDCl₃, 600MHz): δ 4.68 (m, 1H), 0.24-0.01 (m, 70H). ¹³C NMR (CDCl₃, 150MHz): δ 1.27, -0.84 ppm. ²⁹Si NMR (CDCl₃, 119MHz, Cr(acac)₃): δ 7.69, -21.65, -36.49 ppm. MALDI m/z = 3753. GPC Mn: 3700, Mw: 7300, PDI: 1.95.

Me₃SiO(Me₂SiO)_n(MeHSiO)_m]_zSiMe₃, n = 17, m = 1 z~ 20 MW = 25200 g/mol 6

¹H NMR (CDCl₃, 600MHz): δ 4.69 (m, 1H), 0.17-0.08 (m, 101.7H) ppm. ²⁹Si NMR (CDCl₃, 119MHz, Cr(acac)₃): δ 7.26, -21.64, -37.57 ppm. GPC Mn: 25188, Mw: 36538, PDI: 1.45.

General Procedure for the Preparation of Branched Silicones 7-9 (shown for 8-2-5')

5 (3.8285 g, 5.76 mmol SiH) was weighed out into a 25 mL round-bottomed flask before capping and stirring under nitrogen for 5 min. The **2** branch (1.6043 g, 2.8751 mmol) was added to the flask using a syringe and needle and left stirring for 10 min prior to adding of Karstedt's catalyst (109 mL of 0.011 g/mL of toluene, 6.29 x 10⁻⁵ mmol) through the septum. The reaction was left for overnight at room temperature (this reaction has been shown to finish to completion within 24 h); ¹H NMR confirmed that **2** had been consumed and therefore this reaction was shown to be complete. Activated carbon (~0.1 g) was added to the reaction to quench the catalyst and this was stirred for 3 h prior to adding ~10 mL of hexanes. The mixture was left overnight and filtered through Celite

packed with hexanes. Hexanes were removed under reduced pressure to yield 1.5 g of **8-2-5'** (28 % yield).

^1H NMR (CDCl_3 , 600MHz): δ 4.68 (s, 0.85H), 1.47-1.41 (m, 2H), 0.59-0.56 (m, 4H), 0.19 to -0.3 (m, 170H) ppm. ^{13}C NMR (CDCl_3 , 150MHz): δ 22.60, 19.43, 17.32, 2.04, 1.24, -0.28 ppm. ^{29}Si NMR (CDCl_3 , 119MHz, $\text{Cr}(\text{acac})_3$): δ 7.25-6.96, -20.56 to -22.91, -37.58, -69.22 ppm.

NOTE: The ^1H NMR given is for a polymer with a type **2** branch. The ^1H NMR data for polymers modified with branch type **1** vs **2** vs **3** were virtually identical, differing only in the integration of residual SiH and the large SiMe peaks near 0 ppm. We provide representative data for polymers bearing each of the branch types. A full listing of reaction formulations is provided in Table S1.

Type **1** branch polymer

^1H , ^{13}C and ^{29}Si NMR for **8-1-5** (polymer **5** to bearing 5.3% linear type **1** branches):

^1H NMR (CDCl_3 , 600MHz): δ 4.68 (m, 0.8H), 1.32-1.29 (m, 4H), 0.89-0.87 (t, 3H, $J=6.65$ Hz), 0.55-0.52 (t, 2H, 8.6 Hz), 0.46-0.40 (m, 4H), 0.18-0.07 (m, 191H) ppm. ^{13}C NMR (CDCl_3 , 150MHz): δ 26.64-25.67, 18.19, 14.02, 9.55, 8.95, 1.27-0.43, -0.37 ppm. ^{29}Si NMR (CDCl_3 , 119MHz, $\text{Cr}(\text{acac})_3$): δ 8.29-7.26, -20.55 to -22.13, -37.57 ppm.

Type **3** branch polymer

^1H , ^{13}C and ^{29}Si NMR for **8-3-5** (polymer **5** to bearing 5.3% linear type **3** branches):

^1H NMR (CDCl_3 , 600MHz): δ 4.68 (m, 1H), 1.45-1.44 (m, 2H), 0.62-0.58 (m, 4H), 0.10-0.07 (m, 187H) ppm. ^{13}C NMR (CDCl_3 , 150MHz): δ 22.81, 19.43, 16.89, 2.32, 1.48, -1.69 ppm. ^{29}Si NMR (CDCl_3 , 119MHz, $\text{Cr}(\text{acac})_3$): δ 7.60-7.12, -20.56 to -22.77, -37.58, -65.92 to -66.42 ppm.

Table S1: Recipes for Branched Silicone Polymers and Viscosity ^a

Backbone	Type of Branch	Backbone (g)	mmol SiH	Branch (g)	Branch mmol	Branched Monomers %	Yield g (%)	NMR MW	GPC MW	Viscosity (Pa·s) ^b
4 ^c	N/A									0.04
7-1-9	1	2.4001	3.6154	3.9612	4.8921	9.0	4.7 (88)	14490		0.05
7-1-5		3.3092	4.9849	2.0162	2.4901	5.1	4.6 (86)	3610		0.06
7-1-3		3.9056	5.8833	1.4371	1.7749	3.2	4.6 (86)	2550		0.04
7-1-2		4.3718	6.5856	0.8302	1.0253	1.6	4.4 (85)	2810		0.04
7-2-8	2	3.5523	5.3511	2.9850	5.3495	8.5	5.5 (84)	3140		0.08
7-2-8'		3.3594	5.0606	2.9082	5.2118	8.2	4.3 (59)	3490	5630	0.09
7-2-7		3.8069	5.7347	1.6240	2.9103	6.5	2.7 (50)	3300		0.10
7-2-6		3.9995	6.1154	1.6845	3.0188	5.6	2.1 (37)	2850		0.10
7-2-3		4.1740	6.2877	1.0800	1.9355	3.4	4.1 (78)	2670		0.05
7-2-3'		4.5025	6.885	1.1045	1.979	3.3	0.64 (64)	2490		0.06
7-2-2		4.5934	6.9194	0.6505	1.1658	1.9	4.0 (76)	2480		0.04
7-2-2'		5.0021	7.6	0.6224	1.1154	1.6	0.60 (60)	2140		0.05
7-3-8	3	3.1481	4.7423	4.1601	5.3335	8.4	5.4 (66)	5060		0.21
7-3-8'		2.9994	4.5183	3.5244	4.5185	8.2	2.86 (44)	3990		0.13
7-3-6		3.5400	5.3326	2.2086	2.8315	5.8	5.0 (87)	3340		0.15
7-3-3		3.8475	5.7958	1.3545	1.7365	3.3	4.5 (87)	2880		0.09
7-3-2		4.2348	6.3792	0.7451	0.9552	1.8	4.4 (88)	2570		0.05
5 ^c	N/A									0.07
8-1-9	1	2.4001	3.6155	4.0273	4.9738	9.1	4.1 (53)	12620	10580	0.14
8-1-6		3.3119	4.9890	2.3776	2.9364	6.2	5.1 (90)	7290	5460	0.26
8-1-5		3.3183	4.9986	2.0183	2.4927	5.3	4.4 (82)	7060	11100	0.25
8-1-3		3.9086	5.8879	1.4217	1.7558	3.0	3.9 g (73)	5670	5250	0.20
8-1-2		4.3010	6.4790	0.7912	0.9772	1.6	4.0 (78)	5720	12170	0.15
8-2-9	2	3.3045	4.9779	3.0142	5.5408	9.1	3.1 (51)	7620	11020	0.64
8-2-6		3.8265	5.7642	1.5925	2.8539	5.9	1.5 (28)	5580	36600	0.80
8-2-5		15.2271	22.9669	6.3109	11.3099	5.3	16.48 (77)	5960	5350	0.23
8-2-5'		3.8285	5.76	1.6043	2.8751	4.9	(60)	5300		0.21
8-2-3		4.2707	6.4333	1.0224	1.8323	3.3	2.8 (53)	4760	5450	0.24
8-2-3'		4.2129	6.3413	1.0617	1.9027	3.0	0.73 (70)	4860		0.26
8-2-2		4.6210	6.9610	0.5821	1.0432	1.7	.4 (85)	5950	6700	0.22
8-2-2'		4.5918	6.9116	0.5808	1.0408	1.5	0.73 (70)	4590		0.12
8-3-9	3	3.0298	4.5641	4.1502	5.3208	8.7	4.0 (62)	8950	6470	0.70
8-3-9'		3.0018	4.5183	3.5262	4.5208	8.6	5.78 (88)	8470		0.36
8-3-8		3.0057	4.5242	4.0060	5.1359	8.1	6.25 (95)	9080		0.32
8-3-5		3.5092	5.2862	2.0601	2.6411	5.3	3.2 (57)	5930	7640	2.23
8-3-3		3.8722	5.833	1.3623	1.7465	3.2	4.5 (86)	5290	4660	0.22
8-3-2		4.2626	6.4211	0.7491	9.6038	1.6	4.4 (88)	5710	4240	0.27

6^c	N/A							25200	0.40
9-1-5	1	4.9953	3.7900	1.9781	2.4430	4.6	4.99 (72)	49210	0.65 ^d
9-1-3		5.0031	3.7960	1.1242	1.3884	2.6	5.14 (84)	42360	0.52 ^d
9-1-1		4.5750	3.4712	0.4991	0.6164	0.8	1.51 (75)	32070	0.33 ^d
9-2-6	2	4.9891	3.7854	2.2520	4.0358	5.5	3.96 (50)	32680	1.38 ^d
9-2-5		5.0781	3.8529	1.7794	3.1889	4.6	4.87 (71)	30940	4.78 ^d
9-2-4		5.0772	3.8522	1.3645	2.4453	3.5	4.99 (77)	29280	1.85 ^d
9-2-3		5.0648	3.8428	0.7669	1.3744	2.6	3.87 (66)	38550	0.71 ^d
9-2-1		5.0099	3.8011	0.3809	0.6826	1.1	4.96 (92)	30340	0.60 ^d
6^{cd}	N/A								0.74 ^d
9-2-5''	2	4.9891	3.7854	2.2520	4.0358	5.5	3.96 (50)	32680	2.07
9-2-3''		5.0288	3.8155	1.4210	2.5466	3.4	0.54 (54)	27700	2.53
9-2-3'''		4.5337	3.4398	0.9888	1.7720	2.6	4.32 (80)	26220	3.14
9-2-2''		5.0244	3.8121	0.7760	1.3907	1.9	0.64 (64)	25860	0.98
9-2-1''		5.0252	3.8127	0.4132	0.7405	1.1	0.81 (81)	26840	1.08
9-3-5	3	4.9226	3.7349	3.2247	4.1342	5.2	5.99 (74)	38770	0.80 ^d
9-3-5'		4.9958	3.7904	2.9967	3.8419	4.8	6.63 (83)	35880	0.91 ^d
9-3-3		5.0047,	3.7972	1.9478	2.4972	3.2	4.130 (59)	30970	0.88 ^d
9-3-2		5.0537	3.8344	1.0668	1.3677	1.9	4.64 (76)	26210	0.66 ^d
9-3-1		5.0145	3.8046	0.5234	0.6710	0.9	3.83 (69)	28110	0.49 ^d
PHMS									
10-1	1	0.0970	1.6167	1.3645	1.6581	60.0			N/A
10-2	2	0.0962	1.6033	0.9292	1.6652	61.0			N/A
10-3	3	0.0965	1.6083	1.3679	1.7537	60.0			N/A

^a The concentration of Karstedt's catalyst was set to ~20 ppm, relative to the available SiH content. Depending on the specific reaction different concentrations of Karstedt's catalyst in toluene were used (e.g., 0.0171, 0.0058, 0.0123 g/mL in toluene).

^b Except for polymers noted by footnote d, viscosity measurements were performed using a cone-and-plate Stresstech Rheometer by ATS RheoSystems.

^c The Mn of the backbone silicone polymers was **7** 2200 g/mol; **8** 3700 g/mol, and **9** 25200 g/mol

^d Viscosity of these samples we obtained using a TA Instruments Discovery HR-3 Hybrid Rheometer.

General Procedure for Control Reactions – Branching an HPDMS Backbone

The following NMR survey experiments were carried out to simply follow the conversion of SiH to SiC with compound **10**. Conversion was shown in ^1H NMR spectra by analyzing the SiH resonances (1H, 4.68 ppm) relative to the Si-CH₂CH₂-Si bond formation (4H, ~0.6 ppm). Conversions of ~60% were observed from the crude ^1H NMR spectra; note, the NMR spectra contained residual vinyl groups from unreacted starting branch materials, presumably for steric reasons. These signals are not included in the listings below.

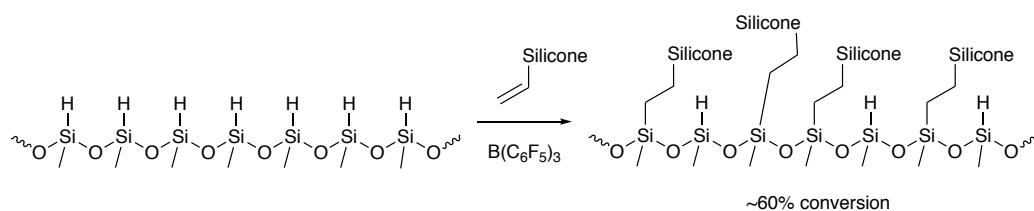


Figure S2: Branching of poly(hydromethylsiloxane) **10**.

Addition of **1** to **10** HMS-992

HMS-992 (0.0970 g, 1.6167 mmol of SiH); **1** (1.3645 g, 1.6851 mmol); Karstedt's catalyst (26 mL of 0.0110 g/mL of toluene, 1.50×10^{-5} mmol). The reaction was left stirring overnight until completion.

^1H NMR (CDCl_3 , 600MHz): δ 4.71 (s, 0.68H), 1.33-1.29 (m, 4H), 0.89-0.87 (m, 3H), 0.56-0.52 (m, 2H), 0.46 (bs, 4H), 0.15-0.05 (m, 29`0H) ppm.

Addition of **2** to **10** HMS-992

10 (0.0962 g, 1.6033 mmol of SiH) was added to a round-bottomed flask and capped. Compound **2** (0.9292 g, 1.6652 mmol, excess) was added by syringe through a septum. The mixture was left to stir under nitrogen for 5 min before adding Karstedt's catalyst (26 mL of 0.0110 g/mL of toluene, 1.50×10^{-5} mmol). The reaction was left stirring for 2 d and no further changes were observed using ^1H NMR. Activated carbon (~0.1 g) was added to quench the catalyst. This was stirred for several hours before adding ~2 mL of dry hexanes. The mixture was left overnight prior to filtering through Celite packed with dry hexane. Hexanes were removed under reduced pressure.

^1H NMR (CDCl_3 , 600MHz): δ 4.68 (s, 0.64H), 1.53-1.41 (m, 2H), 0.62-0.51 (m, 4H), 0.21 to -0.1 (m, 80H) ppm.

Addition of 3 to 10 HMS-992

10 (0.0965 g, 1.6083 mmol of SiH); **3** branch (1.3679 g, 1.7537 mmol); Karstedt's catalyst (26 mL of 0.0110 g/mL of toluene, 1.50×10^{-5} mmol). The reaction was left stirring overnight until completion.

^1H NMR (CDCl_3 , 600MHz): δ 4.68 (s, 0.74H), 1.46-1.42 (m, 2H), 0.61-0.54 (m, 4H), 0.19 to -0.1 (m, 125H) ppm.