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"*A posteriori*" modification of carbosilane dendrimers and dendrons: their activation in core and branch positions

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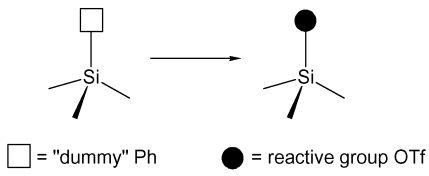
The introduction of phenyl groups at different points on carbosilane dendrimers allows their acidolytic conversion to highly reactive triflato groups which in turn are readily substituted by anionic nucleophiles. Core phenylated first–fourth generation dendrimers were synthesized from tri(allyl)phenylsilane by an alternating sequence of hydrosilylation and allylation steps. Similarly, carbosilane dendrimers containing phenyl-Si groups at the branching points and in the periphery were prepared from tetraallylsilane which was hydrosilylated with $PhHSiCl_2$. Reaction of the phenylated dendrimers with triflic acid in toluene cleanly gave the silyl triflate derivatives, provided that the correct stoichiometry of the reagents was used. In the presence of a large excess of triflic acid the $SiMe_3$-end groups are slowly converted to $SiMe_2(OTf)$-units. The proof of concept was provided by the fixation of a $\{Ph_2PCH_2\}$ group using the lithiated diphenylphosphinomethanide Ph_2PCH_2Li, obtained by cleavage of $Ph_3SnCH_2PPh_2$ with PhLi, as well as a lithiated ether-alcohol functionalized triphos derivative to the core of a third generation carbosilane dendrimer.

Introduction

Among the many known classes of dendrimers which have been developed during the past 2.5 decades,[1] dendritic carbosilanes were found to be particularly suited as platforms for further functionalization.[2] This is due to their high kinetic and thermodynamic stability and the low polarity of the Si–C bond. This inertness has even enabled the selective oxygenation of the end groups in carbosilane dendrimers with H_2O_2 and wide diversity of types of functionalization even under harsh reaction conditions.[3]

The first carbosilane dendrimer was reported as early as 1978 by Fetters and co-workers,[4] however, the field really opened up in the 1990s after the seminal contributions by van der Made and van Leeuwen *et al.*,[5] Roovers *et al.*,[6] Muzafarov *et al.*[7] as well as from Seyferth's group.[8]

The aim of this work was the possibility of selectively functionalizing carbosilane dendrimers in the core, the branching units and at end groups *subsequent* to their divergent synthesis. The key step in the growth sequence is the hydrosilylation of olefinic end groups, a catalytic reaction which is not very tolerant towards functional groups. It was thus desirable to convert relatively inert molecular fragments to highly reactive functionalities within the dendrimer structure. A well established method of functionalization in carbosilane chemistry is the cleavage of Si-phenyl units by strong mineral acids, in particular trifluoromethansulfonic acid.[9] While frequently employed in the synthesis of "simple" silicon compounds this method has not been used in dendrimer chemistry.



The strategy is thus straightforward: introducing phenyl groups at different points of a carbosilane dendrimer as "dummy" functions which can be selectively converted to highly reactive triflato groups which in turn are readily substituted by anionic nucleophiles. To which degree dummy functions in topologically different environments are completely convertible to triflates was a practical question to be resolved in this study. Finally, we were interested in establishing the possibility of using these activated dendrimers for the immobilization of phosphine ligands, which may be employed in catalytic applications of these systems.

Results and discussion

Synthesis of G1–G4 carbosilane dendrimers containing a $PhSiR_3$ core

The syntheses of the core phenylated first–fourth generation dendrimers **1**–**10** were carried out according to the method established for carbosilane dendrimers by Roovers, van Leeuwen and Seyferth.[5,6,8] As the core molecule we chose tri(allyl)phenylsilane from which the dendrimer growth was achieved by an alternating sequence of hydrosilylation and allylation steps (Scheme 1).

The hydrosilylations were carried out in benzene using Karsted's catalyst which avoided the formation of possible regioisomers. The chloroterminated carbosilanes were then reacted with (allyl)MgBr giving the next-generation dendrimers containing allyl end groups. While compounds **3**–**6**, which were employed as branching elements in composite polymers with polyolefins, have been reported previously,[10] they remained incompletely characterized. The final step in the dendrimer synthesis was the methylation of the end groups using MeMgCl (Scheme 2).

The third- and fourth-generation core-phenylated dendritic carbosilanes **7** and **10** were the objects of study in the subsequent acidolytic activation and functionalization steps.

Synthesis of carbosilane dendrimers containing phenyl-Si groups at the branching points and at the periphery

With the aim of synthesizing a carbosilane dendrimer which is phenylated both at the branching points as well as the end groups, tetraallylsilane[11] was hydrosilylated with $PhHSiCl_2$ giving compound **11** (Scheme 3). In the ^1H NMR spectrum of the compound the outer methylene groups of the propylene units resonate as triplets at δ 0.58 and 1.35 ppm, the latter being assigned to the protons adjacent to the $SiPhCl_2$ groups, while

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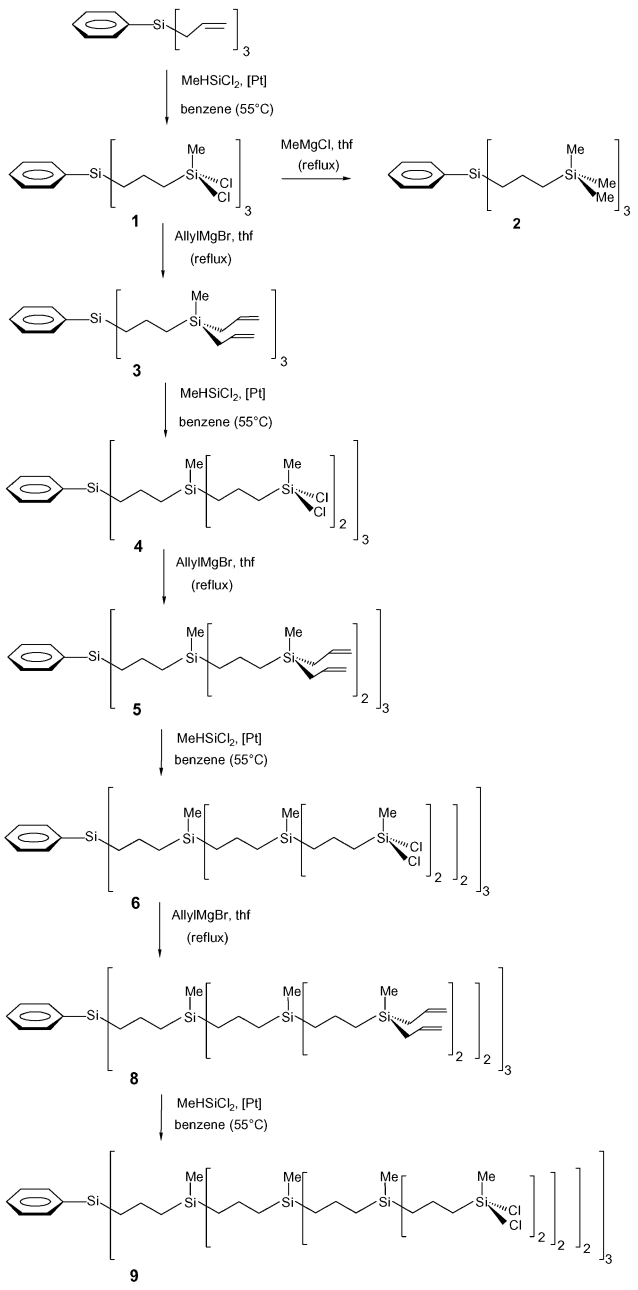


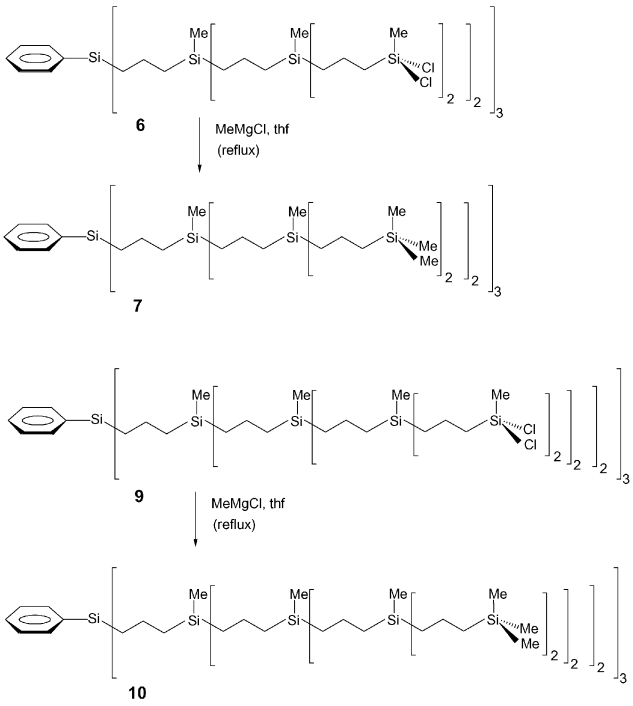
Scheme 1 Synthesis of the G0–G3 carbosilane dendrimers **1**–**7**, **8**, **9** containing a $PhSiR_3$ core.

signal of the CH_2-group in the middle is observed as a multiplet at δ 1.46–1.77. The ^{13}C NMR signals are observed at δ 15.8, 17.3 and 24.9 ppm. The ^{29}Si nucleus at the core position resonates at δ 1.5 ppm whereas the peripheral $SiPhCl_2$ groups give rise to a ^{29}Si NMR signal at δ 18.3 ppm.

Reacting **11** with allylmagnesium bromide in thf giving compound **12** and a subsequent further hydrosilylation step with $PhHSiCl_2$ yielded the first-generation dendrimer **13** which was subsequently methylated with MeMgCl in THF to give $Si[CH_2CH_2CH_2Si(Ph)[CH_2CH_2CH_2Si(Ph)Me_2]_2]_4$ (**14**) (Scheme 3) which was characterized, similar to the other compounds, by elemental analysis, ^1H, ^{13}C, ^{29}Si NMR and IR spectroscopy, as well as FAB mass spectrometry.

Acidolytic cleavage of the phenyl-Si groups in dendrimers with triflic acid giving triflato-Si core units

The acidolytic cleavage of the core-phenylated carbosilane dendrimers was carried out using compounds **2**, **7** and **10** (Scheme 4). Reaction of carbosilane **2** with three molar equivalents of triflic acid in toluene cleanly gave the silyl triflate derivative (a complete



Scheme 2 Methylation of the $SiMeCl_2$ end groups of the G2 and G3 carbosilane dendrimers **6** and **9**.

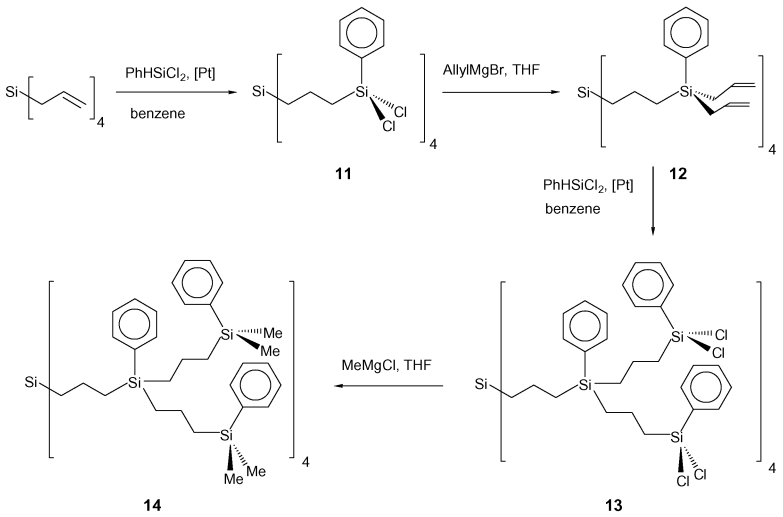
cleavage of the Si-phenyl unit could also be achieved with one molar equivalent of triflic acid albeit at a much slower conversion rate). The quantitative conversion could be readily followed by ^1H NMR spectroscopy which showed the absence of the phenyl resonances at the end of the reaction. The chemical shift of the other resonances of the reaction product **15** differed only slightly from those of **2**. In the $^{13}C\{^1H\}$ NMR spectrum a quartet resonance at δ 118.4 ppm is observed which is due to the CF_3-group of the triflate.

As for the first-generation dendrons **2** and **15**, the ^1H, ^{13}C and ^{29}Si NMR spectra of the third- and fourth-generation products **16** and **17** closely resemble those of the phenylated starting materials **7** and **10**, with only the signals of the phenyl groups being absent. The shift of the resonances in the $^{29}Si\{^1H\}$ NMR spectrum of δ −3.8 ppm for **7** to δ 39.7 ppm for **16** and from δ −3.8 ppm for **10** to δ 39.8 ppm for **17** indicates the substitution of the core phenyl unit by a triflato function.

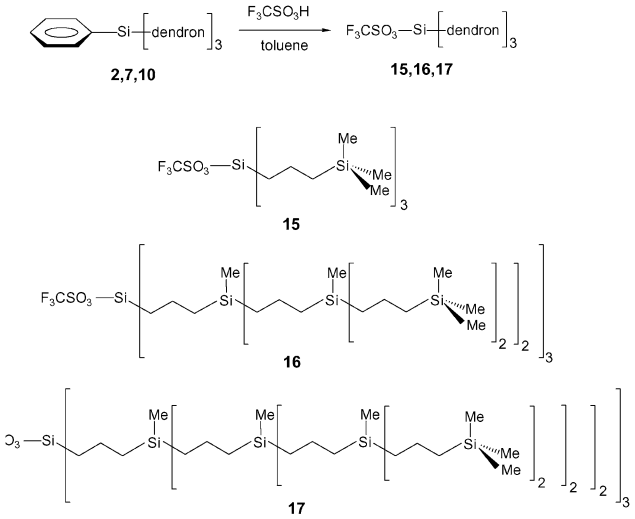
In order to obtain high selectivities in the acidolytic cleavage it is important to closely observe the correct stoichiometry of the reagents. In the presence of an excess of triflic acid the $SiMe_3$-end groups are slowly converted to $SiMe_2(OTf)$-units. To study this side reaction we exposed compound **2** to a tenfold excess of the acid, which not only led to the cleavage of the core-phenyl group but a complete and clean conversion of all three $SiMe_3$ termini to dimethylsilyltriflato units giving compound **18** (Scheme 5). Following the reaction by ^1H NMR spectroscopy showed that the phenyl group is very rapidly eliminated with a subsequent slower cleavage of the Si–CH_3 bonds.

The selectivity of this reaction is remarkable in that only one methyl group per $SiMe_3$ unit is cleaved in spite of the large excess of the acid. This is due to a significant decrease of electron density at the silicon atom upon replacement of a CH_3 group by the triflate thus deactivating this position with respect to further acidolytic transformations, a behaviour which has been previously noted in silicon chemistry.[9b] The subsequent reaction step therefore occurs at a different $SiMe_3$ unit in the periphery.

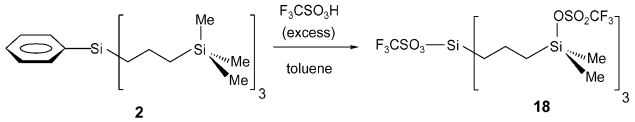
A controlled and rapid acidolytic transformation both at the branching points and the end groups was achieved by reaction of the phenylated first generation dendrimer **14** with 12 equivalents of triflic acid, cleanly giving the dodecatriflate **19** (Scheme 6). In the ^1H NMR spectrum of compound **19** all signals are shifted



Scheme 3 Synthesis of the carbosilane dendrimers **11**–**14** containing phenyl-Si groups at the branching points and in the periphery.



Scheme 4 Acidolytic cleavage of the core phenyl-Si groups in $PhSiR_3$ dendrimers with triflic acid giving triflato-Si core units.



Scheme 5 Acidolytic cleavage of the core phenyl-Si group in **2** and conversion of the $SiMe_3$ end groups into $SiMe_2(OTf)$ groups in the presence of a large excess of triflic acid.

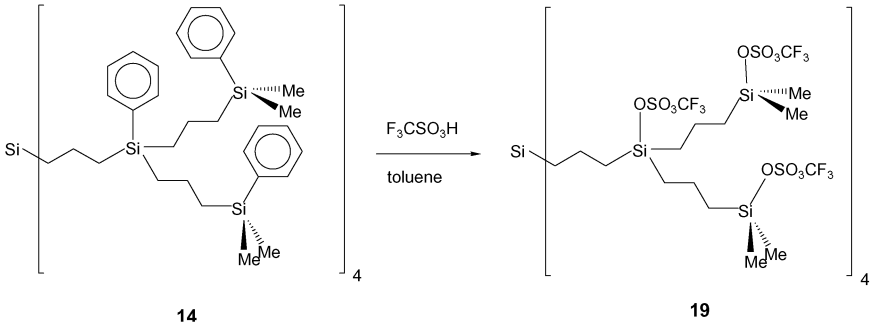
to lower field due to the introduction of twelve electronegative triflato groups, while there is a complete absence of phenyl resonances. The same general trend is observed in the $^{13}C\{^1H\}$ NMR spectrum of the compound. The synthesis of **19** clearly demonstrates the versatility of the acidolytic modification of phenylated dendrimers which is feasible in the core, branching and endgroup positions of a dendritic carbosilane.

Fixation of a monodentate and a tripodal phosphine to the core of a G3–$R_3Si(OTf)$ carbosilane dendrimer

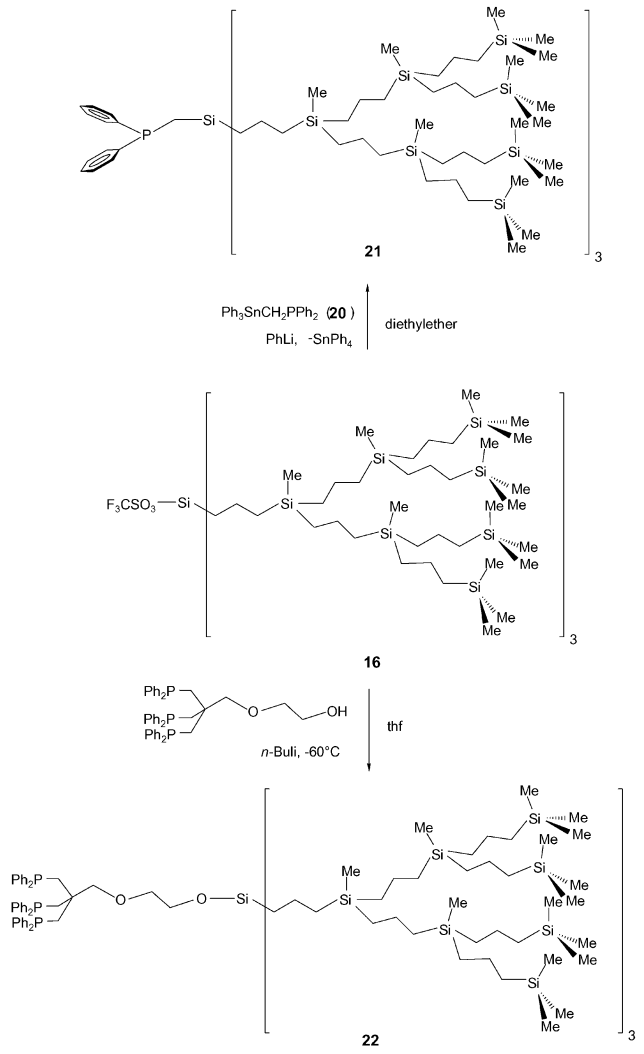
The acidolysis of the phenyl groups provided a means of activation of a relatively inert carbosilane dendrimer. In order to demonstrate the possibility of "*a posteriori*" functionalization we attached two different ligand systems *via* different linker functions to the silyltriflato units of the third generation dendrimer **16**.

The first such modification concerned the introduction of a $\{Ph_2PCH_2\}$ group using the lithiated diphenylphosphinomethanide Ph_2PCH_2Li. The latter may be synthesized by direct lithiation of R_2PCH_3 with lithium alkyls,[12] however, this method generally leads to variable degrees of metallation of the methyl phosphine and consequently to product mixtures. In order to avoid this complication we chose a different synthetic route for Ph_2PCH_2Li by nucleophilic cleavage of $Ph_3SnCH_2PPh_2$ with PhLi. This method is based on previous work by Kauffmann *et al.*[13] as well as the group of one of us,[14] and produced the desired lithium methanide very cleanly. Upon addition of a stoichiometric amount of dendrimer **16** and subsequent work up the target compound **21** was isolated as a colourless oil in good yield (Scheme 7).

As a second target for ligand fixation we employed an ether-alcohol functionalized triphos derivative which we had previously attached to the periphery of carbosilane dendrimers employed in hydrogenation catalysis.[15] Reaction of **16** with the *in situ* lithiated tripodal phosphine readily gave the dendritic



Scheme 6 Acidolytic cleavage of the phenyl-Si groups at the branching points and in the periphery of **14** giving the highly reactive triflato-Si derivative **19**.



Scheme 7 Fixation of a monodentate and a tripodal phosphine to the core of the G3–$R_3Si(OTf)$ carbosilane dendrimer **16**.

derivative **22**. As for compound **21** the main difference in the NMR spectra of this functionalized system with respect to those of **16** concerns the methylene protons adjacent to the Si-core (δ 0.86 ppm) as well as the protons in the ethylene bridge of the linker at the triphos ligand.

Conclusion

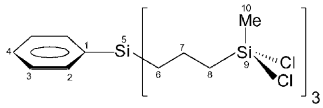
In this work we have presented a convenient strategy to introduce "masked" functionality into carbosilane dendrimers. The dendrimer synthesis is performed with the chemically relatively inert phenylsilane derivatives which do not interfere negatively with hydrosilylation catalysis. Acidolytic cleavage of the phenyl-Si units using stoichiometric amounts of triflic acid then generates highly reactive triflatosilyl units at the core, branching points or the periphery of carbosilane dendrimers which allow a facile subsequent nucleophilic substitution at these points. This method allows the introduction of functional groups, catalytic sites *etc.* into carbosilane dendrimers "*a posteriori*" to their synthesis.

Experimental

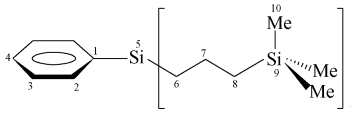
All manipulations were performed under nitrogen. Solvents were dried according to standard methods and saturated with nitrogen. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze–pump–thaw" cycles and stored over 4-Å molecular sieves. Solids were separated from suspensions by filtration through dried Celite or by centrifugation. The ^1H, ^{19}F and ^{13}C Si NMR spectra were recorded on Bruker AC 200, Bruker Avance 250 and Bruker AMX 400 FT NMR spectrometers (reference: tetramethylsilane), using the residual protonated solvent peak (^1H) or the carbon resonance (^{13}C). IR spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out by the microanalytical service at the chemistry department at Strasbourg. Triallylphenylsilane,[16] tetraallylsilane,[11] $HO(CH_2)_2OCH_2C(CH_2PPh_2)_3$[15] and iodomethyltriphenylstannane[17] were prepared according to published procedures. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of the compounds

$PhSi[CH_2CH_2CH_2Si(Me)Cl_2]_3$ (1). Phenyltriallylsilane (1.84 g, 8.07 mmol), $MeHSiCl_2$ (4.18 g, 36.3 mmol) and 50 µl of Karstedt's catalyst were slowly heated in 5 ml of benzene until a weakly exothermic reaction set in and the colourless solution turned pale yellow. The reaction mixture was stirred at 55 °C for 16 h. After cooling to room temperature, the volatiles were removed *in vacuo* and compound **1** was obtained as an analytically pure, pale yellow oil. Yield: 4.63 g (8.07 mmol, 100%). ^1H NMR (400.14 MHz, $CDCl_3$, 295 K): δ 0.76 (s, 9 H, H-10), 0.98 (t, 6 H, $^3J_{HH}$ = 8.5 Hz, H-6), 1.22 (t, 6 H, $^3J_{HH}$ = 7.9 Hz, H-8), 1.56–1.63 (m, 6 H, H-7), 7.38–7.50 (m, 5 H, H-2,H-3, H-4). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 295 K): δ 5.4 (C-10), 15.8 (C-6/7/8), 17.2 (C-6/7/8), 25.7 (C-6/7/8), 128.0 (C-3), 129.2 (C-4), 133.9 (C-2), 136.0 (C-1). $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$, 295 K): δ −3.4 (Si-5), 32.3 (Si-9). IR (neat): ν 3069vw, 2925m, 1451vw, 1427w, 1403w, 1339w, 1261s, 1148m, 1109m, 1021w, 943w, 906m, 815s, 787s, 738m, 700m, 536s cm^{-1}. $C_{18}H_{32}Si_4Cl_6$ (573.51 g mol^{-1}): calc.: C 37.70, H 5.63; found: C 37.76, H 5.68%.

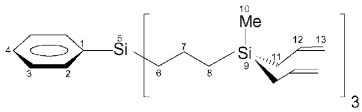


$PhSi[CH_2CH_2CH_2SiMe_3]_3$ (2). To a solution of compound **1** (2.29 g, 4.00 mmol) in 40 ml of thf, which was cooled to −5 °C, were added 11.2 ml (33.6 mmol) of a 3.00 molar solution of methylmagnesium chloride in thf over a period of 1.5 h. The reaction mixture was refluxed for 23 h, cooled to room temperature and then added slowly to 50 ml of a cooled aqueous solution of NH_4Cl. After separation of the organic layer, the aqueous phase was twice extracted with 30 ml of hexane, the combined organic phases were washed with 30 ml of brine and then dried over Na_2SO_4. After removal of the solvent and volatiles *in vacuo*, the residual viscous yellow oil was purified by column chromatography (SiO_2, 15 cm, hexane–ethyl acetate 6 : 1). Compound **2** was obtained as a colourless viscous oil. Yield: 1.25 g (2.77 mmol, 69%). ^1H NMR (400.14 MHz, $CDCl_3$, 295 K): δ −0.05 (s, 27 H, H-10), 0.57 (t, 6 H, $^3J_{HH}$ = 8.2 Hz, H-8), 0.83 (t, 6 H, $^3J_{HH}$ = 8.2 Hz, H-6), 1.33–1.41 (m, 6 H, H-7), 7.31–7.48 (m, 5 H, H-2, H-3, H-4). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 295 K): δ −1.5 (C-10), 17.3 (C-6/7/8), 18.5 (C-6/7/8), 21.6 (C-6/7/8), 127.6 (C-3), 128.5 (C-4), 134.1 (C-2), 138.3 (C-1). $^{29}Si\{^1H\}$ NMR (79.5 MHz, $CDCl_3$, 295 K): δ −3.9 (Si-5), 0.7 (Si-9). IR (neat): ν 3068vw, 3050vw, 2952s, 2913s, 2874m, 1449vw, 1427w, 1412w, 1334w, 1259m, 1247s, 1141m, 1108m, 1022w, 943w, 907m, 862s, 834s, 734m, 698s cm^{-1}. $C_{24}H_{50}Si_4$ (451.00 g mol^{-1}): calc.: C 63.92, H 11.17; found: C 64.03, H 10.84%.

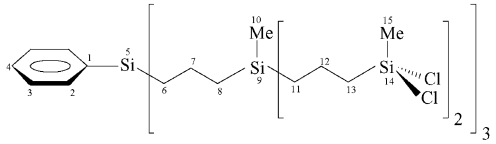


$PhSi[CH_2CH_2CH_2Si(Me)(allyl)_2]_3$ (3). To a solution of **1** (4.63 g, 8.07 mmol) in 5 ml of thf, which was cooled to −5 °C,

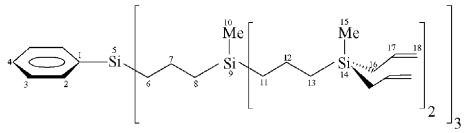
84 ml (67.8 mmol) of a 0.81 molar solution of allylmagnesium bromide were slowly added over a period of 1.5 h. The reaction mixture was heated under reflux for 24 h, then cooled to room temperature and slowly poured into 100 ml of a cooled aqueous solution of NH_4Cl. After separation of the organic layer, the aqueous phase was twice extracted with 50 ml of hexane, the combined organic phases washed with 50 ml of brine and then dried over Na_2SO_4. After the removal of the solvent and volatiles *in vacuo*, the residual viscous yellow oil was purified by column chromatography (SiO_2, 15 cm, hexane). Compound **3** was obtained as a viscous colourless liquid. Yield: 3.92 g (6.46 mmol, 80%).^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ −0.05 (s, 9 H, H-10), 0.63 (t, 6 H, $^3J_{HH}$ = 8.2 Hz, H-8), 0.84 (t, 6 H, $^3J_{HH}$ = 8.2 Hz, H-6), 1.32–1.40 (m, 6 H, H-7), 1.51 (dt, 12 H,$^3J_{HH}$ = 8.2 Hz, $^5J_{HH}$ = 1.2 Hz, H-11), 4.80 (t, 6 H, $^3J_{HH}$ = 1.2 Hz, H(*cis*)-13), 4.81–4.83 (m, 6 H, H(*trans*)-13), 5.68–5.79 (m, 6 H, H-12), 7.32–7.45 (m, 5 H, H-2, H-3, H-4). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ −7.8 (C-10), 17.3 (C-6/7/8), 18.0 (C-6/7/8), 18.2 (C-6/7/8), 21.4 (C-11), 113.1 (C-13), 127.7 (C-3), 128.7 (C-4), 134.0 (C-2), 134.8 (C-12), 137.7 (C-1). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ −3.9 (Si-5), 0.3 (Si-9). IR (neat): ν 3075m, 2994w, 2970m, 2955m, 2914s, 2876m, 1629s, 1427m, 1418m, 1393m, 1335vw, 1252m, 1192w, 1155m, 1108w, 1032m, 990m, 931m, 893s, 825m, 735vw, 699m, 653vw, 591m, 549vw cm^{-1}. $C_{36}H_{62}Si_4$ (607.23 g mol^{-1}): calc.: C 71.15, H 10.28; found: C 70.74, H 10.08%.



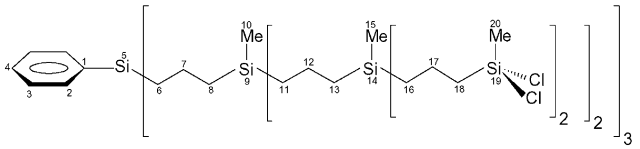
PhSi[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)Cl)$_2$]$_2$]$_3$ (4). Same procedure as for compound **1**, using 3.34 g (5.50 mmol) of **3** and 6.45 g (56.1 mmol) of $MeHSiCl_2$. Compound **4** was obtained as a pale yellow liquid. Yield: 7.14 g (5.50 mmol, 100%). ^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ −0.08 (s, 9 H, H-10), 0.58 (t, 18 H, $^3J_{HH}$ = 8.0 Hz, H-8, H-11), 0.74 (s, 18 H, H-15), 0.83 (t, 6 H,$^3J_{HH}$ = 8.4 Hz, H-6), 1.13 (t, 12 H, $^3J_{HH}$ = 7.9 Hz, H-13), 1.28–1.36 (m, 6 H, H-7), 1.44–1.52 (m, 12 H, H-12), 7.31–7.44 (m, 5 H, H-2, H-3, H-4). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ −5.2 (C-10), 5.5 (C-15), 17.2 (C-11/12/13), 17.4 (C-6/7/8), 17.5 (C-11/12/13), 18.4 (C-6/7/8), 18.6 (C-6/7/8), 25.9 (C-11/12/13), 127.8 (C-3), 128.4 (C-4), 134.0 (C-2), 137.7 (C-1). ^{29}Si{^{1}H} NMR (39.8 MHz, $CDCl_3$, 295 K): δ −4.0 (Si-5), 1.5 (Si-9), 32.2 (Si-14). IR (neat): ν 3069vw, 2925m, 2878m, 1451vw, 1427m, 1403w, 1339vw, 1261s, 1148m, 1109m, 1021w, 1021w, 943w, 906m, 815s, 787s, 738m, 700m, 536s cm^{-1}. $C_{42}H_{86}Si_{10}Cl_{12}$ (1297.43 g mol^{-1}): calc.: C 38.88, H 6.68; found: C 38.67, H 6.49%.



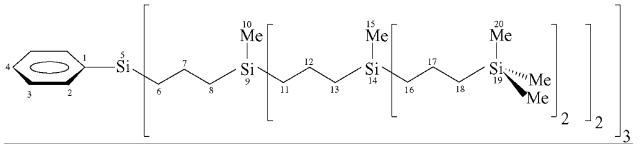
PhSi[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)(allyl)$_2$]$_2$]$_3$ (5). Same procedure as for compound **3** using 7.11 g (5.48 mmol) of compound **4** and 114 ml (92.1 mmol) of a 0.81 molar solution of allylmagnesium bromide. The reaction product, compound **5** was isolated after chromatography as a colourless viscous oil. Yield: 5.00 g (3.66 mmol, 67%). ^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ −0.12 (s, 9 H, H-10), −0.04 (s, 18 H, H-15), 0.48–0.60 (m, 30 H, H-8, H-11, H-13), 0.83 (t, 6 H, $^3J_{HH}$ = 8.4 Hz, H-6), 1.26–1.36 (m, 18 H, H-7, H-12), 1.52 (d, 24 H, $^3J_{HH}$ = 8.2 Hz, H-16), 4.80–4.86 (m, 24 H, H-18),5.70–5.80 (m, 12 H, H-17), 7.30–7.42 (m, 5 H, H-2, H-3, H-4). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ −7.7 (C-15), −5.0 (C-10), 17.6 (C-6/7/8), 17.9 (C-11/12/13), 18.2 (C-11/12/13), 18.5 (C-6/7/8), 18.8 (C-11/12/13), 19.0 (C-6/7/8), 21.5 (C-16), 113.1 (C-18), 127.7 (C-3), 128.6 (C-4), 134.0 (C-2), 135.2 (C-17), 138.0 (C-1). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ −4.0 (Si-5), 0.3 (Si-14), 1.1 (Si-9). IR (neat): ν 3075w, 2994vw, 2970w, 2954w, 2912m, 2876m, 1629s, 1419m, 1333vw, 1252s, 1192vw, 1153s, 1108vw, 1031m, 990m, 931m, 893s, 814br m, 699m, 591m cm^{-1}. $C_{78}H_{146}Si_{10}$ (1364.87 g mol^{-1}): calc.: C 68.64, H 10.77; found: C 68.90, H 10.45%.



PhSi[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$-Si(Me)Cl$_2$]$_2$]$_2$]$_3$ (6). Same general procedure as for compound **4**, using 2.52 g (1.85 mmol) of **5** and 4.34 g (37.7 mmol) of $MeHSiCl_2$. The reaction product, compound **6** was obtained as a pale yellow liquid. Yield: 5.08 g (1.85 mmol, 100%). ^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ −0.12 (s, 9 H, H-10), −0.05 (s, 18 H, H-15), 0.48–0.63 (m, 54 H, H-8, H-11, H-13, H-16), 0.75 (s, 36 H, H-20), 0.82 (t, 6 H, $^3J_{HH}$ = 8.2 Hz, H-6), 1.16 (t, 24 H, $^3J_{HH}$ = 7.9 Hz, H-18), 1.24–1.31 (m, 18 H, H-7, H-12), 1.47–1.53 (m, 24 H, H-17), 7.29–7.46 (m, 5 H, H-2, H-3, H-4). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ −5.1 (C-15), −5.0 (C-10), 5.5 (C-20), 17.3 (C-16), 17.5 (C-17), 17.6 (C-6/7/8), 18.4 (C-11/12/13), 18.5 (C-6/7/8), 18.6 (C-11/12/13), 18.9 (C-11/12/13), 19.0 (C-6/7/8), 25.9 (C-18), 127.6 (C-3), 128.7 (C-4), 134.1 (C-2), 138.0 (C-1). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ −4.0 (Si-5), 1.0 (Si-9), 1.5 (Si-14), 32.2 (Si-19). IR (neat): ν 3065vw, 2918s, 2875s, 1451vw, 1409w, 1336w, 1260s, 1145m, 1083w, 1021m, 943w, 909m, 787s, 745m, 701m, 676m, 538s. $C_{90}H_{194}Si_{22}Cl_{24}$ (2745.28 g mol^{-1}): calc.: C 39.38, H 7.12; found: C 39.36, H 7.15%.

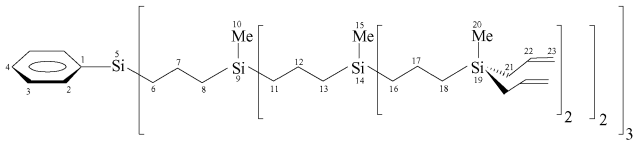


PhSi[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$-SiMe$_3$]$_2$]$_2$]$_3$ (7). Same general procedure as for compound **2**, using 1.92 g (0.70 mmol) of **5** and 7.84 ml (23.5 mmol) of a 3.00 molar solution of methylmagnesium chloride. After work up and purification by column chomatography compound **7** was obtained as a viscous colourless oil. Yield: 1.14 g (0.50 mmol, 71%). ^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ −0.12 (s, 9 H, H-10), −0.10 (s, 18 H, H-15), −0.04 (s, 108 H, H-20), 0.48–0.56 (m, 78 H, H-8, H-11, H-13, H-16, H-18), 0.82 (t, 6 H, $^3J_{HH}$ = 8.2 Hz, H-6), 1.23–1.36 (m, 42 H, H-7, H-12, H-17), 7.29–7.43 (m, 5 H, H-2, H-3, H-4). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ −4.9 (C-10), −4.8 (C-15), −1.5 (C-20), 18.5 (C-16/17/18, C-11/12/13), 18.7 (C-16/17/18), 18.8 (C-6/7/8, C-16/17/18), 18.9 (C-11/12/13), 19.0 (C-11/12/13), 19.1 (C-6/7/8), 19.2 (C-6/7/8), 127.6 (C-3), 128.6 (C-4), 134.1 (C-2), 138.2 (C-1). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ −3.8 (Si-5), 0.8 (Si-9, Si-14), 1.3 (Si-19). IR (neat): ν 2959s, 2910s, 2873m, 1447vw, 1412w, 1333vw, 1256s, 1138vw, 1102s, 1082s, 944vw, 909m, 862s, 827s, 800s, 694s, 690m cm^{-1}. MS (FAB): m/z (relative intensity) 2276.8 (59), [M + Na$^+$]. $C_{114}H_{266}Si_{22}$ (2255.25 g mol^{-1}): calc.: C 60.76, H 11.89; found: C 60.85, H 11.98%.

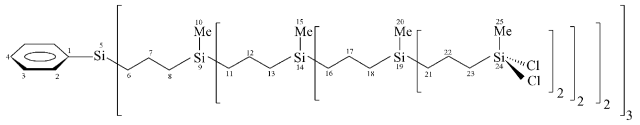


PhSi[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$-Si(Me)(allyl)$_2$]$_2$]$_2$]$_3$ (8). Same procedure as for compound **5**, using 5.02 g (1.83 mmol) of **6** and 92 ml (61.5 mmol) of a

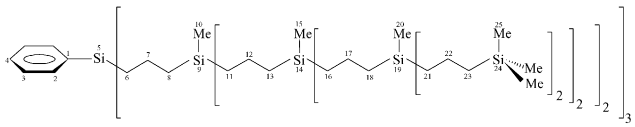
0.67 molar solution of allylmagnesium bromide. After work up and purification by column chromatography the reaction product **8** was isolated as a viscous colourless oil. Yield: 3.64 g (1.26 mmol, 69%). ^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ −0.11 (s, 9 H, H-10), −0.09 (s, 18 H, H-15), −0.02 (s, 36 H, H-20), 0.49–0.63 (m, 78 H, H-8, H-11, H-13, H-16, H-18), 0.82 (t, 6 H, $^{3}J_{HH}$ = 8.1 Hz, H-6), 1.20–1.37 (m, 42 H, H-7, H-12, H-17), 1.54 (d, 48 H, $^{3}J_{HH}$ = 8.2 Hz, H-21), 4.81–4.86 (m, 48 H, H-23), 5.71–5.82 (m, 24 H, H-22), 7.30–7.45 (m, 5 H, H-2, H-3, H-4). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ −5.7 (C-20), −5.02 (C-10), −5.0 (C-15), 17.6 (C-6/7/8), 18.0 (C-11/12/13), 18.2 (C-11/12/13), 18.3 (C-16/17/18), 18.5 (C-6/7/8), 18.5 (C-11/12/13), 18.8 (C-16/17/18), 19.0 (C-16/17/18), 19.1 (C-6/7/8), 21.5 (C-21), 113.1 (C-23), 127.6 (C-3), 128.6 (C-4), 134.1 (C-2), 134.8 (C-22), 138.0 (C-1). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ −4.1 (Si-5), 0.3 (Si-19), 1.0 (Si-9, Si-14). IR (neat): ν 3076m, 2994w, 2970m, 2954m, 2913s, 2876m, 2793vw, 1630s, 1449vw, 1419m, 1333w, 1252s, 1193w, 1153m, 1081vw, 1031m, 990m, 931m, 893s, 814br s, 699m, 654vw, 591m cm^{-1}. $C_{162}H_{314}Si_{22}$ (2880.16 g mol^{-1}): calc.: C 67.56, H 10.99; found: C 66.87, H 9.89%.



PhSi[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$-Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)Cl$_2$]$_2$]$_2$]$_2$]$_3$ (9). Same general procedure as for compound **4**, using 1.58 g (0.55 mmol) of **8** and 49 g (21.7 mmol) of $MeHSiCl_2$. After work-up compound **9** was isolated as a pale yellow liquid. Yield: 3.10 g (0.55 mmol, 100%). ^{1}H NMR (400.13 MHz, $CDCl_3$, 295 K): δ −0.12 (s, 9 H, H-10), −0.09 (s, 18 H, H-15), −0.04 (s, 36 H, H-20), 0.51–0.64 (m, 126 H, H-8, H-11, H-13, H-16, H-18, H-21), 0.75 (s, 72 H, H-25), 0.81 (t, 6 H, $^{3}J_{HH}$ = 8.1 Hz, H-6), 1.16 (t, 48 H, $^{3}J_{HH}$ = 8.0 Hz, H-23), 1.23–1.33 (m, 42 H, H-7, H-12, H-17), 1.48–1.56 (m, 48 H, H-22), 7.29–7.43 (m, 5 H, H-2, H-3, H-4). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ −5.1 (C-10), −5.0 (C-15), −4.9 (C-20), 5.5 (C-25), 17.3 (C-21/22/23), 17.5 (C-21/22/23), 18.0 (C-6/7/8), 18.2 (C-6/7/8), 18.3 (C-6/7/8), 18.5 (C-16/17/18), 18.6 (C-16/17/18), 18.9 (C-16/17/18), 19.0 (C-11/12/12), 19.1 (C-11/12/12), 19.2 (C-11/12/12), 25.9 (C-21/22/23), 127.6 (C-3), 128.6 (C-4), 134.1 (C-2), 138.0 (C-1). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ −4.3 (Si-5), 0.7 (Si-9), 0.8 (Si-14), 1.3 (Si-19), 31.9 (Si-24). IR (neat): ν 2957m, 2917s, 2875s, 2792w, 1451m, 1409m, 1336m, 1260s, 1217m, 1145s, 1084m, 1021m, 979w, 943m, 909s, 817s, 787s, 746s, 700m, 677m, 539s cm^{-1}.

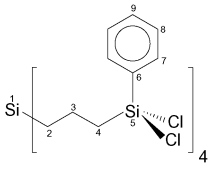


PhSi[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$-Si(Me)[CH$_2$CH$_2$CH$_2$SiMe$_3$]$_2$]$_2$]$_2$]$_3$ (10). Same general procedure as for compounds **2** and **7**, using 2.99 g (0.53 mmol) of **9** and 11.9 ml (35.6 mmol) of a 3.0 molar solution of methylmagnesium chloride. After work-up and purification by column chromatography, compound **10** was obtained as a viscous, colourless liquid. Yield: 1.72 g (0.37 mmol, 69%). ^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ −0.11 (s, 9 H, H-10), −0.10 (s, 18 H, H-15), −0.09 (s, 36 H, H-20), −0.04 (s, 216 H, H-25), 0.54 (t, $^{3}J_{HH}$ = 8.3 Hz, 174 H, H-8, H-11, H-13, H-16, H-18, H-21, H-23), 0.82 (t, 6 H, $^{3}J_{HH}$ = 8.2 Hz, H-6), 1.24–1.36 (m, 90 H, H-7, H-12, H-17, H-22), 7.27–7.44 (m, 5 H, H-2, H-3, H-4). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 295 K): δ −4.5 (C-25, C-20), −4.4 (C-15, C-10), 19.1 (C-21/22/23), 9.2 (C-21/22/23, C-16/17/18), 19.3 (C-6/7/8), 19.4 (C-6/7/8), 19.5 (C-6/7/8, C-16/17/18), 19.6 (C-16/17/18, C-11/12/13), 19.7 (C-11/12/13, C-11/12/13), 21.9 (C-21/22/23), 127.9 (C-2/3), 128.0 (C-1), 128.1 (C-2/3), 128.3 (C-4). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ −3.8 (Si-5), 0.8 (Si-9, Si-14), 1.2 (Si-19), 1.3 (Si-24). IR (neat): ν 2952s, 2930s, 2873s, 2790vw, 1449w, 1412m, 1333m, 1247s, 1215w, 1141s, 1080m, 1022m, 979w, 944m, 909s, 862s, 834s, 796s, 756m, 690m, 664w cm^{-1}. MS (FAB): *m/z* (relative intensity) 4680.5 (98), [M + Na$^+$]. $C_{234}H_{554}Si_{46}$ (4660.91 g mol^{-1}): calc.: C 60.25, H 11.98; found: C 60.22, H 11.94%.

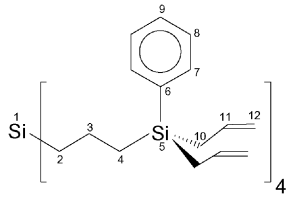


Si[CH$_2$CH$_2$CH$_2$Si(Ph)Cl$_2$]$_4$ (11). Tetraallylsilane (934 mg, 4.85 mmol), $PhHSiCl_2$ (5.85 g, 33.0 mmol) and 60 µl of Karstedt's catalyst were slowly warmed in 15 ml of benzene until an exothermic reaction set in and the colourless solution turned bright yellow. The reaction mixture was stirred at 60 °C for 48 h. After cooling to room temperature, the solution was filtered through 5 cm of silica and the solvent and volatiles were then removed *in vacuo*. After leaving under high vacuum for 1.5 h, compound **11** was obtained as a pure pale yellow liquid.

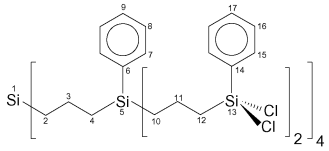
Yield: 4.37 g (4.85 mmol, 100%). ^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ 0.58 (t, 8 H, $^{3}J_{HH}$ = 5.9 Hz, H-2), 1.35 (t, 8 H, $^{3}J_{HH}$ = 7.6 Hz, H-4), 1.46–1.77 (m, 8 H, H-3), 7.41–7.71 (m, 20 H, H-7, H-8, H-9). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ 15.8 (C-2/3/4), 17.3 (C-2/3/4), 24.9 (C-2/3/4), 128.3 (C-8), 131.6 (C-9), 131.7 (C-6), 132.2 (C-7). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ 1.5 (Si-1), 18.3 (Si-5). IR (neat): ν 3073w, 3058vw, 2963m, 2924m, 2876m, 2209w, 1590w, 1429s, 1337 w; 1262m, 1117s, 1020m, 797s, 737m, 694s, 565m, 510m cm^{-1}. $C_{36}H_{44}Si_5Cl_8$ (900.80 g mol^{-1}): calc.: C 47.96, H 4.92; found: C 47.05, H 4.91%.



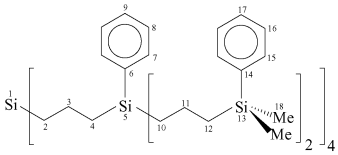
Si[CH$_2$CH$_2$CH$_2$Si(Ph)(allyl)$_2$]$_4$ (12). To a solution of compound **11** (4.36 g, 4.85 mmol) in 10 ml of thf, which was cooled to –5 °C, 116 ml (54.5 mmol) of a 0.47 molar solution of allylmagnesium bromide were added over a period of 1.5 h. The reaction mixture was heated under reflux for 48 h, then cooled to room temperature and slowly poured into a cooled aqueous solution (100 ml) of NH_4Cl. After separation of the organic layer the aqueous phase was twice extracted with 50 ml of hexane, the combined organic phases were washed with brine and then dried over Na_2SO_4. After removal of the volatiles the residue was purified by column chromatography (SiO_2, 15 cm, hexane–ethyl acetate 6 : 1) giving compound **12** as a viscous colourless oil. Yield: 3.21 g (3.40 mmol, 70%). ^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ 0.50 (t, 8 H, $^{3}J_{HH}$ = 8.2 Hz, H-2), 0.87 (t, 8 H, $^{3}J_{HH}$ = 8.2 Hz, H-4), 1.28–1.39 (m, 8 H, H-3), 1.83 (d, 16 H, $^{3}J_{HH}$ = 7.6 Hz, H-10), 4.85–4.93 (m, 16 H, H-12), 5.73–5.85 (m, 8 H, H-11), 7.34–7.51 (m, 20 H, H-7, H-8, H-9). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ 16.7 (C-2/3/4), 17.4 (C-2/3/4), 18.2 (C-2/3/4), 20.1 (C-10), 113.9 (C-12), 127.7 (C-8), 129.1 (C-9), 134.1 (C-7/11), 134.2 (C-7/11), 136.1 (C-6). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ −6.5 (Si-5), 0.9 (Si-1). IR (neat): ν 3075s, 3053m, 3021m, 2998m, 2972m, 2918m, 2883m, 2125s, 1812w, 1630s, 1486w, 1427s, 1416m, 1399m, 1300w, 1261w, 1191m, 1156m, 1114m, 1038m, 990m, 929m, 896s, 848s, 824m, 786m, 738m, 699s, 660w, 600m, 571w cm^{-1}. $C_{60}H_{84}Si_5$ (945.75 g mol^{-1}): calc.: C 76.14, H 8.95; found: C 76.12, H 8.80%.



Si[CH$_2$CH$_2$CH$_2$Si(Ph)[CH$_2$CH$_2$CH$_2$Si(Ph)Cl$_2$]$_2$]$_4$ (13). Same procedure as in the preparation of **11**, using 361 mg (0.38 mmol) of compound **12** and 757 mg (4.28 mmol) of PhHSiCl$_2$. After work-up, compound **13** was obtained as a pale yellow oil. Yield: 897 mg (0.38 mmol, 100%). ^{1}H NMR (400.14 MHz, CDCl$_3$, 295 K): δ 0.92–1.01 (m, 24 H, H-2, H-10), 1.41–1.46 (m, 24 H, H-4, H-12), 1.60–1.70 (m, 24 H, H-3, H-11), 7.45–7.73 (m, 60 H, H-7, H-8, H-9, H-15, H-16, H-17). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, 295 K): δ 15.8 (C-10/11/12), 16.0 (C-2/3/4), 16.3 (C-2/3/4), 17.3 (C-10/11/12), 24.7 (C-2/3/4, C-10/11/12), 127.9 (C-8), 128.3 (C-16), 129.2 (C-9), 131.6 (C-17), 132.7 (C-6, C-14), 133.3 (C-15), 133.9 (C-7). ^{29}Si{^{1}H} NMR (79.5 MHz, CDCl$_3$, 295 K): δ −12.1 (Si-1), −4.0 (Si-5), 18.1 (Si-13). IR (neat): ν 3072w, 3051vw, 2956m, 2925s, 2878m, 1618w, 1590m, 1487w, 1429s, 1337w, 1259w, 1145m, 1117s, 1028m, 998m, 901m, 793m, 738m, 695s, 564s, 549m, 510s cm^{-1}. C$_{108}$H$_{132}$Si$_{13}$Cl$_{16}$ (2362.59 g mol^{-1}): calc.: C 54.86, H 5.63; found: C 54.55, H 5.74%.



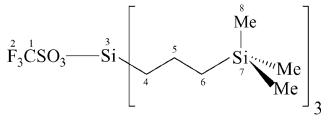
Si[CH$_2$CH$_2$CH$_2$Si(Ph)[CH$_2$CH$_2$CH$_2$Si(Ph)Me$_2$]$_2$]$_4$ (14). To a solution of compound **13** (874 mg, 0.37 mmol) in 40 ml of thf, which was cooled to −5 °C, 2.84 ml (8.51 mmol) of a 3.0 molar solution of methylmagnesium chloride were slowly added. After refluxing for 48 h, the reaction mixture was cooled to room temperature and then poured into a cooled aqueous solution (50 ml) of NH$_4$Cl. After separation of the organic layer, the aqueous phase was twice extracted with 30 ml of hexane, the combined organic phases were washed with 30 ml of brine and then dried over Na$_2$SO$_4$. After removal of the volatiles *in vacuo*, the residual yellow oil was purified by column chromatography (SiO$_2$, 15 cm, hexane–ethyl acetate 6 : 1). Compound **14** was obtained as a viscous colourless liquid. Yield: 482 mg (0.24 mmol, 65%). ^{1}H NMR (400.13 MHz, CDCl$_3$, 295 K): δ 0.22 (s, 48 H, H-18), 0.80 (t, 48 H, $^3J_{HH}$ = 8.0 Hz, H-2, H-4, H-10, H-12), 1.30–1.39 (m, 24 H, H-3, H-11), 7.33–7.48 (m, 60 H, H-7, H-8, H-9, H-15, H-16, H-17). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, 295 K): δ −2.9 (C-18), 17.2 (C-10/11/12), 17.4 (C-2/3/4), 18.3 (C-2/3/4), 18.4 (C-10/11/12), 20.3 (C-2/3/4), 20.4 (C-10/11/12), 127.6 (C-8), 127.3 (C-16), 128.6 (C-9), 128.7 (C-17), 133.5 (C-15), 134.0 (C-7), 137.9 (C-6), 139.7 (C-14). ^{29}Si{^{1}H} NMR (79.5 MHz, CDCl$_3$, 295 K): δ −22.1 (Si-1), −4.1 (Si-5/13), −4.0 (Si-5/13). IR (neat): ν 3068w, 3046vw, 2961s, 2908m, 2873w, 2851w, 2790vw, 1447w, 1426m, 1412m, 1258s, 1110s, 1023s, 863m, 819s, 728m, 699m, 661m cm^{-1}. MS (FAB): *m*/*z* (relative intensity) 2058.1 (25), [M + Na$^+$].



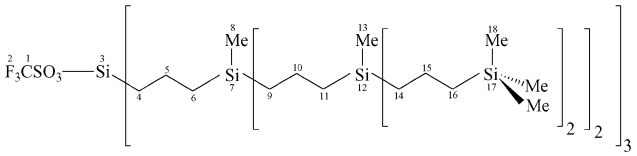
General procedure for the preparation of the dendritic silyl triflates

To a solution of the dendritic phenylcarbosilane (0.6 mmol) in 10 ml of toluene, which was cooled to −40 °C, 91.5 mg (0.61 mmol) of trifluoromethanesulfonic acid were added dropwise. The reaction mixture was then warmed to −20 °C and stirred for 30 min at that temperature. After stirring for another 45 min while warming the solution to room temperature, the acid was completely dissolved. After removal of the volatiles *in vacuo*, the reaction product was left in a high vacuum (10^{-5} mbar) for 2.5 h. The yield of the silyltriflates, which are pale yellow oils was quantitative in all cases.

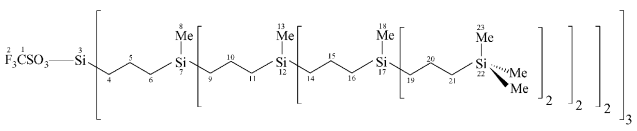
F$_3$CSO$_3$Si[CH$_2$CH$_2$CH$_2$SiMe$_3$]$_3$ (15). ^{1}H NMR (400.14 MHz, CDCl$_3$, 295 K): δ −0.03 (s, 27 H, H-8), 0.58 (t, 6 H, $^3J_{HH}$ = 8.2 Hz, H-6), 0.95 (t, 6 H, $^3J_{HH}$ = 8.2 Hz, H-4), 1.39–1.47 (m, 6 H, H-5). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, 295 K): δ −1.7 (C-8), 17.0 (C-4/5/6), 18.3 (C-4/5/6), 21.0 (C-4/5/6), 118.4 (q, C-1). ^{29}Si{^{1}H} NMR (79.5 MHz, CDCl$_3$, 295 K): δ 1.3 (Si-7), 37.1 (Si-3). ^{19}F NMR (376.4 MHz, CDCl$_3$, 295 K): δ −76.8 (F-2). IR (neat): ν 2953m, 2916m, 2874m, 2205br w, 1394w, 1248s, 1209s,1027s, 946vw, 909m, 862s, 835s, 770vw, 693m, 638m, 577vw, 513w cm^{-1}.



F$_3$CSO$_3$Si[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$-CH$_2$CH$_2$SiMe$_3$]$_2$]$_2$]$_3$ (16). ^{1}H NMR (300.17 MHz, CDCl$_3$, 295 K): δ −0.11 (s, 9 H, H-8), −0.10 (s, 18 H, H-13), −0.05 (s, 108 H, H-18), 0.53 (t, 84 H, $^3J_{HH}$ = 7.9 Hz, H-4, H-6, H-9, H-11, H-14, H-16), 1.24–1.43 (m, 42 H, H-5, H-10, H-15). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, 295 K): δ −5.1 (C-8), −4.8 (C-13), −1.4 (C-18), 18.5 (C-14/15/16), 18.6 (C-9/10/11), 18.8 (C-14/15/16, C-4/5/6), 19.0 (C-9/10/11), 19.1 (C-9/10/11), 19.2 (C-4/5/6), 19.3 (C-4/5/6), 21.6 (C-14/15/16), 128.6 (q, C-1). ^{29}Si{^{1}H} NMR (79.5 MHz, CDCl$_3$, 295 K): δ 0.3 (Si-12), 0.9 (Si-17), 3.2 (Si-7), 39.7 (Si-3). ^{19}F NMR (376.4 MHz, CDCl$_3$, 295 K): δ −77.2 (F-2). IR (neat): ν 2952s, 2911s, 2873m, 2791vw, 1448vw, 1411w, 1333vw, 1258s,1248s, 1215vw, 1141m, 1081m, 1081m, 1026m, 981vw, 944w, 910m, 862s, 834s, 807m,750m, 691m cm^{-1}.

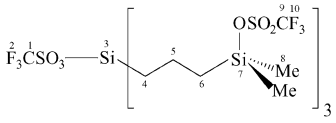


F$_3$CSO$_3$Si[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$-CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$SiMe$_3$]$_2$]$_2$]$_2$]$_3$ (17). ^{1}H NMR (300.17 MHz, CDCl$_3$, 295 K): δ −0.12 (s, 9 H, H-8), −0.11 (s, 18 H, H-13), −0.10 (s, 36 H, H-18), −0.05 (s, 216 H, H-23), 0.53 (t, 180 H, $^3J_{HH}$ = 7.9 Hz, H-4, H-6, H-9, H-11, H-14, H-16, H-19, H-21), 1.24–1.34 (m, 90 H, H-5, H-10, H-15, H-20). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 295 K): δ −5.1 (C-8), −5.0 (C-13), −4.9 (C-18), −1.4 (C-23), 18.5 (C-19/20/21), 18.6 (C-14/15/16), 18.7 (C-19/20/21, C-9/10/11), 18.8 (C-4/5/6, C-4/5/6), 18.9 (C-4/5/6), 19.0 (C-14/15/16, C-14/15/16), 19.1 (C-9/10/11), 19.2 (C-9/10/11), 21.5 (C-19/20/21), 128.7 (q, C-1). ^{29}Si{^{1}H} NMR (79.5 MHz, CDCl$_3$, 295 K): δ 0.3 (Si-12, Si-17), 0.8 (Si-22), 3.2 (Si-7), 39.8 (Si-3). ^{19}F NMR (376.5 MHz, CDCl$_3$, 295 K): δ −76.7 (F-2). IR (neat): ν 2952s, 2911s, 2872m, 2793vw, 1453vw, 1411w, 1333vw, 1248s, 1217vw, 1141m, 1080m, 1025m, 978vw, 943w, 909m, 862s, 834s, 809m, 751m, 691m cm^{-1}.

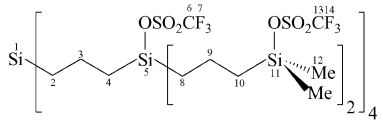


F$_3$CSO$_3$Si[CH$_2$CH$_2$CH$_2$Si(Me)$_2$OSO$_2$CF$_3$]$_3$ (18). To a solution of compound **2** (242 mg, 0.54 mmol) in 10 ml of toluene, which was cooled at −40 °C, were added dropwise 810 mg (5.40 mmol) of trifluoromethanesulfonic acid over a period of 10 min. The reaction mixture was warmed to −20 °C and stirred

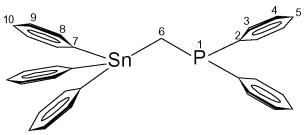
for another 30 min at that temperature. After subsequent stirring at room temperature for 45 min, all the volatiles were removed *in vacuo* yielding compound **19** as a light yellow oil. Yield: 497 mg (0.54 mmol, 100%). ^{1}H NMR (400.14 MHz, $CDCl_3$, 295 K): δ 0.47 (s, 18 H, H-8), 0.98–1.05 (m, 12 H, H-4, H-6), 1.53–1.62 (m, 6 H, H-5). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ −1.4 (C-8), 15.4 (C-4/5/6), 17.4 (C-4/5/6), 20.3 (C-4/5/6), 118.3 (q, C-1, C-9). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$, 295 K): δ 38.7 (Si-3), 43.1 (Si-7). ^{19}F NMR (376.4 MHz, $CDCl_3$, 295 K): δ −76.9 (F-10), −76.6 (F-2). IR (neat): ν 2952m, 2927m, 2875m, 2204br w, 1388s, 1343m, 1247s, 1200 br s, 1156s, 1030s, 967m, 909m, 860m, 807m, 717w, 629s, 550w, 530w, 515w cm^{-1}.



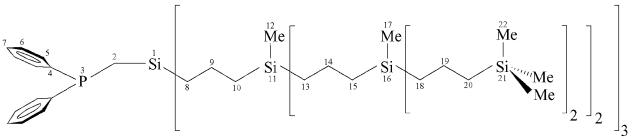
Si[CH$_2$CH$_2$CH$_2$Si(OSO$_2$CF$_3$)[CH$_2$CH$_2$CH$_2$Si(OSO$_2$CF$_3$)-Me$_2$]$_2$]$_4$ (19). To a solution of compound **14** (143 mg, 0.07 mmol) in 5 ml of toluene, which was cooled at −40 °C, were added dropwise 127 mg (0.84 mmol) of trifluoromethanesulfonic acid. After stirring at −20 °C for 30 min and at room temperature for another 50 min, the solvent and volatiles were removed. After leaving the reaction product under high vacuum (10^{-5} mbar) for 5 h, compound **19** was obtained as a pale yellow oil. Yield: 84.1 mg (0.07 mmol, 100%). ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ 0.47 (s, 48 H, H-12), 0.98–1.06 (m, 48 H, H-2, H-4, H-8, H-10), 1.52–1.63 (m, 24 H, H-3, H-9). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 295 K): δ −1.4 (C-12), 15.4 (C-8/9/10), 17.4 (C-8/9/10, C-2/3/4), 17.9 (C-2/3/4), 19.9 (C-2/3/4), 20.2 (C-8/9/10), 116.2 (q, C-6, C-13). IR (neat): ν 2861s, 2925s, 2874s, 2217 br w, 1512vw, 1450m, 1394s, 1260s, 1205s, 1160s, 1107s, 1030s, 976s, 911s, 865s, 822s, 712w, 633s, 570vw, 514m cm^{-1}.



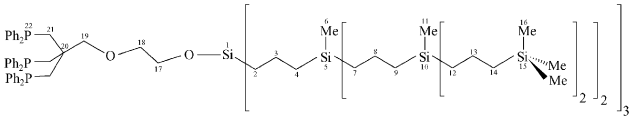
Ph$_3$SnCH$_2$PPh$_2$ (20). To a stirred solution of iodomethyltriphenylstannane[17] (2.01 g, 4.09 mmol) in 60 ml of toluene, which was cooled to −55 °C, were added 2.57 ml (4.09 mmol) of a 1.59 molar solution of *n*-BuLi in hexane. After stirring for 30 min at that temperature 951 mg (8.19 mmol) of TMEDA were added and the clear solution further cooled to −90 °C. At this temperature 902 mg (4.09 mmol) of Ph_2PCl were added dropwise over a period of 10 min. The yellow solution was then warmed to −80 °C and stirred for another 45 min. After slowly warming to room temperature, the reaction mixture was hydrolyzed with 15 ml of degassed water, the organic layer was then separated, twice extracted with 10 ml of degassed water and then dried over Na_2SO_4. After removal of all the volatiles *in vacuo*, the oily residue was taken up in 3 ml of pentane and subjected to column chromatography on Al_2O_3 (basic, activity III) with pentane as eluent. After collection of the product fraction, all volatiles were removed *in vacuo* and the colourless solid residue dried in high vacuum to give pure **20**. Yield: 1.95 g (3.56 mmol, 87%). ^{1}H NMR (300.17 MHz, C_6D_6, 295 K): δ 1.96 (d, 2 H, $^{2}J_{HP}$ = 2.2 Hz, H-6), 6.96–7.05 (m, 10 H, H-3, H-4, H-5), 7.32–7.46 (m, 15 H, H-8, H-9, H-10). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 295 K): δ 8.7 (d, J_{PC} = 34.2 Hz, C-6), 128.2 (d, J_{PC} = 6.1 Hz, C-4), 128.4 (C-10), 128.9 (C-9), 132.3 (d, J_{PC} = 19.5 Hz, C-2), 136.8 (C-5), 136.9 (C-8), 138.3 (d, J_{PC} = 2.4 Hz, C-7), 141.1 (d, J_{PC} = 14.7 Hz, C-3). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 295 K): δ −20.2 (J($^{119/117}$SnP) = 50.9 Hz, P-1). $C_{31}H_{27}SnP$ (549.24 g mol^{-1}) calc.: C 67.85, H 4.96; found: C 68.02, H 5.14%.



Ph$_2$PCH$_2$Si[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$-CH$_2$CH$_2$SiMe$_3$]$_2$]$_2$]$_3$ (21). To a solution of $Ph_3SnCH_2PPh_2$ (65.9 mg, 0.12 mmol) in 2 ml of diethyl ether, which was stirred at room temperature, were added 64 µl (0.12 mmol) of a 1.8 molar solution of PhLi in cyclohexane–ether with the aid of a Hamilton syringe. After stirring for 16 h, a colourless solid had precipitated. The suspension was cooled to −78 °C and 13.9 mg (0.12 mmol) of TMEDA and then 279 mg (0.12 mmol) of compound **16** (dissolved in 2 ml of diethyl ether) were added. After stirring at that temperature for 30 min, the reaction mixture was warmed to room temperature and stirred for another 30 min. After removal of the volatiles *in vacuo*, the residue was extracted with 20 ml of hexane. The solvent of the extract was again removed leaving an oily residue which was taken up in 1 ml of pentane and subjected to column chromatography (Al_2O_3 basic, activity I, eluent: pentane) giving the reaction product **21** as a colourless oil. Yield: 214 mg (0.09 mmol, 74%). ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ −0.09 (s, 9 H, H-12), −0.08 (s, 18 H, H-17), −0.03 (s, 108 H, H-22), 0.55 (t, 78 H, $^{2}J_{HH}$ = 7.5 Hz, H-10, H-13, H-15, H-18, H-20), 0.87 (t, 2 H, $^{3}J_{HH}$ = 6.6 Hz, H-8), 1.25–1.41 (m, 42 H, H-9, H-14, H-19), 1.61 (d, 2 H, $^{3}J_{HP}$ = 3.5 Hz, H-2), 7.30–7.41 (m, 10 H, H-5, H-6, H-7). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K): δ −5.0 (C-12), −4.9 (C-17), −1.5 (C-22), 12.5 (d, J_{PC} = 13.2 Hz, C-2), 18.5 (C-18/19/20, C-13/14/15), 18.7 (C-18/19/20, C-8/9/10), 18.9 (C-13/14/15), 19.0 (C-13/14/15), 19.1 (C-8/9/10), 19.2 (C-8/9/10), 21.5 (C-18/19/20), 128.3 (d, J_{PC} = 3.0 Hz, C-6), 132.1 (d, J_{PC} = 18.3 Hz, C-4), 137.2 (C-7), 140.2 (d, J_{PC} = 11.2 Hz, C-5). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 295 K): δ −26.9 (P-3). IR (neat): ν 3060vw, 2952s, 2910s, 2875s, 2795vw, 1480vw, 1451vw, 1432w, 1412w, 1383vw, 1332w, 1247s, 1215vw, 1141m, 1063w, 1141m, 944vw, 909m, 861s, 833s, 737m, 694m cm^{-1}. $C_{121}H_{273}Si_{22}P$ (2377.35 g mol^{-1}): calc.: C 61.07, H 11.58; found: C 61.08, H 11.75%.



[Ph$_2$PCH$_2$]$_3$CCH$_2$OCH$_2$CH$_2$OSi[CH$_2$CH$_2$CH$_2$Si(Me)[CH$_2$-CH$_2$CH$_2$Si(Me)[CH$_2$CH$_2$CH$_2$SiMe$_3$]$_2$]$_2$]$_3$ (22). To a solution of $[Ph_2PCH_2]_3CCH_2OCH_2CH_2OH$ (47.9 mg, 0.07 mmol) in 1 ml of thf, which was cooled to −60 °C, 44 µl (0.07 mmol) of a 1.59 molar solution of *n*-BuLi in hexane were added with the aid of a Hamilton syringe. The resulting yellow solution was warmed to room temperature and stirred for 30 min. After re-cooling the reaction mixture to −90 °C, compound **16** (163 mg, 0.07 mmol) dissolved in 1 ml of thf was added. After stirring for another 15 min at that temperature, the solution was warmed to room temperature and stirred for 16 h. After removal of the volatiles *in vacuo*, the residue was taken up in 10 ml of toluene and the colourless precipitate separated by centrifugation. The solvent of the centrifugate was removed *in vacuo* and the reaction product left under high vacuum (10^{-5} mbar) for another 5 h to afford compound **22** as a colourless oil. Yield: 190 mg (0.07 mmol, 95%). ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ −0.09 (s, 9 H, H-6), −0.08 (s, 18 H, H-11), −0.03 (s, 108 H, H-16), 0.55 (t, 78 H, $^{3}J_{HH}$ = 7.8 Hz, H-4,



H-7, H-9, H-12, H-14), 0.86 (t, 6 H, $^{3}J_{HH}$ = 8.3 Hz, H-2), 1.25–1.38 (m, 42 H, H-3, H-8, H-13), 2.44 (d, 6 H, $^{2}J_{HP}$ = 1.7 Hz, H-21), 2.87 (t, 2 H, $^{3}J_{HH}$ = 4.2 Hz, H-17/18), 3.30–3.34 (m, 4 H, H-17/18, H-19), 7.15–7.31 (m, 30 H, H-aromat.). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 295 K): δ −5.0 (C-6), −4.9 (C-11), −1.4 (C-16), 18.5 (C-12/13/14), 18.6 (C-7/8/9), 18.7 (C-12/13/14), 18.8 (C-2/3/4), 18.9 (C-7/8/9), 19.0 (C-7/8/9), 19.1 (C-2/3/4), 19.2 (C-2/3/4), 21.5 (C-12/13/14), 38.3–39.0 (m, C-21), 42.4–42.9 (m, C-20), 61.1 (C-17/18), 71.4 (C-17/18), 76.9 (C-19), 128.3 (d, J_{PC} = 7.3 Hz, C-aromat.), 132.9 (d, J_{PC} = 20.7 Hz, C-aromat.), 133.0 (C-aromat.), 139.5 (d, J_{PC} = 11.3 Hz, $C_{quartär}$-aromat.). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 295 K): δ −26.6 (P-22). $^{29}Si\{^{1}H\}$ NMR (79.5 MHz, $CDCl_3$, 295 K): δ 0.4 (Si-15), 0.9 (Si-10), 3.2 (Si-5), 15.3 (Si-1). IR (neat): ν 2952s, 2910s, 2873s, 2792vw, 1450vw, 1233w, 1247s, 1215w, 1141m, 1082m, 1024m, 978w, 943w, 909m, 862s, 834s, 822s, 802m, 691m cm^{-1}. $C_{151}H_{303}Si_{22}O_2P_3$ (2861.87 g mol^{-1}): calc.: C 63.37, H 10.67; found: C 62.54, H 11.23%.

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