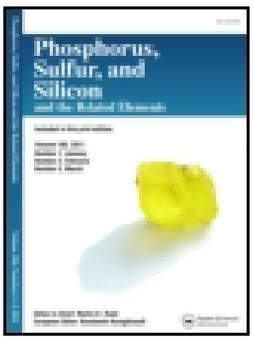

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Dendritic structures incorporating P, S, and Si

SYNTHESIS AND CHARACTERIZATION OF DENDRITIC STRUCTURES INCORPORATING PHOSPHORUS, SULFUR, AND SILICON

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Dedicated to the memory of Prof. Dr. Reinhard Schmutzler

Abstract

Two new families of small phosphorus-containing dendrons, having as core either a phenol protected by a *t*-butyldimethylsilyl group, or a terminal alkyne protected by a trimethylsilyl group have been synthesized. Both families comprise P, S, and Si (and other elements) in their structure. The structure of one of the smallest dendron, having a $P(S)Cl_2$ terminal group, has

been determined by X ray crystallography, showing an almost planar arrangement of a large part of the structure. The $P(S)Cl_2$ terminal group is particularly suitable for further functionalization, as illustrated by the grafting of amines, aldehydes, and dansyl derivatives. These functions were grafted thanks to the reactivity of amines and phenols in basic conditions, demonstrating the compatibility of these reactions with the presence of the protecting groups. Deprotection attempts proved to be difficult, in particular for the purification of the deprotected products. All compounds have been characterized at least by ^{1}H, ^{13}C, and ^{31}P NMR.

Keywords

Dendron, dendrimer, protection/deprotection, phosphorus

INTRODUCTION

Dendrimers are hyperbranched macromolecules which have induced an increasing interest over years, mainly due to their precisely defined structure, and the easy functionalization of their terminal groups for diverse applications.[1] In particular the so-called "dendrimer effect"[2] may modify the properties of the terminal functions, when considered alone or linked to a dendrimer. In most cases, all the terminal groups of a dendrimer are identical. However, it is often desirable to have two types (or more) of terminal groups, for instance a fluorescent group together with a drug and water-solubilizing functions.[3] In many cases, a stochastic functionalization on the surface of the dendrimer is carried out to have multiple types of functions.[4] Such approach is paradoxical, as the synthesis of dendrimers is tedious to obtain pure compounds, whereas the stochastic functionalization in the last step affords a mixture of compounds. Furthermore, the batch-to-batch inconsistencies of such stochastic approach may also induce inconsistencies in the biological response.[5] Thus, it is highly desirable to develop tools for the precise diversification of the terminal groups of dendrimers. Several approaches can be proposed, but dendrons (dentritic wedges) have been used very early to diversify the terminal groups of dendrimers, by grafting them to a core.[6]

We are specialized since a long time in the synthesis of phosphorus-containing dendrimers.[7] Indeed, phosphorus is a very precious tool for the synthesis and the characterization of such complex molecules.[8,9] With specific surface functionalizations, these phosphorus-containing dendrimers have many properties, in particular for catalysis,[10,11] for materials,[12] and above all for biology.[13-15] We have already synthesized dendrons for obtaining Janus dendrimers[16] (two faces

obtained by associating two dendrons by their core),[17] or complex molecular architecture.[18] We report here the synthesis of new small dendrons, which were tentatively designed to be grafted to the core of dendrimers, in order to obtain two types of functions in dendritic molecules. We have synthesized dendrons in which the function at the core is protected by a silyl group, and the surface functions can afford either solubility in water, or the possibility to continue the growing of the dendron, or fluorescence properties. The protected function at the core of the dendrons is either a phenol, particularly suitable for reacting with PCl_2 functions, or a terminal alkyne, suitable for Sonogashira couplings with halogenated aromatics, or for click chemistry.

RESULTS AND DISCUSSION

Trimethylsilyl chloride reacts readily with alcohols and phenols, but the trimethylsilylethers are too susceptible to solvolysis to be used as efficient protecting groups. However, the *t*-butyldimethylsilyloxy group is ca. 10^4 times more hydrolytically stable,[19] and is widely used as protecting group. The protected 4-hydroxybenzaldehyde **1** is classically obtained by reaction with *t*-butyldimethylchlorosilane.[20] The condensation of **1** with the phosphorhydrazide **2** affords easily the dendron **3-G_1** (Scheme 1). This reaction generates water, but no hydrolysis on the $P(S)Cl_2$ function is observed. This stability towards water in the absence of base is in perfect agreement with all our previous observations concerning this function in the chemistry of dendrimers.[7,8,13,18] Compound **3-G_1** is in particular characterized by the presence of a singlet in ^{31}P NMR (δ = 63.3 ppm). The disappearance of the singlet corresponding to the aldehyde of **1** in ^1H NMR (δ = 9.87 ppm) on behalf of the appearance of another singlet (δ = 7.71 ppm) corresponding to the CH = N group of dendron **3-G_1** is characteristic of the condensation. It has

been shown that the $P(S)Cl_2$ groups have a versatile reactivity with amines.[21-23] As an illustration of this reactivity, the reaction with N,N-diethylethylenediamine has been attempted. Such reaction was previously carried out on the terminal groups of several generations of phosphorus dendrimers, to afford ammonium terminal groups, the tertiary amines being used for trapping HCl generated by the substitution reaction on the $P(S)Cl_2$ functions.[12,24] The resulting compounds are most generally soluble in water and not in organic solvents. For practical purposes, in the case of the reactivity of compound **3-G$_1$**, we preferred to avoid the presence of ammonium groups, to keep the solubility in organic solvents for reagents and products. Thus the substitution reaction is carried out in the presence of potassium carbonate, for trapping HCl. Dendron **4-G$_1$** is obtained in this way (Scheme 1). This compound is in particular characterized by the appearance of a new singlet in ^{31}P NMR at δ = 71.4 ppm ($\Delta\delta$ = +8.1 ppm relative to **3-G$_1$**).

The deprotection of the phenol of dendron **4-G$_1$** has been attempted by adding 1.3 equiv. of tetrabutylammonium fluoride (TBAF overnight at room temperature).[25] No clear change could be detected on the ^1H NMR spectrum, which displayed the presence of large quantities of silyl derivatives after work-up. However, the cleavage of the protecting group is clearly detected by $^{13}C\{^1H\}$ NMR, with the presence of a new signal at 115.9 ppm for the carbon *ortho* to the OH group, instead of 120.5 ppm for the carbon *ortho* to the OSi group in **4-G$_1$**. Despite several attempts to remove the *t*-butyldimethylsilyl derivatives from the reaction mixture, the purification was unsuccessful, thus another approach to have a protected group at the core of dendrons was attempted.

The new starting compound is the 4-ethynylbenzaldehyde, protected by a trimethylsilyl group on the terminal alkyne (compound **5**), terminal alkynes react easily with alkene halides[26] or arene halides[27] by Sonogashira couplings. Compound **5** was obtained by Sonogashira coupling between *p*-bromobenzaldehyde and trimethylsilylacetylene.[28] The condensation reaction between **5** and the phosphorhydrazide **2** affords readily the dendron **6-G_1** (Scheme 2).

This dendron is characterized by NMR as was **3-G_1**, but it was also possible to grow single crystals suitable for X-ray diffraction. The X-ray diffraction structure of dendron **6-G_1** is shown in Figure 1; the crystallographic data, the bond lengths and bond angles are gathered in Tables 1, 2, and 3, respectively. At first glance, most part of the molecule is almost flat, from Si to S, including also the carbon C10 linked to N2 (Figure 1B). The main deviations from the plane defined by the carbon atoms of the aromatic ring are 0.31 Å for Si(1), 0.53 Å for P(1), and 0.35 Å for S(1). N2 is planar (sum of angles around N2 = 360°), and the N2-P1 bond length is short (1.637 Å); it corresponds more to a double bond than to a single bond. Such behavior was already observed in other X-ray diffraction structure of phosphorhydrazone-containing dendritic structures,[29-32] and contributes to the planarity of the structure. The most acute angle in the structure is the Cl1-P1-Cl2 angle (99.82°); this value is also comparable to that found in the previously reported structures having such function.

Dendron **6-G_1** is the starting point for the synthesis of two other dendrons, by using the well-established reactivity of phenols with the $P(S)Cl_2$ function,[33-36] in the presence of bases. The first phenol used is 4-hydroxybenzaldehyde (**7**), which is one of the building blocks for the classical growing of the phosphorhydrazone dendrimers.[37,38] The reaction carried out in the presence of

cesium carbonate, affords readily dendron **8-G_1** (Scheme 3). This dendron is in particular characterized by ^{31}P NMR, which displays a signal at δ = 60.1 ppm. The difference with the signal of the starting compound (δ = 62.7 ppm for **6-G_1**) is relatively small, but an intermediate signal at ca 69 ppm, corresponding to the monosubstitution, was observed during the monitoring of the reaction.

Dendron **6-G_1** was also used as starting material for the grafting of dansyl derivatives. Such derivative was chosen as fluorescent dendritic compounds are of particular interest.[3,39] We have already synthesized the phenol dansyl compound **9**, and used it for the synthesis of several types of fluorescent dendritic structures.[40,41] The reaction with dendron **6-G_1** is carried out in the presence of cesium carbonate as the base, to afford dendron **10-G_1** (Scheme 3). The ^{31}P NMR spectrum of **10-G_1** displays a singlet at δ = 62.4 ppm. In this case also, an intermediate signal at ca 69 ppm was observed during the course of the reaction, corresponding to the monosubstitution; this signal disappeared progressively, on behalf of the increase of the signal corresponding to the full substitution.

Several attempts have been carried out for the deprotection of the alkyne group of dendrons **8-G_1** and **10-G_1**, using classical methods. Potassium carbonate in methanol,[42] or TBAF in THF[43] induces the degradation of the product (cleavage of some P-O-Aryl groups) before the end of the deprotection. Cesium fluoride and crown ether[44] in THF induce no reaction.

EXPERIMENTAL

General

All manipulations were carried out with standard high-vacuum and dry-argon techniques. The solvents were freshly dried and distilled (THF and diethylether over sodium/benzophenone, pentane and CH_2Cl_2 over phosphorus pentoxide). Preparative chromatography was performed with Merck Kieselgel. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AC 200, AC250, ARX250 spectrometers. All spectra were measured at 25°C in the indicated deuterated solvents. Proton and carbon chemical shifts (δ) are reported in ppm and coupling constants (*J*) are reported in Hertz (Hz). The signals in the spectra are described as s (singlet), d (doublet), t (triplet), and m (multiplet). References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR and $SiMe_4$ for ^{1}H and ^{13}C NMR. The numbering used for NMR assignments is depicted in Figure 2. Compounds **1**,[20] **2**,[30] **5**,[28] and **9**[41] were synthesized according to methods previously reported.

Synthesis of dendron 3-G_1.

A solution [0.20 mol/L] of compound **2** in chloroform (130 mL, 26 mmol) was added at 0°C to a solution of compound **1** (4.85 g, 21.0 mmol) in dichloromethane (20 mL). The resulting solution was stirred for 2 h. at room temperature, then concentrated to a few mL. This concentrated solution was purified by column chromatography on silica gel, with dichloromethane as eluent. The solution was evaporated to dryness, then the resulting powder was dissolved in pentane, and left slowly evaporated, to afford dendron **3-G_1** as a white powder in 56% yield.

3-G_1: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 63.3 (s) ppm. ^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 6H, CH_3Si), 1.04 (s, 9H, CH_3C), 3.50 (d, $^{3}J_{HP}$ = 14.3 Hz, 3H, CH_3NP), 6.92 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H, C_0^{2}), 7.67 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H, C_0^{3}), 7.71 (s, 1H, CH = N) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = -4.4 (s, CH_3Si), 18.3 (s, $\underline{C}CH_3$), 25.7 (s, $C\underline{C}H_3$), 31.7 (d, $^{2}J_{CP}$ = 13.2 Hz, CH_3NP), 120.5 (s, C_0^{2}), 127.5 (s, C_0^{4}),

128.9 (s, C_0^3), 141.9 (d, $^3J_{CP}$ = 20 Hz, CH = N), 157.8 (s, C_0^1) ppm. MS (DCI/NH_3) m/z = 397 $[M+1]^+$

Synthesis of dendron 4-G_1

N,N-diethylethylenediamine (1.35 g, 8.2 mmol) was added at 0°C to a solution of dendron **3-G_1** (1.500 g, 3.77 mmol) in THF (25 mL), containing K_2CO_3 (3.75 g, 27.1 mmol). The resulting mixture was stirred overnight at room temperature, then filtered. The resulting solution was evaporated to dryness. The residue was dissolved in toluene (25 mL) and evaporated to dryness (3 times), then in CH_2Cl_2 (3 times) to eliminate the slight excess of N,N-diethylethylene diamine. Dendron **4-G_1** was obtained as a white powder in 99% yield.

4-G_1: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 71.4 (s) ppm. ^1H NMR ($CDCl_3$): δ = 0.18 (s, 6H, CH_3Si), 0.96 (s, 9H, CH_3C), 1.01 (t, $^3J_{HH}$ = 7 Hz, 12H, $\underline{CH_3}CH_2N$), 2.63 (m, 12H, $\underline{CH_2}N(\underline{CH_2}CH_3)$, 3.04 (m, 4H, CH_2NP), 3.16 (d, $^3J_{HP}$ = 10 Hz, 3H, CH_3NP), 4.15 (br s, 2H, NH), 6.79 (d, $^3J_{HH}$ = 8.6 Hz, 2H, C_0^2), 7.46 (br s, 1H, CH = N), 7.50 (d, $^3J_{HH}$ = 8.6 Hz, 2H, C_0^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = -3.6 (s, CH_3Si), 11.2 (s, $CH_2\underline{C}H_3$), 19.4 (s, $\underline{C}CH_3$), 25.6 (s, $C\underline{C}H_3$), 30.4 (d, $^2J_{CP}$ = 11 Hz, CH_3NP), 38.3 (s, CH_2NP), 46.4 (s, $\underline{C}H_2CH_3$), 53.1 (d, $^3J_{CP}$ = 7.5 Hz, $\underline{C}H_2CH_2NP$), 120.5 (s, C_0^2), 126.5 (s, C_0^4), 128.2 (s, C_0^3), 137.3 (d, $^3J_{CP}$ = 12 Hz, CH = N), 158.7 (s, C_0^1) ppm.

Synthesis of dendron 6-G_1.

A solution [0.24 mol/L] of compound **2** in chloroform (10.5 mL, 2.52 mmol) was added at 0°C to a solution of compound **5** (0.500 g, 2.47 mmol) in chloroform (5 mL). The resulting solution was stirred overnight at room temperature, then evaporated to dryness. The residue was

dissolved in a minimum amount of pentane, and cooled to induce the crystallization of **6-G$_1$** as colorless crystals in 75% yield. A single crystal obtained in this way was suitable for X-ray diffraction studies.

6-G$_1$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.7 (s) ppm. ^1H NMR ($CDCl_3$): δ = 0.31 (s, 9H, CH_3Si), 3.48 (d, $^3J_{HP}$ = 13.8 Hz, 3H, CH_3NP), 7.51 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_0^2), 7.63 (d, $^4J_{HP}$ = 2.4 Hz, 1H, CH = N), 7.67 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_0^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.0 (CH_3Si), 31.9 (d, $^2J_{CP}$ = 13.3 Hz, CH_3NP), 96.6 (s, Ca), 104.7 (s, Cb), 124.8 (s, C_0^1), 127.2 (s, C_0^2), 132.3 (s, C_0^3), 134.0 (s, C_0^4), 141.0 (d, $^3J_{CP}$ = 18.7 Hz, CH = N) ppm.

Synthesis of dendron 8-G$_1$.

THF (20 mL) was added to a mixture of dendron **6-G$_1$** (0.500 g, 1.37 mmol), of 4-hydroxybenzaldehyde **7** (0.350 g, 2.87 mmol), and cesium carbonate (1.00 g, 3.07 mmol). The resulting mixture was stirred overnight at room temperature. The suspension was filtered over Celite, then the solution was evaporated to dryness. The resulting powder was washed 3 times with 25 mL of a mixture diethylether/pentane (1:1), affording dendron **8-G$_1$** as a white powder in 65% yield.

8-G$_1$: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 60.1 (s) ppm. ^1H NMR ($CDCl_3$): δ = 0.25 (s, 9H, CH_3Si), 3.40 (d, $^3J_{HP}$ = 10.8 Hz, 3H, CH_3NP), 7.47 (d, $^3J_{HH}$ = 8.4 Hz, 4H, C_1^2), 7.59 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_0^2), 7.65 (d, $^4J_{HP}$ = 1.2 Hz, 1H, CH = N), 7.68 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_0^3), 7.84 (d, $^3J_{HH}$ = 8.4 Hz, 4H, C_1^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.0 (CH_3Si), 33.0 (d, $^2J_{CP}$ = 13.3 Hz, CH_3NP), 96.4 (s, Ca), 104.7 (s, Cb), 122.0 (s, C_1^2), 124.4 (s, C_0^1), 126.8 (s, C_0^2), 131.5 (s, C_1^3), 132.4 (s,

C_0^3), 133.7 (s, C_0^4), 134.4 (s, C_1^4), 140.0 (d, $^3J_{CP}$ = 13.8 Hz, CH = N), 155.2 (d, $^2J_{CP}$ = 7.3 Hz, C_1^1), 190.7 (s, CHO) ppm. MS (DCI/NH_3) *m/z* = 535 $[M+H]^+$, 552 $[M+NH_4]^+$.

Synthesis of dendron 10-G_1.

A solution of dendron **8-G_1** (0.250 g, 0.68 mmol) in THF (5 mL) was added to a suspension of compound **9** (0.540 g, 1.44 mmol) and cesium carbonate (0.500g, 1.54 mmol) in THF (30 mL). The resulting mixture was stirred at room temperature for two days. This mixture was then filtered over Celite, and the solution was evaporated to dryness. The resulting powder was purified by column chromatography on silica gel, with a gradient of polarity for the eluent, from ethylacetate/hexane (1:1) to ethylacetate/1% methanol. Dendron **10-G_1** was isolated as a yellow powder in 40% yield.

10-G_1: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.4 (s) ppm. ^1H NMR ($CDCl_3$): δ = 0.30 (s, 9H, CH_3Si), 2.58 (t, $^3J_{HH}$ = 6.2 Hz, 4H, CH_2Ar), 2.84 (s, 12H, $N(CH_3)_2$), 3.10 (t, $^3J_{HH}$ = 6.5 Hz, 4H, CH_2N), 3.30 (d, $^3J_{HP}$ = 10.2 Hz, 3H, CH_3NP), 5.28 (br s, 2H, NH), 6.84 (d, $^3J_{HH}$ = 8.2 Hz, 4H, C_1^2), 6.99 (d, $^3J_{HH}$ = 8.2 Hz, 4H, C_1^3), 7.11 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H_{Dns}), 7.48 (m, 6H, C_0^2, $2H_{Dns}$), 7.65 (m, 3H, C_0^3, CH = N), 8.22 (m, 4H, $2H_{Dns}$), 8.51 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_{Dns}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.0 (s, CH_3Si), 33.1 (d, $^2J_{CP}$ = 12.7 Hz, CH_3NP), 35.1 (s, CH_2Ar), 44.3 (s, CH_2N), 45.4 (s, $N(CH_3)_2$), 96.0 (s, Ca), 104.9 (s, Cb), 115.3 (s, C_{Dns}), 118.8 (s, C_{Dns}), 121.3 (s, C_1^2), 123.2 (s, C_0^1), 126.8 (s, C_0^2), 128.5 (s, C_{Dns}), 129.5 (s, C_{Dns}), 129.7 (s, C_1^3), 129.8 (s, C_{Dns}), 130.4 (s, C_{Dns}), 132.3 (s, C_0^3), 134.8 (s, C_{Dns}), 134.9 (s, C_0^4), 135.0 (s, C_1^4), 139.1 (d, $^3J_{CP}$ = 10 Hz, CH = N), 149.2 (d, $^2J_{CP}$ = 7.1 Hz, C_1^1), 151.9 (s, C_{Dns}) ppm.

Methods of data collection and structure solving and refinement

Intensity data were collected at 180K on an IPDS STOE diffractometer. Structure was solved by direct methods using SIR92, and refined by full-matrix least-squares procedures using the programs of CRYSTALS. Atomic scattering factors were taken from the International tables for X-ray Crystallography. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using a riding model. Absorption corrections were introduced using the program MULTISCAN.

CCDC 1410508 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, B2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

CONCLUSION

We have synthesized two new families of small phosphorus-containing dendrons, having as core either a phenol protected by a *t*-butyldimethylsilyl group, or a terminal alkyne protected by a trimethylsilyl group. The structure of one of the smallest dendron, having a $P(S)Cl_2$ terminal group, has been determined by X ray crystallography. The $P(S)Cl_2$ terminal group is particularly suitable for further functionalization, as illustrated by the grafting of amines (potentially protonable for inducing solubility in water), aldehydes (potentially usable for continuing the growing of the dendron), and dansyl derivatives (potentially usable as fluorescent marker). This work demonstrates that the known reaction of the $P(S)Cl_2$ functions with amines and with

phenols in basic conditions is compatible with the presence of the protecting groups at the core. Unfortunately, the deprotection of the core was difficult. In the case of the *t*-butyldimethylsilyloxy group, the deprotection is quantitative with tetrabutylammonium fluoride, but the *t*-butyldimethylsilyl derivatives are very difficult to remove from the reaction mixture. In the case of the trimethylsilyl group protecting the alkyne, despite 3 different attempts, degradation of the dendrons was observed together with the deprotection. It is clear that other protection and deprotection methods have to be found, but the concept of using dendrons for the specific functionalization of dendrimers remains an interesting target for the precise functionalization of dendrimers with two or more types of functions.

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Table 1 Crystallographic data and refinement for dendron **6-G_1**

Formula	$C_{13}H_{17}Cl_2N_2PSSi$
M	363.32
Temperature K	180
Cryst. Syst.	monoclinic
Space group	C 2/c
a/Å	34.971(7)
b/Å	6.9711(14)
c/Å	15.192(3)
β/deg	96.70(3)
V/Å^3	3678.2(13)
Z	8
μ(Mo-Kα)/mm^{-1}	0.611
Reflections measured	14747
Reflections unique	3516 (Rint = 0.069)
Parameters	181
Reflections used in the calculations [I>1.2σ(I)]	R1 = 0.0458, wR2 = 0.0531

Table 2 Selected bond lengths (Å) for dendron **6-G$_1$**.

Bond	**Bond Length (Å)**	**Bond**	**Bond Length (Å)**	**Bond**	**Bond Length (Å)**
C1 -- C2	1.211(6)	C6 -- C7	1.395(5)	C13 -- Si1	1.843(5)
C1 -- Si1	1.832(4)	C6 -- C9	1.465(5)	P1 -- Cl2	2.0232(15)
C2 -- C3	1.439(5)	C7 -- C8	1.382(5)	P1 -- Cl1	2.0162(15)
C3 -- C4	1.410(6)	C9 -- N1	1.281(5)	P1 -- S1	1.8936(15)
C3 -- C8	1.397(6)	C10 -- N2	1.464(5)	P1 -- N2	1.637(3)
C4 -- C5	1.379(5)	C11 -- Si1	1.854(5)	N2 -- N1	1.391(4)
C5 -- C6	1.396(5)	C12 -- Si1	1.852(5)		

Table 3 Selected bond angles (°) for dendron **6-G_1**.

Bonds	**Angle (°)**	**Bonds**	**Angle (°)**	**Bonds**	**Angle (°)**
C2 -- C1 -- Si1	177.8(4)	C6 -- C7 -- C8	120.1(4)	C11 -- Si1 -- C13	111.9(3)
C1 -- C2 -- C3	176.8(4)	C3 -- C8 -- C7	121.0(4)	C12 -- Si1 -- C13	110.4(2)
C2 -- C3 -- C4	120.9(4)	C6 -- C9 -- N1	119.3(3)	C1 -- Si1 -- Cl1	108.4(2)
C2 -- C3 -- C8	120.2(4)	Cl2 -- P1 -- Cl1	99.82(7)	C1 -- Si1 -- Cl2	108.3(2)
C4 -- C3 -- C8	118.9(3)	Cl2 -- P1 -- S1	114.17(7)	C1 -- Si1 -- Cl3	108.2(2)
C3 -- C4 -- C5	119.7(4)	Cl1 -- P1 -- S1	114.78(7)	C10 -- N2 -- P1	124.2(2)
C4 -- C5 -- C6	121.2(4)	Cl2 -- P1 -- N2	105.62(13)	C10 -- N2 -- N1	121.7(3)
C5 -- C6 -- C7	119.1(3)	Cl1 -- P1 -- N2	103.92(12)	P1 -- N2 -- N1	113.8(2)
C5 -- C6 -- C9	119.0(3)	S1 -- P1 -- N2	116.63(12)	C9 -- N1 -- N2	118.6(3)
C7 -- C6 -- C9	121.9(3)	C11 -- Si1 -- C12	109.6(2)		

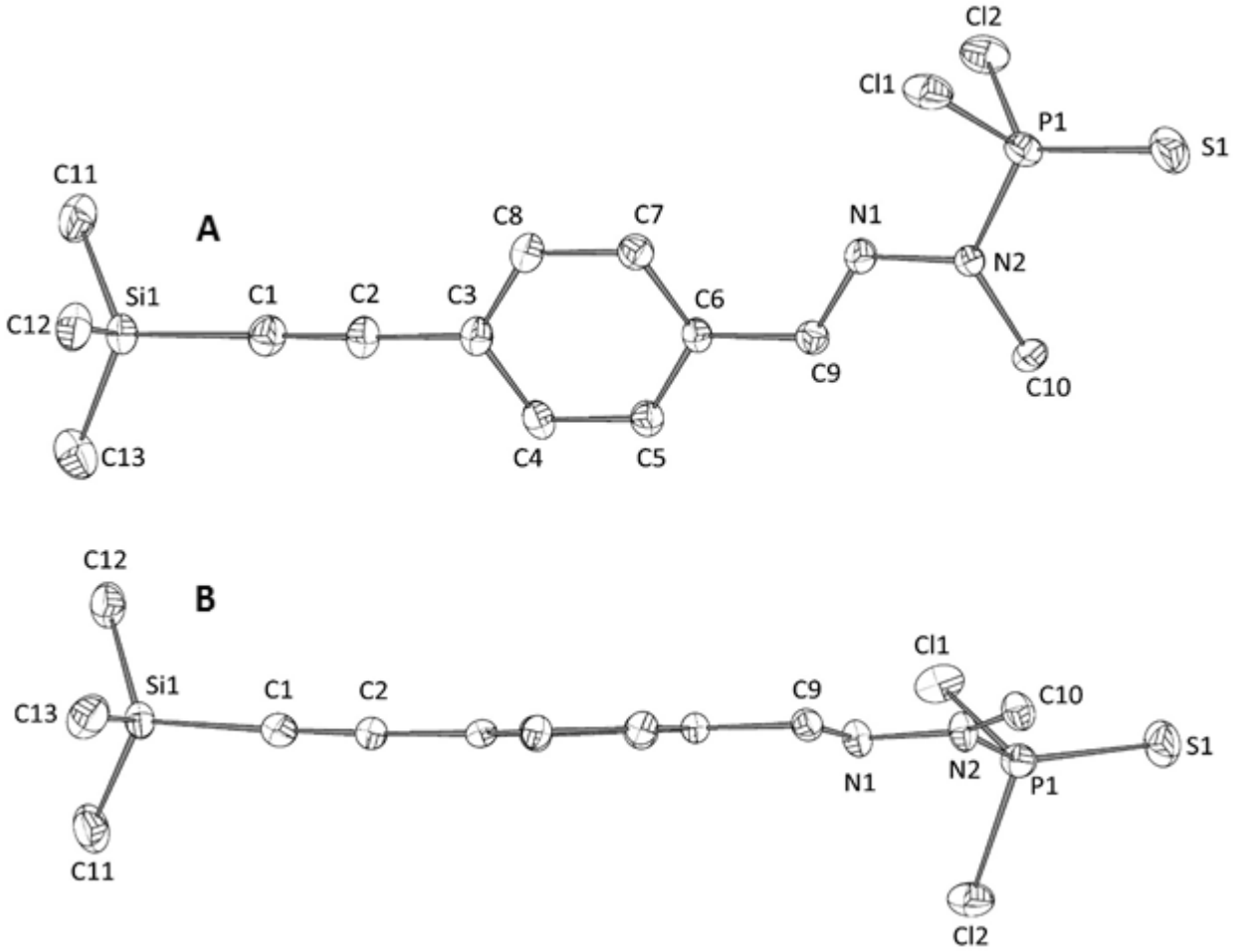


Figure 1 A) X-ray diffraction structure of dendron **6-G$_1$** (H atoms are omitted for clarity). B) Other view of the structure of dendron **6-G$_1$**.

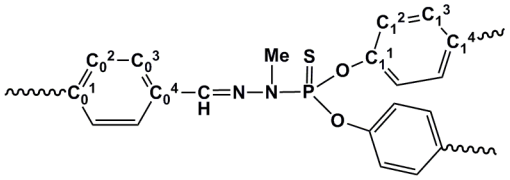
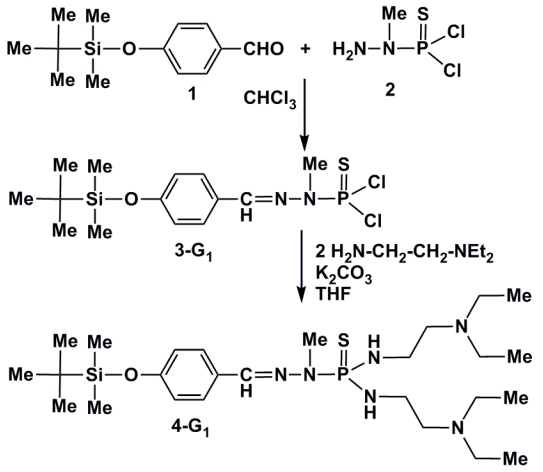
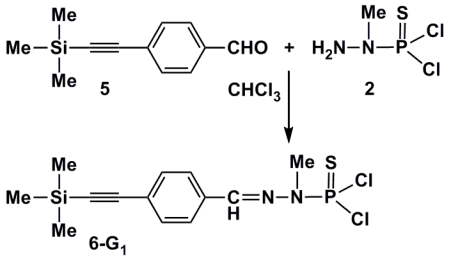


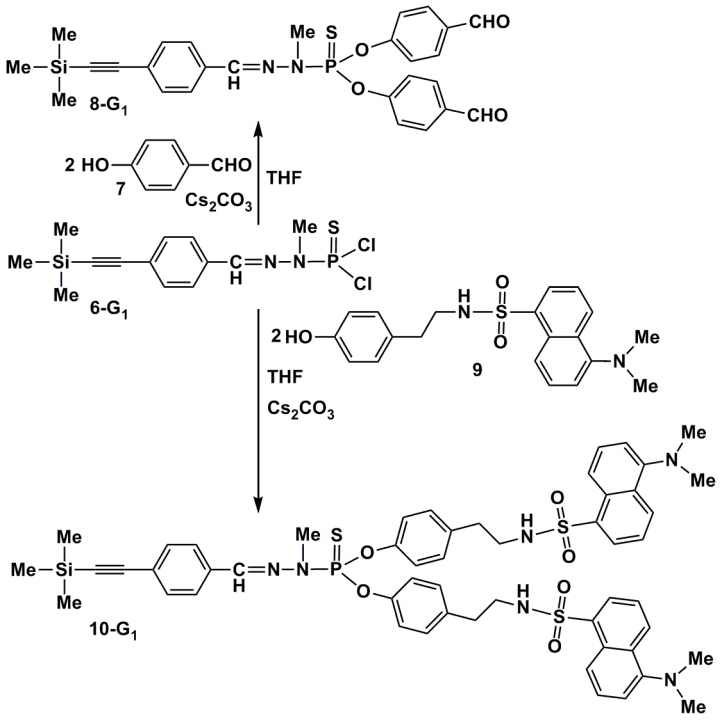
Figure 2 Numbering used for the assignment of NMR signals.



Scheme 1 Synthesis of dendrons **3-G_1** and **4-G_1**.



Scheme 2 Synthesis of dendron **6-G_1**.



Scheme 3 Synthesis of dendrons **8-G$_1$** and **10-G$_1$**.