

# Synthesis and Characterization of Phosphorus Dendrimers Containing Long, Conjugated Branches

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*Dedicated to Prof. Dr. Michael Veith on the occasion of his 60th birthday*

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The synthesis of a new family of phosphorus dendrimers is described up to the fifth generation (96 end-groups). The reaction is based on the nucleophilic substitution of P(S)Cl<sub>2</sub> end-groups by 4-hydroxy-3-methoxycinnamaldehyde, and by the condensation of CHO end-groups with a dichlorophosphorhydrazide. The structure of the first generation has been determined by X-ray diffraction. This structure shows

that the OC<sub>6</sub>H<sub>3</sub>CH=CHCH=NNMeP(S) linkage is close to planarity, which indicates an extended conjugation of this linkage that leads to a semi-rigid skeleton for these dendrimers.

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## Introduction

Dendrimers are a very special type of hyperbranched and monodisperse polymers that are built step by step by the repetition of a sequence of reactions.<sup>[1–3]</sup> They constitute one of the most important new fields of research in chemistry, as shown by the large number of publications, patents or reports listed in Chemical Abstracts (more than 7000), 97% of them having been published within the last ten years. In more recent years the emphasis has been mainly on the properties and applications of dendrimers, although a large part of the work is still devoted to synthesis. In most cases, the synthetic aspects mainly concern modification of the end-groups, whereas changes of the monomeric units constituting the skeleton of dendrimers remain rare. However, the nature of the interior plays an important role in the properties of dendrimers, particularly in terms of flexibility or rigidity, which dictates the possibility or not for the end-groups to be backfolded.<sup>[4]</sup> PAMAM,<sup>[5]</sup> PPI,<sup>[6]</sup> or polysiloxane<sup>[7]</sup> dendrimers and arborols<sup>[8]</sup> have flexible branches, constituted at least in part of alkyl linkages, whereas poly(aryl ether) dendrimers<sup>[9]</sup> are less flexible, and polyphenylene dendrimers<sup>[10]</sup> possess a highly rigid skeleton. The phosphorus dendrimers we synthesize<sup>[11]</sup> have some of the longest branches, constituted of P(S)OC<sub>6</sub>H<sub>4</sub>CH=NNMeP(S) linkages, which afford a semi-rigid

structure. The rigid part is due to the conjugated OC<sub>6</sub>H<sub>4</sub>CH=NNMeP(S) moieties, in which all atoms lie approximately in the same plane.<sup>[12]</sup> These phosphorus dendrimers possess many original properties in various fields such as the modification<sup>[13]</sup> or creation<sup>[14]</sup> of materials, catalysis,<sup>[15]</sup> or various biological uses.<sup>[16]</sup> In most cases, the hydrophobicity and the semi-rigidity of the interior of these dendrimers is believed to play a key role in determining their properties. If this semi-rigidity could be found also for longer branches, some properties of these dendrimers could be modified, particularly those connected to the size of the internal cavities or those connected to the density of end-groups. In order to be able to detect the modifications induced by the lengthening of the branches without changing other parameters, we decided to build dendrimers from 4-hydroxy-3-methoxycinnamaldehyde instead of the 4-hydroxybenzaldehyde used in our classical method of synthesis.<sup>[11]</sup> We report here the synthesis and characterization of this new series of semi-rigid dendrimers up to generation 5, as well as the crystal structure of the first generation obtained by X-ray diffraction.

## Results and Discussion

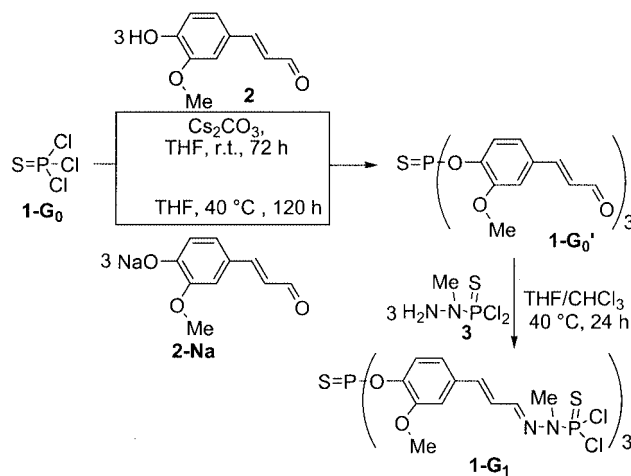
The first step of the synthesis is the nucleophilic substitution of the three chlorines of P(S)Cl<sub>3</sub> (**1-G<sub>0</sub>**) by 4-hydroxy-3-methoxycinnamaldehyde (**2**) under basic conditions. Two methods were used, but the reaction is very slow in both cases. The first method consists of reacting the cinnamaldehyde **2** and P(S)Cl<sub>3</sub> in THF, in the presence of Cs<sub>2</sub>CO<sub>3</sub>,

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for three days at room temperature. Under these conditions, dendrimer **1-G<sub>0</sub>'** was isolated in 52% yield after workup. The second method necessitates the preliminary synthesis of the sodium salt of 4-hydroxy-3-methoxycinnamaldehyde (**2-Na**), which is obtained by reaction of NaH with **2** in THF. A heterogeneous solution of this sodium salt in THF reacts with P(S)Cl<sub>3</sub> at 40 °C and this reaction needs five days to go to completion, as shown by <sup>31</sup>P NMR monitoring of the crude solution; compound **1-G<sub>0</sub>'** was isolated in 63% yield after workup (Scheme 1). This reaction is very slow, especially when compared to that involving the sodium salt of 4-hydroxybenzaldehyde, which reacts in a few hours at room temperature with P(S)Cl<sub>3</sub>.<sup>[11]</sup> Thus, the methoxy group in the *ortho* position relative to the site of the reaction seems to have a major influence on the reaction rate.

The condensation reaction between the aldehyde groups of **1-G<sub>0</sub>'** and the phosphorhydrazide **3** is more rapid and occurs in 24 h at room temperature. The first generation of the dendrimer, **1-G<sub>1</sub>**, was isolated in good yield after workup (90%). The condensation reaction induces the total disappearance of the signals corresponding to the aldehydes in the <sup>1</sup>H and <sup>13</sup>C NMR spectra, as well as in the IR spectra. Furthermore, this reaction induces the appearance of a new signal in the <sup>31</sup>P NMR spectrum at  $\delta = 61.3$  ppm, which corresponds to the P(S)Cl<sub>2</sub> end-groups, besides the signal at  $\delta = 54.6$  ppm corresponding to the core. In order to ascertain the structure of dendrimer **1-G<sub>1</sub>**, and, especially, to know whether the expected semi-rigidity of the lengthened branches is observed or not, single crystals suitable for X-ray diffraction were grown from acetonitrile solution.

The CAMERON drawing of compound **1-G<sub>1</sub>** is shown in Figure 1; bond lengths are given in Table 1, and bond



Scheme 1.

angles in Table 2. Despite the long time needed for the nucleophilic substitution, it appears that there is no particular steric hindrance at the level of the core because the three methoxy groups move away from the central phosphorus (P1). Thus, the slowness of the nucleophilic substitution observed for the synthesis of **1-G<sub>0</sub>'** is more likely due to the electronic influence of the methoxy group than to its steric influence. The arrangement of atoms close to the core is relatively symmetric, but all three branches of **1-G<sub>1</sub>** are different in the crystal, contrary to the structure of the related compound (S)P[OC<sub>6</sub>H<sub>4</sub>CH=NNMeP(S)Cl<sub>2</sub>]<sub>3</sub> (**4-G<sub>1</sub>**), which has also been determined by X-ray diffraction and which has the symmetrical structure of a three-blade propeller.<sup>[12]</sup> However, all three OC<sub>6</sub>H<sub>3</sub>CH=CHCH=NNMeP branches are relatively planar, thus illustrating the expected rigidity

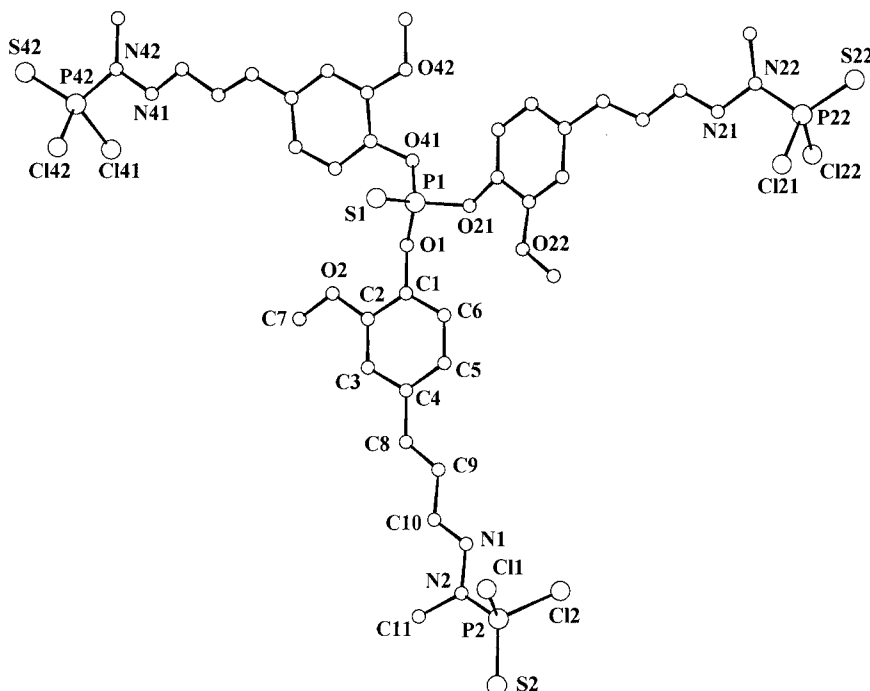
Figure 1. CAMERON drawing of **1-G<sub>1</sub>**.

Table 1. Bond lengths (Å) for **1-G<sub>1</sub>**.

P(1)–S(1)	1.888(4)	C(22)–O(22)	1.360(10)
P(1)–O(1)	1.573(6)	C(23)–C(24)	1.395(12)
P(1)–O(21)	1.572(6)	C(24)–C(25)	1.401(11)
P(1)–O(41)	1.579(6)	C(24)–C(28)	1.480(12)
P(2)–S(2)	1.887(4)	C(25)–C(26)	1.396(12)
P(2)–Cl(1)	2.020(5)	C(27)–O(22)	1.427(12)
P(2)–Cl(2)	1.989(4)	C(28)–C(29)	1.338(12)
P(2)–N(2)	1.644(8)	C(29)–C(30)	1.460(13)
C(1)–C(2)	1.375(11)	C(30)–N(21)	1.272(11)
C(1)–C(6)	1.381(11)	C(31)–N(22)	1.449(13)
C(1)–O(1)	1.407(10)	N(21)–N(22)	1.420(11)
C(2)–C(3)	1.387(12)	P(42)–S(42)	1.904(3)
C(2)–O(2)	1.378(10)	P(42)–Cl(41)	2.001(4)
C(3)–C(4)	1.387(11)	P(42)–Cl(42)	2.012(4)
C(4)–C(5)	1.397(12)	P(42)–N(42)	1.643(7)
C(4)–C(8)	1.463(13)	C(41)–C(42)	1.380(11)
C(5)–C(6)	1.364(12)	C(41)–C(46)	1.383(11)
C(7)–O(2)	1.410(10)	C(41)–O(41)	1.392(9)
C(8)–C(9)	1.338(12)	C(42)–C(43)	1.381(11)
C(9)–C(10)	1.431(12)	C(42)–O(42)	1.377(9)
C(10)–N(1)	1.278(11)	C(43)–C(44)	1.397(11)
C(11)–N(2)	1.460(11)	C(44)–C(45)	1.401(12)
N(1)–N(2)	1.408(10)	C(44)–C(48)	1.454(11)
P(22)–S(22)	1.885(4)	C(45)–C(46)	1.380(11)
P(22)–Cl(21)	2.012(4)	C(47)–O(42)	1.427(10)
P(22)–Cl(22)	1.990(4)	C(48)–C(49)	1.331(11)
P(22)–N(22)	1.644(8)	C(49)–C(50)	1.441(12)
C(21)–C(22)	1.386(11)	C(50)–N(41)	1.286(10)
C(21)–C(26)	1.357(11)	C(51)–N(42)	1.455(11)
C(21)–O(21)	1.409(9)	N(41)–N(42)	1.411(9)
C(22)–C(23)	1.382(11)		

of this linkage. The branch linked to P2 is the most planar: the maximum deviations to the mean plane defined by the aromatic ring are  $-0.268$  Å for P2 and  $0.169$  Å for O1; the branch linked to P22 is the least planar: the maximum deviations to the mean plane defined by the aromatic ring are  $1.976$  Å for P22 and  $1.343$  Å for N22. All the CH=CH–CH=N linkages retain the all-*trans* configuration, thereby ensuring a maximum elongation of the branches. To the best of our knowledge, these arms are the longest ever reported for dendrimers characterized by X-ray diffraction (P1...P2 =  $12.20$  Å, P1...P22 =  $12.49$  Å, P1...P42 =  $12.02$  Å for dendrimer **1-G<sub>1</sub>**; cf  $9$  Å for **4-G<sub>1</sub>**). Furthermore, the distance between two arms in the same molecule is large (P2...P22 =  $17.02$  Å, P22...P42 =  $23.86$  Å, P42...P2 =  $20.82$  Å for dendrimer **1-G<sub>1</sub>**; cf  $17$  Å for **4-G<sub>1</sub>**). In the packing, two molecules appear to interact through two aromatic groups of each dendrimers ( $\pi$ – $\pi$  interactions; Figure 2). In addition, short distances are found between the central sulfur atom (S1) of one molecule and a chlorine (Cl41) of another molecule, as well as between two chlorines of two molecules (Cl42 and Cl21) (Figure 3).

The very large distance between each end-group found in **1-G<sub>1</sub>** indicates that there should be no particular problem to continue the growth of the dendrimer. Starting from **1-G<sub>1</sub>**, the growth of the dendrimer was pursued by treatment with six equivalents of the salt **2-Na**. In this case also, the reaction is slow and again needs five days at  $40$  °C in THF to go to completion. The nucleophilic substitution induces a slight deshielding of the signal corresponding to the phos-

Table 2. Bond angles (°) for **1-G<sub>1</sub>**.

S(1)–P(1)–O(1)	117.2(3)	C(23)–C(24)–C(25)	120.0(8)
S(1)–P(1)–O(21)	118.4(2)	C(23)–C(24)–C(28)	120.6(8)
O(1)–P(1)–O(21)	100.3(3)	C(25)–C(24)–C(28)	119.4(8)
S(1)–P(1)–O(41)	117.3(3)	C(24)–C(25)–C(26)	119.4(9)
O(1)–P(1)–O(41)	99.8(3)	C(21)–C(26)–C(25)	119.2(8)
O(21)–P(1)–O(41)	100.4(3)	C(24)–C(28)–C(29)	125.7(10)
S(2)–P(2)–Cl(1)	113.5(2)	C(28)–C(29)–C(30)	122.3(10)
S(2)–P(2)–Cl(2)	115.1(2)	C(29)–C(30)–N(21)	116.5(9)
Cl(1)–P(2)–Cl(2)	101.0(2)	C(30)–N(21)–N(22)	117.5(9)
S(2)–P(2)–N(2)	115.8(3)	P(22)–N(22)–C(31)	125.1(7)
C(1)–C(2)–C(3)	118.6(8)	P(22)–N(22)–N(21)	112.9(7)
C(1)–C(2)–O(2)	116.0(8)	C(31)–N(22)–N(21)	121.7(8)
C(3)–C(2)–O(2)	125.4(8)	P(1)–O(21)–C(21)	126.6(5)
C(2)–C(3)–C(4)	121.3(8)	C(22)–O(22)–C(27)	117.8(7)
C(3)–C(4)–C(5)	118.4(9)	S(42)–P(42)–Cl(41)	114.43(17)
C(3)–C(4)–C(8)	119.6(8)	S(42)–P(42)–Cl(42)	115.51(18)
C(5)–C(4)–C(8)	122.0(8)	Cl(41)–P(42)–Cl(42)	100.05(17)
C(4)–C(5)–C(6)	120.6(8)	S(42)–P(42)–N(42)	114.9(3)
C(1)–C(6)–C(5)	120.0(8)	Cl(41)–P(42)–N(42)	105.9(3)
C(4)–C(6)–C(9)	128.2(8)	Cl(42)–P(42)–N(42)	104.4(3)
C(8)–C(9)–C(10)	122.7(8)	C(42)–C(41)–C(46)	121.2(8)
C(9)–C(10)–N(1)	119.1(8)	C(42)–C(41)–O(41)	116.8(7)
C(10)–N(1)–N(2)	118.8(8)	C(46)–C(41)–O(41)	121.9(8)
P(2)–N(2)–C(11)	122.7(7)	C(41)–C(42)–C(43)	119.6(7)
P(2)–N(2)–N(1)	113.5(6)	C(41)–C(42)–O(42)	115.0(7)
C(11)–N(2)–N(1)	121.0(7)	C(43)–C(42)–O(42)	125.3(8)
P(1)–O(1)–C(1)	127.3(5)	C(42)–C(43)–C(44)	120.4(8)
C(2)–O(2)–C(7)	117.7(7)	C(43)–C(44)–C(45)	118.9(7)
S(22)–P(22)–Cl(21)	113.7(2)	C(43)–C(44)–C(48)	119.7(8)
S(22)–P(22)–Cl(22)	115.4(2)	C(45)–C(44)–C(48)	121.4(7)
Cl(21)–P(22)–Cl(22)	99.85(19)	C(44)–C(45)–C(46)	120.6(8)
S(22)–P(22)–N(22)	115.7(3)	C(41)–C(46)–C(45)	119.3(8)
Cl(21)–P(22)–N(22)	104.2(3)	C(44)–C(48)–C(49)	126.2(9)
Cl(22)–P(22)–N(22)	106.1(3)	C(48)–C(49)–C(50)	123.6(9)
C(22)–C(21)–C(26)	122.3(8)	C(49)–C(50)–N(41)	117.1(8)
C(22)–C(21)–O(21)	114.7(8)	C(50)–N(41)–N(42)	118.0(8)
C(26)–C(21)–O(21)	122.2(7)	P(42)–N(42)–C(51)	124.3(6)
C(21)–C(22)–C(23)	119.2(8)	P(42)–N(42)–N(41)	113.3(6)
C(21)–C(22)–O(22)	115.5(7)	C(51)–N(42)–N(41)	122.3(7)
C(23)–C(22)–O(22)	125.3(8)	P(1)–O(41)–C(41)	123.9(5)
C(22)–C(23)–C(24)	119.6(8)	C(42)–O(42)–C(47)	117.4(6)

phorus that undergo the reaction, from  $\delta = 61.3$  ppm for **1-G<sub>1</sub>** to  $\delta = 62.0$  ppm for **1-G<sub>1</sub>'** in the  $^{31}\text{P}$  NMR spectra. The  $^1\text{H}$  NMR spectrum of **1-G<sub>1</sub>'** shows that the CH=CH linkages included in CH=CH–CH=O and in CH=CH–CH=N linkages have retained their (*E*)-configuration as expected, as shown by the value of the  $^3J_{\text{H,H}}$  coupling constant ( $15.9$  Hz). The condensation reaction with the phosphorhydrazide **3** and the nucleophilic substitution were each repeated four times from **1-G<sub>1</sub>'** to afford finally the fifth generation dendrimer **1-G<sub>5</sub>'** (96 aldehyde end-groups; Scheme 2).

In all cases the nucleophilic substitution is slow, but we do not observe a lengthening of the reaction time with increasing generations. This suggests that there is no increase in the steric hindrance, and the slowness of the reaction is due to electronic influences and not to steric constraints. Obviously, all the intermediate compounds shown in Scheme 2 were isolated and characterized by multinuclear NMR and IR spectroscopy, and elemental analysis.  $^{31}\text{P}$  NMR spectroscopy appears, as usual, to be a very sensitive tool.<sup>[17]</sup> It is especially useful during the nucleophilic substitution. Indeed, on going from the P(S)Cl<sub>2</sub> end-groups ( $\delta = 61.3$  ppm) to the P(S)(OAr)<sub>2</sub> end-groups ( $\delta = 62.0$  ppm), a signal corresponding to the intermediate P(S)Cl(OAr) ( $\delta = 67$  ppm) is always observed, and disappears when the reac-

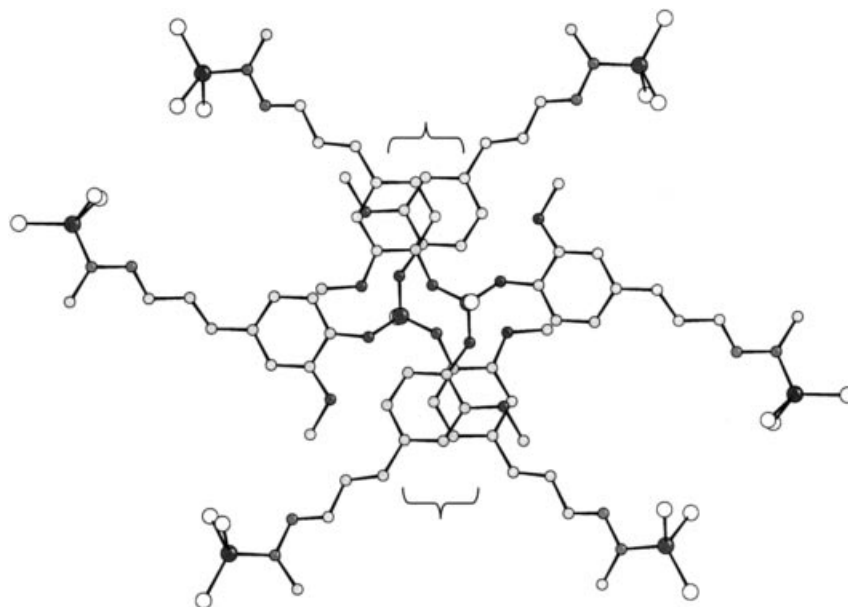


Figure 2.  $\pi$ - $\pi$  interactions between two molecules of **1-G<sub>1</sub>**.

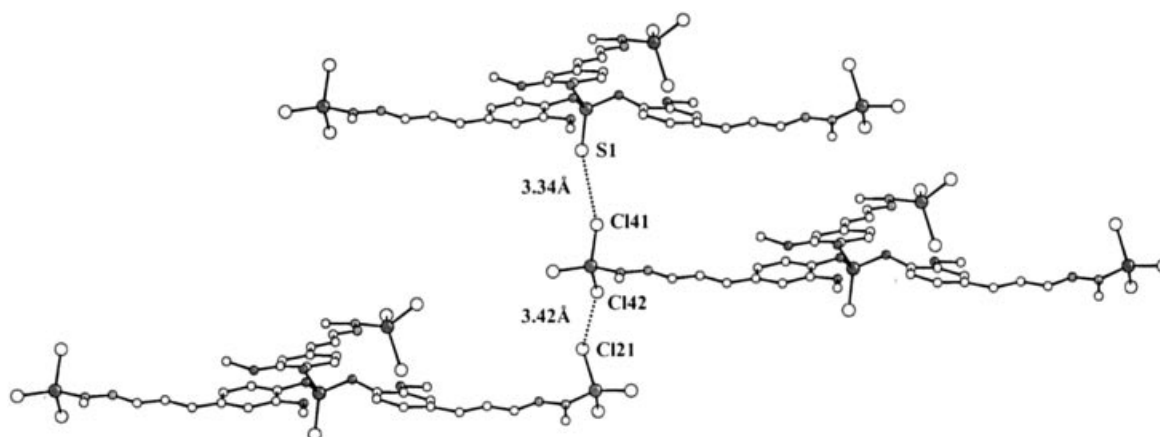


Figure 3. Short distances found in the crystal of **1-G<sub>1</sub>**.

tion has gone to completion. Interestingly, the condensation reaction with the phosphorhydrazide **3** is also detectable by  $^{31}\text{P}$  NMR spectroscopy: it produces a slight deshielding from  $\delta = 62.0$  ppm to  $\delta \approx 62.5$  ppm for the phosphorus that bears the cinnamaldehyde groups, despite the very long distance (9 bonds!) between these phosphorus centres and the sites of reaction. Furthermore, at this step,  $^1\text{H}$  NMR spectroscopy shows the total disappearance of the signals corresponding to the aldehydes. The signals corresponding to the  $\text{CH}=\text{CH}$  linkages are not detected by  $^1\text{H}$  NMR spectroscopy due to overlap of signals. However, we have already shown for phosphorus dendrimers containing photoisomerisable azobenzene linkages as branches that dramatic changes occur in the  $^{31}\text{P}$  NMR spectra upon isomerization;<sup>[18]</sup> this phenomenon is not observed for compounds **1-G<sub>n</sub>**, thus the *trans* configuration is retained.

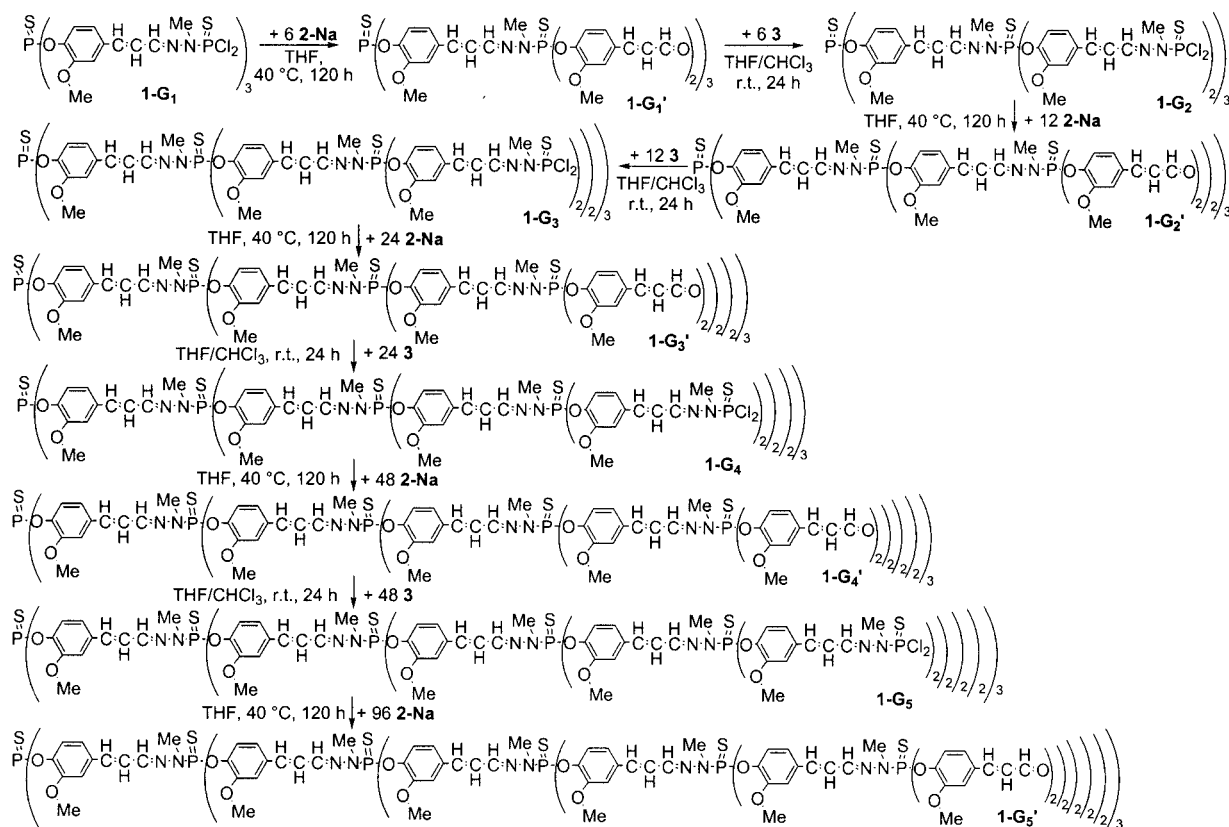
All reactions are quantitative on the crude products: NMR monitoring shows the total disappearance of the signals corresponding to the dendrimer end-groups at each

step. However, the yields of isolated products are not quantitative due to several washings carried out to eliminate the (slight) excess of reagents used. The yields of isolated compounds after the condensation steps are always better than the yields after the nucleophilic substitution steps because an excess of the salt **2-Na** is used in order to accelerate the reaction, and the total elimination of this excess by successive washings also eliminates part of the dendrimer.

## Conclusions

We have reported the synthesis of a new family of dendrimers made of very long branches containing 11 bonds between each branching point. The determination of the structure of the first generation by X-ray diffraction shows that these long branches are relatively planar due to their conjugation, thereby providing a semi-rigid skeleton to the dendrimers. To the best of our knowledge the length of each





Scheme 2.

arm (12 Å) is the largest value determined by X-ray diffraction for any type of regular dendrimer. The synthesis has been carried out up to the fifth generation, thus demonstrating the viability of the synthetic pathway up to high generations. No steric hindrance is observed, and the synthesis could have been pursued, although the lengthy nucleophilic substitution process did not incite us to continue the growth. The compounds obtained are large enough to possess all the properties of dendrimers, and work is in progress to compare the properties of these new compounds with those of dendrimers having shorter branches.

## Experimental Section

**General Remarks:** All manipulations were carried out with standard high-vacuum and dry-argon techniques. The solvents were freshly dried and distilled (THF and diethyl ether over sodium/benzophenone; pentane and  $\text{CH}_2\text{Cl}_2$  over phosphorus pentoxide; toluene over sodium). All experiments were protected against light by aluminium foils.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded with Bruker AC 200, AC 250, DPX 300 or AMX 400 spectrometers. References for NMR chemical shifts are 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$

and  $\text{SiMe}_4$  for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The assignment of  $^{13}\text{C}$  NMR signals was performed using  $J_{\text{mod}}$ , two dimensional HMBC, and HMQC, Broad Band or CW  $^{31}\text{P}$  decoupling experiments where necessary. The numbering scheme used for the NMR assignments is shown in Figure 4.

**Dendrimer (1- $G_0$ ). First Method:** Thiophosphoryl trichloride (313  $\mu\text{L}$ , 3.08 mmol) was added under argon to a solution of cinnamaldehyde (1.65 g, 9.26 mmol, 3 equiv.) and  $\text{C}_2\text{CO}_3$  (2.93 g, 9.5 mmol, 4 equiv.) in anhydrous THF (10 mL). The suspension was stirred for 3 d at room temp. The solution was half evaporated and dichloromethane was added (10 mL). The solution was filtered twice and the resulting orange solution was evaporated. The crude solid was dissolved in THF and a large amount of pentane was added, the suspension was vigorously stirred and the solvent was removed. The solid was washed again with THF/pentane and then with  $\text{Et}_2\text{O}$  (two times) and finally with ethanol. Yield: 52%, pale-yellow solid.

**Second Method:** Thiophosphoryl chloride (0.15 mL, 1.5 mmol) was added to a heterogeneous solution of the sodium salt of 4-hydroxy-3-methoxycinnamaldehyde (1 g, 5 mmol, obtained by reaction of 1 equiv. of NaH with 4-hydroxy-3-methoxycinnamaldehyde) in THF. The resulting mixture was stirred for 5 d at 40 °C. The heterogeneous solution was then centrifuged for 30 min at 10 000 rpm.

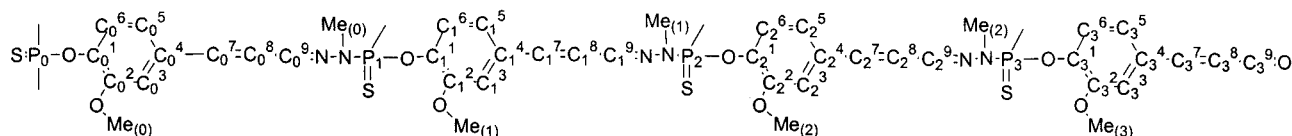


Figure 4. Numbering used for the NMR spectra.

The solution was recovered, evaporated to dryness, and washed three times with THF/pentane (1:5). Yield: 63%, pale-yellow powder, m.p. 196–198 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200.1 MHz):  $\delta$  = 3.87 (s, 9 H, O-Me<sub>0</sub>), 6.66 (dd,  $^3J_{\text{H,Htrans}} = 15.9$ ,  $^3J_{\text{H,H}} = 7.6$  Hz, 3 H, H-C<sub>0</sub><sup>8</sup>), 7.15 (s, 3 H, H-C<sub>0</sub><sup>3</sup>), 7.17 (d,  $^3J_{\text{H,H}} = 8$  Hz, 3 H, H-C<sub>0</sub><sup>5</sup>), 7.44 (d,  $^3J_{\text{H,Htrans}} = 15.9$  Hz, 3 H, H-C<sub>0</sub><sup>7</sup>), 7.55 (dd,  $^3J_{\text{H,H}} = 8$ ,  $^4J_{\text{H,P}} = 1.5$  Hz, 3 H, H-C<sub>0</sub><sup>6</sup>), 9.69 (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 3 H, H-C<sub>0</sub><sup>9</sup>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$  = 56.1 (s, O-Me<sub>0</sub>), 111.8 (s, C<sub>0</sub><sup>3</sup>), 121.7 (s, C<sub>0</sub><sup>5</sup>), 122.9 (d,  $^3J_{\text{C,P}} = 1$  Hz, C<sub>0</sub><sup>6</sup>), 128.8 (s, C<sub>0</sub><sup>8</sup>), 132.4 (s, C<sub>0</sub><sup>4</sup>), 142.1 (d,  $^2J_{\text{C,P}} = 7.8$  Hz, C<sub>0</sub><sup>1</sup>), 151.6 (s, C<sub>0</sub><sup>7</sup>, C<sub>0</sub><sup>2</sup>), 193.3 (s, C<sub>0</sub><sup>9</sup>) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 81.01 MHz):  $\delta$  = 53.8 (s, P<sub>0</sub>) ppm. IR (KBr):  $\nu_{\text{C=O}} = 1671$  cm<sup>-1</sup>. C<sub>30</sub>H<sub>27</sub>O<sub>9</sub>PS (594.6): calcd. C 60.60, H 4.58; found C 60.68, H 4.61.

**General Method for the Synthesis of Dendrimers with P(S)Cl<sub>2</sub> End-Groups (Series G<sub>n</sub>) (n = 1–5):** A solution of H<sub>2</sub>NNMeP(S)Cl<sub>2</sub> (10% excess) in CHCl<sub>3</sub> was added at room temp. to a solution of dendrimer 1-G<sub>n-1</sub>' dissolved in a minimum amount of THF. The resulting solution was stirred for 24 h at room temperature then evaporated to dryness, and the resulting powder was washed at least three times with diethyl ether/pentane (1:5), to afford dendrimer 1-G<sub>n</sub> as a pale-yellow powder.

**General Method for the Synthesis of Dendrimers with CHO End-Groups (Series G<sub>n</sub>') (n = 1–5):** The dendrimer 1-G<sub>n</sub> dissolved in a minimum amount of THF was added to a heterogeneous solution of the sodium salt of 4-hydroxy-3-methoxycinnamaldehyde (10% excess) in THF. The resulting mixture was stirred for 5 d at 40 °C. The heterogeneous solution was centrifuged, and the solution was recovered, evaporated to dryness, and washed three times with THF/pentane (1:5).

**Dendrimer 1-G<sub>1</sub>:** Yield: 90%, pale-yellow powder. Single crystals suitable for X-ray diffraction were grown from a saturated acetonitrile solution at room temperature.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200.1 MHz):  $\delta$  = 3.44 (d,  $^3J_{\text{H,P}} = 13.9$  Hz, 9 H, N-Me<sub>0</sub>), 3.87 (s, 9 H, O-Me<sub>0</sub>), 6.87 (d,  $^3J_{\text{H,Htrans}} = 16.0$  Hz, 3 H, H-C<sub>0</sub><sup>7</sup>), 7.00 (dd,  $^3J_{\text{H,Htrans}} = 16.0$ ,  $^3J_{\text{H,H}} = 8.0$  Hz, 3 H, H-C<sub>0</sub><sup>8</sup>), 7.03 (d,  $^3J_{\text{H,H}} = 8.4$  Hz, 3 H, H-C<sub>0</sub><sup>5</sup>), 7.11 (s, 3 H, H-C<sub>0</sub><sup>3</sup>), 7.50 (dd,  $^3J_{\text{H,H}} = 8.4$ ,  $^4J_{\text{H,P}} = 1.7$  Hz, 3 H, H-C<sub>0</sub><sup>6</sup>), 7.56 (dd,  $^3J_{\text{H,H}} = 8$ ,  $^4J_{\text{H,P}} = 2.3$  Hz, 3 H, H-C<sub>0</sub><sup>9</sup>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$  = 32.1 (d,  $^2J_{\text{C,P}} = 11.8$  Hz, N-Me<sub>0</sub>), 56.1 (s, O-Me<sub>0</sub>), 110.3 (s, C<sub>0</sub><sup>3</sup>), 120.2 (s, C<sub>0</sub><sup>5</sup>), 122.6 (d,  $^3J_{\text{C,P}} = 3.7$  Hz, C<sub>0</sub><sup>6</sup>), 125.4 (s, C<sub>0</sub><sup>8</sup>), 134.1 (s, C<sub>0</sub><sup>4</sup>), 138.8 (s, C<sub>0</sub><sup>7</sup>), 140.6 (d,  $^2J_{\text{C,P}} = 7.3$  Hz, C<sub>0</sub><sup>1</sup>), 144.2 (d,  $^3J_{\text{C,P}} = 19.6$  Hz, C<sub>0</sub><sup>9</sup>), 151.3 (d,  $^3J_{\text{C,P}} = 5.8$  Hz, C<sub>0</sub><sup>2</sup>) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 81.01 MHz):  $\delta$  = 54.6 (s, P<sub>0</sub>), 61.3 (s, P<sub>1</sub>) ppm. C<sub>33</sub>H<sub>36</sub>Cl<sub>6</sub>N<sub>6</sub>O<sub>6</sub>P<sub>4</sub>S<sub>4</sub> (1077.6): calcd. C 36.78, H 3.37, N 7.80; found C 36.82, H 3.39, N 7.76.

**Dendrimer 1-G<sub>1</sub>':** Yield: 80%, pale-yellow powder, m.p. 165–166 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250.1 MHz):  $\delta$  = 3.42 (d,  $^3J_{\text{H,P}} = 10.5$  Hz, 9 H, N-Me<sub>0</sub>), 3.83 (s, 9 H, O-Me<sub>0</sub>), 3.87 (s, 18 H, O-Me<sub>1</sub>), 6.64 (dd,  $^3J_{\text{H,Htrans}} = 15.9$ ,  $^3J_{\text{H,H}} = 7.6$  Hz, 6 H, H-C<sub>1</sub><sup>8</sup>), 6.81 (d,  $^3J_{\text{H,Htrans}} = 15.9$  Hz, 3 H, H-C<sub>0</sub><sup>7</sup>), 7.00 (m, 6 H, H-C<sub>0</sub><sup>8</sup>, H-C<sub>0</sub><sup>5</sup>), 7.08 (s, 3 H, H-C<sub>0</sub><sup>3</sup>), 7.12 (s, 6 H, H-C<sub>1</sub><sup>3</sup>), 7.13 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 6 H, H-C<sub>1</sub><sup>5</sup>), 7.36 (dd,  $^3J_{\text{H,H}} = 8.8$ ,  $^4J_{\text{H,P}} = 1.7$  Hz, 6 H, H-C<sub>1</sub><sup>6</sup>), 7.41 (d,  $^3J_{\text{H,Htrans}} = 15.9$  Hz, 6 H, H-C<sub>1</sub><sup>7</sup>), 7.47 (dd,  $^3J_{\text{H,H}} = 8.4$ ,  $^4J_{\text{H,P}} = 1.6$  Hz, 3 H, H-C<sub>0</sub><sup>6</sup>), 7.59 (dd,  $^3J_{\text{H,H}} = 8.7$ ,  $^4J_{\text{H,P}} = 1.8$  Hz, 3 H, H-C<sub>0</sub><sup>9</sup>), 9.67 (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 6 H, H-C<sub>1</sub><sup>9</sup>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$  = 32.8 (d,  $^2J_{\text{C,P}} = 11.8$  Hz, N-Me<sub>0</sub>), 56.0 (s, O-Me<sub>0</sub>), 56.2 (s, O-Me<sub>1</sub>), 110.0 (s, C<sub>0</sub><sup>3</sup>), 111.9 (s, C<sub>1</sub><sup>3</sup>), 119.9 (s, C<sub>0</sub><sup>5</sup>), 121.8 (s, C<sub>1</sub><sup>5</sup>), 122.5 (d,  $^3J_{\text{C,P}} = 3.1$  Hz, C<sub>0</sub><sup>6</sup>), 122.9 (d,  $^3J_{\text{C,P}} = 3.7$  Hz, C<sub>1</sub><sup>6</sup>), 126.4 (s, C<sub>0</sub><sup>8</sup>), 128.5 (s, C<sub>1</sub><sup>8</sup>), 132.0 (s, C<sub>1</sub><sup>4</sup>), 134.6 (s, C<sub>0</sub><sup>4</sup>), 136.5 (s, C<sub>0</sub><sup>7</sup>), 140.3 (d,  $^2J_{\text{C,P}} = 7.8$  Hz, C<sub>0</sub><sup>1</sup>), 141.8 (d,  $^3J_{\text{C,P}} = 15.3$  Hz, C<sub>0</sub><sup>2</sup>), 142.3 (d,  $^2J_{\text{C,P}} = 7.7$  Hz, C<sub>1</sub><sup>1</sup>), 151.3 (d,  $^3J_{\text{C,P}} = 5.8$  Hz, C<sub>0</sub><sup>9</sup>), 151.7 (d,  $^3J_{\text{C,P}} = 6$  Hz, C<sub>1</sub><sup>2</sup>), 151.9 (s, C<sub>1</sub><sup>7</sup>), 193.4 (s, C<sub>1</sub><sup>9</sup>) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 81.01 MHz):  $\delta$  = 54.7 (s, P<sub>0</sub>), 62.0

(s, P<sub>1</sub>) ppm. IR (KBr):  $\nu_{\text{C=O}} = 1676$  cm<sup>-1</sup>. C<sub>93</sub>H<sub>90</sub>N<sub>6</sub>O<sub>24</sub>P<sub>4</sub>S<sub>4</sub> (1928): calcd. C 57.94, H 4.71, N 4.36; found C 58.06, H 4.77, N 4.31.

**Dendrimer 1-G<sub>2</sub>:** Yield: 85%, pale-yellow powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250.1 MHz):  $\delta$  = 3.44 (d,  $^3J_{\text{H,P}} = 14.0$  Hz, 27 H, N-Me<sub>0</sub>, N-Me<sub>1</sub>), 3.83 (s, 9 H, O-Me<sub>0</sub>), 3.86 (s, 18 H, O-Me<sub>1</sub>), 7.00 (m, 36 H, H-C=), 7.29 (d,  $^3J_{\text{H,H}} = 8.2$  Hz, 6 H, H-C<sub>1</sub><sup>6</sup>), 7.52 (m, 12 H, H-C=) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$  = 32.1 (d,  $^2J_{\text{C,P}} = 10.5$  Hz, N-Me<sub>1</sub>), 32.8 (d,  $^2J_{\text{C,P}} = 9.8$  Hz, N-Me<sub>0</sub>), 56.1 (s, O-Me<sub>0</sub>), 56.2 (s, O-Me<sub>1</sub>), 110.0 (s, C<sub>0</sub><sup>3</sup>), 110.2 (s, C<sub>1</sub><sup>3</sup>), 120.0 (s, C<sub>0</sub><sup>5</sup>), 120.3 (s, C<sub>1</sub><sup>5</sup>), 122.4 (d,  $^3J_{\text{C,P}} = 3.9$  Hz, C<sub>0</sub><sup>6</sup>), 122.6 (d,  $^3J_{\text{C,P}} = 4.0$  Hz, C<sub>1</sub><sup>6</sup>), 125.3 (s, C<sub>1</sub><sup>8</sup>), 126.6 (s, C<sub>0</sub><sup>8</sup>), 134.0 (s, C<sub>1</sub><sup>4</sup>), 134.6 (s, C<sub>0</sub><sup>4</sup>), 136.3 (s, C<sub>0</sub><sup>7</sup>), 138.9 (s, C<sub>1</sub><sup>7</sup>), 140.6 (d,  $^2J_{\text{C,P}} = 7.8$  Hz, C<sub>0</sub><sup>1</sup>), 140.8 (d,  $^2J_{\text{C,P}} = 7.8$  Hz, C<sub>1</sub><sup>1</sup>), 141.5 (d,  $^3J_{\text{C,P}} = 13.8$  Hz, C<sub>0</sub><sup>9</sup>), 144.3 (d,  $^3J_{\text{C,P}} = 14.0$  Hz, C<sub>1</sub><sup>9</sup>), 151.3 (d,  $^3J_{\text{C,P}} = 5.5$  Hz, C<sub>0</sub><sup>2</sup>), 151.6 (d,  $^3J_{\text{C,P}} = 5.6$  Hz, C<sub>1</sub><sup>2</sup>) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 81.01 MHz):  $\delta$  = 54.8 (s, P<sub>0</sub>), 61.4 (s, P<sub>2</sub>), 62.7 (s, P<sub>1</sub>) ppm. C<sub>99</sub>H<sub>108</sub>Cl<sub>12</sub>N<sub>18</sub>O<sub>18</sub>P<sub>10</sub>S<sub>10</sub> (2894): calcd. C 41.09, H 3.76, 8.71; found C 41.21, H 3.82, N 8.65.

**Dendrimer 1-G<sub>2</sub>':** Yield: 81%, pale-yellow powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250.1 MHz):  $\delta$  = 3.42 (d,  $^3J_{\text{H,P}} = 10.3$  Hz, 27 H, N-Me<sub>0</sub>, N-Me<sub>1</sub>), 3.85 (br. s, 63 H, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>), 6.63 (dd,  $^3J_{\text{H,Htrans}} = 15.8$ ,  $^3J_{\text{H,H}} = 7.7$  Hz, 12 H, H-C<sub>2</sub><sup>8</sup>), 6.70–7.60 (m, 102 H, H-C=), 9.67 (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 12 H, H-C<sub>2</sub><sup>9</sup>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 50.3 MHz):  $\delta$  = 32.6 (d,  $^2J_{\text{C,P}} = 12$  Hz, N-Me<sub>0</sub>, N-Me<sub>1</sub>), 55.8 (s, O-Me<sub>0</sub>), 55.9 (s, O-Me<sub>1</sub>), 56.0 (s, O-Me<sub>2</sub>), 109.8 (br. s, C<sub>0</sub><sup>3</sup>, C<sub>1</sub><sup>3</sup>), 111.6 (s, C<sub>2</sub><sup>3</sup>), 119.9 (br. s, C<sub>0</sub><sup>5</sup>, C<sub>1</sub><sup>5</sup>), 121.6 (s, C<sub>2</sub><sup>5</sup>), 123.2 (br. s, C<sub>0</sub><sup>6</sup>, C<sub>1</sub><sup>6</sup>), 123.7 (d,  $^3J_{\text{C,P}} = 3.5$  Hz, C<sub>2</sub><sup>6</sup>), 126.0 (br. s, C<sub>0</sub><sup>8</sup>, C<sub>1</sub><sup>8</sup>), 128.3 (s, C<sub>2</sub><sup>8</sup>), 131.8 (s, C<sub>2</sub><sup>4</sup>), 134.2 (br. s, C<sub>0</sub><sup>4</sup>, C<sub>1</sub><sup>4</sup>), 136.5 (s, C<sub>0</sub><sup>7</sup>, C<sub>1</sub><sup>7</sup>), 140.2 (br. s, C<sub>0</sub><sup>1</sup>, C<sub>1</sub><sup>1</sup>), 141.8 (br. s, C<sub>0</sub><sup>9</sup>, C<sub>1</sub><sup>9</sup>), 142.2 (d,  $^2J_{\text{C,P}} = 7.3$  Hz, C<sub>2</sub><sup>1</sup>), 151.2 (br. s, C<sub>0</sub><sup>2</sup>, C<sub>1</sub><sup>2</sup>), 151.6 (d,  $^3J_{\text{C,P}} = 5.9$  Hz, C<sub>2</sub><sup>2</sup>), 151.8 (s, C<sub>2</sub><sup>7</sup>), 193.3 (s, C<sub>2</sub><sup>9</sup>) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 81.01 MHz):  $\delta$  = 54.7 (s, P<sub>0</sub>), 62.0 (s, P<sub>2</sub>), 62.5 (s, P<sub>1</sub>) ppm. IR (KBr):  $\nu_{\text{C=O}} = 1676$  cm<sup>-1</sup>. C<sub>219</sub>H<sub>216</sub>N<sub>18</sub>O<sub>54</sub>P<sub>10</sub>S<sub>10</sub> (4595): calcd. C 57.25, H 4.74, N 5.49; found C 57.33, H 4.81, N 5.41.

**Dendrimer 1-G<sub>3</sub>:** Yield: 83%, pale-yellow powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250.1 MHz):  $\delta$  = 3.41 (br. d,  $^3J_{\text{H,P}} = 11.5$  Hz, 63 H, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>), 3.85 (br. s, 63 H, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>), 6.80–7.60 (m, 126 H, H-C=) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$  = 32.1 (d,  $^2J_{\text{C,P}} = 13.6$  Hz, N-Me<sub>2</sub>), 32.8 (d,  $^2J_{\text{C,P}} = 10.9$  Hz, N-Me<sub>0</sub>, N-Me<sub>1</sub>), 56.2 (s, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>), 110.0 (br. s, C<sub>0</sub><sup>3</sup>, C<sub>1</sub><sup>3</sup>), 110.2 (s, C<sub>2</sub><sup>3</sup>), 120.0 (br. s, C<sub>0</sub><sup>5</sup>, C<sub>1</sub><sup>5</sup>), 120.4 (s, C<sub>2</sub><sup>5</sup>), 122.6 (br. s, C<sub>0</sub><sup>6</sup>, C<sub>1</sub><sup>6</sup>, C<sub>2</sub><sup>6</sup>), 125.2 (s, C<sub>2</sub><sup>8</sup>), 126.4 (br. s, C<sub>0</sub><sup>8</sup>, C<sub>1</sub><sup>8</sup>), 133.8 (s, C<sub>2</sub><sup>4</sup>), 134.4 (br. s, C<sub>0</sub><sup>4</sup>, C<sub>1</sub><sup>4</sup>), 136.3 (s, C<sub>0</sub><sup>7</sup>, C<sub>1</sub><sup>7</sup>), 139.0 (s, C<sub>2</sub><sup>7</sup>), 140.2 (br. s, C<sub>0</sub><sup>1</sup>, C<sub>1</sub><sup>1</sup>), 140.7 (d,  $^2J_{\text{C,P}} = 7.5$  Hz, C<sub>2</sub><sup>1</sup>), 141.8 (br. s, C<sub>0</sub><sup>9</sup>, C<sub>1</sub><sup>9</sup>), 144.4 (d,  $^3J_{\text{C,P}} = 19.9$  Hz, C<sub>2</sub><sup>9</sup>), 151.5 (br. s, C<sub>0</sub><sup>2</sup>, C<sub>1</sub><sup>2</sup>, C<sub>2</sub><sup>2</sup>) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 81.01 MHz):  $\delta$  = 54.7 (s, P<sub>0</sub>), 61.3 (s, P<sub>3</sub>), 62.4 (s, P<sub>1</sub>, P<sub>2</sub>) ppm. C<sub>231</sub>H<sub>252</sub>Cl<sub>24</sub>N<sub>42</sub>O<sub>42</sub>P<sub>22</sub>S<sub>22</sub> (6527): calcd. 42.51, H 3.89, N 9.01; found C 42.66, H 3.95, N 8.94.

**Dendrimer 1-G<sub>3</sub>':** Yield: 65%, pale-yellow powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200.1 MHz):  $\delta$  = 3.38 (br. d,  $^3J_{\text{H,P}} = 11.9$  Hz, 63 H, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>), 3.82 (br. s, 135 H, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>, O-Me<sub>3</sub>), 6.50–7.60 (m, 246 H, H-C=), 9.63 (d,  $^3J_{\text{H,H}} = 7.1$  Hz, 24 H, H-C<sub>3</sub><sup>9</sup>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 50.3 MHz):  $\delta$  = 32.6 (d,  $^2J_{\text{C,P}} = 11.9$  Hz, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>), 55.7 (s, O-Me<sub>0</sub>), 55.8 (s, O-Me<sub>1</sub>), 55.9 (s, O-Me<sub>2</sub>), 56.0 (s, O-Me<sub>3</sub>), 109.8 (br. s, C<sub>0</sub><sup>3</sup>, C<sub>1</sub><sup>3</sup>, C<sub>2</sub><sup>3</sup>), 111.7 (s, C<sub>3</sub><sup>3</sup>), 119.9 (br. s, C<sub>0</sub><sup>5</sup>, C<sub>1</sub><sup>5</sup>, C<sub>2</sub><sup>5</sup>), 121.6 (s, C<sub>3</sub><sup>5</sup>), 122.3 (br. s, C<sub>0</sub><sup>6</sup>, C<sub>1</sub><sup>6</sup>, C<sub>2</sub><sup>6</sup>), 122.6 (d,  $^3J_{\text{C,P}} = 4.0$  Hz, C<sub>3</sub><sup>6</sup>), 126.0 (br. s, C<sub>0</sub><sup>8</sup>, C<sub>1</sub><sup>8</sup>, C<sub>2</sub><sup>8</sup>), 128.3 (s, C<sub>3</sub><sup>8</sup>), 131.8 (s, C<sub>3</sub><sup>4</sup>), 134.1 (br. s, C<sub>0</sub><sup>4</sup>, C<sub>1</sub><sup>4</sup>, C<sub>2</sub><sup>4</sup>), 136.5 (br. s, C<sub>0</sub><sup>7</sup>, C<sub>1</sub><sup>7</sup>, C<sub>2</sub><sup>7</sup>), 140.2 (br. s, C<sub>0</sub><sup>1</sup>, C<sub>1</sub><sup>1</sup>, C<sub>2</sub><sup>1</sup>), 141.7 (br. s, C<sub>0</sub><sup>9</sup>, C<sub>1</sub><sup>9</sup>, C<sub>2</sub><sup>9</sup>), 142.2 (d,  $^2J_{\text{C,P}} = 7.5$  Hz, C<sub>3</sub><sup>1</sup>), 151.3 (br. s, C<sub>0</sub><sup>2</sup>, C<sub>1</sub><sup>2</sup>, C<sub>2</sub><sup>2</sup>), 151.5 (d,  $^3J_{\text{C,P}} = 4.8$  Hz, C<sub>3</sub><sup>2</sup>), 151.8 (s, C<sub>3</sub><sup>7</sup>), 193.3 (s, C<sub>3</sub><sup>9</sup>) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 81.01 MHz):  $\delta$  = 54.7 (s, P<sub>0</sub>), 61.9 (s, P<sub>3</sub>), 62.5 (br. s, P<sub>1</sub>, P<sub>2</sub>) ppm. IR (KBr):  $\nu_{\text{C=O}} = 1676$  cm<sup>-1</sup>.

C<sub>471</sub>H<sub>468</sub>N<sub>42</sub>O<sub>114</sub>P<sub>22</sub>S<sub>22</sub> (9928): calcd. C 56.98, H 4.75, N 5.93; found C 57.07, H 4.82, N 5.87.

**Dendrimer 1-G<sub>4</sub>**: Yield: 80%, pale-yellow powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ = 3.40 (br. d, <sup>3</sup>J<sub>H,P</sub> = 13 Hz, 135 H, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>, N-Me<sub>3</sub>), 3.83 (br. s, 135 H, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>, O-Me<sub>3</sub>), 6.70–7.60 (m, 270 H, H-C=) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.9 MHz): δ = 32.0 (d, <sup>2</sup>J<sub>C,P</sub> = 13.1 Hz, N-Me<sub>3</sub>), 32.7 (d, <sup>2</sup>J<sub>C,P</sub> = 11.5 Hz, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>), 56.0 (s, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>, O-Me<sub>3</sub>), 109.7 (br. s, C<sub>0</sub><sup>3</sup>, C<sub>1</sub><sup>3</sup>, C<sub>2</sub><sup>3</sup>), 110.0 (s, C<sub>3</sub><sup>3</sup>), 119.9 (br. s, C<sub>0</sub><sup>5</sup>, C<sub>1</sub><sup>5</sup>, C<sub>2</sub><sup>5</sup>), 120.2 (s, C<sub>3</sub><sup>5</sup>), 122.4 (br. s, C<sub>0</sub><sup>6</sup>, C<sub>1</sub><sup>6</sup>, C<sub>2</sub><sup>6</sup>, C<sub>3</sub><sup>6</sup>), 125.0 (s, C<sub>3</sub><sup>8</sup>), 126.2 (br. s, C<sub>0</sub><sup>8</sup>, C<sub>1</sub><sup>8</sup>, C<sub>2</sub><sup>8</sup>), 133.7 (s, C<sub>3</sub><sup>4</sup>), 134.2 (br. s, C<sub>0</sub><sup>4</sup>, C<sub>1</sub><sup>4</sup>, C<sub>2</sub><sup>4</sup>), 136.2 (br. s, C<sub>0</sub><sup>7</sup>, C<sub>1</sub><sup>7</sup>, C<sub>2</sub><sup>7</sup>), 138.8 (s, C<sub>3</sub><sup>7</sup>), 140.1 (br. d, <sup>2</sup>J<sub>C,P</sub> = 8.0 Hz, C<sub>0</sub><sup>1</sup>, C<sub>1</sub><sup>1</sup>, C<sub>2</sub><sup>1</sup>), 140.5 (d, <sup>2</sup>J<sub>C,P</sub> = 7.0 Hz, C<sub>3</sub><sup>1</sup>), 141.4 (br. m, C<sub>0</sub><sup>9</sup>, C<sub>1</sub><sup>9</sup>, C<sub>2</sub><sup>9</sup>), 144.2 (d, <sup>3</sup>J<sub>C,P</sub> = 18.5 Hz, C<sub>3</sub><sup>9</sup>), 151.3 (br. d, <sup>3</sup>J<sub>C,P</sub> = 4.5 Hz, C<sub>0</sub><sup>2</sup>, C<sub>1</sub><sup>2</sup>, C<sub>2</sub><sup>2</sup>, C<sub>3</sub><sup>2</sup>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 81.01 MHz): δ = 54.7 (s, P<sub>0</sub>), 61.4 (s, P<sub>4</sub>), 62.9 (s, P<sub>3</sub>), 63.0 (s, P<sub>2</sub>), 63.1 (s, P<sub>1</sub>) ppm. C<sub>495</sub>H<sub>540</sub>Cl<sub>48</sub>N<sub>90</sub>O<sub>90</sub>P<sub>46</sub>S<sub>46</sub> (13 792): calcd. C 43.11, H 3.95, N 9.14; found C 43.28, H 4.02, N 9.06.

**Dendrimer 1-G<sub>4</sub>'**: Yield: 70%, pale-yellow powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ = 3.38 (br. s, 135 H, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>, N-Me<sub>3</sub>), 3.84 (br. s, 279 H, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>, O-Me<sub>3</sub>, O-Me<sub>4</sub>), 6.50–7.60 (m, 510 H, H-C=), 9.64 (br. s, 48 H, H-C<sub>4</sub><sup>9</sup>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.9 MHz): δ = 32.7 (d, <sup>2</sup>J<sub>C,P</sub> = 11.9 Hz, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>, N-Me<sub>3</sub>), 56.1 (s, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>, O-Me<sub>3</sub>), 56.2 (s, O-Me<sub>4</sub>), 110.0 (br. s, C<sub>0</sub><sup>3</sup>, C<sub>1</sub><sup>3</sup>, C<sub>2</sub><sup>3</sup>, C<sub>3</sub><sup>3</sup>), 111.9 (s, C<sub>4</sub><sup>3</sup>), 120.0 (br. s, C<sub>0</sub><sup>5</sup>, C<sub>1</sub><sup>5</sup>, C<sub>2</sub><sup>5</sup>, C<sub>3</sub><sup>5</sup>), 121.8 (s, C<sub>4</sub><sup>5</sup>), 122.6 (br. s, C<sub>0</sub><sup>6</sup>, C<sub>1</sub><sup>6</sup>, C<sub>2</sub><sup>6</sup>, C<sub>3</sub><sup>6</sup>), 122.8 (br. s, C<sub>4</sub><sup>6</sup>), 126.2 (br. s, C<sub>0</sub><sup>8</sup>, C<sub>1</sub><sup>8</sup>, C<sub>2</sub><sup>8</sup>, C<sub>3</sub><sup>8</sup>), 128.5 (s, C<sub>4</sub><sup>8</sup>), 132.0 (s, C<sub>4</sub><sup>4</sup>), 134.3 (br. s, C<sub>0</sub><sup>4</sup>, C<sub>1</sub><sup>4</sup>, C<sub>2</sub><sup>4</sup>, C<sub>3</sub><sup>4</sup>), 136.5 (br. s, C<sub>0</sub><sup>7</sup>, C<sub>1</sub><sup>7</sup>, C<sub>2</sub><sup>7</sup>, C<sub>3</sub><sup>7</sup>), 140.3 (br. s, C<sub>0</sub><sup>1</sup>, C<sub>1</sub><sup>1</sup>, C<sub>2</sub><sup>1</sup>, C<sub>3</sub><sup>1</sup>), 141.8 (br. s, C<sub>0</sub><sup>9</sup>, C<sub>1</sub><sup>9</sup>, C<sub>2</sub><sup>9</sup>, C<sub>3</sub><sup>9</sup>), 142.3 (d, <sup>2</sup>J<sub>C,P</sub> = 7.2 Hz, C<sub>4</sub><sup>1</sup>), 151.3 (br. d, <sup>3</sup>J<sub>C,P</sub> = 5.4 Hz, C<sub>0</sub><sup>2</sup>, C<sub>1</sub><sup>2</sup>, C<sub>2</sub><sup>2</sup>, C<sub>3</sub><sup>2</sup>), 151.5 (d, <sup>3</sup>J<sub>C,P</sub> = 4.8 Hz, C<sub>4</sub><sup>2</sup>), 151.9 (s, C<sub>4</sub><sup>7</sup>), 193.5 (s, C<sub>4</sub><sup>9</sup>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101.2 MHz): δ = 54.9 (s, P<sub>0</sub>), 62.4 (s, P<sub>4</sub>), 63.2 (br. s, P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>) ppm. IR (KBr): ν<sub>C=O</sub> = 1676 cm<sup>-1</sup>. C<sub>975</sub>H<sub>972</sub>N<sub>90</sub>O<sub>234</sub>P<sub>46</sub>S<sub>46</sub> (20 595): calcd. C 56.86, H 4.76, N 6.12; found C 56.99, H 4.83, N 6.05.

**Dendrimer 1-G<sub>5</sub>**: Yield: 79%, pale-yellow powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200.1 MHz): δ = 3.40 (br. s, 279 H, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>, N-Me<sub>3</sub>, N-Me<sub>4</sub>), 3.82 (br. s, 279 H, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>, O-Me<sub>3</sub>, O-Me<sub>4</sub>), 6.70–7.60 (m, 558 H, H-C=) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 50.3 MHz): δ = 32.9 (d, <sup>2</sup>J<sub>C,P</sub> = 13.0 Hz, N-Me<sub>4</sub>), 32.6 (d, <sup>2</sup>J<sub>C,P</sub> = 11.7 Hz, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>, N-Me<sub>3</sub>), 56.0 (s, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>, O-Me<sub>3</sub>, O-Me<sub>4</sub>), 109.8 (br. s, C<sub>0</sub><sup>3</sup>, C<sub>1</sub><sup>3</sup>, C<sub>2</sub><sup>3</sup>, C<sub>3</sub><sup>3</sup>), 110.0 (s, C<sub>4</sub><sup>3</sup>), 119.9 (br. s, C<sub>0</sub><sup>5</sup>, C<sub>1</sub><sup>5</sup>, C<sub>2</sub><sup>5</sup>, C<sub>3</sub><sup>5</sup>), 120.2 (s, C<sub>4</sub><sup>5</sup>), 122.4 (br. s, C<sub>0</sub><sup>6</sup>, C<sub>1</sub><sup>6</sup>, C<sub>2</sub><sup>6</sup>, C<sub>3</sub><sup>6</sup>, C<sub>4</sub><sup>6</sup>), 125.0 (s, C<sub>4</sub><sup>8</sup>), 126.2 (br. s, C<sub>0</sub><sup>8</sup>, C<sub>1</sub><sup>8</sup>, C<sub>2</sub><sup>8</sup>, C<sub>3</sub><sup>8</sup>), 133.7 (s, C<sub>4</sub><sup>4</sup>), 134.2 (br. s, C<sub>0</sub><sup>4</sup>, C<sub>1</sub><sup>4</sup>, C<sub>2</sub><sup>4</sup>, C<sub>3</sub><sup>4</sup>), 136.1 (br. s, C<sub>0</sub><sup>7</sup>, C<sub>1</sub><sup>7</sup>, C<sub>2</sub><sup>7</sup>, C<sub>3</sub><sup>7</sup>), 138.8 (s, C<sub>4</sub><sup>7</sup>), 140.1 (br. d, <sup>2</sup>J<sub>C,P</sub> = 8.0 Hz, C<sub>0</sub><sup>1</sup>, C<sub>1</sub><sup>1</sup>, C<sub>2</sub><sup>1</sup>, C<sub>3</sub><sup>1</sup>), 140.5 (d, <sup>2</sup>J<sub>C,P</sub> = 7.0 Hz, C<sub>4</sub><sup>1</sup>), 141.5 (br. m, C<sub>0</sub><sup>9</sup>, C<sub>1</sub><sup>9</sup>, C<sub>2</sub><sup>9</sup>, C<sub>3</sub><sup>9</sup>), 144.2 (d, <sup>3</sup>J<sub>C,P</sub> = 18.6 Hz, C<sub>4</sub><sup>9</sup>), 151.3 (br. s, C<sub>0</sub><sup>2</sup>, C<sub>1</sub><sup>2</sup>, C<sub>2</sub><sup>2</sup>, C<sub>3</sub><sup>2</sup>, C<sub>4</sub><sup>2</sup>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 81.01 MHz): δ = 54.7 (s, P<sub>0</sub>), 61.4 (s, P<sub>5</sub>), 63.0 (s, P<sub>4</sub>), 63.1 (s, P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>) ppm. C<sub>1023</sub>H<sub>1116</sub>Cl<sub>96</sub>N<sub>186</sub>O<sub>186</sub>P<sub>94</sub>S<sub>94</sub> (28 322): calcd. C 43.38, H 3.97, N 9.20; found C 43.46, H 4.02, N 9.14.

**Dendrimer 1-G<sub>5</sub>'**: Yield: 63%, pale-yellow powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ = 3.40 (br. d, <sup>3</sup>J<sub>H,P</sub> = 9.5 Hz, 279 H, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>, N-Me<sub>3</sub>, N-Me<sub>4</sub>), 3.85 (br. s, 567 H, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>, O-Me<sub>3</sub>, O-Me<sub>4</sub>, O-Me<sub>5</sub>), 6.50–7.60 (m, 1038 H, H-C=), 9.66 (br. d, <sup>3</sup>J<sub>H,H</sub> = 5 Hz, 96 H, H-C<sub>5</sub><sup>9</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.9 MHz): δ = 32.7 (d, <sup>2</sup>J<sub>C,P</sub> = 11.8 Hz, N-Me<sub>0</sub>, N-Me<sub>1</sub>, N-Me<sub>2</sub>, N-Me<sub>3</sub>, N-Me<sub>4</sub>), 56.1 (s, O-Me<sub>0</sub>, O-Me<sub>1</sub>, O-Me<sub>2</sub>, O-Me<sub>3</sub>, O-Me<sub>4</sub>), 56.2 (s, O-Me<sub>5</sub>), 110.0 (br. s, C<sub>0</sub><sup>3</sup>, C<sub>1</sub><sup>3</sup>, C<sub>2</sub><sup>3</sup>, C<sub>3</sub><sup>3</sup>, C<sub>4</sub><sup>3</sup>), 111.9 (s, C<sub>5</sub><sup>3</sup>), 120.0 (br. s, C<sub>0</sub><sup>5</sup>, C<sub>1</sub><sup>5</sup>, C<sub>2</sub><sup>5</sup>, C<sub>3</sub><sup>5</sup>), 121.8 (s, C<sub>4</sub><sup>5</sup>), 122.6 (br. s,

C<sub>0</sub><sup>6</sup>, C<sub>1</sub><sup>6</sup>, C<sub>2</sub><sup>6</sup>, C<sub>3</sub><sup>6</sup>), 122.8 (br. s, C<sub>4</sub><sup>6</sup>), 126.2 (br. s, C<sub>0</sub><sup>8</sup>, C<sub>1</sub><sup>8</sup>, C<sub>2</sub><sup>8</sup>, C<sub>3</sub><sup>8</sup>, C<sub>4</sub><sup>8</sup>), 128.5 (s, C<sub>5</sub><sup>8</sup>), 132.0 (s, C<sub>5</sub><sup>4</sup>), 134.3 (br. s, C<sub>0</sub><sup>4</sup>, C<sub>1</sub><sup>4</sup>, C<sub>2</sub><sup>4</sup>, C<sub>3</sub><sup>4</sup>, C<sub>4</sub><sup>4</sup>), 136.7 (br. s, C<sub>0</sub><sup>7</sup>, C<sub>1</sub><sup>7</sup>, C<sub>2</sub><sup>7</sup>, C<sub>3</sub><sup>7</sup>, C<sub>4</sub><sup>7</sup>), 140.4 (br. s, C<sub>0</sub><sup>1</sup>, C<sub>1</sub><sup>1</sup>, C<sub>2</sub><sup>1</sup>, C<sub>3</sub><sup>1</sup>, C<sub>4</sub><sup>1</sup>), 142.0 (br. s, C<sub>0</sub><sup>9</sup>, C<sub>1</sub><sup>9</sup>, C<sub>2</sub><sup>9</sup>, C<sub>3</sub><sup>9</sup>, C<sub>4</sub><sup>9</sup>), 142.4 (d, <sup>2</sup>J<sub>C,P</sub> = 7.0 Hz, C<sub>5</sub><sup>1</sup>), 151.3 (br. d, <sup>3</sup>J<sub>C,P</sub> = 5 Hz, C<sub>0</sub><sup>2</sup>, C<sub>1</sub><sup>2</sup>, C<sub>2</sub><sup>2</sup>, C<sub>3</sub><sup>2</sup>, C<sub>4</sub><sup>2</sup>), 151.5 (d, <sup>3</sup>J<sub>C,P</sub> = 5 Hz, C<sub>5</sub><sup>2</sup>), 151.9 (s, C<sub>5</sub><sup>7</sup>), 193.4 (s, C<sub>5</sub><sup>9</sup>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 81.0 MHz): δ = 54.9 (s, P<sub>0</sub>), 62.4 (s, P<sub>5</sub>), 63.2 (br. s, P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, P<sub>4</sub>). IR (KBr): ν<sub>C=O</sub> = 1676 cm<sup>-1</sup>. C<sub>1983</sub>H<sub>1980</sub>N<sub>186</sub>O<sub>474</sub>P<sub>94</sub>S<sub>94</sub> (41 928): calcd. C 56.81, H 4.76, N 6.21; found C 56.96, H 4.82, N 6.17.

**X-ray Crystallographic Study:** Crystal structure information is given in Table 3. Data were collected at low temperature on a IPDS STOE diffractometer equipped with graphite-monochromated Mo-K<sub>α</sub> radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream Cooler Device. The final unit-cell parameters were obtained by means of a least-squares refinement performed on a set of 8000 well-measured reflections; crystal decay was monitored during the data collections, no significant fluctuations of intensities were observed. The structure was solved by direct methods using SIR92,<sup>[19]</sup> and refined by means of least-squares procedures on *F* using the programs of the PC version of CRYSTALS.<sup>[20]</sup> Atomic scattering factors were taken from the International tables for X-ray Crystallography.<sup>[21]</sup> All final phosphorus, chlorine and sulfur atom positions were refined anisotropically. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter. A weighting scheme of the form  $w = w'[1 - \{(|F_o| - |F_c|)/6\sigma(F_o)\}^2]$  with  $w' = 1/\sum_r A_r T_r(X)$  with coefficients 1.44, 0.859 and 0.977 for a Chebyshev series for which  $X = F_c/F_c(\max.)$  was used. CAMERON<sup>[22]</sup> was used for the drawing. CCDC-249559 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Table 3. Crystal data, data collection, and structure refinement.

Empirical formula	C <sub>35</sub> H <sub>39</sub> Cl <sub>6</sub> N <sub>7</sub> O <sub>6</sub> P <sub>4</sub> S <sub>4</sub>
Molecular mass	1118.61
Wavelength	0.71073 Å
Crystal system, space group	triclinic, <i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 12.865(1) Å <i>b</i> = 13.974(2) Å <i>c</i> = 14.279(2) Å $\alpha$ = 94.10(1)° $\beta$ = 97.34(1)° $\gamma$ = 98.08(1)°
Volume	2510.2(5) Å <sup>3</sup>
<i>Z</i> , calculated density	2, 1.48
Absorption coefficient	0.685 mm <sup>-1</sup>
<i>F</i> <sub>000</sub>	1144
Crystal size	0.05 × 0.25 × 0.30 mm
Crystal colour and form	pale-yellow plate
θ range for data collection	2.16–26.19°
Index ranges	−15 ≤ <i>h</i> ≤ 15 −17 ≤ <i>k</i> ≤ 17 −17 ≤ <i>l</i> ≤ 17
Reflections collected/unique	24992/9244 [ <i>R</i> (int) = 0.049]
Refinement method	Full matrix least-squares on <i>F</i>
Data/restraints/parameters	3339/0/320
Goodness of fit on <i>F</i>	1.124
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0700, <i>wR</i> 2 = 0.0726
Largest diff. peak and hole	(0.79 and −0.59) e Å <sup>-3</sup>

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