

# Choice of strategies for the divergent synthesis of phosphorus-containing dendrons, depending on the function located at the core†

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The use of divergent strategies is a fruitful approach for the synthesis of phosphorus-containing dendrons (dendritic wedges). Different synthetic processes have been devised, depending on the type of function located at the core (alkenyl groups, pyridine derivatives, chloromethyl or azidomethyl groups). In all cases, the divergent strategy easily allows one to have very reactive functional groups such as P–Cl, amine, phosphine or aldehyde groups on the surface of the dendron.

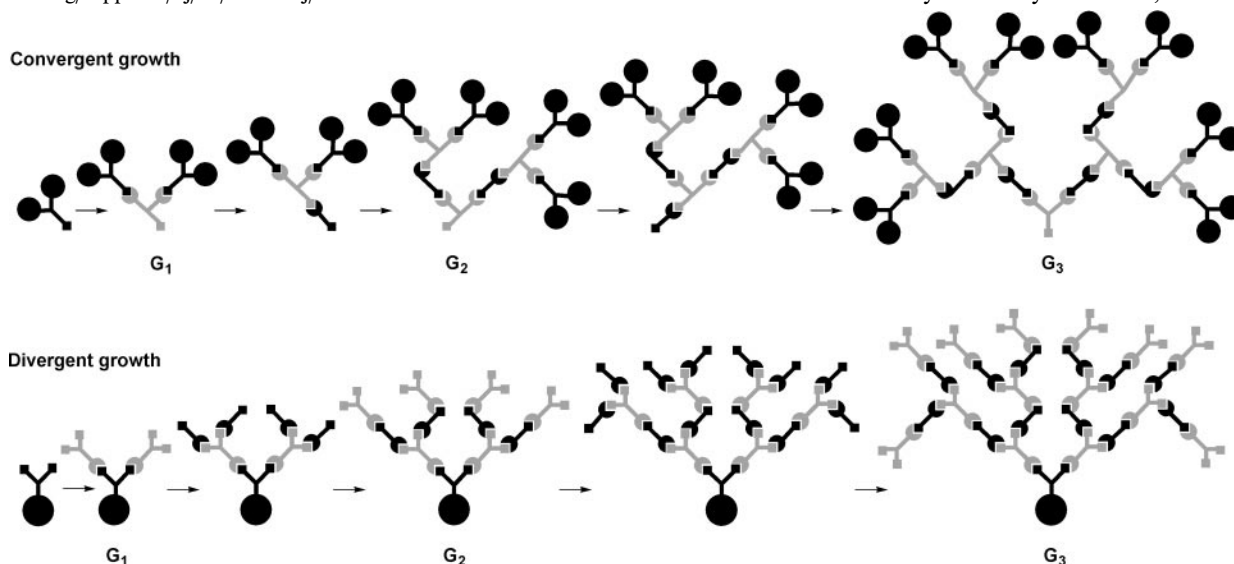
Numerous publications dealing with dendrimers<sup>1</sup> have appeared in the last fifteen years, due to the wide range of unique chemical and physical properties of these hyperbranched macromolecules. Among these papers, the construction of multidendritic systems by connecting preconstructed dendrons<sup>2</sup> (dendritic wedges) appears as an area of growing interest due to the possibilities for controlling the structure and topology of very complex frameworks. Dendrimers and dendrons are built using either divergent or convergent processes, the former being mainly used for dendrimers and the latter for dendrons. Scheme 1 illustrates both processes applied to the synthesis of dendrons. In convergent growth, the periphery of the dendron never reacts, only one reaction occurs at the level of the core, and each generation is created by associating two dendrons, which become larger at each generation. However, in divergent growth the periphery reacts at each step, no reaction occurs at the core, and each gener-

ation is created by associating a large number of small molecules to the dendron. The consequence is that it is much easier to have a variety of functional groups on the periphery of a dendron using divergent growth than with convergent growth. Thus, divergent growth ought to be the most widely used for the synthesis of dendrons, but this feeling is in sharp contrast with reality.<sup>2f,2t,2u,3</sup> Indeed, the drawback of divergent growth is that the function located at the core must not react during the synthesis of the dendron, but must be reactive enough to be activated after the synthesis, despite the steric hindrance of the core.

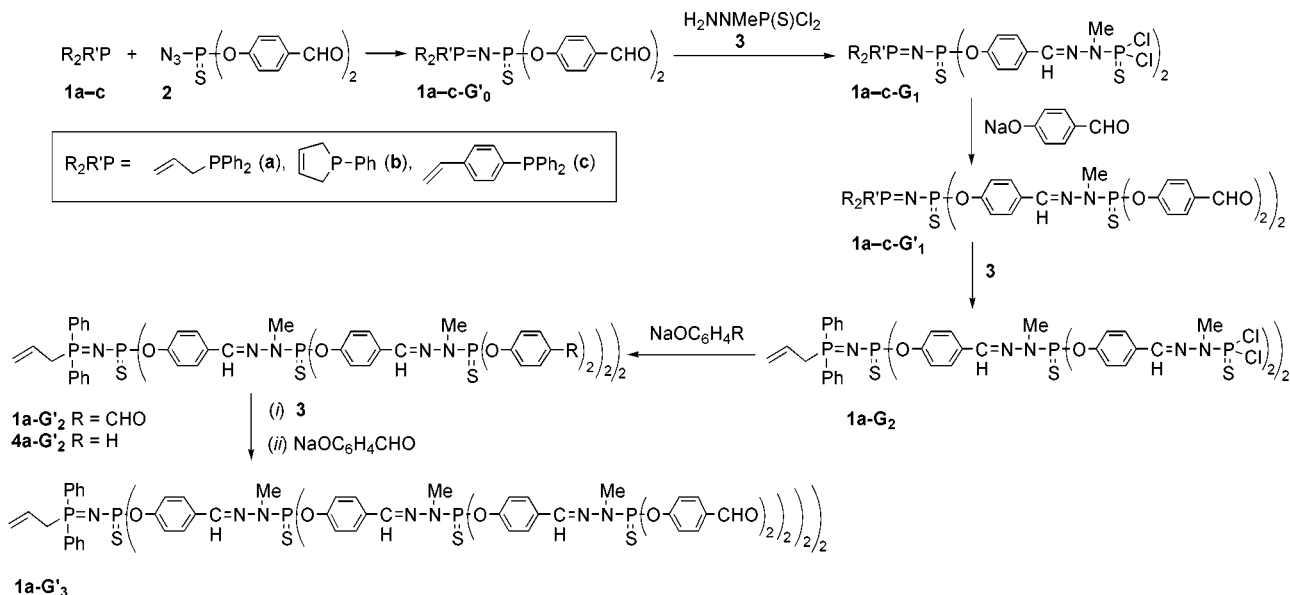
We have already reported several methods of synthesis of P-containing dendrimers using divergent strategies.<sup>4</sup> We present here our efforts to apply these methods to the synthesis of dendrons, and the modifications needed, depending on the type of functional group located at the core.

## Results and discussion

Most of the synthetic methods we developed for dendrimers are based on the reactivity of aldehydes.<sup>4</sup> Thus, in order to



Scheme 1 Schematized convergent and divergent growth schemes for dendrons.

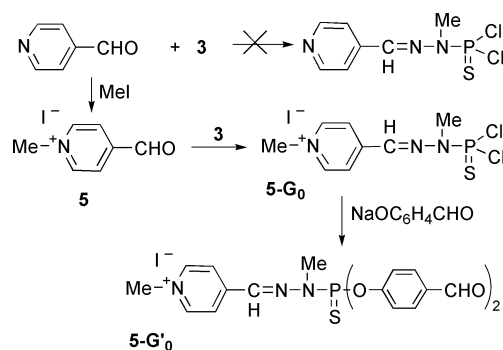


**Scheme 2** Synthesis of dendrons from alkenylphosphines.

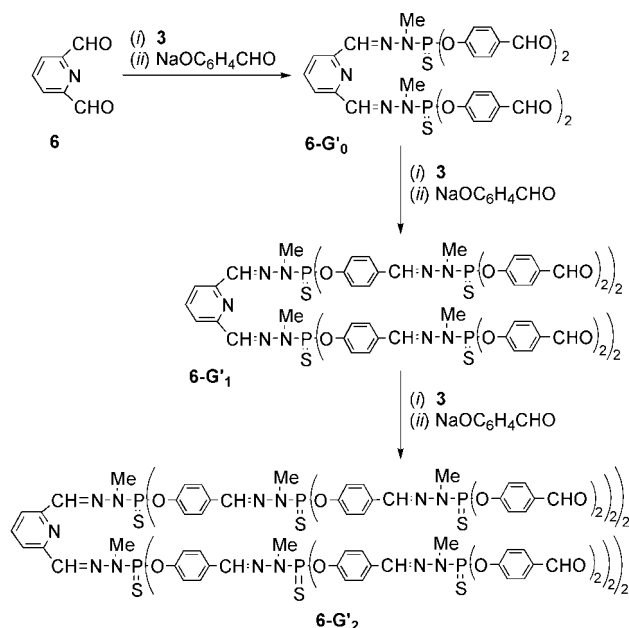
synthesize a dendron having a particular functional group at the core, we decided to design molecules possessing on one side two aldehyde groups and on the other side the desired functional group. The first type of function we tried to have was alkenes, due to the wide range of reactions (additions, substitutions, polymerizations, . . .) that could be carried out later with these functions. For this purpose, we have chosen alkenylphosphines such as allyldiphenylphosphine **1a**, 1-phenylphosphol-3-ene **1b**, and diphenylstyrylphosphine **1c**, for use in Staudinger reactions with the azidodialdehyde **2** (Scheme 2). Such reactions lead to the formation of compounds **1a-c-G'**<sub>0</sub>, possessing one alkenyl and two aldehyde groups, and characterized in <sup>31</sup>P NMR by the presence of two doublets, typical of the P=N-P=S linkage. The dendrons are grown from **1a-c-G'**<sub>0</sub>, with the alternating use of H<sub>2</sub>NNMeP(S)Cl<sub>2</sub> (**3**) in CHCl<sub>3</sub>-THF and NaOC<sub>6</sub>H<sub>4</sub>CHO in THF, both reactions being quantitative before work-up as we have already shown for dendrimers.<sup>4a-c,4e-f</sup> In all cases, the dendrons are characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR and IR spectroscopies, as well as elemental analyses. In particular, <sup>31</sup>P NMR is a precious tool at each step to check the total reaction of the outer layer, and the P=N-P=S group at the core is a sensitive probe to ensure that no reaction occurs at this level. The growth of the dendron has been stopped at the first generations **1b-G'**<sub>1</sub> and **1c-G'**<sub>1</sub> (4 aldehyde groups) from phenylphosphol-3-ene and diphenylstyrylphosphine, respectively. However, the growth could have been pursued to higher generations, as illustrated by the formation of the third generation dendron **1a-G'**<sub>3</sub> from allyldiphenylphosphine. The synthesis has been stopped at this step in order to be able to detect easily the signals corresponding to the P=N-P=S group of the core in <sup>31</sup>P NMR. Dendron **1a-G'**<sub>3</sub> possesses one allyl function at the core and 16 aldehyde functions on the periphery. The presence of aldehyde groups is important since they offer a wide range of possibilities to graft other functions onto the surface of the dendron.<sup>4b-c,4e-f,4k,4o</sup> However, it could be interesting also, for technical reasons, to have non reactive groups on the surface, in order to study more easily the reactivity of the core. This is achieved using NaOC<sub>6</sub>H<sub>5</sub> instead of NaOC<sub>6</sub>H<sub>4</sub>CHO in the last step. For instance, the reaction of **1a-G**<sub>2</sub> with sodium phenate gives dendron **4a-G**<sub>2</sub>, possessing a protected surface and only one allyl group at the core (Scheme 2).

The second type of functional group that we intended to introduce at the core of dendrons was pyridine derivatives, whose complexing and basic properties could be used later. In

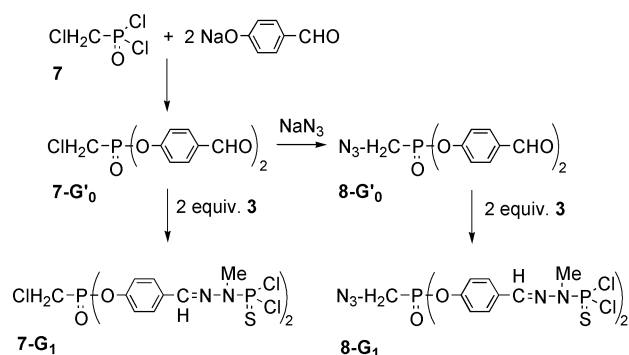
fact, the basicity of pyridine rapidly appeared to be a problem. Indeed, the reaction of pyridine-4-carboxaldehyde with phosphorhydrazide **3** does not give the expected condensation product, but induces the formation of a precipitate (Scheme 3). This precipitate has not been fully characterized, but it seems to correspond to the polymerization of **3**, which occurs in basic conditions, accompanied by the formation of the chlorhydrate of pyridine-4-carboxaldehyde. In order to avoid this reaction, the pyridine is alkylated by methyl iodide in THF, leading to the pyridinium salt **5**, which precipitates. Starting from **5**, we tried to apply the method of synthesis used for dendrons **1-G**<sub>n</sub>, but in a different solvent (acetonitrile). The first step, that is the condensation with phosphorhydrazide **3**, occurs without any problem, leading to **5-G**<sub>0</sub>. However, the next step, the reaction with NaOC<sub>6</sub>H<sub>4</sub>CHO, is not quantitative. The expected product **5-G**<sub>0</sub> is obtained but it appears difficult to isolate from side products, probably due to a reaction with iodide. Thus, we decided to change the type of pyridine derivative used as starting product. Pyridine-2,6-dicarboxaldehyde, **6**, appears as a good candidate, because the nitrogen is hindered and partially deactivated by the inductive effect of both aldehydes. The use of phosphorhydrazide **3** and NaOC<sub>6</sub>H<sub>4</sub>CHO in alternation allows us to grow the dendron starting from **6**, by applying exactly the method used for the synthesis of **1-G**<sub>n</sub>. The construction has been successfully carried out up to the second generation dendron **6-G**<sub>2</sub>, which possesses 16 aldehyde end groups (Scheme 4). However, it must be noted that a strictly quantitative amount of phosphorhydrazide **3** must be used in the condensation step. Indeed, an excess induces the poly-



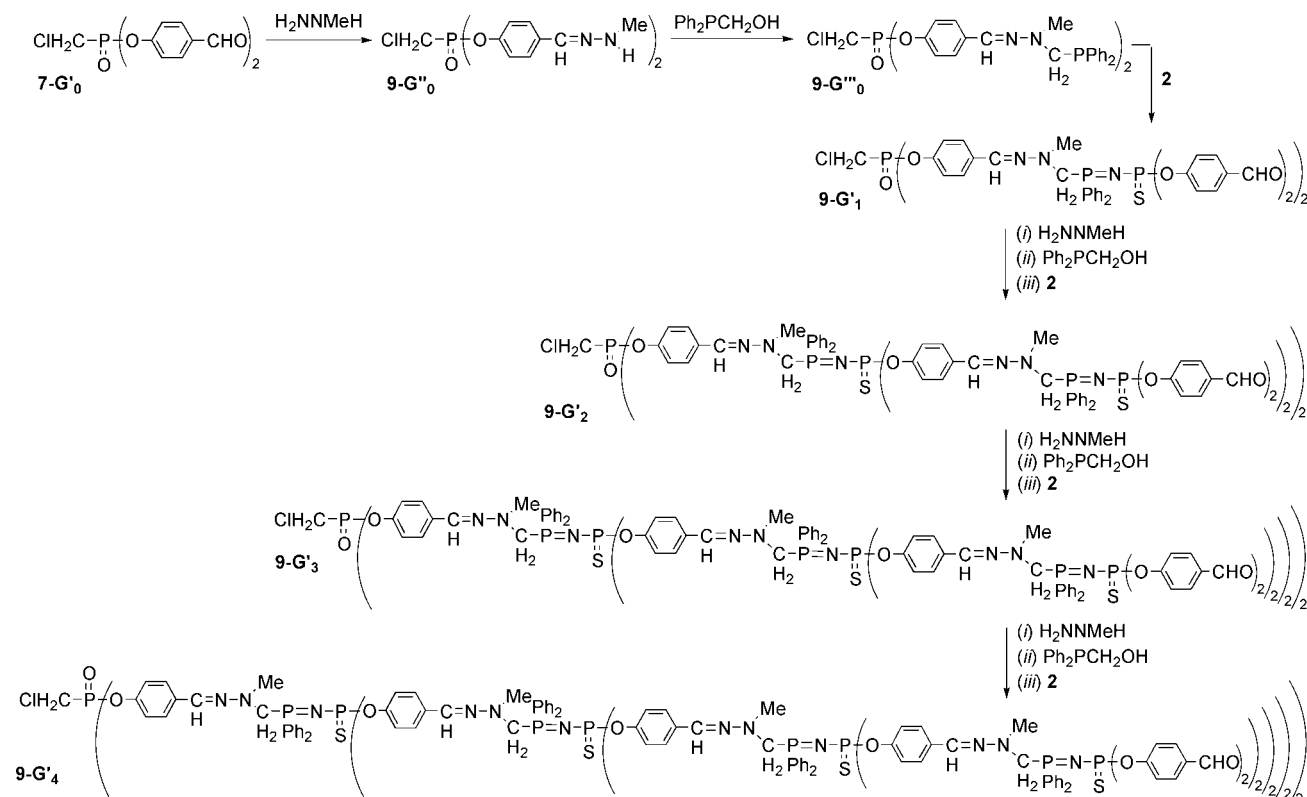
**Scheme 3** Attempted synthesis of a dendron from a monosubstituted pyridine.



**Scheme 4** Synthesis of a dendron from a disubstituted pyridine.



**Scheme 5** Attempted synthesis of dendrons from a chloromethyl or azidomethyl phosphine oxide derivative.



**Scheme 6** Synthesis of a dendron from a chloromethyl phosphine oxide derivative up to the fourth generation.

merization of **3** and the formation of pyridinium chlorhydrate, which is the type of problem already encountered with pyridine-4-carboxaldehyde. Furthermore, we have not isolated compounds **6-G'<sub>n</sub>** ( $n = 0-2$ ) with P(S)Cl<sub>2</sub> end groups, but used them immediately to react with NaOC<sub>6</sub>H<sub>4</sub>CHO. Thus, only compounds with aldehyde end groups **6-G'<sub>n</sub>** ( $n = 0-2$ ) are isolated and fully characterized in this series.

The third type of function we tried to graft at the core of dendrons is a chloromethyl group, which could be used in various substitution reactions. The starting compound is chloromethylphosphonic acid dichloride **7**. The expected difference in reactivity between the P-Cl and C-Cl groups is observed when hydroxybenzaldehyde sodium salt is reacted with compound **7**, only substitutions on the P(O)Cl<sub>2</sub> group occur to yield **7-G'<sub>0</sub>** (Scheme 5). The C-Cl is much less reactive, but it reacts for instance with NaN<sub>3</sub>, even if it is under drastic conditions (70 °C in pyridine for 20 days). The azide **8-G'<sub>0</sub>** is isolated, and characterized in particular by the presence of the ν N<sub>3</sub> band at 2101 cm<sup>-1</sup> in IR spectroscopy. Compounds **7-G'<sub>0</sub>** and **8-G'<sub>0</sub>** could be starting products for the synthesis of dendrons functionalized with C-Cl and C-N<sub>3</sub> groups, respectively. Thus we tried first to react phosphorhydrazide **3** with both compounds. These reactions occur without any problem to yield **7-G'<sub>1</sub>** and **8-G'<sub>1</sub>**, respectively. However, the next step to grow the dendron, the reaction with hydroxybenzaldehyde sodium salt, does not lead cleanly to the expected dendron with four aldehyde groups. Indeed, <sup>31</sup>P NMR indicates in both cases that a reaction occurred also at the level of the core. We did not try to isolate any compound, since the growing of dendrons or dendrimers necessitates absolutely clean and quantitative reactions. Thus, we decided to apply another method to synthesize dendrons from compound **7-G'<sub>0</sub>**, avoiding the use of any sodium salt.

We have already described a three-step synthesis of branches within dendrimers, which necessitates the alternating use of methylhydrazine, Ph<sub>2</sub>PCH<sub>2</sub>OH, and the azide **2**.<sup>4g</sup> Such a process for the growing of dendrons from **7-G'<sub>0</sub>** is depicted in Scheme 6. The repetition of these three steps has been carried out up to the formation of the fourth generation dendron

**9-G<sub>4</sub>**, possessing 32 aldehyde end groups. In this series, only compounds **9-G<sub>n</sub>** ( $n = 1-4$ ) with aldehyde end groups have been isolated and fully characterized. In all cases, the reactions are monitored by  $^{31}\text{P}$  NMR, which indicates a slight shifting of the signals corresponding to the phosphorus of the outer layer. The condensation step with methylhydrazine is characterized by a slight shielding of the doublet corresponding to  $\text{Ph}_2\text{P}=\text{N}$  from  $\delta = 13.1$  to  $\delta = 11.7$ , and a slight deshielding for the doublet corresponding to  $\text{N}=\text{P}=\text{S}$  from  $\delta = 50.9$  to  $\delta = 52.6$  for the **9-G<sub>n</sub>'**  $\rightarrow$  **9-G<sub>n</sub>''** reaction. The condensation step with  $\text{Ph}_2\text{PCH}_2\text{OH}$  is characterized by the appearance of a singlet at  $\delta = -23.4$  for the diphenylphosphino group grafted to the dendron, and a very slight shifting of both doublets corresponding to the  $\text{P}=\text{N}=\text{P}=\text{S}$  linkage ( $\Delta\delta = 0.1$ ) for the **9-G<sub>n</sub>''**  $\rightarrow$  **9-G<sub>n</sub>'''** reaction. The Staudinger reaction with the azide **2** induces the disappearance of the singlet of the diphenylphosphino group and the appearance of two doublets corresponding to the formation of the new  $\text{P}=\text{N}=\text{P}=\text{S}$  linkages at  $\delta = 13.2$  and  $50.9$  for the **9-G<sub>n</sub>'''**  $\rightarrow$  **9-G<sub>n+1</sub>** reaction.

## Conclusion

We have demonstrated in this paper that the use of the divergent strategy is not only a fruitful approach for the synthesis of dendrimers but also for the synthesis of dendrons. The main drawback of this method is that different synthetic processes have to be devised, depending on the type of function located at the core, and no general procedure can be applied. However, the divergent strategy easily allows having very reactive functional groups on the surface of the dendron such as  $\text{P}-\text{Cl}$ , amine, phosphine, and aldehyde groups, whose reactivities were fully studied on the surface of dendrimers.<sup>1h,4k</sup> Furthermore, the variety of functional groups located at the core should offer a versatile reactivity, leading to new means to synthesize multidendritic systems with complex architectures, as we have recently demonstrated for dendrons of type **1-G<sub>n</sub>** having a vinyl group at the core.<sup>5</sup> Work is in progress to study the synthetic properties of the core and of the outer layer of these phosphorus-containing dendrons.

## Experimental

### General

All manipulations were carried out with standard high vacuum and dry-argon techniques.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR spectra were recorded with Bruker AC 200, AC 250 or AMX 400 spectrometers. References for NMR chemical shifts are 85%

$\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  NMR,  $\text{SiMe}_4$  for  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The attribution of  $^{13}\text{C}$  NMR signals has been done using Jmod, two dimensional HMBC, and HMQC, broad band or CW  $^{31}\text{P}$  decoupling experiments when necessary. The labelling scheme used for NMR is depicted on Scheme 7. Only  $^{31}\text{P}$  NMR data are given in this section. Full spectroscopic data and elemental analyses are deposited as Electronic Supplementary Information. Compounds **1a**,<sup>6</sup> **1b**,<sup>7</sup> **1c**,<sup>8</sup> **2**<sup>9</sup> and  $\text{Ph}_2\text{PCH}_2\text{OH}$ <sup>10</sup> were prepared according to published procedures. The reactions are carried out at room temperature, unless otherwise stated.

### General procedure for the synthesis of **1a-c-G<sub>0</sub>**

To a solution of phosphine **1a-c** (**a**: 1.5 g, 6.631 mmol; **b**: 1.5 g, 9.248 mmol, **c**: 1.5 g, 5.202 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was slowly added at  $0^\circ\text{C}$  1 equiv. of the azide **2** (**a**: 2.303 g, 6.631 mmol; **b**: 3.212 g, 9.248 mmol, **c**: 1.807 g, 5.202 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL). Ten minutes after the addition was ended, the solution temperature was raised to room temperature. The evolution of nitrogen ceased after 3 h. The solvent was eliminated under vacuum to yield an oil, which was washed 5 times with THF-pentane (1 : 5).

**1a-G<sub>0</sub>**. White powder, 72% yield.  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 17.8$  (d,  $^2J_{\text{PP}} = 32.9$  Hz,  $\text{P}'_0$ ), 50.8 (d,  $^2J_{\text{PP}} = 32.9$  Hz,  $\text{P}_0$ ).

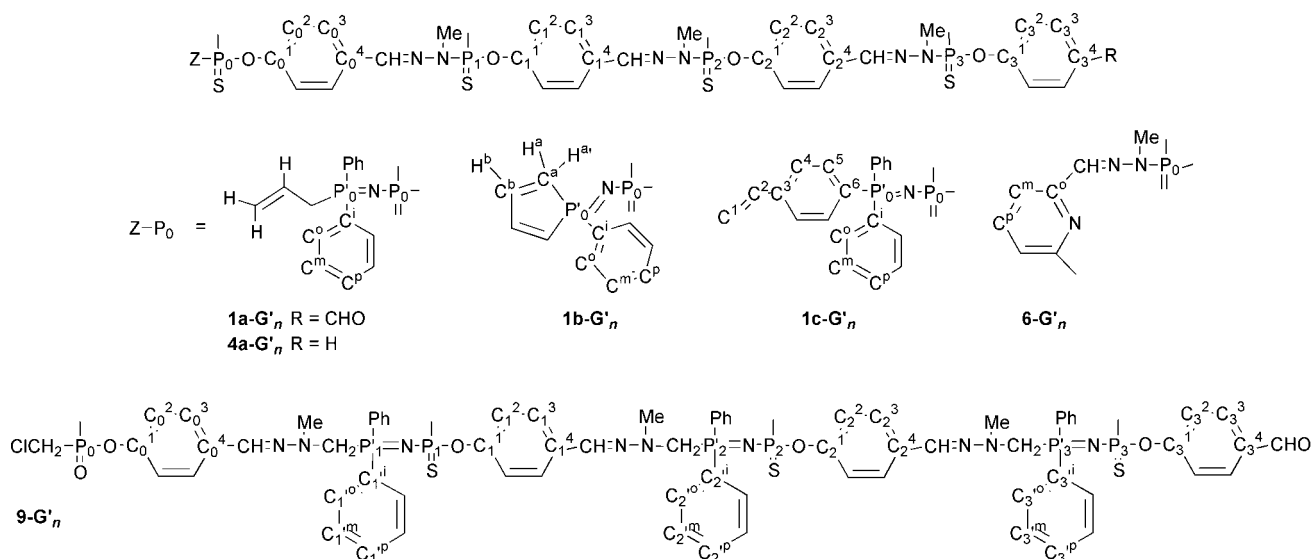
**1b-G<sub>0</sub>**. Yellow oil, 80% yield.  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 40.8$  (d,  $^2J_{\text{PP}} = 29.8$  Hz,  $\text{P}'_0$ ), 52.3 (d,  $^2J_{\text{PP}} = 29.8$  Hz,  $\text{P}_0$ ).

**1c-G<sub>0</sub>**. Pale beige powder, 93% yield.  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 13.3$  (d,  $^2J_{\text{PP}} = 31.3$  Hz,  $\text{P}'_0$ ), 49.9 (d,  $^2J_{\text{PP}} = 31.3$  Hz,  $\text{P}_0$ ).

### General procedure for the synthesis of dendrons **1-G<sub>n</sub>** ( $n = 1-3$ ) with $\text{P}(\text{S})\text{Cl}_2$ end groups

To a solution of dendron **1-G<sub>n-1</sub>** (CHO end groups) (5 mmol) in THF (10 mL) was added a solution of dichloromethylhydrazinothiophosphine **3** (10% excess) in  $\text{CHCl}_3$ . The resulting mixture was stirred for 12 h, then evaporated to dryness. The residue was washed several times with THF-pentane (1 : 5) to afford **1-G<sub>n</sub>**.

**1a-G<sub>1</sub>**. White powder, 88% yield.  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 18.0$  (d,  $^2J_{\text{PP}} = 33.5$  Hz,  $\text{P}'_0$ ), 52.4 (d,  $^2J_{\text{PP}} = 33.5$  Hz,  $\text{P}_0$ ), 63.5 (s,  $\text{P}_1$ ).



Scheme 7 Labelling scheme used for NMR.

**1b-G<sub>1</sub>.** Pale beige powder, 95% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 40.1 (d, <sup>2</sup>J<sub>PP</sub> = 30.2 Hz, P<sub>0</sub>), 53.5 (d, <sup>2</sup>J<sub>PP</sub> = 30.2 Hz, P<sub>0</sub>), 62.1 (s, P<sub>1</sub>).

**1c-G<sub>1</sub>.** Pale beige powder, 92% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 12.4 (d, <sup>2</sup>J<sub>PP</sub> = 31.3 Hz, P<sub>0</sub>), 51.0 (d, <sup>2</sup>J<sub>PP</sub> = 31.3 Hz, P<sub>0</sub>), 62.1 (s, P<sub>1</sub>).

**1a-G<sub>2</sub>.** White powder, 82% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 16.6 (d, <sup>2</sup>J<sub>PP</sub> = 33.5 Hz, P<sub>0</sub>), 51.9 (d, <sup>2</sup>J<sub>PP</sub> = 33.5 Hz, P<sub>0</sub>), 61.5 (s, P<sub>1</sub>), 62.1 (s, P<sub>2</sub>).

**1a-G<sub>3</sub>.** White powder, 92% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 17.6 (d, <sup>2</sup>J<sub>PP</sub> = 33.6 Hz, P<sub>0</sub>), 52.4 (d, <sup>2</sup>J<sub>PP</sub> = 33.6 Hz, P<sub>0</sub>), 62.1 (s, P<sub>1</sub>), 62.3 (s, P<sub>2</sub>), 63.2 (s, P<sub>3</sub>).

#### General procedure for the synthesis of dendrons 1-G'<sub>n</sub> (n = 1–3) with CHO end groups

To a solution of dendron 1-G<sub>n</sub> [P(S)Cl<sub>2</sub> end groups] (5 mmol) in THF (10 mL) was added hydroxybenzaldehyde sodium salt (10% excess). The resulting mixture was stirred overnight, then centrifuged. The solution was then evaporated to dryness to afford a powder, which was washed several times with THF–pentane (1 : 5).

**1a-G'<sub>1</sub>.** White powder, 93% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 17.6 (d, <sup>2</sup>J<sub>PP</sub> = 33.5 Hz, P<sub>0</sub>), 52.6 (d, <sup>2</sup>J<sub>PP</sub> = 33.5 Hz, P<sub>0</sub>), 60.7 (s, P<sub>1</sub>).

**1b-G'<sub>1</sub>.** Pale beige powder, 96% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 39.9 (d, <sup>2</sup>J<sub>PP</sub> = 30.4 Hz, P<sub>0</sub>), 53.6 (d, <sup>2</sup>J<sub>PP</sub> = 30.4 Hz, P<sub>0</sub>), 60.2 (s, P<sub>1</sub>).

**1c-G'<sub>1</sub>.** Pale beige powder, 90% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 12.4 (d, <sup>2</sup>J<sub>PP</sub> = 32.1 Hz, P<sub>0</sub>), 51.5 (d, <sup>2</sup>J<sub>PP</sub> = 32.1 Hz, P<sub>0</sub>), 59.7 (s, P<sub>1</sub>).

**1a-G'<sub>2</sub>.** White powder, 91% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 16.6 (d, <sup>2</sup>J<sub>PP</sub> = 35.0 Hz, P<sub>0</sub>), 52.6 (d, <sup>2</sup>J<sub>PP</sub> = 35.0 Hz, P<sub>0</sub>), 60.6 (s, P<sub>2</sub>), 62.5 (s, P<sub>1</sub>).

**1a-G'<sub>3</sub>.** White powder, 92% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 17.6 (d, <sup>2</sup>J<sub>PP</sub> = 32.0 Hz, P<sub>0</sub>), 52.6 (d, <sup>2</sup>J<sub>PP</sub> = 32.0 Hz, P<sub>0</sub>), 60.5 (s, P<sub>3</sub>), 62.4 (s, P<sub>2</sub>), 62.5 (s, P<sub>1</sub>).

#### Synthesis of dendron 4a-G'<sub>2</sub>

To a solution of 1a-G<sub>2</sub> (3.000 g, 1.618 mmol) in THF (30 mL) was added phenol sodium salt (1.520 g, 13.106 mmol). The resulting mixture was stirred overnight, then centrifuged. The solution was evaporated to dryness to afford a powder, which was washed 3 times with THF–pentane (1 : 5). Dendron 4a-G'<sub>2</sub> was obtained as a white powder in 95% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 17.4 (d, <sup>2</sup>J<sub>PP</sub> = 33.2 Hz, P<sub>0</sub>), 52.6 (d, <sup>2</sup>J<sub>PP</sub> = 33.2 Hz, P<sub>0</sub>), 62.5 (s, P<sub>1</sub>), 62.7 (s, P<sub>2</sub>).

#### Synthesis of 5,5-G<sub>0</sub> and 5-G'<sub>0</sub>

**5.** To a solution of pyridine-4-carboxaldehyde (1.0 mL, 10.46 mmol) in THF (10 mL) were added 5 equiv. of methyl iodide (3.3 mL, 52.38 mmol). The resulting mixture was stirred for 1 day. A precipitate appeared, which was recovered and dried under vacuum, to afford compound 5 as an orange powder in 99% yield. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ = 4.4 (s, 3H, CH<sub>3</sub>), 8.4 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 2H, *o*-C<sub>5</sub>H<sub>4</sub>N), 8.7 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 2H, *m*-C<sub>5</sub>H<sub>4</sub>N), 10.3 (s, 1H, CHO).

**5-G<sub>0</sub>.** To a solution of 5 (1.00 g, 4.01 mmol) in CH<sub>3</sub>CN (40 mL) at 0 °C was added a solution of 3 (4.42 mmol) in CHCl<sub>3</sub> (15.8 mL). The resulting mixture was stirred for 12 h, then evaporated to dryness to give a powder, which was washed several times with pentane. 5-G<sub>0</sub> was obtained as a yellow

powder in 97% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>3</sub>CN): δ = 61.6 (s, P<sub>1</sub>).

**5-G'<sub>0</sub>.** To a solution of 5-G<sub>0</sub> (0.2 g, 0.49 mmol) in MeCN (20 mL) was added hydroxybenzaldehyde sodium salt (0.14 g, 0.98 mmol). The resulting mixture was stirred for 12 h, then centrifuged. The solution was evaporated to dryness to give a yellow powder, which could not be perfectly purified by washing (with diethyl ether). <sup>31</sup>P {<sup>1</sup>H} NMR (CH<sub>3</sub>CN): δ = 58.9 (s, P<sub>1</sub>).

#### General procedure for the synthesis of dendrons 6-G'<sub>n</sub>

To a solution of dialdehyde 6 (5.000 mmol) or dendron 6-G'<sub>n-1</sub> (2.000 mmol) in a minimum amount of THF (10 mL) was added compound 3 (10.000 mmol for 6-G<sub>0</sub>; 8.000 mmol for 6-G<sub>1</sub>; 16.000 mmol for 6-G<sub>2</sub>). The reaction was monitored by <sup>31</sup>P NMR until the disappearance of the signal corresponding to compound 3 (70.5 ppm), then a slight excess of hydroxybenzaldehyde sodium salt was added. The resulting mixture was stirred for 12 h, then centrifuged. The solution was evaporated to dryness to afford a powder, which was washed several times with THF–pentane (1 : 5). Dendrons 6-G'<sub>n</sub> were isolated as white powders.

**6-G'<sub>0</sub>.** 82% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 60.0 (s, P<sub>0</sub>).

**6-G'<sub>1</sub>.** 90% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = 60.5 (s, P<sub>1</sub>), 61.8 (s, P<sub>0</sub>).

**6-G'<sub>2</sub>.** 92% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 60.0 (s, P<sub>2</sub>), 61.2 (s, P<sub>0</sub>), 61.4 (s, P<sub>1</sub>).

#### Synthesis of 7-G'<sub>0</sub> and 7-G<sub>1</sub>

**7-G'<sub>0</sub>.** To a solution of ClCH<sub>2</sub>P(O)Cl<sub>2</sub> (2.00 g, 11.97 mmol) in THF (20 mL), was added 4-hydroxybenzaldehyde sodium salt (3.43 g, 23.94 mmol). The resulting mixture was stirred for 2 h, then centrifuged. The solution was evaporated under vacuum to afford 7-G'<sub>0</sub> as a yellow oil in 80% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 12.2 [s, P<sub>0</sub>(O)].

**7-G<sub>1</sub>.** To a solution of 7-G'<sub>0</sub> (0.200 g, 0.591 mmol) in THF (5 mL), was added a solution of 3 (1.182 mmol) in chloroform (concentration 0.32 M). The resulting solution was stirred for 3 h, then evaporated to dryness to afford a powder. Washing this powder twice with diethyl ether–pentane (2 : 1) afforded 7-G<sub>1</sub> as a yellow powder in 70% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 12.0 [s, P<sub>0</sub>(O)], 61.9 [s, P(S)Cl<sub>2</sub>].

#### Synthesis of 8-G'<sub>0</sub> and 8-G<sub>1</sub>

**8-G'<sub>0</sub>.** To a solution of 7-G'<sub>0</sub> (2.00 g, 5.904 mmol) in pyridine (40 mL) was added a large excess of sodium azide. The resulting mixture was heated at 70 °C for 20 days, then centrifuged. The solution was evaporated under vacuum, and the residue was purified on silica gel (eluent diethyl ether, then methanol) to afford 8-G'<sub>0</sub> as a yellow oil in 60% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 7.3 [s, P<sub>0</sub>(O)].

**8-G<sub>1</sub>.** To a solution of 8-G'<sub>0</sub> (0.065 g, 0.188 mmol) was added a solution of 3 (0.376 mmol) in chloroform (concentration 0.32 M). The solution was stirred for 3 h, then evaporated to dryness to afford a powder, which was washed twice with Et<sub>2</sub>O–pentane (2 : 1). Compound 8-G<sub>1</sub> was obtained as a yellow powder in 71% yield. <sup>31</sup>P {<sup>1</sup>H} NMR (THF): δ = 6.8 [s, P<sub>0</sub>(O)], 62.1 [s, (S)PCl<sub>2</sub>].

#### General procedure for the synthesis of dendrons 9-G'<sub>n</sub> (n = 1–4)

To a solution of 7-G'<sub>0</sub> or dendron 9-G'<sub>n-1</sub> (n = 2–4), in THF (30 mL) was added a stoichiometric amount of methylhydrazine. The resulting mixture was stirred overnight, then evaporated to dryness. The residue was washed two or three

times with diethyl ether to afford dendron **9-G''<sub>n-1</sub>**. To a THF solution of this compound was added a slight excess of Ph<sub>2</sub>PCH<sub>2</sub>OH. The resulting mixture was stirred overnight at 40 °C, then evaporated to dryness. The residue was washed at least 4 times with pentane–Et<sub>2</sub>O (3 : 1), then with pure Et<sub>2</sub>O to afford dendron **9-G'''<sub>n-1</sub>**. To a THF solution of this compound was added a slight excess of the azide **2**. The solution was stirred till the evolution of nitrogen ceased (30 min), then evaporated to dryness. The residue was washed with CH<sub>3</sub>CN–Et<sub>2</sub>O to afford **9-G'<sub>n</sub>** as a white powder. Only dendrons **9-G'<sub>n</sub>** were isolated and fully characterized.

**9-G'<sub>1</sub>**. White powder, 50% yield. <sup>31</sup>P{<sup>1</sup>H} NMR (THF): δ = 11.6 [s, P<sub>0</sub>(O)], 13.1 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P'<sub>1</sub>), 50.9 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P<sub>1</sub>).

**9-G'<sub>2</sub>**. White powder, 55% yield. <sup>31</sup>P{<sup>1</sup>H} NMR (THF): δ = 11.6 [s, P<sub>0</sub>(O)], 11.9 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P'<sub>1</sub>), 13.2 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P'<sub>2</sub>), 50.9 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P<sub>2</sub>), 52.5 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P<sub>1</sub>).

**9-G'<sub>3</sub>**. White powder, 57% yield. <sup>31</sup>P{<sup>1</sup>H} NMR (THF): δ = 12.0 (br d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P'<sub>1</sub>, P'<sub>2</sub>), 13.3 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P'<sub>3</sub>), 50.9 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P<sub>3</sub>), 52.5 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P<sub>1</sub>, P<sub>2</sub>).

**9-G'<sub>4</sub>**. White powder, 50% yield. <sup>31</sup>P{<sup>1</sup>H} NMR (THF): δ = 11.9 (br d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P'<sub>1</sub>, P'<sub>2</sub>, P'<sub>3</sub>), 13.2 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P'<sub>4</sub>), 50.8 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P<sub>4</sub>), 52.4 (d, <sup>2</sup>J<sub>PP</sub> = 32 Hz, P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>).

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