Phosphorus-Containing Dendrimers: Synthesis of Macromolecules with Multiple Tri- and Tetrafunctionalization

Marie-Laure Lartigue, Michael Slany, Anne-Marie Caminade,* and Jean-Pierre Majoral*

Abstract: A variety of dendrimers up to generation 7 possessing terminal $P(S)Cl_2$ (**3-[G_1]**–**3-[G_7]**) or $P(O)Cl_2$ (**7-[G_1]**–**7-[G_3]**, **7-[G_5]**, **7-[G_7]**) have been tri- and tetrafunctionalized. Selective monosubstitution of $P(X)Cl_2$ (X = S, O) termini with allylamine or propargylamine gave the trifunctionalized dendrimers **5-[G_1]**–**5-[G_7]**, **8-[G_1]**–**8-[G_3]**, **10-[G_1]**, **11-[G_1]**, **11-[G_4]**, **12-[G_1]**–**12-[G_3]**, **12-[G_5]**, and **12-[G_7]**. Reaction of dendrimers **4-[G_1]** and **4-[G_4]**, possessing terminal P(S)[N-(allyl)$_2$](Cl) fragments, with propargylamine afforded trifunctionalized dendrimers **14-[G_1]** and **14-[G_4]**. Multiply trifunctionalized macromolecules **13-[G_2]** and **13-[G_3]** with P(S)(NH-allyl)(NH-propargyl) moieties at the surface were prepared by treatment of **8-[G_2]** and **8-[G_3]** with propargylamine. Dendrimers **15-[G_1]**–**15-[G_3]** and **16-[G_1]**–**16-[G_3]** with P(O)(NH-allyl)(OC_6H_4CHO) and P(O)(NH-propargyl)(OC_6H_4CHO) termini were also synthesized. Reaction of hydrazine or cyanomethylenetriphenylphosphorane (**17**) with compounds **15-[G_1]**, **15-[G_3]**, and **16-[G_1]**–**16-[G_3]** led to the multiply tetrafunctionalized dendrimers **18-[G_1]**, **18-[G_3]**, **19-[G_1]**, **20-[G_1]**–**20-[G_3]**, **21-[G_1]**, and **21-[G_2]**.

Keywords
dendrimers · macromolecules · phosphorus compounds · substitutions

Introduction

Dendrimers, a new class of polymers, offer novel properties and features not found in classical systems. These three-dimensional globular polymers have been attracting a great deal of interest due to their unusual architectures, which induce, for example, high chemical reactivity, low viscosity, high solubility, and miscibility. Many of the applications that are being proposed for dendrimers exploit their unique physical properties, or take advantage of the high density of functionalities at the chain ends and the large number of terminal groups at the periphery, which provide numerous possibilities for tailoring the polymer for particular applications.[1]

Although there have been significant advances in the preparation of these monodisperse, unimolecular species, investigations into the synthesis of dendrimers possessing more than one type of functionality at the surface are rare. A limiting feature of most of the known methods is the difficulty in *selectively* modifying peripheral functionalities.

In pioneering work Tomalia reported the formation up to the tenth generation of polyamidoamine-containing dendrimers,[1a, 2a–d] that is, species having two types of functionalities at the periphery. Recently the first preparations of highly unsymmetrical dendritic macromolecules containing predetermined and well-defined numbers of functional groups at the chain ends was accomplished by Fréchet et al.[3] Nonuniformly functionalized dendrimers containing two different functional groups were prepared, as well as other unsymmetrical macromolecules possessing electron withdrawing cyano groups and electron donating benzyloxy groups in segmentally opposed regions of the dendrimer surface.

Therefore, procedures reported up to now describe the introduction of no more than two different types of functionalities.[2e–g] Because surface modifications have a large effect on the properties of these polymers, there is a need to develop versatile new strategies for anchoring a large variety of reactive groups at the surface.

Herein we report approaches to the straightforward control of reactivity at the periphery of phosphorus-containing dendrimers allowing the introduction of sets of three or four different functional groups.

Results and Discussion

Experiments were conducted first with dendrimers **3-[G_1]**–**3-[G_7]** (generations 1 to 7 containing 3 to 192 $P(S)Cl_2$ units). The preparation of these derivatives required, as already reported,[4] reiteration of a two-step sequence: addition of the sodium salt of 4-hydroxybenzaldehyde to the halogenated phosphine sulfide, followed by treatment of the resulting polyaldehyde with dichloro(methylhydrazino)phosphine sulfide (Scheme 1).

In a preliminary communication[5] we described an interesting observation: addition of bisallylamine to dendrimers **3-[G_1]**–**3-[G_4]** (generations 1 to 4) possessing 3, 6, 12, and 24 terminal $P(S)Cl_2$ groups, respectively, led *selectively* to monosubstitution of the $P(S)Cl_2$ moieties, regardless of the number of equivalents of bisallylamine used, with the formation of compounds **4-[G_1]**–**4-[G_4]** (Scheme 2). This prompted us to study the potential of these unexpected reactions in order to diversify the nature of chain ends in our dendritic systems.

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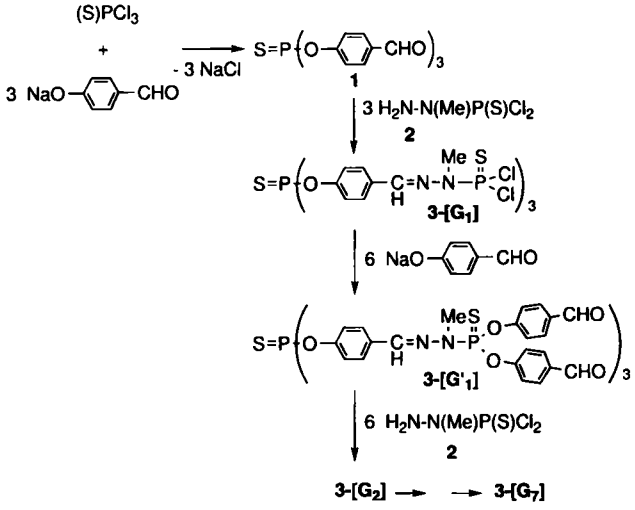
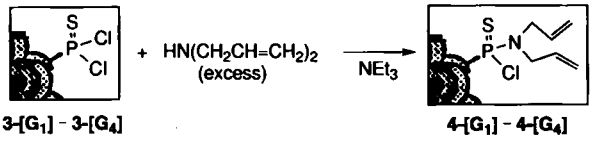
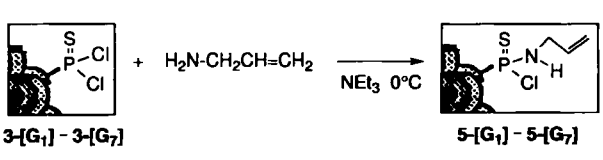


Scheme 1.



Scheme 2.

Trifunctionalization was first attempted by treating **3-[G$_1$]** with 3 equiv of allylamine in the presence of triethylamine (3 equiv) in THF at 0 °C for 3 h. Quantitative and selective monosubstitution occurred giving rise to dendrimer **5-[G$_1$]** with (S)P(Cl)(NH-allyl) moieties as chain ends (Scheme 3). The reaction could be easily followed by ^{31}P NMR spectroscopy, which showed the disappearance of the signal due to the three P(S)Cl$_2$ groups (δ = 63.1) with concomitant appearance of the corresponding P(S)(Cl)(NH-allyl) signal (δ = 72.9). Disubstitution could also be achieved with 6 equiv of allylamine instead of 3. Here again, ^{31}P NMR was useful in following the reaction, since the signal due to the disubstituted derivatives appeared at δ = 68.6.[6] Similarly selective monosubstitutions could be performed with the higher-generation dendrimers **3-[G$_2$]**–**3-[G$_7$]** allowing the anchoring up to 192 NH(allyl) moieties and the formation of the new dendrimers **5-[G$_2$]**–**5-[G$_7$]** (Scheme 3, Table 1). Remarkably, regardless of the generation considered, each -P(S)Cl$_2$ group behaved as a monomeric species, and no disubstitution reaction was detected. As for **3-[G$_1$]**, disubstitution of the P(S)Cl$_2$ chain termini could be achieved for the higher generations by using appropriate amounts of allylamine (reactions followed by ^{31}P NMR).[6]



Scheme 3.

All new materials **5-[G$_1$]**–**5-[G$_7$]** were isolated and fully characterized. Their spectral data and elemental analyses are in agreement with the proposed structures. These new polymers, and further dendrimers reported below, have been identified mainly by NMR, which provides strong support for the interpretation. Any faulty sequence can be detected, even if slight alteration at the surface cannot be totally ruled out. Indeed, ^{31}P NMR appears to be the method of choice to follow rigorously the construction of dendrimers, since, up to generation 6, the signal of the phosphorus atom of the core can be detected; lack of substitution at one or several of the terminal functional groups of dendrimers from generation 1–6 would thus be observed (this is the case when dendrimers are treated with a slight deficiency of reagent). Moreover, substitution reactions on the surface generally result in a shielding or deshielding effect (depending on the type of substitution) of the signal due to the phosphorus atoms of the top generation n and a slight deshielding effect for the phosphorus atom of generation $n-1$.

We now have a useful and convenient entry to multiply "trifunctionalized" dendrimers up to generation 7. In order to check whether reactions involving terminal P(S)Cl$_2$ fragments can be generalized to other phosphorus chain termini, we prepared the new dendrimers **7-[G$_1$]**–**7-[G$_3$]**, **7-[G$_5$]**, and **7-[G$_7$]**, each having a (P=S) group at each branching site at the interior of the cascade framework and P(O)Cl$_2$ groups on the surface. The same reiterative two-step procedure as for the construction of compounds **3-[G$_1$]**–**3-[G$_7$]** was employed, except that dichloro(methylhydrazino)phosphine oxide **6** replaced the corresponding phosphine sulfide **2** in the last step of each elaboration to higher generations (Scheme 4). Dendrimer **7-[G$_1$]** thus has a P=S moiety as its core and three P(O)Cl$_2$ groups on the

Table 1. Number of terminal functional groups (P–Cl, NH-allyl, NH-propargyl, NH-bisallyl, CHO) in multiply trifunctionalized dendrimers.

	X	P–Cl	NH-allyl	NH-propargyl		X	NH-allyl	NH-propargyl	CHO	NH-bisallyl
5-[G$_1$]	S	3	3	–	**13-[G$_2$]**	O	6	6	–	
5-[G$_2$]	S	6	6	–	**13-[G$_3$]**	O	12	12	–	
5-[G$_3$]	S	12	12	–						
5-[G$_4$]	S	24	24	–	**15-[G$_1$]**	O	3	–	3	
5-[G$_5$]	S	48	48	–	**15-[G$_2$]**	O	6	–	6	
5-[G$_6$]	S	96	96	–	**15-[G$_3$]**	O	12	–	12	
5-[G$_7$]	S	192	192	–						
8-[G$_1$]	O	3	3	–	**16-[G$_1$]**	O	–	3	3	
8-[G$_2$]	O	6	6	–	**16-[G$_2$]**	O	–	6	6	
8-[G$_3$]	O	12	12	–	**16-[G$_3$]**	O	–	12	12	
10-[G$_1$]	O	3	3	–						
11-[G$_1$]	S	3	–	3	**14-[G$_1$]**	S	3			3
11-[G$_4$]	S	24	–	24	**14-[G$_4$]**	S	24			24
12-[G$_1$]	O	3	–	3						
12-[G$_2$]	O	6	–	6						
12-[G$_3$]	O	12	–	12						
12-[G$_5$]	O	48	–	48						
12-[G$_7$]	O	192	–	192						

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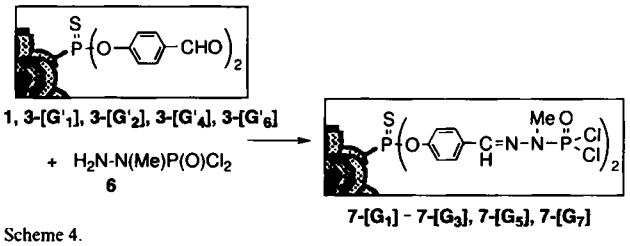
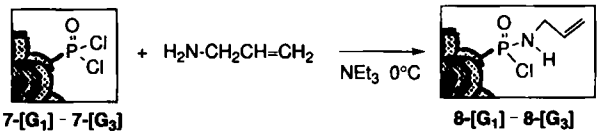


Scheme 4.

surface layer, while dendrimer **7-[G$_7$]** possesses 190 thiophosphoryl groups within the cascade superstructure and 192 $P(O)Cl_2$ groups at the periphery. As previously mentioned for derivatives **3-[G$_1$]**–**3-[G$_7$]**, ^{31}P NMR spectra clearly distinguish between each type of phosphorus site within the dendrimer and on the surface and allow the construction of each compound to be followed in a straightforward manner.

The replacement of thiophosphoryl by phosphoryl fragments did not cause any change in reactivity regardless of the generation considered. Selective monosubstitution took place smoothly when dendrimers **7-[G$_1$]**–**7-[G$_3$]** were treated with the appropriate amount of allylamine to afford the new "trifunctionalized" macromolecules **8-[G$_1$]**–**8-[G$_3$]** (Scheme 5, Table 1). Thus, for example, addition of 6 equiv of allylamine at 0 °C to a THF solution of **7-[G$_2$]** gave **8-[G$_2$]** quantitatively. The reaction was monitored by ^{31}P NMR spectroscopy (disappearance of a singlet at $\delta = 18.6$ assigned to the $P(O)Cl_2$ moieties, and appearance of a singlet at $\delta = 20.6$ corresponding to the P(O)(Cl)(NH-allyl) fragments) as well as by ^1H and ^{13}C NMR spectroscopy (appearance of signals due to the allylic systems).



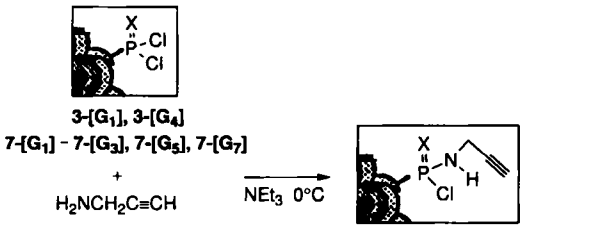
Scheme 5.

A similar reaction of dendron **9-[G$_1$]**, in which a phosphoryl group acts a core and three $P(O)Cl_2$ moieties are present at the periphery, with 3 equiv of allylamine led to formation of **10-[G$_1$]** (Table 1).

Our next aim was to extend the monosubstitution reaction to the introduction of other reagents and thus to prepare a variety of multiply "trifunctionalized" dendrimers. The reactions of compounds **3-[G$_1$]**, **3-[G$_4$]**, **7-[G$_1$]**–**7-[G$_3$]**, **7-[G$_5$]**, and **7-[G$_7$]** with propargylamine were investigated. Reaction with 1 equiv of propargylamine and 1 equiv of triethylamine per $P(S)Cl_2$ or $P(O)Cl_2$ chain terminus led to clean monosubstitutions with the formation of the dendritic systems **11-[G$_1$]**, **11-[G$_4$]**, **12-[G$_1$]**–**12-[G$_3$]**, **12-[G$_5$]**, and **12-[G$_7$]**, respectively, in very high yields (Scheme 6, Table 1). As in the case of the monosubstitution with allylamine, reactions were followed by NMR; here also, no trace of disubstituted products was detected. In contrast to the reactions with bisallylamine, disubstitution was observed with 2 equiv of allylamine and 2 equiv of triethylamine per $P(X)Cl_2$ group (X = S, O).[6]

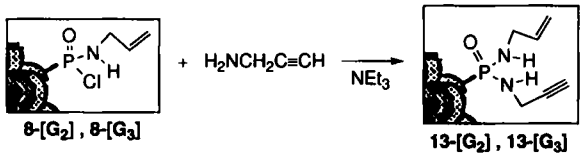
In line with results obtained with monomers such as $(R_2N)_2P(X)Cl$ (X = S or O), which show that the remaining P–Cl bond is still reactive towards a variety of reagents, we expected that dendrimers **8-[G$_n$]** would react with a number of difunctionalized species to give other new macromolecules incorporating three different functionalities.

Treatment of species **8-[G$_2$]**, which has six P(S)Cl(NH-allyl) fragments, with propargylamine (6 equiv) in the presence of triethylamine gave **13-[G$_2$]**, whose surface is covered by six allyl,



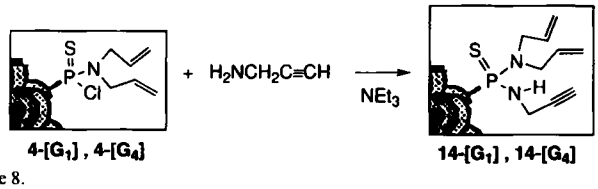
Scheme 6.

six propargyl, and twelve NH groups. Similarly, **8-[G$_3$]** (12 P(S)Cl(NH-allyl) fragments) reacted with propargylamine (12 equiv)/triethylamine to give **13-[G$_3$]**, containing 12 allyl, 12 propargyl, and 24 NH groups (Scheme 7, Table 1).



Scheme 7.

Remarkably, while attempts to disubstitute dendrimers **3-[G$_1$]**–**3-[G$_4$]** with bisallylamine failed (see above), the corresponding monosubstituted compounds **4-[G$_1$]**–**4-[G$_4$]** were still reactive towards propargylamine. Thus, addition of propargylamine to **4-[G$_1$]** and **4-[G$_4$]** afforded derivatives **14-[G$_1$]** and **14-[G$_4$]**, respectively, incorporating both bisallylamino and propargylamino groups on the same phosphorus atom (Scheme 8, Fig. 1, Table 1). These compounds were characterized by NMR, IR, and elemental analysis.



Scheme 8.

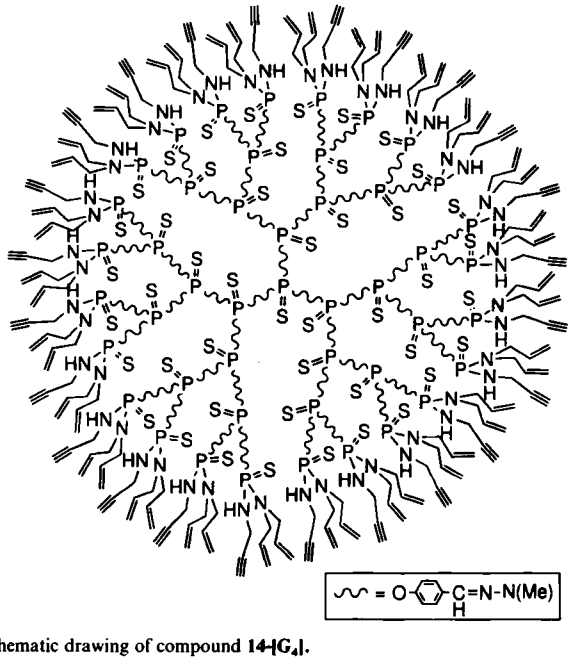
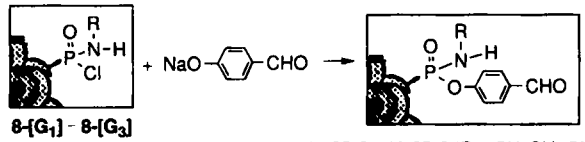


Fig. 1. Schematic drawing of compound **14-[G$_4$]**.

The usefulness of this strategy, which allows the high-yield synthesis of various multiply "trifunctionalized" dendrimers, can also be illustrated by treating species **8-[G_1]–8-[G_3]** and **12-[G_1]–12-[G_3]** with the sodium salt of 4-hydroxybenzaldehyde. Substitution reactions occurred smoothly giving rise to compounds **15-[G_1]–15-[G_3]** and **16-[G_1]–16-[G_3]**, respectively, in which the surfaces are covered by NH, aldehyde, and allyl (**15-[G_1]–15-[G_3]**) or propargyl groups (**16-[G_1]–16-[G_3]**) (Scheme 9). These syntheses were carried out with high yields and were monitored mainly by ^{31}P NMR spectroscopy.



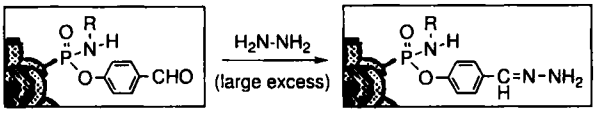
8-[G_1] - 8-[G_3]
12-[G_1] - 12-[G_3]

15-[G_1] - 15-[G_3] (R = $CH_2CH{=}CH_2$)
16-[G_1] - 16-[G_3] (R = $CH_2C{\equiv}CH$)

Scheme 9.

Dendrimers **15-[G_n]** and **16-[G_n]** are good models for the preparation of the first multiply "tetrafunctionalized" macromolecules. This can be exemplified by two types of reaction involving terminal aldehyde groups: reaction with hydrazine and a Wittig reaction with $Ph_3P{=}CH{-}CN$ (**17**).

As expected, addition of hydrazine to **15-[G_1]** and **15-[G_3]** led to the dendrimers **18-[G_1]** and **18-[G_3]**, respectively, possessing four different and compatible functionalities: NH, NH_2, allyl, and hydrazono groups (Scheme 10, Table 2). A similar reaction



15-[G_1], 15-[G_3]
16-[G_1]

18-[G_1], 18-[G_3] (R = $CH_2CH{=}CH_2$)
19-[G_1] (R = $CH_2C{\equiv}CH$)

Scheme 10.

Table 2. Number of terminal functional groups (NH-allyl, $CH{=}N{-}NH_2$, NH-propargyl, $CH{=}CH{-}CN$) in multiply tetrafunctionalized dendrimers.

	X	NH-allyl	$CH{=}N{-}NH_2$	NH-propargyl	$CH{=}CH{-}CN$
18-[G_1]	O	3	3	–	–
18-[G_3]	O	12	12	–	–
19-[G_1]	O	–	3	3	–
20-[G_1]	O	–	–	3	3
20-[G_2]	O	–	–	6	6
20-[G_3]	O	–	–	12	12
21-[G_1]	O	3	–	–	3
21-[G_2]	O	6	–	–	6

with **16-[G_1]** led to the dendron **19-[G_1]**. ^1H NMR, ^{13}C NMR, and IR spectroscopies appear to be very suitable techniques for monitoring the reaction (disappearance of the singlet due to aldehyde protons in the ^1H NMR and disappearance of the singlet due to carbonyl groups in the ^{13}C NMR spectra). However, ^{31}P NMR spectroscopy remains the most important means of following the formation of these compounds, as shown in Figure 2 for the sequence of reactions **3-[G'_2]** → **7-[G_3]** → **8-[G_3]** → **15-[G_3]** → **18-[G_3]**.

Wittig reactions of $Ph_3P{=}CH{-}CN$ with dendrimers **16-[G_1]–16-[G_3]** allowed the isolation and fully characterization of fur-

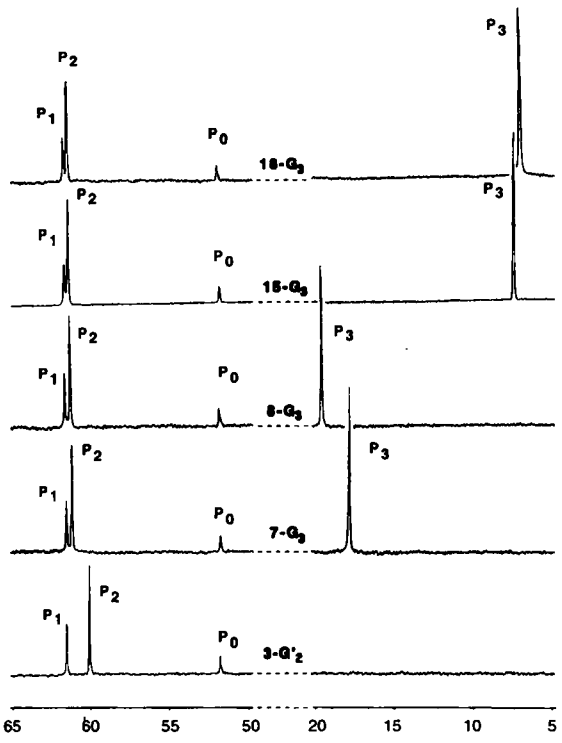
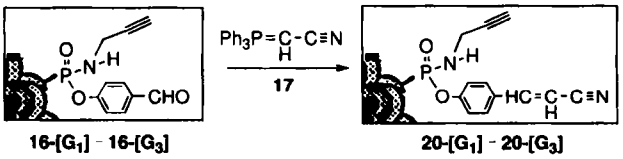


Fig. 2. ^{31}P NMR spectra of compounds **3-[G'_2]**, **7-[G_3]**, **8-[G_3]**, **15-[G_3]**, and **18-[G_3]**.

ther multiply "tetrafunctionalized" species **20-[G_1]–20-[G_3]** (Scheme 11, Table 2, Fig. 3). ^1H NMR spectra for **20-[G_1]–20-[G_3]** show the disappearance of the signal due to the aldehyde groups and the appearance of two doublets assigned to the methine proton in the α position relative to the phenyl group;



16-[G_1] - 16-[G_3]

20-[G_1] - 20-[G_3]

Scheme 11.

the doublet at $\delta = 5.34–5.36$ ($^3J_{HH} = 12.1$ Hz) corresponds to the *cis* isomer and that at $\delta = 5.71–5.74$ ($^3J_{HH} = 16.6$ Hz) to the *trans* isomer (*cis*/*trans* ratio, 1:1.5). The proton in the α position relative to the cyano group only appears as a doublet at $\delta = 6.99–7.01$ ($J_{HH} = 12.1$ Hz) for the *cis* isomer; the signal for the *trans* isomer is obscured by aromatic protons. The formation of the two isomers is also clearly observed in the ^{13}C NMR spectra, which, for example, exhibit two singlets at $\delta = 94.4–95.8$ for the sp^2 carbon α to the phenyl group and two singlets at $\delta = 117.2–117.9$ for the sp^2 carbon α to the cyano group. In addition to NMR characterizations, the formation of **20-[G_1]** and **20-[G_2]** is confirmed by the presence of the molecular ion peaks (**20-[G_1]**: 1243 $[M+1]^+$; **20-[G_2]**: 3055 $[M+1]^+$) in the FAB-MS spectra.

A similar Wittig reaction was undertaken with derivatives **15-[G_1]** and **15-[G_2]** leading to compounds **21-[G_1]** and **21-[G_2]**, respectively (Scheme 12, Table 2).

It should be mentioned that terminal phosphorus units of all the tri- or tetrafunctionalized dendrimers reported in this paper

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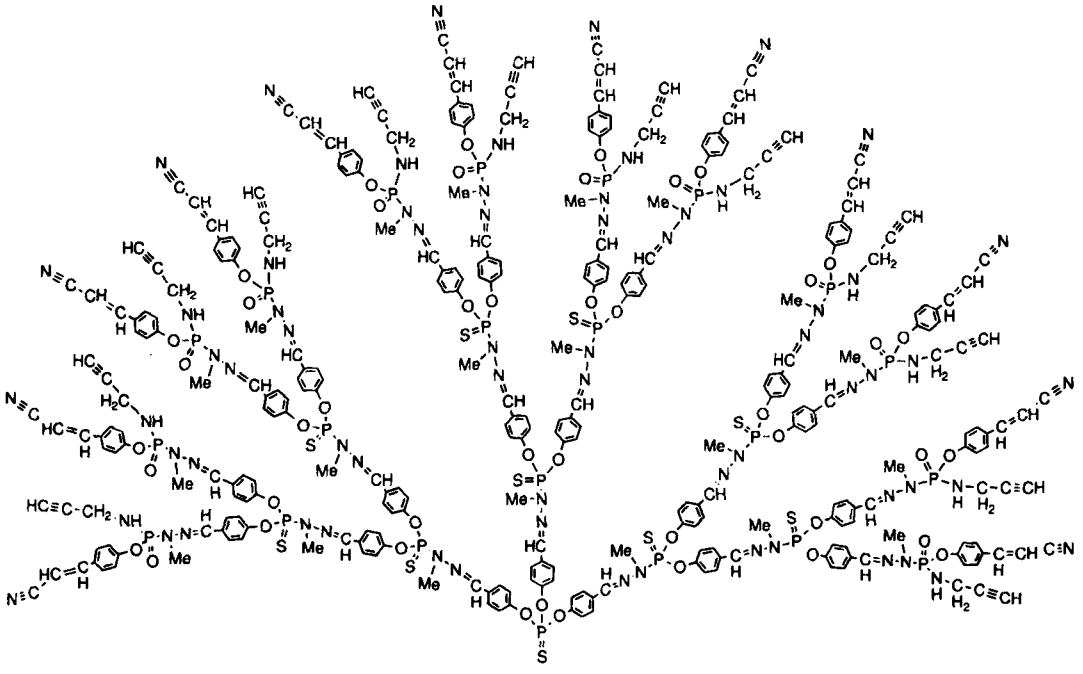
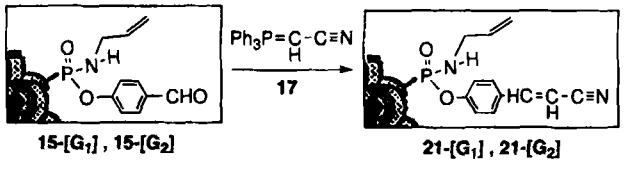


Fig. 3. Compound **20-[G$_3$]**.



15-[G$_1$], 15-[G$_2$] **21-[G$_1$], 21-[G$_2$]**

Scheme 12.

are chiral. As a result, the ^{31}P NMR signal due to the phosphorus fragments of generation $n-1$ is broadened, while the signal of the phosphorus groups at the surface (generation n) remain sharp.

Remarkably, all the polymers reported remain, independently of generation, perfectly soluble in most organic solvents (THF, CH_2Cl_2, $CHCl_3$).

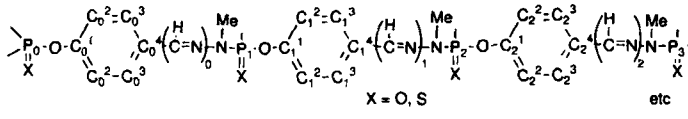
Conclusion

All the experiments reported clearly confirm the unique specificity of the substitution reactions of phosphorus-containing dendrimers **3-[G$_1$]–3-[G$_7$]**, **7-[G$_1$]–7-[G$_3$]**, **7-[G$_5$]**, **7-[G$_7$]**. The presence of phosphorus not only allows the construction of these macromolecules to be monitored without difficulty, but also permits the formation in high yield of a large number of dendrimers with multiple tri- and tetrafunctionalization. In this paper the syntheses and full characterizations of 40 new dendrimers of this type are reported. Each $P(X)Cl_2$ (X = S, O) terminal fragment is found to behave as a monomer, which can be successively monosubstituted and then disubstituted with a variety of difunctionalized reagents such as allylamine, bisallylamine, propargylamine, 4-hydroxybenzaldehyde, phosphorus ylides, and hydrazine.

These results should open new perspectives in dendrimer chemistry. For example, the attachment of several active substances showing different properties can now be envisaged, or the grafting of dendrimers to a second polymer by means of a suitable functionality, leaving other functional groups available for further reaction. Studies in these fields are in progress.

Experimental Section

General: All manipulations were carried out with standard high-vacuum or dry argon atmosphere techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC200 spectrometer. ^{31}P NMR chemical shifts were reported in ppm relative to 85% H_3PO_4. Mass spectra were recorded on a Finniganmat TSQ 700 or 95 spectrometer (FAB). The numbering used for ^{1}H, ^{13}C and ^{31}P NMR assignments is shown in Scheme 13.



Scheme 13.

General procedure for the synthesis of dendrimers 4-[G$_1$]–4-[G$_4$]: To a solution of 0.200 g of dendrimer **3-[G$_n$]** ($n = 1$, 0.22 mmol; $n = 2$, 0.084 mmol; $n = 3$, 0.037 mmol; $n = 4$, 0.018 mmol) in THF (20 mL) was added triethylamine ($n = 1$, 92 µL, 0.66 mmol; $n = 2$, 70 µL, 0.504 mmol; $n = 3$, 62 µL, 0.444 mmol; $n = 4$, 60 µL, 0.432 mmol) and diallylamine ($n = 1$, 82 µL, 0.66 mmol; $n = 2$, 62 µL, 0.504 mmol; $n = 3$, 55 µL, 0.444 mmol; $n = 4$, 53 µL, 0.432 mmol) at room temperature. This mixture was stirred for one week. The precipitate was then eliminated by centrifugation, and the solvent evaporated under vacuum. The resulting oil ($n = 1$) or powder ($n = 2$, 3, 4) was purified by column chromatography (eluent: ethyl acetate).

4-[G$_1$]: Yellow oil; 60% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 52.6$ (brs, P_0), 77.7 (s, P_1); ^{1}H NMR ($CDCl_3$): $\delta = 3.2$ (d, $^3J_{HP_1} = 12.3$ Hz, 9H, P_1–N–CH_3), 4.0 (m, 12H, CH_2–CH=CH_2), 5.2 (m, 12H, CH_2–CH=CH_2), 5.8 (m, 6H, CH_2–CH=CH_2), 7.3 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HP_0} = 1.1$ Hz, 6H, C_0^2-H), 7.6 (d, $^3J_{HP_1} = 2.1$ Hz, 3H; CH=N), 7.7 (d, $^3J_{HH} = 8.6$ Hz, 6H, C_0^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.5$ (d, $^2J_{CP_1} = 11.3$ Hz, P_1–N–CH_3), 49.1 (d, $^2J_{CP_1} = 2.9$ Hz, CH_2–CH=CH_2), 118.0 (s, CH_2–CH=CH_2), 120.8 (d, $^3J_{CP_0} = 4.9$ Hz, C_0^2), 127.5 (s, C_0^3), 132.2 (s, C_0^4), 132.9 (d, $^3J_{CP_1} = 2.6$ Hz, CH_2–CH=CH_2), 137.3 (d, $^3J_{CP_1} = 15.9$ Hz, CH=N), 150.3 (d, $^2J_{CP_0} = 7.4$ Hz, C_0^1). IR (THF): 1642 (m, $\tilde{\nu}_{C=C}$) cm^{-1}. MS *m/z*: 1090 $[M+1]^+$ (Cl = 35) and isotopic repartition (1092: 100%). Anal. calcd for $C_{42}H_{54}Cl_3N_9O_3P_4S_4$: C, 46.22; H, 4.99; N, 11.55. Found: C, 45.98; H, 4.87; N, 11.35.

4-[G$_2$]: White powder; 65% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 52.7$ (s, P_0), 62.3 (brs, P_1), 77.7 (s, P_2); ^{1}H NMR ($CDCl_3$): $\delta = 3.2$ (d, $^3J_{HP_2} = 12.4$ Hz, 18H, P_2–N–CH_3), 3.4 (d, $^3J_{HP_1} = 10.5$ Hz, 9H, P_1–N–CH_3), 4.0 (m, 24H, CH_2–CH=CH_2), 5.2 (m, 24H, CH_2–CH=CH_2), 5.8 (m, 12H, CH_2–CH=CH_2), 7.2 (d, $^3J_{HH} = 8.0$ Hz, 12H, C_1^2-H), 7.3 (d, $^3J_{HH} = 8.6$ Hz, 6H, C_0^2-H), 7.5 (d, $^3J_{HP_2} = 2.0$ Hz, 6H, $(CH=N)_1$), 7.6 (d, $^3J_{HH} = 8.0$ Hz, 12H, C_1^3-H), 7.7 (brs, 3H, $(CH=N)_0$), 7.8 (d,

$^3J_{HH}$ = 8.6 Hz, 6H, C_0^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.5 (d, $^2J_{CP2}$ = 10.7 Hz, P_2-N-CH_3), 32.5 (d, $^2J_{CP1}$ = 12.7 Hz, P_1-N-CH_3), 49.1 (d, $^2J_{CP2}$ = 2.7 Hz, CH_2-CH=CH_2), 118.0 (s, CH_2-CH=CH_2), 120.9 (d, $^3J_{CP0}$ = 3.8 Hz, C_0^2), 121.1 (d, $^3J_{CP1}$ = 4.6 Hz, C_1^2), 127.4 (s, C_1^3), 127.8 (s, C_0^3), 131.8 (s, C_1^4), 132.0 (s, C_0^4), 132.8 (brs, CH_2-CH=CH_2), 137.5 (d, $^3J_{CP1\ 2}$ = 16.1 Hz, (CH=N)$_{0-1}$), 150.5 (d, $^2J_{CP0-1}$ = 7.4 Hz, C_0^1, C_1^1). IR (KBr): 1641 (m, $\tilde{\nu}_{C=C}$) cm^{-1}. Anal. calcd for $C_{108}H_{132}Cl_6N_{24}O_9P_{10}S_{10}$: C, 47.11; H, 4.83; N, 12.21. Found: C, 46.89; H, 4.71; N, 12.06.

4-[G_3]: White powder; 75% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 52.7 (s, P_0), 62.3 (brs, P_2), 62.5 (s, P_1), 77.7 (s, P_3); ^1H NMR ($CDCl_3$): δ = 3.2 (d, $^3J_{HP3}$ = 12.3 Hz, 36H, P_3-N-CH_3), 3.3 (d, $^3J_{HP1\ 2}$ = 9.9 Hz, 27H, $P_{1\ 2}$-N-CH_3), 4.0 (m, 48H, CH_2-CH=CH_2), 5.1 (m, 48H, CH_2-CH=CH_2), 5.8 (m, 24H, CH_2-CH=CH_2), 7.2–7.8 (m, 105H, $(C_6H_4)_{0-1\ 2}$ and (CH=N)$_{0-1\ 2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.4 (d, $^2J_{CP3}$ = 11.3 Hz, P_3-N-CH_3), 32.5 (d, $^2J_{CP1-2}$ = 12.8 Hz, P_{1-2}-N-CH_3), 49.1 (d, $^2J_{CP3}$ = 2.4 Hz, CH_2-CH=CH_2), 118.0 (s, CH_2-CH=CH_2), 120.8 (d, $^3J_{CP0-1}$ = 3.0 Hz, C_0^2, C_1^2), 121.1 (d, $^3J_{CP2}$ = 3.3 Hz, C_2^2), 127.4 (s, C_2^3), 127.6 (s, C_1^3), 127.9 (s, C_0^3), 131.5 (s, C_1^4), 131.7 (s, C_2^4), 132.0 (s, C_0^4), 132.8 (s, CH_2-CH=CH_2), 137.7 (d, $^3J_{CP3}$ = 15.9 Hz, (CH=N)$_2$), 138.3 (d, $^3J_{CP1\ 2}$ = 15.5 Hz, (CH=N)$_{0-1}$), 150.5 (d, $^2J_{CP2}$ = 7.3 Hz, C_2^1), 150.7 (d, $^2J_{CP0-1}$ = 8.9 Hz, C_0^1, C_1^1). IR (KBr): 1641 (m; $\tilde{\nu}_{C=C}$) cm^{-1}. Anal. calcd. for $C_{240}H_{288}Cl_{12}N_{54}O_{21}P_{22}S_{22}$: C, 47.43; H, 4.78; N, 12.44. Found: C, 47.17; H, 4.65; N, 12.27.

4-[G_4]: White powder; 63% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 52.6 (s, P_0), 62.3 (brs, P_3), 62.6 (s, P_2), 62.9 (s, P_1), 77.7 (s, P_4); ^1H NMR ($CDCl_3$): δ = 3.2 (d, $^3J_{HP4}$ = 13.3 Hz, 72H, P_4-N-CH_3), 3.3 (d, $^3J_{HP1\ 2-3}$ = 10.2 Hz, 63H, P_{1-2-3}-N-CH_3), 4.0 (m, 96H, CH_2-CH=CH_2), 5.1 (m, 96H, CH_2-CH=CH_2), 5.8 (m, 48H, CH_2-CH=CH_2), 7.2–7.8 (m, 225H, $(C_6H_4)_{0\ 1-2-3}$ and (CH=N)$_{0-1-2-3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.4 (d, $^2J_{CP4}$ = 11.2 Hz, P_4-N-CH_3), 32.5 (d, $^2J_{CP1-2-3}$ = 13.0 Hz, $P_{1-2\ 3}$-N-CH_3), 49.1 (d, $^2J_{CP4}$ = 2.9 Hz, CH_2-CH=CH_2), 118.0 (s, CH_2-CH=CH_2), 120.8 (brs, C_0^2, C_1^2, C_2^2), 121.1 (d, $^3J_{CP3}$ = 4.0 Hz, C_3^2), 127.4 (s, C_3^3), 127.6 (s, C_2^3), 127.8 (s, C_0^3, C_1^3), 131.5 (s, C_0^4, C_1^4, C_2^4), 131.7 (s, C_3^4), 132.7 (d, $^3J_{CP4}$ = 2.4 Hz, CH_2-CH=CH_2), 137.7 (d, $^3J_{CP4}$ = 15.8 Hz, (CH=N)$_3$), 138.2–138.5 (m, (CH=N)$_{0-1-2}$), 150.5 (d, $^2J_{CP3}$ = 7.6 Hz, C_3^1), 150.7 (d, $^2J_{CP0-1-2}$ = 7.9 Hz, C_0^1, C_1^1, C_2^1). IR (KBr): 1641 (m; $\tilde{\nu}_{C=C}$) cm^{-1}. Anal. calcd. for $C_{504}H_{600}Cl_{24}N_{114}O_{45}P_{46}S_{46}$: C, 47.57; H, 4.75; N, 12.55. Found: C, 47.51; H, 4.68; N, 12.40.

General procedure for the synthesis of dendrimers 5-[G_1]–5-[G_7]: To a solution of 0.100 g of dendrimer **3**-[G_n] (n = 1, 0.11 mmol; n = 2, 0.042 mmol; n = 3, 0.0187 mmol; n = 4, 0.0089 mmol; n = 5, 0.0043 mmol; n = 6, 0.00214 mmol; n = 7, 0.00106 mmol) in THF (10 mL) was added triethylamine (n = 1, 46 µL, 0.33 mmol; n = 2, 35 µL, 0.252 mmol; n = 3, 31 µL, 0.224 mmol; n = 4, 30 µL, 0.213 mmol, n = 5, 29 µL, 0.21 mmol; n = 6, 29 µL, 0.206 mmol; n = 7, 28 µL, 0.204 mmol). The solution was cooled to 0 °C, and allylamine was then added dropwise with a microsyringe (n = 1, 25 µL; n = 2, 19 µL; n = 3, 17 µL; n = 4, 16 µL; n = 5, 16 µL; n = 6, 15 µL; n = 7, 15 µL). The mixture was slowly warmed to room temperature and stirred overnight. After filtration, the solvent was removed under vacuum to give **5**-[G_n] as a powder which was washed with pentane/ether (1/1) (2 × 10 mL).

5-[G_1]: White powder; 95% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 51.9 (s, P_0), 72.9 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.3 (d, $^3J_{HP1}$ = 13.5 Hz, 9H, P_1-N-CH_3), 3.9 (m, 6H, CH_2-CH=CH_2), 4.6 (m, 3H, NH), 5.2 (m, 6H, CH_2-CH=CH_2), 5.9 (m, 3H, CH_2-CH=CH_2), 7.3 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HP0}$ = 1.5 Hz, 6H, C_0^2-H), 7.6 (d, $^3J_{HP1}$ = 3.1 Hz, 3H, CH=N), 7.7 (d, $^3J_{HH}$ = 8.6 Hz, 6H, C_0^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.9 (d, $^2J_{CP1}$ = 10.5 Hz, P_1-N-CH_3), 44.6 (s, CH_2-CH=CH_2), 116.5 (s, CH_2-CH=CH_2), 121.4 (d, $^3J_{CP0}$ = 4.8 Hz, C_0^2), 128.3 (s, C_0^3), 132.2 (s, C_0^4), 134.8 (d, $^3J_{CP1}$ = 9.6 Hz, CH_2-CH=CH_2), 139.1 (d, $^3J_{CP1}$ = 15.5 Hz, (CH=N)$_0$), 150.1 (d, $^2J_{CP0}$ = 8.4 Hz, C_0^1). MS m/z: 972 $[M+1]^+$. IR(KBr): 3338 (m, $\tilde{\nu}_{NH}$) cm^{-1}. Anal. calcd. for $C_{33}H_{42}Cl_3N_9O_3P_4S_4$: C, 40.82; H, 4.36; N, 12.98. Found: C, 40.70; H, 4.22; N, 12.86.

5-[G_2]: White powder; 95% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 51.8 (s, P_0), 61.7 (s, P_1), 73.1 (s, P_2); ^1H NMR ($CDCl_3$): δ = 3.3 (d, $^3J_{HP2}$ = 13.6 Hz, 18H, P_2-N-CH_3), 3.4 (d, $^3J_{HP1}$ = 10.7 Hz, 9H, P_1-N-CH_3), 3.8 (m, 12H, CH_2-CH=CH_2), 4.6 (m, 6H, NH), 5.2 (m, 12H, CH_2-CH=CH_2), 5.9 (m, 6H, CH_2-CH=CH_2), 7.2–7.3 (m, 18H, C_0^2-H, C_1^2-H), 7.5–7.6 (m, 9H, (CH=N)$_{0-1}$), 7.7–7.8 (m, 18H, C_0^3-H, C_1^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.9 (d, $^2J_{CP2}$ = 11.0 Hz, P_2-N-CH_3), 33.0 (d, $^2J_{CP1}$ = 13.1 Hz, P_1-N-CH_3), 44.5 (s, CH_2-CH=CH_2), 116.4 (s, CH_2-CH=CH_2), 121.4 (d, $^3J_{CP0}$ = 4.6 Hz, C_0^2), 121.7 (d, $^3J_{CP1}$ = 4.0 Hz, C_1^2), 128.1 (s, C_1^3), 128.3 (s, C_0^3), 131.7 (s, C_1^4); 132.5 (s, C_0^4), 134.8 (d, $^3J_{CP2}$ = 9.5 Hz; CH_2-CH=CH_2), 138.6 (d, $^3J_{CP1}$ = 13.5 Hz, (CH=N)$_0$), 139.3 (d, $^3J_{CP2}$ = 14.5 Hz, (CH=N)$_1$), 150.0 (d, $^2J_{CP0}$ = 7.9 Hz, C_0^1), 151.3 (d, $^2J_{CP1}$ = 7.0 Hz, C_1^1). IR (KBr): 3350 (m, $\tilde{\nu}_{NH}$) cm^{-1}. Anal. calcd. for $C_{90}H_{108}Cl_6N_{24}O_9P_{10}S_{10}$: C, 43.02; H, 4.33; N, 13.38. Found: C, 42.81; H, 4.21; N, 13.14.

5-[G_3]: White powder; 91% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 51.9 (s, P_0), 61.7 (s, P_1), 61.9 (s, P_2), 73.1 (s, P_3); ^1H NMR ($CDCl_3$): δ = 3.3 (d, $^3J_{HP3}$ = 13.4 Hz, 36H, P_3-N-CH_3), 3.3 (m, 27H, P_{1-2}-N-CH_3), 3.8 (m, 24H, CH_2-CH=CH_2), 4.5 (m, 12H, NH), 5.2 (m, 24H, CH_2-CH=CH_2), 5.8 (m, 12H, CH_2-CH=CH_2), 7.2–7.7 (m, 105H, $(C_6H_4)_{0-1-2}$ and (CH=N)$_{0-1-2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.9 (d, $^2J_{CP3}$ = 11.2 Hz, P_3-N-CH_3), 33.0 (d, $^2J_{CP1-2}$ = 12.9 Hz, P_{1-2}-N-CH_3), 44.5 (s, CH_2-CH=CH_2), 116.5 (s, CH_2-CH=CH_2), 121.4 (m, C_0^2, C_1^2), 121.7 (d, $^3J_{CP2}$ = 3.3 Hz, C_2^2), 128.1 (s, C_2^3), 128.3 (s, C_1^3), 128.4 (s, C_0^3), 131.7 (s, C_2^4), 132.0 (s, C_1^4), 132.5 (s, C_0^4), 134.7 (d, $^3J_{CP3}$ = 9.2 Hz, CH_2-CH=CH_2), 139.0 (m, (CH=N)$_{0-1}$), 139.2 (d, $^3J_{CP3}$ = 15.4 Hz, (CH=N)$_2$), 151.3 (m, C_0^1, C_1^1), 150.7 (d, $^2J_{CP2}$ = 6.9 Hz, C_2^1). IR (KBr): 3358 (m, $\tilde{\nu}_{NH}$) cm^{-1}. Anal. calcd. for $C_{204}H_{240}Cl_{12}N_{54}O_{21}P_{22}S_{22}$: C, 43.78; H, 4.32; N, 13.51. Found: C, 43.44; H, 4.25; N, 13.46.

5-[G_4]: White powder; 92% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 51.8 (s, P_0), 61.4 (s, P_3), 61.7 (s, P_2), 62.2 (s, P_1), 73.1 (s, P_4); ^1H NMR ($CDCl_3$): δ = 3.3 (d, $^3J_{HP4}$ = 15.0 Hz, 72H, P_4-N-CH_3), 3.4 (m, 63H, P_{1-2-3}-N-CH_3), 3.8 (m, 48H, CH_2-CH=CH_2), 4.5 (m, 24H, NH), 5.2 (m, 48H, CH_2-CH=CH_2), 5.8 (m, 24H, CH_2-CH=CH_2), 7.2–7.7 (m, 225H, $(C_6H_4)_{0-1-2-3}$ and (CH=N)$_{0-1-2-3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.8 (d, $^2J_{CP4}$ = 11.0 Hz, P_4-N-CH_3), 33.0 (d, $^2J_{CP1-2-3}$ = 12.6 Hz, P_{1-2-3}-N-CH_3), 44.5 (s, CH_2-CH=CH_2), 116.5 (s, CH_2-CH=CH_2), 121.3 (brs, C_0^2, C_1^2, C_2^2), 121.7 (d, $^3J_{CP3}$ = 3.2 Hz, C_3^2), 128.1 (s, C_3^3), 128.6 (s, C_0^3, C_1^3, C_2^3), 131.6 (s, C_3^4), 132.0 (s, C_0^4, C_1^4, C_2^4), 134.7 (d, $^4J_{CP4}$ = 9.0 Hz, CH_2-CH=CH_2), 139.0 (m, (CH=N)$_{0-1-2}$), 139.3 (d, $^3J_{CP4}$ = 15.8 Hz, (CH=N)$_3$), 151.3 (m, C_0^1, C_1^1, C_2^1, C_3^1). IR (KBr): 3363 (m, $\tilde{\nu}_{NH}$) cm^{-1}. Anal. calcd. for $C_{432}H_{504}Cl_{24}N_{114}O_{45}P_{46}S_{46}$: C, 44.11; H, 4.32; N, 13.57. Found: C, 44.01; H, 4.28; N, 13.41.

5-[G_5]: White powder; 93% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 51.8 (s, P_0), 61.4 (s, P_4), 61.5 (s, P_3), 61.7 (s, P_2), 62.1 (s, P_1), 73.1 (s, P_5); ^1H NMR ($CDCl_3$): δ = 3.2 (d, $^3J_{HP5}$ = 14.9 Hz, 144H, P_5-N-CH_3), 3.4 (m, 135H, $P_{1-2-3-4}$-N-CH_3), 3.8 (m, 96H, CH_2-CH=CH_2), 4.5 (m, 48H, NH), 5.2 (m, 96H, CH_2-CH=CH_2), 5.8 (m, 48H, CH_2-CH=CH_2), 7.1–7.7 (m, 465H, $(C_6H_4)_{0-1-2-3-4}$ and (CH=N)$_{0-1-2-3-4}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.8 (d, $^2J_{CP5}$ = 11.0 Hz, P_5-N-CH_3), 32.9 (d, $^2J_{CP1-2-3-4}$ = 13.3 Hz, $P_{1-2-3-4}$-N-CH_3), 44.4 (s, CH_2-CH=CH_2), 116.5 (s, CH_2-CH=CH_2), 121.7 (brs, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2), 128.1 (s, C_4^3), 128.6 (s, C_0^3, C_1^3, C_2^3, C_3^3), 131.6 (s, C_4^4), 132.0 (s, C_4^3), 132.7 (s, C_0^4, C_1^4, C_2^4), 134.7 (d, $^4J_{CP5}$ = 9.5 Hz, CH_2-CH=CH_2), 139.0 (m, (CH=N)$_{0-1-2-3}$), 139.3 (d, $^3J_{CP5}$ = 15.4 Hz, (CH=N)$_4$), 151.3 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1). IR (KBr): 3350 (m, $\tilde{\nu}_{NH}$) cm^{-1}. Anal. calcd. for $C_{888}H_{1032}Cl_{48}N_{234}O_{93}P_{94}S_{94}$: C, 44.27; H, 4.31; N, 13.60. Found: C, 44.01; H, 4.24; N, 13.34.

5-[G_6]: White powder; 93% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 51.8 (s, P_0), 61.6 (s, P_5), 61.7 (s, P_4), 61.8 (s, P_3), 62.1 (s, P_1, P_2), 73.1 (s, P_6); ^1H NMR ($CDCl_3$): δ = 3.3 (brs, 567H, $P_{1\ 2\ 3-4-5}$-N-CH_3), 3.8 (m, 192H, CH_2-CH=CH_2), 4.5 (brs, 96H, NH), 5.2 (m, 192H, CH_2-CH=CH_2), 5.8 (m, 96H, CH_2-CH=CH_2), 7.1–7.7 (m, 945H, $(C_6H_4)_{0-1-2-3-4-5}$ and (CH=N)$_{0-1-2-3-4-5}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.8 (d, $^2J_{CP6}$ = 10.8 Hz, P_6-N-CH_3), 32.9 (d, $^2J_{CP1-2-3-4-5}$ = 13.1 Hz, $P_{1-2-3-4-5}$-N-CH_3), 44.4 (s, CH_2-CH=CH_2), 116.5 (s, CH_2-CH=CH_2), 121.7 (brs, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2), 128.1 (s, C_5^3), 128.3 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3), 131.6 (s, C_5^4), 132.0 (s, C_4^4), 132.7 (s, C_0^4, C_1^4, C_2^4), 134.7 (d, $^4J_{CP6}$ = 9.5 Hz, CH_2-CH=CH_2), 139.0 (m, (CH=N)$_{0-1-2-3-4}$), 139.3 (d, $^3J_{CP6}$ = 15.0 Hz, (CH=N)$_5$), 151.2 (brs, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1). IR (KBr): 3360 (m, $\tilde{\nu}_{NH}$) cm^{-1}. Anal. calcd. for $C_{1800}H_{2088}Cl_{96}N_{474}O_{189}P_{190}S_{190}$: C, 44.34; H, 4.31; N, 13.61. Found: C, 44.19; H, 4.18; N, 13.36.

5-[G_7]: White powder; 93% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 61.6 (s, P_6), 61.7 (s, P_5), 61.8 (s, P_4), 62.1 (s, P_1, P_2, P_3), 73.1 (s, P_7); ^1H NMR ($CDCl_3$): δ = 3.3 (brs, 1143H, $P_{1\ 2\ 3-4-5-6}$-N-CH_3), 3.8 (m, 384H, CH_2-CH=CH_2), 4.5 (brs, 96H, NH), 5.2 (m, 384H, CH_2-CH=CH_2), 5.8 (m, 192H, CH_2-CH=CH_2), 7.1–7.7 (m, 1905H, $(C_6H_4)_{0-1\ 2-3-4-5-6}$ and (CH=N)$_{0-1-2-3-4-5-6}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.8 (d, $^2J_{CP7}$ = 10.4 Hz, P_7-N-CH_3), 32.9 (d, $^2J_{CP1-2-3-4-5-6}$ = 14.5 Hz, $P_{1-2-3-4-5-6}$-N-CH_3), 44.4 (s, CH_2-CH=CH_2), 116.5 (s, CH_2-CH=CH_2), 121.7 (brs, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2), 128.1 (s, C_6^3), 128.3 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3), 131.6 (s, C_6^4), 132.0 (s, C_5^4), 132.7 (s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4), 134.7 (d, $^3J_{CP7}$ = 9.5 Hz, CH_2-CH=CH_2), 139.0 (m, (CH=N)$_{0-1-2-3-4-5}$), 139.3 (d, $^3J_{CP7}$ = 15.0 Hz, (CH=N)$_6$), 151.2 (brs, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1, C_6^1). IR (KBr): 3350 (m, $\tilde{\nu}_{NH}$) cm^{-1}. Anal. calcd. for $C_{3624}H_{4200}Cl_{192}N_{954}O_{381}P_{382}S_{382}$: C, 44.36; H, 4.31; N, 13.62. Found: C, 44.22; H, 4.24; N, 13.36.

General procedure for the synthesis of dendrimers 7-[G_1]–7-[G_3], 7-[G_5], 7-[G_7] : To a solution of 1.75 g of **1** (4.11 mmol) or dendrimer **3**-[G'_n] (n = 1, 1.23 mmol; n = 2, 0.512 mmol; n = 4, 0.114 mmol; n = 6 , 0.0277 mmol) in chloroform was added a solution (240 mmol L^{-1}) of dichlorophosphonomethylhydrazide (**6**) in chloroform (for **1**, 56 mL; n = 1, 34 mL; n = 2, 28 mL; n = 4, 25 mL; n = 6, 24 mL, 10% excess) at room temperature. The resulting solution was stirred overnight. Then the solvent was removed under vacuum to give a white paste of **7**-[G_{n+1}] which was washed with ether (2 × 50 mL)

7-[G_1]: Pale yellow powder; 78% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 18.8 (s, P_1), 52.3 (s, P_0); ^1H NMR ($CDCl_3$): δ = 3.3 (d, $^3J_{HP1}$ = 10.9 Hz, 9H, P_1-N-CH_3), 7.3 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HP0}$ = 1.5 Hz, 6H, C_0^2-H), 7.7 (d, $^4J_{HP1}$ = 3.1 Hz, 3H, CH=N), 7.7 (d, $^3J_{HH}$ = 8.3 Hz, 6H, C_0^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.6 (d, $^2J_{CP1}$ = 10.9 Hz, P_1-N-CH_3), 120.9 (d, $^3J_{CP0}$ = 5.1 Hz, C_0^2), 128.1 (s, C_0^3), 131.1 (s,

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C_0^4), 139.9 (d, $^3J_{CP_1}$ = 20.7 Hz, CH=N), 151.0 (d, $^2J_{CP_0}$ = 7.6 Hz, C_0^1). MS *m/z*: 859 $[M+1]^+$ (Cl = 35) and isotopic repartition (861:100%). Anal. calcd. for $C_{24}H_{24}Cl_6N_6O_6P_4S$: C, 33.47; H, 2.81; N, 9.76. Found: C, 33.38; H, 2.73; N, 9.63.

7-[G_2]: white powder; 90% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 18.6 (s, P_2), 52.3 (s, P_0), 61.7 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.29 (d, $^3J_{HP_2}$ = 11.0 Hz, 18H, CH_3-N-P_2), 3.37 (d, $^3J_{HP_1}$ = 10.8 Hz, 9H, CH_3-N-P_1), 7.23–7.75 (m, 45H, $(C_6H_4)_{0-1}$ and $(CH{=}N)_{0-1}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 (d, $^2J_{CP_2}$ = 10.5 Hz, P_2-N-CH_3), 32.9 (d, $^2J_{CP_1}$ = 13.0 Hz, P_1-N-CH_3), 121.4 (brs, C_0^2), 121.7 (d, $^3J_{CP_1}$ = 4.6 Hz, C_0^2), 128.5 (brs, C_0^3, C_1^3), 131.1 (s, C_0^4), 132.5 (s, C_0^4), 138.6 (d, $^3J_{CP_1}$ = 14.9 Hz, $(CH{=}N)_0$), 140.8 (d, $^3J_{CP_2}$ = 20.9 Hz, $(CH{=}N)_1$), 150.6 (d, $^2J_{CP_0}$ = 7.6 Hz, C_0^1), 151.7 (d, $^2J_{CP_1}$ = 7.6 Hz, C_1^1). Anal. calcd. for $C_{72}H_{72}Cl_{12}N_{18}O_{15}P_{10}S_4$: C, 37.72; H, 3.16; N, 10.99. Found: C, 37.28; H, 3.01; N, 10.92.

7-[G_3]: white powder; 88% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 18.5 (s, P_3), 52.3 (s, P_0), 61.6 (s, P_2), 62.0 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.26 (d, $^3J_{HP_3}$ = 11.0 Hz, 36H, CH_3-N-P_3), 3.34 (d, $^3J_{H-P_{1-2}}$ = 10.3 Hz, 27H, CH_3-N-P_{1-2}), 7.22–7.77 (m, 105H, $(C_6H_4)_{0-1-2}$ and $(CH{=}N)_{0-1-2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.2 (d, $^2J_{CP_3}$ = 10.9 Hz, CH_3-N-P_3), 33.1 (d, $^2J_{CP_{1-2}}$ = 13.2 Hz, CH_3-N-P_{1-2}), 121.5 (brs, C_0^2), 121.8 (brs, C_1^2, C_2^2), 128.3 (s, C_0^3, C_1^3), 128.6 (s, C_2^3), 131.2 (s, C_2^4), 132.2 (s, C_1^4), 132.7 (s, C_0^4), 139.0 (d, $^3J_{CP_{1-2}}$ = 13.8 Hz, $(CH{=}N)_{0-1}$), 140.9 (d, $^3J_{CP_3}$ = 20.4 Hz, $(CH{=}N)_2$), 151.4 (d, $^2J_{CP_{0-1}}$ = 9.4 Hz, C_0^1, C_1^1), 151.9 (d, $^2J_{CP_2}$ = 6.3 Hz, C_2^1). Anal. calcd. for $C_{168}H_{168}Cl_{24}N_{42}O_{33}P_{22}S_{10}$: C, 39.13; H, 3.28; N, 11.40. Found: C, 38.79; H, 3.11; N, 11.21.

7-[G_4]: white powder; 86% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 18.5 (s, P_5), 61.7 (s, P_4), 61.9 (s, P_3), 62.0 (s, P_2), 62.6 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.30 (m, 279H, CH_3-N-$P_{1\ 2-3-4-5}$), 7.24–7.63 (m, 465H, $(C_6H_4)_{0-1-2-3-4}$ and $(CH{=}N)_{0-1-2-3-4}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 (d, $^2J_{CP_5}$ = 10.3 Hz, CH_3-N-P_5), 32.9 (d, $^2J_{CP_{1-2-3-4}}$ = 12.5 Hz, CH_3-N-$P_{1-2-3-4}$), 121.7 (brs, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2), 128.1 (brs, C_0^3, C_1^3, C_2^3, C_3^3), 128.4 (s, C_4^3), 131.0 (s, C_4^4), 131.9 (s, C_0^4, C_1^4, C_2^4, C_3^4), 140.8 (d, $^3J_{CP_{1-2-3-4-5}}$ = 16 Hz, $(CH{=}N)_{0-1-2-3-4}$), 151.2 (d, $^2J_{CP}$ = 6.5 Hz, C_0^1, C_1^1, C_2^1, C_3^1), 151.7 (d, $^2J_{CP_4}$ = 7.0 Hz, C_4^1). Anal. calcd. for $C_{744}H_{744}Cl_{96}N_{186}O_{141}P_{94}S_{46}$: C, 40.00; H, 3.35; N, 11.66. Found: C, 39.80; H, 3.28; N, 11.45.

7-[G_7]: white powder; 87% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 18.5 (s, P_7), 61.7 (s, P_6), 61.9 (s, P_5), 62.0 (s, P_4), 62.4 (brs, P_1, P_2, P_3); ^1H NMR ($CDCl_3$): δ = 3.14 (m, 1143H, CH_3-N-$P_{1-2-3-4-5-6-7}$), 7.24–7.63 (m, 1905H, $(C_6H_4)_{0-1-2-3-4-5-6}$ and $(CH{=}N)_{0-1-2-3-4-5-6}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 (d, $^2J_{CP_7}$ = 10.4 Hz, CH_3-N-P_7), 32.9 (d, $^2J_{CP_{1-2-3-4-5-6}}$ = 12.8 Hz, CH_3-N-$P_{1-2-3-4-5-6}$), 121.7 (brs, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2), 128.1 (brs, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3), 128.4 (s, C_6^3), 131.1 (s, C_6^4), 131.9 (brs, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4), 138.9 (m, $(CH{=}N)_{0-1-2-3-4-5}$), 140.8 (d, $^3J_{CP_7}$ = 21.5 Hz, $(CH{=}N)_6$), 151.4 (d, $^2J_{CP}$ = 5.9 Hz, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1), 151.5 (d, $^2J_{CP_6}$ = 7.1 Hz, C_6^1). Anal. calcd. for $C_{3048}H_{3048}Cl_{384}N_{762}O_{573}P_{382}S_{190}$: C, 40.21; H, 3.37; N, 11.72. Found: C, 39.97; H, 3.24; N, 11.59.

General procedure for the synthesis of dendrimers 8-[G_1]–8-[G_3]: To a solution of 0.30 g of **7-[G_n]** (n = 1, 0.348 mmol; n = 2, 0.131 mmol; n = 3, 0.0582 mmol) in THF (20 mL) was added triethylamine (n = 1, 145 µL, 1.045 mmol; n = 2, 110 µL, 0.786 mmol; n = 3, 97 µL, 0.698 mmol). The resulting solution was cooled to 0 °C, and a solution of allylamine (n = 1, 78 µL; n = 2, 59 µL; n = 3, 52 µL) in THF (10 mL) was then added. The mixture was stirrred for 3 h at room temperature, then filtered. The solvent was removed under vacuum to give **8-[G_n]** as a powder, which was washed with ether (2 × 30 mL).

8-[G_1]: white powder; 65% yield; $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 19.1 (s, P_1), 52.0 (s, P_0); ^1H NMR ($CDCl_3$): δ = 3.18 (d, $^3J_{HP_1}$ = 10.0 Hz, 9H, CH_3-N-P_1), 3.76 (m, 6H, CH_2-CH=CH_2), 4.12 (brs, 3H, NH), 5.15 (dd, $^3J_{HHcis}$ = 7.6 Hz, $^2J_{HHgem}$ = 1.3 Hz, 3H, $CH_2(H)C{=}C(H_{cis})H$), 5.29 (dd, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HHgem}$ = 1.5 Hz, 3H, $CH_2(H)C{=}C(H)H_{trans}$), 5.91 (m, 3H, CH_2-CH=CH_2), 7.25 (d, $^3J_{HH}$ = 8.4 Hz, 6H, C_0^2-H), 7.59 (s, 3H, $(CH{=}N)_0$), 7.64 (d, $^3J_{HH}$ = 8.4 Hz, 6H, C_0^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 29.9 (d, $^2J_{CP_1}$ = 8.4 Hz, CH_2-N-P_1), 43.1 (s, CH_2-CH=CH_2), 116.0 (s, CH_2-CH=CH_2), 120.8 (d, $^3J_{CP_0}$ = 4.5 Hz, C_0^2), 127.7 (s, C_0^3), 131.7 (s, C_0^4), 134.2 (d, $^3J_{CP_1}$ = 7.9 Hz, CH_2-CH=CH_2), 138.2 (d, $^3J_{CP_1}$ = 17.3 Hz, $(CH{=}N)_0$), 150.6 (d, $^2J_{CP_0}$ = 8.4 Hz, C_0^1). Anal. calcd. for $C_{33}H_{42}Cl_3N_9O_6P_4S$: C, 42.94; H, 4.58; N, 11.52. Found: C, 42.88; H, 4.55; N, 11.47.

8-[G_2]: white powder; 62% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.6 (s, P_2), 52.3 (s, P_0), 61.8 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.13 (d, $^3J_{HP_2}$ = 10.1 Hz, 18H, CH_3-N-P_2), 3.34 (d, $^3J_{HP_1}$ = 10.5 Hz, 9H, CH_3-N-P_1), 3.65 (m, 12H, CH_2-CH=CH_2), 4.21 (m, 6H, NH), 5.10 (dd, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HHgem}$ = 1.2 Hz, 6H, $CH_2(H)C{=}C(H_{cis})H$), 5.24 (dd, $^3J_{HHtrans}$ = 16.9 Hz, $^2J_{HHgem}$ = 1.2 Hz, 6H, $CH_2(H)C{=}C(H)H_{trans}$), 5.88 (m, 6H, CH_2-CH=CH_2), 7.19–7.74 (m, 45H, $(C_6H_4)_{0-1}$ and $(CH{=}N)_{0-1}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.3 (d, $^2J_{CP_2}$ = 8.4 Hz, CH_3-N-P_2), 32.9 (d, $^2J_{CP_1}$ = 13.1 Hz, CH_3-N-P_1), 43.5 (s, CH_2-CH=CH_2), 116.5 (s, CH_2-CH=CH_2), 121.4 (brs, C_0^2), 121.7 (d, $^3J_{CP_1}$ = 4.6 Hz, C_1^2), 128.0 (brs, C_0^3), 128.3 (brs, C_1^3), 131.6 (s, C_1^4), 132.5 (s, C_0^4), 134.6 (d, $^3J_{CP_2}$ = 8.2 Hz, CH_2-CH=CH_2), 139.0 (d, $^3J_{CP_{1-2}}$ = 17.8 Hz, $(CH{=}N)_{0-1}$), 151.0 (d, $^2J_{CP_0}$ = 7.0 Hz, C_0^1), 151.1 (d, $^2J_{CP_1}$ = 6.9 Hz, C_1^1). IR(KBr): 3400 (m, $\tilde{\nu}_{N-H}$) cm^{-1}. Anal. calcd. for $C_{90}H_{108}Cl_6N_{14}O_{15}P_{10}S_4$: C, 44.73; H, 4.50; N, 13.91. Found: C, 44.57; H, 4.36; N, 13.75.

8-[G_3]: white powder; 59% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.7 (s, P_3), 52.4 (s, P_0), 61.7 (s, P_2), 62.1 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.14 (d, $^3J_{HP_3}$ = 9.9 Hz, 36H, CH_3-N-P_3), 3.32 (d, $^3J_{HP_{1-2}}$ = 10.1 Hz, 27H, CH_3-N-P_{1-2}), 3.71 (m, 24H, CH_2-CH=CH_2), 4.12 (m, 12H, NH), 5.11 (d, $^3J_{HHcis}$ = 9.9 Hz, 12H, $CH_2(H)C{=}C(H_{cis})H$), 5.25 (d, $^3J_{HHtrans}$ = 17.4 Hz, 12H, $CH_2(H)C{=}C(H)H_{trans}$), 5.84 (m, 12H, CH_2-CH=CH_2), 7.19–7.74 (m, 105H, $(C_6H_4)_{0-1-2}$ and $(CH{=}N)_{0-1-2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 29.9 (d, $^2J_{CP_3}$ = 8.6 Hz, CH_3-N-P_3), 32.4 (d, $^2J_{CP_{1-2}}$ = 13.3 Hz, CH_3-N-P_{1-2}), 43.1 (s, CH_2-CH=CH_2), 115.9 (s, CH_2-CH=CH_2), 121.0 (brs, C_0^2, C_2^2), 121.2 (brs, C_1^2), 127.5 (brs, C_0^3, C_1^3, C_2^3), 131.2 (s, C_2^4), 131.5 (s, C_1^4), 132.0 (s, C_0^4), 134.2 (d, $^3J_{CP_3}$ = 7.7 Hz, CH_2-CH=CH_2), 138.5 (d, $^3J_{CP_{1-2-3}}$ = 17.3 Hz, $(CH{=}N)_{0-1-2}$), 151.3 (d, $^2J_{CP_{0-1-2}}$ = 7.2 Hz, C_0^1, C_1^1, C_2^1). IR(KBr): 3370 (m, $\tilde{\nu}_{N-H}$), 3067 (m, $\tilde{\nu}_{=CH_2}$) cm^{-1}. Anal. calcd. for $C_{204}H_{240}Cl_{12}N_{54}O_{33}P_{22}S_{10}$: C, 45.34; H, 4.47; N, 13.99. Found: C, 45.18; H, 4.37; N, 13.78.

Synthesis of compound 10-[G_1]: To a solution of **9-[G_1]** (0.320 g, 0.379 mmol) in THF (20 mL) was added triethylamine (158 µL, 1.14 mmol). The solution was cooled to 0 °C, and a solution of allylamine (85 µL, 1.14 mmol) in 10 mL of THF was then added dropwise. The mixture was stirred for 3 h then filtered. The solvent was removed to give a white powder, which was washed with ether (2 × 2 mL).

10-[G_1]: white powder; 63% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −18.3 (s, P_0), 20.4 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.18 (d, $^3J_{CP_1}$ = 10 Hz, 9H, CH_3-N-P_1), 3.74 (m, 6H, CH_2-CH=CH_2), 3.99 (m, 3H, NH), 5.15 (dd, $^3J_{HHcis}$ = 10.1 Hz, $^2J_{HHgem}$ = 1.4 Hz, 3H, $CH_2(H)C{=}C(H_{cis})H$), 5.28 (dd, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HHgem}$ = 1.4 Hz, 3H, $CH_2(H)C{=}C(H)H_{trans}$), 5.92 (m, 3H, CH_2-CH=CH_2), 7.25 (d, $^3J_{HH}$ = 8.4 Hz, 6H, C_0^2-H), 7.59 (s, 3H, CH=N), 7.61 (d, $^3J_{HH}$ = 8.7 Hz, 6H, C_0^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.4 (d, $^2J_{CP_1}$ = 8.2 Hz, CH_3-N-P_1), 43.6 (s, CH_2-CH=CH_2), 116.6 (s, CH_2-CH=CH_2), 120.3 (d, $^3J_{CP_0}$ = 4.3 Hz, C_0^2), 128.3 (s, C_0^3), 132.0 (brs, C_0^4), 134.6 (d, $^3J_{CP_1}$ = 7.8 Hz, CH_2-CH=CH_2), 138.6 (d, $^3J_{CP_1}$ = 17.2 Hz, $(CH{=}N)_0$), 150.8 (d, $^2J_{CP_0}$ = 6.7 Hz, C_0^1). MS *m/z*: 906 $[M+1]^+$ (Cl: 35). IR(KBr): 3400 (m, $\tilde{\nu}_{N-H}$), 3070 (m, $\tilde{\nu}_{=CH_2}$) cm^{-1}. Anal. calcd. for $C_{33}H_{42}Cl_3N_9O_7P_4$: C, 43.70; H, 4.66; N, 13.89. Found: C, 43.41; H, 4.59; N, 13.84.

General procedure for the synthesis of dendrimers 11-[G_1], 11-[G_4]: To a solution of 0.150 g of dendrimer **3-[G_n]** (n = 1, 0.165 mmol; n = 4, 0.0133 mmol) in THF (7 mL) at 0 °C was slowly added a solution of propargylamine (n = 1, 34 µL, 0.495 mmol; n = 4, 22 µL, 0.319 mmol) and triethylamine (n = 1, 69 µL, 0.495 mmol; n = 4, 45 µL, 0.319 mmol) in THF (7 mL). The resulting mixture was left overnight at room temperature, and the precipitate was then removed by centrifugation. The solvent was evaporated, and the resulting powder was purified by column chromatography on silica gel (eluent: ethyl acetate).

11-[G_1]: Yellow powder; 88% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 52.6 (s, P_0), 72.1 (s, P_1); ^1H NMR ($CDCl_3$): δ = 2.33 (t-like, $^4J_{HHA}$ = 2.5 Hz, $^4J_{HHB}$ = 2.6 Hz, 3H, CH_AH_B-C≡CH), 3.35 (d, $^3J_{HP_1}$ = 13.5 Hz, 9H, P_1-N-CH_3), 4.11 (dddd, $^2J_{HH}$ = 20.4 Hz, $^3J_{HP_1}$ = 15.9 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.5 Hz, 3H, CH_2-C≡CH) , 4.13 (dddd, $^2J_{HH}$ = 20.4 Hz, $^3J_{HP_1}$ = 14.1 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 2.4 Hz, 3H, CH_2-C≡CH), 4.65 (t-like, $^3J_{HHA}$ = 6.5 Hz, $^3J_{HHB}$ = 6.9 Hz, 3H, NH-CH_AH_B-C≡CH), 7.31 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HPD}$ = 1.4 Hz, 6H, C_0^2-H), 7.64 (d, $^4J_{HP_1}$ = 3.0 Hz, 3H, CH=N), 7.70 (d, $^3J_{HH}$ = 8.6 Hz, 6H, C_0^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.4 (d, $^2J_{CP_1}$ = 11.5 Hz, P_1-N-CH_3), 31.2 (s, CH_2-C≡CH), 71.9 (s, CH_2-C≡CH), 79.5 (d, $^3J_{CP_1}$ = 11.4 Hz, CH_2-C≡CH), 120.9 (d, $^3J_{CP_0}$ = 4.7 Hz, C_0^2), 127.9 (s, C_0^3), 131.5 (s, C_0^4), 138.8 (d, $^3J_{CP_1}$ = 15.5 Hz, CH=N), 150.6 (d, $^2J_{CP_0}$ = 8.3 Hz, C_0^1). IR(KBr): 3295 (m, $\tilde{\nu}_{N-H}$), 3291 (m, $\tilde{\nu}_{\equiv CH}$) cm^{-1}. MS *m/z*: 964 $[M+1]^+$ (Cl = 35) and isotopic repartition (966: 100%). Anal. calcd. for $C_{33}H_{36}Cl_3N_9O_3P_4S_4$: C, 41.04; H, 3.76; N, 13.06. Found: C, 39.83; H, 3.68; N, 12.95.

11-[G_4]: Pale yellow powder; 60% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 52.6 (s, P_0), 62.2 (s, P_1), 62.3 (s, P_2), 62.4 (s, P_3), 72.3 (s, P_4); ^1H NMR ($CDCl_3$): δ = 2.2 (brs, 24H, CH_2-C≡CH), 3.2 (d, $^3J_{HP_4}$ = 14.8 Hz, 72H, P_1-N-CH_3), 3.3 (d, $^3J_{HP_{1-2-3}}$ = 12.8 Hz, 63H, P_{1-2-3}-N-CH_3), 3.9 (m, 48H, CH_2-C≡CH), 4.6–4.8 (m, 24H, NH), 7.1–7.6 (m, 225H, $(C_6H_4)_{0-1-2-3}$ and $(CH{=}N)_{0-1-2-3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.3 (d, $^2J_{CP_4}$ = 11.4 Hz, P_4-N-CH_3), 31.2 (s, CH_2-C≡CH), 32.4 (d, $^2J_{CP_{1-2-3}}$ = 10.8 Hz, P_{1-2-3}-N-CH_3), 71.9 (s, CH_2-C≡CH), 80.1 (d, $^3J_{CP_4}$ = 8.8 Hz, CH_2-C≡CH), 121.1 (brs, C_0^2, C_1^2, C_2^2, C_3^2), 127.7 (s, C_0^3, C_1^3, C_2^3, C_3^3), 131.0 (s, C_0^4, C_1^4, C_2^4), 131.5 (s, C_3^4), 138.4 (d, $^3J_{CP_{1-2-3}}$ = 11.8 Hz, $(CH{=}N)_{0-1-2}$), 139.1 (d, $^3J_{CP_4}$ = 15.7 Hz, $(CH{=}N)_3$), 150.5–150.7 (m, C_0^1, C_1^1, C_2^1, C_3^1). IR(KBr): 3368 (m, $\tilde{\nu}_{N-H}$), 3292 (m, $\tilde{\nu}_{\equiv C-H}$) cm^{-1}. Anal. calcd. for $C_{432}H_{456}Cl_{24}N_{114}O_{45}P_{46}S_{46}$: C, 44.29; H, 3.92; N, 13.63. Found: C, 44.07; H, 3.79; N, 13.48.

General procedure for the synthesis of dendrimers 12-[G_1]–12-[G_3], 12-[G_8], 12-[G_7]: To a solution of 0.200 g of **7-[G_n]** (n = 1, 0.232 mmol; n = 2, 0.087 mmol; n = 3, 0.0387 mmol; n = 5, 0.0089 mmol, n = 7, 0.0021 mmol) in THF (20 mL) was added triethylamine (n = 1, 97 µL, 0.696 mmol; n = 2, 73 µL, 0.522 mmol; n = 3, 65 µL, 0.464 mmol; n = 5, 60 µL, 0.427 mmol; n = 7, 56 µL, 0.403 mmol). This solution

was cooled to 0 °C, and a solution of propargylamine ($n = 1$, 48 μL, 0.696 mmol; $n = 2$, 36 μL, 0.522 mmol; $n = 3$, 32 μL, 0.464 mmol; $n = 5$, 29 μL, 0.427 mmol; $n = 7$, 28 μL, 0.403 mmol) in 10 mL of THF was then added dropwise. The mixture was stirrred for 3 h then filtered and the solution was evaporated under vacuum to give a powder which was washed with ether (2 × 20 mL).

12-[G_1]: pale yellow powder; 55% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 20.3$ (s, P_1), 52.2 (s, P_0); ^1H NMR ($CDCl_3$): $\delta = 2.26$ (t-like, $^4J_{HHA} = {}^4J_{HHB} = 2.3$ Hz, 3H, $CH_AH_B-C\equiv CH$), 3.12 (d, $^3J_{HP1} = 10.2$ Hz, 9H, CH_3-N-P_1), 3.90 (m, 6H, $CH_2-C\equiv CH$), 4.75 (m, 3H, NH), 7.20 (d, $^3J_{HH} = 8.4$ Hz, 6H, C_0^4-H), 7.55 (s, 3H, $(CH=N)_0$), 7.63 (d, $^3J_{HH} = 8.6$ Hz, 6H, C_0^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.5$ (d, $^2J_{CP1} = 8.6$ Hz, CH_3-N-P_1), 30.9 (s, $CH_2-C\equiv CH$), 72.1 (s, $CH_2-C\equiv CH$), 79.8 (d, $^3J_{CP1} = 8.9$ Hz, $CH_2-C\equiv CH$), 121.3 (d, $^3J_{CP0} = 4.8$ Hz, C_0^2), 128.3 (brs, C_0^3), 132.1 (brs, C_0^4), 138.9 (d, $^3J_{CP1} = 17.5$ Hz, $(CH=N)_0$), 150.9 (d, $^2J_{CP0} = 7.6$ Hz, C_0^1). Anal. calcd. for $C_{33}H_{36}Cl_3N_9O_6P_4S_1$: C, 43.22; H, 3.95; N, 13.74. Found: C, 43.01; H, 3.80; N, 13.62.

12-[G_2]: yellow powder; 51% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 20.3$ (s, P_2), 52.8 (s, P_0), 62.1 (s, P_1); ^1H NMR ($CDCl_3$): $\delta = 2.26$ (t-like, $^4J_{HHA} = {}^4J_{HHB} = 2.5$ Hz, 6H, $CH_AH_B-C\equiv CH$), 3.16 (d, $^3J_{HP2} = 10.2$ Hz, 18H, CH_3-N-P_2), 3.36 (d, $^3J_{HP1} = 10.5$ Hz, 9H, CH_3-N-P_1), 3.89 (m, 12H, $CH_2-C\equiv CH$), 4.29 (m, 6H, NH), 7.21–7.75 (m, 45H, $(C_6H_4)_{0-1}$ and $(CH=N)_{0-1}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.3$ (d, $^2J_{CP2} = 9.0$ Hz, CH_3-N-P_2), 30.9 (s, $CH_2-C\equiv CH$), 32.9 (d, $^2J_{CP1} = 13.1$ Hz, CH_3-N-P_1), 72.3 (s, $CH_2-C\equiv CH$), 79.6 (d, $^3J_{CP2} = 8.5$ Hz, $CH_2-C\equiv CH$), 121.4 (brs, C_0^2), 121.6 (brs, C_1^2), 128.1 (s, C_1^3), 128.3 (s, C_0^3), 131.6 (s, C_1^4), 132.5 (s, C_0^4), 138.4 (d, $^3J_{CP1} = 13.1$ Hz, $(CH=N)_0$), 139.2 (d, $^3J_{CP2} = 17.4$ Hz, $(CH=N)_1$), 151.0 (d, $^2J_{CP0} = 6.0$ Hz, C_0^1), 151.3 (d, $^2J_{CP1} = 8.0$ Hz, C_1^1). Anal. calcd. for $C_{90}H_{96}Cl_6N_{24}O_{15}P_{10}S_4$: C, 44.96; H, 4.02; N, 13.98. Found: C, 44.70; H, 3.93; N, 13.79.

12-[G_3]: yellow powder; 48% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 20.1$ (s, P_3), 52.3 (s, P_0), 61.6 (s, P_2), 61.9 (s, P_1); ^1H NMR ($CDCl_3$): $\delta = 2.15$ (brs, 12H, $CH_2-C\equiv CH$), 3.10 (d, $^3J_{HP3} = 9.5$ Hz, 36H, CH_3-N-P_3), 3.29 (d, $^3J_{HP1-2} = 10.4$ Hz, 27H, CH_3-N-P_{1-2}), 3.87 (m, 24H, $CH_2-C\equiv CH$), 4.56 (m, 12H, NH), 7.16–7.62 (m, 105H, $(C_6H_4)_{0-1-2}$ and $(CH=N)_{0-1-2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.0$ (d, $^2J_{CP3} = 8.5$ Hz, CH_3-N-P_3), 30.5 (s, $CH_2-C\equiv CH$), 32.5 (d, $^2J_{CP} = 11.9$ Hz, CH_3-N-P_{1-2}), 71.7 (s, $CH_2-C\equiv CH$), 79.5 (d, $^3J_{CP3} = 8.3$ Hz, $CH_2-C\equiv CH$), 121.2 (m, C_0^2, C_1^2, C_2^2), 127.7 (m, C_0^3, C_1^3, C_2^3), 131.3 (s, C_2^4), 131.6 (s, C_1^4), 132.1 (s, C_0^4), 138.8 (d, $^3J_{CP1-2-3} = 17.7$ Hz, $(CH=N)_{0-1-2}$), 150.8 (d, $^2J_{CP0-1-2} = 6.1$ Hz, C_0^1, C_1^1, C_2^1). Anal. calcd. for $C_{204}H_{216}Cl_{12}N_{54}O_{33}P_{22}S_{10}$: C, 45.55; H, 4.04; N, 14.05. Found: C, 45.44; H, 3.92; N, 13.88.

12-[G_5]: white yellow powder; 52% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 20.4$ (s, P_5), 61.8 (s, P_4), 63.1 (brs, P_1, P_2, P_3); ^1H NMR ($CDCl_3$): $\delta = 2.24$ (brs, 48H, $CH_2-C\equiv CH$), 3.10 (m, 144H, CH_3-N-P_3), 3.30 (m, 135H, $CH_3-N-P_{1-2-3-4}$), 3.89 (m, 96H, $CH_2-C\equiv CH$), 4.44 (m, 48H, NH), 7.20–7.60 (m, 465H, $(C_6H_4)_{0-1-2-3-4}$ and $(CH=N)_{0-1-2-3-4}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.3$ (d, $^2J_{CP5} = 8.0$ Hz, CH_3-N-P_5), 30.9 (s, $CH_2-C\equiv CH$), 32.9 (d, $^2J_{CP1-2-3-4} = 13.2$ Hz, $CH_3-N-P_{1-2-3-4}$), 72.3 (s, $-CH_2-C\equiv CH$), 81.5 (d, $^3J_{CP5} = 8.4$ Hz, $CH_2-C\equiv CH$), 121.6 (brs, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2), 128.1 (brs, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3), 131.5 (s, C_4^4), 131.9 (s, C_0^4, C_1^4, C_2^4, C_3^4), 139.3 (d, $^3J_{CP1-2-3-4-5} = 17.1$ Hz, $(CH=N)_{0-1-2-3-4}$), 151.2 (brs, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1). Anal. calcd. for $C_{888}H_{936}Cl_{48}N_{234}O_{141}P_{94}S_{46}$: C, 45.91; H, 4.06; N, 14.10. Found: C, 45.41; H, 3.94; N, 13.81.

12-[G_7]: Pale yellow powder; 49% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 20.3$ (s, P_7), 62.0 (s, P_6), 62.1 (s, P_5), 62.2 (brs, P_1, P_2, P_3, P_4); ^1H NMR ($CDCl_3$): $\delta = 2.15$ (brs, 192H, $CH_2-C\equiv CH$), (m, 1143H, $CH_3-N-P_{1-2-3-4-5-6-7}$), 3.87 (m, 384H, $CH_2-C\equiv CH$), 4.53 (m, 192H, NH), 7.20–7.62 (m, 1905H, $(C_6H_4)_{0-1-2-3-4-5-6}$ and $(CH=N)_{0-1-2-3-4-5-6}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.3$ (d, $^2J_{CP7} = 7.0$ Hz, CH_3-N-P_7), 30.9 (s, $CH_2-C\equiv CH$), 32.9 (d, $^2J_{CP1-2-3-4-5-6} = 13.1$ Hz, $CH_3-N-P_{1-2-3-4-5-6}$), 72.3 (s, $CH_2-C\equiv CH$), 79.6 (d, $^3J_{CP7} = 8.5$ Hz, $CH_2-C\equiv CH$), 121.7 (brs, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2), 128.1 (brs, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3), 128.4 (s, C_6^3), 131.6 (s, C_6^4), 131.9 (brs, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4), 139.3 (d, $^3J_{CP1-2-3-4-5-6} = 17.8$ Hz, $(CH=N)_{0-1-2-3-4-5}$), 140.8 (d, $^3J_{CP7} = 21.9$ Hz, $(CH=N)_6$), 151.2 (d, $^2J_{CP0-1-2-3-4-5} = 5.8$ Hz, C_0^1, C_2^1, C_3^1, C_4^1, C_5^1), 151.7 (d, $^2J_{CP6} = 7.0$ Hz, C_6^1). Anal. calcd. for $C_{3624}H_{3816}Cl_{192}N_{954}O_{573}P_{382}S_{190}$: C, 46.00; H, 4.06; N, 14.12. Found: C, 45.65; H, 3.88; N, 14.00.

General procedure for the synthesis of dendrimers 13-[G_2], 13-[G_3]: To a solution of 0.300 g of **8-[G_n]** ($n = 2$, 0.124 mmol; $n = 3$, 0.0555 mmol) in THF (20 mL) was added triethylamine ($n = 2$, 104 μL, 0.744 mmol; $n = 3$, 93 μL, 0.666 mmol) and then propargylamine ($n = 2$, 51 μL, 0.744 mmol; $n = 3$, 46 μL, 0.666 mmol) at room temperature. The resulting mixture was stirrred for 3 h and then filtered. The solvent was evaporated under vacuum to give a powder, which was washed with ether (2 × 20 mL).

13-[G_2]: yellow powder; 73% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.5$ (s, P_2), 52.4 (s, P_0), 62.0 (s, P_1); ^1H NMR ($CDCl_3$): $\delta = 2.14$ (t-like, $^4J_{HHA} = {}^4J_{HHB} = 2.4$ Hz, 6H, $CH_AH_B-C\equiv CH$), 3.00 (m, 6H, $NH-CH_2-C\equiv CH$), 3.12 (d, $^3J_{HP2} = 6.9$ Hz, 18H, CH_3-N-P_2), 3.24 (d, $^3J_{HP1} = 6.9$ Hz, 9H, CH_3-N-P_1), 3.52 (m, 12H, $CH_2-C\equiv CH$), 3.67 (m, 18H, $CH_2-CH=CH_2$ and $NH-CH_2-CH=CH_2$), 5.00 (dd, $^3J_{HHcis} = 10.1$ Hz, $^2J_{HHgem} = 1.1$ Hz, 6H, $CH_2(H)C=C(H_{cis})H$), 5.17 (dd, $^3J_{HHtrans} = 17.1$ Hz, $^2J_{HHgem} = 1.0$ Hz, 6H, $CH_2(H)C=C(H)H_{trans}$), 5.82 (m, 6H, $CH_2-CH=CH_2$), 7.15–7.76 (m, 45H, $(C_6H_4)_{0-1}$ and $(CH=N)_{0-1}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.6$ (s, $CH_2-C\equiv CH$), 31.1 (d, $^2J_{CP2} = 9.1$ Hz, CH_3-N-P_2), 32.9 (d, $^2J_{CP1} = 12.9$ Hz, CH_3-N-P_1), 43.3 (s, $CH_2-CH=CH_2$), 70.9 (s, $CH_2-C\equiv CH$), 81.8 (d, $^3J_{CP2} = 6.8$ Hz, $CH_2-C\equiv CH$), 115.0 (s, $CH_2-CH=CH_2$), 121.3 (brs, C_0^2), 121.4 (d, $^3J_{CP1} = 4.9$ Hz, C_1^2), 127.3 (s, C_1^3), 128.3 (s, C_0^3), 132.6 (s, C_0^4), 132.9 (s, C_1^4), 135.2 (d, $^3J_{CP2} = 13.7$ Hz, $(CH=N)_1$), 136.4 (d, $^3J_{CP2} = 5.7$ Hz, $CH_2-CH=CH_2$), 138.3 (d, $^3J_{CP1} = 14.5$ Hz, $(CH=N)_0$), 150.4 (d, $^2J_{CP1} = 7.4$ Hz, C_1^1), 150.9 (d, $^2J_{CP0} = 7.5$ Hz, C_0^1). IR(KBr): 3391 (m, $\tilde{\nu}_{N-H}$), 3075 (m, $\tilde{\nu}_{=CH2}$) cm^{-1}. Anal. calcd. for $C_{108}H_{132}N_{30}O_{15}P_{10}S_4$: C, 51.31; H, 5.26; N, 16.61. Found: C, 50.97; H, 5.19; N, 16.44.

13-[G_3]: yellow powder; 73% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.5$ (s, P_3), 52.4 (s, P_0), 62.1 (brs, P_1, P_2); ^1H NMR ($CDCl_3$): $\delta = 2.14$ (t-like, $^4J_{HHA} = {}^4J_{HHB} = 2.3$ Hz, 12H, $CH_AH_B-C\equiv CH$), 3.05 (m, 12H, $NH-CH_2-C\equiv CH$), 3.12 (d, $^3J_{HP3} = 6.6$ Hz, 36H, CH_3-N-P_3), 3.31 (d, $^3J_{HP1-2} = 10.0$ Hz, 27H, CH_3-N-P_{1-2}), 3.56 (m, 24H, $CH_2-C\equiv CH$), 3.70 (m, 36H, $CH_2-C(H)=CH_2$ and $NH-CH_2-CH=CH_2$), 5.00 (dd, $^3J_{HHcis} = 10.3$ Hz, $^2J_{HHgem} = 1.4$ Hz, 12H, $CH_2(H)C=C(H_{cis})H$), 5.17 (dd, $^3J_{HHtrans} = 17.3$ Hz, $^2J_{HHgem} = 1.4$ Hz, 12H, $CH_2(H)C=C(H)H_{trans}$), 5.80 (m, 12H, $CH_2-CH=CH_2$), 7.14–7.75 (m, 105H, $(C_6H_4)_{0-1-2}$ and $(CH=N)_{0-1-2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.7$ (s, $CH_2-C\equiv CH$), 31.1 (d, $^2J_{CP3} = 9.5$ Hz, CH_3-N-P_3), 32.9 (d, $^2J_{CP1-2} = 13.6$ Hz, CH_3-N-P_{1-2}), 43.3 (s, $CH_2-CH=CH_2$), 70.9 (s, $CH_2-C\equiv CH$), 81.8 (d, $^3J_{CP3} = 6.1$ Hz, $CH_2-C\equiv CH$), 115.0 (s, $CH_2-CH=CH_2$), 121.4 (brs, C_0^2, C_1^2, C_2^2), 127.3 (s, C_2^3), 128.1 (brs, C_0^3, C_1^3), 131.3 (s, C_2^4), 132.0 (s, C_1^4), 132.8 (s, C_0^4), 135.3 (d, $^3J_{CP3} = 13.6$ Hz, $(CH=N)_2$), 136.4 (d, $^3J_{CP3} = 6.6$ Hz, $CH_2-CH=CH_2$), 138.4 (d, $^3J_{CP1-2} = 10.6$ Hz, $(CH=N)_{0-1}$), 150.4 (d, $^2J_{CP2} = 6.5$ Hz, C_2^1), 151.1 (d, $^2J_{CP0-1} = 6.5$ Hz, C_0^1, C_1^1). IR(KBr): 3400 (m, $\tilde{\nu}_{N-H}$) cm^{-1}. Anal. calcd. for $C_{240}H_{288}N_{66}O_{33}P_{22}S_{10}$: C, 51.23; H, 5.15; N, 16.42. Found: C, 51.04; H, 5.08; N, 16.22.

General procedure for the synthesis of dendrimers 14-[G_1], 14-[G_4]: To a solution of 0.150 g of dendrimer **4-[G_n]** ($n = 1$, 0.138 mmol; $n = 4$, 0.0118 mmol) in THF (7 mL) was added a solution of triethylamine ($n = 1$, 57 μL, 0.412 mmol; $n = 4$, 40 μL, 0.283 mmol) and propargylamine ($n = 1$, 28 μL, 0.412 mmol; $n = 4$, 20 μL, 0.283 mmol) in THF (7 mL) at room temperature. This mixture was stirred for 4 d, the precipitate removed by centrifugation, and the solution evaporated to dryness. The residue thus obtained was purified by column chromatography on silica gel (eluent: ethyl acetate).

14-[G_1]: yellow oil; 71% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 52.8$ (s, P_0), 72.0 (s, P_1); ^1H NMR ($CDCl_3$): $\delta = 2.2$ (t-like, $^4J_{HHA} = {}^4J_{HHB} = 2.5$ Hz, 3H, $CH_AH_B-C\equiv CH$), 3.2 (d, $^3J_{HP1} = 9.4$ Hz, 9H, P_1-N-CH_3), 3.6 (q-like, $^2J_{HP1} = {}^4J_{HH} = 6.5$ Hz, 3H, NH), 3.9 (m, 18H, $CH_2-CH=CH_2$ and $CH_2-C\equiv CH$), 5.1 (m, 12H, $CH_2-CH=CH_2$), 5.7 (m, 6H, $CH_2-CH=CH_2$), 7.3 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HP0} = 1.5$ Hz, 6H, C_0^2-H), 7.5 (s, 3H, CH=N), 7.7 (d, $^3J_{HH} = 8.6$ Hz, 6H, C_0^3-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.4$ (d, $^2J_{CP1} = 2.7$ Hz, $CH_2-C\equiv CH$), 31.1 (d, $^2J_{CP1} = 11.8$ Hz, P_1-N-CH_3), 47.9 (d, $^2J_{CP1} = 4.5$ Hz, $CH_2-CH=CH_2$), 69.6 (s, $CH_2-C\equiv CH$), 80.8 (d, $^3J_{CP1} = 10.1$ Hz, $CH_2-C\equiv CH$), 117.1 (s, $CH_2-CH=CH_2$), 120.8 (d, $^3J_{CP0} = 4.7$ Hz, C_0^2), 127.1 (s, C_0^3), 132.6 (s, C_0^4), 134.0 (d, $^3J_{CP1} = 2.5$ Hz, $CH_2-CH=CH_2$), 135.1 (d, $^3J_{CP1} = 11.9$ Hz, CH=N), 149.9 (d, $^2J_{CP0} = 8.6$ Hz, C_0^1). MS *m/z*: 1147 $[M+1]^+$. IR(THF): 3262 (m, $\tilde{\nu}_{N-H}$), 3083 (m, $\tilde{\nu}_{=CH2}$) cm^{-1}. Anal. calcd. for $C_{51}H_{66}N_{12}O_3P_4S_4$: C, 53.40; H, 5.80; N, 14.66. Found: C, 53.15; H, 5.67; N, 14.39.

14-[G_4]: Yellow powder; 57% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 52.7$ (s, P_0), 62.6 (brs, P_1, P_2, P_3), 72.0 (s, P_4); ^1H NMR ($CDCl_3$): $\delta = 2.2$ (brt, 24H, $CH_2-C\equiv CH$), 3.3 (brd, 135H, $P_{1-2-3}-N-CH_3$), 3.5–4.0 (m, 168H, $CH_2-CH=CH_2$ and $NH-CH_2-C\equiv CH$), 5.1 (m, 96H, $CH_2-CH=CH_2$), 5.8 (m, 48H, $CH_2-CH=CH_2$), 7.2–7.8 (m, 225H, $(C_6H_4)_{0-1-2-3}$ and $(CH=N)_{0-1-2-3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.4$ (d, $^2J_{CP4} = 1.2$ Hz, $CH_2-C\equiv CH$), 31.1 (d, $^2J_{CP4} = 11.8$ Hz, P_4-N-CH_3), 32.4 (d, $^2J_{CP3} = 12.8$ Hz, P_3-N-CH_3), 32.5 (d, $^2J_{CP1-2} = 14.0$ Hz, $P_{1-2}-N-CH_3$), 47.7 (d, $^2J_{CP4} = 4.5$ Hz, $CH_2-CH=CH_2$), 69.6 (s, $CH_2-C\equiv CH$), 117.0 (s, $CH_2-CH=CH_2$), 121.1 (brs, C_0^2, C_1^2, C_2^2, C_3^2), 126.9 (s, C_3^3), 127.6 (brs, C_0^3, C_1^3, C_2^3), 131.5 (brs, C_0^4, C_1^4, C_2^4), 132.1 (s, C_3^4), 134.0 (brs, $CH_2-CH=CH_2$), 135.4 (d, $^3J_{CP4} = 14.6$ Hz, $(CH=N)_3$), 138.0–139.0 (m, $(CH=N)_{0-1-2}$), 150.0–151.0 (m, C_0^1, C_1^1, C_2^1, C_3^1). IR(KBr): 3265 (m, $\tilde{\nu}_{N-H}$), 3076 (m, $\tilde{\nu}_{=CH2}$) cm^{-1}. Anal. calcd. for $C_{576}H_{696}N_{138}O_{45}P_{46}S_{46}$: C, 52.52; H, 5.33; N, 14.67. Found: C, 55.27; H, 5.25; N, 14.51.

General procedure for the synthesis of dendrimers 15-[G_1]–15-[G_3]: To a solution of 0.300 g of dendrimer **8-[G_n]** ($n = 1$, 0.325 mmol; $n = 2$, 0.124 mmol; $n = 3$, 0.0555 mmol) in THF (20 mL) was added powdered 4-hydroxybenzaldehyde sodium salt ($n = 1$, 0.162 g, 1.121 mmol; $n = 2$, 0.123 g, 0.856 mmol; $n = 3$, 0.109 g, 0.760 mmol, 15% excess). The resulting heterogeneous mixture was stirred for 45 min and then filtered. The solvent was removed under vacuum to give a powder which was washed with ether (3 × 20 mL).

15-[G_1]: white powder; 83% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.0$ (s, P_1), 52.4 (s, P_0); ^1H NMR ($CDCl_3$): $\delta = 3.16$ (d, $^3J_{HP1} = 7.6$ Hz, 9H, CH_3-N-P_1), 3.33 (m, 3H,

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NH), 3.77 (m, 6H, CH_2–CH=CH_2), 5.08 (dd, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HHgem}$ = 1.4 Hz, 3H, CH_2(H)C=C(H_{cis})H), 5.22 (dd, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HHgem}$ = 1.5 Hz, 3H, CH_2(H)C=C(H)H_{trans}), 5.86 (m, 3H, CH_2–CH=CH_2), 6.92–7.84 (m, 27H, $(C_6H_4)_{0-1}$ and (CH=N)$_0$), 9.90 (s, 3H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.9 (d, $^2J_{CP1}$ = 9.2 Hz, CH_3–N–P_1), 44.1 (s, CH_2–CH=CH_2), 116.0 (s, CH_2–CH=CH_2), 121.2 (d, $^3J_{CP0}$ = 3.4 Hz, C_0^2), 121.5 (d, $^3J_{CP1}$ = 3.8 Hz, C_1^2), 127.9 (s, C_0^3), 131.5 (s, C_1^3), 132.2 (s, C_0^4), 132.9 (s, C_1^4), 135.7 (d, $^3J_{CP0}$ = 6.1 Hz, CH_2–CH=CH_2), 137.0 (d, $^3J_{CP1}$ = 14.9 Hz, (CH=N)$_0$), 150.8 (d, $^2J_{CP0}$ = 7.8 Hz, C_0^1), 155.7 (d, $^2J_{CP1}$ = 3.2 Hz, C_1^1), 190.8 (s, CHO). IR(KBr): 1700 (S, $\tilde{\nu}_{CHO}$) cm^{-1}. Anal. calcd. for $C_{54}H_{57}N_9O_{12}P_4S$: C, 54.96; H, 4.86; N, 10.68. Found: C, 54.89; H, 4.82; N, 10.64.

15-[G_2]: white powder; 78% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 8.0 (s, P_2), 52.4 (s, P_0), 62.1 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.11 (d, $^3J_{HP2}$ = 7.0 Hz, 18H, CH_3–N–P_2), 3.25 (m, 6H, NH), 3.33 (d, $^3J_{HP1}$ = 10.7 Hz, 9H, CH_3–N–P_1), 3.71 (m, 12H, CH_2–CH=CH_2), 5.03 (dd, $^3J_{HHcis}$ = 11.1 Hz, $^2J_{HHgem}$ = 1.2 Hz, 6H, CH_2(H)C=C(H_{cis})H), 5.18 (dd, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HHgem}$ = 1.2 Hz, 6H, CH_2(H)C=C(H)H_{trans}), 5.81 (m, 6H, CH_2–CH=CH_2), 7.17–7.72 (m, 69H, $(C_6H_4)_{0-1-2}$ and (CH=N)$_{0-1}$), 9.85 (s, 6H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.8 (d, $^2J_{CP2}$ = 8.6 Hz, CH_3–N–P_2), 33.1 (d, $^2J_{CP1}$ = 12.6 Hz, CH_3–N–P_1), 44.0 (s, CH_2–CH=CH_2), 115.9 (s, CH_2–CH=CH_2), 121.2 (brs, C_2^2), 121.6 (brs, C_0^2), 121.8 (brs, C_1^2), 127.7 (s, C_1^3), 128.5 (s, C_0^3), 131.5 (s, C_2^3), 132.2 (s, C_2^4), 132.4 (s, C_1^4), 133.0 (s, C_0^4), 135.7 (d, $^3J_{CP2}$ = 3.5 Hz, CH_2–CH=CH_2), 137.3 (d, $^3J_{CP2}$ = 15.1 Hz, (CH=N)$_1$), 138.6 (d, $^3J_{CP1}$ = 18.6 Hz, (CH=N)$_0$), 151.0 (d, $^2J_{CP0\ 1}$ = 7.9 Hz, C_0^1, C_1^1), 155.7 (d, $^2J_{CP2}$ = 7.2 Hz, C_2^1), 190.9 (s, CHO). IR(KBr): 3392 (m, $\tilde{\nu}_{N-H}$), 1701 (S, $\tilde{\nu}_{CHO}$) cm^{-1}. Anal. calcd. for $C_{132}H_{138}N_{24}O_{27}P_{10}S_4$: C, 54.10; H, 4.74; N, 11.47. Found: C, 53.89; H, 4.66; N, 11.29.

15-[G_3]: white powder; 75% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 8.1 (s, P_3), 52.4 (s, P_0), 61.8 (s, P_2), 62.1 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.10 (d, $^3J_{HP3}$ = 7.2 Hz, 36H, CH_3–N–P_3), 3.25 (m, 12H, NH), 3.33 (d, $^3J_{HP1\ 2}$ = 9.8 Hz, 27H, CH_3–N–P_{1-2}), 3.72 (m, 24H, CH_2–CH=CH_2), 5.02 (dd, $^3J_{HHcis}$ = 9.7 Hz, $^2J_{HHgem}$ = 1.2 Hz, 12H, CH_2(H)C=C(H_{cis})H), 5.17 (dd, $^3J_{HHtrans}$ = 16.5 Hz, $^2J_{HHgem}$ = 1.2 Hz, 12H, CH_2(H)C=C(H)H_{trans}) 5.81 (m, 12H, CH_2–CH=CH_2), 7.16–7.71 (m, 153H, $(C_6H_4)_{0\ 1\ 2\ 3}$ and (CH=N)$_{0\ 1-2}$), 9.85 (s, 12H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.8 (d, $^2J_{CP3}$ = 9.3 Hz, CH_3–N–P_3), 33.0 (d, $^2J_{CP1-2}$ = 12.3 Hz, CH_3–N–P_{1-2}), 44.0 (s, CH_2–CH=CH_2), 115.9 (s, CH=CH_2), 121.2 (brs, C_3^2), 121.8 (brs, C_0^2, C_1^2, C_2^2), 127.8 (s, C_2^3), 128.3 (s, C_1^3), 128.6 (s, C_0^3), 131.5 (s, C_3^3), 132.3 (brs, C_1^4, C_2^4, C_3^4), 133.0 (s, C_0^4), 135.7 (d, $^3J_{CP3}$ = 6.2 Hz, CH_2–CH=CH_2), 137.4 (d, $^3J_{CP3}$ = 14.2 Hz, (CH=N)$_3$), 138.9 (d, $^3J_{CP1-2}$ = 14.1 Hz, (CH=N)$_{0\ 1}$), 151.0 (d, $^2J_{CP2}$ = 6.7 Hz, C_2^1), 151.3 (d, $^2J_{CP}$ = 6.0 Hz, C_0^1, C_1^1), 155.6 (d, $^2J_{CP3}$ = 7.6 Hz, C_3^1), 190.9 (s, CHO). IR(KBr): 3438 (m, $\tilde{\nu}_{N\ H}$), 1701 (S, $\tilde{\nu}_{CHO}$) cm^{-1}. Anal. calcd. for $C_{288}H_{300}N_{54}O_{57}P_{22}S_{10}$: C, 53.78; H, 4.70; N, 11.76. Found: C, 53.38; H, 4.57; N, 11.44.

General procedure for the synthesis of dendrimers 16-[G_1]–16-[G_3]: To a solution of 0.300 g of dendrimer **12-[G_n]** (n = 1, 0.327 mmol; n = 2, 0.125 mmol; n = 3, 0.0557 mmol) in THF (20 mL) was added powdered 4-hydroxybenzaldehyde sodium salt (n = 1, 0.162 g, 1.128 mmol; n = 2, 0.124 g, 0.862 mmol; n = 3, 0.111 g, 0.769 mmol, 15% excess). The resulting heterogeneous mixture was stirred for 45 min and then filtered. The solvent was removed under vacuum to give a powder, which was washed with ether (3 × 20 mL).

16-[G_1]: Yellow-white powder; 75% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 6.5 (s, P_1), 51.9 (s, P_0); ^1H NMR ($CDCl_3$): δ = 2.21 (t-like, $^4J_{HHA}$ = $^4J_{HHB}$ = 2.1 Hz, 3H, CH_AH_B–C≡CH), 3.18 (d, $^3J_{HP1}$ = 7.8 Hz, 9H, CH_3–N–P_1), 3.77 (m, 3H, NH), 3.94 (m, 6H, CH_2–C≡CH), 6.93–7.83 (m, 27H, $(C_6H_4)_{0-1}$ and (CH=N)$_0$), 9.92 (s, 3H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 (s, CH_2–C≡CH), 31.6 (d, $^2J_{CP1}$ = 9.4 Hz, CH_3–N–P_1), 71.8 (s, CH_2–C≡CH), 80.4 (d, $^3J_{CP1}$ = 9.2 Hz, CH_2–C≡CH), 121.1 (brs, C_1^2), 121.3 (brs, C_0^2), 127.9 (s, C_0^3), 131.4 (s, C_1^3), 132.6 (s, C_1^4), 133.0 (s, C_0^4), 137.3 (d, $^3J_{CP}$ = 15.0 Hz, (CH=N)$_0$), 150.8 (d, $^2J_{CP0}$ = 7.4 Hz, C_0^1), 155.2 (d, $^2J_{CP1}$ = 7.2 Hz, C_1^1), 190.7 (s, CHO). IR(KBr): 3391 (w, $\tilde{\nu}_{N-H}$), 3291 (m, $\tilde{\nu}_{\equiv C-H}$), 1699 (w, $\tilde{\nu}_{CHO}$) cm^{-1}. Anal. calcd. for $C_{54}H_{51}N_9O_{12}P_4S$: C, 55.25; H, 4.37; N, 10.73. Found: C, 55.14; H, 4.10; N, 10.59.

16-[G_2]: Yellow powder; 76% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 7.4 (s, P_2), 52.9 (s, P_0), 62.4 (s, P_1); ^1H NMR ($CDCl_3$): δ = 2.18 (t-like, $^4J_{HHA}$ = $^4J_{HHB}$ = 2.1 Hz, 6H, CH_AH_B–C≡CH), 3.13 (d, $^3J_{HP2}$ = 7.6 Hz, 18H, CH_3–N–P_2), 3.37 (d, $^3J_{HP1}$ = 10.3 Hz, 9H, CH_3–N–P_1), 3.74 (m, 6H, NH), 3.89 (m, 12H, CH_2–C≡CH), 7.18–7.79 (m, 69H, $(C_6H_4)_{0-1-2}$ and (CH=N)$_{0\ 1}$), 9.75 (s, 6H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.2 (s, CH_2–C≡CH), 31.7 (d, $^2J_{CP2}$ = 9.8 Hz, CH_3–N–P_2), 33.0 (d, $^2J_{CP1}$ = 12.0 Hz, CH_3–N–P_1), 71.9 (s, CH_2–C≡CH), 83.5 (d, $^3J_{CP2}$ = 9.1 Hz, CH_2–C≡CH), 121.1 (brs, C_2^2), 121.7 (brs, C_0^2, C_1^2), 127.9 (s, C_1^3), 128.5 (s, C_0^3), 131.6 (s, C_2^3), 132.3 (brs, C_1^4, C_2^4), 132.7 (s, C_0^4), 137.8 (d, $^3J_{CP2}$ = 16.3 Hz, (CH=N)$_1$), 138.7 (d, $^3J_{CP1}$ = 14.2 Hz, (CH=N)$_0$), 151.1 (brs, C_0^1, C_1^1), 155.3 (brs, C_1^1), 191.0 (s, CHO). IR(KBr): 3379 (w, $\tilde{\nu}_{N-H}$), 3291 (m, $\tilde{\nu}_{\equiv C-H}$), 1701 (m, $\tilde{\nu}_{CHO}$) cm^{-1}. Anal. calcd. for $C_{132}H_{126}N_{24}O_{27}P_{10}S_4$: C, 54.33; H, 4.35; N, 11.51. Found: C, 54.17; H, 4.26; N, 11.40.

16-[G_3]: Yellow powder; 74% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 7.4 (s, P_3), 52.8 (s, P_0), 62.4 (s, P_1, P_2); ^1H NMR ($CDCl_3$): δ = 2.15 (t-like, $^4J_{HHA}$ = $^4J_{HHB}$ = 2.3 Hz, 12H, CH_AH_B–C≡CH), 3.11 (d, $^3J_{HP3}$ = 7.2 Hz, 36H, CH_3–N–P_3), 3.32 (d, $^3J_{HP1-2}$ = 9.7 Hz, 27H, CH_3–N–P_{1-2}), 3.73 (m, 12H, NH), 3.87 (m, 24H, CH_2–C≡CH), 7.20–7.77 (m, 153H, $(C_6H_4)_{0-1-2-3}$ and (CH=N)$_{0-1-2}$), 9.51 (s, 12H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 (s, CH_2–C≡CH), 31.6 (d, $^2J_{CP3}$ = 9.4 Hz, CH_3–N–P_3), 33.0 (d, $^2J_{CP1-2}$ = 12.5 Hz, CH_3–N–P_{1-2}), 71.8 (s, CH_2–C≡CH), 80.8 (d, $^3J_{CP3}$ = 9.0 Hz, CH_2–C≡CH), 121.0 (brs, C_3^2), 121.6 (brs, C_0^2, C_1^2, C_2^2), 127.8 (s, C_3^3), 128.1 (s, C_1^3), 128.8 (s, C_0^3), 131.4 (s, C_3^3), 132.3 (brs, C_1^4, C_2^4, C_3^4), 133.0 (s, C_0^4), 137.9 (d, $^3J_{CP3}$ = 15.2 Hz, (CH=N)$_2$), 138.9 (d, $^3J_{CP0-1}$ = 14.6 Hz, (CH=N)$_{0-1}$), 151.1 (d, $^2J_{CP2}$ = 6.7 Hz, C_2^1), 151.4 (d, $^2J_{CP0\ 1}$ = 6.0 Hz, C_0^1, C_1^1), 155.3 (d, $^2J_{CP3}$ = 7.6 Hz, C_3^1), 190.9 (s, CHO). IR(KBr): 3380 (w, $\tilde{\nu}_{N-H}$), 3291 (m, $\tilde{\nu}_{\equiv C-H}$), 1702 (m, $\tilde{\nu}_{CHO}$) cm^{-1}. Anal. calcd. for $C_{288}H_{276}N_{54}O_{57}P_{22}S_{10}$: C, 53.99; H, 4.34; N, 11.80. Found: C, 53.59; H, 4.22; N, 11.59.

General procedure for the synthesis of dendrimers 18-[G_1], 18-[G_3]: To an emulsion of 1.2 mL of N_2H_4, $x$$H_2O$ (37 mmol, large excess) in 20 mL of CH_2Cl_2 vigorously stirred at room temperature was added dropwise a solution of 0.200 g of dendrimer **15-[G_n]** (n = 1, 0.169 mmol; n = 3, 0.0311 mmol). The vigorous stirring was maintained for 2 h then stopped to separate two layers. The solvent of the organic layer (lower) was removed under vacuum and the powder thus obtained was washed with ether (3 × 30 mL).

18-[G_1]: White powder; 91% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 7.9 (s, P_1), 52.6 (s, P_0); ^1H NMR ($CDCl_3$): δ = 3.07 (d, $^3J_{HP1}$ = 7.4 Hz, 9H, CH_3–N–P_1), 3.52 (m, 3H, NH), 3.72 (m, 6H, CH_2–CH=CH_2), 5.01 (dd, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HHgem}$ = 1.4 Hz, 3H, CH_2(H)C=C(H_{cis})H), 5.17 (dd, $^3J_{HHtrans}$ = 17.0 Hz, $^2J_{HHgem}$ = 1.4 Hz, 3H, CH_2(H)C=C(H)H_{trans}) 5.51 (brs, 6H, NH_2), 5.81 (m, 3H, CH_2–CH=CH_2), 6.77–7.63 (m, 30H, $(C_6H_4)_{0-1}$ and (CH=N)$_{0-1}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.8 (d, $^2J_{CP1}$ = 9.0 Hz, CH_3–N–P_1), 44.0 (s, CH_2–CH=CH_2), 115.6 (s, CH_2–CH=CH_2), 120.7 (d, $^3J_{CP1}$ = 4.4 Hz, C_1^2), 121.2 (d, $^3J_{CP0}$ = 3.9 Hz, C_0^2), 127.1 (s, C_0^3), 127.7 (s, C_1^3), 131.8 (s, C_1^4), 132.7 (s, C_0^4), 135.8 (d, $^3J_{CP1}$ = 6.5 Hz, CH_2–CH=CH_2), 136.3 (d, $^3J_{CP1}$ = 14.9 Hz, (CH=N)$_0$), 141.7 (s, (CH=N)$_1$), 149.9 (m, C_0^1, C_1^1). IR(KBr): 3401 (w, $\tilde{\nu}_{N-H}$), 3282 (m, $\tilde{\nu}_{N-H}$) cm^{-1}. Anal. calcd. for $C_{54}H_{63}N_{15}O_9P_4S$: C, 53.09; H, 5.19; N, 17.18. Found: C, 52.84; H, 5.14; N, 17.01.

18-[G_3]: White powder; 90% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 7.9 (s, P_3), 52.3 (s, P_0), 61.8 (s, P_2), 62.0 (s, P_1); ^1H NMR ($CDCl_3$): δ = 3.04 (d, $^3J_{HP3}$ = 6.8 Hz, 36H, CH_3–N–P_3), 3.31 (d, $^3J_{HP1-2}$ = 9.8 Hz, 27H, CH_3–N–P_{1-2}), 3.56 (m, 12H, NH), 3.68 (m, 24H, CH_2–CH=CH_2), 5.00 (dd, $^3J_{HHcis}$ = 9.4 Hz, $^2J_{HHgem}$ = 1.2 Hz, 12H, CH_2(H)C=C(H_{cis})H), 5.16 (dd, $^3J_{HHtrans}$ = 16.0 Hz, $^2J_{HHgem}$ = 1.2 Hz, 12H, CH_2(H)C=C(H)H_{trans}), 5.50 (brs, 24H, NH_2), 5.78 (m, 12H, CH_2–CH=CH_2), 6.70–7.66 (m, 165H, $(C_6H_4)_{0\ 1\ 2\ 3}$ and (CH=N)$_{0-1-2-3}$); $^{13}C\{^1H\}$ NMR (CD-Cl_3): δ = 31.9 (d, $^2J_{CP3}$ = 9.4 Hz, CH_3–N–P_3), 33.1 (d, $^3J_{CP1-2}$ = 13.2 Hz, CH_3–N–P_{1-2}), 44.1 (s, CH_2–CH=CH_2), 115.7 (s, CH_2–CH=CH_2), 120.9 (brs, C_3^2), 121.7 (brs, C_0^2, C_1^2, C_2^2), 127.2 (s, C_2^3), 127.7 (s, C_3^3), 128.3 (brs, C_0^3, C_1^3), 131.9 (s, C_3^4), 132.7 (brs, C_0^4, C_1^4, C_2^4), 136.0 (d, $^3J_{CP3}$ = 6.0 Hz, CH_2–CH=CH_2), 136.7 (d, $^3J_{CP1-2-3}$ = 10.7 Hz, (CH=N)$_{0\ 1\ 2}$), 141.9 (s, (CH=N)$_3$), 150.9 (d, $^2J_{CP0\ 1-2}$ = 3.9 Hz, C_0^1, C_1^1, C_2^1), 151.3 (d, $^2J_{CP3}$ = 3.8 Hz, C_3^1). IR(KBr): 3400 (w, $\tilde{\nu}_{N\ H}$), 3282 (w, $\tilde{\nu}_{N-H}$) cm^{-1}. Anal. calcd. for $C_{288}H_{324}N_{78}O_{45}P_{22}S_{10}$: C, 52.41; H, 4.94; N, 16.55. Found: C, 52.07; H, 4.85; N, 16.36.

Synthesis of dendrimer 19-[G_1]: To an emulsion of 0.8 mL of N_2H_4, $x$$H_2O$ (25 mmol, large excess) in 10 mL of CH_2Cl_2 vigorously stirred at room temperature was added dropwise a solution of **16-[G_1]** (0.100 g, 0.0852 mmol). The vigorous stirring was maintained for 2 h and then stopped to separate two layers. The solvent of the organic layer (lower) was removed under vacuum, and the powder thus obtained washed with ether (3 × 30 mL).

19-[G_1]: white-yellow powder; 90% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 7.2 (s, P_1), 52.6 (s, P_0); ^1H NMR ($CDCl_3$): δ = 2.15 (t-like, $^4J_{HHA}$ = $^4J_{HHB}$ = 2.3 Hz, 3H, CH_AH_B–C≡CH), 3.07 (d, $^3J_{HP1}$ = 7.4 Hz, 9H, CH_3–N–P_1), 3.50 (m, 3H, NH), 3.89 (m, 6H, CH_2–C≡CH), 5.53 (brs, 6H, NH_2), 6.77–7.63 (m, 30H, $(C_6H_4)_{0-1}$ and (CH=N)$_{0-1}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.7 (s, CH_2–C≡CH), 31.0 (d, $^2J_{CP1}$ = 9.0Hz, CH_3–N–P_1), 71.0 (s, CH_2–C≡CH), 80.4 (d, $^3J_{CP1}$ = 7.2 Hz, CH_2–C≡CH), 120.3 (brs, C_1^2), 120.6 (brs, C_0^2), 126.7 (s, C_0^3), 127.2 (s, C_1^3), 131.5 (s, C_0^4), 132.4 (s, C_1^4), 136.0 (d, $^3J_{CP1}$ = 15.1 Hz, (CH=N)$_0$), 141.2 (s, (CH=N)$_1$), 149.9 (m, C_0^1, C_1^1). IR(KBr): 3380 (w, $\tilde{\nu}_{N-H}$), 3290 (m, $\tilde{\nu}_{N-H}$) cm^{-1}. Anal. calcd. for $C_{54}H_{57}N_{15}O_9P_4S$: C, 53.34; H, 4.72; N, 17.27. Found: C, 53.26; H, 4.67; N, 17.18.

General procedure for the synthesis of dendrimers 20-[G_1]–20-[G_3]: To a solution of 0.300 g of dendrimer **16-[G_n]** (n = 1, 0.255 mmol; n = 2, 0.103 mmol; n = 3, 0.0468 mmol) in THF (20 mL) was added powdered Ph_3P=CH–C≡N **17** (n = 1, 0.300 g, 0.996 mmol; n = 2, 0.241 g, 0.802 mmol; n = 3, 0.220 g, 0.730 mmol, 30% excess). The resulting mixture was stirred overnight, and the solution was then concentrated under vacuum to ca. 2 mL. An ether/pentane (1/1) solution (20 mL) was added to the remaining solution to precipitate **20-[G_n]**. The resulting mixture was filtered, and the precipitate was then recovered, solubilized in a minimum amount of THF and precipitated again with a ether/pentane solution. The precipitate was recovered and washed with ether (20 mL).

20-[G$_1$]: Yellow powder; 59% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 7.3$ (s, P_1), 52.8 (s, P_0); ^1H NMR ($CDCl_3$): $\delta = 2.20$ (t-like, $^4J_{HHA} = {}^4J_{HHB} \approx 2.3$ Hz, 3H, CH_AH_B-C≡C*H*), 3.15 (d, $^3J_{HP1} = 7.5$ Hz, 9H, CH_3-N-P_1), 3.64 (m, 3H, NH), 3.92 (m, 6H, CH_2-C≡CH), 5.36 (d, $^3J_{HHcis} = 12.1$ Hz, (3×0.4)H, (C*H*=CH-CN)$_{cis}$), 5.74 (d, $^3J_{HHtrans} = 16.6$ Hz, (3×0.6)H, (C*H*=CH-CN)$_{trans}$), 7.02 (d, $^3J_{HHcis} = 12.1$ Hz, (3×0.4)H, (CH=C*H*-CN)$_{cis}$), 7.20–7.87 (m, (27+3×0.6)H, $(C_6H_4)_{0-1}$, $(CH=N)_0$ and (CH=C*H*-CN)$_{trans}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.1$ (s, CH_2-C≡CH), 31.6 (d, $^2J_{CP1} = 9.4$ Hz, CH_3-N-P_1), 71.6 (s, CH_2-C≡*C*H), 80.6 (d, $^3J_{CP1} = 8.9$ Hz, CH_2-*C*≡CH), 94.4 (s, (CH=CH-CN)$_{cis}$), 95.8 (s, (*C*H=CH-CN)$_{trans}$), 117.2 (s, (CH=*C*H-C≡N)$_{cis}$), 117.9 (s, (CH=CH-*C*≡N)$_{trans}$), 121.0 (d, $^3J_{CP0} = 5.0$ Hz, C_0^2), 121.1 (d, $^3J_{CP1} = 6$Hz, C_{1cis}^2), 121.2 (d, $^3J_{CP1} = 5$ Hz, C_{1trans}^2), 127.8 (s, C_0^3), 128.7 (s, C_{1trans}^3), 130.5 (s, C_{1cis}^3), 131.3 (s, C_{1trans}^4), 131.8 (s, C_0^4), 132.7 (s, C_{1cis}^4), 136.9 (d, $^3J_{CP1} = 15.0$ Hz, $(CH=N)_0$), 147.3 (s, (CH=*C*H-CN)$_{cis}$), 149.2 (s, (CH=CH-CN)$_{trans}$), 150.7 (d, $^2J_{CP0} = 7.4$ Hz, C_0^1), 152.2 (d, $^2J_{CP1} = 7.3$ Hz, C_1^1 cis), 152.5 (d, $^2J_{CP1} = 7.3$ Hz, C_{1trans}^1). MS *m/z*: 1243 $[M+1]^+$. IR(KBr): 3401 (w, $\tilde{\nu}_{N-H}$), 3291 (m, $\tilde{\nu}_{\equiv C-H}$), 2215 (m, $\tilde{\nu}_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{60}H_{54}N_{12}O_9P_4S$: C, 57.97; H, 4.37; N, 13.52. Found: C, 57.61; H, 4.18; N, 13.39.

20-[G$_2$]: Yellow powder; 60% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 7.4$ (s, P_2), 52.8 (s, P_0), 62.4 (s, P_1); ^1H NMR ($CDCl_3$): $\delta = 2.17$ (t-like, $^4J_{HHA} = {}^4J_{HHB} \approx 2.3$ Hz, 6H, CH_2-C≡C*H*), 3.12 (d, $^3J_{HP2} = 6.0$ Hz, 18H, CH_3-N-P_2), 3.37 (d, $^3J_{HP1} = 10.2$ Hz, 9H, CH_3-N-P_1), 3.70 (m, 6H, NH), 3.88 (m, 12H, CH_2-C≡CH), 5.34 (d, $^3J_{HHcis} = 12.1$ Hz, (6×0.4)H, (C*H*=CH-C≡N)$_{cis}$), 5.71 (d, $^3J_{HHtrans} = 16.7$ Hz, (6×0.6)H, (C*H*=CH-CN)$_{trans}$), 6.99 (d, $^3J_{HHcis} = 12.1$ Hz, (6×0.4)H, (CH=C*H*-CN)$_{cis}$), 7.21–7.86 (m, (69+6×0.6)H, $(C_6H_4)_{0-1-2}$, $(CH=N)_{0-1}$ and (CH=C*H*-CN)$_{trans}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.1$ (s, CH_2-C≡CH), 31.6 (d, $^2J_{CP2} = 8.8$ Hz, CH_3-N-P_2), 32.9 (d, $^2J_{CP1} = 12.5$ Hz, CH_3-N-P_1), 71.6 (s, CH_2-C≡*C*H), 80.8 (d, $^3J_{CP2} = 8.8$ Hz, CH_2-*C*≡CH), 94.3 (s, (CH=CH-CN)$_{cis}$), 95.8 (s, (CH=CH-CN)$_{trans}$), 117.2 (s, (CH=CH-*C*≡N)$_{cis}$), 117.9 (s, (CH=CH-*C*≡N)$_{trans}$), 121.2 (m, C_0^2, C_1^2, C_{2cis}^2, C_{2trans}^2), 127.7 (s, C_1^3), 128.3 (C_0^3), 128.7 (s, C_{2trans}^3), 130.5 (s, C_{2cis}^3), 131.8 (s, C_{2trans}^4), 132.3 (brs, C_0^4, C_1^4), 132.6 (s, C_{2cis}^4), 137.1 (d, $^3J_{CP2} = 14.4$ Hz, $(CH=N)_1$), 138.4 (d, $^3J_{CP1} = 12.8$ Hz, $(CH=N)_0$), 147.4 (s, (CH=*C*H-CN)$_{cis}$), 149.2 (s, (CH=*C*H-CN)$_{trans}$), 150.9 (brs, C_0^1, C_1^1), 152.2 (d, $^2J_{CP2} = 7.3$ Hz, C_{2cis}^1), 152.6 (d, $^2J_{CP2} = 7.1$ Hz, C_{2trans}^1). MS *m/z*: 3055 $[M+1]^+$. IR(KBr): 3402 (w, $\tilde{\nu}_{N-H}$), 3291 (m, $\tilde{\nu}_{\equiv C-H}$), 2212 (m, $\tilde{\nu}_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{144}H_{132}N_{30}O_{21}P_{10}S_4$: C, 56.58; H, 4.35; N, 13.74. Found: C, 56.37; H, 4.17; N, 13.54.

20-[G$_3$]: Yellow powder; 60% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 7.4$ (s, P_3), 52.8 (s, P_0), 62.4 (brs, P_1, P_2); ^1H NMR ($CDCl_3$): $\delta = 2.15$ (t-like, $^4J_{HHA} = {}^4J_{HHB} = 2.3$ Hz, 12H, CH_2-C≡C*H*), 3.09 (d, $^3J_{HP3} = 6.9$ Hz, 36H, CH_3-N-P_3), 3.33 (d, $^3J_{HP1-3} \approx 9.9$ Hz, 27H, CH_3-N-P_{1-2}), 3.80 (m, 36H, NH and CH_2-C≡CH), 5.34 (d, $^3J_{HHcis} = 12.1$ Hz, (12×0.4)H, (C*H*=CH-C≡N)$_{cis}$), 5.72 (d, $^3J_{HHtrans} = 16.6$ Hz, (12×0.6)H, (C*H*=CH-CN)$_{trans}$), 7.01 (d, $^3J_{HHcis} = 12.1$ Hz, (12×0.4)H, (CH=C*H*-CN)$_{cis}$), 7.19–7.69 (m, (153+12×0.6)H, $(C_6H_4)_{0-1-2-3}$, $(CH=N)_{0-1-2}$ and (CH=C*H*-CN)$_{trans}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.1$ (s, CH_2-C≡CH), 31.6 (d, $^2J_{CP3} = 10.5$ Hz, CH_3-N-P_3), 32.9 (d, $^2J_{CP1-2} = 13.1$ Hz, CH_3-N-P_{1-2}), 71.5 (s, CH_2-C≡*C*H), 80.8 (d, $^3J_{CP3} = 8.0$ Hz, CH_2-*C*≡CH), 94.4 (s, (CH=CH-CN)$_{cis}$), 95.8 (s, (*C*H=CH-C≡N)$_{trans}$), 117.2 (s, (CH=CH-C≡N)$_{cis}$), 117.9 (s, (CH=CH-*C*≡N)$_{trans}$), 121.3 (m, C_0^2, C_1^2, C_2^2, C_{3cis}^2, C_{3trans}^2), 127.6 (s, C_1^3, C_2^3), 128.2 (C_0^3), 128.7 (s, C_{3trans}^3), 130.4 (s, C_{3cis}^3), 131.8 (s, C_{3trans}^4), 132.0 (s, C_2^4), 132.3 (brs, C_0^4, C_1^4), 132.5 (s, C_{3cis}^4), 137.1 (d, $^3J_{CP3} = 14.2$ Hz, $(CH=N)_2$), 138.7 (d, $^3J_{CP1-2} = 10.1$ Hz, $(CH=N)_{0-1}$), 147.3 (s, (CH=*C*H-CN)$_{cis}$), 149.2 (s, (CH=CH-CN)$_{trans}$), 150.8 (brs, C_0^1, C_1^1, C_2^1), 152.2 (d, $^2J_{CP3} = 8.2$ Hz, C_{3cis}^1), 152.6 (d, $^2J_{CP3} = 8.2$ Hz, C_{3trans}^1). IR(KBr): 3401 (w, $\tilde{\nu}_{N-H}$), 3291 (m, $\tilde{\nu}_{\equiv C-H}$), 2215 (m, $\tilde{\nu}_{\equiv C-N}$) cm^{-1}. Anal. calcd. for $C_{312}H_{288}N_{66}O_{45}P_{22}S_{10}$: C, 56.07; H, 4.34; N, 13.83. Found: C, 55.87; H, 4.28; N, 13.64.

General procedure for the synthesis of dendrimers 21-[G$_1$]–21-[G$_3$]: To a solution of 0.300 g of dendrimer **15-[G$_n$]** ($n = 1$, 0.254 mmol; $n = 2$, 0.102 mmol) in 20 mL of *THF* was added Ph_3P=CH-C≡N (**17**) ($n = 1$, 0.298 g, 0.992 mmol; $n = 2$, 0.239 g, 0.798 mmol; 30% excess) at room temperature. The resulting mixture was stirred overnight, and the solution was then concentrated to ca. 2 mL. A mixture of ether and pentane (1/1) was added to the former solution to precipitate **21-[G$_n$]**. After filtration, the precipitate was solubilized in a minimum amount of THF and then precipitated again with a pentane/ether (1/1) mixture. The precipitate was recovered and washed with ether (20 mL).

21-[G$_1$]: White powder; 60% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 7.2$ (s, P_1), 52.0 (s, P_0); ^1H NMR ($CDCl_3$): $\delta = 3.08$ (d, $^3J_{HP1} = 6.9$ Hz, 9H, CH_3-N-P_1), 3.58 (m, 3H, NH), 3.66 (m, 6H, CH_2-CH=CH_2), 4.99 (d, $^3J_{HHcis} = 10.1$ Hz, 3H, CH_2(H)C=C(H_{cis})H), 5.16 (d, $^3J_{HHtrans} = 16.9$ Hz, 3H, CH_2(H)C=C(H)H_{trans}), 5.29 (d, $^3J_{HHcis} = 12.1$ Hz, (3×0.4)H, CH=CH-CN)$_{cis}$), 5.69 (d, $^3J_{HHtrans} = 16.6$ Hz, (3×0.6)H, (CH=CH-CN)$_{trans}$), 5.80 (m, 3H, CH_2-CH=CH_2), 6.95 (d, $^3J_{HHcis} = 12.2$ Hz, (3×0.4), (H, CH=CH-C≡N)$_{cis}$), 7.14–7.74 (m, (27+3×0.6)H, $(C_6H_4)_{0-1}$, $(CH=N)_0$ and (CH=C*H*-CN)$_{trans}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.9$ (d, $^2J_{CP1} = 9.3$ Hz, CH_3-N-P_1), 44.0 (s, CH_2-CH=CH_2), 94.3 (s, (CH=CH-C≡N)$_{cis}$), 95.8 (s, (CH=CH-C≡N)$_{trans}$), 115.6 (s, CH_2-CH=CH_2), 117.4 (s, (CH=CH-*C*≡N)$_{cis}$), 118.1 (s, (CH=CH-*C*≡N)$_{trans}$), 121.1 (d, $^3J_{CP1} = 3.3$ Hz, C_{1cis}^2), 121.3 (m, C_{1trans}^2 and C_0^2), 127.9 (s, C_0^3), 128.8 (s, C_{1trans}^3), 130.6 (s, C_{1cis}^3), 131.4 (s, C_{1cis}^4), 131.9 (s, C_{1trans}^4), 133.1 (s, C_0^4), 136.0 (d, $^3J_{CP1} = 5.6$ Hz, CH_2-*C*H=CH_2), 136.7 (d, $^3J_{CP1} = 14.7$ Hz, $(CH=N)_0$), 147.5 (s, (CH=*C*H-C≡N)$_{cis}$), 149.4 (s, (CH=CH-C≡N)$_{trans}$), 150.7 (d, $^2J_{CP0} = 7.8$ Hz, C_0^1), 152.7 (d, $^2J_{CP1} = 7.5$ Hz, C_{1cis}^1), 153.1 (d, $^2J_{CP1} = 6.7$ Hz, C_{1trans}^1). IR(KBr): 3400 (m, $\tilde{\nu}_{N-H}$), 2210 (m, $\tilde{\nu}_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{60}H_{60}N_{12}O_9P_4S$: C, 57.69; H, 4.84; N, 13.45. Found: C, 57.31; H, 4.70; N, 13.28.

21-[G$_2$]: White powder; 61% yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.0$ (s, P_2), 52.8 (s, P_0), 62.5 (s, P_1); ^1H NMR ($CDCl_3$): $\delta = 3.10$ (d, $^3J_{HP2} = 5.2$ Hz, 18H, CH_3-N-P_2), 3.37 (d, $^3J_{HP1} = 10.3$ Hz, 9H, CH_3-N-P_1), 3.46 (m, 6H, NH), 3.72 (m, 12H, CH_2-CH=CH_2), 5.03 (d, $^3J_{HHcis} = 10.2$ Hz, 6H, CH_2(H)C=C(H_{cis})H), 5.18 (d, $^3J_{HHtrans} = 17.0$ Hz, 6H, CH_2(H)C=C(H)H_{trans}), 5.33 (d, $^3J_{HHcis} = 12.1$ Hz, (6×0.4)H, (CH=CH-CN)$_{cis}$), 5.71 (d, $^3J_{HHtrans} = 16.7$ Hz, (6×0.6)H, (CH=CH-CN)$_{trans}$), 5.80 (m, 6H, CH_2-CH=CH_2), 6.99 (d, $^3J_{HHcis} = 12.2$ Hz, (6×0.4)H, (CH=CH-CN)$_{cis}$), 7.20–7.78 (m, (69+6×0.6)H, $(C_6H_4)_{0-1-2}$, $(CH=N)_{0-1}$ and (CH=C*H*-CN)$_{trans}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.7$ (d, $^2J_{CP2} = 8.6$ Hz, CH_3-N-P_2), 32.9 (d, $^2J_{CP1} = 12.6$ Hz, CH_3-N-P_1), 43.9 (s, CH_2-CH=CH_2), 94.2 (s, (CH=CH-CN)$_{cis}$), 95.7 (s, (CH=CH-C≡N)$_{trans}$), 115.6 (s, (CH_2-CH=CH_2), 117.2 (s, (CH=CH-*C*≡N)$_{cis}$), 118.0 (s, (CH=CH-*C*≡N)$_{trans}$), 121.3 (m, C_0^2, C_1^2, C_{2cis}^2, C_{2trans}^2), 127.6 (s, C_1^3), 128.3 (s, C_0^3), 128.7 (s, C_{2trans}^3), 130.4 (s, C_{2cis}^3), 131.3 (s, C_{2cis}^4), 132.4 (brs, C_0^4, C_1^4), 132.6 (s, C_{2cis}^4), 135.7 (d, $^3J_{CP2} = 4.3$ Hz, CH_2-*C*H=CH_2), 136.8 (d, $^3J_{CP2} = 14.3$ Hz, $(CH=N)_1$), 138.5 (d, $^3J_{CP1} = 11.4$ Hz, $(CH=N)_0$), 147.4 (s, (CH=*C*H-CN)$_{cis}$), 149.2 (s, (CH=*C*H-CN)$_{trans}$), 150.9 (m, C_0^1, C_1^1), 152.5 (d, $^2J_{CP2} = 6.1$ Hz, C_{2cis}^1), 152.9 (d, $^2J_{CP2} = 7.0$ Hz, C_{2trans}^1). IR(KBr): 3401 (m, $\tilde{\nu}_{N-H}$), 2215 (m, $\tilde{\nu}_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{144}H_{144}N_{30}O_{21}P_{10}S_4$: C, 56.36; H, 4.73; N, 13.69. Found: C, 56.09; H, 4.61; N, 13.55.

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[1] Reviews: a) D. A. Tomalia, A. M. Naylor, W. A. Goddart III, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138; b) H. B. Mekelburger, W. Jaworek, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1571; c) D. A. Tomalia, H. D. Durst in *Topics in Current Chemistry, Vol. 165* (Ed.: E. Weber), Springer, Berlin, Heidelberg, **1993**, pp. 193; d) M. F. Ottaviani, S. Bossmann, N. J. Turro, D. A. Tomalia, *J. Am. Chem. Soc.* **1994**, *116*, 661; e) J. M. J. Fréchet, *Science* **1994**, *263*, 1710; f) J. Issberner, R. Moors, F. Vögtle, *Angew. Chem.* **1994**, *106*, 2507; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413; g) C. N. Moorefield, G. R. Newkome in *Advances in Dendritic Molecules, Vol. 1* (Ed.: G. R. Newkome), JAI Press, Greenwich CT, USA **1994**, p. 1; h) A.-M. Caminade, J.-P. Majoral, *Main Group Chemistry News* **1995**, *1*, 14; i) N. Ardoin, D. Astruc, *Bull. Soc. Chim. Fr.* **1995**, *132*, 876; j) P. J. Dandliker, F. Diederich, J. P. Gisselbrecht, A. Louati, M. Gross, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2725; k) S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto, V. Balzani, *Chem. Eur. J.* **1995**, *1*, 211; l) G. R. Newkome, R. Güther, C. N. Moorefield, F. Cardiello, L. Echegoyen, E. Perez-Cordero, H. Luftmann, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2023; m) R. G. Duan, L. L. Miller, D. A. Tomalia, *J. Am. Chem. Soc.* **1995**, *117*, 10783; n) M. F. Ottaviani, E. Cossu, J. N. Turro, D. A. Tomalia, *J. Am. Chem. Soc.* **1995**, *117*, 4387; o) J. F. G. A. Jansen, H. W. I. Peerlings, E. M. M. de Brabander-van der Berg, E. W. Meijer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1207.

[2] See for example: a) D. A. Tomalia, H. Baker, H. Dewald, M. Hall, C. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polym. J.* **1985**, *17*, 117; b) D. A. Tomalia, H. Baker, J. Dewald, M. Hall, C. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Macromolecules* **1986**, *19*, 2466; c) A. D. Meltzer, D. A. Tinell, A. A. Jones, D. Inglefield, M. Hedstrand, D. A. Tomalia, *ibid.* **1992**, *25*, 4541; d) D. A. Tomalia, *Top. Curr. Chem.* **1993**, *165*, 193; e) F. G. A. Jansen, E. M. M. de Brabander-van der Berg, E. W. Meijer, *Science* **1994**, *266*, 1226; f) K. Kadei, R. Moors, F. Vögtle, *Chem. Ber.* **1994**, *127*, 897; g) G. R. Newkome, X. Lin, *Macromolecules* **1991**, *24*, 1443.

[3] a) C. J. Hawker, J. M. J. Fréchet, *Macromolecules* **1990**, *23*, 4726; b) K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1993**, *115*, 11496; c) C. J. Hawker, K. L. Wooley, J. M. J. Fréchet, *J. Chem. Soc. Perkin Trans 1* **1993**, 1287.

[4] a) N. Launay, A.-M. Caminade, R. Lahana, J.-P. Majoral, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1589; b) C. Galliot, D. Prévoté, A.-M. Caminade, J.-P. Majoral, *J. Am. Chem. Soc.* **1995**, *117*, 5470; c) M. Slany, M. Bardaji, M. J. Casanove, A.-M. Caminade, J.-P. Majoral, B. Chaudret, *ibid.* **1995**, *117*, 9764.

[5] N. Launay, A.-M. Caminade, J.-P. Majoral, *J. Am. Chem. Soc.* **1995**, *117*, 3282.

[6] N. Launay, A.-M. Caminade, J.-P. Majoral, *J. Org. Chem.* **1996**, *61*, 3799.

0947-6539/96/0211-1426 $ 15.00+.25/0