Varying Topology of Dendrimers − A New Approach toward the Synthesis of Di-Block Dendrimers

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A new way to synthesise di-block dendrimers having two types of end groups located in two different areas of their surface is reported. It consists in growing, step-by-step, a second dendritic wedge from the core of a first dendron. This method is mainly applied to the synthesis of di-block dendrimers having phosphanyl groups on one part of the surface.

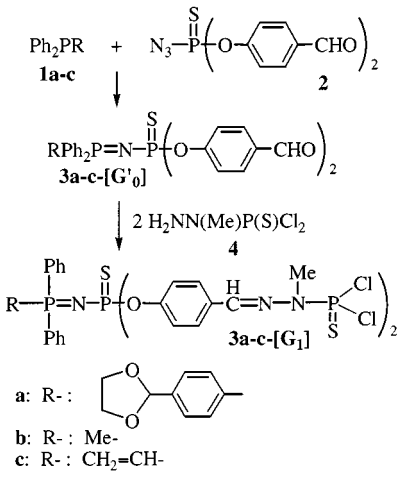
Introduction

The need for advanced materials has created a tremendous area of research in which dendrimers occupy a growing place.[1−8] Indeed, their very particular, highly branched architectures often exhibit unusual behaviours and properties. It has been largely demonstrated that both the nature of the branches and the nature of the terminal functions influence these properties, but less attention has been paid to the modification of shape or topology. One of the challenges in this area consists of synthesising dendritic molecules having two different properties, due to the location of two types of functional groups in definite areas of the molecular surface. Very few papers have reported the synthesis of this type of di-block dendrimer,[9−18] and all of them to date concern the grafting of two different dendrons by their cores. This type of approach appears to be the most straightforward, but is inapplicable when the surface functions of one dendron may interact with the core function of the other dendron. An alternative route to avoid this problem should consist in a step-by-step, divergent synthesis of a new dendritic wedge starting from the core of a dendron.

In the course of our research on the synthesis[19−29] and applications[30−38] of phosphorus-containing dendrimers, we report here our efforts to find suitable methodologies for obtaining di-block dendrimers by growing a second dendritic wedge from the core of one dendron. The crucial point in the envisaged strategy is the choice of the function that will be located at the core of the first dendron. We decided to use R−P=N−P=S linkages, since we have already demonstrated on one hand that the P=S group can be easily desulfurized to yield a tricoordinated phosphorus atom usable in Staudinger reactions,[24−27,39] and on the other hand that the electronic influence of the P=N−P=S group upon R, when R is a vinyl group, allows us to perform Michael-type additions of amines.[17−18] Depending on the nature of R, other reactions could be envisaged, and chosen in order to be compatible with the nature of the terminal functions. Due to their wide range of uses, particularly in catalysis, phosphanyl groups appear as an interesting function to be linked to one part of the surface of the final dendrimer, the other part of the surface being variously functionalized, for instance with ammonium salts, leading to water-soluble derivatives.

Results and Discussion

Most of the work that will be described here was carried out with low generation of dendrons, in order to be able to detect any defects. In fact, our aim was to validate, on relatively small compounds, methods that could also be used for larger compounds. The desired P=N−P=S linkages are easily obtained using the Staudinger reaction between phosphanes **1a−c** and the azide-dialdehyde **2**,[40] leading to dendrons **3a−c-[G′0]**. The next step in growing these dendrons was the condensation with the phosphorus hydrazide **4**, affording the first generation dendron **3a−c-[G1]** (Scheme 1).



Scheme 1

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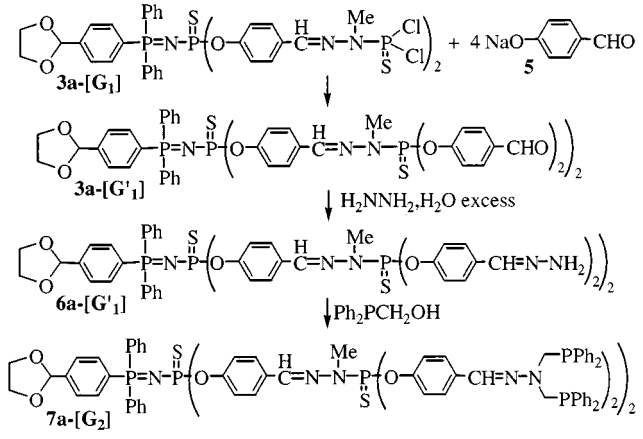
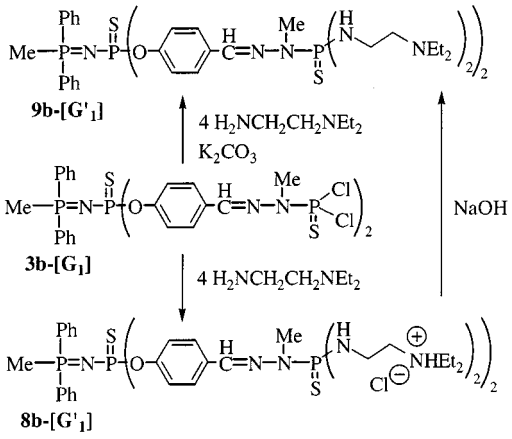
The continuation of the synthesis depends on the type of reactions envisaged at the core after the growing of the first dendron. For instance, the deprotection of the core of **3a-[G_1]** should regenerate an aldehyde group, whose reactivity with various amines could allow us to grow the second dendritic wedge. Thus, the functions located on the surface of the first dendron must be neither aldehydes, nor any group able to react with primary amines. We decided to graft diphosphanyl groups to the surface, using three steps from **3a-[G_1]**: i) substitution with hydroxybenzaldehyde sodium salt (**5**) leading to **3a-[G'_1]**, ii) condensation with hydrazine leading to **6a-[G'_1]**, iii) condensation with Ph_2PCH_2OH leading finally to **7a-[G_2]** (Scheme 2). The characterisation of compound **7a-[G_2]** shows that none of the preceding steps has damaged the acetal function, with the presence of multiplets at $\delta = 4.0$ for the CH_2CH_2 group and one singlet at $\delta = 5.79$ for the OCHO group in the ^1H NMR spectrum. Furthermore, no aldehyde group is detectable by ^1H or ^{13}C NMR. The next step should be the deprotection of the core. For this purpose, we used the classical method already applied to the deprotection of **1a**,[41] i.e. a catalytic amount (5%) of *p*-toluenesulfonic acid in acetone at 60 °C. However, a side reaction occurs at the level of the external groups of **7a-[G_2]**, which induces the total disappearance of the signal corresponding to the diphosphanyl groups in the ^{31}P NMR spectrum ($\delta = -25$) in favour of the appearance of new signals, in particular a singlet at $\delta = -41$, corresponding to Ph_2PH. The cleavage of the surface end groups precludes any use of **7a-[G_2]** for the growing of a second dendron from its core, consequently we decided to study the reactivity of **3b-[G_1]**, applying another strategy to obtain di-block dendrimers.



Scheme 2

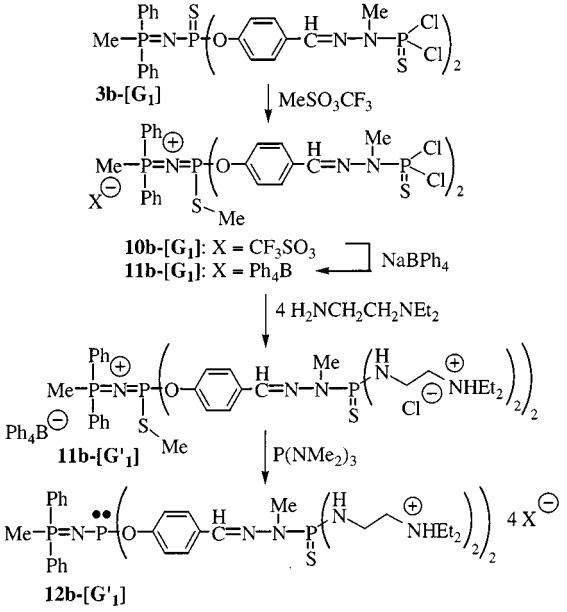
The only possible reactivity at the core of compound **3b-[G_1]** concerns the alkylation and desulfurization of the P=N−P=S linkage using $MeSO_3CF_3$ and $P(NMe_2)_3$ successively.[24−27,39] The first reagent is incompatible with the presence of phosphane groups on the surface of the first dendron, and the second one is incompatible with the P−Cl groups of **3b-[G_1]**, due to Cl/NMe_2 exchanges. Taking into account these constraints, we decided to graft ammonium groups to the surface of **3b-[G_1]**. Indeed, these functions should render the future di-block dendrimer water-soluble. The reaction of **3b-[G_1]** with 4 equiv. of $H_2NCH_2CH_2NEt_2$ affords compound **8b-[G'_1]** (Scheme 3) as expected.[17−18] This compound is soluble in a variety of solvents, either organic solvents such as chloroform and dichloromethane, or protic solvents such as ethanol, methanol, or water. Remarkably, compound **8b-[G'_1]** is stable for more than three weeks in water, even under acidic conditions at pH = 4.



Scheme 3

We tried to apply the first step of the desulfurization process, i.e. the alkylation of the P=S group by $MeSO_3CF_3$ to **8b-[G'_1]** in CH_2Cl_2 solution. Unexpectedly, addition of an excess of $MeSO_3CF_3$ is needed to observe the alkylation, characterised in the ^{31}P NMR spectra by the total disappearance of both doublets corresponding to the PNPS linkage at $\delta = 15.8$ (P=N) and 52.4 (P=S) ($^2J_{PP} = 32$ Hz) and the appearance of a singlet at $\delta = 23.6$. This signal is an AB system, totally degenerated, corresponding to the PNPSMe linkage.[24−27,39] However, other signals are also observed, corresponding to a side reaction presumably inducing the cleavage of the PNP linkage. This side reaction could be due to a reaction with CF_3SO_3H, which could be generated by an H/Me exchange on some ammonium groups. A way of avoiding this problem could be to deprotonate the ammonium groups before using CF_3SO_3Me. The neutral compound **9b-[G'_1]** is easily obtained from **8b-[G'_1]**, using NaOH in water. However, it was extremely difficult to eliminate the last traces of water, which should also generate triflic acid, thus we synthesised **9b-[G'_1]** by another way, the direct reaction of *N*,*N*-diethylethylenediamine with **3b-[G_1]** in the presence of potassium carbonate (Scheme 3); 3 equiv. of CF_3SO_3Me are then added to **9b-[G'_1]**, in order to alkylate both the PNPS and the NEt_2 groups. However, a side and unidentified product appears along with the expected product, thus we decided to avoid the presence of amine in the molecule, and to directly treat **3b-[G_1]** with CF_3SO_3Me.

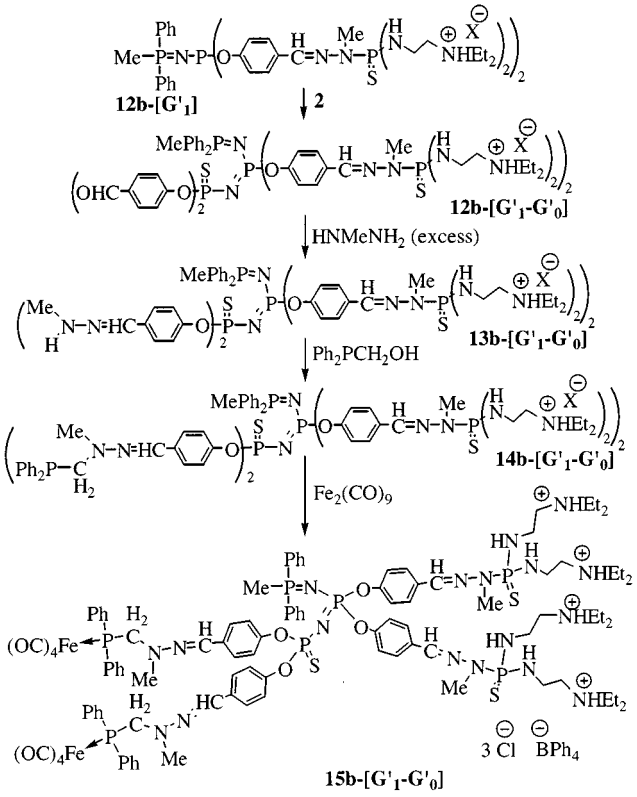
Addition of methyl triflate to **3b-[G_1]** cleanly affords compound **10b-[G_1]**, characterised in the ^{31}P NMR spectrum by the presence of two doublets (AB system) at $\delta = 23.8$ and 24.1 ($^2J_{PP} = 18.2$ Hz) for the PNPSMe linkage and one



Scheme 4

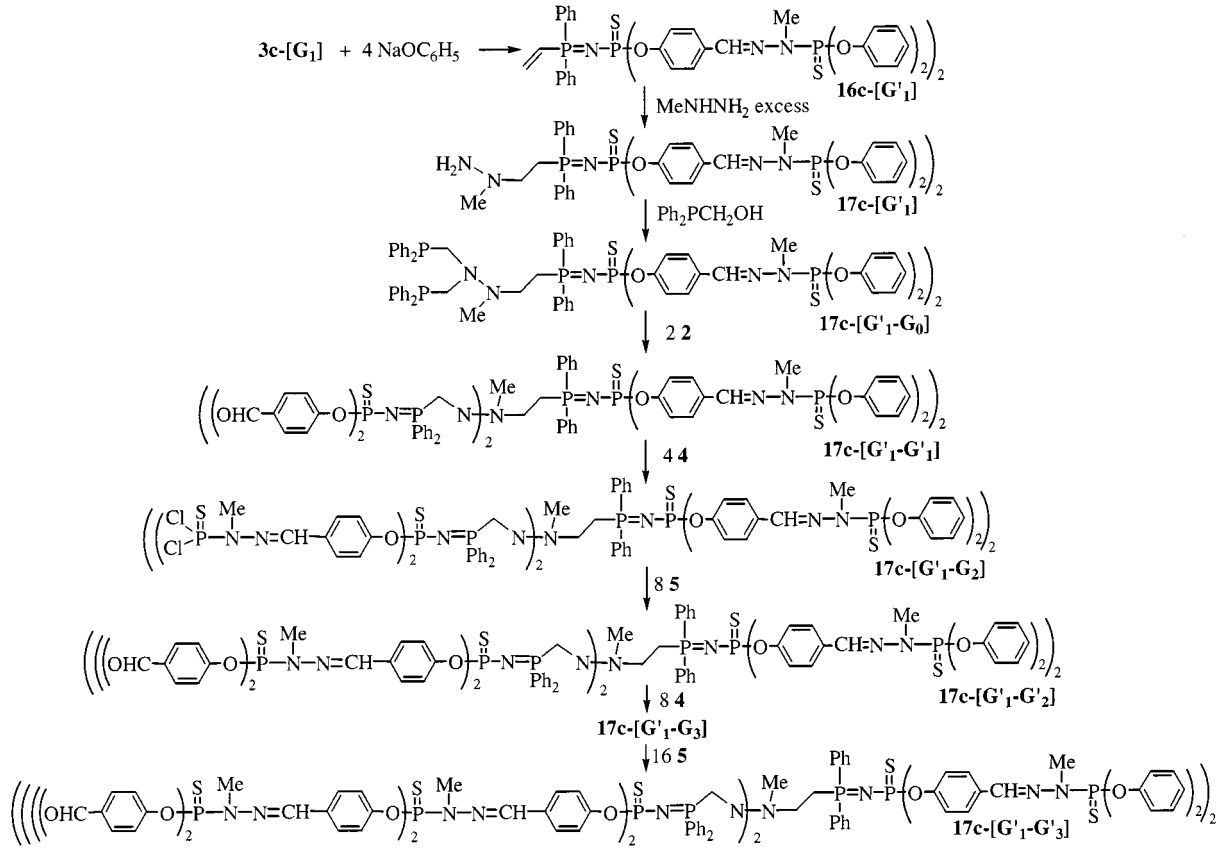
singlet at δ = 62.8 for the $P(S)Cl_2$ groups (Scheme 4). The second step of the desulfurization process, i.e. the reaction with $P(NMe_2)_3$ cannot be used with **10b-[G$_1$]**. Indeed, exchange reactions can take place, leading to partial or total substitution of the P−Cl bonds, with formation of $P(S)Cl(NMe_2)$ or $P(S)(NMe_2)_2$ end groups; thus, the P−Cl functions must be substituted first. The reaction of **10b-[G$_1$]** with *N*,*N*-diethylethylenediamine did not appear desirable, since it could also generate triflic acid. Thus, we decided first to proceed to an anion exchange with $NaBPh_4$. Elimination of CF_3SO_3Na allowed us to isolate **11b-[G$_1$]**. The anion exchange induces a broadening of the AB system, which gives only a signal having the appearance of a singlet for **11b-[G$_1$]**. No signal is detectable in the ^{19}F NMR spectrum, confirming the total exchange. Compound **11b-[G$_1$]** reacts cleanly with *N*,*N*-diethylenediamine to afford **11b-[G′$_1$]** (Scheme 4). The full substitution of the chlorine atoms is characterised in the ^{31}P NMR spectrum by the deshielding of the signal corresponding to the end groups from δ = 62.7 for **11b-[G$_1$]** to δ = 68.5 for **11b-[G′$_1$]**.

Reaction of **11b-[G′$_1$]** with $P(NMe_2)_3$ induces the expected desulfurization, as shown by the appearance of two doublets for the core at δ = 144.2 (P:) and δ = 10.3 (P=N) ($^2J_{PP}$ = 31.6 Hz) for **12b-[G′$_1$]**. This compound was not fully characterised due to its high sensitivity toward oxidation, but directly treated with the azide **2** (Scheme 5). The formation of the P=N−P=N−P=S linkage of compound **12b-[G′$_1$-G′$_0$]** is characterised by the appearance of two doublets at δ = 18.4 (P=N, $^2J_{PP}$ = 26 Hz) and δ = 47.5 (P=S, $^2J_{PP}$ = 58.4 Hz), and a doublet of doublet at δ = −9.6 (central P=N). The ^1H NMR spectrum shows the remaining end groups are in the cationic form. Indeed, all CH_2 and CH_3N groups form a multiplet for **12b-[G′$_1$-G′$_0$]**, as well as for the other compounds having a cationic form (see data for **8b-[G′$_1$]** and **11b-[G′$_1$]**), whereas the neutral form gives a quadruplet at δ = 3.39 for the NCH_2CH_3 groups, clearly distinguishable and separated from all the other CH_2 and CH_3N groups[32] (see data for **9b-[G′$_1$]**). Concerning the nature of the anionic part of **12b-[G′$_1$-G′$_0$]** (only Cl or a mixture of Cl and BPh_4), one can say that all the signals attributed to BPh_4 in the ^{13}C NMR spectra of **11b-[G$_1$]** and **11b-[G′$_1$]** are also detected for **12b-[G′$_1$-G′$_0$]**, and that the integration of the ^1H NMR spectrum indicates the presence of 1 equiv. of BPh_4. At least 95% of the initial quantity of BPh_4 remains in **12b-[G′$_1$-G′$_0$]**, thus its anionic part is constituted by 3 Cl^- and 1 BPh_4^-.



Scheme 5

Compound **12b-[G′$_1$-G′$_0$]** possesses two aldehyde groups that could allow the growing of the second dendritic wedge, using for instance the phosphorus hydrazide **4** followed by hydroxybenzaldehyde sodium salt (**5**). However, we decided to try the grafting of phosphanes. The first step in this process is the condensation of the aldehyde groups with methylhydrazine, leading to **13b-[G′$_1$-G′$_0$]**, characterised by the disappearance of the aldehyde signals in the ^1H and ^{13}C NMR and IR spectra. The grafting of phosphanes is carried out with Ph_2PCH_2OH, affording **14b-[G′$_1$-G′$_0$]**. Then, the phosphanes are readily complexed, in order to avoid any oxidation problem. As an example, the complexation was carried out with $Fe_2(CO)_9$ (Scheme 5). The formation of the complex **15b-[G′$_1$-G′$_0$]** is characterised by the large deshielding of the signal corresponding to the phosphane from δ = −22.9 for **14b-[G′$_1$-G′$_0$]** to δ = 67.5 for **15b-[G′$_1$-G′$_0$]**. The grafting of phosphanes at the previous step is confirmed by the deshielding of the signal of the methyl



Scheme 6

groups in the ^{13}C NMR spectrum from $\delta = 34.0$ for CH_3NH in **13b-[G′$_1$-G′$_0$]** to $\delta = 39.0$ for CH_3NCH_2 in **15b-[G′$_1$-G′$_0$]**.

Compound **15b-[G′$_1$-G′$_0$]** is a rather small compound, but it possesses all the characteristics of a di-block dendrimer, and the methodology developed here should be applicable to the synthesis of larger compounds. However, the full process is rather lengthy, thus we tried to find a more rapid method. Compound **3c-[G$_1$]** should offer such opportunity, since we have shown that a vinyl group linked to a P=N−P=S moiety reacts with primary and secondary amines under mild conditions.[17−18] However, amines also react with the P−Cl groups, so such reactions are inapplicable to **3c-[G$_1$]**. In order to avoid any problem in the future reactions, we decided to react **3c-[G$_1$]** with sodium phenolate, which gives neutral and poorly reactive end groups (Scheme 6). The reaction of **16c-[G′$_1$]** thus obtained with methylhydrazine leads to compound **17c-[G′$_1$]** by a Michael-type addition of the NHMe moieties on the vinyl group. The phosphanes are then grafted using again Ph_2PCH_2OH, leading to **17c-[G′$_1$-G$_0$]**. This compound is another example of a small di-block dendrimer possessing phosphanes in one part of the molecule.

It would be interesting to complex these phosphanes with transition metal ions, but we decided to use them to grow the second part of the di-block dendrimer by a Staudinger reaction with the azide **2**. The formation of **17c-[G′$_1$-G′$_1$]** is characterised in the ^{31}P NMR spectrum by the presence of two sets of two doublets corresponding to two types of P=N−P=S linkages in a 2:1 ratio at $\delta = 14.0$ and 50.0 ($^2J_{PP}$ = 26.0 Hz) for the NCH_2P=N−P=S groups and at $\delta = 16.7$ and 50.2 ($^2J_{PP}$ = 33.9 Hz) for the CH_2CH_2P=N−P=S group. The growing of the molecule is then carried out without any problem, using alternatively the phosphorus hydrazide **4** and hydroxybenzaldehyde sodium salt (**5**) (Scheme 6). The synthesis was stopped after obtaining dendrimer **17c-[G′$_1$-G′$_3$]** (Figure 1), but it could have been continued to higher generations. The presence of aldehyde groups on part of the surface of **17c-[G′$_1$-G′$_3$]** will open the way to a versatile reactivity, including for instance the grafting of phosphanyl groups, using the method already described in Scheme 2.

Conclusion

We have demonstrated that the growing of a second dendritic wedge from the core of a first dendron is an alternative route for the obtaining di-block dendrimers. This approach is less straightforward than the direct coupling of two dendrons by their cores, but it offers the possibility to have a variety of functional groups located in different areas. Even if several of the molecules presented in this paper are relatively small, we have shown that the methodologies developed here can also be applied to larger com-

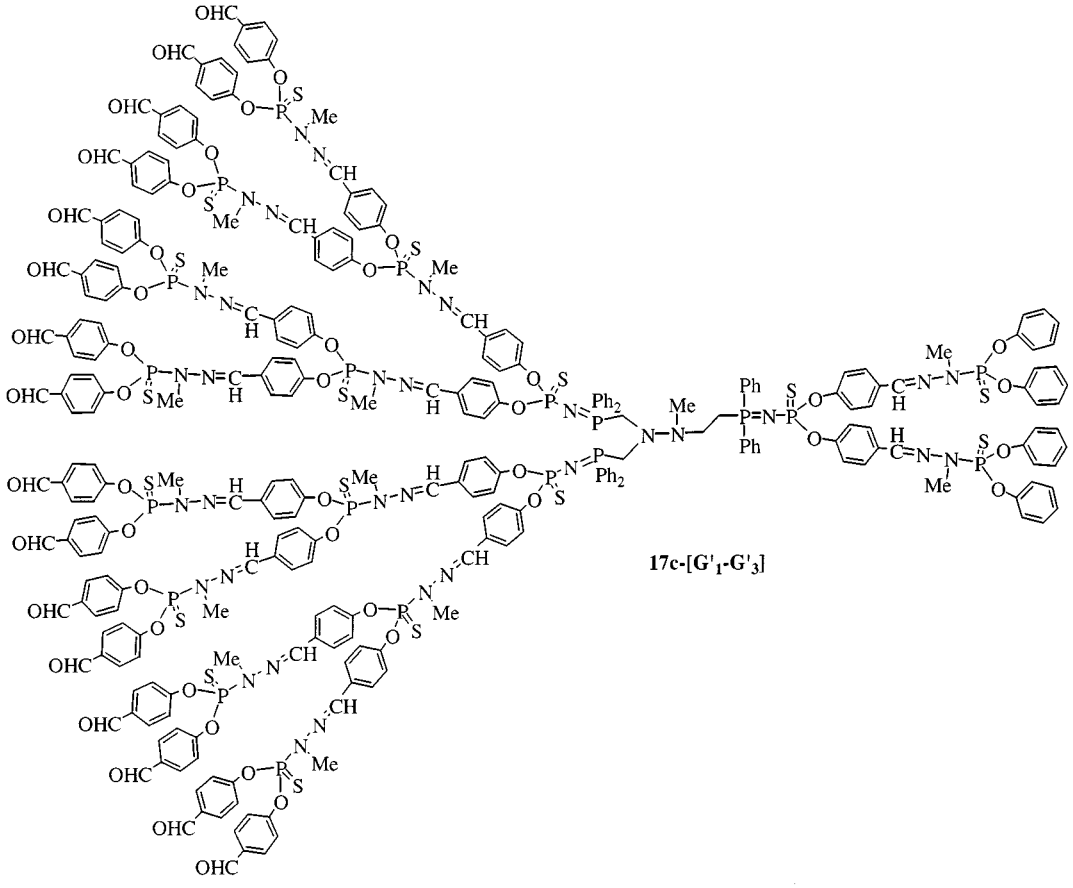


Figure 1. The di-block dendrimer **17c-[G′$_1$-G′$_3$]**

pounds, as indicated by the synthesis of the unsymmetrical third generation dendrimer **17c-[G′$_1$-G′$_3$]**. The presence of two types of end groups should provide new tools for chemistry. The presence of ammonium salts on one side and phosphanes on the other side, i.e. compounds such as **14b-[G′$_1$-G′$_0$]** should lead to biphasic dendritic catalysts. Furthermore, the presence of aldehydes on one side and of other functional groups on the other side of a di-block dendrimer should lead to covalent tailored material surface modifications as already shown with more classical dendrimers.[30−31]

Experimental Section

General Remarks: All reactions except those done in water, were carried out under argon, in the absence of air, using standard Schlenk techniques and vacuum-line manipulations. All solvents were dried and distilled before use. Solvents were also degassed when phosphanes were used. − Perkin−Elmer 1725X was used for FT-IR. − NMR spectra were recorded with Bruker AC80, AC200, or AM250 for ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR, with $SiMe_4$, H_3PO_4, and CF_3CO_2H as references, respectively. The attribution of ^{13}C NMR signals was done using Jmod, two-dimensional HMBC and HMQC, broad-band or CW ^{31}P decoupling experiments when necessary. The numbering scheme used for NMR is depicted Figure 2. − Compounds **1a**,[41] **2**,[40] **3c-[G′$_0$]** and **3c-[G$_1$]**[17] were synthesised according to published procedures.

Synthesis of 3a-[G′$_0$] and 3b-[G′$_0$]: A solution of azide **2** (1.911 g, 5.5 mmol) in THF (20 mL) was added to a solution of phosphane **1a** or **1b** (5 mmol) in THF (10 mL). The reaction induces a strong evolution of N_2. The reaction mixture was stirred for 6 h (**1a**) or 1 h (**1b**) at room temperature, then concentrated to dryness. The residue was dissolved in a minimum amount of CH_2Cl_2 (**1a**) or THF (**1b**) and precipitated with pentane (twice). Compound **3a-[G′$_0$]** was isolated as a white powder (2.482 g, 76% yield), and **3b-[G′$_0$]** was isolated as a pale beige oil (2.031 g, 78% yield).

3a-[G′$_0$]: ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 14.6 (d, $^2J_{PP}$ = 30.6 Hz, P_{00}), 50.2 (d, $^2J_{PP}$ = 30.6 Hz, P_0). − ^{1}H NMR ($CDCl_3$): δ = 4.03 (m, 2 H, CH_2), 4.11 (m, 2 H, CH_2), 5.82 (s, 1 H, OCHO), 7.28 (d, $^3J_{HH}$ = 8.5 Hz, 4 H, $C_0{}^2$H), 7.24−7.69 (m, 14 H, C_6H_5, C_6H_4), 7.77 (d, $^3J_{HH}$ = 8.5 Hz, 4 H, $C_0{}^3$H), 9.92 (s, 2 H, CHO). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 65.5 (s, CH_2), 102.7 (s, OCHO), 122.1 (d, $^3J_{CP}$ = 5 Hz, $C_0{}^2$), 126.8 (d, $^3J_{CP}$ = 14 Hz, $C^{3\prime}$), 128.0 (dd, $^1J_{CP}$ = 106 Hz, $^3J_{CP}$ = 4 Hz, $C_0{}^i$), 128. 8 (d, $^3J_{CP}$ = 14 Hz, $C_0{}^m$), 129.2 (br. d, $^1J_{CP}$ = 106 Hz, $C^{1\prime}$), 131.2 (s, $C_0{}^3$), 132.6 (s, $C_0{}^4$), 132.7 (d, $^2J_{CP}$ = 12 Hz, $C_0{}^o$), 132.9 (d, $^2J_{CP}$ = 11 Hz, $C^{2\prime}$), 132.9 (s, $C_0{}^p$), 142.9 (s, $C^{4\prime}$), 156.9 (d, $^2J_{CP}$ = 10 Hz, $C_0{}^1$), 191.1 (s, CHO). − IR (KBr): 1702 cm^{-1} ($\nu_{C=O}$). − $C_{35}H_{29}NO_6P_2S$ (653.63): calcd. C 64.32, H 4.47, N 2.14; found C 64.25, H 4.50, N 2.09.

3b-[G′$_0$]: ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 16.8 (d, $^2J_{PP}$ = 32.2 Hz, P_{00}), 51.0 (m, $^2J_{PP}$ = 32.2 Hz, P_0). − ^{1}H NMR ($CDCl_3$): δ = 2.19 (d, $^2J_{HP}$ = 13.2 Hz, 3 H, CH_3−P), 7.25−7.69 (m, 18 H, C_6H_5,

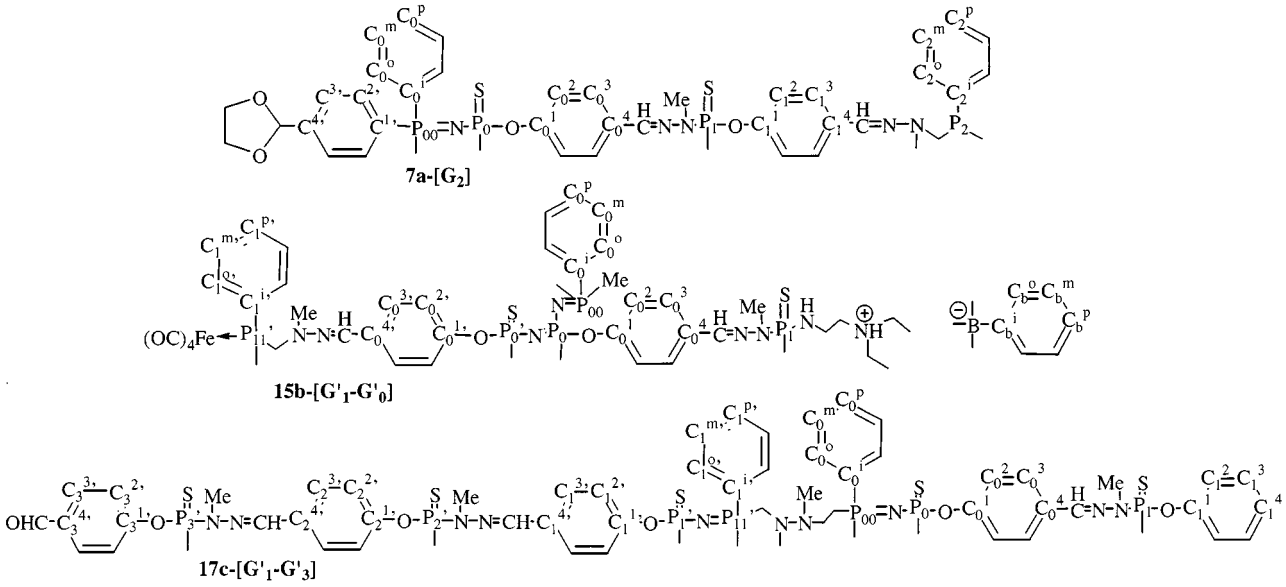


Figure 2. Numbering scheme used for NMR

C_6H_4), 9.77 (s, 2 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.4 (d, $^1J_{CP}$ = 67.4 Hz, CH_3−P), 122.0 (d, $^3J_{CP}$ = 5.9 Hz, C_0^2), 128.8 (s, C_0^3), 128.9 (d, $^3J_{CP}$ = 13.4 Hz, C_0^m), 129.7 (dd, $^1J_{CP}$ = 102.6 Hz, $^3J_{CP}$ = 6.5 Hz, C_0^i), 130.9 (d, $^2J_{CP}$ = 9.7 Hz, C_0^o), 131.2 (s, C_0^p), 132.7 (s, C_0^4), 156.8 (d, $^2J_{CP}$ = 9.9 Hz, C_0^1), 190.9 (s, CHO). − IR (KBr): 1702 cm^{-1} ($\nu_{C=O}$). − $C_{27}H_{23}NO_4P_2S$ (519.50): calcd. C 62.42, H 4.46, N 2.69; found C 62.28, H 4.41, N 2.75.

Synthesis of 3a-[G$_1$] and 3b-[G$_1$]: To a solution of compound **3a-[G′$_0$]** or **3b-[G′$_0$]** (1 mmol) in THF (20 mL) was added a 0.3 M solution of dichloro(1-methylhydrazido)thiophosphane (**4**) (2.2 mmol, slight excess). The reaction mixture was stirred overnight, then concentrated to dryness. Washing the residue twice with CH_2Cl_2/pentane afforded compounds **3a-[G$_1$]** (0.820 g, 84% yield) and **3b-[G$_1$]** (0.724 g, 86% yield) as white powders.

3a-[G$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 13.8 (d, $^2J_{PP}$ = 30.2 Hz, P_{00}), 51.4 (d, $^2J_{PP}$ = 30.2 Hz, P_0), 63.5 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 3.45 (d, $^3J_{HP}$ = 14.1 Hz, 6 H, CH_3N), 4.03 (m, 2 H, CH_2), 4.11 (m, 2 H, CH_2), 5.81 (s, 1 H, OCHO), 7.20 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HP}$ = 1 Hz, 4 H, C_0^2H), 7.39−7.69 (m, 16 H, C_6H_5, C_6H_4), 7.62 (d, $^3J_{HH}$ = 8.1 Hz, 4 H, C_0^3H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.9 (d, $^2J_{CP}$ = 13 Hz, CH_3N), 65.5 (s, CH_2), 102.7 (s, OCHO), 122.1 (d, $^3J_{CP}$ = 6 Hz, C_0^2), 126.7 (d, $^3J_{CP}$ = 14 Hz, C$^{3\prime}$), 128.4 (dd, $^1J_{CP}$ = 106 Hz, $^3J_{CP}$ = 4 Hz, C_0^i), 128.5 (s, C_0^3), 128.8 (d, $^3J_{CP}$ = 12 Hz, C_0^m), 129.5 (br. d, $^1J_{CP}$ = 106 Hz, C$^{1\prime}$), 130.2 (s, C_0^4), 132.8 (d, $^2J_{CP}$ = 11 Hz, C_0^o), 132.8 (s, C_0^p), 132.9 (d, $^2J_{CP}$ = 12 Hz, C$^{2\prime}$), 141.5 (d, $^3J_{CP}$ = 18 Hz, CH=N), 142.6 (s, C$^{4\prime}$), 153.6 (d, $^2J_{CP}$ = 10 Hz, C_0^1). − $C_{37}H_{35}Cl_4N_5O_4P_4S_3$ (975.62): calcd. C 45.55, H 3.62, N 7.18; found C 45.47, H 3.55, N 7.21.

3b-[G$_1$]: $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ = 15.5 (d, $^2J_{PP}$ = 34.6 Hz, P_{00}), 52.4 (d, $^2J_{PP}$ = 34.6 Hz, P_0), 62.1 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 2.28 (d, $^2J_{HP}$ = 13.2 Hz, 3 H, CH_3−P), 3.46 (d, $^2J_{HP}$ = 14.1 Hz, 6 H, CH_3−N−P), 7.24−7.65 (m, 20 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.6 (d, $^1J_{CP}$ = 68 Hz, CH_3−P), 31.8 (d, $^2J_{CP}$ = 14 Hz, CH_3−N−P), 122.0 (d, $^3J_{CP}$ = 4 Hz, C_0^2), 128.4 (s, C_0^3), 128.8 (d, $^3J_{CP}$ = 14 Hz, C_0^m), 130.2 (s, C_0^p), 131.0 (d, $^2J_{CP}$ = 12 Hz, C_0^o), 132.5 (d, $^4J_{CP}$ = 3 Hz, C_0^4), 141.3 (d, $^3J_{CP}$ = 19 Hz, CH=N), 153.5 (d, $^2J_{CP}$ = 8 Hz, C_0^1). − $C_{29}H_{29}Cl_4N_5O_2P_4S_3$ (841.48): calcd. C 41.39, H 3.47, N 8.32; found C 41.27, H 3.42, N 8.25.

Synthesis of 3a-[G′$_1$]: A solution of **3a-[G$_1$]** (0.293 g, 0.3 mmol) in THF (20 mL) was added to hydroxybenzaldehyde sodium salt (**5**) (0.181 g, 1.26 mmol, 5% excess). The resulting mixture was stirred overnight at room temperature, then centrifuged. The solution was concentrated to dryness and the residue was washed with THF/pentane. Compound **3a-[G′$_1$]** was isolated as a white powder (0.308 g, 78% yield).

3a-[G′$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 13.8 (d, $^2J_{PP}$ = 30.0 Hz, P_{00}), 51.6 (d, $^2J_{PP}$ = 30.0 Hz, P_0), 60.8 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 3.37 (d, $^3J_{HP}$ = 10.8 Hz, 6 H, CH_3N), 4.01 (m, 2 H, CH_2), 4.04 (m, 2 H, CH_2), 5.79 (s, 1 H, OCHO), 7.19 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, C_0^2H), 7.38 (d, $^3J_{HH}$ = 7.9 Hz, 8 H, C_1^2H), 7.4−7.7 (m, 16 H, CH=N, C_6H_5, C_6H_4), 7.57 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, C_0^3H), 7.85 (d, $^3J_{HH}$ = 7.9 Hz, 8 H, C_1^3H), 9.91 (s, 4 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.5 (d, $^2J_{CP}$ = 13 Hz, CH_3N), 65.5 (s, CH_2), 102.7 (s, OCHO), 122.0 (d, $^3J_{CP}$ = 6 Hz, C_0^2, C_1^2), 126.7 (d, $^3J_{CP}$ = 14 Hz, C$^{3\prime}$), 128.1 (s, C_0^3), 128.4 (dd, $^1J_{CP}$ = 106 Hz, $^3J_{CP}$ = 4 Hz, C_0^i), 128.8 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 129.5 (br. d, $^1J_{CP}$ = 106 Hz, C$^{1\prime}$), 130.5 (s, C_0^4), 131.5 (s, C_1^3), 132.8 (d, $^2J_{CP}$ = 9 Hz, C_0^o), 132.8 (s, C_0^p), 132.9 (d, $^2J_{CP}$ = 12 Hz, C$^{2\prime}$), 133.7 (s, C_1^4), 140.3 (d, $^3J_{CP}$ = 14 Hz, CH=N), 142.7 (s, C$^{4\prime}$), 153.3 (d, $^2J_{CP}$ = 10 Hz, C_0^1), 155.2 (d, $^2J_{CP}$ = 6 Hz, C_1^1), 190.8 (s, CHO). − IR (KBr): 1702 cm^{-1} ($\nu_{C=O}$). − $C_{65}H_{55}N_5O_{12}P_4S_3$ (1318.27): calcd. C 59.22, H 4.21, N 5.31; found C 59.10, H 4.15, N 5.24.

Synthesis of 6a-[G′$_1$]: A solution of **3a-[G′$_1$]** (0.264 g, 0.2 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a strongly stirred solution of hydrazine hydrate (40 mmol, very large excess) in CH_2Cl_2 (30 mL). The resulting mixture was stirred for 2 h at room temperature. The organic phase was separated, dried with Na_2SO_4, filtered, and concentrated to dryness. The residue was washed twice with CH_2Cl_2/pentane to give **6a-[G′$_1$]** as a white powder (0.256 g, 93% yield).

6a-[G′$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 13.8 (d, $^2J_{PP}$ = 29.0 Hz, P_{00}), 51.5 (d, $^2J_{PP}$ = 29.0 Hz, P_0), 62.4 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 3.30 (d, $^3J_{HP}$ = 10.7 Hz, 6 H, CH_3N), 3.99 (m, 2 H, CH_2), 4.02 (m, 2 H, CH_2), 5.48 (br. s, 8 H, NH_2), 5.78 (s, 1 H, OCHO), 7.17 (d, $^3J_{HH}$ = 8.5 Hz, 12 H, C_0^2H, C_1^2H), 7.45 (d, $^3J_{HH}$ = 8.5 Hz, 8 H, C_1^3H), 7.4−7.7 (m, 24 H, CH=N, C_6H_5, C_6H_4). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.9 (d, $^2J_{CP}$ = 13 Hz, CH_3N), 65.3 (s, CH_2), 102.5 (s, OCHO), 121.5 (d, $^3J_{CP}$ = 5 Hz, C_1^2), 121.8 (d, $^3J_{CP}$ = 5 Hz, C_0^2), 126.6 (d, $^3J_{CP}$ = 13 Hz, $C^{3\prime}$), 127.0 (s, C_1^3), 127.8 (s, C_0^3), 128.2 (dd, $^1J_{CP}$ = 106 Hz, $^3J_{CP}$ = 3 Hz, C_0^i), 128.5 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 130.0 (dd, $^1J_{CP}$ = 106 Hz, $^3J_{CP}$ = 4 Hz, $C^{1\prime}$), 130.7 (s, C_0^4), 132.4 (s, C_1^4), 132.6 (d, $^2J_{CP}$ = 10 Hz, C_0^o), 132.7 (s, C_0^p), 132.8 (d, $^2J_{CP}$ = 11 Hz, $C^{2\prime}$), 139.2 [d, $^3J_{CP}$ = 13 Hz, $(CH=N)_1$], 141.7 [s, $(CH=N)_2$], 142.4 (s, $C^{4\prime}$), 150.6 (d, $^2J_{CP}$ = 7 Hz, C_1^1), 152.9 (d, $^2J_{CP}$ = 9 Hz, C_0^1). − $C_{65}H_{63}N_{13}O_8P_4S_3$ (1374.4): calcd. C 56.81, H 4.62, N 13.25; found C 56.96, H 4.57, N 13.16.

Synthesis of 7a-[G$_2$]: A mixture of 1.0 mmol of paraformaldehyde and 1.0 mmol of diphenylphosphane was heated without solvent for 2 h at 120 °C in a closed reactor to afford Ph_2PCH_2OH. To this crude product was added a solution of **6a-[G′$_1$]** (0.137 g, 0.1 mmol) in THF (10 mL). The resulting mixture was stirred overnight at 80 °C, then concentrated to dryness. The residue was washed first with CH_2Cl_2/pentane, then with ether/pentane to afford **7a-[G$_2$]** as a white powder (0.219 g, 74% yield).

7a-[G$_2$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −25.1 (s, P_2), 13.7 (d, $^2J_{PP}$ = 29.6 Hz, P_{00}), 51.7 (d, $^2J_{PP}$ = 29.6 Hz, P_0), 63.2 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 3.33 (d, $^3J_{HP}$ = 9.3 Hz, 6 H, CH_3N), 3.98 (m, 2 H, CH_2), 4.03 (m, 2 H, CH_2), 4.19 (s, 16 H, CH_2), 5.79 (s, 1 H, OCHO), 7.10−7.80 (m, 124 H, CH=N, C_6H_5, C_6H_4). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.0 (d, $^2J_{CP}$ = 13 Hz, CH_3N), 56.8 (d, $^1J_{CP}$ = 7 Hz, CH_2P), 65.4 (s, CH_2O), 102.6 (s, OCHO), 121.5 (d, $^3J_{CP}$ = 5 Hz, C_1^2), 121.8 (d, $^3J_{CP}$ = 5 Hz, C_0^2), 126.6 (d, $^3J_{CP}$ = 14 Hz, $C^{3\prime}$), 127.2 (s, C_0^3, C_1^3), 128.2 (dd, $^1J_{CP}$ = 106 Hz, $^3J_{CP}$ = 3 Hz, C_0^i), 128.5 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 128.6 (d, $^3J_{CP}$ = 13 Hz, C_2^m), 128.9 (s, C_2^p), 129.9 (dd, $^1J_{CP}$ = 106 Hz, $^3J_{CP}$ = 4 Hz, $C^{1\prime}$), 130.7 (s, C_0^4), 131.3 (s, C_1^4), 132.6 (d, $^2J_{CP}$ = 10 Hz, C_0^o), 132.7 (s, C_0^p), 132.8 (d, $^2J_{CP}$ = 11 Hz, $C^{2\prime}$), 133.1 (d, $^2J_{CP}$ = 20 Hz, C_2^o), 133.1 [s, $(CH=N)_2$], 137.3 (d, $^1J_{CP}$ = 14 Hz, C_2^i), 139.3 [d, $^3J_{CP}$ = 13 Hz, $(CH=N)_1$], 142.5 (s, $C^{4\prime}$), 150.6 (d, $^2J_{CP}$ = 8 Hz, C_1^1), 152.9 (d, $^2J_{CP}$ = 9 Hz, C_0^1).

Synthesis of 8b-[G′$_1$]: To a solution of compound **3b-[G$_1$]** (0.500 g, 0.594 mmol) in THF (20 mL) was added dropwise a solution of *N*,*N*-diethylethylenediamine (334 μL, 2.377 mmol) in THF (20 mL). The reaction mixture was stirred for 12 h at room temperature, and a precipitate of compound **8b-[G′$_1$]** appears. The precipitate was recovered by filtration and washed twice with ether. Compound **8b-[G′$_1$]** was obtained as a white powder (0.528 g, 68% yield).

8b-[G′$_1$]: $^{31}P\{^1H\}$ NMR (THF): δ = 15.8 (d, $^2J_{PP}$ = 32 Hz, P_{00}), 52.4 (d, $^2J_{PP}$ = 32 Hz, P_0), 69.2 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 1.29 (t, $^3J_{HH}$ = 7 Hz, 24 H, CH_2-CH_3), 2.27 (d, $^2J_{HP}$ = 13.2 Hz, 3 H, CH_3-P), 3.16 (m, 6 H, CH_3-N), 3.27 (br. s, 16 H, CH_2-CH_2), 3.44 (q, $^3J_{HH}$ = 7 Hz, 16 H, CH_2-CH_3), 5.31 (d, $^2J_{HP}$ = 5.5 Hz, 4 H, NH), 7.13−7.70 (m, 20 H, C_6H_5, C_6H_4, CH=N), 9.18 (br. s, 4 H, NH^+). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 8.7 (s, CH_2-CH_3), 14.7 (d, $^2J_{CP}$ = 68 Hz, CH_3-P), 32.2 (d, $^2J_{CP}$ = 11 Hz, CH_3-N), 36.5 (s, CH_2-N^+), 47.4 (s, CH_2-CH_3), 52.9 (s, $NH-CH_2$), 121.7 (s, C_0^2), 127.7 (s, C_0^3), 128.9 (d, $^3J_{CP}$ = 12 Hz, C_0^m), 130.9 (d, $^2J_{CP}$ = 11 Hz, C_0^o), 131.7 (s, C_0^p), 132.5 (s, C_0^4), 137.3 (br. s, CH=N), 152.3 (d, $^2J_{CP}$ = 9 Hz, C_0^1). − $C_{53}H_{93}Cl_4N_{13}O_2P_4S_3$ (1306.3): calcd. C 48.73, H 7.17, N 13.93; found C 48.65, H 7.14, N 13.89.

Synthesis of 9b-[G′$_1$]: To a solution of compound **3b-[G$_1$]** (0.400 g, 0.473 mmol) and potassium carbonate (0.263 g, 1.9 mmol) in CH_2Cl_2 (20 mL), was added *N*,*N*-diethylethylenediamine (267 μL, 1.9 mmol). The reaction mixture was stirred for 6 h at room temperature, then centrifuged (10000 rpm) and filtered. The resulting solution was concentrated to dryness to give compound **9b-[G′$_1$]** as a white powder after two washings with ether (0.423 g, 77% yield).

9b-[G′$_1$]: $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ = 16.2 (d, $^2J_{PP}$ = 31 Hz, P_{00}), 52.7 (d, $^2J_{PP}$ = 31 Hz, P_0), 68.1 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 1.25 (t, $^3J_{HH}$ = 6.9 Hz, 24 H, CH_2-CH_3), 2.21 (d, $^2J_{HP}$ = 13.2 Hz, 3 H, CH_3-P), 3.08 (m, 6 H, CH_3-N), 3.19 (br. s, 16 H, CH_2-CH_2), 3.39 (q, $^3J_{HH}$ = 6.9 Hz, 16 H, CH_2-CH_3), 5.21 (d, $^2J_{HP}$ = 5.4 Hz, 4 H, NH), 7.10−7.64 (m, 20 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 8.7 (s, CH_2-CH_3), 14.7 (d, $^1J_{CP}$ = 68 Hz, CH_3-P), 32.1 (d, $^2J_{CP}$ = 11 Hz, CH_3-N-P), 36.6 (s, CH_2-N), 47.4 (s, CH_2-CH_3), 53.1 (d, $^2J_{CP}$ = 6 Hz, $NH-CH_2$), 121.7 (s, C_0^2), 127.7 (s, C_0^3), 128.9 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 130.9 (d, $^2J_{CP}$ = 10 Hz, C_0^o), 131.7 (s, C_0^p), 132.5 (s, C_0^4), 137.3 (d, $^3J_{CP}$ = 13 Hz, CH=N), 152.4 (d, $^2J_{CP}$ = 8 Hz, C_0^1). − $C_{53}H_{89}N_{13}O_2P_4S_3$ (1160.5): calcd. C 54.85, H 7.72, N 15.69; found C 54.86, H 7.59, N 15.58.

Synthesis of 10b-[G$_1$]: To a solution of compound **3b-[G$_1$]** (0.500 g, 0.594 mmol) in CH_2Cl_2 (20 mL), was added methyl triflate (68 μL, 0.601 mmol). The reaction mixture was stirred for 2 h at room temperature, then concentrated to dryness. The residue was washed twice with pentane to afford compound **10b-[G$_1$]** as a white powder (0.561 g, 94% yield).

10b-[G$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 23.8 (d, $^2J_{PP}$ = 18.2 Hz, P_{00} or P_0), 24.1 (d, $^2J_{PP}$ = 18.2 Hz, P_{00} or P_0), 62.8 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 2.18 (d, $^2J_{HP}$ = 12.4 Hz, 3 H, CH_3-P), 2.52 (d, $^3J_{HP}$ = 17.7 Hz, 3 H, CH_3-S), 3.48 (d, $^2J_{HP}$ = 13.9 Hz, 6 H, CH_3-N-P), 7.16−7.82 (m, 20 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.6 (s, CH_3-S), 15.1 (d, $^1J_{CP}$ = 73 Hz, CH_3-P), 32.1 (d, $^2J_{CP}$ = 13 Hz, CH_3-N-P), 120.9 (d, $^3J_{CP}$ = 4 Hz, C_0^2), 125.8 (d, $^1J_{CP}$ = 112 Hz, C^i), 129.6 (s, C_0^3), 129.7 (d, $^3J_{CP}$ = 14 Hz, C_0^m), 130.7 (d, $^2J_{CP}$ = 11 Hz, C_0^o), 133.4 (s, C_0^p), 134.2 (s, C_0^4), 140.5 (d, $^3J_{CP}$ = 18 Hz, CH=N), 150.1 (d, $^2J_{CP}$ = 10 Hz, C_0^1). − $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ = −1.9 (s, $CF_3SO_3^-$). − $C_{31}H_{32}Cl_4F_3N_5O_5P_4S_4$ (1005.6): calcd. C 37.02, H 3.20, N 6.96; found C 36.94, H 3.11, N 6.91.

Synthesis of 11b-[G$_1$]: To a solution of compound **10b-[G$_1$]** (0.420 g, 0.417 mmol) in CH_2Cl_2 (30 mL), was added $NaBPh_4$ (0.143 g, 0.417 mmol). The reaction mixture was stirred for 24 h, then filtered. The resulting solution was concentrated to dryness to afford compound **11b-[G$_1$]** as a white powder (0.436 g, 89% yield).

11b-[G$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 23.8 (br. s, P_{00} and P_0), 62.7 (s, $P(S)Cl_2$). − ^1H NMR ($CDCl_3$): δ = 1.50 (d, $^2J_{HP}$ = 12.3 Hz, 3 H, CH_3-P), 2.26 (d, $^3J_{HP}$ = 17.9 Hz, 3 H, CH_3-S), 3.30 (d, $^2J_{HP}$ = 13.9 Hz, 6 H, CH_3-N-P), 6.76−7.61 (m, 40 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.4 (d, $^2J_{CP}$ = 6 Hz, CH_3-S-P), 14.6 (d, $^1J_{CP}$ = 73 Hz, CH_3-P), 32.0 (d, $^2J_{CP}$ = 12 Hz, CH_3-N-P), 120.7 (d, $^3J_{CP}$ = 4 Hz, C_0^2), 121.7 (s, C_b^o), 125.5 (s, C_b^m), 125.6 (d, $^1J_{CP}$ = 112 Hz, C^i), 129.5 (s, C_0^3), 129.7 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 130.6 (d, $^2J_{CP}$ = 11 Hz, C_0^o), 133.4 (s, C_0^p), 134.3 (s, C_0^4), 136.3 (s, C_b^p), 139.9 (d, $^3J_{CP}$ = 19 Hz, CH=N), 149.9 (d, $^2J_{CP}$ = 11 Hz, C_0^1), 164.2 (q, $^1J_{CB}$ = 49 Hz, C_b^i). − $C_{54}H_{52}BCl_4N_5O_2P_4S_3$ (1175.7): calcd. C 55.16, H 4.45, N 5.95; found C 55.06, H 4.40, N 5.87.

Synthesis of 11b-[G′$_1$]: A solution of *N*,*N*-diethylethylenediamine (0.180 mL, 1.280 mmol) in CH_2Cl_2 (80 mL) was added to a solu-

tion of compound **11b-[G$_1$]** (0.360 g, 0.306 mmol) in CH_2Cl_2 (80 mL). The resulting mixture was stirred for 2 h, then concentrated to dryness. Compound **11b-[G′$_1$]** was obtained as a white powder after washings with ether (0.361 g, 71% yield).

11b-[G′$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 23.7 (br. s, P_{00} and P_0), 68.5 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 1.23 (t, $^3J_{HH}$ = 7.3 Hz, 24 H, CH_2-CH_3), 1.74 (d, $^2J_{HP}$ = 12.2 Hz, 3 H, CH_3-P), 2.34 (d, $^3J_{HP}$ = 17.7 Hz, 3 H, CH_3-S), 2.86−3.23 (m, 38 H, CH_2-CH_2, CH_2-CH_3, CH_3-N), 5.03 (d, $^2J_{HP}$ = 6 Hz, 4 H, NH−P), 6.78−7.77 (m, 40 H, C_6H_5, C_6H_4, CH=N), 10.00 (br. s, 4 H, NH^+). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 8.6 (s, CH_2-CH_3), 13.5 (d, $^2J_{CP}$ = 11 Hz, CH_3-S-P), 14.7 (d, $^1J_{CP}$ = 64 Hz, CH_3-P), 32.2 (d, $^2J_{CP}$ = 11 Hz, CH_3-N-P), 36.4 (s, CH_2-NH^+), 47.3 (s, CH_2-CH_3), 53.1 (s, $NH-CH_2$), 120.7 (d, $^3J_{CP}$ = 4 Hz, C_0^2), 121.9 (s, C_b^o), 125.6 (s, C_b^m), 125.7 (d, $^1J_{CP}$ = 110 Hz, C_0^i), 128.8 (s, C_0^3), 129.8 (d, $^3J_{CP}$ = 12 Hz, C_0^m), 130.7 (d, $^2J_{CP}$ = 10 Hz, C_0^o), 134.4 (s, C_0^4), 134.8 (d, $^3J_{CP}$ = 10 Hz, CH=N), 136.0 (s, C_b^p), 149.0 (d, $^2J_{CP}$ = 10 Hz, C_0^1), 164.0 (q, $^1J_{CB}$ = 49 Hz, C_b^i). − $C_{78}H_{116}BCl_4N_{13}O_2P_4S_3$ (1640.6): calcd. C 57.10, H 7.12, N 11.09; found C 56.97, H 7.04, N 10.98.

Synthesis of 12b-[G′$_1$]: To a solution of compound **11b-[G′$_1$]** (0.300 g, 0.204 mmol) in CH_2Cl_2 (30 mL), was added $P(NMe_2)_3$ (0.270 mL, 1.428 mmol, excess). The resulting mixture was stirred for 1 h, then concentrated to dryness. Compound **12b-[G′$_1$]** was extracted with toluene; this solution was concentrated to dryness to afford compound **12b-[G′$_1$]**, which was used without further purification.

12b-[G′$_1$]: $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ = 10.3 (d, $^2J_{PP}$ = 31.6 Hz, P_{00}), 68.5 (s, P_1), 144.2 (d, $^2J_{PP}$ = 31.6 Hz, P_0).

Synthesis of 12b-[G′$_1$-G′$_0$]: To a solution of compound **12b-[G′$_1$]** (0.253 g, 0.200 mmol) in CH_2Cl_2 (10 mL), was added a solution of azide **2** (0.083 g, 0.234 mmol, slight excess) in CH_2Cl_2 (10 mL). The resulting mixture was stirred for 1 h, then concentrated to dryness. The residue was washed three times with pentane to afford compound **12b-[G′$_1$-G′$_0$]** as a white powder (0.315 g, 84% yield).

12b-[G′$_1$-G′$_0$]: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −9.6 (dd, $^2J_{PP}$ = 26 Hz, $^2J_{PP}$ = 58.4 Hz, P_0), 18.4 (d, $^2J_{PP}$ = 26 Hz, P_{00}), 47.5 (d, $^2J_{PP}$ = 58.4 Hz, P_0'), 70.4 (s, P_1). − ^1H NMR (CD_2Cl_2): δ = 1.26 (t, $^3J_{HH}$ = 6.8 Hz, 24 H, CH_2-CH_3), 2.28 (d, $^2J_{HP}$ = 15.8 Hz, 3 H, CH_3-P), 2.41−3.29 (m, 38 H, CH_2-CH_2, CH_2-CH_3, CH_3-N-P), 5.40 (br. s, 4 H, NH−P), 6.84−7.81 (m, 48 H, C_6H_5, C_6H_4, CH=N), 9.93 (s, 2 H, CHO). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 8.7 (s, CH_2-CH_3), 15.6 (d, $^1J_{CP}$ = 69 Hz, CH_3-P), 32.3 (d, $^2J_{CP}$ = 11 Hz, CH_3-N-P), 36.8 (s, CH_2-NH^+), 47.6 (s, CH_2-CH_3), 53.2 (s, $NH-CH_2$), 121.0 (d, $^3J_{CP}$ = 6 Hz, $C_0^{2\prime}$), 121.4 (d, $^3J_{CP}$ = 4 Hz, C_0^2), 122.0 (s, C_b^0), 125.8 (s, C_b^m), 127.9 (s, $C_0^{3\prime}$), 128.1 (s, C_0^3), 129.3 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 131.2 (d, $^2J_{CP}$ = 12 Hz, C_0^o), 132.2 (s, C_0^4), 132.7 (br. s, $C_0^{4\prime}$), 133.1 (s, C_0^p), 136.1 (s, C_b^p), 137.1 (d, $^3J_{CP}$ = 13 Hz, CH=N), 151.9 (d, $^2J_{CP}$ = 10 Hz, C_0^1), 157.1 (d, $^2J_{CP}$ = 8 Hz, $C_0^{1\prime}$), 164.2 (q, $^1J_{CB}$ = 49 Hz, C_b^i), 191.6 (s, CHO). − IR (KBr): 1701 cm^{-1} ($\nu_{C=O}$). − $C_{91}H_{123}BCl_3N_{14}O_6P_5S_3$ (1877.3): calcd. C 58.22, H 6.60, N 10.44; found C 58.14, H 6.54, N 10.38.

Synthesis of 13b-[G′$_1$-G′$_0$]: To a solution of compound **12b-[G′$_1$-G′$_0$]** (0.250 g, 0.158 mmol) in CH_2Cl_2 (15 mL) was added a large excess of methylhydrazine (0.168 mL, 3.15 mmol). The reaction mixture was stirred for 12 h, then concentrated to dryness. The residue was washed several times with ether to afford compound **13b-[G′$_1$-G′$_0$]** as a white powder (0.223 g, 73% yield).

13b-[G′$_1$-G′$_0$]: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −9.6 (dd, $^2J_{PP}$ = 26.3 Hz, $^2J_{PP}$ = 57 Hz, P_0), 17.9 (d, $^2J_{PP}$ = 26.3 Hz, P_{00}), 48.7 (d, $^2J_{PP}$ = 57 Hz, P_0'), 70.3 (s, P_1). − ^1H NMR (CD_2Cl_2): δ = 1.06 (t, $^3J_{HH}$ = 7.2 Hz, 24 H, CH_2-CH_3), 2.23 (d, $^2J_{HP}$ = 15.6 Hz, 3 H, CH_3-P), 2.58−2.80 (m, 16 H, CH_2-CH_2), 2.92 (s, 6 H, CH_3-NH), 3.05−3.20 (m, 22 H, CH_2-CH_3, CH_3-N-P), 4.43 (s, 2 H, CH_3-N*H*), 5.22 (br. s, 4 H, NH−P), 6.84−7.57 (m, 50 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 8.7 (s, CH_2-CH_3), 15.5 (d, $^1J_{CP}$ = 67 Hz, CH_3-P), 32.3 (d, $^2J_{CP}$ = 11 Hz, CH_3-N-P), 34.0 (s, CH_3NH), 36.8 (s, CH_2-NH^+), 47.5 (s, CH_2-CH_3), 53.2 (s, $NH-CH_2$), 121.2 (d, $^3J_{CP}$ = 5 Hz, $C_0^{2\prime}$), 121.5 (d, $^3J_{CP}$ = 4 Hz, C_0^2), 121.9 (s, C_b^0), 125.8 (s, C_b^m), 126.4 (s, $C_0^{3\prime}$), 128.0 (s, C_0^3), 129.2 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 131.2 (d, $^2J_{CP}$ = 12 Hz, C_0^o), 132.0 (s, C_0^4), 132.5 (br. s, $C_0^{4\prime}$), 133.1 (s, C_0^p), 133.8 (s, CH=N-NH), 136.1 (s, C_b^p), 137.2 (d, $^3J_{CP}$ = 13 Hz, CH=N-NP), 151.8 (d, $^2J_{CP}$ = 9 Hz, C_0^1), 153.9 (d, $^2J_{CP}$ = 8 Hz, $C_0^{1\prime}$), 164.2 (q, $^1J_{CB}$ = 49 Hz, C_b^i). − $C_{93}H_{131}BCl_3N_{18}O_4P_5S_3$ (1933.4): calcd. C 57.77, H 6.82, N 13.04; found C 57.64, H 6.75, N 12.94.

Synthesis of 14b-[G′$_1$-G′$_0$]: To a solution of compound **13b-[G′$_1$−G′$_0$]** (0.100 g, 0.062 mmol) in CH_2Cl_2 (5 mL) was added a solution 0.119 M of Ph_2PCH_2OH (1.04 mL, 0.124 mmol) in CH_2Cl_2. The reaction mixture was stirred for 12 h at 40 °C, then was concentrated to dryness. The residue was washed three times with pentane to afford **14b-[G′$_1$-G′$_0$]** as a white powder (0.101 g, 76% yield).

14b-[G′$_1$-G′$_0$]. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ = −22.9 (s, P_{11}'), −11.8 (dd, $^2J_{PP}$ = 26.5 Hz, $^2J_{PP}$ = 56.6 Hz, P_0), 15.6 (d, $^2J_{PP}$ = 26.5 Hz, P_{00}), 46.5 (d, $^2J_{PP}$ = 56.6 Hz, P_0'), 68.1 (s, P_1).

Synthesis of 15b-[G′$_1$-G′$_0$]: To a solution of compound **14b-[G′$_1$-G′$_0$]** (0.101 g, 0.049 mmol) in CH_2Cl_2 (10 mL) was added a solution of $Fe_2(CO)_9$ (0.054 g, 0.147 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred for 12 h, then filtered. The solution was concentrated to dryness, and the residue was washed twice with ether to afford compound **15b-[G′$_1$-G′$_0$]** as a brown powder (0.106 g, 81% yield).

15b-[G′$_1$-G′$_0$]: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −9.3 (m, P_0), 17.4 (d, $^2J_{PP}$ = 26.5 Hz, P_{00}), 48.4 (d, $^2J_{PP}$ = 54.9 Hz, P_0'), 69.5 (s, P_{11}'), 70.9 (s, P_1). − ^1H NMR (CD_2Cl_2): δ = 1.28 (br. s, 24 H, CH_2-CH_3), 2.26 (d, $^2J_{HP}$ = 15.7 Hz, 3 H, CH_3-P), 2.70−2.94 (m, 38 H, CH_3-N-CH_2, CH_2-CH_2, CH_2-CH_3), 3.26 (m, 6 H, CH_3-N-P), 5.05 (br. s, 4 H, CH_2-P-Fe), 6.74−7.89 (m, 70 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 8.9 (s, CH_2-CH_3), 15.4 (d, $^1J_{CP}$ = 67 Hz, CH_3-P), 32.1 (br. s, CH_3-N-P), 37.0 (s, CH_2-NH^+), 39.0 (s, CH_2NCH_3), 47.4 (s, CH_2-CH_3), 52.9 (s, $NH-CH_2$), 56.3 (d, $^1J_{CP}$ = 74 Hz, CH_2-P), 121.3 (d, $^3J_{CP}$ = 5 Hz, $C_0^{2\prime}$) 121.6 (d, $^3J_{CP}$ = 4 Hz, C_0^2), 121.9 (s, C_b^o), 125.8 (s, C_b^m), 126.3 (br. s, $C_0^{3\prime}$), 127.9 (br. s, C_0^3), 128.7 (br. s, $C_1^{m\prime}$), 129.1 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 130.5 (s, $C_1^{p\prime}$), 131.2 (d, $^2J_{CP}$ = 12 Hz, C_0^o), 131.2 (s, CH=N-NH), 131.7 (br. s, C_0^4), 132.3 (br. s, $C_0^{4\prime}$), 132.8 (d, $^1J_{CP}$ = 32 Hz, $C_1^{i\prime}$), 132.9 (d, $^2J_{CP}$ = 10 Hz, $C_1^{o\prime}$), 133.2 (s, C_0^p), 136.1 (s, C_b^p), 137.3 (br. s, CH=N), 149.6 (d, $^2J_{CP}$ = 8 Hz, $C_0^{1\prime}$), 151.8 (d, $^2J_{CP}$ = 9 Hz, C_0^1), 164.2 (q, $^1J_{CB}$ = 49 Hz, C_b^i), 213.1 (d, $^2J_{CP}$ = 18 Hz, CO). − IR (KBr): 2043, 1972, 1939 cm^{-1} (ν_{CO}). − $C_{127}H_{153}BCl_3Fe_2N_{18}O_{12}P_7S_3$ (2665.6): calcd. C 57.22, H 5.78, N 9.45; found C 57.13, H 5.69, N 9.39.

Synthesis of 16c-[G′$_1$]: NaOPh (0.487 g, 4.2 mmol) was added to a solution of **3c-[G$_1$]** (0.854 g, 1 mmol) in THF (20 mL). The resulting mixture was stirred overnight at room temperature, then centrifuged. The solution was concentrated to dryness and the residue was washed several times with THF/pentane (1:5). Compound **16c-[G′$_1$]** was isolated as a pale beige powder (1.062 g, 98% yield).

16c-[G′$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 9.6 (d, $^2J_{PP}$ = 31.3 Hz, P_{00}), 52.2 (d, $^2J_{PP}$ = 31.3 Hz, P_0), 61.8 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 3.34 (d, $^3J_{HP}$ = 10.6 Hz, 6 H, CH_3N-P), 6.12 (ddd, $^3J_{HP}$ = 24.1 Hz, $^3J_{HH}$ = 18.3 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, HC=CH_EH_Z*), 6.43 (ddd, $^3J_{HP}$ = 45.9 Hz, $^3J_{HH}$ = 12.4 Hz, $^2J_{HH}$ = 1.1 Hz, 1 H, HC=CH_EH_Z*), 6.82 (dddd, $^2J_{HP}$ = 25.2 Hz, $^3J_{HH}$ = 18.3 Hz, $^3J_{HH}$ = 12.4 Hz, $^4J_{HP}$ = 1.1 Hz, 1 H, HC=CH_EH_Z*), 7.20−7.70 (m, 40 H, C_6H_5, C_6H_4, CH=N) (*: *E* and *Z* refer to the relative position of H versus H through C=C). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.9 (d, $^2J_{CP}$ = 13 Hz, CH_3N-P), 121.3 (d. $^3J_{CP}$ = 4 Hz, C_1^2), 121.8 (d, $^3J_{CP}$ = 5 Hz, C_0^2), 125.2 (s, C_1^4), 127.8 (dd, $^1J_{CP}$ = 100 Hz, $^3J_{CP}$ = 4 Hz, C_0^i), 127.8 (s, C_0^3), 128.6 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 129.3 (s, C_1^3), 130.9 (s, C_0^4), 132.0 (d, $^2J_{CP}$ = 11 Hz, C_0^o), 132.5 (d, $^4J_{CP}$ = 2 Hz, C_0^p), 136.6 (s, CH_2=), 138.9 (d, $^3J_{CP}$ = 13 Hz, C_0^4-*C*H=N), 150.5 (d, $^2J_{CP}$ = 7 Hz, C_0^1), 152.8 (d, $^2J_{CP}$ = 9 Hz, C_1^1). − $C_{54}H_{49}N_5O_6P_4S_3$ (1084.1): calcd. C 59.83, H 4.55, N 6.46; found C 59.76, H 4.48, N 6.40.

Synthesis of 17c-[G′$_1$]: To a solution of compound **16c-[G′$_1$]** (0.542 g, 0.500 mmol) in THF (20 mL) were added 30 equiv. of methylhydrazine (0.800 mL, 15 mmol). The resulting solution was stirred for 3 h at room temperature, then concentrated to dryness. Washing several times with a mixture THF/pentane (1:5) afforded compound **17c-[G′$_1$]** as a white powder (0.537 g, 95% yield).

17c-[G′$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 17.9 (d, $^2J_{PP}$ = 32.9 Hz, P_{00}), 52.0 (d, $^2J_{PP}$ = 32.9 Hz, P_0), 62.4 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 2.33 (s, 3 H, CH_3-N-NH_2), 2.65 (m, 2 H, CH_2-CH_2-P), 2.71 (br. s, 2 H, NH_2), 3.02 (m, 2 H, CH_2CH_2-P), 3.34 (d, $^3J_{HP}$ = 10.7 Hz, 6 H, CH_3N-P), 7.20−7.70 (m, 40 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.4 (d, $^1J_{CP}$ = 66 Hz, CH_2CH_2-P), 33.1 (d, $^2J_{CP}$ = 13 Hz, CH_3N-P), 50.6 (s, CH_3-N-NH_2), 54.4 (s, CH_2-CH_2-P), 121.5 (s, C_1^2), 122.1 (d, $^3J_{CP}$ = 3 Hz, C_0^2), 125.4 (s, C_1^4), 127.9 (s, C_0^3), 128.8 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 129.5 (s, C_1^3), 131.1 (s, C_0^4), 131.4 (d, $^2J_{CP}$ = 10 Hz, C_0^o), 132.5 (s, C_0^p), 139.0 (d, $^3J_{CP}$ = 14 Hz, C_0^4-*C*H=N), 150.7 (d, $^2J_{CP}$ = 7 Hz, C_0^1), 153.0 (d, $^2J_{CP}$ = 8 Hz, C_1^1). − $C_{55}H_{55}N_7O_6P_4S_3$ (1130.2): calcd. C 58.45, H 4.90, N 8.67; found C 58.38, H 4.85, N 8.63.

Synthesis of 17c-[G′$_1$-G$_0$]: A solution of compound **17c-[G′$_1$]** (0.150 g, 0.133 mmol) in THF (15 mL) was added to Ph_2PCH_2OH (obtained as described for **7a-[G$_2$]**) and heated at 90 °C under stirring for 12 h, then concentrated to dryness. Washing several times with a mixture THF/pentane (1:5) afforded compound **17c-[G′$_1$-G$_0$]** as a white powder (0.177 g, 87% yield).

17c-[G′$_1$-G$_0$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −24.1 (s, P_{11}'), 18.2 (d, $^2J_{PP}$ = 30.3 Hz, P_{00}), 51.6 (d, $^2J_{PP}$ = 30.3 Hz, P_0), 62.9 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 2.12 (s, 3 H, CH_3-N-CH_2), 2.42−2.75 (m, 4 H, CH_2-CH_2-P), 3.34 (d, $^3J_{HP}$ = 10.2 Hz, 6 H, CH_3-N-P), 3.54 (br. s, 4 H, $N-CH_2-P$), 7.20−7.80 (m, 60 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 26.4 (d, $^1J_{CP}$ = 58 Hz, CH_2CH_2-P), 33.4 (d, $^2J_{CP}$ = 13 Hz, CH_3-N-P), 33.9 (s, CH_3-N-CH_2), 47.3 (s, CH_2-CH_2-P), 53.0 (s, NCH_2-P), 121.9 (d, $^3J_{CP}$ = 5 Hz, C_1^2), 122.4 (d, $^3J_{CP}$ = 5 Hz, C_0^2), 125.8 (s, C_1^4), 128.4 (s, C_0^3), 128.6 (d, $^3J_{CP}$ = 7 Hz, $C_1^{m\prime}$), 129.0 (d, $^3J_{CP}$ = 13 Hz, C_0^m), 129.1 (s, $C_1^{p\prime}$), 129.9 (s, C_1^3), 131.4 (s, C_0^4), 131.7 (d, $^2J_{CP}$ = 9 Hz, C_0^o), 132.6 (s, C_0^p), 133.6 (d, $^2J_{CP}$ = 19 Hz, $C_1^{o\prime}$), 138.1 (d, $^1J_{CP}$ = 14 Hz, $C_1^{i\prime}$), 139.4 (d, $^3J_{CP}$ = 14 Hz, C_0^4-*C*H=N), 151.1 (d, $^2J_{CP}$ = 7 Hz, C_0^1), 153.6 (d, $^2J_{CP}$ = 9 Hz, C_1^1). − $C_{81}H_{77}N_7O_6P_6S_3$ (1526.6): calcd. C 63.73, H 5.08, N 6.42; found C 63.67, H 5.01, N 6.39.

Synthesis of 17c-[G′$_1$-G′$_1$]: A solution of azide **2** (0.073 g, 0.210 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of **17c-[G′$_1$-G$_0$]** (0.135 g, 0.100 mmol) in CH_2Cl_2 (15 mL). The resulting solution was stirred overnight at room temperature, then concentrated to dryness. The residue was washed with THF/pentane (1:5) to give **17c-[G′$_1$-G′$_1$]** as a white powder (0.201 g, 93% yield).

17c-[G′$_1$-G′$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 14.0 (d, $^2J_{PP}$ = 26.0 Hz, P_{11}'), 16.7 (d, $^2J_{PP}$ = 33.9 Hz, P_{00}), 50.0 (d, $^2J_{PP}$ = 26.0 Hz, P_1'), 50.2 (d, $^2J_{PP}$ = 33.9 Hz, P_0), 62.5 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 1.83 (s, 3 H, CH_3-N-CH_2), 2.40−2.72 (m, 4 H, CH_2-CH_2-P), 3.34 (d, $^3J_{HP}$ = 10.5 Hz, 6 H, CH_3-N-P), 4.32 (m, 4 H, NCH_2-P), 7.00−7.80 (m, 76 H, C_6H_5, C_6H_4, CH=N), 9.92 (s, 4 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.8 (d, $^1J_{CP}$ = 64 Hz, CH_2CH_2-P), 33.0 (d, $^2J_{CP}$ = 13 Hz, CH_3-N-P), 35.3 (s, CH_3-N-CH_2), 46.4 (s, CH_2-CH_2-P), 50.4 (d, $^1J_{CP}$ = 87 Hz, NCH_2-P), 121.4 (d, $^3J_{CP}$ = 4 Hz, C_1^2), 121.7 (d, $^3J_{CP}$ = 5 Hz, C_0^2, $C_1^{2\prime}$), 125.4 (s, C_1^4), 128.0 (s, C_0^3), 128.8 (d, $^3J_{CP}$ = 11 Hz, C_0^m, $C_1^{m\prime}$), 129.5 (s, C_1^3), 131.2 (s, $C_1^{3\prime}$), 131.4 (s, C_0^4), 132.2 (d, $^2J_{CP}$ = 9 Hz, C_0^o, $C_1^{o\prime}$), 132.6 (s, C_0^p, $C_1^{p\prime}$, $C_1^{4\prime}$), 138.7 (d, $^3J_{CP}$ = 14 Hz, C_0^4-*C*H=N), 150.6 (d, $^2J_{CP}$ = 6 Hz, C_0^1), 152.8 (d, $^2J_{CP}$ = 10 Hz, C_1^1), 156.5 (d, $^2J_{CP}$ = 8 Hz, $C_1^{1\prime}$), 190.0 (s, CHO). − IR (KBr): 1702 cm^{-1} ($\nu_{C=O}$). − $C_{109}H_{97}N_9O_{14}P_8S_5$ (2165.1): calcd. C 60.47, H 4.52, N 5.82; found C 60.45, H 4.48, N 5.75.

Synthesis of 17c-[G′$_1$-G$_n$] (*n* = 2, 3): A slight excess (5%) of phosphorus hydrazide **4** in solution in $CHCl_3$ was added to a solution of **17c-[G′$_1$-G′$_{n-1}$]** in THF. The resulting solution was stirred overnight at room temperature, then concentrated to dryness. The residue was washed several times with THF/pentane (1:5) to afford **17c-[G′$_1$-G$_2$]** (0.404 g, 96% yield) or **17c-[G′$_1$-G$_3$]** (0.510 g, 97% yield) as white powders.

Synthesis of 17c-[G′$_1$-G′$_n$] (*n* = 2, 3): A solution of compound **17c-[G′$_1$-G$_n$]** in solution in THF was added to the sodium salt **5** (5% excess) in THF. The resulting mixture was stirred overnight, then centrifuged and concentrated to dryness. The residue was washed several times with THF/pentane (1:5) to afford **17c-[G′$_1$-G′$_2$]** (0.418 g, 92% yield) or **17c-[G′$_1$-G′$_3$]** (0.448 g, 91% yield) as white powders.

17c-[G′$_1$-G$_2$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 13.6 (d, $^2J_{PP}$ = 25.1 Hz, P_{11}'), 16.9 (d, $^2J_{PP}$ = 33.3 Hz, P_{00}), 50.3 (d, $^2J_{PP}$ = 25.1 Hz, P_1'), 51.2 (d, $^2J_{PP}$ = 33.3 Hz, P_0), 62.5 (s, P_1), 62.9 (s, P_2'). − ^1H NMR ($CDCl_3$): δ = 1.82 (s, 3 H, CH_3-N-CH_2), 2.45−2.70 (m, 4 H, CH_2-CH_2-P), 3.34 (d, $^3J_{HP}$ = 10.5 Hz, 6 H, CH_3-N-P_1), 3.43 (d, $^3J_{HP}$ = 14.2 Hz, 12 H, CH_3-N-P_2'), 4.23−4.40 (m, 4 H, NCH_2-P), 7.00−7.70 (m, 80 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.7 (d, $^1J_{CP}$ = 65 Hz, CH_2CH_2-P), 31.9 (d, $^2J_{CP}$ = 13 Hz, CH_3-N-P_2'), 33.1 (d, $^2J_{CP}$ = 13 Hz, CH_3-N-P_1), 35.4 (s, CH_3-N-CH_2), 46.4 (s, CH_2-CH_2-P), 50.5 (d, $^1J_{CP}$ = 87 Hz, NCH_2-P), 121.4 (d, $^3J_{CP}$ = 4 Hz, C_1^2), 121.7 (d, $^3J_{CP}$ = 5 Hz, C_0^2, $C_1^{2\prime}$), 125.4 (s, C_1^4), 128.0 (s, C_0^3), 128.4 (s, $C_1^{3\prime}$), 128.8 (d, $^3J_{CP}$ = 13 Hz, C_0^m, $C_1^{m\prime}$), 129.5 (s, C_1^3), 130.2 (s, $C_1^{4\prime}$), 131.3 (d, $^2J_{CP}$ = 10 Hz, C_0^o, $C_1^{o\prime}$), 132.2 (s, C_0^4), 132.6 (s, C_0^p, $C_1^{p\prime}$), 138.8 (d, $^3J_{CP}$ = 14 Hz, C_0^4-*C*H=N), 141.2 (d, $^3J_{CP}$ = 18 Hz, $C_1^{4\prime}$-*C*H=N), 150.6 (d, $^2J_{CP}$ = 7 Hz, C_1^1), 152.8 (d, $^2J_{CP}$ = 10 Hz, C_0^1), 153.3 (d, $^2J_{CP}$ = 8 Hz, $C_1^{1\prime}$). − $C_{113}H_{109}Cl_8N_{17}O_{10}P_{12}S_9$ (2809.1): calcd. C 48.31, H 3.91, N 8.48; found C 48.24, H 3.87, N 8.40.

17c-[G′$_1$-G′$_2$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 14.0 (d, $^2J_{PP}$ = 24.6 Hz, P_{11}'), 17.5 (d, $^2J_{PP}$ = 33.1 Hz, P_{00}), 50.7 (d, $^2J_{PP}$ = 24.6 Hz, P_1'), 51.7 (d, $^2J_{PP}$ = 33.1 Hz, P_0), 60.8 (s, P_2'), 63.0 (s, P_1). − ^1H NMR ($CDCl_3$): δ = 1.82 (s, 3 H, CH_3-N-CH_2), 2.43−2.70 (m, 4 H, CH_2-CH_2-P), 3.34 (m, 18 H, CH_3-N-P), 4.22−4.45 (m, 4 H, NCH_2-P), 7.00−7.80 (m, 112 H, C_6H_5, C_6H_4, CH=N), 9.91 (s, 8 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.7 (d, $^1J_{CP}$ =

64 Hz, CH_2CH_2−P), 33.0 (m, CH_3−N−P), 35.5 (s, CH_3−N−CH_2), 46.2 (s, CH_2−CH_2−P), 50.6 (d, $^1J_{CP}$ = 89 Hz, NCH_2−P), 121.4 (d, $^3J_{CP}$ = 4 Hz, C_1^2), 121.7 (d, $^3J_{CP}$ = 4 Hz, C_0^2, $C_1^{2\prime}$), 122.0 (d, $^3J_{CP}$ = 5 Hz, $C_2^{2\prime}$), 125.4 (s, C_1^4), 128.0 (s, C_0^3), 128.7 (s, $C_1^{3\prime}$), 128.8 (d, $^3J_{CP}$ = 13 Hz, C_0^m, $C_1^{m\prime}$), 129.5 (s, C_1^3), 130.6 (s, $C_1^{4\prime}$), 131.2 (d, $^2J_{CP}$ = 11 Hz, C_0^o, $C_1^{o\prime}$), 131.5 (s, $C_2^{3\prime}$), 132.2 (s, C_0^4), 132.4 (s, C_0^p, $C_1^{p\prime}$), 133.6 (s, $C_2^{4\prime}$), 138.8 (d, $^3J_{CP}$ = 14 Hz, C_0^4-*C*H=N), 140.1 (d, $^3J_{CP}$ = 14 Hz, $C_1^{4\prime}$-*C*H=N), 150.6 (d, $^2J_{CP}$ = 6 Hz, C_0^1), 152.8 (d, $^2J_{CP}$ = 8 Hz, C_1^1), 153.0 (d, $^2J_{CP}$ = 9 Hz, $C_1^{1\prime}$), 155.1 (d, $^2J_{CP}$ = 7 Hz, $C_2^{1\prime}$), 190.8 (s, CHO). − IR (KBr): 1702 cm^{-1} ($\nu_{C=O}$). − $C_{169}H_{149}N_{17}O_{26}P_{12}S_9$ (3494.4): calcd. C 58.08, H 4.29, N 6.81; found C 58.05, H 4.22, N 6.76.

17c-[G′$_1$-G$_3$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 13.5 (d, $^2J_{PP}$ = 24.5 Hz, $P_{11}\prime$), 16.9 (d, $^2J_{PP}$ = 33.1 Hz, P_{00}), 50.2 (d, $^2J_{PP}$ = 24.5 Hz, $P_1\prime$), 51.3 (d, $^2J_{PP}$ = 33.1 Hz, P_0), 61.9 (s, $P_2\prime$), 62.5 (s, P_1), 62.9 (s, $P_3\prime$). − ^1H NMR ($CDCl_3$): δ = 1.84 (s, 3 H, C*H*$_3$−N−CH_2), 2.42−2.74 (m, 4 H, CH_2−CH_2−P), 3.32−3.51 (m, 42 H, CH_3−N−P), 4.22−4.45 (m, 4 H, NCH_2−P), 7.00−7.70 (m, 120 H, C_6H_5, C_6H_4, CH=N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.8 (d, $^1J_{CP}$ = 65 Hz, CH_2CH_2−P), 31.9 (d, $^2J_{CP}$ = 13 Hz, CH_3N−$P_3\prime$), 33.0 (d, $^2J_{CP}$ = 13 Hz, CH_3N−P_1, CH_3N−$P_2\prime$), 35.5 (s, *C*H$_3$−N−CH_2), 46.4 (s, CH_2−CH_2−P), 50.6 (d, $^1J_{CP}$ = 88 Hz, NCH_2−P), 121.4−121.9 (m, C_0^2, C_1^2, $C_1^{2\prime}$, $C_2^{2\prime}$), 125.4 (s, C_1^4), 128.0 (s, C_0^3, $C_1^{3\prime}$), 128.7 (m, C_0^m, $C_1^{m\prime}$, $C_2^{3\prime}$), 129.5 (s, C_1^3), 130.9 (s, $C_1^{4\prime}$), 131.3 (d, $^2J_{CP}$ = 11 Hz, C_0^o, $C_1^{o\prime}$), 131.5 (s, $C_2^{4\prime}$), 132.2 (s, C_0^4), 132.5 (s, C_0^p, $C_1^{p\prime}$), 138.8 (d, $^3J_{CP}$ = 14 Hz, C_0^4-*C*H=N), 139.5 (d, $^3J_{CP}$ = 13 Hz, $C_1^{4\prime}$-*C*H=N), 140.7 (d, $^3J_{CP}$ = 19 Hz, $C_2^{4\prime}$-*C*H=N), 150.7 (d, $^2J_{CP}$ = 7 Hz, C_0^1, C_1^1), 151.9 (d, $^2J_{CP}$ = 7 Hz, $C_2^{1\prime}$), 152.9 (d, $^2J_{CP}$ = 9 Hz, $C_1^{1\prime}$). − $C_{177}H_{173}Cl_{16}N_{33}O_{18}P_{20}S_{17}$ (4782.3): calcd. C 44.45, H 3.64, N 9.66; found C 44.41, H 3.59, N 9.64.

17c-[G′$_1$-G′$_3$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 14.0 (d, $^2J_{PP}$ = 24.2 Hz, $P_{11}\prime$), 17.3 (d, $^2J_{PP}$ = 32.5 Hz, P_{00}), 50.5 (d, $^2J_{PP}$ = 24.2 Hz, $P_1\prime$), 51.8 (d, $^2J_{PP}$ = 32.5 Hz, P_0), 60.5 (s, $P_3\prime$), 62.7 (s, $P_2\prime$), 62.8 (s, P_1),. − ^1H NMR ($CDCl_3$): δ = 1.84 (s, 3 H, C*H*$_3$−N−CH_2), 2.42−2.74 (m, 4 H, CH_2−CH_2−P), 3.34 (m, 42 H, CH_3−N−P), 4.20−4.43 (m, 4 H, NCH_2−P), 7.00−7.80 (m, 184 H, C_6H_5, C_6H_4, CH=N), 9.91 (s, 16 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.7 (d, $^1J_{CP}$ = 64 Hz, CH_2CH_2−P), 32.8 (d, $^2J_{CP}$ = 13 Hz, CH_3−N−P), 35.5 (s, *C*H$_3$−N−CH_2), 46.2 (s, CH_2−CH_2−P), 50.5 (d, $^1J_{CP}$ = 88 Hz, NCH_2−P), 121.2−121.8 (m, C_0^2, C_1^2, $C_1^{2\prime}$, $C_2^{2\prime}$, $C_3^{2\prime}$), 125.2 (s, C_1^4), 127.8−128.5 (m, C_0^3, $C_1^{3\prime}$, C_0^m, $C_1^{m\prime}$), 129.4 (s, C_1^3, $C_2^{3\prime}$), 130.7−132.3 (m, C_0^4, C_1^4, $C_1^{4\prime}$, C_0^o, $C_1^{o\prime}$, C_0^p, $C_1^{p\prime}$, $C_3^{3\prime}$), 133.4 (s, $C_3^{4\prime}$), 139.5 (br. d, $^3J_{CP}$ = 14 Hz, CH=N), 150.4 (d, $^2J_{CP}$ = 7 Hz, C_0^1), 151.3 (d, $^2J_{CP}$ = 7 Hz, $C_2^{1\prime}$), 152.7 (d, $^2J_{CP}$ = 9 Hz, $C_1^{1\prime}$, C_1^1), 154.9 (d, $^2J_{CP}$ = 7 Hz, $C_3^{1\prime}$), 190.6 (s, CHO). − IR (KBr): 1702 cm^{-1} ($\nu_{C=O}$). − $C_{289}H_{253}N_{33}O_{50}P_{20}S_{17}$ (6152.9): calcd. C 56.41, H 4.14, N 7.51; found C 56.31, H 4.05, N 7.44.

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