Polyaminophosphines Containing Dendrimers. Syntheses and Characterizations

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Abstract: The synthesis of phosphorus containing dendrimers **2-[G$_0$]−2-[G$_3$] and 3-[G″$_0$]−3-[G″$_1$]** is achieved from the hexapodant $N_3P_3(OC_6H_4CHO)_6$**2-[G$_0$]** used as a core. It involves iterative reaction sequences: condensation reaction of **2[G$_0$]** with methylhydrazine followed by treatment of the resulting hydrazone with either chlorodiphenylphosphine or chlorodiazaphospholane, the last step being the reaction of the dendrimer possessing terminal aminophosphino groups with the azido thio phosphine $N_3P(S)(OC_6H_4CHO)_2$ **4**. The construction of the dendrimer of the third generation **2-[G$_3$]** is accomplished by reacting the arborol **2-[G″$_2$]** possessing 24 phosphino groups at the periphery with **4**. The same reactions conducted with the ligand $(S)P(OC_6H_4CHO)_3$ **6-[G$_0$]** used as a core, instead of **2-[G$_0$]**, allow the preparation of dendrimers of the first, second, and third generation **6-[G$_1$]−6-[G″$_3$]**.

Introduction

A number of reports describe recent efforts to develop and characterize new three dimensional organizations of ordered macromolecules such as dendrimers. These covalent or ionic architectures can be systematically controlled by stepwise iterative reaction sequences from an initiator core which is usually an atom or a simple molecule.[1] Most of the constructions dealt with a core possessing three reactive sites (Nc = 3). Nevertheless a few reactions involved higher initiator core multiplicity (Nc = 4,[2a−f] Nc = 5,[3a] Nc = 6[4]), but to our knowledge these reactions were rarely conducted beyond the second generation, probably because of steric hindrance.

The first phosphorus cascade molecules were reported a few years ago.[3b,c] They have been generated either from a phosphonium core (Nc = 4) with each branch point being an additional phosphonium ion site or from a phosphine oxide (Nc = 3) or a phosphorane core,[3a] the latter representing the unique cascade structure bearing a penta directional core. We recently described the synthesis up to the seventh generation of neutral phosphorus containing dendrimers (Nc = 3) possessing either aldehyde or $P(S)Cl_2$ end groups.[5] A few recent papers concerned the formation of other phosphorus arborols such as small organophosphine dendrimers[6] or dendrimers having cyclotriphosphazene units in the cascade structure.[4c]

We now report the synthesis of phosphorus containing dendrimers elaborated up to the third generation from a cyclotriphosphazene core $N_3P_3(OC_6H_4CHO)_6$ **2-[G$_0$]** possessing six reactive aldehyde groups (Nc = 6). Simple iterative reactions lead in turn to hydrazone, aminophosphine, or aldehyde functionalized surfaces and provide the first dendrimer with 24 terminal phosphino groups. The same strategy conducted with $(S)P(OC_6H_4CHO)_3$ instead of **2-[G$_0$]** also allows the preparation of dendrimers up to the third generation and possessing the same number of terminal functionalities.

Results and Discussion

The hexapodant $N_3P_3(OC_6H_4CHO)_6$ **2-[G$_0$]** is readily prepared by reacting hexachlorocyclotriphosphazene **1** (1 equiv) with the triethylammonium salt of 4-hydroxybenzaldehyde (6 equiv). The first step of the elaboration of the dendrimer consists of the treatment of **2-[G$_0$]**, used as a core, with methylhydrazine (6 equiv) and gives rise to the hexahydrazono species **2-[G′$_0$]**. Addition of diphenylchlorophosphine to **2-[G′$_0$]** in the presence of triethylamine affords the dendron **2-[G″$_0$]** possessing six terminal aminophosphine groups. The last step involves a Staudinger type reaction between **2-[G″$_0$]** and the azide $N_3P(S)(OC_6H_4CHO)_2$ **4**[7] leading to the dendrimer of the first generation **2-[G$_1$]** (Scheme 1). These iterative reaction sequences using alternatively the three reagents—methylhydrazine, diphenylchlorophosphine and the azide **4**—give rise further to the aminophosphine cascade structures **2-[G″$_1$]** and **2-[G″$_2$]** possessing 12 and 24 terminal diphenyl phosphino groups, respectively (Scheme 2). Dendrimer construction with this synthetic strategy occurs with quantitative yield/conversion syntheses; moreover all the byproducts (water, triethylamine hydrochloride and nitrogen) are easily removed.

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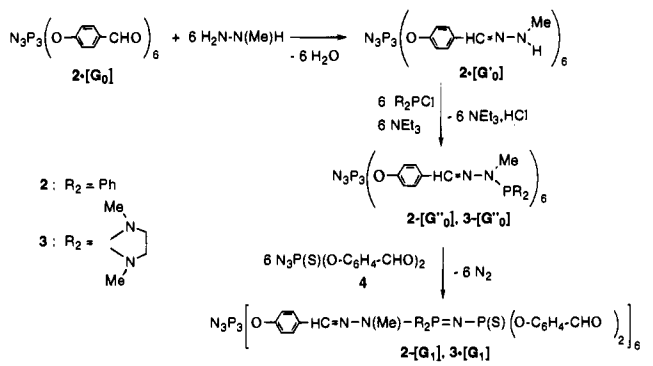
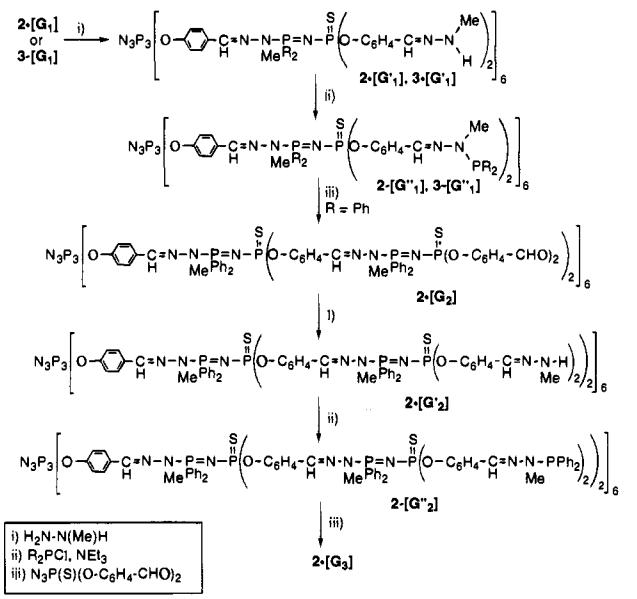
Scheme 1



Scheme 2



Analogous experiments can be done with the chlorodiazaphospholane **5** instead of chlorodiphenylphosphine. In this case, the derivatives **3-[G″$_0$]** and **3-[G″$_1$]** with 6 or 12 terminal phospholane groups, respectively, are isolated.

All the intermediates during the preparation of **2-[G″$_1$]**, **3-[G″$_1$]**, and **2-[G″$_2$]**, i.e., compounds with either terminal hydrazone or aldehyde groups, are also isolated and fully characterized. All new materials exhibit spectral data and elemental analysis in agreement with their proposed structures. Indeed, reactions can be easily monitored by NMR and IR spectroscopies. Thus, for example, addition of methylhydrazine to compounds **2-[G$_0$]**, **2-[G$_1$]**, or **2-[G$_2$]** possessing 6, 12, or 24 aldehyde end-groups, respectively, can be followed by examining ^{1}H and ^{13}C NMR spectra for the disappearance of the singlet due to aldehydic protons (^{1}H NMR: $9.83 < \delta_{CH=N} < 10.12$ ppm) and the disappearance of the singlet due to carbonyl groups (^{13}C{^{1}H} NMR: $189.6 < \delta_{CHO} < 191.6$ ppm). A deshielding effect of 1.2−1.5 ppm is also detected in ^{31}P NMR when moving from terminal aldehyde groups (compounds **2-[G$_0$]**, **2-[G$_1$]**, and **2-[G$_2$]**) to terminal hydrazono groups (compounds **2-[G′$_0$]**, **2-[G′$_1$]**, and **2-[G′$_2$]**). Similarly, the formation of dendrimers **2-[G″$_0$]**, **2-[G″$_1$]**, and **2-[G″$_2$]** from **2-[G′$_0$]**, **2-[G′$_1$]**, and **2-[G′$_2$]**, respectively, can be monitored by ^{31}P and ^{13}C NMR. ^{31}P NMR spectra of **2-[G″$_0$]**, **2-[G″$_1$]**, and **2-[G″$_2$]** exhibit a characteristic singlet at 67.7−67.8 ppm due to the terminal N-P(C_6H_5)$_2$ groups. In ^{13}C{^{1}H} NMR the singlet at $\delta = 34.7$ ppm corresponding to H-N-*C*H$_3$ groups in **2-[G′$_0$]**, **2-[G′$_1$]**, and **2-[G′$_2$]** disappears and a doublet at 37.0−37.1 ppm ($16.2 < {}^2J_{CP} < 16.6$ Hz) grows in. Furthermore, ^{31}P NMR spectra clearly distinguish each type of phosphorus site within the dendrimers (Table 1) and allow one to easily follow the construction of each species. Characteristic doublets are observed for each phosphorus atom of the P=N−P sequences with $33 < {}^2J_{PP} < 35.1$ Hz for **2-[G$_1$]**, **2-[G$_2$]** and ${}^2J_{PP} = 54.3$ Hz for **3-[G$_1$]**.

All these arborols are soluble in a variety of organic solvents (chloroform, THF) except **2-[G″$_2$]** which appears insoluble after removal of the solvent of the reaction (THF). Therefore, a THF solution of **2-[G″$_2$]** (1 equiv) is directly treated with the azide **4** (24 equiv) to give finally the dendrimer of the third generation **2-[G$_3$]** possessing 48 aldehyde functions (Chart 1). Compound **2-[G$_3$]** is fully characterized by ^{31}P, ^{1}H, and ^{13}C NMR as well as elemental analysis. The ^{31}P NMR spectrum of **2-[G$_3$]** exhibits, besides a singlet at 7.9 ppm due to the P_3N_3 core, three sets of doublet of doublets for the three different P=N−P inorganic fragments of the dendrimer backbone at 21.4 (PPh_2) and 49.8 (P(S)) ppm with ${}^2J_{PP} = 34.0$ Hz for the P=N−P fragments closest to the core, 21.0 (PPh_2) and 49.8 (P(S)) ppm (${}^2J_{PP} = 34.0$ Hz) for the next P=N−P fragments, and 21.9 (PPh_2) and 48.7 (P(S)) ppm (${}^2J_{PP} = 34.0$ Hz) for the P=N−P fragments closest to the periphery.

The same dendrimer construction using SP(OC_6H_4CHO)$_3$ as a core (Scheme 3) was investigated in order to check if the dramatic lack of solubility of dendrimer **2-[G$_3$]** of the third generation is due to the high initiator core multiplicity or to the presence of a large number of phenyl groups or is inherent in the method of synthesis.

As previously mentioned for the preparation of ligands **2-[G′$_0$]**, **2-[G″$_0$]**, and **3-[G″$_0$]** and dendrimers **2-[G$_1$]**−**2-[G$_3$]**, **3-[G$_1$]**, and **3-[G′$_1$]** reactions leading to the new dendrons **6-[G′$_0$]** and **6-[G″$_0$]** and the new dendrimers **6-[G$_1$]**−**6-[G″$_3$]** (Scheme 3 and Chart 2) are monitored by NMR. ^{31}P{^{1}H} NMR spectral data for all these species are summarized in Table 2. A significant shielding effect is observed, for example, when the azide **4** is added to **6-[G″$_0$]**, **6-[G″$_1$]**, or **6-[G″$_2$]** leading to compounds **6-[G$_1$]**, **6-[G$_2$]**, or **6-[G$_3$]**, respectively. While the resonance for the terminal N-P(Ph)$_2$ groups is a singlet at 67.6−68.5 ppm in **6-[G″$_0$]**, **6-[G″$_1$]**, or **6-[G″$_2$]**, the resonance for the N-P(Ph)$_2$=N-P(S)= fragments in **6-[G$_1$]**, **6-[G$_2$]**, or **6-[G$_3$]** is a doublet of doublet at 48.6−48.7 and 21.4−22.8 ppm ($33.0 \leq {}^2J_{PP} \leq 35.0$ Hz). Here also, all phosphorus atoms within the cascade structure are distinguishable.

All the species **6-[G′$_0$]**−**6-[G$_3$]** are soluble in common organic solvents except the dendrimer **6-[G′$_3$]** which presents a weaker solubility and dendrimer **6-[G″$_3$]** which appears poorly soluble. Nevertheless, characteristic NMR data for **6-[G′$_3$]** and **6-[G″$_3$]** are also obtained and support the proposed structures.

Although only structures of derivatives **2-[G$_0$]**−**2-[G$_1$]**, **3-[G″$_0$]**−**3-[G$_1$]**, and **6-[G$_0$]**−**6-[G″$_1$]** are corroborated by mass spectrometry (FAB), one can reject structure defects in other dendrimers by taking into account that, even for the dendrimers of the third generation, i.e., **2-[G$_3$]** or **6-[G$_3$]**−**6-[G″$_3$]**, the resonance of the phosphorus core in ^{31}P NMR (three phosphorus atoms for **2-[G$_3$]**, one phosphorus atom for **6-[G$_3$]**−**6-[G″$_3$]**) is still detectable. Therefore, uncompleted substitution at the periphery should be unambiguously seen by ^{31}P NMR.

In conclusion, these new ways of constructing phosphorus containing dendrimers offer several significant advantages including a high initiator core multiplicity allowing one to quickly reach a large external shape, and the possibility to introduce inorganic P=N−P linkages which are useful probes for controlling branch cells assembling. This three step procedure leading to electrophilic or nucleophilic surfaces permits the introduction of three different reactive groups at

Table 1. ^{31}P NMR Spectral Data (δ ppm, J Hz) and Number of Terminal Functions for Compounds **2-[G$_0$]**−**2-[G$_3$]** and Compounds **3-[G″$_0$]**−**3-[G″$_1$]**[a]

	P_0^1	P_0^2	$(J_{P_0^1P_0^2})$	P_1^1	P_1^2	$(J_{P_1^1P_1^2})$	P_2^1	P_2^2	$(J_{P_2^1P_2^2})$	P_3^1	no. of terminal functions CHO	NH	R_2P^-
2-[G$_0$]	7.1										6		
2-[G′$_0$]	8.6											6	
2-[G″$_0$]	8.6	67.8											6
2-[G$_1$]	7.9	22.8	(34.0)	48.7							12		
2-[G′$_1$]	8.0	21.6	(33.1)	50.1								12	
2-[G″$_1$]	8.1	21.6	(33.0)	50.3	67.7								12
2-[G$_2$]	7.8	22.0	(34.9)	50.1	22.6	(34.8)	48.7				24		
2-[G′$_2$]	7.8	20.9	(35.1)	49.0	20.5	(34.8)	50.0					24	
2-[G″$_2$]	7.7	21.7	(34.0)	49.7	21.2	(34.0)	49.7	67.7					24
2-[G$_3$]	7.9	21.4	(34.0)	49.8	21.0	(34.0)	49.8	21.9	(34.0)	48.7	48		
3-[G″$_0$]	8.9	111.4											6
3-[G$_1$]	7.4	24.2	(54.3)	49.3							12		
3-[G′$_1$]	7.6	23.3	(55.2)	50.5								12	
3-[G″$_1$]	7.6	23.4	(53.0)	50.7	111.4								12

[a] For numbering used see Chart 3.

the periphery such as aldehydes and (for the first time) hydrazones >C=N−N(CH$_3$)H and aminophosphines.

Experimental Section

General Methods. All manipulations were carried out with standard high vacuum or dry argon atmosphere techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 200 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).

Synthesis of Dendrimers. The numbering used for ^{13}C and ^{31}P NMR is depicted on Chart 3. **2-[G$_0$]:** To a solution of hexachlorocyclotriphosphazene **1** (0.521 g, 1.5 mmol) in 10 mL of THF was added a solution of triethylamine (2.5 mL, 18 mmol) and 4-hydroxybenzaldehyde (2.20 g, 18 mmol) in 30 mL of THF. The resulting mixture was refluxed for 16 h and then filtered, and the solvent evaporated. The resulting oil was washed with methanol (2 × 50 mL) to give **2-[G$_0$]** as a white powder: mp 141−142 °C; 90% yield.

2-[G$_0$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 7.1 (s) ppm; ^1H NMR ($CDCl_3$) δ 7.1 (d, $^3J_{HH}$ = 8.0 Hz, 12H, $P_0^1OC_6H_4$), 7.7 (d, $^3J_{HH}$ = 8.0 Hz, 12H, $P_0^1OC_6H_4$), 9.9 (s, 6H, CHO) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 120.6 (d, $^3J_{CP}$ = 6.8 Hz, C_0^2), 130.7 (br, s, C_0^3), 133.2 (s, C_0^4), 154.0 (br s, C_0^1), 189.6 (s, CHO) ppm; IR (KBr) 1704 ($\nu_{C=O}$) cm^{-1}; MS *m/z* 862 [M + 1]$^+$. Anal. Calcd for $C_{42}H_{30}N_3O_{12}P_3$: C, 58.54; H, 3.51; N, 4.87. Found: C, 57.90; H, 3.88; N, 4.89.

2-[G′$_0$]: To a solution of **2-[G$_0$]** (2 g, 2.32 mmol) in 50 mL of THF was added methylhydrazine (815 μL, 15.3 mmol) in the presence of molecular sieve 4 Å. After stirring 24 h at room temperature, the solution was filtered, and the solvent evaporated. The residue was washed with ether (2 × 20 mL) to give **2-[G′$_0$]** as a white powder: mp 92 °C dec; 81% yield.

2-[G′$_0$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 8.6 (s, P_0^1) ppm; ^1H NMR ($CDCl_3$) δ 2.93 (s, 18H, $C_0^6H_3$), 5.55 (br s, 6H, NH), 6.90 (d, $^3J_{HH}$ = 8.6 Hz, 12H, $P_0^1OC_6H_4$), 7.32 (d, $^3J_{HP}$ = 8.6 Hz, 12H, $P_0^1OC_6H_4$), 7.40 (s, 6H, C_0^5H) ppm; ^{13}C NMR ($CDCl_3$) δ 34.1 (q, $^1J_{CH}$ = 135.7 Hz, C_0^6), 120.3 (d, $^1J_{CH}$ = 164.6 Hz, C_0^2), 126.1 (d, $^1J_{CH}$ = 154.6 Hz, C_0^3), 132.7 (s, C_0^4), 133.6 (d, $^1J_{CH}$ = 100.5 Hz, C_0^5), 149.3 (m, C_0^1) ppm; IR (KBr) 3351 (ν_{NH}) cm^{-1}; MS *m/z* 1030 [M + 1]$^+$. Anal. Calcd for $C_{48}H_{54}N_{15}O_6P_3$: C, 55.98; H, 5.28; N, 20.40. Found: C, 55.78; H, 5.24; N, 20.33.

2-[G″$_0$]: To a solution of **2-[G′$_0$]** (0.750 g, 0.73 mmol) in 20 mL of THF was added triethylamine (670 μL, 4.8 mmol). After the solution was stirred for 30 min chlorodiphenylphosphine (863 μL, 4.8 mmol) was added. The resulting solution was stirred for 24 h and then filtered, and the solvent evaporated. The residue was washed with ether (3 × 20 mL) to give **2-[G″$_0$]** as a white powder: mp 104 °C dec; 94% yield.

2-[G″$_0$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 8.6 (s, P_0^1), 67.8 (s, P_0^2) ppm; ^1H NMR ($CDCl_3$) δ 3.04 (d, $^3J_{HP}$ = 7.8 Hz, 18H, $C_0^6H_3$), 6.80−7.80 (m, 90H, C_0^5H, $P_0^1OC_6H_4$, $C_6H_5P_0^2$) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 37.0 (d, $^2J_{CP}$ = 16.2 Hz, C_0^6), 120.8 (s, C_0^2), 126.9 (s, C_0^3), 128.0−134.0 (m, $C_6H_5P_0^2$, C_0^4), 138.2 (s, C_0^5). 149.8 (m, C_0^1) ppm; MS *m/z* 2134 [M + 1]$^+$. Anal. Calcd for $C_{120}H_{108}N_{15}O_6P_9$: C, 67.51; H, 5.10; N, 9.84. Found: C, 67.40; H, 4.99; N, 9.74.

2-[G$_1$]: To a solution of **2-[G″$_0$]** (1.200 g, 0.56 mmol) in 20 mL of THF was added the azido thiophosphine **4** (1.284 g, 3.7 mmol) dissolved in 30 mL of THF. The evolution of nitrogen started immediately. After the solution was stirred for 5 h the solvent was evaporated, and the residue was washed with toluene (2 × 10 mL) and then ether (2 × 20 mL) to give **2-[G$_1$]** as a white powder: mp 122−124 °C; 93% yield.

2-[G$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 7.9 (s, P_0^1), 22.8 (d, $^2J_{PP}$ = 34.0 Hz, P_0^2), 48.7 (d, $^2J_{PP}$ = 34.0 Hz, P_1^1) ppm; ^1H NMR ($CDCl_3$) δ 3.13 (d, $^3J_{HP}$ = 8.4 Hz, 18H, $C_0^6H_3$), 6.77 (d, $^3H_{HH}$ = 8.5 Hz, 12H, $P_0^1OC_6H_4$), 7.11 (d, $^3J_{HH}$ = 8.5 Hz, 12H, $P_0^1OC_6H_4$), 7.29 (d, $^3J_{HH}$ = 8.1 Hz, 24H, $P_1^1OC_6H_4$), 7.71 (d, $^3J_{HH}$ = 8.1 Hz, 24H, $P_1^1OC_6H_4$), 7.18−7.71 (m, 66H, $C_6H_5P_0^2$, C_0^5H), 9.83 (s, 12H, CHO) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 32.2 (d, $^2J_{CP}$ = 6.0 Hz, C_0^6), 120.8 (br s, C_0^2), 121.8 (d, $^3J_{CP}$ = 5.5 Hz, C_1^2), 127.6 (s, C_0^3), 128.2−132.0 (m, C_0^4, C_1^4, $C_6H_5P_0^2$), 131.0 (s, C_1^3), 138.1 (d, $^3J_{CP}$ = 12.5 Hz, C_0^5), 150.6 (m, C_0^1), 156.5 (d, $^2J_{CP}$ = 8.7 Hz, C_1^1). 190.8 (s, CHO) ppm; IR (KBr) 1701 ($\nu_{C=O}$) cm^{-1}; MS *m/z* 4048 [M + 1]$^+$. Anal. Calcd for $C_{204}H_{168}N_{21}O_{30}P_{15}S_6$: C, 60.49; H, 4.18; N, 7.26. Found: C, 60.34; H, 4.14; N, 7.17.

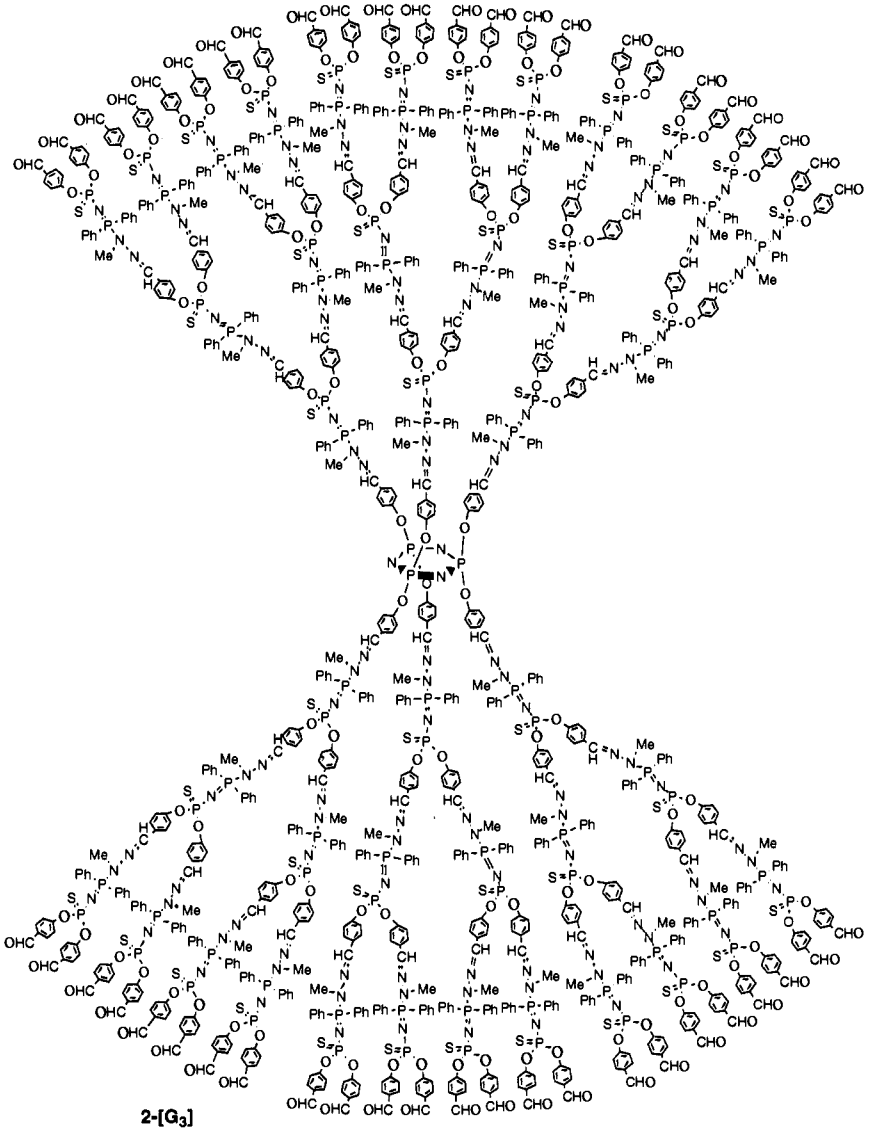
2-[G′$_1$]: To a solution of **2-[G$_1$]** (1.200 g, 0.3 mmol) in 30 mL of THF was added methylhydrazine (208 μL, 3.9 mmol) in the presence of molecular sieves 4 Å. After the solution was stirred for 24 h at room temperature the solution was filtered, and the solvent evaporated to give a residue which was washed with ether (2 × 20 mL). **2-[G′$_1$]** (12 terminal NH functions) was obtained as a white powder: mp 138 °C dec; 87% yield.

2-[G′$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 8.0 (s, P_0^1), 21.6 (d, $^2J_{PP}$ = 33.1 Hz, P_0^2), 50.1 (d, $^2J_{PP}$ = 33.1 Hz, P_1^1) ppm; ^1H NMR ($CDCl_3$) δ 2.86 (s, 36H, $C_1^6H_3$), 3.09 (d, $^3J_{HP}$ = 8.2 Hz, 18H, $C_0^6H_3$), 5.54 (br s, 12H, NH), 6.76 (d, $^3J_{HH}$ = 8.3 Hz, 12H, $P_0^1OC_6H_4$), 7.08 (d, $^3H_{HH}$ = 8.3 Hz, 12H, $P_0^1OC_6H_4$), 7.12 (d, $^3J_{HH}$ = 8.0 Hz, 24H, $P_1^1OC_6H_4$), 7.38 (d, $^3J_{HH}$ = 8.0 Hz, 24H, $P_1^1OC_6H_4$), 7.20−7.73 (m, 78H, C_0^5H, C_1^5H, $C_6H_5P_0^2$) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.9 (d, $^2J_{CP}$ = 6.1 Hz, C_0^6), 34.7 (s, C_1^6), 120.8 (br s, C_0^2), 121.5 (d, $^3J_{CP}$ = 5.0 Hz, C_1^2), 126.4 (s, C_1^3), 127.6 (s. C_0^3), 126.8−133.0 (m, C_0^4, C_1^4, $C_6H_5P_0^2$), 134.6 (s, C_1^5), 137.3 (d, $^3J_{CP}$ = 13.0 Hz, C_0^5), 150.5 (m, C_0^1), 151.5 (d, $^2J_{CP}$ = 9.9 Hz, C_1^1) ppm; IR (KBr) 3366 (ν_{NH}) cm^{-1}. Anal. Calcd for $C_{216}H_{216}N_{45}O_{18}P_{15}S_6$: C, 59.13; H, 4.96; N, 14.37. Found: C, 58.97; H, 4.78; N, 14.20.

2-[G″$_1$] was obtained from **2-[G′$_1$]** (0.900 g, 0.2 mmol), triethylamine (377 μL, 2.7 mmol); and chlorodiphenylphosphine (486 μL, 2.7 mmol) following the procedure described for the synthesis of **2-[G″$_0$]**. **2-[G″$_1$]** was obtained as a white powder: mp 139 °C dec; 87% yield.

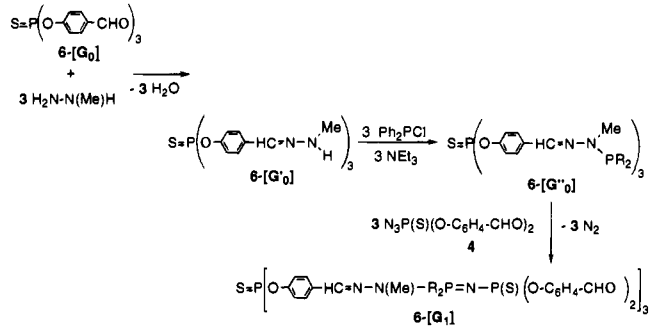
2-[G″$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 8.1 (s, P_0^1), 21.6 (d, $^2J_{PP}$ = 33.0 Hz, P_0^2), 50.3 (d, $^2J_{PP}$ = 33.0 Hz, P_1^1), 67.7 (s, P_1^2) ppm; ^1H NMR ($CDCl_3$) δ 3.12 (m, 54H, $C_0^6H_3$, $C_1^6H_3$), 6.79−7.73 (m, 270H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, C_0^5H, C_1^5H, $C_6H_5P_0^2$, $C_6H_5P_1^2$) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.9 (d, $^2J_{CP}$ = 8.6 Hz, C_0^6), 37.1 (d, $^2J_{CP}$ = 16.6 Hz, C_1^6), 120.8 (br s, C_0^2), 121.5 (br s, C_1^2), 126.8 (s, C_1^3), 127.7 (s, C_0^3), 128.1−134.6 (m, $C_6H_5P_0^2$, $C_6H_5P_1^2$, C_0^4, C_1^4), 137.3 (d, $^3J_{CP}$ = 10.5 Hz, C_0^5),

Chart 1



2-[G_3]

Scheme 3



138.4 (d, $^3J_{CP}$ = 9.5 Hz, C_1^5), 150.5 (m, C_0^1), 150.6 (d, $^2J_{CP}$ = 9.5 Hz, C_1^1) ppm. Anal. Calcd for $C_{360}H_{324}N_{45}O_{18}P_{27}S_6$: C, 65.54; H, 4.95; N, 9.55. Found: C, 65.39; H, 4.71; N, 9.38.

2-[G_2]: Same procedure as for **2-[G''_1]** (0.900 g, 0.14 mmol) and **4** (0.625 g, 1.8 mmol). **2-[G_2]** was obtained as a white powder: mp 133 °C dec; 90% yield.

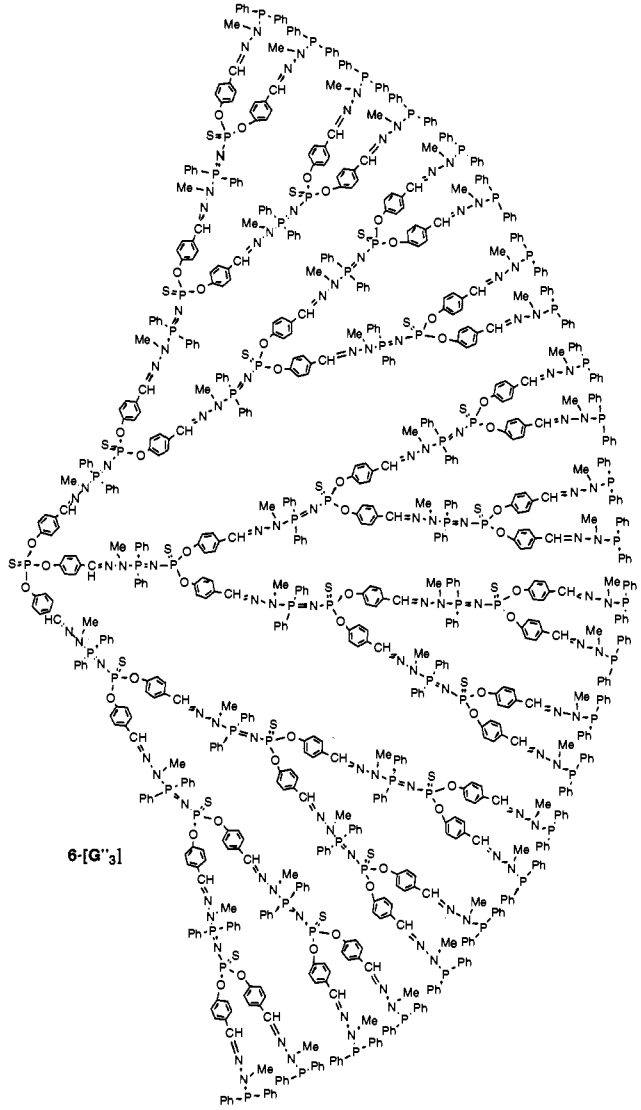
2-[G_2]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 7.8 (s, P_0^1), 22.0 (d, $^2J_{PP}$ = 34.9 Hz, P_0^2), 22.6 (d, $^2J_{PP}$ = 34.8 Hz, P_1^2), 48.7 (d, $^2J_{PP}$ = 34.8 Hz, P_2^1), 50.1 (d, $^2J_{PP}$ = 34.9 Hz, P_1^1) ppm; ^1H NMR ($CDCl_3$) δ 3.17 (m, 54H, $C_0^6H_3$, $C_1^6H_3$), 6.87–7.97 (m, 366H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $P_2^1OC_6H_4$, C_0^5H, C_1^5H, $C_6H_5P_0^2$, $C_6H_5P_1^2$), 9.84 (s, 24H, CHO) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.8 (m, C_0^6, C_1^6), 120.7 (br s, C_0^2), 121.5 (br s, C_1^2), 121.8 (d, $^3J_{CP}$ = 5.6 Hz, C_2^2), 126.5–132.7 (m, $C_6H_5P_0^2$, $C_6H_5P_1^2$, C_0^3, C_1^3, C_0^4, C_1^4, C_2^4), 131.0 (s, C_2^3), 137.3 (m, C_0^5), 138.4 (d, $^3J_{CP}$ = 15.1 Hz, C_1^5), 150.6 (m, C_0^1), 152.5 (d, $^2J_{CP}$ = 8.9 Hz, C_1^1), 156.6 (d, $^2J_{CP}$ = 9.0 Hz, C_2^1), 190.8 (s, CHO) ppm; IR (KBr) 1699 ($\nu_{C=O}$). Anal. Calcd for $C_{528}H_{444}N_{57}O_{66}P_{39}S_{18}$: C, 60.81; H, 4.29; N, 7.66. Found: C, 60.66; H, 4.17; N, 7.47.

2-[G'_2]: Same procedure as for **2-[G'_1]**, starting from **2-[G_2]** (1.000 g, 0.096 mmol) and methylhydrazine (135 μL, 2.5 mmol). **2-[G'_2]** was obtained as a white powder: mp 132 °C dec; 78% yield.

2-[G'_2]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 7.8 (s, P_0^1), 20.5 (d, $^2J_{PP}$ = 34.8 Hz, P_1^2), 20.9 (d, $^2J_{PP}$ = 35.1 Hz, P_0^2), 49.0 (d, $^2J_{PP}$ = 35.1 Hz, P_1^1), 50.0 (d, $^2J_{PP}$ = 34.8 Hz, P_2^1) ppm; ^1H NMR ($CDCl_3$) δ 2.85 (s, 72H, $C_2^6H_3$), 3.11 (m, 54H, $C_0^6H_3$, $C_1^6H_3$), 5.52 (br. s, 24H, N-H), 6.8–7.7 (m, 390H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $P_2^1OC_6H_4$, C_0^5H, C_1^5H, C_2^5H, $C_6H_5P_0^2$, $C_6H_5P_1^2$) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 32.0 (m, C_0^6, C_1^6), 35.2 (s, C_2^6), 121.2 (m, C_0^2, C_1^2), 122.0 (d, $^3J_{CP}$ = 5.0 Hz, C_2^2), 126.9 (s, C_2^3), 127.5–133.3 (m, $C_6H_5P_0^2$, $C_6H_5P_1^2$, C_0^3, C_1^3, C_0^4, C_1^4, C_2^4), 135.2 (br s, C_2^5), 138.2 (m, C_0^5, C_1^5), 151.0 (m, C_0^1), 152.1 (d, $^2J_{CP}$ = 9.3 Hz, C_2^1), 152.8 (d, $^2J_{CP}$ = 7.9 Hz, C_1^1) ppm; IR (KBr) 3369 (ν_{NH}) cm^{-1}. Anal. Calcd for $C_{552}H_{540}N_{105}O_{42}P_{39}S_{18}$: C, 59.72; H, 4.90; N, 13.25. Found: C, 59.48; H, 4.68; N, 13.11.

2-[G''_2]: To a solution of **2-[G'_2]** (0.100 g, 0.009 mmol) in 2 mL of THF-d_8 was added triethylamine (33 μL, 0.24 mmol) and chlorodiphenylphosphine (39 μL, 0.22 mmol). The mixture was stirred for 2 h and then filtered. The resulting solution of **2-[G''_2]** was directly used for the synthesis of **2-[G_3]**.

Chart 2



2-[G''2]: $^{31}P\{^1H\}$ NMR (THF-d_8) δ 7.7 (s, P_0^1), 21.2 (d, $^2J_{PP}$ = 34.0 Hz, P_1^2), 21.7 (d, $^2J_{PP}$ = 34.0 Hz, P_0^2), 49.7 (br d, $^2J_{PP}$ = 34.0 Hz, P_1^1, P_2^1), 67.7 (s, P_2^2) ppm.

2-[G3]: To the preceding solution of **2-[G''2]** (0.009 mmol) in 2 mL of THF-d_8 was added the azide **4** (0.075 **g**, 0.22 mmol) dissolved in 2 mL of THF-d_8. After the solution was stirred for 2 h at room temperature **12a** was directly characterized by NMR and then evaporated to give an insoluble white powder.

2-[G3]: $^{31}P\{^1H\}$ NMR (THF-d_8) δ 7.9 (s, P_0^1), 21.0 (d, $^2J_{PP}$ = 34.0 Hz, P_1^2), 21.4 (d, $^2J_{PP}$ = 34.0 Hz, P_0^2). 21.9 (d, $^2J_{PP}$ = 34.0 Hz, P_2^2), 48.7 (d, $^2J_{PP}$ = 34.0 Hz, P_3^1), 49.8 (br d, $^2J_{PP}$ = 34.0 Hz, P_1^1, P_2^1) ppm; ^1H NMR (THF-d_8) δ 3.0 (m, 126H, $C_0^6H_3$, $C_1^6H_3$, $C_2^6H_3$), 7.1−8.5 (m, 822H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $P_2^1OC_6H_4$, $P_3^1OC_6H_4$, C_0^5H, C_1^5H, C_2^5H, $C_6H_5P_0^2$. $C_6H_5P_1^2$, $C_6H_5P_2^2$), 10.12 (br s, 48H, CHO) ppm; $^{13}C\{^1H\}$ NMR (THF-d_8) δ 33.1 (m, C_0^6, C_1^6, C_2^6), 123.4 (br s, C_0^2, C_1^2, C_2^2, C_3^2), 127.2−136.3 (m, $C_6H_5P_0^2$, $C_6H_5P_1^2$, $C_6H_5P_2^2$, C_0^3, C_1^3, C_2^3, C_0^4, C_1^4, C_2^4, C_3^4), 132.3 (s, C_3^3), 137.2 (m, C_0^5, C_1^5), 140.5 (d, $^2J_{CP}$ = 10.0 Hz, C_2^5), 153.0 (m, C_0^1), 154.6 (br d, $^2J_{CP}$ = 7.0 Hz, C_1^1, C_2^1), 158.7 (d, $^2J_{CP}$ = 9.2 Hz, C_3^1), 191.6 (s, CHO) ppm. Anal. Calcd for $C_{1176}H_{996}N_{129}O_{138}P_{87}S_{42}$: C, 60.92; H, 4.33; N, 7.79. Found: C, 60.63; H, 4.14; N, 7.67.

3-[G''0]: Same procedure as for **2-[G''0]** with **2-[G'0]** (1.500 g, 1.46 mmol) triethylamine (1.34 mL, 9.6 mmol) and chlorodiazaphospholane **5** (1.460 g, 9.6 mmol). **3-[G''0]** was obtained as a white powder: 90% yield.

3-[G''0]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 8.9 (s, P_0^1), 111.4 (s, P_0^2) ppm; ^1H NMR ($CDCl_3$) δ 2.50 (d, $^3J_{HP}$ = 14.2 Hz, 36H, $C_0^7H_3$), 2.87 (d, $^3J_{HP}$ = 4.3 Hz, 18H, $C_0^6H_3$), 3.05 (m. 24H, $C_0^8H_2$), 6.82 (d, $^3J_{HH}$ = 8.9 Hz, 12H, $P_0^1OC_6H_4$), 7.30 (d, $^3J_{HP}$ = 8.9 Hz, 12H, $P_0^1OC_6H_4$), 7.35 (br s, 6H, C_0^5) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 32.3 (d, $^2J_{CP}$ = 12.5 Hz, C_0^6), 34.3 (d, $^2J_{CP}$ = 21.0 Hz, C_0^7), 53.2 (d, $^2J_{CP}$ = 9.5 Hz, C_0^8), 120.7 (s, C_0^2), 126.4 (s, C_0^3), 131.5 (d, $^3J_{CP}$ = 10.5 Hz, C_0^5), 133.1 (s, C_0^4), 149.6 (m, C_0^1) ppm; MS *m/z* 1726 $[M + 1]^+$. Anal. Calcd for $C_{72}H_{108}N_{27}O_6P_9$: C, 50.08; H, 6.30; N, 21.90. Found: C, 49.91; H, 6.18; N, 21.71.

3-[G1]: Same procedure as for **2-[G1]** with **3-[G''0]** (1.000 g, 0.58 mmol) and **4** (1.328 g, 3.83 mmol). **3-[G1]** was obtained as a white powder: 92% yield.

3-[G1]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 7.4 (s, P_0^1), 24.2 (d, $^2J_{PP}$ = 54.3 Hz, P_0^2), 49.3 (d, $^2J_{PP}$ = 54.3 Hz, P_1^1) ppm; ^1H NMR ($CDCl_3$) δ 2.39 (d, $^3J_{HP}$ = 10.9 Hz, 36H, $C_0^7H_3$), 3.08 (d, $^3J_{HP}$ = 7.0 Hz, 18H, $C_0^6H_3$), 3.23 (br s, 24H, $C_0^8H_2$). 7.41 (d, $^3J_{HH}$ = 8.1 Hz, 24H, $P_1^1OC_6H_4$), 7.80 (d, $^3J_{HH}$ = 8.1 Hz, 24H, $P_1^1OC_6H_4$), 7.05−7.50 (m, 30H, C_0^5H, P_0^1-OC_6H_4), 9.87 (s, 12H. CHO) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.7 (d, $^2J_{CP}$ = 4.4 Hz, C_0^7), 31.9 (d, $^2J_{CP}$ = 7.3 Hz, C_0^6), 47.2 (d, $^2J_{CP}$ = 12.4 Hz, C_0^8), 120.4 (br s, C_0^2), 121.5 (d, $^3J_{CP}$ = 5.5 Hz, C_1^2), 126.9 (s, C_0^3), 130.5 (s, C_1^3), 132.1 (s, C_1^4), 133.6 (s, C_0^4), 136.9 (d, $^3J_{CP}$ = 17.9 Hz, C_0^5), 150.4 (m, C_0^1), 156.2 (d, $^2J_{CP}$ = 8.6 Hz, C_1^1), 190.2 (s, CHO) ppm; IR (KBr) 1700 ($\nu_{C=O}$) cm^{-1}; MS *m/z* 3640 $[M + 1]^+$. Anal. Calcd for $C_{156}H_{168}N_{33}O_{30}P_{15}S_6$: C, 51.44; H, 4.65; N, 12.69. Found: C, 51.29; H, 4.51; N, 12.47.

3-[G'1] was obtained from **3-[G1]** (1.090 g, 0.3 mmol) and methylhydrazine (208 μL, 3.9 mmol) following the procedure reported above for **2-[G'1]**.

3-[G'1]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 7.6 (s, P_0^1), 23.3 (d, $^2J_{PP}$ = 55.2 Hz, P_0^2), 50.5 (d, $^2J_{PP}$ = 55.2 Hz, P_1^1) ppm; ^1H NMR ($CDCl_3$) δ 2.37 (d, $^3J_{HP}$ = 10.8 Hz, 36H, $C_0^7H_3$), 2.87 (s, 36H, $C_1^6H_3$), 3.06 (d, $^3J_{HP}$ = 7.0 Hz, 18H, $C_0^6H_3$), 3.21 (m, 24H, $C_0^8H_2$), 5.60 (br s, 12H, NH), 7.0−7.5 (m, 90H, C_0^5H, C_1^5H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.7 (d, $^2J_{CP}$ = 4.3 Hz, C_0^7), 31.9 (d, $^2J_{CP}$ = 7.3 Hz, C_0^6), 34.2 (s, C_1^6), 47.2 (d, $^2J_{CP}$ = 12.7 Hz, C_0^8), 120.4 (br s, C_0^2), 121.0 (d, $^3J_{CP}$ = 5.2 Hz, C_1^2), 125.8 (s, C_1^3) 126.8 (s, C_0^3), 131.9 (s, C_1^4), 132.9 (s, C_0^4), 134.1 (s, C_1^5), 136.2 (d, $^3J_{CP}$ = 12.0 Hz, C_0^5), 150.1 (m, C_0^1), 151.2 (d, $^2J_{CP}$ = 9.4 Hz, C_1^1) ppm; IR (KBr) 3360 (ν_{NH}) cm^{-1}. Anal. Calcd for $C_{168}H_{216}N_{57}O_{18}P_{15}S_6$: C, 50.71; H. 5.47; N, 20.06. Found: C, 50.41; H, 5.34; N, 19.88.

3-[G''1]: Same procedures as for **2-[G''1]** starting from **3-[G'1]** (12 terminal NH functions) (0.700 g, 0.176 mmol), triethylamine (323 μL, 2.32 mmol), and chlorodiazaphospholane **5** (0.350 g, 2.32 mmol).

3-[G''1]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 7.6 (s, P_0^1), 23.4 (d, $^2J_{PP}$ = 53.0 Hz, P_0^2), 50.7 (d, $^2J_{PP}$ = 53.0 Hz, P_1^1), 111.4 (s, P_1^2) ppm; ^1H NMR ($CDCl_3$) δ 2.40 (m, 108H, $C_0^7H_3$, $C_1^7H_3$), 2.87 (d, $^3J_{HP}$ = 4.5 Hz, 36H, $C_1^6H_3$), 3.08 (d, $^3J_{HP}$ = 6.8 Hz, 18H, $C_0^6H_3$). 3.15 (m, 72H, $C_0^8H_2$, $C_1^8H_2$) 7.0−7.6 (m, 90H, C_0^5H, C_1^5H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.7 (d, $^2J_{CP}$ = 4.0 Hz, C_0^7), 31.6 (m, C_0^6, C_1^6), 32.6 (d, $^2J_{CP}$ = 18.0 Hz, C_1^7), 47.2 (d, $^2J_{CP}$ = 9.3 Hz, C_0^8), 52.9 (d, $^2J_{CP}$ = 9.7 Hz, C_1^8), 120.4 (br s, C_0^2), 120.9 (d, $^3J_{CP}$ = 5.0 Hz, C_1^2), 125.8 (s, C_1^3). 126.8 (s, C_0^3), 131.3−134.1 (m, C_0^4, C_1^4, C_0^5, C_1^5), 150.1 (m, C_0^1), 151.2 (d, $^2J_{CP}$ = 8.9 Hz, C_1^1) ppm. Anal. Calcd for $C_{216}H_{324}N_{81}O_{18}P_{27}S_6$: C, 48.29; H, 6.08; N, 21.12. Found: C, 47.98; H, 5.91; N, 20.81.

6-[G0]: To a solution of 4-hydroxybenzaldehyde (9.160 g, 75 mmol) in 300 mL of THF was added freshly distilled triethylamine (10.45 mL, 75 mmol) at room temperature. After the solution was stirred for 1 h trichlorothiophosphine (2.53 mL, 25 mmol) was added at 0 °C. The resulting mixture was stirred overnight at room temperature and then filtered, and the solvent evaporated to give a solid residue that was washed with methanol (2 × 200 mL) to give a white powder: mp 105−106 °C; 90% yield.

6-[G0]: $^{31}P\{^1H\}$NMR ($CDCl_3$) δ 49.5 (s) ppm; ^1H NMR ($CDCl_3$) δ 7.3 (d, $^3J_{HH}$ = 8.0 Hz, 6 H, $P_0^1OC_6H_4$), 7.8 (d, $^3J_{HH}$ = 8.0 Hz, 6 H, $P_0^1OC_6H_4$), 9.9 (s, 3 H, CHO) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 121.6 (d, $^3J_{CP}$ = 5.0 Hz, $C_0^{2,6}$), 131.6 (br s. $C_0^{3,5}$), 133.9 (s, C_0^4), 154.3 (d, $^2J_{CP}$ = 7.0 Hz, C_0^1), 190.6 (s. CHO) ppm; IR (KBr) 1700 ($\nu_{C=O}$) cm^{-1}; MS *m/z* 427 $[M + 1]^+$. Anal. Calcd for $C_{21}H_{15}O_6PS$: C, 59.13; H, 3.54. Found: C, 59.08; H, 3.46.

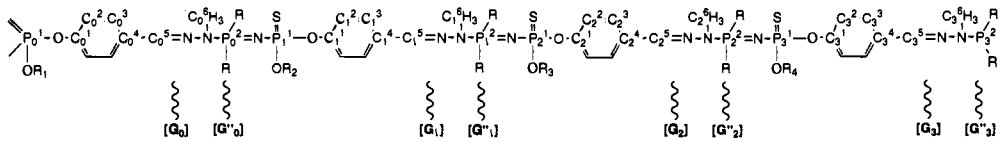
6-[G'0]: To a solution of **6-[G0]** (1.323 g, 3.1 mmol) in 10 mL of THF was added methylhydrazine (542 μL, 10.2 mmol) in the presence of molecular sieves 4 Å. After the solution was stirred overnight at room temperature the solution was filtered, and the solvent evaporated

Table 2. ^{31}P NMR Spectral Data (δ ppm, J Hz) and Number of Terminal Functions for Compounds **6-[G$_0$]**–**6-[G″$_3$]**[a]

	P_0^1	P_0^2	$(J_{P_0^1P_0^2})$	P_1^1	P_1^2	$(J_{P_1^1P_1^2})$	P_2^1	P_2^2	$(J_{P_2^1P_2^2})$	P_3^1	P_3^2	no. of terminal functions CHO	NH	R_2P^-
6-[G$_0$]	49.5											3		
6-[G′$_0$]	52.6												3	
6-[G″$_0$]	53.2	68.5												3
6-[G$_1$]	52.3	22.8	(35.0)	48.8								6		
6-[G′$_1$]	52.3	21.6	(34.0)	50.2									6	
6-[G″$_1$]	52.4	21.6	(34.0)	50.3	67.7									6
6-[G$_2$]	52.5	22.1	(33.0)	50.2	22.6	(33.0)	48.7					12		
6-[G′$_2$]	52.7	22.5	(33.0)	50.1	21.7	(33.0)	50.2						12	
6-[G″$_2$]	52.3	21.7	(33.5)	50.0	21.2	(33.5)	50.0	67.7						12
6-[G$_3$]	52.3	21.8	(33.4)	48.2	21.6	(34.0)	49.9	22.4	(33.1)	48.6		24		
6-[G′$_3$]	52.4	21.9	(34.0)	49.8	21.6	(34.0)	49.8	21.2	(34.0)	50.0			24	
6-[G″$_3$]	52.2	20.8	(34.0)	50.0	20.8	(34.0)	50.0	20.6	(34.0)	50.0	67.6			24

[a] For numbering used see Chart 3.

Chart 3



to give a residue that was washed with ether (2 × 20 mL) to give a colorless oil, 80% yield.

6-[G′$_0$]: $^{31}P\{^1H\}$NMR (C_6D_6) δ 52.6 (s) ppm; ^1H NMR (C_6D_6) δ 2.45 (s, 9 H, $C_0^6H_3$), 5.07 (br s, 3H, NH), 7.05 (s, 3H, C_0^5), 7.29 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{H1P}$ = 1.5 Hz, 6 H, C_0^2H), 7.32 (d, $^3J_{HH}$ = 8.6 Hz, 6 H, C_0^3H) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 34.7 (s, C_0^6), 121.9 (d, $^3J_{CP}$ = 5.0 Hz, C_0^2), 127.3 (d, $^4J_{CP}$ = 1.3 Hz, C_0^3), 132.9 (d, $^6J_{CP}$ = 1.0 Hz, C_0^5), 135.2 (d, $^5J_{CP}$ = 2.2 Hz, C_0^4), 150.6 (d, $^2J_{CP}$ = 8.4 Hz, C_0^1) ppm; IR (KBr) 3430 (ν_{NH}) cm^{-1}; MS *m/z* 511 [M + 1]$^+$. Anal. Calcd for $C_{24}H_{27}N_6O_3PS$: C, 56.45; H, 5.33; N, 16.46. Found: C, 56.21; H, 5.17; N, 16.35.

6-[G″$_0$]: To a solution of **6-[G′$_0$]** (1.580 g, 3.09 mmol) in 10 mL of THF was added chlorodiphenylphosphine (1.83 mL, 10.2 mmol) and freshly distillated triethylamine (1.42 mL, 10.2 mmol). The resulting solution was stirred for 2 h at room temperature and then filtered, and the solvent evaporated. The residue was washed with pentane (2 × 20 mL) to give **6-[G″$_0$]** as a white powder: mp 85 °C dec, 85% yield.

6-[G″$_0$]: $^{31}P\{^1H\}$NMR ($CDCl_3$) δ 53.2 (s, P_0^1), 68.5 (s, P_0^2) ppm; ^1H NMR ($CDCl_3$) δ 3.14 (d, $^3J_{HP}$ = 6.0 Hz, 9 H, $C_0^6H_3$), 7.1–7.9 (m., 45 H, $P_0^1OC_6H_4$, $C_6H_5P_0^2$, C_0^5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 37.1 (d, $^2J_{CP}$ = 17.0 Hz, C_0^6), 121.0 (d, $^3J_{CP}$ = 4.8 Hz, C_0^2), 127.1 (s, C_0^3), 128.0–135.4 (m, $C_6H_5P_0^2$, C_0^4), 138.2 (d, $^3J_{CP}$ = 13.6 Hz, C_0^5), 149.8 (d, $^2J_{CP}$ = 7.1 Hz, C_0^1) ppm; MS *m/z* 1063 [M + 1]$^+$. Anal. Calcd for $C_{60}H_{54}N_6O_3P_4S$: C, 67.79; H, 5.12; N, 7.91. Found: C, 67.28; H, 5.08; N, 7.84.

6-[G$_1$]: To a solution of **6-[G″$_0$]** (3.280 g, 3.09 mmol) in 20 mL of THF was added the azide **4** (3.50 g, 10 mmol) in solution in 5 mL of THF. Evolution of nitrogen started immediately. After stirring 3 h at room temperature, the solvent was evaporated, and the residue washed with ether (3 × 20 mL) to give a white powder: mp 137–138 °C; 95% yield.

6-[G$_1$]: $^{31}P\{^1H\}$NMR ($CDCl_3$) δ 22.8 (d, $^2J_{PP}$ = 35.0 Hz, P_0^2), 48.8 (d, $^2J_{PP}$ = 35.0 Hz, P_1^1), 52.3 (s, P_0^1) ppm; ^1H NMR ($CDCl_3$) δ 3.21 (d, $^3J_{HP}$ = 8.5 Hz, 9 H, $C_0^6H_3$), 7.28 (d, $^3J_{HH}$ = 8.2 Hz, 12 H, P_0^1-OC_6H_4), 7.75 (d, $^3J_{HH}$ = 8.2 Hz, 12 H, $P_0^1OC_6H_4$), 7.09–7.96 (m, 45 H, $P_0^1OC_6H_4$, $C_6H_5P_0^2$, C_0^5H). 9.87 (s, 6 H, CHO) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.8 (d, $^2J_{CP}$ = 6.9 Hz, C_0^6), 121.2 (d, $^3J_{CP}$ = 4.4 Hz, C_0^2), 121.8 (d, $^3J_{CP}$ = 4.9 Hz, C_1^2), 127.8 (s, C_0^3), 128.2–132.8 (m, C_0^4, C_1^4, $C_6H_5P_0^2$), 131.0 (s, C_1^3), 137.6 (d, $^3J_{CP}$ = 14.9 Hz, C_0^5), 150.7 (d, $^2J_{CP}$ = 7.5 Hz, C_0^1), 156.6 (d, $^2J_{CP}$ = 8.5 Hz, C_1^1), 190.8 (s, CHO) ppm; IR (KBr) 1695 ($\nu_{C=O}$) cm^{-1}; MS *m/z* 2020 [M + 1]$^+$. Anal. Calcd for $C_{102}H_{84}N_9O_{15}P_7S_4$: C, 60.62; H, 4.18; N, 6.24. Found: C, 60.45; H, 4.12; N, 6.17.

6-[G′$_1$]: Same procedure as for **6-[G′$_0$]** with **6-[G$_1$]** (1.216 g, 0.6 mmol) and methylhydrazine (211 μL, 4 mmol): mp 105–106 °C, 90% yield.

6-[G′$_1$]: $^{31}P\{^1H\}$NMR ($CDCl_3$) δ 21.6 (d, $^2J_{PP}$ = 34.0 Hz, P_0^2), 50.2 (d, $^2J_{PP}$ = 34.0 Hz, P_1^1), 52.3 (s, P_0^1) ppm; ^1H NMR ($CDCl_3$) δ 2.89 (s, 18 H, $C_1^6H_3$), 3.15 (d, $^3J_{HP}$ = 7.3 Hz, 9 H, $C_0^6H_3$), 4.09 (br s, 6 H, NH), 7.10–7.8 (m, 75 H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $C_6H_5P_0^2$, C_0^5H, C_1^5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.6 (d, $^2J_{CP}$ = 7.0 Hz, C_0^6), 34.7 (s, C_1^6), 121.1 (br s, C_0^2), 121.6 (d, $^3J_{CP}$ = 4.8 Hz, C_1^2), 126.4 (s, C_1^3), 127.8 (s, C_0^3), 128.1–132.7 (m, C_0^4, C_1^4, $C_6H_5P_0^2$), 135.0 (s, C_1^5), 137.6 (d, $^3J_{CP}$ = 13.0 Hz, C_0^5), 150.5 (d, $^2J_{CP}$ = 7.0 Hz, C_0^1), 151.6 (d, $^2J_{CP}$ = 9.7 Hz, C_1^1) ppm; IR (KBr) 3350 (ν_{NH}) cm^{-1}; MS *m/z* 2188 [M + 1]$^+$. Anal. Calcd for $C_{108}H_{108}N_{21}O_9P_7S_4$: C, 59.25; H, 4.97; N, 13.40. Found: C, 59.03; H, 4.84; N, 13.32.

6-[G″$_1$] was obtained from **6-[G′$_1$]** (1.241 g, 0.57 mmol), triethylamine (521 μL, 3.74 mmol), and chlorodiphenylphosphine (671 μL, 3.74 mmol): mp 105–106 °C; 85% yield.

6-[G″$_1$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 21.6 (d, $^2J_{PP}$ = 34.0 Hz, P_0^2), 50.3 (d, $^2J_{PP}$ = 34.0 Hz, P_1^1), 52.4 (s, P_0^1), 67.7 (s, P_1^2) ppm; ^1H NMR ($CDCl_3$) δ 3.13 (d, $^3J_{HP}$ = 6.4 Hz, 18 H, $C_1^6H_3$), 3.17 (d, $^3J_{HP}$ = 7.4 Hz, 9 H, $C_0^6H_3$), 7.08–7.83 (m, 135 H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $C_6H_5P_0^2$, $C_6H_5P_1^2$, C_0^5H, C_1^5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.6 (d, $^2J_{CP}$ = 7.0 Hz, C_0^6), 37.1 (d, $^2J_{CP}$ = 17.3 Hz, C_1^6), 121.1 (d, $^3J_{CP}$ = 3.3 Hz, C_0^2), 121.5 (d, $^3J_{CP}$ = 4.5 Hz, C_1^2), 126.7 (s, C_1^3) 127.8 (s, C_0^3), 128.0–134.5 (m,C_0^4, C_1^4, $C_6H_5P_0^2$. $C_6H_5P_1^2$), 137.8 (d, $^3J_{CP}$ = 13.8 Hz, C_0^5), 138.4 (d, $^3J_{CP}$ = 13.4 Hz, C_1^5), 150.5 (d, $^2J_{CP}$ = 7.9 Hz, C_0^1), 151.6 (d, $^2J_{CP}$ = 10.0 Hz, C_1^1) ppm; MS *m/z* 3292 [M + 1]$^+$. Anal. Calcd for $C_{180}H_{162}N_{21}O_9P_{13}S_4$: C, 65.62; H, 4.95; N, 8.93. Found: C, 65.32; H, 4.89; N, 8.81.

6-[G$_2$] was obtained from **6-[G″$_1$]** (1.867 g, 0.567 mmol) and the azide **4** (1.300 g, 3.74 mmol): mp 150–151 °C; 95% yield.

6-[G$_2$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 22.1 (d, $^2J_{PP}$ = 33.0 Hz, P_0^2), 22.6 (d, $^2J_{PP}$ = 33.0 Hz, P_1^2), 48.7 (d, $^2J_{PP}$ = 33.0 Hz, P_2^1), 50.2 (d, $^2J_{PP}$ = 33.0 Hz, P_1^1), 52.5 (s, P_0^1) ppm; ^1H NMR ($CDCl_3$) δ 3.17 (d, $^3J_{HP}$ = 7.0 Hz, 9 H, $C_0^6H_3$), 3.20 (d, $^3J_{HP}$ = 8.2 Hz, 18 H, $C_1^6H_3$), 7.05–7.95 (m, 183 H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $P_2^1OC_6H_4$, $C_6H_5P_0^2$, $C_6H_5P_1^2$, C_0^5H, C_1^5H), 9.86 (s, 12 H, CHO) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.5 (d, $^2J_{CP}$ = 4.0 Hz, C_0^6), 31.7 (d, $^2J_{CP}$ = 7.2 Hz, C_1^6), 121.2 (br s, C_0^2), 121.6 (d, $^3J_{CP}$ = 5.2 Hz, C_1^2), 121.8 (d, $^3J_{CP}$ = 5.5 Hz, C_2^2), 127.5–132.7 (m, C_0^3, C_1^3, C_0^4, C_1^4, $C_6H_5P_0^2$, $C_6H_5P_1^2$), 131.1 (s, C_2^3), 137.5 (d, $^3J_{CP}$ = 16.0 Hz, C_0^5), 138.4 (d, $^3J_{CP}$ = 14.2 Hz, C_1^5), 150.5 (d, $^2J_{CP}$ = 7.6 Hz, C_0^1), 152.4 (d, $^2J_{CP}$ = 8.9 Hz, C_1^1), 156.6 (d, $^2J_{CP}$ = 8.9 Hz, C_2^1), 190.9 (s, CHO) ppm; IR (KBr) 1699 ($\nu_{C=O}$) cm^{-1}. Anal. Calcd for $C_{264}H_{222}N_{27}O_{33}P_{19}S_{10}$: C, 60.86; H, 4.29; N, 7.26. Found: C, 60.74; H, 4.22; N, 7.18.

6-[G′$_2$]: Same procedure as for **6-[G′$_1$]** with **6-[G$_2$]** (0.960 g, 0.184 mmol) and methylhydrazine (130 μL, 2.43 mmol): mp 165 °C dec; 90% yield.

6-[G′$_2$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 21.7 (d, $^2J_{PP}$ = 33.0 Hz, P_1^2), 22.5 (d, $^2J_{PP}$ = 33.0 Hz, P_0^2), 50.1 (d, $^2J_{PP}$ = 33.0 Hz, P_1^1), 50.2 (d, $^2J_{PP}$ = 33.0 Hz, P_2^1), 52.7 (s, P_0^1) ppm; ^1H NMR ($CDCl_3$) δ 2.83 (s, 36 H, $C_2^6H_3$), 3.12 (m, 27 H, $C_0^6H_3$, $C_1^6H_3$), 5.57 (br s, 12 H, N-H), 7.10–7.75 (m, 195 H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $P_2^1OC_6H_4$, $C_6H_5P_0^2$, $C_6H_5P_1^2$, C_0^5H, C_1^5H, C_2^5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.5 (br d, $^2J_{CP}$ = 7.0 Hz, C_0^6, C_1^6), 34.7 (s, C_2^6), 120.5 (m, C_0^2, C_1^2), 121.5 (d, $^3J_{CP}$ = 4.2 Hz, C_2^2), 126.4 (s, C_2^3), 126.7–132.8 (m, C_0^3, C_1^3, C_0^4, C_1^4, C_2^4, $C_6H_5P_0^2$, $C_6H_5P_1^2$), 134.5 (s, C_2^5), 137.3 (d, $^3J_{CP}$ = 13.0 Hz, C_0^5), 137.7 (d, $^3J_{CP}$ = 14.0 Hz, C_1^5) 150.5 (d, $^2J_{CP}$ = 5.0 Hz, C_0^1), 151.6 (d, $^2J_{CP}$ = 9.6 Hz, C_2^1), 152.4 (d, $^2J_{CP}$ = 10.3 Hz, C_1^1) ppm; IR (KBr) 3369 (ν_{NH}) cm^{-1}. Anal. Calcd for $C_{276}H_{270}N_{51}O_{21}P_{19}S_{10}$: C, 59.76; H, 4.91; N, 12.88. Found: C, 59.68; H, 4.87; N, 12.79.

6-[G″$_2$]: Same procedure as for **6-[G″$_1$]** with **6-[G′$_2$]** (1.020 g, 0.184 mmol), triethylamine (339 μL, 2.43 mmol), and chlorodiphenylphosphine (436 μL, 2.43 mmol): mp 115 °C dec; 85% yield.

6-[G″$_2$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 21.2 (d, $^2J_{PP}$ = 33.5 Hz, P_1^2), 21.7 (d, $^2J_{PP}$ = 33.5 Hz, P_0^2), 50.0 (d, $^2J_{PP}$ = 33.5 Hz, P_1^1, P_2^1), 52.3 (s, P_0^1), 67.7 (s, P_2^2) ppm; ^1H NMR ($CDCl_3$) δ 3.10 (m, 63 H, $C_0^6H_3$, $C_1^6H_3$, $C_2^6H_3$), 7.0–7.8 (m, 315 H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $P_2^1OC_6H_4$, $C_6H_5P_0^2$, $C_6H_5P_1^2$, $C_6H_5P_2^2$, C_0^5H, C_1^5H, C_2^5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.1 (br d, $^3J_{CP}$ = 7.4 Hz, C_0^6, C_1^6), 37.0 (d, $^3J_{CP}$ = 16.0 Hz, C_2^6), 120.9 (m, C_0^2, C_1^2), 121.1 (d, $^3J_{CP}$ = 4.8 Hz, C_2^2), 125.9–132.7 (m, C_0^3, C_1^3, C_2^3, C_0^4, C_1^4, C_2^4, $C_6H_5P_0^2$, $C_6H_5P_1^2$, $C_6H_5P_2^2$), 136.5–137.7 (m, C_0^5, C_1^5, C_2^5), 149.7 (d, $^2J_{CP}$ = 6.0 Hz, C_0^1), 151.2 (d, $^2J_{CP}$ = 10.0 Hz, C_2^1), 151.9 (d, $^2J_{CP}$ = 8.0 Hz, C_1^1) ppm. Anal. Calcd for $C_{420}H_{378}N_{51}O_{21}P_{31}S_{10}$: C, 65.03; H, 4.91; N, 9.21. Found: C, 64.55; H, 4.75; N, 9.12.

6-[G$_3$]: Same procedure as for **6-[G$_1$]** with **6-[G″$_2$]** (1.427 g, 0.184 mmol) and the azide **4** (0.843 g, 2.43 mmol): mp 124 °C dec; 92% yield.

6-[G$_3$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 21.6 (d, $^2J_{PP}$ = 34.0 Hz, P_1^2), 21.8 (d, $^2J_{PP}$ = 33.4 Hz, P_0^2), 22.4 (d, $^2J_{PP}$ = 33.1 Hz, P_2^2), 48.2 (d, $^2J_{PP}$ = 33.4 Hz, P_1^1), 48.6 (d, $^2J_{PP}$ = 33.1 Hz, P_3^1), 49.9 (d, $^2J_{PP}$ = 34.0 Hz, P_2^1), 52.3 (s, P_0^1) ppm; ^1H NMR ($CDCl_3$) δ 3.16 (m, 63 H, $C_0^6H_3$, $C_1^6H_3$, $C_2^6H_3$), 7.0–8.0 (m, 411 H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $P_2^1OC_6H_4$, $P_3^1OC_6H_4$, $C_6H_5P_0^2$, $C_6H_5P_1^2$, $C_6H_5P_2^2$, C_0^5H, C_1^5H, C_2^5H), 9.84 (s, 24 H, CHO) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.4 (m, C_0^6, C_1^6, C_2^6), 120.7 (m, C_0^2, C_1^2), 120.9 (d, $^3J_{CP}$ = 5.4 Hz, C_2^2), 121.4 (d, $^3J_{CP}$ = 5.4 Hz, C_3^2), 126.6–132.5 (m, C_0^3, C_1^3, C_2^3, C_0^4, C_1^4, C_2^4, C_3^4, $C_6H_5P_0^2$, $C_6H_5P_1^2$, $C_6H_5P_2^2$), 130.6 (s, C_3^3), 137.2–137.9 (m, C_0^5, C_1^5, C_2^5), 150.2 (m, C_0^1, C_1^1), 152.0 (d, $^2J_{CP}$ = 9.0 Hz, C_2^1), 156.2 (d, $^2J_{CP}$ = 9.2 Hz, C_3^1), 190.2 (s, CHO) ppm; IR (KBr) 1699 ($\nu_{C=O}$)cm^{-1}. Anal. Calcd for $C_{588}H_{498}N_{63}O_{69}S_{22}$: C, 60.94; H, 4.33; N, 7.61. Found: C, 60.82; H, 4.25; N, 7.55.

6-[G′$_3$]: Same procedure as for **6-[G′$_2$]** with **6-[G$_3$]** (0.200 g, 0.017 mmol) and methylhydrazine (24 μL, 0.449 mmol): mp 110 °C dec; 82% yield.

6-[G′$_3$]: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 21.2 (d, $^2J_{PP}$ = 34.0 Hz, P_2^2), 21.6 (d, $^2J_{PP}$ = 34.0 Hz, P_1^2), 21.9 (d, $^2J_{PP}$ = 34.0 Hz, P_0^2), 49.8 (d, $^2J_{PP}$ = 34.0 Hz, P_1^1, P_2^1), 50.0 (d, $^2J_{PP}$ = 34.0 Hz, P_3^1), 52.4 (s, P_0^1) ppm; ^1H NMR ($CDCl_3$) δ 2.84 (s, 72 H, $C_3^6H_3$), 3.11 (m, 63 H, $C_0^6H_3$, $C_1^6H_3$, $C_2^6H_3$), 5.54 (br s, 24 H, N–H), 7.0–7.8 (m, 435 H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, $P_2^1OC_6H_4$, $P_3^1OC_6H_4$, $C_6H_5P_0^2$, $C_6H_5P_1^2$, $C_6H_5P_2^2$, C_0^5H, C_1^5H, C_2^5H, C_3^5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.5 (m, C_0^6, C_1^6, C_2^6), 34.6 (s, C_3^6), 121.2 (m, C_0^2, C_1^2, C_2^2), 121.5 (d, $^3J_{CP}$ = 4.1 Hz, C_3^2), 126.4 (s, C_3^3), 126.7–133.0 (m, C_0^3, C_1^3, C_2^3, C_0^4, C_1^4, C_2^4, C_3^4, $C_6H_5P_0^2$, $C_6H_5P_1^2$, $C_6H_5P_2^2$), 134.7 (s, C_3^5), 137.8 (m, C_0^5, C_1^5, C_2^5), 151.6 (br d, $^2J_{CP}$ = 10.1 Hz, C_0^1, C_3^1), 152.1 (d, $^2J_{CP}$ = 9.0 Hz, C_1^1), 152.4 (d, $^2J_{CP}$ = 8.3 Hz, C_2^1) ppm; IR (KBr) 3369 (ν_{NH}) cm^{-1}. Anal. Calcd for $C_{612}H_{594}N_{111}O_{45}P_{43}S_{22}$: C, 59.95; H, 4.88; N, 12.68. Found: C, 59.78; H, 4.81; N, 12.60.

6-[G″$_3$]: The reaction was directly performed in a NMR tube with **6-[G′$_3$]** (0.200 g, 0.016 mmol), triethylamine (60 μL, 0.43 mmol), and chlorodiphenylphosphine (77 μL, 0.43 mmol).

6-[G″$_3$]: $^{31}P\{^1H\}$ NMR (THF-d_8) δ 20.6 (d, $^2J_{PP}$ = 34.0 Hz, P_2^2), 20.8 (br d, $^2J_{PP}$ = 34.0 Hz, P_0^2, P_1^2), 50.0 (m, P_1^1, P_2^1, P_3^1), 52.2 (s, P_0^1), 67.6 (s, P_2^2) ppm; ^1H NMR (THF-d_8) δ 3.12 (m, 135 H, $C_0^6H_3$, $C_1^6H_3$, $C_2^6H_3$, $C_3^6H_3$), 7.0–7.8 (m, 675 H, $P_0^1OC_6H_4$, $P_1^1OC_6H_4$, P_2^1-OC_6H_4, $P_3^1OC_6H_4$, $C_6H_5P_0^2$, $C_6H_5P_1^2$, $C_6H_5P_2^2$, $C_6H_5P_3^2$, C_0^5H, C_1^5H, C_2^5H, C_3^5H) ppm; $^{13}C\{^1H\}$ NMR (THF-d_8): δ 32.3 (m, C_0^6, C_1^6, C_2^6), 38.0 (d, $^3J_{CP}$ = 20.0 Hz, C_3^6), 122.0 (m, C_0^2, C_1^2, C_2^2), 122.5 (br s, C_3^2), 126.6–134.0 (m, C_0^3, C_1^3, C_2^3, C_3^3, C_0^4, C_1^4, C_2^4, C_3^4, $C_6H_5P_0^2$, $C_6H_5P_1^2$, $C_6H_5P_2^2$, $C_6H_5P_3^2$), 139.1–139.5 (m, C_0^5, C_1^5, C_2^5), 140.1 (d, $^3J_{CP}$ = 14.3 Hz, C_3^5), 151.8 (m, C_0^1, C_1^1), 152.4 (d, $^2J_{CP}$ = 8.3 Hz, C_2^1), 153.0 (d, $^2J_{CP}$ = 8.3 Hz, C_3^1) ppm.

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