Phosphorus-Containing Dendrimers. Easy Access to New Multi-Difunctionalized Macromolecules

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Phosphorus-containing dendrimers **1-[G′$_1$]**−**1-[G′$_4$]** (generation 1 to generation 4) possessing terminal aldehyde groups reacted with a variety of hydrazino compounds. Addition of hydrazine itself to **1-[G′$_1$]**−**1-[G′$_4$]** afforded the corresponding dendrimers **2-[G$_1$]**−**2-[G$_4$]** with hydrazono groups at the periphery. Addition of methylhydrazine to **1-[G′$_1$]**, **1-[G′$_4$]** gave the dendrimers **3-[G$_1$]**, **3-[G$_4$]**. A Schiff reaction between **1-[G′$_1$]**−**1-[G′$_4$]** and 1-amino-4-(2−hydroxyethyl)piperazine led to dendrimers **5-[G$_1$]**−**5-[G$_4$]** possessing up to 48 alcohol chain ends. Treatment of **1-[G′$_1$]**, **1-[G′$_3$]** with fluorenone hydrazone gave rise to macromolecules **7-[G$_1$]**, **7-[G$_3$]** while the reaction of **1-[G′$_1$]**, **1-[G′$_2$]**, **1-[G′$_4$]** with 4-aminobenzo-15-crown-5 afforded the macromolecules **9-[G$_1$]**, **9-[G$_2$]**, **9-[G$_4$]** in which up to 48 crown ether units are anchored on the surface. Wittig reactions between **1-[G′$_1$]**−**1-[G′$_4$]** with (acetylmethylene)triphenylphosphorane (**10**) or (cyanomethylene)triphenylphosphorane (**12**) allowed the formation of dendrimers **11-[G$_1$]**−**11-[G$_4$]** or **13-[G$_1$]**, **13-[G$_4$]** with α,β unsaturated ketones or cinnamonitrile units, respectively, on the surface. Disubstitution of terminal P(S)Cl$_2$ groups of dendrimers **1-[G$_1$]**−**1-[G$_7$]** with allylamine, propargylamine, or *N*-(trimethylsilyl)imidazole easily occurred to give macromolecules **14-[G$_1$]**−**14-[G$_7$]**, **15-[G$_1$]**, **15-[G$_4$]**, **16-[G$_1$]**, **16-[G$_4$]**.

When a new field of research in chemistry is particularly appealing, a number of assumptions concerning properties and applications of structures resulting from this new area are postulated but need to be checked before going further on investigations. Dendrimer chemistry, a relatively recent branch of polymer chemistry, obeys this observation.[1] Among all the expected properties of these three-dimensional globular compounds, those related to the reactivity of the peripheral functionalities are often cited: the presence of a large number of free chain ends should offer perspectives to develop all the facets of chemistry (organic, inorganic, organometallic...) on the surface of these macromolecules.

Surprisingly very little is known about surface reactivity[2] of dendrimers even if several reports claim how useful such a reactivity might be.

Therefore a part of the work within our research group is targeted toward this goal. As an extension of some of our previous studies[3] we now propose to demonstrate hereafter that chain end functionalities such as aldehyde moieties or phosphorus−chlorine bonds of phosphorus-containing dendrimers **1-[G′$_1$]**−**1-[G′$_4$]** (generation 1 to generation 4, aldehyde functions) or **1-[G$_1$]**−**1-[G$_7$]** (generation 1 to generation 7, P−Cl functions), respectively, are as reactive as monomer species i.e. RCHO or RP(X)Cl$_2$ (X = S, O). As a consequence a large number of multi-difunctionalized dendrimers can be prepared; up to now only a few species of this type were already reported.[4]

Results and Discussion

Dendrimers **1-[G$_1$]**−**1-[G$_7$]** or **1-[G′$_1$]**−**1-[G′$_4$]**, with either terminal P−Cl bonds or terminal aldehyde groups,[3a] were prepared by the reiteration of a two-step sequence: treatment of halogenated phosphane sulfide with the sodium salt of 4-hydroxybenzaldehyde followed by the reaction of the resulting polyaldehyde with dichloro(methylhydrazino) sulfide (Scheme 1). The behavior of these macromolecules toward different reagents was examined in order to determine the influence of the size of these polymers.

Reactivity of Aldehyde Chain Ends. Two well known reactions involving aldehydes were investigated: Schiff reactions and Wittig reactions. Schiff reactions were performed with hydrazine, methylhydrazine, fluorenone hydrazone, and 1-amino-4-(2-hydroxyethyl)piperazine in order to anchor at the periphery of dendrimers, amino, fluorenone, or alcohol groups, respectively, while Schiff reaction was also attempted with 4-aminobenzo-15-crown-5 in order to cover the surface of dendrimers with a large number of crown-ether units.

Treatment of a chloroform solution of **1-[G′$_1$]**, **1-[G′$_2$]**, **1-[G′$_3$]**, or **1-[G′$_4$]** with a large excess of hydrazine at room

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(2) See for example (a) Jansen, J. F. G. A.; De Brabander van der Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *32*, 1226. (b) Lee, J. J.; Ford, W. T.; Moore, J. A.; Li, Y. F. *Macromolecules* **1994**, *27*, 4632. (c) Van der Made, A. W.; Van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400. (d) Knapen, J. W. J.; Van der Made, A. W.; De Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659.

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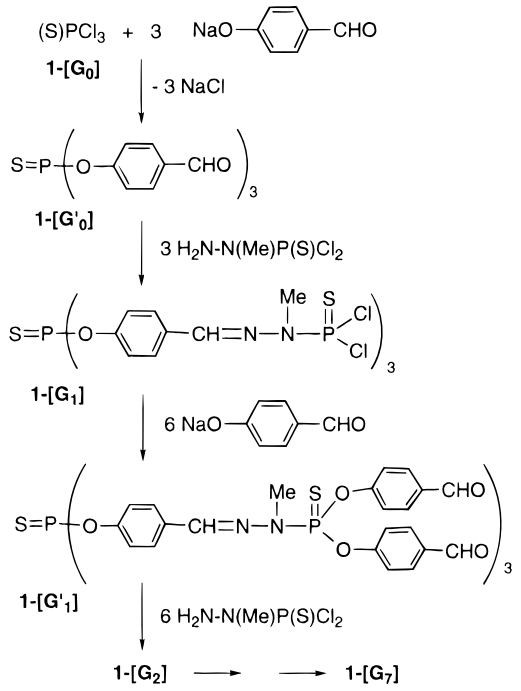
(4) See for example: (a) Tomalia, D. A.; Baker, H.; Dewald, H.; Hall, M.; Kallos, C.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polymer J.* **1985**, *17*, 117. (b) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, C.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466. (c) Meltzer, A. D.; Tinell, D. A.; Jones, A. A.; Inglefield, D.; Hedstrand, M.; Tomalia, D. A. *Macromolecules* **1992**, *25*, 4541. (d) Tomalia, D. A. *Top. Curr. Chem.* **1993**, *165*, 193. (e) Hawker, C. J.; Fréchet, J. M. J. *Macromolecules* **1990**, *23*, 4726. (f) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, *115*, 11496. (g) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc. Perkin Trans 1* **1993**, 1287.

S0022-3263(96)00045-X CCC: $12.00

Scheme 1



temperature for 2 h gave rise to the dendrimers **2-[G$_1$]**−**2-[G$_4$]** in quantitative yields (Scheme 2). Reactions were monitored by ^{31}P NMR which show the disappearance of the signal due to the external thiophosphoryl groups (δ ^{31}P = 60.4 ppm) on behalf of a new signal at 62.2 ppm corresponding to the terminal (S)P(OC$_6$H$_4$CH=NNH$_2$)$_2$ groups of dendrimers **2-[G$_1$]**−**2-[G$_4$]**. Formation of the hydrazono moieties was corroborated by the absence of signals due to aldehyde groups in ^{1}H and ^{13}C NMR as well as in IR spectroscopies. Moreover ^{1}H and ^{13}C NMR confirmed the presence of hydrazono CH=NNH$_2$ protons (δ_H = 7.4 ppm) and carbon (δ_{CH} = 141.6 ppm) while mass spectrometry (fast atom bombardment) indicated that the six condensation reactions took place (MS *m*/*z*: 1507 [M + 1]$^+$) for **2-[G$_1$]**.

The same reactions were conducted with **1-[G′$_1$]** or **1-[G′$_4$]** and monomethylhydrazine leading in high yield to dendrimers **3-[G$_1$]** or **3-[G$_4$]**: here also, reactions needed 2 h to go to completion. In contrast the reaction of **1-[G′$_1$]**−**1-[G′$_4$]** with 1-amino-4-(2-hydroxyethyl)piperazine (**4**) necessitated two days in refluxing chloroform and led to **5[G$_1$]**−**5-[G$_4$]**. A deshielding effect of ≈2 ppm was detected in ^{31}P NMR when moving from terminal aldehyde groups (δ ^{31}P = 60.4 ppm) to terminal hydrazono groups (δ ^{31}P = 62.4 ppm); furthermore a signal corresponding to the condensation of one of the two aldehydic fragments of each terminal (S)P-(OC$_6$H$_4$CHO)$_2$ moieties with **4** was observed at 61.1 ppm. Such a signal further disappeared on behalf of that at 62.4 ppm. Such a phenomenon also occurred when **1-[G′$_1$]** or **1-[G′$_3$]** were treated with the fluorenone hydrazone **6** to give **7-[G$_1$]** or **7-[G$_3$]**: reactions are extremely slow (one week for **1-[G′$_1$]**, 3 weeks for **1-[G′$_3$]**, room temperature) and monocondensation (δ ^{31}P = 60.7 ppm) and then dicondensation (δ ^{31}P = 61.6 ppm) can be easily detected. Steric hindrance introduced by the fluorenone groups probably explains why the reaction is so slow and why attempts to fully substituted **1-[G′$_4$]** with **6** failed up to now. Compounds **3-[G$_1$]**, **3-[G$_4$]**, **5-[G$_1$]**−**5[G$_4$]**, **7-[G$_1$]**, **7-[G$_3$]** were fully characterized by ^{1}H and ^{13}C NMR as well as by elemental analysis and mass spectra (for compounds **3-[G$_1$]**, **5-[G$_1$]**, **7-[G$_1$]**). It is quite likely that all the hydrazono fragments present a trans configuration by analogy with a variety of derivatives possessing such a linkage and characterized by X-ray diffraction studies.[5]

Therefore Schiff reactions allowed us to graft easily on the surface of dendrimers NH$_2$, N(CH$_3$)H, or OH groups which potentially are new anchoring moieties extending the possible applications of these macromolecules.

Of interest was also the reaction of **1-[G′$_1$]**, **1-[G′$_2$]**, **1-[G′$_4$]** with 4-aminobenzo-15-crown-5 **8** leading to dendrimers **9-[G$_1$]**, **9-[G$_2$]**, **9-[G$_4$]** possessing from 6 to 48 crown ether units on the surface (Scheme 2). Formation of **9-[G$_1$]** necessitated one week of stirring in refluxing THF while that of **9-[G$_4$]** (Scheme 3) necessitated three weeks in the same experimental conditions! Here once again steric hindrance played a key role but did not prevent the reactions from going to completion.

None of the ^{1}H and ^{13}C NMR or IR spectra of compounds **9-[G$_1$]**, **9-[G$_2$]**, **9-[G$_4$]** exhibited any signal that could be attributed to unreacted carbonyl functions. ^{1}H or ^{13}C NMR spectra showed singlets at 8.4 ppm (*H*C=NC) or 156.5 ppm (H*C*=NC) due to the protons and carbons, respectively, of the imine functions. Elemental analysis confirmed the structure of all these compounds as well as mass spectrometry (fast atom bombardment) for **9-[G$_1$]** (*m*/*z*: 3013 [M + 1]$^+$).

Some features of interest can be mentioned for dendrimers **9-[G$_1$]**, **9-[G$_2$]**, **9-[G$_4$]**. First, terminal crown ethers acted as shields against hydrolysis of imine functions. Indeed no hydrolysis was observed for example after stirring a THF/water (80/20) solution of **9-[G$_4$]** for 48 h at room temperature.

Secondly a preliminary study concerning the complexation properties of these compounds showed that treatment of **9-[G$_2$]** possessing 12 crown ether units with 12 equiv of sodium tetraphenylborate led after workup to a white powder insoluble in common organic solvents and in water. Elemental analysis of this powder showed that the Na/P ratio is 12/10, thus demonstrating that the twelve sodium cations are trapped by the dendrimer **9-[G$_2$]**. Nevertheless experiments have to be done to confirm this observation and to extend this study in dendrimers **9-[G$_1$]** and **9-[G$_4$]**.

Wittig Reactions. Dendrimers **1-[G′$_1$]**−**1-[G′$_4$]** were reacted with (acetylmethylene)triphenylphosphorane (**10**) for 48 h in refluxing THF. The new dendrimers **11-[G$_1$]**−**11-[G$_4$]** (Scheme 4) were isolated in high yields and characterized by NMR, IR, elemental analysis, and mass spectrometry for **11-[G$_1$]** (FAB, *m*/*z*: 1663 [M + 1]$^+$). Reactions were monitored by ^{31}P NMR which allow to observe the disappearance of the singlet due to **10** (δ ^{31}P = 14.3 ppm) on behalf of that of triphenylphosphine oxide at 23.1 ppm and the deshielding of the signal due to terminal P-(OC$_6$H$_4$CH=CHCOCH$_3$)$_2$ fragments in comparison with that of terminal P-OC$_6$H$_4$CHO groups. (δ = 60.4 ppm for **1-[G′$_1$]**−**1-[G′$_4$]**; 61.6 ppm for **11-[G$_1$]**−**11-[G$_4$]**). ^{1}H NMR spectra clearly established a trans

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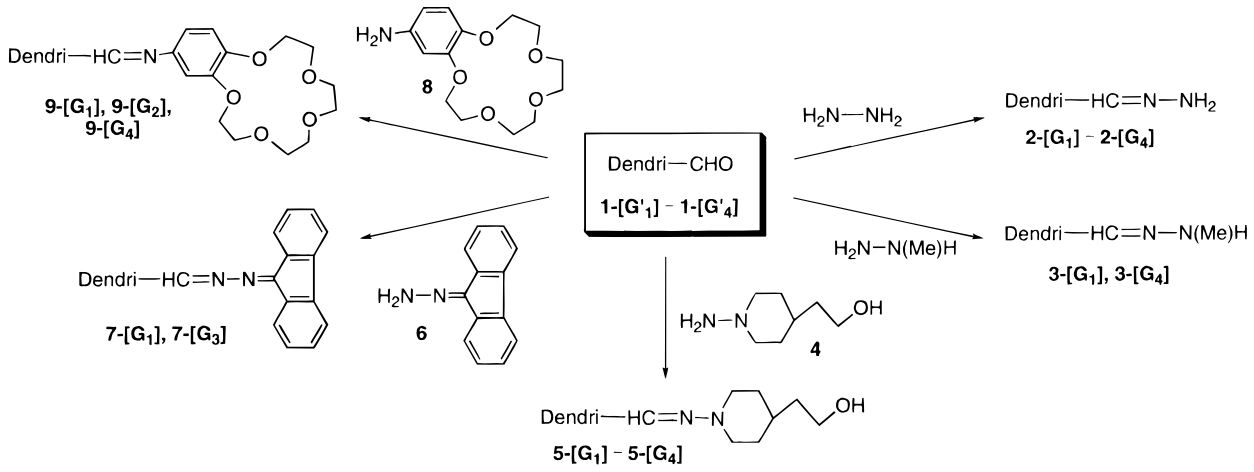
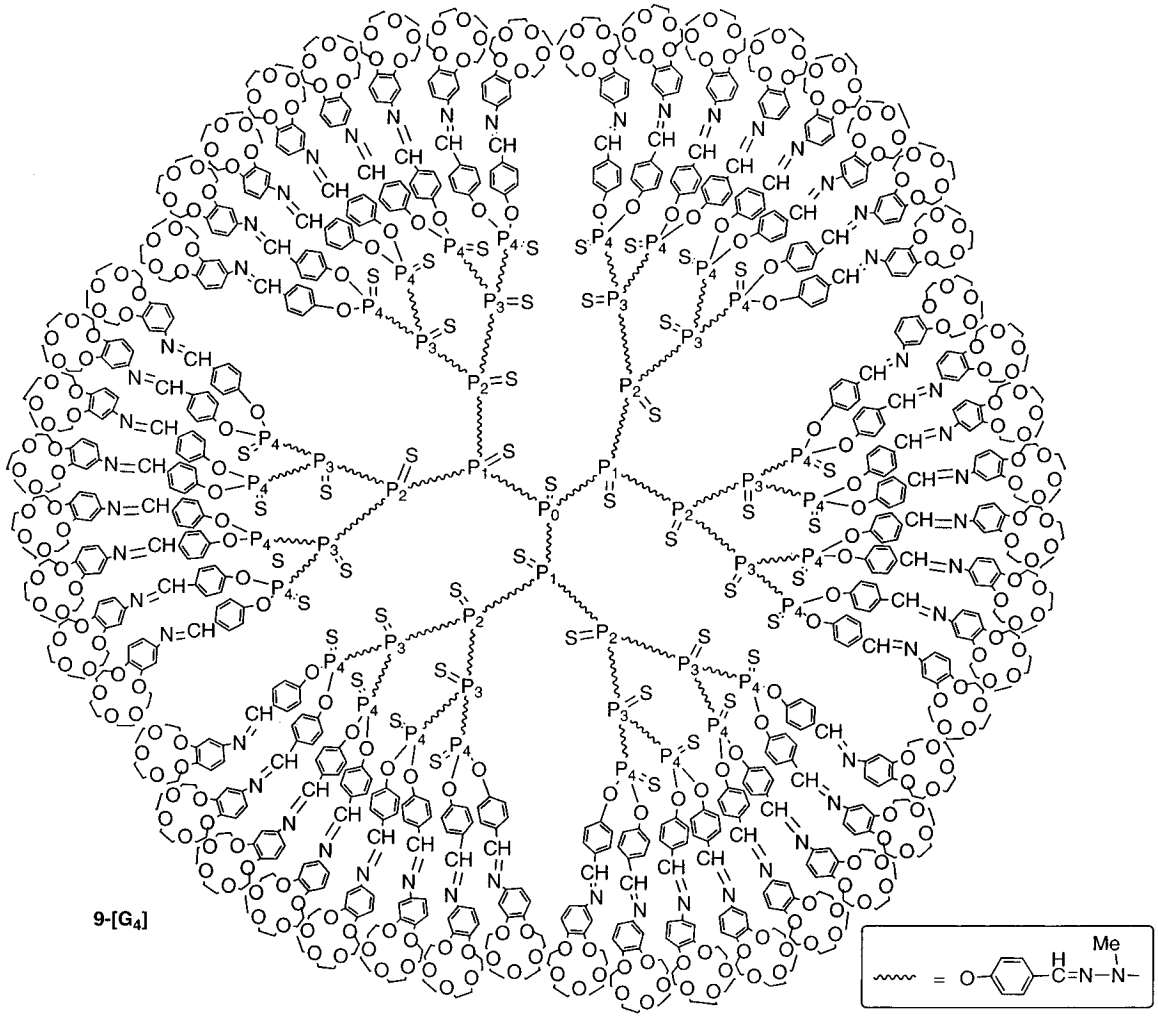
Scheme 2



Scheme 3

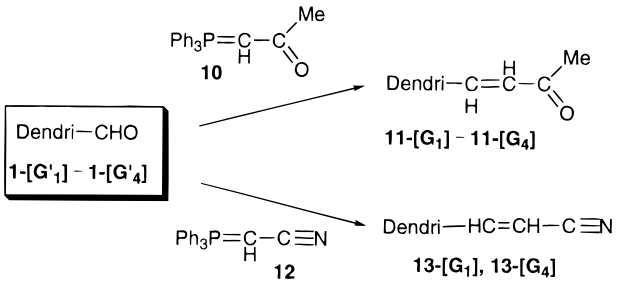


configuration for the olefinic chain ends (CH=CH, $^3J_{HH}$ = 16.3 Hz). IR spectra display two strong absorptions in the carbonyl stretching region, presumably due to s-cis and s-trans conformations of the HC=CHC=O fragments.[6]

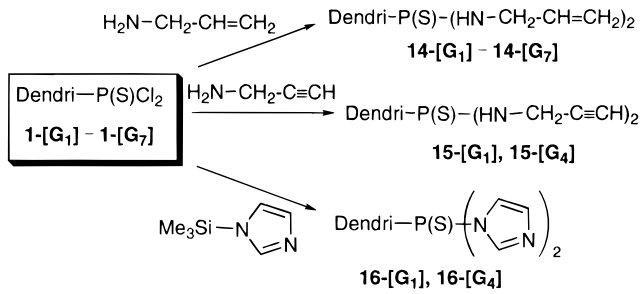
Therefore the Wittig reaction allowed us to anchor up to 48 α,β unsaturated ketones on the surface of our dendrimers. A similar experiment can be done with (cyanomethylene)triphenylphosphorane **12**. Reactions of **12** with **1-[G′1]** and **1-[G′4]** were achieved in 12 h in refluxing THF and led in 58−62% yield to the new macromolecules **13-[G1]** or **13-[G4]** possessing either 6 or 48 terminal cinnamonitrile type groups (Scheme 4). Contrary to what was observed for the reactions of **1-[G′1]**−**1-[G′4]** with the phosphorus ylide **10**, a mixture of trans/cis isomers in a 4/1 ratio was obtained for **13-[G1]** as well as for **13-[G4]**, as indicated by ^{1}H NMR. (δ PhCH = 5.4 ppm, $^3J_{HH}$ = 12.2 Hz cis form; δ PhCH =

(6) Fachin, G.; Bertani, R.; Berton, A.; Gleria, M. *Inorg. Chim. Acta* **1988**, *147*, 165.

Scheme 4



Scheme 5



5.8 ppm, $^3J_{HH}$ = 16.6 Hz trans form; δ CHCN = 7.1 ppm, J_{H-H} = 12.2 Hz cis form; δ CHCN obscured by signals due to aromatic protons for the trans form). ^{13}C NMR corroborated the presence of the two forms (see Experimental Section). These observations concerning the stereospecificity of the Wittig reaction involving dendrimers were in agreement with that reported in the literature for the reactions between "classical" aldehydes and phosphorus ylides **10** or **12**.[6] Remarkably no difference of reactivity was detected when moving from dendrimer of generation 1 to dendrimers of generation 2, 3, or 4.

Reactivity of (S)PCl$_2$ Chain Ends. Nucleophilic substitutions of the terminal P(S)Cl$_2$ moieties easily occurred when dendrimers **1-[G$_1$]**−**1-[G$_7$]** were reacted with monoallylamine (2 equiv of amine per P(S)Cl$_2$ fragments) in the presence of triethylamine (2 equiv per PSCl$_2$ fragments). Dendrimers **14-[G$_1$]**−**14-[G$_7$]** arising from disubstitutions were formed in 92−95% yield (Scheme 5). As mentioned for the preparation of the other dendrimers these reactions can be followed rigorously by ^{31}P NMR, and the seven new dendrimers were fully characterized. The resonance of the phosphorus atom of the core being detected up to the sixth generation, even *one* uncompleted substitution should be detected without any doubt by ^{31}P NMR. For the seventh generation (compound **14-[G$_7$]**, 384 peripheral NH allyl groups), even under the best conditions, structure defects cannot be totally ruled out in the limit of NMR precision (1%). All these macromolecules were found to be soluble in a variety of organic solvents (THF, chloroform, dichloromethane ...) and perfectly stable. No difference of reactivity was observed from generation 1 to generation 7.

Analogous experiments can be performed using other unsaturated amines. For example addition of monopropargylamine (6 or 48 equiv) to a THF solution of **1-[G$_1$]** or **1-[G$_4$]** in the presence of triethylamine (6 or 48 equiv.) led, after stirring for 12 h at room temperature, to derivatives **15-[G$_1$]** or **15-[G$_4$]** possessing 6 or 48 terminal NH propargyl units. Similarly treatment of **1-[G$_1$]** or **1-[G$_4$]** in THF solution with *N*-(trimethylsilyl)imidazole (6 or 48 equiv) gave the dendrimers **16-[G$_1$]** or **16-[G$_4$]** obtained quantitatively after stirring for 1 hour at room temperature. No structure defects can be detected for all these new dendrimers.

Conclusion

It was demonstrated that classical organic chemistry can be developed on the surface of phosphorus-containing dendrimers whatever the size of these macromolecules, i.e. whatever the number of generation. Dense packing effects did not prevent the preparation of a variety of multi-difunctionalized species possessing various peripheral functionalities such as hydrazones, alcohols, allyl or propargylamines, α,β unsaturated ketones, or cinnamonitrile. Thus, 33 new dendrimers were synthesized and fully characterized. The same reactivity was observed for generation 1 or generation 4 or generation 7. Two exceptions have to be mentioned: due to steric effects condensation reactions of aldehyde groups with fluorenone hydrazone or 4-aminobenzo-15-crown-5 appeared to be more and more difficult to achieve when moving from generation 1 to generation 3 or 4. Nevertheless, dendrimers with 24 fluorenone or 48 crown ether moieties on the surface were isolated. Investigations concerning the chemical and physical properties of all these macromolecules are underway.

Experimental Section

General Procedure for the Synthesis of Dendrimers 2-[G$_1$]−2-[G$_4$]. To a solution of 0.100 g of dendrimer **1-[G′$_n$]** (n = 1, 0.070 mmol; n = 2, 0.029 mmol; n = 3, 0.0135 mmol; n = 4, 0.0065 mmol) in 10 mL of CH_2Cl_2 was added dropwise under strong stirring to a suspension of hydrazine hydrate (n = 1, 1.3 mL; n = 2, 2.0 mL; n = 3, 4.0 mL; n = 4, 10.0 mL, large excess) in 10 mL of CH_2Cl_2. After stirring for 2 h at room temperature, two layers were separated. The organic layer (lower layer) was recovered and evaporated to dryness. The residue thus obtained was washed with ether (3 × 10 mL). Compounds **2-[G$_n$]** must be used rapidly, they become insoluble when kept as a powder.

2-[G$_1$]: White powder. Mp 138 °C dec. 92% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.2, 61.9; ^{1}H NMR ($CDCl_3$) δ 3.3 (d, J = 10.5 Hz, 9H), 5.5 (br s, 12H), 7.2−7.6 (m, 45H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 32.9 (d, J = 13.1 Hz), 121.4 (d, J = 4.9 Hz), 127.1, 128.3, 132.4, 138.4 (d, J = 14.0 Hz), 141.6, 150.5 (d, J = 8.1 Hz), 151.0 (d, J = 8.6 Hz). IR (KBr): 3378 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{66}H_{66}N_{18}O_9P_4S_4$: C, 52.59; H, 4.41; N, 16.72. Found: C, 52.36; H, 4.28; N, 16.52.

2-[G$_2$]: White powder. Mp 151 °C dec. 93 % yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.6, 62.2 (br s). ^{1}H NMR ($CDCl_3$) δ 3.3 (d, J = 10.4 Hz, 27H), 5.5 (br s, 24H), 7.2−7.6 (m, 105H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 32.9 (d, J = 11.9 Hz), 121.4 (d, J = 4.3 Hz), 121.4 (br s), 127.1, 128.1, 128.3, 132.0, 132.4, 138.5 (d, J = 14.7 Hz), 141.6, 150.5 (d, J = 7.1 Hz), 151.1 (m). IR (KBr): 3391 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{156}H_{156}N_{42}O_{21}P_{10}S_{10}$: C, 52.26; H, 4.38; N, 16.40. Found: C, 51.86; H, 4.25; N, 16.22.

2-[G$_3$]: White powder. Mp 164 °C dec. 91 % yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.7, 62.1, 62.2. ^{1}H NMR ($CDCl_3$) δ 3.3 (d, J = 10.0 Hz, 63 H), 5.5 (br s, 48 H), 7.1−7.6 (m, 225 H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 32.9 (d, J = 10.4 Hz), 121.4 (br s), 127.1, 128.1 (br s), 132.0, 132.3, 138.6 (m), 141.6, 150.4 (d, J = 6.8 Hz), 151.1 (m). IR (KBr): 3392 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{336}H_{336}N_{90}O_{45}P_{22}S_{22}$: C, 52.13; H, 4.37; N, 16.28. Found: C, 51.86; H, 4.19; N, 16.09.

2-[G$_4$]: White powder. Mp 170 °C dec. 90 % yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.7, 62.1, 62.2. ^{1}H NMR ($CDCl_3$) δ 3.3 (d, J = 10.2 Hz, 135 H), 5.5 (br s, 96 H), 7.1−7.6 (m, 465 H). IR (KBr): 3390 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{696}H_{696}N_{186}O_{93}P_{46}S_{46}$: C, 52.07; H, 4.37; N, 16.22. Found: C, 51.91; H, 4.27; N, 16.10.

General Procedure for the Synthesis of Dendrimers 3-[G$_1$], 3-[G$_4$]. To a solution of 0.300 g of dendrimer **1-[G′$_n$]** (***n*** = 1, 0.211 mmol; n = 4, 0.0195 mmol) in 10 mL of chloroform was added dropwise a solution of methylhydrazine (n = 1, 135 μL, 2.53 mmol; n = 4, 100 μL, 1.87 mmol, 100% excess) in 10 mL of chloroform, at room temperature. The mixture was stirred for 2 h and then evaporated to dryness. The powder thus obtained was washed with ether (10 mL).

3-[G$_1$]: White powder. Mp 153 °C dec. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.4, 62.4. ^{1}H NMR ($CDCl_3$) δ 2.9 (s, 18 H), 3.3 (d, J = 10.4 Hz, 9 H), 5.5 (br s, 6 H), 7.0 (dd, J = 8.5 Hz, J = 1.4 Hz, 12 H), 7.3 (dd, J = 8.5 Hz, J = 1.1 Hz, 6 H), 7.4 (s, 6 H), 7.5 (d, J = 8.5 Hz, 12 H), 7.6 (s, 3 H), 7.7 (d, J = 8.5 Hz, 6 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.4 (d, J = 12.8 Hz), 34.0, 120.9 (d, J = 4.2 Hz), 126.0, 127.8, 132.0, 133.0, 133.8, 137.6 (d, J = 13.8 Hz), 149.5 (d, J = 7.6 Hz), 150.5 (d, J = 8.5 Hz). IR (KBr) 3376 (m, ν_{NH}) cm^{-1}. MS m/z 1591 [M + 1]$^+$. Anal. Calcd for $C_{72}H_{78}N_{18}O_9P_4S_4$: C, 54.33; H, 4.93; N, 15.84. Found: C, 54.07; H, 4.81; N, 15.71.

3-[G$_4$]: White powder. Mp: 150 °C dec. 85% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.4, 62.4, 62.5 (br s). ^{1}H NMR ($CDCl_3$) δ 2.8 (s, 144 H), 3.4 (m, 135 H), 5.5 (br s, 48 H), 7.0−7.8 (m, 465 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.3 (m), 34.0, 121.2 (d, J = 4.3 Hz), 127.6, 130.8, 131.1, 131.5, 132.9, 133.8, 139.0, 150.3 (m), 150.8 (d, J = 6.2 Hz), 154.4 (d, J = 7.4 Hz). IR (KBr) 3412 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{744}H_{792}N_{186}O_{93}P_{46}S_{46}$: C, 53.42; H, 4.77; N, 15.57. Found: C, 53.09; H, 4.63; N, 15.41.

General Procedure for the Synthesis of Dendrimers 5-[G$_1$]−5-[G$_4$]. A solution of 0.300 g of dendrimer **1-[G′$_n$]** (n = 1, 0.211 mmol; n = 2, 0.0877 mmol; n = 3, 0.0405 mmol; n = 4, 0.0195 mmol) and 1-amino-4-(2-hydroxyethyl)piperazine (**4**) (n = 1, 0.368 g, 2.532 mmol; n = 2, 0.306 g, 2.105 mmol; n = 3, 0.282 g, 1.944 mmol; n = 4, 0.272 g, 1.872 mmol, 100% excess) in 20 mL of chloroform was refluxed for 48 h in the presence of molecular sieve (4 Å). Molecular sieve was eliminated by centrifugation, and then the solution was evaporated to dryness. The resulting powder was washed with 2 × 10 mL of a chloroform/ether (1/10) mixture to eliminate excess of **4**.

5-[G$_1$]: White powder. Mp 67 °C dec. 78% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.4, 62.4. ^{1}H NMR ($CDCl_3$) δ 2.5−2.6 (m, 36 H), 2.85 (m, 6 H), 3.1 (m, 24 H), 3.3 (d, J = 10.4 Hz, 9 H), 3.6 (m, 12 H), 7.1 (d, J = 8.0 Hz, 12 H), 7.3 (d, J = 8.4 Hz, 6 H), 7.45 (s, 6 H), 7.5 (d, J = 8.0 Hz, 12 H), 7.6 (s, 3H), 7.7 (d, J = 8.4 Hz, 6 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.4 (d, J = 13.0 Hz), 50.4, 51.5, 57.3, 58.5, 120.9 (d, J = 4.3 Hz), 126.5, 127.7, 132.0, 132.9, 134.1, 137.6 (d, J = 14.9 Hz), 149.7 (d, J = 7.3 Hz), 150.5 (d, J = 7.3 Hz). IR (KBr) 3400 (br, ν_{OH}) cm^{-1}. MS m/z 2185 [M + 1]$^+$. Anal. Calcd for $C_{102}H_{132}N_{24}O_{15}P_4S_4$: C, 56.03; H, 6.08; N, 15.37. Found: C, 55.81; H, 7.95; N, 15.03.

5-[G$_2$]: Pale yellow powder. Mp 72 °C dec. 95% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.6, 62.4, 62.6. ^{1}H NMR ($CDCl_3$) δ 2.5−2.6 (m, 72 H), 2.85 (m, 12 H), 3.1 (br s, 48 H), 3.3 (d, J = 10.4 Hz, 18 H), 3.35 (d, J = 10.4 Hz, 9 H), 3.6 (m, 24 H), 7.1 (d, J = 8.0 Hz, 24 H), 7.2−7.3 (m, 18 H), 7.4 (s, 12 H), 7.5 (d, J = 8.0 Hz, 24 H), 7.6 (s, 9 H), 7.65 (d, J = 8.6 Hz, 12 H), 7.7 (d, J = 8.6 Hz, 6 H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.4 (d, J = 13.0 Hz), 50.4, 51.5, 57.3, 58.5, 120.9 (d, J = 4.5 Hz), 121.1 (d, J = 4.3 Hz), 126.5, 127.6, 127.8, 131.6, 132.0, 132.9, 134.1, 138.0 (d, J = 13.1 Hz), 149.7 (d, J = 7.5 Hz), 150.3 (d, J = 7.3 Hz), 150.6 (d, J = 7.4 Hz). IR (KBr) 3400 (br, ν_{OH}) cm^{-1}. Anal. Calcd for $C_{228}H_{288}N_{54}O_{33}P_{10}S_{10}$: C, 55.40; H, 5.87; N, 15.30. Found: C, 55.28; H, 5.78; N, 15.11.

5-[G$_3$]: Pale yellow powder. Mp 53 °C dec. 85% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.4, 62.3, 62.5 (br s). ^{1}H NMR ($CDCl_3$) δ 2.5−2.6 (m, 144 H), 3.0 (m, 24 H), 3.1 (m, 96 H), 3.4 (d, J = 7.0 Hz, 63 H), 3.6 (m, 48 H), 7.0−7.6 (m, 225 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.3 (d, J = 12.6 Hz), 50.2, 51.6, 57.3, 58.5, 120.8 (d, J = 3.6 Hz), 121.1 (m), 126.5, 127.5 (br s), 131.4, 131.8, 134.0, 138.0−139.0 (m), 149.7 (d, J = 7.3 Hz), 150.5 (d, J = 7.3 Hz), 150.6 (d, J = 6.9 Hz). IR (KBr) 3400 (br, ν_{OH}) cm^{-1}. Anal. Calcd for $C_{480}H_{600}N_{114}O_{69}P_{22}S_{22}$: C, 55.13; H, 5.78; N, 15.27. Found: C, 55.01; H, 5.59; N, 15.03.

5-[G$_4$]: Pale yellow powder. Mp 83 °C dec. 51% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.4, 62.4, 62.5 (br s). ^{1}H NMR ($CDCl_3$) δ 2.5−2.6 (m, 288 H), 2.8 (m, 48 H), 3.1 (m, 192 H), 3.2 (d, J = 9.3 Hz, 135 H), 3.6 (m, 96 H), 7.0−7.6 (m, 465 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.3 (d, J = 13.0 Hz), 50.1, 51.5, 57.3, 58.5, 120.8 (d, J = 3.6 Hz), 120.8 (m), 126.5, 127.6 (br s), 131.5, 131.8, 134.1, 138.0−139.0 (m), 149.7 (d, J = 7.3 Hz), 150.5 (d, J = 6.6 Hz), 150.9 (d, J = 6.4 Hz). IR (KBr): 3400 (br; ν_{OH}) cm^{-1}. Anal. Calcd for $C_{984}H_{1224}N_{234}O_{141}P_{46}S_{46}$: C, 55.01; H, 5.74; N, 15.25. Found: C, 54.73; H, 5.70; N, 15.16.

General Procedure for the Synthesis of Dendrimers 7-[G$_1$], 7-[G$_3$]. A solution of 0.300 g of dendrimer **1-[G′$_n$]** (n = 1, 0.211 mmol; n = 3, 0.0405 mmol) and 9-fluorenone hydrazone **6** (n = 1, 0.492 g, 2.532 mmol; n = 3, 0.378 g, 1.944 mmol) in 20 mL of chloroform was stirred at room temperature (n = 1, 1 week; n = 3, 3 weeks) in the presence of molecular sieve (4 Å). Molecular sieve was eliminated by centrifugation and then the solution was evaporated to dryness. The resulting powder was washed with 2 × 10 mL of a chloroform/ether (1/1) mixture to eliminate excess of **6**.

7-[G$_1$]: Orange yellow powder. Mp 155 °C dec. 70% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.6, 61.6. ^{1}H NMR ($CDCl_3$) δ 3.4 (d, J = 10.3 Hz, 9 H). 7.4−8.4 (m, 87 H), 8.5 (s, 6 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.5 (d, J = 13.1 Hz), 119.1, 121.0 (d, J = 3.2 Hz), 121.4 (d, J = 4.8 Hz), 122.2, 127.4, 127.5, 127.9, 129.5, 130.0, 130.5, 130.8, 130.9, 131.1, 131.9, 136.1, 138.3 (d, J = 13.5 Hz), 140.9, 141.7, 150.6 (d, J = 7.3 Hz), 152.1 (d, J = 7.3 Hz), 158.0, 160.0, 160.1. UV (CH_2Cl_2): 372 (ϵ = 5.1 × 10^4), 354 (ϵ = 8.7 × 10^4), 338 (ϵ = 9.4 × 10^4), 304 (ϵ = 8.5 × 10^4), 296 (ϵ = 9.9 × 10^4), 284 (ϵ = 11.6 × 10^4), 268 (ϵ = 17.4 × 10^4), 266 (ϵ = 17.9 × 10^4), 260 (ϵ = 17.3 × 10^4) nm. MS: m/z 2479 [M + 1]$^+$. Anal. Calcd for $C_{144}H_{102}N_{18}O_9P_4S_4$: C, 69.72; H, 4.14; N, 10.16. Found: C, 69.69; H, 4.11; N, 10.07.

7-[G$_3$]: Orange yellow powder. Mp 135 °C dec. 40% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.6, 61.6, 62.4, 62.6. ^{1}H NMR ($CDCl_3$) δ 3.3 (m, 63 H), 7.2−8.3 (m, 393 H), 8.4 (s, 24 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.4 (d, J = 12.6 Hz), 119.2, 121.0−121.4 (m), 122.2, 127.2, 127.5, 127.7 (br s), 129.4, 130.0, 130.5, 130.8 (br s), 131.0, 131.3−131.5 (m), 136.0, 138.5 (m), 140.8, 141.7, 150.5 (d, J = 7.3 Hz), 150.7 (d, J = 6.6 Hz), 152.1 (d, J = 7.1 Hz), 158.1, 159.9 (br s). Anal. Calcd for $C_{648}H_{480}N_{90}O_{45}P_{22}S_{22}$: C, 66.90; H, 4.16; N, 10.84. Found: C, 66.71; H, 4.01; N, 10.75.

General Procedure for the Synthesis of Dendrimers 9-[G$_1$], 9-[G$_2$], 9-[G$_4$]. A solution of 0.300 g of dendrimer **1-[G′$_n$]** (n = 1, 0.211 mmol; n = 2, 0.0877 mmol; n = 4, 0.0195 mmol) and 4′-aminobenzo-15-crown-5 **8** (n = 1, 0.717 g, 2.532 mmol; n = 2, 0.596 g, 2.105 mmol; n = 4, 0.531 g, 1.872 mmol; 100% excess) in 20 mL of THF was refluxed (n = 1, 1 week; n = 2, 2 weeks, n = 4, 3 weeks) in the presence of molecular sieve (4 Å). After centrifugation, the solution was evaporated to dryness. The resulting powder was washed with 3 × 15 mL of a THF/ether (1/10) mixture to eliminate excess of **8**.

9-[G$_1$]: Yellow powder. Mp 70 °C dec. 70% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.5, 61.6. ^{1}H NMR ($CDCl_3$) δ 3.3 (d, J = 10.6 Hz, 9 H), 4.0 (m, 96 H), 6.8 (m, 18 H), 7.3 (d, J = 8.6 Hz, 18 H), 7.6 (s, 3 H), 7.7 (d, J = 8.6 Hz, 6 H), 7.9 (d, J = 8.4 Hz, 12 H), 8.4 (s, 6 H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.4 (d, J = 13.0 Hz), 68.2−70.4 (m), 107.1, 112.2, 113.8, 120.9 (d, J = 4.4 Hz), 121.1 (d, J = 4.7 Hz), 127.8, 129.3, 131.9, 133.0, 138.1 (d, J = 13.5 Hz), 144.8, 147.2, 148.9, 150.5 (d, J = 7.9 Hz), 152.0 (d, J = 7.6 Hz), 156.5. MS: m/z 3013 [M + 1]$^+$. Anal. Calcd for $C_{150}H_{168}N_{12}O_{39}P_4S_4$: C, 59.73; H, 5.62; N, 5.58. Found: C, 59.51; H, 5.57; N, 5.41.

9-[G$_2$]: Pale yellow powder. Mp 106 °C dec. 60% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.6, 61.8, 65.4. ^{1}H NMR ($CDCl_3$) δ 3.3 (d, J = 10.5 Hz, 27 H), 3.7−4.2 (m, 192 H), 6.7−6.9 (m, 36 H), 7.2−7.8 (m, 93 H), 8.4 (s, 12 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.3 (d, J = 13.0 Hz), 32.4 (d, J = 13.1 Hz), 68.1−70.4 (m), 107.1, 112.2, 113.7, 120.8 (d, J = 4.4 Hz), 121.1 (d, J = 4.3 Hz), 127.6, 127.8, 129.3, 131.2, 132.0, 133.0, 138.0−140.0 (m), 144.8, 147.1, 148.8, 150.5 (d, J = 7.3 Hz), 150.9 (d, J = 8.7 Hz), 151.9 (d, J = 7.4 Hz), 156.2. Anal. Calcd for $C_{324}H_{360}N_{30}O_{81}P_{10}S_{10}$: C, 58.95; H, 5.50; N, 6.37. Found: C, 58.61; H, 5.37; N, 6.21.

9-[G$_4$]: Yellow powder. Mp 116 °C dec. 50% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.6, 61.8, 62.1, 62.4, 62.6. ^{1}H NMR ($CDCl_3$) δ 3.2−3.3 (m, 135 H), 3.7−4.2 (m, 768 H), 6.7−6.9 (m, 144 H), 7.2−7.8 (m, 417 H), 8.3 (br s, 48 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.3 (m), 68.2−70.3 (m), 107.1, 112.2, 113.8, 121.1 (d, J = 3.6

Hz), 127.6, 129.3, 131.4 (m), 133.0, 138.0−140.0 (m), 144.8, 147.1, 148.8, 150.0−156.0 (m), 156.5. Anal. Calcd for $C_{1368}H_{1512}N_{138}O_{333}P_{46}S_{46}$: C, 58.44; H, 5.42; N, 6.87. Found: C, 58.33; H, 5.38; N, 6.74.

General Procedure for the Synthesis of Dendrimers 11-[G$_1$]−11-[G$_4$]. A solution of 0.300 g of dendrimer **1-[G′$_n$]** (n = 1, 0.211 mmol; n = 2, 0.0877 mmol; n = 3, 0.0405 mmol; n = 4, 0.0195 mmol) and (acetylmethylene)triphenylphosphorane (**10**) (n = 1, 0.403 g, 1.266 mmol; n = 2, 0.335 g, 1.052 mmol; n = 3, 0.309 g, 0.972 mmol; n = 4, 0.298 g, 0.936 mmol) in 20 mL of THF was refluxed for 48 h. The solution was then evaporated to dryness. The resulting past was washed with 3 × 20 mL of a THF/pentane/ether (1/10/10) mixture to eliminate triphenylphosphine oxide. Dendrimers **11-[G$_n$]** were obtained as powders.

11-[G$_1$]: Pale yellow powder. Mp 59 °C dec. 59% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.6, 61.6. ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 18 H), 3.4 (d, J = 10.6 Hz, 9 H), 6.6 (d, J = 16.3 Hz, 6 H), 7.2 (dd, J = 6.7 Hz, J = 1.4 Hz, 12 H), 7.3 (dd, J = 8.6 Hz, J = 1.2 Hz, 6 H), 7.4 (d, J = 16.3 Hz, 6 H), 7.5 (d, J = 6.7 Hz, 12 H), 7.6 (s, 3 H), 7.7 (d, J = 8.6 Hz, 6 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 26.9, 32.4 (d, J = 13.1 Hz), 120.9 (d, J = 4.2 Hz), 121.3 (d, J = 4.7 Hz), 126.5, 127.8, 128.9, 131.1, 131.9, 138.2 (d, J = 14.3 Hz), 141.5, 150.5 (d, J = 8.0 Hz), 154.4 (d, J = 7.2 Hz), 197.5. IR (KBr) 1689 (s, $\nu_{C=O(s\text{-}cis)}$), 1666 (s, $\nu_{C=O(s\text{-}trans)}$) cm^{-1} IR (THF) 1695 (s, $\nu_{C=O(s\text{-}cis)}$), 1672 (s, $\nu_{C=O(s\text{-}trans)}$) cm^{-1}. MS: m/z 1663 [M + 1]$^+$. Anal. Calcd for $C_{84}H_{78}N_6O_{15}P_4S_4$: C, 60.64; H, 4.73; N, 5.05. Found: C, 60.57; H, 4.63; N, 4.95.

11-[G$_2$]: Yellow powder. Mp: 56 °C dec. 60% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.8, 61.7, 62.4. ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 36 H), 3.3 (d, J = 10.5 Hz, 18 H), 3.4 (d, J = 9.3 Hz, 9 H), 6.6 (d, J = 16.2 Hz, 12 H), 7.1−7.3 (m, 42 H), 7.3 (d, J = 16.2 Hz, 12 H), 7.5 (d, J = 7.9 Hz, 24 H), 7.6 (s, 9 H), 7.65 (d, J = 8.6 Hz, 12 H), 7.75 (d, J = 8.7 Hz, 6 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 27.0, 32.4 (d, J = 13.0 Hz), 120.8 (d, J = 3.4 Hz), 121.3 (d, J = 4.7 Hz), 126.4, 127.6, 127.8, 128.9, 131.1, 131.4, 131.5, 138.5 (d, J = 13.9 Hz), 141.4, 150.5 (d, J = 5.8 Hz), 150.7 (d, J = 7.1 Hz), 151.4 (d, J = 7.3 Hz), 197.5. IR (KBr) 1689 (s, $\nu_{C=O(s\text{-}cis)}$), 1666 (s, $\nu_{C=O(s\text{-}trans)}$) cm^{-1}. Anal. Calcd for $C_{192}H_{180}N_{18}O_{33}P_{10}S_{10}$: C, 59.16; H, 4.65; N, 6.47. Found: C, 58.95; H, 4.51; N, 6.35.

11-[G$_3$]: Pale yellow powder. Mp 63 °C dec. 72% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.6, 61.7, 62.4, 62.7. ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 72 H), 3.3 (d, J = 10.5 Hz, 63 H), 6.6 (d, J = 16.0 Hz, 24 H), 7.2−7.8 (m, 225 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 26.9, 32.3 (d, J = 12.9 Hz), 121.3 (d, J = 4.8 Hz), 126.5, 127.7, 127.6, 128.9, 131.1, 131.3, 131.5, 132.0, 138.0−138.6 (m), 141.4, 150.5−151.8 (m), 151.4 (d, J = 7.3 Hz), 197.5. IR (KBr) 1689 (s, $\nu_{C=O(s\text{-}cis)}$), 1666 (s, $\nu_{C=O(s\text{-}trans)}$) cm^{-1}. Anal. Calcd for $C_{408}H_{384}N_{42}O_{69}P_{22}S_{22}$: C, 58.57; H, 4.63; N, 7.03. Found: C, 58.41; H, 4.53; N, 6.89.

11-[G$_4$]: Pale yellow powder. Mp 148 °C dec. 65% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.5, 61.6, 62.3, 62.7, 63.0. ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 144 H), 3.3 (d, J = 10.2 Hz, 135 H), 6.5 (d, J = 16.1 Hz, 48 H), 7.2−7.8 (m, 465 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 26.9, 32.3 (d, J = 13.2 Hz), 121.3 (d, J = 4.9 Hz), 126.5, 127.6, 127.8 (br s), 128.9, 131.1, 131.3, 131.5, 138.5−139.0 (m), 141.4, 150.5−151.8 (m), 151.4 (d, J = 8.1 Hz), 197.5. IR (KBr) 1689 (s, $\nu_{C=O(s\text{-}cis)}$), 1666 (s, $\nu_{C=O(s\text{-}trans)}$) cm^{-1}. Anal. Calcd for $C_{840}H_{792}N_{90}O_{141}P_{46}S_{46}$: C, 58.31; H, 4.61; N, 7.28. Found: C, 58.12; H, 4.47; N, 7.21.

General Procedure for the Synthesis of Dendrimers 13-[G$_1$], 13-[G$_4$]. A solution of 0.300 g of dendrimer **1-[G′$_n$]** (n = 1, 0.211 mmol, n = 4, 0.0195 mmol) and (cyanomethylene)triphenylphosphorane (**12**) (n = 1, 0.381 g, 1.266 mmol; n = 4, 0.282 g, 0.936 mmol) in 20 mL of THF was refluxed for 12 h. The solution was then evaporated to dryness. The resulting paste was washed with 3 × 15 mL of a THF/pentane (1/1) mixture to eliminate triphenylphosphine oxide. Dendrimers **11-[G$_n$]** were obtained as powders.

13-[G$_1$]: Pale yellow powder. Mp 128 °C dec. 58% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.7, 61.5. ^{1}H NMR ($CDCl_3$) δ 3.4 (d, J = 10.6 Hz, 9 H), 5.4 (d, J = 12.2 Hz, (6 × 0.2) H), 5.8 (d, J = 16.6 Hz, (6 × 0.8) H), 7.1 (d, J = 12.2 Hz, (6 × 0.2) H), 7.2−7.8 (m, (39 + 6 × 0.8) H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.4 (d, J = 13.2 Hz), 94.4, 95.8, 116.6, 117.3, 120.9 (d, J = 3.9 Hz), 121.2 (d, J = 5.8 Hz), 121.5 (d, J = 4.7 Hz), 127.8, 128.2, 130.0, 130.2, 131.8, 132.0, 138.4 (d, J = 10.8 Hz), 146.8, 148.6, 150.6 (d, J = 7.4 Hz), 151.5 (d, J = 7.3 Hz), 151.9 (d, J = 7.4 Hz). IR (KBr): 2216 (s; $\nu_{C\equiv N}$) cm^{-1}. MS: m/z 1561 [M + 1]$^+$. Anal. Calcd for $C_{78}H_{60}N_{12}O_9P_4S_4$: C, 60.00; H, 3.87; N, 10.76. Found: C, 59.64; H, 3.73; N, 10.59.

13-[G$_4$]: Pale yellow powder. Mp 133 °C dec. 62% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.6, 61.4 62.3 (br s), 62.8, 63.0. ^{1}H NMR ($CDCl_3$) δ 3.3 (d, J = 10.0 Hz, 135 H), 5.3 (d, J = 12.1 Hz, (48 × 0.2) H), 5.7 (d, J = 16.3 Hz, (48 × 0.8) H), 7.0 (d, J = 12.1 Hz, (48 × 0.2) H), 7.2−7.7 (m, (417 + 48 × 0.8) H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 32.3 (d, J = 13.6 Hz), 94.3, 95.7, 116.6, 117.4, 120.9 (d, J = 3.9 Hz), 121.2 (d, J = 9.2 Hz), 121.3 (d, J = 8.7 Hz), 127.5 (br s), 127.8, 128.2, 129.9, 130.1, 131.3, 131.5, 132.0, 138.7 (m), 146.7, 148.5, 150.6 (d, J = 7.4 Hz), 150.5−150.8 (m), 151.4 (d, J = 7.3 Hz), 151.8 (d, J = 7.7 Hz). IR (KBr): 2216 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. Calcd for $C_{792}H_{648}N_{138}O_{93}P_{46}S_{46}$: C, 57.70; H, 3.96; N, 11.72. Found: C, 54.47; H, 3.81; N, 11.51.

General Procedure for the Synthesis of Dendrimers 14-[G$_1$]−14-[G$_7$]. To a solution of 0.100 g of dendrimer **1-[G$_n$]** (n = 1, 0.110 mmol; n = 2, 0.0418 mmol; n = 3, 0.0186 mmol; n = 4, 0.0088 mmol; n = 5, 0.0043 mmol; n = 6, 0.00214 mmol; n = 7, 0.00106 mmol) in 10 mL of THF was added triethylamine (n = 1, 101 μL, 0.726 mmol; n = 2, 77 μL, 0.552 mmol; n = 3, 68 μL, 0.491 mmol; n = 4, 65 μL, 0.465 mmol; n = 5, 63 μL, 0.454 mmol; n = 6, 63 μL, 0.452 mmol; n = 7, 62 μL, 0.448 mmol; 10% excess) then allylamine (n = 1, 55 μL, 0.726 mmol; n = 2, 41 μL, 0.552 mmol; n = 3, 37 μL, 0.491 mmol; n = 4, 35 μL, 0.465 mmol; n = 5, 34 μL, 0.454 mmol; n = 6, 34 μL, 0.452 mmol; n = 7, 34 μL, 0.448 mmol; 10% excess). The resulting mixture was stirred for 12 h at room temperature and then filtered. The solution was evaporated to dryness to give an oil (**14-[G$_1$]**) or a powder, which was washed with 2 × 10 mL of a pentane/ether (1/1) mixture.

14-[G$_1$]: Yellow oil: 92% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 52.2, 68.6. ^{1}H NMR ($CDCl_3$) δ 3.1 (d, J = 9.5 Hz, 9 H), 3.3 (m, 6 H), 3.6 (m, 12H), 5.1 (m, 12H), 5.8 (m, 6H), 7.1 (dd, J = 8.6 Hz, J = 1.5 Hz, 6H), 7.4 (s, 3H), 7.7 (d, J = 8.6 Hz, 6 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 30.9 (d, J = 11.2 Hz), 43.7, 115.4, 121.2 (d, J = 4.5 Hz), 127.5, 133.1, 135.7 (d, J = 12.2 Hz), 136.0 (d, J = 7.9 Hz), 150.3 (d, J = 8.3 Hz). IR (THF): 3376 (m, ν_{NH}) cm^{-1}. MS: m/z 1033.2 [M]$^+$. Anal. Calcd for $C_{42}H_{60}N_{12}O_3P_4S_4$: C, 48.83; H, 5.85; N, 16.27. Found: C, 48.49; H, 5.68; N, 16.12.

14-[G$_2$]: White powder. Mp 98 °C dec. 95% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 51.8, 61.8, 68.7. ^{1}H NMR ($CDCl_3$) δ 3.0 (d, J = 7.3 Hz, 18 H), 3.1 (d, J = 9.3 Hz, 9 H), 3.3 (m, 12H), 3.5 (m, 24 H), 5.1 (m, 24 H), 5.8 (m, 12 H), 7.1−7.7 (m, 45 H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 30.8 (d, J = 11.2 Hz), 33.0 (d, J = 12.8 Hz), 43.7, 115.4, 121.5 (m), 127.4, 128.3, 132.5, 132.7, 136.0 (m), 138.5 (d, J = 12.1 Hz), 150.5 (d, J = 7.2 Hz), 150.9 (d, J = 8.2 Hz). IR (KBr): 3367 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{108}H_{144}N_{30}O_9P_{10}S_{10}$: C, 49.19; H, 5.50; N, 15.94. Found: C, 48.91; H, 5.41; N, 15.79.

14-[G$_3$]: White powder. Mp 109 °C dec. 95% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 51.8, 61.7, 68.7. ^{1}H NMR ($CDCl_3$) δ 3.1 (d, J = 9.5 Hz, 36H), 3.2 (d, J = 9.3 Hz, 27H), 3.3 (m, 24H), 3.5 (m, 48H), 5.1 (m, 48H), 5.8 (m, 24H), 7.1−7.7 (m, 105H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 30.8 (d, J = 10.9 Hz), 32.9 (d, J = 12.7 Hz), 43.7, 115.4, 121.5 (m), 127.4, 128.2, 128.4, 132.0, 132.7, 136.0 (m), 138.7 (d, J = 12.4 Hz), 150.5 (d, J = 7.2 Hz), 150.9 (m). IR (KBr): 3367 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{240}H_{312}N_{66}O_{21}P_{22}S_{22}$: C, 49.32; H, 5.38; N, 15.82. Found: C, 49.11; H, 5.24; N, 15.61.

14-[G$_4$]: White powder: Mp 112 °C dec. 94% yield. ^{31}P {^{1}H} NMR ($CDCl_3$) δ 51.5, 61.3, 61.7, 68.7. ^{1}H NMR ($CDCl_3$) δ 3.1 (d, J = 9.4 Hz, 72H), 3.2 (m, 63H), 3.3 (m, 48H), 3.5 (m, 96H), 5.1 (m, 96H), 5.8 (m, 48H), 7.1−7.7 (m, 225H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 30.8 (d, J = 11.3 Hz), 32.9 (d, J = 12.7 Hz), 43.7, 115.4, 121.5 (m), 127.4, 128.2, 132.0, 132.6, 136.0 (m), 138.7 (m), 150.5 (d, J = 7.0 Hz), 151.1 (d, J = 6.9 Hz). IR (KBr): 3369 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{504}H_{648}N_{138}O_{45}P_{46}S_{46}$: C, 49.38; H, 5.33; N, 15.77. Found: C, 49.06; H, 5.21; N, 15.67.

14-[G_5]: White powder: Mp 111 °C dec. ^{31}P {^1H} NMR ($CDCl_3$) δ 51.8, 61.8 (br s), 68.6. ^1H NMR ($CDCl_3$) δ 3.1 (d, J = 9.1 Hz, 144H), 3.2 (m, 135H), 3.3 (m, 96H), 3.5 (m, 192H), 5.1 (m, 192H), 5.8 (m, 96H), 7.1−7.7 (m, 465H). ^{13}C {^1H} NMR ($CDCl_3$) δ 30.8 (d, J = 11.3 Hz), 32.9 (d, J = 12.8 Hz), 43.7, 115.5, 121.6 (m), 127.4, 128.2, 132.0, 132.7, 136.0 (m), 138.7 (d, J = 13.0 Hz), 150.6 (d, J = 7.4 Hz), 151.1 (d, J = 6.8 Hz). IR (KBr): 3366 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{1032}H_{1320}N_{282}O_{93}P_{94}S_{94}$: C, 49.41; H, 5.30; N, 15.74. Found: C, 49.18; H, 5.16; N, 15.52.

14-[G_6]: White powder: Mp 117 °C dec. 95% yield. ^{31}P {^1H} NMR ($CDCl_3$) δ 51.8, 61.8 (br s), 68.5. ^1H NMR ($CDCl_3$) δ 3.1 (d, J = 9.1 Hz, 288H), 3.2 (m, 279H), 3.3 (m, 192H), 3.5 (m, 384H), 5.1 (m, 384H), 5.7−5.9 (m, 192H), 7.1−7.7 (m, 945H). ^{13}C {^1H} NMR ($CDCl_3$) δ 30.8 (d, J = 11.3 Hz), 32.9 (d, J = 12.8 Hz), 43.7, 115.3, 121.5 (br s), 127.4, 128.1, 128.2, 132.0, 132.7, 135.9 (d, J = 14.5 Hz), 136.0 (d, J = 7.2 Hz), 138.7 (m), 150.5 (d, J = 7.3 Hz), 151.2 (d, J = 6.9 Hz). IR (KBr): 3369 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{2088}H_{2664}N_{570}O_{189}P_{190}S_{190}$: C, 49.42; H, 5.29; N, 15.73. Found: C, 49.21; H, 5.17; N, 15.39.

14-[G_7]: White powder: Mp 122 °C dec. 94% yield. ^{31}P {^1H} NMR ($CDCl_3$) δ 61.7 (br s), 68.5. ^1H NMR ($CDCl_3$) δ 3.1 (d, J = 9.4 Hz, 576H), 3.2 (m, 567H), 3.4 (m, 384H), 3.5 (m, 768H), 5.0 (m, 768H), 5.7 (m, 384H), 7.1−7.7 (m, 1905H). ^{13}C {^1H} NMR ($CDCl_3$) δ 30.8 (d, J = 10.9 Hz), 32.9 (d, J = 13.0 Hz), 43.7, 115.3, 121.4 (br s), 127.4, 128.1, 128.2, 132.0, 132.7, 135.8 (d, J = 15.6 Hz), 136.0 (d, J = 7.2 Hz), 139.0 (m), 150.5 (d, J = 6.7 Hz), 151.0 (m). IR (KBr): 3369 (m, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{4200}H_{5352}N_{1146}O_{381}P_{382}S_{382}$: C, 49.42; H, 5.29; N, 15.73. Found: C, 49.18; H, 5.14; N, 15.41.

General Procedure for the Synthesis of Dendrimers 15-[G_1], 15-[G_4]. To a solution of 0.300 g of dendrimer **1-[G_n]** (n = 1, 0.330 mmol; n = 4, 0.0266 mmol) in 10 mL of THF was added a solution of triethylamine (n = 1, 276 μL, 1.98 mmol; n = 4, 178 μL, 1.278 mmol) and propargylamine (n = 1, 136 μL, 1.98 mmol; n = 4, 88 μL, 1.278 mmol) in 10 mL of THF. The mixture was stirred for 12 h at room temperature. The precipitate was eliminated by centrifugation, and then the solution was evaporated to dryness. The resulting powder was purified by column chromatography on silica gel (eluent: ethyl acetate).

15-[G_1]: Yellow powder. Mp 39 °C dec. 93% yield. ^{31}P {^1H} NMR ($CDCl_3$) δ 52.8, 67.5. ^1H NMR ($CDCl_3$) δ 2.24 (t like, J = 2.5 Hz, 6 H), 3.33 (d, J = 9.8 Hz, 9 H), 3.53 (q like, J = 6.5 Hz, J = 6.6 Hz, J = 6.7 Hz, 6 H), 3.83 (dddd, J = 17.7 Hz, J = 13.0 Hz, J = 6.6, Hz, J = 2.5 Hz, 6 H), 3.85 (dddd, J = 17.7 Hz, J = 13.0 Hz, J = 6.7 Hz, J = 2.5 Hz, 6 H), 7.26 (dd, J = 8.6 Hz, J = 1.3 Hz, 6 H), 7.53 (br s, 3 H), 7.63 (d, J = 8.6 Hz, 6 H). ^{13}C {^1H} NMR ($CDCl_3$) δ 30.3, 30.4 (d, J = 12.0 Hz), 70.8, 80.6 (d, J = 8.2 Hz), 120.8 (d, J = 4.9 Hz), 127.3, 132.4, 136.0 (d, J = 12.5 Hz), 150.0 (d, J = 8.2 Hz). IR (KBr): 3330 (br, ν_{N-H}), 3290 (m, $\nu_{\equiv C-H}$) cm^{-1}. MS: m/z 1021 $[M + 1]^+$. Anal. Calcd for $C_{42}H_{48}N_{12}O_3P_4S_4$: C, 49.40; H, 4.74; N, 16.46. Found: C, 49.18; H, 4.61; N, 16.40.

15-[G_4]: Pale yellow powder. Mp 60 °C dec. 58% yield. ^{31}P {^1H} NMR ($CDCl_3$) δ 52.6, 62.5 (br s), 67.5. ^1H NMR ($CDCl_3$) 2.2 (br s, 48 H), 3.1 (d, J = 9.1 Hz, 72 H), 3.3 (d, J = 8.2 Hz, 63 H), 3.4 (m, 48 H), 3.7−3.8 (m, 96 H), 7.1−7.6 (m, 225 H). ^{13}C {^1H} NMR ($CDCl_3$) δ 30.3, 30.5 (d, J = 10.8 Hz), 30.9 (d, J = 9.8 Hz), 31.9 (d, J = 13.0 Hz), 70.8, 80.7 (d, J = 8.0 Hz), 121.0 (d, J = 3.6 Hz), 127.1, 127.7, 131.6, 132.0, 136.2 (d, J = 12.5 Hz), 138.0−139.0 (m), 150.3 (d, J = 7.7 Hz), 150.7 (d, J = 8.3 Hz). IR (KBr): 3401 (br, ν_{N-H}), 3292 (m, $\nu_{\equiv C-H}$) cm^{-1}. Anal. Calcd for $C_{504}H_{552}N_{138}O_{45}P_{46}S_{46}$: C, 49.77; H, 4.57; N, 15.89. Found: C, 49.51; H, 4.45; N, 15.71.

General Procedure for the Synthesis of Dendrimers 16-[G_1], 16-[G_4]. To a solution of 0.300 g of dendrimer **1-[G_n]** (n = 1, 0.330 mmol; n = 4, 0.0266 mmol) in 10 mL of THF was added 1-(trimethylsilyl)imidazole (n = 1, 319 μL, 2.178 mmol; n = 4, 206 μL, 1.406 mmol; 10% excess). The mixture was stirred for 1 h at room temperature and then evaporated to dryness. The resulting oil was washed with a THF/ether (1/10) mixture to give dendrimers **16-[G_n]** as unstable powders, extremely sensitive to moisture.

16-[G_1]: Yellow powder. 54% yield. ^{31}P {^1H} NMR (THF-d_8) δ 43.4, 49.5. ^1H NMR (THF-d_8) δ 3.5 (d, J = 11.4 Hz, 9 H), 7.1 (br s, 6 H), 7.3 (dd, J = 8.5 Hz, J = 1.6 Hz, 6 H), 7.4 (br s, 6 H), 7.6 (d, J = 8.5 Hz, 6 H), 7.9 (br s, 6 H), 8.0 (d, J = 1.9 Hz, 3 H). ^{13}C {^1H} NMR (THF-d_8) δ 31.2 (d, J = 14.3 Hz), 120.9 (d, J = 7.7 Hz), 120.8 (d, J = 5.2 Hz), 129.0, 131.9 (d, J = 13.4 Hz), 132.7, 140.4 (d, J = 5.3 Hz), 142.5 (d, J = 14.4 Hz), 152.1 (d, J = 7.4 Hz).

16-[G_4]: Yellow powder. 45% yield. ^{31}P {^1H} NMR (THF-d_8) δ 43.1, 49.8, 59.4, 59.9, 60.1. ^1H NMR (THF-d_8) δ 3.3−3.5 (m, 135 H), 7.1 (br s, 48 H), 7.2−8.0 (m, 321 H). ^{13}C {^1H} NMR (THF-d_8) δ 31.3 (d, J = 12.6 Hz), 32.5−33.1 (m), 120.9 (d, J = 7.4 Hz), 122.1 (br s), 128.5, 128.7, 131.9 (d, J = 13.5 Hz), 132.9−133.1 (m), 140.4 (d, J = 4.3 Hz), 142.5 (d, J = 12.7 Hz), 142.8 (d, J = 13.1 Hz), 151.0−152.0 (m), 152.5 (d, J = 7.9 Hz).

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