Synthesis and reactivity of small phosphorus-containing dendritic wedges (dendrons)

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Dedicated to Professor Marcial Moreno-Manas on the occasion of his 60th birthday
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Abstract
The synthesis of two small dendrons (dendritic wedges) is reported and the reactivity of the functionality located at the core is studied. The first dendron has no reactive functionality on the surface, but possesses a vinyl group activated by a P=N-P=S linkage at the core; this vinyl group reacts slowly but cleanly with 2,3-dimethylbutadiene in Diels-Alder additions. The second dendron has aldehyde groups on the surface and one protected phenol group at the core. The deprotection occurs in very mild conditions, leading to a dendron having one phenol and four aldehyde groups. The reactivity of the phenol is demonstrated by the addition of a diisocyanate, affording a carbamate function and the grafting of an isocyanate group at the core of the dendron.

Keywords: Dendron, dendrimer, phosphorus, vinyl, phenol

Introduction

Dendritic macromolecules are highly branched nanosized compounds having well defined three-dimensional size, shape, topology and functionalities. These aesthetic molecules have attracted considerable attention over the past decade, reinforced by promising applications.1 The initial compounds in this field were dendrimers,2 i.e. dendritic compounds having functionalities only on the surface. However, the usefulness of dendritic wedges (also called dendrons),3 having functionalities on the surface and another single functionality at the core was rapidly demonstrated after these pioneering investigations (Figure 1).
Pursuing our work dealing with the synthesis and study of properties of phosphorus-containing dendrimers, we have developed several strategies to functionalize the surface or even the branches of dendritic compounds. Recently, we became interested in the synthesis of phosphorus-containing dendrons, that allowed us to obtain macromolecules having original architectures. The chemical diversity of the functionality located at the core, its reactivity and its compatibility with the functionalities located on the surface remains an interesting problem. We wish to report some examples dealing with the synthesis and reactivity at the core of phosphorus-containing dendrons, potentially useful building blocks for the synthesis of more complex macromolecules.

**Results and Discussion**

We have already demonstrated that a vinyl group activated by a P=N-P=S linkage located at the core of dendrons possesses an interesting reactivity toward primary and secondary amines. We decided to test another type of reactivity of this group, that is Diels-Alder additions. In order to avoid any side reactions, we utilized a dendron having no reactive functional groups on the surface. For this purpose, phenoxy groups are reacted with dendron 1-Gₙ, having two P(S)Cl₂ groups, to yield compound 1-G'. A large excess of 2,3-dimethylbutadiene is then used to ascertain the reactivity of the vinyl group of dendron 1-G'. Scheme 1. The reaction proceeds slowly and necessitates 4 days in toluene at 100°C for completion. The reaction is monitored by ³¹P NMR, which displays in particular the deshielding of the doublet corresponding to the PPh₂ group from 9.6 ppm for 1-G' to 19.9 ppm for 2-G'. Dendron 2-G' is isolated in good yield after work up (82%), but this Diels-Alder reaction is quite slow and necessitates drastic conditions, which could be inapplicable to dendrons having also functionalities on the surface. Thus, it appears that this pathway to functionalize the core of dendrons is not particularly attractive, despite the presence of the P=N-P=S linkage, for which we have demonstrated a useful reactivity toward electrophiles.
Scheme 1. Synthesis of dendron 1-G'₁ and Diels-Alder reaction at its core.

Furthermore, it would be desirable to have dendrons possessing a single reactive group at the core to avoid side reactions. For this purpose, we decided to apply our "classical" method of synthesis of phosphorus-containing dendrimers¹ᵃ, ⁴ᵇ, ⁴ᵈ to 4-acetoxy-benzaldehyde. Indeed, this compound possesses a protected phenol, which could be deprotected in mild conditions after the synthesis of the dendron. The first step of the synthesis is the condensation with H₂NNMeP(S)Cl₂, the second step is the nucleophilic substitution of Cl by hydroxybenzaldehyde in basic conditions, leading to compound 3-G'₀ (Scheme 2). The repetition of these two steps leads finally to the dendron 3-G'₁, possessing one ester functionality at the core and four aldehyde groups on the surface. These reactions are monitored by ¹H NMR for the condensation reactions (disappearance of the signal corresponding to CHO) and by ³¹P NMR for the substitution reactions (slight shielding on going from P(S)Cl₂ to P(S)(OAr)₂).

Scheme 2. Synthesis of dendron 3-Gₙ (n = 0, 1) from the 4-acetoxy-benzaldehyde core.
Contrary to the previous series of dendrons 1-G'1 and 2-G'1, compounds 3-G'n also have functionalities (aldehydes) on the surface; thus, the reactivity carried out at the core must not interfere with the surface. First, we attempted to deprotect the phenol in a classical way, using a mixture of organic solvents and water or methanol, in the presence of KOH or K2CO3. In all cases, the deprotection is only partial and a degradation of the dendron is observed. Consequently, we decided to apply a very mild method, using guanidine as desacetylating agent.8 The reaction is almost instantaneous, no side reaction is observed with the aldehydes, but the phenol is totally deprotected, leading to compound 4-G'1 in a very good yield (89% after work-up) (Scheme 3). This compound is characterized by NMR and Mass spectrometry (FAB).

The presence of a phenol group at the core of dendron 4-G'1 offers a number of possibilities for further functionalizations. As an example, an excess (6 equivalents) of 1,6-diisocyanatohexane is reacted with 4-G'1 (Scheme 3). The expected addition occurs, affording an isocyanate core and a carbamate function, characterized in particular by 13C NMR by the appearance of a singlet at 154.3 ppm. Dendron 5-G'1 also is characterized by Mass spectrometry (FAB).

![Scheme 3. Reactivity at the core of the dendron 3–G'1.](image)

**Conclusions**

We have synthesized two small dendrons and studied the reactivity of the functionality located at the core, a vinyl group in one case (1-G'1), and a protected phenol in the second case (3-G'1). It appears that, for practical reasons, Diels-Alder reaction is not the best way to modify the core of dendron 1-G'1, even if the resulting product is isolated in good yield. On the other hand, the very easy deprotection of the phenol group of 3-G'1, leading to 4-G'1, should open the way to a versatile reactivity. Indeed, we have shown that dendron 4-G'1 adds easily to isocyanate functionalities, and it is well known that phenols offer a very large palette of reactions. Thus,
dendron 4-G'₁ should be considered as an AB₄ monomer (with A = OH and B = CHO) suitable for the synthesis of compounds possessing complex macromolecular dendritic architectures, or for the grafting on various compounds, polymers, or materials.

**Experimental Section**

**General Procedures.** All reactions were carried out in the absence of air, under argon, using standard Schlenk techniques and vacuum-line manipulations. All solvents were dried and distilled before use. Perkin Elmer 1725X was used for FT-IR. NMR spectra were recorded on Bruker AC80, AC200, or AM250 for ¹H, ¹³C, and ³¹P NMR, with SiMe₄, and H₂PO₄ as references, respectively. The attribution of ¹³C NMR signals was done using Jmod, two-dimensional HMBC and HMQC, broad band or CW ³¹P decoupling experiments when necessary. The numbering scheme used for NMR is depicted in Figure 2. Compound 1-G₁ was synthesised according to a published procedure.⁷a, ⁷d

![Numbering used for NMR.](image)

**Figure 2.** Numbering used for NMR.

**Synthesis of dendron 1-G₁.** To a solution of dendron 1-G₁ (0.2 g, 0.234 mmol) in THF (10 mL) was added a slight excess of NaOPh (0.11 g, 0.95 mmol). The resulting mixture was stirred overnight at room temperature, then centrifuged. The solution was recovered and evaporated to dryness to afford a powder, which was washed several times with THF/pentane (1:5) to yield dendron 1-G₁.

1-G₁ Pale beige powder. 88 % yield. ³¹P ⁷¹H NMR (CDCl₃): δ 9.6 (d, ²Jₚₚ = 31.3 Hz, P₀), 52.2 (d, ²Jₚₚ = 31.3 Hz, P₀), 61.8 (s, P₁); ¹H NMR (CDCl₃): δ 3.3 (6H, d, ³Jₚₚ = 10.6 Hz, CH₃N), 6.1 (1H, ddd, ³Jₚₚ = 24.1 Hz, ³Jₕₚₚ = 18.3 Hz, ⁵Jₚₚ = 1.1 Hz, CH₂trans=CH), 6.4 (1H, ddd, ³Jₚₚ = 45.9 Hz, ³Jₕₚₚ = 12.4 Hz, ³Jₚₚ = 1.1 Hz, CH₂cis=CH), 6.8 (1H, ddddd, ²Jₚₚ = 25.2 Hz, ³Jₕₚₚ = 18.3 Hz, ³Jₕₚₚ = 12.4 Hz, ⁴Jₚₚ = 1.1 Hz, CH=), 7.2-7.7 (40H, m, C₆H₅, C₆H₄, CH=N); ¹³C ⁷¹H NMR (CDCl₃): δ 32.9 (d, ²Jₙₙ = 13.1 Hz, P₇-NCH₃), 121.3 (d, ³Jₚₚ = 4.3 Hz, C₁), 121.8 (d, ³Jₚₚ = 4.7 Hz, C₀), 125.2 (s, C₁'), 127.8 (dd, ¹Jₚₚ = 100.0 Hz, ³Jₚₚ = 4.3 Hz, C₀'), 127.8 (s, C₀'), 128.6
(\text{d}, 2^1J_{CP} = 13.1 \text{ Hz, } C^0), 129.3 (s, C_1^4), 130.9 (s, C_4^4), 130.4 (dd, 1^1J_{CP} = 135.9 \text{ Hz, } 3^1J_{CP} = 4.7 \text{ Hz, CH=}), 132.0 (d, 3^1J_{CP} = 10.5 \text{ Hz, } C^m), 132.5 (d, 4^1J_{CP} = 2.4 \text{ Hz, } C^0), 136.6 (s, CH_2=), 138.9 (d, 3^1J_{CP} = 13.4 \text{ Hz, CH=N}), 150.5 (d, 2^1J_{CP} = 7.2 \text{ Hz, } C_0^1), 152.8 (d, 2^1J_{CP} = 9.2 \text{ Hz, } C_1^1). \text{ Anal. Calcd for } C_{54}H_{49}N_5O_6P_4S_3 (1084.10): C, 59.82; H, 4.55; N, 6.46. \text{ Found: C, 60.03; H, 4.67; N, 6.32.}

**Synthesis of dendron 2-G'1.** To a solution of dendron 1-G'1 (0.2 g, 0.18 mmol) in toluene (3 mL) was added a large excess of 2,3-dimethylbutadiene (3 mL, 26.5 mmol). The resulting solution was heated at 100 °C for 4 days in a sealed reactor. Then the solution was evaporated to dryness to give a white powder, which was washed twice with pentane. 2-G'1 \text{ White powder. 82 % yield.} 31P \{1H\} NMR (THF-d8): \( \delta \) 19.9 (d, 2\(^1J_{PP} = 33.2 \text{ Hz, P}^0_0), 50.7 (d, 2\(^1J_{PP} = 33.2 \text{ Hz, P}_0), 61.5 (s, P_1); \) \text{1H NMR (THF-d8): } \( \delta \) 1.64 (3H, s, CH_3), 1.69 (3H, s, CH_3), 1.7-2.4 (7H, m, CH_2, CH), 3.45 (6H, d, 3\(^1J_{HP} = 10.6 \text{ Hz, CH}_2N), 7.0-8.0 (40H, m, C_6H_5, C_6H_4, CH=N); \) \text{13C \{1H\} NMR (THF-d8): } \( \delta \) 19.3 and 19.4 (s, CH_3-C=), 23.8 (s, =C-CH_2-CH_3), 31.1 (s, CH_2-CH_2-CHP'_0), 32.3 (d, 2\(^1J_{CP} = 13.8 \text{ Hz, } =C-CH_2-CHP'_0), 33.5 (d, 2\(^1J_{CP} = 12.2 \text{ Hz, P}_1-NCH_3), 34.2 (d, 1\(^1J_{CP} = 67.0 \text{ Hz, CH-P}), 122.5 (d, 3\(^1J_{CP} = 4.6 \text{ Hz, } C_1^2), 123.0 (d, 3\(^1J_{CP} = 4 \text{ Hz, } C_0^2), 125.1 (d, 3\(^1J_{CP} = 13.8 \text{ Hz, } =C-CH_2-CHP'_0), 126.1 (s, C_1^4), 128.7 (s, C_0^3), 129.2 (dd, 1^1J_{CP} = 120 \text{ Hz, } 3^1J_{CP} = 5.8 \text{ Hz, } C_0^5), 129.3 (s, =CH-CH_2-CH), 129.6 (d, 3\(^1J_{CP} = 12 \text{ Hz, } C^0), 130.4 (s, C_1^3), 132.4 (s, C_0^4), 133.3 (d, 1\(^1J_{CP} = 10.5 \text{ Hz, } C^m), 133.5 (s, C^0), 140.8 (d, 3\(^1J_{CP} = 13.3 \text{ Hz, CH=N}), 152.2 (d, 2\(^1J_{CP} = 7.9 \text{ Hz, } C_0^1), 154.7 (d, 2\(^1J_{CP} = 7.9 \text{ Hz, } C_1^1). \text{ Anal. Calcd for } C_{60}H_{59}N_5O_6P_4S_3 (1166.24): C, 61.79; H, 5.09; N, 6.00. \text{ Found: C, 61.50; H, 4.97; N, 5.81.}

**General procedure for the synthesis of dendrons 3-G_n (P(S)Cl_2 end groups, n = 0, 1)**

To a solution of 1 g of dendron 3-G'_0 (aldehyde end groups) or MeCO_2C_6H_4CHO in chloroform (20 mL) was added at room temperature 5% molar excess of a solution of H_2NNMeP(S)Cl_2 in chloroform (0.3 M). The resulting solution was stirred overnight, then evaporated to dryness to afford 3-G_n as a white powder, which was washed three times with ether/pentane 1/1.

**General procedure for the synthesis of dendrons 3-G'_n (aldehyde end groups, n = 0, 1)**

To a solution of 1 g of dendron 3-G_n (P(S)Cl_2 end groups) in THF (20 mL) was added at room temperature 3% molar excess of 4-hydroxybenzaldehyde, sodium salt (powder). The resulting heterogeneous mixture was stirred overnight, then centrifuged (10000 turns per min). The solution was recovered and evaporated to dryness to give 3-G'_n as a white powder, which was washed three times with ether.

3-G'_0. White powder, 97% yield. 31P \{1H\} NMR (CDCl_3) \( \delta \) 63.5; \text{1H NMR (CDCl_3) } \( \delta \) 2.31 (3H, s, CH_3CO), 3.48 (3H, d, 3\(^1J_{HP} = 13.9 \text{ Hz, CH}_3NPO_0), 7.14 (2H, d, 3\(^1J_{HH} = 8.6 \text{ Hz, } HC_0^2), 7.64 (1H, d, 4\(^1J_{HP} = 2.6 \text{ Hz, } HC_0^5), 7.75 (2H, d, 3\(^1J_{HH} = 8.6 \text{ Hz, } HC_0^5); \) \text{13C \{1H\} NMR (CDCl_3) } \( \delta \) 21.2 (s, CH_3CO), 31.8 (d, 2\(^1J_{CP} = 13.5 \text{ Hz, CH}_3NPO_0), 122.1 (s, C_0^2), 128.5 (s, C_0^3), 131.8 (s, C_0^4), 140.8 (d, 3\(^1J_{CP} = 17.9 \text{ Hz, } C_0^5), 152.0 (s, C_1^1), 169.2 (s, CH_3CO). \text{ Anal. Calcd for } C_{10}H_{11}N_2Cl_2O_2PS (325.1): C, 34.1; H, 3.34; N, 8.01. \text{ Found: C, 36.03; H, 2.99; N, 8.21.}
3-G'. White powder, 98% yield. $^31$P $^1$H NMR (CDCl$_3$) $\delta$ 60.6; $^1$H NMR (CDCl$_3$) $\delta$ 2.30 (3H, s, CH$_3$CO), 3.37 (3H, d, J$_{HP}$ = 11.0 Hz, CH$_3$NP$_0$), 7.10 (2H, d, J$_{HH}$ = 8.6 Hz, HC$_0^5$), 7.36 (4H, dd, J$_{HP}$ = 1.5 Hz, J$_{HH}$ = 8.5 Hz, HC$_1^5$), 7.65 (1H, s, HC$_0^5$), 7.67 (2H, d, J$_{HH}$ = 8.6 Hz, HC$_2^5$), 7.86 (4H, d, J$_{HH}$ = 8.5 Hz, HC$_1^3$), 9.94 (2H, s, CHO); $^{13}$C $^1$H NMR (CDCl$_3$) $\delta$ 21.2 (s, CH$_3$CO), 32.9 (d, J$_{CP}$ = 13.8 Hz, CH$_3$NP$_0$), 120.0 (s, C$_0^5$), 122.1 (d, J$_{CP}$ = 3.5 Hz, C$_1^5$), 128.1 (s, C$_0^3$, C$_1^3$), 131.5 (s, C$_0^4$, C$_1^4$), 139.8 (d, J$_{CP}$ = 13.8 Hz, C$_0^5$), 151.7 (s, C$_0^1$), 155.1 (d, J$_{CP}$ = 8.2 Hz, C$_1^1$), 169.2 (s, CH$_3$CO), 190.9 (s, CHO). Anal. Calcd for C$_{24}$H$_{21}$N$_2$O$_6$PS (496.5): C, 58.06; H, 4.26; N, 5.64. Found: C, 57.80; H, 3.98; N, 5.33.

3-G'. White powder, 97% yield. $^31$P $^1$H NMR (CDCl$_3$) $\delta$ 61.4 (s, P$_0$), 62.5 (s, P$_1$); $^1$H NMR (CDCl$_3$) $\delta$ 2.30 (3H, s, CH$_3$CO), 3.36 (3H, d, J$_{HP}$ = 10.8 Hz, CH$_3$NP$_0$), 3.47 (6H, d, J$_{HP}$ = 13.9 Hz, CH$_3$NP$_1$), 7.14 (2H, d, J$_{HH}$ = 8.6 Hz, HC$_0^5$), 7.28 (4H, m, HC$_1^5$), 7.60-7.77 (7H, m, HC$_0^3$, HC$_0^1$, HC$_1^3$); $^{13}$C $^1$H NMR (CDCl$_3$) $\delta$ 21.2 (s, CH$_3$CO), 31.8 (d, J$_{CP}$ = 13.3 Hz, CH$_3$NP$_1$), 33.1 (d, J$_{CP}$ = 13.3 Hz, CH$_3$NP$_0$), 122.0 (d, J$_{CP}$ = 4.5 Hz, C$_1^5$), 121.1 (s, C$_0^5$), 128.1 (s, C$_0^3$, C$_1^3$), 131.5 (s, C$_0^4$, C$_1^4$), 139.1 (d, J$_{CP}$ = 16.7 Hz, C$_0^5$), 140.8 (d, J$_{CP}$ = 18.4 Hz, C$_1^5$), 151.7 (s, C$_0^1$), 155.1 (d, J$_{CP}$ = 8.2 Hz, C$_1^1$), 169.3 (s, CH$_3$CO). Anal. Calcd for C$_{26}$H$_{27}$N$_6$Cl$_4$O$_4$P$_3$S$_3$ (818.5): C, 38.15; H, 3.32; N, 10.27. Found: C, 37.89; H, 3.07; N, 9.97.

3-G'. White powder, 98% yield. $^31$P $^1$H NMR (CDCl$_3$) $\delta$ 60.8 (s, P$_1$), 62.7 (s, P$_0$); $^1$H NMR (CDCl$_3$) $\delta$ 2.30 (3H, s, CH$_3$CO), 3.37 (3H, d, J$_{HP}$ = 10.7 Hz, CH$_3$NP$_0$), 3.38 (6H, d, J$_{HP}$ = 10.7 Hz, CH$_3$NP$_1$), 7.12 (2H, d, J$_{HH}$ = 8.6 Hz, HC$_0^5$), 7.25 (4H, dd, J$_{HP}$ = 1.6 Hz, J$_{HH}$ = 8.6 Hz, HC$_1^5$); 7.36 (4H, dd, J$_{HP}$ = 1.3 Hz, J$_{HH}$ = 8.4 Hz, HC$_2^5$), 7.60-7.70 (7H, m, HC$_0^3$, HC$_0^1$, HC$_1^3$), 7.74 (2H, d, J$_{HH}$ = 8.6 Hz, HC$_2^5$), 7.85 (8H, d, J$_{HH}$ = 8.4 Hz, HC$_2^3$), 9.93 (4H, s, CHO); $^{13}$C $^1$H NMR (CDCl$_3$) $\delta$ 21.1 (s, CH$_3$CO), 32.9 (d, J$_{CP}$ = 13.1 Hz, CH$_3$NP$_1$), 33.1 (d, J$_{CP}$ = 9.9 Hz, CH$_3$NP$_0$), 122.0 (m, C$_0^5$, C$_1^5$, C$_2^5$), 128.1 (s, C$_0^3$), 128.3 (s, C$_1^3$), 131.5 (s, C$_2^3$), 132.2 (s, C$_0^4$), 132.4 (s, C$_1^4$), 133.6 (s, C$_2^4$), 139.1 (d, J$_{CP}$ = 13.7 Hz, C$_0^5$), 139.6 (d, J$_{CP}$ = 13.7 Hz, C$_1^5$), 151.5 (m, C$_0^1$, C$_1^1$), 155.2 (d, J$_{CP}$ = 6.7 Hz, C$_2^1$), 169.4 (s, CHO). Anal. Calcd for C$_{54}$H$_{47}$N$_6$O$_{12}$P$_3$S$_3$ (1161.1): C, 55.86; H, 4.08; N, 7.24. Found: C, 55.49; H, 3.87; N, 7.03.

Synthesis of dendron 4-G'. A freshly prepared solution of guanidine, obtained from guanidine hydrochloride (0.026 g, 0.44 mmol) and sodium ethoxide (0.03 g, 0.44 mmol) in ethanol (10 mL) was added to a solution of dendron 3-G' (0.50 g, 0.43 mmol) in CH$_2$Cl$_2$ (10 mL)). The resulting mixture was stirred for 5 minutes, the solvents were removed under vacuum. The resulting powder was dissolved in CH$_2$Cl$_2$ (10 mL), then dendron 4-G' was purified by flash chromatography.

4-G'. White powder, 89% yield. $^31$P $^1$H NMR (CDCl$_3$) $\delta$ 60.1 (s, P$_0$), 62.7 (s, P$_1$); $^1$H NMR (CDCl$_3$) $\delta$ 2.33 (3H, d, J$_{HP}$ = 10.6 Hz, CH$_3$NP$_0$), 3.37 (6H, d, J$_{HP}$ = 10.9 Hz, CH$_3$NP$_1$), 6.85 (2H, d, J$_{HH}$ = 8.5 Hz, HC$_0^5$), 7.25 (4H, dd, J$_{HP}$ = 1.4 Hz, J$_{HH}$ = 8.3 Hz, HC$_1^5$), 7.35 (8H, d, J$_{HH}$ = 8.4 Hz, HC$_2^5$), 7.50-7.70 (9H, m, HC$_0^3$, HC$_1^3$, HC$_0^5$, HC$_1^5$), 7.85 (8H, d, J$_{HH}$ = 8.4 Hz, HC$_2^3$), 9.92 (4H, s, CHO); $^{13}$C $^1$H NMR (CDCl$_3$) $\delta$ 21.1 (s, CH$_3$CO), 32.9 (d, J$_{CP}$ = 13.1 Hz, CH$_3$NP$_1$), 33.1 (d, J$_{CP}$ = 9.9 Hz, CH$_3$NP$_0$), 122.0 (m, C$_0^5$, C$_1^5$, C$_2^5$), 128.1 (s, C$_0^3$), 128.3 (s, C$_1^3$), 131.5 (s, C$_2^3$), 132.2 (s, C$_0^4$), 132.4 (s, C$_1^4$), 133.6 (s, C$_2^4$), 139.1 (d, J$_{CP}$ = 13.7 Hz, C$_0^5$), 139.6 (d, J$_{CP}$ = 13.7 Hz, C$_1^5$), 151.5 (m, C$_0^1$, C$_1^1$), 155.2 (d, J$_{CP}$ = 6.7 Hz, C$_2^1$), 169.4 (s, CH$_3$CO), 190.8 (s, CHO). MS
(FAB) m/z: 1119 [MH]+. Anal. Caled for C_{52}H_{45}N_{6}O_{11}P_{3}S_{3} (1119.1): C, 55.81; H, 4.05; N, 7.51. Found: C, 55.49; H, 3.89; N, 7.25.

**Synthesis of dendron 5-G'_{1}**. To a solution of dendron 4-G'_{1} (0.15 g, 0.134 mmol) in THF (10 mL) were added 1 equivalent of triethylamine (20 µL, 0.15 mmol) and 6 equivalents of diisocyanohexane (130 µL, 0.80 mmol). The resulting solution was stirred overnight at room temperature, then evaporated to dryness, to afford a powder, which was washed with Et_{2}O till the obtaining of 5-G'_{1} as a white powder.

5-G'_{1}. White powder, 89 % yield. 31P {1H} NMR (CDCl_{3}) δ 60.1 (s, P_{1}), 61.9 (s, P_{0}); 1H NMR (CDCl_{3}) δ 1.38 (4H, m, (CH_{2})^{3}, (CH_{2})^{6}), 1.59 (4H, m, (CH_{2})^{2}, (CH_{2})^{5}), 3.20 (4H, m, (CH_{2})^{1}, (CH_{2})^{6}), 3.32 (3H, d, J_{HP} = 10.6 Hz, CH_{3}NP_{0}), 3.37 (6H, d, J_{HP} = 10.9 Hz, CH_{3}NP_{1}), 5.42 (1H, t, J_{HH} = 6.0 Hz, HNCO), 7.15 (2H, d, J_{HH} = 8.5 Hz, HC_{0}^{2}), 7.25 (4H, dd, J_{HP} = 1.2 Hz, J_{HH} = 8.5 Hz, HC_{1}^{2}), 7.36 (8H, dd, J_{HP} = 1.0 Hz, J_{HH} = 8.5 Hz, HC_{2}^{2}), 7.60-7.70 (9H, m, HC_{0}^{3}, HC_{1}^{3}, HC_{2}^{3}), 7.85 (8H, d, J_{HH} = 8.5 Hz, HC_{3}^{2}), 9.93 (4H, s, CHO); 13C {1H} NMR (CDCl_{3}) δ 25.9 and 26.1 (2s, (CH_{2})^{3} and (CH_{2})^{6}), 29.6 (s, (CH_{2})^{2}), 31.0 (s, (CH_{2})^{5}), 32.9 (d, J_{CP} = 13.1 Hz, CH_{3}NP_{1}), 33.1 (d, J_{CP} = 9.9 Hz, CH_{3}NP_{0}), 41.1 (s, (CH_{2})^{1}), 42.8 (s, (CH_{2})^{6}), 121.9 (m, C_{0}^{2}, C_{0}^{3}, C_{2}^{2}, NCO), 128.0 (s, C_{0}^{3}), 128.3 (s, C_{1}^{2}), 131.5 (s, C_{1}^{3}), 131.7 (s, C_{0}^{4}, C_{1}^{4}), 133.6 (s, C_{2}^{4}), 139.3 (d, J_{CP} = 13.7 Hz, C_{0}^{5}), 139.7 (d, J_{CP} = 13.8 Hz, C_{1}^{5}), 151.6 (d, J_{CP} = 6.8 Hz, C_{1}^{4}), 152.0 (s, C_{0}^{1}), 154.3 (s, NCOO), 155.2 (d, J_{CP} = 7.3 Hz, C_{2}^{1}), 190.8 (s, CHO). MS (FAB) m/z: 1287 [MH]+. Anal. Caled for C_{60}H_{57}N_{8}O_{13}P_{3}S_{3} (1287.3): C, 55.98; H, 4.46; N, 8.70. Found: C, 55.69; H, 4.19; N, 8.41.

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**References**


