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Design of phosphonium ended dendrimers bearing functionalized amines

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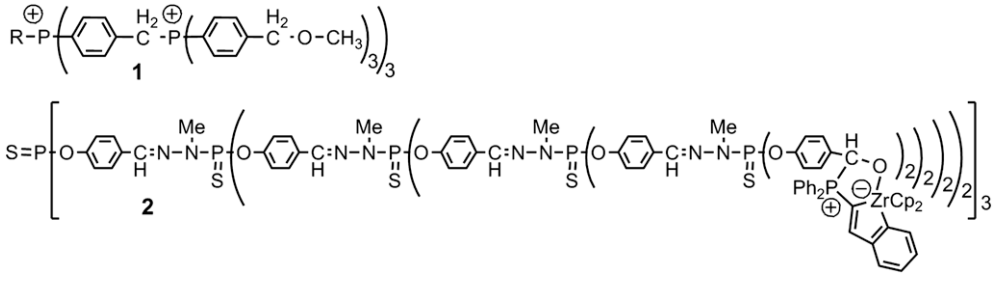
ABSTRACT

Synthesis of unprecedented phosphorus dendrimers from generations 1 to 3 capped with functionalized phosphonium units bearing both P–C and P–N bonds is reported.

Among the large variety of organic, inorganic or metalladendrimers those bearing ionic sites appear of great interest due to their properties and uses in different fields ranging from biology, material sciences and catalysis.[1] This is specially the case of polyanionic phosphorus dendrimers bearing carboxylic, sulfonic, phosphonic or bisphosphonic end groups[2] and of polycationic phosphorus dendrimers decorated on their surface with ammonium groups.[3] In marked contrast very little is known about the design of dendrimers incorporating phosphonium end groups. This is quite surprising taking into account the importance of phosphonium or polyphosphoniums in organic synthesis and related fields.[4] Indeed in a pioneering work Rengan and Engel[5] reported an elegant synthesis of phosphorus dendrimers **1** in which the core and branches are phosphonium ion sites. Phosphorus dendrimers containing zwitterionic anionic zirconocene complexes **2** were also described via formal cycloaddition reactions between phosphino zirconocene and dendrimers with terminal aldehyde groups.[6] However, the design of all these cationic or zwitterionic phosphonium dendrimers is restricted up to now to species incorporating exclusively phosphorus carbon bonds thus limiting their use. Therefore there is a need to diversify the methods of synthesis allowing to substitute some phosphorus carbon bonds with more reactive phosphorus bonds. To this end we here report on an efficient synthetic strategy allowing to create on the outer shell of original dendrimers of generations 1–3 phosphonium centres bearing both P–C and P–N bonds using various functionalized (or not) primary or secondary amines.

On the basis of the work of some of us on metallated ylides exhibiting a high nucleophilicity,[7] we investigated two ways to prepare



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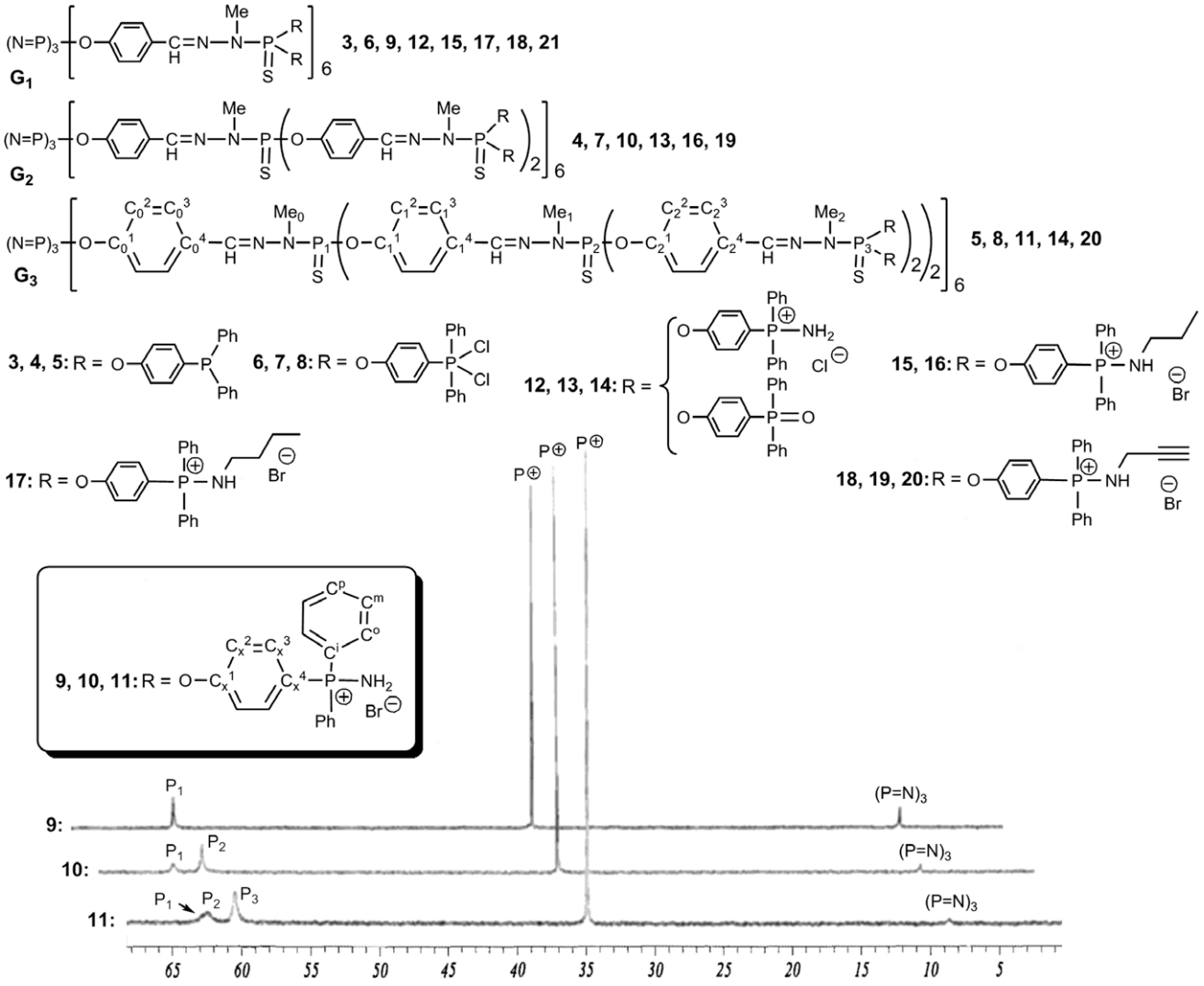
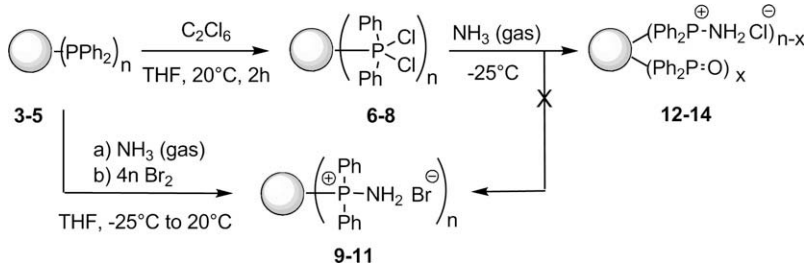


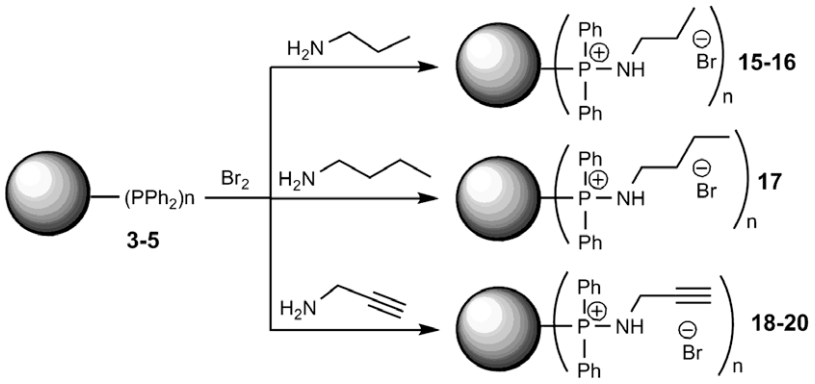
Figure 1. General structures of the new neutral and charged dendrimers. The numbering used for NMR signals assignment is shown on G_3 and on one R. Lower part: ^{31}P NMR spectra of compounds **9**, **10** and **11**.



Scheme 1. Synthesis of phosphonium ended dendrimers **9**–**11**.

aminophosphonium dendrimers (Fig. 1). The first one consists in the treatment of dendrimers **3**–**5** of generation 1, 2 or 3 bearing, respectively, 12, 24 or 48 terminal phosphino groups[8] with C_2Cl_6 giving rise to the halogeno phosphorane dendrimers **6–8** which in the presence of NH_3 should afford dendrimers incorporating aminophosphonium groups[7a,b] (Scheme 1). However the high sensitivity to oxidation of the halogenophosphorane moieties in **6–8** prevents from the isolation of the final monodisperse dendrimers **9**–**11**. Inseparable polydisperse dendrimers **12–14** bearing both terminal aminophosphonium and phosphino oxide groups in various ratios were formed.

To overcome these difficulties another strategy was successfully developed as it is described in Scheme 1, based on the use of both excess of ammonia and bromine.[7e] Reactions were monitored by NMR. As an example the formation of the dendrimer of generation 1, **9** (Scheme 1, Fig 1) results in the disappearance in ^{31}P NMR of the signal of the twelve terminal phosphino groups in **3** (δ = −5.9 ppm) on behalf of a new signal at 36.4 ppm characteristic



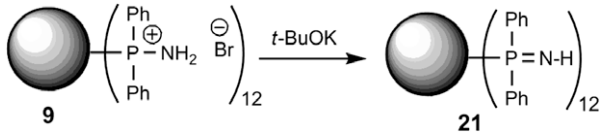
Scheme 2. Synthesis of phosphonium ended dendrimers **15**–**20**.

of aminophosphonium units (δ = 36.5 ppm for [$ArPh_2P$–NH_2] Br). ^1H NMR spectra exhibit a new broad signal at 6.92 ppm due to the presence of P–NH_2 pattern. MALDI-TOF mass spectrometry shows a peak at 4909 (expected mass: 4921 for the cationic part of **9**) arising from the loss of HBr (12 equiv) with the formation of a dendrimer bearing twelve iminophosphorane linkages (terminal –PPh_2 = NH groups). This phenomenon was also observed with the monomer [Ph_3P–NH_2] Br (observed mass 277 instead of 278 resulting from elimination of HBr and formation of Ph_3P=NH).

Such a methodology of incorporation of aminophosphonium was extended to dendrimers of generations 2 and 3, that is, **4** and **5** allowing the isolation and the characterization of the unique aminophosphonium dendrimers **10** and **11**.[9] Here also the course of the reactions is followed by ^{31}P NMR spectroscopy which shows a new broad signal at 34.8 ppm for **10** and **11** in addition to the other unchanged characteristic signals of the phosphorus backbone of the two dendrimers. Similarly the formation of NH_2 is observed in ^1H NMR (δ = 6.97 and 7.24 ppm, respectively, for **10** and **11**).

The next step was to generalize this method to the grafting of various functionalized amines or amines which might increase the solubility of the resulting polycationic dendrimers. Reactions were conducted with *n*-propylamine, *n*-butylamine and dendrimers **3** and **5**. The resulting dendrimers **15** and **16** (generations 1 and 2, *n*-propylaminophosphonium end groups), **17** (generation 1, *n*-butylamino phosphonium end groups) were isolated in good to excellent yields (60–91%) (Scheme 2).[10] ^{13}C NMR data afford additional proof to the formation of the desired polycationic dendrimers since in all cases the signal of the carbon atom α to nitrogen ($PNHCH_2$) on the surface of dendrimers appears as a doublet or a broad singlet due to carbon–phosphorus coupling (e.g., δ_C = 23.4 ppm, $^2J_{CP}$ = 7.3 Hz in **16**). As expected the solubility of the dendrimers increases dramatically from **12–14** to **15–16** and finally **17** in various organic solvents.

Similarly the treatment of dendrimers **3–5** with a functionalized amine as propargylamine in the presence of an excess of bromine led to the formation of propargylaminophosphonium dendrimers **18–20** obtained in 71–91% yield.[11] The grafting of the propargylamine on the dendrimeric scaffold is corroborated by ^{31}P NMR spectroscopy. Indeed, the signals of the phosphino groups for **3–5** at −5.86 to −6.17 ppm disappear on behalf of the signals due to the resulting phosphonium moieties at 39.0–39.1 ppm for **18–20** (Scheme 3).



Scheme 3. Formation of iminophosphorane ended dendrimer **21**.

In conclusion we have demonstrated that it is possible to prepare a variety of new polycationic dendrimers based on surface modification of phosphorus dendrimers bearing terminal phosphino groups. A set of original aminophosphonium ended dendrimers with P–N and P–C bonds was prepared. Their reactivity and properties will be investigated but in a preliminary experiment we observed that the treatment of **9** with *t*BuOK allows a clean deprotonation of the surface of such a dendrimer with the formation of the dendrimer **21** bearing 12 iminophosphorane units (Scheme 3), thus opening new perspectives for their use due to the versatile reactivity of iminophosphorane monomers.[7a,12]

Acknowledgments

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8. The new dendrimers **3–5** are prepared by reacting the corresponding dendrimers of generation 1, 2 or 3 incorporating on the surface $P(S)Cl_2$ units with respectively 12, 24 or 48 equiv of 4-hydroxyphenyldiphenyl phosphine, as reported previously for other types of phosphorus-containing dendrimers. See in particular: Merino, S.; Brauge, L.; Caminade, A. M.; Majoral, J. P.; Taton, D.; Gnanou, Y. *Chem. Eur. J.* **2001**, *7*, 3095–3105.
9. *General procedures for the synthesis of aminophosphonium ended dendrimers:* After standard cycles of evacuation and back-filling with dry and pure nitrogen, we placed the dendrimer **3–5** (generations 1–3) in anhydrous THF (10 mL) in a two-necked Schlenk. The solution was cooled at −30 °C and gaseous ammonia was bubbled for 30 min. Then, bromine was added dropwise. The temperature was raised to 25 °C and the mixture was stirred overnight. The solvent was removed under reduced pressure, and the solid residue was washed with 10 mL water and extracted with 3 × 20 mL of chloroform. Sometimes, it is necessary to use some drops of ethanol to solubilize all residues. The organic extracts were dried with magnesium sulfate, filtered and evaporated. Finally, the residue was dissolved in a minimum of chloroform/methanol mixture (1/1, v/v) and precipitated with diethyl ether (50 mL). Mass spectrometry gave the expected molecular peaks, but was not usable to ascertain the purity of these compounds due to MS-induced rearrangements at the level of the hydrazone linkages.[13] Compound **9** was prepared following this general procedure from dendrimer G_1 (**3**) (200 mg, 0.042 mmol) and bromine (0.1 mL, 2.03 mmol) and was obtained as a white powder with 79% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75–7.27 (m, 198H, CH_{arom}+CH=N), 6.94–6.87 (m, 24H, P^+NH_2), 3.37 (d, $^3J_{H-P}$ = 10.9 Hz, 18H, CH_3N); $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 154.5 (C_1^1), 150.5 (C_0^1), 135.3 (d, $^2J_{C-P}$ = 13.2 Hz, C_1^3, CH=N), 134.6 (C^p), 132.6 (d, $^2J_{C-P}$ = 11.7 Hz, C^o), 131.8 (C_0^4), 129.7 (d, $^3J_{C-P}$ = 12.4 Hz, C^m), 128.6 (C_0^3), 122.9 (d, $^1J_{C-P}$ = 105.4 Hz, C^i), 122.3 (d, $^3J_{C-P}$ = 3.5 Hz, C_0^2, C_1^2), 120.2 (d, $^1J_{C-P}$ = 106.1 Hz, C_1^4), 33.3 (d, $^2J_{C-P}$ = 11.7 Hz, CH_3N); $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6) δ 60.95 (P_1), 34.82 (P^+), 7.99 ($(P{=}N)_3$). Compound **10** was prepared following the general procedure from dendrimer G_2 (**4**) (200 mg, 0.019 mmol) and bromine (0.09 mL, 1.82 mmol) and was obtained as a white powder with 58% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24–7.08 (m, 426H, CH_{arom}+CH=N), 6.97 (br s, 48H, P^+NH_2), 3.37 (m, 54H, CH_3N); $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 154.5 (C_2^1), 150.5 (C_0^1, C_1^1), 135.3 (d, $^2J_{C-P}$ = 12.4 Hz. C_2^3, CH=N), 134.6 (C^p), 132.6 (d, $^2J_{C-P}$ = 11.0 Hz, C^o), 131.9 (C_0^4, C_1^4), 129.7 (d, $^3J_{C-P}$ = 13.2 Hz, C^m), 128.5 (C_0^3, C_1^3), 123.0 (d, $^1J_{C-P}$ = 102.4 Hz, C^i), 122.2 (C_2^2), 121.5 (C_0^2, C_1^2), 120.2 (d, $^1J_{C-P}$ = 105.4 Hz, C_2^4), 33.1 (d, $^2J_{C-P}$ = 12.9 Hz, CH_3N); $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6) δ 62.92 (P_1), 60.83 (P_2), 34.83 (P^+), 8.19 ($(P{=}N)_3$). Compound **11** was prepared following the general procedure from dendrimer G_3 (**5**) (185 mg, 0.008 mmol) and bromine (0.08 mL, 1.59 mmol) and was obtained as a white powder with 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79–7.60 (m, 882H, CH_{arom}+CH=N), 7.24 (br s, 96H, P^+NH_2), 3.41 (d, $^3J_{H-P}$ = 4.0 Hz, 126H, CH_3N); $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 154.5 (C_3^1), 150.9 (m, C_0^1, C_1^1, C_2^1), 135.3 (d, $^2J_{C-P}$ = 11.7 Hz, C_3^3, CH=N), 134.6 (C^p), 132.6 (d, $^2J_{C-P}$ = 11.7 Hz, C^o), 131.8(C_0^4, C_1^4, C_2^4), 129.7 (d, $^3J_{C-P}$ = 13.2 Hz, C^m), 128.5 (m, C_0^3, C_1^3, C_2^3), 122.9 (d, $^1J_{C-P}$ = 103.2 Hz, C^i), 122.2 (C_3^2), 121.3(C_0^2, C_1^2, C_2^2), 120.2 (d, $^1J_{C-P}$ = 105.4 Hz, C_3^4), 33.0 (m, CH_3N); $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6) δ 62.81 (P_1), 62.78 (P_2), 60.66 (P_3), 34.82 (P^+), 8.13 ($(P{=}N)_3$).
10. *General procedures for the synthesis of alkylaminophosphonium ended dendrimers*: After standard cycles of evacuation and back-filling with dry and pure nitrogen, we placed the dendrimer (generation 1–3) and an excess of amine in anhydrous THF (10 mL) in a two-necked Schlenk. The solution was cooled at −30 °C and bromine was added dropwise. The temperature was raised to 25 °C and the mixture was stirred overnight. The solvent was removed under reduce pressure, and the solid residue was washed with 10 mL water and extracted with 3 × 20 mL of chloroform. The organic extracts were dried with magnesium sulfate, filtered and evaporated. Finally, the residue was dissolved in a minimum of chloroform/methanol mixture (1/1, v/v) and precipitated with diethyl ether (50 mL). Compound **15** was prepared following this general procedure from dendrimer G_1 (**3**) (200 mg, 0.042 mmol), *n*-propylamine (0.5 mL, 6.1 mmol) and bromine (0.1 mL, 2.03 mmol) and was obtained as a yellow powder with 81% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75–7.27 (m, 198H, CH_{arom}+CH=N), 6.81 (m, 12H, P^+NHR), 3.41 (br d, 18H, CH_3N), 3.18 (m, 24H, CH_2N), 1.75 (m, 24H, CH_2), 0.88 (m, 36H, CH_3C); $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6) δ 60.20 (P_1), 37.91 (P^+), 8.57 ($(P{=}N)_3$). Compound **16** was prepared following this general procedure from dendrimer G_2 (200 mg, 0.019 mmol), *n*-propylamine (0.5 mL, 6.1 mmol) and bromine (0.09 mL, 1.82 mmol) and was obtained as an orange powder with 60% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82–7.61 (m, 426H, CH_{arom}+CH=N), 7.16–7.10 (br s, 24H, P^+NHR), 3.45 (br s, 54H, CH_3N), 2.74 (m, 48H, CH_2N), 1.54 (m, 48H, CH_2), 0.91 (m, 72H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 154.5 (C_2^1), 150.4 (C_0^1, C_1^1), 135.9 (d, $^2J_{C-P}$ = 11.7 Hz, C_2^3, CH=N), 135.0 (C^p), 133.2 (d, $^2J_{C-P}$ = 11.0 Hz, C^o), 131.9 (C_0^4, C_1^4), 130.0 (d, $^3J_{C-P}$ = 13.2 Hz, C^m), 128.5 (C_0^3, C_1^3), 122.5 (C_2^2), 122.3 (C_0^2, C_1^2), 120.7 (d, $^1J_{C-P}$ = 102.5 Hz, C^i), 118.0 (d, $^1J_{C-P}$ = 107.6 Hz, C_2^4), 33.3 (br s, CH_3N), 23.9 (d, $^2J_{C-P}$ = 7.3 Hz, CH_2N), 20.4 (CH_2CH_3), 10.9 (CH_2CH_3); $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6) δ 62.83 (P_1), 60.46 (P_2), 36.90 (P^+), 8.19 ($(P{=}N)_3$). Compound **17** was prepared following this general procedure from dendrimer G_1 (**3**) (200 mg, 0.042 mmol), *n*-butylamine (0.5 mL, 5.1 mmol) and bromine (0.1 mL, 2.03 mmol) and was obtained as a cream powder with 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.32 (m, 198H, CH_{arom}+CH=N), 6.76 (d, $^2J_{H-P}$ = 8.4 Hz, 12H, P^+NHR), 3.40 (d, 18H, CH_3N), 2.82 (m. 24H, NCH_2), 1.43 (m, 24H, NCH_2CH_2–), 1.03 (m, 24H, CH_2CH_3), 0.57 (m, 36H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.3 (d, $^2J_{C-P}$ = 3.7 Hz, C_1^1), 151.2 (C_0^1), 135.6 (d, $^2J_{C-P}$ = 12.4 Hz, C_1^3, CH=N), 135.0 (C^p), 133.5 (d, $^2J_{C-P}$ = 11.0 Hz, C^o), 132.0 (C_0^4), 130.0 (d, $^3J_{C-P}$ = 13.2 Hz. C^m), 128.7 (C_0^3), 122.7 (m, C_0^2, C_1^2), 121.0 (d, $^1J_{C-P}$ = 103.2 Hz, C^i), 117.8 (d, $^1J_{C-P}$ = 104.7 Hz, C_1^4), 42.3, NCH_2CH_2), 33.9 (d, $^2J_{C-P}$ = 12.5 Hz, NCH_3), 33.3 (d, $^2J_{C-P}$ = 6.6 Hz, NCH_2), 19.7 (CH_2CH_3), 13.5 (CH_3); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 59.84 (P_1), 37.44 (P^+), 7.99 ($(P{=}N)_3$).
11. Compound **18** was prepared following the general procedure from dendrimer G_1 (**3**) (200 mg, 0.042 mmol), propargylamine (0.5 mL, 7.8 mmol) and bromine (0.1 mL, 2.03 mmol) and was obtained as a brown powder with 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–7.34 (m, 198H, CH_{arom}+CH=N), 6.80 (s, 12H, P^+NHR), 3.69 (d, $^3J_{H-P}$ = 13.9 Hz, NCH_2), 3.40 (br s, 18H, CH_3N), 2.04 (s, 12H, CH); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.7 (d, $^2J_{C-P}$ = 3.7 Hz, C–OC_6H_4), 151.2 (C_0^1), 136.0 (d, $^2J_{C-P}$ = 12 Hz, C_1^3, CH=N), 135.2 (C^p), 133.7 (d, $^2J_{C-P}$ = 11.7 Hz, C^o), 132.4 (C_0^4), 130.0 (d, $^3J_{C-P}$ = 13 Hz. C^m), 128.6 (C_0^3), 122.6 (m, C_0^2, C_1^2), 121.1 (d, $^1J_{C-P}$ = 103.2 Hz, C^i), 117.8 (d, $^1J_{C-P}$ = 104.7 Hz, C_1^4), 77.8 (C≡CH), 74.3 (C≡CH), 33.9 (br s, NCH_3), 31.5 (br s, NCH_2); $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6) δ 59.76 (P_1), 39.12 (P^+), 8.06 ($(P{=}N)_3$). Compound **19** was prepared following the general procedure from dendrimer G_2 (**4**) (200 mg, 0.019 mmol), propargylamine (0.5 mL, 7.8 mmol) and bromine (0.09 mL, 1.82 mmol) and was obtained as a brown powder with 71% yield., Compound **20** was prepared following the general procedure from dendrimer G_3 (**5**) (200 mg, 0.009 mmol), propargylamine (0.5 mL, 7.8 mmol) and bromine (0.08 mL, 1.59 mmol) and was obtained as a beige powder with 88% yield.
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