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Alkylation of Enolates : A New Approach to Dendrons.

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Abstract. The synthesis of new polyketonic dendrons is described. These compounds are representative of a new connectivity in dendrimers. The alkylation of enolates and easy functional group interconversion reactions provides a versatile and efficient procedure for the synthesis of this kind of dendron.

Convergent methodology has provided a huge number of efficient syntheses of dendrimers. The methodology described here is based on the disconnection method in organic synthesis and permits a choice for the surface functional groups in the first step of growth. Moreover, a convergent methodology reduces the possibility of side and incomplete reactions and leads to high control over both the chain ends and the interior structure of the dendrimer. This methodology has been extensively used for the synthesis of various dendrimers, and six main connectivities can be considered: ether, amine, amide, ester, phosphate and urethane. Several examples consisting of a combination of two connectivities have also been described. The Suzuki coupling and the Heck reaction have been used to provide the C–C connectivity in dendrimers.[1,2]

All these connectivities provide efficient routes for the synthesis of dendrimers, although any modification of these functional groups can be performed while preserving the dendrimeric structure. Therefore, we believe it necessary to explore new and useful dendrons for novel applications. A connectivity based on the α-alkylation of ketones incorporates two interesting features: (i) a rapid dendrimeric growth may be achieved by double alkylation,[3] and (ii) the carbonyl group may permit a wide range of possibilities for the modification of the functional group at the interior of a dendrimer while maintaining the dendrimeric structure.

With this aim we have initiated a project focused on the synthesis of dendrimeric polyketones. The first attempt consisted of a divergent methodology based on the alkylation of polyacetylbenzenes, a method that provided good results for the first generation dendrimers. However, reaction yields using this method were

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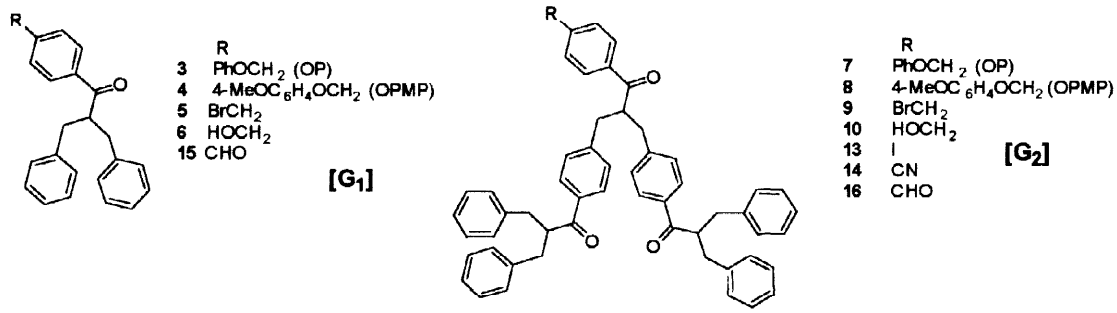
very poor for the synthesis of the second generation dendrimers.[4] Subsequently, we decided to plan the synthesis of dendrons (see Scheme 1) by taking advantage of convergent methodology and the efficient double benzylation of acetophenones. In this way, completion of reactions in each step can be controlled and monitored, and large excesses of reagents are not required even for the preparation of higher generation dendrimers. Moreover, if imperfection does occur during the construction of the dendrimer due to incomplete reaction, the defective dendrimers will generally differ greatly in polarity and size from the desired dendrimer.[5]

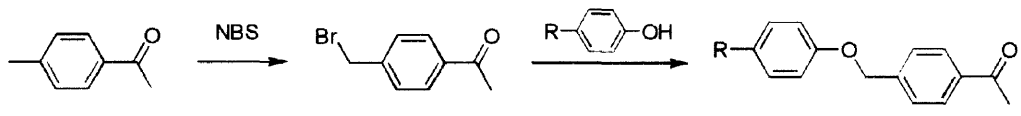


Scheme 1

Results and Discussion

For a convergent synthesis it is necessary to use a starting material bearing two functional groups, one of which permits dendrimeric growth, and one that can be easily transformed into a functional group, called the "focal point", which is able to react with the former group.

In order to employ the convergent methodology efficiently, judicious selection of a focal protective group compatible with the propagation step was essential. We chose to use either the phenyl or *p*-methoxyphenyl ether group due to their stability under the basic conditions of the alkylation reactions. Thus, for this purpose we selected *p*-(phenyloxymethyl)acetophenone (**1**) and *p*-(4-methoxyphenyloxymethyl) acetophenone (**2**) as monomers. The desired starting materials **1** and **2** were synthesised using a two-step procedure (Scheme 2). *p*-Methylacetophenone was first converted into *p*-bromomethylacetophenone by radical bromination with NBS in acetonitrile under irradiation.[4] This benzyl bromide was subsequently protected, in excellent yields, by Williamson ether synthesis using potassium carbonate and Aliquat 336 at 80 °C in the absence of solvent.[6]

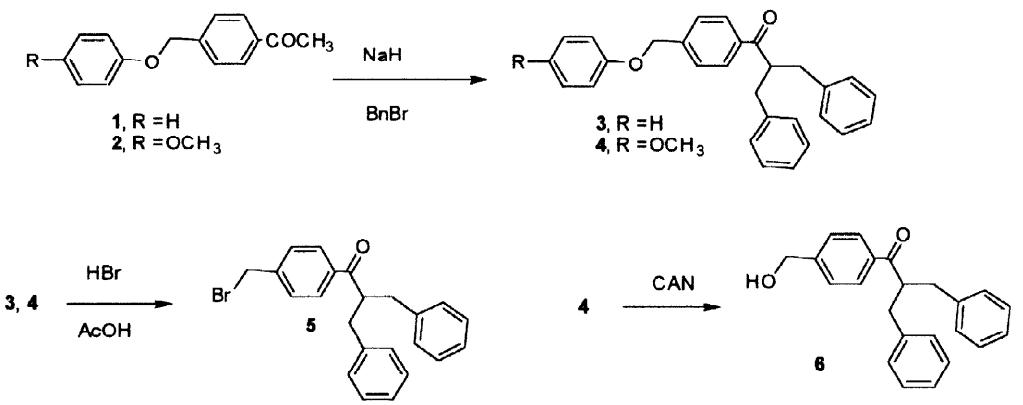


1, R= H; **2**, R =OCH_3

Scheme 2

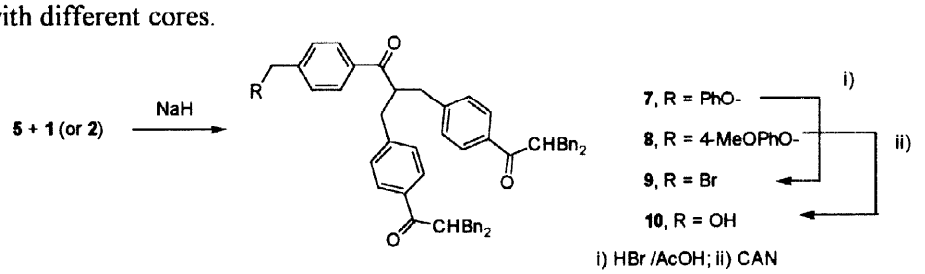
Acetophenones **1** and **2** were reacted with two equivalents of benzyl bromide, in the presence of sodium hydride in THF at room temperature, to give the corresponding dibenzyl derivatives **3** and **4** in

satisfactory yields. Small amounts of *O*-alkylated compounds were also detected. Compounds **3** and **4** were converted into the corresponding compounds containing the focal point functional groups (bromide or alcohol). The phenyl group was removed using refluxing HBr/AcOH[7] to afford a new benzylic bromide **5**, as a white solid in 75% yield, which was suitable for reaction with **1** and **2**. In another approach the *p*-methoxyphenyl group of **2** was oxidatively cleaved with cerium ammonium nitrate (CAN) in acetonitrile/water at room temperature[8] to give the corresponding benzylic alcohol **6** in 80% yield. Compound **6** could then be transformed into the benzylic bromide **5**[9] or be used as the dendron itself for ester or ether connectivities (Scheme 3).



Scheme 3

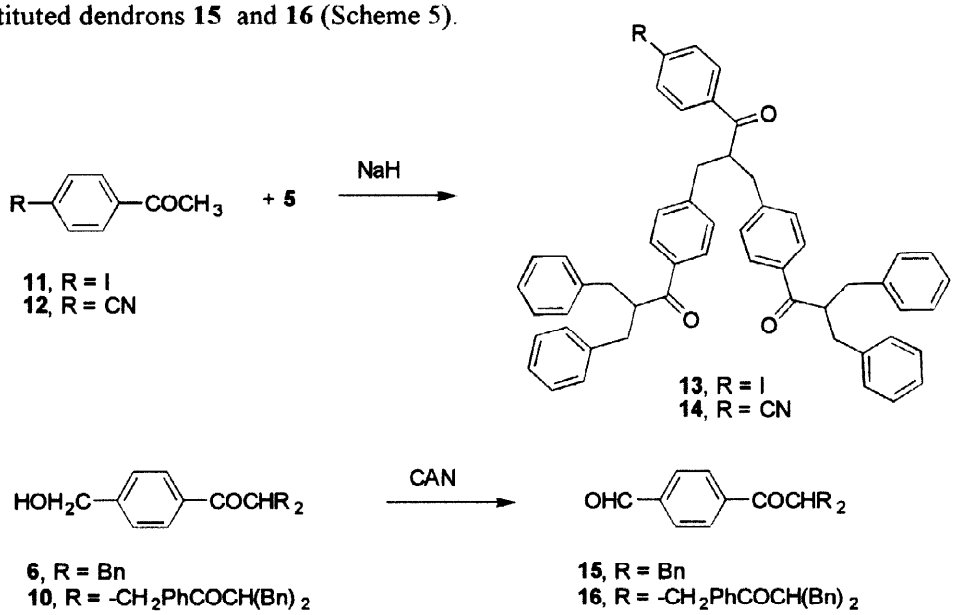
By repeating the procedure shown in Scheme 3 the second generation dendrons **7** and **8** were obtained in satisfactory yield (Scheme 4). Thus, the coupling reaction of the first generation bromide **5** with the monomers **1** and **2** under standard alkylation conditions (NaH in THF at room temperature) afforded the corresponding protected bromide **7** and alcohol **8**, respectively. Once again, small amounts of *O*-alkylated products were present as contaminants, but these were easily removed by column chromatography. The hydrolysis of **7** and the oxidation of **8**, using the same conditions as indicated previously, afforded a new benzylic bromide **9** and a new benzylic alcohol **10**, which could be used for a new growth step and for coupling with different cores.



Scheme 4

Two methods were considered to obtain other dendrons bearing different functionalities at the focal point in order to increase the synthetic possibilities. The first method entailed the use of the commercially

available *p*-iodo and *p*-cyano acetophenones **11** and **12**. The coupling reactions of **11** and **12** with the first generation bromide **5** were performed under standard alkylation conditions. The iodo- and cyano- substituted dendrons **13** and **14** were also obtained in satisfactory yield using this method. The second method considered, involving the oxidation of the benzylic alcohols **6** and **10** promoted by CAN[10] or PCC,[11] afforded two new formyl-substituted dendrons **15** and **16** (Scheme 5).



Scheme 5

The structures of all these compounds were readily assigned by their ^{1}H- and ^{13}C-NMR spectra. For compounds **3** and **7**, **5** and **9**, and **6** and **10**, the unique benzylic signals at $\delta = 5.0$, 4.4 and 4.6, respectively, allow unambiguous identification of these compounds. ^{13}C-NMR spectroscopy is also a useful technique to determine the purity of, and to detect structural defects in, the dendritic fragments. In general, any defective dendron will be unsymmetrical and additional carbon signals will be observed. In contrast, perfect dendrimers or dendrons will have very sharp and simple signals because of their symmetrical structures. The ^{1}H-NMR and ^{13}C-NMR spectra permit differentiation between the first and second generation structures. The ^{1}H-NMR signals of the CH_2–CH–CH_2 fragment show a clear AA'BB'C pattern in the first generation. For example, the AA'BB' part of **3** shows a doublet of doublets with J_{AB} = 13.7 Hz, while the C part appears as a triplet of triplets with J_{AC} = 7.8 Hz and J_{BC} = 6.1 Hz. In the second generation the signal pattern is complicated by the presence of at least two different AA'BB'C systems. For example, the AA'BB' part of **7** appears as two complex multiplets. In the ^{13}C-NMR spectra, signals from the CH_2–CH–CH_2 fragment can also be differentiated in the first and second generation. The ^{13}C-NMR spectrum of **3** shows a signal at δ = 38.25 for the CH_2 and a signal at δ = 50.53 for the CH, while the ^{13}C-NMR spectrum of the second generation compound, **7**, shows three signals at δ = 37.97, 38.16 and 38.70 for the CH_2 and two signals at δ = 49.58 and 50.37 for the CH, with the more deshielded signals corresponding to the external fragments.

Conclusion

A convergent methodology based on acetophenone enolate alkylation as the growth step has been successfully used for the synthesis of polyketonic dendrons. Easy functional group interconversions, or the use of commercially available acetophenones, allows access to a variety of functionalised dendrons.

Experimental

General Considerations. All starting materials were purchased from Aldrich Chemical Co. and Acros and were used without further purification. All solvents used for extractions or reactions were dried according to standard procedures and kept over molecular sieves. Flash chromatography was run on 230-400 mesh silica gel (Merck). NMR spectra were recorded in $CDCl_3$ using a VARIAN UNITY 300 spectrometer operating at 299.980 MHz for proton and 75.423 MHz for carbon-13 at a temperature of 293 K. Mass spectrometry was performed at the SIDI (Universidad Autónoma of Madrid). Elemental analysis were performed on a Perkin Elmer PE 2400CHN microanalyzer. IR spectra were recorded on a Nicolet 550 FT-IR spectrometer as KBr pellet or film on KBr disc where noted.

General procedure for the synthesis of monomers **1** and **2**. A mixture of the appropriate phenol (1 equiv.) and potassium carbonate (1.1 equiv.) was stirred in an oil-bath at 80 °C for 10 min., then *p*-bromomethylacetophenone (1.1 equiv.) was added. The mixture was heated at 80 °C for the required time. After cooling at room temperature the mixture was dissolved in dichloromethane and filtered off. The crude product was purified as described below.

***p*-(Phenyloxymethyl)acetophenone (1)**. Reaction time: 3 h. Flash chromatography of the crude product on silica gel (hexane/ethyl acetate = 95/5) afforded the pure product as a white solid. Yield: 95%. Mp: 102-103°C (hexane). IR (ν_{max}, cm^{-1}): 1685, 1239, 1032. ^{1}H-NMR, δ: 2.61 (s, 3H); 5.14 (s, 2H); 6.90-7.26 (m, 3H); 7.27 (d, 2H, J = 8.3); 7.53 (d, 2H, J = 8.1); 7.97 (d, 2H, J = 8.3). ^{13}C-NMR, δ: 197.69; 158.33; 142.47; 136.55; 129.51; 128.59; 127.08; 121.18; 114.75; 69.10; 26.65. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.51; H, 6.20.

***p*-(4-Methoxyphenyloxymethyl)acetophenone (2)**. Reaction time: 4 h. Flash chromatography of the crude product on silica gel (hexane/ethyl acetate = 95/5) afforded the pure product as a white solid. Yield: 85%. Mp: 109-110°C (hexane/toluene, 20/1). IR (ν_{max}, cm^{-1}): 1685, 1233, 1036. ^{1}H-NMR, δ: 2.61 (s, 3H); 3.77 (s, 3H); 5.08 (s, 2H); 6.81-6.91 (m, 4H); 7.52 (d, 2H, J = 8.4); 7.97 (d, 2H, J = 8.4). ^{13}C-NMR, δ: 197.72; 154.13; 152.53; 142.76; 136.57; 128.59; 127.12; 115.83; 114.68; 69.98; 55.71; 26.66. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.19; H, 6.21.

General procedure for the synthesis of [Gn]-OP and [Gn]-OPMP. Sodium hydride (60% dispersion in mineral oil, 25 mmol) was added to a stirred solution of monomer **1** or **2** (25 mmol) in dry THF (50 ml) at room temperature under argon. After stirring for 1 h the corresponding bromide (25 mmol), benzyl bromide for [G_1] or compound **5** ([G_1]-Br) for [G_2], was added to the solution. After 2 h a new portion of HNa (25 mmol) was added and stirred again for 1 h. Finally anxother portion of the corresponding bromide (25 mmol) was added. The mixture was stirred at room temperature for 15 hours and quenched with water (25 ml). The aqueous phase was extracted with dichloromethane (3 x 20 ml), and the combined organic layers were washed with brine, dried (Na_2SO_4), and filtered. The filtrate was concentrated and the crude product purified as described below.

[G_1]-OP (3). Flash chromatography of the crude product on silica gel (hexane/ethyl acetate = 20/1) afforded the pure product as a white solid. Yield: 70%. Mp:76-77°C (hexane). IR (ν_{max}, cm^{-1}): 1666, 1221, 1053. ^{1}H-NMR, δ: 2.80 (dd, 2H, J = 13.7; 6.1); 3.12 (dd, 2H, J = 13.7; 7.8); 4.00 (tt, 1H, J = 7.8; 6.1); 5.05 (s, 2H); 6.93 (dd, 2H, J = 8.5; 1.0); 6.96 (tt, 1H, J = 7.6; 1.0); 7.09-7.24 (m, 8H); 7.28 (dd, 4H, J = 8.8; 7.3); 7.39 (d, 2H, J = 8.5); 7.73 (d, 2H, J = 8.5). ^{13}C-NMR, δ: 202.82; 158.38; 142.09; 139.42; 136.86; 129.48; 128.94; 126.94; 126.22; 121.17; 114.78; 69.12; 50.33; 38.25. Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.41; H, 6.22.

[G_1]-OPMP (4). Flash chromatography of the crude product on silica gel (hexane/ethyl acetate = 20/1) afforded the pure product as a white solid. Yield: 70%. Mp:82-83°C (hexane). IR (ν_{max}, cm^{-1}): 1666, 1236, 1056. ^{1}H-NMR, δ: 2.80 (dd, 2H, J = 13.7; 6.3); 3.13 (dd, 2H, J = 13.7; 7.9); 3.76 (s, 3H); 4.00 (tt, 1H, J = 7.9; 6.3); 5.01 (s, 2H); 6.80-6.88 (m, 4H); 7.11-7.26 (m, 10H); 7.38 (d, 2H, J = 8.3); 7.73 (d, 2H, J = 8.3). ^{13}C-NMR, δ: 202.88; 154.12; 152.54; 142.37; 139.44; 136.80; 128.97; 128.38; 126.98; 126.25; 115.80; 114.65; 69.94; 55.70; 50.53; 38.23. Anal. Calcd for $C_{30}H_{28}O_3$: C, 82.54; H, 6.46. Found: C, 82.31; H, 6.44.

[G_2]-OP (7). Flash chromatography of the crude product on silica gel (hexane/ethyl acetate = 9/1) afforded the pure product as a white solid. Yield: 60%. Mp:67-68°C (toluene/hexane). IR (ν_{max}, cm^{-1}): 1673, 1237, 1034. ^{1}H-NMR, δ: 2.70 (dd, 3H, J = 14.1; 6.4); 2.73 (ddd, 3H, J = 13.6; 6.1; 2.9); 3.06 (dd, 3H, J =13.6; 11.1); 3.07 (ddd, 3H, J = 14.1; 6.1; 2.9); 3.93 (dddd, 3H, J = 11.1; 6.4; 6.1; 6.1); 4.97 (s, 2H); 6.87 (dd, 2H, J = 8.6; 2.2); 6.95 (tt, 1H, J = 7.6; 1.0); 7.04-7.19 (m, 20H); 7.14 (d, 4H, J = 8.6); 7.25 (dd, 2H, J = 8.5; 2.2); 7.37 (d, 2H, J = 8.5); 7,58 (d, 4H, J = 8.6); 7.68 (d, 2H, J = 8.5). ^{13}C-NMR, δ: 202.70; 201.60; 158.21; 144.39; 142.67; 139.46; 139.43; 136.16; 135.75; 129.50; 129.02; 128.93; 128.36; 128.31; 127.08; 126.18; 121.24; 114.72; 68.94; 50.37; 49.58; 38.20; 38.16; 37.97. MS (FAB, m/z): 851.4 (M^+, 12.4).

[G_2]-OPMP (8). Flash chromatography of the crude product on silica gel (hexane/ethyl acetate = 9/1) afforded the pure product as a white solid. Yield: 60%. Mp:140-141°C (toluene/hexane). IR (ν_{max}, cm^{-1}): 1671, 1230, 1034. ^{1}H-NMR, δ: 2.67-2.79 (m, 6H); 3.02-3.12 (m, 6H); 3.75 (s, 3H); 3.86-3.97 (m, 3H); 4.93 (s, 2H); 6.81 (s, 4H); 7.06-7.20 (m, 24H); 7.37 (d, 2H, J = 8.3); 7.58 (d, 4H, J = 8.3); 7.68 (d, 2H, J = 8.3). ^{13}C-NMR, δ: 202.74; 201.62; 154.09; 152.41; 144.42; 142.91; 139.44; 139.41; 136.14; 135.64: 129.04; 128.93; 128.37; 128.32; 127.09; 126.19; 115.64; 114.63; 69.65, 55.67, 50.35, 49.55; 38.10; 37.91. MS (FAB, m/z): 881.4 (M^+, 8.4).

General procedure for the synthesis of the dendritic bromides [Gn]-Br. A stirred mixture of the corresponding phenyl ether ([Gn]-OP) (16 mmol), hydrobromic acid (80 mmol, 47%), acetic acid (ratio 1/8 v/v in rapport to HBr) and Aliquat 336 (10% mol) was heated under reflux for 18 h. Upon cooling to room temperature the reaction was quenched with saturated potassium carbonate solution and extracted with dichlorometane. The organic layer was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The product was purified by flash chromatography on silica gel to afford the desired bromide.

[G_1]-Br (5). The phenyl group of compound **3** was removed in refluxing HBr/AcOH according to the general procedure detailed above and purified by flash chromatography on silica gel (hexane/ ethyl acetate, 20/1) to afford the title compound **5** (75% yield) as a white solid. Mp, 62-63°C (hexane). IR (ν_{max}, cm^{-1}): 1670, 604. ^{1}H-NMR, δ: 2.80 (dd, 2H, J = 13.6; 6.3); 3.11 (dd, 2H, J = 13.6; 8.1); 3.98 (tt, 1H, J = 8.1; 6.3); 4.42 (s, 2H); 7.11-7.25 (m, 10H); 7.31 (d, 2H, J = 8.5); 7.65 (d, 2H, J = 8.5). ^{13}C-NMR, δ: 202.63; 142.30; 139.34; 137.20; 129.02; 128.95; 128.54; 128.39; 126.29; 50.67; 38.27; 32.07. Anal. Calcd for $C_{23}H_{21}BrO$: C, 70.58; H, 5.15. Found: C, 70.44; H, 5.15.

[G_2]-Br (9). The phenyl group of compound **7** was removed in refluxing HBr/AcOH according to the general procedure detailed above and purified by flash chromatography on silica gel (hexane) to afford the title compound **9** (70% yield) as a white solid. Mp, 79-80°C (toluene/hexane). IR (ν_{max}, cm^{-1}): 1677, 606. ^{1}H-NMR, δ: 2.70 (dd, 3H, J = 14.7; 6.1); 2.75 (ddd, 3H, J = 13.6; 6.1; 2.9); 3.05 (dd, 3H, J =13.6; 3.5); 3.07 (ddd, 3H, J = 14.7; 8.0; 2.9); 3.93 (dddd, 3H, J = 8.0; 6.1; 6.1; 3.5); 4.35 (s, 2H); 7.05-7.26 (m, 24H); 7.31 (d, 2H, J = 8.5); 7,58 (d, 4H, J = 8.5); 7.62 (d, 2H, J = 8.5). ^{13}C-NMR, δ: 202.63; 201.63; 144.27; 142.85; 139.42; 136.56; 135.76; 129.12; 128.99; 128.92; 128.46; 128.35; 128.30; 126.17; 50.36; 49.67; 38.19; 38.15; 37.95; 31.72. MS (FAB, m/z): 839.2 (M+2, 28.2); 837.3 (M^+, 22.6).

General procedure for the synthesis of the dendritic alcohols [Gn]-OH. A mixture of the corresponding *p*-methoxyphenylether (5 mmol) and ceric ammonium nitrate (15 mmol) in 40 ml acetonitrile/water (70/30) was stirred at room temperature for 6 h. The mixture was extracted with

dichloromethane (2 x 20 ml) and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified as described below.

[G_1]-OH (6). The *p*-methoxyphenylether **4** was oxidatively cleaved using the general procedure detailed above and purified by flash chromatography on silica gel (hexane/ethyl acetate, 5/1) to afford the benzylic alcohol **6** as an oil in a 80% yield. IR (film / ν_{max}, cm^{-1}): 3610-3100, 1672, 1234. ^{1}H-NMR, δ: 2.80 (dd, 2H, J = 13.7; 6.1); 3.12 (dd, 2H, J = 13.6; 7.9); 4.00 (tt, 1H, J = 7.9; 6.1); 4.70 (s, 2H); 7.11-7.27 (m, 10H); 7.32 (d, 2H, J = 8.3); 7.71 (d, 2H, J = 8.3). ^{13}C-NMR, δ: 203.22; 145.93; 139.30; 136.35; 128.87; 128.30; 128.38; 128.26; 126.17; 64.28; 50.37; 38.18. Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.56; H, 6.99.

[G_2]-OH (10) The *p*-methoxyphenylether **8** was oxidatively cleaved using the general procedure detailed above and purified by flash chromatography on silica gel (hexane/ethyl acetate, 2/1) to afford **10** as an oil in a 69% yield. IR (film / ν_{max}, cm^{-1}): 3850-3193, 1675, 1233. ^{1}H-NMR, δ: 2.67-2.78 (m, 6H); 3.01-3.09 (m, 6H); 3.88-3.90 (m, 3H); 4.58 (s, 2H); 7.04-7.18 (m, 24H); 7.25 (d, 2H, J = 8.3); 7.55 (d, 4H, J = 8.3); 7.62 (d, 2H, J = 8.6). ^{13}C-NMR, δ: 202.87; 201.80; 146.44; 144.43; 139.34; 139.32; 135.88; 135.55; 129.01; 128.88; 128.27; 128.21; 126.45; 126.15; 64.22; 50.31; 49.46; 38.06; 37.99. MS (FAB, m/z): 775.32 (M^+, 1.47).

[G_2]-I (13). This product was prepared following the general method for the synthesis of compounds **7** and **8**, but using the ketone **11** as monomer and the benzylic bromide **5** as alkylating agent. The crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate, 9/1) to give **13** as a white solid in a 52% yield. Mp, 123-123.5°C (hexane-toluene). IR (ν_{max}, cm^{-1}): 1669. ^{1}H-NMR, δ: 2.67-2.79 (m, 6H); 3.03-3.95 (m, 6H); 3.82 (tt, 1H, J = 13.9; 7.3); 3.92 (tt, 2H, J = 14.2; 7.1); 7.02-7.19 (m, 24H); 7.30 (d, 2H, J = 8.5); 7.56 (d, 4H, J = 7.9); 7.64 (d, 2H, J = 8.6). ^{13}C-NMR, δ: 202.73; 201.60; 144.13; 139.38; 137.80; 136.03; 135.71; 129.25; 128.96; 128.91; 128.37; 128.30; 126.17; 101.28; 50.34; 49.52; 38.20; 38.04. MS (FAB, m/z): 871.2 (M^+, 15.76).

[G_2]-CN (14). This product was prepared following the general method for the synthesis of compounds **7** and **8**, but using the ketone **12** as monomer and the benzylic bromide **5** as alkylating agent. The crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate, 5/1) to give **14** as a colourless oil in a 68% yield. IR (film / ν_{max}, cm^{-1}): 2230, 1677. ^{1}H-NMR, δ: 2.71-2.80 (m, 6H); 3.01-3.10 (m, 6H); 3.80-3.97 (m, 3H); 7.02-7.20 (m, 24H); 7.50-7.60 (m, 8H). ^{13}C-NMR, δ: 202.67; 201.45; 143.73; 139.87; 135.88; 132.31; 128.93; 128.92; 128.43; 128.32; 128.15; 126.21; 117.57; 116.27; 50.42; 50.24; 38.24; 38.12. MS (FAB, m/z): 770.3 (M^+, 13.80).

[G_1]-CHO (15). A stirred mixture of the dendritic benzyl alcohol **6** (1 mmol), sodium bromate (1 mmol), ammonium cerium nitrate (0.01 mmol) in acetonitrite / water (7:3, 5 mL) was heated at 80°C under argon for 5 hours. After cooling water (5 mL) was added and the mixture extracted with dichloromethane (2 x 5 mL). The dried (Na_2SO_4) extracts were evaporated and the product was purified by flash chromatography (hexane / ethyl acetate, 5:1) to yield **15** as an oil (65% yield). IR (film / ν_{max}, cm^{-1}): 2854, 2747, 1692, 1679. ^{1}H-NMR, δ: 2.88 (dd, 2H, J = 13.6; 5.9); 3.13 (dd, 2H, J = 13.6; 8.6); 4.03 (tt, 1H, J = 8.6; 5.9); 7.13-7.22 (m, 10H); 7.72 (d, 2H, J = 8.5); 7.78 (d, 2H, J = 8.5). ^{13}C-NMR, δ: 203.48; 191.48; 141.93; 138.98; 138.45; 129.48; 128.90; 128.44; 128.35; 126.41; 51.36; 38.61. Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.94; H, 6.02.

[G_2]-CHO (16). A mixture of the dendritic benzyl alcohol **10** (1 mmol), pyridinium chlorochromate (1 mmol) in dichloromethane (5 mL) was stirred at room temperature for 16 hours. The oxidising agent excess was eliminated by filtering the reaction crude over silica gel. After flash chromatography (hexane / ethyl acetate, 3:1) the pure product **16** was isolated as an oil (90% yield). IR (film / ν_{max}, cm^{-1}): 2852, 2746, 1706, 1678. ^{1}H-NMR, δ: 2.74 (dd, 4H, J = 13.6; 6.1); 2.75 (dd, 2H, J = 13.6; 6.1); 3.01-3.11 (m, 6H); 3.91 (tt, 3H, J = 7.8; 6.1); 7.04-7.19 (m, 24H); 7.57 (d, 4H, J = 8.3); 7,71 (d, 2H, J = 8.5); 7.77 (d, 2H, J = 8.5); 9.94 (s, 1H). ^{13}C-NMR, δ: 202.68; 202.00; 191.16; 143.93; 141.09; 139.37; 138.81; 135.80; 129.64; 129.01; 128.92; 128.41; 128.37; 128.31; 126.19; 50.38; 50.23; 38.14; 38.06. MS (FAB, m/z): 773.1 (M^+, 19.0).

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References

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