# Rapid and Efficient Synthesis of Aliphatic Ester Dendrons and Dendrimers

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ABSTRACT: A divergent approach to synthesize dendritic aliphatic polyester structures based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) is described. The key building block is the anhydride of isopropylidene-2,2-bis(methoxy)propionic acid which is synthesized in high yields through self-dehydration, utilizing *N*,*N*′-dicyclohexylcarbodiimide (DCC) as reagent. The high reactivity of the anhydride toward hydroxyl groups makes the divergent synthesis of dendrimers and dendrons viable. Dendritic growth occurs in the presence of protecting groups sensitive toward hydrogenolysis, such as benzyl esters and ethers. The acetonide-protecting group is easily removed under acidic conditions using DOWEX 50W-X2 resin in methanol. Fourth-generation dendrons and dendrimers were successfully synthesized in high yields utilizing 1.3−1.5 equiv of anhydride per hydroxyl group. Common characteristics of the esterification reaction were short reaction time, mild reaction conditions, easy monitoring by NMR analysis, and simple workup. This synthetic approach opens up the possibility to utilize orthogonal protecting groups of acetonide-protected 2,2-bis(hydroxymethyl)propionic anhydride as a novel building block.

## Introduction

Dendrimers and dendrons represent a unique class of macromolecules that has gained increasing attention from both academia and industry. The area first became a focus of interest in the early 1980s when Tomalia et al.[1] followed by Newkome et al.[2] described the divergent synthesis of poly(amidoamine) (PAMAM) and arborol dendrimers. The dendritic compounds, with high branching and monodisperse globular shape,[3] offer physical and thermal properties significantly different from linear polymers, which fascinate and challenge scientists all over the world. This has led to the construction of a large number of dendritic materials,[4] and several application areas have been suggested, such as liquid crystalline systems,[5,6] molecular encapsulation,[7,8] catalysis,[9] and biomedicine.[10−13]

The routes generally employed to construct dendrimers are divided into two approaches: the convergent growth, described by Hawker and Fréchet,[14] and the divergent growth.[1,2] In the convergent approach, the growth is started from the terminal groups toward a focal point to afford wedges of desired generation that subsequently can be coupled to a core. The last step involves few coupling sites, making the formation of dendrimers well controlled. However, drawbacks such as the loss of valuable higher generation dendrons and steric hindrance disfavor the use of the convergent approach, especially at higher generations. In the divergent approach, the dendrimer is grown radially outward by the addition of monomers layer-by-layer (generation by generation) from a central moiety. The molecular size and the number of chain ends increase with each new generation in proportion to the functionality of the $AB_x$ monomer.

To obtain a monodisperse higher-generation dendrimer, complete substitution in each step is necessary. A defect at a low generation will have a significant impact on the perfection of a higher-generation dendrimer. However, the divergent growth is the preferred approach as it uses less refined starting materials, i.e., only the protected $AB_x$ monomer. This renders it possible to use larger excess of reagents, increasing the probability of full substitution in each layer. The divergent approach also circumvents the steric hindrance when coupling the higher-generations dendrons to the core.

Previously, a disadvantage with the divergent approach containing a large number of sites was the lack of effective characterization techniques to monitor the progress of the synthesis. This is most crucial since the chemical difference between nearly fully substituted and fully substituted compounds is essentially negligible. Today, this limitation is almost avoided since powerful analytical techniques such as high-resolution NMR and MALDI−TOF have been developed.

In the mid-1990s, Hult et al. presented the first dendrimer based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA).[15] Hydroxyl-terminated dendrimers up to the fourth generation were achieved by introducing the acetonide-protecting group and *N*,*N*′-dicyclohexylcarbodiimide (DCC) as the dehydration agent.[16]

However, DCC has several drawbacks, which decrease the yield at higher generation due to reduced solubility of hydroxyl functional compounds, steric hindrance, loss of dendrons used in excess, and the formation of byproducts (*N*-acylurea).[17] Despite the detrimental disadvantages of the DCC chemistry, all bis-MPA-based dendrons and dendrimers, reported in the literature, have been synthesized in this fashion.

Recently, Fréchet et al.[18] described a divergent route to prepare aliphatic polyester dendrimers based on benzylidene-protected 2,2-bis(hydroxymethyl)propionic anhydride, offering advantages such as low-temperature esterification, short reaction time, facile workup, and high yields. The removal of the benzylidene group was quantitative and accomplished by hydrogenolysis ($H_2$, Pd/C) between each new generation.

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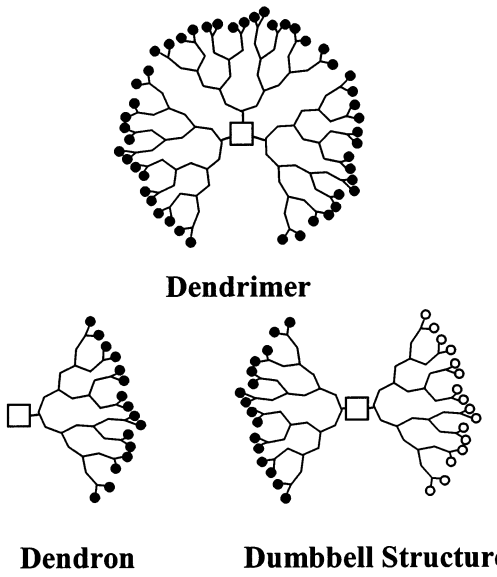



**Figure 1.** Schematic dendritic library: (□) focal point/core: such as aromatic, aliphatic, protected, functionalized, or metal ions; (● or ○) exterior layer with different end groups, i.e., protected, hydroxyl, carboxylic, amine, etc.

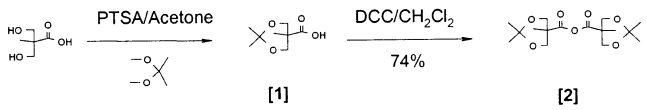
In our efforts to establish a large dendritic library comprising dendritic compounds based on bis-MPA, we became inspired by the efficiency of the anhydride chemistry. However, the synthesis of dumbbell-shaped dendrimers often requires the use of orthogonally protected dendrons (Figure 1). An obvious drawback with the benzylidene-protected anhydride in this respect is that it does not allow selective deprotection in the presence of other groups susceptible toward hydrogenolysis, such as a benzyl ester. The benzyl ester is commonly employed in the synthesis of bis-MPA dendrons. The 2,2-bis(hydroxymethyl)propionic anhydride was introduced to combine the anhydride chemistry with the use of the benzyl ester protected focal point. The acetonide-protected 2,2-bis(hydroxymethyl)propionic anhydride was conveniently employed to construct a variety of fourth-generation dendrons. The growth was demonstrated for three different focal point moieties. Acetonide-protected dendrimers, grown from the second to fourth generation, were also successfully synthesized in the same fashion.

This synthetic route complements the benzylidene-protected anhydride esterification strategy reported by Fréchet et al.[18] in the synthesis of aliphatic polyester dendrons and dendrimers. The acetonide-protected anhydride potentially enables the synthesis of a large number of novel orthogonally protected dendritic building blocks. During the course of this work a paper by Fréchet et al. appeared describing the use of the acetonide-protected 2,2-bis(hydroxymethyl)propionic anhydride, but no synthetic details are given.[19]

## Results and Discussion

To address a modular synthetic approach, the dendron synthesis requires two protecting groups, different at the focal point and the terminal groups. Ideally, these should allow independent, convenient, and quantitative deprotection. The first targeted molecule was a dendron containing a protecting group other than the usual benzyl ester at the focal point.[13,15,16] 2,2,2-Trichloroethanol was first chosen because it is widely used in organic synthesis and also in combination with other protecting groups. However, after successfully constructing benzylidene-[G#2]-$CH_2CCl_3$, we encountered difficulties in the deprotection step of the benzylidene group. It seems that the employed deprotection procedure using hydrogenolysis catalyzed by palladium on carbon is affecting and degrading the 2,2,2-trichloroethyl ester. Why the focal protecting group, which is normally stable to hydrogenolysis, degrades under these conditions is unknown. No further investigations have been conducted to elucidate the cause of this. Attempts to selectively cleave the benzylidene group under acidic conditions were less successful due to long deprotection time and tedious workup as described previously.[18] Hence, a modification of the anhydride building block was preferable in order to afford dendrons of higher generation carrying groups labile during hydrogenolysis. As a natural choice we employed the commonly used acetonide-protected bis-MPA[16] **1** (Scheme 1).

**Scheme 1. Synthesis of Acetonide-Protected Bis-MPA Anhydride 2**



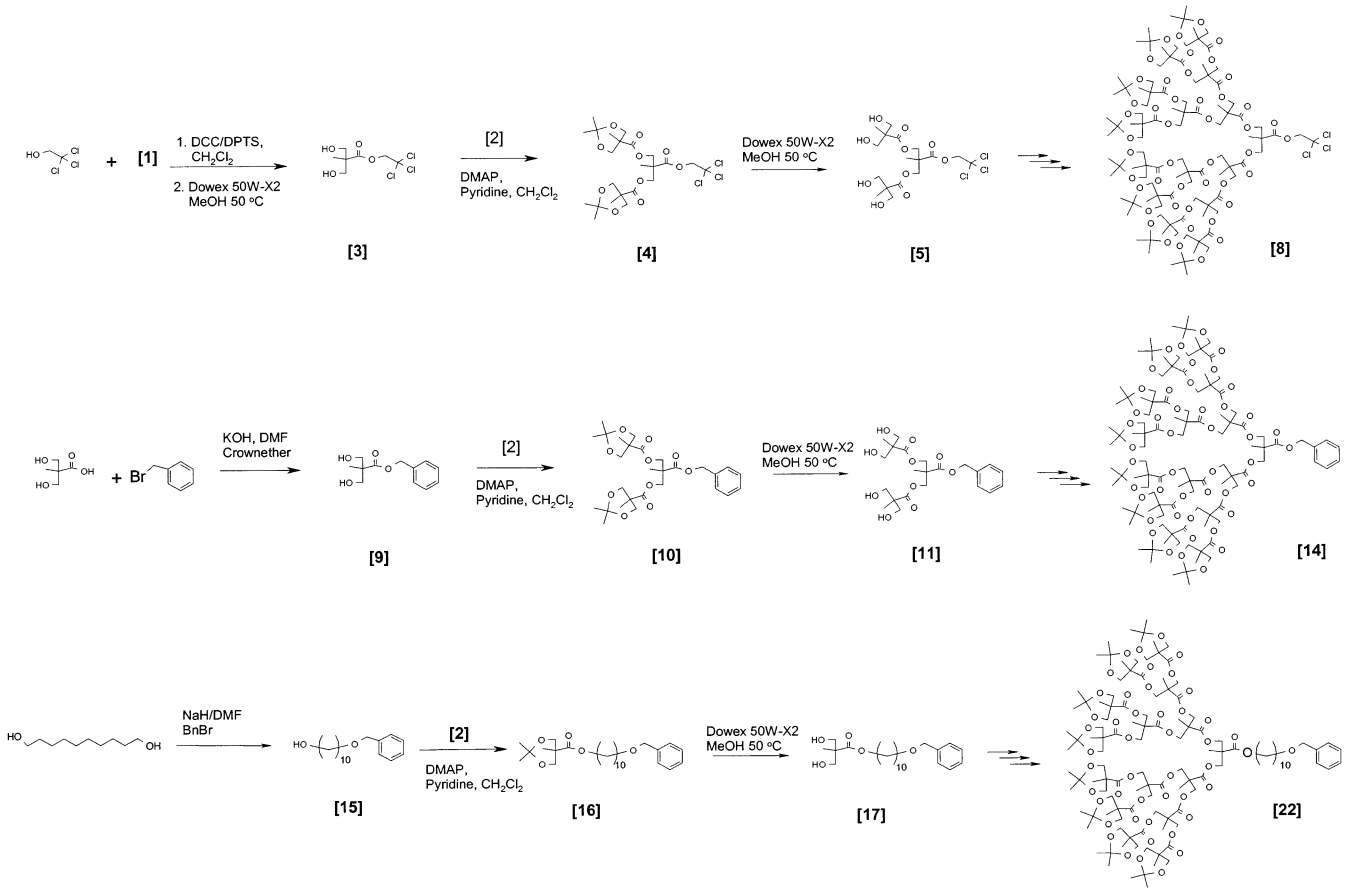

**Synthesis.** The anhydride **2** was afforded in 74% yield, as a white solid, by dehydration of the acetonide-protected bis-MPA using DCC chemistry (Scheme 1). The purification through precipitation into cold hexane is a crucial and tedious step since **2** is soluble in a wide range of aprotic solvents at ambient temperature, such as hexane, $CH_2Cl_2$, diethyl ether, and $CHCl_3$.

The anhydride's susceptibility toward hydrolysis was evaluated after 90 days storage under ambient conditions. The degree of degradation of the anhydride bond was significant; thus, **2** was stored under dry conditions. This was determined by $^{13}C$ NMR spectroscopy where the anhydride carbonyl carbon resonates at 169 ppm and the corresponding acid at 178 ppm. The acetonide-protected anhydride is significantly more sensitive toward hydrolysis than the corresponding benzylidene-protected compound, most likely due to the crystalline nature of the benzylidene compound.

Three different fourth-generation acetonide-protected dendrons based on 2,2,2-trichloroethyl ester **8**, benzyl ester **14**, and decanoyl benzyl ether **22** as the focal point were synthesized (Scheme 2). The 2,2,2-trichloroethyl ester of bis-MPA, **3**, was obtained in 92% yield via the in-situ reaction first involving the DCC esterification of **1** with 2,2,2-trichloroethanol followed by the deprotection of the acetonide groups using DOWEX 50W-X2 in methanol. The benzyl ester of bis-MPA, **9**, was afforded by reacting bis-MPA with benzyl bromide according to a procedure described previously.[16] The monoprotected diol, **15,** of 1,10-decanediol was obtained by reacting the diol with sodium hydride in DMF to form the monoalcoholate. Benzyl bromide was added dropwise to the mixture to obtain the monoprotected diol in 52% yield.

**General Esterification Procedure of Dendrons and Dendrimers (Schemes 2 and 3)**. The success of using the acetonide-protected anhydride **2** as a reagent in the divergent synthesis depends on several key factors. The stoichiometry of reagents, the concentration of the anhydride, and workup procedures are all crucial factors to obtain dendritic materials in high yields and are well discussed in an earlier paper.[18]

**Scheme 2. Divergent Synthesis of Fourth-Generation Dendrons 8, 14, and 22**




In this work, different ratios of reagents to hydroxyl groups were examined. The ratios of 5 equiv of pyridine, 0.15 equiv of DMAP, and 1.3 equiv of anhydride **2** to hydroxyl group resulted in the desired products in high yields. Larger quantities of anhydride were insoluble in the pyridine solution, and thus it was necessary to use a complementary solvent such as $CH_2Cl_2$. The volume proportion of pyridine and $CH_2Cl_2$ used was 1:3; however, it was found that a smaller amount of $CH_2Cl_2$ was sufficient to obtain satisfactory solubility. After completion the reaction was quenched with water, transforming the excess of anhydride to the corresponding acid, diluted, and extracted with $NaHSO_4$ (10%), $Na_2CO_3$ (10%) with no trace of degradation of the products.

The divergent approach utilizing large amounts of anhydride accumulates small amounts of *N*-acylurea; thus further purification by liquid chromatography was necessary after each esterification step. Fortunately, the acetonide-protected dendrons have low polarity and are simply dissolved in 10:90 EtOAc:hexane or solvent mixtures of lower polarity. This allows a simple column procedure where all the low molecular weight byproducts are easily flushed through the column, isolating the larger molecules, i.e., dendritic materials.

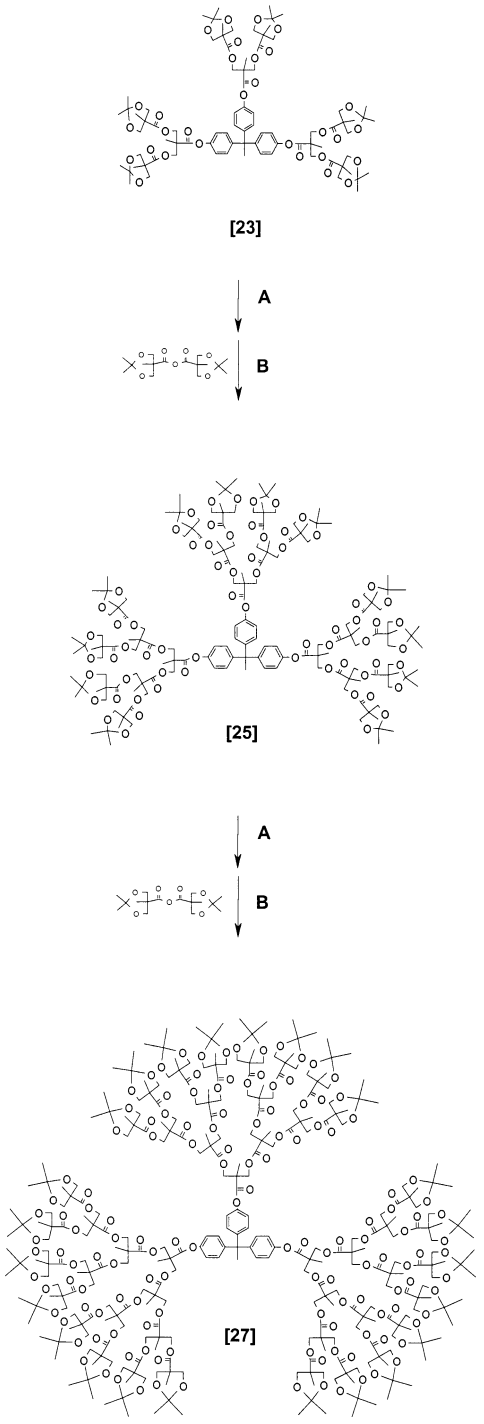
The above-described procedure was successfully employed to synthesize the fourth-generation dendron acetonide-[G#4]-$CH_2CCl_3$, **8**, in 65% overall yield. Other synthesized dendrons, such as acetonide-[G#4]-$CO_2$-$CH_2C_6H_5$, **14**, and acetonide-[G#4]-$CO_2(CH_2)_{10}CO_2C_6H_5$, **22**, were also obtained in high yields. Also, the targeted fourth-generation dendrimer, acetonide-[G#4]-dendrimer, **27**, was grown divergently from the HO-[G#2]-dendrimer, **24**, in order to demonstrate the versatility of the anhydride chemistry also on preformed dendrimers.

The possibility of excluding the column chromatography from the workup procedure was also investigated. NMR results showed that all hydroxyl functional dendrons of the second-generation **5**, **11**, and **19** or higher; i.e., **7**, **13**, and **21** could easily be purified from the accumulated byproducts formed in the esterification steps. This was accomplished through precipitation into cold diethyl ether from methanol.

**General Procedure for Deprotection of Acetonide-Protected Dendrons and Dendrimers.** The acetonide derivatives were easily deprotected by stirring in methanol in the presence of an acidic resin, DOWEX 50W-X2, as described previously.[16] Higher temperature, 50 °C, was employed to increase the solubility of the dendritic compounds in methanol and decrease the deprotection time with no traces of skeletal degradation. Typically, the dendron, such as acetonide-[G#2]-$CH_2$-$CCl_3$, **5**, was dissolved in methanol, and the acetonide groups were selectively removed at 50 °C (ca. 1 teaspoon of DOWEX 50W-X2/g of dendron). The deprotection was easily monitored by TLC, $^{13}C$ NMR, and $^1H$ NMR, and all compounds were fully deprotected within 1−2 h. The DOWEX 50W-X2 resin was filtered off, and the solvent removed in a vacuum to afford the hydroxyl functional dendrons and dendrimers in high yields.

**Characterization of Dendrons and Dendrimers. $^1H$ NMR, $^{13}C$ NMR, and MALDI−TOF Characterization.** Previous NMR analysis, both $^1H$ and $^{13}C$ NMR, of bis-MPA based dendrons and dendrimers featured unique shifts specific to groups in different layers in the

**Scheme 3. Generational Growth of Acetonide-Protected Dendrimers through the Use of Anhydride Esterification: (A) Dowex 50W-X2, MeOH, 50 °C, 3 h; (B) Pyridine/$CH_2Cl_2$ and DMAP**




structure.[15,16] In monitoring the divergent procedure, the $^{13}C$ NMR analysis was a vital tool, revealing an unique resonance related to the farthest layer from the core. The shifts involved in the anhydride esterification initialized from $(HO)_2$-[G#1]-$CH_2CCl_3$, **3**, are shown in Figure 2. The methyl, methylene, and carbonyl carbons (F, D, and C) in the repeating unit are seen as singlets at 17.03, 67.69, and 173.98 ppm. Each new generation has a new set of specific singlets, making it possible to accurately monitor the generational growth. The peaks (A and B) emanating from the focal trichloroethyl group were observed with decreasing intensity at higher generations.

The reactions were easily monitored by the unique shift of the quaternary carbon situated on the outer layer. The quaternary carbon resonance (E) of **3** shifts downfield from 49.64 to 41.80 ppm as the reaction progresses and disappears totally when substitution is complete, forming **4**. In addition, the appearance of a doublet at 22.14 and 25.31 ppm and a singlet at 98.19 ppm (H, H′, and G) is related to the acetonide-protecting group. The excess of anhydride **2** was quenched to the corresponding acid **1** and could easily be distinguished by the shift of the carbonyl carbon at 169.68−178.04 ppm. Utilizing the same monitoring procedure, the deprotection step was followed by observing the upfield shift of the quaternary carbon from 41.80 to around 49 ppm and the disappearance of the resonances representing the protecting group. The fourth generation dendron **8** reveals the same unique $^{13}C$ NMR pattern as the low-generation molecules.

The $^1H$ NMR analysis of the fourth-generation dendron **8** verified the $^{13}C$ NMR results. Different generational segments give unique resonances such as the methyl groups at 1.12, 1.24, 1.25, and 1.36 ppm (F, $F^2$, $F^3$, and $F^4$). Unfortunately, in the same region the acetonide-protecting group has a doublet at 1.32 and 1.38 ppm, and for the higher generations this resonance is predominant, hence overlapping the methyl resonances of the interior. The methylene groups emanating from various generations (D, $D^2$, $D^3$, and $D^4$) and the focal group (B) appears at higher fields.

MALDI−TOF has been employed for the determination of purity and molecular weight of different dendrons and dendrimers. Results from the analysis are in agreement with the calculated values, and an example is shown in Figure 3.

## Conclusions

Different dendritic structures have been successfully synthesized through a divergent growth approach by the use of acetonide-protected 2,2-bis(hydroxymethyl)propionic anhydride as a new building block. The anhydride allows the construction of dendrons up to the fourth generation having focal groups sensitive toward hydrogenolysis. The fourth-generation acetonide-protected dendrimer is easily afforded in the same manner. All materials were obtained in high yields due to high coupling efficiency and straightforward workup procedures. All compounds were analyzed by $^1H$ and $^{13}C$ NMR spectroscopy and MALDI−TOF.

This novel reagent is a versatile building block, requiring mild reaction conditions, for orthogonally protected dendritic compounds since it allows the coexistence of protecting groups sensitive toward hydrogenolysis. An example could be the employment of the anhydride in combination with the particularly important carbobenzyloxy protecting group in peptide chemistry. The use of orthogonal protecting groups allows the buildup of a dendritic library with a wide range of compounds.

## Experimental Section

**Materials and Techniques.** 2,2-Bis(hydroxymethyl)propionic acid (bis-MPA) was kindly supplied by Perstorp AB, Sweden. Compounds **1**, **9**, and **23** were synthesized according to a procedure described by Hult et al.[16] Commercially available DMAP (99%) was purchased from Aldrich. The DOWEX

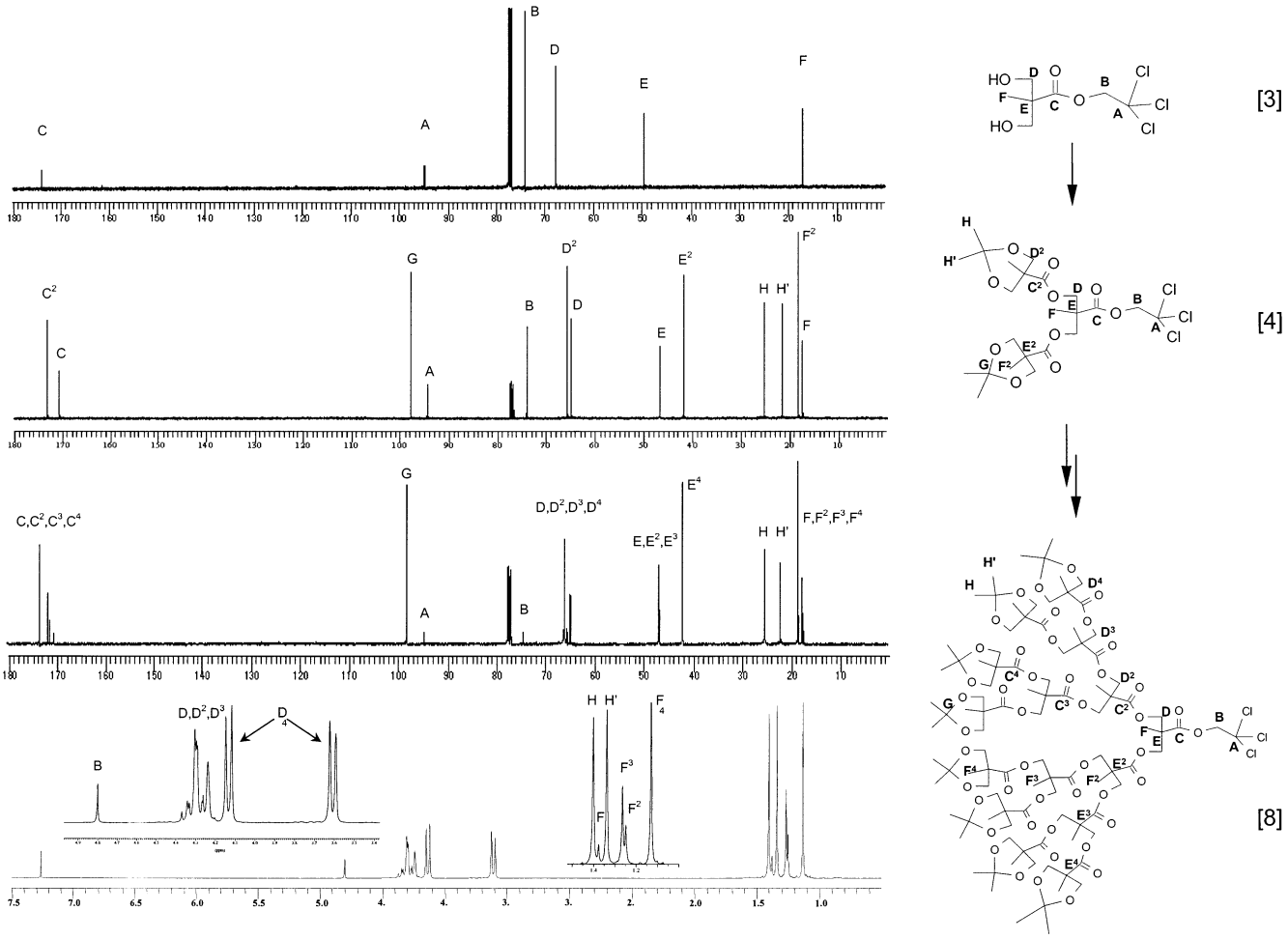



**Figure 2.** $^{13}C$ NMR spectra of **3**, **4**, and the fourth-generation dendron **8** in $CDCl_3$. $^1H$ NMR spectra of **8**.

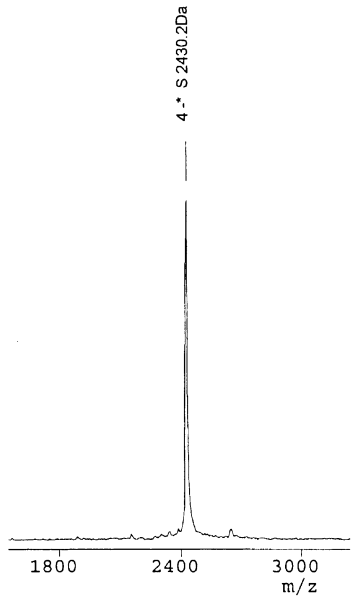



**Figure 3.** MALDI−TOF of the fourth-generation dendron **22** with theoretical molecular weight of 2326.6 Da.

50W-X2 ion-exchange resin was obtained from Acros Organics. $CH_2Cl_2$, methanol, and pyridine were H.P.L.C. grade and purchased from Lab-Scan. Ethyl acetate and hexane were P.A. grade and obtained from Fischer. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AM 400 using $CDCl_3$, MeOD, or DMSO-$d_6$. The solvent signal was used as internal standard. All purifications were performed by medium-pressure liquid chromatography or by flash chromatography. MALDI−TOF experiments were conducted on a Hewlett-Packard G2025 at ~1.5 $\mu$J and ~2 × $10^{-6}$ Torr. Matrix preparation: 9-Nitroanthracene (20 mg) was dissolved in THF (1 mL), and trifluoroacetic acid silver salt (one tip of a knife) was added. Sample preparation: 10 mg of sample was dissolved in 1 mL of THF overnight and filtered through 0.45 $\mu$m Teflon filter. The sample solution (5 $\mu$L) was added to the matrix solution (20 $\mu$L).

**Preparation of Acetonide-2,2-bis(methoxy)propionic Anhydride (2).** Acetonide-2,2-bis(methoxy)propionic acid (**1**) (50.0 g, 287 mmol) was stirred in $CH_2Cl_2$ (200 mL). *N,N′*-Dicyclohexylcarbodiimide (DCC) (29.6 g, 144 mmol) was added to the mixture, and stirring was continued for 48 h at room temperature. The reaction was allowed to reach completion as monitored by $^{13}C$ NMR. This was determined by the appearance of the anhydride carbonyl carbon at 169 ppm and the disappearance of the acid carbonyl carbon corresponding to **1** at 178 ppm. The DCC−urea was filtered off and the solvent evaporated. The viscous residue was diluted in 1 L of hexane and stirred until a white solid formed. Thereafter, the solution was cooled to −78 °C for 1 h, filtered through a glass filter, and dried under vacuum to afford **2** as white crystals (35.1 g, 74%). $^1H$ NMR ($CDCl_3$): $\delta$ 1.21 (s, 6H, $-CH_3$), 1.36 (s, 6H, $-CH_3$), 1.41 (s, 6H, $-CH_3$), 3.66 (d, 4H, $J$ = 12.0 Hz,, $-CH_2O$), 4.18 (d, 4H, $J$ = 12.0 Hz, $-CH_2O$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 17.83, 21.75, 25.72, 43.83, 65.85, 98.56, 169.68.

**Preparation of 2,2,2-Trichloroethyl-2,2-bis(methylol)-propionate (3), in Situ.** 2,2,2-Trichloroethanol (3.00 g, 20.1 mmol) and acetonide-2,2-bis(methoxy)propionic acid (**1**) (3.00 g, 17.2 mmol) were stirred in $CH_2Cl_2$ (20 mL). 4-(Dimethylamino)pyridinium *p*-toluenesulfonate (DPTS)[17] (1.02 g, 3.45 mmol) was first added to the mixture followed by DCC (3.90 g, 19.0 mmol). Stirring was continued at room temperature

for 18 h, and thereafter the DCC−urea was filtered off. The filtrate was evaporated; the byproducts were precipitated in cold hexane and once more filtered through a glass filter. After evaporation of the hexane, the mixture was dissolved in 30 mL of MeOH, and a teaspoon of DOWEX 50W-X2 was added. The reaction was monitored with $^{13}C$ NMR until the disappearance of the assignment related to the acetonide group (at ∼21, 24, 42, and 98 ppm). Then after the resin was filtered off and the solvent evaporated. The crude product were precipitated in EtOAc:hexane (20:80) to afford $(HO)_2$-[G#1]-$CH_2CCl_3$, **3** as white crystals (4.23 g, 92%). $^1H$ NMR ($CDCl_3$): $\delta$ 1.17 (s, 3H, $-CH_3$), 2.81 (s, 2H, −OH), 3.78 (d, 2H, $J = 11.2$ Hz, $-CH_2$-OH), 3.97 (d, 2H, $J = 11.2$ Hz), 4.81 (s, 2H, $-CH_2CCl_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 17.03, 49.64, 67.69, 73.94, 94.72, 173.98.

**General Procedure: Esterification through Anhydride Coupling, Acetonide-[G#2]-$CH_2CCl_3$ (4).** $(HO)_2$-[G#1]-$CH_2CCl_3$ **(3)** (2.05 g, 7.78 mmol) and DMAP (0.43 g, 3.50 mmol) were dissolved in 6 mL (5 equiv./OH-group) of pyridine at room temperature. A solution of **2** (7.70 g, 23.3 mmol) in 20 mL of $CH_2Cl_2$ was added to the vessel. The solution was monitored with $^{13}C$ NMR until the reaction reached completion (determined by the disappearance of the quaternary carbon of **3** at ∼ 49 ppm and the appearance of additional peaks at e.g. ∼42 ppm). The excess anhydride was quenched with 1−2 mL of water under vigorous stirring. The reaction was then diluted with 500 mL of $CH_2Cl_2$ and extracted with 10% of $NaHSO_4$ (3 × 50 mL), 10% of $Na_2CO_3$ (3 × 50 mL), and brine (1 × 50 mL). The organic phase was dried ($MgSO_4$), filtered, concentrated, and purified by liquid column chromatography on silica gel, eluting with hexane and gradually increasing the polarity to 40:60 EtOAc:hexane to give **4** as yellow oil (4.31 g, 96%). TLC (silica) EtOAc:hexane (40:60), $R_f$ 0.63. $^1H$ NMR ($CDCl_3$): $\delta$ 1.02 (s, 6H, $-CH_3$), 1.24 (s, 6H, $-CH_3$), 1.28 (s, 3H, $-CH_3$), 1.31 (s, 6H, $-CH_3$), 3.04 (d, 4H, $J = 12.0$ Hz, $-OCH_2$), 3.52 (d, 4H, $J = 12.0$ Hz, $-OCH_2$), 4.29 (s, 4H, $-CH_2C$), 4.69 (s, 2H, $-CH_2$-$CCl_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 17.30, 18.18, 21.47, 25.22, 41.81, 46.75, 64.76, 65.69, 73.88, 94.38, 97.79, 170.65, 173.16.

**General Deprotection Procedure of the Acetonide Group: $(HO)_4$-[G#2]-$CH_2CCl_3$ (5).** Two teaspoons of DOWEX 50W-X2 was added to a solution of acetonide-[G#2]-$CH_2CCl_3$ **4** (4.31 g, 7.46 mmol) in 200 mL of methanol. The mixture was stirred at 50 °C, and the deprotection was followed with $^{13}C$ NMR until the disappearance of peaks unique for the acetonide group, such as the quaternary carbon at ∼98 ppm. Once the reaction was complete, the resin was filtered off and washed with MeOH. The filtrate was evaporated to give **5** as white crystals (3.30 g, 89%). TLC (silica) EtOAc:hexane (80:20), $R_f$ 0.39. $^1H$ NMR ($CDCl_3$): $\delta$ 1.03 (s, 6H, $-CH_3$), 1.40 (s, 3H, $-CH_3$), 3.67−3.87 (m, 8H, $-CH_2OH$), 4.34 (d, 2H, $J = 11.4$ Hz, $-CH_2C$), 4.53 (d, 2H, $J = 11.4$ Hz, $-CH_2C$), 4.79 (s, 2H, $-CH_2CCl_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 17.52, 18.52, 47.08, 50.04, 64.91, 68.87, 74.62. 77.63, 171.72, 175.49.

**Acetonide-[G#3]-$CH_2CCl_3$ (6).** $(HO)_4$-[G#2]-$CH_2CCl_3$ **5** (2.56 g, 5.15 mmol), DMAP (0.49 g, 4.02 mmol), 8 mL of pyridine, 20 mL of $CH_2Cl_2$, and **2** (8.83 g, 26.8 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluted from hexane, and increasing the polarity gradually to 60:40 EtOAc:hexane giving **6** as colorless viscous oil (5.36 g, 93%). TLC (silica) EtOAc:hexane (40:60), $R_f$ 0.34. $^1H$ NMR ($CDCl_3$): $\delta$ 1.07 (s, 12H, $-CH_3$), 1.21 (s, 3H, $-CH_3$), 1.28 (s, 12H, $-CH_3$), 1.30 (s, 6H, $-CH_3$), 1.34 (s, 12H, $-CH_3$), 3.55 (d, 8H, $J = 11.6$ Hz, $-CH_2OH$), 4.08 (d, 8H, $J = 11.6$ Hz, $-CH_2$-OH), 4.20−4.35 (m, 12H, $-CH_2C$), 4.75 (s, 2H, $-CH_2CCl_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 17.45, 17.65, 18.50, 21.89, 25.34, 42.04, 46.90, 46.91, 65.73, 65.90, 65.96, 94.59, 98.07, 170.54, 171.82, 173.46.

**$(HO)_6$ -[G#3]-$CH_2CCl_3$ (7).** Acetonide-[G#3]-$CH_2CCl_3$ **(6)** (5.83 g, 5.20 mmol), three teaspoons of DOWEX 50W-X2, and 100 mL of MeOH were allowed to react according to the general deprotection procedure to give **7** (4.87 g, 97%) as white crystals. $^1H$ NMR (MeOD): $\delta$ 1.11 (s, 12H, $-CH_3$), 1.26 (s, 6H, $-CH_3$), 1.36 (s, 3H, $-CH_3$), 3.54−3.65 (m, 16H, $-CH_2OH$), 4.18−4.37 (m, 12H, $-CH_2C$), 4.87 (s, 2H, $-CH_2CCl_3$). $^{13}C$ NMR (MeOD): $\delta$ 17.27, 17.92, 18.20, 47.86, 48.04, 51.71, 65.74, 66.08, 66.99, 75.28, 96.07, 172.13, 173.64, 175.82.

**Acetonide-[G#4]-$CH_2CCl_3$ (8).** $(HO)_6$-[G#3]-$CH_2CCl_3$ **(7)** (2.00 g, 2.08 mmol), 0.40 g (3.24 mmol) of DMAP, 7 mL of pyridine, 15 mL of $CH_2Cl_2$, and 7.14 g (21.6 mmol) of **2** were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluted from hexane, and gradually increasing the polarity to 60:40 EtOAc:hexane to give **6** as colorless viscous oil (3.88 g, 85%). $^1H$ NMR ($CDCl_3$): $\delta$ 1.12 (s, 24H, $-CH_3$), 1.24 (s, 6H, $-CH_3$), 1.25 (s, 12H, $-CH_3$), 1.32 (s, 24H, $-CH_3$), 1.32 (s, 3H, $-CH_3$), 1.39 (s, 24H, $-CH_3$), 3.59 (d, 16H, $J = 11.8$ Hz, $-CH_2$-OH), 4.12 (d, 16H, $J = 11.8$ Hz, $-CH_2OH$), 4.23−4.36 (m, 28H, $-CH_2C$), 4.79 (s, 2H, $-CH_2CCl_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 17.41, 17.60, 17.77, 18.60, 22.14, 25.30, 42.13, 46.83, 46.93, 47.01, 64.92, 65.58, 66.00, 66.30, 74.41, 94.71, 98.19, 170.56, 171.49, 171.91, 173.57. Calcd: $[M]^+$ $m/z = 2211.64$. Found: MALDI−TOF: $[M + Ag]^+ = 2315.6$.

**Acetonide-[G#2]-$CO_2CH_2C_6H_5$ (10).** Compound **9** (3.00 g, 13.4 mmol), DMAP (0.64 g, 5.22 mmol), 10 mL of pyridine, 20 mL of $CH_2Cl_2$, and **2** (11.5 g, 34.8 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluted from hexane, and gradually increasing the polarity to 60:40 EtOAc:hexane to give **10** as colorless viscous oil (6.76 g, 94%). The spectral data were in accordance with published data.[16] Calcd: $[M]^+$ $m/z = 536.61$. Found: MALDI−TOFMS-ES: $[M + Ag]^+ = 642.9$.

**$(HO)_6$-[G#2]-$CO_2CH_2C_6H_5$ (11).** Acetonide-[G#2]-$CO_2CH_2$-$C_6H_5$ **(10)** (5.00 g, 9.33 mmol), three teaspoons of DOWEX 50W-X2, and 100 mL of MeOH were allowed to react according to the general deprotection procedure to give **11** (4.10 g, 97%) as white crystals. The spectral data were in accordance with published data.[16]

**Acetonide-[G#3]-$CO_2CH_2C_6H_5$ (12).** $(HO)_6$-[G#2]-$CO_2$-$CH_2C_6H_5$ **(11)** (2.00 g, 4.40 mmol), DMAP (0.42 g, 5.12 mmol), 7 mL of pyridine, 20 mL of $CH_2Cl_2$, and **2** (7.55 g, 22.9 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluting from hexane, and gradually increasing the polarity to 80:20 EtOAc:hexane to give **12** as colorless viscous oil (4.41 g, 93%). TLC (silica) EtOAc:hexane 60:40, $R_f$ 0.40. $^1H$ NMR ($CDCl_3$): $\delta$ 1.09 (s, 12H), 1.14 (s, 3H), 1.22 (s, 6H), 1.30 (s, 24H), 3.53 (d, 8H, $J = 12.60$ Hz), 4.10 (d, 8H, $J = 12.60$ Hz), 4.15−4.20 (m, 8H), 4.23−4.26 (m, 4H), 5.09 (s, 2H), 7.28 (m, 5H). $^{13}C$ NMR ($CDCl_3$): $\delta$ 17.96, 17.98, 18.88, 22.39, 25.61, 42.41, 47.08, 47.19, 65.25, 66.08, 66.31, 66.36, 66.46, 67.58, 98.49, 128.86, 128.93, 129.08, 135.74, 172.33, 173.96.

**$(HO)_8$-[G#3]-$CO_2CH_2C_6H_5$ (13).** Acetonide-[G#3]-$CO_2CH_2$-$C_6H_5$ **(12)** (3.00 g, 2.78 mmol), two teaspoons of DOWEX 50W-X2, and 75 mL of MeOH were allowed to react according to the general deprotection procedure to give **13** (2.36 g, 93%) as white crystals. $^1H$ NMR (DMSO-$d_6$): $\delta$ 0.95 (s, 12H) 0.97 (s, 6H), 1.02 (s, 3H), 3.34−3.44 (m, 16H), 4.01−4.12 (m, 8H), 4.22 (q, 4H, $J = 11.08$ Hz), 5.18 (s, 2H), 7.35 (m, 5H, ArH). $^{13}C$ NMR (DMSO): $\delta$ 16.81, 17.11, 17.15, 46.36, 46.41, 50.38, 63.81, 64.60, 65.90, 66.49, 128.01, 128.31, 128.63, 135.79, 138.02, 171.96, 172.02, 174,19.

**Acetonide-[G#4]-$CO_2CH_2C_6H_5$ (14).** $(HO)_8$-[G#3]-$CO_2$-$CH_2C_6H_5$ **(13)** (1.17 g, 1.27 mmol), DMAP (0.31 g, 2.51 mmol), 4 mL of pyridine, 10 mL of $CH_2Cl_2$, and **2** (4.36 g, 13.2 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluted from hexane, and gradually increasing the polarity to 80:20 EtOAc:hexane to give **14** as colorless viscous oil (2.44 g, 89%). The spectral data were in accordance with published data.[16]

**Preparation of 1-Benzyl-10-decanediol (15).** NaH (60%) (0.917 g, 23.0 mmol) was stirred in 80 mL of DMF, and a solution of 1,10-decanediol in 10 mL of DMF (4.00 g, 23.0 mmol) was added dropwise. The mixture was stirred for an hour using $N_2$ gas as an inert atmosphere, and then 3.14 g (18.7 mmol) of benzyl bromide was dropwise added at −78 °C. The reaction was quenched with 5 mL of saturated ammonium chloride after stirring for an additional 30 min at −78 °C and 18 h at room temperature. The mixture was then diluted with

1 L of water and extracted with diethyl ether (3 × 100 mL). The organic phase was washed with brine, dried ($MgSO_4$), filtered, concentrated, and finally purified by medium-pressure liquid chromatography (MPLC) on silica gel, eluted with hexane, and gradually increasing the polarity to 40:60 EtOAc/hexane to give **15** as colorless oil (2.52 g, 52%). TLC (silica) EtOAc:hexane (20:80), $R_f$ 0.27. $^1$H NMR ($CDCl_3$): $\delta$ 1.20−1.40 (m, 12H, $-CH_2CH_2$), 1.54−1.62 (m, 4H, $-CH_2CH_2O$), 3.47 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCH_2Ar$), 3.62 (t, 2H, $J$ = 13.2 Hz, $-CH_2OH$), 4.51 (s, 2H, $-CH_2Ar$), 7.26−7.35 (m, 5H, ArH). $^{13}$C NMR ($CDCl_3$): $\delta$ 25.63, 26.04, 29.30, 29.33, 29.40, 29.60, 32.61, 62.70, 70.36, 72.71, 76.68, 127.35, 127.51, 128.20, 138.48.

**Acetonide-[G#1]-$CO_2(CH_2)_{10}OCH_2C_6H_5$ (16).** 1-Benzyl-10-decanediol (**15**) (0.30 g, 1.14 mmol), DMAP (31.3 mg, 0.26 mmol), 0.7 mL of pyridine, 3 mL of $CH_2Cl_2$, and **2** (564 mg, 1.71 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluted from hexane, and gradually increasing the polarity to 30:70 EtOAc:hexane to give **16** as a yellow oil (0.45 g, 94%). TLC (silica) EtOAc:hexane (20:80), $R_f$ 0.54. $^1$H NMR ($CDCl_3$): $\delta$ 1.19 (s, 3H, $-CH_3$), 1.26−1.35 (m, 12H, $-CH_2CH_2$), 1.38 (s, 3 H, $-CH_3$), 1.42 (s, 3 H, $-CH_3$), 1.56−1.66 (m, 4H, $-CH_2CH_2O$), 3.45 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCH_2Ar$), 3.63 (d, 2H, $J$ = 12,0.0 Hz, $-OCH_2$), 4.12 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCO$), 3.18 (d, 2H, $J$ = 12.0 Hz, $-OCH_2$), 4.49 (s, 2H, $-CH_2Ar$), 7.24−7.35 (m, 5H, −ArH). $^{13}$C NMR ($CDCl_3$): $\delta$ 18.64, 24.22, 25.72, 26.09, 28.47, 29.10, 29.35, 29.40, 29.68, 41.67, 64.88, 65.93, 70.40, 72.75, 94.92, 127.38, 127.53, 128.25, 138.60, 174.21.

**$(HO)_2$-[G#1]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (17).** Acetonide-[G#1]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (**16**) (0.45 g, 1.07 mmol), half a teaspoon of DOWEX 50W-X2, and 10 mL of MeOH were allowed to react according to the general deprotection procedure to give **17** (0.37 g, 91%) as a colorless oil. TLC (silica) EtOAc:hexane (60:40), $R_f$ 0.43. $^1$H NMR ($CDCl_3$): $\delta$ 1.09 (s, 3H, $-CH_3$), 1.30−1.42 (m, 12H, $-CH_2CH_2$), 1.60−1.70 (m, 4H, $-CH_2CH_2O$), 3.47 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCH_2Ar$), 3.69 (d, 2H, $J$ = 11.2 Hz, $-CH_2OH$), 3.87 (d, 2H, $J$ = 11.2 Hz, $-CH_2$-OH), 4.12 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCO$), 4.52 (s, 2H, $-CH_2$-Ar), 7.25−7.35 (m, 5H, −ArH). $^{13}$C NMR ($CDCl_3$): $\delta$ 17.60, 26.58, 26.66, 28.93, 29.57, 29.82, 29.86, 30.15, 49.61, 65.56, 67.99, 70.91, 73.27, 127.90, 128.04, 128.75, 139.07, 176.07.

**Acetonide-[G#2]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (18).** $(HO)_2$-[G#1]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (**17**) (0.37 g, 0.97 mmol), DMAP (47.5 mg, 0.39 mmol), 1 mL of pyridine, 4 mL of $CH_2Cl_2$, and **2** (1.28 g, 3.90 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluted from hexane, and gradually increasing the polarity to 40:60 EtOAc:hexane to give **18** as a yellow oil (0.61 g, 91%). TLC (silica) EtOAc:hexane (40:60), $R_f$ 0.65. $^1$H NMR ($CDCl_3$): $\delta$ 1.08 (s, 6H, $CH_3$), 1.20−1.32 (m, 15H, br), 1.28 (s, 6H, $-CH_3$), 1.33 (s, 6H, $-CH_3$), 1.49−1.57 (m, 4H m, $-CH_2CH_2O$), 3.38 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCH_2Ar$), 3.54 (d, 4H, $J$ = 12.0 Hz, $-OCH_2$), 4.01−4.09 (m, 6H, br), 4.24 (s, 4H, $-CH_2C$), 4.42 (s, 2H, $-CH_2Ar$), 7.17−7.30 (m, 5H, ArH). $^{13}$C NMR ($CDCl_3$): $\delta$ 17.60, 18.34, 22.05, 24.80, 25.68, 26.00, 28.32, 29.02, 29.24, 29.32, 29.58, 41.82, 46,51, 65,12, 65.77, 65.11, 70.28, 72.64, 97.87, 127.26, 127.40, 128.14, 138.51, 172.42, 174.21.

**$(HO)_4$-[G#2]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (19).** Acetonide-[G#2]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (**18**) (0.61 g, 0.88 mmol), half a teaspoon of DOWEX 50W-X2, and 10 mL of MeOH were allowed to react according to the general deprotection procedure to give **19** (0.49 g, 91%) as white crystals. $^1$H NMR ($CDCl_3$): $\delta$ 1.04 (s, 6H, $-CH_3$), 1.20−1.40 (m, 15H, br), 1.55−1.67 (m, 4H, $-CH_2CH_2O$), 3.46 (t, 2H, $J$ = 13.2 Hz, $CH_2OCH_2$-Ar), 3.66−3.83 (m, 8H, $-CH_2OH$), 4.12 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCO$), 4,25 (d, 2H, $J$ = 12.0 Hz, $-CH_2C$), 4,43 (d, 2H, $J$ = 12.0 Hz, $-CH_2C$), 4.45 (s, 2H, $-CH_2Ar$), 7.25−7.35 (m, 5H, −ArH). $^{13}$C NMR ($CDCl_3$): $\delta$ 17.00, 18.11, 25.68, 26.02, 28.33, 29.02, 29.29, 29.32, 29.58, 46.12, 49,35, 64,80, 65.64, 66.37, 70.46, 72.82, 127.45, 127.60, 128.30, 138.59, 173.02, 175.08. Calcd: $[M]^+$ $m/z$ = 612.75. Found: MALDI−TOF: $[M + Ag]^+$ = 719.0.

**Acetonide-[G#3]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (20).** $(HO)_4$-[G#2]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (**19**) (0 0.49 g, 0.80 mmol), DMAP (87.0 mg, 0.71 mmol), 1.5 mL of pyridine, 3 mL of $CH_2Cl_2$, and **2** (1.58 g, 4.79 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluting from hexane, and gradually increasing the polarity to 60:40 EtOAc:hexane to give **20** as a colorless viscous oil (0.81 g, 82%). TLC (silica) EtOAc:hexane (40:60), $R_f$ 0.55. $^1$H NMR ($CDCl_3$): $\delta$ 1.07 (s, 12H, $-CH_3$), 1.20−1.31 (m, 33H, br), 1.34 (s, 12H, $-CH_3$), 1.50−1.59 (m, 4H, $-CH_2CH_2O$), 3.39 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCH_2Ar$), 3.55 (d, 8H, $J$ = 12.0 Hz, $-OCH_2$), 4.02−4.09 (m, 10 H, br), 4.18−4.24 (m, 12 H, $-CH_2C$), 4.43 (s, 2H, $-CH_2$-Ar), 7.17−7.30 (m, 5H, ArH). $^{13}$C NMR ($CDCl_3$): $\delta$ 17.56, 17.60, 18.43, 22.06, 25.00, 25.76, 26.11, 28.45, 29.12, 29.37, 29.43, 29.69, 41.95, 46.50, 46,77, 64.83, 65,60, 65.83, 65.88, 70.42, 72.76, 98.00, 127.36, 127.51, 128.23, 138.65, 170.99, 171.70, 173.37. Calcd: $[M]^+$ $m/z$ = 1237.46. Found: MALDI−TOF: $[M + Ag]^+$ = 1345.5.

**$(HO)_8$-[G#3]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (21).** Acetonide-[G#3]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (**20**) (0.52 g, 0.42 mmol), half a teaspoon of DOWEX 50W-X2, and 10 mL of MeOH were allowed to react according to the general deprotection procedure to give **21** (0.46 g, 88%) as white crystals. $^1$H NMR (MeOD): $\delta$ 1.15 (s, 12H, $-CH_3$), 1.29−1.45 (m, 21H, br), 1.57−1.70 (m, 4H, $-CH_2CH_2O$), 3.49 (t, 2H, $J$ = 13.2 Hz, $-CH_2$-$OCH_2Ar$), 3.58−3.69 (m, 16H, $-CH_2OH$), 4.15 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCO$), 4.24−4.33 (m, 12H, br), 4.49 (s, 2H, $-CH_2$-Ar), 7.26−7.34 (m, 5H, −ArH). $^{13}$C NMR (MeOD): $\delta$ 17.73, 18.55, 18.68, 37.44, 27.65, 30.05, 30.69, 30.90, 30.98, 31.13, 48.99, 50.05, 52.18, 66.28, 66.57, 67.34, 67.23, 71.86, 74.26, 129.06, 129.28, 129.78, 140.26, 174.15, 174.42, 176.29. Calcd: $[M]^+$ $m/z$ = 1077.21. Found: MALDI−TOF: $[M + Ag]^+$ = 1182.3.

**Acetonide-[G#4]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (22).** $(HO)_8$-[G#3]-$CO_2(CH_2)_{10}-O-CH_2C_6H_5$ (**21**) (2.70 g, 3.44 mmol), DMAP (0.60 g, 4.92 mmol), 10 mL of pyridine, 25 mL of $CH_2Cl_2$, and **2** (9.96 g, 35.74 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluting from hexane, and gradually increasing the polarity to 60:40 EtOAc:hexane to give **22** as a colorless viscous oil (5.71 g, 98%). TLC (silica) EtOAc:hexane (60:40), $R_f$ 0.53. $^1$H NMR ($CDCl_3$): $\delta$ 1.01 (s, 24, $-CH_3$), 1.12−1.25 (m, 23H, br), 1.21 (s, 24H, $-CH_3$), 1.27 (s, 24H, $-CH_3$), 1.42−1.54 (m, 4H, $-CH_2CH_2O$), 3.33 (t, 2H, $J$ = 13.2 Hz, $-CH_2OCH_2Ar$), 3.48 (d, 16H, $J$ = 12.0 Hz, $-OCH_2$), 4.00−4.18 (m, 44 H, br), 4.36 (s, 2H, $CH_2Ar$), 7.14−7.30 (m, 5H, ArH). $^{13}$C NMR ($CDCl_3$): $\delta$ 17.45, 17.51, 17.62, 18.45, 22.09, 25.04, 25.77, 26.15, 28.49, 29.20, 29.43, 29.50, 29.72, 41.96, 46.55, 46,63, 46.76, 65.44, 65,65, 65.84, 65.90, 66.28, 70.44, 72.78, 98.02, 127.39, 127.53, 128.26, 138.66, 171.33, 171.74, 171.83, 173.38. Calcd: $[M]^+$ $m/z$ = 2326,6. Found: MALDI−TOF: $[M + Ag]^+$ = 2430.2.

**$(HO)_{12}$-[G#2]-Dendrimer (24).** Acetonide-[G#2]-dendrimer (**23**) (2.00 g, 1.26 mmol), two teaspoons of DOWEX 50W-X2, and 50 mL of MeOH were allowed to react according to the general deprotection procedure to give **24** (1.57 g, 92%) as white crystals. $^1$H NMR (MeOD): $\delta$ 1.17 (s, 18 H, $-CH_3$), 1.44 (s, 9 H, $-CH_3$), 2.22 (s, 3 H, $-CH_3$), 3.62 (d, 12 H, $J$ = 11.2 Hz, $-CH_2OH$), 3.70 (d, 12H, $J$ = 11.2 Hz, $-CH_2OH$), 4.42 (dd, 12H, $J$ = 25.2 Hz, $-CH_2C$), 7.07 (d, 6H, $J$ = 9.6 Hz, −ArH), 7.15 (d, 6H, $J$ = 9.6 Hz, −ArH). $^{13}$C NMR (MeOD): $\delta$ 18.12, 18.96, 49.00, 52.66, 53.76, 66.62, 67.28, 122.96, 131.67, 151.48, 151.05, 174.14, 176.71. Calcd: $[M]^+$ $m/z$ = 1351.39. Found: MALDI−TOF: $[M + Ag]^+$ = 1456.8.

**Acetonide-[G#3]-Dendrimer (25).** $(HO)_{12}$-[G#2]-dendrimer (**24**) (3.14 g, 2.33 mmol, DMAP (0.66 g, 5.44 mmol), 11 mL of pyridine, 20 mL of $CH_2Cl_2$, and **2** (11.9 g, 5.44 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluted from hexane, and gradually increasing the polarity to 60:40 EtOAc:hexane to give **25** as colorless viscous oil (6.11 g, 81%). TLC (silica) EtOAc:hexane (70:30), $R_f$ 0.55. $^1$H NMR ($CDCl_3$): $\delta$ 1.08 (s, 36H, $-CH_3$), 1.26 (s, 18H, $-CH_3$), 1.29 (s, 36H, $-CH_3$), 1.36 (s, 36H, $-CH_3$), 1.37 (s, 9H, $-CH_3$), 2.12 (s,

3H, $-CH_3$), 3.56 (d, 24H, $J = 11.6$ Hz, $-OCH_2$), 4.09 (d, 24H, $J = 11.6$ Hz, $-OCH_2$), 4.25−4.41 (m, 36H, $-CH_2C$), 6.93 (d, 6H, $J = 7.2$ Hz, $-CH_2C$), 7.06 (d, 6H, $J = 7.2$ Hz, $-CH_2C$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 17.54, 17.58, 18.30, 21.80, 25.15, 41.87, 46.75, 46.84, 51.53, 65,59, 65.75, 65.80, 77.20, 97.92, 120.57, 129.65, 146.36, 146.21, 170.61, 171.72, 173.33. Calcd: $[M]^+$ $m/z$ = 3225.54. Found: MALDI−TOF: $[M + Ag]^+ = 3329.5$.

**$(HO)_{24}$-[G#3]-Dendrimer (26).** Acetonide-[G#3]-dendrimer **(25)** (2.00 g, 0.62 mmol), two teaspoons of DOWEX 50W-X2, and 50 mL of MeOH were allowed to react according to the general deprotection procedure to give **26** (1.60 g, 94%) as white crystals. $^1H$ NMR (MeOD): $\delta$ 0.96 (s, 36H, $-CH_3$), 1.10 (s, 18H, $-CH_3$), 1.25 (s, 9H, $-CH_3$), 2.01 (s, 3H, $-CH_3$), 3.37 (d, 24H, $J = 10.8$ Hz, $-CH_2OH$), 4.45 (d, 24H, $J = 11.6$ Hz, $-CH_2OH$), 4.06 (d, 12H, $J = 11.2$ Hz, $-CH_2C$), 4.13 (d, 12H, $J = 11.2$ Hz, $-CH_2C$), 4.23 (dd, 12H, $-CH_2C$), 6.88 (d, 6H, $J = 8.4$ Hz, $-CH_2C$, $-ArH$), 6.98 (d, 6H, $J = 8.4$ Hz, $-ArH$). $^{13}C$ NMR (DMSO): $\delta$ 16.75, 17.03, 17.22, 46.42, 46.60, 50.33, 63.73, 64.60, 65.89, 121.05, 129.49, 146.24, 148.35, 170.98, 171.95, 174.13.

**Acetonide-[G#4]-Dendrimer (27).** $(HO)_{24}$-[G#3]-dendrimer (**26**) (1.52 g, 0.55 mmol), DMAP (0.31 g, 2.57 mmol), 5 mL of pyridine, 10 mL of $CH_2Cl_2$, and **2** (5.66 g, 17.2 mmol) were reacted according to the general esterification procedure to give a residue that was purified by liquid chromatography on silica gel, eluted from hexane, and gradually increasing the polarity to 80:20 EtOAc:hexane to give **27** as colorless viscous oil (3.13 g, 88%). The spectral data were in accordance with published data.[16] Calcd: $[M]^+$ $m/z$ = 6437.05. Found: MALDI−TOF: $[M + Ag]^+ = 6593.6$.

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## References and Notes

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