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Synthesis of dendrimers with terminal formyl groups

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A method for preparation of dendrons and dendrimers with formyl groups at the terminal aromatic rings, ether bonds in the branching blocks, and ester bonds in the core of the macromolecules is proposed. A way for the selective synthesis of *p*-hydroxymethylbenzaldehyde is described.

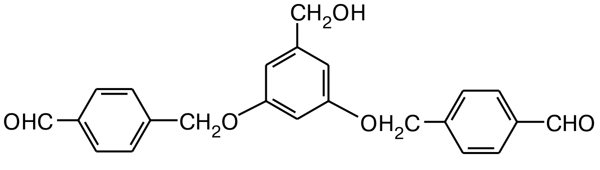
Key words: dendrimer, dendrimer branch, dendrimer core, formyl groups.

Chemistry of dendrimers is an actively developing area of monodisperse polymeric compounds (both organic and organoelement) with a cascade architecture. This area opens new perspectives for developing substances, reagents, and molecular devices to be used in different fields of technology, materials science, organic synthesis, and asymmetric catalysis.[1—8]

An important stage in the synthesis of dendrimers with required properties and structures includes, in particular, the controlled modification of the peripheral layer of a molecule by the transformation of terminal functional groups. These functions are, first of all, various amino and hydroxyl groups of phenols and alcohols.[9—13] Denrimers containing at the periphery ether and ester groups and fragments of carboxylic acids, amides, acid chlorides, and nitriles are also described.[14—17] Unfortunately, many of these groups are poorly reactive, which impedes their use for the modification of dendrimers. In this work, we proposed an approach to the synthesis of dendrimers with formyl groups at the periphery. High and diverse reactivity of aldehydes makes it possible to modify the nature of the terminal layer of dendrimers in a wide range.

The approach to the synthesis of dendrimers containing formyl groups at the periphery is based on the synthesis of dendron **1** from 4-hydroxymethylbenzaldehyde (**2**) and 3,5-dihydroxybenzyl alcohol (**3**). The latter is the main building block in the convergent scheme of synthesis of dendrimers of the Frechet type using the Williamson reaction.[9,10]

Although the synthesis and use of bifunctional compound **2** has been described,[18,19] its yield, including that in the reduction of teraphthalic aldehyde (**4**) with hydrides, does not exceed 65%.[18] Searching for a more efficient method of the synthesis of **2**, we studied a possibility of the selective synthesis of monoacetal **5**, whose subsequent reduction and substitution of the OH group in **7** by bromine, would allow one to obtain benzylating agent **8** (Scheme 1).



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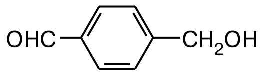

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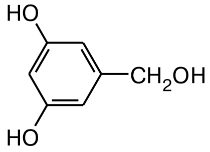

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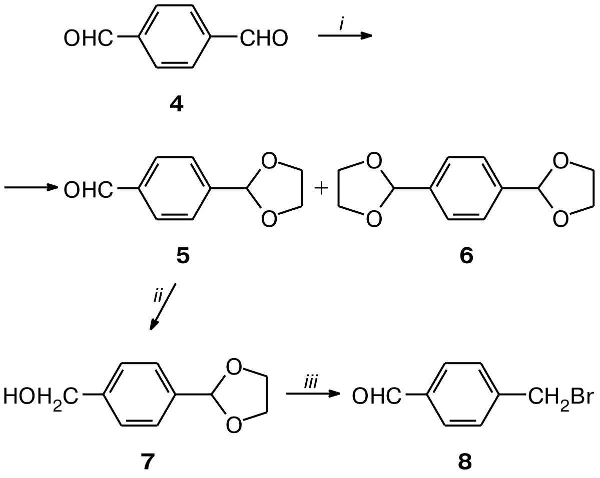
Scheme 1



Reagents and conditions: *i.* $HOCH_2CH_2OH$, benzene, TsOH; *ii.* $NaBH_4$, EtOH; *iii.* CBr_4, PPh_3, CH_2Cl_2.

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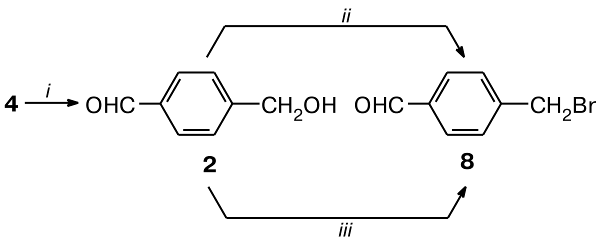
However, it turned out that the rate of formation of diprotected derivative **6** substantially exceeds the rate of the first step of the reaction with ethylene glycol, so that monoacetal **5** is formed with an admixture of 10% compound **6** even when the 1 : 5 ratio of ethylene glycol to **4** is used.

Nevertheless, we succeeded to find a way for increasing the yield of **2** to 90—95% by the reduction of dialdehyde **4** using 0.25 equiv. $NaBH_4$ in an EtOH—THF mixture at −5 °C (Scheme 2). For the bromination of aldehydoalcohol **2** with a CBr_4—PPh_3 system, as well as the bromination of its acetal **7**, the yield of the target *p*-bromomethylbenzaldehyde (**8**) is low, and a large amount of by-products is mainly formed. A more successful method of hydroxyl group substitution by bromine is the use of a mixture of PPh_3 with *N*-bromosuccinimide (NBS).

Scheme 2



i. 0.25 equiv. $NaBH_4$, 90—95% yield; *ii*. CBr_4/PPh_3, 45% yield; *iii*. NBS/PPh_3, 65% yield.

The reaction of benzylating agent **8** with compound **3** or methyl 3,5-dihydroxybenzoate (**9**) in acetone or DMF in the presence of 18-crown-6 and K_2CO_3 afforded the corresponding dendron of zero generation with terminal formyl groups, *viz*., 3,5-bis(4-formylbenzyloxy)benzyl alcohol (**1**) or methyl 3,5-bis(4-formylbenzyloxy)benzoate (**10**) (Scheme 3).

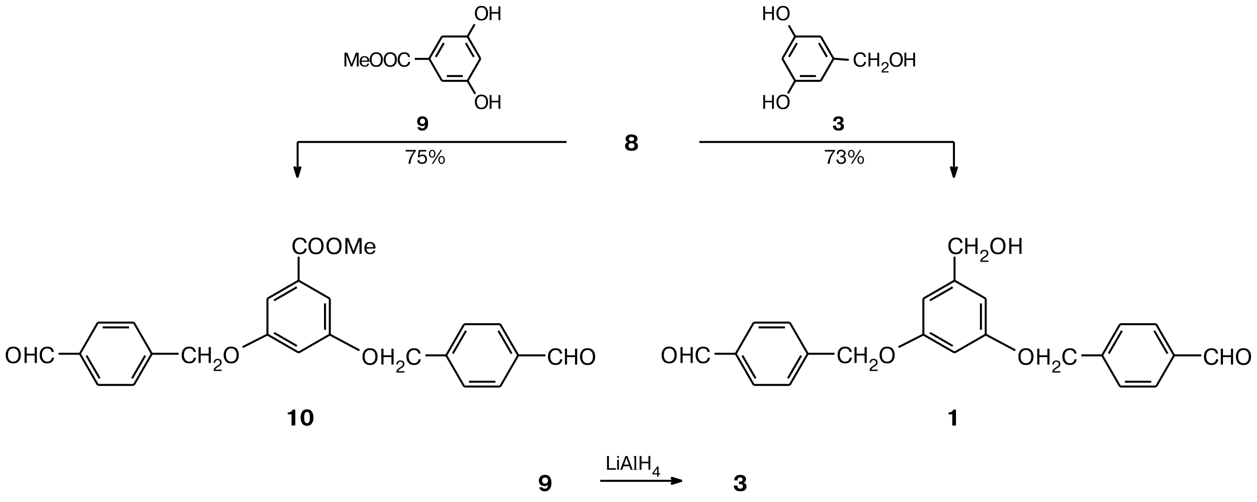
Aforementioned difficulties in the synthesis and isolation of compound **8** compelled us to search for a more convenient reagent for constructing dendrimers of the Frechet type with an ether bond between structural units. We chose (4-formylbenzyl) methanesulfonate (**11**), because it possesses a better leaving group than the Br^- anion. We found that the reaction of methanesulfonate **11**, which is formed in high yield from alcohol **2**, is an efficient method for obtaining dendron **1**. The overall yield of **11**, which is a key compound in the synthesis of formyl-containing dendrimers *via* the scheme proposed by us, is 68% calculated to terephthalic aldehyde (Scheme 4).

In this work, we used benzene-1,3,5-tricarboxylic acid trischloride (**12**) as a core for the formation of dendrimers.[21] Its interaction with dendron **1** on refluxing in benzene in the presence of excess DMAP affords a dendrimer of first generation (**13**) with six terminal formyl groups in 55% yield (Scheme 5).

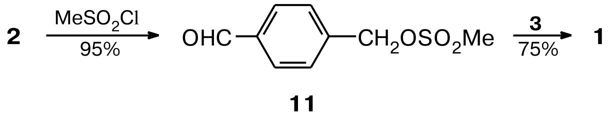
A dendrimer of zero generation (**14**) with three terminal formyl groups was synthesized similarly from acid trischloride **12** and compound **2** (Scheme 6).

The data obtained indicate high purity and individual character of dendrimers **13** and **14**. They are solid white and light yellow substances, respectively, well soluble in $CHCl_3$ and DMF but poorly soluble or virtually insoluble in alcohols, benzene, and acetone. This fact was used to isolate the reaction products from the starting compounds that are easily soluble in acetone. Analytical TLC of isolated samples **13** and **14** (R_f in an AcOEt—$CHCl_3$ (1 : 1) system was 0.45 and 0.52, respectively) confirms the complete removal of compounds **1**, **2**, **12**, and DMAP (R_f 0.75, 0.82, 0.85, and 0.05, respectively) and the absence of

Scheme 3



Scheme 4

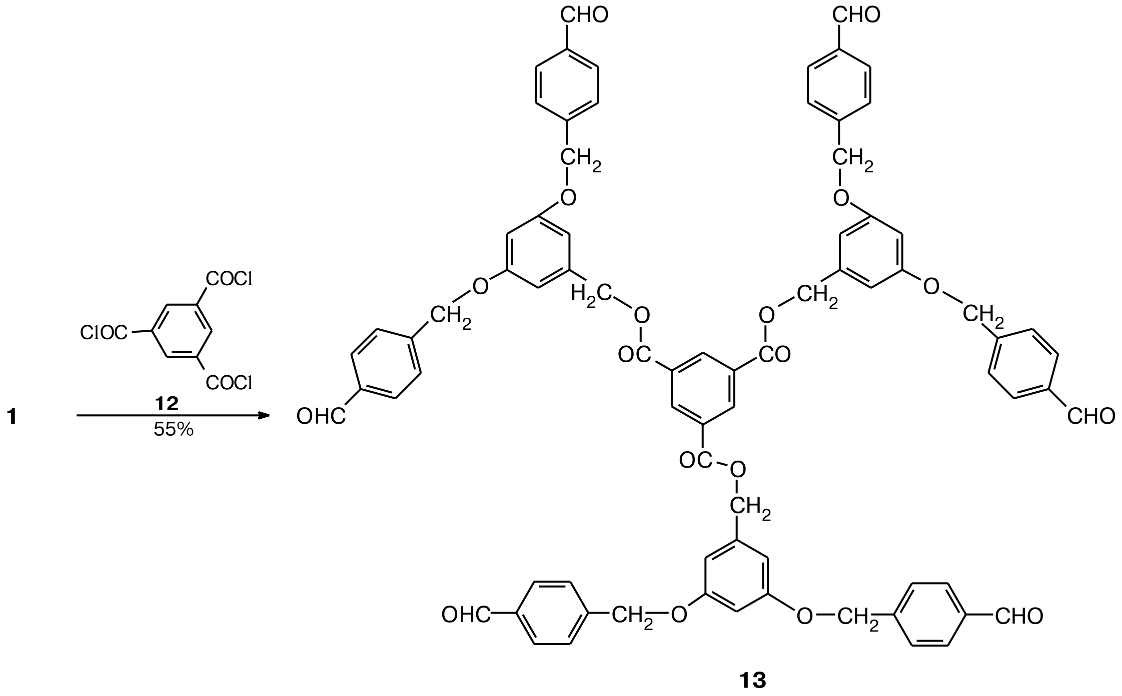


significant amounts of any other admixtures. The structures of dendrimers **13** and **14** agree with the data of elemental analysis and ^{1}H NMR spectra. The spectra contain a singlet signal at δ 8—9 ppm, indicating the presence of three same substituents at the central aromatic ring in both compounds. In the case of addition of only one or two fragments of dendrons **1** and **2** to **12**, two multiplets with a ratio of 1 : 2 should be expected in this region of the ^{1}H NMR spectra; however, they are not observed. Thus, the degree of purity and individual character of dendrimers **13** and **14** is at least 95—97%.

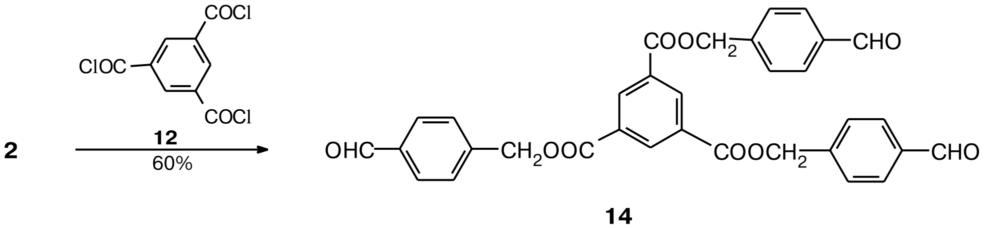
Unlike direct methods of benzene ring formylation, our procedure provides the complete and selective introduction of the formyl group at the periphery of a dendrimer resulting in macromolecules with a highly defined structure.

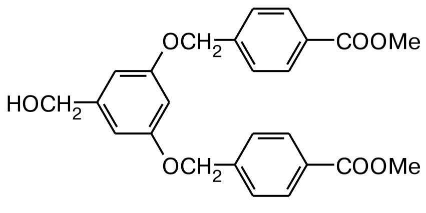
The above-considered approach to the synthesis of dendrimers with formyl groups at the periphery can naturally be used to construct cascade molecules with other terminal functional groups and use other types of reactions for introducing fragments containing a functional substituent. For example, the reaction of methyl (*p*-bromomethylbenzoate) (**15**) with **3** produced dendron (**16**) having ester groups at the periphery, whereas the reaction of perfluorobenzaldehyde (**17**) with ester **9**, under the conditions of nucleophilic aromatic substitution rarely used in dendrimer synthesis, afforded methyl 3,5-bis(4-formyl-2,3,5,6-tetrafluorophenyloxy)benzoate (**18**), *i.e.*, fluorinated analog of dendron **10**, in 96% yield.

Scheme 5



Scheme 6





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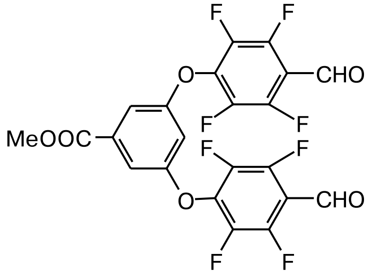

18

Experimental

^{1}H (solvent as the internal standard, δ from Me_4Si) and ^{19}F (CF_3COOH as the external standard) NMR spectra were recorded on Bruker WP-200 SY instruments with working frequencies of 200.13 and 188.3 MHz, respectively. The reaction courses and purity of products were monitored by analytical TLC on Silufol UV-245 plates (Czech Republic). Silica gel 60 (Merck) was used for column chromatography.

Commercial reagents **9**, **12**, and **17** (Aldrich) were used in syntheses.

4-(1,3-Dioxolan-2-yl)benzaldehyde (5) and 1,4-bis(1,3-dioxolan-2-yl)benzene (6). A catalytic amount of TsOH was added to a solution of terephthalic aldehyde **4** (2.0 g, 14.9 mmol) and ethylene glycol (0.5 g, 7.45 mmol, 0.4 mL) in benzene (150 mL). The mixture was refluxed with a Dean—Stark trap for 2 h. After cooling, the reaction mixture was washed with a 15% solution of $NaHCO_3$ and a saturated solution of NaCl and dried with $MgSO_4$ + Na_2SO_4. The solvent was distilled off *in vacuo*, and the residue was purified by column chromatography using a petroleum ether—AcOEt (4 : 1) mixture as an eluent. Fractions of **4** (0.94 g), monoacetal **5** (1.05 g, oil), and diacetal **6** (0.15 g, oil) were consequently collected. ^{1}H NMR of compound **5** (acetone-d_6), δ: 3.95—4.20 (m, 4 H, $(CH_2)_2$); 5.84 (s, 1 H, CHO_2); 7.66—7.70 (m, 2 H, BB´, C_6H_4); 7.92—7.96 (m, 2 H, AA´, C_6H_4); 10.07 (s, 1 H, CHO); compound **6**: 3.95—4.20 (m, 8 H, 2 $(CH_2)_2$); 5.75 (s, 2 H, 2 CHO_2); 7.46 (s, 4 H, C_6H_4). Compound 5. Found (%): C, 67.28; H, 5.71. $C_{10}H_{10}O_3$. Calculated (%): C, 67.41; H, 5.66. Compound 6. Found (%) C, 64.92; H, 6.30. $C_{12}H_{14}O_4$. Calculated (%): C, 64.85; H, 6.35.

4-(1,3-Dioxolan-2-yl)benzyl alcohol (7). $NaBH_4$ (0.19 g, 1.5 mmol) was added with continuous stirring at room temperature (~20 °C) for 30 min to a solution of monoacetal **5** (0.71 g, 4 mmol) in 95% EtOH (50 mL). After evaporation of EtOH, the residue was dissolved in water, products were extracted with AcOEt, volatile components were again evaporated, and the residue was purified by column chromatography on silica gel using an AcOEt—hexane (1 : 4) mixture as an eluent. The yield of **7** (oil) was 0.43 g (60%). ^{1}H NMR (acetone-d_6), δ: 3.13 (br.s, 1 H, OH); 4.15 (m, AA´BB´, 4 H, $(CH_2)_2$); 4.62 (s, 2 H, CH_2); 5.82 (s, 1 H, CHO_2); 7.30—7.50 (m, 4 H, C_6H_4). Found (%): C, 66.72; H, 6.57. $C_{10}H_{12}O_3$. Calculated (%): C, 66.65; H, 6.71.

4-Bromomethylbenzaldehyde (8). ***A.*** Solutions of Ph_3P (1.63 g, 6.2 mmol) and CBr_4 (2.03 g, 6.2 mmol) in anhydrous THF (25 and 20 mL, respectively) were consequently added at 0 °C in an argon flow in the dark to a solution of alcohol **7** (0.9 g, 5 mmol) in anhydrous THF (20 mL). The reaction mixture was stirred for 1 h at 0 °C and then for 8 h at room temperature (~20 °C). After the solvent was removed, the residue was purified by column chromatography on silica gel using an AcOEt—hexane (1 : 3) mixture as an eluent. The yield of **8** was 0.3 g (25%), m.p. 102 °C (from hexane). ^{1}H NMR (acetone-d_6), δ: 4.74 (s, 2 H, CH_2); 7.70—7.93 (q, 4 H, Ph); 10.05 (s, 1 H, CHO). Found (%): C, 48.24; H, 3.58. C_8H_7BrO. Calculated (%): C, 48.19; H, 3.45.

B. Solutions of Ph_3P (10.2 g, 39 mmol) and CBr_4 (12.8 g, 39 mmol) in anhydrous THF (25 and 40 mL, respectively) were consequently added at 0 °C in an argon flow in the dark to a solution of hydroxymethylbenzaldehyde **2** (3.5 g, 26 mmol) in anhydrous THF (20 mL). The reaction mixture was stirred for 1 h at 0 °C and then for 24 h at room temperature (~20 °C). After the solvent was removed, products were isolated by column chromatography using an AcOEt—hexane (1 : 3) mixture as an eluent. The yield of **8** was 2.3 g (45%), m.p. 102—103 °C (from hexane).

C. A mixture of alcohol **2** (2 g, 15 mmol) and PPh_3 (4.7 g, 18 mmol) in anhydrous CH_2Cl_2 (50 mL) was cooled to 0 °C, and NBS (3.4 g, 19 mmol) in anhydrous CH_2Cl_2 (50 mL) was added dropwise with stirring to the cooled solution. After 20 min, water (100 mL) was added to the reaction mixture, and products were extracted with CH_2Cl_2. After the solvent was removed, the residue was treated with hot hexane (4×100 mL), the combined solution was concentrated by evaporation to 100 mL, and crystals of **8** were separated. The yield was 1.9 g (65%), m.p. 102—102.5 °C.

4-Hydroxymethylbenzaldehyde (2). $NaBH_4$ (1.7 g, 37 mmol) was added at −5 °C with continuous stirring for 30 min to a solution of dialdehyde **4** (20 g, 0.15 mol) in a mixture of 95% EtOH (250 mL) and THF (350 mL). Then the mixture was stirred for 6 h, while the temperature was maintained in an interval of 0—2 °C. Then the reaction mixture was neutralized with 2 *M* HCl to pH 5, the solvents were evaporated, water (200 mL) was added to the residue, and products were extracted with AcOEt. Combined organic extracts were dried with $MgSO_4$, and the solvent was evaporated. The yield of nonpurified product **2** was 19.1 g (94%). The product was purified by column chromatography using an AcOEt—hexane (1 : 1) mixture of solvents. The yield was 17.9 g (88%), m.p. 40 °C. TLC (eluent AcOEt—$CHCl_3$ (1 : 1)): R_f 0.82. ^{1}H NMR (acetone-d_6), δ: 4.50 (t, 1 H, OH, J = 5.7 Hz); 4.76 (d, 2 H, CH_2, J = 5.7 Hz); 7.60—7.90 (q, 4 H, Ph); 10.03 (s, 1 H, CHO). Found (%): C, 70.69; H, 5.94. $C_8H_8O_2$. Calculated (%): C, 70.58; H, 5.92.

3,5-Dihydroxybenzyl alcohol (3). Compound **9** (10.3 g, 61 mmol) in anhydrous THF (100 mL) was added dropwise with stirring to a suspension of $LiAlH_4$ (7 g, 184 mmol) in anhydrous THF (300 mL). After 12 h, ether (400 mL) was added to the reaction mixture, and then a saturated solution of Na_2SO_4 (75 mL) was added dropwise. The mixture was neutralized with 15% HCl to pH 5.5, the solution was decanted, the residue was dissolved in 15% HCl, and products were extracted with AcOEt.

Combined organic solutions were concentrated to dryness, and the residue was crystallized from an AcOEt—acetone (10 : 1) mixture. The yield of **3** was 6 g (70%), m.p. 182 °C. ^{1}H NMR (acetone-d$_6$), δ: 4.01 (t, 1 H, OH, *J* = 5.8 Hz); 4.38 (d, 2 H, CH$_2$, *J* = 5.8 Hz); 6.13 (m, 1 H, C_6H_3); 6.26 (m, 2 H, C_6H_3); 8.04 (s, 2 H, 2 OH).

Methyl 3,5-bis(4-formylbenzyloxy)benzoate (10). K_2CO_3 (5.0 g, 36 mmol) and 18-crown-6 (0.4 g, 1.6 mmol) were added to a solution of ether **9** (1.4 g, 8 mmol) in anhydrous DMF (25 mL). Then bromide **8** (4.2 g, 21 mmol) was added dropwise with stirring, and the reaction mixture was kept for 4 h at 50—60 °C. The solvent was removed, water (100 mL) was added to the residue, and products were extracted with AcOEt. Organic extracts were dried with $MgSO_4$, the solvent was evaporated, and the residue was purified with column chromatography using an AcOEt—hexane (2 : 1) mixture as an eluent. The yield was 2.5 g (75%). ^{1}H NMR (acetone-d$_6$), δ: 4.02 (s, 3 H, CH$_3$); 4.46 (s, 4 H, CH$_2$); 6.53 (s, 1 H, C_6H_3); 6.58 (s, 2 H, C_6H_3); 7.80—7.60 (m, 8 H, C_6H_4); 10.01 (s, 2 H, CHO). Found (%): C, 71.05; H, 4.43. $C_{24}H_{20}O_6$. Calculated (%): C, 71.26; H, 4.49.

Methyl 3,5-bis(4-formyl-2,3,5,6-tetrafluorophenyloxy)benzoate (18). K_2CO_3 (5.52 g, 40 mmol) was added with stirring in an argon flow to a solution of ester **9** (3.1 g, 18 mmol), aldehyde **17** (7.9 g, 40 mmol), and 18-crown-6 (1.21 g, 4.5 mmol) in anhydrous acetone (50 mL), maintaining the temperature of the reaction mixture at 15—18 °C. After 2 h, the precipitate was filtered off, the solvent was removed, water (200 mL) was added to the residue, and products were extracted with AcOEt. Organic extracts were dried with $MgSO_4$, the solvent was evaporated, and the residue was purified by column chromatography using an AcOEt—hexane (2 : 1) mixture as an eluent. The yield was 8.98 g (96%), m.p. 137 °C. ^{1}H NMR (acetone-d$_6$), δ: 3.85 (s, 3 H, CH$_3$); 7.46 (t, 1 H, C_6H_3, *J* = 2 Hz); 7.54 (d, 2 H, C_6H_3, *J* = 2 Hz); 10.31 (s, 2 H, CHO). ^{19}F NMR, δ: 65.61 (dd, 4 F, *J* = 8 and 19.5 Hz); 74.51 (dd, 4 F, *J* = 9.3 and 19.7 Hz). Found (%): C, 51.05; H, 1.43; F, 28.92. $C_{22}H_8F_8O_6$. Calculated (%): C, 50.79; H, 1.55; F, 29.21.

(4-Formylbenzyl) methanesulfonate (11). Anhydrous CH_2Cl_2 (200 mL) was added to a solution of alcohol **2** (17.8 g, 0.13 mol) in Et_3N ((36.6 mL, 0.26 mol). The reaction mixture was cooled to –5 °C, and $MeSO_2Cl$ (15.3 mL, 0.20 mol) in anhydrous CH_2Cl_2 (50 mL) was added dropwise. The reaction was carried out for 15 min, after which the reaction mixture was treated with water (2×200 mL), a saturated solution of $NaHCO_3$ (200 mL), and a saturated solution of NaCl. The organic layer was dried with $MgSO_4$. After the solvent was removed, compound **11** was isolated in 95% yield (26.6 g), m.p. 58—59 °C. ^{1}H NMR (acetone-d$_6$), δ: 3.34 (s, 3 H, CH$_3$); 5.56 (s, 2 H, CH$_2$); 7.85—8.13 (m, 4 H, C_6H_4); 10.23 (s, 1 H, CHO). Found (%): C, 50.48; H, 4.87. $C_9H_{10}O_4S$. Calculated (%): C, 50.45; H, 4.71.

3,5-Bis(4-formylbenzyloxy)benzyl alcohol (1). ***A.*** K_2CO_3 (1.7 g, 125 mmol) and 18-crown-6 (0.13 g, 0.5 mmol) were added with stirring in argon to a solution of triol **3** (0.35 g, 2.5 mmol) in anhydrous acetone (100 mL). Then a solution of bromide **8** (1.0 g, 5.0 mmol) in anhydrous acetone (50 mL) was added dropwise. The reaction mixture was stirred for 48 h, the solvent was removed, water (100 mL) was added to the residue, and products were extracted with AcOEt. Organic extracts were dried with $MgSO_4$, the solvent was evaporated, and the residue was purified by column chromatography using an AcOEt—hexane (2 : 1) mixture as an eluent. The yield of **1** was 0.87 g (73.5%), m.p. 72 °C. TLC (eluent AcOEt—CHCl$_3$ (1 : 1)): R_f 0.75. ^{1}H NMR (acetone-d$_6$), δ: 4.57 (s, 4 H, CH$_2$); 5.23 (s, 2 H, CH$_2$OH); 6.60 (s, 1 H, C_6H_3); 6.69 (s, 2 H, C_6H_3); 7.68—7.94 (m, 8 H, C_6H_4); 10.04 (s, 2 H, CHO). Found (%): C, 73.46; H, 5.30. $C_{23}H_{20}O_5$. Calculated (%): C, 73.38; H, 5.37.

B. Dendron **1** was obtained by a similar procedure from **3** (0.65 g, 4.7 mmol) and mesylate **11** (2 g, 9.4 mmol). The yield was 1.4 g (75%), m.p. 71—72 °C.

1,3,5-Tris[3,5-bis(4-formylbenzyloxy)benzyloxycarbonyl]benzene (13). A solution of alcohol **1** (3.3 g, 8.8 mmol) and DMAP (2.9 g, 23 mmol) in benzene (250 mL) was refluxed with a Dean—Stark trap for 2 h and then cooled to ~20 °C. Acid chloride **12** (0.7 g, 2.7 mmol) was added to the reaction mixture, and refluxing was continued for 4 h. The precipitate was filtered off, 5% HCl was added (pH 3), and products were extracted with chloroform. A benzene solution was concentrated, 5% HCl was added, and products were extracted with chloroform. Combined organic extracts were dried with $MgSO_4$, the solvent was evaporated, and the crystalline residue was washed with acetone and kept *in vacuo* at 60—70 °C. The yield of **13** was 1.9 g (55%), m.p. >300 °C; TLC (eluent AcOEt—CHCl$_3$ (1 : 1)): R_f 0.45. ^{1}H NMR (CDCl$_3$), δ: 5.11 (s, 12 H, CH$_2$OAr); 5.33 (s, 6 H, CH$_2$OCO); 6.55 (s, 3H, C_6H_3); 6.68 (s, 6 H, C_6H_3); 7.54—7.84 (m, 24 H, C_6H_4); 8.87 (s, 3 H, C_6H_3 ring); 9.97 (s, 6 H, CHO). Found (%): C, 72.77; H, 4.78. $C_{78}H_{60}O_{18}$. Calculated (%): C, 72.89; H, 4.71.

1,3,5-Tris(4-formylbenzyloxycarbonyl)benzene (14). Zero-generation dendrimer **14** was obtained according to a procedure described above from acid chloride **12** (1.0 g, 5.7 mmol), **2** (2.5 g, 18 mmol), and DMAP (5.9 g, 49 mmol) in benzene (250 mL). Dendrimer **14** was isolated in 59% yield (1.9 g), m.p. >300 °C. TLC (eluent AcOEt—CHCl$_3$ (1 : 1)): R_f 0.52. ^{1}H NMR (CDCl$_3$), δ: 5.45 (s, 6 H, CH$_2$); 7.60—7.86 (m, 12 H, C_6H_4); 8.88 (s, 3 H, C_6H_3 ring); 10.10 (s, 3 H, CHO). Found (%): C, 70.34; H, 4.18. $C_{33}H_{24}O_9$. Calculated (%): C, 70.20; H, 4.29.

3,5-Bis(4-methoxycarbonylbenzyloxy)benzyl alcohol (16). Dendron **16** was obtained similarly to dendron **1** from **3** (0.71 g, 5.0 mmol) and bromide **15** (2.29 g, 10 mmol). The yield was 1.56 g (72%), m.p. 49—50 °C. ^{1}H NMR (acetone-d$_6$), δ: 3.87 (s, 6 H, 2 Me); 4.22 (t, 1 H, HO, *J* = 5.2 Hz); 4.57 (d, 2 H, HOCH$_2$, *J* = 5.2 Hz); 5.19 (s, 4 H, 2 OCH$_2$); 6.56 (t, 1 H, C_6H_3, *J* = 2 Hz); 6.69 (d, 2 H, C_6H_3, *J* = 2 Hz); 7.57—7.61 (m, 4 H, BB´, C_6H_4); 8.02—8.04 (m, 4 H, AA´, C_6H_4). Found (%): C, 68.52; H, 5.47. $C_{25}H_{24}O_7$. Calculated (%): C, 68.80; H, 5.54.

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