Synthesis and Structure–Optical Rotation Relationships of Homochiral, Monodisperse, Tartaric Acid-based Dendrimers

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Optically active, homochiral dendrimers of both the zeroth generation **1** and first generation **2** have been synthesized from (2*R*,3*R*)-tartaric acid and phloroglucinol by an iterative, convergent method. These chiral dendrimers comprise 4-*tert*-butylphenoxy as the surface groups and phloroglucinol as the branching junctures. The chiral element, which is a derivative of L-tartaric acid, serves as the connecting unit between the surface group and the branching juncture, or between two branching junctures. Homochiral (2*S*,3*S*)-(−)-2,3-*O*-isopropylidene-1,4-di-*O*-tosyl-L-threitol **3** was first connected to the surface moiety *via* mono-O-arylation with 4-*tert*-butylphenol to generate the optically active mono-*O*-tosyl ester **4**. Excessive O-alkylation of the branching juncture, 5-benzyloxyresorcinol **5**, with 2 molar equivalents of the mono-*O*-tosyl derivative **4**, followed by activation of the benzyl-protected phenol moiety at the focal point, led to dendritic 'wedge' **7**. Treatment of the phenol **7** with a further molar equivalent of intermediate **4** gave the zeroth generation dendrimer **1** in 36% overall yield from the di-*O*-tosyl ester **3**. By application of the same reaction sequence, the phenol **7** could similarly be transformed into the first generation dendrimer **2** in 13% overall yield from homochiral diester **3**. Investigation on the optical rotation properties of these dendritic compounds showed that their specific rotations remained essentially constant and that the molar rotations were roughly proportional to the number of chiral tartrate units in the molecule.

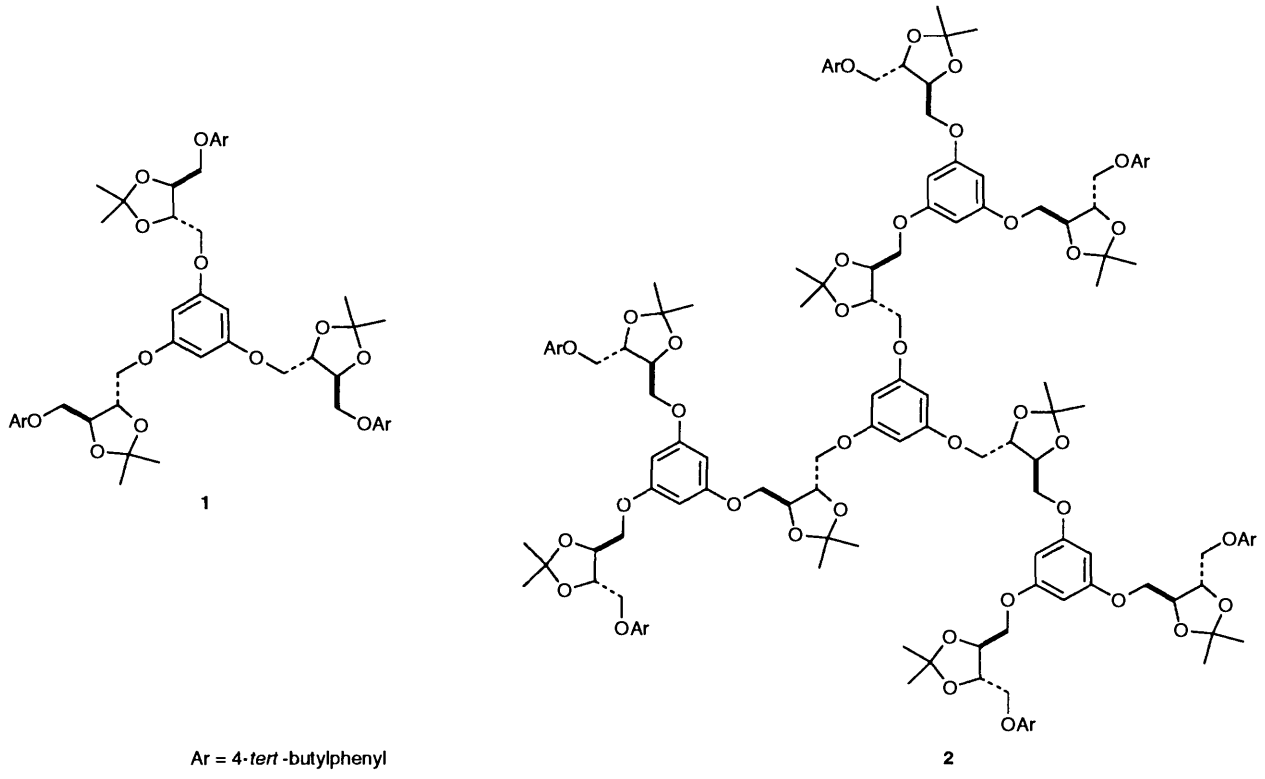
The synthesis of nanometer-size macromolecules with novel architecture and properties has spurred increasing research interest in the preparation of a new class of polymeric materials called hyperbranched polymers and dendrimers. These are highly branched macromolecules with a dendritic, treelike structure. The interest in such macromolecules arises from the possibility that, owing to their novel, unentangled structure, they may be expected to show new and interesting behaviour both in solution and in bulk.[1,2] The synthesis of both of these requires monomers with an AB_n functionalization. While hyperbranched polymers[1] are normally prepared in one step, they are polydisperse and structurally imperfect and unsymmetrical. Dendrimers,[2] on the other hand, are constructed by stepwise processes and are structurally and topologically defined, monodisperse unimolecular species. Both of these polymers have found potential applications as novel materials for engineering plastics,[3] redox devices,[4] molecular magnets,[5] liquid crystals[6] and mimics of biological systems.[7]

Although there have been significant advances[8] in the synthesis of dendrimers with novel core structures, branching skeletons, connectivity units, surface structures and topological morphology, little investigation has been conducted into the synthesis and optical rotation properties of chiral dendrimers.[9] In the past, there were several reports[10] describing the use of biomolecules such as nucleotides or amino acids as building blocks for the construction of chiral nucleic acid or peptide dendrimers. However, apart from the report by Newkome,[10e] none of these papers gave detailed spectroscopic and optical rotation properties of these biodendritic macromolecules. Recently, Seebach disclosed[11] the first synthesis of starburst dendrimers with chiral core and chiral branch units. We are also interested in the optical rotation properties and the use of chiral dendrimers in material applications. In a preliminary communication,[12] we reported the successful synthesis and characterization of a series of optically active, homochiral, monodisperse dendrimers, in which the chiral units are derived from optically active L-tartaric acid. In addition, the number of chiron units inside these chiral dendrimers increases geometrically with increasing dendrimer generation. As a result, this class of dendrimer provides us with the opportunity to study the quantitative relationship between the optical rotation properties and the number of chiral units residing within the molecule. In this article, we report the details of the synthesis, characterization and structure–optical rotation relationship of optically active C_3-symmetrical dendritic molecules **1** and **2**, as well as those of their synthetic intermediates.

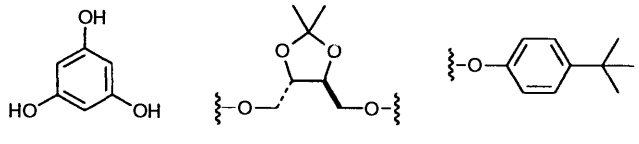
Results and Discussion

Synthesis.—Dendrimer synthesis usually utilizes a stepwise, iterative reaction procedure and therefore the synthetic sequence should be short in terms of its number of steps, easy to perform and high yielding. For our optically active dendrimer, a *tert*-butylphenoxy group is chosen as the surface functionality because it gives us an easy handle with which to measure the number of surface groups in the molecule. The branching juncture should be simple in structure and chemically it can be linked to more than two chiral connecting units under mild reaction conditions. In this case, phloroglucinol is an appropriate choice. The chiral unit chosen is a derivative of tartaric acid, because it is readily available in large quantities and in both enantiomeric pure forms.

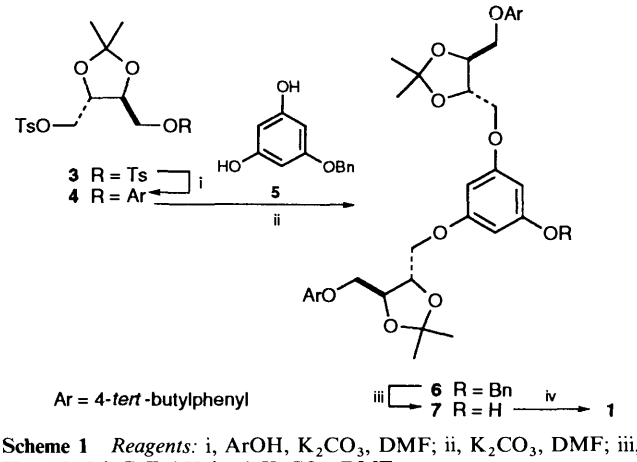
The convergent method[13] was adopted in the synthesis of our target molecules (Scheme 1). In this approach, the synthesis initiates from the dendrimer surface and develops towards the central core. Hence, the surface-group 4-*tert*-butylphenoxy moiety was first attached to the chiral tartrate unit. Treatment of (2*S*,3*S*)-(−)-2,3-*O*-isopropylidene-1,4-di-*O*-tosyl-L-threitol[14] **3** with 0.5 mol equiv. of 4-*tert*-butylphenol in the presence of potassium carbonate in dimethylformamide (DMF) gave the mono-O-arylation product **4** (m.p. 65–67 °C) in 74% yield together with a small amount (9%) of the bis-O-arylation compound. The methyl groups of the isopropylidene moiety in compound **4** are significantly different and appear as two singlets (δ 1.38 and 1.40) in the ^{1}H NMR spectrum. Bis-O-alkylation of 5-benzyloxyresorcinol **5**[15] with 2.1 mol equiv. of compound **4** under similar conditions (K_2CO_3 in DMF, 100 °C) afforded the C_2-symmetric product **6** in 65% yield.



The zeroth generation (**1**) and first generation (**2**) dendrimers



Architecture of the optically active dendrimers



Scheme 1 *Reagents:* i, ArOH, K_2CO_3, DMF; ii, K_2CO_3, DMF; iii, H_2, 10% Pd–C, EtOH; iv, **4**, K_2CO_3, DMF

The phloroglucinolic protons appear as a doublet (δ 6.23) and a triplet (δ 6.18) with a relative integration of 2 to 1. The isopropylidene methyl groups all appear at a single resonance position (δ 1.49). No C-alkylation product could be isolated from the reaction mixture. Hydrogenolysis of the benzyl ether **6** in the presence of 10% palladium on charcoal gave the C_2-symmetric phenol **7** in 94% yield. The presence of the phenolic hydrogen is supported by the presence of a broad singlet (δ 5.02) and the disappearance of the benzylic proton signal. The phloroglucinolic protons again are non-equivalent and appear as a doublet (δ 6.05) and a triplet (δ 6.13). Coupling of the phenol **7** with another mole equivalent of the mono-*O*-tosyl compound **4** (K_2CO_3 in DMF, 120 °C) gave the G0 dendrimer **1** as an oil in 80% yield. In contrast, direct tris-O-alkylation of phloroglucinol with an excess of compound **4** gave dendrimer **1** in relatively poor yield (26%). This could be due to the poor solubility of the phloroglucinol anion in DMF.

The G0 dendrimer **1** contains three chiral tartrate derivative units and has a C_3 symmetry. As a result, both the ^1H NMR and ^{13}C NMR spectra (Fig. 1) of compound **1** are relatively simple as compared with those of the C_2-symmetrical precursors **6** and **7**. There are five regions of interest in the ^1H NMR spectrum of the G0 dendrimer: (a) the aromatic protons of the 4-*tert*-butylphenoxy moiety at δ 7.3–6.8, (b) the aromatic protons (δ 6.18) of phloroglucinol, (c) the aliphatic protons on the tartrate units (δ 4.4–4.0), (d) the isopropylidene methyl groups (δ 1.49) and (e) the *tert*-butyl groups (δ 1.28). The relative integration of these five regions has the proportions 12.0:2.9:18.2:17.8:27.2, which is very close to the theoretical value of 12:3:18:18:27. In contrast to those of compounds **6** and **7**, the phloroglucinolic protons of G0 appear as a sharp singlet (δ 6.18). The phloroglucinolic carbons, as expected, give two resonance signals (δ_C 95.1 and 160.6) in the ^{13}C NMR spectrum. The IR spectrum and elemental analysis are also in accord with the proposed structure.

The synthesis of the first-generation dendrimer **2** (Scheme 2) was accomplished by employing the iterative reaction sequence as described above. Thus, mono-O-alkylation of the phenol **7** with an excess of the di-*O*-tosyl compound **3** in DMF gave compound **8** in 82% yield. The presence of the tosyl functionality was confirmed by the appearance of the methyl singlet (δ 2.42) signal. The isopropylidene group adjacent to the tosyl group appears as two methyl singlets in different positions (δ 1.36 and 1.39). The other two isopropylidene groups appear as a singlet at δ 1.50. Treatment of mono-*O*-tosyl compound **8** (2.1 mol equiv.) with 5-benzyloxyresorcinol **5** gave the dendritic 'wedge' **9** in 70% yield. Hydrogenolysis of the benzyl ether **9** in

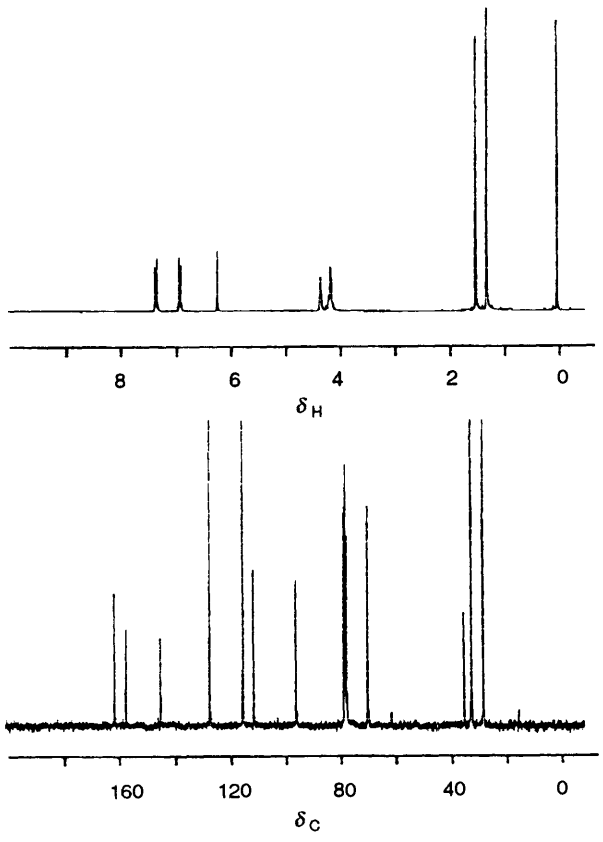
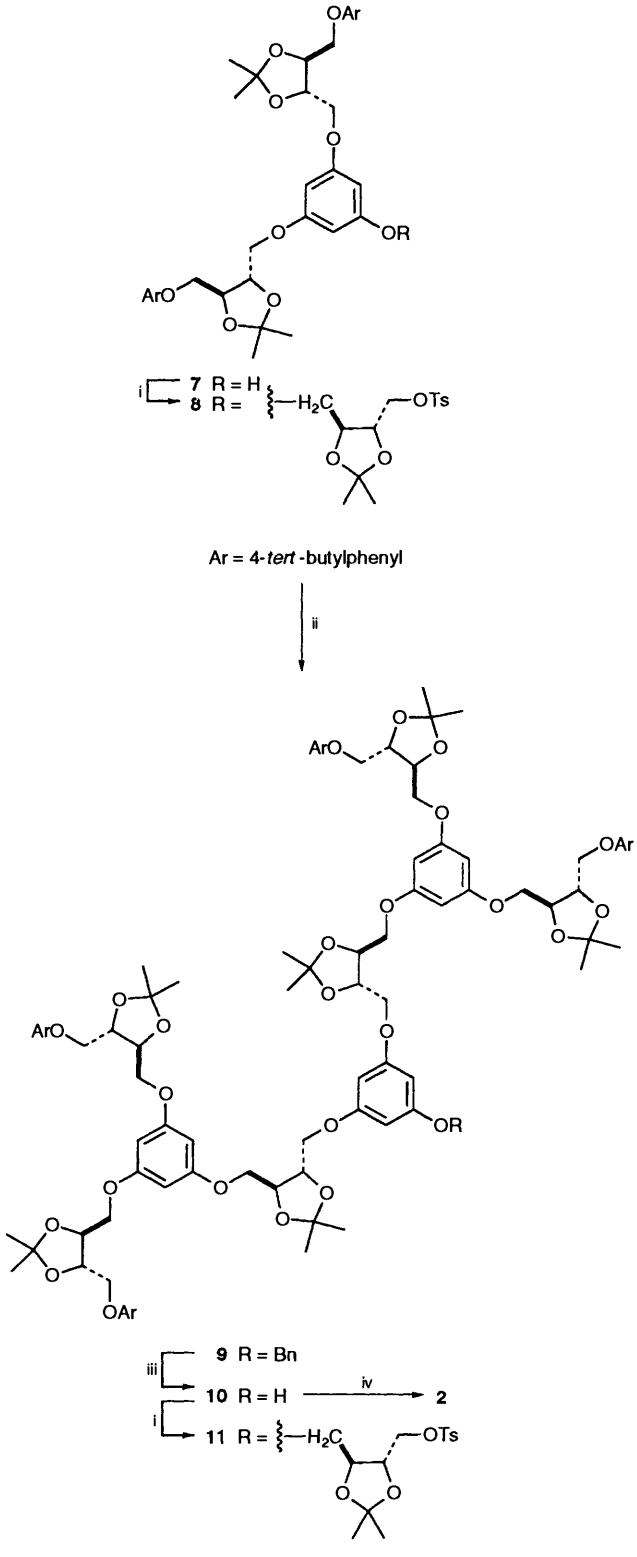


Fig. 1 The ^1H NMR (top) and ^{13}C NMR (bottom) spectra of G0 **1**

the presence of 10% palladium on charcoal afforded the phenol **10** as an oil in 73% yield. Finally, O-alkylation of phenol **10** with compound **8** gave the first-generation dendrimer **2** in 68% yield as a viscous oil.

This first-generation dendrimer **2** has 18 chiral centres and is one out of 262 144 possible stereoisomers. Similar to the zeroth generation dendrimer **1**, the ^1H NMR and ^{13}C NMR spectra (Fig. 2) of G1 dendrimer **2** are relatively simple. In the ^1H NMR spectrum, the relative integration of the above mentioned protons is 24.0:11.1:52.9:50.4:54.4 (calculated: 24:12:54:54:54). The core and the peripheral phloroglucinolic protons appear as sharp singlets at slightly different places (δ 6.15 and 6.16 respectively, relative intensity 1:3). It is interesting to note that the peripheral phloroglucinolic protons have the same chemical shift although they are chemically non-equivalent. The peripheral isopropylidene groups also appear at slightly different positions as compared with the internal isopropylidene groups (δ 1.47 and 1.48 respectively, relative intensity ~2:1). There is no ^{13}C chemical-shift difference between the central and the corresponding peripheral phloroglucinol carbons. The core and the corresponding peripheral chiral tartrate carbons also have the same ^{13}C chemical shifts. This suggested that the core group has nearly the same chemical environment as the peripheral groups. When one compares across different dendrimer generations, the ^{13}C NMR spectrum of G1 is almost identical with that of G0, except that the relative intensities of each peak are different.

The dendritic 'wedge' **10** could be similarly mono-O-alkylated to give the mono-*O*-tosyl compound **11** in 71% yield. We were unable to arylate compound **11** with phenol **5**. The reaction was very sluggish, probably because of steric problems, and at high reaction temperature (110 °C) compound **11** began to decompose. We are currently investigating alternative procedures to solve this problem.



Scheme 2 *Reagents:* i, **3**, K_2CO_3, DMF; ii, **5**, K_2CO_3, DMF; iii, H_2, 10% Pd–C, EtOH; iv, **8**, K_2CO_3, DMF

Structure–Optical Rotation Relationships.—The specific rotations and molar rotations of these compounds are tabulated in Table 1. The specific rotations of these optically active dendrimers remain essentially constant and fall within the range -50 to -70×10^{-1} deg cm^2 g^{-1}. However, we noticed that the measured molar rotation is proportional to the total number of chiral tartrate units. The contribution per tartrate unit towards the molar rotation is approximately ~ -185 °,

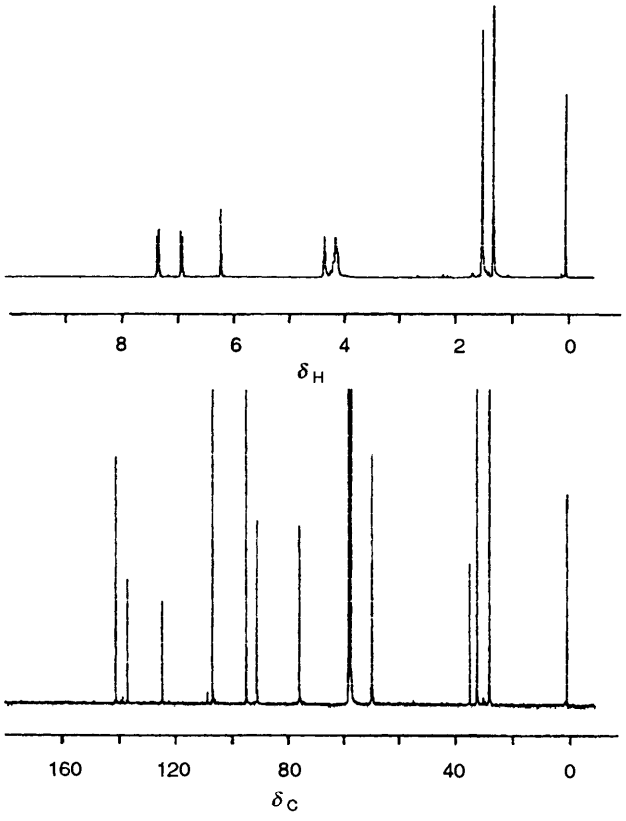


Fig. 2 The ^1H NMR (top) and ^{13}C NMR (bottom) spectra of G1 **2**

Table 1 Optical activity of selected compounds (20 °C in $CHCl_3$, D-line)

Compound	Specific rotation $[\alpha]^a$	Molar rotation (deg)	Molar rotation per tartrate unit (deg)
1	−59.6 (*c* 2.60)	−569	−190
2	−69.7 (*c* 0.37)	−1769	−197
6	−55.3 (*c* 0.38)	−425	−212
7	−52.4 (*c* 0.53)	−355	−178
8	−56.0 (*c* 0.41)	−547	−182
9	−60.1 (*c* 0.38)	−1096	−183
10	−57.3 (*c* 0.47)	−994	−166

[a] In units of 10^{-1} deg cm^2 g^{-1}.

irrespective of the structure of the dendrimer. This is in agreement with the report by Newkome,[10e] in which a direct relationship between the molar ellipticity and the number of surface chiral groups has been demonstrated. In our dendrimers, the chiral tartrate groups occupy both the central and peripheral positions. Our experiment suggests that the molar optical rotation properties of these dendritic molecules can be considered as the sum of the optical-rotation contributions from all the constituent chiral units, irrespective of their locations in the molecule. This again is consistent with the observation in NMR spectroscopy that each chiral tartrate derivative unit has nearly the same chemical environment.

Conclusions.—The present paper demonstrates the syntheses of optically active, homochiral, monodisperse dendrimers. We have initiated a systematic study of the structure–optical rotation relationship of this class of molecules. We show that the molar rotation is proportional to the number of chiral tartaric acid units within a particular molecule. In order to define quantitatively the relationships between the optical-rotation strength and the number of chiral centres in these dendrimers, we are in the process of preparing layer-block dendrimers[16] with alternating D- and L-tartrate units, taking advantage of the fact that both enantiomers are readily available. An alternative synthetic strategy is being explored in order to synthesize other, higher generation dendrimers. The use of this novel class of chiral material in synthetic applications will also be disclosed in due course.

Experimental

General.—M.p.s were determined on a Reichert microscope apparatus and are uncorrected. IR spectra were recorded on a Nicolet (205) FT-IR spectrophotometer for samples as neat films on KBr disks. Proton NMR spectra were recorded on a Bruker Cryospec WM 250 (250 MHz) spectrometer for samples in $CDCl_3$ solution with tetramethylsilane as internal standard. Chemical shifts are reported as parts per million (ppm) in δ-scale downfield from $SiMe_4$ and coupling constants (J) are reported in Hz. ^{13}C NMR spectra were obtained for samples in $CDCl_3$ on a Bruker WM 250 spectrometer at 62.9 MHz. Mass spectra were recorded on a VG Micromass 7070F spectrometer with EI ionization. Optical rotations were measured with sodium D light at 20 °C on a JASCO DIP-370 digital polarimeter using chloroform as solvent, and are given in units of 10^{-1} deg cm^2 g^{-1}. Elemental analyses were carried out by Medac Ltd, Uxbridge, UK.

Synthesis of Chiral Intermediate **4** *from the Homochiral Ditosyl Compound* **3**.—A mixture of *p*-(*tert*-butyl)phenol (0.50 g, 3.30 mmol), di-*O*-tosyl compound **3** (3.00 g, 6.34 mmol) and potassium carbonate (1.38 g, 10.0 mmol) in DMF (50 cm^3) was heated at 100 °C under nitrogen for 48 h. The reaction mixture was cooled, and evaporated under reduced pressure to remove the solvent. The residue was washed with ethyl acetate and filtered through Celite. The filtrate was concentrated, and purified by flash chromatography on silica gel with hexane–ethyl acetate (7:1) as eluent to give the *mono-O-alkylation product* **4** (1.10 g, 74%) as a solid, R_f 0.31 (5:1 hexane–ethyl acetate); m.p. 65-67 °C (from diethyl ether–hexane) (Found: C, 64.1; H, 7.3. $C_{24}H_{32}O_6S$ requires C, 64.3; H, 7.2%); $[\alpha]_D^{20}$ −15.6 (*c* 1.31); ν_{max}/cm^{-1} 1365, 1247, 1218 and 1178; δ_H 1.30 (9 H, s, Bu^t), 1.38 (3 H, s, Me), 1.40 (3 H, s, Me), 2.43 (3 H, s, Ar*Me*), 3.92–4.31 (6 H, m, OCH and OCH_2), 6.78 (2 H, d, *J* 8.9, ArH), 7.29 (2 H, d, *J* 8.8, ArH), 7.32 (2 H, d, *J* 8.4, OSO_2ArH) and 7.80 (2 H, d, *J* 8.3, OSO_2ArH); δ_C 21.5, 26.9, 27.0, 31.5, 34.1, 68.4, 69.3, 76.0, 76.6, 110.6, 114.2, 126.3, 128.1, 129.8, 133.2, 144.3, 144.9 and 156.2; *m/z* 449 ($M^+ + H$, 96%), 434 ($M^+ + H - Me$, 100), 357 ($M^+ - PhCH_3$, 14), 155 ($SO_2PhCH_3^+$, 13) and 91 ($PhCH_3^+$, 15).

Synthesis of the Benzyl Ether **6**.—A mixture of the mono-*O*-tosyl compound **4** (9.00 g, 20.0 mmol), 5-benzyloxyresorcinol **5** (2.00 g, 9.30 mmol) and potassium carbonate (6.50 g, 47.0 mmol) in DMF (150 cm^3) was heated at 120 °C under nitrogen for 40 h. The reaction mixture was cooled, and the solvent was evaporated off under reduced pressure. The residue was washed with ethyl acetate and filtered through Celite. The filtrate was concentrated, and purified by flash chromatography on silica gel with hexane–ethyl acetate (7:1) as eluent to give the C_2-*symmetric product* **6** (4.60 g, 65%) as a viscous liquid, R_f 0.38 (5:1 hexane–ethyl acetate) (Found: C, 73.5; H, 8.0. $C_{47}H_{60}O_9$ requires C, 73.4; H, 7.9%); $[\alpha]_D^{20}$ −55.3 (*c* 0.38); ν_{max}/cm^{-1} 1390, 1370, 1247 and 1217; δ_H 1.28 (18 H, s, 2 × Bu^t), 1.49 (12 H, s, 4 × Me), 4.10–4.29 (8 H, m, OCH_2), 4.30–4.34 (4 H, m, OCH), 4.98 (2 H, s, $PhCH_2$), 6.18 (1 H, t, *J* 1.8, ArH), 6.23 (2 H, d, *J* 1.8, ArH), 6.86 (4 H, d, *J* 8.8, ArH), 7.28 (4 H, d, *J* 8.7, ArH) and 7.28–7.42 (5 H, m, $PhCH_2$); δ_C 27.1, 31.6, 34.1, 68.9, 69.0,

70.3, 77.0, 77.3, 95.0, 95.5, 110.4, 114.3, 126.3, 127.5, 128.0, 128.6, 137.0, 144.2, 156.5, 160.6 and 160.9.

Synthesis of the Phenol **7**.—The benzyl ether **6** (0.30 g, 0.38 mmol) in ethanol (20 cm^3) was hydrogenated (1 atm) in the presence of a catalytic amount of 10% palladium on charcoal (30 mg) at room temperature for 4 h. The mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with hexane–ethyl acetate (4:1) as eluent to give the *phenol* **7** (0.25 g, 94%) as a viscous liquid, R_f 0.13 (5:1 hexane–ethyl acetate) (Found: C, 70.6; H, 8.0. $C_{40}H_{54}O_9$ requires C, 70.75; H, 8.0%); $[\alpha]_D^{20}$ −52.4 (*c* 0.53); ν_{max}/cm^{-1} 3387, 3375, 3367, 3358, 1380, 1368, 1247 and 1220; δ_H 1.29 (18 H, s, 2 × Bu^t), 1.49 (12 H, s, 4 × Me), 4.07–4.25 (8 H, m, OCH_2), 4.26–4.34 (4 H, m, OCH), 5.02 (1 H, s, OH), 6.05 (2 H, d, *J* 2.0, ArH), 6.13 (1 H, t, *J* 2.0, ArH), 6.86 (4 H, d, *J* 8.8, ArH) and 7.30 (4 H, d, *J* 8.8, ArH); δ_C 27.1, 31.5, 34.1, 68.8, 76.9, 77.2, 94.5, 95.7, 110.4, 114.2, 126.3, 144.1, 156.3, 157.8 and 160.6.

Synthesis of the Zeroth Generation Dendrimer **1**.—A mixture of dendritic branch **4** (0.16 g, 0.35 mmol), the phenol **7** (0.24 g, 0.35 mmol) and potassium carbonate (0.10 g, 0.70 mmol) in DMF (10 cm^3) was heated at 120 °C under nitrogen for 6 h. The reaction mixture was cooled, and the solvent was evaporated off under reduced pressure. The residue was washed with ethyl acetate and filtered through Celite. The filtrate was concentrated, and purified by flash chromatography on silica gel with hexane–ethyl acetate (7:1) as eluent to give the *G0 dendrimer* **1** (0.27 g, 80%) as a viscous liquid, R_f 0.30 (5:1 hexane–ethyl acetate) (Found: C, 71.4; H, 8.2. $C_{57}H_{78}O_{12}$ requires C, 71.65; H, 8.2%); $[\alpha]_D^{20}$ −59.6 (*c* 2.60); ν_{max}/cm^{-1} 1381, 1371, 1247 and 1218; δ_H 1.28 (27 H, s, 3 × Bu^t), 1.49 (18 H, s, 6 × Me), 4.07–4.22 (12 H, m, OCH_2), 4.24–4.39 (6 H, m, OCH), 6.18 (3 H, s, core ArH), 6.86 (6 H, d, *J* 8.8, ArH) and 7.29 (6 H, d, *J* 8.9, ArH); δ_C 27.1, 31.5, 34.1, 68.9, 69.0, 76.9, 77.2, 95.1, 110.4, 114.3, 126.3, 144.1, 156.4 and 160.6.

Synthesis of Compound **8**.—A mixture of ditosyl ester **3** (7.00 g, 14.8 mmol), phenol **7** (3.40 g, 5.01 mmol) and potassium carbonate (3.50 g, 25.4 mmol) in DMF (75 cm^3) was heated at 110 °C under nitrogen for 2 h. The reaction mixture was cooled, and the solvent was evaporated off under reduced pressure. The residue was washed with ethyl acetate and filtered through Celite. The filtrate was concentrated, and purified by flash chromatography on silica gel with hexane–ethyl acetate (4:1) as eluent to give the *mono-O-alkylation product* **8** (4.00 g, 82%) as a foam, R_f 0.25 (4:1 hexane–ethyl acetate) (Found: C, 66.4; H, 7.5. $C_{54}H_{72}O_{14}S$ requires C, 66.4; H, 7.4%); $[\alpha]_D^{20}$ −56.0 (*c* 0.41); δ_H 1.29 (18 H, s, 2 × Bu^t), 1.36 (3 H, s, Me), 1.39 (3 H, s, Me), 1.50 (12 H, s, 4 × Me), 2.42 (3 H, s, OSO_2ArMe), 3.90–4.34 (18 H, m, OCH and OCH_2), 6.13 (2 H, d, *J* 2.0, ArH), 6.20 (1 H, t, *J* 1.9, ArH), 6.87 (4 H, d, *J* 8.8, ArH), 7.30 (4 H, d, *J* 8.8, ArH), 7.31 (2 H, d, *J* 8.2, OSO_2ArH) and 7.78 (2 H, d, *J* 8.3, OSO_2ArH); δ_C 21.5, 26.9, 27.0, 27.1, 31.5, 34.1, 68.4, 68.9, 69.0, 69.2, 76.0, 76.4, 76.9, 77.3, 95.1, 95.3, 110.4, 110.6, 114.3, 126.3, 128.0, 129.9, 133.3, 144.1, 144.9, 156.4, 160.3 and 160.6.

Synthesis of Compound **9**.—A mixture of the mono-*O*-tosyl compound **8** (4.00 g, 4.10 mmol), 5-benzyloxyresorcinol **5** (0.40 g, 2.0 mmol) and potassium carbonate (1.40 g, 10.1 mmol) in DMF (70 cm^3) was heated at 115 °C under nitrogen for 44 h. The reaction mixture was cooled, and the solvent was evaporated off under reduced pressure. The residue was washed with ethyl acetate and filtered through Celite. The filtrate was concentrated, and purified by flash chromatography on silica gel with hexane–ethyl acetate (5:1) as eluent to give the C_2-*symmetric product* **9** (2.35 g, 70%) as a viscous liquid, R_f 0.30 (5:1 hexane–ethyl acetate) (Found: C, 70.1; H, 7.8. $C_{107}H_{140}O_{25}$ requires C, 70.4; H, 7.7%); $[\alpha]_D^{20}$ −60.1 (*c* 0.38); ν_{max}/cm^{-1} 1382, 1372, 1247 and 1217; δ_H 1.28 (36 H, s, 4 × Bu^t), 1.48 (36 H, s, 12 × Me), 4.04–4.19 (24 H, m, OCH_2), 4.26–4.34 (12 H, m, OCH), 4.95 (2 H, s, $PhCH_2$), 6.16–6.20 (3 H, m, ArH), 6.17 (6 H, s, ArH), 6.85 (8 H, d, *J* 8.9, ArH), 7.28 (8 H, d, *J* 8.9, ArH) and 7.26–7.40 (5 H, m, $PhCH_2$); δ_C 27.2, 31.6, 34.1, 68.9, 69.0, 70.3, 77.0, 77.3, 94.9, 95.1, 95.4, 110.4, 114.3, 126.3, 127.5, 128.0, 128.6, 136.9, 144.1, 156.5, 160.6 and 160.9.

Synthesis of the Phenol **10**.—The benzyl ether **9** (2.30 g, 1.26 mmol) and a catalytic amount of 10% palladium on charcoal (0.23 g) in an ethanol–ethyl acetate (60 cm^3:10 cm^3) mixture was hydrogenated (1 atm) at room temperature for 3 days. The mixture was filtered through Celite and the filtrate was concentrated. The residue was purified by flash chromatography on silica gel with hexane–ethyl acetate (3:1) as eluent to give the *phenol* **10** (1.60 g, 73%) as a viscous liquid, R_f 0.25 (3:1 hexane–ethyl acetate) (Found: C, 69.0; H, 8.2. $C_{100}H_{134}O_{25}$ requires C, 69.2; H, 7.8%); $[\alpha]_D^{20}$ −57.3 (*c* 0.47); ν_{max}/cm^{-1} 3404, 3392, 1392, 1381, 1372, 1247 and 1217; δ_H 1.28 (36 H, s, 4 × Bu^t), 1.47 (12 H, s, 4 × Me), 1.49 (24 H, s, 8 × Me), 4.00–4.39 (36 H, m, OCH_2 and OCH), 6.00 (1 H, s, OH), 6.06 (2 H, d, *J* 2.0, ArH), 6.10 (1 H, t, *J* 1.9, ArH), 6.14–6.20 (6 H, m, ArH), 6.85 (8 H, d, *J* 8.9, ArH) and 7.29 (8 H, d, *J* 8.8, ArH); δ_C 27.2, 31.6, 34.2, 68.9, 69.0, 76.9, 77.3, 94.2, 95.1, 95.2, 96.0, 110.5, 114.3, 126.3, 144.2, 156.4, 157.9 and 160.6.

Synthesis of the First Generation Dendrimer **2**.—A mixture of dendritic branch **8** (17 mg, 0.017 mmol), the phenol **10** (30 mg, 0.017 mmol) and potassium carbonate (12 mg, 0.087 mmol) in DMF (20 cm^3) was heated at 120 °C under nitrogen for 4 days. The reaction mixture was cooled and the solvent was evaporated off under reduced pressure. The residue was washed with ethyl acetate and filtered through Celite. The filtrate was concentrated, and purified by flash chromatography on silica gel with hexane–ethyl acetate (4:1) as eluent to give the *G1 dendrimer* **2** (30 mg, 68%) as a viscous liquid, R_f 0.24 (4:1 hexane–ethyl acetate) (Found: C, 68.8; H, 8.3. $C_{147}H_{198}O_{36}$ requires C, 69.5; H, 7.9%); $[\alpha]_D^{20}$ −69.7 (*c* 0.37); ν_{max}/cm^{-1} 1381, 1372, 1247 and 1217; δ_H 1.28 (54 H, s, 6 × Bu^t), 1.47 (18 H, s, 6 × Me), 1.48 (36 H, s, 12 × Me), 4.04–4.22 (36 H, m, OCH_2), 4.25–4.37 (18 H, m, OCH), 6.15 (3 H, s, core ArH), 6.16 (9 H, s, ArH), 6.85 (12 H, d, *J* 8.9, ArH) and 7.28 (12 H, d, *J* 8.9, ArH); δ_C 27.2, 31.6, 34.1, 68.9, 69.0, 76.9, 77.2, 95.2, 110.4, 114.3, 126.3, 144.2, 156.4 and 160.6.

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