Synthesis and Chiroptical Analysis of Optically Active Chiral Shell Dendrons

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We have prepared a series of chiral dendrons (**1**−**4**) in which chiral subunits are placed in individual generational shells at varying distances from the focal point. The optical activity of these chiral dendritic structures is successfully modeled using structurally similar low-molecular weight model compounds. In dendrons **1a** and **1b** a chiral subunit is directly adjacent to the focal point, whereas in dendrons **2**, **3**, and **4a**,**b** the chiral subunits are incorporated in the interior of the dendron. A marked difference in optical activity between the former (**1a** and **1b**) and latter (**2**, **3**, **4a**,**b**) dendrons is mirrored in the optical activities of model compounds **12a**, **12b**, **19a**, and **19b**. These model compounds directly mimic the surrounding constitution of the chiral subunits in the dendrons. This successful analysis of the chiroptical data using low-molecular weight model compounds suggests that these dendrons do not possess conformational order in solution.

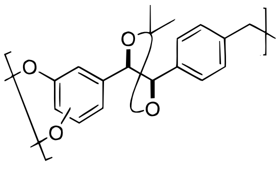
Introduction

Interest in chiral dendritic structures has increased in recent years because of their potential as supports for asymmetric catalysis and stereoselective recognition. In addition, attention has been paid to the effect of chiral subunits on the conformational order of dendritic structures, the fractal nature of dendritic surfaces, and the connection between microscopic and macroscopic chirality.[1−3] Reported chiral dendritic structures have included molecules with (a) a chiral core, (b) chiral terminal units, (c) chiral branching units, and (d) combinations thereof, yet there have been no reports of chiral branching units isolated within individual generational shells of a dendrimer.[4] The isolation of chiral units at different positions within dendritic structures would allow the study of the effect of subunit position on dendrimer conformation, catalytic activity, and clathration ability.

As part of our program to develop strategies for the incorporation of asymmetric units into dendrimers,[5−9] we present here the preparation of a series of dendrons (**1**−**4**) where a generational shell of chiral subunits is placed at varying distances from the focal point of the dendron (Chart 1). In the analysis of the chiroptical properties of these structures, as well as related dendrons containing the same chiral subunits in different relative placements, our newly demonstrated approach[8] to modeling the optical activity of chiral dendritic systems by using structurally similar low-molecular-weight model compounds is shown here to be successful. The data reveal a consistent picture of the effect of chiral subunit placement on observed optical activity, and the implications of this interpretation for dendrimer conformation in solution are discussed.

Results and Discussion

The dendrons prepared in this study consist of both chiral and achiral branching units. The achiral branching units are 3,5-substituted benzyl aryl ethers, the basis for the ubiquitous Fréchet dendrons.[10] The chiral subunits (**5a** and **5b**) are derivatives of (*R*,*R*)-hydrobenzoin and



5a: 3,4
5b: 3,5

have been reported previously.[6,11] The central design criterion of these chiral subunits was that they contain functionality appropriate for hydrogen bonding within

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† University of Arizona.

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[2] Thomas, C. W.; Tor, Y. *Chirality* **1998**, *10*, 53.

[3] Seebach, D.; Rheiner, P. B.; Greiveldinger, G.; Butz, T.; Sellner, H. *Top. Curr. Chem.* **1998**, *197*, 125.

[4] For a preliminary account of this work see: Junge, D. M.; McGrath, D. V. *Tetrahedron Lett.* **1998**, *39*, 1701.

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[12] Hanessian, S.; Simard, M.; Roelens, S. *J. Am. Chem. Soc.* **1995**, *117*, 7630.

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[15] Dobashi, Y.; Kobayashi, K.; Dobashi, A. *Tetrahedron Lett.* **1998**, *39*, 93.

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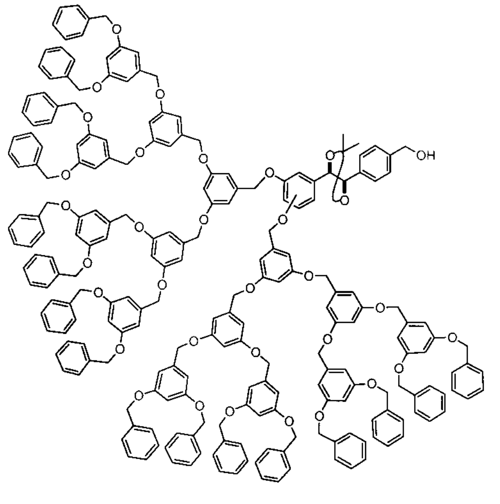
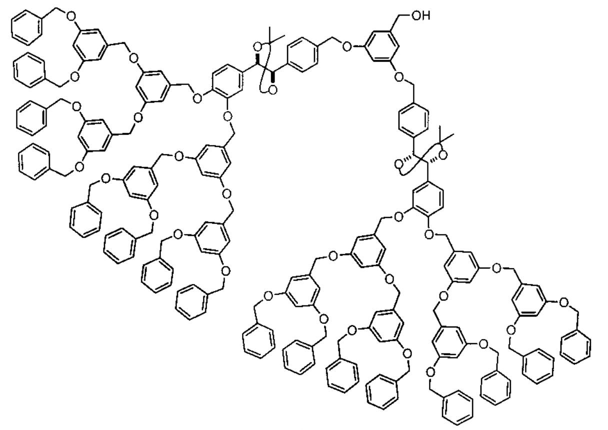
Chart 1



1a: 3,4
1b: 3,5



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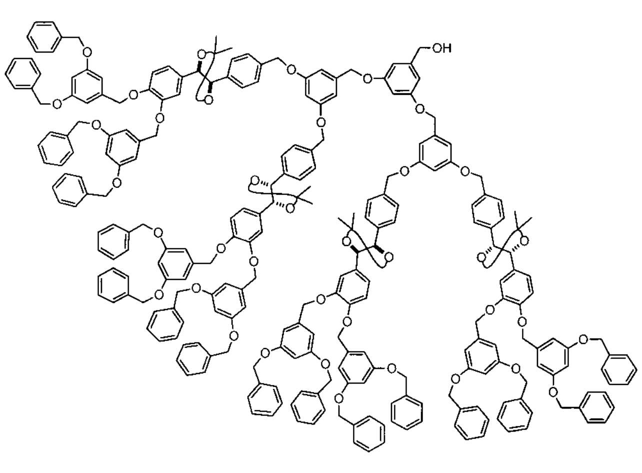

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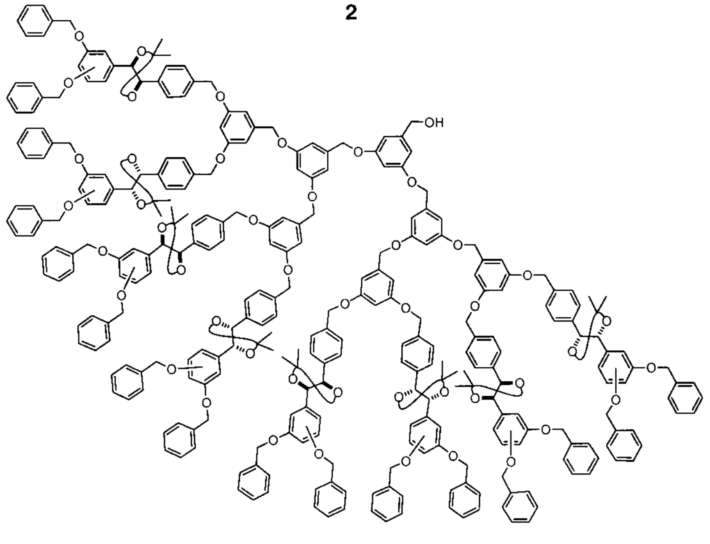
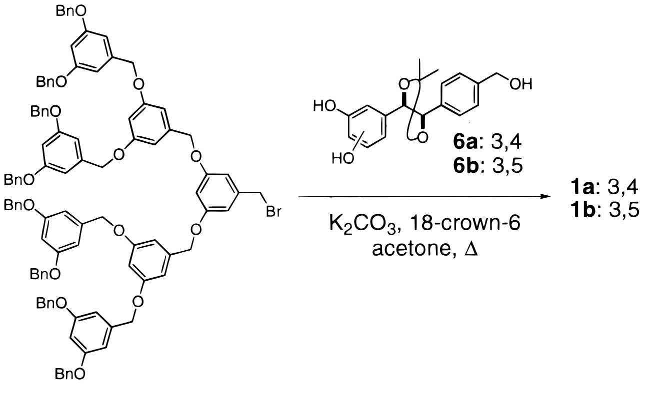
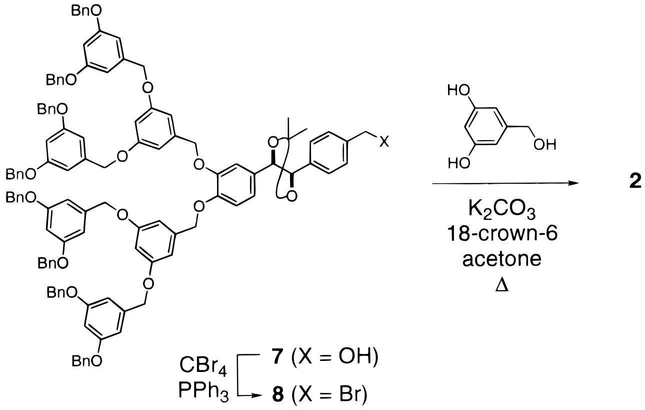


4a: 3,4
4b: 3,5

Scheme 1



Scheme 2



the interior cavities of dendrimers.[11] For this we chose chiral vicinal diols, which have been successfully utilized in such applications as molecular recognition[12–15] and asymmetric catalysis,[16–18] but are here acetonide-protected for synthetic purposes. A secondary design criterion of the chiral subunits was that they possess appropriate functionality to allow incorporation into a convergent growth strategy. Hence, monomer units **6a** and **6b** contain two phenolic residues and a benzylic hydroxyl group rendering them suitable for incorporation into Fréchet dendrons.

Preparation of Dendrons. Synthesis of first- and second-shell chiral dendrons **1a**, **1b**, and **2** followed a

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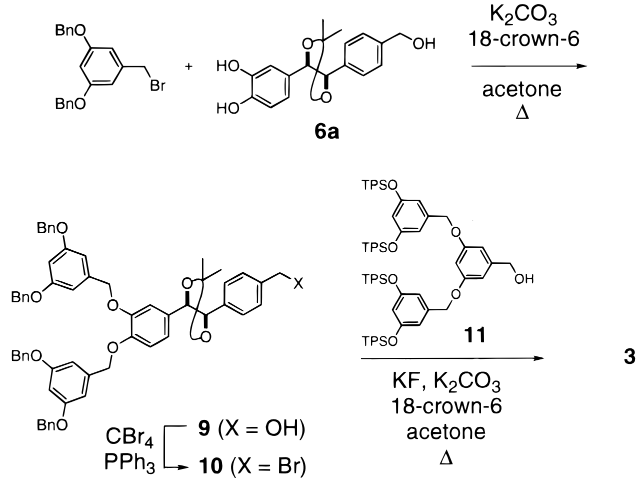
[17] Rosini, C.; Fansini, L.; Pini, D.; Salvadori, P. *Tetrahedron: Asymmetry* **1990**, *1*, 587.

[18] Devine, P. N.; Oh, T. *J. Org. Chem.* **1992**, *57*, 396.

[19] L'abbé, G.; Forier, B.; Dehaen, W. *J. Chem. Soc., Chem. Commun.* **1996**, 2143.

[20] Forier, B.; Dehaen, W. *Tetrahedron* **1999**, *55*, 9829.

Scheme 3

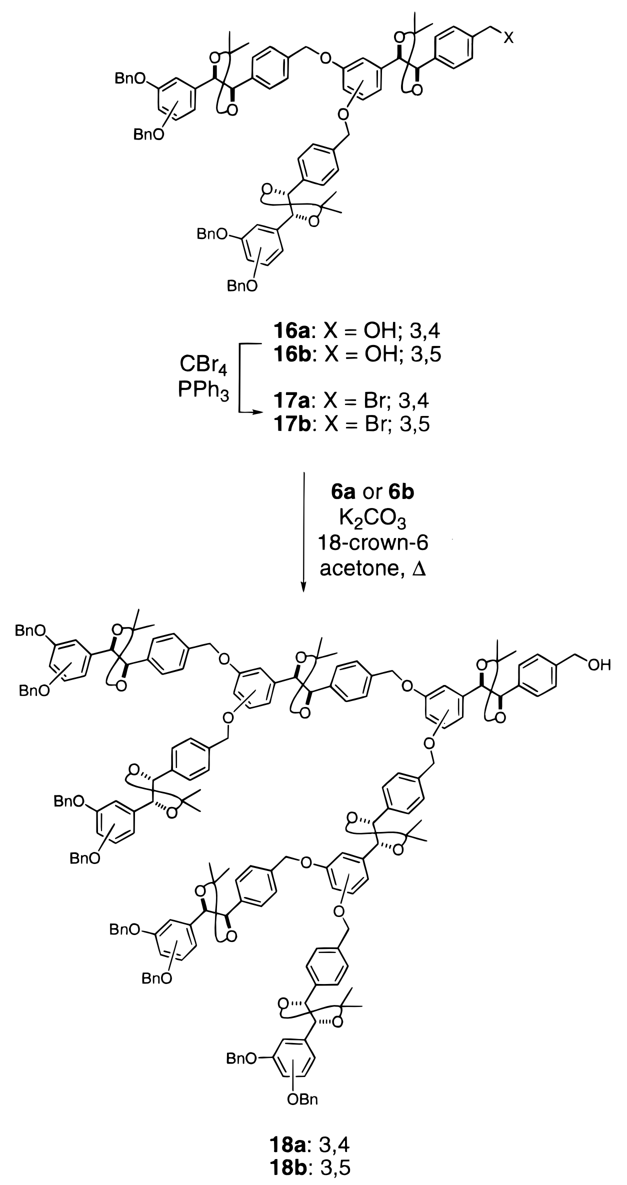


convergent approach (Schemes 1 and 2). Dialkylation of chiral diphenols **6a** and **6b**[11] with a third generation dendritic bromide of the Fréchet type[10] ([G-3]-Br) provided first-shell chiral dendrons **1a** and **1b** (59 and 85% yields, respectively). To prepare second-shell chiral dendron **2**, dendritic alcohol **7** was first obtained from [G-2]-Br and **6a** in 89% yield (not shown). Alcohol **7** was then converted to bromide **8** (86%) which was allowed to react with 3,5-dihydroxybenzyl alcohol to yield chiral second-shell dendron **2** (92%).

Chiral third- and fourth-shell dendrons **3**, **4a**, and **4b** were prepared by a combination of convergent and divergent techniques using the key tetrakis(*tert*-butyldiphenylsilyl)-protected trimer **11** as pioneered by L′abbé and Dehaen.[19,20] Accordingly, third-shell dendron **3** was prepared from alcohol **9**, itself prepared from [G-1]-Br and **6b** in 93% yield (Scheme 3). Conversion of **9** to bromide **10** (95%) proceeded smoothly, and then **10** was allowed to react with trimer **11**[19] in the presence of both potassium fluoride and 18-crown-6 in acetone to provide **3** (75%). Fourth-shell chiral dendrons **4a** and **4b** were prepared in a parallel manner (Scheme 4). Alcohols **12a** and **12b**[11] were converted to bromides **13a** and **13b** (92 and 81%) and then coupled to 3,5-dihydroxy benzyl alcohol to give second generation dendrons **14a** and **14b** (49 and 73%). Subsequent bromination yielded **15a** and **15b** (86 and 92%) which were used to provide **4a** and **4b** (83 and 70%), again by the method of L′abbé and Dehaen.[19,20]

Fully chiral dendrons—those containing only chiral branching units of type **5a** or **5b**—were prepared for comparison purposes with the chiral shell dendrons (Scheme 5).[6] First generation dendrons **16a** and **16b** were prepared in 66 and 85% yields by allowing 2 equiv of bromides **13a** and **13b** to react with **6a** and **6b**, respectively, under standard conditions (not shown). Bromination of **16a** and **16b** to give **17a** and **17b** (69 and 93%) was followed by coupling to compounds **6a** and **6b**, respectively, to yield second generation dendrons **18a** and **18b** (52 and 95%).

Scheme 5



Scheme 4

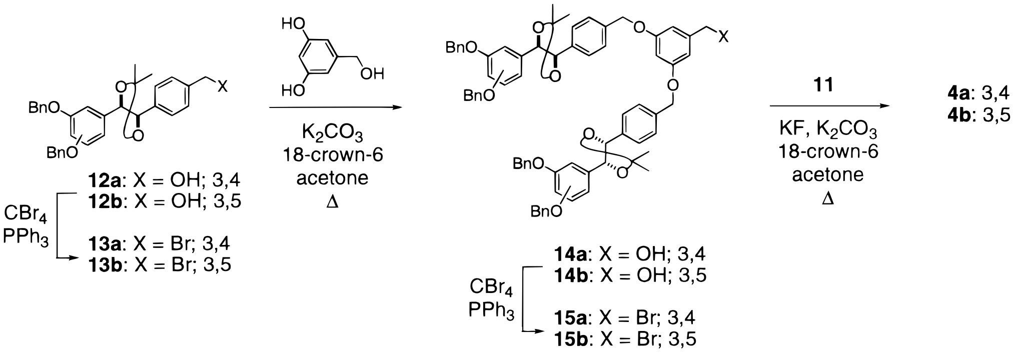
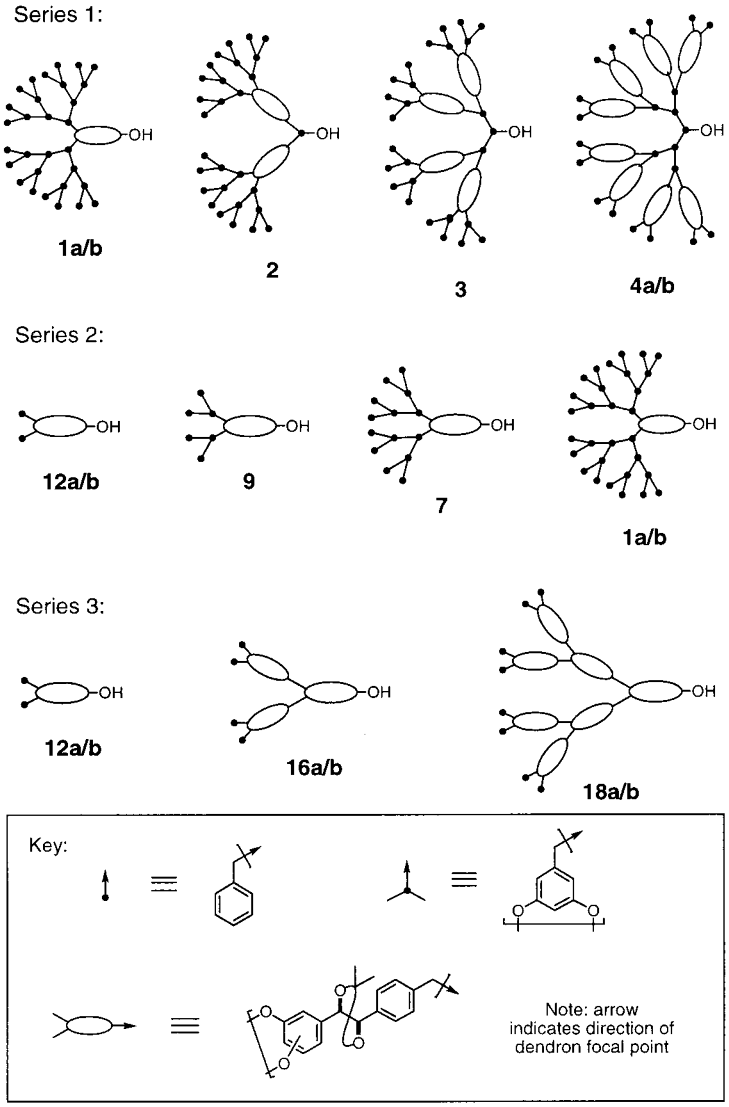


Chart 2



The dendrons prepared in this study are summarized in schematic form in Chart 2. The six compounds **1a/b** **2**, **3**, and **4a/b** constitute the "chiral shell" series of dendrons (Chart 2, series 1). Compounds **1a**, **2**, **3**, and **4a** are fourth generation dendrons containing chiral subunit **5a** in the first, second, third, and fourth generational shells, respectively. Compounds **1b** and **4b** are analogous dendrons that contain chiral subunit **5b** in the first and fourth generational shells, respectively. In addition, dendrons **12a**, **9**, **7**, and **1a**, in that order, constitute a series of structures in which achiral dendritic fragments of increasing size are attached to chiral focal subunit **5a** (Chart 2, series 2). The fully chiral series of dendrons consists of **12a**, **16a**, and **18a** (subunit **5a**), and **12b**, **16b**, and **18b** (subunit **5b**) (Chart 2, series 3). All dendrons are colorless glasses that are readily soluble in common organic solvents (e.g., acetone, ether, CH_2Cl_2, ethyl acetate). Structural characterization was carried out principally by ^1H and ^{13}C NMR spectroscopy and combustion analysis. In addition, mass spectrometry data (MALDI-TOF) confirms the expected molecular masses for all dendrons reported.

Chiroptical Studies. We have demonstrated in previous reports that, in analogy to work in linear polymer systems,[21,22] it is possible to gain information on the conformation of chiral dendrimers by comparing their chiroptical properties with those of structurally similar low-molecular-weight model compounds.[6-9,21,22] In the chiral shell systems presented here, agreement between the molar optical rotation ($[\Phi]_D$) value of the dendrimer and the sum of the $[\Phi]_D$ values of appropriate model compound(s) would indicate that the conformational equilibria for the model compound(s) and the chiral monomeric units of the dendrimer are similar, i.e., conformational order has not developed in the larger molecule. It would also indicate that the chiral subunits have not induced chiral, nonracemic conformations in configurationally achiral portions of the dendron. If some form of conformational order exists, it would manifest itself in a marked change in optical activity of the dendrons with respect to the model compounds.

The chiroptical data for dendrons based on subunit **5a** is presented in Table 1. From the chiroptical data of dendrons **12a**, **9**, **7**, and **1a** we can establish that the

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(21) Pino, P.; Salvadori, P.; Chiellini, E.; Luisi, P. L. *Pure Appl. Chem.* **1968**, *16*, 469.

(22) For a recent example see: Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270.

Table 1. Chiroptical[a] Data for Reported Dendrons Based on Chiral Unit 5a

compd	no. of chiral units	FW	$[\alpha]_D^{26}$ [b]	$[\Phi]_D$ [c]	$[\Phi]_D/n$ [d]
1a	1	3468.08	+17.3	+600	+600
2	2	3644.29	+41.6	+1516	+758
3	4	3996.72	+77.9	+3113	+778
4a	8	4701.58	+123	+5783	+723
7	1	1770.09	+36.0	+637	+637
9	1	921.10	+65.8	+606	+606
12a	1	496.60	+119	+591	+591
14a	2	1097.31	+135	+1481	+740
16a	3	1273.53	+151.6	+1931	+643
18a	7	2827.38	+156.4	+4422	+632
19a	1	572.70	+134	+767	+767

[a] All rotations measured in CH_2Cl_2. [b] Specific rotation (10^{-1} deg cm^2 g^{-1}). [c] Molar rotation (10 deg cm^2 mol^{-1}). [d] Number of chiral units = n.

chiral focal subunit appears to have no increased influence on the molar optical activity of the dendrons as the attached achiral wedges increase in size. The molar optical rotation per chiral unit ($[\Phi]_D/n$) of these dendrons varies only ± 4.6% from the median value of +608. This also implies that the conformational equilibria of the chiral subunits are similar in all four dendrons.[21] An increasing amount of data presented in the literature to date strongly suggests high conformational flexibility of benzyl aryl ether dendrons of the Fréchet type.[23−26] Hence, it is not surprising that a chiral subunit installed at the focal point of such dendrons does not appear to influence their conformation in solution.

However, in consideration of the series of chiral shell dendrons **1a**, **2**, **3**, and **4a**, a seeming chiroptical anomaly is observed. As the chiral units proceed from the focal point (dendron **1a**) to shells further into the interior of the dendron (**2** → **3** → **4a**), an immediate increase is seen in the $[\Phi]_D/n$ value which seems to saturate. The $[\Phi]_D/n$ values of second-, third-, and fourth-shell chiral dendrons **2**, **3**, and **4a** are approximately 26% greater, on average, than that of first-shell dendron (**1a**). That the chiral unit has a larger effect on the optical rotatory power of the molecule when it is not placed near the periphery of the dendron could be due to a degree of conformational order in dendrons **2**, **3**, and **4a** not present in **1a**.

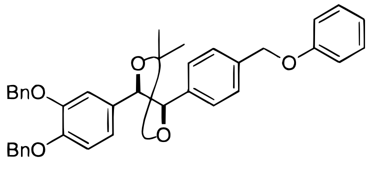
However, slight changes in constitution, rather than conformation, could also be responsible for the observed changes in optical activity.[6−9] Subunits closer to the core of a dendrimer, or focal point of a dendron, are different in constitution than subunits in other regions of the structure (interior, periphery). These differences in constitution can be manifest in dramatically different optical activities. While the chiral subunits of **1a**, **7**, **9**, and **12a** are extremely similar to each other in surrounding constitution—being directly adjacent to the focal hydroxyl group—they are constitutionally dissimilar to those in dendrons **2**, **3**, and **4a**, which are more remote from the focal hydroxyl group. In essence, subunit **5a** can be considered two different subunits, one when it is at the focal point, and one when it is in the interior of the dendron. Therefore, two different low-molecular-weight model compounds would be appropriate here.

Table 2. Chiroptical[a] Data for Reported Dendrons Based on Chiral Unit 5b

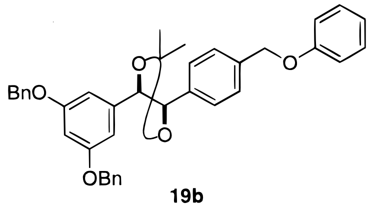
compd	no. of chiral units	FW	$[\alpha]_D^{26}$ [b]	$[\Phi]_D$ [c]	$[\Phi]_D/n$ [d]
1b	1	3468.08	+15.1	+523	+523
4b	8	4701.58	+103	+4843	+605
12b	1	496.60	+94.2	+468	+468
14b	2	1097.31	+112	+1229	+614
16b	3	1273.53	+128	+1634	+545
18b	7	2827.38	+134	+3775	+539
19b	1	572.70	+102	+584	+584

[a] All rotations measured in CH_2Cl_2. [b] Specific rotation (10^{-1} deg cm^2 g^{-1}). [c] Molar rotation (10 deg cm^2 mol^{-1}). [d] Number of chiral units = n.

To investigate the effect of this constitutional difference, we prepared compound **19a** from **12a**. Compound **19a** differs from **12a** only in the replacement of a proton with a phenyl group at the focal point and more closely matches the constitution of chiral subunits in **2**, **3**, and **4a**. The increased $[\Phi]_D$ value of **19a** (+767) with respect to that of **12a** (+591) confirms that a slight constitutional difference in subunit **5a** can alter its contribution to the overall optical activity of a dendron. Hence, contribution of the chiral subunit **5a** to the overall optical activity of the dendrons should vary with relative placement in the larger structure, i.e., whether it is possesses a constitution similar to **12a** or **19a**. This strongly suggests that the difference in $[\Phi]_D/n$ values between first-shell chiral dendron **1** and second-, third-, and fourth-shell chiral dendrons **2**, **3**, and **4a** is based solely on constitutional changes in the dendritic structure and not conformational order. The $[\Phi]_D/n$ value of intermediate **14a** (+740) is also consistent with this observed effect of structure on optical activity.



19a



19b

As further confirmation of the relative contributions of chiral subunits similar to **12a** and those similar to **19a**, we considered the observed molar rotations of fully chiral dendrons **16a** and **18a** which contain both types of subunit. As expected, the $[\Phi]_D/n$ values of these dendrons (+643 and +632) are intermediate between the $[\Phi]_D$ values of **12a** and **19a**. However, the limitations of the accuracy of this analysis are evident here as well. One would expect the $[\Phi]_D/n$ value for **18a** to be slightly greater than **16a** since it contains a greater fraction of subunits of type **19a**, but the converse is true.

A parallel analysis of the chiroptical properties of the compounds constructed from subunit **5b** is possible (Table 2). Compounds **12b** and **19b** now serve as appropriate model compounds for subunit **5b** when it is at the focal point or interior of a dendron, respectively. We note here

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(23) Gorman, C. B.; Parkhurst, B. L.; Su, W. Y.; Chen, K.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 1141.

(24) Peerlings, H. W. I.; Meijer, E. W. *Eur. J. Org. Chem.* **1998**, 573.

(25) Peerlings, H. W. I.; Trimbach, D. C.; Meijer, E. W. *Chem. Commun.* **1998**, 497.

(26) Junge, D. M.; McGrath, D. V. *J. Am. Chem. Soc.* **1999**, *121*, 4912.

as well an increased $[\Phi]_D$ value of **19b** (+584), the internal version of **5b**, with respect to that of **12b** (+591), the focal point version of **5b**. This is mirrored in the relative difference in $[\Phi]_D/n$ values among fourth generation dendrons **1b** (+523) and **4b** (+605) and first generation dendron **14b** (+614). The fully chiral dendrons **16b** and **18b** exhibit $[\Phi]_D/n$ values (+545 and +539) intermediate between the $[\Phi]_D$ values of **12a** and **19a**. We again see a slight, unexplained—at this juncture—decrease in $[\Phi]_D/n$ value on proceeding from first generation **16b** to second generation **18b**.

This close agreement between the optical activity of the dendrons and that of the model compounds indicates that the conformational equilibria of the chiral subunits are not perturbed relative to those of the model compounds. It also indicates that these subunits have a negligible influence on the conformation of the other, achiral subunits throughout the structure. Therefore, chiral conformational order is not evident in these compounds under these solvent and temperature conditions.

Summary

We have prepared a series of chiral dendrons (**1**−**4**) in which chiral subunits are placed in individual generational shells at varying distances from the focal point. Analysis of the chiroptical properties of these structures reveals that changes in optical activity with increasing generation is a result of constitutional effects rather than chiral conformational order. This successful analysis of the chiroptical data using low-molecular weight model compounds suggests that these dendrons do not possess conformational order in solution. The incorporation of these dendrons into dendrimers and further investigation of the effect of chiral dendrimer subunits on macromolecular asymmetry are ongoing efforts in our laboratory.

Experimental Section

Materials and Methods. Optical rotation measurements, NMR spectroscopy, and mass spectrometry (MS) were obtained using commercially available instrumentation. Tetrahydrofuran (THF) was distilled under N_2 from sodium−benzophenone ketyl. Acetone was dried over crushed 3 Å molecular sieves. Potassium carbonate (granular, J. T. Baker) was dried at 100 °C at reduced pressure and stored in a vacuum oven. Fréchet-type bromides[10] ([G-1]-Br, [G-2]-Br, [G-3]-Br) and compounds **6a**,[11] **6b**,[11] **11**,[19] **12a**,[11] **12b**,[11] and **19b**[8] were prepared according to the literature. All other reagents were purchased from commercial suppliers and used as received. Flash chromatography was performed by the method of Still et al.[27] using silica gel (32−63 μm, Scientific Adsorbants, Inc., Atlanta GA). Thin-layer chromatography (TLC) was performed on precoated plates (Silica Gel HLO, F-254, Scientific Adsorbants, Inc.).

4-{5-[3,4-Bis(3,5-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)benzyloxy)phenyl]-2,2-dimethyl-[1,3]dioxolan-4-yl}benzyl Alcohol (i.e., First chiral shell dendron-[3,4]) (1a). To a solution of [G-3]-Br (480 mg, 0.29 mmol) and compound **6a** (46 mg, 0.14 mmol) in acetone (20 mL) were added K_2CO_3 (51 mg, 0.37 mmol) and 18-crown-6 (8.1 mg, 0.029 mmol). The reaction mixture was refluxed under nitrogen until TLC (SiO_2, CH_2Cl_2) indicated consumption of starting materials. The reaction mixture was allowed to cool and concentrated in vacuo, and the product was partitioned in CH_2Cl_2 (20 mL) and H_2O (20 mL). The organic layer was separated, and the aqueous layer was further extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. Purification of the residue by flash chromatography (SiO_2, CH_2Cl_2 gradient to 1:49 EtOAc−CH_2Cl_2) yielded dendron **1a** (290 mg, 59%) as a colorless glass: ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.11 (m, 84H), 6.80−6.43 (m, 45H), 4.99 (s, 2H), 4.97 (s, 2H), 4.90 (s, 32H), 4.79 (s, 16H), 4.73 (s, 8H) 4.61 (d, J = 8.4 Hz, 1H), 4.55 (d, J = 8.4 Hz, 1H), 4.54 (s, 2H), 1.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 160.2, 149.2, 149.0, 141.2, 140.0, 139.9, 139.5, 137.0, 136.6, 136.4, 128.8, 128.64, 128.58, 128.2, 128.0, 127.8, 127.21, 127.18, 127.0, 120.5, 109.4, 106.6, 106.3, 101.8, 85.32, 85.25, 71.4, 70.2, 70.1, 65.1, 27.5, 27.4; $[\alpha]_D$ = +17.3 (c = 1.34, CH_2Cl_2); MS (MALDI) m/z 3496.0 (M + Na), 3507.1 (M + K). Anal. Calcd for $C_{228}H_{200}O_{33}$: C, 78.95; H, 5.82. Found: C, 78.34; H, 5.95.

4-{5-[3,5-Bis(3,5-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)benzyloxy)phenyl]-2,2-dimethyl-[1,3]dioxolan-4-yl}benzyl Alcohol (i.e., First chiral shell dendron-[3,5]) (1b). Following the procedure for the preparation of **1a**, [G-3]-Br (299 mg, 0.18 mmol), compound **6b** (28 mg, 0.09 mmol), acetone (15 mL), K_2CO_3 (33 mg, 0.24 mmol), and 18-crown-6 (6.7 mg, 0.025 mmol) yielded, after purification by flash chromatography (SiO_2, CH_2Cl_2 gradient to 1.5% EtOAc/CH_2Cl_2), dendron **1b** (264 mg, 85%) as a colorless glass: ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.14 (m, 84H), 6.64−6.38 (m, 45H), 4.95 (s, 32H), 4.89 (s, 16H), 4.88 (s, 8H), 4.83 (s, 4H), 4.64 (d, J = 8.4 Hz, 1H), 4.58 (d, J = 8.4 Hz, 1H), 4.50 (d, J = 6.0 Hz, 2H), 1.71 (t, J = 6.0, 1H), 1.58 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 160.0, 159.8, 141.1, 139.3, 139.19, 139.16, 136.8, 128.5, 128.0, 127.5, 126.9, 109.6, 106.5, 106.4, 101.6, 86.1, 86.0, 70.1, 70.01, 69.96,64.9, 27.2, 27.1; $[\alpha]_D$ = +15.07 (c = 2.03, CH_2Cl_2); MS (MALDI) m/z 3494.5 (M + Na). Anal. Calcd for $C_{228}H_{200}O_{33}$: C, 78.95; H, 5.82. Found: C, 78.95; 5.54.

3,5-Bis([*R*,*R*]-4-{5-[3,4-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)benzyl Alcohol (i.e., Second chiral shell dendron-[3,4]) (2). To a solution of benzyl alcohol **7** (490 mg, 0.28 mmol) and CBr_4 (118 mg, 0.35 mmol) in THF (5 mL) was added PPh_3 (92 mg, 0.35 mmol). The reaction mixture was allowed to stir at room temperature and was monitored by TLC (SiO_2, CH_2Cl_2). Excesses of CBr_4 (0.36 mmol) and PPh_3 (0.36 mmol) were added to the reaction mixture in 20 min intervals until all starting materials were consumed (45 min). Upon completion of the reaction, water (5 mL) and CH_2Cl_2 (5 mL) were added, the organic layer was separated, and the aqueous layer was further extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. Purification of the residue by flash chromatography (SiO_2, CH_2Cl_2) yielded bromide **8** (440 mg, 86%) as a colorless glass: ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.23 (m, 44H), 6.68−6.64 (m, 21H), 5.06 (s, 2H), 4.99 (d, J = 7.1 Hz, 2H), 4.93 (s, 16H), 4.81 (s, 4H), 4.80 (s, 4H), 4.62 (d, J = 8.4 Hz, 1H), 4.58 (d, J = 8.4 Hz, 1H), 4.40 (s, 2H), 1.61 (s, 6H). Following the procedure for the preparation of **1a**, bromide **8** (252 mg, 0.14 mmol), 3,5-dihydroxybenzyl alcohol (11 mg, 0.07 mmol), K_2CO_3 (53 mg, 0.38 mmol), 18-crown-6 (4 mg, 0.01 mmol), and acetone (10 mL) yielded, after flash chromatography (SiO_2, CH_2Cl_2), dendron **2** (228 mg, 92%) as a colorless glass: ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.13 (m, 84H), 6.78−6.42 (m, 45H), 5.02−4.99 (m, 10H), 4.91 (s, 16H), 4.89 (s, 16H), 4.79 (s, 8H), 4.77 (s, 8H), 4.64 (d, J = 8.5 Hz, 2H), 4.59 (d, J = 8.5 Hz, 2H), 4.46 (d, J = 5.8 Hz, 2H), 1.59 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 160.04, 160.06, 160.0, 148.9, 148.8, 143.5, 139.7, 139.6, 139.2, 136.80, 136.76, 136.7, 129.9, 128.5, 128.0, 127.9, 127.7, 127.5, 127.2, 126.8, 120.3, 114.7, 113.6, 109.2, 106.4, 106.1, 106.0, 105.6, 101.6, 101.1, 85.0, 84.9, 71.2, 71.1, 69.9, 69.8, 69.7, 65.1, 27.2, 27.1; $[\alpha]_D$ = +41.6 (c = 1.02, CH_2Cl_2); MS (MALDI) m/z 3670.5 (M + Na), 3684.7 (M + K). Anal. Calcd for $C_{239}H_{212}O_{35}$: C, 78.76; H, 5.87. Found: C, 78.70; H 5.97.

3,5-Bis{3,5-bis[(*R*,*R*)-4-(5-{3,4-Bis[3,5-bis(benzyloxy)benzyloxy]phenyl}-2,2-dimethyl[1,3]dioxolan-4-yl)benzyloxy]benzyloxy}benzyl Alcohol (i.e., Third chiral shell dendron-[3,4]) (3). To a solution of benzyl alcohol **9**

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(27) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(756 mg, 0.82 mmol) and CBr$_4$ (340 mg, 1.02 mmol) in THF (20 mL) was added PPh$_3$ (274 mg, 1.04 mmol). The reaction mixture was allowed to stir at room temperature and was monitored by TLC (SiO$_2$, 3:7 EtOAc−petroleum ether). Excesses of CBr$_4$ (1.02 mmol) and PPh$_3$ (1.02 mmol) were added to the reaction mixture in 20 min intervals until all starting materials were consumed (25 min). Upon completion of the reaction, water (5 mL) and CH$_2$Cl$_2$ (5 mL) were added, the organic layer was separated, and the aqueous layer was further extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic extracts were dried (MgSO$_4$) and concentrated. Purification of the residue by flash chromatography (SiO$_2$, 1:4 EtOAc−petroleum ether) yielded bromide **10** (770 mg, 95%) a colorless glass: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34−7.12 (m, 24H), 6.84−6.71 (m, 3H), 6.69 (d, J = 2.1 Hz, 2H), 6.67 (d, J = 2.1 Hz, 2H), 6.48 (t, J = 2.1 Hz, 1H), 6.47 (t, J = 2.1 Hz, 1H), 5.06 (s, 2H), 5.04 (d, J = 12.6 Hz, 1H), 4.99 (d, J = 12.6 Hz, 1H), 4.91 (s, 4H), 4.90 (s, 4H), 4.63 (d, J = 8.4 Hz, 1H), 4.57 (d, J = 8.4 Hz, 1H), 4.42 (s, 2H), 1.61 (s, 3H), 1.60 (s, 3H). A solution of bromide **10** (320 mg, 0.33 mmol), AB$_4$ monomer **11**^{19} (110 mg, 0.82 mmol), KF (29 mg, 0.49 mmol), 18-crown-6 (10 mg, 0.033 mmol), and acetone (10 mL) was maintained at reflux for 24 h under nitrogen. K$_2$CO$_3$ (57 mg, 0.41 mmol) was then added to the reaction mixture. The reaction was kept at reflux until TLC (SiO$_2$, CH$_2$Cl$_2$) indicated consumption of starting materials. The reaction mixture was allowed to cool and concentrated in vacuo, and the product was partitioned in CH$_2$Cl$_2$ (20 mL) and H$_2$O (20 mL). The organic layer was separated, and the aqueous layer was further extracted with CH$_2$Cl$_2$ (3 × 20 mL). The combined organic extracts were dried (Na$_2$SO$_4$) and concentrated. Purification of the residue by flash chromatography (SiO$_2$, CH$_2$Cl$_2$ gradient to 1:24 EtOAc−CH$_2$Cl$_2$) yielded dendron **3** (0.24 g, 75%) as a colorless glass: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31−7.13 (m, 96H), 6.85−6.78 (m, 12H), 6.67−6.44 (m, 33H), 5.03 (d, J = 12.2 Hz, 4H), 5.02 (s, 8H), 4.98 (d, J = 12.2 Hz, 4H), 4.91 (s, 8H), 4.88 (s, 20H), 4.86 (s, 16H), 4.63 (d, J = 8.5 Hz, 4H), 4.57 (d, J = 8.5 Hz, 4H), 4.49 (d, J = 6.0 Hz, 2H), 1.60 (s, 12H), 1.59 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.1, 160.0, 148.9, 148.8, 139.7, 139.6, 139.3, 136.8, 136.75, 136.71, 129.9, 128.5, 127.9, 127.5, 126.8, 120.3, 114.7, 113.6, 109.2, 106.3, 106.1, 106.06, 105.6, 101.6, 101.5, 101.49, 85.0, 84.9, 71.2, 71.1, 69.9, 69.87, 69.8, 65.0, 27.2, 27.1; $[\alpha]_D$ = +77.94 (c = 0.51, CH$_2$Cl$_2$); MS (MALDI) m/z 4021.9 (M + Na), 4037.4 (M + K). Anal. Calcd for C$_{261}$H$_{236}$O$_{39}$: C, 78.43; H, 5.95. Found: C, 78.53; H 6.03.

3,5-Bis{3,5-Bis[3,5-Bis([*R*,*R*]-4-{5-[3,4-bis(benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)benzyloxy]benzyloxy}benzyl Alcohol (i.e., Fourth chiral shell dendron-[3,4]) (4a). To a solution of benzyl alcohol **14a** (278 mg, 0.25 mmol) and CBr$_4$ (170 mg, 0.51 mmol) in THF (5 mL) was added PPh$_3$ (134 mg, 0.51 mmol). The reaction mixture was allowed to stir at room temperature, and the reaction was monitored by TLC (SiO$_2$, 3:7 EtOAc−petroleum ether) until all starting materials were consumed (45 min). Upon completion of the reaction, water (5 mL) and CH$_2$Cl$_2$ (5 mL) were added, the organic layer was separated, and the aqueous layer was further extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic extracts were dried (MgSO$_4$) and concentrated. Purification of the residue by flash chromatography (SiO$_2$, 3:7 EtOAc−petroleum ether) yielded bromide **15a** (322 mg, 83%) as a colorless glass: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41−7.14 (m, 28H), 6.84−6.67 (m, 6H), 6.59 (d, J = 2.2 Hz, 2H), 6.50 (t, J = 2.2 Hz, 1H), 5.12 (s, 2H), 5.10 (d, J = 12.2 Hz, 2H), 5.06 (d, J = 12.2 Hz, 2H), 4.98 (s, 2H), 4.62 (d, J = 8.5 Hz, 2H), 4.57 (d, J = 8.5 Hz, 2H), 4.37 (s, 2H), 1.61 (s, 6H), 1.60 (s, 6H). Following the procedure for the preparation of **3**, bromide **15a** (250 mg, 0.22 mmol), **11**^{19} (77 mg, 0.057 mmol), KF (19 mg, 0.34 mmol), K$_2$CO$_3$ (37 mg, 0.27 mmol), 18-crown-6 (9.2 mg, 0.035 mmol), and acetone (10 mL) yielded after flash chromatography (SiO$_2$, CH$_2$Cl$_2$ gradient to 1:24 EtOAc−CH$_2$Cl$_2$) dendron **4a** (0.18 g, 70%) as a colorless glass: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34−7.20 (m, 112H), 6.63−6.43 (m, 45H), 4.94 (s, 16H), 4.92 (s, 4H), 4.91 (s, 32H), 4.88 (s, 8H), 4.68 (d, J = 8.4 Hz, 8H), 4.61 (d, J = 8.4 Hz, 8H), 4.49 (d, J = 6.0 Hz, 2H), 1.61 (s, 24H), 1.59 (s, 24H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.1, 160.0, 159.9, 149.0, 148.8, 143.6, 139.3, 139.2, 137.2, 137.1, 136.8, 136.6, 134.7, 129.7, 128.4, 127.7, 127.6, 127.5, 127.3, 127.2, 126.8, 120.2, 114.8, 113.7, 109.2, 106.4, 106.3, 105.7, 101.6, 101.5, 101.1, 85.0, 84.8, 71.3, 71.2, 70.0, 69.9, 69.8, 65.0, 27.2, 27.1; $[\alpha]_D$ = +123.2 (c = 1.02, CH$_2$Cl$_2$); MS (MALDI) m/z 4705.4 (M + H), 4728.1 (M + Na). Anal. Calcd for C$_{305}$H$_{284}$O$_{47}$: C, 77.91; H, 6.09. Found: C, 77.49; H 6.15.

3,5-Bis{3,5-Bis[3,5-Bis([*R*,*R*]-4-{5-[3,5-bis(benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)benzyloxy]benzyloxy}benzyl Alcohol (i.e., Fourth chiral shell dendron-[3,5]) (4b). Following the procedure for the preparation of **8**, benzyl alcohol **14b** (0.60 mg, 0.55 mmol), CBr$_4$ (0.72 mg, 2.2 mmol in two portions), THF (20 mL), and PPh$_3$ (0.52 g, 2.0 mmol in two portions) yielded, after purification by flash chromatography (SiO$_2$, 1:3 EtOAc-petroleum ether), bromide **15b** (0.58 g, 92%) as a colorless glass. Following the procedure for the preparation of **3**, bromide **15b** (486 mg, 0.42 mmol), **11**^{19} (162 mg, 0.12 mmol), KF (45 mg, 0.77 mmol), K$_2$CO$_3$ (166 mg, 1.20 mmol in two portions), 18-crown-6 (8.1 mg, 0.031 mmol), and acetone (30 mL) yielded after flash chromatography (SiO$_2$, gradient 1:99 to 3:97 EtOAc−CH$_2$Cl$_2$) dendron **4b** (397 mg, 70%) as a colorless glass: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35−7.18 (m, 112H), 6.63 (d, J = 2.1 Hz, 4H), 6.61 (d, J = 2.1 Hz, 8H), 6.54−6.48 (m, 17H), 6.43 (d, J = 2.2 Hz, 16H), 4.95 (s, 16H), 4.92 (s, 4H), 4.91 (s, 32H), 4.88 (s, 8H), 4.68 (d, J = 8.4 Hz, 8H), 4.62 (d, J = 8.4 Hz, 8H), 4.49 (d, J = 6.0 Hz, 2H), 1.74 (t, J = 6.0, 1H), 1.61 (s, 24H), 1.60 (s, 24H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.97, 160.95, 160.8, 143.5, 140.2, 140.1, 137.7, 137.6, 129.4, 128.9, 128.5, 128.4, 127.9, 126.7, 110.4, 107.31, 107.26, 106.7, 106.6, 102.8, 102.4, 102.3, 86.1, 85.7, 70.93, 70.85, 70.7, 65.2, 28.1, 28.0; $[\alpha]_D$ = +103 (c = 2.01, CH$_2$Cl$_2$); MS (MALDI) m/z 4732.9 (M + Na). Anal. Calcd for C$_{305}$H$_{284}$O$_{47}$: C, 77.91; H, 6.09. Found: C, 77.63; H 5.91.

(*R*,*R*)-4-[5-(3,4-Bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}phenyl)-2,2-dimethyl[1,3]dioxolan-4-yl]benzyl Alcohol (7). Following the procedure for the preparation of **1a**, [G-2]-Br (844 mg, 1.05 mmol), **6a** (166 mg, 0.52 mmol), K$_2$CO$_3$ (184 mg, 1.33 mmol), 18-crown-6 (28 mg, 0.11 mmol), and acetone (50 mL) yielded after flash chromatography (SiO$_2$, 2:3 EtOAc−petroleum ether) dendron **7** (830 mg, 89%) as a colorless glass: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36−7.13 (m, 44H), 6.83−6.43 (m, 21H), 5.05 (s, 2H), 5.01 (d, J = 7.6 Hz, 2H), 4.93 (s, 8H), 4.92 (s, 8H), 4.81 (s, 4H), 4.79 (s, 4H), 4.63 (d, J = 8.4 Hz, 1H), 4.57 (d, J = 5.8 Hz, 2H), 4.56 (d, J = 8.4 Hz, 1H), 1.60 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.1, 160.0, 148.9, 148.8, 140.9, 139.7, 139.22, 139.19, 137.8, 136.3, 128.5, 127.9, 127.6, 126.9, 126.8, 125.9, 109.2, 106.4, 106.4, 106.1, 106.0, 101.6, 101.54, 101.53, 85.1, 85.0, 70.0, 69.9, 69.8, 65.0, 27.2, 27.15; $[\alpha]_D$ = +26.07 (c = 1.45, CH$_2$Cl$_2$); MS (MALDI) m/z 1795.7 (M + Na), 1811.7 (M + K). Anal. Calcd for C$_{116}$H$_{104}$O$_{17}$: C, 78.70; H, 5.93. Found: C, 78.92; H 6.03.

(*R*,*R*)-4-(5-{3,4-Bis[3,5-bis(benzyloxy)benzyloxy]phenyl}-2,2-dimethyl[1,3]dioxolan-4-yl)benzyl Alcohol (9). Following the procedure for the preparation of **1a**, [G-1]-Br (1.00 g, 2.62 mmol), **6a** (415 mg, 1.31 mmol), K$_2$CO$_3$ (460 mg, 3.33 mmol), 18-crown-6 (71 mg, 0.27 mmol), and acetone (100 mL) yielded after flash chromatography (SiO$_2$, 2:3 EtOAc−petroleum ether) dendron **9** (1.13 g, 93%) as a colorless glass: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34−7.13 (m, 24H), 6.84−6.70 (m, 3H), 6.68 (d, J = 2.2 Hz, 2H), 6.65 (d, J = 2.2 Hz, 2H), 6.48 (t, J = 2.2 Hz, 1H), 6.47 (t, J = 2.2 Hz, 1H), 5.06 (s, 2H), 5.04 (d, J = 12.6 Hz, 1H), 4.99 (d, J = 12.6 Hz, 1H), 4.91 (s, 4H), 4.90 (s, 4H), 4.63 (d, J = 8.5 Hz, 1H), 4.60 (d, J = 6.0 Hz, 2H), 4.57 (d, J = 8.6 Hz, 1H), 1.62 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.43, 160.41, 149.2, 149.0, 141.2, 140.0, 137.13, 137.10, 136.6, 130.3, 128.8, 128.2, 127.8, 127.3, 127.1, 120.5, 115.1, 114.1, 109.5, 106.4, 101.9, 101.8, 85.4, 85.3, 77.6, 71.6, 71.5, 70.4, 65.3, 27.51, 27.47; $[\alpha]_D$ = +65.79 (c = 1.22, CH$_2$Cl$_2$); MS (MALDI) m/z 945.5 (M + Na), 962.2 (M + K). Anal. Calcd for C$_{60}$H$_{56}$O$_9$: C, 78.23; H, 6.13. Found: C, 78.34; H 6.16.

3,5-Bis([*R*,*R*]-4-{5-[3,4-bis(benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)benzyl Alcohol (14a). Following the procedure for the preparation of **15a**, benzyl alcohol **12a** (3.32 g, 5.92 mmol), CBr_4 (3.95 g, 11.9 mmol in two portions), PPh_3 (3.12 g, 11.9 mmol in two portions), and THF (25 mL) yielded, after purification by flash chromatography (SiO_2, 3:7 EtOAc−petroleum ether), bromide **13a** (3.39 g, 92%) as a colorless thick oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.10 (m, 14H), 6.85 (d, $J = 8.3$ Hz, 1H), 6.82 (d, $J = 2.0$ Hz, 1H), 6.60 (dd, $J = 8.3, 2.0$ Hz, 1H), 5.14 (s, 2H), 5.12 (d, $J = 13.7$ Hz, 1H), 5.07 (d, $J = 12.2$ Hz, 1H), 4.61 (d, $J = 8.5$ Hz, 1H), 4.56 (d, $J = 8.5$ Hz, 1H), 4.46 (s, 2H), 1.61 (s, 3H), 1.60 (s, 3H). Following the procedure for the preparation of **1a**, bromide **13a** (520 mg, 1.35 mmol), 3,5-dihydroxybenzyl alcohol (96 mg, 0.68 mmol), K_2CO_3 (0.24 g, 1.7 mmol), 18-crown-6 (37 mg, 0.14 mmol), and acetone (50 mL) yielded after flash chromatography (SiO_2, 2:3 EtOAc−petroleum ether) dendron **14a** (360 mg, 49%) as a colorless glass: ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.25 (m, 24H), 7.15 (d, $J = 8$ Hz, 4H), 6.84 (dd, $J = 3, 5$ Hz, 4H), 6.69 (dd, $J = 2, 8$ Hz, 2H), 6.58 (d, $J = 2.3$ Hz, 2H), 6.50 (t, $J = 2.3$ Hz, 1H), 5.12 (s, 2H), 5.10 (d, $J = 12.2$ Hz, 2H), 5.05 (d, $J = 12.2$ Hz, 2H), 4.99 (s, 4H), 4.62 (d, $J = 8.5$ Hz, 2H), 4.59 (d, $J = 6.0$ Hz, 2H), 4.57 (d, $J = 8.5$ Hz, 2H), 1.61 (s, 6H), 1.59 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 149.1, 148.8, 143.5, 137.21, 137.18, 136.8, 129.8, 128.4, 127.8, 127.5, 127.4, 127.3, 126.8, 125.9, 120.2, 114.8, 113.8, 109.2, 105.7, 101.9, 85.0, 84.9, 71.4, 71.3, 69.8, 65.2, 27.2, 27.1; $[\alpha]_D = +135.2$ ($c = 1.19$, CH_2Cl_2); MS (MALDI) *m/z* 1120.9 (M + Na), 1145.5 (M + K). Anal. Calcd for $C_{71}H_{68}O_{11}$: C, 77.72; H, 6.25. Found: C, 77.88; H 6.41.

3,5-Bis([*R*,*R*]-4-{5-[3,5-bis(benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)benzyl Alcohol (14b). Following the procedure for the preparation of **8**, benzyl alcohol **12b** (1.00 g, 2.01 mmol), PPh_3 (1.06 g, 4.02 mmol in two portions), CBr_4 (1.33 g, 4.02 mmol in two portions), and THF (10 mL) yielded, after purification by flash chromatography (SiO_2, 1:4 petroleum ether−ethyl acetate), bromide **13b** as a colorless oil (911 mg, 81%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.18−7.38 (m, 14H), 6.55 (t, $J = 2.3$ Hz, 1H), 6.44 (d, $J = 2.3$ Hz, 2H), 4.95, (s, 4H), 4.67 (d, $J = 8.4$ Hz, 1H), 4.61 (d, $J = 8.4$ Hz, 1H), 4.47 (s, 2H), 1.63 (s, 3H), 1.61 (s, 3H). Following the procedure for the preparation of **1a**, bromide **13b** (1.44 g, 2.58 mmol), 3,5-dihydroxybenzyl alcohol (181 mg, 1.29 mmol), K_2CO_3 (0.45 g, 3.26 mmol), 18-crown-6 (73 mg, 0.28 mmol), and acetone (75 mL) yielded after flash chromatography (SiO_2, 2:3 EtOAc−petroleum ether) dendron **14b** (1.03 mg, 73%) as a colorless glass: ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.20 (m, 28H), 6.55 (d, $J = 2$ Hz, 2H), 6.54 (t, $J = 2$ Hz, 2H), 6.50 (t, $J = 2$ Hz, 1H), 6.44 (d, $J = 2$ Hz, 4H), 5.00 (s, 4H), 4.95 (s, 8H), 4.69 (d, $J = 8.5$ Hz, 2H), 4.63 (d, $J = 8.5$ Hz, 2H), 4.55 (d, $J = 5.5$ Hz, 2H), 1.63 (s, 6H), 1.61 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 160.1, 159.9, 143.4, 139.3, 136.9, 136.74, 136.68, 128.6, 128.0, 127.53, 127.51, 127.0, 109.5, 105.8, 105.7, 101.9, 101.3, 85.2, 84.9, 70.1, 69.8, 65.1, 27.2, 27.1; MS (FAB) *m/z* 1097.1 (M^+, 4%, $C_{71}H_{69}O_{11}$ requires 1097.4); $[\alpha]_D = +112$ ($c = 1.03$, CH_2Cl_2). Anal. Calcd for $C_{71}H_{68}O_{11}$: C, 77.72; H, 6.25. Found: C, 77.10; H 6.20.

4-{5-[3,4-Bis-(4-{5-[3,4-bis(benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyl Alcohol (16a). Following the procedure for the preparation of **1a**, compound **6a** (424 mg, 1.34 mmol), benzyl bromide **13a** (1.50 g, 2.69 mmol), acetone (25 mL), K_2CO_3 (925 mg, 6.70 mmol), and 18-crown-6 (43 mg) yielded **16a** (1.12 g, 66%) as a colorless glass after purification by flash chromatography (SiO_2, 2:3 EtOAc−petroleum ether): ^1H NMR (400 MHz, $CDCl_3$) δ 7.11−7.41 (m, 32H), 6.64−6.84 (m, 9H), 5.05−5.12 (m, 12H), 4.55−4.64 (m, 8H), 1.59−1.64 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.9, 148.8, 148.77, 148.71, 140.9, 137.2, 137.13, 137.10, 136.5, 136.2, 129.7, 128.4, 127.7, 127.33, 127.31, 127.27, 127.25, 126.9, 126.74, 126.68, 126.66, 125.8, 120.3, 120.2, 120.1, 114.7, 113.6, 109.2, 109.18, 85.1, 85.00, 84.89, 84.87, 84.84, 71.29, 71.26, 71.17, 71.14, 71.0, 70.9, 64.9, 27.19, 27.15, 27.12; $[\alpha]_D = +151.6$ ($c = 2.42$, CH_2Cl_2). Anal. Calcd for $C_{82}H_{80}O_{13}$: C, 77.34; H, 6.33. Found: C, 76.99; H, 6.47.

4-{5-[3,5-Bis-(4-{5-[3,5-bis(benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyl Alcohol (16b). Following the procedure for the preparation of **1a**, compound **6b** (257 mg, 0.81 mmol), benzyl bromide **13b** (911 mg, 1.63 mmol), acetone (10 mL), K_2CO_3 (1.12 g, 8.14 mmol), and 18-crown-6 (5 mg) yielded, after purification by flash chromatography (SiO_2, 55:45 petroleum ether−ethyl acetate), **16b** (878 mg, 85%) as a colorless glass: ^1H NMR: 7.18−7.37 (m, 32H), 6.54 (t, $J = 2.3$ Hz, 2H), 6.51 (t, $J = 2.2$ Hz, 1H), 6.45 (d, $J = 2.3$ Hz, 4H), 6.43 (d, $J = 2.2$ Hz, 2H), 4.95 (s, 8H), 4.93 (s, 4H), 4.703 (d, $J = 8.4$ Hz, 2H), 4.702 (d, $J = 8.4$ Hz, 1H), 4.627 (s, 2H), 4.625 (d, $J = 8.4$ Hz, 2H), 4.61 (d, $J = 8.6$ Hz, 1H), 1.63 (s, 6H), 1.620 (s, 3H), 1.617 (s, 6H), 1.61 (s, 3H); ^{13}C NMR: d 160.39, 160.36, 141.5, 139.9, 139.8, 137.26, 137.2, 136.7, 129.0, 128.4, 127.97, 127.93, 127.41, 127.39, 127.35, 109.96, 109.89, 106.33, 106.25, 102.4, 102.3, 85.63, 85.61, 85.36, 85.28, 70.5, 70.2, 65.3, 27.61, 27.56; MS (ES) *m/z* 1296 (M + Na); $[\alpha]_D = +128.3$ ($c = 1.45$, CH_2Cl_2). Anal. Calcd for $C_{82}H_{80}O_{13}$: C, 77.34; H, 6.33. Found: C, 77.06; H, 6.59.

4-{5-[3,4-Bis(4-{5-[3,4-bis-(4-{5-[3,4-bis(benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyl Alcohol (18a). Following the procedure for **8**, benzyl alcohol **17a** (569 mg, 0.45 mmol), THF (10 mL), PPh_3 (235 mg, 0.89 mmol in two portions), and CBr_4 (296 mg, 0.89 mmol in two portions) yielded benzyl bromide **17a** as a colorless glass (411 mg, 69%) after flash chromatography (SiO_2, 6:4 petroleum ether−ethyl acetate): ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.10 (m, 32H), 6.86−6.79 (m, 6H), 6.68−6.62 (m, 3H), 5.02−5.11 (m, 12H), 4.63−4.54 (m, 6H), 4.45 (s, 2H), 1.61 (s, 9H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.87, 148.85, 148.83, 148.7, 137.7, 137.3, 137.18, 137.16, 137.10, 137.07, 136.58, 136.56, 129.73, 129.70, 129.68, 129.1, 128.4, 127.8, 127.35, 127.34, 127.29, 126.9, 127.8, 127.7, 120.3, 120.2, 120.1, 114.8, 114.7, 113.7, 113.6, 113.4, 109.3, 109.2, 85.1, 85.0, 84.94, 84.89, 84.87, 84.7, 71.3, 71.22, 71.18, 71.0, 70.94, 3.2, 27.18, 27.13, 27.09. Following the procedure for the preparation of **1a**, compound **6a** (60 mg, 0.19 mmol), benzyl bromide **17a** (510 mg, 0.38 mmol), acetone (10 mL), K_2CO_3 (263 mg, 1.90 mmol), and 18-crown-6 (5 mg) yielded **18a** (281 mg, 52%) as a colorless glass after purification by flash chromatography (SiO_2, 95:5 ether−CH_2Cl_2): ^1H NMR: δ 7.39−7.26 (m, 68H), 7.10−7.02 (m, 14H), 6.84−6.60 (m, 7H), 5.10−5.02 (m, 22H), 4.62−4.54 (m, 16H), 1.60−1.55 (m, 42H); ^{13}C NMR: δ 149.0, 148.91, 148.88, 148.84, 148.7, 141.0, 137.18, 137.15, 137.10, 136.57, 136.55, 136.52, 136.1, 129.9, 129.85, 129.83, 129.75, 129.70, 128.4, 127.8, 127.37, 127.33, 127.30, 126.9, 126.75, 126.72, 126.70, 126.65, 120.32, 120.25, 120.19, 114.77, 114.73, 114.68, 114.63, 113.70, 113.66, 113.5, 113.41, 113.35, 109.21, 109.17, 109.15, 85.06, 85.02, 84.9, 71.32, 71.21, 71.18, 71.03, 71.00, 71.98, 70.9, 69.5, 64.8, 60.4, 53.8; MS (MALDI) *m/z* 2852.1 (M + Na), 2868.5 (M + K); $[\alpha]_D = +156.4$ ($c = 1.08$, CH_2Cl_2).

4-{5-[3,5-Bis(4-{5-[3,5-bis(4-{5-[3,5-bis(benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyloxy)phenyl]-2,2-dimethyl[1,3]dioxolan-4-yl}benzyl Alcohol (18b). Following the procedure for **15a**, dendron **16b** (880 mg, 0.69 mmol), CBr_4 (357 mg, 1.08 mmol), PPh_3 (279 mg, 1.06 mmol), and THF (15 mL) yielded, after purification by flash chromatography (SiO_2, 4:1 petroleum ether−ethyl acetate), bromide **17b** (859 mg, 93%) as a colorless glassy solid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.17 (m, 32H), 6.54 (t, $J = 2.3$ Hz, 2H), 6.52 (t, $J = 2.2$ Hz, 1H), 6.45 (d, $J = 2.3$ Hz, 4H), 6.43 (d, $J = 2.2$ Hz, 2H), 4.95 (s, 8H), 4.91 (s, 4H), 4.70 (d, $J = 8.4$ Hz, 2H), 4.67 (d, $J = 8.5$ Hz, 1H), 4.62 (d, $J = 8.4$ Hz, 2H), 4.59 (d, $J = 8.4$ Hz, 1H), 4.43 (s, 2H), 1.63−1.60 (m, 18H). Following the procedure for **1a**, bromide **17b** (848 mg, 0.635 mmol), compound **6b** (99 mg, 0.31 mmol), K_2CO_3 (224 mg, 1.62 mmol), and 18-crown-6 (20.3 mg, 0.0768 mmol) yielded dendron **18b** (855 mg, 95%) as a colorless glassy solid after purification by flash chromatography (SiO_2, 7:3 petroleum ether-ethyl acetate): ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.10 (m, 68H), 6.53 (t, $J = 2.3$ Hz, 4H), 6.51 (t, $J = 2.3$ Hz, 2H), 6.50 (t, $J = 2.3$

Hz, 1H), 6.45 (d $J = 2.3$ Hz, 2H), 6.44 (d $J = 2.3$ Hz, 4H), 6.42 (d, $J = 2.3$ Hz, 8H), 4.93 (s, 16H), 4.91 (s, 8H), 4.90 (s, 4H), 4.73−4.56 (m, 16H), 1.62 (s, 12H), 1.60 (s, 24H), 1.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.94, 159.93, 159.90, 141.0, 139.49, 139.45, 139.32, 136.82, 136.79, 136.76, 136.1, 128.6, 128.0, 127.56, 127.51, 127.0, 126.96, 126.91, 126.89, 109.52, 109.50, 109.44, 105.85, 105.76, 101.9, 101.8, 85.2, 85.1, 84.9, 84.83, 84.80, 70.1, 69.8, 64.8, 27.16, 27.12; MS (MALDI) m/z 2853.0 (M + Na), 2868.1 (M + K); $[\alpha]_D$ +133.5 ($c = 1.19$, CH_2Cl_2). Anal. Calcd for $C_{182}H_{176}O_{29}$: C, 77.32; H, 6.27. Found: C, 76.94; H, 6.05.

(*R*,*R*)-4-[4-(Phenoxymethyl)phenyl]-5-[3,4-bis(benzyloxy)phenyl]-2,2-dimethyl-1,3-dioxolane (19a). A slurry of bromide **13a** (412 mg, 0.81 mmol), phenol (76 mg, 0.81 mmol), K_2CO_3 (168 mg, 1.22 mmol), and 18-crown-6 (42 mg, 0.16 mmol) in acetone (20 mL) was heated at reflux under nitrogen. After TLC (SiO_2, 1:4 EtOAc−petroleum ether) indicated consumption of starting materials, the reaction mixture was concentrated in vacuo, and the product was partitioned in water (20 mL) and CH_2Cl_2 (20 mL). The organic layer was separated, and the aqueous layer was then extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were washed with 5% NaOH solution (2 × 20 mL), dried (Na_2SO_4), and concentrated. Purification of the residue by flash chromatography (SiO_2, 1:19 EtOAc−petroleum ether) yielded dendron **19a** (396 mg, 85%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.24 (m, 14H), 7.15 (d, $J = 8.2$ Hz, 2H), 6.95−6.92 (m, 3H), 6.84 (d, $J = 8.3$ Hz, 1H), 6.83 (d$J = 2.0$ Hz, 1H), 6.69 (dd, $J = 2.0$, 8.3 Hz, 1H), 5.13 (s, 2H), 5.11 (d, $J = 12.6$ Hz, 1H), 5.06 (d, $J = 12.6$ Hz, 1H), 5.03 (s, 2H), 4.62 (d, $J = 8.5$ Hz, 1H), 4.58 (d, $J = 8.5$ Hz, 1H), 1.61 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 149.0, 148.8, 137.2, 137.1, 137.0, 136.6, 129.7, 129.4, 128.4, 127.7, 127.4, 127.28, 127.26, 126.7, 120.9, 120.1, 114.8, 113.7, 109.2, 85.0, 84.8, 71.3, 71.2, 69.6, 27.2, 27.1; $[\alpha]_D$ = +133.9 ($c = 1.38$, CH_2Cl_2); MS (FAB) m/z 573. Anal. Calcd for $C_{38}H_{36}O_5$: C, 79.70; H, 6.34. Found: C, 79.77; H 6.05.

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