Upper Rim Substitution of Calix[4]arenes via Their Upper Rim A,C Dinitro Compounds[1]

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p-tert-Butylcalix[4]arene, easily accessible via base-induced condensation of *p-tert*-butylphenol and formaldehyde,[2] provides a convenient starting material for the preparation of calixarenes[3] carrying a wide variety of groups on both the upper and lower rims. An earlier publication[4] in this series detailed the preparation of upper rim 5,17-substituted calix[4]arenes and described their use in the selective introduction of lower rim groups which established conformational immobility. In the present paper the focus shifts to the upper rim of these compounds, employing the nitro groups as precursors to amino groups and various functionalities derived therefrom.

Although *p*-tetranitrocalix[4]arene[5] as well as its alkyl ethers are effectively reduced to the corresponding tetraamines[6] with $SnCl_2$, this reagent failed with the 5,17-dinitro compounds **1a**−**c**, probably because of their limited solubility. With Raney Ni and NH_2NH_2 in EtOAc,[7] however, smooth reduction occurs to afford the diamines **2a**−**c**. As shown in Figure 1, these in turn have been converted to a variety of amides **3a**−**h** (O-dealkylation of **3a**−**c** yields the calix[4]arenetetrols **5a** from **3a**−**c, 5b** from **3d**−**f,** and **5c** from **2a**−**c**), *p*-toluenesulfonamide **4**, the "deep pocket" imines **12a**−**d**, and the intramolecularly bridged compounds **6a**−**c**, **7a**−**c**, and **8a**−**d**.

The building of upper rim bridged and deep pocket calixarenes is of particular interest to a program in this laboratory involving calixarenes as catalysts.[8] Treatment of **2a**−**c** with diacid chlorides containing four or more methylene groups separating the chlorocarbonyl moieties resulted in intramolecular bridging to yield **6a**−**c** from **2a**, **7a**−**c** from **2b**, and **8a**−**d** from **2c**, as shown in Figure 2. The shorter succinoyl dichloride, however, failed to bridge the amino groups and, instead, gave **9** (after ethanolysis of the intially formed diacid chloride) which was also prepared by treatment with ethyl succinoyl monochloride. Similarly, terphthaloyl dichloride yielded **10** (after hydrolysis of the initially formed diacid chloride) (for structures, see Chart 1). A reaction reciprocally related to the conversion of **2c** to **10** has been reported by Jørgensen and co-workers[9] in which a 5,17-bischlorocarbonylcalix[4]arene was treated with *p*-phenylenediamine. In this case only intermolecularly bridged compounds were isolated, the biscalix[4]arene in 19.5% yield along with much smaller amounts of higher oligomers including a trace of the tetrakiscalix[4]arene.

Compounds **3d**,**f**,**g**, **4**, and **10** might be considered as members of the deep pocket family of calixrenes in which substituents of significant bulk occupy the upper rim, as also are the imines **11a**−**d** and **12a,b** obtained by reaction of **2c** with aromatic aldehydes and ketones.

Experimental Section[10]

5,17-Bisamino-25,26,27,28-tetrakis(benzyloxy)calix[4]-arene (2a) (Cone Conformer). A 1.0-g sample of Raney nickel was added to a solution of 8.80 g (10 mmol) of 5,17-bisnitro-25,26,27,28-tetrakis(benzyloxy)calix[4]arene (**1a)** in 200 mL of EtOAc. MeOH (150 mL) was added followed by 30 mL of $NH_2NH_2{\cdot}H_2O$ in portions at room temperature with occasional stirring. The reaction mixture was refluxed 5 h, another 20 mL of $NH_2NH_2{\cdot}H_2O$ was added, and the mixture was refluxed another 6 h. It was filtered, and the residue was washed with CH_2Cl_2 and Me_2CO. The combined filtrate was concentrated under reduced pressure and poured dropwise over ice cold water with stirring to give a white precipitate (turned to light brown on exposure to air) which was removed by filtration, dried, and trituarated with MeOH to give 6.2 g (76%) of **2a**: mp 210−211

(1) Paper no. 50 in a series entitled *Calixarenes*. For paper no. 49 cf.: Xie, D.; Gutsche, C. D. *J. Org. Chem*. **1999**, *64*, 9270.

(2) Gutsche, C. D.; Iqbal, M. *Org. Synth*. **1990**, *68*, 234.

(3) (a) Gutsche, C. D. Calixarenes Revisited. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry: London, 1998. (b) Böhmer, V. Calixarenes, Macrocycles with (Almost) Unlimited Possibilties. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713−745. (c) Gutsche, C. D. Calixarenes. *Aldrichimica Acta* **1995**, *28*, 3−9. (d) *Calixarenes, A Versatile Class of Macrocyclic Compounds*; Vicens, J., Böhmer, V., Eds.; Kluwer: Dordrecht, The Netherlands, 1991. (e) Gutsche, C. D. Calixarenes. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry: London, 1989.

(4) Sharma, S. K.; Gutsche, C. D. *J. Org. Chem*. **1996**, *61*, 2564.

(5) Zhang, W.-C.; Zheng, Y.-S.; Huang, Z.-T. *Synthetic Commun*. **1997**, *27*, 3763 have described a nitration procedure using KNO_3 and $AlCl_3$ in MeCN at 0 °C that is stated to give pure *p*-nitrocalix[4]arene, *p*-nitrocalix[6]arene, and *p*-nitrocalix[8]arene in yields of 84, 89, and 84%, respectively. Attempts in our laboratories to reproduce these results, however, have yielded mixtures in all cases, leading to considerably lower yields of pure *p*-nitrocalix[4]arene in the first case and to no isolable product in the other two cases. The procedure for generating *p*-nitrocalix[4]arene and *p*-nitrocalix[8]arene were studied under a variety of conditions in which the ratio of reactants, the temperature, and the time of reaction were varied. Under none of these conditions could the reported data be reproduced.

(6) (a) van Loon, J.-D.; Arduini, A.; Coppi, L.; Verboom, W.; Pochini, A.; Ungaro, R.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem*. **1990**, *55*, 5639. (b) van Loon, J.-D.; Arduini, A.; Verboom, W.; Ungaro, R.; van Hummel, G. J.; Harkema, S. Reinhoudt, D. N. *Tetrahedron Lett*. **1989**, *30*, 2681. (c) Verboom, W.; Durie, A.; Egberink, R. J. M.; Asfari, Z.; Reinhoudt, D. N. *J. Org. Chem*. **1992**, *57*, 1313. (d) Timmerman, P.; Verboom, W.; Reinhoudt, D. N.; Arduini, A.; Grandi, S.; Sicuri, A. R.; Pochini, A.; Ungaro, R. *Synthesis* **1994**, 185.

(7) Yang, X.; McBranch, D.; Swanson, B.; Li, DeQuan *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 538.

(8) Xie, D.; Gutsche, C. D. *J. Org Chem*. **1999**, *64*, 9270.

(9) Jøorgensen, M.; Larsen, M.; Sommer-Larsen, P.; Petersen, W. B.; Eggert, H. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2851.

(10) Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Dichloromethane was used as HPLC-grade. Column chromatography was carried out with Aldrich 70−230 mesh, 60-Å silica gel. Thin-layer chromatography (TLC) was performed on 250-μm silica gel plates containing a fluorescent indicator. Melting points were taken in sealed and evacuated melting point capillary tubes on a MEL-Temp apparatus (Laboratory Devices, Cambridge, MA) using a 400 °C thermometer calibrated against a thermocouple and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer, and the chemical shifts are reported as δ values with units of parts-per-million (ppm). ^{1}H NMR spectra are referenced to tetramethylsilane (TMS) at 0.00 ppm as an internal standard and recorded at room temperature (20 ± 1 °C), and ^{13}C NMR spectra are referenced to either $CDCl_3$ (77.00 ppm), DMSO-d_6 (40.0 ppm) or to TMS (0.00 ppm) and also recorded at room temperature (20 ± 1 °C). Microanalytical samples were dried for at least 48−72 h at 111 °C (toluene) or at 140 °C (xylene) at 1−2 mm, and the analyses were carried out by Desert Laboratories, Tucson, AZ. Solvent of crystallization was retained in some of the analytical samples and affected the elemental analysis. In such cases, best fits between the analytical values and appropriate increments of the solvents were used.[11]

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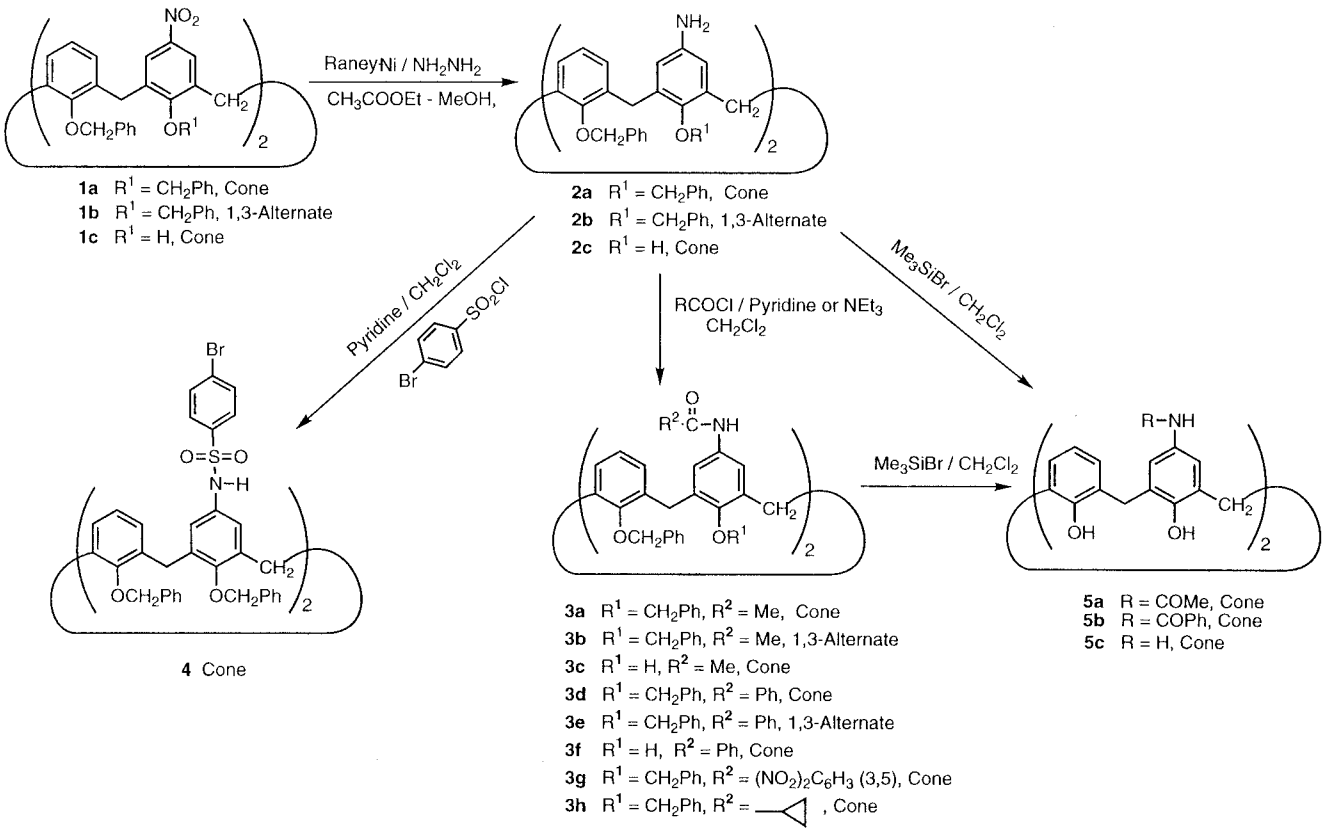


Figure 1. Synthesis and derivatization of 5,17-diaminocalix[4]arenes.

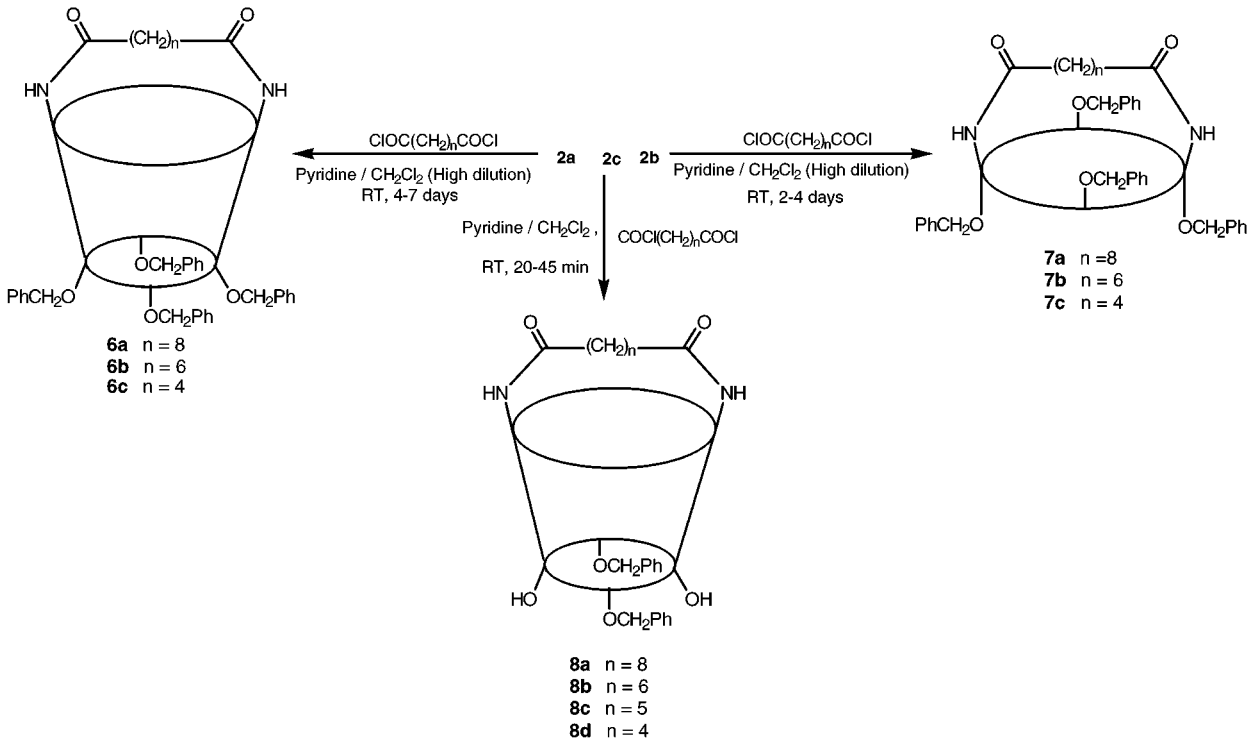
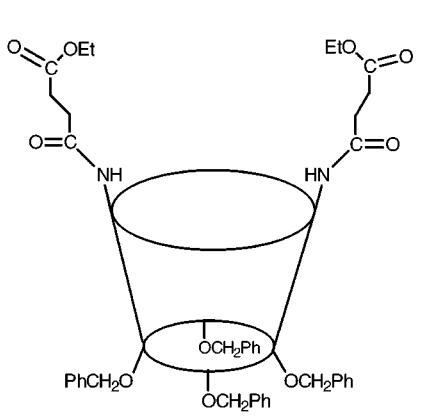


Figure 2. Upper rim bridged 5,17-diaminocalix[4]arenes.

°C; ^{1}H NMR ($CDCl_3$) δ 7.32−7.15 (m, 20), 6.58−6.56 (m, 6), 5.88 (s, 4), 4.91 (s, 4), 4.83 (s, 4), 4.13 (d, 4, J = 13.5 Hz), 2.81 (d, 4, J = 13.5 Hz), 2.90 (bs, 4); ^{13}C NMR ($CDCl_3$) δ 155.91, 149.10, 141.13, 138.48, 138.28, 136.17, 135.84, 130.03, 128.73, 128.60, 128.39, 128.29, 128.11, 128.07, 122.51, 116.27, 76.87, 76.58, 31.84. Anal. Calcd for $C_{56}H_{50}N_2O_4$: C, 82.53; H, 6.18. Found C, 82.63; H, 6.26.

5,17-Bisamino-25,26,27,28-tetrakis(benzyloxy)calix[4]-arene (2b) (1,3-Alternate Conformer). To a mixture of 1.0 g of Raney nickel and 4.40 g (5 mmol) of 5,17-bisnitro-25,26,27,28-tetrakis(benzyloxy)calix[4]arene (**1b**) in 100 mL of EtOAc and 50 mL of MeOH was added 50 mL of $NH_2NH_2 \cdot H_2O$ in portions. The reaction mixture was refluxed 10 h and then worked up as described above for **2a** to give 2.84 g (70%) of **2b**: mp 212−214

Chart 1



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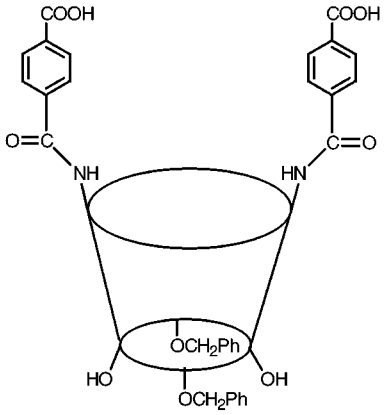

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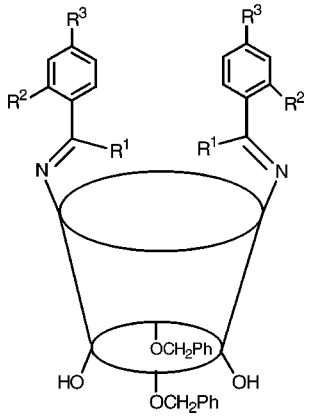
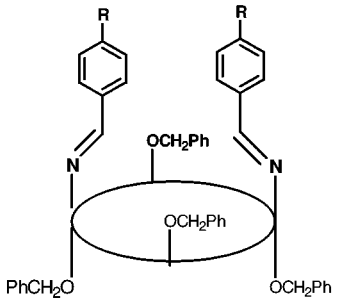


11a $R^1 = R^2 = R^3 = H$
11b $R^1 = R^2 = H$, $R^3 = OMe$
11c $R^1 = R^3 = H$, $R^2 = OMe$
11d $R^1 = Me$, $R^2 = R^3 = H$



12a R = H
12b R = OCH_3

°C; ^{1}H NMR ($CDCl_3$) δ 7.55 (t, 4, J = 7.5 Hz), 7.45−7.35 (m, 12), 7.20 (d, 4, J = 6.6 Hz), 6.69 (d, 4, J = 7.5 Hz), 6.48 (t, 2, J = 7.2 Hz), 6.05 (s, 4), 4.93 (s, 4), 4.87 (s, 4), 3.58 (dd, 8, J = 14.7 Hz), 2.82 (bs, 4); ^{13}C NMR ($CDCl_3$) δ 156.06, 148.99, 140.53, 139.33, 138.79, 134.71, 134.10, 131.60, 128.53, 128.38, 128.05, 127.12, 127.05, 126.83, 122.56, 118.69, 72.23, 71.52, 37.75. Anal. Calcd for $C_{56}H_{50}N_2O_4$: C, 82.53; H, 6.18, N, 3.44. Found: C, 82.08; H, 6.21; N, 3.30.

5,17-Bisamino-26,28-dibenzyloxycalix[4]arene-25,27-diol (2c) (Cone Conformer). To a mixture of 0.5 g of Raney nickel and 3.50 g (5 mmol) of 5,17-bisnitro-26,28-dibenzyloxycalix[4]-arene-25,27-diol (**1c**) in 100 mL of EtOAc and 100 mL of MeOH was added 20 mL of $NH_2NH_2 \cdot H_2O$ in portions. The reaction mixture was refluxed 10 h and then worked up as described above for **2a** to give 2.28 g (72%) of **2c**: mp 170 °C (softening), 246−250 °C; ^{1}H NMR ($CDCl_3$) δ 7.70−7.58 (m, 4), 7.34−7.32 (m, 6), 7.08 (s, 2), 6.86 (d, 4, J = 7.5 Hz), 6.70 (t, 2, J = 8.4 and 7.2 Hz), 6.44 (s, 4), 5.00 (s, 4), 4.25 (d, 4, J = 13.2 Hz), 3.17 (d, 4, J = 13.2 Hz), 3.20−2.90 (b, 4); ^{13}C NMR ($CDCl_3$) δ 152.33, 146.61, 138.31, 137.11, 133.65, 129.24, 129.01, 128.29, 127.95, 127.87, 125.53, 116.34, 78.56, 31.83.

5,17-Bis(*N*-acetamido)-25,26,27,28-tetrakis(benzyloxy)-calix[4]arene (3a) (Cone Conformer). A stirred solution of 0.21 g (0.25 mmol) of **2a** in 20 mL of HPLC-grade CH_2Cl_2 was treated with 0.5 mL of pyridine or triethylamine followed by 1.0 mL of acetyl chloride (vigorous reaction). The reaction mixture was stirred at room temperature for 10 min, and another 10 mL of CH_2Cl_2 was added to reduce the viscosity. After 3 h of standing at room temperature, the contents of the flask were poured over ice-cold water and neutralized with 20% HCl to give a white solid which was removed by filtraton and triturated with *n*-hexane followed by MeOH to yield 0.20 g (90%) of **8a**: mp 144−146 (softening), 240−241 °C; ^{1}H NMR ($CDCl_3$) δ 7.31 (m, 20), 6.78 (bs, 6), 6.78−6.76 (m, 6), 6.34 (s, 4), 5.06 (s, 4), 4.75 (s, 4), 4.15 (d, 4, J = 13.5 Hz), 2.89 (d, 4, J = 13.5 Hz), 1.93 (s, 6); ^{13}C NMR ($CDCl_3$) δ 168.67, 155.78, 152.76, 137.87, 136.47, 134.92, 131.88, 130.46, 129.56, 129.21, 128.99, 128.74, 128.60, 128.30, 128.15, 122.80, 121.64, 77.39, 76.14, 31.74, 24.49. Anal. Calcd for $C_{60}H_{54}N_2O_6 \cdot H_2O$:[11] C, 78.60; H, 5.90. Found: C, 78.58; H, 6.15.

Using the procedure described above for the preparation of **3a**, the following compounds were synthesized.

5,17-Bis(*N*-acetamido)-25,26,27,28-tetrakis(benzyloxy)-calix[4]arene (3b) (1,3-alternate conformer): yield, 86%; mp 255−257 °C; ^{1}H NMR ($CDCl_3$) δ 7.44−7.37 (m, 12), 7.24−7.12 (m, 18), 6.71 (s, 4), 6.69 (d, 4, J = 7.5 Hz), 6.45 (t, 2, J = 7.2 Hz), 6.13 (bs, 2), 4.82 (s, 8), 3.60 (s, 8), 1.96 (s, 6). Anal. Calcd for $C_{60}H_{54}N_2O_6 \cdot {}^1/_2H_2O$:[11] C, 79.05; H, 5.94. Found: C, 79.36; H, 6.10.

5,17-Bis(*N*-acetamido)-26,28-dibenzyloxycalix[4]arene-26,28-diol (3c) (cone conformer): yield, 80%; mp 285−286 °C; ^{1}H NMR ($CDCl_3$) δ 8.64 (s, 2), 7.83 (s, 2), 7.63−7.60 (m, 4), 7.41−7.36 (m, 6), 7.25 (s, 4), 6.96 (d, 4, J = 7.8 Hz), 6.77 (t, 2, J = 7.5 Hz), 5.09 (s, 4), 4.26 (d, 4, J = 12.9 Hz), 3.39 (d, 4, J = 12.9 Hz), 2.08 (s, 6). Anal. Calcd for $C_{46}H_{42}N_2O_6 \cdot {}^1/_2H_2O$:[11] C, 75.91; H, 5.95. Found: C, 75.78; H, 5.85.

5,17-Bis(*N*-benzamido)-25,26,27,28-tetrakis(benzyloxy)-calix[4]arene (3d) (cone conformer): yield, 82%; mp 282−284 °C; ^{1}H NMR ($CDCl_3$) δ 7.66−7.60 (m 6), 7.35−7.19 (m, 24), 6.79 (s, 4), 6.71−6.70 (m, 6), 5.02 (s, 4), 4.87 (s, 4), 4.19 (d, 4, J = 13.5 Hz), 2.93 (d, 4, J = 13.8 Hz). Anal. Calcd for $C_{70}H_{58}N_2O_6$: C, 82.17; H, 5.71. Found: C, 82.24; H, 5.85.

5,17-bis(*N*-benzamido)-25,26,27,28-tetrakis(benzyloxy)-calix[4]arene (3e) (1,3-alternate conformer): yield, 90%; mp 282−283 °C; ^{1}H NMR ($CDCl_3$) δ 7.66−7.53 (m, 6), 7.48−7.38 (m, 10), 7.21−7.15 (m, 12), 7.03−7.02 (m, 2), 6.92 (s, 4), 6.84 (s, 2), 6.69 (d, 4, J = 7.5 Hz), 6.47 (t, 2, J = 7.5 Hz), 4.86 (s, 8), 3.65 (s, 8). Anal. Calcd for $C_{70}H_{58}N_2O_6$: C, 82.17; H, 5.71. Found: C, 82.40; H, 5.64.

5,17-Bis(*N*-benzamido)-26,28-dibenzyloxycalix[4]arene-25,27-diol (3f) (cone conformer): yield, 78%; mp 274−275 °C;

(11) The presence of a complexed water molecule was qualitatively supported by the appearance of a broad signal in its ^{1}H NMR spectrum. A spectrum in $CDCl_3$ alone showed a peak at δ 1.6 ppm and DMSO-d_6 at δ 3.4 ppm.

^{1}H NMR ($CDCl_3$) δ 8.16 (d, 4, J = 7.5 Hz), 7.86 (d, 4, J = 6.9 Hz), 7.75 (s, 1), 7.68−7.62 (m, 6), 7.55−7.44 (m, 6), 7.40−7.39 (m, 6), 6.94 (d, 4, J = 7.5 Hz), 6.74 (t, 2, J = 7.5 Hz), 5.06 (s, 4), 4.31 (d, 4, J = 13.2 Hz), 3.35 (d, 4, J = 13.2 Hz). Anal. Calcd for $C_{56}H_{46}N_2O_6 \cdot {}^1/_2H_2O$:[11] C, 78.95; H, 5.56. Found: C, 79.17; H, 5.35.

5,17-Bis(*N*-[3,5-dinitrobenz]amido)-25,26,27,28-tetrakis-(benzyloxy)calix[4]arene (3g) (cone conformer): yield, 51%; mp 254−255 °C; ^{1}H NMR ($CDCl_3$) δ 8.94 (s, 2), 8.78 (bs, 4), 8.29 (s, 2), 7.34−7.18 (m, 20), 6.83−6.72 (m, 10), 5.09 (s, 4), 4.82 (s, 4), 4.19 (d, 4, J = 13.5 Hz), 2.91 (d, 4, J = 13.2 Hz). Anal. Calcd for $C_{70}H_{54}N_6O_{14} \cdot {}^1/_2H_2O$:[11] C, 69.35; H, 4.57. Found: C, 69.19; H, 4.52.

5,17-Bis(*N*-cyclopropylamido)-26,28-dibenzyloxycalix[4]-arene-25,27-diol (3h) (cone conformer): yield, 67%; mp 290−293 °C; ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ 7.12 (s, 2), 7.79 (s, 2), 7.61 (bs, 4), 7.35 (bs, 6), 7.28 (s, 4), 6.95 (d, 4, J = 5.4 Hz), 6.93 (t, 2), 5.00 (s, 4), 4.23 (d, 4, J = 12.3 Hz), 3.27 (d, 4, J = 12.9 Hz), 1.68 (bs, 2), 0.93 (bs, 4), 0.74 (bs, 4H). Anal. Calcd for $C_{50}H_{46}N_2O_6 \cdot {}^1/_2H_2O$:[11] C, 77.00; H, 6.07. Found: C, 76.82; H, 5.71.

5,17-Bis(*N*-[4′-bromobenzenesulfanamido)-25,26,27,28-tetrakis(nenzyloxy)calix[4]arene (4) (Cone Conformer). To a solution of 0.20 g (0.25 mmol) of **2a** in 20 mL of HPLC-grade CH_2Cl_2 was added 5 drops of pyridine followed by 0.9 g of 4-bromobenzenesulfonyl chloride, and the reaction mixture was stirred at room temperature for 1 h (color becomes dark brown to red). It was poured into cold water and neutralized with 50% HCl to give a brown semisolid which was removed by spatula and allowed to dry for 30 min. Trituration with MeOH left a solid that was dried to give 0.26 g (85%) of **4a**: mp 115−117 °C; ^{1}H NMR ($CDCl_3$) δ 7.54 (d, 4, J = 8.1 Hz), 7.45 (d, 4, J = 7.8 Hz), 7.31−7.17 (m, 20), 6.57 (bs, 6), 6.08 (s, 4), 4.97 (s, 4), 4.76 (s, 4), 4.04 (d, 4, J = 13.2 Hz), 2.74 (d, 4, J = 13.5 Hz); ^{13}C NMR ($CDCl_3$) δ 155.53, 153.56, 138.55, 137.80, 137.40, 136.01, 135.88, 132.22, 130.44, 130.25, 129.30, 128.89, 128.48, 128.44, 128.27, 127.80, 123.66, 123.08, 77.15, 76.43, 31.49. Anal. Calcd for $C_{68}H_{56}N_2S_2Br_2O_8 \cdot H_2O$:[11] C, 64.26; H, 4.43. Found: C, 64.25; H, 4.60.

5,17-Bis(*N*-benzamido)calix[4]arene-25,26,27,28-tetrol (5a) (Cone Conformer). A mixture of 0.42 g (0.5 mmol) of **3f** in 15 mL of HPLC-grade CH_2Cl_2 and 0.5 mL of Me_3SiBr in a l50-mL round-bottomed flask was stirred for 2 h at room temperature. Some white solid material separated, and the mixture was left overnight at room temperature. Excess CH_2Cl_2 was removed under reduced pressure, and the concentrated material was poured into ice-cold water to give a precipitate which was removed by filtration. It was triturated with *n*-hexane to yield 0.27 g (82%) of **5a** as a white solid: mp 354−355 °C; ^{1}H NMR ($CDCl_3$ + 2 drops of DMSO-d_6) δ 9.87 (s, 4), 8.92 (s, 2), 7.84(d, 4, J = 7.8 Hz), 7.47−7.35 (m, 10), 7.10 (d, 4, J = 7.5 Hz), 6.72 (t, 2, J = 7.8 and 7.5 Hz), 4.22 (b, 4), 3.56 (b, 4); ^{13}C NMR ($CDCl_3$ + 2 drops of DMSO-d_6) δ 166, 149.49, 145.10, 135.13, 133.00, 131.41, 129.03, 128.67, 128.32, 128.13, 127.64, 122.40, 121.94, 31.55. Anal. Calcd for $C_{42}H_{34}N_2O_6 \cdot {}^1/_2H_2O$:[11] C, 75.10; H, 5.25. Found: C, 75.15; H, 5.11.

5,17-Bis(*N*-acetamido)calix[4]arene-25,26,27,28-tetrol (5b) (Cone Conformer). A mixture of **3c** (0.35 g, 0.5 mmol) and 0.5 mL of Me_3SiBr in 15 mL of HPLC-grade CH_2Cl_2 was stirred for 2 h at room temperature, and the reaction was worked up as described above to give the crude product. An analytical sample of **5b** was obtained by stirring with *n*-hexane to yield 0.24 g (90%) of a colorless solid: mp 297−301 °C; ^{1}H NMR ($CDCl_3$ + 1 drop of DMSO-d_6) δ 9.80 (bs, 4), 9.16 (s, 4), 7.04 (d, 4, J = 7.5 Hz), 6.60 (t, 2, J = 7.2 and 7.5 Hz), 3.70−3.90 (b, 8), 2.02 (s, 6); ^{13}C NMR (DMSO-d_6) δ 167.91, 150.22, 144.75, 133.28, 128.85, 128.56, 121.12, 120.03, 31.15, 30.92, 23.97. Anal. Calcd for $C_{32}H_{30}N_2O_6 \cdot {}^3/_4H_2O\,{}^1/_4CH_2Cl_2$:[11] C, 67.56; H, 5.63. Found: C, 67.46; H, 5.40.

5,17-Diaminocalix[4]arene-25,26,27,28-tetrol (5c) (Cone Conformer). A mixture of **2a** (0.40 g, 0.5 mmol) and 0.8 mL of Me_3SiBr in 15 mL of CH_2Cl_2 was stirred for 2 h at room temperature, and the reaction was worked up as described above. An analytical sample of **5c** was obtained by stirring the product with *n*-hexane to yield 0.16 g (72%)of a colorless solid: mp 330 °C (softening), 345 (dec) °C; ^{1}H NMR (DMSO-d_6) δ 9.80−9.50 (b, 4), 7.12 (d, 4, J = 7.5 Hz), 7.06 (s, 4), 6.64 (t, 2, J = 7.2 Hz), 4.20−3.50 (b, 12); ^{13}C NMR (DMSO-d_6) δ 150.39, 149.73, 130.09, 129.03, 127.95, 123.69, 123.27, 120.96, 30.53. Compound **5c** was converted to **5a** (vide supra) to confirm its structure.

Bridged Compound 6a (Cone Conformer). A 0.81-g (0.1 mmol) sample of **2a** dissolved in 500 mL of HPLC-grade CH_2Cl_2 was placed in a 500-mL dropping funnel, and 0.40 g (0.15 mmol, 1.5 equiv) of sebacoyl chloride was dissolved in 250 mL of CH_2Cl_2 was placed in a 250-mL dropping funnel. To a stirred mixture of 750 mL of CH_2Cl_2 and 0.5 mL of pyridine in a 3-L round-bottomed flask at room temperature were added 10 mL from the 500-mL funnel and 5 mL from the 250-mL funnel. This addition procedure was repeated every 30 min over a period of 5 days. The reaction mixture was stirred an addtional 2 days, and the solvent was removed under reduced pressure to leave a brownish semisolid. This was triturated with *n*-hexane to leave a light yellow material which was separated by filtration and dissolved in MeOH. The hexane-soluble portion, consisting of unreacted acid chloride and pyridine, was discarded. The hexane-insoluble portion was again dissolved in a minimum amount of CH_2Cl_2, poured over *n*-hexane to produce a light yellow precipitate, filtered, and dried to give 0.82 g of solid. This was dissolved in 100 mL of CH_2Cl_2 and treated with activated charcoal to remove the color and then filtered, concentrated, and passed through a silica gel column (eluted with 1:3 EtOAc−CH_2Cl_2) to give 0.63 g (64%) of **6a** as a white powder. An analytical sample was obtained by triturating with *n*-hexane: mp 264−267 °C; ^{1}H NMR ($CDCl_3$) δ 7.33 (bs, 8), 7.25−7.08 (m, 12), 7.04−7.01 (m, 4), 6.93−6.85 (m, 4), 6.20 (s, 4), 5.22 (s, 4), 4.62 (s, 4), 4.13 (d, 4, J = 13.3 Hz), 2.88 (d, 4, J = 13.5 Hz), 2.08 (t, 4, J = 5.7 Hz), 1.61 (m, 4), 1.31 (m, 8); ^{13}C NMR ($CDCl_3$) δ 171.52, 156.02, 152.54, 137.96, 137.82, 137.36, 133.90, 132.12, 130.87, 129.38, 129.33, 128.76, 128.40, 128.11, 128.03, 122.86, 121.35, 78.00, 75.69, 36.01, 31.84, 27.06, 24.90, 22.91; FAB MS *m/e* 981.8 [M^+, calcd 981.24]. Anal. Calcd for $C_{66}H_{64}N_2O_6$: C, 80.79; H, 6.57. Found: C, 80.22; H, 6.62.

Bridged compound 6b (cone conformer) was prepared in similar fashion from **2a** and suberoyl chloride and obtained in 67% crude yield as a white solid: mp 168−170 °C; ^{1}H NMR ($CDCl_3$) δ 7.32 (s, 8), 7.30−7.09 (m, 12), 7.05 (d, 4, J = 7.5 Hz), 6.93 (t, 2, J = 6.7 Hz), 6.34 (s, 4), 5.24 (s, 4), 4.78 (b, 2), 4.62 (s, 4), 4.13 (d, 4, J = 13.3 Hz), 2.86 (d, 4, J = 13.4 Hz), 2.14 (bs, 4), 1.60 (b, 4), 1.20 (b, 4); ^{13}C NMR ($CDCl_3$) δ 171.52, 155.95, 151.94, 137.91, 137.71, 137.57, 133.81, 132.91, 130.90, 129.48, 129.33, 128.74, 128.42, 128.14, 128.03, 122.74, 119.23, 78.05, 75.70, 36.58, 31.88, 26.92, 24.90; FAB MS *m/e* 953.9 [M^+, calcd 953.19]. Anal. Calcd for $C_{64}H_{60}N_2O_6 \cdot {}^3/_2H_2O$:[11] C, 78.42; H, 6.48. Found: C, 78.45; H, 6.68.

Bridged compound 6c (cone conformer) was prepared in similar fashion from **2a** and adipoyl chloride and obtained in 64% yield: mp 125 (softening), 202−204 °C; ^{1}H NMR ($CDCl_3$) δ 7.38−7.30 (m, 10), 7.22−7.00 (m, 16), 6.93−6.88 (m, 2), 6.09 (s, 4), 5.16 (s, 4), 4.61 (s, 4), 4.15 (d, 4, J = 13.5 Hz), 2.89 (d, 4, J = 13.8 Hz), 2.17 (bs, 4), 1.67 (bs, 4); ^{13}C NMR ($CDCl_3$) 171.62, 156.08, 152.39, 137.88, 137.81, 137.53, 134.11, 132.24, 130.78, 129.45, 129.09, 128.79, 128.35, 128.09, 127.99, 122.57, 120.13, 77.81, 75.71, 35.50, 31.77, 24.59; FAB MS *m/e* 925.7 [M^+, calcd 925.17]. Anal. Calcd for $C_{62}H_{56}N_2O_6 \cdot 2H_2O$:[11] C, 77.48; H, 6.29. Found: C, 77.48; H, 6.14.

Bridged compound 7a (1,3-alternate conformer) was prepared in similar fashion from **2b** and sebacoyl chloride and obtained in 57% yield as a white powder which was triturated with *n*-hexane followed by MeOH to give an analytical sample: mp 295−296 °C, ^{1}H NMR ($CDCl_3$) δ 7.47−7.38 (m, 16), 7.24−7.22 (m, 4), 6.87 (s, 4), 6.67 (d, 4, J = 7.2 Hz), 6.50−6.47 (m, 4), 4.83 (s, 8), 3.46 (s, 8), 2.26 (t, 4, J = 6.4 Hz), 1.87 (b, 4), 1.64 (s, 8); ^{13}C NMR ($CDCl_3$ + 2 drops of DMSO-d_6) δ 170.86, 155.83, 152.21, 138.00, 137.81, 133.85, 133.10, 131.99, 131.29, 128.58, 128.17, 127.62, 127.20, 126.87, 126.67, 122.36, 121.54, 73.69, 71.72, 37.35, 36.77, 29.03, 28.81, 25.10. Anal. Calcd for $C_{66}H_{64}N_2O_6$: C, 80.79; H, 6.57. Found: C, 80.45; H, 6.45.

Bridged compound 7b (1,3-alternate conformer) was prepared in similar fashion from **2b** and suberoyl chloride and obtained in 55% yield as a white powder: mp 229−231 °C, ^{1}H NMR ($CDCl_3$) δ 7.64 (d, 4, J = 7.0 Hz), 7.53−7.36 (m, 16), 6.89 (s, 4), 6.78 (d, 4, J = 6.0 Hz), 6.57 (t, 2, J = 7.2 and 7.3 Hz), 6.40 (s, 2), 4.84 (s, 4), 4.79 (s, 4), 3.40 (dd, 8, J = 13.44 Hz), 2.32 (bs, 4), 1.91 (bs, 4), 1.63 (bs, 4); ^{13}C NMR ($CDCl_3$) δ 169.96, 156.61, 152.07, 138.60, 138.09, 133.50, 132.89, 131.63, 131.31, 129.50,

128.51, 128.12, 127.86, 127.34, 127.17, 121.41, 121.29, 75.21, 73.25, 37.24, 36.03, 28.39, 25.42. Anal. Calcd for $C_{64}H_{60}N_2O_6$: C, 80.65; H, 6.34. Found: C, 80.41; H, 6.32.

Bridged compound 7c (1,3-alternate conformer) was prepared in similar fashion from **2b** and adipoyl chloride and obtained in 58% yield as a white powder: mp 210−211 °C; ^{1}H NMR ($CDCl_3$) δ 7.69 (d, 4, J = 7.5 Hz), 7.55−7.38 (m, 16), 6.91 (s, 4), 6.85 (d, 4, J = 7.5 Hz), 6.59 (t, 2, J = 7.5 Hz), 6.49 (s, 2), 4.81 (s, 4), 4.77 (s, 4), 3.38 (dd, 8, J = 12.9 Hz), 2.39 (s, 4), 1.90 (s, 4); ^{13}C NMR ($CDCl_3$) δ 170.47, 156.05, 152.08, 138.19, 138.07, 133.50, 132.94, 131.32, 130.59, 129.39, 128.72, 128.36, 128.11, 127.57, 127.46, 121.55, 121.51, 75.84, 74.53, 37.20, 35.07, 25.84. Anal. Calcd for $C_{64}H_{60}N_2O_6$: C, 80.65; H, 6.34. Found: C, 80.75; H, 6.12.

Bridged compound 8a (cone conformer) was prepared in similar fashion via high dilution from **2c** and sebacoyl chloride and obtained in 89% yield as a slightly pink powder. Alternatively, it was prepared via low dilution as follows: 0.62 g (0.1 mmol) of **2c** was dissolved in 150 mL of HPLC-grade CH_2Cl_2, treated with 0.5 mL of pyridine, and stirred for 2 min. A solution of 0.31 g (1.5 equiv) of sebacoyl chloride in 10 mL of CH_2Cl_2 was added dropwise with stirring at room temperature (pale pink color precipitate formed at the time of addition). After all of the sebacoyl chloride had been added, a brown semisolid settled to the bottom of the flask and was partially removed by spatula. The remaining solution was concentrated under reduced pressure and stirred with *n*-hexane, and the pale pink precipitate was removed by filtration and mixed with the previously separated semisolid. This was stirred with MeOH for 2 h to give a pink powder which was further stirred with EtOAc followed by Me_2CO and finally with MeOH to give 0.71 g (85%) of an analytical sample: mp 222−224 °C; ^{1}H NMR (DMSO-d_6) δ 9.51 (s, 2), 7.88 (s, 2), 7.63 (s, 2), 7.39 (s, 6), 7.31 (s, 4), 6.94 (s, 4), 6.81 (s, 2), 5.00 (s, 4), 4.15 (d, 4, J = 15.6 Hz), 3.32 (d, 4, J = 15.6 Hz), 2.21 (s, 4), 1.55 (bs, 4), 1.27 (s, 8); ^{13}C NMR (DMSO-d_6) δ 170.47, 151.72, 148.40, 136.47, 133.39, 130.97, 128.81, 128.53, 128.02, 127.52, 127.29, 125.40, 120.07, 78.08, 36.19, 30.80, 28.72, 25.16. Anal. Calcd for $C_{52}H_{52}N_2O_6 \cdot {}^1/_2H_2O$:[11] C, 77.10; H, 6.60. Found: C, 77.05; H, 6.39.

Bridged compound 8b (cone conformer) was preapred by the low dilution procedure described above from **2c** and suberoyl chloride and obtained in 82% yield: mp 227−228 °C; ^{1}H NMR (DMSO-d_6) δ 9.52 (s, 2), 7.89 (s, 2), 7.63 (s, 4), 7.39 (s, 6), 7.31 (s, 4), 6.95 (d, 4, J = 6.8 Hz), 6.81 (m, 2), 5.01 (s, 4), 4.16 (d, 4, J = 12.2 Hz), 3.30 (b, 4), 2.21 (s, 4), 1.55 (bs, 4), 1.29 (s, 4); ^{13}C NMR (DMSO-d_6) δ 170.49, 151.73, 148.42, 136.47, 133.39, 130.97, 128.75, 128.45, 128.02, 127.48, 127.30, 125.39, 120.13, 78.11, 36.18, 30.80, 28.56, 25.12. Anal. Calcd for $C_{50}H_{48}N_2O_6 \cdot H_2O$:[11] C, 75.93; H, 6.37. Found: C, 75.96; H, 5.96.

Bridged compound 8c (cone conformer) was prepared by the low dilution procedure described above from **2c** and pimeloyl chloride and obtained in 82% yield: mp 230−232 °C; ^{1}H NMR (DMSO-d_6) δ 9.51 (s, 2), 7.87 (s, 2), 7.63 (s, 4), 7.39 (s, 6), 7.31 (s, 4), 6.94 (s, 4), 6.80 (b, 2), 5.00 (s, 4), 4.16 (d, 4, J = 10.74 Hz), 3.34 (b, 4), 2.22 (s, 4), 1.58 (s, 4), 1.31 (s, 2); ^{13}C NMR (DMSO-d_6) δ 170.42, 151.72, 148.41, 136.46, 133.38, 130.92, 128.81, 128.52, 128.01, 127.52, 127.30, 125.35, 120.14, 78.09, 36.03, 30.75, 28.41, 24.97. Anal. Calcd for $C_{49}H_{46}N_2O_6 \cdot H_2O$:[11] C, 75.75; H, 6.23. Found: C, 75.71; H, 5.99.

Bridged compound 8d (cone conformer) was prepared by the low dilution procedure described above from **2c** and adipoyl chloride and obtained in 79% yield: mp 236−238 °C; ^{1}H NMR (DMSO-d_6) δ 9.53 (s, 2), 7.88 (s, 2), 7.64 (s, 4), 7.40 (s, 6), 7.31 (s, 4), 6.95 (d, 4, J = 6.4 Hz), 6.80 (m, 2), 5.01 (s, 4), 4.16 (d, 4, J = 15.9 Hz), 3.30 (bd, 4), 2.24 (s, 4), 1.58 (bs, 4); ^{13}C NMR (DMSO-d_6) δ 170.31, 151.72, 148.44, 136.47, 133.38, 130.89, 128.82, 128.52, 128.02, 127.54, 127.30, 125.37, 120.15, 78.10, 36.06, 30.77, 24.98. Anal. Calcd for $C_{48}H_{44}N_2O_6 \cdot H_2O$:[11] C, 75.57; H, 6.08. Found: C, 75.48; H, 5.87.

5,17-Bis(*N*-3′-carboethoxypropionamido)-25,26,27,28-tetrakis(benzyloxy)calix[4]arene (9) (Cone Conformer). A stirred solution of 0.40 g (0.05 mmol) of **2a** in 50 mL of CH_2Cl_2 was treated with 0.5 mL of pyridine followed by 1.5 mL of ethyl succinoyl monochloride. The reaction mixture was stirred at room temperature for 6 h, and the solvent was removed under reduced pressure to give a semisolid which was passed through a silica gel column (eluted with CH_2Cl_2). The product was dissolved in MeOH and poured over 10% HCl to give a white precipitate which was removed by filtration and dried to yield 0.38 g (67%) of **9**: mp 84−86 °C; ^{1}H NMR (DMSO-d_6) δ 7.51 (s, 2), 7.30−7.00 (m, 2), 6.60 (m, 6), 6.32 (s, 4), 4.93 (s, 4), 4.63 (s, 4), 4.08 (d, 8, J = 7.5 Hz), 2.82 (d, 4, J = 13.5 Hz), 2.60 (bs, 4), 2.40 (bs, 4), 1.21 (t, 6, J = 7.0 Hz); ^{13}C NMR (DMSO-d_6) δ 173.73, 169.71, 155.67, 137.90, 135.94, 135.45, 132.12, 130.23, 129.74, 128.81, 128.50, 128.22, 128.14, 122.65, 120.85, 77.10, 76.37, 61.22, 31.82, 31.70, 29.80, 14.54. Anal. Calcd for $C_{68}H_{66}N_2O_{10}$: C, 76.24; H, 6.21. Found: C, 75.97; H, 6.40.

5,17-Bis(*N*-4′-carboxybenzamido)-26,28-bis(benzyloxy)-calix[4]-arene-25,27-diol (10) (Cone Conformer). A stirred solution of 0.32 g (0.05 mmol) of **2c** in 50 mL of CH_2Cl_2 was treated with 0.5 mL of pyridine followed by 0.5 g (0.25 mmol) of perthaloyl dichloride. The reaction mixture was stirred at room temperature for 6 h, and the solvent was removed under reduced pressure to give a semisolid which was stirred with ice-cold water to furnish a light yellow precipitate. This was stirred with *n*-hexane followed by MeOH to give a white precipitate which was removed by filtration and dried to yield 0.36 g (77%) of **10**: mp 260 °C (softening), 295−296 °C (dec); ^{1}H NMR (DMSO-d_6) δ 13.30 (s, 2), 10.10 (s, 2), 8.06−8.04 (bs, 8), 7.67 (m, 4), 7.53 (s, 4), 7.43 (m, 6), 7.03 (d, 4, J = 6.0 Hz), 6.85 (b, 2), 5.06 (s, 4), 4.23 (d, 4, J = 11.28 Hz), 3.42 (d, 4, J = 11.6 Hz); ^{13}C NMR (DMSO-d_6) δ 166.60, 164.02, 151.75, 149.22, 137.29, 136.48, 134.38, 133.35, 130.02, 129.61, 129.52, 129.39, 128.54, 128.04, 127.57, 127.43, 124.38, 121.25, 78.14, 30.81. Anal. Calcd for $C_{58}H_{46}N_2O_{10} \cdot H_2O$:[11] C, 73.41; H, 5.10. Found: C, 73.65; H, 4.77.

5,17-Bis(*N*-benzylidene)amino-26,28-dibenzyloxycalix-[4]arene-25,27-diol (11a) (Cone Conformer). To a slurry of 0.32 g (0.5 mmol) of **2c** in 50 mL of absolute EtOH was added 1 mL of glacial HOAc followed by dropwise addition of 1.0 mL of benzaldehyde. The resulting yellow solution was refluxed for 2 h and stirred at room temperature an additional 18 h. The solvent was removed under reduced pressure, and the residue was stirred with *n*-hexane to give a light yellow precipitate which was removed by filtration and dried. The product was triturated with MeOH to give 0.33 g (82%) of an analytical sample of **11a** as a white powder: mp 231−233 °C; ^{1}H NMR ($CDCl_3$) δ 8.15 (s, 2), 7.89 (s, 6), 7.66 (m, 4), 7.45 (m, 6), 7.44 (m, 6), 7.09 (s, 4), 6.87 (d, 4, J = 7.1 Hz), 6.61 (t, 2, J = 7.65 and 7.00 Hz), 5.08 (s, 4), 4.34 (d, 4, J = 13.32 Hz), 3.39 (d, 4, J = 12.87 Hz); ^{13}C NMR ($CDCl_3$) δ 157.46, 152.54, 151.88, 142.95, 136.75, 136.66, 132.74, 130.90, 129.33, 128.88, 128.80, 128.56, 128.14, 127.49, 125.62, 121.45, 78.45, 31.62. Anal. Calcd for $C_{56}H_{46}N_2O_4$: C, 82.94; H, 5.72. Found C, 83.31; H, 5.61.

5,17-Bis(*N*-[4′-methoxybenzylidene])amino-26,28-dibenzyloxycalix[4]arene-25,27-diol (11b) (cone conformer) was prepared as described above from **2c** and *p*-methoxybenzaldehyde and obtained as a white powder in 78% yield: mp 262−264 °C; ^{1}H NMR ($CDCl_3$) δ 8.42 (s, 2), 7.84 (s, 2), 7.81 (s, 4), 7.67−7.64 (m, 4), 7.39−7.38 (m, 6), 7.04 (s, 4), 6.97 (d, 4, J = 8.6 Hz), 6.90 (d, 4, J = 7.5 Hz), 6.67 (t, 2, J = 7.53 and 7.1 Hz), 5.07 (s, 4), 4.34 (d, 4, J = 13.3 Hz), 3.85 (s, 6), 3.38 (d, 4, J = 13.32 Hz); ^{13}C NMR ($CDCl_3$) δ 161.84, 156.94, 152.08, 151.89, 143.36, 136.74, 132.87, 130.16, 129.68, 129.28, 128.83, 128.46, 128.09, 127.47, 125.55, 121.25, 114.17, 78.42, 55.30, 31.60. Anal. Calcd for $C_{58}H_{50}N_2O_6$: C, 79.98; H, 5.79. Found: C, 79.74; H, 5.69.

5,17-Bis(*N*-[2′-methoxybenzylidene])amino-26,28-dibenzyloxycalix[4]arene-25,27-diol (11c) (cone conformer) was prepared as described above from **2c** and *o*-methoxybenzaldehyde and obtained as a white powder in 76% yield: mp 287−288 °C; ^{1}H NMR ($CDCl_3$) δ 8.94 (s, 2), 8.13 (d, 2, J = 7.8 Hz), 7.77 (s, 2), 7.66 (m, 4), 7.43−7.38 (m, 8), 7.07 (s, 4), 7.03 (m, 2), 7.94 (m, 6), 6.72 (t, 2, J = 7.5 Hz), 5.08 (s, 4), 4.34 (d, 4, J = 13.02 Hz), 3.91 (s, 6), 3.39 (d, 4, J = 13.8 Hz); ^{13}C NMR ($CDCl_3$) δ 158.89, 152.69, 151.67, 143.43, 136.13, 132.99, 131.95, 129.02, 128.52, 127.92, 127.26, 126.76, 125.84, 124.59, 121.17, 120.41, 110.90, 78.33, 55.33, 31.16. Anal. Calcd for $C_{58}H_{50}N_2O_6 \cdot H_2O$:[11] C, 79.16; H, 5.84. Found: C, 78.98; H, 5.67.

5,17-Bis(*N*-[α-methylbenzylidene])amino-26,28-dibenzyloxycalix[4]arene-25,27-diol (11d) (cone conformer) was prepared as described above from **2c** and acetophenone and obtained in 62% yield: mp 263−265 °C; ^{1}H NMR ($CDCl_3$) δ 7.96 (m, 4), 7.66 (m, 4), 7.59 (s, 2), 7.44 (b, 6), 7.38 (b, 6), 6.85 (d, 4, J = 7.1 Hz), 6.66−6.59 (m, 6), 5.05 (s, 4), 4.35 (d, 4, J = 12.9

Hz), 3.32 (d, 4, J = 13.0 Hz), 2.24 (s, 6); ^{13}C NMR ($CDCl_3$) δ 165.29, 151.88, 149.70, 143.02, 139.95, 136.88, 132.87, 130.16, 129.18, 128.79, 128.30, 127.97, 127.49, 127.42, 127.11, 125.44, 120.02, 78.31, 31.55, 17.36. Anal. Calcd for $C_{58}H_{50}N_2O_4 \cdot H_2O$:[11] C, 81.28; H, 6.12. Found: C, 81.03; H, 5.81.

5,17-Bis(*N*-benzylidene)amino-25,26,27,28-tetrakis-(benzyloxy)calix[4]arene (12a) (1,3-alternate conformer) was prepared as described above from **2b** and benzaldehyde and obtained as a white powder in 76% yield: mp 147−149 °C; ^{1}H NMR ($CDCl_3$) δ 7.66 (s, 2), 7.60−7.57 (m, 4), 7.45−7.33 (m, 12), 7.20−7.11 (m, 12), 6.97−6.95 (m, 2), 6.75−6.72 (m, 8), 6.49 (t, 2, J = 7.2 Hz), 4.87 (s, 8), 3.66 (dd, 8, J = 13.5 Hz); ^{13}C NMR ($CDCl_3$) δ 157.29, 156.08, 154.73, 144.92, 138.04, 137.76, 136.82, 134.63, 133.66, 131.21, 130.41, 128.67, 128.42, 128.35, 127.92, 127.13, 127.07, 126.68, 123.54, 122.33, 72.26, 37.40. Anal. Calcd for $C_{70}H_{58}N_2O_4 \cdot H_2O$:[11] C, 84.06; H, 5.95. Found: C, 84.00; H, 5.83.

5,17-Bis(*N*-[4′-methoxybenzylidene])amino-25,26,27,28-tetrakis(benzyloxy)calix[4]arene (12b) (1,3-alternate conformer) was prepared as described above from **2b** and *p*-methoxybenzaldehyde and obtained in 71% yield: mp 239−241 °C; ^{1}H NMR ($CDCl_3$) δ 7.60 (s, 2), 7.53 (d, 4, J = 7.6 Hz), 7.45−7.38 (m, 6), 7.20−7.12 (m, 12), 7.00−6.95 (m, 2), 6.88 (d, 4, J = 7.8 Hz), 6.74−6.69 (m, 8), 6.49 (t, 2, J = 7.2 Hz), 4.87 (s, 4), 4.86 (s, 4), 3.88 (s, 6), 3.64 (dd, 8, J = 14.9 Hz); ^{13}C NMR ($CDCl_3$) δ 161.50, 156.72, 156.11, 154.38, 145.22, 138.12, 137.83, 134.54, 133.69, 131.21, 130.30, 129.95, 128.42, 127.92, 127.10, 126.90, 126.78, 126.68, 123.41, 122.27, 113.76, 72.37, 72.26, 55.38, 37.38. Anal. Calcd for $C_{72}H_{62}N_2O_6$: C, 82.26; H, 5.94. Found: C, 82.21; H, 6.14.

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