Calixarenes. 40. Arylmethylenation of *p*-(Cyanomethyl)calix[4]arene

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Treatment of tetra-O-substituted *p*-(cyanomethyl)calix[4]arenes **3** and **6** with aromatic aldehydes yields aldol product resulting from condensation at the carbons α to the cyano groups. The products **4** from the tetra-*O*-benzyl compound **3** retain the benzyl groups and are formed in the 1,3-alternate conformation. The products **7** from the tetra-*O*-benzoyl compounds **6**, however, involve loss of the benzoyl groups and are formed in the cone conformation. The same phenolic compounds **7** can be obtained from the *O*-benzyl compounds **4** by Lewis acid-induced removal of the benzyl groups. Reintroduction of the benzyl groups by treating **7** with benzyl bromide produces the tetra-*O*-benzylated product in the cone conformation (**12**) when NaH is used as the base or in the 1,3-alternate conformation (**4**) when K_2CO_3 is used as the base. Benzoylation of **7** produces the tetra-*O*-benzoyl compound in the 1,3-alternate conformation (**10**) when 1-methylimidazole is used as the base or the 1,3-di-*O*-benzoyl compound in a flattened cone conformation (**11**) when $AlCl_3$ is used as the catalyst. ^1H NMR and ^{13}C NMR data provide support for the conformational assignments, and UV data suggest a twisting of the conjugated system in the 2′-substituted compounds **4b/7b** (2′-methoxyphenyl), **4e/7e** (2′-methylphenyl), and **4g/7g** (2′-chlorophenyl).

Calixarenes[1] are cavity-containing macrocyclic compounds[2] that are of interest, *inter alia*, because of their potential to serve as polyfunctional catalysts. For this purpose it is necessary that the calixarenes carry functional groups of one sort or another, and to this end a variety of functionalization procedures have been devised. One of these, designated as the "quinone methide route" is exemplified by the synthesis of *p*-(cyanomethyl)calix[4]arene (**2**) which is readily prepared[3] from *p-tert*-butylcalix[4]arene (**1**)[4] by $AlCl_3$-induced de-*tert*-butylation, aminomethylation with HCHO and Me_2NH, quaternization with MeI, and treatment with NaCN. Earlier work in this laboratory[5–7] focused on the synthetic utility of **2** through the use of aroylation and arylmethylation reactions. The present communication extends this synthetic utility by showing that aromatic aldehydes undergo aldol condensations at the carbons α to the cyano groups of **2**.

When *p*-(cyanomethyl)calix[4]arene (**2**) is treated with benzyl bromide in the presence of K_2CO_3 it undergoes benzylation at all four of the phenolic oxygen atoms to give **3** in the 1,3-alternate conformation,[6,7] in contrast to *p-tert*-butylcalix[4]arene (**1**) which under the same conditions forms the 1,3-dibenzyl ether in a flattened cone conformation.[8] In the presence of stronger bases such as NaH and NaOH, benzylation of **2** occurs not only at the phenolic oxygens but also at the carbons α to the cyano groups.[6,7] We have now shown that treatment of **3** with aromatic aldehydes in the presence of NaH likewise involves reaction at the α-position and yields the aldol products **4a–j** and **5a–d** which are assumed, without substantiating evidence, to adopt the configuration in which the aryl moieties are *trans* to one another (*Z* configuration; priorities are CN > aryl and Ar > H). Since the starting material **3** is frozen in the 1,3-alternate conformation, its products are similarly frozen in this conformation. It is possible, however, to obtain these same structures in the cone conformation by removing and then reintroducing the benzyl groups. Thus, treatment of **4a–j** and **5a–d** with $AlCl_3$ in toluene at room temperature or Me_3SiBr in $CHCl_3$ at reflux temperature provides good yields of the corresponding free phenols **7a–j** and **8a–d** for which the stable conformation is the cone. Treatment of **7a** with benzyl bromide in THF–DMF solution using NaH as the base yields **12**, which is the cone analog of the 1,3-alternate conformer **4a**. Almost certainly the other members of the series **4b–j** and **5a–d** should behave in an identical fashion to give the corresponding cone conformers. Treatment of **7a** with MeI using either NaH or K_2CO_3 as the base yields the corresponding tetramethyl ether **13** which, like the tetramethyl ethers of calix[4]arenes in general, exists as a mixture of rapidly interconverting conformers.[9] On the other hand, treatment of **7a** with *p*-bromobenzenesulfonyl chloride yields a mixture of noninterconverting conformers of the tetra-*p*-bromobenzenesulfonate **14** with NaH as the base; with K_2CO_3 as the base the product is predominately the 1,3-alternate conformer.

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(1) The term "calixarene" is variously employed in different contexts. In colloquial usage (as employed in the Discussion), it implies the presence of hydroxyl groups, as, for instance, in *p-tert*-butylcalix[4]-arene for **1** and *p*-(cyanomethyl)calix[4]arene for **2**. In the more precise and complete specification of a compound (as used in the Experimental Section), it implies only the basic sketeton to which the substituents, including the OH groups, are attached at positions designated by appropriate numbers.

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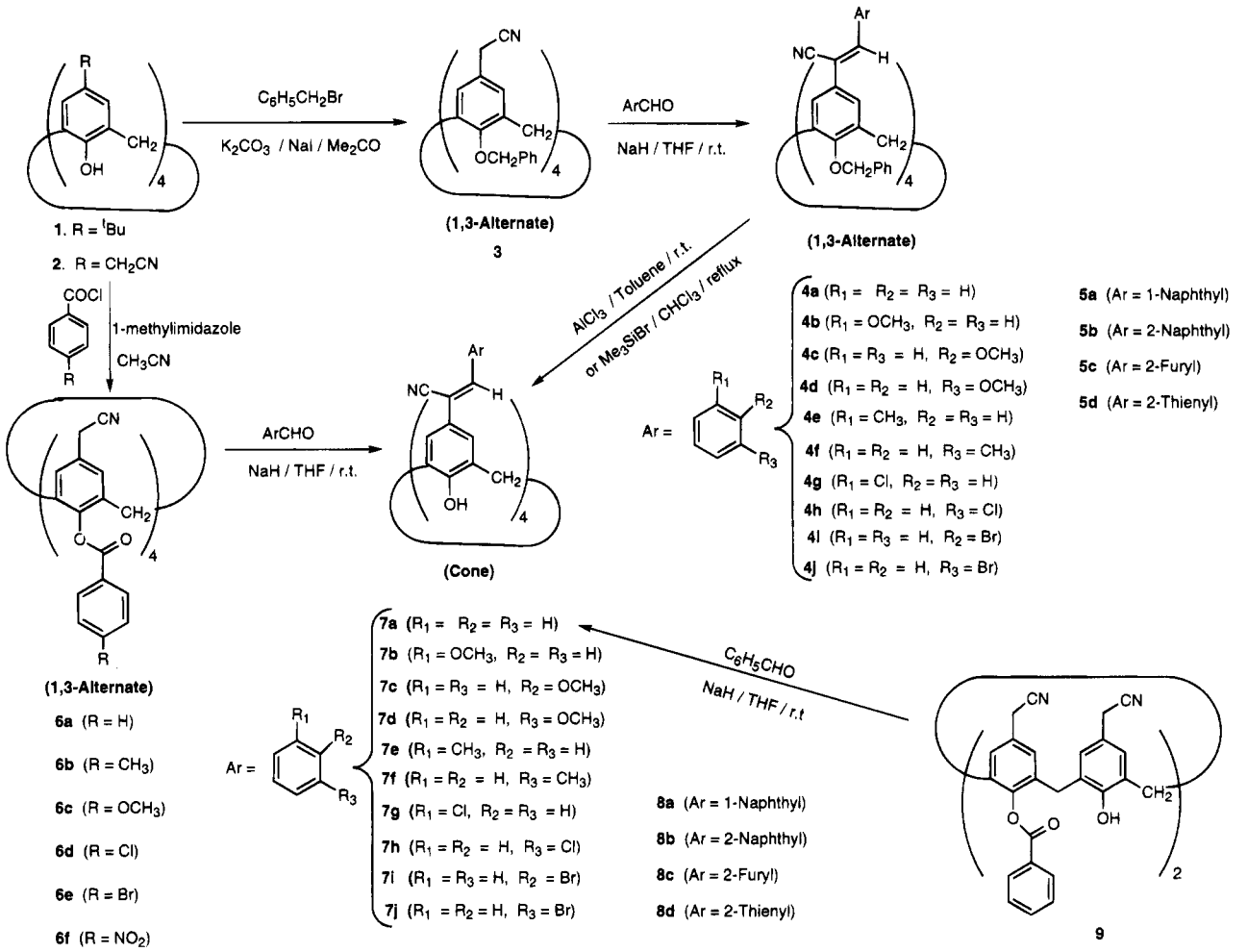
(9) Groenen, L. C.; van Loon, J.-D.; Verboom, W.; Harkema, S.; Casnati, A.; Ungaro, R.; Pochini, A.; Ugozzoli, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 2385.

0022-3263/94/1959-6030$04.50/0

Scheme 1



An easier route to the compounds of series **7** and **8** involves the action of aromatic aldehydes on any of the tetrabenzoates **6a–f**, which can be prepared in good yield by the action of aroyl chlorides on **2** in CH_3CN solution with 1-methylimidazole as the base.[5] Under the same conditions that convert the tetrabenzyl ether **3** to the benzyl ether **4a** upon treatment with ArCHO the tetrabenzoates **6a–f** lose their four aroyl groups and yield the free phenolic aldol products **7a–j** and **8a–d**. The facility with which this cleavage occurs suggests that it might involve an intramolecular route such as that depicted in Scheme 3. In similar fashion the 1,3-dibenzoate **9** yields **7a** when treated with benzaldehyde.

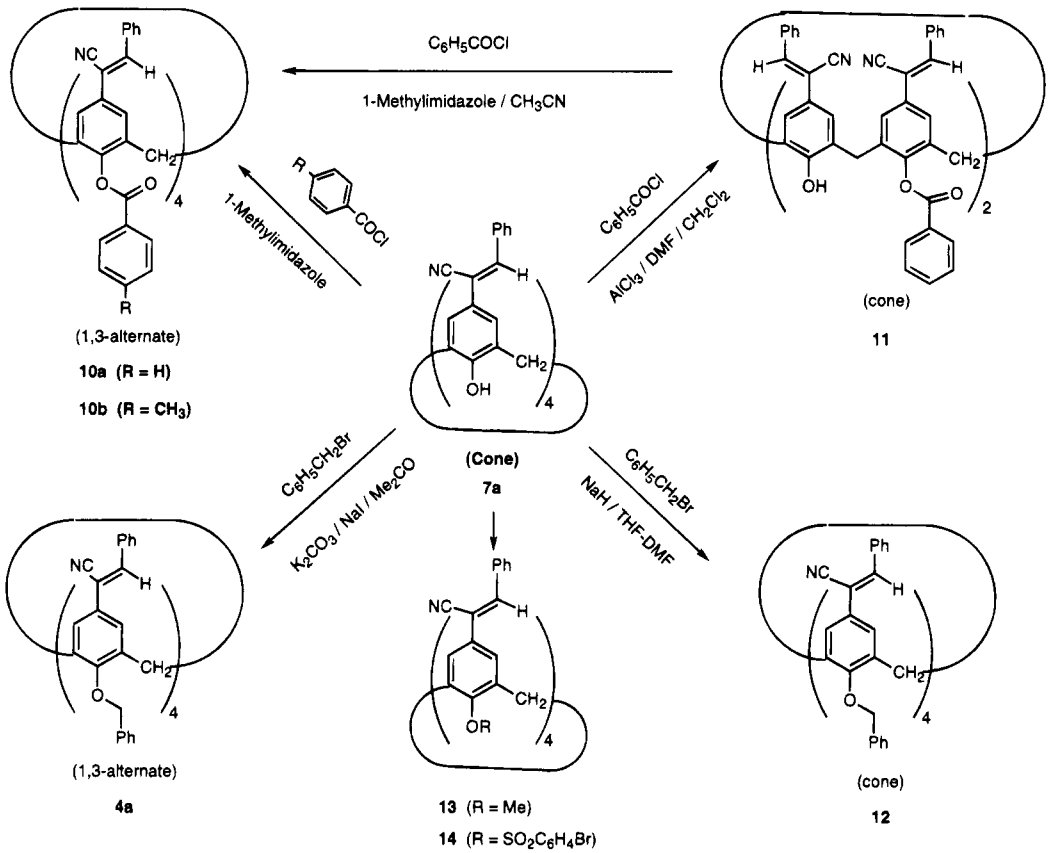
Although the aroylates of the condensation products **7a–j** and **8a–d** are not directly obtainable from **6**, the benzoyl groups that are lost in the fashion described above can be reintroduced in a second step. Thus, treatment of **7a** with aroyl chlorides in CH_3CN solution using 1-methylimidazole as the base provides the tetrabenzoates **10a** and **10b** in the 1,3-alternate conformations. Presumably, the other members of the series **7a–j** should react in a comparable fashion. On the other hand, treatment of **7a** with benzoyl chloride in DMF–CH_2Cl_2 solution with $AlCl_3$ as the catalyst produces the 1,3-dibenzoate **11** in the cone conformation. Similar conformational control through the use of appropriate reaction conditions is demonstrated by the conversion of **7a** to the tetrabenzyl ether in the cone conformation (**12**) by using benzyl bromide in the presence of NaH or in the 1,3-alternate conformation (**4a**) by using benzyl bromide in the presence of K_2CO_3.

The reaction of several other aldehydes and ketones in the base-induced aldol condensation with **3** was investigated, but only starting material was recovered in all cases. Included in the study was acetaldehyde, propionaldehyde, acetone, acetophenone, and benzophenone. Reaction did occur with benzene-1,3-dicarbaldehyde and benzene-1,4-dicarbaldehyde, but the highly refractory and insoluble products could not be characterized and are assumed to be intermolecular condensation products of **3**.

It was anticipated that the cyano groups in the products of arylmethylenation would provide an easy route to the corresponding carboxylic acids. However, treatment of **4a** with H_2SO_4/HOAc under relatively mild conditons simply removed the benzyl groups without affecting the cyano groups, and more strenuous acid treatment of **7a** left it unchanged. Similarly, the action of KOH in aqueous EtOH on **7a** failed to effect hydrolysis, and only starting compound was recovered.

Spectral Properties of the Aldol Products. Tabulations of some of the ^1H NMR and ^{13}C NMR resonances along with the UV absorption characteristics of the aldol products **4**, **5**, **7**, **8**, **10**, and **12** are contained in Tables 1 and 2. The ^1H NMR and ^{13}C NMR spectral data shown in these tables provide strong support for the conformational assignments that have been made. Thus, the appearance of a singlet resonance at δ 3.72 ($\pm$0.09) in the ^1H NMR spectra and a line at δ 37.22 ($\pm$0.70) in the

Scheme 2



Scheme 3

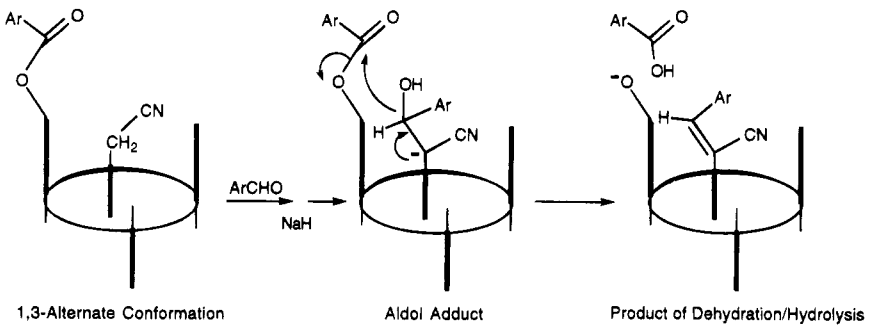


Table 1. ^{1}H NMR, ^{13}C NMR, and UV Spectral Data for 4, 5, and 12

	^{1}H NMR resonances			^{13}C NMR resonances				UV absorptions	
compounds	$ArCH_2Ar$	$ArCH_2O$	HC=	$ArCH_2Ar$	$ArCH_2O$	=C[CN]	CN	λ_{max}	ϵ
4a	3.73	4.90	6.62	37.58	72.54	110.79	117.96	332	81 890
4b	3.63	4.84	7.32	37.86	72.35	111.12	118.10	345	67 820
4c	3.72	4.89	6.58	37.60	72.45	110.94	117.97	337	87 620
4d	3.70	4.89	6.55	37.72	73.19	108.34	118.91	346	95 050
4e	3.72	4.88	6.99	37.85	72.25	112.96	117.60	327	55 450
4f	3.72	4.89	6.57	37.57	72.53	109.58	118.21	336	65 840
4g	3.69	4.88	7.19–7.24	37.84	72.26	113.92	117.14	331	74 260
4h	3.69	4.89	6.54	37.06	73.28	11.18	117.29	332	78 710
4i	3.73	4.89	6.45	37.13	73.18	112.12	117.48	335	79 700
4j	3.69	4.88	6.52	36.50	71.51	110.94	117.35	340	84 650
5a	3.81	4.94	7.44–7.50	37.94	72.37	114.37	117.60	347	47 230
5b	3.76	4.94	6.76	36.80	74.07	110.61	118.47	350	59 510
5c	3.65	4.86	6.37	37.30	72.85	106.91	117.74	354	72 280
5d	3.72	4.90	6.63	36.57	71.32	106.59	117.73	353	60 640
12	2.98 (J = 13.8 Hz) 4.20 (J = 13.8 Hz)	5.00	7.22	31.43	77.05	110.66	118.09	327	53 170

^{13}C NMR spectra accords with a 1,3-alternate conformation for compounds in the benzylated series **4** and **5**, while the appearance of a pair of doublets in the δ 3.56–4.38 region of the ^{1}H NMR spectra and a line at δ 31.24 (±0.50) in the ^{13}C NMR spectra accords with a cone conformation for compounds in the phenolic series **7** and **8** as well as the benzylated compound **12**. Another item of note in the ^{1}H NMR spectra is the downfield shift for

Table 2. ^{1}H NMR, ^{13}C NMR, and UV Spectral Data for 7, 8, and 10

	^{1}H NMR resonances		^{13}C NMR resonances			UV absorptions	
compounds	$ArCH_2Ar$	HC=	$ArCH_2Ar$	=*C*[CN]	CN	λ_{max}	ϵ
7a	3.71 (bs) and 4.34 (bs)	7.32–7.41	30.75	110.29	117.91	324	59 600
7b	3.77 (bs) and 4.35 (bs)	7.76	31.73	110.40	118.17	341	69 300
7c	3.72 (bs) and 4.32 (bs)	7.22–7.40	31.61	110.12	118.19	324	56 310
7d	3.74 (d, J = 15.2 Hz) 4.34 (d, J = 13.5 Hz)	7.28	31.69	107.37	118.75	343	88 120
7e	3.73 (d, J = 12.90 Hz) 4.38 (d, J = 12.90 Hz)	7.57	31.70	112.50	117.78	318	54 360
7f	3.62 (bs) and 4.32 (bs)	7.44	31.68	109.12	118.42	329	62 030
7g	3.74 (bs) and 4.36 (bs)	7.70	31.72	113.53	117.18	321	54 360
7h	3.72 (bs) and 4.32 (bs)	7.29	30.92	111.06	117.67	331	73 270
7i	4.06 (bs)[a]	7.63	30.88	111.62	117.44	328	68 320
7j	4.08 (bs)[a]	7.66	30.86	111.11	117.66	332	81 680
8a	4.12 (bs)[a]	7.79–8.02	30.74	114.33	117.54	346	52 970
8b	4.06 (bs)[a]	7.62	30.78	110.14	118.00	343	67 820
8c	3.56 (bs) and 4.32 (bs)	7.17	31.64	106.25	117.94	345	97 430
8d	3.56 (bs) and 4.34 (bs)	7.46	31.64	106.87	118.32	344	61 390
10a	3.78 (singlet)[b]	7.06	36.23	108.59	116.42	330	85 150
10b	3.76 (singlet)[b]	6.97	36.32	108.28	116.28	329	87 620

[a] Values in DMSO-d_6. [b] 1,3-Alternate conformer.

the HC= proton that occurs when a subsitutuent is present in the 2′ position of the arylmethylene moieties in compounds in the series **4** and **5** (benzyloxy compounds) and the series **7** and **8** (phenolic compounds). Thus, **4b** (2′-methoxyphenyl), **4e** (2′-methylphenyl), **4g** (2′-chlorophenyl), and **5a** (1-naphthyl) all have resonances well above the δ 6.6 position where most of the other compounds of the benzoxy series show this resonance. Similarly, **7b** (2′-methoxypheny), **7e** (2′-methylphenyl), **7g** (2′-chlorophenyl), and **8a** (1-naphthyl) all have resonances above the δ 7.4 position where most of the other compounds of the phenolic series show this resonance.

The effect of a 2′-substituent in the arylmethylene moiety is also manifested in the ^{13}C NMR spectra and, in some cases, the UV spectra. The compounds containing 2′ substituents (**4b/7b**, **4e/7e**, and **4g/7g**) as well as 1-naphthyl (**5a/8a**) all show the =*C*(CN) resonance 1–3 ppm further downfield than their 3′ and/or 4′ counterparts. In compounds **4e/7e** (2′-methylphenyl) and **4g/7g** (2′-chlorophenyl) the positions of absorption (λ_{max}) are at shorter wavelengths than in the 3′ and/or 4′ counterparts, and the extinction coefficients (ϵ) are lower. In like fashion there is a demonstrable difference in the UV behavior for the furyl compounds **5c/8c** and the thienyl compounds **5d/8d**. These effects may arise from steric hindrance between the aryl rim and the cyano group, resulting in interference with the ability of the conjugated system to assume the conformation most conducive to efficient absorption. However, no independence evidence in support of this has been adduced.

Conclusion. The aldol condensations described above provide still another useful procedure for introducing bulky groups onto the upper rim of calix[4]arenes. Through the use of appropriately functionalized aromatic aldehyhdes it should also provide the means for introducing functional groups at the upper rim. Although the method has not yet been tested with calixarenes larger than the calix[4]arene, it seems likely that the reactions will proceed in comparable fashion in these cases as well.

Experimental Section

Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was always freshly distilled from Na-benzophenone, while *N*,*N*-dimethylformamide (DMF), acetonitrile, and acetone were distilled and stored over molecular sieves (3 and 4 Å Linde sieves) for at least 10 d. Flash chromatography was carried out by using J. T. Baker 40 μm silica gel, and column chromatography using Aldrich 70–230 mesh, 60 Å silica gel. Thin layer chromatography (TLC) was performed on 250 μm silica gel plates, and preparative thin layer chromatography (PTLC) on 1000 μm silica gel plates containing a fluorescent indicator. Melting points of all compounds were taken in sealed and evacuated melting point capillary tubes using a 500 °C thermometer calibrated against a thermocouple and are uncorrected. ^{1}H NMR spectra, recorded at 300 MHz, 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, recorded at 75 MHz, 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). UV spectra were measured at 1.0 × 10^{-5} M solutions in $CHCl_3$. Microanalytical samples were dried for at least 72 h at 111 °C using (toluene) or at 140 °C (xylene) at 1–2 mm, and the analyses were carried out by Desert Laboratories, Tucson, AZ.

5,11,17,23-Tetrakis(cyanomethyl)-25,26,27,28-tetrabenzoxycalix[4]arene (3) (1,3-alternate conformer) was obtained as previously described[7] in 91% yield; mp 188–190 °C (reported 188–190 °C).

5,11,17,23-Tetrakis(1-cyano-2-phenylethenyl)-25,26,-27,28-tetrabenzoxycalix[4]arene (4a) (1,3-alternate conformer): An amount 0.60 g (15 mmol, 30 equiv) of NaH (60% in oil dispersion) was placed in a 150 mL three-necked round-bottomed flask followed by freshly distilled and dry THF (90 mL), and the air in the flask was replaced with N_2. The flask was placed in an ice bath, maintaining the temperature approximately 2–3 °C, and 0.47 g (0.5 mmol) of **3** was added, the flask was allowed to warm to rt, and the contents were stirred for 30 min under a stream of N_2. A solution of benzaldehyde (1.60 g, 15 mmol) in 10 mL of dry THF was then added dropwise over a period of 30 min, and the reaction content was allowed to stir at rt for an additional 8 h. The solvent was removed under reduced pressure on a rotary evaporator, and the concentrated residue was neutralized with ice-cold 10% HCl to produce a light yellow precipitate. This was separated by filtration and triturated 30 m with MeOH (100 mL) followed by hexane to leave a white solid. The product was purified by column chromatography using $CHCl_3$ as an eluent followed by recrystallization from $CHCl_3$–n-C_6H_{14} (2:1) to give 0.62 g (92%) of a white powder: mp 259–261 °C; ^{1}H NMR ($CDCl_3$) δ 7.57–7.54 (m, 8 H), 7.39–7.37 (m, 12 H), 7.23–7.18 (m, 8 H), 7.12 (s, 8 H), 7.10–7.03 (m, 12 H), 6.62 (s, 4 H), 4.90 (s, 8 H), 3.73 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 156.80, 140.01, 136.73, 134.44, 133.83, 129.88, 129.20, 128.61, 128.56, 127.90, 127.81, 127.69, 126.93, 117.96, 110.79, 72.54, 37.58.

Anal. Calcd for $C_{92}H_{68}N_4O_4$: C, 85.42; H, 5.30. Found: C, 85.34; H, 5.32.

5,11,17,23-Tetrakis[1-cyano-2-(2′-methoxyphenyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (4b) (1,3-alternate conformer) was obtained in 85% yield following the procedure described above for **4a** using 2-methoxybenzaldehyde. The crude product was purified by column chromatography [$CHCl_3$–CH_2Cl_2 (3:1) eluant], recrystallization from CH_2Cl_2–n-C_6H_{14} (4:1), and trituration with anhydrous MeOH: mp 247–248 °C; ^{1}H NMR ($CDCl_3$) δ 7.87 (d, J = 7.74 Hz, 4 H), 7.38 (t, J = 7.71 and 7.98 Hz, 4 H), 7.32 (s, 4 H), 7.22–7.19 (m, 8 H), 7.11 (s, 8 H), 7.07–7.01 (m, 8 H), 6.96–6.89 (m, 12 H), 4.84 (s, 8 H), 3.83 (s, 12 H), 3.63 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 157.58, 156.67, 136.76, 135.12, 134.41, 131.26, 128.91, 128.62, 128.32, 127.61, 127.40, 127.29, 123.39, 120.63, 118.10, 111.12,110.42, 72.35, 55.49, 37.86. Anal. Calcd for $C_{96}H_{76}N_4O_8$: C, 81.56; H, 5.42. Found: C, 81.27; H, 5.20.

5,11,17,23-Tetrakis[1-cyano-2-(3′-methoxyphenyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (4c) (1,3-alternate conformer) was obtained in 91% yield following the procedure described above for **4a** using 3-methoxybenzaldehyde. The crude product was purified by column chromatography [$CHCl_3$-CH_2Cl_2 (5:2) eluant] and recrystallization from $CHCl_3$–MeOH (1:3) to give a white powder: mp 216–218 °C; ^{1}H NMR ($CDCl_3$) δ 7.32–7.24 (m, 8 H), 7.22–7.15 (m, 12 H), 7.11 (bs, 12 H), 7.03 (d, J = 7.4 Hz, 8 H), 6.95–6.92 (m, 4 H), 6.58 (s, 4 H), 4.89 (s, 8 H), 3.85 (s, 12 H), 3.72 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 159.56, 156.80, 139.92, 136.73, 135.07, 134.46, 129.56, 128.62, 128.55, 127.91, 127.71, 126.91, 122.05, 117.97, 116.31, 113.57, 110.94, 72.45, 55.38, 37.60. Anal. Calcd for $C_{96}H_{76}N_4O_8$: C, 81.56; H, 5.42. Found: C, 81.27; H, 5.46.

5,11,17,23-Tetrakis[1-cyano-2-(4′-methoxyphenyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (4d) (1,3-alternate conformer) was obtained in 88% yield following the procedure described above for **4a** using 4-methoxybenzaldehyde. The crude product was purified by column chromatography [$CHCl_3$–CH_2Cl_2 (3:1) eluant] and recrystallization from $CHCl_3$–n-C_6H_{14} (3:1) to give a fine, white powder: mp 221–224 °C; ^{1}H NMR ($CDCl_3$) δ 7.52 (d, J = 8.79 Hz, 8 H), 7.23–7.18 (m, 8 H), 7.10 (s, 8 H), 7.09 (bs, 12 H), 6.88 (d, J = 8.73 Hz, 8 H), 6.55 (s, 4 H), 4.89 (s, 8 H), 3.87 (s, 12 H), 3.70 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 161.15, 156.80, 140.08, 137.19, 134.68, 131.43, 129.15, 128.95, 128.04, 127.39, 126.95, 118.91, 114.30, 108.34, 73.19, 55.72, 37.72. Anal. Calcd for $C_{96}H_{76}N_4O_8$: C, 81.56; H, 5.42. Found: C, 81.55; H, 5.26.

5,11,17,23-Tetrakis[1-cyano-2-(2′-methylphenyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (4e) (1,3-alternate conformer) was obtained in 94% yield following the procedure described above for **4a** using 2-methylbenzaldehyde. The crude product was purified by column chromatography ($CHCl_3$ eluant) and recrystallization from $CHCl_3$–n-C_6H_{14} (5:2) to give a white powder: mp 226–228 °C; ^{1}H NMR ($CDCl_3$) δ 7.68 (dd, J = 5.61 and 6.0 Hz, 4 H), 7.32–7.29 (m, 8 H), 7.25–7.18 (m, 12 H), 7.14 (m, 4 H), 7.11 (s, 8 H), 6.99 (s, 4 H) , 6.96 (s, 8 H), 4.88 (s, 8 H), 3.72 (s, 8 H), 2.16 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 156.90, 138.79, 137.10, 136.70, 134.52, 133.36, 130.20, 129.69, 128.56, 128.44 , 128.14, 127.72, 127.58, 126.99, 126.20, 117.60, 112.96, 72.25, 37.85, 19.91. Anal. Calcd for $C_{96}H_{76}N_4O_4$: C, 85.43; H, 5.68. Found: C, 85.38; H, 5.67.

5,11,17,23-Tetrakis[1-cyano-2-(3′-methylphenyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (4f) (1,3-alternate conformer) was obtained in 90% yield following the procedure described above for **4a** using 3-methylbenzaldehyde. The crude product was purified by column chromatography [$CHCl_3$–CH_2Cl_2 (4:1) eluant] and recrystallization from CH_2Cl_2–n-C_6H_{14} (3:1) to give a fine, white powder: mp 207 °C; ^{1}H NMR ($CDCl_3$) δ 7.45 (d, 8 H), 7.22–7.17 (m, 16 H), 7.10 (s, 8 H), 7.07–7.02 (m, 12 H), 6.57 (s, 4 H), 4.89 (s, 8 H), 3.72 (s, 8 H), 2.40 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 156.65, 140.27, 140.08, 136.78, 134.43, 131.12, 129.62, 129.32, 128.77, 128.56, 127.68, 126.88, 126.98, 118.21, 109.58, 72.53, 37.57, 21.58. Anal. Calcd for $C_{96}H_{76}N_4O_4$: C, 85.43; H, 5.68. Found: C, 85.31; H, 5.56.

5,11,17,23-Tetrakis[1-cyano-2-(2′-chlorophenyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (4g) (1,3-alternate conformer) was obtained in 89% yield following the procedure described above for **4a** using 2-chlorobenzaldehyde. The crude product was purified by column chromatography [$CHCl_3$–CH_2Cl_2 (4:1) eluant] and recrystallization from CH_2Cl_2–n-C_6H_{14} (3:1) to give a fine, white powder: mp 235–237 °C; ^{1}H NMR ($CDCl_3$) δ 7.85–7.82 (m, 4 H), 7.45–7.40 (m, 4 H), 7.38-7.34 (m, 8 H), 7.24–7.19 (m, 12 H), 7.14 (s, 8 H), 7.09 (m, 4 H), 6.94 (d, J = 7.2 Hz, 8 H), 4.88 (s, 8 H), 3.69 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 157.14, 136.55, 136.11, 134.55, 134.42, 132.52, 130.75, 129.65, 129.41, 128.41, 128.20, 127.80, 127.52, 127.27, 127.03, 117.14, 113.92, 72.26, 37.84. Anal. Calcd for $C_{92}H_{64}N_4O_4Cl_4$: C, 77.20; H, 4.51. Found: C, 77.18; H, 4.43.

5,11,17,23-Tetrakis[1-cyano-2-(4′-chlorophenyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (4h) (1,3-alternate conformer) was obtained in 92% yield following the procedure described above for **4a** using 4-chlorobenzaldehyde. The crude product was purified by column chromatography [$CHCl_3$–CH_2Cl_2 (5:2) eluant] and recrystallization from CH_2Cl_2–n-C_6H_{14} (5:2) to give a light yellow powder which upon stirring with MeOH gave a white powder: mp 244–247 °C; ^{1}H NMR ($CDCl_3$) δ 7.45 (d, J = 8.46 Hz, 8 H), 7.33 (d, J = 8.04 Hz, 8 H), 7.21 (d, J = 7.65 Hz, 8 H), 7.15 (s, 8 H), 7.13 (bs, 12 H), 6.54 (s, 4 H), 4.89 (s, 8 H), 3.69 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 156.86, 138.43, 136.70, 135.85, 134.33, 132.07, 130.43, 128.86, 128.69, 128.20, 127.96, 127.89, 127.35, 128.20, 117.79, 111.18, 73.28, 37.06. Anal. Calcd for $C_{92}H_{64}N_4O_4Cl_4$: C, 77.20; H, 4.51. Found: C, 77.35; H, 4.37.

5,11,17,23-Tetrakis[1-cyano-2-(3′-bromophenyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (4i) (1,3-alternate conformer): Treatment of **3** (0.47 g, 0.5 mmol) with 1.85 g (10 mmol) of 3-bromobenzaldehyde in the procedure described above for the preparation of **4a** yielded **4i** after trituration with MeOH. The product was purified by column chromatography (CH_2Cl_2 eluent) to yield 0.70 g (88%) of a colorless powder. An analytical sample was obtained by crystallization from CH_2Cl_2–n-C_6H_{14} (3:1): mp 238–241 °C; ^{1}H NMR ($CDCl_3$) δ 7.62 (d, J = 8.04 Hz, 4 H), 7.49–7.45 (m, 8 H), 7.29–7.25 (m, 16 H), 7.19–7.15 (m, 8 H), 7.13 (s, 8 H), 6.45 (s, 4 H), 4.89 (s, 8 H), 3.73 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 158.98, 138.01, 136.60, 135.56, 134.38, 132.72, 132.62, 130.12, 128.77, 128.09, 127.96, 127.27, 126.88, 122.58, 117.48, 112.12, 73.18, 37.13. Anal. Calcd for $C_{92}H_{64}N_4O_4Br_4$: C, 68.67; H, 4.01. Found: C, 69.02; H, 4.04.

5,11,17,23-Tetrakis[1-cyano-2-(4′-bromophenyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (4j) (1,3-alternate conformer). Following the procedure for the prepartion of **4a**, compound **4j** was obtained in 91% yield by the reaction of **3** (0.47 g, 0.5 mmol) and 1.85 g (10 mmol) of 4-bromobenzaldehyde. An analytical sample was obtained as a white powder by column chromatography [$CHCl_2$–$CHCl_3$ (2:5) eluant] followed by crystallization from CH_2Cl_2–n-C_6H_{14} (4:1): mp 248–249 °C; ^{1}H NMR ($CDCl_3$) δ 7.49 (d, J = 8.61 Hz, 8 H), 7.37 (d, J = 8.61 Hz, 8 H), 7.22 (d, J = 7.29 Hz, 8 H), 7.15 (s, 8 H), 7.14–7.10 (m, 12 H), 6.52 (s, 4 H), 4.88 (s, 8 H), 3.69 (s, 8 H); ^{13}C NMR (DMSO-d_6) δ 156.63, 138.22, 136.94, 134.38, 132.96, 131.64, 130.58, 127.75, 127.40, 127.27, 126.92, 126.73, 123.06, 117.35, 110.94, 71.51, 36.50. Anal. Calcd for $C_{92}H_{64}N_4O_4Br_4$: C, 68.67; H, 4.01. Found: C, 68.68; H, 4.03.

5,11,17,23-Tetrakis[1-cyano-2-(1′-naphthyl)ethenyl]-25,26,27,28-tetrabenzoxycalix[4]arene (5a) (1,3-alternate conformer) was prepared following the procedure for **4a** by treating of **3** (0.47 g, 0.5 mmol) with 1.56 g (20 mmol) of 1-naphthaldehyde. After stirring at rt for 24 h the reaction mixture was worked up, and the crude product was purified by column chromatography (CH_2Cl_2 eluant) to give 0.63 g (85%) of a white powder. An analytical sample was obtained by crystallization from a mixture of CH_2Cl_2–n-C_6H_{14} (3:1): mp 154–156 °C; ^{1}H NMR ($CDCl_3$) δ 7.91–7.80 (m, 8 H), 7.70–7.44 (m, 24 H), 7.38–7.20 (m, 20 H), 7.11–7.05 (m, 8 H), 4.94 (s, 8 H), 3.81 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 157.12, 137.72, 136.67, 134.59, 133.41, 131.40, 130.19, 128.79, 128.72, 128.64, 128.46, 127.75, 127.69, 127.16, 126.99, 126.58, 126.23, 125.45, 123.66, 117.60, 114.37, 72.37, 37.94.

O-Debenzylation of **5a** (*vide infra*) yielded **8a** for which elemental analytical data are given.

5,11,17,23-Tetrakis[1-cyano-2-(2′-naphthyl)ethenyl]-25,-26,27,28-tetrabenzoxycalix[4]arene (5b) (1,3-alternate

conformer) was prepared in 88% yield by following the procedure for **4a** by treating 0.23 g (0.25 mmol) of **3** with 1.20 g (30 mmol) of 2-naphthaldehyde, purifying the crude product by column chromatography (CH_2Cl_2 eluant). An analytical sample was obtained as a white powder by crystallization from CH_2Cl_2–n-C_6H_{14} (4:1): mp 181 °C (softening) and 191–193 °C (liquid); ^{1}H NMR ($CDCl_3$) δ 8.00–7.92 (m, 4 H), 7.77–7.63 (m, 12 H), 7.52–7.43 (m, 16 H), 7.33–7.25 (m, 20 H), 7.12–7.05 (m, 4 H), 6.76 (s, 4 H), 4.94 (s, 8 H), 3.76 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 156.78, 140.34, 136.75, 134.22, 133.65, 132.78, 131.05, 130.64, 128.90, 128.68, 128.63, 128.21, 128.14, 127.99, 127.81, 127.61, 127.10, 126.39, 124.95, 118.47, 110.61, 74.07, 36.80. Anal. Calcd for $C_{108}H_{76}N_4O_4.H_2O$:[10] C, 85.80; H, 5.20. Found: C, 85.62; H, 4.95.

5,11,17,23-Tetrakis[1-cyano-2-**(2′-furanyl)ethenyl]-25,-26,27,28- tetrabenzoxycalix[4]arene (5c) (1,3-alternate conformer)** was prepared in 72% yield by the reaction of 0.23 g (0.25 mmol) of **3** and 0.72 g (7.5 mmol) of 2-furancarboxaldehyde using 0.30 g of NaH (7.5 mmol) in 30 mL of THF with stirring at rt for 4 h. The product was purified by column chromatography (CH_2Cl_2 eluant) and recrystallization from CH_2Cl_2–n-hexane (4:1) and obtained as light yellow neddles: mp 225–228 °C; ^{1}H NMR ($CDCl_3$) δ 7.53 (d, J = 2.1 Hz, 4 H), 7.22 (d, J = 7.5 Hz, 8 H), 7.17–7.07 (m, 12 H), 7.05 (s, 8 H), 6.88 (d, J = 2.4 Hz, 4 H), 6.51 (dd, J = 2.4 and 2.4 Hz, 4 H), 6.37 (s, 4 H), 4.86 (s, 8 H), 3.65 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 156.67, 150.29, 144.16 , 136.81, 134.35, 128.60, 127.89, 127.71, 127.57, 127.02, 126.30, 117.74, 114.36, 112.44, 106.91, 72.85, 37.30. Anal. Calcd for $C_{84}H_{60}N_4O_8$: C, 80.50; H, 4.82. Found: C, 81.00; H, 4.73.

5,11,17,23-Tetrakis[1-cyano-2-**(2′-thienyl)ethenyl]-25,-26,27,28-tetrabenzoxycalix[4]arene (5d) (1,3-alternate conformer)** was prepared in 82% yield following the procedure for **4a** and was purified by column chromatography [$CHCl_3$–CH_2Cl_2 (5:1) eluant]. An analytical sample was obtained by crystallization from CH_2Cl_2–n-C_6H_{14} (4:1) as a light yellow powder: mp 234–236 °C; ^{1}H NMR ($CDCl_3$) δ 7.46 (d, J = 4.0 Hz, 4 H), 7.28–7.20 (m, 16 H), 7.14–7.01 (m, 20 H), 6.63 (s, 4 H), 4.90 (s, 8 H), 3.72 (s, 8 H); ^{13}C NMR (DMSO-d_6) δ 156.27, 137.56, 136.96, 134.46, 132.60, 132.41, 130.17, 127.65, 127.60, 127.28, 127.01, 126.57, 117.73, 106.59, 71.32, 36.57. Anal. Calcd for $C_{84}H_{60}N_4O_4S_4$: C, 76.57; H, 4.59. Found: C, 76.67; H, 4.58.

Debenzylation Reactions. (A) via Lewis Acid-induced Cleavage: (1) With Trimethylsilyl Bromide. A 0.20 mmol sample of **4a–j** in 30 mL of dry $CHCl_3$ containing some molecular sieves was placed in a 150 mL three-necked round-bottomed flask. The reaction mixture was heated for 10 min in an oil bath at 50–55 °C, and a solution of 30 equiv of Me_3-SiBr in $CHCl_3$ was added dropwise with stirring. The reaction mixture was refluxed for 36–72 h in an atmosphere of N_2. The progress of the reaction was monitored by TLC, and when it was complete the solvent was removed under reduced pressure using a rotary evaporator, and the concentrated material was poured into MeOH (50 mL). The white to yellow precepitate was separated by filtration and washed thoroughly with MeOH to remove unreacted Me_3SiBr and benzyl alcohol (if formed during the course of the reaction). The product was purified by crystallization using the appropriate solvent combination.

(2) With Aluminum Chloride. Anhydrous white powdered $AlCl_3$ (1.33 g, 10 mmol, 50 equiv) and 15 mL of toluene (dried over molecular sieves for 10 d) were placed in a 100 mL three-necked, round-bottomed flask and stirred for 5 min at rt. A slurry of 0.20–0.25 mmol of **4a–j** or **5a–d** in 5 mL of toluene was added with stirring. The reaction mixture was stirred for 5–15 min in an atmosphere of N_2, the completion of reaction being assessed by TLC. The reaction mixture was poured into 100 mL of ice-cold water, and unreacted $AlCl_3$ was neutralized with 10% HCl. The organic layer and aqueous layer were separated, and the water layer was again extracted with 100 mL of $CHCl_3$ or CH_2Cl_2. The combined organic layer extract was concentrated under reduced pressure on a rotary evaporator, and the residue was poured into MeOH (50 mL) to give a white to light pale-yellow precipitate which was removed by filtration, washed several times with MeOH, and purified by the same procedure described above in method **1**.

(B) By the Reaction of 5,11,17,23-tetrakis(cyanomethyl)-25,26,27,28-tetrakis(aroyloxy)calix[4]arenes (6) with Aromatic Aldehyde. A 30 equiv sample of NaH (60% in oil dispersion) was placed in a 150 mL three-necked round-bottomed flask followed by 30–40 mL of dry, freshly distilled THF, and the air in the flask was replaced with N_2. The flask was placed in an ice bath, 0.20–0.25 mmol of **6** was added, the flask was allowed to warm to rt, and the contents were stirred for 30 min. A solution of benzaldehyde or substituted benzaldehydes (20–30 equiv) in dry THF (5 mL) was then added dropwise over a period of 30 min, and reaction content was allowed to stir for 24–48 h at rt. The solvent was removed under reduced pressure, and treatment of the residue with 10% HCl produced a light yellow precipitate. This was removed by filtration and stirred for 30 min with 50 mL of MeOH to leave a white to light yellow (in some cases light brown) solid powder which was stirred with hexane.The product was triturated with MeOH to give **7a–i** and **8a–d**.

5,11,17,23-Tetrakis[1-cyano-2-phenylethenyl]-25,26,27,-28-tetrahydroxycalix[4]arene (7a) (cone conformer) was prepared in 92 and 95% by the reaction of **4a** with Me_3SiBr or $AlCl_3$ following the procedures A1 and A2, respectively. Crystallization from CH_2Cl_2 –hexane (5:1) afforded **7a** as a white powder which was triturated with 30 mL of MeOH to yield an analytical sample: mp 312–314 °C; ^{1}H NMR ($CDCl_3$) δ 10.11–10.09 (bs, 4 H), 7.84–7.82 (m, 8 H), 7.44 (bs, 8 H), 7.41–7.32 (m, 16 H), 4.34 (bs, 4 H), 3.71 (bs, 4 H); ^{13}C NMR (DMSO-d_6) δ 152.11, 140.52, 133.89, 129.99, 129.15, 128.76, 128.69, 126.42, 126.31, 117.91, 110.29, 30.75. Anal. Calcd. for $C_{64}H_{44}N_4O_4$ 0.5 H_2O:[10] C, 81.60; H, 4.81; Found C, 81.50; H, 4.79. Compound **7a** was also prepared in 83% by the reaction of 0.25 g (0.25 mmol) of **6a** with 0.53 g (5 mmol) of benzaldehyde by following the method B as described above.

5,11,17,23-Tetrakis[1-cyano-2-(2′-methoxyphenyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (7b) (cone conformer) was prepared in 90 and 91% by the reaction of **4b** with Me_3SiBr or $AlCl_3$ using procedures A1 and A2, respectively. Crystallization from CH_2Cl_2–hexane (4:1) afforded **7b** as white powder which was triturated with 40 mL of MeOH to give an analytical sample: mp 290–292 °C; ^{1}H NMR ($CDCl_3$) δ 10.15 (bs, 4 H), 8.05 (d, J = 7.80 Hz, 4 H), 7.76 (s, 4 H), 7.45 (s, 8 H), 7.34 (t, J = 7.80 and 8.10 Hz, 4 H), 6.98 (t, J = 7.80 Hz, 4 H), 6.85 (d, J = 8.10 Hz, 4 H), 4.35 (bs, 4 H), 3.77 (bs, 4 H), 3.73 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 157.90, 149.47 (COH), 136.79, 131.76, 129.52, 128.52, 128.30, 126.96, 123.03, 120.57, 118.17, 110.59, 110.40, 55.51, 31.73. Anal. Calcd for $C_{68}H_{52}N_4O_8$: C, 77.55; H, 4.98; Found: C, 77.70; H, 4.90. Compound **7b** was also prepared in 80% yield by the reaction of 0.25 g (0.25 mmol) of **6** and 0.68 g (5 mmol) of 2-methoxybenzaldehyde using method B as described above.

5,11,17,23-Tetrakiskis[1-cyano-2-(3′-methoxyphenyl)-ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (7c) (cone conformer) was prepared in 89 and 87% by the reaction of **4c** with Me_3SiBr or $AlCl_3$ using procedures A1 and A2, respectively. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (4:1) and trituration with 30 mL of MeOH: mp 150 °C (softening) and 162–163 °C; ^{1}H NMR ($CDCl_3$) δ 10.08 (bs, 4 H), 7.44 (s, 8 H), 7.40–7.22 (m, 16 H), 6.95 (m, 4 H), 4.32 (bs, 4 H), 3.81 (s, 12 H), 3.72 (bs, 4 H); ^{13}C NMR ($CDCl_3$) δ 159.74, 149.51, 141.80, 134.83, 129.84, 128.64, 127.03, 122.08, 122.07, 118.19, 117.06, 113.44, 110.12, 55.34, 31.61. Anal. Calcd for $C_{68}H_{52}N_4O_8$: C, 77.55; H, 4.98. Found: C, 77.24; H, 4.91. Compound **7c** was also prepared in 83% yield by the reaction of **6** (0.25 g, 0.25 mmol) and 3-methoxybenzaldehyde (0.68 g, 5 mmol) using method B as described above.

5,11,17,23-Tetrakis[1-cyano-2-(4′-methoxyphenyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (7d) (cone conformer) was prepared in 91 and 90% by the reaction of **4d**

(10) The presence of the water molecule inside the cavity of the molecule was qualitatively supported by the appearance of a broad signal in the ^{1}H NMR spectrum at ca. δ 1.6–1.8 ppm. A spectrum of $CDCl_3$ alone shows a sharp peak at δ 1.5 ppm. With two exceptions (**5b** and **13**) the occlusion of H_2O occurred with compounds in the cone conformation.

with Me_3SiBr or $AlCl_3$ using procedures A1 and A2, respectively. Crystallization from CH_2Cl_2–hexane (4:1) afforded **7b** as white powder which was triturated with 30 mL of MeOH to give an analytical sample: mp 172–174 °C; ^1H NMR ($CDCl_3$) δ 10.09 (bs, 4 H), 7.84 (d, J = 9.0 Hz, 8 H), 7.40 (s, 8 H), 7.28 (s, 4 H), 6.93 (d, J = 9.0 Hz, 8 H), 4.34 (d, J = 13.5 Hz, 4 H), 3.83 (s, 12 H), 3.74 (d, J = 15.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 161.28, 149.21, 141.54, 131.19, 129.75, 128.60, 126.75, 126.51, 118.75, 114.31, 107.37, 55.40, 31.69. Anal. Calcd for $C_{68}H_{52}N_4O_8$: C, 77.55; H, 4.98. Found: C, 77.47; H, 4.84. Compound **7d** was also prepared in 81% yield by the reaction of **6** (0.25 g, 0.25 mmol) and 4-methoxybenzaldehyde (0.68 g, 5 mmol) using method B as described above.

5,11,17,23-Tetrakis[1-cyano-2-(2′-methylphenyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (7e) (cone conformer) was obtained in 90 and 86% by the reaction of **4e** with Me_3SiBr or $AlCl_3$ using procedures A1 and A2, respectively. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (4:1) and trituration with 20 mL of MeOH: mp 264–268 °C; ^1H NMR ($CDCl_3$) δ 10.16 (bs, 4 H), 7.81 (d, J = 9.0 Hz, 4 H), 7.57 (s, 4 H), 7.45 (s, 8 H), 7.30–7.19 (m, 12 H), 4.38 (d, J = 12.90 Hz, 4 H), 3.73 (d, J = 12.90 Hz, 4 H), 2.31 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 149.66, 140.56, 137.66, 133.05, 130.44, 130.19, 129.12, 128.65, 127.96, 127.04, 126.28, 117.78, 112.50, 31.70, 19.99. Anal. Calcd for $C_{68}H_{52}N_4O_4 \cdot 0.5\ H_2O$:[10] C, 81.82; H, 5.35. Found: C, 81.66; H, 5.10. Compound **7e** was also prepared in 81% yield by the reaction of **6** (0.25 g, 0.25 mmol) and 2-methylbenzaldehyde (0.60 g, 5 mmol) using method B as described above.

5,11,17,23-Tetrakis[1-cyano-2-(4′-methylphenyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (7f) (cone conformer) was obtained in 87 and 90% yield by the reaction of **4f** with Me_3SiBr or $AlCl_3$ using procedures A1 and A2, respectively. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (4:1) and trituration with MeOH: mp 195–197 °C; ^1H NMR ($CDCl_3$) δ 10.08 (bs, 4 H), 7.74 (d, J = 8.10 Hz, 8 H), 7.44 (s, 4 H), 7.32–7.20 (m, 16 H), 4.32 (bs, 4 H), 3.62 (bs, 4 H), 2.39 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 149.41, 141.89, 141.02, 130.97, 129.85, 129.61, 129.31, 128.60, 126.91, 118.42, 109.12, 31.68, 21.56. Anal. Calcd for $C_{68}H_{52}N_4O_4$: C, 82.57; H, 5.30. Found: C, 82.42; H, 5.15. Compound **7f** was also prepared in 85% by the reaction of **6** (0.25 g, 0.25 mmol) and 4-methylbenzaldehyde (0.60 g, 5 mmol) using method B as described above.

5,11,17,23-Tetrakis[1-cyano-2-(2′-chlorophenyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (7g) (cone conformer) was prepared in 87 and 82% yield by the reaction of **4g** with Me_3SiBr and $AlCl_3$ using procedures A1 and A2, respectively. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (3:1) and tituration with 30 mL of MeOH: mp 286–288 °C; ^1H NMR ($CDCl_3$) δ 10.18 (s, 4 H), 8.00 (dd, J = 4.77 and 4.65 Hz, 4 H), 7.70 (s, 4 H), 7.49 (s, 8 H), 7.42–7.39 (m, 4 H), 7.35–7.30 (m, 8 H), 4.36 (bs, 4 H), 3.74 (bs, 4 H); ^{13}C NMR ($CDCl_3$) δ 149.98, 137.80, 134.83, 132.10, 131.16, 129.77, 129.26, 128.70, 128.60, 127.26, 127.13, 117.18, 113.53, 31.72. Anal. Calcd for $C_{64}H_{40}N_4O_4Cl_4$: C, 71.78; H, 3.77. Found: C, 72.65; H, 3.85. Compound **5g** was also prepared in 85% by reaction of **6** (0.20 g, 0.2 mmol) and 2-chlorobenzaldehyde (0.56 g, 4 mmol) using method B as described above.

5,11,17,23-Tetrakis[1-cyano-2-(4′-chlorophenyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (7h) (cone conformer) was obtained in 84% yield by the reaction of **4h** with $AlCl_3$ using procedure A2. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (3:1) and trituration with 30 mL of MeOH: mp 335–336 °C; ^1H NMR ($CDCl_3$) δ 10.06 (bs, 4 H), 7.76 (d, J = 7.20 Hz, 8 H), 7.41–7.37 (s+d, 16 H), 7.29 (s, 4 H), 4.32 (bs, 4 H), 3.72 (bs, 4 H); ^{13}C NMR ($CDCl_3$) δ 152.85, 138.79, 134.37, 132.82, 130.33, 129.32, 128.89, 126.40, 125.69, 117.67, 111.06, 30.92. Anal. Calcd. for $C_{64}H_{40}N_4O_4Cl_4$: C, 71.78; H, 3.77. Found: C, 72.49; H, 3.66. Compound **7h** was also prepared in 89% yield by the reaction of **6** (0.25 g, 0.25 mmol) and 0.70 g (5 mmol) of 4-chlorobenzaldehyde using method B.

5,11,17,23-Tetrakis-[1-cyano-2-(3′-bromophenyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (7i) (cone conformer) was obtained in 85% yield by the reaction of **4i** with $AlCl_3$ by following procedure A2. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (4:1) and trituration with MeOH: mp 270–272 °C; ^1H NMR (DMSO-d_6) δ 7.91 (s, 4 H), 7.70 (d, J = 8.10 Hz, 4 H), 7.63 (s, 4 H), 7.55 (s, 8 H), 7.48 (d, J = 8.1 Hz, 4 H), 7.28 (m, 4 H), 4.06 (bs, 8 H); ^{13}C NMR (DMSO-d_6) δ 152.78, 138.23, 136.12, 132.35, 131.11, 130.75, 129.18, 127.26, 126.49, 125.60, 121.92, 117.44, 111.62, 30.88. Compound **7i** was also prepared in 87% yield by the reaction of **6** (0.25 g, 0.25 mmol) and 3-bromobenzaldehyde (0.92 g, 5 mmol) using method B.

5,11,17,23-Tetrakis[1-cyano-2-(4′-bromophenyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (7j) (cone conformer) was obtained in 88% yield by the reaction of **4j** with $AlCl_3$ using procedure A2. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (4:1) and trituration with MeOH: mp 331–333 °C; ^1H NMR (DMSO-d_6) δ 7.71–7.69 (m, 16 H), 7.66 (s, 4 H), 7.55 (s, 8 H), 4.08 (bs, 8 H); ^{13}C NMR (DMSO-d_6) δ 152.65, 138.94, 133.14, 131.82, 130.52, 129.26, 126.46, 125.83, 123.2, 117.66, 111.11, 30.86. Anal. Calcd for $C_{64}H_{40}N_4O_4Br_4 \cdot C_6H_{14}$: C, 62.99; H, 4.08. Found: C, 62.92; H, 3.54.

5,11,17,23-Tetrakis-[1-cyano-2-(1′-naphthyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (8a) (cone conformer) was obtained in 90% yield by the reaction of **5a** with $AlCl_3$ using procedure A2. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (4:1) and trituration with MeOH: mp 335–337 °C; ^1H NMR (DMSO-d_6) δ 8.42 (s, 4 H), 8.02–7.79 (m, 28 H), 7.50 (t, J = 8.10 and 6.60 Hz, 4 H), 7.41 (t, J = 6.60 and 7.20 Hz, 4 H), 7.22 (t, J = 7.50 and 7.50 Hz, 4 H), 4.12 (bs, 8 H); ^{13}C NMR (DMSO-d_6) δ 152.46, 138.24, 132.87, 131.53, 130.87, 129.91, 129.29, 128.38, 128.25, 126.69, 126.48, 126.27, 125.80, 125.29, 123.93, 117.54, 114.33, 30.74. Anal. Calcd for $C_{80}H_{52}N_4O_4$: C, 84.78; H, 4.62. Found: C, 84.93; H, 4.70. Compound **8a** was also prepared in 89% yield by the reaction of **6** (0.25 g, 0.25 mmol) and 1-naphthaldehyde (1.20 g, 7.5 mmol) using method B.

5,11,17,23-Tetrakis[1-cyano-2-(2′-naphthyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (8b) (cone conformer) was obtained in 92% yield by the reaction of **5b** with $AlCl_3$ using procedure A2. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (4:1) and tituration with MeOH: mp 180 °C (softening) and 192–194 °C (liquid); ^1H NMR (DMSO-d_6) δ 8.14 (s, 4 H), 8.00-7.72 (m, 24 H), 7.62 (s, 4 H), 7.56–7.43 (m, 12 H), 4.06 (bs, 8 H); ^{13}C NMR (DMSO-d_6) δ 152.05, 140.25, 133.12, 132.37, 131.37, 129.60, 129.04, 128.20, 128.13, 127.41, 127.30, 126.72, 126.59, 126.51, 124.59, 118.00, 110.14, 30.78. Anal. Calcd for $C_{80}H_{52}N_4O_4.0.5\ H_2O$:[10] C, 84.23; H, 4.68. Found: C, 84.21; H, 4.69. Compound **8b** was also prepared in 91% yield by the reaction of **6** (0.25 g, 0.25 mmol) and 2-naphthaldehyde (1.20 g, 7.5 mmol) using method B.

5,11,17,23-Tetrakis[1-cyano-2-(2′-furanyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (8c) (cone conformer) was obtained in 78% yield by the reaction of **5c** with $AlCl_3$ using procedure A2. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (4:1) and trituration with MeOH: mp 196–197 °C; ^1H NMR ($CDCl_3$) δ 10.09 (bs, 4 H), 7.55 (d, J = 1.5 Hz, 4 H), 7.38 (s, 8 H), 7.17 (s, 4 H), 7.07 (d, J = 3.3 Hz, 4 H), 6.51 (t, J = 1.5 and 3.6 Hz, 4 H), 4.32 (bs, 4 H), 3.56 (bs, 4 H); ^{13}C NMR ($CDCl_3$) δ 149.99, 149.44, 144.76, 128.60, 128.48, 127.48, 126.66, 117.94, 115.55, 112.66, 106.25, 31.64. Anal. Calcd for $C_{56}H_{36}N_4O_8.0.5\ H_2O$:[10] C, 74.58; H, 4.13. Found: C, 74.64; H, 4.01. Compound **8c** was prepared in 86% yield by the reaction of **6** (0.25 g, 0.25 mmol) and 2-furancarboxaldehyde (0.96 g, 10 mmol) using method B as described above.

5,11,17,23-Tetrakis[1-cyano-2-(2′-thienyl)ethenyl]-25,26,27,28-tetrahydroxycalix[4]arene (8d) (cone conformer) was obtained in 82% yield by the reaction of **5d** with $AlCl_3$ using procedure A2. An analytical sample was prepared by crystallization from CH_2Cl_2–hexane (4:1) and trituration with MeOH: mp 190–191 °C; ^1H NMR ($CDCl_3$) δ 10.12 (bs, 4 H), 7.80 (d, 4 H), 7.76–7.72 (m, 4 H), 7.48 (s, 8 H), 7.46 (s, 4 H), 7.06 (m, 4 H), 4.34 (bs, 4 H), 3.56 (bs, 4 H); ^{13}C NMR ($CDCl_3$) δ 149.35, 137.83, 134.12, 132.97, 129.79, 128.88, 128.64,

127.70, 126.74, 118.32, 106.87, 31.64. Anal. Calcd for $C_{56}H_{36}N_4O_4S_4 \cdot 0.5\ H_2O$:[10] C, 69.60; H, 3.96. Found: C, 69.29; H, 3.88. Compound **8d** was prepared in 85% yield by the reaction of **6** (0.25 g, 0.25 mmol) and 2-thiophenecarboxaldehyde (0.56 g, 5 mmol) using procedure B as described above .

5,11,17,23-Tetrakis[1-cyano-2-phenylethenyl]-25,26,27,-28-tetrakis(benzoyloxy)calix[4]arene (10a) (1,3-alternate conformer). A solution of 0.18 g (0.2 mmol) of **7a** and 1 mL of 1-methylimidazole in 30 mL of CH_3CN was stirred 5 min and treated with 0.85 g (6 mmol) of benzoyl chloride. The reaction mixture was stirred for 6 h and poured over ice cold water to give a semisolid material which was extracted into CH_2Cl_2, concentrated, and poured over MeOH (20 mL) to afford 0.24 g (91%) of a white solid. An analytical sample was obtained as a white powder by trituration with MeOH: mp 380–382 °C; ^{1}H NMR (DMSO-d_6) δ 7.75 (d, J = 6.90 Hz, 8 H), 7.50 (bs, 24 H), 7.42 (d, J = 7.5 Hz, 8 H), 7.34 (s, 8 H), 7.06 (s, 4 H), 3.78 (s, 8 H); ^{13}C NMR (DMSO-d_6) δ 163.62, 148.71, 141.04, 134.15, 133.77, 133.11, 130.45, 130.17, 129.19, 129.12 , 128.92, 129.81, 127.63, 116.42, 108.59, 36.23. Anal. Calcd for $C_{92}H_{60}N_4O_8$: C, 81.88; H, 4.48. Found: C, 82.06; H, 4.57.

5,11,17,23-Tetrakis[1-cyano-2-phenylethenyl]-25,26,27,-28-tetrakis[(4′-methylbenzoyl)oxy]calix[4]arene (10b) (1,3-alternate conformer). The above procedure for **10a** was followed, and 0.18 g (0.2 mmol) of **7a** was treated with 0.94 g (6 mmol) of 4-methylbenzoyl chloride. The product was purified by trituration with MeOH (3 × 50 mL) and obtained as 0.25 g (90%) of a white powder: mp 360–362 °C; ^{1}H NMR (DMSO-d_6) δ 7.63 (d, J = 7.92 Hz, 8 H), 7.51 (m, 20 H), 7.34 (s, 8 H), 7.18 (d, J = 8.04 Hz, 8 H), 6.97 (s, 4 H), 3.76 (s, 8 H), 1.82 (s, 12 H); ^{13}C NMR (DMSO-d_6) δ 163.40, 148.63, 144.14, 140.88, 134.06, 133.02, 130.26, 130.50, 130.16, 129.64, 128.87, 128.81, 127.62, 124.92, 116.28, 108.28, 36.32, 20.54. Anal. Calcd for $C_{96}H_{68}N_4O_8$: C, 82.03; H, 4.88. Found: C, 81.86; H, 4.93.

5,11,17,23-Tetrakis(1-cyano-2-phenylethenyl)-25,27-bis-(benzoyloxy)-26,28-dihydroxycalix[4]arene (11) (cone conformer). A 1.35 g sample of white, finely powdered, anhydrous $AlCl_3$ (10 mmol) was stirred with 60 mL of CH_2Cl_2–DMF (5:1) for 2 min, and 0.47 g (0.5 mmol) of **7a** was added. The reaction mixture was stirred for 10 min, 1.40 g (10 mmol) of benzoyl chloride was added, and stirring at rt under N_2 was continued 16 h. The reaction mixture was poured over ice-cold water and extracted into CH_2Cl_2. The organic layer was separated, concentrated, and poured over 50 mL of MeOH to give a white precipitate which was removed by filtration and dried to yield 0.52 g (92%) of **11**. An analytical sample was obtained as a white powder by stirring the product with 50 mL of MeOH: mp 317–319 °C; ^{1}H NMR (DMSO-d_6) δ 7.96 (bs, 2 H), 7.85–7.78 (m, 14 H), 7.46–7.42 (m, 18 H), 7.41–7.34 (m, 4 H), 7.05 (bs, 4 H), 6.83 (bs, 2 H), 4.02 (d, J = 13.98 Hz, 4 H), 3.57 (d, J = 14.07 Hz, 4 H); ^{13}C NMR (DMSO-d_6) δ 163.80, 154.87, 148.75, 141.92, 137.55, 133.62, 133.44, 133.24, 130.32, 130.18, 129.68, 129.10, 128.80, 128.67, 128.56, 128.42, 128.32, 128.13, 127.97, 126.98, 126.89, 126.77, 117.74, 116.96, 110.33, 109.76, 35.59, 35.48, 34.42. Anal. Calcd for $C_{78}H_{52}N_4O_6$: C, 82.09; H, 4.59. Found: C, 82.04 ; H, 4.64.

5,11,17,23-Tetrakis[1-cyano-2-phenylethenyl]-25,26,27,-28-tetrakis(benzyloxy)calix[4]arene (12) (cone conformer). To a slurry of 0.40 g (10 mmol) of NaH (60% oil dispersion) and 35 mL of freshly distilled THF–DMF (5:1) in a 150 mL three-necked, round-bottomed flask 0.18 g (0.2 mmol) was added **7a**. The reaction mixture was stirred for 10 min and 0.85 g (6 mmol) of benzyl bromide in 5 mL of THF was added. The reaction mixture was stirred at rt. for 19 h under N_2. It was then poured over ice-cold 10% HCl which produced a light yellow oil that was extracted into CH_2Cl_2. The organic layer was separated, solvent was removed under reduced pressure, and the residue was poured over hexane to give a white product that was removed by filtration and twice trituration with MeOH. An analytical sample was obtained as 0.22 g (88%) of a white powder by column chromatography ($CHCl_3$ eluant) followed by crystallization from $CHCl_3$–n-C_6H_{14} (3:1): mp 122–124 °C; ^{1}H NMR ($CDCl_3$) δ 7.66 (m, 8 H), 7.42–7.24 (m, 32 H), 7.22 (s, 4 H), 6.99 (s, 8 H), 5.00 (s, 8 H), 4.20 (d, J = 13.80 Hz, 4 H), 2.98 (d, J = 13.80 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 156.14, 140.89, 136.85, 135.68, 133.68, 129.91, 129.25 , 129.09, 128.67, 128.48, 128.40, 128.32, 126.11, 118.09, 110.66, 77.05, 31.43. Anal. Calcd for $C_{92}H_{68}N_4O_4 \cdot 0.5\ H_2O$:[10] C, 84.83; H, 5.34; N, 4.30. Found: C, 84.71; H, 5.31; N, 3.96.

5,11,17,23-Tetrakis[1-cyano-2-phenylethenyl]-25,26,27,-28-tetramethoxycalix[4]arene (13) (mixture of all conformers) was prepared by the reaction of 0.23 g (0.25 mmol) of **7a** with 1.0 mL of MeI and 0.30 g (7.5 mmol) of NaH (60% in oil dispersion), following the procedure described above for **12**, and was isolated in 87% yield. The product was purified by column chromatography ($CHCl_3$ eluant) and an analytical sample was obtained as a white powder by crystallization from $CHCl_3$–n-C_6H_{14} (3:1) and tituration with 40 mL of MeOH: mp 153–155 °C; ^{1}H NMR ($CDCl_3$) δ 7.92–6.62 (m, 32 H), 4.46–3.24 (m, 20 H). Anal. Calcd for $C_{68}H_{52}N_4O_4 \cdot 0.5\ H_2O$:[10] C, 81.82; H, 5.35; Found: C, 81.76; H, 5.05. The same mixtures of conformer was obtained in 85% by the reaction of **7a** (0.23 g, 0.25 mmol) with 1.0 mL of MeI using 1.38 g (40 mmol) of K_2CO_3 for 6 h refluxing.

5,11,17,23-Tetrakis(α-cyano-β-phenylethenyl)-25,26,-27,28-tetrakis(4-bromobenzenesulfonyl)calix[4]arene (14) (mixture of all conformers) was prepared by the reaction of **7a** (0.47 g, 0.5 mmol) with 4-bromobenzenesulfonyl chloride (2.55 g, 10 mmol), following the procedure for **12**, and isolated the product (0.77 g, 86%). The product was purified by column chromatography (CH_2Cl_2) and an analytical sample was obtained by crystallization with CH_2Cl_2–n-C_6H_{14} (3:1) and trituration further with MeOH into white powder: mp 179–81 °C; ^{1}H NMR ($CDCl_3$) δ 8.02–6.94 (complex multiplets, 48 H), 3.90–2.58 (m, 8 H). Anal. Calcd for $C_{88}H_{56}N_4O_{12}S_4Br_4$: C, 58.42; H, 3.12, Found: C, 58.80; H, 3.12. When the reaction of **7a** with 4-bromobenzenesulfonyl chloride was carried in the presence of 1-methylimidazole in CH_3CN, the product showed predominantly 1,3-alternate conformer (>90%): ^{13}C NMR ($CDCl_3$) δ 146.27, 143.37, 135.16, 133.66, 133.60, 133.07, 132.79, 132.33, 130.83, 129.76, 129.67, 128.90, 128.24, 117.91, 107.97, 34.93.

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