Interplay of Steric Hindrance and Hydrogen Bonding To Restrict Mono-*O*-substituted *p-tert*-Butylcalix[6]arenes in Cone Conformation

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The simple mono-*O*-benzyl-*p-tert*-butylcalix[6]arene (**2a**) has been reported to display a cone conformation with a slow inversion rate at room temperature. Here, a series of mono-*O*-substituted *p-tert*-butylcalix[6]arenes (**2a**−**g**, **3**−**9**) has been studied by 2D and variable-temperature NMR spectroscopies. Cone conformations with slow macrocyclic inversion were found for calix[6]arenes whose *O*-substituent was larger than butyl, whereas freezing of the conformation was observed for substituents larger than benzyl. Steric effects and preservation of the cyclic array of hydrogen bonds are suggested as the main cause for the high inversion barriers.

Introduction

Calixarenes are useful building blocks in supramolecular chemistry. In particular, calix[4]arenes can be specifically obtained in any of their four well-defined conformational families (cone, partial cone, 1,3-alternate, and 1,2-alternate), with partial or full functionalization at either the lower or upper rim positions.[1] The resulting shape- and size-controlled molecular platforms have been employed mainly for the development of new selective ionophores and chromoionophores, making use of the available hydroxy groups at the lower rim.[2] For the smaller members of the series, the calix[4]arenes, the size of the cavities, even in the cone conformation, is simply too small to find extensive applications in host−guest chemistry, and only some ions or small molecules can be accommodated inside.[1]

To take advantage of the macrocyclic cavity for guest inclusion, calix[6]arenes are more promising building blocks. In an ideal cone conformation, calix[6]arenes could encapsulate aromatic rings, as well as *tert*-butyl or trimethylammonium groups, within their cavities. Complexation of trimethylammonium groups is a particularly attractive issue since three well-oriented cation−π-stabilizing interactions could be established between the methyl groups and three aromatic rings of the cavity. The importance of this interaction has been pointed out by Dougherty et al. with cyclophanes[3] and, more recently, cation−π interactions have been shown to play an important role in the binding of choline derivatives in biological systems, like *Torpedo californica* acetylcholinesterase.[4]

In a collaborative effort, we have described procedures for the partial and selective functionalization of calix[6]arenes at either the lower and the upper rims.[5] Other functionalized calix[6]arenes have been recently reported by others.[6] These functionalization methods have opened the way to use calix[6]arenes as building blocks for more sophisticated receptors of choline derivatives.[7]

However, a major problem of calix[6]arenes as cavities for molecular recognition is their poor preorganization. In general, calix[6]arenes display a much higher conformational freedom than their tetramer analogues. Up to 90 energy minima have been calculated for the parent

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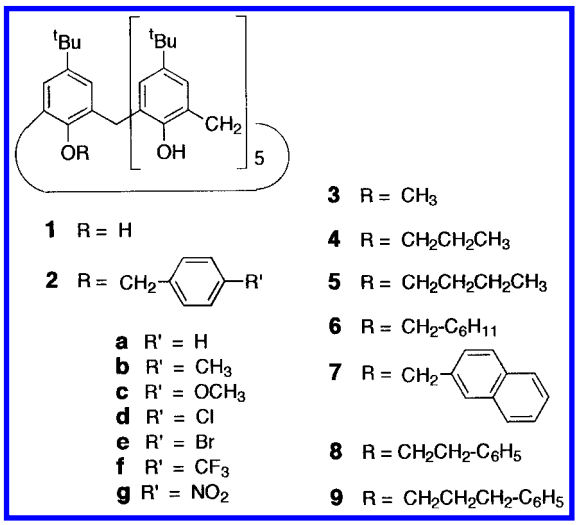
calix[6]arene.[8] For *O*-unsubstituted calix[6]arenes, a full array of hydrogen bonds results in a pinched cone preferred conformation in the solid state[9] and probably also in solution.[10] However, in solution, *O*-unsubstituted calix[6]arenes display fast equilibria between degenerated conformations, leading to ring inversion. Additionally, pseudorotation or pinched cone interconversion produces C_n symmetric average structures from the essentially asymmetric static structrures found at low temperature.[11] At very low temperature in CD_2Cl_2 upper rim substituted trichlorocalix[6]arene shows a completely unsymmetrical conformation compatible with the pinched cone conformation but also with other conformations of higher energy in vacuo.[10a] However, in $CDCl_3$ at higher temperature two exchange processes of similar energy could be identified.[10a] We assigned them to pseudorotation and inversion.[12] In contrast to calix[4]arenes, full substitution of the phenolic positions by bulky groups does not result in immobilized calix[6]arenes,[13] since macrocycle inversion may occur as well by the passage of the upper rim groups through the central cavity, even when these groups are as large as *tert*-butyl residues.[14] For this reason, a considerable effort has been devoted to the synthesis of immobilized calix[6]arenes by means of a covalent union of two or more phenolic hydroxyls with appropriate bridging or capping subunits.[15] Some of these compounds have been shown to complex quaternary ammonium salts with moderate efficiency.[15d]

Quite surprisingly, some simple substitution patterns of *p-tert*-butylcalix[6]arene (**1**) (Chart 1) result in partially

Chart 1



immobilized derivatives without the need of a synthetically costly covalent bridge between aromatic rings. For example, many 1,3,5-tri-*O*-methyl-*p-tert*-butylcalix[6]arenes present a considerably slower rate of macrocycle inversion than their *O*-unsubstituted analogues.[14,16] This effect has been attributed to CH$-\pi$ interactions between the methoxy groups pointing inside the cavity and the corresponding aromatic rings in front of them. As a result, the cavity size is significantly reduced by the self-inclusion process. Even more interesting, the simple mono-*O*-benzyl-*p-tert*-butylcalix[6]arene (**2a**) has been reported by Gutsche to show also a slow inversion rate with a $\Delta G^{\ddagger} > 18$ kcal/mol in $C_2D_2Cl_4$.[17] Apparently, the substituent is not self-included, so the cavity remains free for encapsulation of suitable guests, a fact that has yet to be exploited in supramolecular chemistry. A similar effect has been recently observed for mono- and di-*O*-phosphorylated derivatives.[18]

The interplay between the steric hindrance of the benzyl substituent and the conservation of an extended array of intramolecular hydrogen bonds (five OH groups) has been suggested by Gutsche as a rationale for the cone "fixation" of this simple monosubstituted derivative.[17] However, some questions remain to be answered: Is the substituent effect purely steric, or is there some participation of the aromatic benzyl ring to stabilize the cone conformation? What is the minimum size required for a single *O*-substituent to "fix" the cone conformation? To what extent does the intramolecular hydrogen bonding network play a role? Herein, we address these questions through an analysis of the conformational behavior of a series of mono-*O*-substituted *p-tert*-butylcalix[6]arenes (**2a**−**g**, **3**−**9**) (Chart 1) studied by 2D and variable-temperature NMR spectroscopies.

Results and Discussion

Conformational Study. In unsubstituted *p-tert*-butylcalix[6]arene (**1**), cone−cone inversion is fast at room

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(11) Inversion is the result of flipping the four phenol rings in an "up" position to a "down" position and vice versa. This process exchanges the relative position of the calixarene benzylic protons with respect to the plane defined by the phenolic oxygens (see ref 10a). Pseudorotation was defined by us (see ref 10a) as the process that exchanges the phenolic rings that are projecting outside in a winged cone conformation, all atoms being thus virtually rotated over an angle of 120°. This process does not exchange the relative positions of the calixarene benzylic protons with respect to the plane defined by the phenolic oxygens. Pinched cone interconversion is a different pseudorotation process implying the exchange of four methylene groups between inside and outside positions. This process could be independent from inversion, but energy calculations suggest that a combined inversion−pseudorotation pathway has the lowest activation energy in vacuo (see ref 10b).

(12) By comparison with energy calculations suggesting that pseudorotation and inversion should be concerted in the pinched cone conformation present in vacuo, the similarity of the two activation barriers has been taken as experimental evidence for a single concerted process.[10b] A detailed analysis of the exchange pattern does not support this interpretation. We had previously suggested that $CDCl_3$ could be interacting with calix[6]arene's stabilizing winged conformation.[10a] This possibility was not considered in the calculations.[10b]

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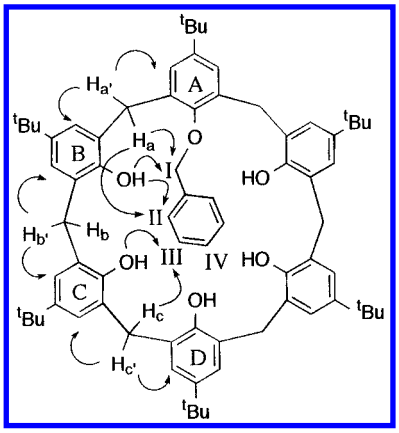

Figure 1. Selected through-space connectivities observed in **2a** by a ROESY experiment in $CDCl_3$ (298 K).

temperature, leading to complete coalescence of each group of constitutionally equivalent nuclei.[10a,19] In contrast, for mono-*O*-benzyl *p-tert*-butylcalix[6]arene (**2a**), a much lower conformational freedom has been reported.[17] In agreement with these observations, the ^{1}H NMR spectrum of **2a** in $CDCl_3$ at room temperature shows three AX systems for the methylene protons of the macrocycle, indicative of a slow ring inversion on the NMR time scale. The spectrum is in agreement with the presence of an average symmetry plane bisecting the *O*-substituted ring. Unambiguous assignment of most signals was achieved by a set of 2D NMR experiments (COSY-45, HMQC, and ROESY in $CDCl_3$ at 298 K). Unassigned signals correspond to calixarene aromatic and *tert*-butyl protons which showed extensive overlap. Pairs of methylene protons were unequivocally assigned from ROESY experiments. Exchange peaks between geminal methylene protons were not detected in ROESY experiments with mixing times up to 300 ms, indicating that inversion was also slow on this time scale.

Diagnostic ROE contacts of **2a** are shown in Figure 1 (see Supporting Information for full ROESY spectra). Protons a, b, and c present cross relaxation peaks only with phenolic OH groups and substituent signals, whereas protons a′, b′, and c′ show ROEs only with calixarene aromatic signals. From this, it may be concluded that the macrocycle is in a cone conformation. This is in agreement with the corresponding ^{13}C NMR signals for the methylenic carbons appearing between 30 and 32 ppm, as is expected for a syn arrangement of the neighboring aromatic rings.[17,20] Other cross peaks of medium to strong intensity are observed between lower rim and substituent protons.[21] These peaks were best observed in the experiments recorded at longer mixing times (τ_m = 300 ms) and further confirm the overall macrocyclic cone conformation. Since only protons b do not have contacts with the substituent, a predominant winged or pinched cone conformation, with the *O*-substituted ring and the ring in front of it pointing outward, is suggested.

The ^{1}H NMR spectra of compounds **2b**−**g** and **5**−**9**, in $CDCl_3$ at room temperature, show also three AX systems

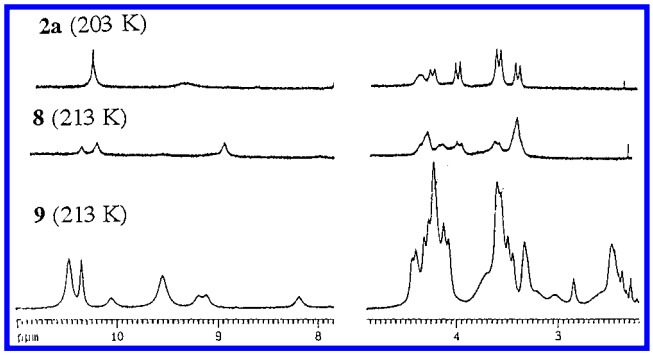

Figure 2. Methylene and OH regions of ^{1}H NMR spectra of compounds **2a**, **8**, **9** at low temperatures.

for the calixarene methylenes, whereas singlets and broad singlets were observed for the same protons of compounds **3** and **4**, respectively. A 2D NMR study of compounds **6** and **8** revealed that these compounds, and presumably all the bulky-substituted compounds of the series (**2a**−**g**, **5**−**9**), display a close conformational similarity to the benzyl derivative **2a**. Indeed, (i) methylene geminal protons did not show mutual exchange cross peaks, (ii) each of the protons within a methylene group showed ROEs only with either lower or upper rim protons of the macrocycle. From this observation it may be concluded that these compounds are also in a frozen cone conformation at room temperature. Thus, the conformation of the mono-*O*-substituted *p-tert*-butylcalix[6]arenes with bulky substituents does not appear to be dependent on the aromatic or aliphatic nature of the substituent. The lower limit for the size of the *O*-substituent chain to freeze the macrocyclic ring inversion is established to be the butyl substituent.

^{1}H NMR spectra of **2a**, **8**, and **9**, forming a homologous series with one, two, or three methylene groups acting as spacers between the phenyl ring and the macrocycle, were recorded in $CDCl_3$ at 213 K (**8** and **9**) and 203 K (**2a**) (Figure 2). A clear trend was observed in the methylene region of the three compounds. While **2a** shows only a slight broadening of one of the methylene groups, **8** and **9** show a number of broad lines. Compound **2a** has considerably broader lines for the OH signals than **8** and **9**. On the other hand, signals arising from a second conformation are barely visible in the OH region of the spectra of **2a** but can be observed in the case of **8** and have a population of ca. 50% of the main species in the calixarene **9** with a three-methylene spacer. Reinhoudt has found that mono-*O*-phosphoryl-*p-tert*-butylcalix[6]arene shows a rather complex spectrum at low temperatures, due to the slow interconversion rate between pinched cone isomers by pseudorotation.[18] A similar effect is probably operating in the monosubstituted calixarenes studied by us. However, the length of the spacer clearly affects the population of the nonsymmetrical conformation. Presumably, the possible orientations of the substituted ring are restricted by the shorter spacer (**2a**). With a longer spacer with three methylene groups as in **9**, the energy difference between the two conformations is around 1.2 kJ mol^{-1} at 213 K (calculated from the integration of OH signals). Interestingly, this shows that at room-temperature rapid pseudorotational interconversion is taking place without inversion of the cone. Thus, pseudorotation is not concerted with inversion at least in the case of these monosubstituted calix[6]arenes.

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(21) For example, methylene proton a shows strong and medium ROESY signals with protons I and II; phenol B with I, II, and III; and phenol C and methylene proton *c* with III (Figure 1).

Table 1. Coalescence Temperature and Free Energies of Activation for the Conformational Inversion of Calix[6]arenes 2−9

compd	solvent	T_c (K)	$\Delta G^{\ddagger}$ (kJ/mol)
2a	$C_2D_2Cl_4$	>396	>77
	DMSO-d_6	320	65
2b	$C_2D_2Cl_4$	>396	>77
2c	DMSO-d_6	>400	>79
2d	$C_2D_2Cl_4$	>396	>77
2f	$C_2D_2Cl_4$	>396	>77
2g	$C_2D_2Cl_4$	>396	>77
	DMSO-d_6	>400	>79
3	$CDCl_3$	<300	<58
4	$CDCl_3$	300	58
5	$C_2D_2Cl_4$	350	69
	DMSO-d_6	<300	<58
6	$C_2D_2Cl_4$	>400	>77
	DMSO-d_6	355	71
7	$C_2D_2Cl_4$	>400	>77
8	$C_2D_2Cl_4$	>363	>72
	DMSO-d_6	>363	>72
9	$C_2D_2Cl_4$	>363	>72

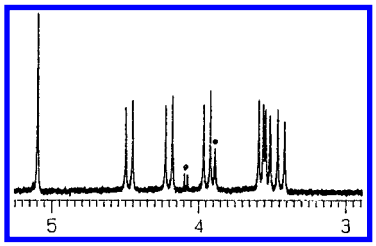

Figure 3. Methylene region of ^{1}H NMR spectra of **2b** in $C_2D_2Cl_4$ at 396 K. (• minor impurities).

Steric Effect of the Substituent. Variable-temperature spectra of mono-*O*-substituted *p-tert*-butylcalix[6]arenes in $CDCl_3$, $C_2D_2Cl_4$, or DMSO were recorded. Coalescence temperatures for methylene AX systems and activation barriers ($\Delta G^{\ddagger}$) for calixarene inversion are collected in Table 1. The parent compound **1**, endowed with a full cyclic array of hydrogen bonds, has an inversion barrier of 53.5 kJ/mol in $CDCl_3$.[10a,19] In contrast, monomethyl derivative **3** appears to be more flexible (no coalescence was observed above or at room temperature). However, barriers raised significantly as the size of the substituent was increased. For example, coalescence is observed at 300 K ($CDCl_3$) for propyl derivative **4** ($\Delta G^{\ddagger}$ = 58 kJ/mol) and at 350 K ($C_2D_2Cl_2$) for the butyl homologue **5** ($\Delta G^{\ddagger}$ = 69 kJ/mol). The rest of the compounds, bearing residues larger than benzyl, can be considered "fixed" ($\Delta G^{\ddagger}$ > 77 kJ/mol) (Figure 3). For *p-tert*-butylcalix[5]arene *O*-derivatives, a single propyl group has been reported to fix the conformation.[22]

The fact that inversion barriers are so strongly dependent on substituent size suggests that for monosubstituted *p-tert*-butylcalix[6]arenes inversion must occur via the lower rim through the annulus. As for bridged *p-tert*-butylcalix[6]arene derivatives, it is likely that inversion is prevented under the usual experimental conditions as the substituent becomes larger than the available hole of the macrocycle.

Intramolecular Hydrogen Bonding. The intramolecular cyclic array of hydrogen bonds stabilizing cone conformations is perturbed when one or several OH hydrogens are replaced by substituents. Thus, in calix[6]arenes, a single substituent results in a broken array

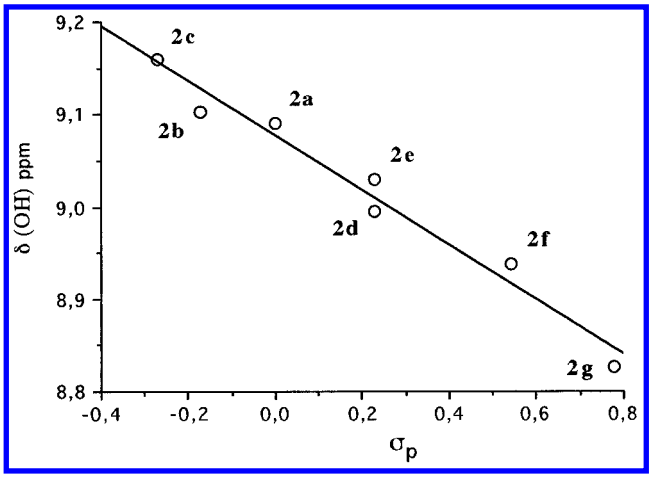

Figure 4. Hammett correlation between OH protons of B rings and σ_p parameters in calix[6]arenes **2a**-**g** (R^2 = 0.97; ρ = −0.29).

with six hydrogen acceptors but only five hydrogen donors. Monosubstitution reduces the inherent symmetry of the macroring, and the expected three signals of relative intensities 2:2:1 for the OH resonances were indeed observed at room temperature for the whole series. Chemical shifts, in the range δ 8.70−9.19, 9.36−9.95, and 9.80−10.15 ppm, respectively, are in accord with highly chelated structures.[23]

The participation of the substituent's oxygen as hydrogen acceptor in the hydrogen-bonded network was clearly established by a simple Hammett correlation. In general, calixarene ^{1}H NMR ($CDCl_3$) signals at room temperature are quite independent of the benzylic substituent. This was not the case, however, for the OH protons neighboring the substituted ring, whose chemical shifts vary considerably depending on the nature of the *O*-substituent. For example, these signals are 0.4 ppm upfield shifted in **2g** (*p*-nitrobenzyl) with respect to the less basic **2c** (*p*-methoxybenzyl), which presents a weaker hydrogen bond.[24] For the larger set of differently *para*-substituted benzyl derivatives **2a**−**g** a good correlation with σ_p was observed (Figure 4).

Since hydrogen-bond strength with the neighboring OH's is likely to be dependent on the oxygen basicity, this long distance Hammett correlation could only be explained by assuming that the substituted oxygen participates as a hydrogen acceptor with neighboring phenols. Thus, the hydrogen bond network is only partially destroyed when only one OH is replaced by an ether substituent, and the cone conformation is still stabilized. The highly preserved hydrogen-bond network prevents monosubstituted *p-tert*-butylcalix[6]arenes from inversion via the upper rim through the annulus, and this could explain the high inversion barriers observed for the compounds carrying a bulky substituent.

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(23) At room temperature phenol protons are differentially broadened in the order B < C ≪ D. The same trend is observed in monosubstituted calix[6]arenes with a variety of substituents, including those that produce "fixed cone" conformations (like **2a**) or mobile structures (like **3**). This suggests that differential broadening is a property of monosubstituted calix[6]arenes reflecting differential mobility, a range of chemical shift differences in the OH groups between the exchanging species, or a combination of both.

(24) In hydrogen-bonded phenols, chemical shifts values are related to the strength of hydrogen bonds, the stronger ones appearing at lower fields. (See Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: New York, 1969.

Participation of hydrogen bonding was further confirmed by the decrease of the inversion barriers of some compounds (**2a**, **5**, and **6**) in DMSO. It is noteworthy that, even in DMSO, the *p-tert*-butylcalix[6]arenes carrying the bulkier groups (**2c**, **2g**, and **8**) did not coalesce even at 400 K, indicating that cone interconversion follows the lower-rim-through-the-annulus pathway also in DMSO (Table 1).

Conclusions

Mono-*O*-substitution of *p-tert*-butylcalix[6]arenes at the lower rim with substituents as large as a butyl group slows ring inversion, while substitution with groups larger than benzyl freezes the conformation. Participation of the ether oxygen of the substituent as hydrogen-bond acceptor has been demonstrated by the Hammett correlation of the vicinal OH's chemical shifts with σ_p for a series of *p*-substituted benzyl derivatives. Steric effects seem to be partly responsible for the high inversion barriers. However, preservation of a cyclic hydrogen-bond array is also a necessary requirement for their effectiveness, as it raises the energy of the alternative upper-rim-through-the-annulus pathway, which would otherwise be insensitive to substitution at the lower rim. In the case of monosubstituted calix[6]arenes, it has been demonstrated that pseudorotation and inversion are not concerted processes.

Experimental Section

Solvents were dried before use by standard methods. Most chemicals were purchased from Aldrich Co. and used as received without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer at 300 and 75 MHz, respectively. ROESY (mixing times 300 and 500 ms), COSY-45, and HMQC were recorded using standart Bruker microprograms using TPPI with TD = 256 or higher. The typical matrix size was 1K × 1K. Low-temperature spectra were recorded in CD_2Cl_2 and/or $CDCl_3$, and high-temperature spectra were recorded in $C_2D_2Cl_4$. Fast atom bombardment (FAB, NBA matrix) spectra were recorded on a VG AutoSpec instrument. TLC analyses were carried out on Alugram Si G/UV254 (Macheray-Nagel). Chromatographic separation was performed with flash grade silica gel SDS 60 (230−400 mesh). Compounds **1**,[25] **2a**,[5a] and **3**[5a] were obtained according to described procedures.

General Procedure for Monoalkylation. To a solution of 200 mg (0.2 mmol) of **1** in acetone (15 mL) was added 30 mg (0.22 mmol) of K_2CO_3. After refluxing for 2 h and cooling to room temperature, the corresponding halide was added and the mixture was refluxed until the reaction was completed. The reaction mixture was cooled to room temperature, quenched with NH_4OH (25%) (2 mL), and stirred for 1 h, HCl (1 N) was added, and the solvent was removed under vacuum. CH_2Cl_2 (10 mL) was added and the aqueous layer was separated and extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layer was washed with water and brine and dried (Na_2SO_4). Evaporation of the solvent and treatment with hexane gave some unreacted **1**, which was filtered off. The filtrate was evaporated and the residue treated with cold MeOH to give the crude mono-*O*-alkylated product.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41-pentahydroxy-42-(4′-methylbenzyloxy)calix[6]arene (2b). Calix[6]arene **2b** was obtained with 4-methylbenzyl bromide (0.2 mmol) as alkylating agent. Time for the reaction was 66 h, to yield 55% (117 mg) after chromatography (CH_2Cl_2−AcOEt 1:1): mp 210−215 °C; ^{1}H NMR ($CDCl_3$) δ 9.93 (s, 2H, OH), 9.72 (s, 1H, OH), 9.10 (s, 2H, OH), 7.63, 7.41 (AA′BB′ system, 4H, ArH), 7.26−7.06 (m, 12H, ArH), 5.14 (s, 2H, OCH_2Ar), 4.42 (d, 2H, J = 13.5 Hz, $ArCH_2Ar$), 4.25 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 3.98 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 3.55 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 3.52 (d, 2H, J = 13.5 Hz, $ArCH_2Ar$), 3.35 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 2.41 (s, 3H, CH_3), 1.27 [s, 18H, $C(CH_3)_3$], 1.26 [s, 18H, $C(CH_3)_3$], 1.22 [s, 9H, $C(CH_3)_3$], 1.17 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.5, 149.3, 148.2, 147.9, 146.6, 144.3, 144.2, 143.5, 142.8, 138.3, 133.3, 132.5, 127.5, 127.0, 126.8, 126.7 (ArC), 129.7, 127.5, 126.2, 126.1, 126.0, 125.9, 125.7, 125.4 (ArCH), 78.0 (OCH_2-Ar), 34.2, 34.0, 33.91, 33.89, [$C(CH_3)_3$], 33.3, 32.7, 32.6 ($ArCH_2$-Ar), 31.6, 31.5, 31.4, 31.2 [$C(CH_3)_3$], 21.4 (CH_3); HRMS (FAB$^+$) calcd for $C_{74}H_{92}O_6$ (M^+) 1076.6894, found 1076.6884.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41-pentahydroxy-42-(4′-methoxybenzyloxy)calix[6]arene (2c). Calix[6]arene **2c** was obtained with 4-methoxybenzyl chloride (0.6 mmol) as alkylating agent. Time for the reaction was 24 h, to yield 31% (69 mg) after chromatography (hexane−CH_2Cl_2 1:1): mp 162−166 °C; ^{1}H NMR ($CDCl_3$) δ 9.95 (s, 2H, OH), 9.76 (s, 1H, OH), 9.16 (s, 2H, OH), 7.71 (AA′BB′ system, 2H, ArH), 7.22−7.12 (m, 14H, ArH), 5.18 (s, 2H, OCH_2Ar), 4.48 (d, 2H, J = 13.4 Hz, $ArCH_2Ar$), 4.30 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 4.03 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 3.90 (s, 3H, OCH_3), 3.60 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 3.58 (d, 2H, J = 13.4 Hz, $ArCH_2Ar$), 3.44 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 1.33 [s, 18H, $C(CH_3)_3$], 1.31 [s, 18H, $C(CH_3)_3$], 1.27 [s, 9H, $C(CH_3)_3$], 1.23 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 159.8, 149.3, 149.2, 148.1, 148.0, 146.7, 144.2, 143.5, 142.9, 132.5, 128.3, 127.3, 127.2, 127.0, 126.7, 126.6 (ArC), 129.2, 126.1, 126.0, 125.9, 125.8, 125.3, 114.4 (ArCH), 77.5 (OCH_2Ar), 55.3 (OCH_3), 34.2, 34.0, 33.9, 33.8 [$C(CH_3)_3$], 33.1, 32.7, 32.5 ($ArCH_2$-Ar), 31.6, 31.5, 31.4, 31.2 [$C(CH_3)_3$]; MS (FAB$^+$) m/z 1092.7 (M^+). Anal. Calcd for $C_{74}H_{92}O_7$·CH_3OH: C, 80.02; H, 8.60. Found: C, 79.71; H, 8.74.

5,11,17,23,29,35-Hexa-*tert*-butyl-42-(4′-chlorobenzyloxy)-37,38,39,40,41-pentahydroxycalix[6]arene (2d). Calix[6]arene **2d** was obtained with 4-chlorobenzyl chloride (0.2 mmol) as alkylating agent. Time for the reaction was 66 h, to yield 55% (120 mg): mp 195−196 °C; ^{1}H NMR ($CDCl_3$) δ 9.97 (s, 2H, OH), 9.84 (s, 1H, OH), 8.99 (s, 2H, OH), 7.68, 7.60 (AA′BB′ system, 4H, ArH), 7.00−7.14 (m, 12H, ArH), 5.14 (s, 2H, OCH_2-Ar), 4.39 (d, 2H, J = 13.5 Hz, $ArCH_2Ar$), 4.27 (d, 2H, J = 13.9 Hz, $ArCH_2Ar$), 3.99 (d, 2H, J = 13.9 Hz, $ArCH_2Ar$), 3.57 (d, 2H, J = 13.9 Hz, $ArCH_2Ar$), 3.49 (d, 2H, J = 13.5 Hz, $ArCH_2$-Ar), 3.38 (d, 2H, J = 13.9 Hz, $ArCH_2Ar$), 1.27 [s, 18H, $C(CH_3)_3$], 1.26 [s, 18H, $C(CH_3)_3$], 1.22 [s, 9H, $C(CH_3)_3$], 1.17 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.3, 149.1, 148.2, 148.1, 146.6, 144.4, 143.6, 143.0, 134.9, 134.4, 132.4, 127.5, 127.4, 127.0, 126.7 (ArC), 129.3, 128.6, 126.2, 126.1, 126.0, 125.7, 125.5 (ArCH), 77.0 (OCH_2Ar), 34.3, 34.0, 33.92, 33.90 [$C(CH_3)_3$], 33.3, 32.6 ($ArCH_2Ar$), 31.6, 31.5, 31.4, 31.2 [$C(CH_3)_3$]; HRMS (FAB$^+$) calcd for $C_{73}H_{89}ClO_6$ (M^+) 1096.63477, found 1096.63280.

42-(4′-Bromobenzyloxy)-5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41-pentahydroxycalix[6]arene (2e). Calix[6]arene **2e** was obtained with 4-bromobenzyl bromide (0.6 mmol) as alkylating agent. Time for the reaction was 24 h, to yield 30% (70 mg) after chromatography (hexane−CH_2Cl_2 2:1): mp 140−142 °C; ^{1}H NMR ($CDCl_3$) δ 9.98 (s, 2H, OH), 9.86 (s, 1H, OH), 9.03 (s, 2H, OH), 7.77, 7.66 (AA′BB′ system, 4H, ArH), 7.20−7.15 (m, 8H, ArH), 7.14 (s, 2H, ArH), 7.12 (s, 2H, ArH), 5.16 (s, 2H, OCH_2Ar), 4.41 (d, 2H, J = 13.4 Hz, $ArCH_2Ar$), 4.31 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 4.03 (d, 2H, J = 13.8 Hz, $ArCH_2Ar$), 3.61 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 3.56 (d, 2H, J = 13.4 Hz, $ArCH_2Ar$), 3.41 (d, 2H, J = 13.8 Hz, $ArCH_2Ar$), 1.31 [s, 18H, $C(CH_3)_3$], 1.30 [s, 18H, $C(CH_3)_3$], 1.26 [s, 9H, $C(CH_3)_3$], 1.20 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.3, 149.1, 148.2, 148.1, 146.6, 144.4, 143.6, 143.0, 135.4, 132.4, 127.5, 127.4, 127.1, 126.7, 122.6 (ArC), 132.2, 128.9, 126.2, 126.1, 126.0, 125.7, 125.5 (ArCH), 77.1 (OCH_2-Ar), 34.3, 34.0, 33.93, 33.91 [$C(CH_3)_3$], 33.3, 32.7 ($ArCH_2Ar$), 31.6, 31.5, 31.4, 31.2 [$C(CH_3)_3$]; MS (FAB$^+$) m/z 1139.4 (M^+). Anal. Calcd for $C_{73}H_{89}O_6Br$: C, 76.75; H, 7.85. Found: C, 76.35; H, 8.33.

(25) Gutsche, C. D.; Dhawan, B.; Leonis, M.; Stewart, D. *Org. Synth.* **1989**, *68*, 238.

5,11,17,23,29,35-Hexa-*tert*-butyl-42-(4′-trifluoromethylbenzyloxy)-37,38,39,40,41-pentahydroxycalix[6]arene (2f). Calix[6]arene **2f** was obtained with 4-trifluoromethylbenzyl chloride (0.2 mmol) as alkylating agent. Time for the reaction was 66 h, to yield 45% (100 mg) after chromatography (hexane−AcOEt 15:1): mp 210−212 °C; ^{1}H NMR ($CDCl_3$) δ 9.96 (s, 2H, OH), 9.87 (s, 1H, OH), 8.94 (s, 2H, OH), 7.90 (s, 4H, ArH), 7.12−7.14 (m, 8H, ArH), 7.07−7.09 (m, 4H, ArH), 5.23 (s, 2H, OCH_2Ar), 4.38 (d, 2H, J = 13.2 Hz, $ArCH_2Ar$), 4.24 (d, 2H, J = 14.3 Hz, $ArCH_2Ar$), 4.01 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 3.56 (d, 2H, J = 14.3 Hz, $ArCH_2Ar$), 3.54 (d, 2H, J = 13.2 Hz, $ArCH_2Ar$), 3.39 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 1.27 [s, 18H, $C(CH_3)_3$], 1.26 [s, 18H, $C(CH_3)_3$], 1.22 [s, 9H, $C(CH_3)_3$], 1.17 [s, 9H, $C(CH_3)_3$];^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.3, 149.1, 148.4, 148.1, 146.4, 144.5, 144.3, 143.7, 143.1, 140.5, 132.4, 126.6, 127.4, 127.1, 126.7 (ArC), 127.2, 126.2, 126.1, 126.06, 126.0, 125.7, 125.6 (ArCH), 76.9 (OCH_2Ar), 34.3, 34.0, 33.9 [$C(CH_3)_3$], 33.3, 32.6, 32.5 ($ArCH_2Ar$), 31.6, 31.5, 31.4, 31.2 [$C(CH_3)_3$]; MS (FAB$^+$) m/z 1130.9 (M$^+$). Anal. Calcd for $C_{74}H_{89}O_6F_3$·1.5H_2O: C, 76.71; H, 8.01 Found: C, 76.63; H, 8.10.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41-pentahydroxy-42-(4′-nitrobenzyloxy)calix[6]arene (2g). Calix[6]arene **2g** was obtained with 4-nitrobenzyl bromide (0.2 mmol) as alkylating agent. Time for the reaction was 66 h, to yield 50% (112 mg). An analytical sample was obtained by chromatography (hexane−AcOEt 15:1): mp 230−235 °C; ^{1}H NMR ($CDCl_3$) δ 9.92 (s, 2H, OH), 9.85 (s, 1H, OH), 8.83 (s, 2H, OH), 8.49, 7.94 (AA′BB′ system, 4H, ArH), 7.12−7.14 (m, 8H, ArH), 7.07−7.09 (m, 4H, ArH), 5.27 (s, 2H, OCH_2Ar), 4.36 (d, 2H, J = 13.5 Hz, $ArCH_2Ar$), 4.24 (d, 2H, J = 14.2 Hz, $ArCH_2Ar$), 4.01 (d, 2H, J = 13.8 Hz, $ArCH_2Ar$), 3.58 (d, 2H, J = 14.2 Hz, $ArCH_2Ar$), 3.55 (d, 2H, J = 13.5 Hz, $ArCH_2Ar$), 3.40 (d, 2H, J = 13.8 Hz, $ArCH_2Ar$), 1.27 [s, 18H, $C(CH_3)_3$], 1.26 [s, 18H, $C(CH_3)_3$], 1.22 [s, 9H, $C(CH_3)_3$], 1.17 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.2, 149.0, 148.5, 147.9, 146.4, 144.5, 144.2, 143.8, 143.6, 143.2, 132.3, 127.4, 127.2, 127.0, 126.7, 126.6 (ArC), 127.6, 126.2, 126.0, 125.7, 125.6, 124.2 (ArCH), 76.2 (OCH_2Ar), 34.3, 33.92, 33.90, 33.0 [$C(CH_3)_3$], 33.2, 32.6, 32.1 ($ArCH_2Ar$), 31.53, 31.51, 31.4, 31.2 [$C(CH_3)_3$]; HRMS (FAB$^+$) calcd for $C_{73}H_{89}NO_8$ (M$^+$) 1107.65882, found 1107.65970.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41-pentahydroxy-42-(propyloxy)calix[6]arene (4). Calix[6]arene **4** was obtained with 1-bromopropane (0.6 mmol) as alkylating agent. Time for the reaction was 48 h, to yield 31% (65 mg) after chromatography (hexane−CH_2Cl_2 1:1): mp 162−164 °C; ^{1}H NMR ($CDCl_3$) δ 9.91 (s, 2H, OH), 9.49 (s, 1H, OH), 9.17 (s, 2H, OH), 7.16−7.13 (m, 8H, ArH), 7.11 (s, 2H, ArH), 7.05 (s, 2H, ArH), 4.15 (t, 2H, J = 7.3 Hz, OCH_2), 4.5−3.6 (sa, 12H, $ArCH_2Ar$), 2.16−2.10 (m, 2H, OPr), 1.41 (t, 3H, J = 7.3 Hz, OPr), 1.31 [s, 18H, $C(CH_3)_3$], 1.29 [s, 18H, $C(CH_3)_3$], 1.24 [s, 9H, $C(CH_3)_3$], 1.22 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.5, 149.4, 148.2, 147.7, 146.6, 144.3, 143.5, 142.9, 132.5, 127.4, 127.3, 127.0, 126.79, 126.78 (ArC), 126.2, 126.0, 125.9, 125.8, 125.7, 125.4 (ArCH), 77.5 (OCH_2), 34.2, 34.0, 33.94, 33.92 [$C(CH_3)_3$], 33.2, 32.6, 32.5 ($ArCH_2Ar$), 31.6, 31.5, 31.4, 31.2 [$C(CH_3)_3$], 23.5 (OPr), 10.7 (OPr); MS (FAB$^+$) m/z 1014.7 (M$^+$). Anal. Calcd for $C_{69}H_{90}O_6$·MeOH: C, 80.26; H, 9.04. Found: C, 80.37; H, 8.79.

5,11,17,23,29,35-Hexa-*tert*-butyl-42-(butyloxy)-37,38,39,40,41-pentahydroxycalix[6]arene (5). Calix[6]arene **5** was obtained with 1-iodobutane (0.8 mmol) as alkylating agent. Time for the reaction was 24 h, to yield 26% (56 mg) after chromatography (hexane−CH_2Cl_2 3:2): mp 182−184 °C; ^{1}H NMR ($CDCl_3$) δ 9.97 (s, 2H, OH), 9.64 (s, 1H, OH), 9.15 (s, 2H, OH), 7.15−7.12 (m, 8H, ArH), 7.10 (s, 2H, ArH), 7.04 (s, 2H, ArH), 4.36 (d, 2H, J = 13.4 Hz, $ArCH_2Ar$), 4.24 (d, 2H, J = 14.4 Hz, $ArCH_2Ar$), 4.17 (t, 2H, J = 6.0 Hz, OCH_2), 4.03 (d, 2H, J = 13.9 Hz, $ArCH_2Ar$), 3.59 (d, 2H, J = 14.4 Hz, $ArCH_2$-Ar), 3.53 (d, 2H, J = 13.4 Hz, $ArCH_2Ar$), 3.47 (d, 2H, J = 13.9 Hz, $ArCH_2Ar$), 2.09−2.05 (m, 2H, OBu), 1.94−1.84 (m, 2H, OBu), 1.30 [s, 18H, $C(CH_3)_3$], 1.28 [s, 18H, $C(CH_3)_3$], 1.23 [s, 9H, $C(CH_3)_3$], 1.22 (t, 3H, J = 6.0 Hz, OBu), 1.18 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.5, 149.4, 148.2, 147.7, 146.6, 144.3, 143.5, 142.8, 132.4, 127.4, 127.3, 126.9, 126.8, 126.7 (ArC), 126.2, 126.0, 125.9, 125.8, 125.7, 125.4 (ArCH), 75.8 (OCH_2), 34.2, 34.0, 33.9, 33.8 [$C(CH_3)_3$], 33.2, 32.5, 32.3 ($ArCH_2Ar$), 32.5 (OBu), 31.6, 31.5, 31.4, 31.2 [$C(CH_3)_3$], 19.6 (OBu), 14.1 (OBu); MS (FAB$^+$) m/z 1028.7 (M$^+$). Anal. Calcd for $C_{70}H_{92}O_6$·CH_2Cl_2: C, 76.52; H, 8.50. Found: C, 75.64; H, 8.79.

5,11,17,23,29,35-Hexa-*tert*-butyl-42-(cyclohexylmethyloxy)-37,38,39,40,41-pentahydroxycalix[6]arene (6). Calix[6]arene **6** was obtained with cyclohexylmethyl bromide (0.8 mmol) as alkylating agent and acetonitrile as solvent. Time for the reaction was 4 days, to yield 50% (111 mg) after chromatography (hexane−CH_2Cl_2 2:1): mp 160−164 °C; ^{1}H NMR ($CDCl_3$) δ 10.15 (s, 2H, OH), 9.95 (s, 1H, OH), 9.19 (s, 2H, OH), 7.17−7.11 (m, 8H, ArH), 7.08 (s, 2H, ArH), 7.01 (s, 2H, ArH), 4.36 (d, 2H, J = 13.4 Hz, $ArCH_2Ar$), 4.25 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 4.03 (d, 2H, J = 13.8 Hz, $ArCH_2Ar$), 3.95 (d, 2H, J = 5.7 Hz, OCH_2Cy), 3.54 (d, 2H, J = 13.8 Hz, $ArCH_2Ar$), 3.47 (d, 2H, J = 13.4 Hz, $ArCH_2Ar$), 3.39 (d, 2H, J = 14.0 Hz, $ArCH_2Ar$), 2.17−2.12 (m, 1H, Cy), 1.98−1.93 (m, 4H, Cy), 1.79−1.75 (m, 4H, Cy), 1.47−1.43 (m, 2H, Cy), 1.28 [s, 18H, $C(CH_3)_3$], 1.26 [s, 18H, $C(CH_3)_3$], 1.21 [s, 9H, $C(CH_3)_3$], 1.15 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.5, 149.4 148.2, 147.7, 146.5, 144.4, 143.6, 142.9, 132.4, 127.7, 127.5, 127.0, 126.8, 126.7 (ArC), 126.2, 126.1, 126.0, 125.9, 125.7, 125.5 (ArCH), 81.9 (OCH_2), 39.1 (Cy), 34.0, 33.98, 33.93, 33.91 [$C(CH_3)_3$], 33.4, 32.7, 32.5 ($ArCH_2Ar$), 31.6, 31.5, 31.4, 31.2 [$C(CH_3)_3$], 30.2, 26.5, 26.1 (Cy); MS (FAB$^+$) m/z 1068.8 (M$^+$). Anal. Calcd for $C_{73}H_{96}O_6$·$^1/_2CH_2Cl_2$: C, 79.39; H, 8.99. Found: C, 79.59; H, 9.46.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41-pentahydroxy-42-(2′-naphthylmethyloxy)calix[6]arene (7). Calix[6]arene **7** was obtained with 2-(bromomethyl)naphthalene (0.26 mmol) as alkylating agent. Time for the reaction was 70 h, to yield 28% (60 mg) after chromatography (hexane−AcOEt 25:1): mp 176−180 °C; ^{1}H NMR ($CDCl_3$) δ 9.91 (s, 2H, OH), 9.58 (s, 1H, OH), 9.10 (s, 2H, OH), 8.25 (d, 1H, J = 8.4 Hz, ArH), 8.12 (s, 1H, ArH), 8.10 (d, 1H, J = 8.6 Hz, ArH), 8.03−7.96 (m, 2H, ArH), 7.57−7.54 (m, 2H, ArH), 7.22 (s, 2H, ArH), 7.19−7.18 (m, 8H, ArH), 7.16 (s, 2H, ArH), 5.41 (s, 2H, OCH_2Ar), 4.58 (d, 2H, J = 13.4 Hz, $ArCH_2Ar$), 4.20 (d, 2H, J = 14.1 Hz, $ArCH_2Ar$), 4.04 (d, 2H, J = 13.8 Hz, $ArCH_2Ar$), 3.62 (m, 4H, $ArCH_2Ar$), 3.46 (d, 2H, J = 13.8 Hz, $ArCH_2Ar$), 1.35 [s, 18H, $C(CH_3)_3$], 1.33 [s, 18H, $C(CH_3)_3$], 1.30 [s, 9H, $C(CH_3)_3$], 1.26 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.53, 149.5, 148.2, 148.1, 146.6, 144.4, 143.6, 142.9, 133.8, 133.5, 133.4, 132.7, 127.6, 127.5, 126.8, 126.7, 126.3 (ArC), 129.3, 128.3, 128.0, 126.7, 126.3, 126.0, 125.9, 125.7, 125.4, 125.3 (ArCH), 78.4 (OCH_2Ar), 34.3, 34.1, 34.0, 33.9 [$C(CH_3)_3$], 33.4, 32.8, 32.6 ($ArCH_2Ar$), 31.7, 31.6, 31.5, 31.3 [$C(CH_3)_3$]; MS (FAB$^+$) m/z 1112.6 (M$^+$). Anal. Calcd for $C_{77}H_{92}O_6$·$^1/_2CH_2Cl_2$: C, 81.78; H, 8.24. Found: C, 81.37; H, 8.27.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41-pentahydroxy-42-(2′-phenylethyloxy)calix[6]arene (8). Calix[6]arene **8** was obtained with 2-chloro-1-phenylethane (1.05 mmol) and NaI (0.8 mmol). Time for the reaction was 5 days, to yield 34% (73 mg) after chromatography (hexane−CH_2Cl_2 2:1) and trituration with methanol: mp 171−174 °C; ^{1}H NMR ($CDCl_3$) δ 9.80 (s, 2H, OH), 9.51 (s, 1H, OH), 8.70 (s, 2H, OH), 7.47 (dd, 2H, J = 6.9 Hz, J = 1.4 Hz, ArH), 7.38 (t, 2H, J = 7.6 Hz, ArH), 7.23 (tt, 1H, J = 7.2 Hz, J = 1.4 Hz), 7.18−7.08 (m, 10H, ArH), 7.12 (s, 2H, ArH), 6.98 (s, 2H, ArH), 4.31 (t, 2H, J = 6.9 Hz, OCH_2), 4.24 (d, 4H, J = 13.9 Hz, $ArCH_2Ar$), 3.98 (d, 2H, J = 13.9 Hz, $ArCH_2Ar$), 3.63 (d, 2H, J = 14.3 Hz, $ArCH_2Ar$), 3.50 (d, 2H, J = 13.9 Hz, $ArCH_2Ar$), 3.46 (d, 2H, J = 13.8 Hz, $ArCH_2Ar$), 3.38 (t, 2H, J = 6.8 Hz, OCH_2CH_2Ar), 1.30 [s, 18H, $C(CH_3)_3$], 1.28 [s, 18H, $C(CH_3)_3$], 1.24 [s, 9H, $C(CH_3)_3$], 1.14 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.7, 149.3, 148.1, 147.7, 146.8, 144.3, 143.6, 142.9, 137.8, 132.2, 127.4, 127.2, 126.9, 126.8, 126.6 (ArC), 128.9, 128.7, 126.7, 126.1, 126.0, 125.9, 125.8, 125.7, 125.4 (ArCH), 76.8 (OCH_2), 36.5 (OCH_2CH_2Ar), 34.2, 33.93, 33.89 [$C(CH_3)_3$], 33.1, 32.6, 32.3 ($ArCH_2Ar$), 31.55, 31.52, 31.4, 31.2 [$C(CH_3)_3$]; MS (FAB$^+$) m/z 1076.6 (M$^+$). Anal. Calcd for $C_{74}H_{92}O_6$: C, 82.47; H, 8.61. Found: C, 81.98; H, 8.64.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41-pentahydroxy-42-(3′-phenylpropyloxy)calix[6]arene (9). Calix[6]arene **9** was obtained with 1-chloro-3-phenylpropane (1.04 mmol) and NaI (0.8 mmol). Time for the reaction was 5 days, to yield 25% (74 mg) after chromatography (hexane−CH_2Cl_2 2:1) and trituration with methanol: mp 174−176 °C; ^{1}H NMR ($CDCl_3$) δ 9.90 (s, 2H, OH), 9.36 (s, 1H, OH), 9.07 (s, 2H, OH), 7.40 (dd, 2H, J = 7.0 Hz, J = 1.4 Hz, ArH), 7.31 (t, 2H, J = 7.5 Hz, ArH), 7.20 (tt, 1H, J = 7.2 Hz, J = 1.3 Hz, ArH), 7.14 (d, 6H, J = 1.9 Hz, ArH), 7.09 (d, 2H, J = 1.3 Hz, ArH), 7.07 (s, 2H, ArH), 7.00 (s, 2H, ArH), 4.35 (d, 2H, J = 13.6 Hz, $ArCH_2Ar$), 4.15 (d, 2H, J = 14.4 Hz, $ArCH_2Ar$), 4.14 (t, 2H, J = 7.5 Hz, OCH_2), 4.00 (d, 2H, J = 13.9 Hz, $ArCH_2Ar$), 3.55 (d, 2H, J = 14.6 Hz, $ArCH_2Ar$), 3.49 (d, 4H, J = 13.7 Hz, $ArCH_2$-Ar), 3.15 (t, 2H, J = 7.5 Hz, $OCH_2CH_2CH_2Ar$), 2.46−2.37 (m, 2H, $OCH_2CH_2CH_2Ar$), 1.30 [s, 18H, $C(CH_3)_3$], 1.27 [s, 18H, $C(CH_3)_3$], 1.22 [s, 9H, $C(CH_3)_3$], 1.15 [s, 9H, $C(CH_3)_3$]; ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT) δ 149.7, 149.4, 148.2, 147.8, 146.8, 144.3, 143.6, 143.0, 141.3, 132.3, 127.3, 127.2, 127.0, 126.8 (ArC), 128.7, 128.5, 126.2, 126.03, 126.01, 125.9, 125.8, 125.4 (ArCH), 75.2 (OCH_2), 34.2, 33.97, 33.96, 33.94, [$C(CH_3)_3$], 33.2, 32.6, 32.5, 32.3, 31.9 ($ArCH_2Ar$ and $OCH_2CH_2CH_2Ar$), 31.6, 31.5, 31.4, 31.2 [$C(CH_3)_3$]; MS (FAB$^+$) m/z 1090.8 (M^+). Anal. Calcd for $C_{75}H_{94}O_6$: C, 82.51; H, 8.68. Found: C, 82.49; H, 8.51.

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Supporting Information Available: Copies of 1D ^{1}H NMR spectra of **3** and **4** at room temperature; **9**, **8**, **2a** in $CDCl_3$ at 213 and 203 K; **2g**, **5** in DMSO-d_6 at 300−400 K; **2f** and **5** in $C_2D_2Cl_4$ at 300−396 K and 2D NMR spectra of **6** and **2a** (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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