A Convenient Preparation of C-Silylated Calixarenes

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Abstract: Calix[4]arenes having multiple silyl groups on the upper (wide) rim were prepared from the corresponding bromocalixarenes by halogen–metal exchange with *t*-BuLi followed by silylation. The best results were obtained using the clear supernatant from a mixture of chlorosilane and triethylamine. With the higher molecular weight chlorosilanes, an aqueous workup was replaced by a filtration through a column of silica gel. *p*-(Trimethylsilyl)calixarene **17**, the silicon analogue of the well-studied *p*-*tert*-butylcalixarene **1**, formed a crystalline complex with toluene having a toluene molecule in the cone cavity with the toluene methyl protruding out at an angle.

Key words: calixarenes, silicon, halogen–metal exchange

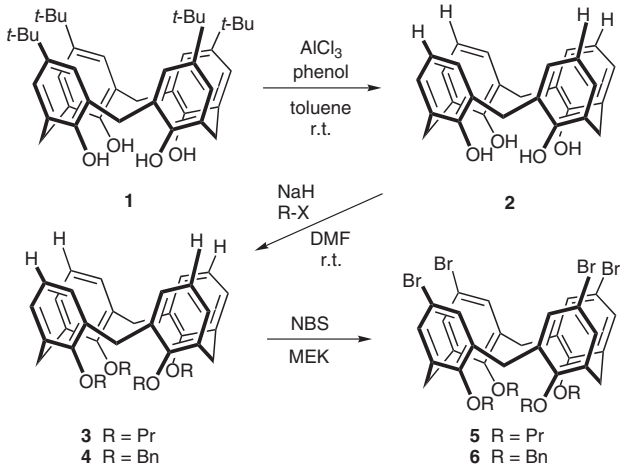
Calixarenes[1] are of considerable current interest in molecular recognition and supramolecular chemistry, and as building blocks for more complicated structures. They are easily prepared from inexpensive starting materials, are easily modified at the upper (wide) and lower (narrow) rims, and have been shown to exist in several well-defined conformations (for calix[4]arenes: cone, partial cone, 1,2-alternate, and 1,3-alternate). Many functional groups have been introduced onto the upper rim of calixarenes, primarily by electrophilic aromatic substitution reactions.

Silylated calixarenes are of potential interest in molecular recognition because some tetracoordinate silicon compounds can form relatively stable hypercoordinate compounds with nucleophiles,[2] suggesting the possibility that silylated calixarenes may be useful for recognition of anionic guests.[3–6] Silyl ethers of calixarenes (lower rim) are well known.[7] We became interested in the preparation of calixarenes having multiple silicon groups, especially at the upper (wide) rim. Upper rim substituents are frequently introduced onto calixarenes by electrophilic substitution reactions. However, the introduction of silyl groups onto aromatic rings by electrophilic aromatic substitution, although known, is not a general method.[8] More commonly, carbon–silicon bonds are made by reactions of organometallic reagents with chlorosilanes. These reactions have not generally been used for the introduction of multiple silyl groups. If such reactions did not proceed in high yield, attempted introduction of multiple silyl groups onto large molecules would produce mixtures of completely and partially silylated compounds, which might be difficult to separate. We have reported the use of the Wurtz–Fittig reaction for the preparation of *p*-C-silylated calixarenes.[5a,b] Two examples of *p*-C-silylated calix[4]arenes have been reported using halogen–metal exchange on bromocalixarenes with *t*-BuLi in THF, followed by treatment with Me_3SiCl.[6,9] In each case, products were purified by chromatography. In one case, fractional crystallization was also employed to separate the tetrakis-Me_3Si compound from the tris.[6] We report here a convenient method to introduce multiple silyl groups onto calix[4]arenes (using readily available halogenated calixarenes) via halogen–metal exchange, which generally does not require chromatography. In principle, this methodology should be applicable to the preparation of other multiply silylated molecules as well.

Preparation of Substrates

Halogenated calix[4]arenes were prepared using standard procedures as outlined below. All the reactions gave good yields, and products were easily purified by crystallization without chromatography.

The preparation of the tetrabromocalix[4]arene substrates is shown in Scheme 1. Thus, *p*-*tert*-butylcalix[4]arene (**1**)[10] was dealkylated using $AlCl_3$ and phenol in toluene[11] to give *p*-H-calixarene **2**[12] (50–74% yield). Calixarene **2** was treated with NaH/PrI in DMF[11] to give the tetrapropyl ether **3** (80–88% yield), and with NaH/BnBr in DMF to give tetrabenzyl ether **4**[13] (76–81% yield). This procedure[11,14] is known to give calix[4]arenes fixed in the cone conformation[15] when propyl or larger groups are introduced. The tetrabromo substrates **5**[16] (86–93% yield)



Scheme 1

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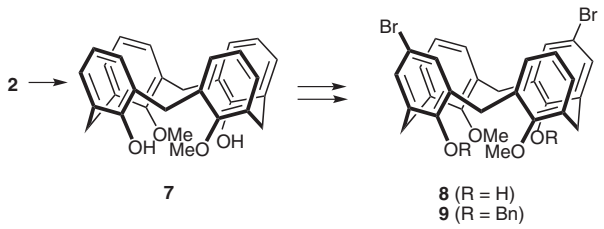


Scheme 2

and **6**[17] (78–88% yield) were prepared by treatment of **3** and **4** , respectively, with NBS in methyl ethyl ketone (MEK). [18]

A substrate for the preparation of disilylated calix[4]arenes, the dibromide **9**, was prepared as shown in Scheme 2. Dimethoxycalixarene **7** was prepared in 70–95% yields by selective alkylation of tetrahydroxycalixarene **2** with MeOTs and K_2CO_3 in MeCN.[19] Taking advantage of the fact that the phenolic rings are more reactive toward electrophilic substitution than are the corresponding ethers, **7** can be converted to the dibromide **8**. Although attempts to effect this conversion with bromine[19] did not lead cleanly to **8** in our hands, when **7** was treated with NBS in MEK,[18,20] the dibromide **8**[19] was produced cleanly in 73–96% yields. Treatment of **8** with NaH/BnBr in DMF yielded benzyl ether **9**[5c] in 80–92% yields.

Halogen–Metal Exchange Reactions

Our initial attempts to prepare C-silylated calixarenes by halogen–metal exchange[21] followed by silylation led to the desired product as the major component of a mixture. For example, treatment of tetrabromide **5** with *t*-BuLi in THF at –78 °C followed by Me_3SiCl (distilled from CaH_2), gave an oily crude product. MALDI-TOF mass spectral analysis indicated that the tetrakis(trimethylsilyl)calixarene **10** was the major product, but that the corresponding tris(trimethylsilyl)calixarene **11** was also present (Figure 1). The ^{1}H NMR spectrum showed the peaks expected for **10** and additional small peaks, including those expected for **11**. (Samples of calixarenes **10** and **11** were available from a Wurtz–Fittig silylation reaction,[5b] and they can be easily distinguished in the ^{1}H NMR spectra. The propyl OCH_2 groups of **11** give rise to multiplets of equal size at about δ = 4.0 and 3.7; the propyl OCH_2 groups of **10** give a triplet at about δ = 3.85. The

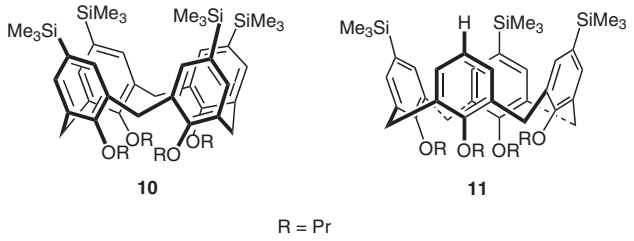


Figure 1 Calixarenes **10** and **11**

spectrum of **11** indicates a flattened cone conformation.[5c,22]) The product was purified by column chromatography, and **10** was obtained pure as white crystals in 62% yield.

We believe that the initially-generated tetralithio intermediate was reacting in part with traces of HCl in the chlorosilane. We therefore tried repeating the reaction, and adding Et_3N to the reaction mixture before adding the chlorosilane. There was little change in the spectra of the crude product. We therefore decided to try mixtures of the amine and the chlorosilane.[23]

When Me_3SiCl is mixed with Et_3N, a fine white precipitate ($Et_3N{\cdot}HCl$) immediately appears (even when each reagent is freshly distilled from CaH_2). The precipitate settles after a few days, and the mixture can be stored for several days, especially if kept cold. However, we centrifuged the mixture, and used the clear supernatant shortly afterwards.

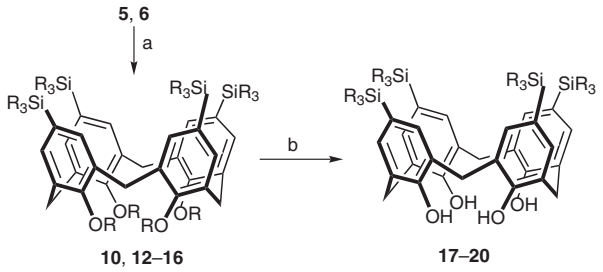
Typically, the Me_3SiCl and Et_3N were premixed in a nitrogen- or argon-flushed, septum-capped centrifuge tube, the resulting white precipitate was compacted by centrifuge, and the supernatant was withdrawn by a syringe, and added to the cold mixture of **5** and *t*-BuLi. This procedure gave a crystalline crude product after workup. MALDI-TOF MS of the crude product showed a peak at *m*/*z* 903.8 corresponding to the tetrasilyl compound **10** (as the Na adduct); partially silylated compounds were not observed. In addition, the ^{1}H NMR spectrum indicated the product was rather pure **10** with no evidence for the tris(trimethylsilyl)calixarene **11**. Calixarene **10** could be purified by a simple recrystallization, and was obtained in 79% yield.

This procedure was carried out using several chlorosilanes, and using both the propyl and benzyl ether substrates **5** and **6**. The results are summarized in Table 1. Using Me_3SiCl or $PhMe_2SiCl$ with **6** gave the tetrasilylated calixarenes **12** (86–92% yields), and **13** (92% yield), respectively. In both cases, the products were purified only by simple recrystallization; chromatography was not necessary.

When $Ph_2MeSiCl$ and (allyl)Me_2SiCl were used as silylating agents in the above procedure, chromatography was necessary to purify the products **14**, **15**, and **16**. [In all of these reactions, the reaction mixtures were worked up by concentration on the rotary evaporator, partitioning between aqueous $NaHCO_3$ and Et_2O,[24] drying, and again concentrating. The products were routinely placed under oil-pump vacuum (ca. 0.05 mm) for about two hours. The aqueous workup would be expected to convert any remaining chlorosilane into silanol and disiloxane, and the higher molecular weight disiloxanes are not volatile.]

For benzyl ether substrate **6** with $Ph_2MeSiCl$, a solid crude product was obtained, but recrystallization did not provide a pure product. Chromatography resulted in silylated calixarene **14** in 61% yield, which appeared to be almost pure by ^{1}H NMR spectroscopy. For propyl ether substrate **5** and (allyl)Me_2SiCl, a crude product consisting of an oil and solid was obtained, and chromatography resulted in

Table 1 Silylations of Tetraabromocalixarenes and Removal of Benzyl Ethers



10, **12–16** **17–20**

(a) (1) *t*-BuLi, THF, –78 °C; (2) R_3SiCl, Et_3N. (b) H_2, Pd/C, EtOAc.

OR	Product	R_3Si	Yield (%)	Product	Yield (%)
OPr	**10**	Me_3Si	79	–	–
OBn	**12**	Me_3Si	92	**17**	88
OBn	**13**	$PhMe_2Si$	92	**18**	92
OBn	**14**	Ph_2MeSi	79[a]	**19**	68
OPr	**15**	(allyl)Me_2Si	86[a]	–	–
OBn	**16**	(allyl)Me_2Si	65	**20**[b]	86

[a] Non-aqueous workup.
[b] $PrMe_2Si$.

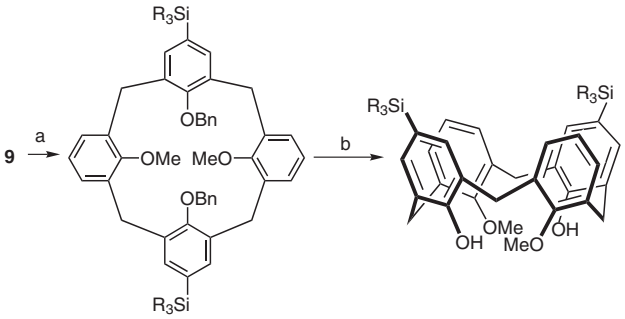
pure silylated calixarene **15** in 52% yield. For **6** and (allyl)Me_2SiCl, an oily crude product was obtained, and chromatography resulted in pure silylated calixarene **16** as a colorless oil in 48–65% yields. In this reaction, MALDI-TOF MS was run on the crude product, and a large peak for the tetrasilylated compound **16** (as Na adduct) was observed; no trisilylated material was detected.

To avoid the problem of separating the product from the higher molecular weight disiloxanes, we developed a non-aqueous workup procedure in which the crude product was concentrated by rotary evaporator as before, and then immediately passed through a silica gel column without taking fractions. The chlorosilanes presumably react with the silica gel and do not elute. The reactions which were rerun using this procedure gave products that could be purified by crystallization, and yields were better. Thus, treatment of benzyl ether substrate **6** with *t*-BuLi followed by the supernatant from $Ph_2MeSiCl/Et_3N$, and using the nonaqueous workup procedure, resulted in pure silylated calixarene **14** in 79% yield. A similar reaction using the propyl ether substrate **5** and (allyl)Me_2SiCl resulted in silylated calixarene **15** in 86% yield.

The benzyl groups in calixarenes **12–14** and **16** were removed by hydrogenolysis (treatment with H_2 in the presence of Pd/C) to give the hydroxycalixarenes **17–20** (see Table 1). Hydrogenolysis of the Ph_2MeSi calixarene **14** to give **19** was slow (complete in 6 h), while with the other substrates, the reactions were complete in two hours. (The product from the hydrogenolysis of allyldimethylsilylcalixarene **16** was propyldimethylsilylcalixarene **20**.) The Ph_2MeSi calixarenes **14** and **19** are notable in that four very bulky groups have been incorporated on the upper rim.

Dibromide **9** was used as a substrate for reactions to introduce two silicon groups. As in the above silylations, compound **9** was treated with *t*-BuLi in THF followed by the chlorosilane/Et_3N mixture (clear supernatant after centrifugation). Disilylated calixarenes **21–24** were obtained in good yields in most cases. The results are summarized in Table 2.

Table 2 Silylations of Dibromocalixarene **9** and Removal of Benzyl Ethers



21–24 **25–27**

(a) (1) *t*-BuLi, THF, –78 °C; (2) R_3SiCl, Et_3N.
(b) H_2, Pd/C, EtOAc.

R_3Si	Product	Yield (%)	Product	Yield (%)
Me_3Si	**21**	84	**25**	78
$PhMe_2Si$	**22**	57	**26**	84
Ph_2MeSi	**23**	79[a]	–	–
(allyl)Me_2Si	**24**	60	**27**[b]	95

[a] Non-aqueous workup.
[b] $PrMe_2Si$.

Initially the aqueous workup procedure was used for these reactions. When Me_3SiCl was used as the silylating agent, the product **21** was purified by only recrystallization (81–84% yields). Chromatography was initially used for purification of the other products, giving **22** from $PhMe_2SiCl$ in 57–66% yields as a crystalline product and **24** from (allyl)Me_2SiCl in 60% yield as an oil. Attempts were made to purify calixarene **23** (from **9** and $Ph_2MeSiCl$) by recrystallization, but the product was not pure by ^1H NMR spectroscopic analysis. A reaction in which the product was purified by careful chromatography resulted in pure **23** in 65% yield.

When the nonaqueous workup procedure became available, this was applied to the reaction of **9** and $Ph_2MeSiCl$, giving pure **23** as a white powder in 79% yield. The other silylations were not repeated using the nonaqueous workup procedure, but that is expected to be the better procedure for reactions with the higher molecular weight chlorosilanes.

The benzyl groups were removed from calixarenes **21**, **22**, and **24** uneventfully by treating with H_2 in the presence of

Pd/C in ethyl acetate, giving the hydroxycalixarenes **25**–**27** (**27** as the $PrMe_2Si$ compound, Table 2). However, attempted debenzylation of the Ph_2MeSi calixarene **23** under the same conditions (2 h) led to recovered **23**. Use of reaction times up to seven hours led to small amounts of product, but the reaction did not go to completion.

The conformations and NMR spectra of these calixarenes deserve comment. All of the previously reported calixarenes prepared in this work, and most of the new calixarenes (except as noted below) were in the cone conformation as shown by NMR spectroscopy.[25,26] The cone conformation of the tetrahydroxy and dihydroxycalixarenes is presumably due to the stability provided by hydrogen bonding, while that of the tetrapropyloxy and tetrabenzyloxy calixarenes arises from the method of preparation[14] of **3** and **4**, and the fact that conformational interconversion of calix[4]arenes is blocked when the phenolic oxygens are alkylated with propyl (or larger) groups.[15] However, while dihydroxy(dimethoxy) calixarene **8** is a cone, the benzylated compound **9** (drawn as a cone) appeared to be a mixture, and the silylation products **21**–**24** showed broad resonances in the ^1H NMR spectra, suggesting conformational equilibrium on the ^1H NMR time scale. Removal of the benzyl groups gave calixarenes **25**–**27**, which again showed sharp ^1H NMR spectra characteristic of the cone conformation, presumably because the H-bonding ability was restored.

The ^1H NMR spectrum of tetrahydroxy(tetrakis)TMS calixarene **17** showed the presence of CH_2Cl_2 (ca. 1:1 ratio) when it was recrystallized from CH_2Cl_2–MeOH, even after placing under oil-pump vacuum (0.1 mm) for two hours. (The elemental analysis showed the presence of $CHCl_3$, which was used in the preparation of the analytical sample.) Some samples of the other calixarenes showed smaller amounts of CH_2Cl_2 by ^1H NMR spectroscopy, suggesting an affinity for complexing with these solvents.

Complexation Studies

Although complexation of the silylated calixarenes with nucleophilic or anionic groups is expected to be more favorable if there are electron-withdrawing groups on the silicon, we briefly studied some of the calixarenes synthesized here. We did not observe complex-induced shifts by ^1H NMR titration (using $MeNO_2$ and calixarenes **12**, **17**, or **25** in $CDCl_3$, or calixarene **10** in xylene-d_{10}; an attempt with calixarene **18** suffered from low solubility in xylene). A brief extraction study[27] showed some extraction of tetrabutylammonium benzoate[28] from water into $CDCl_3$ using the tetrahydroxycalixarene **20** (with *p*-xylene as standard). Suspecting this might be due to an acid-base interaction with the calixarene hydroxyls, we also tried using the dihydroxycalixarene **25**, which should have a considerably higher pK_a value,[29] and did not observe any extraction of the benzoate. We have prepared a complex of tetrakis(trimethylsilyl)calixarene **17** with toluene, and obtained a crystal structure by X-ray diffraction (below).

Calixarene **17** is the silicon analogue of the well-studied *p-tert*-butylcalix[4]arene **1**. The complex of **1** and toluene is well known,[30] and was the first[30a] solid state complex involving a calixarene to be reported.[31] The X-ray crystal structure showed a cone conformation of the calixarene, with the methyl group of the toluene inserted well into the cone cavity. (Further refinement aided by solid-state NMR indicated that the toluene symmetry axis is slightly tilted off the axis of symmetry of the calixarene,[30d,e] and that about 5–10% of the toluene has the methyl protruding out of rather than into the calix cavity.[30d])

A diametrically dimethylated (25,27-dimethoxy-26,28-dihydroxy)-*tert*-butylcalixarene formed a complex with toluene analogous to that of **1**.[32] A number of X-ray structures of *tert*-butylcalixarenes complexed with metals at the oxygens have been reported, many including a toluene in the calix cavity. Different orientations of toluene in the cavities have been observed,[33] possibly due to differences in pitch of the cavity due to hydrogen bonding or metal complexation at the oxygen atoms.[32]

The *tert*-butyl groups extend the calix cavity, and are believed to be instrumental in the complexation of neutral guests by simple calixarenes.[30d] Removal of the *tert*-butyl group from **1** (to give **2**) dramatically reduces the ability of the calixarene to complex simple aromatic guest molecules.[34] X-ray crystal structures of toluene complexes of simple calix[4]arenes having some other *para* substituents have been reported. An analogue of **1** having 1,1,3,3-tetramethylbutyl groups showed a cone structure with toluene in the lattice,[34] while the isopropyl analog of **1** showed a structure with toluene in the cavity, but with the opposite orientation, with the methyl group pointing straight out.[35]

We obtained crystals by allowing a solution of **17** in toluene immersed in a hot water bath to cool to room temperature overnight. Diffraction data were collected at 93 K. The structure is shown in Figure 2. There is no crystallographically imposed symmetry on the molecule – every atom is unique. The structure has two molecules of toluene per calixarene. One toluene is in the lattice. The other is in the cone cavity with the methyl group pointing out, with the symmetry axis of the toluene tilted by about 60° from that of the calixarene.

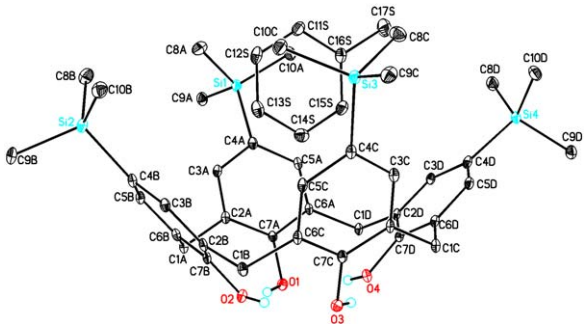


Figure 2 Structure of the toluene complex with calixarene **17**; the toluene in the lattice is omitted[36]

If the four rings in the calixarene system are consecutively labeled as A, B, C, and D, then the plane of the encapsulated toluene is parallel to the B–D vector and perpendicular to the A–C vector. With the CH_3 group of the toluene tilted by 60° from the vertical plane it is expected that the H's attached to this group and those attached to ring carbons C13S, C14S, and C15S would make the closest contacts with the calixarene skeleton. There are no close contacts involving the hydrogen attached to C14S as it projects into the cavity between the four oxygen atoms.

However, there are close contacts involving the H's attached to C13S and C15S (H13A and H15A) and the phenyl carbon atoms of ring B and D (Table 3). There are also close contacts between the toluene methyl H's (H17A) and the methyl H's (H10L) of the calixarene *tert*-butyl groups. As is usual in calixarenes, the protons attached to the four oxygen atoms are involved in hydrogen bonding interactions in a head to tail fashion.

Table 3 Closest Contacts between the Toluene and Calixarene Skeletons

Atom 1	Atom 2	H···X distance (Å)	C–H···X angle (°)
H13A	C3B	2.924	158.4
H13A	C4B	2.802	173.4
H13A	C5B	2.955	147.8
H15A	C2D	2.934	141.8
H15A	C3D	2.975	160.2
H15A	C4D	2.948	168.9
H17A	H10L (C10D)	2.363	158.5
H17B[a]	H8BA (C8B)	2.513	132.0

[a] Intermolecular contact.

Conclusion

Calixarenes with multiple silyl groups on the upper rim can be easily prepared in high yields from the corresponding halogenated calixarenes by halogen–metal exchange followed by silylation. Yields and purities are improved when the silylation is carried out using the clear supernatant from a mixture of chlorosilane and triethylamine. Presumably this removes the proton source as $Et_3N{\cdot}HCl$. Silylation reactions using higher molecular weight chlorosilanes were further improved by omitting an aqueous workup, and instead passing the concentrated reaction mixture through a silica gel column. In principle, this methodology should be applicable to the preparation of other multiply silylated molecules,[37] such as organosilicon dendrimers and hyper-branched polymers,[38] and silicon-bridged macrocycles, such as siloxane-bridged cyclophanes.[39] A complex of toluene with calixarene **17**, the silicon analogue of *p-tert*-butylcalixarene **1**, was prepared and a toluene was shown by X-ray to be in the cone cavity with the toluene methyl protruding out of the cavity.

Unless otherwise stated, all reactions were carried out under argon or N_2, and transfers of liquids were carried out with N_2- or argon-flushed syringes. For experiments requiring anhydrous conditions, glassware was dried overnight at 120 °C, and cooled in a desiccator. The verb 'concentrated' refers to removal of solvent using a rotary evaporator. THF was distilled from sodium and benzophenone. DMF, Et_3N, and Me_3SiCl were distilled from CaH_2. Petroleum ether (PE) used refers to the fraction boiling in the range 30–60 °C. The chlorosilane/Et_3N mixtures were prepared by mixing equal volumes of the chlorosilane and Et_3N in a centrifuge tube (which had been flushed with argon, capped with a septum, and connected to the argon line via a syringe needle), centrifuging for 3 min, and taking the supernatant solution by a syringe. Column chromatography was done as flash chromatography using 200–425 mesh silica gel. All products were placed under oil pump vacuum (0.1–0.05 mm) at r.t. for at least 2 h. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were obtained in $CDCl_3$. Chemical shifts were reported in δ using $CHCl_3$ (7.26) or CH_2Cl_2 (5.32) for ^1H NMR (indicated as standard), and $CDCl_3$ (77.00) for ^{13}C NMR as internal references. ^{13}C NMR assignments were made using DEPT. MALDI-TOF mass spectra were performed using 2,5-dihydroxybenzoic acid as the matrix.

Silylation of Calixarenes 5, 6, and 9; Typical Procedures

1. Procedure Using Aqueous Workup; Preparation of Compound 13

A solution of tetrabromocalixarene **6** (0.30 g, 0.27 mmol) in THF (15 mL) was cooled to –78 °C. A solution of *t*-BuLi (2.0 mL, 1.5 M in pentane, 3.0 mmol) was slowly added to the stirred mixture and the stirring was continued for 2 h. A mixture of $PhMe_2SiCl$ and Et_3N (1:1 v/v; 1.0 mL, ca. 3 mmol of chlorosilane) was slowly added at –78 °C. The resulting mixture was slowly warmed to r.t. in 45 min and stirred for 2 h at r.t. The mixture was then transferred to a one-necked flask and concentrated giving a solid, which was partitioned between Et_2O (20 mL) and H_2O (15 mL). The organic layer was washed with brine (15 mL), dried ($MgSO_4$), and concentrated giving a solid product. Recrystallization from MeOH–CH_2Cl_2 (9:1) yielded 0.33 g (92%) of **13** as white crystals.

2. Procedure Using Non-aqueous Workup; Preparation of Compound 15

A solution of tetrabromotetrapropoxycalixarene **5** (0.348 g, 0.38 mmol) in THF (15 mL) was cooled to –78 °C, and a solution of *t*-BuLi (3.0 mL, 1.5 M in pentane, 4.5 mmol) was added slowly. The mixture was stirred for 1.5 h at –78 °C. A mixture of allyldimethylchlorosilane and Et_3N (1:1 v/v; 1.0 mL, ca. 3.3 mmol of chlorosilane) was slowly added at –78 °C. The mixture was then allowed to warm up to r.t. gradually in about 45 min and was stirred at r.t. for 2 h. The mixture was then transferred to a one-necked flask and concentrated. The crude mixture was immediately passed through a silica gel chromatography column (9.0 g, 1.2 × 22 cm) using PE–CH_2Cl_2 (1:1) as eluent. The eluent (ca. 150 mL) was concentrated and the residue recrystallized from MeOH–CH_2Cl_2 (9:1) to give 0.324 g (86%) of **15** as white crystals.

Hydrogenation of Benzyl Ethers; Typical Procedure

Preparation of Compound 18

A three-necked 50 mL flask, fitted with a stopcock adapter attached to a H_2-filled balloon, was placed under argon on an argon line. The tetrakis(dimethylphenylsilyl)calix[4]arene **13** (0.12 g, 0.091 mmol), 10% Pd/C (0.10 g), and EtOAc (20 mL) were added to the

flask. The connection to the argon bubbler was closed, the stopcock to the H_2-filled balloon was opened, and a small amount of H_2 was allowed to sweep through the flask for a few seconds by slightly opening a septum on one of the necks. The mixture was stirred for 2 h. The mixture was then filtered using Celite and concentrated. The crude solid was recrystallized from MeOH–CH_2Cl_2 (9:1) to give 0.080 g (92%) of **18** as white crystals.

Tetrakis(trimethylsilyl)calixarenes
5,11,17,23-Tetrakis(trimethylsilyl)-25,26,27,28-tetrapropoxycalix[4]arene (10)
The crude product was recrystallized from 4:1 MeOH–acetone; white powder; mp 196–197 °C; 198–199 °C (analytical sample).

IR ($CHCl_3$): 2953, 2871, 1464, 1382, 1267, 1247, 1122, 1006, 881, 833 cm^{-1}.

^1H NMR ($CHCl_3$ standard): δ = 6.89 (s, 8 H, ArH), 4.44 (d, *J* = 12.5 Hz, 4 H, ArC*H*$_2$Ar), 3.85 (t, *J* = 7.6 Hz, 8 H, OC*H*$_2$CH$_2$), 3.17 (d, *J* = 12.5 Hz, 4 H, ArC*H*$_2$Ar), 2.03 (m, 8 H, OCH$_2$C*H*$_2$), 1.00 (t, *J* = 7.4 Hz, 12 H, OCH$_2$CH$_2$C*H*$_3$), 0.05 [s, 36 H, Si(CH$_3$)$_3$].

^{13}C NMR: δ = 156.8 (C), 133.9 (C), 133.3 (CH), 132.8 (C), 77.0 (CH_2), 30.6 (CH_2), 23.3 (CH_2), 10.3 (CH_3), –0.9 (CH_3).

MALDI-TOF MS (crude product): *m*/*z* calcd for $[M + Na]^+$: 903.5; found: 903.8; with no visible peak at *m*/*z* = 832 [**11** + Na]$^+$ (less than 1% would have been visible).

Anal. Calcd for $C_{52}H_{80}O_4Si_4$: C, 70.85; H, 9.15. Found: C, 70.99; H, 9.57.

25,26,27,28-Tetrabenzyloxy-5,11,17,23-tetrakis(trimethylsilyl)calix[4]arene (12)
The crude product crystallized out from the Et_2O solution in white crystals; mp 176–177 °C.

IR (KBr): 3032, 2955, 1465, 1245, 1209, 1117, 984, 891, 830, 748, 692 cm^{-1}.

^1H NMR (CH_2Cl_2 standard): δ = 7.31–7.24 (m, 20 H, C_6H_5), 6.84 (s, 8 H, ArH), 4.92 (s, 8 H, OC*H*$_2$Ph), 4.20 (d, *J* = 12.7 Hz, 4 H, ArC*H*$_2$Ar), 2.93 (d, *J* = 12.8 Hz, 4 H, ArC*H*$_2$Ar), 0.07 [s, 36 H, Si(CH$_3$)$_3$].

^{13}C NMR: δ = 155.9 (C), 138.1 (C), 133.9 (C), 133.4 (CH), 133.1 (C), 129.8 (CH), 128.0 (CH), 127.7 (CH), 76.6 (CH_2), 31.1 (CH_2), –0.9 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for $[M + Na]^+$: 1095.5; found: 1096.0.

25,26,27,28-Tetrahydroxy-5,11,17,23-tetrakis(trimethylsilyl)calix[4]arene (17)
The crude product was recrystallized from 9:1:1 MeOH–acetone–CH_2Cl_2; white crystals; mp 265–267 °C; 263.6–264.6 °C (analytical sample recrystallized from MeOH–acetone–$CHCl_3$).

IR (KBr): 3155, 3012, 2950, 1588, 1470, 1245, 1127, 906, 835, 753 cm^{-1}.

^1H NMR ($CHCl_3$ standard): δ = 10.2 (s, 4 H, ArO*H*), 7.18 (s, 8 H, ArH), 4.26 (d, *J* = 14.0 Hz, 4 H, ArC*H*$_2$Ar), 3.55 (d, *J* = 13.8 Hz, 4 H, ArC*H*$_2$Ar), 0.17 [s, 36 H, Si(CH$_3$)$_3$].

In the ^1H NMR spectrum of the original sample, an additional peak was present at δ = 5.3, assigned to CH_2Cl_2. The integration suggested a 1:1 complex (area ratio of the peaks at δ = 5.3 to 4.26 is 1.7:4.0).

^{13}C NMR: δ = 149.6 (C), 134.2 (CH), 133.6 (C), 127.8 (C), 31.7 (CH_2), –1.1 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for $[M + Na]^+$: 735.3; found: 737.0.

Anal. Calcd for $C_{40}H_{56}O_4Si_4 \cdot 0.5\ CHCl_3$: C, 62.94; H, 7.37. Found: C, 62.65; H, 7.37.

Tetrakis(phenyldimethylsilyl)calixarenes
25,26,27,28-Tetrabenzyloxy-5,11,17,23-tetrakis(phenyldimethylsilyl)calix[4]arene (13)
The crude product was recrystallized from 9:1 MeOH–CH_2Cl_2; white crystals: mp 170–172 °C.

IR (KBr): 3062, 3021, 2955, 1465, 1424, 1255, 1245, 1209, 1116, 1107, 983, 830, 805, 774, 697 cm^{-1}.

^1H NMR (CH_2Cl_2 standard): δ = 7.37–7.27 (m, 40 H, C_6H_5), 6.86 (s, 8 H, ArH), 4.98 (s, 8 H, OC*H*$_2$Ph), 4.18 (d, *J* = 12.8 Hz, 4 H, ArC*H*$_2$Ar), 2.86 (d, *J* = 12.9 Hz, 4 H, ArC*H*$_2$Ar), 0.33 [s, 24 H, Si(CH$_3$)$_2$].

^{13}C NMR: δ = 156.2 (C), 139.5 (C), 137.8 (C), 134.3 (CH), 134.2 (C), 134.0 (CH), 130.4 (C), 130.0 (CH), 128.7 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 76.5 (CH_2), 31.3 (CH_2), –2.2 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for $[M + Na]^+$: 1343.6; found: 1344.4.

25,26,27,28-Tetrahydroxy-5,11,17,23-tetrakis(phenyldimethylsilyl)calix[4]arene (18)
The crude product was recrystallized from 9:1 MeOH–CH_2Cl_2; white crystals: mp 194–196 °C; 192.9–193.4 °C (analytical sample).

IR (KBr): 3206, 3170, 3017, 2950, 1588, 1475, 1245, 1127, 906, 835, 753 cm^{-1}.

^1H NMR ($CHCl_3$ standard): δ = 10.35 (s, 4 H, ArO*H*), 7.50 (d, *J* = 1.7 Hz, 8 H, C_6H_5), 7.35 (m, 12 H, C_6H_5), 7.15 (s, 8 H, C_6H_5), 4.25 (d, *J* = 13.9 Hz, 4 H, ArC*H*$_2$Ar), 3.53 (d, *J* = 13.9 Hz, 4 H, ArC*H*$_2$Ar), 0.45 [s, 24 H, Si(CH$_3$)$_2$].

^{13}C NMR: δ = 150.0, 138.2, 135.1, 134.1, 131.4, 129.1, 127.8, 127.7, 31.8, –2.2.

MALDI-TOF MS: *m*/*z* calcd for $[M + Na]^+$: 983.4; found: 983.4.

Anal. Calcd for $C_{60}H_{64}O_4Si_4$: C, 74.95; H, 6.71. Found: C, 74.61; H, 6.85.

Tetrakis(diphenylmethylsilyl)calixarenes
25,26,27,28-Tetrabenzyloxy-5,11,17,23-tetrakis(diphenylmethylsilyl)calix[4]arene (14)
The reaction mixture was concentrated on the rotary evaporator, and immediately passed through a silica gel column (2.5 × 10 cm) using ca. 150 mL of 1:1 hexane–CH_2Cl_2. The solution was concentrated and recrystallized from 9:1 MeOH–$CHCl_3$; white powder; mp 94–97 °C.

IR (KBr): 3062, 3022, 2950, 2919, 1460, 1424, 1250, 1209, 1122, 1107, 974, 784, 723, 697 cm^{-1}.

^1H NMR (CH_2Cl_2 standard): δ = 7.31–7.16 (m, 60 H, C_6H_5), 6.83 (s, 8 H, ArH), 5.03 (s, 8 H, OC*H*$_2$Ph), 4.16 (d, *J* = 12.7 Hz, 4 H, ArC*H*$_2$Ar), 2.82 (d, *J* = 12.9 Hz, 4 H, ArC*H*$_2$Ar), 0.46 (s, 12 H, SiCH$_3$).

^{13}C NMR: δ = 156.4 (C), 137.6 (C), 137.0 (C), 135.5 (CH), 135.2 (CH), 134.4 (C), 130.1 (CH), 129.0 (CH), 128.4 (C), 127.9 (CH), 127.6 CH), 76.3 (CH_2), 31.7 (CH_2), –3.1 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for $[M + Na]^+$: 1591.6; found: 1594.0.

25,26,27,28-Tetrahydroxy-5,11,17,23-tetrakis(diphenylmethylsilyl)calix[4]arene (19)
The crude product was recrystallized from 9:1 MeOH–acetone; white powder; mp 241–243 °C; 249–250 °C (analytical sample).

IR (KBr): 3219, 3167, 3068, 3045, 3016, 2955, 1476, 1451, 1424, 1249, 1127, 1108, 787, 739, 725, 701 cm^{-1}.

^1H NMR (CH_2Cl_2 standard): δ = 10.63 (s, 4 H, ArO*H*, exch. D_2O), 7.46–7.21 (m, 40 H, C_6H_5), 7.14 (s, 8 H, ArH), 4.28 (d, *J* = 13.6 Hz, 4 H, ArC*H*$_2$Ar), 3.52 (d, *J* = 13.7 Hz, 4 H, ArC*H*$_2$Ar), 0.71 (s, 12 H, SiCH$_3$).

^{13}C NMR: δ = 150.3 (C), 136.3 (CH), 136.2 (C), 135.2 (CH), 129.3 (CH), 129.2 (C), 127.8 (CH), 127.7 (C), 31.9 (CH_2), –3.0 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for [M + Na]$^+$: 1231.4; found: 1232.1.

Anal. Calcd for $C_{80}H_{72}O_4Si_4$: C, 79.42; H, 6.00. Found: C, 79.29; H, 5.74.

Tetrakis(allyldimethylsilyl) and (Propyldimethylsilyl)calixarenes

5,11,17,23-Tetrakis(allyldimethylsilyl)-25,26,27,28-tetrapropoxycalix[4]arene (15)

The reaction mixture was concentrated on the rotary evaporator, and immediately passed through a silica gel column (1.2 × 22 cm) using ca. 150 mL of 1:1 PE–CH_2Cl_2. The solution was concentrated and recrystallized from 9:1 MeOH–CH_2Cl_2; white crystals; mp 142–143 °C; 145.9–146.5 °C (analytical sample).

^{1}H NMR ($CHCl_3$ standard): δ = 6.89 (s, 8 H, ArH), 5.76–5.65 (m, 4 H, C*H*=CH_2), 4.78 (d, *J* = 12.9 Hz, 8 H, CH=CH_2), 4.45 (d, *J* = 12.6 Hz, 4 H, ArCH_2Ar), 3.86 (t, *J* = 7.7 Hz, 8 H, OC$H_2$$CH_2$), 3.18 (d, *J* = 12.7 Hz, 4 H, ArCH_2Ar), 2.05–2.00 (m, 8 H, OCH_2CH_2), 1.56 (d, *J* = 8.1 Hz, 8 H, CH_2CH=CH_2), 1.01 (t, *J* = 7.5 Hz, 12 H, $OCH_2CH_2CH_3$), 0.07 [s, 24 H, Si$(CH_3)_2$].

^{13}C NMR: δ = 157.1 (C), 135.0 (CH), 133.9 (C), 133.6 (CH), 131.2 (C), 113.0 (CH_2), 77.2 (CH_2), 30.7 (CH_2), 24.0 (CH_2), 23.3 (CH_2), 10.3 (CH_3), –3.4 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for [M + Na]$^+$: 1007.6; found: 1008.8.

Anal. Calcd for $C_{60}H_{88}O_4Si_4$: C, 73.11; H, 9.00. Found: C, 72.78; H, 9.05.

5,11,17,23-Tetrakis(allyldimethylsilyl)-25,26,27,28-tetrabenzyloxycalix[4]arene (16)

The crude product was chromatographed (silica gel, 2.5 × 12 cm, PE, 10 mL fractions, fractions 20–24); colorless oil.

IR ($CHCl_3$): 3028, 3009, 2960, 2925, 1631, 1583, 1470, 1455, 1256, 1245, 1124, 989, 897, 830, 698 cm^{-1}.

^{1}H NMR (CH_2Cl_2 standard): δ = 7.36–7.27 (m, 20 H, C_6H_5), 6.86 (s, 8 H, ArH), 5.75–5.66 (m, 4 H, C*H*=CH_2), 4.97 (s, 8 H, OCH_2Ph), 4.83–4.78 (m, 8 H, CH=CH_2), 4.21 (d, *J* = 12.8 Hz, 4 H, ArCH_2Ar), 2.93 (d, *J* = 12.9 Hz, 4 H, ArCH_2Ar), 1.60 (d, *J* = 8.1 Hz, 8 H, CH_2CH=CH_2), 0.12 [s, 24 H, Si$(CH_3)_2$].

^{13}C NMR: δ = 156.0 (C), 137.9 (C), 135.1 (CH), 134.1 (C), 133.7 (CH), 131.5 (C), 129.9 (CH), 128.0 (CH), 127.8 (CH), 113.0 (CH_2), 76.6 (CH_2), 31.3 (CH_2), 24.2 (CH_2), –3.4 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for [M + Na]$^+$: 1199.6; found: 1200.2.

25,26,27,28-Tetrahydroxy-5,11,17,23-tetrakis(propyldimethylsilyl)calix[4]arene (20)

The crude product was recrystallized from 10:1 MeOH–acetone; white crystals; mp 153–155 °C; 156–157 °C (analytical sample).

IR (KBr): 3165, 3012, 2955, 2863, 1588, 1475, 1455, 1245, 1158, 1127, 1102, 1061, 902, 830, 799 cm^{-1}.

^{1}H NMR ($CHCl_3$ standard): δ = 10.32 (s, 4 H, ArO*H*, exch. D_2O), 7.19 (s, 8 H, ArH), 4.28 (d, *J* = 14.0 Hz, 4 H, ArCH_2Ar), 3.58 (d, *J* = 13.9 Hz, 4 H, ArCH_2Ar), 1.57–1.32 (m, 8 H, $SiCH_2$CH_2CH_3), 0.96 (t, *J* = 7.2 Hz, 12 H, $SiCH_2CH_2$CH_3), 0.67 (crude t, *J* = 8.4 Hz, 8 H, Si$CH_2CH_2CH_3$), 0.17 [s, 24 H, Si$(CH_3)_2$].

^{13}C NMR: δ = 149.6 (C), 134.5 (CH), 132.9 (C), 127.7 (C), 31.8 (CH_2), 18.6 (CH_2), 18.4 (CH_3), 17.4 (CH_2), –2.9 (CH_3).

MALDI-TOF MS *m*/*z* calcd for [M + Na]$^+$: 847.4; found: 847.8.

Anal. Calcd for $C_{48}H_{72}O_4Si_4$: C, 69.84; H, 8.79. Found: C, 69.52; H, 8.78.

Bis(trimethylsilyl)calixarenes

26,28-Dibenzyloxy-25,27-dimethoxy-5,17-bis(trimethylsilyl)calix[4]arene (21)

The crude product was crystallized from CH_2Cl_2–MeOH; white crystals; mp 148–150 °C.

IR ($CHCl_3$): 3007, 2950, 2920, 2848, 1583, 1496, 1460, 1419, 1373, 1260, 1246, 1112, 1025, 917, 835, 690 cm^{-1}.

^{1}H NMR (CH_2Cl_2 standard): δ = 7.55–6.61 (m, 20 H), 5.00–3.11 (m, 18 H), two singlets at 0.11 and –0.10 in 4:1 ratio (total integration 18 H).

^{13}C NMR: δ (major peaks) = 157.0, 138.1, 133.0, 128.1, 127.7, 127.4, 30.9, –0.9.

MALDI-TOF MS: *m*/*z* calcd for [M + Na]$^+$: 799.4; found: 800.0.

26,28-Dihydroxy-25,27-dimethoxy-5,17-bis(trimethylsilyl)calix[4]arene (25)

The crude product (in EtOAc) was concentrated to give a white powder; mp 301–302 °C; 301–302 °C (analytical sample).

IR (KBr): 3390, 3012, 2950, 2925, 2899, 2822, 1583, 1460, 1428, 1290, 1245, 1204, 1163, 1113, 912, 835, 774, 754 cm^{-1}.

^{1}H NMR ($CHCl_3$ standard): δ = 8.01 (s, 2 H, ArO*H*), 7.18 (s, 4 H, ArH), 6.90 (d, *J* = 7.3 Hz, 4 H, ArH), 6.77 (t, *J* = 7.3 Hz, 2 H, ArH), 4.30 (d, *J* = 13.0 Hz, 4 H, ArCH_2Ar), 4.00 (s, 6 H, OCH_3), 3.43 (d, *J* = 13.0 Hz, ArCH_2Ar), 0.24 [s, 18 H, Si$(CH_3)_3$].

^{13}C NMR: δ = 153.9 (C), 153.1 (C), 133.7 (CH), 133.1 (C), 129.7 (C), 129.0 (CH), 127.6 (C), 125.4 (CH), 63.7 (CH_3), 31.2 (CH_2), –0.76 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for [M + Na]$^+$: 619.3; found: 620.96.

Anal. Calcd for $C_{36}H_{44}O_4Si_2$: C, 72.44; H, 7.43. Found: C, 72.66; H, 7.28.

Bis(phenyldimethylsilyl)calixarenes

26,28-Dibenzyloxy-25,27-dimethoxy-5,17-bis(phenyldimethylsilyl)calix[4]arene (22)

The crude product was chromatographed (silica gel, 1.2 × 21 cm, 4:1 PE–CH_2Cl_2, 7 mL fractions, fractions 5–8); colorless oil; R_f = 0.4 (3:2 PE–CH_2Cl_2).

IR ($CHCl_3$): 3012, 2950, 2919, 1583, 1460, 1424, 1260, 1112, 1015, 835, 810, 702, 671 cm^{-1}.

^{1}H NMR (CH_2Cl_2 standard): δ = 7.52–6.72 (m, 30 H), 4.93–3.12 (m, 18 H), 0.36 (s, major), 0.11 (s, minor), overlapping with 0.0–0.5 (m, small) (total integration 12 H).

^{13}C NMR: δ (major peaks) = 157.4, 139.1, 138.0, 136.3, 135.2, 134.2, 132.7, 131.3, 130.3, 128.7, 128.1, 127.9, 127.6, 122.8, 60.6, 30.9, –2.0.

MALDI-TOF MS: *m*/*z* calcd for [M + Na]$^+$: 923.4; found: 923.8.

26,28-Dihydroxy-25,27-dimethoxy-5,17-bis(phenyldimethylsilyl)calix[4]arene (26)

The crude product was recrystallized from 9:1 MeOH–acetone; white crystals; mp 249–251 °C; 255–256 °C (analytical sample).

IR (KBr): 3380, 3063, 3017, 2945, 2925, 2822, 1583, 1470, 1424, 1286, 1250, 1209, 1158, 1117, 1020, 994, 912, 815, 769, 733, 702 cm^{-1}.

^{1}H NMR (CH_2Cl_2 standard): δ = 8.14 (s, 2 H, ArO*H*), 7.52 (br, 4 H, C_6H_5), 7.38 (br, 6 H, C_6H_5), 7.23 (s, 4 H, ArH), 6.88 (d, *J* = 7.4 Hz, 4 H, ArH), 6.78 (t, *J* = 7.3 Hz, 2 H, ArH), 4.32 (d, *J* = 13.1 Hz, 4 H, ArCH_2Ar), 4.01 (s, 6 H, OCH_3), 3.42 (d, *J* = 13.1 Hz, 4 H, ArCH_2Ar), 0.54 [s, 12 H, Si$(CH_3)_2$].

^{13}C NMR: δ = 154.3 (C), 153.1 (C), 139.3 (C), 134.8 (CH), 134.3 (CH), 133.0 (C), 129.1 (CH), 128.9 (CH), 127.7 (CH), 127.1 (C), 125.5 (CH), 63.7 (CH_3), 31.2 (CH_2), –1.9 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for $[M + Na]^+$: 743.3; found: 743.6.

Anal. Calcd for $C_{46}H_{48}O_4Si_2$: C, 76.62; H, 6.71. Found: C, 76.13; H, 6.97.

Bis(diphenylmethylsilyl)calixarenes
26,28-Dibenzyloxy-25,27-dimethoxy-5,17-bis(diphenylmethylsilyl)calix[4]arene (23)

The reaction mixture was concentrated on the rotary evaporator, and immediately passed through a silica gel column (1.2 × 20 cm) using ca. 150 mL of 4:1 PE–CH_2Cl_2. The solution was concentrated and recrystallized from 9:1 MeOH–$CHCl_3$; white powder; mp 84–86 °C.

^{1}H NMR (CH_2Cl_2 standard): δ = 7.6–6.8 (40 H), 5.1–2.8 (18 H), 0.8–0.3 (6 H).

^{13}C NMR: δ (major peaks) = 137.8, 136.8, 135.5, 135.3, 135.2, 134.9, 134.5, 134.3, 128.9, 128.8, 128.3, 128.1, 127.6, 127.5, 127.4, 127.3, –2.9.

MALDI-TOF MS: *m*/*z* calcd for $[M + Na]^+$: 1047.4; found: 1047.8.

Bis(allyldimethylsilyl) and (Propyldimethylsilyl)calixarenes
5,17-Bis(allyldimethylsilyl)-26,28-dibenzyloxy-25,27-dimethoxycalix[4]arene (24)

The product was chromatographed (silica gel, 4:1 PE–CH_2Cl_2) to give a cloudy oil.

IR ($CHCl_3$): 3063, 2955, 2925, 1630, 1460, 1419, 1260, 1113, 1025, 989, 917, 902, 825, 671 cm^{-1}.

^{1}H NMR (CH_2Cl_2 standard): δ = 7.54–6.65 (m, 20 H), 5.60 (m, 2 H), 4.95–3.09 (m, 22 H), 1.55 (unresolved doublet, 4 H), two singlets at 0.14 and –0.05 in 4:1 ratio (total integration 12 H) (s, 12 H).

^{13}C NMR: δ (major peaks) = 157.3, 138.1, 136.3, 135.0, 134.5, 133.2, 132.4, 131.4, 128.6, 128.2, 127.9, 127.5, 122.8, 113.0, 30.9, 24.1, –3.5.

MALDI-TOF MS: *m*/*z* calcd for $[M + Na]^+$: 851.4; found: 851.7.

26,28-Dihydroxy-25,27-dimethoxy-5,17-bis(propyldimethylsilyl)calix[4]arene (27)

The crude product was recrystallized from 9:1 MeOH–CH_2Cl_2; white powder; mp 239–241 °C.

IR (KBr): 3391, 3012, 2950, 2919, 2863, 1588, 1573, 1465, 1429, 1286, 1250, 1199, 1158, 1117, 994, 912, 820, 769 cm^{-1}.

^{1}H NMR ($CHCl_3$ standard): δ = 8.01 (s, 2 H, ArO*H*), 7.17 (s, 4 H, ArH), 6.90 (d, *J* = 7.5 Hz, 4 H, ArH), 6.76 (m, 2 H, ArH), 4.30 (d, *J* = 13.0 Hz, 4 H, ArCH_2Ar), 4.00 (s, 6 H, OCH_3), 3.42 (d, *J* = 13.1 Hz, ArCH_2Ar), 1.36 (m, 4 H, $SiCH_2CH_2CH_3$), 0.96 (t, *J* = 7.2 Hz, 6 H, $SiCH_2CH_2CH_3$), 0.71 (crude t, *J* = 8.5 Hz, 4 H, $SiCH_2CH_2CH_3$), 0.23 [s, 12 H, $Si(CH_3)_2$].

^{13}C NMR: δ = 153.9 (C), 153.1 (C), 134.0 (CH), 133.0 (C), 129.0 (CH), 128.9 (C), 127.5 (C), 125.4 (CH), 63.7 (CH_3), 31.2 (CH_2), 18.8 (CH_2), 18.4 (CH_3), 17.5 (CH_2), –2.7 (CH_3).

MALDI-TOF MS: *m*/*z* calcd for major component $[M + Na]^+$: 675.3; found: 675.7; *m*/*z* calcd for the monsilylated minor component $[M + Na]^+$: 575.3; found: 575.5.

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