Calix[4]arene Sulfonates: Palladium-Catalyzed Intermolecular Migration of Sulfonyl Groups and Isolation of a Calix[4]arene in a Chiral 1,2-Alternate Conformation†

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An intermolecular migration of sulfonyl groups in 1,3-bistriflate and 1,3-bismesylate derivatives of *p-tert*-butylcalix[4]arene (**1**) takes place in the presence of both a palladium catalyst and chloride anion. The process leads to the clean formation of 1:1 mixtures of mono- and trisubstituted derivatives that could not be prepared directly from **1** by sulfonylation reactions. A trismesylate **7b** is obtained as a minor derivative under the conditions required for the mesylation of **1**. Compound **7b** exists in a 1,2-alternate conformation, which is chiral due to the pattern of substituents.

Introduction

Calix[4]arenes are not planar and can adopt four different stable conformations [cone, partial cone (paco), 1,2-alternate (1,2-alt), and 1,3-alternate (1,3-alt)] when bulky groups substitute the phenolic hydroxyls ("lower rim") to prevent free rotation of the aromatic rings.[1,2] These compounds are increasingly used as building blocks for the construction of more elaborate structures used for the complexation of cations and neutral substrates.[1,3] We have sought to extend current methodologies for the functionalization of calixarenes by using palladium-catalyzed cross-coupling reactions at the lower rim of calix[4]arenes. Among common activating groups for phenol hydroxyls,[4,5] trifluoromethanesulfonates (triflates) have been extensively used in recent years.[6–8] In particular, their palladium-catalyzed coupling with organostannanes[6] provides a simple solution for carbon–carbon bond formation on an aromatic ring.[9] Palladium-catalyzed procedures for the functionalization of calixarenes have been recently described by using *p*-bromo substituents in the upper rim.[10]

Unexpectedly, we found that the bistriflate and bismethanesulfonate (bismesylate) of *p-tert*-butylcalix[4]arene (**1**) undergo a facile intermolecular rearrangement in the presence of both a palladium catalyst and chloride anion, providing new mono- and trisulfonate derivatives of the parent calixarene **1**. Despite the widespread use of sulfonates as activating[6–8] or protecting groups for phenols,[11] this type of intermolecular migration of sulfonyl groups is unprecedented. Previously, exchange of sulfonyl groups has only been observed intermolecularly in the reaction of aryl triflates with the potassium salts of phenols in liquid ammonia.[12] Additionally, in the course of this study we have prepared the first calix[4]-

† This paper is dedicated to the memory of the late Professor Francisco Fariña.

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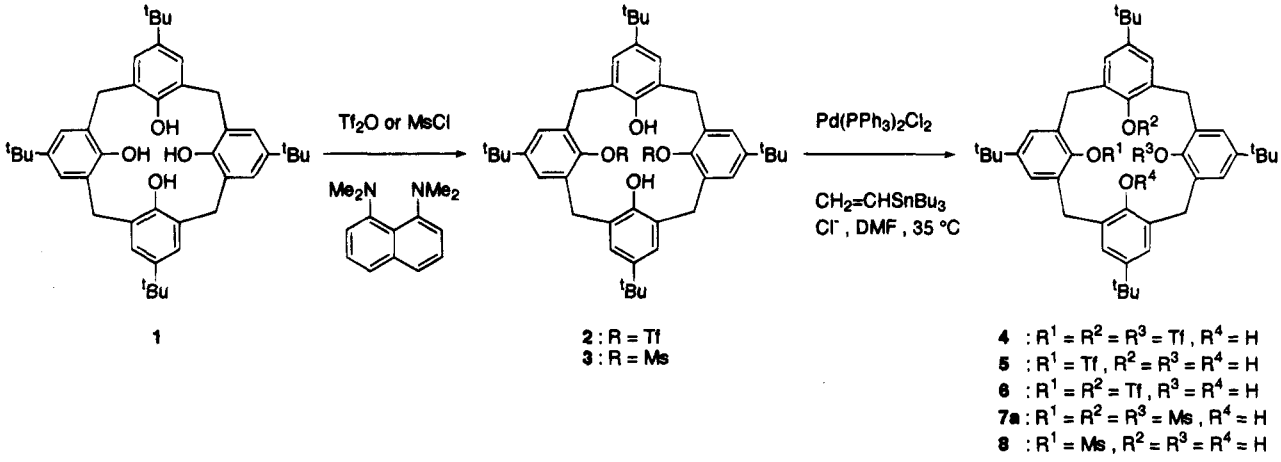
Scheme 1



arene which exists in a stable chiral 1,2-alternate conformation.

Results and Discussion

1. Palladium-Catalyzed Migration of Sulfonyl Groups. Treatment of **1** with excess triflic anhydride in the presence of a variety of bases led to the exclusive formation of the 1,3-bistriflate **2**. None of the other possible derivatives were observed in the crude reaction mixtures. The best conditions for the preparation of **2** were obtained by using 1,8-bis(dimethylamino)naphthalene (proton sponge) as the base, leading to an almost quantitative yield. Similarly, when **1** was treated with methanesulfonyl chloride under the same reaction conditions, the 1,3-bismesylate **3** was obtained in 70% yield. In this reaction a trismesylate was also obtained in low yield (*vide infra*).

Surprisingly, when **2** was submitted to the standard coupling conditions with ethenyltributylstannane (excess LiCl, in DMF, $Pd(PPh_3)_2Cl_2$ as the catalyst),[6] a 1:1 mixture of tristriflate (**4**) and triflate (**5**) was isolated (Scheme 1). Similar results were obtained by using $Pd(PPh_3)_4$ as the catalyst, tetraalkylammonium chloride as the added salt, or DMSO as the solvent. It is noteworthy that only a trifluromethanesulfonyl group migrates under all the reaction conditions examined. No rearrangement was observed in the absence of palladium catalysts, chloride salts, or less polar solvents. $Pd(MeCN)_2Cl_2$ and Pd(dppf)Cl_2 [dppf = 1,1′-bis(diphenylphosphine)ferrocene] were also effective as the catalysts, while $Pd_2(dba)_4$ (dba = dibenzylideneacetone) in the presence or absence of LiCl gave negative results. The stannane apparently behaves as a reductant for Pd(II), leading to a highly reactive coordinatively unsaturated Pd(0) catalyst by transmetallation followed by reductive elimination.[6,7] In fact, it sufficed to add a catalytic amount of the stannane to generate the active catalyst. However, addition of phosphites, known to reduce Pd(II) to active catalysts,[13] gave only unchanged starting bistriflate. By using an excess (3−10 equiv) of LiCl in DMF and $Pd(PPh_3)_2Cl_2$ as the catalyst, the 1,2-bistriflate **6** was also formed in this reaction. Derivative **6** probably arises by cleavage of a sulfonate group of tristriflate **5** assisted by the chloride or adventitious water.

Remarkably, bismesylate **3** also suffered smooth disproportionation under the conditions developed for **2**. Thus, reaction of **3** with ethenyltributylstannane and benzyltriethylammonium chloride in the presence of catalytic amounts of $Pd(PPh_3)_2Cl_2$ in DMF proceeded at 35 °C to yield a mixture of trismesylate **7a** and mesylate **8**. In the absence of palladium catalyst no intermolecular migration of the mesylate was observed.

At present we can only speculate about the role played by the palladium catalyst in these rearrangements. Although cleavage of aryl triflates has been observed as a side reaction in several palladium-catalyzed reactions,[6-8] probably promoted by the added halide,[14] the present process required the addition of both palladium and chloride ion. The need of added chloride anion suggests that anionic $[Pd(L)_2Cl_2]^{2-}$ (L = phosphine) or a related species[15] may be involved in the catalysis. The reaction proceeds satisfactorily at 50 °C with 1 equiv of $Pd(PPh_3)_4$ and 2 equiv of LiCl in DMSO-d_6 as the solvent. Under these reaction conditions good conversions of **2** into a 1:1 mixture of **4** and **5** (*ca.* 90 %, 24 h) were obtained. By monitoring the reaction in $CDCl_3$ by ^1H NMR, a transient broad signal at −0.08 ppm was observed, which disappeared after the addition of D_2O. However, a definitive assignment of this transient species could not be made.

Although Ag(I) is known to complex with calixarenes,[16] a similar Pd(0) complex appears unlikely.[17] In fact, no changes were observed in the ^1H NMR spectrum of **1** or calix[4]arene 1,3-dimethyl ether in DMSO-d_6 after addition of $Pd(PPh_3)_4$ or $Pd(PPh_3)Cl_2$. On the other hand, although intramolecular transacylation reactions of calix[4]arene 1,3-diesters have been described by Guts-

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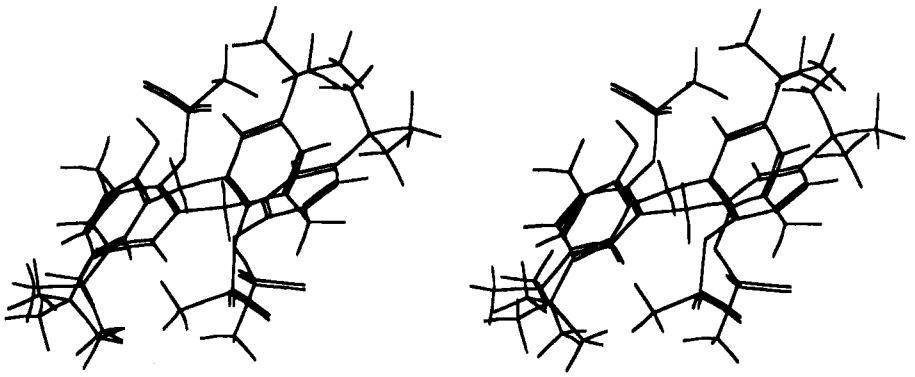
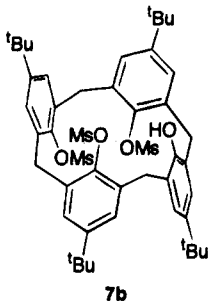


Figure 1. Stereoview of an energy-minimized structure of calixarene **7b**.

che,[18] the involvement of a related mechanism is highly unlikely in our case since it would be difficult to rationalize the formation of 1:1 mixtures of mono- and trisubstituted derivatives in the process. Additionally, intramolecular migrations of sulfonyl groups are, to the best of our knowledge, unknown. Regardless of the particular mechanism of these deproportionations, this unconventional procedure allows for the synthesis in one step of mono- and trisulfonate derivatives, potentially useful substrates for the elaboration of more complex calixarenes. Current methods for the synthesis of mono- and trisubstituted derivatives of parent calix[4]arene **1** often require complex transformations or lead to poor conversions of the desired products.[18,19]

2. Conformation of Calix[4]arene 7b. The new calixarenes **2**–**6** and **8** showed NMR data consistent with cone conformations. Particularly diagnostic were the chemical shifts for the methylene carbons of these derivatives which appeared at 31.1–33.3 ppm, characteristic of syn-oriented adjacent phenol rings.[20] On the other hand, trismesylate **7a** showed two signals for the methylene carbons (36.7 and 32.2 ppm), corresponding to a partial cone (paco) conformation.

As mentioned above, mesylation of **1** furnished a 1,3-bismesylate (**3**) as the major product. Additionally, a trismesylate, **7b**, could be obtained in 5% yield whose NMR data were clearly different to those of its conformer **7a** obtained by the palladium-catalyzed reaction of **3**. The NMR spectra of **7b** in $CDCl_3$ at 23 °C are in agreement with an asymmetric structure in a 1,2-alt or a paco conformation. In DMSO-d_6 four AX systems were observed for the methylene hydrogens. Addition of 1 equiv of Pirkle's chiral shift reagent (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol to the $CDCl_3$ solution led to splitting of several signals. Full assignment of **7b** by COSY and NOESY experiments was consistent with a 1,2-alt conformation as shown in Figure 1. On the other hand, NMR data indicated that **7b** possessed a rigid conformation in the range of −68 to +66 °C ($CDCl_3$ solution). Additionally, no exchange cross-peaks were observed in the ROESY experiments carried out at 23 °C, excluding fast equilibria between several interconverting conformers. Furthermore, neither **7b** nor its conformer **7a** led to equilibration after being heated at 125 °C for 24 h in DMSO-d_6 solution.



7b

The NMR results are fully consistent with fixed chiral 1,2-alt conformation for the trismesylate **7b**. Molecular mechanics calculations were performed using a CVFF force field,[21] starting with **7b** in a idealized symmetrical 1,2-alt conformation. The optimized final structure (Figure 1),[22] is fully compatible with the results of the NOESY experiments.

Usually, chiral calix[4]arenes have been prepared by attaching chiral residues to the tetramer.[23] Calix[4]-arenes possessing three or four different substituents at the *para* position[24] or *meta* substituents[25] are also chiral when ring inversion is frozen by substitution at the lower rim.[26,27] Chiral calixarenes have also been obtained with fixed cone,[4e,28,29] paco,[28,29] or 1,3-alternate[29] conformations. However, no examples of chiral calix[4]arenes with 1,2-alt conformations had been described so far. Our results

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therefore indicate that **7b** is the first example of a calix[4]arene which exists in a chiral 1,2-alt conformation.

Conclusions

We have uncovered a surprisingly facile migration of sulfonyl groups on two 1,3-sulfonates of the parent *p-tert*-butylcalix[4]arene (**1**) which proceeded in the presence of both a palladium catalyst and chloride anion. This process leads to the clean formation of 1:1 mixtures of mono- and trisubstituted derivatives that could not be prepared directly from **1** by sulfonylation reactions. In the preparation of the expected 1,3-bismesylate **1** we have obtained a trismesylate **7b** as a minor derivative which was demonstrated (NMR) to exist in a 1,2-alternate conformation, which is chiral due to the pattern of substituents.

Experimental Section

Solvents were dried before use by standard methods. All reactions were carried out under an atmosphere of Ar. Chromatography was performed with flash grade silica gel. Unless otherwise stated, the more stable conformation of the obtained calix[4]arenes was the cone.

***p-tert*-Butylcalix[4]arene 1,3-Bistriflate (2).** To a suspension of *p-tert*-butylcalix[4]arene (**1**) (300 mg, 0.46 mmol) and 1,8-bis(dimethylamino)naphthalene (proton sponge) (513 mg, 2.39 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added trifluoromethanesulfonic anhydride (0.3 mL, 1.8 mmol). After being stirred for 2 h at 25 °C, the mixture was partitioned between CH_2Cl_2 and aqueous HCl (10%). The organic layer was dried (Na_2SO_4) and evaporated. The residue was chromatographed (10:1 hexane–EtOAc) to give **2** as a white solid (410 mg, 97%): mp 305 °C (MeOH–benzene); IR (KBr) 3600, 1200, 1180 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.18 (s, 4 H), 6.71 (s, 4 H), 4.20 (d, J = 14.4 Hz, 4 H), 4.13 (s, 2 H, OH), 3.52 (d, J = 14.4 Hz, 4 H), 1.32 (s, 18 H), 0.91 (s, 18 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz; DEPT) δ 150.8 (2 C, s, Ar), 149.8 (2 C, s, Ar), 143.5 (2 C, s, Ar), 141.4 (2 C, s, Ar), 132.7 (4 C, s, Ar), 127.8 (4 C, s, Ar), 126.7 (4 C, d, ArH), 125.9 (4 C, d, ArH), 118.7 [2 C, q, $^1J(^{13}C-^{19}F)$ = 320.5 Hz], 34.1 (2 C, s, $C(CH_3)_3$), 34.0 ((2 C, s, $C(CH_3)_3$), 32.4 (4 C, t, $ArCH_2Ar$), 31.6 (6 C, q, $C(CH_3)_3$), 30.7 ((6 C, q, $C(CH_3)_3$); MS (FAB) *m/z* 913 (30) (M^+), 780 (10), (base peak = 57); HRMS (FAB) *m/z* calcd 912.3164, found 912.3161 (M^+). Anal. Calcd for $C_{46}H_{54}F_6O_8S_2 \cdot 1/2$ benzene: C, 61.81; H, 6.03. Found: C, 61.59; H, 5.88. (The presence of benzene from the recrystallization was confirmed by ^1H NMR.)

***p-tert*-Butylcalix[4]arene Tristriflate (4).** A mixture of **2** (100 mg, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (8 mg, 0.01 mmol), ethenyltributylstannane (*ca.* 10 mg), and $BnNEt_3Cl$ (42 mg, 0.22 mmol) in DMF (6 mL) was stirred at 35 °C for 24 h. The mixture was partitioned between EtOAc (50 mL) and aqueous HCl (10%). The organic layer was dried (Na_2SO_4) and evaporated. ^1H NMR showed a 1:1 mixture of **4** and **5**. The residue was chromatographed (10:1 hexane–EtOAc) to give a mixture of **4** and **5**. Trituration with hexane gave **4** as a white solid (30 mg, 26%). Evaporation of the hexane solution gave **5** (23 mg, 26%). **4**: mp 239–240 °C (hexane); IR (KBr) 3600, 3400, 1240, 1210, 1135 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.38 (s, 2 H), 7.19 (s, 2 H), 6.76 (d, J = 2.5 Hz, 2 H), 6.69 (d, J = 2.5 Hz, 2H), 4.63 (d, J = 14.1 Hz, 2 H), 4.14 (d, J = 14.5 Hz, 2 H), 3.75 (s, 1 H, OH), 3.58 (d, J = 14.5 Hz, 2H), 3.55 (d, J = 14.1 Hz, 2 H), 1.39 (s, 9 H), 1.34 (s, 9 H), 0.91 (s, 18 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz; DEPT) δ 151.9 (1 C, s, Ar), 150.1 (2 C, s, Ar), 150.08 (1 C, s, Ar), 143.1 (1 C, s, Ar), 142.1 (1 C, s, Ar), 139.5 (1 C, s, Ar), 136.1 (2 C, s, Ar), 133.3 (2 C, s, Ar), 130.4 (2 C, s, Ar), 127.8 (2 C, d, ArH), 127.0 (2 C, d, ArH), 126.9 (2 C, s, Ar), 126.3 (2 C, d, ArH), 125.8 (2 C, d, ArH), 118.6 [2 C, q, $^1J(^{13}C-^{19}F)$ = 321 Hz], 118.4 [1 C, q, $^1J(^{13}C-^{19}F)$ = 320 Hz], 34.6 (1 C, q, $C(CH_3)_3$), 34.1 (2 C, s, $C(CH_3)_3$), 34.0 (1 C, s, $C(CH_3)_3$), 33.3 (2 C, t, $ArCH_2Ar$), 31.5 (3 C, q, $C(CH_3)_3$), 31.3 (3 C, q, $C(CH_3)_3$), 31.1 (2 C, t, $ArCH_2Ar$), 30.8 [6 C, q, $C(CH_3)_3$)], (one quaternary Ar carbon signal overlaps); MS (FAB) *m/z* 1045 (9.9) (M^+), 1029 (3), 990 (1), (base peak = 57); HRMS (FAB) *m/z* calcd 1044.2657, found 1044.2590 (M^+).

***p-tert*-Butylcalix[4]arene Triflate (5).** This calix[4]arene was prepared, along with **4**, from **2** as a white solid. **5**: mp 228–230 °C (hexane); IR (KBr) 3520, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.13 (d, J = 2.3 Hz, 2 H), 7.08 (d, J = 2.4 Hz, 2 H), 6.94 (s, 2 H), 6.92 (s, 2 H), 5.5–5.0 (br, 3 H, OH), 4.33 (d, J = 14.1 Hz, 2 H), 4.13 (d, J = 14.1 Hz, 2 H), 3.55 (d, J = 14.2 Hz, 2 H), 3.46 (d, J = 14.1 Hz, 2 H), 1.28 (s, 18 H), 1.13 (s, 9 H), 0.97 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz; DEPT) δ 151.0 (1 C, s, Ar), 149.0 (2 C, s, Ar), 146.7 (1 C, s, Ar), 144.1 (1 C, s, Ar), 143.6 (2 C, s, Ar), 141.2 (1 C, s, Ar), 133.1 (2 C, s, Ar), 127.6 (2 C, d, ArH), 127.4 (2 C, s, Ar), 127.3 (2 C, s, Ar), 127.2 (2 C, s, Ar), 126.0 (2 C, d, ArH), 125.9 (2 C, d, ArH), 125.8 (2 C, d, ArH), 119.8 [1 C, q, $^1J(^{13}C-^{19}F)$ = 321 Hz], 34.2 (1 C, s, $C(CH_3)_3$), 34.0 (2 C, s, $C(CH_3)_3$), 32.5 (2 C, t, $ArCH_2Ar$), 32.4 (2 C, t, $ArCH_2Ar$), 31.6 (6 C, q, $C(CH_3)_3$), 31.3 (3 C, q, $C(CH_3)_3$), 30.7 (3 C, q, $C(CH_3)_3$), (one quaternary $C(CH_3)_3$) carbon signal overlaps); MS (EI) *m/z* 780 (3) (M^+), 648 (3), (base peak = 57); HRMS (FAB) *m/z* calcd 780.3671, found 780.3681 (M^+).

***p-tert*-Butylcalix[4]arene 1,2-Bistriflate (6).** When the synthesis of **4** and **5** from **2** and the palladium catalyst was carried out in the presence of excess LiCl (3–10 equiv), 1,2-bistriflate **6** was obtained (*ca.* 20–60% yield). This derivative could not be obtained pure and was isolated contaminated with variable amounts of **5**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.12 (d, J = 2.5 Hz, 2 H), 7.08 (d, J = 2.5 Hz, 2 H), 7.05 (d, J = 2.5 Hz, 2 H), 7.04 (d, J = 2.5 Hz, 2 H), 5.67 (br s, 2 H, OH), 4.60 (d, J = 14.4 Hz, 1 H), 4.35 (d, J = 15.3 Hz, 2 H), 3.84 (d, J = 14.1 Hz, 1 H), 3.69 (d, J = 15.3 Hz, 2 H), 3.63 (d, J = 14.4 Hz, 1 H), 3.57 (d, J = 14.4 Hz, 1 H), 1.23 (s, 18 H), 1.17 (s, 18 H).

***p-tert*-Butylcalix[4]arene 1,3-Bismesylate (3).** To a suspension of **1** (300 mg, 0.46 mmol) and proton sponge (500 mg, 2.39 mmol) in $CHCl_3$ (10 mL) at 0 °C was added methanesulfonyl chloride (2 mL, 25.7 mmol). After being stirred for 4 days at 25 °C, the mixture was partitioned between CH_2Cl_2 and a saturated aqueous solution of NH_4Cl (pH 8). The organic layer was dried (Na_2SO_4) and evaporated. The residue was chromatographed (10:1 hexane–EtOAc) to give *p-tert*-butylcalix[4]arene trismestylate (1,2-alt) (**7b**) (20 mg, 5%). Elution with 5:1 hexane–EtOAc gave **3** as a white solid (260 mg, 70%). **3**: mp > 300 °C ($CHCl_3$); IR (KBr) 3570 1190, 1160 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.16 (s, 4 H), 6.80 (s, 4 H), 4.48 (s, 2 H, OH), 4.29 (d, J = 14.2 Hz, 4 H), 3.51 (d, 14.2 Hz, 4 H), 3.30 (s, 6 H), 1.34 (s, 18 H), 0.92 (s, 18 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, DEPT) δ 150.0 (2 C, s, Ar), 149.8 (2 C, s, Ar), 142.8 (2 C, s, Ar), 141.2 (2 C, s, Ar), 133.2 (4 C, s, Ar), 127.9 (4 C, s, Ar), 126.4 (4 C, d, ArH), 125.6 (4 C, d, ArH), 38.1 (2 C, q, OSO_2CH_3), 34.0 (2 C, s, $C(CH_3)_3$), 33.9 (2 C, s, $C(CH_3)_3$), 33.0 (4 C, t, $ArCH_2Ar$), 31.6 (6 C, q, $C(CH_3)_3$), 30.8 (6 C, q, $C(CH_3)_3$); MS (FAB) *m/z* 937 (26) (M^+ + Cs), 804 (67) (M^+), 693 (22), (base peak = 57). Anal. Calcd for $C_{46}H_{60}F_6O_8S_2 \cdot 1/2H_2O$: C, 67.87; H, 7.55. Found: C, 67.57; H, 7.46. (The presence of water was confirmed by ^1H NMR.)

***p-tert*-Butylcalix[4]arene Trismesylate (paco) (7a).** A mixture of **3** (170 mg, 0.21 mmol), $Pd(PPh_3)_2Cl_2$ (16 mg, 0.02 mmol), ethenyltributylstannane (*ca.* 10 mg), and $BnEt_3NCl$ (77 mg, 0.42 mmol) in DMF (10 mL) was stirred at 35 °C for 24 h. The mixture was partitioned between EtOAc (50 mL) and

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aqueous HCl (10%). The organic layer was dried (Na_2SO_4) and evaporated. ^1H NMR showed a 1:1 mixture of **7a** and **8**. The residue was chromatographed (10:1 hexane–EtOAc) to give **7a** (40 mg, 22%) and **8** (30 mg, 20%) as white solids. **7a**: mp > 300 °C ($CHCl_3$); IR (KBr) 3510, 1190, 1160 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.32 (s, 2 H), 7.28 (s, 2 H), 7.04 (d, J = 2.4 Hz, 2 H), 6.74 (d, J = 2.4 Hz, 2 H), 4.78 (d, J = 13.4 Hz, 2 H), 4.37 (d, J = 14.7 Hz, 2 H), 3.78 (s, 1 H, OH), 3.69 (d, J = 14.7 Hz, 2 H), 3.35 (d, J = 13.4 Hz, 2 H), 3.25 (s, 6 H), 3.09 (s, 3 H), 1.37 (s, 9 H), 1.35 (s, 9 H), 1.01 (s, 18 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz; DEPT) δ 151.7 (1 C, s, Ar), 150.8 (1 C, s, Ar), 149.6 (2 C, s, Ar), 142.8 (1 C, s, Ar), 142.3 (1 C, s, Ar), 141.1 (1 C, s, Ar), 136.4 (2 C, s, Ar), 134.7 (2 C, s, Ar), 132.1 (1 C, s, Ar), 127.4 (1 C, d, ArH), 127.3 (1 C, d, ArH), 126.8 (1 C, d, ArH + 1 C, s, Ar), 126.4 ((1 C, d, ArH), 38.2 (2 C, q, OSO_2CH_3), 38.1 (1 C, q, OSO_2CH_3), 36.7 (2 C, t, $ArCH_2Ar$), 34.5 (2 C, s, $C(CH_3)_3$), 34.1 (2 C, s, $C(CH_3)_3$), 32.2 (2 C, t, $ArCH_2Ar$), 31.7 (3 C, q, $C(CH_3)_3$), 31.4 (3 C, q, $C(CH_3)_3$), 31.0 (6 C, q, $C(CH_3)_3$), (one quaternary Ar carbon signal overlaps); MS (FAB) *m/z* 882 (100) (M^+), 867 (21), 804 (32). Anal. Calcd for $C_{47}H_{62}S_3O_{10}\cdot 2H_2O$: C, 61.55; H, 7.03. Found: C, 61.60; H, 6.88. (The presence of water was confirmed by ^1H NMR.)

***p-tert*-Butylcalix[4]arene Mesylate (8).** This calix[4]arene was prepared, along with **7**, from **3**: mp 162–164 °C (hexane); IR (KBr) 1190, 1155 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 9.14 (s, 1 H, OH), 7.76 (s, 2 H, OH), 7.10 (s, 2H), 7.08 (d, J = 2.4 Hz, 2 H), 7.04 (s, 2 H), 7.02 (d, J = 2.4 Hz, 2 H), 4.44 (d, J = 14 Hz, 2 H), 4.16 (d, J = 14 Hz, 2 H), 3.58 (d, J = 14 Hz, 2 H), 3.53 (d, J = 14 Hz, 2 H), 3.43 (s, 3 H), 1.23 (s, 18 H), 1.21 (s, 9 H), 1.15 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz; DEPT) δ 150.5 (1 C, s, Ar), 148.4 (2 C, s, Ar), 147.2 (1 C, s, Ar), 143.9 (1 C, s, Ar), 143.5 (2 C, s, Ar), 140.8 (1 C, s, Ar), 134.1 (2 C, s, Ar), 127.7 (2 C, s, Ar), 127.2 (2 C, s, Ar), 127.1 (2 C, d, ArH), 126.9 (2 C, s, Ar), 125.9 (2 C, d, ArH), 125.85 (2 C, d, ArH), 125.7 (2 C, d, ArH), 38.9 (1 C, q, OSO_2CH_3), 34.3 (1 C, s, $C(CH_3)_3$), 34.0 (1 C, s, $C(CH_3)_3$), 33.9 (2 C, s, $C(CH_3)_3$), 33.2 (2 C, t, $ArCH_2Ar$), 32.7 (2 C, t, $ArCH_2Ar$), 31.5 (6 C, q, $C(CH_3)_3$), 31.4 (3 C, q, $C(CH_3)_3$), 31.0 (3 C, q, $C(CH_3)_3$); MS (FAB) *m/z* 726 (100) (M^+), 711 (10).

***p-tert*-Butylcalix[4]arene Trismesylate (1,2-alt) (7b).** This calixarene was obtained as a minor product in the mesylation of **1**: mp > 300 °C (MeOH); IR (KBr) 3565, 1190, 1140 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 2.6 Hz, 1 H), 7.40 (d, J = 2.6 Hz, 1 H), 7.38 (d, J = 2.5 Hz, 1 H), 7.33 (d, J = 2.4 Hz, 1 H), 7.21 (d, J = 2.5 Hz, 1 H), 7.19 (d, J = 2.5 Hz, 1 H), 7.16 (d, J = 2.4 Hz, 1 H), 7.03 (d, J = 2.4 Hz, 1 H), 5.22 (s, 1 H, OH), 4.80 (d, J = 13.3 Hz, 1 H), 4.50 (d, J = 15.1 Hz, 1 H), 4.48 (d, J = 14.0 Hz, 1 H), 4.26 (br, s, 2 H), 3.93 (d, J = 15.1 Hz, 1 H), 3.43 (d, J = 13.3 Hz, 1 H), 3.42 (d, J = 14.1 Hz, 1 H), 3.09 (s, 3 H), 1.47 (s, 6 H), 1.36 (s, 18 H), 1.25 (s, 9 H), 1.24 (s, 9 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; DEPT) δ 150.1 (1 C, s, Ar), 150.08 (1 C, s, Ar), 149.4 (1 C, s, Ar), 149.2 (1 C, s, Ar), 143.3 (1 C, s, Ar), 142.6 (1 C, s, Ar), 142.5 (1 C, s, Ar), 141.7 (1 C, s, Ar), 136.7 (1 C, s, Ar), 136.0 (1 C, s, Ar), 135.8 (1 C, s, Ar), 133.0 (1 C, s, Ar), 132.6 (1 C, s, Ar), 132.2 (1 C, s, Ar), 129.0 (1 C, d, ArH), 128.7 (1 C, d, ArH), 128.6 (1 C, d, ArH), 127.5 (1 C, d, ArH), 126.5 (2 C, d, ArH), 125.9 (1 C, s, Ar), 125.8 (1 C, d, ArH), 125.6 (1 C, d, ArH), 124.7 (1 C, s, Ar), 40.1 (1 C, t, $ArCH_2Ar$), 38.7 (1 C, t, $ArCH_2Ar$), 37.3 (1 C, q, OSO_2CH_3), 36.1 (1 C, q, OSO_2CH_3), 35.8 (1 C, q, OSO_2CH_3), 34.5 (2 C, s, $C(CH_3)_3$), 34.4 (1 C, s, $C(CH_3)_3$), 33.9 (1 C, s, $C(CH_3)_3$), 31.5 (3 C, q, $C(CH_3)_3$), 31.4 (2 C, t, $ArCH_2Ar$), 31.3 (9 C, q, $C(CH_3)_3$); MS (FAB) *m/z* 882 (100) (M^+), 804 (28), 611 (16); HRMS (FAB) *m/z* calcd 882.3505, found 882.3479 (M^+).

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Supporting Information Available: Copies of 1D and 2D ^1H NMR spectra of **7b** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered form the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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