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Synthetic and NMR Studies on Calix[*n*]Arene ($n = 4, 6, 8$) Triflates, Mesylates, and Tosylates

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The synthesis and full characterization of eight new calix[*n*]arene sulfonate esters including their conformational analysis were carried out. While *p*-*t*Bu-calix[6]arene and *p*-*t*Bu-calix[8]arene esters are conformationally labile in the temperature interval of 25–100°C, *p*-*t*Bu-calix[4]arene mono- and diesters were isolated as stable conformers at ambient temperature. Two 1,3-functionalised compounds of these derivatives, *p*-*tert*-butylcalix[4]arene ditriflate (5) and dimesylate (6) were shown unexpectedly high conformational stability up to 100°C by dynamic NMR measurements. The NMR measurements confirm the pinched-cone conformation for both derivatives. For the dealkylated calix[4]arene derivatives the partial cone conformer of the triesters have been obtained as major products in all cases.

Keywords: Calixarene, sulfonate esters, 'pinched cone' conformation, NMR

INTRODUCTION

In the last decade extensive studies have been carried out on calixarenes as superior complexing agents. Especially calix[4]arenes proved to be attractive building blocks for the construction of hollow molecules with specific host properties [1–2]. These cyclic tetramers exist as cone, partial cone, 1,2-alternate, and 1,3-alternate conformational isomers. Due to its importance as a molecular host the cone conformer received the greatest attention [3–6]. Although the parent *p*-*tert*-butyl-calix[4]arene (**1**) is conformationally mobile it can be rendered rigid by the introduction of various substituents at the lower rim. The synthesis of tetraethers and esters is the most obvious way to curtail the conformational motion [7–10]. The OH group are conveniently used for the introduction of OR type functional groups but they can act as an obstacle when introducing other groups than OR [11].

The sulfonate esters are widely used in synthetic chemistry due to the presence of facile leaving groups [12]. Especially aryl and enol triflates are favourite substrates in various high-yielding coupling reactions of synthetic interest [13]. The ester formation could be an important step also for the synthesis of a wide variety of

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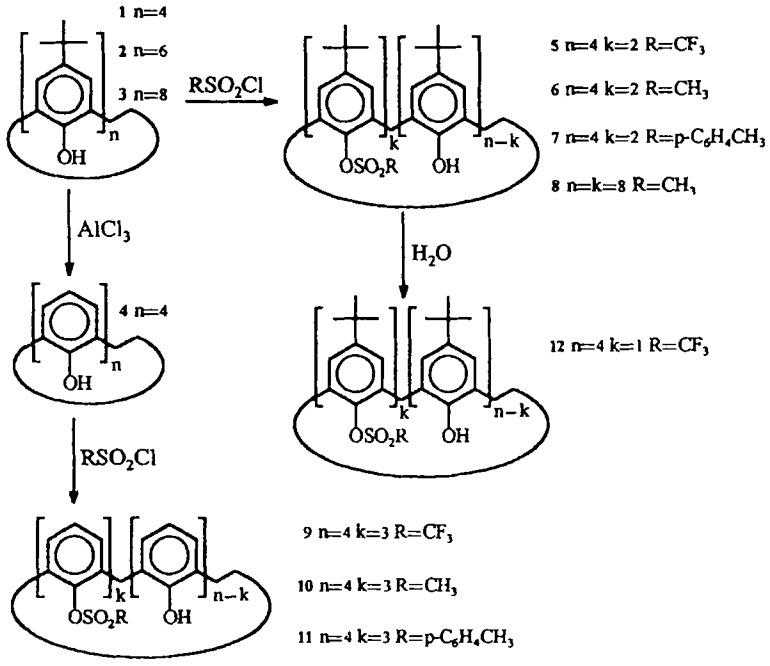
calixarenes due to the easy substitution of the facile leaving groups like the trifyloxi and mesyloxi moieties. Surprisingly, to the best of our knowledge, there is no example for the synthesis of calixarene sulfonate esters, which can be considered as key intermediates in the 'low rim' functionalisation of calixarenes.

We report here the high-yielding synthesis of some calixarene sulfonate esters, among them the symmetrically substituted diesters (**5** and **6**). Furthermore, the synthesized new calix[4]arene diesters themselves represent host molecules of high conformational stability and of special type of cavity.

RESULTS AND DISCUSSION

Compounds **5**, **6** and **7** were obtained in 85, 65, and 80% isolated yield by treating **1** with trifluoromethanesulfonic anhydride, methanesulfonyl chloride, and toluene-4-sulfonyl chloride, respectively (Scheme 1).

The NMR investigations revealed that the major component formed almost exclusively is a kind of 'pinched cone' conformer published earlier as a labile conformer of carboxylic acid (upper rim) derivatives [14]. The ^{1}H NMR of **6** at 20°C shows a well-defined pair of doublets of the bridging methylenes at 4.29, 3.51 ppm (Fig. 1, top spectrum) both in $CDCl_3$ and in DMSO-d_6. The aromatic protons and the methyl protons of the *t*Bu group appear as pairs of singlets at 7.15, 6.80 ppm and 1.33, 0.92 ppm, respectively. The methyl singlet of CH_3SO_3 is in accordance with the two equivalent pairs of aromatic moieties. Both the ^{13}C and ^{1}H NMR spectra support the c2 symmetry of the molecules in solution. Differential steady-state NOE experiments in $CDCl_3$ suggest the spatial proximity of the aromatic protons and the methyls of the *t*Bu groups of the two rings. Furthermore, the existence of sizeable, positive NOE effect between the low-frequency methylene protons and the aromatic protons, and the lack of any NOE between the high-frequency methylene



SCHEME 1 Reaction pathways for the synthesis of calixarene derivatives (**5**–**12**).

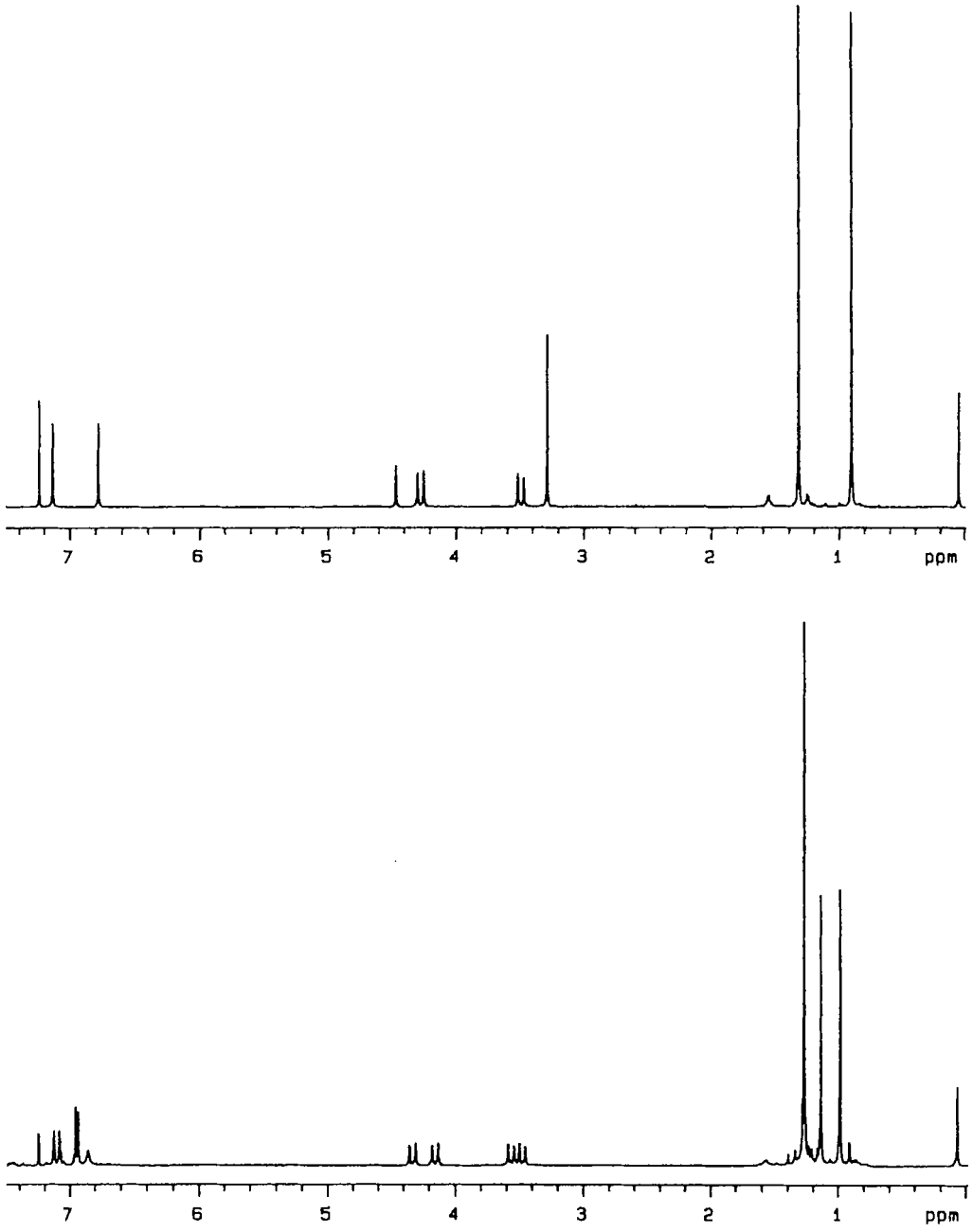


FIGURE 1 The ^{1}H NMR of **6** and **12** in $CDCl_3$ at 20°C.

protons and the aromatic protons refer to the 'cone' character of the molecule. Additionally, the absence of the especially strong 'circular hydrogen bonding' [15] characteristic for the unfunctionalized cyclic tetramer is proved by the high frequencies in the IR and the low-frequency position of the OH protons in the ^{1}H NMR.

Surprisingly, the variable temperature measurements show an *unexpectedly high stability* of the proposed distorted cone ("pinched cone")

conformer in d_8-toluene. The pair of methylene doublets is unusually sharp at room temperature. *Up to 100°C there were no substantial changes neither in the shape nor in chemical shifts and coupling constant of the pair of doublets of CH_2 protons* which are considered as excellent indicators of conformational motions. Furthermore, it seems that the intramolecular hydrogen bonding of the 1,3-OH groups is hindered by the two ester groups. The conformational stability of the analogous ditosylate (**7**) was found similar to **5** and **6**.

On the basis of further NMR and FAB-MS studies carried out on the separated mixture of minor products, the partial cone conformers of diesters (**5a, 6a**) (pair of doublets for CH_2 protons and 1:1:2 ratio for *t*Bu groups) and triesters (**5b, 6b**) were identified.

The trifluoromethanesulfonic anhydride (methanesulfonyl chloride)/**1** molar ratio was increased from 2/1 to 20/1. Interestingly, neither the composition of the reaction mixture nor the isolated yields were affected substantially by the excess of sulfonic acid derivatives.

A typical composition of the reaction mixtures is as follows (determined by ^{1}H NMR) [16].

R=CF_3	94–96%(**5**)	1–3%(**5a**)	2–3%(**5b**)
R=CH_3	71–75%(**6**)	10–12%(**6a**)	15–17%(**6b**)

The predominant formation of diesters has been observed even at low sulfonic acid derivatives to *p-tert*-butylcalix[4]arene ratio. However, the monoester **12** (cone conformer) can be isolated from the ditriflate **5** by hydrolysis carried out only in the presence of $Pd(PPh_3)_4$ or other Pd(0) catalysts (Fig. 1, bottom spectrum).

The selective synthesis of *p-tert*-butyl-calix[6]-arene esters was not successful. Since the mixture of various esters possesses an extremely complex ^{1}H NMR due to overlapping of the characteristic CH_2 patterns, only a qualitative analysis by FAB-MS can be carried out. The investigation revealed that the esterification with the above reagents at the same ratio of calixarene/sulfonating reagent resulted in the formation of different mixtures consisting of triflate and tosylate ($k=2,3,4,5$) as well as mesylate ($k=4,5,6$) esters of different substitution patterns.

The esterification of *p-tert*-butyl-calix[8]arene (**3**) both by trifluoromethanesulfonic anhydride and toluene-**4**-sulfonyl chloride results in a rather complex reaction mixtures. At methanesulfonyl chloride/**3** = 24 ratio complete conversion to octaester **8** takes place, which could be isolated and fully characterised.

The dealkylation of the upper rim of **1** results in the formation of **4** which is much less stabilised in cone conformation by steric effects and circular hydrogen bonding than the parent compound, **1** [17]. Unlike the reaction of **1**, the esterification does not stop at diesters. The triesters were isolated from the reaction mixtures in all cases. The *'in situ'* NMR investigations show rather high chemoselectivity towards triesters.

The synthesis of tetraesters proved to be unsuccessful even in the case of methanesulfonyl chloride as sulfonating agent, which yields sulfonate esters of the smallest sterical congestion at the low ring. The absence of substituents at the upper ring enables the phenylene rings to bent 'in' (pointing towards the interior of the pocket) and, as a consequence of that, the higher esterification of the hydroxi groups directed towards the exterior of the pocket.

A typical composition of the reaction mixtures using **4** is as follows (determined by ^{1}H NMR) [16].

	diester	*triester*	*tetraester*
R=CF_3	14–15%(**9a**)	84–86%(**9**)	–
R=CH_3	10–11%(**10a**)	58–60%(**10**)	29–31%(**10b**)
R=4-CH_3-C_6H_4	–	98–100%(**11**)	–

9, 10 and **11** are the partial cone conformers of the corresponding triesters. The conformation could easily be determined by NMR analysis (^{1}H NOE and ^{19}F NOESY measurements for **9**).

In spite of exhibiting a singlet–pair of doublet (**9**) and two pairs of doublets patters for the CH_2 groups (**11**), respectively (Fig. 2), both compounds possess the partial cone conformer. The "middle" ester group of the three ester functionalities (on the C-ring) is on the side of

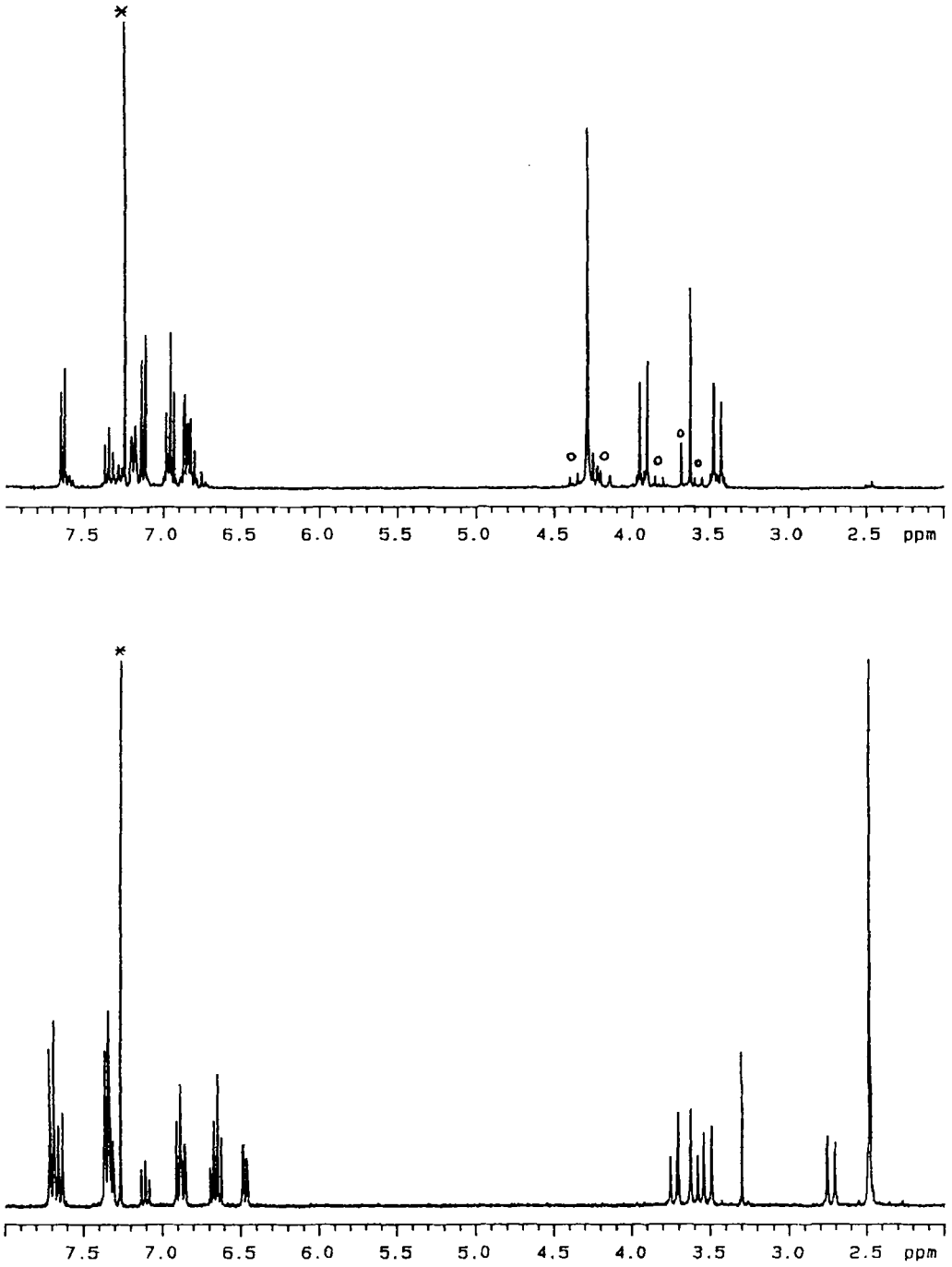


FIGURE 2 The ^1H NMR of **9** and **11** in $CDCl_3$ at 20°C (* and ° stand for $CHCl_3$ and impurity (diester), respectively).

the three *t*Bu groups bonded to the other three aromatic moieties.

As a conclusion it can be stated, that these rigid conformers substituted with facile leaving groups provide a promising route for the synthesis of a variety of functionalised products. The carbonylation (alkoxycarbonylation, aminocarbonylation) and various coupling reactions based on the above esters as substrates may yield new classes of functionalised calixarenes.

EXPERIMENTAL SECTION

^1H, ^{13}C, and ^{19}F NMR spectra were obtained on a Varian UNITY 300 spectrometer using $CDCl_3$ solvent. ^1H chemical shifts are reported relative to the residual nondeuterated solvent of chloroform at 7.24 ppm. The ^{13}C chemical shifts are referenced relative to $CDCl_3$ at 77.0 ppm. The ^{19}F NMR spectra are referenced to $CF_3C_6H_5$ at -63.75 ppm. IR spectra were recorded on a Specord 75 spectrometer in KBr pellets. FAB-MS spectra were obtained on a ZAB-2SEQ spectrometer. Elemental analysis were performed on a 1108 Carlo Erba instrument.

p-tert-Butylcalix[*n*]arenes ($n = 4, 6, 8$) and trifluoromethanesulfonic anhydride were purchased from Aldrich. Methanesulfonyl chloride was a Fluka product.

The dealkylation of *p-tert*-butylcalix[4]arene by $AlCl_3$ was carried out as described in the literature [17].

Preparation of 5

649 mg (1 mmol) of **1** was dissolved in 30 mL dry pyridine. The solution was cooled to 0°C and 1.32 g (4.68 mmol) trifluoromethanesulfonic anhydride was added and stirred for 5 hours. Some white solid powder-like material (pyridinium salt) precipitated which was filtered off. The pale yellow filtrate was poured onto approximately 50 g ice. Immediately white precipitate was formed which was filtered and washed with cold water. The crude product was dried and its composition was determined by ^1H NMR. It was subjected to column cromatography (silica gel, chloroform) in order to obtain conformationally pure **5**. Yield: 775 mg (85%).

m.p. 255°C; IR (KBr, cm^{-1}): 3580 (νOH); ^1H NMR (300 MHz, $CDCl_3$, 20°C): 0.91 (s, 18H, $C(CH_3)_3$); 1.34 (s, 18H, $C(CH_3)_3$); 3.53 (d, J = 14 Hz, 4H, H_{eq} of $ArCH_2Ar$); 4.12 (brs, 2H, OH); 4.21 (d, J = 14 Hz, 4H, H_{ax} of $ArCH_2Ar$); 6.80 (s, 4H, ArH); 7.19 (s, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 20°C): 30.72 ($C(\mathbf{C}H_3)_3$); 31.58 ($C(\mathbf{C}H_3)_3$); 32.41 ($\mathbf{C}H_2$); 34.01 ($\mathbf{C}(CH_3)_3$); 34.09 ($\mathbf{C}(CH_3)_3$); 119.10 (q, J(C–F) = 310 Hz, $OSO_2\mathbf{C}F_3$); 125.86, 126.87; 127.76; 132.68; 141.39; 143.55; 149.75; 150.83; ^{19}F NMR (282 MHz, $CDCl_3$, 20°C): -74.52 ppm; FAB-MS: 912 (M^+); 855 ($M^+ - t$Bu); 778 ($M^+ - HSO_2CF_3$); 762 ($M^+ - HSO_3CF_3$); 722 ($M^+ - SO_2CF_3$-*t*Bu); Analysis calculated for $C_{46}H_{54}F_6O_8S_2$ (M = 913.012) C, 60.51; H, 5.96; S, 7.02%; Found: C, 60.38; H, 5.71; S, 6.80%.

Preparation of 6

649 mg (1 mmol) of **1** was dissolved in 30 mL dry pyridine. The solution was cooled to 0°C and 527 mg (4.6 mmol) methanesulfonyl chloride was added and stirred for 5 hours. Some white solid powder-like material (pyridinium salt) precipitated which was filtered off. The pale yellow filtrate was poured onto approximately 50 g ice. Immediately white precipitate was formed which was filtered and washed with cold water. The crude product was dried and its composition was determined by ^1H NMR. It was subjected to column cromatography (silica gel, chloroform) in order to obtain conformationally pure **6**. Yield: 523 mg (65%).

m.p. 253°C; IR (KBr, cm^{-1}) 3525 (νOH); ^1H NMR (300 MHz, $CDCl_3$, 20°C): 0.92 (s, 18H, $C(CH_3)_3$); 1.33 (s, 18H, $C(CH_3)_3$); 3.30 (s, 6H, CH_3); 3.51 (d, J = 14.1Hz, 4H, H_{eq} of $ArCH_2Ar$); 4.29 (d, J = 14.1Hz, 4H, H_{ax} of $ArCH_2Ar$); 4.49 (brs, 2H, OH); 6.80 (s, 4H, ArH); (meta to OH); 7.15 (s, 4H, ArH (meta to OSO_2 CH_3)); ^{13}C NMR

(75 MHz, $CDCl_3$, 20°C):30.82 ($C(CH_3)_3$); 31.67 ($C(CH_3)_3$); 33.10 (CH_2); 33.99 ($C(CH_3)_3$); 34.04 ($C(CH_3)_3$); 38.20 (CH_3SO_3); 125.66, 126.51; 127.94; 133.27; 141.28; 142.88 149.84; 150.02; FAB-MS: 805 ($M^+ + H$); Analysis calculated for $C_{46}H_{60}S_2O_8$ (M = 805.06) C, 68.62; H, 7.51; S, 7.96 %; Found: C, 68.45; H, 7.67; S, 7.81%.

Preparation of 7

649 mg (1 mmol) of **1** was dissolved in 30 mL dry pyridine. The solution was cooled to 0°C and 877 mg (4.6 mmol) toluene-4-sulfonyl chloride was added and stirred for 5 hours. Some white solid powder-like material (pyridinium salt) precipitated which was filtered off. The pale yellow filtrate was poured onto approximately 50 g ice. Immediately white precipitate was formed which was filtered off. The solid was dissolved in chloroform and washed successively with dilute hydrochloric acid and brine. After drying over $MgSO_4$, the solvent was evaporated under reduced pressure. Yield: 767 mg (80%).

m.p. 295°C; IR (KBr, cm^{-1}): 3575 (νOH); ^1H NMR (300 MHz, $CDCl_3$, 20°C): 0.83 (s, 18H, $C(CH_3)_3$); 1.27 (s, 18H, $C(CH_3)_3$); 2.47 (s, 6H, $ArCH_3$); 3.04 (d, J = 14.2 Hz, 4H, H_{eq} of $ArCH_2$-Ar); 3.92 (d, J = 14.2 Hz, 4H, H_{ax} of $ArCH_2Ar$); 4.52 (s, 2H, OH); 6.62 (s, 4H, ArH); 6.99 (s, 4H, ArH); 7.34 and 7.80 (AA'XX' spin system, 8H, SO_3 $ArCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 20°C): 21.80 (SO_3ArCH_3); 30.80 ($C(CH_3)_3$); 31.64 ($C(CH_3)_3$); 32.14 (CH_2); 33.89 ($C(CH_3)_3$); 33.95 ($C(CH_3)_3$); 125.33; 126.03; 127.99; 128.53; 129.95; 133.16; 133.24; 141.98; 142.42; 145.30; 149.24; 149.95; FAB-MS: 956 (M^+); 802 ($M^+ - SO_2ArCH_2$); 648 ($M^+ - 2SO_2ArCH_2$); Analysis calculated for $C_{58}H_{68}S_2O_8$ (M = 957.29) C, 72.77; H, 7.16; S, 6,7%; Found: C, 72.55; H, 7.28; S, 6.52%.

Preparation of 8

649 mg (0.5 mmol) of **3** was dissolved in 30 mL dry pyridine. The solution was cooled to 0°C and 1.375 g (12 mmol) methanesulfonyl chloride was added and stirred for 5 hours. Some white solid powder-like material (pyridinium salt) precipitated which was filtered off. The pale yellow filtrate was poured onto approximately 50 g ice. Immediately white precipitate was formed which was filtered and washed with cold water. The crude product was dried and its composition was determined by ^1H NMR. Yield: 740 mg (77%).

m.p. 335°C; ^1H NMR (300 MHz, $CDCl_3$, 20°C): 1.08 (s, 72H, $C(CH_3)_3$); 2.96 (s, 24H, SO_3CH_3); 4.14 (brs, 16H, $ArCH_2Ar$); 6.95 (s, 16H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 20°C): 31.12 ($C(CH_3)_3$); 32.07 (CH_2); 34.40 ($C(CH_3)_3$); 38.46 (SO_3CH_3); 126.99; 133.44; 143.20; 149.69; FAB-MS: 1920 (M^+); Analysis calculated for $C_{96}H_{128}S_8O_{24}$ (M = 1922.54) C, 59.98; H, 6.71; S, 13.34%; Found: C, 60.15; H, 6.53; S, 13.4%.

Preparation of 9

424 mg (1 mmol) of **4** was dissolved in 30 mL dry pyridine. The solution was cooled to 0°C and 2.257 g (8 mmol) trifluoromethanesulfonic anhydride was added and stirred for 5 hours. Some white solid powder-like material (pyridinium salt) precipitated which was filtered off. The pale yellow filtrate was poured onto approximately 50 g ice. Immediately white precipitate was formed which was filtered and washed with cold water. The crude product was dried and its composition was determined by ^1H NMR. Yield: 574 mg (70%).

m.p. 185°C; IR (KBr, cm^{-1}): 3625 (νOH); ^1H NMR (300 MHz, $CDCl_3$, 20°C): 3.45 (d, J = 14.5Hz, 2H, H_{eq} of $ArCH_2Ar$); 3.62 (s, 1H, ArOH); 3.92 (d, J = 14.5 Hz, 2H, H_{ax} of $ArCH_2Ar$); 4.30 (s, 4H, $ArCH_2Ar$); A ring (Ar-OH): 6.82 (t, J = 7.5 Hz, 1H); 7.12 (d, J = 7.5 Hz, 2H); B and D rings (Ar-OSO_2CF_3): 6.85 (dd, J_{ortho} = 7.5 Hz, J_{meta} = 1.5 Hz, 2H); 6.96 (t, J = 7.5 Hz, 2H); 7.18 (brd, J = 7.5 Hz, 2H); C ring (Ar-OSO_2CF_3): 7.34 (t, J = 7.6 Hz, 1H); 7.64 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 20°C):

31.03 (CH_2); 36.18 (CH_2); 116.42; 120.58; 124.62; 127.43; 128.02; 129.06; 130.50; 131.09; 132.34; 132.91; 133.76; 134.23; 143.46; 151.95; ^{19}F NMR (282 MHz, $CDCl_3$ 20°C): −74.88; −76.94 ppm; Analysis calculated for $C_{31}H_{21}F_9S_3O_{10}$ (M = 820.51) C, 45.38; H, 2.56; S, 11.72%; Found: C, 45.20; H, 2.51; S, 11.81 %.

Preparation of 10

424 mg (1 mmol) of **4** was dissolved in 30 mL dry pyridine. The solution was cooled to 0°C and 1.375 g (12 mmol) methanesulfonyl chloride was added and stirred for 5 hours. Some white solid powder-like material (pyridinium salt) precipitated which was filtered off. The pale yellow filtrate was poured onto approximately 50 g ice. Immediately white precipitate was formed which was filtered and washed with cold water. The crude product was dried and its composition was determined by ^1H NMR. Yield: 556 mg (85%).

Selected data for **10**: ^1H NMR (300 MHz, $CDCl_3$, 20°C): 2.57 (s, 3H, CH_3); 2.89 (s, 6H, CH_3); 3.59 (d, J = 14.9 Hz, 2H, H_{eq} of $ArCH_2Ar$); 4.26 (d, J = 14.9 Hz, 2H, H_{ax} of $ArCH_2Ar$); 4.36 (s, 4H, $ArCH_2Ar$); FAB-MS: 659 ($M^+ + H$).

Preparation of 11

424 mg (1 mmol) of **4** was dissolved in 30 mL dry pyridine. The solution was cooled to 0°C and 2.288 g (12 mmol) toluene-4-sulfonyl chloride was added and stirred for 5 hours. Some white solid powder-like material (pyridinium salt) precipitated which was filtered off. The pale yellow filtrate was poured onto approximately 50 g ice. Immediately white precipitate was formed which was filtered off. The solid was dissolved in chloroform and washed successively with dilute hydrochloric acid and brine. After drying over $MgSO_4$, the solvent was evaporated under reduced pressure. Yield: 665 mg (75%).

m.p. 125°C; IR (KBr, cm^{-1}): 3580 (νOH); ^1H NMR (300 MHz, $CDCl_3$, 20°C): 2.46 (s, 9H, SO_3ArCH_3), 2.71 (d, J = 14.5Hz, 2H, H_{eq} of $ArCH_2Ar$); 3.28 (s, 1H, ArOH); 3.50 (d, J = 14.5 Hz, 2H, H_{ax} of $ArCH_2Ar$); 3.58 and 3.71 (AB spin system, J = 14.4 Hz, 4H, $ArCH_2Ar$); A ring (ArOH): 6.65 (t, J = 7.6 Hz, 1H); 6.88 (d, J = 7.6 Hz, 2H); B and D rings (Ar-$OSO_2C_6H_4CH_3$): 6.45 (dd, J_{orto} = 7.7 Hz, J_{meta} = 1.4 Hz, 2H); 6.62 (t, J = 7,7 Hz, 2H); 6.85 (dd, J_{orto} = 7.7 Hz, J_{meta} = 1.4 Hz, 2H); C ring (Ar-$OSO_2C_6H_4CH_3$): 7.09 (t, J = 7.8 Hz, 1H); 7.33 (d, J = 7.8 Hz, 2H); 7.30 and 7.63 (AA'XX' spin system, 4H, SO_3ArCH_3); 7.33 and 7.68 (AA'XX' spin system, 8H, SO_3ArCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 20°C): 21.77 (SO_3ArCH_3); 30.95 (CH_2); 35.45 (CH_2); 119.41; 124.61; 126.13; 126.18; 126.81; 127.99; 128.43; 128.61; 129.48; 129.68; 129.88; 129.96; 130.05; 131.76; 133.23; 133.77; 134.08; 145.36; 145.45; 145.55; 145.66; 152.07; FAB-MS: 887 ($M^+ + H$); Analysis calculated for $C_{49}H_{42}S_3O_{10}$ (M = 887.05) C, 66.35; H, 4.74; S, 10.84%; Found: C, 66.21; H, 4.82; S, 10.62%.

Preparation of 12

456 mg (0.5 mmol) of **5** and 11.5 mg (0.01 mmol) of $Pd(PPh_3)_4$ were dissolved in 10 mL DMF under an inert atmosphere, then 100 µl H_2O was added. The reaction mixture was stirred for 10 hours at 60°C and filtered off. The yellow filtrate was evaporated to dryness, and subjected to column cromatography (silica gel, chloroform) in order to obtain conformationally pure **12**. The crude product was dried and its composition was determined by ^1H NMR. Yield: 195 mg (50%).

m.p. 225°C; IR (KBr, cm^{-1}): 3210 (νOH); ^1H NMR (300 MHz, $CDCl_3$, 20°C): 0.96 (s, 9H, $C(CH_3)_3$); 1.12 (s, 9H, $C(CH_3)_3$); 1.25 (s, 18H, $C(CH_3)_3$); 3.45 (d, J = 14 Hz, 2H, H_{eq} of $ArCH_{eq}$ $H_{ax}Ar$); 3.54 (d, J = 14 Hz, 2H, H_{eq} of $ArC'H_{eq}H_{ax}Ar$); 4.13 (d, J = 14 Hz, 2H, H_{ax} of $ArCH_{eq}H_{ax}Ar$); 4.30 (d, J = 14 Hz, 2H, H_{ax} of

ArC'$H_{eq}H_{ax}$Ar); 6.86 (brs, ArOH); A ring: 6.91 (s, 2H); C ring: 6.94 (s, 2H); B and D rings (AB spin system): 7.06 (d, J = 2.3 Hz, 2H); 7.11 (d, J = 2.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 20°C): 30.74 ($C(CH_3)_3$); 31.27 ($C(CH_3)_3$); 31.55 ($C(CH_3)_3$); 32.35 (CH_2); 32.47(CH_2); 33.93 ($C(CH_3)_3$); 33.98 ($C(CH_3)_3$); 34.22 ($C(CH_3)_3$); 125.60; 125.68; 125.95; 127.15; 127.21; 127.28; 127.58; 133.05; 141.13; 143.61; 144.14; 146.53; 148.97; 150.99; FAB MS: 780 (M^+); Analysis calculated for $C_{45}H_{55}F_3O_6S$ (M = 780.98) C, 69.21; H, 7.10; S, 4.11%; Found: C, 69.05; H, 7.2; S, 4.24%.

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[16] Selected NMR and FAB-MS data for the minor products. **5a**: 1.17(s, 9H, $C(CH_3)_3$); 1.21 (s, 18H, $2 \times C(CH_3)_3$); 1.23(s, 9H, $C(CH_3)_3$); **5b**: 0.99(s, 9H, $C(CH_3)_3$); 1.14 (s, 9H, $C(CH_3)_3$; 1.27 (s, 9H, $C(CH_3)_3$); **6a**: 1.02 (s, 18H, $C(CH_3)_3$); 1.35 (s, 9H, $C(CH_3)_3$); 1.38 (s, 9H, $C(CH_3)_3$); 3.24 (s, 6H, OSO_2CH_3); 3.36 (d, 2H, H_{eq} of $ArCH_2Ar$); 3.69 (d, 2H, H_{eq} of $ArCH_2Ar$); 4.38 (d, 2H, H_{ax} of $ArCH_2Ar$); 4.79 (d, 2H, H_{ax} of $ArCH_2Ar$); 6.76. (brs, 2H, ArH); 7.07 (brs, 2H, ArH); 7.28 (s, 2H, ArH); 7.3 (s, 2H, ArH); FAB MS: 805 ($M^+ + H$); **6b**: 1.25(s, 18H, $C(CH_3)_3$); 1.26 (s, 9H, $C(CH_3)_3$); 1.34 (s, 9H, $C(CH_3)_3$; 2.04 (s, 3H, OSO_2CH_3); 2.58 (s, 6H, OSO_2CH_3); 3.69 (d, J = 15.6 Hz, 2H, H_{eq} of $ArCH_2Ar$); 4.31(s, 4H, $ArCH_2Ar$); 4.34 (d, J = 15.6 Hz, 2H, H_{ax} of $ArCH_2Ar$); 7.13 (s, 2H, ArH); 7.17 (dd, J_{meta} = 2.15 Hz, 2H, ArH); 7.31 (dd, J_{meta} = 2.15 Hz, 2H, ArH); 7.34 (s, 2H, ArH); FAB MS: 883 ($M^+ + H$); **9a**: 3.68 (d, J = 14.3 Hz, 4H, H_{eq} of $ArCH_2Ar$); 4.57 (d, J = 14.3 Hz, 4H, H_{ax} of $ArCH_2Ar$); ^{19}F NMR (282 MHz, $CDCl_3$, 20°C): −76.88 ppm; **10a**: 2.49 (s, 3H, CH_3); 2.67 (s, 3H, CH_3);3.83 (d, J = 14 Hz, 2H, H_{eq} of $ArCH_2Ar$); 4.07 (d, J = 14 Hz, 2H, H_{eq} of $ArCH_2Ar$); 4.38 (d, J = 14 Hz, 2H, H_{ax} of $ArCH_2Ar$); 4.53 (d, J = 14 Hz, 2H, H_{ax} of $ArCH_2Ar$); FAB-MS: 581 ($M^+ + H$); **10b**: 3.34 (d, J = 13.9 Hz, 2H, H_{eq} of $ArCH_2Ar$); 4.73 (d, J = 13.9 Hz, 2H, H_{ax} of $ArCH_2Ar$); FAB MS: 737 ($M^+ + H$).

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