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Chiral 1,10-Phenanthroline-Bridged Calix[6]arenes[‡]

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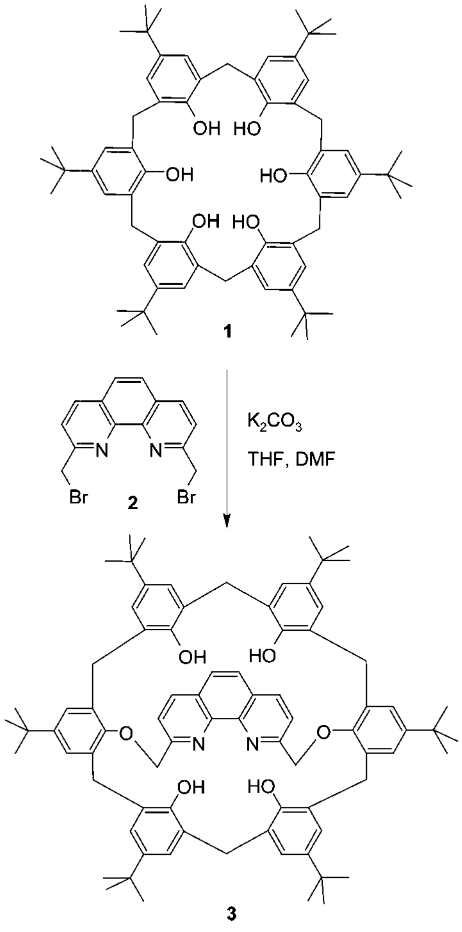
Several approaches to chiral derivatives of the 1,10-phenanthroline-bridged calix[6]arene **3** have been investigated, and seven new chiral calix[6]arenes have been synthesized. The C_2-symmetric axially chiral bimacrocycle **5** has been synthesized as racemic mixture; calixarenes **8**, **14**, **18**, **19**, **20** and **21** carrying chiral substituents (camphorsulfonyl, myrtanyl) have been prepared using enantiomerically pure reagents. Three chiral bimacrocycles **5**, **19** and **20** have also been analyzed by X-ray analyses. All compounds have been tested as ligands for copper ions in the Cu^I-catalyzed cyclopropanation of styrene and indene.

Introduction

Calixarenes are a versatile platform for the construction of compounds with well-defined spatial orientation of functional groups.[1–5] With just a few synthetic steps, interesting geometries can be derived from the macrocyclic calixarenes, including baskets or cages. Functionalized calixarenes have been employed in innumerable applications from “simple” molecular recognition to catalysis.[6,7]

In the past decade, we have synthesized a number of calixarenes which are spanned by bridges that contain functional groups.[8] One such bimacrocyclic calixarene derivative is the calix[6]arene **3**,[9] in which the phenol groups of the aryl rings A and D have been connected by a 1,10-phenanthroline-containing bridge. By reacting the calix[6]arene **1**[10] with 2,9-bis(bromomethyl)-1,10-phenanthroline (**2**),[11] **3** can be synthesized in 62% yield and in gram quantity.[11]

The nitrogen atoms of the 1,10-phenanthroline bridge enable the functionalized calix[6]arene **3** to chelate metal ions. The resulting complexes may be catalytically active, and we have investigated the power of its Cu^I complex to catalyze the cyclopropanation of olefins, for instance styrene or indene.[12,13] Remarkable *syn* selectivities have been found for **3** which complement the *anti* selectivities found with other concave 1,10-phenanthrolines.[12]



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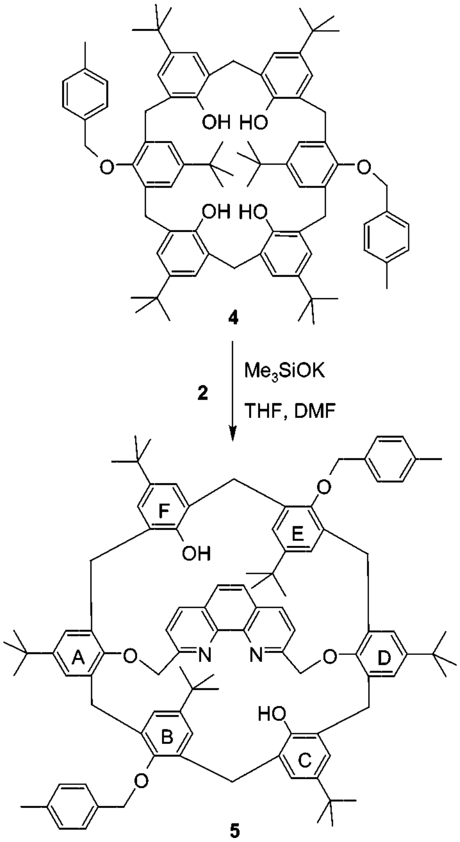
Many efforts have been undertaken to carry out Cu^{I}-catalyzed[14] cyclopropanation enantioselectively.[15–18] However, only some catalysts are able to combine a good enantioselectivity with good diastereoselectivity.[19]

In this work, we investigate approaches to turn the 1,10-phenanthroline-bridged calix[6]arene **3** into a chiral ligand. In principle, there are several approaches conceivable: the chiral information can stem from chiral substituents which have been connected to the calixarene, either before bridging or afterwards. Or the bridged calixarene **3** may carry two additional substituents in B and E position resulting in a C_2-symmetrical molecule with axial chirality. As shown in many enantioselective catalyses, C_2-chiral ligands are of special value because the symmetry allows two identical approaches for a substrate. In a C_1-symmetrical molecule, one of these routes would have to be hindered, or it would influence the selectivity. Therefore, we investigated C_2-symmetrical 1,10-phenanthroline-bridged calix[6]arenes first.



4

2

5

C_2-Symmetrical 1,10-Phenanthroline-Bridged Calix[6]Arenes with Axial Chirality

A C_2-chiral 1,10-phenanthroline-bridged calix[6]arene as envisioned above would contain two kinds of substituents: the 1,10-phenanthroline bridge connecting the aryl rings A and D, and two additional substituents at the aryl rings B and E. In principle, these substituents can be connected with the calixarene framework in either sequence. However, the substitution of only two of the remaining four OH groups in the 1,10-phenanthroline-bridged calix[6]arene **3** allows the formation of isomers. The B,C, B,E and B,F regioisomers can be formed in addition to mono-, tri- or tetrasubstitution of the remaining OH groups.

Therefore, we have chosen the opposite synthetic approach and have started from an A,D-disubstituted calix[6]arene. Gutsche[20] has shown that an A,D-disubstituted isomer **4** can be synthesized in good yield when 4-methylbenzyl bromide is used as reagent. In all experiments in which a calix[6]arene was bridged with the 1,10-phenanthroline unit, A,D spanning has been observed exclusively. Therefore, the reaction of **4** with bis(bromomethyl)-1,10-phenanthroline (**2**)[11] should only give one product, and indeed, only one bimacrocyclic product **5** was isolated in 33% yield.

Spectroscopic analysis revealed the symmetry of calixarene **5**, but it was difficult to assign all signals in the NMR spectra. The application of 2D-NMR techniques and low-temperature measurements suggest that the substituted calix[6]arene **5** adopts a conformation differing from that of the non-alkylated bimacrocycle **3**. Fortunately, crystals could be grown for an X-ray analysis (see Figure 1).

In the crystal of **5**, the arene rings of the calixarene macrocycle adopt an *udiudi* conformation.[21] This conformation is stabilized (i) by a close interaction of the two 4-methylbenzyl residues which are in a distance to allow π–π interaction, and (ii) by hydrogen bonds which involve the two remaining free phenol groups and a water molecule. This conformation for **5** is unexpected because an NMR analysis of the starting material **4** reveals a predominant existence of an all-*up* conformation (the differences in chemical shift for the doublets of the methylene groups connecting the phenol rings are 0.3 to 0.7 ppm,[22] clearly indicating a *syn* orientation, i.e. *uu*, for all neighboring arene rings). This means that during the bridging process from **4** to **5**, two arene rings must invert from an *up* to a *down* orientation.

Temperature-dependent NMR studies show further splitting of signals. Remarkably, one of the three signals for the *tert*-butyl groups considerably splits into two signals (see Figure 2). At the first glance, such a split is not in accordance with the *udiudi* symmetry seen in the X-ray structure. But besides the *up*, *down* or *in* orientation of the arene rings, there is an additional mobility: the 1,10-phenanthroline bridge does not symmetrically bridge the macrocycle but is shifted along the A,D axis. At higher temperature, a quick rocking along this axis probably takes place resulting in three signals for the *tert*-butyl groups of the *up*-, *down*- or *in*-oriented arene rings, respectively. But if on time-average the bridge is displaced towards ring A or D, the molecule looses its symmetry and thus shows splitting of the *tert*-butyl signals.

At 333 K, three sharp *tert*-butyl signals are detectable. At 243 K, the signal at $\delta = 0.60$ ppm splits into two signals with 117 Hz difference. For the signal at $\delta = 1.35$ ppm, also a splitting can be detected but it is considerably smaller (12.8 Hz). The coalescence temperatures have been determined (288 and 264 K, respectively), and from both values,

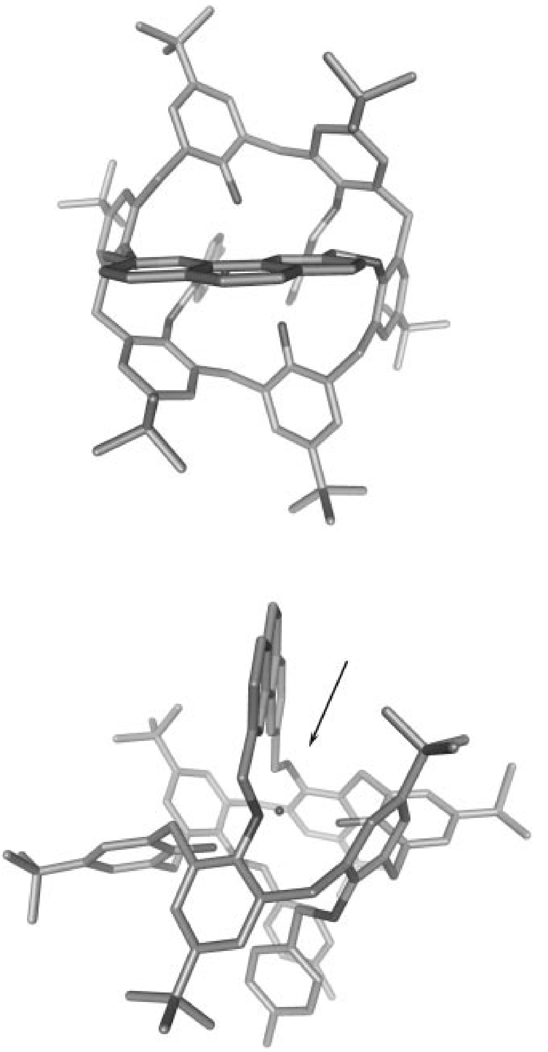


Figure 1. X-ray structure of the 1,10-phenanthroline-bridged bis(4-methylbenzyl) ether **5**. Both enantiomers crystallize within the same crystal, only one is shown here. Top: View from above showing the perpendicular orientation of the 1,10-phenanthroline bridge with respect to the plane of the calix[6]arene macrocycle. Bottom: The two benzylated phenol rings are inverted giving rise to an *ud-iudi* conformation.[21] The two benzyl groups are packed to allow a π–π contact. The two *in*-oriented phenol groups are stabilized by a water molecule. Its oxygen atom is visible in the structure on the bottom. An arrow points at it.

the free enthalpy of activation has been estimated to be 57 kJ/mol.[23]

Compound **5** crystallizes in the centrosymmetrical monoclinic space group $P2_1/n$. This implies that the crystal contains both enantiomers of **5**. Several attempts to separate the enantiomers including fractionating crystallization in the presence of enantiomerically pure auxiliaries from the chiral pool have not been successful up to now. In addition, **5** was subjected to chiral reagents in order to functionalize the remaining OH group(s). But up to now, we were not able to detect any functionalized product. Maybe the phenol groups are shielded too much in their *in* position (see Figure 1) to allow further functionalization.

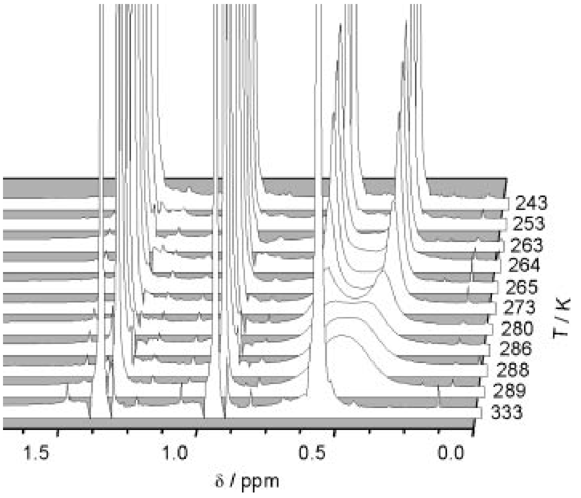


Figure 2. Part of the 500-MHz NMR spectrum of **5** at different temperatures.

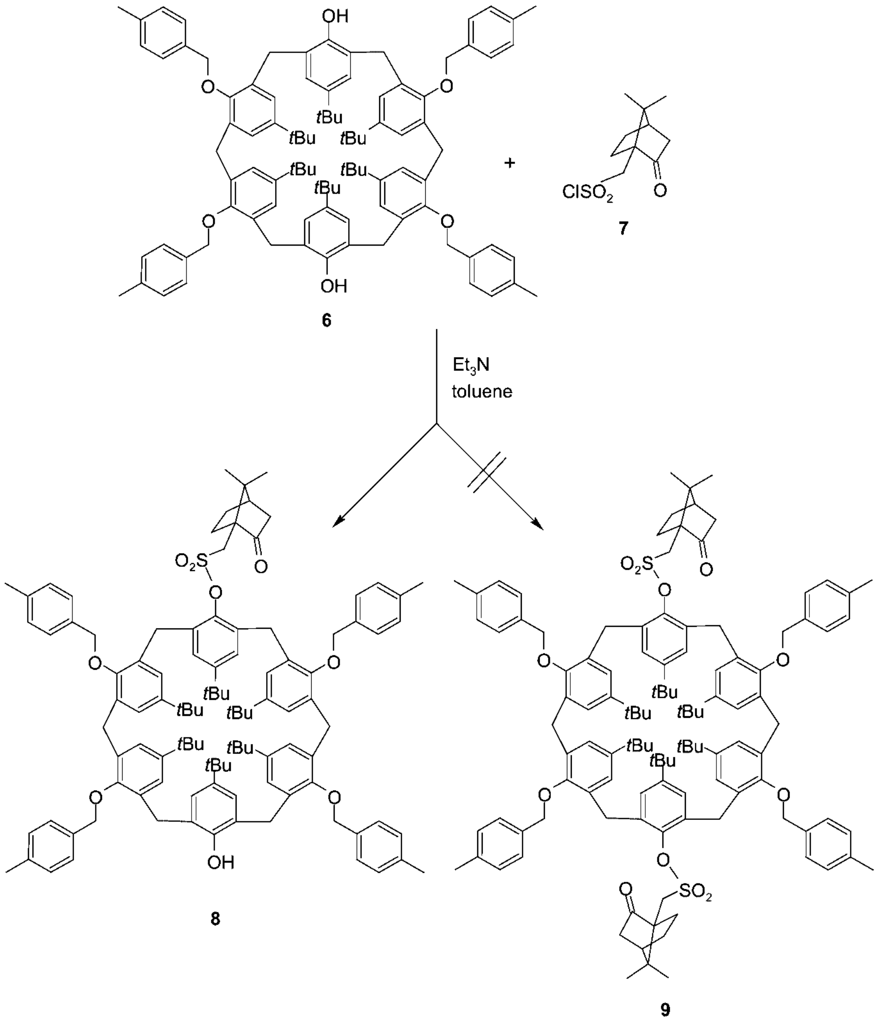
Attempts to Convert C_2-Symmetrical 1,10-Phenanthroline-Bridged Calix[6]arenes into Diastereoisomers

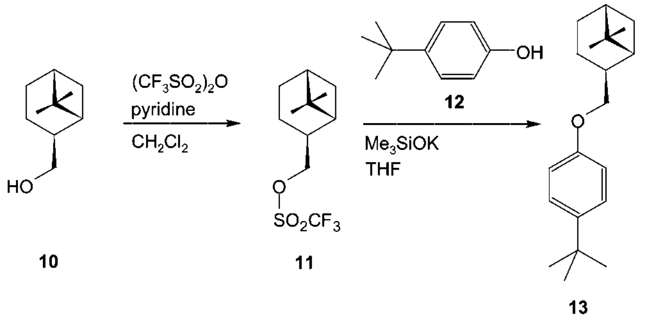
The introduction of an additional chiral element into a chiral compound will turn pairs of enantiomers into pairs of diastereoisomers if the additional chiral element is enantiomerically pure. In the case of the C_2-symmetrical calixarene **5**, chiral residues at the phenol groups in position B and E would lead to a pair of diastereoisomers. Therefore as starting material, a calix[6]arene was sought after which carried two chiral groups in position A and D (i.e. position B and E after bridging).

When thinking about the chiral pool, terpene derivatives seem to be suitable candidates to introduce a chiral substituent. Camphorsulfonic acid derivatives have often been used for such a task. But with calix[6]arene **1**, the reaction with camphorsulfonyl chloride (**7**) only resulted in mono- or hexasubstitution.[24] Nevertheless, the hexasubstitution proved that the sulfonylation of all OH groups in a calix[6]-arene derivative is possible. Thus, an A,D-disubstituted chiral compound should be accessible if one started from a tetra-protected calix[6]arene.

A convenient A,B,D,E-tetraalkylated starting material **6** was reported,[25] using again the 4-methylbenzyl group. Reaction of **6** with camphorsulfonyl chloride (**7**) indeed resulted in the formation of 31% of a chiral derivative **8**, but unfortunately, the sulfonyl group was only introduced once. In contrast to the full sulfonylation of calix[6]arene **1**, the 4-methylbenzyl derivative could not be sulfonylated twice to give the disulfonate **9**. It can be speculated whether the mono-sulfonate **8** adopts a conformation in which the last remaining OH group is not accessible anymore.

A further approach to A,D-disubstituted calix[6]arenes is the formation of diethers. In alkylation reactions, the yield of A,D-disubstituted products is considerably better than in the formation of esters, see for instance the formation of the diether **4**. Respectively, a terpene derivative was looked for which would rather alkylate than esterificate, and myrtanol derivatives were chosen which can easily be ob-





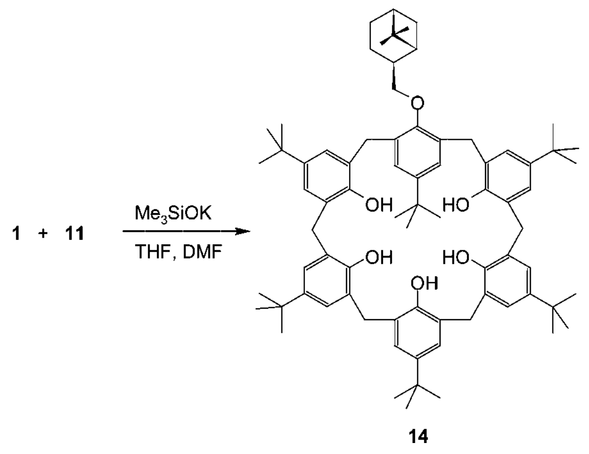
tained by transformation of β-pinene. The *cis*- and *trans*-myrtanyl isomers are possible and even a CPK model suggests that *cis*-myrtanyl residues should give a larger asymmetric shielding of the transition metal ion binding region in the resulting substituted calix[6]arene than *trans* derivatives. But alkylations with *cis*-myrtanyl derivatives are difficult.[26,27] S_N2 reactions are extremely hindered due to shielding by the isopropylidene bridge, and S_N1 reactions lead to many side products due to rearrangements and subsequent decompositions.

Triflates are often more reactive than iodides, and we have therefore prepared the triflate of *cis*-myrtanol **11** by reacting *cis*-myrtanol (**10**) with triflic anhydride. The resulting triflate **11** is a very reactive compound which can only be isolated if the temperature is kept low.

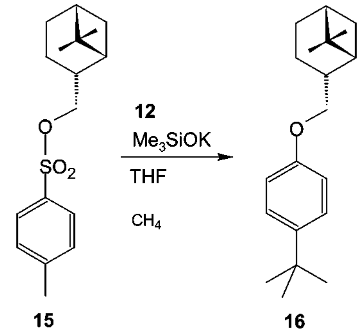
Nevertheless, *cis*-myrtanyl triflate (**11**) can be generated in 90% yield and in 90% purity at 0 °C, and it is usable as alkylating reagent if one offers a substrate immediately. Its potential as an alkylating reagent for phenols was tested with 4-*tert*-butylphenol (**12**). The resulting *cis*-myrtanyl ether **13** could be obtained in 36% yield.

When calix[6]arene **1** was treated with an excess of *cis*-myrtanyl triflate (**11**), alkylation took place, too, and the monoether **14** could be isolated, although only in small yield (3%). This small yield and the short survival time of the *cis*-triflate **11** argue against further alkylation experiments of calix[6]arene **1** with *cis*-myrtanyl triflate (**11**). For the formation of the corresponding diether, the reaction time would have to be even longer but **11** would not survive long enough.

In contrast to *cis*-myrtanyl derivatives, the respective *trans*-myrtanyl compounds should be less hindered for a nucleophilic attack by an oxygen atom. Therefore, we have tested *trans*-myrtanyl tosylate (**15**) in the alkylation of 4-



tert-butylphenol (**12**) and have found a much better alkylation yield: **16** could be isolated in 84% yield.



Next, this tosylate **15**[27] but also the bromide **17**[28] were used to alkylate calix[6]arene **1**.

Analogous to the reaction with the *cis*-myrtanyl reagent, a monoether could also be synthesized in the *trans* series. Reaction of calix[6]arene **1** with 2.5 equiv. of *trans*-myrtanyl tosylate (**15**) led to 19% of the monoether **18**, and with a larger quantity (four- to sixfold excess) of *trans*-myrtanyl bromide (**17**), a double alkylation was also possible, and 8% of the diether **19** was isolated. To elucidate the conformation of the product **19**, again the differences in chemical shifts for all pairs of doublets of the methylene groups connecting adjacent arene rings were examined.[22] Due to very small differences in the chemical shifts of the different pairs, the analysis was not trivial but gave results which are interpretable for a *uduudu* conformation (only one set of doublets shows a large difference in chemical shifts). From dichloromethane/acetonitrile single crystals of **19** suitable for X-ray analysis could be obtained. The result is shown in Figure 3.

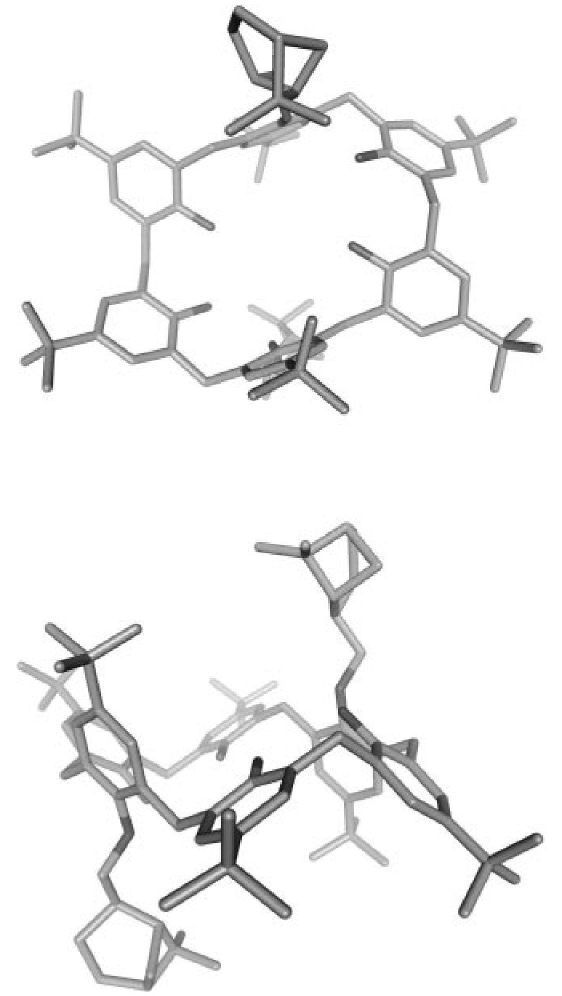
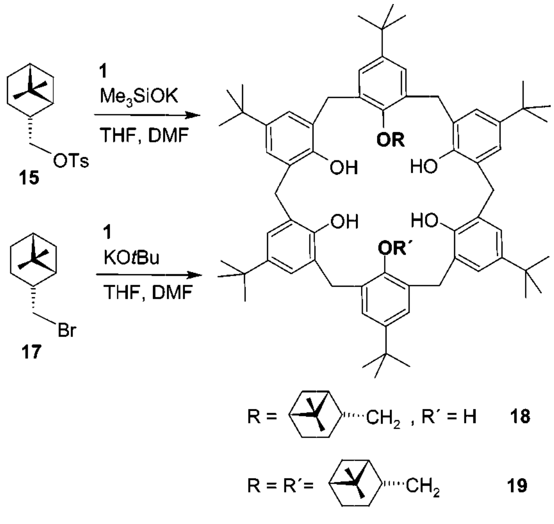


Figure 3. X-ray structure of the di-*trans*-myrtanyl ether of calix[6]arene **19**. Top: View perpendicular to the plane of the calixarene macrocycle. Bottom: View along the B,E arene rings[21] showing that the two myrtanyl residues are located on the opposite sides of the calixarene macrocycle. The overall conformation is *uuiddi*.[21]



In the X-ray analysis, the two myrtanyl residues are located on opposite sides of the calixarene ring of **19**, a conformation seemingly not suggested by the NMR analysis. But an NMR spectrum analyses the dynamic behavior and gives information on the averaged conformation while in the crystal, one conformation is frozen out. Furthermore, the applied NMR analysis[22] simplifies the conformation of neighboring arene rings into *uu* (*syn*, large difference of chemical shifts) or *ud* (*anti*, almost no difference in chemical shift). And finally, the rules of thumbs for *syn* or *anti* orientation of adjacent arene rings does not account for influences of substituents if the rings possess a different substitution pattern.

With the syntheses of the mono- and dimyrtanyl-substituted calix[6]arenes **14**, **18** and **19**, chiral starting materials for a further bridging with 2,9-bis(bromomethyl)-1,10-phenanthroline (**2**) have been made available. But unfortunately, neither of the respective bridging experiments was successful to give isolable material of an A,D-1,10-phenanthroline-bridged calixarene which carried one or two additional terpene-derived chiral groups. At mild reaction conditions, no conversion was observed, with harsher reaction conditions, only decomposed or polymeric material was formed. The bridging experiments were also carried out with a mono-camphorsulfonyl-substituted calix[6]arene,[24] but also in vain. One can only speculate about the reasons. The X-ray structures known so far (see Figure 3, and ref.[24] for a camphorsulfonylated calix[6]arene) suggest that the phenol groups may be oriented in such a way that the second alkylation within one molecule is hindered, but the respective not yet bimacrocyclic [1+1] product could not be detected by mass spectral analyses. Furthermore, the monofunctionalized compounds have to be alkylated in position B or C first, to allow A,D bridging. An alkylation in D position will obviously not allow an A,D bridging with the 1,10-phenanthroline bridge. But an alkylation of a monosubstituted calix[6]arene is not unreasonable to occur in D-position first, because position D is sterically least hindered and a D-centered anion can perfectly be stabilized by a chain of hydrogen bonds on both sides.

Reaction of 1,10-Phenanthroline-Bridged Calix[6]arene 3 with Chiral Reagents

Finally, a third approach to chiral 1,10-phenanthroline-bridged calix[6]arenes was checked, the reaction of the 1,10-phenanthroline-bridged calix[6]arene **3** with chiral reagents. As stated above, the chances of getting the envisaged C_2-chiral bimacrocycle were not high but nevertheless, the other products are chiral calixarenes, too.

When the bridged calixarene **3** was treated with 3 equiv. of camphorsulfonyl chloride (**7**), indeed a doubly sulfonylated derivative **20** could be isolated in 76% yield. In principle, there are several possible regio- and diastereoisomers. (Figure 4)

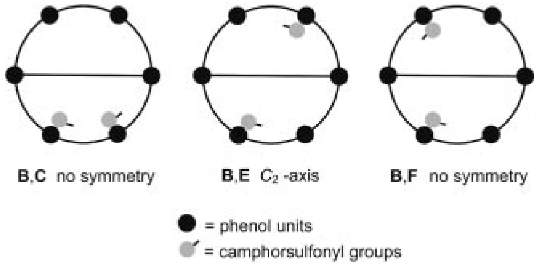
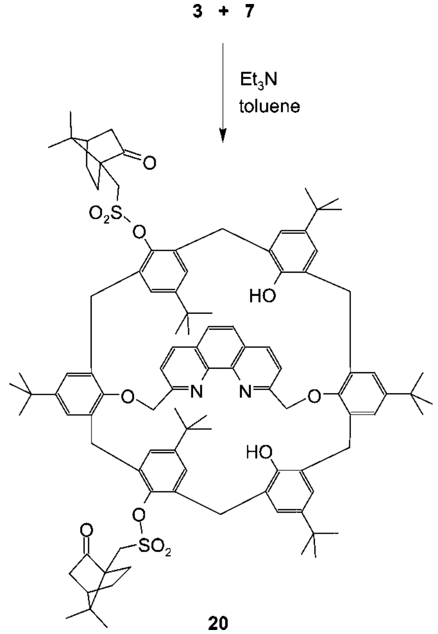


Figure 4. When an A,D-bridged calix[6]arene is treated with two equivalents of a chiral sulfonylating agent, three regioisomers can be formed one of which possesses C_2 symmetry.

Concerning regiochemistry, the camphor residues may be connected to the rings: B and C, B and E, as well as B and F, with only the B,E combination having C_2 symmetry.



20

All compounds are chiral but due to the substitution pattern, not all regioisomers exist as pairs of diastereoisomers. If one looks at the starting material **3** with the aryl rings labeled A through F, a B,E substitution is different from a C,F substitution (diastereoisomeric C_2-symmetrical products are formed), but B,C and E,F as well as B,F and C,E substitution give identical molecules. The NMR analysis showed more signals than expected for C_2 symmetry, and an X-ray analysis proved the substitution pattern to be B,F (see Figure 5).

This B,F pattern is not easy to understand. X-ray analyses[11] and calculations[29] of the 1,10-phenanthroline-bridged calix[6]arene **3** show that the bridge is not perpendicular to the plane of the calixarene macrocycle. Therefore, two neighboring OH groups (B and C) should be more accessible than the other two (E and F). The tendency to form a tilt structure should be even larger once the first OH group (B) is sulfonylated. How can the B,F substitution be explained?

The X-ray structures of **3**[11] and of the disulfonylated derivative **20** tell that the 1,10-phenanthroline bridge is shifted along the A,D axis. Already in the starting material **3**, this shift will differentiate between the remaining phenol groups (but with no effect on the product as all positions are equal in **3**). However, due to steric repulsion, a substituent in position B will probably shift the bridge even more towards ring D. In such a situation, the F phenol group may become accessible for the next attack. Undoubtedly, the B,F isomer **20** is formed and was isolated as the only product.

In enantioselective catalyses however, this compound does not seem to be unsymmetrical enough, and we expected only marginal enantiomeric excesses. Therefore, we also used a different stoichiometry in the reaction of the calixarene **3** with camphorsulfonyl chloride (**7**) to only add one camphor residue to the bimacrocycle **3** to give the

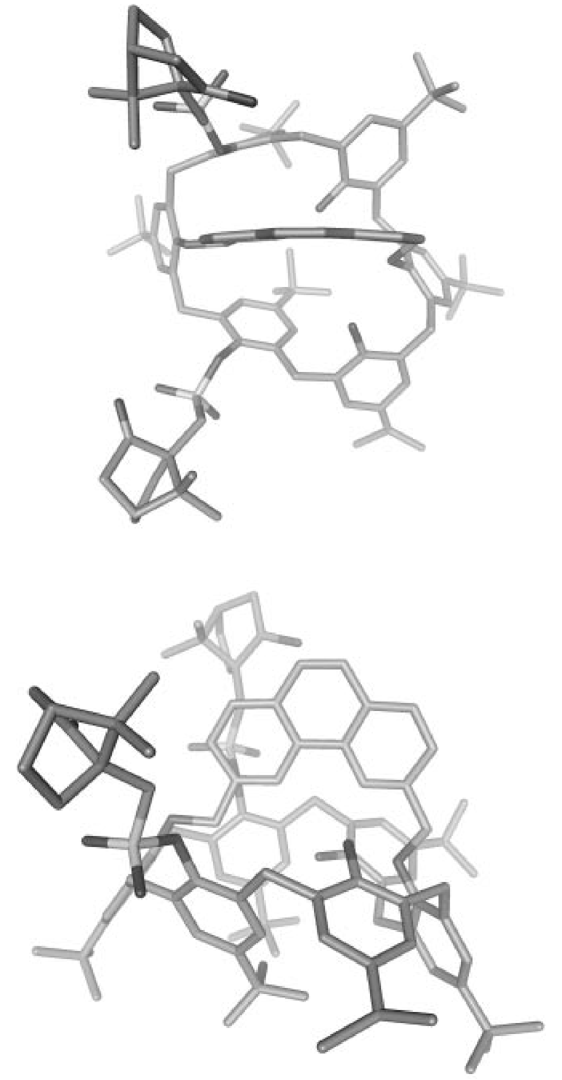
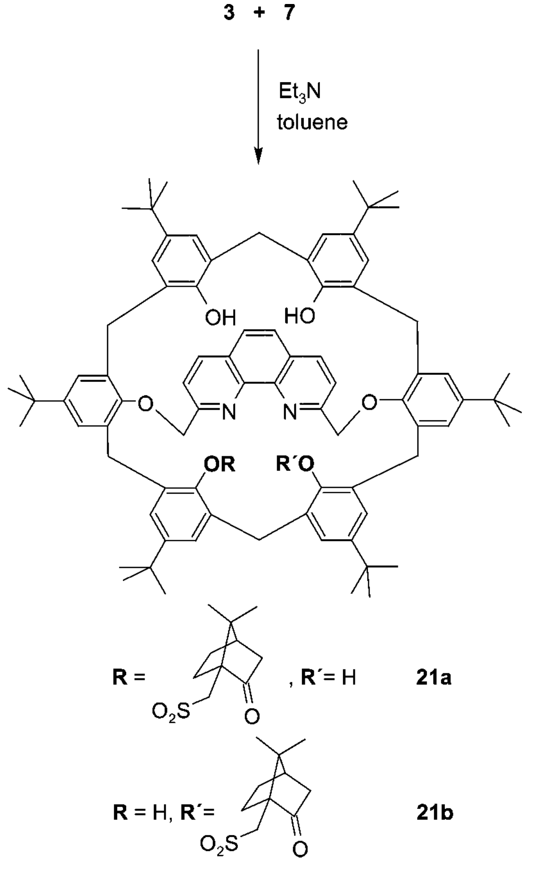


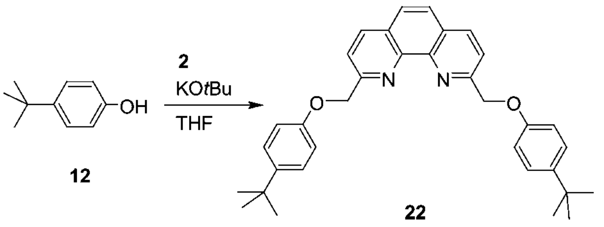
Figure 5. X-ray analysis of the doubly sulfonylated derivative **20**. Top: View perpendicular to the plane of the B,F-disulfonylated calixarene macrocycle. Bottom: View perpendicular to the 1,10-phenanthroline bridge. The 1,10-phenanthroline moiety is shifted along the A,D axis towards bridgehead D minimizing steric repulsion with the two camphor residues in positions B and F.



monosulfonylate **21** in 49% yield. This one residue can become attached to ring B or to ring C. Consequently, the product **21** was found as a mixture of diastereoisomers **21a** and **21b**. By tedious chromatography, one diastereoisomer **21x**[30] could be enriched to 90% purity with 3% yield and the resulting sample was tested as ligand in an enantioselective copper(I)-catalyzed cyclopropanation.

Application of 1,10-Phenanthroline-Bridged Calix[6]arenes in Cyclopropanations

1,10-Phenanthroline-bridged calix[6]arenes are interesting ligands for copper in the Cu^I-catalyzed cyclopropanation of alkenes with diazoacetates.[13] In order to evaluate the influence of the bimacrocyclic structure, a nonmacrocyclic analog was synthesized by reacting the bridging components **2** with 4-*tert*-butylphenol (**12**). The resulting diether **22** was obtained in 88% yield.



It has been shown for many concave 1,10-phenanthrolines that copper(I) complexes are easily formed.[12] For a 1:1 mixture of the axially chiral calix[6]arene **5** with copper(I) trifluoromethanesulfonate, a 500-MHz NMR spectrum in $C_2D_2Cl_4/CD_3CN$ (10:1, 60 °C) has been recorded showing sharp signals for the complex $\mathbf{5}\cdot Cu^+$. Its signals for the 1,10-phenanthroline moiety are shifted upfield upon complexation while the signals of the calixarene part are hardly affected. These data suggest that the overall conformation of the complex does not differ much from the conformation of the free ligand.

Model compound **22** and the calixarene derivatives **5**, **20** and one enriched diastereoisomer of **21** were tested in the cyclopropanation of styrene (**23**) and indene (**24**) with ethyl diazoacetate (**25**). The *cis*/*trans* and the *endo*/*exo* ratios, respectively, for the cyclopropanes **26** and **27** are compared in Table 1. Although the best *cis* or *endo* values were found with *tert*-butyl diazoacetate, the measurements listed in Table 1 were carried out with ethyl diazoacetate (**25**) for the

Table 1. Results of the copper(I)-catalyzed cyclopropanation of styrene (**23**) and indene (**24**) with ethyl diazoacetate (**25**) employing several chiral 1,10-phenanthroline-bridged calix[6]arenes. Besides the *cis*/*trans* and the *endo*/*exo* ratios of the cyclopropanes **26** and **27**, also the ratios of the *cis* and *trans* side products diethyl maleate and diethyl fumarate are listed. The yields are not optimized because all reactions are carried out under standardized conditions to ensure comparability of the selectivities.

Ligand	Styrene (**23**) **26** *cis*/*trans* [% yield]	maleate/fumarate	Indene (**24**) **27** *endo*/*exo* [% yield]	maleate/fumarate
without	36:64 [67]	48:52	30:70 [69][13]	28:72[13]
3	67:33 [54][13]	86:14[13]	76:24 [45][13]	89:11[13]
5	61:39 [67]	66:34	57:43 [37]	78:22
20	51:49 [43]	65:35	33:67 [42]	53:47
21x [30]	42:58 [60]	53:47	–	–
22	41:59 [56]	46:54	20:80 [49]	47:53

following reasons: Only **25** is commercially available and has therefore been chosen as the standard cyclopropanating diazo compound in the literature, and for the examination of selectivity trends, the ethyl derivatives are as good as other esters. Besides the *cis*/*trans* and the *endo*/*exo* selectivities for the cyclopropanes **26** and **27**, also the maleate/fumarate ratios of a competing side reaction, the dimerization of the carbene, are listed. These ratios also strongly depend on the nature of the ligand at the copper ion.

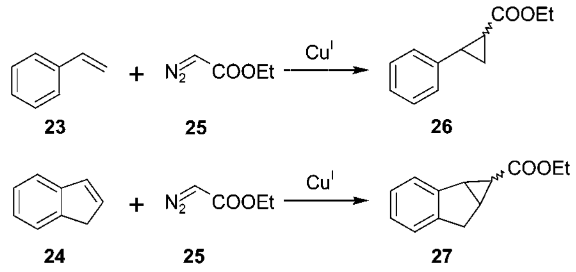


Table 1 shows that the use of the chiral calixarenes alters the stereoselectivities in the same direction (towards *cis* or *endo*) as the use of the bridged calix[6]arene **3**. These results argue for a complexation of copper ions by the 1,10-phenanthroline moieties. The change in stereoselectivities depends strongly on the ligand but all calixarene derivatives shift the *cis*/*trans* or *endo*/*exo* ratio, respectively, towards *cis* or *endo*. The nonmacrocyclic analog **22** shows the smallest deviation from the ratios obtained with ligand-free copper(I). While with styrene (**23**), slightly less *trans* cyclopropane **26** is formed than with copper(I) ions alone, the *exo* fraction of the indene-derived cyclopropane **27** is even larger than in the absence of ligand **22**.

With the sulfonylated calixarenes **20** and **21x**,[30] the difference to experiments without a ligand is also small. Only with the axially chiral calix[6]arene **5**, distinctly more *cis* than *trans* or *endo* than *exo* products, respectively, were found. Unfortunately, the changes never reached the values found for the nonmodified 1,10-phenanthroline-bridged calix[6]arene **3**.

Although the diastereoselectivity (*cis*/*trans* or *endo*/*exo*) was small in the case of the enantiomerically pure compounds **20** and **21x**, the enantiomeric excess of these cyclopropanations was determined by transesterification to menthyl esters and subsequent GC analysis as described by Pfaltz.[31] However, within the accuracy of the measurements, no enantiomeric excess was found for these ligands: 2% *ee* (1*S*,2*S*) for **20**, 4% *ee* (1*S*,2*S*) for **21x**[30].

Conclusions

Several synthetic pathways towards chiral 1,10-phenanthroline-bridged calix[6]arenes have been examined and several new calix[6]arenes have been made accessible some of which exist in unusual conformations. These calixarenes are active as ligands in the stereoselective cyclopropanation of alkenes such as styrene or indene but most exhibited selectivities were only marginal. Only in the case of the C_2-chiral calixarene **5** were the stereoselectivities in the range of the parent compound **3**. Therefore for further work, these ligands shall be produced enantiomerically pure to evaluate their enantioselectivity.

Experimental Section

General Remarks: The following chemicals were obtained commercially and were used without further purification: (+)-camphor-10-sulfonyl chloride (**7**, Fluka), potassium trimethylsilanolate (Aldrich), potassium *tert*-butoxide (Fluka), 4-*tert*-butylphenol (**12**, Fluka), sodium hydride, 60% dispersion in oil (Aldrich), styrene (**23**, Fluka), indene (**24**, Fluka). **1**,[10] **2**,[11] **3**,[9] **4**,[20] **6**,[25] **10**,[32] **15**[26] and **17**[28] were prepared according to literature procedures. HPLC-grade tetrahydrofuran was used. Other dry solvents were obtained with suitable desiccants. Column chromatography was carried out on neutral alumina (Fluka) or silica gel (Macherey–Nagel). Chromatography on the chromatotron (model 7924T from Harrison Research) was carried out with silica gel type 7749 (Merck) or neutral alumina (Merck), both with gypsum and fluorescence indicator. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker ARX 300 (300 MHz or 75 MHz) or DRX 500 (500 MHz or 125 MHz), using tetramethylsilane as internal standard. For the assignment of signals, the following abbreviations have been used: phen = 1,10-phenanthroline, PMB = 4-methylbenzyl, cam = camphor, myr = myrtanyl. For further details see ref.[33–36,41,42,44] IR spectra were measured with Perkin–Elmer 1600 Series. MS spectra were recorded with Finnigan MAT 8200 or 8230, with MALDI-TOF mass spectrometer Biflex III (Bruker-Daltonics, using 2,4-dihydroxybenzoic acid as matrix). Elemental analyses were carried out with EuroEA3000 Elemental Analyzer from Euro Vector. Rotation angles $[\alpha]_D^{20}$ have been determined by using a Perkin–Elmer Polarimeter 341. Gaschromatography was performed with 6890 N (Agilent); split/splitless injector, split ratio 11:1, injector temp. 250 °C, FID detector temp. 300 °C, or on Varian 3400CX (Varian Associates); injector: split/splitless, split ratio 20:1, injector temp. 250 °C, FID detector temp. 300 °C.

5,11,17,23,29,35-Hexa-*tert*-butyl-39,42-dihydroxy-38,41-bis[(4-methylbenzyl)oxy]-37,40-[1,10-phenanthroline-2,9-diylbis(methyleneoxy)]-calix[6]arene (5): Under nitrogen, the A,D-benzylated calix[6]arene **4** (1.16 g, 982 µmol) and sodium hydride (314 mg, 7.86 mmol, 60% dispersion in oil, washed with *n*-pentane) as base were stirred in a mixture of dry tetrahydrofuran (100 mL) and dry dimethylformamide (10 mL). After 45 min, 2,9-bis(bromomethyl)-1,10-phenanthroline (**2**) (539 mg, 1.47 mmol) in dry tetrahydrofuran (50 mL) was added dropwise over 30 min to the slightly yellow suspension and the mixture was stirred for 18 h. The turbid solution was neutralized with 0.2 M hydrochloric acid and the solvents were evaporated to dryness. After dissolving in chloroform (100 mL), the organic layer was washed with water (2×30 mL). For the separation of the layers, centrifugation was necessary. The aqueous layers were extracted with chloroform (50 mL). The organic layer was dried with magnesium sulfate and the solvents were evaporated to dryness. The brown crude residue was purified by chromatography [silica gel, 0.04–0.063 mm, cyclohexane/ethyl acetate (8:1)]. Recrystallization from dichloromethane/methanol led to the colorless crystalline product **5** (448 mg, 33%). M.p. 252 °C. ^{1}H NMR[33] (500 MHz, $C_2D_2Cl_4$, 60 °C): δ = 0.56 [s, 18 H, 17-C(C*H*$_3$)$_3$, 35-C(C*H*$_3$)$_3$], 0.94 [s, 18 H, 5-C(C*H*$_3$)$_3$, 23-C(C*H*$_3$)$_3$], 1.35 [s, 18 H, 11-C(C*H*$_3$)$_3$, 29-C(C*H*$_3$)$_3$], 2.22 (s, 6 H, Ar-C*H*$_3$), 3.28 (d, $^{2}J_{\mathrm{H,H}}$ = 15.9 Hz, 2 H, 8-*H*, 26-*H*), 3.38 (d, $^{2}J_{\mathrm{H,H}}$ = 16.1 Hz, 2 H, 14-*H*, 32-*H*), 3.70 (br. d, $^{2}J_{\mathrm{H,H}}$ ≈ 12 Hz, 2 H, O-C*H*$_2$-Ar), 4.12 (d, $^{2}J_{\mathrm{H,H}}$ = 14.6 Hz, 2 H, 2-*H*, 20-*H*), 4.18 (d, $^{2}J_{\mathrm{H,H}}$ = 14.7 Hz, 2 H, 2-*H*, 20-*H*), 4.32 (br. d, $^{2}J_{\mathrm{H,H}}$ = 16.0 Hz, 2 H, 14-*H*, 32-*H*), 4.39 (br. s, 2 H, 8-*H*, 26-*H*), 4.55 (br. s, 2 H, *), 5.00 (br. d, $^{2}J_{\mathrm{H,H}}$ ≈ 12 Hz, 2 H, O-C*H*$_2$-Ar), 5.79 (br. d, $^{2}J_{\mathrm{H,H}}$ = 15.7 Hz, 2 H, *), 6.35 (d, $^{4}J_{\mathrm{H,H}}$ = 2.6 Hz, 2 H, 16-*H*, 34-*H*), 6.78 (m$_{c}$, 6 H, 6-*H*, 24-*H*, PMB 3-*H*, 5-*H*), 6.93 (d, $^{3}J_{\mathrm{H,H}}$ = 8.3 Hz, 4 H, PMB 2-*H*, 6-*H*), 7.07 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 2 H, 10-*H*, 28-*H*), 7.09 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 2 H, 12-*H*, 30-*H*), 7.12 (d, $^{4}J_{\mathrm{H,H}}$ = 2.6 Hz, 2 H, 4-*H*, 22-*H*), 7.19 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 2 H, 18-*H*, 36-*H*), 7.74 (br. d, $^{3}J_{\mathrm{H,H}}$ ≈ 8 Hz, 2 H, phen 3-*H*, 8-*H*), 7.83 (br. s, 2 H, phen 5-*H*, 6-*H*), 8.25 (d, $^{3}J_{\mathrm{H,H}}$ = 8.3 Hz, 2 H, phen 4-*H*, 7-*H*) ppm. ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 60 °C):[34] δ = 20.8 (Ar-*C*H$_3$), 30.5 [17-C(*C*H$_3$)$_3$, 35-C(*C*H$_3$)$_3$], 30.7 (*C*-8, *C*-26), 30.8 [5-C(*C*H$_3$)$_3$, 23-C(*C*H$_3$)$_3$], 31.5 [11-C(*C*H$_3$)$_3$, 29-C(*C*H$_3$)$_3$], 31.6 (*C*-14, *C*-32), 33.2 [17-*C*(CH$_3$)$_3$, 35-*C*(CH$_3$)$_3$], 33.5 [11-*C*(CH$_3$)$_3$, 29-*C*(CH$_3$)$_3$], 33.7 [5-*C*(CH$_3$)$_3$, 23-*C*(CH$_3$)$_3$], 38.9 (*C*-2, *C*-20), 72.7 (O-*C*H$_2$-Ar), 72.8 (O-*C*H$_2$-phen), 119.7 (phen *C*-3, *C*-8), 124.4 (*C*-16, *C*-34), 125.0 (*C*-6, *C*-24), 125.6 (phen *C*-5, *C*-6), 125.7 (*C*-18, *C*-36), 125.8 (PMB *C*-2, *C*-6), 125.9 (*C*-4, *C*-22), 127.1 (*C*-12, *C*-30), 127.2 (*C*-10, *C*-28), 127.7 (*), 127.8 (phen *C*-4a, *C*-6a), 128.1 (PMB *C*-3, *C*-5), 133.5 (*C*-7, *C*-25, #), 133.7 (*C*-9, *C*-27 #), 134.3 (*C*-15, *C*-33, #), 135.1 (PMB *C*-4), 136.0 (phen *C*-2, *C*-9), 136.5 (phen *C*-4, *C*-7), 141.3 (*C*-11, *C*-29), 144.7 (phen *C*-10a, *C*-10b), 145.1 (*C*-17, *C*-35), 146.5 (*C*-5, *C*-23), 150.6 (*C*-38, *C*-41), 152.3 (*C*-39, *C*-42), 153.4 (*C*-37, *C*-40) ppm. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, –30 °C):[35] δ = 0.31 [s, 9 H, C^{k}(C*H*$_3$)$_3$], 0.54 [s, 9 H, C^{k}(C*H*$_3$)$_3$], 0.90 [s, 9 H, C^{j}(C*H*$_3$)$_3$], 0.93 [s, 9 H, C^{j}(C*H*$_3$)$_3$], 1.26 [s, 9 H, C^{i}(C*H*$_3$)$_3$], 1.27 [s, 9 H, C^{i}(C*H*$_3$)$_3$], 2.21 (s, 3 H, Ar-C*H*$_3$), 2.23 (s, 3 H, Ar-C*H*$_3$), 3.11 (d, $^{2}J_{\mathrm{H,H}}$ = 14.9 Hz, 1 H, Ar-C^{z}H*H*-Ar), 3.16 (d, $^{2}J_{\mathrm{H,H}}$ = 17.0 Hz, 1 H, Ar-C^{q}H*H*-Ar), 3.27 (d, $^{2}J_{\mathrm{H,H}}$ = 15.7 Hz, 1 H, Ar-C^{v}H*H*-Ar), 3.33 (d, $^{2}J_{\mathrm{H,H}}$ = 15.9 Hz, 1 H, Ar-C^{t}H*H*-Ar), 3.40 (d, $^{2}J_{\mathrm{H,H}}$ = 16.8 Hz, 1 H, Ar-C^{w}H*H*-Ar), 3.73 (d, $^{2}J_{\mathrm{H,H}}$ = 11.5 Hz, 1 H, Ar-C^{u}H*H*-Ar), 3.81 (d, $^{2}J_{\mathrm{H,H}}$ = 14.9 Hz, 1 H, Ar-C^{z}*H*H-Ar), 3.86 (d, $^{2}J_{\mathrm{H,H}}$ ca. 12 Hz, 1 H, Ar-C^{s}H*H*-Ar), 3.99 (d, $^{2}J_{\mathrm{H,H}}$ = 14.4 Hz, 1 H, Ar-C^{y}H*H*-Ar), 4.01 (d, $^{2}J_{\mathrm{H,H}}$ = 14.6 Hz, 1 H, Ar-C^{x}H*H*-Ar), 4.06 (d, $^{2}J_{\mathrm{H,H}}$ = 14.4 Hz, 1 H, Ar-C^{y}*H*H-Ar), 4.08 (d, $^{2}J_{\mathrm{H,H}}$ = 14.6 Hz, 1 H, Ar-C^{x}*H*H-Ar), 4.16 (d, $^{2}J_{\mathrm{H,H}}$ = 16.7 Hz, 1 H, Ar-C^{w}*H*H-Ar), 4.33 (d, $^{2}J_{\mathrm{H,H}}$ = 15.4 Hz, 1 H, Ar-C^{v}*H*H-Ar), 4.67 (d, $^{2}J_{\mathrm{H,H}}$ = 12.1 Hz, 1 H, Ar-C^{u}*H*H-Ar), 4.73 (d, $^{2}J_{\mathrm{H,H}}$ = 16.2 Hz, 1 H, Ar-C^{t}*H*H-Ar), 5.04 (d, $^{2}J_{\mathrm{H,H}}$ = 11.9 Hz, 1 H, Ar-C^{s}*H*H-Ar), 5.12 (d, $^{2}J_{\mathrm{H,H}}$ = 14.5 Hz, 1 H, Ar-C^{r}H*H*-Ar), 5.63 (d, $^{2}J_{\mathrm{H,H}}$ = 14.8 Hz, 1 H, Ar-C^{r}*H*H-Ar), 5.82 (d, $^{2}J_{\mathrm{H,H}}$ = 16.2 Hz, 1 H, Ar-C^{q}*H*H-Ar), 6.20 (d, $^{4}J_{\mathrm{H,H}}$ = 2.4 Hz, 1 H, Ar^{b}-*H*), 6.28 (d, $^{4}J_{\mathrm{H,H}}$ = 2.4 Hz, 1 H, Ar^{a}-*H*), 6.62 (s, 1 H, O*H*), 6.71 (d, $^{4}J_{\mathrm{H,H}}$ = 2.4 Hz, 1 H, Ar^{e}-*H*), 6.78 (d, $^{4}J_{\mathrm{H,H}}$ = 2.2 Hz, 1 H, Ar^{d}-*H*), 6.86 (d, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz, 2 H, PMB Ar^{g}-*H*), 6.89 (d, $^{3}J_{\mathrm{H,H}}$ = 8.1 Hz, 2 H, PMB Ar^{h}-*H*), 6.94 (d, $^{3}J_{\mathrm{H,H}}$ = 8.0 Hz, 2 H, PMB Ar^{h}-*H*), 7.00 (d, $^{3}J_{\mathrm{H,H}}$ = 7.6 Hz, 2 H, PMB Ar^{g}-*H*), 7.01 (d, $^{4}J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, Ar^{f}-*H*), 7.03 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 1 H, Ar^{f}-*H*), 7.06 (d, $^{4}J_{\mathrm{H,H}}$ = 2.6 Hz, 1 H, Ar^{e}-*H*), 7.09 (d, $^{4}J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, Ar^{d}-*H*), 7.10 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 1 H, Ar^{c}-*H*), 7.11 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 1 H, Ar^{c}-*H*), 7.13 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 1 H, Ar^{b}-*H*), 7.20 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 1 H, Ar^{a}-*H*), 7.47 (d, $^{3}J_{\mathrm{H,H}}$ = 8.3 Hz, 1 H, phen 8-*H*), 7.72 (d, $^{3}J_{\mathrm{H,H}}$ = 8.6 Hz, 1 H, phen 6-*H*), 7.76 (d, $^{3}J_{\mathrm{H,H}}$ = 8.9 Hz, 1 H, phen 5-*H*), 8.14 (d, $^{3}J_{\mathrm{H,H}}$ = 8.3 Hz, 1 H, phen 3-*H*), 8.14 (s, 1 H, O*H*), 8.22 (d, $^{3}J_{\mathrm{H,H}}$ = 8.4 Hz, 1 H, phen 7-*H*), 8.32 (d, $^{3}J_{\mathrm{H,H}}$ = 8.4 Hz, 1 H, phen 4-*H*) ppm. IR (KBr): $\tilde{\nu}$ = 792, 854, 874, 1120, 1194, 1361, 1458, 1478, 1557, 1595, 2865, 2901, 2960, 3504 cm^{-1}. MALDI-MS: *m*/*z* = 1281 [M – PMB + H]$^{+}$, 1386 [M + H]$^{+}$, 1408 [M + Na], 1424 [M + K]$^{+}$. $C_{96}H_{108}N_2O_6 \cdot H_2O$ (1403.99): calcd. C 82.13, H 7.90, N 2.00; found C 82.48, H 8.15, N 2.01.

5·Copper(I) Trifluoromethanesulfonate: ^{1}H NMR[36] (500 MHz, $C_2D_2Cl_4$/CD_3CN 10:1, 60 °C): δ = 0.40 [s, 18 H, C(C*H*$_3$)$_3$], 0.90 [s, 18 H, C(C*H*$_3$)$_3$], 1.23 [s, 18 H, C(C*H*$_3$)$_3$], 1.93 (s, C*H*$_3$CN), 2.26 (s, 6 H, Ar-C*H*$_3$), 3.40 (d, $^{2}J_{\mathrm{H,H}}$ = 15.7 Hz, 2 H, Ar-C*H*$_2$-x), 3.63 (d, $^{2}J_{\mathrm{H,H}}$ ca. 16 Hz, 2 H, Ar-C*H*$_2$-x), 3.95 (d, $^{2}J_{\mathrm{H,H}}$ = 14.8 Hz, 2 H, Ar-C*H*$_2$-x), 4.07 (d, $^{2}J_{\mathrm{H,H}}$ = 16.6 Hz, 2 H, Ar-C*H*$_2$-x), 4.09 (d, $^{2}J_{\mathrm{H,H}}$ = 15.2 Hz, 2 H, Ar-C*H*$_2$-x), 4.12 (d, $^{2}J_{\mathrm{H,H}}$ = 15.3 Hz, 2 H, Ar-C*H*$_2$-x), 4.66 (d, $^{2}J_{\mathrm{H,H}}$ ≈ 11 Hz, 2 H, Ar-C*H*$_2$-x), 4.67 (d, $^{2}J_{\mathrm{H,H}}$ = 16.2 Hz, 2 H, Ar-C*H*$_2$-x), 4.75 (d, $^{2}J_{\mathrm{H,H}}$ = 11.1 Hz, 2 H, Ar-C*H*$_2$-x), 5.76 (d, $^{2}J_{\mathrm{H,H}}$ = 16.2 Hz, 2 H, Ar-C*H*$_2$-x), 6.59 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 2 H, arom. C*H*), 6.84 (d, $^{4}J_{\mathrm{H,H}}$ = 2.6 Hz, 2 H, arom. C*H*), 7.01 (d, $^{3}J_{\mathrm{H,H}}$ = 8.0 Hz, 4 H, arom. C*H*), 7.03 (d, $^{4}J_{\mathrm{H,H}}$ = 2.7 Hz, 2 H, arom. C*H*), 7.04 (d, $^{4}J_{\mathrm{H,H}}$ = 2.5 Hz, 2 H, arom. C*H*), 7.05 (d, $^{4}J_{\mathrm{H,H}}$ = 2.3 Hz, 2 H, arom. C*H*), 7.06 (d, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz, 4 H, PMB arom. C*H*), 7.14 (d, $^{4}J_{\mathrm{H,H}}$ = 2.4 Hz, 2 H, arom. C*H*), 7.96 (s, 2 H, phen 5-*H*, 6-*H*), 8.07 (d, $^{3}J_{\mathrm{H,H}}$ = 8.4 Hz, 2 H, phen 3-*H*, 8-*H*), 8.55 (d, $^{3}J_{\mathrm{H,H}}$ = 8.4 Hz, 2 H, phen 4-*H*, 7-*H*) ppm.

X-ray Crystal Structure Determination of 5: Empirical formula $C_{96}H_{108}N_2O_6 \cdot H_2O$, *MW* = 1403.99 g/mol, a = 21.370 (2) Å, b = 20.973 (2) Å, c = 22.378 (2) Å, α = 90.00°, β = 116.44°, γ = 90.00°, V = 8980 (1) Å^{3}, T = 170 K, $\rho_{\mathrm{calcd.}}$ = 1.038 g cm^{-3}, μ = 0.06 mm^{-1}, monoclinic, space group $P2_1/n$, Z = 4, STOE Imaging Plate Diffraction System (IPDS-1), Mo-K_{α} (λ = 0.71073 Å), 55915 measured reflections in the range of $3° \leq 2\theta \leq 52°$, 16649 independent reflections used for refinement and 13988 reflections with $I \geq 2\sigma(I)$, R_{int} = 0.0388. Structure solution was done by using SHELXS-97. Structure refinement against F^2 was performed by using SHELXL-97; 976 refined parameters, R_1 for all reflections with $I \geq 2\sigma(I)$ = 0.0579, wR_2 for all reflections = 0.1752, GoF = 1.077, residual electron density 0.39/–0.27 e/Å^{3}. All non hydrogen atoms were refined using anisotropic displacement parameters. The C–H hydrogen atoms were positioned with idealized geometry and refined with isotropic displacement parameters using a riding model. The C atoms of one *tert*-butyl group are disordered in two positions and were refined using split model. The crystal contained two chloroform molecules for which no reasonable structure model was found. Therefore, the data were corrected for disordered solvent by using the "Squeeze" option in Platon.

(1′*S*,4′*R*)-5,11,17,23,29,35-Hexa-*tert*-butyl-39-(camphor-10-sulfonyloxy)-42-hydroxy-37,38,40,41-tetrakis(4-methylbenzyloxy)calix[6]arene (8): Under nitrogen at 90 °C, (+)-camphor-10-sulfonyl chloride (**7**) (1.29 g, 5.14 mmol) and triethylamine (4.0 mL) were added to a solution of the tetra-benzylated calix[6]arene **6** (595 mg, 428 µmol) in dry toluene (30 mL). After 15 h of stirring, the solvents were evaporated to dryness. The residue was dissolved in dichloromethane (100 mL) and the solution was washed with water (3 × 30 mL). The organic layer was dried with magnesium sulfate, evaporated to dryness and filtered through a short silica gel column using dichloromethane/methanol (10:1) as eluent. Final purification was accomplished by chromatography using a chromatotron (silica gel, 4 mm) and dichloromethane/cyclohexane (1:1) as eluents. The first fraction consisted of unreacted calixarene **6** followed by the colorless crystalline product **8** (210 mg, 31%). M.p. 154 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.35–1.48 [m, 61 H, $C(CH_3)_3$, cam CH_3, cam *H*], 1.57–1.68 (m, 1 H, cam *H*), 2.30–2.65 (m, 17 H, PMB CH_3, cam *H*), 3.02–5.17 (m, 22 H, Ar-CH_2-Ar, CH_2SO_3, OCH_2), 5.75–7.82 (m, 29 H, arom. C*H*, O*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, selected signals[37]): δ = 19.70, 19.96 (cam CH_3), 21.33, 25.89, 26.85 (cam CH_2), 31.16, 31.34, 31.68, 31.78 [PMB CH_3, $C(CH_3)_3$], 33.94, 34.06, 34.22, 34.49 [$C(CH_3)_3$], 42.47, 43.51, 47.70 [cam CH, cam $C(CH_3)_2$], 126.54, 127.66, 128.06, 128.57, 128.79, 129.04, 129.13 (arom. *C*H), 133.03, 133.99, 141.78, 148.55, 151.02 (arom. C_q) ppm. MALDI-MS: *m*/*z* = 1626 [M + Na]$^+$, 1642 [M + K]$^+$. IR (KBr): $\tilde{\nu}$ = 802, 842, 1191, 1361, 1480, 1750, 2956, 3410 cm^{-1}. $C_{108}H_{130}O_9S\cdot 1.5C_6H_{12}$ (1730.58): calcd. C 81.18, H 8.59, S 1.86; found C 81.31, H 8.27, S 1.54. $[\alpha]_D^{20}$ = +0.6 (*c* = 10.0 mg/mL, CH_2Cl_2).

(1*R*,2*S*,5*R*)-*cis*-Myrtanyl Triflate (11): At 0 °C, trifluoromethanesulfonic acid anhydride (2.82 g, 10.0 mmol) in dry dichloromethane (10 mL) was slowly added to a solution of (1*R*,2*S*,5*R*)-*cis*-myrtanol (**10**) (1.54 g, 10.0 mmol) and dry pyridine (791 mg, 10.0 mmol) in dry dichloromethane (20 mL). After room temperature was reached, stirring was continued 30 min. The slightly pink solution was filtered through a short silica gel column and the column was washed with dichloromethane. The filtrate was cooled to 0 °C, and in vacuo, the solvent was condensed into flask which was cooled with liquid nitrogen. At 0 °C, **11** is stable only for a few minutes. 2.57 g of **11** remained as a slightly pink residue. The purity was determined by NMR to be 90%, leading to a corresponding yield of 90%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.99 (d, $^3J_{H,H}$ = 9.5 Hz, 1 H, 7-H_a), 1.00 (s, 3 H, 8-*H*), 1.22 (s, 3 H, 9-*H*), 1.40–1.55 (m, 1 H, 3-H_a), 1.90–2.08 (m, 5 H, 1-*H*, 3-H_b, 4-$H_{a,b}$, 5-*H*), 2.38–2.48 (m, 1 H, 2-*H*), 2.52–2.66 (m, 1 H, 7-H_b), 4.44 (dd, $^2J_{H,H}$ = 9.4 Hz, $^3J_{H,H}$ ≈ 7 Hz, 1 H, 10-H_a), 4.50 (dd, $^2J_{H,H}$ = 9.4 Hz, $^3J_{H,H}$ ≈ 8 Hz, 1 H, 10-H_b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 17.6 (*C*-3), 23.1 (*C*-9), 25.4 (*C*-4), 27.6 (*C*-8), 32.5 (*C*-7), 38.4 (*C*-6), 40.4 (*C*-5), 40.9 (*C*-1), 42.1 (*C*-2), 81.0 (*C*-10), 118.7 (q, $^1J_{C,F}$ = 318 Hz, CF_3) ppm. MS (GC-MS, EI, 70 eV): *m*/*z* (%) = 67 (30), 81 (100), 93 (38), 95 (38), 107 (10), 121 (23), 123 (12), 285 (2) [M – H]$^+$. IR (film): $\tilde{\nu}$ = 612, 930, 1146, 1207, 1246, 1412, 1470, 2921 cm^{-1}. $[\alpha]_D^{20}$ = –10.6 (*c* = 20 mg/mL, CH_2Cl_2). Remark: $[\alpha]_D^{20}$ was determined by measuring 90% pure **11**. It cannot be ruled out that the impurities have an influence on the specific rotation value. Due to the tendency of **11** to decompose quickly, neither a high resolution mass spectrum nor an elemental analysis could be obtained.

(1′*R*,2′*S*,5′*R*)-4-*tert*-Butylphenyl *cis*-Myrtanyl Ether (13): 4-*tert*-Butylphenol (**12**) (380 mg, 2.53 mmol) and potassium trimethylsilanolate (648 mg, 5.06 mmol) in dry tetrahydrofuran (20 mL) were stirred for 30 min. (1*R*,2*S*,5*R*)-*cis*-Myrtanyl triflate (**11**) (ca. 5 mmol) in dry tetrahydrofuran (30 mL) was added quickly at 0 °C, and the solution was warmed to room temp. slowly. After 3 h, the mixture was neutralized with 0.1 M hydrochloric acid and the solvents were evaporated. The oily residue was dissolved in dichloromethane (50 mL) and washed with water (3 × 15 mL). The organic layer was dried with magnesium sulfate, the solvent was evaporated and the residue was purified by chromatography on a chromatotron (silica gel, 4 mm) using cyclohexane/dichloromethane (10:1) as eluent yielding a colorless oil (260 mg, 36%). ^{1}H NMR[38] (300 MHz, $CDCl_3$, 25 °C): δ = 0.97 (d, $^3J_{H,H}$ = 9.5 Hz, 1 H, 7-H_a), 1.01 (s, 3 H, 8-*H*), 1.20 (s, 3 H, 9-*H*), 1.30 [s, 9 H, $C(CH_3)_3$], 1.48–1.63 (m, 1 H, 3-H_a), 1.86–2.15 (m, 5 H, 1-*H*, 3-H_b, 4-$H_{a,b}$, 5-*H*), 2.32–2.44 (m, 1 H, 2-*H*), 2.46–2.61 (m, 1 H, 7-H_b), 3.84 (dd, $^2J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 7.4 Hz, 1 H, 10-H_a), 3.91 (dd, $^2J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, 10-H_b), 6.83 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, arom. C*H*), 7.29 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, arom. C*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 19.0 (*C*-3), 23.4 (*C*-8), 26.0 (*C*-4), 28.0 (*C*-9), 31.6 [$C(CH_3)_3$], 33.2 (*C*-7), 34.1 [$C(CH_3)_3$], 38.6 (*C*-6), 40.9 (*C*-5), 41.4 (*C*-1), 43.2 (*C*-2), 72.6 (*C*-10), 113.9 (arom. *C*H), 126.2 (arom. *C*H), 143.0 [*C*-$C(CH_3)_3$], 156.9 (arom. *C*-O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 55 (10), 67 (17), 69 (19), 81 (44), 95 (22), 107 (16), 135 (100), 150 (17), 229 (15) [M – *t*Bu]$^+$, 271 (14) [M – CH_3]$^+$, 286 (14) [M]$^+$. IR (film): $\tilde{\nu}$ = 827, 1044, 1183, 1363, 1381, 1592, 1612, 2962 cm^{-1}. $C_{20}H_{30}O$ (286.47): calcd. C 83.86, H 10.56. $C_{20}H_{30}O\cdot 0.2CH_3COOC_2H_5\cdot 0.9C_6H_{12}$ (295.46):[39] calcd. C 82.85, H 11.25; found C 83.07, H 11.16. $[\alpha]_D^{20}$ = –9.2 (*c* = 10 mg/mL, CH_2Cl_2).

(1′*R*,2′*S*,5′*R*)-5,11,17,23,29,35-Hexa-*tert*-butyl-38,39,40,41,42-pentahydroxy-37-(*cis*-myrtanyloxy)calix[6]arene (14): Under nitrogen, calix[6]arene **1** (2.92 g, 3.00 mmol) and potassium trimethylsilanolate (960 mg, 7.50 mmol) were stirred in a mixture of dry tetrahydrofuran (50 mL) and dry dimethylformamide (5 mL). After 30 min at 0 °C, (1*R*,2*S*,5*R*)-*cis*-myrtanyl triflate (**11**) (approx. 9 mmol) in dry tetrahydrofuran (30 mL) was rapidly added and the solution was stirred for another 15 h while heated to room temperature. After neutralization with 0.5 M hydrochloric acid, the solvents were evaporated to dryness and the crude residue was dissolved in dichloromethane (100 mL). The organic layer was washed with satd. sodium hydrogen carbonate solution (50 mL), water (50 mL) and brine (50 mL) followed by drying with magnesium sulfate. The residue was partly solid, partly oily. Treatment with methanol led to a suspension which was filtered. The filter cake was treated with *n*-pentane and the filtrate was evaporated to dryness. The residue was purified by chromatography on a chromatotron (aluminium oxide, 2 mm) with cyclohexane as eluent followed by recrystallization from dichloromethane/methanol leading to the colorless product **14** (85 mg, 3%). M.p. 195 °C. ^{1}H NMR (200 MHz, $C_2D_2Cl_4$, 75 °C): δ = 0.95 (d, $^3J_{H,H}$ = 9.7 Hz, 1 H, myr *H*), 1.22 (s, 3 H, myr CH_3), 1.24 (s, 3 H, myr CH_3), 1.31 [s, 9 H, $C(CH_3)_3$], 1.33–1.37 [s, 45 H, $C(CH_3)_3$], 1.57–3.20 (m, 8 H, myr *H*), 3.37–3.71 (m, 5 H, Ar-CH_2-Ar, O-CH_2), 3.90–4.54 (m, 9 H, Ar-CH_2-Ar), 7.08 (br. s, 1 H, Ar-*H*), 7.12 (br. s, 1 H, Ar-*H*), 7.15–7.26 (m, 10 H, Ar-*H*), 8.88 (br. s, 1 H, O*H*), 9.12 (br. s, 1 H, O*H*), 9.95–10.34 (m, 3 H, O*H*) ppm. ^{13}C NMR (50 MHz, $C_2D_2Cl_4$, 75 °C, selected signals[40]): δ = 19.37 (myr *C*-3), 23.61 (myr *C*-8), 26.29 (myr *C*-7), 26.35 (myr *C*-4), 28.33 (myr *C*-9), 31.39, 31.58, 31.71, [$C(CH_3)_3$], 32.91, 33.03, 33.48, 33.96, 34.02, 34.07, 34.25 [Ar-CH_2-Ar, $C(CH_3)_3$], 38.85 (myr *C*-6), 42.03 (myr *C*-5), 42.47 (myr *C*-1), 43.96 (myr *C*-2), 81.20 (myr *C*-10), 126.04, 126.11, 126.33, 126.61, 126.72, 126.93, 127.12, 127.23, 127.36, 127.73, 128.05, 128.13, 132.55, 132.61 (arom. *C*H, arom. *C*-CH_2), 143.12, 143.21, 143.94, 143.99, 144.59, 144.69, 146.94, 147.60, 147.81, 148.81, 149.47, 149.62, 149.67, 149.72, 149.78, 149.96, 149.99, 150.12, 150.20 [*C*-C(CH_3)$_3$, *C*-OH, *C*-O-CH_2] ppm. IR (KBr): ṽ = 870, 1203, 1291, 1362, 1484, 2960, 3315 cm^{-1}. MALDI-MS: *m/z* = 1132 [M + Na]$^+$, 1148 [M + K]$^+$. $C_{76}H_{100}O_6$ (1109.67): calcd. C 82.27, H 9.08. $C_{76}H_{100}O_6\cdot 0.2C_6H_{12}$ (1126.50): calcd. C 82.46, H 9.40; found C 82.69, H 9.53. $[\alpha]_D^{20}$ = –0.2 (*c* = 13 mg/mL, CH_2Cl_2).

(1′*R*,2′*R*,5′*R*)-4-*tert*-Butylphenyl *trans*-Myrtanyl Ether (16): 4-*tert*-Butylphenol (**12**) (70 mg, 0.47 mmol) and potassium *tert*-butoxide (57 mg, 0.47 mmol) in dry tetrahydrofuran (20 mL) were stirred for 10 min and then (1*R*,2*R*,5*R*)-*trans*-myrtanyl tosylate (**15**) (216 mg, 700 µmol) was added. After 17 h of refluxing, the mixture was neutralized with 0.1 M hydrochloric acid and the solvents were evaporated. The oily residue was dissolved in dichloromethane (50 mL) and washed with water (3 × 15 mL). The organic layer was dried with magnesium sulfate, the solvent was evaporated and the residue was purified by chromatography on a chromatotron (silica gel, 1 mm) using cyclohexane/ethyl acetate (15:1) as eluents yielding a colorless oil (112 mg, 84 %). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.86 (s, 3 H, 9-*H*), 1.23 (s, 3 H, 8-*H*), 1.29 [s, 9 H, C(C*H*$_3$)$_3$], 1.36 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, 7-*H*$_a$), 1.32–1.40 (m, 1 H, 3-*H*$_a$), 1.68–1.92 (m, 4 H, 3-*H*$_b$, 4-*H*$_{a,b}$, 5-*H*), 1.98–2.02 (m, 1 H, 1-*H*), 2.03–2.10 (m, 1 H, 7-*H*$_b$), 2.43–2.51 (m, 1 H, 2-*H*), 3.72 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H, 10-*H*$_{a,b}$), 6.82 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, arom. C*H*), 7.27 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 18.4 (*C*-3), 20.2 (*C*-9), 23.6 (*C*-7), 24.2 (*C*-4), 26.7 (*C*-8), 31.6 [C(*C*H$_3$)$_3$], 34.0 [*C*(CH$_3$)$_3$], 34.9 (*C*-2), 39.2 (*C*-6), 41.0 (*C*-5), 42.6 (*C*-1), 71.8 (*C*-10), 113.9, 126.1 (arom. *C*H), 143.0 [*C*-C(CH$_3$)$_3$], 157.1 (arom. *C*-O) ppm. MS (EI, 70 eV): *m/z* (%) = 67 (21), 69 (44), 81 (48), 95 (28), 135 (100), 150 (29), 229 (10) [M – *t*Bu]$^+$, 271 (6) [M – CH_3]$^+$, 286 (12) [M]$^+$. IR (film): ṽ = 827, 1031, 1183, 1363, 1381, 1462, 1592, 1612, 2962 cm^{-1}. $C_{20}H_{30}O$ (286.47): calcd. C 83.86, H 10.56. $C_{20}H_{30}O\cdot 0.5H_2O$ (295.46): calcd. C 81.30, H 10.58; found C 81.23, H 10.62. $[\alpha]_D^{20}$ = –11.8 (*c* = 6 mg/mL, CH_2Cl_2).

(1′*R*,2′*R*,5′*R*)-5,11,17,23,29,35-Hexa-*tert*-butyl-38,39,40,41,42-pentahydroxy-37-(*trans*-myrtanyloxy)calix[6]arene (18): Under nitrogen, *p*-*tert*-butylcalix[6]arene **1** (1.26 g, 1.30 mmol) and potassium *tert*-butoxide (792 mg, 6.49 mmol) were stirred in a mixture of dry tetrahydrofuran (50 mL) and dry dimethylformamide (5 mL). After 30 min, (1*R*,2*R*,5*R*)-*trans*-myrtanyl tosylate **15** (1.00 g, 3.25 mmol) in dry tetrahydrofuran (30 mL) was slowly added and the solution was stirred for 15 h. After neutralization with 0.5 M hydrochloric acid, the solvents were evaporated to dryness and the crude residue was dissolved in dichloromethane (50 mL). The organic layer was washed with satd. sodium hydrogen carbonate solution (30 mL), water (30 mL) and brine (30 mL) followed by drying with magnesium sulfate. After evaporation to dryness, the residue was purified by chromatography on silica gel (0.04–0.063 mm) with cyclohexane/dichloromethane (1:1) as eluents followed by recrystallization from dichloromethane/methanol. A colorless crystalline product was obtained (269 mg, 19 %). M.p. 208–215 °C. ^{1}H NMR[41] (500 MHz, $CDCl_3$, 25 °C): δ = 1.03 (s, 3 H, myr 9-*H*), 1.15 [s, 9 H, C(C*H*$_3$)$_3$], 1.21 [s, 9 H, C(C*H*$_3$)$_3$], 1.27 [s, 18 H, C(C*H*$_3$)$_3$], 1.282 [s, 9 H, C(C*H*$_3$)$_3$], 1.286 [s, 9 H, C(C*H*$_3$)$_3$], 1.33 (s, 3 H, myr 8-*H*), 1.58 (d, $^3J_{H,H}$ = 9.9 Hz, 1 H, myr 7-*H*$_a$), 1.76–1.88 (m, 1 H, myr 3-*H*$_a$), 1.90–1.96 (m, 1 H, myr 4-*H*$_a$), 1.97–2.10 (m, 3 H, myr 3-*H*$_b$, 4-*H*$_b$, 5-*H*), 2.18–2.22 (m, 1 H, myr 1-*H*), 2.10–2.28 (m, 1 H, myr 7-*H*$_b$), 2.76–2.85 (m, 1 H, myr 2-*H*), 3.40 (d, $^2J_{H,H}$ = 13.9 Hz, 1 H, Ar-C^a*H*$_2$-Ar), 3.41 (d, $^2J_{H,H}$ = 13.7 Hz, 1 H, Ar-C^b*H*$_2$-Ar), 3.48 (d, $^2J_{H,H}$ = 13.5 Hz, 1 H, Ar-C^c*H*$_2$-Ar), 3.49 (d, $^2J_{H,H}$ = 13.4 Hz, 1 H, Ar-C^d*H*$_2$-Ar), 3.54 (d, $^2J_{H,H}$ = 14.3 Hz, 1 H, Ar-C^e*H*$_2$-Ar), 3.56 (d, $^2J_{H,H}$ = 14.0 Hz, 1 H, Ar-C^f*H*$_2$-Ar), 3.91 (dd, $^2J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 6.5 Hz, 1 H, myr 10-*H*$_a$), 3.94 (dd, $^2J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 6.7 Hz, 1 H, myr 10-*H*$_b$), 4.02 (d, $^2J_{H,H}$ = 13.7 Hz, 1 H, Ar-C^b*H*$_2$-Ar), 4.04 (d, $^2J_{H,H}$ = 13.9 Hz, 1 H, Ar-C^a*H*$_2$-Ar), 4.24 (d, $^2J_{H,H}$ = 14.0 Hz, 1 H, Ar-C^f*H*$_2$-Ar), 4.26 (d, $^2J_{H,H}$ = 14.3 Hz, 1 H, Ar-C^e*H*$_2$-Ar), 4.32 (d, $^2J_{H,H}$ = 13.5 Hz, 1 H, Ar-C^c*H*$_2$-Ar), 4.41 (d, $^2J_{H,H}$ = 13.4 Hz, 1 H, Ar-C^d*H*$_2$-Ar), 7.00 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, arom. C*H*), 7.02 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, arom. C*H*), 7.09 (s, 2 H, arom. C*H*), 7.11 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, arom. C*H*), 7.12 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, arom. C*H*), 7.13–7.16 (m, 6 H, arom. C*H*), 8.96 (s, 1 H, O*H*), 9.19 (s, 1 H, O*H*), 9.95 (br. s, 1 H, O*H*), 10.04 (br. s, 1 H, O*H*), 10.18 (br. s, 1 H, O*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 18.9 (myr *C*-3), 20.2 (myr *C*-9), 24.1 (myr *C*-7), 24.3 (myr *C*-4), 26.8 (myr *C*-8), 31.3, 31.4, 31.6, 31.6, 31.7, 31.7 [C(*C*H$_3$)$_3$], 32.5 (Ar-*C*^{d}H$_2$-Ar), 32.6 (Ar-*C*^{c}H$_2$-Ar), 32.7 (Ar-*C*^{e}H$_2$-Ar), 32.7 (Ar-*C*^{f}H$_2$-Ar), 33.3 (Ar-*C*^{b}H$_2$-Ar), 33.4 (Ar-*C*^{a}H$_2$-Ar), 33.9, 33.9, 34.0, 34.0, 34.1, 34.3 [*C*(CH$_3$)$_3$], 36.1 (myr *C*-2), 39.6 (myr *C*-6), 41.1 (myr *C*-5), 43.0 (myr *C*-1), 81.0 (myr *C*-10), 125.5, 125.6, 125.7, 125.8, 125.9, 125.95, 125.95, 126.0, 126.05, 126.1, 126.2, 126.3 (arom. *C*H), 126.7, 126.7, 126.8, 126.8, 126.9, 127.1, 127.5, 127.6, 127.7, 127.9, 132.3, 132.5 (arom. *C*-CH$_2$), 142.9, 143.0, 143.6, 143.7, 144.4 [*C*-C(CH$_3$)$_3$], 146.6 (*C*-OH), 147.7 [*C*-C(CH$_3$)$_3$], 148.2, 148.3, 149.5, 149.6, 149.6 (*C*-OH, *C*-O-CH$_2$) ppm. IR (KBr): ṽ = 871, 1203, 1292, 1362, 1484, 2959, 3318 cm^{-1}. MALDI-MS: *m/z* = 1132 [M + Na]$^+$, 1148 [M + K]$^+$. $C_{76}H_{100}O_6$ (1109.67): calcd. C 82.27, H 9.08. $C_{76}H_{100}O_6\cdot 0.5C_6H_{12}$ (1151.75): calcd. C 82.39, H 9.28; found C 82.25, H 9.43. $[\alpha]_D^{20}$ = –3.2 (*c* = 14.5 mg/mL, CH_2Cl_2).

(1′*R*,2′*R*,5′*R*)-5,11,17,23,29,35-Hexa-*tert*-butyl-38,39,41,42-tetrahydroxy-37,40-bis(*trans*-myrtanyloxy)calix[6]arene (19): Under nitrogen, *p*-*tert*-butylcalix[6]arene **1** (4.87 g, 5.00 mmol) and potassium trimethylsilanolate (3.78 g, 30.0 mmol) were stirred in a mixture of dry tetrahydrofuran (80 mL) and dry dimethylformamide (8 mL). After 15 min (1*R*,2*R*,5*R*)-*trans*-myrtanyl bromide (**17**) (4.34 g, 20.0 mmol) was rapidly added and the solution was headed to reflux. The progress of the reaction was monitored by HPLC (RP-18, dichloromethane/methanol, 1:4). After 3 d, additional potassium trimethylsilanolate (3.00 g, 23.8 mmol) was added. After 5 d, no unreacted calixarene **1** was left (HPLC analysis). The reaction mixture was neutralized with 1 M hydrochloric acid and the solvents were evaporated to dryness. The crude residue was treated with methanol and the insoluble part was separated by filtration. The filter cake was washed with *n*-pentane (150 mL) and the filtrate concentrated to dryness. Flash-chromatography of the crude product (silica gel, 0.04–0.063 mm, cyclohexane/dichloromethane 3:1) led to the colorless crystalline product **19** (498 mg, 8 %). M.p. 250 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.60 (d, $^3J_{H,H}$ = 10.1 Hz, 2 H, myr 7-*H*$_a$), 0.70–0.80 (m, 2 H, myr 4-*H*$_a$), 0.75 (s, 6 H, myr 9-*H*), 0.83–0.95 (m, 2 H, myr 3-*H*$_a$), 1.02 (s, 6 H, myr 8-*H*), 1.10–1.20 (m, 2 H, myr 4-*H*$_b$), 1.21 [s, 18 H, 5-C(C*H*$_3$)$_3$, 23-C(C*H*$_3$)$_3$], 1.22 [s, 18 H, 17-C(C*H*$_3$)$_3$, 35-C(C*H*$_3$)$_3$], 1.26 [s, 18 H, 11-C(C*H*$_3$)$_3$, 29-C(C*H*$_3$)$_3$], 1.45–1.52 (m, 2 H, myr 5-*H*), 1.55–1.68 (m, 4 H, myr 3-*H*$_b$, 7-*H*$_b$), 1.80–1.85 (m, 2 H, 1-*H*), 2.52–2.61 (m, 2 H, myr 2-*H*), 3.59 (d, $^2J_{H,H}$ = 15.4 Hz, 2 H, 14-*H*, 32-*H*), 3.62–3.75 (m, 4 H, myr 10-*H*$_{a,b}$), 3.86 (d, $^2J_{H,H}$ = 4.4 Hz, 4 H, 2-*H*, 20-*H*), 3.90 (d, $^2J_{H,H}$ = 5.8 Hz, 4 H, 8-*H*, 26-*H*), 4.06 (d, $^2J_{H,H}$ = 15.4 Hz, 2 H, 14-*H*, 32-*H*), 6.90 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, 4-*H*, 22-*H*), 7.02 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, 12-*H*, 30-*H*), 7.05 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, 16-*H*, 34-*H*), 7.08 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, 6-*H*, 24-*H*), 7.09 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, 18-*H*, 36-*H*), 7.15 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, 10-*H*, 28-*H*), 9.09 (s, 2 H, 38-O*H*, 41-O*H*), 9.41 (s, 2 H, 39-O*H*, 42-O*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 17.52 (myr *C*-3), 20.30 (myr *C*-9), 22.81 (myr *C*-7), 23.10 (myr *C*-4), 26.55 (myr *C*-8), 31.44 [17-C(*C*H$_3$)$_3$, 35-C(*C*H$_3$)$_3$], 31.53 [5-

C(*C*H$_3$)$_3$, 23-C(*C*H$_3$)$_3$], 31.63 [11-C(*C*H$_3$)$_3$, 29-C(*C*H$_3$)$_3$], 32.46 (*C*-8, *C*-26), 32.75 (*C*-2, *C*-20), 33.29 (*C*-14, *C*-32), 33.95 [5-*C*(CH$_3$)$_3$, 11-*C*(CH$_3$)$_3$, 23-*C*(CH$_3$)$_3$, 29-*C*(CH$_3$)$_3$], 34.30 [17-*C*(CH$_3$)$_3$, 35-*C*(CH$_3$)$_3$], 34.95 (myr *C*-2), 39.09 (*C*-6), 40.96 (myr *C*-5), 41.66 (myr *C*-1), 78.92 (myr *C*-10), 124.97 (*C*-4, *C*-22), 125.60 (*C*-6, *C*-24), 125.74 (*C*-16, *C*-34), 125.90 (*C*-10, *C*-28), 126.25 (*C*-13, *C*-31), 126.34 (*C*-12, *C*-30), 126.59 (*C*-18, *C*-36), 126.74 (*C*-7, *C*-25), 127.05 (*C*-3, *C*-21), 127.29 (*C*-9, *C*-27), 131.93 (*C*-1, *C*-19), 132.64 (*C*-15, *C*-33), 142.18 (*C*-5, *C*-23), 142.62 (*C*-11, *C*-29), 147.77 (*C*-17, *C*-35), 149.29 (*C*-39, *C*-42), 149.52 (*C*-38, *C*-41), 150.56 (*C*-37, *C*-40) ppm. IR (KBr): ṽ = 871, 1202, 1362, 1483, 1601, 2953, 3321 cm^{-1}. MALDI-MS: *m*/*z* = 1268 [M + Na]$^+$, 1284 [M + K]$^+$. $C_{86}H_{116}O_6$ (1245.91): calcd. C 82.91, H 9.39. $C_{86}H_{116}O_6\cdot2.5H_2O$ (1290.95): calcd. C 80.02, H 9.45; found C 80.19, H 9.61. $[\alpha]_D^{20}$ = +38.4 (*c* = 22 mg/mL, CH_2Cl_2).

X-ray Crystal Structure Determination of 19: Suitable crystals of **19** for X-ray analysis have been obtained by recrystallization from a 1:1 mixture of dichloromethane and acetonitrile. A small hole in the cap of the vial allowed a slow evaporation of the solvent(s). Empirical formula $C_{86}H_{116}O_6\cdot2CH_3CN\cdot2CH_2Cl_2$, *MW* = 1497.75 g/mol, *a* = 12.9649 (5) Å, *b* = 16.7786 (6) Å, *c* = 21.2513 (9) Å, α = 90.00°, β = 103.544 (3)°, γ = 90.00°, *V* = 4494.3 (3) Å^3, *T* = 173 (2) K, $\rho_{calcd.}$ = 1.107 g cm^{-3}, μ = 0.182 mm^{-1}, monoclinic, space group *P*2$_1$/*n*, *Z* = 2, STOE Imaging Plate Diffraction System (IPDS-II), Mo-K_α (λ = 0.71073 Å), 47490 measured reflections in the range of 3.58° ≤ 2θ ≤ 25.62°, 8402 independent reflections used for refinement. R_{int} = 0.0553. Structure solution was done by using SHELXS-97. Structure refinement against F^2 was performed by using SHELXL-97; 528 refined parameters, R_1 for all reflections = 0.1820, wR_2 for all reflections = 0.5500, GoF = 2.780, residual electron density 1.592/–1.884 e/Å^3.

(1′*S*,4′*R*)-5,11,17,23,29,35-Hexa-*tert*-butyl-37,39-bis(camphor-10-sulfonyloxy)-40,42-dihydroxy-38,41-[1,10-phenanthroline-2,9-diylbis(methyleneoxy)]calix[6]arene (20): Under nitrogen, (+)-camphor-10-sulfonyl chloride (**7**) (1.62 g, 6.47 mmol) and the 1,10-phenanthroline-bridged calix[6]arene **3** (2.54 g, 2.16 mmol) were stirred in a mixture of dry toluene (50 mL) and dry triethylamine (5 mL). After 18 h at 90 °C, the solvents were evaporated to dryness. The residue was dissolved in dichloromethane (100 mL) and washed with water (2 × 30 mL) and brine (30 mL). The organic layer was dried with magnesium sulfate, evaporated to dryness. The crude residue was dissolved in little dichloromethane and purified by flash chromatography on silica gel (0.04–0.063 mm) with cyclohexane/ethyl acetate (1:1) as eluents. The product-containing fraction was further purified. Recrystallization from dichloromethane/methanol led to a colorless product **20** (2.62 g, 76%). Single crystals were obtained by crystallization from dichloromethane/acetonitrile. M.p. 260 °C (dec.). ^{1}H NMR[42] (500 MHz, CDCl$_3$, 25 °C): δ = 0.76 [s, 18 H, C^a(C*H*$_3$)$_3$, C^b(C*H*$_3$)$_3$], 0.80 (s, 3 H, cam 8-*H*), 0.84 (s, 3 H, cam 8-*H*), 1.00 (s, 3 H, cam 9-*H*), 1.04 (s, 3 H, cam 9-*H*), 1.09 [s, 9 H, C^c(C*H*$_3$)$_3$], 1.15–1.23 (m, 1 H, cam 6-*H*$_a$), 1.25 [s, 9 H, C^d(C*H*$_3$)$_3$], 1.28 [s, 9 H, C^e(C*H*$_3$)$_3$], 1.30–1.38 (m, 1 H, cam 6-*H*$_b$), 1.45 [s, 9 H, C^f(C*H*$_3$)$_3$], 1.47–1.56 (m, 1 H, cam 5-*H*$_a$), 1.58–1.67 (m, 1 H, cam 5-*H*$_b$), 1.74–1.83 (m, 1 H, cam 6-*H*$_b$), 1.84 (d, $^2J_{H,H}$ = 18.4 Hz, 1 H, cam 3-*H*$_a$), 1.89–2.01 (m, 2 H, cam 4-*H*, 6-*H*$_b$), 1.91 (d, $^2J_{H,H}$ = 18.4 Hz, 1 H, cam 3-*H*$_a$), 2.03–2.07 (m, 1 H, cam 4-*H*), 2.30–2.48 (m, 4 H, cam 3-*H*$_b$, 5-*H*$_b$), 2.87 (d, $^2J_{H,H}$ = 14.8 Hz, 1 H, C^a*H*$_2$SO$_3$), 3.15 (d, $^2J_{H,H}$ = 14.9 Hz, 1 H, C^b*H*$_2$SO$_3$), 3.24 (d, $^2J_{H,H}$ = 15.9 Hz, 1 H, Ar-C^c*H*$_2$-Ar), 3.40 (d, $^2J_{H,H}$ = 16.2 Hz, 1 H, Ar-C^d*H*$_2$-Ar), 3.56–3.72 (m, 6 H, C^a*H*$_2$SO$_3$, C^b*H*$_2$SO$_3$, Ar-C^c*H*$_2$-Ar, Ar-C^e*H*$_2$-Ar, Ar-C^f*H*$_2$-Ar, Ar-C^g*H*$_2$-Ar), 3.74–3.90 (m, 4 H, Ar-C^d*H*$_2$-Ar, Ar-C^g*H*$_2$-Ar, Ar-C^h*H*$_2$-Ar, Ar-C^h*H*$_2$-Ar), 3.98 (d, $^2J_{H,H}$ = 15.4 Hz, 1 H, OC^i*H*$_2$-phen), 4.17 (d, $^2J_{H,H}$ = 15.4 Hz, 1 H, OC^i*H*$_2$-phen), 4.68 (d, $^2J_{H,H}$ = 15.2 Hz, 1 H, Ar-C^e*H*$_2$-Ar), 4.75 (d, $^2J_{H,H}$ = 15.0 Hz, 1 H, Ar-C^f*H*$_2$-Ar), 5.16 (br. s, 1 H, OC^k*H*$_2$-phen), 5.36 (br. s, 1 H, OC^k*H*$_2$-phen), 6.24 (br. s, 1 H, Ar^u-*H*), 6.30 (br. s, 1 H, Ar^v-*H*), 6.72 (br. s, 1 H, O*H*), 6.85 (br. s, 1 H, Ar^v-*H*), 6.86 (br. s, 1 H, Ar^u-*H*), 6.92 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^w-*H*), 6.93 (br. s, 1 H, Ar^x-*H*), 6.98 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^y-*H*), 7.01 (br. s, 1 H, Ar^x-*H*), 7.13 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^w-*H*), 7.18 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^y-*H*), 7.41 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^z-*H*), 7.43 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^z-*H*), 7.45 (br. s, 1 H, O*H*), 7.49 (br. d, $^3J_{H,H}$ = 8.1 Hz, 1 H, phen 8-*H*), 7.71 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, phen 6-*H*), 7.86 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, phen 5-*H*), 8.17 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, phen 7-*H*), 8.45 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, phen 3-*H*), 8.57 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, phen 4-*H*) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 19.71 (2 × cam *C*-8), 19.92, 20.00 (cam *C*-9), 25.02, 25.12 (cam *C*-5), 26.72, 26.83 (cam *C*-6), 30.65 (Ar-*C*^{e}H$_2$-Ar), 30.78 (Ar-*C*^{f}H$_2$-Ar), 30.97 [C^a(*C*H$_3$)$_3$, C^b(*C*H$_3$)$_3$], 31.39 [C^c(*C*H$_3$)$_3$], 31.64 [C^d(*C*H$_3$)$_3$], 31.69 [C^e(*C*H$_3$)$_3$], 31.70 [C^f(*C*H$_3$)$_3$], 31.85 (Ar-*C*^{c}H$_2$-Ar, Ar-*C*^{d}H$_2$-Ar), 31.92 (Ar-*C*^{g}H$_2$-Ar), 32.33 (Ar-*C*^{h}H$_2$-Ar), 33.95, 33.99, 34.05, 34.07, 34.14 [*C*^{a,b,c,d,e}(CH$_3$)$_3$], 34.37 [*C*^{f}(CH$_3$)$_3$], 42.38, 42.39 (cam *C*-3), 42.90, 42.91 (cam *C*-4), 47.70 (2 × cam *C*-7), 48.34 (*C*^{a}H$_2$SO$_3$), 48.56 (*C*^{b}H$_2$SO$_3$), 58.10, 58.14 (cam *C*-1), 73.04 (O*C*^{i}H$_2$–phen), 76.92 (O*C*^{k}H$_2$-phen), 120.50 (phen *C*-3), 121.14 (phen *C*-8), 124.04, 124.16, 124.27, 124.41, 124.70, 125.26 (arom. *C*H), 125.28 (phen *C*-6), 126.24, 126.31 (arom. *C*H), 126.60 (phen *C*-5), 127.10, 127.32 (arom. *C*H), 127.44, 127.56, 127.81, 127.85 (phen *C*-4a, *C*-6a, *C*-10a, *C*-10b), 128.09 ppm. 128.19 (arom. *C*H), 133.14, 133.47, 133.52 (2×), 133.77, 134.08, 134.61, 134.68 (arom. *C*$_q$), 136.64 (phen *C*-7), 136.73 (phen *C*-4), 142.10, 142.38 (arom. *C*$_q$), 142.43, 142.62 [*C*–C(CH$_3$)$_3$], 144.76, 145.33 (arom. *C*$_q$), 146.37, 146.85, 148.62, 148.69 [*C*–C(CH$_3$)$_3$], 50.84, 150.91, 152.10, 152.25 (arom. *C*O), 156.50 (phen *C*-9), 160.17 (phen *C*-2), 213.92, 213.97 (C=O) ppm. IR (KBr): ṽ = 853, 1193, 1362, 1482, 1747, 2958, 3388 cm^{-1}. MALDI-MS: *m*/*z* = 1606 [M + H]$^+$, 1628 [M + Na]$^+$, 1644 [M + K]$^+$. $C_{100}H_{120}N_2O_{12}S_2$ (1606.24): calcd. C 74.78, H 7.53, N 1.74, S 3.99. $C_{100}H_{120}N_2O_{12}S_2\cdot0.5CH_3OH$ (1622.26): calcd. C 74.41, H 7.58, N 1.73, S 3.95; found C 74.40, H 7.76, N 1.74, S 3.76. $[\alpha]_D^{20}$ = +7.5 (*c* = 14 mg/mL, CH_2Cl_2).

X-ray Crystal Structure Determination of 20: Suitable crystals of **20** for X-ray analysis have been obtained by recrystallization from a 1:1 mixture of dichloromethane and acetonitrile. A small hole in the cap of the vial allowed slow evaporation of the solvent(s). Empirical formula $C_{100}H_{120}N_2O_{12}S_2\cdot2.5CH_2Cl_2$, *MW* = 1818.42 g/mol, *a* = 15.5926 (7) Å, *b* = 17.7189 (8) Å, *c* = 22.1072 (11) Å, α = 69.976 (4)°, β = 81.544 (4)°, γ = 77.676 (4)°, *V* = 5588.2 (5) Å^3, *T* = 173 (2) K, $\rho_{calcd.}$ = 1.081 g cm^{-3}, μ = 0.220 mm^{-1}, triclinic, space group P1, *Z* = 2, STOE Imaging Plate Diffraction System (IPDS-II), Mo-K_α (λ = 0.71073 Å), 102508 measured reflections in the range of 3.71° ≤ 2θ ≤ 27.59°, 48827 independent reflections used for refinement. R_{int} = 0.1223. Structure solution was done by using SHELXS-97. Structure refinement against F^2 was performed by using SHELXL-97; 2224 refined parameters, 71 restraints, R_1 for all reflections = 0.1944, wR_2 for all reflections = 0.4177, GoF = 1.489, Flack × parameter = 0.03(11), residual electron density 3.526/–0.767 e/Å^3.

(1′*S*,4′*R*)-5,11,17,23,29,35-Hexa-*tert*-butyl-38-(camphor-10-sulfonyloxy)-39,41,42-trihydroxy-37,40-[1,10-phenanthroline-2,9-diylbis(methyleneoxy)]calix[6]arene (21): Under nitrogen, (+)-camphor-10-sulfonyl chloride (**7**) (379 mg, 1.51 mmol) and 1,10-phenanthroline-bridged calix[6]arene **3** (1.37 g, 1.16 mmol) were stirred in a mixture of dry toluene (20 mL) and dry triethylamine (3 mL). After 18 h at 95 °C, the solvents were evaporated to dryness. The residue was dissolved in dichloromethane (100 mL) and washed with water (2 × 30 mL) and brine (30 mL). The organic layer was dried with magnesium sulfate, evaporated to dryness. The crude residue was dissolved in little dichloromethane and purified by flash chromatography on silica gel (0.04–0.063 mm) with dichloromethane/ethyl acetate (50:1) as eluents. Only the first fraction was isolated being a mixture of both possible diastereoisomers **21a** and **21b** (790 mg, 49 %). Threefold chromatography on a chromatotron (silica gel, 2 mm) with cyclohexane/ethyl acetate (4:1 + 1 % triethylamine) as eluents enriched one diastereoisomer to approx. 90 %. The product was colorless and crystalline (43 mg, 3 %).[43] M.p. 230 °C (dec.). ^{1}H NMR[44] (500 MHz, CDCl$_3$, 25 °C): δ = 0.69 [s, 9 H, $C^a(CH_3)_3$], 0.78 (s, 3 H, cam 8-*H*), 0.97 (s, 3 H, cam 9-*H*), 1.09 [s, 9 H, $C^b(CH_3)_3$], 1.18 [s, 9 H, $C^c(CH_3)_3$], 1.25 [s, 9 H, $C^d(CH_3)_3$], 1.26 [s, 9 H, $C^e(CH_3)_3$], 1.35 [s, 9 H, $C^f(CH_3)_3$], 1.45–1.55 (m, 1 H, cam 6-H_a), 1.59–1.74 (m, 1 H, cam 5-H_a), 1.78–1.88 (m, 1 H, cam 5-H_b), 1.85 (d, $^2J_{H,H}$ = 18.4 Hz, 1 H, cam 3-H_a), 1.94–1.98 (m, 1 H, cam 4-*H*), 2.27–2.35 (m, 1 H, cam 3-H_b), 2.38–2.50 (m, 1 H, cam 6-H_b), 3.28 (d, $^2J_{H,H}$ = 13.7 Hz, 1 H, Ar-C^aH_2-Ar), 3.32 (d, $^2J_{H,H}$ = 15.0 Hz, 1 H, $C^bH_2SO_3$), 3.35 (d, $^2J_{H,H}$ = 16.5 Hz, 1 H, Ar-C^cH_2-Ar), 3.45 (d, $^2J_{H,H}$ = 15.3 Hz, 1 H, Ar-C^dH_2-Ar), 3.67 (d, $^2J_{H,H}$ = 14.1 Hz, 1 H, Ar-C^eH_2-Ar), 3.79 (d, $^2J_{H,H}$ = 16.5 Hz, 1 H, Ar-C^fH_2-Ar), 3.85 (d, $^2J_{H,H}$ = 16.0 Hz, 1 H, Ar-C^gH_2-Ar), 3.87 (d, $^2J_{H,H}$ = 13.7 Hz, 1 H, Ar-C^aH_2 Ar), 3.92 (d, $^2J_{H,H}$ = 15.0 Hz, 1 H, $C^bH_2SO_3$), 4.29 (d, $^2J_{H,H}$ = 14.1 Hz, 1 H, Ar-C^eH_2 Ar), 4.30 (d, $^2J_{H,H}$ = 16.5 Hz, 1 H, Ar-C^fH_2-Ar), 4.31 (d, $^2J_{H,H}$ = 15.3 Hz, 1 H, Ar-C^dH_2-Ar), 4.75 (d, $^2J_{H,H}$ = 16.0 Hz, 1 H, Ar-C^gH_2-Ar), 4.85 (d, $^2J_{H,H}$ = 16.5 Hz, 1 H, Ar-C^cH_2-Ar), 4.87 (d, $^2J_{H,H}$ = 16.6 Hz, 1 H, OC^hH_2-phen), 5.48 (d, $^2J_{H,H}$ = 15.0 Hz, 1 H, OC^iH_2-phen), 5.71 (d, $^2J_{H,H}$ = 15.0 Hz, 1 H, OC^iH_2-phen), 5.81 (d, $^2J_{H,H}$ = 16.6 Hz, 1 H, OC^hH_2-phen), 6.11 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^u-*H*), 6.52 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^v-*H*), 6.57 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^u-*H*), 6.81 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^w-*H*), 6.96 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^x-*H*), 7.04 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^y-*H*), 7.08 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^y-*H*), 7.12 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^z-*H*), 7.13 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^w-*H*), 7.20 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^x-*H*), 7.23 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^v-*H*), 7.32 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, Ar^z-*H*), 7.47 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, phen 8-*H*), 7.68 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, phen 6-*H*), 7.74 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, phen 5-*H*), 7.77 (br. s, 1 H, O*H*), 8.18 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, phen 7-*H*), 8.19 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, phen 3-*H*), 8.28 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, phen 4-*H*) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 19.67 (cam *C*-8), 19.91 (cam *C*-9), 25.09 (cam *C*-6), 26.82 (cam *C*-5), 30.67 [$C^a(CH_3)_3$], 31.25 [$C^b(CH_3)_3$], 31.40 (Ar-C^gH_2-Ar), 31.55 [$C^c(CH_3)_3$, $C^d(CH_3)_3$], 31.68 [$C^e(CH_3)_3$], 31.72 [$C^f(CH_3)_3$], 32.06 (Ar-C^cH_2-Ar), 32.19 (Ar-C^eH_2-Ar, Ar-C^fH_2-Ar), 32.56 (Ar-C^aH_2-Ar), 32.78 (Ar-C^dH_2-Ar), 33.76, 33.83, 34.07, 34.15, 34.23, 34.26 [$C^{a,b,c,d,e,f}(CH_3)_3$], 42.39 (cam *C*-3), 42.90 (cam *C*-4), 47.74 (cam *C*-7), 48.87 ($C^bH_2SO_3$), 58.20 (cam *C*-1), 72.82 (OC^hH_2-phen), 73.92 (OC^iH_2-phen), 119.35 (phen *C*-8), 119.76 (phen *C*-3), 123.19 (arom. C_q), 123.88, 124.28, 124.64, 124.87, 124.92 (arom. *C*H), 125.10 (arom. C_q), 125.28 (phen *C*-6, arom. *C*H), 125.99, 126.16, 126.45 (arom. *C*H), 126.48 (phen *C*-5), 126.72, 126.92 (arom. C_q), 127.35, 127.47 (arom. *C*H), 127.59, 127.63, 128.01, 128.25 (phen *C*-4a, *C*-6a, *C*-10a, *C*-10b), 128.33, (arom. *C*H), 131.21, 131.69, 132.69, 133.84, 134.79, 135.74 (arom. C_q), 136.75 (phen *C*-7), 136.87 (phen *C*-4), 141.12, 142.15, 142.89 [*C*-C(CH$_3$)$_3$], 143.01 (arom. *C*O), 144.90, 145.35 (arom. C_q), 146.09, 147.75 [*C*-C(CH$_3$)$_3$], 148.95 (arom. *C*O), 149.57 [*C*-C(CH$_3$)$_3$], 149.62 (*C*-O-CH$_2$), 150.04, 150.88 (arom. *C*O), 151.73 (*C*-O-CH$_2$), 155.44 (phen *C*-9), 160.85 (phen *C*-2), 213.88 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 852, 1193, 1362, 1454, 1482, 1749, 2956, 3382 cm^{-1}. MALDI-MS: *m/z* = 1392 [M + H]$^+$, 1414 [M + Na]$^+$, 1430 [M + K]$^+$. $C_{90}H_{106}N_2O_9S$ (1391.95): calcd. C 77.66, H 7.68, N 2.01 S 2.30. $C_{90}H_{106}N_2O_9S \cdot 0.5 C_6H_{12} \cdot CH_3COOC_2H_5$ (1522.14): calcd. C 76.54, H 7.95, N 1.84, S 2.11; found C 76.48, H 7.94, N 1.94, S 2.03. $[\alpha]_D^{20}$ = +5.9 (*c* = 16 mg/mL, CH$_2$Cl$_2$).

2,9-Bis(4-*tert*-butylphenoxymethyl)-1,10-phenanthroline (22): 4-*tert*-Butylphenol (**12**) (1.21 g, 8.07 mmol) and potassium *tert*-butoxide (2.44 g, 20.0 mmol) were stirred in dry tetrahydrofuran (30 mL). After 20 min, 2,9-bis(bromomethyl)-1,10-phenanthroline (**2**) (1.31 g, 3.60 mmol) was added and the solution was stirred for another 15 h. After neutralization with 0.1 M hydrochloric acid, the organic layer was evaporated to dryness. The residue was dissolved in dichloromethane (150 mL) and the solution was washed with satd. sodium hydrogen carbonate solution (50 mL) and brine (50 mL). After drying with magnesium sulfate, the solvents were evaporated to dryness and the crude residue was purified by chromatography (silica gel, 0.04–0.063 mm) with cyclohexane/ethyl acetate (2:1) as eluents. The second fraction was purified by chromatography using a chromatotron (silica gel, 4 mm) with cyclohexane/ethyl acetate (4:1) as eluents leading to the colorless crystalline product **22** (1.60 g, 88 %). M.p. 151 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 1.31 [s, 18 H, C(CH_3)$_3$], 5.65 (s, 4 H, CH_2), 7.02 (d, $^3J_{H,H}$ = 8.9 Hz, 4 H, 2-*H′*, 6-*H′*), 7.34 (d, $^3J_{H,H}$ = 8.9 Hz, 4 H, 3-*H′*, 5-*H′*), 7.78 (s, 2 H, 5-*H*, 6 *H*), 7.97 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 3-*H*, 8-*H*), 8.29 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 4-*H*, 7-*H*) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 31.5 [C(*C*H$_3$)$_3$], 34.1 [*C*(CH$_3$)$_3$], 71.3 (*C*H$_2$), 114.2 (*C′*-2, *C′*-6), 120.8 (*C*-3, *C*-8), 126.3 (*C*-5, *C*-6), 126.4 (*C′*-3, *C′*-5), 128.2 (*C*-4a, *C*-6a), 137.1 (*C*-4, *C*-7), 143.8 (*C′*-4), 145.1 (*C*-10a, *C*-10b), 156.1 (*C′*-1), 158.7 (*C*-2, *C*-9) ppm. MS (EI, 70 eV): *m/z* (%) = 135 (29), 207 (66), 237 (36), 299 (97), 355 (92), 487 (55), 505 (100) [M$^+$]. IR (KBr): $\tilde{\nu}$ = 824, 860, 1043, 1183, 1256, 1365, 1512, 1608, 2951 cm^{-1}. $C_{34}H_{36}N_2O_2$ (504.69): calcd. C 80.92, H 7.19, N 5.55. $C_{34}H_{36}N_2O_2 \cdot 0.1C_6H_{12} \cdot 0.2CH_3COOC_2H_5$ (530.72): calcd. C 80.11, H 7.37, N 5.28; found C 80.17, H 7.47, N 5.50.

Cyclopropanation: Under argon, ca. 3.6 to 9.1 mg (+/– 0.01 mg) of copper(I) triflate–hemibenzene complex (Aldrich) were placed in a vial. 440 equiv. [based on copper(I)] of alkene **23** or **24**, and 1.2 equiv. of the ligands, dissolved in 1,2-dichloroethane (*c* = 0.01 mol/L), were added. After addition of 50 equiv. of the ethyl diazoacetate (**25**), the mixture was stirred at room temp. for 24 h. At the beginning of the reaction, a quick development of gas was noticed frequently. After filtration of the mixture through silica gel using diethyl ether as eluent, most of the solvent mixture was evaporated in vacuo until ca. 5 mL remained. Then, 1,2-dichloroethane was added to give ca. 10 mL of solution. After addition of ca. 25 mg of *n*-hexadecane (+/– 0.01 mg) as GC standard, the products were analyzed by GC. For characterization of the products **26** and **27** see ref.[45]. Cyclopropanation of styrene (**23**) with **3** and **5** and without ligand: Optima 1/25 m, 80 °C for 5 min, 10 °C/min until 140 °C, 1 min, 2 °C/min until 160 °C, 1 min, 20 °C/min until 240 °C, 2 min. Cyclopropanation of indene (**24**) with **3** and **5** and without ligand: Optima 1/25 m, 80 °C for 5 min, 2 °C/min until 140 °C, 1 min, 1 °C/min until 160 °C, 3 min, 20 °C/min until 240 °C, 2 min. Cyclopropanation of styrene (**23**) and indene (**24**) with **20**, **21x**[30] and **22** as ligand: HP-5/30 m, 80 °C for 5 min, 2 °C/min until 140 °C, 1 min, 1 °C/min until 160 °C, 3 min, 20 °C/min until 240 °C, 2 min.

To determine the enantiomeric excess, the complete reaction mixture of the cyclopropanation was mixed with methanol (10 mL) and 30 % sodium hydroxide (3 mL). After heating to reflux for 4 h, the mixture was diluted with water (30 mL) and extracted with diethyl ether (3 × 10 mL). The aqueous layer was acidified with concd. hydrochloric acid and extracted with diethyl ether (3 × 20 mL). The combined ether layer was washed with brine (20 mL) and dried with magnesium sulfate. After evaporation of the solvent, 120 mg of a yellow viscous residue remained which was dissolved in toluene (8 mL) and pyridine (64 mg, 0.81 mmol). After addition of thionyl chloride (270 mg, 2.27 mmol) in toluene (4 mL) and (–)-menthol (700 mg, 4.49 mmol) in toluene (4 mL), the mixture was stirred for 1 h at 100 °C. Then, water (20 mL) was added, the organic layer was washed with sodium hydrogen carbonate solution (ca. 15 mL) and the solvents were evaporated to dryness. As preparation for GC analysis, a solution of the residue in dichloromethane was filtered through a Pasteur pipette filled with 3 cm of silica gel (0.04–0.063 mm). The *trans* esters could be separated by GC (HP-5/30 m, start at 100 °C, 1 °C/min until 200 °C, 20 °C/min until 240 °C, 20 min). The assignment (1*S*,2*S*): t_r = 63.8 min, (1*R*,2*R*): t_r = 65.5 min was based on results obtained on a SE-52 column.[31]

CCDC-603012 (for **5**), -603011 (for **19**), and -603010 (for **20**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[33] * = The assignments may be interchanged.

[34] * = The assignments are uncertain, # = assignments may be interchanged. Signals for C atoms 1, 3, 13, 19, 21 und 31 could not be found, they are probably superimposed by other signals.

[35] Protons carrying the same letter are bound to the same aromatic ring or are part of the same methylene group. *tert*-Butyl groups with the same index give rise to one signal at higher temperature (60 °C).

[36] The assignment does not differentiate between the methylene groups between the aryl rings and the methylene groups next to an ether oxygen atom (x = O, Ar).

[37] Not all signals could be identified and assigned.

[38] The aromatic signals are interpreted as doublets although being part of a AA′MM′ system.

[39] After evaporating excess solvent for days at <0.1 mbar, still solvent can be found by NMR and elemental analysis.

[40] Not all signals could be identified and assigned. The signals of the myrtanyl subunit were assigned in analogy to **13**.

[41] Corresponding signals of the calixarene CH_2 groups carry the letters *a–f*. These letters do not correspond to the labeling of the phenol rings A–F.

[42] Hydrogen atoms within the same aryl ring or the same CH_2 group are labeled with the same letter. Two signals for aromatic *C*–O atoms could not be found in the ^{13}C NMR spectrum.

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