The Preparation and Absolute Configurations of Enantiomerically Pure C4 Symmetric Tetraalkoxyresorcin[4]arenes Obtained from Camphorsulfonate Derivatives

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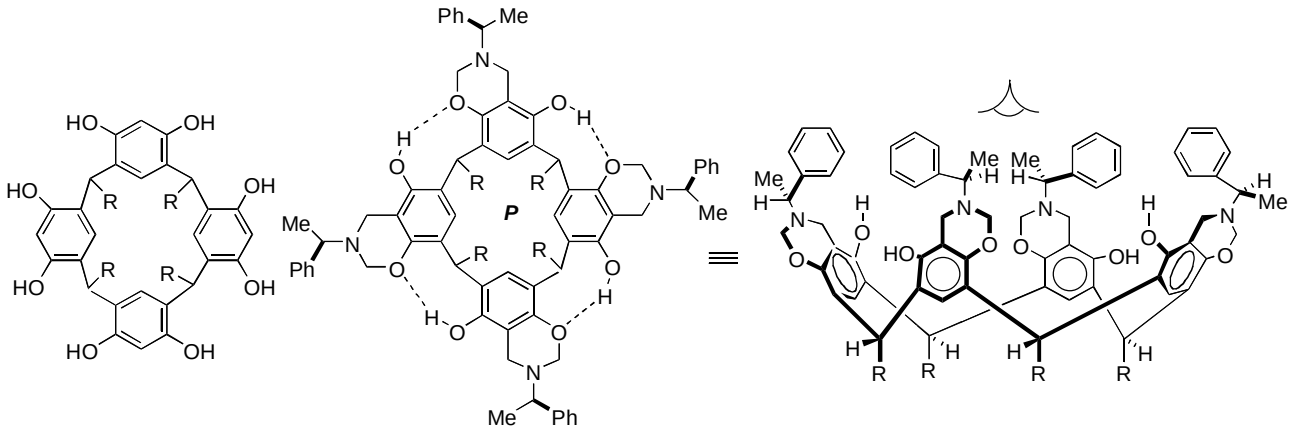
ABSTRACT

The preparation of a series of diastereoisomeric tetracamphorsulfonates derived from racemic tetramethoxyresorcin[4]arenes was achieved by reactions using an excess of (*S*)-(+)-10-camphorsulfonyl chloride in pyridine followed by isolation using flash chromatography. The same tetracamphorsulfonates were obtained in reactions of (*S*)-(+)-10-camphorsulfonyl chloride with the anions obtained by tetradeprotonation of a number of tetramethoxyresorcin[4]arenes using *n*-butyllithium in tetrahydrofuran. Mono-, di-, and tricamphorsulfonates were also prepared following selective deprotonation. In the case of reactions using tetraisopropyloxy- and tetracyclopentyloxyresorcin[4]arenes, only the mono- and dicamphorsulfonates were formed. X-ray crystallographic analysis established the absolute configurations in the case of three diastereoisomerically pure tetracamphorsulfonates, including a diastereoisomer prepared from 2,8,14,20-tetra-2-methylpropyl-6,12,18,24-tetramethoxyresorcin[4]arene. An additional pair of diastereoisomers was also prepared from (*R*)-(–)-10-camphorsulfonyl chloride and 2,8,14,20-tetra-2-methylpropyl-6,12,18,24-tetramethoxyresorcin[4]arene. Hydrolytic removal of the camphorsulfonyl residue(s) from the various diastereoisomers gave enantiomers of known absolute configurations. In some cases the chiral non-racemic tetraalkoxyresorcin[4]arenes were converted into known tetrabenzoxazine derivatives using *N*,*N*-bis(methoxymethyl)-(*S*)-(–)-*N*-α-methylbenzylamine in thermal or microwave enhanced reactions.

Introduction

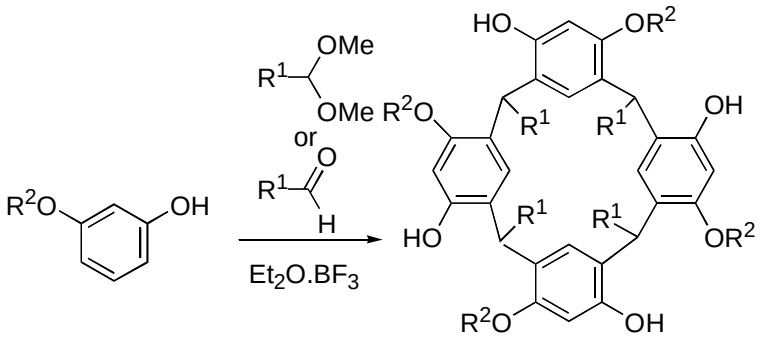
The chemistry of calixarenes is widely studied and has provided a diverse range of molecular assemblies that have been used for a variety of purposes; the topic continues to generate considerable interest.[1] The acid catalysed interaction of aldehydes with resorcinol provides a high yielding route to a range of cyclic tetramers that has made the study of resorcin[4]arenes, for example **1**, particularly attractive.[2] The dissymmetry generated by unsymmetrical substitution of calixarenes is recognized as being related to the non-planar structures of the parent compounds,[3a] although a number of chiral calixarene conformers are racemized thermally by processes involving 'through-the-annulus rotation'.[3b] The first example of the optical resolution of a chiral calixarene used chiral liquid chromatography.[3c] Although considerable effort has been devoted to the synthesis of inherently chiral calixarenes, in the vast majority of published examples the products have been obtained as racemates, which have defied resolution except by using chiral HPLC techniques.[4] This has inevitably meant that only very small amounts of optically pure material has been available for use in other studies. A solution to this problem was provided by studies carried out by us[5a,b] and others[5c] using chiral non-racemic α-methylbenzylamines, and resulted in the highly diastereoselective formation of tetrabenzoxazines derived from a number of resorcin[4]arenes, for example the compounds **2**. The methylation of the residual phenolic hydroxy groups present in the single diastereoisomers was achieved in high yields on multigram scales in order to preclude diastereoisomerization as well as the loss of axial chirality after ring opening of the 1,3-oxazine ring and removal of the chiral auxiliary.[6a] The representation of the compounds **2**, in **Figure 1**, is drawn using the convention that the polar groups are viewed from above and the depending groups (R) are in pseudo-axial orientations: the stereogenic centres at the inter-ring positions are therefore of *S*-chirality with the axis of chirality being *P* (= axial-*R*).[6b] Additional examples, including where in excess of 10 g of chiral non-racemic resorcin[4]arenes have been prepared, have also been reported.[6b]



1, R = *n*-C_5H_{11}, *n*-$C_{11}H_{23}$, Ph.CH_2.CH_2 (*P*,*R*,*S*)-**2**, R = *n*-C_5H_{11}, *n*-$C_{11}H_{23}$, Ph.CH_2.CH_2

Figure 1. Representation of Resorcin[4]arenes, including Axial Stereochemistry

The boron trifluoride catalysed reaction of, for example, octanal with 3-methoxyphenol, that resulted in the formation of a racemic tetramethoxyresorcin[4]arene, provided a route to a range of tetramethoxyresorcin[4]arene derivatives.[7] We extended the method to the preparation of additional tetraalkoxyresorcin[4]arene derivatives:[8] the racemic tetraalkoxyresorcin[4]arenes **4a**–**4f** were prepared, in each case in good to excellent yields, as shown in **Scheme 1**, by the interaction of boron trifluoride (200 mol%) with, for example 1,1-dimethoxyalkanes or aldehydes, and for example the 3-alkoxyphenol derivatives **3a**-**3c**.



Racemic

3a, R^2 = Me
3b, R^2 = *i*-Pr
3c, R^2 = cyclopentyl

4a, R^1 = *n*-C_3H_7, R^2 = Me
4b, R^1 = *n*-C_5H_{11},R^2 = Me
4c, R^1 = *n*-C_7H_{15}, R^2 = Me
4d, R^1 = *n*-$C_{11}H_{23}$, R^2 = Me
4e, R^1 = *n*-C_5H_{11}, R^2 = *i*-Pr
4f, R^1 = *n*-C_5H_{11}, R^2 = cyclopentyl

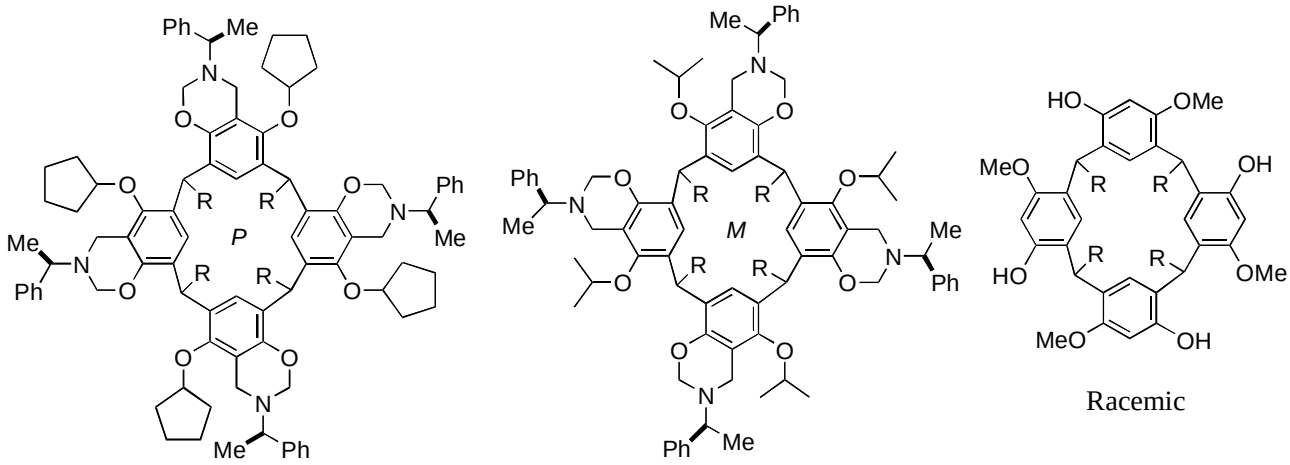
Scheme 1. Formation of Racemic Tetraalkoxyresorcinarenes

The preparation of the racemic tetramethoxyresorcin[4]arene related to **4a-f**, derived by the interaction of 3-methylbutanal with 3-methoxyphenol, conversion into a pair of

monocamphorsulfonates, and their separation and isolation on a small scale by chiral HPLC in 13% and 16% yields has been reported previously.[4k,l] However, the absolute configurations of the enantiomers that were obtained after hydrolysis were not established.

Results and Discussion

In our related work we initially studied reactions of the resorcinarenes **4a** to **f**. The conversion into diastereoisomeric camphorsulfonates could be achieved, in principle, either by a reaction of the racemic tetramethoxyresorcin[4]arenes with (*S*)-(+)-10-camphorsulfonyl chloride in pyridine or by using our low temperature deprotonation protocol,[6] in which hydroxyresorcin[4]arenes are reacted with *n*-butyllithium at –78 °C in THF followed by reaction with the electrophile, in this case (*S*)-(+)-10-camphorsulfonyl chloride. It is clear that the establishment of the absolute configurations of the (*S*)-(+)-10-camphorsulfonates followed by hydrolysis would allow the determination of the absolute configurations of the enantiomers of the tetraalkoxyresorcin[4]arenes. The absolute configurations of the enantiomeric tetraalkoxyresorcin[4]arenes could also be established by reference to the known absolute configurations of chiral non-racemic tetrabenzoxazines such as the compounds **5** and **6**, shown in **Figure 2**, whose structures were known from X-ray crystallographic data.[6b] When the study, conducted at Loughborough and Curtin, including the determination of the absolute configurations of a number of camphorsulfonates, derived from racemic tetraalkoxyresorcin[4]arenes, and their hydrolysis products, was almost ready for publication, the absolute configurations of the tetramethoxyresorcinarenes **7**, derived from 3-methylbutanal and 3-methoxyphenol were published.[9] The Loughborough and Curtin groups were surprised that the results of their study were not in accord with the published results and the Loughborough group therefore repeated their experiments. The Loughborough group also prepared and used the racemic mixture of resorcin[4]arenes **7** in order to prepare tetracamphorsulfonates also using (*S*)-(+)-10-camphorsulfonyl chloride. A very recent publication[10] also used the absolute configurations that were reported earlier.[9] Our repeated reactions, including a complete repetition of the experiments using an enantiomerically pure sample of the compound **7,** that involved the formation of a crystalline amide, was carried out by the Bielefeld group,[11] confirmed the initial results of the Loughborough and Curtin group. We now report a full account of all of our studies.

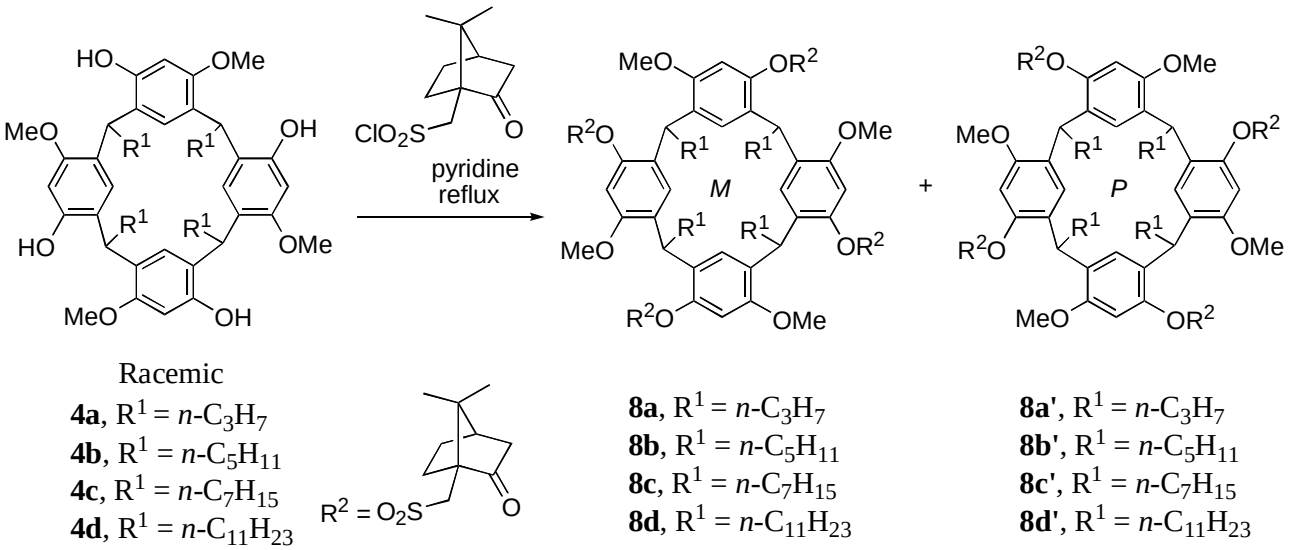


(*P*,*R*,*S*)-**5**, R = *n*-C_5H_{11} (*M*,*S*,*R*)-**6**, R = *n*-C_5H_{11} **7**, R = 2-methylpropyl

Figure 2. Absolute Configurations of Chiral Non-racemic Tetrabenzoxazines and a Racemic Resorcinarene

We were able to prepare tetracamphorsulfonate derivatives **8a-d** and **8a'-d'** shown in **Scheme 2**, in high yields, from the tetraalkoxyresorcin[4]arenes **4a-d** by heating them under reflux in pyridine with an excess of freshly prepared (*S*)-(+)-10-camphorsulfonyl chloride. Lower yields were obtained when using commercial (*S*)-(+)-10-camphorsulfonyl chloride. Separation of the 1:1 mixtures of diastereoisomers was achieved by chromatography on silica gel. However, we were only able to obtain a good recovery of the faster running diastereoisomer in some cases, possibly due to instability towards the isolation process in one isomer in each case. For example, using the resorcinarene **4a**, although NMR spectra of the crude reaction mixtures indicated, as expected, that the diastereoisomers of the 2,8,14,20-tetra-*n*-propyl-4,10,16,22-tetracamphorsulfonyloxy-6,12,18,24-tetramethoxyresorcin[4]arenes were formed as a 1:1 mixture, they were isolated in 46% and 23% yields. In one reaction using the resorcinarene **4b,** we isolated a pair of diastereoisomeric tricamphorsulfonates in addition to the expected tetracamphorsulfonates. Thus, when we heated a solution of the resorcinarene **4b** under reflux for 15 h in pyridine together with 12 equivalents of (*S*)-(+)-10-camphorsulfonyl chloride we obtained a mixture of two tricamphorsulfonates **9b** and **9b'** in 22% yield together with the two tetracamphorsulfonates **8b** and **8b'** in 28% yield. The tricamphorsulfonates were formed in a 1:4 ratio while the tetracamphorsulfonates were formed in a 4:1 ratio as shown in **Scheme 3**. This suggests that there is increasing difficulty in the sequential addition of camphorsulfonyl residues to the hydroxy groups that results from steric problems that particularly affect the slower eluting diastereoisomer of the tricamphorsulfonate. That effect provides an explanation of the apparent diastereoselectivity in the latter reaction. Crystals of the first eluting diastereoisomers **8a** and **8b** were obtained that were suitable for X-ray crystallographic

analysis, and the crystal structures are shown in **Figures 3** and **4**. Because of potential confusion that has arisen in defining the absolute configuration of some C_4 symmetric resorcin[4]arenes we introduced the convention of using the prefix (*P*)- or (*M*)- when defining the priority of substituents around an axis of chirality,[6b] by reference to the Cahn, Ingold, and Prelog convention,[12a] and subsequent discussions concerning axial chirality,[12b,c,d] together with Prelog and his co-workers' discussion of a new kind of stereoisomerism, cycloenantiomerism and cyclodiastereomerism, that can be considered when the two directions in a cyclic structure can be distinguished.[13] The crystal structures established that the two diastereoisomers were (*M,S,R*)-2,8,14,20-tetra-*n*-propyl-4,10,16,22-tetracamphorsulfonyloxy-6,12,18,24-tetramethoxyresorcin[4]arene **8a** and (*M,S,R*)-2,8,14,20-tetra-*n*-pentyl-4,10,16,22-tetracamphorsulfonyloxy-6,12,18,24-tetramethoxyresorcin[4]arene **8b**.



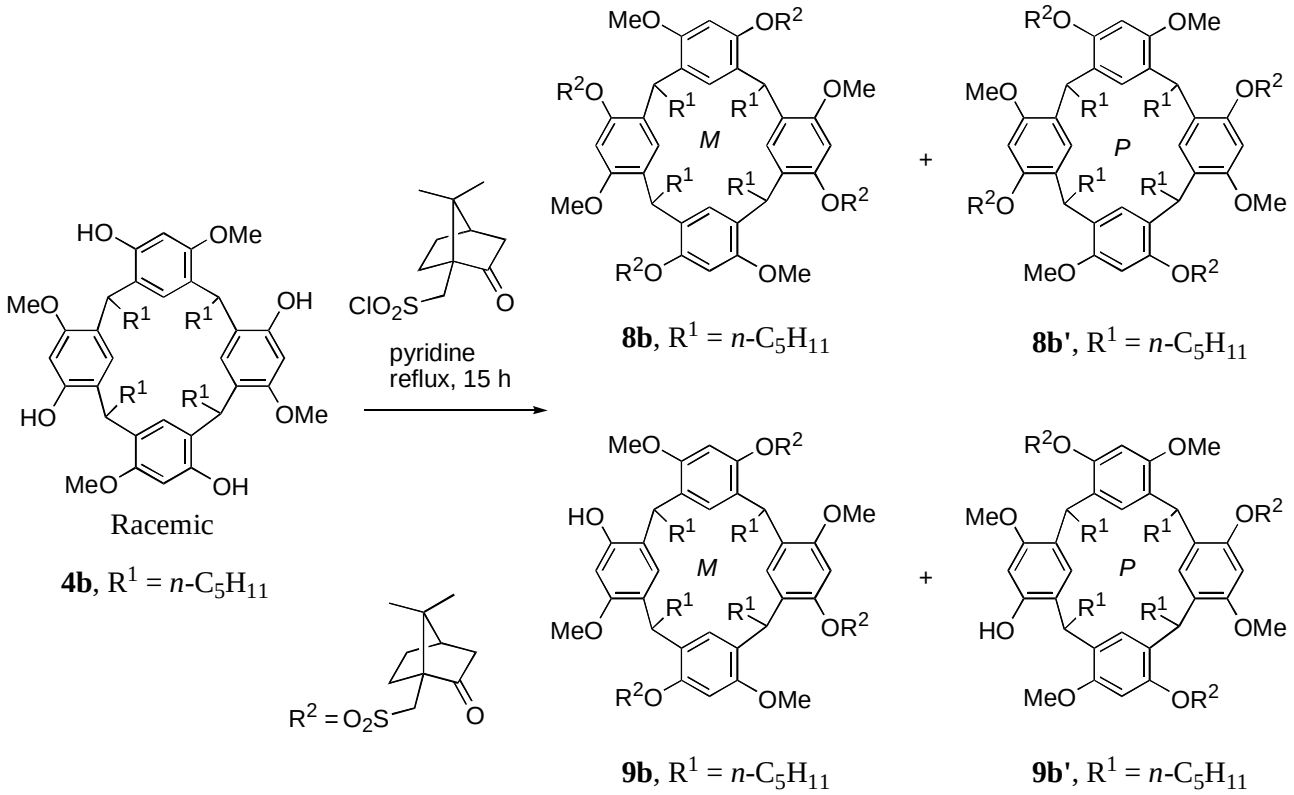
Racemic

4a, $R^1 = n\text{-}C_3H_7$
4b, $R^1 = n\text{-}C_5H_{11}$
4c, $R^1 = n\text{-}C_7H_{15}$
4d, $R^1 = n\text{-}C_{11}H_{23}$

8a, $R^1 = n\text{-}C_3H_7$
8b, $R^1 = n\text{-}C_5H_{11}$
8c, $R^1 = n\text{-}C_7H_{15}$
8d, $R^1 = n\text{-}C_{11}H_{23}$

8a', $R^1 = n\text{-}C_3H_7$
8b', $R^1 = n\text{-}C_5H_{11}$
8c', $R^1 = n\text{-}C_7H_{15}$
8d', $R^1 = n\text{-}C_{11}H_{23}$

Scheme 2. The Formation of Tetracamphorsulfonates from Racemic Resorcinarenes



Scheme 3. The Formation of Tri- and Tetracamphorsulfonates from the Racemic Resorcinarene **4b**

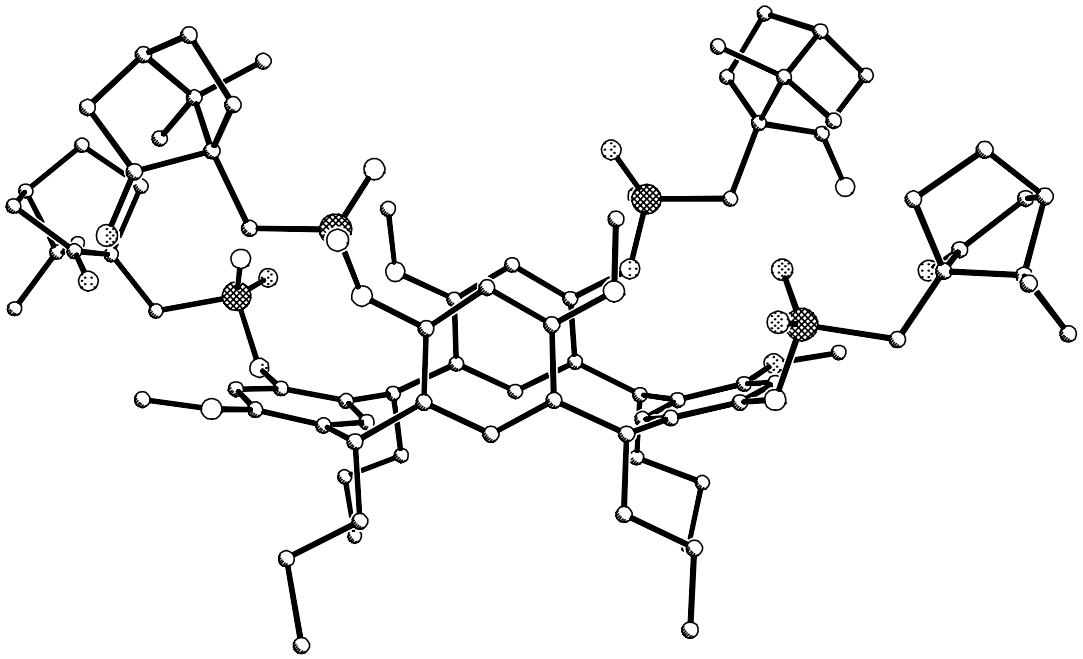


Figure 3. X-ray Structure of the Tetracamphorsulfonate (*M*,*S*,*R*)-**8a**; the hydrogen atoms are omitted for clarity.

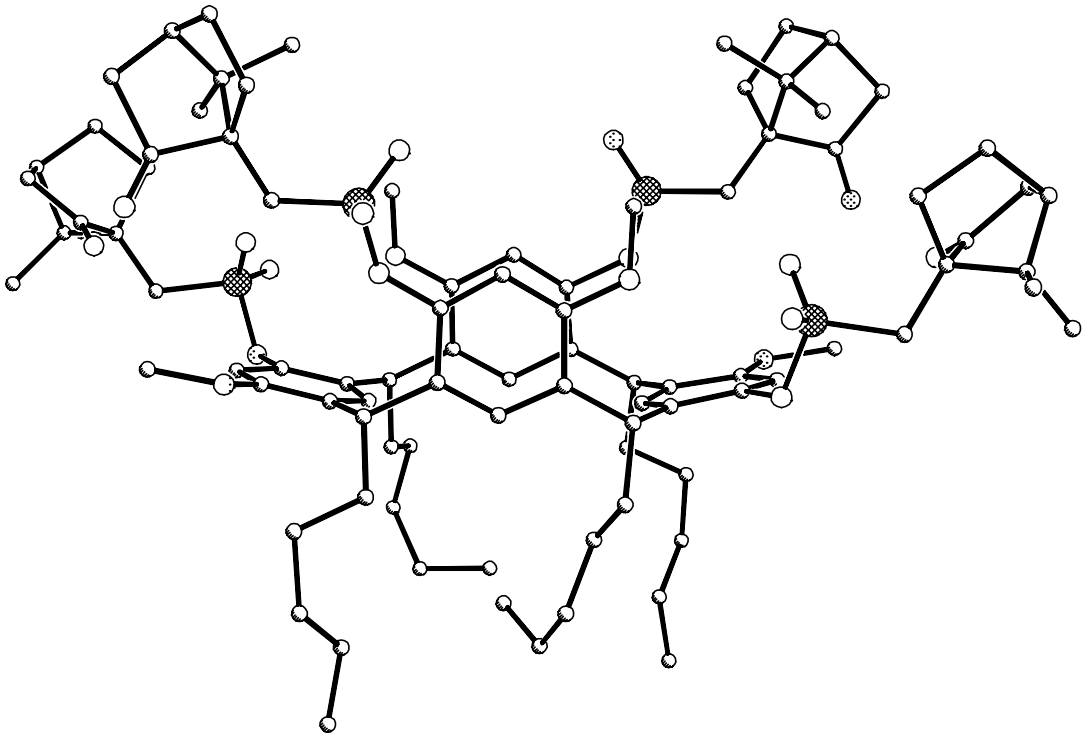
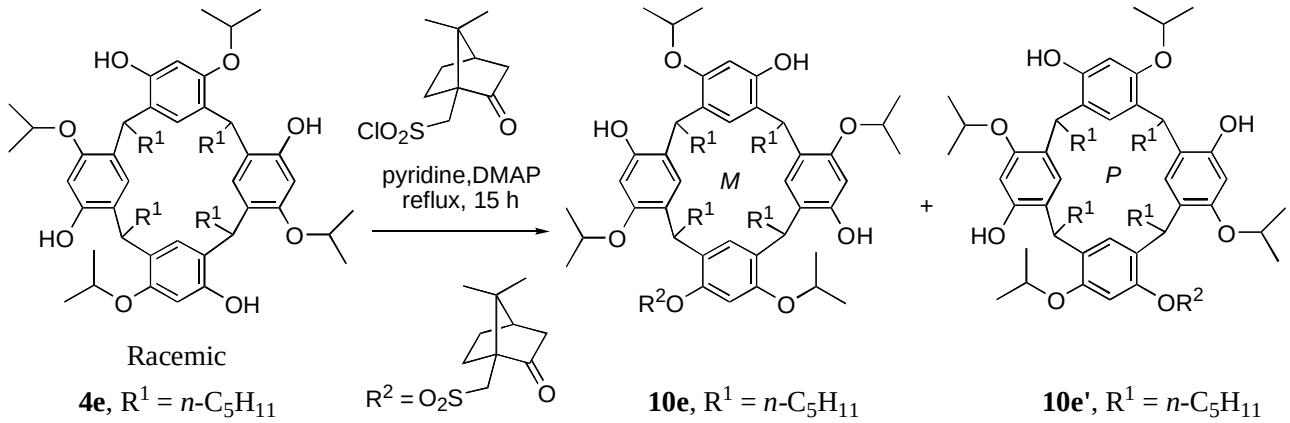


Figure 4. X-ray Structure of the Tetracamphorsulfonate (*M*,*S*,*R*)-**8b**; the hydrogen atoms are omitted for clarity.

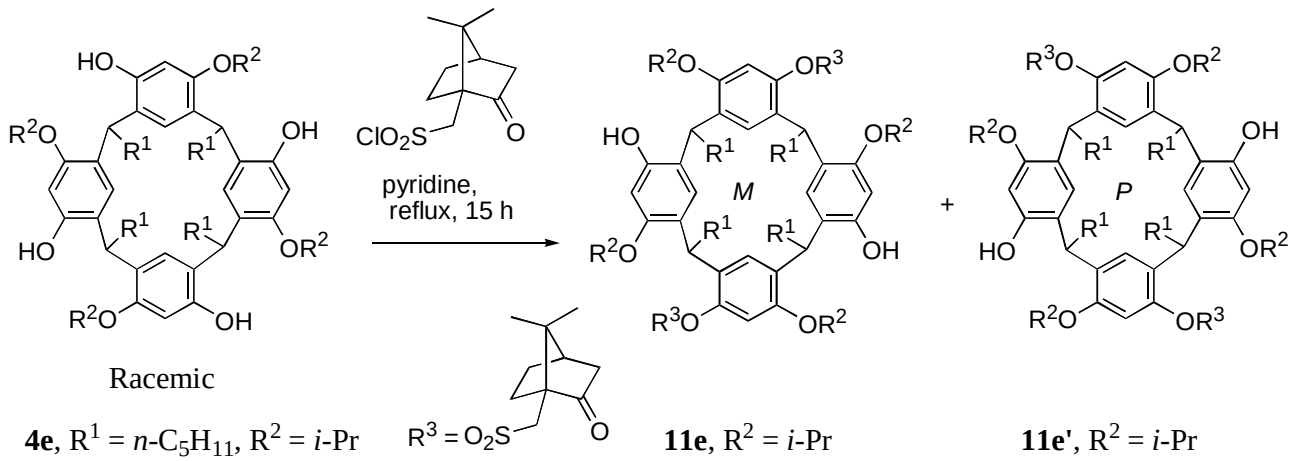
The influence of steric problems became even more evident when we studied the reactions of (*S*)-(+)-10-camphorsulfonyl chloride with the tetraalkoxyresorcin[4]arenes **4e** and **4f** with bulkier head

groups. In a reaction in which 8 equivalents of freshly prepared (*S*)-(+)-10-camphorsulfonyl chloride, the tetraisopropyloxyresorcin[4]arene **4e**, and DMAP were heated under reflux in pyridine, we were only able to obtain a mixture of diastereoisomeric monocamphorsulfonates in a combined yield of 56%. The products **10e** and **10e'**, shown in **Scheme 4**, were separated by flash chromatography on silica gel after the prior separation from unchanged tetraisopropyloxyresorcin[4]arene **4e**. In similar reactions, in which we omitted the DMAP, using the resorcinarenes **4e** or **4f** in pyridine, we obtained mixtures of two dicamphorsulfonates in a combined yield of 64% using **4e** and in 46% yield using **4f**. Although we do not have a crystal structure of any of the diastereoisomers of those dicamphorsulfonates, the steric problems noted above suggest that it is most likely that they are the distally substituted compounds **11e** and **11f**, and **11e'** and **11f'** shown in **Scheme 5**. We will return to this question below, in connection with reactions of anions generated using an excess of *n*-butyllithium in tetrahydrofuran.



Racemic
4e, R^1 = *n*-C_5H_{11}
10e, R^1 = *n*-C_5H_{11}
10e', R^1 = *n*-C_5H_{11}

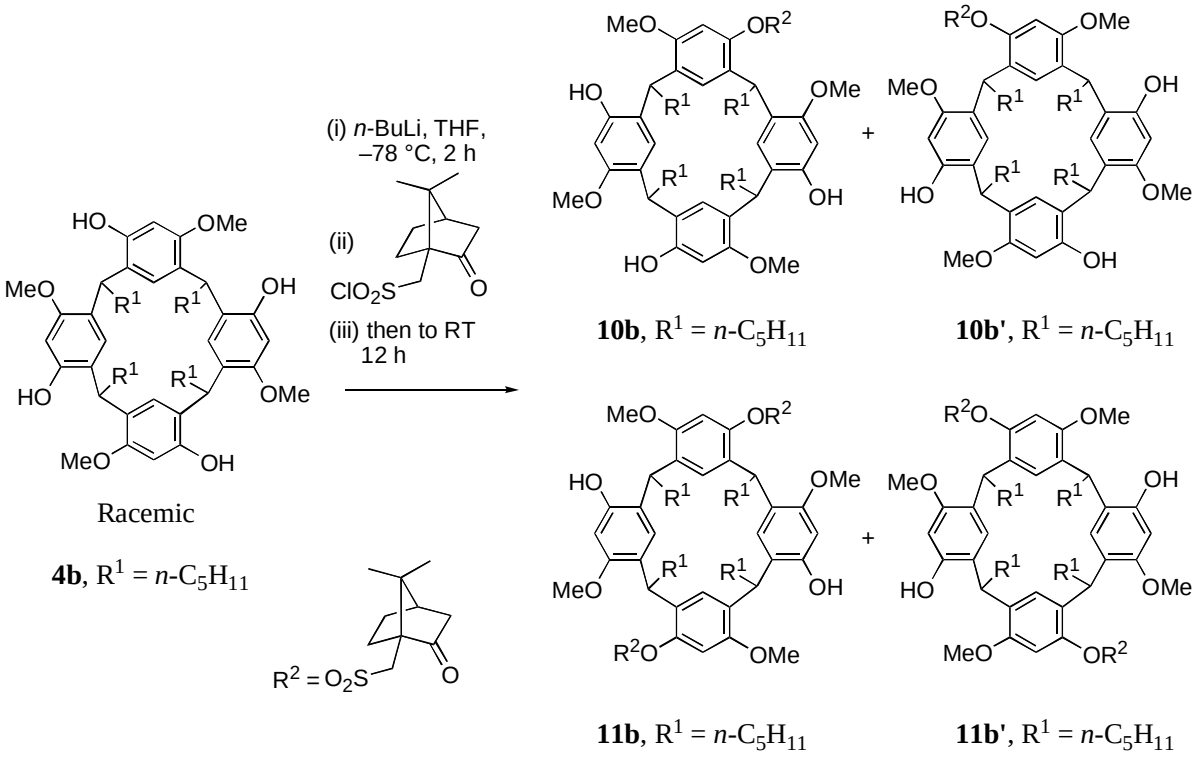
Scheme 4. The Formation of Monocamphorsulfonates from the Racemic Resorcinarene **4e**



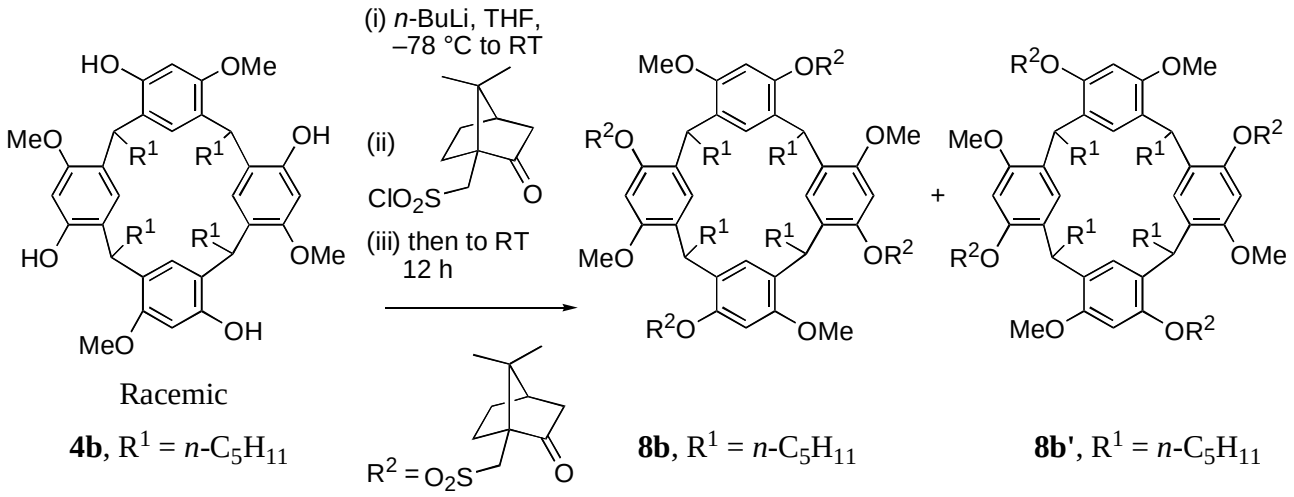
Racemic
4e, R^1 = *n*-C_5H_{11}, R^2 = *i*-Pr
4f, R^1 = *n*-C_5H_{11}, R^2 = cyclopentyl
11e, R^2 = *i*-Pr
11f, R^2 = cyclopentyl
11e', R^2 = *i*-Pr
11f', R^2 = cyclopentyl

Scheme 5. The Formation of Dicamphorsulfonates from the Racemic Resorcinarenes **4e** and **4f**

We next turned our attention to deprotonation of the racemic tetraalkoxyresorcin[4]arenes using our previously disclosed deprotonation protocol,[6a] in which *n*-butyllithium in hexanes is added to a solution of an appropriate resorcin[4]arene derivative in anhydrous tetrahydrofuran at –78 °C. As well as allowing the possibility of preparing mono- and dicamphorsulfonates, we hoped to access some of the tetracamphorsulfonates in improved yields. In a reaction of the racemic tetramethoxyresorcin[4]arene **4b**, the addition of 1.2 mol equivalents of *n*-butyllithium at –78 °C was followed, after 2 hours, by the addition of a THF solution of freshly prepared (*S*)-(+)-10-camphorsulfonyl chloride (1.3 mol equivalents). After allowing the reaction mixture to warm to room temperature over 12 h, normal work up was followed by initial chromatographic separation of the reaction mixture on silica gel to give unchanged tetramethoxyresorcin[4]arene **4b** together with mixtures of diastereoisomeric mono- and dicamphorsulfonates. Repeated chromatography of the mono- and dicamphorsulfonate mixtures allowed the isolation of a pair of monocamphorsulfonates each in 25% yield, together with a pair of dicamphorsulfonates each in 9% yield. In a reaction in which the amounts of *n*-butyllithium and (*S*)-(+)-10-camphorsulfonyl chloride were increased to 2.2 and 2.3 mol equivalents respectively, we obtained the mono- and dicamphorsulfonates each in 33% yield, as shown in **Scheme 6**. Finally, the diastereoisomeric tetracamphorsulfonates were obtained in combined yields of 60% and 74% when reactions of the tetra-anion with freshly prepared (*S*)-(+)-10-camphorsulfonyl chloride were carried out as shown in **Scheme 7**, in the first case initially at –78 °C and in the latter case initially at 0 °C.



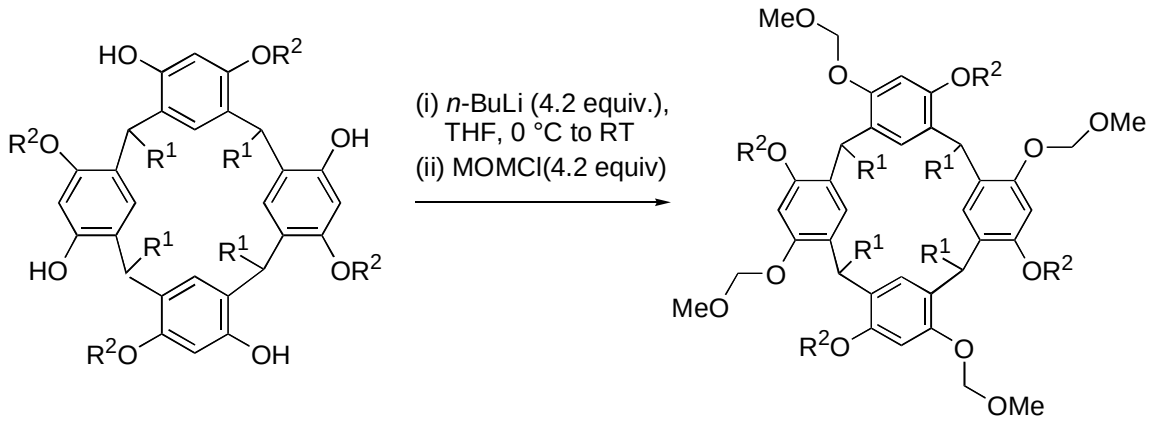
Scheme 6. The Formation of Mono- and Dicamphorsulfonates from the Anions of the Racemic Resorcinarene **4b**



Scheme 7. The Formation of Tetracamphorsulfonates from a Tetra-anion

Reactions of (*S*)-(+)-10-camphorsulfonyl chloride with anions derived from the racemic tetraisopropyloxy- and tetracyclopentyloxyresorcin[4]arenes **4e** and **4f** provided an interesting confirmation of the steric problems associated with the introduction of more than two camphorsulfonyl residues on the tetraalkoxyresorcin[4]arene scaffold. That we were able to prepare a tetra-anion from the tetraisopropyloxyresorcin[4]arene **4e** was shown by the reaction with methoxymethyl chloride, which gave the racemate of the MOM ethers **12e** in 46% yield, shown in

Scheme 8. This result may be compared to the analogous reaction using the tetramethoxyresorcin[4]arene **4b**, from which the MOM ethers **12b** were obtained in 90% yield.



Racemic

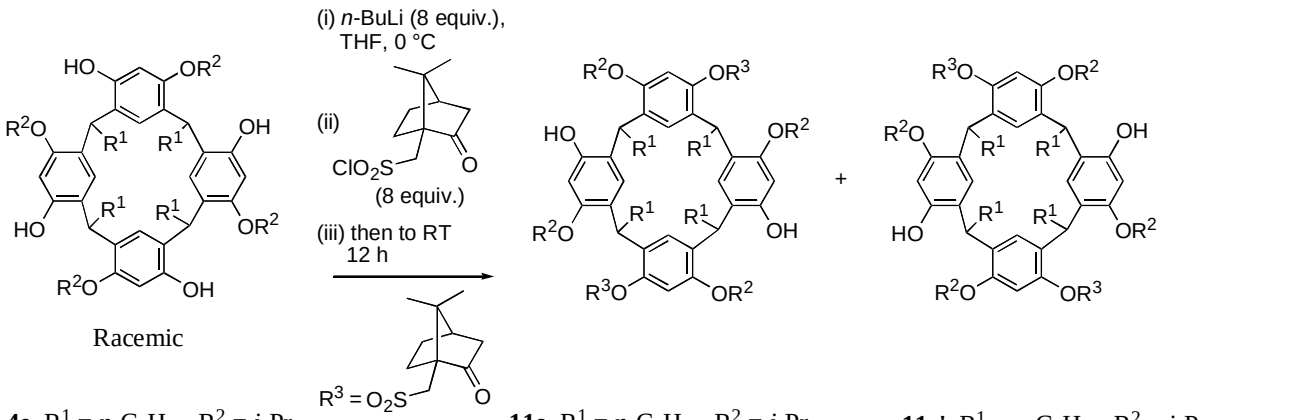
4b, R^1 = *n*-C_5H_{11}, R^2 = Me
4e, R^1 = *n*-C_5H_{11}, R^2 = *i*-Pr

Racemic

12b, R^1 = *n*-C_5H_{11}, R^2 = Me
12e, R^1 = *n*-C_5H_{11}, R^2 = *i*-Pr

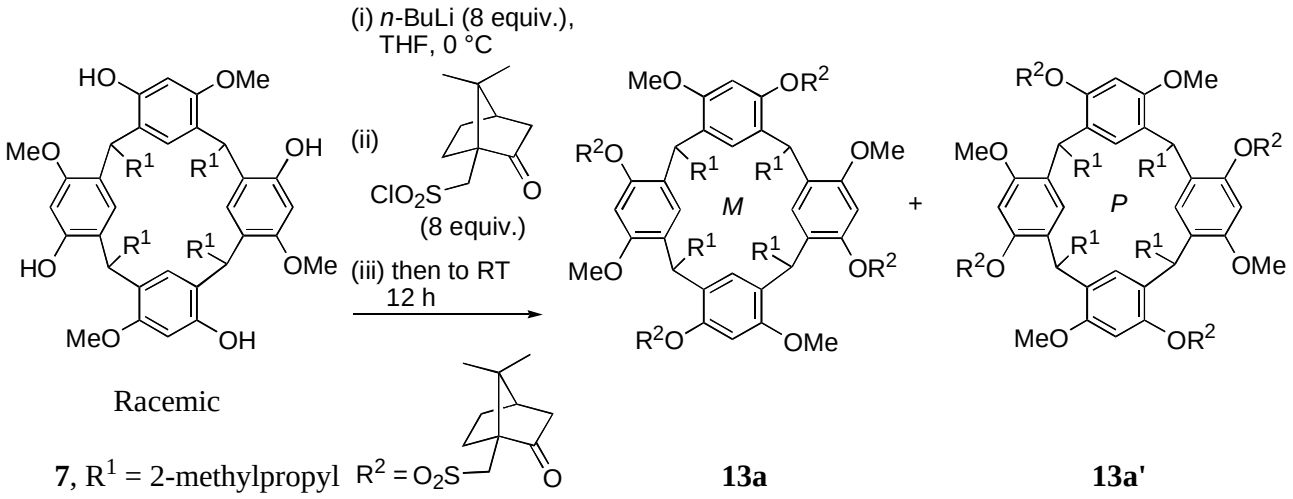
Scheme 8. The Formation of Tetra(methoxymethyl)ethers from Tetra-anions

Our initial reactions with anions derived from the racemic tetraisopropyloxy- and tetracyclopentyloxyresorcin[4]arenes **4e** and **4f** were carried out using 2.1 equivalents of *n*-butyllithium and 2.1 equivalents of (*S*)-(+)-10-camphorsulfonyl chloride. In the case of the reactions using racemic **4e**, we obtained the monocamphorsulfonates **10e** and **10e'** in a combined yield of 48% together with a mixture of dicamphorsulfonates in 18% yield. Similarly, a reaction using the racemic **4f** gave the monocamphorsulfonates **10f** and **10f'** in 46% yield together with the dicamphorsulfonates **11f** and **11f'** in 22% yield. In view of the fact that we had found the more highly substituted derivatives easier to separate, we decided to attempt to prepare tetracamphorsulfonates from the resorcinarenes **4e** and **4f**. A reaction of the racemic tetraisopropyloxyresorcin[4]arene **4e** with *n*-butyllithium (8 equivalents) at 0 °C followed by the addition of an excess of (*S*)-(+)-10-camphorsulfonyl chloride gave, however, a mixture of the diastereoisomeric dicamphorsulfonates **11e** and **11e'** in a combined yield of 82%, as shown in **Scheme 9**. No trace of a tri- or tetracamphorsulfonate was detected. A similar reaction using the racemic compound **4f** gave a mixture of the diastereoisomeric dicamphorsulfonates **11f** and **11f'** in a combined yield of 56%, also shown in **Scheme 9**. We ascribe the failure to form tetracamphorsulfonates in these latter reactions to steric hindrance to the sulfonylation reaction that we noted to a lesser extent in the reaction with methoxymethyl chloride, illustrated in **Scheme 8**.

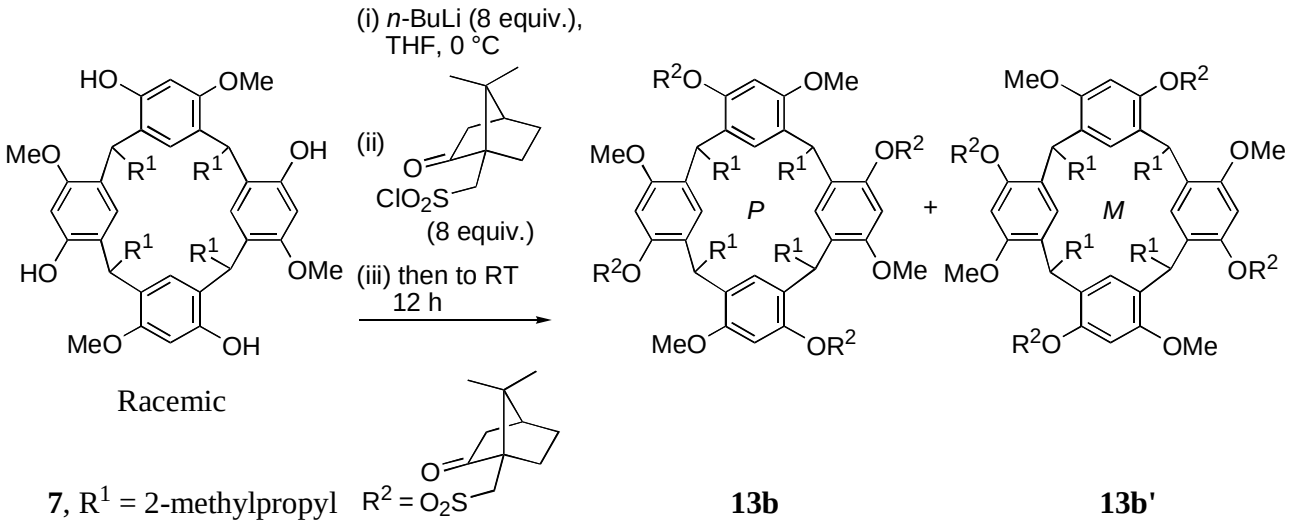


Scheme 9. The Formation of Dicamphorsulfonates from Tetra-anions

Finally, we prepared the tetracamphorsulfonates **13a** and **13a'** using (*S*)-(+)-10-camphorsulfonyl chloride [shown in **Scheme 10**] and **13b** and **13b'** using freshly prepared (*R*)-(–)-10-camphorsulfonyl chloride [shown in **Scheme 11**] from the racemic resorcin[4]arene **7** using the tetra-anion route. The structures of the tetracamphorsulfonates **13a** and **13b** were confirmed by the X-ray crystal structures, shown in **Figures 5** and **6**.[14]



Scheme 10. The Formation of Tetracamphorsulfonates from the Racemic Resorcinarene **7** Using (*S*)-(+)-10-Camphorsulfonyl chloride



Scheme 11. The Formation of Tetracamphorsulfonates from the Racemic Resorcinarene **7** Using (*R*)-(–)-10-Camphorsulfonyl chloride

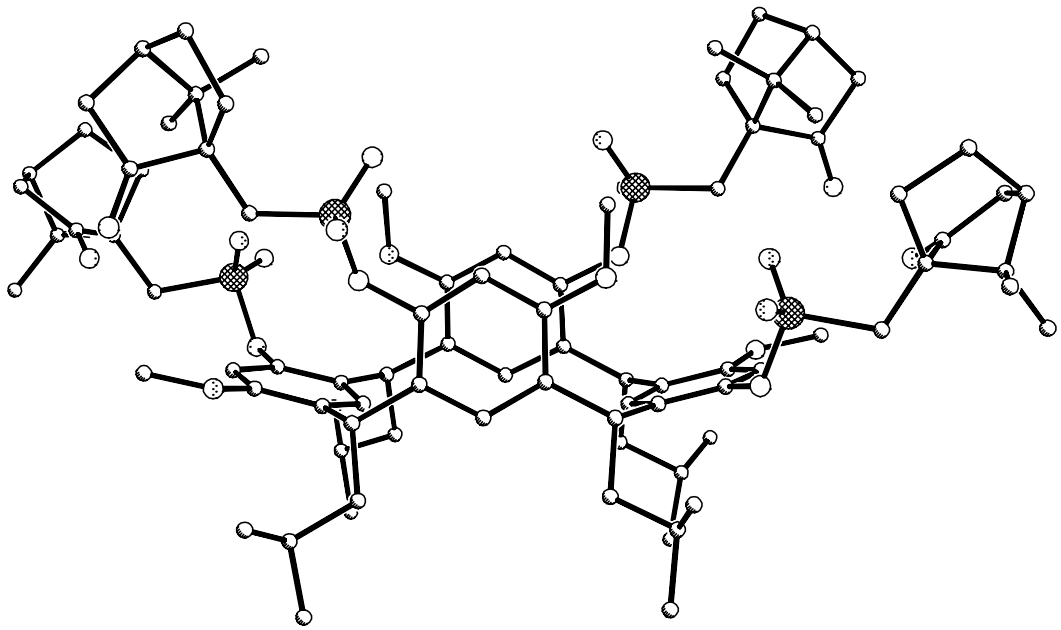


Figure 5. X-ray Structure of the Tetracamphorsulfonate (*M*,*S*,*R*)-**13a**; the hydrogen atoms are omitted for clarity.

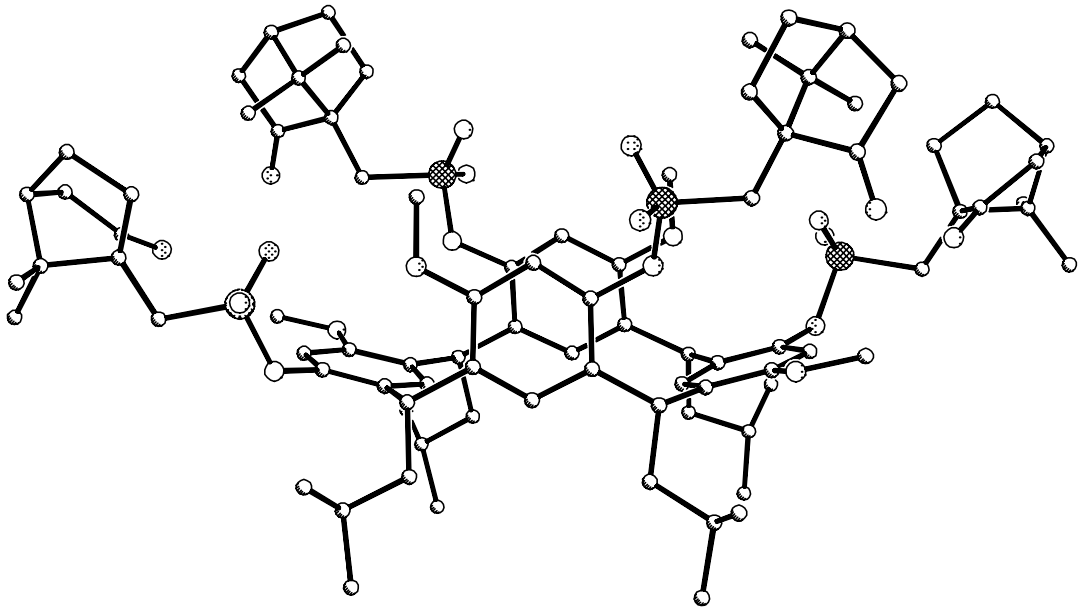


Figure 6. X-ray Structure of the Tetracamphorsulfonate (*P*,*R*,*S*)-**13b**; the hydrogen atoms are omitted for clarity.

The structures of the various camphorsulfonates were established using a variety of analytical techniques in addition to X-ray crystallography.[14] The number of camphorsulfonyl residues present in each of the products followed from high resolution (MALDI-TOF) mass spectrometric data in which the observed ion clusters in the molecular ion region matched the calculated intensities. ^{1}H and ^{13}C NMR data, in the case of the mono-, tri- and tetracamphorsulfonates, were unexceptional. The identification of the diastereoisomeric tetracamphorsulfonates was facilitated by inspection of the ^{1}H NMR spectra. The difference in the chemical shifts of the two aromatic methine hydrogen atoms was *ca*. 0.08 ppm in the case of the first eluting diastereoisomer and *ca*. 0.17 ppm in the case of the second eluting diastereoisomer: illustrated for the compounds **8b** and **8b'** in **Figures 7** and **8**. In the case of the dicamphorsulfonates two possible mixtures could have been formed. However, at present it has not been possible to obtain crystals that are suitable for X-ray analysis from any of the dicamphorsulfonates reported in this paper. Also, it was not possible to distinguish between the two possible regioisomers on the basis of NMR measurements carried out at different temperatures. The steric problems that we observed in the reactions of the racemic tetraisopropyloxy- and tetracyclopentyloxyresorcin[4]arenes **4e** and **4f** strongly support our suggestion that the tetraalkoxyresorcinarenes are distally disubstituted in the dicamphorsulfonates.

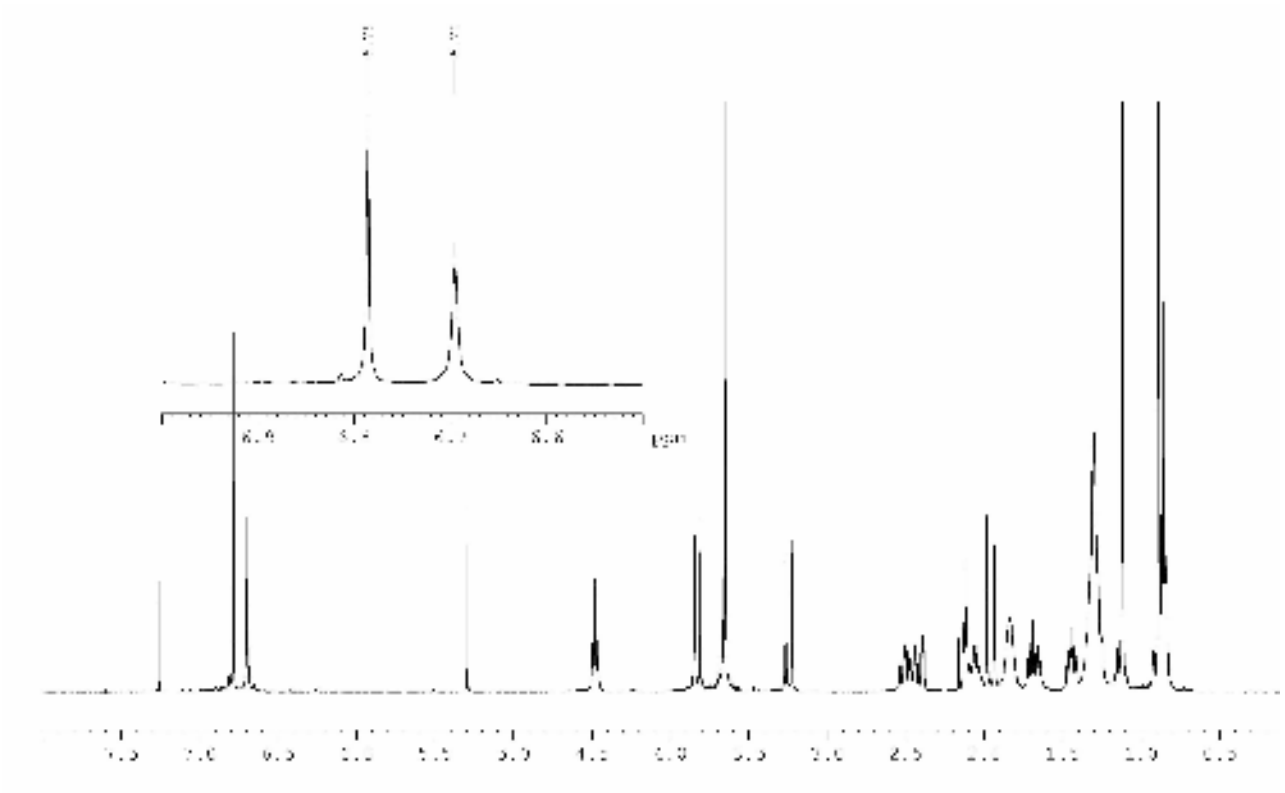


Figure 7. The ^{1}H NMR spectrum of Tetracamphorsulfonate (*M*,*S*,*R*)-**8b**

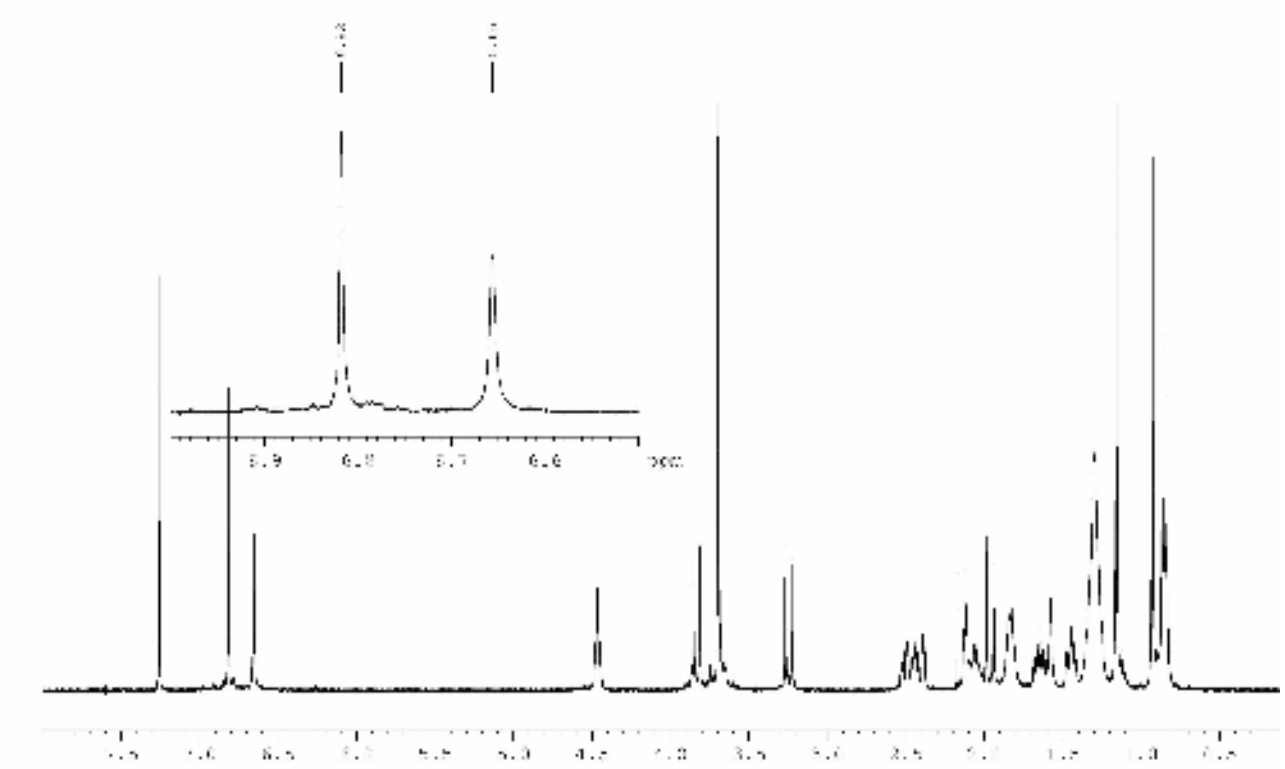
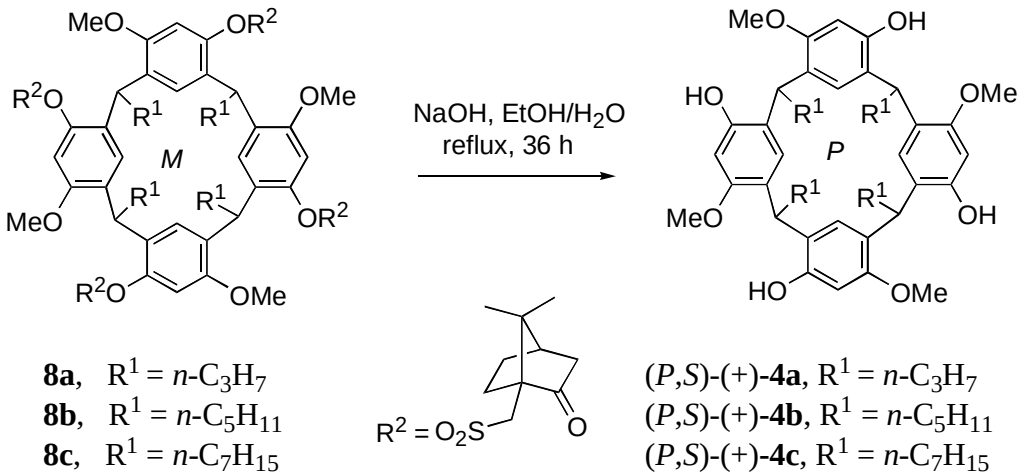


Figure 8. The ^{1}H NMR spectrum of Tetracamphorsulfonate (*P*,*S*,*S*)-**8b'**

We turned our attention next to the hydrolysis of the pure diastereoisomeric camphorsulfonates in order to obtain enantiomerically pure tetraalkoxyresorcin[4]arenes. Hydrolysis of the

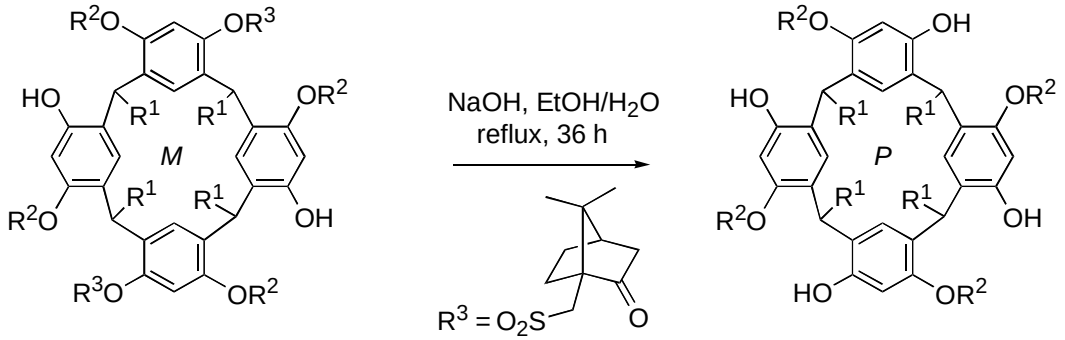
camphorsulfonates was achieved by heating aqueous alcoholic sodium hydroxide solutions under reflux. The results, illustrated for the first eluting diastereoisomer derived from (*S*)-(+)-10-camphorsulfonyl chloride, are shown for the hydrolyses of the tetracamphorsulfonates in **Scheme 12**, and for the hydrolyses of the dicamphorsulfonates in **Scheme 13**. The most important conclusion that emerged from those reactions is that, as expected, the hydrolyses of each of the first eluting diastereoisomers derived from reactions using (*S*)-(+)-10-camphorsulfonyl chloride gave enantiomerically pure tetraalkoxyresorcin[4]arenes that each had specific rotations with the same sign: in the case of the first eluting diastereoisomers a (+)-specific rotation. The hydrolysis of the second eluting diastereoisomer in each case gave the (–)-enantiomer; for example **13a'** gave (*M*,*R*)-(–)-**7**. In the case of the hydrolysis of the diastereoisomers **13b** and **13b'** that were obtained using (*R*)-(–)-10-camphorsulfonyl chloride hydrolysis of the first eluting diastereoisomer gave, as anticipated, the enantiomer (*M*,*R*)-(–)-**7**, shown in **Scheme 14**, and the second eluting diastereoisomer gave the enantiomer (*P*,*S*)-(+)-**7**.



8a, R^1 = *n*-C_3H_7
8b, R^1 = *n*-C_5H_{11}
8c, R^1 = *n*-C_7H_{15}
8d, R^1 = *n*-$C_{11}H_{23}$
13a, R^1 = 2-methylpropyl

(*P*,*S*)-(+)-**4a**, R^1 = *n*-C_3H_7
(*P*,*S*)-(+)-**4b**, R^1 = *n*-C_5H_{11}
(*P*,*S*)-(+)-**4c**, R^1 = *n*-C_7H_{15}
(*P*,*S*)-(+)-**4d**, R^1 = *n*-$C_{11}H_{23}$
(*P*,*S*)-(+)-**7**, R^1 = 2-methylpropyl

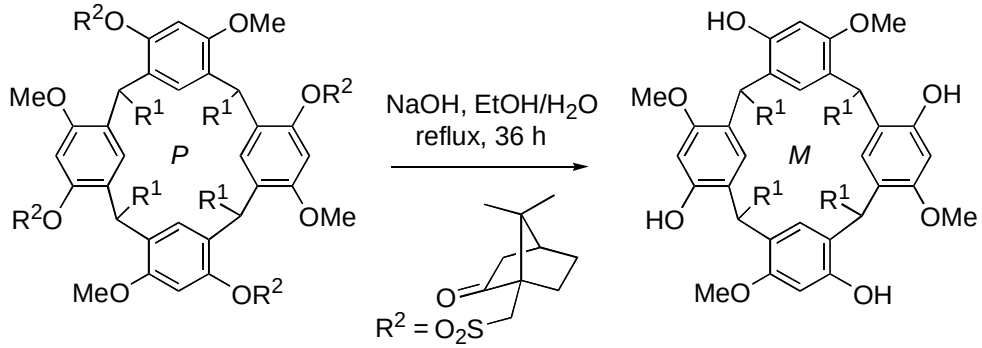
Scheme 12. Hydrolyses of the First Eluting Tetracamphorsulfonates Derived from (*S*)-(+)-10-Camphorsulfonyl chloride



11e, R^1 = *n*-C_5H_{11}, R^2 = *i*-Pr — (*P*,*S*)-(+)-**4e**, R^1 = *n*-C_5H_{11}, R^2 = *i*-Pr

11f, R^1 = *n*-C_5H_{11}, R^2 = cyclopentyl — (*P*,*S*)-(+)-**4f**, R^1 = *n*-C_5H_{11}, R^2 = cyclopentyl

Scheme 13. Hydrolyses of the First Eluting Dicamphorsulfonates Derived from (*S*)-(+)-10-Camphorsulfonyl chloride

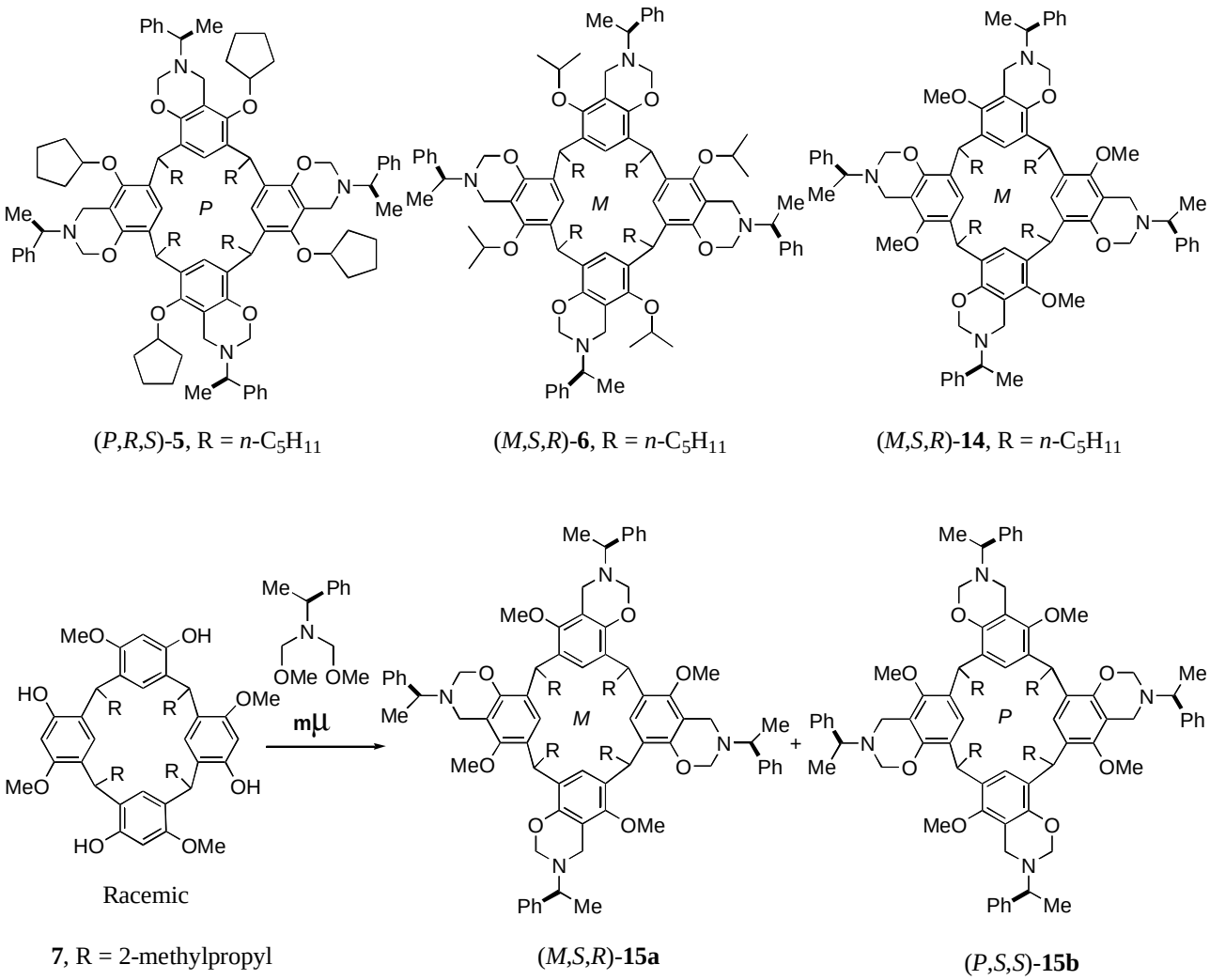


13b, R^1 = 2-methylpropyl — (*M*,*R*)-(–)-**7**, R^1 = 2-methylpropyl

Scheme 14. Hydrolysis of the First Eluting Tetracamphorsulfonate Derived from (*R*)-(–)-10-Camphorsulfonyl chloride

We had available, as an additional confirmation of the absolute configurations of some of the chiral non-racemic tetraalkoxyresorcinarenes, the possibility of comparing NMR data for some tetrabenzoxazine derivatives, which we had obtained from reactions of tetraalkoxyresorcinarenes with chiral non-racemic *N*,*N*-bis(methoxymethyl)-*N*-α-methylbenzylamine derivatives.[6b] The compound **14** was prepared from (*P*,*S*)-(+)-**4b** using (*S*)-(–)-*N*,*N*-bis(methoxymethyl)-*N*-α-methylbenzylamine in 46% yield; its absolute configuration was known from an earlier study.[6a] The structures of the diastereoisomers (*P*,*R*,*S*)-**5** and (*M*,*S*,*R*)-**6** were known from the results of X-ray structure determinations.[6b] We prepared compound (*P*,*R*,*S*)-**5** and compound (*M*,*R*,*R*)-**6'**, the diastereoisomer of compound (*M*,*S*,*R*)-**6**, from (*M*,*R*)-(–)-**4f** in 58% yield and (*P*,*S*)-(+)-**4e** in 53% yield respectively using (*R*)-(+)-*N*,*N*-bis(methoxymethyl)-*N*-α-methylbenzylamine. These experiments also confirmed the assignments of the absolute configurations of enantiomerically pure tetraalkoxyresorcin[4]arenes. In the case of the racemic tetramethoxyresorcin[4]arene **7**, we

prepared the diastereoisomeric tetrabenzoxazines using the microwave enhanced method, shown in **Scheme 15**. Separation of the diastereoisomers gave compounds whose NMR spectra could be compared with compounds that had been obtained previously.[6b] We also prepared the diastereoisomer **15a** from the chiral non-racemic tetramethoxyresorcin[4]arene (*P*,*S*)-(+)-**7** using the microwave enhanced method. The spectra confirmed the anticipated structure as **15a** for the first eluting diastereoisomer and **15b** for the second eluting diastereoisomer and as a result provided additional confirmation of the structures of the enantiomeric tetramethoxyresorcin[4]arenes (*P*,*S*)-(+)-**7** and (*M*,*R*)-(–)-**7**.



Scheme 15 The Synthesis of Tetrabenzoxazines from Racemic 2,8,14,20-tetra-2-methylpropyl-6,12,18,24-tetramethoxyresorcin[4]arene

Conclusions

In this study we have shown that it is possible to prepare and isolate diastereoisomeric mono-, di-, tri-, and tetracamphorsulfonates from a range of tetraalkoxyresorcin[4]arenes. The absolute

configurations of the diastereoisomers were established by a combination of X-ray crystallographic and NMR spectroscopic studies. Hydrolysis of the single diastereoisomeric camphorsulfonates gave a series of tetraalkoxyresorcin[4]arenes in which the (+)-rotatory enantiomers were shown to be of (*P*,*S*)- chirality and the (–)-rotatory enantiomers were of (*M*,*R*)- chirality. Further confirmation of the absolute stereochemistry of the tetramethoxyresorcin[4]arene (*P*,*S*)-(+)-**7** was provided by its conversion into the tetrabenzoxazine derivative **15a**. These results correct the assignment of the absolute stereochemistry of the tetramethoxyresorcin[4]arene (+)-**7** and also of (–)-**7**: also the absolute stereochemistries of diastereoisomeric tetra-2-methylbutyloxy- ethers derived from the compounds (*P*,*S*)-(+)-**7** and (*M*,*R*)-(–)-**7** and a pair of diastereoisomeric tetra-2-methylbutyloxyresorcin[4]arenes that were reported in the earlier study.[9]

Experimental Section

General Experimental Detail. All infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FT-IR and a Bruker Vector 22 FTIR spectrophotometers; thin film spectra were acquired using sodium chloride plates. All ^{1}H and ^{13}C NMR spectra were measured at 400.13 and 100.62 MHz with a Bruker DPX 400 / Avance 400 MHz spectrometer, in deuteriochloroform solution unless otherwise stated, using TMS (tetramethylsilane) as the internal reference. Mass spectra were recorded using a Jeol-SX102 instrument utilizing electron-impact (EI), fast atom bombardment (FAB), and by the EPSRC national mass spectrometry service at the University of Wales, Swansea, utilizing electrospray (ES) and MALDI-TOF. Analysis by GCMS utilized a Fisons GC 8000 series (AS 800), using a 15 m x 0.25 mm DB-5 column and an electron-impact low resolution mass spectrometer. Melting points were recorded using an Electrothermal-IA 9100 melting point instrument and are uncorrected. Optical rotation values were measured with an Optical Activity-polAAar 2001 instrument and a Perkin-Elmer 141 polarimeter, operating at λ=589 nm, corresponding to the sodium D line, at the temperatures indicated. Microanalyses were performed on a Perkin Elmer Elemental Analyser 2400 CHN. All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored using thin layer chromatography (TLC) on aluminium-backed plates coated with Merck Kieselgel 60 F254 silica gel. TLC plates were visualized by UV radiation at a wavelength of 254 nm, or stained by exposure to an ethanolic solution of phosphomolybdic acid (acidified with concentrated sulfuric acid), followed by charring where appropriate. Reactions requiring anhydrous conditions were carried out using flame dried glassware under a nitrogen atmosphere unless otherwise stated. Reaction solvents were used as obtained commercially unless otherwise stated. Light petroleum (b.p. 40-60 ºC) was distilled from calcium chloride prior to use. Ethyl acetate was distilled over calcium sulfate or chloride. Dichloromethane was distilled over calcium hydride. Tetrahydrofuran was distilled under a nitrogen atmosphere from the sodium/benzophenone ketyl radical. Microwave reactions were carried out in a CEM Discover focused microwave set at a maximum of 300 W.

General procedure 1:

The corresponding resorcinarene was dissolved in dry pyridine (10 mL) under a nitrogen atmosphere and (*S*)-(+)-camphorsulfonyl chloride added in several portions at room temperature. The mixture was then heated under reflux overnight. The bulk of the pyridine was removed at reduced pressure and the residue stirred with dilute hydrochloric acid (30 mL) for 30 minutes. The mixture was then extracted with ether (2 x 30 mL) and the combined organic phases washed with dilute hydrochloric acid (2 x 30 mL), water (1 x 30 mL), brine (1 x 30 mL) and dried over anhydrous magnesium sulfate

(or anhydrous sodium sulfate). The ether was removed under reduced pressure to give a mixture of the desired compounds.

General procedure 2:

The corresponding resorcinarene was dissolved in tetrahydrofuran (50 mL) and the solution was cooled down to −78 °C (or 0 °C). *n*-Butyllithium (2.5M in hexanes) was slowly added to the solution and the reaction mixture was stirred for 30 minutes at −78 °C (or 0 °C). A solution of a camphorsulfonyl chloride in tetrahydrofuran (10 mL) was then slowly added using a cannula to the reaction mixture. The mixture was allowed to warm to room temperature and was stirred for 12 hours. A solution of hydrochloric acid (3.5 M) was then added to bring the pH below 7 and the phases were separated. The aqueous phase was then extracted with diethyl ether (3 x 25 mL). The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate (or anhydrous sodium sulfate) and concentrated under reduced pressure to give a mixture of the desired compounds.

General procedure 3:

The corresponding resorcinarene was dissolved in methanol or ethanol (10 mL). Water (1 mL) and sodium hydroxide were added, and the mixture was heated under reflux overnight. The solvent was removed under reduced pressure. Water (approx. 10 mL) was then added to the residue. The pH of the mixture was then adjusted to pH 2 with hydrochloric acid (conc.) and the acidified mixture extracted with dichloromethane (2 x 10 mL). The combined organic phases were dried over anhydrous magnesium sulfate (or anhydrous sodium sulfate) and the solvent was removed under reduced pressure.

2,8,14,20-Tetrapropyl-4,10,16,22-tetra-(*S*)-camphorsulfonyloxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*S*,*R*)-8a and (*P*,*S*,*S*)-8a':

Using general procedure 1:

General procedure 1 followed using 2,8,14,20-tetrapropyl-6,12,18,24-tetramethoxyresorcin[4]arene **4a**[6b] (2.00 g, 2.8 mmol) and (*S*)-(+)-camphorsulfonyl chloride (5.63 g, 22.5 mmol) to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (93:7). The resulting glassy solids were crystallized from methanol to give:

Compound (*M*,*S*,*R*)-8a: as colourless crystals (2.02 g, 46%). M.p. 189-191 °C (Softens 165 °C). $[\alpha]_D^{25}$ +61.3 (*c* 6.2). ν_{max} ($CHCl_3$)/cm^{-1} 2958, 2873, 1748, 1498, 1357; δ_H (400 MHz, $CDCl_3$) 0.90 (12 H, s), 0.95 (12 H, t, *J* 7.4 Hz), 1.14 (12 H, s), 1.30-1.50 (12 H, m), 1.65-1.75 (4 H, m), 1.79-1.90 (8 H, m), 1.97 (4 H, d, *J* 18.8 Hz), 2.01-2.16 (8 H, m), 2.38-2.57 (8 H, m), 3.26 and 3.84 (8 H, AB, *J* 14.8 Hz), 3.67 (12 H, s), 4.52 (4 H, t, *J* 7.4 Hz), 6.73 (4 H, s), 6.80 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.9, 20.4, 20.6, 21.7, 25.8, 27.6, 36.4, 37.7, 43.2, 43.6, 48.5, 49.1, 56.6, 58.8, 105.4, 126.9, 129.0, 131.7, 146.4, 156.1, 214.7.

Compound (*P*,*S*,*S*)-8a': as a glassy solid (1.02 g, 23%). $[\alpha]_D^{25}$ +2.6 (*c* 4.2). ν_{max} ($CHCl_3$)/cm^{-1} 2957, 2872, 1749, 1498, 1357; δ_H (400 MHz, $CDCl_3$) 0.92-0.96 (24 H, m), 1.17 (12 H, s), 1.30-1.51 (12 H, m), 1.61-1.71 (4 H, m), 1.79-1.88 (8 H, m), 1.97 (4 H, d, *J* 18.4 Hz), 2.00-2.16 (8 H, m), 2.37-2.56 (8 H, m), 3.26 and 3.85 (8 H, AB, *J* 15.0 Hz), 3.70 (12 H, s), 4.50 (4 H, t, *J* 7.3 Hz), 6.68 (4 H, s), 6.83 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.9, 20.4, 20.7, 21.7, 25.8, 27.6, 36.6, 37.5, 43.1, 43.7, 48.5, 49.3, 56.6, 58.8, 105.5, 126.9, 128.8, 131.5, 146.5, 156.1, 214.6. MS *m/z* 1568.6 (M^+).

2,8,14,20-Tetrapentyl-4,10,16,22-tetra-(*S*)-camphorsulfonyloxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*S*,*R*)-8b and (*P*,*S*,*S*)-8b' and 2,8,14,20-tetrapentyl-4,10,16-tri-(*S*)-camphorsulfonyloxy-22-hydroxy-6,12,18,24-tetramethoxyresorcin[4]arene 9b and 9b':

Using general procedure 1:

General procedure 1 followed using 22,8,14,20-tetrapentyl-6,12,18,24-tetramethoxyresorcin[4]arene **4b** (0.20 g, 0.24 mmol) and (*S*)-(+)-camphorsulfonyl chloride (0.72 g, 2.88 mmol) to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/Et_2O (96:4) to give:

Compound (*M*,*S*,*R*)-8b: as a colourless foam (0.095 g, 23%). $[\alpha]_D^{25}$ +41.8 (*c* 1.1, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 2955, 2929, 2858, 1747, 1497, 1455, 1356, 1193, 1129, 1068, 1053, 831 and 810; δ_H (400 MHz, $CDCl_3$) 0.85 (12 H, t, *J* 7.0 Hz), 0.89 (12 H, s), 1.12 (12 H, s), 1.24-1.35 (24 H, m), 1.44 (4 H, ddd, *J* 12.7, 9.3, 3.8 Hz), 1.68 (4 H, ddd, *J* 14.0, 9.3 , 4.3 Hz), 1.79-1.86 (8 H, m), 1.99 (4 H, d, *J* 18.4 Hz), 2.03-2.13 (8 H, m), 2.41 (4 H, dt, *J* 9.3, 3.8 Hz), 2.51 (4 H, ddd, *J* 14.0, 11.9, 4.3 Hz), 3.24 and 3.82 (8 H, AB, *J* 15.0 Hz), 3.65 (12 H, s), 4.48 (4 H, t, *J* 7.3 Hz), 6.69 (4 H, s), 6.78 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.2, 19.7, 19.9, 22.6, 25.1, 26.9, 27.7, 32.1, 34.7, 36.0, 42.5, 42.9, 47.9, 48.5, 55.9, 58.1, 104.7, 126.2, 128.3, 131.1, 145.7, 155.4, 214.0; *m/z* (FAB): 1681.7935; $[C_{92}H_{128}O_{20}S_4+H]^+$ requires 1681.7960.

Compound (*P,S,S*)-8b': as a colourless foam (0.023 g, 5.5%). $[\alpha]_D^{25}$ +12.3 (*c* 1.2, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 2954, 2928, 2856, 1747, 1613, 1582, 1496, 1356, 1277, 1193, 1179, 1067, 1053, 832 and 810; δ_H (400 MHz, $CDCl_3$) 0.85 (12 H, t, *J* 7.0 Hz), 0.93 (12 H, s), 1.16 (12 H, s), 1.25-1.36 (24 H, m), 1.38-1.49 (4 H, m), 1.65 (4 H, ddd, *J* 14.0, 9.2, 4.4 Hz), 1.79-1.85 (8 H, m), 1.97 (4 H, d, *J* 18.4 Hz), 2.01-2.17 (8 H, m), 2.41 (4 H, dt, *J* 9.3, 3.6 Hz), 2.46 (4 H, ddd, *J* 14.0, 12.0, 3.8 Hz), 3.25 and 3.85 (8 H, AB, *J* 14.8 Hz), 3.70 (12 H, s), 4.47 (4 H, t, *J* 7.2 Hz), 6.66 (4 H, s), 6.82 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 19.7, 20.0, 22.6, 25.1, 26.9, 27.7, 32.0, 34.6, 36.2, 42.4, 43.0, 47.8, 48.6, 55.9, 58.1, 104.8, 126.2, 128.2, 130.9, 145.8, 155.5, 213.8; *m/z* (MALDI-TOF): 1704.8 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 9b: as a colourless foam (0.017 g, 4.8%). $[\alpha]_D^{25}$ +34.4 (*c* 1.0, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3478, 2956, 2927, 2855, 1746, 1495, 1356, 1262, 1193, 1179, 1068, 1053, 1022, 809; δ_H (400 MHz, $CDCl_3$) 0.84 (12 H, m), 0.89 (3 H, s), 0.91 (3 H, s), 1.15 (3 H, s), 1.16 (3 H, s), 1.18 (3 H, s), 1.23 (3 H, s), 1.38-1.27 (24 H, m), 1.46 (1 H, m), 1.78-1.60 (3 H, m), 2.00-1.82 (11 H, m), 2.18-2.02 (6 H, m), 2.61-2.39 (6 H, m), 3.22 and 3.87 (2 H, AB, *J* 14.8 Hz), 3.25 and 3.89 (2 H, AB, *J* 14.8 Hz), 3.32 and 3.77 (2 H, AB, *J* 14.8 Hz), 3.60 (3 H, s), 3.66 (3 H, s), 3.74 (3 H, s), 3.86 (3 H, s), 4.24 (1 H, t, *J* 7.1 Hz), 4.57 (3 H, m), 6.27 (1 H, s), 6.75 (1 H, s), 6.78 (1 H, s), 6.85 (1 H, s), 6.89 (1 H, s), 6.90 (1 H, s), 6.92 (1 H, s), 7.06 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 19.8, 19.9, 20.0, 22.4, 22.5, 22.6, 22.7, 25.1, 25.2, 26.8, 27.4, 27.5, 27.6, 27.7, 29.7, 31.9, 32.0, 32.1, 34.3, 34.7, 35.1, 35.2, 35.3, 35.5, 35.8, 42.5, 42.8, 42.9, 47.8, 47.9, 48.1, 48.2, 48.3, 55.7, 55.8, 55.9, 56.1, 58.1, 58.2, 99.8, 104.3, 104.4, 104.8, 120.9, 123.9, 125.1, 125.7, 126.1, 126.8, 127.9, 129.7, 129.9, 130.5, 131.1, 131.5, 145.6, 145.8, 146.0, 152.6, 154.1, 155.1, 155.5, 156.4, 214.1; *m/z* (MALDI-TOF): 1490.7 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 9b': as a colourless foam (0.065 g, 18%). $[\alpha]_D^{25}$ −46.7 (*c* 1.2, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3482, 2954, 2928, 2857, 1748, 1496, 1356, 1278, 1194, 1179, 1067, 1053, 832, 811; δ_H (400 MHz, $CDCl_3$) 0.85 (12 H, m), 0.86 (3 H, s), 0.91 (3 H, s), 0.92 (3 H, s), 1.14 (3 H, s), 1.17 (3 H, s), 1.18 (3 H, s), 1.36-1.25 (24 H, m), 1.45 (3 H, m), 1.61 (1 H, m), 1.73 (2 H, m), 2.00-1.86 (11 H, m), 2.14-2.04 (6 H, m), 2.58-2.38 (6 H, m), 3.21 and 3.78 (2 H, AB, *J* 14.9 Hz), 3.29 and 3.89 (2 H, AB, *J* 14.9 Hz), 3.29 and 3.93 (2 H, AB, *J* 14.9 Hz), 3.61 (3 H, s), 3.65 (3 H, s), 3.79 (3 H, s), 3.86 (3 H, s), 4.24 (1 H, t, *J* 7.2 Hz), 4.52 (2 H, m), 4.59 (1 H, t, *J* 7.1 Hz), 6.26 (1 H, s), 6.67 (1 H, s), 6.79 (1 H, s), 6.80 (1 H, s), 6.91 (1 H, s), 6.93 (1 H, s), 6.94 (1 H, s), 7.07 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 19.7, 19.9, 20.1, 22.5, 22.6, 22.7, 25.1, 25.2, 25.3, 26.8, 26.9, 27.4, 27.5, 27.6,

27.7, 31.9, 32.0, 32.1, 34.5, 34.9, 35.2, 35.4, 35.6, 42.4, 42.5, 42.9, 43.0, 47.8, 47.9, 48.3, 48.4, 48.5, 55.6, 55.8, 55.9, 56.1, 58.1, 99.7, 104.3, 104.4, 105.0, 120.5, 123.5, 125.0, 125.7, 126.0, 126.8, 127.6, 129.6, 129.8, 130.1, 131.1, 131.6, 145.6, 145.7, 146.0, 152.7, 154.2, 154.9, 155.6, 156.4, 214.1; *m/z* (MALDI-TOF): 1490.7 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Using general procedure 2:

General procedure 2 followed using 2,8,14,20-tetrapentyl-6,12,18,24-tetramethoxyresorcin[4]arene **4b** (1.0 g, 1.2 mmol), *n*-butyllithium (2.5M in hexanes, 4.9 mL, 9.7 mmol) and (*S*)-(+)-camphorsulfonyl chloride (3.0 g, 12.1 mmol) at 0 °C to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/Et_2O (96:4) to give compound (*M*,*S*,*R*)-**8b** (0.683 g, 33%) and compound (*P*,*S*,*S*)-**8b'** (0.675 g, 33%).

2,8,14,20-Tetraheptyl-4,10,16,22-tetra-(*S*)-camphorsulfonyloxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*S*,*R*)-8c and (*P*,*S*,*S*)-8c':

Using general procedure 1:

General procedure 1 followed using 2,8,14,20-tetraheptyl-6,12,18,24-tetramethoxyresorcin[4]arene **4c** (0.50 g, 0.53 mmol) and (*S*)-(+)-camphorsulfonyl chloride (1.07 g, 4.3 mmol) to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (95:5) to give:

Compound (*M*,*S*,*R*)-8c: as a colourless solid (0.38 g, 39%). $[\alpha]_D^{25}$ +46.7 (*c* 4.1). ν_{max} (DCM)/cm^{-1} 2928, 2856, 1749, 1498, 1358; δ_H (400 MHz, $CDCl_3$) 0.86 (12 H, t, *J* 6.8 Hz), 0.90 (12 H, s), 1.13 (12 H, s), 1.18-1.39 (40 H, m), 1.41-1.48 (4 H, m), 1.66-1.75 (4 H, m), 1.79-1.89 (8 H, m), 1.97 (4 H, d, *J* 18.4 Hz), 2.02-2.16 (8 H, m), 2.38-2.57 (8 H, m), 3.26 and 3.84 (8 H, AB, *J* 14.8 Hz), 3.67 (12 H, s), 4.49 (4 H, t, *J* 7.2 Hz), 6.71 (4 H, s), 6.80 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.8, 20.4, 20.6, 23.4, 25.8, 27.6, 28.7, 30.0, 30.6, 32.7, 35.5, 36.8, 43.2, 43.6, 48.5, 49.1, 56.6, 58.8, 105.4, 126.9, 129.0, 131.8, 146.4, 156.1, 214.7. MS *m/z* 1793.9 (M^+).

Compound (*P*,*S*,*S*)-8c': as a colourless solid (0.16 g, 17%). $[\alpha]_D^{25}$ +5.6 (*c* 5.7). ν_{max} (DCM)/cm^{-1} 2928, 2856, 1749, 1498, 1358; δ_H (400 MHz, $CDCl_3$) 0.86 (12 H, t, *J* 6.7 Hz), 0.94 (12 H, s), 1.167 (12 H, s), 1.17-1.38 (40 H, m), 1.40-1.56 (4 H, m), 1.60-1.70 (4 H, m), 1.77-1.88 (8 H, m), 1.97 (4 H, d, *J* 18.4 Hz), 2.01-2.15 (8 H, m), 2.36-2.55 (8 H, m), 3.25 and 3.84 (8 H, AB, *J* 15.0 Hz), 3.70 (12 H, s), 4.47 (4 H, t, *J* 7.3 Hz), 6.66 (4 H, s), 6.83 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.8, 20.4,

20.7, 23.4, 25.8, 27.6, 28.7, 30.0, 30.5, 32.7, 35.3, 36.9, 43.1, 43.6, 48.5, 49.3, 56.5, 58.8, 105.5, 126.9, 128.8, 131.6, 146.4, 156.1, 214.6. MS *m/z* 1793.9 (M^+).

2,8,14,20-Tetraundecyl-4,10,16,22-tetra-(*S*)-camphorsulfonyloxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*S*,*R*)-8d and (*P*,*S*,*S*)-8d':

Using general procedure 1:

General procedure 1 followed using 2,8,14,20-tetraundecyl-6,12,18,24-tetramethoxyresorcin[4]arene **4d** (0.50 g, 0.43 mmol) and (*S*)-(+)-camphorsulfonyl chloride (0.86 g, 3.4 mmol) to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (93:7) to give:

Compound (*M*,*S*,*R*)-8d: as a glassy solid (0.33 g, 38%). $[\alpha]_D^{25}$ +51.4 (*c* 3.6). ν_{max} (DCM)/cm^{-1} 2925, 2854, 1749, 1498, 1358; δ_H (400 MHz, $CDCl_3$) 0.83-0.92 (24 H, m), 1.15 (12 H, m), 1.17-1.37 (72 H, m), 1.40-1.50 (4 H, m), 1.65-1.75 (4 H, m), 1.78-1.90 (8 H, m), 1.97 (4 H, d, *J* 18.5 Hz), 2.01-2.16 (8 H, m), 2.37-2.56 (8 H, m), 3.25 and 3.83 (8 H, AB, *J* 15.0 Hz), 3.66 (12 H, s), 4.48 (4 H, t, *J* 7.2 Hz), 6.70 (4 H, s), 6.79 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.8, 20.4, 20.6, 23.4, 25.8, 27.6, 28.7, 30.1, 30.4, 30.5, 30.6, 30.7, 32.6, 35.5, 36.8, 43.2, 43.6, 48.5, 49.1, 56.6, 58.8, 105.4, 126.9, 129.0, 131.8, 146.4, 156.1, 214.6. MS *m/z* 2018.0 (M^+).

Compound (*P*,*S*,*S*)-8d': as a glassy solid (0.17 g, 20%). $[\alpha]_D^{25}$ +0.14 (*c* 7.02). ν_{max} (DCM)/cm^{-1} 2928, 2856, 1749, 1498, 1358; δ_H (400 MHz, $CDCl_3$) 0.87 (12 H, t, *J* 6.5 Hz), 0.94 (12 H, s), 1.167 (12 H, s), 1.17-1.37 (72 H, m), 1.38-1.50 (4 H, m), 1.60-1.71 (4 H, m), 1.76-1.87 (8 H, m), 1.97 (4 H, d, *J* 18.5 Hz), 2.00-2.15 (8 H, m), 2.35-2.54 (8 H, m), 3.25 and 3.84 (8 H, AB, *J* 15.0 Hz), 3.70 (12 H, s), 4.47 (4 H, t, *J* 7.2 Hz), 6.65 (4 H, s), 6.82 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.8, 20.4, 20.7, 23.4, 25.8, 27.6, 28.8, 30.1, 30.4, 30.5, 30.57, 30.64, 32.6, 35.3, 36.9, 43.1, 43.6, 48.5, 49.3, 56.5, 58.8, 105.5, 126.9, 128.8, 131.6, 146.4, 156.1, 214.6; MS *m/z* 2018.3 (M^+).

2,8,14,20-Tetrapentyl-4-(*S*)-camphorsulfonyloxy-10,16,22-trihydroxy-6,12,18,24-tetraisopropyloxyresorcin[4]arene 10e and 10e' and 2,8,14,20-tetrapentyl-4,16-di-(S)-camphorsulfonyloxy-10,22-dihydroxy-6,12,18,24-tetraisopropyloxyresorcin[4]arene 11e and 11e':

Using general procedure 2:

General procedure 2 followed using 2,8,14,20-tetrapentyl-6,12,18,24-tetraisopropopyloxyresorcin[4]arene **4e** (1.0 g, 1.07 mmol), *n*-butyllithium (2.5M in hexanes, 0.86 mL, 2.14 mmol) and (*S*)-(+)-camphorsulfonyl chloride (0.540 g, 2.14 mmol) at −78 °C to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (99:1) to give:

Compound 10e: as a yellow foam (0.310 g, 25%). $[\alpha]_D^{25}$ +60.0 (*c* 2.0, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3395, 2955, 2928, 2858, 1747, 1493, 1373, 1111, 846; δ_H (400 MHz, $CDCl_3$) 0.84-0.91 (15 H, m), 1.15 (3 H, s), 1.19-1.38 (31 H, m), 1.39-1.43 (18 H, m), 1.67-1.75 (1 H, m), 1.95 (1 H, d, *J* 18.5 Hz), 2.07-2.23 (10 H, m), 2.40-2.47 (1 H, m), 2.56-2.64 (1 H, m), 3.25 and 3.80 (2 H, AB, *J* 14.9 Hz), 4.22-4.32 (3 H, m), 4.38 (1 H, septet, *J* 6.1 Hz), 4.54-4.60 (2 H, m), 4.68-4.72 (2 H, m), 6.26 (1 H, s), 6.32 (1 H, s), 6.40 (1 H, s), 6.87 (1 H, s), 7.14 (1 H, s), 7.21 (1 H, s), 7.24 (1 H, s), 7.25 (1 H, s), 7.31 (1 H, s), 7.32 (1 H, s), 7.55 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 14.2, 19.7, 20.0, 21.6, 21.8, 21.8, 21.9, 22.0, 22.03, 22.2, 22.6, 22.7, 22.74, 22.8, 25.2, 26.9, 27.5, 27.7, 27.8, 31.8, 32.0, 32.1, 33.4, 33.5, 34.7, 42.5, 42.9, 47.9, 58.2, 70.0, 71.4, 71.7, 72.1, 101.6, 101.8, 102.7, 107.2, 122.6, 122.6, 123.2, 123.4, 123.9, 124.1, 125.1, 125.6, 126.1, 128.1, 132.2, 132.4, 145.0, 150.8, 151.4, 152.2, 152.4, 153.3, 214.02; *m/z* (MALDI-TOF): 1173.7 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 10e': as a yellow foam (0.30 g, 24%). $[\alpha]_D^{25}$ −31.3 (*c* 1.5, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3385, 2954, 2927, 2857, 2360 1747, 1493, 1373, 1111, 845; δ_H (400 MHz, $CDCl_3$) 0.84-0.91 (15 H, m), 1.14 (3 H, s), 1.19-1.43 (49 H, m), 1.70-1.79 (1 H, m), 1.97 (1 H, d, *J* 18.5 Hz), 2.07-2.22 (10 H, m), 2.37-2.43 (1 H, m), 2.49-2.60 (1 H, m), 3.23 and 3.88 (2 H, AB, *J* 14.5 Hz), 4.24-4.33 (3 H, m), 4.38 (1 H, septet, *J* 6.3 Hz), 4.50-4.60 (2 H, m), 4.64-4.72 (2 H, m), 6.26 (1 H, s), 6.32 (1 H, s), 6.40 (1 H, s), 6.90 (1 H, s), 7.12 (1 H, s), 7.21 (1 H, s), 7.23 (1 H, s), 7.24 (1 H, s), 7.27 (1 H, s), 7.33 (1 H, s), 7.57 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 14.2, 19.7, 19.9, 21.6, 21.7, 21.8, 21.9, 22.0, 22.1, 22.2, 22.6, 22.68, 22.74, 22.8, 25.1, 26.9, 27.6, 27.75, 27.8, 31.8, 32.0, 32.1, 33.4, 33.5, 34.7, 42.5, 42.9, 46.7, 47.9, 58.0, 70.1, 71.4, 71.7, 71.9, 101.6, 101.7, 102.7, 107.3, 122.5, 122.6, 123.1, 123.4, 124.1, 125.4, 125.7, 126.1, 127.2, 132.0, 132.1, 145.1, 150.8, 151.4, 152.2, 152.4, 153.3, 153.4, 154.6, 213.8; *m/z* (FAB): 1168.8 $[M+NH_4]^+$; the isotopic distribution of the observed data matched the theoretical $[M+NH_4]^+$ isotopic distribution.

Compound 11e: as a colourless foam (0.120 g, 8%), $[\alpha]_D^{25}$ +27.8 (*c* 1.2, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3500, 2954, 2928, 2857, 1748, 1494, 1372, 1189, 1114, 1053, 850; δ_H (400 MHz, $CDCl_3$) 0.81-0.92 (24 H, m), 1.01 (3 H, s), 1.17 (3 H, s), 1.23-1.44 (46 H, m), 1.59-1.67 (2 H, m), 1.70-2.14 (12 H, m), 2.38-2.44 (3 H, m), 2.49-2.60 (1 H, m), 3.29 and 3.65 (2 H, AB, *J* 15.2 Hz), 3.34 and 3.84

(2 H, AB, *J* 15.2 Hz), 4.20-4.32 (3 H, m), 4.51-4.61 (4 H, m), 4.75 (1 H, t, *J* 7.6 Hz), 6.22 (1 H, s), 6.42 (1 H, s), 6.52 (1 H, s), 6.54 (1 H, s), 6.80 (1 H, s), 6.86 (1 H, s), 6.89 (1 H, s), 6.92 (1 H, s), 7.08 (1 H, s), 7.33 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 14.1, 19.66, 19.74, 19.8, 20.0, 21.5, 21.7, 21.8, 21.86, 21.87, 21.9, 22.18, 22.2, 22.57, 22.60, 22.61, 22.8, 25.1, 25.2, 26.8, 26.9, 27.5, 27.6, 29.7, 31.9, 32.0, 32.2, 34.3, 34.5, 34.54, 34.8, 35.7, 36.2, 42.4, 42.5, 43.0, 47.6, 47.8, 48.1, 58.1, 58.2, 69.9, 70.9, 71.5, 71.6, 101.9, 102.0, 107.2, 107.6, 114.5, 122.5, 123.5, 123.97, 124.0, 124.1, 128.1, 125.8, 125.9, 126.5, 128.6, 130.9, 132.0, 133.0, 145.2, 146.1, 152.0, 152.2, 152.3, 152.8, 152.9, 154.7, 214.0; *m/z* (MALDI-TOF): 1387.8 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 11e': as a colourless foam (0.120 g, 8%). $[\alpha]_D^{25}$ +11.2 (*c* 1.3, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3500, 2954, 2927, 2857, 1748, 1495, 1373, 1190, 1114, 1053, 850; δ_H (400 MHz, $CDCl_3$) 0.81-0.92 (24 H, m), 1.06 (3 H, s), 1.24 (3 H, s), 1.23-1.44 (46 H, m), 1.50-1.59 (1 H, m), 1.67-1.75 (1 H, m), 1.77-2.14 (12 H, m), 2.34-2.43 (3 H, m), 2.52-2.64 (1 H, m), 3.12 and 3.68 (2 H, AB, *J* 14.7 Hz), 3.25 and 3.93 (2 H, AB, *J* 14.7 Hz), 4.23-4.32 (3 H, m), 4.51-4.59 (4 H, m), 4.74 (1 H, t, *J* 7.6 Hz), 6.23 (1 H, s), 6.42 (1 H, s), 6.49 (1 H, s), 6.50 (1 H, s), 6.81 (1 H, s), 6.90 (1 H, s), 6.91 (1 H, s), 6.93 (1 H, s), 7.06 (1 H, s), 7.32 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.09, 14.1, 14.13, 19.7, 19.8, 19.9, 20.0, 21.4, 21.7, 21.76, 21.8, 21.85, 21.9, 22.1, 22.2, 22.58, 22.59, 22.62, 22.8, 25.2, 25.6, 26.8, 26.9, 27.4, 27.5, 28.0, 31.9, 31.94, 32.0, 32.2, 33.4, 34.3, 34.5, 35.7, 36.3, 42.4, 42.5, 43.0, 43.2, 47.7, 47.76, 47.82, 48.3, 58.09, 58.11, 70.1, 70.9, 71.0, 71.4, 101.7, 102.0, 106.8, 107.1, 114.5, 122.3, 123.9, 123.95, 124.0, 125.7, 125.9, 126.4, 128.4, 130.5, 131.9, 132.6, 145.0, 146.2, 152.1, 152.2, 152.3, 152.8, 152.9, 154.7, 213.6, 213.9; *m/z* (MALDI-TOF): 1387.8 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

2,8,14,20-Tetrapentyl-4,16-di-(*S*)-camphorsulfonyloxy-10,22-dihydroxy-6,12,18,24-tetraisopropyloxyresorcin[4]arene 11e and 11e':

Using general procedure 1:

General procedure 1 followed using 2,8,14,20-tetrapentyl-6,12,18,24-tetraisopropopyloxyresorcin[4]arene **4e** (0.10 g, 0.11 mmol) and (*S*)-(+)-camphorsulfonyl chloride (0.43 g, 1.90 mmol) to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (96:4) to give compound **11e** (0.049 g, 34%) and compound **11e'** (0.044 g, 30%).

Using general procedure 2:

General procedure 2 followed using 2,8,14,20-tetrapentyl-6,12,18,24-tetraisopropopyloxyresorcin[4]arene **4e** (0.20 g, 0.21 mmol), *n*-butyllithium (2.5M in hexanes, 0.68 mL, 1.71 mmol) and (*S*)-(+)-camphorsulfonyl chloride (0.54 g, 2.14 mmol) at 0 °C to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (98:2) to give compound **11e** (0.13 g, 41%) and compound **11e'** (0.13 g, 41%).

2,8,14,20-Tetrapentyl-4-(*S*)-camphorsulfonyloxy-10,16,22-trihydroxy-6,12,18,24-tetracyclopentyloxyresorcin[4]arene 10f and 10f'and 2,8,14,20-tetrapentyl-4,16-di-(*S*)-camphorsulfonyloxy-10,22-dihydroxy-6,12,18,24-tetracyclopentyloxyresorcin[4]arene 11f and 11f'and:

Using general procedure 2:

General procedure 2 followed using 2,8,14,20-tetrapentyl-6,12,18,24-tetracyclopentyloxyresorcin[4]arene **4f** (1.0 g, 0.96 mmol), *n*-butyllithium (2.5M in hexanes, 0.76 mL, 1.92 mmol) and (*S*)-(+)-camphorsulfonyl chloride (0.48 g, 1.92 mmol) at −78 °C to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2 to give:

Compound 10f: as a yellow foam (0.28 g, 23%). $[\alpha]_D^{25}$ +26.7 (*c* 0.9, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3393, 2954, 2927, 1747, 1618, 1493, 1172; δ_H (400 MHz, $CDCl_3$) 0.83-0.89 (12 H, m), 0.90 (3 H, s), 1.15 (3 H, s), 1.16-1.36 (24 H, m), 1.39-1.56 (2 H, m), 1.59-1.71 (9 H, m), 1.77-2.00 (25 H, m), 2.08-2.19 (9 H, m), 2.38-2.44 (1 H, m), 2.54-2.61 (1 H, m), 3.21 and 3.80 (2 H, AB, *J* 14.8 Hz), 4.19-4.28 (3 H, m), 4.54-4.63 (2 H, m), 4.72-4.75 (1 H, m), 4.84 (1 H, quintet, *J* 4.0 Hz), 4.93 (1 H, quintet, *J* 2.8 Hz), 6.22 (1 H, s), 6.31 (1 H, s), 6.41 (1 H, s), 6.87 (1 H, s), 7.06 (1 H, s), 7.08 (1 H, s), 7.12 (1 H, s), 7.17 (1 H, s), 7.22 (1 H, s), 7.32 (1 H, s), 7.42 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 14.2, 19.7, 20.0, 22.6, 22.66, 22.7, 22.8, 23.7, 23.8, 23.83, 24.0, 24.1, 24.12, 24.4, 24.5, 25.3, 27.4, 27.7, 27.8, 29.7, 31.6, 31.8, 31.9, 32.0, 32.3, 32.4, 32.5, 32.7, 32.8, 32.9, 32.9, 33.0, 33.2, 33.24, 33.3, 33.5, 33.7, 34.6, 34.8, 35.8, 42.5, 42.9, 47.5, 47.8, 58.2, 79.0, 80.8, 80.9, 81.2, 101.2, 101.6, 102.4, 106.7, 121.8, 122.1, 122.9, 123.2, 123.3, 124.8, 125.1, 125.4, 125.8, 127.4, 132.0, 132.1, 144.9, 151.1, 151.6, 151.9, 152.9, 153.1, 153.2, 154.9, 214.0; *m/z* (MALDI-TOF): 1277.8 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 10f': as a yellow foam (0.27 g, 22%). $[\alpha]_D^{25}$ +4.6 (*c* 1.3, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3393, 2953, 2928, 1747, 1583, 1493, 1169; δ_H (400 MHz, $CDCl_3$) 0.83-0.92 (15 H, m), 1.15 (3 H, s), 1.16-1.36 (24 H, m), 1.39-1.56 (2 H, m), 1.59-2.00 (34 H, m), 2.09-2.21 (9 H, m), 2.39-2.43 (1

H, m), 2.48-2.59 (1 H, m), 3.21 and 3.86 (2 H, AB, *J* 14.5 Hz), 4.19-4.30 (3 H, m), 4.54-4.62 (2 H, m), 4.71-4.74 (1 H, m), 4.82 (1 H, quintet, *J* 4.1 Hz), 4.93 (1 H, m), 6.22 (1 H, s), 6.31 (1 H, s), 6.42 (1 H, s), 6.89 (1 H, s), 7.06 (1 H, s), 7.07 (1 H, s), 7.09 (1 H, s), 7.16 (1 H, s), 7.22 (1 H, s), 7.33 (1 H, s), 7.44 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 14.2, 19.7, 20.0, 22.6, 22.66, 22.74, 22.8, 23.7, 23.8, 23.9, 24.0, 24.1, 24.2, 24.4, 24.5, 25.1, 26.9, 27.4, 27.6, 27.8, 31.6, 31.8, 31.9, 32.0, 32.3, 32.4, 32.5, 32.7, 32.8, 32.9, 33.0, 33.1, 33.2, 33.5, 33.7, 34.6, 35.0, 36.0, 42.5, 42.9, 47.9, 48.0, 58.0, 79.1, 80.8, 80.9, 81.1, 101.3, 101.6, 102.5, 106.7, 121.8, 122.1, 122.9, 123.2, 123.4, 124.9, 125.0, 125.4, 125.8, 127.4, 131.8, 132.0, 144.5, 151.0, 151.5, 151.9, 152.9, 153.2, 153.3, 155.0, 213.8; *m/z* (MALDI-TOF): 1277.8 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 11f: as a colourless foam (0.15 g, 10%), $[\alpha]_D^{25}$ +25.7 (*c* 1.3, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3501, 2954, 2928 2869, 2358, 1748, 1493, 1454, 1357, 1171 and 832; δ_H (400 MHz, $CDCl_3$) 0.77 (3 H, s), 0.82-0.89 (12 H, m), 0.92 (3 H, s), 0.97 (3 H, s), 1.18 (3 H, s), 1.20-1.36 (24 H, m), 1.37-1.56 (2 H, m), 1.59-2.19 (48 H, m), 2.33-2.45 (3 H, m), 2.55-2.63 (1 H, m), 3.14 and 3.61 (2 H, AB, *J* 14.9 Hz), 3.29 and 3.82 (2 H, AB, *J* 14.9 Hz), 4.17-4.25 (2 H, m), 4.47-4.54 (2 H, m), 4.70-4.84 (4 H, m), 6.19 (1 H, s), 6.33 (1 H, s), 6.34 (1 H, m), 6.41 (1 H, s), 6.74 (1 H, s), 6.88 (3 H, s), 7.05 (1 H, s) and 7.30 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 14.14, 19.6, 19.7, 19.8, 20.0, 22.58, 22.6, 22.7, 23.9, 24.0, 24.10, 24.14, 24.2, 24.3, 25.2, 25.3, 26.8, 26.9, 27.4, 27.6, 27.9, 31.88, 31.9, 32.0, 32.1, 32.3, 32.5, 32.6, 32.7, 32.8, 32.92, 33.1, 33.4, 34.3, 34.5, 35.8, 36.5, 42.4, 42.5, 43.0, 47.4, 47.77, 47.8, 48.1, 58.1, 58.2, 78.9, 80.1, 80.8, 101.0, 101.6, 106.5, 106.8, 121.6, 123.2, 123.7, 124.0, 125.5, 125.8, 125.9, 126.4, 128.2, 130.3, 131.4, 132.5, 145.2, 146.1, 152.0, 152.3, 152.57, 152.6, 153.0, 154.9, 213.9, 217.1; *m/z* (MALDI-TOF): 1491.8 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 11f': as a colourless foam (0.15 g, 10%), $[\alpha]_D^{25}$ +5.8 (*c* 1.2, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3500, 2954, 2928, 2868, 1749, 1494, 1455, 1356, 1172, 1051 and 833; δ_H (400 MHz, $CDCl_3$) 0.87 (3 H, s), 0.90-0.96 (12 H, m), 0.97 (3 H, s), 1.11 (3 H, s), 1.23 (3 H, s), 1.25-1.37 (24 H, m), 1.39-1.56 (2 H, m), 1.59-2.17 (47 H, m), 2.20 (1 H, t, *J* 4.3 Hz), 2.38-2.51 (3 H, m), 2.61-2.67 (1 H, m), 3.14 and 3.61 (2 H, AB, *J* 14.9 Hz), 3.29 and 3.82 (2 H, AB, *J* 14.9 Hz), 4.17-4.25 (2 H, m), 4.47-4.54 (2 H, m), 4.70-4.84 (4 H, m), 6.19 (1 H, s), 6.33 (1 H, s), 6.34 (1 H, m), 6.41 (1 H, s), 6.74 (1 H, s), 6.88 (3 H, s), 7.05 (1 H, s), 7.30 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 14.14, 19.6, 19.7, 19.8, 20.0, 22.58, 22.6, 22.7, 23.9, 24.0, 24.1, 24.14, 24.2, 24.3, 25.2, 25.3, 26.8, 26.9, 27.4, 27.6, 27.9, 31.88, 31.9, 32.0, 32.1, 32.3, 32.5, 32.6, 32.7, 32.8, 32.9, 33.1, 33.4, 34.3, 34.5, 35.8, 36.5, 42.4, 42.5, 43.0, 47.4, 47.7, 47.8, 48.1, 58.1, 58.2, 78.9, 80.1, 80.8, 101.0, 101.6, 106.6, 106.8, 121.6,

123.2, 123.7, 124.0, 125.5, 125.8, 125.9, 126.4, 128.2, 130.3, 131.4, 132.5, 145.2, 146.1, 152.0, 152.3, 152.57, 152.6, 153.0, 154.9, 213.9, 217.1; *m/z* (MALDI-TOF): 1491.8 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

2,8,14,20-Tetrapentyl-4,16-di-(*S*)-camphorsulfonyloxy-10,22-dihydroxy-6,12,18,24-tetracyclopentyloxyresorcin[4]arene 11f and 11f':

Using general procedure 1:

General procedure 1 followed using 2,8,14,20-tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetracyclopentyloxyresorcin[4]arene **4f** (0.50 g, 0.48 mmol) and (*S*)-(+)-camphorsulfonyl chloride (1.44 g, 5.77 mmol) to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (98:2) to give compound **11f** (0.16 g, 23%) and compound **11f'** (0.16 g, 23%).

Using general procedure 2:

General procedure 2 followed using 2,8,14,20-tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetracyclopentyloxyresorcin[4]arene **4f** (0.20 g, 0.19 mmol), *n*-butyllithium (2.5M in hexanes, 0.62 mL, 1.54 mmol) and (*S*)-(+)-camphorsulfonyl chloride (0.48 g, 1.92 mmol) at 0 °C to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (99:1) to give compound **11f** (0.08 g, 28%) and compound **11f'** (0.08 g, 28%).

2,8,14,20-Tetrapentyl-4-(*S*)-camphorsulfonyloxy-10,16,22-trihydroxy-6,12,18,24-tetramethoxyresorcin[4]arene 10b and 10b' and 2,8,14,20-tetrapentyl-4,16-di-(*S*)-camphorsulfonyloxy-10,22-dihydroxy-6,12,18,24-tetramethoxyresorcin[4]arene 11b and 11b':

Using general procedure 2:

General procedure 2 followed using 2,8,14,20-tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene **4b** (0.20 g, 0.24 mmol), *n*-butyllithium (2.5M in hexanes, 0.12 mL, 0.29 mmol) and (*S*)-(+)-camphorsulfonyl chloride (0.80 g, 0.31 mmol) at −78 °C to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (98:2) to give:

Compound 10b: as a yellow foam (0.06 g, 25%). $[\alpha]_D^{25}$ +48.8 (*c* 1.7, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3402, 2923, 2856, 1732, 1614, 1494, 1455, 1372, 1291, 1238, 1193, 1169, 902, 835, 810; δ_H (400 MHz, $CDCl_3$) 0.79 (12 H, t, *J* 7.2 Hz), 0.84 (3 H, s), 1.07 (3 H, s), 1.12-1.35 (24 H, m), 1.62 (1 H,

m), 1.98-2.10 (11 H, m), 2.35 (1 H, td, *J* 14.4, 4.2 Hz), 2.46 (1 H, m), 3.23 and 3.76 (2 H, AB, *J* 15.0 Hz), 3.65 (3 H, s), 3.75 (6 H, s), 3.76 (3 H, s), 3.84 (3 H, s), 4.24 (3 H, m), 4.64 (1 H, t, *J* 7.1 Hz), 6.23 (1 H, s), 6.27 (1 H, s), 6.28 (1 H, s), 7.05 (1 H, s), 7.06 (1 H, s), 7.11 (1 H, s), 7.12 (1 H, s), 7.13 (1 H, s), 7.18 (1 H, s), 7.20 (1 H, s), 7.25 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 19.7, 19.9, 22.6, 22.7, 25.5, 26.8, 27.5, 27.6, 27.7, 31.8, 31.9, 32.0, 32.1, 33.1, 33.3,33.5, 34.2, 34.3, 35.7, 42.5, 43.0, 47.7, 47.8, 55.7, 55.8, 56.3, 58.2, 99.8, 99.9, 104.6, 122.7, 123.6, 123.7, 123.9, 124.2, 124.5, 124.7, 124.9, 126.1, 131.3, 131.8, 145.4, 152.5, 153.0, 153.1, 153.2, 153.7, 154.1, 156.1, 214.1; *m/z* (MALDI-TOF): 1061.7 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 10b': as a yellow foam (0.06 g, 25%). $[\alpha]_D^{25}$ –27.6 (*c* 1.8, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3405, 2928, 2856, 1745, 1614, 1586, 1494, 1445, 1353, 1291, 1194, 903, 835, 809; δ_H (400 MHz, $CDCl_3$) 0.70-0.84 (18 H, m), 1.18-1.28 (24 H, m), 1.66 (1 H, m), 1.89 (1 H, m), 1.97-2.08 (11 H, m), 2.30 (1 H, td, *J* 14.0, 4.0 Hz), 2.48 (1 H, m), 3.19 and 3.84 (2 H, AB, *J* 14.7 Hz), 3.66 (3 H, s), 3.74 (3 H, s), 3.75 (3 H, s), 3.85 (3 H, s), 4.19 (3 H, m), 4.61 (1 H, t, *J* 7.2 Hz), 6.23 (1 H, s), 6.27 (1 H, s), 6.28 (1 H, s), 6.85 (1 H, s), 7.12 (2 H, s), 7.13 (1 H, s), 7.18 (1 H, s), 7.20 (1 H, s), 7.24 (1 H, s), 7.27 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 19.7, 19.9, 22.6, 22.7, 25.1, 26.9, 27.5, 27.7, 31.8, 31.9, 32.0, 33.1, 33.3, 33.4, 34.0, 34.4, 35.8, 37.6, 42.6, 42.9, 47.7, 47.8, 55.6, 55.8, 56.3, 58.0, 99.7, 99.9, 100.3, 104.4, 108.6, 122.7, 122.8, 123.6, 124.0, 124.1, 124.6, 124.7, 124.9, 126.2, 131.1, 131.6, 145.1, 152.5, 153.0, 153.1, 153.2, 153.6, 154.1, 156.1, 214.0; *m/z* (FAB): 1061.7 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 11b: as a yellow foam (0.027 g, 9%). $[\alpha]_D^{25}$ −6.3 (*c* 1.0, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3468, 2928, 2856, 1746, 1615, 1585, 1495, 1463, 1356, 1290, 1193, 1067, 1053, 905, 831, 736; δ_H (400 MHz, $CDCl_3$) 0.79 (12 H, m), 0.85 (3 H, s), 0.91 (3 H, s), 1.09 (3 H, s), 1.16 (3 H, s), 1.18-1.38 (24 H, m), 1.44 (1 H, m), 1.62-1.74 (2 H, m), 1.80-1.98 (3 H, m), 2.04-2.16 (5 H, m), 2.38-2.61 (3 H, m), 3.22 and 3.79 (2 H, AB, *J* 15.0 Hz), 3.32 and 3.86 (2 H, AB, *J* 15.0 Hz), 3.60 (3 H, s), 3.82 (6 H, s), 3.83 (3 H, s), 4.23 (2 H, m), 4.55 (1 H, t, *J* 6.7 Hz), 4.75 (1 H, t, *J* 7.7 Hz), 6.23 (1 H, s), 6.41 (1 H, s), 6.86 (1 H, s), 6.89 (2 H, s), 6.99 (1 H, s), 7.11 (1 H, s), 7.36 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.2, 19.8, 20.0, 20.1, 22.7, 25.4, 27.0, 27.5, 27.6, 27.7, 32.0, 32.1, 33.1, 34.0, 34.3, 34.5, 36.1, 36.3, 42.6, 43.0, 47.7, 47.9, 48.2, 55.6, 56.0, 56.2, 58.2, 99.5, 100.1, 104.3, 104.9, 121.9, 123.5, 123.8, 125.2, 125.4, 126.2, 129.3, 130.3, 131.2, 131.6, 145.7, 146.0, 152.5, 153.0, 153.8, 153.9, 154.9, 156.5, 214.2; *m/z* (MALDI-TOF): 1275.6 $[M+Na]^+$; the isotopic distribution of the observed data matched the theoretical $[M+Na]^+$ isotopic distribution.

Compound 11b': as a yellow foam (0.027 g, 9%). $[\alpha]_D^{25}$ −10.4 (*c* 1.3, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3482, 2927, 2856, 1748, 1497, 1466, 1356, 1291, 1194, 1067, 905, 832; δ_H (400 MHz, $CDCl_3$) 0.79 (6 H, m), 0.80 (6 H, m), 0.82 (3 H, m), 0.84 (3 H, s), 1.06 (3 H, s), 1.10 (3 H, s), 1.12-1.30 (24 H, m), 1.39 (1 H, m), 1.50-1.60 (2 H, m), 1.69 (1 H, m), 1.87 (3 H, m), 2.15 (3 H, m), 2.37 (3 H, m), 2.53 (1 H, m), 3.15 and 3.73 (2 H, AB, *J* 14.9 Hz), 3.22 and 3.88 (2 H, AB, *J* 14.9 Hz), 3.57 (3 H, s), 3.78 (6 H, s), 3.79 (3 H, s), 4.17 (2 H, m), 4.49 (1 H, t, *J* 7.0 Hz), 4.67 (1 H, t , *J* 7.8 Hz), 6.18 (1 H, s), 6.35 (1 H, s), 6.60 (s1 H, s), 6.61 (1 H, s), 6.82 (1 H, s), 6.84 (1 H, s), 6.85 (1 H, s), 6.95 (1 H, s), 7.04 (1 H, s), 7.29 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 19.7, 19.9, 20.0, 22.5, 22.6, 22.7, 25.4, 25.5, 26.8, 26.9, 27.4, 27.5, 27.6, 27.7, 31.9, 32.0, 32.1, 33.1, 33.9, 34.2, 34.4, 36.0, 36.2, 42.4, 42.5, 42.9, 43.1, 47.8, 47.9, 48.0, 48.2, 55.5, 56.0, 56.1, 56.2, 58.2, 99.4, 100.0, 104.3, 104.7, 122.0, 123.3, 123.4, 123.7, 125.1, 125.2, 125.4, 126.0, 129.0, 130.1, 131.0, 131.4, 145.5, 145.9, 152.5, 152.9, 153.8, 153.9, 154.9, 156.4, 214.1; *m/z* (MALDI-TOF): 1252.7 (M^+); the isotopic distribution of the observed data matched the theoretical (M^+) isotopic distribution..

2,8,14,20-Tetrapentyl-4,10,16,22-tetramethoxymethyl--6,12,18,24-tetramethoxyresorcin[4]arene 12b:

2,8,14,20-Tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene **4b** (0.50 g, 0.6 mmol) was dissolved in tetrahydrofuran (20 mL) under nitrogen and the solution was cooled down to −78 °C. *n*-Butyllithium (2.5M in hexanes, 2.0 mL, 4.9 mmol) was slowly added to the solution and the reaction mixture was stirred for 30 minutes at −78 °C. Methoxymethyl chloride (370 µL, 4.9 mmol) was then added to the reaction mixture. The mixture was allowed to warm to room temperature and was stirred for 12 hours. Brine (20 mL) was then added and the phases were separated. The aqueous phase was then extracted with diethyl ether (3 x 10 mL). The combined organic phases were washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was placed on a column of silica gel and eluted with EtOAc/hexane (15:85) to give compound **12b** as a colourless foam (0.55 g, 90%). ν_{max} (DCM)/cm^{-1} 2924, 1610, 1582, 1495, 1279, 1147, 731; δ_H (400 MHz, $CDCl_3$) 0.87 (12 H, t, *J* 7.0 Hz), 1.22-1.39 (24 H, m), 1.80-1.87 (8 H, m), 3.34 (12 H, s), 3.64 (120 H, s), 4.50 (4 H, t, *J* 7.6 Hz), 4.74 and 4.86 (8 H, AB, *J* 6.4 Hz), 6.51 (4 H, s), 6.66 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.2, 22.7, 27.8, 32.2, 34.9, 35.5, 55.9, 55.7, 95.6, 99.9, 126.0, 126.9, 127.4, 153.5, 155.5; *m/z* (FAB): 1000.6293 $[M]^+$; $[C_{60}H_{88}O_{12}]^+$ requires 1000.6276.

2,8,14,20-Tetrapentyl-4,10,16,22-tetramethoxymethyl--6,12,18,24-tetraisopropyloxyresorcin[4]arene 12e:

2,8,14,20-Tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetraisopropyloxyresorcin[4]arene **4e** (0.35 g, 0.4 mmol) was dissolved in tetrahydrofuran (10 mL) under nitrogen and the solution was cooled down to 0 °C. *n*-Butyllithium (2.5M in hexanes, 0.9 mL, 2.2 mmol) was slowly added to the solution and the reaction mixture was stirred for 30 minutes at 0 °C. Methoxymethyl chloride (170 µL, 2.2 mmol) was then added to the reaction mixture. The mixture was allowed to warm to room temperature and was stirred for 12 hours. Brine (20 mL) was then added and the phases were separated. The aqueous phase was then extracted with diethyl ether (3 x 10 mL). The combined organic phases were washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was placed on a column of silica gel and eluted with EtOAc/hexane (20:80) to give compound **12e** as a colourless foam (0.191 g, 46%). ν_{max} (DCM)/cm^{-1} 2953, 2928, 2857, 1609, 1581, 1496, 1284, 1149, 1117, 1058, 1101; δ_H (400 MHz, $CDCl_3$) 0.84 (12 H, t, *J* 6.9 Hz), 0.94-1.03 (8 H, m), 1.19-1.41 (40 H, m), 1.74-1.85 (8 H, m), 3.38 (12 H, s), 4.34 (4 H, septet, *J* 5.3 Hz), 4.50 (4 H, t, *J* 7.5 Hz), 4.86 (8 H, m), 6.49 (4 H, s), 6.66 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.2, 21.8, 22.3, 22.7, 27.8, 32.1, 35.0, 35.4, 55.7, 69.8, 95.2, 101.6, 126.4, 128.2, 153.4, 153.5; *m/z* (FAB): 1113.7624 $[M+H]^+$; $[C_{68}H_{104}O_{12}+H]^+$ requires 1113.7608.

2,8,14,20-Tetra-(2-methylpropyl)-4,10,16,22-tetracamphorsulfonyloxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*S*,*R*)-13a and (*P*,*S*,*S*)-13a':

Using general procedure 2:

General procedure 2 followed using 2,8,14,20-tetra-(2-methylpropyl)-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene **7** (1.0 g, 1.3 mmol), *n*-butyllithium (2.5M in hexanes, 4.2 mL, 10.4 mmol) and (*S*)-(+)-camphorsulfonyl chloride (2.6 g, 10.4 mmol) at 0 °C to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (97:3) to give:

Compound (*M*,*S*,*R*)-13a: as colourless crystals (0.54 g, 26%). M.p.>248 °C (decomp.); $[\alpha]_D^{25}$ +43.3 (*c* 0.49, $CHCl_3$); ν_{max} ($CHCl_3$) /cm^{-1} 2954, 1748, 1611, 1496, 1366, 1178, 1073, 1005, 924, 835; δ_H (400 MHz, $CDCl_3$) 0.89 (12 H, s), 0.94 (12 H, d, *J* 6.0 Hz), 0.96 (12 H, d, *J* 6.0Hz), 1.12 (12 H, s), 1.40-1.50 (4 H, ddd, *J* 4.0, 8.0, 13.5 Hz), 1.57-1.64 (4 H, m), 1.66-1.71 (12 H, m), 1.96 (4 H, d, *J* 18.6 Hz), 2.01-2.10 (4 H, m), 2.13 (4 H, t, *J* 4.1 Hz), 2.36-2.53 (8 H, m), 3.26 and 3.84

(8 H, AB, *J* 15.2 Hz), 3.67 (12 H, s), 4.63 (4 H, t, *J* 6.8 Hz), 6.65 (4 H, s), 6.82 (4 H, s); δ_C (100 MHz, $CDCl_3$) 19.7, 19.9, 22.8, 22.9, 25.1, 25.8, 26.9, 33.9, 42.5, 42.9, 43.9, 47.9, 48.5, 55.9, 58.1, 104.9, 126.4, 128.3, 131.0, 145.7, 155.4, 214.0; *m/z* (FAB): 1625.7352 $[M+H]^+$; $[C_{88}H_{120}O_{20}S_4+H]^+$ requires 1625.7334.

Compound (*P,S,S*)-13a': as a colourless foam (0.51 g, 24%). $[\alpha]_D^{25}$ +10.0 (*c* 1.2, $CHCl_3$); ν_{max} (DCM)/cm^{-1} 2953, 1747, 1496, 1362, 1179, 1067, 924, 834; δ_H (400 MHz, $CDCl_3$) 0.93 (24 H, t, *J* 5.0 Hz), 0.95 (12 H, s), 1.16 (12 H, s), 1.42-1.48 (4 H, ddd, *J* 3.4, 9.2, 12.4 Hz), 1.56-1.66 (8 H, m), 1.71 (8 H, t, *J* 7.0 Hz), 1.96 (4 H, d, *J* 18.4 Hz), 2.02-2.09 (4 H, m), 2.12 (4 H, t, *J* 4.4 Hz), 2.37-2.52 (8 H, m), 3.25 and 3.84 (8 H, AB, *J* 15.0 Hz), 3.71 (12 H, s), 4.61 (4 H, t, *J* 7.4 Hz), 6.59 (4 H, s), 6.85 (4 H, s); δ_C (100 MHz, $CDCl_3$) 19.7, 20.0, 22.76, 22.77, 25.1, 25.8, 26.9, 34.2, 42.4, 43.0, 43.5, 47.8, 48.6, 55.9, 58.1, 104.9, 126.3, 128.1, 130.7, 145.9, 155.5, 213.8; *m/z* (FAB): 1624.7234; $[C_{88}H_{120}O_{20}S_4]^+$ requires 1624.7256.

2,8,14,20-Tetra-(2-methylpropyl)-4,10,16,22-tetracamphorsulfonyloxy-6,12,18,24-tetramethoxyresorcin[4]arene (*P,R,S*)-13b and (*M,R,R*)-13b':

Using general procedure 2:

General procedure 2 followed using 2,8,14,20-tetra-(2-methylpropyl)-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene **7** (1.0 g, 1.3 mmol), *n*-butyllithium (2.5M in hexanes, 4.2 mL, 10.4 mmol) and (*R*)-(–)-camphorsulfonyl chloride (2.6 g, 10.4 mmol) at 0 °C to give the diastereoisomeric mixture which was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (97:3) to give:

Compound (*P,R,S*)-13b: as colourless crystals (0.76 g, 36%). $[\alpha]_D^{25}$ −49.6 (*c* 1.1, $CHCl_3$); ν_{max} ($CHCl_3$) /cm^{-1} 2955, 1747, 1612, 1496, 1366, 1180, 1067, 1005, 917, 835; δ_H (400 MHz, $CDCl_3$) 0.89 (12 H, s), 0.94 (12 H, d, *J* 6.0 Hz), 0.96 (12 H, d, *J* 6.0 Hz), 1.12 (12 H, s), 1.40-1.50 (4 H, ddd, *J* 4.0, 8.0, 13.5 Hz), 1.57-1.64 (4 H, m), 1.66-1.71 (12 H, m), 1.96 (4 H, d, *J* 18.4 Hz), 2.01-2.10 (4 H, m), 2.13 (4 H, t, *J* 4.1 Hz), 2.36-2.53 (8 H, m), 3.26 and 3.83 (8 H, AB, *J* 14.8 Hz), 3.66 (12 H, s), 4.63 (4 H, t, *J* 7.4 Hz), 6.64 (4 H, s), 6.82 (4 H, s); δ_C (100 MHz, $CDCl_3$) 19.7, 19.9, 22.8, 22.9, 25.1, 25.8, 26.9, 33.9, 42.5, 42.9, 43.9, 47.9, 48.5, 55.9, 58.1, 104.9, 126.4, 128.3, 131.0, 145.7, 155.4, 214.0; *m/z* (FAB): 1624.7395 $[M]^+$; $[C_{88}H_{120}O_{20}S_4]^+$ requires 1624.7256.

Compound (*M,R,R*)-13b': as a colourless foam (0.74 g, 35%). $[\alpha]_D^{25}$ −12.8 (*c* 1.6, $CHCl_3$); ν_{max} (DCM)/cm^{-1} 2955, 1747, 1497, 1367, 1179, 918, 836; δ_H (400 MHz, $CDCl_3$) 0.92 (12 H, s, *J* 5.0 Hz), 0.94 (24 H, d, *J* 6.4 Hz), 1.15 (12 H, s), 1.42-1.48 (4 H, ddd, *J* 3.4, 9.2, 12.4 Hz), 1.56-1.66 (8

H, m), 1.71 (8 H, t, *J* 7.0 Hz), 1.96 (4 H, d, *J* 18.4 Hz), 2.02-2.09 (4 H, m), 2.12 (4 H, t, *J* 4.4 Hz), 2.37-2.52 (8 H, m), 3.25 and 3.84 (8 H, AB, *J* 15.2 Hz), 3.70 (12 H, s), 4.60 (4 H, t, *J* 7.2 Hz), 6.59 (4 H, s), 6.85 (4 H, s); δ_C (100 MHz, $CDCl_3$) 19.7, 20.0, 22.76, 22.77, 25.1, 25.8, 26.9, 34.2, 42.4, 43.0, 43.5, 47.8, 48.6, 55.9, 58.1, 104.9, 126.3, 128.1, 130.7, 145.9, 155.5, 213.8; *m/z* (FAB): 1624.7480; $[C_{88}H_{120}O_{20}S_4]^+$ requires 1624.7256.

2,8,14,20-Tetrapropyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*P*,*S*)-(+)-4a:

Using general procedure 3:

General procedure 3 followed using (*M*,*S*,*R*)-**8a** (0.52 g, 0.33 mmol) and sodium hydroxide (1.32 g, 33.1 mmol). The residue was crystallized from methanol to yield compound (*P*,*S*)-(+)-**4a** as pale orange plates (0.21 g, 89 %). M.p. 212-213 °C**.** $[\alpha]_D^{25}$ +88.5 (*c* 2.6); δ_H (500 MHz, $CDCl_3$) 0.99 (12 H, t, *J* 7.4 Hz), 1.32 (8 H, hex, *J* 7.4 Hz), 2.20 (8 H, q, *J* 7.4 Hz), 3.84 (12 H, s), 4.31 (4 H, t, *J* 8.0 Hz), 6.35 (4 H, s), 7.24 (4 H, s), 7.51 (4 H, s); δ_C (125 MHz, $CDCl_3$) 14.7, 21.7, 33.4, 36.7, 56.6, 100.7, 124.5, 125.3, 125.4, 153.7, 154.4; Found: C, 73.8; H, 7.8; $C_{44}H_{56}O_8$; requires C, 74.1; H, 7.9 %.

2,8,14,20-Tetrapropyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*R*)-(−)-4a:

Using general procedure 3:

General procedure 3 followed using (*P*,*S*,*S*)-**8a'** (0.16 g, 0.10 mmol) and sodium hydroxide (0.41 g, 10.2 mmol). The residue was crystallized from methanol to yield compound (*M*,*R*)-(−)-**4a** as pale orange plates (0.057 g, 78 %), M.p. 212-213 °C**.** $[\alpha]_D^{25}$ −89.2 (*c* 1.2). δ_H (500 MHz, $CDCl_3$) 0.99 (12 H, t, *J* 7.4 Hz), 1.32 (8 H, hex, *J* 7.2 Hz), 2.20 (8 H, q, *J* 7.2 Hz), 3.84 (12 H, s), 4.31 (4 H, t, *J* 8.0 Hz), 6.35 (4 H, s), 7.24 (4 H, s), 7.50 (4 H, s); δ_C (125 MHz, $CDCl_3$) 14.7, 21.7, 33.4, 36.7, 56.6, 100.7, 124.5, 125.3, 125.4, 153.7, 154.4; Found: C, 72.7; H, 8.0; $C_{44}H_{56}O_8.CH_3OH$; requires C, 72.6; H, 8.1 %.

2,8,14,20-Tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*P*,*S*)-(+)-4b:

Using general procedure 3:

General procedure 3 followed using **11b** (0.1 g, 0.08 mmol) and sodium hydroxide (0.6 g, 15.0 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (98:2) to yield compound (*P*,*S*)-(+)-**4b** as a colourless foam (0.05 g, 70%). $[\alpha]_D^{25}$ +52.5 (*c* 1.1, $CHCl_3$); ν_{max} (DCM)/cm^{-1} 3403, 2927, 2856, 1619, 1588, 1495, 1464, 1335, 1293, 1239, 1196, 1166, 1089, 1018, 901, 836; δ_H (400 MHz, $CDCl_3$) 0.89 (12 H, t, *J* 7.0 Hz), 1.25-1.38 (24 H, m), 2.15-2.20 (8 H, m), 3.83 (12 H, s), 4.26 (4 H, t, *J* 7.6 Hz), 6.34 (4 H, s), 7.21 (4 H, s), 7.52 (4 H, s); δ_C (100 MHz, $CDCl_3$) 13.1, 21.7, 26.8, 30.9, 32.1, 32.9, 54.8, 98.9, 122.6, 123.6, 123.7, 151.9, 152.6; *m/z* (FAB): 825.5306 $[M+H]^+$; $[C_{52}H_{72}O_8+H]^+$ requires 825.5319.

General procedure 3 followed using (*M*,*S*,*R*)-**8b** (0.4 g, 0.23 mmol) and sodium hydroxide (3.0 g, 75 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (98:2) to yield compound (*P*,*S*)-(+)-**4b** as a colourless foam (0.126 g, 65%).

2,8,14,20-Tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*R*)-(−)-4b:

Using general procedure 3:

General procedure 3 followed using **11b'** (0.1 g, 0.08 mmol) and sodium hydroxide (0.6 g, 15.0 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (98:2) to yield compound (*M*,*R*)-(−)-**4b** as a colourless foam (0.05 g, 70%). $[\alpha]_D^{25}$ −51.6 (*c* 1.1, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3403, 2927, 2856, 1619, 1588, 1495, 1464, 1335, 1293, 1239, 1196, 1166, 1089, 1018, 901, 836; δ_H (400 MHz, $CDCl_3$) 0.89 (12 H, t, *J* 7.0 Hz), 1.25-1.38 (24 H, m), 2.15-2.20 (8 H, m), 3.83 (12 H, s), 4.26 (4 H, t, *J* 7.6 Hz), 6.34 (4 H, s), 7.21 (4 H, s), 7.52 (4 H, s); δ_C (100 MHz, $CDCl_3$) 13.1, 21.7, 26.8, 30.9, 32.1, 32.9, 54.8, 98.9, 122.6, 123.6, 123.7, 151.9, 152.6; *m/z* (FAB): 842.5558 $[M+NH_4]^+$; $[C_{52}H_{72}O_8+NH_4]^+$ requires 842.5565.

General procedure 3 followed using (*P*,*S*,*S*)-**8b'** (0.34 g, 0.20 mmol) and sodium hydroxide (2.5 g, 62.5 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (98:2) to yield compound (*M*,*R*)-(−)-**4b** as a colourless foam (0.105 g, 64%).

2,8,14,20-Tetraheptyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*P*,*S*)-(+)-4c:

Using general procedure 3:

General procedure 3 followed using (*M*,*S*,*R*)-**8c** (0.37 g, 0.2 mmol) and sodium hydroxide (1.6 g, 40 mmol). The residue was crystallized from methanol to yield compound (*P*,*S*)-(+)-**4c** as colourless plates (0.16 g, 84%). M.p. 141.7–142.5 °C. $[\alpha]_D^{25}$ +65.4 (*c* 1.3). δ_H (500 MHz, $CDCl_3$) 0.90 (12 H, m), 1.20-1.42 (40 H, m), 2.10-2.28 (8 H, m), 3.84 (12 H, s), 4.27 (4 H, t, *J* 8.0 Hz), 6.35 (4 H, s), 7.23 (4 H, s), 7.52, (4 H, s); δ_C (125 MHz, $CDCl_3$) 14.8, 23.3, 28.8, 30.0, 30.3, 32.6, 33.8, 34.7, 56.6, 100.7, 124.4, 125.3, 125.4, 153.7, 154.3; Found: C, 76.9; H, 9.6; $C_{60}H_{88}O_8$; requires C, 76.9; H, 9.5 %.

2,8,14,20-Tetraheptyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*R*)-(−)-4c

Using general procedure 3:

General procedure 3 followed using (*P*,*S*,*S*)-**8c'** (0.32 g, 0.18 mmol) and sodium hydroxide (0.71 g, 17.8 mmol). The residue was crystallized from methanol to yield compound (*M*,*R*)-(−)-**4c** as colourless plates (0.12 g, 70%). M.p. 140.6–141.8 °C. $[\alpha]_D^{25}$ −66.1 (*c* 1.9). δ_H (500 MHz, $CDCl_3$) 0.90 (12 H, m), 1.17-1.46 (40 H, m), 2.10-2.28 (8 H, m), 3.84 (12 H, s), 4.27 (4 H, t, *J* 7.8 Hz), 6.35 (4 H, s), 7.22 (s, 4 H), 7.54 (4 H, s); δ_C (125 MHz, $CDCl_3$) 14.8, 23.3, 28.8, 30.0, 30.4, 32.6, 33.8, 34.7, 56.6, 100.7, 124.4, 125.3, 125.4, 153.7, 154.3; *m/z* (FAB): 936.6469 $[M^+]$; $[C_{60}H_{88}O_8]^+$ requires 936.6479.

2,8,14,20-Tetraundecyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*P*,*S*)-(+)-4d:

Using general procedure 3:

General procedure 3 followed using (*M*,*S*,*R*)-**8d** (0.11 g, 0.05 mmol) and sodium hydroxide (0.22 g, 5.5 mmol). The residue was crystallized from methanol to yield compound (*P*,*S*)-(+)-**4d** as tan micro-crystals (0.05 g, 79%). M.p. 148.5-149.5 °C. $[\alpha]_D^{25}$ +51.0 (*c* 1.3). δ_H (500 MHz, $CDCl_3$) 0.89 (12 H, m), 1.12-1.48 (72 H, m), 2.07-2.29 (8 H, m), 3.84 (12 H, s), 4.27 (4 H, t, *J* 7.4 Hz), 6.35 (4 H, s), 7.22 (4 H, s), 7.53 (4 H, s); δ_C (125 MHz, $CDCl_3$) 14.8, 23.4, 28.8, 30.1, 30.42, 30.44, 30.5, 32.6, 33.8, 34.7, 56.6, 100.7, 124.4, 125.3, 125.4, 153.6, 154.3; Found: C, 77.9; H, 10.7; $C_{44}H_{56}O_8.CH_3CH_2OH$; requires C, 77.6; H, 10.5 %.

2,8,14,20-Tetraundecyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*R*)-(−)-4d:

Using general procedure 3:

General procedure 3 followed using (*P*,*S*,*S*)-**8d'** (0.064 g, 0.03 mmol) and sodium hydroxide (0.15 g, 3.8 mmol). The residue was crystallized from methanol to yield compound (*M*,*R*)-(−)-**4d** as pale orange waxy micro-crystals (0.022 g, 60%), M.p. 146.5-147.5 °C (softens 141-143). $[\alpha]_D^{25}$ –46.9 (*c* 1.0); δ_H (500 MHz, $CDCl_3$) 0.90 (12 H, m), 1.22-1.42 (72 H, m), 2.16-2.23 (8 H, m), 3.84 (12 H, s), 4.28 (4 H, t, *J* 7.8 Hz), 6.35 (4 H, s), 7.22 (4 H, s), 7.52 (4 H, s); δ_C (125 MHz, $CDCl_3$) 14.8, 23.4, 28.8, 30.1, 30.41, 30.44, 30.5, 32.6, 33.7, 34.7, 56.5, 100.7, 124.4, 125.3, 125.4, 153.6, 154.3.

2,8,14,20-Tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetraisopropoxyresorcin[4]arene (*P*,*S*)-(+)-4e:

Using general procedure 3:

General procedure 3 followed using **10e** (0.09 g, 0.08 mmol) and sodium hydroxide (0.2 g, 5.0 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (99:1) to yield compound (*P*,*S*)-(+)-**4e** as a colourless foam (0.065 g, 89%). $[\alpha]_D^{25}$ +36.8 (*c* 1.3, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3372, 2928, 2858, 1618, 1584, 1492, 1111, 939, 849, 735; δ_H (400 MHz, $CDCl_3$) 0.90 (12 H, t , *J* 7.0 Hz), 1.19-1.38 (48 H, m), 2.10-2.29 (8 H, m), 4.28 (4 H, t, *J* 7.9 Hz), 4.55 (4 H, septet, *J* 6.1 Hz), 6.35 (4 H, s), 7.23 (4 H, s), 7.72 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.2, 21.8, 21.9, 22.7, 27.8, 33.4, 34.0, 37.6, 71.7, 102.5, 123.7, 125.4, 125.6, 151.7, 152.8; *m/z* (FAB): 937.6571 $[M+H]^+$; $[C_{60}H_{88}O_8+H]^+$ requires 937.6557.

General procedure 3 followed using **11e** (0.11 g, 0.08 mmol) and sodium hydroxide (0.44 g, 11.0 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (99:1) to yield compound (*P*,*S*)-(+)-**4e** as a colourless foam (0.06 g, 82%)

2,8,14,20-Tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetraisopropoxyresorcin[4]arene (*M*,*R*)-(−)-4e:

Using general procedure 3:

General procedure 3 followed using **10e'** (0.09 g, 0.08 mmol) and sodium hydroxide (0.2 g, 5.0 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (99:1) to yield compound (*M*,*R*)-(−)-**4e** as a colourless foam (0.06 g, 82%). $[\alpha]_D^{25}$ −36.5 (*c* 1.2, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3372, 2928, 2858, 1618, 1584, 1492, 1111, 939, 849, 735; δ_H (400 MHz, $CDCl_3$) 0.90 (12 H, t , *J* 7.0 Hz), 1.19-1.38 (48 H, m), 2.10-2.29 (8 H, m), 4.28 (4 H, t, *J* 7.9 Hz), 4.55 (4 H, septet, *J* 6.1 Hz), 6.35 (4 H, s), 7.23 (4 H, s), 7.72 (4 H, s); δ_C (100 MHz, $CDCl_3$) 14.2, 21.8, 21.9, 22.7, 27.8, 33.4, 34.0, 37.6, 71.7, 102.5, 123.7, 125.4, 125.6, 151.7, 152.8; *m/z* (FAB): 936.6474 (M^+); $[C_{60}H_{88}O_8]^+$ requires 936.6474.

General procedure 3 followed using **11e'** (0.175 g, 0.13 mmol) and sodium hydroxide (0.90 g, 22.5 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2/EtOAc (99:1) to yield compound (*M*,*R*)-(−)-**4e** as a colourless foam (0.10 g, 83%)

2,8,14,20-Tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetracyclopentyloxyresorcin[4]arene (*P*,*S*)-(+)-4f:

Using general procedure 3:

General procedure 3 followed using **11f** (0.10 g, 0.07 mmol) and sodium hydroxide (0.44 g, 11.0 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2 to yield compound (*P*,*S*)-(+)-**4f** as a colourless foam (0.051 g, 72%). $[\alpha]_D^{25}$ +12.0 (*c* 1.0, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3370, 2927, 2857, 1619, 1585, 1493, 1166, 973; δ_H (400 MHz, $CDCl_3$) 0.90 (12 H, t, *J* 7.0 Hz), 1.20-1.37 (24 H, m), 1.60-1.75 (8 H, m), 1.83-1.97 (24 H, m), 2.03 (4 H, m), 2.13 (4 H, m), 4.24 (4 H, t, *J* 7.8 Hz), 4.78 (4 H, m), 6.36 (4 H, s), 7.23 (4 H, s), 7.62 (4 H, s); δ_C (100 MHz, $CDCl_3$); 14.2, 22.7, 23.7, 24.0, 27.7, 31.9, 32.4, 32.9, 33.2, 34.0, 81.1, 102.5, 123.6, 125.1, 125.3, 152.0, 152.7; *m/z* (FAB): 1041.7179 $[M+H]^+$; $[C_{68}H_{96}O_8+H]^+$ requires 1041.7183.

General procedure 3 followed using **10f** (0.10 g, 0.08 mmol) and sodium hydroxide (0.22 g, 5.5 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2 to yield compound (*P*,*S*)-(+)-**4f** as a colourless foam (0.062 g, 75%).

2,8,14,20-Tetrapentyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetracyclopentyloxyresorcin[4]arene (*M*,*R*)-(−)-4f:

Using general procedure 3:

General procedure 3 followed using **11f'** (0.11 g, 0.07 mmol) and sodium hydroxide (0.44 g, 11.0 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2 to yield compound (*M*,*R*)-(−)-**4f** as a colourless foam (0.06 g, 76%). $[\alpha]_D^{25}$ −12.3 (*c* 1.1, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3370, 2927, 2857, 1619, 1585, 1493, 1166, 973; δ_H (400 MHz, $CDCl_3$) 0.90 (12 H, t, *J* 7.0 Hz), 1.20-1.37 (24 H, m), 1.60-1.75 (8 H, m), 1.83-1.97 (24 H, m), 2.03 (4 H, m), 2.13 (4 H, m), 4.24 (4 H, t, *J* 7.8 Hz), 4.78 (4 H, m), 6.36 (4 H, s), 7.23 (4 H, s), 7.62 (4 H, s); δ_C (100 MHz, $CDCl_3$); 14.2, 22.7, 23.7, 24.0, 27.7, 31.9, 32.4, 32.9, 33.2, 34.0, 81.1, 102.5, 123.6, 125.1, 125.3, 152.0, 152.7; *m/z* (FAB): 1041.7176 $[M+H]^+$; $[C_{68}H_{96}O_8+H]^+$ requires 1041.7183.

Using general procedure 3:

General procedure 3 followed using **10f'** (0.11 g, 0.09 mmol) and sodium hydroxide (0.22 g, 5.5 mmol). The residue was placed on a column of silica gel and eluted with CH_2Cl_2 to yield compound (*M*,*R*)-(−)-**4f** as a colourless foam (0.071 g, 78%)

2,8,14,20-Tetra-2-methylpropyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*P*,*S*)-(+)-7:

Using general procedure 3:

General procedure 3 followed using **13a** (0.24 g, 0.15 mmol) and sodium hydroxide (2.0 g, 50.0 mmol). The residue was placed on a column of silica gel and eluted with Petroleum Ether/EtOAc (8:2) to yield compound (*P*,*S*)-(+)-**7** as a colourless foam (0.09 g, 80%). $[\alpha]_D^{25}$ +65.3 (*c* 1.1, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3397, 2952, 2866, 1618, 1588, 1496, 1089, 908; δ_H (400 MHz, $CDCl_3$) 0.94 (12 H, d, *J* 6.8 Hz), 0.94 (12 H, d, *J* 6.8 Hz), 1.44 (4 H, septet, *J* 6.8 Hz), 2.07 (8 H, t, *J* 7.2 Hz), 3.83 (12 H, s), 4.41 (4 H, t, *J* 7.8 Hz), 6.35 (4 H, s), 7.21 (4 H, s), 7.54 (4 H, s); δ_C (100 MHz, $CDCl_3$) 22.7, 22.8, 26.0, 30.6, 42.9, 55.9, 100.0, 124.0, 124.5, 124.6, 152.9, 153.6.

2,8,14,20-Tetra-2-methylpropyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxyresorcin[4]arene (*M*,*R*)-(−)-7:

Using general procedure 3:

General procedure 3 followed using **13a'** (0.2 g, 0.12 mmol) with sodium hydroxide (2.0 g, 50.0 mmol). The residue was placed on a column of silica gel and eluted with Petroleum Ether/EtOAc

(8:2) to yield (*M*,*R*)-(−)-**7** as a colourless foam (0.07 g, 74%). $[\alpha]_D^{25}$ −65.5 (*c* 1.0, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3397, 2952, 2866, 1618, 1588, 1496, 1089, 908; δ_H (400 MHz, $CDCl_3$) 0.94 (12 H, d, *J* 6.8 Hz), 0.94 (12 H, d, *J* 6.8 Hz), 1.44 (4 H, septet, *J* 6.8 Hz), 2.07 (8 H, t, *J* 7.2 Hz), 3.83 (12 H, s), 4.41 (4 H, t, *J* 7.8 Hz), 6.35 (4 H, s), 7.21 (4 H, s), 7.54 (4 H, s); δ_C (100 MHz, $CDCl_3$) 22.7, 22.8, 26.0, 30.6, 42.9, 55.9, 100.0, 124.0, 124.5, 124.6, 152.9, 153.6.

Using general procedure 3:

General procedure 3 followed using **13b** (0.22 g, 0.14 mmol) with sodium hydroxide (2.0 g, 50.0 mmol). The residue was placed on a column of silica gel and eluted with Petroleum Ether/EtOAc (8:2) to yield (*M*,*R*)-(−)-**7** as a colourless foam (0.08 g, 78%). $[\alpha]_D^{25}$ −65.6 (*c* 6.2, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 3397, 2952, 2866, 1618, 1588, 1496, 1089, 908; δ_H (400 MHz, $CDCl_3$) 0.94 (12 H, d, *J* 6.8 Hz), 0.94 (12 H, d, *J* 6.8 Hz), 1.44 (4 H, septet, *J* 6.8 Hz), 2.07 (8 H, t, *J* 7.2 Hz), 3.83 (12 H, s), 4.41 (4 H, t, *J* 7.8 Hz), 6.35 (4 H, s), 7.21 (4 H, s), 7.54 (4 H, s); δ_C (100 MHz, $CDCl_3$) 22.7, 22.8, 26.0, 30.6, 42.9, 55.9, 100.0, 124.0, 124.5, 124.6, 152.9, 153.6.

Tetrabenzoxazine (*P*,*R*,*S*)-5: [6b]

Tetracyclopentyloxyresorcinarene (*M*,*R*)-(−)-**4f** (0.04 g, 0.04 mmol) was dissolved in dry toluene (5 mL) in a 25 mL oven dried round-bottomed flask under nitrogen. *N*,*N*-bis(methoxymethyl)-(*R*)-(+)-*N*- -methylbenzylamine (0.08 g, 0.38 mmol) in toluene (1 mL) was added in one portion and the reaction mixture heated under reflux for 5 days. After this time, the reaction was allowed to cool to room temperature and the solvent removed under reduced pressure. The residue was placed on a column of silica gel and eluted with Petroleum Ether/EtOAc (85:15) to yield tetrabenzoxazine (*P*,*R*,*S*)-**5** as a colourless foam (0.036 g, 58%). $[\alpha]_D^{25}$ +129.8 (*c* 1.6, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 2953, 2867, 1583, 1464, 1321, 1228, 1170, 1117, 939; δ_H (400 MHz, 50 °C, $CDCl_3$) 0.87 (12 H, t, *J* 5.8 Hz), 1.12-1.33 (40 H, m), 1.39 (12 H, d, *J* 6.0 Hz), 1.44-1.59 (16 H, m), 1.62-1.81 (4 H, m), 1.93-2.08 (4 H, m), 3.84 (4 H, q, *J* 6.5 Hz), 3.87 and 4.18 (8 H, AB, *J* 17.0 Hz), 4.29 (4 H, m), 4.44 (4 H, t, *J* 7.2 Hz), 4.66 (8 H, m), 6.87 (4 H, m), 7.19-7.36 (20 H, m); δ_C (100 MHz, $CDCl_3$) 14.2, 21.5, 22.7, 23.6, 23.7, 28.1, 32.1, 32.6, 32.8, 36.1, 36.7, 45.4, 57.1, 79.6, 84.5, 112.5, 125.4, 125.5, 127.2, 127.5, 128.4, 144.3, 150.0, 152.4; *m/z* LRMS (ESI): 1623 $[M+H]^+$; $[C_{108}H_{140}O_8N_4+H]^+$ requires 1623 (the isotopic distribution of the observed data matched the theoretical $[M+H]^+$ isotopic distribution).

Tetrabenzoxazine (*M*,*R*,*R*)-6':[6b]

Tetraisopropyloxyresorcinarene (*P*,*S*)-(+)-**4e** (0.06 g, 0.06 mmol) was dissolved in dry toluene (5 mL) in a 25 mL oven-dried round-bottomed flask under nitrogen. *N*,*N*-bis(methoxymethyl)-(*R*)-(+)-*N*- -methylbenzylamine (0.13 g, 0.64 mmol) in toluene (1 mL) was added in one portion and the reaction mixture was heated under reflux for 5 days under nitrogen. After this time, the reaction was allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was placed on a column of silica gel and eluted with Petroleum Ether/EtOAc (8:2) to yield tetrabenzoxazine (*M*,*R*,*R*)-**6** as a yellow foam (0.097 g, 53%). $[\alpha]_D^{25}$ −9.1 (*c* 1.5, $CHCl_3$). ν_{max} (DCM)/cm^{-1} 2968, 2926, 2857, 1461, 1110, 942, 700; δ_H (400 MHz, 50 °C, $CDCl_3$) 0.82-0.94 (24 H, m), 1.03 (12 H, d, *J* 5.2 Hz), 1.18-1.32 (24 H, m), 1.41 (12 H, d, *J* 6.4 Hz), 1.67-1.76 (4 H, m), 1.92-2.04 (4 H, m), 3.72-3.92 (12 H, m), 4.10 (4 H, m), 4.34 (4 H, t, *J* 7.2 Hz), 4.52 and 4.93 (8 H, AB, *J* 10.0 Hz), 6.86 (4 H, s), 7.18-7.34 (20 H, m); δ_C (100 MHz, $CDCl_3$) 14.2, 21.2, 22.3, 22.5, 22.7, 27.9, 32.0, 36.3, 36.5, 46.7, 57.8, 74.0, 78.8, 113.3, 125.7, 127.0, 127.4, 128.3, 144.5, 150.1, 152.0; *m/z* (FAB): 1518.0123 $[M+H]^+$; $[C_{100}H_{132}O_8N_4+H]^+$ requires 1518.0144.

Tetrabenzoxazine (*M*,*S*,*R*)-14: [6b]

Tetramethoxyresorcinarene (*P*,*S*)-(+)-**4b** (0.17 g, 0.21 mmol) was dissolved in dry toluene (5 mL) in a 25 mL oven dried round-bottomed flask under nitrogen. *N*,*N*-bis(methoxymethyl)-(*S*)-(–)-*N*- -methylbenzylamine (0.258 g, 1.24 mmol) in toluene (1 mL) was added in one portion and the reaction mixture heated under reflux for 4 days. After this time, the reaction was allowed to cool to room temperature and the solvent removed under reduced pressure. The residue was placed on a column of silica gel and eluted with Petroleum Ether/EtOAc (8:2) to yield tetrabenzoxazine (*M*,*S*,*R*)-**14** as a colourless foam (0.133 g, 46%). $[\alpha]_D^{25}$ −131.2 (*c* 1.1, $CHCl_3$). δ_H (400 MHz, $CDCl_3$) 0.87 (12 H, t, *J* 6.4 Hz), 1.32-1.38 (24 H, m), 1.37 (12 H, d, *J* 6.4 Hz), 1.78-1.91 (8 H, m), 3.26 (12 H, s), 3.68 (4 H, q, *J* 6.4Hz), 3.77 and 4.14 (8 H, AB, *J* 16.8 Hz), 4.35 (4 H, t, *J* 7.4 Hz), 4.51 and 4.56 (8 H, AB, *J* 10.0 Hz), 6.66 (4 H, s), 7.15-7.10 (20 H, s); δ_C (100 MHz, $CDCl_3$) 14.2, 21.2, 22.7, 27.9, 32.3, 35.4, 35.8, 44.7, 57.3, 60.0, 79.5, 112.2, 124.5, 127.3, 127.5, 127.8, 128.4, 128.8, 144.1, 150.1, 153.6.

Tetrabenzoxazine (*M*,*S*,*R*)-15a: [6b]

Tetramethoxyresorcinarene (*P*,*S*)-(+)-**7** (0.10 g, 0.16 mmol) was suspended in *N*,*N*-bis(methoxymethyl)-(*S*)-(–)-*N*- -methylbenzylamine (0.33 g, 1.56 mmol) in a CEM microwave tube. The suspension was heated under microwave irradiation at 140 ºC for 2 x 10 min (without cooling). The orange oil obtained was placed on a column of silica gel and eluted with light petroleum/ethyl acetate (6:4) to yield tetrabenzoxazine (*M*,*S*,*R*)-**15a** as a colourless foam (0.15 g, 71%). $[\alpha]_D^{25}$ –124.7 (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$) /cm^{-1} 2951, 2864, 2359, 1589, 1469, 1365, 1235, 1095, 942, 753; δ_H (400 MHz, $CDCl_3$) 0.94 (12 H, d, *J* 10.0 Hz), 0.96 (12 H, d, *J* 10.0 Hz), 1.39 (12 H, d, *J* 6.5 Hz), 1.52-1.61 (4 H, m), 1.65-1.72 (4 H, m), 1.76-1.83 (4 H, m), 3.26 (12 H, s), 3.80 (4 H, q, *J* 6.5 Hz), 3.86 (4 H, d, *J* 17.0 Hz), 4.17 (4 H, d, *J* 16.9 Hz), 4.55-4.62 (12 H, m), 6.70 (4 H, s), 7.17-7.35 (20 H, m); δ_C (100 MHz, $CDCl_3$) 21.3, 22.8, 22.9, 25.9, 33.1, 44.6, 44.9, 57.2, 60.1, 79.6, 112.3, 124.7, 127.3, 127.6, 128.4, 128.7, 144.0, 150.0, 153.6; *m/z* (FAB) 1348.8189; $C_{88}H_{108}O_8N_4$ (M^+) requires 1348.8167.

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Captions

Figure 1. Representation of Resorcin[4]arenes, including Axial Stereochemistry

Scheme 1. Formation of Racemic Tetraalkoxyresorcinarenes

Figure 2. Absolute Configurations of Chiral Non-racemic Tetrabenzoxazines and a Racemic Resorcinarene

Scheme 2. The Formation of Tetracamphorsulfonates from Racemic Resorcinarenes

Scheme 3. The Formation of Tri- and Tetracamphorsulfonates from the Racemic Resorcinarene **4b**

Figure 3. X-ray Structure of the Tetracamphorsulfonate (*M*,*S*,*R*)-**8a**; the hydrogen atoms are omitted for clarity.

Figure 4. X-ray Structure of the Tetracamphorsulfonate (*M*,*S*,*R*)-**8b**; the hydrogen atoms are omitted for clarity.

Scheme 4. The Formation of Monocamphorsulfonates from the Racemic Resorcinarene **4e**

Scheme 5. The Formation of Dicamphorsulfonates from the Racemic Resorcinarenes **4e** and **4f**

Scheme 6. The Formation of Mono- and Dicamphorsulfonates from the Anions Of the Racemic Resorcinarene **4b**

Scheme 7. The Formation of Tetracamphorsulfonates from a Tetra-anion

Scheme 8. The Formation of Tetra(methoxymethyl)ethers from Tetra-anions

Scheme 9. The Formation of Dicamphorsulfonates from Tetra-anions

Scheme 10. The Formation of Tetracamphorsulfonates from the Racemic Resorcinarene **7** Using (*S)*-(+)-10-Camphorsulfonyl chloride

Scheme 11. The Formation of Tetracamphorsulfonates from the Racemic Resorcinarene **7** Using (*R*)-(–)-10-Camphorsulfonyl chloride

Figure 5. X-ray Structure of the Tetracamphorsulfonate (*M*,*S*,*R*)-**13a**; the hydrogen atoms are omitted for clarity.

Figure 6. X-ray Structure of the Tetracamphorsulfonate (*P*,*R*,*S*)-**13b**; the hydrogen atoms are omitted for clarity.

Figure 7. The ^{1}H NMR spectrum of Tetracamphorsulfonate (*M*,*S*,*R*)-**8b**

Figure 8. The ^{1}H NMR spectrum of Tetracamphorsulfonate (*P*,*S*,*S*)-**8b'**

Scheme 12. Hydrolyses of the First Eluting Tetracamphorsulfonates Derived from (*S*)-(+)-10-Camphorsulfonyl chloride

Scheme 13. Hydrolyses of the First Eluting Dicamphorsulfonates Derived from (*S*)-(+)-10-Camphorsulfonyl chloride

Scheme 14. Hydrolysis of the First Eluting Tetracamphorsulfonate Derived from (*R*)-(–)-10-Camphorsulfonyl chloride

Scheme 15. The Synthesis of Tetrabenzoxazines from Racemic 2,8,14,20-tetra-2-methylpropyl-6,12,18,24-tetramethoxyresorcin[4]arene

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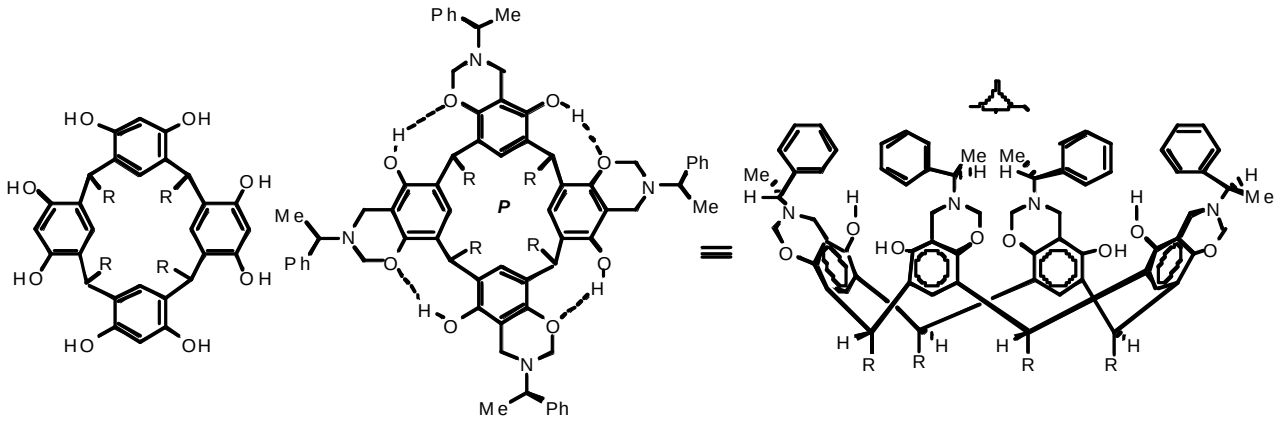
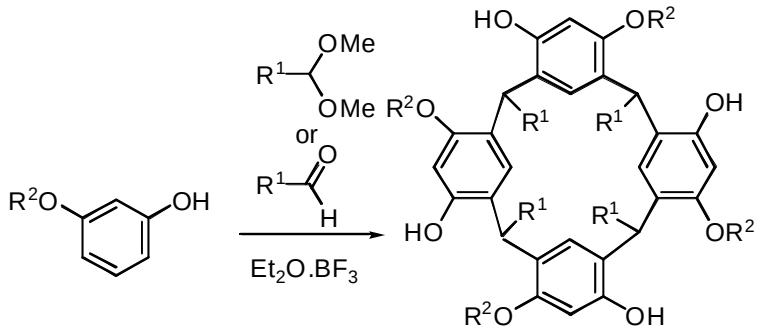
14. CCDC 609240 and 614078-614080 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/

Schemes and Figures



1, R = *n*-C_5H_{11}, *n*-$C_{11}H_{23}$, Ph.CH_2.CH_2 (*P*,*R*,*S*)-**2**, R = *n*-C_5H_{11}, *n*-$C_{11}H_{23}$, Ph.CH_2.CH_2

Figure 1. Representation of Resorcin[4]arenes, including Axial Stereochemistry

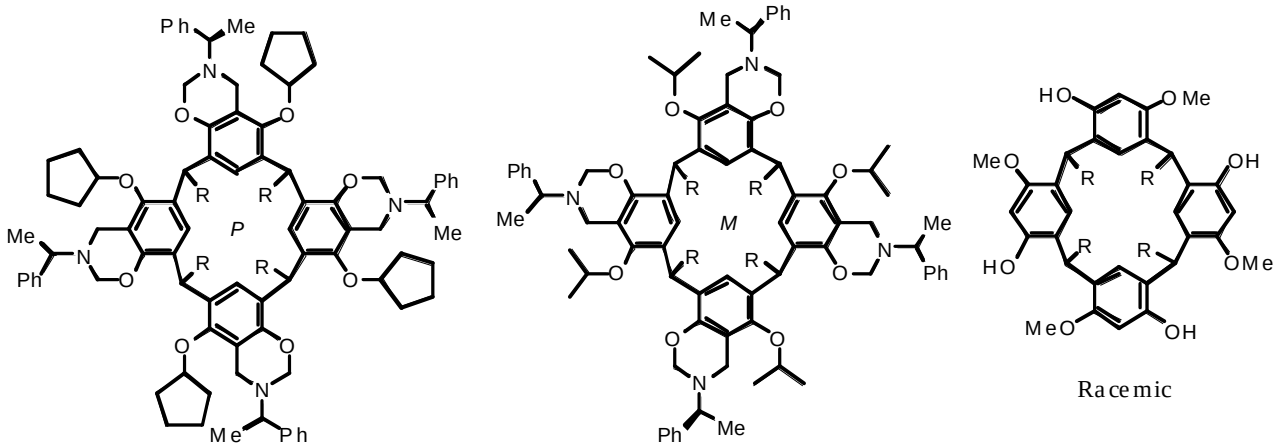


Racemic

3a, R^2 = Me
3b, R^2 = *i*-Pr
3c, R^2 = cyclopentyl

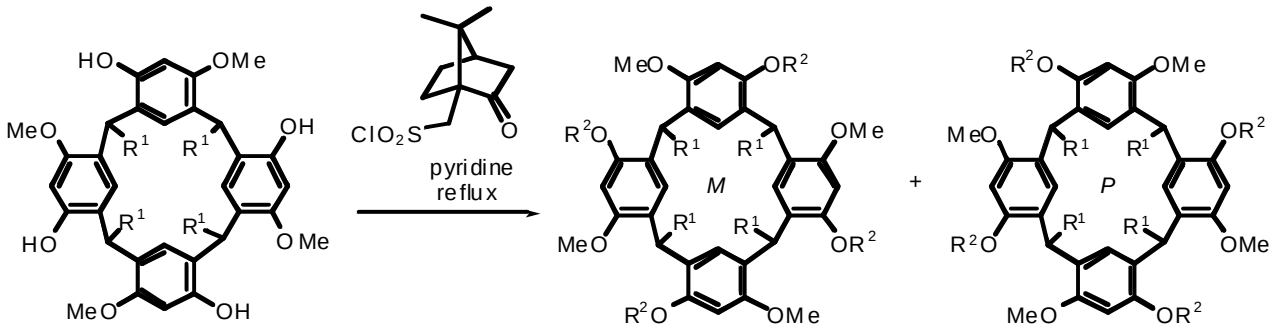
4a, R^1 = *n*-C_3H_7, R^2 = Me
4b, R^1 = *n*-C_5H_{11},R^2 = Me
4c, R^1 = *n*-C_7H_{15}, R^2 = Me
4d, R^1 = *n*-$C_{11}H_{23}$, R^2 = Me
4e, R^1 = *n*-C_5H_{11}, R^2 = *i*-Pr
4f, R^1 = *n*-C_5H_{11}, R^2 = cyclopentyl

Scheme 1. Formation of Racemic Tetraalkoxyresorcinarenes



(*P*,*R*,*S*)-**5**, R = *n*-C_5H_{11} (*M*,*S*,*R*)-**6**, R = *n*-C_5H_{11} **7**, R = 2-methylpropyl

Figure 2. Absolute Configurations of Chiral Non-racemic Tetrabenzoxazines and a Racemic Resorcinarene



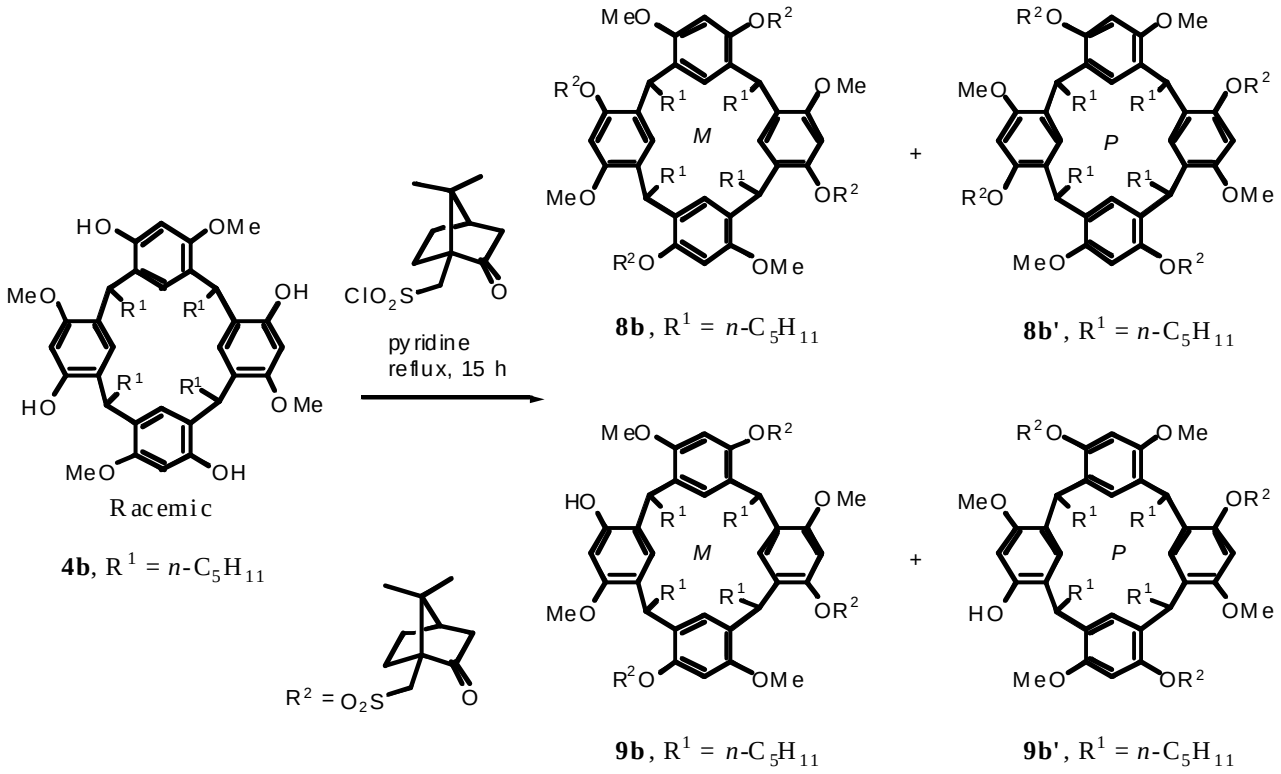
Racemic

4a, R^1 = *n*-C_3H_7
4b, R^1 = *n*-C_5H_{11}
4c, R^1 = *n*-C_7H_{15}
4d, R^1 = *n*-$C_{11}H_{23}$

8a, R^1 = *n*-C_3H_7
8b, R^1 = *n*-C_5H_{11}
8c, R^1 = *n*-C_7H_{15}
8d, R^1 = *n*-$C_{11}H_{23}$

8a', R^1 = *n*-C_3H_7
8b', R^1 = *n*-C_5H_{11}
8c', R^1 = *n*-C_7H_{15}
8d', R^1 = *n*-$C_{11}H_{23}$

Scheme 2. The Formation of Tetracamphorsulfonates from Racemic Resorcinarenes



Scheme 3. The Formation of Tri- and Tetracamphorsulfonates from the Racemic Resorcinarene **4b**

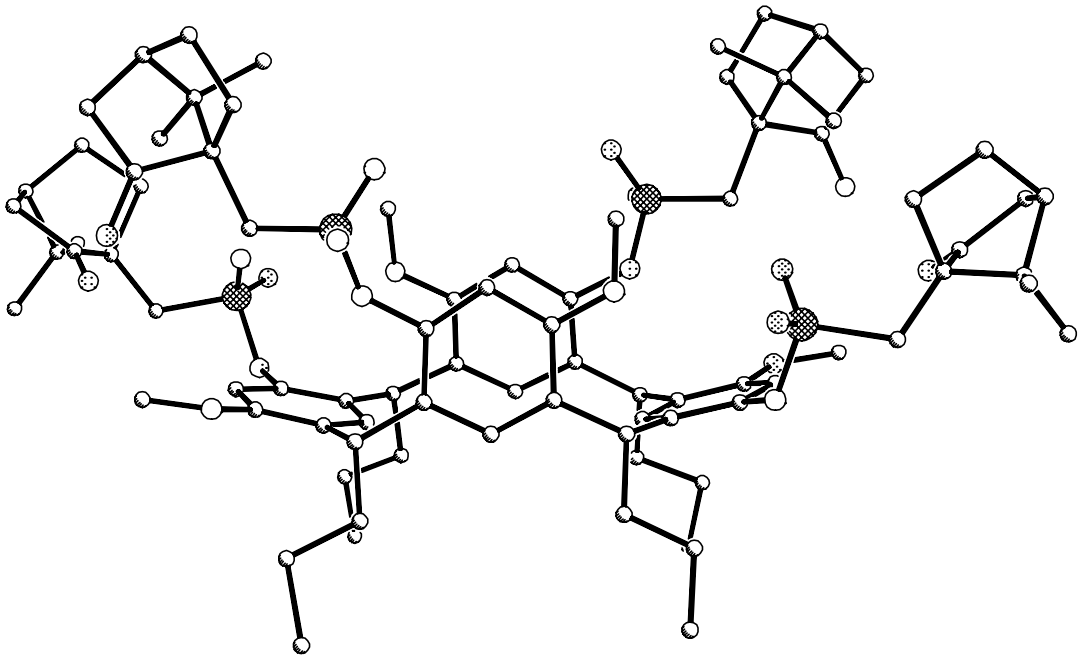


Figure 3. X-ray Structure of the Tetracamphorsulfonate (*M*,*S*,*R*)-**8a**; the hydrogen atoms are omitted for clarity.

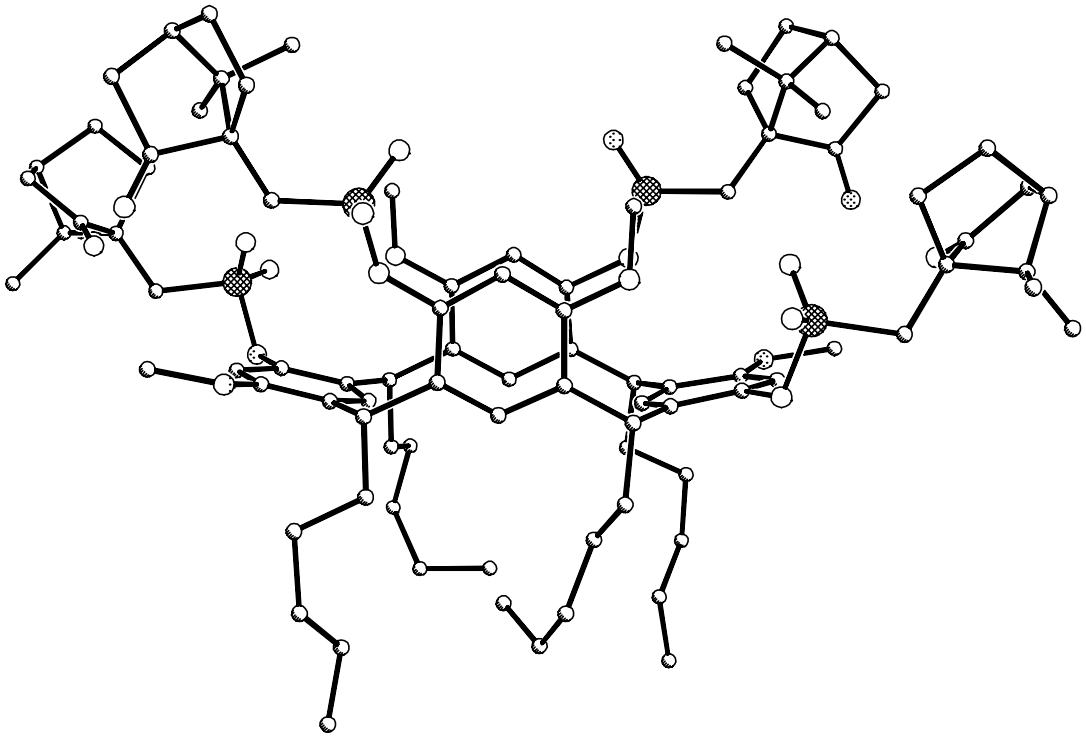
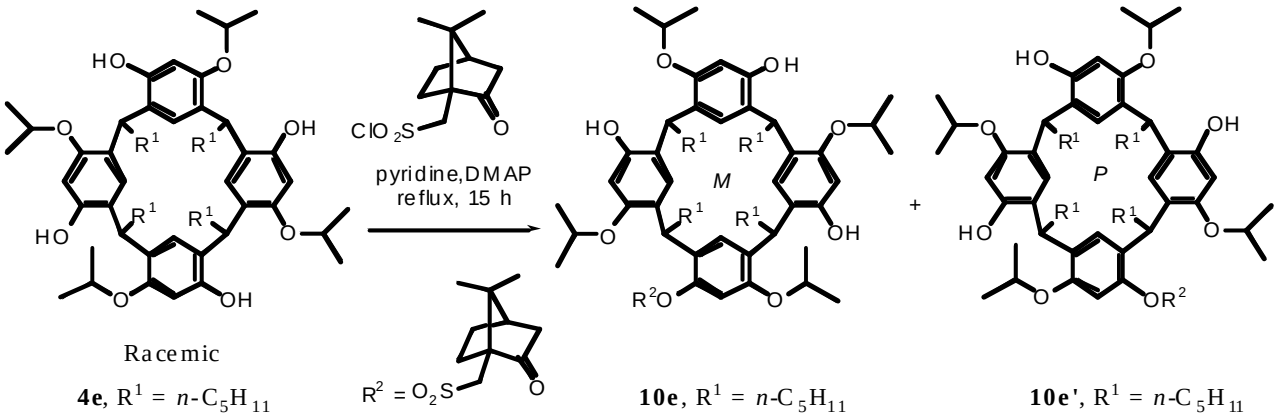
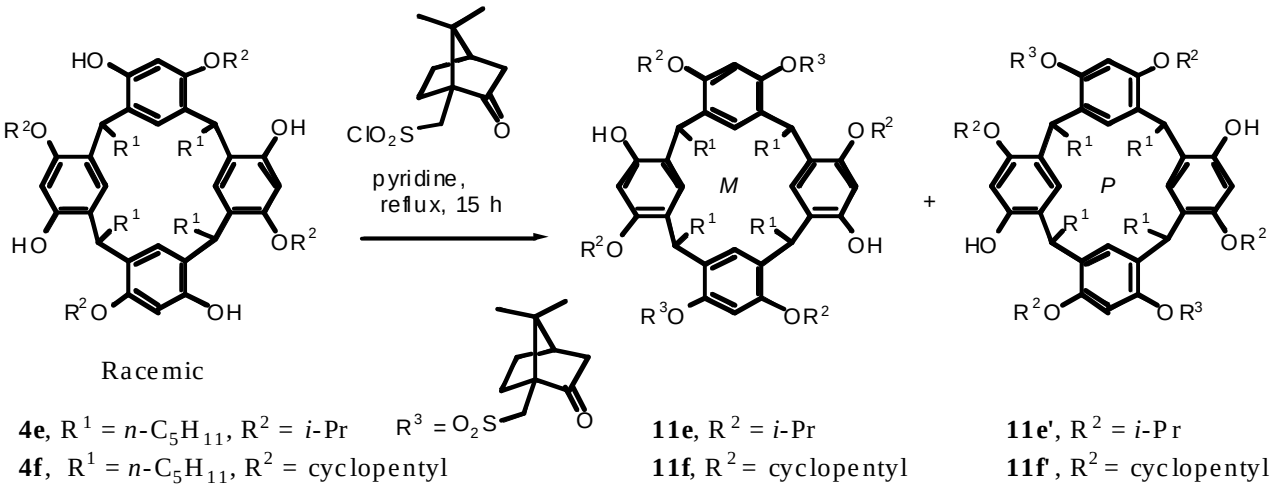


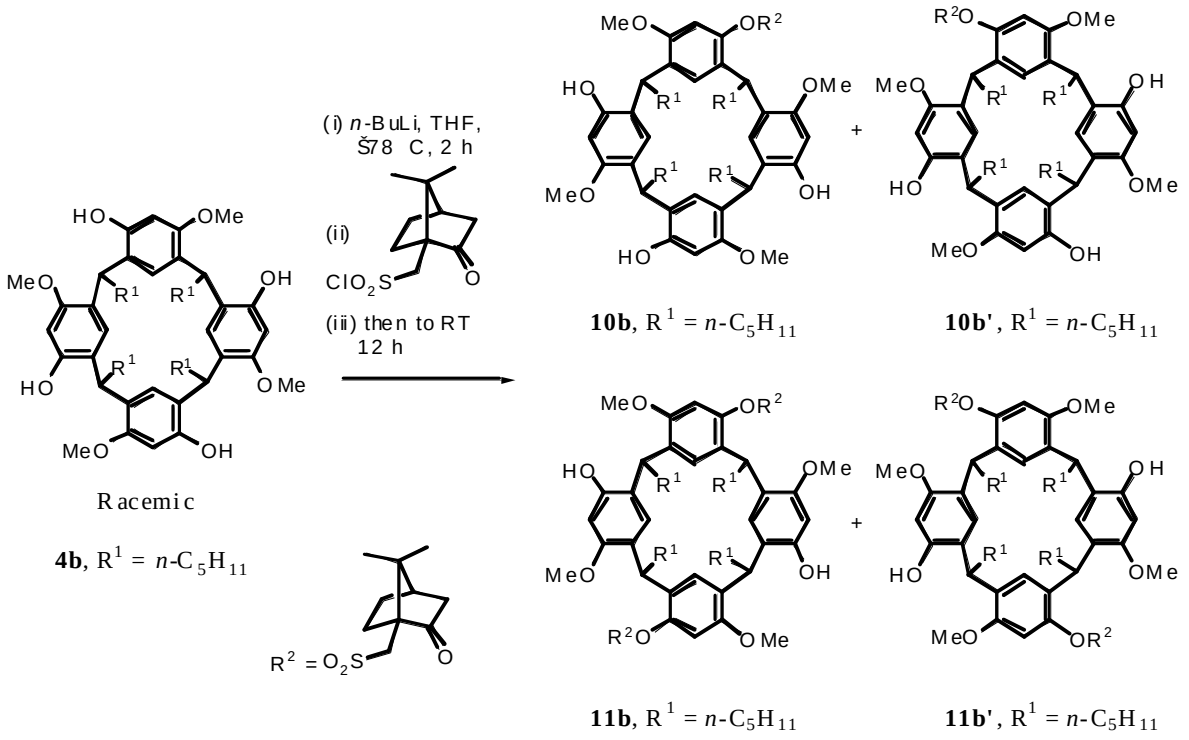
Figure 4. X-ray Structure of the Tetracamphorsulfonate (*M*,*S*,*R*)-**8b**; the hydrogen atoms are omitted for clarity.



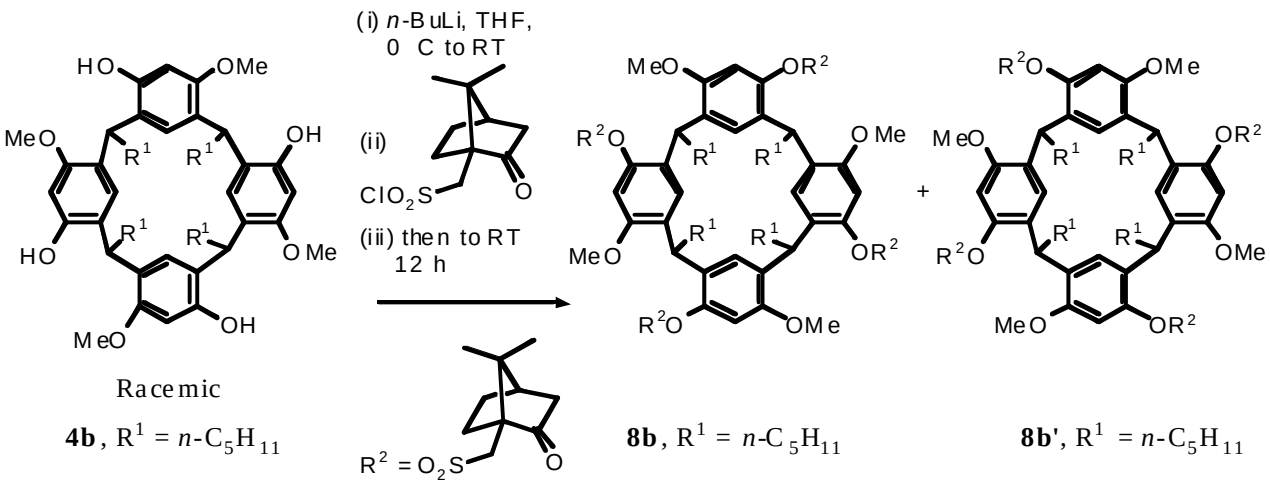
Scheme 4. The Formation of Monocamphorsulfonates from the Racemic Resorcinarene **4e**



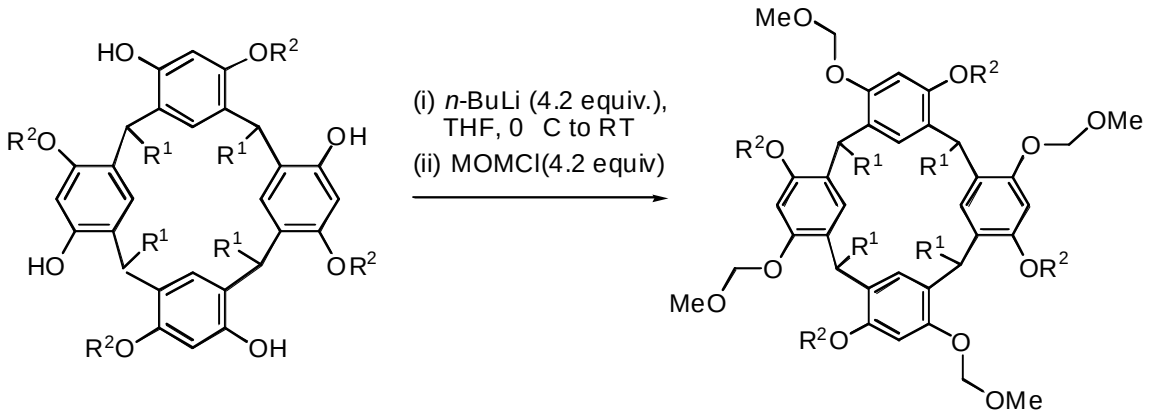
Scheme 5. The Formation of Dicamphorsulfonates from the Racemic Resorcinarenes **4e** and **4f**



Scheme 6. The Formation of Mono- and Dicamphorsulfonates from the Anions of the Racemic Resorcinarene **4b**



Scheme 7. The Formation of Tetracamphorsulfonates from a Tetra-anion



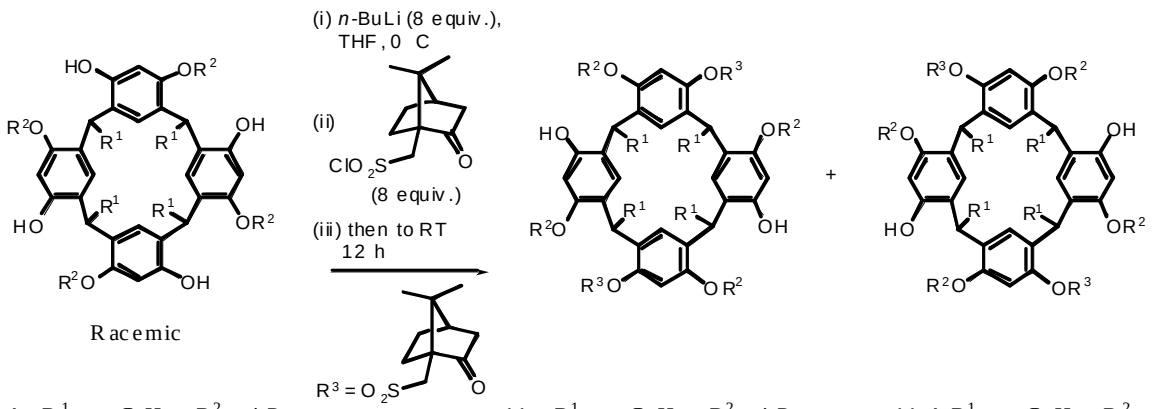
Racemic

4b, $R^1 = n\text{-}C_5H_{11}$, R^2 = Me
4e, $R^1 = n\text{-}C_5H_{11}$, $R^2 = i$-Pr

Racemic

12b, $R^1 = n\text{-}C_5H_{11}$, R^2 = Me
12e, $R^1 = n\text{-}C_5H_{11}$, $R^2 = i$-Pr

Scheme 8. The Formation of Tetra(methoxymethyl)ethers from Tetra-anions

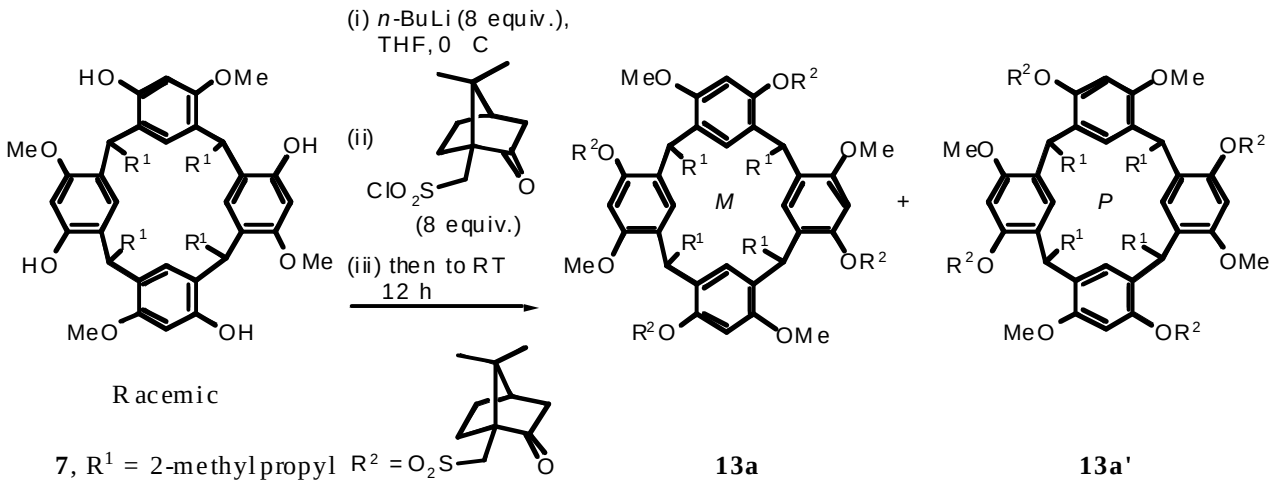


4e, $R^1 = n\text{-}C_5H_{11}$, $R^2 = i$-Pr
4f, $R^1 = n\text{-}C_5H_{11}$, R^2 = cyclopentyl

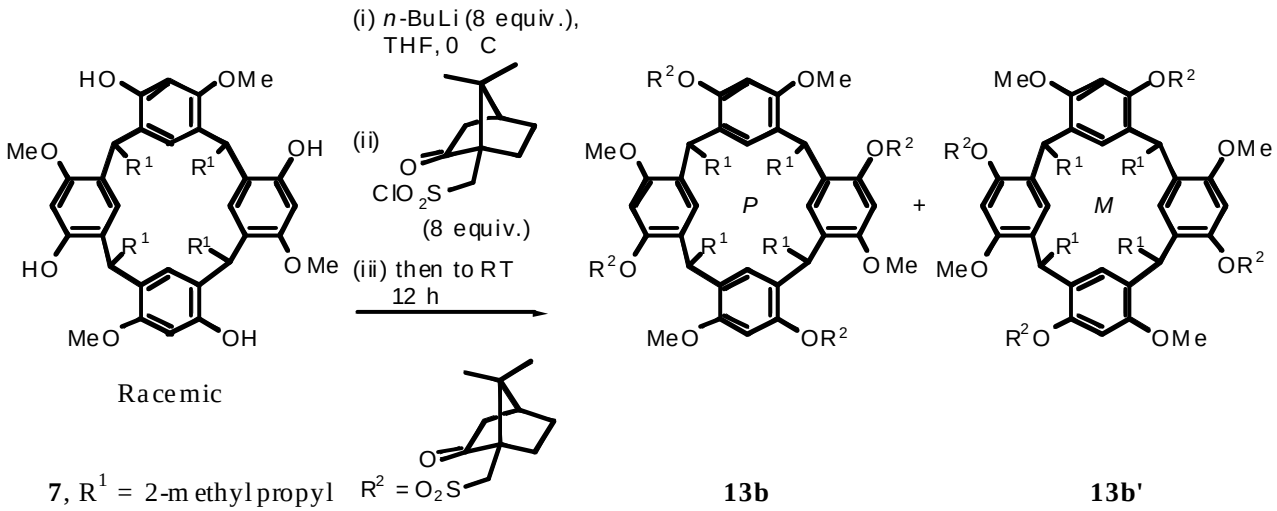
11e, $R^1 = n\text{-}C_5H_{11}$, $R^2 = i$-Pr
11f, $R^1 = n\text{-}C_5H_{11}$, R^2 = cyclopentyl

11e', $R^1 = n\text{-}C_5H_{11}$, $R^2 = i$-Pr
11f', $R^1 = n\text{-}C_5H_{11}$, R^2 = cyclopentyl

Scheme 9. The Formation of Dicamphorsulfonates from Tetra-anions



Scheme 10. The Formation of Tetracamphorsulfonates from the Racemic Resorcinarene **7** Using (*S*)-(+)-10-Camphorsulfonyl chloride



Scheme 11. The Formation of Tetracamphorsulfonates from the Racemic Resorcinarene **7** Using (*R*)-(Š)-10-Camphorsulfonyl chloride

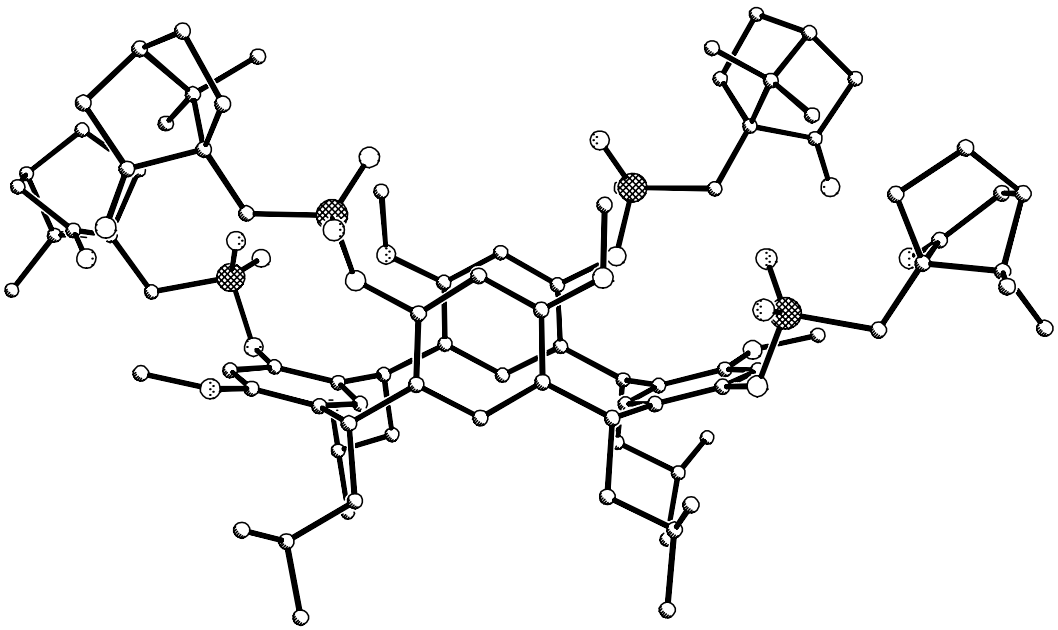


Figure 5. X-ray Structure of the Tetracamphorsulfonate (*M*,*S*,*R*)-**13a**; the hydrogen atoms are omitted for clarity.

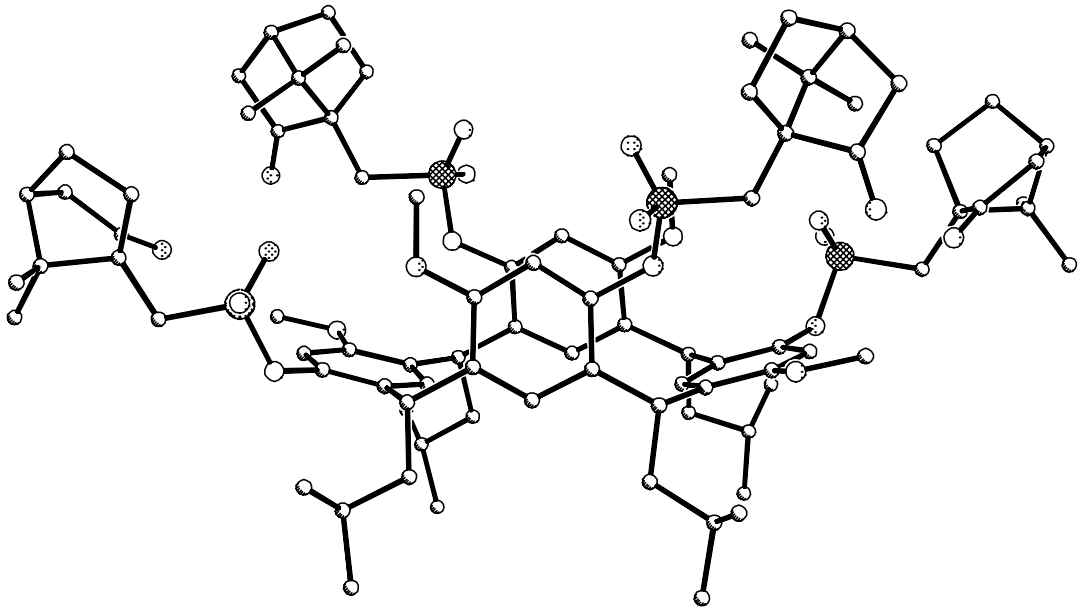


Figure 6. X-ray Structure of the Tetracamphorsulfonate (*P*,*R*,*S*)-**13b**; the hydrogen atoms are omitted for clarity.

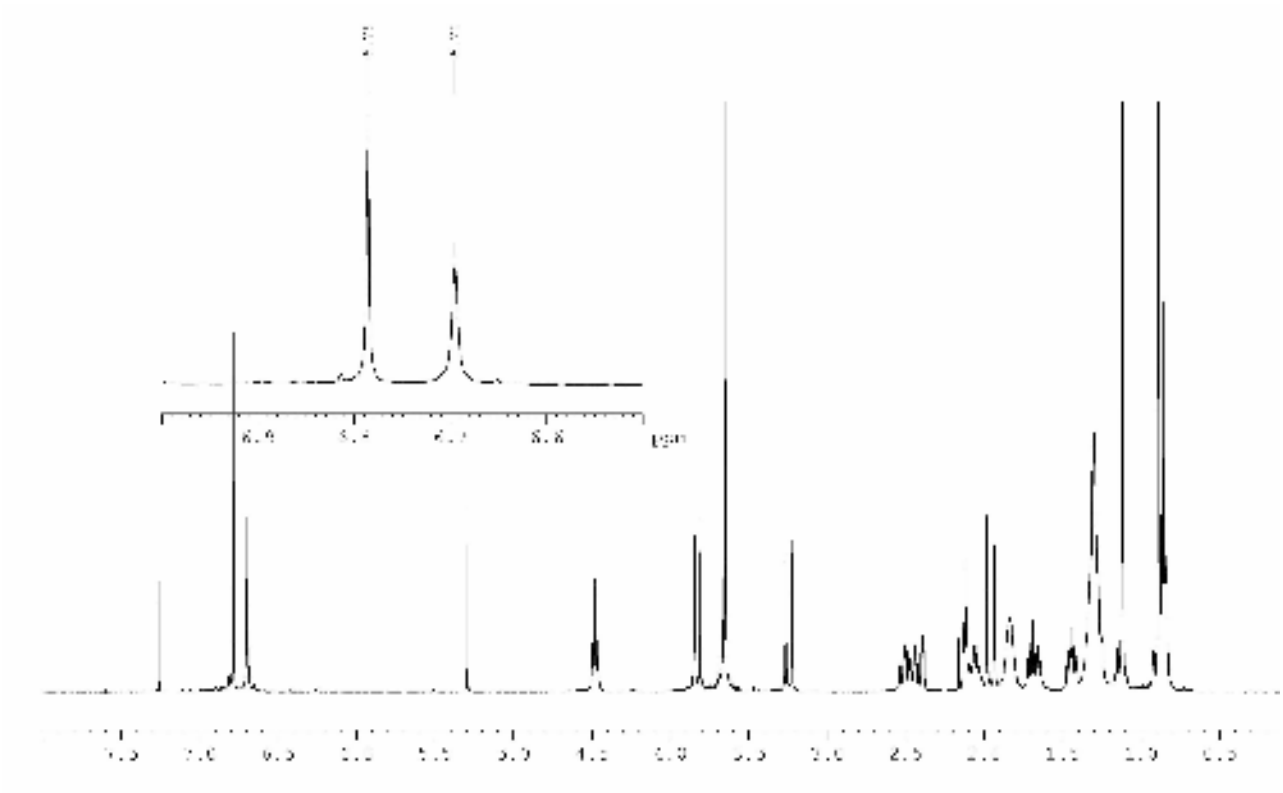


Figure 7. The ^{1}H NMR spectrum of Tetracamphorsulfonate (*M*,*S*,*R*)-**8b**

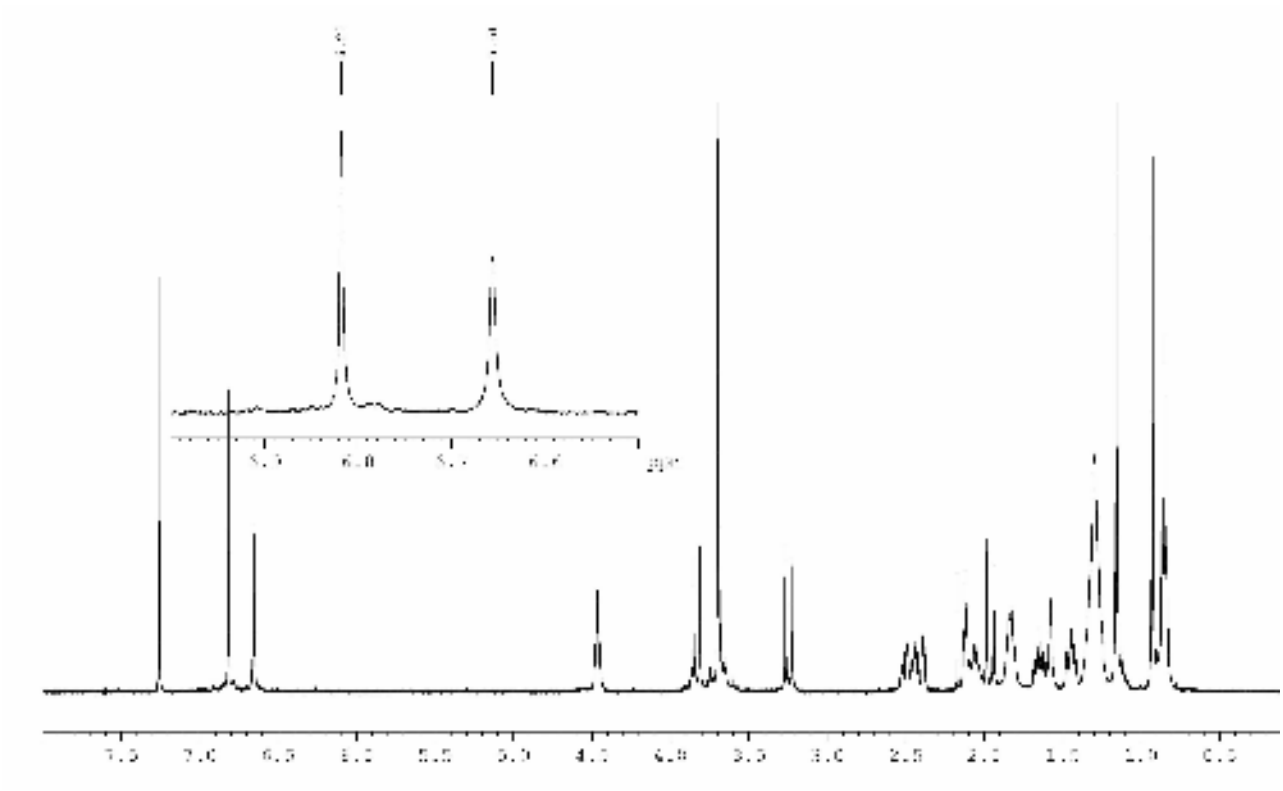
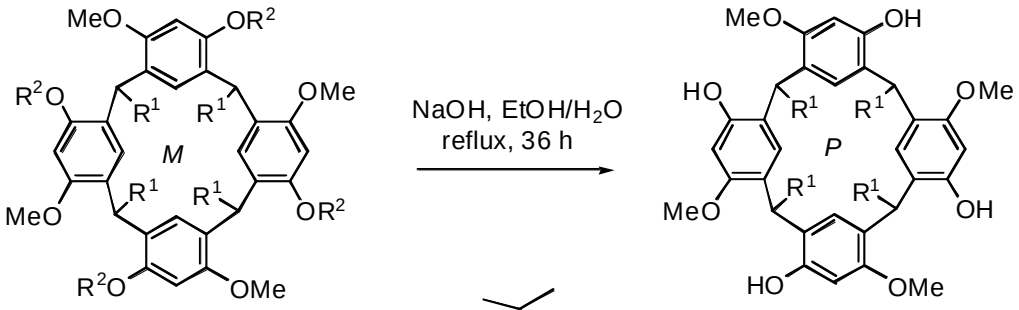
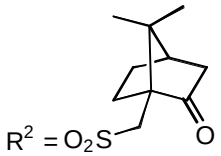


Figure 8. The ^{1}H NMR spectrum of Tetracamphorsulfonate (*P*,*S*,*S*)-**8b'**

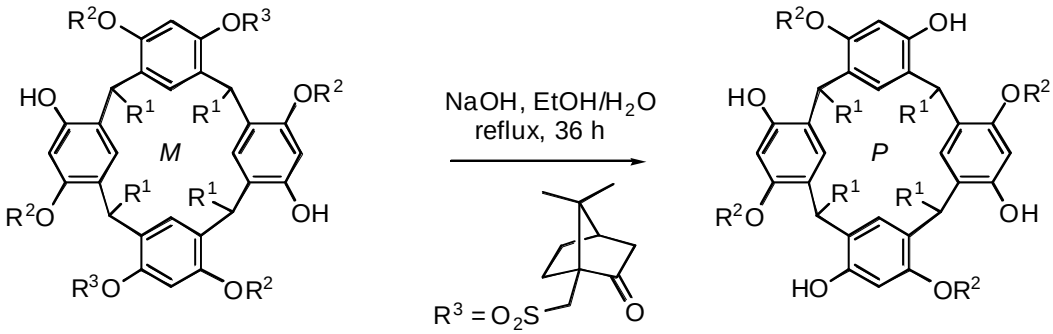




8a, $R^1 = n\text{-}C_3H_7$
8b, $R^1 = n\text{-}C_5H_{11}$
8c, $R^1 = n\text{-}C_7H_{15}$
8d, $R^1 = n\text{-}C_{11}H_{23}$
13a, R^1 = 2-methylpropyl

(*P*,*S*)-(+)-**4a**, $R^1 = n\text{-}C_3H_7$
(*P*,*S*)-(+)-**4b**, $R^1 = n\text{-}C_5H_{11}$
(*P*,*S*)-(+)-**4c**, $R^1 = n\text{-}C_7H_{15}$
(*P*,*S*)-(+)-**4d**, $R^1 = n\text{-}C_{11}H_{23}$
(*P*,*S*)-(+)-**7**, R^1 = 2-methylpropyl

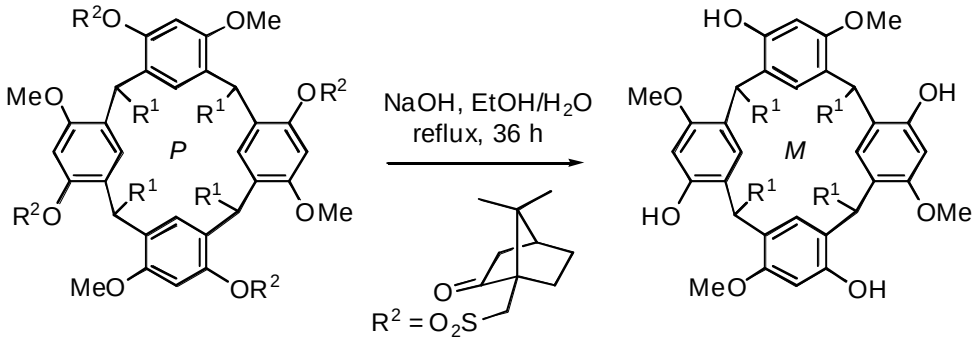
Scheme 12. Hydrolyses of the First Eluting Tetracamphorsulfonates Derived from (*S*)-(+)-10-Camphorsulfonyl chloride



11e, $R^1 = n\text{-}C_5H_{11}$, $R^2 = i$-Pr
11f, $R^1 = n\text{-}C_5H_{11}$, R^2 = cyclopentyl

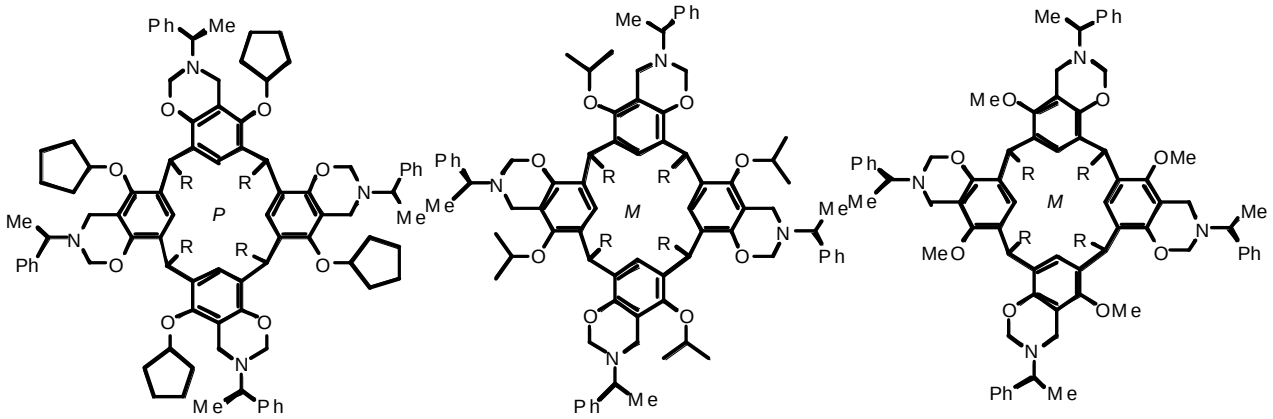
(*P*,*S*)-(+)-**4e**, $R^1 = n\text{-}C_5H_{11}$, $R^2 = i$-Pr
(*P*,*S*)-(+)-**4f**, $R^1 = n\text{-}C_5H_{11}$, R^2 = cyclopentyl

Scheme 13. Hydrolyses of the First Eluting Dicamphorsulfonates Derived from (*S*)-(+)-10-Camphorsulfonyl chloride

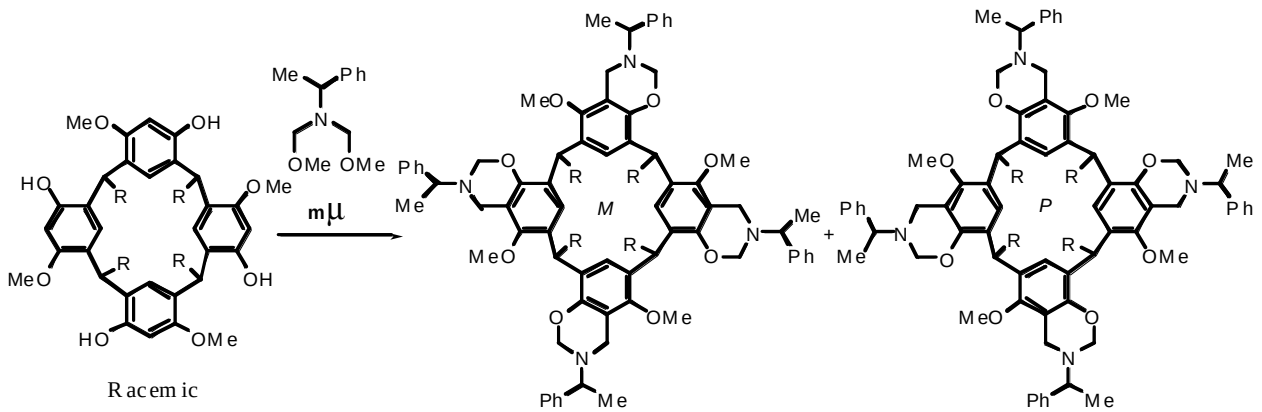


13b, R^1 = 2-methylpropyl (*M*,*R*)-(Š)-**7**, R^1 = 2-methylpropyl

Scheme 14. Hydrolysis of the First Eluting Tetracamphorsulfonate Derived from (*R*)-(Š)-10-Camphorsulfonyl chloride



(*P*,*R*,*S*)-**5**, R = *n*-C_5H_{11} (*M*,*S*,*R*)-**6**, R = *n*-C_5H_{11} (*M*,*S*,*R*)-**14**, R = *n*-C_5H_{11}



Racemic

7, R = 2-methylpropyl (*M*,*S*,*R*)-**15a** (*P*,*S*,*S*)-**15b**

Scheme 15 The Synthesis of Tetrabenzoxazines from Racemic 2,8,14,20-tetra-2-methylpropyl-6,12,18,24-tetramethoxyresorcin[4]arene