Review

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Chiral Calixarenes

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Introduction

Calixarenes, obtained in the condensation reaction of formaldehyde and *p*-substituted phenols, are often referred to as the third generation of supramolecular receptors after crown ethers and cyclodextrins.[1,2] They have 2 well-defined rims, an upper rim defined by the para substituents of the phenolic rings and a lower rim defined by the phenolic hydroxyl groups (Figure 1). This excellent skeleton enables calixarenes to act as "molecular baskets" towards neutral or ionic guests.[3]

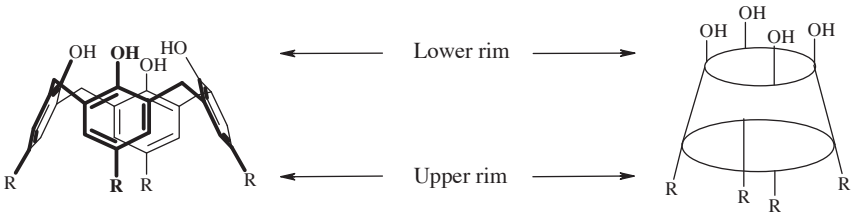

Figure 1. Representation of calix[4]arenes and designation of the faces.

By comparing with naturally occurring host molecules, such as cyclodextrins, the calix[n]arenes provide a very flexible template for building numerous structures with potentially useful host–guest properties. The easy accessibility and the selective functionalizations at one of the calix rims have made this class of compounds competitive candidates for studying the interactions involved in host–guest recognition as well as useful receptors

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in separation processes. Calix[n]arenes are readily converted into a wide range of derivatives containing various functional groups such as ketone,[4] amine, [5] ester,[6–8] amide,[9–12] alcohol,[13,14] ether,[15] carboxylic acid,[16] crown ether,[17] or other functional groups. The complexation properties of these molecules depend on the ring size of the calix[n]arene, the nature of the groups attached, the number of donor atoms, and the conformation of the macrocycle. Calixarene-based receptors find remarkable applications in molecular recognition studies consistent with the principles of host–guest chemistry, phase transfer catalysis, chromatography, ion-selective electrodes, and liquid membrane technology. The chemistry of calixarenes is well documented in the literature, including journal articles, published conference proceedings, books, chapters in books, reviews, patents, doctoral theses, and reports.[18–35]

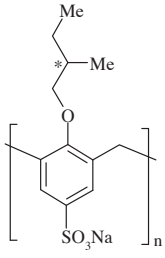
Chiral calixarenes have attracted increasing attention in recent years due to their potential as enantioselective artificial receptors and asymmetric catalysts. Two principal approaches have been used for the preparation of chiral calixarenes. The first one is synthesis of 'inherently' chiral calixarenes, built up of achiral moieties and consequently owe their chirality only to the fact that the calixarene molecule is not planar. In the literature, several strategies, including fragment condensation, and regio- and stereoselective functionalization at the lower rim, have been reported for the preparation of inherently chiral calixarenes. The second approach is an attachment of chiral moieties at the upper or lower rim of calixarene macrocycle.

From a practical point of view, the second approach appears to be preferable, because enantiomerically pure derivatives can be obtained relatively easily, provided the derivatization reaction proceeds without racemization if homochiral reagents are used. However, the inherently chiral calixarenes generally require more complex synthetic procedures and a difficult resolution on an appropriate scale.

Only a few reviews[36–43] or chapters in books on chiral calixarenes concerning their synthesis, applications, and properties as well as chiral recognition are available.

This review covers both the synthesis and applications of the chiral calixarenes bearing enantiomerically pure substituents developed by us and other groups and is organized according to the type of chiral unit attached to the calixarene framework for the synthesis of chiral calixarenes.

In 1987, Shinkai and co-workers synthesized a chiral calixarene derivative **1** for the first time (Figure 2), from the reaction of (*S*)-1-bromo-2-methylbutane with calix[6]arene-*p*-hexasulphonate.[44,45] Since then, a number of research groups have incorporated various chiral subunits at either the upper or lower rims of the calixarene macrocyclic ring. Thus, chiral receptors based on the calixarene platform provide a new approach



1 n = 4
2 n = 6
3 n = 8

Figure 2. *p*−sulfonatocalix[n]arenes bearing (*S*)-2-methylbutoxy groups.

for studies of the host–guest chemistry of calixarenes and may have potential applications in the preparation, separation, and analysis of enantiomers and asymmetric synthesis.

Amines and Amino Alcohols

Many approaches have been developed with chiral amino alcohols and amines as chiral sources in the synthesis of calixarenes. We have constructed novel chiral mono and diamide derivatives of calix[4]arene from the aminolysis reaction of calix[4]arene diester with appropriate primary amine or amino alcohols (Figure 3) and examined their binding abilities by UV–Vis absorption and ^{1}H-NMR spectroscopy.[46,47] All chiral receptors have greater K values toward the enantiomers of phenylethylamine (PEA) than cyclohexylethylamine (CHEA), the nonaromatic analog of PEA, due to $\pi-\pi$ interactions as well as hydrogen bonding. Furthermore, somewhat greater K values were obtained for chiral receptors **7-14**, bearing the alcohol–OH group. Such an additional functional group seems to work for better complexation and chiral recognition because of hydrogen bonding with -OH groups. It seems that chiral calix[4]arenes **4-14** interact with a minimum of 3 of the possible recognition groups (carbonyl oxygen, amide nitrogen, phenoxy oxygen, phenyl group, and hydroxy groups) in order to exhibit enantioselective binding to the chiral amines. The extraction properties of compounds **9-14** toward selected α-amino acid methyl esters were also studied in a liquid–liquid extraction system.

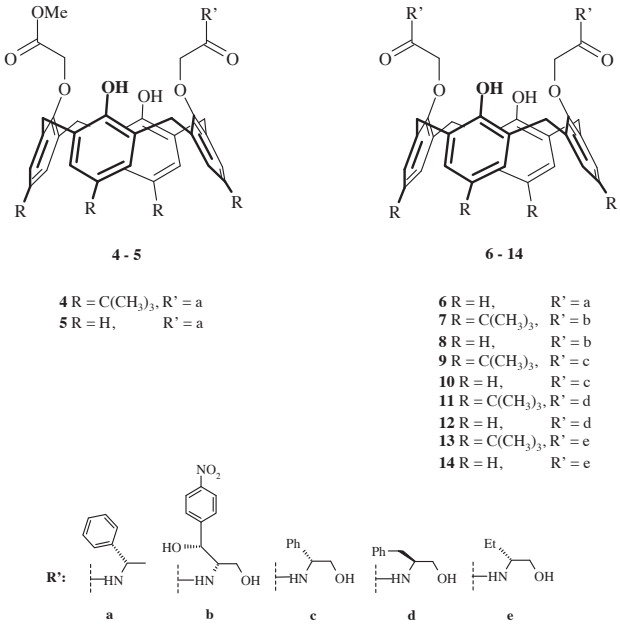


Figure 3. Mono and diamide derivatives of calix[4]arene.

Zheng and co-workers have reported a series of chiral nitrogen-containing calix[4]arene and calix[4]crown derivatives (Figure 4) bearing optically pure amine, 1,2-diphenyl-1,2-oxyamino, αsβ-amino alcohol, and $\alpha-\beta$-diamine groups at the lower rim.[13,48–50] Chiral receptors **18, 19,** and **23** showed good to excellent chiral recognition abilities towards the enantiomers of mandelic acid, dibenzoyltartaric acid, and 2-hydroxy-3-methylbutyric acid. They have also demonstrated that chiral calix[4]arenes **(15-17)** bearing long tertiary alkyl groups at the

upper rim and (*S*)-1-phenylethylamine groups at the lower rim can form heat-set gels and egg-like vesicles enantioselectively with *D*-2,3-dibenzoyltartaric acid in cyclohexane, which is the first example of heat-set gels resulting from a difference in interactions between 2 component gelators.[51]

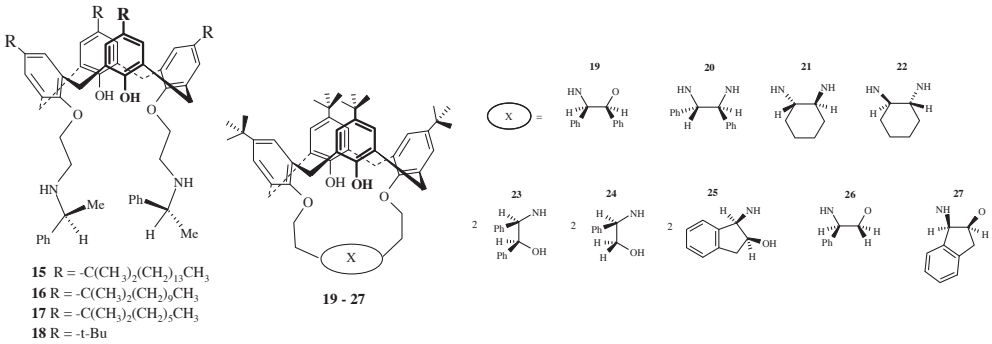


Figure 4. Chiral nitrogen-containing calix[4]arene and calix[4]crown derivatives.

Our group has also described the synthesis of novel chiral calix[4](azoxa)crown ethers **28** and **29** (Figure 5) from the reaction of calix[4]arene diacid chloride with a chiral diamine.[52,53] In liquid–liquid extraction experiments, **29** exhibits selectivity for Li^+ among the other alkali metals and a good extraction ability for transition metal cations, suggesting its potential use in different fields, such as a sensor for ions as well as for chiral molecules.

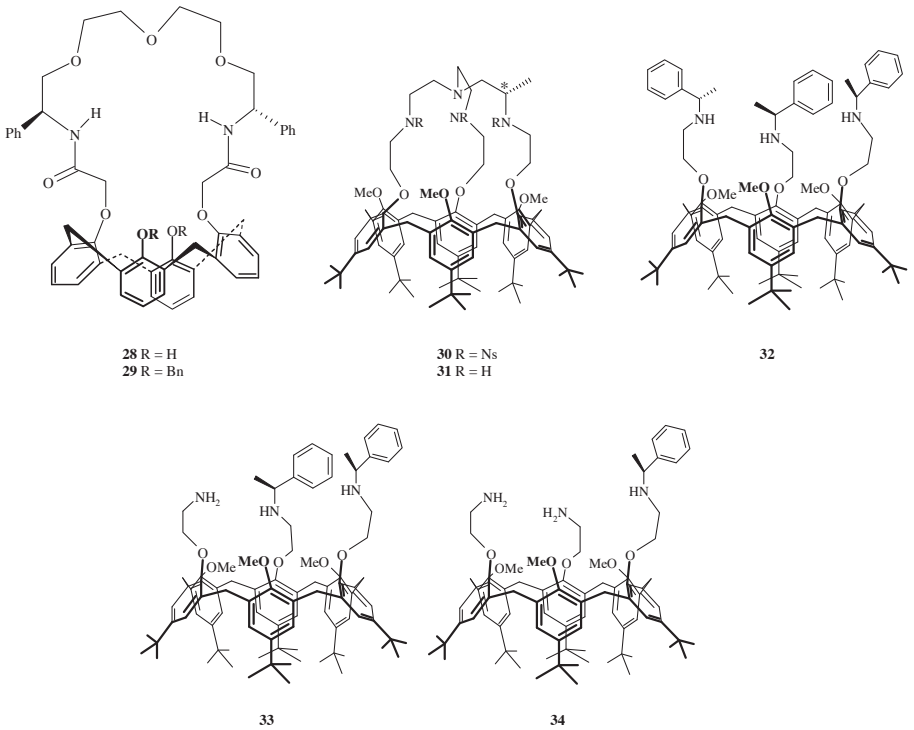


Figure 5. Chiral calix[4](azoxa)crown ethers and calix[6]aza-cryptands.

Jabin and co-workers synthesized the first enantiopure calix[6]aza-cryptands from 1,3,5-tris-*O*-methylated calix[6]arene.[54] NMR studies showed that the tetra protonated derivative **30.4H**$^+$ displays remarkable host–guest properties towards polar neutral molecules and enantioselective recognition processes with chiral guests. Similarly optically pure calix[6]arenes bearing chiral amino arms **32, 33,** and **34** have been synthesized in high yields from the known symmetrically 1,3,5-trismethylated calix[6]arene.[55] The chiral derivative **34** undergoes a conformational change with the 3 ammonium arms, forming a tris-cationic chiral binding site that caps the cavity. The obtained polarized host **(34.3H**$^+$**)** behaves as a remarkable endo-receptor for small polar neutral molecules.

Yilmaz et al. have reported the synthesis of chiral calix[4]arene **36-38** and calix[6]arene **39, 40** (Figures 6 and 7) derivatives possessing phenylalaninol and phenylethylamine substituents.[56–58] Liquid–liquid extraction studies of ligands towards some selected α-amino acid methylesters, amino alcohols, and α-amines displayed good affinity towards all amino acid species without any remarkable discrimination.

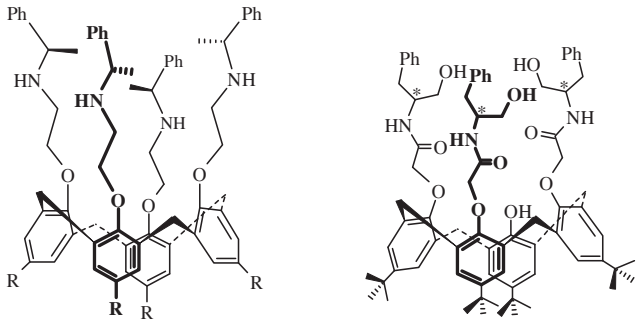


Figure 6. Chiral calix[6]arene derivatives possessing phenylalaninol and phenylethylamine substituents.

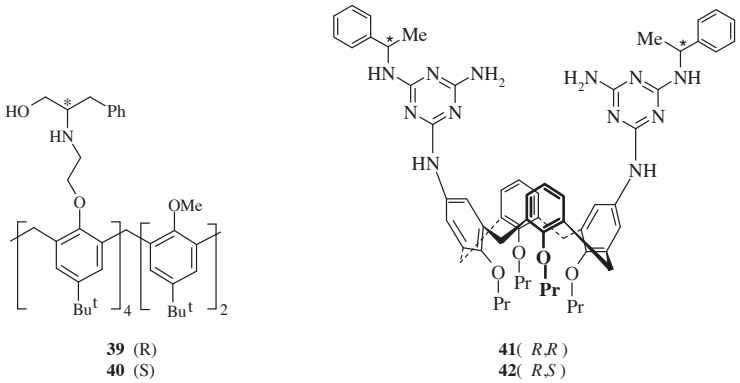


Figure 7. Enantiomerically pure phenylethylamine and dimelamine derivatives of calix[n]arene.

Timmerman, Reinhoudt, and co-workers have reported synthesis and complexation studies of the dimelamine derivatives **41** and **42** of calix[4]arene starting from the reaction of diamine calix[4]arene with cya-

nurchloride, followed by stepwise substitution of the remaining chlorine atoms by ammonia and (*R*)- or (*S*)-methylbenzylamine in several steps.[59,60]

We have also reported the synthesis of chiral calix[4]arene Schiff base derivatives **43-45** by attaching chiral amines at the upper rim of the calix[4]arene (Figure 8) and their recognition abilities for certain chiral and achiral amines by a UV–Vis titration method in $CHCl_3$.[61] Chiral receptor **44** showed the enantioselective recognition ability toward (*R*)- and (*S*)-phenylethylamine (up to $K_R/K_S = 2.67$) among all of the chiral hosts studied and more stable complexes were obtained with *n*-butylamine compared with 3-morpholinopropylamine. The results revealed that the size/shape-fit concept plays a crucial role in the formation of inclusion complexes of host compounds with guest molecules of various structures.

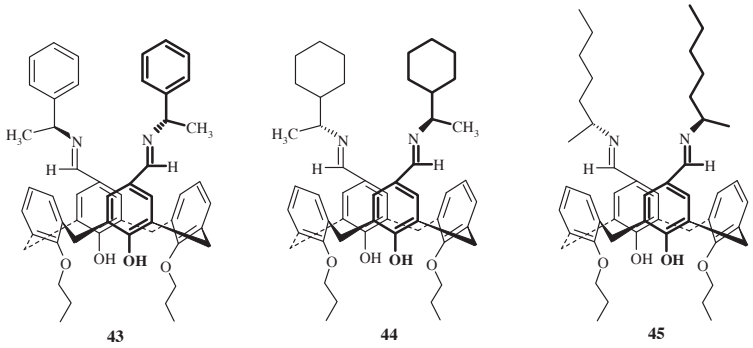


Figure 8. Calix[4]arene Schiff base derivatives from chiral amines.

Amino Acid Derivatives and Peptides

In biological systems, the cooperative action of peptide hydrogen bonds plays an important role in organization, assembly, and molecular recognition processes.[62] On the other hand, specially engineered synthetic peptides are able to assemble into nanotubes or other supramolecular structures or act as hosts for a variety of guest molecules. The attachment of *R*-amino acids or peptides to the calixarene framework can be achieved through the terminal amino or carboxylic groups.[63]

Ungaro et al. have reported the synthesis and inclusion properties of new chiral hosts (Figure 9), having 2 or 4 *L*-alanine or *L*-alanyl-*L*-alanine units at the upper rim *N*-linked calix[4]arenes.[64,65] The water soluble peptidocalix[4]arenes **48** and **52** exhibited noticeable recognition ability toward amino acids and aromatic ammonium cations. No inclusion for the very hydrophilic glycine (Gly) and its methyl ester and a very modest chiral discrimination between *L*-and *D*-amino acids are observed. A remarkable influence of the rigidity of the calix[4]arene platform in determining the recognition properties of mobile **48** and rigid cone **52** water soluble peptidocalix[4]arene receptors has been found.

The same group has also described the synthesis and properties of upper rim C-linked peptidocalix[4]arenes **55-68** containing 2 or 4 *L*-alanine or *L*-phenylalanine units (Figure 10), which represent a novel class of chiral receptors in that the amino acid units are linked to the calix[4]arene platform through their carboxy groups rather than through nitrogen as in all previously described *N*-linked peptidocalix[4]arenes.[66,67] In designing these receptors, it was anticipated that they would show different conformational and binding properties as compared with their *N*-linked analogues.

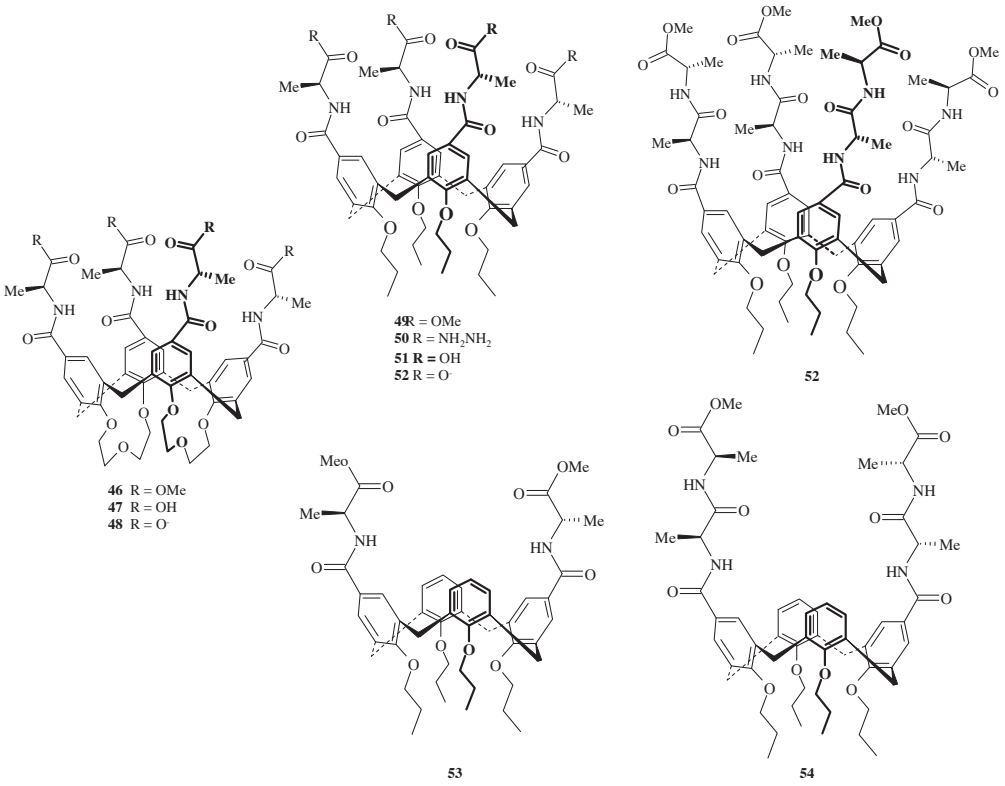


Figure 9. *N*-linked calix[4]arenes bearing *L*-alanine units at the upper rim.

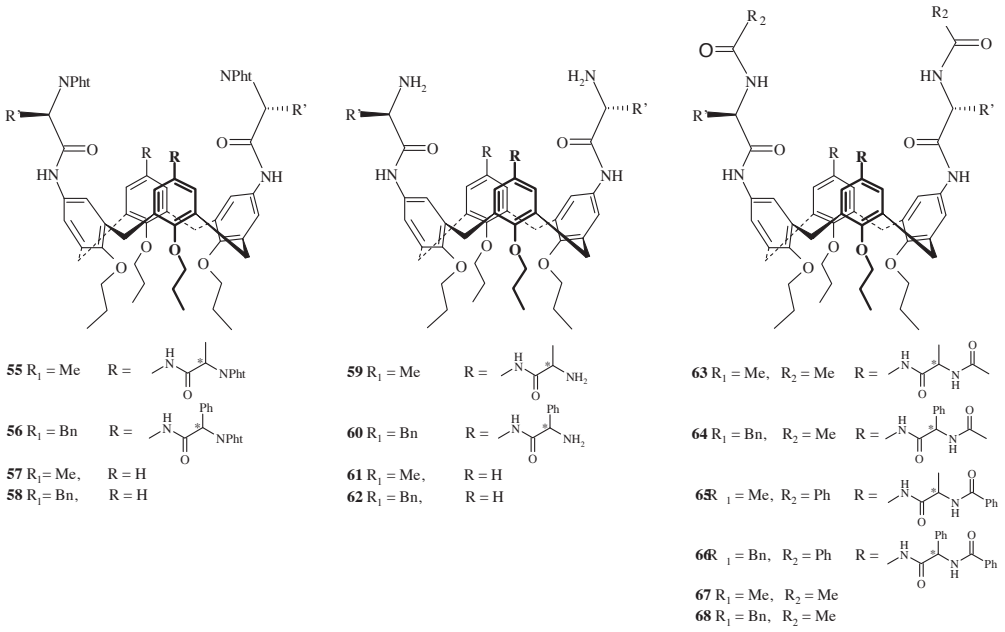


Figure 10. C-linked peptidocalix[4]arenes containing *L*-alanine or *L*-phenylalanine units.

Interestingly, some of the upper rim bridged N-linked peptidocalix[4]arenes (e.g., **69**) behaved as vancomycin mimics (Figure 11) and showed promising antibiotic activity toward gram-positive bacterial strands as a consequence of their ability to bind the D-alanyl-D-alanine (D-ala-D-ala) terminal part of peptoglycans[68,69] while 2 neutral macrobicyclic anion receptors **70** and **71** display good complexation ability for carboxylate anions.[70]

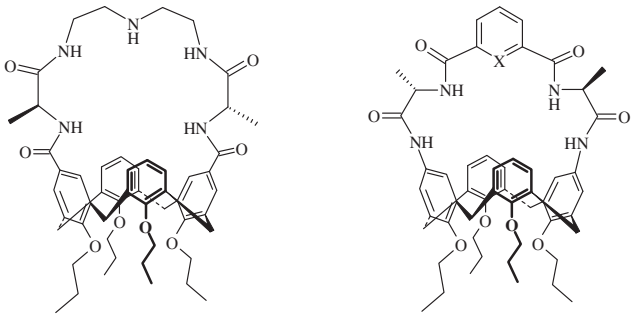


Figure 11. Upper rim bridged N-linked peptidocalix[4]arenes.

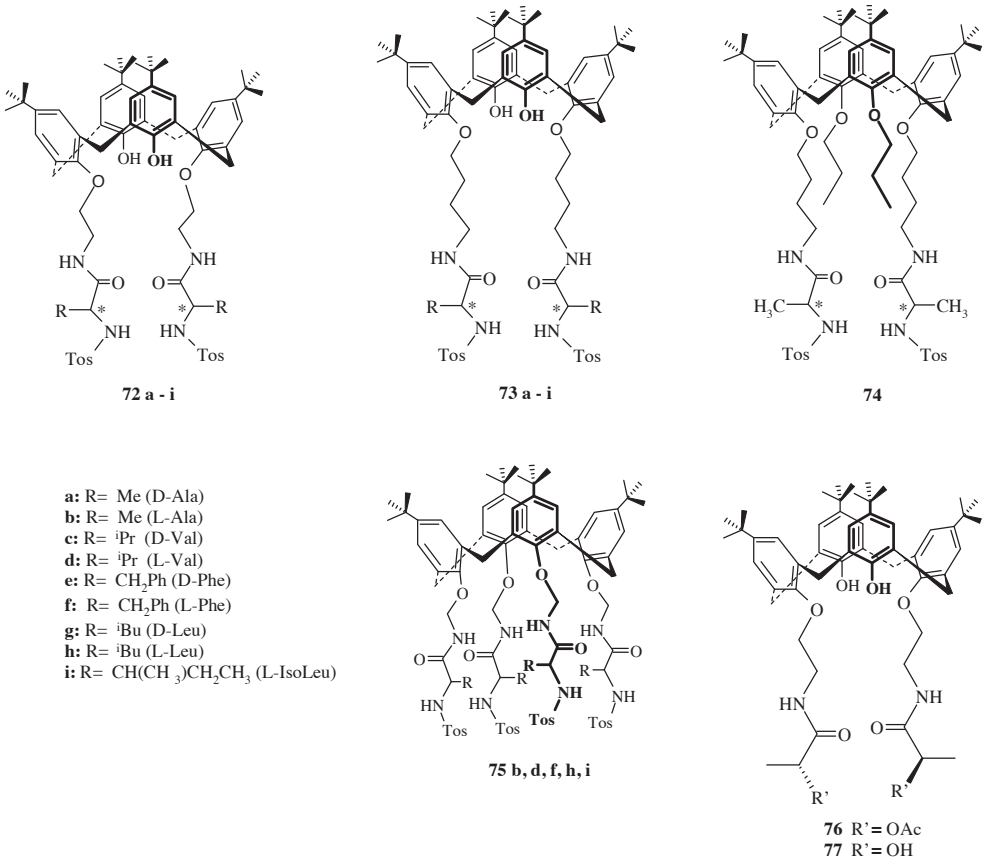


Figure 12. Chiral calix[4]arenes functionalized with α-hydroxyamide and amino acid functions.

New chiral calix[4]arenes functionalized at the lower rim with α-hydroxyamide and amino acid functions have been prepared (Figure 12) as a class of receptors selective for anions that are bound through hydrogen bonding with the NH group.[71−73] Host–guest complexation properties of these ligands towards various anions have been studied by ^{1}H-NMR spectroscopy. It was found that the chiral calix[4]arene derivatives **72-74** and **77** might be suitable for the synthesis of hydrophobic neutral anion receptors, which are able to bind anions in a 1:1 stoichiometry through hydrogen bonding. High binding constants are observed and better selectivity is obtained for N-tosyl-(L)-alaninate presumably due to additional πtπ interactions between the tosyl groups.

Bisurea calix[4]arene-based receptors **78-83** possessing amino acid moieties were obtained by means of nucleophilic addition reactions of the methyl esters of glycine, L-alanine, or L-isoleucine with isocyanatocalix[4]arenes (Figure 13). Ligand **81**, having alanine residues close to the urea binding groups, shows a remarkable ability to recognize $D-N$-acetylphenylalaninate from the corresponding L-isomer.[74]

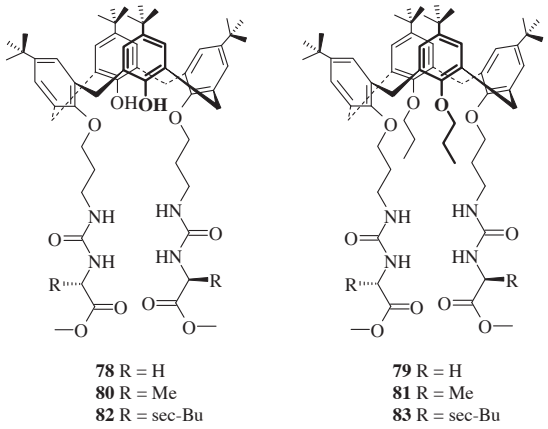


Figure 13. Bisurea calix[4]arene-based receptors possessing amino acid moieties.

Huang and co-workers have reported that calixarenes or their diamino derivatives were reacted with N-Boc-L-amino acids or N-chloroacetyl amino acid ester to give the calixarene diamide (Figure 14) **(84-89)** or diester (Figure 15) **(90-92)** derivatives.[75,76]

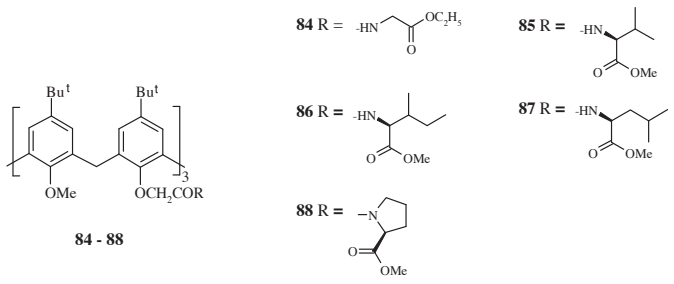


Figure 14. Chiral calix[6]arene diamide derivatives containing amino acid residues.

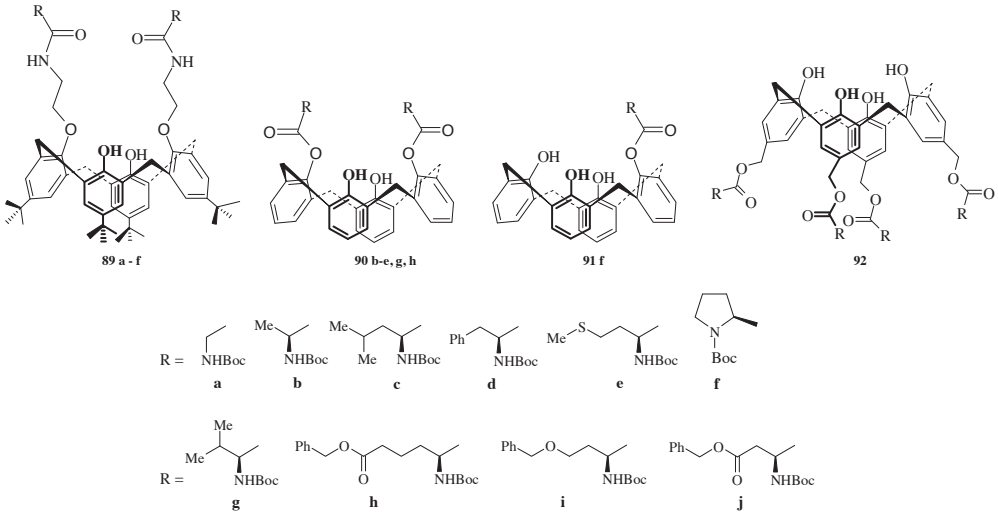


Figure 15. Chiral calix[4]arene amide and ester derivatives containing *N*-Boc-*L*-amino acids.

Mono, di, and tetrasubstituted chiral calix[4]arene derivatives bearing amino acid residues **(93-97)** at the lower rim have been prepared (Figure 16) to investigate possible hydrogen-bonding motifs with OH and amidic functions.[77]

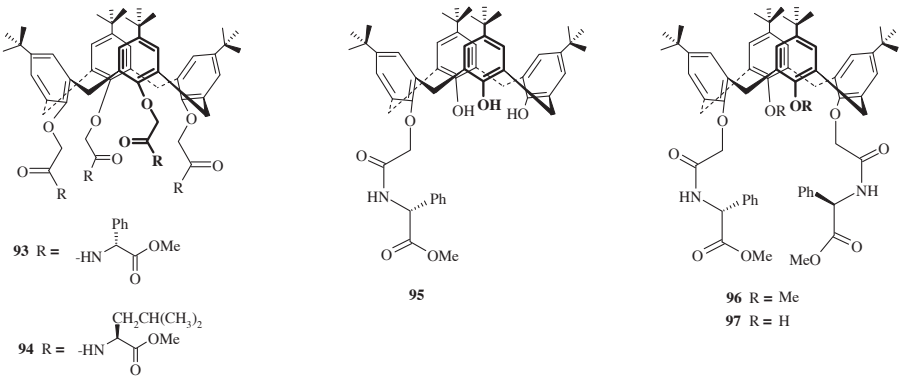


Figure 16. Mono, di, and tetrasubstituted chiral calix[4]arene derivatives bearing amino acid subunits.

Rudkevich et al. have described the design and synthesis of calix[4]arene amino acids (Figure 17) **98-103**, which were used as construction blocks to assemble nanoscale, multivalent entities—calix–peptides **104** and **105** and calix–peptide-dendrimers **106** and **107**.[78]

Neri et al. have described a series of *N*-linked tetrapeptidocalix[4]arene diversomers (Figure 18), **108-123**, by coupling of a cone calix[4]arene tetracarboxylic acid chloride with tetrapeptides obtained in a parallel fashion.[79] The inhibition activity of tetrapeptidocalix[4]arenes towards tissue and microbial transglutaminase was evaluated by in vitro assays with a labeled substrate.

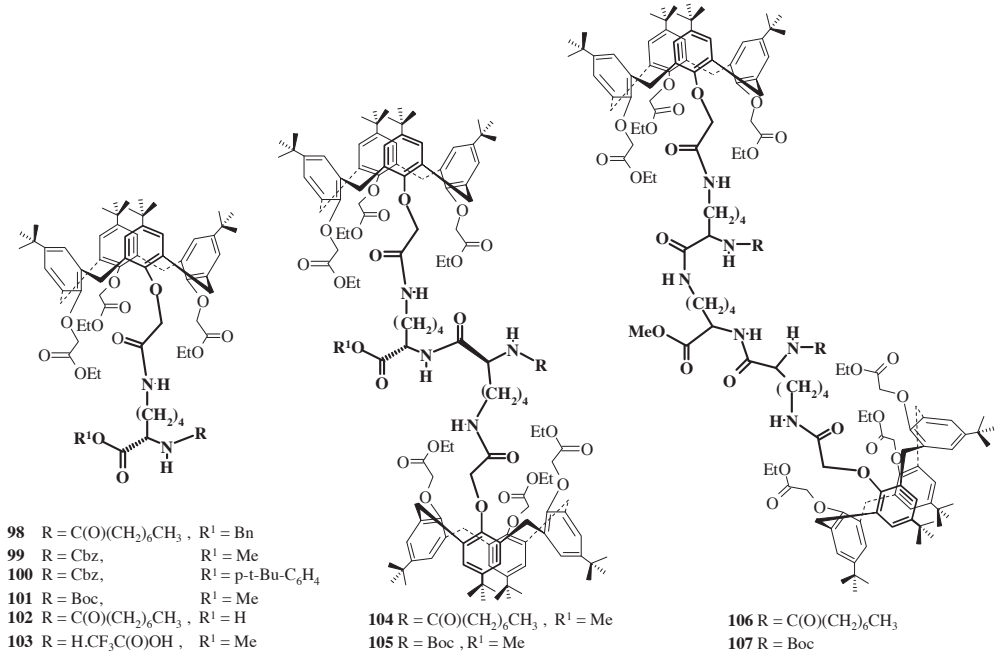


Figure 17. Calix[4]arene amino acids, calix–peptides, and calix–peptide-dendrimers.

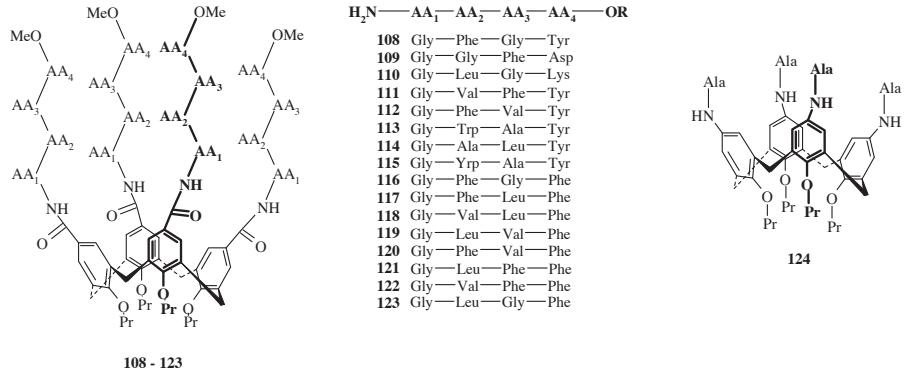


Figure 18. *N*-linked tetrapeptido- and alanine-substituted calix[4]arene derivatives.

Synthesis of alanine-substituted calix[4]arene (Figure 18) **124** from the acid chloride of Fmoc-alanine has been described by Shuker et al.[80] The dimerization and binding properties of compound **124** were also investigated by NMR spectroscopy. It was reported that this is the first example of a calix[4]arene derivative that self-associates in polar, protic solvent.

Water-soluble calix[4]resorcinarenes (Figure 19) **128-133** with 3- and 4-hydroxyproline substituent groups are evaluated as chiral NMR solvating agents on a series of monosubstituted phenyl-containing compounds. They suggested that the substrates interact with the calixresorcinarene through insertion of the aromatic ring into the cavity. Cationic, anionic, and neutral substrates were examined, and all exhibited enantiomeric discrimination in the ^{1}H-NMR spectrum with one or more of the calixresorcinarenes.[81–83]

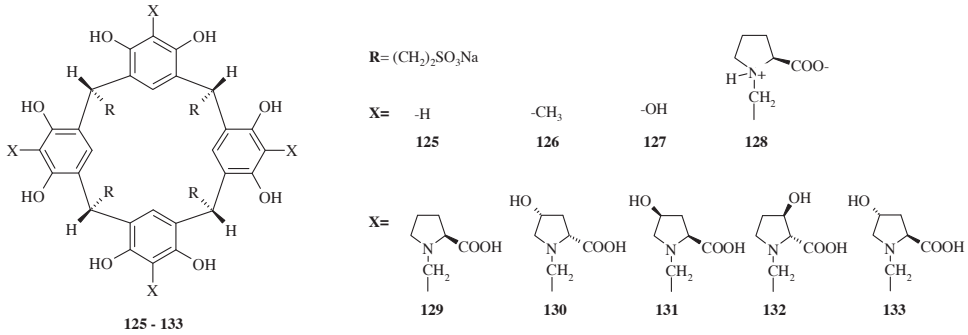
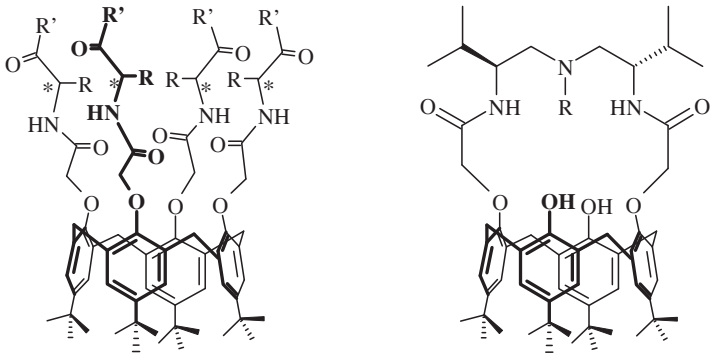


Figure 19. Water-soluble calix[4]resorcinarenes.

Warner et al. described the first chiral separations of 3 binaphthyl derivatives (BNHP, BINOL, and BNA) using ($N-L$-alaninoacyl)calix[4]arene **(135)** and ($N-L$-valinoacyl)calix[4]arene (Figure 20) **(136)** as pseudostationary phases in capillary electrophoresis.[84,85] All 3 binaphthyl derivatives were baseline resolved when chiral selector **136** or a mixture of sodium dodecyl sulfate and **135** was used as an additive to the buffer. The results showed that the optimum buffer pH was 11, and the buffer concentration was 40 mM Na_2HPO_4 for the separation.

New types of chiral calix[4](aza)crowns **(137, 138)** containing L-valine were synthesized by Wu and co-workers.[86] Chiral recognition properties of host **137** was studied by ^{1}H- and ^{13}C-NMR, and UV spectroscopy. It was found that host **138** exhibited different recognition ability towards the (R)- or (S)-mandelic acid and (L)- or (D)-dibenzoyltartaric acid.



134 R = Me; R' = OBu^t
135 R = $CH(CH_3)_2$; R' = OH
136 R = Me; R' = OH

137 R= Me
138 R= H

Figure 20. N-linked amino acid-substituted calix[4]arene and calix[4]azacrown derivatives.

Wenzel and co-workers have prepared a series of chiral calix[4]arenes **139-148**, by attaching optically pure amino acid esters of alanine, valine, leucine, and proline (Figure 21) through the phenolic oxygen atoms and calix[4]resorcarenes with primary and secondary amines and examined as CSAs in NMR spectroscopy.[87] Although there were a few examples when enantiomeric discrimination occurred in the ^{1}H-NMR spectra of substrates, the calix[4]arenes and calix[4]resorcarenes that were synthesized were generally unsuccessful at producing the intended effect.

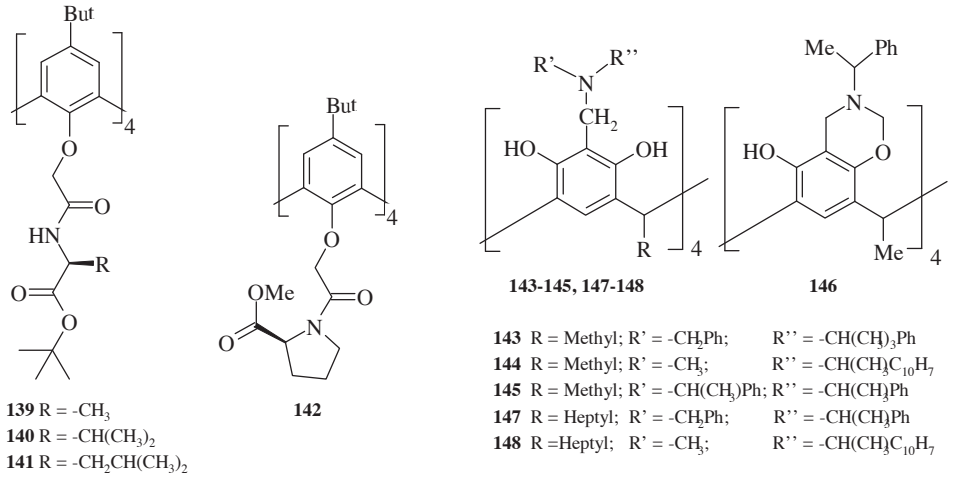


Figure 21. Chiral calix[4]arenes bearing optically pure amino acid esters of alanine, valine, leucine, and proline.

Two-armed chiral calix[4]arenes **(149-151)** functionalized at the lower rim with *L*-tryptophan units have been prepared by He and co-workers (Figure 22).[88] The enantioselective recognition of these receptors towards a series of chiral carboxylates has been studied by fluorescence titration and ^{1}H-NMR spectroscopy. Receptor **149** has been demonstrated to be a highly selective fluorescent sensor for *N*-Boc-protected alanine anion and **150** reveals good enantioselective recognition ability towards the enantiomers of mandelate. According to the results, a relatively rigid structure, good structural preorganization, steric effects, and multiple hydrogen bonds induce the enantioselective recognition ability of **149** and **150**.

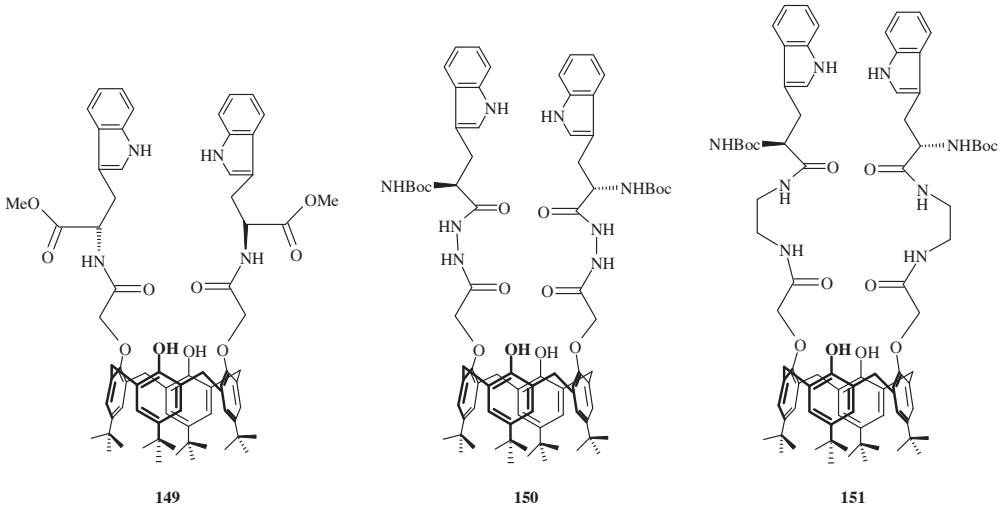


Figure 22. Two-armed chiral calix[4]arenes functionalized with *L*-tryptophan units.

Cheng and co-workers have reported the synthesis of a series of chiral calix[4]arene derivatives by the reaction of calix[4]arene diacid dichloride with various amino acid derivatives (Figure 23).[89–91] Receptors **152-154** were found to bind much more favorably with (*R*)-methyl lactate than with its (*S*)-enantiomer by using the quartz crystal microbalance (QCM) method, and thus render it as a good new candidate for chiral gas sensor

coatings, whereas receptor **159** was found to be an efficient receptor for the biologically important phosphate molecule whose neutral receptors are only scarcely reported (Figure 24).

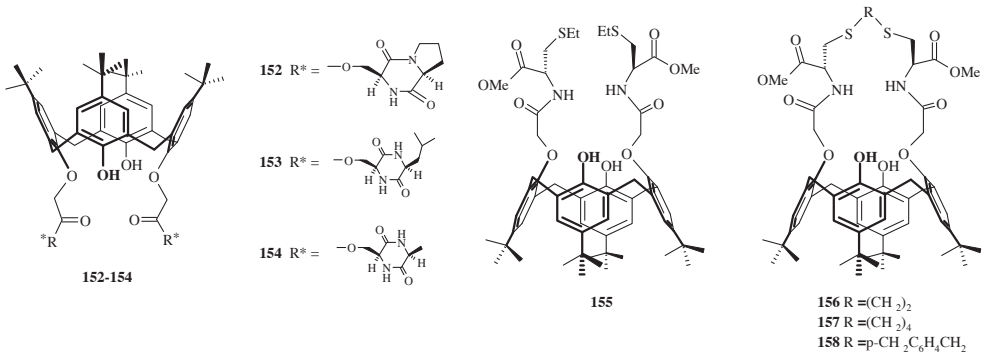


Figure 23. Dicyclopeptide-bearing calix[4]arene derivatives.

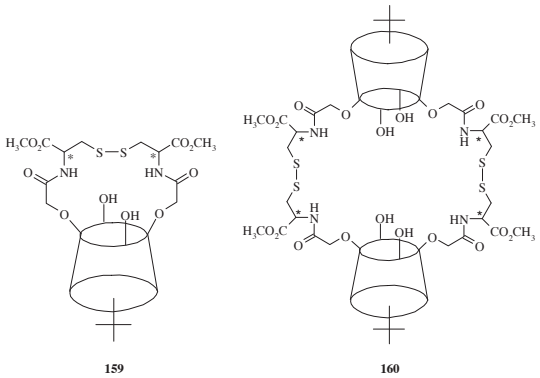


Figure 24. Cystine-containing calix[4]arene derivatives.

Neri and colleagues have described the synthesis of some new optically active calix[4]arene derivatives bearing chiral pendant units, which include amino acids, and pinene-like and binaphthyl groups (Figure 25).[92] The application of these derivatives in enantioselective catalysis was studied by testing the catalytic activities of the corresponding Ti(IV)/calixarene complexes, prepared in situ, in an asymmetric aldol reaction. Unfortunately, only limited enantioselectivities were observed.

Huang et al. have synthesized the Boc-*L*-proline-appended calix[4]arene derivatives **170-175** (Figure 26) and used them for the preparation of pure *m*-dimethylamino substituted inherently chiral calix[4]arenes.[93−95] Their applications as novel bifunctional organocatalysts in the enantioselective direct aldol reaction were also reported. It was found that the inherently chiral catalysts **173** and **175** could promote the aldol reaction between 4-nitrobenzaldehyde and cyclohexanone in the presence of acetic acid in high yields and with good enantioselectivities.

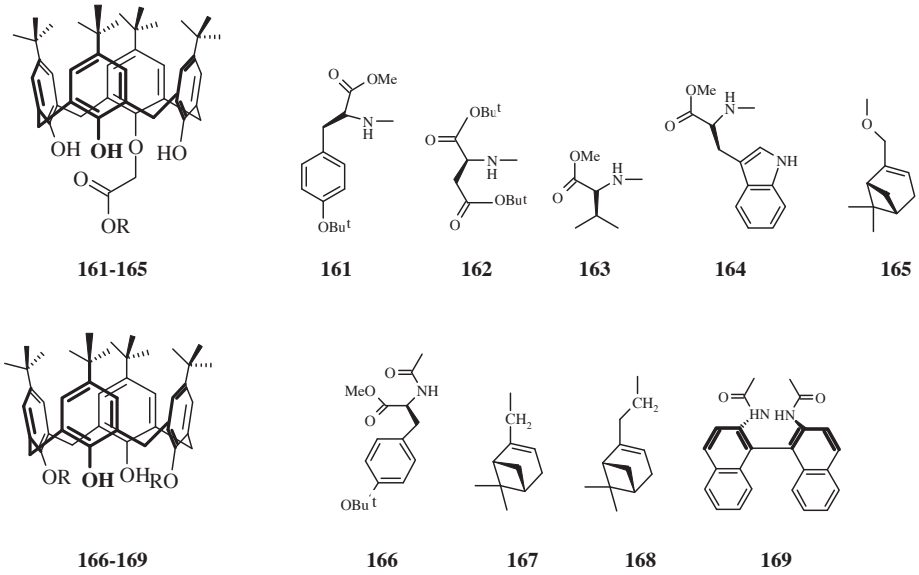


Figure 25. Optically active calix[4]arene derivatives bearing amino acids, pinene-like, and binaphthyl groups.

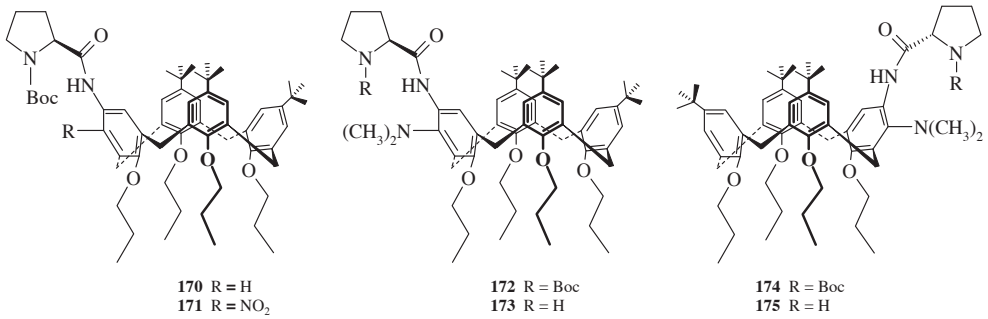
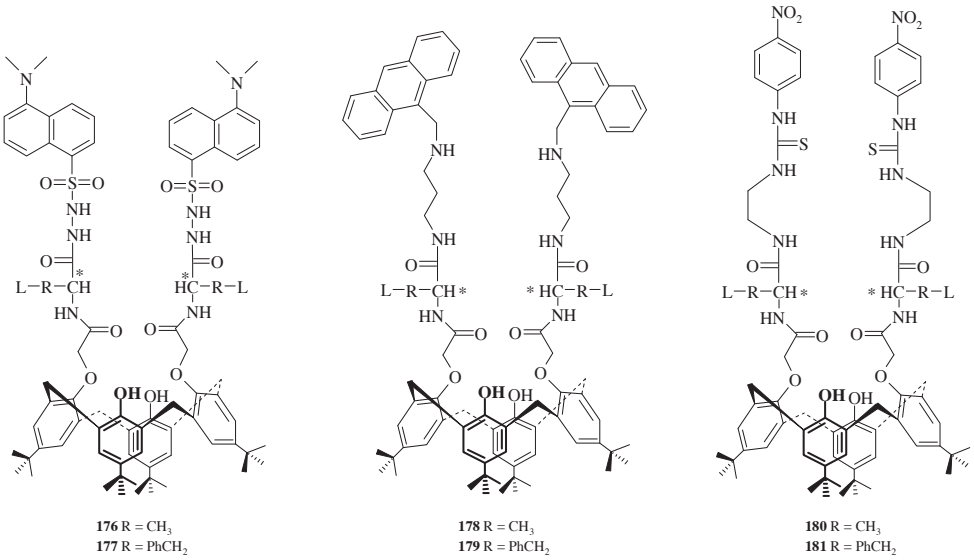


Figure 26. Boc-*L*-proline-appended calix[4]arene derivatives.

He et al. have constructed a series of chiral calix[4]arenes **(176-179)** (Figure 27) containing hydrazide, dansyl, and anthracene groups and examined them for their enantioselective recognition abilities by the fluorescence and ^{1}H-NMR spectra in $CHCl_3$.[96,97] The results indicate that both **176** and **177** exhibit excellent enantioselectivities towards *N*-protected alanine or phenylalanine anions due to the cooperative act of the hydrazide and amide in the binding amino acid anion by multiple hydrogen bonds, whereas receptors **178** and **179** exhibit good chiral recognition abilities towards the enantiomers of *D*- and *L*-tetrabutylammonium malate, and formed a 1:1 complex between the host and guest.

Similarly 2 chiral chromogenic sensors **180** and **181** containing both thiourea and amino acid binding units have been synthesized and examined for their chiral anion-binding abilities by UV/Vis absorption and ^{1}H-NMR spectroscopy.[98] The results reveal that **180** exhibits good enantioselective recognition for the enantiomers of the α-phenylglycine anion. Moreover, the marked color changes observed for the complexation of **180** with the chiral anions reveal that receptor **180** could be used as a good chiral chromogenic chemosensor for the enantiomers of the α-phenylglycine anion.



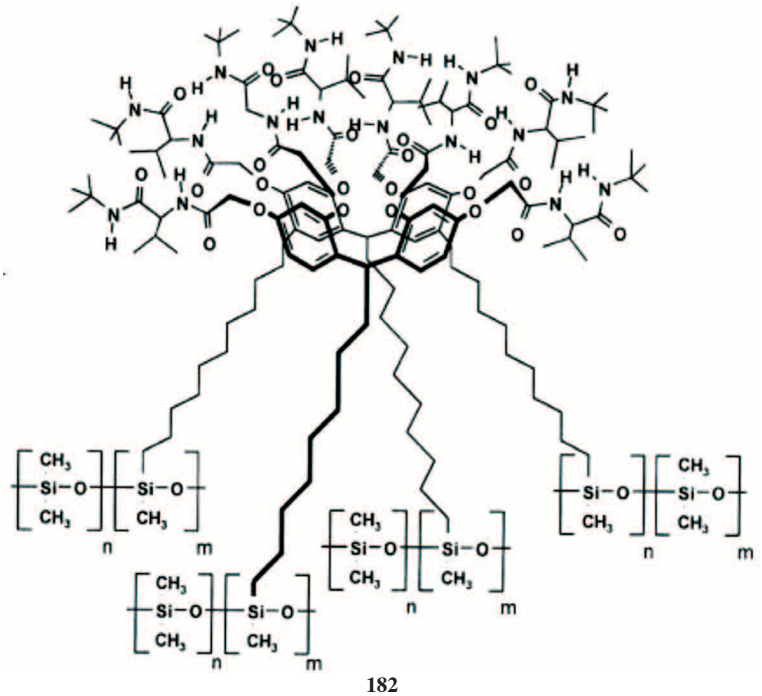
176 R = CH_3
177 R = $PhCH_2$

178 R = CH_3
179 R = $PhCH_2$

180 R = CH_3
181 R = $PhCH_2$

Figure 27. Chiral calix[4]arenes containing hydrazide, dansyl and anthracene groups.

The synthesis of a new enantiomerically pure resorcinarene by linking *L*-valine tert butylamide to the 8 hydroxy groups of a resorc[4]arene was described by Schurig and co-workers.[99,100] The chiral macrocyclic product was chemically bonded to a poly(hydro)dimethylsiloxane by hydrosilylation using a platinum catalyst (Figure 28). The resulting chiral polysiloxane Chirasil-Calix **182** can be used as chiral stationary phase (CSP) in capillary gas chromatography.



182

Figure 28. Chirasil-Calix as chiral stationary phase (CSP) in capillary gas chromatography.

Fluorescent Groups

Calixarene-based enantioselective fluorescence receptors are generally composed of a fluorophore and a chiral moiety attached to the calix[4]arene skeleton and organic fluorophores are usually arranged in proximity to hydrogen bonding and chiral centers in the host molecule in such a way that binding of the guest species results in quenching of the fluorescence.[101] The use of fluorescently labeled chiral calixarenes for enantioselective recognition of chiral amines and amino alcohols have attracted considerable interest because such receptors potentially provide a real-time technique that can be used to determine the enantiomeric composition of chiral molecules.[102−105]

The excellent chiral recognition ability of 1,1-binaphthocrowns was utilized in calixarene chemistry for the first time by Kubo et al., who prepared chromogenic receptors **(*S*)-183** and **184** containing indophenol indicator units as part of the calixarene core (Figure 29).[106−108] Ligand **(*S*)-183** and to some extent **(*S*)-184** was disclosed to selectively recognize (*R*)-phenylglycinol in EtOH solution associated with a remarkable change of color, thus representing the first chiral sensor for the colorimetric determination of amine enantiomers.

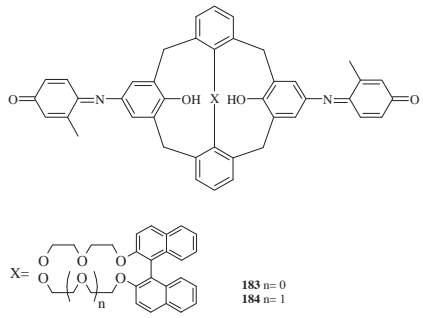


Figure 29. Chiral calix[4]arene derivatives containing indophenol indicator units.

Chiral calixarene derivatives **(185-187)** bearing (*S*)-di-2-naphthylprolinol and (*R*/*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol groups have been synthesized by Diamond and co-workers (Figure 30).[109−111] One of these, an (*S*)-di-2-naphthylprolinol tetramer **185**, is shown to exhibit significant ability to discriminate between enantiomers of 1-phenylethylamine (PEA), phenylglycinol, and norephedrine on the basis of the quenching of the (*S*)-di-2-naphthylprolinol fluorescence emission in chloroform. In these guest molecules, the common feature is the positioning of hydrogen bonding sites and a chiral center immediately adjacent to an aryl ring. The aryl ring is known to be a crucial feature, as cyclohexylethylamine, the nonaromatic analogue of phenylethylamine, has no quenching effect at all.

Similarly, a propranolol amide derivative of *p*-allylcalix[4]arene **188** in which binding sites and the chiral center separated from the fluorescent naphthyl groups by an additional ether group has been designed to behave as a molecular sensor capable of distinguishing chiral amines on the basis of their shape and chirality.[112] This ligand was found to successfully discriminate between the enantiomers of phenylalaninol, which possesses a methylene spacer between its aromatic moiety and chiral center. It was also found that a significant enhancement in the observed enantiomeric discrimination would occur on binding of the calixarene with potassium cation.

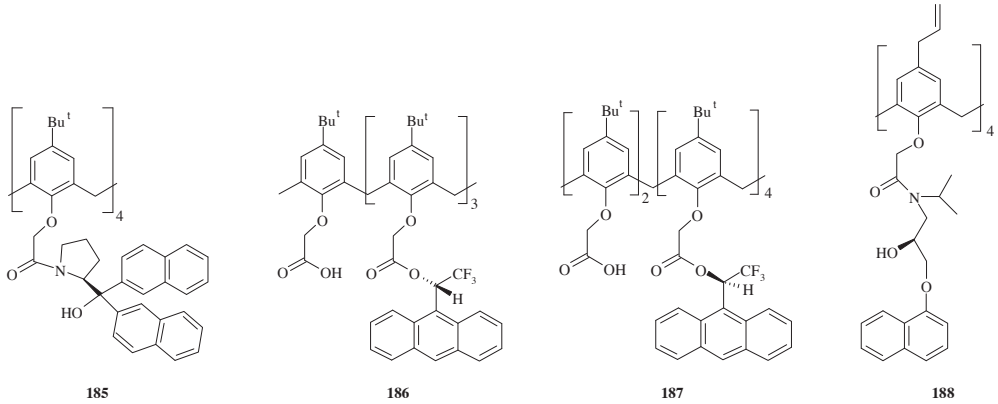


Figure 30. Chiral calixarene derivatives bearing (*S*)-di-2-naphthylprolinol and (*R*/*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol groups.

Recently Huang et al. reported the synthesis of a series of tri-*O*-alkylated and tetra-*O*-alkylated inherently chiral fluorescent calix[4]crowns in the cone and partial cone conformations respectively using (S)-BINOL attached calix[4]arenes **(189-194, 198-200)** (Figure 31).[113−115] One of the tetra-*O*-alkylated inherently chiral fluorescent calix[4]crown-6 in the partial cone conformation **197** was found to exhibit considerable enantioselective recognition capability towards the enantiomers of leucinol.

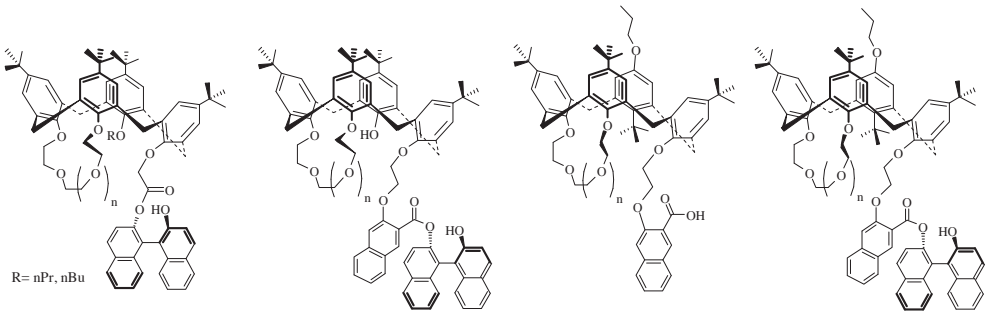


Figure 31. Chiral fluorescent calix[4]crowns in the cone and partial cone conformations.

The same group have also presented the preparation of chiral calix[4]arenes **201-204** derived from (*S*)-BINOL or (*R*)-phenylglycinol (Figure 32) and employed in the synthesis of a series of inherently chiral calix[4]quinolines on the upper rim.[116] Their optical resolutions were conveniently achieved through the separation of their diastereomers.

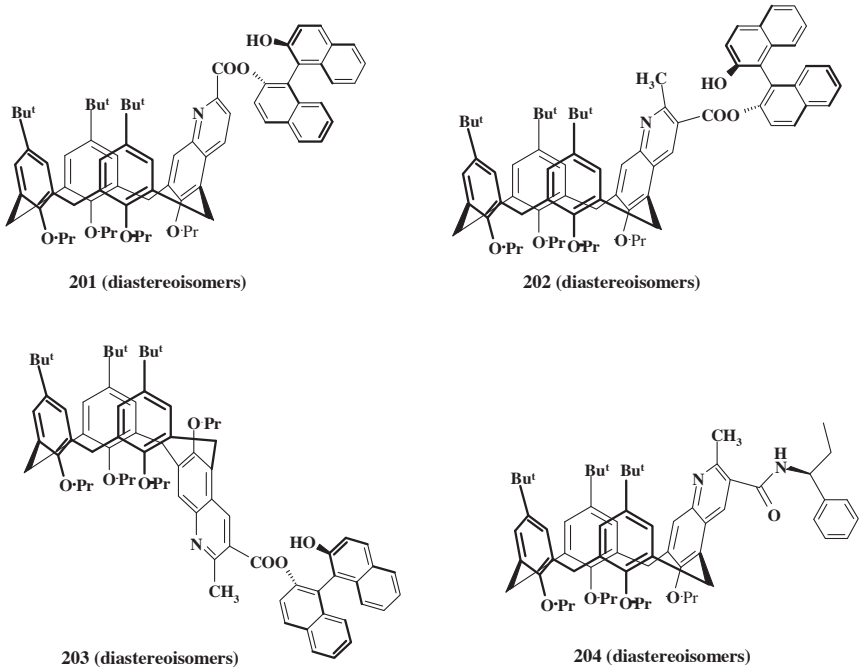


Figure 32. Chiral calix[4]arenes derived from (*S*)-BINOL and (*R*)-phenylglycinol.

Chiral calix[5]arenes bearing a binaphthyl crown on the lower rim, **(*R*)-, (*S*)-205** and **(*R*)-, (*S*)-206** were successfully synthesized (Figure 33).[117] The complexes [**(*R*)-205.Cu**$^{2+}$] and [**(*S*)-205.Cu**$^{2+}$] were used as binary hosts to recognize carbohydrates. The fluorescent titration experiments showed that the binary hosts can selectively recognize *D*-(+)-gluconic acid δ-lactone between various carbohydrates.

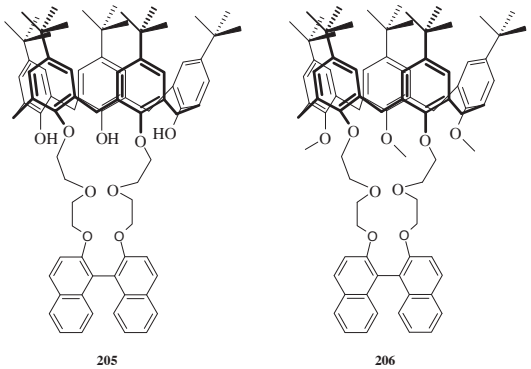


Figure 33. Chiral calix[5]arenes bearing a binaphthyl crown unit at the lower rim.

New chiral upper and lower rim (*R*)-binaphthyl-bridged calix[4]arenes **(207-212)** have been synthesized by exploiting the selective functionalization of the calix[4]arene skeleton (Figure 34).[118] Their complexation properties toward neutral molecules, alkali metal, and silver(I) cations have also been explored.

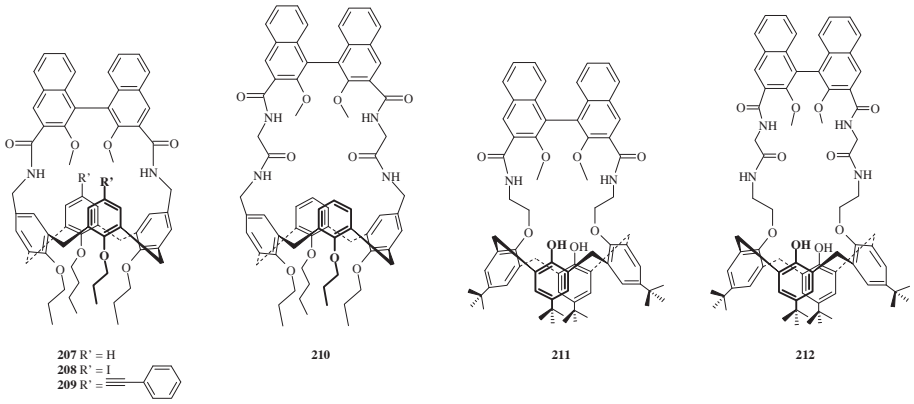


Figure 34. (*R*)-binaphthyl-bridged chiral calix[4]arenes.

Sugars

Model *O*-glycosylation reactions at either rim of calix[4]arenes are described by Dondoni and Ungaro with the aim of providing access to a new family of carbohydrate-containing calixarene derivatives named calixsugars.[119,120] One or 2 sugar moieties (*D*-mannofuranose and *D*-glucopyranose) were introduced at the lower rim of the calix[4]arene **(213-218)** by glycosylation of the phenolic hydroxyl groups by means of a Mitsunobu reaction whereas tetrapropoxy calix[4]arenes bearing 2 or 4 hydroxymethyl groups at the upper rim were coupled with perbenzoylated thioethyl *D*-galactoside and *D*-lactoside and β-linked bis- and tetrakis-*O*-galactosyl calix[4]arenes were obtained **(219-222)** (Figure 35). The galactose-containing calixsugars showed some affinity toward charged carbohydrates and dihydrogen phosphate anion.

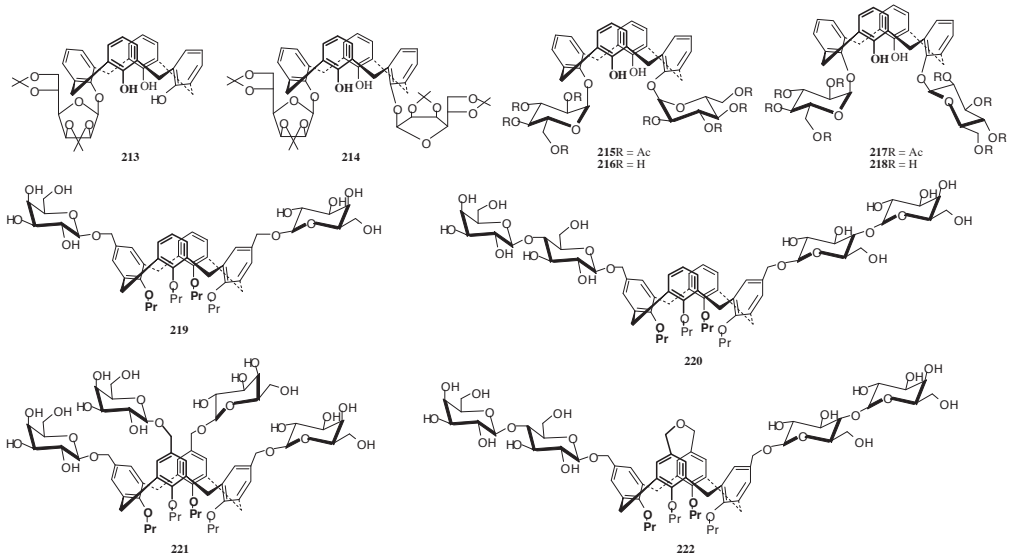


Figure 35. Carbohydrate-containing calixarene derivatives.

Lhotak and co-workers have described new calixarene–saccharide conjugates **223-225** using the reaction between the appropriate acyl chloride and an amino calix[4]arene or an aminosaccharide derivative (Figure

36).[121] The introduction of sugar moieties into the lower rim of calix[4]arene leads to novel receptors, the usefulness of which has been demonstrated by their interaction with various monosaccharide derivatives.

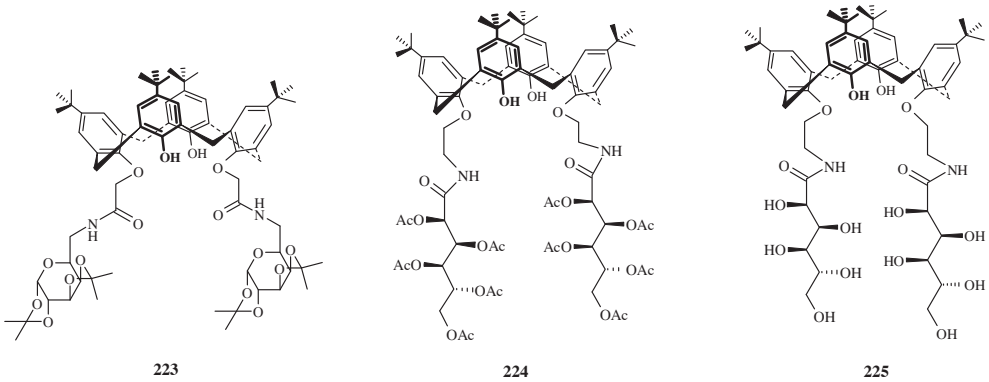


Figure 36. Calix[4]arene–saccharide conjugates.

Consoli and co-workers have also described an efficient approach for the introduction of 8 mono- or disaccharide sugar moieties (*D*-glucose, *N*-acetyl-*D*-glucosamine, *D*-galactose, *L*-fucose, *D*-maltose, and *D*-cellobiose) at the upper rim of calix[8]arene, using thioureido linkers (Figure 37).[122] It was reported that the glycocalix[8]arenes **226-237** may act as biomimetic carbohydrate systems and as hosts for highly polar organic molecules.

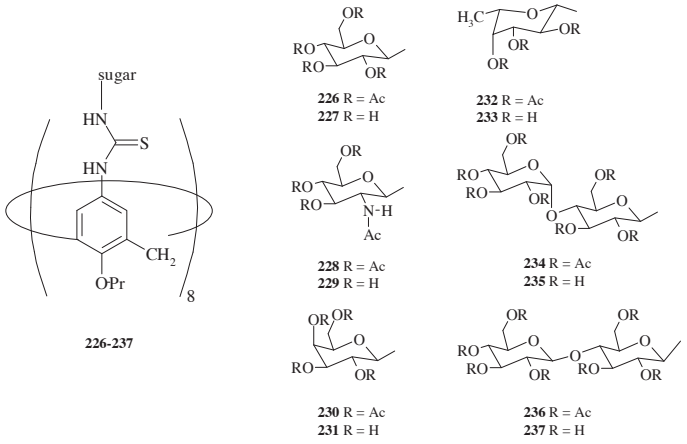


Figure 37. Calix[8]arene bearing sugar moieties.

The synthesis and biological activity of new tetrakis(mannopyranosyl) calix[4]arenes **(238-241)** with a deepened cavity were described using the Sonogashira reaction for the assembly of the sugar moieties onto the calix[4]arene scaffolds (Figure 38).[123]

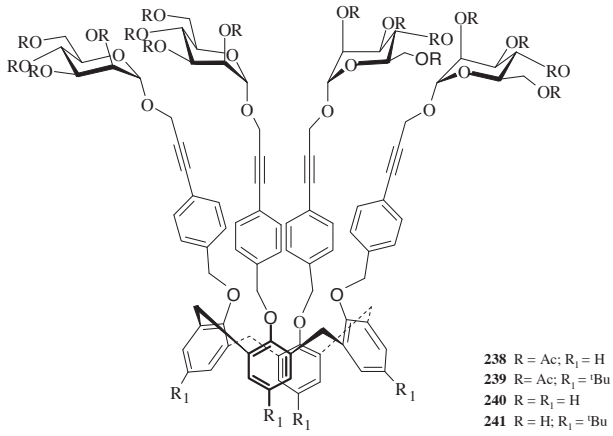


Figure 38. Tetrakis(mannopyranosyl) calix[4]arenes.

Bitter, Kubinyi, and co-workers have produced novel chromogenic 1,3-calix[4](crown-6) derivatives (Figure 39) composed of 1,1'-binaphthyl, $\alpha - D$-glucoside, and D-mannitol moieties in the crown ether ring and supplied with 2,4-dinitrophenylazo indicator groups.[124,125] Receptors **242e** and **243g** exhibited noticeable chiral recognitions toward α-methylbenzylamine enantiomers. The UV fluorescence of **(*R*)-242e/(*S*)-242e** arising from the binaphthyl moiety is quenched by K^+ ions, but not by the amine guests, showing that the interaction between the binaphthyl group and the complexed amines is weak.

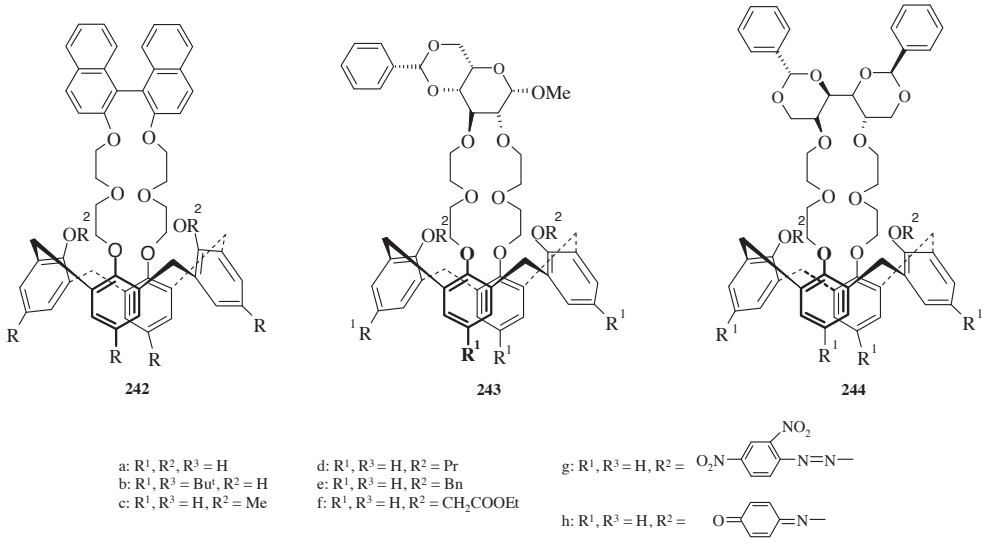


Figure 39. Chromogenic 1,3-calix[4](crown-6) derivatives from 1,1'-binaphthyl, $\alpha - D$-glucoside and D-mannitol moieties.

The synthesis of molecular capsules using non-covalent interactions is a very attractive area of supramolecular chemistry. Rebek et al. described the optically active tetraureas **247-258,** prepared through reaction of the tetraamine calix[4]arene with the appropriate isocyanates derived from amino acid methyl esters, which have self-complementary recognition sites and assemble into dimeric structures (Figure 40).[126,127]

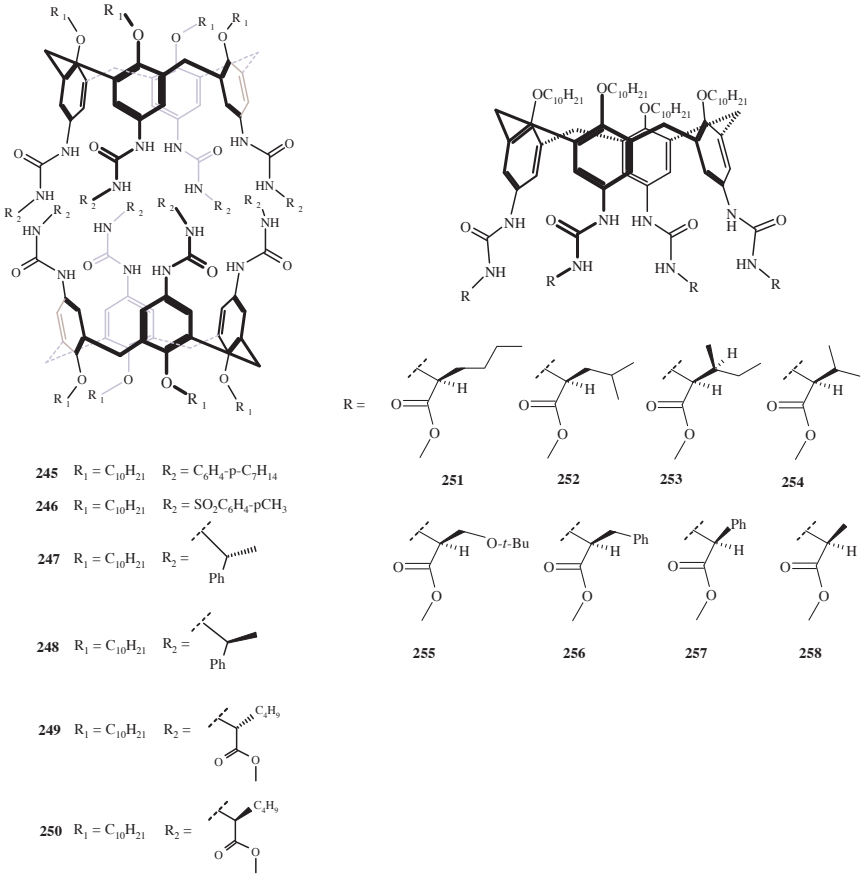


Figure 40. Tetraureas of calix[4]arene derivatives and calixarene-based dimers.

Tartaric Acid Derivatives

Tartaric acid derivatives are useful building blocks for the synthesis of chiral calixarenes. The attachment of homochiral residues to the lower rim provides a calixarene with novel properties and the synthesis of calixcrowns has been reported. For example, tartaric ester chloroacetates can be easily prepared by the reactions of chloroacetyl chloride with esters of tartaric acid. Attaching of these chiral fragments to the platforms of calix[4]arenes affords a new kind of chiral calix[4]arene derivatives **259-261** (Figure 41).[128]

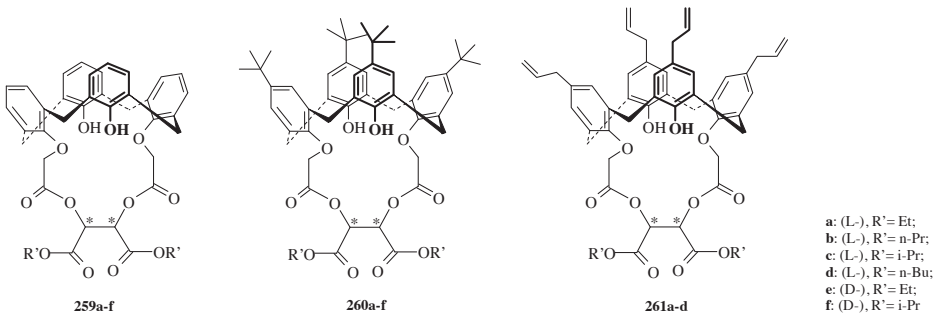


Figure 41. Chiral calix[4]arenes bearing tartaric ester moieties.

Our group has also described the synthesis of new chiral calix[4]arene derivatives **263-267** containing tartaric acid ester moieties at the lower rim and various functionalities including aldehyde, nitro and Schiff base at the upper rim (Figure 42).[129,130] The chiral recognition capabilities of calix[4]arene derivatives toward the guests, 1,2-propanediol and α-aminoacid esters, were investigated by ^{1}H-NMR and UV-vis spectroscopy. Chiral hosts **262** and **263** showed enantiomeric recognition toward *rac*-serine methyl ester hydrochloride and 1,2-propanediol, respectively, due to the multiple hydrogen bonding. On the other hand, chiral selectors **265-267** show good recognition ability for the enantiomers of phenylalanine and alanine methyl ester hydrochlorides (up to $K_D/K_L = 4.36$, $\Delta\Delta G_0 = -3.65$ kJ mol^{-1}). The D/L-enantioselectivities are found to be highly sensitive to the Schiff base moiety attached to the upper rim of calix[4]arene and the shape of the substituted group in amino acid derivatives. The steric hindrance between the ammonium cation and Schiff base moiety around the stereogenic centre of the host may play an important role in chiral recognition and is expected to be minimized for the D-isomer in all cases. Therefore, the D-isomers of amino acid ester hydrochlorides form more favorable complexes with the chiral selectors than the L-isomers.

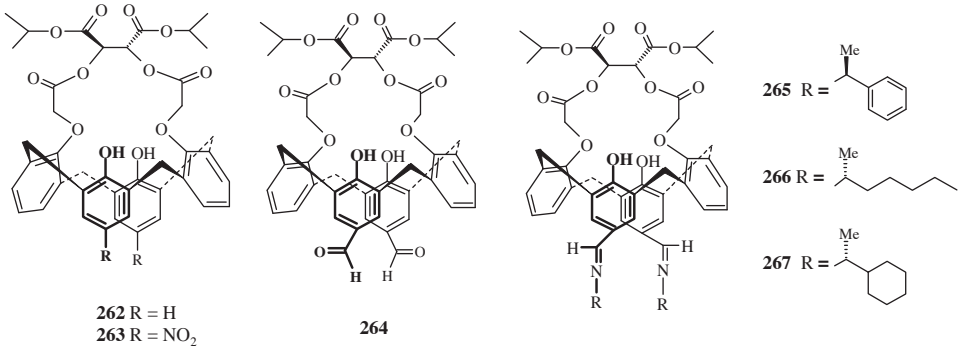


Figure 42. Tartaric ester derivatives of calix[4]arenes with various functionalities including aldehyde, nitro and Schiff base at the upper rim.

Menthone Derivatives

The synthesis of new chiral calix[n]arenes **268-271** was reported by Schurig et al. similar to the one-pot procedure described by Gutsche and co-workers using (p-hydroxy-phenyl)-menthone and (-)-menthone (Figure 43).[131,132] Calix[n]arenes with different ring sizes were obtained in reasonable yields.

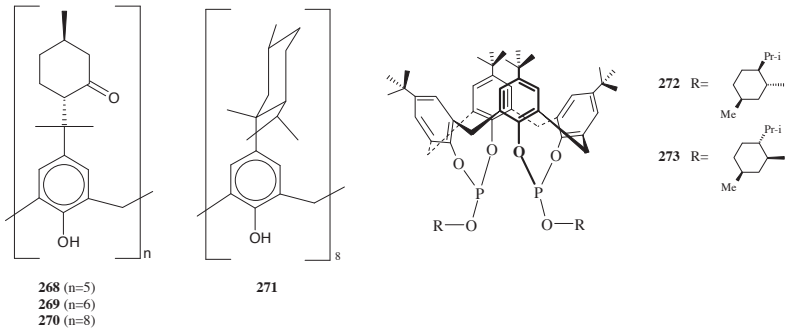
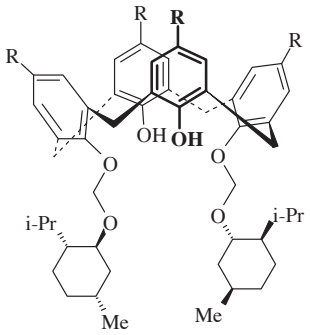


Figure 43. Calix[n]arenes from (p-hydroxy-phenyl)-menthone and (-)-menthone.

Chiral *p-tert*-butyl-calix[4]arene bisphosphites **(272-273)** have been synthesized by the reaction of *p-tert*-butyl-calix[4]arene and the phosphorodichloridites, $ROPCl_2$ [R = (1*S*,2*R*,5*R*)-(+)-iso-menthyl or (1*R*,2*S*,5*R*)-(-)-menthyl.[133]

Lopez and co-workers have investigated the complex formation between the antibiotic levofloxacin and a series of chiral calix[4]arene derivatives **274-279** possessing 2 (+)-isomenthyl substituents at the lower rim (Figure 44).[134]



274: R= H
275: R= CH_3
276: R= ^{t}Bu
277: R= CH_2CHCH_2
278: R= $COCH_3$
279: R= NO_2

Figure 44. Chiral calix[4]arene derivatives possessing (+)-isomenthyl substituents.

Cinchona Alkaloids

Cinchona alkaloids have served extensively as the primary source of effective chiral catalysts and resolving agents. These inexpensive commercially available alkaloids can be used as chiral residues in the synthesis of calixarenes. Recently, the synthesis of the first calixarene-based chiral phase-transfer catalysts derived from cinchona alkaloids has been achieved by our group in 2 steps from *p-tert*-butylcalix[4]arene (Figure 45).[135] The catalytic efficiency of the chiral calix[4]arenes **280-282** was evaluated by carrying out the phase transfer alkylation of *N*-(diphenylmethylene)glycine ethyl ester with benzyl bromide. Benzylation of glycine imine using calix[4]arene-based dimeric catalyst **280** as a chiral phase-transfer catalyst in toluene/$CHCl_3$ mixture (7:3 v/v) at 0 °C gave the best enantioselectivities up to 57% ee and yields in the presence of aqueous NaOH.

The synthesis and chromatographic evaluation of novel carbamate and urea-linked cinchona-calixarene hybrid-type receptors **283-286** and chiral stationary phases (**287-290**) being derived from 9-amino(9-deoxy)-quinine (AQN), 9-amino(9-deoxy)-epiquinine (eAQN), quinine (QN) and its corresponding C9-epimer (eQN) were described (Figure 45).[136,137] The receptors display complementary enantiomer separation profiles in terms of elution order, chiral substrate specificity, and mobile phase characteristics, indicating the existence of 2 distinct chiral recognition mechanisms. The QN-and AQN-derived CSPs **288** and **290** showed enantioselectivities for open-chained amino acids, preferentially binding the (*S*)-enantiomers. In contrast, the eQN and eAQN congeners **287** and **289** exhibited broad chiral recognition capacity for open-chained as well as cyclic amino acids, and preferential binding of the (*R*)-enantiomers.

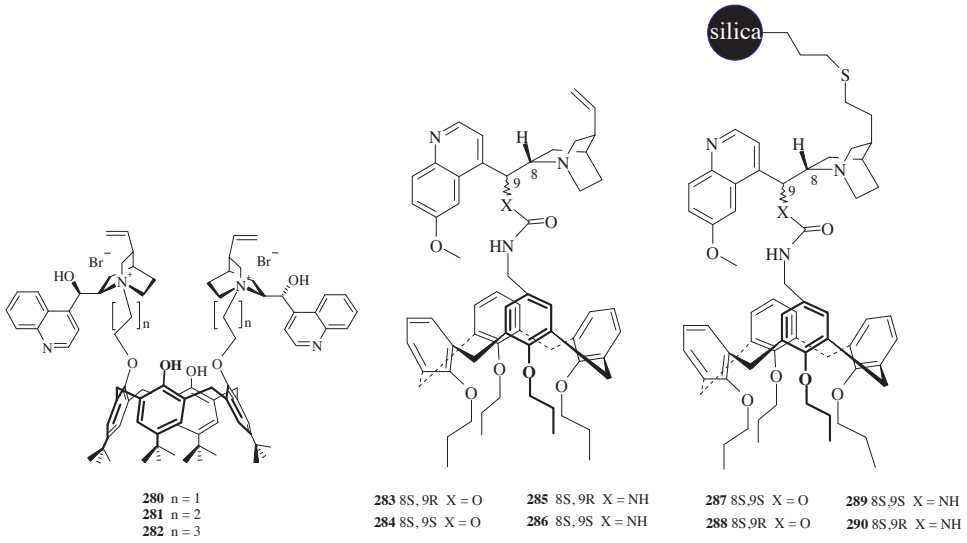


Figure 45. Chiral calix[4]arenes from cinchona alkaloids as chiral phase-transfer catalysts and stationary phases.

Camphor Sulfonyl Chloride

Camphor sulfonyl chloride has also been employed for the introduction of chirality into calixarenes. Kalchenko and co-workers have reported the preparation of chiral calix[4]arenes **(291-295)** from the reaction of calix[4]arene monoalkyl ethers with 1(S)-camphor-10-sulfonyl chloride and (R)- or (S)$-N$-(1-phenylethyl)bromoacetamides (Figure 46).[138−140] Enantiomerically pure inherently chiral calix[4]arene derivatives **294d,e** and **295d,e** have been synthesized using chiral receptors **291d,e** in preparative yields and high diastereomeric excess.

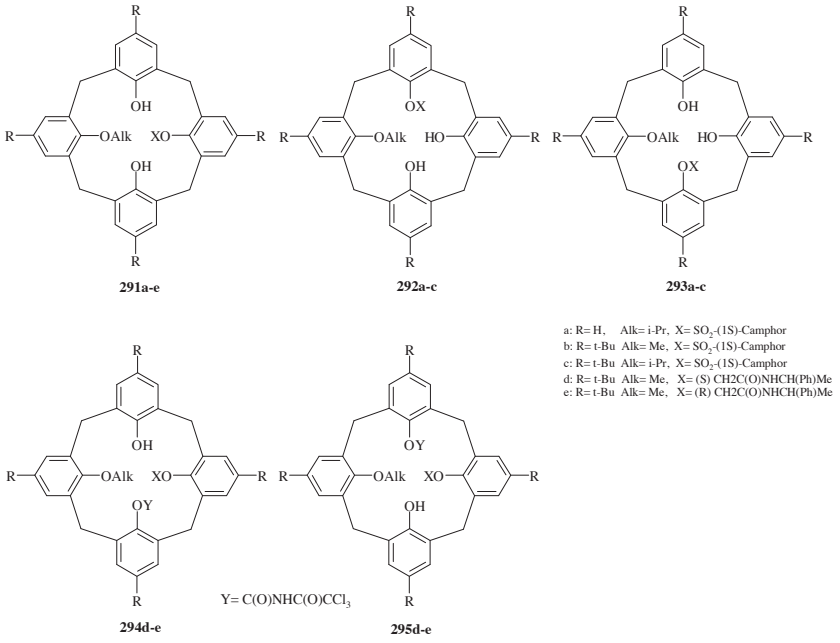


Figure 46. Chiral calix[4]arenes from camphor sulfonyl chloride.

Shimizu et al. have prepared the chiral calix[4]arene derivatives **297** and **298** bearing a chiral residue (camphorsulfonyl group) for the optical resolution of racemic inherently chiral wide rim ABCD-type calix[4]arene **296** fixed in a cone conformation (Figure 47).[141] The chiral calix[4]arene **296** was used as an organocatalyst in asymmetric Michael addition reactions of thiophenols.

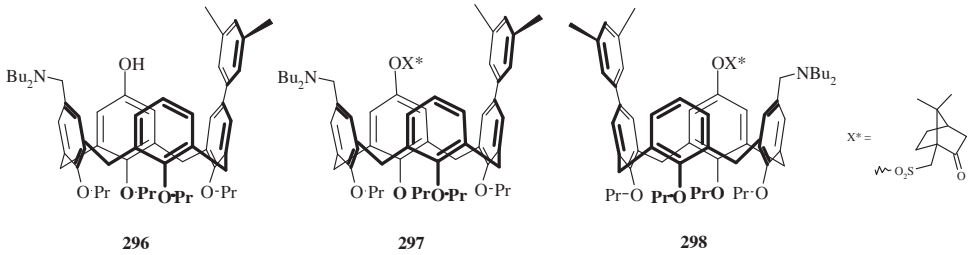


Figure 47. Inherently chiral calix[4]arene derivatives bearing camphor sulfonyl group.

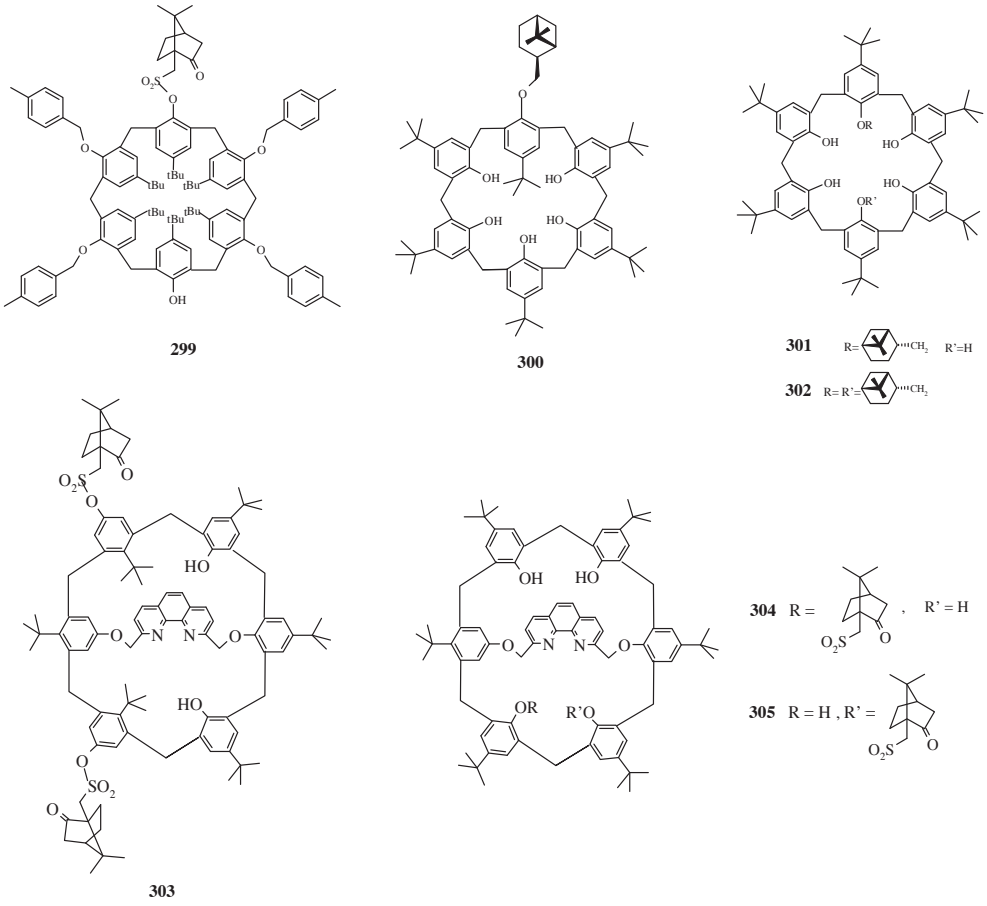


Figure 48. Chiral derivatives of the 1,10-phenanthroline-bridged calix[6]arene.

Luning et al. have investigated several approaches to chiral derivatives of the 1,10-phenanthroline-bridged calix[6]arene, and a series of new chiral calix[6]arenes has been synthesized (Figure 48).[142] The calixarenes **299-305** carrying chiral substituents (camphorsulfonyl, myrtanyl) have been prepared using enantiomerically pure

reagents. All compounds have been tested as ligands for copper ions in the CuI-catalyzed cyclopropanation of styrene and indene but most exhibited selectivities were only marginal.

Epoxides and Glycidyl groups

For the first time, Neri and co-workers reported calixarenes bearing chiral glycidyl groups at the lower rim by treatment of *p-tert*-butylcalix[4]arene and *p-tert*-butylcalix[6]arene with glycidyl tosylate.[143] Regio- and stereoselective ring-opening reaction of **307** with amines led to chiral β-aminoalcohols **(308 and 309)** (Figure 49).

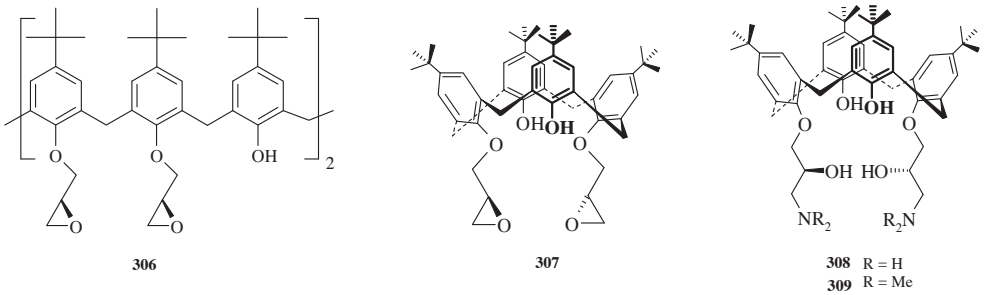


Figure 49. Calixarenes bearing chiral glycidyl groups at the lower rim.

A new series of chiral calix[4]arenes bearing β-amino alcohol groups have been synthesized by conducting through the binding of glycidyl groups followed by the regioselective opening by 2 different amines (Figure 50).[14] In the presence of $[Ru(p\text{-cymene})Cl_2]_2$, the monofunctionalized ligands **313** and **314** proved to be useful catalysts in the asymmetric transfer hydrogenation of acetophenone and showed good enantioselectivities (ee max = 90%) and very good conversions (conversion max = 97%).

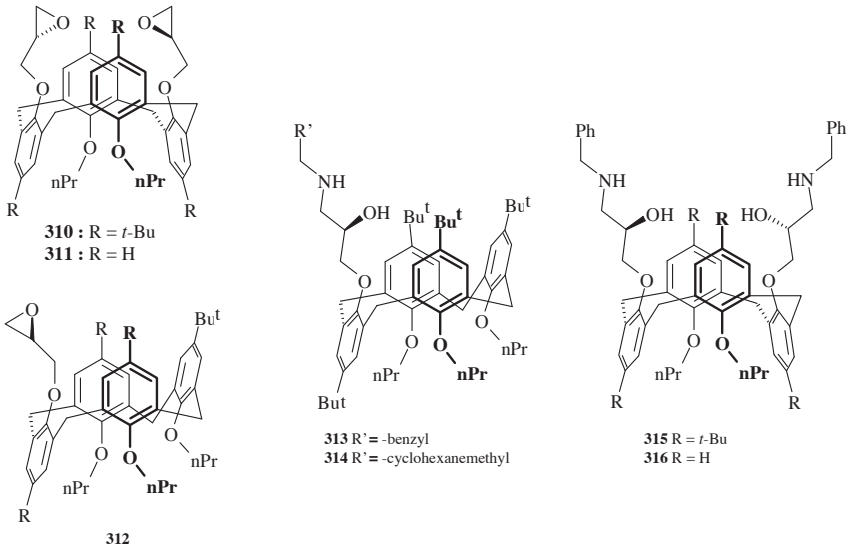


Figure 50. Chiral calix[4]arenes bearing glycidyl groups as chiral catalysts.

We have also used (*R*)-styrene oxide as a chiral source in the synthesis of chiral calix[4]azacrown ethers **317-320** (Figure 51).[144,145] The chiral recognition of these receptors towards the enantiomers of carboxylic acids and α-amino acid esters has been studied by ^{1}H-NMR spectroscopy.

Chiral selectors **318** and **319** showed strong binding and some chiral recognition ability for the enantiomers of racemic carboxylic acids and α-amino acid esters, respectively, whereas **317** exhibited different chiral recognition abilities towards both enantiomers of carboxylic acids and α-amino acid esters. The molar ratio and the association constants of the chiral hosts with each of the enantiomers of guest molecules were determined by using Job plots and a nonlinear least-squares fitting method, respectively. The results indicate that the multiple hydrogen bonding, steric hindrance, structural rigidity or flexibility and $\pi-\pi$ stacking between the aromatic groups may be responsible for the enantiomeric recognition.

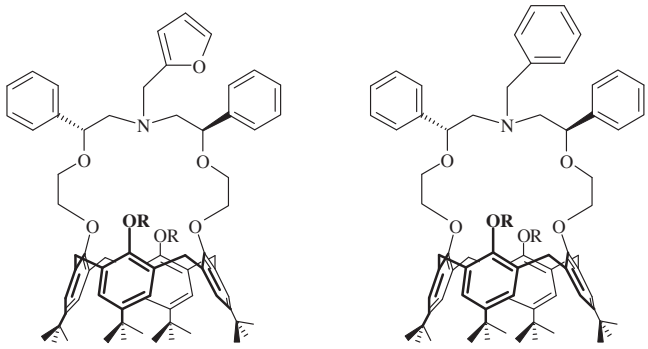


Figure 51. Chiral calix[4]azacrown ethers selectors from (*R*)-styrene oxide as a chiral source.

Ethyl Lactate

Recently, Barretta et al. reported a series of ethyl lactate derivatives **321-323** of *p-tert*-butylcalix[4]arene as chiral solvating agent (CSA) (Figure 52) for the differentiation of the NMR spectra of enantiomeric mixtures of amino acid derivatives.[146] The origin of enantiodiscrimination in solution was investigated by NMR spectroscopy and comparison with model chiral auxiliaries.

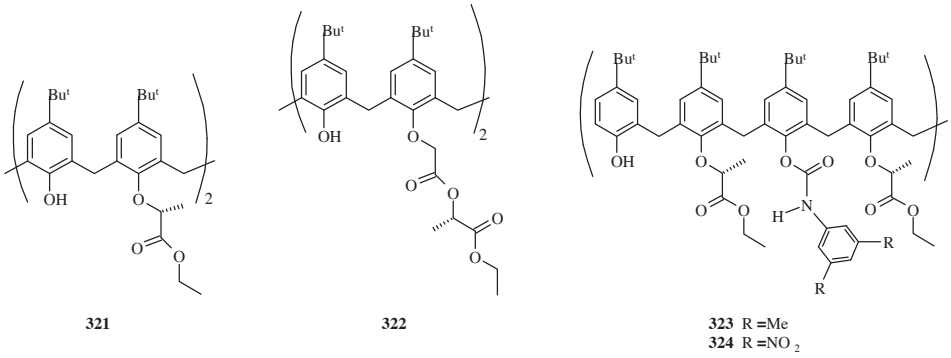


Figure 52. Ethyl lactate derivatives of *p-tert*-butylcalix[4]arene as chiral solvating agents.

Guanidinium Salts

Monolayers of the amphiphilic calix[4]arene derivatives **(323-325)** bearing chiral bicyclic guanidinium on the surface of pure water and of aqueous subphases containing *L*-phenylalanine or *D*-phenylalanine (*L* / *D*-Phe) were studied by film balance measurements (Figure 53). The results indicate that **325-327** can form stable monolayers at the air–water interface and their capacities of the enantioselective recognition for *L* / *D*-Phe depend on their molecular structures.[147,148]

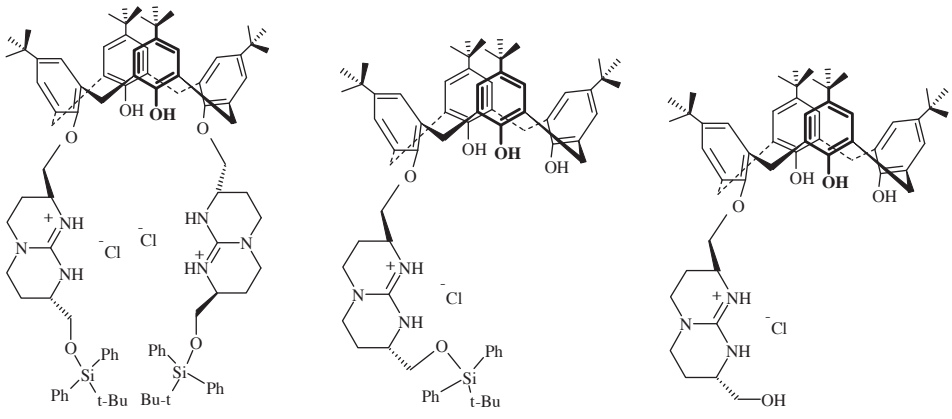


Figure 53. Calix[4]arene derivatives bearing chiral bicyclic guanidinium moieties.

Cyclodextrins

A new type of calix[4]arene-capped [3-(2-*O* − *β*-cyclodextrin)-2-hydroxypropoxy]-propylsilyl-appended silica particles has been successfully synthesized and used as chiral stationary phase (CSP) to separate chiral drugs in HPLC.[149] This new type of CSP **328** has a chiral selector with 2 recognition sites: calix[4]arene and *β*-CD. The C4CD-HPS has shown excellent selectivity for the separation of aromatic positional isomers and enantiomers of chiral aromatic compounds due to the cooperative functioning of calix[4]arenes and *β*-CDs (Figure 54).

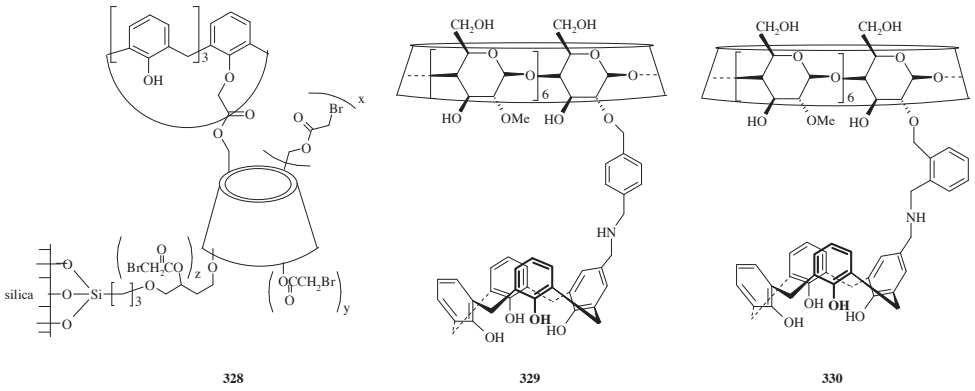


Figure 54. *β*-cyclodextrin-based chiral calixarene derivatives.

Reinhoudt and co-workers have described the preparation of novel host molecules **329** and **330** from reaction of the secondary hydroxy face of heptakis(6-0-tert-butyldimethylsilyl) β-cyclodextrin with alpha-bromotolunitrile, methylation of the remaining C(2)-hydroxys, conversion of the cyano group to the aminomethyl group, and reductive coupling with formylcalix[4]arene followed by desilylation.[150] The cyclodextrin-calix[4]arene receptor molecules **329** and **330** were found to be very effective hosts for the fluorescent dyes 1-anilino-8-naphthalenesulfonate and 2-p-toluidino-6- naphthalene-sulfonate and the strongly increased binding capacity is attributed to the additional environmental shielding of the guest by the upper rim of the calix[4]arene, which can move over the secondary hydroxy face of the cyclodextrin cavity.

The syntheses of novel calix[4]arene-tethered mono- **(331)** and bis(beta-cyclodextrin) **(332)** and their molecular recognition behavior with fluorescence dyes, i.e. acridine red (AR) and sodium 2-($p-$toluidino)-6-naphthalenesulfonate (TNS), as well as some structurally related guests, i.e. methyl orange (MO), ethyl orange (EO), tropaeolin OO (TOO), brilliant green (BG), crystal violet (CV), and rhodamine B (RhB), in aqueous buffer solution were presented by Liu, Inoue, and co-workers (Figure 55).[151]

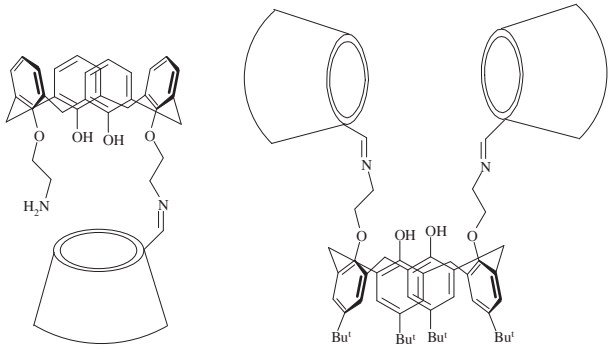


Figure 55. Mono and bis β-cyclodextrin-based chiral calixarene derivatives for molecular recognition of fluorescence dyes.

Miscellaneous

In order to provide tools for investigations of amphotericin B (AmB) ion channels, new conjugates bearing a calix[4]arene scaffold covalently linked to 4 amphotericin B molecules were synthesized (Figure 56).[152] The antifungal activity of the conjugates **333** and **334** was superior or similar to that of native amphotericin B, with minimal inhibitory concentration values of 0.10 and 0.25 μM, respectively. Investigation of the hemotoxicity also revealed that these macromolecules are 10 times less toxic than native AmB.

Thondorf et al. have prepared the chiral derivatives of a mesitylene-based calix[4]arene **335** and **336** known to exist in the 1,3-alternate conformation by the attachment of homochiral residues to the 4 exo-hydroxy groups (Figure 56).[153]

In order to develop calixarene-based podands shaped as potent drug dispensers, 2 penicillin arms have been grafted at the lower rim of the *p-tert*-butylcalix[4]arene (Figure 57), giving a new kind of podand **(337)**, which was fully characterized.[154]

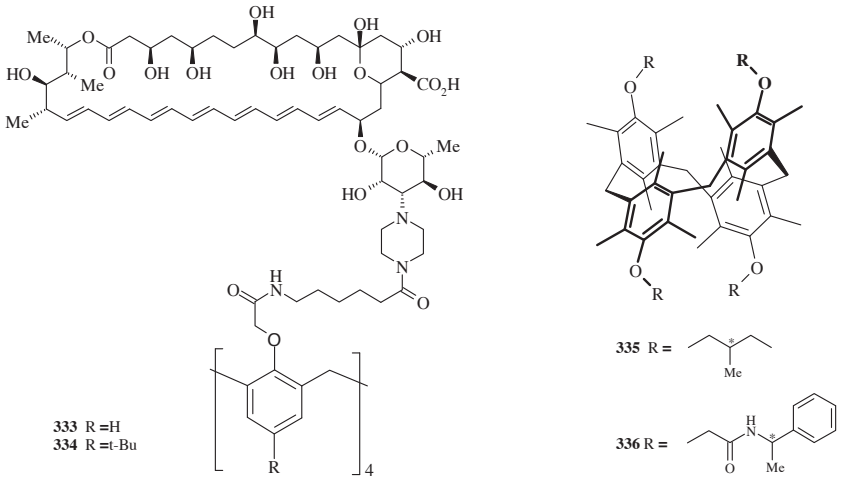
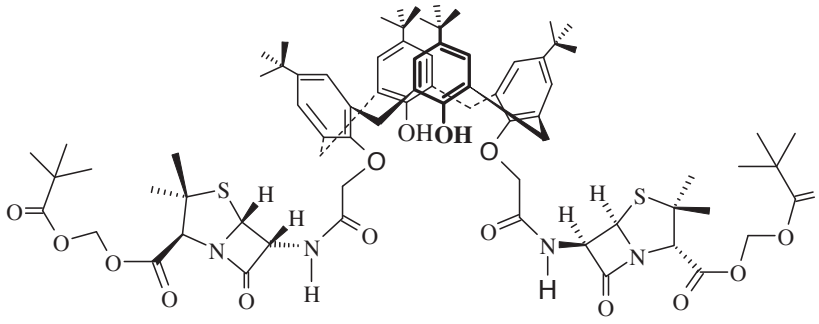


Figure 56. Conjugates bearing a calix[4]arene scaffold covalently linked to amphotericin B and mesitylene-based calix[4]arenes.



337

Figure 57. Penicillin grafted *p-tert*-butylcalix[4]arene.

Kalchenko and co-workers have described that the chiral calix[4]arene alpha-aminophosphonic acids **338d** and **339d** were obtained through diastereoselective Pudovik-type addition of sodium ethyl phosphites to the chiral calixarene imines **(338a** and **339a)**, removal of chiral auxiliary groups, and mild dealkylation of phosphonate fragments (Figure 58).[155] The diacids obtained show inhibitory activity toward porcine kidney alkaline phosphatase that depends considerably on the absolute configuration of the α-carbon atoms.

Recently Haino et al. synthesized a calix[5]arene-based artificial receptor **340** capped with a chiral macrocycle and showed strong binding towards ethyltrimethylammonium derivatives via cation-π and/or hydrogen bonding interactions (Figure 59). [156]

Parisi et al. have also reported that *p-tert*-butylcalix[5]arenes **341** and **342** in a fixed cone conformation, endowed with a urea functionality at the upper rim (Figure 59), behave as remarkably efficient receptors of α-amino acids and biogenic amines, which are bound with one end of the chain within the π-basic cavity (primary recognition site) and the other grasped by the secondary hydrogen bonding donor/acceptor binding site.[157]

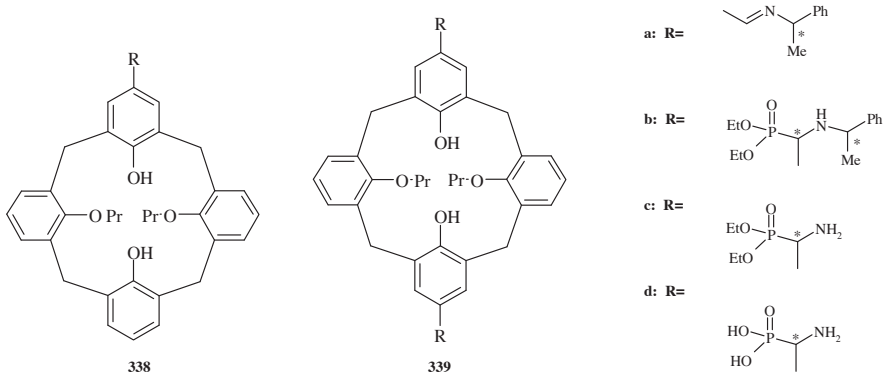


Figure 58. Chiral calix[4]arene alpha-aminophosphonic acids.

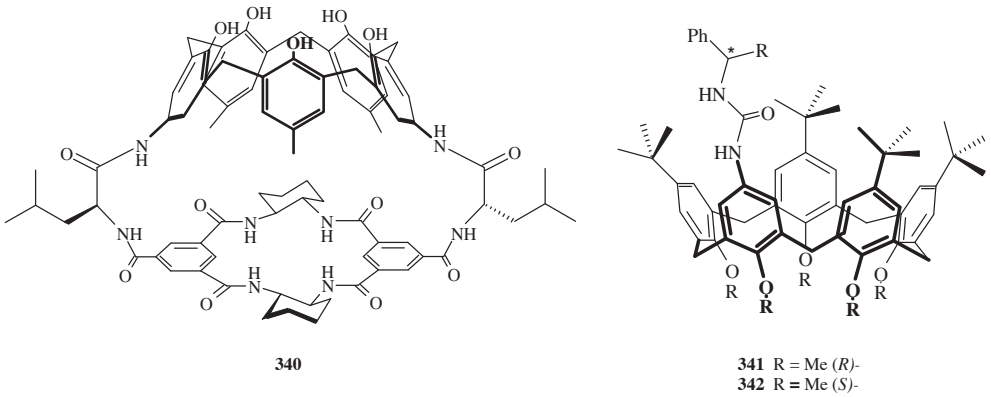


Figure 59. Chiral calix[5]arene-based artificial receptors.

Recently, Wenzel and co-workers introduced a water-soluble tetra *L*-prolinylmethyl derivative of tetrasulfonated calix[4]resorcarene **343** as an effective chiral NMR solvating agent for compounds with bicyclic aromatic or indole rings (Figure 60).[158] It was found that the bicyclic substrates have larger association constants with the calix[4]resorcarene than similar phenyl-containing compounds. Substantial enantiomeric discrimination is observed for several resonances in the ^{1}H-NMR spectra of these substrates.

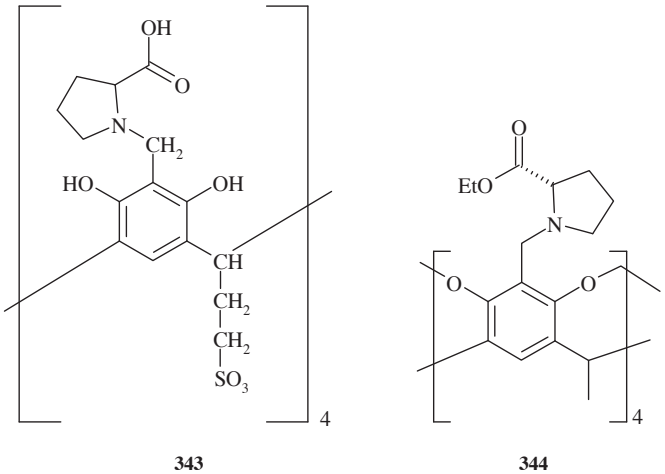


Figure 60. Chiral calix[4]resorcinarenes from *L*-proline derivatives.

Harrison and co-workers have also reported the synthesis and structural characterization of a calix[4]resorcinarene based molecule that has helical chirality in the solid state.[159] The calix[4]resorcinarene **344** has chiral *L*-proline ethyl ester substituents positioned perpendicular to the cavity (Figure 60).

Tomaselli et al. have produced the first example of (salen) Mn^{III} and UO_2 complexes **(345** and **346)** containing a chiral calix[4]arene unit in the ligand framework.[160] (Salen) Mn^{III} calix[4]arene complexes were employed as catalysts in epoxidation reactions of styrene, dihydronaphtalene and of some standard *cis*-β-alkylstyrenes and high enantioselectivity up to 72% ee has been obtained.

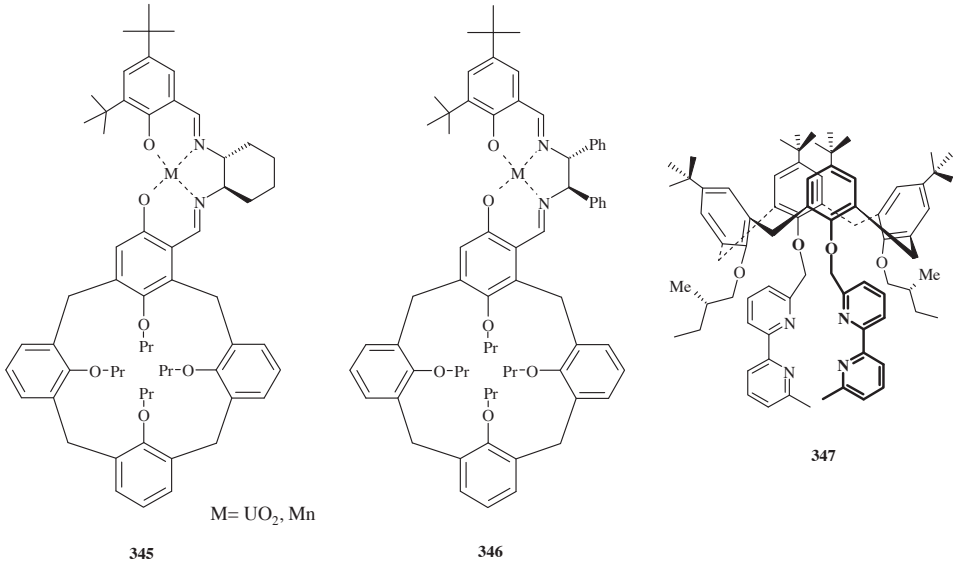


Figure 61. Chiral calix[4]arene-metal complexes as chiral catalysts.

Regnouf-de-Vains et al. have introduced the non-complexing chiral (*S*)-2-methylbutyl substituent close to the complexing site of a bis[(bipyridinyl)methoxy]-calixarene podand **(347),** resulting in the induction of an enantiomeric excess of *ca.* 30% in the corresponding Cu(I) complex.[161]

Leeuwen, Kamer, and co-workers have introduced the first chiral calix[4]arene-modified ligands that induce high enantioselectivity in metal-catalyzed asymmetric reactions.[162] Chiral calixarene-based diphosphite ligands **348-351** have been obtained via lower-rim functionalization of the *p-tert*-butylcalix[4]arene core. High enantiomeric excess (up to 94%) and good activities were obtained in the rhodium-catalyzed asymmetric hydrogenation of prochiral olefins with TADDOL-containing diphosphites **350** and **351** (Figure 62).

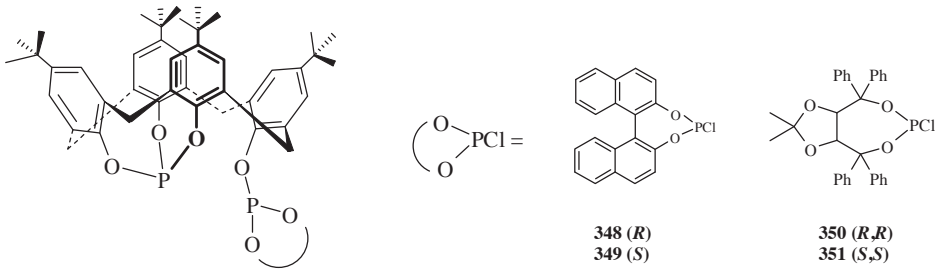


Figure 62. Chiral calixarene-based diphosphite ligands.

Consoli et al. have reported the first example of the chiral calix[4]arenes **352a-d** and **353a-d** bearing thymine, adenine, cytosine, guanine 2'-deoxynucleotide residues via phosphoester linkage (Figure 63).[163,164] Preliminary studies about their assembling in apolar solvent and host properties toward biologically interesting guests are also reported.

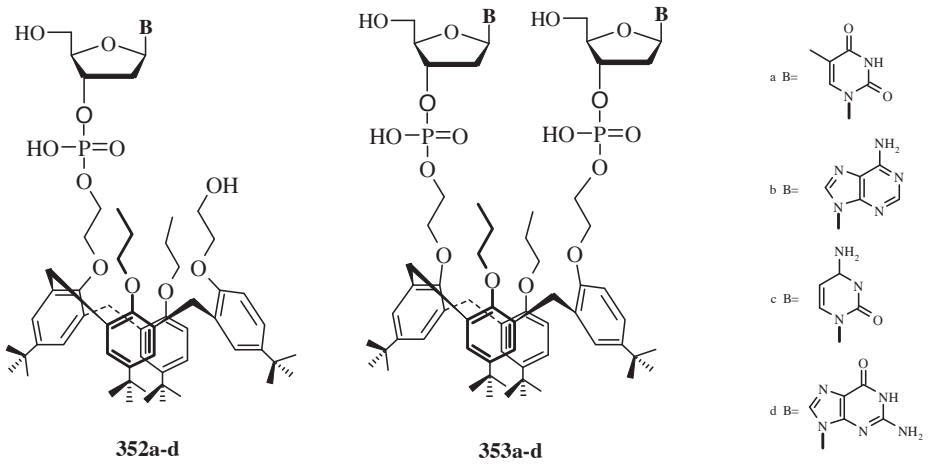


Figure 63. Nucleotide-calixarene conjugates via phosphoester linkage.

Bonini and co-workers have introduced the first example of an enantioselective preparation of a chiral calix[4]arene bis-epoxide **354** via a direct asymmetric reaction on the parent 1,3-diformyl calix[4]arene in excellent chemical yield and >99% ee, and its enantiospecific conversion to the corresponding bis-dioxolane **355** (Figure 64).[165]

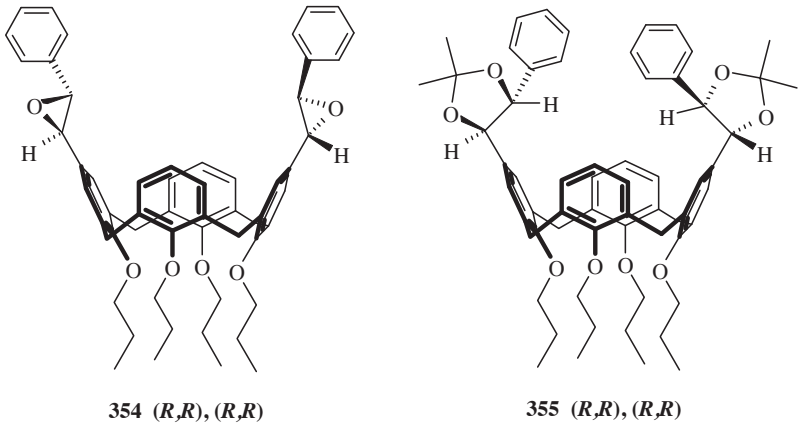
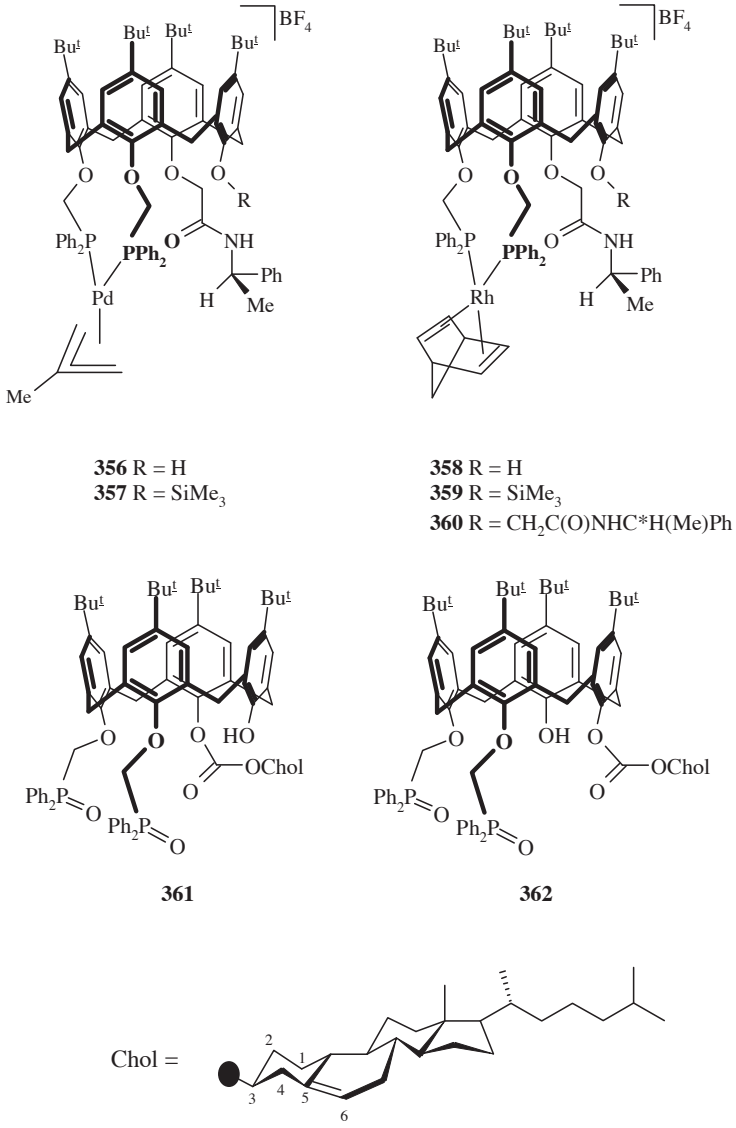


Figure 64. Chiral calix[4]arene bis-epoxide and bis-dioxolane derivatives.

Matt et al. have reported the synthesis of chiral diphosphine and phosphinite calix[4]arenes **356-362** and used them in allylic alkylation with 67% ee and hydrogenation with 48% ee. Despite these poor transfers of chirality, they obtained excellent results in terms of conversion (100%).[166,167]



356 R = H
357 R = $SiMe_3$

358 R = H
359 R = $SiMe_3$
360 R = $CH_2C(O)NHC^*H(Me)Ph$

361

362

Figure 65. Chiral diphosphine and phosphinite calix[4]arenes.

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