Functionalization reactions of calixarenes

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Abstract
In this review examples of functionalization reactions of calixarenes are presented with those involving the wide rim being presented first, followed by those involving the narrow rim, and then by reactions involving functionalization of both rims. The application possibilities of the obtained compounds are also described.

Keywords: Calixarenes, chirality, conformation, functionalization, narrow rim, wide rim

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1. Introduction

Calixarenes are widely studied due to their interesting properties,[1-9] including the fact that they are valuable receptors besides cyclodextrins,[10-13] and cucurbiturils.[14-17] An advantageous feature of calixarenes is their easy availability. Functionalization of calixarenes at their wide and at their narrow rims, permits the synthesis of a variety of derivatives having desired properties and is the topic of the present review.

The large number of publications dealing with calixarenes is a reflection of their various applications. Calixarenes are receptors for neutral and charged species,[18-20] they form complexes

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with metal ions,[21-23] and are promising for environment protection due to their ability to extract cesium and lanthanides from radioactive waste.[24,25] They are of interest for the design of sensor,[26-28] and catalysts,[29,30] and are useful in chiral recognition,[31,32] as well, polymers,[33-35] and supramolecular structures,[36-38] containing calixarenes exist. It is worthnoting that calixarenes may be applied in the design of metal-organic nanotubes,[39,40] vesicles,[41] and nanoparticles.[42] Attention should be paid also to capped calixarenes,[43] and calixtubes,[44] along with their complexation properties.

Compounds related to calixarenes include resorcinarenes[45-47] bearing two hydroxyl groups on the phenyl moieties able to form cavitands[48,49] which are precursors of capsules.[50] An interesting class are the pyrogallolarenes built from pyrogallol units[51] which are components of metal-organic nanocapsules.[52]

Related to calixarenes also are the calixcrowns,[53,54] which are calixarenes bearing crown ether units; calixquinones,[55,56] containing one or two quinone units instead of phenol moieties of calixarenes; calixpyrroles,[57-59] built from pyrrole units, and calixphyrins,[60,61] formed by the reduction of porphyrins. Pillarenes,[62-64] in which benzene rings are linked by para, and not by meta positions as in calixarenes should also be included. A special group are the thia, oxa and azacalixarenes, in which the linking methylene groups of calixarenes are formally replaced by sulfur,[65-67] oxygen,[68-70] or nitrogen,[71-73] atoms, respectively.

This contribution is a continuation of our previous works concerning calixarenes,[74] their complexes with metal ions,[75,76] covalently and noncovalently bound calixarene assemblies,[77] and cavitands,[78] forming dimeric,[79] as well as trimeric and hexameric,[80] capsules. Since the amount of reports dealing with calixarenes is enormous, only selected examples are described in this review. The text consists of three chapters; two of them concern functionalization of the wide and the narrow rims of calixarenes, and in the third chapter the functionalization of both rims is presented.

2. Functionalization of the wide rim of calixarenes

Many calixarenes functionalized at the wide rim are known,[81-86] It should be noted that functionalization of the wide rim is more difficult than of the narrow rim. Functionalization of the wide rim requires protection of the narrow rim hydroxyl groups and also removal of the *t*-butyl groups from the wide rim. Some selected examples of functionalizations of calixarene at the wide rim are shown below.

In a study of calixarene monophosphines as supramolecular receptors, reactions leading to **1**-**4** have been performed.[87] The synthesis of calixarene monophosphines **1** and **2** begins with the nickel-catalyzed reactions of dibromocalixarene **5** and of tetrabromocalixarene **6** with Ph_2POEt affording calixarene phosphine oxides **7** and **8**, which were reduced with $PhSiH_3$ to give **1** and **2**, respectively.

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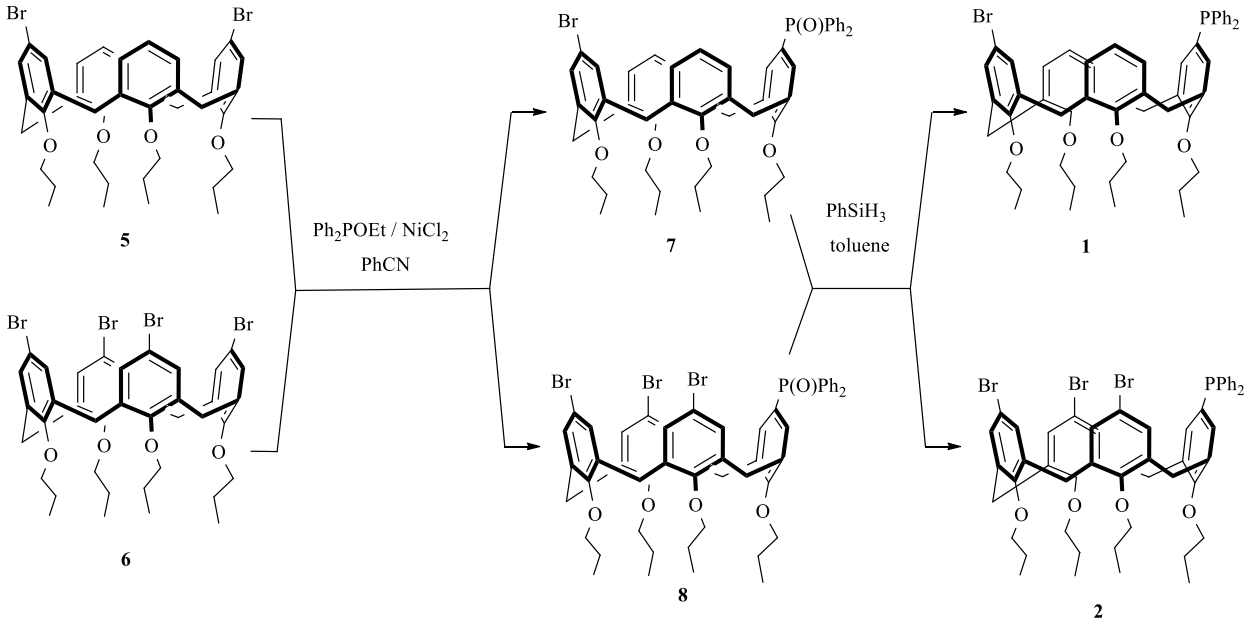
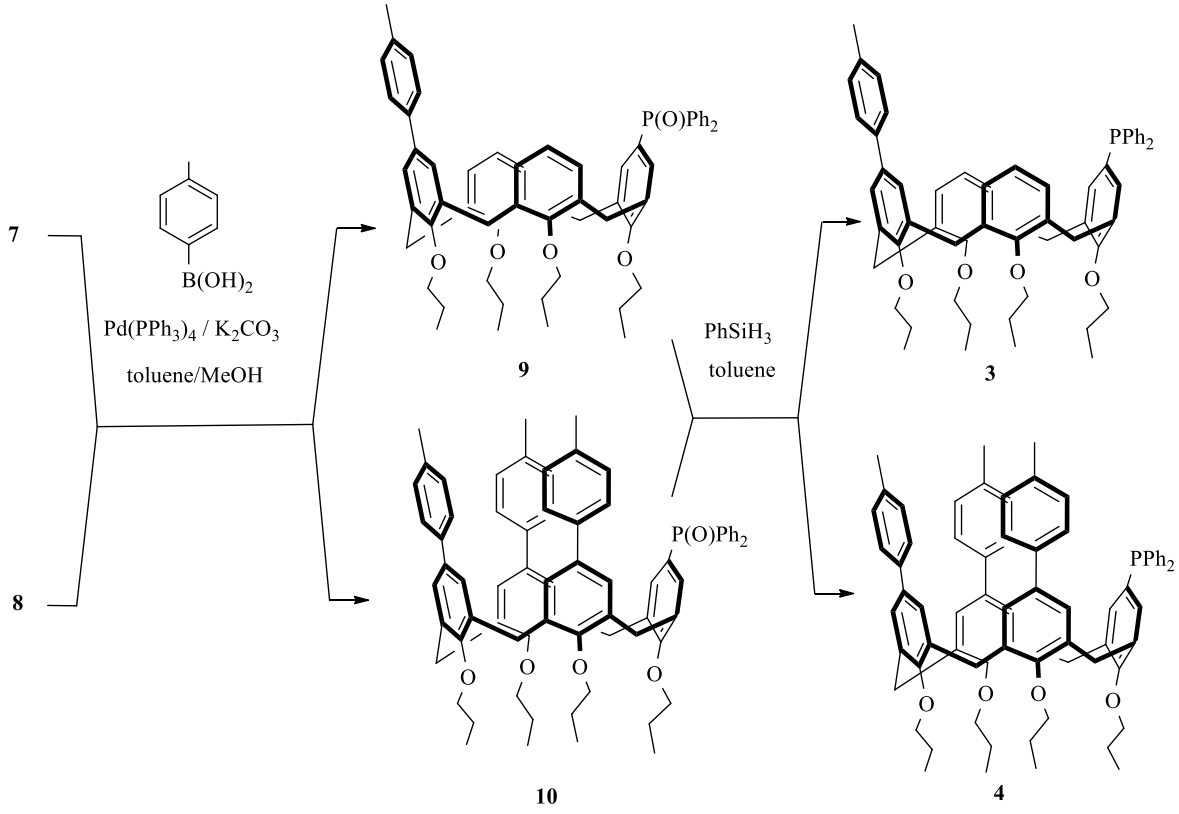


Scheme 1

The synthesis of **3** and **4** involves the Suzuki-Miyaura coupling of **7** and **8** with *p*-tolylboronic acid yielding **9** and **10**, which upon reduction afford **3** and **4**.



Scheme 2

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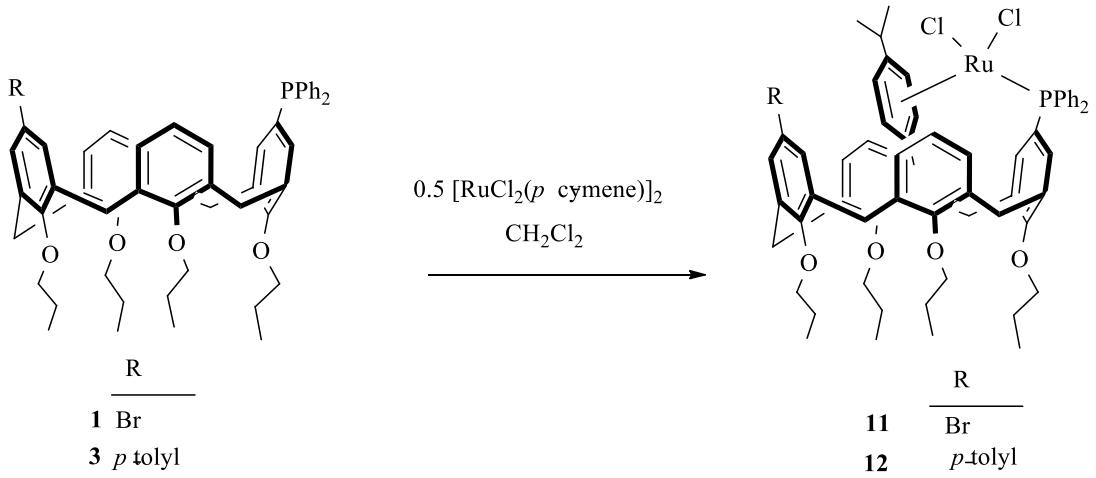
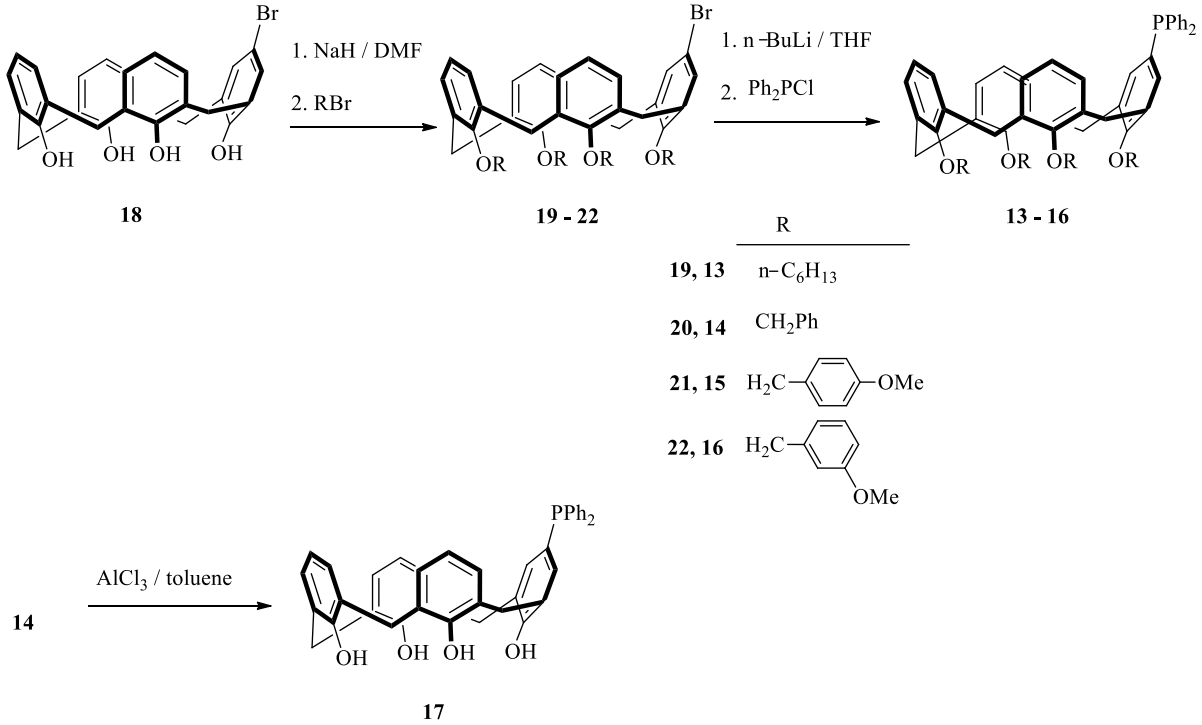
It was found that compounds **1-4** form with $[RuCl_2(p\text{-cymene})]_2$ inclusion complexes; the complexation of **1** and **3** leads to $[RuCl_2(p\text{-cymene})L]$ complexes **11** (L=**1**) and **12** (L=**3**).



Scheme 3

In continuation of the above experiments concerning calixarene monophosphines, compounds **13-17** have been synthesized for use in preparation of Suzuki-Miyaura cross-coupling catalysts.[88] Thus, bromocalixarene **18** was alkylated in the presence of sodium hydride to afford **19-22** which, upon halogen-lithium exchange, followed by reaction with Ph_2PCl yielded **13-16**. Debenzylation of **14** using $AlCl_3$ gave **17**.



Scheme 4

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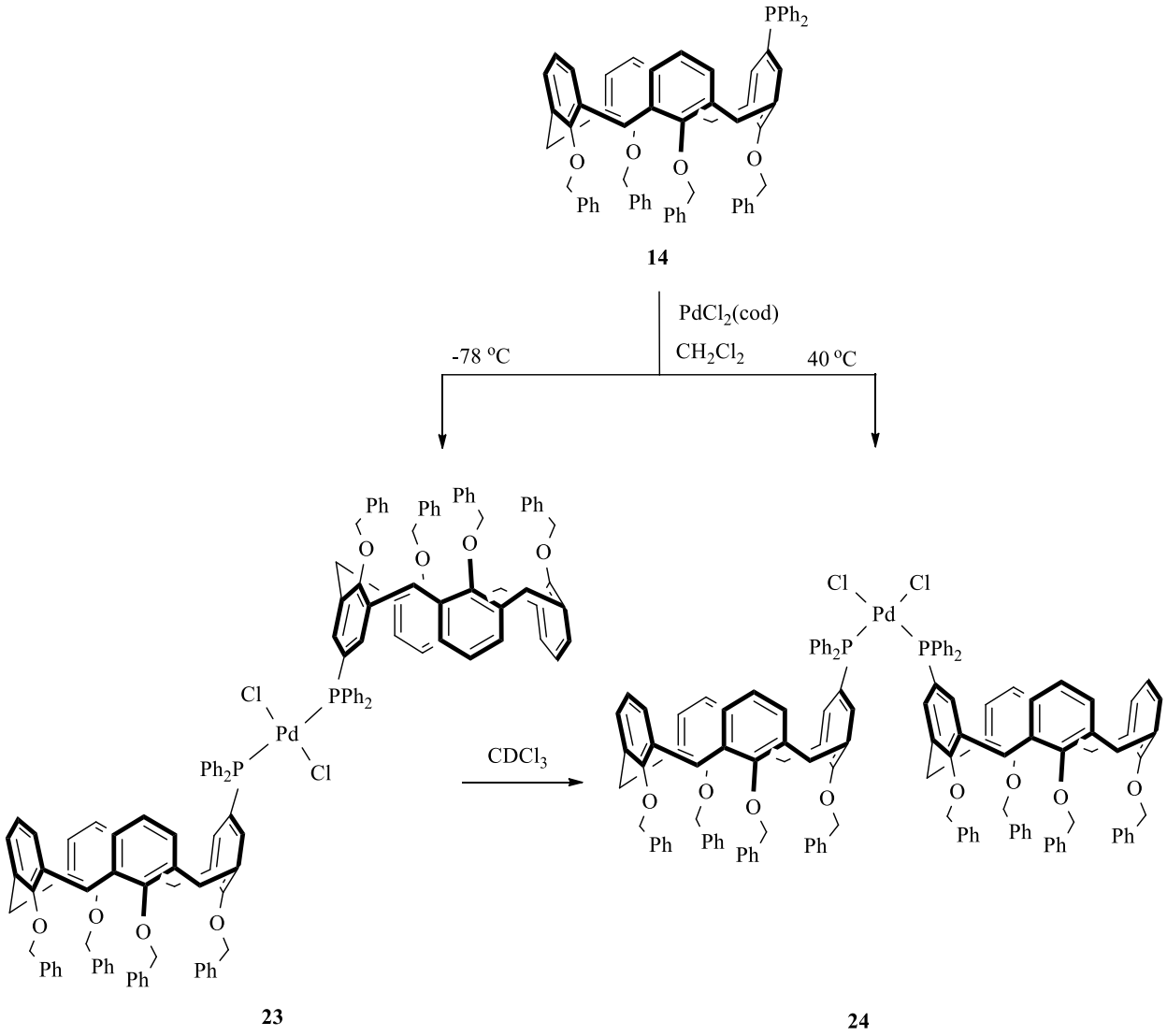
In order to investigate the coordination ability of phosphines **13**-**17**, the reaction of **14** with [$PdCl_2$(cod)] leading to trans-**23** and cis-**24** was performed.[88] It was found that **23** upon treatment with $CDCl_3$ undergoes isomerization into **24**.



cod = 1,5–cyclooctadiene

Scheme 5

The reaction of **14** with [Pd(*o*-$C_6H_4NMe_2$)Cl]$_2$ affords complex **25** which was treated with $AgBF_4$ in THF to give the complex **26**; recrystallization of **26** performed by slow diffusion of hexane into a commercial undried dichloromethane solution of **26** yields the aquo complex **27**.

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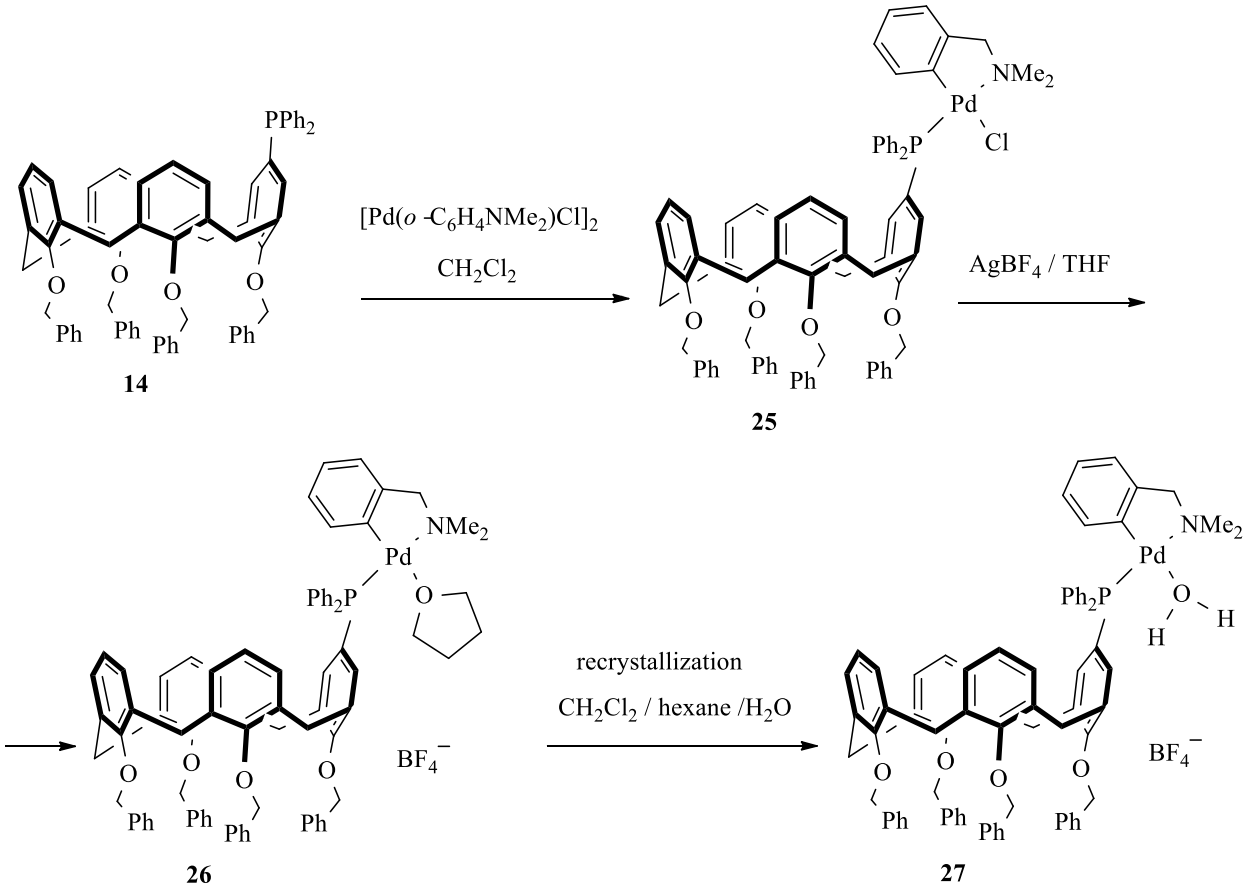
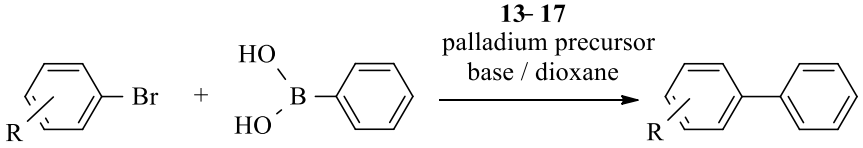


Scheme 6

For the study of Suzuki-Miyaura cross-coupling reactions, the catalysts were generated in situ by mixing the respective monophosphines from among **13-17** with the palladium precursor. In these experiments, bromobenzene, 2-3-and 4-bromotoluene, 2-and 4-bromoanisole, 1-bromonaphthalene and 2-bromo-6-methoxynaphthalene served as aryl bromides, while $[Pd(OAc)_2]$, $[Pd(dba)_2]$ and $[PdCl_2(cod)]_2$ were used as the palladium precursors; NaH, NaOH, KOH, K_2CO_3, Cs_2CO_3 and CsF were used as the bases.



Scheme 7

It was found that combining each of the monophosphines **13-17** with $[Pd(OAc)_2]$ and NaH in dioxane, yielded a highly efficient catalytic system for the Suzuki-Miyaura cross-coupling of aryl bromides with phenylboronic acid. Notably also, these catalysts remained stable for several days.[88]

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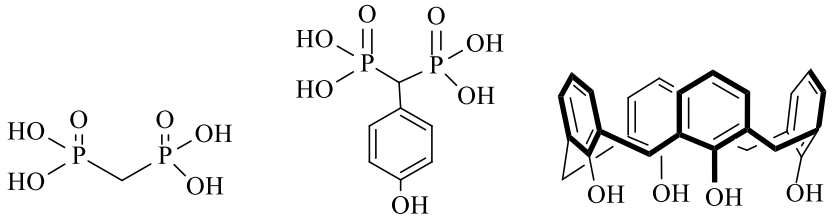
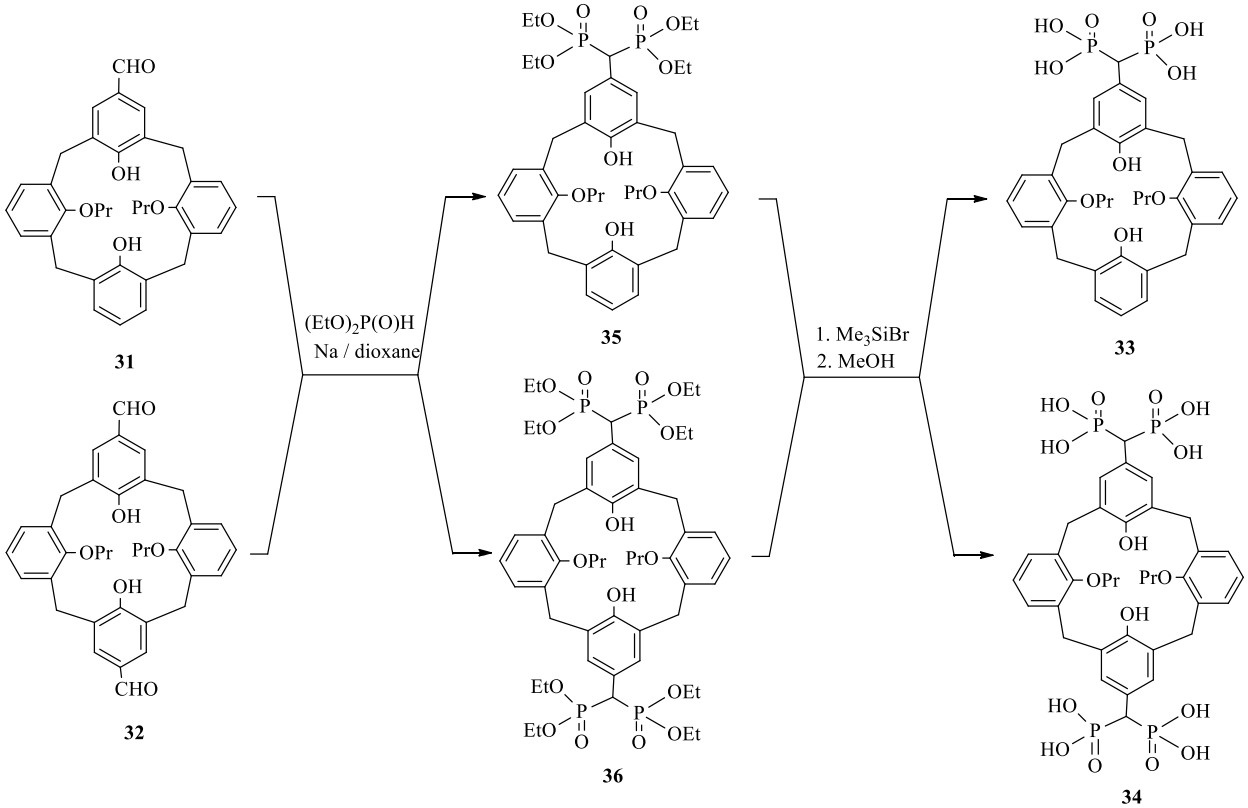
In order to study phosphorylation which occurs in biochemical processes, the phosphatase inhibitory properties of compounds **28** and **29** have been investigated.[89] In these experiments it was found that the introduction of methylenebisphosphonic acid **28** onto calix[4]arene **30** to form compounds such as **33** and **34**, results in the efficient inhibition of alkaline phosphatase whereas this inhibition of **28** itself is only very low. For these phosphatase inhibitory studies, calixarenes **33** and **34** containing one and two units of **28**, respectively, were synthesized via the reactions of calixarene aldehydes **31** and **32**.



Scheme 8

Treatment of calixarenes **31** and **32** with sodium diethylphosphite generated in situ from diethylhydrogenphosphite and sodium in dioxane afforded esters **35** and **36** which were then converted to the corresponding acids **33** and **34** by reaction with Me_3SiBr followed by methanol.



Scheme 9

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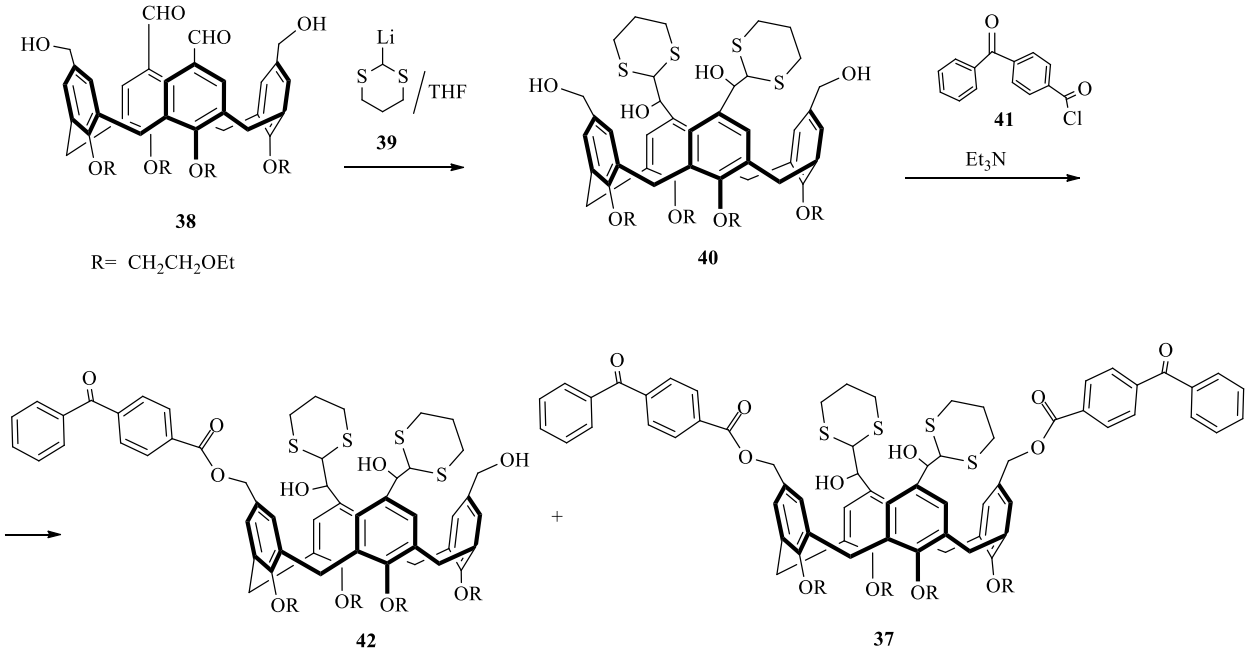
The phosphatase inhibitory activities of **28**, **29**, **33**, **34** and **36** which were found to decrease in the order **34** > **33** > **29** >**28** were examined in the hydrolysis reactions of *p*-nitrophenylphosphate catalyzed by calf intestine alkaline phosphatase. The esterified calixarene **36** showed no inhibitory activity and therefore one may conclude that the free phosphonyl groups are responsible for the inhibitory properties of **28**, **29**, **33** and **34**. The activity of these compounds as phosphatase inhibitors likely results from their coordination to the metal (Zn^{2+} and Mg^{2+}) ions in the enzyme active site.

Properties of a photolabile calixarene bearing an internal sensitizer have been examined. Considering the fact that α-hydroxyalkyldithianes are known to undergo photofragmentation in the presence of an electron transfer sensitizer, such as benzophenone, the synthesis of calixarene **37** bearing two photocleavable dithianylhydroxymethyl groups and two benzophenonecarboxylate groups was performed. It was found that **37** indeed undergoes a photoinduced fragmentation.[90]



Scheme 10

The synthesis of **37** begins with the reaction of dialdehyde **38** with lithiated dithiane **39** to afford compound **40**. Benzophenone-4-carboxylic acid was used as the tethered internal sensitizer and it was coupled to **40** via its chloride **41** formed by treatment with oxalyl chloride. The coupling of **40** with **41** in the presence of triethylamine yielded the mono and disubstituted products **42** and **37**, respectively.

For the photochemical study, **37** was irradiated with a medium pressure mercury lamp; the process was monitored by ^{1}H NMR and confirmed the ability of **37** to self-sensitized photofragmentation.

In a study of calixarenes with ferrocenyl redox-active units,[91] calixarenes **43** and **44** bearing ferrocenyl units were synthesized for investigation of their electrochemical properties.[92] The synthesis involves the reaction of calixarene dialdehyde **45** with 4-ferrocenylaniline, affording the

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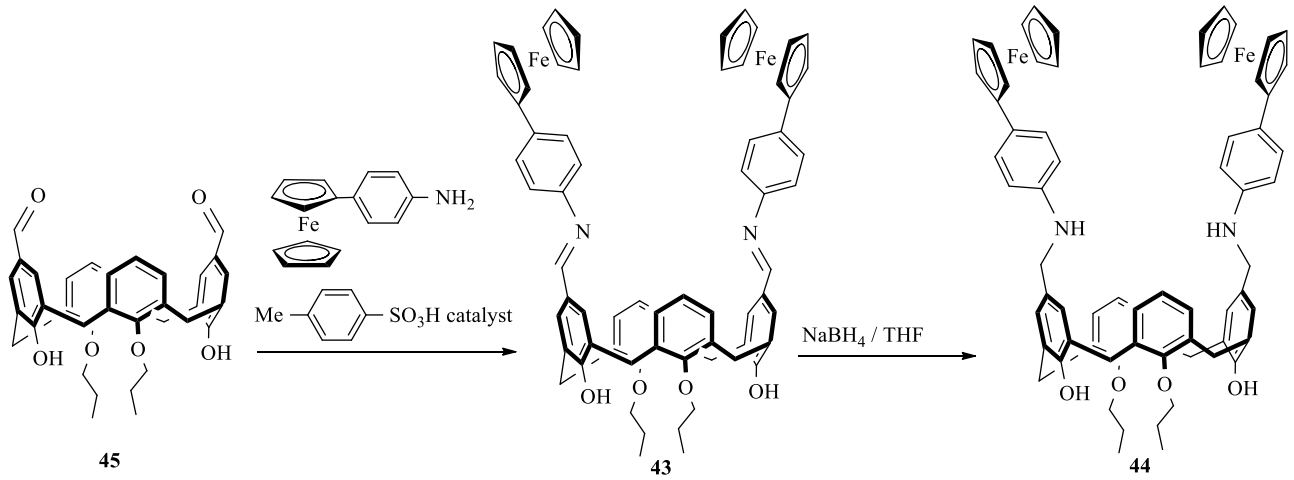
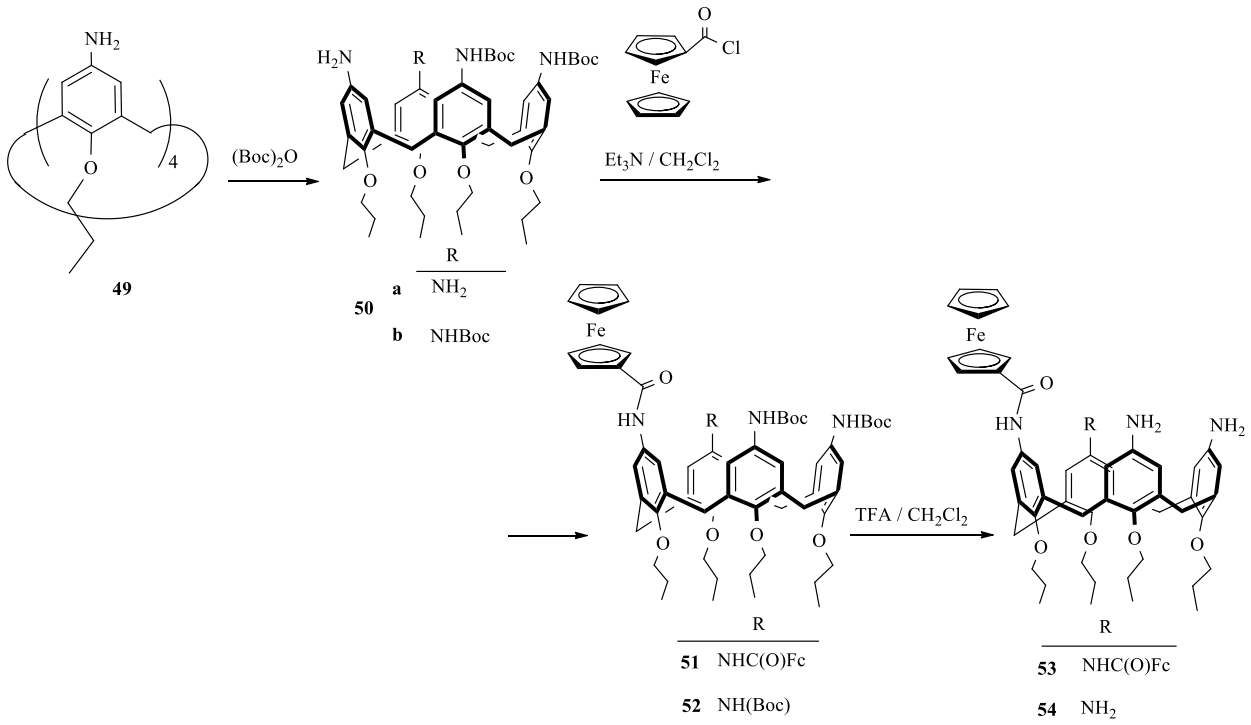
Schiff base **43**, which upon reduction, yields calixarene **44**. It was found that **43** and **44** electrochemically recognize La^{3+}, Ce^{3+}, Pb^{2+} and Cu^{2+} ions and the study of the extraction properties toward metal ions showed selectivity of **44** for Cu^{2+}, Fe^{3+}, Pb^{2+} and Cd^{2+} ions over Co^{2+} and Ni^{2+}.



Scheme 11



Scheme 12

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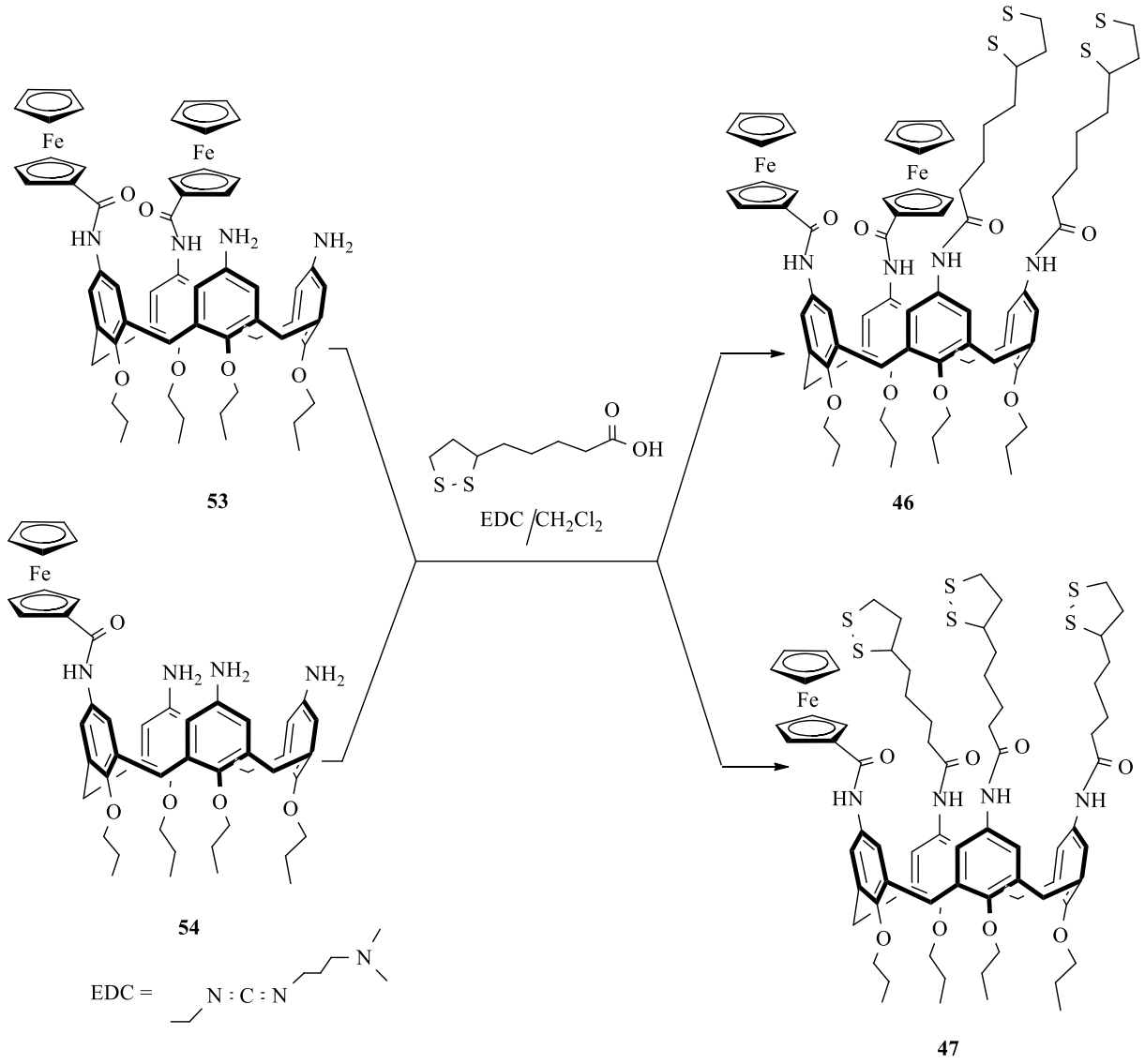
Redox-active anion sensors have also been widely investigated and the use of ferrocene units in these species should be noted. It has been established that anion sensors adsorbed on surfaces in SAMs are advantageous since they are robust and portable, and moreover, the preorganization of receptors onto a surface enhances the thermodynamic driving force associated with receptor/analyte binding. With these considerations in mind, the disulfide-functionalized calixarenes bearing ferrocene units, **46**-**48** were synthesized for construction of SAM redox-active anion sensors adsorbed on gold surfaces.[93]

The synthesis of **46** and **47** started with the reaction of tetraaminocalixarene **49** with BOC anhydride affording **50a** and **50b** which upon treatment with ferroceneacid chloride, give **51** and **52**, respectively. Their deprotection by TFA leads to **53** and **54** which react with thioctic acid in the presence of the carbodiimide coupling reagent, EDC, yielding **46** and **47**, respectively.



Scheme 13

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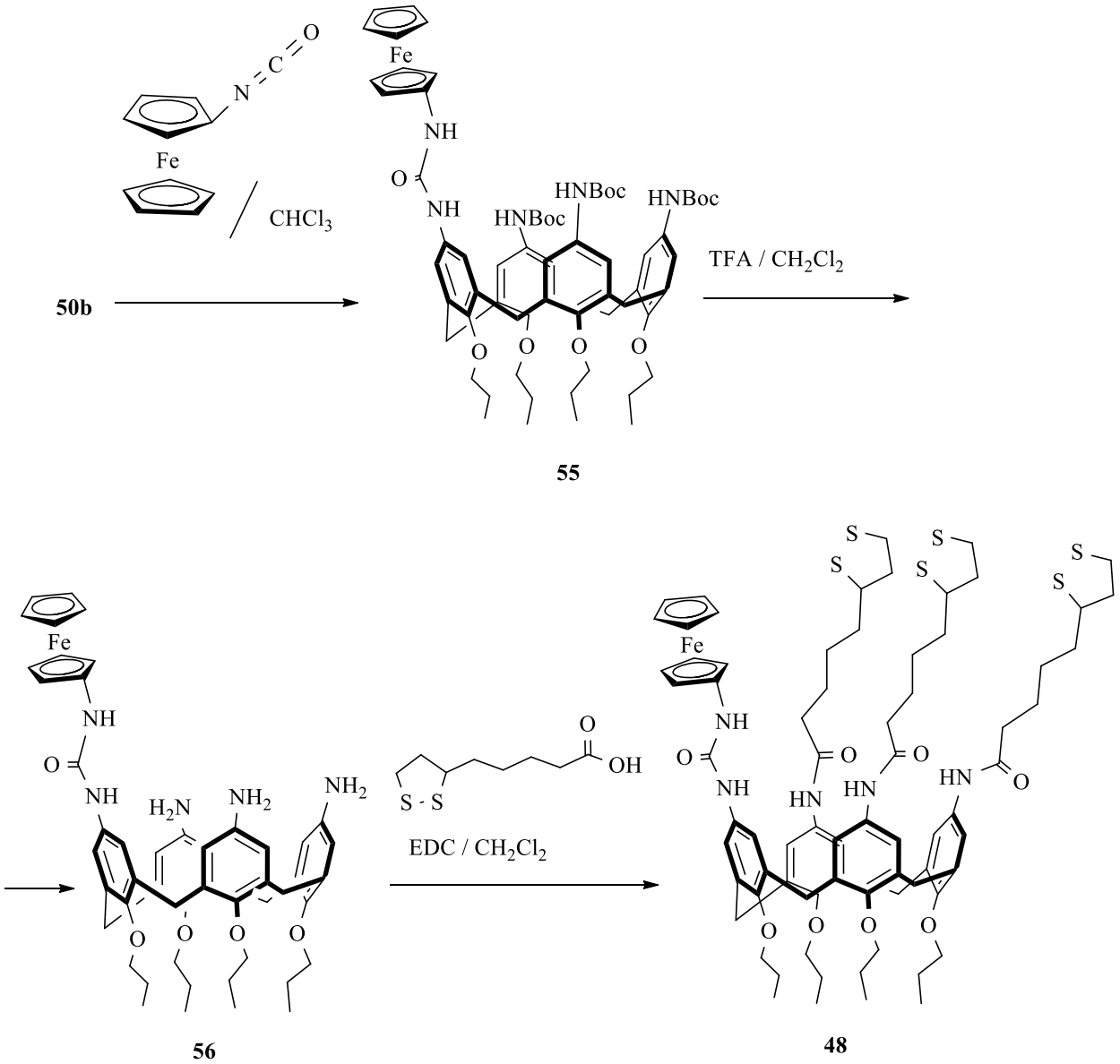
In order to obtain **48** bearing the ferrocene unit linked by the urea moiety to the calixarene platform, the reaction of calixarene **50b** with isocyanatoferrocene leading to calixarene **55** was performed. Deprotection of **55** afforded **56**, which upon treatment with thioctic acid and EDC, yielded **48**.



Scheme 14

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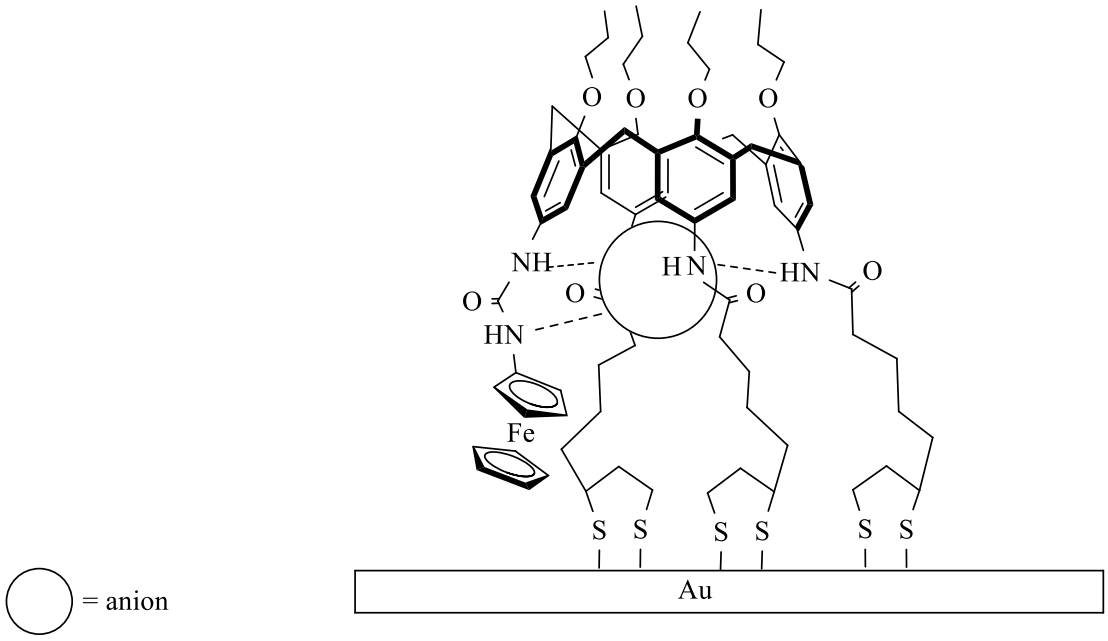

Anion sensing by receptor **48** adsorbed on gold electrode

Scheme 15

The anion sensing properties of **46**-**48** were studied using chloride, benzoate, dihydrogen phosphate and perrhenate anions. The cathodic shifts of the respective ferrocene/ferrocenium redox couple, resulting from the anion binding, were measured. It was established that SAMs of **48** adsorbed onto a gold electrode, selectively recognized perrhenate anions in aqueous solution in the presence of equimolar amount of dihydrogen phosphate, and are thus promising for the design of electrochemical anion sensors.[93]

Surfactant triscarboxycalixarenes **57a-k** bearing *n*-alkyl chains with 1-12 carbon atoms have been synthesized with the aim of investigating their self-assembly properties.[94] The synthesis begins with the treatment of calixarenes **58a-k** with methyl iodide to form quaternary ammonium salts which, upon reaction with sodium cyanide yield tris(cyanomethyl)calixarenes **59a-k**. The hydrolysis of **59a-k** with alcoholic potassium hydroxide affords triscarboxycalixarenes **57a-k**, all of which were found to form typical micelles in aqueous media at biologically relevant pH 6 and pH 8 values.

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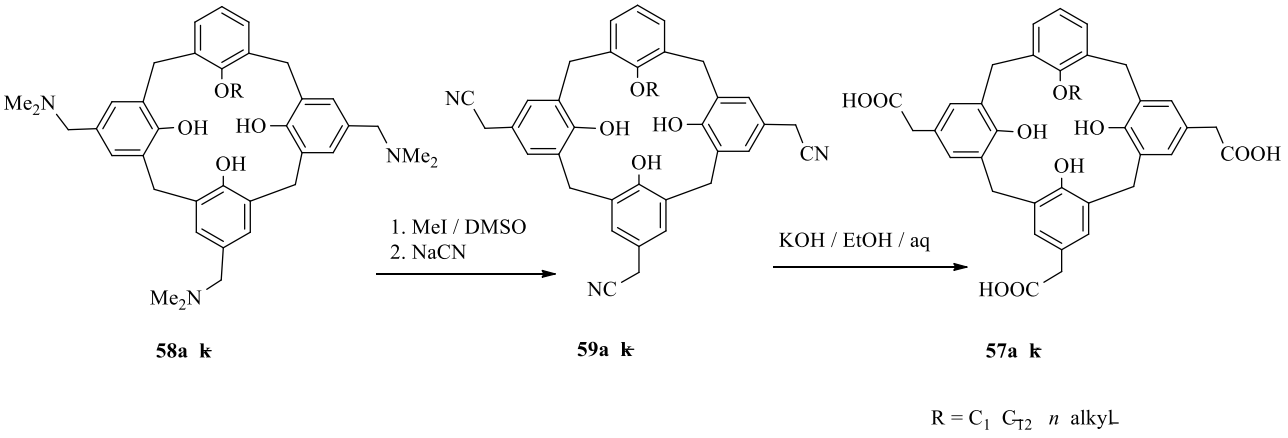

Scheme 16

A convenient method of regioselective functionalization of calix[8]arenes at the wide rim of aromatic rings 1 and 5 has been reported. This functionalization was performed using a protection-deprotection procedure, the protected derivatives were the xylylene-bridged calix[8]arenes **61a** and **61b**,[95] synthesized by the reaction of *p*-*t*-butylcalix[8]arene **60** with *m*-and *p*-bis(bromomethyl)benzenes, respectively. Hexamethylation of calixarenes **61a**,**b** with methyl iodide afforded **62a**,**b** and hexapropylation with *n*-propyl iodide afforded **63a**,**b**. The removal of the xylylene bridge from **62a**,**b** and **63a**,**b** was achieved by hydrogenolysis (H_2, Pd/C) to give hexasubstituted calix[8]arenes **64** and **65** having two free hydroxyl groups on rings 1 and 5.

It was found that upon treatment with nitric acid, **64** and **65** undergo selective *ipso*-nitration of rings 1 and 5 to afford 1,5-dinitrocalix[8]arenes **66** and **67**, respectively. Calixarene **67** was exhaustively propylated to give **68**, which upon reduction with H_2/Raney Ni yielded the corresponding diamino-derivative **69**, whose amino groups can undergo further reactions. The selective *de*-*t*-butylation of **64** and **65** using $AlCl_3$ in the presence of toluene or phenol gave *de*-*t*-butylated calix[8]arenes **70** and **71**.

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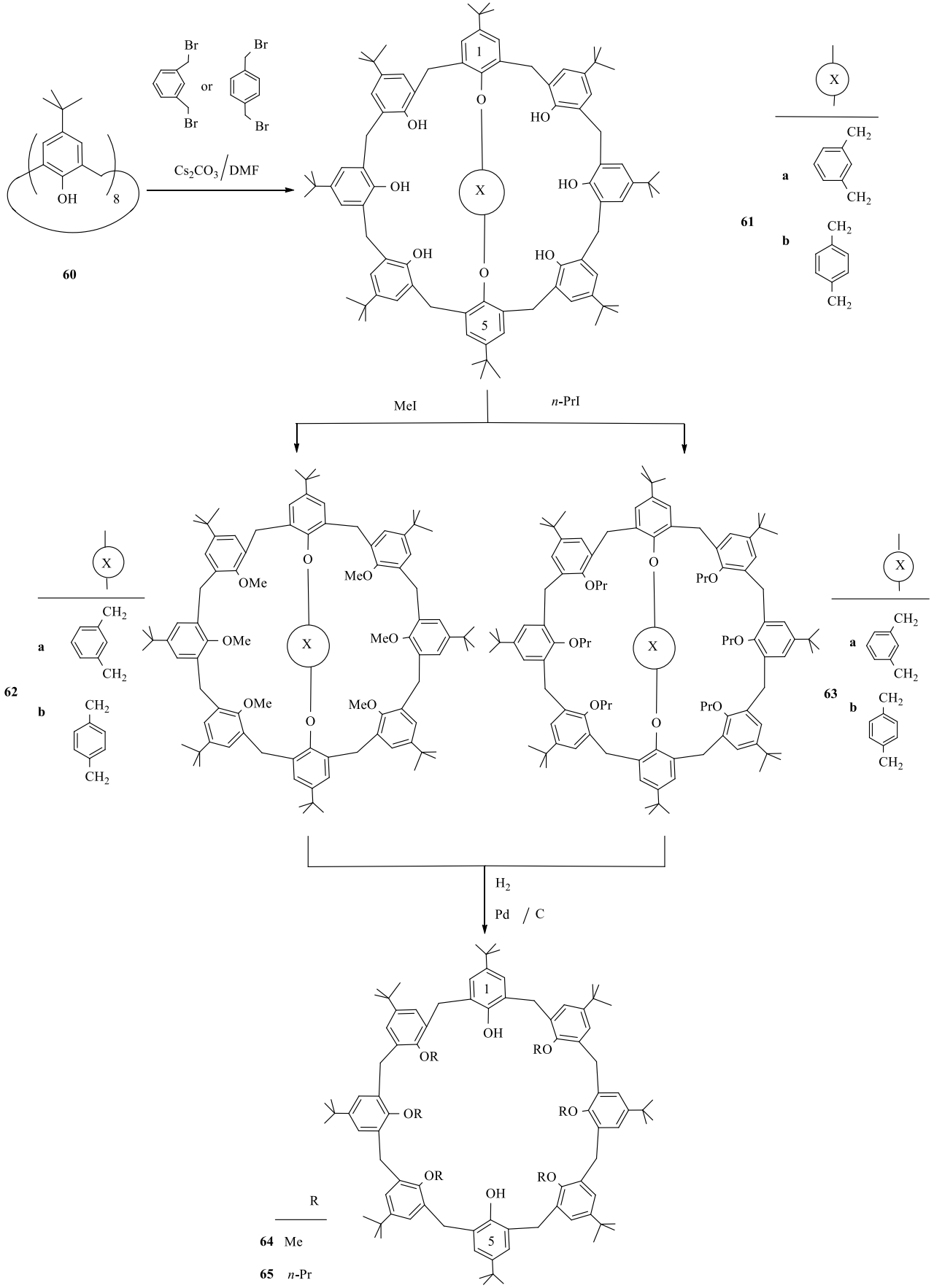

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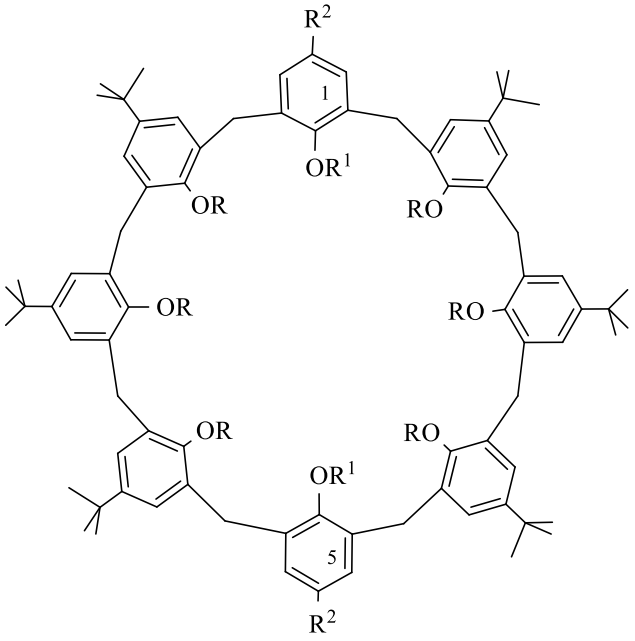
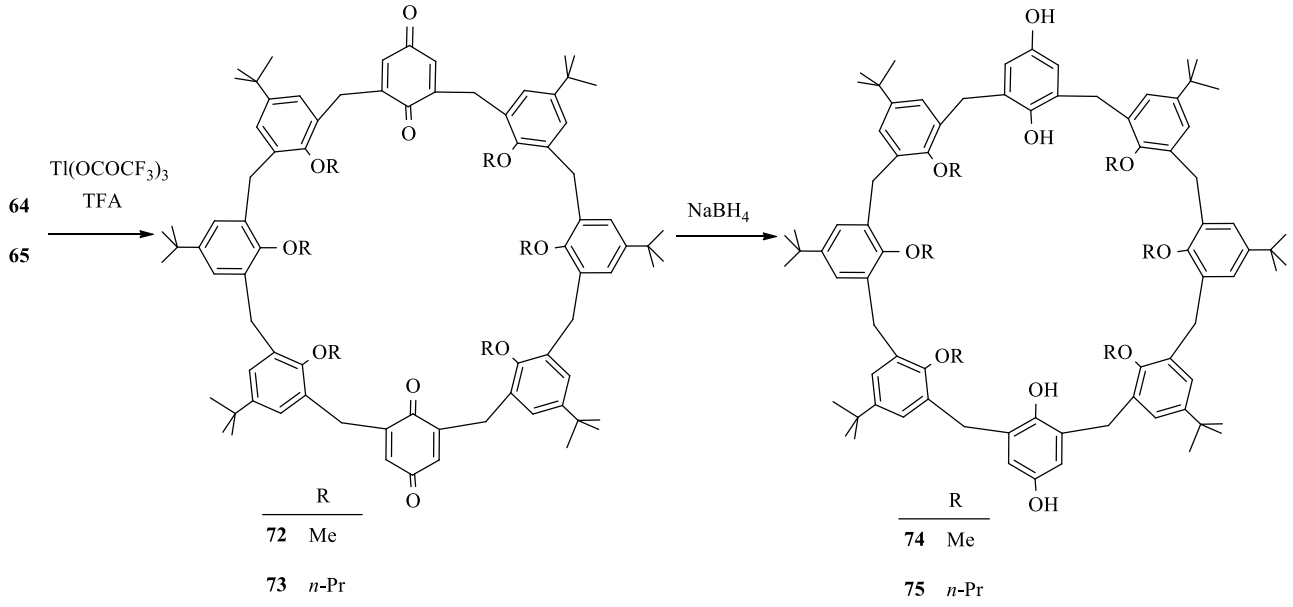


	R	R^1	R^2
64	Me	H	*t*-Bu
65	*n*-Pr	H	*t*-Bu
66	Me	H	NO_2
67	*n*-Pr	H	NO_2
68	*n*-Pr	*n*-Pr	NO_2
69	*n*-Pr	*n*-Pr	NH_2
70	Me	H	H
71	*n*-Pr	H	H

Scheme 18

Upon oxidation with $Tl(OCOCF_3)_3$ in the presence of trifluoroacetic acid, calixarenes **64** and **65** afforded 1,5-calix[8]diquinones **72** and **73** which when subjected to reduction with $NaBH_4$ gave 1,5-calix[8]dihydroquinones **74** and **75**.



Scheme 19

The above methodology enables access to calix[8]arenes selectively substituted at the wide rim of aromatic rings 1 and 5 and as a result, calix[8]arenes containing nitro, amino, quinone and hydroquinone functionalities can be easily synthesized.[95]

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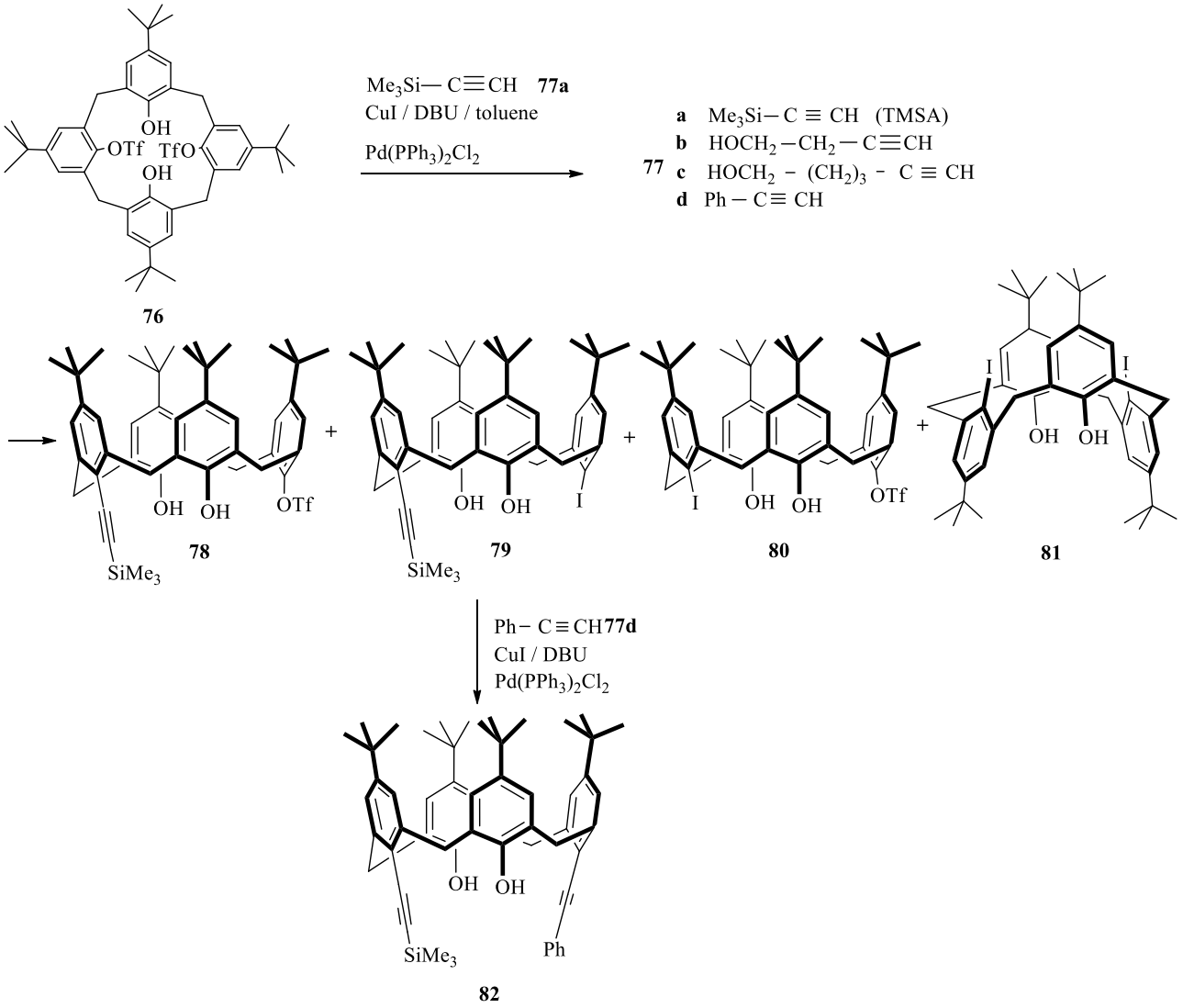
3. Functionalization of the narrow rim of calixarenes

Some examples of functionalization of the calixarene narrow rim, selected from a large number of such processes,[96-101] are presented. For the functionalization of calixarene narrow rim using Pd-catalyzed Sonogashira coupling reactions, the bis-triflate calixarene **76** and alkynes **77a-d** have been employed.[102] The reaction of **76** with trimethylsilylacetylene **77a** affords monoalkynylcalixarenes **78** and **79** along with derivatives **80** and **81**, the formation of **79-81** containing iodine atoms, which were obtained *via* direct metal-assisted substitution by a halide was rather unexpected. It was also observed that calixarene **79** treated with phenylacetylene **77d** yields dialkynylcalixarene **82**.



Scheme 20

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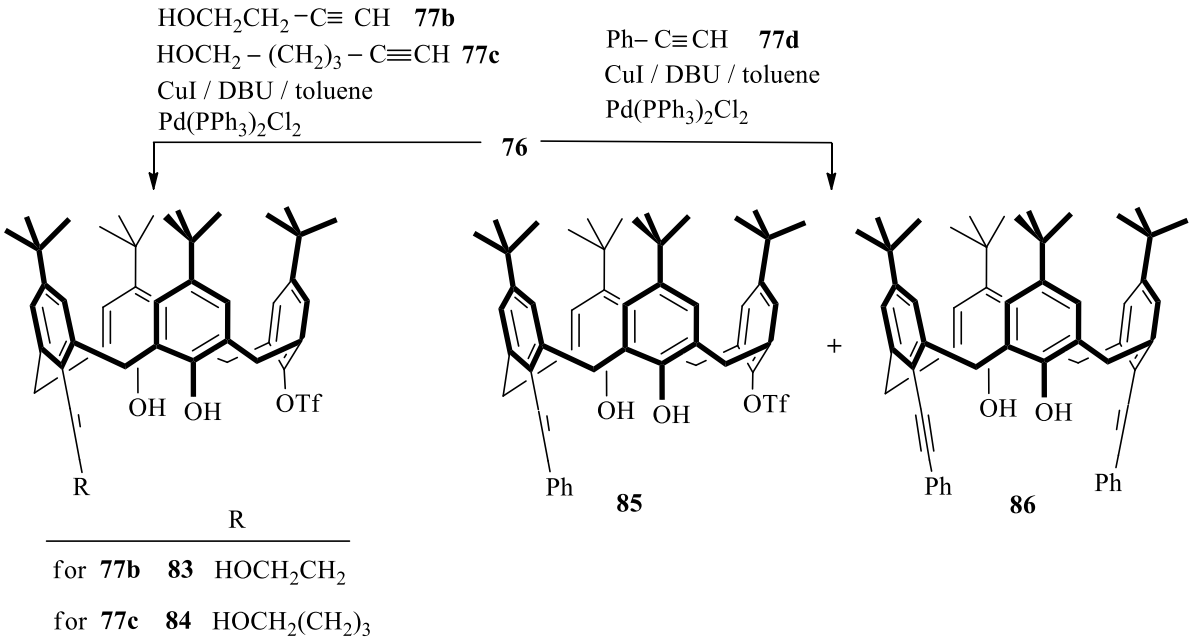
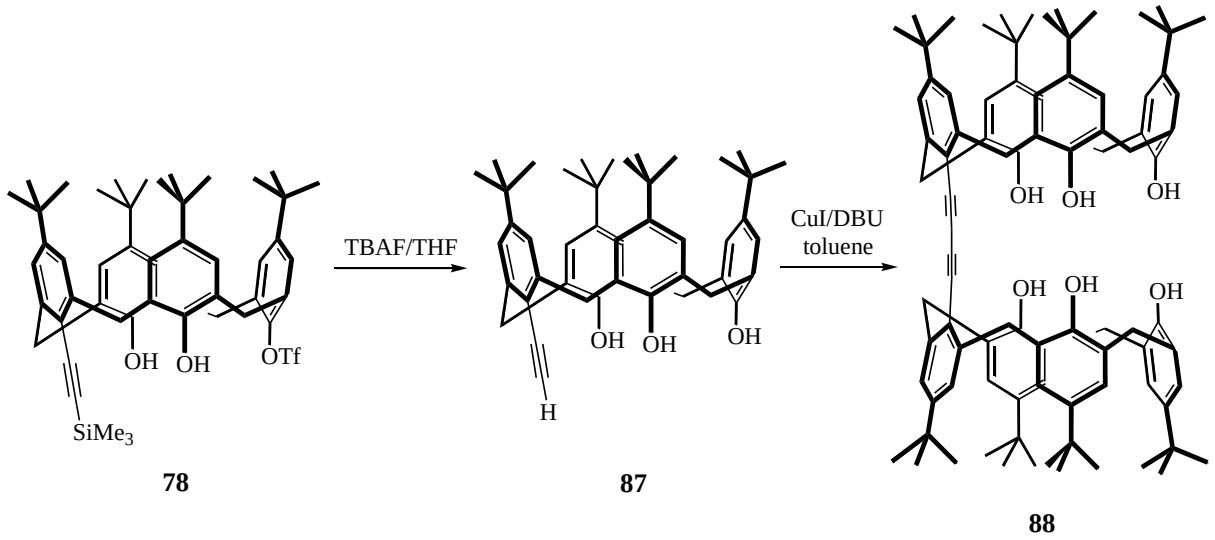
Reactions of **76** with alkynes **77b** and **77c** afforded monoalkynylcalixarenes **83** and **84**, respectively, however the dialkynyl products were not formed. On the other hand, the reaction of **76** with **77d** yielded both expected monoalkynyl and dialkynylcalixarenes **85** and **86**, respectively.



Scheme21



Scheme 22

The homocoupling of monoethynylcalixarene **87** leading to bis-calixarene **88** has also been achieved. For this purpose **78** was treated with tetrabutylammonium fluoride (TBAF) to remove the

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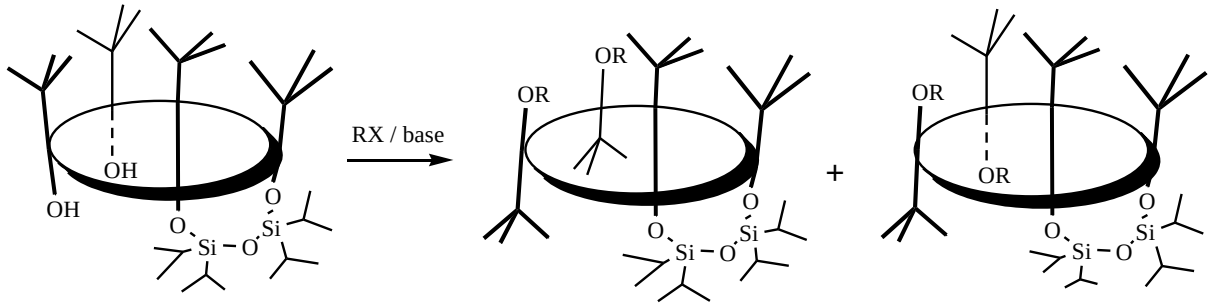
TMS group, the formed **87**, upon reaction with CuI in the presence of DBU, afforded the rigid narrow-rim-bridged bis-calixarene **88**.[102]

It is well-known that the narrow-rim *O*-alkylation of calix[4]arenes with alkyl halides proceeds favorably at the distal hydroxyl groups. This behavior results from a circular intramolecular hydrogen bonding in the monoalkylated intermediate and has been extensively studied.

However, the dialkylation at proximal hydroxyl groups, which is very important for the design of synthetic receptors, has been less intensively investigated. A convenient method for such syntheses is to "cap" two proximal hydroxyls with a disiloxane bridge as in **89**. In these alkylation reactions, organohalides such as BuI or $BrCH_2COOEt$ were used and *t*-BuOK, K_2CO_3 or Cs_2CO_3 served as bases. The reactions of capped **89** with the organohalides in the presence of a base afforded syn and anti products **90** and **91**, respectively, which upon subsequent desilylation with TBAF, gave the corresponding *syn* and anti proximally-dialkylated products. The syn/anti ratio of these dialkylation products depends on the alkyl halide and the base used. Dialkylation of calixarene **89** in the presence of *t*-BuOK gives syn product exclusively, as did the use of K_2CO_3, however the use of Cs_2CO_3 strongly shifts the stereoselectivity toward the anti product.[103]



syn *anti*

89 **90** **91**

Scheme 23

In the experiments the reaction of **92** with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in the presence of imidazole afforded disiloxane bridged **89**. The treatment of **89** with the organohalides MeI, $BrCH_2COOEt$ or $PhCH_2Br$ yielded 1,2-alt **93 a-c** which upon desilylation by TBAF gave *O,O'*-dialkylated 1,2-alt calixarenes **94a-c**.[104]

However, it was found that the treatment of **89** with methyl iodide under changed conditions may give monomethylated product **95**. The reaction of the remaining hydroxyl group of **95** with benzyl bromide completed the alkylation yielding 1,2-alt **96** which upon deprotection with TBAF afforded 1,2-alt **97**. It is noteworthy that compounds of the type of **96** and **97** are inherently chiral due to the presence of two differently substituted adjacent aromatic rings.[104] All of these reactions proceeded smoothly and with excellent yields

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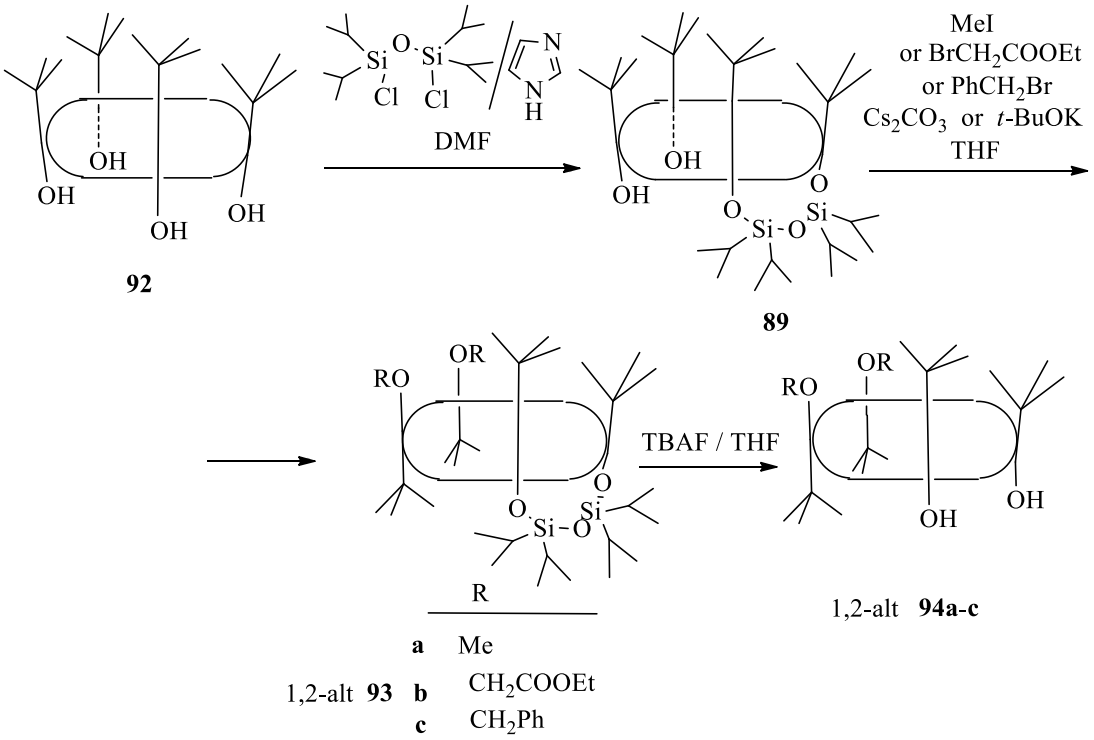
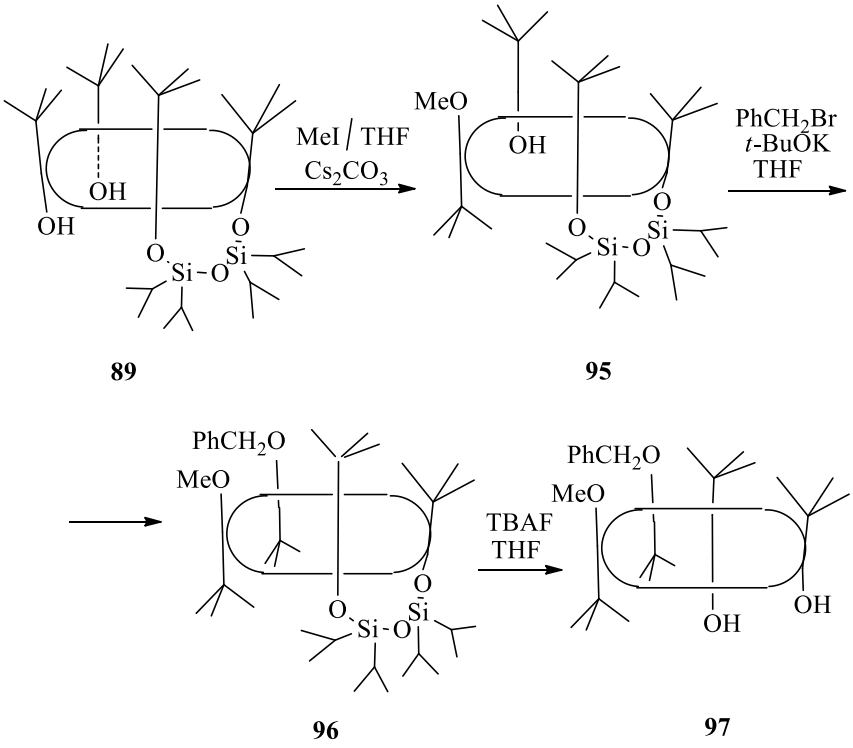


Scheme 24



Scheme 25

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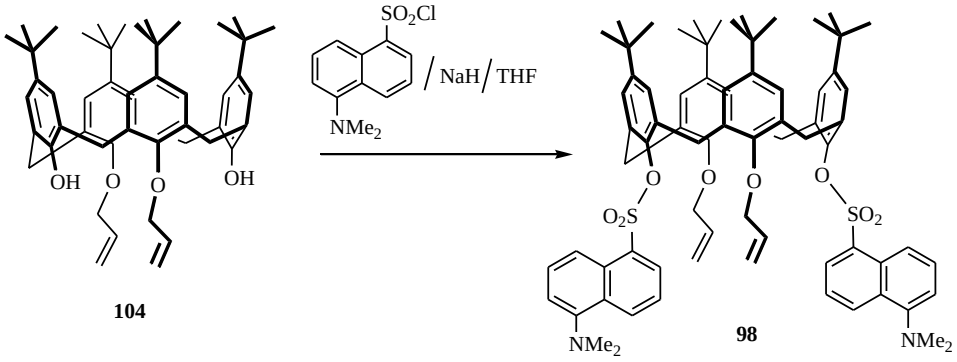
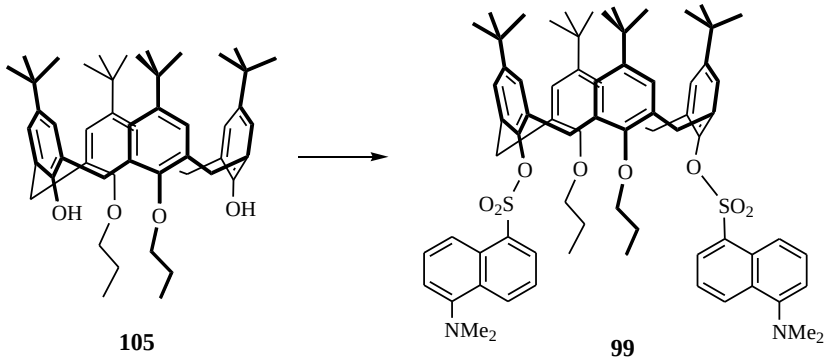
In recent years, fluorescent molecular sensors for the detection of environmentally important heavy metals, such as copper,[105,106] and mercury,[107,108] have received increasing interest. To this aim, calixarenes **98-103** bearing attached dansyl groups have been synthesised and investigated for their use as fluorescent sensors for metal ions.[109] Their syntheses involve the treatment of the appropriate calixarenes with dansyl chloride and sodium hydride, in THF. In this way calixarenes **104-106** were converted into **98-100**, respectively.

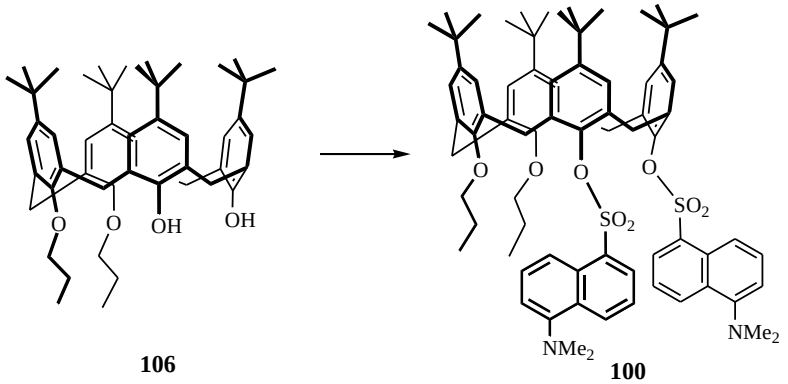


104 **98**

Scheme 26



105 **99**



106 **100**

Scheme 27

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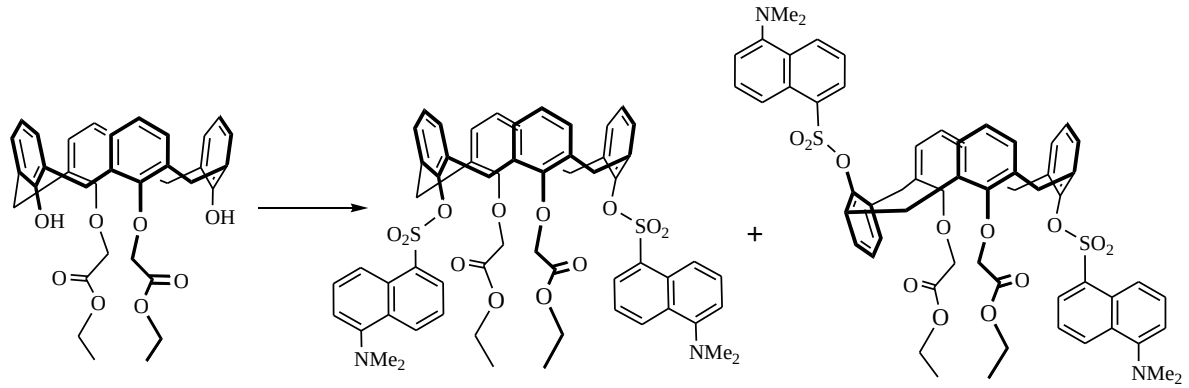
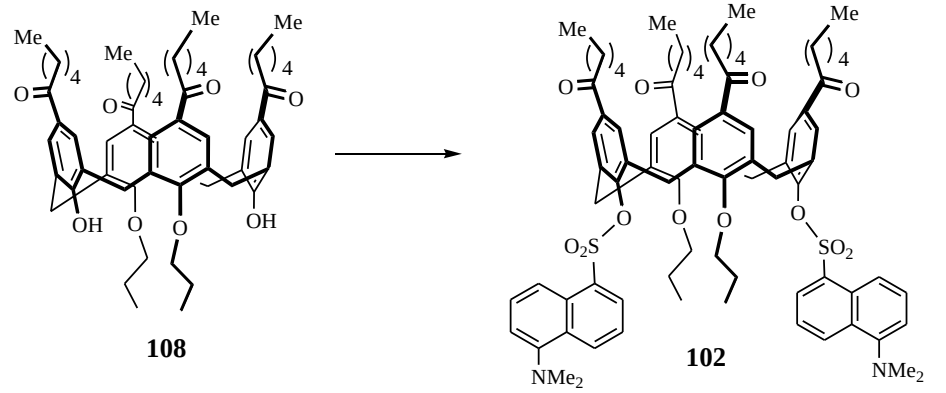
Similar reaction of calixarene **107** affords the mixture of cone **101a** and paco **101b**, which could be separated by column chromatography. Using the same procedure, calixarenes **108** and **109** yielded **102** and **103**, respectively.

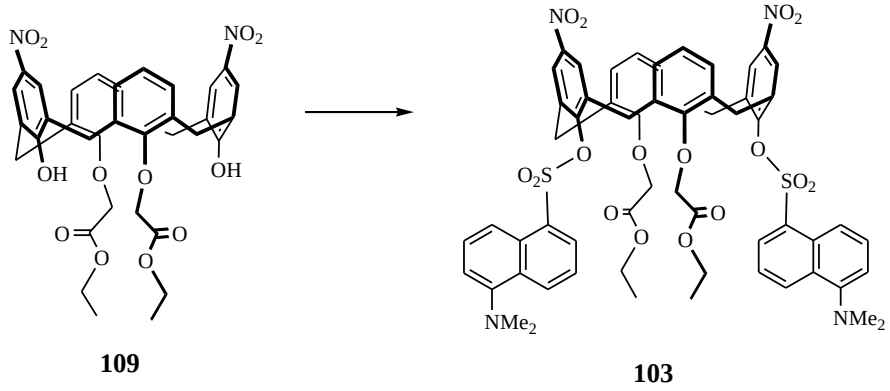


107 **101a** **101b**

Scheme 28



108 **102**



109 **103**

Scheme 29

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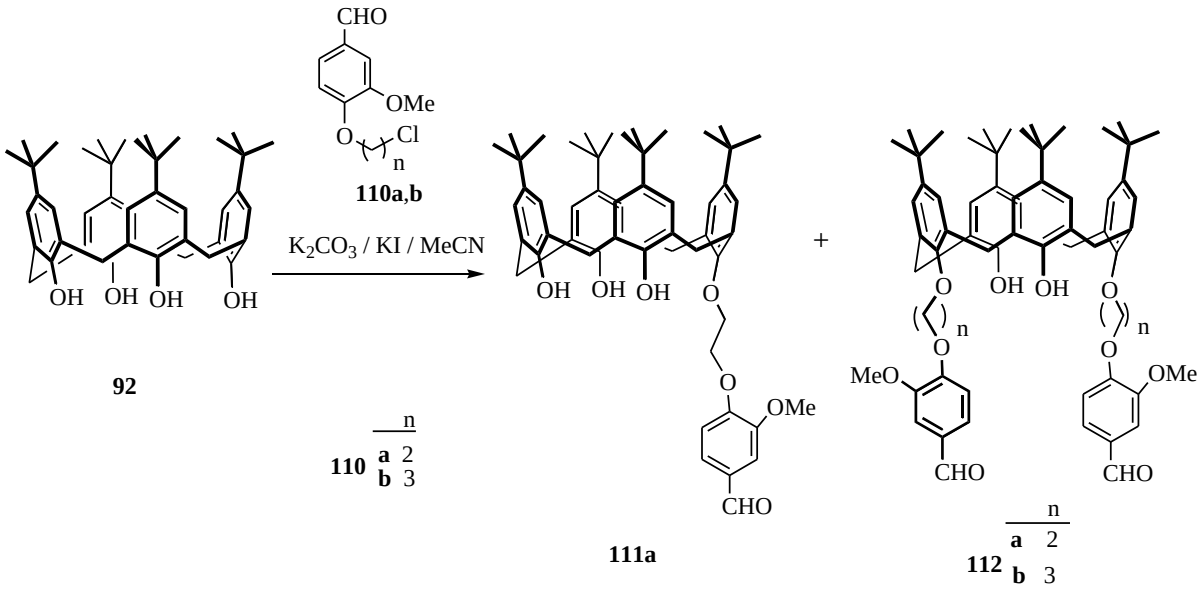
The crystal structures of dansylated calixarenes, namely the unsolvated **101b**, and two solvated species **98**•$CH_2(OH)CN$ and **99**•$3CH_3CN$ have been described, in the crystal structure of **101b**, the calixarene is in a paco conformation, while in the solvates of **98** and **99** the calixarenes are fixed in cone conformations. Fluorescence measurements have shown that calixarenes **98**-**102** selectively recognize Cu^{2+} ions; moreover, **101a** may be used for simultaneous determination of Cu^{2+} and Hg^{2+} ions.[109]

The direct alkylation of calixarene **92** with substituted benzaldehydes **110a**,**b** has been reported. The reaction of **92** with **110a** affords the mono-and dialdehydes **111a** and **112a**, respectively. However, in the case of **110b** the dialdehyde **112b** was obtained as the sole product.[110]



Scheme 30

The introduction of aldehyde groups into calixarenes can enable further functionalization reactions. Thus, the condensation of **111a** and **112a**,**b** with *S*-methyl-and *S*-benzyl-dithiocarbazates affords the sulfur-containing Schiff bases, from **111a** two products **113a**,**b** were obtained, while the reaction of **112a**,**b** yielded four products **114a-d**.[110] It is noteworthy that syntheses of mono-functionalized calixarenes,[111] such as **111a** and **113a,b** are not as common as those leading to fully functionalized species.

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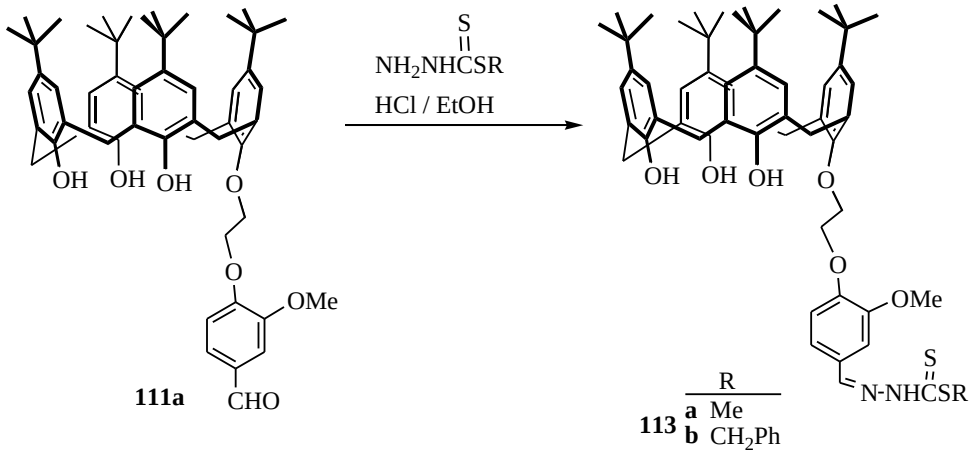
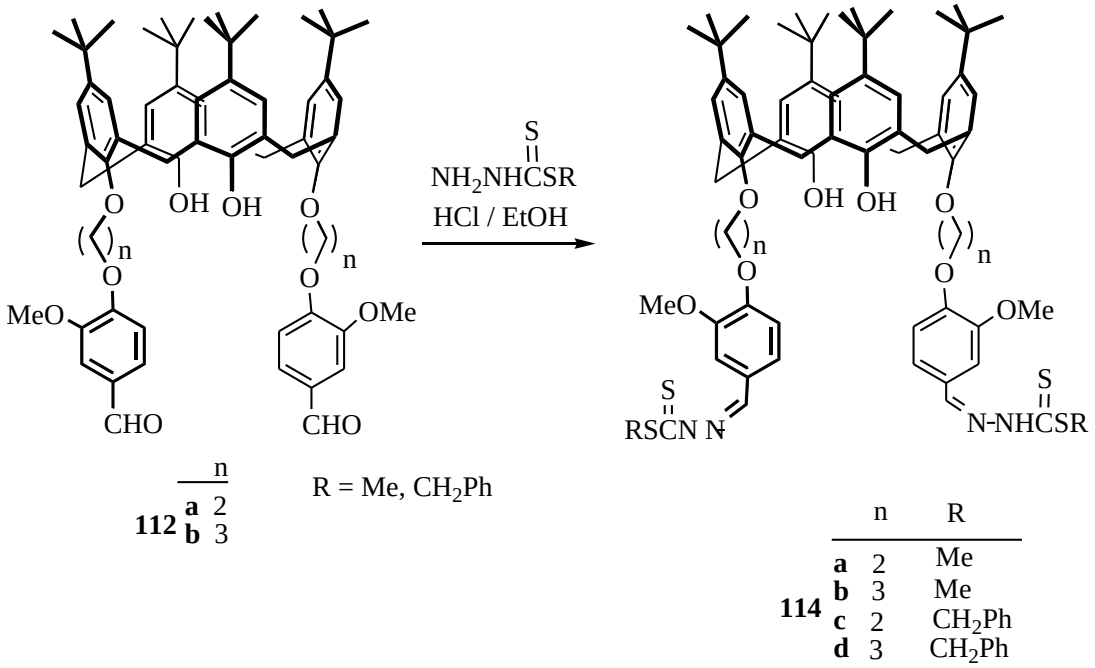


Scheme 31



Scheme 32

In order to investigate the reactivity of the aldehyde groups of calixarene **115**, it was submitted to reactions with hydrazine hydrate and with diaminomaleonitrile affording **116** and **117**, with salicylaldehyde hydrazone and 2-pyridinaldehyde hydrazone, compounds **118** and **119** were formed, respectively.[112] All reactions proceed at room temperature, the ^{1}H NMR data indicate that the products are in cone conformations. In all cases it was found that the pendant arms of the compounds do not adopt a face-to-face structure but are bent away from each other.

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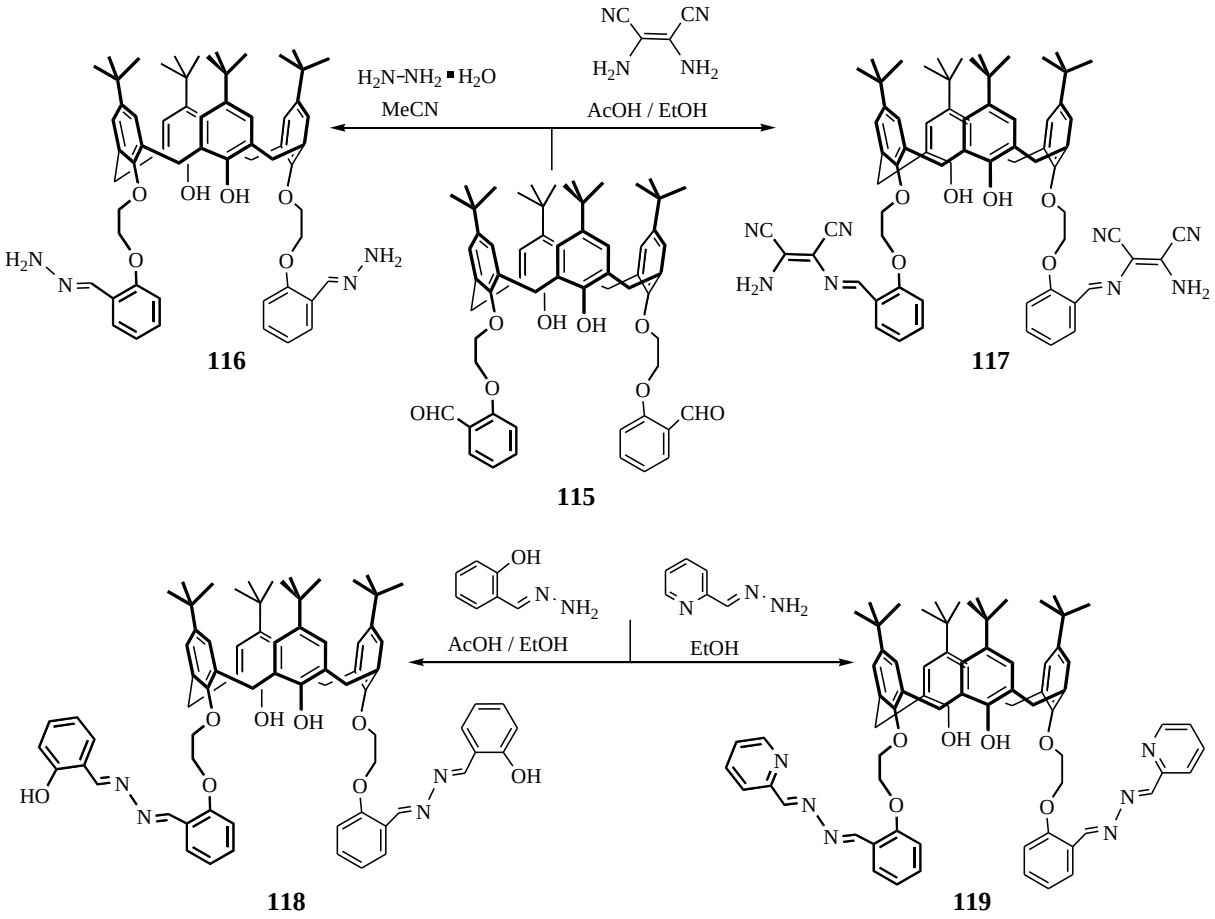

Scheme 33

For a study using calixarenes as receptors for the colorimetric detection of fluoride ions,[113] compounds **120**-**123** were synthesized. It should be noted that due to its high electronegativity and small size, fluoride ion can form strong hydrogen bonds at low concentrations, and is a sufficiently strong base to promote deprotonation at higher concentrations. The synthesis of the receptors commenced with the treatment of calixarene **124** with *p*-hydroxybenzaldehyde and *p*-hydroxyacetophenone, leading to **125a** and **125b**, respectively. Reaction of **125a** with *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine affords calixarenes **120** and **121**, while **125b** with the same reagents yields **122** and **123**.[114]

It was found that **120** selectively recognizes F^- ions; among $H_2PO_4^-$, AcO^- and F^- ions, the solution color changes from yellow to purple only with F^- ions, whereas with **121** the color also changes with $H_2PO_4^-$ and AcO^- ions. The observation that the limiting value in the absorption maximum of **120** was achieved at four F^- equivalents instead of only two equivalents was unexpected. This behavior is explained by the fact that addition of one F^- equivalent results in the hydrogen bonding with the NH protons in **120** and formation of a 1:1 complex, **120** • F^-. Upon addition of a second F^- equivalent, the complex **120** • $2F^-$ is formed, and further addition of F^-

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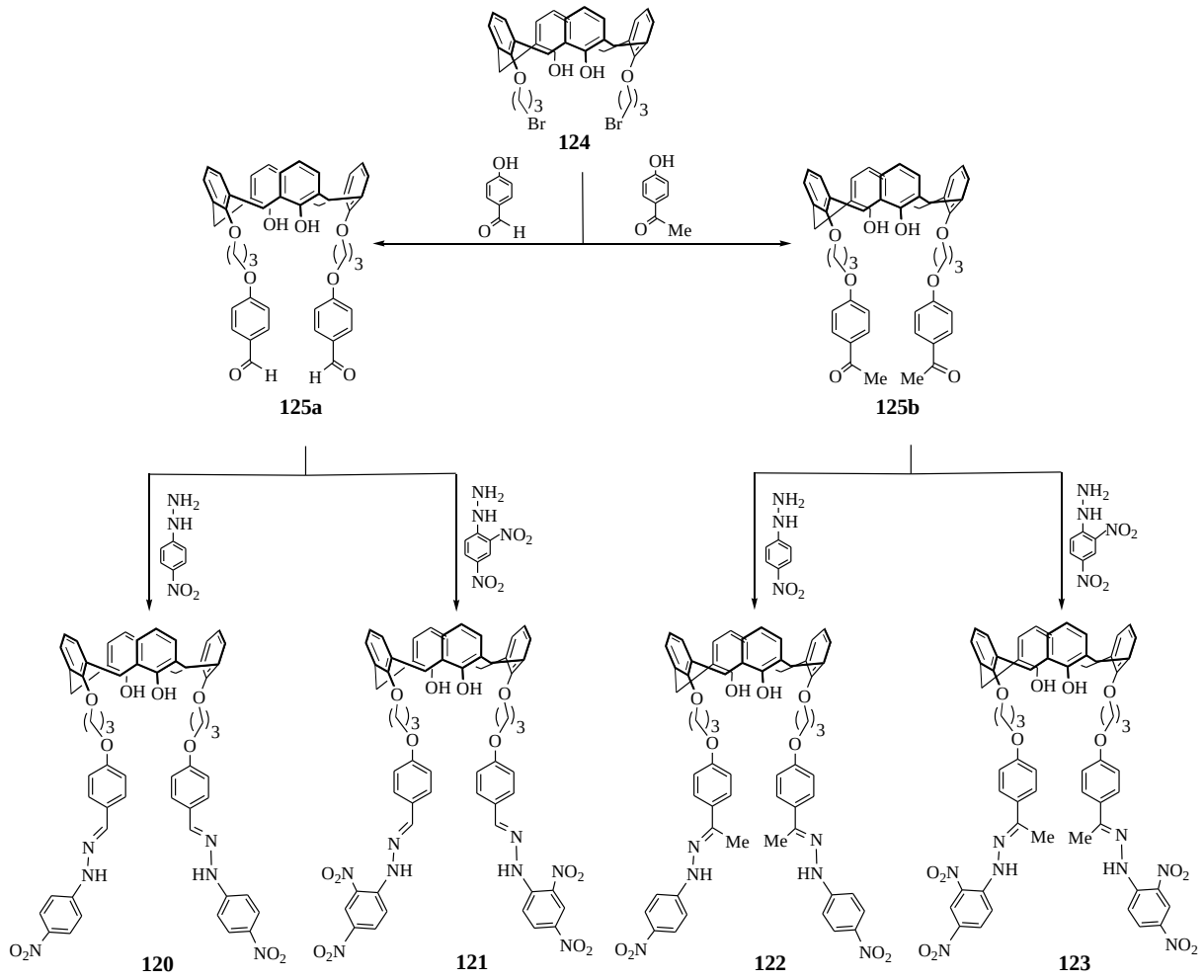
equivalents causes deprotonation of the NH groups. The above studies are promising for further design of colorimetric sensors of fluoride ions.[114]



Scheme 34

In a study of calixarenes containing tethered drug moieties, calixarene **126** substituted by nalidixic acid, a quinolone antibiotic, has been synthesized; for this purpose calixarene **92** was treated with bromopropyl ester of nalidixic acid **127**.[115]

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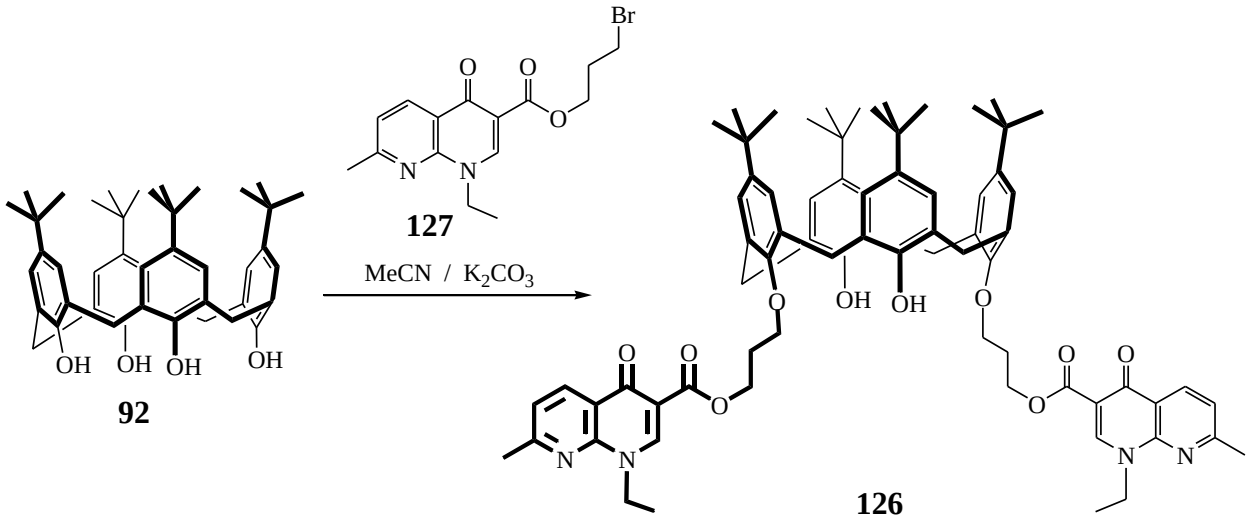
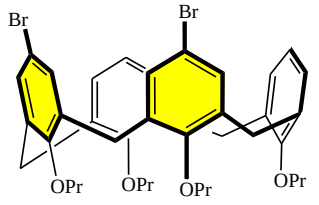
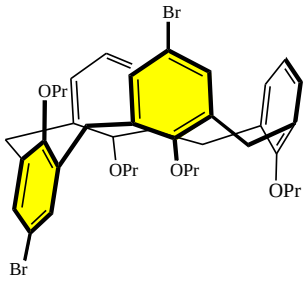


Scheme 35

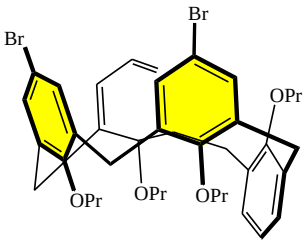
All six possible conformational isomers of the proximally para-disubstituted calixarene **128** were selectively synthesized and isolated; they are one cone, two paco, two 1,2-alt and one 1,3-alt conformers. It was established that the two paco **128b*** and **128c***, one 1,2-alt **128e*** and one 1,3-alt **128f*** conformers are inherently chiral.[116]



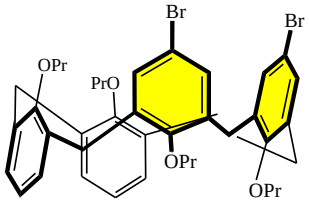
128a
cone



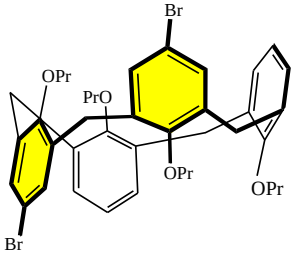
128b*
paco



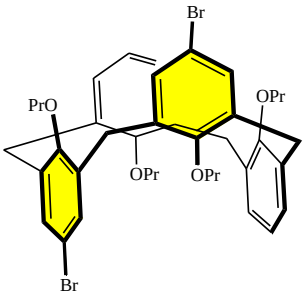
128c*
paco



128d
1,2-alt



128e*
1,2-alt



128f *
1,3-alt

(in the structures of **128a-f** the disubstituted rings are darkened)

Scheme 36

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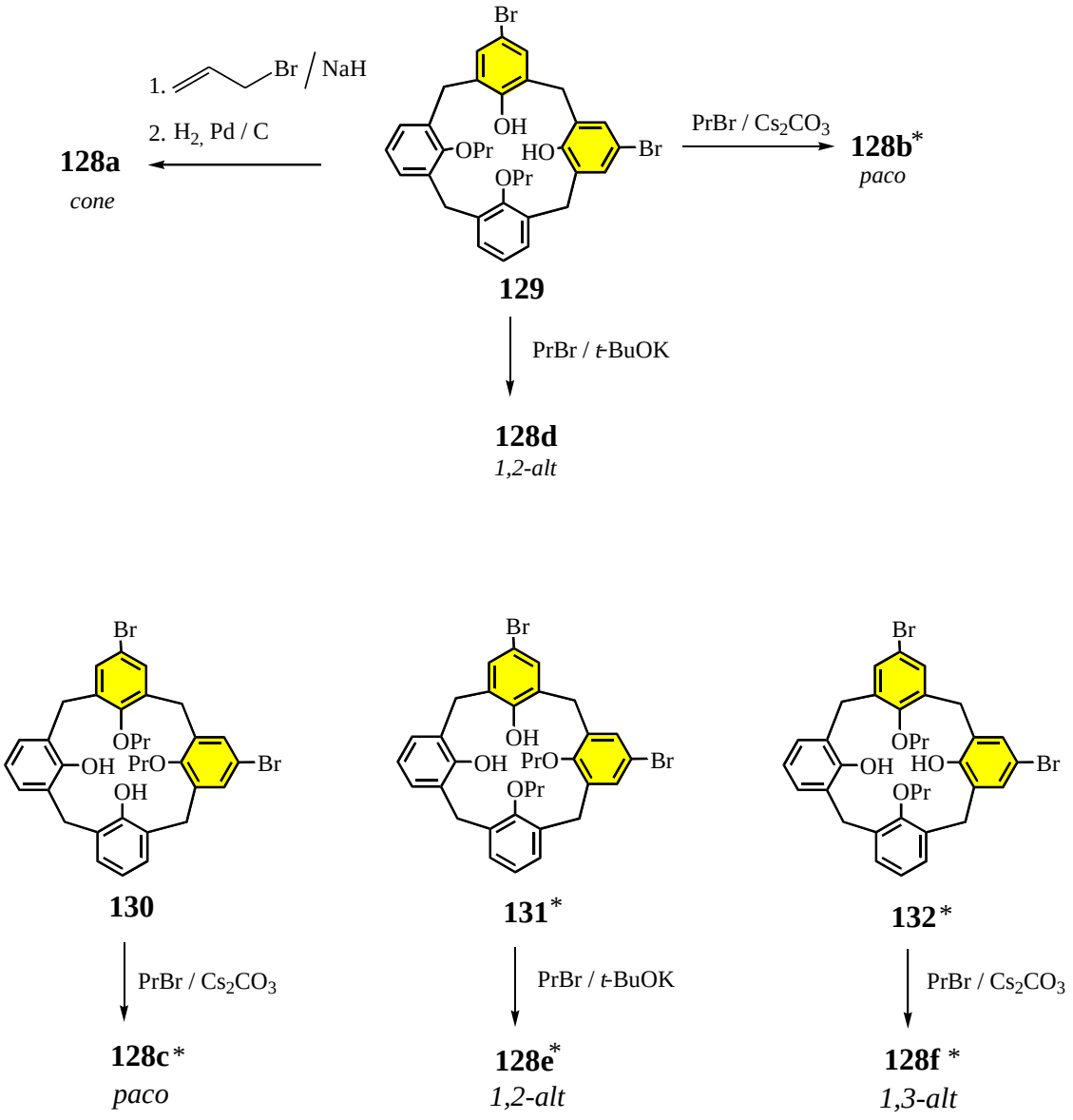
The above compounds were synthesized by propylation of calixarenes **129**, **130**, **131*** and **132*** in the presence of a base. The role of the base in this process is very important: *e.g.* for **129** the use of NaH leads preferentially to *cone* **128a**, whereas in the presence of Cs_2CO_3 and *t*-BuOK, conformers *paco* **128b*** and 1,2-*alt* **128d**, respectively, are obtained.



Scheme 37

Calixarenes **128b***, **128c***,**128e*** and **128f*** are promising precursors for the design of synthetic receptors capable of chiral discrimination, since bromine atoms may be readily replaced by other substituents.

The tannin-like calixarene **133a**, bearing two gallate units was synthesized along with calixarenes **133b** and **133c**.[117] Gallic acid is present in the plant tannin in form of condensed

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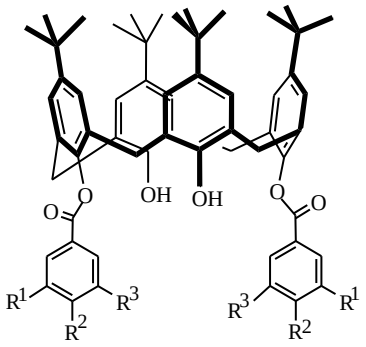
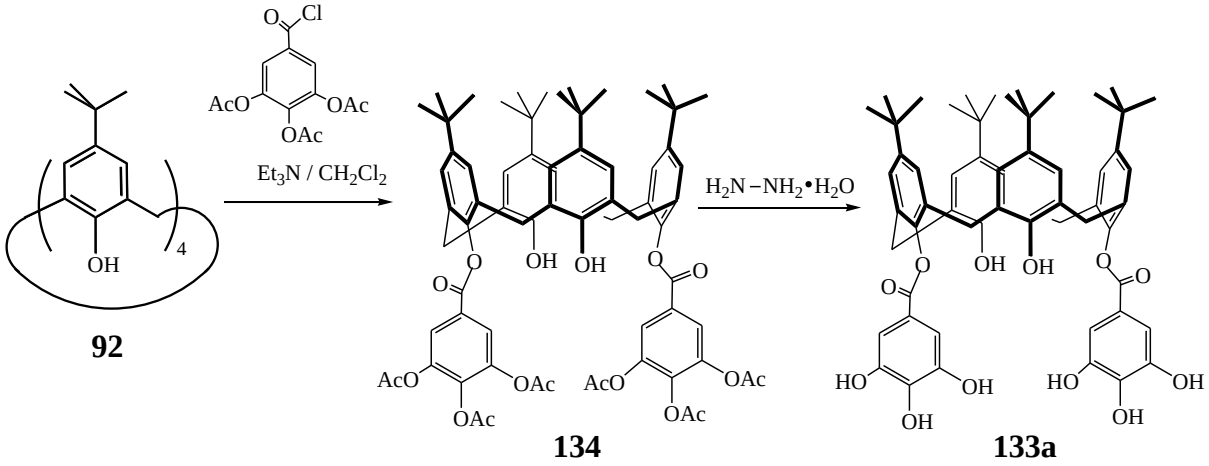
compounds, *e.g.* with glucose or quinic acid, tannins have biological properties and are able to bind proteins and metal ions.



		R^1	R^2	R^3
133	**a**	OH	OH	OH
	b	H	OH	OH
	c	H	OH	H

Scheme 38

The synthesis of **133a** begins with the reaction of calixarene **92** with 3,4,5-triacetoxybenzoyl chloride affording **134** which, upon deacetylation with hydrazine monohydrate, yields the desired product. Calixarenes **133b** and **133c** were obtained by a similar procedure.



92 **134** **133a**

Scheme 39

The ^{1}H NMR spectra show that calixarenes **133a-c** are in *cone* conformations and have C_2 symmetry. The galloyl groups in **133a** are situated near to each other, allowing an unusual nonbonding close contact, the OH-π interaction between the hydroxyl group and the aromatic ring of the galloyl unit is therefore possible.

The reactions of easily-accessible calixarene phosphoric esters **135-138** with bromotrimethylsilane, followed by methanol, have been reported to yield water soluble calixarene phosphoric acids **139-142**.[11]

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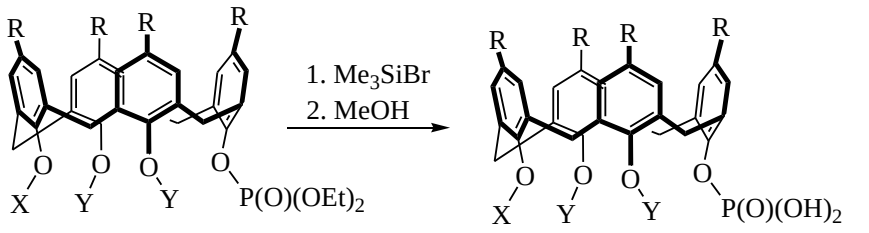


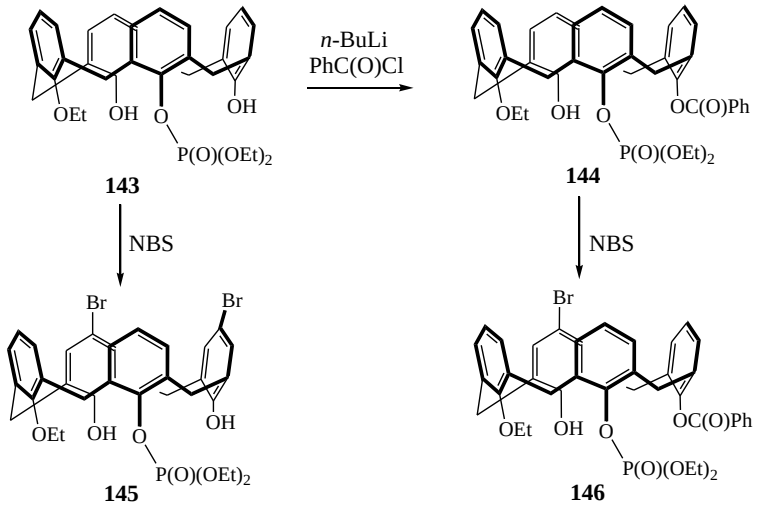
135 - 138 **139 - 142**

	R	X	Y
135	H	Et	H
136	H	$P(O)(OEt)_2$	H
137	*t*-Bu	$P(O)(OEt)_2$	H
138	*t*-Bu	$P(O)(OEt)_2$	$P(O)(OEt)_2$

	R	X	Y
139	H	Et	H
140	H	$P(O)(OH)_2$	H
141	*t*-Bu	$P(O)(OH)_2$	H
142	*t*-Bu	$P(O)(OH)_2$	$P(O)(OH)_2$

Scheme 40

The reactions of chiral calixarene **143**, leading to inherently chiral calixarenes **144**-**146** have also been reported.[118] These begin with the acylation of **143** by benzoyl chloride affording calixarene **144**, bromination of **143** and **144** with NBS yields calixarenes **145** and **146**, respectively. Calixarenes **143**-**146** react with bromotrimethylsilane forming trimethylsilyl esters **147**-**150** which, without isolation, were treated with methanol to give inherently chiral calixarene phosphoric acids **151**–**154**, formed as racemic mixtures of two enantiomers, similarly to **143**-**146**.



143 **144** **145** **146**

Scheme 41

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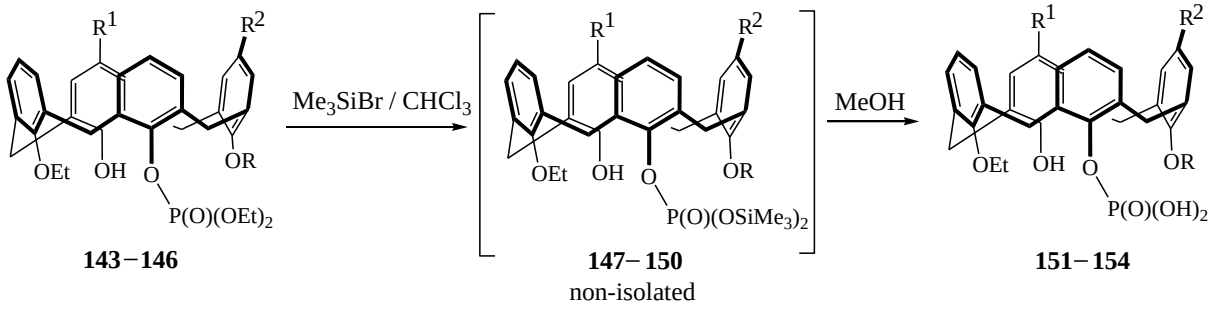
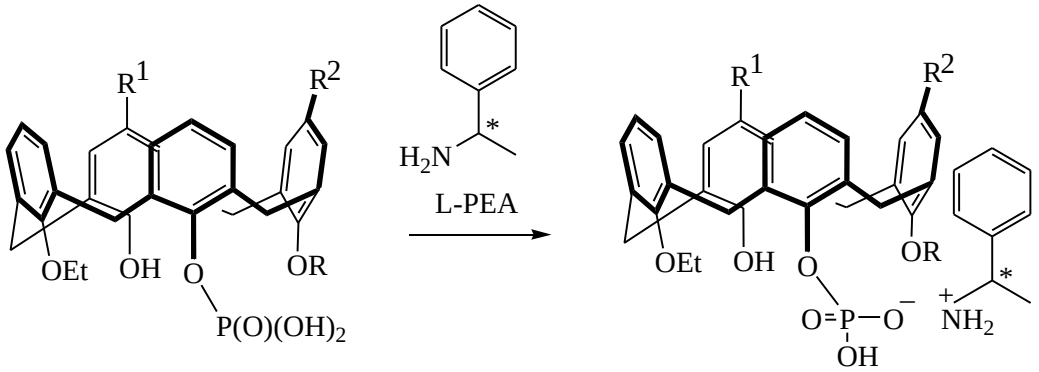


143−146 **147−150** non-isolated **151−154**

			R	R^1	R^2
143	**147**	**151**	H	H	H
144	**148**	**152**	C(O)Ph	H	H
145	**149**	**153**	H	Br	Br
146	**150**	**154**	C(O)Ph	Br	H

Scheme 42



151−154 **155−158**

		R	R^1	R^2
151	**155**	H	H	H
152	**156**	C(O)Ph	H	H
153	**157**	H	Br	Br
154	**158**	C(O)Ph	Br	H

Scheme 43

Reactions of **151**–**154** with L-(-)-α-phenylethylamine (PEA) afford weakly dissociated diastereomeric salts **155-158**, respectively, which could be easily separated into diastereomers by RP HPLC on Separon SGX C18 or Partisil 5 ODS 3 achiral columns. Other chiral amines may also be used besides L-PEA.[118]

Due to their conformational flexibility the chemistry of large calix[*n*]arenes (*n* = 6,8) has been less investigated than that of calix[4]arenes. It should be pointed out that large calixarenes have

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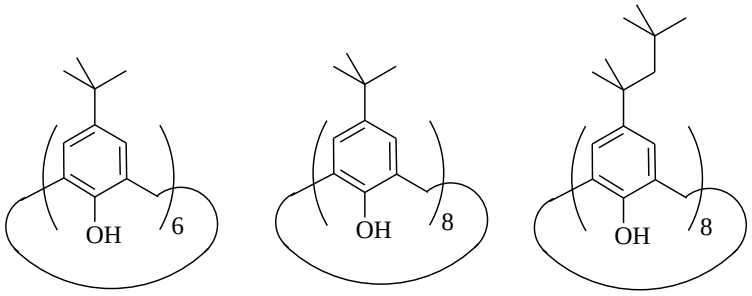
some advantages since they may serve as receptors for bulky guest molecules and as enzyme mimics. Considering the many applications of calixarenes, as well as the potentially valuable properties of calix[*n*]arenes (*n* = 6,8), synthetic methods for preparation of water-soluble large calixarenes functionalized at the narrow rim have been reported,[119] using calixarenes **159**-**161** as starting materials.

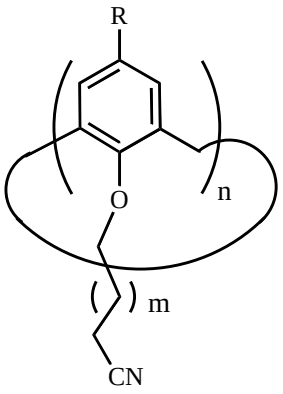


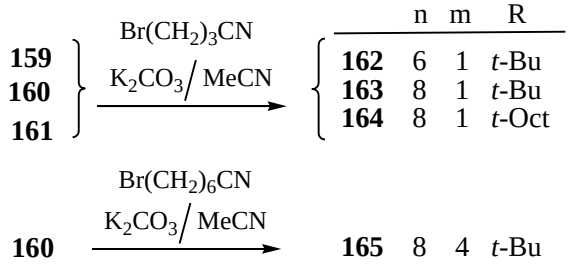
159 **160** **161**

Scheme 44

Two types of reagents were chosen: *bromoalkanenitriles and oligo(ethylene glycol)* derivatives, in both cases, calixarenes which can be further functionalized are obtained. Moreover, the reactions with oligo(ethylene glycol) derivatives afford hydrophillic calixarenes. A simple synthetic procedure involves the use of 4-bromobutyronitrile, 7-bromoheptanenitrile as well as activated tri, hexa-and dodeca(ethylene glycol) derivatives.

In reactions with bromoalkanenitriles the full alkylation of **159**-**161** performed with bromobutyronitrile in the presence of K_2CO_3 yielded **162**-**164**, and reaction of **160** with bromoheptanenitrile yielded **165**.





	n	m	R
159 **160** **161**			
162	6	1	*t*-Bu
163	8	1	*t*-Bu
164	8	1	*t*-Oct
160			
165	8	4	*t*-Bu

Scheme 45

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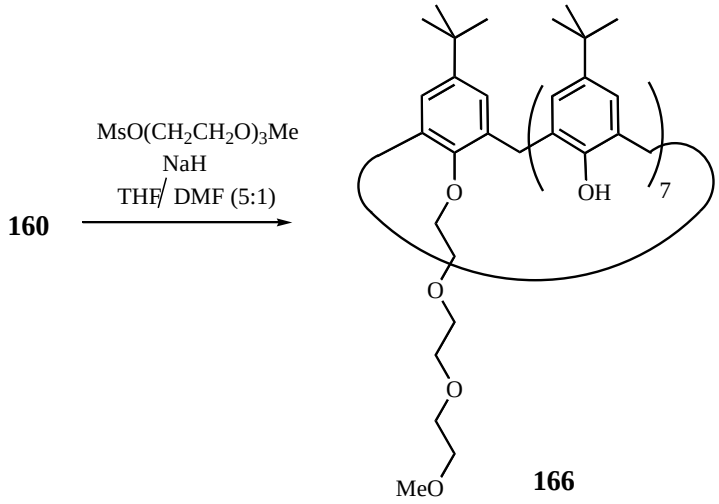
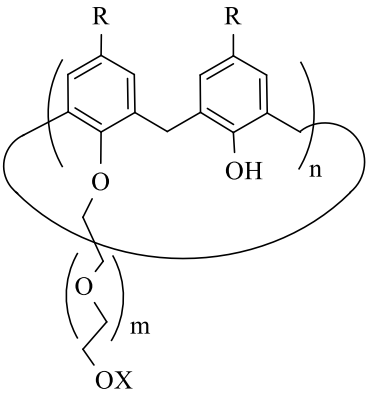
In reactions with oligo(ethylene glycol) derivatives, the monoalkylation of **160** with 3,6,9-trioxadecyl mesylate, carried out in the presence of sodium hydride afforded **166**.



Scheme 46

Partial alkylation of **160** and **161** with $Br(CH_2CH_2O)_3Me$ gave rise to **167** and **168**, while the partial alkylation of **159**–**161** using $Br(CH_2CH_2O)_6THP$ afforded **169**–**171**, respectively.



			n	m	R	X
160, **161**	$Br(CH_2CH_2O)_3Me$, K_2CO_3 / MeCN	**167**	4	2	*t*-Bu	Me
		168	4	2	*t*-Oct	Me
159–**161**	$Br(CH_2CH_2O)_6THP$, K_2CO_3 / MeCN	**169**	3	5	*t*-Bu	THP
		170	4	5	*t*-Bu	THP
		171	4	5	*t*-Oct	THP

THP = 3,4-dihydro-2*H*-pyrane (protecting agent)

Scheme 47

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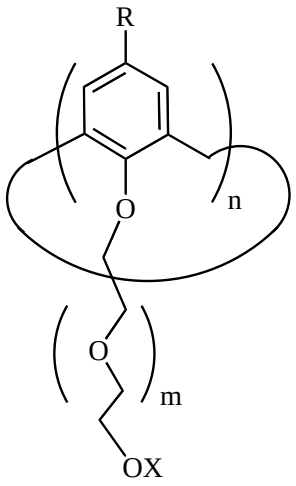
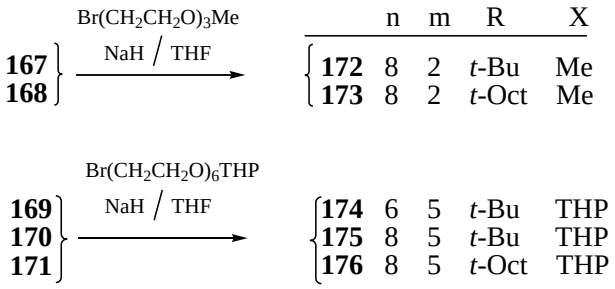
In order to obtain fully alkylated products, second alkylations of **167** and **168** with $Br(CH_2CH_2O)_3Me$ and of **169-171** with $Br(CH_2CH_2O)_6THP$ afforded **172, 173**, and **174-176**, respectively.





	n	m	R	X
172	8	2	*t*-Bu	Me
173	8	2	*t*-Oct	Me
174	6	5	*t*-Bu	THP
175	8	5	*t*-Bu	THP
176	8	5	*t*-Oct	THP

Scheme 48

The above syntheses of calix[6]arenes and calix[8]arenes functionalized at the narrow rim extend the possibilities of their applications by introduction of various, *e.g.* solubilizing or fluorescent groups, which could be promising for the design of biological models or molecular sensors.[119]

A large class of calixarenes bridged by crown ethers *i.e.* calixcrowns, exists,[120,121] and these are efficient acceptors of metal ions. A related class of compounds are the calixaza-crowns,[122-124] which also show complexing properties.

The synthesis of an interesting spirobiscalixazacrown **177** has been reported. Its structure consists of two calixazacrown moieties connected by a spiro-carbon atom, for comparison purposes calixazacrown **178**, *i.e.* half-part of **177** was also synthesized. Both **177** and **178** were obtained by the reaction of calixarene **179** with appropriate diamino derivatives **180** and **181**, respectively, and were investigated for their complexing properties.[125]

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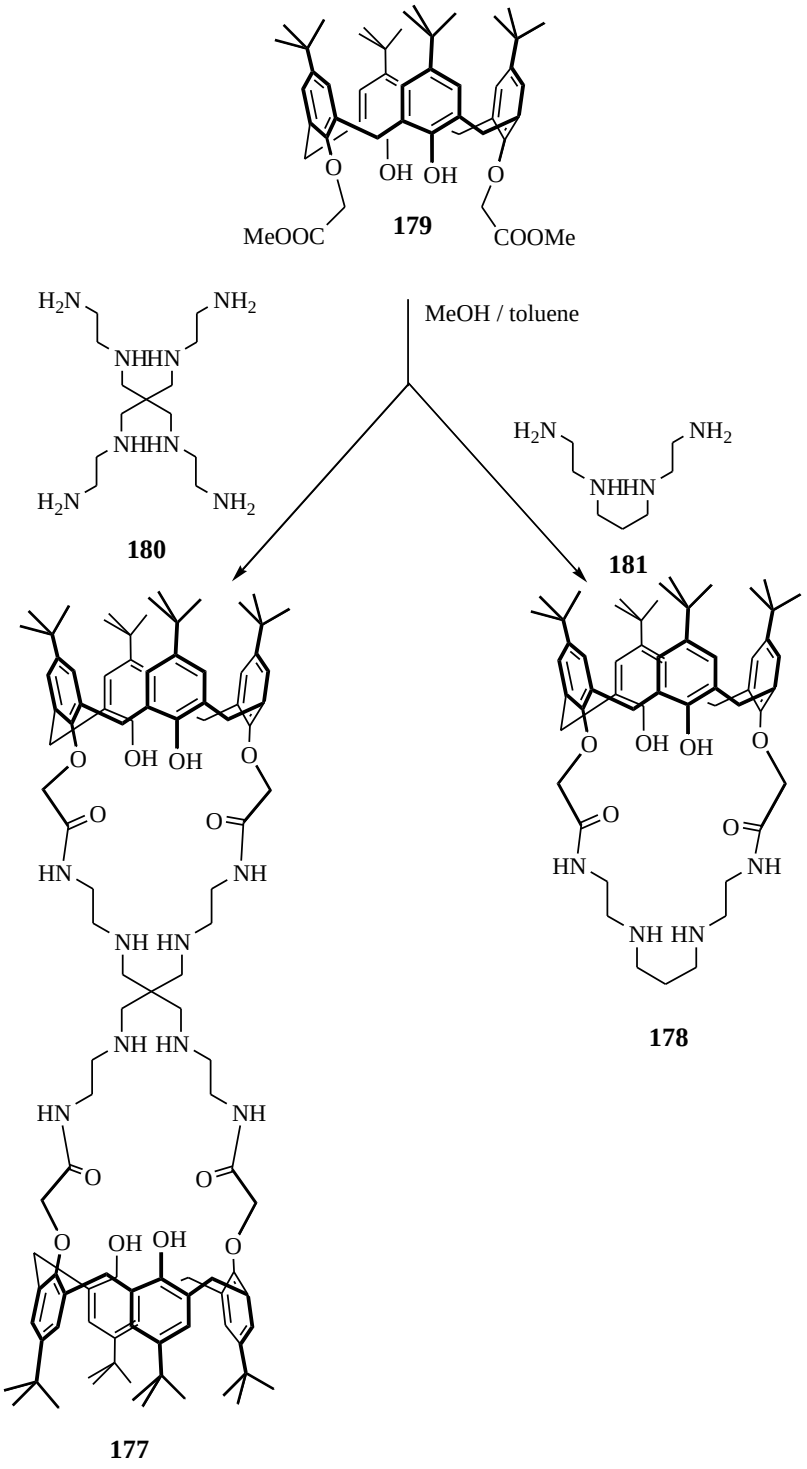

Scheme 49

It was observed that **177** forms 1:2 complexes, **177•M**$_2$, with Ag^+, Zn^{2+} and Fe^{2+} ions, whereas **178** affords 1:1 **178•M** complexes. In the **177•M**$_2$ complexes, one metal ion is situated in each cavity. The complexation of **177** with metal ions proceeds slower than complexation of **178** since the next metal ion enters the second cavity of **177** with more difficulty than does the first.

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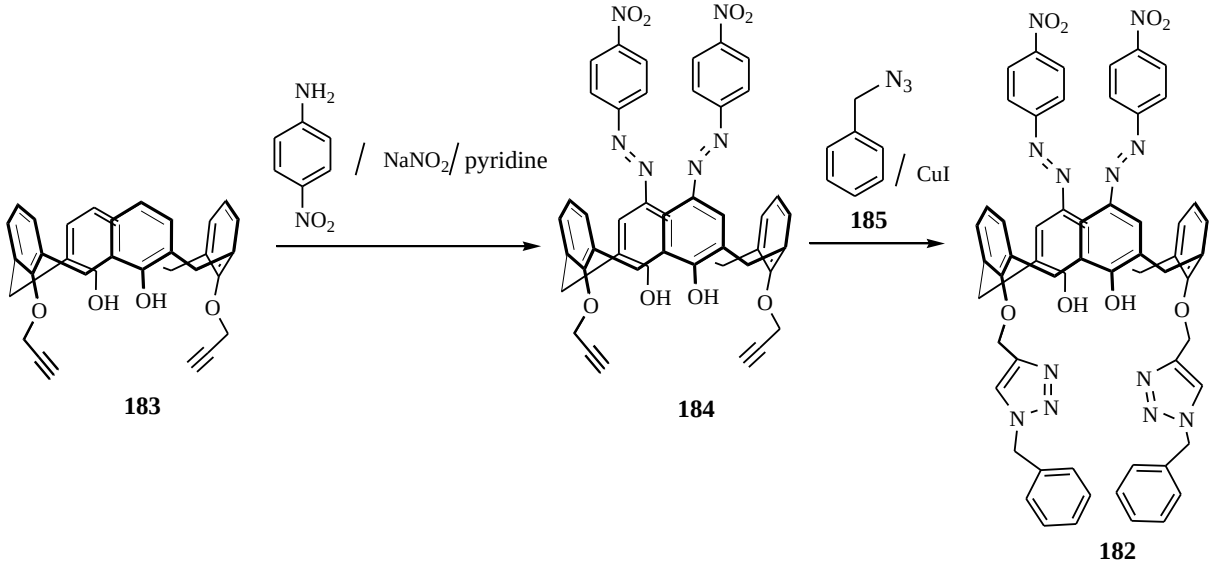
4. Functionalization of both rims of calixarenes

Many functionalization reactions of calixarenes at both rims are known,[126-131] and some examples are described below. In a study of calixarene chromogenic chemosensors for both cations and anions,[132] and with the aim to construct molecular logic gates,[133,134] calixarene **182** recognizing Ca^{2+} and I^- ions has been synthesized.[135] The process involves the treatment of dipropargylcalixarene **183** with *p*-nitroaniline and $NaNO_2$ affording calixarene **184** containing azo groups which upon click reaction with azide **185** yields calixarene **182**.



Scheme 50

Calixarene **182** has triazole units as metal-ligating groups responsible for recognition of Ca^{2+}, Pb^{2+} and Ba^{2+} ions, while its phenol hydroxyl groups are responsible for binding of F^-, AcO^- and $H_2PO_4^-$ anions. The color changes resulting from the presence of azo groups are distinct and may be detected by naked eye. The UV/Vis spectral behavior of **182** toward Ca^{2+} and F^- ions enables the construction of a dual output molecular switch, as an INHIBIT logic gate with a YES logic function; the system is operated by inputs of Ca^{2+} and F^- ions. The above experiments are promising for design of miniaturized molecular level devices.

Synthesis of 1,3-*alt* calixarenes bearing imidazolyl (**186**–**188**) and pyrazolyl (**189**–**191**) units has been performed for design of the directional 2D coordination network.[136,137] In this process the starting calixarene **192** containing mesitylene rings was chloromethylated to give derivative **193** which reacted with sodium imidazolate and pyrazolate affording compounds **186** and **189**, respectively.

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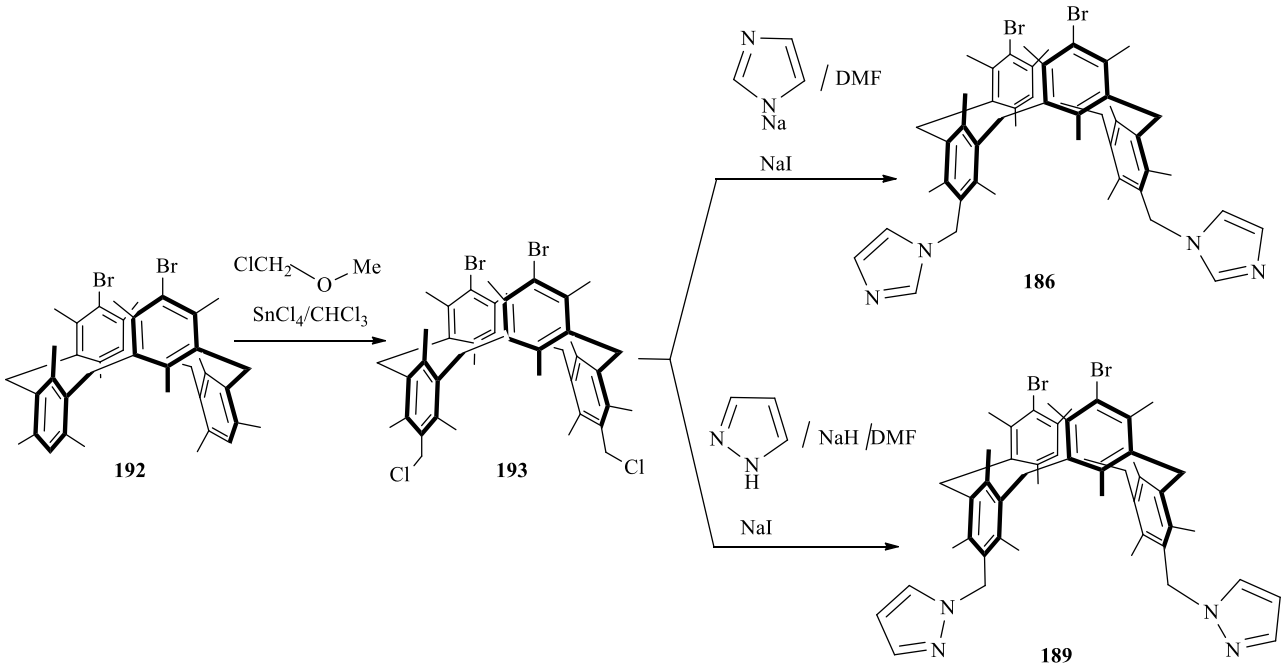
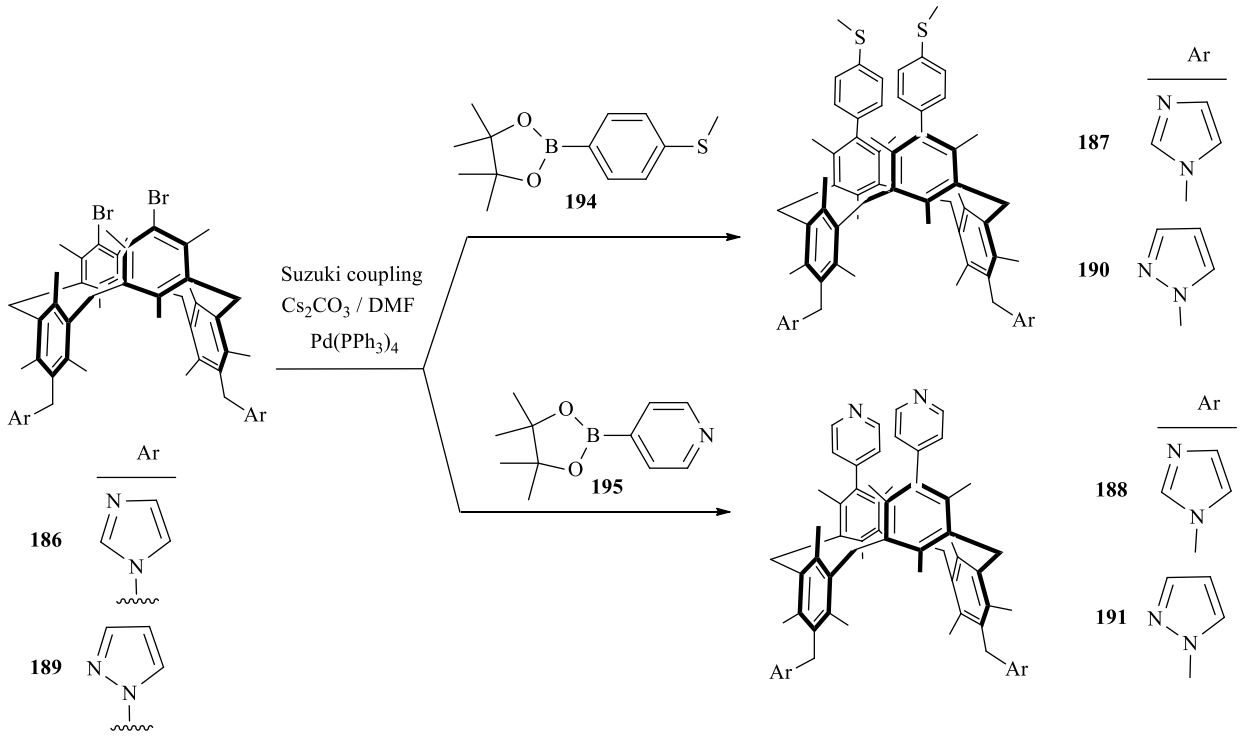


Scheme 51

Compounds **186** and **189** upon Suzuki coupling with boronic esters **194** and **195** bearing *p*-methylthiophenyl and pyridyl groups, respectively, performed with the use of $Pd(PPh_3)_4$ as a catalyst, yielded in the case of **186** compounds **187** and **188**, and in the case of **189** compounds **190** and **191**.



Scheme 52

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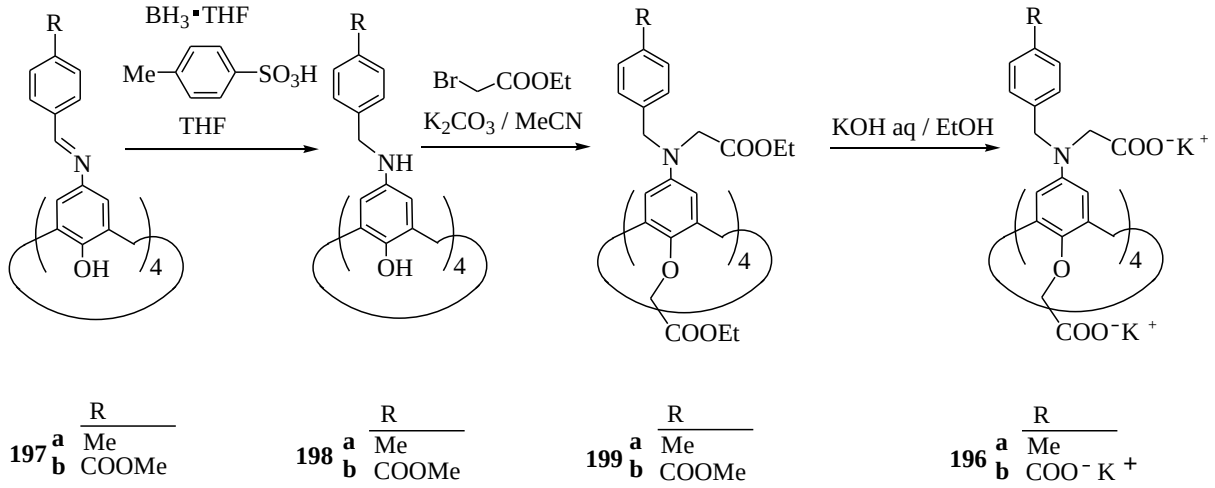
The structural investigation has shown that **186** affords crystalline discrete metallamacrobicycles in the presence of metal halides MX_2 (M = Co, Zn, Cu, Hg; X = Cl or Br), whereas **189** forms infinite 1D coordination networks with CoX_2 (X = Cl or Br) and with $ZnCl_2$. It was found however that the acentric **191** bearing two pyrazolyl and two pyridyl groups forms the desired directional 2D coordination network with $ZnCl_2$.

The water soluble calixarenes **196a**,**b** having deep cavities were synthesized with the aim to investigate their inclusion complexation with pyridines and with aromatic cations.[138] The synthesis begins with the reduction of calixarenes **197a**,**b** with BH_3•THF complex affording **198a**,**b** which upon treatment with ethyl bromoacetate yield esters **199a**,**b**. The subsequent hydrolysis of **199a**,**b** leads to **196a**,**b** as potassium salts, bearing eight and twelve potassium carboxylate units, respectively.



197 **a** R = Me; **b** R = COOMe

198 **a** R = Me; **b** R = COOMe

199 **a** R = Me; **b** R = COOMe

196 **a** R = Me; **b** R = COO^-K^+

Scheme 53

It is noteworthy that **196a** and **196b** are both water soluble and highly stable, calixarene **196a** has a hydrophobic, and **196b** a hydrophilic cavity. It was found that **196a**,**b** form 1:1 inclusion complexes with pyridines **200**, **201** and aromatic cations **202**–**206**. The **196b•203** complex showed the highest binding constant.

Comparing complexing properties of **196a** and **196b**, it was found that **196a** binds **200** and **201** more strongly than **196b** does, whereas **196b** binds **202**-**206** more strongly than **196a** does. Comparing properties of guests it was observed that **196a** binds more strongly with **200** and **201** than with **202**-**206**. The affinity of **202** and **203** as guests of **196a** and of **196b** is higher for **203** than for **202**, this fact showing that the presence of the methyl group in the ring of **203** enhances its binding strength. All of the above experiments were performed in aqueous medium and therefore they are of interest for investigation of biological processes.

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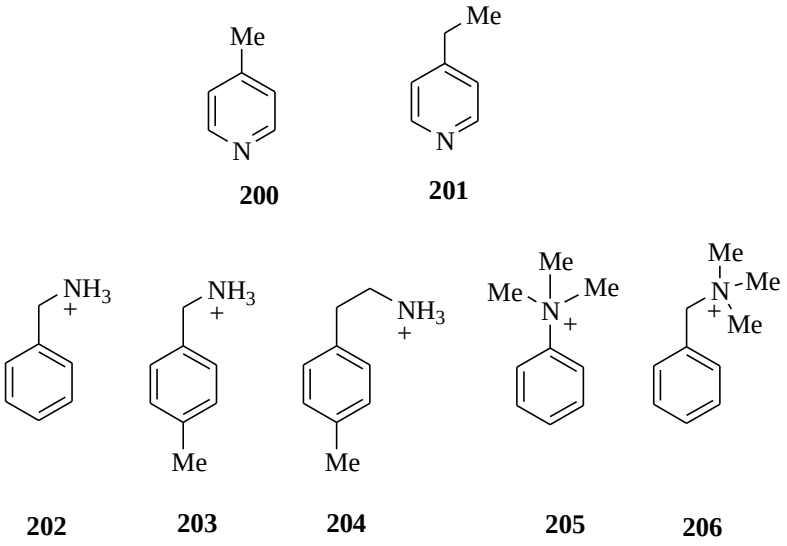

200 **201** **202** **203** **204** **205** **206**

Pyridines and aromatic cations used as guest molecules of **196a**,**b**

Scheme 54

It is known that chiral, especially inherently chiral calixarenes are able to include enantiomers of chiral guest molecules, this property being of a great value, *e.g.* in the design of chiral advanced materials, in the preparation of enantioselective sensors and in asymmetric synthesis. In this aspect both enantiomers of inherently chiral calixarenecarboxylic acids **207a** and **207b** with ABCD substitution patterns have been prepared.[139]

Calixarene **208** was reacted with (*R*+)-*N*-(α-phenylethyl)bromoacetamide affording calixarene **209** and benzoylation of one its hydroxyl groups leads to the mixture of *paco* diastereomers **210a** and **210b**. Diastereotopicity of **210a** and **210b** results both from the presence of the chiral carbon atom of phenylethylamide group and of the ABCD asymmetrical substitution of the calixarene macrocycle. Diastereomers **210a** and **210b** were separated by column chromatography and regioselectively brominated with NBS to give monobromocalixarenes **211a** and **211b**. The phenylethylamide and benzoyl groups of **211a** and **211b** were removed by treatment with KOH in ethanol/water medium affording chiral *cone* carboxylic acids **207a** and **207b** which are promising for the chiral recognition of organic compounds.

In the study of calixarene self-organized solids, the calixarenequinhydrone charge-transfer complex **212** has been synthesized.[140] For this purpose, dimethoxycalixarene **213** was oxidized with thallium (III) trifluoroacetate to give calixarenediquinone **214** which, upon reduction with sodium borohydride, yielded calixarenedihydroquinone **215**.

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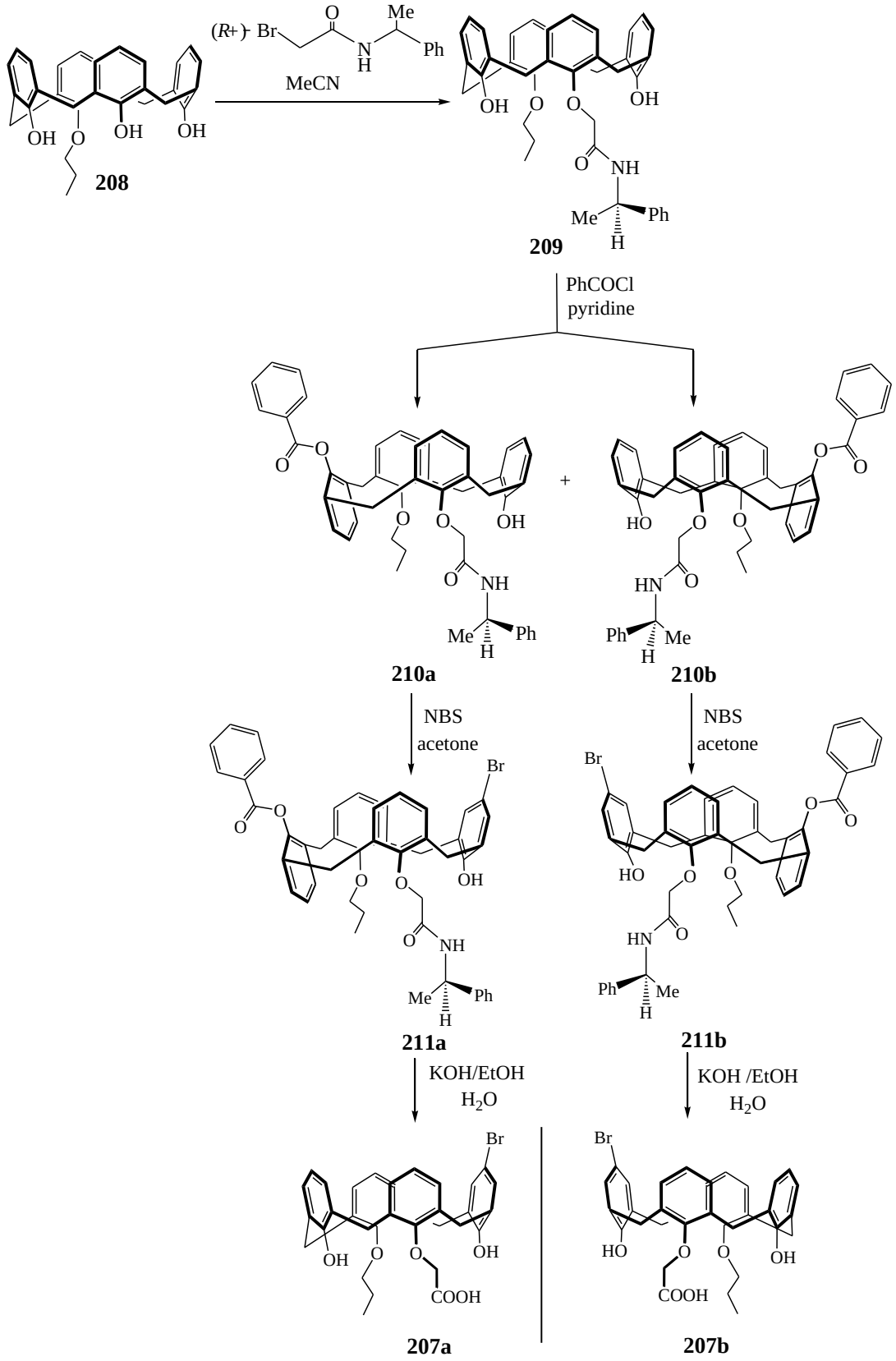

Scheme 55

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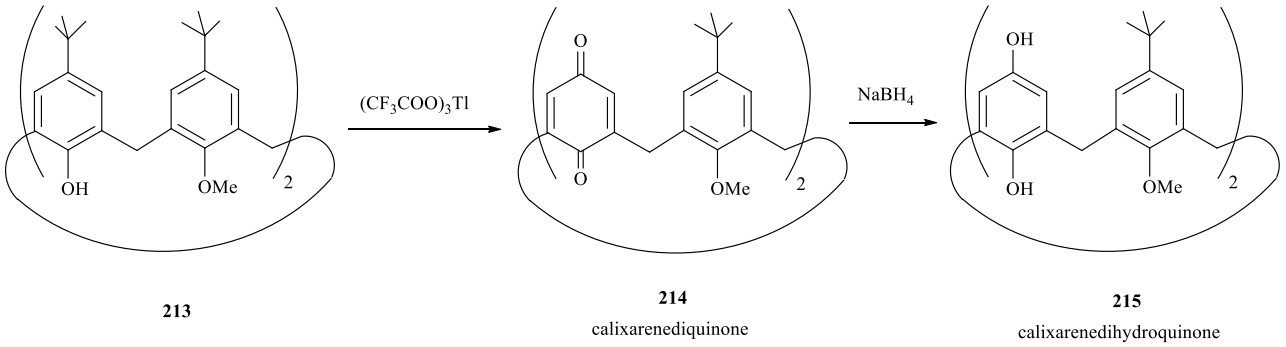
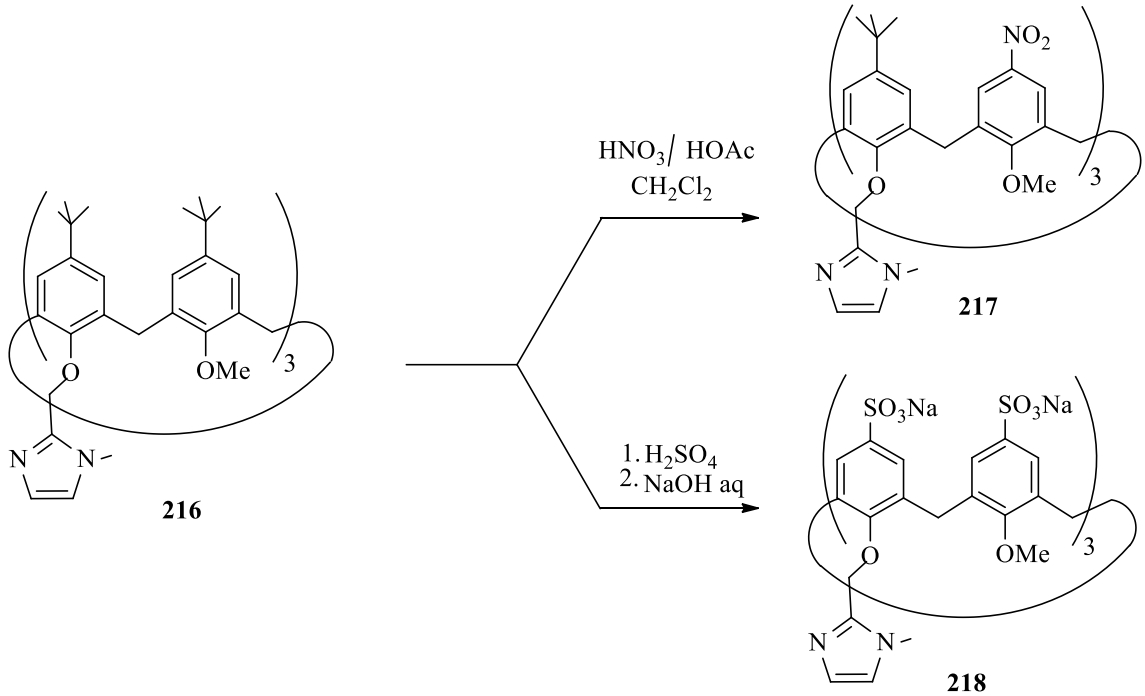


Scheme 56

The direct synthesis of **212** by mixing calixarenediquinone **214** and calixarenedihydroquinone **215** was impossible due to the lack of solubility of **215**. Therefore, **212** was prepared by partial reduction of **214** with NaH, leading to formation of the sodium salt of **212**. It was observed that **212** shows solvatochromism in the visible region and this result is promising for use of quinhydrone type calixarenes in the design of sensors.

The electrophilic *ipso*-nitration reactions of calix[6]arene **216** bearing three methylimidazolyl groups in alternate ring positions have been performed. It was observed that the reaction of **216** with fuming nitric acid and glacial acetic acid at room temperature in CH_2Cl_2 leads to partial *ipso*-nitration, affording tris-nitrated product. However, the reaction of **216** with concentrated sulfuric acid at 60 ºC leads to *ipso*-sulfonation of all benzene rings, affording hexa-sulfonated compound **218**.[141]



Scheme 57

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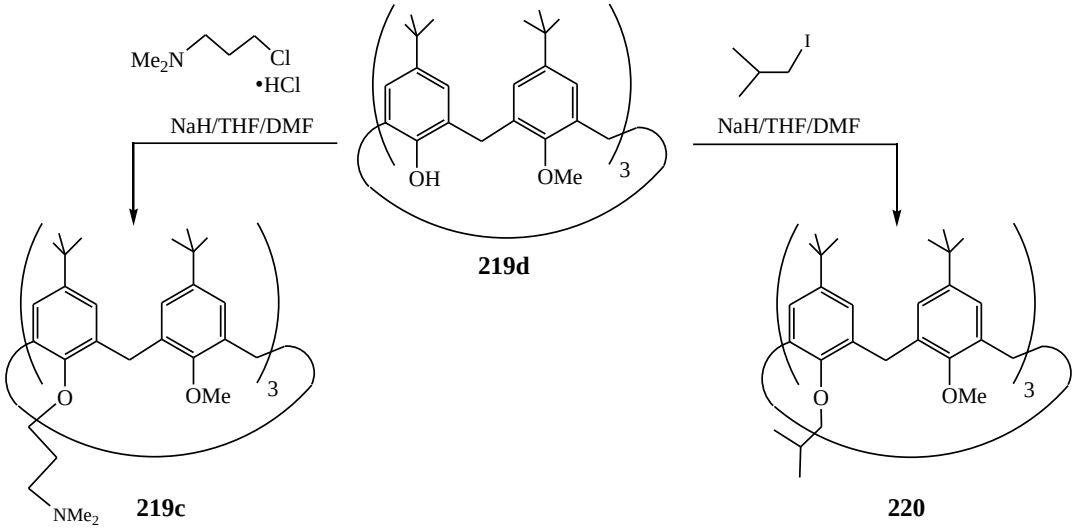
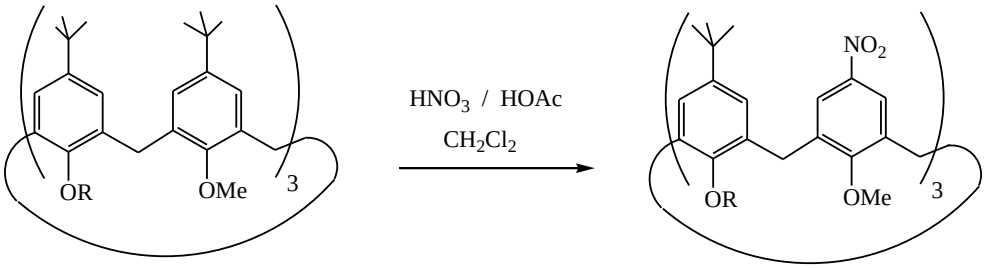
In order to understand why the nitration proceeds only on the anisole rings in preference to imidazolyl-substituted rings, the nitration was performed on calix[6]arenes bearing other than methylimidazolyl groups, for this purpose, calixarenes **219a-c** containing amino groups and **220** containing *i*-butyl groups have been used. Calixarenes **219a**,**b** were obtained by known procedures,[142] calixarenes **219c** and **220** were synthesized from **219d** by treatment with 3-(*N*,*N*-dimethylamino)propylchloride and *i*-butyl iodide, respectively.



219d **219c** **220**

Scheme 58

Calixarenes **219a-c** and **220** were nitrated as in the case of **216**, it was observed that **219a-c** afforded the tris-nitrated products **221a-c**, whereas from **220** the hexa-nitrated product **222** has been obtained.



		R
219	**a**	$CH_2CH_2NH_2$
	b	$CH_2CH_2NMe_2$
	c	$CH_2CH_2CH_2NMe_2$
	d	H

		R
221	**a**	$CH_2CH_2NH_2$
	b	$CH_2CH_2NMe_2$
	c	$CH_2CH_2CH_2NMe_2$

Scheme 59

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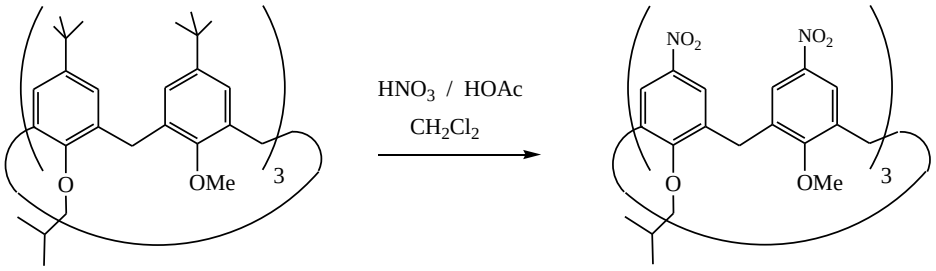
The crucial role of the substituent **R** may be explained by the presence of a protonable site in this group. Calixarene **216** containing methylimidazolyl groups as well as calixarenes **219a-c** containing arms with primary and tertiary amino groups, are protonated under the strongly acid nitration conditions. These protonated amino groups form hydrogen bonds with the phenolic oxygen atoms of calixarene, therefore the whole aromatic ring has lower electron density, *i.e.* is deactivated toward electrophilic attack of nitronium ion NO_2^+. As a result, in **219a-c**, the nitration proceeds only on the anisole rings and not on the rings containing amino groups. However, in **220**, where the amino groups are absent, such deactivation does not exist and therefore the nitration affords hexa-nitrated product **222**.



220 **222**

Scheme 60

It should be pointed out that the studied selective *ipso*-nitration of calix[6]arenes allows the direct introduction of three nitro groups in alternate rings, therefore the disymmetrization of the wide rim is possible. This selectivity depends on the nature of the substituents on the phenolic rings of the calixarenes. Facile reduction of the nitro groups leading to amino groups opens further synthetic perspectives for selectively functionalized calix[6]arenes.[141]

With the consideration of usefulness of amino groups, 1,3-*alt* calix[4]arenes bearing four or eight amino groups have been synthesized.[143]

In order to obtain tetraaminocalixarenes the following reactions were performed. The reaction of calixarene **92** with *N*-bromopropylphthalimide affords **223** which with bromopropylnitrile gives **224**, this compound can be also obtained from **92** by treatment with bromopropylnitrile yielding **925**, subsequently reacted with *N*-bromopropylphthalimide. Cleavage of **224** with hydrazine in ethanol proceeds without reduction of the nitrile groups to give **226**, this compound was acetylated affording **227** which upon reduction yielded **228**.

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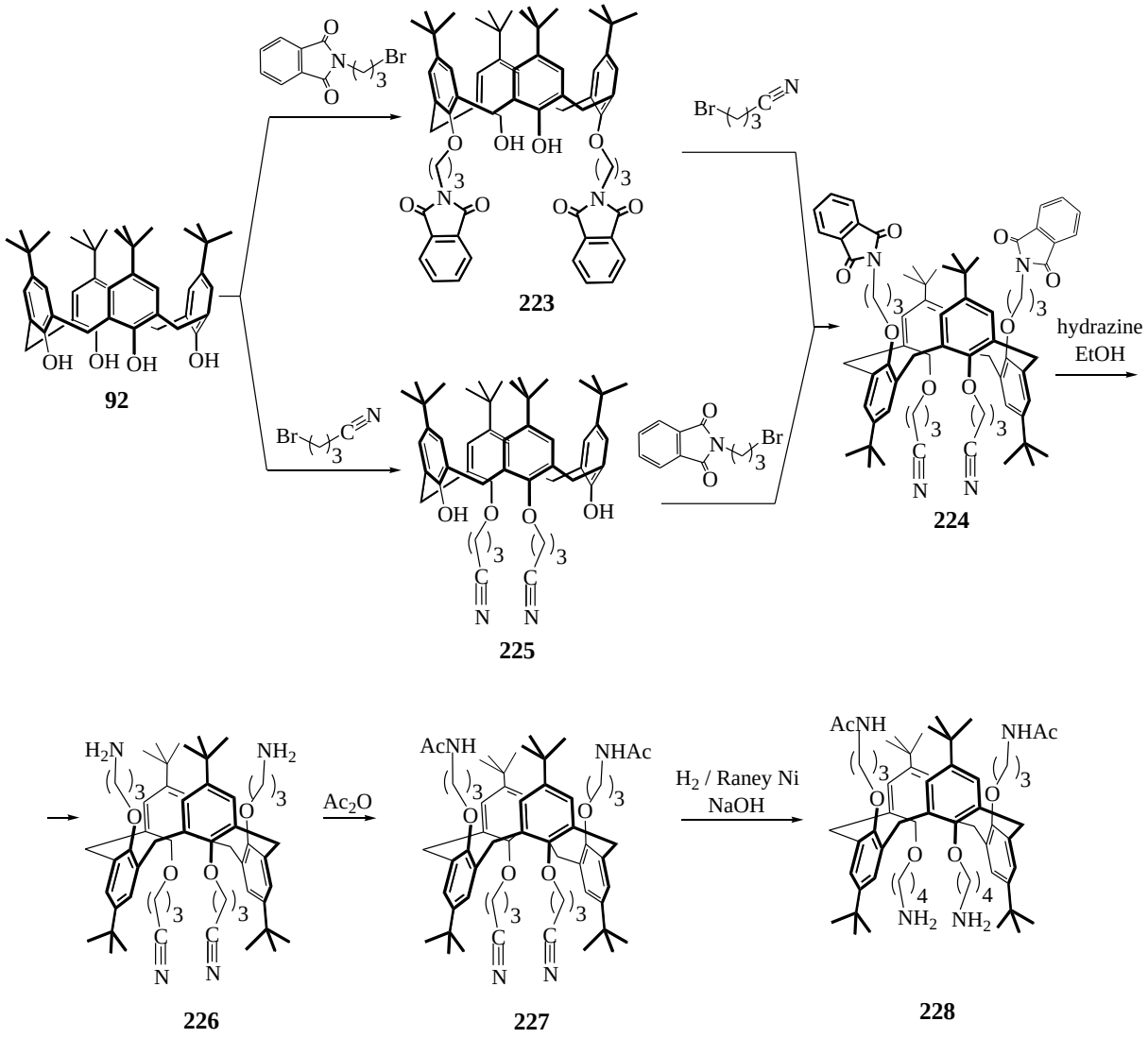

Scheme 61

The *O*-allylation of **229** with allylbromide gives rise to **230** which by simultaneous reduction of nitro groups and hydrogenation of C = C double bonds affords diaminocalixarene **231**. The protection of amino groups of **231** by phthalimide units leads to **232**, which was submitted to *ipso*-nitration yielding dinitrocalixarene **233**.The treatment of compound **233** with hydrazine in ethanol by cleavage of the phthalimide groups gives **234**, and catalytic hydrogenation of the nitro groups affords **235**.

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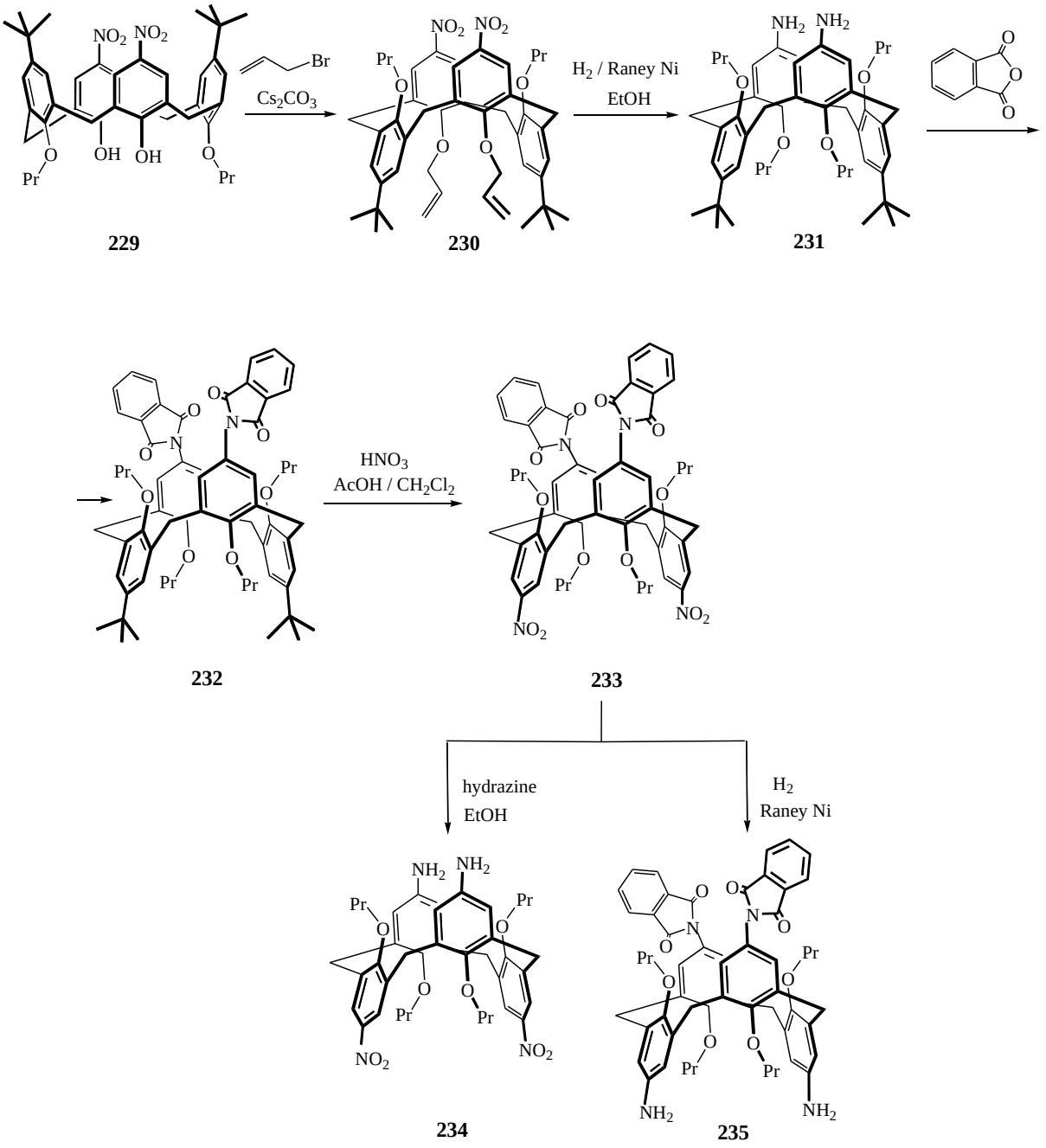

Scheme 62

Investigation of the partial protection of **236** by Boc has shown that the reaction with two Boc anhydride equivalents leads to mono-and diprotected calixarenes **237** and **238**, while the use of three Boc anhydride equivalents affords tri-and tetraprotected **239** and **240**, respectively.

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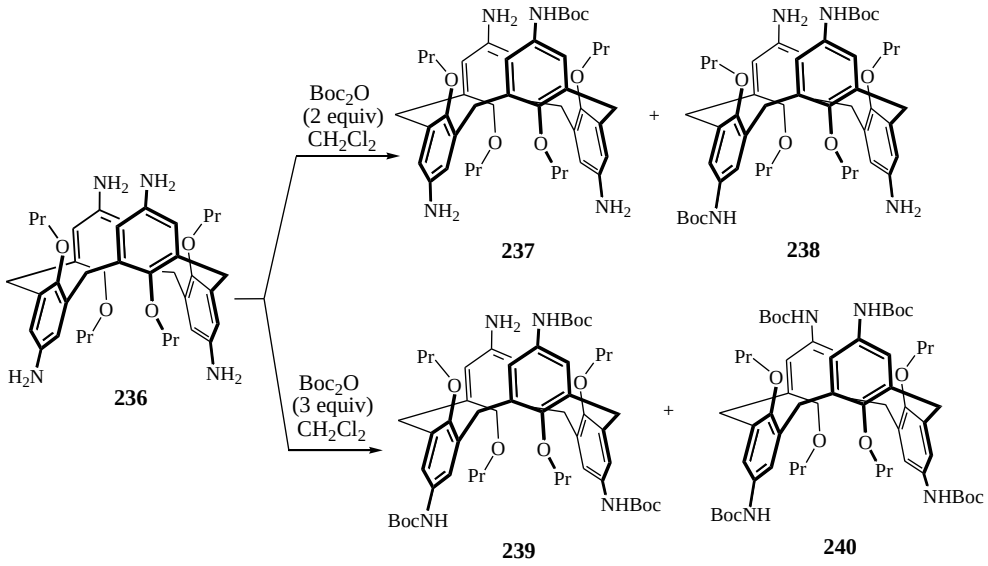
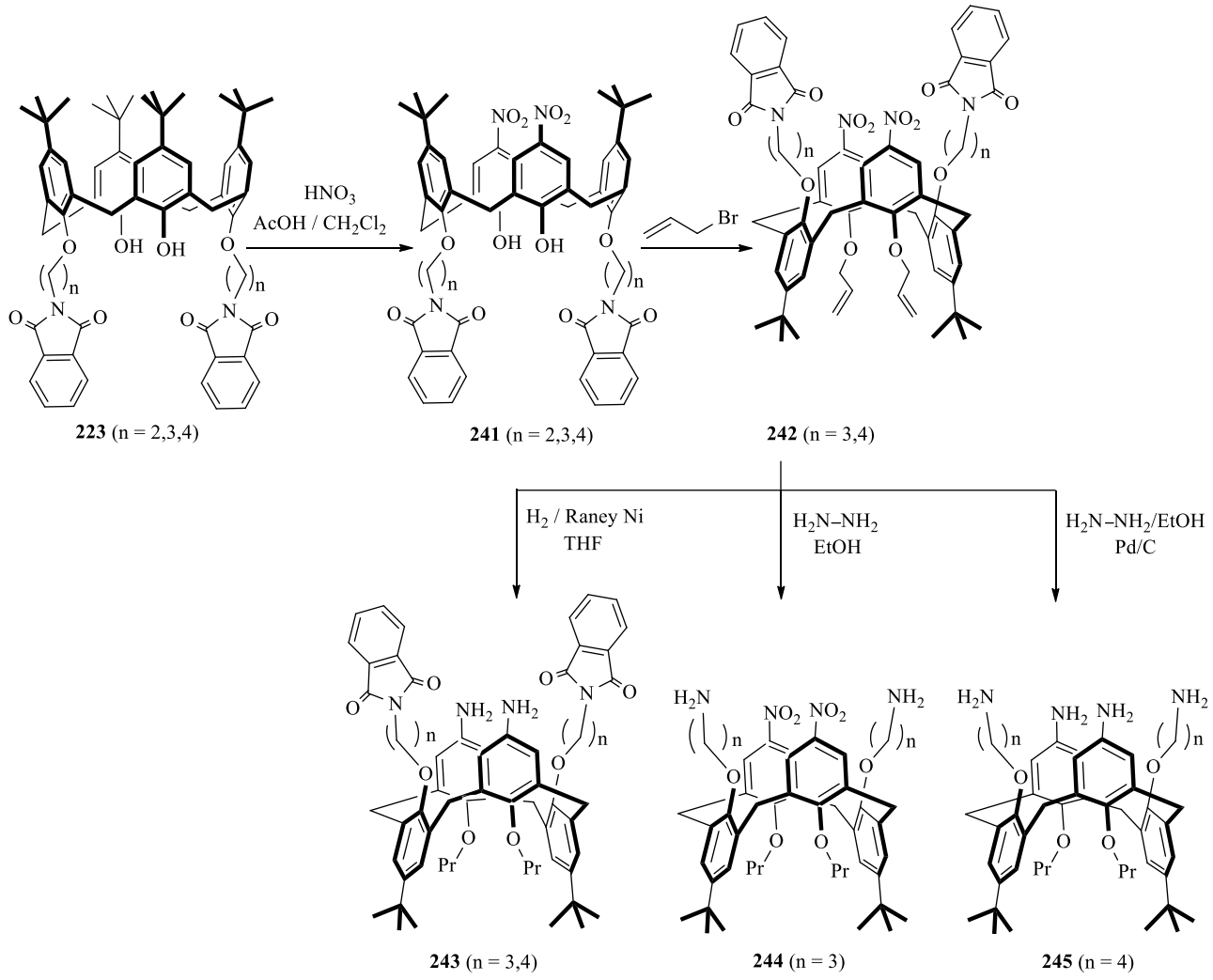


Scheme 63



Scheme 64

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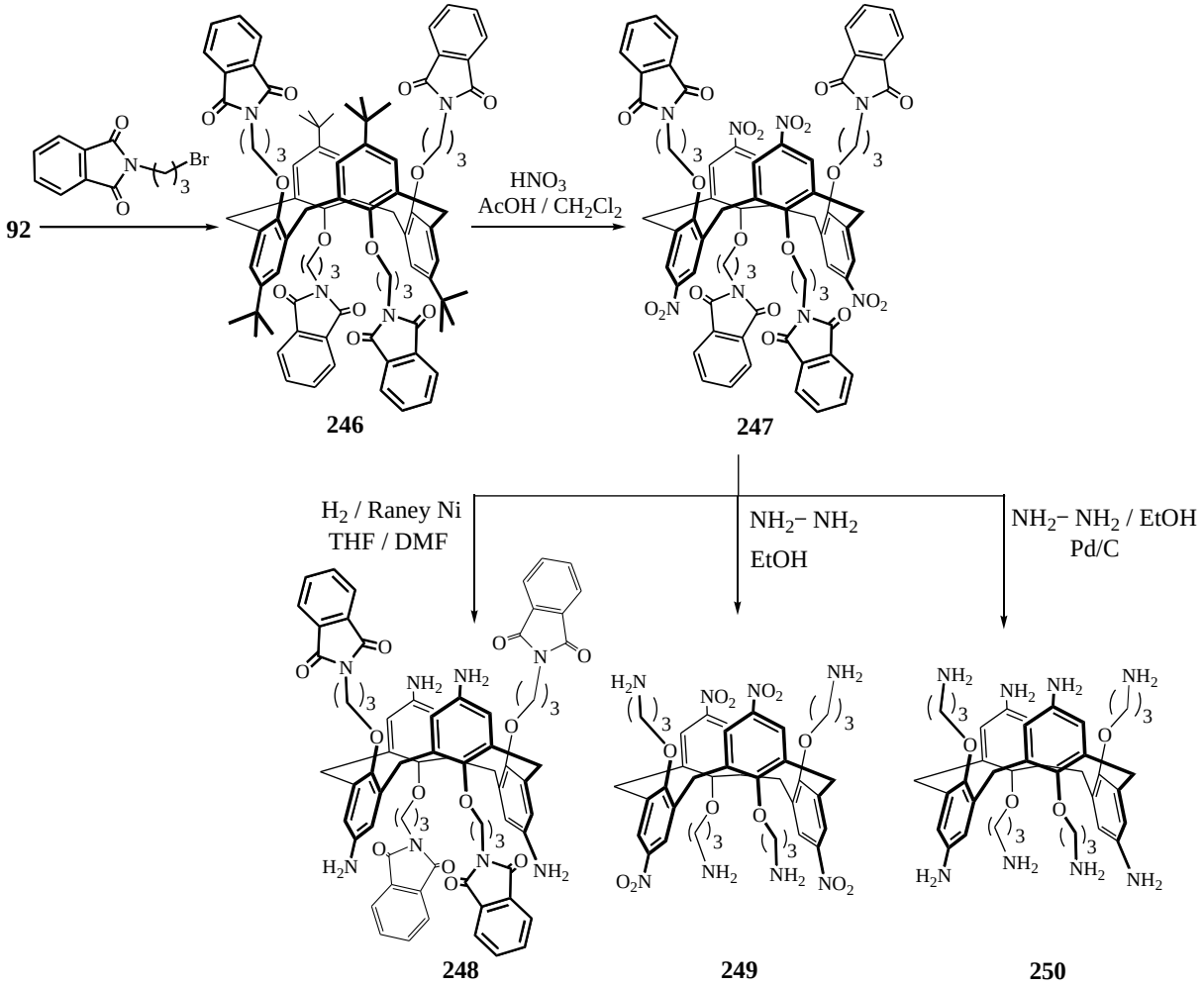
Calixarene **223** was *ipso*-nitrated to give **241** which, with allyl bromide yields **242**, which in turn, is catalytically reduced to **243**. Compound **242** treated with hydrazine in EtOH affords **244** in which the nitro groups are retained, however when this reaction proceeds in the presence of Pd/C catalyst it leads to tetraaminocalixarene **245**.

In order to obtain octaaminocalixarenes, the following reactions were performed. Calixarene **92** was treated with *N*-bromopropylphthalimide to give **246** which upon *ipso*-nitration yields **247**. The catalytic reduction of the nitro groups of **247** affords **248**, while reaction of **247** with hydrazine in EtOH results in the cleavage of the phthalimido groups affording **249**. Reaction of **247** with hydrazine in EtOH in the presence of Pd/C causes simultaneous cleavage of the phthalimido groups and reduction of the nitro groups leading to the octaaminocalixarene **250**. The presence of amino groups in calixarenes is of a great importance for their further reactions.[143]



Scheme 65

Due to their redox properties, porphyrins are important components in crucial biological electron-transport systems such as respiration and photosynthesis. Porphyrins have high electronic excitation energy, allowing light/electricity conversion and are thus promising for their use in solar

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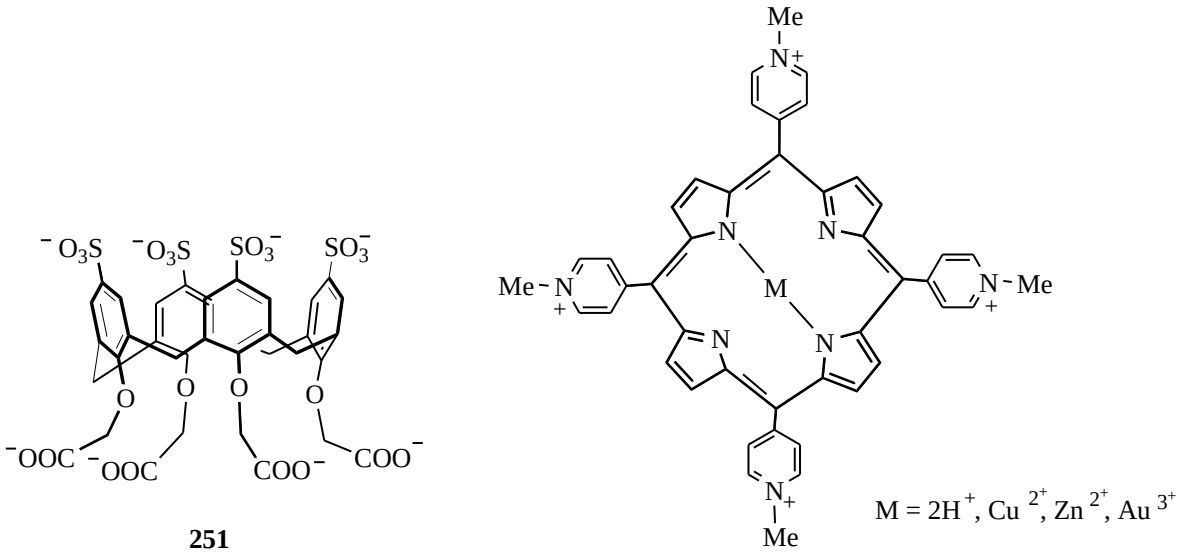
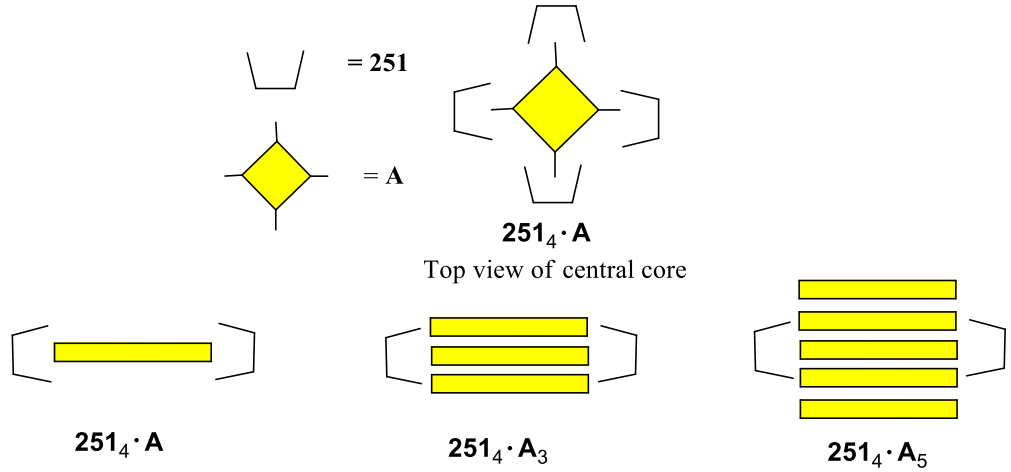
cells.[144-147] It has been reported that anionic calixarene **251** may form noncovalent assemblies with free base or metallated (M = Cu^{2+}, Zn^{2+}, Au^{3+}) cationic porphyrins **A**.[148]



251 **A**

Scheme 66

The titration of **251** with aliquots of porphyrins **A** initially forms the central core, *i.e.* **251**$_4$•**A** serving as a template for complexing further porphyrin units. The subsequent addition of two equivalents of porphyrin **A** leads to formation of the assembly **251**$_4$•**A**$_3$ in which the added **A** molecules are situated above and below the central core plane (*i.e.* before and behind the top view plane), the next two **A** molecules afford **251**$_4$•**A**$_5$ assembly, and addition of further two **A** molecules leads to **251**$_4$•**A**$_7$ assembly.



Side view of central core **251**$_4$· **A** along with **251**$_4$ · **A**$_3$ and **251**$_4$ · **A**$_5$ assemblies (two calixarene molecules of the central core, which are situated before and behind the figure plane are omitted for clarity)

Scheme 67

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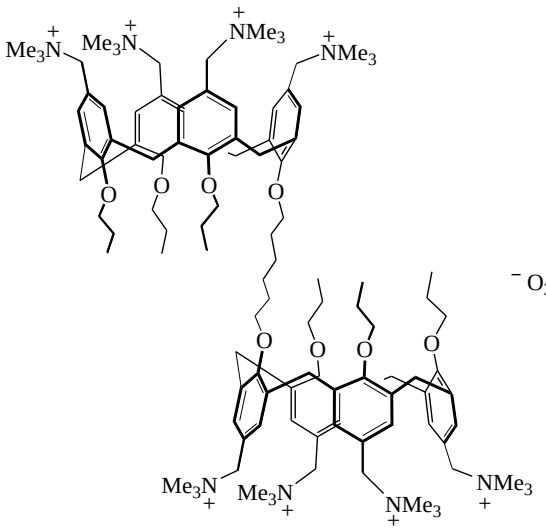
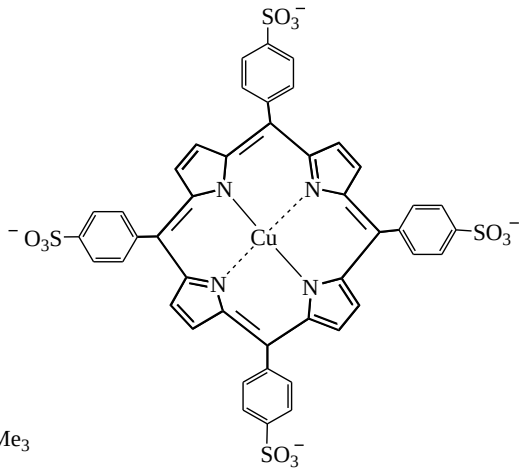
Porphyrins used may be different and the core porphyrin may be metallated or not; the sequence and stoichiometry of formed assemblies depend on the order of addition and number of used porphyrin equivalents. The above assemblies with desired porphyrin sequences are promising for construction of molecular devices.

As a continuation of the above investigations,[148] the noncovalent assemblies of octacationic bis-calixarene **252** with tetraanionic copper porphyrin **B** have been synthesized,[149] the templating agent **252** is water soluble and has cavities oriented in a divergent fashion.

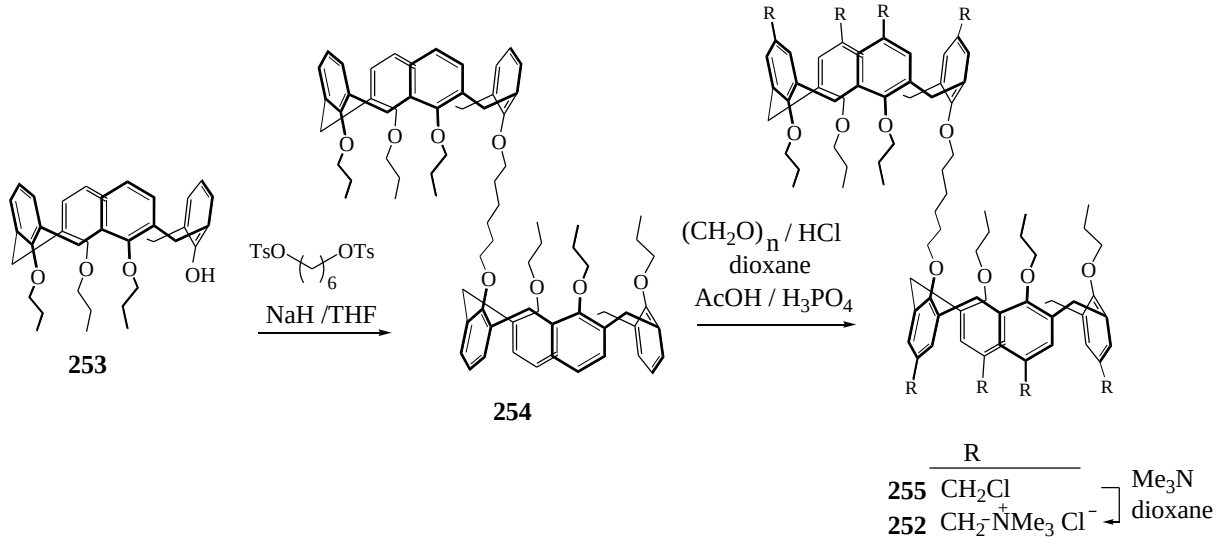


252



B

Scheme 68



Scheme 69

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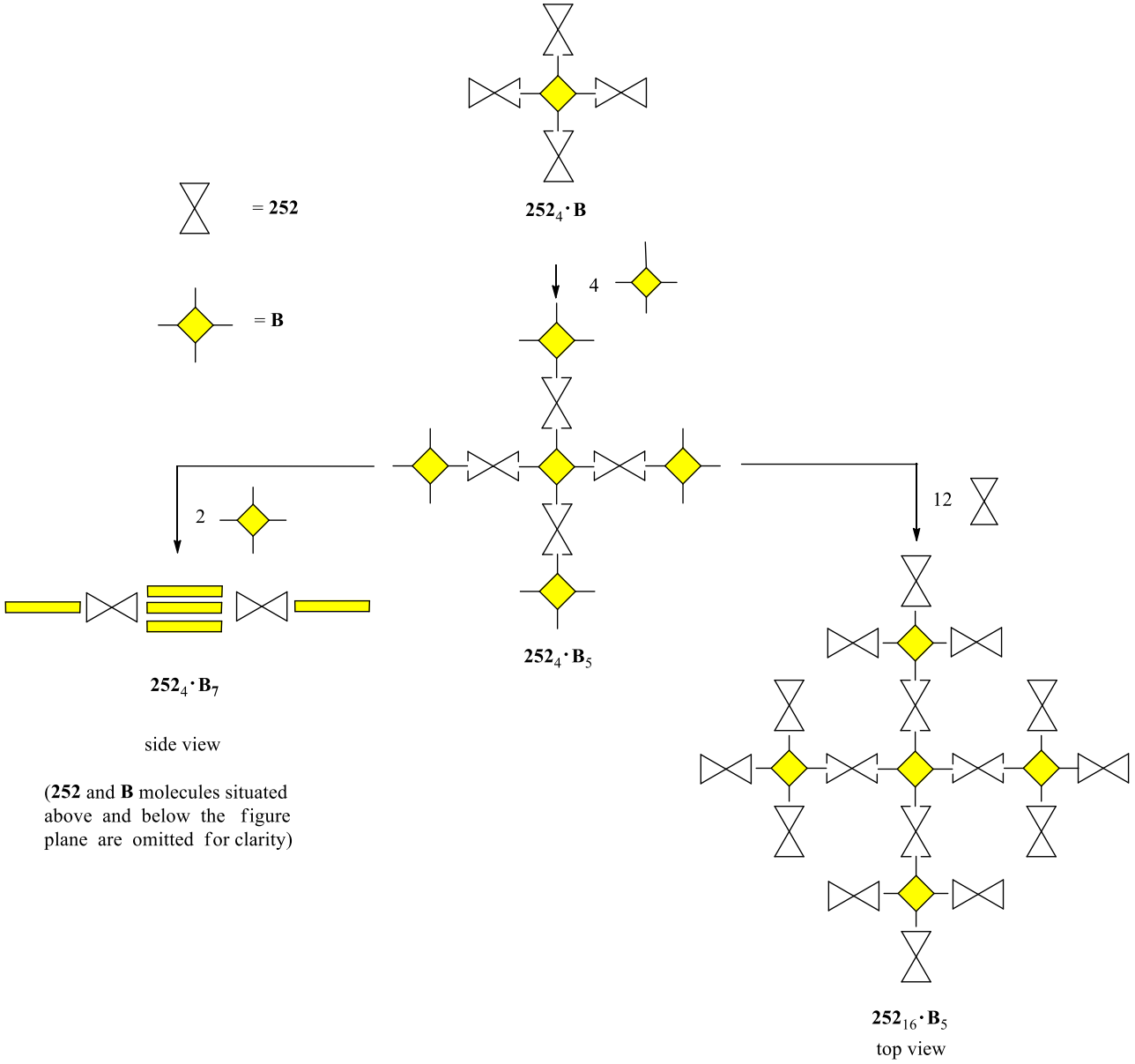
The synthesis of **252** begins by the treatment of calixarene **253** with 1,6-hexanediyl ditosylate affording **254** which reacts with paraformaldehyde and HCl in dioxane to give **255**. The amination of **255** with Me_3N yields bis-calixarene **252**.

During the UV/Vis titration, the aqueous solution of **252** was treated stepwise with **B** aliquots. Initially the central core $\mathbf{252}_4$•**B** is formed, which upon addition of four **B** equivalents affords the $\mathbf{252}_4$•$\mathbf{B}_5$ assembly. The subsequent treatment of $\mathbf{252}_4$•$\mathbf{B}_5$ with two **B** equivalents yields the 3D $\mathbf{252}_4$•$\mathbf{B}_7$ assembly, (*i.e.* $\mathbf{252}_4$•$\mathbf{B}_5$ in which two added **B** equivalents are situated below and above the central core), whereas the treatment of $\mathbf{252}_4$•$\mathbf{B}_5$ with twelve **252** equivalents leads to the 2D assembly $\mathbf{252}_{16}$•$\mathbf{B}_5$. It is noteworthy that in experiments the different porphyrins may be used.



Scheme 70

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5. Conclusion

The rapid development of research area of calixarenes observed today, results in a large amount of reports. One may believe that examples shown in the present review, albeit only selected, could provide some information connected with functionalization of these compounds. It is noteworthy that the properties of obtained functionalized calixarenes strongly depend on their structure.

Many works deal with calixarene complexes,[150-153] among them complexes with metal ions,[152,153] are of a great importance so for recovery as well as for removal of toxic metals from industrial sewages. Having in view the ecological safety one should also point out studies concerning the nuclear waste management.[153]

The works aiming to use calixarenes for construction of systems adsorbing gases such as hydrogen,[154] or methane,[155] are of interest in the field of energetics, and the development of these investigations is expected. A growing attention is paid today to a wide range of sensors,[156,157] as well as to removal of undesired compounds from industrial waste,[158-160] this research area being strongly connected with the environment protection.

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