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Synthesis, Conformational Analysis and Extraction Studies of *p*-isopropylcalix[*n*]arene Derivatives ($n = 4$, 6, 8). A New Family of Molecular Receptors

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Ethers, esters and ketones, derivatives of *p*-isopropylcalix[*n*]arenes ($n = 4$, 6, 8), have been prepared; 33 new molecular receptors have been isolated and fully characterized. ^{1}H NMR and ^{13}C NMR measurements reveal that tetraester and tetraketone derivatives are in cone conformation at room temperature when hexa and octa derivatives look like flexible flattened cones. Extraction studies with metal picrates from aqueous solution into dichloromethane were used to assess the ionophoric activity of the *p*-isopropylcalix[*n*]arene derivatives. The better E% are obtained with tetrameric derivatives in cone conformation, fully functionalized on the phenolic oxygens by ester or ketonic groups. The tetraamide derivative is the most efficient binder; the E% values are around 100 for Li, Na, K, Rb, Cs, Ca and Ba.

Keywords: Calixarenes; Functionalization; Conformation; Complexation

INTRODUCTION

Calixarenes are cyclic oligomers produced by condensation of *p*-substituted phenols with formaldehyde [1]. Calixarenes are cavity-shaped cyclic molecules made up of phenol units linked *via* alkylidene groups. The "lower rim" of the calixarenes is already functionalized with hydroxyl groups which provide excellent sites for the introduction of other moieties. The "upper rim" bears alkyl groups, like *tert*-butyl, which has been largely used over the last few years [2–5].

Probably due to the fact that the parent *p*-isopropylcalix[*n*]arenes ($n = 4$, 6, 8) were obtained with a low yield, the *p*-isopropylcalixarene series has been to a considerably less extent than the *p-tert*-butylcalixarene series. In 1987, Gutsche [6] indicated procedures to obtain *p*-isopropylcalix[*n*]arenes with ratios of 10% for $n = 4$ and 26% for $n = 6$ [7]. In a work [8] carried out in 1989, we improved the yield to 18% for $n = 4$, 54% for $n = 6$ and 32% for $n = 8$. Very recently Meziani [9] has optimized the synthesis of *p*-isopropylcalix[4]arene by the method of

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experimental plan, and the ratio rises above 40%. For the *p*-isopropylcalix[6] and [8]arenes the yields reach 62 and 42%.

The objective of the work reported here was to use the *p*-isopropylcalix[*n*]arenes ($n = 4, 6, 8$) as molecular platforms on which to assemble groups of covalently bound ligands capable of acting as ion and molecule receptors. By attaching various groups to the parent *p*-isopropylcalix[*n*]arenes through the phenolic oxygen atom, 33 new calixarenes have been synthesized; some of them are partially functionalized. Their conformations were ^{1}H NMR and ^{13}C NMR studied in solution. Extraction studies with alkali metal picrates from aqueous solution into dichloromethane were used to assess the ionophoric activity. The results are discussed according to the nature of the functional group, the steric hindrance of the functional group, the size of the parent calixarenes and the conformation of the calixarene derivatives.

RESULTS AND DISCUSSION

Synthesis

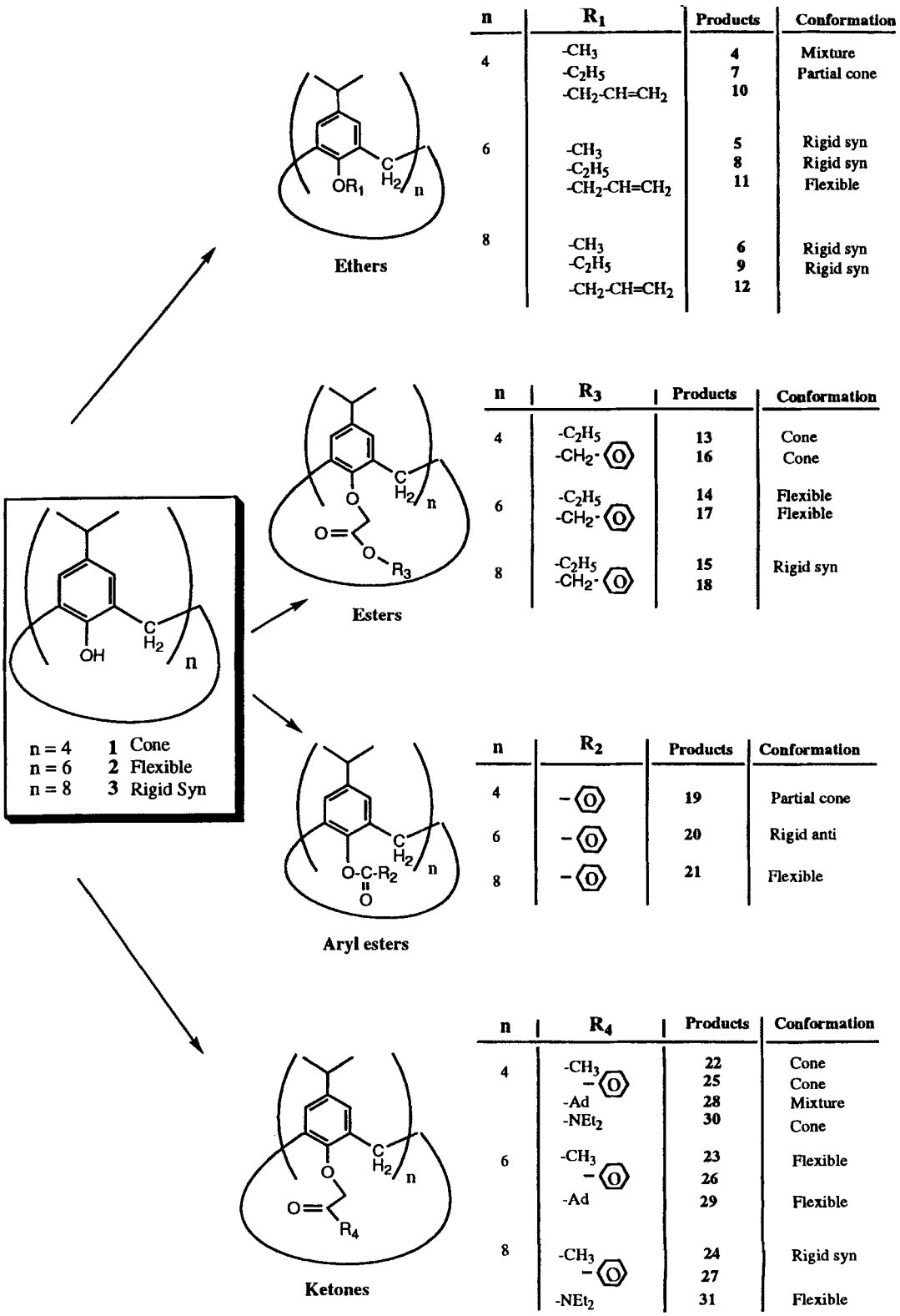
By exhaustive functionalization of the parent *p*-isopropylcalix[*n*]arene (**1**) (**2**) (**3**) new derivatives were synthesized and characterized. The functionalization on the calixarene lower rim consists in doing a hydrogen phenolic substitution by alkylhalides with enough strong base to deprotonate all the phenol hydroxyles. Functionalization of calix[6]arene and calix[8]arene usually is more complicated than that of calix[4]arene due to several factors, including bad solubility and the variety of conformational isomers [10, 11]. As shown in Figure 1, and given in the experimental part, functional groups are introduced into the lower rim by means of Williamson-type OH – modifications [12–23]. Literature procedures were generally used to introduce on the *p*-isopropylcalix[4]arene lower rim ether, ester, acyl, ketone and amide groups. For exhaustive functionalization of the *p*-isopropylcalix[6]arene and *p*-isopropylcalix[8]arene lower rims, the literature procedures were sometimes modified and optimized.

Treatment of *p*-isopropylcalix[*n*]arenes (**1**) (**2**) (**3**) with methyliodide and ethyliodide in tetrahydrofuran in the presence of sodium hybride produced methyl ether (**4**) (**5**) (**6**) and ethyl ether (**7**) (**8**) (**9**) derivatives. The allyl ether derivatives (**10**) (**11**) (**12**) were prepared by using the allylbromide as alkylating agent. Only the hexaallyl ether derivative (**11**) has been completely characterized; the tetra allyl ether (**10**) appeared to be very insoluble and the octa allyl ether (**12**) was obtained as the major product in a non-isolable mixture with partially functionalized derivatives.

Esterification was carried out according to the method described by McKervey *et al.* [18]. Treatment of parent calixarenes (**1**) (**2**) (**3**) with ethyl bromoacetate in dry acetone under reflux furnished the crystalline derivatives (**13**) (**14**) (**15**); the octa acetate derivative (**15**) was formed with a large excess of alkylating agent. The benzyl acetate derivatives (**16**) (**17**) (**18**) were obtained in good yields, by transesterification of the ethyl acetate derivatives (**13**) (**14**) (**15**) in benzylic alcohol in the presence of catalytic quantities of *p*-toluenesulfonic acid. The octabenzyl acetate (**18**) obtained was not pure.

Aroylation was carried out by a new procedure including the dimethylaminopyridine, DMAP, as catalyst. Treatment of the calixarenes (**1**) (**2**) (**3**) with benzoïc anhydride in the presence of triethylamine afforded the three benzoyl derivatives (**19**) (**20**) (**21**) with a good yield.

The introduction of ketonyl carbonyl groups was brought about by exhaustive alkylation with selected electrophiles. The methyl ketone derivatives (**22**) (**23**) (**24**) were prepared by treating the parent *p*-isopropylcalix[*n*]arenes with iodoacetone, obtained *in situ* from chloroacetone with sodium iodide and potassium carbonate in dry acetone. The phenyl ketone derivatives (**25**) (**26**) (**27**) were prepared with



n	R_1	Products	Conformation
4	$-CH_3$	4	Mixture
	$-C_2H_5$	7	Partial cone
	$-CH_2-CH=CH_2$	10	
6	$-CH_3$	5	Rigid syn
	$-C_2H_5$	8	Rigid syn
	$-CH_2-CH=CH_2$	11	Flexible
8	$-CH_3$	6	Rigid syn
	$-C_2H_5$	9	Rigid syn
	$-CH_2-CH=CH_2$	12	

n	R_3	Products	Conformation
4	$-C_2H_5$	13	Cone
	$-CH_2-$	16	Cone
6	$-C_2H_5$	14	Flexible
	$-CH_2-$	17	Flexible
8	$-C_2H_5$	15	Rigid syn
	$-CH_2-$	18	

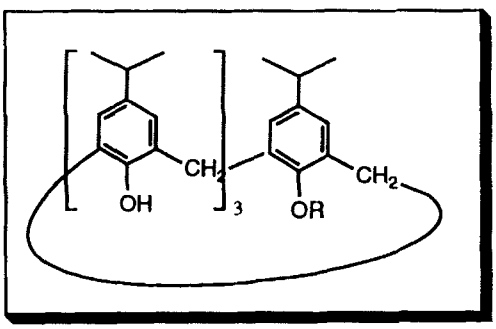
n	R_2	Products	Conformation
4	–	19	Partial cone
6	–	20	Rigid anti
8	–	21	Flexible

n	R_4	Products	Conformation
4	$-CH_3$	22	Cone
	–	25	Cone
	-Ad	28	Mixture
	$-NEt_2$	30	Cone
6	$-CH_3$	23	Flexible
	–	26	
	-Ad	29	Flexible
8	$-CH_3$	24	Rigid syn
	–	27	
	$-NEt_2$	31	Flexible

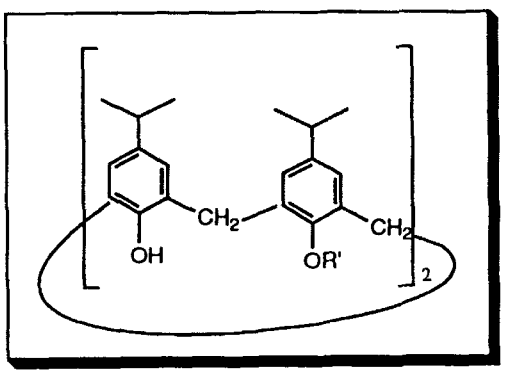
FIGURE 1 Exhaustive functionalization of *p*-isopropylcalixarenes.

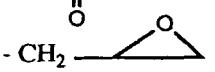
phenacyl chloride according to the same procedure. The adamantyl ketone derivatives (**28**) (**29**) were synthesized by using the alkylbromide, 1-adamantyl bromoethyl ketone, in slight excess.

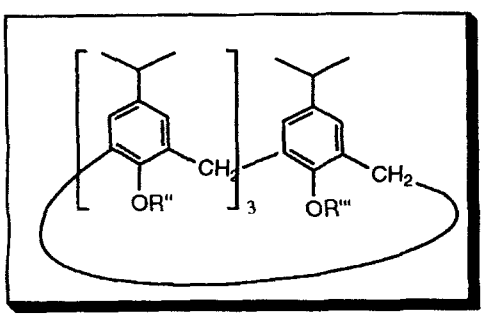
Amide derivatives were synthesized according to a modified procedure; the *p*-isopropylcalixarene dissolved in dry acetone was treated with α-chloro-*N*, *N*-diethylacetamide in the presence of sodium iodide and potassium carbonate. The tetra amide ketone (**30**) was obtained in a good yield. After extensive purification, the octa amide ketone (**31**) crystallizes.



R	Product	Conformation
$-CH_3$	32	Cone
$-CH_2-CH=CH_2$	33	Cone
$-CH_2-C(=O)-O-C_2H_5$	34	Cone



R'	Product	Conformation
$-CH_2-CH=CH_2$	35	Flattened cone
$-CH_2-C(=O)-O-C_2H_5$	36	Flattened cone
	37	Flattened cone



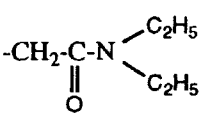
R"	R'''	Product	Conformation
$-CH_2-C(=O)-CH_3$	$-CH_2-C(=O)-OC_2H_5$	38	Flattened cone
	CH_3	39	

FIGURE 2 *p*-isopropylcalix[4]arenes with mixed functional groups.

Selective functionalization of the *p*-isopropylcalixarenes has been carried out with the cyclic tetramer (**1**) (Fig. 2). In this work, literature procedures [24–33] were modified and adjusted to the *p*-isopropylcalixarenes. A kinetic control of the reactions allowed the monoalkylated derivatives to be produced without dialkylated derivatives.

Monoalkylated derivatives were obtained in the presence of potassium carbonate (0.5 equiv.) by direct methods. Treatment of (**1**) with methyliodide in dry acetonitrile under reflux furnished the mono methyl ether (**32**) in a good yield (63%), the mono allyl ether (**33**) was produced at room temperature in acetone with a 70% yield, and the mono ethyl acetate (**34**) was easily separated from unsubstituted *p*-isopropylcalix[4]arene by column chromatography and obtained pure in a 60% ratio.

Dialkylated derivatives (**35**), (**36**), (**37**) have been synthesized. As shown by the NMR studies, the distal derivatives were formed. The diallyl ether (**35**) was obtained in acetone reflux, the diethyl acetate (**35**) was produced in dry acetone in the presence of potassium carbonate (2 equiv.) and the diepoxide (**37**) was synthesized (85% yield) with a large excess of epichlorhydrine in the presence of tetrabutyl ammonium bromide.

We have extended our study of chemically modified *p*-isopropylcalix[4]arene to include derivatives with more than one type of functionality around the calix and we have prepared tetramers bearing one ethyl acetate and three methyl ketone groups (**38**) and one methyl ether and three diethylacetamide groups (**39**).

Conformation

Basically, *p*-alkylphenol derived calix[4]arenes can exist in four different conformations: cone, partial cone, 1,2 alternate and 1,3 alternate. Calix[6]arenes can assume eight "up-down" conformations and because of the increased flexibility of this system additional conformations are possible in which one or more aromatic rings assume a position approximatively in the average plane of the molecule. For calix[8]arenes, there are sixteen "up-down" forms as well as many others in which one or more aromatic groups assume the "out" alignment.

All of the calixarenes derivatives, regardless of ring size, are conformationally flexible in solution at room temperature. The rate at which they undergo conformational interconversion is most easily studied by NMR spectroscopy. The most useful methods to distinguish the four main conformations of calixarenes are those based on ^{1}H NMR methylene and aromatic signals and their multiplicities [34–37]. For calix[4]arene with the same substituent at each *para* position, the AB system is usually observed below the coalescence temperature for the methylene protons in the cone conformation. Both singlet and AB system should be present in partial cone or in 1,2-alternate conformation. The number and multiplicity of aromatic signals permit them to be differentiated. The conformation of calix[4]-arene can also be deduced from the ^{13}C NMR chemical shifts of the methylene groups. Jaime *et al.* [38] have shown that the methylene signals appear around δ 31 ppm when the phenol rings beside each methylene are in syn orientation (*i.e.*, in cone conformation) whereas they appear around δ 37 ppm when both phenol rings are in anti orientation (*i.e.*, 1,3-alternate conformation). Two differentiated signals of almost equal intensities are observed at δ 31 and 37 ppm when the calixarenes are in the partial cone or in 1,2-alternate conformation (two syn and two anti orientations). In this work ^{1}H and ^{13}C NMR were used to probe the conformation of all the *p*-isopropylcalix[*n*]arenes derivatives in solution.

At 25°C, the ^{1}H NMR spectrum shows that the tetra methylether (**4**) is conformationally flexible. At −12°C and −20°C, (**4**) appears to be a mixture of conformers where the partial cone predominates. In fact, in the upfield $C(CH_3)_2$ give three doublets and OCH_3 three singlets (Fig. 3a). This pattern is only consistent with a

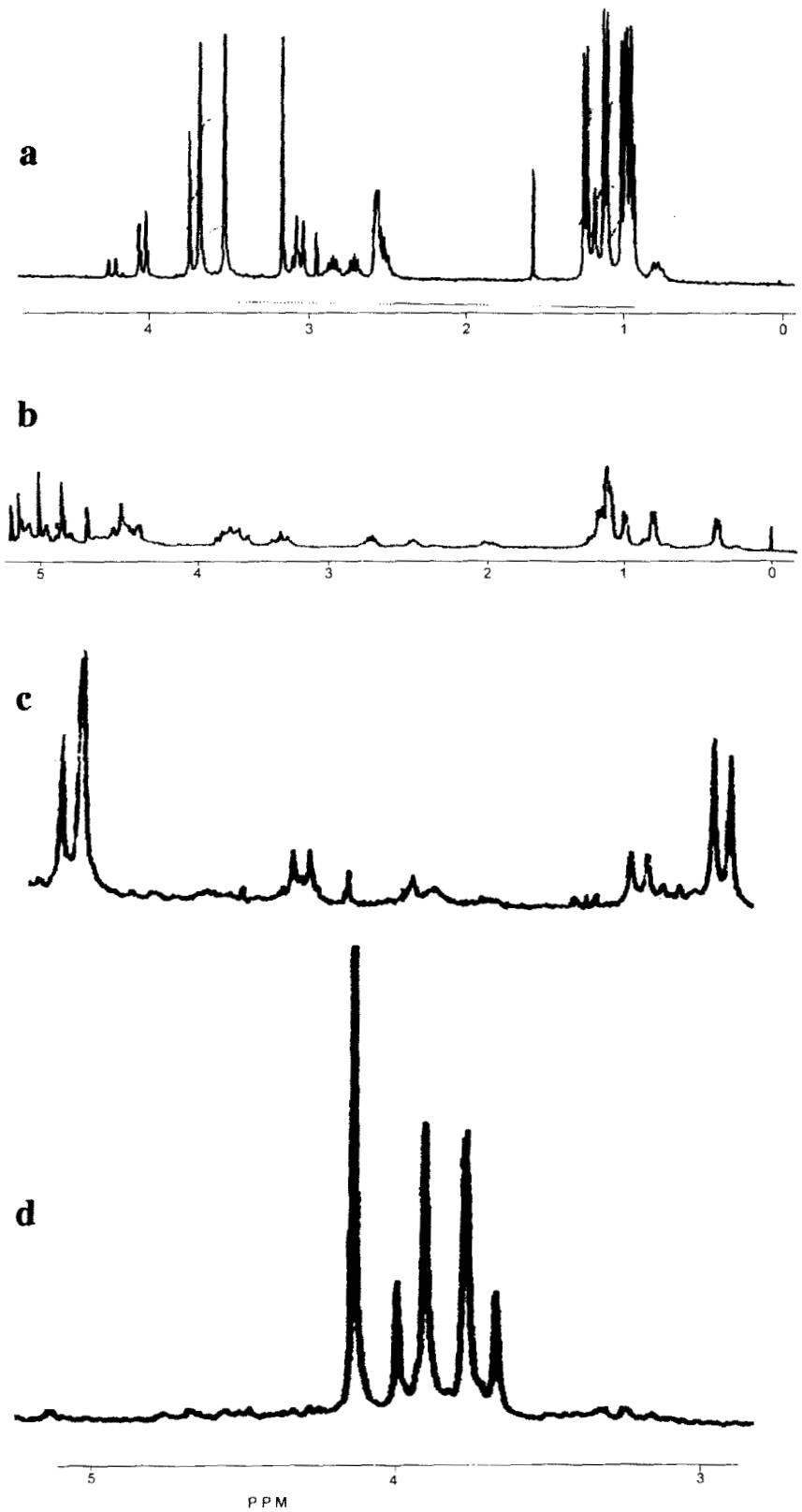


FIGURE 3 Partial ^{1}H NMR spectra in $CDCl_3$ a:(4) at $-20°C$, b:(17) at $-60°C$, c: (22) at $-60°C$ recrystallized from methanol, d: (22) at 25°C, recrystallized from toluene.

partial cone conformation. However, there exist additional peaks, which were assigned [14] to the three other conformers in the case of *p-tert*-butylcalix[4]arene. ^{13}C NMR spectrum of (**4**) shows three singlets at δ 29.79, 30.97 and 37.13 ppm assigned to methylene signals, therefore (**4**) in $CDCl_3$ at 25°C appears to be a mixture of conformers. Hexa (**5**) and octa (**6**) methyl ether give at room temperature ^1H NMR spectra containing thin and well-resolved resonances in good agreement with rigid conformations. In the ^{13}C NMR spectrum of (**5**), the methylene signal appears at δ 30.46 ppm, for (**6**) it appears at δ 30.15 ppm. Thus, the phenolic units of the hexa (**5**) and octa (**6**) derivatives are in syn orientation.

For (**7**) in downfield, the aryl group hydrogens are resolved on four singlets and in upfield, the $C(CH_3)_2$ hydrogens on three doublets. The ^{13}C NMR spectrum of (**7**) is also in substantial agreement with a partial cone conformation: it shows two singlets at δ 30.45 and 37.44 ppm assigned to methylene carbon atoms. Clearly, the tetraethyl (**7**) is conformationally less flexible than the tetramethyl (**4**).

In ^1H NMR spectra of (**8**) and (**9**), the methylene and the aryl hydrogens are resolved on thin singlets with prevailing rigid conformations for the two compounds. In the ^{13}C NMR spectrum of (**8**), the methylene signal appears at δ 30.76 and in the (**9**) spectrum it appears at δ 30.03 ppm; this pattern shows that the phenolic units of the two compounds are in syn orientation. (**11**) gives at room temperature ^1H NMR spectrum containing large signals, which shows that (**11**) is conformationally flexible.

^1H NMR spectrum of tetraester (**13**) contains well-resolved resonances in agreement with a cone conformation; it shows a singlet in the aromatic field arising from the phenolic units and a pair of doublets δ 3.15 and 4.85 ppm arising from the AB system of the methylene hydrogens. The ^{13}C NMR spectrum and DEPT experiment reveal a single resonance δ 31.7 ppm for the methylene carbons in close agreement with a cone conformation. In the ^1H NMR spectrum of (**14**), the methylene hydrogens give a large singlet no rigid pattern is prevailing. The ^{13}C NMR spectrum shows a single resonance δ 30.97 ppm for the methylene carbons, in agreement with a syn orientation of the phenolic units. The ^1H NMR spectrum of (**15**) contains well-resolved resonances, indicating rigid conformation. The ^{13}C NMR spectrum shows a single resonance δ 30.23 ppm for the methylene carbons, in accordance with a syn orientation of the phenolic units.

The benzyl acetate (**16**) adopts a cone conformation whereas (**17**) is conformationally flexible at 25°C; it exists as a mixture of interconvertible conformers at −60°C (Fig. 3b).

The benzoyl ester (**19**) shows two pairs of doublets δ 4.06; 3.95; 3.77; 3.45 ppm for the methylene protons, consistent with a partial cone conformation. The hexa benzoyl ester (**20**) shows in the methylene field a pair of doublets and a singlet in agreement with a "up-down" organization similar to a partial cone conformation. The octa benzoyl ester (**21**) is conformationally flexible.

In the ketones series, ^1H NMR data established that the tetramer derivatives (**22**), (**25**) and (**30**) possess the cone conformation and (**28**) is conformationally flexible. The hexa derivatives like (**23**) and (**29**) are conformationally flexible whereas the octa derivatives (**24**) adopt a rigid conformation. However, the conformation of the calixarene derivatives can be slightly changed by the synthesis procedures (Figs. 3c and d). When (**22**) is obtained by recrystallization from toluene, it exists essentially as a cone conformer; we observe a perturbation of the methylene protons indicating that toluene is inside the lipophilic cavity of the calixarene. Whereas, when (**22**) is obtained from methanol it looks like a mixture of conformers; at −60°C ^1H NMR spectrum shows two different cone conformers resulting of a conformational inversion probably by a "lower rim through the annulus" pathway.

Selective mono functionalization in compounds (**32**) (**33**) (**34**) induces the non-equivalence of the four aromatic rings. The presence of

methoxy (**32**), propenoxy (**33**) and ethylcarbonyl (**34**) groups induces a specific pattern of the signals in the aromatic field (two singlets and two doublets) and the methylene groups show two different signals: a doublet whose intensity corresponds to two hydrogens and a doublet with an intensity of four hydrogens. The NMR data of (**32**) (**33**) (**34**) are fully in accord with this pattern and indicate a cone conformation for the monoalkylated *p*-isopropylcalix[*n*]arene.

The introduction of two alkyl groups on the lower rim of the *p*-isopropylcalix[4]arene has a significant influence on the conformation of the parent-calixarene. The ^{1}H NMR spectra of (**35**), (**36**) and (**37**) exhibit two doublets for $(\text{-}CH_3)_2$ groups on very different shift positions (δ 1 ppm and δ 1,3 ppm), an abnormal OH upfield shift (δ 7,3 ppm) and a single AB system for the bridging methylene groups (He and Ha are equivalent). These results suggest a flattened cone conformation for the distal derivatives (**35**), (**36**) and (**37**).

The ^{1}H NMR spectra of polysubstituted derivative (**38**) contains well-resolved resonances showing a rigid conformation. It can be interpreted compared with the ^{1}H NMR spectra of tetraacetate (**13**) and tetraketone (**22**) derivatives. Two doublets and one triplet are observed for the bridging methylene groups; the triplet appears as the composition of two doublets, suggesting a flattened cone conformation for this compound.

Ionophoric Ability

The phase transfer data for *p*-isopropylcalixarene derivatives and metal picrates which are presented as E% (percent cation extracted) are given in Table I. These data were obtained by using dichloromethane solutions of the *p*-isopropylcalixarene derivative to extract metal picrate from neutral aqueous solution, the equilibrium concentration of picrate in the organic phase then being determined by UV spectrophotometry [9, 39–42]. The %E values reveal a wide range of phase transfer ability within the *p*-isopropylcalixarene derivatives and the most significant indications are as follow.

(a) Parent *p*-isopropylcalixarenes (**1**), (**2**), (**3**) and ether derivatives (**4**) to (**12**) show very low levels of phase transfer. (b) The ketone derivatives are more efficient than the ester derivatives for phase transfer. (c) The tetraamide derivative (**30**) is the most efficient binder; the %E values are around 100 for all alkali and alkaline earth cations studied. (d) The tetraadamantyl (**28**), phenyl (**25**) and methyl (**22**) ketones show a similar profile. They have a high ability of complexing Na^+, Ba^{2+}, K^+ and Li^+ and they are not efficient for Ca^{2+}, Rb^+ and Cs^+. (e) In the ketone series the adamantyl (**28**) is better than the phenyl (**25**) and the methyl (**22**) for extraction of alkali and alkaline earth cations. (f) The tetraethyl ester derivative (**13**) displays a selectivity peak for Na^+ and low levels of phase transfer for other cations. (g) Ethyl ester derivatives display different profiles. The tetramer (**13**) presents a peak of selectivity for Na^+, the hexamer (**14**) for Cs^+ and the octamer (**15**) for Ba^{2+}. (h) Incomplete functionalization of parent isopropylcalixarene, as in (**36**) diminished the extraction ability. (i) The benzoyl derivatives, (**19**), (**20**), (**21**), exhibit low extraction ability; the tetrameric derivative (**19**) is in partial cone conformation, (**20**) is in similar partial cone conformation and (**21**) is flexible. (j) In general, the tetrameric derivatives show the broadest extraction ability, the octameric derivatives are generally the least efficient.

From these results it appears that the better E% (percent extraction cations) are obtained with tetrameric derivatives in cone conformation, functionalized on the phenolic oxygens by ester or ketonic groups. The tetraester and tetraketone derivatives in the cone conformation show a hydrophobic cavity created by the four phenolic rings; the oxygenated pendant chains define a hydrophilic cavity closed by the four phenoxy oxygen atoms and four ester or ketone carbonyl groups [43–47]. As shown in the X-ray

TABLE I Percent extraction of metal picrate into CH_2Cl_2 at 20°C

Cation product	Li	Ca	Na	Ba	K	Rb	Cs
Parent							
1	< 4	< 4	< 4	< 4	< 4	< 4	< 4
2	< 4	< 4	< 4	6	< 4	< 4	< 4
3	< 4	< 4	< 4	5	< 4	< 4	5
Ether							
4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
5	< 4	< 4	< 4	< 4	< 4	< 4	< 4
6	< 4	< 4	< 4	< 4	< 4	< 4	< 4
7	< 4	< 4	< 4	< 4	< 4	< 4	< 4
8	< 4	< 4	< 4	< 4	< 4	< 4	< 4
9	< 4	< 4	< 4	< 4	< 4	< 4	< 4
10	< 4	< 4	< 4	< 4	< 4	< 4	< 4
11	< 4	< 4	< 4	< 4	< 4	< 4	< 4
Ester							
13	17	17	54	24	16	10	13
14	9	4	11	7	18	11	47
15	4	7	5	22	5	< 4	< 4
17	4	4	7	13	13	9	–
19	< 4	5	4	< 4	< 4	< 4	< 4
20	< 4	4	< 4	5	< 4	< 4	< 4
21	4	7	6	5	5	< 4	< 4
Ketone							
22	58	33	83	56	59	18	22
23	< 4	7	< 4	4	< 4	< 4	4
25	69	17	90	70	68	6	9
26	7	< 4	11	13	8	10	23
28	72	38	90	84	81	18	18
29	6	4	41	39	48	6	14
30	98	100	98	97	98	98	98
Dialkylated							
35	< 4	< 4	< 4	< 4	< 4	< 4	< 4
36	6	7	14	5	6	5	7
37	< 4	< 4	< 4	< 4	< 4	< 4	< 4

structure of the tetraethyl ester (**13**) (Fig. 4), the cone conformation persists in the solid state, the ethyl ester chains fix the conformation with a high degree of primary preorganization, and the carbonyl groups are toward the interior of the cavity. In this arrangement the ligating groups of four phenoxy oxygen atoms and four ester carbonyl groups are mutually syn and present eight binding sites toward the guest cation. The cavity dimensions may allow the inclusion of appropriate cation [48]; clearly with the tetraethyl ester (**13**) the cavity dimensions are well adapted to accommodate the Na^+ cation. The same conclusion can be drawn with the tetraketone derivatives where the tetramethyl (**22**), phenyl (**25**) and adamantyl (**28**) present a high ability of complexing Na^+. The ability to complex the smaller Li^+ cation or the larger K^+ cation is probably due to a flexing movement of the oxygenated pendant chains which modifies the cavity dimensions. The preorganization of the hydrophilic cavity is also disturbed by the steric hindrance and the electronic properties of the alkyl moieties in the oxygenated

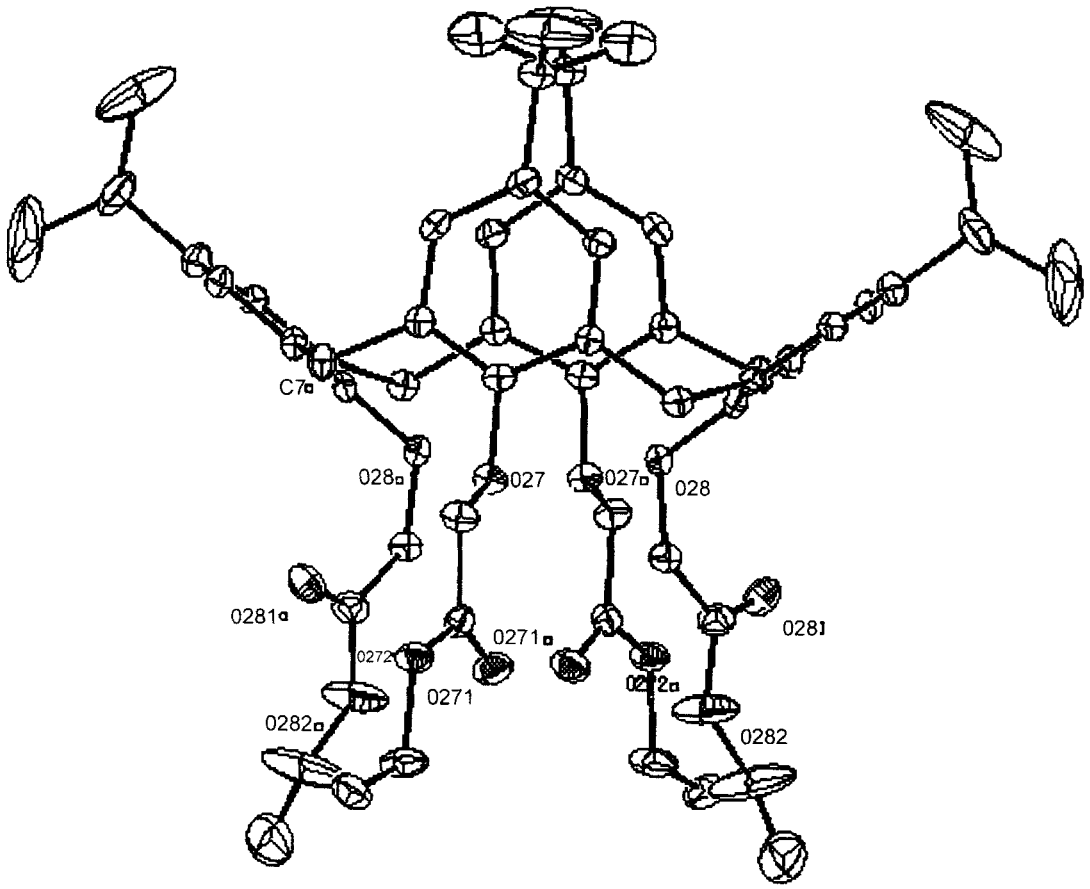


FIGURE 4 Structure of the tetraethyl ester **(13)** showing the hydrophilic cavity closed by the four phenoxy oxygen atoms and four ester carbonyl groups. Ellipsoids are drawn at 30% probability level.

pendant chains. The steric hindrance of R_4 modifies E% slightly; the methyl ketone (**22**) is less effective than the phenyl ketone (**25**) and less effective than the adamantyl ketone (**28**). On the other hand the donor group -N-$(Et)_2$ clearly enhances the extraction ability of the calixarene ketone (**30**) towards all the cations studied.

EXPERIMENTAL SECTION

General

Melting points (°C, uncorrected) were determined on an Electrothermal 9100 capillary apparatus. Elemental analyses were performed at SCA, CNRS, Solaize, France. Mass Spectra (MS): Electrospray (ES) or Fast-Atom-Bombardment (FAB) were recorded on a Platform Micromass apparatus at the SCA, CNRS, Solaize, France. ^{1}H NMR spectra were recorded on a Brucker AM 200 (200 MHz) for all the compounds except for **7**, **11**, **20**, **24**, **32**, **33**, **34** which were recorded on a Brucker AM 300 (300 Mhz); ^{13}C NMR spectra were obtained on a Brucker AC 200 (50.3 MHz) (TMS as internal standard, chemical shifts in ppm). Infra-Red was performed on a Mattson 5000 FT apparatus (ν in cm $^{-1}$) and UV Spectra were recorded on a Shimadzu UV 2401 PC apparatus. Macherey-Nagel TLC plates were used for chromatography analysis (SiO_2, Polygram SIL G/UV254, Ref.

805021). All commercially available products were used without further purification unless otherwise specified.

Picrate Extraction Measurements

Neutral metal picrates ($2.5\ 10^{-4}$ M) were prepared from picric acid ($2.5\ 10^{-4}$ M) and metal hydroxide titrisol solutions (10^{-1} M) according to a potentiometric method. Distilled, deionized water was used for aqueous solutions. Solutions ($2.5\ 10^{-4}$ M) of the isopropylcalixarenes were prepared in dichloromethane. Equal volumes (5 mL) of the two solutions were shaken vigorously for 1 min. This was repeated 4 times, and the solutions were left standing until phase separation was complete. The concentration of disappeared picrate ion in the aqueous phase was then determined spectrophotometrically. The percentage cation extracted (E%) was calculated as the ratio $100 \times (A_0 - A)/A_0$.

Preparation of *p*-isopropylcalix[*n*]arenes (1–3)

30 g of each parent calixarenes **1**, **2** and **3** were prepared according to the optimized procedures given Reference [9].

25,26,27,28-Tetrakis(methoxy)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (4)

0.5 g of (**1**) in THF (25 ml) and DMF (2.5 ml) was treated with NaH (0.5 g) and MeI (5 ml). The mixture was heated 1.50 h at 38°C. The excess of NaH was neutralized with EtOH, the solvent was evaporated, and the residue treated with 100 ml water. After extraction with $CHCl_3$, the organic solution was dried and concentrated to leave ether as white powder that was recrystallized to be purified from $CHCl_3$–MeOH. Mp = 133–134°C; ^{1}H NMR ($CDCl_3$): δ 0.8–1.5 (*m*, 24 H, -C(CH_3)$_2$), 2.5–3 (*m*, 4H, ArCH-), 3–3.4 (*m*, 4H, Ar-CH_2-Ar), 3.4–4 (*t*, 12H, -OCH_3); 4–4.4 (*m*, 4H, Ar-CH_2-Ar), 7.09–6.55 (*m*, 8H, ArH); ^{13}C NMR ($CDCl_3$): δ 24.13 (-C(CH_3)$_2$), 29.78–31.02 (Ar-CH_2-Ar), 33.24 (ArCH_{iso}), 60.31 (OCH_3), 126.4–126.9–128.1 (Cm), 133.8 (Co), 142.21 (Cp), 155.71 (Ci); IR ν max (KBr) 2960, 2942, 1468 cm^{-1}; FAB MS *m*/*z* 655.5 [**4** + Li]$^+$; Anal. Calcd. for $C_{44}H_{56}O_4$: C, 81.44; H, 8.70; O, 9.86. Found: C, 81.69; H, 8.70; O, 9.61.

37,38,39,40,41,42-Hexakis(methoxy)-5,11,17,23,29,35-hexa-p-iso-propylcalix[6]arene (5)

0.5 g of (**2**) in THF (25 ml) and DMF (2.5 ml) was treated with NaH (0.5 g) and MeI (5 ml). The mixture was heated 3.50 h at 38°C. The reaction mixture was then processed exactly as described above to furnish (**5**). Yield = 98%; Mp = 260°C; ^{1}H NMR ($CDCl_3$): δ 1.1(*d*, 36H, C(CH_3)$_2$), 2.7(*m*, 6H, ArCH), 3.4(*s*, 18H, OCH_3), 4(*s*, 12H, ArCH_2-Ar), 6.7(*s*, 12H, ArH); ^{13}C NMR ($CDCl_3$): δ 24.11(*s*, C, C(CH_3)$_2$), 30.46(*s*, CH_2, ArCH_2Ar), 33.39(*s*, C, ArCH), 60.03(*s*, CH_3, OCH_3), 126.85(*s*, C, Cm), 134.09(*s*, C, CO), 143.52(*s*, C, Cp), 154.20(*s*, C, Ci); IR ν max (KBr) 2957, 2928, 1475 cm^{-1}; FAB MS *m*/*z* 973.5 [**5** + H]$^+$; Anal. Calcd. for $C_{66}H_{84}O_6$: C, 81.44; H, 8.70; O, 9.86. Found: C, 81.51; H, 8.72; O, 9.77.

49,50,51,52,53,54,55,56-Octakis(methoxy)-5,11,17,23,29,35,41,47-octa-p-iso-propylcalix[8]arene (6)

0.5 g of (**3**) in THF (25 ml) and DMF (2.5 ml) was treated with NaH (1 g) and MeI (10 ml). The mixture was heated 6 h at 38°C. The reaction mixture was then processed exactly as described above to furnish (**6**) in 95%. Mp = 200°C; ^{1}H NMR ($CDCl_3$): δ 1.1(*d*, 48H, C(CH_3)$_2$), 2.6(sept, 8H, ArCH), 3.4(*s*, 24H, OCH_3), 4(*s*, 16H, ArCH_2 Ar), 6.75(*s*, 16H, ArH); ^{13}C NMR ($CDCl_3$): δ 24.76(*s*, C, C(CH_3)$_2$), 29.77 and 30.15(2*s*, CH_2, ArCH_2Ar), 33.45(*s*, C, ArCH), 60.58(*s*, CH_3, OCH_3), 126.85(*s*, C, Cm), 133.67(*s*, C, CO), 143.87(*s*, C, Cp), 154.67(*s*, C, Ci); IR ν max (KBr) 2960, 2942, 1468 cm^{-1}; ES-MS (pos.mode)

m/z 1320.8 [**6** + H + Na]$^+$; Anal. Calcd. For $C_{88}H_{112}O_8$: C, 81.44; H, 8.70; O, 9.86. Found: C, 81.38; H, 8.80; O, 9.77.

25,26,27,28-Tetrakis(ethoxy)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (7)

0.5 g of (**1**) in THF (25 ml) and DMF (2.5 ml) was treated with NaH (0.5 g) and EtI (5 ml). The mixture was refluxed 2 h. The reaction mixture was then processed as described above to furnish (**7**) in 26%. Mp = 137 – 138°C; ^{1}H NMR ($CDCl_3$): δ 0.91 – 1.03 (2d and 1m, 24H, -C(CH_3)$_2$), 1.29 (t, 12 H, -OC-CH_3), 2.55 (sept, 4H, ArCH-), 3.15 (d, 24H,Ar-CH_2-Ar, J = 13 Hz), 4.2 (q, 8H, CH_2-C), 4.8 (s, 8H, OCH_2), 4.85 (d, 4H, Ar-CH_2-Ar, J = 13 Hz), 6.55 (s, 8H, ArH); ^{13}C NMR ($CDCl_3$): δ 15.75 – 16.37(CH_3,OCH_2CH_3), 23.49 – 24.53(CH_3,C(CH_3)$_2$), 30.75 – 37.44(CH_2, $ArCH_2Ar$), 32.8 – 33.69(C,ArCH), 67 – 69.3(CH_2, OCH_2CH_3), 125.97 – 128.99(C, Cm), 131.97 – 136.6(C, Co), 140.62 – 142.81(C, Cp), 153.66 – 155.53(t, C, Ci); IR ν max (KBr) 2957, 2914, 1457 cm^{-1}; FAB MS m/z 711.7 [**7** + Li]$^+$; Anal. Calcd. For $C_{48}H_{64}O_4$: C, 81.77; H, 9.15; O, 9.08. Found: C, 81.67; H, 9.13; O, 9.20.

37,38,39,40,41,42-Hexakis(ethoxy)-5,11,17,23,29,35-hexa-p-iso-propylcalix[6]arene (8)

0.5 g of (**2**) in dry THF (25 ml) and DMF (2.5 ml) was treated with NaH (0.5 g) and EtI (5 ml). The mixture was refluxed 2 days. The reaction mixture was then processed exactly as described above to furnish (**8**) in 40%. Mp = 291°C; ^{1}H NMR ($CDCl_3$): δ 0.93(s, 18H, CCH_3), 1.1(d, 36H, C(CH_3)$_2$), 2.6(sept, 6H, ArCH), 3.2(t, 12H, OCH_2C), 3.9(s, 12H, $ArCH_2Ar$), 6.9(s, 12H, ArH); ^{13}C NMR ($CDCl_3$): δ 15.63(s, CH_3, OCH_2 CH_3), 24.06(s, C, C(CH_3)$_2$), 30.76(s, CH_2, $ArCH_2$-Ar), 33.28(s, C, ArCH), 68.29(s, CH_2, OCH_2CH_3), 126.90(s, C, Cm), 133.97(s, C, CO), 143.09(s, C, Cp), 153.28(s, C, Ci); IR ν max (KBr) 2963, 2960, 1497 cm^{-1}; FAB MS m/z 1057.7[**8** + H]$^+$; Anal. Calcd. for $C_{72}H_{96}O_6$: C, 81.77; H, 9.15; O, 9.08. Found: C, 81.60; H, 9.30; O, 9.12.

49,50,51,52,53,54,55,56-Octakis(ethoxy)-5,11,17,23,29,35,41,47-octa-p-iso-propylcalix[8]arene (9)

0.5 g of (**3**) in dry THF (25 ml) and DMF (2.5 ml) was treated with NaH (1 g) and EtI (10 ml). The mixture was refluxed 4 h. The reaction mixture was then processed exactly as described above to furnish (**9**) in 25%. Mp = 188°C; ^{1}H NMR: ($CDCl_3$): δ 1(d, 48H, C(CH_3)$_2$), 1.15(t, 24H, CCH_3), 2.6(sept, 8H, ArCH), 3.6 (q, 16H, OCH_2C), 4(s, 16H, $ArCH_2Ar$), 6.75(s, 16H, ArH); ^{13}C NMR ($CDCl_3$), δ 15.65(s, CH_3, OCH_2CH_3), 24.03(s, C, C(CH_3)$_2$), 30.03(s, CH_2, $ArCH_2Ar$), 33.41(s, C, ArCH), 68.58(s, CH_2, OCH_2CH_3), 126.71(s, C, Cm), 131.28(s, C, CO), 143.47(s, C, Cp), 153.81(s, C, Ci);); IR ν max (KBr) 2958, 2916, 1456 cm^{-1}; ES MS (pos. mode) m/z 1409.9 [**9** + H]$^+$; Anal. Calcd. for $C_{96}H_{128}O_8$: C, 81.77; H, 9.15; O, 9.08; Found: C, 81.48; H, 9.35; O, 9.22.

25,26,27,28-Tetrakis(propenoxy)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (10)

0.5 g of (**1**) in dry THF (25 ml) and DMF (2.5 ml) was treated with NaH (0.5 g) and allyl bromide (5 ml). The mixture was refluxed 2 h. The reaction mixture was then processed exactly as described above to furnish (**10**) in 24%. Mp = 128 – 130°C; ^{1}H NMR (insoluble). IR ν max (KBr) 2960, 2928, 1463 cm^{-1}; FAB MS m/z 759.5[**10** + Li]$^+$; Anal. Calcd. for $C_{52}H_{64}O_4$: C, 82.99; H, 8.50; O, 8.50. Found: C, 82.88; H, 8.47; O, 8.55.

37,38,39,40,41,42-Hexakis(propenoxy)-5,11,17,23,29,35-hexa-p-iso-propylcalix[6]arene (11)

0.5 g of (**2**) in dry THF (25 ml) and DMF (2.5 ml) was treated with NaH (0.5 g) and allyl bromide (5 ml). The mixture was refluxed 12 h. The reaction mixture was then processed exactly as

described above to furnish (**11**) in 26%. Mp = 224°C; ^{1}H NMR ($CDCl_3$): δ 1.1(*d*, 36 H, -C(CH_3)$_2$), 2.7 (sept, 6H, ArCH), 3.85 (*s*, 16 H, $ArCH_2Ar$), 4.79 (*s* large, 16 H, OCH_2R), 5.69 (*s* large, 4H, -HC = C), 6.95 (*s*, 16 H, ArH);). IR ν max (KBr) 2956, 2934, 1462 cm^{-1}; FAB MS *m/z* 1129.7[**11** + H]$^+$; Anal.Calcd. for $C_{78}H_{96}O_6$: C, 82.94; H, 8.57; O, 8.50; Found: C, 82.92; H, 8.69; O, 8.66.

25,26,27,28-Tetrakis (ethoxycarbonylmethoxy)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (13)

0.5 g of (**1**) in dry acetone (10 ml) was treated with K_2CO_3 (0.5 g) and ethyl bromoacetate (0.8 ml). The mixture was refluxed 48 h under N_2. The cooled mixture was filtered, the solid residue was washed several times with CH_2Cl_2. The organic solution was dried and concentrated to an oil that was recrystallized to be purified from EtOH to leave ethylacetate derivative. Yield = 85%; Mp = 118 – 119°C; ^{1}H NMR ($CDCl_3$): δ 1(*d*, 24H, C(CH_3)$_2$), 1.29(*t*, 12H, $OCCH_3$), 2.55(sept, 4H, ArCH), 3.15(*d*, 24H, $ArCH_2Ar$, *J* = BHz), 4.2(*q*, 8H, CH_2C), 4.8 (*s*, 8H, OCH_5ArCH_2Ar, *J* = 13 Mz), 6.55 (*s*, 8H, ArH); ^{13}C NMR ($CDCl_3$), δ 14.25(*s*, CH_3, OCH_2CH_3), 24 (*s*, CH3, C(CH_3)$_2$), 31.68(*s*, CH_2, $ArCH_2Ar$), 33.01(*s*, C, ArCH), 60.37(*s*, CH_2, OCH_2CH_3), 71.40 (*s*, CH2, OCH2, R), 126.35(*s*, C, Cm), 133.96(*s*, C, CO), 124.58(*s*, C, Cp), 153.58(*s*, C, Ci), 170.51(*s*, C, C = O); IR ν max (KBr) 2974, 2940, 1756 cm^{-1}; ES MS (pos. mode) *m/z* 960.2 [**13** + Na]$^+$; Anal. Calc. for $C_{56}H_{72}O_{12}$: C, 71.76: H, 7.76; O, 20.5; Found: C, 71.40; H, 7.58; O, 20.48.

37,38,39,40,41,42-Hexakis(ethoxycarbonylmethoxy)-5,11,17,23,29,35-hexa-p-iso-propylcalix[6]arene (14)

0.5 g of (**2**) in dry acetone (10 ml) was treated with K_2CO_3 (0.5 g) and ethyl bromoacetate (0.8 ml). The mixture was refluxed 3 days under N_2. The reaction mixture was then processed exactly as previously to furnish (**14**). Yield = 67%; Mp = 179 – 180°C; ^{1}H NMR ($CDCl_3$): δ 0.8 (large, 36H, C(CH_3)$_2$), 1.3(*t*, 18H, C-CH_3), 2.5(sept, 6H, ArCH), 3.9(*s*,12H, $ArCH_2Ar$), 4.3(*q*, 12H, CH_2-C), 4.7(*s*,12H, OCH_2), 6.8(*s*, 12H, ArH); ^{13}C NMR($CDCl_3$): δ 14.28 (CH_3,-OCH_2CH_3), 23.70 (CH_3,-C(CH_3)$_2$), 30.97 (CH_2, Ar-CH_2-Ar), 33.10 (C, ArCH), 60.92 (CH_2,-OCH_2CH_3), 71 (CH_2, -OCH_2R), 127.25 (C, Cm), 133.18 (C, Co), 144.64 (C, Cp), 153.5 (C, Ci), 168.57 (C, C = O); IR ν max (KBr) 2954, 2940, 1756 cm^{-1}; ES MS (pos. mode) *m/z* 1405 [**14** + Na]$^+$; Anal. Calc. for $C_{84}H_{108}O_{18}$: C, 71.76; H, 7.75; O, 20.50. Found: C, 71.42; H, 7.71; O, 20.13.

49,50,51,52,53,54,55,56 Octakis(ethoxycarbonylmethoxy)-5,11,17,23,29,35,41,47-octa-p-iso-propylcalix[8]arene (15)

0.5 g of (**3**) in dry acetone (10 ml) was treated with K_2CO_3 (0.7 g) and ethyl bromoacetate (1.5 ml). The mixture was refluxed 7 days under N_2. The reaction mixture was then treated as previously to furnish (**15**) in 73%. Mp = 205 – 206°C; ^{1}H NMR ($CDCl_3$): δ 1(*d*, 48H, C(CH_3)$_2$), 1(*t*, 24H, C-CH_3), 2.6(sept, 8H, ArCH), 4(*s*,16H, $ArCH_2Ar$), 4(*q*, 16H, CH_2-C), 4.2(*s*,16H, OCH_2), 6.7(*s*, 16H, ArH); ^{13}C NMR($CDCl_3$): δ 13.97 (*s*,CH_3,-OCH_2CH_3), 23.96 (*s*,CH_3, -C(CH_3)$_2$), 30.23 (*s*, CH_2, Ar-CH_2-Ar), 33 (*s*, C, ArCH-), 60.98 (*s*, CH_2, -OCH_2CH_3), 70.03 (*s*, CH_2, -OCH_2R), 127.03 (*s*, C, Cm), 133. 23 (*s*, C, Co), 144.61 (*s*, C, Cp), 153.11 (*s*, C, Ci), 168.87 (*s*, C, C = O); IR ν max (KBr) 2966, 2931, 1757 cm^{-1}; ES MS *m/z* 1875.6 [**15** + H]$^+$; Anal. Calcd. for $C_{112}H_{144}O_{24}$: C, 71.76; H, 7.75; O, 20.5; Found: C, 71.69; H, 7.37; O, 20.96.

25,26,27,28-Tetrakis(benzyloxycarbonylmethoxy)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (16)

0.5 g of (**1**) was refluxed under nitrogen for 3 days in benzylic alcohol (3.6 g) containing *p*-toluenesulfonic acid (5 mg). The solution was

then concentrated under reduced pressure; the residue was taken up in dichloromethane and washed with 2N aqueous NaOH and thoroughly with water. The organic solution was dried and concentrated to leave ester (**16**) as white powder. Yield = 67%; ^{1}H NMR ($CDCl_3$): δ 1.24 and 1.5 (2 *m*, 24 H, -C(CH_3)$_2$), 2.61 (sept, 4H, ArCH-), 3.06 and 3.12 (2 *d*, 4H, Ar-CH_2-Ar, J = 13 Hz), 4.78 (*s*, 8H, OCH_2C=O), 4.76 and 4.82 (2 *d*, 4H, $ArCH_2Ar$, J = 13 Hz), 5.09 (*s*, 8H, OCH_2Bz), 6.53 (*s*, 8H, ArH), 7.27 (*s*, 20H, BzH); IR ν max (KBr) 2970, 1752 cm^{-1}; ES-MS (pos. mode) *m/z* 1208 [**16** + Na]$^+$; Anal. Calcd. for $C_{76}H_{80}O_{12}$: C, 77.24; H, 6.89; O, 15.86. Found: C, 77.17; H, 6.82; O, 15.98.

37,38,39,40,41,42-Hexakis(benzyloxycarbonylmethoxy)-5,11,17,23,29,35-hexa-p-isopropylcalix[6]arene (17)

0.5 g of (**2**) was refluxed under nitrogen for 3 days in benzylic alcohol 3.6 g containing *p*-toluenesulfonic acid (5 mg). The reaction mixture was then treated as previously to furnish (**17**). Yield = 65%; Mp = 216–217°C; ^{1}H NMR (Pyridine): δ 1.16–1.33 (*m*, 36H, C(CH_3)$_2$), 2.68 (*s*, 6H, ArCH), 4.28 (*s*, 12 H, Ar-CH_2-Ar), 5.01 (*s*, 12 H, OCH_2C=O), 5.34 (*s*, 12 H, OCH2Bz), 7.21 (*s*, 12H, ArH), 8.73 (*s*, 30 H, BzH); IR ν max (KBr) 2966, 1750 cm^{-1}; ES MS (pos. mode) *m/z* 1801.1 [**17** + Na]$^+$; Anal. Calcd. for $C_{114}H_{120}O_{18}$: C, 77.24; H, 6.89; O, 15.86. Found: C, 77.09; H, 6.80; O, 16.19.

25,26,27,28-Tetrakis(benzoyloxy)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (19)

0.5 g of (**1**) was treated with triethylamine (0.56 g), DMAP (0.063 g) and benzoic anhydride (0.906 g). The mixture was heated 16 h at 80°C. The residue was treated with 100 ml of water. After extraction with $CHCl_3$, the organic solution was treated with 100 ml of HCl (1N) and 100 ml of NaOH (2N). The organic solution was dried and concentrated to leave benzoyl as white powder. Yield = 60%; ^{1}H NMR ($CDCl_3$): δ 0.6 (*d*, 6 H, C(CH_3)$_2$, J = 7 Hz), 0.72 (*d*, 6 H, C(CH_3)$_2$, J = 6 Hz), 0.81 (*d*, 6 H, C(CH_3)$_2$, J = 6 Hz), 1.28 (*d*, 6 H, C(CH_3)$_2$, J = 7 Hz), 1.82, 2.16, 2.87 (3 sept, 4H, ArCH), 3.45 (*d*, 2 H, Ar-CH_2-Ar, J = 13.7 Hz), 3.77 (*d*, 2 H, Ar-CH_2-Ar, J = 16 Hz), 3.95 (*d*, 2 H, Ar-CH_2-Ar, J = 16 Hz), 4.06 (*d*, 2 H, Ar-CH_2-Ar, J = 13,7 Hz), 6.04, 6.43, 6.76 (2 *s* + 1 *m*, 28H, ArH); IR ν max (KBr) 2960, 1728 cm^{-1}; ES MS (pos. mode) *m/z* 1031.4 [**19** + Na]$^+$; Anal. Calcd. for $C_{68}H_{64}O_8$: C, 81.11; H, 6.45; O, 12.43; Found: C, 80.92; H, 6.39; O, 12.68.

37,38,39,40,41,42-Hexakis(benzoyloxy)-5,11,17,23,29,35-hexa-p-iso-propylcalix[6]arene (20)

0.5 g of (**2**) was treated with triethylamine (0.56 g), DMAP (0.063 g) and benzoic anhydride (0.906 g). The mixture was heated 16 h at 80°C. The reaction mixture was then processed exactly as previously to furnish (**20**) in 71%; ^{1}H NMR ($CDCl_3$): δ 0.78–1.1 (1 *m*, 36 H, C(CH_3)$_2$), 2.5 (3 sept, 6H, ArCH), 3.3–3.77 (2*d* + 1*s*: large, 12 H, Ar-CH_2-Ar, J = 13,7 Hz), 6.46, 6.43-7 (3 *s*, 42H, ArH); IR ν max (KBr) 2960, 1730 cm^{-1}; ES MS (pos. mode) *m/z* 1536.9 [**20** + Na]$^+$; Anal. Calcd. for $C_{102}H_{96}O_{12}$: C, 81.11; H, 6.45; O, 12.43; Found: C, 81.15; H, 6.41; O, 12.33.

49,50,51,52,53,54,55,56-Octakis(benzoyloxy)-5,11,17,23,29,35,41,47-octa-p-iso-propylcalix[8]arene (21)

0.5 g of (**3**) was treated with triethylamine (1 g), DMAP (0.08 g) and benzoic anhydride (1.15 g). The mixture was heated one day at 80°C. The reaction mixture was then processed exactly as previously to furnish (**21**) in 60%; Mp = 219°C; ^{1}H NMR ($CDCl_3$): δ 0.93 (*s*, 48H, C(CH_3)$_2$), 2.6 (*s*, 8H, ArCH), 3.65 (*s*, 16H, $ArCH_2$-Ar), 6.83 (*s* + *m*, 56H, ArH); IR ν max (KBr) 2960, 1728 cm^{-1}; ES MS (pos. mode) *m/z* 2040.4 [**21** + Na]$^+$; Anal.

Calcd. for $C_{136}H_{128}O_{16}$: C, 80.92; H, 6.39; O, 12.68; Found: C, 81.11; H, 6.45; O, 12.43.

25,26,27,28-Tetrakis (methoxycarbonyl)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (22)

To a stirred mixture of (**1**) (0.5 g) and potassium carbonate (0.93 g) in dry acetone (30 ml) was added after 20 min, a mixture of chloroacetone (0.54 ml) and sodium iodide (1.012 g) in dry acetone (3.5 ml). The reaction mixture was refluxed for 24 h under nitrogen, and after cooling was filtered and washed several times with acetone. The solvent was removed by evaporation and an orange solid residue was stirred for 2 h in 100 ml water at 60°C. The product was extracted into dichloromethane and then washed with 0.1 N sodium thiosulfate and water. The organic solution was dried and concentrated to give a brown solid which was boiled in methanol and filtered. The solid was recrystallized from toluene to give tetraketone derivative as yellow powder. Yield = 52%; Mp = 105–106°C; ^{1}H NMR ($CDCl_3$): δ 0.94 (*s*, 8H, OCH_2R), 1.2 (*d* + *t*, 36 H, $-C(CH_3)_2 + CH_3$), 2.8 (*m*, 4H, ArCH), 3.8 (*d*, 4 H, Ar-CH_2-Ar, $J = 15.4$ Hz), 4 (*d*, 4 H, Ar-CH_2-Ar, $J = 15.4$ Hz), 6.9 and 7.04 (2 *s*, 8H, ArH); ^{13}C NMR ($CDCl_3$): δ 21.47, 23.72, 26.57 ($-C(CH_3)_2 + -CH_3$), 30.45 (*s*, CH_2, Ar-CH_2-Ar), 33.2 (*m*, 4H, ArCH), 61.5 (CH_2, OCH_2R), 125.34, 127.18, 128.26, 129.08 (Cm), 134.62, 137.91 (Co), 145.91 (Cp), 150.32 (Ci), 206.04 (C=O); IR ν max (KBr) 2966, 1724 cm^{-1}; ES MS (pos. mode) *m/z* 839.5 [**22** + Na]$^+$; Anal. Calcd. for $C_{52}H_{64}O_8$: C, 76.44; H, 7.89; O, 15.66. Found: C, 76.22; H, 7.93; O, 15.85.

37,38,39,40,41,42-Hexakis (methoxycarbonyl)-5,11,17,23,29,35-hexa-p-iso-propylcalix[6]arene (23)

To a stirred mixture of (**2**) (0.5 g) and potassium carbonate (0.93 g) in dry acetone (30 ml) was added after 20 min, a mixture of chloroacetone (0.54 ml) and sodium iodide (1.012 g) in dry acetone (3.5 ml). The reaction mixture was then treated as previously to furnish (**23**). Yield = 50%, Mp = 128–129°C; ^{1}H NMR ($CDCl_3$): δ 0.9 (*m*, 36 H, $-C(CH_3)_2$), 2.8 (*m*, 24H, ArCH + CCH_3), 3 (*m*, 12H, OCH_2R), 3 (*m*, 12H,Ar-CH_2-Ar), 6.8 (1*s*, 12H, ArH); IR ν max (KBr) 2959, 1729 cm^{-1}; ES MS (pos. mode) *m/z* 1247.8 [**23** + Na]$^+$; Anal. Calcd. for $C_{78}H_{96}O_{12}$: C, 76.44; H, 7.89; O, 15.66. Found: C, 76.14; H, 7.89; O, 15.66.

49,50,51,52,53,54,55,56-Octakis(methoxycarbonyl)-5,11,17,23,29,35,41,47-octa-p-iso-propylcalix[8]arene (24)

To a stirred mixture of (**3**) (0.5 g) and potassium carbonate (0.93 g) in dry acetone (30 ml) was added after 20 min, a mixture of chloroacetone (0.54 ml) and sodium iodide (1.012 g) in dry acetone (3.5 ml). The reaction mixture was refluxed for 48 h under nitrogen and treated as previously to furnish (**24**). Yield = 40%; ^{1}H NMR ($CDCl_3$): δ 1.05 (*d*, 48 H, $-C(CH_3)_2$), 2 (*s*, 24 H, O=C-CH_3), 2.8 (*m*, 8H, ArCH), 3.94 (*s*, 16H, OCH_2R), 4.10 (*s*, 16 H,Ar-CH_2-Ar), 6.78 (*s*, 16H, ArH); IR ν max (KBr) 2965, 1724 cm^{-1}; ES MS (pos. mode) *m/z* 1656.9 [**24** + Na]$^+$; Anal. Calcd. for $C_{104}H_{128}O_{16}$: C, 76.44; H, 7.89; O, 15.66. Found: C, 76.28; H, 7.89; O, 15.83.

25,26,27,28-Tetrakis (benzocarbonylmethoxy)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (25)

To a stirred mixture of (**1**) (0.5 g) and potassium carbonate (0.93 g) in dry acetone (30 ml) was added after 20 min, a mixture of chloroacetophenone (1.04 g) and sodium iodide (1.012 g) in dry acetone (3.5 ml). The reaction mixture was refluxed for 48 h under nitrogen, and after cooling was filtered and washed several times with acetone. The solvent was removed by

evaporation and solid residue was suspended in 100 ml. The product was extracted into dichloromethane and then washed with 5% aqueous sodium bisulfite, 3% aqueous sulfuric acid and water. The organic solution was dried and concentrated to give a dark brown solid which was boiled in methanol and filtered to give tetraketone derivative as light brown powder. Yield = 50%; Mp = 130–131°C; ^{1}H NMR ($CDCl_3$): δ 1.05 (*d*, 24 H, -C(CH_3)$_2$), 2.6 (sept, 4H, ArCH), 3.29 (*d*, H,Ar-CH_2-Ar, J = 13 Hz), 5.66 (*s*, 8 H, OCH_2R), 6.63 (*s*, 8H, ArH), 7.27 and 7.42 (2*t*, 20 H, J = 7 Hz); IR ν max (KBr) 2960, 1702 cm^{-1}; ES MS (pos. mode) *m/z* 1087.7 [**25** + Na]$^+$; Anal. Calcd. for $C_{72}H_{72}O_8$: C, 81.20; H, 6.76; O, 12.03. Found: C, 81.08; H, 6.68; O, 12.20.

25,26,27,28-Tetrakis (adamantyloxycarbonyl)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (28)

0.5 g of (**1**) in dry acetone (30 ml) was treated with K_2CO_3 (0.6 g) and adamantylbromomethylketone (1.084 g). The mixture was refluxed 4 days under N_2. After cooling the mixture was filtered and washed several times with acetone. The solvent was removed by evaporation. The residue was boiled in methanol and filtered to give tetraketone derivative as yellow powder. Yield = 50%; ^{1}H NMR ($CDCl_3$): δ 0.8–1.5 (*m*, 24 H, -C(CH_3)$_2$), 1.5–2.3 (*m*, 60H, HAd), 2.4–3.2 (3 sept, 4H, ArCH-), 3.5–4.8 (*m* + 2*d*, 8H, Ar-CH_2-Ar), 5.1 (*s*, 8H, -OCH_2C=O), 6.3–7.2 (*m*, 8H, ArH); ES MS (pos. mode) *m/z* 1320 [**28** + Na]$^+$; Anal. Calcd. for $C_{88}H_{112}O_8$: C, 81.48; H, 8.64; O, 9.87. Found: C, 81.30; H, 8.66; O, 9.93.

37,38,39,40,41,42-Hexakis(adamantyloxycarbonyl)-5,11,17,23,29,35-hexa-p-iso-propylcalix[6]arene (29)

To a stirred mixture of (**2**) (0.5 g) and potassium carbonate (0.93 g) in dry acetone (30 ml) was added, after 20 min, a mixture of adamantylbromomethylketone (1.084 g) and sodium iodide (1.012 g) in dry acetone (3.5 ml). The reaction mixture was refluxed for 24 h under nitrogen, and after cooling was filtered and washed several times with acetone. The solvent was removed by evaporation and an orange solid residue was stirred for 2 h in 100 ml water at 60°C. The product was extracted into dichloromethane and then washed with 0.1 N sodium thiosulfate and water. The organic solution was dried and concentrated to give a brown solid which was boiled in methanol and filtered to obtaine a brown powder. The hexaketone derivative was purified by column chromatography (eluent: $CHCl_3$/heptane, 6:4). Yield = 50%; ^{1}H NMR ($CDCl_3$): δ 0.6–1.4 (*m*, 36 H, -C(CH_3)$_2$), 1.5–2.4 (*m*, 90H, HAd), 2.5–3.9 (*m*, 6H, ArCH-), 3.5 (*m* + 2*d*, 32H, Ar-CH_2-Ar + -OCH_2C=O), 6.6–7.2 (*m*, 16H, ArH); ES MS (pos. mode) *m/z* 1968.5 [**29** + Na]$^+$; Anal. Calcd. for $C_{132}H_{168}O_{12}$: C, 81.48; H, 8.64; O, 9.87. Found: C, 81.25; H, 8.58; O, 10.01.

25,26,27,28-Tetrakis(N,N-diethylaminocarbonylmethoxy)-5,11,17,23-tetra-p-iso-propylcalix[4]arene (30)

0.5 g of (**1**) in dry acetone (30 ml) was treated with K_2CO_3 (0.6 g) and α-chloro-*N,N*-diethylacetamide (0.8 ml). The mixture was refluxed 4 days under N_2. After cooling the mixture, the solvent was evaporated, and the residue treated with 100 ml of HCl (10%). After extraction with $CHCl_3$, the organic solution was dried and concentrated to oily residue which was treated with diethyl ether as white powder that was recrystallized to be purified from $CHCl_3$-MeOH. Yield = 25%; Mp = 188–188.5°C; ^{1}H NMR ($CDCl_3$): δ 1.1 (*d*, 24 H, -C(CH_3)$_2$ J = 7Hz), 1.1 (*t*, 24 H, N-C-CH_3), 2.6 (sept, 4H, ArCH-), 3.2 and 3.5 (2*q*, 16H, NCH_2C), 3.26 (*d*, 4H,Ar-CH_2-Ar, J = 12 Hz), 4.5 (*s*, 8H, OCH_2), 4.4 (*d*, 4H, Ar-CH_2-Ar, J = 12 Hz), 6.96 (*s*, 8H, ArH); ES MS (pos. mode) *m/z* 1067.7 [**30** + Na]$^+$; Anal. Calcd.

for $C_{64}H_{92}O_8N_4$: C, 73.56; H, 8.81; O, 12.26. Found: C, 73.50; H, 8.88; O, 12.32.

49,50,51,52,53,54,55,56-Octakis(N,N-diethylaminocarbonylmethoxy-5,11,17,23,29,35,41,47-octa-p-iso-propylcalix[8]arene (31)

0.5 g of (**3**) in dry acetone (30 ml) was treated with K_2CO_3 (1 g) and α-chloro-*N,N*-diaethylacetamide (1.6 ml). The mixture was refluxed 4 days under N_2. After cooling the mixture, the solvent was evaporated, and the residue treated as above; after recrystallization in $CHCl_3$-MeOH for 2 months, few crystals were recovered. ^{1}H NMR ($CDCl_3$): δ 0.8–1.5 (*m*, 48 H, -C(CH_3)$_2$), 1.6 (large *S*, 48 H, N-C-CH_3), 2.6 (*m*, 8H, ArCH-), 3.3–3.4 (*m*, 32H, NCH_2C), 3.6–5.4(*d*, 32H,Ar-CH_2-Ar + OCH_2); 6.6–7.4 (*m*, 16H, ArH); ES MS (pos. mode) *m/z* 2112 [**31**+Na]$^+$; Anal. Calcd. for $C_{128}H_{184}O_{16}N_8$: C, 73.56; H, 8.81; O, 12.26. Found: C, 73.45; H, 8.77; O, 12.28.

25-methoxy-26,27,28-trihydroxy-5,11,17,23-p-iso-propylcalix[4]arene (32)

1 g of (**1**) in dry acetonitrile (50 ml) was treated with K_2CO_3 (0.084 g) and 4 equiv. MeI (0.260 g). The mixture was refluxed for 3 days under nitrogen atmosphere. After cooling the solvent was removed under reduced pressure. The residue was taken up in 100 ml aqueous HCl (10%). After extracted with CH_2Cl_2, the organic solution was dried and evaporated to give a crude product. TLC of product shows traces of unsubstitued *p*-isopropylcalix[4]arene. A purified monomethyl derivative was easily obtained by column chromatography (eluent: $CHCl_3$/hexane, 7:3). Yield = 63%; ^{1}H NMR ($CDCl_3$): δ 1.05 (2*d*, 24 H, -C(CH_3)$_2$), 2.7 (sept, 4H, ArCH), 3.37 (*d*, 2H, H,Ar-CH_2-Ar eq., J = 13 Hz), 4.2 (*d*, 2H, H,Ar-CH_2-Ar ax., J = 13 Hz), 4.37 (*d*, 2H, H,Ar-CH_2-Ar ax′, J = 13 Hz), 4.1 (*s*, 3H, OCH_3), 6.82–7.87 (*s*, 4H, ArH), 6.89–6.93 (*d*, 4H, ArH), 9.5 (*s*, 2H, OH), 10 (*s*, 1H, OH); ES MS (neg. mode) *m/z* 605.5 [**32**-H]$^-$.

25-propenoxy-26,27,28-trihydroxy-5,11,17,23-p-iso-propylcalix[4] (33)

1g of (**1**) in dry acetonitrile (50 ml) was treated with K_2CO_3 (0.084 g) and 10 equiv. allylbromide (2.04 g). The mixture was stirred at room temperature for 6 days in a nitrogen atmosphere. After cooling the solvent was removed under reduced pressure. The residue was taken up in 100 ml aqueous HCl (10%), and extracted with CH_2Cl_2. The organic solution was dried and evaporated to give (**33**) that was recrystallized from MeOH-$CHCl_3$. Yield = 70%; ^{1}H NMR ($CDCl_3$): δ 1 (2*d*, 24 H, -C(CH_3)$_2$), 2.7 (sept, 4H, ArCH), 3.4 (*d*, 2H, H,Ar-CH_2-Ar eq., J = 13 Hz), 4.2 (*d*, 2H, H,Ar-CH_2-Ar ax., J = 13 Hz), 4.37 (*d*, 2H, H,Ar-CH_2-Ar ax′., J = 13 Hz), 4.8 (*d*, 2H, OCH_2C=C), 5.4–5.8 (2*d*, 2H, C=CH_2), 6.8 (*m*, 1 H, -CH=CH), 6.82–7.87 (*s*, 4H, ArH), 6.89–6.93 (*d*, 4H, ArH), 9.5 (*s*, 2H, OH), 10 (*s*, 1H, OH); ES MS (pos. mode) *m/z* 655.5 [**33**+Na]$^+$.

25-ethoxycarbonylmethoxy-26,27,28-trihydroxy-5,11,17,23-p-iso-propylcalix[4]arene (34)

1g of (**1**) in dry acetonitrile (50 ml) was treated with K_2CO_3 (0.084 g) and ethylbromoacetate (2.82 g). The mixture was refluxed for 5 days in a nitrogen atmosphere. After cooling the solvent was removed under reduced pressure. The residue was taken up in 100 ml aqueous HCl (10%). After extracted with CH_2Cl_2, the organic solution was dried and evaporated to give a crude product. TLC of product shows trace of unsubstitued *p*-isopropylcalix[4]arene. A purified derivative was easily obtained by column chromatography (eluent: CH_2Cl_2/heptane, 7:3). Yield = 60%; ^{1}H NMR ($CDCl_3$): δ 1.1 (2*d*, 24 H, -C(CH_3)$_2$), 1.4 (*t*, 3H, -CH_3), 2.7 (sept, 4H, ArCH), 3.4 (*d*, 2H, H,Ar-CH_2-Ar, J = 13 Hz), 4.3 (*d*, 2H, H,Ar-CH_2-Ar., J = 13 Hz), 4.8 (*s*, 2H, OCH_2R),

4.4 (*q*, 2H, OCH_2), 6.88, 6.93 (*s*, 4H, ArH), 6.83 (*d*, 4H, ArH), 9.2 (*s*,2H, OH), 10 (*s*, 1H, OH).

25,27,26,28-dipropenoxy-5,11,17,23-p-isopropylcalix[4]arene (35)

0.5 g of (**1**) in dry acetone (10 ml) was treated with K_2CO_3 (0.5 g) and 8 equiv. allylebromide (0.82 g). The mixture was refluxed 48 h under N_2. The cooled mixture was filtered, and the solid residue was washed several times with CH_2Cl_2. The organic solution was dried and concentrated to an oil that was recrystallized to be purified from EtOH to leave diallylether derivative. Yield = 70%; ^{1}H NMR ($CDCl_3$): δ 0.99 – 1.17 (*d*, 24 H, -C$(CH_3)_2$), 2.53 – 2.73 (sept, 4H, ArCH), 3.28 (*d*, 2H, H,Ar-CH_2-Ar eq, J = 13 Hz), 4.26 (*d*, 2H, H,Ar-CH_2-Ar.ax, J = 13 Hz), 4.5 (*s*, OCH_2R), 6.7 – 6.74 – 6.86 (2*s*, H, ArH), 7.9 (*s*, 2H, OH);); ES MS (pos. mode) m/z 695.6 **[35** + Na$]^+$.

25,27-Diethoxycarbonylmethoxy-26,28-dihydroxy-5,11,17,23-p-isopropylcalix[4]arene (36)

1g of (**1**) in dry acetone (50 ml) was treated with K_2CO_3 (0.33 g) and 2 equiv. ethylbromoacetate (0.564 g). The mixture was refluxed for 27 h under nitrogen atmosphere. The cooled mixture was filtered, the solid residue was washed several times with CH_2Cl_2. The organic solution was dried and evaporated to give a pure product. Yield = 80%; ^{1}H NMR ($CDCl_3$): δ 1 – 1.2 (*d*, 24 H, -C$(CH_3)_2$), 1.4 (*t*, 6H, -CH_3), 2.7 (sept, 4H, ArCH), 3.4 (*d*, 2H, H,Ar-CH_2-Ar eq, J = 13 Hz), 4.5 (*d*, 2H, H,Ar-CH_2-Ar. ax, J = 13 Hz), 4.4 (*q*,4H, OCH_2), 4.8 (*s*, 4H, OCH_2R), 6.7 – 6.89 (*s*, 8H, ArH), 7.4 (*s*,2H, OH); ES MS (pos. mode) m/z 787.8 **[36** + Na$]^+$.

25,27-Diepoxide-26,28-dihydroxy-5,11,17,23-p-iso-propylcalix[4]arene (37)

1 g of (**1**) was treated with 19 equiv. epichlorhydrine (2.94 g) in a presence of 0.08 equiv. Bu_4NBr. The stirred mixture was heated for 18 h at 85°C and then refluxed for 4 h. To the reaction mixture was added 2-propanol and 8 equiv. aqueous NaOH, and this was heated for 45 h at 70°C. After cooling, the solvent was removed under reduced pressure. The residue was taken up in 100 ml aqueous HCl (10%). After extraction with toluene, the organic solution was dried and evaporated to give (**37**) as a white powder. Yield = 85%; ^{1}H NMR ($CDCl_3$): δ 1 – 1.2 (*d*, 24 H, -C$(CH_3)_2$), 2.7 (sept, 4H, ArCH), 3.34 (*d*, 2H, H, Ar-CH_2-Ar eq, J = 13 Hz), 4.5 (*d*, 2H, H,Ar-CH_2-Ar. ax, J = 13 Hz), 4.27 (*s*, OCH_2R), 6.7 – 6.87 (*s*, 8H, ArH), 7.26 (*s*, 2H, OH); ES MS (pos. mode) m/z 727.7**[37** + Na$]^+$.

25-ethoxycarbonylmethoxy-26,27,28-tris(methoxycarbonyl)-5,11,17,23-p-isopropylcalix[4]arene (38)

1 g of (**34**) in dry acetone (50 ml) was treated with K_2CO_3 (1.46 g) and 17 equiv. chloroacetone (2.32 g) in a presence of NaI (1.33 g). The mixture was refluxed 3 days under nitrogen. The reaction mixture was treated in the same way as (**22**). Yield = 40%; ^{1}H NMR ($CDCl_3$): δ 1 (*d*, 24 H, -C$(CH_3)_2$), 1.45 (*t*, 6H, -CH_3), 2.25 (sept, 4H, ArCH), 2.3 (*s*, O = CC H_3), 3.3 (*t*, 2H, H,Ar-CH_2-Ar, J = 13 Hz), 4.2 (*d*, 2H, H,Ar-CH_2-Ar, J = 13 Hz), 4.4 (*q*, OCH_2), 4.5 (*s*, OCH_2R ester), 4.5 (*s*, OCH_2R ketone), 7 (*s*, 8H, ArH); ES MS (pos. mode) m/z 869.7 **[38** + Na$]^+$.

25-methoxy-26,27,28-tris(N,N-diethylaminocarbonylmethoxy)-5,11,17,23-p-iso-propylcalix[4]arene (39)

1g of (**32**) in dry acetone (50 ml) was treated with K_2CO_3 (0.735 g) and 23 equiv. α-chloro-*N,N*-diethylacetamide (5.66 g) in a presence of NaI (1.48 g). The mixture was refluxed for 4 days under nitrogen. The reaction mixture was treated in the same way as (**30**). Yield = 20%; ^{1}H NMR ($CDCl_3$): δ 1 – 1.4 (*m*, -C$(CH_3)_2$)calix + CH_3 amide), 2.7 (sept, ArCH), 2.3 (*s*, O = CCH_3),

3.4 (*m*, Ar-CH_2-Ar), 3.35 (*s*, OCH_3R ether), 4. 25 (*s*, OCH_2R amide), 7(*m*, ArH); ES MS (pos. mode) *m/z* 968.7[**39** + Na]$^+$.

X-ray Crystal Structure Analysis of (13)

Data were measured on an Enraf-Nonius Kappa – CCD diffractometer. X-ray data for (**13**): monoclinic, $a = 22.905$, $b = 13.219$, $c = 19.624$ Å, $\beta = 118.71$, $U = 5211$ Å^3, space groups C_2/c, $Z = 4$. The refinement leads to an *R* value of 0. 16.

CONCLUSION

In conclusion, a new family of calixarenes has been synthesized; 33 *p*-isopropylcalixarenes derivatives have been obtained as pure products and fully characterized. The ^{1}H NMR and ^{13}C NMR data established that the *p*-isopropylcalix[4]arene derivatives exist preferentially in the cone conformation at ordinary temperatures. However, the tetraadamantyl ketone derivative (**28**) appears as a mixture of cone and partial cone conformers, the tetramethyl ether (**4**) is a mixture of conformers with a preferred partial cone conformation, and tetraethyl ether (**7**) and tetrabenzoyl ester (**19**) derivatives adopt a partial cone conformation.

Herein, we have reviewed the ionophoric activity of these derivatives. It is undoubted that *p*-isopropylcalixarene derivatives can provide a wide variety of receptors for selective ion or molecular recognition and transport. The tetraamide derivative (**30**) is the most efficient binder, and the tetraketone derivatives (**22**), (**25**), (**28**) have a high ability to complex Na^+, Ba^{2+}, K^+ and Li^+. The tetraester (**13**) displays a selectivity peak for Na^+, the hexaester (**14**) presents a peak of selectivity for Cs^+ and the octaester (**15**) shows a preference for Ba^{2+} extraction. X-Ray structure of the tetraethyl ester shows that the cone conformation persists in the solid state and confirms that the cation is inserted into the hydrophilic cavity closed by the four phenoxy oxygen atoms and four ester or ketone carbonyl groups.

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[48] In order to appreciate the hydrophilic cavity dimensions of the empty form of (**13**), selected bond lengths (Å) are given: O(27)–O(28) = 3.308; O(28)–O(28a) = 3.388; O(27)–O(28a) = 2.988; O(271)–O(281) = 5.676; O(281)–O(271a) = 3.252; O(271)–O(271a) = 5.829. Symmetry transformations were used to generate equivalent (a) atoms.