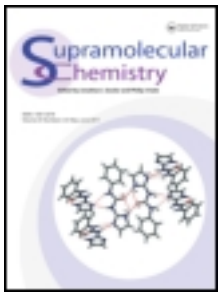


Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

New conjugates of calix[4]arenes bearing dipyridine and indolizine heterocycles

Ramona Danac [a], Raluca Rusu [a], Alexandru Rotaru [b], Aurel Pui [a] & Sergiu Shova [b]

[a] Department of Chemistry, Alexandru Ioan Cuza University of Iasi, 14 Carol I, Iasi, 700506, Romania

[b] Petru Poni Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, Iasi, 700487, Romania

Available online: 24 May 2012

To cite this article: Ramona Danac, Raluca Rusu, Alexandru Rotaru, Aurel Pui & Sergiu Shova (2012): New conjugates of calix[4]arenes bearing dipyridine and indolizine heterocycles, Supramolecular Chemistry, DOI:10.1080/10610278.2012.688122

To link to this article: http://dx.doi.org/10.1080/10610278.2012.688122

Supramolecular Chemistry
iFirst article, 2012, 1–13

Taylor & Francis
Taylor & Francis Group

New conjugates of calix[4]arenes bearing dipyridine and indolizine heterocycles

Ramona Danac[a]*, Raluca Rusu[a], Alexandru Rotaru[b], Aurel Pui[a] and Sergiu Shova[b]

[a]*Department of Chemistry, Alexandru Ioan Cuza University of Iasi, 14 Carol I, Iasi 700506, Romania;* [b]*Petru Poni Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, Iasi 700487, Romania*

(*Received 15 February 2012; final version received 4 April 2012*)

A simple route to introduce various heterocycles, derivatives of dipyridyls and indolizines on the lower rim of the *para-tert*-butylcalix[4]arene via ester bond formation to afford 1,3-disubstituted conjugates is described. The conformation of the new compounds and some intermolecular interactions are discussed on the basis of X-ray and NMR analyses. Preliminary complexation properties of some of the new *tert*-butylcalix[4]arene heterocyclic conjugates with Cu (II), Co (II) and Ni (II) were studied by means of UV–Vis titration.

Keywords: calixarenes; heterocycles; metal complexes

Introduction

Calixarenes are versatile molecular scaffolds for the design of wide variety of structural entities. Through the pioneering studies of Gutsche in the late 1970s, calixarenes have rapidly become the most employed macrocyclic compounds in supramolecular chemistry (*1*). By tethering various functional groups, calixarenes have also become an important class of macrocyclic receptors able to complex various metal ions (*2*).

Heterocycles, as molecules of life, are ubiquitous in biological systems and are involved in many biological functions because of their ability to undergo various non-covalent interactions with ions as well as neutral species. Thus, by equipping the upper or the lower rim of calixarenes with heterocycles, new compounds as functional materials or multifunctional enzyme models were elaborated (*3*). Particularly, nitrogen-containing functional groups suitable for transition metal binding are of great interest due to the combination of the complexation features of nitrogen ligands with the hydrophobic cavity of calixarenes within the same molecule (*3*, *4*). Calixarenes with covalently attached fluorophores and coordinating properties, bear a great potential in terms of an easy monitoring of the complexation processes (*5*).

Although many methods that allow their straightforward functionalisation are now available, the selective introduction of functional groups into the calixarenes on both narrow or wide rim is still an interesting and challenging subject to study. Earlier, different groups reported the synthesis and metal complexation features of dipyridyl-based calix[4] arenes (*5a*, *6*), emphasising their affinity for transition metal cations. Furthermore, incorporation of these moieties into calixarenes allows the combination of the peculiar features of the macrocycle with the photochemical and electrochemical properties displayed by the metal complexes of these heterocyclic units (*7*, *8*). Dipyridyl podants were introduced in several synthetic steps via either ether calixarene bonds (*6c–l*), C—C bonds (*6a*) or amide bonds (*6b*) on both the lower rim (*6c–l*) and the upper rim (*6a,b*) of the calixarene scaffold.

In this study we report a simple way of selective introduction of nitrogen-containing heterocycles on the lower rim of the *tert*-butylcalix[4]arene by esterification reaction. Despite the labile properties of the phenol ester bond, we succeeded both the synthesis and some preliminary studies of binding properties for new conjugates towards transition metal cations (Cu^{2+}, Co^{2+} and Ni^{2+}).

From the previous reports on the narrow rim esterification (*9*), using acid halides and sodium hydride, acid anhydrides and sulphuric acid, the acylation or aroylation generally involves all of the OH groups if the derivatising agent is used in excess. By using acid halides in the presence of bases weaker than NaH and limiting amounts of the esterifying reagent, it is possible to obtain partially substituted calixarenes in a selective fashion (*10*).

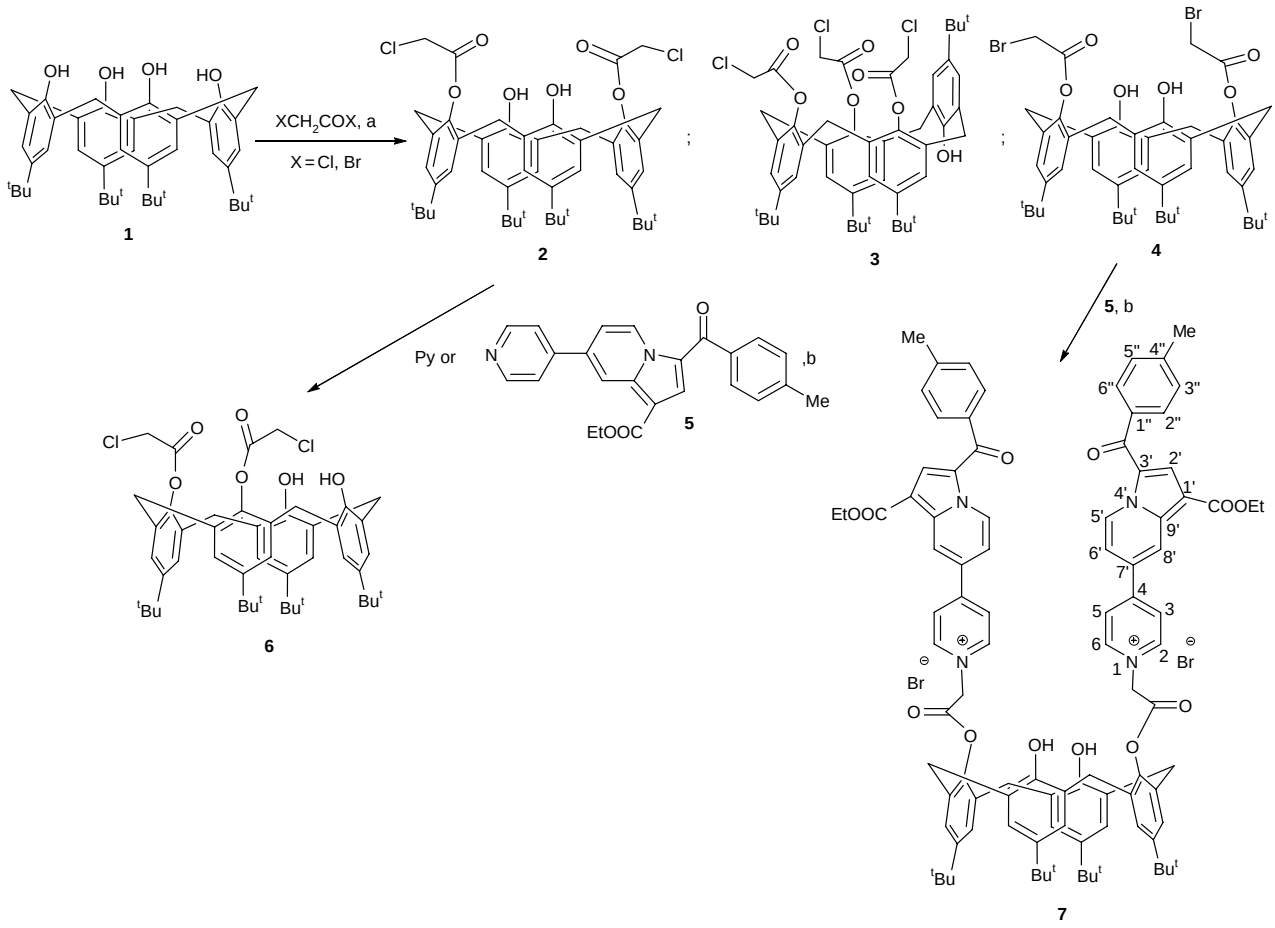
Results and discussions

One of the first goals of our research aiming to obtain new calixarenes bearing heterocycles on the lower rim of their scaffold was to investigate the reaction conditions for the introduction of reactive halogen groups able to get easily

*Corresponding author. Email: rdanac@uaic.ro

ISSN 1061-0278 print/ISSN 1029-0478 online

http://dx.doi.org/10.1080/10610278.2012.688122
http://www.tandfonline.com



Scheme 1. Reaction of *tert*-butylcalix[4]arene with halogenoacyl halides at the lower rim. (a) Et_3N, MeCN, rt; (b) MeCN, reflux.

functionalised. Thus, treating *tert*-butylcalix[4]arene **1** with chloroacetyl chloride or bromoacetyl bromide in acetonitrile in the presence of triethylamine (TEA), we afforded different compounds depending on the number of equivalents of acyl halide used. Reacting **1** with 5 equivalents of chloroacetyl chloride in dry acetonitrile in the presence of TEA resulted in the corresponding 1,3-diester **2** isolated in good yield (Scheme 1). The ^{1}H NMR spectra showed a cone conformation of this compound with the characteristic AB pattern for bridging CH_2 groups whereas the IR spectra showed strong absorption band for C═O ester bond at 1763 cm^{-1} and for the free OH groups at 3512 cm^{-1}.

When the ratio of number of equivalents was increased (**1**/chloroacetyl chloride/TEA: 1/8/9), the triester derivative **3** was obtained. The ^{1}H NMR spectra showed spectral patterns (three singlets from *tert*-Bu hydrogen atoms and four doublets from the bridging methylene groups) compatible with either a cone or a partial cone conformation of this triester derivative in solution, while the solid-state structure was assigned on the basis of X-ray diffraction which showed whereas triester **3** in a *uudu* flattened partial cone conformation with the phenol OH group laying on the opposite side of the ester groups (Figure 1).

The perspective view of the molecular structure of **3**, investigated by single-crystal X-ray diffraction analysis, along with the atomic labelling scheme, is shown in Figure 1. Crystal **3** has a molecular structure, in which the calix[4]arene core adopts a partial cone conformation. This conformation seems to be facilitated by two C—H···O hydrogen bonds between methylene group, denoted by C37 carbon atom, and two ester oxygen atoms O2 and O6 (Figure 1), whereas the free OH group does not exhibit any hydrogen bonding. An examination of the torsion angles (Table 1) shows the sequence of signs for ϕ and χ to be $+\,-\,,+\,-\,,++,--$ as expected for partial cone conformation (*11*).

The same triester **3** was isolated when we continued to increase the number of equivalents of chloroacetyl chloride, being unable to obtain the corresponding tetraester under these conditions (Scheme 1).

In order to obtain pyridinium quaternary salt derivatives, the next step in our research plan was to

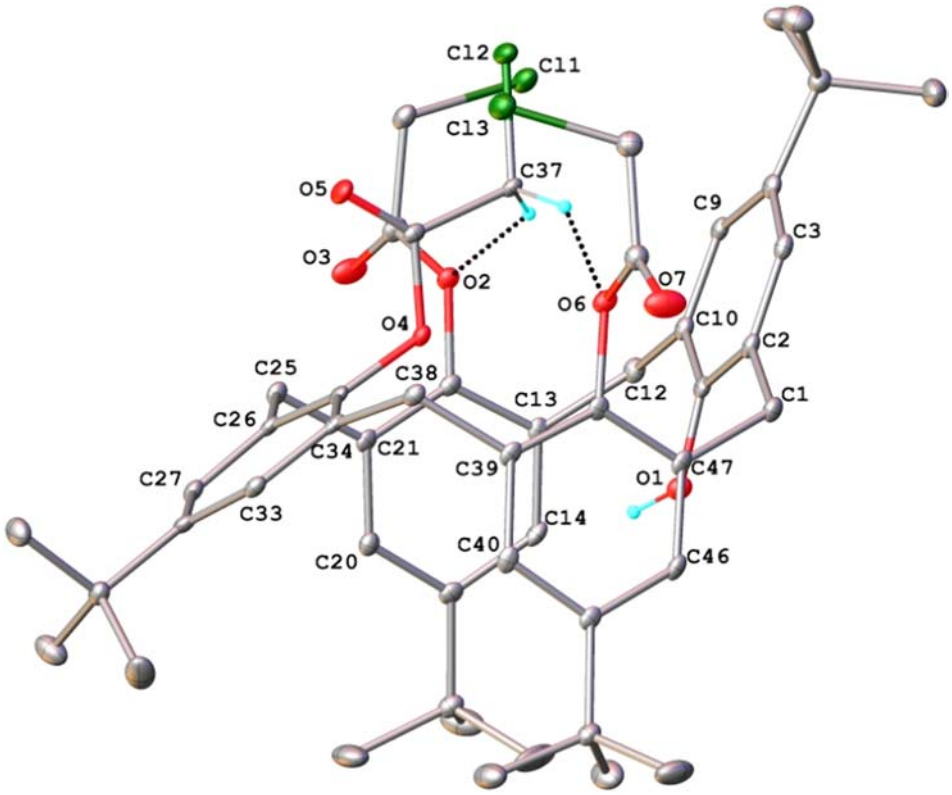


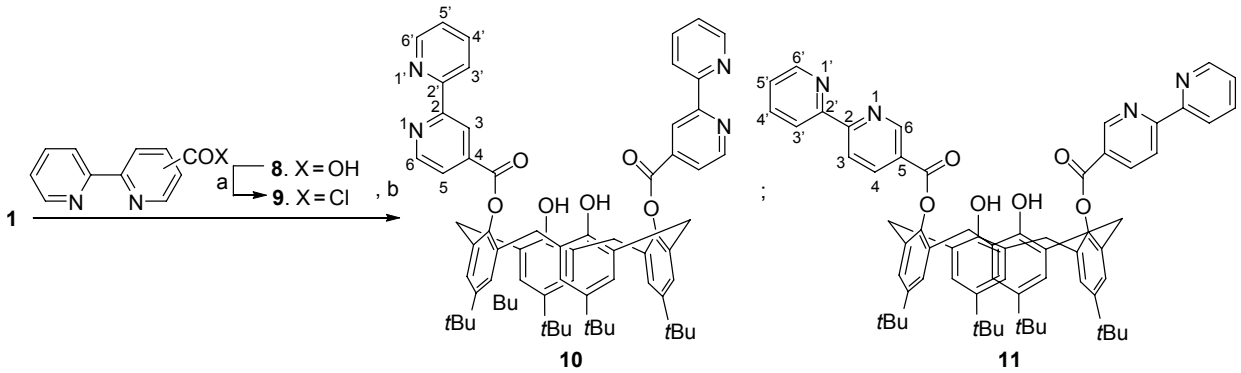
Figure 1. X-ray molecular structure of compound **3**. Thermal ellipsoids are drawn at 40% probability level. Non-relevant hydrogen atoms are omitted for clarity. H-bond parameters: C37—H···O6 [C37—H 0.97 Å, H···O6 2.27 Å, C37···O6 3.115(4) Å, C37—H···O6 145.6°]; C37—H···O2 [C37—H 0.97 Å, H···O2 2.25 Å, C37···O2 3.038(4) Å, C37—H···O6 137.7°].

Table 1. Torsion angles to define the calixarene conformation in compound **3**.

Torsion angle	ϕ (°)	Torsion angle	χ (°)
C20–C21–C25–C26	67.8 (4)	C21–C25–C26–C27	−110.0 (4)
C33–C34–C38–C39	104.5 (4)	C34–C38–C39–C40	−58.6 (4)
C46–C47–C1–C2	117.1 (4)	C47–C1–C2–C3	129.4 (4)
C9–C10–C12–C13	−135.8 (3)	C10–C12–C13–C14	−110.2 (4)

carry out the reaction between the resulted calixarene-1,3-diester **2** and the fluorescent pyridylindolizine derivative **5** which was recently synthesised in our group (*12*). First we treated diester **2** with a simpler N-heterocycle as pyridine in anhydrous acetonitrile, but instead of obtaining the corresponding salt, a migration of one of the ester groups occurred and 1,2 diester **6** was afforded in a cone conformation, the structure being confirmed by ^{1}H NMR (two singlets from *tert*-Bu groups and six doublets for methylene bridging groups). This is in agreement with literature reports, in which these migrations were observed on different aroyl esters (*10*), the cleavage being facilitated by a phenolic OH proximate to the ester carbonyl function. The same migration was observed when diester **2** reacted in the same conditions with indolizine **5**, when an amine induced cleavage of one ester group occurred to obtain compound **6** in the same conformation. No ester cleavage was observed when triester **3** was treated in the same conditions (no proximate OH to the ester groups), but only traces of desired pyridinium salts were observed to be formed in this reaction.

Interestingly, treating **1** with five or more equivalents of bromoacetyl bromide, in order to synthesise esters bearing a more reactive halogen, only the corresponding 1,3-diester **4** in cone conformation was obtained. The treatment of **4** with monoindolizine **5** in refluxing anhydrous acetonitrile gave indeed the corresponding dipyridinium dibromide **7** in a cone conformation to the detriment of the migration observed in case of compound **2**. This salt becomes bright red coloured when treated with



Scheme 2. Reaction of *tert*-butylcalix[4]arene **1** with acyl chlorides of 2,2′-dipyridine-4 carboxylic and 2,2′-dipyridine-5 carboxylic acids. (a) $(COCl)_2$, DMF, C_6H_6; (b) Et_3N, MeCN, rt.

bases (e.g TEA), the fact which probably indicates their transformation to the corresponding ylides, which can be interesting candidates for cycloaddition reactions.

In our further investigation using the previously described conditions, we tethered the 2,2′-dipyridine units to the 1,3 positions of *tert*-butylcalix[4]arene *via* ester bonds (Scheme 2) in order to obtain compounds possessing heteroaromatic substituents which can provide donor atoms for binding metal ions.

Thus, treating **1** with 5 equivalents of 2,2′-dipyridine-4-carbonyl chloride or 2,2′-dipyridine-5-carbonyl chloride (obtained from the corresponding commercial available carboxylic acids), we were able to isolate only the 1,3-disubstituted products **10** or **11**. Both compounds showed ^{1}H NMR spectra with the same spectral patterns corresponding to a cone conformation, their structures being finally confirmed by X-ray diffraction (Figures 2 and 4).

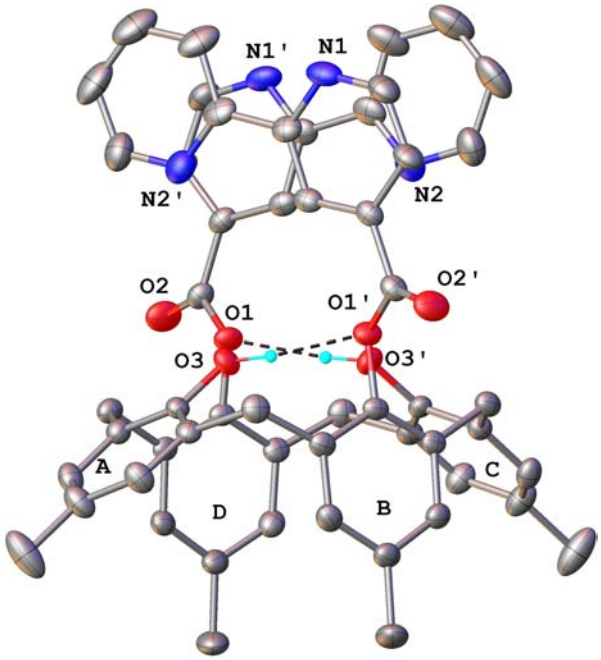


Figure 2. X-ray molecular structure of compound **10**. Thermal ellipsoids are drawn at 40% probability level. Non-relevant hydrogen atoms, as well as the *tert*-Bu atoms, are omitted for clarity. Symmetry code for equivalent atoms: 1/2 − *x*, 2 − *y*, *z*. H-bond parameters: O3—H···O1 [O3—H 0.89 Å, H···O1 2.01 Å, O3···O1′ (1/2 − *x*, 2 − *y*, *z*) 2.893(4) Å, O3—H···O1 174.0°].

The conformation of compound **10** can be described as 'distorted cone' facilitated by two O—H···O intramolecular hydrogen bonds, formed between OH groups and ester oxygen atoms. This conclusion is confirmed by the values and the sequences of sign (+ −, + −, + −, + −) for torsion angles (*11*), given in Table 2.

Two phenolic units B and D are almost perpendicular to the mean plane through the C atoms of the methylene bridges with the values of dihedral angles being equal to 84.89(9)° and 84.9(1)°, respectively, which is in a good correlation with the intramolecular distance between two symmetrically related 2,2-dipyridine units. This is evidenced by the centroid-to-centroid distances of 3.585 Å between adjacent overlapping aromatic rings. Two aryl rings carrying the free OH groups are splayed outward resulting in 'flattened cone' conformation. It is important to note that the π−π stacking interaction is extending in the crystal to the intermolecular system, which determined the association of compound **10** molecules into the infinite ribbon running 010 direction (Figure 3).

The crystal has a molecular structure constructed from neutral molecules **11**, depicted in Figure 4, and solvate water molecules in 1:1.8 ratio.

Table 2. Torsion angles to define the calixarene conformation in compound **10**.

Torsion angle	ϕ (°)	χ (°)
A–B	106.4 (5)	− 64.3 (5)
B–C	64.2 (5)	− 105.0 (5)
C–D	106.4 (5)	− 64.3 (5)
D–A	64.2 (5)	− 105.0 (5)

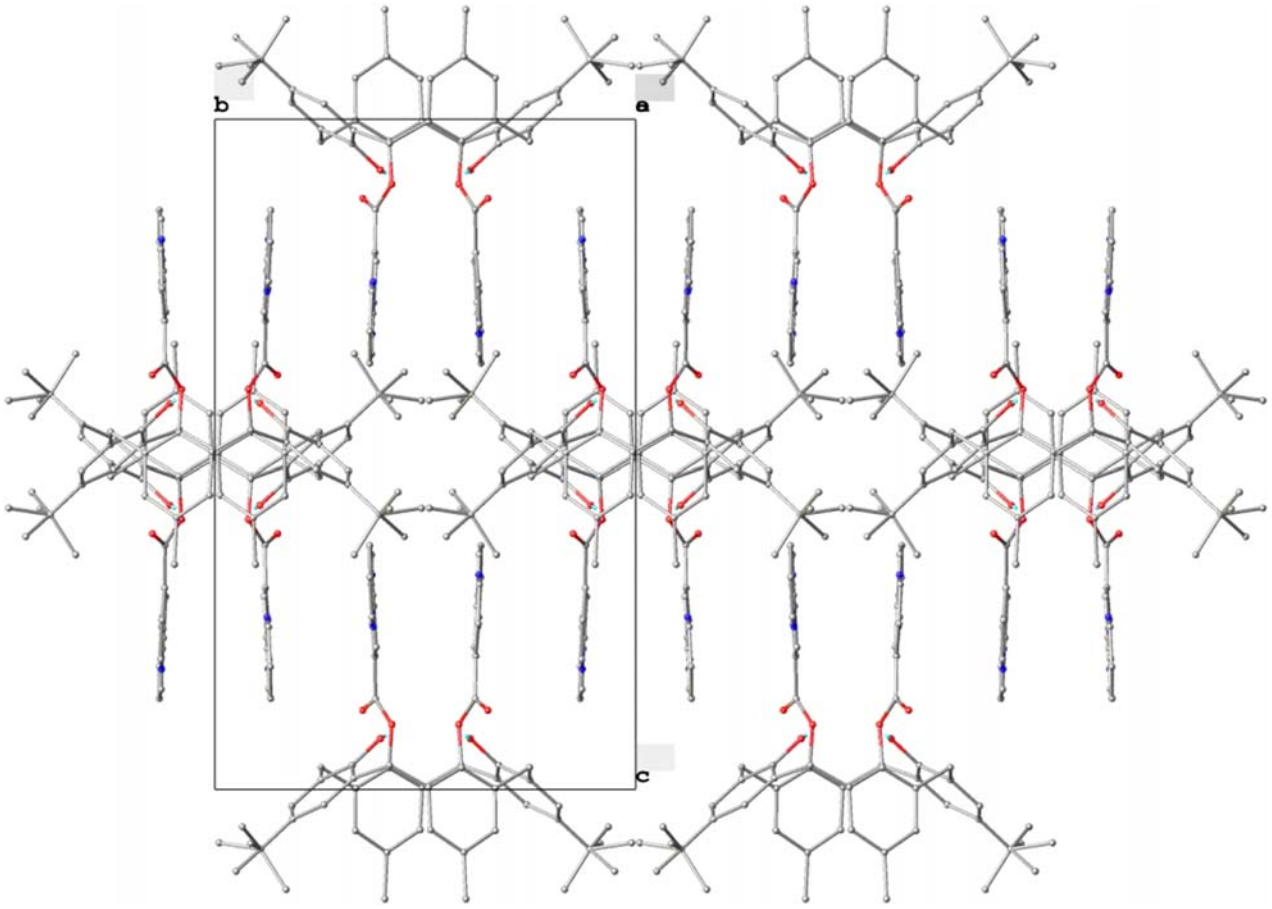


Figure 3. $\pi-\pi$ Stacking interaction in structure of **10**.

This molecule is characterised by own symmetry, determined by crystallographically imposed mirror plane of *C2/m* space group. The molecule contains two free OH groups in opposite orientation and exhibits partial cone conformation even though the cone conformation is the major species at equilibrium in solution. The characterisation of partial cone conformation in terms of torsion angles is presented in Table 3. The sequence of signs $(+\,-\,,\,+\,-\,,\,++,\,--)$ for ϕ and χ dihedral angles, confirms the partial cone conformation (*11*).

It is important to note that the crystal structure motif of **11** is characterised by the formation of the channel which contains statistically distributed solvate water molecules. The projection of the crystal structure packing is shown in Figure 5.

The next goal of our investigation was to synthesise, using the same method, fluorescent calixarenes which can be used as potential ligands in metals complexation. Thus, the hydrolysis of the ethyl ester group of our fluorescent pyridylindolizine derivative **5** was carried out in basic conditions giving the corresponding carboxylic acid **12**, which was transformed in more reactive acyl chloride **13**. Keeping the equivalents of reactants ratio as previously described for esterification reactions (**1**/**13**/TEA: 1/5/6), we could isolate only the corresponding fluorescent 1,3-diester in a cone conformation (*13*), even though the thin layer chromatography (TLC) plate of the reaction mixture showed few other fluorescent compounds as by-products (Scheme 3).

A preliminary complexation study by UV–Vis titrations in ethanol at 25°C was carried out using the ester derivative **10** with Ni^{2+}, Co^{2+} and Cu^{2+} inorganic salts. Typically, a solution of M^{2+} (2×10^{-3} mol l^{-1}) with a total volume of 10 µl was added stepwise in portions of 1 µl to a solution of 2 ml of **10** (1×10^{-5} mol l^{-1}), and the absorption spectra were measured using a Cintra 101 spectrophotometer in the range of 200–400 nm (Figure 6).

The free ligand **10** (**L**) shows two absorption maxima at 232 and 260 nm (Figure 3), the latter one being characteristic to the absorption of the bipyridyl moiety of compound **10**. The addition of M(II) solution causes a bathochromic shift of the absorption maximum from 260

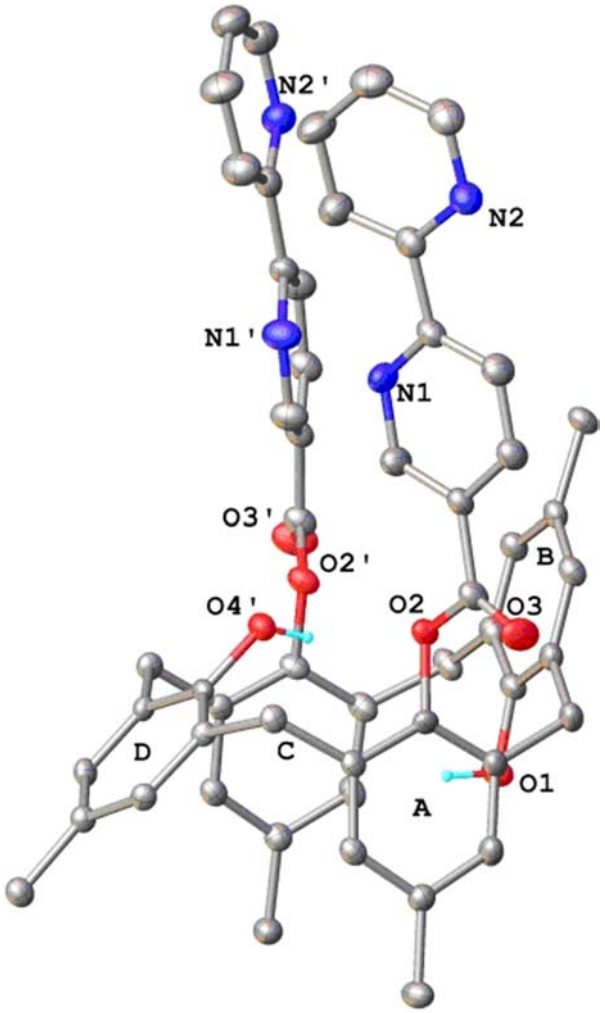


Figure 4. X-ray molecular structure of compound **11**. Thermal ellipsoids are drawn at 40% probability level. Non-relevant hydrogen atoms, as well as the *tert*-Bu atoms, are omitted for clarity. Symmetry code for equivalent atoms: x, $1 - y$, z.

Table 3. Torsion angles to define the calixarene conformation in compound **11**.

Torsion angle	ϕ (°)	χ (°)
C–D	63.7 (4)	−97.2 (4)
D–A	97.2 (4)	−63.7 (4)
A–B	117.2 (4)	122.4 (4)
B–C	−122.4 (4)	−117.2 (4)

to 310 nm for Co**L**, 313 nm for Ni**L** and 311 nm for Cu**L** correspondingly (for details, see Supplementary Information, available online).

As shown in Figure 6, increases in absorbance at around 310 nm and reduction in free ligand absorbance at 260 nm with the formation of two clear isosbestic points were observed, which indicates that the ligand and its metal complex are in equilibrium in solution. The stoichiometry of metal/ligand (M/L) main species was determined by mole ratio (*14*) and Job plot methods (*15*). Interestingly, both methods indicated the presence of only one complexation species with molar ratio M/L: 1/1, which corresponds to the previously reported data in case of Co^{2+}(*6e*). The stability constants obtained by the two different methods are comparable and are presented in Table 4, showing a good stability of these complexes.

Conclusions

In this study, selective introduction of heterocycles into the lower rim of *tert*-butylcalix[4]arene via ester bond formation was studied. Different approaches were tested but the direct esterification of the OH groups of the *tert*-butylcalix[4]arene by heterocyclic acyl chloride derivatives was the most effective. By this way, only 1,3-disubstituted *tert*-butylcalix[4]arenes with 2,2′-dipyridine or fluorescent indolizine units were afforded. In contrast to the bulky heterocyclic moieties, during the optimisation of esterification reaction, also a trisubstituted derivative of *tert*-butylcalix[4]arene with chloroacetyl chloride was obtained.

The complexes of heterocyclic derivative **10** with Ni^{2+}, Co^{2+} and Cu^{2+} were investigated by UV–Vis titrations, providing the insight into the ratio between the metal and ligand in the studied complexation system. From the obtained results, it may be concluded that all three metal ions form only one complexation species with molar ratio 1:1 between metal and compound **10**.

Expanded complexation studies and investigation of the electric, fluorescence and transport properties of the synthesised compounds are currently under progress.

Experimental

Melting points were recorded on an A. Krüss Optronic Melting Point Meter KSPI (Kruss, Hamburg, Germany) and are uncorrected. Proton and carbon nuclear magnetic resonance (δ_H, δ_C) spectra were recorded on a Bruker Avance 400 DRX (400 MHz, Bruker BioSpin GmbH, Rheinstetten, Germany). All chemical shifts are quoted on the δ-scale in ppm using TMS or residual solvents ($CHCl_3$, DMSO) as internal standards. Coupling constants are given in Hz. IR spectra were recorded on an FT-IR Shimadzu (Shimadzu, Japan) or Jasco 660 *plus* (Jasco Inc, Easton, USA) FT-IR spectrophotometers. Low-resolution mass spectra were recorded on a Bruker micrOTOF-Q II Electrospray Ionization Mass Spectrometer (Bruker Daltonics Inc, Bremen, Germany), ESI in the positive mode; *m/z* values are reported in Daltons. TLC was carried out on Merck silica gel $60F_{254}$ plates (Merck, USA). Column chromatography was carried out on silica gel (Roth 60, 0.04–0.063 mm). Visualisation of the plates was achieved using a UV lamp ($\lambda_{max} = 254$ or

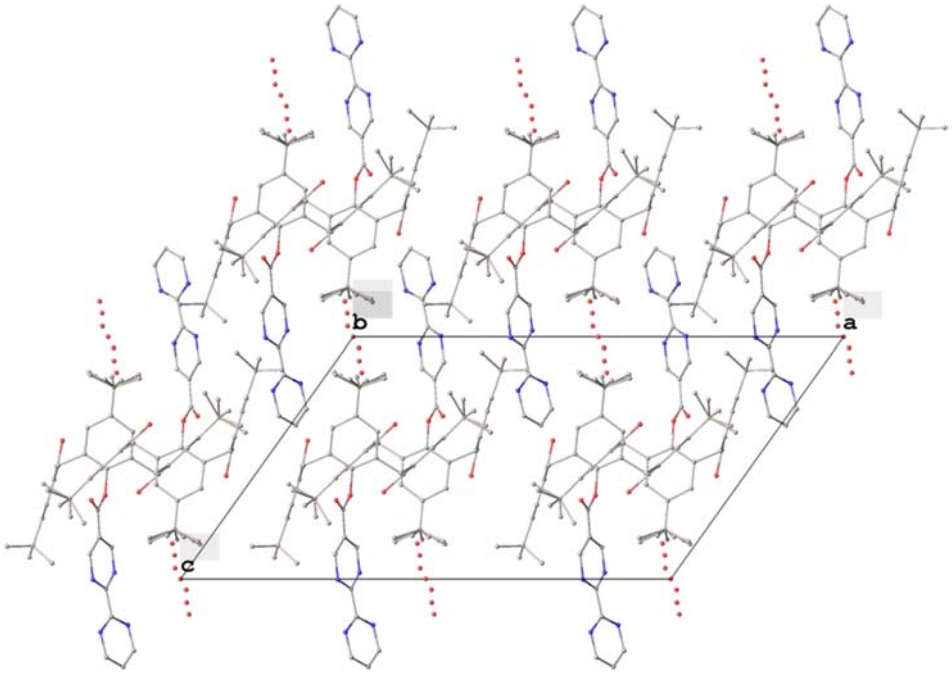
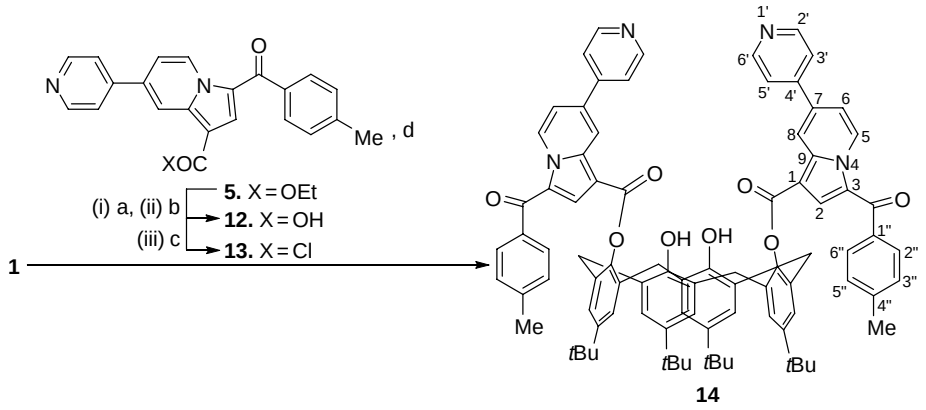


Figure 5. The view of crystal structure of **11** along *b* crystallographic axis.



Scheme 3. Reaction of *tert*-butylcalix[4]arene with indolizinylacyl chloride **13**. (a) MeOH, EtOH, NaOH 4 M, 60°C; (b) citric acid; (c) $(COCl)_2$, DMF, C_6H_6; (d) Et_3N, MeCN, rt.

365 nm). Spectrophotometric measurements were carried out at 25°C in EtOH solution using a Cintra 101 spectrophotometer (GBC Scientific Equipment Pty Ltd, Braeside, Australia) in the range 200–400 nm. All commercially available products were used without further purification unless otherwise specified.

General procedure for preparation of compounds 2–4

Tert-butylcalix[4]arene (1.5 mmol, 1 equiv., 1 g) and TEA (9 mmol, 6 equiv., 1.29 ml for compounds **2** and **4**; 13.5 mmol, 9 equiv., 1.93 ml for compound **3**) were added to 30 ml of anhydrous acetonitrile, and the obtained suspension was stirred under nitrogen at room temperature (rt) for 20 min. Chloroacetyl chloride (7.5 mmol, 5 equiv., 0.61 ml for compound **2**; 12 mmol, 8 equiv., 0.98 ml for compound **3**) or bromoacetyl bromide (7.5 mmol, 5 equiv., 0.67 ml for compound **4**) was added dropwise for 15 min (magnetic stirring) and the resulting mixture was then stirred over night at rt. The solid was collected by filtration to give a powder which was then washed with methanol. The solution was concentrated *in vacuo* and the residue was dissolved in $CHCl_3$ and extracted with saturated solutions of $NaHCO_3$, NaCl and finally water. The organic layer was dried (Na_2SO4), filtered and concentrated *in vacuo*. The residue was mixed with the solid obtained after initial filtration and purified by crystallisation from methanol–chloroform (1:1, *v/v*).

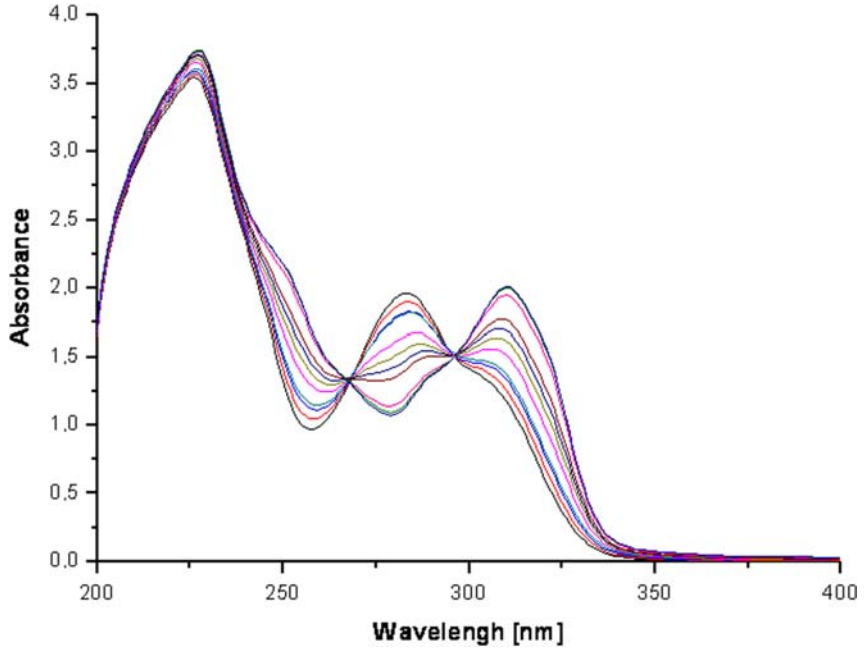


Figure 6. UV–Vis titration curves for diester **10** with Ni^{2+}.

Table 4. Log β values for the complex formation of Co^{2+}, Ni^{2+} and Cu^{2+} and ligand **10s**.

Reaction	Log β[a]	Log β[b]
$Co^{2+} + L = [CoL]^{2+}$	6.8	6.7
$Ni^{2+} + L = [NiL]^{2+}$	6.9	6.9
$Cu^{2+} + L = [CuL]^{2+}$	7.1	7.3

[a] Mole ratio method.
[b] Job method.

General procedure for preparation of compound 6

A solution of pyridine (1.05 mmol, 2.1 equiv., 0.082 g) or ethyl-3-(4-methylbenzoyl)-7-(pyridine-4-yl)-indolizine-1-carboxylate **5** (*12*) (0.40 g) and 5,11,17,23-tetra-*tert*-butyl-25,27-di(chloroacetyloxy)-26,28-dihydroxy-calix[4]arene **2** (0.5 mmol, 1 equiv., 0.39 g) in anhydrous acetonitrile (20 ml) was magnetically stirred for 20 h at reflux. The resulting yellow precipitate was removed by filtration and then washed with acetonitrile. The product was purified by crystallisation ($CHCl_3$: MeOH 3:1, *v/v*).

General procedure for preparation of compound 7

A solution of monoindolizine **5** (*12*) (2.1 mmol, 2.1 equiv., 0.80 g) and 5,11,17,23-tetra-*tert*-butyl-25,27-di(bromoacetyloxy)-26,28-dihydroxy-calix[4]arene **4** (1 mmol, 1 equiv., 0.88 g) in anhydrous acetonitrile (20 ml) was magnetically stirred for 20 h at reflux. The resulting yellow precipitate was removed by filtration and then washed with acetonitrile. The product was purified by crystallisation ($CHCl_3$: MeOH 3:1, *v/v*).

General procedure for preparation of compounds 9

To a solution of 2.2′-dipyridine-4-carboxylic acid or 2.2′-dipyridine-5-carboxylic acid (0.5 mmol, 1 equiv., 0.1 g) in 5 ml of benzene or dichloromethane (DCM) were added 0.127 g (1 mmol, 2 equiv.) of oxalyl chloride and catalytic DMF. After 1 h at rt, the solvent and excess oxalyl chloride were removed *in vacuo* to afford the corresponding 2,2′-dipyridine carbonyl chlorides **9** which were used in the next step without any further purification.

General procedure for preparation of compounds 10–11 and 14

Tert-butylcalix[4]arene (0.3 mmol, 1 equiv., 0.2 g) and TEA (1.8 mmol, 6 equiv., 0.26 ml) were added to 7 ml of anhydrous acetonitrile, and the obtained suspension is stirred under nitrogen at rt for 20 min. 2,2′-Dipyridine-4-carbonyl chloride or 2,2′-dipyridine-5-carbonyl chloride (1.5 mmol, 5 equiv., 0.34 g) or ethyl 3-(4-methylbenzoyl)-7-(pyridine-4-yl)indolizine-1-carbonyl chloride **13** (1.5 mmol, 5 equiv., 0.57 g) suspended in 5 ml of acetonitrile was added dropwise over 15 min (magnetic stirring), and the resulting mixture was then stirred over night at rt. The solid was collected by filtration to give a powder which was then washed with methanol. The solution was concentrated *in vacuo* and the residue was dissolved in $CHCl_3$ and extracted with saturated solutions

of $NaHCO_3$, NaCl and water. The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was mixed with the solid obtained after initial filtration and purified by crystallisation from methanol–chloroform (1:1, *v/v*; for compounds **10** and **11**) or column chromatography using $CHCl_3$:MeOH (9.8:0.2; for compound **14**).

General procedure for preparation of compound 12

Ethyl 3-(4-methylbenzoyl)-7-(pyridine-4-yl) indolizine-1-carboxylate **5** (*12*) (2.1 mmol, 2.1 equiv., 0.80 g) was hydrolysed in EtOH:MeOH:4 M KOH (25:25:8, 150 ml) at 60°C for 3 h. After cooling, the reaction mixture was poured into ice water (100 ml) and acidified by slow addition of 10% citric acid until pH 6. The resulted solid was separated by filtration and dried to give 3-(4-methylbenzoyl)-7-(pyridine-4-yl)indolizine-1-carboxylic acid **12** as a yellow solid, which was used in the next step without any further purification due to the poor solubility in common solvents.

General procedure for preparation of compound 13

To a solution of 3-(4-methylbenzoyl)-7-(pyridine-4-yl)indolizine-1-carboxylic acid (0.5 mmol, 1 equiv., 0.1 g) in 5 ml of benzene or dry DCM were added 0.071 g (1 mmol, 2 equiv.) of oxalyl chloride and catalytic amount of DMF. After 1 h at rt, the solvent and excess oxalyl chloride were removed *in vacuo* to afford the corresponding indolizinylacyl chloride **13**, which was used in the next step without any further purification.

5,11,17,23-Tetra-tert-*butyl-25,27-bis-(chloroacetyloxy)-26,28-dihydroxy-calix[4]arene* ***2***

Compound **2** was obtained as white powder in 75% yield (0.92 g), mp 309–311°C; ^{1}H NMR ($CDCl_3$): δ 1.14 (s, 18H, *t*Bu-H), 1.31 (s, 18H, *t*Bu-H), 3.68 (d, 4H, $ArCH_2Ar$, $J = 15.2$ Hz), 3.76 (d, 4H, $ArCH_2Ar$, $J = 15.2$ Hz), 3.85 (s, 4H, CH_2Cl), 4.45 (s, 2H, OH), 7.00 (s, 4H, Ar-H), 7.09 (s, 4H, Ar-H); ^{13}C NMR ($CDCl_3$): 31.1 ($6 \times CH_3$), 31.7 ($6 \times CH_3$), 34.0 ($2 \times C(CH_3)_3$), 34.3 ($2 \times C(CH_3)_3$), 35.7 ($4 \times ArCH_2Ar$), 40.3 ($2 \times CH_2Cl$), 125.4 ($4 \times$ Ar-CH), 126.7 ($4 \times$ Ar-Cq), 126.9 ($4 \times$ Ar-CH), 131.8 ($4 \times$ Ar-Cq), 142.5 ($2 \times$ Ar-Cq), 144.3 ($2 \times$ Ar-Cq), 149.8 ($2 \times$ Ar-Cq-OCOR), 150.9 ($2 \times$ Ar-Cq-OH), 164.7 ($2 \times$ C═O); IR (KBr, cm^{-1}): 3512, 2952, 1763, 1461, 1168, 1138, 1108; MS (ESI^+): 823 ($M + Na^+$), 839 ($M + K^+$); anal. calcd. for $C_{48}H_{58}Cl_2O_6$: C, 71.90; H, 7.29. Found: C, 71.81; H, 7.20%.

5,11,17,23-Tetra-tert-*butyl-25,26,27-tris-(chloroacetyloxy)-28-hydroxy-calix[4]arene* ***3***

Compound **3** was obtained as colourless crystals in 79% yield (1.07 g), mp 326–328°C. ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 18H, *t*Bu-H), 1.38 (s, 9H, *t*Bu-H), 1.42 (s, 9H, *t*Bu-H), 3.29 (d, 2H, $ArCH_2Ar$, $J = 14$ Hz), 3.54(d, 2H, $ArCH_2Ar$, $J = 14$ Hz), 3.72 (d, 2H, $ArCH_2Ar$, $J = 16.8$ Hz), 3.74 (d, 2H, $ArCH_2Ar$, $J = 16.8$ Hz), 3.83 (s, 1H, OH), 3.99 (s, 2H, CH_2Cl), 4.29 (d, 2H, CH_2Cl, $J = 14$ Hz), 4.31(d, 2H, CH_2Cl, $J = 14$ Hz), 6.70 (d, 2H, Ar-H, $J = 2.4$ Hz), 7.07 (d, 2H, Ar-H, $J = 2.4$ Hz), 7.16 (s, 2H, Ar-H), 7.25 (s, 2H, Ar-H); ^{13}C NMR ($CDCl_3$): 31.1 ($6 \times CH_3$, $2 \times ArCH_2Ar$), 31.5 ($3 \times CH_3$), 31.7 ($3 \times CH_3$), 32.1 ($2 \times C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 36.7 ($2 \times ArCH_2Ar$), 40.5 (CH_2Cl), 40.9 ($2 \times CH_2Cl$), 126.2 ($2 \times$ Ar-CH), 126.31 ($2 \times$ Ar-CH), 126.33 ($2 \times$ Ar-CH), 126.5 ($2 \times$ Ar-CH), 128.3 ($2 \times$ Ar-Cq), 131.4 ($2 \times$ Ar-Cq), 131.6 ($2 \times$ Ar-Cq), 133.9 ($2 \times$ Ar-Cq), 143.2 (Ar-Cq), 143.4 ($2 \times$ Ar-Cq), 144.7 (Ar-Cq), 149.0 ($2 \times$ Ar-Cq-OCOR), 149.8 ($2 \times$ Ar-Cq-OCOR), 152.1 (Ar-Cq-OH), 165.7 ($2 \times$ C═O), 166.6 (C═O); IR (KBr, cm^{-1}): 3522, 2951, 1768, 1477, 1153, 871; MS (ESI^+): 899 ($M + Na^+$), 915 ($M + K^+$); anal. calcd. for $C_{50}H_{59}Cl_3O_7$: C, 68.37; H, 6.77. Found: C, 68.29; H, 6.85.

5,11,17,23-Tetra-tert-*butyl-25,27-di(bromoacetyloxy)-26,28-dihydroxy-calix[4]arene* ***4***

Compound **4** was obtained as white powder in 71% yield (0.97 g), mp 316–319°C; ^{1}H NMR ($CDCl_3$): δ 1.06 (s, 18H, *t*Bu-H), 1.33 (s, 18H, *t*Bu-H), 3.54 (d, 4H, $ArCH_2Ar$, $J = 14.8$ Hz), 3.83 (d, 4H, $ArCH_2Ar$, $J = 14.8$ Hz), 3.87 (s, 4H, CH_2Br), 4.74 (s, 2H, OH), 6.98 (s, 4H, Ar-H), 7.06 (s, 4H, Ar-H); ^{13}C NMR ($CDCl_3$): 25.26 ($2 \times CH_2Br$), 31.0 ($6 \times CH_3$), 31.7 ($6 \times CH_3$), 34.0 ($2 \times C(CH_3)_3$), 34.4 ($2 \times C(CH_3)_3$), 34.4 ($4 \times ArCH_2Ar$), 125.4 ($4 \times$ Ar-CH), 127.0 ($4 \times$ Ar-Cq), 126.5 ($4 \times$ Ar-CH), 131.7 ($4 \times$ Ar-Cq), 142.5 ($2 \times$ Ar-Cq), 144.4 ($2 \times$ Ar-Cq), 149.5 ($2 \times$ Ar-Cq-OCOR), 150.6 ($2 \times$ Ar-Cq-OH), 164.9 ($2 \times$ C═O); IR (KBr, cm^{-1}): 3128, 2952, 2865, 1764, 1479, 1200, 745; anal. calcd. for $C_{48}H_{58}Br_2O_6$: C, 64.72; H, 6.56. Found: C, 64.66; H, 6.66.

5,11,17,23-Tetra-tert-*butyl-25,26-bis-(chloroacetyloxy)-27,28-dihydroxy-calix[4]arene* ***6***

Compound **6** was obtained as white powder in 75% yield (0.29 g), mp 332–334°C; ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 18H, *t*Bu-H), 1.32 (s, 18H, *t*Bu-H), 2.75 (d, 2H, $ArCH_2Ar$, $J = 16.0$ Hz), 3.17 (d, 2H, $ArCH_2Ar$, $J = 16.0$ Hz), 3.31 (d, 1H, $ArCH_2Ar$, $J = 14.0$ Hz), 3.46 (d, 1H, $ArCH_2Ar$, $J = 14$ Hz), 3.54 (d, 1H, $ArCH_2Ar$, $J = 14.0$ Hz), 3.87 (d, 2H, CH_2Cl, $J = 16.8$ Hz), 4.06 (d, 2H, CH_2Cl, $J = 16.8$ Hz), 4.14 (d, 1H, $ArCH_2Ar$, $J = 14.0$ Hz), 5.98 (s, 2H, OH), 6.98 (d, 2H, Ar-H, $J = 2$ Hz), 7.15 (d, 2H, Ar-H, $J = 2$ Hz), 7.23 (d, 2H, Ar-H, $J = 2$ Hz), 7.28 (d, 2H, Ar-H, $J = 2$ Hz); ^{13}C NMR ($CDCl_3$): 31.2 ($6 \times CH_3$), 31.6 ($6 \times CH_3$), 34.1 ($2 \times C(CH_3)_3$), 34.5 ($2 \times C(CH_3)_3$), 37.6 ($4 \times ArCH_2Ar$), 39.6 ($2 \times CH_2Cl$), 125.4 ($2 \times$ Ar-Cq),

125.8 (2 × Ar-CH), 125.9 (2 × Ar-CH), 126.1 (2 × Ar-CH), 126.8 (2 × Ar-CH), 128.2 (2 × Ar-Cq), 130.5 (2 × Ar-Cq), 133.8 (2 × Ar-Cq), 144.2 (2 × Ar-Cq), 144.3 (2 × Ar-Cq), 149.7 (2 × Ar-Cq-OCOR), 149.8 (2 × Ar-Cq-OH), 166.0 (2 × C═O); IR (KBr, cm^{-1}): 3492, 2960, 1773, 1482, 1202, 1143; MS (ESI^+): 823 ($M + Na^+$); anal. calcd. for $C_{48}H_{58}Cl_2O_6$: C, 71.90; H, 7.29. Found: C, 71.85; H, 7.27.

5,11,17,23-Tetra-tert-*butyl-25,27-bis[4-[1-(ethoxycarbonyl)-3-(4-methylbenzoyl) indolizin-7-yl]-1-(2-acetyloxy)pyridinium]-26,28-dihydroxy-calix[4]arene dibromide* ***7***

Compound **7** was obtained as yellow powder in 69% yield (0.86 g), mp 280–282°C; ^1H NMR ($CDCl_3$): δ 1.12 (s, 18H, *t*Bu-H), 1.18 (s, 18H, *t*Bu-H), 1.42 (t, 6H, 2 × CH_2CH_3, $J = 7.2$ Hz), 2.47 (s, 6H, 2 × CH_3), 3.42 (d, 4H, $ArCH_2Ar$, $J = 13.2$ Hz), 4.38 (d, 4H, $ArCH_2Ar$, $J = 13.2$ Hz), 4.42 (q, 4H, 2 × CH_2CH_3, $J = 7.2$ Hz), 6.96 (s, 4H, Ar-H), 7.05 (s, 4H, Ar-H), 7.11 (s, 4H, 2 × CH_2N), 7.35 (ad, 6H, 2 × H-3″, 2 × H-5″, 2 × H-6′), 7.63 (s, 2H, OH), 7.76 (d, 4H, 2 × H-2″, 2 × H-16″, $J = 7.6$ Hz), 7.90 (s, 2H, 2 × H-2′), 8.25 (as, 4H, 2 × H-2, 2 × H-6), 8.87 (as, 2 × H-8′), 9.78 (as, 4H, 2 × H-3, 2 × H-5), 10.02 (d, 2H, 2 × H-5′, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$): 14.6, 21.7, 31.4, 31.2, 31.8, 32.6, 33.8, 34.0, 34.3, 60.7, 109.7, 112.1, 119.9, 124.0, 125.5, 128.9, 129.3, 129.9, 130.6, 132.0, 136.3, 138.0, 143.0, 144.4, 147.2, 163.4 (2 × COOEt), 185.8 (2 × C═O); IR (KBr, cm^{-1}): 3186, 2958, 1758, 1701, 1618, 1202; anal. calcd. for $C_{96}H_{98}N_4O_{12}$: C, 69.47; H, 5.95; N, 3.38. Found: C, 69.39; H, 5.97; N, 3.35.

5,11,17,23-Tetra-tert-*butyl-25,27-bis-[2-(pyrid-2′-yl)pyridin-4-carbonyloxy]-26,28-dihydroxy-calix[4]arene* ***10***

Compound **10** was obtained as pale pink crystals in 70% yield (0.22 g), mp 305–307°C; ^1H NMR ($CDCl_3$): δ 1.02 (s, 18H, *t*Bu-H), 1.17 (s, 18H, *t*Bu-H), 3.54 (d, 4H, $ArCH_2Ar$, $J = 14.4$ Hz), 3.97 (d, 4H, $ArCH_2Ar$, $J = 14.4$ Hz), 5.09 (s, 2H, OH), 6.94 (s, 4H, Ar-H), 7.04 (s, 4H, Ar-H), 7.26 (m, 2H, H-5′, $CDCl_3$ overlapped signal), 7.80 (dt, 2H, H-4′, $J = 7.6$ and 1.6 Hz), 8.03 (dd, 2H, H-5, $J = 4.8$ and 1.2 Hz), 8.40 (d, 2H, H-3′, $J = 8.0$ Hz), 8.59 (d, 2H, H-6′, $J = 4.4$ Hz), 8.72 (d, 2H, H-6, $J = 4.8$ Hz), 9.47 (s, 2H, H-3); ^{13}C NMR ($CDCl_3$): 31.0 (6 × CH_3), 31.5 (6 × CH_3), 33.3 (4 × CH_2), 33.9 (2 × $C(CH_3)_3$), 34.1 (2 × $C(CH_3)_3$), 121.3 (2 × C-3), 121.4 (2 × C-3′), 122.7 (2 × C-5), 124.2 (2 × C-5′), 125.7 (4 × Ar-CH), 126.3 (4 × Ar-CH), 127.8 (4 × Ar-Cq), 131.7 (4 × Ar-Cq), 136.9 (2 × C-4′), 137.7 (2 × Ar-Cq), 142.9 (2 × Ar-Cq), 143.1 (2 × C2), 149.2 (2 × C4), 149.4 (2 × C6′), 150.3 (2 × C6), 150.4 (2 × Ar-C-OH), 154.9 (2 × C2′), 157.8 (2 × Ar-Cq-OCOR), 163.8 (2 × C═O); IR (KBr, cm^{-1}): 3568, 2952, 2866, 1740, 1458, 1224, 1209, 754; MS (ESI^+): 1012 ($M + H^+$), 1035 ($M + Na^+$); anal. calcd. for $C_{66}H_{68}N_4O_6$: C, 78.23; H, 6.76; N, 5.53. Found: C, 78.18; H, 6.83; N, 5.55.

5,11,17,23-Tetra-tert-*butyl-25,27-bis-[2-(pyrid-2′-yl)pyridin-5-carbonyloxy]-26,28-dihydroxy-calix[4]arene* ***11***

Compound **11** was obtained as pale yellow crystals in 77% yield (0.24 g), mp 284–287°C; ^1H NMR ($CDCl_3$): δ 1.07 (s, 18H, *t*Bu-H), 1.10 (s, 18H, *t*Bu-H), 3.58 (d, 4H, $ArCH_2Ar$, $J = 14.4$ Hz), 3.92 (d, 4H, $ArCH_2Ar$, $J = 14.4$ Hz), 4.95 (s, 2H, OH), 6.98 (s, 4H, Ar-H), 7.01 (s, 4H, Ar-H), 7.27 (m, 2H, H-5′, $CDCl_3$ overlapped signal), 7.50 (dt, 2H, H-4′, $J = 7.6$ and 0.8 Hz), 8.43 (d, 2H, H-3′, $J = 8.0$ Hz), 8.55 (ad, 2H, H-6′, $J = 4.4$ Hz), 8.66 (dd, 2H, H-3, $J = 8.4$ and 1.6 Hz), 8.74 (d, 2H, H-4, $J = 8.4$ Hz), 9.47 (as, 2H, H-6); ^{13}C NMR ($CDCl_3$): 31.1 (6 × CH_3), 31.4 (6 × CH_3), 33.8 (2 × $C(CH_3)_3$), 34.1 (2 × $C(CH_3)_3$), 34.2 (4 × $ArCH_2Ar$), 121.3 (2 × C-4), 122.3 (2 × C-3′), 124.3 (2 × C-5′), 124.6 (2 × C-5), 125.7 (4 × Ar-CH), 126.5 (4 × Ar-CH), 127.5 (4 × Ar-Cq), 132.1 (4 × Ar-Cq), 136.9 (2 × C-4′), 138.8 (2 × Ar-Cq), 144.7 (2 × Ar-Cq), 143.5 (2 × C2), 149.2 (2 × C6′), 150.5 (2 × Ar-C-OH), 151.3 (2 × C6), 155.0 (2 × C2′), 160.2 (2 × Ar-Cq-OCOR), 163.8 (2 × C═O). IR (KBr, cm^{-1}): 3533, 2959, 1728, 1591, 1480, 1177, 1117, 757; MS (ESI^+): 1012 ($M + H^+$), 1035 ($M + Na^+$); anal. calcd. for $C_{66}H_{68}N_4O_6$: C, 78.23; H, 6.76; N, 5.53. Found: C, 78.18; H, 6.82; N, 5.55.

3-(4-Methylbenzoyl)-7-(pyridine-4-yl)indolizine-1-carboxylic acid ***12***

Compound **12** was obtained as yellow solid in 90% yield (0.67 g), mp 284–286°C; IR (KBr, cm^{-1}): 3427 (bb), 2922, 1698, 1606, 1213.

5,11,17,23-Tetra-tert-*butyl-25,27-bis-[3-(4-methylbenzoyl)-7-(pyridin-4-yl)indolizine-1-carbonyloxy]-26,28-dihydroxy-calix[4]arene* ***14***

Compound **14** was obtained as yellow powder in 50% yield (0.20 g), mp >360°C; ^1H NMR ($CDCl_3$): δ 0.94 (s, 18H, *t*Bu-H), 1.35 (s, 18H, *t*Bu-H), 2.15 (s, 6H, 2 × CH_3) 3.31 (d, 2H, $ArCH_2Ar$, $J = 12.4$ Hz), 3.62 (d, 2H, $ArCH_2Ar$, $J = 10.4$ Hz), 4.04 (d, 2H, $ArCH_2Ar$, $J = 12.4$ Hz), 4.28 (d, 2H, $ArCH_2Ar$, $J = 10.4$ Hz), 6.17 (s, 2H, OH), 6.42 (as, 4H, 2 × H-3″, 2 × H-5″), 6.80 (bs, 2H, Ar-H), 6.88 (bs, 2H, Ar-H), 7.12 (bs, 2H, Ar-H), 7.24 (bs, 2H, Ar-H), 7.37 (d, 4H, 2 × H-2″, 2 × H-6″, $J = 5.6$ Hz), 7.56 (as, 2H, 2 × H-6), 7.76 (as, 4H, H-3′, H-5′), 8.17 (s, 2H, 2 × H-2), 8.83 (ad, 6H, 2 × H-2′, 2 × H-6′, 2 × H-8), 10.17 (as, 2H, 2 × H-5); ^{13}C NMR ($CDCl_3$):

21.5 (2 × CH_3), 30.9 (6 × CH_3), 31.4 (2 × CH_2), 31.7 (6 × CH_3), 31.8 (2 × CH_2), 34.0 (4 × $C(CH_3)_3$), 113.9 (2 × C-6), 116.7 (2 × C-8), 104.6 (2 × Ar-Cq), 121.1 (2 × C-3′, 2 × C-5′), 123.0 (2 × Ar-Cq), 125.4 (4 × Ar-CH), 125.5 (4 × Ar-CH), 125.9 (2 × Ar-Cq), 127.9 (2 × C-3″, 2 × C-5″), 128.4 (2 × C-2), 129.1 (2 × C-2″, 2 × C-6″), 129.8 (2 × C-5), 131.2 (2 × Ar-Cq), 135.5 (2 × Ar-Cq), 137.0 (2 × Ar-Cq), 140.4 (2 × Ar-Cq), 141.6 (2 × Ar-Cq), 142.1 (2 × Ar-Cq), 142.8 (2 × Ar-Cq), 145.0 (2 × Ar-Cq), 148.8 (2 × Ar-Cq), 150.1 (2 × Ar-Cq), 150.8 (2 × C-2′, 2 × C-6′), 161.9 (2 × COOR), 184.4 (2 × C═O); IR (KBr, cm^{-1}): 3547, 2957, 2868, 1720, 1619, 1184, 1167, 1070; anal. calcd. for $C_{88}H_{84}N_4O_8$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.68; H, 6.44; N, 4.26.

X-ray crystallography

X-ray data for compound **3** were collected at the Aarhus University using an Agilent SuperNova diffractometer (Agilent Technologies, Santa Clara, USA) equipped with an Atlas CCD detector. The crystal was cooled to 100K using Oxford Cryosystems Cryostream 700 (Oxford Cryosystems, Oxford, UK). Crystallographic measurements for **10** and **11** were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer (Oxford Diffraction Limited, Abingdon, UK) using graphite-monochromated Mo-Kα radiation. The crystals were placed 40 mm from the CCD detector. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction (Oxford Diffraction Limited, Abingdon, UK) (*16*). All structures were solved by direct methods using SHELXS-97 (*17*) and refined by full-matrix least squares on Fo^2 with SHELXL-97 (*17*) with anisotropic displacement parameters for non-hydrogen atoms. All H atoms attached to carbon were introduced in idealised positions (dCH = 0.96 Å) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom. Positional parameters of the H attached to O atoms were obtained from difference Fourier syntheses and verified by the geometric parameters of the corresponding hydrogen bonds. All carbon atoms of *tert*-Bu groups in structures **3** and **11** presented too large thermal ellipsoids, so that disordered models in combination with the available tools (PART, DFIX and SADI) of SHELXL97 were applied in order to better fit the electron density. The same approach was applied in order to fit two disordered positions of BiPy fragment in structure **11**. The main crystallographic data together with refinement details are summarised in Table 5.

CCDC-864665 (**3**), CCDC-864663 (**10**) and CCDC-864664 (**11**) contain the supplementary crystallographic data for this contribution. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data

Table 5. Crystallographic data, details of data collection and structure refinement parameters for compounds **3**, **10** and **11**.

Empirical formula	$C_{50}H_{59}Cl_3O_7$ (**3**)	$C_{66}H_{68}N_4O_6$ (**10**)	$C_{132}H_{142}N_8O_{14.8}$ (**11**)
Molecular weight, g/mol	878.32	1013.24	2077.34
Temperature (K)	100	200	293
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	*Pnma*	*C2/m*
a (Å)	10.4314 (6)	19.9520 (10)	25.613 (3)
b (Å)	13.3835 (10)	13.7058 (10)	17.9021 (15)
c (Å)	17.7391 (10)	21.7492 (12)	15.5182 (17)
α (°)	69.535 (6)	90	90
β (°)	87.247 (5)	90	125.531 (16)
γ (°)	84.853 (5)	90	90
V (Å^3)	2310.5 (3)	5947.5 (6)	5790.6 (10)
Z	2	4	2
D_{calc} (g/cm^3)	1.262	1.132	1.191
μ (mm^{-1})	0.249	0.072	0.078
θ_{min}, θ_{max} (°)	2.29–26.00	2.99–25.05	3.00–26.00
Crystal size (mm)	0.21 × 0.08 × 0.05	0.20 × 0.20 × 0.15	0.10 × 0.10 × 0.05
Reflections collected/unique	34892/9069 (R_{int} = 0.0755)	17115/5183 (R_{int} = 0.0678)	14129/5872 (R_{int} = 0.0768)
Data/restraints/parameters	9069/0/553	5183/66/361	5872/46/407
R_1 ($I > 2\sigma(I)$)[a]	0.0776	0.0860	0.0840
wR_2 ($I > 2\sigma(I)$)[b]	0.1790	0.2018	0.1014
R_1 (all data)[a]	0.1345	0.1686	0.2602
wR_2 (all data)[b]	0.2027	0.2364	0.1322
GOF[c]	1.008	1.007	1.031
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e/Å^3)	0.485 and −0.455	0.432 and −0.406	0.418 and −0.220

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.ca.ac.uk).

Acknowledgements

This study was supported by the National Council for Research in Higher Education Institutions (CNCSIS), Ministry of Education, Research and Innovation, Romania, through the IDEI Grant No. 2023/2008, European Regional Development Fund, Sectoral Operational Programme 'Increase of Economic Competitiveness,' Priority Axis 2 (SOP IEC-A2-O2.1.2-2009-2, ID 570, COD SMIS CSNR: 12473, Contract 129/2010-POLISILMET) and European Union's Seventh Framework Programme (FP7/2007-2013) under agreement 264115 – STREAM. Authors are also grateful to Dr Jacob Overgaard, Aarhus University, for structure determination of compound **3**.

References

(1) (a) Gutsche, C.D. *Calixarenes Revisited*, *Monographs in Supramolecular Chemistry*; Stoddart, J.F., Ed.; The Royal Society of Chemistry: Cambridge, 1998; (b) Asfari, Z.V.; Bohmer, V.; Harrowfield, J.M., Vicens, J.; Eds.; *Calixarenes 2001*; Kluwer Academic Publishers: Dordrecht, 2001; (c) Vicens, J.Z.; Asfari, Z.; Harrowfield, J.M.; Eds.; *Calixarenes 50th Anniversary: Commemorative Issue*; Kluwer Academic Publishers: Dordrecht, 1994; (d) Vicens, J.; Bohmer, V.; Eds.; *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer Academic Publishers: Dordrecht, 1991; (e) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713–1734; (f) Bohmer, V. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713–745.

(2) (a) Sémeril, D.; Matt, D.; Toupet, L. *Chem. Eur. J.* **2008**, *14*, 7144–7155; (b) Monnereau, L.; Sémeril, D.; Matt, D. *Eur. J. Org. Chem.* **2010**, 3068–3073; (c) Lejeune, M.; Jeunesse, C.; Matt, D.; Sémeril, D.; Peruch, F.; Toupet, L.; Lutz, P.J. *Macromol. Rapid Commun.* **2006**, *27*, 865–870; (d) Sémeril, D.; Jeunesse, C.; Matt, D.*C. R. Chim.* **2008**, *11*, 583–594.

(3) (a) Kumar, S.; Luxami, V.; Singh, H. Conjugates of Calixarenes and Heterocycles in the Design of Newer Chemical Entities. In *Advances in Heterocycles Chemistry*: Katritzky, A.; Ed.; Elsevier: San Diego, California, USA, 2009; Vol. 97; (b) Rondelez, Y.; Bertho, G.; Reinaud, O. *Angew. Chem. Int. Ed.* **2002**, *41*, 1044–1046.

(4) Izzet, G.; Douziech, B.; Prange, T.; Tomas, A.; Jabin, I.; Le Mest, Y.; Reinaud, O. *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 6831–6836.

(5) (a) Pellet-Rostaing, S.; Regnouf-de-Vains, J.B.; Lamartine, R. *Tetrahedron Lett*. **1996**, *37*, 5889–5892; (b) Pellet-Rostaing, S.; Regnouf-de-Vains, J.B.; Lamartine, R., Meallier P.; Guittonneau, S.; Fenet, B. *Helv. Chim. Acta* **1997**, *80*, 1229–1243; (c) Talanov, V.S.; Roper, E.D.; Buie, N.M.; Talanova, G.G. *Tetrahedron Lett*. **2007**, *48*, 8022–8025; (d) Chang, K.C.; Senthivelan, A.; Chung, W.S. *Org. Lett*. **2007**, *9*, 3363–3366.

(6) (a) Regnouf-de-Vains, J.B.; Lamartine, R. *Tetrahedron Lett*. **1996**, *37*, 6311–6314; (b) Creaven, B.S.; Gernon, T.L.; McGinley, J.; Moore, A.M.; Toftlund, H. *Tetrahedron* **2006**, *62*, 9066–9071; (c) Arena, G.; Contino, A.; Longo, E.; Sciotto, D.; Sgarlata, C.; Spoto, G. *Tetrahedron Lett*. **2003**, **44**, 5415–5418; (d) Arena, G.; Bonomo, R.P.; Contino, A.; Sgarlata, C.; Spoto, G.; Tabbi, G. *Dalton Trans*. **2004**, 3205–3211; (e) Arena, G.; Contino, A.; Maccarone, G.; Sciotto, D.; Sgarlata, C. *Tetrahedron Lett*. **2007**, *48*, 8274–8276; (f) Psychogios, N.; Regnouf-de-Vains, J.B. *Tetrahedron Lett*. **2001**, *42*, 2799–2800; (g) Psychogios, N.; Regnouf-de-Vains, J.B. *Tetrahedron Lett*. **2002**, *43*, 77–80; (h) Mourer, M.; Regnouf-de-Vains, J.B. *Tetrahedron Lett*. **2006**, *47*, 1895–1899; (i) Regnouf-de-Vains, J.B.; Lamartine, R.; Fenet, B.; Bavoux, C.; Thozet, A.; Perrin, M. *Helv. Chem. Acta* **1995**, *78*, 1607–1619; (j) Pellet-Rostaing, S.J.; Regnouf-de-Vains, B.; Lamartine, R. *Tetrahedron Lett*. **1995**, *36*, 5745–5748; (k) Regnouf-de-Vains, J.B.; Lamartine, R. *Helv. Chem. Acta* **1994**, *77*, 1817–1824; (l) Beer, P.D.; Martin J.P.; Drew, M.G.B. *Tetrahedron* **1992**, *48*, 9917–9928.

(7) (a) Sabbatini, N.; Guardigli, M.; Lehn, J.M. *Coord. Chem. Rev.* **1993**, *123*, 201–228; (b) Balzani, V.; Credi, A.; Venturi, M. *Coord. Chem. Rev.* **1998**, *171*, 3–16.

(8) (a) Arena, G.; Contino, A.; Longo, E.; Sgarlata, C.; Spoto, G.; Zito, V. *Chem. Comm*. **2004**, 1812–1813; (b) Arena, G.; Bonomo, R.P.; Contino, A.; Sgarlata, C.; Spoto, G.; Tabbi, G. *Dalton Trans*. **2004**, 3205–3211.

(9) Gutsche, C.D. *Calixarenes, An Introduction*; The Royal Society of Chemistry: Cambridge, 2008; pp 116–118.

(10) (a) See, K.A.; Fronczek, F.R.; Watson, W.H.; Kashyap, R.P.; Gutsche, C.D.J. *Org. Chem*. **1991**, *56*, 7256–7268; (b) Lynch, J.A.; Mestayer, J.J.; Blanda, M.T. *J. Supramol. Chem*. **2001**, 139–145.

(11) Ugozzoli, F.; Andretti, G.D. *J. Incl. Phenom. Mol. Recognit. Chem.* **1992**, *13*, 337–348.

(12) Rotaru, A.; Avram, E.; Druta, I.; Danac, R. *Arkivoc* **2009**, *13*, 287–299.

(13) Jaime, C.; De Mendoza, J.; Prados, P.; Nieto, P.M.; Sanchez, C. *J. Org. Chem.* **1991**, *56*, 3372–3376.

(14) Yoe, J.H.; Harvey, A.E. *J. Am. Chem. Soc.* **1948**, *70*, 648–654.

(15) Job, P. *Ann. Chim.* **1928**, *9*, 113–117.

(16) CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.34.76, **2003**.

(17) Sheldrick, G.M. *Acta Crystallogr.* **2008**, *A64*, 112–122.