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Synthesis of upper rim-double-bridged calix[4]arenes bearing seven membered rings and related compounds†

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Meta/*meta*- and *meta*/*para*-disubstituted organomercury calix[4]arenes in the cone conformation were transformed into corresponding amino derivatives. Acylation and subsequent intramolecular cyclization using the Bischler–Napieralski reaction provided, in the case of the *meta*/*meta*-series, double bridged calixarenes possessing seven membered rings on the upper rim. A similar synthetic strategy applied to *meta*/*para*-isomers allowed for the isolation of monobridged compounds bearing an additional trifluoroacetamido group located distally to seven-membered rings. Both series represent inherently chiral systems, which were successfully resolved using preparative chiral HPLC. The pure enantiomers exhibited a recognition ability towards selected chiral guest molecules as documented by the ^{1}H NMR titration experiments. The absolute configuration of the phenyl-substituted enantiomer (*meta*/*meta*-) was confirmed by single crystal structure determination (X-ray).

Introduction

Calix[n]arenes,[1] a well-known family of macrocyclic oligophenols, possess many properties which make them perfect candidates for the role of building blocks and molecular scaffolds in supramolecular chemistry. Due to their easy multi-gram preparation, simple chemical transformation, well-defined and/or tuneable 3D shapes of the cavity, and very good complexation abilities, these compounds are frequently used in the design of more complex supramolecular systems including various receptors applicable in host–guest chemistry.

Over the years, the chemistry of calix[4]arenes in particular has become well-established, and currently many regioselective transformations of the basic skeleton are available. In this context, while the *para* position of the phenolic moiety is well accessible *via* electrophilic aromatic substitution (nitration,[2] sulfonation,[3] halogenation, Friedel–Crafts reactions,[4] *etc.*), the *meta* positions remained almost unused due to the lack of suitable chemical tools.

Recently we reported direct mercuration of calix[4]arenes leading to *meta*-substituted organomercury derivatives (Fig. 1).[5] This unprecedented regioselectivity enabled transformation of basic skeleton leading to so far inaccessible derivatization patterns. Among them, a direct connection (*via* a single-bond-bridge) between the *meta*-positions of two neighbouring aromatic subunits led to a novel type of the upper-rim bridged calix[4]arenes (Fig. 1, structure **A**).[6] Similarly, organomercurials served as a starting point for the introduction of one-atom bridge, represented by carbonyl group (structure **B**),[7] or even two-atoms bridge (structure **C**).[8] All the above mentioned compounds exhibit rigid and highly distorted cavities with interesting complexation properties and surprisingly amended

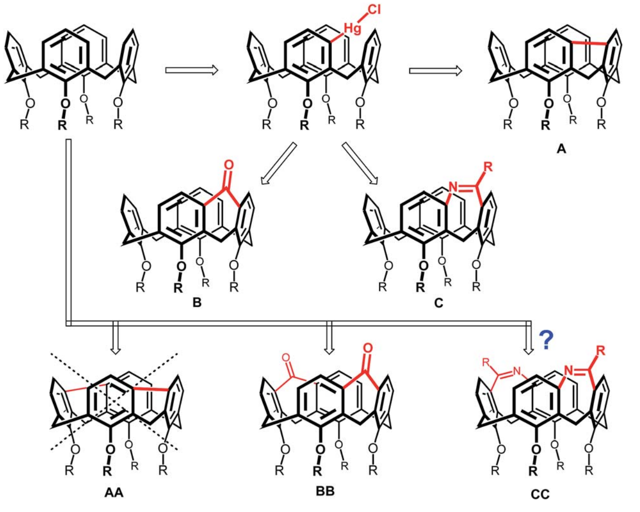

Fig. 1 *Meta*-bridged calix[4]arenes in mono- and di-substituted versions.

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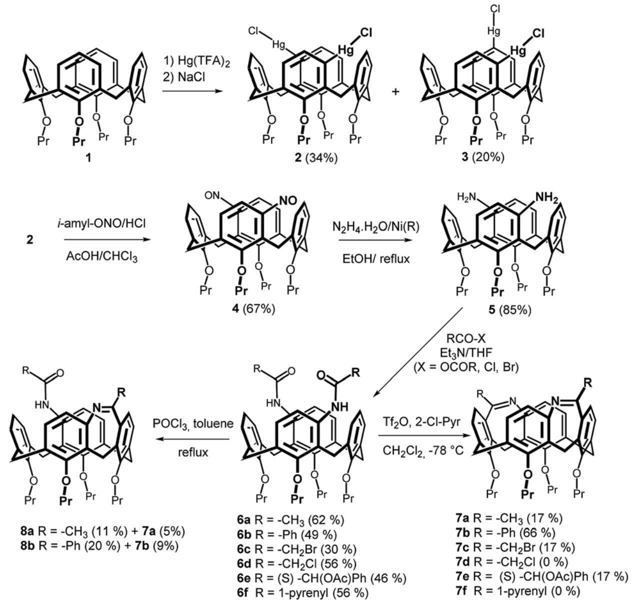
chemical behaviour if compared with the systems without such bridges.

Double *meta*-mercuration[9] should enable the construction of bis-bridged calixarenes. Unfortunately, despite our efforts the corresponding single-bond-bridged isomer **AA** was never isolated. Obviously, two single-bond bridges would impose too high internal strain on the molecule to be stable at common conditions. On the other hand, the isomer **BB** possessing a well-preorganised cavity, was prepared successfully, and showed the ability to form the solid-state complexes using the cooperative effect of various interactions (hydrogen bonding, CH–π interactions, or halogen bonding).[10]

Previously, we have reported the synthesis of bridged calixarenes containing a seven membered ring (structure **C**).[8] These compounds with enlarged and rigidified cavities represent inherently chiral systems potentially useful in the design of chiral receptors. In this paper, we report on our continuous synthetic effort to synthesise analogous bis-*meta*-bridged calix[4]arenes of type **CC** and some related compounds with previously unknown derivatization patterns in calixarene chemistry.

Results and discussion

As shown in Scheme 1, the starting tetrapropoxy-calix[4]arene **1** immobilized in the cone conformation was reacted (using a recently described procedure)[9] with 2.0 equiv. of $Hg(TFA)_2$ providing a mixture of *meta*/*meta*- and *meta*/*para*-organomercury derivatives **2** and **3** in 34% and 20% yield, respectively. The *meta*/*meta*-regioisomer was than transformed into the corresponding nitroso compound **4** by reaction[11] with isopentyl nitrite and HCl at 0 °C. A subsequent reduction of the nitroso groups, accomplished by RANEY® nickel and $N_2H_4 \cdot H_2O$ in refluxing EtOH, provided smoothly the key diamine **5** in 85% yield.



Scheme 1 Synthesis of bridged calix[4]arenes (*meta*/*meta*-isomers).

The acylation step was carried out using various carboxylic acid derivatives (bromide, chloride, anhydride). Thus, reaction with acetic anhydride in THF in the presence of triethylamine (TEA) provided amide **6a** in 62% yield (Scheme 1). A similar reaction using benzoyl chloride or 1-pyrenecarbonyl chloride gave the corresponding amides **6b** and **6f** in 49% and 56% yields, respectively. To achieve intermediates capable of further derivatization, compounds **6c** (30%) and **6d** (56%) bearing the halomethyl groups were prepared from bromoacetyl bromide and chloroacetyl chloride. The introduction of stereogenic centrum into the inherently chiral (racemic) amine **5** should lead to a diastereomeric mixture potentially separable by common chromatographic techniques. Accordingly, compound **5** was acylated by (*S*)-*O*-acetylmandelic acid using standard DCC coupling conditions (THF, 24 h at rt) to provide amide **6e** in 46% yield. Unfortunately, despite our efforts, we were unable to isolate the individual isomers using silica gel chromatography.

The bridging of amidic functions was accomplished using Bischler–Napieralski reaction,[8] which is well-known from the synthesis of various heterocyclic systems. The reaction conditions (**6a**, $POCl_3$ in refluxing toluene) previously applied to monosubstituted derivatives of type **C** (Fig. 1) led to a rather complex reaction mixture. The preparative TLC on silica gel provided low yields of two compounds **7a** (5%) and **8a** (11%). As revealed by HRMS ESI$^+$, compound **7a** represents the expected bis-bridged derivative (m/z = 671.38433 (predicted) *vs.* 671.38404 (found) for $[M + H]^+$), while **8a** is in agreement with a mono-bridged system (m/z = 689.39490 (predicted) *vs.* 689.39445 (found) for $[M + H]^+$). A similar result was obtained for the cyclization step of **6b** where the products **7b** and **8b** were isolated in 9% and 20% yields, respectively.

These findings indicated that the reaction conditions were unsuitable for the efficient formation of the expected product. Moreover, the assumed lower stability of products obviously was not compatible with high reaction temperature. To solve the above-mentioned issues we applied much milder reaction conditions reported[12] for Bischler–Napieralski reaction, where the cyclization is accomplished using a mixture of triflic anhydride and 2-chloropyridine. Indeed, the reaction of **6b** with Tf_2O/2-ClPyr in CH_2Cl_2 at −78 °C afforded the double-bridged product **7b** in 66% yield. On the contrary, the corresponding methyl derivative **7a** was isolated only in 17% yield, and the same yield was obtained for compounds **7c** ($R = CH_2Br$) and **7e** (R = (*S*)-CH_2(OAc)Ph), while the reaction of **6d** and **6f** did not lead to any isolable products.

Although the structures of **7a** and **7b** were normally assigned using the combination of HRMS ESI$^+$ analysis and the $^1H/^{13}C$ NMR spectroscopy, in the case of compound **7c** only MS and ^1H NMR spectra were acquired, as compound did not survive the measurement of ^{13}C NMR spectrum. This trend was even more pronounced for derivative **7e**, where we obtained successfully only the HRMS analysis, while the attempt to acquire the ^1H NMR spectrum was accompanied by very fast decomposition of compound in $CDCl_3$ solution.

The ^1H NMR spectrum ($CDCl_3$) of **7a** showed four doublets at 4.59, 4.53, 3.25 and 2.72 ppm in the 2 : 2 : 2 : 2 ratio possessing typical geminal coupling constants (11.7–12.3 Hz) corresponding to the Ar–CH_2–Ar bridges. Moreover, a singlet of the methyl groups from the bridging moieties (2.49 ppm), together with the four doublets with a characteristic *ortho*-splitting from the aromatic hydrogens, are in a perfect agreement with the splitting pattern expected for the C_2 symmetry of the product.

The single crystal X-ray analysis of the first eluting enantiomer from the resolution of **7b** (enantiomer assigned as **7b_1**, see later for the resolution of the racemate) crystallized in a hexagonal system in the $P6_1$ space group. As follows from Fig. 2, the absolute configuration of enantiomer **7b_1** can be assigned as *P*.[13] The presence of the two bridges resulted in a slightly distorted square shape of the cavity, as can be documented by the length of both diagonals (6.944 and 7.352 Å, Fig. 2a). If we define the main plane of the molecule by the four carbon atoms of the CH_2 bridges, the corresponding interplanar angles Φ with aromatic subunits were 69.46°, 67.33°, 72.95°, and 71.84°, starting clockwise from aromatic unit bearing amidic moiety (Fig. 2a). This reflects the almost ideal C_{4v} symmetry of the phenolic skeleton creating a rigid cavity suitable for the inclusion. Indeed, the crystal packing consists of the infinite inclusion motif (Fig. 2c) where the methyl group of one propyl moiety is immersed into the cavity of neighbouring calixarene. As shown in Fig. 2d, the methyl group exhibits at least seven close contacts between the C–H bonds and aromatic C atoms of the cavity (distances from 2.714 to 2.889 Å). As a result, the crystal packing of enantiomer (*P*) **7b** is formed by infinite right-handed helices possessing *P* chirality. The pitch of this helix (the vertical distance between the two consecutive turns) is 36.443 Å, where one turn consists of six calixarene molecules (Fig. 2e).

The exact structure of isomer **8b** was also confirmed by the single crystal X-ray analysis. Compound crystallized (EtOH/CH_2Cl_2) in the monoclinic system with $P2_1/c$ space group (Fig. 3) and formed a solvate with one molecule of EtOH. The presence of the two-atom-bridge does not impose to the molecule so huge distorsion as observed for a single-bond-bridge derivative of type **A**.[6] It can be demonstrated by almost the same lengths (7.077 Å *vs.* 7.225 Å) of both diagonals (see Fig. 3a). Consequently, the pinched cone conformation, a typical motif of calix[4]arenes in the cone conformation, is substituted here by much more squared shape with the corresponding interplanar angles

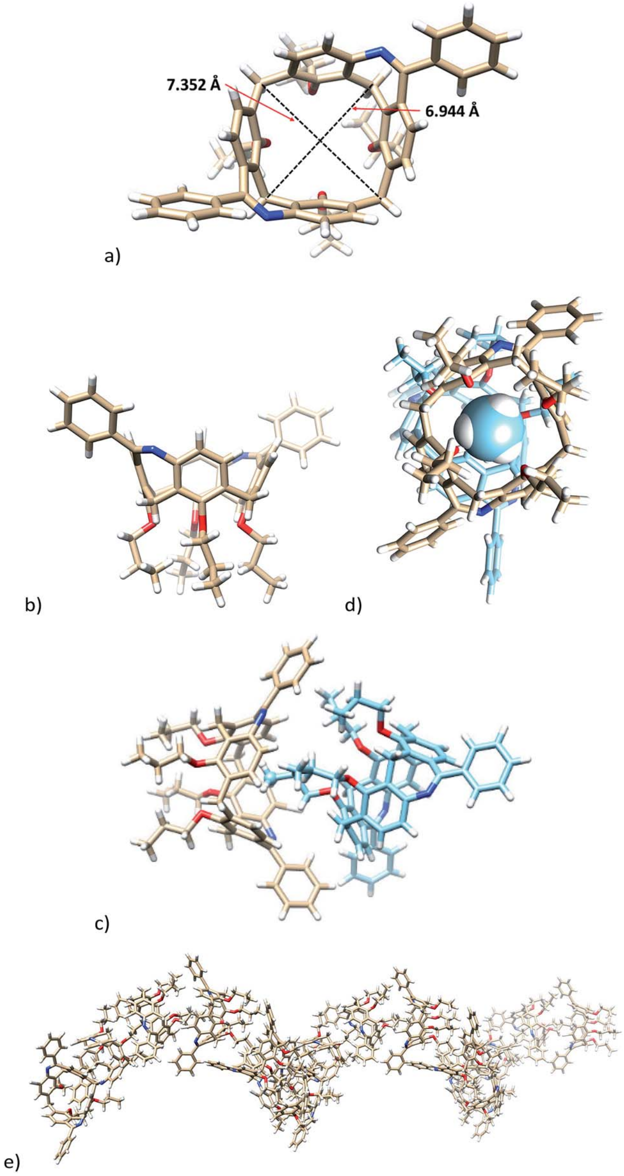


Fig. 2 X-ray structure of (*P*-) enantiomer **7b_1**: (a) top view, (b) side view, (c) inclusion motif with the methyl group immersed into the next cavity. (d) Top view of the same motif (methyl group shown as spacefill). (e) The helical arrangement of the molecules.

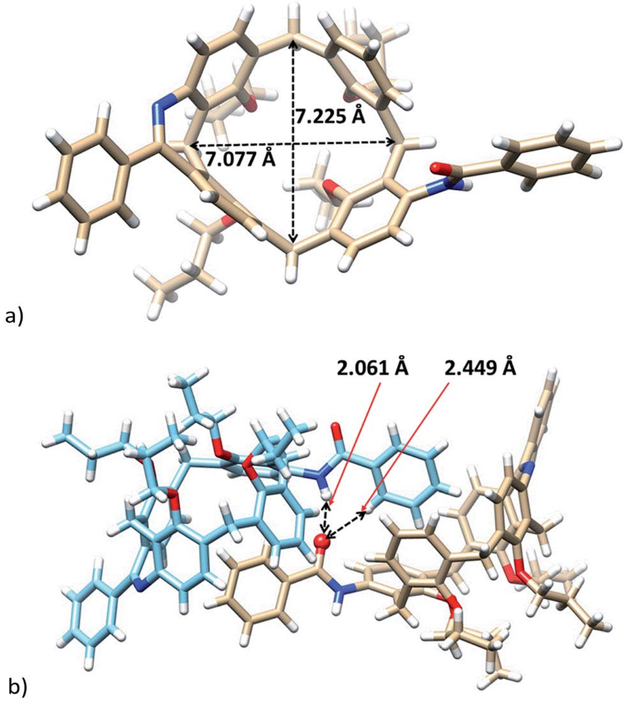


Fig. 3 X-ray structure of **8b** (molecules of solvent (EtOH) were removed for better clarity): (a) top view; (b) hydrogen bonded dimer.

Φ (see above) 43.67°, 79.23°, 65.82°, and 74.47°, starting clockwise from aromatic unit bearing amidic moiety (Fig. 3a).

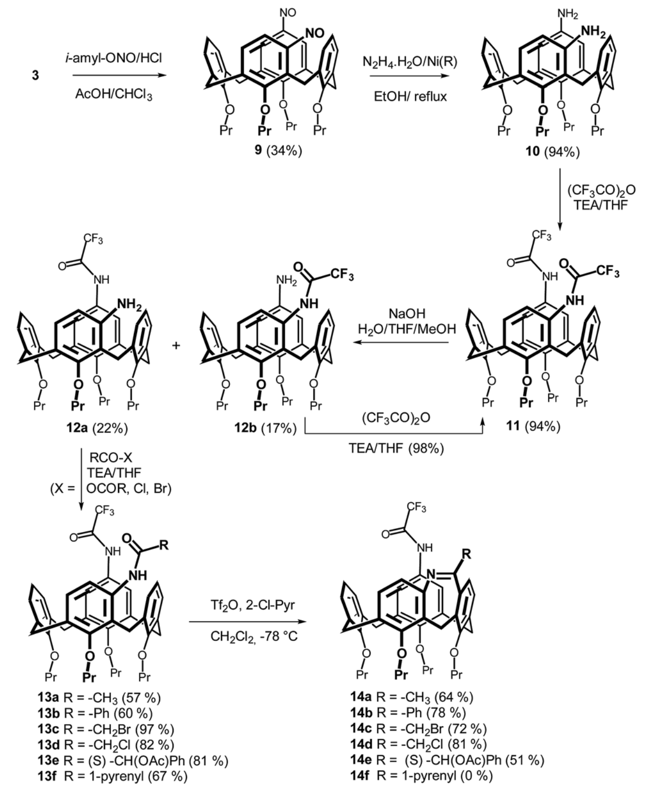
The crystal packing of **8b** shows a dimeric motif held together by hydrogen bonds from the carbonyl group to the amidic proton of the second molecule (C═O⋯H–N, 2.061 Å). The same carbonyl group is bonded simultaneously to the *ortho* hydrogen atom (2.449 Å) thus orienting the phenyl moiety into the cavity of calixarene (Fig. 3b). Interestingly, the individual dimeric assemblies within the crystal lattice are formed by the same enantiomers of **8b**.

The synthesis in *meta*/*para*-series (Scheme 2) started with the corresponding nitroso derivative **9** (obtained from chloromercurio derivative **3**) which was reduced to yield amine **10** in 94% yield. To achieve the intramolecular Bischler–Napieralski reaction (bridging) in the *meta* position, the *para* amino group should be deactivated towards this reaction, otherwise intermolecular reaction cannot be avoided. From our previous study we knew that TFA amide was inert towards the appropriate reaction conditions. Based on this knowledge, the amine **10** was acylated with trifluoroacetic acid anhydride (TFAA)/TEA to provide diamide **11** (94%). A careful hydrolysis of this diamide allowed the isolation of monoamides **12a** (*para*) and **12b** (*meta*) in 22 and 17% yield, respectively. In this context, it is important to carry out this reaction using lower overall conversion (40%), since at higher conversion fully deprotected amine **10** was formed again. Moreover, the *para*-deprotected isomer **12b** can be smoothly recycled to the starting diamide **11** (98% yield) just repeating the acylation step (TFAA/TEA).

The protected *meta*-amine derivative **12a** was then acylated using similar reaction conditions described above for the *meta*/*meta*- compounds. The corresponding amides **13a–13f** were isolated in good to excellent yields (57–97%) depending on the substitution. Finally, the intramolecular bridging was accomplished *via* the reaction with Tf_2O/2-ClPyr at −78 °C in CH_2Cl_2. As can be seen in Scheme 2, the bridged products **14a–14e** were obtained in good yields (51–81%) irrespective of the substitution, the only exception being amide **13f** which did not give any reaction. As expected, the trifluoroacetamido group in the *para* position remained untouched in all the cases.

The structures of the bridged products were confirmed by a combination of NMR and MS techniques. Thus, the HRMS ESI^+ analysis of **14b** showed signals at *m*/*z* = 805.38297 and 827.36360, which were in good agreement with the $[M + H]^+$ (805.38228) and $[M + Na]^+$ (827.36360) cations predicted for the bridged product. The ^1H NMR spectrum of **14b** ($CDCl_3$) revealed the presence of four doublets at 3.32, 3.25, 3.19 and 2.89 ppm (equatorial) and another four doublets at 4.69, 4.61, 4.48 and 4.43 ppm (axial), representing the CH_2 bridges of the calixarene skeleton ($J \cong 12.1$–12.5 Hz). This splitting pattern is consistent with the absence of any symmetry elements in the product (C_s symmetry).

Moreover, the unambiguous structural evidence was obtained by a single crystal X-ray crystallography. Calixarene **14a** crystallized ($EtOH/CH_2Cl_2$) in the monoclinic system with $P\,2_1/c$ space group. As shown in Fig. 4, the shape of the cavity is slightly distorted by the presence of the additional bridge. The length of the short diagonal (the C⋯C distance of two opposite methylene bridges) was 6.918 Å, while the longer diagonal was



Scheme 2 Synthesis of bridged calix[4]arenes (*meta*/*para*-isomers).

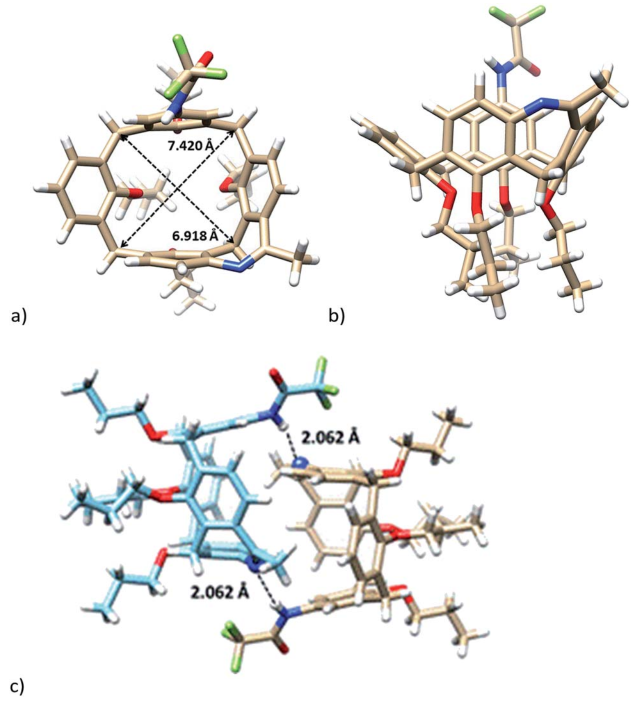


Fig. 4 X-ray structure of **14a**: (a) top view, (b) side view, (c) dimeric structure with hydrogen bonding interactions.

7.420 Å. The corresponding interplanar angles Φ with aromatic subunits (see above) were 82.97°, 62.03°, 83.26°, and 37.46°, starting clockwise from aromatic unit bearing amidic function (Fig. 4a and b). An interesting packing motif is represented (Fig. 4b) by dimeric structure held by $C{=}N\cdots H{-}N$ hydrogen bond (2.062 Å).

Chiral separation of **7b** was performed using an automated preparative system Autopurification (Waters, USA) consisting of a binary pump module, PDA detector, column manager and fraction collector with separated fluidic ways for preparative and analytical mode. The suitable conditions allowing for efficient enantioseparation were first proven on the analytical scale using chiral polysaccharide column ChiralArt Amylose-SA (250 × 4.6 mm ID, 5 μm). In preparative mode, a polysaccharide column Chiralpak IA (250 × 20 mm ID, 5 μm) was employed using the optimum mobile phase heptane/propan-2-ol (9/1, v/v) with diethylamine 0.1% as a basic additive (Fig. 5a). The enantiomeric character of the separated fractions **7a_1** and **7a_2** was verified with ECD spectroscopy, which showed the typical mirror images (Fig. 5b). The optical purity of both enantiomers was found to be >99.5% ee (see ESI†).

Compound **14b** was also successfully separated on a preparative column using almost the same conditions as mentioned above (hexane/propan-2-ol (9/1, v/v) with diethylamine 0.05%) to yield two enantiomers **14b_1** and **14b_2**.

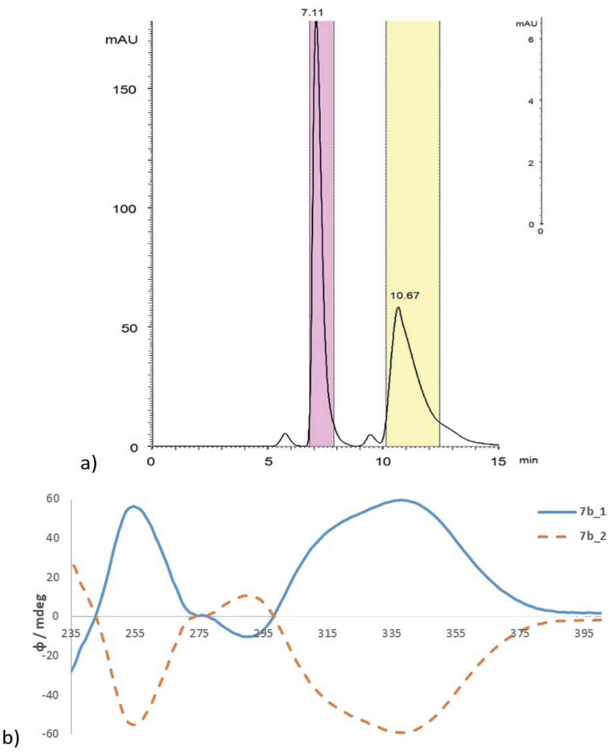


Fig. 5 (a) Preparative enantioseparation of **7b** on Chiralpak IA (250 × 20 mm i.d., 5 μm) in heptane/propan-2-ol (9/1, v/v) with diethylamine 0.1% as a basic additive at 15 °C, flow rate 15 mL min^{-1}, sample concentration 4.28 mg mL^{-1}, injection volume 0.6 mL, detection wavelength 350 nm. (b) ECD spectra of both separated enantiomers of **7b** in MeOH, the first eluting enantiomer **7b_1** full (blue) line, the second eluting enantiomer **7b_2** dashed (orange) line.

The ^{1}H NMR titration experiments ($CDCl_3$) carried out with racemic **7a** indicated that the cavity of double-bridged calixarene can interact with MeCN, although the corresponding complexation constant was very low $K = 2.8 \pm 0.2\ M^{-1}$ (see ESI†). Based on this result, we attempted the enantioselective resolution of a chiral guest molecule bearing more acidic CH_3 group that could be complexed by the combination of CH–π and/or cation–π interactions.

For this purpose, a natural (*S*)-nicotine was methylated on pyridine nitrogen atom and the resulting (*S*)-*N*-methylnicotinium iodide[8] (NMNI) was used as a guest molecule. The ^{1}H NMR titration experiments with resolved enantiomers **7b_1** and **7b_2** as the host molecules and *N*-methylpyridinium iodide (NMPI) as the guest in 1,1,2,2-$C_2D_2Cl_4$ revealed that the complexation occurred under fast-exchange conditions. The titration curves (see ESI†) were constructed from the CIS (the Complexation Induced Shift) values of the host aromatic signals and they were analysed using the online available software Bindfit.[14]

Surprisingly, the titration curves with NMNI gave the best fits using 2 : 1 (host : guest) stoichiometry[15] with very similar overall binding constants: $K_{11} = 330 \pm 10$ and $K_{21} = 5900 \pm 270$ for **7b_1**; $K_{11} = 450 \pm 15$ and $K_{21} = 5760 \pm 270$ for **7b_2**. From this point of view, much bigger differences were found during the titration of separated enantiomers of **14b** with NMNI: $K_{11} = 720 \pm 25$ and $K_{21} = 4900 \pm 260$ for **14b_1**, and $K_{11} = 440 \pm 20$ and $K_{21} = 1150 \pm 90$ for **14b_2**, indicating potential applicability of these compounds in the role of receptors (see ESI†).

A suitable shape of the cavity of **14b** (racemic) for the complexation of guest molecules bearing acidic methyl groups was demonstrated on the complexation of acetonitrile as a neutral guest molecule ($K = 72 \pm 5\ M^{-1}$) in $CDCl_3$. Moreover, a synchronous effect of CH–π, π–π and/or cation–π interactions was demonstrated using the ^{1}H NMR titrations (1,1,2,2-$C_2D_2Cl_4$) of **14b** with *N*-methylpyridinium (NMP), *N*-methylquinolinium (NMQ) and *N*-methylisoquinolinium (NMIQ) iodides. The analysis of the binding isotherms showed the 1 : 1 stoichiometry in all cases, with the highest complexation constants for NMP ($K = 615 \pm 15\ M^{-1}$) indicating the best fit between the shape of the cavity and the shape of the guest molecule (Fig. 6). The NMQ and NMIQ derivatives showed

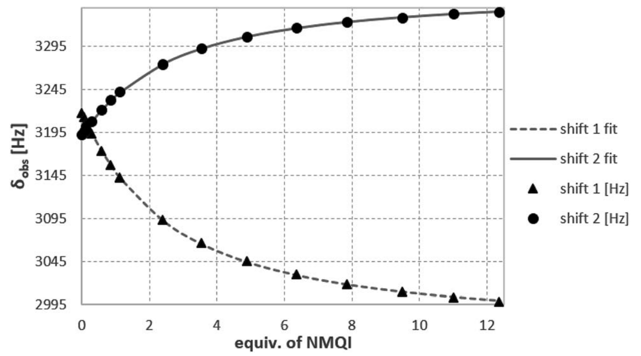


Fig. 6 ^{1}H NMR titration curve of **14b** with *N*-methylquinolinium iodide (NMQ) ($C_2D_2Cl_4$, 298 K, 400 MHz).

much worse complexation abilities ($K = 395 \pm 4\ \mathrm{M}^{-1}$ and $K = 211 \pm 2\ \mathrm{M}^{-1}$, respectively).

Conclusion

Meta/*meta*- and *meta*/*para*-disubstituted organomercurials, easily obtainable by direct mercuration of starting calix[4]arene, immobilised in the cone conformation, were transformed into corresponding amino derivatives. Acylation and subsequent intramolecular cyclization using the conditions of Bischler–Napieralski reaction provided in the case of *meta*/*meta*-series double bridged calixarenes possessing seven membered rings on the upper rim. A similar synthetic strategy applied to *meta*/*para*-isomers allowed for the isolation of monobridged compounds bearing an additional trifluoroacetamido group located distally to seven-membered ring. Both series represent inherently chiral systems, which were successfully resolved using preparative chiral HPLC. The rigidified cavities of bridged calixarenes can interact with guest molecules bearing acidic methyl groups, as documented by the shape selective complexation of *N*-methylpyridinium, *N*-methylquinolinium and *N*-methylisoquinolinium iodides using racemic **14b**. Moreover, the ^{1}H NMR titration experiments indicated the recognition ability of pure enantiomers of **14b** towards selected chiral guest molecules. The absolute configuration of phenyl-substituted enantiomer (*meta*/*meta*-) was confirmed by single crystal structure determination (X-ray).

Experimental

General experimental procedures

All chemicals were purchased from commercial sources, and used without further purification. Chloroform, tetrahydrofuran and dichloromethane used for the reactions were dried with CaH_2 or $MgSO_4$ and stored over molecular sieves. Melting points were measured on Heiztisch Mikroskop-Polytherm A (Wagner & Munz, Germany) and were not corrected. The IR spectra were measured on FT-IR spectrometer Nicolet 740 in KBr transmission mode. NMR spectra were recorded on spectrometer Agilent 400-MR DDR2 (^{1}H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts (δ) are expressed in parts per million and are referenced to the residual peak of solvent or TMS as an internal standard, coupling constants (J) are in Hertz. The mass analyses were performed using ESI technique on a FT-MS (LTQ Orbitrap Velos) spectrometer. Purity of the substances and the courses of the reactions were monitored by TLC using aluminum sheets with Silica gel 60 F_{254} (Merck) and analysed at 254 or 365 nm. Preparative TLC chromatography was carried out on a Chromatotron (Harrison Research) with plates covered by Silica gel 60 GF_{254} (Merck).

General procedure for preparation of *m*,*m*-diamides

m,*m*-Diamino calixarene **5** was dissolved in 10 mL of THF at room temperature and Et_3N and corresponding carboxylic acid derivative were added. The solution was stirred for 24 h at room temperature, and diluted with dichloromethane (10 mL) was added. The crude reaction mixture was washed with water (3×20 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield crude product which was further purified by preparative TLC on silica gel.

4,16-Di(acetamido)-25,26,27,28-tetrapropoxycalix[4]arene (6a). Compound **6a** was prepared according to the general procedure by reacting calixarene **5** (0.152 g, 0.24 mmol) and acetic anhydride (0.062 mL, 0.66 mmol) in the presence of triethylamine (0.620 mL, 4.47 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 2 : 15, v/v) to give title compound **6a** as a colourless amorphous solid (0.080 g, 46%), mp 288–290 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.20–6.75 (m, 7H, Ar–*H*, Ar–*NH*–CO), 6.73–6.59 (m, 2H, Ar–*H*), 6.53–6.42 (m, 1H, Ar–*H*), 6.36–6.08 (m, 2H, Ar–*H*), 4.49 (d, 2H, $J = 14.1$ Hz, Ar–CH_2–Ar), 4.42 (d, 2H, $J = 13.3$ Hz, Ar–CH_2–Ar), 4.16–3.99 (m, 2H, O–CH_2), 3.97–3.80 (m, 2H, O–CH_2), 3.77–3.61 (m, 4H, O–CH_2), 3.23 (d, 2H, $J = 14.5$ Hz, Ar–CH_2–Ar), 3.16 (d, 2H, $J = 13.7$ Hz, Ar–CH_2–Ar), 1.99 (s, 3H, CO–CH_3), 1.97–1.76 (m, 8H, O–CH_2–CH_2), 1.12–1.00 (m, 6H, O–CH_2–CH_2–CH_3), 0.94–0.81 (m, 6H, O–CH_2–CH_2–CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz, 298 K) δ 168.0, 157.9, 156.6, 134.8 (2×), 134.3, 134.2, 133.6, 129.0, 128.7, 127.3, 121.8, 120.1, 76.9, 76.7, 31.1, 29.7, 23.9, 23.4, 22.7, 10.6, 9.9 ppm.

IR (KBr) ν 2961.0, 2934.4, 2874.8, 1661.9, 1521.9, 1455.4, 1206.3 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{44}H_{54}N_2O_6$ 729.38741 $[M + Na]^+$, 745.36135 $[M + K]^+$, found *m*/*z* 729.38820 $[M + Na]^+$ (100%), 745.36046 $[M + K]^+$ (5%).

4,16-Di(benzoylamido)-25,26,27,28-tetrapropoxycalix[4]arene (6b). Compound **6b** was prepared according to the general procedure by reacting calixarene **5** (0.100 g, 0.16 mmol) and benzoyl chloride (0.120 mL, 1.03 mmol) in the presence of triethylamine (0.420 mL, 3.03 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 5 : 1, v/v) to give title compound **6b** as a colourless amorphous solid (0.056 g, 41%) mp 314–317 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.72–7.62 (m, 4H, Ar–*H*), 7.57–7.52 (m, 2H, Ar–*H*), 7.49–7.44 (m, 2H, Ar–*H*), 7.21 (br s, 2H, Ar–*NH*–CO), 7.10–6.94 (m, 2H, Ar–*H*), 6.90–6.67 (m, 6H, Ar–*H*), 6.46–6.32 (m, 2H, Ar–*H*), 4.57–4.45 (m, 4H, Ar–CH_2–Ar), 4.16–4.05 (m, 2H, O–CH_2), 3.92–3.70 (m, 6H, O–CH_2), 3.29 (d, 2H, $J = 14.5$ Hz, Ar–CH_2–Ar), 3.23 (d, 2H, $J = 13.7$ Hz, Ar–CH_2–Ar), 1.98–1.78 (m, 8H, O–CH_2–CH_2), 1.06 (t, 6H, $J = 7.4$ Hz, O–CH_2–CH_2–CH_3), 0.90 (t, 6H, $J = 7.4$ Hz, O–CH_2–CH_2–CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz, 298 K) δ 165.7, 156.8, 145.5, 134.8, 134.2, 134.1, 133.6, 131.6, 129.0 (2×), 128.6 (2×), 127.4, 122.2, 120.2, 77.0, 76.8, 31.3, 31.2, 23.4, 22.7, 10.6, 9.9 ppm. IR (KBr) ν 3300.8, 2959.7, 2927.8, 2873.5, 1649.8, 1580.7, 1516.3, 1487.6, 1268.3 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{54}H_{58}N_2O_6$ 853.41871 $[M + Na]^+$, 869.39265 $[M + K]^+$, found *m*/*z* 853.41870 $[M + Na]^+$ (100%), 869.39185 $[M + K]^+$ (13%).

4,16-Di(bromoacetamido)-25,26,27,28-tetrapropoxycalix[4]arene (6c). Compound **6c** was prepared according to the general procedure by reacting calixarene **5** (0.100 g, 0.16 mmol) and bromoacetyl bromide (0.092 mL, 1.06 mmol) in the presence of triethylamine (0.420 mL, 3.03 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 1 : 1, v/v) to give title compound **6c** as a red amorphous solid (0.042 g, 30%), mp 273–276 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.46 (br s, 2H, Ar–*NH*–CO), 6.96–6.29 (m, 10H, Ar–*H*), 4.50–4.39 (m, 4H, Ar–*CH*$_2$–Ar), 4.02–3.71 (m, 10H, O–*CH*$_2$, CO–*CH*$_2$–Br), 3.28 (d, 2H, $J = 14.1$ Hz, Ar–*CH*$_2$–Ar), 3.17 (d, 2H, $J = 13.7$ Hz, Ar–*CH*$_2$–Ar), 1.98–1.78 (m, 8H, O–CH$_2$–*CH*$_2$), 1.01 (t, 6H, $J = 7.4$ Hz, O–CH$_2$–CH$_2$–*CH*$_3$), 0.94 (t, 6H, $J = 7.4$ Hz, O–CH$_2$–CH$_2$–*CH*$_3$) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 163.7, 157.2, 157.1, 133.6, 133.5, 132.8, 132.7, 128.7, 128.3, 127.8, 122.3, 119.6, 76.9, 76.8, 31.0, 29.7, 29.4, 23.3, 22.8, 10.4, 10.1 ppm. IR (KBr) ν 3261.1, 2960.1, 2925.7, 2873.9, 1663.0, 1527.0, 1454.9, 1207.3 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{44}H_{52}Br_2N_2O_6$ 887.20639 [M + Na]$^+$, 903.18032 [M + K]$^+$, found *m*/*z* 887.20630 [M + Na]$^+$ (100%), 903.17920 [M + K]$^+$ (17%).

4,16-Di(chloroacetylamido)-25,26,27,28-tetrapropoxycalix[4] arene (6d). Compound **6d** was prepared according to the general procedure by reacting calixarene **5** (0.100 g, 0.16 mmol) and chloroacetyl chloride (0.077 mL, 0.97 mmol) in the presence of triethylamine (0.42 mL, 3.03 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 1 : 1, v/v) to give title compound **6d** as a colourless solid (0.071 g, 56%), mp 240–243 °C.

^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.82–7.61 (m, 2H, Ar–*H*), 6.95–6.82 (m, 2H, Ar–*H*), 6.77–6.46 (m, 8H, Ar–*H*, Ar–*NH*–CO), 4.51–4.39 (m, 4H, Ar–*CH*$_2$–Ar), 4.15–4.10 (m, 2H, CO–*CH*$_2$–Cl), 4.02–3.67 (m, 8H, O–*CH*$_2$), 3.29 (d, 2H, $J = 14.5$ Hz, Ar–*CH*$_2$–Ar), 3.18 (d, 2H, $J = 13.7$ Hz, Ar–*CH*$_2$–Ar), 1.99–1.79 (m, 8H, O–CH$_2$–*CH*$_2$), 1.05–0.89 (m, 12H, O–CH$_2$–CH$_2$–*CH*$_3$) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 164.2, 157.3, 156.7, 143.4, 133.9, 133.3, 132.5, 129.3, 128.7, 128.3, 127.9, 122.3, 119.7, 76.9, 76.8, 42.9, 31.0, 30.8, 23.3, 22.9, 10.4, 10.2 ppm. IR (KBr) ν 3282.0, 2960.9, 2932.5, 2874.6, 1671.1, 1520.0, 1455.7, 1207.3, 1085.1 cm^{-1}.

HRMS (ESI$^+$) calcd for $C_{44}H_{52}Cl_2N_2O_6$ 797.30946 [M + Na]$^+$, 813.28340 [M + K]$^+$, found *m*/*z* 797.30895 [M + Na]$^+$ (100%), 813.28276 [M + K]$^+$ (25%).

(*S*,*S*)-4,16-Di(*O*-acetylmandelylamido)-25,26,27,28-tetrapropoxycalix[4]arene (6e). Compound **6e** was prepared using DCC as coupling reagent. (*S*)-*O*-acetylmandelic acid (0.125 g, 0.64 mmol) was dissolved in 5 mL of THF at room temperature. DCC (0.133 g, 0.64 mmol) was added and the solution was stirred for 10 min. Calixarene **5** (0.100 g, 0.16 mmol) was added afterwards, and the solution was stirred for 24 h at room temperature. The crude reaction mixture was diluted by 10 mL of dichloromethane, washed with water (3 × 20 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure to yield crude product which was further purified by preparative TLC (cyclohexane : ethylacetate 2 : 1, v/v) to give title compound **6e** as a colourless amorphous solid (0.092 g, 46%), mp > 330 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.58–7.26 (m, 23H, Ar–*H*), 7.14 (m, 16H, Ar–*H*, Ar–*NH*–CO), 6.17–6.03 (m, 2H, Ar–*H*), 5.93–5.70 (m, 2H, Ar–*H*), 4.51–4.32 (m, 8H, Ar–*CH*$_2$–Ar), 4.10–3.91 (m, 4H, O–*CH*$_2$), 3.88–3.59 (m, 14H, O–*CH*$_2$, CO–*CH*(OAc)–Ar), 3.27–3.08 (m, 8H, Ar–*CH*$_2$–Ar), 2.22 (s, 3H, O–CO–*CH*$_3$), 2.19 (s, 3H, O–CO–*CH*$_3$), 2.00–1.72 (m, 16H, O–CH$_2$–*CH*$_2$), 1.08–0.96 (m, 12H, O–CH$_2$–CH$_2$–*CH*$_3$), 0.93 (t, 6H, $J = 7.4$ Hz, O–CH$_2$–CH$_2$–*CH*$_3$), 0.85 (t, 6H, $J = 7.4$ Hz, O–CH$_2$–CH$_2$–*CH*$_3$) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 169.9, 169.1, 166.4, 166.3, 158.2, 158.1, 157.1, 156.5, 135.4, 134.7, 134.2, 133.7, 133.2, 133.0, 132.5 (2×), 132.1, 132.0, 129.5, 129.4, 129.2, 129.0, 128.9, 128.8, 128.6, 128.1, 127.7, 127.6, 127.4, 127.1, 122.2, 122.0, 119.8, 119.4, 76.9 (2×), 76.8, 76.7, 75.8, 75.7, 31.1, 31.0, 29.7, 28.5, 23.3, 23.2, 22.8, 22.5, 21.2, 20.9, 10.6, 10.4, 10.1, 9.8 ppm. IR (KBr) ν 3369.4, 2961.3, 2933.0, 2875.0, 1746.3, 1686.3, 1517.1, 1455.2, 1233.0 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{60}H_{66}N_2O_{10}$ 997.46097 [M + Na]$^+$, 1013.43490 [M + K]$^+$, found *m*/*z* 997.46149 [M + Na]$^+$ (100%), 1013.43352 [M + K]$^+$ (10%).

4,16-Di(1-pyrenoylamido)-25,26,27,28-tetrapropoxy-calix[4] arene (6f). Compound **6f** was prepared according to the general procedure by reacting calixarene **5** (0.147 g, 0.24 mmol) and 1-pyrenecarbonyl chloride (0.190 g, 0.72 mmol) in the presence of triethylamine (0.62 mL, 4.47 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 5 : 1, v/v) to give title compound **6f** as a yellow amorphous solid (0.142 g, 56%), mp 187–190 °C. Compound **6f** was also prepared using DCC as coupling reagent. 1-pyrenecarboxylic acid (0.120 g, 0.49 mmol) was dissolved in 5 mL of THF at room temperature. DCC (0.100 g, 0.64 mmol) was added and the solution was stirred for 10 minutes. Calixarene **5** (0.100 g, 0.16 mmol) was added afterwards and the solution was stirred for 24 h at room temperature. 10 mL of dichloromethane were added. The crude reaction mixture was washed with water (3 × 20 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure to yield crude product which was further purified by preparative TLC (cyclohexane : ethyl acetate 5 : 1, v/v) to give title compound **6f** (0.023 g, 11%). ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 8.61 (d, 2H, $J = 9.4$ Hz, Ar–*H*), 8.32–8.00 (m, 15H, Ar–*H*), 7.47–7.41 (m, 3H, Ar–*H*), 6.81 (br s, 2H, Ar–*NH*–CO), 6.66–6.19 (m, 6H, Ar–*H*), 6.14–6.02 (m, 2H, Ar–*H*), 4.59 (d, 2H, $J = 14.1$ Hz, Ar–*CH*$_2$–Ar), 4.48 (d, 2H, $J = 13.7$ Hz, Ar–*CH*$_2$–Ar), 4.21–4.00 (m, 2H, O–*CH*$_2$), 3.93–3.70 (m, 6H, O–*CH*$_2$), 3.33 (d, 2H, $J = 14.1$ Hz, Ar–*CH*$_2$–Ar), 3.22 (d, 2H, $J = 13.3$ Hz, Ar–*CH*$_2$–Ar), 2.01–1.75 (m, 8H, O–CH$_2$–*CH*$_2$), 1.07 (t, 6H, $J = 7.0$ Hz, O–CH$_2$–CH$_2$–*CH*$_3$), 0.86 (t, 6H, $J = 7.0$ Hz, O–CH$_2$–CH$_2$–*CH*$_3$) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 167.9, 156.9, 156.8, 134.1, 133.8 (2×), 132.7, 131.2, 131.1, 130.8, 130.7 (2×), 139.0, 128.8 (2×), 128.7, 128.4, 127.7, 127.2, 126.3, 125.8 (2×), 124.9, 124.8, 124.4 (2×), 124.3, 122.2, 119.4, 76.8, 76.7, 33.9, 31.2, 23.4, 22.7, 10.6, 9.9 ppm. IR (KBr) ν 3372.2, 2959.6, 2928.5, 2874.0, 1650.1, 1588.4, 1511.8, 1455.7, 1087.8 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{74}H_{66}N_2O_6$ 1101.48131 [M + Na]$^+$, 1117.45525 [M + K]$^+$, found *m*/*z* 1101.48226 [M + Na]$^+$ (100%), 1117.45522 [M + K]$^+$ (35%).

General procedure for preparation of bis-bridged calixarenes

Calixarene **6a–f** was dissolved under argon atmosphere in 5 mL of dry CH$_2$Cl$_2$. The solution was cooled down to −78 °C, and 2-chloropyridine and triflic anhydride were added. The mixture was stirred for 5 min, then the solution was warmed to 0 °C and stirred for another 5 min. After that, the mixture was warmed to room temperature and stirred for one more hour. The reaction was quenched by a solution of NaHCO$_3$. The organic layer was separated, washed with water (10 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure to yield crude product, which was further purified by preparative TLC on silica gel.

Alternative procedure was also examined. Corresponding calixarene was dissolved in 5 mL of toluene. $POCl_3$ was added afterwards, and the reaction mixture was heated to reflux and stirred for 24 hours. The solution was washed with $NaHCO_3$ (10 mL) and then with water (2 × 10 mL). The separated organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure to yield crude product, which was further purified by preparative TLC on silica gel.

Methylimine-bis-bridged-25,26,27,28-tetrapropoxycalix[4]arene (7a). Calixarene **7a** was prepared according to general procedure by reacting calixarene **6a** (0.093 g, 0.13 mmol), 2-chloropyridine (0.030 mL, 0.32 mmol) and triflic anhydride (0.049 mL, 0.29 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 4 : 5, v/v) to give title compound **7a** as a yellow amorphous solid (0.015 g, 17%), mp 130–133 °C.

Alternative procedure was also examined by reacting calixarene **6a** (0.066 g, 0.09 mmol) and $POCl_3$ (0.085 mL, 0.91 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 1 : 1, v/v) to give title compound as a yellow amorphous solid (0.003 g, 5%).

^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ 6.97 (d, 2H, J = 7.8 Hz, Ar–*H*), 6.87 (d, 2H, J = 8.2 Hz, Ar–*H*), 6.79 (d, 2H, J = 7.8 Hz, Ar–*H*), 6.58 (d, 2H, J = 8.2 Hz, Ar–*H*), 4.59 (d, 2H, J = 12.1 Hz, Ar–CH_2–Ar), 4.53 (d, 2H, J = 11.7 Hz, Ar–CH_2–Ar), 3.94–3.72 (m, 8H, O–CH_2), 3.25 (d, 2H, J = 11.7 Hz, Ar–CH_2–Ar), 2.72 (d, 2H, J = 11.7 Hz, Ar–CH_2–Ar), 2.49 (s, 6H, N═C(Ar)–CH_3), 2.07–1.85 (m, 8H, O–CH_2–CH_2), 1.14 (t, 6H, J = 7.4 Hz, O–CH_2–CH_2–CH_3), 1.09 (t, 6H, J = 7.4 Hz, O–CH_2–CH_2–CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz, 298 K) δ 167.3, 153.0, 152.6, 146.2, 138.3, 136.1, 133.7, 131.9, 127.3, 127.2, 126.7, 121.1, 118.9, 77.4, 77.5, 30.7, 29.7, 27.5, 23.4, 23.3, 10.5 (2×) ppm. IR (KBr) ν 3363.1, 2959.3, 2928.3, 2874.8, 1418.8, 1066.7 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{44}H_{50}N_2O_4$ 671.38433 [M + H]$^+$, 693.36628 [M + Na]$^+$, found *m/z* 671.38404 [M + H]$^+$ (100%), 693.36582 [M + Na]$^+$ (60%).

Phenylimine-bis-bridged-25,26,27,28-tetrapropoxycalix[4]arene (7b). Calixarene **7b** was prepared according to general procedure by reacting calixarene **6b** (0.068 g, 0.08 mmol), 2-chloropyridine (0.020 mL, 0.21 mmol) and triflic anhydride (0.030 mL, 0.18 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 6 : 1, v/v) to give title compound **7b** as a yellow amorphous solid (0.043 g, 66%), mp 175–178 °C.

Alternative procedure was also examined by reacting calixarene **6b** (0.056 g, 0.07 mmol) and $POCl_3$ (0.062 mL, 0.66 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 7 : 1, v/v) to give title compound as a yellow amorphous solid (0.005 g, 9%).

^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.84–7.78 (m, 4H, Ar–*H*), 7.49–7.35 (m, 6H, Ar–*H*), 6.97 (d, 2H, J = 7.8 Hz, Ar–*H*), 6.94 (d, 2H, J = 8.2 Hz, Ar–*H*), 6.73 (d, 2H, J = 8.2 Hz, Ar–*H*), 6.59 (d, 2H, J = 8.2 Hz, Ar–*H*), 4.72 (d, 2H, J = 12.1 Hz, Ar–CH_2–Ar), 4.62 (d, 2H, J = 11.7 Hz, Ar–CH_2–Ar), 4.07–3.99 (m, 2H, O–CH_2), 3.93–3.79 (m, 6H, O–CH_2), 3.32 (d, 2H, J = 12.1 Hz, Ar–CH_2–Ar), 2.86 (d, 2H, J = 12.1 Hz, Ar–CH_2–Ar), 2.17–1.88 (m, 8H, O–CH_2–CH_2), 1.22 (t, 6H, J = 7.4 Hz, O–CH_2–CH_2–CH_3), 1.11 (t, 6H, J = 7.4 Hz, O–CH_2–CH_2–CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz, 298 K) δ 166.3, 153.0, 152.8, 146.4, 140.4, 138.5, 137.6, 132.2, 131.6, 129.9, 129.5, 128.0, 127.4, 126.8, 126.7, 123.9, 119.4, 77.5, 77.4, 30.7, 23.9, 23.6, 23.3, 10.7, 10.6 ppm. IR (KBr) ν 2959.6, 1933.0, 2875.1, 1572.0, 1466.4, 1417.5, 1217.1, 1062.6 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{54}H_{54}N_2O_4$ 795.41563 [M + H]$^+$, 817.39758 [M + Na]$^+$, found *m/z* 795.41581 [M + H]$^+$ (100%), 817.39702 [M + Na]$^+$ (35%).

Brommethylimine-bis-bridged-25,26,27,28-tetrapropoxycalix[4]arene (7c). Calixarene **7c** was prepared according to general procedure by reacting calixarene **6c** (0.055 g, 0.06 mmol), 2-chloropyridine (0.015 mL, 0.16 mmol) and triflic anhydride (0.026 mL, 0.15 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethylacetate 3 : 1, v/v) to give title compound **7c** as a red amorphous solid (0.009 g, 17%). ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.00 (d, 2H, J = 8.2 Hz, Ar–*H*), 6.90 (d, 2H, J = 8.2 Hz, Ar–*H*), 6.84 (d, 2H, J = 8.2 Hz, Ar–*H*), 6.58 (d, 2H, J = 8.2 Hz, Ar–*H*), 4.62 (d, 2H, J = 12.1 Hz, Ar–CH_2–Ar), 4.61 (d, 2H, J = 9.8 Hz, N═C(Ar)–CH_2–Br), 4.55 (d, 2H, J = 11.7 Hz, Ar–CH_2–Ar), 4.28 (d, 2H, J = 9.8 Hz, N═C(Ar)–CH_2–Br), 3.98–3.91 (m, 2H, O–CH_2), 3.88–3.75 (m, 6H, O–CH_2), 3.28 (d, 2H, J = 11.7 Hz, Ar–CH_2–Ar), 2.80 (d, 2H, J = 12.1 Hz, Ar–CH_2–Ar), 2.06–1.86 (m, 8H, O–CH_2–CH_2), 1.16 (t, 6H, J = 7.4 Hz, O–CH_2–CH_2–CH_3), 1.08 (t, 6H, J = 7.4 Hz, O–CH_2–CH_2–CH_3) ppm. HRMS (ESI$^+$) calcd for $C_{44}H_{48}Br_2N_2O_4$ 829.20331 [M + H]$^+$, 851.18526 [M + Na]$^+$, found *m/z* 829.20333 [M + H]$^+$ (30%), 851.18539 [M + Na]$^+$ (100%).

(Phenyl-acetoxymethyl)imine-bis-bridged-25,26,27,28-tetrapropoxycalix[4]arene (7e). Compound **7e** was prepared according to general procedure by reacting amide **6e** (0.075 g, 0.08 mmol), 2-chloropyridine (0.018 mL, 0.19 mmol) and triflic anhydride (0.029 mL, 0.17 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 3 : 1, v/v) to give the title compound **7e** as a yellow amorphous solid (0.016 g, 17%). HRMS (ESI$^+$) calcd for $C_{60}H_{62}N_2O_8$ 939.45789 [M + H]$^+$, 961.43984 [M + Na]$^+$, found *m/z* 939.45758 [M + H]$^+$ (75%), 961.43933 [M + Na]$^+$ (100%).

4-Acetamido-methylimine-bridged-25,26,27,28-tetrapropoxycalix[4]arene (8a). Compound **8a** was obtained as a byproduct in the alternative procedure ($POCl_3$/toluene) for the synthesis of compound **7a**. The title compound **8a** was obtained as a yellow amorphous solid (0.007 g, 11%), mp 92–95 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.08–6.90 (m, 4H, Ar–*H*), 6.90–6.75 (m, 2H, Ar–*H*), 6.75–6.66 (m, 1H, Ar–*H*), 6.61–6.51 (m, 1H, Ar–*H*), 6.45–6.34 (m, 1H, Ar–*H*), 4.58 (d, 1H, J = 12.3 Hz, Ar–CH_2–Ar), 4.49 (d, 1H, J = 12.9 Hz, Ar–CH_2–Ar), 4.45 (d, 1H, J = 13.5 Hz, Ar–CH_2–Ar), 4.37 (d, 1H, J = 13.5 Hz, Ar–CH_2–Ar), 4.00–3.52 (m, 8H, O–CH_2), 3.32–3.18 (m, 3H, Ar–CH_2–Ar), 2.78 (d, 1H, J = 11.7 Hz, Ar–CH_2–Ar), 2.53 (s, 3H, N═C(Ar)–CH_3), 2.29–1.82 (m, 8H, O–CH_2–CH_2), 2.12 (s, 3H, Ar–CO–CH_3), 1.17–0.92 (m, 12H, O–CH_2–CH_2–CH_3) ppm. IR (KBr) ν 2919.3, 2850.7, 1622.4, 1407.7, 1118.7, 1046.1 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{44}H_{52}N_2O_5$ 689.39490 [M + H]$^+$, 711.37684 [M + Na]$^+$, found *m/z* 689.39445 [M + H]$^+$ (95%), 711.37628 [M + Na]$^+$ (100%).

4-Benzamido-phenylimine-bridged-25,26,27,28-tetrapropoxycalix[4]arene (8b). Compound **8b** was obtained by the alternative procedure (POCl$_3$/toluene) during the synthesis of compound **7b**. The title compound **8b** was obtained as a yellow amorphous solid (0.011 g, 20%), mp 177–180 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.90–7.84 (m, 2H, Ar–*H*), 7.81–7.74 (m, 2H, Ar–*H*), 7.67 (br s, 1H, Ar–*NH*–Ph), 7.57–7.51 (m, 1H, Ar–*H*), 7.50–7.37 (m, 5H, Ar–*H*), 7.05 (dd, 1H, J = 7.4, 1.6 Hz, Ar–*H*), 6.81–6.75 (m, 2H, Ar–*H*), 6.73–6.66 (m, 2H, Ar–*H*), 6.64 (d, 1H, J = 7.8 Hz, Ar–*H*), 4.70 (d, 1H, J = 11.7 Hz, Ar–CH_2–Ar), 4.60 (d, 1H, J = 12.1 Hz, Ar–CH_2–Ar), 4.49 (d, 1H, J = 12.5 Hz, Ar–CH_2–Ar), 4.45 (d, 1H, J = 13.7 Hz, Ar–CH_2–Ar), 4.01–3.84 (m, 5H, O–CH_2), 3.80–3.64 (m, 3H, O–CH_2), 3.36 (d, 1H, J = 12.1 Hz, Ar–CH_2–Ar), 3.29 (d, 1H, J = 13.7 Hz, Ar–CH_2–Ar), 3.27 (d, 1H, J = 12.9 Hz, Ar–CH_2–Ar), 2.92 (d, 1H, J = 11.7 Hz, Ar–CH_2–Ar), 2.32–2.21 (m, 2H, O–CH$_2$–CH_2), 2.12–1.99 (m, 4H, O–CH$_2$–CH_2), 1.96–1.85 (m, 2H, O–CH$_2$–CH_2), 1.18 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3), 1.08 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3), 1.03 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3), 0.97 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 166.0, 165.6, 157.0, 156.4, 153.3, 153.2, 139.9, 137.4 (2×), 136.7 (2×), 134.8, 134.7, 133.5, 132.0, 131.7, 131.6, 130.6, 130.0, 129.5 (2×), 129.1, 128.6, 128.4 (2×), 128.0, 127.3 (2×), 127.0, 126.7, 123.1, 122.6, 120.4, 118.7, 78.2, 77.8 (2×), 76.3, 31.3, 30.2, 27.6, 23.9, 23.6, 23.3, 23.0, 22.2, 10.8 (2×), 10.3, 9.9 ppm. IR (KBr) ν 2960.0, 2932.3, 2874.4, 1651.2, 1582.9, 1464.2, 1417.8, 1213.6, 1054.2 cm^{-1}. HRMS (ESI$^+$) calcd for $\mathrm{C_{54}H_{56}N_2O_5}$ 813.42620 [M + H]$^+$, 835.40814 [M + Na]$^+$, found *m*/*z* 813.42661 [M + H]$^+$ (85%), 835.40788 [M + Na]$^+$ (100%).

4,17-Di(trifluoroacetamido)-25,26,27,28-tetrapropoxycalix[4]arene (11). *m*-*p*-Diamino calixarene **10** (0.773 g, 1.24 mmol) was dissolved in 10 mL of THF at room temperature. Et$_3$N (3.300 mL, 23.80 mmol) and trifluoroacetic anhydride (0.380 mL, 2.74 mmol) were added. The solution was stirred for 2 h at room temperature. 10 mL of dichloromethane were added. The crude reaction mixture was washed with water (3 × 20 mL) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield crude product which was further purified by column chromatography on silica gel (cyclohexane : ethyl acetate 5 : 1, v/v) to give title compound **11** as a yellow amorphous solid (0.829 g, 82%), mp 236–238 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 8.47 (br s, 1H, Ar–*NH*–CO), 7.38 (br s, 1H, Ar–*NH*–CO), 7.19 (dd, 1H, J = 7.4, 1.6 Hz, Ar–*H*), 7.14 (dd, 1H, J = 7.4, 1.6 Hz, Ar–*H*), 7.11–7.06 (m, 2H, Ar–*H*), 7.00 (t, 1H, J = 7.4 Hz, Ar–*H*), 6.90 (t, 1H, J = 7.4 Hz, Ar–*H*), 6.36 (d, 1H, J = 6.36 Hz, Ar–*H*), 6.23 (d, 1H, J = 2.7 Hz, Ar–*H*), 6.13 (d, 1H, J = 8.6 Hz, Ar–*H*), 5.83 (d, 1H, J = 2.7 Hz, Ar–*H*), 4.60 (d, 1H, J = 14.5 Hz, Ar–CH_2–Ar), 4.50–4.41 (m, 3H, Ar–CH_2–Ar), 4.12–4.03 (m, 2H, O–CH_2), 3.99–3.88 (m, 2H, O–CH_2), 3.71–3.57 (m, 4H, O–CH_2), 3.26–3.10 (m, 4H, Ar–CH_2–Ar), 1.94–1.80 (m, 8H, O–CH$_2$–CH_2), 1.14–1.08 (m, 6H, O–CH$_2$–CH$_2$–CH_3), 0.87 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3), 0.81 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 158.1, 157.8, 156.5, 153.7, 137.3, 137.2, 136.0, 134.5 (2×), 133.6, 133.2, 130.3, 130.0, 129.6, 129.4, 129.3, 129.2, 128.5, 127.8, 122.3, 121.6, 121.5, 120.6, 119.4, 117.5, 117.4, 114.6, 114.5, 77.2, 76.9, 76.8, 76.1, 31.4, 31.3, 30.6, 28.9, 23.5 (2×), 23.1, 22.4, 10.9, 10.8, 9.8, 9.6 ppm. IR (KBr) ν 3289.8, 2963.1, 1932.8, 2876.3, 1706.5, 1462.9, 1200.0, 1159.4 cm^{-1}. HRMS (ESI$^+$) calcd for $\mathrm{C_{44}H_{48}F_6N_2O_6}$ 837.33088 [M + Na]$^+$, 853.30481 [M + K]$^+$, found *m*/*z* 837.33243 [M + Na]$^+$ (100%), 853.30555 [M + K]$^+$ (60%).

4-Amino-17-trifluoroacetamido-25,26,27,28-tetrapropoxycalix[4]arene (12a). Calixarene **11** (2.177 g, 2.67 mmol) was dissolved in 5 mL of MeOH : THF (1 : 1, v/v) at room temperature. NaOH (0.110 g, 2.75 mmol) and water (0.500 mL, 27.78 mmol) were added. The solution was stirred for 50 h at room temperature. 20 mL of dichloromethane were added. The crude reaction mixture was washed with water (3 × 20 mL) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield crude product which was further purified by column chromatography on silica gel (cyclohexane : ethyl acetate 5 : 1, v/v) to give title compound **12a** as a yellow amorphous solid (0.426 g, 22%), mp 215–218 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.45 (br s, 1H, Ar–*NH*–CO), 7.02 (d, 1H, J = 7.4 Hz, Ar–*H*), 6.94–6.84 (m, 8H, Ar–*H*), 6.82–6.75 (m, 2H, Ar–*H*), 6.56 (d, 1H, J = 2.0 Hz, Ar–*H*), 6.26 (d, 1H, J = 2.0 Hz, Ar–*H*), 6.21 (d, 1H, J = 8.2 Hz, Ar–*H*), 5.80 (d, 1H, J = 8.2 Hz, Ar–*H*), 4.52–4.44 (m, 3H, Ar–CH_2–Ar), 4.34 (d, 1H, J = 13.3 Hz, Ar–CH_2–Ar), 4.09–3.99 (m, 1H, O–CH_2), 3.96–3.82 (m, 3H, O–CH_2), 3.80–3.62 (m, 4H, O–CH_2), 3.22–3.06 (m, 4H, Ar–CH_2–Ar), 1.95–1.81 (m, 8H, O–CH$_2$–CH_2), 1.10–1.01 (m, 6H, O–CH$_2$–CH$_2$–CH_3), 0.97–0.86 (m, 6H, O–CH$_2$–CH$_2$–CH_3) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 157.7, 157.3, 157.1, 154.5, 143.2, 136.8, 136.5, 136.1, 135.6, 135.5, 134.4, 129.0, 128.9, 128.8 (2×), 128.2, 128.1, 124.5, 122.0 (3×), 119.9, 117.3, 114.4, 110.7, 76.8 (3×), 31.5, 31.0, 30.5, 27.8, 23.4, 23.3, 23.2, 22.6, 10.6 (2×), 10.1, 9.9 ppm. IR (KBr) ν 3312.4, 2962.3, 2933.3, 2875.7, 1712.6, 1463.4, 1216.1, 1184.0 cm^{-1}. HRMS (ESI$^+$) calcd for $\mathrm{C_{42}H_{49}F_3N_2O_5}$ 719.36663 [M + H]$^+$, 741.34858 [M + Na]$^+$, 757.32252 [M + K]$^+$, found *m*/*z* 719.36658 [M + H]$^+$ (100%), 741.34772 [M + Na]$^+$ (15%), 757.32153 [M + K]$^+$ (7%).

4-Trifluoroacetamido-17-amino-25,26,27,28-tetrapropoxycalix[4]arene (12b). Calixarene **12b** was isolated from the same reaction mixture as calixarene **12a** as a yellow amorphous solid (0.316 g, 17%), mp 215–218 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.58 (br s, 1H, Ar–*NH*–CO), 7.10–6.99 (m, 4H, Ar–*H*), 6.94–6.84 (m, 3H, Ar–*H*), 6.33 (d, 1H, J = 8.2 Hz, Ar–*H*), 5.53 (d, 1H, J = 1.6 Hz, Ar–*H*), 5.39 (d, 1H, J = 1.6 Hz, Ar–*H*), 4.64 (d, 1H, J = 14.5 Hz, Ar–CH_2–Ar), 4.51 (d, 1H, J = 13.3 Hz, Ar–CH_2–Ar), 4.47–4.38 (m, 2H, Ar–CH_2–Ar), 4.13–3.89 (m, 4H, O–CH_2), 3.82–3.64 (m, 4H, O–CH_2), 3.26–3.16 (m, 2H, Ar–CH_2–Ar), 3.15–3.08 (m, 2H, Ar–CH_2–Ar), 1.99–1.82 (m, 8H, O–CH$_2$–CH_2), 1.16–1.06 (m, 6H, O–CH$_2$–CH$_2$–CH_3), 0.94 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3), 0.88 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 158.0, 157.9, 156.5, 154.9, 154.5, 149.1, 140.6, 138.1, 136.9, 136.0, 134.4, 134.2, 133.3, 133.1, 130.6, 129.7, 129.1, 128.7, 128.6, 128.4, 126.9, 122.0 (2×), 118.4, 115.1, 114.3, 77.2, 76.9, 76.8, 76.2, 31.4, 31.1, 30.8, 28.7, 23.4 (2×), 23.1, 22.4, 10.8, 10.7, 10.0, 9.7 ppm. IR (KBr) ν 3345.1, 2961.9, 2930.6, 2875.3, 1722.8, 1464.4, 1211.9, 1159.2 cm^{-1}. HRMS (ESI$^+$) calcd for $\mathrm{C_{42}H_{49}F_3N_2O_5}$ 719.36663 [M + H]$^+$, found *m*/*z* 719.36746 [M + H]$^+$ (100%).

General procedure for preparation of *p*-trifluoroamido-*m*-amides

p-Trifluoroamido-*m*-amino calixarene **12a** was dissolved in 10 mL of THF at room temperature. Et$_3$N and corresponding carboxylic acid derivative were added. The solution was stirred for 24 h at room temperature. 10 mL of dichloromethane were added. The crude reaction mixture was washed with water (3 × 20 mL) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield crude product which was further purified by preparative TLC on silica gel.

4-Acetamido-17-trifluoroacetamido-25,26,27,28-tetrapropoxycalix[4]arene (13a). Compound **13a** was prepared according to the general procedure by reacting calixarene **12a** (0.071 g, 0.10 mmol) and acetic anhydride (0.012 mL, 0.12 mmol) in the presence of triethylamine (0.120 mL, 0.86 mmol). The title compound **13a** was isolated without further purification as a colourless amorphous solid (0.043 g, 57%), mp 277–279 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 9.58 (br s, 1H, Ar–*NH*–CO), 7.19–7.05 (m, 4H, Ar–*H*), 6.97 (t, 1H, J = 7.4 Hz, Ar–*H*), 6.89 (t, 1H, J = 7.4 Hz, Ar–*H*), 6.56–6.52 (m, 1H, Ar–*NH*–CO), 6.50 (d, 1H, J = 8.2 Hz, Ar–*H*), 6.25 (d, 1H, J = 2.4 Hz, Ar–*H*), 6.07 (d, 1H, J = 8.2 Hz, Ar–*H*), 5.62 (d, 1H, J = 2.4 Hz, Ar–*H*), 4.58 (d, 1H, J = 14.5 Hz, Ar–CH_2–Ar), 4.49–4.40 (m, 3H, Ar–CH_2–Ar), 4.11–4.00 (m, 2H, O–CH_2), 3.99–3.88 (m, 2H, O–CH_2), 3.72–3.53 (m, 4H, O–CH_2), 3.22 (d, 1H, J = 13.7 Hz, Ar–CH_2–Ar), 3.19–3.06 (m, 3H, Ar–CH_2–Ar), 1.95 (s, 3H, CO–CH_3), 1.93–1.78 (m, 8H, O–CH$_2$–CH_2), 1.14–1.06 (m, 6H, O–CH$_2$–CH$_2$–CH_3), 0.87 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3), 0.81 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 167.6, 158.2, 158.1, 156.1, 155.0, 154.7, 153.5, 137.4, 163.2, 134.3, 134.2, 134.0, 132.9, 131.1, 129.8, 129.4 (2×), 129.2, 127.5, 126.2, 122.2 (2×), 120.8, 120.7, 119.3, 117.6, 114.8, 77.0, 76.8, 76.6, 76.1, 31.3, 30.5, 29.7, 29.1, 24.1, 23.5 (2×), 23.0, 22.3, 10.9, 10.8, 9.8, 9.6 ppm. IR (KBr) ν 3344.6, 3065.4, 2962.6, 2933.1, 2876.0, 1706.7, 1674.0, 1463.8, 1214.1 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{44}H_{51}F_3N_2O_6$ 783.35914 [M + Na]$^+$, 799.33308 [M + K]$^+$, found *m/z* 783.35923 [M + Na]$^+$ (100%), 799.33191 [M + K]$^+$ (12%).

4-Benzoylamido-17-trifluoroacetamido-25,26,27,28-tetrapropoxycalix[4]arene (13b). Compound **13b** was prepared according to the general procedure by reacting calixarene **12a** (0.061 g, 0.08 mmol) and benzoyl chloride (0.012 mL, 0.10 mmol) in the presence of triethylamine (0.110 mL, 0.79 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 5 : 1, v/v) to give title compound **13b** as a colourless amorphous solid (0.042 g, 60%), mp 280–283 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 9.65 (br s, 1H, Ar–*NH*–CO), 7.76 (d, 2H, J = 7.0 Hz, Ar–*H*), 7.61–7.55 (m, 1H, Ar–*H*), 7.55–7.48 (m, 2H, Ar–*H*), 7.25 (s, 1H, Ar–*NH*–CO), 7.20–7.13 (m, 2H, Ar–*H*), 6.99 (t, 1H, J = 7.4 Hz, Ar–*H*), 6.94 (dd, 1H, J = 7.4, 1.2 Hz, Ar–*H*), 6.72 (dd, 1H, J = 7.4, 1.2 Hz, Ar–*H*), 6.60 (d, 1H, J = 8.22 Hz, Ar–*H*), 6.31 (t, 1H, J = 7.4 Hz, Ar–*H*), 6.27 (d, 1H, J = 2.4 Hz, Ar–*H*), 6.14 (d, 1H, J = 8.2 Hz, Ar–*H*), 5.78 (d, 1H, J = 2.4 Hz, Ar–*H*), 4.61 (d, 1H, J = 14.5 Hz, Ar–CH_2–Ar), 4.52–4.40 (m, 3H, Ar–CH_2–Ar), 4.14–4.03 (m, 2H, O–CH_2), 4.01–3.87 (m, 2H, O–CH_2), 3.74–3.57 (m, 4H, O–CH_2), 3.27–3.19 (m, 2H, Ar–CH_2–Ar), 3.17–3.08 (m, 2H, Ar–CH_2–Ar), 1.97–1.79 (m, 8H, O–CH$_2$–CH_2), 1.15–1.08 (m, 6H, O–CH$_2$–CH$_2$–CH_3), 0.88 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3), 0.81 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 164.6, 158.2, 157.8, 156.2, 155.1, 154.8, 153.6, 137.3, 137.2, 136.2, 134.7, 134.4, 134.3, 133.7, 133.1, 131.6, 131.6, 130.6, 130.1, 129.4 (2×), 129.2, 128.5, 127.7, 127.2, 126.5, 122.3, 122.2, 121.1, 120.9, 119.2, 77.1, 76.8, 76.7, 76.1, 31.3 (2×), 30.6, 29.4, 23.5 (2×), 23.0, 22.4, 10.9, 10.8, 9.8, 9.6 ppm. IR (KBr) ν 3250.8, 3066.0, 2962.5, 2933.5, 2875.7, 1706.6, 1463.6, 1214.7, 1004.4 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{49}H_{53}F_3N_2O_6$ 845.37479 [M + Na]$^+$, 861.34873 [M + K]$^+$, found *m/z* 845.37536 [M + Na]$^+$ (100%), 861.34718 [M + K]$^+$ (8%).

4-Bromoacetamido-17-trifluoroacetamido-25,26,27,28-tetrapropoxycalix[4]arene (13c). Compound **13c** was prepared according to the general procedure by reacting calixarene **12a** (0.100 g, 0.14 mmol) and bromoacetyl chloride (0.020 mL, 0.23 mmol) in the presence of triethylamine (0.180 mL, 1.29 mmol). The title compound **13c** was isolated without further purification as a colourless amorphous solid (0.113 g, 97%), mp 151–154 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 9.48 (br s, 1H, Ar–*NH*–CO), 7.62 (s, 1H, Ar–*NH*–CO), 7.29–7.25 (m, 1H, Ar–*H*), 7.18 (dd, 1H, J = 7.4, 1.2 Hz, Ar–*H*), 7.13 (dd, 1H, J = 7.4, 1.2 Hz, Ar–*H*), 7.06 (dd, 1H, J = 7.4, 1.2 Hz, Ar–*H*), 7.01–6.96 (m, 1H, Ar–*H*), 6.87 (t, 1H, J = 7.4 Hz, Ar–*H*), 6.44 (d, 1H, J = 8.2 Hz, Ar–*H*), 6.34 (d, 1H, J = 2.4 Hz, Ar–*H*), 6.12 (d, 1H, J = 8.2 Hz, Ar–*H*), 5.55 (d, 1H, J = 2.4 Hz, Ar–*H*), 4.59 (d, 1H, J = 14.5 Hz, Ar–CH_2–Ar), 4.50–4.41 (m, 3H, Ar–CH_2–Ar), 4.13–4.03 (m, 2H, O–CH_2), 3.99–3.91 (m, 2H, O–CH_2), 3.84 (s, 1H, CO–CH_2–Br), 3.83 (s, 1H, CO–CH_2–Br), 3.73–3.57 (m, 4H, O–CH_2), 3.27–3.18 (m, 2H, Ar–CH_2–Ar), 3.16–3.09 (m, 2H, Ar–CH_2–Ar), 1.94–1.80 (m, 8H, O–CH$_2$–CH_2), 1.15–1.08 (m, 6H, O–CH$_2$–CH$_2$–CH_3), 0.88 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3), 0.83 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 162.3, 158.2, 158.1, 156.3, 153.5, 137.4 (2×), 153.9, 134.4, 134.1, 133.6, 132.2, 131.9, 129.6, 129.5, 129.3, 129.2, 127.8, 126.8, 125.5, 122.3 (2×), 120.8, 120.6, 119.2, 117.6, 114.7, 77.2, 76.8, 76.8, 76.1, 34.2, 31.3 (2×), 30.1, 29.9, 23.7, 23.5 (2×), 23.0, 10.9, 10.8, 9.8, 9.6 ppm. IR (KBr) ν 3265.2, 2961.6, 2933.7, 2875.2, 1705.6, 1683.6, 1463.6, 1215.0, 1159.1 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{44}H_{50}BrF_3N_2O_6$ 861.2697 [M + Na]$^+$, 877.2436 [M + K]$^+$, found *m/z* 861.2702 [M + Na]$^+$ (100%), 877.2434 [M + K]$^+$ (55%).

4-Chloroacetamido-17-trifluoroacetamido-25,26,27,28-tetrapropoxycalix[4]arene (13d). Compound **13d** was prepared according to the general procedure by reacting calixarene **12a** (0.101 g, 0.14 mmol) and chloroacetyl chloride (0.017 mL, 0.21 mmol) in the presence of triethylamine (0.180 mL, 1.29 mmol). The title compound **13d** was isolated without further purification as a colourless amorphous solid (0.092 g, 82%), mp 113–116 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 9.56 (br s, 1H, Ar–*NH*–CO), 7.66 (s, 1H, Ar–*NH*–CO), 7.24 (dd, 1H, J = 7.4, 1.2 Hz, Ar–*H*), 7.20 (dd, 1H, J = 7.4, 1.6 Hz, Ar–*H*), 7.14 (dd, 1H, J = 7.4, 1.2 Hz, Ar–*H*), 7.07 (dd, 1H, J = 7.4, 1.2 Hz, Ar–*H*), 6.99 (t, 1H, J = 7.4 Hz, Ar–*H*), 6.87 (t, 1H, J = 7.4 Hz, Ar–*H*), 6.46 (d, 1H, J = 8.2 Hz, Ar–*H*), 6.37 (d, 1H, J = 2.4 Hz, Ar–*H*), 6.14 (d, 1H, J = 8.6 Hz, Ar–*H*), 5.52 (d, 1H, J = 2.4 Hz, Ar–*H*), 4.60 (d, 1H, J = 14.1 Hz, Ar–CH_2–Ar), 4.52–4.42 (m, 3H, Ar–CH_2–Ar), 4.14–4.04 (m, 2H, O–CH_2), 4.02 (s, 1H, CO–CH_2–Cl), 4.00–3.90 (m, 3H, O–CH_2, CO–CH_2–Cl), 3.75–3.58 (m, 4H, O–CH_2), 3.26 (d, 1H, J = 13.7 Hz, Ar–CH_2–Ar), 3.21 (d, 1H, J = 14.5 Hz, Ar–CH_2–Ar), 3.17–3.09 (m, 2H, Ar–CH_2–Ar), 1.97–1.81 (m, 8H, O–CH$_2$–CH_2), 1.16–1.09 (m, 6H, O–CH$_2$–CH$_2$–CH_3), 0.89 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3), 0.83 (t, 3H, J = 7.4 Hz, O–CH$_2$–CH$_2$–CH_3) ppm. ^{13}C-

NMR ($CDCl_3$, 100 MHz, 298 K) δ 162.9, 158.2, 158.1, 156.3, 153.4, 137.4 (2×), 135.9, 134.3, 134.0, 133.5, 132.2, 131.6, 129.7, 129.6, 129.5, 129.4, 129.2, 127.8, 126.8, 122.3 (2×), 120.8, 120.6, 119.3, 117.6, 114.8, 77.2, 76.8, 76.6, 76.1, 43.0, 31.3 (2×), 30.5, 29.3, 23.5 (2×), 23.0, 22.4, 10.9, 10.8, 9.8, 9.6 ppm. IR (KBr) ν 3265.1, 2962.6, 2932.5, 2875.8, 1685.0, 1463.9, 1215.0, 768.8 cm^{-1}.

HRMS (ESI^+) calcd for $C_{44}H_{50}ClF_3N_2O_6$ 817.3202 $[M + Na]^+$, 833.2941 $[M + K]^+$, found *m*/*z* 817.3207 $[M + Na]^+$ (100%), 833.2940 $[M + K]^+$ (90%).

(*S*)-4-*O*-Mandelylamido-17-trifluoroacetamido-25,26,27,28-tetrapropoxycalix[4]arene (13e). Compound **13e** was prepared according to the general procedure by reacting calixarene **12a** (0.100 g, 0.14 mmol) and (*S*)-*O*-acetylmandelyl chloride (0.040 g, 0.19 mmol) in the presence of triethylamine (0.180 mL, 1.29 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 3 : 1, v/v) to give title compound **13e** as a colourless amorphous solid (0.101 g, 81%), mp 124–127 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ 9.34 (br s, 1H, Ar–*NH*–CO), 8.61 (br s, 1H, Ar–*NH*–CO), 7.53–7.47 (m, 3H, Ar–*H*), 7.44–7.32 (m, 7H, Ar–*H*), 7.19–6.83 (m, 13H, Ar–*H*), 6.67 (d, 1H, *J* = 8.6 Hz, Ar–*H*), 6.35–6.30 (m, 3H, Ar–*H*), 6.08 (s, 1H, Ph–*CH*(OAc)–CO), 6.06 (t, 2H, *J* = 7.8 Hz, Ar–*H*), 5.96 (d, 1H, *J* = 2.4 Hz, Ar–*H*), 5.85 (s, 1H, Ph–*CH*(OAc)–CO), 5.62 (d, 1H, *J* = 2.4 Hz, Ar–*H*), 4.63–4.53 (m, 2H, Ar–CH_2–Ar), 4.50–4.39 (m, 6H, Ar–CH_2–Ar), 4.13–4.00 (m, 4H, O–CH_2), 3.98–3.87 (m, 4H, O–CH_2), 3.73–3.51 (m, 8H, O–CH_2), 3.27–3.05 (m, 8H, Ar–CH_2–Ar), 2.34 (s, 3H, CO–CH_3), 2.18 (s, 3H, CO–CH_3), 1.95–1.77 (m, 16H, O–CH_2–CH_2), 1.14–1.03 (m, 12H, O–CH_2–CH_2–CH_3), 0.91–0.77 (m, 12H, O–CH_2–CH_2–CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz, 298 K) δ 170.2, 168.6, 165.6, 165.5, 158.2, 158.1 (3×), 156.3, 156.0, 154.8, 154.6, 154.4, 153.7, 153.4, 137.8, 137.5, 137.4, 136.9, 136.5, 135.9 (2×), 135.7, 135.0, 134.5, 134.4, 134.3, 134.2, 134.0, 133.3, 132.5, 132.1, 131.6, 131.1, 129.8, 129.5 (3×), 129.4, 129.3, 129.2 (3×), 128.8, 128.5, 128.1 (2×), 127.7, 127.4, 127.1, 125.5, 122.3 (2×), 122.0, 121.6, 121.5, 120.9, 120.8, 119.9 (2×), 117.6 (2×), 114.6, 114.5, 77.1, 77.0, 76.9, 76.8 (2×), 76.6, 76.1 (2×), 75.4, 75.2, 31.4, 31.3 (2×), 31.2, 30.6, 30.5, 29.6, 29.2, 23.5 (2×), 23.4 (2×), 23.0 (2×), 22.4, 22.2, 21.3, 20.9, 10.9, 10.8 (3×), 9.8 (2×), 9.6, 9.5 ppm. IR (KBr) ν 3260.5, 2962.8, 2934.0, 2875.8, 1711.3, 1675.1, 1517.6, 1464.1, 1216.5 cm^{-1}. HRMS (ESI^+) calcd for $C_{52}H_{57}F_3N_2O_8$ 917.39592 $[M + Na]^+$, 933.36986 $[M + K]^+$, found *m*/*z* 917.39736 $[M + Na]^+$ (100%), 933.37037 $[M + K]^+$ (55%).

4-(1-Pyrenecarbonylamido)-17-trifluoroacetamido-25,26,27,28-tetrapropoxycalix[4]arene (13f). Compound **13f** was prepared according to the general procedure by reacting calixarene **12a** (0.100 g, 0.14 mmol) and 1-pyrenecarbonyl chloride (0.060 g, 0.23 mmol) in the presence of triethylamine (0.180 mL, 1.29 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 4 : 1, v/v) to give title compound **13f** as a yellow amorphous solid (0.088 g, 67%), mp 160–163 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ 9.89 (br s, 1H, Ar–*NH*–CO), 8.54 (d, 1H, *J* = 9.4 Hz, Ar–*H*), 8.31–8.07 (m, 8H, Ar–*H*), 7.35 (br s, 1H, Ar–*NH*–CO), 7.25–7.19 (m, 2H, Ar–H), 7.08–7.02 (m, 2H, Ar–*H*), 6.98–6.94 (m, 1H, Ar–*H*), 6.42 (d, 1H, *J* = 7.4 Hz, Ar–*H*), 6.39 (d, 1H, *J* = 2.4 Hz, Ar–*H*), 6.28 (d, 1H, *J* = 8.2 Hz), 5.98 (d, 1H, *J* = 2.0 Hz, Ar–*H*), 5.93 (t, 1H, *J* = 7.4 Hz, Ar–*H*), 4.64 (d, 1H, *J* = 14.5 Hz, Ar–CH_2–Ar), 4.57–4.47 (m, 3H, Ar–CH_2–Ar), 4.16–3.89 (m, 4H, O–CH_2), 3.79–3.61 (m, 4H, O–CH_2), 3.31 (d, 1H, *J* = 13.7 Hz, Ar–CH_2–Ar), 3.24–3.18 (m, 2H, Ar–CH_2–Ar), 3.16 (d, 1H, *J* = 14.9 Hz, Ar–CH_2–Ar), 2.00–1.79 (m, 8H, O–CH_2–CH_2), 1.18–1.09 (m, 6H, O–CH_2–CH_2–CH_3), 0.91 (t, 3H, *J* = 7.4 Hz, O–CH_2–CH_2–CH_3), 0.81 (t, 3H, *J* = 7.4 Hz, O–CH_2–CH_2–CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz, 298 K) δ 167.0, 158.2, 157.9, 156.3, 155.6, 155.2, 153.8, 137.3 (2×), 136.3, 136.6, 134.5, 133.8, 133.5, 133.1, 131.2, 131.1, 130.7, 130.2, 129.5 (2×), 129.3, 129.2, 129.0, 128.6, 128.0, 127.2, 126.4, 126.0, 125.9, 125.5, 125.4, 124.9 (2×), 124.4, 124.3, 123.0, 122.4, 121.7, 121.0, 117.9, 117.7, 114.8, 77.1, 76.9, 76.7, 76.2, 31.4, 31.3, 30.7, 29.3, 23.5 (2×), 23.1, 22.3, 10.9, 10.8, 9.9, 9.6 ppm. IR (KBr) ν 3248.1, 3050.6, 2961.6, 2932.3, 2875.2, 1713.3, 1654.2, 1464.0, 1214.2 cm^{-1}. HRMS (ESI^+) calcd for $C_{59}H_{57}F_3N_2O_6$ 969.40609 $[M + Na]^+$, 985.38003 $[M + K]^+$, found *m*/*z* 969.40613 $[M + Na]^+$ (100%), 985.37960 $[M + K]^+$ (80%).

General procedure for preparation of bridged calixarenes

Corresponding calixarene was dissolved in the argon atmosphere in 5 mL of dry CH_2Cl_2. The solution was cooled down to −78 °C. 2-chloropyridine and trifluoromethanesulfonic anhydride were added afterwards. After 5 minutes of stirring the solution was warmed to 0 °C and stirred for another 5 min. The mixture was then warmed to room temperature and stirred for one more hour. The reaction was quenched by a solution of $NaHCO_3$. The organic layer was separated, washed with water (1×10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield crude product which was further purified by preparative TLC on silica gel.

17-Trifluoracetamido-methylimine-bridged-25,26,27,28-tetrapropoxycalix[4]arene (14a). Calixarene **14a** was prepared according to general procedure by reacting calixarene **13a** (0.043 g, 0.06 mmol), 2-chloropyridine (0.010 mL, 0.11 mmol) and triflic anhydride (0.010 mL, 0.06 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 3 : 1, v/v) to give title compound **14a** as a yellow amorphous solid (0.027 g, 64%), mp 122–125 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) δ 8.22 (br s, 1H, Ar–*NH*–CO), 7.16 (d, 1H, *J* = 2.4 Hz, Ar–*H*), 7.07–6.99 (m, 2H, Ar–*H*), 6.96 (dd, 1H, *J* = 7.4, 1.2 Hz, Ar–*H*), 6.86 (d, 1H, *J* = 7.8 Hz, Ar–*H*), 6.80 (d, 1H, *J* = 2.4 Hz, Ar–*H*), 6.72 (t, 1H, *J* = 7.4 Hz, Ar–*H*), 6.61 (d, 1H, *J* = 8.2 Hz, Ar–*H*), 6.20 (d, 1H, *J* = 8.2 Hz, Ar–*H*), 4.61–4.54 (m, 2H, Ar–CH_2–Ar), 4.45–4.37 (m, 2H, Ar–CH_2–Ar), 4.01–3.68 (m, 8H, O–CH_2), 3.31 (d, 1H, *J* = 12.1 Hz, Ar–CH_2–Ar), 3.23–3.15 (m, 2H, Ar–CH_2–Ar), 2.75 (d, 1H, *J* = 11.7 Hz, Ar–CH_2–Ar), 2.51 (s, 3H, N═C(Ar)–CH_3), 2.29 (sex, 2H, *J* = 7.8 Hz, O–CH_2–CH_2), 2.05–1.83 (m, 6H, O–CH_2–CH_2), 1.14 (t, 3H, *J* = 7.4 Hz, O–CH_2–CH_2–CH_3), 1.09–0.96 (m, 9H, O–CH_2–CH_2–CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz, 298 K) δ 166.9, 156.1, 153.6, 153.2 (2×), 143.2, 140.3, 136.9, 135.8, 135.4, 135.3, 135.1, 135.0, 133.8, 130.6, 129.3, 128.8, 127.4, 127.1, 126.8, 123.0, 121.8, 121.2, 120.4, 118.1, 117.3, 115.5, 77.9, 77.8, 77.6, 76.3, 31.0, 30.5, 26.8, 23.5, 23.3 (2×), 23.2, 23.0, 22.7, 10.7, 10.3 (2×), 9.9 ppm. IR (KBr) ν 2960.6, 2930.2, 2874.8, 1721.0, 1610.7, 1463.4, 1215.5 cm^{-1}. HRMS

(ESI$^+$) calcd for $C_{44}H_{49}F_3N_2O_5$ 743.36663 [M + H]$^+$, 765.34858 [M + Na]$^+$, found *m*/*z* 743.36721 [M + H]$^+$ (100%), 765.34773 [M + Na]$^+$ (27%).

17-Trifluoracetamido-phenylimine-bridged-25,26,27,28-tetrapropoxycalix[4]arene (14b). Calixarene **14b** was prepared according to general procedure by reacting calixarene **13b** (0.042 g, 0.05 mmol), 2-chloropyridine (0.010 mL, 0.11 mmol) and triflic anhydride (0.010 mL, 0.06 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 3 : 1, v/v) to give title compound **14b** as a yellow amorphous solid (0.032 g, 78%), mp 127–130 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.89–7.84 (m, 2H, Ar–*H*), 7.54 (bs s, 1H, Ar–*NH*–CO), 7.45–7.35 (m, 3H, Ar–*H*), 7.17 (d, 1H, $J =$ 2.4 Hz, Ar–*H*), 7.05 (dd, 1H, $J =$ 7.8, 1.6 Hz, Ar–*H*), 6.99 (d, 2H, J = 7.8 Hz. Ar–*H*), 6.85 (d, 1H, $J =$ 2.7 Hz, Ar–*H*), 6.80–6.74 (m, 2H, Ar–*H*), 6.67–6.63 (m, 2H, Ar–*H*), 4.69 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 4.61 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 4.48 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 4.43 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 4.05–3.94 (m, 2H, O–*CH$_2$*), 3.92–3.81 (m, 2H, O–*CH$_2$*), 3.81–3.69 (m, 4H, O–*CH$_2$*), 3.32 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 3.25 (d, 1H, J = 12.5 Hz, Ar–*CH$_2$*–Ar), 3.19 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 2.89 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 2.32 (sex, 2H, $J =$ 7.4 Hz, O–CH$_2$–*CH$_2$*), 2.10–1.99 (m, 4H, O–CH$_2$–*CH$_2$*), 1.94–1.84 (m, 2H, O–CH$_2$–*CH$_2$*), 1.18 (t, 3H, $J =$ 7.4 Hz, O–CH$_2$–CH$_2$–*CH$_3$*), 1.10–0.99 (m, 9H, O–CH$_2$–CH$_2$–*CH$_3$*) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 165.9, 156.2, 154.5, 153.6, 153.4, 153.3, 145.9, 139.8, 136.9, 135.9, 135.4, 135.2, 135.0, 131.8, 130.8, 130.1, 129.4, 129.2, 128.8 (2×), 128.0, 127.1, 127.0, 126.9, 123.3, 123.0, 121.3, 120.8, 118.6, 117.2, 114.3, 78.0, 77.8, 77.6, 76.4, 31.1, 30.6, 30.5, 23.8, 23.6, 23.3, 23.0, 22.8, 10.7, 10.4, 10.3, 9.9 ppm. IR (KBr) ν 3331.0, 2924.0, 2872.4, 1459.9, 1383.6, 1212.5, 1195.5, 1056.2 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{49}H_{51}F_3N_2O_5$ 805.38228 [M + H]$^+$, 827.36423 [M + Na]$^+$, found *m*/*z* 805.38297 [M + H]$^+$ (100%), 827.36360 [M + Na]$^+$ (35%).

17-Trifluoracetamido-bromomethylimine-bridged-25,26,27,28-tetrapropoxycalix[4]arene (14c). Calixarene **14c** was prepared according to general procedure by reacting calixarene **13c** (0.071 g, 0.08 mmol), 2-chloropyridine (0.010 mL, 0.11 mmol) and trifluoromethansulphonic anhydride (0.020 mL, 0.12 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 4 : 1, v/v) to give title compound **14c** as a yellow amorphous solid (0.050 g, 72%), mp 145–148 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.70 (br s, 1H, Ar–*NH*–CO), 7.19 (d, 1H, $J =$ 2.4 Hz, Ar–*H*), 7.07 (d, 1H, $J =$ 7.8 Hz, Ar–*H*), 7.02 (dd, 1H, $J =$ 7.4, 1.6 Hz, Ar–*H*), 6.98 (dd, 1H, $J =$ 7.4, 1.6 Hz, Ar–*H*), 6.88 (d, 1H, $J =$ 8.2 Hz, Ar–*H*), 6.82 (d, 1H, $J =$ 2.7 Hz, Ar–*H*), 6.78–6.72 (m, 2H, Ar–*H*), 6.42 (d, 1H, $J =$ 7.8 Hz, Ar–*H*), 4.66–4.60 (m, 2H, Ar–*CH$_2$*–Ar, CO–*CH$_2$*–Br), 4.58 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 4.46 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 4.41 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 4.24 (d, 1H, $J =$ 10.2 Hz, CO–*CH$_2$*–Br), 4.03–3.90 (m, 2H, O–*CH$_2$*), 3.87–3.68 (m, 6H, O–*CH$_2$*), 3.33 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 3.23 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 3.18 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 2.86 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 2.33–2.23 (m, 2H, O–CH$_2$–*CH$_2$*), 2.07–1.82 (m, 6H, O–CH$_2$–*CH$_2$*), 1.14 (t, 3H, $J =$ 7.4 Hz, O–CH$_2$–CH$_2$–*CH$_3$*), 1.10–0.97 (m, 9H, O–CH$_2$–CH$_2$–*CH$_3$*) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 164.6, 156.2, 153.6 (2×), 153.3, 144.0, 137.9, 136.6, 135.7, 135.3, 135.2, 134.9, 131.9, 131.0, 129.3, 128.9, 128.8, 127.6, 127.2, 127.1, 123.1, 121.8, 121.4, 119.5, 118.2, 117.2, 114.3, 78.0, 77.9, 77.6, 76.3, 35.2, 31.1, 30.6, 30.5, 23.6, 23.3, 23.2, 23.1, 22.7, 10.7, 10.6, 10.3, 9.9 ppm. IR (KBr) ν 3300.8, 2962.1, 2934.4, 2875.7, 1721.8, 1464.2, 1422.7, 1217.4, 1158.1 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{44}H_{48}BrF_3N_2O_5$ 821.2771 [M + H]$^+$, 843.2591 [M + Na]$^+$, 861.2315 [M + K]$^+$, found *m*/*z* 821.2768 [M + H]$^+$ (100%), 843.2585 [M + Na]$^+$ (60%), 861.2330 [M + K]$^+$ (30%).

17-Trifluoracetamido-chloromethylimine-bridged-25,26,27,28-tetrapropoxycalix[4]arene (14d). Calixarene **14d** was prepared according to general procedure by reacting calixarene **13d** (0.066 g, 0.08 mmol), 2-chloropyridine (0.010 mL, 0.11 mmol) and triflic anhydride (0.020 mL, 0.12 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 4 : 1, v/v) to give title compound **14d** as a yellow amorphous solid (0.052 g, 81%), mp 153–156 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.16 (d, 1H, $J =$ 2.7 Hz, Ar–*H*), 7.08 (d, 1H, $J =$ 8.2 Hz, Ar–*H*), 7.03 (dd, 1H, $J =$ 7.4, 1.6 Hz, Ar–*H*), 6.98 (dd, 1H, $J =$ 7.4, 1.6 Hz, Ar–*H*), 6.87 (d, 1H, $H =$ 7.8 Hz, Ar–*H*), 6.82 (d, 1H, $J =$ 2.7 Hz, Ar–*H*), 6.74 (t, 1H, $J =$ 7.4 Hz, Ar–*H*), 6.68 (d, 1H, $J =$ 8.2 Hz, Ar–*H*), 6.28 (d, 1H, $J =$ 7.8 Hz, Ar–*H*), 4.71 (d, 1H, $J =$ 11.7 Hz, CO–*CH$_2$*–Br), 4.64 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 4.59 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 4.46 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 4.41 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 4.33 (d, 1H, $J =$ 11.7 Hz, CO–*CH$_2$*–Br), 4.03–3.92 (m, 2H, O–*CH$_2$*), 3.87–3.68 (m, 6H, O–*CH$_2$*), 3.33 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 3.23 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 3.18 (d, 1H, $J =$ 12.5 Hz, Ar–*CH$_2$*–Ar), 2.81 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 2.35–2.24 (m, 2H, O–CH$_2$–*CH$_2$*), 2.07–1.96 (m, 4H, O–CH$_2$–*CH$_2$*), 1.95–1.82 (m, 2H, O–CH$_2$–*CH$_2$*), 1.15 (t, 3H, O–CH$_2$–CH$_2$–*CH$_3$*), 1.10–0.98 (m, 9H, O–CH$_2$–CH$_2$–*CH$_3$*) ppm. ^{13}C-NMR (CDCl$_3$, 100 MHz, 298 K) δ 164.3, 156.1, 153.6, 153.5, 153.3, 144.1, 137.9, 136.6, 135.7, 135.3, 135.1, 134.9, 131.8, 130.8, 129.3, 128.9, 128.8, 127.6, 127.2, 127.1, 123.1, 121.7, 121.2, 119.8, 118.2, 117.2, 114.3, 78.0, 77.9, 77.6, 76.4, 47.7, 31.1, 30.6, 30.5, 23.6, 23.3 (2×), 23.0, 22.7, 10.7, 10.6, 10.3, 9.9 ppm. IR (KBr) ν 3300.8, 2962.1, 2934.4, 2875.7, 1721.8, 1464.2, 1217.4, 1158.1, 1005.5 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{44}H_{48}ClF_3N_2O_5$ 777.32766 [M + H]$^+$, 799.30961 [M + Na]$^+$, 815.28354 [M + K]$^+$, found *m*/*z* 777.32712 [M + H]$^+$ (20%), 799.30930 [M + Na]$^+$ (100%), 815.28301 [M + K]$^+$ (55%).

(*S*)-17-Trifluoracetamido-(phenyl-acetoxymethyl)imine-bridged-25,26,27,28-tetrapropoxycalix[4]arene (14e). Calixarene **14e** was prepared according to general procedure by reacting calixarene **13e** (0.113 g, 0.13 mmol), 2-chloropyridine (0.020 mL, 0.21 mmol) and triflic anhydride (0.025 mL, 0.15 mmol). The crude reaction mixture was purified by preparative TLC on silica gel (cyclohexane : ethyl acetate 3 : 2, v/v) to give title compound **14e** as a yellow amorphous solid (0.018 g, 16%), mp 130–133 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz, 298 K) δ 8.15–8.11 (m, 2H, Ar–*H*), 7.58 (tt, 1H, $J =$ 7.4, 1.2 Hz, Ar–*H*), 7.55 (br s, 1H, Ar–*NH*–CO), 7.49–7.44 (m, 2H, Ar–*H*), 7.11 (d, 1H, $J =$ 2.7 Hz, Ar–*H*), 7.03 (dd, 1H, $J =$ 7.8, 1.6 Hz, Ar–*H*), 7.00 (d, 2H, $J =$ 7.8 Hz, Ar–*H*), 6.93 (d, 1H, $J =$ 2.7 Hz, Ar–*H*), 6.86 (d, 1H, $J =$ 8.2 Hz, Ar–*H*), 6.78 (d, 2H, J = 7.8 Hz, Ar–*H*), 6.73 (d, 1H, $J =$ 8.2 Hz, Ar–*H*), 4.76 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 4.59 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 4.51 (d, 1H, $J =$ 12.1 Hz, Ar–*CH$_2$*–Ar), 4.43 (d, 1H, $J =$ 12.9 Hz, Ar–

CH_2–Ar), 4.08–3.90 (m, 3H, O–CH_2), 3.89–3.70 (m, 6H, O–CH_2, AcO–CH(Ph)–C=N), 3.31 (d, 1H, J = 12.1 Hz, Ar–CH_2–Ar), 3.28 (d, 1H, J = 12.5 Hz, Ar–CH_2–Ar), 3.20 (d, 1H, J = 12.9 Hz, Ar–CH_2–Ar), 2.95 (d, 1H, J = 12.1 Hz, Ar–CH_2–Ar), 2.32–2.25 (m, 2H, O–$\mathrm{CH_2}$–CH_2), 2.17 (s, 3H, O–CO–CH_3), 2.06–1.86 (m, 6H, O–$\mathrm{CH_2}$–CH_2), 1.15 (t, 3H, J = 7.4 Hz, O–$\mathrm{CH_2}$–$\mathrm{CH_2}$–CH_3), 1.08 (t, 3H, J = 7.4 Hz, O–$\mathrm{CH_2}$–$\mathrm{CH_2}$–CH_3), 1.03 (t, 3H, J = 7.4 Hz, O–$\mathrm{CH_2}$–$\mathrm{CH_2}$–CH_3), 1.02 (t, 3H, J = 7.4 Hz, O–$\mathrm{CH_2}$–$\mathrm{CH_2}$–CH_3) ppm. ^{13}C-NMR ($\mathrm{CDCl_3}$, 100 MHz, 298 K) δ 194.3, 163.9, 156.1, 153.6, 153.5, 144.5, 138.0, 136.7, 136.1, 135.4 (2×), 135.1, 134.9, 133.4, 133.3, 130.8, 130.7, 129.4, 129.0, 128.7, 128.4, 127.4, 127.3, 127.2, 123.1, 121.7, 121.3, 120.7, 119.4, 113.9, 78.0 (2×), 77.6, 76.7, 76.4, 31.2 (2×), 30.8, 30.5, 23.5 (2×), 23.3, 23.0, 22.8, 10.6 (2×), 10.3, 9.9 ppm. IR (KBr) ν 2961.3, 2929.7, 2875.6, 1724.0, 1465.2, 1220.0 cm^{-1}. HRMS (ESI$^+$) calcd for $\mathrm{C_{52}H_{55}F_3N_2O_7}$ 877.40341 [M + H]$^+$, 899.38536 [M + Na]$^+$, 915.35929 [M + K]$^+$, found m/z 877.40344 [M + H]$^+$ (20%), 899.38502 [M + Na]$^+$ (100%), 915.35644 [M + K]$^+$ (25%).

X-ray crystallography

Crystallographic data for 7b. The structure of **7b** was measured using D8 VENTURE equipped with Photon CMOS detector with Cu-Kα (λ = 1.54178 Å) radiation at 180 K. The structure was in hexagonal system, P61 space group with lattice parameters a = 14.5403(3) Å, b = 14.5403(3) Å, c = 36.4429(8) Å, α = 90° β = 90° γ = 120°, Z = 6, V = 6672.5(4) Å^3, D_c = 1.199 g cm^{-3}, μ (Cu-Kα) = 0.713 mm^{-1}. The data reduction and absorption correction were done with Apex3 software. The structure was solved by direct method using SIR92 software[17] and refined by full matrix least squares on F squared value using Crystals software[18] to final values R = 0.0438 and wR = 0.1004 using 8653 independent reflections ($\theta_{\max}$ = 72.100°), 609 parameters and 42 restraint. MCE software was used for visualization of residual electron density maps. According to common practice the hydrogen atoms attached to carbon atoms were place geometrically with U_{iso}(H) in range 1.2–1.5 U_{eq} of parent atom (C). The crystal is a solid solution of two chemical entities.[19] The difference between them is the chlorine atom bonded in the *para* position to the one of propoxy group. The occupancy of the molecule, which contains chlorine, is 0.23. The ordering is random, there are no peaks in the pattern which can show the supercell. The disordered functional groups were refined with restrained geometry and occupancy constrained to full for each atomic position. The structure was deposited into Cambridge Structural Database under number CCDC 1918213.

Crystallographic data for 8b. Larger prism crystal of **8b** was selected, immersed in high viscosity PEG oil and cut to size appropriate for data collection. Data were collected at 180 (2) K on a D8 Venture Photon CMOS diffractometer with Incoatec microfocus sealed tube Cu-Kα radiation. The crystal s found to be in monoclinic space group $P2_1/c$ with lattice parameters a = 12.0248 (3) Å, b = 20.0249 (4) Å, c = 40.0398 (9) Å, β = 93.8505 (12) °, V = 9619.6 (4) Å^3, Z = 8. The structure was solved by charge flipping[16] and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs[18] to final value R = 0.064 and wR = 0.153 using 17 623 independent reflections ($\theta_{\max}$ = 68.5°), 1456 parameters and 491 restrains. The disordered propoxy groups and solvent were refined with restrained geometry and thermal parameters. The sum occupancy of disordered positions was restrained to 1 for each group. The hydrogen atoms attached to carbon atoms were placed in calculated positions. The hydrogen atoms attached to oxygen and nitrogen atoms were found in difference electron density maps. In both cases were the hydrogen atoms refined with riding constrains after initial refinement of geometry. The MCE program[20] was used for visualization of residual electron density maps. The structure was deposited into Cambridge Structural Database under number CCDC 1918371.

Crystallographic data for 14a. Larger prism crystal of **14a** was selected, immersed in high viscosity PEG oil and cut to size appropriate for data collection. Data were collected at 180 (2) K on a D8 Venture Photon CMOS diffractometer with Incoatec microfocus sealed tube Cu-Kα radiation. The crystal s found to be in monoclinic space group $P2_1/c$ with lattice parameters a = 13.9434 (6) Å, b = 17.1880 (8) Å, c = 17.1967 (8) Å, β = 105.4889 (17)°, V = 3971.7 (3) Å^3, Z = 4. The structure was solved by charge flipping[16] and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs[18] to final value R = 0.045 and wR = 0.113 using 7210 independent reflections ($\theta_{\max}$ = 68.4°), 546 parameters and 58 restrains. The disordered propoxy groups were refined with restrained geometry and thermal parameters. The sum occupancy of disordered positions was restrained to 1 for each group. The hydrogen atoms attached to carbon atoms were placed in calculated positions. The hydrogen atoms attached to nitrogen atoms were found in difference electron density maps. In both cases were the hydrogen atoms refined with riding constrains after initial refinement of geometry. The MCE program[19] was used for visualization of residual electron density maps. The structure was deposited into Cambridge Structural Database under number CCDC 1918372.

Conflicts of interest

There are no conflicts to declare.

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