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Regioselective *ipso*-nitration of calix[4]arenes

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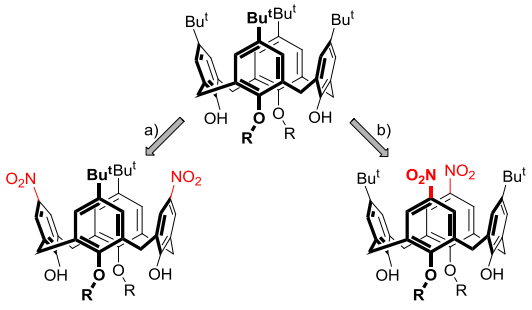
ABSTRACT

A novel protection/deprotection method leading to the regioselective *ipso*-substitution of calix[4]arenes is described. The introduction of nosyl (*p*-nitrobenzenesulfonyl) groups into the lower rim of partly alkylated *tert*-butylcalix[4]arenes leads subsequently to the exclusive *ipso*-nitration of the alkylated phenol rings, while the protecting groups can be easily removed in the next step. This method gives dialkoxy- or trialkoxy-substituted calix[4]arenes with nitro groups on the alkylated rings and *tert*-butyl groups on the remaining ones. The above substitution pattern is complementary to the isomers so far known in the chemistry of calix[4]arenes and could be used in the design of novel type of calixarene-based receptors.

1. Introduction

Contemporary supramolecular chemistry mostly relies on several families of macrocyclic compounds capable of preorganization. Among them, calix[*n*]arenes[1] are especially popular for their easy preparation and almost limitless derivatization potential, which makes them ideal candidates for various applications in supramolecular chemistry.[2] Because of their tuneable three-dimensional shapes, calix[4]arenes became indispensable in the design of sophisticated receptors and host–guest systems. Over last three decades a plethora of regioselective and/or stereoselective derivatisation methods of the basic skeleton was described,[1] thus enabling the application of calix[4]arene as a molecular scaffold. In this context, a calixarene macrocycle is usually frozen in one of the four common conformations (*cone*, *partial cone*, *1,2-alternate*, or *1,3-alternate*), and selected structural fragments responsible for the recognition are introduced into the molecule. These highly preorganised systems, with precisely defined 3-D shapes and mutual spatial arrangement of functional groups, can then be used as receptors for ions or neutral molecules.[3]

Nitro-substituted calix[4]arenes are frequently used as intermediates for the design and preparation of novel receptors or calixarene-based building blocks (usually via reduction to amino groups and subsequent derivatisation with suitable agent). Therefore, the nitration of calix[4]arenes represents an important and well-established method, which can be carried out either directly,[4] or via the *ipso*-substitution[5] of *tert*-butyl groups. *ipso*-Substitution is usually used for tetranitration of peralkylated calix[4]arenes where all four *tert*-butyl groups can be changed for nitro groups in high yields.[6] On the other hand, it can be also used for regioselective substitution of the upper rim through the partial alkylation of the lower rim. Thus, introduction of two alkyl groups into the distal positions makes these two aromatic rings less reactive compared with those bearing free hydroxyl groups. Consequently, subsequent *ipso*-nitration proceeds selectively[7] on the unsubstituted rings (Scheme 1, path a).



Scheme 1. Two different substitution patterns in dialkylated calix[4]arenes: (a) common *ipso*-nitration, (b) *ipso*-nitration using nosyl protection/deprotection method.

During our ongoing research on calix[4]arene derivatization we found that nosyl-substituted derivatives can be used for regioselective introduction of various functional groups through direct

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electrophilic substitution of the free (de-*tert*-butylated) upper rim.[8] In this paper we report a straightforward regioselective *ipso*-nitration in the calix[4]arene series starting from nosyl-substituted *tert*-butyl derivatives. The whole strategy, consisting of lower-rim protection/*ipso*-nitration/deprotection steps, allows the introduction of nitro groups to the alkylated phenolic units, thus representing so far almost inaccessible substitution pattern (Scheme 1, path b) in calix[4]arene chemistry complementary to commonly used isomers.

2. Results and discussion

To check the general applicability of regioselective *ipso*-nitration three different partly alkylated isomers were prepared using known procedures. Thus, the alkylation of starting *tert*-butylcalix[4]arene (PrI/K_2CO_3/MeCN)[9] gave a distal dipropoxy derivative **2** in 74% yield. Proximally disubstituted compound **3** was obtained in 53% yield using PrBr/NaOH in aqueous DMSO,[10] while the trialkylated isomer **4** was isolated in 51% yield using PrI/BaO/$Ba(OH)_2$ system in DMF.[11] These partly alkylated calixarenes were reacted with *p*-nitrobenzenesulfonyl chloride (nosyl chloride) in the presence of NaH as a base. Reaction was carried out either in DMF at 0 °C (for **2**, **4**) or in THF under reflux (for **3**) and the isomers **5**–**7** were obtained in acceptable yields (78, 75 and 69% yield, respectively). The ^{1}H NMR spectra of **5**–**7** confirmed the exclusive formation of the *cone* conformation. Thus, the presence of two doublets at 3.91 and 2.76 ppm for $-CH_2-$ bridges with typical geminal coupling constants ($J\approx13$ Hz) clearly showed the *cone* conformation for distal derivative **5**. Analogously, the expected splitting pattern (three doublets for equatorial protons of $-CH_2-$ bridging units at 3.10, 2.76 and 2.74 ppm in 1:2:1 integral ratio) is in perfect accord with the lower symmetry of derivative **6**.

The *ipso*-nitration of compounds **5**–**7** was carried out using 100% HNO_3 in an AcOH/DCM mixture at room temperature. In all cases, nitration proceeded almost quantitatively and the corresponding nitro-substituted compounds **8**–**10** were obtained in 99, 98 and 99% yields, respectively. The ^{1}H NMR spectrum of **8** clearly proves the regioselective formation of distally *p*-nitro-substituted product where both NO_2 groups are on the alkylated rings. Thus, compound **8** possesses one singlet of nitro-substituted phenyl rings (δ 7.94 ppm), and one singlet from *tert*-butyl substituted rings (δ 6.52 ppm). The unequivocal structural evidence was obtained by X-ray crystallography, which fully proved the expected structure of compound **8** (see Supplementary data).

Nitro-substituted derivatives **8**–**10** were finally deprotected by basic hydrolysis of nosyl groups with KOH in EtOH/dichloromethane mixture. The corresponding calixarenes **11**–**13** with partly unsubstituted lower rims were obtained in essentially quantitative yields ($\geq$96% after isolation). The ^{1}H NMR spectrum of **11** in $CDCl_3$ clearly shows the *cone* conformation (pair of doublets at 4.36 and 3.48 ppm, J=13 Hz), with two nitro groups introduced into the upper rim of calixarene (two singlets for aromatic protons at 7.87 and 7.13 ppm). Similarly, the isomers **12** and **13** also adopt the *cone* conformation as ascertained by series of doublets for equatorial and axial protons in $-CH_2-$ bridging units with typical geminal coupling constants $J\approx13$ Hz (Scheme 2).

The exact position of the nitro groups in derivative **11** was also confirmed by direct comparison with the corresponding regioisomer **17** having NO_2 groups on the unsubstituted aromatic rings. This compound can be prepared[5a,7a] by direct *ipso*-nitration of dipropoxy derivative **2** and possesses the same type of splitting pattern and signal multiplicity as compound **11** (Scheme 3). However, the chemical shifts of some signals are significantly different, proving the different positions of nitro groups on calixarene skeleton (see Fig. 1). While the signal of free phenolic OH group in **11** can be found at 7.91 ppm, the same signal in **17** is shifted to much lower field (9.50 ppm) because of the presence of the nitro group on the same ring.

The final unambiguous structural evidence for compound **12** was obtained by X-ray crystallography. It proved that proximal derivative adopts the *cone* conformation with NO_2 groups being introduced into the *para* positions of alkoxy-substituted rings (Fig. 2a). The main motif of crystal packing is represented by self-inclusion of one *tert*-butyl group into the cavity of the neighbour macrocycle (Fig. 2b) leading to the formation of self-included dimers.

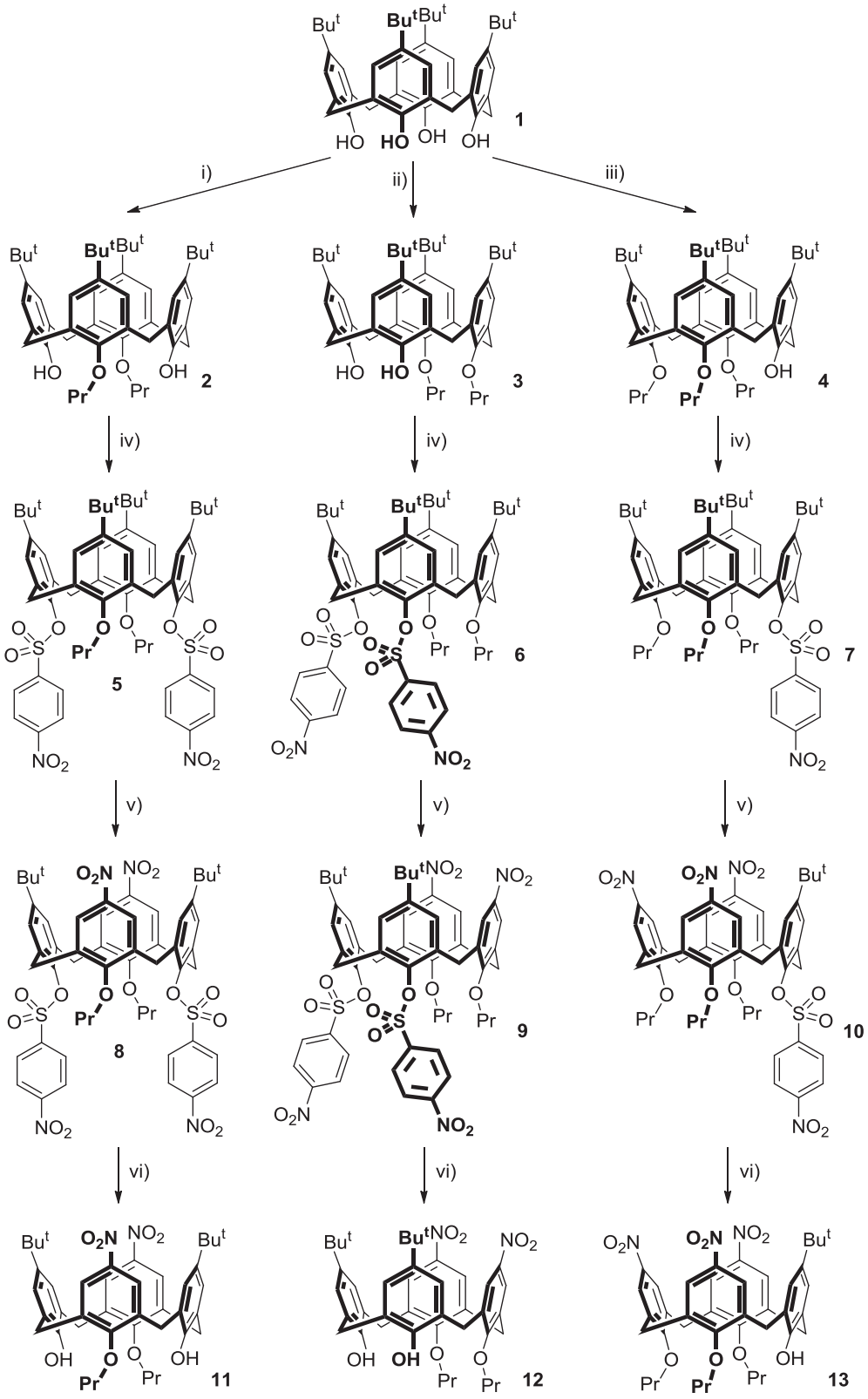
To show the usefulness of this novel synthetic approach in calix[4]arene chemistry we attempted the transformation of nitro derivative **11** into the corresponding anion receptor **15** and to compare its complexation ability with a recently reported[8] analogue **16** without *tert*-butyl groups on the upper rim. Thus, dinitro derivative **11** was reduced using Raney nickel[11] in methanol under reflux conditions to yield amino substituted compound **14** in 97% yield. This compound was then reacted with phenyl isocyanate in DCM at room temperature to give the target receptor **15** in 29% yield. The low yield of receptor is probably a consequence of the repeated chromatographic purifications, which were necessary to remove the impurities formed by the quenching of phenyl isocyanate with MeOH.

The complexation ability of ligand **15** was studied by standard ^{1}H NMR titration experiments using an increasing concentration of appropriate anion to obtain different host/guest ratios (1–20:1). To ensure the solubility of both ligand **15** and anion (tetrabutylammonium salts of benzoate, acetate, chloride) a mixed solvent system ($CDCl_3$/DMSO-d_6=4:1, v/v) was used. As the same solvent system was recently used for the measuring of the complexation properties of **16**,[8] it also allowed us a direct comparison with our receptor.

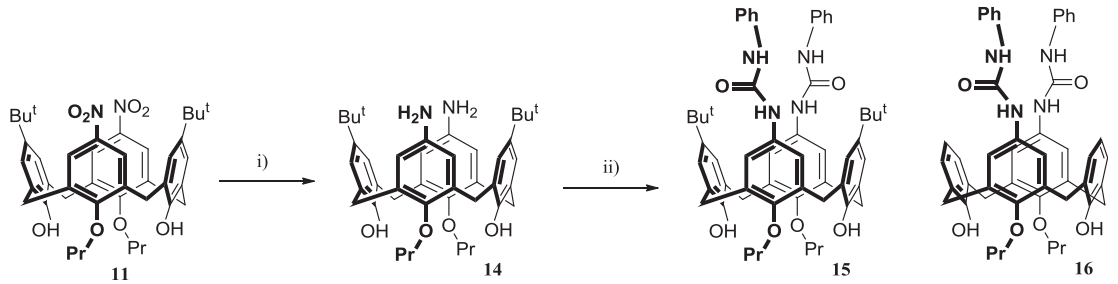
The addition of anions to **15** led to the remarkable down-field shifts of ureido NH signals supporting the complexation phenomenon under fast exchange conditions. A typical titration curve constructed from the complexation induced chemical shifts (CIS) for compound **15**/benzoate system is shown in Fig. 3a. The addition of 20 equiv of BzO^- led to the CIS value higher than 3.3 ppm. This is an unusually high value indicating very strong hydrogen-bonding interactions between the ureido functions and benzoate. On the other hand, data obtained could not be analysed as 1:1 complex, which was recently observed for receptor **16**.[8] The Job plot analysis (Fig. 3b) revealed the more complex behaviour corresponding to a 2:1 stoichiometry (anion/calix). As the same stoichiometries were observed also for other anions studied (acetate, chloride) we assumed that this behaviour is general for receptor **15**. The most likely explanation of the difference between the operating of receptors **15** and **16** lies in the steric hindrance on the upper rim of calixarene receptors. Derivative **16** can use both ureido functions for cooperative binding of anions leading always to 1:1 stoichiometry. On the other hand, the presence of *tert*-butyl groups in receptor **15** does not allow efficient cooperation of the ureido units. Consequently, both urea moieties behave independently and prefer the separate binding of anions leading to the 2:1 complexes.

3. Conclusions

In conclusion, we have demonstrated the usefulness of nosyl groups in the selective *ipso*-nitration of calix[4]arenes. The introduction of nosyl groups into the lower rim of calix[4]arene enables a highly regioselective *ipso*-nitration of the alkoxy-substituted aromatic rings. The whole strategy, consisting of the lower-rim protection/*ipso*-nitration/deprotection steps, leads to so far almost inaccessible substitution pattern, which can be useful in the design of novel calixarene-based receptors.



Scheme 2. Regioselective nitration of partly alkylated calix[4]arenes: (i) PrI/K_2CO_3/MeCN (**2**,74%); (ii) PrBr/NaOH/DMSO/H_2O (**3**, 53%); (iii) PrI/BaO/$Ba(OH)_2$/DMF (**4**, 51%); (iv) nosyl chloride/NaH/DMF, 0 °C (**5**, 78%; **7**, 69%); nosyl chloride/NaH/THF, reflux (**6**, 75%); (v) 100% HNO_3/AcOH/DCM, 0 °C (**8**, 99%, **9**, 98%, **10**, 99%); (vi) KOH/DCM/EtOH, rt (**11**, 96%, **12**, 99%, **13**, 98%).



Scheme 3. Preparation of anion receptor: (i) Ni(R)/$NH_2NH_2 \cdot H_2O$/MeOH, reflux (**14**, 97%); (ii) phenyl isocyanate/DCM, rt (**15**, 29%).

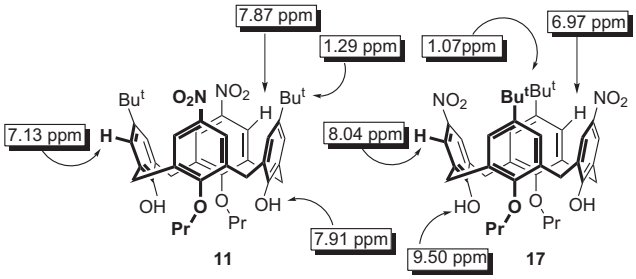


Fig. 1. Differences in ^{1}H NMR spectra of regioisomers **11** and **17** ($CDCl_3$, 300 MHz, 298 K).

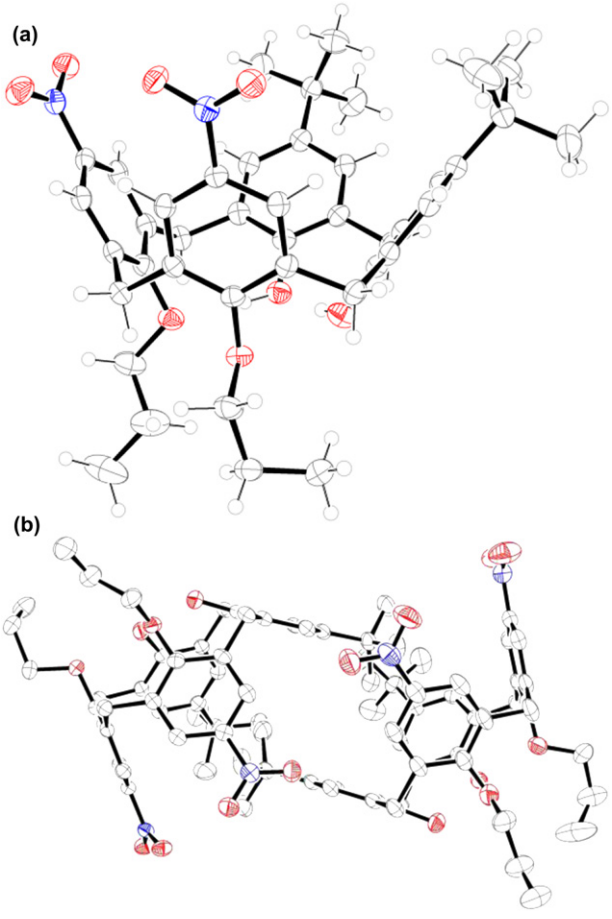


Fig. 2. (a) ORTEP drawing of proximal dinitro derivative **12**, (b) self-inclusion motif in crystal packing of **12** (hydrogens omitted for better clarity).

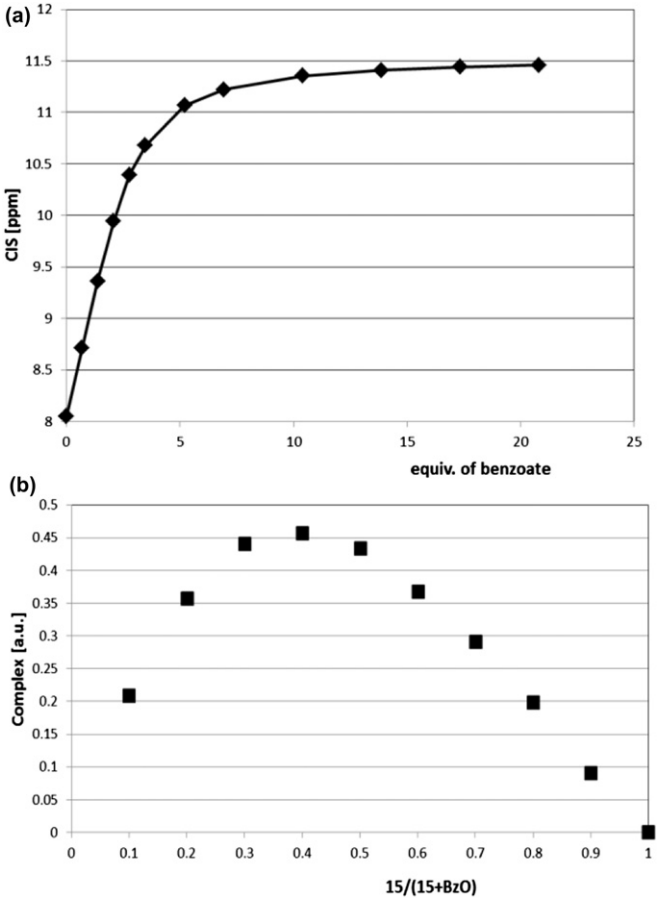


Fig. 3. (a) Binding isotherm of ligand **15** with benzoate anion; (b) Job plot for the same system in $CDCl_3$/DMSO-d_6 4:1 v/v system (^{1}H NMR titration, 300 MHz, 298 K).

4. Experimental

4.1. General

Melting points were determined on a Boetius block (Carl Zeiss Jena, Germany) and are not corrected. The IR spectra were measured on an FT-IR spectrometer Nicolet 740 in $CHCl_3$ and/or in KBr. ^{1}H NMR spectra were recorded on a Varian Gemini 300 spectrometer. Dichloromethane used for the reaction was dried with CaH_2 and stored over molecular sieves. The purity of the substances and the courses of reactions were monitored by TLC using TLC aluminium sheets with Silica gel 60 F_{254} (Merck). Preparative TLC chromatography was carried out on 20×20 cm glass plates covered by Silica gel 60 GF_{254} (Merck).

Starting compounds **2**–**4** were prepared according to known procedures.

4.2. Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-bis(*p*-nitrobenzenesulfonyloxy)-26,28-dipropoxycalix[4]arene (*cone*) 5

A mixture of 5,11,17,23-tetra-*tert*-butyl-26,28-dipropoxycalix[4]arene-25,27-diol **2** (5.00 g, 6.82 mmol) and sodium hydride (1.1 g, 27.50 mmol, 60% suspension in mineral oil) was stirred for 30 min at 0 °C in anhydrous DMF (300 ml). Then, *p*-nitrobenzenesulfonyl chloride (7.80 g, 34.13 mmol, 97% purity) was added and the reaction mixture was stirred at room temperature for 5 days. The resulting mixture was acidified with 1 M HCl (aq) and extracted with CH_2Cl_2 (3×100 ml). The combined organic layers were washed with water (300 ml), brine (300 ml) and dried over $MgSO_4$. Organic solvent was removed under reduced pressure, and the oily residue was dissolved in CH_2Cl_2 (15 ml) and precipitated by addition of methanol (150 ml). The precipitate was filtered off, washed twice with methanol and dried to give 5.92 g of title compound **5** as a yellowish powder (78%), mp: 261–264 °C. ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ_H 8.39–8.36 (m, 4H, Ar*H*–Ns), 7.98–7.96 (m, 4H, Ar*H*–Ns), 7.02 (s, 4H, Ar*H*), 6.48 (s, 4H, Ar*H*), 3.91 (d, 4H, *J*=12.9 Hz, ArC*H*$_2$Ar *ax*), 3.82 (t, 4H, *J*=6.6 Hz, OC*H*$_2$), 2.76 (d, 4H, *J*=13.2 Hz, ArC*H*$_2$Ar *eq*), 2.15–2.02 (m, 4H, OCH$_2$C*H*$_2$), 1.28 (s, 18H, ^{t}*Bu*), 0.99 (t, 6H, *J*=7.5 Hz, C*H*$_3$), 1.09 (s, 18H, ^{t}*Bu*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 154.4, 151.1, 148.6, 145.9, 142.1, 141.7, 134.7, 133.2, 130.3, 126.0, 125.7, 124.4, 76.9, 34.3, 34.1, 32.0, 31.9, 31.1, 29.9, 23.4. TOF MS (ESI$^+$): calcd for $C_{62}H_{74}N_2O_{12}S_2$: 1103.42. Found: *m*/*z* (rel int. %) 1125.63 (100) [M+Na]$^+$. IR (KBr) ν cm^{-1}: 2963, 1536, 1350, 1312, 1195; EA calcd for $C_{62}H_{74}N_2O_{12}S_2$: C, 67.49; H, 6.76; N, 2.54; S, 5.81%. Found: C, 67.35; H, 6.80; N, 2.53; S, 5.77%.

4.3. Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,26-bis(*p*-nitrobenzenesulfonyloxy)-27,28-dipropoxycalix[4]arene (*cone*) 6

Proximal derivative **3** (3.00 g, 4.09 mmol) was added into the suspension of sodium hydride (0.98 g, 24.5 mmol, 60% suspension in mineral oil, washed with hexane) in 200 ml of dried THF, and the mixture was heated to reflux. Then, the solution of *p*-nitrobenzenesulfonyl chloride (3.62 g, 16.36 mmol, 97% purity) in dry THF (20 ml) was added dropwise during 30 min. The reaction mixture was refluxed for 24 h and the solvent was removed under reduced pressure. The solid residue was dissolved in CH_2Cl_2 (150 ml) and the resulting solution was carefully poured into the water (1 l) while stirring. Water phase was separated and extracted with CH_2Cl_2 (2×100 ml). Combined organic layers were washed with water (300 ml), brine (300 ml) and dried over $MgSO_4$. The solvent was removed by evaporation and the oily residue was dissolved in CH_2Cl_2 (5 ml) and precipitated by addition of methanol (120 ml). The precipitate was filtered off, washed twice with methanol and dried to give 3.40 g of title compound **6** (75% yield) as a yellow powder, mp: 214–217 °C. ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ 8.37–8.34 (m, 4H, Ar*H*–Ns), 8.04–8.01 (m, 4H, Ar*H*–Ns), 6.81 (d, 2H, *J*=2.3 Hz, Ar*H*), 6.76–6.74 (m, 4H, Ar*H*), 6.65 (d, 2H, *J*=2.6 Hz, Ar*H*), 4.39 (d, 1H, *J*=12.6 Hz, ArC*H*$_2$Ar *ax*), 4.09 (d, 2H, *J*=13.2 Hz, ArC*H*$_2$Ar *ax*), 3.91 (td, 2H, *J*=10.1, 5.8 Hz, OC*H*$_2$), 3.82–3.71 (m, 3H, m, OC*H*$_2$+ArC*H*$_2$Ar *ax*), 3.10 (d, 1H, *J*=12.6 Hz, ArC*H*$_2$Ar *eq*), 2.76 (d, 2H, *J*=13.2 Hz, ArC*H*$_2$Ar *eq*), 2.74 (d, 1H, *J*=14.4 Hz, ArC*H*$_2$Ar *eq*), 2.11–1.87 (m, 4H, OCH$_2$C*H*$_2$), 1.07 (s, 18H, ^{t}*Bu*), 1.03 (s, 18H, ^{t}*Bu*), 0.99 (t, 6H, *J*=7.5 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 153.4, 151.0, 149.6, 145.0, 142.2, 141.5, 135.8, 134.2, 133.8, 132.6, 131.0, 126.8, 126.1, 125.9, 124.6, 124.2, 77.3, 34.4, 34.1, 31.8, 31.6, 31.4. TOF MS (ESI$^+$): calcd for $C_{62}H_{74}N_2O_{12}S_2$: 1103.42. Found: *m*/*z* (rel intensity, %) 1125.53 (100) [M+Na]$^+$. IR (KBr) ν cm^{-1}: 2964, 1537, 1350, 1312, 1196; EA calcd for $C_{62}H_{74}N_2O_{12}S_2$: C, 67.49; H, 6.76; N, 2.54; S, 5.81%. Found: C, 67.45; H, 6.71; N, 2.51; S, 5.79%.

4.4. Synthesis of 5,11,17,23-tetra-*tert*-butyl-25-(*p*-nitrobenzenesulfonyloxy)-26,27,28-tripropoxycalix[4]arene (*cone*) 7

A mixture of trialkyl derivative **4** (1.10 g, 1.42 mmol) and sodium hydride (0.11 g, 4.58 mmol, 60% suspension in mineral oil) was stirred for 30 min at 0 °C in anhydrous DMF (50 ml). Then, *p*-nitrobenzenesulfonyl chloride (0.63 g, 2.84 mmol, 97% purity) was added and the reaction mixture was stirred at room temperature for 5 days. The resulting mixture was acidified by 1 M aqueous HCl and extracted with CH_2Cl_2 (3×60 ml). The combined organic layers were washed with water (150 ml), brine (150 ml) and dried over $MgSO_4$. Organic solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 (5 ml) and reprecipitated by addition of methanol (60 ml). The precipitate was filtered off, washed twice with methanol and dried to give 0.94 g of product **7** as a white powder (69% yield), mp: 217–219 °C. ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ 8.38–8.34 (m, 2H, Ar*H*–Ns), 7.99–7.94 (m, 2H, Ar*H*–Ns), 7.09 (d, 2H, *J*=2.6 Hz, Ar*H*), 6.98 (d, 2H, *J*=2.4 Hz, Ar*H*), 6.53 (s, 2H, Ar*H*), 6.40 (s, 2H, Ar*H*), 4.38 (d, 2H, *J*=12.9 Hz, ArC*H*$_2$Ar *ax*), 4.05 (td, 2H, *J*=10.7, 5.1 Hz, OC*H*$_2$), 3.96 (d, 2H, *J*=12.9 Hz, ArC*H*$_2$Ar *ax*), 3.79 (td, 2H, *J*=10.6, 5.4 Hz, OC*H*$_2$), 3.65 (t, 2H, *J*=7.2 Hz, OC*H*$_2$), 3.11 (d, 2H, *J*=12.6 Hz, ArC*H*$_2$Ar *eq*), 2.75 (d, 2H, *J*=12.9 Hz, ArC*H*$_2$Ar *eq*), 2.23–2.11 (m, 2H, OCH$_2$C*H*$_2$), 2.08–1.98 (m, 2H, OCH$_2$C*H*$_2$), 1.96–1.84 (m, 2H, OCH$_2$C*H*$_2$), 1.29 (s, 18H, ^{t}*Bu*), 1.06 (t, 3H, *J*=7.3 Hz, C*H*$_3$), 0.95 (t, 6H, *J*=7.5 Hz, C*H*$_3$), 0.85 (s, 9H, ^{t}*Bu*), 0.78 (s, 9H, ^{t}*Bu*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 154.7, 152.8, 151.0, 148.5, 145.3, 144.2, 142.2, 141.8, 135.9, 134.5, 133.5, 132.0, 130.4, 126.5, 125.7, 125.1, 124.6, 124.3, 77.8, 34.3, 33.8, 32.1, 31.9, 31.4, 31.1, 23.8, 23.4, 11.0, 10.2. TOF MS (ESI$^+$): calcd for $C_{59}H_{77}NO_8S$: 960.34. Found: *m*/*z* (rel intensity, %) 982.52 (100) [M+Na]$^+$. IR (KBr) ν cm^{-1}: 2963, 1537, 1481, 1362, 1311, 1196. EA calcd for $C_{59}H_{77}NO_8S$: C, 73.79; H, 8.08; N, 1.46; S, 3.34%. Found: C, 73.68; H, 8.01; N, 1.42; S, 3.37%.

4.5. *ipso*-Nitration (general procedure)

The corresponding derivatives **5**–**7** were dissolved in the mixture of CH_2Cl_2 (10 ml for 1 mmol) and glacial acetic acid (10 ml for 1 mmol). Nitric acid (100%, 80 equiv) was added dropwise to the solution while cooling to 0 °C in an ice bath. The reaction mixture was then stirred until the colour changed from deep purple to light yellow, poured into water and extracted with CH_2Cl_2. The combined organic layers were washed with water, saturated aqueous $NaHCO_3$, then with brine and dried over $MgSO_4$. Organic solvent was removed under reduced pressure to give the corresponding *ipso*-nitrated products **8**–**10**.

*4.5.1. Synthesis of 11,23-di-tert-butyl-5,17-dinitro-25,27-bis(p-nitrobenzenesulfonyloxy)-26,28-dipropoxycalix[4]arene (cone) **8**.* General procedure was applied to compound **5** (4.00 g, 3.63 mmol) and product was isolated as an orange powder (3.9 g, 99% yield), mp: 280 °C (dec). ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ_H 8.43–8.40 (m, 4H, Ar*H*–Ns), 8.01–7.97 (m, 4H, Ar*H*–Ns), 7.94 (s, 4H, Ar*H*), 6.52 (s, 4H, Ar*H*), 4.02–3.95 (m, 8H, ArC*H*$_2$Ar *ax*+OC*H*$_2$), 2.96 (d, 4H, *J*=13.5 Hz, ArC*H*$_2$Ar *eq*), 2.11–1.98 (m, 4H, OCH$_2$C*H*$_2$), 1.02 (t, 6H, *J*=7.5 Hz, C*H*$_3$), 0.83 (s, 18H, ^{t}*Bu*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ 162.3, 151.4, 150.2, 143.0, 142.0, 141.4, 136.7, 132.1, 130.3, 126.3, 124.6, 124.4, 31.8, 31.1, 23.4, 10.1. TOF MS (ESI$^+$): calcd for $C_{54}H_{56}N_4O_{16}S_2$: 1081.19. Found: *m*/*z* (rel intensity, %) 1103.50 (100) [M+Na]$^+$. IR (KBr) ν cm^{-1}: 2967, 1534, 1348, 1314, 1195. EA calcd for

$C_{54}H_{56}N_4O_{16}S_2$: C, 59.99; H, 5.22; N, 5.18; S, 5.93%. Found: C, 60.03; H, 5.20; N, 5.12; S, 5.88%.

4.5.2. Synthesis of 17,23-di-tert-butyl-5,11-dinitro-25,26-bis(p-nitrobenzenesulfonyloxy)-27,28-dipropoxycalix[4]arene (cone) ***9***. Calixarene **6** (1.00 g, 0.90 mmol) was *ipso*-nitrated according to general procedure, product **9** was isolated as an orange powder (0.96 g, 98% yield), mp: 137–141 °C. ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ_H 8.41–8.36 (m, 4H, Ar*H*–Ns), 8.02–7.98 (m, 4H, Ar*H*–Ns), 7.62–7.60 (m, 4H, Ar*H*), 6.71–6.68 (m, 4H, Ar*H*), 4.56 (d, 1H, *J*=13.8 Hz, ArC*H*$_2$Ar *ax*), 4.19 (d, 2H, *J*=13.5 Hz, ArC*H*$_2$Ar *ax*), 4.11 (td, 2H, *J*=10.1, 6.1 Hz, OC*H*$_2$), 3.95 (td, 2H, *J*=10.1, 5.8 Hz, OC*H*$_2$), 3.68 (d, 1H, *J*=14.1 Hz, ArC*H*$_2$Ar *ax*), 3.36 (d, 1H, *J*=13.8 Hz, ArC*H*$_2$Ar *eq*), 2.93 (d, 2H, *J*=14.1 Hz, ArC*H*$_2$Ar *eq*), 2.74 (d, 1H, *J*=14.1 Hz, ArC*H*$_2$Ar *eq*), 2.03–1.83 (m, 4H, OCH$_2$C*H*$_2$), 1.08–0.93 (m, 24H, 2× C*H*$_3$+2× ^{t}*Bu*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 161.8, 151.3, 150.9, 142.8, 142.5, 140.9, 135.7, 135.3, 134.1, 130.8, 126.9, 126.7, 124.4, 124.3, 78.2, 34.3, 31.8, 31.7, 31.5, 31.2, 29.9, 23.6, 10.3. TOF MS (ESI$^+$): calcd for $C_{54}H_{56}N_4O_{16}S_2$: 1081.19. Found: *m*/*z* (rel intensity, %) 1103.48 (100) [M+Na]$^+$. IR (KBr) ν cm^{-1}: 2965, 1535, 1347, 1313, 1195. EA calcd for $C_{54}H_{56}N_4O_{16}S_2$: C, 59.99; H, 5.22; N, 5.18; S, 5.93%. Found: C, 59.83; H, 5.19; N, 5.15; S, 5.90%.

4.5.3. Synthesis of 23-tert-butyl-5,11,17-trinitro-25-(p-nitrobenzenesulfonyloxy)-26,27,28-tripropoxycalix[4]arene (cone) ***10***. General procedure was applied to calixarene **7** (1.4 g, 1.46 mmol), product **10** was isolated as an orange powder (1.34 g, 99% yield), mp: 166–168 °C. ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ_H 8.44–8.41 (m, 2H, Ar*H*–Ns), 8.03–8.00 (m, 2H, Ar*H*–Ns), 7.93 (d, 2H, *J*=2.6 Hz, Ar*H*), 7.86 (d, 2H, *J*=2.9 Hz, Ar*H*), 7.34 (s, 2H, Ar*H*), 6.45 (s, 2H, Ar*H*), 4.52 (d, 2H, *J*=13.5 Hz, ArC*H*$_2$Ar *ax*), 4.17–4.08 (m, 4H, ArC*H*$_2$Ar+OC*H*$_2$), 3.95 (td, 2H, *J*=10.4, 5.8 Hz, OC*H*$_2$), 3.86 (t, 2H, *J*=7.2 Hz, OC*H*$_2$), 3.39 (d, 2H, *J*=13.8 Hz, ArC*H*$_2$Ar *eq*), 3.00 (d, 2H, *J*=14.1 Hz, ArC*H*$_2$Ar *eq*), 1.99–1.83 (m, 6H, OCH$_2$C*H*$_2$), 1.09 (t, 3H, *J*=7.5 Hz, C*H*$_3$), 0.97 (t, 6H, *J*=7.3 Hz, C*H*$_3$), 0.80 (s, 9H, ^{t}*Bu*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 162.4, 161.1, 151.3, 150.6, 143.2, 143.0, 142.5, 141.5, 136.7, 136.1, 134.4, 132.8, 130.3, 126.5, 124.7, 124.6, 123.9, 78.5, 77.7, 32.0, 31.3, 30.9, 23.6, 23.4, 10.7, 10.1; TOF MS (ESI$^+$): calcd for $C_{47}H_{50}N_4O_{14}S$: 927.00. Found: *m*/*z* (rel intensity, %) 949.29 (100) [M+Na]$^+$. IR (KBr) ν cm^{-1}: 2966, 1523, 1460, 1346, 1313, 1196. EA calcd for $C_{54}H_{56}N_4O_{16}S_2$: C, 60.90; H, 5.44; N, 6.04; S, 3.46%. Found: C, 60.81; H, 5.44; N, 6.02; S, 3.44%.

4.6. Deprotection of nosyl group (general procedure)

The corresponding calixarenes **8**–**10** were dissolved in a mixture of dichloromethane and ethanol (1:1, v/v, 150 ml for 1 g) and 50 equiv of powdered potassium hydroxide was added. The reaction mixture was stirred at room temperature for 24 h, then acidified with 1 M hydrochloric acid and extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, and dried over $MgSO_4$. Organic solvent was then removed under reduced pressure to give the corresponding products **11**–**13** bearing free hydroxyl groups.

4.6.1. Synthesis of 11,23-di-tert-butyl-5,17-dinitro-26,28-dipropoxycalix[4]arene-25,27-diol (cone) ***11***. General procedure was applied to calixarene **8** (3.5 g, 3.24 mmol), product **11** was isolated as a yellow powder (2.23 g, 96% yield), mp: >250 °C (dec). ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ_H 7.91 (s, 2H, ArO*H*), 7.87 (s, 4H, Ar*H*), 7.13 (s, 4H, Ar*H*), 4.36 (d, 4H *J*=12.9 Hz, ArC*H*$_2$Ar *ax*), 4.04 (t, 4H, *J*=6.2 Hz, OC*H*$_3$), 3.48 (d, 4H, *J*=13.2 Hz, ArC*H*$_2$Ar *eq*), 2.17–2.05 (m, 4H, OCH$_2$C*H*$_2$), 1.33 (t, 6H, *J*=7.3 Hz, C*H*$_3$), 1.29 (s, 18H, s, ^{t}*Bu*). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 157.5, 150.9, 145.0, 143.2, 135.7, 126.4, 126.2, 124.9, 79.4, 34.3, 32.1, 31.9, 23.8, 11.2. TOF MS (ESI$^-$): calcd for $C_{42}H_{50}N_2O_8$: 710.88. Found: *m*/*z* (rel intensity, %) 709.34 (100) [M–H]$^-$. IR (KBr) ν cm^{-1}: 3359, 2963, 1522, 1487, 1344, 1212. EA calcd for $C_{42}H_{50}N_2O_8$: C, 70.96; H, 7.09; N, 3.94%. Found: C, 70.91; H, 7.04; N, 3.93%.

4.6.2. Synthesis of 17,23-di-tert-butyl-5,11-dinitro-27,28-dipropoxycalix[4]arene-25,26-diol (cone) ***12***. General procedure was applied to calixarene **9** (0.8 g, 0.74 mmol), product was obtained as a yellow powder (0.52 g, 99% yield), mp: 216–220 °C. ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ_H 8.65 (m, 2H, ArO*H*), 7.99 (d, 2H, *J*=2.6 Hz, Ar*H*), 7.95 (d, 2H, *J*=2.9 Hz, Ar*H*), 7.05 (d, 2H, *J*=2.3 Hz, Ar*H*), 7.02 (d, 2H, *J*=2.6 Hz, Ar*H*), 4.69 (d, 1H, *J*=12.9 Hz, ArC*H*$_2$Ar *ax*), 4.39 (d, 2H, *J*=12.9 Hz, ArC*H*$_2$Ar *ax*), 4.20 (d, 1H, *J*=13.5 Hz, ArC*H*$_2$Ar *ax*), 4.15–3.98 (m, 2H, OC*H*$_2$), 4.06–3.98 (m, 2H, OC*H*$_2$), 3.60 (d, 1H, *J*=12.6 Hz, ArC*H*$_2$Ar *eq*), 3.50 (d, 2H, *J*=13.2 Hz, ArC*H*$_2$Ar *eq*), 3.39 (d, 1H, *J*=13.5 Hz, ArC*H*$_2$Ar *eq*), 2.18–2.06 (m, 4H, OCH$_2$C*H*$_2$), 1.25–1.16 (m, 24H, C*H*$_3$+^{t}*Bu*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 159.4, 148.8, 144.4, 144.0, 136.5, 135.2, 128.2, 127.0, 126.6, 125.7, 125.3, 124.1, 79.3, 34.4, 32.9, 32.6, 31.8, 30.3, 30.0, 23.6, 10.5. TOF MS (ESI$^+$): calcd for $C_{42}H_{50}N_2O_8$: 710.88. Found: *m*/*z* (rel intensity, %) 733.57 (100) [M+Na]$^+$. IR (KBr) ν cm^{-1}: 3369, 2962, 1517, 1456, 1346, 1214. EA calcd for $C_{42}H_{50}N_2O_8$: C, 70.96; H, 7.09; N, 3.94%. Found: C, 70.90; H, 7.05; N, 3.96%.

4.6.3. Synthesis of 23-tert-butyl-5,11,17-trinitro-26,27,28-tripropoxycalix[4]arene-25-ol (cone) ***13***. General procedure was applied to calixarene **10** (1.24 g, 1.34 mmol), product was isolated as a slightly yellowish powder (0.97 g, 98% yield), mp: 116–117 °C. ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ_H 8.21 (s, 2H, Ar*H*), 7.34 (d, 2H, *J*=2.4 Hz, Ar*H*), 7.23 (d, 2H, *J*=2.6 Hz, Ar*H*), 7.17 (s, 2H, Ar*H*), 4.68 (s, 1H, ArO*H*), 4.51 (d, 2H, *J*=13.5 Hz, ArC*H*$_2$Ar *ax*), 4.34 (d, 2H, *J*=14.1 Hz, ArC*H*$_2$Ar *ax*), 3.99–3.93 (m, 2H, OC*H*$_2$), 3.82 (td, 4H, *J*=6.6, 2.2 Hz, OC*H*$_2$), 3.44 (d, 2H, *J*=13.8 Hz, ArC*H*$_2$Ar *eq*), 3.40 (d, 2H, *J*=13.8 Hz, ArC*H*$_2$Ar *eq*), 2.20–2.12 (m, 2H, OCH$_2$C*H*$_2$), 1.99–1.86 (m, 4H, OCH$_2$C*H*$_2$), 1.38 (s, 9H, C(C*H*$_3$)$_3$), 1.13 (t, 6H, *J*=7.5 Hz, C*H*$_3$), 0.95 (t, 3H, *J*=7.5 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 162.4, 159.8, 150.5, 143.8, 143.6, 143.4, 137.4, 135.3, 133.8, 128.0, 126.4, 125.4, 124.3, 123.2, 78.6, 34.4, 31.9, 31.5, 31.1, 30.0, 23.6, 22.8, 10.9, 9.7. TOF MS (ESI$^+$): calcd for $C_{41}H_{47}N_3O_{10}$: 741.85. Found: *m*/*z* (rel intensity, %) 764.31 (100) [M+Na]$^+$. IR (KBr) ν cm^{-1}: 3557, 2965, 1524, 1344, 1216. EA calcd for $C_{41}H_{47}N_3O_{10}$: C, 66.38; H, 6.39; N, 5.66. Found: C, 66.33; H, 6.35; N, 5.62%.

4.7. Synthesis of 5,17-diamino-11,23-di-*tert*-butyl-26,28-dipropoxycalix[4]arene-25,27-diol (*cone*) 14

A catalytic amount of Raney nickel (10 mg) was added to the solution of nitro-substituted calix[4]arene **11** (200 mg, 0.28 mmol) and hydrazine monohydrate (0.7 ml) in methanol (50 ml), and the mixture was heated to reflux. After 1 h the same amount of hydrazine monohydrate (0.7 ml) was added and mixture was refluxed for further 4 h. After cooling to room temperature, the resulting suspension was filtered through a short column of Celite, the column was washed by additional MeOH. The evaporation of solvent gave product as a slightly brown powder (178 mg, 0.27 mmol, 97%), mp: 293–298 °C. ^{1}H NMR (300 MHz; $CDCl_3$, 298 K): δ_H 8.29 (s, 2H, ArO*H*), 6.99 (s, 4H, Ar*H*), 6.25 (s, 4H, Ar*H*), 4.24 (d, 4H, *J*=12.9 Hz, ArC*H*$_2$Ar *ax*), 3.90 (t, 4H, *J*=6.2 Hz, OC*H*$_2$), 3.24–3.20 (m, 8H, ArC*H*$_2$Ar *eq*+N*H*$_2$), 2.05–1.94 (m, 4H, OCH$_2$C*H*$_2$), 1.30–1.25 (m, 24H, ^{t}*Bu*+C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ 151.4, 145.2, 142.8, 141.3, 134.5, 127.5, 125.4, 116.3, 78.5, 32.2, 32.0, 29.9, 23.7, 11.2; TOF MS (ESI$^+$): calcd for $C_{42}H_{54}N_2O_4$: 650.91. Found: *m*/*z* (rel intensity, %) 651.416 (100) [M+H]$^+$. ν (KBr, cm^{-1}): 3366, 2959, 1636, 1485, 1225; Anal. Calcd for $C_{42}H_{54}N_2O_4$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.45; H, 8.33; N, 4.30.

4.8. Synthesis of 11,23-di-*tert*-butyl-5,17-bis(*N'*-phenyl-ureido)-26,28-dipropoxycalix[4]arene-25,27-diol (*cone*) 15

Phenyl isocyanate (93 mg, 0.78 mmol) was added to a solution of calix[4]arene **14** (100 mg, 0.15 mmol) in 30 ml of dry CH_2Cl_2 under nitrogen atmosphere. The resulting solution was stirred for 2 days at room temperature. Then, 5 ml of MeOH was added to quench the reaction and the mixture was stirred for further 1 h. Solvents were removed under reduced pressure and the residue was purified by column chromatography (Al_2O_3, eluent CH_2Cl_2/MeOH=100:1) and then using preparative TLC (SiO_2, eluent CH_2Cl_2/MeOH=50:1) to give a product as a slightly brown powder (40 mg, 0.045 mmol, 29%), mp: 315–317 °C. ^{1}H NMR (300 MHz; DMSO-d_6, rt): δ_H 8.54 (s, 2H, N*H*), 8.42 (s, 2H, ArO*H*), 8.14 (s, 2H, N*H*), 7.36 (d, 4H, *J*=8.8 Hz, Ar*H*), 7.21 (t, 4H, *J*=7.5 Hz, Ar*H*), 7.10 (s, 8H, Ar*H*), 6.90 (d, 2H, *J*=7.3 Hz, Ar*H*), 4.16 (d, 4H *J*=12.3 Hz, ArCH_2Ar *ax*), 3.91 (t, 4H, *J*=5.4 Hz, OCH_2), 3.39 (d, 4H, *J*=12.6 Hz, ArCH_2Ar *eq*), 2.00–1.94 (m, 4H, OCH$_2$CH_2), 1.31 (t, 6H, *J*=7.3 Hz, CH_3), 1.23 (s, 18H, ^{t}*Bu*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ 153.9, 151.1, 148.5, 141.9, 138.7, 134.8, 134.3, 129.0, 127.2, 125.6, 123.0, 121.6, 119.5, 78.5, 34.0, 32.0, 31.7, 23.6, 11.0; TOF MS (ESI$^+$): calcd for $C_{56}H_{64}N_4O_6$: 889.16. Found: *m*/*z* (rel intensity, %) 911.472 (80) [M+Na]$^+$. ν (KBr, cm^{-1}): 3365, 2958, 1650, 1465, 1364, 1216; Anal. Calcd for $C_{56}H_{64}N_4O_6$: C, 75.65; H, 7.26; N, 6.30. Found: C, 75.62; H, 7.24; N, 6.28.

4.9. Crystallographic measurements

*4.9.1. Crystallographic data for $C_{54}H_{56}N_4O_{16}S_2\cdot 2(C_3H_6O)$ (**8**·2 acetone).* M=1197.35, monoclinic system, space group $C2/c$, a=28.894(5) Å, b=11.6449(8) Å, c=24.271(4) Å, β=131.44(3)°, Z=4, V=6122(3) Å^3, D_c=1.299 g cm^{-3}, μ(Cu Kα)=1.41 mm^{-1}, crystal dimensions of 0.32×0.43×0.54 mm. Data were collected at 150(2) K on a Xcalbur OnyxCCD diffractometer with graphite monochromated Cu Kα radiation. The structure was solved by direct methods[12] using the CRYSTALS suite of programs[13] and anisotropically refined by full matrix least squares on F value to final R=0.0644 and R_w=0.0760 using 5614 independent reflections (Θ_{max}=77.9°), 406 parameters and 48 restrains. The positions of disordered *tert*-butyl group were found from the electron density maps. All distances between neighbouring atoms and angles were fixed. Site occupancies were assigned resulting in similar thermal parameters for both group positions. The hydrogen atoms were placed in calculated positions. The structure was deposited into Cambridge Structural Database under number CCDC 826041.

*4.9.2. Crystallographic data for $C_{42}H_{50}N_2O_8$: (**12**).* M=710.87, monoclinic system, space group $P2_1/n$, a=11.6699(8) Å, b=30.6312(12) Å, c=21.9350(11) Å, β=103.653(6)°, Z=8, V=7619.4(7) Å^3, D_c=1.239 g cm^{-3}, μ(Cu Kα)=0.69 mm^{-1}, crystal dimensions of 0.24×0.37×0.49 mm. Data were collected at 170(2) K on a Xcalbur OnyxCCD diffractometer with graphite monochromated Cu Kα radiation. The structure was solved by direct methods[12] using the CRYSTALS suite of programs[13] and anisotropically refined by full matrix least squares on F^2 value to final R=0.051 and R_w=0.097 using 15,627 independent reflections (Θ_{max}=76.4°), 991 parameters and 62 restrains. The positions of disordered propoxy groups were found from the electron density maps. All distances between neighbouring atoms and angles were fixed. Site occupancies were assigned resulting in similar thermal parameters for both group positions. The hydrogen atoms attached to carbon atoms were placed in calculated positions. The hydrogen atoms attached to oxygen atoms were found from differential electron density map and refined with soft restraints to regularize their geometry after which the positions were refined with riding constraints. The structure was deposited into Cambridge Structural Database under number CCDC 846881.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.03.102.

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