SELECTIVE DERIVATIZATION OF CALIX[4]ARENES VIA AMINO GROUPS ATTACHED TO THE WIDE RIM

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Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday in acknowledgement of his contributions to the chemistry of calixarenes.

A new strategy is proposed for the synthesis of tetraether derivatives of calix[4]arenes bearing at the wide rim nitro and phthalimido groups in well defined positions. Since both groups are precursors of amino functions, calix[4]arenes substituted by different *N*-acylamino residues are easily available in four steps. The essential steps during the synthesis of the precursor consist in the protection of amino groups by the formation of their phthalimides followed by *ipso*-nitration of the remaining *tert*-butylphenol ether units. This nitration occurs without side reactions at the phthalimido substituted units, in contrast to simple *N*-acyl derivatives.

Keywords: Acylations; Calixarenes; *ipso*-Nitration; Hydrogenation; Regioselectivity; Nitro compounds; Amines; Anilines; NMR spectroscopy.

Calixarenes[1] represent a class of macrocyclic molecules which is readily available in large quantities by condensation of *tert*-butylphenol with formaldehyde under alkaline conditions[2]. Thus, they have established themselves as a universal platform on which a variety of functional groups can be easily attached. Especially the chemistry of calix[4]arenes is well developed. Numerous residues have been attached via ether links (less frequently via ester links) to the narrow rim[3], simultaneously fixing the molecule in one of the four possible conformations (*cone*, *partial cone*, *1,2-alternate*, *1,3-alternate*). Due to the shape of the *cone* conformer of a calix[4]arene four residues attached to the narrow rim have a "convergent" orientation, while an attachment to the wide rim leads to a "divergent" orientation which may be used also to "enlarge" the cavity of the calixarene[4].

One of the most appropriate starting materials for the preparation of derivatives at the wide rim are amino substituted calix[4]arenes[5] which can be easily *N*-acylated[6]. Examples for acyl groups thus attached comprise such different functions or compounds as carbamoyl-methylphosphineoxide (CMPO) derivatives[7] as extractants for lanthanides and actinides[8], ureas[9] or thio ureas[10], interesting as anion receptors[11,12] and especially as building blocks for self-assembled dimeric capsules[13]. Amino acids[14] and small peptides[15], which can be obtained as combinatorial libraries by solid-phase synthesis, and glycoconjugates[16] for various biomimetic applications are further examples. Tetraamino calix[4]arenes have been used as building blocks for carcerands[17] and recently also as scaffold for the attachment of perylene dyes via imide functions[18].

In all these cases it can be of interest, not to attach four identical (acyl) residues, but in consecutive steps two different residues in a controlled manner. Since the tetraamino derivatives are easily available by exhaustive *ipso*-nitration of *tert*-butylcalix[4]arene tetraethers we formerly tried a partial protection of the amino groups[19]. However, although the mono-Boc (36%), 1,2-di-Boc (48%) and tri-Boc (54%) derivatives were available in preparatively useful amounts after chromatographic isolation, the 1,3-Boc derivative[20] could neither be obtained, nor even detected. Partial acylation with various reagents (acyl chlorides, *p*-nitrophenyl esters or carbamates) also did not lead to the 1,3-derivative, which may be understood by the formation of a strong trans cavity hydrogen bond between the first amide function and the opposite amino group, strongly lowering its nucleophilicity.

In the following we present a strategy to prepare calix[4]arene derivatives having different *N*-acylamino residues attached to the wide rim in 1,3 and 2,4 positions. It is based on subsequent *ipso*-nitration steps and can be extended also to the preparation of other regioisomeric derivatives with *N*-acyl (thio)urea, etc. functions.

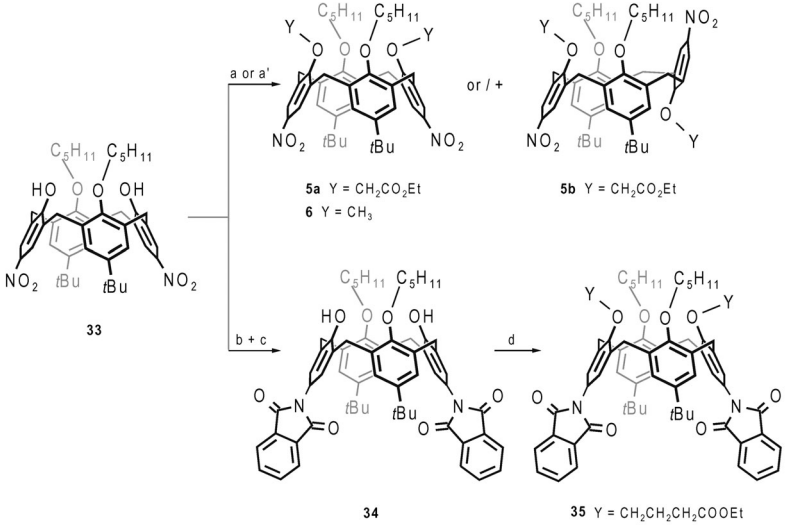
RESULTS AND DISCUSSION

Syntheses

The *ipso*-nitration of the tetrapentyl ether of *tert*-butylcalix[4]arene (*cone* conformer) can be adjusted to obtain not only the tetranitro derivative in excellent yield (85%), but also the mononitro (**1**, 76%), a mixture of the two dinitro (**2**, **3**, 60%), and the trinitro (**4**, 57%) derivative in reasonable to

good yields[21]. In CH_2Cl_2 at room temperature increasing amounts of nitric acid and acetic acid lead to an increase in the degree of nitration[22]. The individual compounds may be obtained by recrystallization, but especially for the dinitro derivatives (**2** and **3**) the separation by column chromatography seems advantageous also on a preparative scale. An alternative route, especially for the diametrically nitrated compound **3** consists in the *ipso*-nitration of the easily available 1,3-diether, which occurs selectively in the phenolic units[23], followed by *O*-alkylation. It has the advantage, that also two different ether residues can be introduced in positions 2 and 4. Compounds **5** and **6** were obtained in this way (Scheme 1).

The partially nitrated compounds **1**–**6** can be easily reduced to the corresponding amino compounds **7**–**12** (Scheme 2) and acylated by various acylating agents[24]. However, a subsequent *ipso*-nitration of the remaining *tert*-butyl phenyl ether units fails. It has been shown for simple amides derived from calix[4]arenes that under nitration conditions preferentially to *ipso*-nitration or nitration of free *para*-positions, the position *ortho* to the *N*-acylamino group is substituted[25]. The amino compounds **7**–**12** can be easily converted into the corresponding phthalimide derivatives **13**–**18** by reaction with 10–20% excess of phthalic anhydride in refluxing toluene (2 days, triethylamine as catalyst, 70–85%). These phthalimide compounds

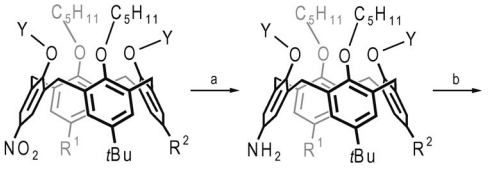


SCHEME 1

(a) Na_2CO_3, alkylating reagent, acetonitrile; (a′) K_2CO_3, alkylating reagent, acetonitrile (just for the compound **5b**); (b) H_2, Ra-Ni, toluene, r.t.; (c) phthalic anhydride, toluene, triethylamine, reflux, 1–2 days; (d) NaH, ethyl 4-bromobutyrate, DMF, r.t.

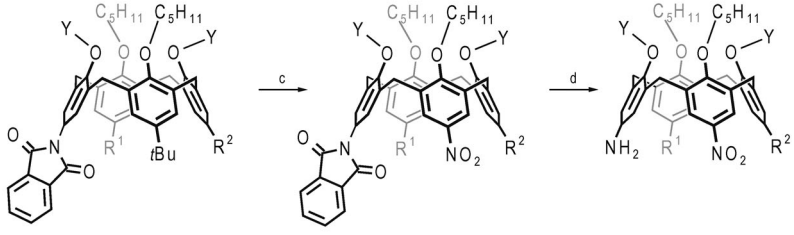
undergo a clean *ipso*-nitration at the *tert*-butyl phenyl ether units without any observable side reaction. Compounds **19**–**22**, **25**, **26** and **36** were thus obtained with yields ranging from 55 to 90%. Lowering the concentration of the starting material in the reaction mixture allows the conversion of **14** and **15** into the mononitro derivatives **23** (86%, inherently chiral) and **24** (70%) in preparatively useful amounts.

To avoid the *O*-alkylation of *p*-nitrophenol units which usually requires reactive alkyl halides such as benzyl bromides or bromoacetates[26] the nitro groups of **33** can be first reduced to amino groups and directly reacted with



	R^1	R^2	Y
1	*t*Bu	*t*Bu	C_5H_{11}
2	NO_2	*t*Bu	C_5H_{11}
3	*t*Bu	NO_2	C_5H_{11}
4	NO_2	NO_2	C_5H_{11}
5	*t*Bu	NO_2	CH_2CO_2Et
6	*t*Bu	NO_2	Me

	R^1	R^2	Y
7	*t*Bu	*t*Bu	C_5H_{11}
8	NH_2	*t*Bu	C_5H_{11}
9	*t*Bu	NH_2	C_5H_{11}
10	NH_2	NH_2	C_5H_{11}
11	*t*Bu	NH_2	CH_2CO_2Et
12	*t*Bu	NH_2	Me



	R^1	R^2	Y
13	*t*Bu	*t*Bu	C_5H_{11}
14	Phth	*t*Bu	C_5H_{11}
15	*t*Bu	Phth	C_5H_{11}
16	Phth	Phth	C_5H_{11}
17	*t*Bu	Phth	CH_2CO_2Et
18	*t*Bu	Phth	Me
35	*t*Bu	Phth	$(CH_2)_3CO_2Et$

	R^1	R^2	Y
19	NO_2	NO_2	C_5H_{11}
20	Phth	NO_2	C_5H_{11}
21	NO_2	Phth	C_5H_{11}
22	Phth	Phth	C_5H_{11}
23	Phth	*t*Bu	C_5H_{11}
24	*t*Bu	Phth	C_5H_{11}
25	NO_2	Phth	CH_2CO_2Et
26	NO_2	Phth	Me
36	NO_2	Phth	$(CH_2)_3CO_2Et$

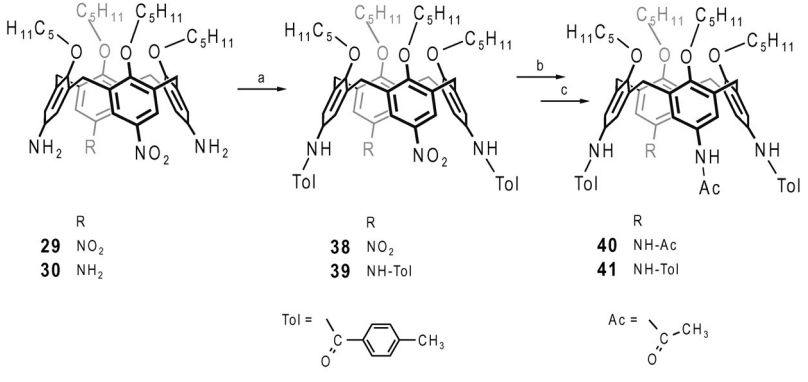
	R^1	R^2	Y
27	NO_2	NO_2	C_5H_{11}
28	NH_2	NO_2	C_5H_{11}
29	NO_2	NH_2	C_5H_{11}
30	NH_2	NH_2	C_5H_{11}
31	NO_2	NH_2	CH_2CO_2Et
32	NO_2	NH_2	Me
37	NO_2	NH_2	$(CH_2)_3CO_2Et$

SCHEME 2

(a) Toluene, H_2, Ra-Ni, r.t.; (b) phthalic anhydride, toluene, triethylamine, reflux, 1–2 days; (c) HNO_3 fuming, dichloromethane/acetic acid (19:1), r.t.; (d) hydrazine hydrate or HCl, ethanol/toluene (3:1), reflux (this step was not done with **23** and **24**)

phthalic anhydride before the second alkylation step (Scheme 1). Compound **34** was thus available in 83% yield. Its *O*-alkylation carried out under the usual conditions (NaH, DMF, room temperature) led to **35** in 26% yield due to difficulties during the purification. Nevertheless, this sequence represents an alternative route to tetraethers substituted at the wide rim by *tert*-butyl and phthalimido groups.

Compounds **19**–**26** and **36** are substituted by two precursors of an amino group, the nitro and the phthalimido group, which in principle may be converted to an amino function independently. Up to now, we have cleaved the phthalimido group with hydrazine hydrate (ethanol/toluene 3:1, reflux) to obtain the aminonitro derivatives **27**–**30** and **32**. They may be acylated, subsequently the nitro group(s) may be reduced and finally a different acyl group may be introduced in the second acylation step. The compounds in Scheme 3 serve as examples to demonstrate this strategy[27]. In principle it should be also possible to reduce first the nitro groups (e.g. by catalytic hydrogenation) and to cleave the phthalimido groups after the first acylation step. The choice of the strategy depends on the resistance of the first *N*-acylamino group to the conditions of the hydrazinolysis[28]. On the other hand, deprotection of the phthalimido groups is possible also under acidic conditions (HCl 37%, ethanol/toluene 3:1, reflux, 1–2 days), as shown for **31** and **37**. Their alkyl ester groups at the narrow rim were not affected, but transesterification may occur with ester groups different from ethyl.



SCHEME 3
(a) Toluoyl chloride, triethylamine, THF, reflux for 2 h; (b) H_2, Ra-Ni, toluene; (c) acetic anhydride, pyridine, 12 h, r.t.

NMR Studies

All compounds were characterized by NMR and mass spectra. Especially the typical pattern of the aromatic protons of the calixarene skeleton and the doublets of the methylene bridges (geminal coupling $^2J \approx 13.2–14.5$) in the ^{1}H NMR spectra are useful. Compounds of the ABAB type (**37**, as an example) show two singlets for Ar-H (7.55 and 5.96 ppm) and one pair of doublets for Ar-CH_2-Ar (4.35 and 3.13 ppm), while the AABB type (**28**) shows two pairs of m-coupled doublets for Ar-H (7.60 and 7.52, 5.97 and 5.89 ppm, J = 2.2) and three pairs of doublets (ratios 1:2:1, 4.51 and 3.31, 4.38 and 3.12, 4.24 and 2.91 ppm) for Ar-CH_2-Ar. Two singlets (e.g. 7.39 and 5.79 ppm) and one pair of m-coupled doublets (6.26 and 6.22 ppm, not well resolved) for Ar-H and two pairs of doublets (ratios 1:1, 4.38 and 3.07, 4.24 and 2.90 ppm) for Ar-CH_2-Ar are found for the AAAB type (**30** as an example). For the inherently chiral AABC type (**23**) four pairs of m-coupled doublets for Ar-H (7.28 and 7.25, 7.25 and 7.20, 7.07 and 7.05, 6.47 and 6.44 ppm, J = 2.4) and four pairs of doublets for Ar-CH_2-Ar are expected, which are partially overlapped (4.56, 4.51 and 4.50 ppm for axial, and 3.30, 3.29, 3.24 and 3.23 ppm for equatorial protons).

As expected, the spectra are more complicated for the dimethyl ether derivatives which are not fixed in the *cone* conformation but exist as a mixture of *partial cone* and *cone*. Interestingly the ratio is 10:1 for **6**, 3.5:1 for **26** (Fig. 1) while both conformers are found in a 1:1 ratio in the case of **32**.

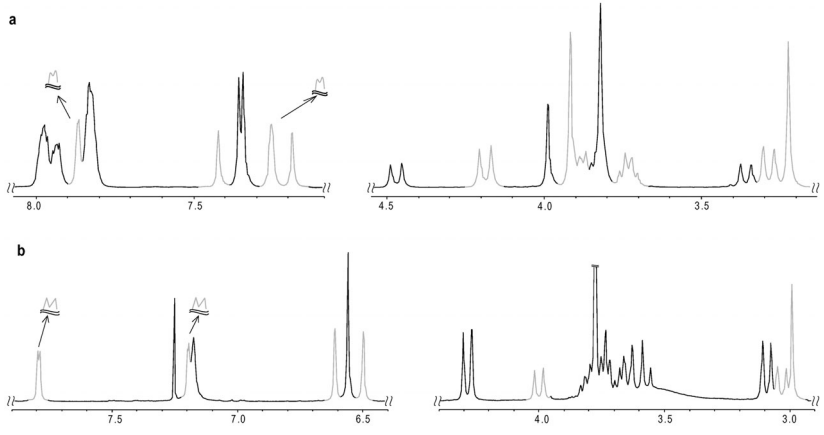


FIG. 1
Sections of the ^{1}H NMR spectra a of **26** (in CD_2Cl_2) and b of **32** (in $CDCl_3$) showing different ratio between the two conformers. Grey signals correspond to the *partial cone* conformer while signals of the *cone* conformer and overlapping signals are drawn in black

CONCLUSIONS

Calix[4]arenes substituted at the wide rim with nitro and phthalimido groups are suitable precursors for derivatives bearing different *N*-acylamino groups at the wide rim. They are easily obtained by a reaction sequence involving partial *ipso*-nitration of a tetraether of *tert*-butylcalix[4]arene, reduction of the nitro groups, protection of the amino groups as phthalimides and *ipso*-nitration of the remaining *para*-positions, as shown for various examples. One example, the propyl ether analogue of **21**, has been described before and it is interesting to compare the different strategies. The published synthesis involves the following steps starting with *tert*-butylcalix[4]arene[17]: (i) debutylation (66–80%); (ii) tetra-*O*-alkylation (61–80%); (iii) partial nitration in positions 1 and 3 (30%); (iv) iodination in positions 2 and 4 (93%); (v) aromatic substitution with potassium phthalimide (70%) with an overall yield of 8–12%.

The synthesis described above for **21** involves also five steps[29]: (i) tetra-*O*-alkylation (90%); (ii) partial *ipso*-nitration in 1,3-position (33%); (iii) reduction of the nitro groups; (iv) protection of the amino groups as phthalimides (80% (iii) + (iv)); (v) *ipso*-nitration in 2,4-position (90%) with an overall yield of 21%.

In both cases the partial (*ipso*-)nitration is responsible for the low overall yield, which, however, is twice as high in the second sequence. Not only due to this higher overall yield we prefer this strategy. The single steps are preparatively easier, especially since the bothersome Ullmann-type substitution is avoided.

To introduce two different acyl residues, we used the reaction sequence (vi) cleavage of the phthalimide groups (vii) first *N*-acylation (viii) reduction of the nitro groups, and (ix) second *N*-acylation. The alternative route (vi) reduction of the nitro groups (vii) first *N*-acylation (viii) cleavage of the phthalimide groups, and (ix) second *N*-acylation should be possible, too.

EXPERIMENTAL

Solvents and all other chemicals were purchased and used without further purification, if not stated otherwise. Column chromatography was performed with silica gel (Merck, 0.040–0.063 mm). ^{1}H and ^{13}C NMR spectra (δ, ppm; *J*, Hz) were recorded on a Bruker DRX400 Avance Instrument (^{1}H at 400 and ^{13}C at 100 MHz at room temperature, if not stated otherwise). Chemical shifts were referenced to the residual signal of a deuterated solvent. Mass spectra were obtained on a Finnigan MAT 8230 spectrometer. Melting points were not corrected.

Abbreviations for assignment of ^{1}H NMR spectra: Ar-H, hydrogen atoms attached to a phenyl ring; Ar_{phth}-H, hydrogen atoms attached to a phthalimido group, Ar-CH_2-Ar ax and eq, hydrogen atoms of the methylene bridge axial and equatorial, respectively.

Compounds **1**–**4**, **7**–**12**[30] were obtained as described in the literature.

General Procedure for the Alkylation of Nitro Derivative **33**

A slurry of **33**, Na_2CO_3 (3 mmol/1 mmol dihydroxy derivative) and alkylating reagent (3 mmol ethyl bromoacetate/1 mmol **33** or 12 mmol methyl iodide) in acetonitrile was refluxed for 2 days. The solvent was evaporated to dryness under reduced pressure and the crude product precipitated from a dichloromethane/methanol mixture. Yield of crystalline compound 82–92%.

5,17-Di-tert-butyl-11,23-dinitro-25,27-bis[(ethoxycarbonyl)methoxy]-26,28-bis(pentyloxy)calix-[4]arene (**5**). Yield 82%, m.p. 146–147 °C. ^{1}H NMR ($CDCl_3$): 7.32 s, 4 H (Ar-H); 6.92 s, 4 H (Ar-H); 4.69 s, 4 H (OCH_2-CO); 4.57 d, 4 H, *J* = 13.4 (Ar-CH_2-Ar ax); 4.22 q, 4 H, *J* = 7.2 (OC**H**$_2$$CH_3$); 3.93 t, 4 H, *J* = 7.8 (OCH_2-); 3.27 d, 4 H, *J* = 13.7 (Ar-CH_2-Ar eq); 1.88 m, 4 H (-CH_2-); 1.37–1.34 m, 8 H (-CH_2-); 1.29 t, 6 H, *J* = 7.2 (CH_2C**H**$_3$); 1.19 s, 18 H (*t*-Bu); 0.92 t, 6 H, *J* = 7.1 (-CH_3). ^{13}C NMR ($CDCl_3$): 168.67, 160.05, 154.12, 145.99, 142.91, 135.81, 133.33, 126.06, 123.24, 75.47, 71.01, 61.02, 34.05, 31.69, 31.41, 29.64, 28.11, 22.73, 14.17, 14.10. MS (FD), *m/z*: 938.8 (M^+ calculated $C_{54}H_{70}N_2O_{12}$: 938.49).

If potassium carbonate was used the product was obtained in the *partial cone* conformation. Yield after two crystallizations from CH_2Cl_2/MeOH 36%, m.p. 172–173 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): 8.24 s, 2 H (Ar-H); 7.99 s, 2 H (Ar-H); 7.05 and 6.51 2bs, 4 H (Ar-H); 4.37 s, 2 H (OCH_2-CO); 4.13 s, 2 H (OCH_2-CO); 4.25–3.25 m, 16 H (Ar-CH_2-Ar + OCH_2-); 1.82 m, 4 H (-CH_2-); 1.42–1.39 m, 8 H (-CH_2-); 1.29 t, 6 H, *J*=7.1 (CH_2C**H**$_3$); 1.19 t, 6 H, *J* = 7.1 (CH_2C**H**$_3$); 1.02 s, 2 H (*t*-Bu); 0.95 bs, 6 H (-CH_3).

5,17-Di-tert-butyl-11,23-dinitro-25,27-dimethoxy-26,28-bis(pentyloxy)calix[4]arene (**6**). Equilibrium mixture of *partial cone* and *cone* conformations (≈10:1). Yield 92%, m.p. 222–224 °C. ^{1}H NMR ($CDCl_3$, –50 °C): 8.22 s, 2 H (Ar-H); 8.11 s, 0.4 H (Ar-H); 8.05 s, 2 H (Ar-H); 6.91 s, 2 H (Ar-H); 6.45 s, 2 H (Ar-H); 6.35 s, 0.4 H (Ar-H); 4.30 d, 0.4 H, *J* = 13 (Ar-CH_2-Ar ax); 4.03–3.99 m, 2 H (Ar-CH_2-Ar ax); 3.86–3.82 m, 4 H (OCH_2-); 3.68–3.65 m, 2 H (Ar-CH_2-Ar ax); 3.5–3.44 m, 2 H (Ar-CH_2-Ar eq); 3.39 s, 3 H (OCH_3); 3.29 d, 0.4 H, *J* = 13 (Ar-CH_2-Ar eq); 3.21–3.18 m, 2 H (Ar-CH_2-Ar eq); 3.12 s, 3 H (-CH_3); 1.84–1.74 m, 4.4 H (-CH_2-); 1.34 m, 9 H (-CH_2-); 1.00–0.76 m, 27 H (*t*-Bu + -CH_3). ^{13}C NMR ($CDCl_3$, –50 °C): 163.80, 163.58, 154.08, 144.81, 142.67, 141.80, 138.04, 135.20, 131.08, 130.56, 126.34, 125.25, 124.68, 124.11, 123.87, 76.24, 75.79, 74.34, 61.06, 60.50, 58.62, 37.15, 33.69, 31.30, 31.10, 30.29, 30.08, 28.32, 22.56, 13.95, 0.96. MS (FD), *m/z*: 794.8 (M^+ calculated $C_{48}H_{62}N_2O_8$: 794.45).

General Procedure for the Reaction of Amino Derivatives **7**–**12** with Phthalic Anhydride

A toluene solution of **7**–**12** obtained after the reduction was treated with phthalic anhydride (1.1–1.2 mmol of phthalic anhydride per 1 mmol of amino group) and a few drops of triethylamine as catalyst. The reaction mixture was refluxed for 1–2 days to form a clear orange solution. The solvent was evaporated in vacuo and the residue was first passed through a short silica column (eluent ethyl acetate/hexane) and then recrystallised from dichloromethane/methanol or acetonitrile. Yield 70–85%.

5,11,17-Tri-tert-butyl-23-phthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**13**). Yield 72%, m.p. 161–162 °C. ^{1}H NMR ($CDCl_3$): 7.73 m, 2 H (Ar_{phth}-H); 7.72 m, 2 H (Ar_{phth}-H); 7.03 s, 2 H (Ar-H); 6.77 s, 2 H (Ar-H); 6.73 s, 4 H (Ar-H); 4.46 d, 2 H, *J* = 13.4 (Ar-CH_2-Ar ax); 4.42 d, 2 H, *J* = 12.9 (Ar-CH_2-Ar ax); 3.96 t, 2 H, *J* = 7.6 (OCH_2-); 3.90 t, 2 H, *J* = 7.5 (OCH_2-); 3.82 m, 4 H (OCH_2-); 3.17 d, 2 H, *J* = 12.6 (Ar-CH_2-Ar eq); 3.12 d, 2 H, *J* = 12.9 (Ar-CH_2-Ar eq); 2.03 m, 4 H (-CH_2-); 1.96 m, 4 H (-CH_2-); 1.39 m, 16 H (-CH_2-); 1.05 s, 18 H (*t*-Bu); 1.02 s, 9 H (*t*-Bu); 0.96 m, 12 H (-CH_3). ^{13}C NMR ($CDCl_3$): 166.99, 155.64, 153.91, 153.56, 144.41, 144.27, 135.82, 134.16, 133.85, 133.48, 132.59, 131.90, 125.72, 125.20, 125.09, 124.84, 123.28, 75.50, 75.28, 75.20, 33.77, 33.67, 31.38, 31.20, 31.11, 30.06, 30.01, 29.81, 28.39, 28.30, 22.88, 22.86, 22.80, 14.24, 14.14. MS (FD), *m/z*: 1017.9 (M^+ calculated $C_{68}H_{91}NO_6$: 1017.68).

5,11-Di-tert-butyl-17,23-diphthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**14**). Yield 82%, m.p. 293–294 °C. ^{1}H NMR ($CDCl_3$): 7.72 m, 4 H (Ar_{phth}-H); 7.68 m, 4 H (Ar_{phth}-H); 7.06 d, 2 H, *J* = 1.9 (Ar-H); 6.93 d, 2 H, *J* = 1.9 (Ar-H); 6.77 bd, 2 H (Ar-H); 6.74 bd, 2 H (Ar-H); 4.52 d, 1 H, *J* = 13.0 (Ar-CH_2-Ar ax); 4.47 d, 2 H, *J* = 12.7 (Ar-CH_2-Ar ax); 4.46 d, 1 H, *J* = 12.7 (Ar-CH_2-Ar ax); 3.96–3.88 m, 8 H (OCH_2-); 3.26 d, 1 H, *J* = 12.7 (Ar-CH_2-Ar eq); 3.18 d, 2 H, *J* = 13.4 (Ar-CH_2-Ar eq); 3.14 d, 1 H, *J* = 14.3 (Ar-CH_2-Ar eq); 1.99 m, 8 H (-CH_2-); 1.43–1.39 m, 16 H (-CH_2-); 1.01 s, 18 H (*t*-Bu); 0.96 t, 12 H, *J* = 6.2 (-CH_3). ^{13}C NMR ($CDCl_3$): 166.87, 155.37, 153.70, 144.73, 135.36, 134.62, 133.81, 133.65, 133.06, 131.85, 125.87, 125.49, 125.46, 125.33, 124.83, 123.23, 75.50, 75.32, 33.72, 31.21, 31.06, 30.96, 30.07, 29.88, 28.41, 28.32, 22.84, 22.81, 14.19, 14.17. MS (FD), *m/z*: 1106.7 (M^+ calculated $C_{72}H_{86}N_2O_8$: 1106.6).

5,17-Di-tert-butyl-11,23-diphthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**15**). Yield 82%, m.p. 240–241 °C. ^{1}H NMR ($CDCl_3$): 7.35 m, 4 H (Ar_{phth}-H); 7.32 m, 4 H (Ar_{phth}-H); 6.99 s, 4 H (Ar-H); 6.51 s, 4 H (Ar-H); 4.48 d, 4 H, *J* = 13 (Ar-CH_2-Ar ax); 4.01 t, 4 H, *J* = 8.1 (OCH_2-); 3.81 t, 4 H, *J* = 6.8 (OCH_2-); 3.18 d, 4 H, *J* = 13 (Ar-CH_2-Ar eq); 2.01 q, 4 H, *J* = 7.8 (-CH_2-); 1.94 q, 4 H, *J* = 7.5 (-CH_2-); 1.54–1.50 m, 4 H (-CH_2-); 1.45–1.39 m, 8 H (-CH_2-); 1.32–1.28 m, 4 H (-CH_2-); 1.23 s, 18 H (*t*-Bu); 0.98 t, 6 H, *J* = 7.1 (-CH_3); 0.96 t, 6 H, *J* = 7.2 (-CH_3). ^{13}C NMR ($CDCl_3$): 166.33, 154.73, 154.66, 144.84, 134.55, 134.06, 133.13, 131.69, 125.74, 125.56, 125.45, 122.54, 75.35, 75.18, 33.99, 31.53, 31.25, 30.12, 29.86, 28.60, 28.24, 22.93, 22.76, 14.29, 14.12. MS (FD), *m/z*: 1108.0 (M^+ calculated $C_{72}H_{86}N_2O_8$: 1106.6).

5-tert-Butyl-11,17,23-triphthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**16**). Yield 87%, m.p. 290–291 °C (decomp.). ^{1}H NMR (CD_2Cl_2): 7.84 m, 2 H (Ar_{phth}-H); 7.75 m, 2 H (Ar_{phth}-H); 7.35 m, 4 H (Ar_{phth}-H); 7.26 m, 4 H (Ar_{phth}-H); 7.20 s, 2 H (Ar-H); 7.06 s, 2 H (Ar-H); 6.51 d, 2 H, *J* = 2.4 (Ar-H); 6.50 d, 2 H, *J* = 2.4 (Ar-H); 4.57 d, 2 H, *J* = 13.4 (Ar-CH_2-Ar ax); 4.52 d, 2 H, *J* = 13.0 (Ar-CH_2-Ar ax); 4.18 t, 2 H, *J* = 8.3 (OCH_2-); 4.07 t, 2 H, *J* = 8.2 (OCH_2-); 3.86–3.80 m, 4 H (OCH_2-); 3.29 d, 2 H, *J* = 13.4 (Ar-CH_2-Ar eq); 3.22 d, 2 H, *J* = 13.2 (Ar-CH_2-Ar eq); 2.07–2.01 m, 4 H (-CH_2-); 2.00–1.92 m, 4 H (-CH_2-); 1.58–1.53 m, 4 H (-CH_2-); 1.48–1.40 m, 8 H (-CH_2-); 1.37–1.31 m, 4 H (-CH_2-); 1.23 s, 9 H (*t*-Bu); 0.98 t, 6 H, *J* = 7.2 (-CH_3); 0.97 t, 6 H, *J* = 7.2 (-CH_3). ^{13}C NMR (CD_2Cl_2): 167.60, 166.74, 157.17, 155.30, 155.12, 145.40, 136.86, 135.28, 134.45, 134.33, 133.76, 133.61, 132.35, 131.95, 126.68, 126.48, 126.37, 126.18, 126.07, 125.77, 123.59, 122.85, 76.06, 75.78, 75.73, 34.27, 31.60, 31.56, 30.58, 30.34, 30.09, 29.07, 28.65, 28.60, 23.35, 23.14, 14.48, 14.28, 1.13. MS (FD), *m/z*: 1195.5 (M^+ calculated $C_{76}H_{81}N_3O_{10}$: 1195.59).

5,17-Di-tert-butyl-11,23-diphthalimido-25,27-bis[(ethoxycarbonyl)methoxy]-26,28-bis(pentyloxy)-calix[4]arene (**17**). Yield 92%, m.p. 290 °C (decomp.). ^{1}H NMR ($CDCl_3$): 7.51 m, 8 H (Ar_{phth}-H); 6.85 s, 4 H (Ar-H); 6.74 s, 4 H (Ar-H); 4.73 s, 4 H (OCH_2-CO); 4.65 d, 4 H, *J* =

13.2 (Ar-CH_2-Ar ax); 4.23 q, 4 H, *J* = 7.2 (OC**H**$_2$$CH_3$); 3.96 t, 4 H, *J* = 7.6 (OCH_2-); 3.24 d, 4 H, *J* = 13.2 (Ar-CH_2-Ar eq); 1.95 q, 4 H, *J* = 7.5 (-CH_2-); 1.41–1.34 m, 8 H (-CH_2-); 1.30 t, 6 H, *J* = 7.3 (CH_2C**H**$_3$); 1.12 s, 18 H (*t*-Bu); 0.94 t, 6 H, *J* = 7 (-CH_3). ^{13}C NMR ($CDCl_3$): 169.66, 166.60, 154.40, 154.18, 144.99, 134.81, 133.48, 133.28, 131.74, 126.15, 126.04, 125.61, 122.89, 75.43, 71.07, 60.57, 33.90, 31.64, 31.42, 29.74, 28.30, 22.79, 14.21, 14.17. MS (FD), *m/z*: 1140.9 (M^+ calculated $C_{70}H_{78}N_2O_{12}$: 1138.55).

5,17-Di-tert-butyl-11,23-diphthalimido-25,27-dimethoxy-26,28-bis(pentyloxy)calix[4]arene (**18**). Equilibrium mixture of *cone* and *partial cone* (≈1:1.6). Yield 85%, m.p. 235–236 °C (decomp.). ^{1}H NMR ($CDCl_3$): 7.96 m, 10.4 H (Ar_{phth}-H); 7.77 m, 10.4 H (Ar_{phth}-H); 7.26 s, 3.2 H (Ar-H); 7.20 s, 4 H (Ar-H); 7.16 s, 3.2 H (Ar-H); 6.93 bd, 3.2 H (Ar-H); 6.63 bd, 3.2 H (Ar-H); 6.53 s, 4 H (Ar-H); 4.39 d, 4 H, *J* = 12.7 (Ar-CH_2-Ar ax); 4.18 d, 3.2 H, *J* = 12.9 (Ar-CH_2-Ar ax); 4.03 s, 6 H (OCH_3); 3.82–3.55 m, 16.8 H (OCH_2- + Ar-CH_2-Ar ax + Ar-CH_2-Ar eq); 3.46 s, 4.8 H (OCH_3); 3.29 s, 4.8 H (OCH_3); 3.22 d, 4 H, *J* = 12.9 (Ar-CH_2-Ar eq); 3.13 d, 3.2 H, *J* = 13.1 (Ar-CH_2-Ar eq); 1.92 q, 4 H, *J* = 7 (-CH_2-); 1.79 q, 6.4 H, *J* = 7 (-CH_2-); 1.46–1.36 m, 8 H (-CH_2-); 1.27–1.20 m, 12.8 H (-CH_2-); 1.08 s, 28.8 H (*t*-Bu); 0.95 t, 6 H, *J* = 7.12 (-CH_3); 1.08 s, 18 H (*t*-Bu); 0.75 t, 9.6 H, *J* = 7.12 (-CH_3). ^{13}C NMR ($CDCl_3$): 167.57, 158.10, 157.73, 154.52, 153.49, 144.75, 144.14, 137.58, 137.43, 135.18, 134.08, 132.04, 131.26, 131.02, 129.62, 126.70, 126.58, 126.06, 125.67, 125.51, 125.34, 124.81, 124.64, 123.55, 123.44, 75.51, 74.17, 60.56, 58.15, 37.53, 33.70, 31.40, 31.23, 31.10, 30.39, 30.09, 28.49, 28.33, 22.58, 14.10, 13.80. MS (FD), *m/z*: 994.6 (M^+ calculated $C_{64}H_{70}N_2O_8$: 994.51).

5,17-Di-*tert*-butyl-11,23-diphthalimido-25,27-dihydroxy-26,28-bis(pentyloxy)-calix[4]arene (**34**)

A suspension of Raney nickel (0.5 g) in a toluene solution of **33** (1.3 mmol in 35–40 ml) was stirred at room temperature and normal pressure in a hydrogen atmosphere. After 2–3 h, when the hydrogen uptake was finished, the catalyst was filtered off on a paper filter containing some sea sand (≈10 g), washed with toluene (2–3 × 20 ml) and the toluene solution was concentrated to the initial volume and used directly in the next reaction. To this solution phthalic anhydride (2.2 mmol of phthalic anhydride per 1 mmol of **33**) and few drops of triethylamine as catalyst were added. The reaction mixture was refluxed for 1–2 days until it became a clear orange solution. The solvent was evaporated in vacuo and the residue was recrystallized from a dichloromethane/methanol mixture. Yield 83%, m.p. 287–288 °C. ^{1}H NMR ($CDCl_3$): 8.14 s, 2 H (OH); 7.89 m, 4 H (Ar_{phth}-H); 7.69 m, 4 H (Ar_{phth}-H); 7.15 s, 4 H (Ar-H); 6.88 s, 4 H (Ar-H); 4.33 d, 4 H, *J* = 13.2 (Ar-CH_2-Ar ax); 3.98 t, 4 H, *J* = 6.6 (OCH_2-); 3.37 d, 4 H, *J* = 13.2 (Ar-CH_2-Ar eq); 2.03 q, 4 H, *J* = 6.6 (-CH_2-); 1.66 q, 4 H, *J* = 7.6 (-CH_2-); 1.51 m, 4 H (-CH_2-); 1.01–098 m, 24 H (*t*-Bu + CH_3). ^{13}C NMR ($CDCl_3$): 167.60, 153.15, 149.97, 147.51, 133.98, 131.99, 131.77, 128.70, 126.18, 125.95, 123.45, 122.14, 76.68, 34.07, 31.51, 31.14, 29.72, 28.17, 22.53, 14.11. MS (FD), *m/z*: 966 (M^+ calculated $C_{62}H_{66}N_2O_8$: 967.23).

5,17-Di-*tert*-butyl-11,23-diphthalimido-25,27-bis[(3-ethoxycarbonyl)propoxy]-26,28-bis(pentyloxy)calix[4]arene (**35**)

A slurry of **34** (0.54 g, 0.55 mmol) and NaH (40 mg, 1.6 mmol) in DMF (10 ml) was stirred at room temperature for 30 min. After the addition of ethyl 4-bromobutyrate (0.2 ml, 1.39 mmol) stirring was continued for 1–2 days. (The reaction mixture became dark green.) The excess of NaH was destroyed by adding water when a precipitate was formed. Dichloro-

methane was added to this mixture, then the organic layer was separated, washed several times with water, dried over $MgSO_4$ and concentrated in vacuo. The product was precipitated by adding methanol (20– 30 ml). Yield 26%, m.p. 198–199 °C. ^{1}H NMR ($CDCl_3$): 7.35 m, 4 H (Ar_{phth}-H); 7.29 m, 4 H (Ar_{phth}-H); 7.01 s, 4 H (Ar-H); 6.49 s, 4 H (Ar-H); 4.45 d, 4 H, *J* = 13.0 (Ar-CH_2-Ar ax); 4.16 q, 4 H, *J* = 7.1 (OC**H**$_2$$CH_3$); 4.01 t, 4 H, *J* = 8.1 (OCH_2-); 3.83 t, 4 H, *J* = 6.2 (OCH_2-); 3.19 d, 4 H, *J* = 13.0 (Ar-CH_2-Ar eq); 2.61 t, 4 H, *J* = 7.5 (CO-CH_2-); 2.24 q, 4 H, *J* = 7.0 (-CH_2-); 2.00 bq, 4 H (-CH_2-); 1.41–1.38 m, 4 H (-CH_2-); 1.28–1.20 m, 28 H (*t*-Bu + CH_3 + -CH_2-); 0.94 t, 4 H, *J* = 7.2 (-CH_3). ^{13}C NMR ($CDCl_3$): 173.12, 166.24, 154.56, 154.18, 144.99, 134.51, 133.80, 133.14, 131.61, 125.86, 125.72, 125.60, 122.51, 75.14, 74.16, 60.31, 34.00, 31.51, 31.29, 31.18, 29.91, 28.09, 25.65, 22.86, 14.32, 14.23. MS (FD), *m/z*: 1193.5 (M^+ calculated $C_{74}H_{86}N_2O_{12}$: 1194.6).

General Procedure for the Complete *ipso*-Nitration of Phthalimido Compounds

A phthalimide derivative **13**–**18** was dissolved in a mixture of dichloromethane/glacial acetic acid (19:1; 50 ml/1 mmol), and fuming nitric acid (Merck, 100% extra pure; 5–6 mmol acid/1 mmol *tert*-butyl group) was added in one portion while stirring. The reaction mixture become violet and after a few minutes yellow. The course of the reaction could be followed by TLC and if it was not complete, an additional amount of nitric acid had to be added. The reaction mixture was washed with water until a neutral pH was reached and then concentrated in vacuo. The crude product was precipitated with methanol and, in general, it was pure enough for the next reaction. If the phthalimide derivatives **14** or **15** were dissolved in a double amount of solvent, the main products were mono-*ipso*-nitrated compounds **23** or **24**.

5,11,17-Trinitro-23-phthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**19**). Yield 55%, m.p. 272 °C. ^{1}H NMR ($CDCl_3$): 7.88 s, 4 H (Ar-H); 7.83 m, 2 H (Ar_{phth}-H); 7.72 m, 2 H (Ar_{phth}-H); 7.39 s, 2 H (Ar-H); 6.49 s, 2 H (Ar-H); 4.52 d, 2 H, *J* = 13.4 (Ar-CH_2-Ar ax); 4.51 d, 2 H, *J* = 13.7 (Ar-CH_2-Ar ax); 4.22–4.09 m, 4 H (OCH_2-); 3.85–3.83 m, 4 H (OCH_2-); 3.37 d, 4 H, *J* = 13.7 (Ar-CH_2-Ar eq); 1.94–189 m, 4 H (-CH_2-); 1.48–1.32 m, 16 H (-CH_2-); 0.98–0.93 m, 12 H (-CH_3). ^{13}C NMR ($CDCl_3$): 166.55, 162.40, 160.68, 154.90, 143.64, 142.74, 136.82, 135.67, 134.07, 133.92, 133.19, 131.48, 126.51, 126.26, 124.64, 124.03, 123.60, 77.15, 76.31, 76.10, 76.02, 75.83, 31.09, 30.01, 29.90, 29.71, 28.39, 28.21, 27.96, 22.68, 22.65, 22.57, 14.09, 14.01, 13.94. MS (FD), *m/z*: 984.5 (M^+ calculated $C_{56}H_{64}N_4O_{12}$: 984.45).

5,11-Dinitro-17,23-diphthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**20**). Yield 78%, m.p. 197–199 °C. ^{1}H NMR ($CDCl_3$): 7.83 m, 4 H (Ar_{phth}-H); 7.69 m, 4 H (Ar_{phth}-H); 7.68 bd, 2 H (Ar-H); 7.63 bd, 2 H (Ar-H); 6.88 d, 2 H, *J* = 2.4 (Ar-H); 6.79 d, 2 H, *J* = 2.4 (Ar-H); 4.53 d, 4 H, *J* = 13.6 (Ar-CH_2-Ar ax); 4.06–3.92 m, 8 H (OCH_2-); 3.35 d, 1 H, *J* = 13.6 (Ar-CH_2-Ar eq); 3.33 d, 2 H, *J* = 13.2 (Ar-CH_2-Ar eq); 3.31 d, 1 H, *J* = 13.2 (Ar-CH_2-Ar eq); 1.94–1.91 m, 8 H (-CH_2-); 1.44–1.39 m, 16 H (-CH_2-); 0.98–0.93 m, 12 H (-CH_3). ^{13}C NMR ($CDCl_3$): 166.81, 161.64, 155.46, 143.27, 135.86, 135.13, 134.59, 134.00, 133.77, 131.73, 126.61, 126.33, 125.94, 124.60, 123.90, 123.53, 75.94, 75.73, 31.15, 31.08, 29.93, 29.84, 28.31, 28.18, 22.77, 22.69, 14.15, 14.07. MS (FD), *m/z*: 1084.5 (M^+ calculated $C_{64}H_{68}N_2O_{12}$: 1084.48).

5,17-Dinitro-11,23-diphthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**21**). Yield 92%, m.p. 262–264 °C. ^{1}H NMR ($CDCl_3$): 7.95 s, 4 H (Ar-H); 7.39 m, 4 H (Ar_{phth}-H); 7.29 m, 4 H (Ar_{phth}-H); 6.52 s, 4 H (Ar-H); 4.52 d, 4 H, *J* = 13.6 (Ar-CH_2-Ar ax); 4.22 t, 4 H, *J* = 8.1 (OCH_2-); 3.80 t, 4 H, *J* = 6.9 (OCH_2-); 3.37 d, 4 H, *J* = 13.6 (Ar-CH_2-Ar eq); 1.97 q, 4 H, *J* = 7.8 (-CH_2-); 1.91 q, 4 H, *J* = 7.8 (-CH_2-); 1.50–1.20 m, 16 H (-CH_2-); 0.97 t, 6 H, *J* = 7.0 (-CH_3); 0.96 t, 6 H, *J* = 7.0 (-CH_3). ^{13}C NMR ($CDCl_3$): 166.31, 163.04, 154.51, 142.47, 136.87,

133.47, 132.43, 131.39, 126.27, 126.13, 124.37, 122.92, 75.95, 75.75, 31.12, 30.11, 29.79, 28.51, 28.03, 22.78, 22.69, 14.19, 14.05. MS (FD), *m/z*: 1084.5 (M^+ calculated $C_{64}H_{68}N_2O_{12}$: 1084.48).

5-Nitro-11,17,23-triphthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**22**). Yield 86%, m.p. > 200 °C (decomp.). ^{1}H NMR ($CDCl_3$): 7.84 s, 2 H (Ar-H); 7.82 m, 2 H (Ar_{phth}-H); 7.68 m, 2 H (Ar_{phth}-H); 7.39 m, 4 H (Ar_{phth}-H); 7.35 m, 4 H (Ar_{phth}-H); 7.04 s, 2 H (Ar-H); 6.79 d, 2 H, *J* = 1.9 (Ar-H); 6.64 d, 2 H, *J* = 1.9 (Ar-H); 4.54 d, 2 H, *J* = 13.2 (Ar-CH_2-Ar ax); 4.53 d, 2 H, *J* = 13.2 (Ar-CH_2-Ar ax); 4.15 bt, 2 H, *J* = 7.8 (OCH_2-); 4.06 t, 2 H, *J* = 7.9 (OCH_2-); 3.89–3.84 m, 4 H (OCH_2-); 3.34 d, 2 H, *J* = 13.7 (Ar-CH_2-Ar eq); 3.30 d, 2 H, *J* = 13.7 (Ar-CH_2-Ar eq); 2.01–1.92 m, 8 H (-CH_2-); 1.49–1.33 m, 16 H (-CH_2-); 0.99–0.94 m, 12 H (-CH_3). ^{13}C NMR ($CDCl_3$): 166.93, 166.43, 162.59, 156.08, 154.89, 142.72, 136.31, 135.51, 134.12, 133.86, 133.37, 132.65, 131.90, 131.57, 126.49, 126.26, 126.03, 125.95, 125.78, 124.26, 123.34, 122.86, 75.66, 75.49, 31.15, 31.09, 30.02, 29.84, 29.79, 28.44, 28.21, 28.11, 22.83, 22.74, 22.72, 14.22, 14.14, 14.08, 0.97. MS (FD), *m/z*: 1184.1 (M^+ calculated $C_{72}H_{72}N_4O_{12}$: 1184.5).

5-tert-Butyl-11-nitro-17,23-diphthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**23**). Yield 86%, m.p. 211–213 °C. ^{1}H NMR (CD_2Cl_2): 7.88 m, 2 H (Ar_{phth}-H); 7.77 m, 2 H (Ar_{phth}-H); 7.74 m, 2 H (Ar_{phth}-H); 7.68 m, 2 H (Ar_{phth}-H); 7.28 d, 1 H, *J* = 2.7 (Ar-H); 7.26 bs, 1 H (Ar-H); 7.25 bs, 1 H (Ar-H); 7.20 d, 1 H, *J* = 2.4 (Ar-H); 7.07 d, 1 H, *J* = 2.4 (Ar-H); 7.05 d, 1 H, *J* = 2.4 (Ar-H); 6.47 d, 1 H, *J* = 2.4 (Ar-H); 6.44 d, 1 H, *J* = 2.4 (Ar-H); 4.56 d, 2 H, *J* = 13.4 (Ar-CH_2-Ar ax); 4.51 d, 1 H, *J* = 13.2 (Ar-CH_2-Ar ax); 4.50 d, 1 H, *J* = 13.2 (Ar-CH_2-Ar ax); 4.18–4.01 m, 4 H (OCH_2-); 3.87–3.82 m, 4 H (OCH_2-); 3.30 d, 1 H, *J* = 13.4 (Ar-CH_2-Ar eq); 3.29 d, 1 H, *J* = 13.4 (Ar-CH_2-Ar eq); 3.24 d, 1 H, *J* = 13.4 (Ar-CH_2-Ar eq); 3.23 d, 1 H, *J* = 13.2 (Ar-CH_2-Ar eq); 2.03–1.91 m, 8 H (-CH_2-); 1.55–1.50 m, 4 H (-CH_2-); 1.47–1.40 m, 8 H (-CH_2-); 1.34–1.30 m, 4 H (-CH_2-); 1.23 s, 9 H (*t*-Bu); 0.99–0.95 m, 12 H (-CH_3). ^{13}C NMR (CD_2Cl_2): 155.01, 145.84, 143.88, 136.91, 135.87, 135.66, 135.44, 134.94, 134.82, 134.58, 134.33, 134.17, 134.06, 132.23, 132.16, 127.03, 126.92, 126.55, 126.47, 126.41, 126.17, 125.99, 125.58, 124.16, 123.71, 123.46, 76.37, 76.14, 75.86, 75.73, 34.31, 31.55, 31.48, 31.41, 30.54, 30.43, 30.25, 30.11, 29.03, 28.85, 28.60, 28.53, 23.32, 23.30, 23.13, 23.06, 14.44, 14.28, 14.21. MS (FD), *m/z*: 1095.6 (M^+ calculated $C_{68}H_{77}N_3O_{10}$: 1095.55).

5-tert-Butyl-17-nitro-11,23-diphthalimido-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**24**). Yield 70%, m.p. 305–307 °C. ^{1}H NMR (CD_2Cl_2): 7.69 m, 4 H (Ar_{phth}-H); 7.59 m, 4 H (Ar_{phth}-H); 7.61 s, 2 H (Ar-H); 6.97 bs, 2 H (Ar-H); 6.91 bs, 2 H (Ar-H); 6.52 s, 2 H (Ar-H); 4.52 d, 2 H, *J* = 13.3 (Ar-CH_2-Ar ax); 4.47 d, 2 H, *J* = 13.0 (Ar-CH_2-Ar ax); 4.04 m, 2 H (OCH_2-); 3.95 m, 4 H (OCH_2-); 3.85 t, 2 H, *J* = 7.2 (OCH_2-); 3.28 d, 2 H, *J* = 13.3 (Ar-CH_2-Ar eq); 3.22 d, 2 H, *J* = 13.0 (Ar-CH_2-Ar eq); 2.20–1.80 m, 8 H (-CH_2-); 1.50–1.20 m, 16 H (-CH_2-); 1.00–0.90 m, 12 H (-CH_3). ^{13}C NMR ($CDCl_3$): 166.91, 161.84, 155.79, 153.54, 146.22, 145.51, 142.59, 136.22, 135.57, 134.05, 133.79, 132.66, 131.75, 127.07, 125.79, 125.40, 123.81, 123.23, 76.00, 75.45, 33.63, 31.14, 31.06, 30.14, 29.91, 28.48, 28.27, 22.84, 22.68, 14.23, 14.15, 14.07. MS (FD), *m/z*: 1095.4 (M^+ calculated $C_{68}H_{77}N_3O_{10}$: 1095.55).

5,17-Dinitro-11,23-diphthalimido-25,27-bis[(ethoxycarbonyl)methoxy]-26,28-bis(pentyloxy)-calix[4]arene (**25**). Yield 79%, m.p. 290 °C (decomp.). ^{1}H NMR ($CDCl_3$): 7.80 s, 4 H (Ar-H); 7.45 m, 4 H (Ar_{phth}-H); 7.42 m, 4 H (Ar_{phth}-H); 6.71 s, 4 H (Ar-H); 4.70 d, 4 H, *J* = 13.8 (Ar-CH_2-Ar ax); 4.54 s, 4 H (OCH_2-CO); 4.27–4.20 m, 8 H ($OC\mathbf{H}_2CH_3$ + OCH_2-); 3.38 d, 4 H, *J* = 13.8 (Ar-CH_2-Ar eq); 1.93 q, 4 H, *J* = 7.3 (-CH_2-); 1.42–1.36 m, 8 H (-CH_2-); 1.31 t, 6 H, *J* = 7.2 ($CH_2C\mathbf{H}_3$); 0.94 t, 6 H, *J* = 6.9 (-CH_3). ^{13}C NMR ($CDCl_3$): 168.79, 166.39, 162.67,

154.10, 142.57, 136.23, 133.70, 133.05, 131.40, 127.04, 126.52, 124.19, 123.1176.09, 71.54, 60.91, 31.33, 29.63, 28.06, 22.63, 14.21, 14.09. MS (FD), *m/z*: 1117.7 (M^+ calculated $C_{62}H_{60}N_4O_{16}$: 1117.19).

5,17-Dinitro-11,23-diphthalimido-25,27-dimethoxy-26,28-bis(pentyloxy)calix[4]arene (**26**). Equilibrium mixture of *cone* and *partial cone* (≈1:3.5). Yield 88%, m.p. 292–293 °C. ^{1}H NMR (CD_2Cl_2): 7.98–7.92 m, 18 H (Ar_{phth}-H); 7.86 d, 7 H, *J* = 2.2 (Ar-H); 7.83–7.81 m, 18 H (Ar_{phth}-H); 7.41 s, 4 H (Ar-H); 7.35 s, 7 H (Ar-H); 7.34 s, 7 H (Ar-H); 7.25 d, 3.2 H, *J* = 1.9 (Ar-H); 7.18 s, 4 H (Ar-H); 4.47 d, 4 H, *J* = 13.6 (Ar-CH_2-Ar ax); 4.18 d, 7 H, *J* = 14.2 (Ar-CH_2-Ar ax); 3.98 s, 6 H (OCH_3); 3.91 s, 10.5 H (OCH_3); 3.88–3.84 m, 7 H (OCH_2-); 3.82 m, 18 H (OCH_2- + Ar-CH_2-Ar ax + Ar-CH_2-Ar eq); 3.75–3.70 m, 7 H (OCH_2-); 3.36 d, 4 H, *J* = 13.6 (Ar-CH_2-Ar eq); 3.29 d, 7 H, *J* = 14.2 (Ar-CH_2-Ar eq); 3.22 s, 10.5 H (OCH_3); 1.95–1.78 m, 18 H (-CH_2-); 1.45–1.24 m, 36 H (-CH_2-); 0.96 t, 6 H, *J* = 7.2 (-CH_3); 0.78 t, 21 H, *J* = 7.2 (-CH_3). ^{13}C NMR ($CDCl_3$): 167.30, 167.16, 161.67, 157.68, 156.75, 142.43, 136.15, 136.07, 134.98, 134.38, 134.31, 133.67, 132.37, 131.85, 131.73, 129.31, 126.90, 126.82, 125.90, 124.49, 123.70, 123.63, 123.56, 75.20, 60.66, 59.15, 25.62, 30.93, 30.12, 28.27, 22.50, 13.78, 0.98. MS (FD), *m/z*: 974.7 (M^+ calculated $C_{56}H_{52}N_4O_{12}$: 973.06).

5,17-Dinitro-11,23-diphthalimido-25,27-bis[(3-ethoxycarbonyl)propoxy]-26,28-bis(pentyloxy)-calix[4]arene (**36**). Yield 72%, m.p. 228–230 °C. ^{1}H NMR ($CDCl_3$): 7.99 s, 4 H (Ar-H); 7.36 m, 4 H (Ar_{phth}-H); 7.26 m, 4 H (Ar_{phth}-H); 6.48 s, 4 H (Ar-H); 4.50 d, 4 H, *J* = 13.4 (Ar-CH_2-Ar ax); 4.22 t, 4 H, *J* = 8.2 (OCH_2-); 4.20 q, 4 H, *J* = 7.1 ($OC\mathbf{H}_2CH_3$); 3.82 t, 4 H, *J* = 6.7 (OCH_2-); 3.38 d, 4 H, *J* = 13.7 (Ar-CH_2-Ar eq); 3.57 t, 4 H, *J* = 7.5 (CO-CH_2-); 2.22 q, 4 H, *J* = 6.9 (-CH_2-); 1.96 q, 4 H, *J* = 8.1 (-CH_2-); 1.43–1.39 m, 4 H (-CH_2-); 1.34–1.29 m, 4 H (-CH_2-); 1.26 t, 6 H, *J* = 7.2 ($CH_2C\mathbf{H}_3$); 0.94 t, 6 H, *J* = 7.2 (-CH_3). ^{13}C NMR ($CDCl_3$): 172.67, 166.23, 162.97, 153.99, 142.51, 136.82, 133.47, 132.17, 131.31, 126.50, 126.16, 124.49, 122.89, 75.75, 74.68, 60.55, 31.05, 30.99, 29.86, 27.88, 25.56, 22.74, 14.25, 14.20, 0.99. MS (FD), *m/z*: 1172.8 (M^+ calculated $C_{66}H_{68}N_4O_{16}$: 1173.3).

General Procedure for the Cleavage of Phthalimides

Method A (with hydrazine hydrate): A phthalimidonitro derivative **27**–**30** or **32** was dissolved in a warm ethanol/toluene mixture (3:1). When a clear solution was formed, the calculated amount of hydrazine (minimum 10 mmol of hydrazine per 1 mmol phthalimido group) was added and the reaction mixture was refluxed for 2 h. After cooling to room temperature, hydrochloric acid (37%) was added (2–3 ml) and a white precipitate appeared. This mixture was diluted with toluene and washed with water until a neutral pH was reached. The water layer was extracted again with toluene and the combined organic layer was dried over $MgSO_4$ and evaporated to dryness. The product was crystallized from dichloromethane/methanol to give yellow crystals. Yield 85–97%.

Method B (with hydrochloric acid): A phthalimidonitro compound (**25**) was dissolved in a warm ethanol/toluene mixture (3:1; 5–10 ml solvent per 0.1 mmol compound), concentrated hydrochloric acid (50 mmol/phthalimido group) was added and the clear solution refluxed for 1–2 days. The work up was done in a way similar to the method *A*.

5-Amino-11,17,23-trinitro-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**27**) *(method A)*. Yield 85%, m.p. 175–176 °C. ^{1}H NMR ($CDCl_3$): 7.89 s, 4 H (Ar-H); 7.21 s, 2 H (Ar-H); 5.53 s, 2 H (Ar-H); 4.51 d, 2 H, *J* = 13.9 (Ar-CH_2-Ar ax); 4.37 d, 2 H, *J* = 13.7 (Ar-CH_2-Ar ax); 4.16–4.11 m, 4 H (OCH_2-); 4.04–4.00 m, 4 H (OCH_2-); 3.86 t, 2 H, *J* = 6.8 (OCH_2-); 3.66 t, 2 H, *J* = 6.7 (OCH_2-); 3.35 d, 2 H, *J* = 13.9 (Ar-CH_2-Ar eq); 3.18 d, 2 H, *J* = 13.9 (Ar-CH_2-Ar eq); 2.92 bs,

2 H (NH_2); 1.87–1.78 m, 8 H (-CH_2-); 1.47–1.24 m, 16 H (-CH_2-); 0.96–0.90 m, 12 H (-CH_3). ^{13}C NMR ($CDCl_3$): 163.03, 161.23, 148.29, 142.59, 142.46, 141.73, 137.80, 136.00, 134.78, 133.03, 124.84, 123.75, 123.50, 114.42, 76.07, 75.84, 75.60, 31.13, 29.97, 29.93, 29.84, 28.56, 28.32, 27.92, 22.71, 22.60, 14.10, 14.07, 14.01, 1.01. MS (FD), *m/z*: 854.4 (M^+ calculated $C_{48}H_{62}N_4O_{10}$: 854.8).

5,11-Diamino-17,23-dinitro-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**28**) *(method A)*. Yield 90%, m.p. 197–199 °C. ^{1}H NMR ($CDCl_3$): 7.60 d, 2 H, *J* = 2.2 (Ar-H); 7.52 bd, 2 H (Ar-H); 5.97 bd, 2 H (Ar-H); 5.89 bd, 2 H (Ar-H); 4.51 d, 1 H, *J* = 14.0 (Ar-CH_2-Ar ax); 4.38 d, 2 H, *J* = 13.8 (Ar-CH_2-Ar ax); 4.24 d, 1 H, *J* = 13.4 (Ar-CH_2-Ar ax); 4.05–3.99 m, 2 H (OCH_2-); 3.93–3.87 m, 2 H (OCH_2-); 3.08–3.67 m, 4 H (OCH_2-); 3.31 d, 1 H, *J* = 14.0 (Ar-CH_2-Ar eq); 3.12 d, 2 H, *J* = 13.8 (Ar-CH_2-Ar eq); 3.25–3.05 bs, 4 H (NH_2); 2.91 d, 1 H, *J* = 13.4 (Ar-CH_2-Ar eq); 1.85–1.78 m, 8 H (-CH_2-); 1.38–1.33 m, 16 H (-CH_2-); 0.94–0.90 m, 12 H (-CH_3). ^{13}C NMR ($CDCl_3$): 162.40, 149.24, 142.28, 141.17, 137.13, 136.01, 135.25, 133.88, 124.34, 123.22, 115.58, 114.48, 75.65, 75.25, 31.23, 31.14, 31.04, 29.91, 29.79, 28.36, 28.15, 22.77, 22.66, 14.14, 14.06. MS (FD), *m/z*: 824.8 (M^+ calculated $C_{48}H_{64}N_4O_8$: 825.07).

5,17-Diamino-11,23-dinitro-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**29**) *(method A)*. Yield 95%, m.p. ≤ 200 °C (decomp.). ^{1}H NMR ($CDCl_3$): 7.50 s, 4 H (Ar-H); 6.03 s, 4 H (Ar-H); 4.38 d, 4 H, *J* = 13.6 (Ar-CH_2-Ar ax); 3.93 t, 4 H, *J* = 7.3 (OCH_2-); 3.78 t, 4 H, *J* = 7.6 (OCH_2-); 3.25 bs, 4 H (NH_2); 3.11 d, 4 H, *J* = 13.6 (Ar-CH_2-Ar eq); 1.83 q, 8 H, *J* = 7.2 (-CH_2-); 1.45–1.30 m, 16 H (-CH_2-); 0.93 t, 12 H, *J* = 6.7 (-CH_3). ^{13}C NMR ($CDCl_3$): 162.25, 149.25, 142.40, 141.45, 136.42, 134.56, 123.39, 115.98, 75.65, 75.35, 31.16, 29.92, 29.72, 28.32, 28.21, 22.78, 22.67, 14.14, 14.07. MS (FD), *m/z*: 824.7 (M^+ calculated $C_{48}H_{64}N_4O_8$: 825.07).

5,11,17-Triamino-23-nitro-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**30**) *(method A)*. Yield 90%, m.p. > 200 °C (decomp.). ^{1}H NMR ($CDCl_3$): 7.39 s, 2 H (Ar-H); 6.26 bd, 2 H (Ar-H); 6.22 bd, 2 H (Ar-H); 5.79 s, 2 H (Ar-H); 4.38 d, 2 H, *J* = 13.6 (Ar-CH_2-Ar ax); 4.24 d, 2 H, *J* = 13.3 (Ar-CH_2-Ar ax); 3.88–3.83 m, 4 H (OCH_2-); 3.78–3.72 m, 2 H (OCH_2-); 3.65 t, 2 H, *J* = 7.0 (OCH_2-); 3.36 bs, 6 H (NH_2); 3.07 d, 2 H, *J* = 13.6 (Ar-CH_2-Ar eq); 2.90 d, 2 H, *J* = 13.6 (Ar-CH_2-Ar eq); 1.83–1.80 m, 8 H (-CH_2-); 1.38–1.35 m, 16 H (-CH_2-); 0.94–0.89 m, 12 H (-CH_3). ^{13}C NMR ($CDCl_3$): 150.59, 143.14, 142.22, 140.47, 139.31, 137.00, 136.23, 135.06, 134.80, 123.39, 117.15, 116.02, 114.81, 75.43, 75.09, 75.05, 31.17, 31.05, 29.94, 29.65, 28.49, 28.25, 22.81, 22.74, 22.62, 14.17, 14.10, 14.03. MS (FD), *m/z*: 796.5 (M^+ calculated $C_{48}H_{66}N_4O_6$: 795.08).

5,17-Diamino-11,23-dinitro-26,28-dimethoxy-25,27-bis(pentyloxy)calix[4]arene (**32**) *(method A)*. Equilibrium mixture of *cone* and *partial cone* (≈1:1). Yield 93%, m.p. > 200 °C (decomp.). ^{1}H NMR ($CDCl_3$): 7.79 d, 2 H, *J* = 2.7 (Ar-H); 7.19 d, 2 H, *J* = 2.7 (Ar-H); 7.17 s, 4 H (Ar-H); 6.61 s, 2 H (Ar-H); 6.55 s, 4 H (Ar-H); 6.49 s, 2 H (Ar-H); 4.28 d, 4 H, *J* = 13.4 (Ar-CH_2-Ar ax); 4.00 d, 2 H, *J* = 13.7 (Ar-CH_2-Ar ax); 3.90–3.55 m, 29 H (OCH_3 + OCH_2- + Ar-CH_2-Ar ax + Ar-CH_2-Ar eq); 3.09 d, 4 H, *J* = 13.4 (Ar-CH_2-Ar eq); 3.03 d, 7 H, *J* = 14.0 (Ar-CH_2-Ar eq); 2.99 s, 3 H (OCH_3); 1.89–1.82 m, 8 H (-CH_2-); 1.53–1.48 m, 8 H (-CH_2-); 1.45–1.38 m, 8 H (-CH_2-); 0.96–0.91 m, 12 H (-CH_3). ^{13}C NMR ($CDCl_3$): 161.55, 161.15, 142.71, 142.20, 136.30, 136.14, 135.34, 135.21, 133.14, 132.71, 124.24, 123.08, 122.64, 117.78, 116.46, 75.59, 74.74, 61.10, 59.91, 59.49, 35.32, 30.86, 30.72, 30.21, 29.99, 28.27, 22.53, 22.47, 14.08, 14.03, 0.98. MS (FD), *m/z*: 712.7 (M^+ calculated $C_{40}H_{48}N_4O_8$: 712.85).

5,17-Diamino-11,23-dinitro-26,28-bis[(ethoxycarbonyl)methoxy]-25,27-bis(pentyloxy)calix-[4]arene (**31**) *(method B)*. Yield 90%, m.p. ≥ 200 °C (decomp.). ^{1}H NMR ($CDCl_3$): 7.24 s, 4 H (Ar-H); 6.32 s, 4 H (Ar-H); 4.67 d, 4 H, *J* = 13.7 (Ar-CH_2-Ar ax); 4.56 s, 4 H (OCH_2-CO);

4.16 q, 4 H, *J* = 7.2 (OC**H**$_2$CH$_3$); 3.86 t, 4 H, *J* = 7.1 (OCH$_2$-); 3.37 s, 4 H (NH$_2$); 3.12 d, 4 H, *J* = 13.9 (Ar-CH$_2$-Ar eq); 1.83 q, 4 H, *J* = 7.1 (-CH$_2$-); 1.43–1.34 m, 8 H (-CH$_2$-); 1.25 t, 6 H, *J* = 7.1 (CH$_2$C**H**$_3$); 0.91 t, 6 H, *J* = 7 (-CH$_3$). ^{13}C NMR (CDCl$_3$): 169.86, 161.31, 148.83, 142.62, 142.12, 135.46, 135.34, 123.01, 116.22, 75.83, 70.83, 60.38, 31.30, 29.66, 28.19, 22.56, 14.15, 13.98. MS (FD), *m/z*: 858.0 (M^+ calculated $C_{46}H_{56}N_4O_{12}$: 856.98).

5,17-Diamino-11,23-dinitro-26,28-bis[(3-ethoxycarbonyl)propoxy]-25,27-bis(pentyloxy)calix[4]-arene (**37**) *(method B).* Yield 90%, m.p. > 200 °C (decomp.). ^{1}H NMR (CDCl$_3$): 7.55 s, 4 H (Ar-H); 5.96 s, 4 H (Ar-H); 4.35 d, 4 H, *J* = 14.5 (Ar-CH$_2$-Ar ax); 4.13 q, 4 H, *J* = 7.1 (OC**H**$_2$CH$_3$); 3.95 t, 4 H, *J* = 7.6 (OCH$_2$-); 3.79 t, 4 H, *J* = 7.0 (OCH$_2$-); 3.25 bs, 4 H (NH$_2$); 3.13 d, 4 H, *J* = 13.8 (Ar-CH$_2$-Ar eq); 2.42 t, 4 H, *J* = 7.6 (CO-CH$_2$-); 2.13 q, 4 H, *J* = 7.3 (-CH$_2$-); 1.84 q, 4 H, *J* = 7.3 (-CH$_2$-); 1.37–1.31 m, 8 H (-CH$_2$-); 1.24 t, 6 H, *J* = 7.0 (CH$_2$C**H**$_3$); 0.90 t, 6 H, *J* = 6.8 (-CH$_3$). ^{13}C NMR (CDCl$_3$): 172.85, 162.24, 148.68, 142.35, 141.74, 136.43, 134.16, 123.51, 115.91, 75.66, 74.11, 60.34, 31.08, 30.88, 29.81, 27.99, 25.21, 22.57, 14.20, 14.06. MS (FD), *m/z*: 913.4 (M^+ calculated $C_{50}H_{64}N_4O_{12}$: 913.09).

General Procedure for the Reaction of Aminonitro Derivatives with *p*-Toluoyl Chloride

A solution of the aminonitrocalix[4]arene, *p*-toluoyl chloride and triethylamine (NH_2 group: chloride:triethylamine 1:1.1:1) in THF (20–25 ml per 1 mmol) was stirred at reflux over 2 h. The reaction mixture was cooled to room temperature, filtered and evaporated to dryness. The residue was treated with methanol, the white precipitate formed was filtered off, washed with methanol (2 × 5 ml) and dried.

5,17-Bis(4-methylbenzamido)-11,23-dinitro-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**38**). Yield 79%, m.p. 177–190 °C (phase transition), 318–320 °C (melting). ^{1}H NMR (CDCl$_3$): 7.65 s, 2 H (NH); 7.61 d, 4 H, *J* = 8.0 (Ar-H); 7.50 s, 4 H (Ar-H); 7.08 d, 4 H, *J* = 8.0 (Ar-H); 6.96 s, 4 H (Ar-H); 4.45 d, 4 H, *J* = 13.7 (Ar-CH$_2$-Ar ax); 3.96 t, 4 H, *J* = 7.3 (OCH$_2$-); 3.86 t, 4 H, *J* = 7.8 (OCH$_2$-); 3.23 d, 4 H, *J* = 13.7 (Ar-CH$_2$-Ar eq); 2.34 s, 6 H (-CH$_3$); 1.90–1.80 m, 8 H (-CH$_2$-); 1.50–1.30 m, 16 H (-CH$_2$-); 0.93 t, 12 H, *J* = 6.8 (-CH$_3$). ^{13}C NMR (CDCl$_3$): 165.56, 162.06, 153.27, 142.61, 141.90, 136.13, 134.49, 132.56, 131.69, 129.18, 127.03, 123.57, 121.75, 75.83, 75.54, 31.21, 29.89, 29.75, 28.22, 22.75, 22.67, 21.42, 14.12, 14.07. MS (FD), *m/z*: 1029.4 (M^+ calculated $C_{64}H_{76}N_4O_8$: 1029.2).

5,11,17-Tris(4-methylbenzamido)-23-nitro-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**39**). Yield 65%, m.p. 240–250 °C (decomp.). ^{1}H NMR (CDCl$_3$): 7.97 s, 2 H (NH); 7.77 d, 2 H, *J* = 9.0 (Ar-H); 7.75 d, 4 H, *J* = 8.3 (Ar-H); 7.4 s, 1 H (NH); 7.39 d, 2 H, *J* = 2.2 (Ar-H); 7.19 d, 2 H, *J* = 7.7 (Ar-H); 7.18 d, 4 H, *J* = 8.1 (Ar-H); 7.14 s, 2 H (Ar-H); 7.11 d, 2 H, *J* = 2.4 (Ar-H); 6.49 s, 2 H (Ar-H); 4.46 d, 2 H, *J* = 13.8 (Ar-CH$_2$-Ar ax); 4.38 d, 2 H, *J* = 13.4 (Ar-CH$_2$-Ar ax); 4.03–3.97 m, 2 H (OCH$_2$-); 3.92–3.84 m, 4 H (OCH$_2$-); 3.70 t, 2 H, *J* = 6.9 (OCH$_2$-); 3.20 d, 2 H, *J* = 14.0 (Ar-CH$_2$-Ar eq); 3.11 d, 2 H, *J* = 13.4 (Ar-CH$_2$-Ar eq); 2.37 s, 6 H (-CH$_3$); 2.34 s, 3 H (-CH$_3$); 1.88–1.82 m, 8 H (-CH$_2$-); 1.53–1.45 m, 4 H (-CH$_2$-); 1.44–1.33 m, 8 H (-CH$_2$-); 1.29–1.21 m, 4 H (-CH$_2$-); 0.97–0.91 m, 12 H (-CH$_3$). ^{13}C NMR (CDCl$_3$): 165.85, 165.53, 161.54, 154.05, 153.11, 142.32, 142.01, 141.74, 136.77, 135.85, 135.82, 133.88, 132.28, 132.08, 131.96, 131.60, 129.30, 129.10, 127.22, 127.07, 123.16, 121.63, 121.48, 121.32, 75.60, 75.38, 75.22, 31.32, 31.08, 30.06, 29.97, 29.60, 28.58, 28.42, 28.05, 22.83, 22.71, 22.60, 21.46, 14.21, 14.07, 14.04, 1.00. MS (FD), *m/z*: 1149.1 (M calculated $C_{72}H_{84}N_4O_9$: 1149.49).

General Procedure for the Reduction of Nitroamide Derivatives and the Following Second Acylation

The amidonitro derivative (**38** or **39**) was dissolved in toluene (5–10 ml per 1 mmol) and hydrogenated under normal pressure in the presence of Raney nickel at room temperature (see also[31]). After the hydrogen uptake was complete, the catalyst was filtered off, washed with warm toluene and the toluene solution evaporated in vacuo. The crude product was used directly in the next reaction.

A suspension of the crude product in a 1:1 mixture of acetic anhydride and pyridine (15 ml per 0.1 mmol) was stirred at room temperature over 12 h. Then the reaction mixture was poured onto ice and stirred until the whole amount of acetic anhydride was hydrolyzed. Then the pH of the resulting mixture was adjusted to 2–3 using a 2 M solution of HCl and extracted with chloroform (3×). The combined organic solution was washed with water (2×), dried over $MgSO_4$ and evaporated to dryness. The resulting white precipitate was treated with a mixture of ether/dichloromethane (3:1), then hexane was added. The resulting solution was evaporated to half of the initial volume. The white precipitate was filtered off, washed with hexane (3×) and dried.

5,17-Diacetamido-11,23-bis(4-methylbenzamido)-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**40**). Yield 81%, m.p. 188–200 °C (phase transition), 200 °C (melting). ^{1}H NMR (DMSO-d_6): 9.84 s, 2 H (NH); 9.34 s, 2 H (NH); 7.79 d, 4 H, *J* = 8.2 (Ar-H); 7.28 s, 4 H (Ar-H); 7.23 d, 4 H, *J* = 8.2 (Ar-H); 6.76 s, 4 H (Ar-H); 4.36 d, 4 H, *J* = 12.9 (Ar-CH_2-Ar ax); 3.91 t, 4 H, *J* = 7.8 (OCH_2-); 3.77 t, 4 H, *J* = 6.8 (OCH_2-); 3.11 d, 4 H, *J* = 12.9 (Ar-CH_2-Ar eq); 2.36 s, 6 H (-CH_3); 1.92–1.87 m, 8 H (-CH_2-); 1.85 s, 6 H (-CH_3); 1.41–1.36 m, 16 H (-CH_2-); 0.93 t, 6 H, *J* = 7.1 (-CH_3); 0.92 t, 6 H, *J* = 7.1 (-CH_3). ^{13}C NMR (DMSO-d_6): 167.37, 164.63, 152.45, 151.59, 141.07, 134.54, 133.45, 133.16, 132.82, 132.06, 128.66, 127.45, 120.62, 119.68, 74.91, 74.59, 30.76, 29.40, 29.11, 27.95, 27.75, 23.52, 22.26, 22.21, 20.87, 13.92, 13.82. MS (FD), *m/z*: 1085.6 (M^+ calculated $C_{68}H_{84}N_4O_8$: 1085.35).

5-Acetamido-11,17,23-tris(4-methylbenzamido)-25,26,27,28-tetrakis(pentyloxy)calix[4]arene (**41**). Yield 78%, m.p. 200–206 °C (phase transition), 262–264 °C (melting). ^{1}H NMR (DMSO): 9.79 s, 2 H (NH); 9.74 s, 1 H (NH); 9.38 s, 1 H (NH); 7.79 d, 2 H, *J* = 8.5 (Ar-H); 7.76 d, 4 H, *J* = 8.2 (Ar-H); 7.25–7.22 m, 6 H (Ar-H + Ar-H); 7.19 d, 4 H, *J* = 8.2 (Ar-H); 7.14 s, 2 H (Ar-H); 6.87 s, 2 H (Ar-H); 4.41 d, 2 H, *J* = 12.6 (Ar-CH_2-Ar ax); 4.38 d, 2 H, *J* = 12.6 (Ar-CH_2-Ar ax); 3.91–3.81 m, 8 H (OCH_2-); 3.16 d, 2 H, *J* = 13.5 (Ar-CH_2-Ar eq); 3.13 d, 2 H, *J* = 13.5 (Ar-CH_2-Ar eq); 2.34 s, 6 H (-CH_3); 2.33 s, 3 H (-CH_3); 1.96–1.89 m, 8 H (-CH_2-); 1.78 s, 3 H (-CH_3); 1.42–1.38 m, 16 H (-CH_2-); 0.94 t, 12 H, *J* = 6.7 (-CH_3). ^{13}C NMR ($CDCl_3$): 167.36, 164.62, 152.33, 152.17, 151.75, 141.00, 134.20, 134.15, 133.82, 133.77, 133.09, 132.97, 132.02, 128.61, 128.57, 127.52, 127.46, 120.79, 119.73, 74.86, 74.73, 30.86, 30.79, 29.31, 29.20, 27.88, 27.81, 23.45, 22.24, 20.85, 13.91, 13.86. MS (FD), *m/z*: 1161.6 (M^+ calculated $C_{74}H_{88}N_4O_8$: 1161.55).

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