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Synthesis of Derivatives of *p-tert*-Butylcalix[4]arene Containing on Lower Rim Fragments of 2-Aminoalkylbenzimidazoles

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Abstract—Reactions of calix[4]arene carboxymethoxy derivatives with 2-aminoalkylbenzimidazoles in the presence of dicyclohexylcarbodiimide and hydroxybenzotriazole afforded a series of *p-tert*-butylcalix[4]arene derivatives containing on the lower rim *N*-(2-benzimidazolylalkyl)carbamoylmethoxy fragments. The reaction carried out in the absence of hydroxybenzOtriazole resulted in macrocycles containing one *N*-(2-benzimidazolylalkyl)carbamoyl fragment and a fragment of *N*-(acyl)dicyclohexylisourea.

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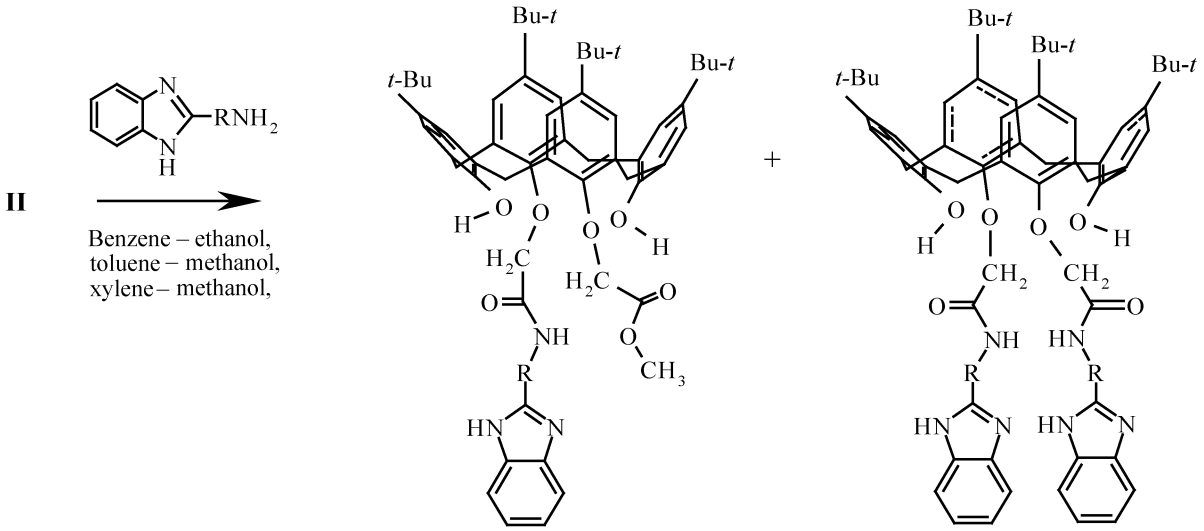
Derivatives of calixarenes containing on the lower or upper rim of the macrocycle amide and heteroaromatic fragments are capable of binding cations of certain metals, of bringing these complexes through hydrophobic membranes, and some among such compounds exhibit a biological activity with respect to pathogenic bacteria and simulate enzymes action [1–8]. Among new efficient receptors underlain by calixarenes exhibiting such properties derivatives are promising containing imidazole and benzimidazole fragments [9–11].

Aiming at preparation of benzimidazolyl derivatives of *p-tert*-butylcalix[4]arene (**I**) we considered the possibility to use two methods of reaction between bis[(methoxycarbonyl)methoxy]- **II** and bis[(chlorocarbonyl)methoxy]- **III** derivatives of calixarene **I** with 2-aminoalkyl-substituted benzimidazoles. This way would introduce into the molecule of the macrocycle an additional binding site, a carbamoyl group [12–14].

The preparation of the calixarene derivatives containing benzimidazole fragments by the first procedure occurred by boiling bis[(methoxycarbonyl) methoxy]-*p-tert*-butylcalix[4]arene (**II**) with 2-aminoalkyl-substituted benzimidazoles in mixed solvents methanol–toluene, ethanol–benzene, xylene–methanol at the ratio calixarene–benzimidazole 1 : 4 [12]. In all events mono- and di(benzimidazolylcarbamoyl) derivatives were isolated in the ratio 2:1 (the conversion of initial calixarene 65–70%); therewith the increase in the number of the carbon atoms in the position *2* of 2-aminoalkylbenzimidazoles resulted in the hgher yield of compounds containing a single benzimidazole group (Scheme 1).

The second procedure consisted in the reaction of acid chloride **III** with 2-aminoalkyl-substituted benzimidazoles [13, 14]. In this case independent of the reagents ratio and the reaction time the acylation proceeded also ambiguously. Compounds formed in the reaction of calixarene carbonyl chloride **III** with 2-(aminoalkyl)benzimidazoles containing one carboxy group and one amide fragment in the course of purification by crystallization from lower alcohols readily transformed into the corresponding derivatives possessing an ester group. The prolonged boiling of calixarene **II** with unsubstituted benzimidazole (6 equiv per each ester group) in xylene did not provide the target products, whereas the reaction of acid chloride **III** with benzimidazole gave calixarene **XII** containing one benzimidazole fragment, although in a low yield. This compound is unstable in acid medium, the formed

Scheme 1.



R = CH_2 (**IV**, **VIII**), $(CH_2)_2$ (**V**, **IX**), CH (**VI**, **X**), $(CH_2)_4$ (**VII**, **XII**).

amide group decomposed even at washing its solution in chloroform with 10% HCl solution.

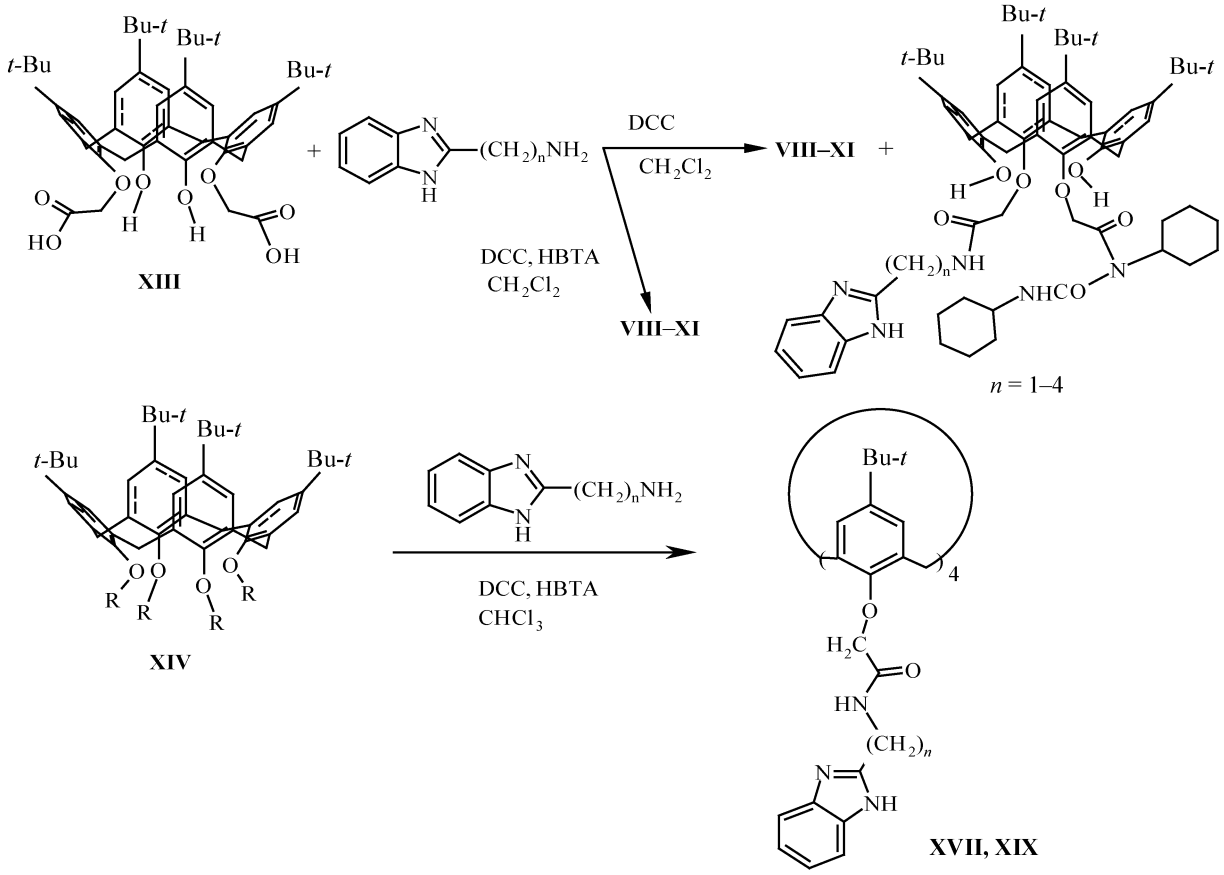
In order to increase the yield of the symmetrically substituted calixarene benzimidazolyl derivatives we considered the possibility to use the carbodiimide method by an example of reaction between dicarboxymethoxy-*p*-*tert*-butylcalix[4]arene (**XIII**) with 2-aminoalkylbenzimidazoles [15]. But in this case alongside the disubstituted compounds with two benzimidazole fragments we also obtained macrocycles where along with the *N*-(2-benzimidazolylalkyl)carbamoyl substituent an *N*-cyclohexyl-*N*-(*N*'-cyclohexyl-carbamoyl)carbonylmethoxy fragment was present.

These data suggest that the reaction involving the carboxy groups in the calixarene molecule is a step-wise process where first one carboxy group is activated, then the second. In no experiments the obtained calixarene contained two N-acylurea residues. The reaction of calixarene **XIV** containing four carboxy groups with aminoalkylbenzimidazoles furnished a mixture of compounds conteining two or three benzimidazole fragments and consequently two or one N-acylurea residue, whereas acylation of 2-aminoalkylbenzimidazoles with mono(carboxymethoxy)-*p*-*tert*-butylcalix[4]arene (**XV**) alongside the target product a calixarene was obtained in minor quantity with an *N*-cyclohexyl-*N*-(*N*'-cyclohexyl-carbamoyl)carbonylmethoxy substituent.

The reaction between calixarene **XIII** and 2-aminoalkylbenzimidazoles in the presence of dicyclohexylcarbodiimide (DCC) and hydroxybenzotriazole (HBTA) proved to be more effective approach to the preparation of *p*-*tert*-butylcalix[4]arenas substituted with two benzimidazole fragments. By the same procedure we obtained from mono- **XV** and tetra- **XIV** carboxy-substituted calixarenes mono- (**XVI**) and tetra-*cis*-[(benzimidazol-2-ylmethyl)carbamoyloxy]- (**XVII**), mono- (**XVIII**) and tetracis[(benzimidazol-2-ylethyl)carbamoyloxy]- (**XIX**) calixarenes (Scheme 2). The yields of the target compounds were 75% for tetraderivatives **XVII, XIX** and 80–85% for mono- and disubstituted calixarenes.

The structure of compounds obtained was proved by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of the obtained disubstituted calix[4]-arene derivatives contained 2 singlets from the protons of the *tert*-butyl groups with the integral intensity 18H each, two doublets from the protons of the methylene bridges of intensity 4H each, *J* 12.7–13.7 Hz, and two singlets from the protons of the aromatic part of the macrocycle with the intensity 4H each. In the spectra of the monosubstituted calixarenes the protons of the *tert*-butyl groups appeared as three singlets (1:2:1), the protons of the methylene bridges, as four doublets of intensity 2H each (*J* 11.4–13.3 Hz), aromatic protons of the macrocycle, as two doublets and two singlets. The tetraderivatives **XVII, XIX** have in

Scheme 2.



R = CH_2COOH (**XIV**); *n* = 1 (**XVII**), 2 (**XIX**).

the ^1H NMR spectra a singlet (36H) from the protons of the *tert*-butyl groups, 2 doublets from the methylene protons, and a singlet from the aromatic protons of the calixarene skeleton. This spectral pattern indicates that the obtained compounds exist in the *cone* conformation and makes it possible to conclude that no conformational isomerization of the macrocycle occurs during the modification of the functional group on the lower rim of the *p-tert*-butylcalix-[4]arene.

Therefore the comparison of approaches to the introduction into the molecule of *p-tert*-butylcalix[4]arene of amidoalkylbenzimidazole fragments demonstrated that the most efficient procedure for the preparation of the benzimidazolyl-substituted macrocycles from the corresponding carboxy derivatives was the carbodiimide method of acylation in the presence of hydroxybenzotriazole.

EXPERIMENTAL

The structure and prevailing conformations of compounds obtained were established by ^1H NMR method on a spectrometer Varian VXR-300 (300 MHz) from ~10% solutions in $CDCl_3$, internal reference TMS. Mass spectra were obtained by FAB method on a mass spectrometer VG 70-70EQ using a X**e** atoms beam of the energy 8 kV, electron impact (70 eV) mass spectra were registered on an instrument MKh-1321.

Bis[(methoxycarbonyl)methoxy]-*p-tert*-butyl-calix[4] arene (**II**), bis[(chlorocarbonyl)methoxy]-*p-tert*-butylcalix[4]arene (**III**), di(carboxymethoxy)-*p-tert*-butylcalix[4]arene (**XIII**), tetra(carboxymethoxy)-*p-tert*-butylcalix[4]arene (**XIV**), and mono(carboxymethoxy)-*p-tert*-butylcalix[4]arene (**XV**) were obtained by procedures [12–14, 16, 17].

Reaction of bis[(methoxycarbonyl)methoxy]-*p-tert*-butylcalix[4]arene (II) with 2-aminoalkylbenzimidazoles. A dispersion of 0.79 g (1 mmol) of calix[4]arene **II**, 12 mmol of an appropriate 2-aminoalkylbenzimidazole in 55 ml of a mixture methanol–xylene, 1:10, was boiled at stirring over 48–52 h. The solvent was removed

at a reduced pressure, the dry residue was treated with hot hexane or heptane (4 × 15 ml). The solution obtained was concentrated to 15 ml and cooled. Unreacted calixarene **II** was filtered off. The solution was evaporated at the reduced pressure, the disubstituted compounds **VIII–XI** were separated from monobenzimidazolyl-substituted calixarenes by the fractional crystallization from the mixture methanol–water, 5 : 1.

Reaction of bis[(chlorocarbonyl)methoxy]-*p-tert*-butylcalix[4]arene (III) with 2-aminoalkylbenzimidazoles. To a dispersion of 2.3 mmol of 2-aminoalkylbenzimidazole dihydrohloride, 0.95 ml (6.9 mmol) of triethylamine in 30 ml of anhydrous chloroform was added dropwise at stirring a solution of 0.8 g (1 mmol) of calixarene **III** in 20 ml of anhydrous chloroform. The reaction mixture was boiled at stirring for 18 h. On completion of the reaction the triethylamine hydrochloride was filtered off, the solvent was evaporated at a reduced pressure, the dry residue was dissolved in 50 ml of chloroform and the solution was several times washed with water. The organic layer was evaporated at a reduced pressure. The purification and separation of the reaction products was carried out as described above.

Reaction of di(carboxymethoxy)-*p-tert*-butylcalix[4]arene (XIII) with 2-aminoalkylbenzimidazoles. To a dispersion of 2.3 mmol of 2-aminoalkylbenzimidazole dihydrochloride, 0.61 ml (4.4 mmol) of triethylamine in 10 ml of chloroform was added at stirring 0.76 g (1 mmol) of calixarene **XIII** in 10 ml of chloroform, 10 min after the addition of calixarene into the reaction mixture was added 0.47 g (2.3 mmol) of *N,N*-dicyclohexylcarbodiimide. The reaction progress was monitored by TLC and mass spectrometry. After 10–15 h the reaction mixture was filtered, the filtrate was evaporated, the dry residue was dissolved in 50 ml of chloroform and the solution was washed with water (2 × 20 ml). The organic layer was evaporated at a reduced pressure. The reaction products containing the acylurea fragment were separated from the disubstituted compounds by fractional crystallization from hexane or heptane.

Reaction of di(carboxymethoxy)-*p-tert*-butylcalix[4]arene (XIII) with 2-aminoalkylbenzimidazoles in the presence of hydroxybenzotriazole. To a dispersion of 0.76 g (1 mmol) of calixarene **XIII**, 0.3 g (2.25 mmol) hydroxybenzotriazole in 30 ml of chloroform cooled to 0°C was added at stirring 0.46 g (2.25 mmol) of dicyclohexylcarbodiimide. The reaction mixture was stirred at room temperature for another 30 min, and a dispersion was added of 2.3 mmol of an appropriate 2-aminoalkylbenzimidazole dihydrochloride and 0.61 ml (4.4 mmol) of triethylamine in 10 ml of chloroform. After 20 h the reaction mixture was filtered, the filtrate was evaporated, the dry residue was dissolved in 50 ml of chloroform and the solution was washed with water (2 × 20 ml). The organic layer was evaporated at a reduced pressure. The crude feaction products were purified by crystallization (from methanol–water, 5:1).

5,11,17,23-Tetra-*tert*-butyl-25-[(methoxycarbonyl)methoxy]-27-[(benzimidazol-2-yl-methyl)carbamoylmethoxy]-26,28-dihydroxycalix[4]arene (IV). ^{1}H NMR spectrum, δ, ppm: 0.97 s [9H, $(CH_3)_3C$], 0.98 s [9H, $(CH_3)_3C$], 1.26 s [9H, $(CH_3)_3C$], 1.30 s [9H, $(CH_3)_3C$], 3.32 d (2H, $ArCH_2Ar$, *J* 13.38 Hz), 3.55 s (2H, $CH_2CO\underline{CH_3}$), 4.07 d (2H, $ArCH_2Ar$, *J* 13.69 Hz), 4.38 s (2H, $\underline{CH_2}COCH_3$), 4.45 d (2H, $ArCH_2Ar$, *J* 13.07 Hz), 4.53 d (2H, $ArCH_2Ar$, *J* 12.76 Hz), 4.62 s (2H, $\underline{CH_2}CONH$), 4.71 s (2H, $\underline{CH_2}NH$), 6.80 d (2H, ArH), 6.83 s (2H, ArH), 6.98 d (2H, ArH), 7.02 s (2H, ArH), 7.12 m (2H, ArH_{benzim}), 7.35 m (2H, ArH_{benzim}), 7.53 br.s (3H, OH, NH), 8.91 br.s (1H, NH). Mass spectrum: *m*/*z* 908 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(benz-imidazol-2-ylmethyl)carbamoylmethoxy]-26,28-dihydroxycalix[4]arene (VIII). ^{1}H NMR spectrum, δ, ppm: 0.97 s [18H, $(CH_3)_3C$], 1.28 s [18H, $(CH_3)_3C$], 3.27 d (4H, $ArCH_2Ar$, *J* 13.38 Hz), 3.95 d (4H, $ArCH_2Ar$, *J* 13.38 Hz), 4.39 d (4H, $\underline{CH_2}CO$), 4.85 s (4H, $\underline{CH_2}NH$), 6.81 s (4H, ArH), 7.03 s (4H, ArH), 7.19 m (4H, ArH_{benzim}), 7.48 m (4H, ArH_{benzim}), 7.55 br.s (4H, OH, NH), 9.02 br.s (2H, NH). Mass spectrum: *m*/*z* 1023 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25-[(methoxycarbonyl)methoxy]-27-[(benzimidazol-2-ylethyl)-carbamoylmethoxy]-26,28-dihydroxycalix[4]arene (V). ^{1}H NMR spectrum, δ, ppm: 0.94 s [9H, $(CH_3)_3C$], 0.96 s [9H, $(CH_3)_3C$], 1.24 s [9H, $(CH_3)_3C$], 1.28 s [9H, $(CH_3)_3C$], 3.28 d (2H, $ArCH_2Ar$, *J* 13.35 Hz), 3.44 t (2H, $CH_2\underline{CH_2}NH$), 3.7 s (2H, $CH_2CO\underline{CH_3}$), 4.1 d (2H, $ArCH_2Ar$, *J* 13.69 Hz), 4.3 s (2H, $\underline{CH_2}COCH_3$), 4.38 m (4H, $ArCH_2Ar$, $\underline{CH_2}CH_2NH$), 4.47 d (2H, $ArCH_2Ar$, *J* 12.67 Hz), 4.52 s (2H, $\underline{CH_2}CONH$), 6.82 d (2H, ArH), 6.86 s (2H, ArH), 6.94 d (2H, ArH), 7.05 s (2H, ArH), 7.12 m (2H, ArH_{benzim}), 7.39 m (2H, ArH_{benzim}), 7.55 br.s (3H, OH, NH), 8.97 br.s (1H, NH). Mass spectrum: *m*/*z* 922 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(benz-imidazol-2-ylethyl)carbamoylmethyloxy]-26,28-dihydroxy-

calix[4]arene (IX). ^{1}H NMR spectrum, δ, ppm: 1.01 s [18H, $(CH_3)_3C$], 1.26 s [18H, $(CH_3)_3C$], 3.28 d (4H, $ArCH_2Ar$, *J* 13.69 Hz), 3.35 t (4H, $CH_2\underline{CH_2}NH$), 3.99 d (4H, $ArCH_2Ar$, *J* 13.07 Hz), 4.46 t (4H, $\underline{CH_2}CH_2NH$), 4.53 s (4H, $\underline{CH_2}CO$), 6.89 s (4H, ArH), 7.00 s (4H, ArH), 7.15 m (4H, ArH_{benzim}), 7.46 m (4H, ArH_{benzim}), 7.64 br.s (4H, OH, NH), 9.0 br.s (2H, NH). Mass spectrum: *m*/*z* 051 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25-[(methoxycarbonyl)methoxy]-27-[(benzimidazol-2-ylpropyl)carbamoylmethoxy]-26,28-dihydroxycalix[4]arene (VI). ^{1}H NMR spectrum, δ, ppm: 0.97 s [9H, $(CH_3)_3C$], 1.01 s [9H, $(CH_3)_3C$], 1.18 s [9H, $(CH_3)_3C$], 1.22 s [9H, $(CH_3)_3C$], 1.85 m (2H, $NHCH_2\underline{CH_2}CH_2$), 2.78 m (2H, $NH\underline{CH_2}CH_2CH_2$), 3.22 m (2H, $NHCH_2CH_2\underline{CH_2}$), 3.35 d (2H, $ArCH_2Ar$, *J* 13.69 Hz), 3.53 s (2H, $CH_2CO\underline{CH_3}$), 3.98 d (2H, $ArCH_2Ar$, *J* 13.48 Hz), 4.25 d (2H, $ArCH_2Ar$, *J* 12.76 Hz), 4.32 s (2H, $\underline{CH_2}COCH_3$), 4.40 d (2H, $ArCH_2Ar$, *J* 12.69 Hz), 4.46 s (2H, $\underline{CH_2}CONH$), 6.86 d (2H, ArH), 6.9 s (2H, ArH), 7.03 d (2H, ArH), 7.1 m (4H, ArH, ArH_{benzim}), 7.34 m (2H, ArH_{benzim}), 7.59 br.s (3H, OH, NH), 8.74 s (1H, NH). Mass spectrum: *m*/*z* 936 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(benz-imidazol-2-ylpropyl)carbamoylmethoxy]-26,28-dihydroxycalix[4]arene (X). ^{1}H NMR spectrum, δ, ppm: 1.14 s [18H, $(CH_3)_3C$], 1.27 s [18H, $(CH_3)_3C$], 1.87 m (4H, $NHCH_2\underline{CH_2}CH_2$), 2.84 m (4H, $NH\underline{CH_2}CH_2CH_2$), 3.65 m (4H, $NHCH_2CH_2\underline{CH_2}$), 3.52 d (4H, $ArCH_2Ar$, *J* 13.6 Hz), 4.2 d (4H, $ArCH_2Ar$, *J* 13.38 Hz), 4.48 s (4H, $\underline{CH_2}CO$), 6.92 s (4H, ArH), 7.06–7.17 m (8H, ArH, ArH_{benzim}), 7.1 s (ArH), 7.35 m (4H, ArH_{benzim}), 7.69 br.s (4H, OH, NH), 8.72 br.s (2H, NH). Mass spectrum: *m*/*z* 1079 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25-[(methoxycarbonyl)methoxy]-27-[(benzimidazol-2-ylbutyl)-carbamoylmethoxy]-26,28-dihydroxycalix[4]arene (VII). ^{1}H NMR spectrum, δ, ppm: 0.95 s [9H, $(CH_3)_3C$], 1.05 s [9H, $(CH_3)_3C$], 1.17 s [9H, $(CH_3)_3C$], 1.23 s [9H, $(CH_3)_3C$], 1.57–1.78 m (4H, $NHCH_2\underline{CH_2}CH_2CH_2$), 2.85 m (2H, $NH\underline{CH_2}CH_2CH_2CH_2$), 3.25 m (2H, $NHCH_2CH_2CH_2\underline{CH_2}$), 3.32 d (2H, $ArCH_2Ar$, *J* 13.38 Hz), 3.6 s (2H, $CH_2CO\underline{CH_3}$), 3.76 d (2H, $ArCH_2Ar$, *J* 13.38 Hz), 4.23 d (2H, $ArCH_2Ar$, *J* 12.76 Hz), 4.36 s (2H, $\underline{CH_2}COCH_3$), 4.41 d (2H, $ArCH_2Ar$, *J* 12.78 Hz), 4.32 s (2H, $\underline{CH_2}CONH$), 6.90 d (2H, ArH), 6.95 s (2H, ArH), 7.01 d (2H, ArH), 7.05 s (2H, ArH), 7.1 m (2H, ArH_{benzim}), 7.35 m (2H, ArH_{benzim}), 7.6 br.s (3H, OH, NH), 8.64 s (1H, NH). Mass spectrum: *m*/*z* 950 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(benz-imidazol-2-ylbutyl)carbamoylmethoxy]-26,28-dihydroxycalix[4]arene (XI). ^{1}H NMR spectrum, δ, ppm: 1.12 s [18H, $(CH_3)_3C$], 1.24 s [18H, $(CH_3)_3C$], 1.60–1.80 m (8H, $NHCH_2\underline{CH_2}CH_2CH_2$), 2.9 m (4H, $NH\underline{CH_2}CH_2CH_2CH_2$), 3.24 m (4H, $NHCH_2CH_2CH_2\underline{CH_2}$), 3.45 d (4H, $ArCH_2Ar$, *J* 13.76 Hz), 4.28 d (4H, $ArCH_2Ar$, *J* 13.38 Hz), 4.45 s (4H, $\underline{CH_2}CO$), 6.89 s (4H, ArH), 7.03 s (4H, ArH), 7.12 m (4H, ArH_{benzim}), 7.34 m (4H, ArH_{benzim}), 7.65 br.s (4H, OH, NH), 9.1 br.s (2H, NH). Mass spectrum: *m*/*z* 1107 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25-[(benzimidazol-2-ylmethyl)carbamoylmethoxy]-26,27,28-trihydroxycalix[4]arene (XVI). ^{1}H NMR spectrum, δ, ppm: 1.15 s [9H, $(CH_3)_3C$], 1.18 s [18H, $(CH_3)_3C$], 1.19 s [9H, $(CH_3)_3C$], 4.06 d (2H, $ArCH_2Ar$, *J* 12.76 Hz), 4.18 d (2H, $ArCH_2Ar$, *J* 13.56 Hz), 4.25 d (2H, $ArCH_2Ar$, *J* 12.76 Hz), 4.34 d (2H, $ArCH_2Ar$, *J* 11.5 Hz), 4.42 s (2H, $\underline{CH_2}CO$), 4.68 s (8H, $\underline{CH_2}NH$), 7.02 d (2H, ArH), 7.06 s (2H, ArH), 7.1 d (2H, ArH), 7.12 s (2H, ArH), 7.25 m (2H, ArH_{benzim}), 7.42 m (1H, ArH_{benzim}), 7.70 m (1H, ArH_{benzim}), 8.49 br.s (1H, NH), 8.58 s (1H, OH), 8.59 s (2H, OH), 8.62 s (1H, NH). Mass spectrum: *m*/*z* 836 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25-[(benzimidazol-2-ylethyl)carbamoylmethoxy]-26,27,28-trihydroxycalix[4]arene (XVIII). ^{1}H NMR spectrum, δ, ppm: 1.13 s [9H, $(CH_3)_3C$], 1.15 s [18H, $(CH_3)_3C$], 1.17 s [9H, $(CH_3)_3C$], 3.88 t (2H, $CH_2\underline{CH_2}NH$), 4.00 d (2H, $ArCH_2Ar$, *J* 13.21 Hz), 4.12 d (2H, $ArCH_2Ar$, *J* 13.45 Hz), 4.22 d (2H, $ArCH_2Ar$, *J* 12.76 Hz), 4.31 d (2H, $ArCH_2Ar$, *J* 11.49 Hz), 4.37 t (2H, $\underline{CH_2}CH_2NH$), 4.62 s (2H, $\underline{CH_2}CO$), 7.01 d (2H, ArH), 7.04 s (2H, ArH), 7.09 d (2H, ArH), 7.12 s (2H, ArH), 7.25 m (1H, ArH_{benzim}), 7.41 m (1H, ArH_{benzim}), 7.70 m (1H, ArH_{benzim}), 8.33 br.s (1H, NH), 8.51 s (1H, OH), 8.59 s (2H, OH), 8.61 s (1H, NH). Mass spectrum: *m*/*z* 850 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-*cis*-[(benzimidazol-2-ylmethyl)carbamo-ylmethoxy]calix[4]arene (XVII). ^{1}H NMR spectrum, δ, ppm: 1.04 s [36H, $(CH_3)_3C$)], 3.04 d (4H, $ArCH_2Ar$, *J* 11.74 Hz), 4.28 d (4H, $ArCH_2Ar$, *J* 11.74 Hz), 4.36 s (8H, $\underline{CH_2}CO$), 4.67 m (8H, $\underline{CH_2}NH$), 5.18 s (4H, NHCO), 6.71 s (8H, ArH), 7.18 m (8H, ArH_{benzim}), 7.49 m (8H, ArH_{benzim}), 8.90 br.s (4H, NH). Mass spectrum: *m*/*z* 1397 $[M + 1]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-*cis*-[(benzimidazol-2-ylethyl)carbamoylmethoxy]calix[4]arene (XIX). ^{1}H NMR spectrum, δ, ppm: 1.02 s [36H, $(CH_3)_3C$], 3.01 t (8H, $CH_2\underline{CH_2}NH$),

3.04 d (4H, $ArCH_2Ar$, *J* 11.98 Hz), 3.66 t (8H, $\underline{CH_2}CH_2NH$), 4.25 d (4H, $ArCH_2Ar$, *J* 11.98 Hz), 4.44 s (8H, $\underline{CH_2}CO$), 5.20 s (4H, NHCO), 6.74 s (8H, ArH), 7.10 m (8H, ArH_{benzim}), 7.40 m (8H, ArH_{benzim}), 8.66 br.s (4H, NH). Mass spectrum: *m*/*z* 1453 $[M + 1]^+$.

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