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Synthesis of new calix[4]pyrrole derivatives via 1,3-dipolar cycloadditions

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ABSTRACT

Octamethylcalix[4]pyrrole-2-carbaldehyde **1** and 3-(octamethylcalix[4]pyrrol-2-yl)propenal **5** were used as precursors of azomethine ylides, which were trapped in situ with a range of dipolarophiles, such as 1,4-benzoquinone, 1,4-naphthoquinone, and fumaronitrile. Aldehyde **1** showed very low reactivity but the azomethine ylide generated from the reaction of aldehyde **5** with *N*-methylglycine could be trapped with those dipolarophiles to afford new β-substituted octamethylcalix[4]pyrrole derivatives in moderate yields. The resulting cycloadducts show high affinity constants for fluoride and acetate anions; compounds **7** and **8** display sharp changes in color in the presence of these anions.

1. Introduction

Calix[4]pyrroles (CP) are easy-to-make fully *meso*-substituted porphyrinogens that interact strongly with small anions, such as fluoride, phosphate, acetate, among others. Moreover being synthesized for the first time by Baeyer in the nineteenth century,[1] calixpyrroles remained almost forgotten until 1996, when it was discovered that they could be used as sensors for anions[2] and neutral substrates.[3] Since then, the chemistry of calixpyrroles has progressed significantly,[4,5] being most part of the studies oriented to the synthesis of calix[4]pyrrole-based anion sensors. Some calixpyrrole derivatives can be used as naked-eye anion sensors[6–11] or as colorimetric chemosensors for neutral substrates (amino acids and amines[12] or nitroaromatic explosives,[13] for instance).

Because anion recognition by calixpyrroles involves the formation of hydrogen bonds between the pyrrolic NH protons and the anion,[2] the introduction of substituents at the β- or *meso*-positions of the calixpyrrole can modify the conformation of the macrocycle or the hydrogen bonding ability of the NH groups, resulting in more efficient and selective sensors. Thus, the chemical functionalization of calixpyrroles is an active field in organic chemistry.[11,14–17]

In contrast to the huge number of known methods to functionalize porphyrins[18] (structural analogues of calix[4]pyrroles), the chemistry of calixpyrroles is still in its infancy. In fact, the methods available for the functionalization of the β-[9,11,19–21] or *meso*-positions[22,23] of CP are scarce and the results are frequently disappointing. Interesting examples of such chemical transformation involve the formylation of *meso*-octamethylcalix[4]pyrrole (OMCP) followed by condensation of the resulting calixpyrrole-2-carbaldehyde **1** with methylene active compounds.[9,21] This type of chemistry was recently extended to 3-(octamethylcalix[4]pyrrol-2-yl)-propenal **5**.[11]

Some years ago we reported the use of porphyrin-2-carbaldehyde,[24] corrole-2-carbaldehyde and corrole-3-carbaldehyde[25,26] to generate azomethine ylides, which were trapped in situ with a range of dipolarophiles. Based on those works, we decided to verify if calixpyrrole-2-carbaldehyde **1** and 3-(octamethylcalix[4]pyrrol-2-yl)propenal **5** can also be used in similar 1,3-dipolar cycloadditions. The results obtained show that the two calixpyrrole derivatives behave quite differently.

2. Results and discussion

2.1. Synthesis

Our first studies involved the in situ generation of azomethine ylide **2** (from the reaction of *meso*-octamethylcalix[4]pyrrole-2-carbaldehyde (**1**) and *N*-methylglycine) in the presence of dipolarophiles (Scheme 1). The formation of cycloadducts **3** was anticipated but, surprisingly, the reaction of calixpyrrole **1** with *N*-methylglycine in the presence of 1,4-benzoquinone, 1,4-naphthoquinone or dimethyl acetylenedicarboxylate afforded only starting aldehyde **1** or decomposition products.

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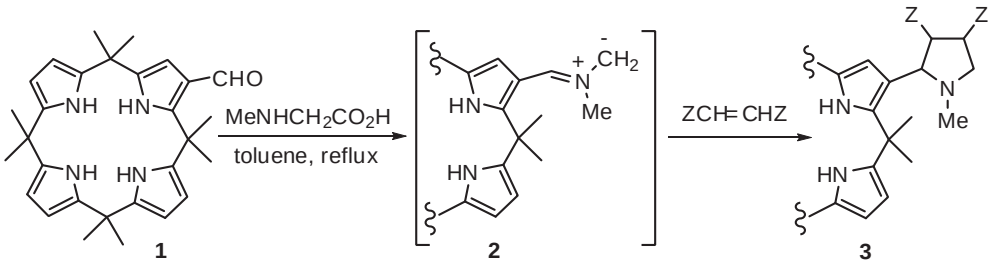


Scheme 1.

A similar reaction in the presence of fumaronitrile afforded the expected cycloadduct **4** in 24% yield (as a mixture of two diastereoisomers, each as a racemate). The two isomers were separated by preparative TLC and, from their ^{1}H NMR spectra, we established structure **4a** for the main product (16% yield, higher R_f) and structure **4b** for the minor one (8% yield)(Fig. 1). Both isomers show the molecular ion peak at m/z 562.

disappointing results prompted us to use calixpyrrole **5** expecting that the spacer (a vinyl group) between the macrocycle and the formyl group would prevent the steric effects and provide a more reactive azomethine ylide. The results below confirm that aldehyde **5** is, in fact, more reactive than **1** in 1,3-dipolar cycloadditions.

The 1,3-dipolar cycloadditions were performed by heating at reflux a toluene solution of aldehyde **5**, *N*-methylglycine and

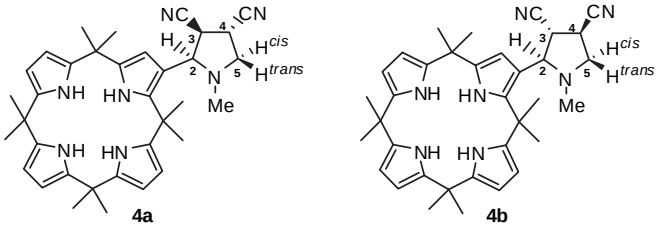
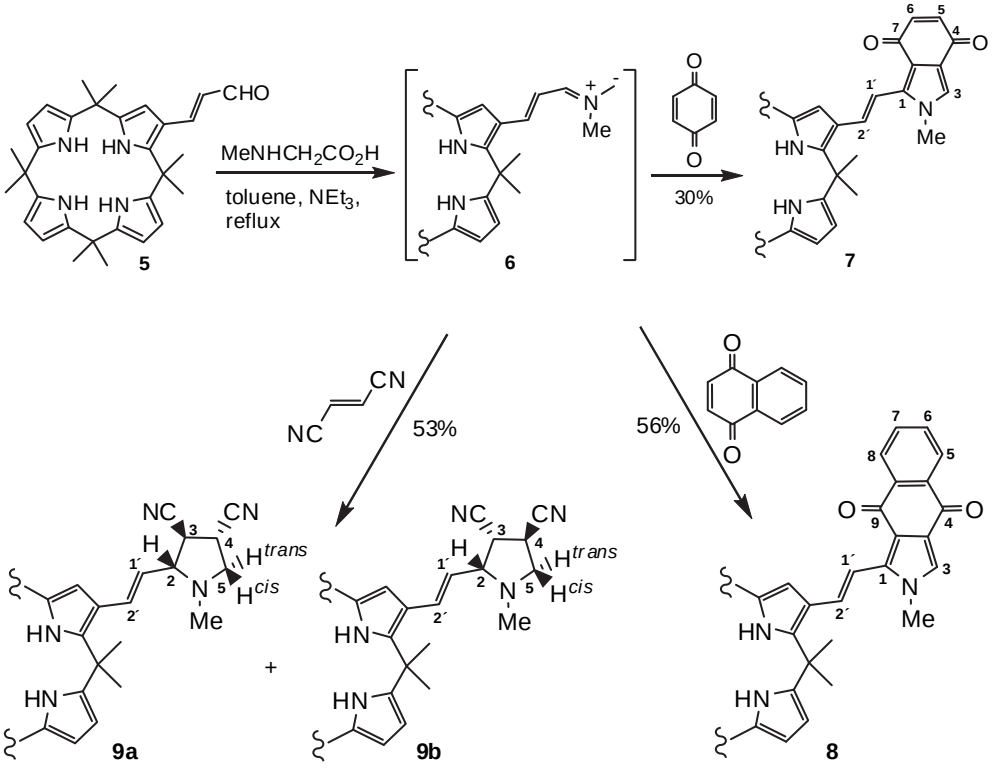


Figure 1. Structures of calixpyrroles **4a** and **4b**.

The low reactivity of CP **1**, when compared with porphyrin-2-carbaldehydes[24] and corrole-2(or 3)-carbaldehyde[25,26] (which are planar systems), is probably due to the conformation adopted by the calixpyrrole, which, somehow prevents the formation of the azomethine ylide or its reaction with the dipolarophiles. These

a dipolarophile. As indicated in Scheme 2, the in situ generated azomethine ylide **6** reacts with the dipolarophile leading to the cycloadduct or to a dehydrogenated cycloadduct derivative. In the reaction with 1,4-benzoquinone, calixpyrrole **5** was completely consumed after 2 h, as revealed by TLC. Separation of the reaction



Scheme 2.

mixture by column chromatography (silica gel) afforded a single product in 30% yield, which was identified as compound **7** (resulted from the dehydrogenation of the expected 1,3-dipolar cycloadduct). Highly polar products remaining on the top of the column were discharged. Calixpyrrole derivative **8** was obtained in 56% yield under similar reaction conditions, but using 1,4-naphthoquinone as dipolarophile.

The reaction with fumaronitrile afforded a mixture of the two diastereoisomers **9a** (22% yield, higher R_f) and **9b** (31% yield, lower R_f), which were separated by preparative TLC. In order to obtain an aromatic ring conjugated with the macrocycle, a mixture of compounds **9a** and **9b** was oxidized with DDQ affording compound **10** (Fig. 2) in 40% yield (or 81% yield based on the consumed starting material).

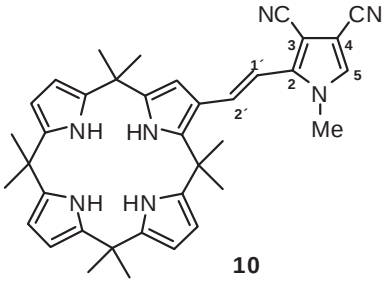


Figure 2. Structure of calixpyrrole **10**.

2.2. Structural characterization

All compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The ^{1}H NMR spectra of compounds **4a** and **4b** show the characteristic resonances of the CP protons: one multiplet due to the *meso*-CH_3 groups (1.46–1.65 ppm), another multiplet due to the β-pyrrolic protons (5.86–5.96 ppm), and four broad singlets corresponding to the resonances of the NH protons. The resonance of the N–CH_3 group appear as a singlet at 2.29 ppm (compound **4a**) or at 2.16 ppm (compound **4b**). The main differences between the two ^{1}H NMR spectra correspond to the resonances of the pyrrolidine protons. The spectrum of compound **4a** shows a doublet at 3.72 ppm (J=8.3 Hz) assigned to H-2, a double doublet at 2.70 ppm assigned to H-3 (J=8.3 and 6.5 Hz), and a multiplet at 3.22–3.30 ppm due to H-4. The resonance of proton H-5*trans* appears at 2.46 ppm as a triplet (J=9.4 Hz) while H-5*cis* appears at 3.53 ppm as a double doublet (J=9.4 and 7.8 Hz). The ^{1}H NMR spectrum of **4b** shows a doublet (J=8.5 Hz) at 3.72 ppm corresponding to H-2 and two double doublets at 2.72 ppm (J=9.9 and 8.5 Hz) and 3.49 ppm (J=9.9 and 1.3 Hz) due to the resonances of H-5*cis* and H-5*trans*, respectively.

The ^{1}H NMR spectrum of compound **7** shows, in addition to the resonances of the CP protons, a singlet at 7.26 ppm due to the resonance of H-3 and a multiplet at 6.61–6.77 ppm corresponding to protons H-1′, H-5, and H-6. The aliphatic region of the spectrum reveals a singlet at 3.79 ppm due to the resonance of the N–CH_3 protons. The resonance of proton H-2′ appears as a doublet at 8.96 ppm (J=15.6 Hz) due to the coupling with H-1′. The ^{1}H NMR spectrum of compound **8** shows two singlets at 3.83 and 7.41 ppm corresponding to the resonances of N–CH_3 and H-3, respectively, and two multiplets at 7.63–7.72 and 8.21–8.23 ppm due to the resonance of H-5, H-8 and H-6, H-7, respectively. The resonances of protons H-1′ and H-2′ appear as doublets at 6.89 and 8.65 ppm (J=15.9 Hz), respectively.

The ^{1}H NMR spectra of diastereoisomers **9a** and **9b** show, in addition to the resonances of the CP protons, the expected signals corresponding to the ethenyl and pyrrolidine protons. For compound **9a**, the resonance of H-1′ appears as a double doublet at 5.57 ppm (J=8.3 and 15.4 Hz) due to coupling with H-2′ (a doublet at 7.00 ppm, J=15.4 Hz) and H-2. The resonance of proton H-2 appears at 2.69 ppm as a double doublet (J=8.3 and 9.8 Hz) due to coupling with H-1′ and H-3 (a double doublet at 3.43 ppm, J=1.9 and 9.8 Hz). The protons H-5*trans* (*trans* position with H-2), H-5*cis* (*cis* position with H-2), and NCH_3 appear as triplet (2.95 ppm), double doublet (3.09 ppm), and singlet (2.35 ppm), respectively. The spectrum of **9b** shows a singlet at 2.34 ppm due to the resonance of the NCH_3 and four multiplets corresponding to the resonance of H-2 (2.45–2.53 ppm), H-5*cis* (3.08–3.12 ppm), H-5*trans* and H-4 (3.37–3.48 ppm), and H-3 (3.57–3.62 ppm), respectively.

The spectrum of the compound **10**, in addition to the resonances of the CP protons, shows two singlets corresponding to the resonance of the N–CH_3 (3.72 ppm) and H-5 (7.05 ppm) protons. The resonances of protons H-1′ and H-2′ appear as doublets at 6.37 and 7.91 ppm (J=15.8 Hz), respectively.

2.3. Anion binding

Due to their interesting absorption spectra (Fig. 3), calixpyrroles **5**, **7**, **8**, and **10** were evaluated as anion sensors. While compounds **5** and **10** are light yellow, **7** is purple and **8** is orange. The anion binding studies were conducted by UV–vis spectroscopy using six anions in their tetrabutylammonium form (F^-, Br^-, NO_2^-, NO_3^-, AcO^-, and $H_2PO_4^-$).

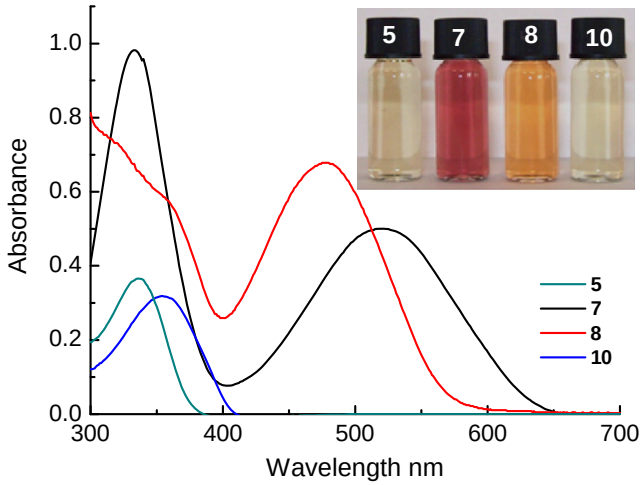


Figure 3. UV–vis spectra of calixpyrroles **5**, **7**, **8**, and **10** in CH_2Cl_2 (5×10^{-5} mol dm^{-3}).

In all cases 1:1 host–guest complexes were inferred from Job's plots and the affinity constants (Table 1) were determined from standard non-linear curve fit of the changes observed in the UV–vis spectra of the sensors (Fig. 4a).[27]

Table 1
Affinity constants (K, M^{-1}) for OMCP, **5**, **7**, **8**, and **10** and anionic substrates

Anion	OMCP	5[c]	7[c]	8[c]	10[c]
F^-	1.7×10^4[a]	4.3×10^6	1.52×10^6	2.04×10^6	4.03×10^6
AcO^-	668[b]	21,700	889	3130	1540
$H_2PO_4^-$	97[a]	2230	95.5	547	80.6
$K_{AcO^-/H2PO4^-}$	6.9	9.7	9.3	5.7	19.1

[a] lit. Ref. 2.
[b] lit. Ref. 28.
[c] Determined in CH_2Cl_2 by UV–vis spectroscopy.

Dichloromethane solutions of sensors **7** and **8** show naked-eye color changes after the addition of tetrabutylammonium fluoride or acetate, and, to a lesser extent, tetrabutylammonium dihydrogen phosphate (Fig. 4b). No color changes are observed after the addition of bromide, nitrate, and nitrite anions. The color changes observed are thus directly related with the values of the affinity constants.

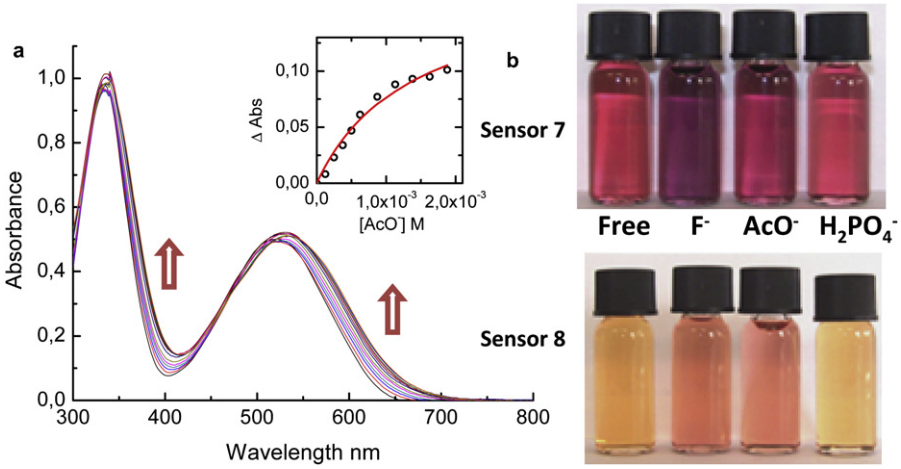


Figure 4. (a) Absorption spectroscopic titration of sensor **7** with acetate anion, *inset:* fit of the experimental data at 570 nm with a non-linear regression; (b) solutions of sensors **7** (top) and **8** (5×10^{-5} mol dm^{-3} in CH_2Cl_2) in the presence of anions (10 equiv).

Using the affinity constants reported for the parent OMCP as reference, it is evident that our four sensors show higher affinities for all studied anions. Comparing our four sensors, compound **5** shows the highest affinity constants, which decrease sharply from fluoride to acetate and to dihydrogen phosphate anions. It is interesting to note that the affinity constants with $H_2PO_4^-$ are much lower for sensors **7** and **10** than for sensors **5** and **8**. Another interesting observation is the excellent selectivity for the acetate anion when compared with $H_2PO_4^-$, being the best affinity constant ratio $K_{AcO^-}/H_2PO_4^-$=19.1 for compound **10** (Table 1).

3. Conclusions

Calix[4]pyrrole derivatives **1** and **5** show a quite distinct reactivity with *N*-methylglycine to generate azomethine ylides. While aldehyde **1** is almost inert to this reaction, the azomethine ylide generated from aldehyde **5** can be successfully trapped in 1,3-dipolar cycloadditions with fumaronitrile and quinones. The resulting cycloadducts show high affinity constants for fluoride anion and a significant selectivity for acetate when compared with dihydrogen phosphate.

4. Experimental section

4.1. General

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 spectrometer at 300 MHz and 75 MHz, respectively. $CDCl_3$ was used as solvent and TMS as an internal reference. Chemical shifts (δ) are quoted in parts per million (ppm) relative to TMS. Mass spectra were recorded on a 4800 MALDI TOF/TOF Analyser (Applied Biosystems). Flash chromatography was carried out with silica gel 0.032–0.063 mm. Melting points were measured in a Buchi Melting Point B-540 apparatus.

4.2. General procedure for the 1,3-dipolar cycloaddition reactions

A mixture of calixpyrrole **1** or **5** (0.01 mmol), *N*-methylglycine (0.07 mmol), dipolarophile (0.02 mmol), and triethylamine (0.02 mmol) in toluene (5 mL) was refluxed for 1–5 h under a nitrogen atmosphere. After cooling to room temperature, toluene was evaporated and the resulting residue dissolved in chloroform and purified by preparative TLC (silica gel) using a mixture of chloroform/ethyl acetate (20:1) as the eluent.

4.2.1. rel-(2R,3S,4S)-1-Methyl-2-(octamethylcalix[4]pyrrol-2-yl)pyrrolidine-3,4-dicarbonitrile, ***4a****.* Yield 16%, mp 119–120 °C. ^{1}H NMR: δ 1.48–1.65 (m, 24H, CH_3), 2.29 (s, 3H, N–CH_3), 2.46 (t, 1H, J=9.4 Hz, H-5*trans*), 2.70 (dd, 1H, J=8.3 and 6.5 Hz, H-3), 3.22–3.30 (m, 1H, H-4), 3.53 (dd, 1H, J=9.4 and 7.8 Hz, H-5*cis*), 3.72 (d, 1H, J=8.3 Hz, H-2), 5.88–5.94 (m, 7H, H-β), 7.10 (br, 1H, NH), 7.42 (br, 1H, NH), 7.47 (br, 1H, NH), 8.28 (br, 1H, NH). ^{13}C NMR: 26.7, 27.6, 27.8, 28.3, 28.5, 29.5, 30.3, 33.6, 34.7, 35.1, 35.2, 36.7, 39.4, 58.4, 65.0, 101.7, 102.1, 102.3, 103.3, 105.0, 135.4, 135.5, 135.7, 136.3, 139.3, 139.4, 139.5, 151.6, 172.9, 178.4. HRMS: calculated for $C_{35}H_{44}N_7$ 562.3653, found 562.3642.

4.2.2. rel-(2R,3R,4R)-1-Methyl-2-(octamethylcalix[4]pyrrol-2-yl)pyrrolidine-3,4-dicarbonitrile, ***4b****.* Yield 8%, mp 182–183 °C. ^{1}H NMR δ: 1.46–1.64 (m, 24H, CH_3), 2.16 (s, 3H, N–CH_3), 2.72 (dd, 1H, J=9.9 and 8.5 Hz, H-5*cis*), 3.21–3.32 (m, 2H, H-3, and H-4), 3.49 (dd, 1H, J=9.9 and 1.3 Hz, H-5*trans*), 3.72 (d, 1H, J=8.5 Hz, H-2), 5.86–5.96 (m, 7H, H-β), 6.90 (br, 1H, NH), 7.05 (br, 1H, NH), 7.14 (br, 1H, NH), 7.20 (br, 1H, NH). ^{13}C NMR: 28.2, 28.4, 28.6, 29.1, 29.2, 29.6, 30.4, 30.5, 35.1, 35.15, 35.18, 36.9, 38.8, 41.8, 58.2, 66.7, 102.1, 102.2, 102.5, 102.6, 103.1, 103.17, 103.22, 113.0, 118.9, 136.0, 137.9, 138.0, 138.1, 138.3, 138.8, 139.1, 171.3, 176.8. HRMS: calculated for $C_{35}H_{44}N_7$ 562.3653, found 562.36334.

4.2.3. (E)-2-Methyl-1-(2-(octamethylcalix[4]pyrrol-2-yl)vinyl)-2H-isoindole-4,7-dione, ***7****.* Yield 30%, mp 247–248 °C. ^{1}H NMR δ: 1.52–1.57 (m, 24H, CH_3), 3.79 (s, 3H, N–CH_3), 5.82–6.00 (m, 6H, H-β), 6.29 (d, J=2.7 Hz, 2H, H-β), 6.61–6.77 (m, 3H, H-1′, H-5, and H-6), 6.97 (br, 2H, NH), 7.26 (s, overlapped with the $CHCl_3$ signal, 1H, H-3), 7.33 (br, 2H, NH), 8.96 (d, J=15.6 Hz, 1H, H-2′). ^{13}C NMR: 28.5, 28.7, 29.1, 29.5, 35.1, 35.2, 35.3, 36.0, 37.2, 101.5, 101.8, 102.8, 102.9, 103.9, 104.0, 109.1, 116.3, 116.4, 121.2, 126.5, 131.9, 137.5, 138.0, 138.1, 139.2, 139.3, 139.4, 142.1, 180.3, 182.3. MS-MALDI: 613.3 $[M]^{\bullet}$, 636.3 $[M+Na]^+$, 652.3 $[M+K]^+$. HRMS-ESI: calculated for $C_{39}H_{44}N_5O_2$ $[M+H]^+$ 614.3490, found 614.3481.

4.2.4. (E)-2-Methyl-1-(2-(octamethylcalix[4]pyrrol-2-yl)vinyl)-2H-benzo[f]isoindole-4,9-dione, ***8****.* Yield 56%, mp >300 °C. ^{1}H NMR δ: 1.49–1.66 (m, 24H, CH_3), 3.83 (s, 3H, N–CH_3), 5.95–5.97 (m, 6H, H-β), 6.33 (d, J=2.6 Hz, 2H, H-β), 6.89 (d, J=15.9 Hz, 1H, H-1′), 6.97 (br, 2H, NH), 7.34 (br, 2H, NH), 7.41 (s, 1H, H-3), 7.63–7.72 (m, 2H, H-5, and H-8), 8.21–8.23 (m, 2H, H-6, and H-7), 8.65 (d, J=15.9 Hz, 1H, H-2′). ^{13}C NMR: 28.6, 28.7, 29.4, 35.1, 35.3, 36.4, 37.3, 101.6, 101.9, 102.8, 103.8, 110.0, 116.5, 126.4, 126.7, 127.1, 127.2, 131.3, 133.0, 133.1, 134.8, 137.5, 137.6, 138.1, 139.1, 179.3,

181.1. MS-MALDI: 663.3 $[M]^{\bullet}$, 686.3 $[M+Na]^{+}$, 702.3 $[M+K]^{+}$. HRMS-ESI: calculated for $C_{43}H_{46}N_5O_2$ $[M+H]^{+}$ 664.3646, found 664.3639.

4.2.5. rel-(E,2R,3S,4S)-1-Methyl-2-(2-(octamethylcalix[4]pyrrol-2-yl) vinyl)pyrrolidine-3,4-dicarbonitrile, ***9a****.* Yield 31%, mp 159–160 °C. ^{1}H NMR δ: 1.42–1.63 (m, 24H, CH_3), 2.35 (s, 3H, N–CH_3), 2.69 (dd, J=8.3 and 9.8 Hz, 1H, H-2), 2.95 (t, J=8,8 Hz, 1H, H-5*trans*), 3.09 (dd, J=5.9 and 8.8 Hz, 1H, H-5*cis*), 3.27–3.32 (m, 1H, H-4), 3.43 (dd, J=9.8 and 1.9 Hz, 1H, H-3), 5.57 (dd, J=8.3 and 15.4 Hz, 1H, H-1′), 5.83–5.98 (m, 6H, H-β), 6.13 (d, J=2.9 Hz, 1H, H-β), 6.90 (br, 1H, NH), 6.94 (br, 1H, NH), 7.00 (d, J=15.4 Hz, 1H, H-2′), 7.20 (br, 1H, NH), 7.26 (br, 1H, NH). ^{13}C NMR: 28.7, 29.2, 29.4, 30.1, 31.7, 35.1, 35.2, 35.3, 35.4, 36.9, 38.8, 39.9, 53.7, 58.2, 69.5, 73.8, 101.6, 102.5, 102.7, 102.8, 102.9, 103.6, 103.8, 114.7, 118.1, 119.7, 120.3, 130.3, 135.7, 137.5, 137.6, 137.6, 138.0, 138.1, 139.1, 210.9. MS-MALDI: 610.3 $[M+Na]^{+}$, 626.3 $[M+K]^{+}$. HRMS-ESI: calculated for $C_{37}H_{46}N_7$ $[M+H]^{+}$ 588.3809, found 588.3793.

4.2.6. rel-(E,2R,3R,4R)-1-Methyl-2-(2-(octamethylcalix[4]pyrrol-2-yl)vinyl)pyrrolidine-3,4-dicarbonitrile, ***9b****.* Yield 22%, mp 194–195 °C. ^{1}H NMR δ: 1.49–1.62 (m, 24H, CH_3), 2.34 (s, 3H, N–CH_3), 2.45–2.53 (m, 1H, H-2), 3.08–3.12 (m, 1H, H-5*cis*), 3.37–3.48 (m, 2H, H-5*trans* and H-4), 3.57–3.62 (m, 1H, H-3), 5.08 (dd, J=8.8 and 15.4 Hz, 1H, H-1′), 5.84–5.98 (m, 7H, H-β), 6.85 (br, 1H, NH), 6.93 (br, 1H, NH), 6.94 (d, J=15.4 Hz, 1H, H-2′), 7.20 (br, 1H, NH), 7.23 (br, 1H, NH). ^{13}C NMR: 28.9, 29.5, 30.6, 31.9, 35.2, 37.0, 38.7, 39.8, 53.6, 58.1, 69.8, 70.3, 101.7, 102.1, 102.6, 102.9, 103.7, 105.6, 115.3, 118.0, 118.9, 131.0, 135.6, 137.8, 138.3, 139.5, 210.9. MS-MALDI: 610.3 $[M+Na]^{+}$, 626.3 $[M+K]^{+}$. HRMS-ESI: calculated for $C_{37}H_{46}N_7$ $[M+H]^{+}$ 588.3809, found 588.3794.

4.2.7. (E)-1-Methyl-2-(2-(octamethylcalix[4]pyrrol-2-yl)vinyl)-1H-pyrrole-3,4-dicarbonitrile, ***10****.* DDQ (77 mg, 0.34 mmol) was added to a mixture of isomers **9a** and **9b** (100 mg, 0.17 mmol) dissolved in toluene (5 mL). The reaction mixture was heated at reflux for 16 h. Then, the mixture was washed with brine (50 mL) and with water (50 mL). The solution was dried (Na_2SO_4), the solvent was evaporated, and the residue was purified by column chromatography (silica gel) using chloroform as the eluent. Compound **10** was then crystallized from dichloromethane/hexane affording 40 mg (40% yield) of a yellow solid with mp 256–257 °C (dec). ^{1}H NMR δ: 1.51–1.57 (m, 24H, CH_3), 3.72 (s, 3H, N–CH_3), 5.89–5.95 (m, 6H, H-β), 6.19 (d, J=2.9 Hz, 1H, H-β), 6.37 (d, J=15.8 Hz, 1H, H-1′), 6.93 (br, 1H, NH), 6.99 (br, 1H, NH), 7.05 (s, 1H, H-5), 7.24 (br, 1H, NH), 7.91 (d, J=15.8 Hz, 1H, H-2′). ^{13}C NMR: 28.6, 28.7, 28.9, 29.1, 29.4, 29.6, 30.5, 35.1, 35.2, 35.4, 35.5, 37.0, 37.2, 96.0, 101.4, 102.0, 102.7, 102.9, 103.1, 103.4, 103.6, 103.9, 104.0, 104.6, 106.7, 108.4, 115.28, 115.32, 115.4, 129.4, 130.6, 130.7, 183.8, 211.3, and 211.4. MS-MALDI: 583.4 $[M]^{\bullet}$, 606.4 $[M+Na]^{+}$, 622.4 $[M+K]^{+}$. HRMS-ESI: calculated for $C_{37}H_{42}N_7$ $[M+H]^{+}$ 584.3496, found 588.3485.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.07.024.

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