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Efficient Synthesis and Host−Guest Properties of a New Class of Calix[6]azacryptands

Stéphane Le Gac, Xianshun Zeng, Camille Girardot, and Ivan Jabin*

Université Libre de Bruxelles, Service de Chimie Organique, Avenue F. D. Roosevelt 50, CP160/06, B-1050 Brussels, Belgium

ijabin@ulb.ac.be

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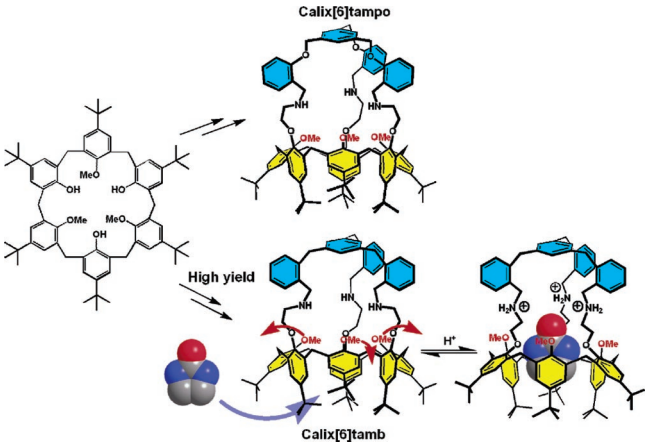

Two members of a new class of calix[6]azacryptands, namely, calix[6]tampo and calix[6]tamb, have been synthesized through an efficient [1 + 1] macrocyclization reaction−reduction sequence. One of them has been obtained in a remarkably high overall yield from the known $X_6H_3Me_3$. In comparison to all the other calix[6]azacryptands, they possess unique conformational properties since they present a rigidified cone conformation with a partial filling of the cavity by the methoxy groups. In contrast to calix[6]tampo, the fully protonated derivative of calix[6]tamb behaves as a remarkable molecular receptor toward polar neutral guests. NMR studies have shown that the intracavity binding process is governed by a conformational flip of the aromatic walls of the calixarene core.

Readily available calixarenes have emerged as very attractive platforms for the design of efficient molecular receptors toward charged or neutral species.[1] In particular, the size of the hydrophobic cavity of calix[6]arenes is well adapted for the inclusion of organic guests. However, these flexible macrocycles have to be constrained in a cone conformation in order to display intracavity host properties.[2] To remedy this problem, a possible strategy consists of introducing intramolecular covalent bridges at either the narrow or the wide rim of the calixarene skeleton.[3] In this regard, we have developed an original class of molecular receptors based on a calix[6]arene core rigidified by an azacryptand unit.[4] These calix[6]azacryptands (Figure 1) present a hydrophobic cavity closed at the narrow rim by a nitrogenous tripodal cap and open at the large rim for guest inclusion. These receptors proved to be extremely versatile since they present outstanding host−guest properties toward either charged (ammonium or metal ions) or neutral species thanks to the azacryptand cap that provides a tunable binding site.[5] Indeed, this basic cap can accommodate either metal ions or protons, offering coordination or hydrogen bonding sites for the molecular recognition processes. Recently, the calix[6]azacryptands have also been successfully used in the intracavity chiral recognition of neutral guests[4d] and in the modeling of active sites of enzymes.[6] In order to develop a new class of calix[6]azacryptands possessing different binding properties, we wanted to graft azacryptand moieties bearing an aromatic ring in place of the central heteroatom. Here, we report on the syntheses, conformational behavior, and preliminary host−guest properties of two new calix[6]-azacryptands displaying this structural feature, the so-called calix[6]tamb and calix[6]tampo.[7]

Either linear or convergent strategies have been used for the syntheses of the previously reported calix[6]azacryptands.[4] For the grafting of tripodal caps displaying a central aromatic ring, we decided to apply a convergent route with a [1 + 1] macrocyclization reaction as the key step. Calix[6]trisamine **4** and trisaldehydes **2** and **3** were chosen as the tripodal partners for the macrocyclization reaction since the formation of a calix[6]-trisimine had already proven to be efficient with compound **4**.[4c]

First, trisaldehydes **2** and **3** were prepared in one step from 1,3,5-tris(bromomethyl)benzene **1** (Scheme 1).[8] The reaction of 2-hydroxybenzaldehyde with **1** in the presence of NaOH led to compound **2** in high yield.[9] Suzuki cross-coupling reaction of **1** and 3.3 equiv of 2-formylphenylboronic acid, in presence of a catalytic amount of $Pd(PPh_3)_4$, led to trisaldehyde **3** in 44% yield. The average 76% yield per coupling reaction corresponds to what is classically obtained with a benzyl halide as the starting material.[10]

The synthesis of calix[6]trisamine **4**[11] from the C_{3v} symmetrical tris-*O*-methylated *tert*-butylcalix[6]arene (namely, X_6H_3-

* To whom correspondence should be addressed. Tel: +32 2 650 35 37. Fax: +32 2 650 27 98.

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(7) Tampo and tamb are related to 1,3,5-tris(2-(aminomethyl)phenoxymethyl)benzene and 1,3,5-tris(2-(aminomethyl)benzyl)benzene, respectively.

(8) 1,3,5-Tris(bromomethyl)benzene **1** was prepared from trimethyl 1,3,5-benzenetricarboxylate according to the literature: Houk, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 6825.

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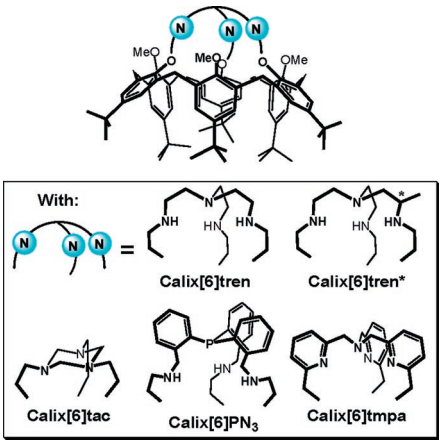
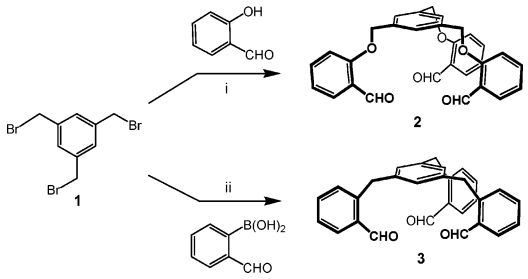


FIGURE 1. The calix[6]azacryptands.[4]

SCHEME 1. Syntheses of the Trisaldehydes 2 and 3[a]



[a] Conditions: (i) NaOH, EtOH, reflux, 88%;[9] (ii) Na_2CO_3, $Pd(PPh_3)_4$, toluene/H_2O, 90 °C, 44%.

Me_3) was already reported by us in a two-step sequence, but in order to avoid delicate chromatographic separation of the intermediate, we decided to develop a new route. Thus, **4** was prepared in an efficient three-step sequence by per-alkylation of $X_6H_3Me_3$ with ethylbromoacetate in presence of a strong base (NaH),[12] reaction with ammonia in MeOH, and subsequent reduction of the obtained amide groups by BH_3/THF (79% overall yield). The [1 + 1] macrocyclization reactions between calix[6]trisamine **4** and either **2** or **3** were carried out under classical conditions (Scheme 2). ^{1}H NMR analyses of the crude reaction mixtures revealed the presence of the expected calix[6]trisimine **8** as the exclusive species, while an unidentified minor calixarene-type species was formed along with the desired calix[6]trisimine **5** (see the Supporting Information for the ^{1}H NMR spectra of crude **5** and **8**). It shows that the trisaldehyde **3** displays a perfect complementarity from a geometrical point of view with the calix[6]arene framework. The calix[6]trisimines **5** and **8** were not isolated and directly reduced with $NaBH_4$, leading to the corresponding calix[6]tampo **6** and calix[6]tamb **9**. It is noteworthy that pure final calix[6]azacryptand **9** was isolated in a remarkably high 93% overall yield from **4** (74% overall yield from $X_6H_3Me_3$), and thus this new calix[6]-azacryptand constitutes a leading example of easily accessible covalently bridged calix[6]arene. As expected, besides the major calix[6]tampo **6**, a minor unidentified calixarene-type species was observed through NMR analysis of the crude reaction mixture. As a consequence, a two-step purification sequence was necessary to isolate pure calix[6]tampo **6**. First, the amino groups of **6** were converted into the corresponding *tert*-butyl carbamate, and the obtained tris-protected calixarene **7**[13] was purified through column chromatography on silica gel (27% overall yield from **4**). Treatment of compound **7** with trifluoroacetic acid (TFA) afforded pure calix[6]tampo **6** in 86% yield.

The two new calix[6]azacryptands **6** and **9** were characterized by ^{1}H NMR spectroscopy in $CDCl_3$ (see Figure 2a,b), and all the signals were attributed through 2D NMR analyses (COSY, HMQC, HMBC). These NMR studies afforded several interesting data on the conformational properties of these two compounds:

(i) Their spectrum recorded at 293 K is characteristic of a major C_{3v}-symmetrical flattened cone conformation ($\Delta\delta_{t\mathrm{Bu}}$ = 0.66 and 0.60 ppm for **6** and **9**, respectively) with the OMe groups directed toward the inside of the cavity (δ_{OMe} = 1.61 and 2.10 ppm for **6** and **9**, respectively).

(ii) HMBC experiments showed that the aromatic units of the anisole moieties present the more downfield shifted resonances, indicating that they are in an *out* position, while those linked to the azacryptand cap are in an *in* position (see the structures displayed Figure 2).

(iii) The methylenic $ArCH_2$ protons display well-defined doublets even at 330 K, indicating an inhibition of the cone−cone inversion thanks to the capping by the azacryptand units.

These conformational features differ from those observed with the previously described calix[6]azacryptands,[4] which all display a major cone conformation with the OMe groups projected toward the outside of the cavity. This original conformational behavior of **6** and **9** may be due to the very different geometry of their cap. Indeed, the central aromatic ring projects the amino arms far away from the C_{3v} axis, allowing the partial inclusion of the OMe groups, which should be stabilized through CH−π interactions with the aromatic rings of the calixarene core.

In the case of calix[6]tren and calix[6]PN_3, it was shown that the full protonation of the azacryptand unit provides a polycationic binding site that can strongly interact with polar neutral molecules, such as ureas, amides, alcohols, sulfoxides, and nitriles.[4d,5b] With such polarized receptors, the guests are stabilized inside the hydrophobic cavity through hydrogen bonding, charge−dipole, and CH−π interactions. Similar host properties have been even evidenced with calix[6]arenes lacking the covalent bridges between the ammonium arms.[14] Thus, we decided to investigate the behavior of the fully protonated calix-

(9) The synthesis of trisaldehyde **2** was reported earlier in 85% yield with a quasi-similar synthetic procedure (3 h of reflux instead of 20 h in our case): Chand, D. K.; Bharadwaj, P. K. *Tetrahedron Lett.* **1996**, *37*, 8443. Complementary characterization data for compound **2**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.5 (CH_2), 113.0 (CH), 121.3 (CH), 125.2 (C), 125.8 (CH), 128.8 (CH), 136.0 (CH), 137.5 (C), 160.7 (C), 189.5 (CH).

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(11) For the spectroscopic characterization of **4**, see ref 4b.

(12) The calix[6]trisester was obtained in 96% yield from $X_6H_3Me_3$ according to a previously described procedure. See: Takeshita, M.; Shinkai, S. *Chem. Lett.* **1994**, 1349.

(13) Similarly to the closely related triscarbamate of calix[6]PN_3,[4c] **7** displayed dissymmetrical ^{1}H and ^{13}C NMR patterns. However, when the ^{1}H NMR spectrum was recorded at high *T* (353 K in toluene-d_8) a C_{3v}-symmetrical profile was observed (see the Supporting Information). The loss of symmetry may be related to a different *Z*/*E* stereochemistry adopted by one of the Boc groups compared to the other two.

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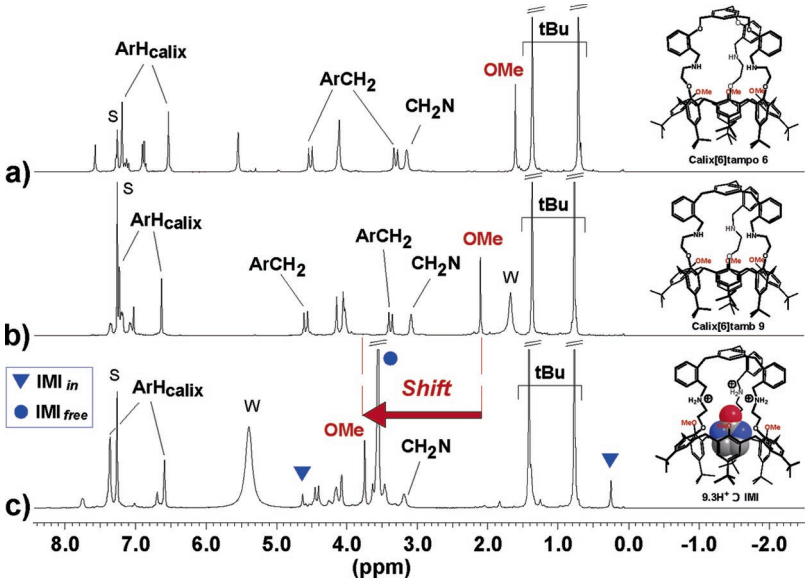
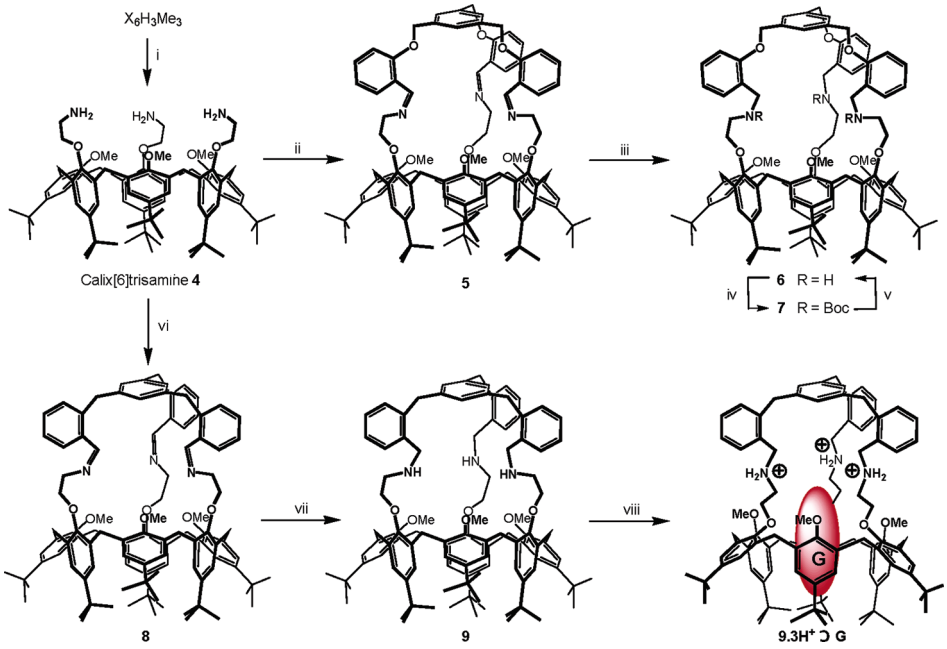


FIGURE 2. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of (a) calix[6]tampo **6**; (b) calix[6]tamb **9**; (c) host−guest complex **9.3H**$^+$⊃**IMI** obtained after addition of TFA (6 equiv) and IMI (24 equiv) to calix[6]tamb **9**. Solvent and water have been labeled "S" and "W", respectively. The H atoms of the included IMI have been omitted for clarity in the structure of the complex **9.3H**$^+$⊃**IMI**.

SCHEME 2. Syntheses of the Calix[6]azacryptands 6 and 9[a]



[a] Conditions: (i) $BrCH_2COOEt$, NaH, THF, reflux;[12] NH_3, MeOH, 55 °C; BH_3/THF, reflux, then EtOH, reflux, 79% (overall yield from $X_6H_3Me_3$); (ii) **2**, CH_2Cl_2, rt; (iii) $NaBH_4$, EtOH/CH_2Cl_2, 0 °C then rt; (iv) Boc_2O, Et_3N, CH_2Cl_2, rt, 27% (overall yield from **4**); (v) TFA, CH_2Cl_2, rt, 86%; (vi) **3**, CH_2Cl_2, rt; (vii) $NaBH_4$, EtOH/CH_2Cl_2, 0 °C then rt, 93% (overall yield from **4**); (viii) TFA, G, $CDCl_3$ (with G = polar neutral guest such as IMI, PYR, or DMSO).

[6]tampo **6.3H**$^+$ and calix[6]tamb **9.3H**$^+$ toward polar neutral guests. Our aim was to study the ability of calix[6]tampo **6** and calix[6]tamb **9** to accommodate a guest inside the hydrophobic cavity despite its partial filling by the methoxy groups. Addition of an excess of TFA (>6 equiv) to a $CDCl_3$ solution of either **6** or **9** led to the corresponding trisammonium salts **6.3H**$^+$ and **9.3H**$^+$, respectively. Evidence of the tris-protonation was observed on their ^{1}H NMR spectra which display a C_{3v}-symmetrical profile with a downfield shift of the CH_2N signals and the presence of a broad singlet at ca. 9.0 ppm integrating for six protons and corresponding to the NH_2^+ resonance. In both cases, the OMe groups were still directed toward the inside of the cavity with even more high-field-shifted resonances than that for the corresponding free amines (i.e., δ_{OMe} = 1.59 and 1.89 ppm for **6.3H**$^+$ and **9.3H**$^+$, respectively). Endo-complexation of imidazolidin-2-one (IMI), pyrrolidin-2-one (PYD), and DMSO was then tested since these polar neutral molecules led to a remarkably strong binding with all the previously described polyammonium calix[6]arene-based receptors.[4d,14] First, the NMR pattern of **6.3H**$^+$ was not affected by the addition of a large excess of these molecules (up to 50 equiv), showing that this polycationic calixarene is unable to host neutral guests. In strong contrast, the addition of IMI (24 equiv) to **9.3H**$^+$ gave rise to the endo-complex **9.3H**$^+$⊃**IMI** as

TABLE 1. Relative Affinities of the Neutral Guests G toward Host $9.3H^+$ and NMR Complexation Induced Upfield Shifts (CIS) Observed upon Their Endo-Complexation (Solvent: $CDCl_3$)

entry	G	relative affinity[a]	CIS[b] (ppm) α	β	γ
1	DMSO	0.0005		−2.49	
2	PYD	0.02		−0.98	−3.21, −3.44[c]
3	IMI	1			−3.31

[a] Relative affinity calculated at 293 K and defined as $[G_{in}]/[IMI_{in}] \times [IMI_{free}]/[G_{free}]$, where index "in" stands for "included". Errors estimated ±10%. [b] CIS calculated at 293 K and defined as $\Delta\delta = \delta$(complexed L) − δ(free L); α, β, and γ refer to the relative position of the protons to the oxygen atom. [c] Values determined for $CH_2CH_2CH_2$ and CH_2N, respectively.

attested by the high-field resonance at 0.24 ppm, which corresponds to the methylenic protons of the guest in the heart of the cavity (Figure 2c).[15] Moreover, major changes were observed in the NMR profile of the calixarene host **9.3H**$^+$: (i) the OMe groups experienced an impressive downfield shift presenting a quasi-normal resonance at 3.76 ppm, showing that they were expulsed from the cavity; (ii) signals of both CH_2N protons were high-field-shifted, indicating a shorter distance from the C_{3v} axis as a consequence of the establishment of H bonds between the NH_2^+ and the carbonyl group of the guest. In addition, HMBC spectrum of the host−guest adduct **9.3H**$^+\supset$**IMI** showed an *in* position of the ArH protons of the anisole units, denoting a conformational flip of the aromatic walls of the calixarene core (Scheme 2). These results highlight the remarkable ability of **9.3H**$^+$ to undergo a deep structural reorganization induced by the complexation of a guest. Similar results were obtained when DMSO or PYD was used instead of IMI. It is noteworthy that, at room temperature, the *in* and *out* exchange process of all these guests within the cavity of **9.3H**$^+$ was slower than the NMR time scale. Moreover, the observed NMR upfield CISs (complexation induced shifts) (Table 1) were close to those observed with the parent chiral calix[6]tren receptor, indicating that the guests adopt a similar positioning inside the cavity.[4d] Finally, NMR competitive binding experiments allowed us to determine the relative affinities of the neutral guests toward host **9.3H**$^+$ (Table 1; see the Supporting Information). Similarly to the closely related polycationic calixarene-based receptors, IMI displayed the highest relative affinity (entry 3) since this urea combines a size well-adapted to the calixarene cavity, a high dipole moment, and ideally located donor and acceptor hydrogen bonding groups.

In conclusion, two members of a new class of calix[6]-azacryptands, calix[6]tampo **6** and calix[6]tamb **9**, have been synthesized in a few steps from the 1,3,5-tris-*O*-methylated *t*Bu-calix[6]arene ($X_6H_3Me_3$). One of them, calix[6]tamb **9**, has been obtained through a remarkably efficient [1 + 1] macrocyclization reaction−reduction sequence. Starting from $X_6H_3Me_3$, the overall yield of the synthesis of **9** is 74%, thus allowing a large-scale preparation. NMR studies of these novel calix[6]-azacryptands have shown that they display unique conformational properties since they present a rigidified cone conformation with the methoxy groups directed toward the inside of the cavity. Such a positioning of the OMe groups contrasts with what was observed with all the other calix[6]azacryptands and is clearly related to the different geometry of the cap. Very interestingly, host−guest NMR studies revealed that the fully protonated derivative **9.3H**$^+$ can perform endo-complexation of polar neutral guests that can induce a conformational flip of the aromatic walls of the calixarene core and thus the expulsion of the OMe groups from the cavity. In contrast, the fully protonated derivative **6.3H**$^+$, which possesses a more flexible cap, is not able to produce such an induced fit process. These results highlight that a small structural change in the cap can greatly influence the host−guest properties of the receptor. We are now investigating the binding properties of these calix[6]azacryptands toward charged species, such as ammonium and metal ions.

(15) The resonance at 0.24 ppm was unambiguously attributed to the included IMI through a 2D NOESY experiment (see the Supporting Information). Similarly, the NH resonance of the included IMI was identified at 4.62 ppm. Moreover, HMQC spectrum allowed us to determine the methylenic carbon resonance of the included IMI at 38.3 ppm.

Experimental Section

Protected Calix[6]tampo 7. A solution of calix[6]trisamine **4** (300 mg, 0.262 mmol) and 1,3,5-tri(2′-formylphenoxymethyl)-benzene **2** (126 mg, 0.262 mmol) in anhydrous CH_2Cl_2 (12 mL) was stirred at rt for 14 h. After concentration, a ^{1}H NMR spectrum ($CDCl_3$) of the resulting solid (410 mg) showed the presence of the calix[6]trisimine **5** as the major species. A part of this crude compound **5** (320 mg) was dissolved in a 3:1 EtOH/CH_2Cl_2 mixture (30 mL), and then $NaBH_4$ (220 mg, 5.82 mmol) was added by small portions at 0 °C. The reaction mixture was stirred for 3 h at rt and then concentrated. The resulting residue was dissolved in CH_2Cl_2 (50 mL) and washed with an aqueous HCl solution (1 M, 20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic layers were washed with an aqueous NaOH solution (1 M, 50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic layers were washed with water (2 × 20 mL). After concentration, the resulting residue was dissolved in anhydrous CH_2Cl_2 (20 mL), and NEt_3 (113 μL, 0.813 mmol) and Boc_2O (178 mg, 0.816 mmol) were added subsequently. The reaction mixture was stirred for 15 h at rt, and then the solvent was removed. The residue was purified by column chromatography (CH_2Cl_2/AcOEt, 98:2), yielding compound **7** (105 mg, 27% overall yield from **4**) as a white solid.

Calix[6]tampo 6. Trifluoroacetic acid (0.5 mL, 6.5 mmol) was added to a solution of calix[6]arene **7** (100 mg, 0.0533 mmol) in anhydrous CH_2Cl_2 (1 mL). The reaction mixture was stirred for 4 h at rt and then concentrated. The resulting residue was dissolved in CH_2Cl_2 (20 mL) and washed vigorously with an aqueous NaOH solution (1 M, 15 mL) for 30 min. The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and the combined organic layers were washed with water (3 × 5 mL). Removal of the solvent led to pure calix[6]tampo **6** (72 mg, 86%) as a white solid.

Calix[6]tamb 9. A solution of calix[6]trisamine **4** (650 mg, 0.568 mmol) and 1,3,5-tri(2′-formylbenzyl)benzene **3** (245 mg, 0.568 mmol) in anhydrous CH_2Cl_2 (30 mL) was stirred at rt for 21 h. After concentration, a ^{1}H NMR spectrum ($CDCl_3$) of the resulting solid (870 mg) showed the presence of the calix[6]trisimine **8** as the exclusive species. A part of this crude compound **8** (850 mg) was dissolved in anhydrous CH_2Cl_2 (10 mL) and then slowly added at 0 °C to a solution of $NaBH_4$ (633 mg, 16.74 mmol) in anhydrous EtOH (45 mL). The reaction mixture was stirred for 1 h at 0 °C and then 2 h at rt, and the solvent was removed. CH_2Cl_2 (5 mL) was added to the resulting residue, and the salts were removed by suction filtration and then washed with CH_2Cl_2 (3 × 2 mL). CH_2Cl_2 (80 mL) was added to the filtrate, and the organic layer was washed with water (2 × 10 mL). Concentration led to pure calix[6]tamb **9** (794 mg, 93% overall yield from **4**) as a white solid.

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Supporting Information Available: Full experimental details spectroscopic data and NMR spectra for all new compounds synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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