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Shaping the cavity of calixarene architecture for molecular recognition: synthesis and conformational properties of new azocalix[4]arenes

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Abstract—A series of new azocalix[4]arenes containing one, two, three, and four free phenolic groups have been synthesized through the reaction of 4-nitro- and 2,4-dinitrophenylhydrazines with flexible calix[4]arene diquinones as well as through diazocoupling reactions of calix[4]arenes. Characterization of synthesized compounds by spectroscopic methods and X-ray diffraction revealed that azocalix[4]arenes adopt a cone conformation if they contain at least one free phenolic group. Partial cone or 1,3-alternate conformers of azocalix[4]arenes result only when they are devoid of free phenolic groups. The results can be utilized to shape calix[4]arene architecture for ionic and molecular recognition.

1. Introduction

Calix[*n*]arenes (*n*=4–20) are phenolic $[1]_n$-metacyclophanes,[1] which can be synthesized through acid or base catalyzed condensation of *p*-substituted phenols and formaldehyde. They possess easily functionalizable hydrophobic upper rim and hydrophilic lower rim to encompass a hollow cavity, the dimensions of which depend upon their conformation and appended functional groups.[2] The observed diversity of calix[*n*]arenes essentially lies in their conformational isomerism due to rotation of Ar–CH_2–Ar bonds or molecular rotation through the annulus.[3] Different stable conformers of calix[4]arenes have different capabilities for ionic and molecular recognition.[4]

Though X-ray structure analysis is the final diagnosis for the determination of conformation of calix[*n*]arenes, it has now been established that ^{1}H NMR and ^{13}C NMR spectral analysis can be effectively employed for conformational analysis. For instance, when the phenolic units around each methylene unit are in a *syn* orientation, the methylene carbon appears around δ 31 when phenolic units are in an *anti* orientation with respect to each other, the methylene carbon appears around δ 37[5] in the ^{13}C NMR spectrum of calix[4]arenes.

Introduction of azo groups into the calix[*n*]arene framework confers chromogenicity to their molecular architecture, which can be utilized for development of specific molecular diagnostics and sensor materials.

A number of azocalix[*n*]arenes have recently been examined for metal ion recognition.[6] Apparently, azocalix[4]arenes devoid of the possibility of intramolecular hydrogen bonding have not been examined to a great extent, as deprotonation of phenolic hydroxyls to elicit shift in the UV–vis spectra as an analytical signal (Fig. 1)[7] is not possible in such cases. Mere involvement of intramolecular hydrogen bonding to explain the observed role of hydrophobic cavity and its size and shape in molecular and ionic recognition needs to be explored further.[8] In order to understand the recognition characteristics of azocalix[*n*]arenes better, one is required to develop rational methods for obtaining cone, partial cone or alternate conformations of chromogenic calixarenes to examine their differential host–guest interaction to arrive at conclusions, which may define the role of weak interaction in the ionic recognition by azocalix[4]arenes. In this paper, we report our exploration in the role of hydrogen bonding in shaping the cavity of azocalixarenes and methods to achieve their different conformers. The choice of pyridylazo- and nitrophenylazo- groups as chromogens was motivated by the assumption that these functions when present in cone, partial cone, and 1,3-alternate conformations would allow better sensing capability for cations and neutral organic guests even in the absence of free phenolic hydroxyls. Assignment of the conformational structure of synthesized azocalix[4]arenes has been inferred from examination of their NMR splitting patterns and structure determination through single crystal X-ray diffraction.

Keywords: Calix[*n*]arenes; Diazotization; Conformation; Hydrogen bond.
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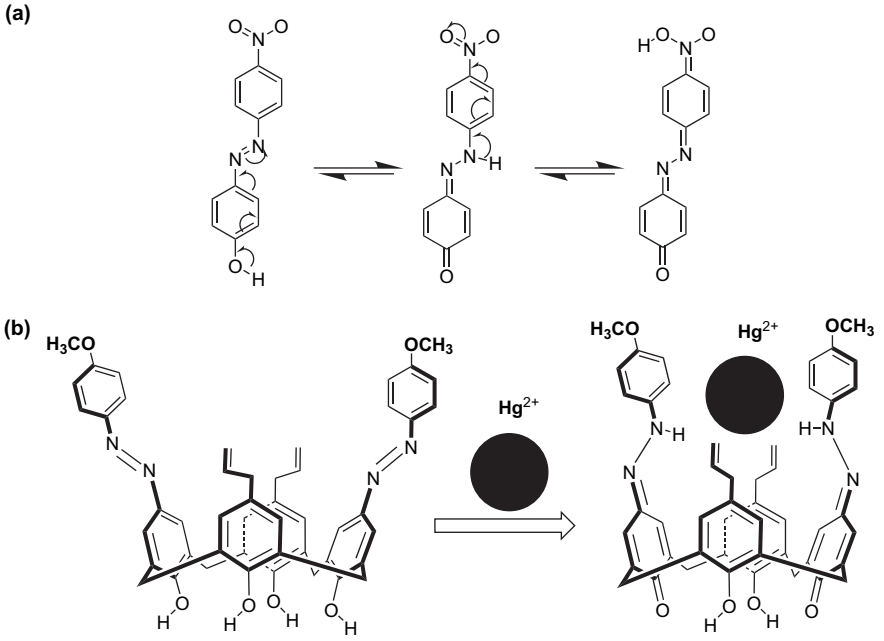


Figure 1. (a) Suggested mechanism of conversion of azo phenol moiety to quinoidal form; (b) an example of ionic recognition through azo quinoidal form.

2. Results and discussion

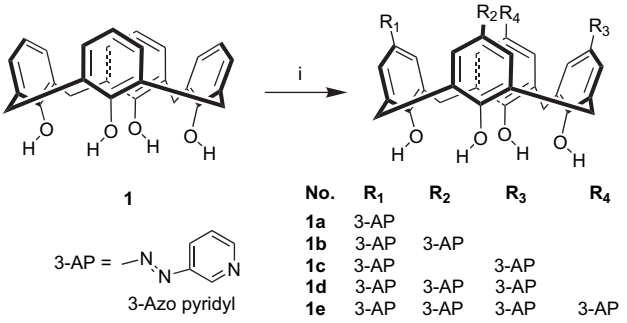
2.1. Results and characterization of the products

Calix[*n*]arenes bearing *p*-nitrophenylazo- and pyridylazo-chromogens containing one, two, three or four free phenolic groups in calix[4]arenes were synthesized either through the diazocoupling reaction of corresponding diazotized amines with calix[4]arene derivatives or through the reaction of nitrosubstituted phenyl hydrazines with calix[4]arene diquinones. Some of the derivatives were afforded through acylation or benzoylation of calix[4]arene derivatives. The choice of calix[4]arene diquinones as the starting materials for affording some of the derivatives was based upon their conformational flexibility and possible availability of partial cone conformation. Reaction conditions described in the Section 4 allowed the isolation of compounds, which were identified by examination of their ^{1}H and ^{13}C NMR and FAB mass spectra, NOESY experiments and X-ray diffraction analysis (for **3b** and **12a**).

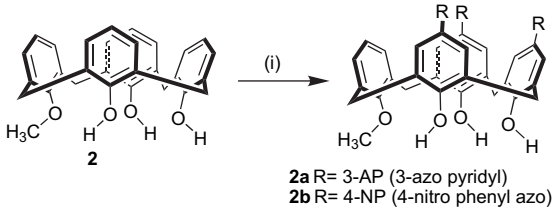
Azocalix[4]arene containing four free phenolic groups (**1a**–**e**) were synthesized by the diazonium coupling reaction of diazotized aromatic amines and calix[4]arene (**1**) by employing the method reported earlier[9] (Scheme 1). The identity of purified products was confirmed by comparison with authentic samples and analysis of their spectral data (IR, NMR).

Azocalix[4]arenes containing three free phenolic groups (**2a**, **2b**) were obtained by the diazonium coupling reaction of pyridyl or 4-nitrophenyl diazonium chloride and monomethoxy-calix[4]arene at 0–5 °C in DMF/methanol (8:5) in the presence of sodium acetate (pH 7–9) (Scheme 2). The products were isolated as red powders, which were characterized as **2a** and **2b** by spectral measurements.

The synthesis of azocalix[4]arenes containing two free phenolic groups (**3a**–**6a**, Scheme 3) was achieved in moderate



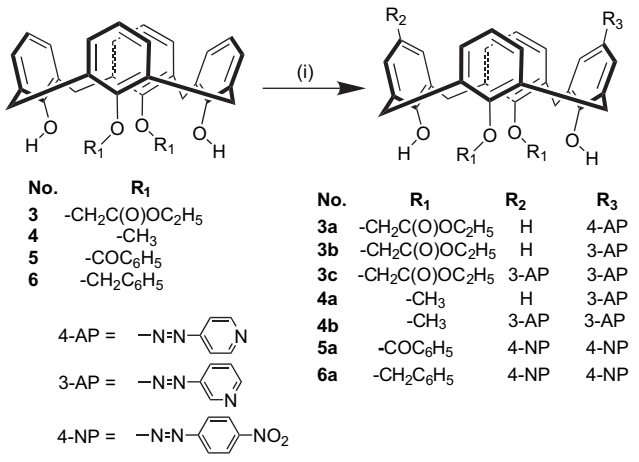
Scheme 1. Synthesis of azocalix[4]arenes with four free phenolic groups. Reagents and conditions (i) diazonium salt obtained from 3-aminopyridine, DMF/MeOH, CH_3COONa, 0–5 °C, 3 h.



Scheme 2. Synthesis of azocalix[4]arenes with three free phenolic groups. Reagents and conditions (i) diazonium salt obtained from respective amine, DMF/MeOH, CH_3COONa, 0–5 °C, 3 h.

yields (21–56%) by reacting dialkylated calix[4]arenes at 0–5 °C with 3 equiv of diazonium salt obtained from the corresponding amine in DMF/methanol (8:5) in the presence of sodium acetate as a base for adjustment of pH of the reaction (pH 7–9).

^{13}C NMR spectra of the synthesized derivatives revealed that their methylene carbon appears at δ 31.0 indicating that the synthesized compounds were in their cone conformation in accordance with the earlier findings on conformational assignment in calix[4]arenes.[5] It was interesting to note that



Scheme 3. Synthesis of dialkyl azocalix[4]arenes with two free phenolic groups. Reagents and conditions (i) diazonium salt obtained from respective amine, DMF/MeOH, CH_3COONa, 0–5 °C, 3 hr.

the diester derivative **3a** and **3b** displayed a quartet or a pair of doublet for the –OCH_2CO– protons at δ 4.71 and 4.75, respectively, in their ^1H NMR spectra as against the expected singlet for these protons (Supplementary data, 1). This is perhaps due to molecular dissymmetry, which then induces a diastereomeric relationship. This conclusion was confirmed by recording the single crystal X-ray (discussed later) and NOESY spectrum[10] of **3b** (Fig. 2b), which revealed the presence of cross peaks for these protons as indicated by arrows in Figure 2a.

A non-diazocoupling route was also used to synthesize azocalix[4]arene derivatives containing two free phenolic groups. Accordingly, dibenzoylated and dibenzylated calix-[4]arene diquinones (**7**, **8**) were prepared by oxidation of dibenzoylated and dibenzylated calix[4]arenes (**5**, **6**) with ClO_2, which were treated with 4-nitro- and 2,4-dinitrophenylhydrazine in $CHCl_3$/EtOH mixture in the presence of H_2SO_4 to give bis(nitrophenylazophenol) derivatives in 78–84% yields. These derivatives were characterized as **5a**, **6a**, **7a**, and **8a** by spectral measurements as given in the Section 4 (Scheme 4).

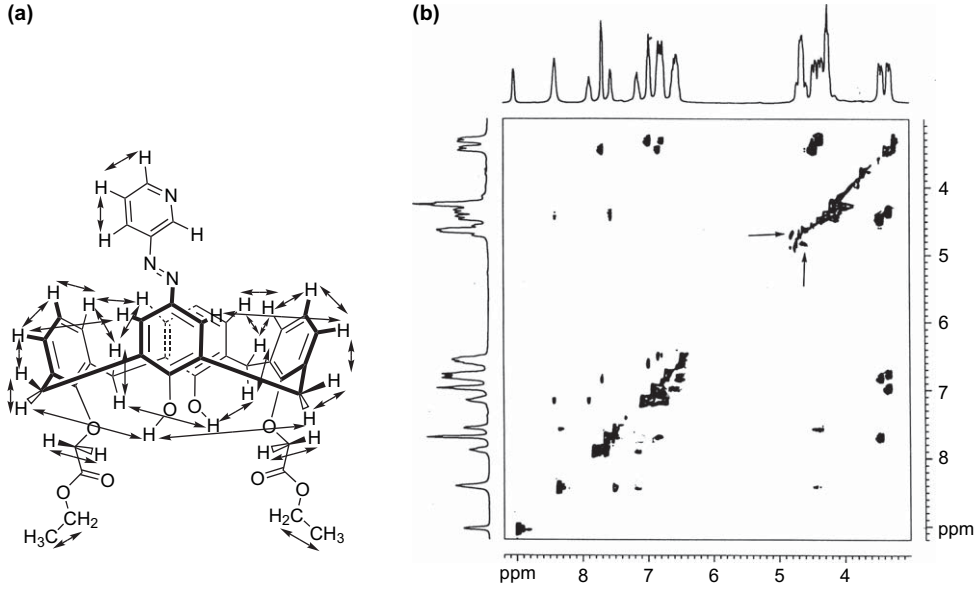
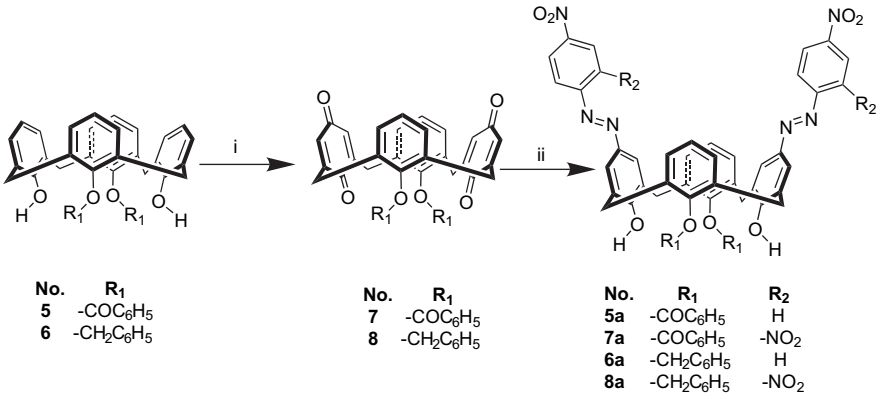


Figure 2. (a) Molecular structure of **3b** and observed correlations in its NOESY spectrum; (b) correlation of aromatic and methylene protons in the NOESY spectrum of **3b** in $CDCl_3$ at 25 °C and 300 MHz.



Scheme 4. Synthesis of dialkyl azocalix[4]arenes with two free phenolic groups via a diquinone route. Reagents and conditions (i) ClO_2, room temperature; (ii) chloroform/ethanol, nitrosubstituted phenyl hydrazines, concn H_2SO_4, 4 h, room temperature.

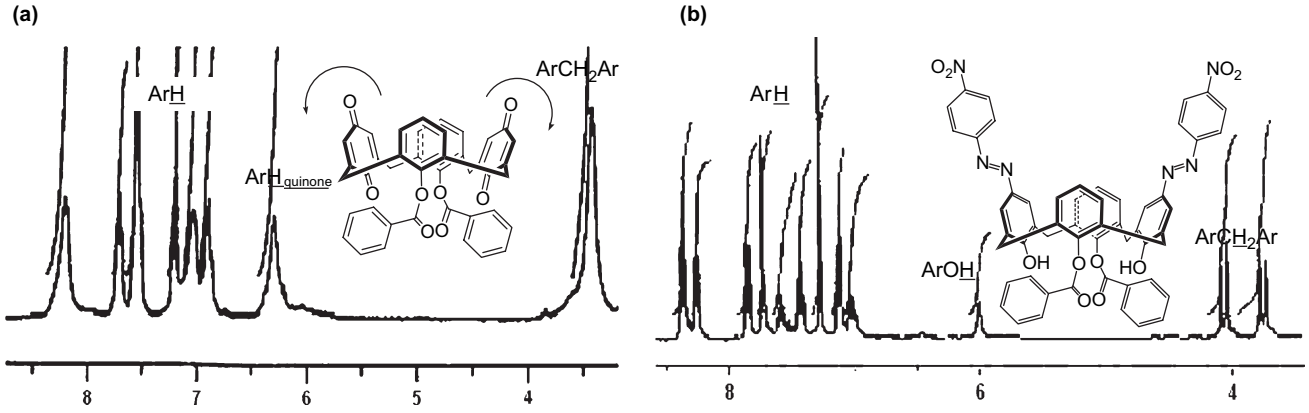
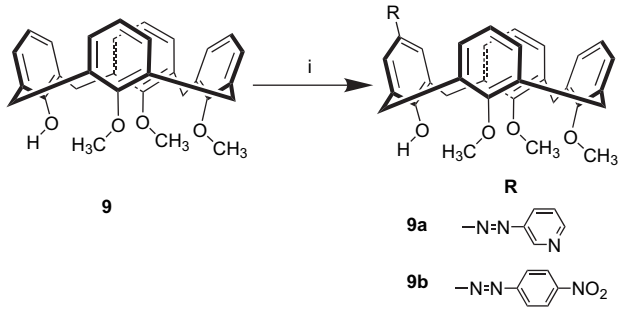


Figure 3. (a) Molecular structure and ^{1}H NMR spectra of dibenzoylcalix[4]diquinone **7**; (b) molecular structure and ^{1}H NMR spectra of 5,17-bis(4′-nitrophenylazo)-25,27-di(benzyloxy)-26,28-dihydroxycalix[4]arene **5a**.

The synthesized dibenzoylcalix[4]arene diquinones exhibited characteristic methylene bridge protons as a broad singlet in their ^{1}H NMR spectrum to reveal their flexible conformational constitution. On conversion into *p*-nitrophenylazocalix[4]arene dibenzoyl derivative, the broad singlet for methylene bridge protons got split into a pair of doublet for azocalix[4]arenes (**6a**, **7a**, and **8a**) indicating that they were present in their cone conformations (Fig. 3).

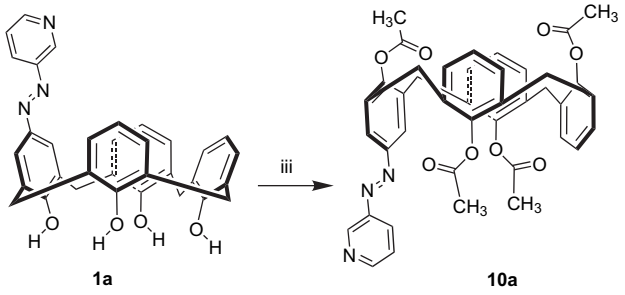
Trimethylated-calix[4]arenes **9** (i.e., containing only one free phenolic group) when reacted with 3 equiv of corresponding diazonium chlorides at 0–5 °C in DMF/methanol (8:5) using sodium acetate (pH 7–9) as a base gave **9a**,**b**.

Examination of the ^{1}H NMR and ^{13}C NMR spectra of tri-*O*-substituted azocalix[4]arenes having only one hydroxyl group (Scheme 5, **9a**, **9b**) indicated that they were also present in their cone conformation albeit the cone conformation was flattened and deviated from its perfect cone structure as revealed by X-ray diffraction analysis.[11]



Scheme 5. Synthesis of azocalix[4]arenes with one free phenolic group. Reagents and conditions (i) diazonium salt obtained from respective amine, DMF/MeOH, CH_3COONa, 0–5 °C, 3 h.

2.1.1. Acylation and benzoylation of azocalix[4]arenes: conformational outcome. When **1a** was reacted with acetic anhydride and pyridine in dichloromethane at room temperature, it gave **10a** as a major product (Scheme 6), which exhibited a singlet and a pair of doublet (1:1) for methylene protons in its ^{1}H NMR spectrum suggesting it to have a partial cone or 1,3-alternate conformation. This dichotomy of ^{1}H NMR spectral interpretation was resolved by the ^{13}C NMR spectrum (DEPT-135) in which methylene carbons appeared at δ 37.5 and 37.4 to reveal its 1,3-alternate conformation. Since no signal was observed at around δ 30, the possibility of a partial cone conformation was not considered on the basis of literature precedents.[5]

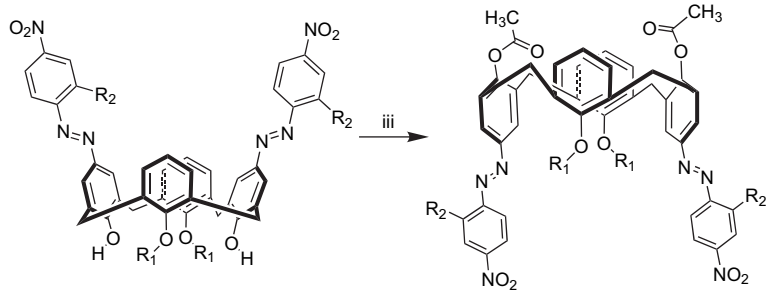


Scheme 6. Synthesis of tetra-alkyl azocalix[4]arenes with one azo substituent. Reagents and conditions (iii) acetic anhydride, dichloromethane/pyridine (10:1), room temperature, 24 h.

When azocalix[4]arenes with two free phenolic groups present in the cone conformation (**5a**–**8a**) were subjected to acetylation in the presence of acetic anhydride and pyridine in dichloromethane at room temperature, they gave **11a**–**12b** in 67–75% yield (Scheme 7), which exhibited a pair of doublet in the ^{1}H NMR spectrum (Supplementary data, 2). The methylene carbons in **11a** and **12a** appeared at δ 37.2 and δ 37.4, respectively, in their ^{13}C NMR spectrum could be attributed to 1,3-alternate conformations that were confirmed by X-ray crystallographic analysis of **12a** (discussed later).

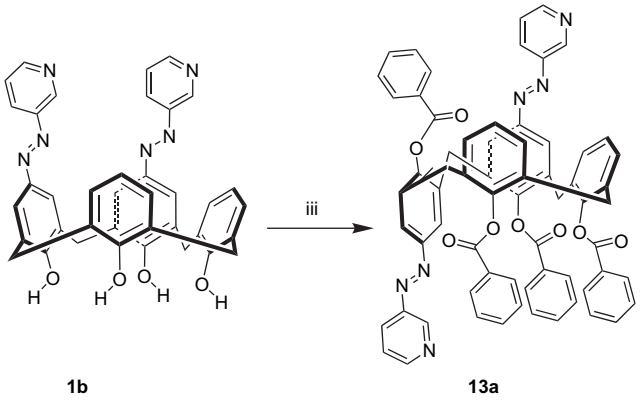
Room temperature benzoylation of **1b** with benzoyl chloride and pyridine in dichloromethane yielded **13a** (Scheme 8) in which methylene protons appeared as a multiplet in its ^{1}H NMR spectrum. The exact conformation for **13a** therefore was difficult to infer from its ^{1}H NMR spectrum, but methylene carbons in its ^{13}C NMR spectrum appeared as four signals at δ 37.8, 36.9, 30.2, 29.6 (Supplementary data, 3), which were possible only if azocalix[4]arenes (**13a**) had a partial cone conformation.

Similarly, room temperature acylation of **2a**,**b** with acetic anhydride and pyridine in dichloromethane yielded **14a**,**b** (Scheme 9). The synthesized derivatives exhibited multiplets for methylene protons in their ^{1}H NMR spectrum, which made it difficult to infer exact information about the conformation. However, ^{13}C NMR spectrum (DEPT-135)



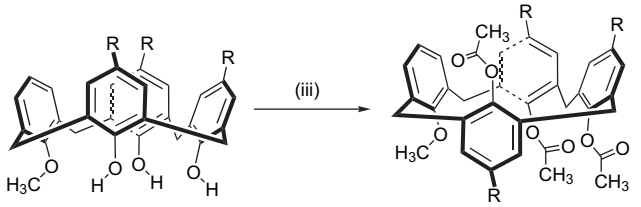
No.	R_1	R_2
11a	$-COC_6H_5$	H
11b	$-CH_2C_6H_5$	H
12a	$-COC_6H_5$	$-NO_2$
12b	$-CH_2C_6H_5$	$-NO_2$

Scheme 7. Synthesis of tetra-alkyl azocalix[4]arenes with two distal azo substituents. Reagents and conditions (iii) acetic anhydride, dichloromethane/pyridine (10:1), room temperature, 24 h.



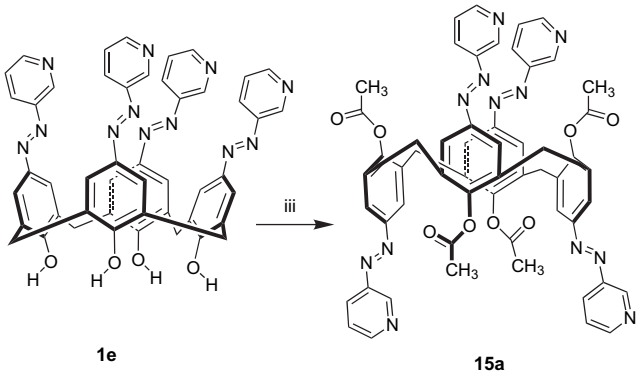
Scheme 8. Synthesis of tetra-alkyl azocalix[4]arenes with two proximal azo substituent. Reagents and conditions (iii) benzoyl chloride, dichloromethane/pyridine (10:1), room temperature, 24 h.

of **14a** revealed the presence of four signals at δ 38.4, 37.8, 31.7, 30.4 for methylene carbons and three signals at δ 21.2, 20.6, 20.2 for –CO*C*H$_3$ carbon suggesting the formation of a partial cone conformer with one azophenol moiety near the anisole unit in the *anti* disposition.



Scheme 9. Synthesis of tetra-alkyl azocalix[4]arenes without free phenolic groups. Reagents and conditions (iii) acetic anhydride, dichloromethane/pyridine (10:1), room temperature, 24 h.

Acetylation of **1e** in the presence of acetic anhydride and pyridine at room temperature resulted in **15a** (Scheme 10), which exhibited a singlet for methylene bridge protons in its ^{1}H NMR spectrum and methylene carbon at δ 38.2 in its ^{13}C NMR spectrum to suggest that it is present in the 1,3-alternate conformation.



Scheme 10. Synthesis of tetra-alkyl azocalix[4]arenes without free phenolic groups. Reagents and conditions (iii) acetic anhydride, dichloromethane/pyridine (10:1), room temperature, 24 h.

A summary of the splitting patterns observed in the ^{1}H NMR spectra, chemical shift values of methylene carbons in their ^{13}C NMR spectra, and the assigned conformation of the synthesized new azocalix[4]arene analogs is given in Table 1.

2.2. X-ray crystallographic analysis

2.2.1. X-ray crystallographic analysis of 3b. An ORTEP diagram of **3b** is shown in Figure 4a. It appears that **3b** crystallizes with chloroform. The torsion angles φ and χ around Ar—CH_2—Ar bonds about C7, C14, C21, and C28 show a −+, −+, −+, −+ pattern, which is consistent with the cone conformation.[12] The inter planer angles between ring A (C1—C6) and its distally positioned ring C (C15—C20) is 34.36° while the inter planer angle between ring B (C8—C13) and D (C22—C27) is 75.90°. This suggests that rings A and C are almost parallel while rings B and D are almost perpendicular to each other. The azopyridyl group has been found to be disordered. The corresponding hydroxyl substituents O1, O2, O3, and O4 are directed inwards the cavity of the calixarene architecture. Both the O2–C33–C34–O7 and O4–C29–C30–O5 are cis thereby

Table 1. Conformational assignment of synthesized azocalix[*n*]arenes. ^{1}H NMR splitting pattern for methylene protons and ^{13}C NMR data for methylene carbons (δ, 300 MHz, 25 °C) in different azocalix[4]arenes

No	^{1}H NMR splitting pattern of methylene protons (ratio of protons)	^{13}C NMR values for methylene carbons	Conformation
2a	Two pair of doublet (1:1:1:1)	31.2, 33.3	Cone
2b	Two pair of doublet (1:1:1:1)	—	Cone
3a	Two pair of doublet (1:1:1:1)	31.3, 29.6	Cone
3b	Two pair of doublet (1:1:1:1)	31.3, 29.6	Cone
3c	One pair of doublet (1:1)	31.4	Cone
4a	One triplet and one pair of doublet (2:1:1)	31.0, 29.5	Cone
4b	One pair of doublet (1:1)	31.1	Cone
5a	One pair of doublet (1:1)	32.9	Cone
6a	One pair of doublet (1:1)	—	Cone
7a	One pair of doublet (1:1)	—	Cone
8a	One pair of doublet (1:1)	—	Cone
9b	Two pair of doublet (1:1:1:1)	—	Cone
10a	One singlet and one pair of doublet (1:1)	38.7, 37.5	1,3-Alternate
11a	One pair of doublet	37.2	1,3-Alternate
11b	One pair of doublet	—	1,3-Alternate
12a	One pair of doublet	37.4	1,3-Alternate
12b	One pair of doublet	—	1,3-Alternate
13a	Multiplet	37.8, 36.9, 30.2, 29.6	Partial cone
14a	Multiplet	38.4, 37.8, 31.7, 30.4	Partial cone
14b	Multiplet	—	Partial cone
15a	One singlet	38.2	1,3-Alternate

making both the carbonyl groups *endo* with respect to the calix cavity.

A significant intramolecular hydrogen bonding has been observed amongst hydroxyl groups and proximal oxygens (O1–H1—O2=1.939 Å, O3–H3—O4=1.970 Å). There is a prominent C–H$\cdots\pi$ interaction among C10–H10$\cdots$ring A (with H$\cdots\pi$ distance 3.395 Å) that brings two phenyl rings much closer thereby resulting in the formation of a dimer. A prominent intermolecular interaction exists between the pyridyl ring and hydrogen of the ester chain to result in a dimeric columnar packing (Fig. 4b). These dimeric columns run parallel and are associated with each other through weak intermolecular hydrogen bonds (C36–H36B$\cdots$N2X–= 2.650 Å) and C–H$\cdots\pi$ interaction among C35–H35A$\cdots$ring A (with H$\cdots\pi$ distance 3.016 Å). The molecular packing of **3b** along the axis *a* is shown in Figure 4b.

2.2.2. X-ray crystallographic analysis of 12a. An ORTEP diagram for **12a** is shown in Figure 5a. Torsion angles φ and χ around Ar—CH_2—Ar bonds about C7, C14, C21, and C28 showing ++, −−, ++, −− are consistent with 1,3-alternate conformation.[13] The inter planar angles between rings A (C1—C6) and its distally positioned ring C (C15—C20) is 25.04° while between ring B (C8—C13) and D (C22—C27) is 20.76°, which suggest that these are almost parallel to each other. Phenyl rings of the benzoyl group are perpendicular to the respective calixaryl aromatic ring plane. The oxygen of the carbonyl group remains *exo* to the cavity. The dihedral angle between the phenylazo group plane (C29–C34) and ring A (C1–C6) is 7.41°, which corroborates that one phenylazo ring is parallel and the other phenylazo ring (C42–C47) is perpendicular to ring C (C15—C20) showing a dihedral angle 70.01° with the nitro group (*ortho* to azo), which remains outward of the calixarene cavity. There are prominent intramolecular C–H$\cdots\pi$ interactions among C34–H34$\cdots$Phenyl ring (C36–C41) and C47–H47$\cdots$Phenyl ring (C49–C54) with H$\cdots\pi$ distance 3.484 Å and 3.493 Å, respectively. This brings the substituted phenylazo group much closer to the adjacent benzoyl ring (Fig. 5b). The molecular packing of **12a** along the axis *a* is shown in Figure 5c.

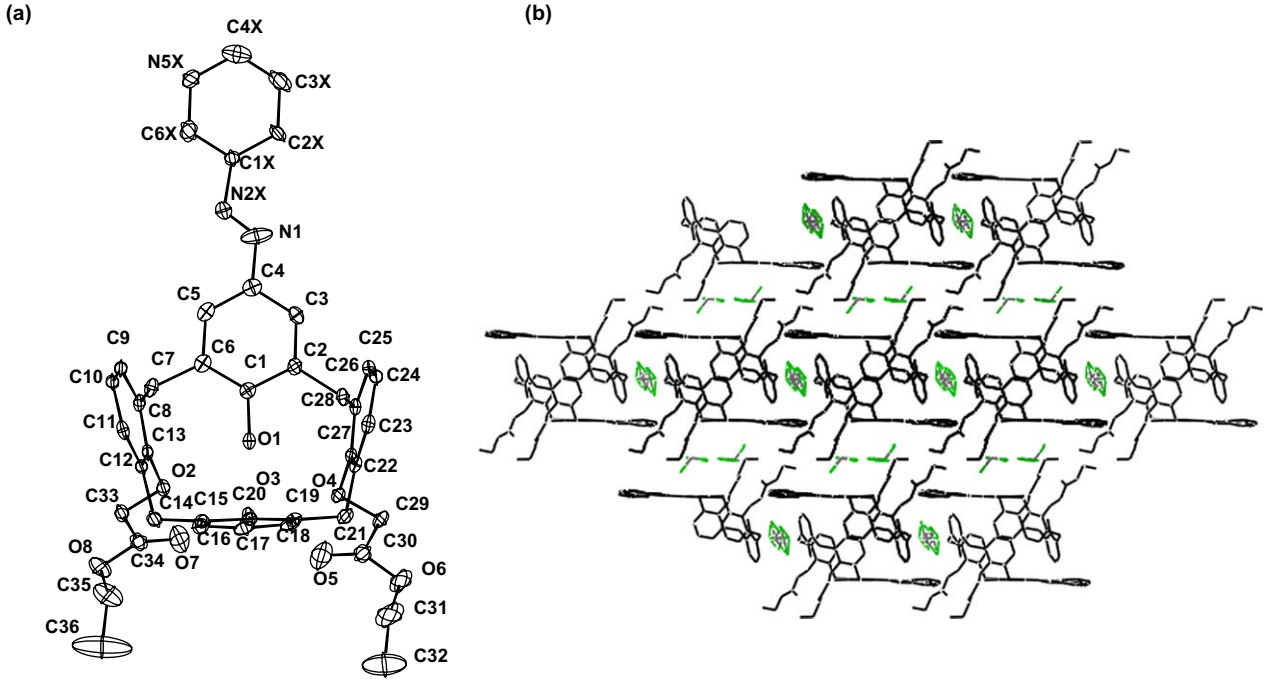


Figure 4. (a) ORTEP diagram of **3b** (hydrogens, solvent molecules, and disordered part have been omitted for clarity); (b) view of the molecular packing along the axis *a*.

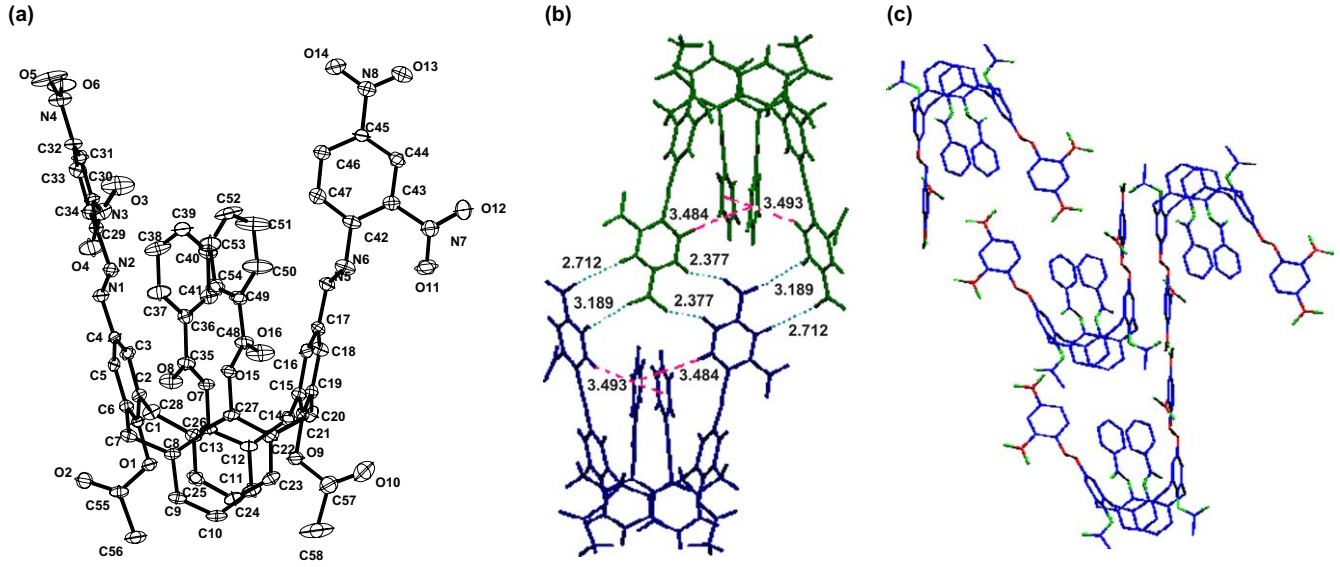


Figure 5. (a) ORTEP diagram showing labeling of atoms in **12a** with 30% probability factor (hydrogen atoms have been omitted for clarity); (b) intermolecular hydrogen bonds and CH–π interactions; (c) view of the molecular packing along the axis *a*.

3. Discussion

The conformational flexibility of calixarene compounds has often been explained by the presence of intramolecular hydrogen bonds, which is directly correlated with the number of free phenolic hydroxyls present in the calix[4]arene. Accordingly, azocalix[4]arenes with four free phenolic groups at the lower rim (**1a**–**e**, Scheme 1) adopt a cone conformation in accordance with the earlier reports.[14] When the number of phenolic groups is decreased, it is apparently expected to exert a profound effect on the conformational outcome. Present investigations however indicate that mono alkyl azocalix[4]-arenes (**2a**–**2d**, Scheme 2) bearing three phenolic hydroxyl groups and the dialkyl azocalix[4]arenes (**3a**–**6a**, Scheme 3) bearing two phenolic hydroxyl groups also exist in their cone conformation.

The use of an alternate route for the synthesis of azocalix[4]-arenes with two free phenolic groups through dialkyl-calix[4]arene diquinones, which are known to be present in their cone and partial cone conformations in equilibrium with each other[15] also resulted in azocalix[4]arenes in their cone conformation. This revealed that the route adopted or the conformation of the starting material does not have any bearing on the conformational outcome of the azocalix[4]arenes.

Examination of spectral characteristics of tri-*O*-substituted azocalix[4]arenes possessing one free phenolic group (**9a**,**b**, Scheme 5) indicate that they were also present in their flattened cone conformation as revealed by their single crystal X-ray diffraction analysis.[11] The flattened cone conformation probably results because these compounds are conformationally flexible due to loss of stabilization owing to decreased strength of intramolecular hydrogen bonding. Nonetheless, it is important to note that even when only one phenolic hydroxyl is present, synthesized azocalix[4]arene is present in the cone conformation.

When free phenolic groups at the lower rim in azocalix-arenes are completely absent, the diazo coupled product may lead to the 1,3-alternate or partial cone conformer. It has been determined that in such cases the 1,3-alternate conformation predominates particularly when the number of azo substituents is one (Scheme 2) or when they are symmetrically positioned at the upper rim (Schemes 7 and 10). However, it seems that in the event, when free phenolic groups at the lower rim were absent and when they possess more than two unsymmetrically positioned azo substituents (Schemes 8 and 9) at the upper rim, a partial cone conformation has been found to be the major conformer.

In conclusion, we report that one can obtain the cone conformation of azocalix[4]arenes if at least one free phenolic groups present at their lower rim. 1,3-alternate and partial cone conformations are only obtained when free phenolic groups are absent. The conformational outcome in azocalix[4]arenes is also dictated by the symmetric disposition of azo substituent at the upper rim.

4. Experimental

4.1. General

All the reagents used in the study were purchased from Sigma–Aldrich or Merck and were chemically pure. The solvents used were distilled (for diazotization reaction) and dried (for acetylation or benzoylation reaction). Column chromatography was performed on silica gel (60–120 mesh) obtained from Merck. ^{1}H NMR, ^{13}C NMR, DEPT-135, and NOESY spectra were recorded on a 300 MHz Bruker DPX 300 instrument at room temperature using tetramethylsilane (TMS) at 0.00 as an internal standard. IR spectra were recorded on a Nicolet Protégé 460 spectrometer in KBr disks while X-ray data was recorded using a Bruker SMART CCD single crystal diffractometer. UV–vis spectra were

obtained on a Perkin–Elmer (Lambda-3B) recording spectrophotometer. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 Mass spectrometer/Data System using argon/xenon (6 kV, 10 mA) as the FAB gas. Melting points were determined on an electrothermal Toshniwal melting point apparatus and were uncorrected.

4.2. General procedure for the synthesis

p-tert-Butylcalix[4]arene and calix[4]arene were synthesized by the method described by Gutsche.[16] Compound **1–10** were synthesized as described in the literature[17] while **1a–e** and **9a** were previously synthesized by our group.[9,11]

4.2.1. Synthesis of azocalix[*n*]arenes through the diazotization reaction (compounds 1a–e, 2a–b, 3a–c, 4a,b, 5a, 6a, 9a, 9b). The pyridyl diazonium chloride solutions were prepared by the addition of an aqueous solution of sodium nitrite (2 equiv of amine) into solution of respective amines in concn HCl (10–20 equiv) and distilled water (5–10 ml) at 0–5 °C. The diazotized solution was slowly added (in standardized 1.5 molar ratio with respect to each free phenolic group in the corresponding calix[*n*]arenes) into an ice-cold (0–5 °C) solution of corresponding calix[*n*]arenes (*n*=4) in DMF/methanol (8:5), sodium acetate (pH 7–9) with constant stirring to give yellow to dark red suspension. The reaction mixture was stirred for 3 h at 0–5 °C and then for 30 min at room temperature. The suspension was poured into water, acidified with concn HCl to give a yellow to dark red precipitate, which was filtered to give a product or a mixture of products. The mixture of products was then separated by column chromatography (silica gel) to give substituted azocalix[*n*]arene derivatives.

4.2.2. Synthesis of azocalix[*n*]arenes through the reaction between quinones and hydrazines (compounds 5a, 6a, 7a, 8a). To a solution of disubstituted-calix[4]arene diquinones (**7**, **8**) in $CHCl_3$ was added ethanol, nitrosubstituted phenyl hydrazines in presence of concn H_2SO_4. The reaction mixture was stirred for 4 h at room temperature and treated with cold water and extracted with chloroform. The organic phase was separated and dried with sodium sulfate and evaporated in vacuo to give orange powder, which was purified by recrystallization from chloroform/methanol.

4.2.3. Synthesis of substituted azocalix[*n*]arenes through the acetylation or benzylation reaction (compounds 10a, 11a,b, 12a,b, 13a, 14a, 14b, 15a). The synthesized azocalix[4]arenes (**1a**, **1b**, **1e**, **5a**, **6a**, **7a**, **8a**) and acetic anhydride (for acetylation) or benzoyl chloride (for benzoylation) (20 equiv) in dichloromethane/pyridine (10:1) were stirred at room temperature for a period of 24 h. The reaction mixture was poured into cold water, washed with 1 M HCl and water, and evaporated in vacuo to give a yellow solid.

4.2.4. 5,11,17-Tris(3′-pyridylazo)-25-(methoxy)-26,27,28-trihydroxycalix[4]arene, 2a. Afforded as an orange solid. Yield: 90%, mp>200 °C (decomposed). IR (KBr pellet, cm^{-1}): 3416, 1580, 1459, 1423. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): δ 9.12 (s, 2H, Py*H*), 9.00 (s, 1H, Py*H*), 8.60 (s, 2H, Py*H*), 8.52 (s, 1H, Py*H*), 8.06 (d, *J*=6.9 Hz, 2H, Py*H*), 7.96 (d, *J*=6.9 Hz, 1H, Py*H*), 7.81 (s, 4H, Ar*H*), 7.69 (s, 2H, Ar*H*), 7.38 (br s, 3H, Py*H*), 6.86 (br s, 2H, Ar*H*), 6.65 (br s, 1H), 4.52 (d, *J*=11.7 Hz, 2H, ArCH_2Ar), 4.39 (d, *J*=12.6 Hz, 2H, ArCH_2Ar), 3.93 (s, 3H, ArOCH_3), 3.64 (d, *J*=12.6 Hz, 2H, ArCH_2Ar), 3.53 (d, *J*=11.7 Hz, 2H, ArCH_2Ar). ^{13}C NMR (300 MHz, $CDCl_3$): 150.3, 149.7, 148.0, 146.4, 132.0, 130.4, 129.7, 128.9, 126.4, 125.4, 124.5, 123.7, 123.1 (Ar*C*H and Ar*C*), 63.6 (ArO*C*H_3), 33.5, 30.4 (Ar*C*H_2Ar). FABMS *m/z*: 754 (M^+). Anal. Calcd for $C_{44}H_{35}N_9O_4$: C, 70.11; H, 4.68; N, 16.72. Found: C, 70.35; H, 4.70; N, 16.65.

4.2.5. 5,11,17-Tris(4′-nitrophenylazo)-25-(methoxy)-26,27,28-trihydroxycalix[4]arene, 2b. Afforded as a red solid. Yield: 94%, mp>200 °C (decomposed). IR (KBr pellet, cm^{-1}): 3423, 1593, 1519, 1467, 1341. ^1H NMR (300 MHz, $CDCl_3$): δ 8.35 (d, *J*=8.7 Hz, 4H, NO_2–Ar*H*), 8.22 (d, *J*=8.4 Hz, 2H, NO_2–Ar*H*), 7.96 (d, *J*=8.7 Hz, 4H, NO_2–Ar*H*), 7.90 (d, *J*=8.4 Hz, 2H, NO_2–Ar*H*), 7.86 (s, 2H, Ar*H*), 7.85 (s, 2H, Ar*H*), 7.82 (s, 2H, Ar*H*), 7.14 (d, *J*=6.9 Hz, 2H, ArH_{meta}), 6.91 (t, *J*=6.9 Hz, 1H, ArH_{para}), 4.47 (t, *J*=13.5 Hz, 4H, ArCH_2Ar), 4.15 (s, 3H, ArOCH_3), 3.77 (d, *J*=13.5 Hz, 2H, ArCH_2Ar), 3.67 (d, *J*=13.2 Hz, 2H, ArCH_2Ar). FABMS *m/z*: 886 (M^+). Anal. Calcd for $C_{47}H_{35}N_9O_{10}$: C, 63.73; H, 3.98; N, 14.23. Found: C, 63.58; H, 4.00; N, 14.17.

4.2.6. 5-(4′-Pyridylazo)-25,27-di(ethoxycarbonyl methoxy)-26,28-dihydroxycalix[4]arene, 3a. Purified by column chromatography using hexane/ethyl acetate (7:3) as the eluent, orange solid. Yield: 10%, mp>230 °C (decomposed). IR (KBr pellet, cm^{-1}): 3262, 1750, 1652, 1584, 1464. ^1H NMR (300 MHz, $CDCl_3$): δ 8.72 (br s, 2H, Py*H*), 8.56 (br s, 1H, D_2O exchangeable, ArO*H*), 7.71 (s, 2H, Ar*H*), 7.62 (br s, 2H, Py*H*), 7.57 (s, 1H, D_2O exchangeable, ArO*H*), 7.00 (d, *J*=7.5 Hz, 2H, ArH_{meta}), 6.92 (d, *J*=7.5 Hz, 2H, ArH_{meta}), 6.89 (d, *J*=7.5 Hz, 2H, ArH_{meta}), 6.73 (t, *J*=7.5 Hz, 2H, ArH_{para}), 6.61 (t, *J*=7.5 Hz, 1H, ArH_{para}), 4.75 (dd, *J*=15.3, 15.9 Hz, 4H, ArOCH_2), 4.50 (d, *J*=13.5 Hz, 2H, ArCH_2Ar), 4.39 (d, *J*=13.2 Hz, 2H, ArCH_2Ar), 4.32 (q, *J*=6.9 Hz, 4H, –OCH_2CH$_3$), 3.48 (d, *J*=13.5 Hz, 2H, ArCH_2Ar), 3.37 (d, *J*=12.9 Hz, 2H, ArCH_2Ar), 1.32 (t, *J*=7.2 Hz, 6H, –OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): 166.5, 157.9, 152.8, 152.2, 151.0, 134.5, 133.2, 129.5, 129.2, 128.8, 128.5, 127.8, 125.7, 124.7, 119.2, 116.1 (Ar*C*H and Ar*C*), 72.4 (ArO*C*H_2), 61.4 (–O*C*H_2CH$_3$), 31.3, 29.6 (Ar*C*H_2Ar), 14.0 (–OCH$_2$*C*H$_3$). ESMS *m/z*: 702.61 (M^++1). Anal. Calcd for $C_{41}H_{39}N_3O_8$: C, 70.17; H, 5.60; N, 5.99. Found: C, 69.99; H, 5.56; N, 5.97. UV (λ_{max}, MeOH): 261, 379 nm.

4.2.7. 5-(3′-Pyridylazo)-25,27-di(ethoxycarbonyl methoxy)-26,28-dihydroxycalix[4]arene, 3b. Purified by column chromatography using hexane/chloroform (6:4) as the eluent, orange solid. Yield: 35%, mp>230 °C (decomposed). IR (KBr pellet, cm^{-1}): 3448, 1754, 1633, 1586, 1471. ^1H NMR (300 MHz, $CDCl_3$): δ 9.04 (s, 1H, Py*H*), 8.43 (br s, 2H, 1H–D_2O exchangeable, Py*H* and ArO*H*), 7.90 (d, *J*=7.2 Hz, 1H, Py*H*), 7.69 (s, 2H, Ar*H*), 7.56 (s, 1H, D_2O exchangeable, ArO*H*), 7.17 (dd, *J*=4.5, 3.3 Hz, 1H, Py*H*), 6.99 (d, *J*=6.9 Hz, 2H, ArH_{meta}), 6.84 (d, *J*=7.2 Hz, 2H, ArH_{meta}), 6.79 (d, *J*=7.2 Hz, 2H, ArH_{meta}), 6.59–6.52 (m, 3H, ArH_{para}), 4.71 (dd, *J*=15.0, 15.6 Hz, 4H, ArOCH_2), 4.47 (d, *J*=13.2 Hz, 2H, ArCH_2Ar), 4.38 (d, *J*=12.9 Hz, 2H, ArCH_2Ar), 4.27 (q, *J*=6.9 Hz, 4H, –OCH_2CH$_3$), 3.46

(d, J=13.2 Hz, 2H, ArCH_2Ar), 3.34 (d, J=12.9 Hz, 2H, ArCH_2Ar), 1.28 (t, J=6.9 Hz, 6H, –OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): 168.6, 157.2, 152.8, 152.1, 150.4, 148.1, 146.6, 145.5, 133.0, 132.1, 130.7, 129.4, 129.1, 128.5, 127.8, 126.6, 125.6, 124.1, 123.8, 119.1 (Ar*C*H and Ar*C*), 72.3 (ArOCH$_2$), 61.4 (–OCH$_2$CH$_3$), 31.3, 29.6 (ArCH$_2$Ar), 14.0 (–OCH$_2$CH$_3$). ESMS *m*/*z*: 702.61 (M^++1). Anal. Calcd for $C_{41}H_{39}N_3O_8$: C, 70.17; H, 5.60; N, 5.99. Found: C, 70.01; H, 5.57; N, 5.94. UV (λ_{max}, MeOH): 263, 372 nm.

4.2.8. 5,17-Bis(3′-pyridylazo)-25,27-di(ethoxycarbonyl methoxy)-26,28-dihydroxycalix[4]arene, 3c. Purified by column chromatography using $CHCl_3$/MeOH (9.9:0.1) as the eluent, red solid. Yield: 25%, mp>230 °C (decomposed). IR (KBr pellet, cm^{-1}): 3374, 1730, 1601, 1466. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.06 (s, 2H, Py*H*), 8.56 (br s, 2H, Py*H*), 8.39 (br s, 2H, D_2O exchangeable, ArO*H*), 8.01 (d, J=6.9 Hz, 2H, Py*H*), 7.70 (s, 4H, Ar*H*), 7.33 (dd, J=4.5, 3.3 Hz, 2H, Py*H*), 6.97 (d, J=6.9 Hz, 4H, ArH_{meta}), 6.76 (t, J=7.2 Hz, 2H, ArH_{para}), 4.69 (s, 4H, ArOCH_2), 4.47 (d, J=12.9 Hz, 4H, ArCH_2Ar), 4.31 (q, J=6.9 Hz, 4H, –OCH_2CH$_3$), 3.51 (d, J=12.9 Hz, 4H, ArCH_2Ar), 1.33 (t, J=6.6 Hz, 6H, –OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): 168.7, 157.2, 152.2, 150.5, 148.2, 146.7, 145.7, 132.4, 129.6, 128.5, 126.7, 125.9, 124.2, 123.8 (ArCH and ArC), 72.4 (ArOCH_2), 61.5 (–OCH_2CH$_3$), 31.4 (ArCH_2Ar), 14.1 (–OCH$_2$CH_3). FABMS *m*/*z*: 806 (M^+). Anal. Calcd for $C_{46}H_{42}N_6O_8$: C, 68.47; H, 5.25; N, 10.42. Found: C, 68.35; H, 5.20; N, 10.34. UV (λ_{max}, MeOH): 257, 370 nm.

4.2.9. 5-(3′-Pyridylazo)-25,27-dimethoxy-26,28-dihydroxycalix[4]arene, 4a. Purified by column chromatography using $CHCl_3$/MeOH (9.95:0.05) as the eluent, yellow solid. Yield: 40%, mp 180 °C. IR (KBr pellet, cm^{-1}): 3274, 1653, 1590, 1470. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (s, 1H, Py*H*), 8.64 (d, J=3.6 Hz, 1H, Py*H*), 8.51 (br s, 1H, D_2O exchangeable, ArO*H*), 8.09 (d, J=8.1 Hz, 1H, Py*H*), 7.78 (s, 2H, Ar*H*), 7.76 (s, 1H, D_2O exchangeable, ArO*H*), 7.40 (dd, J=4.2, 4.2 Hz, 1H, Py*H*), 7.10 (d, J=7.2 Hz, 2H, ArH_{meta}), 6.95 (d, J=7.2 Hz, 2H, ArH_{meta}), 6.90 (d, J=7.5 Hz, 2H, ArH_{meta}), 6.74–6.70 (m, 3H, ArH_{para}), 4.37 (t, J=12.9 Hz, 4H, ArCH_2Ar), 4.00 (s, 6H, ArOCH_3), 3.57 (d, J=13.2 Hz, 2H, ArCH_2Ar), 3.44 (d, J=13.2 Hz, 2H, ArCH_2Ar). ^{13}C NMR (300 MHz, $CDCl_3$): 157.2, 153.0, 150.4, 148.1, 146.6, 145.5, 132.7, 131.8, 129.3, 129.0, 128.5, 127.7, 126.5, 125.3, 124.1, 123.7, 119.1 (Ar*C*H and Ar*C*), 63.5 (ArOCH_3), 31.0, 29.5 (ArCH_2Ar). FABMS *m*/*z*: 558 (M^+). Anal. Calcd for $C_{35}H_{31}N_3O_4$: C, 75.38; H, 5.60; N, 7.54. Found: C, 75.25; H, 5.58; N, 7.51. UV (λ_{max}, MeOH): 260, 369 nm.

4.2.10. 5,17-Bis(3′-pyridylazo)-25,27-dimethoxy-26,28-dihydroxycalix[4]arene, 4b. Purified by column chromatography using $CHCl_3$/MeOH (9.9:0.1) as the eluent, orange solid. Yield: 22%, mp>230 °C (decomposed). IR (KBr pellet, cm^{-1}): 3382, 1630, 1586, 1473. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (s, 2H, Py*H*), 8.64 (br s, 2H, Py*H*), 8.50 (br s, 2H, D_2O exchangeable, ArO*H*), 8.10 (d, J=7.8 Hz, 2H, Py*H*), 7.79 (s, 4H, Ar*H*), 7.43 (dd, J=4.5, 3.3 Hz, 2H, Py*H*), 7.00 (d, J=7.5 Hz, 4H, ArH_{meta}), 6.80 (t, J=7.2 Hz, 2H, ArH_{para}), 4.37 (d, J=13.2 Hz, 4H, ArCH_2Ar), 4.03 (s, 6H, ArOCH_3), 3.60 (d, J=13.2 Hz, 4H, ArCH_2Ar). ^{13}C NMR (300 MHz, $CDCl_3$): 157.2, 153.1, 150.6, 148.1, 146.7, 145.7, 132.1, 129.4, 128.5, 126.6, 125.5, 124.1, 123.8 (ArCH and ArC), 63.8 (ArOCH_3), 31.1 (ArCH_2Ar). FABMS *m*/*z*: 662 (M^+). Anal. Calcd for $C_{40}H_{34}N_6O_4$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.35; H, 5.14; N, 12.62. UV (λ_{max}, MeOH): 258, 372 nm.

4.2.11. 5,17-Bis(4′-nitrophenylazo)-25,27-dibenzoyloxy-26,28-dihydroxycalix[4]arene, 5a. Obtained as a red solid. Yield: 78%, mp>270 °C (decomposed). IR (KBr pellet, cm^{-1}): 3500, 1729, 1655, 1595, 1518, 1461, 1343, 1262. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (d, J=9 Hz, 4H, NO_2–Ar*H*), 8.25 (d, J=7.5 Hz, 4H, *o*-Ar′*H*), 7.84 (d, J=8.7 Hz, 4H, NO_2–Ar*H*), 7.71 (s, 4H, Ar*H*), 7.60 (m, 4H, *m*-Ar′*H*), 7.44 (t, J=7.8 Hz, 2H, *p*-Ar′*H*), 7.12 (d, J=7.2 Hz, 4H, ArH_{meta}), 7.02 (t, J=7.5 Hz, 2H, ArH_{para}), 5.98 (br s, 2H, D_2O exchangeable, ArO*H*), 4.07 (d, J=14.4 Hz, 4H, ArCH_2Ar), 3.71 (d, J=14.4 Hz, 4H, ArCH_2Ar). ^{13}C NMR (300 MHz, $CDCl_3$): 134.0, 133.8, 132.8, 132.0, 130.5, 130.0, 129.7, 128.9, 128.4, 126.9, 126.1, 125.2, 124.6, 123.0 (Ar*C*H and Ar*C*), 32.9 (Ar*C*H$_2$Ar). FABMS *m*/*z*: 930 (M^+). Anal. Calcd for $C_{54}H_{38}N_6O_{10}$: C, 69.67; H, 4.11; N, 9.03. Found: C, 69.65; H, 4.09; N, 9.01.

4.2.12. 5,17-Bis(4′-nitrophenylazo)-25,27-dibenzyloxy-26,28-dihydroxycalix[4]arene, 6a. Obtained as a red solid. Yield: 78%, mp>240 °C (decomposed). IR (KBr pellet, cm^{-1}): 3378, 1588, 1519, 1463, 1262. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (br s, 2H, D_2O exchangeable, ArO*H*), 8.29 (d, J=8.7 Hz, 4H, NO_2–Ar*H*), 7.89 (d, J=8.7 Hz, 4H, NO_2–Ar*H*), 7.73 (s, 4H, Ar*H*), 7.58 (d, J=5.4 Hz, 4H, *o*-Ar′*H*), 7.35 (m, 6H, *m*-Ar′*H* and *p*-Ar′*H*), 6.94 (d, J=7.5 Hz, 4H, ArH_{meta}), 6.75 (t, J=7.5 Hz, 2H, ArH_{para}), 5.05 (s, 4H, Ar′CH_2), 4.30 (d, J=13.2 Hz, 4H, ArCH_2Ar), 3.42 (d, J=13.2 Hz, 4H, ArCH_2Ar). FABMS *m*/*z*: 902 (M^+). Anal. Calcd for $C_{54}H_{42}N_6O_8$: C, 71.83; H, 4.69; N, 9.31. Found: C, 71.81; H, 4.67; N, 9.29.

4.2.13. 5,17-Bis(2′,4′-dinitrophenylazo)-25,27-dibenzoyloxy-26,28-dihydroxycalix[4]arene, 7a. Obtained as a red solid. Yield: 84%, mp>250 °C (decomposed). IR (KBr pellet, cm^{-1}): 3506, 1732, 1660. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.91 (br s, 2H, D_2O exchangeable, ArO*H*), 8.75 (s, 2H, NO_2–Ar*H*), 8.43 (dd, J=2.1, 2.1 Hz, 4H, NO_2–Ar*H*), 8.23 (d, J=7.2 Hz, 4H, *o*-Ar′*H*), 7.77 (s, 4H, Ar*H*), 7.57 (m, 4H, *m*-Ar′*H*), 7.38 (t, J=8.7 Hz, 2H, *p*-Ar′*H*), 7.04 (d, J=8.2 Hz, 4H, ArH_{meta}), 6.95 (t, J=7.5 Hz, 2H, ArH_{para}), 4.04 (d, J=15.3 Hz, 4H, ArCH_2Ar), 3.73 (d, J=15.3 Hz, 4H, ArCH_2Ar). FABMS *m*/*z*: 1020 (M^+). Anal. Calcd for $C_{54}H_{36}N_8O_{14}$: C, 63.53; H, 3.55; N, 10.98. Found: C, 63.50; H, 3.52; N, 10.96.

4.2.14. 5,17-Bis(2′,4′-dinitrophenylazo)-25,27-dibenzyloxy-26,28-dihydroxycalix[4]arene, 8a. Obtained as a red solid. Yield: 81%, mp>280 °C (decomposed). IR (KBr pellet, cm^{-1}): 3206, 1598, 1531, 1461, 1345. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.93 (br s, 2H, D_2O exchangeable, ArO*H*), 8.76 (s, 2H, NO_2–Ar*H*), 8.50 (dd, J=2.4, 2.4 Hz, 4H, NO_2–Ar*H*), 7.84 (d, J=9 Hz, 4H, *o*-Ar′*H*), 7.78 (s, 4H, Ar*H*), 7.64 (m, 4H, *m*-Ar′*H*), 7.43 (d, J=6.3 Hz, 2H, *p*-Ar′*H*), 7.00 (d, J=7.5 Hz, 4H, ArH_{meta}), 6.86 (t, J=7.2 Hz, 2H, ArH_{para}), 5.12 (s, 4H, Ar′CH_2), 4.35 (d, J=13.2 Hz, 4H, ArCH_2Ar), 3.53 (d, J=13.2 Hz, 4H, ArCH_2Ar).

FABMS *m/z*: 992 (M^+). Anal. Calcd for $C_{54}H_{40}N_8O_{12}$: C, 65.32; H, 4.06; N, 11.29. Found: C, 65.30; H, 4.04; N, 11.26.

4.2.15. 5-(4′-Nitrophenylazo)-25,26,27-trimethoxy-28-hydroxycalix[4]arene, 9b. Obtained as a yellow solid. Yield: 12%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, J=8.7 Hz, 2H, NO_2–ArH), 7.90 (d, J=8.7 Hz, 2H, NO_2–Ar*H*), 7.90 (d, J=8.7 Hz, 2H, NO_2–Ar*H*), 7.73 (s, 2H, Ar*H*), 7.30 (d, J=6.9 Hz, 2H, Ar*H*), 7.11 (d, J=6.9 Hz, 2H, Ar*H*), 6.95–6.39 (m, 7H, Ar*H*), 4.33 (t, J=13.2 Hz, 4H, ArCH_2Ar), 3.90 (s, 3H, OCH_3), 3.79 (s, 6H, OCH_3), 3.45 (d, J=13.8 Hz, 2H, ArCH_2Ar), 3.23 (d, J=13.8 Hz, 2H, ArCH_2Ar). FABMS *m/z*: 616 (M^+). Anal. Calcd for $C_{37}H_{33}N_3O_6$: C, 72.18; H, 5.40; N, 6.83. Found: C, 71.93; H, 5.37; N, 6.76.

4.2.16. 5(3′-Pyridylazo)-25,26,27,28-tetracetyloxy-calix[4]arene, 10a. Obtained as a yellow solid. Yield: 72%, mp>230 °C (decomposed). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.16 (s, 1H, Py*H*), 8.73 (br s, 1H, Py*H*), 8.32 (d, 1H, J=6.9 Hz, Py*H*), 7.71 (s, 2H, Ar*H*), 7.48 (br m, 1H, Py*H*), 7.10–6.61 (m, 9H, Ar*H*), 3.88 (d, J=14.1 Hz, 2H, ArCH_2Ar), 3.76 (s, 4H, ArCH_2Ar), 3.60 (d, J=14.1 Hz, 2H, ArCH_2Ar), 2.38 (s, 3H, –COCH_3), 1.78 (s, 3H, –COCH_3), 1.68 (s, 6H, –COCH_3). DEPT-135 NMR (300 MHz, $CDCl_3$): 152.4, 147.7, 129.5, 127.3, 126.1, 125.9, 125.2, 124.4, 124.1, 119.6 (Ar*C*H), 37.5, 37.4 (Ar*C*H_2Ar), 21.5, 20.7, 20.6 (–CO*C*H_3). FABMS *m/z*: 698 (M^+). Anal. Calcd for $C_{41}H_{35}N_3O_8$: C, 70.58; H, 5.06; N, 6.02. Found: C, 70.78; H, 5.08; N, 5.98.

4.2.17. 5,17-Bis(4′-nitrophenylazo)-25,27-diacetyloxy-26,28-benzoyloxycalix[4]arene, 11a. Obtained as an orange solid. Yield: 76%, mp>320 °C. IR (KBr pellet, cm^{-1}): 1754, 1731, 1601, 1521, 1458, 1345. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, J=8.4 Hz, 4H, NO_2–Ar*H*), 7.58 (d, J=7.5 Hz, 4H, *o*-Ar′*H*), 7.40 (d, J=8.7 Hz, 4H, NO_2–Ar*H*), 7.28 (s, 4H, Ar*H*), 7.12 (m, 8H, *m*-Ar′*H* and ArH_{meta}), 6.96 (t, J=7.5 Hz, 4H, *p*-Ar′*H* and ArH_{para}), 3.80 (d, J=15.6 Hz, 4H, ArCH_2Ar), 3.63 (d, J=15.6 Hz, 4H, ArCH_2Ar), 2.00 (s, 6H, –COCH_3). ^{13}C NMR (300 MHz, $CDCl_3$): 148.3, 134.5, 133.3, 132.9, 130.5, 130.2, 128.3, 125.6, 124.9, 124.4, 123.2 (Ar*C*H and Ar*C*), 37.2 (Ar*C*H_2Ar), 21.0 (CO*C*H_3). FABMS *m/z*: 1014 (M^+). Anal. Calcd for $C_{58}H_{42}N_6O_{12}$: C, 68.63; H, 4.17; N, 8.28. Found: C, 68.61; H, 4.13; N, 8.23.

4.2.18. 5,17-Bis(4′-nitrophenylazo)-25,27-diacetyloxy-26,28-benzyloxycalix[4]arene, 11b. Obtained as an orange solid. Yield: 69%, mp 180 °C. IR (KBr pellet, cm^{-1}): 1750, 1589, 1521, 1460, 1341. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (d, J=8.1 Hz, 4H, NO_2–Ar*H*), 7.98 (d, J=8.4 Hz, 4H, NO_2–Ar*H*), 7.78 (s, 4H, Ar*H*), 7.29 (m, 10H, Ar′*H*), 6.87 (m, 6H, Ar*H*), 5.08 (s, 4H, Ar′CH_2), 4.80 (d, J=12 Hz, 4H, ArCH_2Ar), 4.73 (d, J=12 Hz, 4H, ArCH_2Ar), 2.15 (s, 6H, –COCH_3). FABMS *m/z*: 986 (M^+). Anal. Calcd for $C_{58}H_{46}N_6O_{10}$: C, 70.58; H, 4.70; N, 8.51. Found: C, 70.56; H, 4.67; N, 8.50.

4.2.19. 5,17-Bis(2′,4′-dinitrophenylazo)-25,27-diacetyloxy-26,28-benzoyloxycalix[4]arene, 12a. Obtained as an orange solid. Yield: 67%, mp>270 °C (decomposed). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (s, 2H, NO_2–Ar*H*), 8.36 (dd, J=3, 3 Hz, 4H, NO_2–Ar*H*), 7.52 (s, 4H, Ar*H*), 7.24–6.94 (m, 16H, Ar*H* and Ar′*H*), 3.83 (d, J=15.6 Hz, 4H, ArCH_2Ar), 3.70 (d, J=15.6 Hz, 4H, ArCH_2Ar), 1.94 (s. 6H, –COCH_3). ^{13}C NMR (300 MHz, $CDCl_3$): 148.5, 134.7, 134.1, 133.4, 131.6, 126.3, 125.6, 124.9, 124.6, 123.0 (Ar*C*H and Ar*C*), 37.4 (Ar*C*H_2Ar), 21.2 (CO*C*H_3). FABMS *m/z*: 1104 (M^+). Anal. Calcd for $C_{58}H_{40}N_8O_{16}$: C, 63.04; H, 3.65; N, 10.14. Found: C, 63.01; H, 3.62; N, 10.11.

4.2.20. 5,17-Bis(2′,4′-dinitrophenylazo)-25,27-diacetyloxy-26,28-benzyloxycalix[4]arene, 12b. Obtained as an orange solid. Yield: 71%, mp>250 °C (decomposed). IR (KBr pellet, cm^{-1}): 1743, 1728, 1603, 1537, 1456, 1347. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (s, 2H, NO_2–Ar*H*), 8.56 (dd, J=2.2, 2.2 Hz, 4H, NO_2–Ar*H*), 7.71 (s, 4H, Ar*H*), 7.51 (d, J=9 Hz, 4H, *o*-Ar′*H*), 7.23 (m, 6H, *m*-Ar′*H* and *p*-Ar′*H*), 6.77 (d, J=7.2 Hz, 4H, ArH_{meta}), 6.69 (t, J=8.7 Hz, 2H, ArH_{para}), 4.78 (s, 4H, Ar′CH_2), 4.72 (d, J=10.5 Hz, 4H, ArCH_2Ar), 4.64 (d, J=10.5 Hz, 4H, ArCH_2Ar), 1.94 (s, 6H, –COCH_3). FABMS *m/z*: 1076 (M^+). Anal. Calcd for $C_{58}H_{44}N_8O_{14}$: C, 64.68; H, 4.12; N, 10.40. Found: C, 64.63; H, 4.10; N, 10.44.

4.2.21. 5,11-Bis(3′-pyridylazo)-25,26,27,28-tetrabenzyloxycalix[4]arene, 13a. Obtained as an orange solid. Yield: 72%, mp>230 °C (decomposed). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81–6.40 (m, 38H, Ar*H* and Py*H*), 4.09–3.45 (m, 8H, ArCH_2Ar). ^{13}C NMR (300 MHz, $CDCl_3$): 163.7, 152.0, 151.5, 148.1, 147.3, 146.8, 135.4, 133.8, 133.6, 133.3, 132.9, 131.3, 130.6, 129.8, 129.4, 129.1, 128.7, 128.2, 127.9, 126.9, 126.6, 126.0, 125.7, 125.0, 123.6, 122.3 (Ar*C*H and Ar*C*), 37.8, 36.9, 30.2, 29.6 (Ar*C*H_2Ar). FABMS *m/z*: 1051 (M^+). Anal. Calcd for $C_{66}H_{46}N_6O_8$: C, 75.42; H, 4.41; N, 8.00. Found: C, 75.25; H, 4.43; N, 8.05.

4.2.22. 5,11,17-Tris(3′-pyridylazo)-25,26,27-tri-acetyloxy-28-methoxycalix[4]arene, 14a. Obtained as an orange solid. Yield: 70%, mp 155 °C. IR (KBr pellet, cm^{-1}): 1753, 1648, 1575, 1462. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (s, 1H, Py*H*), 9.17 (s, 1H, Py*H*), 9.06 (s, 1H, Py*H*), 8.75–8.67 (m, 3H, Py*H*), 8.21–6.66 (m, 15H, Py*H* and Ar*H*), 4.17–3.42 (m, 11H, ArCH_2Ar and ArOCH_3), 2.27 (s, 3H, –COCH_3), 1.85 (s, 3H, –COCH_3), 1.50 (s, 3H, –COCH_3). DEPT-135 NMR (300 MHz, $CDCl_3$): 152.3, 151.2, 147.7, 147.1, 130.6, 130.2, 128.4, 127.3, 127.0, 126.0, 125.7, 124.6, 124.4, 123.6, 120.3, 120.1 (Ar*C*H), 61.7 (ArO*C*H_3), 38.4, 37.8, 31.7, 30.4 (Ar*C*H_2Ar), 21.2, 20.6, 20.2 (–CO*C*H_3). FABMS *m/z*: 880 (M^+). Anal. Calcd for $C_{50}H_{41}N_9O_7$: C, 68.25; H, 4.70; N, 14.33. Found: C, 68.11; H, 4.71; N, 14.29.

4.2.23. 5,11,17-Tris(4′-nitrophenylazo)-25,26,27-tri-acetyloxy-28-methoxycalix[4]arene, 14b. Obtained as an orange solid. Yield: 83%, mp 162 °C. IR (KBr pellet, cm^{-1}): 1756, 1595, 1522, 1462, 1342. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37–6.60 (m, 21H, Py*H* and Ar*H*), 4.09–3.20 (m, 11H, ArCH_2Ar and ArOCH_3), 2.37 (s, 3H, –COCH_3), 1.91 (s, 3H, –COCH_3), 1.49 (s, 3H, –COCH_3). FABMS *m/z*: 1012 (M^+). Anal. Calcd for $C_{53}H_{41}N_9O_{13}$: C, 62.91; H, 4.08; N, 12.46. Found: C, 62.63; H, 4.10; N, 12.38.

4.2.24. 5,11,17,23-Tetrakis(3′-pyridylazo)-25,26,27,28-tetracetyloxycalix[4]arene, 15a. Obtained as an orange solid. Yield: 92%, mp 180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (s, 4H, Py*H*), 8.63 (d, J=4.2 Hz, 1H, Py*H*), 8.03 (d, J=7.8 Hz, 1H, Py*H*), 7.68 (s, 8H, Ar*H*), 7.39 (dd,

J=4.8, 4.2 Hz, 4H, Py*H*), 3.92 (s, 8H, ArCH_2Ar), 3.76 (s, 4H, ArCH_2Ar), 3.60 (d, J=14.1 Hz, 2H, ArCH_2Ar), 1.50 (s, 12H, –COCH_3). DEPT-135 NMR (300 MHz, $CDCl_3$): 149.4, 144.6, 129.4, 126, 125.2 (Ar*C*H), 38.2 (Ar*C*H_2Ar), 21.0 (–CO*C*H_3). FABMS *m/z*: 1013 (M^+). Anal. Calcd for $C_{56}H_{44}N_{12}O_8$: C, 66.40; H, 4.38; N, 16.59. Found: C, 66.63; H, 4.38; N, 16.64.

4.3. X-ray Structure Determination of 3b

Crystal data: $C_{41}H_{35}N_3O_8\times 2CCl_3$; M=934; triclinic; a=10.2509(18) Å, b=14.302(3) Å, c=14.672(3) Å; α=93.644(3)°, β=97.642(3)°, γ=106.115(3)°; V=2036.7(6) Å^3; Z=2; Dc=1.427 g cm^{-3}; μ=0.381 mm^{-1}; space group=P1. Intensity data were collected up to θ=47.4° by using 2θ scanning mode with graphite filtered Mo Kα radiation (λ=0.71073) on a 0.249×0.116×0.072 mm^3 crystal at 100(2) K. A total of 15,324 reflections were measured, 7481 were independent and of which 5532 [I>2(I)] were considered observed. Final R indices [I>2σ(I)] R1=0.0856, wR2=0.2265, and R indices (all data) R1=0.1093, wR2=0.2436 was found for 7481 observed reflections, 0 restraints, and 605 parameters. The apparent high R values are possibly due to the disorder found in azopyridyl unit and the solvent molecules. The structure was solved by direct methods and refined by full matrix least-square techniques on F^2 using SHELXTL. All the nonhydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions by using a riding model. SADABS was applied for absorption correction. Torsion angles and H-bonding were calculated using PARST. Crystal data have been deposited with the Cambridge Crystallographic Data Center, under reference CCDC 281637.

4.4. X-ray Structure Determination of 12a

Crystal data: $C_{58}H_{40}N_8O_{16}$; M=1104.98; triclinic; a=11.229(3) Å, b=14.397(4) Å, c=17.555(5) Å; α=103.152(5)°, β=102.341(5)°, γ=101.175(6)°; V=2610.6(12) Å^3; Z=2; Dc=1.406 g cm^{-3}; μ=0.105 mm^{-1}; space group=P1. Intensity data were collected up to θ=45° by using 2θ scanning mode with graphite filtered Mo Kα radiation (λ=0.71073) on a 0.219×0.109×0.105 mm^3 crystal at 298(2) K. A total of 20,423 reflections were measured, 6806 were independent and of which 4938 [I>2(I)] were considered observed. The structure was solved by direct methods and refined by full matrix least-square techniques on F^2 using SHELXTL. All the nonhydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions by using a riding model. SADABS was applied for absorption correction. Final R indices [I>2σ(I)] R1=0.0929, wR2=0.1830, and R indices (all data) R1=0.1303, wR2=0.1996 was found for 6806 observed reflections, 0 restraints, and 741 parameters. Torsion angles and H-bonding were calculated using PARST. Crystal data have been deposited with the Cambridge Crystallographic Data Center, under reference CCDC No. 294509.

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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.2006.05.040.

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