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Diallylbis(arylazo)calix[4]arenes: the Syntheses of Calix[4]arenes with Two Different *Para*-Substituents

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Abstract: The diazonium coupling between two kinds of *p*-diallylcalix[4]arenes (**3** and **4**) and *p*-substituted benzenediazonium salts yielded calix[4]arenes with two different substituents on their para-position. The synthesis and the ^{1}H-NMR spectral characteristic features of the two *p*-diallylcalix[4]arenes and their arylazo derivatives are discussed.

INTRODUCTION

Calixarenes, which are cavity-containing compounds, have been proposed in the research areas of host-guest complexation and enzyme-mimic studies.[1] However, the calixarenes which have a potential as the enzyme-mimic model can not be prepared directly from the corresponding phenols and formaldehyde, and hence, the preparation of calixarenes with an appropriate functional group in the proper position is a real challenge for chemists.

It is well-known that most of the functional groups are not able to be incorporated into calixarenes by a direct condensation process.[2] Therefore, the functional groups are introduced into the existing calixarene framework by a functionalized method either in the "lower rim" (the oxygen-position of the phenolic moieties) or in the "upper tim" (the *p*-position of the aromatic nuclei).[1] Literature surveys show that the majority of studies have concentrated on the lower rim functionalization, with only a few concentrating on the calixarene's upper rim. The surveys also show that only one kind of substituent was introduced in these functionalized methods, and calixarenes with two different kinds of substituents could only be achieved by using the long and tedious stepwise method.[3] Among the upper rim functionalized methods, Gutsche and his coworker reported that the allyl group could be introduced by the Claisen rearrangement route,[4] and several research groups reported that the arylazo groups could be introduced by a diazonium coupling method.[5] It is logical to propose a general synthetic method to functionalize calix[4]arene's upper rim with two different kinds of substituents, the allyl groups by Claisen rearrangement and *p*-substituted phenylazo groups by diazonium coupling reaction. In this paper we report the synthesis of diallylbis(arylazo)-calix[4]arenes and diallylmono(arylazo)calix[4]arenes by this synthetic strategy.

RESULTS AND DISCUSSION

***p*-Diallylcalix[4]arenes (3 and 4).** Gutsche and his coworkers reported that the calixarene allyl ethers were able to transform to the corresponding *p*-allylcalixarenes by the heat-induced Claisen rearrangement.[4] It is assumed that the partially *p*-allyl substituted calix[4]arenes could also be prepared from the corresponding partially allyloxylated calix[4]arenes in the same rearrangement. The two diallyl ethers were prepared according to the general procedures reported by Reinhoudt and his coworkers for the calix[4]arene's 1,2-dialkyl ethers and 1,3-dialkyl ethers.[6,7] Calix[4]arene 1,3-diallyl ether **1** was prepared by refluxing calix[4]arene with allyl bromide in CH_3CN in the presence of K_2CO_3, whereas, calix[4]arene 1,2-diallyl ether **2** was prepared by stirring calix[4]arene with allyl bromide in CH_3CN in the presence of NaH at room temperature. In the preparation of 1,2-diallyl ether **2**, we noticed that if the reactions were carried out either at an elevated temperature or for a longer period, a deep purple color solution accompanied with a large amount of tetraallyl ether resulted. In these cases, the final isolated yield of 1,2-diallyl ether **2** was reduced. Therefore, the reaction was quenched by treating with acetic acid as soon as the deep purple color appeared to ensure a maximum yield of 1,2-diallyl ether **2**.

The number of the ether linkages of ethers **1** and **2** was easily determined by their mass spectra, and the similarity of ^{1}H-NMR spectra between diallyl ether **1** and calix[4]arene *syn*-1,3-dibenzoate suggested that compound **1** also possessed *syn*-1,3-diallyl structure.[8] Although, the ^{1}H-NMR spectrum of the diallyl ether **2** did not reveal any information about the positions and the orientation of the two allyloxy moieties, the structure of compounds **1** and **2** can be decided by their ^{13}C-NMR spectral feature.[9] Alternatively, the exact position of the two allyloxy groups in compounds **1** and **2** can be determined by characterization of their Claisen rearrangement products.

The two *p*-diallylcalix[4]arenes **3** and **4** which were prepared by refluxing the corresponding diallyl ethers **1** and **2** in *N,N*-diethylaniline under an inert atmosphere displayed very different ^{1}H-NMR spectra from the starting ethers, and the upfield shift of the allylic methylene hydrogens (from δ=4.5 to δ=3.2) indicated that the allyl moieties had been transferred from the lower rim to the upper rim. When the ^{1}H-NMR spectra of 5,17-diallyl **3** and 5,11-diallyl **4** were measured at room temperature, it surprised us to notice that two indistinguishable spectra which not only displayed the same chemical shifts but also composed of identical splitting patterns for respective hydrogens were recorded. However, when the ^{1}H-NMR spectra of the same compounds were measured at -20°C, a distinct splitting pattern for the calix[4]arene's methylene hydrogens was observed (Figure 1). Compound **3** which was 5,17-diallylcalix[4]arene displayed a pair of doublets, whereas, three pairs of doublets which was known to arise from the 5,11-disubstituted calix[4]arene was observed in the spectrum of compound **4**.[10] This result indicated that compound **2** must be calix[4]arenes 1,2-diallyl ether in order to produce 5,11-diallylcalix[4]arene (**4**) in the Claisen rearrangement.

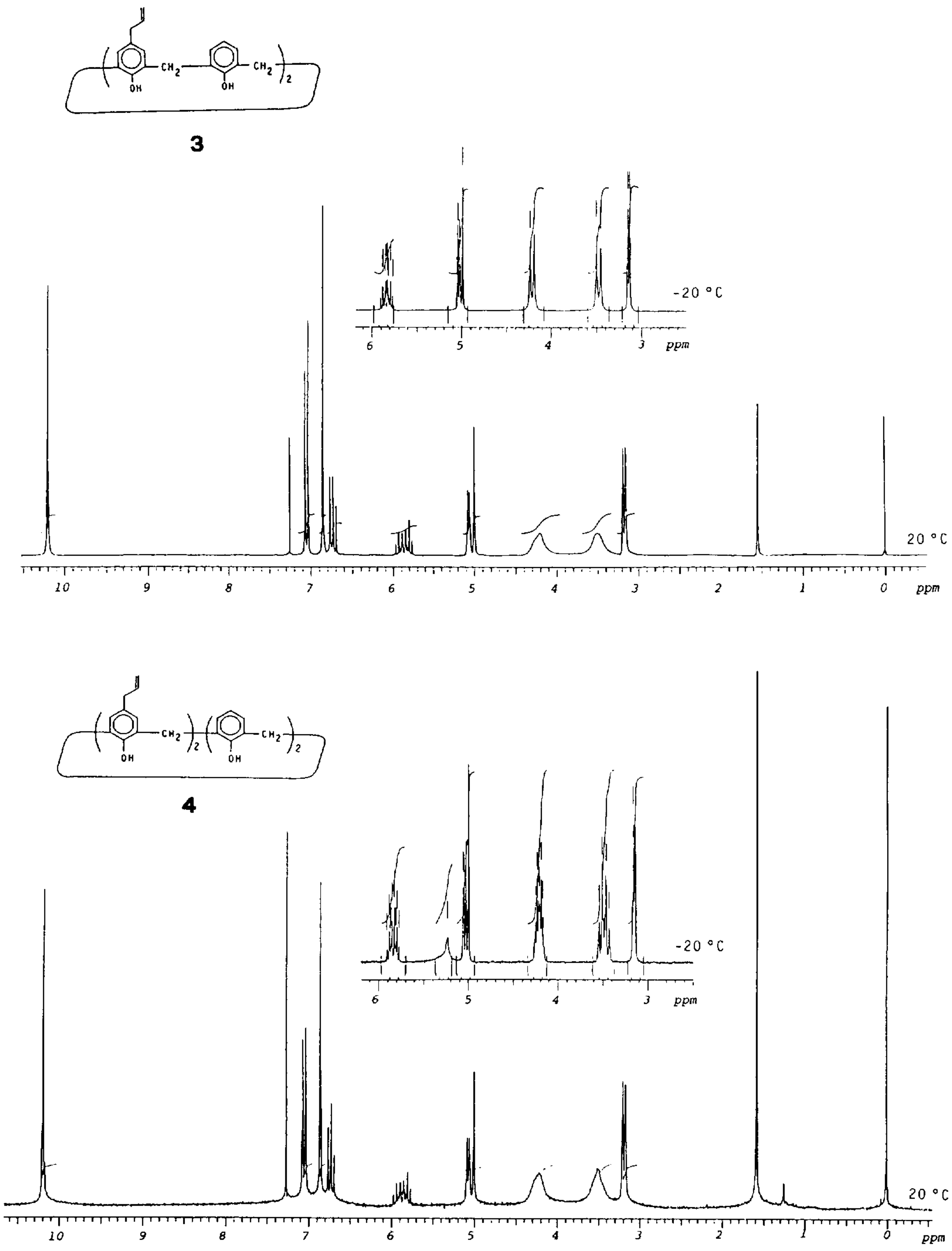
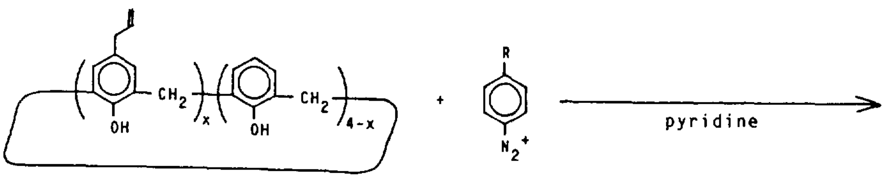
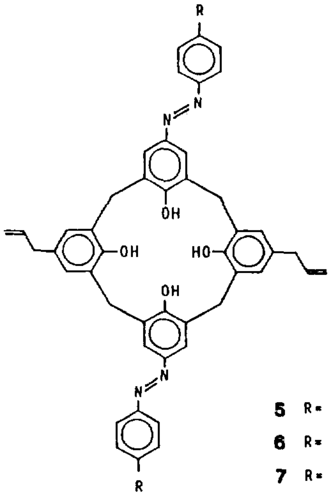


Figure 1. ^{1}H-NMR spectrum of compounds **3** and **4** in $CDCl_3$ at various temperature.



3 x=2, 1,3-diallyl-

4 x=2, 1,2-diallyl-



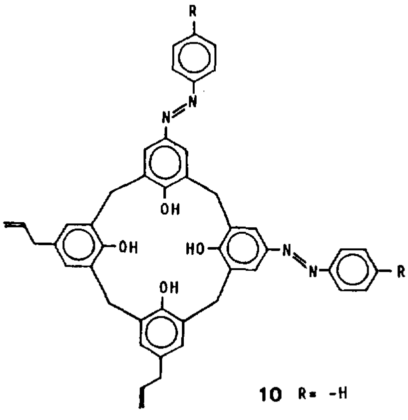
5 R= -H

6 R= $-CH_3$

7 R= -COOH

8 R= $-NO_2$

9 R= $-OCH_3$



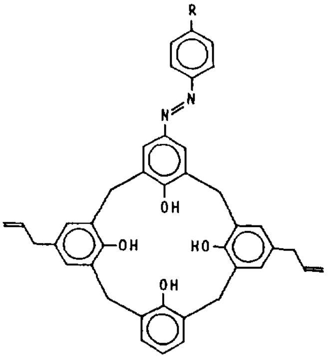
10 R= -H

11 R= $-CH_3$

12 R= -COOH

13 R= $-NO_2$

14 R= $-OCH_3$



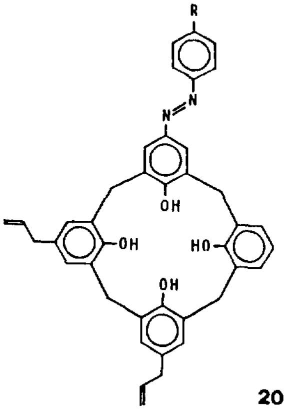
15 R= -H

16 R= $-CH_3$

17 R= -COOH

18 R= $-NO_2$

19 R= $-OCH_3$



20 R= -H

21 R= $-CH_3$

22 R= -COOH

23 R= $-NO_2$

24 R= $-OCH_3$

5,17-Diallyl-11,23-bis(arylazo)calix[4]arenes (5-9) and 5,11-diallyl1-7,23-bis(arylazo)calix[4]arene (10-14). Applying the same methodology for the preparation of the fully substituted *p*-arylazocalixarenes,[5] the syntheses of diallylbis(arylazo)calix[4]arenes were studied. When compounds **3** or **4** were treated with various *p*-substituted benzenediazonium salts in pyridine and THF, the corresponding 5,17-diallyl-11,23-bis[(*p*-substituted phenyl)azo]calix[4]arenes (**5-9**) or 5,11-diallyl-17,23-bis[(*p*-substituted phenyl)azo]calix[4]arenes (**10-14**) were afforded as colorful products, respectively. These bisarylazo products displayed the similar ^{1}H-NMR spectra pattern as starting materials **3** or **4** except for the signals in the aromatic region. In this region, the total disappearance of a set of a doublet and a triplet which arose from the non-substituted calixarene's aromatic ring strongly indicated that the starting materials were converted to the corresponding bisarylazo products.

The 1,3-bisarylazo products **5-9** belong to the same symmetrical point group (C_{2v}) as starting material **3**, and hence, the spectral assignment for the calixarene's aromatic hydrogens was straightforward. Although, the 1,2-bis-arylazo products **10-14** belong to the same symmetrical point group (C_v) as starting material **4**, in contrast to the previous cases, complex ^{1}H-NMR spectra were observed for the same hydrogens. The eight calixarenes' aromatic hydrogens of the 1,2-bisarylazo products located on two different kinds of *p*-substituted aromatic rings, were grouped into four different pairs. Each pair of hydrogens experienced a different magnetic environment from the adjacent p-substituted aromatic rings, and a pattern of four doublets was observed. Most of the 1,2-bisarylazo products showed an overlapping spectra, but four sets of doublets were clearly displayed in the aromatic region in

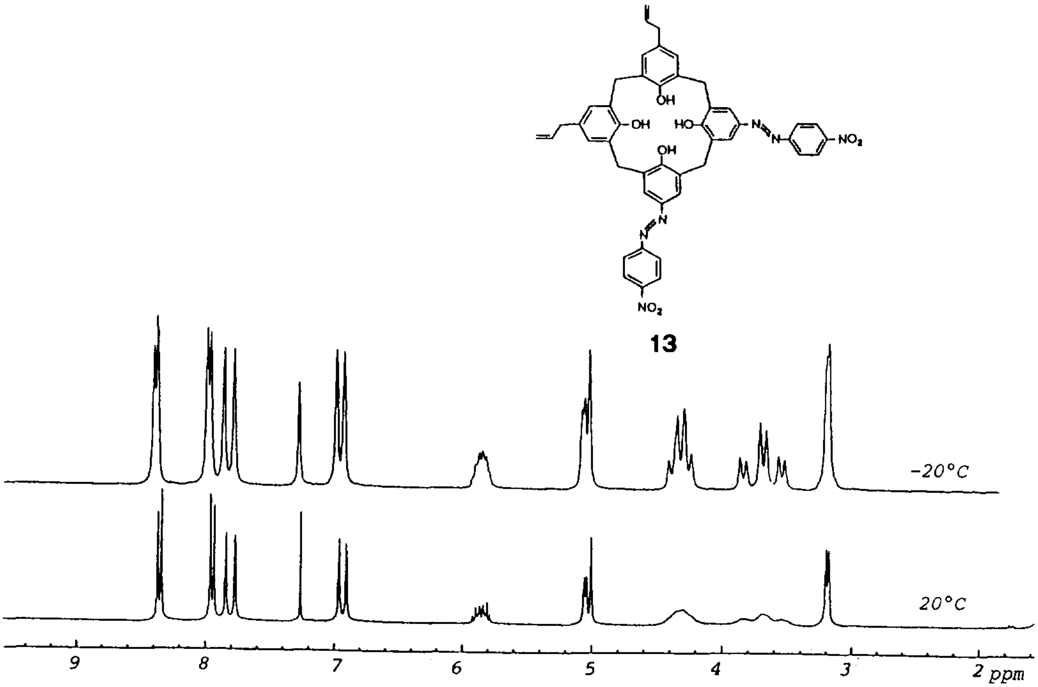


Figure 2. ^{1}H-NMR spectrum of compound **13** in $CDCl_3$ at various temperature.

the case of product **13**, as shown in Figure 2.

A similar broad doublet for the calix[4]arene methylene hydrogens was observed in all of the bisarylazo products, which indicated that the large *p*-substituted phenylazo moieties had no influence on the rate of free rotation around the methylene linkage. As would be in any p-disubstituted calix[4]arenes cases, a characteristic spectral pattern for the methylene hydrogens was displayed when the spectra were taken at low temperature.[10] For example, the low temperature (-20°C) spectrum of compound **13** which displays three sets of double doublets with an integrated ratio of 2:1:1 for the methylene hydrogens is shown in Figure 2.

5,17-Diallyl-11-arylazocalix[4]arenes (15-19). In our earlier studies, we reported that the partial *p*-arylazo substituted calix[4]arenes can be prepared by varying the amount of benzenediazonium salts.[10] When the coupling reaction was carried out under diluted conditions for a brief period and the amount of benzenediazonium salts was reduced, a mixture of the monoarylazocalix[4]arenes and the corresponding bisarylazocalix[4]arenes was produced. It was noticed that the number of arylazo groups dramatically increased the interaction between the products and silica gel, and therefore, the isolation of these monoarylazocalix[4]arenes by column chromatography with a variable elution system were quite easy. These monoarylazo products belong to a lower symmetrical point group (C_v), and the ^{1}H-NMR spectra were expected to be different from the spectrum of compound **3**. A set of doublet and triplet from the non-substituted aromatic ring and a downfield shift singlet from the arylazo substituted aromatic ring clearly indicated that these products contained only one *p*-arylazo substituent. Unlike their bisarylazo counterparts, the four calix[4]arene's aromatic hydrogens which located on the *p*-allyl substituted aromatic rings experienced two different magnetic environ-ments, one from the non-substituted aromatic ring and the other one from the arylazo substituted aromatic ring displayed as four set of doublets. In general, these spectral patterns in aromatic region would be displayed for the calix[4]arenes which possess two different kinds of *p*-substiuents with 1,3-di-2-mono- arrangement.

5,11-Diallyl-17-arylazocalix[4]arenes (20-24). The synthesis of the 5,11-diallyl-17-arylazocalix[4]arenes were studied as in the previous section. These monoarylazo products did not contain any symmetry element (C_1); and hence, the ^{1}H-NMR spectra were expected to be very complex. A distinct pair of doublets for the p-substituted phenylazo group indicated the successful of the diazonium coupling reaction. However, the nine remaining calix[4]arene's aromatic hydrogens behaved as if in seven different magnetic environments; as a result, seven sets of signals were displayed in the aromatic region. For example, the clearly resolved spectrum of 5,11-diallyl-17-(*p*-nitrophenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (**23**) displayed (signals are arranged from downfield to upfield) a singlet, two sets of doublet doublets, two doublets, a singlet, and a triplet for the nine calix[4]arene's aromatic hydrogens as shown in Figure 3. The other monoarylazo products also showed similar spectra but the signals were not as well resolved as compound **23** due to the signals overlap. The calixarenes' methylene hydrogens in these monoarylazo products also displayed a pair of broad signals. In the low temperature spectrum, however, four sets of doublet pairs were displayed as shown in Figure 3. This result is a general characteristic for any totally unsymmetrical *p*-substituted calix[4]arene system.

These unsymmetrical *p*-monoarylazo substituted calix[4]arenes are not superimposable on their mirror images, and enantiomer pairs are expected to exist. However, the free rotation around the methylene linkage transforms the two enantiomers to one another and thus optical resolution is impossible for these products. These enantiomers could be present, as noted by Shinkai in his paper on the "calixarenes"[11] and by Pappalardo et al in their paper on the "inherently chiral calix[4]arenes",[12] in the cases when the free rotation around the methylene linkage is hindered, i.e. a bulky substituent on the calix[4]arene's phenolic hydroxy groups.

We have demonstrated that diallylmonoarylazocalix[4]arenes and diallylbisarylazocalix[4]arenes could be synthesized by the Claisen rearrangement and the diazonium coupling reaction route. We anticipate that the synthesis of the calix[4]arenes with different numbers of *p*-allyl and *p*-arylazo groups would be accomplished via the same synthetic route. Moreover, this synthetic strategy of introducing the *p*-allyl groups by Claisen rearrangement can be further explored for the other calix[4]arene derivatives with various numbers of *p*-allyl and the other *p*-substituents. Finally, the isolation of these diallylmonoarylazocalix[4]arene compounds offers an easy pathway to synthesis the calix[4]arenes with three different kinds of *p*-substituents which may be of use in further studies.

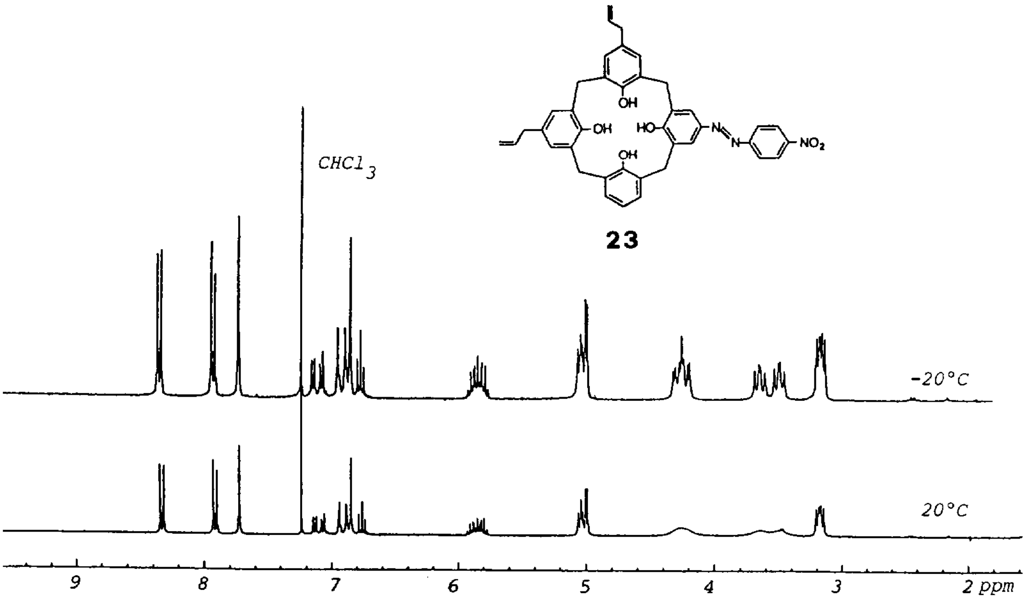


Figure 3. ^{1}H-NMR spectrum of compound **23** in $CDCl_3$ at various temperature.

EXPERIMENTAL

All reagents were obtained from Merck Chemical Company and used without further purification. Melting points were taken in capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature on a Varian Gemini 200 spectrometer and low temperature ^{1}H-NMR spectra were recorded at -20°C on a Bruker MSL-300 spectrometer, and chemical shifts are reported as δ values in ppm relative to TMS (δ=0.00) as an internal standard. Samples for

FAB-MS and elemental analyses were dried at 140°C under vacuum for 72 hours, the FAB-MS spectra were then taken on a JOEL JMS-HX 110 spectrometer and elemental analyses were taken on a Perkin-Elmer 240C analyzer. Chromatographic separations were performed with Merck silica gel (230-400 mesh ASTM) on columns of 25 mm diameter filled to height of 15 cm. TLC analyses were carried out on Merck aluminium back silica gel 60 F_{254} plates (absorbant thickness 0.2 mm).

25,27-Diallyloxy-26,28-dihydroxycalix[4]arene (1). A slurry of 2.12 g (5.0 mmol) of calix[4]arene, 0.68 g (5.0 mmol) of K_2CO_3, and 1.34 g (11.1 mmol) of allyl bromide in 100 mL of CH_3CN was refluxed for 4 h. The solvent was removed, and the residue was treated with diluted HCl to give a white solid. Recrystallization from $CHCl_3$ and CH_3OH afforded 1.56 g (62%) of colorless plate-like crystals: mp 205-207°C; ^{1}H-NMR ($CDCl_3$) δ 8.02 (s, 2H, ArOH), 6.62-7.08 (m, 12H, ArH), 6.18-6.37 (m, 2H, C=CH-C), 5.39-5.85 (m, 4H, $C=CH_2$), 4.54-4.57 (d, J= 5Hz, 4H, OCH_2C), 4.29-4.35 (d, J= 13Hz, 4H, $ArCH_2Ar$), 3.36-3.42 (d, J= 13Hz, 4H, $ArCH_2Ar$); ^{13}C-NMR δ 153.4, 151.8, 133.5, 132.9, 129.0, 128.6, 128.2, 125.6, 119.2, 118.1, 77.0, 31.6; FAB-MS *m/z*: 504 (M^+). Anal. Calcd for $C_{34}H_{32}O_4$: C, 80.95; H, 6.35%. Found: C, 80.97; H, 6.51%.

25,26-Diallyloxy-27,28-dihydroxycalix[4]arene (2). A slurry of 2.12 g (5.0 mmol) of calix[4]arene, 0.90 g (29.8 mmol) of NaH, and 1.34 g (11.1 mmol) of allyl bromide in 100 mL of CH_3CN was stirred at room temperature for 1 h to produce a light purple solution. The reaction was neutralized with diluted HCl, solvent was then removed, and the residue was treated with CH_3OH to leave starting material. Calix[4]arene was filtered out and the filtrate was concentrated to dryness. The product was dissolved in $CHCl_3$ and further recrystallized from $CHCl_3$ and *n*-hexane to afford 0.97 g (48%) of colorless plate-like crystals: mp 145-147°C; ^{1}H-NMR ($CDCl_3$) δ 8.85 (s, 2H, ArOH), 6.63-7.26 (m, 12H, ArH), 6.33-6.53 (m, 2H, C-CH=C), 5.42-5.67 (m, 4H, $C=CH_2$), 4.35-4.77 (m, 8H, OCH_2C and $ArCH_2Ar$), 3.36-3.48 (m, 4H, $ArCH_2Ar$); ^{13}C-NMR δ 152.9, 150.9, 134.5, 134.1, 133.3, 129.1, 128.9, 128.7, 128.6, 127.9, 124.8, 120.4, 119.0, 77.0, 31.8, 31.7, 30.3; FAB-MS *m/z*: 504 (M^+). Anal. Calcd for $C_{34}H_{32}O_4$: C, 80.95; H, 6.35%. Found: C, 80.81; H, 6.63%.

5,17-Diallyl-25,26,27,28-tetrahydroxycalix[4]arene (3). A sample of 1.00 g (1.98 mmol) of 25,27-diallyloxy-26,28-dihydroxycalix[4]arene (**1**) was refluxed in 10 mL of *N,N*-diethylaniline for 4 h under an argon atmosphere. The reaction mixture was poured into 50 mL of diluted HCl to produce an off white solid. The solid was purified with a short column chromatography (6 cm in height, $CHCl_3$/*n*-hexane : 1/4). Recrystallization from $CHCl_3$ and CH_3OH afforded 0.84 g (84%) of pale yellow needle-like crystals: mp 214-216°C (Lit.[7] 85-87.5°C); ^{1}H-NMR ($CDCl_3$): δ 10.21 (bs, 4H, ArOH), 7.04-7.08 (d, J= 8Hz, 4H, ArH), 6.86 (s, 4H, ArH), 6.70-6.78 (t, J= 8Hz, 2H, ArH), 5.77-5.97 (m, 2H, C-CH=C), 5.00-5.10 (m, 4H, $C=CH_2$), 4.15-4.40 (bd, 4H, $ArCH_2Ar$), 3.40-3.65 (bd, 4H, $ArCH_2Ar$), 3.16-3.20 (d, J= 7Hz, 4H, $ArCH_2C$); ^{13}C-NMR δ 148.8, 146.9, 137.5, 133.5, 128.9, 128.2, 128.1, 122.1, 115.6, 39.3, 31.7; FAB-MS *m/z*: 504 (M^+). Anal. Calcd for $C_{34}H_{32}O_4$: C, 80.95; H, 6.35%. Found: C, 80.72; H, 6.47%.

5,11-Diallyl-25,26,27,28-tetrahydroxycalix[4]arene (4). A sample of 1.00 g (1.98 mmol) of 25,26-diallyloxy-27,28-dihydroxycalix[4]arene (**2**) was refluxed in 10 mL of *N,N*-diethylaniline for 4 h under an argon atmosphere. The reaction mixture was poured into 50 mL of diluted HCl to produce an off white solid. The solid was purified with a short column chromatography (6 cm in height, $CHCl_3$/*n*-hexane : 1/4). Recrystallization from $CHCl_3$ and CH_3OH afforded 0.80 g (80%) of colorless solid: mp 201-203°C; ^{1}H-NMR ($CDCl_3$) δ 10.16 (s, 4H, ArOH), 7.02-7.06 (d, J= 8Hz, 4H, ArH), 6.85 (s, 4H, ArH), 6.68-6.76 (t, J= 8Hz, 2H, ArH), 5.76-5.96 (m, 2H, C-CH=C), 4.99-5.08 (m, 4H, C=CH_2), 4.10-4.35 (bs, 4H, ArCH_2Ar), 3.35-3.60 (bs, 4H, ArCH_2Ar), 3.16-3.19 (d, J= 7Hz, 4H, ArCH_2C); ^{13}C-NMR δ 148.7, 146.9, 137.5, 133.4, 128.9, 128.2, 128.1, 122.1, 116.6, 115.6, 112.6, 50.5, 40.5, 39.3, 31.6; FAB-MS *m/z*: 504 (M^+). Anal. Calcd for $C_{34}H_{32}O_4$: C, 80.95; H, 6.35%; calcd for $C_{34}H_{32}O_4 \cdot H_2O$: C, 78.16; H, 6.51%. Found: C, 78.21; H, 6.39%.

General procedure for diallylbisarylazocalix[4]arenes 5-14. In an ice bath temperature, a cold solution of 1.60 mmol of *p*-substituted aniline and 0.17 g (2.46 mmol) of $NaNO_2$ in 5 mL of 4N HCl and 5 mL of acetone was added to a solution of 0.20 g (0.40 mmol) of *p*-diallylcalix[4]arenes (**3** or **4**) in 5 mL of pyridine to produce a colored solution. The reaction mixture was stirred for 1 h and was then treated with 100 mL of diluted HCl to leave a colored residue. This solid residue was further recrystallized to produce the corresponding bisarylazo products.

5,17-Diallyl-11,23-bis(phenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (5). The solid was recrystallized from $CHCl_3$ and CH_3OH to afford 0.21 g (75%) of deep yellow powder: mp 271-273°C; ^{1}H-NMR ($CDCl_3$) δ 10.25 (bs, 4H, ArOH), 7.79-7.83 (m, 4H, Ar'H), 7.69 (s, 4H, ArH), 7.40-7.54 (m, 6H, Ar'H), 6.99 (s, 4H, ArH), 5.79-5.98 (m, 2H, C-CH=C), 5.02-5.10 (m, 4H, C=CH_2), 4.15-4.40 (bd, 4H, ArCH_2Ar), 3.55-3.80 (bd, 4H, ArCH_2Ar), 3.20-3.24 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 713 (M^++1). Anal. Calcd for $C_{46}H_{40}N_4O_4$: C, 77.53; H, 5.62; N, 7.87%; for $C_{46}H_{40}N_4O_4 \cdot CH_3OH$: C, 75.80; H, 5.91; N, 7.53%. Found: C, 75.76; H, 5.97; N, 7.08%.

5,17-Diallyl-11,23-bis-(*p*-methylphenyl)azo-25,26,27,28-tetrahydroxycalix[4]arene (6). The solid was recrystallized from $CHCl_3$ and CH_3OH to afford 0.10 g (35%) of red solid: mp 308-309°C; ^{1}H-NMR ($CDCl_3$) δ 10.25 (bs, 4H, ArOH), 7.68-7.72 (d, J= 8Hz, 4H, Ar'H), 7.65 (s, 4H, ArH), 7.23-7.27 (d, J= 8Hz, 4H, Ar'H), 6.96 (s, 4H, ArH), 5.80-5.91 (m, 2H, C-CH=C), 5.00-5.08 (m, 4H, C=CH_2), 4.20-4.45 (bd, 4H, ArCH_2Ar), 3.50-3.85 (bd, 4H, ArCH_2Ar), 3.18-3.22 (d, J= 7Hz, 4H, ArCH_2C), 2.42 (s, 6H, Ar'CH_3); FAB-MS *m/z*: 741 (M^++1). Anal. Calcd for $C_{48}H_{44}N_4O_4$: C, 77.84; H, 5.95; N, 7.57%. Found: C, 77.79; H, 5.98; N, 7.21%.

5,17-Diallyl-11,23-bis-(*p*-carboxyphenyl)azo-25,26,27,28-tetrahydroxycalix[4]arene (7). The solid was recrystallized from acetone and water to afford 0.28 g (90%) of red solid: mp 320-322°C; ^{1}H-NMR (pyridine-d_5) δ 8.44-8.48 (d, J= 8Hz, 4H, Ar'H), 8.08 (s, 4H, ArH), 7.94-7.98 (d, J= 8Hz, 4H, Ar'H), 7.11 (s, 4H, ArH), 6.82 (bs, 6H, ArOH and Ar'COOH), 5.76-5.98 (m, 2H, C-CH=C), 4.88-5.25 (m, 4H, C=CH_2), 3.40-5.40 (bs, 8H, ArCH_2Ar), 3.04-3.08 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 801 (M^++1). Anal. Calcd for $C_{48}H_{40}N_4O_8$: C, 72.00; H, 5.00; N, 7.00%; for $C_{48}H_{40}N_4O_8 \cdot 2H_2O$: C, 68.90; H, 5.26; N, 6.70%. Found: C, 68.87; H, 5.01; N, 6.59%.

5,17-Diallyl-11,23-bis-(*p*-nitrophenyl)azo-25,26,27,28-tetrahydroxycalix[4]arene (8). The solid was recrystallized from $CHCl_3$ and CH_3OH to afford 0.27 g (84%) of red powder: mp 280-281°C; ^{1}H-NMR ($CDCl_3$) δ 10.25 (bs, 4H, ArOH), 8.33-8.37 (d, J= 9Hz, 4H, Ar'H), 7.90-7.94 (d, J= 9Hz, 4H, Ar'H), 7.76 (s, 4H, ArH), 7.01 (s, 4H, ArH), 5.78-6.00 (m, 2H, C-CH=C), 5.00-5.12 (m, 4H, C=CH_2), 4.20-4.45 (bd, 4H, ArCH_2Ar), 3.55-3.80 (bd, 4H, ArCH_2Ar), 3.21-3.25 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 803 (M^++1). Anal. Calcd for $C_{46}H_{38}N_6O_8$:

C, 68.83; H, 4.74; N, 10.47%; for $C_{46}H_{38}N_6O_8{\cdot}3/2H_2O$: C, 66.58; H, 4.95; N, 10.13%. Found: C, 66.83; H, 4.59; N, 10.25%.

5,17-Diallyl-11,23-bis-(*p*-methoxyphenyl)azo-25,26,27,28-tetrahydroxycalix[4]arene (9). The solid was recrystallized from $CHCl_3$ and CH_3OH to afford 0.26 g (82%) of yellow powder: mp 263-265°C; ^{1}H-NMR ($CDCl_3$) δ 10.25 (bs, 4H, ArOH), 7.79-7.84 (d, J= 9Hz, 4H, Ar'H), 7.64 (s, 4H, ArH), 6.96-7.00 (d; J= 9Hz, 4H, Ar'H), 6.98 (s, 4H, ArH), 5.78-5.98 (m, 2H, C-CH=C), 5.01-5.10 (m, 4H, C=CH_2), 4.15-4.40 (bs, 4H, ArCH_2Ar), 3.87 (s, 6H, Ar'OCH_3), 3.50-3.75 (bs, 4H, ArCH_2Ar), 3.20-3.24 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 773 (M^++1). Anal. Calcd for $C_{48}H_{44}N_4O_6$: C, 74.61; H, 5.70; N, 7.25%. Found: C, 74.85; H, 5.71; N, 7.22%.

5,11-Diallyl-17,23-bis(phenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (10). The solid was recrystallized from $CHCl_3$ and CH_3OH to yield 0.22 g (78.5%) of orange powder: mp 244°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 10.23 (bs, 4H, ArOH), 7.69-7.86 (m, 8H, Ar'H and ArH), 7.40-7.54 (m, 6H, Ar'H), 6.97-6.98 (d, J= 1Hz, 2H, ArH), 6.87-6.88 (d, J= 1Hz, 2H, ArH), 5.77-5.97 (m, 2H, C-CH=C), 5.00-5.12 (m, 4H, C=CH_2), 4.10-4.40 (bs, 4H, ArCH_2Ar), 3.35-3.65 (bs, 4H, ArCH_2Ar), 3.13-3.16 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 713 (M^++1). Anal. Calcd for $C_{46}H_{40}N_4O_4$: C, 77.53; H, 5.62; N, 7.87%, for $C_{46}H_{40}N_4O_4{\cdot}1/2H_2O$: C, 76.56; H, 5.69; N, 7.77%. Found: C, 77.75; H, 5.77; N,7.61%.

5,11-Diallyl-17,23-bis(*p*-methylphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (11). The solid was recrystallized from $CHCl_3$ and CH_3OH to afford 0.20 g (69%) of orange solid: mp 240°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 10.20 (s, 4H, ArOH), 7.68-7.77 (m, 8H, Ar'H and ArH), 7.27-7.31 (d, J= 8Hz, 4H, Ar'H), 6.96-6.97 (d, J= 1Hz, 2H, ArH), 6.88-6.89 (d, J= 1Hz, 2H, ArH), 5.77-5.98 (m, 2H, C-CH=C), 5.00-5.12 (m, 4H, C=CH_2), 4.10-4.40 (bs, 4H, ArCH_2Ar), 3.35-3.65 (bs, 4H, ArCH_2Ar), 3.13-3.16 (d, J= 7Hz, 4H, ArCH_2C), 2.42 (s, 6H, Ar'CH_3); FAB-MS *m/z*: 741 (M^++1). Anal. Calcd for $C_{48}H_{44}N_4O_4$: C, 77.84; H, 5.95; N, 7.57%; for $C_{48}H_{44}N_4O_4{\cdot}1/2H_2O$: C, 76.90; H, 6.01;N, 7.48%. Found: C, 76.91; H, 6.05; N, 7.46%.

5,11-Diallyl-17,23-bis(*p*-carboxyphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (12). The solid was recrystallized from acetone and n-hexane to afford 0.16 g (50%) of dark red solid: mp 253-255°C; ^{1}H-NMR (pyridine-d_5) δ 8.92 (bs, 6H, ArOH and ArCOOH), 8.48-8.52 (d, J= 8Hz, 4H, Ar'H), 8.14-8.15 (d, J= 1Hz, 2H, ArH), 8.06-8.07 (d, J= 1Hz, 2H, ArH), 7.99-8.03 (d, J= 8Hz, 4H, Ar'H), 7.09-7.10 (d, J= 1Hz, 2H, ArH), 7.00-7.01 (d, J= 1Hz, 2H, ArH), 5.65-5.85 (m, 2H, C-CH=C), 4.83-4.97 (m, 4H, C=CH_2), 3.30-5.30 (bs, 8H, ArCH_2Ar), 2.99-3.03 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 801 (M^++1). Anal. Calcd for $C_{48}H_{40}N_4O_8$: C, 72.00; H, 5.00; N, 7.00%; for $C_{48}H_{40}N_4O_8{\cdot}1/2H_2O$: C, 71.20; H, 5.07; N, 6.92%. Found: C,71.22; H, 4.92; N, 6.51%.

5,11-Diallyl-17,23-bis(*p*-nitrophenyl)azo-25,26,27,28-tetrahydroxycalix[4]arene (13). The solid was recrystallized from $CHCl_3$ and CH_3OH to afford 0.22 g (69%) of brick red needle-like crystals: mp 245°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 10.20 (s, 4H, ArOH), 8.33-8.37 (d, J= 9Hz, 4H, Ar'H), 7.92-7.96 (d, J= 9Hz, 4H, Ar'H), 7.82-7.83 (d, J= 1Hz, 2H, ArH), 7.75-7.76 (d, J= 1Hz, 2H, ArH), 6.95-6.96 (d, J= 1Hz, 2H, ArH), 6.90-6.91 (d, J= 1Hz, 2H, ArH), 5.75-5.95 (m, 2H, C-CH=C), 5.00-5.12 (m, 4H, C=CH_2), 4.10-4.40 (bs, 4H, ArCH_2Ar), 3.35-3.65 (bs, 4H, ArCH_2Ar), 3.13-3.16 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 803 (M^++1). Anal. Calcd for $C_{46}H_{38}N_6O_8$: C, 68.83; H, 4.74; N, 10.47%. Found: C, 69.05; H, 4.72; N, 10.31%.

5,11-Diallyl-17,23-bis(*p*-methoxyphenyl)azo-25,26,27,28-tetrahydroxycalix[4]arene (14). The solid was recrystallized from EtOAc and CH$_3$OH to afford 0.19 g (61%) of yellow powder: mp 250-252°C; ^{1}H-NMR (CDCl$_3$) δ 10.17 (s, 4H, ArOH), 7.76-7.80 (d, J= 7Hz, 4H, Ar'H), 7.67-7.68 (d, J= 1Hz, 2H, ArH), 7.58-7.59 (d, J= 1Hz, 2H, ArH), 6.81-6.94 (m, 8H, Ar'H and ArH), 5.77-5.98 (m, 2H, C-CH=C), 4.93-5.01 (m, 4H, C=CH$_2$), 4.10-4.40 (bs, 4H, ArCH$_2$Ar), 3.81 (s, 6H, Ar'OCH$_3$), 3.35-3.65 (bs, 4H, ArCH$_2$Ar), 3.11-3.15 (d, J= 7Hz, 4H, ArCH$_2$C); FAB-MS *m/z*: 773 (M$^+$+1). Anal. Calcd for C$_{48}$H$_{44}$N$_4$O$_6$: C, 74.61; H, 5.70; N, 7.25%. Found: C, 74.34; H, 5.61; N, 7.17%.

General procedure for diallylmonoarylazocalix[4]arenes 15-24. In an ice bath temperature, a cold solution of 0.87 mmol of *p*-substituted aniline and 0.08 g (1.26 mmol) of NaNO$_2$ in 2 mL of 4N HCl and 20 mL of acetone was added to a solution of 0.40 g (0.79 mmol) of *p*-diallylcalix[4]arenes (**3** or **4**) in 5 mL of pyridine and 20 mL of acetone to produce a colored solution. The reaction mixture was stirred for few min, and treated with 200 mL of diluted HCl to leave a colored solid. The solid were isolated by column chromatography with different elutent. The starting materials **3** or **4** were eluted first with 4:1 *n*-hexane/CHCl$_3$ elutent, the corresponding monoarylazo products **15-24** were eluted with 2:1 *n*-hexane/CHCl$_3$ and the 1:1 *n*-hexane/CHCl$_3$ elutent was used to separate the bisarylazo compounds **5-14**.

5,17-Diallyl-11-phenylazo-25,26,27,28-tetrahydroxycalix[4]arene (15). The second eluted compound was recrystallized from CHCl$_3$ and CH$_3$OH to afford 0.16 g (33%) of yellow powder **15**: mp 280-281°C (dec.); ^{1}H-NMR (CDCl$_3$) δ 10.22 (bs, 4H, ArOH), 7.80-7.86 (m, 2H, Ar'H), 7.69 (s, 2H, ArH), 7.44-7.56 (m, 3H, Ar'H), 7.04-7.08 (d, J= 8Hz, 2H, ArH), 6.94-6.95 (d, J= 1Hz, 2H, ArH), 6.87-6.88 (d, J= 1Hz, 2H, ArH), 6.70-6.78 (t, J= 8Hz, 1H, ArH), 5.78-5.98 (m, 2H, C-CH=C), 5.00-5.11 (m, 4H, C=CH$_2$), 4.15-4.35 (bd, 4H, ArCH$_2$Ar), 3.45-3.75 (bm, 4H, ArCH$_2$Ar), 3.18-3.22 (d, J= 7Hz, 4H, ArCH$_2$C); FAB-MS *m/z*: 609 (M$^+$+1). Anal. Calcd for C$_{40}$H$_{36}$N$_2$O$_4$: C, 78.95; H, 5.92; N, 4.61%; for C$_{40}$H$_{36}$N$_2$O$_4$·1/2CH$_3$OH: C, 77.88; H, 6.09; N, 4.49%. Found: C, 78.09, H, 6.08; N, 4.27%.

The third eluted compound which was further recrystallized from CHCl$_3$ and CH$_3$OH was an orange solid **5**, weighed 0.15 g (26%).

5,17-Diallyl-11-(*p*-methylphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (16). The second eluted compound was recrystallized from CHCl$_3$ and CH$_3$OH to afford 0.23 g (46%) of orange crystals **16**: mp 302-304°C (dec.); ^{1}H-NMR (CDCl$_3$) δ 10.22 (bs, 4H, ArOH), 7.72-7.76 (d, J= 8Hz, 2H, Ar'H), 7.67 (s, 2H, ArH), 7.27-7.31 (d, J= 8Hz, 2H, Ar'H), 7.04-7.08 (d, J= 8Hz, 2H, ArH), 6.95-6.96 (d, J= 1Hz, 2H, ArH), 6.88-6.89 (d, J= 1Hz, 2H, ArH), 6.70-6.78 (t, J= 8Hz, 1H, ArH), 5.78-5.98 (m, 2H, C-CH=C), 5.02-5.10 (m, 4H, C=CH$_2$), 4.15-4.35 (bd, 4H, ArCH$_2$Ar), 3.45-3.70 (bm, 4H, ArCH$_2$Ar), 3.18-3.22 (d, J= 7Hz, 4H, ArCH$_2$C), 2.44 (s, 3H, Ar'CH$_3$); FAB-MS *m/z*: 623 (M$^+$+1). Anal. Calcd for C$_{41}$H$_{38}$N$_2$O$_4$: C, 79.10; H, 6.11; N, 4.50%. Found: C, 79.19; H, 6.05; N, 4.19%.

The third eluted compound which was further recrystallized from CHCl$_3$ and CH$_3$OH was an orange solid **6**, weighed 0.22 g (30%).

5,17-Diallyl-11-(*p*-carboxyphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (17). Compound 7 was separated as CHCl$_3$ insoluble solid which upon recrystallization form acetone and water afforded 0.15 g (28%) of red solid. The filtrate was concentrated and separated by column chromatography. The second eluted compound was further recrystallized from $CHCl_3$ and CH_3OH to yield 0.06 g (11%) of orange solid **17**: mp 260-262°C; ^{1}H-NMR ($CDCl_3$) δ 10.22 (bs, 4H, ArOH), 8.22-8.27 (d, J= 9Hz, 2H, Ar'H), 7.86-7.91 (d, J= 9Hz, 2H, Ar'H), 7.73 (s, 2H, ArH), 7.04-7.08 (d, J= 8Hz, 2H, ArH), 6.97-6.98 (d, J= 1Hz, 2H, ArH), 6.90-6.91 (d, J= 1Hz, 2H, ArH), 6.70-6.78 (t, J= 8Hz, 1H, ArH), 5.78-5.99 (m, 2H, C-CH=C), 5.02-5.12 (m, 4H, C=CH_2), 4.15-4.35 (bd, 4H, ArCH_2Ar), 3.45-3.70 (bm, 4H, ArCH_2Ar), 3.18-3.24 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 653 (M^++1). Anal. Calcd for $C_{41}H_{36}N_2O_6$: C, 75.46; H, 5.52; N, 4.29%. Found: C, 75.36; H, 5.81; N, 3.74%.

5,17-Diallyl-11-(*p*-nitrophenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (18). The second eluted compound was recrystallized from $CHCl_3$ and CH_3OH to afford 0.11 g (21%) of brick-red crystals **18**: mp 238-240°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 10.22 (bs, 4H, ArOH), 8.34-8.38 (d, J= 9Hz, 2H, Ar'H), 7.94-7.98 (d, J= 9Hz, 2H, Ar'H), 7.74 (s, 2H, ArH), 7.04-7.08 (d, J= 8Hz, 2H, ArH), 6.97-6.98 (d, J= 1Hz, 2H, ArH), 6.90-6.91 (d, J= 1Hz, 2H, ArH), 6.70-6.78 (t, J= 8Hz, 1H, ArH), 5.78-5.98 (m, 2H, C-CH=C), 5.00-5.08 (m, 4H, C=CH_2), 4.15-4.35 (bd, 4H, ArCH_2Ar), 3.45-3.70 (bm, 4H, ArCH_2Ar), 3.18-3.22 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 654 (M^++1). Anal. Calcd for $C_{40}H_{35}N_3O_6$: C, 73.51; H, 5.36; N, 6.43%. Found: C, 72.26; H, 5.40; N, 5.85%.

The third eluted compound which was further recrystallized from $CHCl_3$ and CH_3OH was an orange solid **8**, weighed 0.22 g (30%).

5,17-Diallyl-11-(*p*-methoxyphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (19). The second eluted compound was recrystallized from $CHCl_3$ and CH_3OH to afford 0.23 g (44%) of yellow solid **19**: mp 234-236°C; ^{1}H-NMR ($CDCl_3$) δ 10.22 (bs, 4H, ArOH), 7.82-7.86 (d, J= 8Hz, 2H, Ar'H), 7.65 (s, 2H, ArH), 7.06-7.10 (d, J= 8Hz, 2H, Ar'H), 6.98-7.02 (d, J= 8Hz, 2H, ArH), 6.97-6.98 (d, J= 1Hz, 2H, ArH), 6.88-6.89 (d, J= 1Hz, 2H, ArH), 6.70-6.78 (t, J= 8Hz, 1H, ArH), 5.78-5.98 (m, 2H, C-CH=C), 5.02-5.12 (m, 4H, C=CH_2), 4.15-4.35 (bd, 4H, ArCH_2Ar), 3.88 (s, 3H, Ar'OCH_3), 3.45-3.70 (bm, 4H, ArCH_2Ar), 3.18-3.22 (d, J= 7Hz, 4H, ArCH_2C); FAB-MS *m/z*: 639 (M^++1). Anal. Calcd for $C_{41}H_{38}N_2O_5$: C, 77.12; H, 5.96; N, 4.39%; for $C_{41}H_{38}N_2O_5\cdot 1/2H_2O$: C,76.04; H, 6.03; N, 4.33%. Found: C, 76.12; H, 5.96; N, 4.10%.

The third eluted compound which was further recrystallized from $CHCl_3$ and CH_3OH was an orange solid **9**, weighed 0.13 g (25%).

5,11-Diallyl-17-phenylazo-25,26,27,28-tetrahydroxycalix[4]arene (20). The second eluted compound was recrystallized from $CHCl_3$ and CH_3OH to afford 0.11 g (22%) of yellow powder **20**: mp 285°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 10.25 (s, 4H, ArOH), 7.82-7.87 (m, 2H, Ar'H), 7.72 (s, 2H, ArH), 7.45-7.56 (m, 3H, Ar'H), 7.17-7.21 (dd, J= 8Hz and 1Hz,, 1H, ArH), 7.08-7.12 (dd, J= 8Hz and 1Hz, 1H, ArH), 6.99-7.00 (d, J= 1Hz, 1H, ArH), 6.91-6.92 (d, J= 1Hz, 1H, ArH), 6.89 (s, 2H, ArH), 6.76-6.83 (t, J= 8Hz, 1H, ArH), 5.77-5.98 (m, 2H, C-CH=C), 5.00-5.12 (m, 4H, C=CH_2), 4.10-4.40 (bd, 4H, ArCH_2Ar), 3.35-3.65 (bm, 4H, ArCH_2Ar), 3.22-3.24 (two d, 4H, ArCH_2C); FAB-MS *m/z*: 609 (M^++1). Anal. Calcd for $C_{40}H_{36}N_2O_4$: C, 78.95; H, 5.92; N, 4.61%: for $C_{40}H_{36}N_2O_4\cdot 1/2H_2O$: C, 77.80; H, 6.00; N, 4.54%. Found: C, 77.52, H, 6.03; N, 4.33%.

The third eluted compound which was further recrystallized from $CHCl_3$ and CH_3OH was an orange solid **10**, weighted 0.13 g (23%).

5,11-Diallyl-17-(*p*-methylphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (21). The second eluted compound was recrystallized from $CHCl_3$ and CH_3OH to afford 0.28 g (43.5%) of orange needle-like crystals **21**: mp 259°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 10.20 (s, 4H, ArOH), 7.74-7.78 (d, J= 8Hz, 2H, Ar'H), 7.69 (s, 2H, ArH), 7.29-7.33 (d, J= 8Hz, 2H, Ar'H), 7.17-7.21 (dd, J= 8Hz and 1Hz, 1H, ArH), 7.09-7.13 (dd, J= 8Hz and 1Hz, 1H, ArH), 6.99-7.00 (d, J= 1Hz, 1H, ArH), 6.90-6.91 (d, J= 1Hz, 1H, ArH), 6.88 (s, 2H, ArH), 6.74-6.84 (t, J= 8Hz, 1H, ArH), 5.77-5.98 (m, 2H, C-CH=C), 5.00-5.12 (m, 4H, $C=CH_2$), 4.10-4.40 (bd, 4H, $ArCH_2Ar$), 3.35-3.65 (bm, 4H, $ArCH_2Ar$), 3.18-3.22 (two d, 4H, $ArCH_2C$), 2.45 (s, 3H, $Ar'CH_3$); FAB-MS *m/z*: 623 (M^++1). Anal. Calcd for $C_{41}H_{38}N_2O_4$: C, 79.10; H, 6.11; N, 4.50%; for $C_{41}H_{38}N_2O_4\cdot 1/2H_2O$: C, 77.97; H, 6.18; N,.4.44%. Found: C, 78.10; H, 6.16; N, 4.44%.

The third eluted compound which was further recrystallized from $CHCl_3$ and CH_3OH was an orange solid **11**, weighed 0.18 g (31%).

5,11-Diallyl-17-(*p*-carboxyphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (22). Compound **12** was separated as $CHCl_3$ insoluble solid which upon recrystallization form acetone and n-hexane afforded 0.04 g (15.5%) of dark red solid. The filtrate was concentrated and further separated by column chromatography. The second eluted compound was recrystallized from $CHCl_3$ and CH_3OH to yield 0.02 g (8%) of orange solid **22**: mp 247-248°C; ^{1}H-NMR (acetone-d_6) δ 10.20 (s, 4H, ArOH), 8.17-8.21 (d, J= 9Hz, 2H, Ar'H), 7.87-7.92 (d, J= 9Hz, 2H, Ar'H), 7.89 (s, 2H, ArH), 7.24-7.28 (dd, J= 8Hz and 1Hz, 1H, ArH), 7.15-7.19 (dd, J= 8Hz and 1Hz, 1H, ArH), 7.01-7.10 (two d, 2H, ArH, and s, 2H, ArH), 6.68-6.76 (t, J= 8Hz, 1H, ArH), 5.77-5.98 (m, 2H, C-CH=C), 5.00-5.12 (m, 4H, $C=CH_2$), 4.10-4.40 (bd, 4H, $ArCH_2Ar$), 3.35-3.65 (bm, 4H, $ArCH_2Ar$), 3.13-3.16 (bd, 4H, $ArCH_2C$); FAB-MS *m/z*: 653 (M^++1). Anal. Calcd for $C_{41}H_{36}N_2O_6$: C, 75.46; H, 5.52; N, 4.29%; for $C_{41}H_{36}N_2O_6\cdot 1/2H_2O$: C, 74.43; H, 5.60; N, 4.24%. Found: C, 74.53; H, 5.23; N, 3.94%.

5,11-Diallyl-17-(*p*-nitrophenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (23). The second eluted compound was recrystallized from $CHCl_3$ and CH_3OH to afford 0.22 g (30%) of brick-red crystals **23**: mp 241-242°C; ^{1}H-NMR ($CDCl_3$) δ 10.20 (s, 4H, ArOH), 8.33-8.37 (d, J= 8Hz, 2H, Ar'H), 7.92-7.96 (d, J= 8Hz, 2H, Ar'H), 7.75 (s, 2H, ArH), 7.14-7.18 (dd, J= 8Hz and 1Hz, 1H, ArH), 7.06-7.10 (dd, J= 8Hz and 1Hz, 1H, ArH), 6.95-6.96 (d, J= 1Hz, 1H, ArH), 6.90-6.91 (d, J= 1Hz, 1H, ArH), 6.87 (s, 2H, ArH), 6.74-6.82 (t, J= 8Hz, 1H, ArH), 5.77-5.98 (m, 2H, C-CH=C), 5.00-5.12 (m, 4H, $C=CH_2$), 4.10-4.40 (bd, 4H, $ArCH_2Ar$), 3.35-3.65 (bm, 4H, $ArCH_2Ar$), 3.16-3.23 (two d, 4H, $ArCH_2C$); FAB-MS *m/z*: 654 (M^++1). Anal. Calcd for $C_{40}H_{35}N_3O_6$: C, 73.51; H, 5.36; N, 6.43%; for $C_{40}H_{35}N_3O_6\cdot CHCl_3$: C, 63.69; H, 4.66; N, 5.44%. Found: C, 63.74; H, 4.85; N, 5.31%.

The third eluted compound which was further recrystallized from $CHCl_3$ and CH_3OH was an orange solid **13**, weighed 0.18 g (30%).

5,11-Diallyl-17-(*p*-methoxyphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (24). The second eluted compound was recrystallized from EtOAc and CH_3OH to afford 0.03 g (15%) of pale yellow solid **24**: mp 250-252°C; ^{1}H-NMR ($CDCl_3$) δ 10.20 (s, 4H, ArOH), 7.82-7.86 (d, J= 8Hz, 2H, Ar'H), 7.64 (s, 2H, ArH), 6.86-7.02 (m, 9H, ArH and Ar'H), 5.77-5.98 (m, 2H, C-CH=C), 5.00-5.12 (m, 4H, $C=CH_2$), 4.10-4.40 (bd, 4H, $ArCH_2Ar$), 3.89 (s, 3H, $Ar'OCH_3$), 3.35-3.65 (bm, 4H, $ArCH_2Ar$), 3.18-3.22 (two d, 4H, $ArCH_2C$); FAB-MS *m/z*: 639 (M^++1). Anal. Calcd for $C_{41}H_{38}N_2O_5$: C, 77.12; H, 5.96; N, 4.39%. Found: C, 76.87; H, 5.90; N, 4.32%.

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9. The 1,2-disubstituted and 1,3-disubstituted calix[4]arenes are belonged to two different symmetrical point groups (C_v and C_{2v}, respectively), and therefore, the number of the ^{13}C-NMR spectral signals are different in those calix[4]arenes. Such difference in the number of the ^{13}C spectral signals can be used to distinguish the structures of two disubstituted calix[4]arenes. The 1,3-disubstituted calix[4]arenes **1** and **3** are expected to display 12 ^{13}C spectral signals, whereas, 18 ^{13}C spectral signals are anticipated for the 1,2-disubstituted calix[4]arenes **2** and **4**. The four calix[4]arene's methylene carbons (δ value around 30 ppm) are equivalent in compounds **1** and **3**, and therefore, only one ^{13}C-signal was observed. Whereas, the four methylene carbons are categorized into three sets in compounds **2** and **4** and three ^{13}C-signals were observed. For example, compound **1** displayed 12 ^{13}C-signals with only one signal at δ= 31.6 ppm; whereas, compound **2** displayed 17 ^{13}C-signals with three signals at δ=31.8, 31.7, and 30.3.
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