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# Studies on the reactivity of calix[4]arene derived bis(spirodienone) with carbo- and hetero-dienophiles and dichlorocarbene: synthesis of highly functionalized macrocycles

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**Abstract**—Calix[4]arene derived bis(spirodienone) can act as a 4π component in cycloaddition reaction with a variety of carbo- and hetero-dienophiles yielding the bisadducts in excellent to quantitative yields. Bis(spirodienone) also undergoes addition reactions with dichlorocarbene resulting in mono- and bis-dichlorocyclopropyl derived bis(spiroenones) in excellent yields.


## 1. Introduction

Calix[*n*]arenes[1] are synthetic macrocycles obtained by the base catalyzed condensation of *p*-substituted phenols and formaldehyde. Because of their unlimited functionalization possibilities at the lower/upper rims and methylene junctions, calix[*n*]arenes are regarded as highly versatile building blocks for the design of selective receptors for the recognition of metal ions, anions, and neutral molecules.[2] Biali and co-workers[3–8] have shown that in the presence of tetraalkylammonium tribromide in a basic medium, the hydroxyl groups bordering the lower rim of calix[4]arene can participate in an intramolecular oxidative cyclization reaction giving rise to an interesting series of multifunctional molecules namely bis(spirodienones) **1a–c** (Fig. 1).

The calix[4]bis(spirodienone) derivatives are remarkable since in a single step the hydroxyl groups are transformed into carbonyl and ether functionalities, two phenolic rings are transformed to cyclohexadienone moieties and in the process, two spiro stereocentres are also introduced in the macrocycle. These functionalities provide potential means for the modification of the calix skeleton. These spirodienone derivatives have been used as synthetic intermediates for achieving selective functionalization of the calixarenes at the intraannular, extraannular and methylene positions.[9]

The bis(spirodienones) appear attractive from the vantage point of their transformations to novel structural frameworks with potentially useful properties. Of special interest to us has been their Diels–Alder reactivity as the dienone moieties in compounds **1a–c** can, in principle, act as efficient 4π components. We undertook some investigations in this area and our preliminary results have been published. The results showed that the most stable isomer bis(spirodienone) **1a** can act as a 4π component in a cycloaddition reaction with activated acetylenes.[10] As part of our continued interest in the cycloaddition chemistry of bis(spirodienones), we undertook a systematic investigation of the cycloaddition reaction of **1a** with various carbo- and hetero-dienophiles. The detailed results of our investigation are presented in the following section.

## 2. Results and discussion

### 2.1. Cycloaddition reactions with carbo-dienophiles

**2.1.1. With triple bonded systems.** As part of our interest in the design of novel macrocyclic systems, we undertook a systematic investigation of the cycloaddition of the calix[4]-arene derived bis(spirodienone) with various dienophiles. We commenced our investigation by reacting a series of acetylenes, both electron deficient and electron rich with the most stable isomer **1a**, which was synthesized following Biali's procedure.[5] Our experiment started with the reaction of 2 equiv of dimethyl acetylenedicarboxylate (DMAD), **2a** with **1a** in dry toluene under ambient conditions (Scheme 1).

After column chromatographic purification, the product **3a** was obtained in quantitative yield and characterized by

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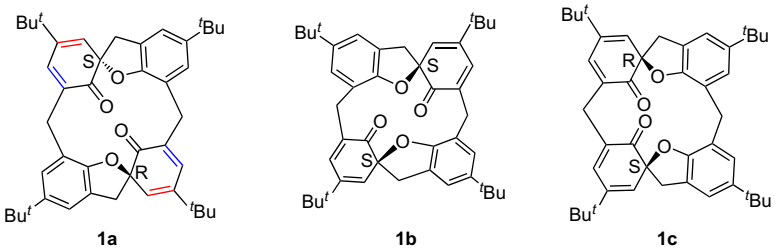
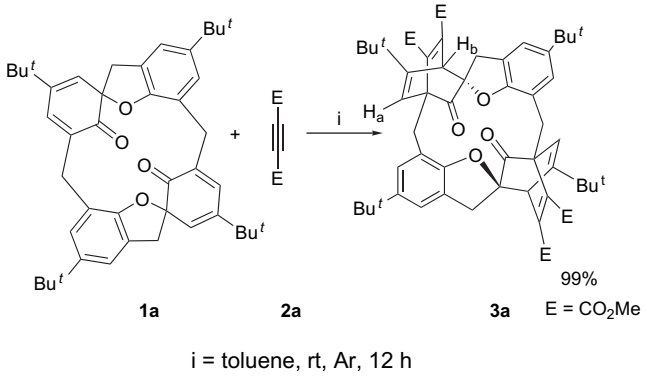



**Figure 1**.




**Scheme 1**.

spectral techniques. The IR spectrum showed the ester carbonyl absorption at 1746 $cm^{-1}$ and the ring carbonyl absorption at 1710 $cm^{-1}$. The highly symmetrical nature of the product was evident from the well-defined $^1H$ NMR spectrum. The aromatic protons resonated at $\delta$ 7.06 and 6.89 as singlets. The olefinic proton $H_a$ and the ring junction proton $H_b$ appeared as close doublets due to allylic coupling at $\delta$ 4.82 ($J$=2.1 Hz) and 4.35 ($J$=2.1 Hz). In the $^{13}C$ NMR spectrum, the signals due to the ring carbonyl, ester carbonyls and the spiro carbons appeared at $\delta$ 192.7, 166.0, 163.0 and 77.2, respectively. The structure and stereochemistry of the product were finally arrived at by single crystal X-ray analysis[11] (Fig. 2). A selective approach of the dienophile from the face opposite to the dihydrofuran oxygen results in the exclusive formation of the *exo–exo* isomer.

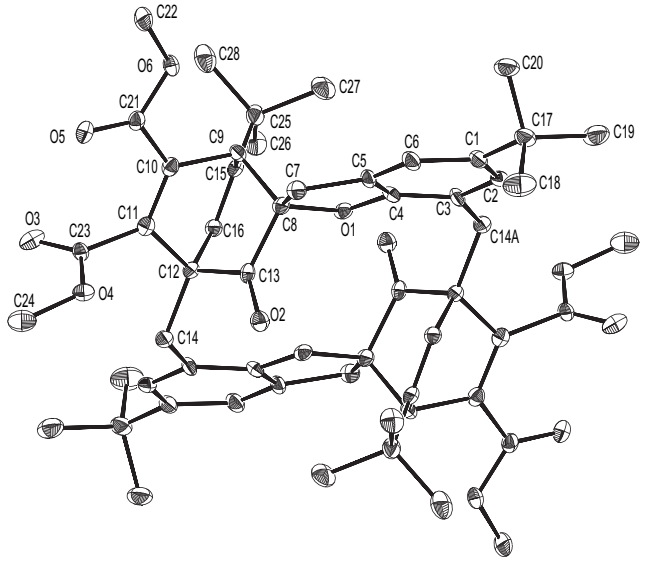
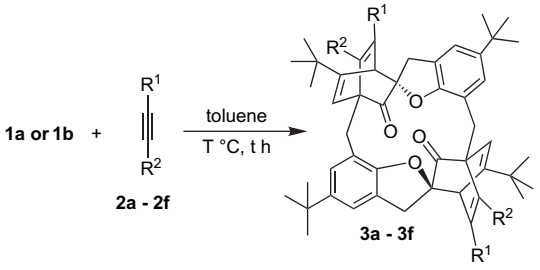



**Figure 2**. ORTEP diagram of **3a** (hydrogen atoms omitted for clarity).

All activated acetylenes with electron withdrawing groups reacted with **1a** yielding the bisbicyclo[2.2.2]octenone derivatives in excellent yields (Table 1). Diphenylacetylene and ethoxyacetylene failed to react with the substrate even in sealed tube conditions probably due to electronic reasons. Even though the products **3c** and **3d** (entries 3 and 4) were obtained exclusively as single isomers, products **3e** and **3f** were obtained as mixtures of two regioisomers. In these cases, the lower regioselectivity might be the result of marginal differences in steric demands of the acetylene substituents. The separation of the regioisomers (**3e**, entry 7) could not be achieved by column chromatography. However, the isomers (**3f**, entry 8) were separated by repeated column

**Table 1**



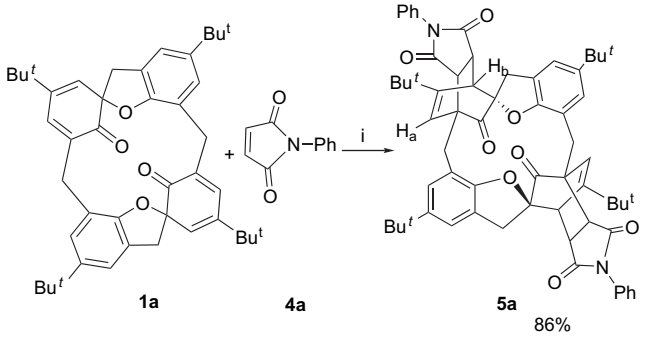

| Entry | Substrate | $R^1$ and $R^2$ | Temp ($T$, °C) | Time ($t$, h) | Product, yield (%) |
|---|---|---|---|---|---|
| 1 | **1a** | $R^1$=$CO_2Me$ $R^2$=$CO_2Me$ | 25 | 12 | **3a**, 99 |
| 2 | **1a** | $R^1$=$CO_2{}^tBu$ $R^2$=$CO_2{}^tBu$ | 110 | 12 | **3b**, 99 |
| 3 | **1a** | $R^1$=Ph $R^2$=$CO_2Me$ | 110 | 12 | **3c**, 88 |
| 4 | **1a** | $R^1$=H $R^2$=$CO_2Me$ | 110 | 12 | **3d**, 94 |
| 5 | **1a** | $R^1$=Ph $R^2$=Ph | 110 | 12 | No reaction |
| 6 | **1a** | $R^1$=H $R^2$=$OC_2H_5$ | 110 | 16 | No reaction |
| 7 | **1a** | $R^1$=$CO^tBu$ $R^2$=$CO_2Me$ | 110 | 18 | **3e**,[a] 98 |
| 8 | **1a** | $R^1$=$CH_3$ $R^2$=$CO_2Et$ | 110 | 18 | **3f**,[a] 66 |
| 9 | **1b** | $R^1$=$CO_2Me$ $R^2$=$CO_2Me$ | 25 | 36 | **3a**, 98 |

[a] Mixture of two regioisomers in the ratio 1:1.

chromatography and characterized. The regiochemistry of **3d** was ascertained by $^1$H NMR spectrum.

When DMAD was reacted with **1b** under ambient conditions, the product obtained was exclusively **3a**. This is easily explainable as the stereoisomers **1a** and **1b** exist in equilibrium in solution.[5]

**2.1.2. With double bonded systems.** In order to study the reactivity of double bonded systems on cycloaddition with bis(spirodienone), we started our investigation by reacting *N*-phenyl maleimide with **1a**. The cycloadduct was obtained in excellent yield (86%) under ambient conditions. (Scheme 2).




**Scheme 2**.

The structure of the adduct was established by spectroscopic methods. In the IR spectrum, the carbonyl peaks were observed as a broad band at 1717 cm$^{-1}$. In the $^1$H NMR spectrum, the aromatic protons appeared as multiplet ranging from $\delta$ 7.60 to 7.37 and one doublet at $\delta$ 7.18 ($J$=2.4 Hz). The olefinic proton H$_a$ resonated as a singlet at $\delta$ 4.83. The singlet at $\delta$ 3.58 was assigned to the ring junction proton H$_b$. In the $^{13}$C NMR spectrum, the cyclohexenone carbonyl resonated at $\delta$ 202 whereas the other two carbonyls appeared at $\delta$ 174.6 and 174.5. The spiro carbon furnished a peak at $\delta$ 82.7.

The reaction was found to be applicable to other symmetric olefinic systems like maleimide and maleic anhydride. The reaction was then extended to asymmetric olefinic systems with electron withdrawing groups. When **1a** was treated with acrylonitrile in toluene under reflux conditions the bisadduct was obtained in good yield (Scheme 3).

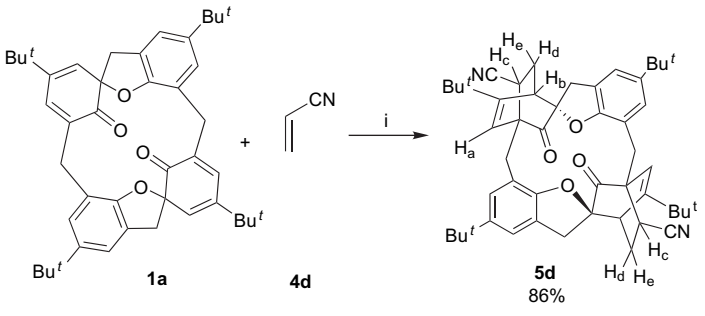
The structure of the adduct **5d** was assigned by spectroscopic methods. In the IR spectrum, the carbonyl peak was observed at 1739 cm$^{-1}$. The aromatic protons appeared as singlets at $\delta$ 7.08 and 7.01. The olefinic proton, H$_a$ appeared as a singlet at $\delta$ 4.76 and the ring junction proton, H$_b$ as a broad singlet at $\delta$ 3.07. The proton, H$_c$ resonated as a doublet of doublet at $\delta$ 2.72. The protons H$_d$ and H$_e$ appeared as multiplets at $\delta$ 2.05 and 1.75, respectively. The regiochemistry of the product was further confirmed by $^1$H–$^1$H COSY experiment. The proton, H$_c$, which appeared as a double doublet showed correlation with the adjacent H$_e$ and H$_d$ protons. The protons H$_d$ and H$_e$ showed correlation with both H$_c$ and the ring junction proton, H$_b$. The ring carbonyl displayed a $^{13}$C resonance signal at $\delta$ 204.0. The signal at $\delta$ 84.3 was assigned to the spiro carbon.

The reaction was repeated with other asymmetric olefinic systems and was found to be of general nature. All the reactions were regiospecific fetching only single products, which showed similar $^1$H NMR spectrum as that of **5a** except for entry 7 where the dimethylfumarate reacted to give two isomeric products in 1:1 ratio. The results are summarized in Table 2.

## 2.2. Cycloaddition reactions with hetero-dienophiles

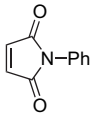
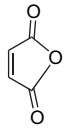
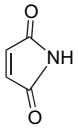
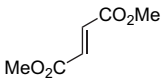
In view of the encouraging results obtained in the cycloaddition of bis(spirodienone) **1a** with double and triple bonded systems, we extended our studies towards its cycloaddition reactions to hetero-dienophiles. With the aim of exploring their potential for the synthesis of complex structures based on the calixarene skeleton, we chose *N*-substituted-1,2,4-triazoline-3,5-diones[12,13] as hetero-dienophiles for our study. 1,2,4-Triazoline-3,5-diones are very reactive cyclic azo-dienophiles and they have an intrinsic capability to introduce an N–N moiety into the structure of the cycloadduct. The resulting biscycloadducts could be potential intermediates for further structural transformations.

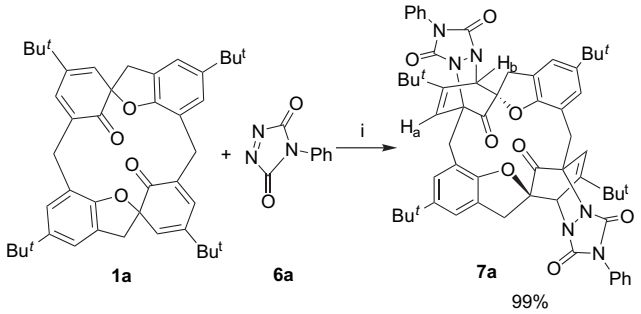
We commenced our study by reacting the bis(spirodienone) **1a** with *N*-phenyl-1,2,4-triazoline-3,5-dione (Scheme 4). A facile reaction occurred at ambient conditions leading to the formation of the cycloadduct in quantitative yield. After purification by column chromatography, to remove the excess of dienophile, the product, **7a** was fully characterized by spectral techniques.




**Scheme 3**.

**Table 2**

| Entry | Substrate | Dienophile | Temp ($T$, °C) | Time ($t$, h) | Product, yield (%) |
|---|---|---|---|---|---|
| 1 | **1a** |  | 25 | 18 | **5a**, 86 |
| 2 | **1a** |  | 110 | 4 | **5b**, 98 |
| 3 | **1a** |  | 110 | 4 | **5c**, 98 |
| 4 | **1a** |  | 110 | 8 | **5d**, 86 |
| 5 | **1a** |  | 110 | 10 | **5e**, 80 |
| 6 | **1a** |  | 110 | 12 | **5f**, 70 |
| 7 | **1a** |  | 110 | 14 | **5g**, 80 |




**Scheme 4**.

The IR spectrum showed strong carbonyl absorptions at 1712 and 1762 $cm^{-1}$ corresponding to the ring carbonyl and the carbonyl groups of the triazoline part, respectively. The highly symmetrical nature of the cycloadduct was evident from the $^1H$ NMR spectrum, which showed well-defined proton resonance signals. In the $^1H$ NMR spectrum the aromatic protons appeared as multiplet centred at $\delta$ 7.45 and as singlets at $\delta$ 7.20 and 7.10. The olefinic proton, $H_a$ displayed a singlet at $\delta$ 5.24. The doublet at $\delta$ 5.11 ($J$=1.8 Hz) was assigned to the ring junction proton $H_b$. All other signals were in good agreement with the assigned structure. In the $^{13}C$ NMR spectrum, the signals due to the ring carbonyl and the carbonyl of the triazoline part appeared at $\delta$ 193.4, 154.6 and 154.3, respectively. The spiro carbon resonated at $\delta$ 81.5. The final conformation and stereochemistry of the structure were obtained from single crystal X-ray analysis[14] (Fig. 3).

The reaction was found to be general for 1,2,4-triazoline-3,5-diones and resulted in the formation of triazoline dione derived macrocycles based on calix[4]arenes in excellent yields (Table 3).

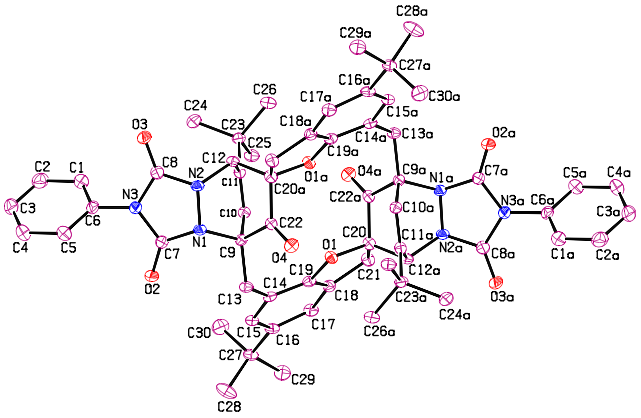
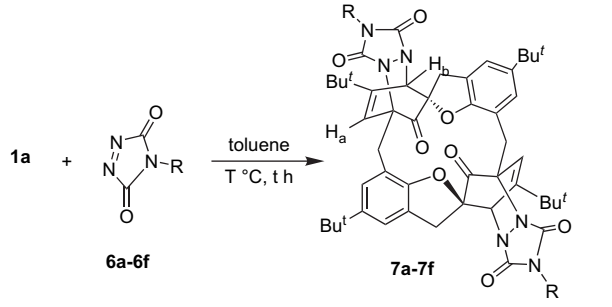


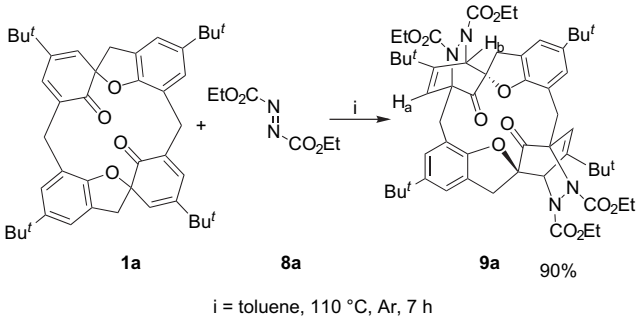

**Figure 3**. ORTEP diagram of the compound **7a** with 40% probability for the thermal ellipsoid (hydrogen atoms omitted for clarity).

**Table 3**




| Entry | Substrate | R | Temp ($T$, °C) | Time ($t$, h) | Product, yield (%) |
|---|---|---|---|---|---|
| 1 | **1a** | –Ph | 25 | 6 | **7a**, 99 |
| 2 | **1a** | Cyclohexyl | 25 | 10 | **7b**, 86 |
| 3 | **1a** | –$CH_2$Ph | 25 | 8 | **7c**, 99 |
| 4 | **1a** | –$CH_2$Ph–OMe | 25 | 8 | **7d**, 98 |
| 5 | **1a** | –$CH_2$Ph–Me | 25 | 10 | **7e**, 98 |
| 6 | **1a** | –$CH_2$Ph–Cl | 25 | 10 | **7f**, 90 |

It was observed that the cycloaddition of **1a** with diethyl azodicarboxylate[15–17] required more stringent conditions and the cycloadduct was obtained by treating **1a** with **8a** in dry toluene under reflux conditions for 7 h (Scheme 5).




**Scheme 5**.

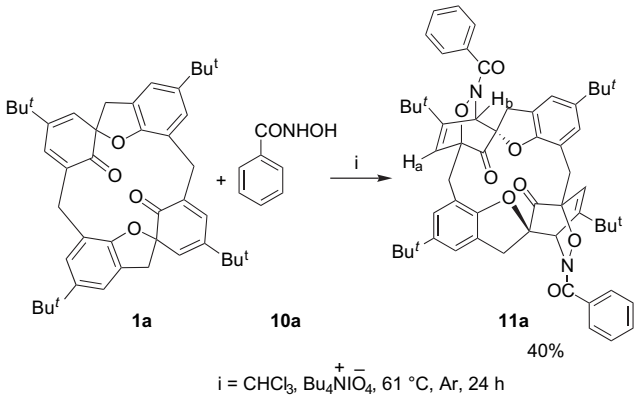
The IR spectrum of the compound displayed strong carbonyl absorptions at 1756, 1737 and 1703 $cm^{-1}$ corresponding to the ester carbonyl groups and the ring carbonyls, respectively. In the $^1H$ NMR spectrum, the aromatic protons

resonated as a singlet at $\delta$ 7.13 and as a multiplet at $\delta$ 7.00. The singlet at $\delta$ 5.43 was assigned to the olefinic proton, $H_a$. The ring junction proton, $H_b$ appeared as a multiplet at $\delta$ 5.15. The $-OCH_2$ protons of the ester group resonated as a multiplet at $\delta$ 4.19. The $CH_3$ protons were observed as a multiplet ranging from $\delta$ 1.26 to 1.15. All other proton signals were in good agreement with the proposed structure. The ester carbonyl and the ring carbonyl displayed $^{13}C$ resonance signals at $\delta$ 196.9, 159.1 and 154.9. The signal at $\delta$ 84.3 was assigned to the spiro carbon.

With diisopropyl azodicarboxylate the reaction occurred in a similar way affording the product in quantitative yield. But the di-*tert*-butyl azodicarboxylate failed to react even under sealed tube conditions probably due to steric reasons (Table 4).

Acylnitroso compounds are also good hetero-dienophiles[18–20] and in principle can participate in cycloaddition reactions with bis(spirodienones). When **1a** was treated with benzohydroxamic acid in dry chloroform in the presence of tetrabutylammonium periodate and heated at 61 °C for 24 h, the 1,2-oxazine derived cycloadduct **11a** was obtained in 40% yield (via cycloaddition of the nitroso derivative generated in situ). The unreacted starting material was recovered. The symmetric nature of the product was evident from the $^1H$ NMR spectrum (Scheme 6).

The IR spectrum showed two carbonyl absorption peaks at 1759 and 1653 $cm^{-1}$. The aromatic protons of the acylnitroso part appeared as a doublet at $\delta$ 7.69 ($J$=6.9 Hz) and as a multiplet ranging from $\delta$ 7.46 to 7.36. The singlets at $\delta$ 7.17 and 6.91 were assigned to the aromatic protons of the calix[4](spiroenone) part. The olefinic proton, $H_a$ and the ring junction proton, $H_b$ appeared as singlets at $\delta$ 5.85 and 5.12, respectively. All other protons were in good agreement with the proposed structure. The signals at $\delta$ 195.1 and 155.1 in the $^{13}C$ NMR spectrum were assigned to the ring




**Scheme 6**.

carbonyl and the carbonyl group of the nitroso species. The spiro carbon appeared at $\delta$ 82.5. The same reactivity pattern was observed for *p-tert*-butyl benzohydroxamic acid (entry 5, Table 4).

In all cases only one isomer was obtained from good to excellent yields. The reaction is highly regio- and stereospecific.

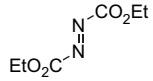
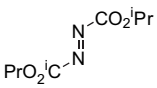
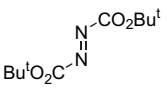
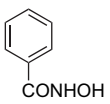
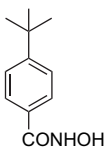
### 2.3. Addition reaction with dichlorocarbene

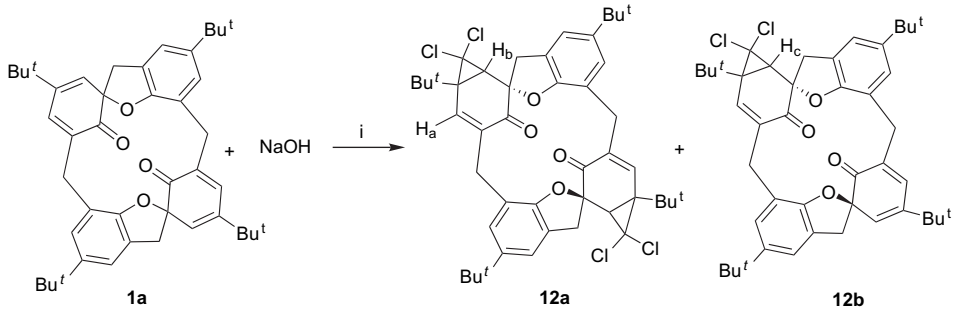
Results from our group have shown that the bis(spirodienone) **1a** acts as 2π component in cycloaddition with 1,2-benzoquinones and the double bond shown in red in Figure 1 has reacted.[21] This prompted us to investigate on the reactivity of **1a** with carbenes. When **1a** was treated with dichlorocarbene generated from chloroform and sodium hydroxide, two products were obtained in good yields (Scheme 7). On spectral analysis **12a** was identified as the bisadduct and **12b** as the monoadduct.

The IR spectrum of the bisadduct showed strong carbonyl absorption at 1686 $cm^{-1}$ corresponding to the enone carbonyl group. In the $^1H$ NMR spectrum, the aromatic protons appeared as singlets at $\delta$ 7.16 and 7.07. The olefinic proton, $H_a$ appeared as a singlet at $\delta$ 6.53 and the ring junction proton, $H_b$ as a singlet at $\delta$ 2.61. All other signals were in good agreement with the assigned structure. In the $^{13}C$ NMR spectrum, the signals due to the ring carbonyl and the spiro carbon resonated at $\delta$ 186.0 and 81.3. From the spectral data it was confirmed that the double bond near to the *tert*-butyl group (shown in red in Fig. 1) has reacted in this case. Conclusive evidence for the structure was obtained by single crystal X-ray analysis[22] (Fig. 4).

The structure of the monoadduct was established by spectroscopic methods. The IR spectrum of the compound showed a broad absorption peak at 1689 $cm^{-1}$ corresponding to the enone carbonyl. In the $^1H$ NMR spectrum, the aromatic protons appeared as singlets at $\delta$ 7.15, 7.09 and 7.05. The singlets observed at $\delta$ 6.62, 6.53 and 5.83 were assigned to the olefinic protons. The ring junction proton, $H_c$ displayed a singlet at $\delta$ 2.62. All other protons were in good agreement with the proposed structure. The cyclohexadienone and hexenone carbonyls displayed $^{13}C$ resonance signals at $\delta$ 194.9 and 186.3. The spiro carbons resonated at $\delta$ 81.6 and 81.3.

**Table 4**

| Entry | Substrate | Dienophile | Temp ($T$, °C) | Time ($t$, h) | Product, yield (%) |
|---|---|---|---|---|---|
| 1 | **1a** |  | 110 | 7 | **9a**, 90 |
| 2 | **1a** |  | 110 | 6 | **9b**, 98 |
| 3 | **1a** |  | 110 | 48 | No reaction |
| 4 | **1a** |  | 61 | 24 | **11a**, 40 |
| 5 | **1a** |  | 61 | 24 | **11b**, 50 |




**Scheme 7**.

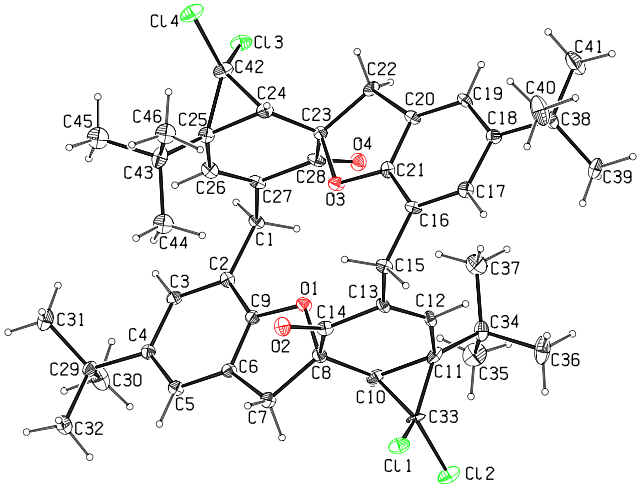



**Figure 4**. ORTEP diagram of the compound **12a** (hydrogen atoms omitted for clarity).

When **1a** was treated with dimethoxycarbene and carbene generated from diethyl diazomalonate, no reaction took place and the starting material was recovered quantitatively.

## 3. Conclusion

In conclusion, we have successfully employed the Diels–Alder chemistry for the synthesis of highly functionalized calixarene analogues. The bisadducts were obtained in excellent to quantitative yields with very good diastereofacial selectivity. The bisbicyclo[2.2.2]octenone, triazoline dione, hydrazine and oxazine derivatives can be potential candidates for further synthetic transformations and it is conceivable that the present strategy may open up possibilities for the construction of highly functionalized macromolecules from the calix[4]arene skeleton.

## 4. Experimental

### 4.1. General

All reactions were conducted in oven-dried glassware under an atmosphere of argon. Progress of the reactions was monitored by thin-layer chromatography and purification was effected using silica gel column chromatography. $^1$H and $^{13}$C NMR spectra were recorded on Bruker DPX300 FTNMR spectrometer at 300 and 75 MHz, respectively. Chemical shifts are reported in $\delta$ (ppm) relative to $Me_4Si$ ($^1$H NMR) or $CDCl_3$ ($^{13}$C NMR) as internal standard. Abbreviations for NMR multiplicities are as follows: s, singlet; d, doublet; m, multiplet; dd, double doublet; coupling constants $J$ are reported in hertz (Hz). IR spectra were recorded on Bomem MB Series FTIR spectrometer and the absorbances are reported in cm$^{-1}$. Recrystallization was done by slow evaporation method from dichloromethane–acetonitrile mixture at rt.

### 4.2. Typical procedure for the preparation of 3a

Calix[4]bis(spirodienone) **1a** (50 mg, 0.078 mmol) was dissolved in dry toluene (8 mL) under inert atmosphere. Dimethyl acetylenedicarboxylate (23 mg, 0.163 mmol) was added to it and stirred at rt for 12 h. The solvent was removed under vacuum and the residue subjected to silica gel column chromatography to remove the excess dienophile using 85:15 hexane–ethylacetate solvent mixture to afford **3a** as a white solid (70 mg, 99%).

### 4.3. Spectroscopic data for new compounds

**4.3.1. Compound 3a.** White crystalline solid; $R_f$: 0.15 (9:1 hexane–ethylacetate); mp>300 °C (decomp.). IR (KBr) $\nu_{max}$: 2957, 1746, 1613, 1480, 1261, 1056, 895 cm$^{-1}$. $^1$H NMR: $\delta$ 7.05 (s, 2H), 6.89 (s, 2H), 4.82 (d, $J$=2.1 Hz, 2H), 4.35 (d, $J$=2.1 Hz, 2H), 4.09 (d, $J$=14.4 Hz, 2H), 3.87 (s, 6H), 3.79 (s, 6H), 3.31 (d, $J$=15.6 Hz, 2H), 3.00 (d, $J$=15.6 Hz, 2H), 2.55 (d, $J$=14.5 Hz, 2H), 1.30 (s, 18H), 0.98 (s, 18H). $^{13}$C NMR: $\delta$ 192.7, 166.0, 163.0, 153.5, 150.8, 144.2, 135.5, 127.5, 125.5, 120.0, 118.3, 77.2, 59.5, 52.5, 38.8, 34.3, 31.7, 27.6. MS (FAB) $m/z$ calcd for $C_{56}H_{64}O_{12}$+H: 929.44. Found: 929.73. Analysis calculated for $C_{56}H_{64}O_{12}$: C, 72.39; H, 6.94. Found: C, 72.04; H, 7.20.

**4.3.2. Compound 3b.** White crystalline solid; $R_f$: 0.48 (9:1 hexane–ethylacetate); mp>298 °C (decomp.). IR (KBr) $\nu_{max}$: 2957, 1744, 1701, 1484, 1367, 1164, 1055, 896 cm$^{-1}$. $^1$H NMR: $\delta$ 7.07 (s, 2H), 6.86 (s, 2H), 4.73 (d, $J$=2.1 Hz, 2H), 4.18 (d, $J$=2.1 Hz, 2H), 4.07 (d, $J$=14.1 Hz, 2H), 3.26 (d, $J$=15.6 Hz, 2H), 3.04 (d, $J$=15.6 Hz, 2H), 2.67 (d, $J$=14.4 Hz, 2H), 1.56 (s, 18H), 1.50 (s, 18H), 1.30 (s, 18H), 0.97 (s, 18H). $^{13}$C NMR: $\delta$ 192.3, 164.6, 162.6, 155.2, 153.1, 149.0, 144.0, 136.7, 127.5, 126.1, 120.2, 119.8, 118.9, 116.5, 82.9, 59.5, 48.2, 38.7, 34.4, 34.3, 31.9, 28.4, 28.2, 27.8, 27.7. MS (FAB) $m/z$ calcd for $C_{68}H_{88}O_{12}$+H: 1097.63. Found: 1097.95.

**4.3.3. Compound 3c.** White crystalline solid; $R_f$: 0.44 (9:1 hexane–ethylacetate); mp>295 °C (decomp.). IR (KBr) $\nu_{max}$: 2955, 1738, 1700, 1483, 1437, 1331, 1247, 1204, 1139, 942, 895, 704 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.35 (m, 7H), 7.25 (s, 2H), 7.05 (s, 3H), 6.67 (s, 2H), 4.92 (s, 2H), 4.41 (d, $J$=2.1 Hz, 2H), 3.80 (d, $J$=14.7 Hz, 2H), 3.50 (s, 6H), 3.41 (d, $J$=15.6 Hz, 2H), 3.14 (d, $J$=15.6 Hz, 2H), 2.24 (d, $J$=15.0 Hz, 2H), 1.28 (s, 18H), 1.01 (s, 18H). $^{13}C$ NMR: $\delta$ 195.1, 165.0, 159.5, 154.5, 153.6, 143.7, 136.2, 134.7, 127.9, 127.6, 127.2, 125.5, 119.9, 118.9, 78.1, 62.2, 51.7, 48.3, 38.9, 34.4, 34.2, 31.2, 29.4, 27.6. MS (FAB) $m/z$ calcd for $C_{64}H_{68}O_8$+H: 965.49. Found: 965.89.

**4.3.4. Compound 3d.** White crystalline solid; $R_f$: 0.39 (9:1 hexane–ethylacetate); mp>300 °C (decomp.). IR (KBr) $\nu_{max}$: 2957, 1742, 1719, 1480, 1363, 1308, 1235, 1059, 942, 902 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.22 (d, $J$=6.6 Hz, 2H), 7.01 (s, 2H), 6.94 (s, 2H), 4.93 (d, $J$=2.1 Hz, 2H), 4.28 (d, $J$=15.0 Hz, 2H), 3.84 (dd, $J_1$=2.4 Hz, $J_2$=2.4 Hz, 2H), 3.77 (s, 6H), 3.38 (d, $J$=15.6 Hz, 2H), 3.18 (d, $J$=15.3 Hz, 2H), 2.80 (d, $J$=15.6 Hz, 2H), 1.30 (s, 18H), 0.96 (s, 18H). $^{13}C$ NMR: $\delta$ 193.3, 164.3, 154.6, 151.8, 144.8, 143.5, 141.1, 127.7, 125.4, 120.2, 118.9, 85.9, 58.0, 51.6, 47.6, 34.1, 33.9, 31.7, 30.7, 27.4. MS (FAB) $m/z$ calcd for $C_{52}H_{60}O_8^{\ddagger}$: 812.43. Found: 812.11.

**4.3.5. Compound 3e (inseparable isomers in the ratio 1:1).** White crystalline solid; $R_f$: 0.41 (9:1 hexane–ethylacetate); mp>302 °C (decomp.). IR (KBr) $\nu_{max}$: 2957, 1742, 1716, 1689, 1483, 1436, 1394, 1364, 1152, 1103, 943, 895 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.08 (s, 4H), 6.90 (m, 4H), 4.94 (m, 4H), 4.37 (s, 2H), 4.20 (d, $J$=14.7 Hz, 2H), 3.91 (d, $J$=14.4 Hz, 2H), 3.82 (s, 2H), 3.76 (s, 12H), 3.34 (br s, 6H), 3.13 (m, 2H), 2.97 (m, 2H), 2.54 (d, $J$=13.8 Hz, 2H), 1.30 (m, 36H), 1.20 (s, 18H), 1.10 (s, 18H), 1.04 (br s, 18H), 0.95 (s, 18H). $^{13}C$ NMR: $\delta$ 213.0, 211.0, 193.8, 192.6, 164.5, 164.0, 157.0, 155.6, 155.2, 154.8, 154.5, 153.8, 150.7, 144.4, 144.1, 136.3, 134.8, 128.0, 127.6, 126.5, 126.3, 125.6, 125.3, 121.3, 120.2, 119.6, 119.3, 78.3, 78.2, 61.5, 57.6, 52.6, 52.3, 51.0, 48.3, 44.8, 44.3, 39.3, 39.1, 34.5, 34.4, 31.9, 28.8, 27.7, 27.5, 27.3. MS (FAB) $m/z$ calcd for $C_{62}H_{76}O_{10}$+Na: 1003.54. Found: 1003.58.

**4.3.6. Compound 3f (two regioisomers in the ratio 1:1).** White crystalline solid; $R_f$: 0.52 (9:1 hexane–ethylacetate); mp>310 °C (decomp.). IR (KBr) $\nu_{max}$: 2957, 1739, 1697, 1483, 1315, 1230, 1055, 898, 836 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.05 (s, 2H), 6.89 (s, 2H), 4.76 (s, 2H), 4.27 (m, 6H), 4.06 (d, $J$=14.5 Hz, 2H), 3.22 (d, $J$=15.4 Hz, 2H), 3.08 (d, $J$=16.1 Hz, 2H), 2.80 (d, $J$=14.6 Hz, 2H), 2.20 (s, 6H), 1.31 (s, 18H), 1.30 (m, 6H), 0.95 (s, 18H). $^{13}C$ NMR: $\delta$ 194.7, 165.5, 158.1, 155.5, 152.6, 144.0, 132.6, 127.7, 126.3, 120.3, 118.8, 78.4, 62.7, 60.9, 48.4, 39.0, 34.4, 32.1, 28.6, 27.8, 15.7, 14.7. MS (FAB) $m/z$ calcd for $C_{56}H_{68}O_8$+H: 869.49. Found: 869.25.

White crystalline solid; $R_f$: 0.44 (9:1 hexane–ethylacetate); mp>310 °C (decomp.). IR (KBr) $\nu_{max}$: 2957, 1739, 1697, 1483, 1315, 1230, 1055, 898, 836 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.03 (s, 2H), 6.86 (s, 2H), 4.84 (d, $J$=2.1 Hz, 2H), 4.28 (m, 6H), 3.95 (d, $J$=15.7 Hz, 2H), 3.34 (d, $J$=15.7 Hz, 2H), 2.94 (d, $J$=15.4 Hz, 2H), 2.60 (d, $J$=14.9 Hz, 2H), 2.10 (s, 6H), 1.33 (s, 18H), 1.30 (m, 6H), 0.96 (s, 18H). $^{13}C$ NMR: $\delta$ 195.0, 165.8, 158.5, 156.4, 151.6, 143.9, 132.8, 128.0, 126.5, 120.6, 118.7, 78.7, 62.9, 61.0, 48.5, 39.2, 34.7, 32.9, 28.9, 27.6, 16.1, 14.9. MS (FAB) $m/z$ calcd for $C_{56}H_{68}O_8$+H: 869.49. Found: 869.25.

### 4.4. Typical procedure for the preparation of 5a

Calix[4]bis(spirodienone) **1a** (50 mg, 0.078 mmol) was dissolved in dry toluene (8 mL) under inert atmosphere. *N*-Phenyl maleimide (28 mg, 0.163 mmol) was added to it and stirred at rt for 18 h. The solvent was removed under vacuum and the residue subjected to silica gel column chromatography to remove excess dienophile using 85:15 hexane–ethylacetate solvent mixture affording **5a** as a white solid (66 mg, 86%). The product was recrystallized from dichloromethane–acetonitrile mixture.

**4.4.1. Compound 5a.** White crystalline solid; $R_f$: 0.079 (9:1 hexane–ethylacetate); mp>275 °C (decomp.). IR (KBr) $\nu_{max}$: 2957, 1717 (br), 1485, 1377, 1201, 901 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.38–7.50 (m, 6H), 7.12 (br s, 8H), 4.83 (s, 2H), 4.02 (d, $J$=14.1 Hz, 2H), 3.58 (s, 2H), 3.49 (d, $J$=14.7 Hz, 4H), 3.33 (d, $J$=15.3 Hz, 2H), 3.07 (d, $J$=6.3 Hz, 2H), 2.88 (dd, $J_1$=3.6 Hz, $J_2$=3.4 Hz, 2H), 1.33 (s, 18H), 0.93 (s, 18H). $^{13}C$ NMR: $\delta$ 202.2, 174.7, 174.5, 154.6, 149.9, 144.8, 129.2, 128.7, 126.1, 124.5, 120.4, 120.0, 118.6, 116.5, 113.0, 112.0, 109.2, 82.7, 51.5, 47.2, 45.3, 37.3, 34.4, 31.9, 28.2, 27.4. MS (FAB) $m/z$ calcd for $C_{64}H_{66}O_8N_2$+H: 991.48. Found: 991.21.

**4.4.2. Compound 5b.** White crystalline solid; $R_f$: 0.053 (9:1 hexane–ethylacetate); mp>277 °C (decomp.). IR (KBr) $\nu_{max}$: 2968, 1784, 1747, 1485, 1365, 1236, 933 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.18 (s, 2H), 7.12 (s, 2H), 4.90 (s, 2H), 4.03 (d, $J$=14.7 Hz, 2H), 3.61 (s, 2H), 3.49 (d, $J$=15.3 Hz, 2H), 3.31 (d, $J$=15.3 Hz, 4H), 3.21 (m, 4H), 1.33 (s, 18H), 0.96 (s, 18H). $^{13}C$ NMR: $\delta$ 199.8, 171.4, 154.5, 151.7, 146.7, 129.7, 125.6, 121.0, 119.7, 117.2, 112.1, 82.9, 51.3, 49.4, 46.0, 42.4, 37.4, 34.6, 34.5, 28.0. MS (FAB) $m/z$ calcd for $C_{52}H_{56}O_{10}$+H: 841.39. Found: 841.34.

**4.4.3. Compound 5c.** White crystalline solid; $R_f$: 0.053 (9:1 hexane–ethylacetate); mp >267 °C (decomp.). IR (KBr) $\nu_{max}$: 2954, 1786, 1720, 1485, 1346, 1288, 1195, 892 $cm^{-1}$. $^1H$ NMR: $\delta$ 9.70 (s, 2H), 7.17 (s, 2H), 7.07 (s, 2H), 4.85 (s, 2H), 4.01 (d, $J$=14.7 Hz, 2H), 3.55 (s, 2H), 3.50 (d, $J$=15.6 Hz, 2H), 3.29 (d, $J_1$=15.9 Hz, $J_2$= 14.4 Hz, 4H), 3.15 (d, $J$=8.1 Hz, 2H), 3.04 (d, $J$=7.8 Hz, 2H), 1.32 (s, 18H), 0.93 (s, 18H). $^{13}C$ NMR: $\delta$ 202.9, 180.6, 179.7, 150.5, 145.8, 128.1, 124.3, 119.7, 118.7, 117.3, 82.7, 51.1, 49.0, 45.4, 42.5, 37.2, 34.4, 31.6, 29.9, 27.7. MS (FAB) $m/z$ calcd for $C_{52}H_{58}N_2O_8^{+}$: 838.42. Found: 838.13.

**4.4.4. Compound 5d.** White crystalline solid; $R_f$: 0.18 (9:1 hexane–ethylacetate); mp>270 °C (decomp.). IR (KBr) $\nu_{max}$: 2954, 2236, 1739, 1483, 1363, 1282, 1203, 1143, 1047, 937 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.08 (s, 2H), 7.01 (s, 2H), 4.76 (s, 2H), 4.05 (d, $J$=14.5 Hz, 2H), 3.40 (d, $J$=15.3 Hz, 2H), 3.07 (br s, 2H), 3.05 (d, $J$=14.9 Hz, 2H), 2.72 (dd, $J_1$=2.9 Hz, $J_2$=2.6 Hz, 2H), 2.45 (d, $J$=14.6 Hz, 2H), 2.05 (uneven t, $J_1$=14.5 Hz, $J_2$=8.3 Hz, 2H), 1.75 (d, $J$=14.1 Hz, 2H), 1.31 (s, 18H), 1.01 (s, 18H). $^{13}C$ NMR: $\delta$ 204.4, 154.5,

145.7, 127.7, 125.0, 120.7, 120.0, 119.3, 117.3, 108.7, 84.3, 51.7, 42.8, 37.4, 37.0, 35.1, 31.5, 30.6, 27.3. MS (FAB) *m/z* calcd for $C_{50}H_{58}N_2O_4$+H: 750.44. Found: 751.04.

**4.4.5. Compound 5e.** White crystalline solid; $R_f$: 0.30 (9:1 hexane–ethylacetate); mp>268 °C (decomp.). IR (KBr) $\nu_{max}$: 2953, 2906, 2727, 1730 (br), 1483, 1436, 1362, 1205, 939 $cm^{-1}$. $^1H$ NMR: $\delta$ 9.47 (s, 2H), 7.08 (s, 2H), 6.84 (s, 2H), 4.72 (d, $J$=1.5 Hz, 2H), 4.16 (d, $J$=14.7 Hz, 2H), 3.50 (d, $J$=15.3 Hz, 2H), 3.10 (d, $J$=15.6 Hz, 2H), 3.08 (s, 2H), 2.46 (d, $J$=14.7 Hz, 2H), 2.44 (m, 2H), 1.89 (br s, 4H), 1.30 (s, 18H), 0.98 (s, 18H). $^{13}C$ NMR: $\delta$ 202.4, 201.0, 154.4, 152.1, 143.8, 126.3, 124.9, 120.0, 119.5, 116.4, 84.3, 55.2, 53.0, 51.5, 42.6, 34.5, 34.1, 31.7, 29.0, 27.4, 23.9. MS (FAB) *m/z* calcd for $C_{50}H_{60}O_6$+H: 756.44. Found: 757.27.

**4.4.6. Compound 5f.** White crystalline solid; $R_f$: 0.32 (9:1 hexane–ethylacetate); mp>283 °C (decomp.): IR (KBr) $\nu_{max}$: 2955, 1738 (br), 1481, 1362, 1258, 1200, 1171, 1049, 935 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.09 (s, 2H), 6.79 (s, 2H), 4.63 (s, 2H), 3.97 (d, $J$=14.6 Hz, 2H), 3.79 (s, 6H), 3.46 (d, $J$=15.5 Hz, 2H), 3.11 (d, $J$=15.6 Hz, 2H), 3.05 (br s, 2H), 2.74 (dd, $J_1$=3.9 Hz, $J_2$=3.8 Hz, 2H), 2.40 (d, $J$=14.7 Hz, 2H), 2.01 (uneven t, $J_1$=12.6 Hz, $J_2$=11.2 Hz, 2H), 1.71 (m, 2H), 1.30 (s, 18H), 0.97 (s, 18H). $^{13}C$ NMR: $\delta$ 203.5, 172.5, 154.7, 149.6, 143.2, 126.6, 124.5, 120.3, 119.3, 116.1, 83.7, 51.9, 51.3, 48.0, 42.4, 36.9, 34.3, 31.6, 28.6, 27.3. MS (FAB) *m/z* calcd for $C_{52}H_{64}O_8^+$: 816.46. Found: 816.48.

**4.4.7. Compound 5g (inseparable isomers in the ratio 1:1).** White crystalline solid; $R_f$: 0.18 (9:1 hexane–ethylacetate); mp>270 °C (decomp.). IR (KBr) $\nu_{max}$: 2957, 1742 (br), 1483, 1437, 1365, 1319, 1199, 1178, 1020, 947 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.20 (s, 2H), 7.11 (s, 2H), 6.99 (s, 2H), 6.77 (s, 2H), 4.91 (s, 2H), 4.60 (s, 2H), 4.05 (d, $J$=15.9 Hz, 2H), 3.89 (s, 6H), 3.85 (s, 6H), 3.81 (s, 6H), 3.78 (s, 6H), 3.63 (s, 4H), 3.50 (s, 2H), 3.35 (m, 8H), 3.22 (s, 4H), 2.88 (s, 2H), 2.79 (m, 2H), 2.47 (d, $J$=3.9 Hz, 2H), 2.42 (d, $J$=3.9 Hz, 2H), 1.31 (s, 36H), 1.01 (s, 18H), 0.87 (s, 18H). $^{13}C$ NMR: $\delta$ 204.0, 203.4, 175.6, 175.1, 154.9, 154.7, 154.1, 153.9, 151.9, 151.7, 150.8, 150.5, 145.5, 128.7, 128.5, 127.4, 127.2, 125.9, 125.7, 125.2, 125.1, 120.8, 117.1, 84.1, 83.1, 54.5, 53.8, 53.7, 53.6, 53.5, 52.9, 50.4, 47.3, 44.4, 44.3, 37.0, 36.7, 35.2, 34.4, 31.2, 30.3, 29.7, 29.4, 27.4. MS (FAB) *m/z* calcd for $C_{56}H_{68}O_{12}^+$: 932.47. Found: 932.56.

### 4.5. Typical experimental procedure for 7a

A solution of **1a** (50 mg, 0.078 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (28 mg, 0.163 mmol) in dry toluene (5 mL) was stirred under an inert atmosphere at rt. The reaction mixture was stirred at this temperature until the reaction was complete as indicated by TLC (6 h). The solvent was removed under reduced pressure and the residue purified by silica gel column chromatography, to remove excess dienophile, using hexane–ethylacetate (90:10) as the eluent to yield **7a** (75 mg, 99%). The product was recrystallized from dichloromethane–acetonitrile mixture by slow evaporation method.

**4.5.1. Compound 7a.** White crystalline solid; $R_f$: 0.24 (9:1 hexane–ethylacetate); mp>274 °C (decomp.). IR (KBr) $\nu_{max}$: 2957, 1764, 1712, 1363, 1219, 1093 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.52–7.37 (m, 10H), 7.20 (s, 2H), 7.11 (s, 2H), 5.24 (s, 2H), 5.11 (d, $J$=1.8 Hz, 2H), 4.28 (d, $J$=15.3 Hz, 2H), 4.18 (d, $J$=15.3 Hz, 2H), 3.63 (d, $J$=16.5 Hz, 2H), 3.52 (d, $J$=16.5 Hz, 2H), 1.33 (s, 18H), 1.07 (s, 18H). $^{13}C$ NMR: $\delta$ 193.4, 154.6, 154.2, 152.3, 146.2, 131.2, 129.4, 128.8, 128.4, 125.9, 124.4, 121.5, 119.4, 118.1, 81.5, 67.8, 60.6, 37.1, 34.8, 33.9, 32.2, 29.9, 27.6, 26.5. MS (FAB) *m/z* calcd for $C_{60}H_{62}N_6O_8$+H: 996.17. Found: 996.01.

**4.5.2. Compound 7b.** White crystalline solid; $R_f$: 0.46 (9:1 hexane–ethylacetate); mp>272 °C (decomp.). IR (KBr) $\nu_{max}$: 2931, 1764, 1711, 1482, 1405, 1372, 1109, 897 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.16 (s, 2H), 7.09 (s, 2H), 5.12 (d, $J$=2.0 Hz, 2H), 4.94 (d, $J$=2.0 Hz, 2H), 4.16 (d, $J$=15.4 Hz, 2H), 4.08 (d, $J$=15.4 Hz, 2H), 3.74 (m, 2H), 3.54 (d, $J$=16.3 Hz, 2H), 3.43 (d, $J$=16.3 Hz, 2H), 2.03 (m, 4H), 1.80 (m, 4H), 1.63 (m, 6H), 1.34 (s, 18H), 1.25 (m, 6H), 0.98 (s, 18H). $^{13}C$ NMR: $\delta$ 193.4, 155.7, 155.4, 154.2, 151.6, 145.7, 128.2, 124.3, 121.1, 118.8, 118.1, 81.3, 67.2, 60.2, 52.7, 36.8, 34.5, 33.5, 31.9, 29.3, 27.4, 26.3, 25.8, 24.9. MS (FAB) *m/z* calcd for $C_{60}H_{74}N_6O_8$+H: 1007.56. Found: 1007.54.

**4.5.3. Compound 7c.** White crystalline solid; $R_f$: 0.27 (9:1 hexane–ethylacetate); mp>278 °C (decomp.). IR (KBr) $\nu_{max}$: 2955, 2914, 1758, 1711, 1556, 1540, 1455, 1430, 1109, 897 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.33 (m, 10H), 7.15 (s, 2H), 7.10 (s, 2H), 5.05 (s, 2H), 4.95 (s, 2H), 4.58 (s, 4H), 4.17 (d, $J$=15.3 Hz, 2H), 4.07 (d, $J$=15.3 Hz, 2H), 3.50 (d, $J$=16.5 Hz, 2H), 3.41 (d, $J$=16.5 Hz, 2H), 1.33 (s, 18H), 0.90 (s, 18H). $^{13}C$ NMR: $\delta$ 191.5, 153.9, 153.7, 153.0, 147.1, 145.3, 139.1, 130.8, 127.5, 127.2, 124.2, 121.5, 119.2, 117.1, 81.4, 68.6, 59.8, 44.4, 36.7, 34.6, 34.3, 33.7, 32.0, 29.9, 26.5. MS (FAB) *m/z* calcd for $C_{62}H_{66}N_6O_8$+H: 1022.49. Found: 1023.22.

**4.5.4. Compound 7d.** White crystalline solid; $R_f$: 0.24 (9:1 hexane–ethylacetate); mp>260 °C (decomp.). IR (KBr) $\nu_{max}$: 2945, 1759, 1709, 1475, 1438, 1415, 1103, 927, 846 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.27 (m, 4H), 7.14 (s, 2H), 7.09 (s, 2H), 6.80 (d, $J$=8.4 Hz, 4H), 5.04 (s, 2H), 4.93 (s, 2H), 4.51 (s, 4H), 4.15 (d, $J$=16.8 Hz, 2H), 4.06 (d, $J$=15.0 Hz, 2H), 3.77 (s, 6H), 3.48 (d, $J$=16.8 Hz, 2H), 3.39 (d, $J$=15.6 Hz, 2H), 1.33 (s, 18H), 0.90 (s, 18H). $^{13}C$ NMR: $\delta$ 192.0, 159.0, 154.0, 153.1, 147.5, 130.4, 128.8, 127.8, 126.6, 124.5, 122.2, 119.5, 117.3, 115.2, 81.6, 68.7, 59.7, 56.1, 44.0, 36.9, 34.8, 34.4, 31.7, 30.2, 29.4, 26.4. MS (FAB) *m/z* calcd for $C_{64}H_{70}N_6O_{10}$+H: 1083.52. Found: 1083.64.

**4.5.5. Compound 7e.** White crystalline solid; $R_f$: 0.30 (9:1 hexane–ethylacetate); mp>265 °C (decomp.). IR (KBr) $\nu_{max}$: 2959, 1745, 1713, 1483, 1437, 1409, 1201, 1169, 1105, 950, 840, 756 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.19 (m, 8H), 7.14 (s, 2H), 7.10 (s, 2H), 5.20 (d, $J$=1.9 Hz, 2H), 5.17 (d, $J$=2.0 Hz, 2H), 4.67 (s, 4H), 4.19 (d, $J$=15.4 Hz, 2H), 3.99 (d, $J$=15.5 Hz, 2H), 3.53 (d, $J$=16.2 Hz, 2H), 3.36 (d, $J$=16.3 Hz, 2H), 2.33 (s, 6H), 1.33 (s, 18H), 0.98 (s, 18H). $^{13}C$ NMR: $\delta$ 191.8, 153.8, 153.0, 147.1, 139.1, 130.8, 128.5, 128.2, 124.2, 121.8, 119.2, 117.1, 81.3, 68.4, 59.4, 44.1, 36.6, 34.6, 34.1, 33.7, 32.1, 29.9, 29.6, 26.1, 20.9. MS (FAB) *m/z* calcd for $C_{64}H_{70}N_6O_8$+: 1050.53. Found: 1050.57.

**4.5.6. Compound 7f.** White crystalline solid; $R_f$: 0.27 (9:1 hexane–ethylacetate); mp>255 °C (decomp.). IR (KBr) $\nu_{max}$: 2955, 1763, 1713, 1485, 1435, 1410, 1199, 1099, 950, 844 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.28 (m, 8H), 7.10 (s, 2H), 7.08 (s, 2H), 5.19 (s, 2H), 5.16 (s, 2H), 4.67 (s, 4H), 4.18 (d, $J$=15.4 Hz, 2H), 3.97 (d, $J$=15.5 Hz, 2H), 3.52 (d, $J$=16.3 Hz, 2H), 3.36 (d, $J$=16.3 Hz, 2H), 1.34 (s, 18H), 0.97 (s, 18H). $^{13}C$ NMR: $\delta$ 191.7, 153.8, 152.8, 147.0, 146.3, 135.2, 132.4, 128.5, 128.0, 126.2, 124.1, 121.8, 119.2, 117.0, 81.2, 68.3, 59.4, 43.5, 36.6, 34.6, 34.15, 32.6, 31.4, 29.9, 26.1. MS (FAB) *m/z* calcd for $C_{62}H_{64}Cl_2N_6O_8$+H: 1091.42. Found: 1091.09.

### 4.6. Typical experimental procedure for 9a

To calix[4]bis(spirodienone) **1a** (50 mg, 0.078 mmol) was added dry toluene (5 mL) and stirred under inert atmosphere. Diethyl azodicarboxylate (27 mg, 0.155 mmol) was added to it and the mixture heated at 110 °C for 7 h. The solvent was removed under vacuum and the residue subjected to silica gel column chromatography using hexane–ethylacetate mixture (90:10) as the eluent to afford **9a** as a white solid (70 mg, 90%).

**4.6.1. Compound 9a.** White crystalline solid; $R_f$: 0.21 (9:1 hexane–ethylacetate); mp>252 °C (decomp.). IR (KBr) $\nu_{max}$: 2958, 1756, 1738, 1703, 1484, 1413, 1311, 1266, 1251, 1112, 843 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.05 (s, 2H), 6.98 (s, 2H), 5.43 (s, 2H), 5.20 (s, 2H), 5.13 (d, $J$=14.1 Hz, 2H), 4.97 (d, $J$=14.1 Hz, 2H), 4.19 (m, 8H), 3.64–3.39 (m, 4H), 1.32 (s, 18H), 1.26–1.15 (m, 12H), 0.99 (s, 18H). $^{13}C$ NMR: $\delta$ 196.9, 159.1, 154.9, 151.3, 144.7, 127.4, 126.9, 125.1, 124.9, 120.6, 119.2, 118.6, 84.3, 68.2, 63.1, 62.7, 56.3, 35.3, 35.2, 34.7, 31.9, 29.1, 27.8, 14.6. MS (FAB) *m/z* calcd for $C_{56}H_{72}O_{12}N_4$+H: 993.52. Found: 993.48.

**4.6.2. Compound 9b.** White crystalline solid; $R_f$: 0.38 (9:1 hexane–ethylacetate); mp>256 °C (decomp.). IR (KBr) $\nu_{max}$: 2960, 1754, 1740, 1486, 1412, 1320, 1276, 1257, 1115, 850 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.23 (s, 2H), 7.01 (s, 2H), 5.41 (s, 2H), 5.22 (m, 2H), 4.91 (m, 4H), 4.17 (d, $J$=15.0 Hz, 2H), 3.62 (m, 2H), 3.45 (m, 2H), 3.34 (br s, 2H), 1.34 (s, 18H), 1.26 (m, 24H), 0.99 (s, 18H). $^{13}C$ NMR: $\delta$ 193.1, 157.0, 156.2, 152.0, 151.7, 135.2, 127.3, 121.0, 88.6, 75.0, 74.5, 73.7, 73.1, 34.5, 33.7, 33.5, 31.6, 29.1, 26.9, 22.0, 21.7, 21.5, 21.3, 21.2, 18.7, 18.4. MS (FAB) *m/z* calcd for $C_{60}H_{80}N_4O_{12}$+H: 1049.58. Found: 1049.25.

### 4.7. Typical experimental procedure for 11a

Calix[4]bis(spirodienone) **1a** (50 mg, 0.078 mmol) was dissolved in dry chloroform (10 mL) under inert atmosphere. Benzohydroxamic acid (22 mg, 0.163 mmol) was added to it and stirred for 5 min at rt. To the reaction mixture was added tetrabutylammonium periodate (135 mg, 0.310 mmol) and heated at 61 °C for 24 h. The solvent was removed under vacuum and the residue subjected to silica gel column chromatography using 95:5 hexane–ethylacetate mixture to afford **11a** (35 mg, 50%) as a white solid.

**4.7.1. Compound 11a.** White crystalline solid; $R_f$: 0.54 (9:1 hexane–ethylacetate); mp>235 °C (decomp.). IR (KBr) $\nu_{max}$: 2961, 1759, 1653, 1540, 1481, 1365, 1255 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.69 (d, $J$=6.9 Hz, 4H), 7.46–7.38 (m, 6H), 7.17 (s, 2H), 6.91 (s, 2H), 5.85 (s, 2H), 5.12 (s, 2H), 4.04 (d, $J$=14.7 Hz, 2H), 3.64 (d, $J$=16.2, 2H), 3.48 (d, $J$=16.2 Hz, 2H), 2.36 (d, $J$=15.3 Hz, 2H), 1.31 (s, 18H), 1.07 (s, 18H). $^{13}C$ NMR: $\delta$ 195.1, 155.1, 153.6, 144.6, 143.4, 139.6, 128.0, 127.8, 126.0, 123.9, 121.5, 120.4, 116.5, 109.9, 82.5, 58.3, 38.1, 35.7, 34.7, 34.4, 32.1, 28.6, 28.1. MS (FAB) *m/z* calcd for $C_{58}H_{62}N_2O_8$+H: 915.45. Found: 915.17.

**4.7.2. Compound 11b.** White crystalline solid; $R_f$: 0.50 (9:1 hexane–ethylacetate); mp>238 °C (decomp.). IR (KBr) $\nu_{max}$: 2965, 1762, 1656, 1640, 1485, 1365, 1257, 867 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.68 (d, $J$=7.8 Hz, 4H), 7.39 (d, $J$=8.1 Hz, 4H), 7.16 (s, 2H), 6.95 (s, 2H), 5.84 (s, 2H), 5.11 (s, 2H), 4.06 (d, $J$=14.7 Hz, 2H), 3.63 (d, $J$=15.9 Hz, 2H), 3.47 (d, $J$=16.5 Hz, 2H), 2.40 (d, $J$=15.6 Hz, 2H), 1.34 (s, 18H), 1.31 (s, 18H), 1.07 (s, 18H). $^{13}C$ NMR: $\delta$ 193.6, 178.1, 152.0, 143.2, 142.8, 142.0, 138.2, 126.4, 125.6, 124.6, 123.8, 122.5, 120.0, 118.5, 115.0, 80.2, 58.7, 36.7, 34.2, 33.8, 33.1, 32.7, 29.0, 29.5, 26.8. MS (FAB) *m/z* calcd for $C_{66}H_{78}N_2O_8$+H: 1027.26. Found: 1027.58.

### 4.8. Experimental procedure for 12a and 12b

Calix[4]bis(spirodienone) **1a** (50 mg, 0.078 mmol) was dissolved in a mixture of chloroform and water (12 mL) in the ratio 1:3. To the reaction mixture sodium hydroxide (>7.8 mmol) and a catalytic amount of tetrabutyl ammoniumbromide were added and stirred at rt for 8 h. To the reaction mixture, 5 mL of $CHCl_3$ and 5 mL water were added, and after phase separation the organic phase was washed with water, brine and then dried over $Na_2SO_4$. After the organic solvent was evaporated, the residue was chromatographed [silica, eluent: hexanes–ethylacetate mixture (98:2)] and the compounds isolated were crystallized from dichloromethane–acetonitrile mixture yielding 30 mg of **12a** (48%) and 25 mg of **12b** (44%).

**4.8.1. Compound 12a.** White crystalline solid; $R_f$: 0.67 (9:1 hexane–ethylacetate); mp>250 °C (decomp.). IR (KBr) $\nu_{max}$: 2956, 1686, 1479, 1365, 1255, 1103, 874 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.15 (s, 2H), 7.07 (s, 2H), 6.53 (s, 2H), 4.08 (uneven t, $J_1$=14.9 Hz, $J_2$=14.1 Hz, 4H), 3.17 (d, $J$=15.8 Hz, 2H), 2.89 (d, $J$=14.8 Hz, 2H), 2.61 (s, 2H), 1.36 (s, 18H), 0.92 (s, 18H). $^{13}C$ NMR: $\delta$ 186.0, 152.6, 144.2, 143.5, 138.7, 125.7, 125.6, 122.6, 120.0, 81.3, 68.3, 41.5, 39.9, 36.0, 34.4, 34.2, 31.9, 27.8, 27.6. MS (FAB): *m/z* calcd for $C_{46}H_{52}Cl_4O_4$+2H: 810.26. Found: 810.46.

**4.8.2. Compound 12b.** Pale yellow solid; $R_f$: 0.63 (9:1 hexane–ethylacetate); mp>260 °C (decomp.). IR (KBr) $\nu_{max}$: 2960, 1689, 1365, 1201, 869 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.15 (s, 1H), 7.09 (s, 1H), 7.05 (s, 2H), 6.62 (s, 1H), 6.53 (s, 1H), 5.83 (s, 1H), 4.12 (m, 3H), 3.71 (d, $J$=15.6 Hz, 1H), 3.18 (d, $J$=16.2 Hz, 1H), 3.03 (d, $J$=15.3 Hz, 1H), 2.85 (uneven t, $J_1$=14.1 Hz, $J_2$=13.2 Hz, 2H), 2.62 (s, 1H), 1.35 (s, 18H), 1.03 (s, 9H), 0.96 (s, 9H). $^{13}C$ NMR: $\delta$ 195.0, 186.5, 153.3, 144.8, 143.7, 143.4, 142.3, 139.1, 138.4, 134.3, 127.3, 126.3, 125.7, 124.4, 123.1, 122.6, 122.5, 120.3, 120.1, 119.6, 119.3, 81.6, 81.3, 68.3, 40.5, 40.1, 38.2, 34.9, 34.3, 31.9, 31.5, 28.7, 28.5, 27.9, 27.6. MS (FAB) *m/z* calcd for $C_{45}H_{52}Cl_2O_4$+H: 727.32. Found: 727.42.

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