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Multifold Photocyclization Reactions of Styrylcalix[4]arenes

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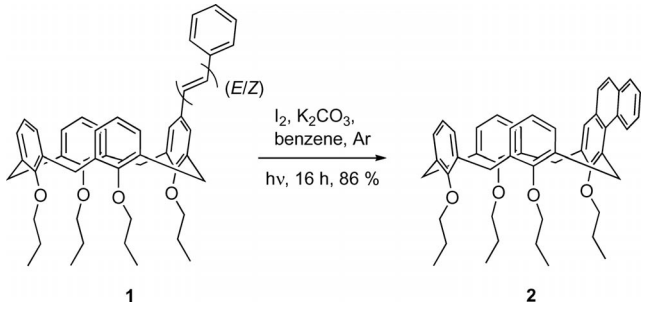
A photochemical transannular [2+2] cycloaddition reaction is the main reaction pathway for 1,3-substituted styrylcalix[4]arenes, whereas 1,2-distyrylcalix[4]arenes give calix[4]diphenanthrenes.

Introduction

Calixarenes and resorcinarenes that provide well-defined electron-rich cavities are favourite systems for studying host–guest interactions.[1,2] Extending and functionalizing the rims of the cavities should give access to tailor-made hosts for molecular recognition.

We have previously reported optimized reaction conditions for the oxidative photocyclization of monostyrylcalixarene **1** to the first calix[4]monophenanthrene **2** by the irradiation of **1** with iodine and potassium carbonate in benzene (Scheme 1).[3] The presence of the base proved to be crucial for inhibiting acid-catalysed ring cleavage at an intermediary enol ether moiety, giving rise to a linear tetramer as the major product. Herein we describe the synthesis of calixarenes with multiple stilbene units and their photochemical cyclization reactions.



Scheme 1. Optimized reaction conditions for the synthesis of calixarene **2**.

Results and Discussion

As an approach to calixphenanthrene **5** we prepared distyrylcalixarene **4** in analogy to the synthesis of monostyrylcalixarene **1** by Wittig reaction of diformylcalixarene[4] **3** with benzyltriphenylphosphonium chloride (Scheme 2). Product **4** was obtained in excellent yield as a mixture of the three different *E*/*Z* isomers and the molecular mass was verified by a peak at *m*/*z* = 796 in the FAB mass spectrum. A 1:2 ratio of the *E* and *Z* stilbene units was determined from the integrals of the bridging methylene proton signals and in comparison with the published ^{1}H NMR spectroscopic data for the pure (*E*,*E*)-distyrylcalixarene (prepared by Horner–Wadsworth–Emmons reaction in 73% yield).[4] We also succeeded in obtaining the sole *E*,*E* isomer by the reported iodine-catalysed isomerization.[4]

The photochemical cyclization of calixarene **4** with a medium-pressure Hg lamp (125 W) in the presence of iodine and potassium carbonate in benzene yielded 90% of cyclization products. In the ^{1}H NMR spectrum the diagnostic signal for the bay-region proton was registered at around 8.63 ppm, proving the formation of phenanthrene. However, HPLC clearly indicated the presence of three different products, two of which were poorly resolved. The cyclobutane-bridged calixarene **6** was the only compound that could be isolated analytically pure in a 37% yield (Scheme 3). Clearly this product is a result of a transannular [2+2] cycloaddition reaction of the stilbene units, comparable to the synthesis of ladderanes from functionalized [2.2]paracyclophanes described by Hopf et al.[5] The ^{13}C NMR spectrum exhibits diagnostic signals at δ = 45.0 and 48.7 ppm arising from cyclobutane carbons. The signals of the corresponding protons appear at δ = 3.76 and 3.86 ppm in the ^{1}H NMR spectrum. In addition, a peak at *m*/*z* = 796 in the FAB mass spectrum confirms the molecular mass, identical to the molecular mass of the starting material, therefore excluding oxidative cyclization to the target calix[4]diphenanthrene **5**. Notably, the extraordinary upfield shift of the *m*-aryl protons of the substituted phenyl units to δ = 5.50 and 5.86 ppm reveals that calixarene **6** is fixed in a pinched cone conformation. The bridging cyclobutane leads to the coplanarity of the opposite benzene rings, whereas the unsubstituted units stick out. The ^{13}C NMR spectrum before crystallization clearly indicates a cone conformation as there are no signals at about 37 ppm for meth-

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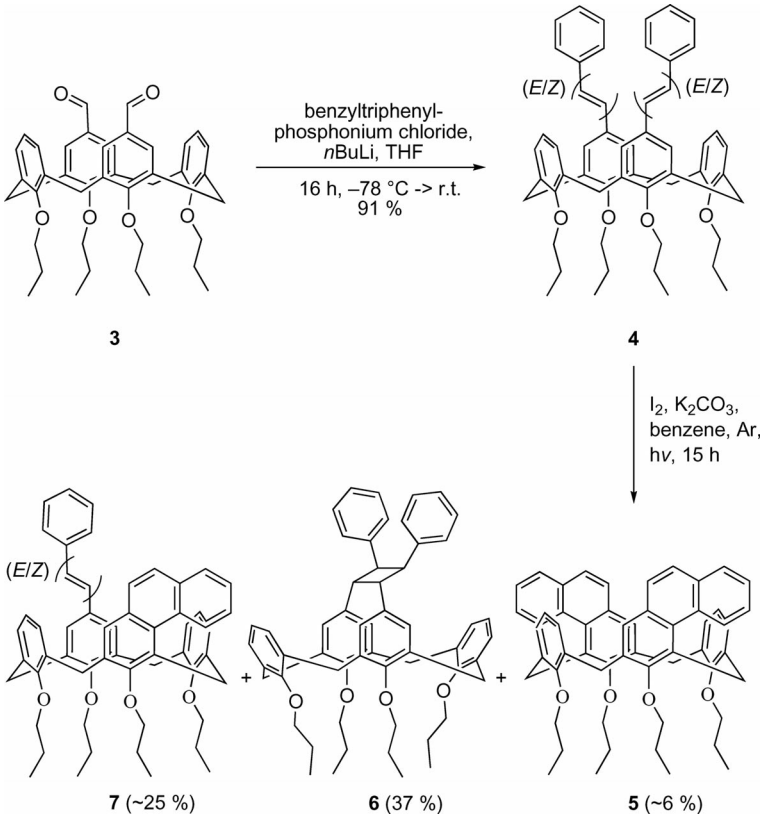
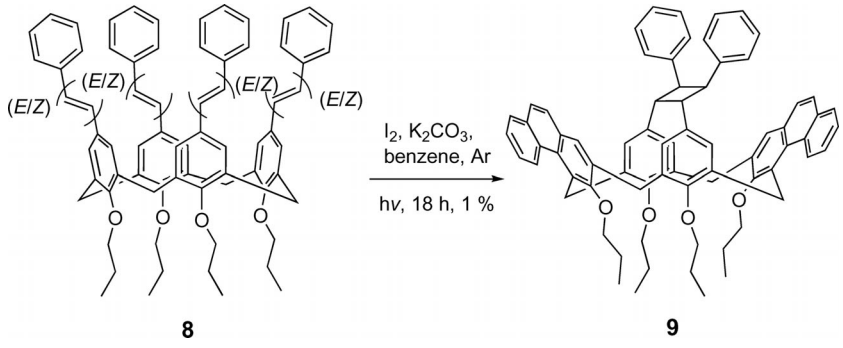


Scheme 2. Synthesis and photolysis of styrylcalix[4]arene **4**.

ylene carbons, which would indicate an *anti* orientation of the adjacent phenyl units in the calixarene ring.[6] However, the crystal structure analysis of a randomly picked single crystal surprisingly showed **6** in a partial cone conformation (Figure 1). According to semi-empirical PM3 calculations the partial cone conformation is minimally favoured by 0.8 kcal mol^{-1} compared with the cone conformation, but interconversion between the two conformations is prevented by the propyl groups.[7] Therefore we assume that the crystals obtained do not represent the bulk material, but a minor impurity not detectable in the NMR spectra. Two additional fractions isolated by HPLC showed diagnostic phenanthrene ^{1}H NMR signals at around 8.6 ppm. Based on the integration of the NMR signals we identified these fractions as calixmonophenanthrene **7**, with the molecular peak at *m*/*z* = 794 in the FAB mass spectrum, and the desired calixdiphenanthrene **5**, unfortunately obtained as a minor by-product. Overall, a product ratio of 6:4:1 was determined for compounds **6**, **7** and **5**.

Photolysis of the four-fold stilbene **8** under the same reaction conditions as for **4** gave a highly complex mixture of cyclization products, as observed by Mattay and Barton.[8] After separation by HPLC we succeeded in isolating an analytically pure sample of the cyclobutane-bridged calix[4]diphenanthrene diastereomer **9** in 1% yield (Scheme 3). The ^{1}H NMR spectrum exhibits a diagnostic signal of the phenanthrene 5-H at δ = 8.51 ppm and diagnostic signals for the cyclobutane ring in the ^{13}C NMR spectrum appear at δ = 44.3, 46.2, 47.7 and 47.9 ppm. The large upfield shift of the *meta* protons of the bridged phenyl units to δ = 5.01,



Scheme 3. [2+2] cycloaddition by photolysis of styrylcalix[4]arene **8**.

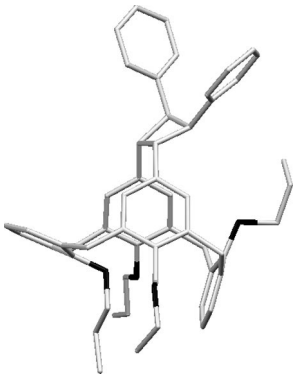
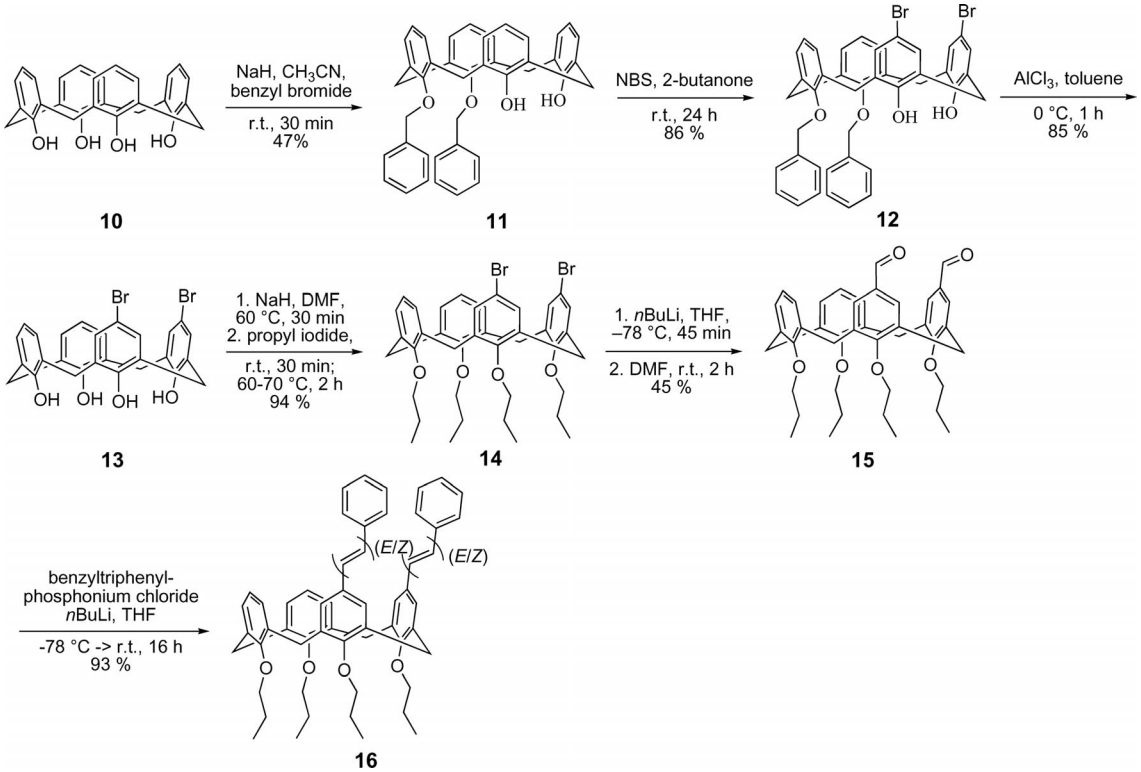


Figure 1. Crystal structure of cyclobutane-bridged calixarene **6** in the partial cone conformation.

5.2, 5.6 and 6.1 ppm reveals that this structure is also fixed in a pinched cone conformation. The upfield shift is further increased by the ring-current effect of the phenanthrene units. The orientation of both phenanthrene moieties in the same direction is verified by an anisotropic downfield shift of two OCH_2 groups to δ = 77.96 and 78.05 ppm in the ^{13}C NMR spectrum, distinct from the signals of the other OCH_2 groups at δ = 76.4 and 76.5 ppm. A peak at m/z = 997 in the FAB mass spectrum also confirms the formation of compound **9**.

Because [2+2] cycloaddition should not take place between adjacent stilbene units in a calixarene, we decided to synthesize the 1,2-distyrylcalix[4]arene **16** as a promising model compound for oxidative bis-cyclization (Scheme 4). Therefore we developed an independent synthetic procedure for the synthesis of diformylcalixarene **15**: Parent calix[4]arene **10** was stirred with sodium hydride and benzyl bromide in acetonitrile at room temperature[9] to yield the proximally substituted dibenzylcalixarene **11** in up to 47% yield. Tetrabenzylcalix[4]arene and monobenzylcalix[4]-arene were isolated in yields of up to 32 and 6% along with traces of the distally substituted dibenzylcalixarene and starting material. Bromination of **11** was achieved according to a literature procedure[9] by treatment with *N*-bromosuccinimide in 2-butanone to give 86% of dibromo compound **12**. Removal of the benzyl groups with aluminium chloride in toluene at 0 °C[8] led to 85% of the 5,11-dibromocalixarene **13**,[10] easily identified by the broad ^1H NMR signals of the methylene protons. Introduction of the propyl groups under standard reaction conditions[11] resulted in an excellent 94% yield of calixarene **14**, which was transformed into the diformylcalixarene **15**[12] by lithiation with *n*-butyllithium in THF and subsequent treatment with DMF in 45% yield. Wittig reaction of **14** with benzyltriphenylphosphonium chloride resulted in a 93% yield of the desired distyrylcalixarene **16**. Due to the formation of a mixture of the possible *E*/*Z* isomers the signal pattern for the bridging methylene protons in the ^1H NMR spectrum was rather complex: six signals for equatorial protons and seven for axial protons. Again, isomerization with iodine led to a simpler spectrum, especially in the aliphatic region, showing only three doublets for equatorial protons and one at δ = 4.46 ppm for the axial ones. In the ^{13}C NMR spectrum of the unisomerized **16**, eight different peaks appear between



Scheme 4. Synthesis of 5,11-distyrylcalix[4]arene (**16**).

δ = 156.2 and 157.2 ppm for the tertiary aromatic carbon atoms substituted by propoxy groups, which indicates that all possible isomers were formed. A signal at *m*/*z* = 796 in the FAB mass spectrum unambiguously identified styrylcalixarene **16**.

The proximally disubstituted distyrylcalixarene was irradiated in accord with our standard photolysis conditions with iodine and potassium carbonate in benzene; purification by flash chromatography yielded the cyclization products in 67% yield. From 235 mg of the material subjected to HPLC three different compounds were isolated, all of which showed a molecular signal at *m*/*z* = 792 in the FAB mass spectra, as expected for the three diastereoisomers of the desired calixphenanthrenes (Scheme 5). Semi-empirical PM3 calculations revealed that the diastereoisomer **17c** should be favoured over structures **17b** and **17a** by about 3.4 and 10.6 kcal mol^{-1}, respectively. However, we were able to clearly identify the main product as structure **17a** by one- and two-dimensional NMR experiments as well as by crystal structure analysis (Figure 2). These findings suggest that attractive π–π interactions predominate over steric repulsion in the first cyclization. Although the configuration of **17a** is that of a *meso* compound, the steric demands of the phenanthrene units pointing towards each other result in an asymmetric conformation of the molecule. The large number of signals, both in the ^{1}H and ^{13}C NMR spectra, and the signal pattern of the propyl groups and bridging methylene groups in the ^{1}H NMR spectrum as well as the crystal structure confirm the chirality of **17a**. Diagnostic signals for Phen-5-H appear at δ = 8.70 and 7.61 ppm. The phenanthrene, tilted towards the cavity, experiences anisotropic effects from the other phenanthrene. The upfield shift of a singlet at δ = 6.00 ppm (Figure 3), assigned to one Phen-1-H, and the aryl protons of an unsubstituted aryl unit prove that these units are tilted towards each other (rings B and D).

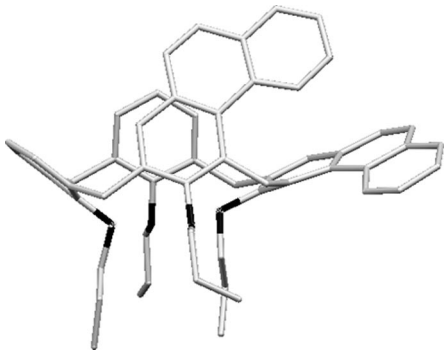
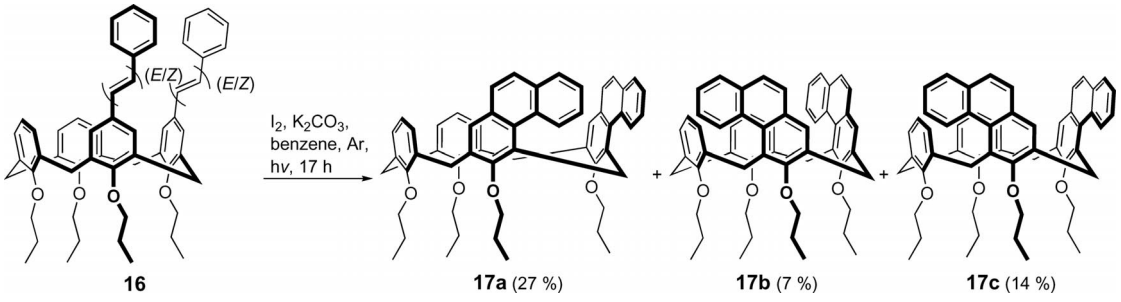


Figure 2. Crystal structure of the proximal substituted calix[4]diphenanthrene **17a**.



Scheme 5. Photolysis of 5,11-distyrylcalix[4]arene **16**.

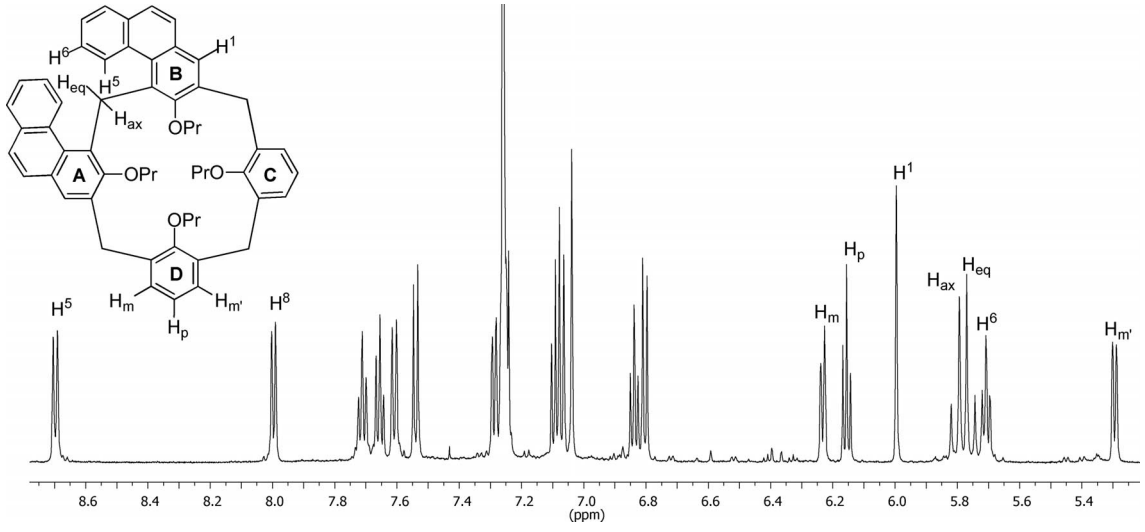


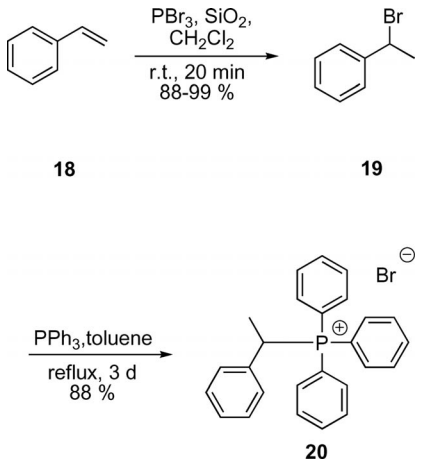
Figure 3. Partial ^{1}H NMR spectrum of **17a**, recorded at 600 MHz in $CDCl_3$.

Thus, the *meta* proton facing the phenanthrene unit exhibits the strongest paratropic shift to δ = 5.30 ppm. This unit exhibits a 1.03 ppm upfield shift for its Phen-5-H as well as an even stronger paratropic shift for the corresponding Phen-6-H, which is found as a triplet at δ = 5.71 ppm. Notably, the two methylene protons at the bridge between the phenanthrene units exhibit an extremely large downfield shift of about 2 ppm, especially in the case of the equatorial proton, appearing at δ = 5.76 and 5.81 ppm. In addition, they exhibit a somewhat enlarged geminal coupling constant of J = 15.9 Hz compared with the normal 13.5 Hz.

The number of signals in the NMR spectra exhibited by the second compound isolated by HPLC indicates a plane of symmetry, which can only be in agreement with structure **17b**. Indeed, there are only two peaks for both the propoxy carbons and the phenyl carbons attached to the oxygen atoms in the ^{13}C NMR spectrum, which confirms two different sets of aryl units. In addition, the three signals for the bridging methylene carbons at δ = 30.5, 30.9 and 31.3 ppm as well as the three sets of doublets, identified by coupling in the two-dimensional NMR spectra, confirm the highly symmetric proximal difunctionalization of the calixarene. The diagnostic phenanthrene signal at δ = 8.78 ppm in the ^{1}H NMR spectrum integrates to two protons, further evidence that two phenanthrene units have been formed. The broad signals assigned to the *m*-aryl protons, at δ = 5.80 and 6.20 ppm, and the *m*-Phen protons at δ = 7.06 ppm suggest a dynamic process. The relative upfield shift of the aryl protons is indicative of a pinched cone conformation whereas the peak-broadening implies an equilibrium of the two conformations with coalescence at room temperature.

The third compound obtained by HPLC shows rather complicated NMR spectra; the number of signals again implies high asymmetry. On the basis of the peak in the FAB mass spectrum at m/z = 792 and the diagnostic signal for the phenanthrene-5-H at δ = 8.73 ppm with an integration of two protons, it is probably the third expected stereoisomer **17c** with both phenanthrene units pointing in the same direction. Regarding the missing symmetry in this isomer, which should exist in a racemic mixture with its enantiomer, complicated NMR spectra are of no surprise. For the bridging methylene units four sets of doublets appear in the ^{1}H NMR spectrum. The signals at δ = 4.52 and 4.66 ppm exhibit the large downfield shifts expected for the equatorial methylene protons in the bay region of the phenanthrene units with their axial partners appearing at δ = 4.94 and 5.31 ppm. The ^{13}C NMR spectrum shows four signals for both the propyl carbons attached to the oxygen atoms and the bridging methylene carbon atoms and three signals for the aryl carbons attached to the oxygen, one of which consists of two superimposed peaks for the PhenC–O. Broad signals at δ = 6.39 and 7.49 ppm might indicate again a dynamic process of the different pinched cone conformations.

After successfully synthesizing the calix[4]diphenanthrenes **17a**–**c**, we decided to introduce an additional methyl group at the stilbene moiety in order to suppress [2+2] cycloaddition by steric hindrance. First, the modified benzyltriphenylphosphonium bromide **20** had to be prepared as depicted in Scheme 6. The first step involved the hydrobromination of styrene (**18**) by a literature procedure[13] to give (1-bromoethyl)benzene (**19**) in 88–99% yield after distillation in vacuo. Subsequent conversion to compound **20**, involving procedures described in the literature,[14,15] resulted in yields lower than 50%, which prompted us to optimize the reaction conditions (Table 1). Benzyltriphenylphosphonium bromide **20** was finally obtained in 88% yield by heating **19** at reflux with triphenylphosphane in toluene for 3 days in a screw-capped flask.



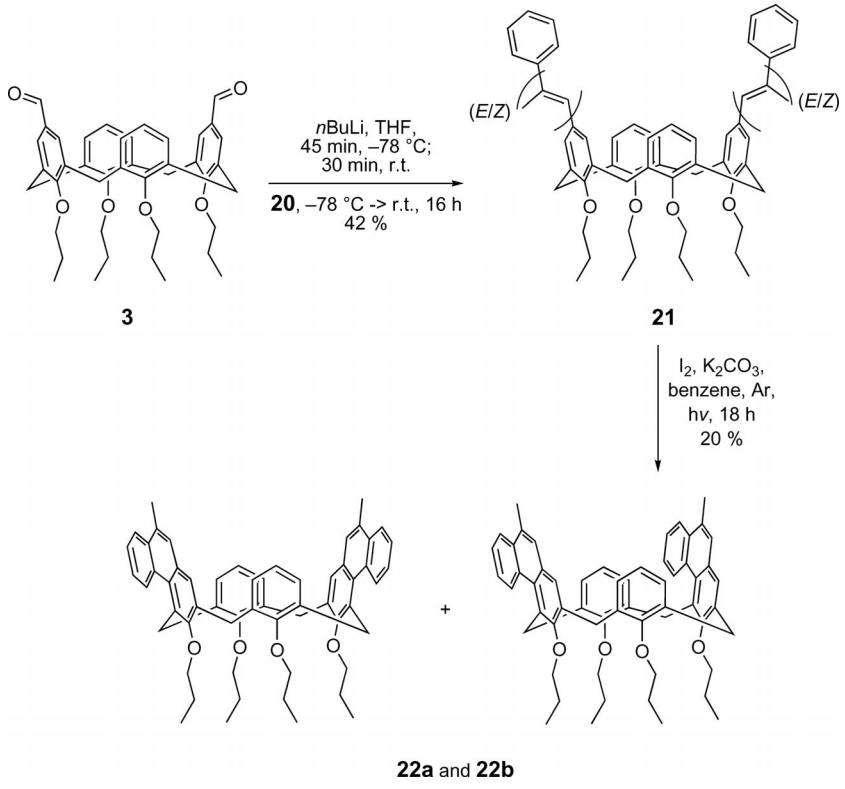
Scheme 6. Synthesis of benzyltriphenylphosphonium bromide **20**.

Table 1. Reaction conditions for the synthesis of (1-phenylethyl)-triphenylphosphonium bromide **20**.

Entry	Solvent	Time	Yield [%]
1	benzene	24 h	44[a]
2	ethyl acetate	24 h	45[b]
3	toluene	24 h	62
4	toluene	3 d	88

[a] Yield of 80% according to the literature.[14] [b] Yield of 78% according to the literature.[15]

Diformylcalixarene **3**[16] was then transformed into the corresponding distyrylcalixarene **21** in 42% yield under Wittig conditions (Scheme 7). Its ^{1}H NMR spectrum is much less complicated than that of the corresponding distyrylcalixarene **4** without the additional methyl groups on the styryl moiety as compound **21** seems to be formed almost exclusively as the *E*,*E* isomer. Signals of the bridging methylene protons of the minor isomers exhibit an upfield shift compared with the *E*,*E* isomer and indicate a 1:10 ratio. In addition, the product is identified by its FAB mass spectrum, which shows a signal at m/z = 824. Consequently, distyrylcalixarene **21** was submitted to photolysis and yielded after HPLC an inseparable mixture of calix[4]di-



Scheme 7. Synthesis and irradiation of styrylcalixarene **21** and calix[4]diphenanthrene **22a** and **22b**.

phenanthrenes **22a** (Figure 4) and **22b** in 20% yield (Scheme 7). The FAB mass spectrum shows a peak at *m*/*z* = 820 and diagnostic signals for the Phen-5-H moiety appear as doublets at δ = 8.57 and 8.60 ppm in the ^{1}H NMR spectrum. Although the ^{1}H NMR spectrum of the mixture is rather complicated, some signals could be assigned to either of the diastereomers (Figure 5). Thus, the *m*-aryl protons of **22a** appear as doublets at δ = 5.33 and 6.03 ppm with the *p*-ArH triplet at δ = 5.94 ppm. The signal at δ = 5.33 ppm exhibits the expected anisotropic upfield shift caused by the adjacent phenanthrene unit. The corresponding *m*-ArH protons of the diastereomer **22b** appear at δ = 5.12 ppm as a doublet, exhibiting an even larger shift, which indicates that both phenanthrene units point towards one aryl ring. The proton at the *para* position of this aryl unit appears at δ = 5.64 ppm, whereas the protons of the opposite aryl ring appear as a multiplet at lower field between 6.26–6.31 ppm, clearly not influenced by the phenanthrenes. Integration of the two different sets of signals reveals a ratio of the two diastereomers **22a**/**22b** of roughly 1:1.1. Crystals of **22a**, with both enantiomers in the unit cell, were obtained from α,α,α-trifluorotoluene/methanol, and crystal analysis confirmed the pinched cone conformation of the molecules (Figure 4).

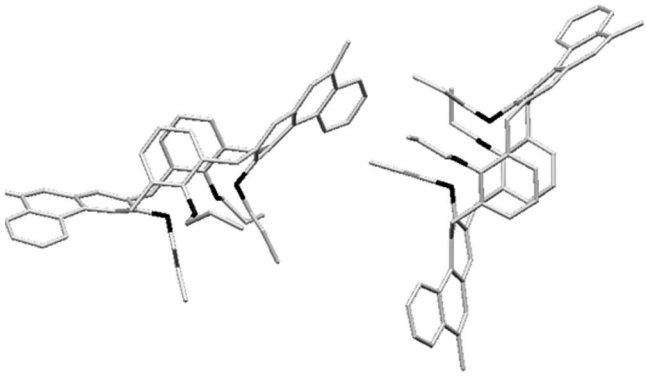


Figure 4. Crystal structure of calix[4]diphenanthrene **22a** with both enantiomers in the unit cell.

The successful suppression of the [2+2] cycloaddition encouraged us to test a four-fold oxidative cyclization. We prepared tetrastyrylcalixarene **24** by Wittig reaction of the tetraformylcalixarene **23** with benzyltriphenylphosphonium bromide **20** in 64% yield (Scheme 8). The peak at *m*/*z* = 1056 in the FAB mass spectrum identifies compound **24**. The relatively simple NMR spectrum suggests that one conformation of the stilbene units is preferred. Irradiation of tetrastyrylcalixarene **24** resulted in a complex mixture of products. The ^{1}H NMR spectrum obtained from one isolated fraction after HPLC shows diagnostic phenanthrene signals above 8 ppm. However, a peak at *m*/*z* = 1052 in the FAB mass spectrum indicates that a maximum of two phenanthrene units are formed.

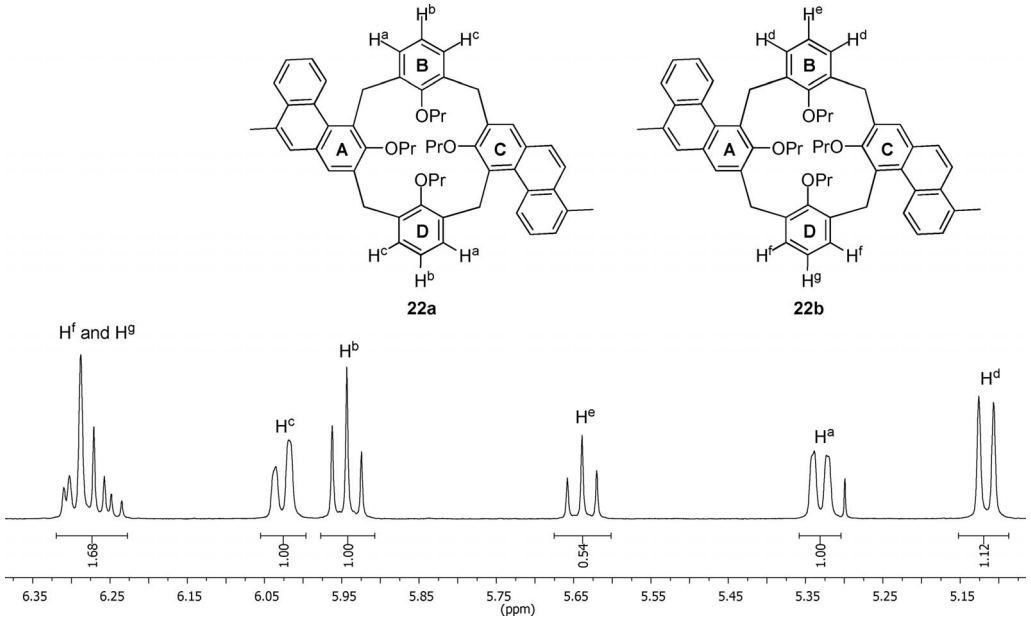
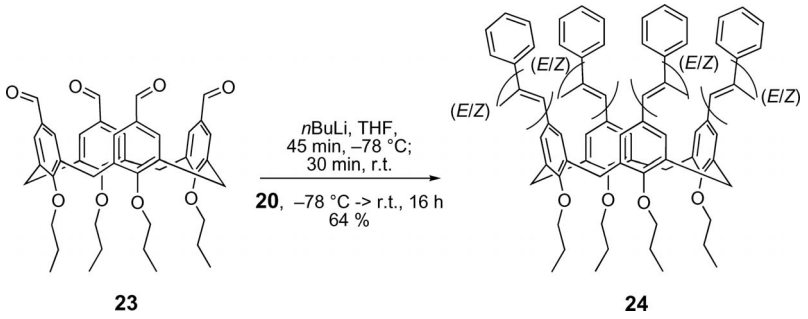


Figure 5. Partial ^{1}H NMR spectrum of a mixture of diasteromers **22a** and **22b** in a ratio of 1:1.1, recorded at 400 MHz in $CDCl_3$.



Scheme 8. Synthesis of tetrastyrylcalixarene **24**.

Conclusions

The photolysis of 1,3-substituted styrylcalixarenes led to cyclobutane-bridged calixarenes by transannular [2+2] cycloaddition reaction. Introducing steric hindrance at the styryl moiety suppressed the photocyclization to give a mixture of the calix[4]diphenanthrene stereoisomers **22a** and **22b**. In the case of proximal disubstitution, the photocyclization proceeded smoothly to yield all the possible diastereoisomeric calixdiphenanthrenes, but favouring the sterically overcrowded and thermodynamically unfavoured isomer. According to the NMR spectroscopic data as well as X-ray crystal structure data the calixphenanthrenes prefer a pinched cone conformation with the phenanthrene units sticking out. We are currently testing palladium-catalysed annulation[8] reactions as a route to calixphenanthrenes and -fluorenes.

Experimental Section

General: Melting points were determined with a Kofler instrument, model Reichert Thermovar. Elemental analyses were performed with a Vario EL instrument. Infrared spectroscopy was performed with a Bruker Equinox 55 FT-IR spectrometer (KBr, $\tilde{\nu}$ in cm^{-1}). UV/Vis spectra were recorded with a Varian Cary 1 (λ_{max} in nm, ε in $cm^2 mmol^{-1}$). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX 200, DPX 400 or DRX 600 spectrometer. The spectra were calibrated relative to the internal solvent peak [$\delta(CHCl_3)$ = 7.26 (^{1}H) and 77.16 ppm (^{13}C); $\delta(CH_2Cl_2)$ = 5.32 (^{1}H) and 54.00 ppm (^{13}C)]. Mass spectrometry was performed with a Varian MAT CH5 or VG Autospec spectrometer. FAB mass spectra were recorded in NBA as matrix. For TLC, SiO_2 plates (Polygram SIL G/UV 254) from Macherey–Nagel & Co were used. All compounds were purified by flash chromatography on Kieselgel 60 (Merck, 0.030–0.060 mm). Light petroleum ether (PE) was used for flash chromatography. HPLC was performed with a Knauer HPLC pump 64, a Knauer differential refractometer and a LiChrospher Si 60 (5 μ) column from Merck. All commercially available chemicals were used without further purification. Solvents were dried by common methods. The calixarenes **3**,[16] **8**,[3] **10**,[17] **11**,[9,18] **12**,[9] **23**[11b] and compound **19**[13] were synthesized according to literature procedures.

***cone*-(*E*,*Z*)-5,17-Bis[2-phenylethenyl]-25,26,27,28-tetra-*n*-propoxycalix[4]arene (4):** *n*BuLi (1.63 mL, 15% in hexane, 2.60 mmol) was added to a cooled (–78 °C) suspension of benzyltriphenylphosphonium chloride (863 mg, 2.22 mmol) in dry THF (20 mL). The reaction mixture was stirred for 45 min at –78 °C and for 30 min at

room temperature. A solution of diformylcalixarene **3** (555 mg, 860 μmol) in dry THF (20 mL) was added to the dark-red suspension at –78 °C. The reaction mixture was stirred overnight while warming up to room temperature. The orange solution was hydrolysed with water (20 mL) and extracted with dichloromethane (100 mL). The organic layer was washed with water (4 × 50 mL) and brine (100 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue (1.29 g) was submitted to flash chromatography (silica, PE/EtOAc, 20:1, R_f = 0.50) to yield 632 mg of a colourless solid, which was further purified by diffusion of methanol into a dichloromethane solution to yield 618 mg (91%) of the (*E*,*Z*)-calixarene **4** after drying in vacuo (0.2 mbar, 50–75 °C, 2 h). Isomerization to the *E*,*E* isomer was achieved by adding a crystal of iodine to the NMR sample and subsequent heating with a heat gun. ^{1}H NMR (200 MHz, $CDCl_3$, *E*,*Z* isomer): δ = 0.88–1.08 (m, 12 H, CH_3), 1.80–2.01 (m, 8 H, CH_2), 2.99 and 3.18 (both d, both J = 13.4 Hz, 4 H, ArCH_2Ar), 3.63–3.78 (m, 4 H, OCH_2), 3.92–4.00 (m, 4 H, OCH_2), 4.36 and 4.46 (both d, J = 13.1, J = 13.4 Hz, 4 H, ArCH_2Ar), 6.19–7.49 (m, 20 H, ArH) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, *E*,*E* isomer): δ = 0.93 (t, J = 7.4 Hz, 6 H, CH_3),1.09 (t, J = 7.5 Hz, 6 H, CH_3), 1.82–2.02 (m, 8 H, CH_2), 3.18 (d, J = 13.4 Hz, 4 H, ArCH_2Ar), 3.75 (t, J = 7.1 Hz, 4 H, OCH_2), 3.99 (t, J = 8.0 Hz, 4 H, OCH_2), 4.46 (d, J = 13.4 Hz, 4 H, ArCH_2Ar), 6.37 (br. s, 6 H, ArH), 6.93 (d, J = 14 Hz, 2 H, alkene-H), 7.02 (d, J = 15 Hz, 2 H, alkene-H), 7.11 (s, 4 H, *m*-ArH), 7.19–7.46 (m, 6, ArH), 7.44 (d, J = 6.8 Hz, 4 H, ArH) ppm. MS (FAB): *m*/*z* (%) = 796 (100) $[M]^+$. The NMR spectroscopic data for the *E*,*E* isomer are in agreement with the literature.[4]

Transannular Cyclization Product (*cone*) 6: In three parallel reactions, a suspension of calixarene **4** (124, 126 and 127 mg, 16 μmol), iodine (91–99 mg, 0.36–0.38 mmol) and potassium carbonate (1.199–1.202 g, 8.68–8.70 mmol) in benzene (200 mL) was degassed with argon (30 min) and irradiated for 15 h (medium-pressure lamp, 125 W, quartz filter) while a permanent stream of argon was bubbled through the solution. Benzene was removed in vacuo and the combined residues were suspended in dichloromethane (600 mL) and insoluble material was filtered off. The solvent was evaporated and the black residue (ca. 600 mg) was purified by flash chromatography [silica, PE to PE/EtOAc, 10:1, R_f (20:1) = 0.42] to yield 339 mg (90%) of cyclization products. By HPLC (*n*-hexane/EtOAc, 80:1, p = 1.6–1.7 MPa, flow = 10 mL/ min) and subsequent drying in vacuo (0.31 mbar, 50 °C, 1.5 h), 141 mg (37%) of **6** were isolated as a colourless solid with m.p. 266–268 °C. Crystals suitable for X-ray crystallography were obtained by crystallization from CH_2Cl_2/MeOH. IR (KBr): $\tilde{\nu}$ = 3056 (w), 3026 (w), 2962 (m), 2930 (m), 2874 (m), 1601 (w), 1584 (w), 1463 (s), 1383 (w), 1278 (w), 1214 (m), 1172 (w), 1128 (w), 1073 (w), 1037 (w), 1008 (m), 966 (m), 920 (w), 890 (w), 870 (w), 833 (w), 799 (w), 768 (w), 721 (w) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} [log(ε/cm^2 $mmol^{-1}$)] = 271 [3.4], 225 [4.8, sh] nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 und 0.86 (t, superimposed, both J = 7.4 Hz, 6 H, CH_3), 1.12 (t, J = 7.4 Hz, 6 H, CH_3), 1.75–1.88 (m, 8 H, CH_2), 3.15 (d, J = 14.4 Hz, 2 H, ArCH_2Ar), 3.21 (d, J = 14.3 Hz, 2 H, ArCH_2Ar), 3.69 (t, J = 6.4 Hz, 4 H, OCH_2), 3.76 ("d", *AA*′BB′, "*J*" = 7.0 Hz, 2 H, cyclobutane-H), 3.86 ("d", AA′*BB*′, "*J*" = 7.0 Hz, 2 H, cyclobutane-H), 3.89–3.93 (m, 4 H, OCH_2), 4.45 and 4.49 (both d, superimposed, both J = 13.9 Hz, 4 H, ArCH_2Ar), 5.50 (d, J = 2.0 Hz, 2 H, *m*-ArH), 5.86 (d, ^3J = 2.0 Hz, 2 H, *m*-ArH), 6.87–6.89 (m, 4 H, *o*-PhH), 6.94–7.05 (m, 8 H, PhH, *p*-ArH), 7.13 (d, J = 7.3 Hz, 2 H, *m*-ArH), 7.21 (d, J = 7.4 Hz, 2 H, *m*-ArH) ppm. ^{13}C{^{1}H} NMR (100 Hz, $CDCl_3$): δ = 10.00, 10.02, 11.1 (all q, *C*H_3), 23.2, 23.3, 23.7 (all t, *C*H_2), 31.4, 31.6 (both t, Ar*C*H_2Ar), 45.0 (d, cyclobutane-*C*-Ph), 48.7 (d, cyclobutane-C), 76.26, 76.31, 76.34 (all t, O*C*H_2), 121.5 (d, *p*-Ar*C*H), 125.1 (d, *m*-Ar*C*H), 125.5 (d, Ph*C*H), 127.7 (d, Ph*C*H), 128.3 (d, *o*-Ph*C*H), 128.7 (*m*-Ar*C*H), 129.4 (d, *m*-Ar*C*H), 129.6 (d, *m*-Ar*C*H), 133.9 (s, Ar*C*CH_2Ar, *p*-Ar*C*), 134.3 (Ar*C*CH_2Ar), 138.0, 138.1 (both s, Ar*C*CH_2Ar), 141.7 (Ph*C*), 154.4, 159.4, 159.5 (all s, Ar*C*O) ppm. MS (FAB): *m*/*z* (%) = 796 (100) $[M]^+$. $C_{56}H_{60}O_4$ (797.07): calcd. C 84.38, H 7.59; found C 83.98, H 7.22. ^{1}H NMR spectra of other HPLC fractions indicated the formation of compounds **5** and **7** in minor amounts and purity: approximate yields were determined from NMR spectra to be about 6% for the desired diphenanthrene **5** and about 25% for compound **7**.

Transannular Cyclization-Product (*cone*) 9: In three parallel reactions, a suspension of calixarene **8** (90 mg, 90 μmol; 110 mg, 110 μmol; 140 mg, 140 μmol), iodine (110–180 mg, 0.43–0.71 mmol) and potassium carbonate (1.90–3.03 g, 13.7–21.9 mmol) in benzene (200 mL) was degassed with argon (30 min) and irradiated for 18 h (125 W medium-pressure lamp, quartz filter). During the reaction a constant stream of argon was bubbled through the solution. Benzene was removed in vacuo, the residue was suspended in dichloromethane (10 mL) and insoluble material was filtered off. The solvent was evaporated and the combined black residue was purified by flash chromatography [silica, PE/EA, 100:1 to 50:1, R_f (100:1) = 0.44, 0.39, 0.09 (**9**), 0.05]. The fraction with R_f = 0.09 yields 81 mg (24%) of slightly impure cyclization products after drying in vacuo (0.73 mbar, 50 °C, 1 h). By HPLC (*n*-hexane/EtOAc, 80:1, p = 1.6–1.7 MPa) and subsequent drying in vacuo, 4 mg (1%) of analytically pure **9** were isolated as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 und 0.93 (2 t, superimposed, both J = 7.3 Hz, 6 H, CH_3), 1.24 and 1.26 (2 t, superimposed, both J = 7.1 Hz, 6 H, CH_3), 1.84–2.06 (m, 8 H, CH_2), 3.38 and 3.39 (m, 2 H, ArCH_2Ar, cyclobutane-H), 3.50 (m, 2 H, ArCH_2Ar, cyclobutane-H), 3.62 (m, 1 H, cyclobutane-H), 3.69 (m, 1 H, cyclobutane-H), 3.76–3.85 (m, 4 H, OCH_2), 4.06–4.15 (m, 2 H, OCH_2), 4.37–4.47 (m, 2 H, OCH_2), 4.60 (d, J = 13.9 Hz, 1 H, ArCH_2Ar), 4.66 (d, J = 13.6 Hz, 1 H, ArCH_2Ar), 4.69 (d, J = 14.1 Hz, 2 H, ArCH_2Ar), 4.90 and 4.91 (2 d, superimposed, J = 14.6, J = 14.9 Hz, 2 H, ArCH_2Ar), 5.01 (s, 1 H, *m*-ArH), 5.18 (s, 1 H, *m*-ArH), 5.56 (s, 1 H, *m*-ArH), 6.14 (s, 1 H, *m*-ArH), 6.44–6.46 (m, 2 H, ArH), 6.75–6.79 (m, 5 H, ArH), 6.88–6.96 (m, 3 H, ArH), 7.52–7.57 (m, 4 H, Phen-6/7-H), 7.62 (s, 1 H, Phen-1-H), 7.68 and 7.70 (2 d, superimposed, J = 9.1, J = 9.6 Hz, 2 H, Phen-9-H), 7.76 (s and d, J = 8.6 Hz, 2 H, Phen-1-H, Phen-10-H), 7.84 (d, J = 8.8 Hz, 1 H, Phen-10-H), 7.90 (m, 2 H, Phen-8-H), 8.51 (m, 2 H, Phen-5-H) ppm. ^{13}C{^{1}H} NMR (100 Hz, $CDCl_3$): δ = 10.1, 10.2, 11.2 (all q, *C*H_3), 23.5, 23.6, 23.89, 23.93 (all t, *C*H_2), 31.0, 31.3, 31.5, 31.7 (all t, Ar*C*H_2Ar), 44.3, 46.2, 47.7, 47.9 (all d, cyclobutane-C), 76.4, 76.5, 77.96, 78.04 (all t, O*C*H_2), 124.2 (d), 124.89 (d), 124.91 (d), 124.97 (s), 125.3 (d), 125.4 (s), 125.47 (d), 125.49 (d), 125.9 (s), 127.3 (d), 127.4 (d), 127.5 (d), 127.7 (d), 127.9 (s), 128.2 (d), 128.27 (d), 128.32 (d), 128.4 (d), 128.5 (d), 128.7 (d), 130.3 (s), 130.4 (s), 132.1 (s), 132.4 (s), 132.6 (s), 133.4 (s), 133.5 (s), 133.76 (s), 133.80 (s), 133.9 (s), 134.5 (s), 135.2 (s), 136.96 (s), 137.02 (s), 140.7 (s), 141.2 (s), 153.7 (s, Ar*C*O), 154.0 (s, Ar*C*O), 160.1 (s, Phen*C*O), 160.2 (s, Phen*C*O) ppm. MS (FAB): *m*/*z* (%) = 997 (82) $[M + H]^+$.

***cone*-5,11-Dibromo-25,26,27,28-tetrahydroxycalix[4]arene (13):** Calixarene **12** (2.89 g, 3.79 mmol) was dissolved in dry toluene (200 mL) and anhydrous $AlCl_3$ (1.01 g, 7.52 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 45 min and for an additional 20 min at room temperature. The reaction was quenched with HCl (1 N, 50 mL) and the separated aqueous layer was extracted twice with dichloromethane (40 mL). The combined organic layers were washed with water (50 mL), dried with $MgSO_4$

and the solvents were removed in vacuo. The residue was treated with CH_2Cl_2/MeOH (1:1), concentrated to 25% of the volume and the resulting precipitate was filtered off and dried in vacuo (0.82–1.7 mbar, 100 °C, 3 h) to give 1.88 g (85%) of calixarene **13** as a colourless solid with m.p. >300 °C (ref.[10] m.p. >300 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.49 (br. s, 4 H, ArCH_2Ar), 4.18 (br. s, 4 H, ArCH_2Ar), 6.77 (t, J = 7.5 Hz, 2 H, *p*-ArH), 7.02–7.11 (m, 4 H, *m*-ArH), 7.14 (d, ^3J = 2.4 Hz, 2 H, BrArH), 7.19 (d, ^3J = 2.4 Hz, 2 H, BrArH), 10.04 (s, 4 H, O*H*) ppm. ^{13}C{^{1}H} NMR (50 Hz, $CDCl_3$): δ = 31.5, 31.6, 31.7 (all t, all Ar*C*H$_2$Ar), 114.1 (s), 122.7 (d), 127.4 (s), 128.3 (s), 129.2 (d), 129.5 (d), 129.6 (s), 130.6 (s), 131.6 (d), 131.9 (d), 148.2, 148.7 (both s) ppm. The NMR spectroscopic data are in accord with the literature.[10]

***cone*-5,11-Dibromo-25,26,27,28-tetra-*n*-propoxycalix[4]arene (14):** NaH (60% in mineral oil, 2.47 g, 61.7 mmol) was washed three times with hexane (15 mL), suspended in dry DMF (80 mL) and after the addition of calixarene **13** (1.80 g, 3.09 mmol) the mixture was heated at 60 °C for 30 min. Then propyl iodide was added and after stirring at room temperature for 30 min the reaction mixture was heated for an additional 2 h at 60–70 °C. The reaction was quenched with ice-cold water (110 mL) and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The organic layer was washed twice with aqueous ammonium chloride (1 N, 50 mL), once with water (50 mL) and brine (50 mL), dried with $MgSO_4$ and the solvent was evaporated. The residue was purified by flash chromatography [silica, PE/CH_2Cl_2, 8:1, R_f (PE/CH_2Cl_2, 2.5:1) = 0.51] and dried in vacuo (1.4–3.9 mbar, 100 °C, 2 h) to give 1.66 g (94%) of calixarene **14** as a colourless solid with m.p. 80–82 °C (ref.[10] 117–119 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.97 and 0.98 (both t, superimposed, J = 7.4, J = 7.5 Hz, 12 H, OCH_3), 1.77–1.97 (m, 8 H, CH_2), 3.04, 3.11 and 3.17 (all d, J = 13.9, J = 13.6, J = 13.0 Hz, 4 H, ArCH_2Ar), 3.75–3.86 (m, 8 H, OCH_2), 4.35, 4.39 and 4.44 (all d, J = 13.6, J = 13.6, J = 13.4 Hz, 4 H, ArCH_2Ar), 6.56–6.72 (m, 10 H, ArH) ppm. ^{13}C{^{1}H} NMR (50 Hz, $CDCl_3$): δ = 10.4, 10.5 (both q, *C*H$_3$), 23.27, 23.28 (both t, *C*H$_2$), 30.9, 31.0, 31.1 (all t, Ar*C*H$_2$Ar), 76.8, 76.9 (both t, O*C*H$_2$), 114.8, 122.4, 128.1, 128.7, 130.6, 131.2, 134.4, 135.4, 136.7, 137.8, 156.0, 156.7 (all s, Ar*C*O) ppm. MS (FAB): m/z (%) = 750 (82) [M]$^+$. The NMR spectroscopic data are in accord with the literature.[9,10]

***cone*-5,11-Diformyl-25,26,27,28-tetra-*n*-propoxycalix[4]arene (15):** *n*BuLi (2.77 mL, 15% in hexane, 4.41 mmol) was added to a cooled (–78 °C) solution of calixarene **14** (1.24 g, 1.65 mmol) in dry THF. The reaction mixture was stirred for 45 min at –78 °C and after the addition of DMF (2.52 mL, 15.5 mmol) for 2 h at room temperature. The reaction was hydrolysed with HCl (1 N, 40 mL), the aqueous layer was extracted with dichloromethane (3 × 30 mL), the organic layers were washed with water (3 × 30 mL) and brine (30 mL) and then dried with $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography [silica, PE/EtOAc, 20:1 to 10:1, R_f (PE/EtOAc, 5:1) = 0.28] to give **15** after drying in vacuo (1.8 mbar, 50 °C, 2.5 h) in 632 mg (45%) yield as a colourless solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.99 and 1.01 (2 t, superimposed, both J = 7.4 Hz, 12 H, CH_3), 1.81–1.99 (m, 8 H, CH_2), 3.16 (d, J = 13.6 Hz, 1 H, ArCH_2Ar), 3.25 (d, J = 14.0 Hz, 2 H, ArCH_2Ar), 3.32 (d, J = 14.7 Hz, 1 H, ArCH_2Ar), 3.77–4.10 (m, 8 H, OCH_2), 4.42 (d, J = 13.4 Hz, 1 H, ArCH_2Ar), 4.47 (d, J = 13.6 Hz, 2 H, ArCH_2Ar), 4.52 (d, J = 13.6 Hz, 1 H, ArCH_2Ar), 6.47–6.61 (m, 6 H, ArH), 7.12 and 7.14 (2 d, both ^3J = 1.9 Hz, 4 H, *m*-Ar*H*), 9.65 (s, 2 H, ArC*H*O) ppm. ^{13}C{^{1}H} NMR (50 Hz, $CDCl_3$): δ = 10.4, 10.5 (both q, *C*H$_3$), 23.4, 23.5 (both t, *C*H$_2$), 31.1 (t, Ar*C*H$_2$Ar), 76.9 (t, O*C*H$_2$), 122.4, 128.2, 128.8, 130.0, 130.8, 131.2, 134.3, 135.5, 135.6, 136.7, 156.6, 162.4, 191.7 ppm. MS (FAB): m/z (%) = 671 (80) [M + Na]$^+$, 648 (100) [M]$^+$. The NMR spectroscopic data are in accord with the literature.[12]

***cone*-5,11-Bis(2-phenylethenyl)-25,26,27,28-tetra-*n*-propoxycalix[4]-arene (16):** *n*BuLi (1.78 mL, 15% in hexane, 2.85 mmol) was added to a cooled (–78 °C) suspension of benzyltriphenylphosphonium chloride (939 mg, 2.42 mmol) in dry THF (20 mL). The reaction mixture was stirred for 45 min at –78 °C and for 30 min at room temperature, during which time the colour changed from yellow to orange and finally to dark red. The reaction mixture was cooled to –78 °C and a solution of diformylcalixarene **15** (607 mg, 0.94 mmol) in dry THF (25 mL) was added. The reaction was warmed to room temperature overnight. After hydrolysing with water (20 mL) the aqueous layer was extracted with dichloromethane (2 × 50 mL), the organic layers were washed with water (4 × 50 mL) and brine (100 mL) and then dried with $MgSO_4$. The solvents were removed in vacuo and the resulting solid (1.463 g) was purified by flash chromatography (silica, PE/EtOAc, 20:1, R_f = 0.35) and dried in vacuo (1.0–5.2 mbar, 50 °C, 2.5 h) to give 691 mg (93%) of distilbene **16** as a colourless solid with m.p. 79–81 °C. Isomerization to the *E*,*E* isomer was achieved by adding a crystal of iodine to the NMR sample and subsequent heating with a heat gun. IR (KBr): $\tilde{\nu}$ = 3055 (w), 3020 (w), 2959 (s), 2930 (s), 2872 (s), 2735 (w), 1631 (w), 1594 (w), 1492 (w), 1461 (s), 1401 (w), 1383 (m), 1304 (w), 1280 (w), 1246 (m), 1216 (s), 1193 (m), 1159 (w), 1125 (m), 1083 (w), 1068 (w), 1037 (m), 1005 (s), 963 (s), 916 (w), 888 (w), 836 (w), 807 (w), 763 (s) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} [log(ε/cm^2 mmol^{-1})] = 296 [4.5] nm. *E*,*Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96–1.04 (m, 12 H, CH_3), 1.85–1.96 (m, 8 H, CH_2), 2.89, 2.98, 2.99, 3.03, 3.16, 3.19 (all d, J = 13.3, J = 13.4, J = 14.0, J = 14.0, J = 13.4, J = 13.4 Hz, 4 H, ArCH_2Ar), 3.76–3.93 (m, 8 H, OCH_2), 4.31, 4.36, 4.37, 4.39, 4.45, 4.46, 4.47 (all d, J = 13.2, J = 13.1, J = 13.3, J = 12.9, J = 13.4, J = 13.4, J = 13.4 Hz, 4 H, ArCH_2Ar), 6.27–6.85 (m, 14 H, ArH, alkene-H), 7.08–7.25 (m, 8 H, ArH), 7.32 (t, J = 7.6 Hz, 1 H, ArH), 7.42–7.54 (m, 1 H, ArH) ppm. ^{13}C{^{1}H} NMR (100 Hz, $CDCl_3$): δ = 10.37, 10.46, 10.48, 10.50, 10.60 (all q, *C*H$_3$), 23.36, 23.38, 23.45 (all t, *C*H$_2$), 31.0, 31.1, 31.2, 31.3 (all t, Ar*C*H$_2$Ar), 76.8 (t, O*C*H$_2$), 122.0, 122.1, 122.2, 126.3, 126.4, 126.5, 126.6, 126.62, 126.66, 126.75, 126.83, 126.9, 127.06, 127.10, 128.0, 128.17, 128.22, 128.35, 128.41, 128.5, 128.6, 128.7, 128.9, 129.2, 129.4, 129.47, 129.53, 130.77, 130.81, 130.9, 131.3, 134.5, 134.7, 134.8, 134.9, 135.0, 135.2, 135.26, 135.33, 135.38, 135.41, 135.60, 135.64, 135.7, 135.9, 137.95, 138.00, 138.12, 138.13, 156.2, 156.3, 156.55, 156.58, 156.64, 156.8, 157.0, 157.2 ppm. MS (FAB): m/z (%) = 796 (100) [M]$^+$. $C_{56}H_{60}O_4$ (797.07): calcd. C 84.38, H 7.59; found C 84.37, H 7.82. *E*,*E* isomer: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.99 and 1.00 (2 t, superimposed, J = 7.3, J = 7.4 Hz, 12 H, CH_3), 1.82–2.01 (m, 8 H, CH_2), 3.15, 3.17 and 3.19 (3 d, superimposed, J = 13.6, J = 13.5, J = 13.6 Hz, 4 H, ArCH_2Ar), 3.81–3.91 (m, 8 H, OCH_2), 4.46 (d, J = 13.5 Hz, 4 H, ArCH_2Ar), 6.48–6.64 (m, 6 H, ArH), 6.73 and 6.77 (d and s, superimposed, J = 16.2 Hz, 6 H, alkene-H, *m*-ArH), 6.87 (d, J = 16.3 Hz, 2 H, alkene H), 7.16–7.24 (m, 2 H, *p*-Ar′H), 7.32 ("t", "J" = 7.7 Hz, 4 H, *m*-Ar′H), 7.45 ("d", "J" = 7.8 Hz, 4 H, *o*-Ar′H) ppm.

Proximal *cone*-Calix[4]bisphenanthrenes 17a–c: In four parallel reactions, a suspension of calixarene **16** (108, 109, 111 and 126 mg, 135–158 μmol), iodine (79–92 mg, 0.31–0.36 mmol) and potassium carbonate (1.05–1.30 g, 7.60–9.41 mmol) in benzene (200 mL) was degassed with argon (30 min) and irradiated for 17 h (medium-pressure Hg lamp, 125 W, quartz filter). During the reaction a permanent stream of argon was bubbled through the solution. Benzene was removed in vacuo and the residue was suspended in dichloromethane and insoluble material was filtered off. The filtrate was

washed with aqueous $Na_2S_2O_3$ (10%, 60 mL) and dried with $MgSO_4$ to give 573 mg of a brown residue. Successive flash chromatography [silica, PE/EtOAc, 50:1 and PE/EtOAc, 20:1, R_f (PE/EtOAc, 20:1) = 0.32] gave 301 mg (67%) of a mixture of cyclization products. A portion of this mixture (235 mg) was subjected to HPLC (PE/EtOAc, 200:1, p = 1.1–1.2 MPa) and the isolated compounds dried in vacuo (1.1–1.8 mbar, 75–100 °C, 1.5 h).

First Fraction: 123 mg (27%) of **17a** were isolated as a colourless solid with m.p. 243–245 °C. Crystals suitable for X-ray crystallography were obtained from chloroform/ethanol. IR (KBr): $\tilde{\nu}$ = 3048 (w), 2959 (s), 2918 (m), 2872 (m), 1590 (w), 1511 (w), 1452 (s), 1442 (s), 1412 (w), 1377 (w), 1330 (w), 1285 (m), 1252 (m), 1206 (m), 1166 (w), 1137 (w), 1096 (w), 1083 (w), 1062 (w), 1033 (w), 1001 (s), 966 (s), 885 (w), 868 (w), 838 (w), 805 (m), 765 (m), 745 (m) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} [log(ε/cm^2 $mmol^{-1}$)] = 309 [4.0, sh], 259 [4.7], 221 [4.6, sh] nm. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.79 (t, J = 7.5 Hz, 3 H, CH_3), 0.94 (t, J = 7.4 Hz, 3 H, CH_3), 1.06 (t, J = 7.4 Hz, 3 H, CH_3), 1.33 (t, J = 7.4 Hz, 3 H, CH_3), 1.72–2.14 (m, 8 H, CH_2), 3.04 (d, J = 14.3 Hz, 1 H, ArCH_2Ar), 3.25 (d, J = 13.3 Hz, 1 H, ArCH_2Ar), 3.31 (d, J = 14.0 Hz, 1 H, ArCH_2Ar), 3.56–3.63 (m, 2 H, OCH_2), 3.90–3.97 (m, 2 H, OCH_2), 4.03–4.07 (m, 1 H, OCH_2), 4.16–4.29 and 4.26 (m and d, superimposed, J = 12.9 Hz, 3 H, OCH_2, ArCH_2Ar), 4.49 (d, J = 13.2 Hz, 1 H, ArCH_2Ar), 4.79 (d, J = 13.8 Hz, 1 H, ArCH_2Ar), 5.30 (d, J = 7.3 Hz, 1 H, *m*-ArH), 5.71 (t, J = 7.2 Hz, 1 H, Phen-6-H), 5.76 (d, J = 15.8 Hz, ArCH_2Ar), 5.81 (d, J = 15.9 Hz, 1 H, ArCH_2Ar), 6.00 (s, 1 H, Phen-1-H), 6.16 (t, J = 7.5 Hz, 1 H, *p*-ArH), 6.23 (d, J = 7.2 Hz, 1 H, *m*-ArH), 6.80 (d, J = 8.6 Hz, 1 H, Phen-10-H), 6.84 (t, J = 7.3 Hz, 1 H, Phen-7-H), 7.04 (s, 1 H, Phen-1-H), 7.07 (d, J = 8.6 Hz, 1 H, Phen-9-H), 7.09 (t, J = 7.5 Hz, 1 H, *p*-ArH), 7.24–7.26 (m, 3 H, *m*-ArH, Phen-8-H, Phen-10-H), 7.54 (d, J = 8.7 Hz, 1 H, Phen-9-H), 7.61 (d, J = 8.4 Hz, 1 H, Phen-5-H), 7.66 (t, J = 7.3 Hz, 1 H, Phen-7-H), 7.71 (t, J = 7.5 Hz, 1 H, Phen-6-H), 8.00 (d, J = 7.5 Hz, 1 H, Phen-8-H), 8.70 (d, J = 8.2 Hz, 1 H, Phen-5-H) ppm. $^{13}C\{^1H\}$ NMR (150 Hz, $CDCl_3$): δ = 9.8, 10.1, 11.0, 11.3 (all q, CH_3), 22.2, 23.1, 23.7, 23.9 (all t, CH_2), 30.7, 31.0, 31.5, 31.6 (all t, ArCH_2Ar), 77.0, 77.2 (both t, OCH_2), 122.1 (d, *p*-ArCH), 122.5 (d, Phen-C-6), 123.3 (d, *p*-ArCH), 123.9 (d, Phen-C-9), 124.3 (d, Phen-C-7), 124.6 (d, Phen-C-9), 124.9 (d, Phen-C-6), 125.8 (d, Phen-C-7), 125.9 (d, *m*-ArCH), 126.6, 126.8, 127.0 (3 d, Phen-C-8, Phen-C-10, *m*-ArCH), 127.3 (d, Phen-C-5), 127.4 (s, Phen-C), 127.8 (d, Phen-C-5), 128.0 (d, Phen-C-1), 128.2 (d, Phen-C-8), 128.3 (s, Phen-C), 128.5, 128.6 (both d, both Phen-C), 129.0 (s, Phen-C), 129.1 (d, *m*-ArCH), 129.5 (s, Phen-C), 129.8 (d, *m*-ArCH), 130.6 (s, PhenCCH$_2$Phen), 131.1 (s, Phen-C), 131.5 (s, PhenCCH$_2$Phen), 132.0 (s, Phen-C), 132.86 (s, ArCCH$_2$Phen), 132.87 (s, ArCCH$_2$Phen), 133.47, 133.49, 133.6 (3 s, PhenCCH$_2$Ar, two Phen-C), 135.7 (s, PhenCCH$_2$Ar), 137.0 (s, ArCCH$_2$Phen), 138.3 (s, ArCCH$_2$Ar), 155.0 (s, ArCO), 156.9 (s, PhenCO), 158.7 (s, ArCO), 159.8 (s, PhenCO) ppm. MS (FAB): *m*/z (%) = 815 (7) $[M + Na]^+$, 792 (100) $[M]^+$. $C_{56}H_{56}O_4$ (793.04): calcd. C 84.81, H 7.12; found C 84.41, H 7.13.

Second Fraction: 31 mg (7%) of **17b** were isolated as a colourless solid with m.p. 129–131 °C. IR (KBr): $\tilde{\nu}$ = 3046 (w), 2959 (s), 2930 (m), 2872 (m), 1592 (w), 1510 (w), 1454 (s), 1441 (s), 1413 (w), 1380 (w), 1332 (w), 1288 (w), 1249 (w), 1214 (m), 1201 (m), 1177 (w), 1134 (w), 1101 (m), 1082 (w), 1064 (w), 1037 (w), 1004 (s), 967 (m), 882 (w), 838 (w), 804 (m), 758 (m), 744 (m), 700 (w) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} [log(ε/cm^2 $mmol^{-1}$)] = 269 [5.0], 310 [4.3] nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.02 (t, J = 7.4 Hz, 6 H, CH_3), 1.08 (t, J = 7.4 Hz, 6 H, CH_3), 1.88–1.96 (m, 4 H, CH_2), 1.98–2.11 (m, 4 H, CH_2), 2.90 (d, J = 14.3 Hz, 1 H, ArCH_2Ar), 3.46 (d, J = 14.2 Hz, 1 H, ArCH_2Ar), 3.79–3.92 (m, 4 H, OCH_2), 4.03–4.09 (m, 2 H, OCH_2) 4.28 (d and m, superimposed, J = 14.2 Hz, 3 H, ArCH_2Ar, OCH_2), 4.73 (d, J = 14.3 Hz, 2 H, ArCH_2Ar), 4.94 and 4.98 (both d, superimposed, J = 14.4, J = 14.6 Hz, 3 H, ArCH_2Ar), 5.84 (br. s, 2 H, *m*-ArH), 6.07 (t, J = 7.3 Hz, 2 H, *p*-ArH), 6.26 (br. s, 2 H, *m*-ArH), 7.04 (br. s, 2 H, Phen-H), 7.38 (s, 2 H, Phen-H), 7.44–7.56 (m, 6 H, Phen-H), 7.78 (d, J = 7.3 Hz, 2 H, Phen-H), 8.78 (d, J = 8.0 Hz, 2 H, Phen-5-H) ppm. $^{13}C\{^1H\}$ NMR (100 Hz, $CDCl_3$): δ = 10.5, 10.7 (both q, CH_3), 23.3, 23.7 (both t, CH_2), 30.5, 30.9, 31.3 (all d, ArCH_2Ar), 76.4, 78.3 (both t, OCH_2), 121.3 (d, *p*-ArCH), 124.3, 124.7, 125.6 (all d, Phen-C), 127.6 (d, Phen-C, *m*-ArCH), 128.1 (d, *m*-ArCH, Phen-C), 128.5 (d, *m*-Phen-C, Phen-C-5), 129.0, 130.5, 130.7, 133.0 (all s, Phen-C), 134.2 (s, PhenCCH$_2$Phen), 134.5 (s, ArCCH$_2$Phen), 134.7 (s, ArCCH$_2$Ar), 156.3 (s, ArCO), 159.0 (s, PhenCO) ppm. MS (FAB): *m*/*z* (%) = 792 (100) $[M]^+$.

Third Fraction: 63 mg (14%) of **17c** were isolated as a colourless solid with m.p. 134–136 °C. IR (KBr): $\tilde{\nu}$ = 3046 (w), 2959 (s), 2930 (m), 2872 (m), 2732 (w), 1590 (w), 1510 (w), 1454 (s), 1440 (s), 1413 (w), 1380 (w), 1335 (w), 1286 (w), 1248 (w), 1215 (m), 1200 (m), 1134 (w), 1101 (m), 1082 (w), 1064 (w), 1036 (w), 1003 (s), 967 (m), 881 (w), 838 (w), 805 (m), 762 (m), 744 (m) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} [log(ε/cm^2 $mmol^{-1}$)] = 258 [4.9], 307 [4.5, sh], 343 [3.3], 359 [3.2] nm. ^1H NMR (400 MHz, $CDCl_3$): δ = δ = 0.94 (t, J = 7.4 Hz, 3 H, CH_3), 1.00 (t, J = 7.4 Hz, 3 H, CH_3), 1.06 (t, J = 7.4 Hz, 3 H, CH_3), 1.11 (t, J = 7.4 Hz, 3 H, CH_3), 1.87–2.03 (m, 8 H, CH_2), 3.04 (d, J = 13.9 Hz, 1 H, ArCH_2Ar), 3.41 (d, J = 13.7 Hz, ArCH_2Ar), 3.74–4.13 (m, 7 H, OCH_2), 4.22–4.28 (m, 1 H, OCH_2), 4.38 (d, J = 13.8 Hz, 1 H, ArCH_2Ar), 4.52 (d, J = 14.8 Hz, 1 H, ArCH_2Ar), 4.66 (d, J = 15.5 Hz, ArCH_2Ar), 4.73 (d, J = 13.6 Hz, 1 H, ArCH_2Ar), 4.94 (d, J = 14.8 Hz, 1 H, ArCH_2Ar), 5.31 (d, J = 15.5 Hz, 1 H, ArCH_2Ar), 6.18 (t, J = 7.5 Hz, 1 H), 6.39 (br. s, 2 H), 6.52 (d, J = 6.9 Hz, 3 H), 6.88 (d, J = 8.5 Hz, 1 H), 7.19 (d, J = 8.7 Hz, 1 H), 7.38–7.44 (m, 4 H), 7.49 (br. s, 2 H), 7.61 and 7.62 (m, 1 H), 7.73 (br. "s", 1 H), 8.73 ("d", "J" = 7.4 Hz, 2 H, Phen-5-H) ppm. $^{13}C\{^1H\}$ NMR (100 Hz, $CDCl_3$): δ = 10.3, 10.5, 10.75, 10.78 (all q, CH_3), 23.0, 23.3, 23.5 (all t, CH_2), 30.0, 30.7, 31.4, 31.5 (all t, ArCH_2Ar), 76.2, 77.0, 77.4, 77.8 (all t, OCH_2), 120.9, 122.5, 123.9, 124.0, 124.8, 125.1, 125.4, 125.6, 127.5, 127.6, 127.75, 127.84, 128.1, 128.2, 128.3, 128.5, 128.7 (s), 128.76 (s), 128.83 (s), 129.2 (s), 129.8 (s), 130.4 (s), 130.5 (s), 130.6 (s), 132.8 (s), 133.2 (s), 133.8 (s), 134.5 (s), 134.87 (s), 134.89 (s), 136.2 (s), 156.4, 157.0 (both s, ArCO), 157.9 (s, PhenCO) ppm. MS (FAB): *m*/*z* (%) = 792 (100) $[M]^+$.

(1-Phenylethyl)triphenylphosphonium Bromide (20): 1-Bromoethylbenzene (**19**; 2.71 g, 14.6 mmol) and triphenylphosphane (4.00 g, 15.3 mmol) were dissolved in toluene (15 mL) and stirred at 110–120 °C for 3 d in a screw-capped flask. The colourless precipitate was filtered off, washed with toluene and dried in vacuo (0.76–2.5 mbar, 100 °C, 3 h) to give 5.77 g (88%) of **20** as a solid with m.p. 229–231 °C (ref.[15] m.p. 231–234 °C). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.82 (dd, J = 19.1, J = 7.2 Hz, 3 H, CH_3), 6.82 (dq, J = 14.2, J = 7.3 Hz, 1 H, C*H*), 7.15–7.26 (m, 5 H, ArH), 7.58–7.88 (m, 15 H, ArH) ppm. MS (FAB): *m*/*z* (%) = 367 (100) $[M]^+$. The NMR spectroscopic data are in accord with the literature.[14,15]

***cone*-5,17-Bis(2-methyl-2-phenylethenyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (21):** *n*BuLi (1.5 mL, 15% in hexane, 2.39 mmol) was added to a cooled (–78 °C) suspension of phosphonium bromide **20** (854 mg, 1.92 mmol) in dry THF (20 mL). The reaction mixture was stirred for 45 min at –78 °C and for 30 min at room temperature. A solution of diformylcalixarene **3** (475 mg, 733 μmol) in dry THF (10 mL) was added at –78 °C. The reaction mixture was warmed to room temperature overnight. The suspen-

sion was hydrolysed with water (25 mL) and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed twice with water (20 mL) and once with brine (30 mL) and then dried with $MgSO_4$. The solvent was evaporated and the residue (1.37 g) purified by flash chromatography (silica, PE/EtOAc, 30:1 to 20:1) and dried in vacuo (0.61 mbar, 75 °C, 2 h) to yield 418 mg (69%) of calixarene **21** [R_f (PE/EtOAc, 20:1) = 0.46] in as a colourless solid. Recrystallization from CH_2Cl_2/MeOH and CH_2Cl_2/*i*PrOH gave 252 mg (42%) of **21** as crystals with m.p. 229–231 °C. IR (KBr): $\tilde{\nu}$ = 3057 (w), 3023 (w), 2958 (m), 2929 (m), 2871 (m), 1592 (w), 1492 (m), 1459 (s), 1383 (m), 1308 (m), 1287 (w), 1247 (m), 1219 (s), 1196 (m), 1169 (w), 1136 (m), 1106 (w), 1082 (m), 1037 (m), 1005 (s), 965 (m), 889 (w), 858 (w), 837 (w), 801 (w), 757 (s) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} [log(ε/$cm^2\,mmol^{-1}$)] = 280 [4.2], 228 [4.3, sh] nm. ^1H NMR (400 MHz, CD_2Cl_2, diagnostic signals of the minor isomer are marked with an asterisk): δ = 0.89*, 0.95*, 0.99*, 1.03, 1.05 (all t, J = 7.4 Hz, 12 H, CH_2CH_3), 1.89 and 2.12* (both br. s, 6 H, CH_3), 1.93–2.08 (m, 8 H, CH_2), 2.88*, 3.16*, 3.19 (all d, J = 13.2, J = 13.1 Hz, 4 H, $ArCH_2Ar$), 3.78*, 3.87, 3.94 (all t, J = 7.3, J = 7.4, J = 7.6 Hz, 8 H, OCH_2), 4.32*, 4.46*, 4.50 (all d, J = 13.1, J = 13.1 Hz, 4 H, $ArCH_2Ar$), 6.23–6.84 (m, 12 H, ArH and alkene-H), 7.10–7.50 (m, 10 H, Ar′H) ppm. $^{13}C\{^1H\}$ NMR (100 Hz, CD_2Cl_2): δ = 10.7, 10.8 (both q, CH_2CH_3), 17.6 (q, CH_3), 23.8, 24.0 (both t, CH_2), 31.6 (t, $ArCH_2Ar$), 77.4, 77.7 (both t, OCH_2), 122.6 (d, ArCH), 126.3 (d, Ar′CH), 127.1, 128.1 (d, alkene-CH), 128.7 (d, Ar′CH), 128.8 (d, ArCH, Ar′CH), 129.03* (d, Ar′CH), 129.68* (d, ArCH), 129.81 (d, *m*-ArCH), 132.4, 135.0, 135.97, 136.00, 144.7 (all s), 155.8 (s, ArCO), 157.2 (s, styryl-CO) ppm. MS (FAB): *m*/*z* (%) = 824 (100) $[M]^+$, 751 (8). $C_{58}H_{64}O_4 \cdot {}^1/_8CH_2Cl_2$ (835.74): calcd. C 83.53, H 7.75; found C 83.41, H 7.34.

***cone*-25,26,27,28-Tetra-*n*-propoxycalix[4]bis(9-methylphenanthrene) (22a and 22b):** In three parallel reactions, a suspension of calixarene **21** (84 mg, 102 μmol and twice 100 mg, 121 μmol), iodine (57 mg, 0.22 mmol; 68 mg, 0.27 mmol) and potassium carbonate (759 mg, 5.49 mmol; 903 mg, 6.51 mmol) in benzene (200 mL) was degassed with argon (30 min) and irradiated for 17 h (125 W medium-pressure lamp, quartz filter) while a permanent stream of argon was bubbled through the solution. Benzene was removed in vacuo, the combined residues were suspended in dichloromethane (20 mL) and insoluble material was filtered off. The solvent was evaporated and the resulting brown solid (307 mg) was purified by flash chromatography [silica, hexane/toluene, 5:1 to 2:1, R_f (5:1) = 0.21; silica, PE/EtOAc, 100:1, R_f = 0.17] to yield 129 mg (46%) of cyclization products. By HPLC (PE/EtOAc, 200:1, p = 1.1 MPa) and subsequent drying in vacuo (0.47 mbar, 75–80 °C, 1.5 h) 57 mg (20%) of a mixture of isomers **22a** and **22b** were obtained as a colourless solid with m.p. 161–163 °C. Single crystals were obtained from trifluorotoluene/methanol. IR (KBr): $\tilde{\nu}$ = 3066 (w), 3020 (w), 2959 (s), 2931 (s), 2872 (s), 2729 (w), 1621 (w), 1589 (w), 1518 (w), 1478 (m), 1452 (s), 1416 (m), 1382 (m), 1338 (m), 1290 (w), 1243 (s), 1196 (m), 1179 (s), 1142 (w), 1128 (w), 1083 (m), 1065 (w), 1036 (m), 1002 (s), 966 (s), 888 (w), 839 (w), 818 (w), 799 (w), 755 (s), 720 (w) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} [log(ε/$cm^2\,mmol^{-1}$)] = 366 [3.3], 348 [3.4], 315 [4.4], 266 [5.1], 218 [4.9] nm. Isomer **22a**: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.5 Hz, 6 H, CH_2CH_3), 1.24 (t, J = 7.4 Hz, 6 H, CH_2CH_3), 1.89–2.16 (m, 8 H, CH_2), 2.74 (s, 6 H, CH_3), 3.35 and 3.39 (2 d, superimposed, J = 14.9, J = 13.8 Hz, 2 H, $ArCH_2Ar$), 3.76–3.86 (m, 4 H, OCH_2), 4.15–4.26 (m, 2 H, OCH_2), 4.32–4.44 (m, 2 H, OCH_2), 4.60 (d, J = 13.4 Hz, 1 H, $ArCH_2Ar$), 4.62 (d, J = 13.2 Hz, 1 H, $ArCH_2Ar$), 4.66 (d, J = 14.9 Hz, 1 H, $ArCH_2Ar$), 4.72 (d, J = 14.6 Hz, 1 H, $ArCH_2Ar$), 4.87 (d, J = 14.7 Hz, 2 H, $ArCH_2Ar$), 5.33 (d, J = 6.4 Hz, 2 H, *m*-ArH **22a**), 5.94 (t, J = 7.6 Hz, 2 H, *p*-ArH **22a**), 6.03 (d, J = 6.7 Hz, 2 H, *m*-ArH **22a**), 7.52–7.62 (m, 8 H, Phen-H), 8.05 ("t", J = 7.5, J = 7.8 Hz, 2 H, Phen-H), 8.60 (d, J = 7.9 Hz, 2 H, Phen-5-H) ppm. Isomer **22b**: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.5 Hz, 6 H, CH_2CH_3), 1.16 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.32 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.89–2.16 (m, 8 H, CH_2), 2.73 (s, 6 H, CH_3), 3.35 and 3.39 (2 d, superimposed, J = 14.9, J = 13.8 Hz, 2 H, $ArCH_2Ar$), 3.74 (t, J = 6.7 Hz, 2 H, OCH_2), 3.87 (t, J = 6.5 Hz, 2 H, OCH_2), 4.15–4.26 (m, 2 H, OCH_2), 4.32–4.44 (m, 2 H, OCH_2), 4.60 (d, J = 13.4 Hz, 1 H, $ArCH_2Ar$), 4.62 (d, J = 13.2 Hz, 1 H, $ArCH_2Ar$), 4.66 (d, J = 14.9 Hz, 1 H, $ArCH_2Ar$), 4.72 (d, J = 14.6 Hz, 1 H, $ArCH_2Ar$), 4.87 (d, J = 14.7 Hz, 2 H, $ArCH_2Ar$), 5.12 (d, J = 7.5 Hz, 2 H, *m*-ArH **22b**), 5.64 (t, J = 7.6 Hz, 1 H, *p*-ArH **22b**), 6.23–6.31 (m, 3 H, *p*-ArH, *m*-ArH **22b**), 7.52–7.62 (m, 8 H, Phen-H), 8.05 ("t", J = 7.5, J = 7.8 Hz, 2 H, Phen-H), 8.57 (d, J = 8.0 Hz, 2 H, Phen-5-H) ppm. $^{13}C\{^1H\}$ NMR (100 Hz, $CDCl_3$): δ = 10.1, 11.0, 11.2, 11.3 (all q, all CH_2CH_3), 19.8 (q, CH_3), 23.3, 23.4, 23.8, 23.9, 24.0 (all t, all CH_2), 30.2, 31.2 (both t, both $ArCH_2Ar$), 76.5, 76.7, 77.0, 77.8, 78.0 (all t, all OCH_2), 122.7, 122.8, 122.9 (all d, all *p*-ArCH), 124.3, 124.4 (both d, both Phen-8-C), 124.5 (d, Phen-6-C), 125.8 (d, Phen-7-C), 126.3, 126.8, 127.1 (all d, all *m*-ArCH), 127.2 (d, Phen-1-C), 127.4 (d, Phen-C), 127.6 (d, *m*-ArCH), 127.7, 128.4 (both s, both Phen-C), 128.5, 128.6 (both d, both Phen-5-C), 130.3 (s), 130.6 (s), 131.0, 131.1 (both s, both Phen-C), 132.2, 132.7 (both s, $ArCCH_2Phen$), 133.27 (s), 133.33 (s), 134.6, 134.9 (both s, both $ArCCH_2Phen$), 136.91, 136.96 (both s), 154.6, 154.9, 155.3 (all s, all ArCO), 159.6, 159.7 (both s, both PhenCO) ppm. MS (FAB): *m*/*z* (%) = 820 (100) $[M]^+$. $C_{58}H_{60}O_4$ (821.09): calcd. C 84.84, H 7.37; found C 84.62, H 7.12.

***cone*-5,11,17,23-Tetrakis(2-methyl-2-phenylethenyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (24):** *n*BuLi (8.55 mL, 15% in hexane, 13.6 mmol) was added to a cooled (–78 °C) suspension of phosphonium bromide **20** (5.09 g, 11.4 mmol) in dry THF (70 mL). The reaction mixture was stirred for 1 h at –78 °C and for 30 min at room temperature. A solution of tetraformylcalixarene **23** (802 mg, 1.13 mmol) in dry THF (15 mL) was added at –78 °C. The reaction mixture was warmed to room temperature overnight. The suspension was hydrolysed with water (80 mL), the aqueous layer was extracted with ethyl acetate (2 × 40 mL) and the organic layers were washed with water (50 mL) and brine (50 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue (3.04 g) purified by flash chromatography (silica, PE/EtOAc, 20:1) and dried in vacuo (1.6–2.1 mbar, 75 °C, 1.5 h) to yield 773 mg (64%) of calixarene **24** [R_f (PE/EtOAc, 10:1) = 0.54] as a colourless solid with m.p. 167–168 °C. IR (KBr): $\tilde{\nu}$ = 3079 (w), 3053 (w), 3020 (w), 2959 (m), 2931 (m), 2873 (m), 1597 (w), 1576 (w), 1542 (w), 1493 (m), 1465 (s), 1444 (m), 1383 (w), 1310 (w), 1288 (w), 1219 (m), 1145 (w), 1126 (w), 1106 (w), 1067 (w), 1036 (w), 1006 (m), 964 (w), 941 (w), 894 (w), 853 (w), 756 (m), 695 (m) cm^{-1}. UV/Vis (*n*-hexane): λ_{max} [log(ε/$cm^2\,mmol^{-1}$)] = 278 [4.5], 228 [4.4] nm. ^1H NMR (400 MHz, $CDCl_3$, diagnostic signals of the minor isomer are marked with an asterisk): δ = 0.96*, 1.00*, 1.02*, 1.05 (all t, J = 7.4, J = 7.3, J = 7.4, J = 7.5 Hz, 12 H, CH_2CH_3), 1.83*, 1.96, 2.16* (all s, CH_3), 1.88–2.08 (m, 20 H), 2.90*, 3.19*, 3.22 (all d, J = 13.0, J = 12.7, J = 13.0 Hz, 4 H, $ArCH_2Ar$), 3.79* (t, J = 7.3 Hz) and 3.88–4.01* (m with 3.94, t, J = 7.6 Hz, 8 H, OCH_2), 4.34*, 4.49*, 4.53 (all d, J = 12.9, 14.0, 13.0 Hz, 4 H, $ArCH_2Ar$), 6.22–6.90 (m, 12 H, C=CH, *m*-ArH), 7.12–7.49 (m, 20 H, Ar′H) ppm. $^{13}C\{^1H\}$ NMR (100 Hz, $CDCl_3$): δ = 10.35* , 10.52, 10.64* (all q, CH_2CH_3), 17.15*, 17.29, 17.68 (all q, CH_3), 23.47, 23.50* (all t, CH_2), 31.22*, 31.30 (all t, $ArCH_2Ar$), 76.96, 77.21 (all t, OCH_2), 125.9, 126.0, 126.1*, 126.7*, 126.8 (all d, *m*-ArCH, Ar′CH), 127.8, 127.9* (both

d, *m*-ArCH, C=*C*H), 128.2*, 128.27, 128.33*, 128.6* (all d, Ar′CH), 129.2*, 129.5 (both d, *m*-ArCH), 132.1*, 132.3, 132.4 (all s), 134.63 (s, Ar*C*CH$_2$Ar), 135.6*, 135.7 (both s), 144.2 (s), 154.8*, 155.2 (both s, Ar*C*O) ppm. MS (FAB): *m*/*z* (%) = 1056 (79) [M]$^+$, 940 (17). $C_{76}H_{80}O_4$ (1057.45): calcd. C 86.32, H 7.63; found C 86.33, H 7.46.

X-ray Crystallography: The intensity data were collected with an Oxford Diffraction Xcalibur2 diffractometer with a Sapphire2 CCD. The crystal structures were solved by direct methods using SHELXS-97[19] and refined with SHELXL-97.[19] For refinement details see the following section.

Crystal Structure of 6: Colourless prisms, $0.42 \times 0.22 \times 0.17$ mm^3, monoclinic, $P2_1/c$, a = 20.5290(7), b = 17.7566(6), c = 24.2824(8) Å, β = 92.535(3)°, V = 8842.9(5) Å^3, Z = 8, $\rho_{calcd.}$ = 1.197 g/cm^3, θ_{max} = 25.0°, λ(Mo-K_α) = 0.71073 Å, T = 110(2) K, 61209 measured reflections, 15535 independent reflections (R_{int} = 0.0963), 6248 reflections [$I > 2\sigma(I)$], 1089 parameters, R = 0.0438, wR = 0.1085 (for all data).

Crystal Structure of 17a: Colourless prisms, $0.22 \times 0.20 \times 0.10$ mm^3, orthorhombic, *P2(1)2(1)2(1)*, a = 11.0221(6), b = 13.3367(8), c = 29.644(2) Å, V = 4357.6(4) Å^3, Z = 4, $\rho_{calcd.}$ = 1.209 g/cm^3, θ_{max} = 26.0°, λ(Mo-K_α) = 0.71073 Å, T = 113(2) K, 28159 measured reflections, 4774 [8555] independent reflections (R_{int} = 0.0420), 3657 [6093] reflections [$I > 2\sigma(I)$], 545 parameters, R = 0.0367 [0.0359], wR = 0.0567 [0.0555] (for all data) [data before merging, Flack: –0.6(7)]. As we were unable to obtain a satisfying dataset using Cu radiation we decided to merge the Mo data as the absolute structure could not be determined exactly. Nevertheless the Flack parameter for the unmerged data set suggests that the enantiomer shown is predominates within the crystal.

Crystal Structure of 22a: Colourless prisms, $0.32 \times 0.27 \times 0.22$ mm^3, triclinic, $P\bar{1}$, a = 11.1909(4), b = 14.9553(6), c = 27.464(1) Å, α = 93.885(4), β = 90.615(3), γ = 93.971(3)°, V = 4574.4(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.192 g/cm^3, θ_{max} = 25.25°, λ(Mo-K_α) = 0.71073 Å, T = 113(2) K, 68021 measured reflections, 16546 independent reflections (R_{int} = 0.1126), 6119 reflections [$I > 2\sigma(I)$], 1129 parameters, R = 0.0502, wR = 0.0997 (for all data).

CCDC-787366 (for **6**), -787367 (for **17a**) and -787368 (for **22a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for all new compounds synthesized.

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