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Photochemistry of Styrylcalix[4]arenes

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The photochemical transformation of the monostyrylcalix[4]-arenes **12a** and **12b** either leads to inherent chiral calix[4]phenanthrenes **13a** and **13b** under basic reaction conditions or to unexpected products of an acid-catalyzed ring cleavage of the macrocycle. Studies towards the reaction mechanism and the optimization of the reaction conditions are presented.

Introduction

Studying molecular recognition with artificial supramolecular systems is of broad interest for understanding weak interactions, which are essential for biological processes on the molecular level.[1] Calix[4]arenes[2] (**1**) fixed in the *cone* conformation are frequently used as scaffold for the design of host molecules containing a rigid π-electron-rich cavity for recognizing cationic,[3] neutral[4] or anionic[5] guests.

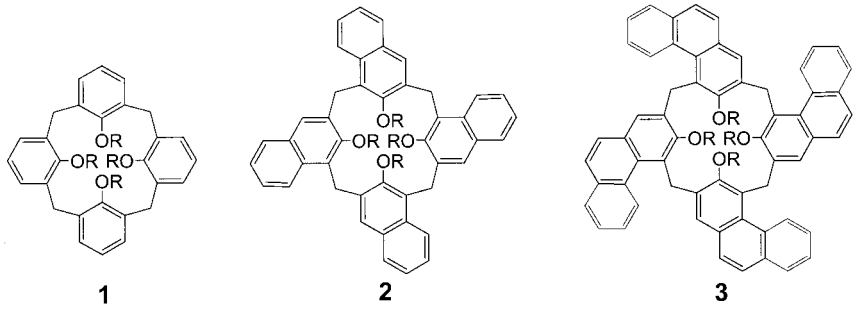
The introduction of chirality in calixarenes should create hosts for the enantioselective recognition of chiral guests.[6] Besides the functionalization with chiral moieties,[7] inherent chirality could be generated by desymmetrization, for instance by introduction of only one substituent in *meta* position of the phenolic unit.[8–10] This is e.g. the case for some calix[4]naphthalenes (for example **2** in Scheme 1), where the inherent chirality is caused by their helical topologies.[8,10a,11] Host–guest complexes of **2** with fullerene C_{60} or TMACl have already been described.[11d,11f] Other calixarenes with macrocyclic aromatic subunits of homologues higher than benzene or naphthalene are rare.[12]

Our intention was to synthesize chiral calixphenanthrenes[13] (e.g. **3** in Scheme 1) from the corresponding styrylcalix[4]arenes by the well-known photochemical oxidative cyclization of stilbenes (Scheme 2).[14] The initial test for the oxidative photocyclization of tetrastyrylcalixarene **9** resulted in an unexpected fragmentation of the calixarene macrocycle, prompting us to thoroughly investigate mechanistic and preparative implications of this observation: Herein we describe the synthesis of monostyrylcalixarenes **12a** and **12b** and their photolysis under various conditions to elaborate the mechanism of the photo-induced macrocycle cleavage.

Results and Discussion

Synthesis and Characterization

In order to find optimized reaction conditions for the oxidative photocyclization we first tested model compound **6**, which had been synthesized in just two preparative steps (Scheme 2): the bromoarene **4** was transformed to the aldehyde **5** by lithiation and subsequent treatment with DMF. The stilbene **6** was then obtained in 78% yield and an (*E*/*Z*) ratio of 60:40 by Wittig reaction. The isomers were separated by flash chromatography and were fully characterized by spectroscopic means. The NMR spectroscopic data of the (*E*) isomer were in agreement with those described in



Scheme 1. Scaffolds of the homologue calix[4]arene (**1**), calix[4]naphthalene (**2**) and calix[4]phenanthrene (**3**).

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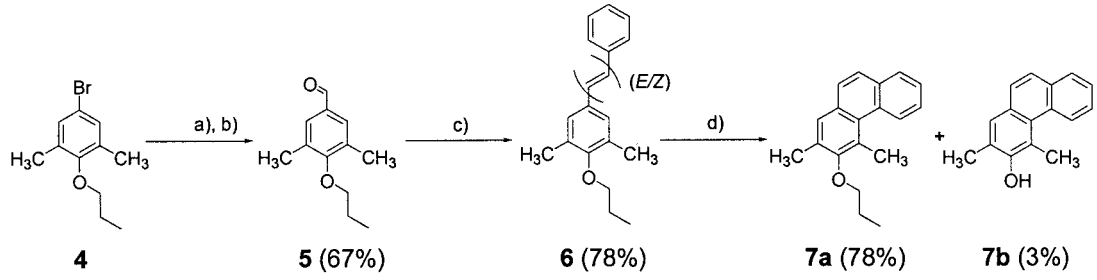


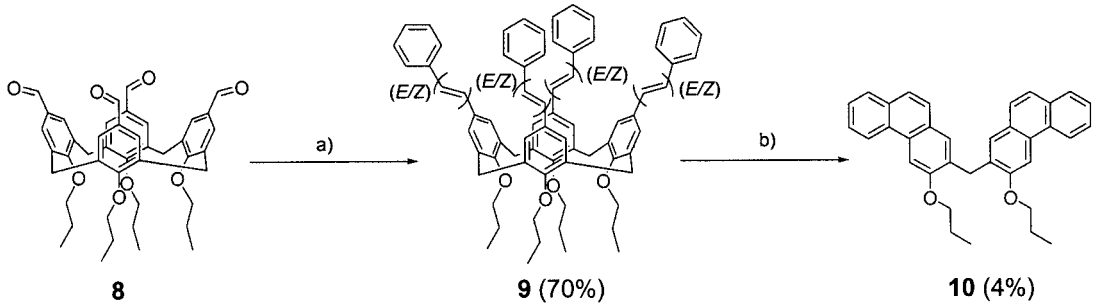
Scheme 2. Synthesis of model compound **7a** by photolysis of the (*E*/*Z*)-stilbene **6**. a) 1 equiv. *n*BuLi, THF, –78 °C, 40 min; b) DMF, 2 h, room temp.; then H^+/H_2O. c) benzylidenetriphenylphosphonium ylide, THF, –78 °C → room temp. d) 1 equiv. I_2, cyclohexane, *hv*, 4 h.

literature.[15] A mixture of the (*E*/*Z*) isomers **6** in cyclohexane with a stoichometric amount of iodine was irradiated with a 125-W Hg medium-pressure lamp. After four hours reaction time we succeeded in isolating a 78% yield of the expected phenanthrene **7a** besides traces of the phenol **7b**. Both compounds were identified by diagnostic ^{1}H NMR signals. For example, phenanthrene **7a** exhibits two 3 H singlets for the methyl groups at δ = 2.51 and 3.03 ppm. Further typical signals are the Phen-5-H at δ = 8.85 ppm and the Phen-8-H at δ = 7.88 ppm. A peak at *m*/*z* = 264 in the EI-mass spectrum confirms the result.

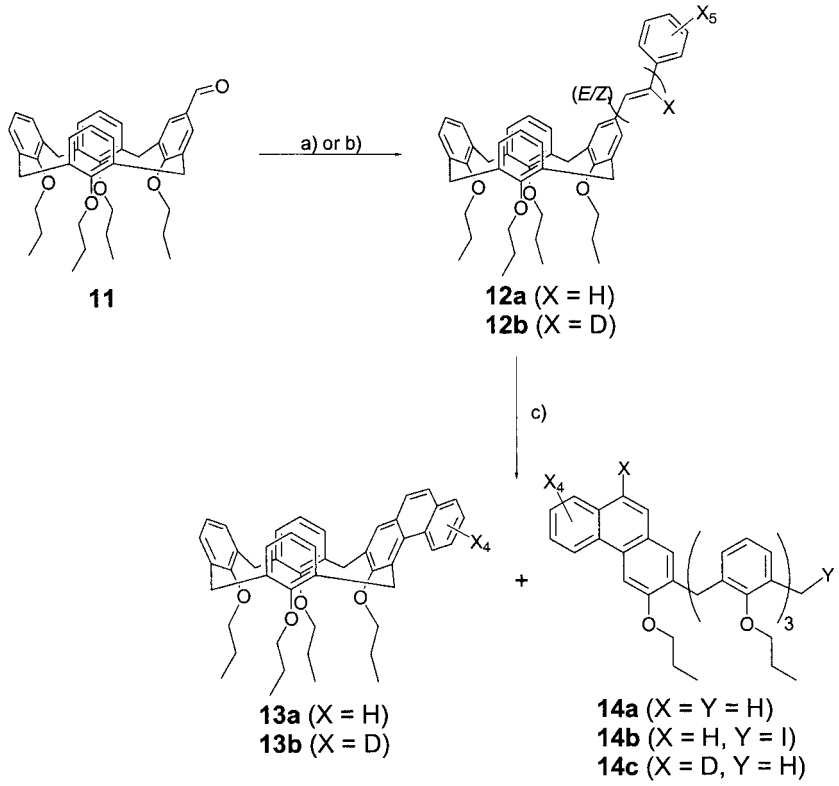
For testing the photochemical cyclization at the calixarene moiety we introduced phenylethenyl units at the upper rim by a fourfold Wittig reaction[16] at the tetraaldehyde **8**.[17] The tetrastilbene **9** was isolated in a 70% yield as a mixture of all possible (*E*/*Z*) isomers (Scheme 3). Although styrylcalix[4]arenes had been synthesized before with a high (*E*) selectivity by Heck reactions or by Horner–Wadsworth–Emmons reactions,[18,19] we applied standard Wittig conditions resulting in excellent yields of mixtures of (*E*/*Z*) isomers: it was not necessary to separate and purify the (*E*/*Z*) isomers, because the quantum yield of the photo-induced (*E*/*Z*) isomerization generally is much higher than that of the subsequent electrocyclic ring closure.[20] Calixarene **9** was identified by a [M + H$^+$] peak at *m*/*z* = 1001 in the FAB mass spectrum and by comparison of integrals of the aromatic region with those of the aliphatic regions in the ^{1}H NMR spectrum. The ^{1}H NMR spectrum was rather complicate because of the mixture of the six possible (*E*/*Z*) isomers. However, the spectrum of the same sample became rather simple within five days, indicating, that isomerization of all alkene units to the thermodynamically preferred (*E*) conformation proceeded smoothly, presumably catalyzed by traces of hydrogen chloride in the solvent $CDCl_3$.

Calixarene **9** was irradiated under the same conditions as the model compound: cyclohexane as solvent, iodine as oxidant (one equiv. per stilbene unit) and four hours reaction time. From the complex product mixture we were able to isolate only one compound by a combination of flash chromatography and multiple crystallizations from dichloromethane/acetone: the methylenebis(phenanthrene) **10** (Scheme 3). This unexpected result led to the question, how the fragmentation of the macrocycle took place. For the formation of **10** obviously at least two CC bond-cleavage reactions had taken place, presumably at the 4-positions of the phenanthrene units, which had been built up during the photochemical process. Consequently the monostilbene **12a** was chosen as another model compound, in order to minimize the possibilities for cleavage reactions to just one. The monostilbene **12a** was synthesized again by Wittig reaction (Scheme 4). Subsequent photolysis in cyclohexane indeed gave the expected linear tetramer **14a** in 7–15% yield, besides a mixture of the reactant **12a** and the calixphenanthrene **13a**, which could not further be separated by column chromatography or fractional crystallization.

Also submolar additions of iodine nevertheless led to the linear compound **14a**. As a key step of the mechanism we considered a [1,9]-sigmatropic H-shift (Scheme 5); in order to prove this hypothesis we synthesized the deuterated calixarene **12b**. If the expected H-shift is part of the ring-cleaving process, the 4-position of the phenanthrene unit of the resulting linear tetramer should be deuterated. After irradiation in the presence of an equimolar amount of iodine we isolated 50% of the deuterated calixphenanthrene **13b**

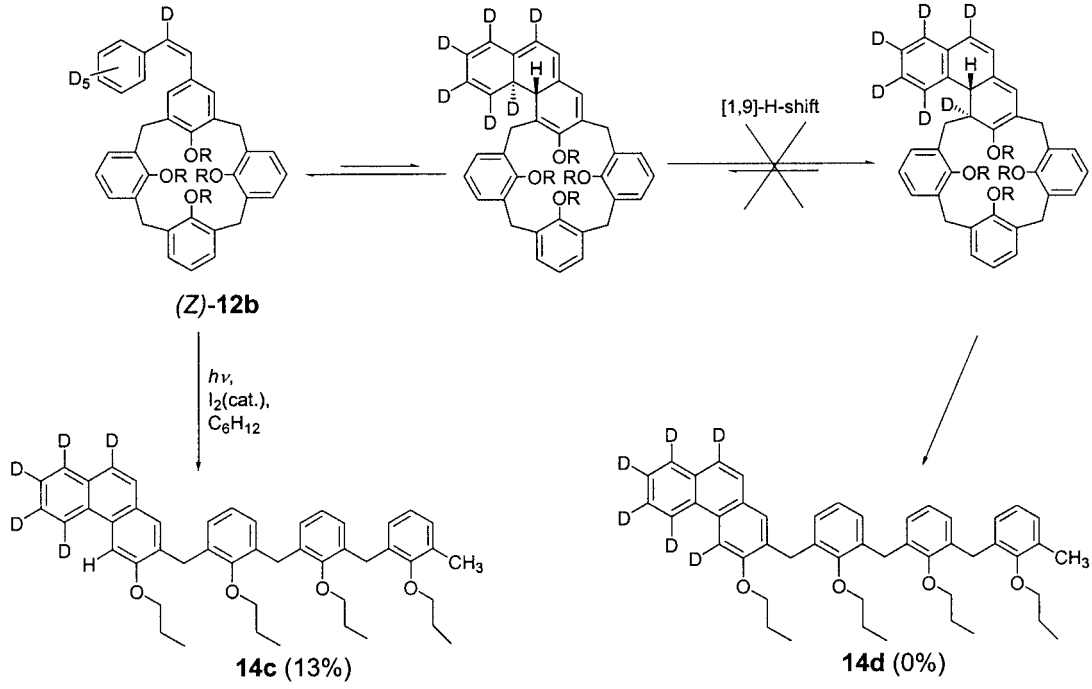


Scheme 3. Unexpected macrocycle fragmentation by photolysis of (*E*/*Z*)-**9**. a) Benzyltriphenylphosphonium chloride, *n*BuLi, THF, 14 h b) 4 equiv. I_2, cyclohexane, 16 h UV irradiation.



Scheme 4. Synthesis and photolysis of monostyrylcalixarenes **12a** and **12b**. a) benzyltriphenylphosphonium chloride, *n*BuLi, THF, room temp., 14 h, yield: 86% **12a**; b) D_7-benzyltriphenylphosphonium chloride, *n*BuLi, THF, room temp., 24 h, yield: 71% **12b**. c) for yields and conditions see Table 1.

besides 13% of the linear tetramer **14c**, with no deuterium in the 4-position of the phenanthrene scaffold (proven by a distinct singlet at δ = 8.00 ppm in the ^{1}H NMR spectrum). This result clearly disproved our initial [1,9]-H-shift hypothesis, but should be regarded as a hint, that hydrogen transfer from the solvent cyclohexane to the linear tetramer **14c** took place. Changing the photolysis conditions for **12a** by the use of benzene as solvent, the reaction gave 22% of the



Scheme 5. Excluding a [1,9]-H-shift during photolysis of the deuterated stilbene **12b**.

Table 1. Reaction conditions and yields of the stilbene photolyses after 16 h of irradiation.

Entry	Reactant	Solvent	Additions	Products (yields)
1	**9**	cyclohexane	I_2	**10** (4%)
2	**12a**	cyclohexane	I_2	**14a** (16%)[a]
3	**12a**	benzene	I_2	**13a** (22%); **14b** (39%)
4	**12a**	benzene	I_2, K_2CO_3	**13a** (86%)
5	**12b**	cyclohexane	I_2	**13b** (50%); **14c** (13%)

[a] Irradiation time 4 h, after chromatography we isolated besides the linear tetramer **14a** a fraction containing a mixture of **12a** and **13a** we were not able to separate. From ^{1}H NMR spectroscopy of the mixed fraction the yield of **13a** was estimated to 15%.

calixphenanthrene **13a** and 39% of the benzyl iodide **14b**. This indicates that the hydrogen iodide, which is produced in the course of the reaction, is crucial for the ring cleavage step. And indeed, if potassium carbonate was added in order to remove hydrogen iodide during irradiation, the ring opening was suppressed to only marginal amounts of less than 1%. Thus, calixphenanthrene **13a** was isolated in a very good yield of 86%.

All compounds were identified by NMR spectroscopy. Typical of the linear tetramers **14a**–**c** is the phenanthrene 4-H appearing as singlet in the ^{1}H NMR spectrum at δ = 8.00 ppm for compound **14a**, at δ = 8.01 ppm for **14c** and at δ = 7.87 ppm for **14b**, thus being indicative for the ring cleavage. Another evidence for the ring opening is the loss of the characteristic pattern of the bridging methylene protons typical of fixed *cone*-conformed calix[4]arenes. Instead of doublets with geminal coupling constants of roughly 14 Hz, four singlets were detected.

The ^{1}H NMR spectrum of the racemic compound **13a** exhibits some remarkable signals with strong relative shifts, caused by the overall topology including the phenanthrene unit (Figure 1): The equatorial methylene proton proximate to the bay-region of the phenanthrene unit (H^d in Figure 1) suffered a strong diatropic shift and appears at δ = 4.70 ppm. This is explained by the ring current effect of the topologically fixed phenanthrene moiety. A similar anisotropic effect could be detected for the protons H^a, H^b and H^c. They were paratropically shifted and gave two doublets at δ = 5.43 ppm (H^a) and 5.86 ppm (H^c) and a triplet at δ = 5.94 ppm (H^b).

Mechanistic Rationale

The proposed reaction mechanism for the ring cleavage is depicted in Scheme 6: (*E*)- and (*Z*)-stilbene **12a** were in a photostationary dynamic equilibrium. The (*Z*)-stilbene **12a** is able to react in a 6π electrocyclic ring closure to the dihydrophenanthrene **15**. Oxidation with half an equivalent of iodine leads to the phenanthryl radical **16**, which profits from the rearomatization of one six-membered ring. The generated hydrogen iodide is a strong Brønstedt acid (pK_a = –10) and therefore able to protonate **16** in the enol ether-type α-positon to give the radical cation **17**. Subsequently the iodide anion cleaves the macrocycle by a nucleophilic substitution at the bridging methylene unit in β-position, which results in the formation of **18**. Subsequent oxidation again results in the iodated linear tetramer **14b**. Addition of

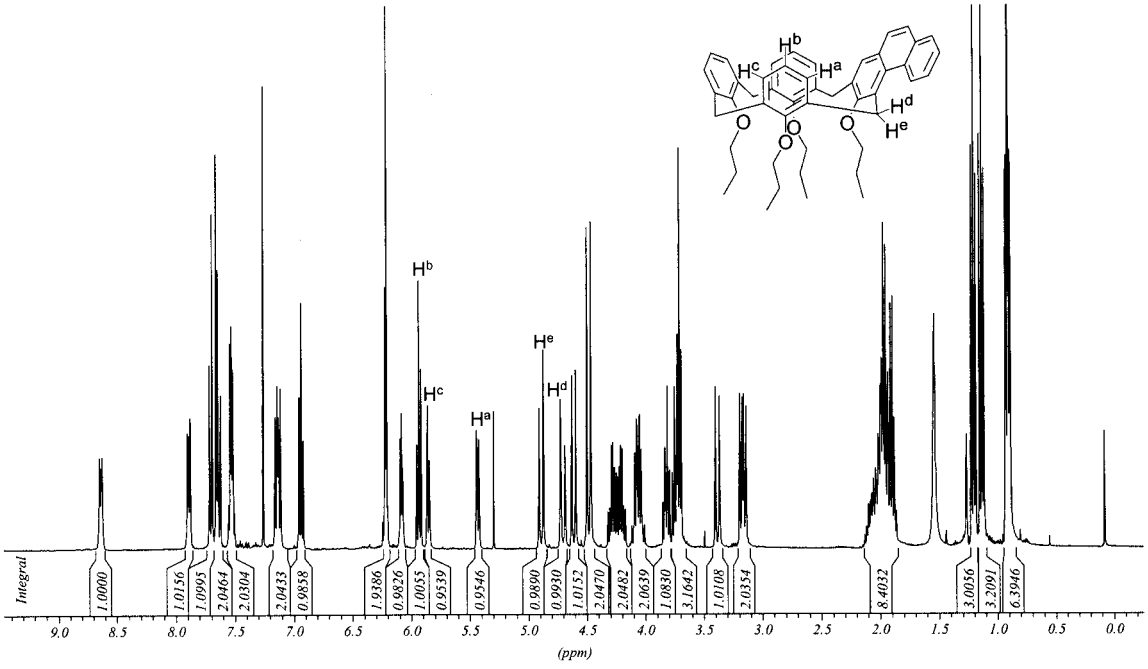
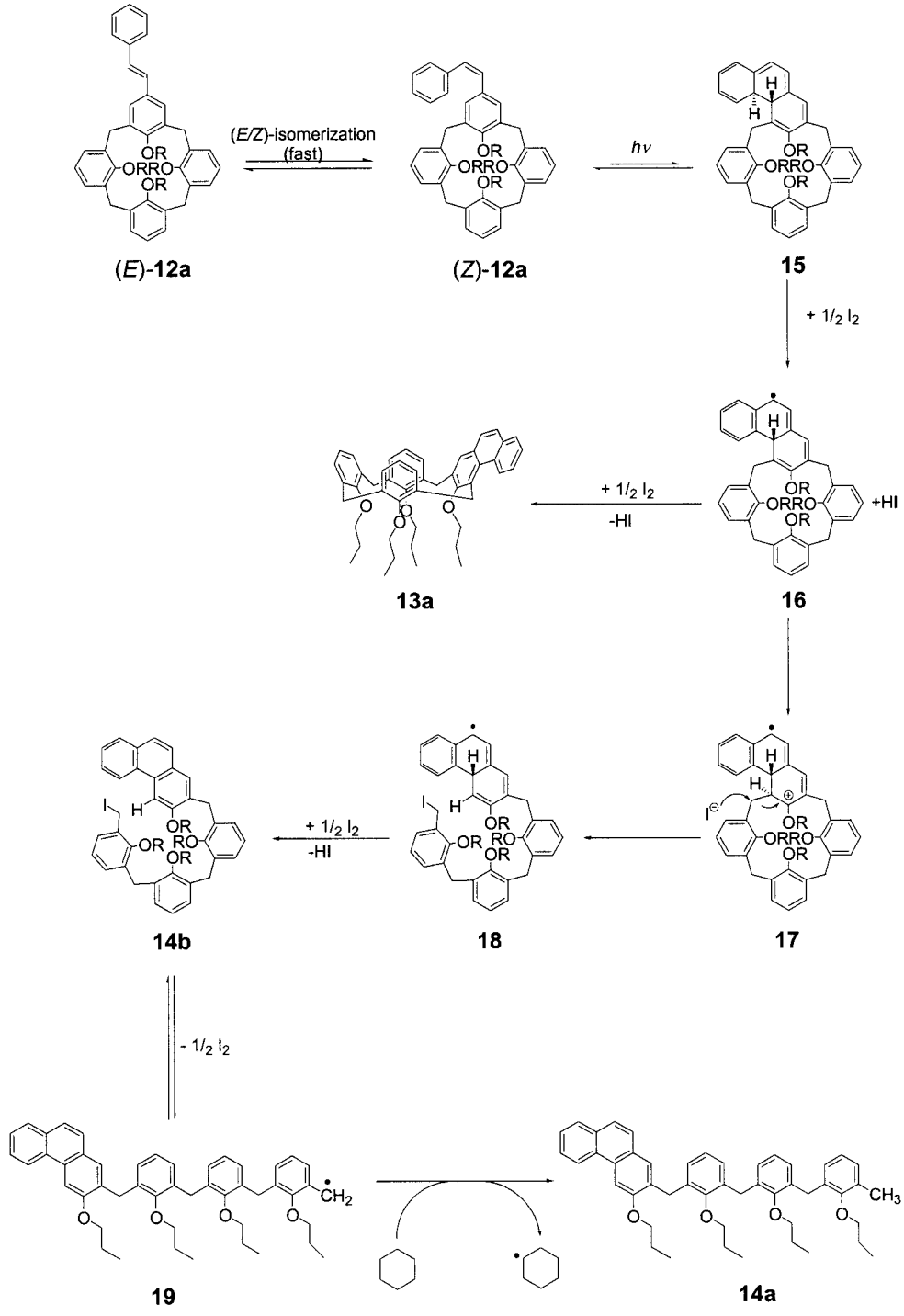


Figure 1. ^{1}H NMR spectrum of compound **13a**, recorded at 400 MHz in $CDCl_3$.

potassium carbonate effectively prevents ring cleavage by trapping the generated hydrogen iodide and therefore **16** is then exclusively converted into the calix[4]phenanthrene **13a**. Performing the photolysis in benzene as solvent gave the iodated compound **14b** as the favoured linear tetramer instead of **14a** in cyclohexane. This result strongly implies that cyclohexane takes part as reactant in the formation of **14a**. Therefore, we proposed an exchange of the benzylic iodine with a hydrogen of cyclohexane by a radical mechanism,[21] although to the best of our knowledge the photochemical reaction between benzyl iodide and cyclohexane has not been described yet.[21c] We tested this final step of our mechanistic hypothesis by monitoring the photolysis of a cyclohexane/benzyl iodide mixture by GC. After 31 h of irradiation, the reaction mixture shows the typical purple colour of I_2. As expected, an increasing concentration of toluene was observed, accompanied by a decreasing concentration of benzyl iodide. We also detected an almost



Scheme 6. Mechanistic rationale for the photochemical transformation of stilbene **12a** to the linear tetramer **14a**.

constant amount of cyclohexyl iodide in the reaction mixture. This result supports the suggested mechanism of the macrocycle cleavage and gives an explanation for the catalytic amount of I_2, which is sufficient for the ring-opening reaction.

Conclusions

With optimized reaction conditions for the oxidative photocyclization of styryl-substituted calixarenes we succeeded in the synthesis of the first calix[4]phenanthrene **13a** in high yields up to 86%. Strongly basic reaction conditions are a prerequisite for the formation of this inherent chiral cavitand; otherwise, cleavage of the macrocycle catalyzed by the strongly acidic hydrogen iodide is observed. Currently we are investigating the preparation of calix[4]phenanthrenes containing two, three and four phenanthrene units and the enantiomeric enrichment of **13a**.

Experimental Section

General Remarks: Melting points (°C, uncorrected values) were determined with a Kofler instrument, model Reichert Thermovar. Elemental analyses were determined with a Vario EL. Infrared spectroscopy was performed with a Bruker Equinox 55, a Perkin–Elmer 983G or a Perkin–Elmer 841 (KBr, $\tilde{\nu}$ in cm^{-1}). UV/Vis-spectra were recorded with a Varian Cary 1 (λ_{max} in nm, ε in $cm^2\,mmol^{-1}$). ^1H and ^{13}C and ^{31}P NMR spectra were recorded with a Bruker DPX 200, a Bruker DRX 400 or a Bruker DRX 600. The spectra were calibrated on the internal solvent peak $\delta(CHCl_3)$ = 7.26 ppm (^1H) and 77.05 ppm (^{13}C), the ^{31}P NMR spectrum was calibrated with phosphourous acid (85%) as external standard (δ = 0.00 ppm). Mass spectroscopy was performed with a Varian MAT CH5 or a VG Autospec. FAB spectra were recorded in NBA as matrix. High-resolution mass spectra were recorded with a Bruker Bio TOF II calibrated with reserpine. For TLC SiO_2 plates (Polygram SIL G/UV 254) from Macherey–Nagel were used. All compounds were purified by flash chromatography on Kieselgel 60 (Merck, 0.030–0.60 mm). All commercially available products were used without further purification. Solvents were dried with common methods. The calixarenes **8**,[17] **11**,[22] and the model compound **4**[23] were synthesized according to literature.

***cone*-5,11,17,23-Tetrakis(2-phenylethenyl)-25,26,27,28-tetrakis(propyloxy)calix[4]arene (9):** To a cooled (–78 °C) suspension of benzyltriphenylphosphonium chloride (2.703 g, 6.95 mmol) in THF (40 mL) *n*BuLi (7.20 mmol) was added. The reaction mixture was stirred 45 min at –78 °C and additional 30 min at room temperature. The orange-coloured solution was cooled again to –78 °C and a solution of the tetracarbaldehyde **8** (400 mg, 0.57 mmol) in THF (10 mL) was added. The reaction mixture was stirred overnight at room temperature. The reaction was quenched with water (50 mL) and the separated organic layer washed once with water (50 mL) and once with brine (50 mL) and dried with magnesium sulfate. Solvents were removed by rotary evaporation to get roughly 2 g of a colourless solid. TLC (PE/EA, 2:1): R_f = 0.87 (**9**), 0.00. After separation by column chromatography the resulting colourless solid was suspended in methanol (8 mL), 30 min sonicated and separated by filtration. The resulting residue was washed with methanol (2 × 2 mL) and dried in vacuo (1.4 mbar, 50 °C) to get 397 mg (70%) of the tetrastilbene **9** as a colourless solid with m.p. 64–69 °C. IR (KBr): $\tilde{\nu}$ = 3022 cm^{-1}, 2959, 2931, 2872, 1631, 1598, 1492, 1465, 1446, 1402, 1384, 1308, 1279, 1249, 1218, 1179, 1130, 1068, 1036, 1005, 961, 917, 887, 839, 774, 748, 695, 592. UV/Vis (*n*-hexane): λ_{max} (lgε) = 295 nm (5.1), 231 (5.3), 202 (5.4). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.94–1.01 ppm (m, 12 H, OCH_2-CH_2-CH_3), 1.87–1.91 (m, 8 H, OCH_2-CH_2-CH_3), 2.83 ("t"), 3.04 ("t"), 3.22 ("d", all together 4 H, all ArCH_2Ar) 3.70–3.90 (m, 8 H, Ar-OCH_2-C_2H_5), 4.27–4.51 (m, 4 H, Ar-CH_2-Ar), 6.00–7.55 (m, 36 H, alkene-H and ArH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.27 ppm, 10.34, 10.45 (all q, O-CH_2-CH_2-CH_3), 23.18, 23.26 (both t, O-CH_2-CH_2-CH_3), 30.97, 31.13 (both t, Ar-CH_2-Ar), 76.90, 77.25 (both t, O-CH_2-CH_2-CH_3), 126.22, 126.38, 126.44, 126.60, 126.68, 126.77, 126.90, 127.59, 127.96, 128.14, 128.19, 128.23, 128.29, 128.39, 128.52, 128.61, 128.71, 128.87, 129.25, 129.38, 130.66, 130.75, 130.86, 131.02, 134.08, 134.46, 134.79, 134.86, 135.03, 137.79, 137.84, 137.88, 137.99, 155.97 (s, Ar*C*-O-), 156.30 (s, Ar*C*-O-). MS (FAB): *m*/*z* (%) = 1001 (100) [M + H^+], 959 (9), 899 (14), 795 (9). $C_{72}H_{72}O_4 \cdot 1/2H_2O$ (1010.37): calcd. C 85.59, H 7.28; found C 85.27, H 7.20.

3,5-Dimethyl-4-(propyloxy)benzaldehyde (5): To a cooled (–78 °C) solution of bromophenol ether **4** (2.190 g, 9.0 mmol) in THF (30 mL) *n*BuLi (6.5 mL of a 1.6 molar hexane solution, 10.4 mmol) was added and the mixture stirred for 40 min at –78 °C. DMF (5 mL) was added and the mixture stirred 2 hours at room temperature. The mixture was quenched with hydrochloric acid (100 mL, 1 N), and extracted 3× with dichloromethane (50 mL). The organic layer was washed once with water (50 mL), once with brine (100 mL) and dried with magnesium sulfate. Solvents were removed by rotary evaporation to give 1.764 g of a yellow liquid. Purification by flash chromatography (PE/EA, 15:1) gave 1.154 g (67%) of the aldehyde **5** as colourless liquid. TLC (PE/EA, 6:1): R_f = 0.35. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 1.08 ppm (t, *J* = 7.3 Hz, 3 H, -$OCH_2CH_2CH_3$), 1.85 (sext, *J* = 7.1 Hz, 2 H, -$OCH_2CH_2CH_3$), 2.34 (s, 6 H, Ar-CH_3), 3.78 (t, *J* = 6.7 Hz, 2 H, O-$CH_2CH_2CH_3$), 7.55 (s, 2 H, Ar-H), 9.87 (s, 1 H, C*H*O). ^1H NMR spectroscopic data were in agreement with the literature.[18b]

2,6-Dimethyl-4-[(*E*/*Z*)-2-phenylethenyl]-1-(propyloxy)benzene (6): To a cooled (–78 °C) solution of benzyltriphenylphosphonium chloride (2.33 g, 5.99 mmol) in THF (50 mL) and *n*BuLi (3.75 mL of a 1.6 molar hexane solution, 6.0 mmol) was added, and the resulting orange suspension stirred 45 min at –78 °C. The aldehyde **5** (1.154 g, 6.00 mmol) was added and the mixture stirred at room temperature. Water (50 mL) was added after 2.5 h and the organic layer separated. The organic layer was washed 3× with water (50 mL), once with brine (50 mL) and dried with magnesium sulfate. Solvents were removed by rotary evaporation and the remaining brown residue separated by flash chromatography (petroleum ether). **1st Fraction [R_f(PE/EA, 6:1) = 0.68]:** 501 mg (31%) of the (*Z*) isomer as colourless oil. IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1}, 3014, 3010, 2962, 2927, 2874, 2855, 1599, 1482, 1383, 1301, 1217, 1179, 1132, 1065, 1041, 1005, 967, 890, 772, 694. UV/Vis (*n*-hexane): λ_{max} (lgε) = 288 nm (3.2), 228 (4.4). ^1H NMR (200.1 MHz, $CDCl_3$): δ = 1.07 ppm (t, *J* = 7.4 Hz, 3 H, -$OCH_2CH_2CH_3$), 1.82 (sext, *J* = 7.1 Hz, 2 H, -$OCH_2CH_2CH_3$), 2.16 (s, 6 H, Ar-CH_3), 3.72 (t, *J* = 6.7 Hz, 2 H, O-$CH_2CH_2CH_3$), 6.49 ("d", „*J*" = 2.3 Hz, 2 H, alkene-H), 6.90 (s, 2 H, Ar-H), 7.17–7.28 (m, 5 H, Ar′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.66 ppm (q, -$OCH_2CH_2CH_3$), 16.23 (t, $OCH_2CH_2CH_3$), 23.69 (q, Ar-CH_3-), 73.90 (t, $OCH_2CH_2CH_3$), 126.97 (s, Ar*C*-CH_3), 128.12, 128.89, 129.26 (all d, all Ar′*C*-H), 129.32 (d, Ar*C*-H), 130.05, 130.66 (both d, both alkene-*C*), 132.52 (s, Ar*C*-CH=CH-Ar′), 137.55 (s, Ar′-C-1), 155.29 (s, Ar*C*-O). MS (EI = 70 eV): *m*/*z* (%) = 267 (12) [M + 1]$^+$, 266 (57) [M]$^+$, 225 (17), 224 (100), 223 (27), 208 (6), 205 (9), 194 (8), 181 (7), 180 (36), 179

(32), 178 (24), 165 (25), 152 (8), 117 (12), 115 (10), 91 (17), 89 (8), 59 (9), 51 (8), 49 (6), 43 (9), 41 (8), 39 (6), 28 (7), 27 (7). $C_{19}H_{22}O$ (266.38): calcd. C 85.67, H 8.32; found C 85.58, H 8.72. **2nd Fraction [R_f(PE/EA, 6:1) = 0.63]:** 752 mg (47%) of the (*E*) isomer as colourless oil. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.10 ppm (t, *J* = 7.5 Hz, 3 H, -OCH$_2$CH$_2$C*H*$_3$), 1.85 (sext, *J* = 7.1 Hz, 2 H, -OCH$_2$C*H*$_2$CH$_3$), 2.32 (s, 6 H, Ar-C*H*$_3$), 3.75 (t, *J* = 6.6 Hz, 2 H, O-C*H*$_2$CH$_2$CH$_3$), 7.01 ("s", 2 H, alkene-H), 7.19 (s, 2 H, Ar-H), 7.24 ("t", "*J*" = 7.3 Hz, 1 H, Ar′-4-H), 7.35 ("t", "*J*" = 7.5 Hz, 2 H, Ar′-3/5-H), 7.50 ("d", "*J*" = 7.3 Hz, 2 H, Ar′-2/6-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.68 ppm (q, -OCH$_2$CH$_2$*C*H$_3$), 16.42 (t, O-CH$_2$*C*H$_2$CH$_3$), 23.70 (q, Ar-*C*H$_3$-), 74.01 (t, O-*C*H$_2$CH$_2$CH$_3$), 126.37, 127.03, 127.31 (all d, all Ar′*C*-H), 127.49 (s, Ar*C*-CH$_3$), 128.48, 128.67 (both d, both alkene-*C*), 131.19 (d, Ar*C*-H), 132.72 (s, Ar*C*-CH=CH-Ar′), 137.72 (s, Ar′-C-1), 156.00 (s, Ar*C*-O). NMR spectroscopic data were in accord with the literature.[18b]

2,4-Dimethyl-3-(propyloxy)phenanthrene (7a) and 2,4-Dimethyl-3-phenanthrenol (7b): A solution of the (*E*/*Z*)-stilbene **6** (134 mg, 0.50 mmol) and iodine (132 mg, 1.04 mmol) in cyclohexane (200 mL) was degassed with argon (30 min) and irradiated for 4 h (125-W Hg medium-pressure lamp, quartz filter). During the reaction period a permanent argon stream was bubbled through the solution. Cyclohexane was removed by rotary evaporation and the remaining residue was separated by flash chromatography (petroleum ether): **1st Fraction (R_f = 0.28):** 4 mg (3%) of the hydroxyphenanthrene **7b** as pale yellow solid. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.53 ppm (s, 3 H, Ar-C*H*$_3$), 3.13 (s, 3 H, Ar-C*H*$_3$), 7.34 (br. s, 1 H, -O*H*), 7.53–7.67 (m, 5 H, Phen-H), 7.90 (m, 1 H, Phen-8-H), 8.89 ("d", 1 H, Phen-5-H). **2nd Fraction (R_f = 0.12):** 103 mg (78%) of the phenanthrene **7a** as pale yellow oil. IR (KBr): $\tilde{\nu}$ = 3083 cm^{-1}, 2963, 2933, 2875, 1602, 1493, 1452, 1379, 1330, 1261, 1217, 1159, 1143, 1118, 1064, 1043, 1005, 961, 876, 806, 745. UV/Vis (*n*-hexane): λ_{max} (lgε) = 352 nm (2.4), 335 (2.5), 300 (3.9), 288 (3.8), 276 (3.9), 254 (4.6), 227 (4.2). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.16 ppm (t, *J* = 7.4 Hz, 3 H, -OCH$_2$CH$_2$C*H*$_3$), 1.95 (sext, *J* = 7.1 Hz, 2 H, -OCH$_2$C*H*$_2$CH$_3$), 2.51 (s, 3 H, Ar-C*H*$_3$), 3.03 (s, 3 H, Ar-C*H*$_3$), 3.89 (t, *J* = 6.6 Hz, 2 H, O-C*H*$_2$CH$_2$CH$_3$), 7.53–7.64 (m, 5 H, Phen-H), 7.88 (dd, *J* = 7.7, 1.9 Hz, 1 H, Phen-8-H), 8.85 (d, *J* = 8.8 Hz, 1 H, Phen-5-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.79 ppm (q, -OCH$_2$CH$_2$*C*H$_3$), 16.97, 18.20 (both q, Ar-*C*H$_3$), 23.71 (t, OCH$_2$*C*H$_2$CH$_3$), 74.64 (t, O*C*H$_2$CH$_2$CH$_3$), 125.11, 125.53, 126.06, 127.24 (all d), 127.53 (s), 127.59 (d, Phen-C-5), 128.59 (d, two superimposed signals, Phen-C-8), 130.07, 130.12, 130.63, 131.49, 133.38 (all s), 156.34 (s, Ar*C*-O). MS (EI = 70 eV): *m*/*z* (%) = 268 (12) [M + 4]$^+$, 264 (57) [M]$^+$, 224 (9), 222 (25), 221 (7), 194 (8), 179 (8), 178 (16), 177 (51), 136 (10), 135 (100), 91 (25), 59 (10), 43 (9), 41 (9). $C_{19}H_{20}O$ (264.37): calcd. C 86.32, H 7.62; found: C 85.33, H 7.86.

3,3′-Bis(propyloxy)-2,2′-methylenebis(phenanthrene) (10): A solution of the calixarene **9** (160 mg, 0.16 mmol) and iodine (92 mg, 0.72 mmol) in cyclohexane (250 mL) was irradiated 16 h (125-W Hg medium-pressure lamp, quartz filter). During the reaction period a permanent argon stream was bubbled through the solution. Cyclohexane was removed by rotary evaporation and the remaining residue separated by flash chromatography. TLC (PE/EA, 8:1): R_f = 0.59, 0.44 (**10**), 0.22. The fraction with R_f = 0.44 was dried by rotary evaporation to get 30 mg of an oily, pale yellow substance. Twofold recrystallization by diffusion of acetone in a dichloromethane solution and subsequent drying in vacuo gave 6 mg (4%) of **10** as a pale yellow solid; m.p. 198–204 °C. UV/Vis (*n*-hexane): λ_{max} (lgε) = 353 nm (3.3), 336 (3.2), 322 (3.1), 305 (3.9), 283 (sh, 4.3), 276 (4.4), 263 (sh, 4.5), 255 (4.6), 221 (4.4), 193 (4.5). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.08 ppm (t, *J* = 7.5 Hz, 6 H, OCH$_2$-CH$_2$-C*H*$_3$), 1.92 (m, *J* = 7.5 Hz, 4 H, OCH$_2$-C*H*$_2$-CH$_3$), 4.19 (t, *J* = 7.5 Hz, 4 H, Phen-OC*H*$_2$-C$_2$H$_5$), 4.38 (s, 2 H, Phen-C*H*$_2$-Phen), 7.55–7.61 (m, 8 H, Phen-6/7/9/10-H), 7.64 (s, 2 H, Phen-1-H), 7.86 (d, *J* = 7.0 Hz, 2 H, Phen-8-H), 8.01 (s, 2 H, Phen-4-H), 8.60 (d, *J* = 8.5 Hz, 2 H, Phen-5-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.81 ppm (q, O-CH$_2$-CH$_2$-*C*H$_3$), 22.82 (t, O-CH$_2$-*C*H$_2$-CH$_3$), 30.84 (t, Phen-*C*H$_2$-Phen), 69.76 (t, O-*C*H$_2$-CH$_2$-CH$_3$), 102.58 (d, Phen-C-4), 122.53 (d, Phen-C-5), 124.23 (d, Phen-C-6), 125.95 (d, Phen-C-9), 126.11 (d, Phen-C-7), 126.46 (s, Phen-C-10a), 126.62 (d, Phen-C-10), 128.63 (d, Phen-C-8), 129. 86 (s, Phen-C-2), 130.11 (s, Phen-C-4b), 130.26 (d, Phen-C-1), 130.51 (s, Phen-C-4a), 132.16 (s, Phen-C-8a), 156.77 (s, Phen*C*-O-). MS (EI = 70 eV): *m*/*z* (%) = 486 (9), 485 (40), 484 (100) [M$^+$], 399 (7), 381 (9), 353 (5), 352 (6), 291 (12), 243 (5), 236 (15), 235 (5), 207 (17), 206 (5), 194 (19), 178 (11), 165 (5), 69 (5), 59 (14), 58 (7), 57 (8), 56 (7), 44 (5), 43 (20), 42 (9), 31 (5), 29 (7), 28 (9), 27 (5). HRMS (ESI-TOF): calcd. for $C_{35}H_{32}O_2Na$ [M + Na$^+$]: 506.2216; found 506.2158.

***cone*-(*E*/*Z*)-5-(2-Phenylethenyl)-25,26,27,28-tetrakis(propyloxy)-calix[4]arene (12a):** To a cooled (–78 °C) solution of benzyltriphenylphosphonium chloride (132 mg, 0.33 mmol) in THF (8 mL) *n*BuLi (0.25 mL of a 1.6 molar hexane solution, 0.40 mmol) was added and the resulting orange suspension stirred 30 min at –78 °C. A solution of calixarene **11** (175 mg, 0.28 mmol) in THF (8 mL) was added and the reaction mixture stirred at room temperature for 14 h. Water (10 mL) and dichloromethane (50 mL) was added and the organic layer separated. The organic layer was washed 2× with water (50 mL), once with brine (50 mL) and dried with magnesium sulfate. Solvents were removed by rotary evaporation to remain 300 mg of a colourless solid. Purification by flash chromatography (PE/EA, 6:1, R_f = 0.50) and additional drying in vacuo (0.2 mbar, 100 °C) gave 168 mg (86%) of the (*E*/*Z*)-calixarene **12a** as colourless solid; m.p. 56–62 °C. IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 2929, 2873, 1590, 1453, 1384, 1290, 1248, 1215, 1194, 1123, 1087, 1037, 1007, 966, 889, 842, 758, 695. UV/Vis (*n*-hexane): λ_{max} (lgε) = 318 nm (3.8), 306 (4.2), 204 (4.1). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.95–1.05 ppm (m, 24 H, OCH$_2$-CH$_2$-C*H*$_3$), 1.84–1.98 (m, 16 H, OCH$_2$-C*H*$_2$-CH$_3$), 3.00 (d, *J* = 13.0 Hz, 2 H, Ar-C*H*$_2$-Ar), 3.16 (d, *J* = 13.1 Hz, 4 H, two superimposed signals, Ar-C*H*$_2$-Ar), 3.19 (d, *J* = 13.5 Hz, 2 H, Ar-C*H*$_2$-Ar), 3.77 (t, *J* = 7.3 Hz, 4 H, Ar-OC*H*$_2$-C$_2$H$_5$), 3.83–3.94 (m, 12 H, Ar-OC*H*$_2$-C$_2$H$_5$), 4.37 (d, *J* = 13.0 Hz, 2 H, Ar-C*H*$_2$-Ar), 4.46 (d, *J* = 13.5 Hz, 2 H, Ar-C*H*$_2$-Ar), 4.47 (d, *J* = 13.5 Hz, 2 H, Ar-C*H*$_2$-Ar), 4.48 (d, *J* = 13.0 Hz, 2 H, Ar-C*H*$_2$-Ar), 6.34 (t, *J* = 4.5 Hz, 2 H, ArH), 6.42–6.47 (m, 6 H, ArH), 6.57–6.63 (m, 8 H, ArH), 6.72–6.75 (m, 4 H, ArH), 6.78–6.81 (m, 6 H, ArH), 7.19–7.25 (m, 6 H, ArH), 7.34 (t, *J* = 7.5 Hz, 2 H, ArH), 7.46 (d, *J* = 7.0 Hz, 2 H, ArH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.19 ppm, 10.34, 10.43, 10.52 (all q, O-CH$_2$-CH$_2$-*C*H$_3$), 23.18, 23.22, 23.29, 23.34 (all t, O-CH$_2$-*C*H$_2$-CH$_3$), 30.97, 31.04 (two superimposed signals), 31.10 (all t, all Ar-*C*H$_2$-Ar), 76.79 (t, O-*C*H$_2$-CH$_2$-CH$_3$), 121.84, 121.93, 121.98, 122.02, 122.29 (all d), 126.22 (d), 126.44 (s), 126.60 (d), 126.70 (s), 126.99 (d), 127.86, 128.01, 128.14, 128.41, 128.45, 128.60, 128.89, 128.94, 129.03, 129.14, 129.27, 130.77, 130.81, 131.08 (s), 134.24, 134.44, 134.75, 135.10, 135.34, 135.65, 135.89, 137.86 (all s), 156.04, 156.53, 156.72, 156.97, 157.12 (all s, all Ar*C*-O-). MS (FAB): *m*/*z* (%) = 694 (100) [M + H$^+$]. $C_{48}H_{54}O_4 \cdot 1/4CH_2Cl_2$ (716.18): calcd. C 80.92, H 7.67; found C 80.90, H 7.56.

***rac-cone*-33,34,35,36-Tetrakis(propyloxy)calix[3]benzene[1]phenanthrene (13a):** A suspension of calixarene **12a** (50 mg, 0.067 mmol), iodine (18 mg, 0.071 mmol) and potassium carbonate (600 mg) in benzene (200 mL) was degassed with argon (30 min) and irradiated for 14 h (125-W Hg medium-pressure lamp, quartz filter). Benzene was removed by rotary evaporation and dichloromethane (10 mL)

added to the remaining residue. Unsoluble material was filtered off and dichloromethane removed in vacuo to give a greenish-black residue. TLC (PE/EA, 15:1): R_f = 0.62, 0.60 (**13a**), 0.48 (**14a**, **14b**), 0.00. Separation by flash chromatography (PE/EA, 50:1) gave after drying in vacuo (50 °C, 0.7 mbar) 40 mg (86%) of the racemic calixphenanthrene **13a** as pale yellow solid; m.p. 88–94 °C. IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1}, 2960, 2932, 2873, 1558, 1455, 1383, 1336, 1289, 1246, 1206, 1105, 1086, 1065, 1036, 1006, 967, 881, 842, 800, 758, 682, 660. UV/Vis (*n*-hexane): λ_{max} (lgε) = 359 nm (3.0), 344 (3.1), 310 (4.2), 263 (4.9). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 ppm (t, *J* = 7.5 Hz, 3 H, O-$CH_2CH_2CH_3$), 0.92 (t, *J* = 7.5 Hz, 3 H, O-$CH_2CH_2CH_3$), 1.14 (t, *J* = 7.5 Hz, 3 H, O-$CH_2CH_2CH_3$), 1.91 (t, *J* = 7.5 Hz, 3 H, O-$CH_2CH_2CH_3$), 1.86–2.13 (m, 8 H, O-$CH_2CH_2CH_3$), 3.16 (d, *J* = 13.6 Hz, 1 H, ArCH_2Ar), 3.18 (d, *J* = 13.1 Hz, 1 H, ArCH_2Ar), 3.38 (d, *J* = 13.4 Hz, 1 H, ArCH_2Ar), 3.71 (t, *J* = 6.8 Hz, 2 H, O-$CH_2CH_2CH_3$), 3.78 (m, 2 H, O-$CH_2CH_2CH_3$), 4.06 (m, 2 H, O-$CH_2CH_2CH_3$), 4.29 (td, ^2J = 10.8 Hz, ^3J = 5.8 Hz, 1 H, Phen-O-$CH_2CH_2CH_3$), 4.31 (td, ^2J = 10.8 Hz, ^3J = 5.7 Hz, 1 H, Phen-O-$CH_2CH_2CH_3$), 4.48 (d, *J* = 13.4 Hz, 2 H, ArCH_2Ar), 4.61 (d, *J* = 13.4 Hz, 1 H, ArCH_2Ar), 4.70 (d, *J* = 14.6 Hz, 1 H, ArCH_2Ar), 4.89 (d, *J* = 14.6 Hz, 1 H, ArCH_2Ar), 5.43 (d, *J* = 7.1 Hz, 1 H, Ar′-3-H), 5.86 (d, *J* = 6.5 Hz, 1 H, Ar′-5-H), 5.94 (t, *J* = 7.6 Hz, 1 H, Ar′-4-H), 6.08 ("t", "*J*" = 6.5 Hz, 1 H, Ar′′′-4-H), 6.22 (m, 2 H, Ar′′′-3/5-H), 6.93 (t, *J* = 7.5 Hz, 1 H, Ar′′-4-H), 7.11–7.16 (m, 2 H, Ar′′-3/5-H), 7.53 (m, 2 H, Phen-6/7-H), 7.63 (d, *J* = 8.5 Hz, 1 H, Phen-9-H), 7.66 (s, 1 H, Phen-1-H), 7.71 (d, *J* = 8.8 Hz, 1 H, Phen-10 H), 7.89 (m, 1 H, Phen-8-H), 8.64 (m, 1 H, Phen-5-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 9.89 ppm, 9.93, 10.91, 11.03 (all q, all $OCH_2CH_2CH_3$), 23.07, 23.13, 23.62, 23.73 (all t, all $OCH_2CH_2CH_3$), 29.60, 31.11, 31.14 (all t, all ArCH_2Ar), 76.58, 76.64, 76.90, 77.55 (all t, all $OCH_2CH_2CH_3$), 121.70, 122.33, 122.40 (all d, all Ar-C-4), 124.86 (d, Phen-C-6), 125.12 (d, Phen-C-9), 125.66 (d, Phen-C-7), 126.78 (d, Ar′-C-3), 127.02 (d, Ar′-C-5), 127.19 (d, Ar′′′-C-3), 127.27 (d, Phen-C-10), 127.59 (d, Ar′′′-C-4), 127.94 (d, Phen-C-5), 128.35 (d, Phen-C-8), 128.58 (s, Phen-C-10a), 128.88, 129.00 (both d, both Ar′′*C*-H), 130,40 (s, Phen-C-4b), 131.21 (s, Phen-C-4a), 132.39, 133.07, 133.33, 133.38, 133.39, 134.39 (all s, all Ar*C*-CH_2-Ar), 136.69 (s, Phen-C-4), 137.42 (s, Phen-C-2), 137.52 (s, Ar*C*-CH_2-Ar), 155.04, 155.18, 158.40 (all s, all ArC-O-), 159.51 (s, Phen-*C*-O-). MS (FAB): *m*/*z* (%) = 692.4 (100) [M^+]. $C_{48}H_{52}O_4 \cdot 1/8CH_2Cl_2$ (703.02): calcd. C 82.16, H 7.49; found C 82.27, H 7.34.

2-{3′-[3′′-(3′′′-Methyl-2′′′-(propyloxy)benzyl)-2′′-(propyloxy)benzyl]-2′-(propyloxy)benzyl}-3-(propyloxy)phenanthrene (14a): A solution of the calixarene **12a** (90 mg, 0.13 mmol) and iodine (31 mg, 0.12 mmol) in cyclohexane (200 mL) was degassed with argon (30 min) and irradiated for 4 h (125-W Hg medium-pressure lamp, quartz filter). Cyclohexane was removed by rotary evaporation to remain a brown residue. TLC (PE/EA, 40:1): R_f = 0.31 (**12a**, **13a**), 0.25 (**14a**). Separation by flash chromatography (PE/EA, 50:1) gave after drying in vacuo: **1st Fraction:** A mixture of **12a** and **13a** as pale yellow solid (detected by ^{1}H NMR spectroscopy), that could not be separated by further column chromatography. **2nd Fraction:** 15 mg (16%) of the linear phenanthrene **14a** as colourless oil of high viscosity. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.98 ppm, 0.99, 1.03 (all t, *J* = 7.5 Hz, 3 H, Ar-$OCH_2CH_2CH_3$), 1.06 (t, *J* = 7.5 Hz, 3 H, Phen-$OCH_2CH_2CH_3$), 1.78–1.79 (m, 6 H, Ar-$OCH_2CH_2CH_3$), 1.89 (sext, *J* = 6.8 Hz, 2 H, Phen-$OCH_2CH_2CH_3$), 2.32 (s, 3 H, Ar-CH_3), 3.72 ("t", "*J*" = 6.4 Hz, two superimposed signals, 4 H, Ar-$OCH_2CH_2CH_3$), 3.77 (t, *J* = 6.4 Hz, 2 H, Ar-$OCH_2CH_2CH_3$), 4.11 (s, 2 H, Ar-CH_2-Ar), 4.15 (s, 2 H, Ar-CH_2-Ar), 4.19 (t, *J* = 6.4 Hz, 2 H, Phen-$OCH_2CH_2CH_3$), 4.25 (s, 2 H, Ar-CH_2-Ar), 6.87–6.97 (m, 8 H, Ar-H), 7.04 (dd, *J* = 2.0 Hz, *J* = 6.8 Hz, 1 H), 7.53 (s, 1 H, Phen-1-H), 7.55–7.63 (m, 4 H, Phen-H), 7.85 (d, *J* = 7.8 Hz, *J* = 1.0 Hz, 1 H, Phen-8-H), 8.00 (s, 1 H, Phen-4-H), 8.59 (d, *J* = 8.0 Hz, 1 H, Phen-5-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.62 ppm, 10.77 (both q, both superimposed signals, O-CH_2-CH_2-CH_3), 16.47 (q, CH_2-Ar′′′-CH_3), 22.77, 23.64, 23.66 (all t, all O-CH_2-CH_2-CH_3), 29.46, 29.56, (all t, all Ar-CH_2-Ar), 30.18 (t, Phen-CH_2-Ar), 69.76 (t, Phen-O-CH_2-CH_2-CH_3), 74.39, 75.02, 75.05, 77.26 (all t, all Ar-O-CH_2-CH_2-CH_3), 102.52 (d, Phen-C-4), 122.51 (d, Phen-C-5), 123.71, 123.81, 123.86 (all d, all Ar*C*-H), 124.27 (d, Phen-C-6), 125.96 (d, Phen-C-9), 126.14, 126.46, 126.62 (all d, all Phen*C*-H), 128.61(s), 128.64 (d, Phen-C-8), 128.83, 128.85, 128.89, 128.93 (all d, all Ar*C*-H), 129.22 (d), 129.81 (s, Phen-C-2), 130.02, 130.08, 131.01, 131.07 (all s), 132.16 (s, Phen-C-8a), 133.73, 134.09, 134.20, 134.22, 134.24 (all s, all Ar*C*-CH_2-Ar), 155.87, 155.98, 156.04 (all s, all Ar*C*-O), 156.58 (s, Phen*C*-O). MS (FAB): *m*/*z* (%) = 694.4 (28) [M^+]. HRMS (ESI-TOF) calcd. for $C_{48}H_{54}O_4Na$ [M + Na^+]: 717.3914; found 717.3874.

2-{3′-[3′′-(3′′′-Iodomethyl-2′′′-(propyloxy)benzyl)-2′′-(propyloxy)benzyl]-2′-(propyloxy)benzyl}-3-(propyloxy)phenanthrene (14b): A solution of calixarene **12a** (100 mg, 0.13 mmol) and iodine (18 mg, 0.071 mmol) in benzene (220 mL) was degassed with argon (30 min) and irradiated for 14 h (125-W Hg medium-pressure lamp, quartz filter). Benzene was removed by rotary evaporation to give a greenish-black residue. TLC (PE/EA, 20:1): R_f = 0.56, 0.45 (**13a**), 0.34 (**14b**), 0.22, 0.16, 0.00. Separation by flash chromatography (PE/EA, 50:1) gave after drying in vacuo (50 °C, 0.7 mbar): **1st Fraction (R_f = 0.45):** 22 mg (22%) of calixphenanthrene **13a**. Analytical data are in agreement to those described above. **2nd Fraction (R_f = 0.34):** 45 mg (39%) of the benzyl iodide **14b** as pale yellow wax, becoming a deep brown oil after a few hours. IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1}, 3028, 2961, 2931, 2873, 1624, 1589, 1519, 1499, 1455, 1384, 1249, 1217, 1156, 1124, 1103, 1081, 1041, 1003, 992, 891, 839, 806, 766, 743, 701, 656. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.00 ppm (t, *J* = 7.5 Hz, 6 H, Ar-$OCH_2CH_2CH_3$), 1.07 (t, *J* = 7.1 Hz, 3 H, Ar-$OCH_2CH_2CH_3$), 1.10 (t, *J* = 7.3 Hz, 3 H, Ar-$OCH_2CH_2CH_3$), 1.76–1.87 (m, 8 H, -$OCH_2CH_2CH_3$), 3.71 (t, *J* = 6.4 Hz, 2 H, Ar-$OCH_2CH_2CH_3$), 3.76 (t, *J* = 6.4 Hz, 2 H, Ar-$OCH_2CH_2CH_3$), 3.93 (t, *J* = 6.4 Hz, 2 H, Ar-$OCH_2CH_2CH_3$), 4.11 (s, 2 H, Ar-CH_2-Ar), 4.15 (s, 2 H, Ar-CH_2-Ar), 4.19 (t, *J* = 6.4 Hz, 2 H, Phen-$OCH_2CH_2CH_3$), 4.25 (s, 2 H, Ar-CH_2-Ar), 4.56 (s, 2 H, Ar-CH_2I), 6.85–6.97 (m, 8 H, Ar-H), 7.27 (m, 1 H, Ar-H), 7.53 (s, 1 H, Phen-1-H), 7.53–7.65 (m, 5 H, Phen-H), 7.87 (d, *J* = 7.6 Hz, 1 H, Phen-8-H), 8.00 (s, 1 H, Phen-4-H), 8.60 (d, *J* = 8.0 Hz, 1 H, Phen-5-H).^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 0.58 ppm (t, ArCH_2I), 10.55, 10.61 (two superimposed signals), 10.76 (all q, all -$OCH_2CH_2CH_3$), 22.76, 23.62, 23.65, 23.70 (all t, all -$OCH_2CH_2CH_3$), 29.43, 29.57, 30.18 (all t, all ArCH_2Ar), 69.75, 74.51, 75.05 (two superimposed signals) (all t, all -$OCH_2CH_2CH_3$), 102.51 (d, Phen-C-4), 122.49 (d, Phen-C-5), 123.82, 123.93 (both d), 124.41 (d, Phen-C-6), 125.96 (d, Phen-C-9), 126.14 (d, Phen-C-7), 126.45 (s, Phen-C-10a), 126.59 (d, Phen-C-10), 128.62 (d, Phen-C-8), 128.83, 128.89, 129.16, 129.35 (all d, all Ar*C*-H), 129.80 (s, Phen-C-2), 130.01 (d, Phen-C-1), 130.08 (s, Phen-C-4b), 130.97 (s), 131.12 (s), 132.14 (d), 132.71 (s, Phen-C-8a), 133.61, 133.77, 134.09, 134.41, 135.02 (all s, all Ar*C*-CH_2-Ar), 155.33, 155.88, 155.97, 156.55 (all s, all Ar*C*-O-). MS (FAB): *m*/*z* (%) = 843 (2) [M + Na^+], 820 (2) [M^+], 699 (8), 692 (14) [M^+ – HI], 677 (13), 651 (3), 619 (5). HRMS (ESI-TOF): calcd. for $C_{48}H_{53}IO_4Na$ [M + Na^+]: 843.2881; found 843.2898.

([D_7]Benzyl)triphenylphosphonium Chloride: To a solution of triphenylphosphane (2.008 g, 7.65 mmol) in [D_8]toluene (4 mL) [D_7]-benzyl chloride (1 mL, 8.98 mmol) was added and heated for 16 h

at 100 °C. After cooling to room temperature, the colourless precipitate was collected by filtration, washed 3 times with diethyl ether (5 mL) and dried in a moderate argon stream. Yield: 1.400 g (46%) of the deuteriophosphonium salt as colourless solid; m.p. >300 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.45 ppm [d, J = 7.3 Hz, $C_6D_5CH_2$-$P^+(C_6H_5)_3$], 5.46 [d, J = 7.5 Hz, C_6D_5CHD-$P^+(C_6H_5)_3$], 7.57–7.62 [m, -$P^+(C_6H_5)_3$], 7.70–7.75 [m, -$P^+(C_6H_5)_3$]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.37 ppm [m, $C_6D_5CH_2$-$P^+(C_6H_5)_3$, C_6D_5CHD-$P^+(C_6H_5)_3$ und $C_6D_5CD_2$-$P^+(C_6H_5)_3$], 118.0 [dd, $^1J_{CP}$ = 85.9 Hz, $^3J_{CD}$ = 3.1 Hz, -P^+(*ipso*-$C_6H_5)_3$], 127.08 [m, *ipso*-$C_6D_5CD_2$-$P^+(C_6H_5)_3$], 128.05 [m, *para*-$C_6D_5CD_2$-$P^+(C_6H_5)_3$], 128.54 [m, *meta*-$C_6D_5CD_2$-$P^+(C_6H_5)_3$], 130.70 [d, $^2J_{CP}$ = 13.1 Hz, -P^+(*ortho*-$C_6H_5)_3$], 131.14 [m, *ortho*-$C_6D_5CD_2$-$P^+(C_6H_5)_3$], 134.40 [d, $^3J_{CP}$ = 10.0 Hz, -P^+(*meta*-$C_6H_5)_3$], 134.89 [d, $^4J_{CP}$ = 3.0 Hz, -P^+(*para*-$C_6H_5)_3$]. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 24.50 ppm ("t", "*J*" s= 11.1 Hz). MS (EI = 70 eV): *m*/*z* = 359 (14), 358 (63), 357 (100), 356 (65), 355 (40), 278 (7), 277 (58), 263 (11), 262 (58), 261 (11), 185 (12), 184 (15), 183 (71), 173 (28), 172 (41), 171 (11), 170 (22), 169 (17), 157 (9), 156 (9), 152 (12), 143 (7), 108 (18), 107 (13), 99 (9), 97 (14), 96 (15), 87 (15), 85 (10), 77 (11), 74 (10), 71 (12), 69 (9), 59 (15), 58 (11), 57 (42), 56 (10), 55 (9), 51 (14), 45 (12), 44 (27), 43 (25), 42 (9), 41 (21), 39 (21), 38 (5), 37 (48), 36 (18), 35 (8), 29 (822), 28 (21), 27 (8). By comparison the ^{1}H NMR spectrum with that of the non-deuterated phosphonium salt the grade of deuteration in the benzylic position could be estimated to 51%.

***cone*-(*E*/*Z*)-5-[2-(2,3,4,5,6-Pentadeuteriophenyl)-2-deuterioethenyl]-25,26,27,28-tetrakis(propyloxy)calix[4]arene (12b):** To a cooled (–78 °C) solution of ([D_7]benzyl)triphenylphosphonium chloride (106 mg, 0.27 mmol) in THF (8 mL) *n*BuLi (0.17 mL of a 1.6 molar hexane solution, 0.27 mmol) was added, and the resulting orange suspension stirred at –78 °C for 30 min. A solution of the calixarene **11** (150 mg, 0.24 mmol) in THF (4 mL) was added and the reaction mixture stirred at room temperature for 24 h. Solvents were removed by rotary evaporation and the remaining residue purified by flash chromatography (PE/EA, 100:1, R_f = 0.24). Additional drying in vacuo gave 120 mg (71%) of (*E*/*Z*)-deuteriocalixarene **12b** as colourless solid; m.p. 53–55 °C. IR (KBr): $\tilde{\nu}$ = 3434 cm^{-1}, 2962, 2932, 2874, 1587, 1558, 1538, 1505, 1456, 1384, 1304, 1289, 1248, 1216, 1195, 1131, 1087, 1067, 1040, 1007, 966, 888, 841, 761. UV/Vis (*n*-hexane): λ_{max} (lg ε) = 308 nm (4.6), 205 (5.1). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.94–1.04 ppm (m, 24 H, OCH_2-CH_2-CH_3), 1.84–1.99 (m, 16 H, OCH_2-CH_2-CH_2-CH_3), 3.00 (d, J = 13.0 Hz, 2 H, Ar-CH_2-Ar), 3.16 (d, J = 13.1 Hz, 4 H, two superimposed signals, Ar-CH_2-Ar), 3.18 (d, J = 13.5 Hz, 2 H, Ar-CH_2-Ar), 3.77 (t, J = 7.3 Hz, 4 H, Ar-OCH_2-C_2H_5), 3.83–3.94 (m, 12 H, Ar-OCH_2-C_2H_5), 4.38 (d, J = 13.0 Hz, 2 H, Ar-CH_2-Ar), 4.46 (d, J = 13.5 Hz, 2 H, Ar-CH_2-Ar), 4.47 (d, J = 13.5 Hz, 2 H, Ar-CH_2-Ar), 4.48 (d, J = 13.0 Hz, 2 H, Ar-CH_2-Ar), 6.34 (t, J = 4.5 Hz, 2 H, ArH), 6.42–6.47 (m, 6 H, ArH), 6.57–6.63 (m, 8 H, ArH), 6.72–6.75 (m, 4 H, ArH), 6.78–6.81 (m, 6 H, ArH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.19 ppm, 10.22, 10.34, 10.35, 10.42, 10.52 (all q, O-CH_2-CH_2-*C*H_3), 23.19, 23.22, 23.28, 23.30, 23.33, 23.36 (all t, O-CH_2-*C*H_2-CH_3), 30.95, 31.06 (two superimposed signals), 31.11 (all t, Ar-*C*H_2-Ar), 76.60, 76.64, 76.66, 76.79 (all t, O-*C*H_2-CH_2-CH_3), 121.84, 121.93, 121.99, 122.02, (all d), 126.41 (s), 126.61, 127.87, 128.03, 128.15, 128.24 128.41, 129.03, 129.18, 129.29, 130.64 (all d), 130.76, 130.85, 131.11, 134.26, 134.46, 134.77, 135.11 135.34, 135.63, 135.88, 137.61, 137.82, 137.88 (all s), 156.06, 156.53, 156.57, 156.73, 156.96, 157.14 (all s, Ar*C*-O-). MS (FAB): *m*/*z* (%) = 700.5 (100) [M + H$^+$]. HRMS (ESI-TOF): calcd. for $C_{48}H_{48}D_6O_4Na$ [M + Na$^+$]: 723.4292; found: 723.4291.

5,6,7,8,9-Pentadeuterio-2-{3′-[3′′-(3′′′-methyl-2′′′-(propyloxy)benzyl)-2′′-(propyloxy)benzyl]-2′-(propyloxy)benzyl}-3-(propyloxy)phenanthrene (14c) and *rac-cone*-9,10,11,12-Tetradeuterio-33,34,35,36-tetrakis(propyloxy)calix[3]benzene[1]phenanthrene (13b): A solution of deuteriocalixarene **12b** (80 mg, 0.11 mmol) and iodine (a tip of a spatula) in cyclohexane (200 mL) was degassed with argon (30 min) and irradiated for 16 h (125-W Hg medium-pressure lamp, quartz filter). Cyclohexane was removed by rotary evaporation to remain a brown residue. TLC (PE/EA, 40:1): R_f = 0.31 (**13b**), 0.25 (**14c**). Separation by flash chromatography (PE/EA, 50:1) gave after drying in vacuo: **1st Fraction (R_f = 0.31):** 38 mg (50%) of deuterated calixphenanthrene **13b** as pale yellow solid. The compound was not further purified. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.93 ppm (t, J = 7.6 Hz, 3 H, O-$CH_2CH_2CH_3$), 0.93 (t, J = 7.3 Hz, 3 H, O-$CH_2CH_2CH_3$), 1.16 (t, J = 7.4 Hz, 3 H, O-$CH_2CH_2CH_3$), 1.22 (t, J = 7.4 Hz, 3 H, O-$CH_2CH_2CH_3$), 1.86–2.13 (m, 8 H, O-$CH_2CH_2CH_3$), 3.16 (d, J = 13.9 Hz, 1 H, ArCH_2Ar), 3.18 (d, J = 13.4 Hz, 1 H, ArCH_2Ar), 3.40 (d, J = 13.4 Hz, 1 H, ArCH_2Ar), 3.73 (t, J = 6.7 Hz, 2 H, O-$CH_2CH_2CH_3$), 3.80 (m, 2 H, O-$CH_2CH_2CH_3$), 4.01–4.15 (m, 2 H, O-$CH_2CH_2CH_3$), 4.23 (td, ^2J = 10.8 Hz, ^3J = 5.8 Hz, 1 H, Phen-O-$CH_2CH_2CH_3$), 4.30 (td, ^2J = 10.8 Hz, ^3J = 5.7 Hz, 1 H, Phen-O-$CH_2CH_2CH_3$), 4.50 (d, J = 13.4 Hz, 2 H, ArCH_2Ar), 4.63 (d, J = 13.4 Hz, 1 H, ArCH_2Ar), 4.72 (d, J = 14.9 Hz, 1 H, ArCH_2Ar), 4.91 (d, J = 14.7 Hz, 1 H, ArCH_2Ar), 5.46 (d, J = 7.1 Hz, 1 H, Ar′-3-H), 5.88 (d, J = 6.8 Hz, 1 H, Ar′-5-H), 5.96 (t, J = 7.6 Hz, 1 H, Ar′-4-H), 6.10 ("t", 1 H, Ar′′′-4-H), 6.23 (m, 2 H, Ar′′′-3/5-H), 6.95 (m, 1 H, Ar′′-4-H), 7.12–7.18 (m, 2 H, Ar′′-3/5-H), 7.66 (d, J = 8.6 Hz 1 H, Phen-9-H), 7.71 (s, 1 H, Phen-1-H), 7.73 (d, J = 8.8 Hz, 1 H, Phen-8-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 9.90 ppm, 9.94, 10.92, 11.03 (all q, all $OCH_2CH_2CH_3$), 23.07, 23.13, 23.63, 23.74 (all t, all $OCH_2CH_2CH_3$), 26.97, 29.55, 31.15 (all t, all Ar*C*H_2Ar), 76.58, 76.64, 76.90, 77.54 (all t, all $OCH_2CH_2CH_3$), 121.70, 122.33, 122.40 (all d, all Ar-C-4), 125.09 (d, Phen-C-9), 126.79 (d, Ar′-C-3), 127.04 (d, Ar′-C-5), 127.19 (d, Ar′′′-C-3), 127.25 (d, Phen-C-10), 127.59 (d, Ar′′′-C-4), 128.35 (d, Phen-C-8), 128.58 (s, Phen-C-10a), 128.88, 129.00 (both d, both Ar′′*C*-H), 130.31 (s, Phen-C-4b), 131.17 (s, Phen-C-4a), 132.39, 133.07, 133.33, 133.38, 133.42, 134.38 (all s, all Ar*C*-CH_2-Ar), 136.67 (s, Phen-C-4), 137.41 (s, Phen-C-2), 137.52 (s, Ar*C*-CH_2-Ar), 155.04, 155.18, 158.40 (all s, all ArC-O-), 159.51 (s, Phen*C*-O-). **2nd Fraction (R_f = 0.25):** 10 mg (13%) of the deuterated phenanthrene **14c** as colourless oil of high viscosity. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.98 ppm, 0.99, 1.03 (all t, J = 7.5 Hz, 3 H, Ar-$OCH_2CH_2CH_3$), 1.06 (t, J = 7.5 Hz, 3 H, Phen-$OCH_2CH_2CH_3$), 1.74–1.83 (m, 6 H, Ar-$OCH_2CH_2CH_3$), 1.89 (sext, J = 6.8 Hz, 2 H, Phen-$OCH_2CH_2CH_3$), 2.32 (s, 3 H, Ar-CH_3), 3.72 ("t", *"J"* = 6.4 Hz, two superimposed signals, 4 H, Ar-O*C*$H_2CH_2CH_3$), 3.77 (t, J = 6.4 Hz, 2 H, Ar-O*C*$H_2CH_2CH_3$), 4.11 (s, 2 H, Ar-CH_2-Ar), 4.15 (s, 2 H, Ar-CH_2-Ar), 4.19 (t, J = 6.4 Hz, 2 H, Phen-O*C*$H_2CH_2CH_3$), 4.25 (s, 2 H, Ar-CH_2-Ar), 6.87–6.97 (m, 8 H, Ar-H), 7.04 (dd, J = 1.9 Hz, J = 6.8 Hz, 1 H), 7.53 (s, 1 H, Phen-1-H), 7.58 (s, 1 H, Phen-10-H), 8.00 (s, 1 H, Phen-4-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.60 ppm, 10.61, 10.63, 10.77 (all q, O-CH_2-CH_2-*C*H_3), 16.47 (q, CH_2-Ar′′′-*C*H_3), 22.77, 23.64, 23.66 (all t, all O-CH_2-*C*H_2-CH_3), 29.46, 29.56, (all t, all Ar-*C*H_2-Ar), 30.18 (t, Phen-*C*H_2-Ar), 69.76 (t, Phen-O-*C*H_2-CH_2-CH_3), 74.39, 75.02, 75.05, 77.26 (all t, all Ar-O-*C*H_2-CH_2-CH_3), 102.53 (d, Phen-C-4), 123.71, 123.81, 123.86 (all d, all Ar*C*-H), 124.22, 126.45, 126.59 (all d, all Phen*C*-H), 128.60 (s), 128.82, 128.84, 128.89, 128.93 (all d, all Ar*C*-H), 129.22 (d), 129.73, 130.02, 130.07, 131.00, 131.07 (all s), 132.16 (s, Phen-C-8a), 133.73, 134.09, 134.20, 134.22, 134.24 (all s, all Ar*C*-CH_2-Ar), 155.87, 155.98, 156.04 (all s, all Ar*C*-O), 156.57 (s, Phen*C*-O). MS (FAB): *m*/*z* (%) = 699.5

(29) [M+]. HRMS (ESI-TOF): calcd. for $C_{48}H_{49}D_5O_4Na$ [M + Na+]: 722.4228; found: 722.4194.

Photolysis of Benzyl Iodide[24] in Cyclohexane: A solution of benzyl iodide (206 mg, 0.945 mmol) in cyclohexane (200 mL) was degassed with argon for 30 min and irradiated 31 h (125-W Hg medium-pressure lamp, quartz filter). The reaction was monitored by taking small aliquots of the reaction mixture after 4, 5, 6, 22.75, 24, 26, 28 and 30 h. The samples were analyzed by GC with a Siemens Sichromat 1–4 with a FID as detector and hydrogen (0.5 bar) as inert gas with a OV1 methylsilicon column (25 m, 0.2 mm) and the software Chromstar version 3.25 S or by GC/MS with a Hewlett–Packard 5890 Series II Gas Chromatographer with a Hewlett–Packard 5972 Series Mass Selective Detector, a ZB-5 w.s.column (30 m, 0.25 mm), thickness 0.25 μm with helium as inert gas. The formation of I_2 was observed by a typical purple colour of the irradiated reaction mixture, which could be decolourized with an aqueous thiosulfate solution.

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