Concave Hydrocarbons

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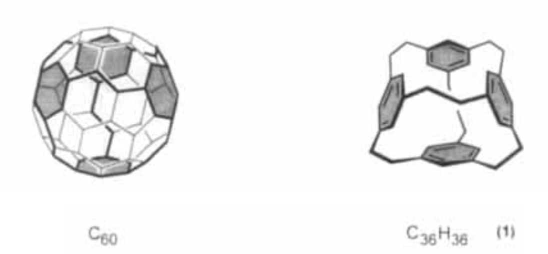
Abstract: Concave hydrocarbons, such as **1** ($C_{36}H_{36}$), **4** ($C_{60}H_{60}$), **5** ($C_{54}H_{48}$), and **6** ($C_{60}H_{52}$), represent three-dimensionally clamped analogues of π-prismands. They encapsulate small metal ions and accomplish metal-ion extraction from aqueous solution. Their remarkable selectivity allows applications such as incorporation in ion-selective electrodes. The synthetic route is based on well-established cyclophane methodology and, thus, offers a general approach to a whole family of concave hydrocarbons.

Keywords
concave hydrocarbons · cyclophanes · host/guest chemistry · ion-selective electrodes · prismands

Introduction

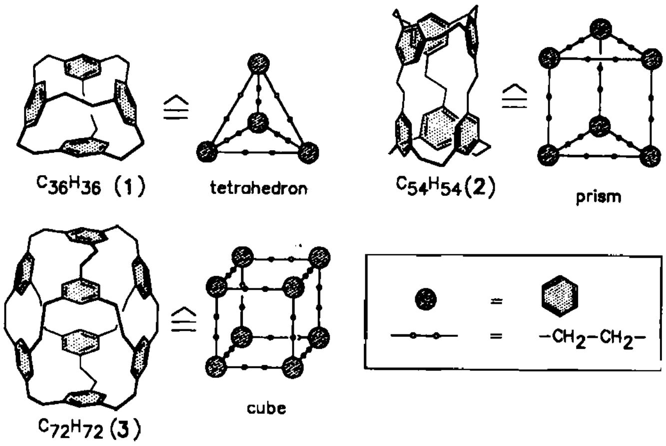
Spherical hydrocarbons with an *intra*molecular cavity are of interest in both fullerene and host/guest chemistry. With their cyclophane-based hydrocarbon cages they define an almost spherical cavity which, in contrast to the inside of fullerenes, can be entered through tailored openings on the surface. The hydrophobic cavities offer considerable potential for the encapsulation of small charged[1] or uncharged[2] organic molecules as well as metal ions like Ag^+ or Ga^+[3, 4] as they constitute three-dimensionally clamped analogues of π-prismands.[5]

In the light of the finding that pyrolysis of simple aromatic compounds such as naphthalene leads to the formation of fullerenes,[6] concave cyclophanes with an appropriate number of carbon atoms and their corresponding host/guest complexes can be envisaged serving as direct precursors for fullerenes or endohedral fullerene complexes[7] that are currently obtained by arc-discharge vaporization of doped graphite. Especially those derivatives linked by etheno rather than ethano bridges are considered to be more stable towards C–C bond cleavage and therefore should be more suitable for the necessary C–C condensation and dehydrogenation reactions. Figure 1 illustrates how the molecular skeleton of $C_{36}H_{36}$ (**1**), described below, is part of the framework of fullerene C_{60}.



Results and Discussion

Earlier, we reported the synthesis of $C_{36}H_{36}$ (**1**), in which four benzene rings are braced by six ethane bridges.[8, 9] $C_{36}H_{36}$ represents the smallest member of a whole family of macropolycyclic hydrocarbons constructed of 1,3,5-trimethylenebenzene subunits and fitting the formula $[C_9H_9]_{2n}$, for example homologues **2** and **3**. We found it helpful to use a symbolic representation as depicted in Figure 2, in which the benzene spacers and the ethane bridges are represented as corners and edges of polyhedra, respectively. Thus, compounds with higher *n* are de-



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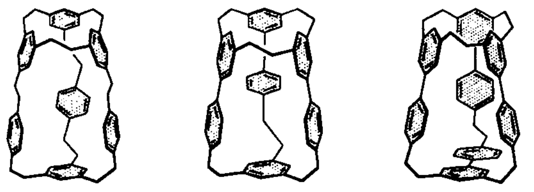
with higher n are described more easily, and conclusions concerning the structure of these spheriphanes can be drawn by applying simple geometrical equations: as three edges form one corner and each edge joins two corners, Equation (1) holds (C = number of corners; E = number of edges), and in addition Euler's polyhedron equation [Eq. (2)] applies, where F = number of faces.

$$E = {}^{3}/_{2}C \tag{1}$$

$$C - E + F = 2 \tag{2}$$

number of faces. Thus, $C_{36}H_{36}$ (**1**) is equivalent to a tetrahedron, $C_{54}H_{54}$ (**2**) to a triangular prism, and $C_{72}H_{72}$ (**3**) to a cube. A hypothetical $C_{180}H_{180}$ built up from 12 trimethylenebenzene subunits would be represented as a dodecahedron. The faces of the polyhedra correspond to the openings on the surface of the molecule, an area surrounded by n corners corresponding to a [2_n]metacyclophane window.

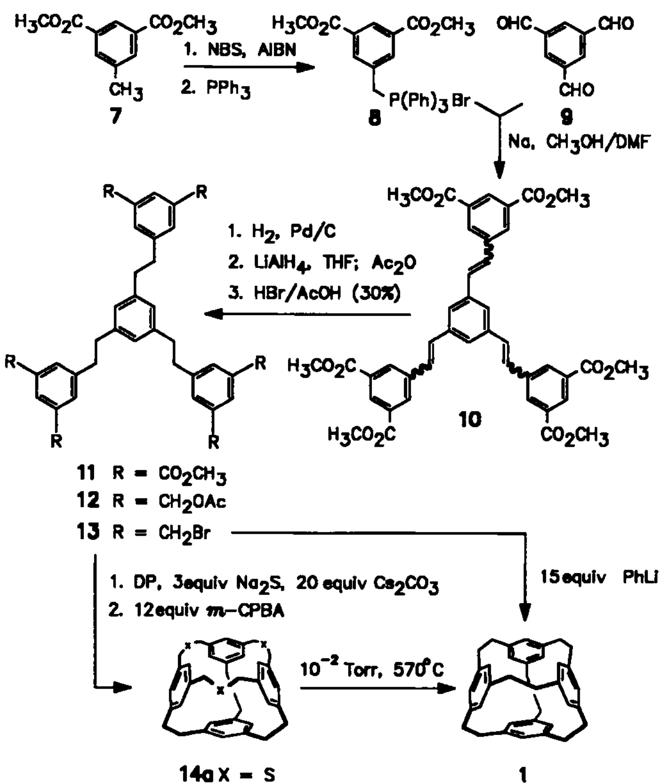
Concave hydrocarbons having 60 or 70 carbon atoms are of special interest as model compounds in an approach towards fullerenes, but they cannot be constructed from 1,3,5-trimethylenebenzene spacers exclusively. With other spacers and different substitution patterns the design of similar concave hydrocarbons such as **4**–**6** can be accomplished (Fig. 3).



$C_{60}H_{60}$ (4) $C_{54}H_{48}$ (5) $C_{60}H_{52}$ (6)

Fig. 3. $C_{60}H_{60}$, $C_{54}H_{48}$, and $C_{60}H_{52}$ constitute spheriphanes built up of other spacers than 1,3,5-connected benzene rings.

We report herein the synthesis of $C_{36}H_{36}$ (**1**), $C_{60}H_{60}$ (**4**), $C_{54}H_{48}$ (**5**), and $C_{60}H_{52}$ (**6**), their ability to complex metal ions in comparison to other π-spherands and π-prismands known from the literature, and their potential use as ionophores in ion-selective electrodes.



Scheme 1. Synthesis of **1** (DP = dilution principle).

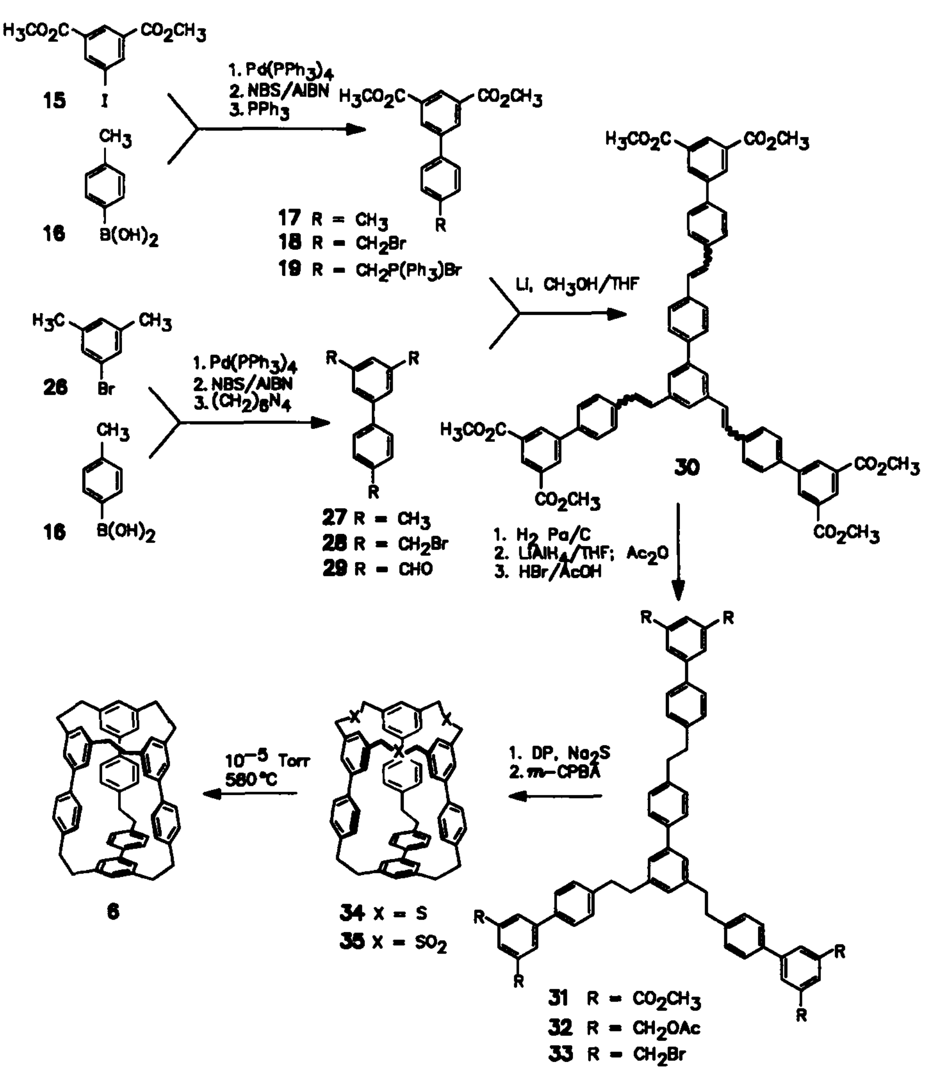
Synthesis: The synthesis of $C_{36}H_{36}$ was accomplished by building up the molecular framework in a stepwise manner, starting from 1,3,5-benzene tricarbaldehyde[10] (**9**), which is reacted in a threefold Wittig reaction with the phosphonium salt **8** (Scheme 1). The resulting hexaester **10** is obtained as a mixture of E/Z isomers and already contains the 36 carbon atoms of the target molecule. Quantitative hydrogenation of the double bonds and derivatization of the six ester moieties gives the hexabromide **13** in high yield in three synthetic steps. Well-established cyclophane methodology, sulfide cyclization[11] under high dilution conditions,[12] followed by oxidation and sulfone pyrolysis[13] of the tricyclic trisulfide **14**, provides the concave hydrocarbon **1**.[14]

This reaction sequence of "folding up" an open-chain precursor by an intramolecular cyclization reaction proved to be applicable for the synthesis of $C_{54}H_{48}$ (**5**) and $C_{60}H_{52}$ (**6**), too. Suzuki coupling of the iodide **15** with p-toluene boronic acid (**16**) affords the 4'-methylbiphenyl-3,5-dicarboxylic acid dimethyl ester **17** (Scheme 2), which was subsequently NBS-brominated and reacted with triphenylphosphine to yield the phosphonium bromide **19**. The trialdehyde **29** was synthezized by Suzuki coupling of p-toluene boronic acid (**16**) with 5-bromo-m-xylene (**26**), NBS-bromination of the obtained trimethylbiphenyl **27** and Sommelet oxidation of the tris(bromomethyl)biphenyl **28**. The Wittig reaction of **9** and **19** (not shown) yielded the triene **20**, which is the precursor of **5**, while the analogous reaction of **29** and **19** afforded triene **30**, the corresponding precursor of **6**.

However, for the synthesis of $C_{60}H_{60}$ (**4**) the Wittig reaction and functionalization sequence had to be carried out repetitively, requiring an almost 20-step synthesis (Scheme 3). The overall yields for the cage compounds **1**, **4**, **5**, and **6** range between 0.8 (for **9** → **4**) and 4.7% (for **9** → **1**).

For the hydrocarbon $C_{54}H_{54}$ (**2**) a more convergent strategy seemed to be feasible by building up the macrotetracyclic skeleton by *inter*molecular cyclization of two trimeric subunits (Scheme 4). The cyclic trimer **55** was built up by an analogous Wurtz reductive coupling as described by Müller and Röscheisen[15] and subsequently functionalized to the bromide **56** and the thiol **57**. However, we found that a conformation in

Abstract in German: *Die Synthese von vier konkaven Kohlenwasserstoffen (1, 4, 5 und 6) über etablierte, konvergente Synthesestrategien mit Sulfidcyclisierung und anschließender Extrusion der Schwefelatome in Form von SO_2 über Sulfonpyrolyse wird beschrieben. Die Synthesestrategie eröffnet den Zugang zu konkaven Kohlenwasserstoffen, die dreidimensional verklammerte Analoga von π-Prismanden repräsentieren. Sie komplexieren Metallionen und sind in der Lage, diese selektiv aus einer wäßrigen Lösung zu extrahieren. Die zum Teil bemerkenswerten Selektivitäten machen die Komplexliganden zu potentiellen Sensormaterialien für ionenselektive Elektroden.*



Scheme 2. Synthesis of **6**. The synthesis of **5** (not shown) is accomplished analogously by treating **19** with **9**; the intermediates are **20**–**25**.

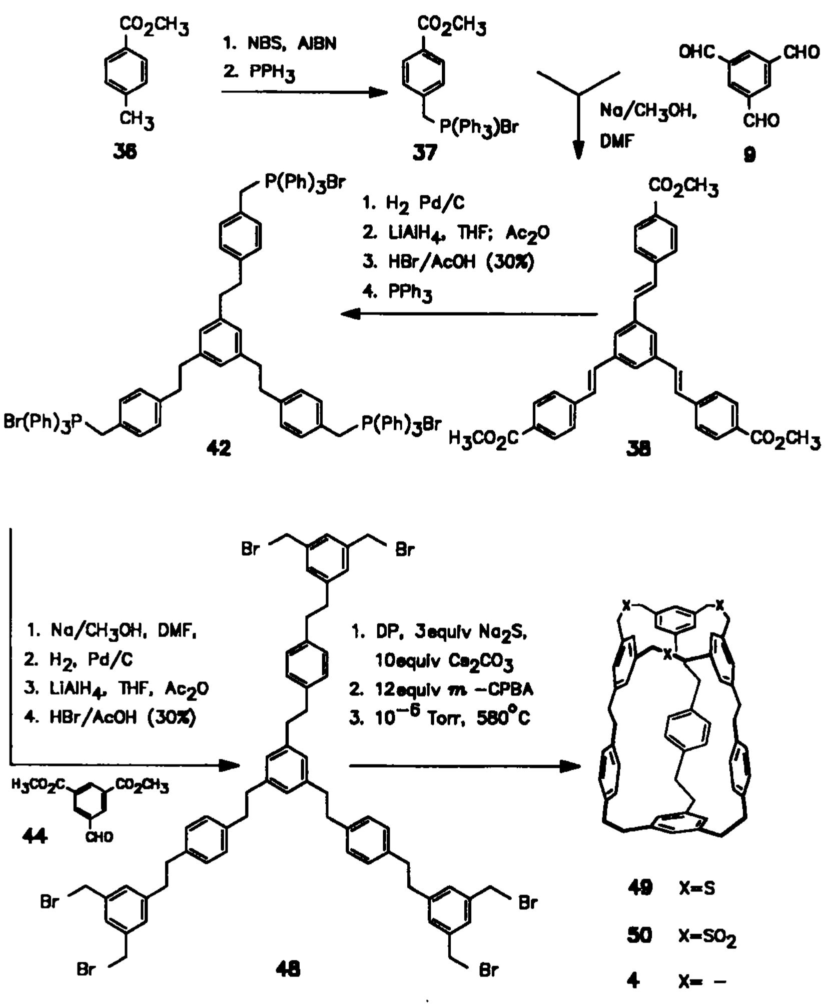
which the three reactive moieties are directed to one side seems to be unfavorable for either the precursor **56** or **57**, and the cyclization reactions proved to be unsuccessful. To avoid the conformational flexibility of the ethylene bridges we replaced them by all-*Z* configurated etheno groups.[16] Compound **59**, which is prepared from **53** by substitution of one bromine, oxidation to monoaldehyde **58**, and subsequent reaction with triphenylphosphine, yielded the all-*Z* preorganized trimer **60** by a threefold *inter*molecular Wittig reaction. The triene **60** is a valuable precursor for the π-conjugated spheriphanes **63** and higher homologues.

Physical properties: The high stability of the spheriphanes **1**, **4**, **5**, and **6** is reflected in their high melting points (> 360 °C) and their mass spectra (EI), which consist exclusively of their M^+ and M^{2+} peaks without any fragmentation. The ^{1}H NMR and ^{13}C NMR spectra of the spheriphanes with C_{3v} symmetry are simple, confirming the symmetrical structures of the products. For example, the ^{1}H spectrum of $C_{36}H_{36}$ shows only two signals, corresponding to the aromatic and benzylic protons, respectively, while the ^{13}C spectrum consists of three peaks arising from the three carbon environments present in the molecule. The molecular skeleton of all spheriphanes is flexible enough to allow rapid twisting of the ethane linkages connecting the aromatic rings. In the case of $C_{36}H_{36}$ low-temperature ^{1}H NMR studies show that this twisting motion is rapid in solution, even below −90 °C; this results in the respective methylene hydrogens appearing equivalent.

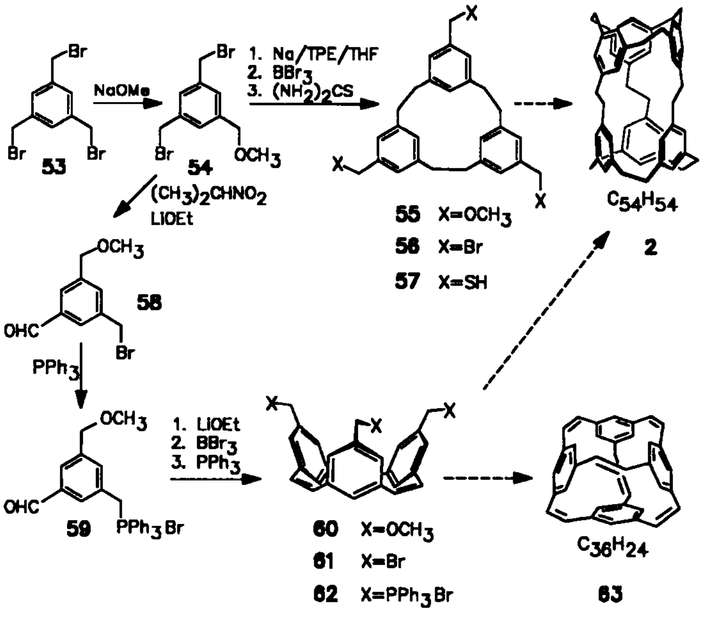
In the solid state, however, the twisted ethane linkages lead to a helical arrangement of the benzene rings; this is confirmed by the X-ray structure analysis (see Fig. 4).[8] In the single crystal analyzed, $C_{36}H_{36}$ adopts a *p*-helical arrangement exclusively. The central cavity of **1** has a diameter of 568 pm. Taking into account the van der Waals radius of the benzene rings, $C_{36}H_{36}$, with a diameter of 228 pm, offers enough room for the encapsulation of small metal ions, but is smaller than the cavity of C_{60} (362 pm). The form of the cage is almost spherical and the centroids of the four benzene rings form a slightly compressed tetrahedron. The compression (4 pm) results from a $CHCl_3$ molecule bound outside the cavity to one of the aromatic rings by an attractive interaction between the hydrogen of the solvent molecule and the π system of the benzene ring.[17]

The molecular skeleton of $C_{60}H_{60}$ is less rigid. Flexibility is a potentially important feature if the cage molecules are to be used as hosts for encapsulating suitable guests. The determination of the geometries and dimensions of $C_{60}H_{60}$ and $C_{54}H_{48}$ by molecular modeling calculations indicates that **4** provides a tailored niche for molecules like adamantylamine or *t*-butylamine and **5** for acetonitrile.[18]

The X-ray structure of $C_{60}H_{60}$ shows the *p*-phenylene rings to be turned to the inside of the molecule, decreasing the cavity size. One of the *p*-phenylene rings is turned perpendicularly to



Scheme 3. Synthesis of 4.



Scheme 4. Attempted synthesis of 2.

the surface, thus providing a large opening for molecules to enter the cavity (see Fig. 5). However, this constricted arrangement of the *p*-phenylene rings in the crystals might be caused by packing effects and might be unfavorable in solution, because it forces the benzene rings of the upper rim into a non-tilted conformation and the hydrogens of the corresponding ethane linkages into an eclipsed conformation.

Complexation of metal ions: We expected the spheriphanes, which are three-dimensionally clamped analogues of π-prismands, to form metal-ion complexes with their benzene rings acting as π donors. Cioslowski et al.[19] used large-scale electronic structure calculations to investigate the guest discrimination in exohedral and endohedral complexes of alkali-metal cations with the $C_{36}H_{36}$ spheriphane (**1**) and revealed qualitative differences among these complexes. Although both endohedral and exohedral isomers are found to be energy minima for Li^+, Na^+, and K^+, the formation of endohedral species proceeds without a barrier only in the first two cases. The endohedral isomers are predicted to be more stable than their exohedral counterparts in the gas phase, but this order of stabilities is expected to be reversed in solvents that form complexes with the metal cations, because the formation of endohedral isomers requires the stripping of all molecules of solvent from the guest cation, whereas retention of some solvent molecules is possible for exohedral species. Though we were unsuccessful in preparing stable complexes of alkali-metal cations in solution, most likely because of the strong solvation energy, $C_{36}H_{36}$ (**1**) formed a stable complex with $AgSO_3CF_3$ that precipitated from THF solutions. The elemental analysis of the colorless light-sensitive material proved a 1:1 (metal:cage) stoichiometry. Though a full characterization of the complex was not possible because of its low solubility, the solid-state NMR spectra indicate that the silver cation is not incorporated in the cage but is externally coordinated to the surface of the hydrocarbon.[20]

Having the spheriphanes $C_{36}H_{36}$ (**1**), $C_{54}H_{48}$ (**5**), $C_{60}H_{60}$ (**4**), and $C_{60}H_{52}$ (**6**) at hand, liquid–liquid extraction experiments were chosen as a practical method with which to obtain precise quantitive data about the ability of the spheriphanes to form complexes with silver metal cations and to compare them with the well-known π-prismand **51** and π-spherand **52**, as well as to the reference compounds **53** and **54** (Fig. 6). Aqueous metal nitrate/picric acid solutions were extracted with a $CHCl_3$ phase containing the hydrocarbon ligand in various concentrations (Fig. 7). Subsequent determination of the metal-ion concentration by the radio tracer method[21] in both layers allowed a comparison of the extraction efficiency and conclusions about the stoichiometry of the complexes. As expected, the reference compounds, having too small a cavity, did not extract silver ions. $C_{36}H_{36}$ (**1**) and the tetraene **52** form complexes of 1:1 stoichiometry but show a relatively poor extraction ability. Larger spheriphanes $C_{54}H_{48}$ (**5**) and $C_{60}H_{52}$ (**6**) extracted silver cations in comparable amounts. Apparently, complex formation is unfavorable owing to the rigid biphenyl units in the molecule. In contrast to this, compounds having only flexible ethane bridges had pronounced favorable properties for the extraction of silver ions. Thus, the [2.2.2]paracyclophane **51** formed a 1:1 complex and allowed efficient extraction over a wide range of concentrations because of its good solubility (at a

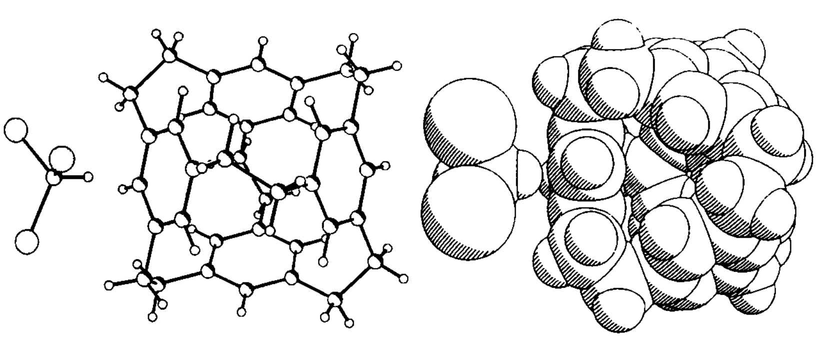


Fig. 4. X-ray structure of $C_{36}H_{36}$. Left: View along the C_{3v} axis; right: a $CHCl_3$ molecule is bound to one of the aromatic rings by a CH–π attraction.

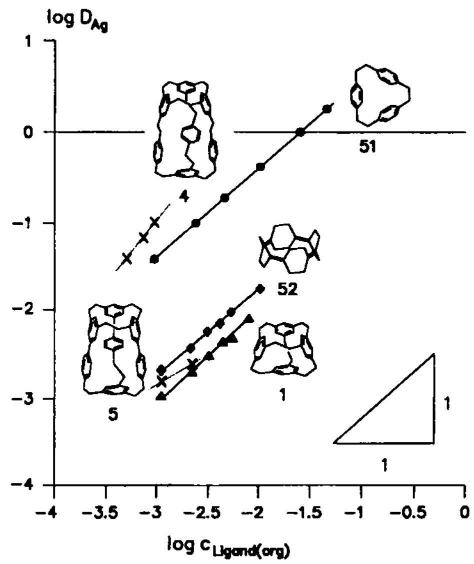


Fig. 7. Extraction of Ag^+ with selected hydrocarbons as a function of ligand concentration ($[AgNO_3] = 2.7 \times 10^{-4}$ M, [picric acid] $= 1 \times 10^{-2}$ M; organic phase: [ligand] $= 5 \times 10^{-4}$–5×10^{-2} M in $CHCl_3$). $D_{Ag} = c_{Ag(org)}/c_{Ag(w)}$.

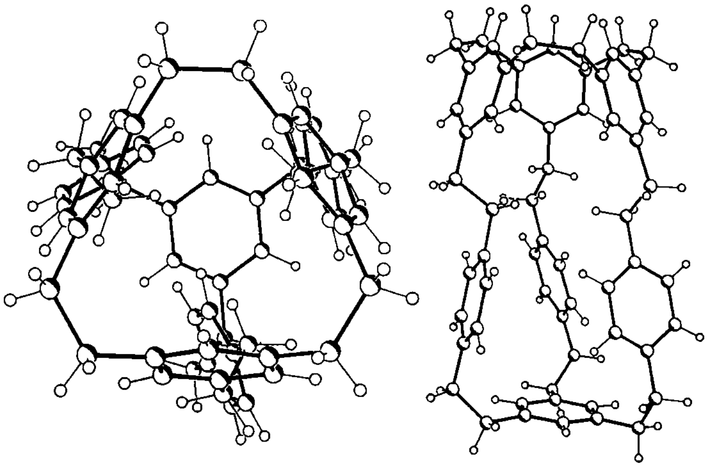


Fig. 5. X-ray structure of $C_{60}H_{60}$.

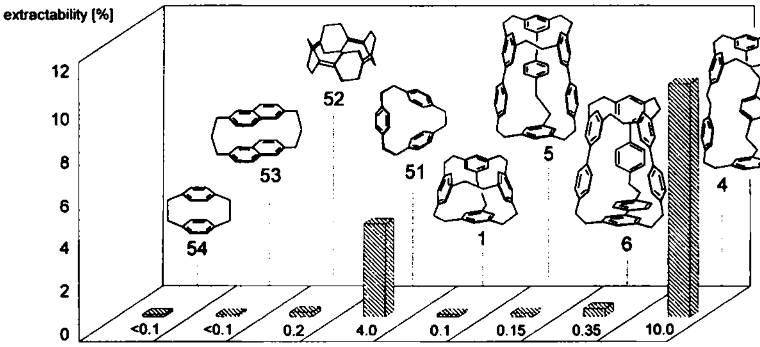


Fig. 6. Extractability of Ag^+ with selected hydrocarbons ($c_{ligand} = 1 \times 10^{-3}$ M in $CHCl_3$, $[AgNO_3] = 2.7 \times 10^{-4}$ M, [picric acid] $= 1 \times 10^{-2}$ M).

ligand concentration of 5×10^{-2} M, 67% of silver was extracted). However, the most efficient silver-ion extraction was accomplished by $C_{60}H_{60}$ (**4**), which extracted more than twice as much Ag^+ compared with **51** at low ligand concentrations (up to 1×10^{-3} M). At higher concentrations the complex precipitated, and thus further investigations are difficult. Because of the limited data readings, a definite determination of the complex composition, or of that for $C_{54}H_{48}$ (**5**), was not possible.[22]

To determine the selectivity of the hydrocarbons **1**, **4**, and **51**, which were obtained in sufficient amounts, we performed extraction experiments for selected alkali-, alkaline-earth- and transition-metal ions (Fig. 8). Compound **51** extracted neither alkali-metal ions nor Tl^+ and Hg^{2+}, which have an ion size comparable to Ag^+, in detectable amounts. With $C_{36}H_{36}$ (**1**) an extractability of 0.1% for Tl^+ (for Na^+, Ca^{2+}, Zn^{2+}, Hg^{2+} <0.1%) was determined, and with $C_{60}H_{60}$ (**4**) the extractability of Na^+, Ca^{2+}, and Zn^{2+} was likewise below 0.1%. For mercury and thallium the values increase slightly to 0.5% and 0.8%, respectively. Thus, $C_{60}H_{60}$ (**4**) showed the highest extractability for Ag^+ paired with a remarkable selectivity.

Ion-selective membranes: Another interesting possible method for the examination of the host/guest properties of the concave hydrocarbons is their incorporation (utilization as ionophores) in ion-selective electrodes.[32] In the course of these studies a number of cyclophanes was tested: the $[2_n]$paracyclophanes **64**, **51**, **65** (with $n = 2,3,4$), [2.2.2](1,4)naphthalenocyclophane (**66**) and $C_{60}H_{60}$ (**4**). The membranes used in these experiments contained ≈30–33 w/w% poly(vinylchloride) (PVC), 67–70% plasticizer (*ortho*-nitrophenyl-*n*-octylether (*o*-NPOE)), ≈0.5% *p*-tetrakis(chlorophenyl)borate potassium salt (KTPB) as an additive and 1–1.5% of the ligand. The potential was measured with an Ag/AgCl system as reference electrode.

The most simple ligand tested, [2.2]paracyclophane (**64**), did not have a particularly high selectivity for Ag^+. The sensitivity towards Tl^+ and H^+ was only slightly lower and the values of other cations did not indicate any special selectivities. In contrast, the PVC/[2.2.2]paracyclophane (**51**) membrane showed a remarkable selectivity towards silver against alkali-metal, alkaline-earth-metal, and thallium ions. On the other hand, it was also sensitive towards Fe^{3+}, Pb^{2+}, Cr^{3+}, Al^{3+}, and Cu^{2+} (Fig. 10). The calibration plot for Ag^+ has a slope of 56.8 mV decade^{-1} and a detection limit of 10^{-6} mol L^{-1}. The electrode parameters of the PVC/[2.2.2.2]paracyclophane (**65**) membrane were substantially worse. The sensitivities for Ag^+ and Tl^+ were much lower than in the case of **51** and no special selectivities were observed. The detection limit was 5×10^{-4} mol L^{-1} for Tl^+ and 10^{-5} mol L^{-1} for Ag^+.

The naphthalenocyclophane **66**, having a more extended π-electron system than the [2.2.2]paracyclophane (**51**), showed a

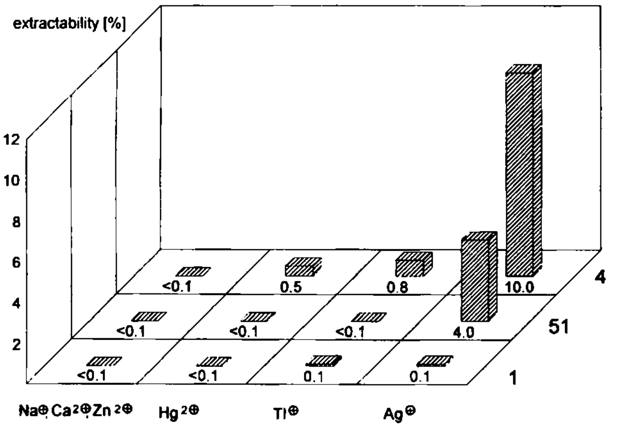


Fig. 8. Extractability of selected cations by the hydrocarbons **1**, **51**, and **4** ($[M(NO_3)_n] = 1 \times 10^{-4}$ M (M = Na^+, Tl^+, Ca^{2+}, Zn^{2+}, Hg^{2+}); $[AgNO_3] = 2.7 \times 10^{-4}$ M, [picric acid] $= 1 \times 10^{-2}$ M; [ligand] $= 1 \times 10^{-3}$ M in $CHCl_3$).

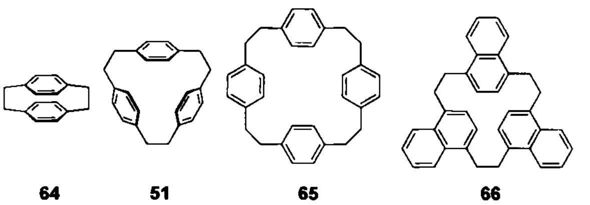


Fig. 9. The macrocyclic hydrocarbons incorporated in ion-selective membranes.

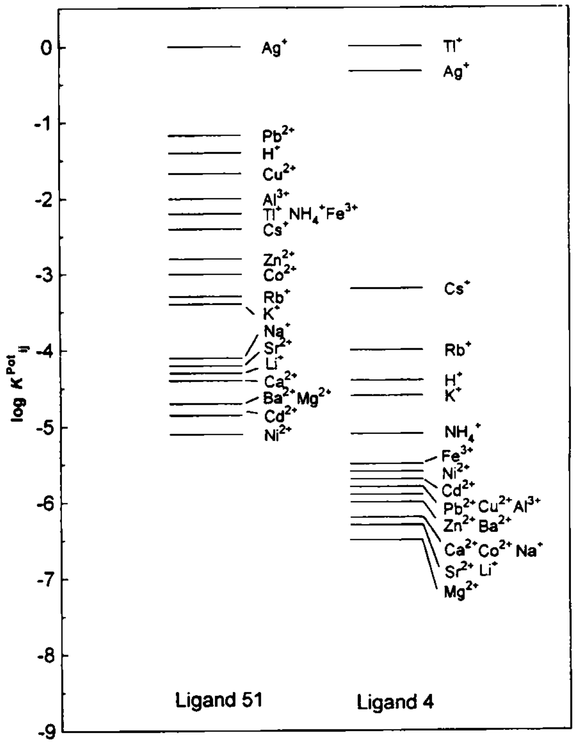


Fig. 10. Selectivity coefficients $\log K_{ij}$ for liquid membrane electrodes based on ligands **4** and **51**. Determination of $\log K_{ij}$ with the mixed solution method [31].

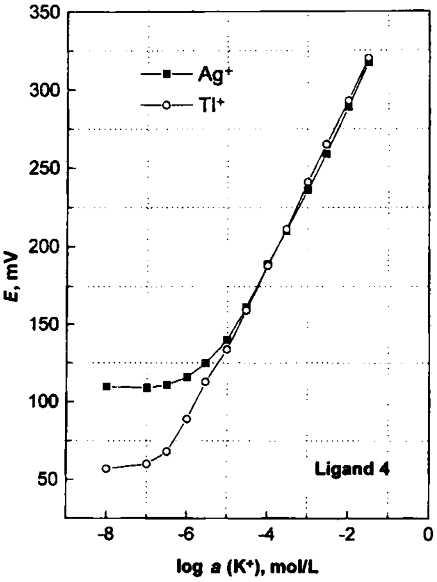


Fig. 11. Calibration plot for liquid membrane based on ligand **4**.

notable sensitivity for alkali-metal ions and ammonia besides the expected sensitivity for silver. The sensitivity for the alkali-metal ions increased with the ion radius. A reasonable explanation is the stronger interaction between the "soft" π-electron system and the "softer" cations.

$C_{60}H_{60}$ (**4**) had the best electrode parameters of the hydrocarbons tested. The electrode displayed excellent selectivity for Ag^+ and Tl^+ and a much lower sensitivity for alkali-metal ions (here again the sensitivity towards the ions is related to the ion radius) whereas it hardly responded to the other heavy metal, alkali and alkaline-earth metal ions tested (Fig. 10). The detection limit of silver was 9×10^{-6} mol L^{-1}; the slope of the calibration curve was 60 mV decade^{-1}. The electrode parameters for Tl^+ were even better, with a detection limit of 2×10^{-7} mol L^{-1} and a slope of 61 mV decade^{-1} (Fig. 11).

Experimental Procedure

General: NMR spectra were recorded on a Bruker AM-250, AM-400 and DRX-500 spectrometer at 250, 400, and 500 MHz for ^{1}H NMR and 62.89, 100.62, and 125.77 MHz for ^{13}C NMR, respectively. Chemical shifts are reported relative to TMS or solvent signals. IR spectra were recorded on a Perkin Elmer model 1600 FT-IR spectrometer. Electron impact mass spectra were recorded on a AIE MS-30 and MS-50, and positive-ion fast atom bombardment mass spectra on a Cratos Concept 1 H, with 4-nitrobenzyl alcohol as matrix in the case of FAB spectra. THF, Et_2O, and toluene were distilled from deep blue sodium/benzophenone solutions. Merck silica gel (63–100 µm mesh) was used for chromatography. 1,3,5-Benzene tricarbaldehyde was prepared by the literature method [9]; **10**, **11**, **12**, and **13** as we reported earlier [23].

Crystal structure analysis of $C_{60}H_{60}$: Crystal data: $C_{60}H_{60}$, $M_r = 781.14$, monoclinic, space group $P2_1/n$ (nonstandard, no. 15), $a = 15.485(2)$, $b = 9.216(1)$, $c = 31.418(5)$ Å, $\alpha = 92.02(1)°$, $V = 4529(1)$ Å^3, $Z = 4$, $\rho_c = 1.146$ g cm^{-3}, $F(000) = 1680$, $T = 296 \pm 1$ K. The data were collected from a colorless crystal of dimensions $0.10 \times 0.15 \times 0.15$ mm. Of 9267 collected reflections, 8369 were unique ($R_{int} = 0.01$), recorded with an Enraf–Nonius CAD4 diffractometer and graphite-monochromated $Cu_{K\alpha}$ radiation [$\lambda(Cu_{K\alpha}) = 1.5418$ Å] and a $\omega/2\theta$ scan mode to $\theta = 73°$ (h: $-18 \rightarrow 18$, k: $0 \rightarrow 11$ and l: $0 \rightarrow 38$); 2056 reflections (only 24.56%) with $I > 2\sigma I$ were used for refinement. Lp correction, but no absorption correction, $\mu(Cu_{K\alpha}) = 0.449$ mm^{-1}. The structure was solved (after several attempts, because of the very weak diffraction by the crystal) by direct methods (SHELXS [24]) and subjected to full-matrix refinement [25]. Because of the very limited number of reflections the anisotropic temperature factors of the phenyl rings were treated as follows: one carbon in each phenyl ring was refined anisotropically and the remaining five temperature factors were set to ride on the one refined. All other non-H atoms were refined anisotropically (X's and U's). In addition, owing to the poor quality of the data 75 geometrical restraints altogether were used to prevent some anomalous bond distances and angles (1.525 Å, $\sigma = 0.01$ Å, for the H_2C-CH_2 bonds, 1.480 Å, $\sigma = 0.01$ Å, for the (arom)C–CH_2, 1.390 Å, $\sigma = 0.01$ Å, for the (arom)C–C(arom), and 120°, $\sigma = 1°$, for the angles in phenyl rings. The hydrogen atoms were calculated to their idealized positions (C–H distance 1.00 Å) with fixed isotropic temperature factors ($U = 0.08$ Å^2) and were included in the final structure factor calculations but were not refined. The F_0/parameter ratio = 6.21; the final R value was 0.119 and $R_w = 0.119$ for 331 parameters: $w = w'[1.0 - (\Delta F/6\sigma F)^2]^2$, where w' = Chebychev polynomial for F_c with five coefficients (0.615, −6.40, −4.55, −4.89, −2.12). $S = 1.17$, convergence, max. shift/error < 0.06. A final difference map displayed no electron density higher than 0.36 e Å^{-3} [26].

4′-Methylbiphenyl-3,5-dicarboxylic acid dimethyl ester (17): A suspension of 5-iodoisophthalic acid dimethyl ester (9.60 g, 30 mmol) and tetrakis(triphenylphosphine)palladium(0) (1035 mg, 3 mol%) in toluene (60 mL) and a Na_2CO_3 solution (2N, 30 mL) were stirred under an inert gas atmosphere. p-Tolueneboronic acid (3.47 g, 11 mmol) dissolved in as little ethanol as possible was added, and the mixture was heated to 95 °C for 8 h. All solvents need to be oxygen-free. After cooling to RT the unreacted boronic acid was oxidized by adding H_2O_2 solution (30%, 1.5 mL) and stirring for 1 h. Et_2O was added to the mixture, the organic layer was separated, washed with saturated NaCl solution and water, and dried with Na_2SO_4. After removal of the solvent in vacuo the residue was recrystallized from methanol yielding colorless needles. Yield: 78%; m.p. 128 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.39 (s, 3H; CH_3), 3.95 (s, 6H; CO_2CH_3), 7.28 (d, ^3J(H,H) = 8 Hz, 2H; Ar–H), 7.55 (d, ^3J(H,H) = 8 Hz, 2H; Ar–H), 8.43 (d, ^4J(H,H) = 1.5 Hz, 2H; Ar–H), 8.62 (t, ^4J(H,H) = 1.5 Hz, 1H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.14 (CH_3), 52.41 (CO_2CH_3), 126.97 (2CH), 129.02 (CH), 129.75 (2CH), 131.08 (CH), 132.02 (2CH), 136.08 (C_q), 138.17 (C_q), 141.81 (C_q), 166.29 (CO); HRMS: calcd 284.1048; found 284.1042.

4′-Bromomethylbiphenyl-3,5-dicarboxylic acid dimethyl ester (18): Compound **17** (5.68 g, 20 mmol) was dissolved in dry CH_2Cl_2 (50 mL) and heated to reflux after adding NBS (1.80 g, 10 mmol) and AIBN while irradiating with a 200 W lamp. Another portion of NBS (1.80 g) and AIBN was added after 1 h. The end of the reaction was indicated by the discoloration of the reddish solution. After cooling to RT the mixture was filtered and the solution was washed with sat. $NaHCO_3$ solution and water and dried with Na_2SO_4. The solvent was removed in vacuo and the residue was recrystallized from CCl_4 (colorless needles). Yield: 73%; m.p. 151 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.96 (s, 6H; CH_3), 4.42 (s, 2H; CH_2Br), 7.48 (d, ^3J(H,H) = 14 Hz, 2H; Ar–H), 7.61 (d, ^3J(H,H) = 14 Hz, 2H; Ar–H), 8.41 (d, ^4J(H,H) = 1.5 Hz, 2H; Ar–H), 8.62 (t, ^4J(H,H) = 1.5 Hz, 1H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 32.95 (CH_2Br), 52.49 (CO_2CH_3), 127.56 (2CH), 129.55 (CH), 129.76 (2CH), 131.22 (CH), 132.15 (2CH), 137.89 (C_q), 139.03 (C_q), 141.07 (C_q), 160.09 (CO); MS: m/z (%) = 362.01 (2.22) [M^+], 283 (100) [$M^+ - Br$].

3,5,4′-Biphenyl tricarbaldehyde (29): 3,5,4′-Tris[bromomethyl]biphenyl (**28**) [27] (8.00 g, 18.5 mmol) and hexamethylene tetraamine (16.00 g) were heated to reflux in half-concentrated acetic acid (120 mL) for 6 h. Half-concentrated HCl (80 mL) was added to the hot solution over a period of 30 min. The solution was cooled to RT and stirred for another 12 h. The resulting precipitate was filtered off, washed with water, and recrystallized from water yielding colorless crystals. Yield: 29%; m.p. 162 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 8.07 (s, 4H; Ar–H), 8.48 (t, ^4J(H,H) = 1.4 Hz, 1H; Ar–H), 8.58 (d, ^4J(H,H) = 1.4 Hz, 2H; Ar–H), 10.1 (s, 1H; CHO), 10.2 (s, 2H; CHO); ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 127.78 (CH), 128.89 (CH), 130.36 (CH), 133.41 (C_q), 135.90 (C_q), 137.53 (C_q), 140.51 (C_q), 143.31 (C_q), 192.76 (CHO), 192.86 (CHO); MS: m/z = 238 [M^+].

General procedure for the interconversion of benzyl bromides to benzyltriphenylphosphonium bromides: A solution of the benzylbromide (10 mmol) and triphenylphosphane (1.1 equiv for each benzylbromide moiety) in $CHCl_3$ (200 mL) was heated to reflux for 3 h. The clear solution was allowed to cool to RT and was added under vigorous stirring to Et_2O (400 mL). The colorless fluffy precipitate was filtered, washed with Et_2O and dried in vacuo.

3,5-Bis(carboxymethyl)biphenyl-4′-methylenetriphenylphosphonium bromide (19): Yield: 99%; ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 3.9 (s, 6H; CO_2CH_3), 5.31 (d, ^2J(H,P) = 16 Hz, 2H; CH_2P), 7.03 (dd, ^3J(H,H) = 13 Hz, ^4J(H,P) = 2 Hz, 2H; Ar–H), 7.62–7.9 (m, 17H; Ar–H), 8.38 (d, ^4J(H,H) = 1.2 Hz, 2H; Ar–H), 8.42 (t, ^4J(H,H) = 1.2 Hz, 1H; Ar–H).

4,4′,4″-[1,3,5-Benzenetriyltris(1,2-ethanediyl)]tris(benzyltriphenylphosphonium bromide) (42): Yield: 99%; m.p. 161–162 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.55 (m, 12H; CH_2), 4.97 (d, ^2J(P,H) = 14 Hz, 6H; CH_2PR_3), 6.52 (s, 3H; Ar–H), 6.65 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 6.78 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 7.4–7.7 (m, 45H; Ar–H); MS (+FAB/m-NBA): m/z = 1375 [$M^+ - Br$], 1295 [$M^+ - Br, -HBr$], 1213 [$M^+ - Br, -2HBr$].

3-Methoxymethyl-5-(triphenylphosphoniumbromide)methylbenzaldehyde (59): Yield: 90%; m.p. 243 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.20 (s, 3H; OCH_3), 4.20 (s, 2H; CH_2O), 5.20 (d, ^2J(P,H) = 15 Hz, 2H; CH_2P), 7.40 (s, 1H; Ar–H), 7.50 (s, 1H; Ar–H), 7.55–7.70 (m, 15H; PPh_3), 7.80 (s, 1H; Ar–H), 9.70 (s, 1H; CHO); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 30.5 (CH_2P), 58.7 (CH_3O), 73.5 (CH_2), 116.6 (CH), 118.6 (CH), 127.3 (CH), 128.9 (CH), 130.1 (CH), 132.6 (CH), 134.4 (C_q), 135.1 (C_q), 136.6 (C_q), 139.9 (C_q), 191.8 (CH); MS (+FAB/m-NBA): m/z (%) = 425 (100) [$M^+ - HBr$], 394 (6) [$M^+ - HBr, -OCH_3$], 165 (5) [$M^+ - PPh_3Br$]; IR (KBr): $\tilde{\nu}$ = 2850–2870 (m), 2990 (s), 1696 (s), 1434 (s), 1107 (vs) cm^{-1}; $C_{28}H_{26}BrO_2P$ (505.39): calcd C 66.54, H 5.19, found C 66.64, H 5.21.

All-(Z) 5,13,21-Tris{(triphenylphosphonium)methyl[2.2.2]metacyclophane-1,9,17-triene}benzene bromide (62): Yield: 57%; m.p. > 320 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.20 (d, ^2J(P,H) = 15 Hz, 6H; CH_2P), 6.10 (s, 6H; CH=CH), 6.35 (s, 3H; Ar–H), 6.55 (d, ^3J(H,H) = 1.25 Hz, 6H; Ar–H), 7.3–7.8 (m, 45H; PPh_3); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 30.5 (CH_2P), 128.4 (CH), 128.7 (CH), 129.3 (CH), 129.5 (CH), 130.4 (CH), 132.1 (CH), 134.3 (C_q), 135.2 (C_q), 137.6 (C_q); MS (MALDI/9-nitroanthracene): m/z (%) = 1292 (10) [$M^+ - Br$], 1212 (100) [$M^+ - 2Br$], 1132 (64) [$M^+ - 3Br$].

General procedure for the double-bond hydrogenation: To a solution of the tris(stilbene) (10 mmol) in toluene (150 mL), Pd (10%) on charcoal (1.00 g) was added and the reaction mixture was hydrogenated at 3 atm H_2 for 12 h at 50 °C with a Parr hydrogenation apparatus. The hot reaction mixture was filtered through Celite and the toluene was evaporated to yield the colorless product.

1,3,5-Tris[4-(carboxymethyl)phenyl-1,2-ethanediyl]benzene (39): Yield: quant.; m.p. 68 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.85 (m, 12H; CH_2), 3.87 (s, 9H; OCH_3), 6.73 (s, 3H; Ar–H), 7.17 (d, 6H; Ar–H), 7.94 (d, 6H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 37.31 (3CH_2), 37.92 (3CH_2), 51.95 (3CH_3), 126.41 (3CH), 127.84 (3C_q), 128.51 (6CH), 129.60 (6CH), 141.26 (3C_q), 142.17 (3C_q), 167.07 (3CO); HRMS: calcd 564.2510, found 564.2521; IR (KBr): $\tilde{\nu}$ = 486 (m), 705 (s), 765 (s), 802 (w), 856 (m), 988 (w), 1019 (m), 1110 (vs), 1177 (s), 1278 (vs), 1412 (m), 1508 (w), 1573 (w), 1607 (s), 1713 (vs), 2855 (m), 2932 (m) cm^{-1}.

1,3,5-Tris{4-{[3,5-bis(carboxymethyl)phenyl]-1,2-ethanediyl}phenyl-1,2-ethanediyl}-benzene (46): Yield: 98%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.85 (s, 12H; CH_2), 2.95 (m, 12H; CH_2), 3.95 (s, 18H; OCH_3), 6.85 (d, ^4J(H,H) = 3.1 Hz, 3H; Ar–H), 7.17 (s, 12H; Ar–H), 8.05 (d, ^4J(H,H) = 1.5 Hz, 6H; Ar–H), 8.52 (t, ^4J(H,H) = 1.5 Hz, 3H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 37.18 (3CH_2), 37.59 (3CH_2), 37.72 (3CH_2), 38.03 (3CH_2), 52.31 (6CH_3), 126.29 (3CH), 128.34 (6CH), 128.57 (6CH), 128.98 (3CH), 130.58 (6CH), 133.89 (6C_q), 138.42 (3C_q), 139.82 (3C_q), 141.87 (3C_q), 142.73 (3C_q), 166.47 (6CO); MS (+FAB/m-NBA + Na^+): m/z = 1073 [$(M+Na)^+$].

4,4′,4″-[1,3,5-benzenetriyltris(1,2-ethanediyl)]-tris(3′,5′-biphenyldicarboxylic acid dimethyl ester) (21): Yield: 99%; m.p. 176–178 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.92 ("s", 12H; CH_2), 3.95 (s, 18H; CO_2CH_3), 6.68 (s, 3H; Ar–H), 7.60 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 7.26 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 8.43 (d; ^4J(H,H) = 1.5 Hz, 6H; Ar–H), 8.62 (t, ^4J(H,H) = 1.5 Hz, 3H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 37.38 (CH_2), 37.90 (CH_2), 52.51 (CO_2CH_3), 126.53 (3CH), 127.13 (CH), 129.16 (3CH), 129.92 (C_q), 132.15 (C_q), 136.69 (C_q), 141.73 (3C_q), 141.82 (C_q) 142.1 (C_q), 166.3 (CO_2CH_3) (+FAB/m-NBA): m/z = 967.4 [M^+].

3,5,4′-Tris[2-(3′,5′-bis(carboxymethyl)biphenyl-4-yl)ethyl]biphenyl (31): Yield: 99%; m.p. 192 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.0 (s, 12H; CH_2), 3.96 (s, 12H; OCH_3), 3.97 (s, 6H; OCH_3), 6.99 (s, 3H; Ar–H), 7.17 (d, ^3J(H,H) = 7.14 Hz, 2H; Ar–H), 7.23–7.33 (m, 4H; Ar–H), 7.29 (d, ^3J(H,H) = 8.17 Hz, 4H; Ar–H), 7.47 (d, ^3J(H,H) = 7.14 Hz, 2H; Ar–H), 7.59 (d, ^3J(H,H) = 8.15 Hz, 4H; Ar–H), 8.46 ("s", 6H; Ar–H), 8.63 ("s", 3H; Ar–H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 37.401 (CH_2), 37.460 (CH_2), 37.671 (2CH_2), 37.912 (2CH_2), 52.421 (OCH_3), 125.085 (CH), 127.084 (CH), 127.106 (CH), 127.580 (CH), 128.216 (CH), 129.023 (CH), 129.088 (CH), 129.200 (CH), 129.290 (CH), 129.424 (CH), 131.087 (C_q), 131.999 (CH), 132.064 (CH), 136.611 (C_q), 136.653 (C_q), 139.032 (C_q), 140.555 (C_q), 141.084 (C_q), 141.721 (C_q), 141.743 (C_q), 141.958 (C_q), 142.003 (C_q), 166.229 (CO), 166.256 (CO); MS (+FAB/m-NBA): m/z = 1043.3 [M^+].

General procedure for the reduction of methyl benzoates to (acetoxymethyl)arenes: To a cooled suspension of LAH (2 equiv for each methyl benzoate moiety) in anhydrous THF (250 mL) a solution of methyl benzoate (20 mmol) in anhydrous THF (100 mL) was added dropwise under an inert gas atmosphere. The reaction mixture was stirred for 2 h at RT and then heated for 2 h under reflux. Under external cooling acetic anhydride (10 mL) was added dropwise, and after complete addition the reaction mixture was heated under reflux for 4 h. The solvent was evaporated in vacuo and the residue was treated with dilute HCl. The clear solution was extracted twice with $CHCl_3$ (2 × 100 mL), then the organic layer was washed with $NaHCO_3$ solution and water and dried ($MgSO_4$). The $CHCl_3$ was removed in vacuo to yield an oily product. TLC and NMR showed that complete conversion had occurred, and the product was used for the following reaction without any further purification.

1,3,5-Tris[4-(acetoxymethyl)phenyl-1,2-ethanediyl]benzene (40): Yield: 95%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.08 (s, 9H; CH_3), 2.87 (s, 12H; CH_2), 5.09 (s, 6H; CH_2O), 6.84 (s, 3H; Ar–H), 7.18 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 7.30 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.01 (3CH_3), 37.74 (3CH_2), 37.84 (3CH_2), 66.23 (3CH_2), 126.36 (3CH), 128.46 (6CH), 128.71 (6CH), 133.51 (3C_q), 141.65 (3C_q), 142.09 (3C_q), 170.95 (3C_q).

1,3,5-Tris{4-{[3,5-bis(acetoxymethyl)phenyl]-1,2-ethanediyl}phenyl-1,2-ethanediyl}-benzene (47): Yield: 95%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.15 (s, 18H; CH_3), 2.85–2.90 (m, 12H; CH_2), 2.96 (s, 12H; CH_2), 5.13 (s, 12H; OCH_2), 6.90 (m, 3H;

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Ar–H), 7.13–7.30 (m, 21 H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 20.83 (3CH$_3$), 37.18 (3CH$_2$), 37.55 (3CH$_2$), 37.89 (3CH$_2$), 37.97 (3CH$_2$), 65.87 (6CH$_2$O), 125.57 (3CH), 126.15 (3CH), 128.10 (6CH), 128.19 (6CH), 128.34 (6CH), 128.82 (3CH), 136.20 (6C$_q$), 138.71 (3C$_q$), 139.48 (3C$_q$), 141.87 (3C$_q$), 142.56 (3C$_q$), 170.60 (6CO); MS (+ FAB/*m*-NBA): *m/z* = 1134.5 [M^+].

4,4′,4″-[1,3,5-benzenetriyltris(1,2-ethanediyl)]tris(3′,5′-bis(acetoxymethyl)biphenyl) (22): Yield: 86%; ^{1}H NMR (80 MHz, CDCl$_3$): δ = 2.05 (s, 18H; CH$_3$), 2.95 (s, 12H; CH$_2$), 5.1 (s, 12H; CH$_2$O), 6.8 (s, 3H; Ar–H), 7.2–7.8 (m, 21 H; Ar–H); MS (+ FAB/*m*-NBA): *m/z* = 1050.5 [M^+].

3,5,4′-Tris[2-(3′,5′-bis(acetoxymethyl)biphenyl-4-yl)ethyl]biphenyl (32): Yield: 92%; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.12 (s, 12H; 4CH$_3$), 2.13 (s, 6H; 4CH$_3$), 2.99 ("s", 12H; CH$_2$), 5.16 ("s"; OCH$_2$), 7.01 ("s", 2H; Ar–H), 7.2–7.38 (m, 12H; Ar–H), 7.41–7.62 (m, 14H; Ar–H); MS (+ FAB/*m*-NBA): *m/z* = 1126.5 [M^+].

General procedure for the interconversion of (acetoxymethyl)arenes to (bromomethyl)arenes: A solution of the (acetoxymethyl)arene (5 mmol) in HBr/AcOH (33%, 50 mL) was stirred for 2 h at RT and 2 h at 50 °C. The reaction mixture was poured into ice water (150 mL) and the resulting precipitate taken up by CH$_2$Cl$_2$. The organic layer was subsequently washed with Na$_2$CO$_3$ solution and water and dried (MgSO$_4$), and the solvent was evaporated. The crude product was taken up by cyclohexane (100 mL), and after addition of silica gel (2 g) heated to reflux for 5 min. The silica gel was filtered off and upon cooling the product crystallized as fine colorless needles.

1,3,5-Tris[4-(bromomethyl)phenyl-1,2-ethanediyl]benzene (41): Yield: 88%; m.p. 72–73 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.85 ("s", 12H; CH$_2$), 4.5 (s, 6H; CH$_2$Br), 6.6 (s, 3H; Ar–H), 7.15 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 7.32 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 33.73 (3CH$_2$), 37.67 (6CH$_2$), 126.37 (3CH), 128.94 (6CH), 129 (6CH), 135.51 (3C$_q$), 141.49 (3C$_q$), 142.23 (3C$_q$); MS (EI, 180 °C): *m/z* (%) = 666 (10) [M^+], 587 (5) [M^+ – Br], 508 (27) [M^+ – 2Br], 429 (12) [M^+ – 3Br]; HRMS: calcd 666.0132, found 666.0106.

1,3,5-Tris{4-{[3,5-bis(bromomethyl)phenyl]-1,2-ethanediyl}phenyl-1,2-ethanediyl}-benzene (48): Yield: 93%; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.95 (s, 12H; CH$_2$), 2.98 (s, 12H; CH$_2$), 4.5 (s, 12H; CH$_2$Br), 6.96 (s, 3H; Ar–H), 7.20 ("s", 18H; Ar–H), 7.32 (s, 3H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 33.05 (6CH$_2$), 37.14 (3CH$_2$), 37.63 (3CH$_2$), 37.69 (3CH$_2$), 38.04 (3CH$_2$), 126.31 (3CH), 127.22 (3CH), 128.35 (6CH), 128.55 (6CH), 129.29 (6CH), 138.28 (6C$_q$), 138.70 (3C$_q$), 139.66 (3C), 141.76 (3C$_q$), 143.11 (3C$_q$).

4,4′,4″-[1,3,5-benzenetriyltris(1,2-ethanediyl)]tris[3,5-bis(bromomethyl)biphenyl] (23): Yield: 73%; m.p. 164 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.92 (s, 12H; CH$_2$), 4.49 (s, 12H; CH$_2$Br), 6.87 (s, 3H; Ar–H), 7.24 (d, ^3J(H,H) = 7.8 Hz, 6H; Ar–H), 7.51 (d, ^3J(H,H) = 7.8 Hz; 6H; Ar–H), 7.39 (t, ^4J(H,H) = 1 Hz, 3H; Ar–H), 7.52 ("s", 6H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 33.98 (CH$_2$Br), 37.79 (3CH$_2$), 37.9 (3CH$_2$), 126.57 (3CH), 127.09 (6CH), 127.78 (6CH), 128.19 (3CH), 137.53 (6CH), 138.9 (3C$_q$), 141.65 (6C$_q$), 141.74 (3C$_q$), 142.37 (3C$_q$); MS (+ FAB/*m*-NBA): *m/z* = 1175.7 [M^+], 1095.8 [M^+ – Br], 1017.9 [M^+ – 2Br], 938.0 [M^+ – 3Br], 858.1 [M^+ – 4Br], 775.2 [M^+ – 5Br], 695.3 [M^+ – 6Br].

3,5,4′-Tris{2-[3′,5′-bis(bromomethyl)biphenyl-4-yl]ethyl}biphenyl (33): Yield: 74%; m.p. 178 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.98 (s, 12H; CH$_2$), 4.51 (s, 8H; CH$_2$Br), 4.52 (s, 4H; CH$_2$Br), 6.95 ("s", 1H; Ar–H), 7.2–7.29 (m, 14H; Ar–H), 7.38 (s, 2H; Ar–H), 7.40 (d, ^3J(H,H) = 8.42 Hz, 2H; Ar–H), 7.48 ("s", 3H; Ar–H), 7.52 ("s", 6H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 32.984 (CH$_2$Br), 37.535 (CH$_2$), 37.634 (CH$_2$), 37.812 (2CH$_2$), 38.064 (2CH$_2$), 125.201 (CH), 127.070 (CH), 127.183 (CH), 127.862 (CH), 128.146 (CH), 128.233 (CH), 128.948 (CH), 129.154 (CH), 129.205 (CH), 129.273 (CH), 129.511 (CH), 129.699 (CH), 137.058 (C$_q$), 137.655 (C$_q$), 138.955 (C$_q$), 139.011 (C$_q$), 140.750 (C$_q$), 141.070 (C$_q$), 141.686 (C$_q$), 142.037 (C$_q$), 142.494 (C$_q$); MS (+ FAB/*m*-NBA): *m/z* = 1251.9 [M^+], 1174.0 [M^+ – Br], 1094.1 [M^+ – 2Br], 1014.2 [M^+ – 3Br].

General procedure for the synthesis of oligo(stilbenes) by Wittig reaction (Method A): Lithium (0.62 g) was dissolved in 140 mL of dry methanol under an inert gas atmosphere. After the solution had been cooled to RT the phosphonium bromide (15 mmol) was added. A solution of the trialdehyde (5 mmol) in dry THF was added dropwise to the bright yellow solution. After complete addition stirring was continued for 12 h. The precipitate was filtered under an inert gas atmosphere, washed with methanol and recrystallized from benzene.

4,4′,4″-[1,3,5-benzenetriyltris(1,2-ethenediyl)]tris(3′,5′-biphenyldicarboxylic acid dimethylester) (20): Yield: 57%; ^{1}H NMR (60 MHz CDCl$_3$): δ = 4.05 (s, 18H; OCH$_3$), 6.4–7.8 (m, 21H; CH, Ar–H), 8.4 ("s", 6H, Ar–H), 8.55 ("s", 3H, Ar–H); MS (+ FAB/*m*-NBA): *m/z* = 960.3 [M^+].

3,5,4′-Tris{2-[3′,5′-bis(carboxymethyl)biphenyl-4-yl]-ethenyl}biphenyl (30): Yield: 64%; ^{1}H NMR: (250 MHz, CDCl$_3$): δ = 3.98 (s, 18H, OCH$_3$), 6.6–6.8 (m, 6H; CH), 7.1–7.7 (m, 16H; Ar–H), 8.3–8.7 (m, 12H; Ar–H); MS (+ FAB/*m*-NBA): *m/z* = 1036.3 [M^+].

General procedure for the synthesis of oligo(stilbenes) by Wittig reaction (Method B): 1,3,5-Benzenetricarbaldehyde (9) (50 mmol) and the phosphonium bromide (150 mmol) were suspended in DMF (250 mL) under an inert gas atmosphere. Sodium methoxide solution (2.5 M) was added dropwise at 50 °C until the orange color of the solution faded. Stirring was continued for a further 2 h and the reaction mixture was adjusted to pH = 7 by addition of dilute HCl. The solvent was removed in vacuo, the residue taken up by CHCl$_3$, washed with water, and dried (Na$_2$SO$_4$). After evaporating the solvent, the crude product was purified as described below.

1,3,5-Tris[4-(carboxymethyl)phenyl-1,2-ethenediyl]benzene (38): The crude product was taken up by toluene (100 mL), a trace of iodine was added, and the mixture of *E*/*Z* isomers was isomerized to the all-*E* product by irradiation for 5 h by means of a 200 W lamp. Upon cooling the all-*E* product crystallized as colorless needles. Yield: 28%; m.p. 232 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.93 (s, 9H; OCH$_3$), 7.20 (d, ^3J(H,H) = 17.5 Hz, 3H; *E*-alkene CH), 7.27 (d, 17.5 Hz, 3H; *E*-alkene CH), 7.60 (d, 8 Hz, 6H; Ar–H), 7.62 (s, 3H; Ar–H), 8.05 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 52.22 (3CH$_3$), 124.95 (3CH), 126.52 (6CH), 128.66 (3CH), 129.29 (3C$_q$), 130.19 (6CH), 130.60 (3CH), 137.64 (3C$_q$), 141.57 (3C$_q$), 166.91 (3CO); MS (EI, 230 °C): *m/z* (%) = 558 (55) [M^+]; HRMS: calcd 558.2024, found 558.2033.

1,3,5-Tris{4-{[3,5-bis(carboxymethyl)phenyl]-1,2-ethenediyl}phenyl-1,2-ethanediyl}-benzene (45): The residue was taken up by hot ethanol. Upon cooling in the freezer (– 20 °C), the product became a glutinous oil. The supernatant solvent was decanted and the product, which was a mixture of isomers, was obtained as a colorless gluey solid (78%) [28].

3,5-Bis(carboxymethyl)benzylhexamethylenetetraammonium bromide (43): 5-(Bromomethyl)isophthalic acid methyl ester (5.00 g, 17.4 mmol) and hexamethylene tetramine (5.40 g, 34.8 mmol) were heated under reflux for 3 h in CHCl$_3$ (100 mL). The reaction mixture was allowed to cool to RT, the salt (6.6 g, 89% yield) was filtered, washed with CHCl$_3$, and dried in vacuo. M.p. 198 °C; ^{1}H NMR (250 MHz, D$_2$O): δ = 2.51 (s, 6H; NCH$_2$N), 2.83 (s, 2H; Ar–CH$_2$), 3.05 (d, ^3J(H,H) = 12.7 Hz, 3H; N$^+$CH$_2$N), 3.24 (d, ^3J(H,H) = 12.7 Hz, 3H; N$^+$CH$_2$N), 3.70 (s, 6H; OCH$_3$) 6.87 (d, J(H,H) = 1.5 Hz, 2H; Ar–H), 7.28 (t, J(H,H) = 1.5 Hz, 1H; Ar–H); MS (+ FAB/*m*-NBA): *m/z* = 773 [$(C_{17}H_{23}N_4O_4Br) + (C_{17}H_{23}N_4O_4)]^+$.

3,5-Bis(carboxymethyl)benzaldehyde (44): 3,5-Bis(carboxymethyl)benzylhexamethylenetetraammonium bromide (6.65 g, 15.6 mmol) was heated under reflux for 3 h in glacial AcOH (90 mL). The same volume of water was added to the hot reaction mixture. The product (1.45 g, 42% yield) crystallized as colorless needles upon cooling. M.p. 84 °C; ^{1}H NMR (80 MHz, CDCl$_3$): δ = 3.95 (s, 6H; OCH$_3$), 8.65 (s, 2H; Ar–H), 8.85 (s, 1H; Ar–H), 10.1 (s, 1H; CHO); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 52.55 (2CH$_3$), 131.45 (CH), 133.97 (2CH), 135.50 (2C$_q$), 136.67 (C$_q$), 164.85 (2CO), 190.24 (CHO); MS *m/z* (%) = 222 (45) [M^+], 191 (100) [M^+ – CH$_3$O].

General procedure for the sulfide cyclization reactions: A refluxing solution of Cs$_2$CO$_3$ (4.9 g, 30 mmol) in a mixture of benzene/ethanol (1:1, 900 mL) in a NORMAG two-component dilution principle apparatus (2-C-DP) under inert gas atmosphere was treated simultaneously over a period of 16 h with a solution of the hexakis(bromomethyl) compound (1 mmol) in benzene (250 mL) and a solution of Na$_2$S·9H$_2$O (3 mmol) in a mixture of ethanol/water (10:1, 250 mL). The reaction mixture was heated for a further 5 h and the solvent was evaporated. The residue was taken up by CHCl$_3$ (50 mL), washed with water, and dried (MgSO$_4$). The colorless product was isolated by column chromatography (silica gel; PE (40/60)/CH$_2$Cl$_2$ (1:1)).

5,13,32-Trithiaheptacyclo[15.13.3.2^{9,24}.1^{3,29}.1^{7,11}.1^{15,19}.1^{22,26}]nonatriaconta-1,3-(36),7(37),8,10,15(38),16,18,22(39),23,35,29-dodecaene (14a): Yield: 18%; R_f = 0.48 (SiO$_2$, PE (40/60)/CHCl$_3$ 1:1); m.p. > 340 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.05 (s, 12H; CH$_2$), 3.25 (d, ^3J(H,H) = 14 Hz, 6H; CH$_2$S), 3.55 (d, ^3J(H,H) = 14 Hz, 6H; CH$_2$S), 6.52 (s, 3H; Ar–H), 6.70 (s, 3H; Ar–H), 6.80 (s, 6H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 31.70 (3CH$_2$), 31.96 (3CH$_2$), 35.97 (6CH$_2$), 125.62 (3C$_q$), 127.04 (3CH), 127.33 (3C$_q$), 136.77 (6CH$_2$), 139.27 (3CH), 140.48 (6C); MS: *m/z* (%) = 564 (100) [M^+], 531 (26) [M^+ – SH], 500 (58) [M^+ – 2S], 465 (36) [M^+ – 3SH]; IR (KBr): $\tilde{\nu}$ = 680 (w), 705 (w), 725 (m), 755 (m), 830 (m), 900 (m), 920 (w), 1155 (w), 1200 (w), 1240 (w), 1470 (vs), 1615 (vs), 1750 (w), 2890 (s), 3060 (vs) cm^{-1}.

18,26,52-Trithiadecacyclo[20.20.8.3.^{14,30}2.^{6,9}2.^{35,38}2.^{45,48}1.^{3,41}1.^{12,16}1.^{20,24}1.^{28,32}]trihexaconta-1,3(60),6,8,12,14,16(61),20,22,24(62),28,30,32(63),35,37,41,45,47,54,56,58-heneicosaene (49): Yield: 14%; R_f = 0.39 (SiO$_2$, PE (40/60)/CH$_2$Cl$_2$ 1:1); m.p. 107 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.64 (s, 12H; CH$_2$), 2.90 (s, 12H; CH$_2$), 3.28 (d, ^3J(H,H) = 13.5 Hz, 6H; CH$_2$S), 3.40 (d, ^3J(H,H) = 13.5 Hz, 6H; CH$_2$S), 6.39 (s, 3H; Ar–H), 6.66 (s, 3H; Ar–H), 6.76 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 6.85 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 6.87 (s, 6H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 35.20 (6CH$_2$), 36.24 (3CH$_2$), 36.60 (3CH$_2$), 36.78 (3CH$_2$), 37.02 (3CH$_2$), 126.75 (3CH), 127.40 (3CH), 128.10 (6CH), 128.39 (6CH), 128.53 (6CH), 137.86 (6C$_q$), 138.11 (3C$_q$), 138.90 (3C$_q$), 140.80 (3C$_q$), 141.74 (3C$_q$); MS (+ FAB/*m*-NBA): m/z (%) = 877.4 [(*M* + H)$^+$]; IR (KBr): $\tilde{\nu}$ = 709 (m), 809 (m), 1225 (m), 1450 (s), 1512 (m), 1600 (s), 2852 (s), 2910 (vs), 3010 (m) cm^{-1}.

16,24,46-Trithiadecacyclo[18.18.6.3^{12,28}.2.^{6,9}.2^{31,34}.2^{41,44}.1^{3,37}.1^{10,14}.1^{18,22}.1^{26,30}] heptapentaconta-1,3(54)6,8,10,12,14(55),18,20,22(56),26,28,30(57),31,33,37,41,43,48,50,52-beneicosaene (24): Yield: 13.5%; R_f = 0.54 (SiO$_2$, PE/CH$_2$Cl$_2$ 1:1); m.p. > 350 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.05 (m, 6H; CH$_2$), 3.15 (m, 6H; CH$_2$), 3.57 (d, ^2J(H,H) = 14.2 Hz, 6H; CH$_2$S), 3.75 (d, ^2J(H,H) = 14.2 Hz, 6H; CH$_2$S), 6.73 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 6.79 (s, 3H; Ar–H), 6.94 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 7.0 (s, 3H; Ar–H), 7.14 (d, 6H, ^4J(H,H) = 1.4 Hz, Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 33.12 (3CH$_2$), 34.6 (3CH$_2$), 35.9 (6CH$_2$S), 125.86 (6CH), 126.47 (3CH), 126.68 (6CH), 128.65 (3CH), 129.03 (6CH), 137.97 (6C$_q$), 139.62 (3C$_q$), 140.26 (3C$_q$), 141.87 (3C$_q$); MS: m/z (%) = 792.29 (100) [*M*$^+$], 760 (30) [*M*$^+$ – S], 728 (65) [*M*$^+$ – 2S], 694 (50) [*M*$^+$ – 3S].

20,28,50-Trithiaundecacyclo[22.18.6.3^{16,32}.2.^{4,7}.2^{10,13}.2^{35,38}.2.$^{45.48}$.1^{3,41}.1^{14,18}.1^{22,26}.1^{30,34}]trihexaconta-1,3(60)6,10,12,14,16,18(61),22,24,26(62)30,32,34(63),35,37,41,45,47,52,54,56,58-tetraeicosaene (34): Yield: 12%; m.p. > 350 °C; ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 3.01 ("s", 12H; CH$_2$), 3.28 (AB, 4H; CH$_2$S), 3.75 (AB, 4H; CH$_2$S), 3.81 (AB, 4H; CH$_2$S), 6.75 (s, 2H; Ar–H), 6.85 (s, 2H; Ar–H), 6.93 (d, ^3J(H,H) = 8.25 Hz, 4H; Ar–H), 6.94 (s, 2H; Ar–H), 6.96 (d, ^3J(H,H) = 8 Hz, 2H; Ar–H), 6.97 (s, 2H; Ar–H) 6.98 (d, ^3J(H,H) = 8 Hz, 2H; Ar–H), 6.99 (d, ^3J(H,H) = 8.25 Hz, 4H; Ar–H), 7.08 (s, 1H; Ar–H), 7.18 (s, 2H; Ar–H), 7.22 (d, ^3J(H,H) = 8.25 Hz, 2H; Ar–H), 7.40 (s, 2H; Ar–H), 7.41 (d, ^3J(H,H) = 8 Hz, 2H; Ar–H); ^{13}C NMR (125.77 MHz, CD$_2$Cl$_2$): δ = 33.035 (2CH$_2$), 34.701 (2CH$_2$), 35.343 (2CH$_2$S), 37.105 (CH$_2$), 37.163 (2CH$_2$S), 37.297 (CH$_2$), 38.880 (2CH$_2$S), 124.928 (CH), 125.024 (CH), 125.433 (CH), 126.609 (CH), 126.825 (CH), 126.891 (4CH), 127.305 (CH), 127.441 (CH), 129.079 (4CH), 129.634 (CH), 129.759 (CH), 129.778 (CH), 136.730 (C$_q$), 137.653 (C$_q$), 137.780 (C$_q$), 138.559 (C$_q$), 138.572 (C$_q$), 139.574 (C$_q$), 139.715 (C$_q$), 140.009 (C$_q$), 140.331 (C$_q$), 140.442 (C$_q$), 140.572 (C$_q$), 140.617 (C$_q$); MS: m/z (%) = 868.1 (100) [*M*$^+$], 835.1 (10) [*M*$^+$ – S], 804.2 (30) [*M*$^+$ – 2S], 770.2 (25) [*M*$^+$ – 3S].

General procedure for the oxidation of the cyclic trisulfides to the corresponding sulfones: A solution of the cyclic trisulfide (0.15 mmol) and *m*-CPBA (1.5 mmol) in CHCl$_3$ (50 mL) was stirred for 2 d at RT. Upon addition of *n*-hexane (150 mL) a colorless fluffy material precipitated; this was filtered and washed with warm ethanol to remove *m*-chloro- and *m*-chloroperoxybenzoic acid.

5,5,13,13,32,32-Hexaoxo-5,13,32-trithiaheptacyclo[15.13.3.2^{9,24}.1^{3,29}.1^{7,11}.1^{15,19}.1^{22,26}]nonatriaconta-1,3(36),7(37),8,10,15(38),16,18,22(39),23,25,29-dodecaene (14b): Yield: 73%; m.p. > 350 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 3.05 (m, 12H; CH$_2$), 3.83 (d, ^3J(H,H) = 15 Hz, 6H; CH$_2$SO$_2$), 4.19 (d, ^3J(H,H) = 15 Hz, 6H; CH$_2$SO$_2$), 6.78 (s, 3H; Ar–H), 6.88 (s, 3H; Ar–H), 6.95 (s, 6H; Ar–H); ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 30.02 (3CH$_2$), 30.76 (3CH$_2$), 57.59 (6CH), 125.29 (3C$_q$), 128.64 (3CH), 129.51 (6CH), 130.59 (3C$_q$), 139.12 (3CH), 139.60 (6C); MS: m/z (%) = 596 (7) [*M*$^+$ – SO$_2$], 532 (8) [*M*$^+$ – 2SO$_2$], 468 (100) [*M*$^+$ – 3SO$_2$].

18,18,26,26,52,52-Hexaoxo-18,26,52-trithiadecacyclo[20.20.8.3^{14,30}.2^{6,9}.2^{35,38}.2^{45,48}.1^{3,41}.1^{12,16}.1^{20,24}.1^{28,32}]trihexaconta-1,3(60),6,8,12,14,16(61),20,22,24(62),28,30,32(63),35,37,41,45,47,54,56,58-heneicosaene (50): Yield: 96%; m.p. 263–264 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 2.40 (s, 12H; CH$_2$), 2.97 (s, 12H; CH$_2$), 3.80 (d, ^3J(H,H) = 14 Hz, 6H; CH$_2$S), 4.07 (d, ^3J(H,H) = 14 Hz, 6H; CH$_2$S), 6.28 (s, 3H; Ar–H), 6.69 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 6.92 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 7.17 (s, 6H; Ar–H); ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 34.58 (3CH$_2$), 34.84 (3CH$_2$), 36.10 (3CH$_2$), 36.46 (3CH$_2$), 56.15 (6CH$_2$), 125.82 (3CH), 127.69 (6CH), 127.83 (6CH), 127.93 (6CH), 129.94 (3CH), 131.54 (6C$_q$), 136.75 (3C$_q$), 138.37 (3C$_q$), 140.14 (3C$_q$), 141.74 (3C$_q$); MS (+ FAB/*m*-NBA): m/z = 974 [(*M* + H)$^+$], 780.5 [*M*$^+$ – 3SO$_2$]; IR (KBr: $\tilde{\nu}$ = 899 (w), 1114 (vs), 1317 (vs), 1455 (m), 1604 (m), 2924 (s) cm^{-1}.

16,16,24,24,46,46-Hexaoxo-16,24,46-trithiadecacyclo-[18.18.6.3^{12,28}.2.^{6,9}.2^{31,34}.2^{41,44}.1^{3,37}.1^{10,14}.1^{18,22}.1^{26,30}]heptapentaconta-1,3(54),6,8,10,12,14(55),18,20,22(56),26,28,30(57),31,33,37,41,43,48,50,52-henicosaene (25): Yield: 71%; m.p. > 350 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 3.0 (m, 12H; CH$_2$), 4.32 (d, ^2J(H,H) = 14.5 Hz, 6H, CH$_2$SO$_2$), 4.48 (d, ^2J(H,H) = 14.5 Hz, 6H; CH$_2$SO$_2$), 6.8 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 6.89 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 7.02 (s, 3H; Ar–H), 7.13 ("s", 6H; Ar–H), 7.22 ("s", 2H; Ar–H); ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 31.2 (3CH$_2$), 34.85 (3CH$_2$), 58.29 (3CH$_2$SO$_2$), 125.68 (CH), 126.06 (CH), 127.68 (CH), 129.07 (CH), 130.02 (CH), 136.51 (C$_q$), 139.28 (C$_q$), 140.35 (C$_q$), 140.84 (C$_q$); MS: m/z = 888.2 [*M*$^+$], 889.2 [(*M* + H)$^+$], 911.2 [(*M* + Na)$^+$, 100%], 696.3 [*M*$^+$ – 3SO$_2$].

20,20,28,28,50,50-Hexaoxo-20,28,50-Trithiaundecacyclo[22.18.6.3^{16,32}.2^{4,7}.2^{10,13}.2^{35,38}.2$^{45.48}$.1^{3,41}.1^{14,18}.1^{22,26}.1^{30,34}]trihexaconta-1,3(60),6,10,12,14,16,18(61),22,24,26(62),30,32,34(63),35,37,41,45,47,52,54,56,58-tetraicosaene (35): Yield: 82%; m.p. > 350 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.03–3.06 (m, 2H; CH$_2$), 3.08–3.1 (m, 2H; CH$_2$), 3.12–3.2 (m, 8H; CH$_2$), 3.5 (d, ^2J(H,H) = 13 Hz, 2H; CH$_2$S), 4.03 (d, ^2J(H,H) = 13 Hz, 2H; CH$_2$S), 4.46 (d, ^2J(H,H) = 14.6 Hz, 2H; CH$_2$S), 4.54 (d, ^2J(H,H) = 13.4 Hz, 2H; CH$_2$S), 4.64 (d, ^2J(H,H) = 13.4 Hz, 2H; CH$_2$S), 4.86 (d, ^2J(H,H) = 14.6 Hz, 2H; CH$_2$S), 6.76 ("s", 3 H, Ar–H), 6.69 (d, ^3J(H,H) = 7.9 Hz, 2 H, Ar–H), 7.02 ("s", 3 H, Ar–H), 7.06 ("s", 3 H, Ar–H), 7.14 (d, ^3J(H,H) = 8.3 Hz, 2 H, Ar–H), 7.17 (d, ^3J(H,H) = 8.1 Hz, 2 H, Ar–H), 7.24 (d, ^3J(H,H) = 7.9 Hz, 2 H, Ar–H), 7.34 (d, ^3J(H,H) = 8.1 Hz, 2 H, Ar–H), 7.40 ("s", 2 H, Ar–H), 7.54 (d, ^3J(H,H) = 8.3 Hz, 2 H, Ar–H), 7.68 ("s", 3 H, Ar–H), 7.84 ("s", 2 H, Ar–H); ^{13}C NMR (100.62 MHz, [D$_6$]DMSO): δ = 31.5083 (2CH$_2$), 33.3207 (2CH$_2$), 35.0193 (CH$_2$), 36.3136 (CH$_2$), 43.5461 (SO$_2$CH$_2$), 59.2022 (SO$_2$CH$_2$), 61.7275 (SO$_2$CH$_2$), 123.2425 (CH), 125.4038 (CH), 126.1697 (CH), 126.2304 (CH), 126.4958 (CH), 126.8522 (CH), 127.2086 (CH), 127.8532 (CH), 128.8532 (CH), 129.3168 (CH), 129.6049 (CH), 130.9851 (CH), 133.5179 (C$_q$), 135.5653 (C$_q$), 135.9445 (C$_q$), 136.4526 (C$_q$), 137.8934 (C$_q$), 138.8413 (C$_q$), 139.3115 (C$_q$), 139.7589 (C$_q$), 140.0470 (C$_q$), 140.2897 (C$_q$), 140.8357 (C$_q$); MS (+ FAB/*m*-NBA): m/z = 868.1 [*M*$^+$].

General procedure for the sulfone pyrolysis: The cyclic trisulfone was sublimed under high vacuum [29] in a quartz tube and passed through the pyrolysis zone, which was heated to 600 °C by a belt oven. After having passed the pyrolysis zone, the product condensed in colder parts of the quartz tube. The crude product was eluted by CHCl$_3$ and purified by column chromatography (SiO$_2$; PE (40/60)/CH$_2$Cl$_2$ (1:1)).

Heptacyclo[13.13.2^{1,15}.2^{8,22}.2^{3,27}.1^{6,10}.1^{13,17}.1^{20,24}]hexatriaconta-1,3(33),6,8,10(34),13,15,17(35),20,22,24(36),27-dodecaene (1): Yield: 45%; R_f = 0.49 (SiO$_2$, PE/CH$_2$Cl$_2$ 2:1); m.p. > 340 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.89 (s, 24H; CH$_2$), 6.47 (s, 12H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 35.52 (12CH$_2$), 126.48 (12CH), 138.67 (12C$_q$); MS: m/z (%) = 468.2831 (100) [*M*$^+$] (calcd 468.2817), 234 (16) [*M*$^{2+}$].

Decacyclo[19.19.8.2.^{6,9}2.^{14,28}2.^{33,36}2.^{43,46}1.^{3,39}1.^{12,16}1.^{19,23}1.^{26,30}]hexaconta-1,3(57),6,8,12,14,16(58),19,21,23(59),26,28,30(60),33,35,39,43,45,49,53,55-heneicosaene (4): Yield: 38%; R_f = 0.24 (SiO$_2$, PE/CH$_2$Cl$_2$ (2:1)); m.p. > 340 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.61 (m, 12H; CH$_2$), 2.70 (m, 12H; CH$_2$), 3.0 (m, 12H; CH$_2$), 6.42 (s, 3H; Ar–H), 6.63 (d, ^3J(H,H) = 1.5 Hz, 6H; Ar–H), 6.67 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H), 6.77 (t, ^3J(H,H) = 1.5 Hz, 3H; Ar–H), 6.80 (d, ^3J(H,H) = 8 Hz, 6H; Ar–H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 34.08 (3CH$_2$), 36.25 (3CH$_2$), 36.31 (3CH$_2$), 37.82 (3CH$_2$), 38.15 (3CH$_2$), 126.34 (6CH), 126.92 (3CH), 126.97 (3CH), 127.94 (6CH), 128.73 (6CH), 138.25 (3C$_q$), 138.94 (3C$_q$), 139.60 (6C$_q$), 140.34 (3C$_q$), 140.81 (3C$_q$); MS (DEI): m/z = 780.4 [*M*$^+$], 390.3 [*M*$^{2+}$].

Decacyclo[17.17.6.2^{6,9}.2^{12,26}.2^{29,32}.2^{39,42}.1^{3,35}.1^{10,14}.1^{17,21}.1^{24,28}]tetrapentaconta-1,3(51),6,8,10,12,14(52),17,19,21(53),24,26,28(54),29,31,35,39,41,43,47,49-heneicosaene (5): Yield: 38%; m.p. > 350 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.04 (s, 12H; CH$_2$), 3.07 (m, 12H; CH$_2$), 6.64 (s, 15H; Ar–H), 6.73 ("s", 6H; Ar–H), 6.95 (s, 3H; Ar–H); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 32.71 (CH$_2$), 33.45 (CH$_2$), 35.12 (CH$_2$), 126.32 (CH), 126.39 (CH), 126.76 (CH), 127.89 (CH), 128.83 (CH), 139.07 (C$_q$), 139.25 (C$_q$), 139.36 (C$_q$), 139.91 (C$_q$), 140.48 (C$_q$); HRMS: m/z calcd 696.3756, found 696.3770.

Undecacyclo[21.17.6.2^{4,7}.2^{10,13}.2^{32,36}.2^{43,46}.2.^{43,46}.1^{3,39}.1^{14,18}.1^{21,25}.1^{28,32}]hexaconta-1,3(57),4,6,10,12,14,16,18(58),21,23,25(59),28,30,32(60),33,35,39,43,45,47,49,53,55-tetraeicosaene (6): Yield: 34%; m.p. > 350 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.95–3.02 (m, 6H; CH$_2$), 3.04–3.11 (m, 6H; CH$_2$), 3.16–3.29 (m, 12H; CH$_2$), 6.66 ("s", 1H; Ar–H), 6.67 ("s", 2H; Ar–H), 6.75 (d, ^3J(H,H) = 7.8 Hz, 2H; Ar–H), 6.76 (d, ^3J(H,H) = 7.8 Hz, 2H; Ar–H), 6.79 (d, ^3J(H,H) = 8 Hz, 4H; Ar–H), 6.88 (d, ^3J(H,H) = 8 Hz, 4H; Ar–H), 6.92 ("s", 2H; Ar–H), 6.93 ("s", 2H; Ar–H), 6.97 ("s", 4H; Ar–H), 7.05 (d, ^3J(H,H) = 7.8 Hz, 2H; Ar–H), 7.06 ("s", 1H; Ar–H), 7.08 (d, ^3J(H,H) = 7.8 Hz, 2H; Ar–H); ^{13}C NMR (125.77 MHz, CDCl$_3$): δ = 33.379 (2CH$_2$), 33.418 (2CH$_2$), 33.915 (2CH$_2$), 34.124 (2CH$_2$), 35.502 (2CH$_2$), 37.348 (CH$_2$), 37.518 (CH$_2$), 124.336 (CH), 125.172 (CH), 125.491 (CH), 126.264 (CH), 126.409 (CH), 126.950 (CH), 127.006 (CH), 127.073 (CH), 129.316 (CH), 129.350 (CH), 129.742 (CH), 138.649 (C$_q$), 138.853 (C$_q$), 138.942 (C$_q$), 138.966 (C$_q$), 139.063 (C$_q$), 139.345 (C$_q$), 139.441 (C$_q$), 139.486 (C$_q$), 139.731 (C$_q$), 139.793 (C$_q$), 140.058 (C$_q$), 140.626 (C$_q$), 141.333 (C$_q$); MS: m/z (%) = 772.4 (100) [*M*$^+$].

Preparation of 1 by cyclization with phenyllithium: To a refluxing solution of phenyllithium (12 mL of 2% solution in *n*-hexane, 24 mmol) in anhydrous Et$_2$O (100 mL) in a NORMAG one-component dilution principle apparatus (1-C DP), **13** (948 mg, 1 mmol) dissolved in a mixture of anhydrous Et$_2$O/THF (1:1, 150 mL) was added over a period of 8 h. The reaction mixture was allowed to cool to RT, the excess of phenyllithium was quenched by addition of water (5 mL), and the solvent was evaporated. The residue was taken up by CHCl$_3$, washed with water, dried (MgSO$_4$), and purified by column chromatography as described above.

3,5-Bis(bromomethyl)methoxymethylbenzene (54): A solution of freshly prepared potassium methoxide (20 mmol/200 mL) was added dropwise under an inert gas atmosphere to a solution of 1,3,5-tris(bromomethyl)benzene (**53**) (20 mmol) [30] in dry methanol (500 mL) over a period of 12 h. The solvent was evaporated in vacuo and the residue was treated with water. After extraction with CH$_2$Cl$_2$ the organic layer was washed with water and dried ($MgSO_4$). The solvent was removed in vacuo to yield an oily product, which was purified by column chromatography (silica gel; CH_2Cl_2). Yield: 40%; $R_f = 0.62$ (SiO_2, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.41$ (s, 3H; OCH_3), 4.42 (s, 2H; CH_2O), 4.45 (s, 4H; CH_2Br), 7.29 (s, 2H; Ar–H), 7.32 (s, 1H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 32.8$ ($2CH_2$), 58.4 (CH_3), 73.9 (CH_2), 128.1 ($2C_q$), 128.8 (2CH), 138.6 (C_q), 139.8 (CH); MS (GC-MS): m/z (%) = 308 (100) [M^+], 277 (5) [$M^+ - OCH_3$], 227 (100) [$M^+ - HBr$].

5,13,21-Tris(methoxymethyl)[2.2.2]metacyclophane (55): Under an inert gas atmosphere tetraphenylethene (TPE) (3.25 mmol) was dissolved in dry THF (250 mL). A suspension of powdered sodium (0.16 mol) [31] in dry THF (250 mL) was added to this solution immediately. After stirring vigorously for 2 h at −78 °C, **54** (13 mmol) dissolved in dry THF (80 mL) was added dropwise by a perfusor over 72 h at −78 °C at such a rate as to ensure that the red color remained present. Afterwards, the mixture was treated with MeOH (2 mL) and the color turned from red to yellow. For safety, the mixture was treated with MeOH once again to be sure that there was no sodium in the mixture before the solvent was evaporated and the residue taken up by $CHCl_3$. The resultant mixture was refluxed for 1 h and the inorganic solid material was filtered off. After evaporating the solvent the product was purified by column chromatography (silica gel; CH_2Cl_2/acetone = 90:1). Yield: 6%; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.80$ (s, 12H; CH_2), 3.30 (s, 9H; OCH_3), 4.38 (s, 6H; CH_2O), 6.10 ("s", 3H; H_i), 6.90 (s, 6H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 36.33$ (CH_2), 57.81 (OCH_3), 74.80 (CH_2O), 125.87 (CH), 129.53 (CH), 137.58 (C_q), 140.62 (C_q); MS (+ FAB/m-NBA): $m/z = 444$ [M^+].

5,13,21-Tris(bromomethyl)[2.2.2]metacyclophane (56): A solution of **55** (0.12 mmol) in HBr (62%, 8 mL) was stirred for 4 h at RT and 2 h at 40 °C. The reaction mixture was poured into ice water (150 mL) and the resulting precipitate was taken up by CH_2Cl_2. The organic layer was subsequently washed with Na_2CO_3 solution and water and dried ($MgSO_4$), and the solvent was evaporated. The crude product was taken up by $CHCl_3$, petroleum ether (40/60) was added, and the powder was filtered off. Yield: 80%; m.p. 244 °C; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.72$ (s, 12H; CH_2), 4.38 (s, 8H; CH_2), 6.05 ("s", 3H; H_i), 6.91 ("s", 6H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 34.18$ (CH_2), 36.21 (CH_2), 127.20 (CH), 130.49 (CH), 137.44 (C_q), 140.95 (C_q); MS (+ FAB/m-NBA): $m/z = 591$ [M^+], 511 [$M^+ - Br$], 431 [$M^+ - 2Br$], 351 [$M^+ - 3Br$].

5,13,21-Tris(mercaptomethyl)[2.2.2]metacyclophane (57): A solution of **56** (0.034 mmol) and thiourea (0.14 mmol) in dry ethanol was heated to reflux for 5 h. The thiouronium salt was collected by filtration and dried. Under an inert gas atmosphere HCl (10%, 3 mL) was added and the mixture was heated under reflux for 4 h. The mixture was cooled to RT, and dilute H_2SO_4 was added, followed by extraction with CH_2Cl_2. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed in vacuo to yield an oily product. Yield: 47%; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.85$ (t, $^3J(H,H) = 8$ Hz, 3H; SH), 2.7 (s, 12H; CH_2), 3.75 (d, $^3J(H,H) = 8$ Hz, 6H; CH_2SH), 6.05 ("s", 3H; H_i), 7.05 (s, 6H; Ar–H); MS (+ FAB/m-NBA): $m/z = 450$ [M^+].

3-Bromomethyl-5-(methoxymethyl)benzaldehyde (58): A solution of potassium 2-nitropropanoate (5.65 mmol) in dry ethanol (20 mL) was added dropwise under an inert gas atmosphere to a solution of **54** (9.75 mmol) in dry ethanol (30 mL) over a period of 2 h. The reaction mixture was stirred for a further 4 h and then treated with water, extracted twice with CH_2Cl_2, and dried ($MgSO_4$). The solvent was evaporated to yield the crude product, which was subjected to column chromatography (silica gel; CH_2Cl_2). Yield: 21%; m.p. 53–56 °C; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.40$ (s, 3H; OCH_3), 4.50 (s, 4H; CH_2Br; CH_2O), 7.61 (s, 1H; Ar–H), 7.75 (s, 1H; Ar–H), 7.80 (s, 1H; Ar–H), 10.00 (s, 1H; CHO); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 32.0$ ($2CH_2Br$), 58.6 (CH_3O), 73.5 (CH_2O), 128.5 (CH), 129.0 (CH), 134.0 (CH), 137.0 (C_q), 139.0 (C_q), 141.0 (C_q), 191.6 (CHO); MS (GC-MS): m/z (%) = 242 and 244 (8) [M^+], 212 (5) [$M^+ - HCHO$], 163 (95) [$M^+ - HBr$], 133 (100) [$M^+ - HBr, -OCH_3$]; IR (KBr): $\tilde{\nu} = 1701$ (s) cm^{-1}.

All-(Z)-5,13,21-tris(methoxymethyl)[2.2.2]metacyclophane-1,9,17-triene (60): **59** (7.91 mmol) was dissolved in DMF (150 mL) and the mixture was cooled to −40 °C. Freshly prepared lithium ethoxide in ethanol was added dropwise to the stirred solution, which slowly changed color from yellow to orange. The addition was complete within a few hours, when no further color change was observed on addition of base. The mixture was warmed to RT, and water (120 mL) was added, followed by extraction with Et_2O. The organic layer was washed with water and dried over Na_2SO_4, and the solvent was removed. The residue was purified by column chromatography (silica gel, PE(40/60)/ethyl acetate (4:1)). Yield: 21%; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.30$ (s, 9H; OCH_3), 4.35 (s, 6H; CH_2O), 6.57 (s, 6H; CH=CH), 6.65 (s, 3H; Ar–H), 6.94 (d, $^3J(H,H) = 1.25$ Hz, 6H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 57.9$ (CH_3O), 74.4 (CH_2), 126.8 (CH), 128.8 (CH), 131.1 (CH), 137.7 (C_q), 138.4 (C_q); MS (MALDI/9-nitroanthracene): m/z (%) = 477 (58) [$(M+K)^+$], 461 (100) [$(M+Na)^+$], 438 (38) [M^+].

All-(Z)-5,13,21-tris(bromomethyl)[2.2.2]metacyclophane-1,9,17-triene (61): A solution of boron tribromide (1 M in CH_2Cl_2, 0.42 mmol) was added dropwise under an inert gas atmosphere to a solution of **60** (0.14 mmol) in dry CH_2Cl_2 (25 mL) at 0 °C. The mixture was warmed to RT and hydrolyzed under vigorous stirring for 3 h followed by extraction with Et_2O. The organic layer was washed with water and dried over Na_2SO_4; after removing the solvent the residue was purified by flash column chromatography (silica gel; CH_2Cl_2/PE(40/60) (3:1)). Yield: 66%; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 4.40$ (s, 6H; CH_2Br), 6.55 (s, 6H; CH=CH), 6.65 (s, 3H; Ar–H), 7.00 (d, $^3J(H,H) = 1.25$ Hz, 6H; Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 33.3$ (CH_2Br), 128.2 (CH), 129.5 (CH), 131.0 (CH), 138.1 (C_q), 138.3 (C_q); MS (+ FAB/m-NBA): m/z (%) = 581 [M^+], 502 [$M^+ - HBr$], 422 [$M^+ - 2HBr$], 344 [$M^+ - 3HBr$].

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