Synthesis of Self-Assembling Resorcin[4]arene Tetrasulfide Adsorbates

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The synthesis of a new type of host adsorbate possessing a large resorcin[4]arene headgroup and four di-*n*-decyl sulfide chains underneath is described. The cross-sectional area of the alkyl chains is equal or larger than that of the headgroups which makes these resorcin[4]arene tetrasulfides suitable for self-assembly onto gold surfaces to form well-packed monolayers of which the outer interface is composed of receptor sites and the alkyl chains underneath the cavity headgroups passivate the gold surface. Resorcin[4]arene tetrasulfides with the following functionalities at the resorcin[4]arene headgroup were synthesized: methylene ether (the so-called *cavitand*), methyl ether, 2-fluoroethyl, several carboxyl esters, *N*-propylacetamide and hydroxy.

Organosulfur compounds bind strongly to gold surfaces and several self-assembled monolayers of adsorbates with a surface-active sulfur group, an alkyl chain, and a terminal functional group have been reported.¹ The self-assembling process opens the route to develop active layers for fast responding sensors² by organizing receptor molecules on top of an appropriate transduction element. Following this strategy, self-assembling adsorbate molecules with, for example, ω -terminated phosphatidylcholine,³ porphyrin,⁴ viologen⁵ and ferrocene⁶ groups have been synthesized.

Adsorbates containing a receptor cavity are particularly interesting for sensing layers capable of the selective binding of small organic molecules. Therefore, β -cyclodextrin has been functionalized with seven dodecylsulfide chains for self-assembling, but it appeared that this adsorbate did not form a density packed monolayer structure.⁷

In order to obtain stable self-assembling monolayers of receptor adsorbates, which completely passivate the gold surface and form a highly ordered outer interface of densely packed receptor sites, we have designed and synthesized various resorcin[4]arene adsorbates with four dialkyl sulfide chains underneath. The sulfide-gold interaction in these adsorbates is well suited for the preparation of stable receptor monolayers, owing to its high strength and specificity, and the length of the alkyl chains can be tuned to optimize the gold passivation.⁸ In this paper the design and synthesis of the receptor adsorbates is discussed. The extensive characterization of assemblies prepared from these adsorbates has been described in a separate paper.⁹ An example of the use of these assemblies for specific gas detecting using a quartz crystal microbalance has been recently reported.¹⁰

Design of Receptor Adsorbates:

Resorcin[4]arenes¹¹ are well suited to the purpose of constructing receptor adsorbates. In addition to the cone-like cavity formed by the four resorcinol units, underneath the cavity four points of attachment for alkyl chains are available at the methine linkages. These chains are oriented mutually parallel and perpendicular with respect to the annulus of the macrocycle at a distance of 5 Å from each other. This parallel orientation of the alkyl

chains at a packing distance commonly found in alkanethiol monolayers^{1f,12,13} renders these resorcin[4]arenes unique molecules for the development of receptor adsorbates. In other potential receptor molecules, like fourfold alkylated *cone*-calix[4]arenes and (heptakis)alkylated β -cyclodextrins, the alkyl chains are not directed parallel, but are diverging from each other. By connecting four 11-thiahenicosyl chains to the methine linkages, eight alkyl chains can become organized underneath the cavity with a total cross-sectional area of ca. 160 Å², which is slightly larger than that of the resorcin[4]arene headgroup (ca. 140 Å²). The dialkyl sulfide chains underneath the headgroups are expected to form a well-packed hydrocarbon layer, capable of passivating the gold surface completely, and excluding undesired interactions between the gold surface and analytes.

In order to investigate the influence of size and polarity of the headgroup on the monolayer formation, adsorbates with various functionalities at the resorcin[4]arene headgroup were synthesized. In addition, the length of the terminal alkyl chain was varied for two of the adsorbates (**4a**, **4c**) in order to study its effect on the monolayer organization.

Synthesis of the Resorcin[4]arene Tetrasulfides:

Most of the resorcin[4]arene tetrasulfides were prepared via the three-step synthesis represented in Scheme 1. First, the resorcin[4]arene tetraolefinic building blocks **2a–c** were prepared. These octols or dodecaols were either completely alkylated or acylated to compounds **3a–i**. Subsequently, addition of decanethiol to the four double bonds then afforded the resorcin[4]arene tetrasulfides **4a–i**.

The resorcin[4]arene cyclotetramer was formed by condensation of undecylenic aldehyde with resorcinol (**1a**), 2-methylresorcinol (**1b**), or pyrogallol (**1c**) in a mixture of ethanol and hydrochloric acid for 16 h at 70 °C. The temperature of 70 °C was necessary in order to shift the thermodynamic equilibrium to the most stable CCC (all-cis) diastereoisomeric form of the cyclotetramers.¹⁴ The resorcin[4]arenes **2a–c** were obtained in 55–64 % yield after repeated triturations. These products appear as a slightly pink powder due to the presence of strongly red-colored impurities which were difficult to remove. However, ¹H NMR, IR and elemental analysis indicated that these contaminations were only present in a minor amount in the products. The colored impurities could easily be removed by column chromatography after functionalization of the hydroxy groups of the resorcin[4]arenes in the second step. In the case of **2a** and **2c** only the CCC diastereoisomeric form of the cyclic tetramer is present in the product, as was inferred from the ¹H NMR spectrum. The product of **2b** was obtained as a mixture of 90 % of the CCC diastereoisomer and about 10 % of

Scheme 1

another diastereoisomer, most probably the CTT (cis-trans-trans).¹² The presence of this diastereoisomeric impurity is probably caused by the limited solubility of **2b** in ethanol which prevents the kinetically formed diastereomeric mixture of **2b** shifting completely to the thermodynamic most stable CCC diastereoisomer. However, separation of the diastereoisomers was possible after cavitand formation (**3b**), and acylation (**3h**) in the second step.

The hydroxy groups of the resorcin[4]arenes **2a–c** were modified with various alkylating and acylating reagents to give eight- or twelvefold functionalized compounds (Scheme 1). Three different types of reactions will be subsequently discussed. Firstly, the alkylation of **2a** and **2c** with bromochloromethane to form the rigid, cone-shaped cavitands **3a** and **3b**, respectively. Secondly, the alkylation of **2a** and **2c** with iodomethane (to **3c** and **3d**, respectively), of **2a** to **3f** with methyl-2-bromoacetate, and of **2a** to **3e** with 2-fluoroethyl tosylate, and thirdly, the acylation of **2a–c** to **3g–i** with acetic anhydride.

Resorcin[4]areneoctol **2a** could be converted in 55% yield into the cavitand **3a** by treatment with sodium hydride and bromochloromethane in DMF at 70 °C for 72 h. In order to obtain the cavitand, the octol **2a** and bromochloromethane had to be added simultaneously to a suspension of the base. Other ways of addition, or the use of different bases (K₂CO₃, Cs₂CO₃), or solvents (DMSO, acetonitrile, THF) resulted in the formation of an insoluble off-white material, in which the resorcin[4]arenes are probably intermolecularly linked by methylene bridges. However, cavitand **3b** could be obtained in 86% yield by alkylation of resorcin[4]arene **2b** with bromochloromethane and potassium carbonate in DMF at 60 °C for 16 h. The remarkable difference in reaction conditions which is required to achieve cavitand

formation for **2b** is probably caused by the four methyl groups which prevent intermolecular reactions.

The resorcin[4]arenes **2a–c** could be completely methylated by treatment with sodium hydride and iodomethane in DMF for 24 h at 50 °C, in 56, 40, and 22% yields, respectively. Complete methylation (eight- or twelvefold) was proven by ¹H NMR spectroscopy and FAB-mass spectrometry. The methylation of the CCC and CTT diastereomeric mixture of **2b** afforded the completely methylated products in the same diastereomeric ratio and separation of this mixture was not successful. 2-Fluoroethylation of resorcin[4]arene **2a** to **3e** could be achieved by a treatment with sodium hydride and 2-fluoroethyl tosylate¹⁵ in DMF, at 80 °C for 16 h, in 47% yield. When other bases (K₂CO₃, Cs₂CO₃) or solvents (acetonitrile, THF) were applied in the alkylation reactions, only partially methylated or 2-fluoroethylated products were obtained. However, with methyl 2-bromoethanolate and potassium carbonate in acetonitrile at 80 °C for 48 h, resorcin[4]arene **2a** was successfully alkylated in 55% yield. The milder conditions necessary for this alkylation can probably be attributed to the higher reactivity of the α-bromocarbonyl compound compared to the former halogenide and tosylate alkylating reagents.

The resorcin[4]arenes **2a–c** could be fully acetylated by treatment with acetic anhydride in the presence of a catalytic amount of pyridine at 100 °C, yielding **3g–i** in 50, 59, and 58% yield, respectively. Lower reaction temperatures or shorter reaction times afforded incompletely acylated products. The ¹H NMR spectra of **3g–i** at room temperature indicate a slow pseudo-rotation of the resorcin[4]arene moiety, causing broadening of the aromatic hydrogen resonances. The ¹H NMR spectra at –50 °C, however, showed distinct signals of a frozen-out boat-conformation. Similar behavior has been reported for a comparable octapropionate resorcin[4]arene.¹⁵

Coupling of 1-decanethiol to the terminal carbon atoms of the fourfold vinylic resorcin[4]arenes **3a–i** could be achieved by anti-Markovnikov addition with 9-borabicyclo[3.3.1]nonane (9-BBN) in THF at 0 °C (Scheme 1).¹⁶ The tetrasulfides **4a–i** formed were subjected to column chromatography to remove excess of 1-decanethiol. Recrystallization from acetone (in most cases) afforded white (microcrystalline) powders in 60–90 % isolated yields. The ¹H NMR and IR spectra clearly indicated that all four double bonds had been transformed into sulfide groups. Furthermore, the ¹H NMR spectrum showed that the addition had occurred exclusively anti-Markovnikov.

Besides 1-decanethiol, primary alkanethiols of different chain length, viz. 1-octanethiol, 1-nonanethiol, 1-undecanethiol, and 1-dodecanethiol, could also be successfully added to the vinylic moieties of **3c**. These tetrasulfides will be referred to as **4c(8)**, **4c(9)**, **4c(11)**, and **4c(12)**, respectively, where the number in parenthesis indicates the carbon length of the terminal alkyl chain. Similarly, 1-octanethiol and 1-dodecanethiol were added to the double bonds of **3a**, affording **4a(8)** and **4a(12)**, respectively.

In addition to the resorcin[4]arene tetrasulfides **4a–i**, two other resorcin[4]arene-modified tetrasulfides were prepared, which could not be synthesized by the three-step route given in Scheme 1. In the synthesis of **5** and **6**, the amide and hydroxy functionalities are not compatible with the 9-BBN catalyst in the alkanethiol addition reaction. Therefore, indirect methods for the synthesis of these compounds were used.

Octa(*N*-propylacetamide)resorcin[4]arene **5** could be obtained in 82 % yield by aminolysis of the octamethyl ester **4f** with a large excess of propylamine in THF for 48 h at room temperature (Scheme 2).

Scheme 2

The octahydroxyresorcin[4]arene tetrasulfide **6** could be prepared by reductive deacetylation of octaacetate **4g** with zinc powder in refluxing methanol/THF in 81 % yield (Scheme 3).¹⁷ The zinc powder had to be activated with 0.1 M hydrochloric acid prior to use, and was employed in large excess, since the octol **6** passivates the zinc surface.

Scheme 3

Self-Assembled Monolayers of the Resorcin[4]arene Adsorbates:

For the formation of monolayers from the prepared receptor adsorbates freshly prepared, cleaned gold substrates were immersed in 1 mM solutions of the resorcin[4]arenes in 7:3 (v/v) ethanol–chloroform (for **5** the ratio 9:1 v/v was used). Remarkably, the degree of organization of the monolayers was strongly dependent on the temperature of the solvent during the adsorption process. At room temperature only disorganized submonolayers with many defects were formed, as was apparent from heterogeneous electron transfer and surface plasmon spectroscopy (SPS) measurements.^{8,9} However, the monolayer quality improved dramatically by adsorption from a heated solution (60 °C) for 13 h and subsequent slow cooling to room temperature over 3 h. This behavior is apparently due to the unique structural architecture of the adsorbates, having four dialkylsulfide legs for binding to the gold surface. At room temperature the kinetically controlled adsorption of the sulfide atoms to the gold surface will not necessarily give a dense packing of the alkyl chains. However, at higher temperatures the reversible sulfur–gold binding allows alkyl chain organization with maximum Van der Waals contact, resulting

Figure 1. Self-assembling of resorcin[4]arene tetrasulfide adsorbates to monolayers on gold

in highly organized monolayers for various adsorbates. The quality of the monolayers thus formed can be broadly divided into two categories, depending on the size of the functionalized headgroups. Adsorbates with resorcin[4]arene headgroups equal to or smaller than the total area (ca. $160 \text{ \AA}^2$) of the eight alkyl chains underneath this headgroup (**4a–c**, **e**, **g**) form well-organized monolayers (Figure 1).

These well-organized monolayers effectively passivate the gold surface in heterogeneous electron transfer experiments. Cyclic voltammograms (1 mM $\text{K}_3\text{Fe}(\text{CN})_6^{3-}$, 0.1 M K_2SO_4) of gold electrodes covered with these monolayers show maximum cathodic current densities less than $5 \mu\text{A cm}^{-2}$ and low capacitance values in the range $0.99\text{--}1.20 \mu\text{F cm}^{-2}$ (0.1 M K_2SO_4 between -100 and $+100 \text{ mV}_{\text{msec}}$ at 100 mVs^{-1}), which is comparatively good blocking behavior to that found for 1-alkanethiol monolayers.^{1f,11} For **4a** and **c**, the substitution of the terminal decyl chain for a shorter or longer chain has a deleterious effect on the monolayer quality. Molecular modeling shows that maximum packing is obtained when the alkyl chains on both sides of the sulfur have equal length.

The adsorbates in which the functionalized resorcin[4]arene headgroup is larger than $160 \text{ \AA}^2$ form monolayers with less densely packed alkyl chains. Significant heterogeneous electron transfer and higher capacitance values are observed for these monolayers (**4d**, **f**, **h**, **i**, **5**). The octol derivative **6** is an adsorbate with a relatively small headgroup. However, due to the strong hydrogen-bonding properties of the free hydroxy groups, a poorly organized bilayer structure is formed by head-to-head interactions.⁹

The functionalized resorcin[4]arenes⁵ which form well-organized monolayers are currently under investigation for their molecular recognition properties in sensing devices. Recently, we have shown that monolayers of the rigid cavitand **4a**, on a quartz microbalance oscillator, respond strongly to tetrachloroethylene in air.¹⁰

In conclusion, resorcin[4]arene adsorbates with four 11-thiahenicosyl chains and various functionalities at the phenolic groups could be prepared as the pure CCC isomers. The modification of the hydroxy functions of the resorcin[4]arene headgroup afforded fully alkylated or acylated products. Also, the aminolysis and deacetylation of the multifunctional compounds **4f** and **4g** could be performed under conditions yielding complete conversion of the functionalities. Functionalities at the resorcin[4]arene headgroup are: methylene (cavitand), methyl ether, 2-fluoroethyl, various carboxyl esters, *N*-propylacetamide and the free hydroxy group. The resorcin[4]arene tetrasulfides are stable compounds, which are soluble in chlorinated alkanes and well suited for self-assembling to monolayers on gold.⁹ The quality of the monolayers obtained from these adsorbates appears to be dependent on the size of the headgroup; adsorbates with functionalized resorcin[4]arene headgroups smaller than or equal to the total area of the four dialkylsulfide chains underneath (ca. $160 \text{ \AA}^2$) give monolayers which show least defects.

^1H and ^{13}C NMR spectra were recorded with a Bruker AC250F (250 MHz) spectrometer in CDCl_3 unless stated otherwise with TMS as an internal standard. FAB-mass spectra were obtained with a Finnigan MAT90 mass spectrometer using *m*-nitrobenzyl alcohol (NBA) or *o*-nitrophenyl octyl ether (NPOE) as a matrix. IR spectra were recorded with a Nicolet 55XC spectrometer. Mps were determined with a Reichert melting point apparatus and are uncorrected. Reagents were obtained from Janssen, Merck, Aldrich, Fluka, or Pfaltz und Bauer. Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl; DMF was stored over molecular sieves (4 Å); pyridine was dried over KOH pellets prior to use. All other solvents and purchased chemicals were reagent grade and were used without purification. Chromatographic separations were performed on silica gel 60 (SiO_2 , Merck, particle size $0.040\text{--}0.063 \text{ mm}$, 230–240 mesh).

Compounds **3a**, **3b** · MeCN, **3c–i**, **4a**, **4a(8)**, **4a(12)**, **4b**, **4c**, **4c(8)**, **4c(9)**, **4c(11)**, **4c(12)**, **4d–i**, **5** and **6** gave C,H analysis $\pm 0.36\%$; except **3f**, C = 0.61; **4c**, H + 0.50. **3b** · MeCN and **5**, and **4b**, **h**, **i** gave N and S analysis, respectively, $\pm 0.21\%$.

2,8,14,20-Tetrakis(9-decenyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (2a):

Into a solution of resorcinol **1a** (22.02 g, 0.2 mol) and 10-undecenal (33.64 g, 0.2 mol) in EtOH (200 mL) was added 12 N hydrochloric acid (32 mL) at 0°C in 10 min. The mixture was stirred at 60°C for 16 h. The red oil was poured into well-stirred demineralized water (600 mL). The orange precipitate was filtered off and washed thoroughly with hot water (80°C , 6 L), dried (28.6 g, 55%) and precipitated three times from MeCN, once from cyclohexane and twice from petroleum ether (bp $60\text{--}80^\circ\text{C}$) to give 10 g (22%) of a slightly pink powder: mp 295°C (dec.). The remaining slight impurity (< 2%) could not easily be removed at this stage of the synthesis and the compound was used for the conversion into the hydroxy-functionalized compounds **3a**, **c**, **e**, **f** and **g**, which were more easily purified.

^1H NMR (acetone- d_6): δ = 8.46 (s, 8 H, ArOH), 7.55 and 6.22 (each s, each 4 H, ArH), 5.80 (m, 4 H, $\text{RCH}=\text{CH}_2$), 5.00 and 4.91 (each d, each 4 H, $J_1 = 18$, $J_2 = 10 \text{ Hz}$, $\text{RC}=\text{CH}_2$), 4.31 (t, 4 H, $J = 7.6 \text{ Hz}$, RCHAr_2), 2.29 (m, 8 H, $\text{RCH}_2\text{C}=\text{C}$), 1.32 (56 H, CH_2), 3.00 (m, 2 H, H_2O).

^{13}C NMR (acetone- d_6 - CDCl_3 , 1:1 v/v): δ = 151.2, 139.0, 124.3, 123.3, 113.9, 102.9, 33.7, 33.4, 33.2, 30.6, 29.6, 29.6, 29.4, 29.0, 28.8, 28.0.

FAB-MS: m/z = 1040.5 ($\text{M}^+ - \text{H}$), 901.4 [$\text{M}^+ - (\text{CH}_2)_8\text{CH} = \text{CH}_2$].

IR (KBr): ν = 3371, 3286 (OH), 3076, 1641, 908 cm^{-1} ($\text{C}=\text{C}$).

2,8,14,20-Tetrakis(9-decenyl)-5,11,17,23-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (2b):

Starting from 2-methylresorcinol **1b** (12.4 g, 0.1 mol) and 10-undecenal (16.84 g, 0.1 mol) compound **2b** was prepared analogously to the preparation of **2a**. The resulting yellow powder was precipitated twice from MeOH, once from 1,1,1-trichloroethane, and finally once from MeCN, giving 15.6 g (57%) of a slightly pink powder: mp 285°C (dec.). The remaining slight impurity (< 2%) could not easily be removed at this stage of the synthesis and the compound was used for the conversion into the hydroxy-functionalized compounds **3b** and **3h**, which were more easily purified.

^1H NMR (acetone- d_6): δ = 7.96 (s, 8 H, ArOH), 7.39 (s, 4 H, ArH), 5.7–5.9 (m, 4 H, $\text{RCH}=\text{CH}_2$), 4.95 and 4.89 (each d, each 4 H, $J_1 = 17$, $J_2 = 10 \text{ Hz}$, $\text{RC}=\text{CH}_2$), 4.37 (t, 4 H, $J = 7.4 \text{ Hz}$, RCHAr_2), 2.83 (s, 12 H, ArCH_3), 2.27 (m, 8 H, $\text{RCH}_2\text{C}=\text{C}$), 1.34 (s, 56 H, CH_2).

FAB-MS: m/z = 1097.6 (M^+), 958.4 [$\text{M}^+ - (\text{CH}_2)_8\text{CH} = \text{CH}_2$].

IR (KBr): ν = 3393 (OH), 3076, 1641, 909 cm^{-1} ($\text{C}=\text{C}$).

2,8,14,20-Tetrakis(9-decenyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecaol (2c):

Starting from pyrogallol **1c** (12.6 g, 0.1 mol) and 10-undecenal (16.84 g, 0.1 mol), compound **2c** was prepared analogously to the preparation of **2a**. The resulting red powder was recrystallized three times from MeCN, giving 17.5 g (64%) of a pink powder: mp 270 °C (dec.). The remaining slight impurity (<2%) could not easily be removed at this stage of the synthesis and the compound was used for the conversion into the methylated compound **3d**, which was more easily purified.

¹H NMR: δ = 8.11 (s, 8 H, ArOH), 7.21 (s, 4 H, ArOH), 7.10 (s, 4 H, ArH), 5.89–5.73 (m, 4 H, RCH=CH₂), 5.01 and 4.91 (each d, each 4 H, RCH=CH₂, J_1 = 17.2, J_2 = 10.2 Hz), 4.33 (t, 4 H, RCHAr₂, J = 7.8 Hz), 2.87 (s, 8 H, H₂O), 2.26 (m, 8 H, RCH₂C=C), 1.30 (s, 56 H, CH₂).

FAB-MS: m/z = 1103.5 (M^+ – H), 963.4 [M^+ – (CH₂)₈CH = CH₂].

IR (KBr): ν = 3471, 3300 (OH), 3076, 1640, 909 cm^{–1} (C=C).

1,21,23,25-Tetrakis[9-deceny]-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-*i*:5',4'-*i'*]benzo[1,2-*d*:5,4-*d'*]-bis[1,3]benzodioxocin (3a**):**

To a suspension of sodium hydride [(0.45 g, 10 mmol); freed from mineral oil by washing with petroleum ether (bp 40–60 °C) (3 × 10 mL)] in DMF (100 mL), was added slowly a solution of **2a** (1.00 g, 0.96 mmol) and bromochloromethane (0.60 g, 4.7 mmol) in DMF (20 mL). After gas evolution ceased the red suspension was heated at 70 °C for 24 h. An extra amount of bromochloromethane (0.56 g, 4.3 mmol) was added and the suspension was heated for another 48 h at 70 °C. After cooling to room temperature the solvent was removed under reduced pressure. The residue was dissolved in Et₂O (300 mL) and washed with water (3 × 250 mL). The solvent was removed under reduced pressure. The residue was ground into a fine powder and Soxhlet extracted with acetone (300 mL) for 48 h. The red filtrate was subjected to column chromatography (SiO₂; Et₂O). The obtained orange oil was precipitated from petroleum ether (40–60 °C) at –15 °C, giving 0.58 g (55%) of a colorless powder, mp 106–108 °C.

¹H NMR: δ = 7.10 and 6.48 (each s, each 4 H, ArH), 5.89–5.77 (m, 4 H, RCH=CH₂), 5.75 and 4.43 (each d, each 4 H, OCH₂O, J = 7.2 Hz), 4.95 and 4.90 (each d, each 4 H, RC=CH₂, J_1 = 17, J_2 = 10 Hz), 4.72 (t, 4 H, RCHAr₂, J = 8.0 Hz), 2.20 (m, 8 H, RCH₂C=C), 2.07 (m, 8 H, RCH₂CHAr₂), 1.5–1.25 (m, 48 H, CH₂).

¹³C NMR: δ = 154.8, 139.2, 138.4, 120.6, 116.5, 114.2, 99.5, 36.3, 33.8, 29.8, 29.7, 29.5, 29.2, 29.0, 27.8.

FAB-MS: m/z = 1088.7 (M^+), 950.0 [M^+ – (CH₂)₈CH = CH₂].

IR (KBr): ν = 1641, 908 (C=C), 968 cm^{–1} (OCH₂O).

1,21,23,25-Tetrakis[9-deceny]-7,11,15,28-tetramethyl-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-*i*:5',4'-*i'*]benzo[1,2-*d*:5,4-*d'*]-bis[1,3]benzodioxocin (3b**):**

To a pink solution of **2b** (5.00 g, 4.56 mmol) in DMF (200 mL) was added bromochloromethane (4.0 g, 31 mmol) and potassium carbonate (7.5 g, 54 mmol) at r.t. The solution was heated to 60 °C and stirred for 16 h. The solution was concentrated under reduced pressure, and diluted with CH₂Cl₂. The red solution was washed three times with water and concentrated. The viscous red oil was subjected to column chromatography (SiO₂; CH₂Cl₂). The resulting yellowish oil crystallized from acetone–MeCN (1:1 v/v) after several days, affording 4.50 g (86%) of a white powder, mp 68 °C.

¹H NMR: δ = 6.95 (s, 4 H, ArH), 5.91 and 4.26 (each d, each 4 H, OCH₂O, J_1 = 7.4, J_2 = 7.5 Hz), 5.90–5.70 (m, 4 H, RCH=CH₂), 4.99 and 4.93 (each d, each 4 H, RCH=CH₂, J_1 = 20, J_2 = 8 Hz), 4.78 (t, 4 H, RCHAr₂, J = 7.8 Hz), 2.30–2.13 (m, 8 H, RCH₂CH=CH₂), 2.09 (m, 8 H, RCH₂CHAr₂), 2.01 (s, 12 H, ArCH₃), 1.5–1.2 (m, 48 H, CH₂).

FAB-MS: m/z = 1144.7 (M^+ – H), 1005 [M^+ – (CH₂)₈CH = CH₂].

IR (KBr): ν = 3073, 1641, 908 (C=C), 978 cm^{–1} (OCH₂O).

2,8,14,20-Tetrakis(9-deceny)-4,6,10,12,16,18,22,24-(octamethoxy)-pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (3c**):**

To a suspension of sodium hydride [(3.00 g, 100 mmol); freed from mineral oil by washing with petroleum ether (bp 40–60 °C) (3 × 30 mL)] in DMF (150 mL) was slowly added a solution of **2a** (10.00 g, 9.6 mmol) and iodomethane (20 g, 142 mmol) in DMF (100 mL). The temperature was kept below 35 °C by adjusting the rate of addition. The brown suspension was stirred for 24 h at r.t. and for a further 24 h at 50 °C. After cooling to r.t. the solvent was removed under reduced pressure. The residue was taken up in CH₂Cl₂ and washed with sat. aq. NH₄Cl (3 × 250 mL) and water (2 × 250 mL). The organic layer was dried (MgSO₄) and concentrated at reduced pressure. The brown oil was subjected to column chromatography (SiO₂; Et₂O) and crystallized once from MeOH–diisopropyl ether and twice from isopropanol giving 6.2 g (56%) of a white powder, mp 124 °C.

¹H NMR: δ = 6.60 and 6.31 (each s, each 4 H, ArH), 5.87–5.71 (m, 4 H, RCH=CH₂), 4.97 and 4.91 (each d, each 4 H, J_1 = 17.0, J_2 = 10.1 Hz, RC=CH₂), 4.44 (t, 4 H, J = 7.4 Hz, RCHAr₂), 3.59 (s, 24 H, ArOCH₃), 2.05–2.00 (m, 8 H, RCH₂C=C), 1.97–1.79 (m, 8 H, RCH₂CHAr₂), 1.40–1.15 (m, 48 H, CH₂).

¹³C NMR: δ = 155.8, 139.6 (RCH=CH₂), 126.3, 126.1, 114.0 (RCH=CH₂), 97.1, 56.2 (ArOCH₃), 35.4, 34.7, 33.8, 29.9, 29.7, 29.6, 29.2, 29.0, 28.2.

FAB-MS: m/z = 1153.3 (M^+), 1013.8 [M^+ – (CH₂)₈CH = CH₂].

IR (KBr): ν = 3077, 1641, 909 (C=C), 2833, 1300 cm^{–1} (OCH₃).

2,8,14,20-Tetrakis(9-deceny)-4,5,6,10,11,12,16,17,18,22,23,24-(decamethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (3d**):**

Starting from compound **2c** (5.0 g, 4.5 mmol), iodomethane (7.8 g, 55 mmol) and sodium hydride (2.12 g, 80% dispersion in oil, 71 mmol) compound **3d** was prepared analogously to the preparation of **3c**. The resulting brown oil was subjected to column chromatography (SiO₂; petroleum ether–EtOAc, 3:1), and subsequent recrystallization from EtOH, afforded 2.00 (22%) of yellowish crystals, mp 75–76 °C.

¹H NMR: δ = 6.42 (s, 4 H, ArH), 5.87–5.71 (m, 4 H, RCH=CH₂), 4.97 and 4.91 (each d, each 4 H, RCH=CH₂, J_1 = 18.1, J_2 = 11.5 Hz), 4.49 (t, 4 H, RCHAr₂, J = 7.4 Hz), 3.78 (s, 12 H, ArOCH₃), 3.61 (s, 24 H, ArOCH₃), 2.01 (m, 8 H, RCH₂C=C), 1.80 (m, 8 H, RCH₂CHAr₂), 1.4–1.2 (m, 48 H, CH₂).

¹³C NMR: δ = 149.5, 145.9, 139.2 (RCH=CH₂), 133.5, 120.3, 114.1 (RCH=CH₂), 60.3, 60.1, 36.6, 35.7, 33.8, 29.9, 29.7, 29.2, 29.0, 28.3.

FAB-MS: m/z = 1272.8 (M^+), 1133.6 [M^+ – (CH₂)₈CH = CH₂].

IR (KBr): ν = 3077, 1641, 910 (C=C), 2978, 1410, 1314 cm^{–1} (OCH₃).

2,8,14,20-Tetrakis(9-deceny)-4,6,10,12,16,18,22,24-octa(2-fluoroethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (3e**):**

To a suspension of sodium hydride [(0.11 g, 2.62 mmol); freed from mineral oil by washing with petroleum ether (bp 60–80 °C) (3 × 20 mL)] in DMF (60 mL) was added **2a** (0.50 g, 0.48 mmol) and 2-fluoroethyl tosylate¹⁴ (1.00 g, 4.62 mmol). The brown suspension was heated for 16 h at 80 °C, quenched with water and concentrated under reduced pressure. The brown residue was dissolved in CH₂Cl₂ (150 mL) and washed with sat. aq. NH₄Cl (3 × 250 mL). The organic layer was dried (MgSO₄) and subjected to column chromatography [SiO₂; EtOAc–petroleum ether (bp 60–80 °C), 1:1 v/v]. Recrystallization from MeOH afforded 0.32 g (47%) of a white powder, mp 94–95 °C.

¹H NMR: δ = 6.63 (s, br, 4 H, ArH), 6.28 (s, 4 H, ArH), 5.71–5.88 (m, 4 H, RCH=CH₂), 4.89 (m, 8 H, RCH=CH₂), 4.45–4.64 (m, 16 H + 4 H, RCH₂F + RCHAr₂), 3.78–4.17 (m, br, 16 H, ArOCH₂R), 1.97–2.05 (m, 8 H, RCH₂C=C), 1.82 (s, 8 H, RCH₂CHAr₂), 1.28 (s, 48 H, CH₂).

^{13}C NMR: $\delta = 80.8$ (RCH_2F).

FAB-MS: $m/z = 1408.9$ (M^+), 1269.5 [$\text{M}^+ - (\text{CH}_2)_8\text{CH}=\text{CH}_2$].

IR (KBr): $\nu = 1641, 912$ ($\text{C}=\text{C}$), 1056 cm^{-1} ($\text{C}-\text{F}$).

2,8,14,20-Tetrakis(9-decenyl)-4,6,10,12,16,18,22,24-octa(methoxycarbonylmethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (3f):

To a suspension of **2a** (5.00 g, 4.81 mmol) and potassium carbonate (7.0 g, 51 mmol) in MeCN was added methyl-2-bromoethanoate (6.0 g, 39 mmol). The suspension was refluxed for 48 h, during which time another portion of methyl-2-bromoethanoate (39 mmol) was added. The reaction mixture was concentrated under reduced pressure, diluted with Et₂O (200 mL) and washed with water (3 × 200 mL). The yellowish organic layer was dried (MgSO_4), and concentrated under reduced pressure. The resulting yellow powder was subjected to column chromatography (SiO_2 ; EtOAc–isohexane, 3:1 v/v), and subsequently crystallized from MeOH, affording 4.28 g (55%) of off-white crystals, mp 93–96°C.

^1H NMR: $\delta = 6.60$ and 6.21 (each s, each 4H, ArH), 5.87–5.71 (m, 4H, $\text{RCH}=\text{CH}_2$), 4.97 and 4.91 (each d, each 4H, $\text{RCH}=\text{CH}_2$, $J_1 = 18$, $J_2 = 10$ Hz), 4.58 (t, 4H, RCHAr_2 , $J = 7.4$ Hz), 4.27, [s, 16H, $\text{ArOCH}_2\text{C}(\text{O})\text{OCH}_3$], 3.75 [s, 24H, $\text{C}(\text{O})\text{OCH}_3$], 2.10–1.95 (m, 8H, $\text{RCH}_2\text{C}=\text{C}$), 1.95–1.78 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.4–1.2 (m, 48H, CH_2).

^{13}C NMR: $\delta = 169.8$ ($\text{C}=\text{O}$), 154.5, 139.2 ($\text{RCH}=\text{CH}_2$), 128.5, 126.5, 114.1 ($\text{RCH}=\text{CH}_2$), 67.1 [$\text{ArOCH}_2\text{C}(\text{O})\text{OCH}_3$], 51.9 [$\text{C}(\text{O})\text{OCH}_3$], 35.7, 34.5, 33.8, 29.9, 29.7, 29.2, 29.0, 28.0.

FAB-MS: $m/z = 1615.2$ ($\text{M}^+ - \text{H}$), 1601.8 ($\text{M}^+ - \text{CH}_3$), 1543.2 [$\text{M}^+ - \text{CH}_2\text{C}(\text{O})\text{OCH}_3$].

IR (KBr): $\nu = 3077, 1642, 904$ ($\text{C}=\text{C}$), 1762, 1731 cm^{-1} ($\text{C}=\text{O}$).

2,8,14,20-Tetrakis(9-decenyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-4,6,10,12,16,18,22,24-octayl Octaacetate (3g):

To a suspension of **2a** (10.00 g, 9.6 mmol) in Ac₂O (100 mL) was added 0.5 mL of pyridine. The mixture was heated at 100°C for 1 h. The orange solution was carefully quenched with MeOH and concentrated under reduced pressure. The orange oil was precipitated once from MeOH and once from 2-propanol. The yellowish powder was subjected to column chromatography [SiO_2 ; petroleum ether (40–60°C)–EtOAc, 1:1 v/v]. The resulting yellowish oil was crystallized from 2-propanol giving 6.61 g (50%) of colorless crystals, mp 123°C.

^1H NMR (r.t.): $\delta = 6.90$ (s br, 4H, ArH), 5.79 (m, 4H, $\text{RCH}=\text{CH}_2$), 4.99 and 4.90 (each d, each 4H, $J_1 = 17.1$, $J_2 = 10.1$ Hz, $\text{RCH}=\text{CH}_2$), 4.14 (t, 4H, RCHAr_2 , $J = 7.23$ Hz), 2.15 [s br, 24H, $\text{ArOC}(\text{O})\text{CH}_3$], 2.01 (m, 8H, $\text{RCH}_2\text{C}=\text{C}$), 1.84 (s br, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.25 (s, 48H, CH_2).

^1H NMR (-50°C): $\delta = 7.35, 7.01, 6.78, 5.99$ (each s, each 2H, ArH), 5.82 (m, 4H, $\text{RCH}=\text{CH}_2$), 5.02 and 4.94 (each d, each 4H, $\text{RCH}=\text{CH}_2$, $J_1 = 18$, $J_2 = 10$ Hz), 4.1 (m, 4H, RCHAr_2), 2.40 and 2.11 (each s, each 12H, ArOCOCH_3), 2.05 (s br, 8H, $\text{RCH}_2\text{C}=\text{C}$), 1.70 (s br, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.22 (s, 48H, CH_2).

FAB-MS: $m/z = 1377.5$ ($\text{M}^+ - \text{H}$), 1335.5 ($\text{M}^+ - \text{CH}_2\text{C}=\text{O}$), 1292.6 [$\text{M}^+ - 2(\text{CH}_2\text{C}=\text{O})$].

IR (KBr): $\nu = 3076, 1641, 915$ ($\text{C}=\text{C}$), 1760 cm^{-1} ($\text{C}=\text{O}$).

2,8,14,20-Tetrakis(9-decenyl)-5,11,17,23-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-4,6,10,12,16,18,22,24-octayl Octaacetate (3h):

To a suspension of **2b** (8.3 g, 7.6 mmol) in Ac₂O (100 mL) was added 0.5 mL of pyridine. The mixture was heated at 120°C for 2 h. The slightly orange solution was cooled, carefully quenched with MeOH and concentrated under reduced pressure. The resulting yellow powder was recrystallized from MeOH, and subjected to column chromatography (SiO_2 ; petroleum ether–EtOAc, 1:1 v/v). The last fraction was collected and crystallized from isopropanol, to give 6.4 g (59%) of a white powder, mp 195–197°C.

^1H NMR (r.t.): $\delta = 5.9$ –5.7 (m, 4H, $\text{RCH}=\text{CH}_2$), 4.98 and 4.86 (each d, each 4H, $\text{RCH}=\text{CH}_2$, $J_1 = 18$, $J_2 = 10$ Hz), 4.1–3.9 (m, 4H, RCHAr_2), 2.4–1.6 (m, 52H, ArCH_3 , $\text{RCH}_2\text{C}=\text{C}$, $\text{ArOC}(\text{O})\text{CH}_3$ and RCHCHAr_2), 1.4–1.2 (s, 48H, CH_2).

^1H NMR (CD_2Cl_2 , -50°C): $\delta = 7.48$ and 6.40 (each d, each 2H, ArH), 5.9–5.7 (m, 4H, $\text{RCH}=\text{CH}_2$), 4.98 and 4.86 (each d, each 4H, $\text{RCH}=\text{CH}_2$, $J_1 = 18$, $J_2 = 10$ Hz), 4.1–3.9 (m, 4H, RCHAr_2), 2.60 (m, 20H, ArCH_3 and $\text{RCH}_2\text{C}=\text{C}$), 2.2 [s, 24H, $\text{ArOC}(\text{O})\text{CH}_3$], 1.7 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.4–1.2 (s, 48H, CH_2).

FAB-MS: $m/z = 1434$ (M^+), 1392 ($\text{M}^+ - \text{CH}_2\text{C}=\text{O}$), 1349 [$\text{M}^+ - 2(\text{CH}_2\text{C}=\text{O})$], 1307 [$\text{M}^+ - 3(\text{CH}_2\text{C}=\text{O})$].

IR (KBr): $\nu = 3076, 904$ ($\text{C}=\text{C}$), 1765, 1720 cm^{-1} ($\text{C}=\text{O}$).

2,8,14,20-Tetrakis(9-decenyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-4,5,6,10,11,12,16,17,18,22,23,24-dodecayl Dodecaacetate (3i):

To a pink suspension of **2c** (10.0 g, 9.05 mmol) in Ac₂O (100 mL) was added 0.5 mL of pyridine. The mixture was heated at 100°C for 2 h. The resulting orange solution was cooled, carefully quenched with MeOH and concentrated under reduced pressure. The orange paste was precipitated once from isopropanol–acetone (2:1 v/v) and once from MeOH– CH_2Cl_2 (4:1 v/v). The yellow needle crystals were subjected to column chromatography (SiO_2 ; EtOAc). The resulting yellowish oil was crystallized from MeOH– CH_2Cl_2 (4:1 v/v), affording 8.53 g (58%) of an off-white microcrystalline powder, mp 206–209°C.

^1H NMR (r.t.): $\delta = 7.0$ –6.8 (s br, 4H, ArH), 5.89–5.68 (m, 4H, $\text{RCH}=\text{CH}_2$), 4.98 and 4.91 (each d, each 4H, $\text{RCH}=\text{CH}_2$, $J_1 = 17.5$, $J_2 = 12.6$ Hz), 4.09 (t, 4H, RCHAr_2 , $J = 7.5$ Hz), 2.4–1.7 [m, 52H, $\text{ArOC}(\text{O})\text{CH}_3$, $\text{RCH}_2\text{C}=\text{C}$ and $\text{RCH}_2\text{CHAr}_2$], 1.4–1.2 (s, 48H, CH_2).

^1H NMR (CD_2Cl_2 , -50°C): $\delta = 7.22$ and 6.03 (each s, each 2H, ArH), 5.85–5.54 (m, 4H, $\text{RCH}=\text{CH}_2$), 4.96 and 4.89 (each d, each 4H, $\text{RCH}=\text{CH}_2$, $J_1 = 18$, $J_2 = 13$ Hz), 4.0–3.8 (m, 4H, RCHAr_2), 2.5–1.4 [m, 52H, $\text{ArOC}(\text{O})\text{CH}_3$, $\text{RCH}_2\text{C}=\text{C}$ and $\text{RCH}_2\text{CHAr}_2$], 1.4–1.0 (s, 48H, CH_2).

FAB-MS: $m/z = 1566.3$ ($\text{M}^+ - \text{CH}_2\text{C}=\text{O}$), 1524.2 [$\text{M}^+ - 2(\text{CH}_2\text{C}=\text{O})$], 1481.2 [$\text{M}^+ - 3(\text{CH}_2\text{C}=\text{O})$], 1439.0 [$\text{M}^+ - 4(\text{CH}_2\text{C}=\text{O})$], 1397.2 [$\text{M}^+ - 5(\text{CH}_2\text{C}=\text{O})$].

IR (KBr): $\nu = 3077, 1641, 899$ ($\text{C}=\text{C}$), 1781 cm^{-1} ($\text{C}=\text{O}$).

1,21,23,25-Tetrakis[11-thiaheicosyl]-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocin[5,4-*i*:5',4'-*i'*]benzo[1,2-*d*:5,4-*d'*]bis[1,3]benzodioxocin (4a):

To a solution of **3a** (1.00 g, 0.92 mmol) in THF (50 mL) was added 1-decanethiol (2 mL, 9.65 mmol) and 9-BBN (0.5 mL, 0.5 M in THF) at 0°C. The mixture was stirred for 16 h during which time it was allowed to warm to r.t. The yellowish solution was concentrated at reduced pressure, diluted with CH_2Cl_2 (200 mL), washed with water (2 × 200 mL), dried (MgSO_4) and concentrated under reduced pressure. The residue was crystallized from diisopropyl ether giving 1.13 g (69%) of a white solid, mp 107–108°C.

^1H NMR: $\delta = 7.08$ and 6.46 (each s, each 4H, ArH), 5.74 and 4.43 (each d, each 4H, OCH_2O , $J = 7.2$ Hz), 4.72 (t, 4H, RCHAr_2 , $J = 7.9$ Hz), 2.49 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7.5$ Hz), 2.21 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.57 (m, 16H, $\text{RCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}'$), 1.32 (m, 112H, CH_2), 0.88 (t, 12H, RCH_3).

FAB-MS: $m/z = 1786.8$ (M^+).

IR (KBr): $\nu = 969\text{ cm}^{-1}$ (OCH_2O).

1,21,23,25-Tetrakis[11-thianonadecyl]-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocin[5,4-*i*:5',4'-*i'*]benzo[1,2-*d*:5,4-*d'*]bis[1,3]benzodioxocin (4a(8)):

Starting from **3a** (0.80 g, 0.73 mmol) and 1-octanethiol (1.5 mL, 8.6 mmol) compound **4a(8)** was prepared analogously to the preparation of **4a**. The product was subjected to column chromatography (SiO_2 ; CH_2Cl_2), and was recrystallized from isopropanol–acetone (3:1 v/v), affording 0.91 g (71%) of a white powder, mp 70–72°C.

^1H NMR: $\delta = 7.09$ and 6.47 (each s, each 4H, ArH), 5.73 and 4.42 (each d, each 4H, OCH_2O , $J = 7.2$ Hz), 4.71 (t, 4H, RCHAr_2 ,

$J = 8.0$ Hz), 2.49 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7.4$ Hz), 2.23–2.15 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.60–1.49 (m, 16H, $\text{RCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}'$), 1.49–1.2 (m, 96H, CH_2), 0.87 (t, 12H, RCH_3 , $J = 6.5$ Hz).

FAB-MS: $m/z = 1674.0$ (M^+), 1561.4 [$\text{M} - (\text{CH}_2)_8\text{H}^+$], 1528.3 [$\text{M} - \text{HS}(\text{CH}_2)_8\text{H}^+$].

IR (KBr): $\nu = 969$ cm^{-1} (OCH_2O).

1,21,23,25-Tetrakis[11-thiatricosyl]-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-*i*:5',4'-*i'*]benzo[1,2-*d*:5,4-*d'*]bis[1,3]benzodioxocin [4a (12)]:

Starting from **3a** (0.84 g, 0.77 mmol) and 1-dodecanethiol (1.00 g, 4.2 mmol) compound **4a (12)** was prepared analogously to the preparation of **4a**. The product was subjected to column chromatography (SiO_2 ; CH_2Cl_2) and recrystallized from isopropanol–acetone (2:1 v/v), affording 1.06 g (73%) of a white powder, mp 67–70°C.

$^1\text{H NMR}$: $\delta = 7.03$ and 6.41 (each s, each 4H, ArH), 5.67 and 4.36 (each d, each 4H, OCH_2O , $J = 7.2$ Hz), 4.65 (t, 4H, RCHAr_2 , $J = 7.9$ Hz), 2.43 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7.4$ Hz), 2.16–2.09 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.54–1.44 (m, 16H, $\text{RCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}'$), 1.4–1.2 (m, 128H, CH_2), 0.81 (t, 12H, RCH_3 , $J = 6.5$ Hz).

FAB-MS: $m/z = 1897.6$ ($\text{M} - \text{H}^+$), 1698.2 [$\text{M} - \text{HS}(\text{CH}_2)_{12}\text{H}^+$].

IR (KBr): $\nu = 969$ cm^{-1} (OCH_2O).

1,21,23,25-Tetrakis[11-thiaheicosyl]-7,11,15,28-tetramethyl-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-*i*:5',4'-*i'*]benzo[1,2-*d*:5,4-*d'*]bis[1,3]benzodioxocin (4b):

Starting from **3b** (5.08 g, 4.44 mmol) and 1-decanethiol (6 mL, 41 mmol) compound **4b** was prepared analogously to the preparation of **4a**. The resulting yellowish oil was subjected to column chromatography (SiO_2 ; CH_2Cl_2 –petroleum ether (60–80°C), 3:1 v/v) and the resulting red powder was subsequently recrystallized from acetone, affording 5.60 g (68%) of a white microcrystalline powder: mp 45–47°C.

$^1\text{H NMR}$: $\delta = 6.95$ (s, 4H, ArH), 5.89 and 4.27 (each d, each 4H, OCH_2O , $J = 7.5$ Hz), 4.76 (t, 4H, RCHAr_2 , $J = 8$ Hz), 2.50 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7$ Hz), 2.19 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.56 (m, 16H, $\text{RCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}'$), 1.43–1.2 (m, 112H, CH_2), 0.90 (t, 12H, RCH_3 , $J = 7.0$ Hz).

FAB-MS: $m/z = 1842$ (M^+), 1701 [$\text{M}^+ - (\text{CH}_2)_{10}\text{H}$].

IR (KBr): $\nu = 979$ cm^{-1} (OCH_2O).

4,6,10,12,16,18,22,24-Octamethoxy-2,8,14,20-tetrakis(11-thiaheicosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4c):

Starting from **3c** (1.00 g, 0.86 mmol) and 1-decanethiol (2 mL, 9.6 mmol) compound **4c** was prepared analogously to the preparation of **4a**. The resulting white paste was subjected to column chromatography (SiO_2 ; CH_2Cl_2) and subsequently crystallized from acetone, affording 1.40 g (88%) of colorless needle-shaped crystals, mp 75–77°C.

$^1\text{H NMR}$: $\delta = 6.51$ and 6.23 (each s, each 4H, ArH), 4.37 (t, 4H, RCHAr_2 , $J = 7.3$ Hz), 3.55 (s, 24H, ArOCH_3), 2.41 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7.4$ Hz), 1.80–1.65 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.55–1.40 (s, 16H, $\text{RCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}'$ and H_2O), 1.32–1.12 (s, 112H, CH_2), 0.82 (t, 12H, RCH_3 , $J = 6.5$ Hz).

FAB-MS: $m/z = 1850.2$ (M^+), 1536.0 [$\text{M}^+ - (\text{CH}_2)_{10}\text{S}(\text{CH}_2)_{10}\text{H}$].

IR (KBr): $\nu = 1299$ cm^{-1} (OCH_3).

4,6,10,12,16,18,22,24-Octamethoxy-2,8,14,20-tetrakis(11-thianonadecyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene [4c(8)]:

Starting from **3c** (0.6 g, 0.52 mmol) and 1-octanethiol (0.5 g, 3.4 mmol) compound **4c(8)** was prepared analogously to the preparation of **4c**. The product was subjected to column chromatography (SiO_2 , CH_2Cl_2 –EtOAc, 5:1 v/v), and subsequently recrystallized from acetone, affording 0.63 g (70%) of white plate crystals, mp 83–85°C.

$^1\text{H NMR}$: $\delta = 6.58$ and 6.31 (each s, each 4H, ArH), 4.43 (t, 4H, RCHAr_2 , $J = 7.2$ Hz), 3.58 (s, 24H, ArOCH_3), 2.48 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7.4$ Hz), 1.85–1.70 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.60–1.45 (m, 16H, $\text{RCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}'$), 1.45–1.2 (m, 96H, CH_2), 0.87 (t, 12H, RCH_3 , $J = 6.6$ Hz).

FAB-MS: $m/z = 1737.2$ (M^+), 1452.1 [$\text{M} - (\text{CH}_2)_{10}\text{S}(\text{CH}_2)_8\text{H}^+$].

IR (KBr): $\nu = 1300$ cm^{-1} (OCH_3).

4,6,10,12,16,18,22,24-Octamethoxy-2,8,14,20-tetrakis(11-thiaicosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene [4c(9)]:

Starting from **3c** (0.6 g, 0.52 mmol) and 1-nonanethiol (2 mL, 10 mmol) compound **4c(9)** was prepared analogously to the preparation of **4a**. The product was subjected to column chromatography (SiO_2 ; CH_2Cl_2) and recrystallized from acetone, affording 0.63 g (68%) of a white microcrystalline powder, mp 83–85°C.

$^1\text{H NMR}$: $\delta = 6.59$ and 6.31 (each s, each 4H, ArH), 4.44 (t, 4H, RCHAr_2 , $J = 7.3$ Hz), 3.59 (s, 24H, ArOCH_3), 2.49 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7.4$ Hz), 1.9–1.7 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.65–1.45 (m, 16H, $\text{RCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}'$), 1.4–1.2 (m, 104H, CH_2), 0.88 (t, 12H, RCH_3 , $J = 6.5$ Hz).

FAB-MS: $m/z = 1795.8$ ($\text{M} + \text{H}^+$), 1494.2 [$\text{M} - (\text{CH}_2)_{10}\text{S}(\text{CH}_2)_9\text{H}^+$].

IR (KBr): $\nu = 1299$ cm^{-1} (OCH_3).

4,6,10,12,16,18,22,24-Octamethoxy-2,8,14,20-tetrakis(11-thiadocosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene [4c(11)]:

Starting from **3c** (0.6 g, 0.52 mmol) and 1-undecanethiol (2 mL, 9 mmol) compound **4c(11)** was prepared analogously to the preparation of **4c**. The product was subjected to column chromatography (SiO_2 ; CH_2Cl_2) and was recrystallized from acetone, affording 0.78 g (77%) of a white powder, mp 82–84°C.

$^1\text{H NMR}$: $\delta = 6.59$ and 6.31 (each s, each 4H, ArH), 4.44 (t, 4H, RCHAr_2 , $J = 7.3$ Hz), 3.59 (s, 24H, ArOCH_3), 2.49 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7.4$ Hz), 1.9–1.7 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.65–1.45 (m, 16H, $\text{RCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}'$), 1.45–1.2 (m, 120H, CH_2), 0.88 (t, 12H, RCH_3 , $J = 6.5$ Hz).

FAB-MS: $m/z = 1906.4$ (M^+), 1719.1 [$\text{M} - \text{S}(\text{CH}_2)_{11}\text{H}^+$].

IR (KBr): $\nu = 1299$ cm^{-1} (OCH_3).

4,6,10,12,16,18,22,24-Octamethoxy-2,8,14,20-tetrakis(11-thiatricosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene [4c(12)]:

Starting from **3c** (0.6 g, 0.52 mmol) and 1-dodecanethiol (2 mL, 8.3 mmol) compound **4c(12)** was prepared analogously to the preparation of **4c**. The product was subjected to column chromatography (SiO_2 ; CH_2Cl_2) and was recrystallized from acetone, affording 0.63 g (62%) of a white microcrystalline powder, mp 76–78°C.

$^1\text{H NMR}$: $\delta = 6.59$ and 6.40 (each s, each 4H, ArH), 4.44 (t, 4H, RCHAr_2 , $J = 7.3$ Hz), 3.59 (s, 24H, ArOCH_3), 2.49 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7.3$ Hz), 1.95–1.7 (m, 8H, $\text{RCH}_2\text{CHAr}_2$), 1.65–1.45 (m, 16H, $\text{RCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}'$), 1.4–1.2 (m, 128H, CH_2), 0.87 (t, 12H, RCH_3 , $J = 6.5$ Hz).

FAB-MS: $m/z = 1962.0$ (M^+), 1621.6 [$\text{M} - (\text{CH}_2)_{10}\text{S}(\text{CH}_2)_{12}\text{H}^+$].

IR (KBr): $\nu = 1300$ cm^{-1} (OCH_3).

4,5,6,10,11,12,16,17,18,22,23,24-Dodecamethoxy-2,8,14,20-tetrakis(11-thiaheicosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4d):

Starting from **3d** (1.25 g, 0.98 mmol) and 1-decanethiol (2 mL, 9.6 mmol) compound **4d** was prepared analogously to the preparation of **4a**. The resulting yellowish oil was subjected to column chromatography (SiO_2 ; petroleum ether–EtOAc, 9:1 v/v) and subsequently crystallized from acetone, affording 1.13 g (58%) of an off-white powder, mp 67–69°C.

$^1\text{H NMR}$: $\delta = 6.41$ (s, 4H, ArH), 4.48 (t, 4H, RCHAr_2 , $J = 7.4$ Hz), 3.78 (s, 12H, ArOCH_3), 3.61 (s, 24H, ArOCH_3), 2.49 (t, 16H, $\text{RCH}_2\text{SCH}_2\text{R}'$, $J = 7.6$ Hz), 1.70–1.85 (m, 8H,

RCH_2CHAr_2), 1.60–1.45 (m, 16 H, $RCH_2CH_2SCH_2CH_2R'$), 1.40–1.20 (m, 112 H, CH_2), 0.86 (t, 12 H, RCH_3 , $J = 6.6$ Hz).

FAB-MS: $m/z = 1970$ ($M - H^+$), 1656.8 [$M - (CH_2)_{10}S(CH_2)_{10}H^+$].

IR (KBr): $\nu = 1410, 1313\text{ cm}^{-1}$ (OCH_3).

4,6,10,12,16,18,22,24-Octa(2-fluoroethoxy)-2,8,14,20-tetrakis(11-thiahenicosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25), 3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4e):

To a solution of **3e** (0.50 g, 0.35 mmol) in THF (25 mL) at 0 °C was added 1-decanethiol (0.69 g, 3.93 mmol) and 9-BBN (0.2 mL of a 0.5 M solution in THF, 0.1 mmol). The solution was stirred for 16 h, during which time it was allowed to warm slowly to r.t. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed with water (2×100 mL). The organic layer was dried ($MgSO_4$), and recrystallized twice from MeOH, affording 0.29 g (39 %) of a white powder, mp 67–70 °C.

1H NMR: $\delta = 6.59$ (s br, 4 H, ArH), 6.27 (s, 4 H, ArH), 4.43–4.62 (m, 16 H + 4 H, RCH_2F and $RCHAr_2$), 3.94–4.06 (br, 16 H, $ArOCH_2R$), 2.44–2.51 (m, 16 H, RCH_2SCH_2R'), 1.81 (s, br, 8 H, RCH_2CHAr_2), 1.55 (s br, 16 H, $RCH_2CH_2SCH_2CH_2R'$), 1.29 (s, 112 H, CH_2), 0.87 (t, 12 H, CH_3 , $J = 6.7$ Hz).

^{13}C NMR: $\delta = 80.9$ (RCH_2F), 31.9 (RCH_2SCH_2R').

FAB-MS: $m/z = 2106.8$ (M^+), 1793.1 [$M^+ - (CH_2)_{10}S(CH_2)_{10}H^+$].

4,6,10,12,16,18,22,24-Octa(methoxycarbonylmethoxy)-2,8,14,20-tetrakis(11-thiahenicosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25), 3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4f):

Starting from compound **3f** (3.28 g, 2.03 mmol) and 1-decanethiol (3 mL, 14.6 mmol) was prepared compound **4f** analogously to the preparation of **4a**. The yellowish reaction mixture was concentrated under reduced pressure, diluted with EtOAc (300 mL) and washed with water (3×500 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The white paste was precipitated from acetone–MeOH, 1:3 (v/v) and the resulting off-white powder was subjected to column chromatography (SiO_2 ; petroleum ether–EtOAc, 2:3 v/v). Subsequent crystallization from acetone–EtOH (1:3 v/v) afforded 3.31 g (72 %) of a white powder, mp 78–81 °C.

1H NMR: $\delta = 6.60$ and 6.21 (each s, each 4 H, ArH), 4.58 (t, 4 H, $RCHAr_2$, $J = 7.2$ Hz), 4.27 [s, 16 H, $ArOCH_2C(O)OCH_3$], 3.75 [s, 24 H, $C(O)OCH_3$], 2.49 (t, 16 H, RCH_2SCH_2R' , $J = 7.3$ Hz), 1.83 (m, 8 H, RCH_2CHAr_2), 1.56 (m, 16 H, $RCH_2CH_2SCH_2CH_2R'$), 1.26 (m, 112 H, CH_2), 0.88 (t, 12 H, RCH_3 , $J = 6.6$ Hz).

FAB-MS: $m/z = 2315.1$ (M^+), 2000.9 [$M^+ - (CH_2)_{10}S(CH_2)_{10}H$].

IR (KBr): $\nu = 1763, 1732\text{ cm}^{-1}$ ($C=O$).

2,8,14,20-Tetrakis(11-thiahenicosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25), 3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octyl Octaacetate (4g):

Starting from **3g** (2.00 g, 1.45 mmol) and 1-decanethiol (2.5 mL, 12 mmol) compound **4g** was prepared analogously to the preparation of **4a**. The resulting colorless oil was subjected to column chromatography (SiO_2 ; CH_2Cl_2) and subsequently crystallized from acetone, affording 2.27 g (75 %) of colorless crystals, mp 100–102 °C.

1H NMR (r.t.): $\delta = 6.90$ (s br, 4 H, ArH), 4.14 (t, 4 H, $J = 7.2$ Hz, $RCHAr_2$), 2.49 (t, 16 H, $J = 7.3$ Hz, RCH_2SCH_2R'), 2.17 [s br, 24 H, $ArOC(O)CH_3$], 1.84 (s, br, 8 H, RCH_2CHAr_2), 1.56 (m, 16 H, $RCH_2CH_2SCH_2CH_2R'$), 1.26 (s, 112 H, CH_2), 0.88 (t, 12 H, $J = 6.6$ Hz, RCH_3).

FAB-MS: $m/z = 2074.4$ (M^+), 2033.5 ($M^+ - CH_2 = C=O$), 1990.8 [$M^+ - 2(CH_2 = C=O)$].

IR (KBr): $\nu = 1766, 1758\text{ cm}^{-1}$ ($C=O$).

2,8,14,20-Tetrakis(11-thiahenicosyl)-5,11,17,23-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25), 3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octyl Octaacetate (4h):

Starting from **3h** (4.00 g, 2.79 mmol) and 1-decanethiol (2.5 mL, 12 mmol) compound **4h** was prepared analogously to the prepara-

tion of **4a**. The resulting yellowish paste was subjected to column chromatography (SiO_2 ; petroleum ether–EtOAc, 2:1, v/v) and subsequently crystallized from isopropanol, affording 4.65 g (79 %) of a white powder, mp 172–173 °C.

1H NMR: $\delta = 4.1$ –3.9 (m, 4 H, $RCHAr_2$), 2.47 (t, 16 H, RCH_2SCH_2R' , $J = 7.6$ Hz), 2.35–2.05 (m, 20 H, $ArCH_3$ and RCH_2CHAr_2), 2.05–1.65 [m, 24 H, $ArOC(O)CH_3$], 1.65–1.45 (m, 16 H, $RCH_2CH_2SCH_2CH_2R'$), 1.40–1.20 (m, 112 H, CH_2), 0.88 (t, 12 H, RCH_3 , $J = 6.5$ Hz).

FAB-MS: $m/z = 2131.6$ (M^+), 2089.0 ($M^+ - CH_2 = C=O$), 2045.8 [$M^+ - 2(CH_2 = C=O)$].

IR (KBr): $\nu = 1765\text{ cm}^{-1}$ ($C=O$).

2,8,14,20-Tetrakis(11-thiahenicosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25), 3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecyl Dodecaacetate (4i):

Starting from **3i** (5.00 g, 3.11 mmol) and 1-decanethiol (6 mL, 29 mmol) compound **4i** was prepared analogously to the preparation of **4a**. The resulting oil was precipitated from isopropanol and subsequently subjected to column chromatography (SiO_2 ; petroleum ether–EtOAc, 2:1 v/v). The first fraction was crystallized from isopropanol, giving 5.05 g (70 %) of a white microcrystalline powder, mp 174–176 °C.

1H NMR: $\delta = 4.12$ (t, 4 H, $RCHAr_2$, $J = 7.5$ Hz), 2.49 (t, 16 H, RCH_2SCH_2R' , $J = 7.5$ Hz), 2.35–1.70 [m, 44 H, $ArOC(O)CH_3$ and RCH_2CHAr_2], 1.55–1.45 (m, 16 H, $RCH_2CH_2SCH_2CH_2R'$), 1.40–1.20 (m, 112 H, CH_2), 0.89 (t, 12 H, RCH_3 , $J = 6.6$ Hz).

FAB-MS: $m/z = 2306.7$ (M^+), 2248.0 ($M^+ - CH_2 = C=O$), 2204.4 [$M^+ - 2(CH_2 = C=O)$], 2161.8 [$M^+ - 3(CH_2 = C=O)$], 2119.0 [$M^+ - 4(CH_2 = C=O)$].

IR (KBr): $\nu = 1782\text{ cm}^{-1}$ ($C=O$).

4,6,10,12,16,18,22,24-Octa(propylcarbamoylmethoxy)-2,8,14,20-tetrakis(11-thiahenicosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25), 3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (5):

To a solution of **4f** (0.2 g, 86.5 μ M) in 20 mL of THF was added propylamine (1 g, 17 mM). After 48 h at r.t. the solution was concentrated under reduced pressure and crystallized from acetone, affording 0.18 g (82 %) of a white powder, mp 153–155 °C.

1H NMR: $\delta = 6.84$ [t, 8 H, $C(O)NHR$, $J = 6.3$ Hz], 6.75 and 6.26 (each s br, each 4 H, ArH), 4.46 (t, 4 H, $RCHAr_2$, $J = 7.3$ Hz), 4.08 (m br, 16 H, $ArOCH_2CONHR$), 3.4–4.1 [m, 16 H, $C(O)NHCH_2CH_2CH_3$], 2.48 (t, 16 H, RCH_2SCH_2R' , $J = 7.3$ Hz), 1.86 (m, 8 H, RCH_2CHAr_2), 1.56 [m, 16 H + 16 H, $RCH_2CH_2SCH_2CH_2R' + C(O)NHCH_2CH_2CH_3$], 1.26 (m, 112 H, CH_2), 0.92 (m, 36 H, RCH_3).

FAB-MS: $m/z = 2531.9$ (M^+),

2430.9 [$M^+ - CH_2C(O)NHCH_2CH_2CH_3$].

IR (KBr): $\nu = 3435, 3350$ (NH), 1693 ($C=O$), 1536 (CONHR), 1302 cm^{-1} ($C-N$).

2,8,14,20-Tetrakis(11-thiahenicosyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25), 3,5,7(28),9,11,13(27),15,17,19(26), 21,23-dodecaene-4,6,10,12,16,18,22,24-octol (6):

To a solution of **4g** (0.56 g, 0.27 mmol) in 200 mL of EtOH and 100 mL of THF was added freshly activated zinc powder (0.5 g, 7.7 mmol). The grey suspension was refluxed for 72 h, and subsequently filtered. The residue was washed with acetone (500 mL). The filtrate was concentrated under reduced pressure. The off-white material was dissolved in CH_2Cl_2 (300 mL) and washed with 1 M hydrochloric acid (3×300 mL), and water (3×300 mL). The CH_2Cl_2 solution was filtered. The filtrate was concentrated under reduced pressure, giving a white compound that was recrystallized once from EtOH, and once from acetone, affording 0.38 g (81 %) of a white powder, mp 222–225 °C.

1H NMR: $\delta = 8.39$ and 7.89 (each s, each 4 H, ArOH), 7.45 and 6.22 (each s, each 4 H, ArH), 4.29 (t, 4 H, $RCHAr_2$, $J = 7.4$ Hz), 2.87 (s, H_2O), 2.50 (t, 16 H, RCH_2SCH_2R' , $J = 7.2$ Hz), 2.25 (m, 8 H, RCH_2CHAr_2), 1.57 (m, 16 H, $RCH_2CH_2SCH_2CH_2R'$), 1.4–1.2 (m, 112 H, CH_2), 0.87 (t, 12 H, RCH_3 , $J = 6.8$ Hz).

FAB-MS: $m/z = 1738.6$ (M^+), 1425.3 [$M^+ - (CH_2)_{10}S(CH_2)_{10}H$].
IR (KBr): $\nu = 3370\text{ cm}^{-1}$ (OH).

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