Synthesis and Properties of 7,7,12,12-Tetramethyl-1,4-dioxacyclotetradecane-8,9,10,11-tetrone

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Dedicated to Professor Werner Tochtermann on the occasion of his 65th birthday

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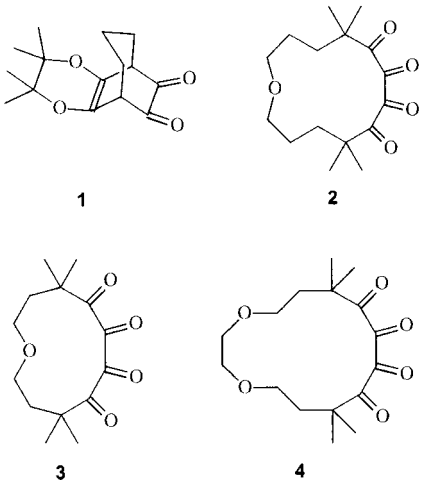
The fourteen-membered ring of 7,7,12,12-tetramethyl-1,4-dioxacyclotetradecane-8,9,10,11-tetrone (**4**) was built up from 1,2-bis(2′-chloroethoxy)ethane, two units derived from isobutyric acid and acetylene. Key intermediates were 2,2,11,11-tetramethyl-5,8-dioxadodecane-1,12-diol (**8**), 7,7,12,12-tetramethyl-1,4-dioxa-9-cyclotetradecyne-2,8-diol protected by one tetrahydropyran group (**15**), and 8,11-dihydroxy-7,7,12,12-tetramethyl-1,4-dioxacyclotetradecane-9,10-dione (**18**). X-ray investigation on single crystals of the (*R*,*S*) isomer **18a** revealed a transannular interaction between the dioxaethane bridge and the dicarbonyl moiety. Calculations (HF/6-31G*) on **4** predict relatively short distances between the oxygen atoms of the dioxyethane bridge and the $(CO)_4$ part. Investigations by means of cyclic voltammetry, PE and UV/Vis spectroscopy on **4** reveal an interaction between the dioxaethane bridge and the $(CO)_4$ group.

The juxtaposition of carbonyl groups increases the acceptor properties of a $(CO)_x$ moiety with increasing x.[1] As a result the tendency to form stable hydrates increases with the number of CO groups.[2] Recently, we explored different ways of stabilizing the $(CO)_x$ moiety. In one approach we explored homoconjugation with an electron-rich double-bond system such as **1**.[3] In another effort the transannular donor−acceptor interactions of a $(CO)_4$ moiety with an ether oxygen atom was probed. In the case of the thirteen-membered ring system **2**[4] we found no interaction between the ether oxygen atom and the $(CO)_4$ unit. However, in the eleven-membered ring system **3**[5] a considerable transannular interaction between the ether oxygen center and the $(CO)_4$ group was evidenced by X-ray and CV studies. To explore donor−acceptor effects of two ether oxygen atoms in the fourteen-membered ring system we embarked in the synthesis of 7,7,12,12-tetramethyl-1,4-dioxacyclotetradecane-8,9,10,11-tetrone (**4**). In this paper we describe in detail our route to **4** and some of its properties.



1 **2** **3** **4**

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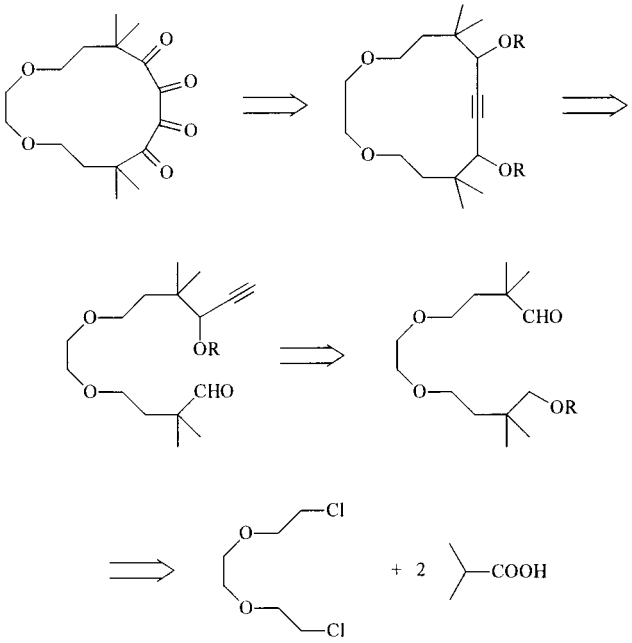
Results

Syntheses

As in our preceding synthesis of cyclic vicinal tetraketones we substitute the carbon atoms adjacent to the $(CO)_4$ moiety by two methyl groups each to prevent enolization. Our strategy to build up the fourteen-membered ring of **4** is outlined in Scheme 1.



Scheme 1. Retrosynthetic analysis of **4**

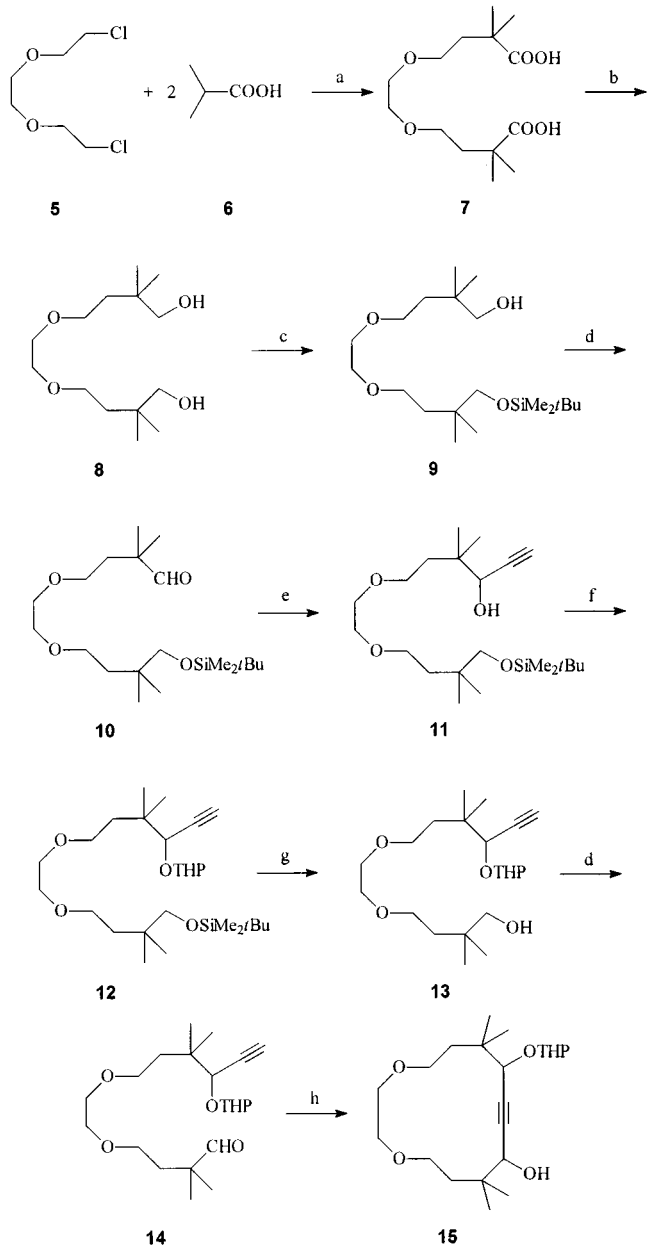
  1434−193X/99/0606−1303 $ 17.50+.50/0

The ring system is built up from 1,2-bis(2′-chloroethoxy)-ethane (**5**),[7] two units derived from isobutyric acid and acetylene. The scheme shows that the central C_2O_2 unit of the tetraketone fragment originates from the acetylene building block, while the terminal CO groups and the adjacent $(CH_3)_2C$ units stem from the isobutyric acid. This route makes use of an earlier observation[5] that the ring closure with an acetylene unit works very well even in the case of an eleven-membered ring.

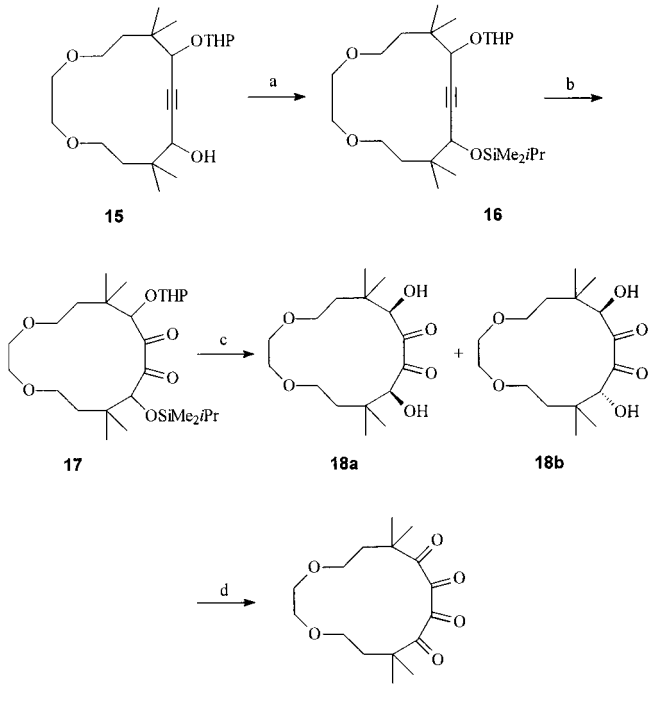
Our synthesis of **4** is outlined in Scheme 2. It makes extensive use of selective protection and deprotection of alcohol functions[6] and starts with the reaction of **5**[7] with the dilithium salt of isobutyric acid (**6**) following a protocol first suggested by Newkome et al.,[8] to give 2,2,11,11-tetramethyl-5,8-dioxadodecanedioic acid (**7**), isolated as bis(diisopropylammonium) salt. The diacid was readily reduced with $LiAlH_4$ and the resulting diol **8** was monoprotected by treating **8** with *tert*-butyldimethylsilyl chloride (TBSCl)[6] in presence of imidazole to yield **9**. The oxidation of the remaining alcohol function in **9** by using the Swern procedure[9] afforded the aldehyde **10**. Reaction of the latter with the lithium salt of acetylene and subsequent protection of the alcohol **11** with dihydropyran (DHP)[10] yielded **12**.

We used this protecting group because it allows at a later stage a selective deprotection of the TBS group introduced before. The disadvantage of introducing the THP group is the generation of a second stereogenic center, which increases the number of isomers of **12** to two diastereomeric pairs of enantiomers. These isomers were not separated and thus the resulting NMR spectra were rather complex. Selective deprotection of the primary alcohol **12** by treatment with tetrabutylammonium fluoride[11] and subsequent oxidation[9] of the alcohol **13** yielded the aldehyde **14**. The ring closure[12] of **14** to **15** could be achieved in 77% yield by transformation of the alkyne unit to the corresponding anion with lithium bis(trimethylsilyl)amide.[13] The ring closure generates a third stereogenic center in **15**. This in turn gave rise to a rather complex NMR pattern.

The resulting alcohol function from the ring closure was protected with the isopropyldimethylsilyl (IPS) group.[14] We chose the IPS group because it can be cleaved under mild conditions together with the THP group, it is stable under the oxidation conditions applied and it is sterically not too demanding. The alkyne unit in the resulting species, **16**, was oxidized with sodium periodate in presence of catalytic amounts of RuO_2[15] to yield the yellow diketone **17**



Scheme 2. a) *n*BuLi, iPr_2NH/THF; b) $LiAlH_4$/THF; c) *t*BuMe$_2$SiCl/CH_2Cl_2; d) DMSO/$(COCl)_2$/NEt_3; e) *n*BuLi, C_2H_2/THF; d) H^+, DHP/CH_2Cl_2; f) Bu_4NF/THF; g) $LiN(SiMe_3)_2$/THF



Scheme 3. a) Me$_2$*i*PrSiCl, 2,6-lutidine/CH_2Cl_2; b) $NaIO_4$, RuO_2/CCl_4; c) H^+/CH_3OH; d) NBS/CCl_4

(Scheme 3). Deprotection afforded a mixture of diastereomers **18a** and **18b**, which could be separated by HPLC into the *meso* derivative (**18a**) and the racemate **18b**. The oxidation of **18** to the tetraketone **4** could be achieved with NBS in CCl_4.[16] The procedure was used because any contact with water and other nucleophiles also during reaction and workup can be avoided.

Structural and Spectroscopic Investigations

We were able to grow single crystals of **18**. The molecular structure of the "*syn*" isomer **18a** is shown in Figure 1. These investigations allowed us to assign the configurations of the two diastereomers **18a** [(*R*,*S*) configuration at the secondary alcohol functions] and **18b** [(*R*,*R*) or (*S*,*S*) configuration at the secondary alcohol functions].

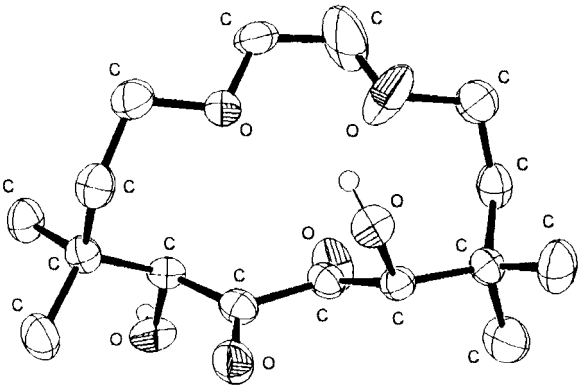


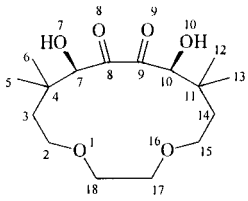
Figure 1. Molecular structure of **18a**

A detailed structural analysis provides information on possible transannular interactions between the C_2O_2 unit and the two ether oxygen atoms. As Figure 1 shows, one of the OH groups of **18a** forms an intramolecular hydrogen bond with the opposite oxygen atom of the ether group. In Table 1 the most relevant distances of **18a** are compared with those of **19a**.[5] It is found that the transannular distances between the ether oxygen atom(s) and the opposite carbonyl groups are 0.3−0.6 Å longer in the 14-membered as compared to the 11-membered ring,[5] but they are still smaller than the expected van der Waals distances (3.4 Å)[17] and the transannular distances encountered in **20a** (4.6−5.3 Å),[5] the precursor to **2**.

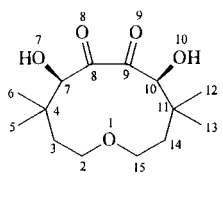
Table 1. Selected geometrical parameters (distances in Å) of **18a** and **19a**

	19a	**18a**
C7−C8	1.511(3)	1.519(7)
C8−C9	1.530(2)	1.551(7)
C9−C10	1.534(3)	1.518(6)
C8−O8	1.210(2)	1.221(6)
C9−O9	1.215(2)	1.211(5)
O1···C8	2.574(2)	3.139(6)
O16···C9	2.913(2)[a]	3.128(7)
O10···O16		2.686(7)

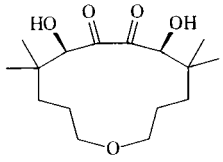
[a] Distance O1···C9.



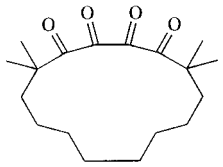
18a



19a



20a



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Since structural data of **4** were not available, we optimized the geometrical parameters of **4** by using the RHF-SCF method applying a 6-31G* basis set.[18] This procedure was used because it reproduced the geometrical parameters of **18a** very close to those found in the crystal. The molecular structure found is shown in Figure 2. The calculation predicts C_2 symmetry for the molecular structure. This was verified by an HF/6-31G* frequency calculation (no imaginary frequencies are found). The torsion angles between the central CO groups in **4** are very similar to those found in **3** while the torsion angles of the peripheral CO groups are considerably larger (see Table 2). The distance between the outer CO groups and the opposite ether oxygen atoms amounts to 2.726 Å. The distance between the inner CO groups and the opposite ether oxygen atoms is predicted to be slightly longer (3.058 Å) than in the case of **3** [2.703(2) Å, 2.794(2) Å] but still smaller than the expected van der Waals distance (3.4 Å). These results suggest that the conformation of **4** favors a donor−acceptor interaction between the two ether oxygen atoms and the $(CO)_4$ moiety. A second-order perturbation-theory treatment with the Fock matrix on the basis of natural bond orbitals (NBO)[19] reveals a stabilizing interaction of twice $E^{(2)} = 4.04$ kcal/mol for the donation of electron density from the ether lone pair into the π* orbital of the terminal carbonyl groups.

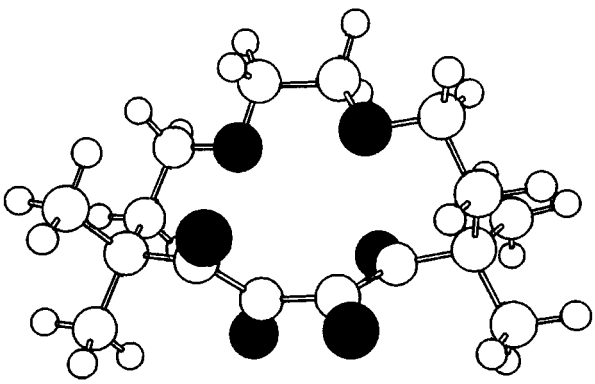

Figure 2. Calculated (HF/6-31G*) structure of **4**; the oxygen atoms are represented by full circles

Table 2. Torsion angles of the carbonyl moiety in **4** (calculated) and **3** (X-ray data)

	3	**4**
Outer torsion angle	−130.2(2)	−198.8
Central torsion angle	107.1(2)	107.8

The electronic structure of **4** was studied by cyclic voltammetry (CV), PE and UV/Vis spectroscopy. The tetraketone **4** can be reduced to its radical anion in a reversible process at −541 mV. This value is closer to that obtained for **3** (−569 mV)[5] than to that reported for **2** (−439 mV)[5] and for 7,7,12,12-tetramethylcyclotetradecane-8,9,10,11-tetrone (**21**) (−389 mV)[7] (see Table 3). We interpret this as evidence for a donor−acceptor interaction between the lone pairs of the ether oxygen atoms and the $(CO)_4$ moiety. This interaction destabilizes the lowest π* orbital (LUMO) and stabilizes the 2p type lone pairs at the oxygen atoms.

Table 3. Comparison between UV/Vis and CV data of **4**, **3**, **2**, and **21**

Compound	UV data λ_{max} [nm] (log ε)		CV data $E_{1/2}$
4	494 (2.08)	374 (3.19)	−541
3	460 (1.44)	362 (1.80)	−569
2	512 (1.40)	380 (2.12)	−439
21	533 (1.94)	385 (1.99)	−389

The destabilization of the LUMO shows also up in the first two absorption bands in the electronic spectrum of **4** (λ_1 = 494 nm and λ_2 = 374 nm). The corresponding values for **2**[4] are: λ_1 = 512 nm, λ_2 = 380 nm, for **3**[5]: λ_1 = 460 nm, λ_2 = 362 nm and for **21**[5]: λ_1 = 533 nm, λ_2 = 385 nm. A comparison yields a blue shift relative to **2** and **21** and a red shift relative to **3**.

The PE spectrum of **4** shows three peaks below 11 eV in the approximate ratio of 1:3:1 (Figure 3). To assign these peaks to individual transitions we compare them with the PE spectrum of **3** (Figure 4). This suggests the assignment of the first band to a lone pair combination (43a) of the p-type lone pairs at the carbonyl oxygen atoms. The same holds for band 2 (41b) followed closely by the 2p lone pair combinations at the ether oxygen atoms (40b, 42a). The band at 10.7 eV is assigned to the third lone pair combination of the carbonyl lone pairs (41a). In Table 4 we compare the calculated orbital energies (ε_j) of **4** with the measured vertical ionization energies ($I_{v,j}$), making use of Koopmans' theorem[20] which allows a direct correlation. The orbital energies were derived by an HF-SCF calculation with a 6-31G* basis set.[18] The calculated orbital energies are based on the fully optimized geometrical parameters of **4**. The HOMO is assigned to the maximal bonding linear combination of the lone pairs at the carbonyl oxygen atoms. The close-lying bands 2 to 4 are assigned to linear combinations of ether lone pairs and lone pairs at the carbonyl oxygen atoms. As can be seen from Table 4, the recorded energy differences between the first four ionization energies correspond closely with the results of the calculations.

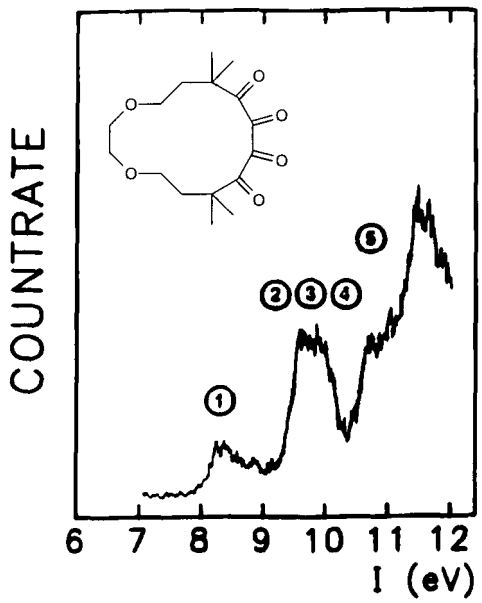

Figure 3. PE spectrum of **4**

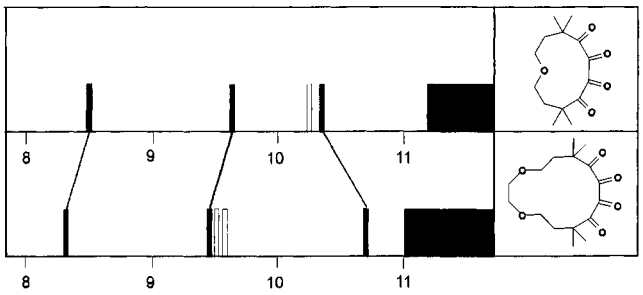

Figure 4. Comparison between the PE spectra of **3** and **4**

Table 4. Comparison between the recorded vertical ionization energies ($I_{v,j}$) of **4** and calculated orbital energies (ε_j), all values given in eV

Band	$I_{v,j}$	Assignment	$-\varepsilon_j$
1	8.3	43a(n_1)	9.79
2	9.6	41b(n_2)	11.44
3	9.7	40b($2p_1$)	11.51
4	9.9	42a($2p_2$)	11.55
5	10.7	41a(n_3)	12.47

Conclusion

Our synthesis of **4** demonstrates that the ring closure with the alkyne unit works well for medium-sized rings. The investigations of the properties of the 14-membered ring of **4** show that there is an efficient transannular interaction of donor−acceptor type between the electron-rich dialkoxyethane unit and the electron-poor tetraketone unit. Especially strong is the donor−acceptor interaction between

the ether oxygen atoms and the peripheral CO groups of the $(CO)_4$ moiety. The two ether oxygen atoms also make a donor−acceptor interaction possible in a 14-membered ring while for one ether oxygen atom a smaller ring (11-membered) is necessary.

Experimental Section

General Procedures: Reactions were carried out under argon with magnetic stirring. Solvents were dried and distilled under argon before use. The buffer solution used for the workup of the reactions was a 1 M aqueous solution prepared from equal parts of H_3PO_4 and NaH_2PO_4. − The ^{1}H- and ^{13}C-NMR spectra were recorded with Bruker WH 300 and Avance 500 instruments, respectively. All compounds containing a THP group exist in several diastereomers (**12**−**17**). This affects the number of ^{1}H and ^{13}C resonances in the NMR spectra of these compounds. − The diastereomers were not separated, because they all lead to the same final product. − Mass spectra were obtained with a Jeol JMS 700 mass spectrometer. − Microanalyses were carried out at the analytical laboratory of the "Chemische Institute der Universität Heidelberg".

2,2,11,11-Tetramethyl-5,8-dioxadodecanedioic Acid (7): A solution of *n*-butyllithium (1.6 M in hexane, 225 mL) was added dropwise at −30°C to a solution of diisopropylamine (35.35 g, 350 mmol) in THF (250 mL). After stirring for 30 min, 14.1 g (160 mmol) of isobutyric acid was added at −20°C. The cooling bath was removed and the reaction mixture was warmed up to 50°C for 2 h. After that, the reaction mixture was cooled again to −20°C, and 1,2-bis(2′-chloroethoxy)ethane **5** (14.96 g, 80 mmol) was added in one portion. The reaction mixture was heated until a white precipitate was formed (ca. 50°C). After being stirred at that temperature for 1 h, the reaction mixture was hydrolyzed with water at 0°C, ether was added, and the phases were separated. The aqueous phase was extracted three times with ether. The organic phases were combined and dried with Na_2SO_4. The solvent was removed in vacuo and the crude product was used for the following reaction without further purification. Diacid **7** was characterized as bis(diisopropylammonium) salt **7a** by recrystallization from ether/pentane (1:1) yielding 18.5 g (55%) of **7a** as white crystals, m.p. 102°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.81 (br., 4 H, NH_2^+), 3.47 (s, 4 H, OCH_2), 3.46 (t, ^3J = 7.5 Hz, 4 H, OCH_2), 3.19−3.13 (m, 4 H, NCH), 1.77 (t, ^3J = 7.5 Hz, 4 H, CH_2), 1.21 (d, ^3J = 6.5 Hz, 24 H, CH_3), 1.08 (s, 12 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.9 (s, COO^-), 70.2 (t, OCH_2), 69.0 (t, OCH_2), 45.9 (d, NCH), 41.0 (s, C), 40.4 (t, CH_2), 26.3 (q, CH_3), 19.9 (q, CH_3).

2,2,11,11-Tetramethyl-5,8-dioxadodecane-1,12-diol (8): A solution of 18 g of **7** (crude product from from preceding procedure) in THF (100 mL) was added dropwise at 0°C to a solution of lithium aluminum hydride (5.0 g, 132 mmol) in THF (150 mL). The cooling bath was removed and the reaction mixture was stirred overnight. After cooling to 0°C, the reaction mixture was hydrolyzed with water, ether and buffer solution were added, and the phases were separated. The aqueous phase was extracted three times with ether. The organic phases were combined and dried with Na_2SO_4. Column chromatography on silica gel with cyclohexane/ethyl acetate (2:1) yielded 11.1 g (90%) of **8** as colorless oil. −^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.52 (s, 4 H, OCH_2), 3.47 (t, ^3J = 5.7 Hz, 4 H, OCH_2), 3.23 (s, 4 H, OCH_2), 1.51 (t, ^3J = 5.7 Hz, 4 H, CH_2), 0.83 (s, 12 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 70.7 (t, OCH_2), 69.7 (t, OCH_2), 67.8 (t, OCH_2), 38.5 (t, CH_2), 34.6 (s, C), 24.8 (q, CH_3). − $C_{14}H_{30}O_4$ (262.2): calcd. C 64.09, H 11.52; found C 63.83, H 11.54.

12-(*tert*-Butyldimethylsiloxy)-2,2,11,11-tetramethyl-5,8-dioxadodecan-1-ol (9): A solution of *tert*-butyldimethylchlorosilane (2.42 g, 16.2 mmol) in dichloromethane (220 mL) was added over 2 h to a solution of diol **8** (8.46 g, 32.3 mmol) and imidazole (2.20 g, 32.3 mmol) in dichloromethane (220 mL). After being stirred overnight, the reaction mixture was hydrolyzed with buffer solution. Ether was added and the phases were separated. The aqueous phase was extracted three times with ether. The organic phases were combined and dried with Na_2SO_4. Column chromatography on silica gel with cyclohexane/ethyl acetate (5:1) yielded 3.76 g (31%) of **9** as colorless oil. Excess **8** could be recovered by eluation with ethyl acetate. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55−3.45 (m, 8 H, OCH_2), 3.25 (s, 2 H, OCH_2), 3.20 (s, 2 H, OCH_2), 1.54−1.50 (m, 4 H, CH_2), 0.86 (s, 6 H, CH_3), 0.85 (s, 9 H, CH_3), 0.82 (s, 6 H, CH_3), −0.02 (s, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 71.9 (t, OCH_2), 71.1 (t, OCH_2), 70.2 (t, OCH_2), 69.8 (t, OCH_2), 68.4 (t, OCH_2), 68.0 (t, OCH_2), 39.1 (t, CH_2), 37.9 (t, CH_2), 34.9 (s, C), 34.5 (s, C), 25.9 (q, CH_3), 25.1 (q, CH_3), 24.3 (q, CH_3), 18.2 (s, C), −5.6 (q, CH_3). − $C_{20}H_{44}O_4Si$ (376.3): calcd. C 63.78, H 11.77; found C 63.88, H 12.05.

12-(*tert*-Butyldimethylsiloxy)-2,2,11,11-tetramethyl-5,8-dioxadodecan-1-al (10): A solution of oxalyl chloride (2.14 g, 17.0 mmol) in dichloromethane (40 mL) was cooled to −50 °C. Dimethyl sulfoxide (2.65 g, 34.0 mmol), dissolved in 10 mL dichloromethane, was added and the reaction mixture was stirred for 3 min. The alcohol **9** (5.86 g, 15.6 mmol), dissolved in 30 mL of dichloromethane, was added within 5 min. After 15 min, triethylamine (7.87 g, 77.9 mmol), was added. After stirring for 5 min, the reaction mixture was allowed to warm to room temperature. Water was added and the phases were separated. The aqueous phase was extracted three times with dichloromethane. The organic phases were combined and dried with Na_2SO_4. Column chromatography on silica gel with cyclohexane/ethyl acetate (5:1) yielded 5.27 g (90%) of **10** as colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.42 (s, 1 H, CHO), 3.48−3.41 (m, 8 H, OCH_2), 3.19 (s, 2 H, OCH_2), 1.76 (t, ^3J = 6.2 Hz, 2 H, CH_2), 1.51 (t, ^3J = 7.4 Hz, 2 H, CH_2), 1.03 (s, 6 H, CH_3), 0.85 (s, 9 H, CH_3), 0.82 (s, 6 H, CH_3), −0.02 (s, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.3 (CHO), 71.9 (t, OCH_2), 70.3 (t, OCH_2), 69.9 (t, OCH_2), 68.3 (t, OCH_2), 67.3 (t, OCH_2), 44.5 (C), 38.0 (t, CH_2), 37.8 (t, CH_2), 34.5 (s, C), 25.9 (q, CH_3), 24.3 (q, CH_3), 21.5 (q, CH_3), 18.2 (s, C), −5.6 (q, CH_3). − $C_{20}H_{42}O_4Si$ (374.3): calcd. C 64.12, H 11.30; found C 64.21, H 11.39.

1-(*tert*-Butyldimethylsiloxy)-12-hydroxy-2,2,11,11-tetramethyl-5,8-dioxa-13-tetradecyne (11): THF (25 mL) was cooled to −45°C, and *n*-butyllithium (1.6 M in hexane, 20 mL) was added. Acetylene was bubbled through the solution. The formation of a white precipitate indicated that the reaction had begun. Acetylene continued to be bubbled through for about 2 h, and the temperature was maintained at −45 °C. The reaction mixture was then cooled to −78 °C, and the aldehyde **10** (5.0 g, 13.4 mmol), dissolved in THF (15 mL), was added. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. Buffer solution and ether were added, and the phases were separated. The aqueous phase was extracted three times with ether. The organic phases were combined and dried with Na_2SO_4. Column chromatography on silica gel with cyclohexane/ethyl acetate (10:1) yielded 4.66 g (87%) of **11** as colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.07 (d, ^4J = 2.0 Hz, 1 H, OCH), 3.64−3.45 (m, 8 H, OCH_2), 3.19 (s, 2 H, OCH_2), 2.37 (d, ^4J = 2.0 Hz, 1 H, C≡CH), 1.98−1.89 (m, 1 H, CH_2), 1.52 (t, ^3J = 7.6 Hz, 2 H, CH_2), 1.41−1.33 (m, 1 H, CH_2), 0.99 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 0.85 (s, 9 H, CH_3), 0.82 (s, 6 H, CH_3), −0.02 (s, 6 H, CH_3). − ^{13}C NMR (75 MHz in $CDCl_3$):

δ = 83.8 (s, C=*C*-C), 73.1 (d, H*C*=C), 71.9 (t, OCH_2), 70.1 (t, OCH_2), 69.7 (t, OCH_2), 69.6 (d, OCH), 68.4 (t, OCH_2), 67.7 (t, OCH_2), 37.9 (t, CH_2), 37.9 (t, CH_2), 34.5 (s, C), 25.9 (q, CH_3), 24.7 (q, CH_3), 24.3 (q, CH_3), 23.7 (q, CH_3), 18.2 (s, C), −5.6 (q, CH_3). − $C_{22}H_{44}O_4Si$ (401.3): calcd. C 65.95, H 11.07; found C 66.05, H 11.31.

1-(*tert*-Butyldimethylsiloxy)-2,2,11,11-tetramethyl-12-(tetrahydropyran-2-yloxy)-5,8-dioxa-13-tetradecyne (12): Alcohol **11** (4.50 g, 11.3 mmol), 3,4-dihydro-2*H*-pyran (1.76 g, 21.0 mmol) and pyridinium *p*-toluenesulfonate (0.29 g, 1.16 mmol) were dissolved in dichloromethane (25 mL). The mixture was stirred overnight and then worked up by addition of ether and buffer solution. The aqueous layer was separated and extracted twice with ether. The organic phases were combined and dried with Na_2SO_4. Column chromatography on silica gel with cyclohexane/ethyl acetate (10:1) yielded 5.04 g (92%) of **12** as colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.99 (t, ^3J = 3.2 Hz, 0.5 H, OCHO), 4.66 (t, ^3J = 3.2 Hz, 0.5 H, OCHO), 4.07 (d, ^4J = 2.1 Hz, 0.5 H, OCH), 3.86 (d, ^4J = 2.1 Hz, 0.5 H, OCH), 3.57−3.46 (m, 10 H, OCH_2), 3.20 (s, 2 H, OCH_2), 2.38 (d, ^4J = 2.2 Hz, 0.5 H, C=CH), 2.33 (d, ^4J = 2.2 Hz, 0.5 H, C=CH), 1.78−1.51 (m, 10 H, CH_2), 1.01 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 0.85 (s, 9 H, CH_3), 0.82 (s, 6 H, CH_3), −0.02 (s, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 100.7 (d, OCHO), 94.8 (d, OCHO), 82.6 (s, C=*C*-C), 81.0 (s, C=*C*-C), 76.7 (d, OCH), 74.6 (d, H*C*=C), 73.5 (d, H*C*=C), 72.8 (d, OCH), 72.0 (t, OCH_2), 70.2 (t, OCH_2), 70.2 (t, OCH_2), 68.4 (t, OCH_2), 68.1 (t, OCH_2), 62.2 (t, OCH_2), 61.8 (t, OCH_2), 38.0 (t, CH_2), 37.8 (s, C), 37.4 (t, CH_2), 37.2 (t, CH_2), 36.8 (s, C), 34.6 (s, C), 30.3 (t, CH_2), 30.3 (t, CH_2), 25.9 (q, CH_3), 25.5 (t, CH_2), 25.4 (t, CH_2), 24.3 (q, CH_3), 23.6 (q, CH_3), 23.5 (q, CH_3), 23.2 (q, CH_3), 23.1 (q, CH_3), 19.0 (t, CH_2), 19.0 (t, CH_2), 18.2 (s, C), −5.6 (q, $SiCH_3$). − $C_{27}H_{52}O_5Si$ (484.4): calcd. C 66.90, H 10.81; found C 66.84, H 11.05.

2,2,11,11-Tetramethyl-12-(tetrahydropyran-2-yloxy)-5,8-dioxa-13-tetradecyne-1-ol (13): To a solution of **12** (4.9 g, 10.1 mmol) in THF (25 mL) was added Bu_4NF (1 M in THF, 10.1 mL), and the reaction mixture was stirred overnight at room temperature. Then buffer solution and ether were added, and the phases were separated. The aqueous phase was extracted three times with ether. The combined organic phases were dried with Na_2SO_4, and the product was isolated by column chromatography on silica gel, with cyclohexane/ethyl acetate (5:1) as eluant, yielding 3.4 g (90%) of **13** as colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.99 (t, ^3J = 3.2 Hz, 0.5 H, OCHO), 4.66 (t, ^3J = 3.2 Hz, 0.5 H, OCHO), 4.07 (d, ^4J = 2.0 Hz, 0.5 H, OCH), 3.87 (d, ^4J = 2.1 Hz, 0.5 H, OCH), 3.55−3.49 (m, 10 H, OCH_2), 3.25 (s, 2 H, OCH_2), 2.39 (d, ^4J = 2.1 Hz, 0.5 H, C=CH), 2.34 (d, ^4J = 2.0 Hz, 0.5 H, C=CH), 1.77−1.51 (m, 10 H, CH_2), 1.01 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 0.89 (s, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 100.5 (d, OCHO), 94.6 (d, OCHO), 82.3 (s, C=*C*-C), 80.8 (s, C=*C*-C), 76.4 (d, OCH), 74.5 (d, H*C*=C), 73.3 (d, H*C*=C), 72.5 (d, OCH), 70.9 (t, OCH_2), 70.0 (t, OCH_2), 69.7 (t, OCH_2), 68.0 (t, OCH_2), 67.8 (t, OCH_2), 62.0 (t, OCH_2), 61.7 (t, OCH_2), 38.9 (t, CH_2), 37.6 (s, C), 37.2 (t, CH_2), 37.0 (t, CH_2), 36.6 (s, C), 34.7 (s, C), 30.1 (t, CH_2), 30.1 (t, CH_2), 25.3 (t, CH_2), 25.2 (t, CH_2), 24.9 (q, CH_3), 23.4 (q, CH_3), 23.3 (q, CH_3), 23.0 (q, CH_3), 22.9 (q, CH_3), 18.8 (t, CH_2), 18.8 (t, CH_2). − $C_{21}H_{38}O_5$ (370.3): calcd. C 68.07, H 10.34; found C 68.06, H 10.38.

2,2,11,11-Tetramethyl-12-(tetrahydropyran-2-yloxy)-5,8-dioxa-13-tetradecyn-1-al (14): A solution of oxalyl chloride (1.19 g, 9.4 mmol) in dichloromethane (25 mL) was cooled to −50 °C. Dimethyl sulfoxide (1.47 g, 18.9 mmol), dissolved in dichloromethane (5 mL), was added and the reaction mixture was stirred for 3 min. The alcohol **13** (3.20 g, 8.7 mmol), dissolved in dichloromethane (15 mL), was added within 5 min. After 15 min, triethylamine (4.36 g, 43.2 mmol) was added. After stirring for 5 min, the reaction mixture was allowed to warm to room temperature. Water was added and the phases were separated. The aqueous phase was extracted three times with dichloromethane. The organic phases were combined and dried with Na_2SO_4. Column chromatography on silica gel with cyclohexane/ethyl acetate (5:1) yielded 2.97 g (93%) of **14** as colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.41 (s, 1 H, CHO), 4.98 (t, ^3J = 2.9 Hz, 0.5 H, OCHO), 4.64 (t, ^3J = 3.2 Hz, 0.5 H, OCHO), 4.06 (d, ^4J = 2.1 Hz, 0.5 H, OCH), 3.86 (d, ^4J = 2.1 Hz, 0.5 H, OCH), 3.53−3.40 (m, 10 H, OCH_2), 2.38 (d, ^4J = 2.2 Hz, 0.5 H, C=CH), 2.33 (d, ^4J = 2.1 Hz, 0.5 H, C=CH), 1.81−1.49 (m, 10 H, CH_2), 1.02 (s, 6 H, CH_3), 1.00 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.1 (d, CHO), 100.5 (d, OCHO), 94.6 (d, OCHO), 82.4 (s, C=*C*-C), 80.8 (s, C=*C*-C), 76.6 (d, OCH), 74.5 (d, H*C*=C), 73.3 (d, H*C*=C), 72.5 (d, OCH), 70.1 (t, OCH_2), 69.8 (t, OCH_2), 69.8 (t, OCH_2), 67.9 (t, OCH_2), 67.1 (t, OCH_2), 62.0 (t, OCH_2), 61.6 (t, OCH_2), 44.3 (s, C), 37.5 (t, CH_2), 37.2 (t, CH_2), 37.0 (t, CH_2), 36.6 (s, C), 30.1 (t, CH_2), 30.1 (t, CH_2), 25.3 (t, CH_2), 25.2 (t, CH_2), 23.4 (q, CH_3), 23.3 (q, CH_3), 23.0 (q, CH_3), 22.9 (q, CH_3), 21.3 (q, CH_3), 18.8 (t, CH_2), 18.7 (t, CH_2). − $C_{21}H_{36}O_5$ (368.3): calcd. C 68.44, H 9.85; found C 68.55, H 9.91.

7,7,12,12-Tetramethyl-11-(tetrahydropyran-2-yloxy)-1,4-dioxa-13-cyclotetradecyn-8-ol (15): A solution of **14** (860 mg, 2.34 mmol) in THF (900 mL) was added slowly during 5 h to a solution of lithium bis(trimethylsilyl)amide (1 M in THF, 7.3 mL) in THF (150 mL). Then ethanol (10 mL) was added and the reaction mixture was concentrated to a volume of 30 mL. Buffer solution and ether were added. The phases were separated and the aqueous layer was extracted three times with ether. The organic phases were combined and dried with Na_2SO_4. Column chromatography on silica gel with cyclohexane/ethyl acetate (2:1) yielded 664 mg (77%) of **15** as colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.44−5.41 (m, 1 H, OCHO), 4.80−4.26 (m, 2 H, OCH), 4.17−3.07 (m, 10 H, OCH_2), 2.42−1.34 (m, 10 H, CH_2), 1.32−0.96 (m, 12 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 100.1 (d, OCHO), 100.1 (d, OCHO), 95.0 (d, OCHO), 94.9 (d, OCHO), 86.4 (s, C=C), 85.2 (s, C=C), 83.7 (s, C=C), 83.6 (s, C=C), 76.5 (d, OCH), 76.4 (d, OCH), 72.7 (d, OCH), 72.5 (d, OCH), 71.7 (t, OCH_2), 70.6 (t, OCH_2), 70.5 (t, OCH), 70.5 (t, OCH), 67.4 (t, OCH_2), 67.4 (t, OCH_2), 67.3 (t, OCH_2), 61.7 (t, OCH_2), 61.2 (t, OCH_2), 38.7 (t, CH_2), 38.6 (t, CH_2), 38.5 (t, CH_2), 38.4 (s, C), 38.3 (s, C), 38.3 (s, C), 30.7 (t, CH_2), 30.4 (t, CH_2), 30.4 (t, CH_2), 28.7 (q, CH_3), 28.6 (q, CH_3), 28.3 (q, CH_3), 28.2 (q, CH_3), 25.8 (t, CH_2), 25.7 (t, CH_2), 25.7 (q, CH_3), 25.7 (q, CH_3), 25.4 (q, CH_3), 24.7 (q, CH_3), 24.7 (q, CH_3), 24.2 (q, CH_3), 24.0 (q, CH_3), 22.9 (q, CH_3), 22.8 (q, CH_3), 22.8 (q, CH_3), 22.7 (q, CH_3), 19.3 (t, CH_2), 19.0 (t, CH_2), 18.7 (t, CH_2). − $C_{21}H_{36}O_5$ (368.3): calcd. C 68.44, H 9.85; found C 68.49, H 9.86.

8-(Isopropyldimethylsiloxy)-7,7,12,12-tetramethyl-11-(tetrahydropyran-2-yloxy)-1,4-dioxa-9-cyclotetradecyne (16): To a solution of **15** (951 mg, 2.58 mmol) and 2,6-lutidin (736 mg, 6.88 mmol) in dichloromethane (5 mL) was added isopropyldimethylchlorosilane (469 mg, 3.44 mmol). After the mixture had been stirred overnight, a white precipitate formed. Buffer solution and ether were added. The phases were separated and the aqueous phase was extracted twice with ether. The organic phases were combined and dried with Na_2SO_4. The product was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (10:1) as eluant, yielding 908 mg (87%) of **16** as colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.00−4.97 (m, 0.5 H, OCHO), 4.67−4.66 (m, 0.5 H, OCHO), 4.17−3.94 (m, 2 H, OCH), 3.77−3.48 (m, 10 H, OCH_2),

1.87−1.50 (m, 10 H, CH_2), 1.02−0.92 (m, 18 H, CH_3), 0.87−0.76 (m, 2 H, SiCH), 0.11−0.04 (m, 6 H, $SiCH_3$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 100.0 (d, OCHO), 95.1 (d, OCHO), 95.0 (d, OCHO), 86.7 (s, C=C), 85.6 (s, C=C), 84.0 (s, C=C), 83.9 (s, C=C), 82.7 (s, C=C), 76.1 (d, OCH), 76.0 (d, OCH), 72.9 (d, OCH), 72.8 (d, OCH), 70.7 (d, OCH), 70.6 (t, OCH_2), 70.5 (t, OCH_2), 70.5 (t, OCH), 70.3 (t, OCH), 70.3 (t, OCH), 67.8 (t, OCH_2), 67.7 (t, OCH_2), 67.6 (t, OCH_2), 67.6 (t, OCH_2), 67.5 (t, OCH_2), 61.9 (t, OCH_2), 61.9 (t, OCH_2), 61.8 (t, OCH_2), 39.6 (t, CH_2), 39.3 (t, CH_2), 39.2 (t, CH_2), 39.2 (t, CH_2), 39.0 (t, CH_2), 39.0 (t, CH_2), 38.6 (s, C), 38.5 (s, C), 38.3 (s, C), 38.3 (s, C), 37.3 (s, C), 30.5 (t, CH_2), 30.2 (t, CH_2), 25.8 (q, CH_3), 25.6 (t, CH_2), 25.4 (q, CH_3), 25.2 (q, CH_3), 25.2 (q, CH_3), 25.1 (q, CH_3), 24.9 (q, CH_3), 24.9 (q, CH_3), 23.9 (q, CH_3), 23.5 (q, CH_3), 23.4 (q, CH_3), 23.2 (q, CH_3), 23.1 (q, CH_3), 19.2 (t, CH_2), 19.1 (t, CH_2), 18.7 (t, CH_2), 16.9 (q, CH_3), 14.8 (d, SiCH), −3.6 (q, $SiCH_3$), −4.3 (q, $SiCH_3$), −4.3 (q, $SiCH_3$). − $C_{26}H_{48}O_5Si$ (468.3): calcd. C 66.62, H 10.32; found C 66.86, H 10.41.

8-(Isopropyldimethylsiloxy)-7,7,12,12-tetramethyl-11-(tetrahydropyran-2-yloxy)-1,4-dioxacyclotetradecane-9,10-dione (17): To a solution of **16** (792 mg, 1.69 mmol) in carbon tetrachloride (8 mL) were added acetonitrile (8 mL), water (12 mL), and sodium periodate (1.41 g, 6.59 mmol). The mixture was stirred vigorously until two clear phases resulted. After that, 1 mg of $RuO_2 \cdot x\,H_2O$ was added, and the vigorous stirring was continued. The mixture immediately turned black, then yellow and a white precipitate was formed. After 1 h, water (10 mL) was added. The phases were separated and the aqueous phase was extracted three times with dichloromethane. The organic phases were combined and dried with Na_2SO_4. The product was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (5:1) as eluant, yielding 709 mg (84%) of **17** as yellow oil. − ^{1}H NMR (300 MHz, C_6D_6): δ = 5.22−4.74 (m, 3 H, OCHO, OCH), 3.93−2.72 (m, 10 H, OCH_2), 2.36−0.98 (m, 28 H, CH_2, CH_3), 0.98−0.75 (m, 2 H, SiCH), 0.28−0.16 (m, 6 H, $SiCH_3$). − ^{13}C NMR (75 MHz, C_6D_6): δ = 200.9 (s, C=O), 200.5 (s, C=O), 195.8 (s, C=O), 195.4 (s, C=O), 193.1 (s, C=O), 191.8 (s, C=O), 101.7 (d, OCHO), 100.8 (d, OCHO), 100.2 (d, OCHO), 100.1 (d, OCHO), 81.9 (d, OCH), 79.9 (d, OCH), 76.3 (d, OCH), 73.6 (d, OCH), 70.6 (d, OCH), 70.0 (t, OCH_2), 69.9 (t, OCH_2), 69.7 (t, OCH), 68.0 (t, OCH), 69.9 (t, OCH), 69.7 (t, OCH_2), 68.0 (t, OCH_2), 67.8 (t, OCH_2), 67.7 (t, OCH_2), 67.2 (t, OCH_2), 63.3 (t, OCH_2), 61.4 (t, OCH_2), 39.7 (t, CH_2), 39.6 (t, CH_2), 39.5 (t, CH_2), 39.4 (t, CH_2), 38.6 (t, CH_2), 38.5 (t, CH_2), 37.6 (s, C), 37.5 (s, C), 37.3 (s, C), 37.3 (s, C), 37.2 (s, C), 31.6 (t, CH_2), 30.8 (t, CH_2), 30.8 (t, CH_2), 27.6 (q, CH_3), 27.2 (q, CH_3), 26.6 (q, CH_3), 26.5 (q, CH_3), 26.4 (q, CH_3), 25.7 (t, CH_2), 25.6 (t, CH_2), 24.7 (q, CH_3), 24.2 (q, CH_3), 23.5 (q, CH_3), 20.7 (t, CH_2), 20.6 (t, CH_2), 19.6 (t, CH_2), 17.3 (q, CH_3), 17.2 (q, CH_3), 16.0 (q, SiCH), 15.8 (d, SiCH), 15.5 (d, SiCH), −3.3 (q, $SiCH_3$), −3.5 (q, $SiCH_3$), −4.0 (q, $SiCH_3$), −4.1 (q, $SiCH_3$). − IR (film): $\tilde{\nu}$ [cm^{-1}] = 2952 (vs), 2867 (vs), 1724 (s), 1469 (m), 1362 (w), 1253 (w), 1203 (w), 1122 (m). − $C_{26}H_{48}O_7Si$ (500.3): calcd. C 62.36, H 9.66; found C 62.42, H 9.62.

8,11-Dihydroxy-7,7,12,12-tetramethyl-1,4-dioxacyclotetradecane-9,10-dione (18): Ion exchange resin AG 500 W-X2 from BioRad in methanol (3 mL) was added to a solution of **17** in methanol (5 mL). The suspension was stirred until **17** was no longer detected by TLC (ca. 4 h). The ion exchange resin was then removed by filtration. Methanol was removed in vacuo, and the products were purified by column chromatography (silica gel; cyclohexane/ethyl acetate, 2:1), yielding 314 mg (84%) of **18**. The isomers **18a** (*R*,*S*) and **18b** (*R*,*R*/*S*,*S*) could be separated by HPLC (silica gel; *n*-hexane/ethanol, 99:1) and were obtained in a 1:1 ratio as yellow crystals.

(*R*,*S*) Isomer 18a: M.p. 91°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.48 (d, ^3J = 9.5 Hz, 2 H, OCH), 4.24 (br., 2 H, OH), 3.65−3.46 (m, 8 H, OCH_2), 2.07−2.01 (m, 2 H, CH_2), 1.46−1.38 (m, 2 H, CH_2), 1.09 (s, 6 H, CH_3), 1.07 (s, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.8 (s, C=O), 78.4 (d, OCH), 70.3 (t, OCH_2), 68.4 (t, OCH_2), 38.6 (t, CH_2), 38.1 (s, C), 26.3 (q, CH_3), 24.2 (q, CH_3). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3390 (vs), 2964 (s), 2909 (s), 2875 (s), 1716 (vs), 1632 (w), 1473 (m), 1363 (m), 1250 (w), 1171 (w), 1122 (s), 1095 (vs), 1031 (s). − UV (CH_2Cl_2): λ_{max} [nm] (log ε) = 222 (2.89), 280 (1.85), 342 (1.40), 416 (1.22). − $C_{16}H_{28}O_6$ (316.2): calcd. C 60.74, H 8.92; found C 60.62, H 8.82.

(*R*,*R*/*S*,*S*) Isomer 18b: M.p. 120°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.61 (br., 2 H, OH), 4.43 (d, ^3J = 10.1 Hz, 2 H, OCH), 3.64−3.47 (m, 8 H, OCH_2), 2.17−2.08 (m, 2 H, CH_2), 1.39−1.32 (m, 2 H, CH_2), 1.14 (s, 6 H, CH_3), 1.06 (s, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.7 (s, C=O), 80.1 (d, OCH), 69.8 (t, OCH_2), 68.4 (t, OCH_2), 38.5 (s, C), 37.6 (t, CH_2), 28.2 (q, CH_3), 24.7 (q, CH_3). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3440 (vs), 2957 (s), 2921 (s), 2872 (s), 1718 (s), 1632 (w), 1473 (w), 1362 (w), 1254 (w), 1180 (w), 1105 (s). − UV (CH_2Cl_2): λ_{max} [nm] (log ε) = 222 (2.93), 282 (1.89), 296 (1.79), 362 (1.34). − $C_{16}H_{28}O_6$ (316.2): calcd. C 60.74, H 8.92; found C 60.61, H 8.86.

7,7,12,12-Tetramethyl-1,4-dioxacyclotetradecane-8,9,10,11-tetrone (4): To a solution of **18** (186 mg, 0.59 mmol) in carbon tetrachloride (10 mL) was added *N*-bromosuccinimide (345 mg, 1.94 mmol). The mixture was heated to reflux for 4 d. Succinimide was filtered off with a frit under argon, and the red solution was then concentrated. The product was purified by HPLC (silica gel, *n*-hexane/ethyl acetate, 84:16), yielding 46 mg (25%) of **4** as red oil. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.48 (t, ^3J = 5.3 Hz, 4 H, OCH_2), 3.29 (s, 4 H, OCH_2), 2.14 (t, ^3J = 5.4 Hz, 4 H, CH_2), 1.30 (s, 12 H, CH_3). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.9 (s, C=O), 188.8 (s, C=O), 70.2 (t, OCH_2), 67.8 (t, OCH_2), 45.2 (s, C), 40.2 (t, CH_2), 25.3 (q, CH_3). − IR (film): $\tilde{\nu}$ [cm^{-1}] = 2968 (s), 2924 (s), 2873 (s), 1784 (w), 1714 (vs), 1469 (s), 1387 (w), 1365 (m), 1259 (m), 1099 (vs), 1039 (s). − UV (CH_2Cl_2): λ_{max} [nm] (log ε) = 222 (3.24), 300 (2.24), 374 (3.19), 494 (2.08). − HRMS (FAB+): *m*/*z* = 313.1679 (calcd. for $C_{16}H_{25}O_6$: *m*/*z* = 313.1651).

X-ray Analysis: The crystallographic data were collected with a Siemens SMART (CCD) diffractometer, Mo-K_α radiation, graphite monochromator, 0.3° ω scan. Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically with a full-matrix least-squares technique (F^2), and the hydrogen atoms were taken into account at calculated positions. Refinement and structure solutions were carried out with SHELXTL-PLUS software package.[21] The crystallographic data and details of the refinement procedure are shown in Table 5. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112909. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

He(I) Photoelectron Spectrum of 18: The He(I) PE spectrum of **18** was recorded with a PS18 spectrometer (Perkin−Elmer) at 86°C. The calibration was performed with Ar and Xe. A resolution of 20 meV on the $^2P3_{3/2}$ Ar line was obtained.

Cyclic Voltammetry: The electrochemical measurements were performed with the METROHM potentiostat system PGSTAT20. As

Table 5. Crystal data and structure refinement of **18a**

Empirical formula	$C_{16}H_{28}O_6$
Formula weight	316.38
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	*Fdd*2
Z	16
Unit cell dimensions	$a = 20.5256(6)$ Å $b = 29.3261(8)$ Å $c = 11.4452(3)$ Å
Volume	6889.3(3) Å^3
Density (calculated)	1.22 Mgm^{-3}
Absorption coefficient	0.09 mm^{-1}
Crystal size	0.24 × 0.16 × 0.16 mm
Theta range for data collection	2.2 to 25.5°
Index ranges	$-24 \le h \le 24$ $-35 \le k \le 34$ $-13 \le l \le 13$
Reflections collected	12600
Independent reflections	2992 [R(int) = 0.0870]
Observed refections	2097 [$I > 2\sigma(I)$]
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2991/26/205
Goodness-of-fit on F^2	1.09
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.068$, $wR2 = 0.126$
Largest diff. peak and hole	0.38 and −0.32 eÅ^{-3}

working electrode a METROHM disc electrode was used (radius ca. 0.3 cm, glassy carbon). The Ag/AgCl reference electrode was separated from the solution by a fine grid and a luggin capillary. A 0.1 M solution of nBu$_4$PF$_6$ in CH_2Cl_2 was used as electrolyte. The potential of the ferrocene/ferrocenium (Fc/Fc^+) system was recorded at 721 mV with an error of ± 5 mV vs. Ag/AgCl. All measurements were recorded at $v = 100$ mV/s.

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