A Repetitive Approach to the Synthesis of Medium and Large Ring Compounds with a Ring-Opening/Ring-Closure Cascade Reaction of Siloxycyclopropane Derivatives as Crucial Step☆

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Starting from siloxycyclopropyl-substituted dimethyl malonates **1** and **2** a chain elongation was performed to give new malonates **8**, **9**, **10**, and **18** in reasonable overall yield. Further elongation by five carbon atoms transforms **10** into **15**. Precursor **21** was prepared by alkylation of cyclopropanecarboxylate **20** with dibromide **17** and subsequent treatment with sodium dimethyl malonate. Compounds **8**, **9**, **10**, **15**, **18**, and **21** were subjected to cesium fluoride under high dilution which induced a ring-opening/ring-closure cascade reaction giving cyclopentadecanone derivatives **11**, **12**, **13**, cycloeicosanone derivative **16**, cyclotetradecanone derivative **19** and cyclononane derivative **22** (together with **23**). The efficiency of this reaction including an intramolecular Michael addition is discussed. The sequence allows efficient synthesis of medium and large carbocycles by a highly flexible building block system involving in principle unlimited repetition of construction steps. An X-ray analysis of **19** reveals its crown-like conformation which is slightly distorted to a more planar skeleton compared with a ten-membered ring analog **24**.

In a recent report[2] we described scope and limitations of a new method leading to functionalized cyclodecanone derivatives **A**. The ten ring atoms of **A** are delivered by 2-alkenyl-substituted methyl 2-siloxycyclopropanecarboxylate **B**, alkyl dihalide **C**, and a CH-acidic component **D** as building blocks. This concept provides various precursor molecules **E** in a highly flexible manner, which undergo a ring-opening/ring-closure cascade by treatment with cesium fluoride furnishing **A** in low to good yields. The efficiency of the crucial intramolecular Michael additions of intermediate carbanion **F** to give **A** is highly dependend on substitutents R, on X and on the nature of the acceptor groups Acc[2].

In this account we want to demonstrate that this flexible concept can easily be extended to the synthesis of other ring sizes thus allowing preparation of functionalized medium and large-ring compounds with almost any number of chain links. We depict a repetitive procedure which elongates **E** by five carbon atoms to new precursor molecules **G**. Their ring-opening/ring-closure cascade furnishes fifteen-membered rings **H**. By change of spacer part X′ synthesis of a fourteen-membered ring is possible. To illustrate the options for even larger ring compounds intermediate **G** was elongated again by five carbon atoms which allowed preparation of a cycloeicosane derivative **I**.

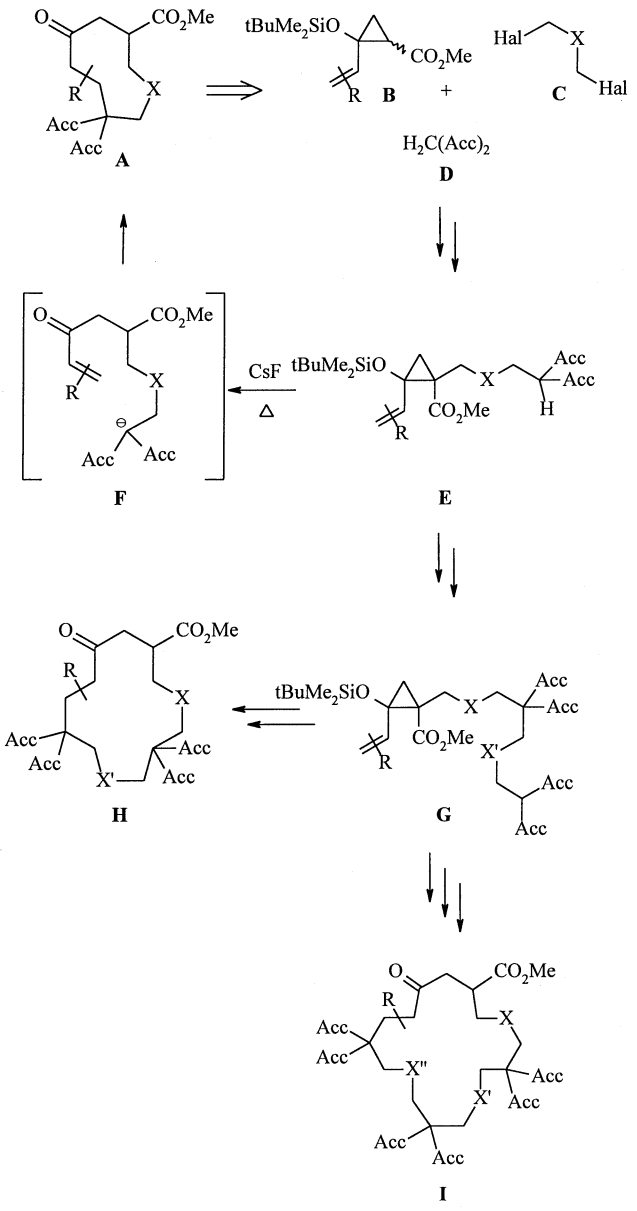
Results

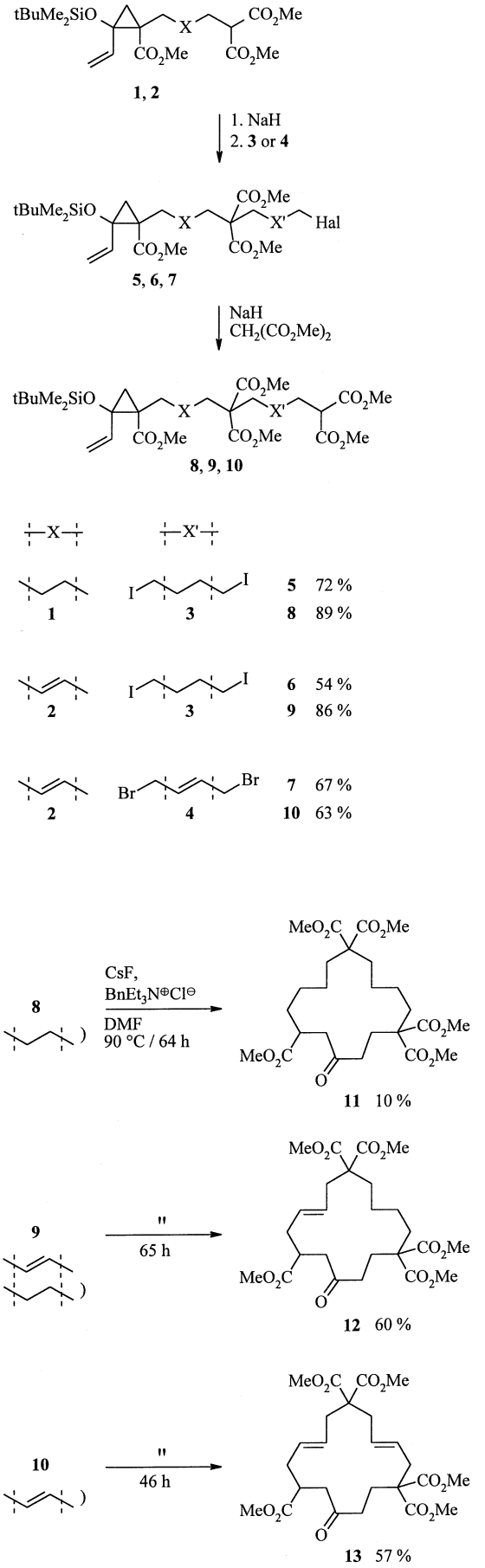
Siloxycyclopropyl-substituted dimethyl malonates **1** and **2** were alkylated with alkyl dihalides **3** or **4** by a standard procedure. The resulting products **5**−**7** reacted with an excess of sodium dimethyl malonate to furnish precursor compounds **8**−**10** in reasonable overall yield. All reactions were only once performed and are therefore not optimized.

The ring-opening/ring-closure cascade was executed under conditions that had proven suitable for the synthesis of cyclodecenone derivatives[2]. Hence precursor compounds were slowly added by syringe pump to a suspension of cesium fluoride and benzyltriethylammonium chloride in hot dimethyl formamide. The final concentration of the products was generally 1−2 mmolar. This proceeding guarantees low concentrations of the intermediate enone, thus increasing the chance for intramolecular Michael addition. Precursor **8** with completely saturated spacer units X, X′ afforded cyclopentadecanone derivative **11** in only 10% yield. No further components could be isolated and characterized in this experiment. Oligomerization, condensation reactions and decarboxylation may be competing processes which

[+] X-ray analysis.

  1434−193X/98/1111−2541 $ 17.50+.50/0



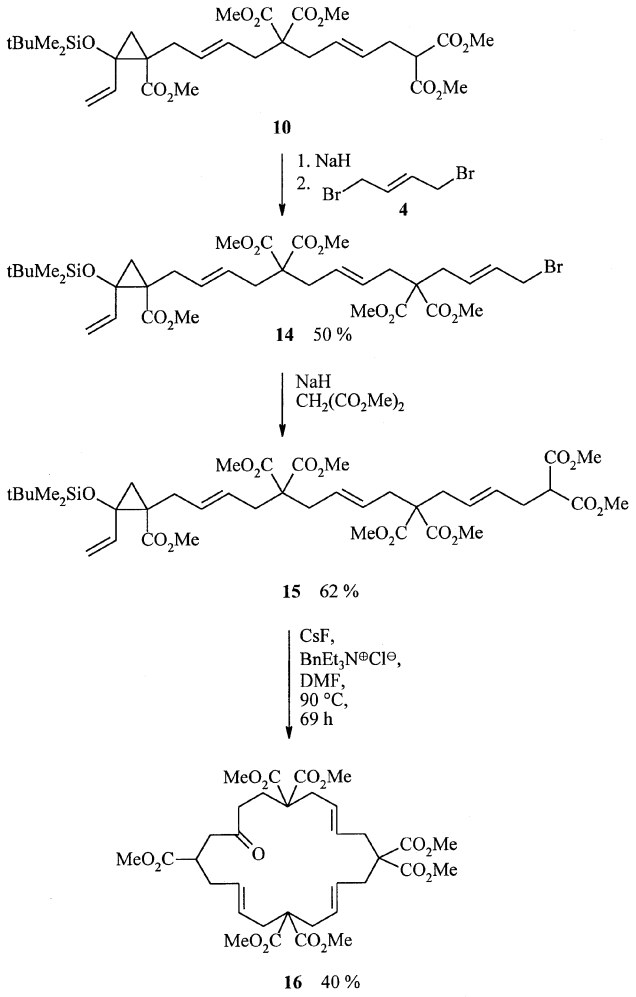


hamper the efficiency of transformation **8** → **11**. However it must be reminded that the corresponding reaction of the ten-carbon system with saturated spacer X (see **E**) did not provide the expected cyclodecanone derivative at all but only a twenty-membered ring in 2% yield[2].

Gratifyingly, fluoride-induced ring-opening/ring-closure of **9** and **10** succeeded with good efficiency and furnished cyclopentadecanone derivatives **12** and **13** in 60% and 57% yield, respectively. These examples demonstrate that unsaturated spacer units X and X′ strongly support cyclization. This effect has already been observed by Deslongchamps and coworkers in related ring syntheses and it can be attributed to lesser degrees of freedom in the open chain cyclization precursors[3]. This entropic effect dramatically favours intramolecular Michael additions as illustrated by comparing the yields of **11**, **12**, and **13**.

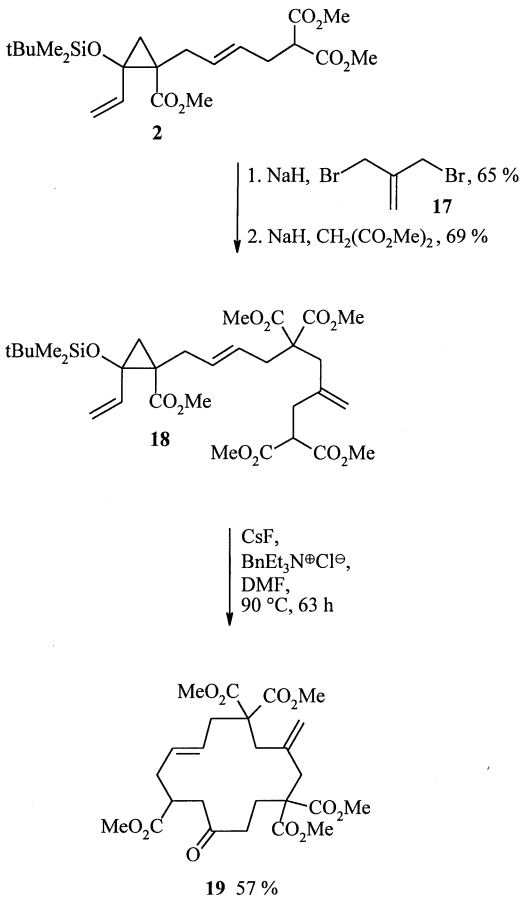
As mentioned in the introduction, we also wanted to demonstrate that other ring sizes are available by repetition

of our chain elongation steps. Thus, compound **10** was alkylated again with (*E*)-1,4-dibromo-2-butene (**4**) and the resulting **14** was reacted with sodium dimethyl malonate furnishing the twenty-carbon chain precursor **15** in reasonable overall yield. Its transformation into cycloeicosanone derivative **16** proceeded under standard conditions with 40% yield.

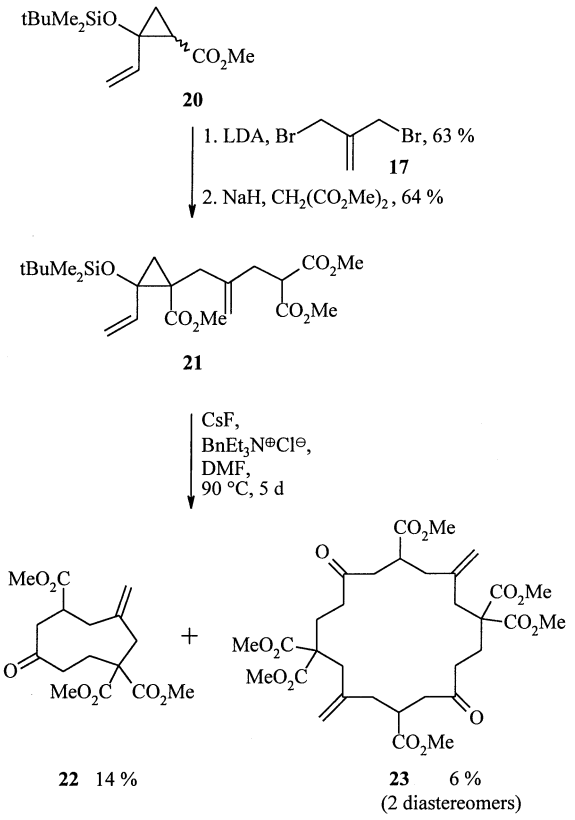


Whereas the examples presented so far illustrate the feasibility of our repetitive approach for preparation of ten-, fifteen-, and twenty-membered rings we could also show that alternative spacer components allow synthesis of other ring sizes. For this purpose precursor **2** was alkylated with 3-bromo-2-bromomethyl-1-propene (**17**) and the intermediate was again treated with an excess of sodium dimethyl malonate. We obtained pentaester **18** in moderate overall yield and subjected it to our standard cesium fluoride protocol which afforded the fourteen-membered ring compound **19** with an *exo*-methylene unit in 57%.

Employing spacer precursor **17** we also tried to synthesize cyclononane derivatives. Therefore, siloxycyclopropane **20** which is the key starting material for almost all compounds investigated in this and the earlier report, was alkylated under standard conditions[4] with **17** and the resulting product was further equipped with the required malonic ester unit. Precursor **21** cyclized to give only 14% of the expected nine-membered ring product **22** together with 6% of the "dimer" **23** which is formed as 1:1 mixture of the two possible diastereomers. This experiment confirms that the ring formation tendency is rather low for nine-membered rings[5].

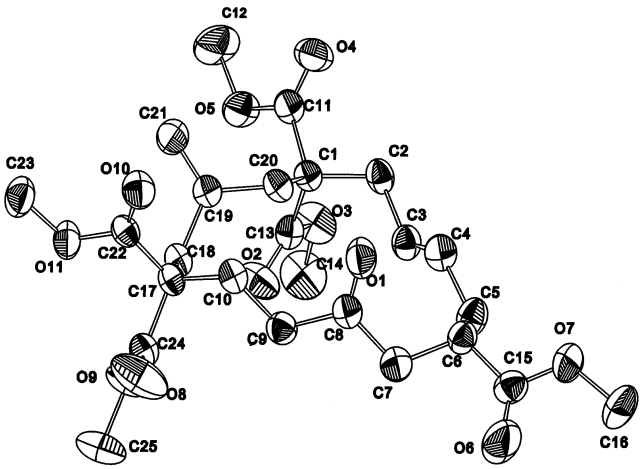


An X-ray analysis[6] of cyclotetradecenepentacarboxylate **19** (Figure 1) acertained its constitution and also allowed comparison of the conformation of this compound with that of a related ten-membered ring system[7]. The elementary cell of the crystal contained four conformationally identical molecules of **19** whereas for **24** two slightly different conformers were observed. The distance of the carbonyl carbon (C-8) to the C−C double bond (C-3, C-4) is as expected considerably larger for the fourteen-membered ring **19** compared with **24** (Table 1). A transannular interaction of these functional groups can therefore be excluded. Whereas an ideal crown-like conformation could be determined for **24** this is slightly pertubated in the fourteen-membered ring **19**. The region of **19** containing the "additional" atoms (C-17, C-18, C-19, C-20) is less ordered and the angle defined by the planes C-1, C-2, C-10 and C-2, C-3, C-9, C-10 (these atoms are almost in plane) is smaller than the corresponding angle in **24** (Table 2). This is probably due to the larger flexibility in **19** which allows avoidance of strain caused by the additional methoxycarbonyl groups at C-17. The angles of other planes in **19** are wid-



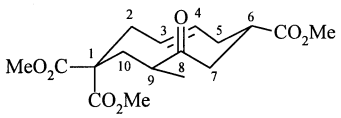
ened for similar reasons leading to a slight deflexion of the crown conformation in the direction to a more planar arrangement of the ring carbon atoms.

Figure 1. X-ray structure of **19** (numbering of atoms does not follow the systematical nomenclature)



Conclusion

In this account we could demonstrate that our approach to ten-membered rings can easily be extended to larger ring sizes by a repetitive sequence. Thus, stepwise elongation of precursors such as **2** by alkyldihalides and dimethyl malonate afforded compounds that furnish fourteen-, fifteen-, and



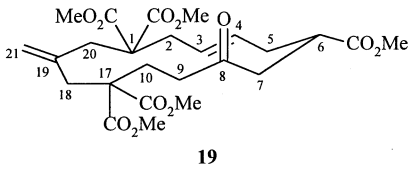


Table 1. Relevant bond lengths in compounds **19** and **24** [Å]

Bond lengths	**19**	**24**[a]	**24**[b]
C5−C7	2.5398 (0.0036)	2.5260	2.5254
C8−C4	3.2949 (0.0033)	2.8344	2.8320
C3−C9	4.3839 (0.0033)	3.0592	3.0388
C2−C10	5.3532 (0.0033)	2.5892	2.5939
C8−C3	3.9057 (0.0032)	3.0832	3.0780
C8−C19	4.5706 (0.0033)		
C8−C21	5.7021 (0.0038)		
C8−C5	3.3140 (0.0035)	3.1543	3.1582
C8−C1	4.9108 (0.0032)	3.5827	3.5881
C1−C6	5.7885 (0.0032)	5.3281	5.3333
C8−C6	2.5553 (0.0033)	2.5272	2.5268
O1−C4	3.3434 (0.0032)	3.1473	3.1592

[a] Conformer A. − [b] Conformer B.

Table 2. Relevant angles between planes of atoms in compounds **19** and **24** [°]

Angles between planes of atoms[a]		**19**	**24**[b]	**24**[c]
C1−C2−C10	C2−C3−C9−C10	49.99 (0.13)	55.30	54.11
C2−C3−C9−C10	C3−C4−C8−C9	64.95 (0.12)	58.56	59.74
C3−C4−C8−C9	C4−C5−C7−C8	61.55 (0.13)	58.77	58.56
C4−C5−C7−C8	C5−C6−C7	66.74 (0.19)	57.57	58.42

[a] When four Atoms are indicated these are roughly in plane. − [b] Conformer A.

twenty-membered rings by a one-pot ring-opening/ring-closure procedure. The advantage of siloxycyclopropanecarboxylates as masked enone moiety whose reactivity can be triggered when required is nicely illustrated by these examples[8]. As shown, medium- and large-ring compounds with almost optional ring size may synthesized by our repetitive approach[9]. Thus, the known spectrum of syntheses leading to large ring compounds is supplemented by a very flexible method[10].

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Table 3. Alkylation of siloxycyclopropanes **1** and **2** with **3**, **4**, and **17**

Precursor	NaH [eq.]	Dihalide	Eq.	Chromatography heptane/ethyl acetate	Product	Amount [g]	Yield [%]
1	5.0	**3**	10	1:0→4:1	**5**[a]	0.506	72
2	5.0	**3**	10	1:0→4:1	**6**[a]	0.381	54
2	2.0	**4**	10	9.5:0.5→8.5:1.5	**7**[a]	0.430	67
2	4.0	**17**	4.0	1:0→4:1	[b][c]	0.419	65

[a] Lightly yellow oil. – [b] Dimethyl (6*E*)-1-Bromo-8-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-2-methylene-6-octene-4,4-dicarboxylate. – [c] Colourless oil.

Experimental Section

All reactions were performed under argon atmosphere in flame-dried flasks, and the components were added by means of syringes. All solvents were dried by standard methods. Silica gel (0.040−0.063 mm, Fa. Merck-Schuchardt) was used for column chromatography. – IR: Nicolet 205 FT-IR. – NMR: Bruker AC 200, AC 300 or DRX-500 (^{1}H and ^{13}C); $CDCl_3$ as solvent, TMS or chloroform (δ_H = 7.25, δ_C = 77.0) as internal standard. – MS: Varian MAT 311 A (FD) and Kratos Analytics Kompact Maldi II (Maldi). – Melting points (uncorrected): Gallenkamp MPD 350. 1,4-Diiodobutane (**3**) and (*E*)-1,4-dibromo-2-butene (**4**) are commercially available and were used as received. Other starting materials: siloxycyclopropanes **1**[1], **2**[2b], and **20**[11], 3-bromo-2-bromomethyl-1-propene (**17**)[12].

General Procedure A for Alkylation of Siloxycyclopropyl-Substituted Dimethyl Malonates with **3**, **4**, *or* **17**: To a suspension of sodium hydride (2.0−5.0 equivalents) in a mixture of THF and DMF (5:1) (30 ml/mmol of cyclopropane) the crude siloxycyclopropyl-substituted dimethyl malonate (0.500 g, 1.13 mmol, 1.0 equivalents) was slowly added at 0°C and the mixture was stirred for 1 h at r.t. Then the dihalide (4.0−10 equivalents) was added at 0°C. After stirring at r.t. for 18 h the mixture was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 ×). The combined organic layers were washed with water and brine and dried ($MgSO_4$). After evaporation of the solvents the unconsumed alkylating reagent was occasionally removed by kugelrohr distillation (0.01 mbar, 100°C). The residue was purified by chromatography as indicated in the individual experiments.

General Procedure B for Reaction of Siloxycyclopropyl-Substituted Halides with Dimethyl Malonate: To a suspension of sodium hydride (1.2−5.0 equivalents) in a mixture of THF and DMF (5:1) (15 ml/mmol of cyclopropane) dimethyl malonate (10.0 equivalents) was slowly added at 0°C and the mixture was stirred for 1 h at r.t. Then the siloxycyclopropyl-substituted halide (1.0 equivalent) was added at 0°C. After stirring at r.t. for 18 h the mixture was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 ×). The combined organic layers were washed with water and brine and dried ($MgSO_4$). After evaporation of the solvents the unconsumed dimethyl malonate was occasionally removed by kugelrohr distillation (0.01 mbar, 70°C). The residue was purified by chromatography as indicated in the individual experiments.

General Procedure C for Fluoride-Induced Cyclization: To a warm suspension (90°C) of cesium fluoride (3.0 equivalents) and benzyltriethylammonium chloride (1.5 equivalents) in dry DMF (ca. 550 ml/mmol cyclopropane) a solution of siloxycyclopropyl-substituted dimethyl malonate (1.0 equivalent) in DMF (50 ml, addition by syringe pump, time given in the individual experiments) was slowly added. After evaporation of all volatile components (16 mbar, 70°C) the residue was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (5 ×). The combined organic layers were washed with brine and dried ($MgSO_4$). After evaporation of solvents the remainder of DMF was removed by kugelrohr distillation (0.01 mbar, 50°C) and the residue was purified by chromatography as indicated in the individual experiments.

Dimethyl 1-[r-2-(tert-Butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-9-iodononane-5,5-dicarboxylate (**5**): IR (neat): $\tilde{\nu}$ = 3100−3000 cm^{-1} (=C−H), 2950, 2930, 2860 (−C−H), 1730 (CO_2Me), 1640 (C=C). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.77 (dd, *J* = 17, 10.5 Hz, 1 H, 1′′-H), 5.20 (dd, *J* = 17, 1.5 Hz, 1 H, *cis*-2′′-H), 5.05 (dd, *J* = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 3.68 (s, 6 H, 2 CO_2Me), 3.59 (s, 3 H, CO_2Me), 3.15 (t, *J* = 7 Hz, 2 H, 9-H), 2.05 (m_c, 1 H), 1.81 (m_c, 8 H), 1.56−1.08 (m, 6 H), 0.92 (d, *J* = 6 Hz, 1 H, *trans*-3′-H), 0.87 (s, 9 H, *t*Bu), 0.08, 0.05 (2 s, 6 H, $SiMe_2$). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 172.4, 172.0*, 52.3*, 51.8 (2 s, 2 q, 3 CO_2Me), 136.9 (d, C-1′′), 114.9 (t, C-2′′), 64.9 (s, C-2′), 57.4 (s, C-5), 37.9 (s, C-1′), 33.3, 32.5, 31.3, 28.7, 27.7, 24.9, 24.2, 23.8 (8 t, C-1, C-2, C-3, C-4, C-6, C-7, C-8, C-3′), 25.8, 18.2 (q, s, *t*Bu), 6.1 (t, C-9), −3.4, −3.6 (2 q, $SiMe_2$), * signal has double intensity. – $C_{26}H_{45}IO_7Si$ (624.6): calcd. C 49.99, H 7.26; found C 50.07, H 7.47.

Dimethyl (2E)-1-[r-2-(tert-Butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-9-iodo-2-nonene-5,5-dicarboxylate (**6**): IR (neat): $\tilde{\nu}$ = 3050−3000 cm^{-1} (=C−H), 2950, 2930, 2890, 2860 (−C−H), 1740 (CO_2Me), 1650 (C=C). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.71 (dd, *J* = 17, 10.5 Hz, 1 H, 1′′-H),

Table 4. Synthesis of dimethyl malonates **8**, **9**, **10**, and **18**

Precursor	Amount [g (mmol)]	NaH [eq.]	Chromatography heptane/ethyl acetate	Product	Yield [g (%)]
5	0.457 (0.732)	5.0	9:1	**8**[a]	0.409 (89)
6	0.339 (0.544)	5.0	9:1→4:1	**9**[a]	0.292 (86)
7	0.287 (0.500)	1.2	4:1→7:3	**10**[b]	0.197 (63)
[c]	0.401 (0.699)	5.0	1:0→7.5:2.5	**18**[a]	0.302 (69)

[a] Colourless oil. – [b] Lightly yellow oil. – [c] Dimethyl (6*E*)-1-Bromo-8-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-2-methylene-6-octene-4,4-dicarboxylate.

Table 5. Synthesis of macrocycles **11**, **12**, **13**, and **19**

Precursor	Amount [g (mmol)]	Time [h]	Chromatography eptane/ethyl acetate	Product	Yield [g (%)]	M.P. [° C]
8	0.368 (0.585)	64	9:1→5:1	**11**[a]	0.030 (10)	158−160°C
9	0.288 (0.459)	65	9:1→7:3	**12**[a]	0.141 (60)	95−97°C
10	0.152 (0.243)	46	9:1→1:1	**13**	0.071 (57)	lightly yellow oil
18	0.276 (0.442)	63	9:1→1.5:1	**19**[a]	0.128 (57)	98−100°C

[a] Colourless crystals.

5.46, 5.18 (2 m_c, 1 H each, 2-H, 3-H), 5.16 (dd, J = 17, 1.5 Hz, 1 H, *cis*-2′′-H), 5.00 (dd, J = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 3.61 (s, 6 H, 2 CO_2Me), 3.54 (s, 3 H, CO_2Me), 3.09 (t, J = 7 Hz, 2 H, 9-H), 2.75 (dd, J = 15.5, 6.5 Hz, 1 H, 1-H), 2.50 (d, J = 7.5 Hz, 2 H, 4-H), 2.08 (dd, J = 15.5, 6.5 Hz, 1 H, 1-H), 1.76−1.67 (m, 5 H), 1.24−1.18 (m, 2 H), 0.91 (d, J = 6.5 Hz, 1 H, *trans*-3′-H), 0.81 (s, 9 H, *t*Bu), 0.03, 0.00 (2 s, 6 H, $SiMe_2$). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 171.5, 171.2*, 52.1*, 51.7 (2 s, 2 q, 3 CO_2Me), 136.5 (d, C-1′′), 132.0, 124.9 (2 d, C-2, C-3), 115.0 (t, C-2′′), 64.9 (s, C-2′), 57.4 (s, C-5), 37.2 (s, C-1′), 35.6, 33.1, 31.6, 30.7, 24.5, 23.5 (6 t, C-1, C-4, C-6, C-7, C-8, C-3′), 25.7, 18.0 (q, s, *t*Bu), 6.1 (C-9), −3.6, −3.7 (2 q, $SiMe_2$), *signal has double intensity. − $C_{26}H_{43}IO_7Si$ (622.6): calcd. C 50.16, H 6.96; found C 50.16, H 7.20.

Dimethyl (2E,7E)-9-Bromo-1-[r-2-(tert-butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-2,7-nonadiene-5,5-dicarboxylate (**7**): IR (CCl_4): ν̃ = 3100−3010 cm^{-1} (=C−H), 2960, 2930, 2870 (−C−H), 1740 (CO_2Me), 1630 (C=C). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 5.74 (dd, J = 17, 10.5 Hz, 1 H, 1′′-H), 5.64−5.42, 5.26−5.14* (2 m, 3 H, 1 H, 2-H, 3-H, 7-H, 8-H), 5.19 (br. d, J = 17 Hz, 1 H, *cis*-2′′-H), 5.02 (dd, J = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 3.82 (d, J = 7 Hz, 2 H, 9-H), 3.63 (s, 6 H, 2 CO_2Me), 3.55 (s, 3 H, CO_2Me), 2.76 (dd, J = 15.5, 6.5 Hz, 1 H, 1-H), 2.50 (m_c, 4 H, 4-H, 6-H), 2.10 (dd, J = 15.5, 6.5 Hz, 1 H, 1-H), 1.75 (d, J = 6.5 Hz, 1 H, *cis*-3′-H), 0.94 (d, J = 6.5 Hz, 1 H, *trans*-3′-H), 0.83 (s, 9 H, *t*Bu), 0.04, 0.01 (2 s, 6 H, $SiMe_2$), * signals are partly overlapped by *cis*-2′′-H signal. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 171.6, 170.7*, 52.2*, 51.7 (2 s, 2 q, 3 CO_2Me), 136.5 (d, C-1′′), 132.5, 130.6, 129.5, 124.5 (4 d, C-2, C-3, C-7, C-8), 115.0 (t, C-2′′), 64.9 (s, C-2′), 57.5 (s, C-5), 37.2 (s, C-1′), 35.7, 34.9, 32.1, 31.6 (4 t, C-1, C-4, C-6, C-9), 25.7, 18.0 (q, s, *t*Bu), 23.5 (t, C-3′), −3.6, −3.7 (2 q, $SiMe_2$), * signal has double intensity. − $C_{26}H_{41}BrO_7Si$ (573.6): calcd. C 54.44, H 7.20; found C 54.43, H 7.29.

Dimethyl (6E)-1-Bromo-8-[r-2-(tert-butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-2-methylene-6-octene-4,4-dicarboxylate: IR (KBr): ν̃ = 3090−3000 cm^{-1} (=C−H), 2950, 2930, 2900, 2850 (−C−H), 1730 (CO_2Me), 1640−1630 (C=C). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.73 (dd, J = 17, 10.5 Hz, 1 H, 1′′-H), 5.47, 5.30−5.20 (m_c, m, 1 H each, 6-H, 7-H), 5.23 (d, J = 0.5 Hz, 1 H, =CH_2), 5.18 (dd, J = 17, 1.5 Hz, 1 H, *cis*-2′′-H), 5.02 (dd, J = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 4.91 (d, J = 0.5 Hz, 1 H, =CH_2), 3.83 (s, 2 H, 1-H), 3.62 (s, 6 H, 2 CO_2Me), 3.56 (s, 3 H, CO_2Me), 2.80−2.74* (m, 1 H, 8-H), 2.77* (s, 2 H, 3-H), 2.53 (d, J = 7.5 Hz, 2 H, 5-H), 2.11 (dd, J = 15.5, 6.5 Hz, 1 H, 8-H), 1.74 (d, J = 6.5 Hz, 1 H, *cis*-3′-H), 0.93 (d, J = 6.5 Hz, 1 H, *trans*-3′-H), 0.83 (s, 9 H, *t*Bu), 0.04, 0.02 (2 s, 6 H, $SiMe_2$), * signals are overlapping. − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 171.6, 171.0*, 52.25, 52.23, 51.7 (2 s, 3 q, 3 CO_2Me), 140.9 (s, C-2), 136.5 (d, C-1′′), 132.5, 124.6 (2 d, C-6, C-7), 120.0 (t, =CH_2), 115.1 (t, C-2′′), 65.0 (s, C-2′), 57.4 (s, C-4), 37.1 (s, C-1′), 36.6, 36.0, 35.2, 31.6 (4 t, C-1, C-3, C-5, C-8), 25.7, 18.0 (q, s, *t*Bu), 23.6 (t, C-3′), −3.2, −3.7 (2 q, $SiMe_2$), * signal has double intensity. − $C_{26}H_{41}BrO_7Si$ (573.6): calcd. C 54.44, H 7.20; found C 53.54, H 6.96.

Tetramethyl 10-[r-2-(tert-Butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl]decane-1,1,6,6-tetracarboxylate (**8**): IR (CCl_4): ν̃ = 3040−3000 cm^{-1} (=C−H), 2950, 2930, 2860 (−C−H), 1740 (CO_2Me), 1640 (C=C). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.74 (dd, J = 17, 10.5 Hz, 1 H, 1′′-H), 5.17 (dd, J = 17, 1.5 Hz, 1 H, *cis*-2′′-H), 5.01 (dd, J = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 3.67, 3.64 (2 s, 6 H each, 4 CO_2Me), 3.56 (s, 3 H, CO_2Me), 3.28 (t, J = 7.5 Hz, 1 H, 1-H), 2.00 (m_c, 1 H), 1.87−1.72 (m, 7 H), 1.52−1.19 (m, 5 H), 1.17−1.04 (m, 4 H), 0.89 (d, J = 6 Hz, 1 H, *trans*-3′-H), 0.84 (s, 9 H, *t*Bu), 0.05, 0.02 (2 s, 6 H, $SiMe_2$). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 172.3, 172.0*, 169.6*, 52.3*, 52.1*, 51.6 (3 s, 3 q, 5 CO_2Me), 136.9 (d, C-1′′), 114.8 (t, C-2′′), 64.8 (s, C-2′), 57.5 (s, C-6), 51.4 (d, C-1), 37.8 (s, C-1′), 32.5, 32.3, 28.6, 28.4, 27.6, 27.4, 24.1, 23.7* (8 t, C-2, C-3, C-4, C-5, C-7, C-8, C-9, C-10, C-3′), 25.7, 18.0 (q, s, *t*Bu), −3.5, −3.8 (2 q, $SiMe_2$), * signal has double intensity. − $C_{31}H_{52}O_{11}Si$ (628.8): calcd. C 59.21, H 8.33; found C 59.27, H 8.67.

Tetramethyl (8E)-10-[r-2-(tert-Butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-8-decene-1,1,6,6-tetracarboxylate (**9**): IR (neat): ν̃ = 3100−3000 cm^{-1} (=C−H), 2960, 2930, 2860 (−C−H), 1730 (CO_2Me), 1680, 1640 (C=C). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.73 (dd, J = 17, 10.5 Hz, 1 H, 1′′-H), 5.43, 5.24−5.14* (m_c, m, 1 H each, 8-H, 9-H), 5.17 (dd, J = 17, 1.5 Hz, 1 H, *cis*-2′′-H), 5.01 (dd, J = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 3.65, 3.61 (2 s, 6 H each, 4 CO_2Me), 3.54 (s, 3 H, CO_2Me), 3.26 (t, J = 7.5 Hz, 1 H, 1-H), 2.75 (dd, J = 15.5, 6.5 Hz, 1 H, 10-H), 2.48 (d, J = 7.5 Hz, 2 H, 7-H), 2.08 (dd, J = 15.5, 6 Hz, 1 H, 10-H), 1.85−1.70 (m, 5 H), 1.28−1.03 (m, 4 H), 0.91 (d, J = 6.5 Hz, 1 H, *trans*-3′-H), 0.82 (s, 9 H, *t*Bu), 0.03, 0.01 (2 s, 6 H, $SiMe_2$), * signal is partly overlapped by *cis*-2′′-H signal. − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 171.6, 171.4*, 169.6*, 52.3−52.1, 51.6 (3 s, several q, 5 CO_2Me), 136.6 (d, C-1′′), 131.8, 125.0 (2 d, C-8, C-9), 115.0 (t, C-2′′), 65.0 (s, C-2′), 57.6 (s, C-6), 51.4 (d, C-1), 37.2 (s, C-1′), 35.8, 31.8, 31.6, 28.4, 27.3, 23.50, 23.46 (7 t, C-2, C-3, C-4, C-5, C-7, C-9, C-3′), 25.7, 18.0 (q, s, *t*Bu), −3.6, −3.7 (2 q, $SiMe_2$), * signal has double intensity. − $C_{31}H_{50}O_{11}Si$ (626.8): calcd. C 59.40, H 8.04; found C 59.46, H 8.36.

Tetramethyl (3E,8E)-10-[r-2-(tert-Butyldimethylsiloxy)-trans-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-3,8-decadiene-1,1,6,6-tetracarboxylate (**10**): IR (CCl_4): ν̃ = 3090, 3040 cm^{-1} (=C−H), 2950, 2930, 2860 (−C−H), 1760−1740 (CO_2Me), 1630 (C=C). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 5.72 (dd, J = 17, 10.5 Hz, 1 H, 1′′-H), 5.47−5.08* (m, 4 H, 3-H, 4-H, 8-H, 9-H), 5.16 (dd, J = 17, 1.5 Hz, 1 H, *cis*-2′′-H), 5.00 (dd, J = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 3.64, 3.59 (2 s, 6 H each, 4 CO_2Me), 3.54 (s, 3 H, CO_2Me), 3.30 (t, J = 7.5 Hz, 1 H, 1-H), 2.74 (dd, J = 15.5, 6.5 Hz, 1 H, 10-H), 2.52−2.41 (m, 6 H, 2-H, 5-H, 7-H), 2.07 (dd, J = 15.5, 6.5 Hz,

1 H, 10-H), 1.73 (d, J = 6.5 Hz, 1 H, *cis*-3′-H), 0.92 (d, J = 6.5 Hz, 1 H, *trans*-3′-H), 0.81 (s, 9 H, *t*Bu), 0.02, 0.00 (2 s, 6 H, $SiMe_2$), * signals are partly overlapped by *cis*-2′′-H signal. – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 171.6, 170.8*, 168.9*, 52.3*, 52.2, 52.1, 51.7, 51.4 (3 s, 4 q, d, 5 CO_2Me, C-1), 136.5, 132.1, 130.0, 127.1, 124.8 (5 d, C-3, C-4, C-8, C-9, C-1′′), 115.0 (t, C-2′′), 64.9 (s, C-2′), 57.6 (s, C-6), 37.2 (s, C-1′), 35.2, 35.1 (2 t, C-2, C-10), 31.6* (t, C-5, C-7), 25.7, 18.0 (q, s, *t*Bu), 23.5 (t, C-3′), −3.6, −3.8 (2 q, $SiMe_2$), * signal has double intensity. – $C_{31}H_{48}O_{11}Si$ (624.8): calcd. C 59.59, H 7.74; found C 59.06, H 8.16.

Tetramethyl (7E)-9-[r-2-(tert-Butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-3-methylene-7-nonene-1,1,5,5-tetracarboxylate (**18**): IR (neat): $\tilde{\nu}$ = 3090−3000 cm^{-1} (=C−H), 2960, 2930, 2900, 2860 (−C−H), 1750−1740 (CO_2Me), 1640 (C=C). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.76 (dd, J = 17, 10.5 Hz, 1 H, 1′′-H), 5.48, 5.26 (2 m_c, 1 H each, 7-H, 8-H), 5.21 (dd, J = 17, 1.5 Hz, 1 H, *cis*-2′′-H), 5.05 (dd, J = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 4.86 (d, J = 1 Hz, 1 H, $=CH_2$), 4.80 (br. s, 1 H, $=CH_2$), 3.68, 3.65 (2 s, 6 H each, 4 CO_2Me), 3.59 (s, 3 H, CO_2Me), 3.58 (t, J = 8 Hz, 1 H, 1-H), 2.80 (dd, J = 15.5, 6.5 Hz, 1 H, 9-H), 2.62 (s, 2 H, 4-H), 2.56 (d, J = 7 Hz, 2 H, 6-H), 2.48 (d, J = 8 Hz, 2 H, 2-H), 2.12 (dd, J = 15.5, 6.5 Hz, 1 H, 9-H), 1.76 (dd, J = 6, 1 Hz, 1 H, *cis*-3′-H), 0.95 (br. d, J = 6 Hz, 1 H, *trans*-3′-H), 0.86 (s, 9 H, *t*Bu), 0.07, 0.04 (2 s, 6 H, $SiMe_2$). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 171.8, 171.22, 171.20, 169.1*, 52.4−51.8 (4 s, several q, 5 CO_2Me), 140.6 (s, C-3), 136.6 (d, C-1′′), 132.2, 125.0 (2 d, C-7, C-8), 116.9, 115.1 (2 t, C-2′′, $=CH_2$), 65.1 (s, C-2′), 57.6 (s, C-5), 50.2 (d, C-1), 37.8, 35.8, 35.2, 31.7 (4 t, C-2, C-4, C-6, C-9), 37.2 (s, C-1′), 25.8, 18.1 (q, s, *t*Bu), 23.6 (t, C-3′), −3.5, −3.7 (2 q, $SiMe_2$), * signal has double intensity. – $C_{31}H_{48}O_{11}Si$ (624.8): calcd C 59.59, H 7.74; found C 59.99, H 7.73.

Pentamethyl 4-Oxocyclopentadecane-1,1,6,11,11-pentacarboxylate (**11**): IR (KBr): $\tilde{\nu}$ = 2950, 2860 cm^{-1} (−C−H), 1740, 1720 (CO_2Me, C=O). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.692, 3.685, 3.67, 3.66, 3.64 (5 s, 15 H, 5 CO_2Me), 2.95 (m_c, 1 H, 6-H), 2.76 (dd, J = 17, 6 Hz, 1 H, 5-H), 2.59 (dd, J = 17, 6.5 Hz, 1 H, 5-H), 2.46 (m_c, 1 H), 2.33 (m_c, 2 H), 1.14 (m_c, 1 H), 2.02−1.72 (m, 6 H), 1.62−1.54 (m, 1 H), 1.43−0.84 (m, 9 H). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 207.2 (s, C=O), 175.4, 172.0, 171.9*, 171.4, 52.54, 52.47, 52.4*, 51.9 (4 s, 4 q, 5 CO_2Me), 57.0, 56.9 (2 s, C-1, C-11), 43.1, 37.5, 31.7, 30.3, 30.2, 29.9, 26.0, 25.2, 24.3, 23.8, 22.0 (11 t, C-2, C-3, C-5, C-7, C-8, C-9, C-10, C-12, C-13, C-14, C-15), 38.8 (d, C-6), * signal has double intensity. – $C_{25}H_{38}O_{11}$ (514.6): calcd. C 58.36, H 7.44; found C 58.47, H 7.69.

Pentamethyl (8E)-4-Oxo-8-cyclopentadecene-1,1,6,11,11-pentacarboxylate (**12**): IR (KBr): $\tilde{\nu}$ = 3040−3000 cm^{-1} (=C−H), 2950, 2900, 2870 (−C−H), 1730 (CO_2Me, C=O), 1630 (C=C). – ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.38 (m_c, 1 H, 8-H), 5.15 (m_c, 1 H, 9-H), 3.665, 3.655, 3.65, 3.63 (4 s, 12 H, 4 CO_2Me), 3.61 (s, 3 H, 6-CO_2Me), 2.97 (m_c, 1 H, 6-H), 2.84 (dd, J = 18, 8.5 Hz, 1 H, 5-H_{ax}), 2.58 (m_c, 2 H, 10-H), 2.44* (dd, J = 18, 4 Hz, 1 H, 5-H_{eq}), 2.41* (m_c, 1 H, 7-H), 2.34−2.26, 2.20−2.09 (2 m, 2 H, 3 H, 2-H, 3-H, 7-H), 1.76 (m_c, 1 H, 15-H), 1.71−1.60 (m, 3 H, 12-H, 15-H), 1.20−1.09 (m, 3 H, 13-H, 14-H), 1.04 (m_c, 1 H, 13-H), * signals are partly overlapping. – ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 207.6 (s, C=O), 174.6, 51.9 (s, q, 6-CO_2Me), 171.6*, 171.4, 171.3, 52.4*, 52.3* (3 s, 2 q, 4 CO_2Me), 131.2 (d, C-8), 127.3 (d, C-9), 56.8 (s, C-1), 56.3 (s, C-11), 42.2 (t, C-5), 39.1 (d, C-6), 37.1 (t, C-3), 36.4 (t, C-10), 33.8 (t, C-7), 31.9 (t, C-12), 30.2 (t, C-15), 25.7 (t, C-2), 23.7 (t, C-13), 23.1 (t, C-14), *signal has double intensity; assignment supported by 2D-NMR experiments. – $C_{25}H_{36}O_{11}$ (512.6): calcd. C 58.58, H 7.08; found C 58.84, H 7.55.

Pentamethyl (3E,8E)-13-Oxo-3,8-cyclopentadecadiene-1,1,6,6,11-pentacarboxylate (**13**): IR (CCl_4): $\tilde{\nu}$ = 3050−3000 cm^{-1} (=C−H), 2950, 2900, 2850 (−C−H), 1740 (CO_2Me), 1710 (C=O), 1680, 1660 (C=C). – ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.41−5.36 (m, 3 H, 3-H, 4-H, 9-H), 5.24 (m_c, 1 H, 8-H), 3.72, 3.71, 3.68*, 3.66 (4 s, 15 H, 5 CO_2Me), 2.97 (m_c, 1 H, 11-H), 2.71 (d, J = 6 Hz, 2 H, 12-H), 2.69−2.63 (m, 6 H, 2-H, 5-H, 7-H), 2.39−2.33 (m, 2 H, 10-H, 14-H), 2.27−2.20 (m, 2 H, 10-H, 14-H), 2.03 (m_c, 2 H, 15-H), *signal has double intensity. – ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 207.8 (s, C=O), 174.7, 52.0 (s, q, 11-CO_2Me), 171.4*, 171.2, 171.1, 52.7*, 52.6* (3 s, 2 q, 4 CO_2Me), 130.7 (d, C-9), 128.6 (d, C-4), 128.1 (d, C-3), 126.9 (d, C-8), 56.1 (s, C-1), 55.8 (s, C-6), 41.3 (t, C-12), 39.0 (d, C-11), 38.4 (t, C-14), 35.8 (t, C-2), 35.4 (t, C-5), 34.9 (t, C-7), 33.7 (t, C-10), 26.8 (t, C-15), *signal has double intensity; assignment supported by 2D-NMR experiments. – $C_{25}H_{34}O_{11}$ (510.5): calcd. C 58.82, H 6.71; found C 58.56, H 6.81.

Pentamethyl (7E)-3-Methylene-12-oxo-7-cyclotetradecene-1,1,5,5,10-pentacarboxylate (**19**): IR (KBr): $\tilde{\nu}$ = 3080−3000 cm^{-1} (=C−H), 2950, 2930, 2850 (−C−H), 1740−1730 (CO_2Me, C=O), 1640 (C=C). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.35, 5.05 (2 m_c, 1 H each, 7-H, 8-H), 4.70 (s, 2 H, $=CH_2$), 3.71, 3.68, 3.66, 3.65* (4 s, 15 H, 5 CO_2Me), 3.14 (m_c, 1 H, 10-H), 2.96−2.01 (m, 14 H), *signal has double intensity. – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 206.3 (s, C=O), 175.0, 171.5, 171.21, 171.18, 171.16, 52.5, 52.4, 52.3, 52.2, 52.0 (5 s, 5 q, 5 CO_2Me), 140.3 (s, C-3), 132.6, 126.4 (2 d, C-7, C-8), 117.5 (t, $=CH_2$), 58.8, 58.2 (2 s, C-1, C-5), 42.8, 39.7, 38.4, 37.8, 37.5, 35.7, 24.6 (7 t, C-2, C-4, C-6, C-9, C-11, C-13, C-14), 37.9 (d, C-10). – $C_{25}H_{34}O_{11}$ (510.5): calcd. C 58.82, H 6.71, found C 59.07, H 6.87.

Tetramethyl (2E,7E,12E)-14-Bromo-1-[r-2-(tert-butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-2,7,12-tetradecatriene-5,5,10,10-tetracarboxylate (**14**): According to *General Procedure A* siloxycyclopropane **10** (1.08 g, 1.74 mmol) was deprotonated with sodium hydride (0.260 g, 8.68 mmol) and alkylated with dihalide **4** (3.71 g, 17.4 mmol). Chromatography (heptane/ethyl acetate, 9.5:0.5 to 4:1) furnished compound **14** (0.657 g, 50%) as colourless oil. – IR (KBr): $\tilde{\nu}$ = 3030−3000 cm^{-1} (=C−H), 2960, 2930, 2860 (−C−H), 1740 (CO_2Me), 1640 (C=C). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.83−5.72, 5.54, 5.37−5.20 (2 m, m_c, 2 H, 2 H, 4 H, 1′′-H, *cis*-2′′-H, 2-H, 3-H, 7-H, 8-H, 12-H, 13-H), 5.07 (dd, J = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 3.88 (d, J = 7.5 Hz, 2 H, 14-H), 3.70, 3.67 (2 s, 6 H each, 4 CO_2Me), 3.61 (s, 3 H, CO_2Me), 2.82 (dd, J = 15.5, 6.5 Hz, 1 H, 1-H), 2.58−2.50 (m, 8 H, 4-H, 6-H, 9-H, 11-H), 2.14 (dd, J = 15.5, 6 Hz, 1 H, 1-H), 1.79 (dd, J = 6.5, 1 Hz, 1 H, *cis*-3′-H), 0.98 (br. d, J = 6.5 Hz, 1 H, *trans*-3′-H), 0.88 (s, 9 H, *t*Bu), 0.09, 0.06 (2 s, 6 H, $SiMe_2$). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 171.8, 171.0*, 170.8*, 52.5*, 52.3*, 51.9 (3 s, 3 q, 5 CO_2Me), 136.7 (d, C-1′′), 132.3, 130.9, 129.6, 129.1, 128.0, 125.0 (6 d, C-2, C-3, C-7, C-8, C-12, C-13), 115.2 (t, C-2′′), 65.0 (s, C-2′), 57.8, 57.5 (2 s, C-5, C-10), 37.4 (s, C-1′), 35.9, 35.52, 35.46, 35.1, 32.3, 31.8 (6 t, C-1, C-4, C-6, C-9, C-11, C-14), 25.8, 18.2 (q, s, *t*Bu), 23.6 (t, C-3′), −3.5, −3.6 (2 q, $SiMe_2$), * signal has double intensity. – $C_{35}H_{53}BrO_{11}Si$ (757.8): calcd. C 55.48, H 7.05; found C 55.50, H 7.17.

Hexamethyl (3E,8E,13E)-15-[r-2-(tert-Butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-3,8,13-pentadecatriene-1,1,6,6,11,11-hexacarboxylate (**15**): According to *General Procedure B* dimethyl malonate (1.55 g, 11.7 mmol) was deprotonated with sodium hydride (0.176 g, 5.85 mmol) and treated with **14** (0.887 g, 1.17 mmol). Chromatography (heptane/ethyl acetate, 9.5:0.5 to 6.5:3.5) afforded **15** (0.589 g, 62%) as colourless oil. – IR (KBr): $\tilde{\nu}$ = 3040−3000 cm^{-1} (=C−H), 2960, 2930, 2860 (−C−H), 1740

(CO_2Me), 1640 (C=C). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.78 (dd, *J* = 17, 10.5 Hz, 1 H, 1′′-H), 5.56–5.42, 5.36–5.20 (2 m, 2 H, 5 H, 3-H, 4-H, 8-H, 9-H, 13-H, 14-H, *cis*-2′′-H), 5.07 (br. d, *J* = 10.5 Hz, 1 H, *trans*-2′′-H), 3.71, 3.68, 3.67 (3 s, 6 H each, 6 CO_2Me), 3.61 (s, 3 H, CO_2Me), 3.39 (t, *J* = 7.5 Hz, 1 H, 1-H), 2.82 (dd, *J* = 15.5, 6.5 Hz, 1 H, 15-H), 2.59–2.49 (m, 10 H, 2-H, 5-H, 7-H, 10-H, 12-H), 2.14 (dd, *J* = 15.5, 6.5 Hz, 1 H, 15-H), 1.79 (d, *J* = 6.5 Hz, 1 H, *cis*-3′-H), 0.98 (d, *J* = 6.5 Hz, 1 H, *trans*-3′-H), 0.88 (s, 9 H, *t*Bu), 0.09, 0.06 (2 s, 6 H, $SiMe_2$). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 171.8, 171.0*, 170.9*, 169.1*, 52.5–51.6 (4 s, several q, 7 CO_2Me), 136.7 (d, C-1′′), 132.3, 130.3, 128.7, 128.3, 127.1, 125.0 (6 d, C-3, C-4, C-8, C-9, C-13, C-14), 115.1 (t, C-2′′), 65.1 (s, C-2′), 57.8, 57.6 (2 s, C-6, C-11), 37.4 (s, C-1′), 35.5–31.8 (several t, C-2, C-5, C-7, C-10, C-12, C-15), 25.8, 18.2 (q, s, *t*Bu), 23.6 (t, C-3′), –3.5, –3.6 (2 q, $SiMe_2$), * signal has double intensity. – $C_{40}H_{60}O_{15}Si$ (809.0): calcd. C 59.39, H 7.48; found C 59.39, H 7.70.

Heptamethyl (3E,8E,13E)-18-Oxo-3,8,13-cycloeicosatriene-1,1,6,6,11,11,16-heptacarboxylate (**16**): According to *General Procedure C* compound **15** (0.580 g, 0.717 mmol) was added during 69 h to a suspension of cesium fluoride (0.327 g, 2.15 mmol) and benzyltriethylammonium chloride (0.245 g, 1.08 mmol) in DMF (260 ml). Chromatography (heptane/ethyl acetate, 9:1 to 1:1) provided **16** (0.197 g, 40%) as colourless crystals, m.p. 135–137°C. – IR (KBr): $\tilde{\nu}$ = 3050–3000 cm^{-1} (=C–H), 2960, 2850 (–C–H), 1730 (CO_2Me, C=O), 1640 (C=C). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.66–5.12 (m, 6 H, 3-H, 4-H, 8-H, 9-H, 13-H, 14-H), 3.64, 3.618, 3.617, 3.61, 3.60, 3.59* (6 s, 21 H, 7 CO_2Me), 2.92 (m_c, 1 H), 2.74 (dd, *J* = 18, 7 Hz, 1 H), 2.55–1.99 (m, 17 H), * signal has double intensity. – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 207.2 (s, C=O), 174.6, 171.1–170.9, 52.5–52.3, 51.8 (several s, several q, 7 CO_2Me), 131.0, 129.0, 128.7, 128.3, 127.9, 126.8 (6 d, C-3, C-4, C-8, C-9, C-13, C-14), 57.5, 56.9, 56.6 (3 s, C-1, C-6, C-11), 42.0, 37.8, 36.2, 35.32, 35.29, 35.14, 35.06, 34.4, 26.4 (9 t, C-2, C-5, C-7, C-10, C-12, C-15, C-17, C-19, C-20), 39.1 (d, C-16). – $C_{34}H_{46}O_{15}$ (694.7): calcd. C 58.78, H 6.67; found C 58.81, H 6.97.

Dimethyl 3-[r-2-(tert-Butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-ylmethyl]-3-butene-1,1-dicarboxylate (**21**): Siloxycyclopropane **20** (0.500 g, 1.95 mmol) was deprotonated with lithium diisopropylamide (generated in situ from 2.93 mmol of diisopropylamine and 2.93 mmol of *n*-butyllithium) in THF (30 ml) at –78°C. After 2 h the dihalide **17** (0.834 g, 3.90 mmol) was added and the mixture was stirred at –78°C for 18 h. The mixture was diluted with saturated aqueous NH_4Cl solution and after warming up it was extracted with ethyl acetate (3 ×). The combined organic layers were washed with water and brine and dried ($MgSO_4$). After evaporation of the solvents the unconsumed dihalide **17** was removed by kugelrohr distillation (0.01 mbar, 75°C). Chromatography (heptane/ethyl acetate, 1:0 to 4:1) gave dimethyl (6*E*)-1-bromo-8-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-2-methylene-6-octene-4,4-dicarboxylate (0.479 g, 63%) as colourless oil. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.80 (dd, *J* = 17, 10.5 Hz, 1 H, 1′′-H), 5.26 (dd, *J* = 17, 1.5 Hz, 1 H, *cis*-2′′-H), 5.17 (br. s, 1 H, 3′-H), 5.11 (dd, *J* = 10.5, 1.5 Hz, 1 H, *trans*-2′′-H), 5.01 (d, *J* = 1 Hz, 1 H, 3′-H), AB system (δ_A = 3.90, δ_B = 3.83, J_{AB} = 10 Hz, 2 H, CH_2Br), 3.59 (s, 3 H, CO_2Me), 3.01 (d, *J* = 17 Hz, 1 H, 1′-H), 2.55 (d, *J* = 17 Hz, 1 H, 1′-H), 1.95 (dd, *J* = 6.5, 1 Hz, 1 H, *cis*-3-H), 1.16 (br. d, *J* = 6.5 Hz, 1 H, *trans*-3-H), 0.91 (s, 9 H, *t*Bu), 0.11, 0.10 (2 s, 6 H, $SiMe_2$). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 171.8, 51.9 (s, q, CO_2Me), 143.7 (s, C-2′), 136.5 (d, C-1′′), 115.8, 115.6 (2 t, C-2′′, C-3′), 64.4 (s, C-2), 36.7, 32.5 (2 t, C-1′, CH_2Br), 36.2 (s, C-1), 25.8, 18.2 (q, s, *t*Bu), 23.6 (t, C-3), –3.4, –3.5 (2 q, $SiMe_2$).

According to *General Procedure A* dimethyl malonate (1.49 g, 11.2 mmol) was deprotonated with sodium hydride (0.169 g, 5.62 mmol) and alkylated with the product obtained above (0.438 g, 1.12 mmol). Chromatography (heptane/ethyl acetate, 1:0 to 8.5:1.5) furnished **21** (0.316 g, 64%) as colourless oil. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.76 (dd, *J* = 17, 10.5 Hz, 1 H, vinyl-1-H), 5.21 (dd, *J* = 17, 1.5 Hz, 1 H, *cis*-vinyl-2-H), 5.07 (dd, *J* = 10.5, 1.5 Hz, 1 H, *trans*-vinyl-2-H), 4.81 (s, 1 H, 4-H), 4.74 (s, 1 H, 4-H), 3.67 (s, 6 H, 2 CO_2Me), 3.58 (t, *J* = 8 Hz, 1 H, 1-H), 3.55 (s, 3 H, CO_2Me), 2.89 (d, *J* = 17 Hz, 1 H, 1′-H), 2.59 (d, *J* = 8 Hz, 2 H, 2-H), 2.21 (d, *J* = 17 Hz, 1 H, 1′-H), 1.91 (dd, *J* = 6.5, 1 Hz, 1 H, *cis*-3′′-H), 1.00 (br. d, *J* = 6.5 Hz, 1 H, *trans*-3′′-H), 0.86 (s, 9 H, *t*Bu), 0.07, 0.04 (2 s, 6 H, $SiMe_2$). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 171.8, 169.3, 169.2, 52.38, 52.36, 51.8 (3 s, 3 q, 3 CO_2Me), 143.5 (s, C-3), 136.4 (d, vinyl-C-1), 115.4 (t, vinyl-C-2), 111.9 (t, C-4), 64.5 (s, C-2′′), 50.2 (d, C-1), 36.3 (s, C-1′′), 35.4, 34.1 (2 t, C-2, C-1′), 25.7, 18.1 (q, s, *t*Bu), 23.7 (t, C-3′′), –3.5, –3.7 (2 q, $SiMe_2$). – $C_{22}H_{36}O_7Si$ (440.6): calcd. C 59.97, H 8.23; found C 61.35, H 8.28. Due to the sensitivity of this compound no satisfactory elemental analysis could be obtained.

Trimethyl 3-Methylene-7-oxocyclononane-1,1,5-tricarboxylate (**22**) *and Hexamethyl 3,12-Dimethylene-7,16-dioxocyclooctadecane-1,1,5,10,10,14-hexacarboxylate* (**23**) : According to *General Procedure C* compound **21** (0.292 g, 0.663 mmol) was added during 5 days to a suspension of cesium fluoride (0.302 g, 1.99 mmol) and benzyltriethylammonium chloride (0.226 g, 0.994 mmol) in DMF (400 ml). Chromatography (heptane/ethyl acetate, 1:0 to 1.5:1) provided **22** (0.031 g, 14%) and **23** (0.013 g, 6%) as colourless oils.

Analytical data of **22**: IR (neat): $\tilde{\nu}$ = 3100–3000 cm^{-1} (=C–H), 2990, 2960, 2930, 2910 (–C–H), 1740–1730, 1710–1700 (CO_2Me, C=O), 1660–1640 (C=C). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.98, 4.69 (2 s, 1 H each, $=CH_2$), 3.720, 3.716, 3.69 (3 s, 9 H, 3 CO_2Me), 3.15 (m_c, 1 H, 5-H), 2.85–2.12 (m, 10 H). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 212.3 (s, C=O), 174.5, 171.70, 171.67, 52.92, 52.88, 52.2 (3 s, 3 q, 3 CO_2Me), 139.1 (s, C-3), 118.4 (t, $=CH_2$), 56.8 (s, C-1), 43.9, 40.2, 37.5, 35.2, 28.2 (5 t, C-2, C-4, C-6, C-8, C-9), 41.0 (d, C-5). – MS (FD); *m/z* (%): 327 (39) [M^+ + 1], 326 (100) [M^+]. – $C_{16}H_{22}O_7$ (326.3): calcd. C 58.89, H 6.79; found C 58.62, H 6.89.

Analytical data of **23** (two diastereomers): IR (CCl_4): $\tilde{\nu}$ = 3080–3000 cm^{-1} (=C–H), 2950, 2900, 2840 (–C–H), 1740 (CO_2Me, C=O), 1650 (C=C). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.84, 4.75, 4.70 (3 s, 2 H, 1 H, 1 H, 2 $=CH_2$), 3.72, 3.71, 3.69, 3.68, 3.66, 3.63 (6 s, 18 H, 6 CO_2Me), 3.09–1.96 (m, 22 H). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 207.0* (s, 2 C=O), 175.10, 175.05, 51.9, 51.7 (2 s, 2 q, 5-CO_2Me, 14-CO_2Me), 171.4, 171.3*, 171.2, 52.7, 52.6, 52.5, 52.4 (3 s, 4 q, 4 CO_2Me), 141.10, 141.05 (2 s, C-3, C-12), 116.6, 115.3 (2 t, 2 $=CH_2$), 57.0, 56.8 (2 s, C-1, C-10), 44.1, 43.2, 40.5, 39.2, 37.6, 36.9, 36.8, 34.6, 25.4, 24.9 (10 t, 10 CH_2), 38.3* (d, C-5, C-14), * signal has double intensity. – MS (MALDI, matrix: sinapinic acid); *m/z* (%): 691 (10) [M^+ – 1 with K], 674 (100) [M^+ – 1 with Na]. – $C_{32}H_{44}O_{14}$ (652.7): calcd. C 58.89, H 6.79; found C 58.48, H 6.66.

X-ray Crystallographic Study[6]: $C_{25}H_{34}O_{11}$, M_r = 510.52, crystal dimensions 0.58 × 0.25 × 0.25 mm, monoclinic, $P2_1/a$, *a* = 14.793(2), *b* = 11.0727(11), *c* = 16.243(3) Å, α = 90(11), β = 100.936(13), γ = 90.000(10)°, *V* = 2612.3(6) $Å^3$, *Z* = 4, ρ_{calcd} = 1.298 g cm^{-3}, Mo-*Kα*, *T* = 293(2) K, μ = 0.102 mm^{-1}. 6403 (3390 unique, 2θ < 45°, R_{int} = 0.0296) data were collected on a NONIUS CAD4 (four-circle) diffractometer. The structure was solved by direct methods (SHELXS-86[13]) and refined by full matrix least-square on F^2 values for all data (SHELXL-97[14]) to give R_1 (all

data) = 0.0577 and R ($I > 2\sigma I$) = 0.0427. Residual electron density extremes were +0.243 and −0.175 e Å $^{-3}$.

☆ Dedicated to Prof. *R. W. Hoffmann* on the occasion of his 65th birthday.

[1] A. Ullmann, Dissertation, Technische Universität Dresden, **1998**.

[2] [2a] A. Ullmann, J. Schnaubelt, H.-U. Reißig, *Synthesis* **1998**, 1052−1066. − [2b] J. Schnaubelt, A. Ullmann, H.-U. Reißig, *Synlett* **1995**, 1223−1225.

[3] [3a] P. Deslongchamps, S. Lamothe, H.-S. Lin, *Can. J. Chem.* **1984**, *62*, 2395−2398. − [3b] P. Deslongchamps, B. L. Roy, *Can. J. Chem.* **1986**, *64*, 2068−2075.

[4] [4a] I. Böhm, E. Hirsch, H.-U. Reißig, *Angew. Chem.* **1981**, *93*, 593−594; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 574. − [4b] I. Reichelt, H.-U. Reißig, *Liebigs Ann. Chem.* **1984**, 531−551. − [4c] Review: H.-U. Reißig, *Top. Curr. Chem.* **1988**, *144*, 73−135.

[5] [5a] Review: K. Ziegler in *Houben-Weyl*, vol. 4/2, 4th ed. (Ed.: E. Müller), Thieme, Stuttgart, **1955**, p. 729−822. − [5b] Review: G. Illuminati, L. Mandolini, *Acc. Chem. Res.* **1981**, *14*, 95−102.

[6] Crystallographic datas (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101681. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CN2 1EZ, UK [Fax: int. code +44(1223)336−033; E-mail: deposit@ccdc.cam.ac.uk].

[7] A. Ullmann, G. Zahn, J. Schnaubelt, H.-U. Reißig, *Z. Kristallogr.*, submitted.

[8] Further recent applications of this concept: [8a] B. Frey, S. Hünig, M. Koch, H.-U. Reißig, *Synlett* **1991**, 854−856. − [8b] J. Schnaubelt, R. Zschiesche, H.-U. Reißig, H. J. Lindner, J. Richter, *Liebigs Ann. Chem.* **1993**, 61−70. − [8c] J. Schnaubelt, H.-U. Reißig, *Synlett* **1995**, 452−454.

[9] For synthesis of a variety of benzanellated compounds (cyclophanes): A. Ullmann, M. Gruner, H.-U. Reißig, *Chem. Eur. J.*, im press.

[10] [10a] J. Breitenbach, J. Boosfeld, F. Vögtle in *Comprehensive Supramolecular Chemistry*, vol. 2, 1st ed. (Ed.: F. Vögtle), Pergamon, Oxford, New York, Tokyo, **1996**, p. 29−67. − [10b] Q. Meng, M. Hesse, *Top. Curr. Chem.* **1992**, *161*, 107−176. − [10c] C. J. Roxburgh, *Tetrahedron* **1995**, *51*, 9767−9822. − [10d] M. A. Titus, *Chem. Rev.* **1988**, *88*, 719−732.

[11] B. Hofmann, H.-U. Reißig, *Chem. Ber.* **1994**, *127*, 2315−2325.

[12] H. Finkelstein, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1528−1532.

[13] G. M. Sheldrick, *SHELXS86*, **1986**, Program for the Solution of Crystal Structures from Diffraction Data, Göttingen.

[14] G. M. Sheldrick, *SHELXL93*, **1993**, Program for the Refinement of Crystal Structures, Göttingen.

[O98252]