Synthesis of Functionalized Cyclophanes by Ring-Opening/Ring-Closure Cascade Reactions of Siloxycyclopropanes

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Dedicated to Professor Gernot Boche on the occasion of his 60th birthday

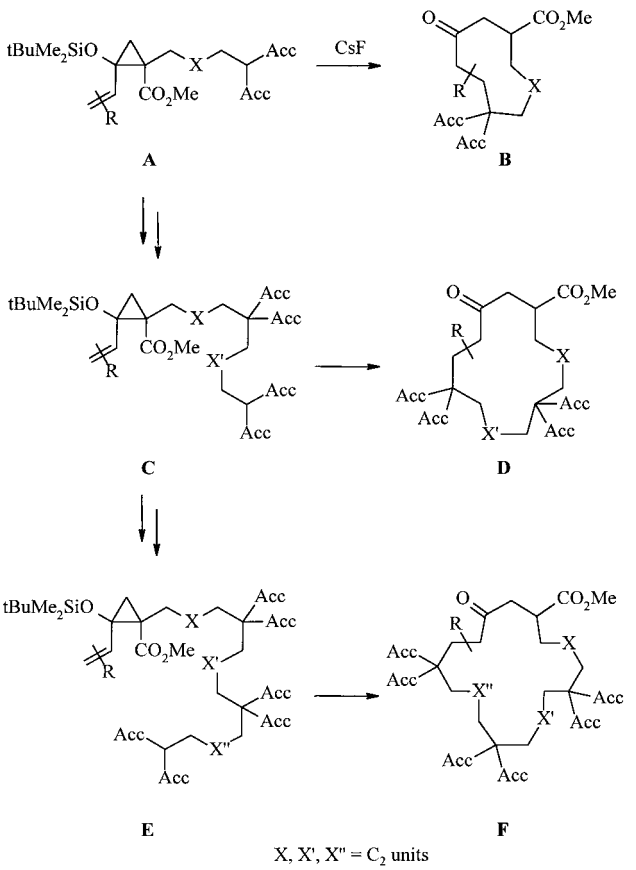
Abstract: Our repetitive approach to the synthesis of large-ring compounds has been extended to the preparation of a number of functionalized cyclophanes. The key components are substituted methyl 2-alkenyl-2-siloxycyclopropanecarboxylates, such as **8**–**10**, **24**–**28**, **36**, and **39**, which are easily prepared by a highly versatile route involving malonate alkylations. Treatment of these precursors with cesium fluoride under appropriate conditions of high dilution causes cascade reactions that proceed with consecutive desilylation, ring-opening, proton transfer, and finally, intramolecular Michael addition to afford benzannulated large-ring compounds in generally good yields. The geometry of the aromatic spacer in precursors **8** and **10** does not allow formation of monomeric cyclic products, but the 'dimers' **12** and **13** were isolated in low yield. However, the functionalized cyclophanes **11**, **29**, **30**, **31**, **33**, and **34** are formed in moderate to good yields. The pyridinophane **37**, its dimer **38**, and [13]pyridinophane **40** (obtainable in excellent yield) may be of particular interest as they could serve as precursors to highly functionalized ligands in supramolecular chemistry.

Keywords: cyclophanes · cyclopropanecarboxylates · enones · macrocyclic ligands · Michael additions

Introduction

Syntheses of cyclophanes[1] have received much attention over the last decades because of the particular properties of this class of compound, such as effects of strain on structure and reactivity, transannular interactions, and the potential to act as hosts for certain guests.[2] Many synthetic methods have been developed in which the ring-closure step is very often crucial. We have recently reported[3, 4] the rather straightforward preparations of ten-membered carbocycles from suitably functionalized methyl 2-alkenyl-2-siloxycyclopropanecarboxylates **A**, which undergo desilylation and ring-opening on treatment with cesium fluoride (Scheme 1). This is followed directly by intramolecular Michael addition[5] to furnish the cyclodecanone derivatives **B** in moderate to good yields. Repetition of the steps followed in the synthesis of **A** allowed us to obtain the precursor compounds **C** or **E**, which undergo the same ring-opening/ring-closure cascade reactions to yield the fifteen-membered ring compounds **D** and twenty-membered ring systems **F**, respectively.[6]

The simplicity, versatility, and often surprising efficiency of these reactions led us to extend this strategy to the synthesis of



Scheme 1. Synthesis of carbocycles **B**, **D**, and **F**.

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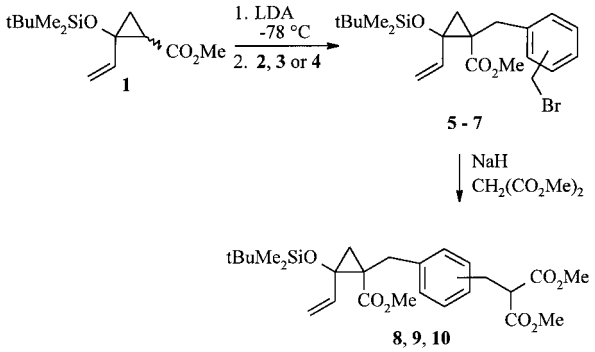
ortho-, meta-, and paracyclophanes, as well as to pyridinophanes. If successful we would establish a very powerful and highly adaptable route to various functionalized cyclophanes.

Results

Methyl 2-siloxy-2-vinylcyclopropanecarboxylate **1**[7] was converted into its alkylation products **5**, **6**, and **7** by deprotonation with lithium diisopropylamide (LDA) and subsequent reaction of the ester enolate[8] with an excess of the dihalides **2**, **3**, or **4**, respectively (Scheme 2). These products were then



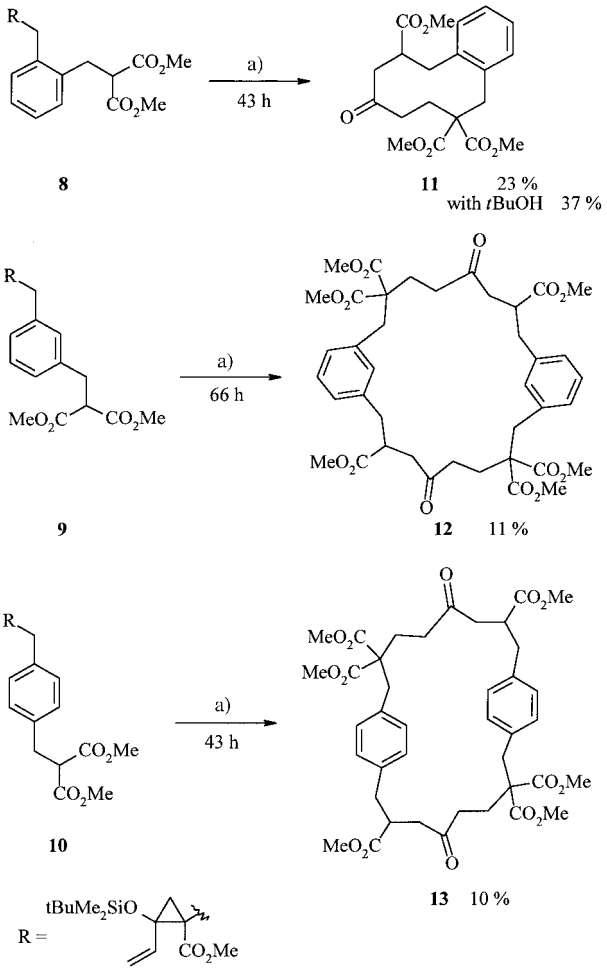
Scheme 2. Synthesis of precursors **8**–**10** via **5**–**7**, respectively. Yields: **8**: 72%; **9**: 62%; **10**: 44%.

Abstract in German: *Unsere repetitiven Synthesen von großen Ringen konnten auf die Darstellung einer Reihe von funktionalisierten Cyclophanen ausgedehnt werden. Als Schlüsselverbindungen dienen dabei die 2-Alkenyl-2-siloxy-cyclopropancarbonsäuremethylester **8**–**10**, **24**–**28**, **36** und **39**, die in flexibler Weise durch Malonesteralkylierung mit den notwendigen funktionellen Gruppen ausgestattet werden konnten. Beim Behandeln dieser Verbindungen mit Cäsiumfluorid unter Hochverdünnungsbedingungen wird eine Reaktionskaskade ausgelöst, bei der nacheinander Desilylierung, Ringöffnung, Protonentransfer und schließlich intramolekulare Michael-Addition ablaufen und die benzannulierte Makrocyclen in meist guten Ausbeuten liefert. Die Geometrie der aromatischen Spacer in den Vorstufen **8** und **10** verhindert die Bildung der monomeren cyclischen Produkte und es entstehen stattdessen die ‚Dimeren' **12** und **13** in niedriger Ausbeute. Die funktionalisierten Cyclophane **11**, **29**, **30**, **31**, **33** und **34** werden dagegen in mäßiger bis guter Ausbeute isoliert. Besonders interessant sind die Pyridinophane **37**, **38** und **40**, letzteres in sehr guter Ausbeute zugänglich, da sie als Vorläufer für funktionalisierte Liganden der Supramolekularen Chemie in Frage kommen.*

treated with sodium dimethyl malonate to furnish the precursors **8**, **9**, and **10** in reasonable overall yields (see Table 1). It should be emphasized that all the reactions described have been performed only once, with no attempt to optimize the yields.

Precursor **8** was added by syringe pump to a suspension of cesium fluoride and benzyltriethylammonium chloride in hot DMF over 43 h. The final concentration of **8** or its reaction products was about 1.6 mmol L^{-1}. These standard conditions proved to be suitable for most ring-opening/ring-closure cascade reactions of this type,[4, 6] but were only moderately successful for the ring expansion of **8**. The benzannulated cyclodecanone derivative **11** was isolated in a yield of 23% that was increased to 37% in the presence of *tert*-butyl alcohol (5.0 equiv). It has not yet been proved whether or not addition of *tert*-butyl alcohol generally improves the yield in such reactions. The role of this additive may be to accelerate the proton transfer required to generate the malonate anion from the ester enolate that is formed initially after the ring-opening of **8** (Scheme 3).

Not unexpectedly,[9] attempts to perform the analogous transformation with the *meta*- and *para*-substituted precursors **9** and **10** failed to provide any of the expected 'monomeric' cyclization products. Rather, the 'dimers' **12** and **13**, respectively, were isolated in low yields. They can be regarded as



Scheme 3. Ring expansion reactions of **8**–**10**. a) CsF, $BnEt_3N^+Cl^-$, DMF, 90 °C.

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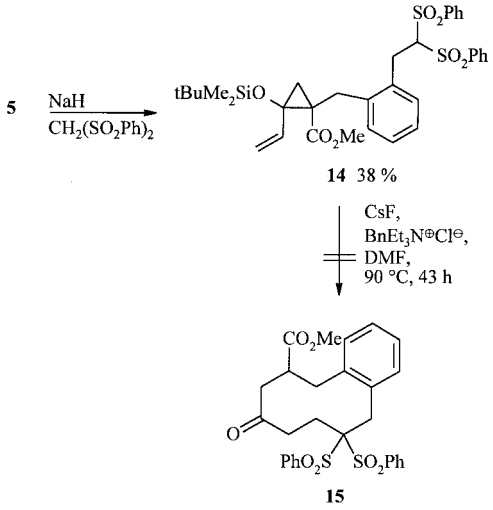
[8,8]metacyclophane and [8,8]paracyclophane, which may be of some interest because of the functionalities present in the spacer unit. The formation of these dimers can be easily confirmed by the appearance of two diastereomers as witnessed by the spectra obtained from 2D NMR ^{1}H-^{1}H COSY and ^{1}H-^{13}C-correlated HSQC and HMBC experiments. In addition, all the dimers were characterized by mass spectrometry (See Experimental Section).

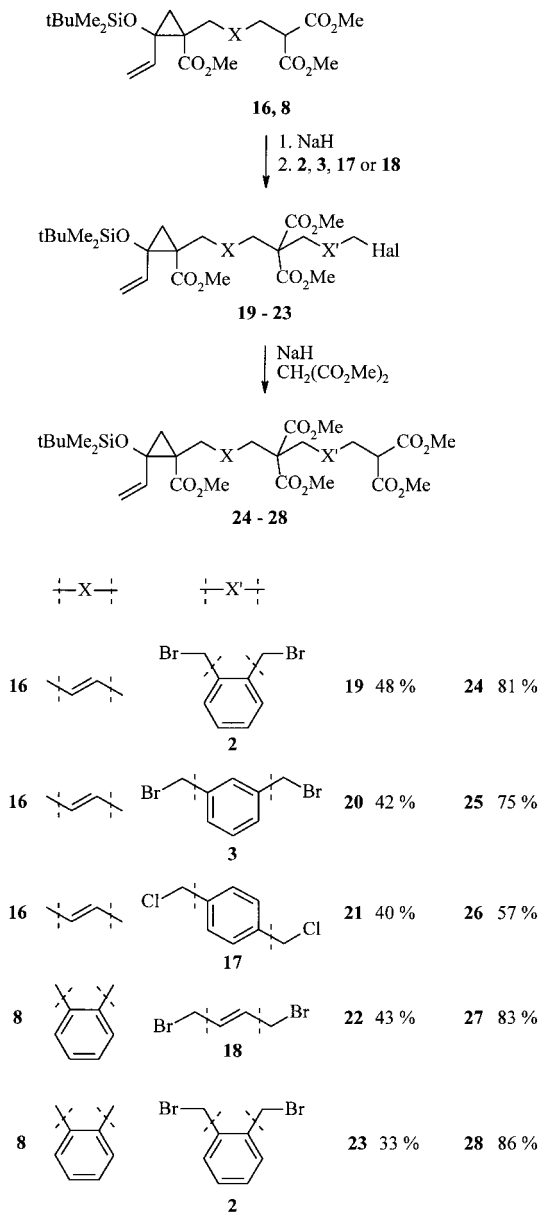
Combination of the intermediate **5** with the sodium salt of bis(phenylsulfonyl)methane produced the potential precursor compound **14** in moderate yield (Scheme 4). Unfortunately, the standard treatment with cesium fluoride did not yield the bicyclic system **15**. We propose that steric hindrance from the bulky bissulfonyl moiety (which already reduces conversion in the alkylation step) efficiently prevents the intramolecular Michael addition to form **15**.[10] In this reaction, as well as in those with low mass balance, no other definite products could be identified. It may be that intermolecular Michael addition, condensation reaction, or dealkylation and decarboxylation produce undefined oligomeric material.

The repetitive character of our strategy permits the facile synthesis of precursors for larger ring sizes. Thus, the dimethyl malonates **16**[4] and **8** underwent chain-elongation by reaction with the dihalides **2**, **3**, **17**, or **18** to give the monohalides **19**–**23** in moderate yields (Scheme 5, see Table 2). These were treated further with sodium dimethyl malonate to form the desired pentaesters **24**–**28** in generally good yields (see Table 3).



Scheme 4. Synthesis of precursor **14**.

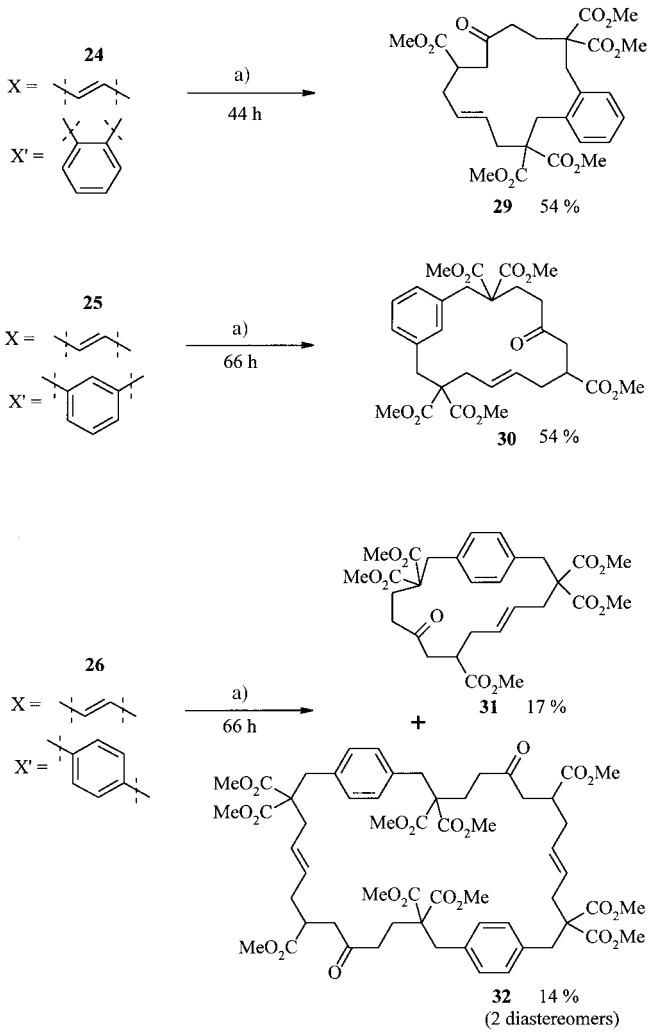
Again only standard conditions were employed for the ring-opening/ring-closure transformations of these precursors. The reactions of **24** and **25** afforded the expected benzannulated fifteen-membered compound **29** and the [13]metacyclophane **30** in yields that are highly acceptable for formation of medium-sized rings (Scheme 6). However, the reaction with precursor **26** incorporating a *para*-substituted spacer unit was less efficient (see Table 4). Only 17% of the 'monomer' **31** was obtained in addition to the [13,13]paracyclophane **32** (two diastereomers), which is actually a 34-membered ring (yield = 14%).



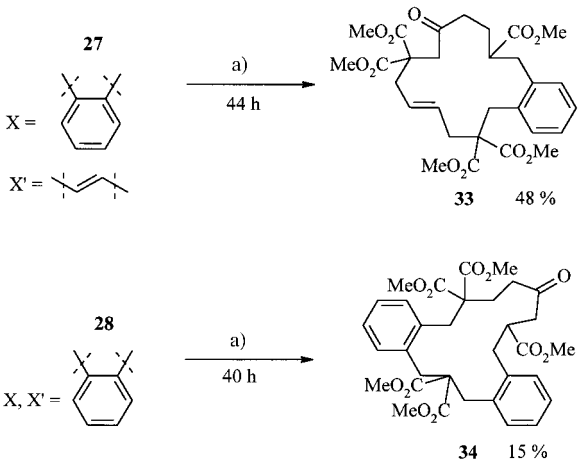
Scheme 5. Synthesis of **24**–**28** via **19**–**23**, respectively.

Precursor **27** (where the two spacer units X and X′ are interchanged with respect to **24**) was transformed with similar efficiency. The benzannulated product **33** was isolated with a yield of 48% (Scheme 7). In contrast, compound **28** (with two *ortho*-substituted benzene units) was converted into the predicted [8,3]orthocyclophane **34** in only 15% yield. Steric hindrance from the two benzene rings may hamper the efficiency of cyclization in this example.

Two further examples demonstrate that our repetitive approach to medium- and large-ring compounds is readily adaptable to systems that contain heterocyclic units. Methyl cyclopropanecarboxylate **1** was deprotonated and then treated with the biselectrophilic component **35**.[11] The resulting 2-bromomethylpyridyl-substituted cyclopropane derivative was combined with an excess of sodium dimethyl malonate to furnish the precursor **36** in a reasonable overall yield (Scheme 8). The ring-opening/ring-closure procedure was



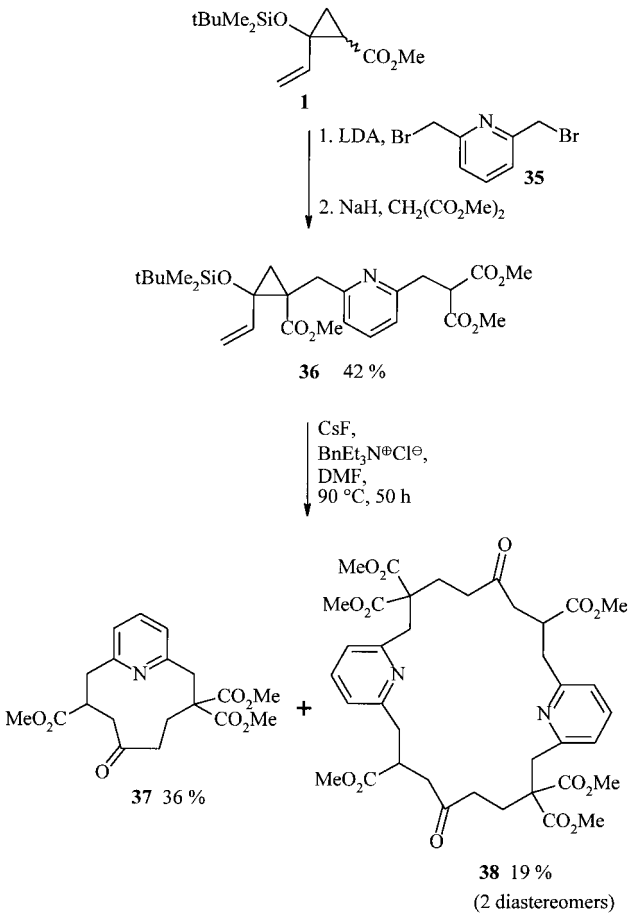
Scheme 6. Ring expansion reactions of **24**–**26**. a) CsF, $BnEt_3N^+Cl^-$, DMF, 90 °C.



Scheme 7. Ring expansion reactions of **27** and **28**. a) CsF, $BnEt_3N^+Cl^-$, DMF, 90 °C.

followed as before and gave a surprisingly large quantity of [8](2,6)pyridinophane **37** (36 %), together with the 'dimer' **38** (19 %, two diastereomers).

This result should be compared with the reaction of precursor **9** (the carbon analogue of **36**) where only the



Scheme 8. Synthesis of **38**.

'dimeric' product **12** was formed in low yield. This difference might be attributable to the smaller size of a nitrogen atom in **36** compared with a C–H unit in **9**, which would cause less strain in the transition state of the Michael addition that produces **37**. The complexating effect of the nitrogen lone pair of **36** may be more important, as it could ligate the cesium ion close to the malonate unit. This would, in turn, limit the degree of freedom and thus favor intramolecular cyclization.

The yield of the [8,8](2,6)pyridinophane **38** was enhanced moderately to 28 % when **36** was treated with cesium fluoride without dilution (Scheme 9). This method may be optimized further for the simple preparation of such [8,8]pyridinophanes or similar compounds.

Finally, we combined the pyridino spacer with one of the carbon spacers used above. The precursor **39** was smoothly synthesized in good yield by the usual two-step method. Subsequent treatment of **39** with cesium fluoride formed the interestingly functionalized [13]metapyridinophane **40** in an excellent yield of 78 % (Scheme 10). The efficiency of ring formation is again considerably higher for this pyridine case compared with the all-carbon example (**25** → **30**, 54 % yield) but is not as striking as for the pair **36**/**9**. Pyridinophanes such as **37**, **38**, and **40** may be of particular interest as ligands for the complexation of metal ions because of their additional donor atoms.[12]

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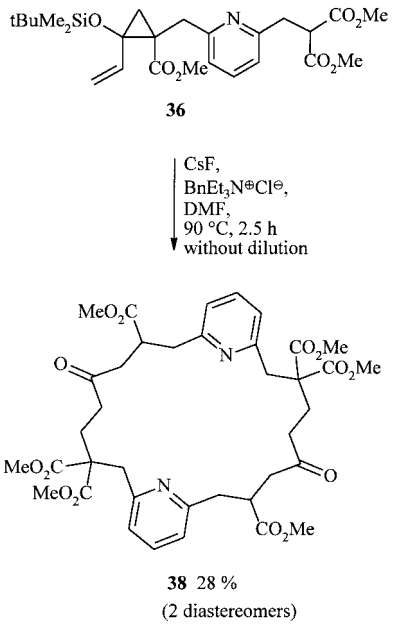
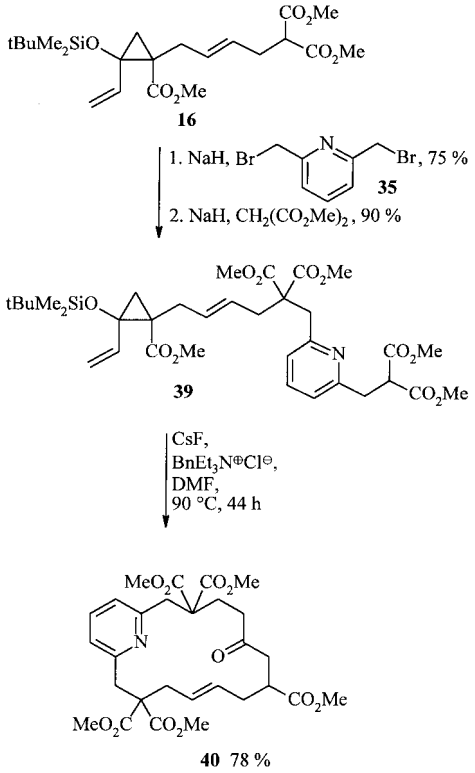


Scheme 9. Synthesis of **38**.



Scheme 10. Synthesis of **40**.

Conclusion

In this report we have demonstrated that our strategy for the synthesis of large-ring compounds could also be applied to the preparation of various benzannulated macrocycles. The efficiency of the crucial intramolecular Michael addition depends strongly on the desired ring size and on the geometric restrictions introduced by the spacer units. While an *ortho*-phenylene unit allowed the synthesis of 10- and 15-membered rings, the corresponding *meta*- and *para*-phenylene spacers could only be introduced successfully into larger ring sizes (16- and 17-membered carbocycles). Compounds with the 2,6-pyridino spacers may be of particular value as the cyclizations occur with considerably higher yields than those of the related all-carbon analogues. Our examples show that the use of alkenyl-substituted siloxycyclopropanes as masked enones can be applied very flexibly to compounds of the cyclophane family, such that many extensions of this strategy are conceivable.

Experimental Section

All reactions were performed under argon atmosphere in flame-dried flasks, and the reactants were introduced by syringe. All solvents were dried by standard methods. Silica gel (0.040 – 0.063 mm, Merck – Schuchardt) was used for the column chromatography. Melting points (uncorrected) were measured with a Gallenkamp MPD 350 instrument. ^{1}H and ^{13}C NMR spectra were recorded with Bruker instruments (AC 200, AC 300, or DRX-500) in $CDCl_3$ solution. The chemical shifts are given relative to TMS from the solvent ($CDCl_3$) signal ($\delta_H = 7.25$, $\delta_C = 77.0$). The 2D NMR COSY, HSQC (heteronuclear single quantum coherence), and HMBC (heteronuclear multiple quantum correlation) spectra were recorded on the DRX 500 spectrometer with an inverse TBI probe-head using pulsed 2-field gradients. The final resolution of the 2D spectra was 2.5 Hz per point for ^{1}H and 20.5 Hz per point for ^{13}C.

IR spectra were measured with a Nicolet 205 FT-IR spectrometer. MS spectra were recorded on a Varian MAT 311 A spectrometer (FD) or on a Kratos Analytics Kompact Maldi II instrument (Maldi). (*E*)-1,4-Dibromo-2-butene (**18**), α,α'-dibromo-*o*-xylene (**2**), α,α'-dibromo-*m*-xylene (**3**), α,α'-dibromo-*p*-xylene (**4**), and α,α'-dichloro-*p*-xylene (**17**) are commercially available and were used as received. The other starting materials were synthesized as described in the literature (siloxycyclopropanes **1**[7] and **16**,[4] 2,6-bis(bromomethyl)pyridine **35**[11]).

General procedure A for alkylation with 2, 3 or 4: Siloxycyclopropane **1** (1.0 equiv) was deprotonated with LDA (1.5 equiv) in THF (10 mL mmol^{-1}) at $-78\,^\circ$C. After 2 h, the dihalide (2.0 equiv) was added and the mixture was stirred at $-78\,^\circ$C for 18 h. Subsequent dilution with saturated NH_4Cl solution and warming of the mixture was followed by extraction with ethyl acetate (3×20 mL). The combined organic layers were washed with water and brine, and then dried over $MgSO_4$. After evaporation of the solvent, the unconsumed alkylating reagent was removed by rotary evaporation (0.01 mbar, 100 °C). The residue was purified by chromatography as described in the individual experiments (Table 1).

Table 1. Alkylation of siloxycyclopropane **1** with **2**, **3**, or **4**.

Amount of **1** [g (mmol)]	Dihalide	Chromatography heptane/ethyl acetate	Product	Amount [g]	Yield [%]	
0.500 (1.95)	**2**	1:0 → 9:1	**5**	0.436	50	yellow oil
1.00 (3.90)	**3**	9.5:0.5 → 7:3	**6**	1.03	60	slightly yellow oil
1.00 (3.90)	**4**	1:0 → 0:1	**7**	1.19	69	slightly yellow oil

Methyl 1-(2-bromomethyl-benzyl)-*t*-2-*tert*-butyldimethylsiloxy-*c*-2-vinyl-*r*-1-cyclopropanecarboxylate (5):

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.25 - 6.98$ (m, 4H; aryl-H), 5.82 (dd, $J =$ 17, 10.5 Hz, 1H; 1″-H), 5.25 (dd, $J = 17$, 1.5 Hz, 1H; *cis*-2″-H), 5.07 (dd, $J =$ 10.5, 1.5 Hz, 1H; *trans*-2″-H), 4.53 (d, $J = 10$ Hz, 1H; CH_2Br), 4.38 (d, $J =$ 10 Hz, 1H; CH_2Br), 3.58 (d, $J = 17.5$ Hz, 1H; 1′-H), 3.37 (s, 3H; CO_2Me), 2.95 (d, $J = 17.5$ Hz, 1H; 1′-H), 2.04 (dd, $J = 6.5$, 1 Hz, 1H; *cis*-3-H), 1.15 (br d, $J = 6.5$ Hz, 1H; *trans*-3-H), 0.82 (s, 9H; *t*Bu), 0.05, 0.00 (2s, 6H; $SiMe_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 171.8$, 51.8 (s, q, CO_2Me), 138.8, 135.7 (2s, aryl-C), 136.5 (d, C-1″), 130.2, 128.8, 127.7, 126.2 (4d, aryl-CH),

115.7 (t, C-2″), 64.8 (s, C-2), 36.4 (s, C-1), 31.7, 30.5 (2t, C-1′, CH_2Br), 25.8, 18.1 (q, s, *t*Bu), 24.5 (t, C-3), −3.4, −3.6 (2q, $SiMe_2$); IR (neat): $\tilde{\nu}$ = 3100–3000 (=C−H), 2950, 2930, 2900, 2860 (C−H), 1730 (CO_2Me), 1640, 1610 cm^{-1} (C=C); elemental analysis: $C_{21}H_{31}BrO_3Si$ (439.5): calcd C 57.40, H 7.11; found C 57.56, H 7.28.

Methyl 1-(3-bromomethyl-benzyl)-*t*-2-*tert*-butyldimethylsiloxy-*c*-2-vinyl-*r*-1-cyclopropanecarboxylate (6): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.22 (m, 4H; aryl-H), 5.87 (dd, *J* = 17, 10.5 Hz, 1H; 1″-H), 5.30 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-2″-H), 5.15 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-2″-H), 4.46 (s, 2H; CH_2Br), 3.57 (s, 3H; CO_2Me), 3.53 (d, *J* = 16 Hz, 1H; 1′-H), 2.86 (d, *J* = 16 Hz, 1H; 1′-H), 1.95 (dd, *J* = 6.5, 1 Hz, 1H; *cis*-3-H), 1.19 (br d, *J* = 6.5 Hz, 1H; *trans*-3-H), 0.93 (s, 9H; *t*Bu), 0.15, 0.13 (2 s, 6H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 51.8 (s, q, CO_2Me), 140.9, 137.7 (2s, aryl-C), 136.6 (d, C-1″), 129.3, 128.7, 128.6, 126.7 (4d, aryl-CH), 115.7 (t, C-2″), 65.2 (s, C-2), 38.4 (s, C-1), 34.2, 33.7 (2t, C-1′, CH_2Br), 25.9, 18.2 (q, s, *t*Bu), 24.1 (t, C-3), −3.3, −3.5 (2q, $SiMe_2$); elemental analysis: $C_{21}H_{31}BrO_3Si$ (439.5): calcd C 57.40, H 7.11; found C 54.80, H 6.35. No correct elemental analysis could be obtained for this sensitive compound.

Methyl 1-(4-bromomethyl-benzyl)-*t*-2-*tert*-butyldimethylsiloxy-*c*-2-vinyl-*r*-1-cyclopropanecarboxylate (7): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.10 (m, 4H; aryl-H), 5.86 (dd, *J* = 17, 10.5 Hz, 1H; 1″-H), 5.30 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-2″-H), 5.15 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-2″-H), 4.48 (s, 2H; CH_2Br), 3.57 (s, 3H; CO_2Me), 3.54 (d, *J* = 15.5 Hz, 1H; 1′-H), 2.86 (d, *J* = 15.5 Hz, 1H; 1′-H), 1.95 (dd, *J* = 6.5, 1 Hz, 1H; *cis*-3-H), 1.18 (br d, *J* = 6.5 Hz, 1H; *trans*-3-H), 0.93 (s, 9H; *t*Bu), 0.15, 0.12 (2s, 6H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 51.8 (s, q, CO_2Me), 140.7, 135.5 (2s, aryl-C), 136.5 (d, C-1″), 129.0,* 128.9* (2d, aryl-CH), 115.7 (t, C-2″), 65.2 (s, C-2), 38.4 (s, C-1), 34.0, 33.5 (2t, C-1′, CH_2Br), 25.9, 18.2 (q, s, *t*Bu), 24.0 (t, C-3), −3.3, −3.5 (2q, $SiMe_2$),* indicates that signal has double intensity; IR (KBr): $\tilde{\nu}$ = 3080–3000 (=C−H), 2960, 2930, 2880, 2850 (C−H), 1720 (CO_2Me), 1640–1630 cm^{-1} (C=C); elemental analysis: $C_{21}H_{31}BrO_3Si$ (439.5): calcd C 57.40, H 7.11; found C 62.25, H 7.52. No correct elemental analysis could be obtained for this sensitive compound.

General procedure B for alkylation of siloxycyclopropyl-substituted dimethyl malonates with 2, 3, 17, or 18: The crude siloxycyclopropyl-substituted dimethyl malonate (1.0 equiv) was added slowly to a suspension of sodium hydride (2.0–5.0 equiv) in THF/DMF (5:1) (30 mL $mmol^{-1}$ of siloxycyclopropyl compound) at 0 °C. The mixture was stirred for 1 h at room temperature. The dihalide (4.0–10.0 equiv) was then added at 0 °C, and after further stirring at room temperature for 18 h, the mixture was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water and brine, and then dried over $MgSO_4$. After evaporation of the solvent, the unconsumed alkylating reagent was removed by rotary evaporation (0.01 mbar, 100 °C). The residue was purified by chromatography as described in the individual experiments (Table 2).

Table 2. Alkylation of siloxycyclopropanes **8** and **16** with **2**, **3**, **17**, or **18**.

Precursor	Amount [g (mmol)]	Dihalide	Chromatography heptane/ethyl acetate	Product	Amount [g]	Yield [%]	
16	0.500 (1.13)	**2**	1:0 → 9:1	**19**	0.340	48	slightly yellow oil
16	0.500 (1.13)	**3**	9:1 → 3:1	**20**	0.299	42	slightly yellow oil
16	0.500 (1.13)	**17**	1:0 → 4:1	**21**	0.261	40	colorless oil
8	1.50 (3.05)	**18**	1:0 → 4:1	**22**	0.827	43	yellow oil
8	1.45 (2.96)	**2**	1:0 → 7:3	**23**	0.666	33	yellow oil

Dimethyl (4E)-1-(2-bromomethyl-phenyl)-6-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-4-hexene-2,2-dicarboxylate (19): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.23–7.00 (m, 4H; aryl-H), 5.70 (dd, *J* = 17, 10.5 Hz, 1H; 1″-H), 5.38 (m_c, 2H; 4-H, 5-H), 5.14 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-2″-H), 4.99 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-2″-H), 4.45 (s, 2H; CH_2Br), 3.53 (s, 3H; CO_2Me), 3.50 (s, 6H; 2CO_2Me), 3.26 (s, 2H; 1-H), 2.76 (dd, *J* = 15.5, 6 Hz, 1H; 6-H), 2.52 (d, *J* = 6.5 Hz, 2H; 3-H), 2.09 (dd, *J* = 15.5, 6 Hz, 1H; 6-H), 1.72 (d, *J* = 6.5 Hz, 1H; *cis*-3′-H), 0.90 (d, *J* = 6.5 Hz, 1H; *trans*-3′-H), 0.79 (s, 9H; *t*Bu), 0.00, −0.02 (2s, 6H; $SiMe_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.8, 171.30, 171.27, 52.3,* 51.9 (3s, 2q, 3CO_2Me), 136.9, 135.3 (2s, aryl-C), 136.6 (d, C-1″), 132.7, 130.9, 130.8, 128.6, 127.4, 125.0 (6d, C-4, C-5, aryl-CH), 115.3 (t, C-2″), 65.1 (s, C-2′), 59.1 (s, C-2), 37.23 (s, C-1′), 37.20, 33.9, 31.8** (3t, C-1, C-3, C-6, CH_2Br), 25.8, 18.2 (q, s, *t*Bu), 23.7 (t, C-3′), −3.5, −3.6 (2q, $SiMe_2$),* signal has double intensity; ** two signals overlap; IR (CCl_4): $\tilde{\nu}$ = 3100–3000 (=C−H), 2950, 2930, 2880, 2860 (C−H), 1730 (CO_2Me), 1640 cm^{-1} (C=C); elemental analysis: $C_{30}H_{43}BrO_7Si$ (623.7): calcd C 57.78, H 6.95; found C 58.25, H 7.17.

Dimethyl (4E)-1-(3-bromomethyl-phenyl)-6-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-4-hexene-2,2-dicarboxylate (20): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–6.98 (m, 4H; aryl-H), 5.83 (dd, *J* = 17, 10.5 Hz, 1H; 1″-H), 5.60, 5.38 (2m_c, 1H each; 4-H, 5-H), 5.27 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-2″-H), 5.10 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-2″-H), 4.43 (s, 2H; CH_2Br), 3.69 (s, 6H; 2CO_2Me), 3.65 (s, 3H; CO_2Me), 3.18 (s, 2H; 1-H), 2.88 (dd, *J* = 15.5, 6.5 Hz, 1H; 6-H), 2.49 (d, *J* = 7 Hz, 2H; 3-H), 2.23 (dd, *J* = 15.5, 6.5 Hz, 1H; 6-H), 1.86 (dd, *J* = 6.5, 1 Hz, 1H; *cis*-3′-H), 1.05 (br d, *J* = 6.5 Hz, 1H; *trans*-3′-H), 0.91 (s, 9H; *t*Bu), 0.12, 0.10 (2s, 6H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 170.9,* 52.3,* 51.9 (2s, 2q, 3CO_2Me), 137.7, 136.7 (2s, aryl-C), 136.6 (d, C-1″), 132.5, 130.7, 129.9, 128.6, 127.5, 125.2 (6d, C-4, C-5, aryl-CH), 115.2 (t, C-2″), 65.1 (s, C-2′), 59.1 (s, C-2), 37.7 (s, C-1′), 37.4, 35.2, 33.3, 31.9 (4t, C-1, C-3, C-6, CH_2Br), 25.8, 18.1 (q, s, *t*Bu), 23.7 (t, C-3′), −3.5, −3.6 (2q, $SiMe_2$),* signal has double intensity; IR (neat): $\tilde{\nu}$ = 3080–3000 (=C−H), 2950, 2930, 2900, 2860 (C−H), 1730 (CO_2Me), 1660, 1640, 1610 cm^{-1} (C=C); elemental analysis: $C_{30}H_{43}BrO_7Si$ (623.7): calcd C 57.78, H 6.95; found C 57.24, H 6.57.

Dimethyl (4E)-6-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-1-(4-chloromethyl-phenyl)-4-hexene-2,2-dicarboxylate (21): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25, 7.05 (2m_c, 4H; aryl-H), 5.81 (dd, *J* = 17, 10.5 Hz, 1H; 1″-H), 5.56, 5.38 (2m_c, 1H each; 4-H, 5-H), 5.26 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-2″-H), 5.10 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-2″-H), 4.52 (s, 2H; CH_2Cl), 3.67 (s, 6H; 2CO_2Me), 3.64 (s, 3H; CO_2Me), 3.18 (s, 2H; 1-H), 2.86 (dd, *J* = 15.5, 6.5 Hz, 1H; 6-H), 2.47 (d, *J* = 7 Hz, 2H; 3-H), 2.21 (dd, *J* = 15.5, 6.5 Hz, 1H; 6-H), 1.84 (dd, *J* = 6.5, 1 Hz, 1H; *cis*-3′-H), 1.02 (br d, *J* = 6.5 Hz, 1H; *trans*-3′-H), 0.90 (s, 9H; *t*Bu), 0.11, 0.09 (2s, 6H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 171.0,* 52.27, 52.26, 51.9 (2s, 3q, 3CO_2Me), 136.6 (d, C-1″), 136.3, 136.1 (2s, aryl-C), 132.5, 125.1 (2d, C-4, C-5), 130.2,* 128.5* (2d, aryl-CH), 115.2 (t, C-2″), 65.1 (s, C-2′), 59.1 (s, C-2), 45.9 (t, CH_2Cl), 37.6, 35.2, 31.8 (3t, C-1, C-3, C-6), 37.3 (s, C-1′), 25.8, 18.1 (q, s, *t*Bu), 23.7 (t, C-3′), −3.5, −3.6 (2q, $SiMe_2$),* signal has double intensity; IR (neat): $\tilde{\nu}$ = 3100–3000 (=C−H), 2950, 2930, 2900, 2860 (C−H), 1740 (CO_2Me), 1640, 1610 cm^{-1} (C=C); elemental analysis: $C_{30}H_{43}ClO_7Si$ (579.2): calcd C 62.21, H 7.48; found C 61.79, H 7.18.

Dimethyl (4E)-6-bromo-1-{2-[*r*-2-(*tert*-butyldimethylsiloxy)-t-1-methoxycarbonyl-2-vinylcycloprop-1-yl-methyl]phenyl}-4-hexene-2,2-dicarboxylate (22): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.28–6.97 (m, 4H; aryl-H), 5.88 (dd, *J* = 17, 10.5 Hz, 1H; vinyl-1-H), 5.72 (m_c, 2H; 4-H, 5-H), 5.29 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-vinyl-2-H), 5.14 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-vinyl-2-H), 3.87 (d, *J* = 6.5 Hz, 2H; 6-H), 3.70, 3.69 (2s, 6H; 2CO_2Me), 3.55 (d, *J* = 16.5 Hz, 1H; 1′-H), 3.49 (s, 3H; CO_2Me), AB system (δ_A = 3.44, δ_B = 3.31, J_{AB} = 15 Hz, 2H; 1-H), 2.87 (d, *J* = 16.5 Hz, 1H; 1′-H), 2.57 (d, *J* = 5.5 Hz, 2H; 3-H), 2.04 (d, *J* = 6.5 Hz, 1H; *cis*-3″-H), 1.18 (d, *J* = 6.5 Hz, 1H; *trans*-3″-H), 0.91 (s, 9H; *t*Bu), 0.14, 0.08 (2s, 6H; $SiMe_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.8, 171.3, 171.2, 52.4, 52.3, 51.8 (3s, 3q, 3CO_2Me), 139.0, 134.4 (2s, aryl-C), 136.5 (d, vinyl-C-1), 130.39, 130.37, 129.7, 128.1, 127.0, 125.9 (6d, C-4, C-5, aryl-CH), 115.6 (t, vinyl-C-2), 64.9 (s, C-2″), 59.2 (s, C-2), 37.7 (s, C-1″), 36.1, 34.9, 32.3, 31.3 (4t, C-1, C-3, C-6, C-1′), 25.9, 18.2 (q, s, *t*Bu), 24.5 (t, C-3″), −3.3, −3.5 (2q, $SiMe_2$); IR (CCl_4): $\tilde{\nu}$ = 3100–3000 (=C−H), 2950, 2930, 2900, 2850 (C−H), 1740 (CO_2Me), 1650–1600 cm^{-1} (C=C); elemental analysis: $C_{30}H_{43}BrO_7Si$ (623.7): calcd C 57.78, H 6.95; found C 57.57, H 6.74.

Dimethyl 3-(2-bromomethyl-phenyl)-1-{2-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl-methyl]phenyl}propane-2,2-dicarboxylate (23): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29–7.09 (m, 8H; aryl-H), 5.87 (dd, *J* = 17, 10.5 Hz, 1H; vinyl-1-H), 5.28 (d, *J* = 17 Hz, 1H; *cis*-vinyl-2-H), 5.14 (d, *J* = 10.5 Hz, 1H; *trans*-vinyl-2-H), 4.36 (s, 2H; CH_2Br), 3.59, 3.56, 3.50 (3s, 9H; 3 CO_2Me), 3.48–3.40 (m, 5H, 1-H, 3-H; 1′-H), 2.86 (d, *J* = 16.5 Hz, 1H; 1′-H), 2.01 (d, *J* = 6.5 Hz, 1H; *cis*-3″-H), 1.14 (d, *J* = 6.5 Hz, 1H; *trans*-3″-H), 0.88 (s, 9H; *t*Bu), 0.12, 0.05 (2s, 6H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 172.0, 171.8, 171.6, 52.5, 52.4, 51.9 (3s, 3q, 3CO_2Me), 139.0, 137.0, 135.6, 134.6 (4s, aryl-C), 136.6 (d, vinyl-C-1), 130.8,

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130.6, 128.60, 128.55, 128.3, 127.4, 126.9, 126.1 (8 d, aryl-CH), 115.6 (t, vinyl-C-2), 65.0 (s, C-2″), 59.3 (s, C-2), 37.4 (s, C-1″), 35.8, 34.7, 31.9, 31.2 (4 t, C-1, C-3, C-1′, CH_2Br), 25.8, 18.1 (q, s, *t*Bu), 24.4 (t, C-3″), −3.3, −3.5 (2 q, $SiMe_2$); IR (KBr): $\tilde{\nu}$ = 3070, 3020 (=C−H), 2950, 2930, 2860 (C−H), 1730 (CO_2Me), 1660–1610 cm^{-1} (C=C); elemental analysis: $C_{34}H_{45}BrO_7Si$ (673.7): calcd C 60.62, H 6.73; found C 61.16, H 6.67.

General procedure C for reaction of siloxycyclopropyl-substituted halides with dimethyl malonate: Dimethyl malonate (10.0 equiv) was added slowly at 0 °C to a suspension of sodium hydride (1.2–5.0 equiv) in THF/DMF (5:1) (15 mL $mmol^{-1}$ of siloxycyclopropyl compound). The mixture was stirred for 1 h at room temperature. The siloxycyclopropyl-substituted halide (1.0 equiv) was then added at 0 °C. After stirring at room temperature for 18 h the mixture was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent the unconsumed dimethyl malonate was removed by rotary evaporation (0.01 mbar, 70 °C). The residue was purified by chromatography as indicated in the individual experiments (Table 3).

Table 3. Reaction of siloxycyclopropyl-substituted halides with dimethyl malonate.[a]

Precursor	Amount [g (mmol)]	NaH [equiv]	Chromatography heptane/ethyl acetate	Product	Amount [g]	Yield [%]	
5	0.383 (0.871)	1.2	1:0 → 9:1	**8**	0.311	72	colorless crystals[b]
6	1.03 (2.35)	5.0	1:0 → 4:1	**9**	0.713	62	slightly yellow oil
7	1.16 (2.65)	5.0	1:0 → 1:1	**10**	0.574	44	slightly yellow oil
19	0.268 (0.430)	1.2	1:0 → 4:1	**24**	0.236	81	colorless oil
20	0.280 (0.449)	5.0	9:1 → 4:1	**25**	0.227	75	colorless oil
21	0.233 (0.402)	5.0	1:0 → 4:1	**26**	0.155	57	colorless oil
22	0.733 (1.18)	5.0	9:1 → 4:1	**27**	0.655	83	colorless oil
23	0.638 (0.947)	5.0	9:1 → 7:3	**28**	0.591	86	slightly yellow oil

[a] 10 equivalents with regard to precursor. [b] M. p. 69–71 °C.

Dimethyl 2-{2-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl-methyl]phenyl}ethane-1,1-dicarboxylate (8): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.23–6.98 (m, 4 H; aryl-H), 5.82 (dd, *J* = 17, 10.5 Hz, 1 H; vinyl-1-H), 5.24 (dd, *J* = 17, 1.5 Hz, 1 H; *cis*-vinyl-2-H), 5.08 (dd, *J* = 10.5, 1.5 Hz, 1 H; *trans*-vinyl-2-H), ABX system (δ_A = 3.20, δ_B = 3.17, δ_X = 3.64,* J_{AB} = 14.5 Hz, J_{AX} = J_{BX} = 8 Hz, 3 H; 1-H, 2-H), 3.587, 3.585 (2 s, 6 H; 2 CO_2Me), 3.49 (d, *J* = 17 Hz, 1 H; 1′-H), 3.41 (s, 3 H; CO_2Me), 2.82 (d, *J* = 17 Hz, 1 H; 1′-H), 2.04 (dd, *J* = 6.5, 1 Hz, 1 H; *cis*-3″-H), 1.14 (br d, *J* = 6.5 Hz, 1 H; *trans*-3″-H), 0.82 (s, 9 H; *t*Bu), 0.06, 0.00 (2 s, 6 H; $SiMe_2$), * signal is partly overlapped by ester signals; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.8, 169.09, 169.06, 52.31, 52.29, 51.80 (3 s, 3 q, 3 CO_2Me), 137.8, 135.6 (2 s, aryl-C), 136.4 (d, vinyl-C-1), 129.3, 127.2, 126.9, 125.9 (4 d, aryl-CH), 115.6 (t, vinyl-C-2), 64.7 (s, C-2″), 51.78 (d, C-1**), 36.6 (s, C-1″), 31.7, 30.6 (2 t, C-2, C-1′), 25.6, 18.0 (q, s, *t*Bu), 24.7 (t, C-3″), −3.5, −3.7 (2 q, $SiMe_2$), ** assignment supported by the lower intensity of the signal compared with the methoxy signals; IR (KBr): $\tilde{\nu}$ = 3100–3000 (=C−H), 2950, 2930, 2890, 2860 (C−H), 1750, 1730 (CO_2Me), 1640, 1610 cm^{-1} (C=C); elemental analysis: $C_{26}H_{38}O_7Si$ (490.7): calcd C 63.64, H 7.81; found C 64.04, H 8.30.

Dimethyl 2-{3-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl-methyl]phenyl}ethane-1,1-dicarboxylate (9): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–6.97 (m, 4 H; aryl-H), 5.85 (dd, *J* = 17, 10.5 Hz, 1 H; vinyl-1-H), 5.29 (dd, *J* = 17, 1.5 Hz, 1 H; *cis*-vinyl-2-H), 5.13 (dd, *J* = 10.5, 1.5 Hz, 1 H; *trans*-vinyl-2-H), 3.69 (s, 6 H; 2 CO_2Me), 3.65 (t, *J* = 8 Hz, 1 H; 1-H), 3.57 (s, 3 H; CO_2Me), 3.51 (d, *J* = 16 Hz, 1 H; 1′-H), 3.18 (d, *J* = 8 Hz, 2 H; 2-H), 2.81 (d, *J* = 16 Hz, 1 H; 1′-H), 1.92 (dd, *J* = 6.5, 1 Hz, 1 H; *cis*-3″-H), 1.18 (br d, *J* = 6.5 Hz, 1 H; *trans*-3″-H), 0.93 (s, 9 H; *t*Bu), 0.15, 0.13 (2 s, 6 H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 169.2,* 52.5,* 51.8 (2 s, 2 q, 3 CO_2Me), 140.5, 137.8 (2 s, aryl-C), 136.6 (d, vinyl-C-1), 129.0, 128.5, 127.0, 126.5 (4 d, aryl-CH), 115.5 (t, vinyl-C-2), 65.2 (s, C-2″), 53.6** (d, C-1), 38.6 (s, C-1″), 34.8, 34.2 (2 t, C-2, C-1′), 25.9, 18.2 (q, s, *t*Bu), 23.9 (t, C-3″), −3.3, −3.5 (2 q, $SiMe_2$), * signal has double intensity; ** assignment supported by the lower intensity of the signal compared with the methoxy signals; IR (neat): $\tilde{\nu}$ = 3100–3000 (=C−H), 2950, 2930, 2900, 2860 (C−H), 1760, 1740 (CO_2Me), 1630, 1610 cm^{-1} (C=C); elemental analysis: $C_{26}H_{38}O_7Si$ (490.7): calcd C 63.64, H 7.81; found C 63.31, H 7.89.

Dimethyl 2-{4-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl-methyl]phenyl}ethane-1,1-dicarboxylate (10): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13–7.06 (m, 4 H; aryl-H), 5.84 (dd, *J* = 17, 10.5 Hz, 1 H; vinyl-1-H), 5.28 (dd, *J* = 17, 1.5 Hz, 1 H; *cis*-vinyl-2-H), 5.13 (dd, *J* = 10.5, 1.5 Hz, 1 H; *trans*-vinyl-2-H), 3.692, 3.690 (2 s, 6 H; 2 CO_2Me), 3.65 (t, *J* = 8 Hz, 1 H; 1-H), 3.56 (s, 3 H; CO_2Me), 3.51 (d, *J* = 15.5 Hz, 1 H; 1′-H), 3.18 (d, *J* = 8 Hz, 2 H; 2-H), 2.81 (d, *J* = 15.5 Hz, 1 H; 1′-H), 1.92 (dd, *J* = 6.5, 1 Hz, 1 H; *cis*-3″-H), 1.16 (br d, *J* = 6.5 Hz, 1 H; *trans*-3″-H), 0.92 (s, 9 H; *t*Bu), 0.14, 0.12 (2 s, 6 H; $SiMe_2$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.9, 169.3,* 52.5,* 51.8 (2 s, 2 q, 3 CO_2Me), 138.6, 135.4 (2 s, aryl-C), 136.6 (d, vinyl-C-1), 128.71,* 128.68* (2 d, aryl-CH), 115.5 (t, vinyl-C-2), 65.1 (s, C-2″), 53.6** (d, C-1), 38.5 (s, C-1″), 34.4, 33.8 (2 t, C-2, C-1′), 25.8, 18.2 (q, s, *t*Bu), 23.8 (t, C-3″), −3.4, −3.5 (2 q, $SiMe_2$), * signal has double intensity; ** assignment supported by the lower intensity of the signal compared with the methoxy signals; IR (KBr): $\tilde{\nu}$ = 3080–3000 (=C−H), 2940, 2910, 2860, 2830 (C−H), 1740, 1730 (CO_2Me), 1630–1620 cm^{-1} (C=C); elemental analysis: $C_{26}H_{38}O_7Si$ (490.7): calcd C 63.64, H 7.81; found C 63.37, H 8.23.

Dimethyl (4E)-6-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-1-{2-[2,2-di(methoxycarbonyl)ethyl]-phenyl}-4-hexene-2,2-dicarboxylate (24): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.08 (s, 4 H; aryl-H), 5.79 (dd, *J* = 17, 10.5 Hz, 1 H; vinyl-1-H), 5.47 (m_c, 2 H; 4-H, 5-H), 5.23 (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), 3.65 (s, 6 H; 2 CO_2Me), 3.61 (s, 9 H; 3 CO_2Me), 3.54* (t, *J* = 8 Hz, 1 H; 2″-H), 3.29 (s, 2 H; 1-H), 3.21 (d, *J* = 8 Hz, 2 H; 1″-H), 2.84 (dd, *J* = 15, 5.5 Hz, 1 H; 6-H), 2.54 (d, *J* = 6.5 Hz, 2 H; 3-H), 2.16 (dd, *J* = 15, 5.5 Hz, 1 H; 6-H), 1.80 (d, *J* = 6.5 Hz, 1 H; *cis*-3′-H), 0.99 (d, *J* = 6.5 Hz, 1 H; *trans*-3′-H), 0.88 (s, 9 H; *t*Bu), 0.09, 0.07 (2 s, 6 H; $SiMe_2$), * signal is partly overlapped by ester signals; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.7, 171.20, 171.18, 169.0,* 52.4,* 52.1,* 51.8 (4 s, 3 q, 5 CO_2Me), 136.8, 134.6 (2 s, aryl-C), 136.6 (d, vinyl-C-1), 132.3, 130.7, 129.5, 127.0, 126.6, 125.3 (6 d, C-4, C-5, aryl-CH), 115.1 (t, vinyl-C-2), 65.0 (s, C-2′), 59.2 (s, C-2), 53.1 (d, C-2″), 37.2 (s, C-1′), 36.9, 33.9, 31.8, 31.2 (4 t, C-1, C-3, C-6, 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; IR (CCl_4): $\tilde{\nu}$ = 3100–3000 (=C−H), 2950, 2930, 2900, 2890, 2860 (C−H), 1750, 1740 (CO_2Me), 1650 cm^{-1} (C=C); elemental analysis: $C_{35}H_{50}O_{11}Si$ (674.9): calcd C 62.29, H 7.47; found C 62.10, H 7.66.

Dimethyl (4E)-6-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-1-{3-[2,2-di(methoxycarbonyl)ethyl]phenyl}-4-hexene-2,2-dicarboxylate (25): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11–7.06, 6.98–6.96, 6.85–6.83 (3 m, 1 H, 1 H, 2 H; aryl-H), 5.75 (dd, *J* = 17, 10.5 Hz, 1 H; vinyl-1-H), 5.52, 5.33 (2 m_c, 1 H each; 4-H, 5-H), 5.19 (dd, *J* = 17, 1.5 Hz, 1 H; *cis*-vinyl-2-H), 5.03 (dd, *J* = 10.5, 1.5 Hz, 1 H; *trans*-vinyl-2-H), 3.61, 3.60 (2 s, 12 H; 4 CO_2Me), 3.57 (s, 3 H; CO_2Me), 3.08 (m_c, 4 H; 1-H, 1″-H), 2.81 (dd, *J* = 15.5, 6.0 Hz, 1 H; 6-H), 2.39 (d, *J* = 7 Hz, 2 H; 3-H), 2.15 (dd, *J* = 15.5, 6.5 Hz, 1 H; 6-H), 1.78 (d, *J* = 6 Hz, 1 H; *cis*-3′-H), 0.98 (d, *J* = 6 Hz, 1 H; *trans*-3′-H), 0.84 (s, 9 H; *t*Bu), 0.05, 0.03 (2 s, 6 H; $SiMe_2$), 2″-H-signal is overlapped by ester signals; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.6, 171.8,* 168.9,* 52.3,* 52.0,* 51.7 (3 s, 3 q, 5 CO_2Me), 137.5, 136.2 (2 s, aryl-C), 136.6 (d, vinyl-C-1), 132.2, 130.3, 128.3, 128.2, 127.2, 125.2 (6 d, C-4, C-5, aryl-CH), 115.0 (t, vinyl-C-2), 65.0 (s, C-2′), 59.0 (s, C-2), 53.3 (d, C-2″), 37.7, 35.0, 35.5, 31.7 (4 t, C-1, C-3, C-6, C-1″), 37.2 (s, C-1′), 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; IR (KBr): $\tilde{\nu}$ = 3050–3000 (=C−H), 2950, 2930, 2860 (C−H), 1740 (CO_2Me), 1640 cm^{-1} (C=C); elemental analysis: $C_{35}H_{50}O_{11}Si$ (674.9): calcd C 62.29, H 7.47; found C 62.31, H 7.63.

Dimethyl (4E)-6-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-1-{4-[2,2-di(methoxycarbonyl)ethyl]phenyl}-4-hexene-2,2-dicarboxylate (26): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06, 6.96 (2 m_c, 4 H; aryl-H), 5.81 (dd, *J* = 17, 10.5 Hz, 1 H; vinyl-1-H), 5.54, 5.38 (2 m_c, 1 H each; 4-H, 5-H), 5.25 (dd, *J* = 17, 1.5 Hz, 1 H; *cis*-vinyl-2-H), 5.09 (dd, *J* = 10.5, 1.5 Hz, 1 H; *trans*-vinyl-2-H), 3.67, 3.66 (2 s, 12 H; 4 CO_2Me), 3.64 (s, 3 H; CO_2Me), 3.62* (t, *J* = 7.5 Hz, 1 H; 2″-H), 3.17–3.14 (m, 4 H; 1-H, 1″-H), 2.85 (dd, *J* = 15.5, 6.0 Hz, 1 H; 6-H), 2.45 (d, *J* = 7 Hz, 2 H; 3-H), 2.20 (dd, *J* = 15.5, 6.5 Hz, 1 H; 6-H), 1.83 (d, *J* = 6.5 Hz, 1 H; *cis*-3′-H), 1.02 (d, *J* = 6.5 Hz, 1 H; *trans*-3′-H), 0.90 (s, 9 H; *t*Bu), 0.11, 0.09 (2 s, 6 H; $SiMe_2$), * signal is partly overlapped by ester signals; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 171.0,* 169.1,* 52.4–51.9 (3 s, several q, 5 CO_2Me), 136.7 (d,

vinyl-C-1), 136.3, 134.5 (2s, aryl-C), 132.4, 125.2 (2d, C-4, C-5), 130.1,* 128.6* (2d, aryl-CH), 115.2 (t, vinyl-C-2), 65.1 (s, C-2′), 59.2 (s, C-2), 53.5 (d, C-2″), 37.6, 35.2, 34.3, 31.8 (4t, C-1, C-3, C-6, C-1″), 37.3 (s, C-1′), 25.8, 18.1 (q, s, *t*Bu), 23.7 (t, C-3′), −3.5, −3.6 (2q, $SiMe_2$), * signal has double intensity; IR (KBr): $\tilde{\nu}$ = 3050 – 3000 (=C−H), 2950, 2930, 2900, 2860 (C−H), 1760, 1740 (CO_2Me), 1640 cm^{-1} (C=C); elemental analysis: $C_{35}H_{50}O_{11}Si$ (674.9): calcd C 62.29, H 7.47; found C 62.57, H 7.13.

Tetramethyl (3E)-7-{2-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl-methyl]phenyl}-3-heptene-1,1,6,6-tetracarboxylate (**27**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.25 – 6.99 (m, 4H; aryl-H), 5.87 (dd, *J* = 17, 10.5 Hz, 1H; vinyl-1-H), 5.46 (m_c, 2H; 3-H, 4-H), 5.27 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-vinyl-2-H), 5.12 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-vinyl-2-H), 3.69, 3.643, 3.640, 3.57* (3s, 13H; 4 CO_2Me, 1′-H), 3.48 (s, 3H; CO_2Me), 3.33 (d, *J* = 10 Hz, 2H; 7-H), 2.86 (d, *J* = 16.5 Hz, 1H; 1′-H), 2.60 – 2.52 (m, 4H; 2-H, 5-H), 2.02 (d, *J* = 6.5 Hz, 1H; *cis*-3″-H), 1.16 (d, *J* = 6.5 Hz, 1H; *trans*-3″-H), 0.90 (s, 9H; *t*Bu), 0.13, 0.07 (2s, 6H; $SiMe_2$), * 1′-H-signal (1H) is partly overlapped by ester signals; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.8, 171.3, 171.2, 169.0,* 52.4, 52.13,* 52.11, 51.7, 51.6 (4s, 4q, d, 5 CO_2Me, C-1), 138.9, 134.6 (2s, aryl-C), 136.6 (d, vinyl-C-1), 129.9, 129.7, 128.0, 127.8, 126.8, 125.7 (6d, C-3, C-4, aryl-CH), 115.5 (t, vinyl-C-2), 64.9 (s, C-2″), 59.2 (s, C-6), 37.6 (s, C-1″), 36.4, 34.4, 31.1, 28.9 (4t, C-2, C-5, C-7, C-1′), 25.8, 18.1 (q, s, *t*Bu), 24.4 (t, C-3″), −3.4, −3.6 (2q, $SiMe_2$), * signal has double intensity; IR (CCl_4): $\tilde{\nu}$ = 3100 – 3000 (=C−H), 2950, 2930, 2900, 2860 (C−H), 1750, 1740 (CO_2Me), 1650, 1600 cm^{-1} (C=C); elemental analysis: $C_{35}H_{50}O_{11}Si$ (674.9): calcd C 62.29, H 7.47; found C 62.35, H 7.54.

Dimethyl 3-{2-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl-methyl]phenyl}-1-{2-[2,2-di(methoxycarbonyl)ethyl]-phenyl}propane-2,2-dicarboxylate (**28**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26, 7.17 – 7.03 (m_c, m, 1H, 7H; aryl-H), 5.88 (dd, *J* = 17, 10.5 Hz, 1H; vinyl-1-H), 5.29 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-vinyl-2-H), 5.14 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-vinyl-2-H), 3.64, 3.63 (2s, 6H; 2 CO_2Me), 3.60, 3.59 (2s, 6H; 2 CO_2Me), 3.52* (t, *J* = 8 Hz, 1H; 2′-H), 3.51 (s, 3H; CO_2Me), 3.46 – 3.34 (m, 5H; 1-H, 3-H, 1″-H), 3.07 (d, *J* = 8 Hz, 2H; 1′-H), 2.85 (d, *J* = 17 Hz, 1H; 1″-H), 2.02 (d, *J* = 6.5 Hz, 1H; *cis*-3‴-H), 1.14 (d, *J* = 6.5 Hz, 1H; *trans*-3‴-H), 0.89 (s, 9H; *t*Bu), 0.13, 0.06 (2s, 6H; $SiMe_2$), * signal is partly overlapped by ester signals; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 171.6, 171.5, 168.9,* 52.9, 52.29,** 52.26, 51.7 (4s, 3q, d, 5 CO_2Me, C-2′), 138.8, 136.8, 134.9, 134.8 (4s, aryl-C), 136.5 (d, vinyl-C-1), 130.1, 129.5, 128.3, 128.1, 126.9, 126.7, 126.5, 125.8 (8d, aryl-CH), 115.4 (t, vinyl-C-2), 64.9 (s, C-2‴), 59.0 (s, C-2), 37.2 (s, C-1‴), 35.1, 34.5, 31.2, 31.1 (4t, C-1, C-3, C-1′, C-1″), 25.7, 18.0 (q, s, *t*Bu), 24.4 (t, C-3‴), −3.5, −3.6 (2q, $SiMe_2$), * signal has double intensity; ** signal has triple intensity; IR (KBr): $\tilde{\nu}$ = 3100 – 3000 (=C−H), 2950, 2930, 2900, 2860 (C−H), 1760 – 1740 (CO_2Me), 1640, 1610 cm^{-1} (C=C); elemental analysis: $C_{39}H_{52}O_{11}Si$ (724.9): calcd C 64.62, H 7.23; found C 64.73, H 7.39.

Dimethyl 2-{6-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl-methyl]-2-pyridyl}ethane-1,1-dicarboxylate (**36**): In accordance with general procedure A, siloxycyclopropane **1** (0.300 g, 1.17 mmol) was deprotonated with lithium diisopropylamide (generated in situ from diisopropylamine (1.76 mmol) and *n*-butyllithium (1.76 mmol)) in THF (18 mL) at −78 °C. After 2 h, the dibromide **35** (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 it was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water and brine, and dried over $MgSO_4$. Evaporation of the solvent was followed by removal of the unused dibromide **35** by rotary evaporation (0.01 mbar, 75 °C). Chromatographic separation (heptane/ethyl acetate, 1:0 → 9:1) gave a yellow oil (0.762 g), which contained colorless crystals. The alkylation product could not be separated from the dibromide **35**; the mixture contained approximately 47% methyl 1-(6-bromomethyl-pyridyl-2-methyl)-*t*-2-*tert*-butyldimethylsiloxy-*c*-2-vinyl-*r*-1-cyclopropanecarboxylate. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 7.5 Hz, 1H; pyridine-4-H), 7.20, 7.07 (2d, *J* = 7.5 Hz, 1H each; pyridine-3-H, pyridine-5-H), 5.89 (dd, *J* = 17, 10.5 Hz, 1H; 1″-H), 5.31 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-2″-H), 5.13 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-2″-H), 4.45 (s, 2H; CH_2Br), 3.61 (d, *J* = 16 Hz, 1H; 1′-H), 3.56 (s, 3H; CO_2Me), 3.07 (d, *J* = 16 Hz, 1H; 1′-H), 1.92 (d, *J* = 6.5 Hz, 1H; *cis*-3-H), 1.27 (d, *J* = 6.5 Hz, 1H; *trans*-3-H), 0.87 (s, 9H; *t*Bu), 0.11, 0.10 (2s, 6H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 172.0, 51.8 (s, q, CO_2Me), 160.2, 155.8 (2s, pyridine-C-2, pyridine-C-6), 136.9, 136.6 (2d, C-1″, pyridine-C-4), 121.6, 120.5 (2d, pyridine-C-3, pyridine-C-5), 115.4 (t, C-2″), 65.3 (s, C-2), 36.7, 34.2 (2t, C-1′, CH_2Br), 25.8, 18.1 (q, s, *t*Bu), 24.5 (t, C-3), −3.6, −3.6 (2q, $SiMe_2$), the spectra also contain signals from the dibromide **35**.

As described in general procedure C**,** dimethyl malonate (1.55 g, 11.7 mmol) was deprotonated with sodium hydride (0.176 g, 5.85 mmol) and subsequently alkylated with the product mixture as obtained above (0.762 g). Chromatographic separation (heptane/ethyl acetate, 1:0 → 4:1) furnished **36** as a pale yellow-brown oil (0.239 g, 42% for two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (t, *J* = 7.5 Hz, 1H: pyridine-4-H): 6.94 (d, *J* = 7.5 Hz, 2H; pyridine-3-H, pyridine-5-H), 5.84 (dd, *J* = 17, 10.5 Hz, 1H, vinyl-1-H), 5.28 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-vinyl-2-H), 5.10 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-vinyl-2-H), 4.20 (t, *J* = 7.5 Hz, 1H; 1-H), 3.66 (s, 6H; 2 CO_2Me), 3.60 (d, *J* = 16 Hz, 1H; 1′-H), 3.54 (s, 3H; CO_2Me), 3.28 (d, *J* = 7.5 Hz, 2H; 2-H), 2.94 (d, *J* = 16 Hz, 1H; 1′-H), 1.87 (d, *J* = 6.5 Hz, 1H; *cis*-3″-H), 1.21 (d, *J* = 6.5 Hz, 1H; *trans*-3″-H), 0.88 (s, 9H; *t*Bu), 0.10, 0.09 (2s, 6H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 172.0, 169.7,* 52.3,* 51.7 (2s, 2q, 3 CO_2Me), 159.5, 156.6 (2s, pyridine-C-2, pyridine-C-6), 136.7, 136.3 (2d, pyridine-C-4, vinyl-C-1), 120.5, 120.4 (2d, pyridine-C-3, pyridine-C-5), 115.3 (t, vinyl-C-2), 65.3 (s, C-2″), 50.1 (d, C-1), 36.5, 36.2 (2t, C-2, C-1′), 37.2 (s, C-1″), 25.8, 18.1 (q, s, *t*Bu), 24.1 (t, C-3″), −3.5, −3.6 (2q, $SiMe_2$), * signal has double intensity; IR (neat): $\tilde{\nu}$ = 3100 – 3000 (=C−H, pyridine), 2960, 2930, 2900, 2890, 2860 (C−H), 1760 – 1730 (CO_2Me), 1640 (C=C), 1590, 1580 cm^{-1} (pyridine); elemental analysis: $C_{25}H_{37}NO_7Si$ (491.7): calcd C 61.07, H 7.58, N 2.85; found C 61.12, H 7.71, N 3.14.

Dimethyl (4E)-6-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-1-{6-[2,2-di(methoxycarbonyl)ethyl]-2-pyridyl}-4-hexene-2,2-dicarboxylate (**39**): As set out in general procedure B**,** crude compound **16** (0.350 g, 0.794 mmol) was added slowly at 0 °C to a suspension of sodium hydride (0.036 g, 1.19 mmol) in THF/DMF (5:1) (21 mL). The mixture was stirred for 1 h at room temperature, and then the dihalide **35** (0.421 g, 1.59 mmol) was added at 0 °C. After stirring at room temperature for 18 h the mixture was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water and brine, and dried over $MgSO_4$. Chromatographic separation (heptane/ethyl acetate, 9.5:0.5 → 7:3) provided dimethyl (4E)-1-(6-bromomethyl-2-pyridyl)-6-[*r*-2-(*tert*-butyldimethylsiloxy)-*t*-1-methoxycarbonyl-2-vinylcycloprop-1-yl]-4-hexene-2,2-dicarboxylate as a colorless oil (0.370 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (t, *J* = 7.5 Hz, 1H; pyridine-4-H), 7.18, 6.96 (2d, *J* = 7.5 Hz, 1H each; pyridine-3-H, pyridine-5-H), 5.76 (dd, *J* = 17, 10.5 Hz, 1H; 1″-H), 5.34 (m_c, 2H; 4-H, 5-H), 5.21 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-2″-H), 5.05 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-2″-H), 4.37 (s, 2H; CH_2Br), 3.68 (s, 6H; 2 CO_2Me), 3.60 (s, 3H; CO_2Me), 3.31 (s, 2H; 1-H), 2.78 (dd, *J* = 15, 5 Hz, 1H; 6-H), 2.46 (d, *J* = 6 Hz, 2H; 3-H), 2.12 (dd, *J* = 15, 5.5 Hz, 1H; 6-H), 1.78 (d, *J* = 6 Hz, 1H; *cis*-3′-H), 0.96 (d, *J* = 6 Hz, 1H; *trans*-3′-H), 0.84 (s, 9H; *t*Bu), 0.06, 0.04 (2s, 6H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.7, 170.9,* 52.27, 52.26, 51.8 (2s, 3q, 3 CO_2Me), 156.8, 155.8 (2s, pyridine-C-2, pyridine-C-6), 137.0, 136.6 (2d, C-1″, pyridine-C-4), 132.1, 125.3, 123.4, 121.0 (4d, C-4, C-5, pyridine-C-3, pyridine-C-5), 115.0 (t, C-2″), 65.0 (s, C-2′), 57.6 (s, C-2), 39.2, 35.2, 33.7, 31.7 (4t, C-1, C-3, C-6, CH_2Br), 37.3 (s, C-1′), 25.7, 18.0 (q, s, *t*Bu), 23.5 (t, C-3′), −3.6, −3.7 (2q, $SiMe_2$), * signal has double intensity; IR (neat): $\tilde{\nu}$ = 3100 – 3000 (=C−H, pyridine), 2950, 2930, 2900, 2890, 2860 (C−H), 1740 – 1730 (CO_2Me), 1640 (C=C), 1590, 1570 cm^{-1} (pyridine); elemental analysis: $C_{29}H_{42}BrNO_7Si$ (624.6): calcd C 55.76, H 6.78, N 2.24; found C 55.44, H 6.80, N 2.60.

In accordance with general procedure C**,** dimethyl malonate (0.683 g, 5.17 mmol) was deprotonated with sodium hydride (0.078 g, 2.59 mmol) and alkylated to give the product as obtained above (0.323 g, 0.517 mmol). Chromatographic purification (heptane/ethyl acetate, 9:1 → 7.5:2.5) furnished **39** as a colorless oil (0.315 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 7.5 Hz, 1H; pyridine-4-H), 6.97, 6.88 (2d, *J* = 7.5 Hz, 1H each; pyridine-3-H, pyridine-5-H), 5.78 (dd, *J* = 17, 10.5 Hz, 1H; vinyl-1-H), 5.34 – 5.32 (m, 2H; 4-H, 5-H), 5.22 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-vinyl-2-H), 5.07 (dd, *J* = 10.5, 1.5 Hz, 1H; *trans*-vinyl-2-H), 4.15 (t, *J* = 7.5 Hz, 1H; 2″-H), 3.69, 3.66 (2s, 6H each; 4 CO_2Me), 3.61 (s, 3H; CO_2Me), 3.31 (s, 2H; 1-H), 3.23 (d, *J* = 7.5 Hz, 1H; 1″-H), 2.80 (br d, *J* = 15.5 Hz, 1H; 6-H), 2.44 (d, *J* = 5 Hz, 2H; 3-H), 2.12 (br d, *J* = 15.5 Hz, 1H; 6-H), 1.79 (d, *J* = 6.5 Hz, 1H; *cis*-3′-H), 0.97 (d, *J* = 6.5 Hz, 1H; *trans*-3′-H), 0.86 (s, 9H; *t*Bu), 0.08, 0.06 (2s, 6H; $SiMe_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 171.2, 171.1, 169.6,* 52.4,* 52.3,* 51.8 (4s, 3q, 5 CO_2Me), 156.8, 156.4 (2s, pyridine-C-2, pyridine-C-6), 136.6, 136.5 (2d, pyridine-C-4, vinyl-C-1), 131.9, 125.5, 122.1, 121.2 (4d, C-4, C-5, pyridine-C-3, pyridine-C-5), 115.1 (t, vinyl-C-2), 65.1 (s,

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C-2′), 57.6 (s, C-2), 50.3 (d, C-2″), 39.3, 36.5, 35.0, 31.7 (4t, C-1, C-3, C-6, C-1″), 37.4 (s, C-1′), 25.8, 18.1 (q, s, *t*Bu), 23.5 (t, C-3′), −3.5, −3.7 (2q, $SiMe_2$), * signal has double intensity; IR (neat): $\tilde{\nu}$ = 3060–3000 (=C−H, pyridine), 2950, 2930, 2860 (C−H), 1760–1720 (CO_2Me), 1640 (C=C), 1590, 1580 cm^{-1} (pyridine); elemental analysis: $C_{34}H_{49}NO_{11}Si$ (675.8): calcd C 60.42, H 7.31, N 2.07; found C 60.05, H 7.39, N 2.48.

General procedure D for fluoride-induced cyclization: A solution of siloxycyclopropyl-substituted dimethyl malonate (1.0 equiv) in DMF (50 mL) was added slowly to a warm suspension (90 °C) of cesium fluoride (3.0 equiv) and benzyltriethylammonium chloride (1.5 equiv) in dry DMF (≈550 mL $mmol^{-1}$ siloxycyclopropyl compound). This addition was performed with a syringe pump over a certain period of time that is detailed in each experiment. After evaporation of all the volatile components (16 mbar, 70 °C), the residue was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (5 × 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. Subsequent removal of solvent was followed by rotary evaporation of the remaining DMF (0.01 mbar, 50 °C). The residue was purified by chromatography as indicated in the individual experiments (Table 4).

Trimethyl 3,4-benzo-8-oxo-cyclodecane-1,1,6-tricarboxylate (**11**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.17–6.99 (m, 3H; aryl-H), 6.74 (d, J = 7 Hz, 1H; aryl-H), 3.87, 3.81, 3.76* (3s, 10H; 6-H, 3CO_2Me), 3.38–2.99 (m, 4H), 2.84–2.79 (m, 1H), 2.69 (m_c, 1H), 2.47–2.35 (m, 2H), 2.09–1.95 (m, 2H), * 6-H-signal is overlapped by ester signals; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 209.3 (s, C=O), 174.3, 172.6, 170.4, 52.9,** 52.1 (3s, 2q, 3CO_2Me), 138.8, 134.6 (2s, C-3, C-4), 130.1, 128.1, 127.3, 126.7 (4d, aryl-CH), 58.2 (s, C-1), 42.0 (d, C-6), 40.3, 38.5, 32.1, 30.0, 27.4 (5t, C-2, C-5, C-7, C-9, C-10), ** signal has double intensity; IR (KBr): $\tilde{\nu}$ = 3080–3020 (=C−H), 2960, 2940, 2850 (C−H), 1740–1720 (CO_2Me, C=O), 1640 cm^{-1} (C=C); elemental analysis: $C_{20}H_{24}O_7$ (376.4): calcd C 63.82, H 6.43; found C 63.42, H 6.79.

5,19-Dioxo-2,2,7,16,16,21-hexa(methoxycarbonyl)-[8$_2$]metacyclophane (**12**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14 (td, J = 7.5, 2.5 Hz, 2H; 11-H, 25-H), 6.98 (d, J = 7.5 Hz, 2H; 10-H, 24-H or 12-H, 26-H), 6.88 (s, 2H; 14-H, 28-H), 6.83 (m_c, 2H; 10-H, 24-H or 12-H, 26-H), 3.72, 3.71 (2s, 12H; 4CO_2Me), 3.64, 3.63 (2s, 6H; 7-CO_2Me, 21-CO_2Me), 3.21, 3.20 (2br s, 4H; 1-H, 15-H), 3.09 (m_c, 2H; 7-H, 21-H), 2.99 (m_c, 2H; 8-H, 22-H), 2.72–2.57 (m, 4H; 6-H, 8-H, 20-H, 22-H), 2.56–2.36* (m, 4H; 4-H, 18-H), 2.38* (m_c, 2H; 6-H, 20-H), 2.01–1.82 (m, 4H; 3-H, 17-H), * signals overlap; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 207.1** (s, C=O), 175.0, 174.9, 51.9** (2s, q, 7-CO_2Me, 21-CO_2Me), 171.4, 171.32, 171.30,** 52.5,** 52.4** (3s, 2q, 4CO_2Me), 138.6** (s, C-9, C-23), 135.70, 135.67 (2s, C-13, C-27), 130.8, 130.7 (2d, C-14, C-28), 128.7, 128.5 (2d, C-11, C-25), 127.9, 127.83, 127.77** (3d, C-10, C-12, C-24, C-26), 57.92, 57.88 (2s, C-2, C-16), 42.6, 42.5 (2t, C-6, C-20), 41.9** (d, C-7, C-21), 39.2, 39.0 (2t, C-1, C-15), 37.9, 37.8 (2t, C-4, C-18), 37.1, 36.9 (2t, C-8, C-22), 25.6, 25.5 (2t, C-3, C-17), ** signal has double intensity; assignment supported by 2D NMR experiments; IR (KBr): $\tilde{\nu}$ = 3050–3000 (=C−H), 2960, 2930, 2890 (C−H), 1730 (CO_2Me, C=O), 1640 cm^{-1} (C=C); MS (Maldi, matrix: gentisinic acid): m/z (%): 793 ([M − K + 2]$^+$, 72), 777 ([M − Na + 2]$^+$, 100); elemental analysis: $C_{40}H_{48}O_{14}$ (752.8): calcd C 63.82, H 6.43; found C 63.44, H 6.70.

5,19-Dioxo-2,2,7,16,16,21-hexa(methoxycarbonyl)-[8$_2$]paracyclophane (**13**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.96 (m_c, 4H; 10-H, 14-H, 24-H, 28-H), 6.90 (m_c, 4H; 11-H, 13-H, 25-H, 27-H), 3.71,* 3.693, 3.688, 3.67* (4s, 18H, 6CO_2Me), 3.21–3.06 (m, 8H; 1-H, 7-H, 8-H or 22-H, 15-H, 21-H), 2.66 (m_c, 4H; 6-H or 20-H, 8-H or 22-H), 2.39 (dd, J = 18, 5 Hz, 1H; 6-H or 20-H), 2.36–2.14** (m, 4H; 4-H, 18-H), 2.23** (dd, J = 18, 4.5 Hz, 1H; 6-H or 20-H), 2.03–1.82 (m, 4H; 3-H, 17-H), * signal has double intensity; ** signals overlap; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 207.5, 207.4 (2s, C=O), 174.8, 174.6, 171.2, 171.11, 171.06, 170.9, 52.55, 52.52,* 52.4, 52.00, 51.98 (6s, 5q, 6CO_2Me), 137.2, 137.1 (2s, C-9, C-23), 133.8* (s, C-12, C-26), 130.0,* 129.9* (2d, C-11, C-13, C-25, C-27), 129.10,* 129.07* (2d, C-10, C-14, C-24, C-28), 57.9, 57.8 (2s, C-2, C-16), 42.0, 41.8 (2t, C-6, C-20), 40.9* (d, C-7, C-21), 38.8, 38.2 (2t, C-1, C-15), 37.8, 37.7 (2t, C-4, C-18), 36.1, 35.9 (2t, C-8, C-22), 26.1, 25.8 (2t, C-3, C-17), * signal has double intensity; assignment supported by 2D NMR experiments; IR (KBr): $\tilde{\nu}$ = 3050–3000 (=C−H), 2950, 2900 (C−H), 1730 (CO_2Me; C=O), 1640 cm^{-1} (C=C); MS (Maldi, matrix: gentisinic acid): m/z (%): 793 ([M − K + 2]$^+$, 75), 777 ([M − Na + 2]$^+$, 100); elemental analysis: $C_{40}H_{48}O_{14}$ (752.8): calcd C 63.82, H 6.43; found C 63.62, H 6.52.

Pentamethyl (8E)-3,4-benzo-13-oxo-8-cyclopentadecene-1,1,6,6,11-pentacarboxylate (**29**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.99–6.83 (m, 4H; aryl-H), 5.36, 5.03 (2m_c, 1H each; 8-H, 9-H), 3.62, 3.58, 3.57, 3.52, 3.30 (5s, 15H; 5CO_2Me), 3.64–1.97 (m, 15H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 205.8 (s, C=O), 174.9, 171.5, 171.4, 171.3, 171.2, 52.5, 52.3, 52.09, 52.06, 51.9 (5s, 5q, 5CO_2Me), 136.5, 135.2 (2s, C-3, C-4), 132.6, 130.9, 129.8, 126.6, 126.4, 126.0 (6d, C-8, C-9, aryl-CH), 59.3, 58.8 (2s, C-1, C-6), 42.8, 40.0, 38.1, 36.1, 35.4, 33.8, 24.5 (7t, C-2, C-5, C-7, C-10, C-12, C-14, C-15), 37.5 (d, C-11); IR (KBr): $\tilde{\nu}$ = 3100–3000 (=C−H), 2950, 2930, 2850 (C−H), 1730 (CO_2Me, C=O), 1640, 1620 cm^{-1} (C=C); elemental analysis: $C_{29}H_{36}O_{11}$ (560.6): calcd C 62.13, H 6.47; found C 62.09, H 6.70.

(4E)-9-Oxo-2,2,7,12,12-penta(methoxycarbonyl)-[13]metacyclophan-4-ene (**30**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11, 6.83, 6.76 (3m_c, 1H, 2H, 1H; aryl-H), 5.35 (m_c, 2H; 4-H, 5-H), 3.70, 3.68, 3.65 (3s, 15H; 5CO_2Me), 3.25–2.99 (m, 5H), 2.77–2.74 (m, 2H), 2.54–1.89 (m, 8H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 206.5 (s, C=O), 174.6, 171.0, 170.92, 170.86, 170.7, 52.5, 52.45,* 52.38, 51.9 (5s, 4q, 5CO_2Me), 135.9, 135.3 (2s, aryl-C), 132.5, 131.7, 128.8, 128.2, 127.4, 125.7 (6d, C-4, C-5, aryl-CH), 58.2, 58.1 (2s, C-2, C-12), 42.4, 38.6,** 38.2, 36.8, 34.5, 33.6, 26.2 (7t, C-1, C-3, C-6, C-8, C-10, C-11, C-13), 38.6** (d, C-7), * signal has double intensity; ** signals overlap; IR (KBr): $\tilde{\nu}$ = 3050–3000 (=C−H), 2950, 2930, 2850 (C−H), 1730 (CO_2Me, C=O), 1640, 1630 cm^{-1} (C=C); elemental analysis: $C_{29}H_{36}O_{11}$ (560.6): calcd C 62.13, H 6.47; found C 62.11, H 6.72.

(4E)-9-Oxo-2,2,7,12,12-penta(methoxycarbonyl)-[13]paracyclophan-4-ene (**31**) and **(4E,23E)-9,28-dioxo-2,2,7,12,12,21,21,26,31,31-deca(methoxycarbonyl)-[13$_2$]paracyclophan-4,23-diene** (**32**): Analytical data for **31**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11, 7.00 (2m_c, 2H each; aryl-H), 4.91 (m_c, 2H; 4-H, 5-H), 3.79, 3.78, 3.76, 3.75, 3.63 (5s, 15H; 5CO_2Me), 3.43–3.28 (m, 4H), 2.71–2.42 (m, 4H), 2.32–1.60 (m, 7H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 208.1 (s, C=O), 174.6, 172.1, 172.0, 171.5, 171.2, 52.8,* 51.8 (5s, 2q, 5CO_2Me), 135.5, 133.9 (2s, aryl-C), 130.5, 129.6,* 126.9 (3d, C-4, C-5, aryl-

Table 4. Cyclization of compounds **8**–**10**, **14**, **24**–**28**, **36**, and **39**.

Precursor	Amount [g (mmol)]	Time [h]	Chromatography heptane/ethyl acetate	Product	Yield [g (%)]	M. p.
8	0.268 (0.546)	43	9:1 → 0.1	**11**	0.048 (23)	slightly yellow crystals (128–130 °C)
8[a]	0.200 (0.408)	62	9:1 → 0.1	**11**	0.057 (37)	slightly yellow crystals (122–125 °C)
9	0.454 (0.925)	66	9:1 → 4.5:5.5	**12**	0.039 (11)	colorless crystals (167–169 °C)
10	0.556 (1.13)	43	9:1 → 1:1	**13**	0.042 (10)	colorless crystals (174–176 °C)
24	0.205 (0.304)	44	9:1 → 7:3	**29**	0.092 (54)	colorless crystals (59–61 °C)
25	0.220 (0.326)	66	9:1 → 1:1	**30**	0.099 (54)	colorless crystals (132–134 °C)
26	0.141 (0.209)	66	1:0 → 5.5:4.5	**31**	0.020 (17)	colorless crystals (50–52 °C)
				32	0.016 (14)	slightly yellow crystals (167–170 °C)
27	0.499 (0.739)	44	9:1 → 7:3	**33**	0.199 (48)	colorless crystals (138–140 °C)
28	0.505 (0.697)	40	9:1 → 7:3	**34**	0.063 (15)	slightly yellow crystals (66–68 °C)
36	0.228 (0.464)	50	9:1 → 7:3	**37**	0.063 (36)	colorless crystals (98–100 °C)
				38	0.034 (19)	slightly yellow crystals (168–170 °C)
39	0.309 (0.457)	44	9:1 → 3:2	**40**	0.199 (78)	colorless crystals (55–57 °C)

[a] Cyclization in the presence of *tert*-butyl alcohol (0.151 g, 2.04 mmol).

CH), 57.1, 56.3 (2s, C-2, C-12), 41.2, 38.7, 38.05, 38.02, 34.7, 33.1, 27.8 (7t, C-1, C-3, C-6, C-8, C-10, C-11, C-13), 39.1 (d, C-7), * signal has multiple intensity; IR (KBr): $\tilde{\nu}$ = 3030 – 3000 (=C–H), 2960, 2930, 2850 (C–H), 1730 (CO_2Me, C=O), 1650 – 1610 cm^{-1} (C=C); MS (FD): *m/z* (%): 562 ([*M* + 2]$^+$, 24), 561 ([*M* + 1]$^+$, 49), 560 (*M*$^+$, 100); elemental analysis: $C_{29}H_{36}O_{11}$ (560.6): calcd C 62.13, H 6.47; found C 62.06, H 6.25.

Analytical data for **32** (two diastereomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94 (br s, 8H; 8 aryl-H), 5.34 (m_c, 4H; 4-H, 5-H, 23-H, 24-H), 3.67, 3.662, 3.659 (3s, 30H; 10 CO_2Me), 3.17, 3.13 (2s, 4H each), 2.92 – 2.76 (m, 4H); 2.52 – 2.16 (m, 14H), 2.03 (m_c, 4H), ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 207.2 (s, 2C=O), 175.0, 171.3, 171.2, 171.1,* 52.4,* 52.3,* 51.9 (4s, 3q, 10 CO_2Me), 134.8, 134.3 (2s, 4 aryl-C), 131.3, 129.94,* 129.85,* 127.2 (4d, C-4, C-5, C-23, C-24, 8 aryl-CH), 59.1, 58.0 (2s, C-2, C-12, C-21, C-31), 43.1, 38.9, 38.0, 37.7, 35.3, 34.7, 25.9 (7t, 14 CH_2), 39.8 (d, C-7, C-26), * signal has multiple intensity; IR (KBr): $\tilde{\nu}$ = 3040 – 3000 (=C–H), 2960, 2920, 2850 (C–H), 1730 (CO_2Me, C=O), 1660 – 1610 cm^{-1} (C=C); MS (Maldi, matrix: sinapinic acid): *m/z* (%): 1164 ([*M* – K – 3]$^+$, 31), 1141 ([*M* – Na – 3]$^+$, 100); elemental analysis: $C_{58}H_{72}O_{22}$ (1121.2): calcd C 62.13, H 6.47; found C 62.12, H 6.72.

Pentamethyl (3E)-8,9-benzo-13-oxo-3-cyclopentadecene-1,1,6,6,11-pentacarboxylate (**33**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14 – 7.07, 6.95 – 6.94 (2m, 3H, 1H; aryl-H), 5.48, 5.29 (2m_c, 1H each; 3-H, 4-H), 3.72, 3.70, 3.69 (3s, 12H; 4 CO_2Me), 3.59 (s, 3H; CO_2Me), 3.24 – 3.12 (m, 3H), 2.98 (dd, *J* = 14.5, 10 Hz, 1H), 2.87 (dd, *J* = 14.5, 5 Hz, 1H), 2.78 – 2.62 (m, 6H), 2.43 (m_c, 2H), 2.12 (t, *J* = 8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 207.2 (s, C=O), 174.2, 171.3, 171.2, 171.1, 171.0, 52.7, 52.6, 52.54, 52.46, 51.8 (5s, 5q, 5 CO_2Me), 137.6, 134.4 (2s, C-8, C-9), 129.2, 128.71, 128.67, 128.6, 126.8, 126.4 (6d, C-3, C-4, aryl-CH), 58.6, 55.4 (2s, C-1, C-6), 44.1, 37.9, 35.2,* 34.2,* 25.1 (5t, C-2, C-5, C-7, C-10, C-12, C-13, C-15), 42.6 (d, C-11), * signal has double intensity; IR (KBr): $\tilde{\nu}$ = 3070 – 3000 (=C–H), 2960, 2930, 2850 (C–H), 1730 (CO_2Me, C=O), 1660 – 1620 cm^{-1} (C=C); elemental analysis $C_{29}H_{36}O_{11}$ (560.6): calcd C 62.13, H 6.47; found C 62.01, H 6.69.

Pentamethyl 3,4,8,9-dibenzo-13-oxo-cyclopentadecane-1,1,6,6,11-pentacarboxylate (**34**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 – 7.01 (m, 8H; aryl-H), 3.64, 3.62, 3.60, 3.55, 3.40 (5s, 15H; 5 CO_2Me), 3.65 – 3.25* (m, 4-H), 3.15 (d, *J* = 14.5 Hz, 1H), 3.09 (m_c, 1H), 3.01 – 2.91 (m, 2H), 3.81 (dd, *J* = 15.5, 8.5 Hz, 1H), 3.65 (dd, *J* = 15.5, 4 Hz, 1H), 2.55 – 2.26 (m, 5H), * signals are partly overlapped by ester signals; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 207.2 (s, C=O), 174.5, 171.5, 171.4,* 171.3, 52.5, 52.4, 52.2, 52.1, 51.9 (4s, 5q, 5 CO_2Me), 137.4, 135.5, 135.4, 135.2 (4s, C-3, C-4, C-8, C-9), 130.7, 130.0, 129.7, 129.2, 127.0, 126.7, 126.6, 126.5 (8d, aryl-CH), 61.2, 58.7 (2s, C-1, C-6), 43.4, 39.3, 38.2, 36.9, 34.2, 33.9, 26.5 (7t, C-2, C-5, C-7, C-10, C-12, C-14, C-15), 42.1 (d, C-11), * signal has double intensity; IR (KBr): $\tilde{\nu}$ = 3070 – 3000 (=C–H), 2950, 2930, 2850 (C–H), 1730 (CO_2Me, C=O), 1660 – 1620 cm^{-1} (C=C); elemental analysis: $C_{33}H_{38}O_{11}$ (610.7): calcd C 64.91, H 6.27; found C 64.52, H 6.52.

5-Oxo-2,2,7-tri(methoxycarbonyl)-[8](2,6)pyridinophane (**37**) and **5,19-oxo-2,2,7,16,16,21-hexa(methoxycarbonyl)-[8$_2$](2,6)pyridinophane** (**38**): Analytical data for **37**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (t, *J* = 7.5 Hz, 1H; pyridine-4-H), 7.02, 7.00 (2d, *J* = 7.5 Hz, 1H each; pyridine-3-H, pyridine-5-H), 3.77, 3.74, 3.72 (6s, 9H; 3 CO_2Me), 3.56 – 3.49 (m, 2H), 3.37 (d, *J* = 14 Hz, 1H), 3.24 (dd, *J* = 15, 3.5 Hz, 1H), 3.10 – 2.92 (m, 2H), 2.78 – 2.73* (m, 1H), 2.68* (dd, *J* = 15.5, 1.5 Hz, 1H), 2.51 (m_c, 1H), 2.27 (m_c, 1H), 2.10 (m_c, 1H), * signals partly overlap; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 207.3 (s, C=O), 175.5, 171.7, 171.5, 52.8, 52.6, 52.0 (3s, 3q, 3 CO_2Me), 157.6, 155.5 (2s, pyridine-C-2, pyridine-C-6), 137.2 (d, pyridine-C-4), 121.9, 121.5 (2d, pyridine-C-3, pyridine-C-5), 58.3 (s, C-2), 43.1, 38.8, 38.6, 38.3, 25.9 (5t, C-1, C-3, C-4, C-6, C-8), 40.5 (d, C-7); IR (KBr): $\tilde{\nu}$ = 3070 – 3000 (pyridine), 2950, 2900, 2850 (C–H), 1730, 1700 (CO_2Me, C=O), 1590, 1580 cm^{-1} (pyridine); MS (FD): *m/z* (%): 379 ([*M* + 2]$^+$, 27), 378 ([*M* + 1]$^+$, 57), 377 ([*M*]$^+$, 100), 317 (45); elemental analysis: $C_{19}H_{23}NO_7$ (377.4): calcd C 60.47, H 6.14, N 3.71; found C 60.18, H 6.11, N 3.70.

Analytical data for **38** (two diastereomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44, 7.43 (2t, *J* = 7.5 Hz, 2H; 13-H, 27-H), 6.88 (m_c, 4H; 2-H, 14-H, 26-H, 28-H), 3.75, 3.71,* 3.70, 3.60, 3.58 (5s, 18H; 6 CO_2Me), 3.69 – 3.48** (m, 2H), 3.36 – 3.26 (m, 4H), 3.03 (m_c, 2H), 2.83 – 2.22 (m, 10H), 2.15 – 1.82 (m, 4H), * signal has double intensity; ** signal is partly overlapped by ester signals; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 207.4, 207.3 (2s, 2C=O), 175.6, 175.3, 51.70, 51.66 (2s, 2q, 7-CO_2Me, 21-CO_2Me), 171.7, 171.5, 171.4, 171.3, 52.5,* 52.4* (4s, 2q, 4 CO_2Me), 158.2, 157.6, 156.4, 156.3 (4s, C-9, C-11, C-23, C-25), 136.72, 136.69 (2d, C-13, C-27), 121.9, 121.8, 121.5 (3d,** C-12, C-14, C-26, C-28), 57.3, 56.8 (2s, C-2, C-16), 43.3, 42.9, 41.3, 40.3, 39.6, 39.4,*** 38.3, 38.0, 26.3, 25.9 (10t, C-1, C-3, C-4, C-6, C-8, C-15, C-17, C-18, C-20, C-22), 40.1, 39.4*** (2d, C-7, C-21), * signal has double intensity; ** fourth doublet is overlapped, the others have same intensity; *** signals overlap; IR (KBr): $\tilde{\nu}$ = 3070 – 3000 (pyridine), 2950, 2930, 2860 (C–H), 1730 (CO_2Me, C=O), 1590, 1580 cm^{-1} (pyridine), MS (FD): *m/z* (%): 756 ([*M* + 2]$^+$, 31), 755 ([*M* + 1]$^+$, 50), 754 ([*M*]$^+$, 100), 377 (25), 375 (21); elemental analysis: $C_{38}H_{46}N_2O_{14}$ (754.8): calcd C 60.47, H 6.14, N 3.71; found C 60.73, H 6.32, N 3.54.

Cyclization of 36 without conditions of dilution: A solution of siloxycyclopropane **36** (0.187 g, 0.380 mmol) in DMF (3.5 mL) was added quickly to a warm suspension (90 °C) of cesium fluoride (0.193 g, 1.27 mmol) and benzyltriethylammonium chloride (0.145 g, 0.636 mmol) in dry DMF (3.5 mL). After stirring for 2.5 h at 90 °C, all the volatile components (16 mbar, 70 °C) were evaporated. The residue was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (5 × 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After removal of solvent, the remaining DMF was removed by rotary evaporation (0.01 mbar, 50 °C). The residue was purified by chromatography (heptane/ethyl acetate 9.5:0.5 → 0:1) to give **38** as colorless crystals (0.040 g, 28 %, m.p. = 167 – 170 °C). The analytical data for this compound are identical to those reported above for **38**.

(4E)-9-Oxo-2,2,7,12,12-penta(methoxycarbonyl)-[13](2,6)pyridinophan-4-ene (**40**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (t, *J* = 7.5 Hz, 1H; pyridine-4-H), 6.86, 6.85 (2d, *J* = 7.5 Hz, 1H each; pyridine-3-H, pyridine-5-H), 5.58, 5.44 (2m_c, 1H each; 4-H, 5-H), 3.69,* 3.68, 3.67, 3.66 (4s, 15H; 5 CO_2Me), 3.35 (s, 2H; 1-H or 13-H), 3.29 (d, *J* = 6.5 Hz, 2H; 8-H), 3.06 (m_c, 1H; 7-H), 2.94 – 2.15 (m, 10H), * signal has double intensity; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 207.1 (s, C=O), 174.9, 171.1, 170.83,* 170.78, 52.5, 52.34, 52.31,* 51.8 (4s, 4q, 5 CO_2Me), 156.6, 156.2 (2s, pyridine-C-2, pyridine-C-6), 136.5, 130.8, 127.3 (3d, C-4, C-5, pyridine-C-4), 122.5, 122.2 (2d, pyridine-C-3, pyridine-C-5), 58.5, 58.1 (2s, C-2, C-12), 42.3, 39.4, 38.98, 38.9, 34.3, 33.9, 25.4 (7t, C-1, C-3, C-6, C-8, C-10, C-11, C-13), 39.03 (d, C-7), * signal has double intensity; IR (KBr): $\tilde{\nu}$ = 3060 – 3000 (=C–H, pyridine), 2960, 2930, 2850 (C–H), 1740 (CO_2Me, C=O), 1640 (C=C), 1590, 1580 cm^{-1} (pyridine); MS (FD): *m/z* (%): 563 ([*M* + 2]$^+$, 25), 562 ([*M* + 1]$^+$, 31), 561 ([*M*]$^+$, 100); elemental analysis: $C_{28}H_{35}NO_{11}$ (561.6): calcd C 59.88, H 6.28, N 2.49; found C 59.75, H 6.45, N 2.48.

Methyl 1-{2-[2,2-di(phenylsulfonyl)ethyl]benzyl}-*t*-2-*tert*-butyldimethylsiloxy-*c*-2-vinyl-*r*-1-cyclopropanecarboxylate (**14**) **and attempts to cyclize to 15**: Di(phenylsulfonyl)methane (3.37 g, 11.4 mmol) was added slowly to a suspension of sodium hydride (0.041 g, 1.37 mmol) in THF/DMF (5:1) (30 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. Crude compound **5** (0.500 g, 1.14 mmol) was then added at 0 °C. After stirring at room temperature for 18 h, the mixture was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water and brine, and dried over $MgSO_4$. After solvent evaporation the residue was purified by chromatography (heptane/ethyl acetate 1:0 → 0:1), which yielded **14** as pale yellow crystals (0.279 g, 38 %, m.p. = 48 – 51 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.77 – 7.71 (m, 4H; SO_2Ph, 4 *o*-CH), 7.54 – 7.47 (m, 2H; SO_2Ph, 2 *p*-CH), 7.40 – 7.30 (m, 4H; SO_2Ph, 4 *m*-CH), 7.15 (m_c, 1H; aryl-H), 7.04 – 6.97 (m, 3H; aryl-H), 5.81 (dd, *J* = 17, 10.5 Hz, 1H; vinyl-1-H), 5.27 (dd, *J* = 17, 1.5 Hz, 1H; *cis*-vinyl-2-H), 5.15 – 5.08 (m, 3H; 2″-H, *trans*-vinyl-2-H), 3.58 (t, *J* = 6.5 Hz, 2H; 1″-H), 3.39 (d, *J* = 16.5 Hz, 1H; 1′-H), 3.32 (s, 3H; CO_2Me), 2.69 (d, *J* = 16.5 Hz, 1H; 1′-H), 2.00 (d, *J* = 6.5 Hz, 1H; *cis*-3-H), 1.14 (d, *J* = 6.5 Hz, 1H; *trans*-3-H), 0.82 (s, 9H; *t*Bu), 0.06, 0.00 (2s, 6H; $SiMe_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.6, 51.7 (s, q, CO_2Me), 138.6, 138.4, 138.2, 133.2 [4s, 2 aryl-C, 2 *i*-C (SO_2Ph)], 136.5 (d, vinyl-C-1), 134.13, 134.06 [2d, 2 *p*-C (SO_2Ph)], 129.9, 127.6, 127.2, 125.9 (4d, 4 aryl-CH), 129.2,* 129.1,* 128.9,* 128.8* [4d, 4 *o*-C, 4 *m*-C (SO_2Ph)], 115.7 (t, vinyl-C-2), 83.5 (d, C-2″), 64.4 (s, C-2), 37.1 (s, C-1), 30.9, 28.3 (2t, C-1′, C-1″), 25.7, 18.0 (q, s, *t*Bu), 25.0 (t, C-3), −3.4, −3.6 (2q, $SiMe_2$), * signal has double intensity; IR (KBr): $\tilde{\nu}$ = 3100 – 3010 (=C–H), 2960, 2930, 2890, 2860 (C–H), 1720 (CO_2Me), 1640 (C=C), 1330, 1150 cm^{-1} (SO_2); elemental analysis: $C_{34}H_{42}O_7S_2Si$ (654.9): calcd C 62.36, H 6.46, S 9.79; found C 62.60, H 6.89, S 9.74.

In accordance with general procedure D, a solution of **14** (0.229 g, 0.350 mmol) in DMF (50 mL) was added to a warm suspension (90 °C) of cesium fluoride (0.159 g, 1.05 mmol) and benzyltriethylammonium chloride

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(0.119 g, 0.524 mmol) in dry DMF (300 mL) over 43 h. After evaporation of all the volatile components (16 mbar, 70 °C) the residue was diluted with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (5 × 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After removal of solvent the remaining DMF was removed by rotary evaporation (0.01 mbar, 50 °C). We tried to purify the residue by chromatography (heptane/ethyl acetate 4:1 → 0:1), but no cyclization product **15** was obtained.

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