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PAPER

One-pot synthesis of cyclophane-type macrocycles using manganese(III)-mediated oxidative radical cyclization†

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Cyclophane-type macrocyclic compounds from 21 to 56 members having two fused dihydrofuran rings were synthesized by the manganese(III)-mediated oxidation of terminal dienes with bis(3-oxobutanoate)s containing aromatics. The reaction detail, characterization and reaction pathways are described.

Introduction

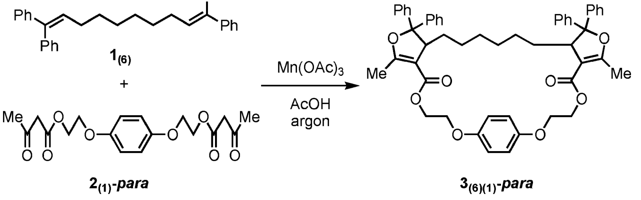
The synthesis of cyclophanes remains an attractive area for investigation from the standpoint of their constitutive and physicochemical properties.[1,2] In particular, macrocyclic compounds reveal supramolecular behaviors such as molecular recognition,[3] anion binding,[4] metal ion transport,[5] enzymatic catalysis,[6] chemical switching,[7] *etc*. Therefore, many chemists have been interested in the synthesis and the properties of macrocyclic compounds for more than five decades.[8] In recent years, we have developed various manganese(III)-based oxidative cyclization reactions.[9] In connection with our study, we found the straightforward access to the functionalized large ring compounds which were obtained by the oxidation of oligomethylene di(3-oxobutanoate)s[10] or *N*,*N*′-oligomethylenebis(3-oxobutanamide)s[11] with manganese(III) acetate in the presence of terminal alkadienes. The reaction gave macrodiolides or macrocyclic diamides containing 11 to 62 members in good yields.[10,11] We also found the intramolecular macrocyclization of 2-propenoxyoligomethylene 3-oxobutanoates and *N*-(ω-alkenyl)-3-oxobutanamides, giving the corresponding macrolides and macrocyclic amides from 8 to 26 members in good yields.[12] These reactions prompted us to investigate the synthesis of cyclophane-type macromolecules using terminal dienes and bis(3-oxobutanoate)s containing aromatics, since some naturally occurring macrocyclic compounds are also known[13] and the manganese(III)-enolate complex prepared *in situ* must undergo a specific reaction during the macrocyclization.[10a] In fact, a mixture of 1,1,10,10-tetraphenyl-1,9-octadiene and *p*-phenylenebis(oxapropyl) bis(3-oxobutanoate) initially underwent the manganese(III)-oxidation to afford the corresponding cyclophane-type macrocyclic compound. In this paper, we report the convenient synthesis and structure determination of the cyclophane-type macrodiolides.

Results and Discussion

Reaction of alkadienes 1 with bis(3-oxobutanoate)s 2 containing aromatics in the presence of manganese(III) acetate

1,9-Octadiene $\mathbf{1}_{(6)}$ was prepared by the Grignard reaction of diethyl octanedioate with phenylmagnesium bromide followed by dehydration. Bis(3-oxobutanoate) containing aromatics, $\mathbf{2}_{(1)}$-***para***, was synthesized by the reaction of hydroquinone with bromoacetate under basic conditions, followed by reduction with lithium aluminium hydride[14] and then esterification with a diketene.[13]

With the diene $\mathbf{1}_{(6)}$ and the bis(3-oxobutanoate) $\mathbf{2}_{(1)}$-***para*** in hand, we examined the reaction of $\mathbf{1}_{(6)}$ with $\mathbf{2}_{(1)}$-***para*** in the presence of manganese(III) acetate. Since it was recognized that the dissolved molecular oxygen influenced the manganese(III)-based oxidation,[10b] the mixture was degassed under reduced pressure using an ultrasonicator, followed by displacement with argon before carrying out the reaction. The reaction was carried out using a stoichiometric amount of the oxidant under high dilution conditions to give the cyclic compound $\mathbf{3}_{(6)(1)}$-***para*** together with the unchanged $\mathbf{1}_{(6)}$ (Scheme 1 and Table 1, Entry 1). Since the diene $\mathbf{1}_{(6)}$ was recovered, an excess amount of the oxidant and



Scheme 1 Reaction of diene $\mathbf{1}_{(6)}$ with bis(3-oxobutanoate) $\mathbf{2}_{(1)}$-***para*** in the presence of manganese(III) acetate.

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† Electronic supplementary information (ESI) available: The synthetic procedures and spectroscopic data of the substrates $\mathbf{1}_{(m)}$, $\mathbf{1}_{(O)}$, $\mathbf{2}_{(n)}$**-arom**, $\mathbf{2}_{(CH_2)_y}$**-arom**, $\mathbf{4}_{(m)}$, **6**, and **8** with references; the X-ray data collection and processing parameters of [22]paracyclophane $\mathbf{3}_{(8)(1)}$-***para***. CCDC reference number CCDC 769197. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00683a

Table 1 Reaction of octadiene $\mathbf{1}_{(6)}$ with bis(3-oxobutanoate) $\mathbf{2}_{(1)}$-***para*** in the presence of manganese(III) acetate[a]

Entry	$\mathbf{1}_{(6)}/\mathbf{2}_{(1)}$-***para***/ Mn(III)[b]	AcOH/ mL	Time/ min	$\mathbf{3}_{(6)(1)}$-***para*** %[c]	Rec. $\mathbf{1}_{(6)}$ %
1	1 : 1.3 : 4	200	150	30	14
2	1 : 1.3 : 4	100	15	51	18
3	1 : 1.3 : 7	100	30	54	—
4	1 : 1.3 : 7	50	90	46	5
5	1 : 1.3 : 10	100	150	43	—

[a] The reaction with $\mathbf{1}_{(6)}$ (0.2 mmol) was carried out in glacial acetic acid at 100 °C under an argon atmosphere. [b] Molar ratio. [c] Isolated yield based on the amount of $\mathbf{1}_{(6)}$ used.

the slightly concentrated conditions were adopted and the desired cyclic compound $\mathbf{3}_{(6)(1)}$-***para*** was obtained with a 54% yield (Entry 3). A greater excess of the oxidant and concentrated conditions led to a decrease in the yield of $\mathbf{3}_{(6)(1)}$-***para*** (Entries 4 and 5).

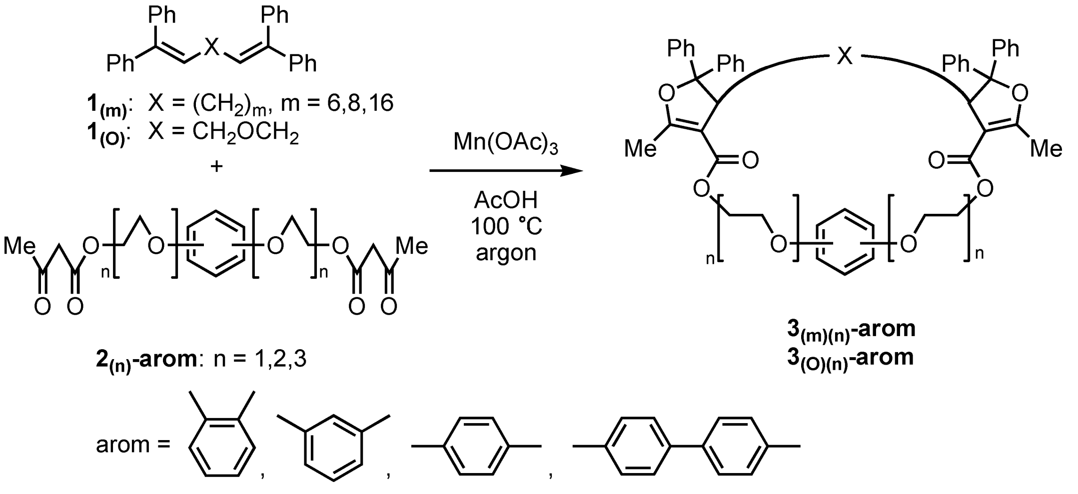
In order to examine other combinations of the terminal alkadienes and bis(3-oxobutanoate)s containing aromatics, alkadienes $\mathbf{1}_{(m)}$ (m = 8,16) were prepared by a manner similar to that of the octadiene $\mathbf{1}_{(6)}$, and 4-oxaheptadiene $\mathbf{1}_{(O)}$ was synthesized by the Reformatsky reaction of benzophenone with ethyl bromoacetate, followed by its reduction and then condensation. Other bis(3-oxobutanoate)s containing aromatics $\mathbf{2}_{(n)}$-**arom** (n = 1,2,3) were also prepared by the Williamson ether synthesis of the corresponding phenolic diols with (chloroethoxy)ethanols followed by esterification with a diketene.[14] When the reaction of the dienes $\mathbf{1}_{(m)}$ and $\mathbf{1}_{(O)}$ with bis(3-oxobutanoate)s $\mathbf{2}_{(n)}$-**arom** was carried out under the optimized reaction conditions (Scheme 2), the desired cyclic compounds, $\mathbf{3}_{(m)(n)}$-**arom** and $\mathbf{3}_{(O)(n)}$-**arom**, were produced in the yields shown in Table 2.

We also applied the reaction to methylene-tethered bis(3-oxobutanoate)s $\mathbf{2}_{(CH_2)_y}$-**arom** (y = 6,8) which were prepared in a manner similar to that of the $\mathbf{2}_{(n)}$-**arom** (Scheme 3). As a result, the corresponding cyclic compounds $\mathbf{3}_{(m)(CH_2)_y}$-**arom** were obtained in the yields shown in Table 3.

Both reactions gave cyclophane-type macrocyclic compounds containing between 21 and 50 members, having two-fused dihydrofurans in moderate yields. The yield of $\mathbf{3}_{(m)(n)}$-***meta*** was slightly lower than those of $\mathbf{3}_{(m)(n)}$-***ortho*** and $\mathbf{3}_{(m)(n)}$-***para*** (Table 2, Entries 1–14). Although the tendency might be assigned to the symmetric and/or steric problem of $\mathbf{3}_{(m)(n)}$-***meta***, we do not have any explanations at this moment. The use of 4-oxaheptadiene $\mathbf{1}_{(O)}$ also afforded $\mathbf{3}_{(O)(n)}$-**arom** in low yields (Table 2, Entries 15–20). Because the oxamethylene chain of $\mathbf{1}_{(O)}$ would be much shorter than that of the reactant bis(3-oxobutanoate)s $\mathbf{2}_{(n)}$-**arom**, the intramolecular cyclization would probably be suppressed. The biphenyl-inserted bis(3-oxobutanoate)s $\mathbf{2}_{(n)}$-**biphen** also gave the corresponding cyclophanes $\mathbf{3}_{(m)(n)}$-**biphen** containing between 28 and 50 members in low yields (Table 2, Entries 21–29). It seemed that the $\mathbf{2}_{(n)}$-**arom** containing the biphenyl chain might be more rigid than that including the phenylene chain. The oxamethylene tethered $\mathbf{2}_{(n)}$-**arom** would undergo an over-oxidation with manganese(III) acetate since the $\mathbf{2}_{(n)}$-**arom**, having the successive ether chain, might be much more sensitive to the metal oxidant than the inactive methylene tethered $\mathbf{2}_{(CH_2)_y}$-**arom**, and therefore, the use of the methylene tethered $\mathbf{2}_{(CH_2)_y}$-**arom** instead of the oxamethylene tethered $\mathbf{2}_{(n)}$-**arom** led to the good yield of the cyclophanes $\mathbf{3}_{(m)(CH_2)_y}$-**arom** (Table 3).

Characterization of $\mathbf{3}_{(6)(1)}$-*para*

The structure of $\mathbf{3}_{(6)(1)}$-***para*** was characterized by a spectroscopic method. All the peaks of the ^{1}H NMR and the ^{13}C NMR spectrum were correlated by the HMQC spectrum. The ^{1}H NMR spectrum showed the existence of two dihydrofurans and a hydroquinone part at δ 3.67 (2H, t, J = 5.4 Hz), 2.29 (6H, s), and 6.74 (4H, s) ppm, assigned to a methine and a methyl proton of the dihydrofuran and aromatic protons of the hydroquinone, respectively. The ^{13}C NMR spectrum also revealed two sp^2 carbons at δ 165.5 and 107.7, a methine carbon at δ 48.9 and a quaternary carbon at δ 95.3 ppm due to the dihydrofuran. These peaks, as well as an ester carbonyl carbon at 167.0 ppm, appeared as two slightly different peaks, due to the diastereomixture of the cyclic compound that contained two asymmetric carbons.[10a] Interestingly, eight protons of the methylene chain were extremely shifted upfield at δ 0.58–0.31 (4H, m) and 0.08–−0.23 (4H, m) ppm because of the strong ring current effect just below the hydroquinone group. These data supported the fact that the terminal diene $\mathbf{1}_{(6)}$ must undergo oxidative macrocyclization with the

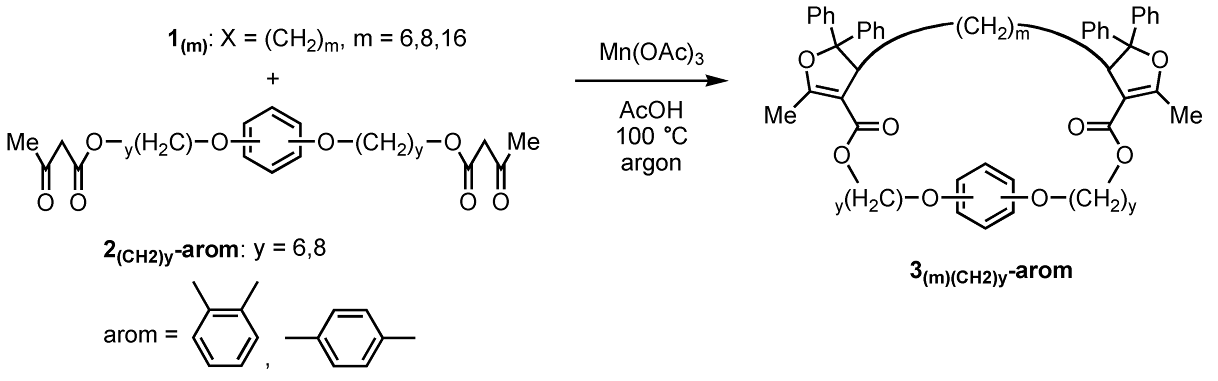


Scheme 2 Reaction of dienes $\mathbf{1}_{(m)}$ and $\mathbf{1}_{(O)}$ with bis(3-oxobutanoate)s $\mathbf{2}_{(n)}$-**arom** in the presence of manganese(III) acetate.

Table 2 Reaction of terminal dienes **1**$_{(m)}$ and **1**$_{(O)}$ with bis(3-oxobutanoate)s **2**$_{(n)}$**-arom** in the presence of manganese(III) acetate[a]

Entry	Diene	Butanoate	**1**/**2**/Mn(III)[b]	Time/ min	Cyclophane (%)[c]	Ring size
1	**1**$_{(6)}$	**2**$_{(1)}$-***para***	1 : 1.3 : 7	30	**3**$_{(6)(1)}$-***para*** (54)	24
2	**1**$_{(6)}$	**2**$_{(2)}$-***ortho***	1 : 1.3 : 7	60	**3**$_{(6)(2)}$-***ortho*** (58)	28
3	**1**$_{(6)}$	**2**$_{(2)}$-***meta***	1 : 1.3 : 7	80	**3**$_{(6)(2)}$-***meta*** (33)	29
4	**1**$_{(6)}$	**2**$_{(2)}$-***para***	1 : 1.3 : 7	60	**3**$_{(6)(2)}$-***para*** (64)	30
5	**1**$_{(6)}$	**2**$_{(3)}$-***ortho***	1 : 1.3 : 7	70	**3**$_{(6)(3)}$-***ortho*** (42)	34
6	**1**$_{(6)}$	**2**$_{(3)}$-***para***	1 : 1.3 : 7	70	**3**$_{(6)(3)}$-***para*** (46)	36
7	**1**$_{(8)}$	**2**$_{(1)}$-***para***	1 : 1.3 : 8	45	**3**$_{(8)(1)}$-***para*** (62)	26
8	**1**$_{(8)}$	**2**$_{(2)}$-***ortho***	1 : 1.3 : 7	60	**3**$_{(8)(2)}$-***ortho*** (60)	30
9	**1**$_{(8)}$	**2**$_{(2)}$-***meta***	1 : 1.3 : 7	60	**3**$_{(8)(2)}$-***meta*** (33)	31
10	**1**$_{(8)}$	**2**$_{(2)}$-***para***	1 : 1.3 : 8	20	**3**$_{(8)(2)}$-***para*** (52)	32
11	**1**$_{(8)}$	**2**$_{(3)}$-***para***	1 : 1.3 : 7	60	**3**$_{(8)(3)}$-***para*** (42)	38
12	**1**$_{(16)}$	**2**$_{(1)}$-***para***	1 : 1.3 : 8	40	**3**$_{(16)(1)}$-***para*** (44)	34
13	**1**$_{(16)}$	**2**$_{(2)}$-***para***	1 : 1.3 : 8	60	**3**$_{(16)(2)}$-***para*** (38)	40
14	**1**$_{(16)}$	**2**$_{(3)}$-***para***	1 : 1.3 : 7	60	**3**$_{(16)(3)}$-***para*** (43)	46
15	**1**$_{(O)}$	**2**$_{(1)}$-***para***	1 : 1.3 : 7	20	**3**$_{(O)(1)}$-***para*** (23)	21
16	**1**$_{(O)}$	**2**$_{(2)}$-***ortho***	1 : 1.3 : 7	80	**3**$_{(O)(2)}$-***ortho*** (30)	25
17	**1**$_{(O)}$	**2**$_{(2)}$-***meta***	1 : 1.3 : 7	90	**3**$_{(O)(2)}$-***meta*** (22)	26
18	**1**$_{(O)}$	**2**$_{(2)}$-***para***	1 : 1.3 : 7	80	**3**$_{(O)(2)}$-***para*** (29)	27
19	**1**$_{(O)}$	**2**$_{(3)}$-***ortho***	1 : 1.3 : 7	80	**3**$_{(O)(3)}$-***ortho*** (19)	31
20	**1**$_{(O)}$	**2**$_{(3)}$-***para***	1 : 1.3 : 7	80	**3**$_{(O)(3)}$-***para*** (20)	33
21	**1**$_{(6)}$	**2**$_{(1)}$**-biphen**	1 : 1.3 : 7	75	**3**$_{(6)(1)}$**-biphen** (28)	28
22	**1**$_{(6)}$	**2**$_{(2)}$**-biphen**	1 : 1.3 : 7	35	**3**$_{(6)(2)}$**-biphen** (41)	34
23	**1**$_{(6)}$	**2**$_{(3)}$**-biphen**	1 : 1.3 : 7	30	**3**$_{(6)(3)}$**-biphen** (33)	40
24	**1**$_{(8)}$	**2**$_{(1)}$**-biphen**	1 : 1.3 : 7	90	**3**$_{(8)(1)}$**-biphen** (35)	30
25	**1**$_{(8)}$	**2**$_{(2)}$**-biphen**	1 : 1.3 : 7	30	**3**$_{(8)(2)}$**-biphen** (43)	36
26	**1**$_{(8)}$	**2**$_{(3)}$**-biphen**	1 : 1.3 : 7	40	**3**$_{(8)(3)}$**-biphen** (22)	42
27	**1**$_{(16)}$	**2**$_{(1)}$**-biphen**	1 : 1.3 : 7	30	**3**$_{(16)(1)}$**-biphen** (43)	38
28	**1**$_{(16)}$	**2**$_{(2)}$**-biphen**	1 : 1.3 : 7	30	**3**$_{(16)(2)}$**-biphen** (23)	44
29	**1**$_{(16)}$	**2**$_{(3)}$**-biphen**	1 : 1.3 : 7	30	**3**$_{(16)(3)}$**-biphen** (30)[d]	50

[a] The reaction with the terminal diene **1** (0.2 mmol) was carried out in glacial acetic acid (100 mL) at 100 °C under an argon atmosphere. [b] Molar ratio of the terminal diene **1**$_{(m)}$, **1**$_{(O)}$: bis(3-oxobutanoate)s **2**$_{(n)}$**arom** : manganese(III) acetate. [c] Isolated yield based on the amount of the terminal diene **1**$_{(m)}$ and **1**$_{(O)}$ used. [d] The corresponding diploid was isolated in 17% yield.



Scheme 3 Reaction of dienes **1**$_{(m)}$ with bis(3-oxobutanoate)s **2**$_{(CH_2)_y}$**-arom** in the presence of manganese(III) acetate.

bis(3-oxobutanoate) **2**$_{(1)}$-***para*** during the double dihydrofuranation. In addition, the exact molecular ion peak appeared at *m/z* 804.3673 (calculated for $C_{52}H_{52}O_8$: 804.3662) in the high-resolution FAB mass spectrum. Therefore, the product **3**$_{(6)(1)}$-***para*** was determined to be a [20]paracyclophane. Fortunately, the product **3**$_{(8)(1)}$-***para*** was crystallized from chloroform–hexane to provide a single crystal, which was measured by X-ray diffraction. As a result, it was confirmed that the product **3**$_{(8)(1)}$-***para*** was a [22]paracyclophane, having two fused dihydrofuran rings (Fig. 1). Although the strong ring current effect of the hydroquinone group was observed in most of the cyclophane-type compounds **3**$_{(m)(n)}$**-arom** and **3**$_{(m)(CH_2)_y}$**-arom** except for **3**$_{(O)(n)}$**-arom** and the macrocyclic compounds produced by the reaction using icosadiene **1**$_{(16)}$, the upfield shift of the methylene protons was particularly remarkable in the **3**$_{(6)(1)}$**-biphen** containing the biphenol part, appearing at δ 0.29 (2H), 0.12 (2H), and −0.20 (4H) ppm, respectively.

The reaction of icosadiene **1**$_{(16)}$ with bis(3-oxobutanoate) **2**$_{(3)}$**-biphen** containing the biphenyl moiety deserves comments. The other cyclic product, which was very similar to the NMR spectrum of **3**$_{(16)(3)}$**-biphen**, was isolated (Table 2, Entry 29). The cyclic product was determined to be the diploid (Fig. 2) since the high-resolution FAB mass spectrum showed a molecular ion peak at *m/z* 2393.3213 (calculated for $C_{152}H_{184}O_{24}$: 2393.3178) (see Experimental section). Another diploid of **3**$_{(6)(CH_2)_6}$-***para*** was also isolated from the reaction of octadiene **1**$_{(6)}$ with bis(3-oxobutanoate) **2**$_{(CH2)6}$-***para*** (Table 3, Entry 2).

Table 3 Reaction of terminal dienes **1**$_{(m)}$ with bis(3-oxobutanoate)s **2**$_{(CH_2)y}$**-arom** in the presence of manganese(III) acetate[a]

Entry	Diene	Butanoate	**1**/**2**/Mn(III)[b]	Time/ min	Cyclophane (%)[c]	Ring size
1	**1**$_{(6)}$	**2**$_{(CH2)6}$-***ortho***	1 : 1.5 : 7	35	**3**$_{(6)(CH2)6}$-***ortho*** (57)	30
2	**1**$_{(6)}$	**2**$_{(CH2)6}$-***para***	1 : 1.5 : 7	25	**3**$_{(6)(CH2)6}$-***para*** (58)[d]	32
3	**1**$_{(6)}$	**2**$_{(CH2)8}$-***para***	1 : 1.5 : 7	25	**3**$_{(6)(CH2)8}$-***para*** (55)	36
4	**1**$_{(8)}$	**2**$_{(CH2)6}$-***ortho***	1 : 1.5 : 7	40	**3**$_{(8)(CH2)6}$-***ortho*** (50)	32
5	**1**$_{(8)}$	**2**$_{(CH2)6}$-***para***	1 : 1.5 : 7	25	**3**$_{(8)(CH2)6}$-***para*** (57)	34
6	**1**$_{(8)}$	**2**$_{(CH2)8}$-***para***	1 : 1.5 : 7	25	**3**$_{(8)(CH2)8}$-***para*** (50)	38
7	**1**$_{(16)}$	**2**$_{(CH2)6}$-***ortho***	1 : 1.5 : 7	30	**3**$_{(16)(CH2)6}$-***ortho*** (50)	40
8	**1**$_{(16)}$	**2**$_{(CH2)6}$-***para***	1 : 1.5 : 7	30	**3**$_{(16)(CH2)6}$-***para*** (60)	42
9	**1**$_{(16)}$	**2**$_{(CH2)8}$-***para***	1 : 1.5 : 7	25	**3**$_{(16)(CH2)8}$-***para*** (50)	46

[a] The reaction with the terminal diene **1** (0.2 mmol) was carried out in glacial acetic acid (100 mL) at 100 °C under an argon atmosphere. [b] Molar ratio of the terminal diene **1**$_{(m)}$: bis(3-oxobutanoate)s **2**$_{(CH2)y}$**-arom** : manganese(III) acetate. [c] Isolated yield based on the amount of the terminal diene **1**$_{(m)}$ used. [d] The corresponding diploid was isolated in 20% yield.

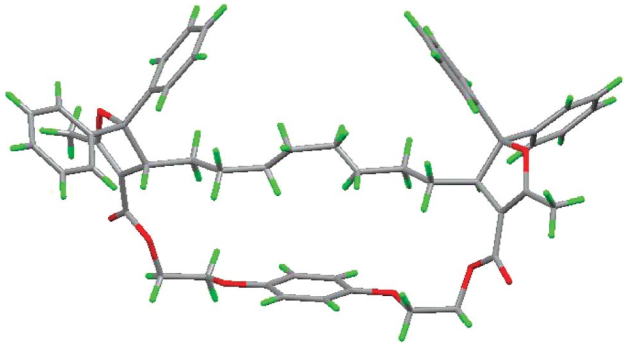


Fig. 1 X-ray crystal structure of [22]paracyclophane **3**$_{(8)(1)}$-***para***.

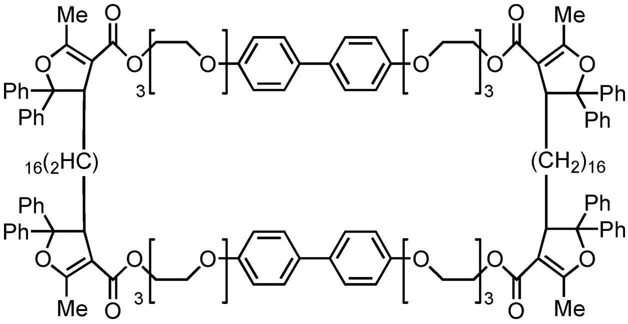


Fig. 2 Diploid of **3**$_{(16)(3)}$**-biphen**.

Reaction of alkadienes 4$_{(m)}$ and 6 with di(3-oxobutanoate)s 2$_{(n)}$-*para* and 8 in the presence of manganese(III) acetate

Since we were delighted to obtain the desired cyclophane-type macrodiolides, we explored the reaction of the terminal alkadienes containing aromatics **4**$_{(m)}$ and **6** with bis(3-oxobutanoate)s **2**$_{(n)}$-***para*** and **8** in order to synthesize the [x.x]cyclophanes (Scheme 4). The terminal alkadienes containing aromatics **4**$_{(m)}$ were prepared by the reaction of hydroquinone with (chloroethoxy)ethanols followed by the reaction with 3-bromo-1,1-diphenylpropene. *p*-phenylenebis(7,7-diphenyl-6-heptene) **6** and *p*-phenylenebis(heptyl) bis(3-oxobutanoate) **8** were synthesized by the reaction of terephthaloyl dichloride with 1-morpholino-1-cyclohexene followed by decomposition with sodium hydroxide in ethanol, the Wolff–Kishner reduction,[15] and then esterification to give diethyl *p*-phenylenebis(heptanoate), which underwent a Grignard reaction followed by dehydration of the reduction product and subsequent esterification with a diketene.

The reaction of *p*-phenylenebis(1,4-oxa-7,7-diphenylhept-6-ene) (**4**$_{(1)}$) with *p*-phenylene-1-oxaethyl bis(3-oxobutanoate) (**2**$_{(1)}$-***para***) was carried out under the same reaction conditions as above to afford the corresponding [12.12]paracyclophane-type macrocyclic compound **5**$_{(1)(1)}$-***para*** with 36% yield (Scheme 4 and Table 4, Entry 1). The existence of two sets of dihydrofuran and hydroquinone parts was confirmed in the NMR spectrum of **5**$_{(1)(1)}$-***para***, and in addition, the molecular ion peak of **5**$_{(1)(1)}$-***para*** was identified at *m*/*z* 944.3765 (calculated for $C_{58}H_{56}O_{12}$ 944.3772) in the high-resolution FAB mass spectrum. The reaction of other terminal dienes with bis(3-oxobutanoate)s also gave the corresponding [x.x]paracyclophane-type macrodiolides containing between 32 and 56 members in the same yields as above (Table 4, Entries 2–13), along with some dipliods as a by-product in some cases (Entries 7,8,10–13). Using the tetrakis(4-chlorophenyl)-substituted terminal diene **4**$_{(1)}$**-Cl** instead of the tetraphenyl-substituted **4**$_{(1)}$ in the reaction with **2**$_{(1)}$-***para*** also afforded the corresponding [12.12]paracyclophane-type macrocyclic compound **5**$_{(1)(1)}$**-Cl,*para*** in 31% yield.

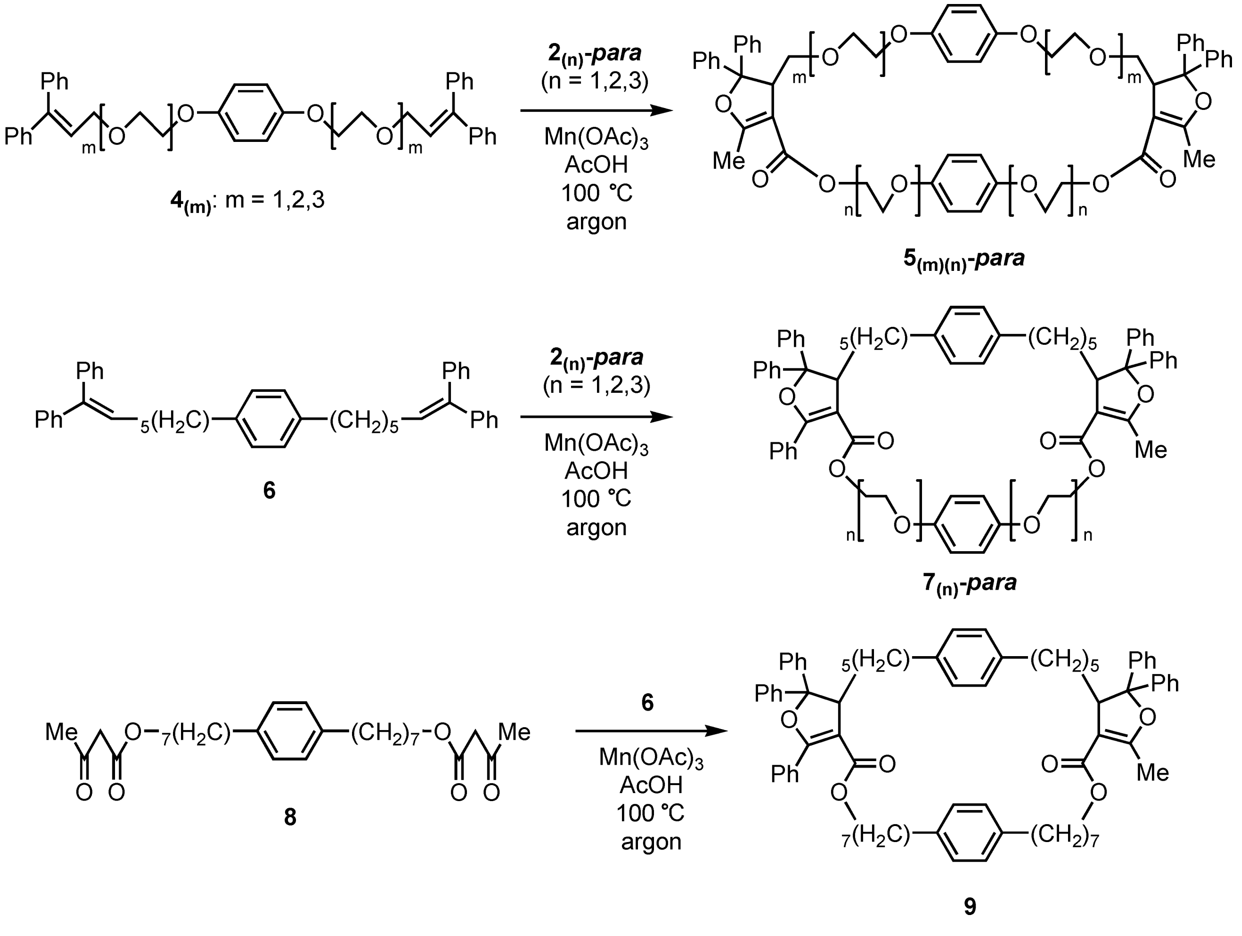
Mechanism for the formation of cyclophane-type macrodiolides

The manganese(III)-mediated macrocyclization was explained by a two-step mechanism. The formation of the dihydrofurans using manganese(III) acetate was first investigated by Heiba and Dessau,[16] and after that, many chemists developed the reaction further.[17,18] Manganese(III)-enolate complexes are formed reversibly by the reaction of manganese(III) acetate with 1,3-dicarbonyl compounds, such as 2,4-pentandione and 3-oxobutanoates, and undergo addition to electron-rich 1,1-disubstituted alkenes *via* a one-electron transfer oxidation to give tertiary radicals followed by oxidative cyclization, producing dihydrofurans.[19,20] In the macrocyclization, the terminal bis(3-oxobutanoate)s **2-arom** would react with manganese(III) acetate to give the corresponding manganese(III)-enolate complexes **A** (Scheme 5) which attack the terminal dienes **1** to produce the monodihydrofuran during the first stage. The intramolecular dihydrofuranation must then occur between the other pair of enolates and the terminal double bond at the second stage *via* the electron donor–acceptor-like interaction such as **B**,[10a,21] and

Table 4 Reaction of terminal dienes **4**$_{(m)}$ and **6** with bis(3-oxobutanoate)s **2**$_{(n)}$-***para*** and **8** in the presence of manganese(III) acetate[a]

Entry	Diene	Butanoate	Diene/butanaoate/Mn(III)[b]	Time/ min	Cyclophane(%)[c]	Diploid (%)[c]	Ring size monomer
1	**4**$_{(1)}$	**2**$_{(1)}$-***para***	1 : 1.5 : 8	40	**5**$_{(1)(1)}$-***para*** (36)	—[d]	32
2	**4**$_{(1)}$	**2**$_{(2)}$-***para***	1 : 1.5 : 9	30	**5**$_{(1)(2)}$-***para*** (46)	—[d]	38
3	**4**$_{(1)}$	**2**$_{(3)}$-***para***	1 : 1.5 : 9	30	**5**$_{(1)(3)}$-***para*** (37)	—[d]	44
4	**4**$_{(2)}$	**2**$_{(1)}$-***para***	1 : 1.5 : 9	40	**5**$_{(2)(1)}$-***para*** (33)	—[d]	38
5	**4**$_{(2)}$	**2**$_{(2)}$-***para***	1 : 1.5 : 7	20	**5**$_{(2)(2)}$-***para*** (35)	—[d]	44
6	**4**$_{(2)}$	**2**$_{(3)}$-***para***	1 : 1.5 : 7	20	**5**$_{(2)(3)}$-***para*** (21)	—[d]	50
7	**4**$_{(3)}$	**2**$_{(1)}$-***para***	1 : 1.5 : 7	30	**5**$_{(3)(1)}$-***para*** (38)	9	44
8	**4**$_{(3)}$	**2**$_{(2)}$-***para***	1 : 1.5 : 9	30	**5**$_{(3)(2)}$-***para*** (41)	8	50
9	**4**$_{(3)}$	**2**$_{(3)}$-***para***	1 : 1.5 : 7	40	**5**$_{(3)(3)}$-***para*** (38)	—[d]	56
10	**6**	**2**$_{(1)}$-***para***	1 : 1.5 : 7	30	**7**$_{(1)}$-***para*** (62)	9	32
11	**6**	**2**$_{(2)}$-***para***	1 : 1.5 : 7	20	**7**$_{(2)}$-***para*** (61)	7	38
12	**6**	**2**$_{(3)}$-***para***	1 : 1.5 : 9	50	**7**$_{(3)}$-***para*** (57)	4	44
13	**6**	**8**	1 : 1.5 : 7	20	**9** (49)	18	40

[a] The reaction with the terminal diene (0.2 mmol) was carried out in glacial acetic acid (100 mL) at 100 °C under an argon atmosphere. [b] Molar ratio of the terminal diene, bis(3-oxobutanoate), and manganese(III) acetate. [c] Isolated yield based on the amount of the terminal diene used. [d] The corresponding diploid was not isolated.

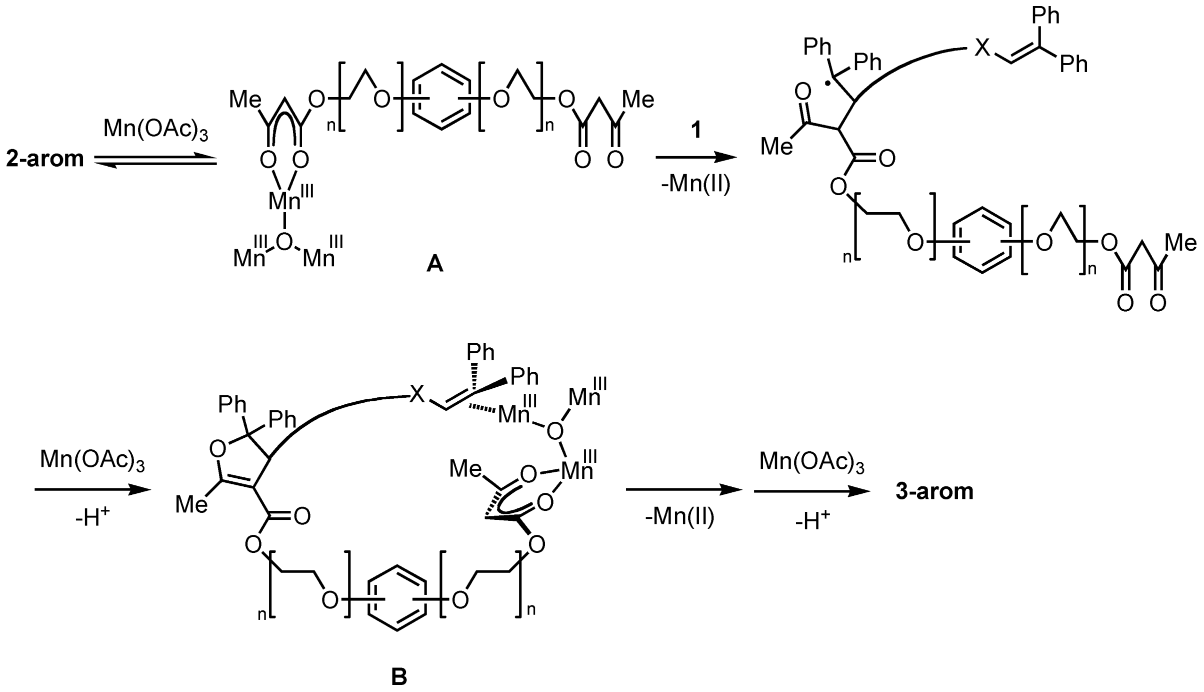


Scheme 4 Reaction of dienes **4**$_{(m)}$ and **6** with bis(3-oxobutanoate)s **2**$_{(n)}$-***para*** and **8** in the presence of manganese(III) acetate.

finally, the cyclophane-type macrodiolides **3-arom** were obtained. The reaction pathway is outlined in Scheme 5. The intramolecular cyclization during the second stage must be specific in the manganese(III) acetate oxidation because of producing a huge ring such as 56 members. The production of other cyclophane-type macrodiolides **5**$_{(m)(n)}$-***para***, **7**$_{(n)}$-***para***, and **9** would be realized by the same reaction pathway.

Conclusions

We have developed the synthesis of cyclophane-type macrodiolides **3**, **5**, **7**, and **9** using the manganese(III)-mediated oxidative radical cyclization of the terminal dienes **1**, **4**, and **6** with bis(3-oxobutanoate)s containing aromatics **2** and **8**. The cyclophanes were obtained as a 1 : 1 diastereomixture because they contain



Scheme 5 Reaction pathway for the reaction of dienes **1** with bis(3-oxobutanoate)s **2-arom** in the presence of manganese(III) acetate.

two asymmetric carbons and the stereoselectivity of the macrocyclization was not observed under the conditions. However, the produced macrocycles were quite stable in air. Although many ionic macrocyclizations promoted by metal cations are known,[8,22] the oxidative radical macrocyclization should be characteristic for the manganese(III)-based oxidation chemistry. Efforts are currently underway in our laboratory to investigate the function of the cyclophane-type macrodiolides.

Experimental section

Measurements

The melting points are uncorrected. The IR spectra were measured neat or in $CHCl_3$ solution and expressed in cm^{-1}. The NMR spectra were measured at 300 MHz for ^1H and at 75 Hz for ^{13}C with tetramethylsilane as the internal standard. The chemical shifts are reported in δ values (ppm) and the coupling constants in Hertz. The EIMS spectra were recorded at the ionizing voltage of 70 eV. The high-resolution mass spectra were measured at the Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan, and the Analytical Center of Kumamoto University, Kumamoto, Japan.

Preparation of terminal alkadienes and bis(3-oxobutanoate)s

$\alpha,\alpha,\omega,\omega$-tetraphenyl-$\alpha$,($\omega$-1)-alkadienes $\mathbf{1}_{(m)}$ (m = 6,8,16) were prepared by the Grignard reaction of the corresponding alkanedioates with phenylmagnesium bromide followed by dehydration. 4-oxa-1,6-heptadiene $\mathbf{1}_{(O)}$ was prepared by the Reformatsky reaction of benzophenone with ethyl α-bromoacetate followed by reduction with lithium aluminium hydride and then dehydration.[14,23] Oxamethylene bis(3-oxobutanoate)s containing aromatics $\mathbf{2}_{(n)}$**-arom** (n = 1,2,3) and *p*-phenylene bis(allyoxy)ethyl ethers $\mathbf{4}_{(m)}$ (m = 1,2,3) were prepared by the Williamson ether synthesis of the corresponding aromatic diols with (chloroethoxy)ethanols, followed by esterification with the diketene or the reaction of 3-bromo-1,1-diphenylpropene under basic conditions.[10a,14] *p*-phenylenebis(7,7-diphenyl-6-heptene) (**6**) and *p*-phenylenebis(heptyl) bis(3-oxobutanoate) (**8**) were synthesized by the modified method described in literature.[15] That is, terephthaloyl dichloride was allowed to react with 1-morpholino-1-cyclohexene followed by the Wolff–Kishner reduction and esterification, giving diethyl *p*-phenylenebis(heptanoate), which underwent same reactions as mentioned above.

General procedure for the manganese(III)-based oxidation of terminal dienes with bis(3-oxobutanoate)s containing aromatics

To a solution of the terminal diene $\mathbf{1}_{(m)}$, $\mathbf{1}_{(O)}$, $\mathbf{4}_{(m)}$, or **6** (0.2 mmol) and bis(3-oxobutanoate) **2(n)-arom**, $\mathbf{2}_{(CH_2)y}$**-arom**, or **8** (0.26 mmol) in glacial acetic acid (100 mL), manganese(III) acetate dehydrate (1.4 mmol) was added and the mixture was sufficiently degassed under reduced pressure for 30 min using an ultrasonicator for exchange with an argon atmosphere. The mixture was then heated at 100 °C under an argon atmosphere for the period described in the tables until the brown color of manganese(III) disappeared. The color typically turned a transparent yellow. The solvent was evaporated and the residue was treated with 2 M HCl (20 mL), which was extracted with $CHCl_3$ (20 mL × 3). The combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ (30 mL) and water, and then concentrated to dryness. The crude products were separated by silica gel TLC (Wakogel B-10) while eluting with $CHCl_3$, $CHCl_3$–MeOH, or Et_2O–hexane. The molar ratio and product yields are summarized in Tables 1, 2, 3, and 4. The specific details are given below. The data were shown as a diastereomixture except for $\mathbf{3}_{(O)(1)}$***-para***.

[20]Paracyclophane $3_{(6)(1)}$-*para*. Diastereomer ratio, 49 : 51. R_f 0.64 ($CHCl_3$–MeOH = 98 : 2 v/v). Colorless microcrystals (from $CHCl_3$–hexane), m.p. 219 °C. IR ($CHCl_3$): ν 1693 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.48 (4H, m, arom. H), 7.31–7.17 (16H, m, arom. H), 6.74 (4H, s, arom. H), 4.90–4.86 (2H, m, -CH_2O-), 4.07–4.02 (6H, m, -CH_2O-), 3.67 (2H, t, *J* = 5.4 Hz, >C*H*-), 2.29 (6H, s, -CH_3), 1.15–0.92 (4H, m, -CH_2-), 0.58–0.31 (4H, m, -CH_2-), 0.08–−0.23 (4H, m, -CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0 (2C, -CO_2-), 165.5 (2C, =CO-), 153.0 (2C, arom. CO-), 145.3 (2C, arom. C), 140.7 (2C, arom. C), 128.0, 127.7, 127.5, 127.0, 126.7, 126.2 (20C, arom. CH), 115.0 (4C, arom. CH), 107.7 (2C, =C<), 95.3 (2C, >C<), 67.2 (2C, -CH_2O-), 61.4 (2C, -CO_2CH_2-), 48.9 (2C, >CH-), 31.7, 31.6, 29.7(2C), 26.8, 26.7 (6C, -CH_2-), 14.4 (2C, -CH_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{52}H_{52}O_8$ 804.3662 (M$^+$); found 804.3673.

[26]Orthocyclophane $3_{(6)(2)}$-*ortho*. Colorless amorphous. IR ($CHCl_3$): ν 1691 (C=O), 1646 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.48 (4H, m, arom. H), 7.31–7.11 (16H, m, arom. H), 6.91 (4H, s, arom. H), 4.37–4.30 (2H, m, -CO_2CH_2-), 4.22–4.18 (2H, m, -CO_2CH_2-), 4.17–4.11 (4H, m, -CH_2OArOCH_2-), 3.84–3.72 (10H, m, -CH_2O-, >CH-), 2.26 (6H, s, -CH_3), 1.26–1.18 (4H, m, -CH_2-), 0.86–0.73 (4H, m, -CH_2-), 0.73–0.64 (4H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5 (2C, -CO_2-), 165.5 (2C, =CO-), 148.9 (2C, arom. CO-), 145.1 (2C, arom. C), 140.7 (2C, arom. C), 128.5, 128.2, 127.9, 127.4, 127.0, 126.8, 126.5, 126.0 (20C, arom. CH), 121.6, 114.8 (4C, arom. CH), 107.9 (2C, =C<), 95.0 (2C, >C<), 69.4 (4C), 68.9 (6C, -CH_2O-), 62.4 (2C, -CO_2CH_2-), 48.4, 48.3 (2C, >CH-), 31.6, 29.2, 25.8 (6C, -CH_2-), 14.4 (2C, -CH_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{56}H_{61}O_{10}$ 893.4265 (M+H); found 893.4326.

[26]Metacyclophane $3_{(6)(2)}$-*meta*. Diastereomer ratio, 49 : 51. Colorless amorphous. IR ($CHCl_3$): ν 1691 (C=O), 1646 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48–7.46 (4H, m, arom. H), 7.16–7.12 (17H, m, arom. H), 6.54–6.46 (3H, m, arom. H), 4.31–4.26 (2H, m, -CO_2CH_2-), 4.22-4.17 (2H, m, -CO_2CH_2-), 4.04 (4H, t, *J* = 4.2 Hz, -CH_2OArOCH_2-), 3.84-3.68 (10H, m, -CH_2O-, >CH-), 2.29 (6H, s, -CH_3), 1.26–1.03 (4H, m, -CH_2-), 1.03–0.80 (2H, m, -CH_2-), 0.80–0.60 (3H, m, -CH_2-), 0.60–0.42 (3H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7 (2C, -CO_2-), 165.7 (2C, =CO-), 159.9 (2C, arom. CO-), 145.3 (2C, arom. C), 140.8 (2C, arom. C), 129.9 (arom. CH), 128.0, 127.6, 127.1, 126.9, 126.7, 126.7, 126.1 (20C, arom. CH), 107.9, 107.8 (2C, =C<), 107.2 (arom. CH), 101.1 (arom. CH), 95.1 (2C, >C<), 69.5, 69.3, 67.5, 67.3 (6C, -CH_2O-), 62.6 (2C, -CO_2CH_2-), 48.8, 48.7 (2C, >CH-), 31.4, 29.6, 29.5, 26.0, 26.9 (6C, -CH_2-), 14.5 (2C, -CH_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{56}H_{61}O_{10}$ 893.4265 (M+H); found 893.4262.

[26]Paracyclophane $3_{(6)(2)}$-*para*. Diastereomer ratio, 50 : 50. Colorless amorphous. IR ($CHCl_3$): ν 1690 (C=O), 1646 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.47 (4H, m, arom. H), 7.33–7.13 (16H, m, arom. H), 6.83 (4H, s, arom. H), 4.27–4.21 (4H, m, -CO_2CH_2-), 4.06 (4H, t, *J* = 4.8, -CH_2OArOCH_2-), 3.80–3.69 (10H, m, -CH_2O-, >CH-), 2.26 (6H, s, -CH_3), 1.30–1.08 (4H, m, -CH_2-), 1.08–0.80 (2H, m, -CH_2-), 0.80–0.49 (4H, m, -CH_2-), 0.49–0.30 (2H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5 (2C, C=O), 165.7 (2C, =CO-), 153.2, 153.1 (2C, arom. CO-), 145.4 (2C, arom. C), 140.8 (2C, arom. C), 129.9, 128.0, 127.63, 127.61, 127.2, 127.0, 126.7, 126.2 (20C, arom. CH), 116.0 (4C, arom. CH), 107.9 (2C, =C<), 95.1 (2C, >C<), 69.5, 68.6, 68.5 (6C, -CH_2O-), 62.5 (2C, -CO_2CH_2-), 49.0, 48.9 (2C, >CH-), 31.4, 29.5, 29.4, 26.1, 26.0 (6C, -CH_2-), 14.6 (2C, -CH_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{56}H_{60}O_{10}$ 892.4186 (M$^+$); found 892.4187.

[32]Orthocyclophane $3_{(6)(3)}$-*ortho*. Colorless amorphous. IR ($CHCl_3$): ν 1691 (C=O), 1646 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.47 (4H, m, arom. H), 7.33–7.14 (16H, m, arom. H), 6.90 (4H, s, arom. H), 4.35–4.27 (2H, m, -CO_2CH_2-), 4.19–4.13 (2H, m, -CO_2CH_2-, 4H, t, *J* = 4.5 Hz, -CH_2OArOCH_2-), 3.85 (4H, t, *J* = 4.5 Hz, -CH_2O-), 3.82–3.68 (10H, m, -CH_2O-), 3.67–3.62 (4H, m, -CH_2O-, >CH-), 2.26 (6H, s, -CH_3), 1.30–1.12 (6H, m, -CH_2-), 0.87–0.71 (3H, m, -CH_2-), 0.71–0.56 (3H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6 (2C, -CO_2-), 165.7 (2C, =CO-), 149.0 (2C, arom. CO-), 145.2 (2C, arom. C), 140.8 (2C, arom. C), 128.0, 127.64, 127.61, 127.1, 127.0, 126.7, 126.2 (20C, arom. CH), 121.6, 114.6 (4C, arom. CH), 108.0 (2C, =C<), 95.2 (2C, >C<), 70.9, 70.6, 69.8, 69.4, 69.0 (10C, -CH_2O-), 62.5 (2C, -CO_2CH_2-), 48.7 (2C, >CH-), 31.7, 29.5, 26.21, 26.15 (6C, -CH_2-), 14.6 (2C, -CH_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{60}H_{69}O_{12}$ 981.4789 (M+H); found 981.4816.

[32]Paracyclophane $3_{(6)(3)}$-*para*. Colorless amorphous. IR ($CHCl_3$): ν 1689 (C=O), 1646 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.48 (4H, m, arom. H), 7.36–7.12 (16H, m, arom. H), 6.85 (4H, s, arom. H), 4.21–4.18 (4H, m, -CO_2CH_2-), 4.09 (4H, t, *J* = 4.5 Hz, -CH_2OArOCH_2-), 3.80 (4H, t, *J* = 4.5 Hz, -CH_2O-), 3.71–3.56 (14H, m, -CH_2O-, >CH-), 2.27 (6H, s, -CH_3), 1.32–1.16 (6H, m, -CH_2-), 0.96–0.88 (1H, m, -CH_2-), 0.75–0.69 (2H, m, -CH_2-), 0.69–0.50 (3H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2 (2C, -CO_2-), 165.6 (2C, =CO-), 153.1(2C, arom. CO-), 145.3 (2C, arom. C), 140.8 (2C, arom. C), 129.9, 128.0, 127.6, 127.2, 127.0, 126.7, 126.2 (20C, arom. CH), 115.9 (4C, arom. CH), 108.1 (2C, =C<), 95.0 (2C, >C<), 70.9, 70.6, 69.8, 69.3, 68.4 (10C, -CH_2O-), 62.6 (2C, -CO_2CH_2-), 48.9 (2C, >CH-), 31.5, 29.6, 29.5, 26.23, 26.16 (6C, -CH_2-), 14.8 (2C, -CH_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{60}H_{69}O_{12}$ 981.4789 (M+H); found 981.4780.

[22]Paracyclophane $3_{(8)(1)}$-*para*. Diastereomer ratio, 50 : 50. R_f 0.67 ($CHCl_3$–MeOH = 98 : 2 v/v). Colorless microcrystals ($CHCl_3$–hexane); m.p. 120 °C. IR ($CHCl_3$): ν 1693 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.51 (4H, m, arom. H), 7.35–7.15 (16H, m, arom. H), 6.77 (4H, s, arom. H), 4.89–4.85 (2H, m, -CO_2CH_2-), 4.11–3.99 (6H, m, -CO_2CH_2-, -CH_2OArOCH_2-), 3.80–3.70 (2H, m, >CH-), 2.30 (6H, s, -CH_3), 1.63 (1H, m, -CH_2-), 1.37–1.14 (4H, m, -CH_2-), 0.82–0.62 (4H, m, -CH_2-), 0.62–0.38 (7H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2 (2C, -CO_2-), 165.7 (2C, =CO-), 152.9 (2C, arom. CO-), 145.3 (2C, arom. C), 140.8 (2C, arom. C), 128.1, 127.7, 127.6, 127.0, 126.7, 126.2 (20C, arom. CH), 115.1 (4C, arom. CH), 107.9 (2C, =C<), 95.3 (2C, >C<), 66.9, (2C, -CH_2O-), 61.5 (2C, -CO_2CH_2-), 49.14, 49.08 (2C, >CH-), 31.9, 30.1, 29.9, 26.9 (8C, -CH_2-), 14.4 (2C, -CH_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{54}H_{56}O_8$ 832.3975 (M$^+$); found 832.3975.

[28]Orthocyclophane $3_{(8)(2)}$-*ortho*. Colorless amorphous. IR (CHCl$_3$): ν 1691 (C=O), 1646 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.52–7.50 (4H, m, arom. H), 7.34–7.17 (16H, m, arom. H), 6.92 (4H, s, arom. H), 4.39–4.31 (2H, m, -CO$_2$C*H*$_2$-), 4.27–4.18 (2H, m, -CO$_2$C*H*$_2$-) 4.20 (4H, t, *J* = 5.1 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.83 (4H, t, *J* = 5.1 Hz, -C*H*$_2$O-), 3.79–3.78 (6H, m, -C*H*$_2$-, >C*H*-), 2.27 (6H, s, -C*H*$_3$), 1.55–1.05 (6H, m, -C*H*$_2$-), 1.05–0.70 (10H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.6 (2C, -*C*O$_2$-), 165.7 (2C, =*C*O-), 149.0 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.9 (2C, arom. C), 128.6, 128.2, 128.0, 127.6, 127.1, 127.0, 126.6, 126.2, 125.7, 125.5, (20C, arom. *C*H), 121.8, 121.6, 115.1 (4C, arom. *C*H), 108.2, 108.1 (2C, =C<), 95.2 (2C, >C<), 69.61, 69.58, 69.0, 68.8 (6C, -*C*H$_2$O-), 62.5 (2C, -CO$_2$*C*H$_2$-), 48.7 (2C, >*C*H-), 31.81, 31.77, 29.5, 28.92, 28.88, 26.02, 25.99 (8C, -*C*H$_2$-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for C$_{58}$H$_{65}$O$_{10}$ 921.4578 (M+H); Found 921.4574.

[28]Metacyclophane $3_{(8)(2)}$-*meta*. Colorless amorphous. IR (CHCl$_3$): ν 1691 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.52–7.49 (4H, m, arom. H), 7.32–7.11 (17H, m, arom. H), 6.52 (2H, m, arom. H), 6.46 (1H, t, *J* = 2.1 Hz, arom. H), 4.38 (2H, dt, *J* = 12.3, 4.5 Hz, -CO$_2$C*H*$_2$-), 4.16 (2H, dt, *J* = 12.3, 4.5 Hz, -CO$_2$C*H*$_2$-), 4.04 (4H, t, *J* = 4.8 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.85–3.70 (10H, m, -C*H*$_2$O-, >CH-), 2.25 (6H, s, -C*H*$_3$), 1.46–1.10 (4H, m, -C*H*$_2$-), 1.04–0.77 (6H, m, -C*H*$_2$-), 0.77–0.59 (6H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.8 (2C, -*C*O$_2$-), 165.8 (2C, =*C*O-), 159.9 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.8 (2C, arom. C), 129.8 (arom. *C*H), 128.0, 127.6, 127.0, 126.7, 126.6, 126.2 (20C, arom. *C*H), 107.99, 107.97 (2C, arom. *C*H), 107.3 (2C, =C<), 101.0 (arom. *C*H), 95.2 (2C, >C<), 69.6, 69.4, 67.4 (6C, -*C*H$_2$O-), 62.6 (2C, -CO$_2$*C*H$_2$-), 48.9 (2C, >*C*H-), 31.7, 29.8, 29.2, 26.2, 26.1 (8C, -*C*H$_2$-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for C$_{58}$H$_{65}$O$_{10}$ 921.4578 (M+H); found 921.4579.

[28]Paracyclophane $3_{(8)(2)}$-*para*. *R*$_f$ 0.60 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): ν 1692 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.53–7.50 (4H, m, arom. H), 7.34–7.17 (16H, m, arom. H), 6.80 (4H, s, arom. H), 4.36–4.31 (2H, m, -CO$_2$C*H*$_2$-), 4.24–4.18 (2H, m, -CO$_2$C*H*$_2$-), 4.03 (4H, t, *J* = 4.5 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.84–3.75 (10H, m, -C*H*$_2$O-, >C*H*-), 2.28 (6H, s, -C*H*$_3$), 1.68 (1H, m, -C*H*$_2$-), 1.41–1.12 (4H, m, -C*H*$_2$-), 0.95–0.68 (4H, m, -C*H*$_2$-), 0.68–0.58 (3H, m, -C*H*$_2$-), 0.58–0.41 (4H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.7 (2C, -*C*O$_2$-), 165.8 (2C, =*C*O-), 153.1 (2C, arom. *C*O-), 145.4 (2C, arom. C), 140.8 (2C, arom. C), 128.1, 127.6, 127.0, 126.8, 126.2 (20C, arom. *C*H), 115.6 (4C, arom. *C*H), 107.9 (2C, =C<), 95.1 (2C, >C<), 69.5, 69.4, 68.3 (6C, -*C*H$_2$O-), 62.5 (2C, -COO*C*H$_2$-), 49.1 (2C, >*C*H-), 31.5, 29.9, 29.3, 26.1 (8C, -*C*H$_2$-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for C$_{58}$H$_{64}$O$_{10}$ 920.4499 (M$^+$); found 920.4498.

[34]Paracyclophane $3_{(8)(3)}$-*para*. *R*$_f$ 0.35 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (neat) ν 1686 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.52–7.50 (4H, m, arom. H), 7.33–7.18 (16H, m, arom. H), 6.83 (4H, s, arom. H), 4.22 (4H, t, *J* = 4.5 Hz, -CO$_2$C*H*$_2$-) 4.07 (4H, t, *J* = 4.5 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.80 (4H, t, *J* = 4.5 Hz, -C*H*$_2$O-), 3.76–3.62 (14H, m, -C*H*$_2$O-, >C*H*-), 2.27 (6H, s, -C*H*$_3$), 1.38–1.18 (4H, m, -C*H*$_2$-), 0.96–0.63 (12H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.4 (2C, -*C*O$_2$-), 165.7 (2C, =*C*O-), 153.1 (2C, arom. *C*O-), 145.4 (2C, arom. C), 140.9 (2C, arom. C), 128.1, 127.7, 127.0, 126.8, 126.2 (20C, arom. *C*H), 115.8 (4C, arom. *C*H), 108.1 (2C, =C<), 95.1 (2C, >C<), 71.0, 70.7, 69.9, 69.4, 68.4 (10C, -*C*H$_2$O-), 62.7 (2C, -CO$_2$*C*H$_2$-), 49.1 (2C, >*C*H-), 31.6, 29.8, 29.2, 26.1 (8C, -*C*H$_2$-), 14.7 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for C$_{62}$H$_{73}$O$_{12}$ 1009.5102 (M+H); found 1009.5050.

[30]Paracyclophane $3_{(16)(1)}$-*para*. *R*$_f$ 0.76 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1693 (C=O), 1645 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.54–7.47 (4H, m, arom. H), 7.34–7.19 (16H, m, arom. H), 6.83 (4H, s, arom. H), 4.53–4.46 (2H, m, -CO$_2$C*H*$_2$-), 4.40–4.33 (2H, m, -CO$_2$C*H*$_2$-), 4.12 (4H, t, *J* = 4.8 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.81 (2H, t, *J* = 5.1 Hz, >C*H*-), 2.29 (6H, s, -C*H*$_3$), 1.47–1.24 (4H, m, -C*H*$_2$-), 1.24–1.04 (16H, m, -C*H*$_2$-), 0.93 (12H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.1 (2C, -*C*O$_2$-), 165.8 (2C, =*C*O-), 153.1 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.9 (2C, arom. C), 128.1, 127.7, 127.0, 126.7, 126.2 (20C, arom. *C*H), 115.5 (4C, arom. *C*H), 108.1 (2C, =C<), 95.4 (2C, >C<), 66.7 (2C, -*C*H$_2$O-), 61.9 (2C, -CO$_2$*C*H$_2$-), 48.7 (2C, >*C*H-), 31.7, 29.4, 29.3, 29.1, 28.9, 25.9 (16C, -*C*H$_2$-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for C$_{62}$H$_{72}$O$_8$ 944.5227 (M$^+$); found 944.5227.

[36]Paracyclophane $3_{(16)(2)}$-*para*. *R*$_f$ 0.52 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): ν 1692 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.54–7.51 (4H, m, arom. H), 7.34–7.18 (16H, m, arom. H), 6.81 (4H, s, arom. H), 4.40–4.35 (2H, m, -CO$_2$C*H*$_2$-), 4.23–4.16 (2H, m, -CO$_2$C*H*$_2$-), 4.04 (4H, t, *J* = 4.8 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.83–3.77 (10H, t, *J* = 4.8 Hz, -C*H*$_2$O-, m, >C*H*-), 2.27 (6H, s, -C*H*$_3$), 1.40–1.27 (4H, m, -C*H*$_2$-), 1.27–1.00 (18H, m, -C*H*$_2$-), 1.00–0.85 (10H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.8 (2C, -*C*O$_2$-), 165.8 (2C, =*C*O-), 153.1 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.9 (2C, arom. C), 128.1, 127.7, 127.0, 126.8, 126.2 (20C, arom. *C*H), 115.4 (4C, arom. *C*H), 108.1 (2C, =C<), 95.2 (2C, >C<), 69.7 (2C), 67.9 (6C, -*C*H$_2$O-), 62.5 (2C, -CO$_2$*C*H$_2$-), 48.9 (2C, >*C*H-), 31.7, 29.8, 29.7, 29.63, 29.58, 29.50, 29.3, 26.2 (16C, -*C*H$_2$-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for C$_{66}$H$_{80}$O$_{10}$ 1032.5751 (M$^+$); found 1032.5754.

[42]Paracyclophane $3_{(16)(3)}$-*para*. Colorless amorphous, IR (neat) ν 1690 (C=O), 1646 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.54–7.51 (4H, m, arom. H), 7.51–7.19 (16H, m, arom. H), 6.83 (4H, s, arom. H), 4.34–4.28 (2H, m, -CO$_2$C*H*$_2$-), 4.24-4.20 (2H, m, -CO$_2$C*H*$_2$-), 4.05 (4H, t, *J* = 4.5 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.82 (4H, t, *J* = 4.5 Hz, -C*H*$_2$O-), 3.79–3.65 (14H, m, -C*H*$_2$O-, >C*H*-), 2.28 (6H, s, -C*H*$_3$), 1.40–1.26 (4H, m, -C*H*$_2$-), 1.26–1.20 (2H, m, -C*H*$_2$-), 1.20–1.00 (16H, m, -C*H*$_2$-), 1.00–0.81 (10H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.6 (2C, -*C*O$_2$-), 165.7 (2C, =*C*O-), 153.0 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.8 (2C, arom. C), 128.1, 127.6, 127.0, 126.7, 126.2 (20C, arom. *C*H), 115.5 (4C, arom. *C*H), 108.1 (2C, =C<), 95.1 (2C, >C<), 70.8, 70.6, 69.9, 69.5, 68.0 (10C, -*C*H$_2$O-), 62.5 (2C, -CO$_2$*C*H$_2$-), 49.0 (2C, >*C*H-), 31.7, 29.8, 29.74, 29.70, 29.64, 29.57, 29.3, 26.1 (16C, -*C*H$_2$-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for C$_{70}$H$_{89}$O$_{12}$ 1121.6354 (M+H); found 1121.6361.

[17]Paracyclophane $3_{(O)(1)}$-*para*. Diastereomer ratio, 49 : 51. *R*$_\mathrm{f}$ 0.38 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1694 (C=O), 1641 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.38–7.06 (20H, m, arom. H), 6.82, 6.79 (4H, s, arom. H), 4.54–4.48 (2H, dt, *J* = 10.8, 2.7 Hz, -CO$_2$C*H*$_2$-), 4.31 (4H, t, *J* = 2.7 Hz, -C*H*$_2$OArOC*H*$_2$-), 4.27–4.23 (2H, m, -CO$_2$C*H*$_2$-), 3.54 (2H, br. d, *J* = 10.2 Hz, >C*H*-), 2.76 (2H, dd, *J* = 10.2, 2.1 Hz, >CHC*H*$_2$O-), 2.33 (6H, s, -C*H*$_3$), 2.27 (2H, m, >CHC*H*$_2$O-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 169.1 (2C, -*C*O$_2$-), 165.3 (2C, =*C*O-), 154.0 (2C, arom. *C*O-), 144.8 (2C, arom. C), 140.7 (2C, arom. C), 128.1, 128.0, 127.8, 127.7, 127.2, 127.1, 127.0, 126.6, 126.4 (20C, arom. *C*H), 116.8, 116.7 (4C, arom. *C*H), 102.5 (2C, =C<), 95.0 (2C, >C<), 68.5 (2C, >CH*C*H$_2$O-), 68.1 (2C, -*C*H$_2$OAr-), 64.1 (2C, -COO*C*H$_2$-), 50.2 (2C, >*C*H-), 14.7 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{48}H_{44}O_9$ 764.2985 (M$^+$); found 764.2957.

Diastereoisomer of $3_{(O)(1)}$-*para*. *R*$_\mathrm{f}$ 0.30 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1694 (C=O), 1641 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.47–7.10 (20H, m, arom. H), 6.82, 6.79 (4H, s, arom. H), 4.46–4.40 (2H, m, -CO$_2$C*H*$_2$-), 4.32–4.30 (2H, m, -CO$_2$C*H*$_2$-), 4.25–4.24 (4H, m, -C*H*$_2$OArOC*H*$_2$-), 3.53 (2H, br. d, *J* = 10.2 Hz, >C*H*-), 2.44 (2H, m, >CHC*H*$_2$O-), 2.27 (6H, s, -C*H*$_3$), 2.18 (2H, dd, *J* = 10.2, 2.0 Hz, >CHC*H*$_2$O-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.8 (2C, -*C*O$_2$-), 165.0 (2C, =*C*O-), 154.0 (2C, arom. *C*O-), 145.0 (2C, arom. C), 140.5 (2C, arom. C), 128.1, 127.8, 127.3, 127.1, 127.0, 126.6, 126.4 (20C, arom. *C*H), 116.7 (4C, arom. *C*H), 102.5 (2C, =C<), 94.7 (2C, >C<), 68.7 (2C, >CH*C*H$_2$O-), 67.8 (2C, -*C*H$_2$OAr-), 63.6 (2C, -CO$_2$*C*H$_2$-), 50.0 (2C, >*C*H-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{48}H_{44}O_9$ 764.2985 (M$^+$); found 764.2977.

[23]Orthocyclophane $3_{(O)(2)}$-*ortho*. Diastereomer ratio, 49 : 51. Colorless amorphous. IR (CHCl$_3$): ν 1694 (C=O), 1645 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.53–7.47 (4H, m, arom. H), 7.36–7.08 (16H, m, arom. H), 6.90 (2H), 6.89, 6.86 (4H, s, arom. H), 4.44–4.36 (2H, m, -CO$_2$C*H*$_2$-), 4.23–4.14 (2H, m, -CO$_2$C*H*$_2$-), 4.10–4.03 (4H, m, -C*H*$_2$OArOC*H*$_2$-), 3.83–3.69 (10H, m, -C*H*$_2$O-, >C*H*-), 3.02 (1H, dd, *J* = 10.2, 2.9 Hz, >CHC*H*$_2$O-), 2.92 (1H, dd, *J* = 10.0, 2.9 Hz, >CHC*H*$_2$O-), 2.83 (1H, dd, *J* = 10.2, 6.9 Hz, >CHC*H*$_2$O-), 2.76 (1H, dd, *J* = 10.0, 6.9 Hz, >CHC*H*$_2$O-), 2.28 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.1, 167.8 (2C, -*C*O$_2$-), 165.3 (2C, =*C*O-), 149.03, 148.96 (2C, arom. *C*O-), 145.5, 145.2 (2C, arom. C), 140.6, 140.4 (2C, arom. C), 128.3, 128.1, 127.64, 127.57, 127.3, 127.0, 126.8, 126.7, 126.4, 126.3 (20C, arom. *C*H), 121.6 (2C), 114.7, 114.4 (4C, arom. *C*H), 103.3, 103.1 (2C, =C<), 94.6, 94.5 (2C, >C<), 69.8, 69.7, 69.5, 69.2, 69.0 (8C, -*C*H$_2$O-), 62.6 (2C, -CO$_2$*C*H$_2$-), 51.33, 51.27 (2C, >*C*H-), 14.7, 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{52}H_{53}O_{11}$ 853.3588 (M+H); found 853.3585.

[23]Metacyclophane $3_{(O)(2)}$-*meta*. Diastereomer ratio, 50 : 50. Colorless amorphous. IR (CHCl$_3$): ν 1693 (C=O), 1646 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.50–7.48 (4H, m, arom. H), 7.39–7.09 (17H, m, arom. H, arom. H), 6.58 (1H, dd, *J* = 8.2, 2.4 Hz, arom. H), 6.49 (1H, dd, *J* = 8.2, 2.4 Hz, arom. H) 6.39 (1H, t, *J* = 2.4 Hz, arom. H), 4.42–4.29 (2H, m, -CO$_2$C*H*$_2$-), 4.14–4.05 (2H, m, -CO$_2$C*H*$_2$-), 4.00 (4H, *J* = 4.5 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.81–3.65 (8H, m, -C*H*$_2$O-), 3.64–3.59 (2H, m, >C*H*-), 2.96 (1H, dd, *J* = 9.2, 2.4 Hz, >CHC*H*$_2$O-), 2.74 (2H, d, *J* = 4.5 Hz, >CHC*H*$_2$O-), 2.67 (1H, dd, *J* = 9.2, 6.6 Hz, >CHC*H*$_2$O-), 2.32, 2.29 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.7, 168.3 (2C, -*C*O$_2$-), 165.3, 165.2 (2C, =*C*O-), 160.1, 159.9 (2C, arom. *C*O-), 145.8, 145.2 (2C, arom. C), 140.8, 140.4 (2C, arom. C), 130.1, 129.8 (1C, arom. *C*H), 128.0, 127.6, 127.42, 127.37, 126.8, 126.5, 126.4, 126.3 (20C, arom. *C*H), 107.0, 106.9 (1C, arom. *C*H), 103.0, 102.7 (2C, =C<), 101.4, 100.9 (2C, arom. *C*H), 94.61, 94.58 (2C, >C<), 69.5, 69.4, 69.1, 69.0, 68.6, 68.3, 68.0, 67.7 (8C, -*C*H$_2$O-), 62.42, 62.36 (2C, -CO$_2$*C*H$_2$-), 51.4, 50.9 (2C, >*C*H-), 14.7, 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{52}H_{53}O_{11}$ 853.3588 (M+H); found 853.3585.

[23]Paracyclophane $3_{(O)(2)}$-*para*. Diastereomer ratio, 49 : 51. Colorless amorphous. IR (CHCl$_3$): ν 1693 (C=O), 1645 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.56–7.52 (4H, m, arom. H), 7.41–7.14 (16H, m, arom. H), 6.81, 6.73 (4H, s, arom. H), 4.31–4.16 (4H, m, -CO$_2$C*H*$_2$-), 4.00 (4H, q, *J* = 4.8 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.76–3.57 (10H, m, -C*H*$_2$O-, >C*H*-), 2.78 (1H, dd, *J* = 9.2, 2.5 Hz, >CHC*H*$_2$O-), 2.64 (1H, d, *J* = 9.2 Hz, >CHC*H*$_2$O-), 2.53–2.43 (2H, m, >CHC*H*$_2$O-), 2.31, 2.27 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.6, 168.2 (2C, -*C*O$_2$-), 165.2, 165.1 (2C, =*C*O-), 153.2 (2C, arom. *C*O-), 145.7, 145.1 (2C, arom. C), 140.7, 140.5 (2C, arom. C), 128.1, 128.0, 127.7, 127.5, 127.4, 127.3, 126.8, 126.6, 126.5 (20C, arom. *C*H), 116.0, 115.9 (4C, arom. *C*H), 102.8 (2C, =C<), 94.7 (2C, >C<), 69.6, 69.5 (2C), 69.4, 69.3, 68.7, 68.6, 68.0 (8C, -*C*H$_2$O-), 62.4 (2C, -CO$_2$*C*H$_2$-), 51.2, 50.8 (2C, >*C*H-), 14.8 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{52}H_{53}O_{11}$ 853.3588 (M+H); found 853.3644.

[29]Orthocyclophane $3_{(O)(3)}$-*ortho*. Diastereomer ratio, 50 : 50. Colorless amorphous. IR (CHCl$_3$): ν 1693 (C=O), 1646 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.57–7.49 (4H, m, arom. H), 7.37–7.12 (16H, m, arom. H), 6.88 (4H, s, arom. H), 4.36–4.29 (2H, m, >CHC*H*$_2$O-), 4.22–4.10 (6H, m, >CHC*H*$_2$O-, -C*H*$_2$OArOC*H*$_2$-), 3.88–3.57 (18H, m, -C*H*$_2$O-, >C*H*-), 3.14 (1H, dd, *J* = 9.5, 2.4 Hz, >CHC*H*$_2$O-), 2.89 (2H, d, *J* = 5.1 Hz, >CHC*H*$_2$O-), 2.74 (1H, dd, *J* = 9.5, 7.8 Hz, >CHC*H*$_2$O-), 2.32 (6H, s, -C*H*$_3$ × 2) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.1, 167.9 (2C, -*C*O$_2$-), 165.2 (2C, =*C*O-), 148.9 (2C, arom. *C*O-), 145.3, 145.1 (2C, arom. C), 140.5, 140.4 (2C, arom. C), 128.1, 127.7, 127.3, 126.92, 126.86, 126.41, 126.35 (20C, arom. *C*H), 121.5, 114.5 (4C, arom. *C*H), 103.2, 103.0 (2C, =C<), 94.7, 94.6 (2C, >C<), 70.9, 70.5, 69.8, 69.3, 69.0 (12C, -*C*H$_2$O-), 62.6, 62.5 (2C, -CO$_2$*C*H$_2$-), 51.2 (2C, >*C*H-), 14.7, 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{56}H_{61}O_{13}$ 941.4112 (M+H); found 941.4114.

[29]Paracyclophane $3_{(O)(3)}$-*para*. Colorless amorphous. IR (CHCl$_3$): ν 1692 (C=O), 1645 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.56–7.50 (4H, m, arom. H), 7.38–7.13 (16H, m, arom. H), 6.82, 6.81 (4H, s, arom. H), 4.21–4.17 (4H, m, >CHC*H*$_2$O-), 4.05 (4H, dd, *J* = 5.3, 3.9 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.79–3.75 (4H, m, -C*H*$_2$O-), 3.68–3.58 (14H, m, -C*H*$_2$O-, >C*H*-), 2.96 (1H, dd, *J* = 9.6, 2.7 Hz, >CHC*H*$_2$O-), 2.78 (1H, dd, *J* = 9.6, 2.7 Hz, >CHC*H*$_2$O-),.2.69 (1H, dd, *J* = 14.4, 7.2 Hz, >CHC*H*$_2$O-), 2.66 (1H, dd, *J* = 14.4, 7.2 Hz, >CHC*H*$_2$O-), 2.30, 2.29 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.9, 167.8 (2C,

-*C*O$_2$-), 165.1 (2C, ═*C*O-), 153.1 (2C, arom. *C*O-), 145.4, 145.1 (2C, arom. C), 140.6, 140.4 (2C, arom. C), 128.1, 128.0, 127.65, 127.38, 126.9, 126.8, 126.7, 126.4 (20C, arom. *C*H), 116.04, 115.99 (4C, arom. *C*H), 103.14, 102.99 (2C, ═C<), 94.6 (2C, >C<), 70.9, 70.7, 69.9, 69.3, 68.7, 68.6, 68.5 (12C, -*C*H$_2$O-), 62.4 (2C, -CO$_2$*C*H$_2$-), 51.2, 50.9 (2C, >*C*H-), 14.9 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{56}H_{61}O_{13}$ 941.4112 (M+H); found 941.4117.

[20]Biphenylcyclophane 3$_{(6)(1)}$-biphen. Diastereomer ratio, 49 : 51. R_f 0.53 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): *ν* 1695 (C═O) 1643 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 7.48–7.42 (4H, m, arom. H), 7.38–7.34 (4H, m, arom. H), 7.33–7.08 (16H, m, arom. H), 6.98–6.91 (4H, m, arom. H), 4.45–4.34 (8H, m, -CO$_2$C*H*$_2$-, -C*H*$_2$OArOC*H*$_2$-), 3.55-3.49 (2H, m, >C*H*-), 2.25, 2.24 (6H, s, -C*H*$_3$), 0.98–0.73 (4H, m, -C*H*$_2$-), 0.44-0.22 (2H, m, -C*H*$_2$-), 0.22–0.03 (2H, m, -C*H*$_2$-), minus 0.06-minus 0.36 (4H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): *δ* 166.6, 166.5 (2C, -*C*O$_2$-), 165.4 (2C, ═*C*O-), 158.1, 158.0 (2C, arom. *C*O-), 145.4, 145.3 (2C, arom. C), 140.7 (2C, arom. C), 133.9 (2C, arom. -*C*–*C*-), 128.1, 127.7, 127.60, 127.55, 127.0, 126.9, 126.8, 126.2, 126.1, 126.1 (20C, arom. *C*H), 116.2 (8C, arom. *C*H), 107.9, 107.7 (2C, ═C<), 95.12, 95.06 (2C, >C<), 67.3 (2C, -*C*H$_2$O-), 63.1 (2C, -CO$_2$*C*H$_2$-), 49.1, 48.9 (2C, >*C*H-), 30.9, 30.7, 29.2 (2C), 26.0, 25.6 (6C, -*C*H$_2$-), 14.7 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{58}H_{56}O_8$ 880.3975 (M$^+$); found 880.3974.

[26]Biphenylcyclophane 3$_{(6)(2)}$-biphen. Diastereomer ratio, 49 : 51. R_f 0.30 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): *ν* 1690 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 7.55–7.35 (8H, m, arom. H), 7.35–7.21 (6H, m, arom. H), 7.20–7.11 (10H, m, arom. H), 7.03–7.00 (4H, m, arom. H), 4.36–4.31 (2H, m, -CO$_2$C*H*$_2$-), 4.23–4.20 (4H, m, -C*H*$_2$OArOC*H*$_2$-), 4.11–4.06 (2H, m, -CO$_2$C*H*$_2$-), 3.83–3.80 (4H, m, -C*H*$_2$O-), 3.79–3.71 (4H, m, -C*H*$_2$O-), 3.65–3.57 (2H, m, >C*H*-), 2.18, 2.17 (6H, s, -C*H*$_3$), 1.21–0.98 (4H, m, -C*H*$_2$-), 0.70–0.53 (2H, m, -C*H*$_2$-), 0.52–0.36 (2H, m, -C*H*$_2$-), 0.36–0.11 (4H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) *δ* 166.2 (2C, -*C*O$_2$-), 165.6 (2C, ═*C*O-), 158.0 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.7 (2C, arom. C), 133.7 (2C, arom. -*C*–*C*-), 128.0, 127.6, 127.0, 126.8, 126.2 (20C, arom. *C*H), 115.8 (8C, arom. *C*H), 108.0 (2C, ═C<), 95.0 (2C, >C<), 70.0, 69.5, 68.3 (6C, -*C*H$_2$O-), 62.6 (2C, -CO$_2$*C*H$_2$-), 49.2, 49.1 (2C, >*C*H-), 31.2, 29.4, 26.2 (6C, -*C*H$_2$-), 14.7 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{62}H_{64}O_{10}$ 968.4499 (M$^+$); found 968.4480.

[32]Biphenylcyclophane 3$_{(6)(3)}$-biphen. R_f 0.21 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): *ν* 1690 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 7.52–7.43 (8H, m, arom. H), 7.43–7.12 (16H, m, arom. H), 7.00–6.97 (4H, m, arom. H), 4.22–4.14 (8H, m, -CO$_2$C*H*$_2$-, -C*H*$_2$OArOC*H*$_2$-), 3.84–3.83 (4H, m, -C*H*$_2$O-), 3.72–3.49 (14H, m, -C*H*$_2$O-, >C*H*-), 2.27, 2.22 (6H, s, -C*H*$_3$), 1.40–1.06 (4H, m, -C*H*$_2$-), 0.83–0.66 (3H, m, -C*H*$_2$-) 0.66–0.54 (3H, m, -C*H*$_2$-), 0.54–0.39 (2H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): *δ* 166.2, 166.0 (2C, -*C*O$_2$-), 165.6 (2C, ═*C*O-), 158.0 (2C, arom. *C*O-), 145.4 (2C, arom. C), 140.8 (2C, arom. C), 133.7 (2C, arom. -*C*–*C*-), 128.0, 127.7, 127.6, 127.0, 126.8, 126.2 (20C, arom. *C*H), 115.4 (8C, arom. *C*H), 108.1 (2C, ═C<), 95.1, 95.0 (2C, >C<), 71.4, 71.1, 70.7, 70.5, 69.9, 69.4, 67.9 (10C, -*C*H$_2$O-), 62.7, 62.5 (2C, -CO$_2$*C*H$_2$-), 49.1, 49.0 (2C, >*C*H-), 42.7, 31.6, 31.4, 29.5, 26.2 (6C, -*C*H$_2$-), 14.8 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{66}H_{72}O_{12}Na$ 1079.4921 (M$^+$ +Na); found 1079.5010.

[22]Biphenylcyclophane 3$_{(8)(1)}$-biphen. Diastereomer ratio, 49 : 51. R_f 0.63 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): *ν* 1693 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 7.52–7.49 (4H, m, arom. H), 7.38–7.37 (4H, m, arom. H), 7.38–7.12 (16H, m, arom. H), 6.94–6.90 (4H, m, arom. H), 4.69–4.64 (2H, m, -CO$_2$C*H*$_2$-), 4.36–4.22 (6H, m, -CO$_2$C*H*$_2$-, -C*H*$_2$OArOC*H*$_2$-), 3.70–3.60 (2H, m, >C*H*-), 2.28 (6H, s, -C*H*$_3$), 1.11–1.04 (4H, m, -C*H*$_2$-), 0.50–0.38 (2H, m, -C*H*$_2$-), 0.19–0.01 (10H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): *δ* 167.1, 167.0 (2C, -*C*O$_2$-), 165.6 (2C, ═*C*O-), 158.0 (2C, arom. *C*O-), 145.4 (2C, arom. C), 140.7 (2C, arom. C), 133.5 (2C, arom. -*C*–*C*-), 128.1, 127.7, 127.5, 127.4, 127.0, 126.9, 126.8, 126.24, 126.20, (20C, arom. *C*H), 115.3 (8C, arom. *C*H), 107.8, 107.7 (2C, ═C<), 95.2 (2C, >C<), 66.9 (2C, -*C*H$_2$O-), 62.3 (2C, -CO$_2$*C*H$_2$-), 49.2, 49.1 (2C, >*C*H-), 31.3, 31.2, 30.1 (2C), 29.8, 29.7, 26.3, 26.2 (8C, -*C*H$_2$-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{60}H_{60}O_8$ 908.4288 (M$^+$); found 908.4299.

[28]Biphenylcyclophane 3$_{(8)(2)}$-biphen. Diastereomer ratio, 50 : 50. R_f 0.33 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): *ν* 1690 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 7.50–7.47 (4H, m, arom. H), 7.43–7.38 (4H, m, arom. H), 7.33–7.12 (16H, m, arom. H), 7.00–6.93 (4H, m, arom. H) 4.36–4.31 (2H, m, -CO$_2$C*H*$_2$-), 4.22–4.15 (6H, m, -CO$_2$C*H*$_2$-, -C*H*$_2$OArOC*H*$_2$-), 3.85–3.82 (4H, m, -C*H*$_2$O-), 3.80–3.75 (4H, m, -C*H*$_2$O-), 3.75–3.68 (2H, m, >C*H*-), 2.27, 2.23 (6H, s, -C*H*$_3$), 1.25–1.20 (6H, m, -C*H*$_2$-), 1.50–0.78 (2H, m, -C*H*$_2$-), 0.63–0.43 (8H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): *δ* 166.44, 166.40 (2C, -*C*O$_2$-), 165.7 (2C, ═*C*O-), 158.0 (2C, arom. *C*O-), 145.4 (2C, arom. C), 140.8 (2C, arom. C), 133.63, 133.59 (2C, arom. -*C*–*C*-), 128.0, 127.6, 127.6, 127.0, 126.8, 126.2 (20C, arom. *C*H), 115.5, 114.8 (8C, arom. *C*H), 108.0 (2C, ═C<), 95.05, 95.03 (2C, >C<), 69.7, 69.6, 68.2 (6C, -*C*H$_2$O-), 62.6 (2C, -CO$_2$*C*H$_2$-), 49.2, 49.1 (2C, >*C*H-), 31.3, 29.8, 29.2, 26.1 (8C, -*C*H$_2$-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{64}H_{68}O_{10}$ 996.4812 (M$^+$); found 996.4874.

[34]Biphenylcyclophane 3$_{(8)(3)}$-biphen. R_f 0.26 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): *ν* 1690 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 7.53–7.42 (8H, m, bip-arom. H), 7.27–7.15 (16H, m, arom. H), 6.98–6.95 (4H, m, arom. H), 4.21–4.17 (8H, m, -CO$_2$C*H*$_2$-, -C*H*$_2$OArOC*H*$_2$-), 3.85 (4H, t, *J* = 3.3 Hz, -C*H*$_2$O-), 3.70–3.63 (14H, m, -C*H*$_2$O-, >C*H*-), 2.28, 2.24 (6H, s, -C*H*$_3$), 1.41–1.22 (4H, m, -C*H*$_2$-), 1.01–0.82 (3H, m, -C*H*$_2$-), 0.82–0.77 (2H, m, -C*H*$_2$-), 0.76–0.69 (3H, m, -C*H*$_2$-), 0.68–0.58 (4H, m, -C*H*$_2$-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): *δ* 166.1 (2C, -*C*O$_2$-), 165.6 (2C, ═*C*O-), 157.9 (2C, arom. *C*O-), 145.4 (2C, arom. C), 140.8 (2C, arom. C), 133.7 (2C, arom. -*C*–*C*-), 128.0, 127.7, 127.6, 127.0, 126.8, 126.2 (20C, arom. *C*H), 115.3 (8C, arom. *C*H), 108.2 (2C, ═C<), 95.0 (2C, >C<), 71.1, 70.7, 69.9, 69.4, 67.9 (10C, -*C*H$_2$O-), 62.7 (2C, -CO$_2$*C*H$_2$-), 49.2 (2C, >*C*H-), 31.5, 29.8, 29.2, 26.1 (8C, -*C*H$_2$-), 14.8 (2C,

-CH_3) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{68}H_{76}O_{12}$ 1084.5337 (M^+ +Na); found 1084.5272.

[30]Biphenylcyclophane $3_{(16)(1)}$-biphen. R_f 0.16 ($CHCl_3$). Colorless amorphous. IR ($CHCl_3$): *ν* 1695 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.54–7.52 (4H, m, arom. H), 7.46–7.43 (4H, m, arom. H), 7.35–7.17 (16H, m, arom. H), 6.95–6.92 (4H, m, arom. H), 4.66 (2H, dt, *J* = 12.0, 4.8 Hz, -CO_2C*H$_2$*-), 4.30 (2H, dt, *J* = 12.0, 4.8 Hz, -CO_2C*H$_2$*-), 4.20 (4H, t, *J* = 4.8 Hz, -C*H$_2$*OArOC*H$_2$*-), 3.80 (2H, t, *J* = 5.4 Hz, >C*H*-), 2.31 (6H, s, -C*H$_3$*), 1.38–1.23 (4H, m, -C*H$_2$*-), 1.16–0.99 (16H, m, -C*H$_2$*-), 0.98–0.77 (12H, m, -C*H$_2$*-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 167.3 (2C, -*C*O$_2$-), 165.8 (2C, ═*C*O-), 157.8 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.8 (2C, arom. C), 133.7 (2C, arom. -*C*–*C*-), 128.1, 127.7, 127.0, 126.7, 126.2 (20C, arom. *C*H), 114.7 (8C, arom. *C*H), 108.1 (2C, ═C<), 95.5 (2C, >C<), 66.2 (2C, -*C*H$_2$O-), 61.7 (2C, -CO$_2$*C*H$_2$-), 48.8 (2C, >*C*H-), 32.0, 29.85, 29.80, 29.7, 29.6, 29.4, 26.4 (16C, -*C*H$_2$-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{68}H_{76}O_8$ 1020.5540 (M^+); found 1020.5518.

[36]Biphenylcyclophane $3_{(16)(2)}$-biphen. R_f 0.29 ($CHCl_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR ($CHCl_3$): *ν* 1692 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.54–7.51 (4H, m, arom. H), 7.44–7.41 (4H, m, arom. H), 7.35–7.18 (16H, m, arom. H), 6.94–6.92 (4H, m, arom. H), 4.40 (2H, dt, *J* = 12.3, 4.2 Hz, -CO_2C*H$_2$*-), 4.19 (2H, dt, *J* = 12.3, 4.2 Hz, -CO_2C*H$_2$*-), 4.12 (4H, t, *J* = 5.1 Hz, -C*H$_2$*OArOC*H$_2$*-), 3.86 (4H, t, *J* = 5.1, 1.8 Hz, -C*H$_2$*-), 3.82–3.77 (6H, m, -C*H$_2$*O-, >C*H*-), 2.29, 2.23 (6H, s, -C*H$_3$*), 1.43–1.28 (4H, m, -C*H$_2$*-), 1.27–1.12 (4H, m, -C*H$_2$*-), 1.11–0.98 (10H, m, -C*H$_2$*-), 0.98–0.76 (14H, m, -C*H$_2$*-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 166.8 (2C, -*C*O$_2$-), 165.8 (2C, ═*C*O-), 157.8 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.7 (2C, arom. C), 133.4 (2C, arom. -*C*–*C*-), 128.0, 127.6, 127.5, 127.0, 126.7, 126.1 (20C, arom. *C*H), 114.6 (8C, arom. *C*H), 107.9 (2C, ═C<), 95.1 (2C, >C<), 69.6, 69.4, 67.4 (6C, -*C*H$_2$O-), 62.5 (2C, -CO$_2$*C*H$_2$-), 49.0 (2C, >*C*H-), 31.6, 29.9, 29.8, 29.4, 26.2 (16C, -*C*H$_2$-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{72}H_{84}O_{10}$ 1108.6064 (M^+); found 1108.6064.

[42]Biphenylcyclophane $3_{(16)(3)}$-biphen. R_f 0.37 ($CHCl_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR ($CHCl_3$): *ν* 1695 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.53–7.51 (4H, m, arom. H), 7.45–7.42 (4H, m, arom. H), 7.42–7.16 (16H, m, arom. H), 6.95–6.93 (4H, m, arom. H), 4.32–4.20 (4H, m, -CO_2C*H$_2$*-), 4.15 (4H, t, *J* = 5.1 Hz, -C*H$_2$*OArOC*H$_2$*-), 3.87 (4H, t, *J* = 5.1 Hz, -C*H$_2$*O-), 3.80–3.64 (14H, m, -C*H$_2$*O-, >C*H*-), 2.28 (6H, s, -C*H$_3$*), 1.46–1.28 (4H, m, -C*H$_2$*-), 1.28–1.16 (4H, m, -C*H$_2$*-), 1.16–1.01 (10H, m, -C*H$_2$*-), 0.98–0.82 (14H, m, -C*H$_2$*-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 166.4 (2C, -*C*O$_2$-), 165.6 (2C, ═*C*O-), 157.8 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.8 (2C, arom. C), 133.5 (2C, arom. -*C*–*C*-), 128.0, 127.6, 127.5, 126.9, 126.7, 126.1 (20C, arom. *C*H), 114.8 (8C, arom. *C*H), 108.0 (2C, ═C<), 95.0 (2C, >C<), 70.9, 70.6, 69.7, 69.4, 67.5 (10C, -*C*H$_2$O-), 62.6 (2C, -CO$_2$*C*H$_2$-), 49.0 (2C, >*C*H-), 31.5, 29.8, 29.8, 29.7, 29.6, 29.2, 26.0 (16C, -*C*H$_2$-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{76}H_{92}O_{12}$ 1196.6589 (M^+); found 1196.6580.

Diploid of $3_{(16)(3)}$-biphen. R_f 0.27 ($CHCl_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR ($CHCl_3$): *ν* 1688 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.54–7.52 (8H, m, arom. H), 7.47–7.44 (8H, m, arom. H), 7.42–7.19 (32H, m, arom. H), 6.98–6.94 (8H, m, arom. H), 4.30–4.24 (8H, m, -CO_2C*H$_2$*-), 4.18 (8H, m, -C*H$_2$*OArOC*H$_2$*-), 3.90–3.79 (8H, m, -C*H$_2$*O-), 3.79–3.59 (28H, m, -C*H$_2$*O-, >C*H*-), 2.28 (12H, s, -C*H$_3$*), 1.53–1.29 (8H, m, -C*H$_2$*-), 1.29–1.00 (40H, m, -C*H$_2$*-), 1.00–0.78 (16H, m, -C*H$_2$*-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 166.3 (4C, -*C*O$_2$-), 165.7 (4C, ═*C*O-), 157.9, 157.8 (4C, arom. *C*O-), 145.4 (4C, arom. C), 140.9 (4C, arom. C), 133.7, 133.6 (4C, arom -*C*–*C*-), 128.3, 128.2, 128.1, 127.7, 127.1, 126.8, 126.3, 125.7, 125.6 (40C, arom. *C*H), 114.9 (16C, arom *C*H), 108.2 (4C, ═C<), 95.1 (4C, >C<), 72.5, 71.4, 70.9, 70.7, 70.6, 70.4, 69.8, 69.4, 67.5 (20C, -*C*H$_2$O-), 62.6, 61.8 (4C, -CO$_2$*C*H$_2$-), 49.1 (4C, >*C*H-), 31.6, 29.7, 29.6, 29.5, 29.2, 26.2, 26.0 (32C, -*C*H$_2$-), 14.8 (4C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{152}H_{184}O_{24}$ 2393.3178 (M^+); found 2393.3213.

[28]Orthocyclophane $3_{(6)(CH2)6}$-*ortho*. Diastereomer ratio, 49 : 51. R_f 0.22 ($CHCl_3$). Colorless amorphous. IR ($CHCl_3$): *ν* 1684 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.51–7.48 (4H, m, arom. H), 7.32–7.13 (16H, m, arom. H), 6.79 (4H, s, arom. H), 4.17–4.11 (2H, m, -CO_2C*H$_2$*-), 4.07–3.96 (6H, m, -C*H$_2$*OArOC*H$_2$*-, -CO_2C*H$_2$*-), 3.70 (2H, t, *J* = 5.4 Hz, >C*H*-), 2.26 (6H, s, -C*H$_3$*), 1.81 (4H, quin, *J* = 6.6 Hz, -C*H$_2$*-), 1.66 (4H, quin, *J* = 6.9 Hz, -C*H$_2$*-), 1.59–1.52 (4H, m, -C*H$_2$*-), 1.49–1.44 (4H, m, -C*H$_2$*-), 1.26–1.16 (4H, m, -C*H$_2$*-), 0.80–0.68 (8H, m, -C*H$_2$*-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 166.23, 166.18 (2C, -*C*O$_2$-), 166.0, 165.9 (2C, ═*C*O-), 149.2 (2C, arom. *C*O-), 145.3 (2C, arom. C), 140.9 (2C, arom. C) 128.0, 127.61, 126.98, 126.74, 126.71, 126.2 (20C, arom. *C*H), 121.2, 114.1 (4C, arom. *C*H), 108.33, 108.30 (2C, ═C<), 95.13, 95.11 (2C, >C<), 69.0 (2C, -*C*H$_2$O-), 63.4 (2C, -CO$_2$*C*H$_2$-), 49.8, 48.7 (2C, >*C*H-), 31.8, 29.4, 29.3, 28.7, 26.3, 26.2, 25.9, 25.8 (14C, -*C*H$_2$-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{60}H_{68}O_8$ 916.4914 (M^+); found 916.4900.

[28]Paracyclophane $3_{(6)(CH2)6}$-*para*. Diastereomer ratio, 49 : 51. R_f 0.35 ($CHCl_3$). Colorless amorphous. IR ($CHCl_3$): *ν* 1697 (C═O), 1653 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.50–7.48 (4H, m, arom. H), 7.33–7.17 (16H, m, arom. H), 6.80–6.70 (4H, m, arom. H), 4.11–4.00 (4H, m, -CO_2C*H$_2$*-), 3.95 (4H, t, *J* = 6.0 Hz, -C*H$_2$*OArOC*H$_2$*-), 3.67 (2H, t, *J* = 5.1 Hz, >C*H*-), 2.31 (6H, s, -C*H$_3$*), 1.73 (4H, quin, *J* = 6.3 Hz, -C*H$_2$*-), 1.62 (4H, quin, *J* = 6.6 Hz, -C*H$_2$*-), 1.53–1.37 (8H, m, -C*H$_2$*-), 1.20–1.31 (4H, m, -C*H$_2$*-), 0.80–0.55 (4H, m, -C*H$_2$*-), 0.55–0.42 (4H, m, -C*H$_2$*-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 165.9, 165.83 (2C, -*C*O$_2$-), 165.79 (2C, ═*C*O-), 152.9 (2C, arom. *C*O-), 145.4 (2C, arom. C), 140.8 (2C, arom. C) 128.0, 127.63, 127.59, 127.0, 126.8, 126.2 (20C, arom. *C*H), 115.81, 115.80 (4C, arom. *C*H), 108.3, 108.2 (2C, ═C<), 95.0 (2C, >C<), 68.2, 68.1 (2C, -*C*H$_2$O-), 63.3 (2C, -CO$_2$*C*H$_2$-), 49.1 (2C, >*C*H-), 31.5, 29.5, 28.6, 28.5, 26.32, 26.28, 25.5, 25.4, 25.3 (14C, -*C*H$_2$-), 14.7 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{60}H_{68}O_8$ 916.4914 (M^+); found 916.4890.

Diploid of $3_{(6)(CH2)6}$-*para*. R_f 0.12 ($CHCl_3$). Colorless amorphous. IR ($CHCl_3$): *ν* 1684 (C═O), 1651 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.60–7.49 (8H, m, arom. H), 7.49–7.05

(32H, m, arom. H), 6.81 (8H, s, arom. H), 4.16–4.00 (8H, m, -CO$_2$CH_2-), 4.00–3.80 (8H, m, -CH_2OArOCH_2-), 3.80–3.70 (4H, m >CH-), 2.32 (12H, s, -CH_3), 1.90–1.70 (8H, m, -CH_2-), 1.70–1.66 (8H, m, -CH_2-), 1.59–1.35 (18H, m, -CH_2-), 1.26–1.04 (8H, m, -CH_2-), 1.04–0.62 (8H, m, -CH_2-), 0.62–0.39 (6H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 165.92 (4C, -CO$_2$-), 165.90 (4C, =CO-), 153.1 (4C, arom. CO-), 145.3 (4C, arom. C), 140.9 (4C, arom. C) 128.1, 127.6, 127.0, 126.8, 126.2 (40C, arom. CH), 115.4 (8C, arom CH), 108.4 (4C, =C<), 95.0 (4C, >C<), 68.4 (4C, -CH$_2$O-), 63.5 (4C, -CO$_2$$CH_2$-), 49.0 (4C, >$C$H-), 31.6, 29.5, 29.3, 28.7, 25.9, 25.8 (28C, -CH$_2$-), 14.7 (4C, -CH$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{120}H_{136}O_{16}$ 1832.9828 (M$^+$); found 1832.9825.

[32]Paracyclophane $3_{(6)(CH2)8}$-*para*. R_f 0.37 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1688 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.51–7.49 (4H, m, arom. H), 7.39–7.15 (16H, m, arom. H), 6.81 (4H, s, arom. H), 4.05 (4H, t, J = 6.6 Hz, -CO$_2$CH_2-), 3.96 (4H, t, J = 6.6 Hz, -CH_2OArOCH_2-), 3.70–3.62 (2H, m, >CH-), 2.26 (6H, s, -CH_3), 1.73 (4H, quin, J = 6.6 Hz, -CH_2-), 1.65–1.53 (4H, m, -CH_2-), 1.44–1.42 (4H, m, -CH_2-), 1.32 (12H, m, -CH_2-), 1.25–1.15 (4H, m, -CH_2-), 0.81–0.60 (4H, m, -CH_2-), 0.60–0.50 (4H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 165.9 (2C, -CO$_2$-), 165.7 (2C, =CO-), 153.0 (2C, arom. CO-), 145.4 (2C, arom. C), 140.9 (2C, arom. C) 128.0, 127.6, 127.0, 126.8, 126.2 (20C, arom. CH), 115.7 (4C, arom. CH), 108.4 (2C, =C<), 95.0 (2C, >C<), 68.3 (2C, -CH$_2$O-), 63.6 (2C, -CO$_2$$CH_2$-), 49.0 (2C, >$C$H-), 31.6, 29.5, 28.8, 28.6, 28.53, 28.47, 26.3, 26.2, 25.7, 25.4 (16C, -CH$_2$-), 14.7 (2C, -CH$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{64}H_{76}O_8$ 972.5540 (M$^+$); found 972.5577.

[30]Orthocyclophane $3_{(8)(CH2)6}$-*ortho*. R_f 0.37 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1686 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.56–7.50 (4H, m, arom. H), 7.32–7.14 (16H, m, arom. H), 6.88 (4H, s, arom. H), 4.21–4.13 (2H, m, -CO$_2$CH_2-), 4.07–3.95 (6H, m, -CO$_2$CH_2-, -CH_2OArOCH_2-), 3.74 (2H, t, J = 5.4 Hz, >CH-), 2.32 (6H, s, -CH_3), 1.81 (4H, quin, J = 6.3 Hz, -CH_2-), 1.67 (4H, quin, J = 6.6 Hz, -CH_2-), 1.60–1.38 (8H, m, -CH_2-), 1.37–1.20 (3H, m, -CH_2-), 1.17–1.15 (1H, m, -CH_2-), 1.00–0.75 (12H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.3 (2C, -CO$_2$-), 166.0 (2C, =CO-), 149.2 (2C, arom. CO-), 145.3 (2C, arom. C), 140.9 (2C, arom. C) 128.2, 128.0, 127.6, 127.0, 126.7, 126.2, 121.1 (20C, arom. CH), 114.1 (4C, arom. CH), 108.4 (2C, =C<), 95.1 (2C, >C<), 69.0 (2C, -CH$_2$O-), 63.4 (2C, -CO$_2$$CH_2$-), 48.9 (2C, >$C$H-), 31.8, 29.6, 29.2, 28.9, 28.7, 26.2, 26.0, 25.7 (16C, -CH$_2$-), 14.5 (2C, -CH$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{62}H_{72}O_8$ 944.5227 (M$^+$); found 944.5233.

[30]Paracyclophane $3_{(8)(CH2)6}$-*para*. R_f 0.45 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1686 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.52–7.50 (4H, m, arom. H), 7.30–7.16 (16H, m, arom. H), 6.78 (4H, s, arom. H), 4.20–4.05 (4H, m, -CO$_2$CH_2-), 3.92 (4H, t, J = 6.3 Hz, -CH_2OArOCH_2-), 3.75–3.70 (2H, m, >CH-), 2.26 (6H, s, -CH_3), 1.74 (4H, quin, J = 6.3 Hz, -CH_2-), 1.65 (4H, quin, J = 6.3 Hz, -CH_2-), 1.57–1.36 (10H, m, -CH_2-), 1.36–1.20 (4H, m, -CH_2-), 1.00–0.68 (10H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.00, 165.97 (2C, -CO$_2$-), 165.90 (2C, =CO-), 153.0 (2C, arom. CO-), 145.4 (2C, arom. C), 140.9 (2C, arom. C) 128.0, 127.6, 127.0, 126.8, 126.2 (20C, arom. CH), 115.7 (4C, arom. CH), 108.3 (2C, =C<), 95.0 (2C, >C<), 68.2 (2C, -CH$_2$O-), 63.3 (2C, -CO$_2$$CH_2$-), 49.1 (2C, >$C$H-), 31.7, 29.8, 29.2, 28.7, 28.6, 26.3, 25.6, 25.4 (16C, -CH$_2$-), 14.5 (2C, -CH$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{62}H_{72}O_8$ 944.5227 (M$^+$); found 944.5226.

[34]Paracyclophane $3_{(8)(CH2)8}$-*para*. R_f 0.36 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1683 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.53–7.51 (4H, m, arom. H), 7.29–7.13 (16H, m, arom. H), 6.79 (4H, s, arom. H), 4.10–4.05 (4H, m, -CO$_2$CH_2-), 3.92 (4H, t, J = 6.3 Hz, -CH_2OArOCH_2-), 3.75 (2H, t, J = 4.8 Hz, >CH-), 2.26 (6H, s, -CH_3), 1.74–1.67 (4H, quin, J = 6.6 Hz, -CH_2-), 1.66–1.54 (4H, m, -CH_2-), 1.53–1.23 (22H, m, -CH_2-), 1.00–0.70 (10H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 165.78 (2C, -CO$_2$-), 165.71 (2C, =CO-), 152.9 (2C, arom. CO-), 145.3 (2C, arom. C), 140.8 (2C, arom. C) 127.9, 127.5, 126.9, 126.7, 126.1 (20C, arom. CH), 115.6, 115.2 (4C, arom. CH), 108.3 (2C, =C<), 94.9 (2C, >C<), 68.2 (2C, -CH$_2$O-), 63.4 (2C, -CO$_2$$CH_2$-), 49.0 (2C, >$C$H-), 31.6, 29.6, 28.9, 28.7, 28.6, 28.5, 26.1, 25.7, 25.4 (20C, -CH$_2$-), 14.5 (2C, -CH$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{66}H_{80}O_8$ 1000.5853 (M$^+$); found 1000.5860.

[38]Orthocyclophane $3_{(16)(CH2)6}$-*ortho*. R_f 0.50 (CHCl$_3$). colorless amorphous. IR (CHCl$_3$): ν 1686 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.45–7.42 (4H, m, arom. H), 7.22–7.06 (16H, m, arom. H), 6.77 (4H, s, arom. H), 4.05–3.95 (4H, m, -CO$_2$CH_2-), 3.89 (4H, t, J = 6.6 Hz, -CH_2OArOCH_2-), 3.71 (2H, t, J = 5.1 Hz, >CH-), 2.18 (6H, s, -CH_3), 1.73 (4H, t, J = 6.6 Hz, -CH_2-), 1.60 (4H, t, J = 6.6 Hz, -CH_2-), 1.61–1.39 (8H, m, -CH_2-), 1.31–1.24 (4H, m, -CH_2-), 1.18–1.01 (18H, m, -CH_2-), 1.01–0.82 (10H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.0 (2C, -CO$_2$-), 165.8 (2C, =CO-), 149.0 (2C, arom. CO-), 145.3 (2C, arom. C), 140.8 (2C, arom. C) 127.9, 127.5, 126.9, 126.6, 126.1 (20C, arom. CH), 114.1 (4C, arom. CH), 108.3 (2C, =C<), 95.0 (2C, >C<), 68.9 (2C, -CH$_2$O-), 63.3 (2C, -CO$_2$$CH_2$-), 48.8 (2C, >$C$H-), 31.7, 29.5, 29.2, 29.1, 29.0, 28.7, 26.1, 25.8, 25.6 (24C, -CH$_2$-), 14.4 (2C, -CH$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{70}H_{89}O_8$ 1057.6557 (M+1); found 1057.6477.

[38]Paracyclophane $3_{(16)(CH2)6}$-*para*. R_f 0.32 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1685 (C=O), 1647 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.54–7.51 (4H, m, arom. H), 7.35–7.20 (16H, m, arom. H), 6.78 (4H, s, arom. H), 4.22 (2H, dt, J = 10.8, 6.0 Hz, -CO$_2$CH_2-), 4.01 (2H, dt, J = 10.8, 6.0 Hz, -CO$_2$CH_2-),3.87 (4H, t, J = 6.6 Hz, -CH_2OArOCH_2-), 3.76 (2H, t, J = 5.1 Hz, >CH-), 2.28 (6H, s, -CH_3), 1.86–1.70 (4H, t, J = 6.6 Hz, -CH_2-), 1.70–1.58 (4H, t, J = 6.6 Hz, -CH_2-), 1.58–1.39 (8H, m, -CH_2-), 1.58–1.24 (6H, m, -CH_2-), 1.24–1.03 (16H, m, -CH_2-), 1.02–0.74 (10H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.3 (2C, -CO$_2$-), 165.9 (2C, =CO-), 153.0 (2C, arom. CO-), 145.2 (2C, arom. C), 140.8 (2C, arom. C) 128.1, 128.0, 127.5, 126.9, 126.7, 126.1 (20C, arom. CH), 115.1 (4C, arom. CH), 108.2 (2C, =C<), 95.0 (2C, >C<), 68.2 (2C, -CH$_2$O-), 63.2 (2C, -CO$_2$$CH_2$-), 48.9 (2C, >$C$H-), 31.9, 29.9, 29.82, 29.79, 29.73, 29.66, 29.4, 29.2, 28.7, 26.4, 26.0, 25.7 (24C, -CH$_2$-), 14.5 (2C, -CH$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{70}H_{88}O_8$ 1056.6479 (M$^+$); found 1056.6432.

[42]Paracyclophane $3_{(16)(CH2)8}$-*para*. R_f 0.43 ($CHCl_3$). Colorless amorphous. IR ($CHCl_3$): *ν* 1683 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.54–7.51 (4H, m, arom. H), 7.33–7.16 (16H, m, arom. H), 6.77 (4H, s, arom. H), 4.18 (2H, dt, *J* = 10.8, 6.3 Hz, -CO$_2$C*H$_2$*-), 4.02 (2H, dt, *J* = 10.8, 6.3 Hz, -CO$_2$C*H$_2$*-), 3.87 (4H, t, *J* = 6.6 Hz, -C*H$_2$*OArOC*H$_2$*-), 3.76 (2H, t, *J* = 5.1 Hz, >C*H*-), 2.28 (6H, s, -C*H$_3$*), 1.73 (4H, quin, *J* = 6.6 Hz, -C*H$_2$*-), 1.64 (4H, quin, *J* = 6.3 Hz, -C*H$_2$*-), 1.55–1.40 (8H, m, -C*H$_2$*-), 1.40–1.26 (16H, m, -C*H$_2$*-), 1.23–1.05 (12H, m, -C*H$_2$*-) 1.00–0.70 (12H, m, -C*H$_2$*-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 166.2 (2C, -*C*O$_2$-), 166.0 (2C, ═*C*O-), 153.1 (2C, arom. *C*O-), 145.4 (2C, arom. C), 140.9 (2C, arom. C) 128.0, 127.6, 127.0, 126.8, 126.2 (20C, arom. *C*H), 115.4 (4C, arom. *C*H), 108.3 (2C, ═C<), 95.1 (2C, >C<), 68.5 (2C, -*C*H$_2$O-), 63.4 (2C, -CO$_2$*C*H$_2$-), 49.1 (2C, >*C*H-), 31.8, 29.91, 28.87, 29.79, 29.7, 29.4, 29.24, 29.19, 29.17, 28.8, 26.9, 26.4, 26.1, 25.9 (28C, -*C*H$_2$-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{74}H_{96}O_8$ 1112.7105 (M$^+$); found 1112.7113.

[12.12]Paracyclophane $5_{(1)(1)}$-*para*. R_f 0.18 ($CHCl_3$). Colorless microcrystals (from $CHCl_3$–hexane), m.p. 208–209 °C. IR ($CHCl_3$): *ν* 1697 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.59–7.57 (4H, m, arom. H), 7.37–7.18 (16H, m, arom. H), 6.70–6.60 (8H, m, arom. H), 4.52–4.45 (2H, m, -CO$_2$C*H$_2$*-), 4.30–4.23 (2H, m, -CO$_2$C*H$_2$*-), 4.12–4.05 (2H, m, >C*H*-), 4.01 (4H, t, *J* = 3.9 Hz, -C*H$_2$*OArOC*H$_2$*-), 3.73 (4H, t, *J* = 4.8 Hz, -OC*H$_2$*-), 3.59 (2H, dt, *J* = 9.0, 2.2 Hz, -OC*H$_2$*-), 3.18 (2H, ddd, *J* = 10.3, 7.7, 2.2 Hz, -OC*H$_2$*-), 3.03–2.90 (4H, m, -OC*H$_2$*-), 2.33 (6H, m, C*H$_3$*) ppm.^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.7 (2C, C═O), 165.4 (2C, ═*C*O-), 153.0, 152.9 (4C, arom. C), 144.8 (2C, arom. C), 140.4 (2C, arom. C), 128.1, 127.8, 127.3, 127.1, 126.4 (20C, arom. *C*H), 115.7, 115.5 (8C, arom. *C*H), 103.1 (2C, >C═), 94.8 (2C, >C<), 69.8, 68.9, 67.8, 66.5 (8C, -*C*H$_2$O-), 62.0 (2C, -CO$_2$*C*H$_2$-), 51.1 (2C, >*C*H-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{58}H_{56}O_{12}$ 944.3772 (M$^+$); found 944.3765.

[15.15]Paracyclophane $5_{(1)(2)}$-*para*. R_f 0.38 ($CHCl_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR ($CHCl_3$): *ν* 1695 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.61–7.59 (4H, m, arom. H), 7.36–7.17 (16H, m, arom. H), 6.89–6.67 (8H, m, arom. H), 4.39 (2H, dt, *J* = 12.3, 4.2 Hz, -CO$_2$C*H$_2$*-), 4.18 (2H, dt, *J* = 12.3, 4.3 Hz, -CO$_2$C*H$_2$*-), 4.10 (2H, d, *J* = 7.2 Hz, >C*H*-), 3.91 (4H, t, *J* = 4.5 Hz, -OC*H$_2$*-), 3.79–3.77 (8H, m, -C*H$_2$*O-), 3.65–3.62 (6H, m, -C*H$_2$*O-), 3.16 (2H, dd, *J* = 7.2, 2.4 Hz, >CHC*H$_2$*-), 3.14 (2H, t, *J* = 4.5 Hz, >CHC*H$_2$*-), 2.95–2.90 (2H, m, -C*H$_2$*O-), 2.32 (6H, s, -C*H$_3$*) ppm.^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.7 (2C, C═O), 165.4 (2C, ═*C*O-), 153.0, 152.9 (4C, arom. C), 144.9 (2C, arom. C), 140.4 (2C, arom. C), 128.1, 127.7, 127.3, 127.2, 127.1, 126.5 (20C, arom. *C*H), 115.39, 115.36 (8C, arom. *C*H), 102.9 (2C, >C═), 94.9 (2C, >C<), 69.8, 69.7, 69.5, 68.9, 67.9, 67.5 (12C, -*C*H$_2$O-), 62.9 (2C, -CO$_2$*C*H$_2$-), 51.4 (2C, >*C*H-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{62}H_{64}O_{14}$ 1032.4296 (M$^+$); found 1032.4261.

[18.18]Paracyclophane $5_{(1)(3)}$-*para*. R_f 0.29 ($CHCl_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR ($CHCl_3$): *ν* 1693 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.63–7.60 (4H, m, arom. H), 7.35–7.18 (16H, m, arom. H), 6.72–6.68 (8H, m, arom. H), 4.37–4.31 (2H, m, -CO$_2$C*H$_2$*-), 4.22–4.15 (2H, m, -CO$_2$C*H$_2$*-), 4.10 (2H, d, *J* = 8.1 Hz, >CH-), 3.99 (4H, t, *J* = 4.6 Hz, -CH$_2$O-), 3.79 (4H, t, *J* = 4.6 Hz, -CH$_2$O-), 3.73–3.60 (18H, m, -CH$_2$O-), 3.28–3.21 (2H, m, -CH$_2$O-), 3.14 (2H, t, *J* = 9.0 Hz, -CH$_2$O-), 2.97–2.90 (2H, m, -CH$_2$O-), 2.34 (6H, s, C*H$_3$*) ppm.^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.5 (2C, C═O), 165.4 (2C, ═*C*O-), 152.98, 152.94 (4C, arom. C), 144.9 (2C, arom. C), 140.4 (2C, arom. C), 128.1, 127.7, 127.6, 127.3, 127.2, 127.1, 126.5 (20C, arom. *C*H), 115.5, 115.3 (8C, arom. *C*H), 102.8 (2C, >C═), 94.8 (2C, >C<), 70.8, 70.7, 69.8, 69.6, 69.4, 68.8, 68.0, 67.5 (16C, -*C*H$_2$O-), 62.9 (2C, -CO$_2$*C*H$_2$-), 51.5 (2C, >*C*H-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{66}H_{72}O_{16}$ 1120.4820 (M$^+$); found 1120.4744.

[15.15]Paracyclophane $5_{(2)(1)}$-*para*. R_f 0.09 ($CHCl_3$). Colorless amorphous. IR ($CHCl_3$): *ν* 1693 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.59–7.57 (4H, m, arom. H), 7.36–7.19 (16H, m, arom. H), 6.81–6.67 (8H, m, arom. H), 4.44–4.29 (4H, m, -CO$_2$C*H$_2$*-), 4.09–4.02 (6H, m, -C*H$_2$*O-, >CH-), 3.97 (4H, t, *J* = 4.5 Hz, -C*H$_2$*O-), 3.68 (4H, *J* = 4.5 Hz, -C*H$_2$*O-), 3.52 (2H, dd, *J* = 9.0, 3.0, >CHC*H$_2$*-), 3.40–3.30 (4H, m, -C*H$_2$*O-), 3.17 (2H, t, *J* = 9.0 Hz, >CHC*H$_2$*-) 2.99–2.92 (2H, m, -C*H$_2$*O-), 2.91–2.84 (2H, m, -C*H$_2$*O-), 2.31 (6H, s, C*H$_3$*) ppm.^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.2 (2C, C═O), 165.3 (2C, ═*C*O-), 153.1, 153.0 (4C, arom. C), 144.9 (2C, arom. C), 140.5 (2C, arom. C), 128.1, 127.8, 127.3, 127.13, 127.06, 126.5 (20C, arom. *C*H), 115.7, 115.6 (8C, arom. *C*H), 103.3 (2C, >C═), 94.7 (2C, >C<), 70.5, 70.0, 69.7, 69.5 (8C, -*C*H$_2$O-), 68.2, 66.6 (4C, -*C*H$_2$OArOC*H$_2$*-), 62.0 (2C, -CO$_2$*C*H$_2$-), 51.1 (2C, >*C*H-), 14.7 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{62}H_{64}O_{14}$ 1032.4296 (M$^+$); found 1032.4297.

[18.18]Paracyclophane $5_{(2)(2)}$-*para*. R_f 0.08 ($CHCl_3$). Colorless amorphous. IR ($CHCl_3$): *ν* 1693 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.61–7.58 (4H, m, arom. H), 7.36–7.19 (16H, m, arom. H), 6.83–6.74 (8H, m, arom. H), 4.38–4.31 (2H, m, -CO$_2$C*H$_2$*-), 4.22–4.16 (2H, m, -CO$_2$C*H$_2$*-), 4.15–4.05 (2H, m, >C*H*-), 3.96 (8H, t, *J* = 4.7 Hz, -C*H$_2$*OArOC*H$_2$*-), 3.79–3.65 (12H, m, -C*H$_2$*O-), 3.56 (2H, dd, *J* = 9.5, 2.2 Hz, >CHC*H$_2$*-), 3.36–3.34 (4H, m, -C*H$_2$*O-), 3.12 (2H, t, *J* = 9.5 Hz, >CHC*H$_2$*-), 3.07–3.00 (2H, m, 3.56 -C*H$_2$*O-), 2.83–2.78 (2H, m, 3.56 -C*H$_2$*O-), 2.33 (6H, s, C*H$_3$*) ppm.^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.3 (2C, C═O), 165.4 (2C, ═*C*O-), 153.0 (4C, arom. C), 144.9 (2C, arom. C), 140.5 (2C, arom. C), 128.1, 127.7, 127.2, 126.5 (20C, arom. *C*H), 115.4 (8C, arom. *C*H), 103.1 (2C, >C═), 94.8 (2C, >C<), 70.5, 70.0, 69.7, 69.5 (12C, -*C*H$_2$O-), 68.0 (4C, -*C*H$_2$OArO*C*H$_2$-), 62.8 (2C, -CO$_2$*C*H$_2$-), 51.3 (2C, >*C*H-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{66}H_{72}O_{16}$ 1120.4820 (M$^+$); found 1120.4827.

[21.21]Paracyclophane $5_{(2)(3)}$-*para*. R_f 0.38 ($CHCl_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR ($CHCl_3$): *ν* 1693 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.62–7.59 (4H, m, arom. H), 7.36–7.18 (16H, m, arom. H), 6.84–6.77 (8H, m, arom. H), 4.34–4.28 (2H, m, -CO$_2$C*H$_2$*-), 4.22–4.17 (2H, m, -CO$_2$C*H$_2$*-), 4.08 (2H, dd, *J* = 6.9 Hz, >CH-), 3.98 (8H, dd, *J* = 9.0, 4.2 Hz, -C*H$_2$*OArOC*H$_2$*-), 3.79–3.76 (4H, m, -C*H$_2$*O-), 3.69–3.66 (16H, m, -C*H$_2$*O-), 3.59 (2H, dd, *J* = 9.5, 2.2 Hz, >CHC*H$_2$*-), 3.37–3.34 (4H, m, -C*H$_2$*O-), 3.12–3.06 (4H, m, -C*H$_2$*O-), 2.78–2.74 (2H, m, -C*H$_2$*O-), 2.33 (6H, s, C*H$_3$*) ppm.^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.3 (2C, C═O), 165.4 (2C, ═*C*O-), 153.0 (4C, arom. C), 144.9 (2C, arom. C), 140.5 (2C, arom. C), 128.1, 127.7, 127.2, 127.1, 126.5 (20C, arom. *C*H), 115.5 (8C, arom. *C*H), 103.0 (2C, >C═), 94.8 (2C, >C<), 70.8, 70.6, 70.4, 69.8, 69.7, 69.5, 69.3 (16C, -*C*H$_2$O-), 67.9 (4C, -*C*H$_2$OAr), 62.7 (2C, -CO$_2$*C*H$_2$-), 51.4 (2C, >*C*H-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{70}H_{80}O_{18}$ 1208.5345 (M$^+$); found 1208.5286.

[18.18]Paracyclophane $\mathbf{5_{(3)(1)}}$-*para*. R_f 0.22 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): ν 1695 (C═O) 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.60–7.53 (4H, m, arom. H), 7.36–7.21 (16H, m, arom. H), 6.84–6.78 (8H, m, arom. H), 4.46–4.40 (2H, m, -CO$_2$C*H*$_2$-), 4.35–4.28 (2H, m, -CO$_2$C*H*$_2$-), 4.12–4.03 (10H, m, >C*H*-, -C*H*$_2$O-), 3.78 (4H, t, *J* = 4.6 Hz, -C*H*$_2$O-), 3.67–3.63 (4H, m, -C*H*$_2$O-), 3.60–3.47 (6H, m, -C*H*$_2$O-, >CHC*H*$_2$-), 3.31–3.29 (4H, m, -C*H*$_2$O-), 3.10 (2H, t, *J* = 9.0 Hz, >CHC*H*$_2$-), 3.00–2.94 (2H, m, -C*H*$_2$O-), 2.82–2.75 (2H, m, -C*H*$_2$O-), 2.31, (6H, s, C*H*$_3$) ppm.^{13}C NMR (75 MHz, CDCl$_3$): δ 168.2 (2C, C═O), 165.2 (2C, ═*C*O-), 153.1, 153.0 (4C, arom. C), 144.9 (2C, arom. C), 140.5 (2C, arom. C), 128.52, 128.47, 128.1, 127.7, 127.2, 127.15, 127.05, 126.5 (20C, arom. *C*H), 115.6, 115.5 (8C, arom. *C*H), 103.1 (2C, >C═), 94.8 (2C, >C<), 70.8, 70.6, 70.3, 69.9, 69.7, 69.4, 68.13, 67.99, 66.6 (16C, -*C*H$_2$O-), 61.9 (2C, -CO$_2$*C*H$_2$-), 51.3 (2C, >*C*H-), 14.7 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{66}H_{72}O_{16}$ 1120.4820 (M$^+$); found 1120.4813.

Diploid of $\mathbf{5_{(3)(1)}}$-*para*. R_f 0.15 (CHCl$_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR (CHCl$_3$): ν 1697 (C═O) 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.60–7.57 (8H, m, arom. H), 7.35–7.16 (32H, m, arom. H), 6.85–6.78 (16H, m, arom. H), 4.51–4.40 (4H, m, -CO$_2$C*H*$_2$-), 4.40-4.30 (4H, m, -CO$_2$C*H*$_2$-), 4.24–3.96 (24H, m, >C*H*-, -C*H*$_2$O-), 3.86–3.76 (8H, m, -C*H*$_2$O-), 3.70–3.60 (8H, m, -C*H*$_2$O-), 3.60–3.53 (8H, m, -C*H*$_2$O-, >CHC*H*$_2$-), 3.37–3.17 (8H, m, -C*H*$_2$O-), 3.17–2.88 (8H, m, -C*H*$_2$O-), 2.80–2.65 (4H, m, -C*H*$_2$O-), 2.25 (12H, s, C*H*$_3$) ppm.^{13}C NMR (75 MHz, CDCl$_3$): δ 168.3 (4C, C═O), 165.3 (4C, ═*C*O-), 153.0 (8C, arom. C), 144.9 (4C, arom. C), 140.5 (4C, arom. C), 128.9, 128.3, 128.1, 127.7, 127.3, 127.2, 126.6, 125.6 (40C, arom. *C*H), 115.6, 115.5 (16C, arom. *C*H), 102.9 (4C, >C═), 94.9 (4C, >C<), 70.8, 70.6, 70.5, 70.2, 69.8, 69.4, 68.0, 66.7, 66.4, 63.7 (32C, -*C*H$_2$O-), 62.0, 61.5 (4C, -CO$_2$*C*H$_2$-), 51.4, 49.9 (4C, >*C*H-), 14.8 (4C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{132}H_{144}O_{32}$ 2240.9641 (M$^+$); found 2240.9675.

[21.21]Paracyclophane $\mathbf{5_{(3)(2)}}$-*para*. R_f 0.44 (CHCl$_3$–MeOH = 95 : 5 v/v). Colorless amorphous. IR (CHCl$_3$): ν 1693 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.61–7.58 (4H, m, arom. H), 7.36–7.18 (16H, m, arom. H), 6.82–6.78 (8H, m, arom. H), 4.32 (2H, dt, *J* = 12.0, 4.8 Hz, -CO$_2$C*H*$_2$-), 4.21 (2H, dt, *J* = 12.0, 4.8 Hz, -CO$_2$C*H*$_2$-), 4.07 (2H, d, *J* = 7.2 Hz, >C*H*-), 4.01 (8H, t, *J* = 3.3 Hz, t, *J* = 3.3 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.80–3.72 (12H, m, -C*H*$_2$O-), 3.65 (4H, t, *J* = 4.2 Hz, -C*H*$_2$O-), 3.61–3.55 (6H, m, -C*H*$_2$O-), 3.30 (4H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 3.10–2.99 (4H, m, -C*H*$_2$O-), 2.80–2.75 (2H, m, -C*H*$_2$O-), 2.34 (6H, s, C*H*$_3$) ppm.^{13}C NMR (75 MHz, CDCl$_3$): δ 168.2 (2C, C═O), 165.4 (2C, ═*C*O-), 153.0 (4C, arom. C), 144.9 (2C, arom. C), 140.5 (2C, arom. C), 128.1, 127.7, 127.2, 127.18, 127.06, 126.5 (20C, arom. *C*H), 115.54, 115.47 (8C, arom. *C*H), 103.0 (2C, >C =), 94.8 (2C, >C<), 70.8, 70.6, 70.3, 69.9, 69.8, 69.7, 69.4, 68.04, 67.99 (20C, -*C*H$_2$O-, -*C*H$_2$OArOC*H*$_2$-), 62.7 (2C, -CO$_2$*C*H$_2$-), 51.4 (2C, >*C*H-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{70}H_{80}O_{18}$ 1208.5345 (M$^+$); found 1208.5341.

Diploid of $\mathbf{5_{(3)(2)}}$-*para*. R_f 0.30 (CHCl$_3$–MeOH = 95 : 5 v/v). Colorless amorphous. IR (CHCl$_3$): ν 1695 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.62–7.59 (8H, m, arom. H), 7.53–7.15 (32H, m, arom. H), 6.85–6.76 (16H, m, arom. H) 4.34–4.28 (4H, m, -CO$_2$C*H*$_2$-), 4.26–4.18 (4H, m, -CO$_2$C*H*$_2$-), 4.10–3.95 (20H, m, >C*H*-, -C*H*$_2$OArOC*H*$_2$-), 3.85–3.71 (24H, m, -C*H*$_2$O-), 3.69–3.61 (12H, m, -C*H*$_2$O-), 3.61–3.55 (8H, m, -C*H*$_2$O-), 3.30 (8H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 3.10–3.01 (8H, m, -C*H*$_2$O-), 2.77–2.70 (4H, m, -C*H*$_2$O-), 2.34 (3H, s, C*H*$_3$), 2.32 (6H, s, C*H*$_3$)–2.27 (3H, s, C*H*$_3$) ppm.^{13}C NMR (75 MHz, CDCl$_3$): δ 165.3 (4C, C═O), 165.3 (4C, ═*C*O-), 153.0 (8C, arom. C), 145.0 (4C, arom. C), 140.5 (4C, arom. C), 128.1, 127.7, 127.2, 127.2, 126.7, 125.6 (40C, arom. *C*H), 115.5 (16C, arom. *C*H), 103.0 (4C, >C =), 94.8 (4C, >C<), 70.8, 70.6, 70.5, 70.2, 69.8, 69.4, 69.0, 68.0 (40C, -*C*H$_2$O-), 62.6 (4C, -CO$_2$*C*H$_2$-), 51.3 (4C, >*C*H-), 14.7 (4C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{140}H_{160}O_{36}$ 2417.0689 (M$^+$); found 2417.0669.

[24.24]Paracyclophane $\mathbf{5_{(3)(3)}}$-*para*. R_f 0.42 (CHCl$_3$–MeOH = 96 : 4 v/v). Colorless amorphous. IR (CHCl$_3$): ν 1692 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.62–7.59 (4H, m, arom. H), 7.37–7.18 (16H, m, arom. H), 6.83–6.79 (8H, m, arom. H), 4.32–4.27 (2H, m, -CO$_2$C*H*$_2$-), 4.21–4.18 (2H, m, -CO$_2$C*H*$_2$-), 4.08–4.02 (10H, m, >C*H*-, -C*H*$_2$OArOC*H*$_2$-), 3.89–3.76 (8H, m, -C*H*$_2$O-), 3.76–3.61 (18H, m, -C*H*$_2$O-), 3.61–3.51 (4H, m, -C*H*$_2$O-), 3.30–3.29 (4H, m, -C*H*$_2$O-), 3.06 (4H, t, *J* = 8.1 Hz, -C*H*$_2$O-), 2.76–2.73 (2H, m, -C*H*$_2$O-), 2.32 (6H, s, C*H*$_3$) ppm.^{13}C NMR (75 MHz, CDCl$_3$): δ 168.2 (2C, C═O), 165.4 (2C, ═*C*O-), 153.0 (4C, arom. C), 145.0 (2C, arom. C), 140.5 (2C, arom. C), 128.1, 127.7, 127.25, 127.2, 127.1, 126.5 (20C, arom. *C*H), 115.5 (8C, arom. *C*H), 103.0 (2C, >C =), 94.8 (2C, >C<), 70.8, 70.6, 70.2, 69.8, 69.4, 69.3 (20C, -*C*H$_2$O-), 68.0 (4C, -*C*H$_2$OAr), 62.7 (2C, -CO$_2$*C*H$_2$-), 51.4 (2C, >*C*H-), 14.7 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{74}H_{88}O_{20}$ 1296.5869 (M$^+$); found 1296.5846.

[12.12]Paracyclophane $\mathbf{7_{(1)}}$-*para*. R_f 0.49 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1693 (C═O), 1643 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.53–7.50 (4H, m, arom. H), 7.34–7.21 (16H, m, arom. H), 6.94–6.80 (4H, m, arom. H), 6.66–6.60 (4H, m, arom. H), 4.54–4.48 (2H, m, -CO$_2$C*H*$_2$-), 4.33–4.27 (2H, m, -CO$_2$C*H*$_2$-), 4.07 (4H, t, *J* = 5.0 Hz, -C*H*$_2$OArOC*H*$_2$-), 3.79–3.76 (2H, m, >C*H*-), 2.40–2.37 (4H, m, -C*H*$_2$Ar-), 2.32 (6H, s, C*H*$_3$), 1.33–1.27 (9H, m, -C*H*$_2$-), 0.98–0.96 (7H, m, -C*H*$_2$-) ppm.^{13}C NMR (75 MHz, CDCl$_3$): δ 167.2 (2C, C═O), 165.8 (2C, ═*C*O-), 152.8 (2C, arom. C), 145.2 (2C, arom. C), 140.8 (2C, arom. C), 139.7 (2C, arom. C), 128.1, 127.7, 127.0, 126.6, 126.1 (20C, arom. *C*H), 115.3 (8C, arom. *C*H), 108.0 (2C, >C =), 95.4 (2C, >C<), 66.5 (2C, -*C*H$_2$OAr), 61.8 (2C, -CO$_2$*C*H$_2$-), 48.6 (2C, >*C*H-), 35.1, 31.7, 30.8, 29.0, 25.9 (10C, -*C*H$_2$-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{62}H_{64}O_8$ 936.4601 (M$^+$); found 936.4615.

Diploid of $\mathbf{7_{(1)}}$-*para*. R_f 0.24 (CHCl$_3$). Colorless amorphous. IR (CHCl$_3$): ν 1690 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.53–7.51 (8H, m, arom. H), 7.32–7.10 (32H, m, arom. H), 6.98–6.49 (16H, m, arom. H), 4.55–4.31 (8H, m, -CO$_2$C*H*$_2$-), 4.16–4.00 (8H, m, -CH_2OArOCH_2-), 3.80–3.701 (4H, m, >C*H*-), 2.38–2.20 (20H, m, -CH_2Ar-, CH_3), 1.33–1.27 (18H, m, -CH_2-), 0.98–0.96 (14H, m, -CH_2-) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2 (4C, C═O), 165.8 (4C, ═*C*O-), 152.8 (4C, arom. C), 145.2 (4C, arom. C), 140.8 (4C, arom. C), 139.7 (4C, arom. C), 128.1, 127.7, 127.1, 126.6, 126.2 (40C, arom. *C*H), 115.5, 115.3 (16C, arom. *C*H), 108.0 (4C, >C =), 95.4 (4C, >C<), 66.7, 66.4 (4C, -*C*H$_2$OAr), 62.5, 61.8 (4C, -CO$_2$*C*H$_2$-), 48.6 (4C, >*C*H-), 35.1, 31.7, 31.0, 29.0, 25.9 (20C, -*C*H$_2$-), 14.6 (4C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{124}H_{128}O_{16}$ 1873.9236 (M$^+$); found 1872.9220.

[15.15]Paracyclophane 7$_{(2)}$-*para*. *R*$_f$ 0.57 ($CHCl_3$). Colorless amorphous. IR ($CHCl_3$): ν 1689 (C═O), 1645 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.50 (4H, m, arom. H), 7.33–7.18 (16H, m, arom. H), 6.90–6.85 (4H, m, arom. H), 6.75–6.73 (4H, m, arom. H), 4.42–4.35 (2H, m, -CO$_2$CH_2-), 4.20–4.15 (2H, m, -CO$_2$CH_2-), 3.96 (4H, t, *J* = 4.8 Hz, -CH_2OArOCH_2-), 3.81–3.73 (10H, m, >C*H*-, -CH_2O-), 2.31–2.26 (10H, m, -CH_2ArCH_2-, CH_3), 1.40–1.20 (8H, m, -CH_2-), 1.00–0.90 (8H, m, -CH_2-) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9 (2C, C═O), 165.8 (2C, ═*C*O-), 153.0 (2C, hyd-arom. C), 145.3 (2C, hyd-arom. C), 140.8 (2C, arom. C), 139.7 (2C, arom. C), 128.1, 128.0, 127.7, 127.0, 126.7, 126.1 (20C, arom. *C*H), 115.4 (8C, arom. *C*H), 108.0 (2C, >C═), 95.2 (2C, >C<), 69.7, 69.6, 67.9 (6C, -*C*H$_2$O-), 62.5 (2C, -CO$_2$*C*H$_2$-), 48.8 (2C, >*C*H-), 35.2, 31.6, 31.0, 29.5, 25.9 (10C, -*C*H$_2$-), 14.6 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{66}H_{72}O_{10}$ 1024.5125 (M$^+$); found 1024.5048.

Diploid of 7$_{(2)}$-*para*. *R*$_f$ 0.28 ($CHCl_3$–MeOH = 98 : 2 v/v). Colorless amorphous. IR ($CHCl_3$): ν 1690 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.50 (8H, m, arom. H), 7.46–7.03 (32H, m, arom. H), 7.00–6.79 (16H, m, arom. H), 4.41–4.14 (8H, m, -CO$_2$CH_2-), 4.09–3.90 (8H, m, -CH_2OArOCH_2-), 3.90–3.66 (20H, m, >C*H*-, -CH_2O-), 2.35–2.24 (20H, m, -CH_2ArCH_2-, CH_3), 1.40–1.20 (16H, m, -CH_2-), 1.00–0.90 (16H, m, -CH_2-) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4 (4C, C═O), 165.7 (4C, ═*C*O-), 153.0 (4C, arom. C), 145.3 (4C, arom. C), 140.8 (4C, arom. C), 140.0, 139.8 (4C, arom. C), 128.7, 128.1, 127.7, 127.2, 127.1, 126.8, 126.2, 125.7, 125.5 (40C, arom. *C*H), 115.5, 115.4 (16C, arom. *C*H), 108.1 (4C, >C =), 95.1 (4C, >C<), 69.8, 69.7, 69.5, 67.9 (12C, -*C*H$_2$O-), 62.5 (4C, -CO$_2$*C*H$_2$-), 49.0 (4C, >*C*H-), 35.2, 31.5, 31.0, 29.4, 28.9, 25.9 (20C, -*C*H$_2$-), 14.8 (4C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{132}H_{144}O_{20}$ 2050.0285 (M$^+$); found 2049.0256.

[18.18]Paracyclophane 7$_{(3)}$-*para*. *R*$_f$ 0.53 ($CHCl_3$–MeOH = 97 : 3 v/v). Colorless amorphous. IR ($CHCl_3$): ν 1690 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.51 (4H, m, arom. H), 7.34–7.18 (16H, m, arom. H), 6.94–6.91 (4H, m, arom. H), 6.81–6.78 (4H, m, arom. H), 4.33–4.17 (4H, m, -CO$_2$CH_2-), 4.02 (4H, t, *J* = 4.9 Hz, -CH_2OArOCH_2-), 3.79 (3H, t, *J* = 4.8 Hz, -CH_2O-), 3.79 (3H, m, >CH-), 3.75–3.60 (12H, m, -CH_2O-), 2.34–2.25 (4H, m, -CH_2ArCH_2-), 2.28 (6H, s, -CH_3), 1.33-1.27 (9H, m, -CH_2-), 1.10–0.90 (7H, m, -CH_2-) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6 (2C, C═O), 165.7 (2C, ═*C*O-), 153.0 (2C, arom. C), 145.3 (2C, arom. C), 140.8 (2C, arom. C), 139.8 (2C, arom. C), 128.1, 127.7, 127.1, 126.7, 126.2 (20C, arom. *C*H), 115.6, 115.5 (8C, arom. *C*H), 108.0 (2C, >C =), 95.1 (2C, >C<), 70.8, 70.6, 69.8, 69.4, 68.1 (10C, -*C*H$_2$O-), 62.6 (2C, -CO$_2$*C*H$_2$-), 48.9 (2C, >*C*H-), 35.2, 31.5, 31.0, 29.5, 25.9 (10C, -*C*H$_2$-), 14.7 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{70}H_{80}O_{12}$ 1112.5650 (M$^+$); found 1112.5647.

Diploid of 7$_{(3)}$-*para*. *R*$_f$ 0.39 ($CHCl_3$–MeOH = 97 : 3 v/v). Colorless amorphous. IR ($CHCl_3$): ν 1686 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.51 (8H, m, arom. H), 7.34–7.15 (32H, m, arom. H), 7.00–6.77 (16H, m, arom. H), 4.31–4.19 (8H, m, -CO$_2$CH_2-), 4.02 (8H, t, *J* = 4.9 Hz, -CH_2OArOCH_2-), 3.79 (8H, t, *J* = 4.8 Hz, -CH_2O-), 3.79 (4H, m, >CH-), 3.73–3.60 (24H, m, -CH_2O-), 2.36–2.16 (8H, m, -CH_2ArCH_2-), 2.25 (12H, s, -CH_3), 1.33–1.26 (18H, m, -CH_2-), 1.10–0.90 (14H, m, -CH_2-) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6 (4C, C═O), 165.7 (4C, ═*C*O-), 153.0 (4C, arom. C), 145.3 (4C, arom. C), 140.8 (4C, arom. C), 139.8 (4C, arom. C), 128.1, 127.7, 127.1, 126.7, 126.2 (40C, arom. *C*H), 115.6, 115.5 (16C, arom. *C*H), 108.0 (4C, >C =), 95.1 (4C, >C<), 70.9, 70.6, 69.8, 69.5, 68.1 (20C, -*C*H$_2$O-), 62.6 (4C, -CO$_2$*C*H$_2$-), 48.9 (4C, >*C*H-), 35.2, 31.6, 31.0, 29.5, 25.9 (20C, -*C*H$_2$-), 14.8, 14.7 (4C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{140}H_{160}O_{24}$ 2226.1334 (M$^+$); found 2225.1331.

[16.16]Paracyclophane 9. *R*$_f$ 0.81 ($CHCl_3$). Colorless amorphous. IR ($CHCl_3$): ν 1686 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.51 (4H, m, arom. H), 7.31–7.19 (16H, m, arom. H), 7.01–6.92 (8H, m, arom. H), 4.16–4.04 (4H, m, -CO$_2$CH_2-), 3.80–3.70 (2H, m, >C*H*-), 2.54–2.50 (4H, m, -CH_2ArCH_2-), 2.32 (6H, s, -CH_3), 2.40–2.25 (4H, m, -CH_2ArCH_2-), 1.75–1.50 (8H, m, -CH_2-), 1.50–1.10 (20H, m, -CH_2-), 1.10–0.80 (8H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2 (2C, *C*═O), 166.0 (2C, ═*C*O-), 145.3 (4C, arom. C), 140.9 (2C, arom. C), 139.8 (2C, arom. C), 128.2, 128.0, 127.6, 127.0, 126.7, 126.2 (28C, arom. *C*H), 108.3 (2C, >C =), 95.0 (2C, >C<), 63.5 (2C, -*C*H$_2$O-), 48.9 (2C, >*C*H-), 35.4, 35.3 (4C, -*C*H$_2$Ar*C*H$_2$), 31.8, 31.2, 31.1, 29.6, 29.0, 28.7, 26.1 (18C, -*C*H$_2$-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{72}H_{84}O_6$ 1044.6268 (M$^+$); found 1044.6274.

Diploid of 9. *R*$_f$ 0.74 ($CHCl_3$). Colorless amorphous. ν 1684 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59–7.51 (8H, m, arom. H), 7.32–7.12 (32H, m, arom. H), 7.09–6.92 (16H, m, arom. H), 4.31–3.91 (8H, m, -CO$_2$CH_2-), 3.80–3.65 (4H, m, >C*H*-), 2.69–2.40 (8H, m, -CH_2ArCH_2-), 2.32–2.23 (8H, m, -CH_2ArCH_2-), 2.25 (6H, s, -CH_3), 2.23 (6H, s, -CH_3), 1.75–1.48 (16H, m, -CH_2-), 1.48–1.10 (40H, m, -CH_2-), 1.10–0.80 (16H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2 (4C, *C*═O), 166.1 (4C, ═*C*O-), 145.4 (8C, arom. C), 140.9 (4C, arom. C), 139.8 (4C, arom. C), 128.7, 128.2, 128.1, 127.7, 127.1, 126.8, 126.2 (56C, arom. *C*H), 108.4 (4C, >C =), 95.1 (4C, >C<), 63.5 (4C, -*C*H$_2$O-), 49.0 (4C, >*C*H-), 35.4, 35.3 (8C, -*C*H$_2$Ar*C*H$_2$), 31.8, 31.5, 31.3, 31.1, 29.6, 29.4, 29.1, 28.8, 26.2, 26.1 (36C, -*C*H$_2$-), 14.5 (4C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{144}H_{168}O_{12}$ 2090.2570 (M$^+$); found 2089.2532.

[12.12]Paracyclophane 5$_{(1)(1)}$-Cl,*para*. *R*$_f$ 0.21 ($CHCl_3$). Colorless microcrystals (from $CHCl_3$–hexane), m.p. 152–153 °C. IR ($CHCl_3$): ν 1699 (C═O), 1647 (C═C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49–7.46 (4H, m, arom. H), 7.38–7.18 (12H, m, arom. H), 6.71–6.68 (8H, s, arom. H), 4.49–4.44 (2H, m, -CO$_2$CH_2-), 4.35–4.30 (2H, m, -CO$_2$CH_2-), 4.06–3.99 (6H, m, >C*H*-, -CH_2OArOCH_2-), 3.76 (4H, t, *J* = 4.4 Hz, -OCH_2-), 3.59 (2H, dt, *J* = 9.5, 2.6 Hz, -OCH_2-), 3.19–3.13 (2H, m, -OCH_2-), 3.13–2.90 (4H, m, -OCH_2-), 2.31 (6H, s, CH_3) ppm.^{13}C NMR (75 MHz, CDCl$_3$): δ 168.39 (2C, C=O), 168.35 (2C, =CO-), 153.0, 152.9 (4C, arom. C), 143.0 (2C, arom. C), 138.6 (2C, arom. C), 133.9 (2C, arom. C), 133.3 (2C, arom. C), 128.6, 128.4, 127.8, 127.6 (16C, arom. *C*H), 115.8, 115.7, 115.6 (8C, arom. *C*H), 103.1 (2C, >C =), 93.9 (2C, >C<), 69.5, 69.0, 67.9, 66.5 (8C, -*C*H$_2$O-), 62.1 (2C, -CO$_2$*C*H$_2$-), 51.2 (2C, >*C*H-), 14.5 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{58}H_{52}O_{12}Cl_4$ 1082.2198 (M$^+$); found 1080.2236.

X-ray analysis of [22]paracyclophane $3_{(8)(1)}$-*para*

A colorless block crystal of $C_{54}H_{56}O_8$ having approximate dimensions of 0.90 × 0.80 × 0.70 mm was mounted on a glass fiber. All measurements were made on a diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range $30.12 < 2\theta < 34.17°$ corresponded to a C-centered monoclinic cell with dimensions: a = 14.5489(17) Å, b = 31.423(9) Å, c = 11.6090(13) Å, β = 118.413(8)°, V = 4668.0(14) Å^3, Z = 4, F.W. = 833.03, the calculated density is 1.185 g cm^{-3}, the space group was determined to be $C2/c$ (#15). The data were collected at a temperature of 25 ± 1 °C using the ω scan technique to a maximum 2θ value of 55.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.27° with a take-off angle of 6.0°. Scans of $(1.73 + 0.30 \tan \theta)°$ were made at a speed of 16.0° min^{-1} (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 235 mm. The computer-controlled slits were set to 3.0 mm (horizontal) and 3.0 mm (vertical). Of the 6419 reflections that were collected, 5364 were unique (R_{int} = 0.124). The intensities of three representative reflections were measured after every 0 reflections. Over the course of data collection, the standards decreased by 36.5%. A polynomial correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.784 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.735 to 0.947. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction[24] was applied (coefficient = 245.440002). The structure was solved by direct methods, SIR92[25] and expanded using Fourier techniques, DIRDIF99.[26] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 2891 observed reflections and 309 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of R^1 = 0.0878 and wR^2 = 0.1042. The standard deviation of an observation of unit weight was 4.75. The weighting scheme was based on counting statistics. Plots of $\Sigma_w (|Fo| - |Fc|)^2$ *versus* $|Fo|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.86 and −0.77 e−/Å^3, respectively. The crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC 769197.†

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