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Stereoselective Synthesis of Meta- and Three-bridged Cyclophanes with Intramolecular [2 + 2] Photocycloaddition by Using the Steric Effect of Methoxyl Group[1)]

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Key Words: Cyclophane; stereoselectivity; conformation; regioisomer; photocycloaddition; torsional angle

Abstract: *Dimethoxy[n.2]metacyclophanes 9 (n=2, 3, 4, 5, and 6) and 10 were stereoselectively obtained in 61 - 87% yields by means of [2 + 2] photocycloaddition. Their conformations, when n=3 - 6, are exclusively of syn, while the dimethoxy[2.2]metacyclophane exists as a mixture of syn and anti isomers with the ratio of 4:3. After their Birch reduction, [n.4]metacyclophanes 11 (n=2 - 6) were successfully obtained in 59 - 94% yields. Their conformations, when n=2 - 4 are of anti or n=5 and 6 are of syn. Dihydroxy[n.4]metacyclophanes 16 (n=2 - 6) and dihydroxy[n.2]metacyclophanes 17 (n=4, 5, and 6) were obtained in 93 - 100% and 78 - 95% yields, respectively, after the demethylation of methoxyl groups. The conformation of 16 and 17 is the same as that of corresponding dimethoxymetacyclophanes. The acidity of phenolic group in 16 and 17 is low like monomeric phenol. After olefination and vinylation via triflate 18, the metacyclophanes 19 and 21 gave the three-bridged [n.2.2](1,3,4)cyclophanes 20 and 22 stereoselectively in 65 - 67% and 42 - 86% yields, respectively, under photoirradiation. The two cyclobutane rings of 20 and 22 face oppositely each other as confirmed by NOESY experiments and the structures are most stable among possible four ones according to the MM2 calculation. And also, three-bridged phanes 22 were converted to [n.4.4](1,3,4)cyclophanes 23 in 61 - 79% yields by the Birch reduction. Another regioisomeric three-bridged [n.2.2](1,3,5)cyclophanes 28 were also obtained stereoselectively as only one isomer in 31 - 78% yields with photocycloaddition by using the steric effect of methoxyl group. The configuration of cyclobutane rings relative to methoxyl groups was confirmed to be anti by NOESY experiments. The torsional angle of methoxyl groups on cyclophanes was estimated from ^{13}C NMR chemical shifts. The angles of metacyclophanes 9, 10, and 11 are 10 - 25° and those of three-bridged cyclophanes 28 are about 54°, which is the largest one among those ever reported.*

Introduction

Cyclophanes have been extensively gathering much attentions to the synthesis of highly strained and fascinating molecules.[2)] In this field, intramolecular [2 + 2] photocycloaddition is one of the excellent synthetic methods for ortho-[3)] meta-,[4)] para-,[5)] and three-bridged[6)] cyclophanes. Styrene derivatives[7)] are used as convenient starting materials for this synthesis (see Chart 1). The products, cyclophanes fused by cyclobutane ring, show unique structural features concerned with the cyclobutane methine configuration and the aromatic ring conformation.[7)] And at the same time, those cyclophanes have attracted much interest on their strain energies and aromatic ring interactions. Recently, we preliminarily reported that an *o*-methoxyl group to a vinyl one of the starting styrene derivatives effectively controls the conformation of the vinyl group and makes the

cyclobutane ring direct exclusively *anti* to the methoxyl group.[8] On the basis of these results, we investigated the steric effect of methoxyl group on the conformer distributions of metacyclophanes which can be readily determined by using the $\Delta\delta$ value defined by Krois and Lehner.[9] Moreover, we studied the detailed structural investigation for the behavior of methoxyl group on cyclophane skeletons; *i.e.*, its effect on the cyclobutane ring cleavage, its torsional angle to the benzene nucleus, and its transformation toward multi-bridged cyclophanes. In this paper we describe some findings of our recent research in this field.

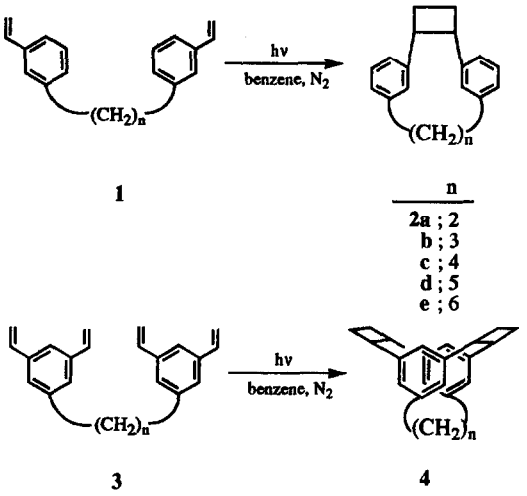


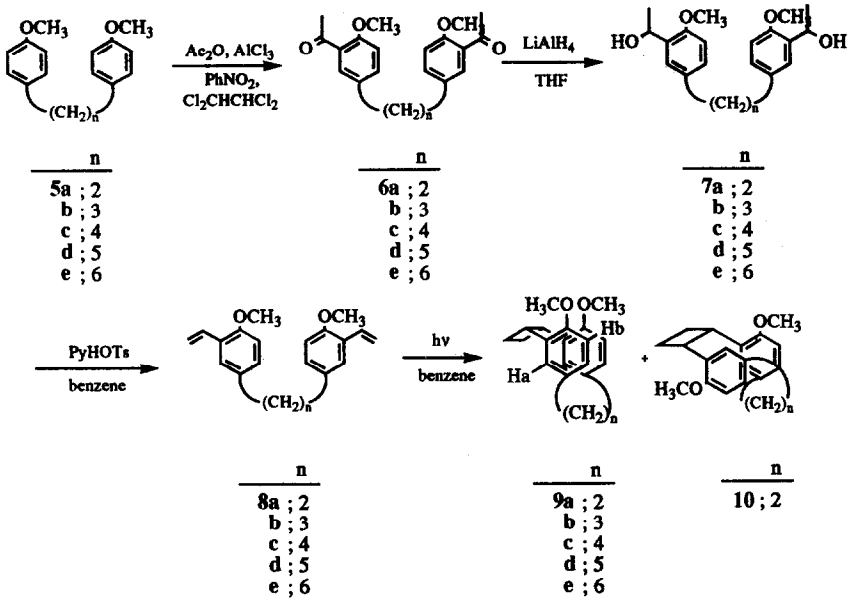
Chart 1.

Results and Discussion

Synthesis. *1) Dimethoxy[n.2]- and dimethoxy[n.4]metacyclophanes.*

The synthetic route of dimethoxy[n.2]metacyclophanes is shown in Scheme 1. α,ω-Bis(*p*-methoxyphenyl)alkanes **5** were used as starting materials.[10] Diketones **6** were obtained by treatment with acetic anhydride and $AlCl_3$ in nitrobenzene and 1,1,2,2-tetrachloroethane in 58 - 93% yields.[11] Diols **7** were obtained by the reduction with $LiAlH_4$ in quantitative yields. Diolefins **8** were obtained by the dehydration with pyridinium *p*-toluenesulfonate in 72 - 92% yields. [2 + 2] Photocycloaddition of diolefins **8** was carried out by the irradiation with a 400 W high-pressure Hg lamp (Pyrex filter) in benzene.[6,12,13] After evaporation, [n.2]metacyclophanes **9b**, **9c**, **9d**, and **9e** were isolated in 61 - 87% yields. [2.2]Metacyclophanes **9a** and **10**, however, were found to be an equilibrium mixture, so that they could not be separated with either HPLC or TLC. But the ^1H NMR peaks for each isomer could be detected separately.

Birch reduction is useful procedure for the cyclobutane ring opening.[14] The reduction of [n.2]metacyclophanes **9** and **10** to [n.4]metacyclophanes **11** was attempted by previously reported method.[15] It was performed with **9** and **10**, Na, liq. NH_3/THF, and EtOH at -60 °C as shown in Scheme 2. The product distribution of this reaction is summarized in Table 1. [n.4]Metacyclophanes **11** were obtained in 59 - 94%



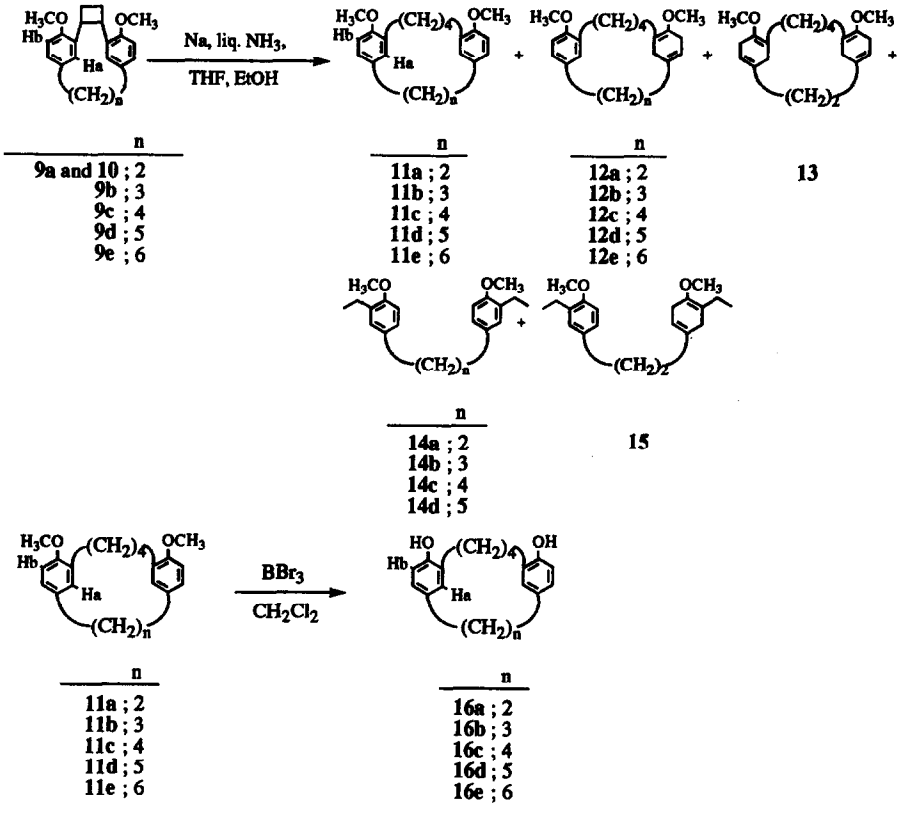
Scheme 1.

yields as main products. Interestingly, cyclophanes **12** and **13**, which were further reduced products on benzene ring, were obtained in 4.4 - 26% and 6.9% yields, respectively, and ring-opening compounds **14** and **15** were obtained in 0.2 - 9.7 and 7.3% yields, respectively, as minor products.[15] It is well known that anisole derivatives were readily reduced on benzene ring.[16,17] Accordingly, these results suggest that the reduction pathways of cyclobutane ring and anisole moiety competed each other.

2) Dihydroxy[n.2]- and dihydroxy[n.4]metacyclophanes by the cleavage of CH_3O groups.

The synthetic route to dihydroxy[n.2]metacyclophanes **17** is shown in Scheme 3. Anisole derivatives **9** were treated with excess of boron tribromide at r.t. for 12 h.[18] Phenol derivatives **17b** and **c** were obtained in 95 and 93% yields, respectively. On the other hand, **9c** did not give any cyclophane products under the same conditions. Since the reaction gave complex product mixture, we made the conditions mild. Thus, **9c** was carefully treated with an equimolar amount of BBr_3 at 0 °C for 2 h to give **17a** in 78% yield. Unfortunately, **9a**, **9b**, and **10** did not give any phenol products.

The same cleavage of [n.4]metacyclophanes **11** is shown in Scheme 2. They were treated with an equimolar amount of BBr_3 at r.t. for 12 h. Phenol derivatives **16** were obtained in 93 - 100% yields.



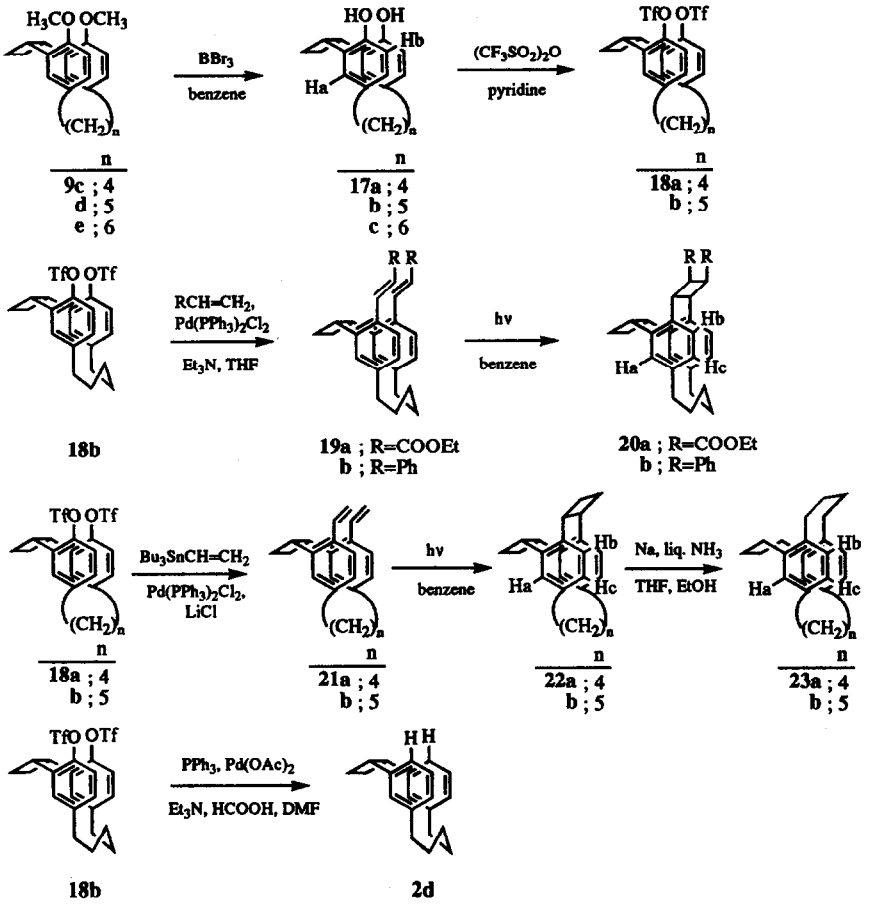
Scheme 2.

Table 1. The product distribution after the Birch reduction of cyclophanes **9** and **10**

	Yield of product (%)				
Compd	**11**	**12**	**13**	**14**	**15**
9a/10	62	8.7	6.9	9.7	7.3
9b	62	26	---	1.8	---
9c	84	5.6	---	0.2	---
9d	94	4.4	---	1.4	---
9e	59	18	---	---	---

3) [n.2.2](1,3,4)-, [n.4.4](1,3,4)-, and [n.2.2](1,3,5)Cyclophanes.

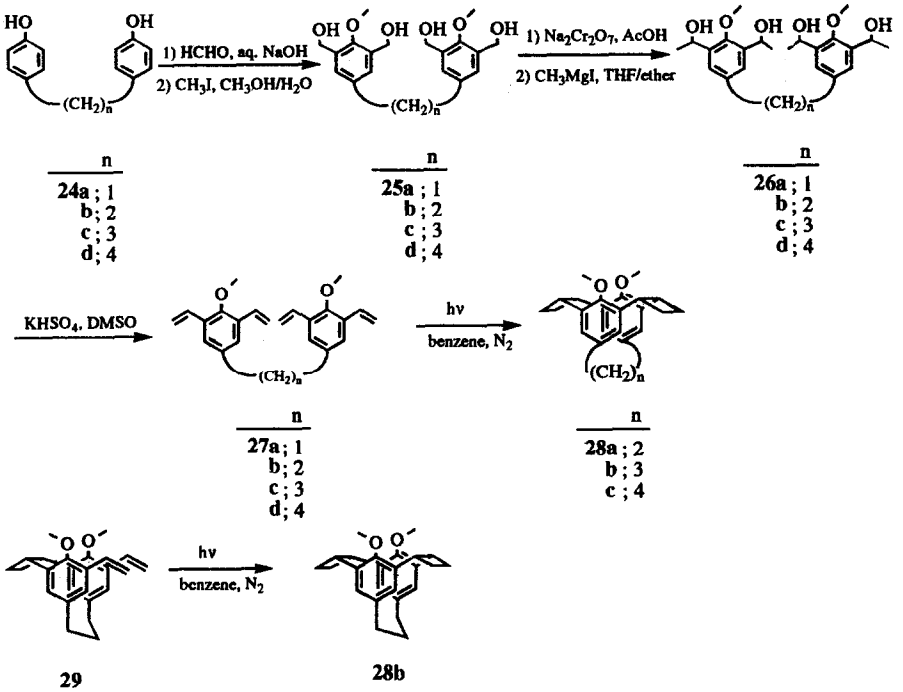
We developed two regioselective synthetic routes toward three-bridged cyclophanes.[19] One is a multi-step synthesis by means of olefination and photocycloaddition. The other is a one-step photochemical synthesis of polyvinylated precursors. The synthetic route to [n.2.2](1,3,4)-, and [n.4.4](1,3,4)cyclophanes was shown in Scheme 3. Triflates **18a** and **b** were obtained from the reactions of **17a** and **b** with $(CF_3SO_2)_2O$ in 87 and 91% yields, respectively. Under the reported olefination conditions,[20,21,22] however, olefins **19** were



Scheme 3.

obtained from **18b** in very low yields. This result suggests that the reactivity of leaving groups on bulky cyclophane skeleton is very low even though they are trifluoroacetoxyl group. So we must make the conditions rather sever ones; *i.e.*, triflate **18b** (34 mmol dm^{-3}) was treated with $Pd(PPh_3)_2Cl_2$ (0.28 equiv.), Et_3N (43 equiv.), and a corresponding olefin (ethyl acrylate or styrene, 14 equiv.) in DMF in a sealed ampule at 130 °C for 24 h. Yields of **19a** and **b** now increased to 88 and 89%, respectively. Olefin moieties in **19a** and **b** were assigned to be of *trans* configuration according to IR and ^1H NMR (see Experimental). Olefins **19a** and **b** were irradiated in benzene to give three-bridged [n.2.2](1,3,4)cyclophanes **20a** and **b** in 67 and 65% yields, respectively.

Since the vinylation of triflates **18** under the reported conditions also gave only the mono-vinyl derivatives,[23,24] the reaction conditions were modified to rather severer ones; *i.e.*, triflates **18a** and **b** (0.20 mol dm^{-3}) were treated with $Pd(PPh_3)_2Cl_2$ (16 mol%), $Bu_3SnCH{=}CH_2$ (1.2 - 2 equiv.),[25] and LiCl (5



Scheme 4.

equiv.) in dry DMF at 100 °C for 2 h. Yields of olefins **21a** and **b** were 78 and 79%, respectively. [2 + 2] Photocycloaddition of olefins **21a** and **b** was performed with a high-pressure Hg lamp (Pyrex filter) in benzene. Three-bridged [n.2.2](1,3,4)cyclophanes **22a** and **b** were obtained in 42 and 86% yields, respectively. And also, triflate **18b** was successfully converted to [5.2]metacyclophane **2d** with $Pd(OAc)_2$, HCO_2H, PPh_3, and Et_3N in DMF in 68% yield as shown in Scheme 3.[26] The reduction of [n.2.2](1,3,4)cyclophanes **22** to [n.4.4](1,3,4)cyclophanes **23** was carried out under the same conditions as that of [n.2]metacyclophanes (see Scheme 2). Cyclophanes **23a** and **b** were obtained in 61 and 79% yields, respectively.

By using the second synthetic method, another three-bridged cyclophanes [n.2.2](1,3,5)cyclophanes **28** were prepared as shown in Scheme 4. Thus, α,ω-bis(*p*-hydroxyphenyl)alkanes **24** were converted to **25** by means of hydroxymethylation with formaldehyde in 78 - 93% yields,[27] followed by the methylation with methyl iodide in MeOH/H_2O in 80 - 99% yields.[28] Tetrols **26** were prepared by the oxidation of **25** with $Na_2Cr_2O_7$ in 61 - 86% yields,[29] followed by Grignard reaction in THF/ether in 73 - 85% yields. Dehydration of tetrols **26** was carried out by $KHSO_4$ in DMSO to afford the desired olefins **27** in 43 - 47% yields.[6] The photocycloaddition of **27** was performed with a high-pressure Hg lamp in benzene. Cyclophanes **28** were gradually decomposed under irradiation, so that their yields decreased after the maximum reached in about 12 h under the conditions applied. After column chromatography, we obtained the desired three-bridged [n.2.2](1,3,5)cyclophanes **28a**, **b**, and **c** in 31%, 78%, and 68% yields, respectively. No isomer except an

intermediate **29** were found in this reaction mixture by a careful chromatographic analysis. Olefin **27a** did not give any cyclophanes, probably because the [1.2.2]cyclophane skeleton is highly strained.[30,31] Eventually here is a limitation of this photocycloaddition method.

Structure Analysis. *1) Dimethoxy[n.2]- and dimethoxy[n.4]metacyclophanes.*

Structural determination was carried out by NMR spectroscopy, including COSY, NOESY, ^{13}C, and DEPT experiments. The cyclobutane ring of metacyclophanes **9** and **10** was assigned to be of *cis* configuration by ^1H NMR chemical shifts (δ3.72 - 4.74) of cyclobutane methine protons, compared with **2d** (see Table 2).[5] The direction of the cyclobutane ring to the methoxyl group was easily confirmed by NOESY experiments; *i.e.*, the methylene protons of the cyclobutane ring clearly show an NOE interaction with Ha aromatic protons. The methoxyl groups possess NOE interactions with not only methine protons of the cyclobutane ring but also Hb aromatic protons. Accordingly, the cyclobutane ring is concluded to face to the opposite direction of the methoxyl groups as shown in Scheme 1. ^1H NMR chemical shifts of Ha and Hb aromatic protons are listed in Table 3. According to the molecular framework examination, dimethoxy[n.2]metacyclophanes **9** and **10** are apt to take *syn* conformation,[32,33] because the steric interaction between methoxyl group and cyclobutane methylene protons seems to be severe, if they take *anti* conformation. The conformation was experimentally determined by Δδ value of Krois and Lehner as shown in Table 3.[34,35,36,37] It was also confirmed by ^1H NMR spectrum, since *syn* conformer showed a symmetrical spectral pattern of C_s symmetry, while *anti* conformer did an unsymmetrical one due to C_1 symmetry. The anisotropic shielding effect of CH_3O group on the chemical shift of Hb was estimated by using 2,4-dimethylanisole as a model, whose proton chemical shifts corresponding to Ha and Hb are δ6.95 and 6.72, respectively. Hence, the chemical shift deviation due to the effect of CH_3O group is calculated 0.23 ppm. Dimethoxy[n.2]metacylophanes **9b-e** are concluded to be of *syn* conformation because the corrected Δδ value is positive and small numbers from 0.26 to 0.58. The strain energy of **9d** is 19.0 kcal/mol larger than that of *syn*-[5.2]metacyclophane **2d**, because of the repulsion between two methoxyl groups calculated by MM2 program (see Table 4). In general, the shorter bridged chain makes the larger ΔSE value. But, the ΔSE from **9b** (n=3) to **9e** (n=6), which take *syn* conformation, only differs about 8 kcal/mol. According to ^1H NMR and COSY spectra, [2.2]metacyclophanes **9a** and **10** formed a mixture of *syn*- and *anti*-isomers in the ratio of 4:3. *syn*-Dimethoxy[2.2]metacyclophane is highly strained, so that the repulsion between benzene rings overcomes the steric hindrance between the methoxyl groups and ethano bridge. In fact, the MM2 calculation shows that the ΔSE value of *syn*-[2.2]metacyclophane **9a** (ΔSE=53.1 kcal/mol) is larger than that of *syn*-[3.2]metacyclophane **9b** (ΔSE=33.3 kcal/mol) as shown in Table 4.

The conformation of [n.4]metacyclophanes **11** was obviously changed as shown in Table 3. In a case of [n.2]metacyclophanes **9** and **10**, *syn* and *anti* conformers could be separated and assigned with the symmetry of C_s and C_1, respectively, by ^1H NMR spectra due to the slow interconversion rate of benzene rings in NMR time scale.[9] Interestingly, these [n.4]metacyclo-phanes **11** show the rapid interconversion in NMR time scale between *syn* and *anti* conformation, judging from C_s symmetrical spectra of all cyclophanes **11**. Since Δδ values of **11d** and **e** are nearly zero and, on the other hand, those of **11a**, **b**, and **c** are clearly large from -0.36

Table 2. The chemical shifts of methine, methoxyl, and hydroxyl groups of cyclophanes[a)]

Compd	Ar-CH	CH_3O		OH
	δ_H	δ_H	δ_C	δ_H
2d[b)]	4.04			
9a	4.74	3.50	55.63	
10	3.72, 4.74	3.81, 3.85		
9b	4.64	3.55	55.52	
9c	4.57	3.59	55.40	
9d	4.52	3.62	55.37	
9e	4.43	3.63	55.30	
11a		3.80	56.10	
11b		3.79	55.87	
11c		3.79	55.90	
11d		3.76	55.62	
11e		3.79	55.66	
16a				4.53
16b				4.52
16c				4.52
16d				4.49
16e				4.53
17a	4.47			4.86
17b	4.43			5.03
17c	4.31			5.43
18a	4.57			
18b	4.51			
19a	4.57			
19b	4.56			
20a	4.12, 4.34			
20b	4.22, 4.41			
21a	4.50			
21b	4.40			
22a	4.11			
22b	4.07			
28a	4.45	3.44		
28b	4.49	3.39	62.58	
28c	4.44	3.40	62.49	
29	4.55	3.50		
anisole		3.80	55.10	
2,4-dimethylanisole		3.79		
2,4-dimethylphenol				4.58

a) In $CDCl_3$, using TMS as an internal standard. b) Reference 5.

to -1.22 (see Table 3), the major conformer of **11** changed from *syn* to *anti*, when n decreased. And also, MM2 calculations show that strain energies (SE) of **11a-e** decrease about 4.2 - 29.4 kcal/mol by the reduction from C_2 to C_4 bridge, compared with those (ΔSE) of [n.2]metacyclophanes **9** and **10**. These results suggest that the free rotation of benzene rings was attained after the Birch reduction of cyclobutane ring. So we concluded that the conformation of **11a**, **b**, and **c** is of *anti* and that of **11d** and **e** is of *syn*.

UV spectra of dimethoxy[n.2]- and -[n.4]metacyclophanes **9**, **10**, and **11** show almost the same absorption maxima (λ_{max}) at 230 and 280 nm except for **9a**, **9b**, and **10** (see Figure 1 and Experimental). The

Table 3. Conformational Analysis of Cyclophanes **9**, **10**, and **11**

Compound	Observed			Corrected	Assignment
	Ha	Hb	$\Delta\delta^{a)}$	$\Delta\delta^{b)}$	
9a	6.72	6.08	0.64	0.41	*syn*
10	4.38, 5.18	6.83, 6.89	-2.45 - -1.71	-2.68 - -1.94	*anti*
9b	7.05	6.24	0.81	0.58	*syn*
9c	7.04	6.32	0.72	0.49	*syn*
9d	7.04	6.43	0.61	0.38	*syn*
9e	6.98	6.49	0.49	0.26	*syn*
11a	5.85	6.84	-0.99	-1.22	*anti*
11b	6.25	6.73	-0.48	-0.71	*anti*
11c	6.59	6.72	-0.13	-0.36	*anti*
11d	6.85	6.71	0.14	-0.09	*syn*
11e	6.78	6.74	0.04	-0.19	*syn*

a) $\Delta\delta=\delta_{Ha} - \delta_{Hb}$. b) Corrected by -0.23 ppm, since 2,4-dimethylanisole gives the chemical shifts difference between Ha (3-) and Hb (6-) positions.

Table 4. Strain Energy (SE) of Cyclophanes[a)]

Compd	SE/kcal mol^{-1}	ΔSE/kcal mol^{-1}
2d[b),c)]	35.4	6.7
9a	81.8	53.1
9b	62.0	33.3
9c	57.0	28.3
9d	54.4	25.7
9e	53.6	24.9
11a	23.7	
11b	16.1	
11c	19.8	
11d	16.8	
11e	20.7	
16a	13.2	
16b	6.37	
16c	10.0	
16d	6.49	
16e	10.8	
17a	47.5	18.8
17b	44.7	16.0
17c	43.8	15.1
22a	93.4	36.0
22b	88.5	31.1
23a	25.4	
23b	27.2	
28a	150.0	92.6
28b	126.7	69.3
28c	121.4	64.0

a) Strain energy was calculated by MM2 program. Strain energy difference (ΔSE) is based on *cis*-diphenylcyclobutane (SE=28.7 kcal/mol) as a standard. b) Reference 15. c) *syn*-Conformer.

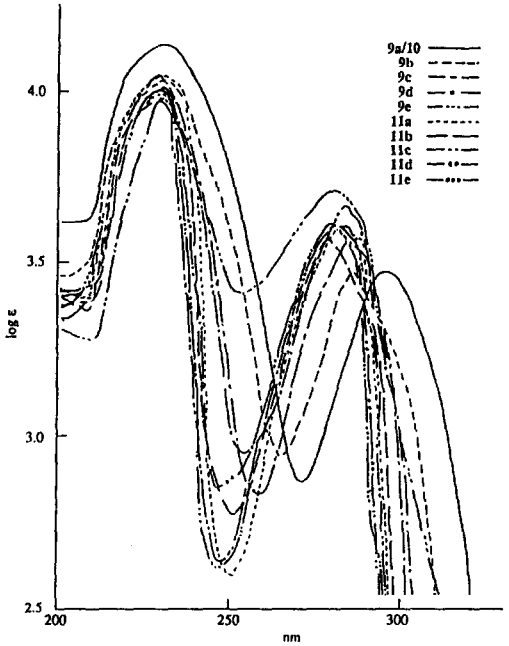


Fig. 1. Ultraviolet absorption spectra of dimethoxymetacyclophanes **9**, **10**, and **11**. 0.18 - 0.25 mol dm^{-3} in 1,4-dioxane at 25 °C.

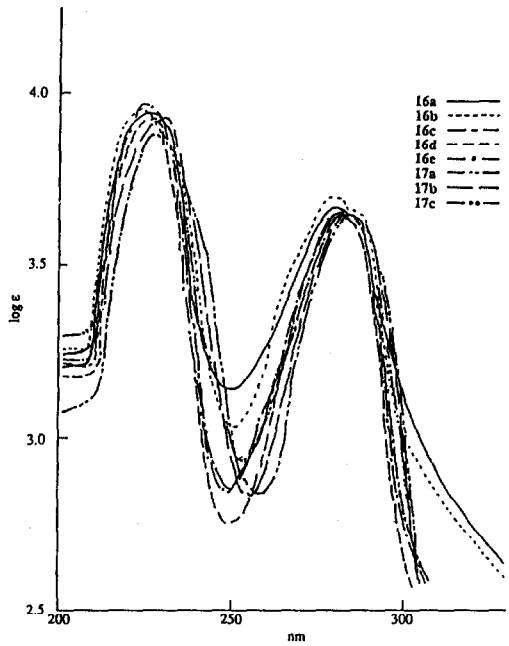


Fig. 2. Ultraviolet absorption spectra of dihydroxymetacyclophanes **16** and **17**. 0.17 - 0.25 mol dm^{-3} in 1,4-dioxane at 25 °C.

absorption bands of **9a/10** and **9b**, which have the face-to-face situation and high strain energy, shift to long wavelength region about 8 - 16 nm and the broaden.[40] And also the end of absorbance notable shifted to long wavelength region. These results suggest that [2.2]- and [3.2]metacyclophanes **9a**, **9b**, and **10** have the strongly interacted benzene rings as mentioned above. The log ε (λ=230 nm) of **9**,**10**, and **11** is nearly equal values in a range of 3.97 - 4.14.

2) Dihydroxy[n.2]- and dihydroxy[n.4]metacyclophanes.

The configuration of cyclobutane ring for dihydroxy[n.2]metacyclophanes **17** was assigned to be of *cis* on the basis of chemical shift of its methine protons (δ4.31 - 4.47, see Table 2). The conformation of **17a-c** was determined by the corrected Δδ value as shown in Table 5. The Δδ values are small and gather in a range from 0.15 to 0.34. Accordingly, we concluded that **17a-c** take *syn* conformation. So the structure of **17a-c** is same as corresponding dimethoxy[n.2]metacyclophanes **9** even after the cleavage of methoxyl groups. The MM2 calculation shows that the strain energies of **17a-c** decrease about 10 kcal/mol by demethylation of **9c-e** (see Table 4). Therefore, the strain energies of metacyclophanes increase about 10 kcal/mol by introducing OH groups on benzene rings and further increase another 10 kcal/mol by substituting CH_3 groups on OH groups.

Table 5. Conformational Analysis of Cyclophanes **16** and **17**

Compound	Observed Ha	Observed Hb	Observed $\Delta\delta^{a)}$	Corrected $\Delta\delta^{b)}$	Assignment
16a	5.82	6.75	-0.93	-1.19	*anti*
16b	6.23	6.67	-0.44	-0.70	*anti*
16c	6.57	6.65	-0.08	-0.34	*anti*
16d	6.79	6.63	0.16	-0.10	*syn*
16e	6.75	6.67	0.08	-0.18	*syn*
17a	6.95	6.35	0.60	0.34	*syn*
17b	6.95	6.46	0.49	0.23	*syn*
17c	6.91	6.50	0.41	0.15	*syn*

a) $\Delta\delta=\delta_{Ha}-\delta_{Hb}$. b) Corrected by -0.26 ppm, since 2,4-dimethylphenol gives the chemical shifts difference between Ha (3-) and Hb (6-) positions.

The conformation of [n.4]metacyclophanes **16** is shown in Table 5. $\Delta\delta$ values of **16d** and **e** are small from -0.10 to -0.18. On the other hand, those of **16a-c** are obviously large from -0.34 to -1.19. So we concluded that **16d-e** take *syn* conformation whereas **16a-c** take *anti* one. In this case, MM2 calculation also shows that the strain energies of **16** decrease about 10 kcal/mol by the demethylation of **11**. Interestingly, these phenol derivatives **16** and **17** are weak acids, which were judged from those chemical shifts of OH groups (δ_{OH}=4.49 - 4.53 for **16** and 4.86 - 5.43 for **17**) compared with that of 2,4-dimethylphenol (δ_{OH}=4.58) as a model of monomeric phenol.[41] Furthermore, [n.2]metacyclophanes **17** are slightly stronger acid ($\Delta\delta_{OH}$=ca. 0.3 - 0.9) than [n.4]metacyclophanes **16**. These results suggest that the face-to-face situation of benzene rings of **17** is caused a weak interaction between two hydroxyl groups.

UV spectra of **16** and **17** are shown in Figure 2. The absorption maxima λ_{max} (227 and 282 nm) and log ε (3.96 at 227 nm) of these cyclophanes are nearly equal because of weak interaction between benzene rings (see Experimental). Only **16a** and **b** retain the absorbance beyond long wavelength region probably due to the weak transannular interaction through the rapid conformational change.

3) [n.2.2](1,3,4)-, [n.4.4](1,3,4)-, and [n.2.2](1,3,5)cyclophanes.

The structures of regioisomeric three-bridged cyclophanes **20**, **22**, **23**, and **28** were confirmed by similar methods as mentioned above. The configuration of two cyclobutane rings of cyclophanes **20** was assigned to be *cis* by the typical methine proton chemical shifts (δ4.12 - 4.41) as shown in Table 2. The benzylic methine protons attaching to new cyclobutane rings of **20** clearly exhibit an NOE interaction with the methine protons of the other cyclobutane rings. Methine protons attaching at the carbons with COOEt or Ph have another NOE interaction with Hb aromatic protons. Accordingly, the directions of two cyclobutane rings are confirmed as shown in Scheme 3.

The *cis* configuration of two cyclobutane rings of cyclophanes **22a** and **b** was assigned from the typical chemical shifts of cyclobutane methine protons which appear at δ4.07 to 4.11 (see Table 2). The aromatic proton peaks of **22** shift to up-field region and gather around the limited region, due to the face-to-face

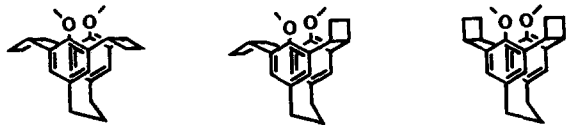
arrangement of benzene rings. The *exo* configuration of cyclobutane rings of **22** was confirmed by NOESY experiments; *i.e.*, the methylene bridges of two cyclobutane rings have the NOE interaction with aromatic Ha and Hb protons. Obviously this fact shows that only [n.2.2](1,3,4)cyclophanes **22** were obtained from possible four isomers in contrast with the isomer mixtures of [n.2.2](1,3,5)cyclophanes **4**[6] and also shows that the ring rotation of cyclophanes **21** could not occur under photoirradiation. In fact, the exclusive formation of cyclophanes **22** was explained by the MM2 calculation; *i.e.*, the strain energies (ΔSE) of **22** are *ca.* 15 kcal/mol less than their isomers whose cyclobutane rings face to each other. Accordingly the obtained cyclophanes **22** are formed from the most stable conformer of olefins under photoirradiation.

The strain energies for aromatic ring moiety of three-bridged cyclophanes **22** increase more than *syn*-[2.5]metacyclophane **2d**. In fact, cyclophanes **22b** have higher strain energies by ΔSE=24.4 and 5.4 kcal/mol than metacyclophane **2d** and **9d**, respectively,[15] according to the MM2 calculation (see Table 4).

The structures of [n.4.4](1,3,4)cyclophanes **23a** and **b** were also determined with ^{1}H NMR spectroscopy. The cyclobutane ring opening was confirmed with the disappearance of cyclobutane methine protons for **22**. Interestingly the aromatic protons of **23** exhibit only small differences from those of **22**. The methylene bridges can not move freely even after the cyclobutane rings opening, which is recognized from unsymmetrical resonance peaks for benzylic or phenethylic protons. These results showed that the conformation of **23** resembles that of **22** due to the same (1,3,4)three-bridged structure.

The MM2 calculation exhibits that the strain energies of **23a** and **23b** are SE=25.4 and 27.2 kcal/mol, respectively (see Table 4). These strain energies of **23** are 3.9 - 10.6 kcal/mol smaller than those of **22** after the compensation of the cyclobutane ring strain energy. This small difference of strain energy between cyclophanes **22** and **23** would be caused by the restricted three-bridged structure, although the bridged chains were reduced from C_2- to C_4-bridges.

The ^{1}H NMR spectra of cyclophanes **28** are extremely simple because of their C_{2v} symmetry of the molecule. The configuration of the cyclobutane ring is assigned *cis* from the chemical shift of cyclobutane methine protons which appear at δ4.44 to 4.49 (see Table 2). Its configuration to the methoxyl group was concluded to be *anti* by the NOESY experiment; *i.e.*, its methylene protons exhibit the NOE interaction with the aromatic protons, but its methine protons indicate NOE interaction with the methoxyl protons. The ^{1}H NMR chemical shifts of the methoxyl groups do not show any down-field shift caused by the compression. On the contrary, they considerably shift to high-field region by 0.36 - 0.41 ppm in comparison with those of anisole, due to the shielding of the aromatic ring (*vide infra*). Accordingly both methoxyl groups are concluded to be directed outside to avoid the steric repulsion with each other, and the structure of cyclophane **28** is determined to be that depicted in Scheme 4. The MM2 calculation also indicates that the vinyl groups of olefins **27** have already *anti* conformation against the methoxyl groups. Hence the stereoselectivity recognized in this cyclization is concluded to be due to the vinyl group conformation. The strain energy difference (ΔSE) of **28** records the largest value (64.0 - 92.6 kcal/mol) among those of all cyclophanes in this study (see Table 4). And also, ΔSE of **28** is 32.9 - 56.6 kcal/mol larger than that of **22** due to the rigid face-to-face situation, which was judged from the considerable up-field shift of aromatic protons (δ6.06 - 6.59). Furthermore, ΔSE of **28b** is ca. 6 - 12 kcal/mol less than its hypothetical isomers as depicted in Chart 2. Actually, **28** is the most stable isomer among possible three ones.



28b
SE=126.7 kcal/mol
ΔSE=69.3

SE=132.7 kcal/mol
ΔSE=75.3

SE=138.7 kcal/mol
ΔSE=81.3

Chart 2.

Although the mechanism has not been thoroughly examined, an experimental run gave intermediate cyclophane **29**. Irradiated through the Pyrex filter, it had been completely converted to cyclophane **28b**. Therefore, this photocycloaddition is believed to proceed stepwise.

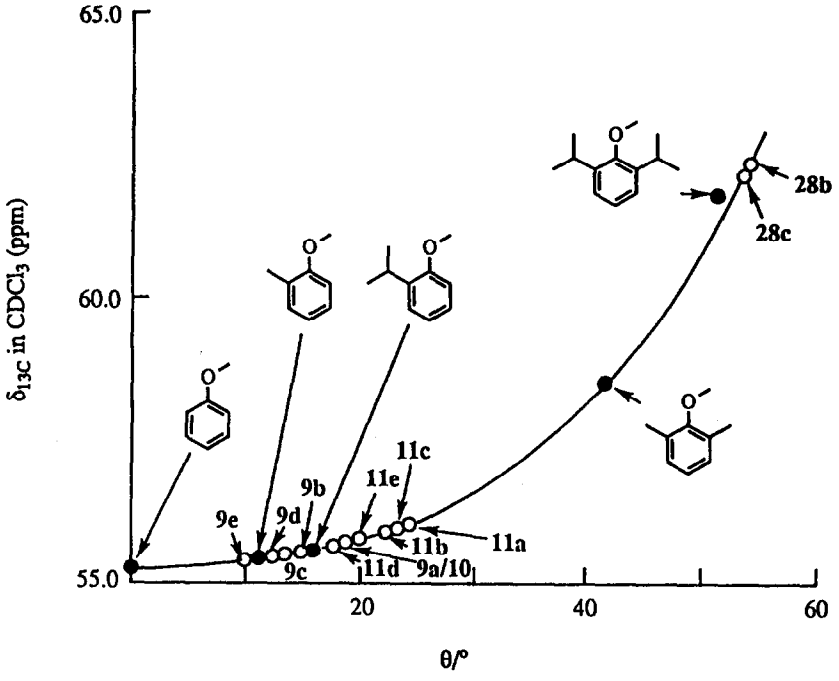


Fig. 3. Torsional angle of CH_3O group for cyclophanes **9**, **10**, **11**, and **28** and anisole derivatives.

The torsional angle of CH_3O group.

The torsional angle of methoxyl group can be estimated by ^{13}C NMR chemical shift.[38,42] The obtained data together with substituted anisoles are shown in Figure 3. The torsional angles of dimethoxy[n.2]-

and -[n.4]metacyclophanes **9**, **10**, and **11** gathered in the range of 10 - 25°, comparable with those of mono-substituted anisoles. Generally speaking, the torsional angle becomes larger when the chain length n decreases. Interestingly, the torsional angle of [n.4]cyclophanes **11** is larger than that of [n.2]cyclophanes **9** and **10**, although the strain energies of the former is far less than those of the laters (see Table 4). This result is explained that the methoxyl groups of **11** can move freely more than those of **9** and **10** due to the rapid interconversion between *syn* and *anti* conformation. The methoxyl group of [n.2.2](1,3,5)cyclophanes **28** has larger angle than that of **9**, **10**, and **11** due to the remarkable repulsion with each other. Although there are no plausible emperical equations to evaluate the angle more than 52°, those for **28b** and **28c** are assumed around 54° extrapolated from the reported data.

Conclusions

Dimethoxy[n.2]metacyclophanes **9** and **10** (n=2, 3, 4, 5, and 6) were stereoselectively obtained by means of [2 + 2] photocycloaddition. Their conformations, when n=3 - 6, are exclusively *syn*, while dimethoxy[2.2]metacylophane exists as a mixture of *syn* and *anti* isomers with the ratio of 4:3. After Birch reduction, [n.4]metacyclophanes **11** (n=2 - 6) were successfully obtained. Their conformation, when n=2 - 4 are *anti* or n=5 and 6 are *syn*. Dihydroxy[n.2]metacyclophanes **17** (n=4, 5, and 6) and dihydroxy[n.4]-metacyclophanes **16** (n=2 - 6) were obtained by the cleavage of methoxyl groups. The conformation of **16** and **17** is same as that of dimethoxymetacyclophanes. The hydroxyl groups of **16** and **17** show weak acidity. These cyclophanes will be able to use as antioxidants or receptor molecules.[43] After olefination via triflate **18**, the metacyclophanes gave three-bridged [n.2.2](1,3,4)cyclophanes **20** and **22** stereoselectively under photoirradiation. And also **22** was converted to [n.4.4](1,3,4)cyclophanes **23** by the reduction. The photocycloaddition combined with the olefination is a reasonable route toward multi-bridged cyclophanes like [n.2.2](1,3,4)- and [n.4.4](1,3,4)cyclophanes. Another three-bridged [n.2.2](1,3,5)cyclophanes **28** are also obtained stereoselectively as only one isomer with photocycloaddition by using the steric effect of methoxyl group. The torsional angles of methoxyl groups of metacyclophanes **9**, **10**, and **11** are 10 - 25° and those of three-bridged cyclophanes **28** are about 54° by ^{13}C NMR experiments.

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Experimental

General. Elemental analyses were performed at the Microanalytical Center of Gunma University. Melting points are not corrected. NMR spectra were recorded on a JEOL JNM-PMX60SI, a Varian Gemini-200, and a JEOL JNM-A500 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Mass spectra were taken on a JEOL JMS-DX302 mass spectrometer. Infrared spectra were recorded on a Hitachi 270-50 infrared spectrophotometer with KBr-disc method. UV spectra were recorded on a Shimadzu UV-160A spectrophotometer in 1,4-dioxane. The MM2 program was cordially given by Prof. Eiji

Osawa, Toyohashi University of Technology. Thin-layer chromatographic analyses (TLC) were performed on Merck silica gel 60 F_{254} plates. Column chromatographic purification of reaction mixture were performed with Merck silica gel 60 (70 - 230 mesh).

Materials. Benzene, ether, 1,4-dioxane, and tetrahydrofuran (THF) were distilled from sodium under nitrogen atmosphere. N,N-Dimethylformamide (DMF) was treated with KOH and distilled under reduced pressure. Dimethyl sulfoxide (DMSO) and dichloromethane were dried over molecular sieves 4A 1/16. Other commercially available reagents were used without further purification.

1,2-Bis(3-acetyl-4-methoxyphenyl)ethane (6a). To a solution of 135 g (0.557 mol) of 1,2-bis(*p*-methoxyphenyl)ethane **5a** in 329 cm^3 of nitrobenzene and 178 cm^3 of 1,1,2,2-tetrachloroethane was slowly added 334 g (2.50 mol) of $AlCl_3$ with mechanical stirring at 0 °C. And a solution of 153 g (1.50 mol) of acetic anhydride in 178 cm^3 of 1,1,2,2-tetrachloroethane was added in this mixture for 3 h at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was poured into cold 10% HCl solution (1.5 dm^3) and extracted with benzene (3 dm^3). After drying over Na_2SO_4 and evaporation, **6a** was isolated in 58.4% yield by column chromatography (SiO_2, benzene/ethyl acetate=9/1). ^1H NMR ($CDCl_3$, 200 MHz) δ=2.60 (6H, s), 2.84 (4H, s), 3.89 (6H, s), 6.85 (2H, d, *J*=8.0 Hz), 7.23 (2H, dd, *J*=3.0 & 8.0 Hz), and 7.55 (2H, d, *J*=3.0 Hz).

1,3-Bis(3-acetyl-4-methoxyphenyl)propane (6b). It was prepared in 68.2% yield from 65.6 g (0.256 mol) of **5b**, 193 g (1.45 mol) of $AlCl_3$, and 78.3 g (0.767 mol) of acetic anhydride in 166 cm^3 of nitrobenzene and 166 cm^3 of 1,1,2,2-tetrachloroethane. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.50 - 2.20 (2H, m), 2.20 - 2.70 (4H, m), 2.61 (6H, s), 3.90 (6H, s), 6,91 (2H, d, *J*=9.0 Hz), 7.30 (2H, dd, *J*=2.2 & 9.0 Hz), and 7.57 (2H, d, *J*=2.2 Hz).

1,4-Bis(3-acetyl-4-methoxyphenyl)butane (6c). It was prepared in 77.1% yield from 102 g (0.378 mol) of **5c**, 254 g (1.90 mol) of $AlCl_3$, and 115 g (1.13 mol) of acetic anhydride in 250 cm^3 of nitrobenzene and 240 cm^3 of 1,1,2,2-tetrachloroethane. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.66 (4H, m), 2.36 - 2.90 (4H, m), 2.61 (6H, s), 3.92 (6H, s), 6.95 (2H, d, *J*=8.2 Hz), 7.32 (2H, dd, *J*=2.2 & 8.2 Hz), and 7.63 (2H, d, *J*=2.2 Hz).

1,5-Bis(3-acetyl-4-methoxyphenyl)pentane (6d). It was prepared in 80.0% yield from 110 g (0.387 mol) of **5d**, 300 g (2.25 mol) of $AlCl_3$, and 130 g (1.27 mol) of acetic anhydride in 250 cm^3 of nitrobenzene and 240 cm^3 of 1,1,2,2-tetrachloroethane. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.02 - 1.95 (6H, m), 2.22 - 2.99 (4H, m), 2.62 (6H, s), 3.90 (6H, s), 6.92 (2H, d, *J*=8.0 Hz), 7.34 (2H, dd, *J*=2.0 & 8.0 Hz), and 7.62 (2H, d, *J*=2.0 Hz).

1,6-Bis(3-acetyl-4-methoxyphenyl)hexane (6e). It was prepared in 92.9% yield from 120 g (0.403 mol) of **5e**, 290 g (2.17 mol) of $AlCl_3$, and 86.4 g (0.846 mol) of acetic anhydride in 250 cm^3 of nitrobenzene and 240 cm^3 of 1,1,2,2-tetrachloroethane. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.00 - 2.00 (8H, m), 2.20 - 2.85 (4H, m), 2.45 (6H, s), 3.80 (6H, s), 6.67 (2H, d, *J*=9.0 Hz), 7.03 (2H, dd, *J*=2.2 & 9.0 Hz), and 7.32 (2H, d, *J*=2.2 Hz).

1,2-Bis[3-(1-hydroxyethyl)-4-methoxyphenyl]ethane (7a). A solution of 75.0 g (0.230 mol) of diketone **6a** in 750 cm^3 of THF was added dropwise into a suspension of 14.0 g (0.369 mol) of $LiAlH_4$ in 250 cm^3 of THF for 2 h below 10 °C. After stirring for 1 h at room temperature, the reaction mixture was poured into cold 10% HCl solution and extracted with 3 dm^3 of benzene. After drying over Na_2SO_4 and evaporation, diol **7a** was obtained in quantitative yield and used in a next step without further purification. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.51 (6H, d, *J*=6.0 Hz), 2.50 - 3.10 (2H, m), 2.82 (4H, s), 3.88 (6H, s), 5.10 (2H, q, *J*=6.0 Hz), 6.82 (2H, d, *J*=9.0 Hz), 6.99 (2H, dd, *J*=2.0 & 9.0 Hz), and 7.41 (2H, d, *J*=2.0 Hz).

1,3-Bis[3-(1-hydroxyethyl)-4-methoxyphenyl]propane (7b). It was obtained in 98.8% yield from 12.6 g (37.1 mmol) of diketone **6b** and 1.79 g (47.2 mmol) of $LiAlH_4$ in 250 cm^3 of THF. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.48 (6H, d, *J*=6.4 Hz), 1.66 - 2.28 (2H, m), 2.28 - 3.01 (6H, m), 3.85 (6H, s), 5.10 (2H, q, *J*=6.4 Hz), 6.81 (2H, d, *J*=8.0 Hz), 7.12 (2H, dd, *J*=1.8 & 8.0 Hz), and 7.18 (2H, d, *J*=1.8 Hz).

1,4-Bis[3-(1-hydroxyethyl)-4-methoxyphenyl]butane (7c). It was obtained in quantitative yield from 83.3 g (0.235 mol) of diketone **6c** and 13.0 g (0.343 mol) of $LiAlH_4$ in 1 dm^3 of THF. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.25 - 1.98 (4H, m), 1.50 (6H, d, *J*=6.0 Hz), 2.22 - 2.95 (6H, m), 3.88 (6H, s), 5.08 (2H, q, *J*=6.0 Hz), 6.87 (2H, d, *J*=7.8 Hz), 7.16 (2H, dd, *J*=2.0 & 7.8 Hz), and 7.24 (2H, d, *J*=2.0 Hz).

1,5-Bis[3-(1-hydroxyethyl)-4-methoxyphenyl]pentane (7d). It was obtained in 99.0% yield from 62.4 g (0.170 mol) of diketone **6d** and 8.77 g (0.231 mol) of $LiAlH_4$ in 800 cm^3 of THF. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.34 (2H, m), 1.47 (6H, d, *J*=6.4 Hz), 1.59 (4H, m), 2.52 (4H, bt), 2.67 (2H, bs), 3.82 (6H, s), 5.03 (2H, q, *J*=6.4 Hz), 6.77 (2H, d, *J*=8.3 Hz), 7.01 (2H, dd, *J*=2.2 & 8.3 Hz), and 7.11 (2H, d, *J*=2.2 Hz).

1,6-Bis[3-(1-hydroxyethyl)-4-methoxyphenyl]hexane (7e). It was obtained in 99.7% yield from 45.4 g (0.119 mol) of diketone **6e** and 6.80 g (0.179 mol) of $LiAlH_4$ in 600 cm^3 of THF. ^1H NMR ($CDCl_3$, 60 MHz) δ=0.90 - 1.87 (8H, m), 1.47 (6H, d, *J*=6.6 Hz), 2.27 - 2.73 (6H, m), 3.75 (6H, s), 5.00 (2H, q, *J*=6.6 Hz), 6.68 (2H, d, *J*=8.2 Hz), 6.97 (2H, dd, *J*=2.0 & 8.2 Hz), and 7.03 (2H, d, *J*=2.0 Hz).

1,2-Bis(3-vinyl-4-methoxyphenyl)ethane (8a). A solution of 78.0 g (0.236 mol) of diol **7a** and 11.6 g (46.2 mmol) of pyridinium *p*-toluenesulfonate in 1.8 dm^3 of benzene was refluxed with a Dean-Stark apparatus for 5 days. After extraction with 2 dm^3 of benzene, drying over Na_2SO_4, and evaporation, pure diolefin **8a** was isolated in 90.7% yield by column chromatography (SiO_2, benzene). Found: C, 81.15; H, 7.37%. Calcd for $C_{20}H_{22}O_2 \cdot 0.1H_2O$: C, 81.10; H, 7.55%. ^1H NMR ($CDCl_3$, 200 MHz) δ=2.84 (4H, s), 3.83 (6H, s), 5.24 (2H, dd, *J*=1.6 & 11 Hz), 5.70 (2H, dd, *J*=1.6 & 18 Hz), 6.78 (2H, d, *J*=8.4 Hz), 7.03 (2H, dd, *J*=11 & 18 Hz), 7.03 (2H, dd, *J*=2.2 & 8.4 Hz), and 7.28 (2H, d, *J*=2.2 Hz).

1,3-Bis(3-vinyl-4-methoxyphenyl)propane (8b). It was prepared in 72.3% yield from 40.6 g (0.118 mol) of diol **7b** and 8.90 g (35.4 mmol) of pyridinium *p*-toluenesulfonate in 900 cm^3 of benzene. Found: C, 80.76; H, 8.00%. Calcd for $C_{21}H_{24}O_2 \cdot 0.25H_2O$: C, 80.60; H, 7.89. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.91 (2H, q, *J*=7.8 Hz), 2.59 (4H, t, *J*=7.8 Hz), 3.82 (6H, s), 5.25 (2H, dd, *J*=1.6 & 11 Hz), 5.73 (2H, dd, *J*=1.6 & 18 Hz), 6.79 (2H, d, *J*=8.4 Hz), 7.03 (2H, dd, *J*=11 & 18 Hz), 7.05 (2H, dd, *J*=1.8 & 8.4 Hz), and 7.28 (2H, d, *J*=1.8 Hz).

1,4-Bis(3-vinyl-4-methoxyphenyl)butane (8c). It was prepared in 88.1% yield from 86.6 g (0.242 mol) of diol **7c** and 12.0 g (47.7 mmol) of pyridinium *p*-toluenesulfonate in 2 dm^3 of benzene. Found: C, 81.67; H, 8.01%. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.37 - 1.95 (4H, m), 2.28 - 2.91 (4H, m), 3.81 (6H, s), 5.28 (2H, dd, *J*=2.2 & 11 Hz), 5.76 (2H, dd, *J*=2.2 & 18 Hz), 6.81 (2H, d, *J*=9.0 Hz), 7.12 (2H, dd, *J*=2.0 & 9.0 Hz), 7.22 (2H, dd, *J*=11 & 18 Hz), and 7.36 (2H, d, *J*=2.0 Hz).

1,5-Bis(3-vinyl-4-methoxyphenyl)pentane (8d). It was prepared in 91.7% yield from 181 g (0.487 mol) of diol **7d** and 35.3 g (0.140 mol) of pyridinium *p*-toluenesulfonate in 2.3 dm^3 of benzene. Found: C, 81.96; H, 8.68%. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39%. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.37 (2H, m), 1.62 (4H, m), 2.54 (4H, bt), 3.81 (6H, s), 5.24 (2H, dd, *J*=1.6 & 11 Hz), 5.71 (2H, dd, *J*=1.6 & 18 Hz), 6.77 (2H, d, *J*=8.3 Hz), 7.02 (2H, dd, *J*=11 & 18 Hz), 7.02 (2H, dd, *J*=2.0 & 8.3 Hz), and 7.25 (2H, d, *J*=2.0 Hz).

1,6-Bis(3-vinyl-4-methoxyphenyl)hexane (8e). It was prepared in 74.8% yield from 96.4 g (0.250 mol) of diol **7e** and 18.8 g (74.8 mmol) of pyridinium *p*-toluenesulfonate in 1.9 dm^3 of benzene. Found: C, 81.97; H, 8.82%. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63%. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.07 - 1.97 (8H, m), 2.20 - 2.73 (4H, m), 3.74 (6H, s), 5.13 (2H, dd, *J*=2.2 & 11 Hz), 5.60 (2H, dd, *J*=2.2 & 18 Hz), 6.63 (2H, d, *J*=8.2 Hz), 6.77 (2H, dd, *J*=2.2 & 8.2 Hz), 6.95 (2H, dd, *J*=11 & 18 Hz), and 7.15 (2H, d, *J*=2.2 Hz).

6,12-Dimethoxy[2^{9,10}][2.2]metacyclophane (9a and 10). Diolefin **8a** (1.98 g, 6.72 mmol) was dissolved in dry benzene (670 cm^3) under nitrogen atmosphere using a Pyrex glass photoreaction apparatus (1 dm^3). The solution was stirred and irradiated with a 400 W high-pressure Hg lamp for 92 h. The disappearance of vinyl groups was confirmed by ^{1}H NMR. After photoreaction, the mixture was evaporated and separated by column chromatography (SiO_2, benzene/hexane=1/1). Pure cyclophane **9a** and **10** was obtained in 61.3% yield; mp 105 - 109 °C. Found: C, 81.74; H, 7.66%. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.48%. EIMS (20 eV) m/z 294 (M^+). IR ν 2945 1500, 1250, 1043, and 815 cm^{-1}. UV λ_{max} (log ε) 230 (4.14) and 294 (3.47) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.73 - 2.15 (m), 2.30 - 2.64 (m), 2.83 - 3.22 (m), 3.50 (s), 3.72 (m), 3.81 (s), 3.85 (s), 4.38 (d, *J*=2.1 Hz), 4.74 (m), 5.18 (d, *J*=2.1 Hz), 6.08 (d, *J*=8.1 Hz), 6.44 (dd, *J*=8.1 & 2.1 Hz), 6.72 (d, *J*=2.1 Hz), 6.83 (d, *J*=8.1 Hz), 6.89 (d, *J*=8.1 Hz), and 7.03 (dd, *J*=8.1 & 2.1 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ=20.84, 34.97, 41.16, 55.63, 109.69, 127.27, 128.01, 131.00, 135.18, and 155.39.

7,13-Dimethoxy[2^{10,11}][3.2]metacyclophane (9b). It was prepared in 77.8% yield from diolefin **8b** (5.98 g, 19.4 mmol) in dry benzene (1.78 dm^3) under nitrogen atmosphere using a Pyrex glass apparatus (2 dm^3) for 26 h; mp 153 - 155 °C. Found: C, 81.74; H, 7.58%. Calcd for $C_{21}H_{24}O_2$: C, 81.80; H, 7.85. EIMS (20 eV) m/z 308 (M^+). IR ν 2925, 1507, 1260, 1045, and 817 cm^{-1}. UV λ_{max} (log ε) 230 (4.04) and 286 (3.45) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.56 (1H, m), 2.22 (1H, m), 2.36 - 2.72 (6H, m), 2.95 (2H, m), 3.55 (6H, s), 4.64 (2H, m), 6.24 (2H, d, *J*=8.3 Hz), 6.62 (2H, dd, *J*=8.3 & 2.2 Hz), and 7.05 (2H, d, *J*=2.2 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ=21.08, 36.77, 38.27, 55.52, 109.76, 125.87, 128.27, 132.39, 133.53, and 154.58.

8,14-Dimethoxy[2^{11,12}][4.2]metacyclophane (9c). It was prepared in 80.8% yield from diolefin **8c** (15.5 g, 48.1 mmol) in dry benzene (1.40 dm^3) under nitrogen atmosphere using a Pyrex glass apparatus (2 dm^3) for 68 h; mp 125 - 130 °C. Found: C, 81.95; H, 8.15%. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. EIMS (20 eV) m/z 322 (M^+). IR ν 2920, 1505, 1255, 1040, and 810 cm^{-1}. UV λ_{max} (log ε) 228 (4.00) and 283 (3.55) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.42 (2H, bt), 1.91 (2H, bt), 2.28 (2H, bt), 2.52 (6H, m), 3.59 (6H, s), 4.57 (2H, m), 6.32 (2H, d, *J*=8.1 Hz), 6.55 (2H, dd, *J*=8.1 & 2.2 Hz), and 7.04 (2H, d, *J*=2.2 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ=21.90, 29.47, 35.08, 37.56, 55.40, 109.07, 126.78, 128.87, 129.72, 133.41, and 154.91.

9,15-Dimethoxy[2^{12,13}][5.2]metacyclophane (9d). It was prepared in 87.2% yield from diolefin **8d** (13.3 g, 39.6 mmol) in dry benzene (1.40 dm^3) under nitrogen atmosphere using a Pyrex glass apparatus (2 dm^3) for 32 h; mp 110 - 113 °C. Found: C, 81.93; H, 8.31%. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39%. EIMS (70 eV) m/z 336 (M^+). IR ν 2952, 1510, 1265, 1142, 1046, and 814 cm^{-1}. UV λ_{max} (log ε) 229 (4.04) and 282 (3.65) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=0.18 (1H, m), 0.90 (1H, m), 1.52 (2H, m), 1.71 (2H, m), 2.30 - 2.74 (8H, m), 3.62 (6H, s), 4.52 (2H, m), 6.43 (2H, d, *J*=8.2 Hz), 6.64 (2H, dd, *J*=8.2 & 2.1Hz), and 7.04 (2H, d, *J*=2.1 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ=22.76, 23.11, 27.93, 32.94, 37.13, 55.37, 109.53, 126.43, 129.35, 130.33, 132.56, and 154.94.

10,16-Dimethoxy[2^{13,14}][6.2]metacyclophane (9e). It was prepared in 61.1% yield from diolefin **8e** (9.50 g, 27.1 mmol) in dry benzene (1 dm^3) under nitrogen atmosphere using a Pyrex glass apparatus (2 dm^3) for 92 h; mp 46 - 50 °C. Found: C, 82.04; H, 8.42%. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63%. EIMS (20 eV) m/z 350 (M^+). IR ν 2920, 1505, 1260, 1040, and 810 cm^{-1}. UV λ_{max} (log ε) 230 (3.99) and 280 (3.70) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=0.98 (4H, m), 1.20 - 1.86 (4H, m), 2.48 (8H, m), 3.63 (6H, s), 4.43 (2H, m), 6.49 (2H, d, *J*=8.2 Hz), 6.76 (2H, dd, *J*=8.2 & 2.1 Hz), and 6.98 (2H, d, *J*=2.1 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ=23.69, 28.60, 29.06, 34.98, 38.03, 55.30, 109.37, 126.63, 127.78, 130.31, 133.06, and 155.17.

6,16-Dimethoxy[4.2]metacyclophane (11a). Liquid ammonia (90 cm^3) was condensed into a 500 ml four-necked flask equipped with a magnetic stirrer and gas inlet tube at -60 °C. 2.79 g (0.121 mol) of Na was gradually added into the flask for 15 min. Metacyclophane **9a** and **10** (509 mg, 1.73 mmol) and 0.50 cm^3 (8.5 mmol) of EtOH in 90 cm^3 of THF were slowly added into the flask. After stirring at -60 °C for 3 h, 90 cm^3 of H_2O was added to consume the excess Na and stop the reaction. And then the reaction mixture was allowed to stand to room temperature and extracted with 500 cm^3 of benzene. After drying over Na_2SO_4 and evaporation, **11a** was isolated in 62.1% yield by column chromatography (SiO_2, benzene); mp. 152 - 153 °C. Found: C, 81.38; H, 8.32%. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%. EIMS (70 eV) m/z 296 (M^+). IR ν 2950, 1505, 1260, 1122, 1040, and 805 cm^{-1}. UV λ_{max} (log ε) 230 (4.03) and 280 (3.59) nm. ^1H NMR ($CDCl_3$, 500 MHz) δ=0.74 - 1.27 (4H, m), 1.94 - 2.58 (4H, m), 2.58 - 3.31 (4H, m), 3.80 (6H, s), 5.85 (2H, d, *J*=1.8 Hz), 6.84 (2H, d, *J*=8.5 Hz), and 7.01 (2H, dd, *J*=1.8 & 8.5 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=24.55, 24.98, 38.47, 56.10, 111.14, 126.61, 128.38, 131.87, 132.81, and 156.91.

Compound **12a** was obtained in 8.7% yield; mp 109 - 110 °C. Found: C, 80.77; H, 8.94%. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78%. EIMS (70 eV) m/z 298 (M^+). IR ν 2970, 1518, 1483, 1270, 1160, 1055, and 820 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.08 (2H, bs), 1.59 (2H, m), 1.78 - 2.36 (2H, m), 1.98 (2H, bs), 2.47 - 3.03 (2H, m), 2.62 (2H, m), 2.70 (2H, bs), 2.89 (2H, m), 3.51 (3H, s), 3.78 (3H, s), 5.60 (1H, bs), 6.76 (1H, d, *J*=7.9 Hz), 6.91 (1H, dd, *J*=2.4 & 7.9 Hz), and 7.03 (1H, d, *J*=2.4 Hz).

Compound **13** was obtained in 6.9% yield; mp 69 - 71 °C. Found: C, 80.18; H, 9.32%. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39%. EIMS (70 eV) m/z 300 (M^+). IR ν 2910, 1458, 1205, and 1135 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.29 (4H, m), 1.84 - 3.04 (8H, m), 2.43 (4H, m), 2.86 (4H, m), 3.50 (6H, s), and 5.49 (2H, bt).

Compound **14a** was obtained in 9.7% yield; mp 67 - 68 °C. Found: C, 80.27; H, 8.72%. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78%. EIMS (70 eV) m/z 298 (M^+). IR ν 2960, 1520, 1265, 1150, 1050, and 830 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.17 (6H, t, *J*=7.3 Hz), 2.61 (4H, q, *J*=7.3 Hz), 2.81 (4H, s), 3.80 (6H, s), 6.75 (2H, d, *J*=7.9 Hz), 6.97 (2H, d, *J*=2.5 Hz), and 6.98 (2H, dd, *J*=2.5 & 7.9 Hz).

Compound **15** was obtained in 7.3% yield; liq. Found: C, 79.71; H, 9.88%. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39%. EIMS (20 eV) m/z 300 (M^+). IR ν (neat) 2910, 1505, 1455, 1243, 1035, and 815 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=0.99 (3H, t, *J*=7.4 Hz), 1.18 (3H, t, *J*=7.4 Hz), 2.13 (2H, q, *J*=7.4 Hz), 2.25 (2H, t-like), 2.61 (2H, q, *J*=7.4 Hz), 2.65 (4H, m), 2.81 (2H, t-like), 3.52 (3H, s), 3.80 (3H, s), 5.42 (1H, bt), 6.76 (1H, d, *J*=9.2 Hz), 6.97 (1H, d, *J*=3.0 Hz), and 6.99 (1H, dd, *J*=3.0 & 9.2 Hz).

6,17-Dimethoxy[4.3]metacyclophane (11b). It was obtained in 61.6% yield from 392 mg (1.27 mmol) of **9b**, 2.00 g (87.0 mmol) of Na, and 0.30 cm^3 (5.1 mmol) of EtOH in 80 cm^3 of liq. ammonia and 80 cm^3 of THF; mp. 94 - 95 °C. Found: C, 80.93; H, 8.45%. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44%. EIMS (70 eV) m/z 310 (M^+). IR ν 2995, 1505, 1258, 1122, 1050, and 815 cm^{-1}. UV λ_{max} (log ε) 229 (3.97) and 278 (3.56) nm. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.54 (4H, m), 2.03 (2H, q, *J*=7.5 Hz), 2.49 (4H, t, *J*=7.5 Hz), 2.54 (4H, bs), 3.79 (6H, s), 6.25 (2H, d, *J*=1.8 Hz), 6.73 (2H, d, *J*=8.5 Hz), and 6.94 (2H, dd, *J*=1.8 & 8.5 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=25.87, 25.91, 29.55, 32.69, 55.87, 110.23, 126.45, 129.46, 130.96, 133.45, and 156.31.

Compound **12b** was obtained in 26.4% yield; mp 80 - 81 °C. Found: C, 79.86; H, 8.82%. Calcd for $C_{21}H_{28}O_2 \cdot 0.2H_2O$: C, 79.82; H, 9.05%. EIMS (70 eV) m/z 312 (M^+). IR ν 2925, 1500, 1461, 1240, 1140, 1037, and 805 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.38 (2H, m), 1.73 (4H, m), 2.08 (4H, m), 2.34 - 2.63 (6H, m), 2.89 (2H, m), 3.54 (3H, s), 3.78 (3H, s), 5.50 (1H, bs), 6.69 (1H, d, *J*=8.1 Hz), 6.75 (1H, d, *J*=2.1 Hz), and 6.89 (1H, dd, *J*=2.1 & 8.1 Hz).

Compound **14b** was obtained in 1.8% yield; liq. Found: C, 80.47; H, 8.53%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%. EIMS (70 eV) m/z 312 (M^+). IR ν (neat) 2925, 1505, 1250, 1140, 1040, and 802 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.18 (6H, t, *J*=7.5 Hz), 1.90 (2H, m), 2.58 (4H, m), 2.61 (4H, q, *J*=7.5 Hz), 3.81 (6H, s), 6.76 (2H, d, *J*=8.8 Hz), 6.97 (2H, d, *J*=2.2 Hz), and 7.00 (2H, dd, *J*=2.2 & 8.8 Hz).

6,18-Dimethoxy[4.4]metacyclophane (11c). It was obtained in 84.2% yield from 459 mg (1.43 mmol) of **9c**, 2.30 g (100 mmol) of Na, and 0.40 cm^3 (6.8 mmol) of EtOH in 80 cm^3 of liq. ammonia and 80 cm^3 of THF; mp. 132 - 133 °C. Found: C, 81.31; H, 8.70%. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70%. EIMS (70 eV) m/z 324 (M^+). IR ν 2910, 1501, 1250, 1119, 1030, and 800 cm^{-1}. UV λ_{max} (log ε) 229 (3.99) and 279 (3.60) nm. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.48 (8H, m), 2.52 (4H, bs), 2.60 (4H, bs), 3.79 (6H, s), 6.59 (2H, d, *J*=1.8 Hz), 6.72 (2H, d, *J*=8.5 Hz), and 6.88 (2H, dd, *J*=1.8 & 8.5 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=26.46, 26.97, 27.57, 33.83, 55.90, 110.11, 127.51, 128.02, 130.61, 133.95, and 156.19.

Compound **12c** was obtained in 5.6% yield; mp 157 - 158 °C. Found: C, 81.12; H, 8.98%. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26%. EIMS (70 eV) m/z 326 (M^+). IR ν 2952, 1510, 1465, 1255, 1150, 1043, and 808 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.14 (4H, m), 1.48 (4H, m), 1.94 (2H, t-like), 2.01 (2H, t-like), 2.15 (2H, t-like), 2.56 (2H, t, *J*=5.9 Hz), 2.68 (2H, t, *J*=5.9 Hz), 2.83 (2H, m), 3.51 (3H, s), 3.79 (3H, s), 5.38 (1H, bs), 6.72 (1H, d, *J*=8.2 Hz), 6.88 (1H, dd, *J*=2.0 & 8.2 Hz), and 7.01 (1H, d, *J*=2.0 Hz).

Compound **14c** was obtained in 0.2% yield; mp 42 - 44 °C. Found: C, 80.44; H, 8.82%. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26%. EIMS (70 eV) m/z 326 (M^+). IR ν 2930, 1502, 1242, 1140, 1035, and 803 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.18 (6H, t, *J*=7.5 Hz), 1.63 (4H, m), 2.55 (4H, m), 2.61 (4H, q, *J*=7.5 Hz), 3.80 (6H, s), 6.75 (2H, d, *J*=8.9 Hz), 6.95 (2H, d, *J*=2.3 Hz), and 6.96 (2H, dd, *J*=2.3 & 8.9 Hz).

9,17-Dimethoxy[5.4]metacyclophane (11d). It was obtained in 94.0% yield from 422 mg (1.26 mmol) of **9b**, 2.02 g (87.8 mmol) of Na, and 0.40 cm^3 (6.8 mmol) of EtOH in 80 cm^3 of liq. ammonia and 80 cm^3 of THF; mp. 92 - 93 °C. Found: C, 81.75; H, 8.76%. Calcd for $C_{23}H_{30}O_2$: C, 81.62; H, 8.93%. EIMS (70 eV) m/z 338 (M^+). IR ν 2930, 1613, 1510, 1255, 1122, 1040, and 802 cm^{-1}. UV λ_{max} (log ε) 229 (4.02) and 278 (3.61) nm. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.19 (2H, m), 1.55 (4H, m), 1.61 (4H, m), 2.56 (4H, t-like), 2.63 (4H, t-like), 3.76 (6H, s), 6.71 (2H, d, *J*=8.6 Hz), 6.85 (2H, d, *J*=2.5 Hz), and 6.88 (2H, dd, *J*=2.5 & 8.6 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=26.11, 28.02, 28.51, 30.41, 34.12, 55.62, 110.60, 126.98, 130.43, 130.88, 133.96, and 155.74.

Compound **12d** was obtained in 4.4% yield; liq. Found: C, 80.66; H, 9.01%. Calcd for $C_{23}H_{32}O_2$: C, 81.13; H, 9.47%. EIMS (30 eV) m/z 340 (M^+). IR ν (neat) 2945, 1515, 1470, 1265, 1150, 1057, and 821 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.12 (2H, m), 1.29 (2H, m), 1.37 (2H, m), 1.56 (2H, m), 1.62 (2H, m), 2.01 (2H, t-like), 2.11 (2H, t-like), 2.37 (2H, t-like), 2.55 (2H, t-like), 2.63 (2H, t-like), 2.76 (2H, bt), 3.47 (3H, s), 3.78 (3H, s), 5.31 (1H, bs), 6.78 (1H, d, *J*=8.5 Hz), 6.93 (1H, d, *J*=2.1 Hz), and 6.94 (1H, dd, *J*=2.1 & 8.5 Hz).

Compound **14d** was obtained in 1.4% yield; liq. Found: C, 81.02; H, 9.86%. Calcd for $C_{23}H_{32}O_2$: C, 81.13; H, 9.47%. EIMS (30 eV) m/z 340 (M^+). IR ν (neat) 2940, 1515, 1255, 1130, 1040, and 810 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.19 (6H, t, *J*=7.6 Hz), 1.61 (6H, m), 2.54 (4H, m), 2.62 (4H, q, *J*=7.6 Hz), 3.80 (6H, s), 6.75 (2H, d, *J*=8.8 Hz), 6.95 (2H, d, *J*=2.8 Hz), and 6.95 (2H, dd, *J*=2.8 & 8.8 Hz).

10,18-Dimethoxy[6.4]metacyclophane (11e). It was obtained in 58.5% yield from 226 mg (0.646 mmol) of **9e**, 1.04 g (45.2 mmol) of Na, and 0.17 cm^3 (2.9 mmol) of EtOH in 40 cm^3 of liq. ammonia and 40 cm^3 of THF; mp. 60 - 61 °C. Found: C, 81.86; H, 9.28%. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15%. EIMS (70 eV) m/z 352 (M^+). IR ν 2925, 1500, 1242, 1119, 1025, and 812 cm^{-1}. UV λ_{max} (log ε) 229 (4.00) and 279 (3.60) nm. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.18 (4H,

m), 1.57 (8H, m), 2.50 (4H, t-like), 2.62 (4H, m), 3.79 (6H, s), 6.74 (2H, d, *J*=8.5 Hz), 6.78 (2H, d, *J*=2.4 Hz), and 6.91 (2H, dd, *J*=2.4 & 8.5 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=27.07, 28.43, 28.58, 30.17, 33.45, 55.66, 110.37, 126.85, 130.13, 130.50, 133.90, and 155.55.

Compound **12e** was obtained in 17.5% yield; liq. Found: C, 79.42; H, 9.43%. Calcd for $C_{24}H_{34}O_2 \cdot 0.5H_2O$: C, 79.30; H, 9.70%. EIMS (20 eV) m/z 354 (M^+). IR ν (neat) 2910, 1495, 1452, 1242, 1212, 1025, and 803 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.17 (4H, m), 1.33 (4H, m), 1.64 (4H, m), 2.01 (2H, t-like), 2.11 (2H, t-like), 2.43 (2H, t-like), 2.54 (2H, t-like), 2.66 (2H, m), 2.83 (2H, m), 3.53 (3H, s), 3.80 (3H, s), 5.39 (1H, bs), 6.76 (1H, d, *J*=9.0 Hz), 6.92 (1H, d, *J*=2.2 Hz), and 6.94 (1H, dd, *J*=2.2 & 9.0 Hz).

6,16-Dihydroxy[4.2]metacyclophane (16a). To a solution of 90 mg (0.30 mmol) of **11a** in 9.0 cm^3 of dry dichloromethane was added 76 mg (0.30 mmol) of boron tribromide at 0 °C under nitrogen atmosphere. After stirring 12 h at room temperature, the mixture was extracted with 100 cm^3 of chloroform and dried over Na_2SO_4. After evaporation, **16a** was isolated in 96% yield by column chromatography (SiO_2, benzene/ethyl acetate=9/1); mp. 214 - 215 °C. Found: C, 80.28; H, 7.71%. Calcd for $C_{18}H_{20}O_2$: C, 80.57; H, 7.51%. EIMS (70 eV) m/z 268 (M^+). IR ν 3420, 2945, 1510, 1435, 1261, 1102, and 820 cm^{-1}. UV λ_{max} (log ε) 228 (3.93) and 283 (3.63) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.25 (2H, m), 1.43 (2H, m), 2.10 - 3.02 (8H, m), 4.53 (2H, s), 5.82 (2H, d, *J*=2.2 Hz), 6.75 (2H, d, *J*=8.1 Hz), and 6.92 (2H, dd, *J*=2.2 & 8.1 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=24.92, 24.98, 38.43, 115.46, 125.48, 126.98, 131.99, 132.99, and 152.67.

6,17-Dihydroxy[4.3]metacyclophane (16b). It was prepared in 98% yield from 80 mg (0.26 mmol) of **11b** and 65 mg (0.26 mmol) of boron tribromide in 8.0 cm^3 of dry dichloromethane; mp. 168 - 169 °C. Found: C, 80.15; H, 7.77%. Calcd for $C_{19}H_{22}O_2 \cdot 0.1H_2O$: C, 80.31; H, 7.87%. EIMS (70 eV) m/z 282 (M^+). IR ν 3400, 2925, 1505, 1445, 1240, 1100, and 820 cm^{-1}. UV λ_{max} (log ε) 227 (3.94) and 281 (3.67) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.61 (4H, m), 2.04 (2H, m), 2.48 (8H, m), 4.52 (2H, s), 6.23 (2H, d, *J*=2.2 Hz), 6.67 (2H, d, *J*=8.1 Hz), and 6.88 (2H, dd, *J*=2.2 & 8.1 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=25.82, 26.08, 29.01, 32.58, 114.85, 126.45, 126.73, 131.29, 133.63, and 152.03.

6,18-Dihydroxy[4.4]metacyclophane (16c). It was prepared in 98.9% yield from 104 mg (0.321 mmol) of **11c** and 80.4 mg (0.321 mmol) of boron tribromide in 10.0 cm^3 of dry dichloromethane; mp. 202 - 203 °C. Found: C, 81.19; H, 8.06%. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%. EIMS (70 eV) m/z 296 (M^+). IR ν 3400, 2930, 1503, 1447, 1241, 1100, and 810 cm^{-1}. UV λ_{max} (log ε) 226 (3.92) and 282 (3.63) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.45 (4H, m), 1.55 (4H, m), 2.51 (4H, m), 2.59 (4H, m), 4.52 (2H, s), 6.57 (2H, d, *J*=1.9 Hz), 6.65 (2H, d, *J*=8.0 Hz), and 6.81 (2H, dd, *J*=1.9 & 8.0 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=26.66, 26.92, 27.69, 33.87, 114.59, 127.66, 127.93, 128.28, 134.46, and 151.90.

9,17-Dihydroxy[5.4]metacyclophane (16d). It was prepared in quantitative yield from 105 mg (0.311 mmol) of **11d** and 77.9 mg (0.311 mmol) of boron tribromide in 10.0 cm^3 of dry dichloromethane; mp. 194 - 196 °C. Found: C, 79.80; H, 8.30%. Calcd for $C_{21}H_{26}O_2 \cdot 0.3H_2O$: C, 79.86; H, 8.49%. EIMS (70 eV) m/z 310 (M^+). IR ν 3340, 2910, 1500, 1425, 1245, 1098, and 820 cm^{-1}. UV λ_{max} (log ε) 228 (3.91) and 281 (3.61) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.15 (2H, m), 1.62 (8H, m), 2.54 (4H, m), 2.63 (4H, m), 4.49 (2H, s), 6.63 (2H, d, *J*=8.6 Hz), 6.79 (2H, d, *J*=2.2 Hz), and 6.81 (2H, dd, *J*=2.2 & 8.6 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=26.01, 28.04, 28.23, 30.33, 34.17, 115.37, 127.37, 127.52, 130.98, 134.46, and 151.49.

10,18-Dihydroxy[6.4]metacyclophane (16e). It was prepared in 93% yield from 56 mg (0.16 mmol) of **11e** and 40 mg (0.16 mmol) of boron tribromide in 7.0 cm^3 of dry dichloromethane; mp. 184 - 185 °C. Found: C, 80.58; H, 8.57%. Calcd for $C_{22}H_{28}O_2 \cdot 0.2H_2O$: C, 80.54; H, 8.73%. EIMS (70 eV) m/z 324 (M^+). IR ν 3310, 2915, 1502, 1425, 1250, 1115, and 820 cm^{-1}. UV λ_{max} (log ε) 227 (3.96) and 281 (3.63) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.16 (4H, m), 1.60 (8H, m),

2.48 (4H, m), 2.62 (4H, m), 4.53 (2H, s), 6.67 (2H, d, *J*=8.1 Hz), 6.75 (2H, d, *J*=2.0 Hz), and 6.84 (2H, dd, *J*=2.0 & 8.1 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ=26.97, 28.30, 28.43, 30.11, 33.45, 115.16, 127.27, 127.61, 130.28, 134.41, and 151.32.

8,14-Dihydroxy[2^{11,12}][4.2]metacyclophane (17a). To a solution of of 638 mg (1.98 mmol) of **9c** in 34 cm^3 of dry dichloromethane was added 496 mg (1.98 mmol) of boron tribromide at -50 °C under nitrogen atmosphere. After stirring for 2 h at 0 °C, the mixture was extracted with 600 cm^3 of chloroform and dried over Na_2SO_4. After evaporation, **17a** was isolated in 77.8% yield by column chromatography (SiO_2, benzene/ethyl acetate=9/1); mp. 187 - 188 °C. Found: C, 78.65; H, 7.37%. Calcd for $C_{20}H_{22}O_2 \cdot 0.6H_2O$: C, 78.71; H, 7.66%. EIMS (30 eV) m/z 294 (M^+). IR ν 3350, 2940, 1503, 1257, 1215, and 820 cm^{-1}. UV λ_{max} (log ε) 230 (3.87) and 285 (3.61) nm. ^{1}H NMR ($CDCl_3$, 500 MHz) δ=1.38 (2H, m), 1.85 (2H, m), 2.25 (2H, m), 2.49 (2H, m), 2.57 (4H, m), 4.47 (2H, m), 4.86 (2H, bs), 6.35 (2H, d, *J*=8.2 Hz), 6.48 (2H, dd, *J*=1.8 & 8.2 Hz), and 6.95 (2H, d, *J*=1.8 Hz).

9,15-Dihydroxy[2^{12,13}][5.2]metacyclophane (17b). It was prepared in 94.7% yield from 16.7 g (49.7 mmol) of **9d** and 37.4 g (0.149 mol) of boron tribromide in 1 dm^3 of dry dichloromethane at room temperature for 12 h; mp 212 - 214 °C. Found: C, 81.19; H, 7.87%. Calcd for $C_{21}H_{24}O_2 \cdot 0.1H_2O$: C, 81.31; H, 7.86%. EIMS (70 eV) m/z 308 (M^+). IR ν 3352, 2932, 1497, 1251, 1212, and 807 cm^{-1}. UV λ_{max} (log ε) 229 (3.89) and 284 (3.61) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=0.12 (1H, m), 0.89 (1H, m), 1.60 (4H, m), 2.40 (2H, m), 2.60 (6H, m), 4.43 (2H, m), 5.03 (2H, bs), 6.46 (2H, d, *J*=8.1 Hz), 6.58 (2H, dd, *J*=8.1 & 2.1 Hz), and 6.95 (2H, d, *J*=2.1 Hz).

10,16-Dihydroxy[2^{13,14}][6.2]metacyclophane (17c). It was prepared in 93.4% yield from 6.97 g (19.9 mmol) of **9e** and 10.0 g (39.9 mmol) of boron tribromide in 350 cm^3 of dry dichloromethane at room temperature for 12 h; mp. 155 - 156 °C. Found: C, 80.16; H, 8.03%. Calcd for $C_{22}H_{26}O_2 \cdot 0.5H_2O$: C, 79.72; H, 8.21%. EIMS (70 eV) m/z 322 (M^+). IR ν 3290, 2949, 1501, 1240, and 820 cm^{-1}. UV λ_{max} (log ε) 228 (3.95) and 283 (3.60) nm. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=0.86 (2H, m), 0.93 (2H, m), 1.44 (2H, m), 1.71 (2H, m), 2.38 - 2.61 (8H, m), 4.31 (2H, m), 5.43 (2H, s), 6.50 (2H, d, *J*=7.0 Hz), 6.65 (2H, dd, *J*=7.0 & 1.8 Hz), and 6.91 (2H, d, *J*=1.8 Hz).

8,14-Bis(trifluoromethylsulfonyloxy)[2^{11,12}][4.2]metacyclophane (18a). To a solution of 453 mg (1.54 mmol) of **17a** in 19 cm^3 of pyridine was slowly added 2.69 g (9.53 mmol) of $(CF_3SO_2)_2O$ at -20 °C under nitrogen atmosphere. After stirring for 42 h at room temperature, the mixture was poured into cold 10% HCl solution and extracted with 100 cm^3 of ether. After drying over Na_2SO_4 and evaporation, triflate **18a** was obtained in 87.2% yield by column chromatography (SiO_2, benzene/hexane=1/1). ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.51 (2H, m), 1.98 (2H, m), 2.43 (2H, bt-like), 2.50 - 2.80 (6H, m), 4.57 (2H, m), 6.71 (2H, dd, *J*=2.1 & 8.3 Hz), 6.80 (2H, d, *J*=8.3 Hz), and 7.18 (2H, d, *J*=2.1 Hz).

9,15-Bis(trifluoromethylsulfonyloxy)[2^{12,13}][5.2]metacyclophane (18b). It was prepared in 91.1% yield from 1.42 g (4.61 mmol) of **17b** and 5.55 g (19.7 mmol) of $(CF_3SO_2)_2O$ in 59 cm^3 of pyridine; mp. 78 - 82 °C. Found: C, 48.09; H, 4.01%. Calcd for $C_{23}H_{22}F_6O_6S_2$: C, 48.25; H, 3.87%. EIMS (70 eV) m/z 572 (M^+). IR ν 2952, 1439, 1220, 1154, and 900 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=0.12 (1H, m), 1.01 (1H, m), 1.67 (4H, m), 2.54 (6H, m), 2.72 (2H, m), 4.51 (2H, m), 6.79 (2H, dd, *J*=2.0 & 8.3 Hz), 6.88 (2H, d, *J*=8.3 Hz), and 7.21 (2H, d, *J*=2.0 Hz).

9,15-Bis[2-(ethoxycarbonyl)ethenyl][2^{12,13}][5.2]metacyclophane (19a). Triflate **18b** (37 mg, 0.065 mmol) was treated with 26 mg (0.037 mmol) of $PdCl_2(PPh_3)_2$, 0.39 cm^3 of triethylamine, and 180 mg (1.8 mmol) of ethyl acrylate in 1.9 cm^3 of DMF into a sealed ampule at 130 °C for 24 h under nitrogen atmosphere. The reaction mixture was cooled to 0 °C and poured into cold 10% HCl solution. After extraction with 100 cm^3 of benzene, drying over Na_2SO_4, and evaporation, diolefin **19a** was isolated in 88% yield by column chromatography (SiO_2, benzene); mp. 145 - 150 °C. Found: C, 78.55; H, 7.69%. Calcd for $C_{31}H_{36}O_4$: C, 78.78; H, 7.68%. EIMS (20 eV) m/z 472 (M^+). IR ν 2926, 1724, 1312, 1164, and 972

cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=0.15 (1H, m), 1.01 (1H, m), 1.34 (6H, t, *J*=7.2 Hz), 1.62 (2H, m), 1.77 (2H, m), 2.51 (2H, m), 2.61 (4H, m), 2.75 (2H, m), 4.24 (4H, q, *J*=7.2 Hz), 4.57 (2H, m), 6.03 (2H, d, *J*=15.8 Hz), 6.72 (2H, dd, *J*=7.8 & 1.5 Hz), 7.14 (2H, d, *J*=7.8 Hz), 7.19 (2H, d, *J*=1.5 Hz), and 7.86 (2H, d, *J*=15.8 Hz).

9,15-Bis(2-phenylethenyl)[$2^{12,13}$][5.2]metacyclophane (19b). It was prepared in 89.0% yield from 186 mg (0.325 mmol) of **18b**, 129 mg (0.184 mmol) of $PdCl_2(PPh_3)_2$, 1.93 cm^3 of triethylamine, 990 mg (9.51 mmol) of styrene in 9.67 cm^3 of DMF; mp. 74 - 76 °C. Found: C, 92.57; H, 7.29%. Calcd for $C_{37}H_{36}$: C, 92.45; H, 7.55%. EIMS (70 eV) m/z 480 (M^+). IR ν 2932, 1495, 960, 890, 720, and 692 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=0.25 (1H, m), 0.98 (1H, m), 1.63 (2H, m), 1.84 (2H, m), 2.58 (6H, m), 2.80 (2H, m), 4.56 (2H, m), 6.64 - 6.80 (6H, m), 7.15 (4H, m), and 7.31 (10H, m).

22,23-Bis(ethoxycarbonyl)[$2^{12,13}$.$2^{20,21}$][5.2.2](1,3,4)cyclophane (20a). Diolefin **19a** (70.3 mg, 0.149 mmol) was dissolved in dry benzene (866 cm^3) under nitrogen atmosphere using a Pyrex glass photoreaction apparatus (1 dm^3). The solution was stirred and irradiated with a 400 W high-pressure Hg lamp for 2.5 h. The disappearance of olefin protons was confirmed by ^1H NMR. After evapolation, the reaction mixture was purified to give **20a** in 66.9% yield by column chromatography (SiO_2, benzene); mp. 42 - 43 °C. Found: C, 78.86; H, 7.70%. Calcd for $C_{31}H_{36}O_4$: C, 78.78; H, 7.68%. EIMS (20 eV) m/z 472 (M^+). IR ν 2925, 1736, 1196, and 790 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=0.34 (2H, m), 1.10 (2H, m), 1.28 (6H, t, *J*=7.0 Hz), 1.56 (2H, m), 2.30 - 2.65 (8H, m), 3.77 (2H, d, *J*=6.5 Hz), 4.12 (2H, m), 4.21 (4H, q, *J*=7.0 Hz), 4.34 (2H, d, *J*=6.5 Hz), 6.61 (2H, dd, *J*=8.5 & 2.0 Hz), 6.68 (2H, d, *J*=8.5 Hz), and 6.74 (2H, d, *J*=2.0 Hz).

22,23-Diphenyl[$2^{12,13}$.$2^{20,21}$][5.2.2](1,3,4)cyclophane (20b). It was prepared in 65% yield from diolefin **19b** (85 mg, 0.18 mmol) in dry benzene (200 cm^3) for 2 h; mp. 157 - 160 °C. Found: C, 92.21; H, 7.70%. Calcd for $C_{37}H_{36}$: C, 92.44; H, 7.56%. EIMS (70 eV) m/z 480 (M^+). IR ν 2940, 1496, and 700 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=0.42 (2H, m), 1.13 (2H, m), 1.58 (2H, m), 2.40 - 2.68 (8H, m), 4.22 (2H, m), 4.41 (4H, m), 6.68 (2H, dd, *J*=8.0 & 1.5 Hz), 6.80 (2H, d, *J*=1.5 Hz), 6.96 (2H, d, *J*=8.0 Hz), and 7.05 - 7.26 (10H, m).

8,14-Divinyl[$2^{11,12}$][4.2]metacyclophane (21a). A mixture of 531 mg (0.952 mmol) of triflate **18a**, 1.20 g (3.78 mmol) of vinyltributyltin, 110 mg (0.157 mmol) of $PdCl_2(PPh_3)_2$, 410 mg (9.67 mmol) of LiCl, and small amount of *p-tert*-butylcatechol in 4.8 cm^3 of DMF was treated at 100 °C for 2 h under nitrogen atmosphere. And then, the mixture was cooled to 0 °C and treated with 2.5 g of KF in 22 cm^3 of H_2O for 30 min. After extraction with 300 cm^3 of benzene, drying over Na_2SO_4, and evaporation, diolefin **21a** was isolated in 78.2% yield by column chromatography (SiO_2, benzene). Found: C, 91.95; H, 8.13%. Calcd for $C_{24}H_{26}$: C, 91.66; H, 8.34%. ^1H NMR ($CDCl_3$, 200MHz) δ=1.67 (2H, m), 2.03 (2H, m), 2.40 (2H, m), 2.62 (6H, m), 4.50 (2H, m), 5.14 (2H, dd, *J*=1.6 & 12 Hz), 5.35 (2H, dd, *J*=1.6 & 16 Hz), 6.64 (2H, dd, *J*=1.4 & 7.9 Hz), 6.86 (2H, dd, *J*=12 & 16 Hz), 7.02 (2H, d, *J*=7.9 Hz), and 7.22 (2H, d, *J*=1.4 Hz).

9,15-Divinyl[$2^{12,13}$][5.2]metacyclophane (21b). It was obtained in 78.7% yield from 606 mg (1.06 mmol) of triflate **18b**, 800 mg (2.52 mmol) of vinyltributyltin, 130 mg (0.185 mmol) of $PdCl_2(PPh_3)_2$, 470 mg (11.1 mmol) of LiCl, and small amount of *p-tert*-butylcatechol in 5.4 cm^3 of DMF. Found: C, 91.36; H, 8.31%. Calcd for $C_{25}H_{28}$: C, 91.41; H, 8.59%. ^1H NMR ($CDCl_3$, 200MHz) δ=0.16 (1H, m), 0.92 (1H, m), 1.56 (2H, m), 1.80 (2H, m), 2.39 - 2.61 (6H, m), 2.74 (2H, m), 4.40 (2H, m), 5.13 (2H, dd, *J*=1.5 & 11 Hz), 5.34 (2H, dd, *J*=1.5 & 17 Hz), 6.70 (2H, dd, *J*=1.7 & 8.0 Hz), 6.88 (2H, dd, *J*=11 & 17 Hz), 7.06 (2H, d, *J*=8.0 Hz), and 7.16 (2H, d, *J*=1.7 Hz).

[$2^{11,12}$.$2^{19,20}$][4.2.2](1,3,4)Cyclophane (22a). Diolefin **21a** (95 mg, 0.30 mmol) was dissolved in 180 cm^3 of dry benzene under N_2 using a 300 cm^3 of Pyrex glass apparatus. The solution was stirred and irradiated with 400 W high-pressure Hg lamp for 2 h. The disappearance of vinyl groups was confirmed by ^1H NMR. After photoreaction, the mixture was evaporated and separated by column chromatography (SiO_2, benzene). Cyclophane **22a** was obtained in 42% yield; mp. 152 - 154

°C. Found: C, 91.46; H, 8.25%. Calcd for $C_{24}H_{26}$: C, 91.66; H, 8.34%. EIMS (70 eV) m/z 314 (M^+). IR ν 2930, 2852, 1488, 1443, 1242, and 820 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.35 (2H, m), 1.68 (2H, m), 2.17 - 2.98 (12H, m), 4.11 (4H, m), 6.55 (2H, dd, J=1.5 & 8.2 Hz), 6.68 (2H, d, J=8.2 Hz), and 6.71 (2H, d, J=1.5 Hz).

[2^{12,13}.2^{20,21}][5.2.2](1,3,4)Cyclophane (22b). It was prepared in 85.8% yield from 400 mg (1.22 mmol) of **21b** in 244 cm^3 of dry benzene; mp. 169 - 172 °C. Found: C, 91.11; H, 8.76%. Calcd for $C_{25}H_{28}$: C, 91.41; H, 8.59%. EIMS (70 eV) m/z 328 (M^+). IR ν 2930, 2850, 1491, 1442, 1240, and 812 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=0.38 (2H, m), 1.13 (2H, m), 1.59 (2H, m), 2.27 - 2.70 (12H, m), 4.07 (4H, m), 6.65 (2H, dd, J=1.6 & 8.1 Hz), 6.76 (2H, d, J=1.6 Hz), and 6.82 (2H, d, J=8.1 Hz).

[4.4.4](1,3,4)Cyclophane (23a). Liquid ammonia (20 cm^3) was condensed into a 100 cm^3 four-necked flask equipped with a magnetic stirrer and gas inlet tube at -60 °C. 0.44 g (19 mmol) of Na was slowly added into the flask for 15 min. Matacyclophane **22a** (42 mg, 0.13 mmol) and 0.05 cm^3 (0.9 mmol) of EtOH in 20 cm^3 of THF were slowly added into the flask. After stirring at -60 °C for 3 h, 20 cm^3 of H_2O was added to consume the excess Na and stop the reaction. And then the reaction mixture was allowed to stand to room temperature and extracted with 100 cm^3 of benzene. After drying over Na_2SO_4 and evaporation, **23a** was obtained in 61% yield by column chromatography (SiO_2, benzene); mp. 121 - 123 °C. Found: C, 88.02; H, 9.31%. Calcd for $C_{24}H_{30}\cdot 0.5H_2O$: C, 88.00; H, 9.56%. EIMS (70 eV) m/z 318 (M^+). IR ν 2948, 2860, 1510, 1456, and 820 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.73 (4H, m), 1.86 - 2.20 (8H, m), 2.32 (4H, m), 2.42 (4H, m), 2.65 (4H, m), 6.50 (2H, dd, J=2.0 & 8.2 Hz), 6.51 (2H, d, J=2.0 Hz), and 6.64 (2H, d, J=8.2 Hz).

[5.4.4](1,3,4)Cyclophane (23b). It was obtained in 79.2% yield from 106 mg (0.323 mmol) of **22b**, 1.10 g (47.8 mmol) of Na, and 0.10 cm^3 (1.7 mmol) of EtOH in 40 cm^3 of liq. ammonia and 40 cm^3 of THF; mp. 37 - 38 °C. Found: C, 89.29; H, 9.57%. Calcd for $C_{25}H_{32}\cdot 0.2H_2O$: C, 89.33; H, 9.71%. EIMS (70 eV) m/z 332 (M^+). IR ν 2920, 2856, 1500, 1454, and 804 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ=0.68 (2H, m), 1.35 (2H, m), 1.50 - 1.82 (4H, m), 2.02 (6H, m), 2.27 - 2.61 (8H, m), 2.75 (4H, m), 6.57 (2H, dd, J=1.8 & 7.8 Hz), 6.63 (2H, d, J=1.8 Hz), and 6.71 (2H, d, J=7.8 Hz).

Bis[3,5-bis(hydroxymethyl)-4-methoxyphenyl]methane (25a). Compound **24a** (56 g, 0.28 mol) was dissolved in 665 cm^3 of 5% NaOH solution and 98 cm^3 of 37% HCHO solution. The reaction mixture were stirred at room temperature for 7 days and poured into 2 dm^3 of 2-propanol at -20 °C. After filtration with suction and drying under reduced pressure, hydroxymethylated product was obtained in 78% yield. A mixture of 63 g (0.17 mol) of hydroxymethylated compound and 97 g (0.68 mol) of CH_3I in 350 cm^3 of H_2O and 350 cm^3 of CH_3OH was heated at 40 °C for 12 h. After acidic extraction with 2 dm^3 of THF/ether (1/5), drying over Na_2SO_4, and evaporation, **25a** was obtained in 99% yield and used in a next step without further purification. ^1H NMR (DMSO-d_6, 500 MHz) δ=3.57 (2H, s), 3.63 (6H, s), 4.44 (4H, bs), 4.48 (8H, s), and 7.15 (4H, s).

1,2-Bis[3,5-bis(hydroxymethyl)-4-methoxyphenyl]ethane (25b). It was prepared in 92% yield from 10 g (27 mmol) of hydroxymethylated compound, which was obtained in 83% yield with 28 g (0.13 mol) of **24b** in 307 cm^3 of 5% NaOH solution and 45 cm^3 of 37% HCHO solution, and 15 g (0.11 mol) of CH_3I in 66 cm^3 of H_2O and 66 cm^3 of CH_3OH. ^1H NMR (DMSO-d_6, 60 MHz) δ=2.78 (4H, bs), 3.67 (6H, s), 4.55 (12H, s), and 7.29 (4H, s).

1,3-Bis[3,5-bis(hydroxymethyl)-4-methoxyphenyl]propane (25c). It was prepared in 99% yield from 2.0 g (5.1 mmol) of hydroxymethylated compound, which was obtained in 93% yield with 10 g (44 mmol) of **24c** in 106 cm^3 of 5% NaOH solution and 15 cm^3 of 37% HCHO solution, and 2.0 g (14 mmol) of CH_3I in 6 cm^3 of H_2O and 6 cm^3 of CH_3OH. ^1H NMR (DMSO-d_6, 60 MHz) δ=1.82 (2H, m), 2.55 (4H, m), 3.66 (6H, s), 4.05 (4H, bs), 4.55 (8H, s), and 7.25 (4H, s).

1,4-Bis[3,5-bis(hydroxymethyl)-4-methoxyphenyl]butane (25d). It was prepared in 80% yield from 5.0 g (12 mmol) of hydroxymethylated compound, which was obtained in 89% yield with 36 g (0.15 mol) of **24d** in 368 cm^3 of 5% NaOH

solution and 54 cm^3 of 37% HCHO solution, and 7.2 g (51 mmol) of CH_3I in 25 cm^3 of H_2O and 25 cm^3 of CH_3OH. ^1H NMR (DMSO-d_6, 60 MHz) δ=1.61 (4H, m), 2.59 (4H, m), 3.76 (6H, s), 4.61 (12H, s), and 7.24 (4H, s).

Bis[3,5-bis(1-hydroxyethyl)-4-methoxyphenyl]methane (26a). To a solution of 60.2 g (0.173 mol) of **25a** in 650 cm^3 of acetic acid was slowly added 100 g (0.336 mmol) of $Na_2Cr_2O_7$ at 50 °C. After stirring for 30 min, the reaction mixture was cooled to room temperature and extracted with 3 dm^3 of ether/THF (5/1). After drying over Na_2SO_4 and evaporation, the aldehyde was isolated in 72.0% yield by column chromatography (SiO_2, benzene). CH_3MgI (92.0 mmol) in 130 cm^3 of ether was dropwised into 3.50 g (10.3 mmol) of the aldehyde in 130 cm^3 of THF at room temperature. After refluxing for 3 h, the mixture was added into 5% HCl solution and extracted with 300 cm^3 of ether/THF (5/1). After drying over Na_2SO_4 and evaporation, **26a** was isolated in 73.0% yield by column chromatography (SiO_2, benzene/ethyl acetate=4/1). ^1H NMR ($CDCl_3$, 60 MHz) δ=1.42 (12H, d, *J*=6.0 Hz), 3.50 (4H, bs), 3.70 (2H, s), 3.78 (6H, s), 5.05 (4H, q, *J*=6.0 Hz), and 7.22 (4H, s).

1,2-Bis[3,5-bis(1-hydroxyethyl)-4-methoxyphenyl]ethane (26b). It was prepared in 85.0% yield from 6.23 g (17.6 mmol) of aldehyde, which was obtained in 61.1% yield with 9.41 g (26.0 mmol) of **25b** and 15.1 g (50.7 mmol) of $Na_2Cr_2O_7$ in 100 cm^3 of acetic acid, in 235 cm^3 of THF and 235 cm^3 of CH_3MgI (163 mmol) in ether. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.47 (12H, d, *J*=6.0 Hz), 2.87 (4H, s), 3.87 (6H, s), 3.92 (4H, s), 5.17 (4H, q, *J*=6.0 Hz), and 7.10 (4H, s).

1,3-Bis[3,5-bis(1-hydroxyethyl)-4-methoxyphenyl]propane (26c). It was prepared in 78% yield from 2.3 g (6.3 mmol) of aldehyde, which was obtained in 85.8% yield with 9.38 g (24.9 mmol) of **25c** and 15.2 g (51.0 mmol) of $Na_2Cr_2O_7$ in 105 cm^3 of acetic acid, in 80 cm^3 of THF and 80 cm^3 of CH_3MgI (50 mmol) in ether. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.50 (12H, d, *J*=7.0 Hz), 2.10 (2H, m), 2.60 (4H, m), 3.83 (10H, s), 5.17 (4H, q, *J*=7.0 Hz), and 7.33 (4H, s).

1,4-Bis[3,5-bis(1-hydroxyethyl)-4-methoxyphenyl]butane (26d). It was prepared in 82% yield from 2.0 g (5.2 mmol) of aldehyde, which was obtained in 78.5% yield with 22.7 g (58.2 mmol) of **25d** and 35.3 g (118 mmol) of $Na_2Cr_2O_7$ in 243 cm^3 of acetic acid, in 67 cm^3 of THF and 67 cm^3 of CH_3MgI (46 mmol) in ether. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.50 (12H, d, *J*=6.2 Hz), 1.53 (4H, m), 2.60 (4H, m), 3.78 (10H, s), 5.13 (4H, q, *J*=6.2 Hz), and 7.22 (4H, s).

Bis(3,5-divinyl-4-methoxyphenyl)methane (27a). A solution of 2.10 g (5.20 mmol) of tetrol **26a** and 3.10 g (22.8 mmol) of $KHSO_4$ in 63 cm^3 of DMSO was heated at 180 °C for 3.5 min. The mixture was poured into ice-water. After extraction with 100 cm^3 of benzene, drying over Na_2SO_4, and evaporation, tetraolefin **27a** was obtained in 43.0% yield by column chromatography (SiO_2, benzene). ^1H NMR ($CDCl_3$, 200 MHz) δ=3.70 (2H, s), 3.82 (6H, s), 5.30 (4H, dd, *J*=1.4 & 10 Hz), 5.71 (4H, dd, *J*=1.4 & 18 Hz), 7.00 (4H, dd, *J*=10 & 18 Hz), and 7.26 (4H, s).

1,2-Bis(3,5-divinyl-4-methoxyphenyl)ethane (27b). It was obtained in 45.7% yield from 1.36 g (3.25 mmol) of **26b** and 1.90 g (14.0 mmol) of $KHSO_4$ in 39 cm^3 of DMSO. Found: C, 82.92; H, 7.81%. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56%. ^1H NMR ($CDCl_3$, 60 MHz) δ=2.87 (4H, s), 3.87 (6H, s), 5.35 (4H, dd, *J*=1.6 & 13 Hz), 5.75 (4H, dd, *J*=1.6 & 18 Hz), 7.00 (4H, dd, *J*=13 & 18 Hz), and 7.31 (4H, s).

1,3-Bis(3,5-divinyl-4-methoxyphenyl)propane (27c). It was obtained in 43.6% yield from 270 mg (0.625 mmol) of **26c** and 364 mg (2.68 mmol) of $KHSO_4$ in 7.3 cm^3 of DMSO. Found: C, 81.02; H, 8.11%. Calcd for $C_{25}H_{28}O_2 \cdot 0.5H_2O$: C, 81.26; H, 7.91%. ^1H NMR ($CDCl_3$, 200 MHz) δ=1.96 (2H, m), 2.62 (4H, m), 3.70 (6H, s), 5.30 (4H, dd, *J*=1.5 & 12 Hz), 5.75 (4H, dd, *J*=1.5 & 18 Hz), 7.01 (4H, dd, *J*=12 & 18 Hz), and 7.26 (4H, s).

1,4-Bis(3,5-divinyl-4-methoxyphenyl)butane (27d). It was obtained in 47.1% yield from 760 mg (1.70 mmol) of **26d** and 1.00 g (7.35 mmol) of $KHSO_4$ in 20 cm^3 of DMSO. Found: C, 81.66; H, 8.14%. Calcd for $C_{26}H_{30}O_2 \cdot 0.5H_2O$: C, 81.42; H, 8.15%. ^1H NMR ($CDCl_3$, 60 MHz) δ=1.69 (4H, m), 2.61 (4H, m), 3.73 (6H, s), 5.36 (4H, dd, *J*=1.8 & 12 Hz), 5.80 (4H, dd, *J*=1.8 & 17 Hz), 7.01 (4H, dd, *J*=12 & 17 Hz), and 7.36 (4H, s).

6,12-Dimethoxy[2^{9,10}.2^{17,18}][2.2.2](1,3,5)cyclophane (28a). Tetraolefin **27b** (98 mg, 0.28 mmol) was dissolved in 94 cm^3 of dry benzene under N_2 using a Pyrex glass photoreaction apparatus (200 cm^3). The solution was irradiated with a 400 W high-pressure Hg lamp for 12 h. The disappearance of vinyl groups was confirmed by ^{1}H NMR. Then, the mixture was evaporated and separated by column chromatography (SiO_2, benzene). Cyclophane **28a** was obtained in 31% yield; mp. 157 - 159 °C. Found: C, 79.02; H, 7.92%. Calcd for $C_{24}H_{26}O_2 \cdot H_2O$: C, 79.09; H, 7.74%. EIMS (70 eV) m/z 346 (M^+). IR ν 2940, 1470, 1426, 1270, 1210, 1140, and 1022 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=2.45 (8H, m), 2.87 (4H, s), 3.44 (6H, s), 4.45 (4H, m), and 6.06 (4H, s).

7,13-Dimethoxy[2^{10,11}.2^{18,19}][3.2.2](1,3,5)cyclophane (28b). It was prepared in 78.3% yield from 184 mg (0.511 mmol) of **27c** in 170 cm^3 of dry benzene under N_2 using a Pyrex glass (200 cm^3) apparatus for 12 h; mp. 182 - 183 °C. Found: C, 81.43; H, 7.82%. Calcd for $C_{25}H_{28}O_2 \cdot 0.5H_2O$: C, 81.26; H, 7.91%. EIMS (70 eV) m/z 360 (M^+). IR ν 2938, 1470, 1425, 1269, 1212, 1140, and 1023 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=2.06 (2H, m), 2.44 (8H, m), 2.72 (4H, bt), 3.39 (6H, s), 4.49 (4H, m), and 6.59 (4H, s). ^{13}C NMR ($CDCl_3$, 50 MHz) δ=19.56, 26.83, 36.19, 44.53, 62.58, 128.58, 133.69, 136.30, and 155.86.

Compound **29** was obtained in 1.3% yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=2.25 (2H, m), 2.60 (6H, m), 3.00 (2H, m), 3.50 (6H, s), 4.54 (2H, m), 5.06 (2H, dd, *J*=1.6 & 12 Hz), 5.46 (2H, dd, *J*=1.6 & 18 Hz), 6.70 (2H, dd, *J*=12 & 18 Hz), 6.83 (2H, d, *J*=2.0 Hz), and 7.15 (2H, d, *J*=2.0 Hz).

8,14-Dimethoxy[2^{11,12}.2^{19,20}][4.2.2](1,3,5)cyclophane (28c). It was prepared in 68.0% yield from 250 mg (0.668 mmol) of **27d** in 223 cm^3 of dry benzene under N_2 using a Pyrex glass (300 cm^3) apparatus for 12 h; mp. 201 - 202 °C. Found: C, 81.13; H, 8.30%. Calcd for $C_{26}H_{30}O_2 \cdot 0.5H_2O$: C, 81.42; H, 8.15%. EIMS (70 eV) m/z 374 (M^+). IR ν 2936, 1469, 1423, 1271, 1210, 1139, and 1027 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=1.82 (4H, m), 2.26 (4H, m), 2.39 (8H, m), 3.40 (6H, s), 4.44 (4H, m), and 6.37 (4H, s). ^{13}C NMR ($CDCl_3$, 50 MHz) δ=19.92, 30.68, 36.21, 43.86, 62.49, 126.51, 133.23, 137.32, and 155.98.

[2^{12,13}][5.2]Metacyclophane (2d). A mixture of 41.3 mg (0.0722 mmol) of triflate **18b**, 0.058 cm^3 (1.5 mmol) of formic acid, 30.4 mg (0.116 mmol) of triphenylphosphine, and 12.2 mg (0.0543 mmol) of $Pd(OAc)_2$ was heated in 0.32 cm^3 (2.3 mmol) of triethylamine and 1.52 cm^3 of DMF at 60 °C for 12 h under nitrogen atmosphere. After extraction with 100 cm^3 of ether, drying over Na_2SO_4, and evaporation, **2d** was isolated in 68.1% yield by column chromatography.

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