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One-pot synthesis of macrocyclic compounds possessing two cyclobutane rings by sequential inter- and intramolecular [2+2] photocycloaddition reactions

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Abstract

Sensitized photocycloaddition reactions of 6,6′-dimethyl-4,4′-[1,3-bis(methylenoxy)phenylene]-di-2-pyrone (**1**) with electron-poor α,ω-diolefins such as ethylene diacrylate (**2a**) and polyoxyethylene dimethacrylates (**2b–d**) afforded site- and stereoselective macrocyclic dioxatetralactones (**3a–d**) and (**4b**) having 18- to 25-membered rings across the C5–C6 and C5′–C6′ double bonds, or C5–C6 and C3′–C4′ double bonds in **1**, respectively. Similar photoreactions of **1** with electron-rich α,ω-diolefins such as poly(ethylene glycol)divinyl ether (**2e** and **2f**) afforded crown ether-type macrocyclic compounds (**5e** and **5f**) having 18- and 21-membered rings across the C3–C4 and C3′–C4′ double bonds in **1**, respectively. The stereochemical features of **3b**, **5e-*xx***, and **5e-*nn*** were determined by the X-ray crystal analysis. The reaction mechanism was inferred by MO methods.

Keywords: Photocycloaddition reactions; Di-2-pyrones; Diolefins; Macrocyclic compounds

1. Introduction

The synthesis of macrocyclic ring systems, involving both natural products and artificial substrates such as crown ethers, cryptands, cyclophanes, porphyrins, and macrolides, is an important area in organic chemistry. These compounds initiated the exciting field of host–guest supramolecular chemistry.[1] There are several strategies for obtaining macrocycles, including cyclization, capping, and condensation using thermal reactions[2] and photochemical methods.[3] Little attention has been paid to the synthesis of macrocyclic compounds from the sequential inter- and intramolecular [2+2] photocycloaddition reactions of α,ω-diolefins, although [2+2] photocycloaddition reaction is a fruitful method in the synthesis of a variety of macrocycles possessing one or two cyclobutane rings.[4] Recently, we have succeeded in achieving one-pot synthesis of macrocyclic compounds from the sequential inter- and intramolecular [2+2] photocycloaddition reactions between polymethylenedioxy-di-2-pyrones and α,ω-diolefins.[5] We also elucidated the origin of remarkable change in regioselectivities on the inter- and intramolecular photocycloadditions by means of MO analysis.[6,7] So, we planed to extend the reaction to investigate the generality of this photochemical method. In this paper, we describe the one-pot synthesis of macrocyclic compounds using photochemical reactions of two 2-pyrones tethered by *m*-position of benzene ring (**1**) with electron-poor and electron-rich α,ω-diolefins (**2a–f**), and MO analysis of the reaction mechanism.

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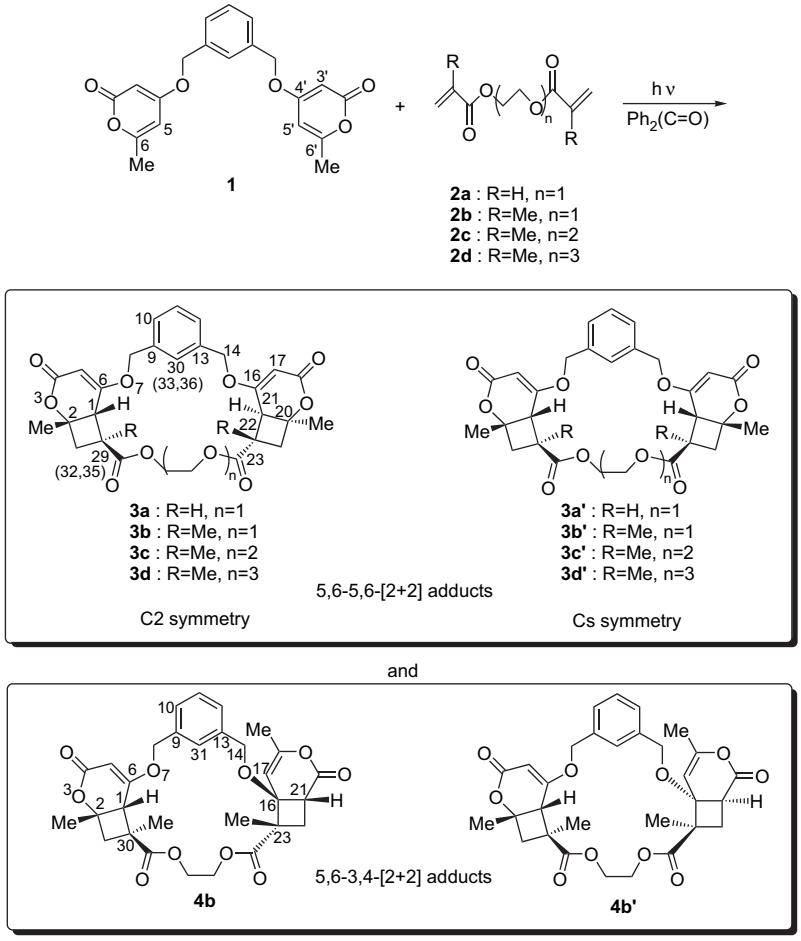
2. Results and discussion

2.1. Photoreaction of *1* with electron-poor diolefins (*2a–d*)

m-Di-2-pyrone (**1**) was prepared from dehydrochlorination of 4-hydroxy-6-methyl-2-pyrone with 1,3-bis(chloromethyl)-benzene using 1,8-diazabicyclo[5.4.0]-7-undecene in 43% yield. A solution of **1** (10 mM) with 2 equiv of ethylene dimethacrylate (**2b**) in acetonitrile was irradiated in the presence of benzophenone as sensitizer with a 300 W high-pressure mercury lamp using a UV cut filter under 320 nm under a nitrogen atmosphere. The reaction was followed by TLC and 6 h irradiation was required to fully convert all of the starting compound **1**. An amount of 2 equiv of **2b** was required because of the polymerization of **2b** by irradiation. After removal of the solvent, the oily residue was chromatographed by silica gel (eluent: ethyl acetate/hexane=2:1, v/v) to give a mixture of **3b** and **3b′** (1:1) (5,6-5,6-[2+2] cycloadducts) in 18% yield, and a mixture of **4b** and **4b′** (2:1) (5,6-3,4-[2+2] cycloadducts) in 18% yield, which were the major products from ^{1}H NMR spectra of the reaction mixture, together with a complex mixture unable to isolate (Scheme 1).

The isomers of **3b** and **3b′**, having C_2 symmetry and C_s symmetry, respectively, were separated by fractional recrystallization from acetonitrile. The structure of **3b** was confirmed as regioselective [2+2] cycloadduct, 2,20,22,29-tetramethyl-3,7,15,19,24,27-hexaoxahexacyclo[27.1^{2,29}.1^{9,13}.1^{20,22}.0.0^{1,6}.0^{16,21}]-nonacosa-5,9,11,13(30),16-pentaen-4,18,23,28-tetraone (22-*exo*, 29-*exo* adduct), across the C5–C6 and C5′–C6′ double bonds in **1** with two olefin parts in **2b** by X-ray crystallographic analysis (Fig. 1). The ORTEP drawing of **3b** shows 19-membered ring structure possessing two cyclobutane rings. Another product **3b′** was estimated as facial selective isomer at the C5–C6 and C5′–C6′ double bonds in **1** with **2b** because of showing similar ^{1}H NMR spectral data to **3b**. The stereochemistry of **3b** in each cyclobutane ring was found as *exo* conformation between 5,6-dihydropyrone ring and alkoxycarbonyl group from the X-ray structural analysis and NOE measurement.

The isomers of **4b** and **4b′** were also separated by fractional crystallization from ethyl acetate but it was difficult to obtain as a single crystal from each product. The structure of **4b** was estimated as 2,18,23,30-tetramethyl-3,7,15,19,25,28-hexaoxahexacyclo[28.1^{2,30}.1^{9,13}.0.0^{1,6}.0^{16,21}.0^{16,23}]triaconta-5,9,11,13(31),17-pentaen-4,20,24,29-tetraone (23-*endo*,30-*exo* adduct), across the C5–C6 and C3′–C4′ double bonds in **1** with two olefin parts in **2b**, on the basis of ^{1}H NMR and IR spectral data. Thus, **4b** showed 1720 cm^{-1} (α,β-unsaturated lactone carbonyl) and 1760 cm^{-1} (γ,δ-unsaturated lactone carbonyl) in IR spectra. The stereochemistry of **4b** in the two cyclobutane rings



Scheme 1.

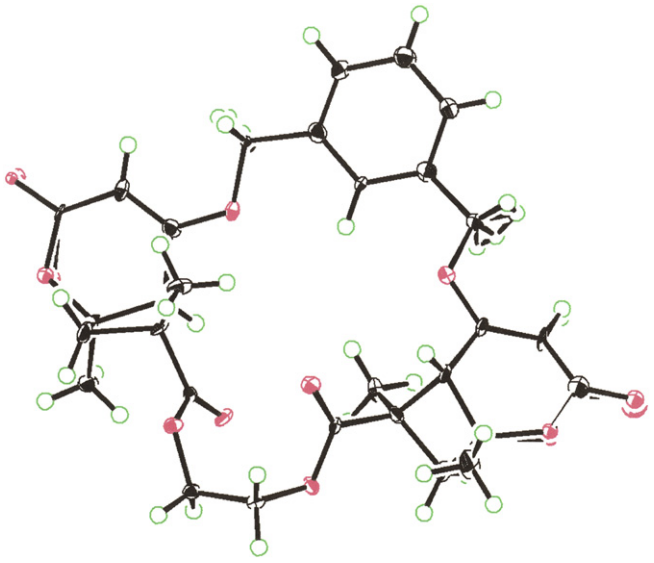


Figure 1. ORTEP drawing of **3b**.

was estimated as *exo* conformation between 5,6-dihydropyrone ring and alkoxycarbonyl group and *endo* conformation between 3,4-dihydropyrone ring and alkoxycarbonyl group from the NOE measurement. Another product **4b′** was estimated as isomer at the C5–C6 and C3′–C4′ double bonds in **1** with two olefin parts in **2b**, from the similar spectral analyses. The results of the similar photoreactions of **1** with **2a**, **2c**, and **2d** are summarized in Table 1. These reactions didn't afford 5,6-3,4-[2+2] adducts (**4**).

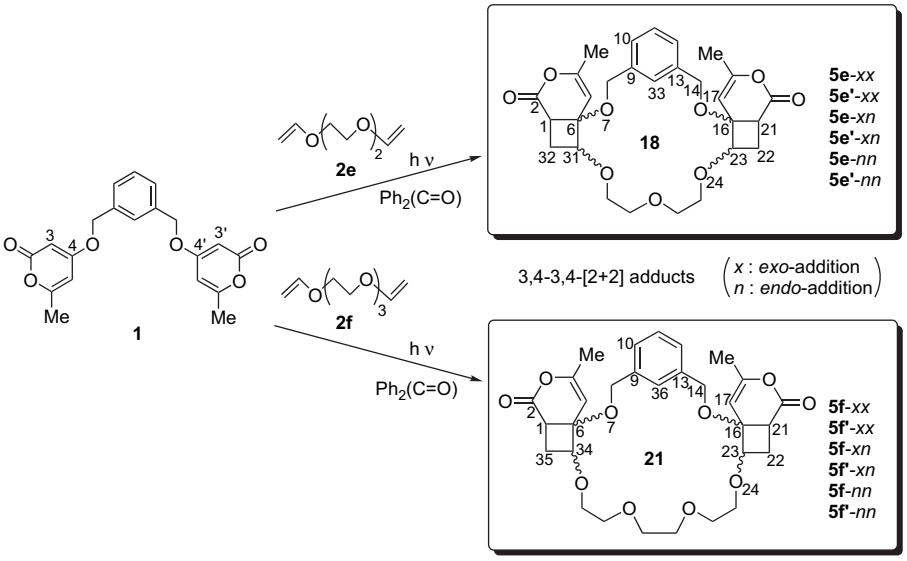
Table 1
Photoreaction of *m*-di-2-pyrone (**1**) with electron-poor diolefins (**2a–d**)

Diolefins	Irradiation time (h)	Conversion of **1** (%)[a]	Product (yield, %)[a]			
			5,6-5,6-[2+2] Adducts		5,6-3,4-[2+2] Adducts	
2a	6	95	**3a** (10)	**3a′** (10)		
2b	6	98	**3b** (9)	**3b′** (9)	**4b** (12)	**4b′** (6)
2c	8	98	**3c** (11)	**3c′** (11)		
2d	10	98	**3d** (12)	**3d′** (12)		

[a] Estimated from NMR spectral analyses using internal standard (pyrazine).

2.2. Photoreaction of *1* with electron-rich diolefins (*2e* and *2f*)

Photoreaction of **1** with di(ethylene glycol)divinyl ether (**2e**) was also carried out in the same reaction conditions mentioned above. After removal of the solvent, the oily residue was chromatographed by silica gel (eluent: ethyl acetate/hexane=2:1, v/v) to give three kinds of 1:1 mixtures of *exo*,*exo*-adducts (**5e-*xx***, **5e′-*xx***), *exo*,*endo*-adducts (**5e-*xn***, **5e′-*xn***), and *endo*,*endo*-adducts (**5e-*nn***, **5e′-*nn***) in yields of 8, 16, and 8%, respectively, together with a complex mixture unable to isolate (Scheme 2). Compounds **5e-*xx*** and **5e′-*xx***, and **5e-*nn*** and **5e′-*nn*** were separated by fractional recrystallization from acetonitrile. The structures of **5e-*xx*** and **5e-*nn*** were confirmed as regioselective [2+2] cycloadduct, 4,18-dimethyl-3,7,15,19,24,27,30-heptaoxahexacyclo[30.1^{9,13}.0.0^{1,6}.0^{6,31}.0^{16,21}.0^{16,23}]dotriaconta-4,9,11,13(33),17-pentaen-2,20-dione (23-*exo*,31-*exo* adduct) and 4,18-dimethyl-3,7,15,19,24,27,30-heptaoxahexacyclo[30.1^{9,13}.0.0^{1,6}.0^{6,31}.0^{16,21}.0^{16,23}]dotriaconta-4,9,11,13(33),17-pentaen-2,20-dione (23-*endo*,31-*endo* adduct), respectively, across the C3–C4 and C3′–C4′ double bonds in **1** with two olefin parts in **2e** by X-ray crystallographic analyses (Figs. 2 and 3). But, a mixture of *exo*,*endo*-adducts (**5e-*xn*** and **5e′-*xn***) was difficult to isolate despite many crystallization trials. The ORTEP drawings of **5e-*xx*** (Fig. 2) and **5e-*nn*** (Fig. 3) show 18-membered ring structures possessing two cyclobutane rings. Compounds **5e-*xx*** and **5e-*nn*** had also C_2 symmetry. The structures of **5e′-*xx*** and **5e′-*nn*** were estimated as facial selective isomers of **5e-*xx*** and **5e-*nn***, respectively, to have C_s symmetry. The result of the similar photoreaction of **1** with **2f** is summarized in Table 2. It was difficult to separate isomers of **5f-*xx*** and **5f′-*xx***, **5f-*xn*** and **5f′-*xn***, and **5f-*nn*** and **5f′-*nn***, respectively, because of using **2f** (n=3), which has longer chain length than **2e** (n=2).



Scheme 2.

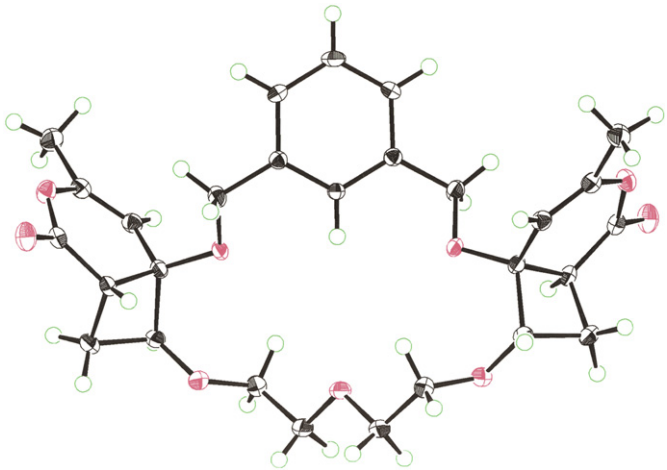


Figure 2. ORTEP drawing of **5e-*xx***.

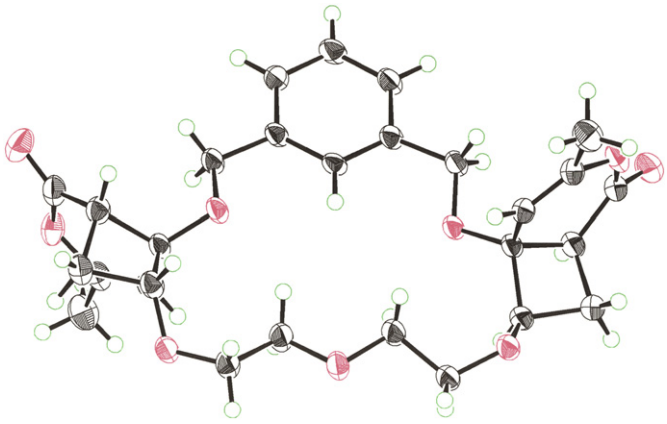


Figure 3. ORTEP drawing of **5e-*nn***.

We next describe the photocycloaddition mechanism by using PM5 level.[6] Figure 4 shows energies and coefficients of higher singly occupied molecular orbital (HSOMO) and lower ones (LSOMO) of the triplet states by means of the PM5 level, and those of LUMO and HOMO of the ground states of two α,ω-diolefins, **2b** and **2e**, by means of the PM5 level. Since these photoadditions were sensitized by some triplet sensitizers, they were inferred to go through two-step radical paths, and that the first steps were mainly influenced by coefficients and energies of the two frontier orbitals, respectively. The reasonable processes via radical intermediates (**I**–**III** in Fig. 5) are inferred from the narrow gap ($\Delta\varepsilon$) of the energies and the large coefficients (C_i and C_r) between two substrates are quantitatively confirmed by large two-center frontier orbital interactions in Table 3. The interactions, $(C_iC_r)^2/\Delta\varepsilon$ (in γ^2/eV) have a tendency to be larger between C6 (**1**) and Cβ (**2**), or C3 (**1**) and Cβ (**2**) than others. In the concrete, with **2a** possessing an electron-withdrawing group, the C6–Cβ interactions between the HSOMO and LUMO are larger than the others, and with **2e** possessing an electron-donating group, the C3–Cβ interactions between the LSOMO and HOMO are far larger. In the case of **2b** having electron-withdrawing and electron-donating groups, respectively, the C6 (**1**, HSOMO)–Cβ (**2**, LUMO) interactions are nearly equal to the C3 (**1**, LSOMO)–Cβ (**2**, HOMO) interactions. The photoreactions of **1** with **2a**, and **1** with **2e** are strongly supported to go through the respective intermediates (**I** and **II**) in Figure 5. The reaction between **1** and **2b** is also supported to proceed via first-step intermediates **I**, followed by intermediates **I** or **III**. Photoreaction of **1** with **2b** gave 5,6-3,4-[2+2] adducts (**4b** and **4b′**) together with 5,6-5,6-[2+2] adducts (**3b** and **3b′**). The former formation was inferred to be caused by the close distance between two reacting points (C3′–Cβ is prior to C6′–Cβ as shown Fig. 6 and Table 4) from the consideration of the optimized geometry for the first-step cycloadduct.

3. Conclusion

Sensitized photocycloaddition reactions of *m*-di-2-pyrone (**1**) with electron-poor α,ω-diolefins (**2a–d**) afforded *exo*,*exo*-addition macrocyclic dioxatetralactones (**3a–d**) across the C5–C6 and C5′–C6′ double bonds in **1** with two olefin parts in **2a–d**, together with dioxatetralactone (**4b**) across the C5–C6 and C3′–C4′ double bonds in **1** with two olefin parts in **2b**, having 18- to 25-membered rings. On the other hand, similar photoreactions of **1** with electron-rich α,ω-diolefins (**2e** and **2f**) afforded crown ether-type macrocyclic compounds (**5e** and **5f**) across the C3–C4 and C3′–C4′ double bonds in **1** with two olefin parts in **2e** and **2f**, having 18- and 21-membered rings. Sequential inter- and intramolecular photocycloaddition mechanism was reasonably explained by MO analyses. It was found that photochemical [2+2] cycloaddition reaction between di-2-pyrone and α,ω-diolefins was effective method to construct macrocyclic compounds.

4. Experimental section

4.1. General

All melting points were measured on a Yanagimoto Meltemp apparatus and uncorrected. NMR spectra were measured at 400 MHz on the JNM GSX-400 (TMS as an internal standard). IR spectra were recorded with a JASCO IR Report-100

Table 2
Photoreaction of *m*-di-2-pyrone (**1**) with diolefins (**2e** and **2f**)

Diolefins	Irradiation time (h)	Conversion of **1**[a] (%)	Product (yield, %)[b]					
			exo,*exo*-[2+2] Adducts		*exo*,*endo*-[2+2] Adducts		*endo*,*endo*-[2+2] Adducts	
2e	6	97	**5e-*xx*** (4)	**5e′-*xx*** (4)	**5e-*xn*** (8)	**5e′-*xn*** (8)	**5e-*nn*** (4)	**5e′-*nn*** (4)
2f	8	98	**5f-*xx*** (8)	**5f′-*xx*** (8)	**5f-*xn*** (9)	**5f′-*xn*** (9)	**5f-*nn*** (4)	**5f′-*nn*** (4)

[a] Estimated from NMR spectral analyses using internal standard (pyrazine).
[b] Isolated yield.

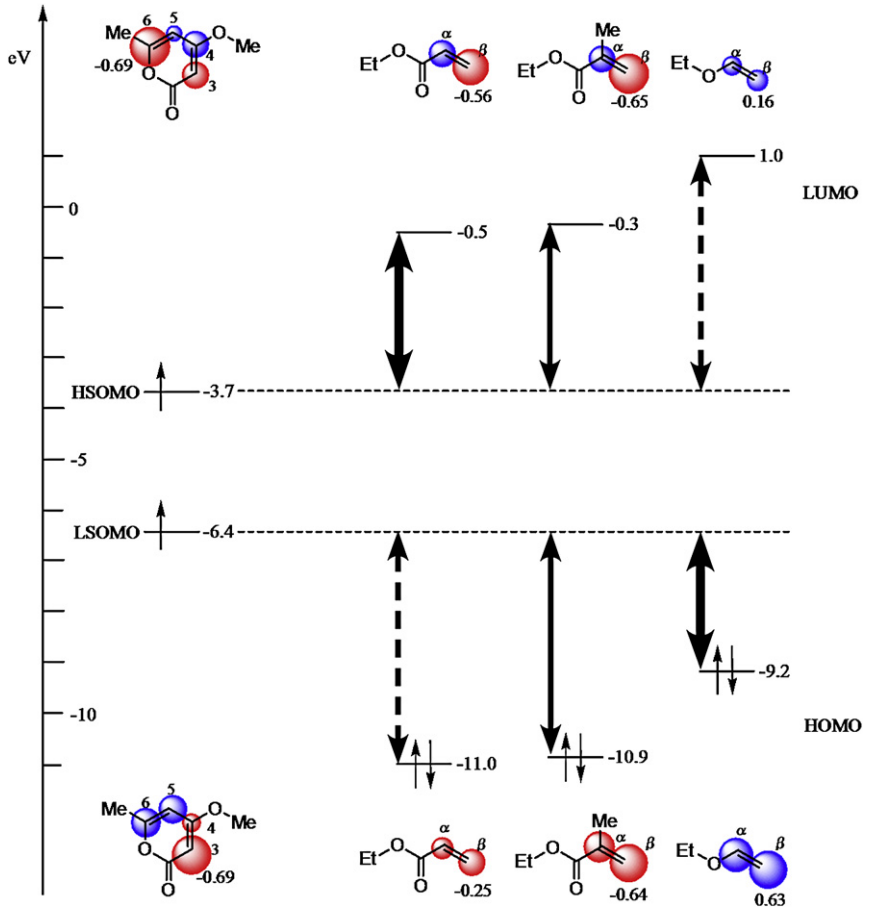


Figure 4. Estimated energies and coefficients of triplet 2-pyrone and ground state olefins by means of PM5 level.

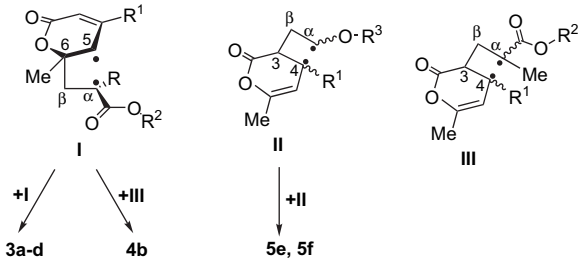


Figure 5. Three types of intermediate structures.

Table 3
Estimated frontier orbital interactions between **1** and **2** by the PM5 calculation (γ^2/eV)

	Position	2a		2b		2e	
		C6–Cβ[a]	C3–Cβ[b]	C6–Cβ	C3–Cβ	C6–Cβ	C3–Cβ
1	$\Delta\varepsilon$	3.2	4.6	3.4	4.5	4.7	2.8
	$(C_iC_r)^2/\Delta\varepsilon$	0.047	0.006	0.059	0.049	0.003	0.067

[a] Left: HSOMO (**1**)–LUMO (**2**) interaction.
[b] Right: LSOMO (**1**)–HOMO (**2**) interaction.

spectrometer. Mass spectra were recorded with a JEOL JMS-HX110A (FABMS) using *m*-nitrobenzyl alcohol as matrix. Elemental analysis was made using a Yanaco MT-5. Single crystal X-ray diffraction analyses of **3b**, **5e-*xx***, and **5e-*nn*** were performed on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo Kα radiation. Lorentz and polarization corrections were applied to the intensity data. The structures were solved by direct methods using SHELX-97[8] or SIR 92[9] and refined by a full-matrix least-squares method. The non-hydrogen atoms were refined anisotopically. All calculations were performed using the teXsan[10] crystallographic software package.[†] Photoirradiations were carried out in the Pyrex tube by using 300 W high-pressure mercury lamp. Wakogel C200 was used for preparative column chromatography. Geometry optimizations of all molecules in Figure 6 were carried out at the improved PM5 level in WinMOPAC version 3.5 by Fujitsu Ltd.[11]

*4.1.1.6,6′-Dimethyl-4,4′-[1,3-bis(methylenoxy)phenylene]-di-2-pyrone (**1**)*

To a refluxing acetonitrile (400 ml) solution of 4-hydroxy-6-methyl-2-pyrone (20.5 g, 160 mmol) and DBU (42.6 g, 208 mmol) was slowly added 1,3-bis(chloromethyl)benzene (14.0 g, 80 mmol) and refluxing was continued for 72 h. After cooling to room temperature, the reaction mixture was

[†] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and diposition numbers CCDC 670628–670630 for **3b**, **5e-*xx***, and **5e-*nn***, respectively.

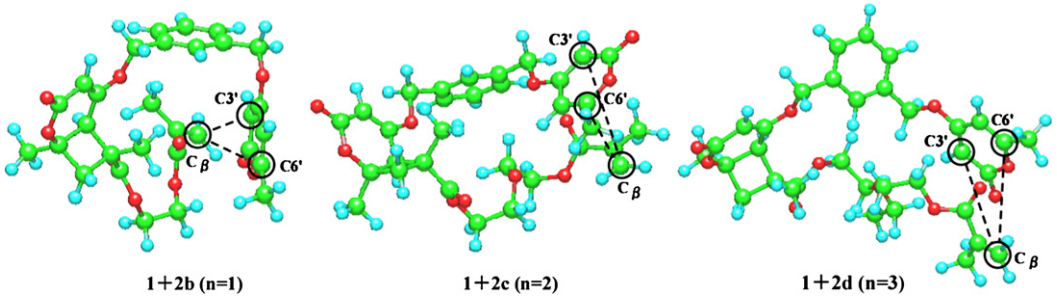


Figure 6. Optimized geometry for the first-step cycloadducts.

Table 4
Estimated distance of reaction point atoms by PM5 level

Reaction	Distance (Å)	
	C6′–Cβ	C3′–Cβ
1+**2b** (*n*=1)→**3b** and **4b**	6.63	4.72
1+**2c** (*n*=2)→**3c**	4.01	4.79
1+**2d** (*n*=3)→**3d**	5.15	6.11

evaporated in vacuo and the resulting oily residue was dissolved in chloroform (400 ml). To the concentrate was added saturated ammonium chloride (100 ml) and the mixture was stirred for 1 h at room temperature. The mixture was washed with brine, dried with anhydrous magnesium sulfate, and filtered. The filtrate was concentrated to dryness under reduced pressure, and the residue was recrystallized from acetonitrile to give **1** (12.2 g, 43%).

Compound **1**: mp 191–194 °C. ^{1}H NMR ($CDCl_3$) δ 2.22 (6H, s, Me), 5.03 (4H, s, OCH_2), 5.48 (2H, s, 3-H), 5.85 (2H, s, 5-H), 7.37 (2H, d, *J*=6.0 Hz, Ar-H), 7.38 (1H, s, Ar-H), 7.44 (1H, t, *J*=6.0 Hz, Ar-H). IR (KBr) 1710, 1680 cm^{-1}. LRMS *m*/*z* 355 (MH^+). Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.88; H, 4.99.

*4.1.2. 2,20-Dimethyl-3,7,15,19,24,27-hexaoxahexacyclo [27.1^{2,29}.1^{9,13}.1^{20,22}.0.0^{1,6}.0^{16,21}]nonacosa-5,9,11,13(30), 16-pentaen-4,18,23,28-tetraone (22-exo,29-exo adduct) (**3a**) (C_2 symmetry) and (**3a′**) (C_s symmetry)*

A solution of **1** (355 mg, 1.00 mmol) with ethylene diacrylate (**2a**) (340 mg, 2.00 mmol) in acetonitrile (200 ml) was irradiated in the presence of benzophenone (182 mg, 1.00 mmol) for 5 h with a 300 W high-pressure mercury lamp using a UV cut filter under 320 nm under a nitrogen atmosphere at room temperature. After removal of the solvent, the oily residue was chromatographed by silica gel (eluent: ethyl acetate/hexane=1:1, v/v) to give a mixture of **3a** and **3a′** (1:1) (109 mg, 21% yield), whose melting point was found to be 106–109 °C.

Compound **3a**: ^{1}H NMR ($CDCl_3$) δ 1.61 (6H, s, Me), 2.48 (2H, ddd, *J*=12.0, 5.2, and 2.0 Hz), 2.78 (2H, t, *J*=12.0 Hz), 3.12 (2H, dt, *J*=12.0 and 5.2 Hz), 3.27 (2H, dd, *J*=5.2 and 2.0 Hz), 4.31 (2H, d, *J*=10.4 Hz, CH_2), 4.49 (2H, d, *J*=10.4 Hz, CH_2), 4.98 (2H, d, *J*=11.2 Hz, OCH_2), 5.04 (2H, d, *J*=11.2 Hz, OCH_2), 5.34 (2H, s, 3-H), 7.30 (2H, dd, *J*=8.4 and 1.6 Hz, Ar-H), 7.41 (1H, t, *J*=8.4 Hz, Ar-H), 7.49 (1H, d, *J*=1.6 Hz, Ar-H). IR (KBr) 1710, 1640 cm^{-1}. HRMS (FAB, MH^+) calcd for $C_{28}H_{29}O_{10}$: *m*/*z* 525.1761; found: *m*/*z* 525.1777. Anal. Calcd for $C_{28}H_{28}O_{10}$: C, 64.12; H, 5.38. Found: C, 64.37; H, 5.67.

Compound **3a′**: ^{1}H NMR ($CDCl_3$) δ 1.60 (6H, s, Me), 2.46 (2H, ddd, *J*=12.0, 5.2, and 2.0 Hz), 2.77 (2H, t, *J*=12.0 Hz), 3.17 (2H, dt, *J*=12.0 and 5.2 Hz), 3.27 (2H, dd, *J*=5.2 and 2.0 Hz), 4.24 (2H, dd, *J*=12.0 and 6.8 Hz, CH_2), 4.51 (2H, dd, *J*=12.0 and 6.8 Hz, CH_2), 4.99 (4H, s, OCH_2), 5.33 (2H, s, 3-H), 7.30 (2H, dd, *J*=8.4 and 1.6 Hz, Ar-H), 7.41 (1H, t, *J*=8.4 Hz, Ar-H), 7.49 (1H, d, *J*=1.6 Hz, Ar-H). IR (KBr) 1710, 1640 cm^{-1}.

*4.1.3. 2,20,22,29-Tetramethyl-3,7,15,19,24,27-hexaoxahexacyclo[27.1^{2,29}.1^{9,13}.1^{20,22}.0.0^{1,6}.0^{16,21}]-nonacosa-5,9,11,13(30),16-pentaen-4,18,23,28-tetraone (22-exo,29-exo adduct) (**3b**) (C_2 symmetry) and (**3b′**) (C_s symmetry), 2,18,23,30-tetramethyl-3,7,15,19,25,28-hexaoxahexacyclo[28.1^{2,30}.1^{9,13}.0.0^{1,6}.0^{16,21}.0^{16,23}]-triaconta-5,9,11,13(31),17-pentaen-4,20,24,29-tetraone (24-endo,30-exo adduct) (**4b**) and (**4b′**)*

A solution of **1** (708 mg, 2.00 mmol) with ethylene dimethacrylate (**2b**) (792 mg, 4.00 mmol) in acetonitrile (200 ml) was irradiated in the presence of benzophenone (182 mg, 1.00 mmol) for 6 h with a 300 W high-pressure mercury lamp using a UV cut filter under 320 nm under a nitrogen atmosphere at room temperature. After removal of the solvent, the oily residue was chromatographed by silica gel (eluent: ethyl acetate/hexane=2:1, v/v) to give a mixture of **3b** and **3b′** (1:1) (200 mg, 18% yield), and a mixture of **4b** and **4b′** (2:1) (202 mg, 18% yield). Compounds **3b** and **3b′**, and **4b** and **4b′** were separated by fractional recrystallization from acetonitrile and ethyl acetate, respectively.

Compound **3b**: mp 272–274 °C. ^{1}H NMR ($CDCl_3$) δ 1.33 (6H, s, Me), 1.54 (6H, s, Me), 2.33 (2H, d, *J*=13.2 Hz), 2.72 (2H, dd, *J*=13.2 and 2.4 Hz), 3.46 (2H, d, *J*=2.4 Hz), 4.31 (2H, dd, *J*=8.8 and 2.0 Hz, CH_2), 4.55 (2H, dd, *J*=8.8 and 2.0 Hz, CH_2), 4.98 (2H, d, *J*=11.2 Hz, OCH_2), 5.02 (2H, d, *J*=11.2 Hz, OCH_2), 5.43 (2H, s, 3-H), 7.28 (2H, dd, *J*=7.2 and 1.2 Hz, Ar-H), 7.39 (1H, t, *J*=7.2 Hz, Ar-H), 7.47 (1H, d, *J*=1.2 Hz, Ar-H). IR (KBr) 1710, 1620 cm^{-1}. LRMS *m*/*z* 553 (MH^+). Anal. Calcd for $C_{30}H_{32}O_{10}$: C, 65.20; H, 5.84. Found: C, 65.06; H, 5.73. *Single crystal X-ray diffraction analyses of **3b***. Crystal structure data for **3b**: formula $C_{30}H_{32}O_{10}$, *M*=552.56, crystal dimensions 0.18×0.10×0.08 mm, triclinic, space group *P*-1 (#2), *a*=8.2172(2) Å, *b*=14.0038(9) Å, *c*=23.3966(14) Å,

α=89.953(8)°, β=89.898(3)°, γ=82.978(7)°, V=2672.1(2) Å^3, Z=4, ρ_{calcd}=1.374 g/m^3, $2\theta_{max}$=55.0°, T=113(2) K, R (Rw)=0.2050 (0.5008) for 11,885 reflection data with $I>2\sigma(I)$ and 721 variables, GOF=1.095.

Compound **3b′**: oil. ^{1}H NMR ($CDCl_3$) δ 1.33 (6H, s, Me), 1.55 (6H, s, Me), 2.32 (2H, d, J=13.2 Hz), 2.70 (2H, dd, J=13.2 and 2.4 Hz), 3.48 (2H, d, J=2.4 Hz), 4.31 (2H, m, CH_2), 4.47 (2H, m, CH_2), 4.97 (4H, s, OCH_2), 5.44 (2H, s, 3-H), 7.31 (2H, d, J=7.2 Hz, Ar-H), 7.40 (1H, t, J=7.2 Hz, Ar-H), 7.46 (1H, s, Ar-H). IR (KBr) 1710, 1630 cm^{-1}. HRMS (FAB, MH$^+$) calcd for $C_{30}H_{33}O_{10}$: *m/z* 553.2074; found: *m/z* 553.2142.

Compound **4b**: mp 127–130 °C. ^{1}H NMR ($CDCl_3$) δ 1.33, 1.52 (each 3H, s, Me), 1.54, 1.96 (each 3H, s, Me), 2.10 (1H, dd, J=11.6 and 10.4 Hz), 2.31 (1H, d, J=13.2 Hz), 2.39 (1H, dd, J=11.6 and 10.4 Hz), 2.70 (1H, dd, J=13.2 and 1.6 Hz), 3.33 (1H, dt, J=10.4 and 1.6 Hz), 3.58 (1H, d, J=1.6 Hz), 4.29 (1H, d, J=11.6 Hz), 4.30–4.36 (2H, m, CH_2), 4.36 (1H, d, J=11.6 Hz), 4.46 (2H, ddd, J=12.8, 8.8, and 1.2 Hz), 4.56 (2H, ddd, J=12.8, 8.8, and 1.2 Hz), 4.76 (1H, s, 5-H), 4.99 (1H, d, J=12.8 Hz, OCH_2), 5.14 (1H, d, J=12.8 Hz, OCH_2), 5.35 (1H, s, 3-H), 7.10 (1H, d, J=7.2 Hz, Ar-H), 7.16 (1H, d, J=7.2 Hz, Ar-H), 7.30 (1H, t, J=7.2 Hz, Ar-H), 7.53 (1H, s, Ar-H). IR (KBr) 1760, 1710, 1670, 1620 cm^{-1}. HRMS (FAB, MH$^+$) calcd for $C_{30}H_{33}O_{10}$: *m/z* 553.2074; found: *m/z* 553.2077.

Compound **4b′**: oil. ^{1}H NMR ($CDCl_3$) δ 1.45, 1.48 (each 3H, s, Me), 1.56, 1.94 (each 3H, s, Me), 2.09 (1H, dd, J=11.6 and 10.4 Hz), 2.34 (1H, d, J=13.2 Hz), 2.35 (1H, dd, J=11.6 and 10.4 Hz), 2.73 (1H, dd, J=13.2 and 1.6 Hz), 3.33 (1H, dt, J=10.4 and 1.6 Hz), 3.56 (1H, d, J=1.6 Hz), 4.29 (1H, d, J=11.6 Hz), 4.30–4.36 (2H, m, CH_2), 4.36 (1H, d, J=11.6 Hz), 4.38 (2H, m), 4.44 (2H, m), 4.81 (1H, s, 17-H), 4.92 (1H, d, J=11.6 Hz, OCH_2), 5.03 (1H, d, J=11.6 Hz, OCH_2), 5.47 (1H, s, 5-H), 7.10 (1H, d, J=7.2 Hz, Ar-H), 7.16 (1H, d, J=7.2 Hz, Ar-H), 7.30 (1H, t, J=7.2 Hz, Ar-H), 7.56 (1H, s, Ar-H). IR (NaCl) 1760, 1710, 1680, 1630 cm^{-1}. HRMS (FAB, MH$^+$) calcd for $C_{30}H_{33}O_{10}$: *m/z* 553.2074; found: *m/z* 553.2077.

*4.1.4. 2,20,22,32-Tetramethyl-3,7,15,19,24,27,30-heptaoxahexacyclo[30.1^{2,32}.1^{9,13}.1^{20,22}.0.0^{1,6}.0^{16,21}]-dotriaconta-5,9,11,13(33),16-pentaen-4,18,23,31-tetraone (22-exo,32-exo adduct) (**3c**) (C_2 symmetry) and (**3c′**) (C_s symmetry)*

A solution of **1** (708 mg, 2.00 mmol) with di(ethylene glycol)dimethacrylate (**2c**) (969 mg, 4.00 mmol) in acetonitrile (200 ml) was irradiated in the presence of benzophenone (182 mg, 1.00 mmol) for 8 h with a 300 W high-pressure mercury lamp using a UV cut filter under 320 nm under a nitrogen atmosphere at room temperature. After removal of the solvent, the oily residue was chromatographed by silica gel (eluent: ethyl acetate/hexane=2:1, v/v) to give a mixture of **3c** and **3c′** (1:1) (238 mg, 20% yield). Compounds **3c** and **3c′** were separated by fractional recrystallization from acetonitrile.

Compound **3c**: mp 241–244 °C. ^{1}H NMR ($CDCl_3$) δ 1.33 (6H, s, Me), 1.53 (6H, s, Me), 2.31 (2H, d, J=13.2 Hz), 2.73 (2H, dd, J=13.2 and 2.0 Hz), 3.42 (2H, d, J=2.0 Hz), 3.58 (4H, ddd, J=9.0, 5.6, and 3.6 Hz), 4.12 (2H, ddd, J=12.0, 5.6, and 3.6 Hz, CH_2), 4.38 (2H, ddd, J=12.0, 5.6, and 3.6 Hz, CH_2), 4.94 (2H, d, J=11.6 Hz, OCH_2), 4.98 (2H, d, J=11.6 Hz, OCH_2), 5.44 (2H, s, 3-H), 7.33 (2H, d, J=8.8 Hz, Ar-H), 7.43 (1H, t, J=8.8 Hz, Ar-H), 7.43 (1H, s, Ar-H). IR (KBr) 1690, 1615 cm^{-1}. LRMS *m/z* 597 (MH$^+$). Anal. Calcd for $C_{32}H_{36}O_{11}$: C, 64.42; H, 6.08. Found: C, 63.60; H, 6.10.

Compound **3c′**: oil. ^{1}H NMR ($CDCl_3$) δ 1.34 (6H, s, Me), 1.52 (6H, s, Me), 2.31 (2H, d, J=13.2 Hz), 2.74 (2H, dd, J=13.2 and 1.6 Hz), 3.42 (2H, d, J=1.6 Hz), 3.59 (4H, t, J=4.8 Hz), 4.13 (2H, dt, J=12.0 and 4.8 Hz, CH_2), 4.39 (2H, dt, J=12.0 and 4.8 Hz, CH_2), 4.99 (4H, s, OCH_2), 5.43 (2H, s, 3-H), 7.34 (2H, d, J=8.8 Hz, Ar-H), 7.42 (1H, t, J=8.8 Hz, Ar-H), 7.43 (1H, s, Ar-H). IR (KBr) 1690, 1615 cm^{-1}. HRMS (MH$^+$) calcd for $C_{32}H_{37}O_{11}$: *m/z* 597.2336; found: *m/z* 597.2340.

*4.1.5. 2,20,22,35-Tetramethyl-3,7,15,19,24,27,30,33-octaoxahexacyclo[33.1^{2,35}.1^{9,13}.1^{20,22}.0.0^{1,6}.0^{16,21}]-pentatriaconta-5,9,11,13(36),16-pentaen-4,18,23,34-tetraone (22-exo,35-exo adduct) (**3d**) (C_2 symmetry) and (**3d′**) (C_s symmetry)*

A solution of **1** (708 mg, 2.00 mmol) with tri(ethylene glycol)dimethacrylate (**2d**) (1145 mg, 4.00 mmol) in acetonitrile (200 ml) was irradiated in the presence of benzophenone (182 mg, 1.00 mmol) for 10 h with a 300 W high-pressure mercury lamp using a UV cut filter under 320 nm under a nitrogen atmosphere at room temperature. After removal of the solvent, the oily residue was chromatographed by silica gel (eluent: ethyl acetate/hexane=2:1, v/v) to give a mixture of **3d** and **3d′** (1:1) (286 mg, 22% yield). Compounds **3d** and **3d′** were separated by fractional recrystallization from acetonitrile.

Compound **3d**: mp 187–190 °C. ^{1}H NMR ($CDCl_3$) δ 1.37 (6H, s, Me), 1.53 (6H, s, Me), 2.30 (2H, d, J=13.6 Hz), 2.73 (2H, dd, J=13.6 and 2.0 Hz), 3.30 (4H, s), 3.40 (2H, d, J=2.0 Hz), 3.58 (4H, t, J=4.4 Hz), 4.20 (2H, dt, J=12.4 and 4.4 Hz, CH_2), 4.31 (2H, dt, J=12.4 and 4.4 Hz, CH_2), 4.91 (2H, d, J=11.6 Hz, OCH_2), 4.95 (2H, d, J=11.6 Hz, OCH_2), 5.46 (2H, s, 3-H), 7.37 (2H, d, J=7.6 Hz, Ar-H), 7.38 (1H, s, Ar-H), 7.43 (1H, t, J=7.6 Hz, Ar-H). IR (KBr) 1690, 1610 cm^{-1}. LRMS *m/z* 640 (MH$^+$). Anal. Calcd for $C_{34}H_{40}O_{12}$: C, 63.74; H, 6.29. Found: C, 63.73; H, 6.30.

Compound **3d′**: oil. ^{1}H NMR ($CDCl_3$) δ 1.37 (6H, s, Me), 1.54 (6H, s, Me), 2.30 (2H, d, J=13.6 Hz), 2.78 (2H, d, J=13.6 Hz), 3.30 (4H, s), 3.42 (2H, s), 3.59 (4H, m), 4.19 (2H, m, CH_2), 4.32 (2H, m, CH_2), 4.94 (4H, s, OCH_2), 5.47 (2H, s, 3-H), 7.38 (2H, d, J=7.6 Hz, Ar-H), 7.39 (1H, s, Ar-H), 7.46 (1H, t, J=7.6 Hz, Ar-H). IR (KBr) 1690, 1610 cm^{-1}. HRMS (MH$^+$) calcd for $C_{34}H_{41}O_{12}$: *m/z* 641.2598; found: *m/z* 641.2607.

*4.1.6. 4,18-Dimethyl-3,7,15,19,24,27,30-heptaoxahexacyclo[30.1^{9,13}.0.0^{1,6}.0^{6,31}.0^{16,21}.0^{16,23}]-dotriaconta-4,9,11,13(33),17-pentaen-2,20-dione (23-exo,31-exo adduct) (**5e-xx**) (C_2 symmetry) and (**5e′-xx**) (C_s symmetry), 4,18-dimethyl-3,7,15,19,24,27,30-heptaoxahexacyclo[30.1^{9,13}.0.0^{1,6}.0^{6,31}.0^{16,21}.0^{16,23}]-dotriaconta-4,9,11,13(33),17-pentaen-2,20-dione*

*(23-endo,31-exo adduct) (**5e-xn**) and (**5e′-xn**), and 4,18-dimethyl-3,7,15,19,24,27,30-heptaoxahexacyclo-[30.1^{9,13}.0.0^{1,6}.0^{6,31}.0^{16,21}.0^{16,23}]dotriaconta-4,9,11,13(33), 17-pentaen-2,20-dione (23-endo,31-endo adduct) (**5e-nn**) (C_2 symmetry) and (**5e′-nn**) (C_s symmetry)*

A solution of **1** (708 mg, 2.00 mmol) with di(ethylene glycol)divinyl ether (**2e**) (633 mg, 4.00 mmol) in acetonitrile (200 ml) was irradiated in the presence of benzophenone (364 mg, 2.00 mmol) for 6 h with a 300 W high-pressure mercury lamp using a UV cut filter under 320 nm under a nitrogen atmosphere at room temperature. After removal of the solvent, the oily residue was chromatographed by silica gel (eluent: ethyl acetate/hexane=1:1, v/v) to give mixtures of **5e-*xx*** and **5e′-*xx*** (1:1) (84 mg, 8% yield), **5e-*xn*** and **5e′-*xn*** (1:1) (161 mg, 16% yield), and **5e-*nn*** and **5e′-*nn*** (1:1) (81 mg, 8% yield), respectively. Compounds **5e-*xx*** and **5e′-*xx***, **5e-*nn*** and **5e′-*nn*** were separated by fractional recrystallization from acetonitrile, respectively.

Compound **5e-*xx***: mp 214–216 °C. ^{1}H NMR ($CDCl_3$) δ 2.04 (6H, s, Me), 2.12 (2H, ddd, J=12.8, 10.4, and 6.0 Hz), 2.28 (2H, dt, J=12.8 and 1.2 Hz), 3.54 (2H, t, J=10.4 Hz), 3.61–3.71, 3.88–3.95 (8H, m, CH_2), 3.93 (2H, dd, J=6.0 and 1.2 Hz), 4.31 (2H, d, J=11.6 Hz), 4.43 (2H, d, J=11.6 Hz), 4.98 (2H, s, 5-H), 7.03 (2H, d, J=7.6 Hz, Ar-H), 7.39 (1H, t, J=7.6 Hz, Ar-H), 7.47 (1H, s, Ar-H). IR (KBr) 1765, 1690 cm^{-1}. HRMS (MH^+) calcd for $C_{28}H_{33}O_9$: *m/z* 513.2125; found: *m/z* 513.2129. Anal. Calcd for $C_{28}H_{32}O_9$: C, 65.61; H, 6.29. Found: C, 64.90; H, 6.23. *Single crystal X-ray diffraction analyses of **5e-xx***. Crystal structure data for **5e-*xx***: formula $C_{28}H_{32}O_9$, M=512.56, crystal dimensions 0.58×0.46×0.10 mm, monoclinic, space group *C*2/*c* (#15), a=11.5555(3) Å, b=15.8026(4) Å, c=13.7876(3) Å, β=105.1059(9)°, V=2430.7(1) Å^3, Z=4, ρ_{calcd}=1.401 g/m^3, $2\theta_{max}$=55.0°, T=−160.0 °C, R (*Rw*)=0.067(0.110) for 2784 reflection data with 2θ<54.96° and 169 variables, GOF=1.55.

Compound **5e′-*xx***: oil. ^{1}H NMR ($CDCl_3$) δ 2.02 (6H, s, Me), 2.12 (2H, ddd, J=12.8, 10.4, and 6.0 Hz), 2.30 (2H, t, J=12.8 Hz), 3.62 (2H, t, J=10.4 Hz), 3.61–3.85 (8H, m, CH_2), 3.93 (2H, d, J=6.0 Hz), 4.34 (2H, d, J=11.6 Hz), 4.43 (2H, d, J=11.6 Hz), 4.96 (2H, s, 5-H), 7.04 (2H, d, J=7.6 Hz, Ar-H), 7.20 (1H, t, J=7.6 Hz, Ar-H), 7.70 (1H, s, Ar-H). IR (KBr) 1765, 1690 cm^{-1}. HRMS (MH^+) calcd for $C_{28}H_{33}O_9$: *m/z* 513.2125; found: *m/z* 513.2123.

Compounds **5e-*xn*** and **5e′-*xn***: mp 45–50 °C (isomers 1:1 mixture). ^{1}H NMR ($CDCl_3$) δ 1.75 or 1.80 (1H, q, J=8.8 Hz), 2.01 or 2.04 (6H, s, Me), 2.11–2.20 (1H, dt, J=10.8 and 6.4 Hz), 2.27 or 2.30 (1H, dt, J=10.8 and 0.8 Hz), 2.52 or 2.54 (1H, q, J=8.8 Hz), 2.83 or 2.86 (1H, dt, J=8.8 and 1.6 Hz), 3.50 or 3.56 (1H, t, J=10.8 Hz), 3.61–3.95 (8H, m, CH_2), 3.96 (1H, dd, J=6.4 and 0.8 Hz), 4.17 or 4.21 (1H, dt, J=8.8 and 1.6 Hz), 4.26–4.33 (2H, m, OCH_2), 4.40–4.48 (2H, m, OCH_2), 4.94 or 4.96 (1H, s, *exo*-5-H), 5.09 or 5.15 (1H, s, *endo*-5-H), 7.01 (1H, d, J=7.6 Hz, Ar-H), 7.05 (1H, d, J=7.6 Hz, Ar-H), 7.21 (1H, t, J=7.6 Hz, Ar-H), 7.66 or 7.68 (1H, s, Ar-H). IR (KBr) 1750, 1680 cm^{-1}. HRMS (MH^+) calcd for $C_{28}H_{33}O_9$: *m/z* 513.2125; found: *m/z* 513.2045.

Compound **5e-*nn***: mp 258–261 °C. ^{1}H NMR ($CDCl_3$) δ 1.79 (2H, dt, J=10.0 and 8.8 Hz), 2.01 (6H, s, Me), 2.54 (2H, dt, J=10.0 and 8.8 Hz), 2.82 (2H, dt, J=10.0 and 2.0 Hz), 3.65–3.89 (8H, m, CH_2), 4.13 (2H, dt, J=8.8 and 2.0 Hz), 4.33 (2H, d, J=12.0 Hz, OCH_2), 4.46 (2H, d, J=12.0 Hz, OCH_2), 5.02 (2H, s, 5-H), 7.02 (2H, d, J=7.6 Hz, Ar-H), 7.22 (1H, t, J=7.6 Hz, Ar-H), 7.57 (1H, s, Ar-H). IR (KBr) 1760, 1700 cm^{-1}. LRMS *m/z* 513 (MH^+). Anal. Calcd for $C_{28}H_{30}O_9$: C, 65.61; H, 6.29. Found: C, 65.38; H, 6.27. *Single crystal X-ray diffraction analyses of **5e-nn***. Crystal structure data for **5e-*nn***: formula $C_{28}H_{32}O_9$, M=512.54, crystal dimensions 0.66×0.45×0.10 mm^3, monoclinic, space group *C*2/*c*, a=17.7604(14) Å, b=11.0086(6) Å, c=12.7521(6) Å, α=90°, β=92.1425(17)°, γ=90°, V=2491.5 (3) Å^3, Z=4, ρ_{calcd}=1.366 g/m^3, $2\theta_{max}$=55.0°, T=113(2) K, R (*Rw*)=0.0598 (0.1664) for 2822 reflection data with R (int)=0.0507 and 170 variables, GOF=1.049.

Compound **5e′-*nn***: oil. ^{1}H NMR ($CDCl_3$) δ 1.77 (2H, dt, J=10.0 and 8.8 Hz), 2.02 (6H, s, Me), 2.55 (2H, dt, J=10.0 and 8.8 Hz), 2.83 (2H, dt, J=10.0 and 1.2 Hz), 3.65–3.90 (8H, m, CH_2), 4.19 (2H, dt, J=8.8 and 1.2 Hz), 4.31 (2H, d, J=12.0 Hz, OCH_2), 4.45 (2H, d, J=12.0 Hz, OCH_2), 5.01 (2H, s, 5-H), 7.01 (2H, d, J=7.6 Hz, Ar-H), 7.22 (1H, t, J=7.6 Hz, Ar-H), 7.57 (1H, s, Ar-H). IR (KBr) 1760, 1695 cm^{-1}. HRMS (MH^+) calcd for $C_{28}H_{31}O_9$: *m/z* 513.2125; found: *m/z* 513.2125.

*4.1.7. 4,18-Dimethyl-3,7,15,19,24,27,30,33-octaoxahexacyclo[33.1^{9,13}.0.0^{1,6}.0^{6,34}.0^{16,21}.0^{16,23}]-pentatriaconta-4,9,11,13(36),17-pentaen-2,20-dione (23-exo,34-exo adduct) (**5f-xx**) (C_2 symmetry) and (**5f′-xx**) (C_s symmetry), 4,18-dimethyl-3,7,15,19,24,27,30,33-octaoxahexacyclo[33.1^{9,13}.0.0^{1,6}.0^{6,34}.0^{16,21}.0^{16,23}]-pentatriaconta-4,9,11,13(36),17-pentaen-2,20-dione (23-endo,34-exo adduct) (**5f-xn**) and (**5f′-xn**), and 4,18-dimethyl-3,7,15,19,24,27,30,33-octaoxahexacyclo-[33.1^{9,13}.0.0^{1,6}.0^{6,34}.0^{16,21}.0^{16,23}]pentatriaconta-4,9,11, 13(36),17-pentaen-2,20-dione (23-endo,34-endo adduct) (**5f-nn**) (C_2 symmetry) and (**5f′-nn**) (C_s symmetry)*

A solution of **1** (708 mg, 2.00 mmol) with tri(ethylene glycol)divinyl ether (**2f**) (810 mg, 4.00 mmol) in acetonitrile (200 ml) was irradiated in the presence of benzophenone (364 mg, 2.00 mmol) for 8 h with a 300 W high-pressure mercury lamp using a UV cut filter under 320 nm under a nitrogen atmosphere at room temperature. After removal of the solvent, the oily residue was chromatographed by silica gel (eluent: ethyl acetate/hexane=2:1, v/v) to give mixtures of **5f-*xx*** and **5f′-*xx*** (1:1) (178 mg, 16% yield), **5f-*xn*** (99 mg, 9% yield) and **5f′-*xn*** (98 mg, 9% yield), and **5f-*nn*** and **5f′-*nn*** (1:1) (89 mg, 8% yield), respectively. Compounds **5f-*nn*** and **5f′-*nn*** were separated by fractional recrystallization from acetonitrile.

Compound **5f-*xx***: oil. ^{1}H NMR ($CDCl_3$) δ 2.04 (6H, s, Me), 2.12 (2H, ddd, J=10.4, 8.8, and 5.6 Hz), 2.27 (2H, t, J=10.4 Hz), 3.54 (2H, t, J=8.8 Hz), 3.56–3.82 (12H, m, CH_2), 3.93 (2H, d, J=5.6 Hz), 4.31 (2H, d, J=12.0 Hz), 4.47 (2H, d, J=12.0 Hz), 5.01 (2H, s, 5-H), 7.10 (2H, d, J=8.0 Hz, Ar-H), 7.24 (1H, t, J=8.0 Hz, Ar-H), 7.46 (1H, s,

Ar-H). IR (NaCl) 1755, 1680 cm^{-1}. HRMS (MH^+) calcd for $C_{30}H_{37}O_{10}$: *m/z* 557.2387; found: *m/z* 557.2451.

Compound **5f′-*xx***: oil. ^1H NMR ($CDCl_3$) δ 2.01 (6H, s, Me), 2.12 (2H, ddd, J=10.4, 8.8, and 5.6 Hz), 2.28 (2H, t, J=10.4 Hz), 3.54 (2H, t, J=8.8 Hz), 3.61–3.89 (12H, m, CH_2), 3.94 (2H, d, J=5.6 Hz), 4.34 (2H, d, J=12.0 Hz), 4.45 (2H, d, J=12.0 Hz), 4.97 (2H, s, 5-H), 7.11 (2H, d, J=8.0 Hz, Ar-H), 7.23 (1H, t, J=8.0 Hz, Ar-H), 7.48 (1H, s, Ar-H). IR (NaCl) 1765, 1690 cm^{-1}. HRMS (MH^+) calcd for $C_{30}H_{37}O_{10}$: *m/z* 557.2387; found: *m/z* 557.2339.

Compound **5f-*xn***: oil. ^1H NMR ($CDCl_3$) δ 1.78 (1H, q, J=8.8 Hz), 2.02, 2.04 (each, 3H, s, Me), 2.13 (1H, dt, J=11.2 and 5.6 Hz), 2.31 (1H, t, J=11.2 Hz), 2.53 (1H, q, J=8.8 Hz), 2.83 (1H, t, J=8.8 Hz), 3.59 (1H, t, J=11.2 Hz), 3.59–3.98 (12H, m, CH_2), 3.93 (1H, d, J=5.6 Hz), 4.19 (1H, t, J=8.8 Hz), 4.24, 4.31 (each 1H, d, J=11.2 Hz, OCH_2), 4.41 (2H, d, J=11.2 Hz, OCH_2), 4.91 (1H, s, *exo*-5-H), 5.28 (1H, s, *endo*-5-H), 7.04 (1H, d, J=7.2 Hz, Ar-H), 7.11 (1H, d, J=7.2 Hz, Ar-H), 7.23 (1H, t, J=7.2 Hz, Ar-H), 7.51 (1H, s, Ar-H). IR (NaCl) 1755, 1685 cm^{-1}. HRMS (MH^+) calcd for $C_{30}H_{37}O_{10}$: *m/z* 557.2387; found: *m/z* 557.2400.

Compound **5f′-*xn***: oil. ^1H NMR ($CDCl_3$) δ 1.75 (1H, q, J=9.2 Hz), 2.01, 2.04 (each, 3H, s, Me), 2.13 (1H, dt, J=11.2 and 5.2 Hz), 2.29 (1H, t, J=11.2 Hz), 2.52 (1H, q, J=9.2 Hz), 2.77 (1H, t, J=9.2 Hz), 3.55 (1H, t, J=11.2 Hz), 3.59–3.80 (12H, m, CH_2), 3.94 (1H, d, J=5.2 Hz), 4.25 (1H, t, J=9.2 Hz), 4.28, 4.31 (each 1H, d, J=11.2 Hz, OCH_2), 4.43, 4.46 (each 1H, d, J=11.2 Hz, OCH_2), 4.97 (1H, s, *exo*-5-H), 5.21 (1H, s, *endo*-5-H), 7.04 (1H, d, J=7.6 Hz, Ar-H), 7.10 (1H, d, J=7.6 Hz, Ar-H), 7.23 (1H, t, J=7.6 Hz, Ar-H), 7.52 (1H, s, Ar-H). IR (NaCl) 1765, 1695 cm^{-1}. HRMS (MH^+) calcd for $C_{30}H_{37}O_{10}$: *m/z* 557.2387; found: *m/z* 557.2386.

Compound **5f-*nn***: mp 176–179 °C. ^1H NMR ($CDCl_3$) δ 1.79 (2H, dt, J=11.6 and 8.8 Hz), 2.04 (6H, s, Me), 2.53 (2H, dt, J=11.6 and 8.8 Hz), 2.82 (2H, dt, J=8.8 and 1.6 Hz), 3.64–3.81 (12H, m, CH_2), 4.16 (2H, dt, J=8.8 and 1.6 Hz), 4.27 (2H, d, J=11.2 Hz, OCH_2), 4.45 (2H, d, J=11.2 Hz, OCH_2), 5.15 (2H, s, 5-H), 7.06 (2H, d, J=7.6 Hz, Ar-H), 7.23 (1H, t, J=7.6 Hz, Ar-H), 7.47 (1H, s, Ar-H). IR (NaCl) 1750, 1680 cm^{-1}. HRMS (MH^+) calcd for $C_{30}H_{37}O_{10}$: *m/z* 557.2387; found: *m/z* 557.2382.

Compound **5f′-*nn***: oil. ^1H NMR ($CDCl_3$) δ 1.76 (2H, dt, J=10.0 and 8.8 Hz), 2.05 (6H, s, Me), 2.53 (2H, dt, J=10.0 and 8.8 Hz), 2.83 (2H, dt, J=8.8 and 2.0 Hz), 3.60–4.03 (12H, m, CH_2), 4.13 (2H, dt, J=8.8 and 2.0 Hz), 4.23–4.37 (2H, d, J=11.2 Hz, OCH_2), 4.45 (2H, d, J=11.2 Hz, OCH_2), 5.09 (2H, s, 5-H), 7.06 (2H, d, J=7.6 Hz, Ar-H), 7.23 (1H, t, J=7.6 Hz, Ar-H), 7.46 (1H, s, Ar-H). IR (NaCl) 1750, 1680 cm^{-1}. HRMS (MH^+) calcd for $C_{30}H_{37}O_{10}$: *m/z* 557.2387; found: *m/z* 557.2330.

References and notes

1. (a) Robbins, T. A.; Konobler, C. B.; Bellow, D. R.; Cram, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 111–122; (b) Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245–255; (c) Fan, E.; Van Arman, S. A.; Kincaid, S.; Hamilton, A. D. *J. Am. Chem. Soc.* **1993**, *115*, 369–370; (d) Yang, J.; Fan, E.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1993**, *115*, 5314–5315; (e) Schneider, H.-J.; Durr, H. *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; VCH: Weinheim, 1991.
2. Dietrich, B.; Viout, P.; Lehn, J.-M. *Macrocyclic Chemistry*; VCH: Weinheim, 1993.
3. Griesbeck, A. G.; Henz, A.; Hirt, J. *Synthesis* **1996**, 1261–1276.
4. (a) Nishimura, J.; Doi, H.; Ohbayashi, A.; Oku, A. *J. Am. Chem. Soc.* **1987**, *109*, 5293–5295; (b) Inokuma, S.; Takezawa, M.; Satoh, H.; Nakamura, Y.; Sasaki, T.; Nishimura, J. *J. Org. Chem.* **1998**, *63*, 5791–5796; (c) Inokuma, S.; Ide, T.; Yonekura, T.; Funaki, T.; Kondo, S.; Shinobara, S.; Yoshihara, T.; Tobita, S.; Nishimura, J. *J. Org. Chem.* **2005**, *70*, 1698–1703.
5. Shimo, T.; Kawamura, M.; Fukushima, E.; Yasutake, M.; Shinmyozu, T.; Somekawa, K. *Heterocycles* **2003**, *60*, 23–27.
6. Odo, Y.; Shimo, T.; Hori, K.; Somekawa, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1209–1215.
7. (a) Omar, H. I.; Shimo, T.; Somekawa, K. *J. Mol. Struct. (Theochem)* **2006**, *763*, 115–121; (b) Tokunaga, D.; Shimo, T.; Hashimoto, H.; Ooto, T.; Somekawa, K. *J. Comput. Chem. Jpn.* **2007**, *6*, 283–294.
8. Sholdrick, G. M. *SHELX-97, Program for the Refinement of Crystal Structures*; University of Gottingen: Gottingen, Germany, 1997.
9. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.
10. Crystal structure analyses package, molecular structure corporation (1985 and 1999).
11. Stewart, J. J. P. *WinMOPAC Version 3.5*; Fujitsu: Tokyo, Japan, 2001.