Superjacent and Subjacent Orbitals Participations for Kinetically-Controlled Cycloaddition Reactions of 2*H*-Cyclohepta[*b*]furan-2-ones and 8,8-Dicyanoheptafulvene to 2,3-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene

Guan Rong TIAN,† Shigeru SUGIYAMA,†† Akira MORI, Hitoshi TAKESHITA,* Miwako HIGASHI,††† and Hiroyuki YAMAGUCHI†††

Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
†††College of Technology, Ibaraki University, 4-12-1, Nakanarusawa, Hitachi 316

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Thermal cycloaddition reactions of 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene with 2*H*-cyclohepta[*b*]furan-2-ones and 8,8-dicyanoheptafulvene gave [4+2]adducts exclusively. This mode is different from the reported [8+2]adduct formations for 2*H*-cyclohepta[*b*]furan-2-ones with enamines and alkoxyethenes. A consideration of the superjacent and subjacent orbitals effects of the MO calculations gave a better result in favor of [4+2]adduct formation. Thermolysis of cycloadducts gave the methylene derivatives of homobarrelenes.

Recently, we investigated thermal cycloaddition reactions of 2*H*-cyclohepta[*b*]furan-2-ones (**1**) to 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (**2**) to give the [4+2]cycloadducts exclusively.[1] This was different from the previously-reported [8+2]cycloadducts formation in the thermal reactions of **1** with enamines[2] and alkoxyethenes.[3] Both reaction modes were explained by molecular orbital (MO) considerations involving not only a frontier molecular orbital approach but also the square of the sum of the products of the coefficients of interacting centers.[1,4] We have proposed that both the [4+2]cycloadducts for **1** and **2** and the [8+2]cycloadducts from **1** and enamines and alkoxyethenes were kinetically-controlled products. However, the above theoretical treatments were not always satisfactory to explain all the experimental results. This was the case for the more complicated molecules; such as substituted **1** and **2**.

Paddon-Row et al. have pointed out[4] the importance of superjacent orbital effects to explain the periselectivity for cycloaddition reactions of nonalternant 6,6-dimethylfulvene and cyclopentadiene, studied by Houk and Luskus.[5] In the case of 2*H*-cyclohepta[*b*]furan-2-ones, nonalternant aromatic compounds, we also found that better results to fit the experiments could be obtained when the calculation was extended to involve both interactions between a superjacent (NLU) and a highest occupied (HO) MOs and a subjacent (NHO) and a lowest unoccupied (LU) MOs. In this paper, we will describe these findings.

Results and Discussion

Cycloadditions of 1 and 2. When 2*H*-cyclohepta[*b*]-furan-2-one (**1a**) amd **2** were heated at 130 °C for 36 h in chlorobenzene, three products (**3a—5a**) were obtained together with 3,4-bis(methoxycarbonyl)furan (**6**). The ^{1}H and ^{13}C NMR spectra of **3a** showed an element of symmetry in a molecule and its structure was determined to be 2-oxatricyclo[6.2.2.0^{1,5}]dodeca-4,6,9,11-tetraen-3-one, a methylenehomobarrelene. Product **4a** was a bis(methoxycarbonyl) derivative of **3a**, a Diels-Alder adduct between **1a** and dimethyl butynedioate. Product **5a** was a [4+2]adduct and its stereochemistry was deduced from the coupling constant of the methine protons. No [8+2]cycloadduct was detected at all. Yields of products are summarized in Table 1.

Next, 3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one (**1b**)[6] and **2** gave two [4+2]cycloadducts (**5b** and **7b**) and cycloreversed product **3b**. The reactions of **2** and 5-chloro-3-methoxycarbonyl (**1c**),[7] 5-methoxy-3-methoxycarbonyl (**1d**),[7] and 6-isopropyl-3-methoxycarbonyl (**1e**)[8] derivatives afforded similar products as shown in Scheme 1. The structures of these products were determined from comparison with the NMR data of the products from **1a** and **2**. In the case of **1e**, a single product (**5e**) was obtained in 8% yield. This low yield might be attributable to steric hindrance of the bulky isopropyl group at the reaction site. A reaction under 3000 bar afforded [4+2]adducts in improved yields; from **1b** and **2**, two [4+2]adducts (**5b** and **7b**) formed in 70% yield together with **3b** in 12% yield.

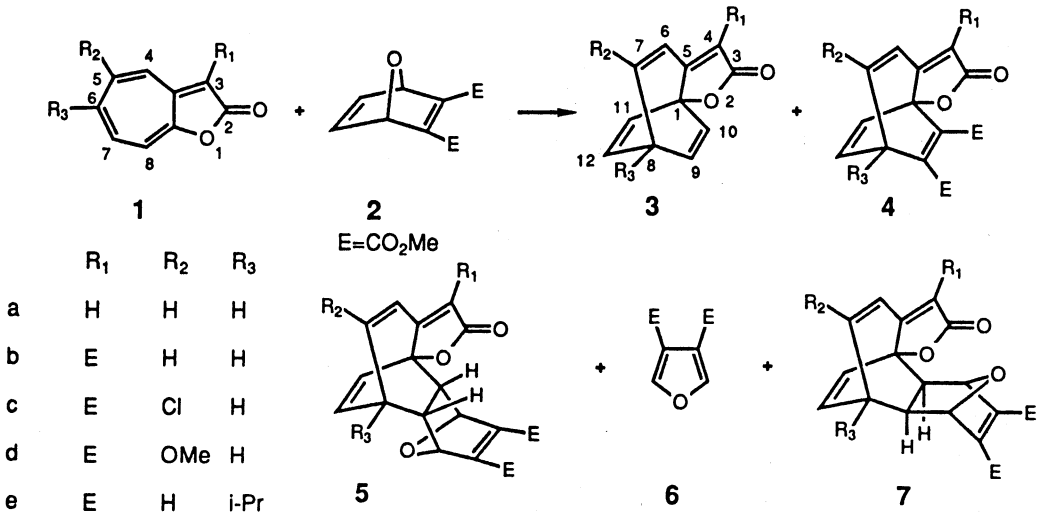
Table 1. Cycloaddition Products from **1** and **2**[a]

Substrate	Products (Yield/%)			
1a	**3a** (35)	**4a** (7)	**5a** (26)	—[b]
1b	**3b** (40)	—	**5b** (43)	**7b** (11)
	3b (12)[c]	—	**5b**+**7b** (70)[c]	
1c	**3c** (33)	**4c** (2)	**5c** (14)	**7c** (6)
1d	**3d** (50)	**4d** (3.6)	**5d** (34)	**7d** (12)
1e	—	—	**5e** (8)	—

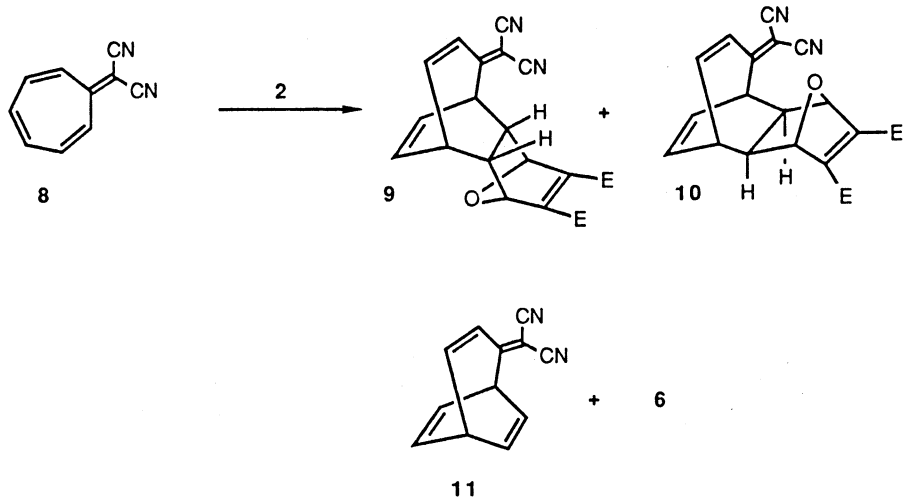
a) Yields shown indicate amounts isolated based on consumed starting materials. b) Not isolated. c) Under 3000 bar.

† On leave from Yanbian University, Yanji, Jilin, People's Republic of China.

†† Present address: Department of Technology, Tokushima University, Tokushima 770.



Scheme 1.



Scheme 2.

Similarly, the reaction of **2** and 8,8-dicyanoheptafulvene (**8**) gave [4+2]adducts (**9** and **10**) in 43 and 10% yields along with a cycloreversed 2-(dicyanomethylene)-homobarrelene (**11**). Yields of **9** and **10** increased to 76 and 13%, but that of **11** was 2.5% under 3000 bar. Thus, cycloreversions to **3** and **11** were suppressed under 3000 bar.

Pyrolysis of Adducts. Thermolyses of **5** and **9** in chlorobenzene gave methylenehomobarrelenes as summarized in Table 2. The chemical shifts of C_9 (δ 131.9—133.6) in **4** were high-field shifted by ca. 11—16 ppm than that of C_{10} (δ 145.0—147.8) and as well as the chemical shift of unsubstituted olefinic carbons, C_{11} and C_{12} (δ 131.0—135.4). From these observations, a methoxycarbonyl group at C_{10} took an out-of-plane conformation due to steric interactions with adjacent substituents.

Molecular Orbital Considerations. As mentioned above, no [8+2]adduct was isolated from the reactions of **1** and **2**. The molecular orbitals of **1** and **2** were calculated by the MNDO method together with (dimethylamino)ethene (**A**) and methoxyethene (**B**). From the energy separation between the frontier orbitals, the [8+2]adducts are preferred in the reactions between **2** and **1** (except for **1c**), whereas the [4+2]adducts are favored in the reactions of **1** with **A** and **B**. These are not in accord to the experimental observations.

Table 2. Thermolysis of **5** and **9** at 130 °C

Compound	Products yield/%		
	3	**6**	**11**
5a	54	54	
5b	57	57	
5c	70	70	
5d	55	55	
9		99	95

Namely, other than the reactions of 5-substituted **1c** and **1d**, the exclusive formation of [4+2]adducts from **1**

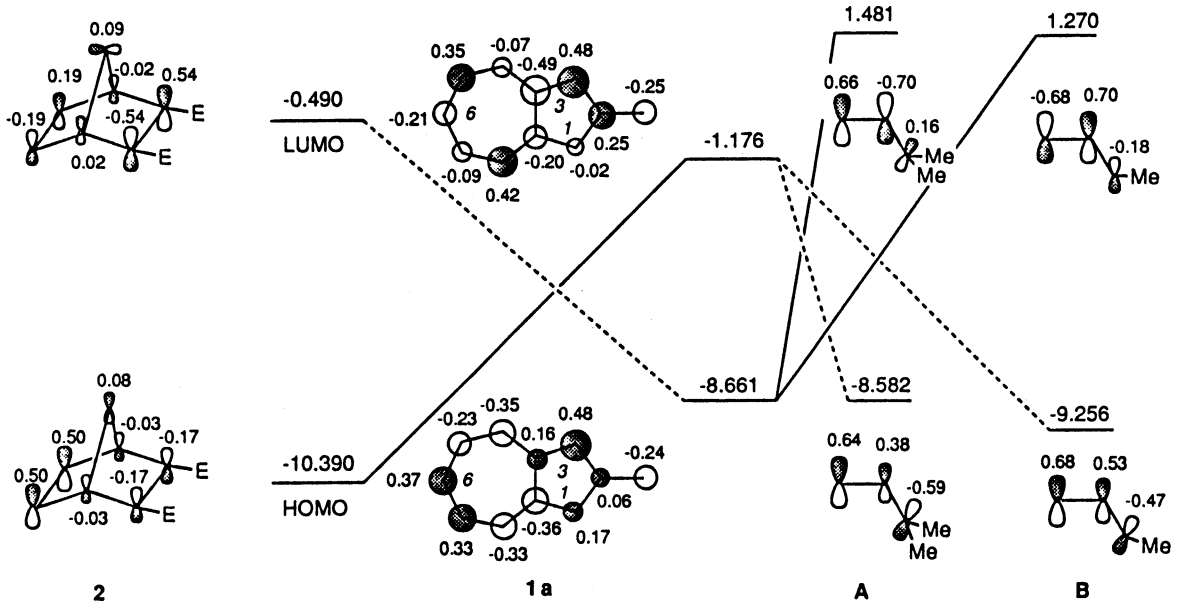


Fig. 1. HOMO-LUMO correlation diagrams of **1a** and olefins

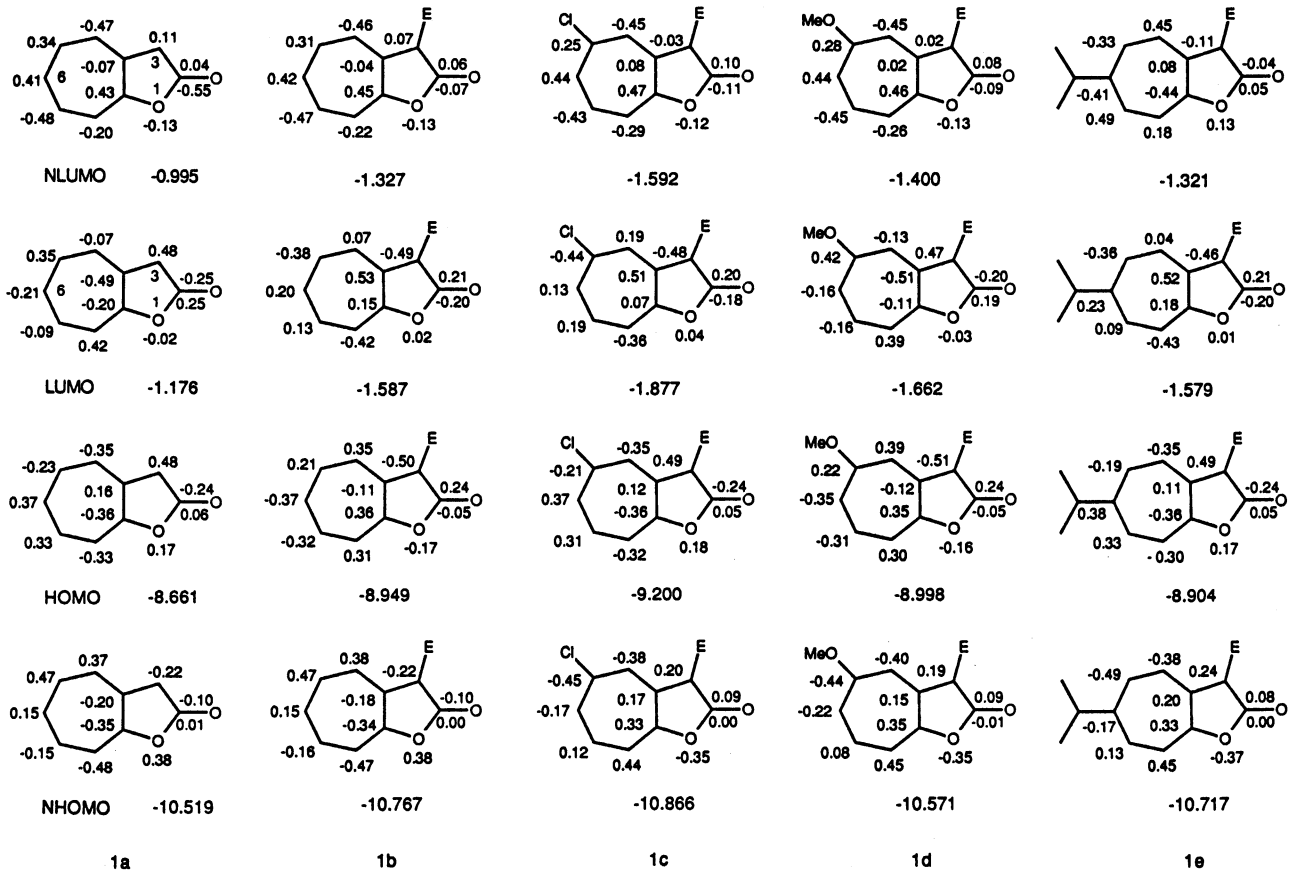
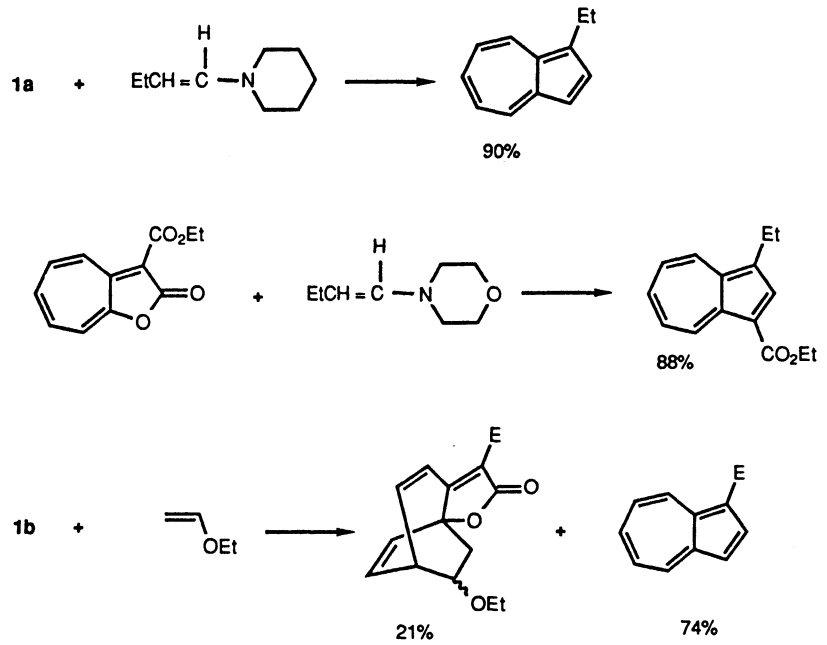


Fig. 2. Coefficients and energy levels of selected molecular orbitals of **1**.

and **2** is consistent with the prediction from the square of the sum of the products of the coefficients of interacting centers:[4] the HOMO(**2**)-LUMO(**1a**) interaction which expected the [4+2]adduct, is more favorable than the [8+2]adduct-forming HOMO(**1a**)-LUMO(**2**) interaction as shown in Fig. 1 and Table 3. In the same time, the antibonding interaction indicated to disfavor a formation of the [8+2]adduct. However, this treatment favored the formation of an [8+2]adduct between 5-substituted **1** and **2**, although it was not



Scheme 3.

Table 3. Calculation of Stabilization Energy ($\times 10^4$)[a] between **1** and **2**

	Reaction mode	**1a**	**1b**	**1c**	**1d**	**1e**
HOMO(**2**)-LUMO(**1**)	[4+2]	46	35	12	21	48
LUMO(**2**)-HOMO(**1**)	[8+2]	31	32	30	31	31
HOMO(**2**)-NLUMO(**1**)	[4+2]	188	209	235	225	199
LUMO(**2**)-NHOMO(**1**)	[4+2]	9	8	9	12	9
[4+2]/[8+2]		243/31	252/32	256/30	258/31	256/31

a) See the Ref. 4.

Table 4. Calculation of Stabilization Energy between **1a** and **A** and **B**

	Reaction mode	**A**	**B**
HOMO(**A** or **B**)-LUMO(**1a**)	[4+2]	0.0058	0.0076
LUMO(**A** or **B**)-HOMO(**1a**)	[8+2]	0.0324	0.0340
HOMO(**A** or **B**)-NLUMO(**1a**)	[4+2]	0.0245	0.0314
LUMO(**A** or **B**)-NHOMO(**1a**)	[4+2]	0.0094	0.0100
[4+2]/[8+2]		397/324	490/340

consistent with the experimental results.

In order to provide a consistent explanation of the results, we took the participations of NLUMO and NHOMO of **1** into account since both pairs of LUMO(**1**) and NLUMO(**1**) and HOMO(**1**) and NHOMO(**1**) have the same pseudosymmetries at C_6 and C_{8a}[4] and the coefficients of the NLUMO(**1**) at these atoms are larger than those of LUMO(**1**). As shown in Table 3, the interaction between HOMO(**2**) and NLUMO(**1**) is the largest and it contributes 77—92% towards the total stabilization energy[4] for the [4+2]cycloaddition reaction. Thus, the formation of the [4+2]adduct could be explained.

On the other hand, the results of **1** and enamines and alkoxyethenes were reported to give rather complicated product distributions; the reactions of **1a** and 1-(1-pyrrolidinyl)-1-butene and 3-ethoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one and 1-morpholino-1-butene gave the [8+2]cycloadducts, 1-ethylazulene, and 1-ethyl-3-ethoxycarbonylazulene in 90 and 88% yields, respectively.[9] No [4+2]adduct formed.

Recently, Nozoe et al. reported the formation of a [8+2]cycloadduct by isolating 1-methoxycarbonylazulene in 74% yield together with an isomeric mixture of three [4+2]adducts in 21% yield, from **1b** and ethoxyethene to reveal two reaction modes.[3] There remained the problem of which cycloadduct is the kinetically-controlled product. From the HOMO-LUMO interactions, the formations of [8+2]adducts were expected, whereas an involvement of NLUMO and NHOMO effects would result in the formation of [4+2]adducts. The calculation of the stabilization energy between **1a** and **A** or **B** is shown in Table 4.

To make these points clear, a further study under high-pressure conditions should be desirable, where a formation of a kinetically-controlled product is expected to be predominant.

Experimental

Elemental analyses were performed by Miss S. Hirashima,

of the Institute of Advanced Material Study, Kyushu University. NMR spectra were measured with JEOL FX 100 Model and GSX 270 H Model spectrometers in $CDCl_3$ solution (unless otherwise specified); chemical shifts are expressed in the unit δ. Mass spectra were measured with a JEOL OlSG-2 spectrometer at 70 eV. IR spectra were taken as KBr disks or as liquid films inserted between NaCl plates using a Jasco IR-A 102 spectrometer. UV spectra were measured with a Hitachi U-3200 spectrophotometer.

Cycloadditions of 1 and 2. General Method. A chlorobenzene solution (1.5 cm^3) of **1** (0.2—1 mmol) and **2** (0.5—1.1 mmol) was heated at 130 °C for 36 h in a sealed ampule, purged with N_2. The mixture was chromatographed on a silica-gel column to give products.

3a: Colorless crystals, 35%; mp 116.5—117.5 °C. ^{1}H NMR δ=3.96 (1H, dtt, J=7.7, 6.6, 1.1 Hz), 5.70 (1H, s), 6.00 (1H, d, J=10.6 Hz), 6.35 (2H, dd, J=7.7, 1.1 Hz), 6.52 (2H, dd, J=7.7, 6.6 Hz), and 6.57 (1H, dd, J=10.6, 7.7 Hz); ^{13}C NMR δ=40.1, 87.8, 111.6, 118.7, 132.1 (2C), 133.0 (2C), 139.8, 158.2, and 173.5; IR 1760, 1620, 1350, 1105, 1025, 905, and 850 cm^{-1}; UV (MeOH) 259.4 (ε 10600) and 297.0 nm (5000); MS m/z (%) 170 (M^+, 10), 116 (62), 115 (base), 89 (29), and 63 (38).

Found: C, 77.03; H, 4.74%. Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68%.

4a: Colorless crystals, 7%; mp 121—123 °C. ^{1}H NMR δ=3.78 (3H, s), 3.83 (3H, s), 4.51 (1H, dd, J=7.7, 7.0 Hz), 5.83 (1H, s), 6.15 (1H, d, J=10.6 Hz), 6.39 (1H, dd, J=7.7, 1.5 Hz), and 6.6 (2H, m); ^{13}C NMR δ=39.5, 52.8, 52.9, 86.4, 113.3, 119.9, 131.9, 132.7, 133.6, 138.2, 145.0, 155.6, 163.1, 163.9, and 171.7; IR 1765, 1720, 1435, 1330, and 1270 cm^{-1}; UV (MeOH) 219.2 (ε 9700), 248.0 (9750), and 293.0 nm (4200); MS m/z (%) 288 (M^+, 19), 229 (57), 228 (34), 197 (30), and 44 (base).

Found: C, 62.57; H, 4.19%. Calcd for $C_{15}H_{12}O_6$: C, 62.50; H, 4.20%.

5a: Colorless crystals, 26%; mp 137—139 °C. ^{1}H NMR δ=2.29 (1H, dd, J=8.1, 1.1 Hz), 2.53 (1H, dd, J=8.1, 1.1 Hz), 3.48 (1H, dd, J=8.8, 7.7 Hz), 3.81 (6H, s), 4.92 (1H, d, J=1.1 Hz), 5.47 (1H, d, J=1.1 Hz), 5.66 (1H, s), 6.09 (1H, d, J=8.4 Hz), 6.21 (1H, dd, J=8.4, 7.7 Hz), 6.33 (1H, d, J=10.6 Hz), and 6.67 (1H, dd, J=10.6, 8.8 Hz); ^{13}C NMR δ =39.4, 44.2, 49.3, 52.7, 52.8, 83.6, 85.5, 88.1, 111.4, 121.7, 130.0, 131.0, 144.2, 145.4, 145.5, 162.7, 162.9, 164.0, and 172.8; IR 1750, 1630, 1435, 1265, and 1210 cm^{-1}; UV (MeOH) 244.2 (ε 11500), 268.2 (10900), and 397.0 nm (1450).

Found: C, 63.95; H, 4.50%. Calcd for $C_{19}H_{16}O_7$: C, 64.04; H, 4.53%.

3b: Colorless crystals, 40%; mp 149—150 °C. ^{1}H NMR δ=3.87 (3H, s), 4.12 (1H, dttd, J=8.1, 6.2, 1.5, 1.1 Hz), 6.39 (2H, dd, J=7.3, 1.5 Hz), 6.65 (2H, dd, J=7.3, 6.2 Hz), 6.78 (1H, dd, J=10.7, 1.1 Hz), and 6.91 (1H, dd, J=10.7, 8.1 Hz); ^{13}C NMR δ=41.5, 52.2, 86.3, 112.2, 118.7, 132.9 (2C), 133.7 (2C), 145.8, 161.7, 162.7, and 168.6; IR 1770, 1710, 1610, 1430, 1260, and 1030 cm^{-1}; UV (MeOH) 212.4 (ε 5300), 276.4 (8900), and 319.0 nm (4600); MS m/z (%) 230 (M^+, base), 198 (46), 170 (39), 115 (85), 91 (69), and 44 (67).

Found: C, 67.67; H, 4.38%. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38%.

5b: Colorless crystals, 43%; mp 138.5—139.5 °C. ^{1}H NMR δ=2.32 (1H, dd, J=8.1, 1.1 Hz), 2.57 (1H, dd, J=8.1, 1.1 Hz), 3.62 (1H, dd, J=8.4, 7.3 Hz), 3.80 (3H, s), 3.82 (3H, s), 3.89 (3H, s), 4.95 (1H, d, J=1.5 Hz), 5.48 (1H, d, J=1.5 Hz), 6.10 (1H, dt, J=8.4, 1.1 Hz), 6.31 (1H, dd, J=8.4, 7.3 Hz), 7.00 (1H, dd, J=10.6, 8.4 Hz), and 7.16 (1H, d, J=10.6 Hz); ^{13}C NMR δ=40.3, 44.4, 49.6, 52.5, 52.7, 52.8, 83.6, 85.4, 86.3, 111.8, 121.6, 129.6, 132.2, 145.3, 145.7, 150.0, 162.0, 162.4, 162.8, 168.0, and 168.2; IR 1770, 1710, 1615, 1430, 1270, and 1210 cm^{-1}; UV (MeOH) 203.6 (ε 8350), 241.8 (7100), and 291.8 nm (10700).

Found: C, 60.91; H, 4.33%. Calcd for $C_{21}H_{18}O_9$: C, 60.87; H, 4.38%.

7b: Colorless crystals, 11%; mp 187—188 °C. ^{1}H NMR δ=2.58 (1H, dd, J=8.8, 5.9 Hz), 3.02 (1H, d, J=8.8 Hz), 3.73 (1H, dddm, J=8.4, 7.0, 5.9 Hz), 3.80 (3H, s), 3.81 (3H, s), 3.89 (3H, s), 4.74 (1H, d, J=1.1 Hz), 4.87 (1H, d, J=1.1 Hz), 6.22 (1H, dd, J=8.4, 0.7 Hz), 6.44 (1H, dd, J=8.4, 7.0 Hz), 6.73 (1H, dd, J=10.6, 8.4 Hz), and 7.41 (1H, d, J=10.6 Hz); ^{13}C NMR δ=38.3, 41.8, 52.1, 52.4, 52.5, 52.6, 79.1, 83.2, 87.4, 113.3, 125.9, 133.1, 135.1, 144.5, 145.4, 146.1, 161.5, 161.8, 162.5, 167.2, and 167.9; IR 1775, 1720, 1620, 1440, 1280, 1210, and 1035 cm^{-1}; UV (MeOH) 243.2 (ε 5900) and 295.8 nm (7600).

Found: C, 60.89; H, 4.40%. Calcd for $C_{21}H_{18}O_9$: C, 60.87; H, 4.38%.

3c: Colorless crystals, 33%; mp 148—149 °C. ^{1}H NMR δ=3.89 (3H, s), 4.26 (1H, tq, J=6.6, 1.5 Hz), 6.48 (2H, dd, J=7.7, 1.5 Hz), 6.72 (2H, dd, J=7.7, 6.6 Hz), and 6.95 (1H, d, J=1.5 Hz); ^{13}C NMR δ=50.5, 52.3, 85.3, 111.6, 115.8, 131.2 (2C), 134.6 (2C), 152.1, 161.5, 162.8, and 168.1; IR 1780, 1710, 1610, 1250, and 1035 cm^{-1}; UV (MeOH) 283.4 (ε 10500) and 321.4 nm (9400); MS m/z (%) 266 (M^++2, 11), 264 (M^+, 34), 229 (base), 197 (61), and 149 (36).

Found: C, 58.80; H, 3.42%. Calcd for $C_{13}H_9O_4Cl$: C, 59.00; H, 3.43%.

4c: Colorless crystals, 2%; mp 155—157 °C. ^{1}H NMR δ=3.83 (3H, s), 3.84 (3H, s), 3.90 (3H, s), 4.82 (1H, ddd, J=7.0, 1.8, 1.5 Hz), 6.51 (1H, dd, J=8.1, 1.5 Hz), 6.82 (1H, dd, J=8.1, 7.0 Hz), and 7.09 (1H, d, J=1.8 Hz); ^{13}C NMR δ=49.7, 52.6, 53.2 (2C), 84.0, 112.8, 117.0, 131.9, 132.8, 133.5, 145.8, 150.6, 160.4, 161.0, 162.2, 163.1, and 166.6; IR 1780, 1730, 1615, 1440, 1275, 1250, 1035, and 1025 cm^{-1}; UV (MeOH) 267.4 (ε 8600) and 322.6 nm (8200); MS m/z (%) 382 (M^++2, 14), 380 (M^+, 42), 349 (29), 323 (35), 321 (base), 292 (47), 289 (45), 277 (33), 207 (33), and 59 (75).

Found: C, 53.92; H, 3.58%. Calcd for $C_{17}H_{13}O_8Cl$: C, 53.63; H, 3.44%.

5c: Colorless crystals, 14%; mp 209—210 °C. ^{1}H NMR δ=2.36 (1H, dd, J=7.7, 1.1 Hz), 2.74 (1H, dd, J=7.7, 1.1 Hz), 3.77 (1H, dm, J=7.7 Hz), 3.81 (3H, s), 3.83 (3H, s), 3.90 (3H, s), 4.97 (1H, d, J=1.1 Hz), 5.47 (1H, d, J=1.1 Hz), 6.15 (1H, dm, J=8.8 Hz), 6.35 (1H, dd, J=8.8, 7.7 Hz), and 7.35 (1H, d, J=1.8 Hz); ^{13}C NMR δ=43.9, 49.5, 50.0, 52.4, 52.5, 52.7, 83.2, 84.8, 84.9, 110.9, 118.9, 129.7, 130.7, 145.0, 145.2, 155.5, 161.5, 162.0, 162.3, 166.7, and 167.2; IR 1775, 1720, 1610, 1438, 1260, and 1220 cm^{-1}; UV (MeOH) 242.6 (ε 8200) and 305.6 nm (13700).

Found: C, 56.29; H, 3.87%. Calcd for $C_{21}H_{17}O_9Cl$: C, 56.20; H, 3.82%.

7c: Colorless crystals, 6%; mp 155—156 °C. ^{1}H NMR δ=2.63 (1H, dd, J=8.8, 6.2 Hz), 3.00 (1H, d, J=8.8 Hz), 3.81 (3H, s), 3.83 (3H, s), 3.90 (3H, s), 3.9 (1H, m), 4.75 (1H, d, J=1.1 Hz), 5.06 (1H, d, J=1.1 Hz), 6.28 (1H, dd J=8.4, 0.7 Hz), 6.50 (1H, dd, J=8.4, 7.3 Hz), and 7.58 (1H, d, J=1.8 Hz); ^{13}C NMR δ=41.8, 48.4, 51.3, 52.4, 52.5, 52.6, 79.2, 82.4, 86.4, 112.6, 123.2, 132.8, 134.3, 145.3, 145.8, 150.2, 161.3, 161.7, 162.4, 165.6, and 167.4; IR 1775, 1720, 1620, 1440, 1335, 1270, 1250, and 1030 cm^{-1}; UV (MeOH) 240.0 (ε 7000) and 312.6

nm (11200).

Found: C, 56.26; H, 3.86%. Calcd for $C_{21}H_{17}O_9Cl$: C, 56.20; H, 3.82%.

3d: Colorless crystals, 50%; mp 136—137 °C. ^{1}H NMR δ=3.78 (3H, s), 3.87 (3H, s), 4.07 (1H, tdt, J=6.6, 2.6, 1.5 Hz), 6.06 (1H, d, J=2.6 Hz), 6.52 (2H, dd, J=7.4, 1.5 Hz), and 6.60 (2H, dd, J=7.4, 6.6 Hz); ^{13}C NMR δ=47.1, 53.1, 56.7, 85.7, 88.6, 106.0, 130.2 (2C), 136.5 (2C), 163.1, 169.1, 169.6, and 172.6; IR 1760, 1710, 1580, 1380, 1360, 1290, 1265, and 1035 cm^{-1}; UV (MeOH) 269.6 (ε 6300) and 344.2 nm (16250): MS m/z (%) 260 (M^+, base), 229 (39), 200 (35), 145 (35), 115 (38), 102 (37), 76 (30), and 65 (31).

Found: C, 64.81; H, 4.65%. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65%.

4d: Colorless crystals, 3.6%; mp 186—187 °C. ^{1}H NMR δ=3.80 (6H, s), 3.84 (3H, s), 3.87 (3H, s), 4.65 (1H, ddd, J=7.0, 2.2, 1.5 Hz), 6.19 (1H, d, J=2.2 Hz), 6.55 (1H, dd, J=7.7, 1.5 Hz), and 6.73 (1H, dd, J=7.7, 7.0 Hz); ^{13}C NMR δ=46.5, 52.6, 53.1 (2C), 56.7, 84.3, 89.6, 107.2, 131.0, 131.9, 135.4, 147.8, 162.5, 162.6, 163.5, 166.8, 167.7, and 170.9; IR 1780, 1730, 1690, 1440, 1285, and 1260 cm^{-1}; UV (MeOH) 208.8 (ε 17900), 263.6 (7900), and 348.4 nm (13900): MS m/z (%) 376 (M^+, 42), 317 (37), 288 (35), 285 (43), 203 (35), 119 (34), 93 (36), 76 (36), 59 (base), and 44 (60).

Found: C, 57.58; H, 4.30%. Calcd for $C_{18}H_{16}O_9$: C, 57.45; H, 4.29%.

5d: Colorless crystals, 34%; mp 232—233 °C. ^{1}H NMR δ=2.35 (1H, dd, J=8.1, 1.1 Hz), 2.61 (1H, dd, J=8.1, 1.5 Hz), 3.56 (1H, dm, J=6.6 Hz), 3.80 (3H, s), 3.82 (3H, s), 3.83 (3H, s), 3.88 (3H, s), 4.97 (1H, d, J=1.1 Hz), 5.47 (1H, d, J=1.1 Hz), 6.19 (1H, dt, J=8.8, 1.1 Hz), 6.26 (1H, dd, J=8.8, 6.6 Hz), and 6.50 (1H, d, J=2.2 Hz); ^{13}C NMR δ=43.4, 45.9, 50.2 (2C), 51.9, 52.6, 56.8, 83.2, 85.0, 85.1, 92.0, 105.2, 128.5, 132.5, 145.2, 145.6, 162.1, 162.5, 163.1, 168.5, 172.8, and 176.7; IR 1760, 1715, 1690, 1440, 1270, and 1235 cm^{-1}; UV (MeOH) 215.0 (ε 13500), 240.8 (10100), and 336.0 nm (18000).

Found: C, 59.33; H, 4.57%. Calcd for $C_{22}H_{20}O_{10}$: C, 59.46; H, 4.54%.

7d: Colorless crystals, 12%; mp 233—234 °C. ^{1}H NMR δ=2.59 (1H, dd, J=8.8, 7.0 Hz), 2.95 (1H, d, J=8.8 Hz), 3.65 (1H, tm, J=7.0 Hz), 3.81 (3H, s), 3.82 (3H, s), 3.84 (3H, s), 3.88 (3H, s), 4.78 (1H, d, J=1.1 Hz), 4.91 (1H, d, J=1.1 Hz), 6.33 (1H, dd, J=8.4, 1.5 Hz), 6.39 (1H, dd, J=8.4, 7.0 Hz), and 6.76 (1H, d, J=2.2 Hz); ^{13}C NMR δ=41.6, 44.7, 51.2, 51.8, 52.5 (2C), 56.8, 79.7, 82.3, 86.3, 96.6, 106.9, 131.6, 136.4, 145.2, 146.1, 161.8, 162.5, 162.9, 168.5, 171.3, and 173.4; IR 1760, 1710, 1695, 1440, and 1230 cm^{-1}; UV (MeOH) 219.2 (ε 12400) and 341.6 nm (16200).

Found: C, 59.27; H, 4.55%. Calcd for $C_{22}H_{20}O_{10}$: C, 59.46; H, 4.54%.

5e: Colorless crystals, 8%; mp 212 °C. ^{1}H NMR δ=1.17 (3H, d, J=6.6 Hz), 1.18 (3H, d, J=6.6 Hz), 2.17 (1H, sept, J=6.6 Hz), 2.34 (1H, d, J=8.1 Hz), 2.55 (1H, d, J=8.1 Hz), 3.80 (3H, s), 3.81 (3H, s), 3.89 (3H, s), 5.13 (1H, d, J=1.1 Hz), 5.49 (1H, d, J=1.1 Hz), 6.05 (1H, dd, J=9.2, 1.1 Hz), 6.10 (1H, dd, J=9.2, 1.1 Hz), 6.82 (1H, d, J=11.0 Hz), and 7.22 (1H, d, J=11.0 Hz); ^{13}C NMR δ=16.2, 18.4, 32.4, 47.6, 49.2, 50.5, 52.3, 52.4, 52.6, 80.5, 83.3, 85.8, 110.9, 121.3, 128.3, 136.3, 145.0, 146.0, 151.1, 161.8, 162.2, 162.6, 167.8, and 168.0; IR 1765, 1735, 1710, 1620, 1435, 1275, and 1225 cm^{-1}; UV (MeOH) 245.8 (ε 9800) and 294.0 nm (15600).

Found: C, 62.96; H, 5.32%. Calcd for $C_{24}H_{24}O_9$: C, 63.15; H, 5.30%.

Cycloaddition of 2 and 8. A chlorobenzene solution, (2 cm^3) of **8** (188 mg) and **2** (265 mg) was heated at 130 °C for 20 h in a sealed tube. The mixture was chromatographed on a silica-gel column to give 54 mg (47%) of **6**, 100 mg (43%) of **9**, 23 mg (10%) of **10**, 38.7 mg (42%) of **11**, and unreacted **8** (78.9 mg).

9: Colorless crystals, mp 164—165 °C; ^{1}H NMR δ=2.38 (1H, dm, J=7.7 Hz), 2.65 (1H, dd, J=7.7, 1.1 Hz), 3.51 (1H, ddm, J=8.1, 7.7 Hz), 3.82 (3H, s), 3.83 (3H, s), 4.17 (1H, dm, J=7.0 Hz), 4.93 (1H, d, J=1.1 Hz), 5.10 (1H, d, J=1.1 Hz), 6.09 (1H, dd, J=7.7, 7.0 Hz), 6.46 (1H, t, J=7.7 Hz), 6.52 (1H, dd, J=10.6, 2.2 Hz), and 7.02 (1H, dd, J=10.6, 8.1 Hz); ^{13}C NMR δ=40.0, 44.0, 46.1, 48.2, 52.5, 52.6, 81.1, 85.5, 86.4, 111.7, 112.8, 125.4, 126.3, 136.6, 144.9, 145.6, 152.0, 162.3, 162.7, and 169.4; IR 2250, 1730, 1610, 1440, 1290, 1255, and 1230 cm^{-1}. UV (MeOH) 243.4 (ε 8600) and 302.6 nm (16200).

Found: C, 65.97; H, 4.47; N, 7.47%. Calcd for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69%.

10: Colorless crystals, mp 183—184 °C; ^{1}H NMR δ=2.63 (1H, dd, J=8.4, 5.8 Hz), 2.78 (1H, dd, J=8.4, 5.5 Hz), 3.64 (1H, td, J=8.0, 5.8 Hz), 3.81 (3H, s), 3.83 (3H, s), 4.27 (1H, dd, J=7.0, 5.5 Hz), 4.82 (2H, s), 6.16 (1H, dd, J=7.3, 7.0 Hz), 6.62 (1H, dd, J=8.0, 7.3 Hz), and 6.7—6.8 (2H, m); ^{13}C NMR δ=38.8, 44.9, 47.3, 48.0, 52.5, 52.6, 81.7, 82.6, 83.2, 111.8, 113.2, 129.2, 129.9, 140.4, 145.3, 146.0, 147.3, 162.4, 162.5, and 169.5; IR 2240, 1725, 1610, 1440, 1290, 1265, and 1230 cm^{-1}; UV (MeOH) 243.4 (ε 7900) and 307.2 nm (12600).

Found: C, 65.76; H, 4.45; N, 7.40%. Calcd for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69%.

11: Colorless needles, mp 71—73 °C; ^{1}H NMR δ=3.98 (1H, dtm, J=8.4, 6.6 Hz), 4.68 (1H, tdd, J=6.6, 2.2, 1.5 Hz), 6.06 (1H, dd, J=10.6, 2.2 Hz), 6.36 (2H, td, J=6.6, 1.5 Hz), 6.84 (2H, td, J=6.6, 1.5 Hz), and 6.95 (1H, dd, J=10.6, 8.4 Hz); ^{13}C NMR δ=41.8, 46.8, 81.8, 111.6, 113.1, 122.3, 128.3 (2C), 140.2 (2C), 149.2, and 164.1; IR 2245, 1600, 1530, 1355, 1290, 930, and 897 cm^{-1}; UV (MeOH) 287.4 (ε 12700) and 390.6 nm (6200); MS m/z (%) 180 (M^+, 28), 153 (35), 115 (base), 76 (36), 75 (34), 63 (50), 62 (38), 51 (34), 50 (71), and 49 (33).

Found: C, 79.94; H, 4.49; N, 15.57%. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.54%.

Cycloadditions under 3000 bar. a) A chlorobenzene solution (2 cm^3) of **1b** (110 mg) and **2** (115 mg) was heated at 120 °C for 36 h. The mixture was purified to give 7.1 mg (11%) of **3b**, 5.7 mg (12%) of **6**, 78.6 mg (70%) of **5b** and **7b**, and unreacted **1b** (53 mg).

b) A chlorobenzene solution (1.5 cm^3) of **8** (153 mg) and **2** (353 mg) was heated at 120 °C to give 210.5 mg (76%) of **9**, 37 mg (13%) of **10**, 3.4 mg (2.5%) of **11**, and unreacted **8** (36.3 mg).

Thermolysis of 5 and 9. A chlorobenzene solution (1 cm^3) of **5** (40 mg) was heated at 130 °C for 24 h. The mixture was chromatographed to give the products. The results were summarized in Table 2.

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