Synthetic Photochemistry. XLVI.[1] Cycloaddition of *exo, endo*-2,7-Bis(methoxycarbonyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene and Conjugated Enones and *p*-Quinones

Guan Rong TIAN,† Akira MORI, Nobuo KATO, and Hitoshi TAKESHITA*
Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
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Photocycloaddition of *exo,endo*-2,7-bis(methoxycarbonyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene with conjugated enones and *p*-quinones occurred exclusively at the exo-addition moiety to give [2+2]-cycloadducts. From cyclohexenone, all four possible photoadducts were obtained. A single photoadduct from cyclopentenone was a cis-transoid-cis isomer. Upon thermolysis, cyclobutene derivatives were formed from these photoadducts. An acid treatment of oxetane derivatives derived from photoadducts of *p*-quinones afforded Michael adducts instead of dienone-phenol rearrangement products.

Recently, we have shown that the thermal cycloaddition of 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]-heptadiene (**1**) and tropones,[2] cyclohepta[*b*]furan-2-ones,[3] and anthracenes[4] gave Diels-Alder adducts. Subsequent thermolysis of the adducts yielded homobarrelenones and dibenzobarrelenes. Therefore, **1** should be a useful "transfer reagent"[5,6] for acetylene. If **1** were applicable as an acetylene substitute in a photochemical version to form cyclobutenes, the utility of **1** should be extended to a great extent, since photoreactions of acetylenes with olefins were known to be contaminated by the formation of bicyclopropyl derivatives.[7] An irradiation of **1** with methyl 2,4-dioxopentanoate (**2**), however, solely gave a photoisomer of **1**, 7-oxaquadricyclane derivative (**3**),[8] but no intermolecular adduct. Instead of **1**, the reaction with *exo,endo*-2,7-bis(methoxycarbonyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (**4**),[9] a 1 : 2-adduct of dimethyl butynedioate to furan, was investigated because the intramolecular process was prohibited. Herein, we describe our findings.

Photoadditions with *p*-Quinones. The UV-irradiation of **4** and *p*-benzoquinone (**5**) by means of a high-pressure mercury lamp gave a single photoadduct (**6**) in 78% yield. The ^{1}H NMR spectrum of **6** showed it to be a 1 : 1-adduct having an oxetane structure. The reactive double bond of **4** was identified as depicted in the structure, since the exo,exo-isomer (**7**) was photochemically inactive toward **5** under the conditions used. In addition, an iodolactonization[10] of **6** gave two isomeric iodo lactones (**8** and **9**), in 32 and 31% yields, respectively. Although the structures of **8** and **9** could not be differentiated at this stage, it is certain that the reaction occurred at the anti C=C bond in **4**.[11] The oxetane ring was deduced to have an exo-stereochemistry from the coupling constants (J_{ab}=J_{cd}= 0 Hz).

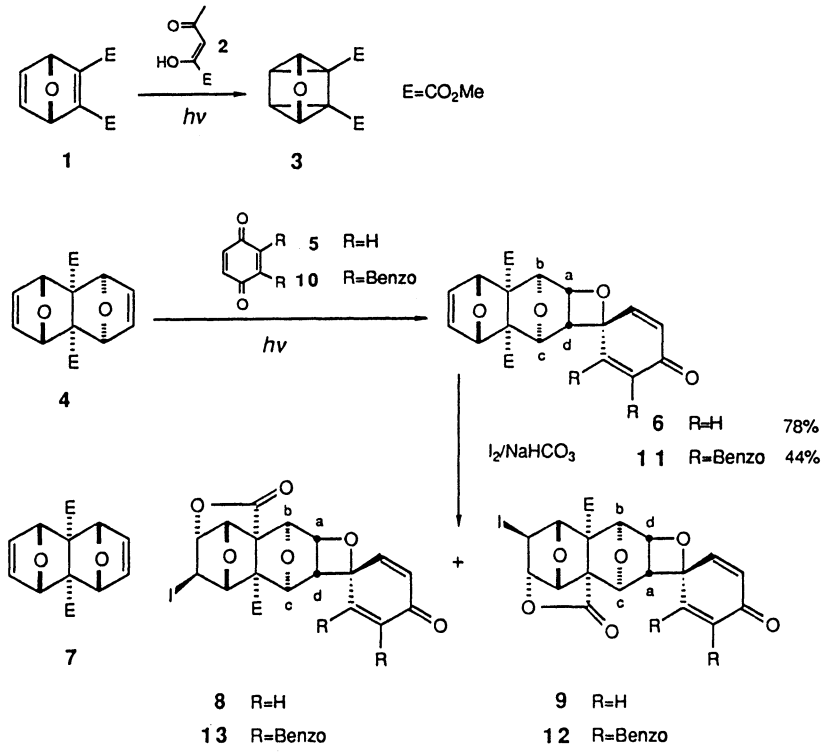
The UV-irradiation of **4** and 1,4-naphthoquinone (**10**) similarly gave a single product (**11**) in 44% yield. Again, the reaction occurred at the exo-C=C bond from the chemical shift of the remaining C=C carbons at δ=137.0 and 138.5 and the formation of two isomeric iodo lactones (**12** and **13**). The oxetane ring of **11** had an exo-stereochemistry according to the coupling constants (J_{ab}=J_{cd}=0 Hz). Its 1,4-dihydronaphthalene ring was exo from the observation of a high-field-shifted H_c signal (δ=4.47), than the H_c signal (δ=4.94 or 5.01) of **6**. An exclusive oxetane formation in *p*-quinones is a well-known reaction mode.[12,13]

It is interesting that in the ^{13}C NMR spectra the olefinic carbon signals of both photoadducts (**6** and **11**) appeared at nearly the same positions; in **6**, they were at 136.9 and 138.5, while those in **11** were at 137.0 and 138.5. These were also the case for photoadducts from the cycloalkanones and **2** (vide infra) and could be employed to deduce the structures of the products.

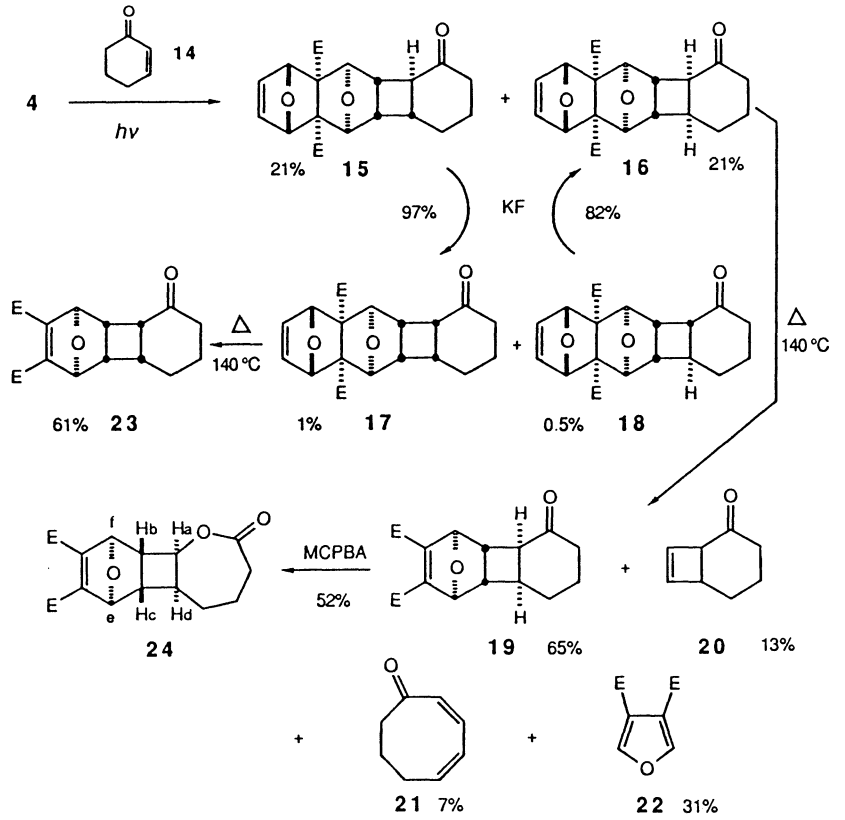
Photoadditions with Cyclic Enones. Similar UV-irradiation of **4** with 2-cyclohexenone (**14**) afforded four 1 : 1-adducts (**15**—**18**). The olefinic carbon signals of **15**—**18** appeared around 138 ppm, showing the occurrence of a reaction at the same C=C bond of **4**. The ^{1}H NMR spectra of **15**—**18** indicated that **14** attacked the exo site of **4**, but no further stereochemical information could be obtained at this stage. However, with potassium fluoride on Florisil,[14] **15** and **18** were converted to **17** and **16**, respectively; the newly-generated ring junctures of **16** and **17** were, thus, established to be cis.

Further chemical transformations clarified the remaining stereochemistry: When **16** was refluxed in xylene for 60 h, thermolysates (**19**—**21**) were obtained together with 3,4-bis(methoxycarbonyl)furan (**22**). Another cis-isomer **17** gave the thermolysate (**23**). Products **20** and **21** were identical with bicyclo[4.2.0]oct-7-en-2-one[15,16] and cyclooctadienone.[17] Since the ^{1}H NMR spectra of **19** and **23** were not informative to elucidate stereochemistries, an oxidation with *m*-chloroperbenzoic acid (MCPBA) was carried out; **19** gave a lactone (**24**), whereas **23** gave no oxidation product. The ^{1}H NMR spectrum of **24** showed a proton on the carbon bearing a lactonic oxygen atom at 4.39 (H_a, dd, J=6.6, 2.6 Hz). The nuclear Overhauser effect (NOE) experiments of **24** showed that the satura-

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



Scheme 1.



Scheme 2.

tion of the lower methine signal (H_f) resulted in an enhancement of both signals of H_a and H_b at 2.73 (1H, ddd, J=6.9, 2.6, 1.0 Hz), and the stereochemistry of **24** must be cis-transoid-cis. From these observations and the epimerization experiments, **16** and **17** were determined to be cis-transoid-cis and cis-cisoid-cis, respectively, and **15** and **18** were the corresponding trans epimers, as shown in Scheme 2.

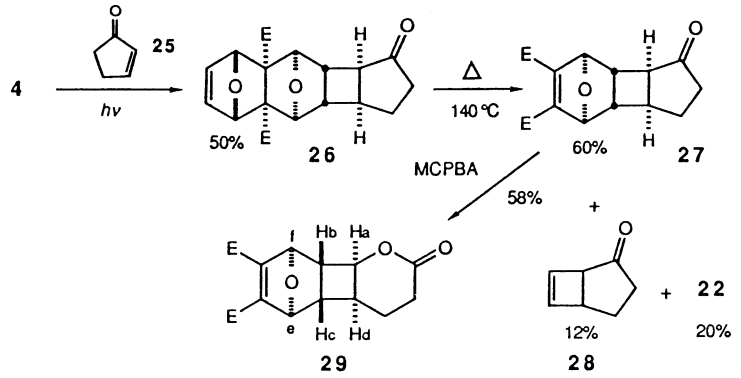
On the other hand, the irradiation of **4** with 2-cyclopentenone (**25**) gave a single product (**26**) in 50% yield. The stereochemistry of **26** was shown to be parallel to that of **16**: its thermolysis gave **27** and **28** in 60 and 12% yields, by refluxing in a xylene solution. The ^{1}H NMR spectrum of **28** was identical with that of the reported bicyclo[3.2.0]hept-6-en-2-one.[18,19] An MCPBA-oxidation of **27** did indeed occur to form a single lactone (**29**), whose ^{1}H NMR spectrum showed a proton signal on the lactonic carbon at δ=4.53 (H_a, dd, J=7.7, 2.9 Hz), which coupled to two signals (H_b and H_d) around 2.4 and 2.6, but not to a signal (H_c) at 2.32, being confirmed from the COSY spectrum. An irradiation of the lower methine signal (H_f) enhanced the signal of H_a.

The difference in the product distributions in reactions with **14** and **25** should be due to, at least in part, a large strain energy for *trans*-bicyclo[3.2.0]heptanone framework, which should have arisen from the latter (**25**).

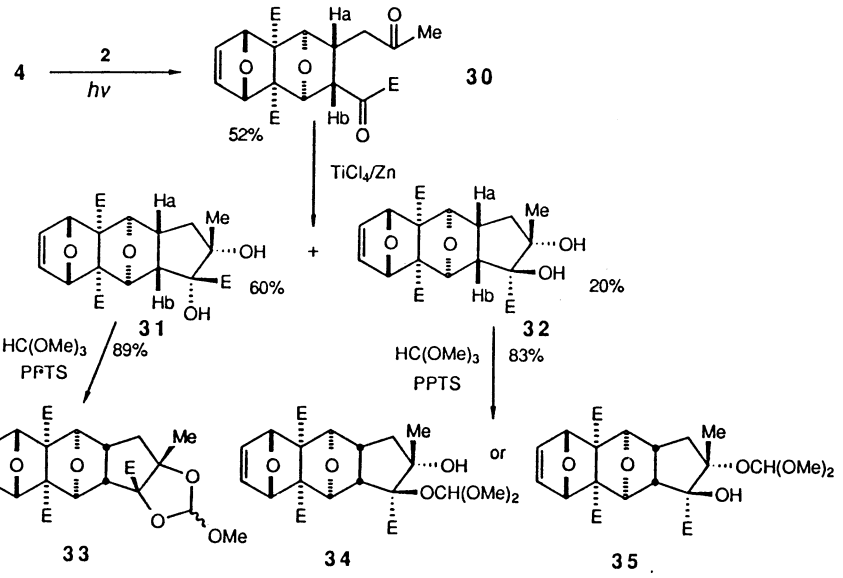
Photoaddition with Methyl 2,4-Dioxopentanoate (2). An irradiation of **4** with **2** gave a single product (**30**) via a [2+2] addition and a retro-aldol process.[20] The stereochemistry of **30** was determined to be as shown in Scheme 4 from the appearance of H_b as a doublet (J=8.4 Hz). A reductive cyclization of **30** with titanium(II) chloride[21] gave two 1,2-diols (**31** and **32**) in 60 and 20% yields. The NOE experiments of **31** and **32** established the cis relationship between the methyl group and protons H_a and H_b. Acetal formations of **31** to dioxolanes (**33**) and **32** to an uncyclized orthoformate (**34** or **35**) determined the *cis*- and *trans*-glycols, respectively.

All of the photoadducts from **4** with enones and *p*-quinones were derived by reactions at the anti C=C bond to the methoxycarbonyl groups. The inertness of the syn C=C bond toward photocycloaddition has been established without exception. The marked difference in the photochemical reactivity of these double bonds is interesting.

Thermal Cycloreversions of Photoadducts. As mentioned in the preparations of **19** and **27**, further cycloreversed products, **20** and **28**, were formed in 13 and 12% yields, respectively. Heating photoadduct **15** at 140 °C gave two products (**23** and **36**) in 44 and 38% yields, respectively. The latter **36** was quantitatively



Scheme 3.

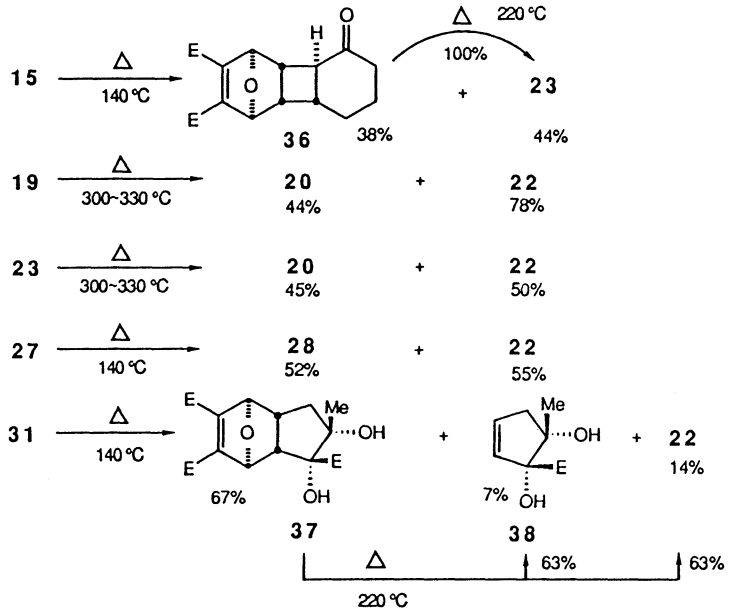


Scheme 4.

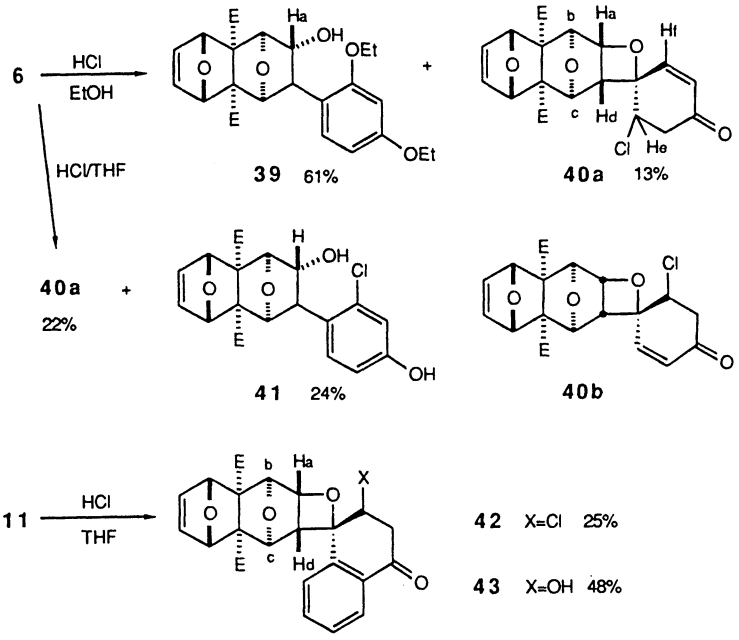
epimerized to **23** at 220 °C and the former **23** was obtained in 61% from the cis-cisoid-cis photoadduct **17**. Thermolysis of **19** and **23** at 330 °C gave **20** in 44 and 45% yields. While **27** was heated at 140 °C for 48 h, **28** was obtained in 52% yield together with **22**.

Subsequently, when **31** was thermolysed at 140 °C, thermolysates (**37** and **38**) were obtained in 67 and 7% yields. The former was converted to the latter in 63% yield at 220 °C.

Acid Treatments of Photoadducts from *p*-Quinones. Since photoadducts from *p*-quinones have a 2,5-cyclohexadienone chromophore, a dienone-phenol rearrangement would be expected.[12,13] When **6** was heated with hydrochloric acid in ethanol, two products (**39** and **40**) were formed in 61 and 13% yields. The major **39** had an aromatic ring with two ethoxyl groups, which were located at C-2 and C-4. The stereochemistry of the hydroxyl group was exo, from the coupling constant of H_a signal. The minor **40** had an enone chromophore and an oxetane ring. From the mass spectrum and an elemental analysis, **40** was shown to be a Michael adduct of hydrochloric acid. Two singlet signals of H_b and H_c appeared at 4.94 and 5.01 in **6**, whereas corresponding signals at 4.97 and 5.35 in **40**. One of them moved to the lower field upon the introduction of a chlorine atom. Therefore, the



Scheme 5.



Scheme 6.

structure **40a** should be as depicted. The stereochemistry of the chlorine atom was quasi-axial due to an observation of a long-range coupling between H_e and H_f. To minimize the Michael adduct formation, the reaction was carried out in tetrahydrofuran; a new chlorophenol derivative (**41**) was obtained along with **40a**. Similarly, **11** gave two Michael adducts (**42** and **43**) as shown in Scheme 6. A chlorine atom of **42** was quasi-equatorial because a methylene signal appeared as two doublets of doublets at 3.02 (J=18.7, 12.8 Hz) and 3.28 (J=18.7, 5.5 Hz), while the hydroxyl group of **43** was quasi-axial from the splittings of the methylene signals at 2.89 (dm, J=18.9 Hz) and 2.98 (dd, J=18.9, 2.7 Hz). The chemical shifts of H_b and H_c (5.10 and 4.24) of **42** were similar to those (5.19 and 4.47) of **11**.

Thus, a dienone-phenol rearrangement did not occur in these particular photoadducts from *p*-quinones.

Conclusion

As has been described, **4** was photochemically reactive with cyclic enones and a further thermal cycloreversion of the photoadducts afforded 1,2-unsubstituted cyclobutene derivatives. Photochemical additions of **4** were regioselective. The cis-transoid-cis isomer formed exclusively from **25** and predominantly from **14**. Ready thermolyses to cyclobutene and cyclopentene derivatives indicate that **4** is useful as cycloaddend in alicyclic synthesis.

Experimental

Elemental analyses were performed by Miss S. Hirashima, of Institute of Advanced Material Study, Kyushu University. NMR spectra were measured by a JEOL 270H spectrometer in $CDCl_3$ solution (unless otherwise specified): chemical shifts are expressed in the unit δ. Mass spectra were measured with a JEOL OISG-2 spectrometer. IR spectra were taken as KBr disks or as a $CHCl_3$ solution using a Jasco IR-A 102 spectrometer. UV spectra were measured by a Hitachi U-3200 spectrophotometer.

Photoreaction of 1 and Methyl 2,4-Dioxopentanoate (2). Formation of 7-Oxaquadricyclane Derivative (3). A $CDCl_3$ solution (0.5 cm^3) of **1** (40 mg) and **2** (16.2 mg) was irradiated with a 400-W high-pressure mercury lamp and the reaction was monitored by ^{1}H NMR spectroscopy. After 1 h, new signals [2.83(2H, d, J=3 Hz), 3.70 (6H, s), and 4.93 (2H, d, J=3 Hz)] of **3** appeared, which was identical with the spectrum of the authentic **3**.[8]

Photoreaction of 4 and *p*-Benzoquinone (5). a) A $CDCl_3$ solution (0.5 cm^3) of **4** (35 mg) and **5** (14.5 mg) was irradiated. After 20 min, the solvent was evaporated and the residue was chromatographed on a silica-gel column to isolate **6** [colorless crystals, mp 191—192 °C, 12.6 mg; 78%. Found: C, 62.19; H, 4.64%. Calcd for $C_{20}H_{18}O_8$: C, 62.18; H, 4.70%. ^{1}H NMR δ=3.26 (1H, d, J=5.1 Hz, H_d), 3.70 (3H, s), 3.74 (3H, s), 4.71 (1H, d, J=1.8 Hz), 4.84 (1H, d, J=1.8 Hz), 4.94 (1H, s, H_b or H_c), 5.01 (1H, s, H_c or H_b), 5.21 (1H, d, J=5.1 Hz, H_a), 6.14 (1H, dd, J=10.3, 2.2 Hz), 6.21 (1H, dd, J=10.3, 2.2 Hz), 6.54 (1H, dd, J=5.9, 1.8 Hz), 6.67 (1H, dd, J=5.9, 1.8 Hz), 7.28 (1H, dd, J=10.3, 2.9 Hz), and 7.69 (1H, dd, J=10.3, 2.9 Hz). ^{13}C NMR δ=49.1, 52.8, 72.0, 72.8, 79.3, 80.0, 80.2, 80.3, 81.2, 84.0, 127.1, 128.3, 130.5, 136.9, 138.5, 144.7, 148.7, 170.4, 170.5, and 185.2. IR ν: 1715, 1665, 1625, 1260, and 1220 cm^{-1}. UV (MeOH): 237.6 nm (ε=12450)] together with **5** [10 mg] and **4** [12 mg]. **b)** A $CDCl_3$ solution (0.8 cm^3) of **5** (138 mg) and a 3 : 1-mixture (476 mg) of **4** and **7** was reacted by similar manner. Product **6** [193 mg, 54%] was obtained together with recovered **5** [10 mg] and a mixture [204 mg] of **4** and **7**.

Photoreaction of 4 and 1,4-Naphthoquinone (10). A $CHCl_3$ solution (1 cm^3) of **4** (341 mg) and **10** (156 mg) was irradiated to give **11** [colorless crystals, mp 179—181 °C, 150 mg; 44%. Found: C, 65.81; H, 4.58%. Calcd for $C_{24}H_{20}O_8$: C, 66.05; H, 4.62%. ^{1}H NMR δ=3.24 (1H, d, J=4.8 Hz, H_d), 3.60 (3H, s), 3.75 (3H, s), 4.47 (1H, s, H_c), 4.66 (1H, br s), 4.87 (1H, br s), 5.19 (1H, s, H_b), 5.36 (1H, d, J=4.8 Hz, H_a), 6.29 (1H, d, J=10.3 Hz), 6.53 (1H, dd, J=5.9, 1.8 Hz), 6.64 (1H, dd, J=5.9, 1.8 Hz), 7.47 (1H, ddd, J=7.7, 7.0, 1.5 Hz), 7.64 (1H, ddd, J=7.7, 7.0, 1.5 Hz), 7.68 (1H, d, J=10.3 Hz), 8.06 (1H, dd, J=7.0, 1.5 Hz), and 8.52 (1H, dd, J=7.0, 1.5 Hz). ^{13}C NMR δ=51.7, 52.7, 52.9, 72.5, 73.6, 79.2, 80.0, 80.2, 81.4, 83.3, 83.7, 126.3, 126.5, 128.6, 129.9, 130.7, 132.3, 137.0, 138.5, 138.7, 153.0, 170.4 (2C), and 184.6. IR ν: 1720, 1670, 1597, and 1260 cm^{-1}. UV (MeOH): 244.2 (ε=11600), 278.8 (5000), and 312.0 nm (2200)] and recovered **4** [211 mg] and **10** [33 mg].

Photoreaction of 4 and Cyclohexenone (14). A $CHCl_3$ solution (2 cm^3) of **4** (824 mg) and **14** (2.03 g) was irradiated for 60 h to give **15** [colorless crystals, mp 126—127 °C, 221 mg: 21%. Found: C, 64.12; H, 5.95%. Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92%. ^{1}H NMR δ=1.6—2.5 (6H, m), 2.45—2.6 (1H, m), 2.83 (1H, dd, J=9.1, 5.5 Hz), 3.05 (1H, dd, J=13.6, 6.6 Hz), 3.33 (1H, dd, J=6.6, 5.5 Hz), 3.68 (3H, s), 3.69 (3H, s), 4.64 (1H, s), 4.71 (1H, br s), 4.76 (1H, br s), 4.97 (1H, s), 6.58 (1H, dd, J=5.5, 1.1 Hz), and 6.64 (1H, dd, J=5.5, 1.1 Hz). ^{13}C NMR δ=24.9, 26.7, 39.3, 41.6, 42.9, 45.9, 51.7, 52.5 (2C), 71.7, 73.8, 79.2, 80.3, 82.2, 83.9, 137.7, 138.9, 171.4, 171.5, and 206.6. IR ν: 1720, 1260, 1207, and 904 cm^{-1}], **16** [colorless crystals, mp 181—183 °C, 220 mg; 21%. Found: C, 64.05; H, 5.87%. Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92%. ^{1}H NMR δ=1.5—1.6 (1H, m), 1.65—1.8 (1H, m), 1.8—1.9 (1H, m), 1.95—2.1 (1H, m), 2.24 (1H, ddd, J=18.0, 8.4, 6.6 Hz), 2.46 (1H, dt, J=18.0, 5.9 Hz), 2.5—2.6 (2H, m), 2.66 (1H, dd, J=8.1, 4.4 Hz), 2.81 (1H, dd, J=5.9, 4.4 Hz). 3.68 (3H, s), 3.69 (3H, s), 4.72 (2H, s), 4.76 (1H, br s), 4.81 (1H, s), 6.58 (1H, dd, J=5.5, 1.8 Hz), and 6.62 (1H, dd, J=5.5, 1.8 Hz). ^{13}C NMR δ=20.3, 27.5, 36.2, 39.6, 43.0, 44.0, 45.9, 52.5 (2C), 72.0, 72.2, 79.9 (2C), 84.5, 84.6, 138.1, 138.3, 171.2, 171.5, and 214.6. IR ν: 1725, 1697, 1262, 1210, and 905 cm^{-1}], **17** [colorless crystals, mp 185 °C, 7.5 mg, 1%. Found: C, 64.32; H, 5.97%. Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92%. ^{1}H NMR δ=1.5—2.0 (4H, m), 2.2—2.35 (2H, m), 2.8—3.0 (3H, m), 3.18 (1H, dd, J=9.2, 6.6 Hz), 3.67 (3H, s), 3.68 (3H, s), 4.69 (1H, br s), 4.73 (1H, br s), 4.89 (1H, s), 4.91 (1H, s), 6.56 (1H, dd, J=5.5, 1.8 Hz), and 6.64 (1H, dd, J=5.5, 1.8 Hz). ^{13}C NMR δ=20.3, 21.5, 34.0, 39.6, 41.0, 42.6, 43.5, 52.8 (2C), 72.6, 72.8, 80.1, 80.2, 81.3, 82.6, 138.0, 138.9, 171.6 (2C), and 214.4. IR ν: 1720, 1695, 1260, and 1207 cm^{-1}], **18** [colorless crystals, mp 162—164 °C, 5 mg, 0.5%. Found: C, 64.30; H, 5.88%. Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92%. ^{1}H NMR δ=1.5—1.9 (3H, m), 2.0—2.2 (4H, m), 2.4—2.5 (1H, m), 2.9—3.1 (2H, m), 3.68 (6H, s), 4.66 (1H, s), 4.72 (2H, br s), 5.28 (1H, s), 6.59 (1H, dd, J=5.5, 1.8 Hz), and 6.64 (1H, dd, J=5.5. 1.8 Hz). ^{13}C NMR δ=26.0, 29.0, 39.1,

42.6, 43.4, 45.1, 52.7, 52.8 (2C), 71.9, 73.8, 79.4, 80.6, 81.0, 83.9, 138.1, 139.1, 171.7, 171.8, and 206.7. IR ν: 1740, 1710, 1280, 1255, 1225, and 1080 cm^{-1}], and recovered **4** [47 mg].

Photoreaction of 4 and Cyclopentenone (25). A $CHCl_3$ solution (2 cm^3) of **4** (584 mg) and **25** (1.76 g) was irradiated for 80 h to give **26** [a colorless oil, 245 mg; 50%. Found: m/z 360.1208 (M^+). Calcd for $C_{19}H_{20}O_7$: 360.1208. ^1H NMR δ=1.9—2.4 (4H, m), 2.55—2.8 (4H, m), 3.69 (3H, s), 3.70 (3H, s), 4.71 (1H, br s), 4.74 (1H, br s), 4.79 (1H, s), 4.81 (1H, s), 6.59 (1H, dd, J=5.5, 1.8 Hz), and 6.62 (1H, dd, J=5.5, 1.8 Hz). ^{13}C NMR δ=27.6, 36.7, 36.9, 42.1, 45.1, 47.2, 52.5 (2C), 72.0, 72.4, 79.8, 79.9, 84.2, 84.9, 138.1, 138.2, 171.1, 171.4, and 221.3. IR ν: 1730, 1265, and 1220 cm^{-1}] and recovered **4** [211 mg] and **25** [454 mg].

Photoreaction of 4 and Methyl 2,4-Dioxopentanoate (2). A $CHCl_3$ solution (2 cm^3) of **4** (485 mg) and **2** (620 mg) was irradiated for 60 h to give **30** [colorless crystals, mp 175—176 °C, 269 mg; 52%. Found: C, 56.78; H, 5.26%. Calcd for $C_{20}H_{22}O_{10}$: C, 56.87; H, 5.25%. ^1H NMR δ=2.10 (3H, s), 2.55 (1H, dd, J=19.0, 8.4 Hz), 2.62 (1H, dd, J=19.0, 7.0 Hz), 3.23 (1H, td, J=8.4, 7.0 Hz, H_a), 3.67 (3H, s), 3.68 (3H, s), 3.89 (3H, s), 4.15 (1H, d, J=8.4 Hz, H_b), 4.48 (1H, d, J=1.5 Hz), 4.83 (1H, d, J=0.7 Hz), 4.95 (1H, d, J=1.1 Hz), 5.01 (1H, d, J=1.5 Hz), 6.62 (1H, dd, J=5.9, 1.5 Hz), and 6.71 (1H, dd, J=5.9, 1.1 Hz). ^{13}C NMR δ=30.2, 40.0, 43.3, 49.4, 52.5, 52.6, 53.3, 72.4, 72.5, 79.7 (2C), 83.2. 86.4, 137.6, 138.8, 161.0, 170.9, 171.1, 193.1, and 207.4. IR ν: 1730, 1270, and 1207 cm^{-1}] and recovered **4** [145 mg] and **2** [192 mg].

Iodolactonization of 6. A CH_3CN solution (6 cm^3) of **6** (100 mg), I_2 (120 mg), and $NaHCO_3$ (210 mg) was stirred for 2 d. A mixture was washed with an $NaHSO_3$ solution and extracted with $CHCl_3$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to give **8** [colorless crystals, mp 240 °C, 36 mg; 32%. Found: C, 46.08; H, 3.19%. Calcd for $C_{19}H_{15}O_8I$: C, 45.80; H, 3.03%. ^1H NMR (DMSO-d_6) δ=3.40 (1H, d, J=5.1 Hz), 3.72 (3H, s), 4.10 (1H, s), 4.82 (1H, s), 4.88 (1H, s), 5.00 (1H, s), 5.11 (1H, d, J=5.5 Hz), 5.21 (1H, d, J=5.1 Hz), 5.51 (1H, J=5.5 Hz), 6.1—6.2 (2H, m), and 7.45—7.5 (2H, m). ^{13}C NMR (DMSO-d_6) δ=46.8, 53.2, 58.0, 74.0, 78.9, 79.1, 79.5, 80.2, 81.3, 81.9, 83.7, 84.5, 126.1, 129.8, 144.6, 149.5, 167.8, 170.5, and 184.7. IR ν: 1800, 1740, 1660, 1620, 1250, and 1000 cm^{-1}. UV (MeOH): 237.6 nm (ε=13500)], **9** [colorless crystals, mp 189—191 °C, 35 mg; 31%. Found: C, 45.99; H, 3.11%. Calcd for $C_{19}H_{15}O_8I$: C, 45.80; H, 3.03%. ^1H NMR (DMSO-d_6) δ=3.25 (1H, d, J=5.1 Hz), 3.74 (3H, s), 4.14 (1H, s), 4.82 (1H, s), 4.92 (1H, s), 5.09 (1H, d, J=5.1 Hz), 5.12 (1H, s), 5.30 (1H, d, J=5.1 Hz), 5.38 (1H, d, J=5.1 Hz), 6.12 (1H, dd, J=9.9, 2.2 Hz), 6.20 (1H, dd, J=10.3, 2.2 Hz), 7.46 (1H, dd, J=9.9, 2.9 Hz), and 7.54 (1H, dd, J=10.3, 2.2 Hz). ^{13}C NMR (DMSO-d_6) δ=46.7, 53.3, 59.0, 73.7, 77.8, 78.9 (2C), 79.1, 82.3, 83.3, 84.4 (2C), 126.3, 129.8, 144.6, 149.5, 167.7, 170.6, and 184.7. IR ν: 1797, 1740, 1660, 1620, and 1250 cm^{-1}. UV (MeOH): 237.4 nm (ε= 14500)], and recovered **6** [12 mg].

Iodolactonization of 11. A CH_3CN solution (6 cm^3) of **11** (117 mg), I_2 (164 mg), and $NaHCO_3$ (210 mg) was stirred for 4 d. A similar work-up as mentioned above gave **12** [colorless crystals, mp 240 °C, 13 mg; 9%. Found: C, 50.00; H, 2.99%. Calcd for $C_{23}H_{17}O_8I$: C, 50.29; H, 3.12%. ^1H NMR (DMSO-d_6) δ=3.16 (1H, d, J=4.8 Hz), 3.75 (3H, s), 4.12 (1H, s), 4.28 (1H, s), 5.05 (1H, d, J=5.1 Hz), 5.08 (1H, s), 5.15 (1H, s), 5.32 (1H, d, J=5.1 Hz), 5.48 (1H, d, J=4.8 Hz), 6.31 (1H, d, J=10.3 Hz), 7.57 (1H, ddd, J=7.7, 7.0, 1.1 Hz), 7.70 (1H, td, J=7.0, 1.5 Hz), 7.85 (1H, d, J=10.3 Hz), 7.94 (1H, dd, J=7.7, 1.5 Hz), and 8.38 (1H, dd, J=7.0, 1.1 Hz). ^{13}C NMR (DMSO-d_6) δ=49.7, 53.3, 59.4, 74.2, 77.8, 78.4, 79.2, 82.3, 82.6, 83.2, 83.9, 84.2, 125.7 (2C), 128.7, 129.4, 130.2, 131.6, 138.6, 153.4, 167.7, 170.5, and 183.5. IR ν: 1800, 1740, 1660, and 1595 cm^{-1}. UV (MeOH): 242.0 (ε=11850) and 277.8 nm (5100)] and **13** [colorless crystals, mp 249 °C, 27 mg: 18%. Found: C, 50.63; H, 3.04%. Calcd for $C_{23}H_{17}O_8I$: C, 50.29; H, 3.12%. ^1H NMR (DMSO-d_6) δ=3.39 (1H, d, J=4.8 Hz), 3.61 (3H, s), 4.04 (1H, s), 4.27 (1H, s), 4.92 (1H, s), 4.99 (1H, s), 5.11 (1H, d, J=5.1 Hz), 5.41 (1H, d, J=4.8 Hz), 5.55 (1H, d, J=5.1 Hz), 6.30 (1H, d, J=10.3 Hz), 7.55 (1H, dd, J=7.7, 7.3 Hz), 7.68 (1H, dd, J=7.7, 7.3 Hz), 7.86 (1H, d, J=10.3 Hz), 7.93 (1H, d, J=7.7 Hz), and 8.36 (1H, d, J=7.7 Hz). ^{13}C NMR (DMSO-d_6) δ=49.6, 53.2, 58.5, 74.5, 78.3, 79.1, 79.8, 81.3, 82.3, 83.1, 83.9, 84.5, 125.6 (2C), 128.7, 129.3, 130.3, 131.7, 138.3, 153.3, 167.8, 170.6, and 183.5. IR ν: 1800, 1750, 1675, 1597, and 1240 cm^{-1}. UV (MeOH): 243.2 (ε=11900) and 278.2 nm (5100)].

Epimerization of 15. An MeOH solution (16 cm^3) of **15** (90 mg) and KF (520 mg) was stirred in the presence of Florisil (540 mg) at room temperature for 2 d. After the solvent was removed, the residue was extracted with $CHCl_3$. The solvent was evaporated and the residue was chomatographed to give **17** [87 mg, 97%].

Epimerization of 18. An MeOH solution (5 cm^3) of **18** (43.6 mg) and KF (250 mg) was stirred with Florisil (300 mg) overnight to give **16** [35.7 mg, 82%].

Thermolysis of 16. A xylene solution (1.5 cm^3) of **16** (110 mg) was refluxed for 60 h in a sealed tube. The solvent was evaporated and the residue was chromatographed on a silica-gel column to give **19** [a colorless oil, 51.6 mg, 65%. Found: C, 62.54; H, 5.90%. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92%. ^1H NMR δ=1.6—2.0 (4H, m), 2.2—2.6 (6H, m), 3.79 (3H, s), 3.81 (3H, s), 5.09 (1H, s), and 5.17 (1H, s). ^{13}C NMR δ=20.2, 27.4, 33.9, 39.5, 39.9, 41.6, 43.4, 52.4 (2C), 82.6, 83.0, 141.8, 142.5, 162.5, 162.9, and 213.3. IR ν: 1720, 1260, and 1206 cm^{-1}], **20**[15,16] [a colorless oil, 4.1 mg, 13%], **21**[17] [a colorless oil, 2.1 mg; 7%], **22** [14.7 mg, 31%], and recovered **16** [12.5 mg].

Thermolysis of 17. A xylene solution (1 cm^3) of **17** (87 mg) was refluxed for 30 h to give **23** [a colorless oil, 26 mg; 61%. Found: C, 62.75; H, 6.02%. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92%. ^1H NMR δ=1.6—2.3 (6H, m), 2.50 (1H, dd, J=8.1, 7.0 Hz), 2.83 (1H, dd, J=9.5, 6.2 Hz), 2.9—3.1 (2H, m), 3.79 (6H, s), 5.20 (1H, s), and 5.32 (1H, s). ^{13}C NMR δ=20.2, 21.3, 30.7, 39.2, 39.4 (2C), 40.5, 52.3 (2C), 79.8, 80.4, 142.4, 142.7, 162.6, 162.7, and 213.0. IR ν: 1730, 1630, and 1215 cm^{-1}] and recovered **17** [34.7 mg].

Thermolysis of 15. A xylene solution (2 cm^3) of **15** (220 mg) was refluxed for 20 h to give **23** [61.8 mg, 44%], **36** [a colorless oil, 52.9 mg, 38%. Found: C, 62.50: H, 5.90%. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92%. ^1H NMR δ=1.8—2.3 (6H, m), 2.35—2.5 (2H, m), 2.89 (1H, dd, J=12.9, 6.6 Hz), 3.15 (1H, dd, J=6.6, 5.5 Hz), 3.79 (3H, s), 3.81 (3H, s), 4.99 (1H, s), and 5.31 (1H, s). ^{13}C NMR δ=25.4, 27.4, 39.7, 40.6, 41.5, 42.6, 50.6, 52.3, 52.4, 81.1, 81.9, 141.9, 144.9, 162.4, 162.8, and 206.7. IR ν: 1735, 1720. 1700, and 1210 cm^{-1}], and recovered **15** [49 mg].

Epimerization of 36 to 23. Compound **36** (19 mg) was placed in a sealed tube and pyrolyzed at 220 °C to give **23** [19 mg; 100%].

Thermolysis of 19. The compound **19** (70 mg) was passed through a glass tube heated at 300—330 °C under an

N_2 stream to give **20** [8 mg; 44%], **22** [21.5 mg; 78%], and recovered **19** [24 mg].

Thermolysis of 23. Similarly, compound **23** (70 mg) was pyrolyzed at 300—330 °C under an N_2 stream to give **20** [6 mg; 45%], **22** [10 mg, 50%], and recovered **23** [36.6 mg].

Thermolysis of 26. A xylene solution (1 cm^3) of **26** (150 mg) was refluxed for 2 d to give **27** [a colorless oil, 48 mg, 60%. Found: *m/z* 292.0948 (M^+). Calcd for $C_{15}H_{16}O_6$: 292.0946. ^1H NMR δ=2.0—2.4 (6H, m), 2.55—2.7 (2H, m), 3.79 (3H, s), 3.81 (3H, s), 5.17 (1H, s), and 5.19 (1H, s). ^{13}C NMR δ=27.3, 36.4, 36.6, 39.3, 42.7, 45.4, 52.4 (2C), 82.7, 83.0, 142.0, 142.3, 162.4, 162.8, and 219.8. IR ν: 1730, 1630, 1260, and 1210 cm^{-1}. UV (MeOH): 227.8 nm (ε=5400)], **28**[18,19] [a colorless oil, 3.5 mg, 12%], **22** [10 mg, 20%], and recovered **26** [51 mg].

Thermolysis of 27. A xylene solution (1 cm^3) of **27** (58 mg) was refluxed for 2 d to give **28** [5 mg, 52%], **22** [9 mg, 55%], and recovered **27** [32.2 mg].

MCPBA-Oxidation of 19. A $CHCl_3$ solution (1.5 cm^3) of **19** (33 mg) and MCPBA (50 mg) was kept in a refrigerator for 10 h. The mixture was washed with aqueous $NaHSO_3$ and $NaHCO_3$ solutions and a $CHCl_3$ layer was dried on Na_2SO_4 and evaporated. The residue was chromatographed on a silica-gel column to give **24** [colorless crystals, mp 107—109 °C, 18 mg, 52%. Found: C, 59.80; H, 5.74%. Calcd for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63%. ^1H NMR δ=1.6—1.8 (1H, m), 1.8—1.95 (3H, m), 2.1—2.2 (1H, m), 2.22 (1H, dd, *J*=7.0, 4.0 Hz), 2.4—2.5 (2H, m, H_c and H_d), 2.73 (1H, ddd, *J*=6.9, 2.6, 1.0 Hz, H_b), 3.80 (3H, s), 3.82 (3H, s), 4.39 (1H, dd, *J*=6.6, 2.6 Hz, H_a), 5.08 (1H, s, H_e), and 5.12 (1H, s, H_f). ^{13}C NMR δ=20.5, 24.8, 31.9, 36.8, 40.5, 43.1, 52.4, 52.5, 73.6, 81.4, 82.1, 141.8, 143.3, 162.2. 162.6, and 172.8. IR ν: 1737, 1690, 1615, and 1290 cm^{-1}. UV (MeOH): 232.2 nm (ε=6000)].

MCPBA-Oxidation of 23. A $CHCl_3$ solution (3 cm^3) of **23** (63 mg) and MCPBA (60 mg) was refluxed for 10 h. Same work-up gave no product.

MCPBA-Oxidation of 27. A $CHCl_3$ solution (3 cm^3) of **27** (97 mg) and MCPBA (80 mg) was kept for 1 d in a refrigerator. Same work-up gave **29** [colorless crystals. mp 144—145 °C, 59 mg, 58%. Found: C, 58.52; H, 5.34%. Calcd for $C_{15}H_{16}O_7$: C, 58.44; H, 5.23%. ^1H NMR δ=1.9—2.0 (1H, m), 2.15—2.2 (1H, m), 2.32 (1H, dd, *J*=7.0, 3.3 Hz, H_c), 2.35—2.5 (2H, m), 2.5—2.6 (2H, m, H_b and H_d), 3.81 (3H, s), 3.82 (3H, s), 4.53 (1H, dd, *J*=7.7, 2.9 Hz, H_a), 5.14 (1H, s, H_e), and 5.22 (1H, s, H_f). ^{13}C NMR δ=22.8, 28.6, 31.3, 40.6, 46.1, 52.5 (2C), 74.0, 81.5, 82.0, 141.7, 143.6, 162.2, 162.7, and 171.2. IR ν: 1720, 1630, and 1230 cm^{-1}. UV (MeOH): 231.8 nm (ε=5900)].

$TiCl_2$-Mediated Cyclization of 30. To an anhydrous THF solution (20 cm^3) of $TiCl_4$ (0.1 cm^3), Zn (0.1 g) was added at −60 °C under stirring. After warming to room temperature, pyridine (0.1 cm^3) was added. To the resultant suspension, a THF solution (10 cm^3) of **30** (102 mg) was added drop by drop. After stirring overnight, the mixture was quenched with aqueous K_2CO_3 and extracted with $CHCl_3$. The organic layer was dried on Na_2SO_4 and evaporated. The residue was chromatographed on silica-gel to give **31** [colorless crystals, mp 200—202 °C, 63 mg; 60%. Found: C, 56.55; H, 5.74%. Calcd for $C_{20}H_{24}O_{10}$: C, 56.60; H, 5.70%. ^1H NMR δ=1.13 (3H, s), 1.75 (1H, dd, *J*=14.3, 4.0 Hz), 2.31 (1H, dd, *J*=14.3, 9.6 Hz), 2.88 (1H, ddd, *J*=9.6, 7.3, 4.0 Hz), 3.15 (1H, d, *J*=7.3 Hz), 3.69 (6H, s), 3.79 (3H, s), 3.80 (1H, s, OH), 4.44 (1H, s, OH), 4.69 (1H, s), 4.77 (1H, s), 4.80 (1H, s), 5.12 (1H, s), and 6.64 (2H, s). ^{13}C NMR δ=22.2, 43.0, 43.7, 52.0, 52.3, 52.6 (2C), 71.6, 72.1, 79.5 (2C), 81.0, 82.6, 85.0, 87.0, 138.2, 138.3, 171.1, 171.2, and 173.9. IR ν: 3370, 1720, 1260, 1235, and 1215 cm^{-1}] and **32** [colorless crystals, mp 199—201 °C, 21 mg; 20%. Found: C, 56.62; H, 5.65%. Calcd for $C_{20}H_{24}O_{10}$: C, 56.60; H, 5.70%. ^1H NMR δ=1.26 (3H, s), 1.46 (1H, dd, *J*=13.2, 9.5 Hz), 2.00 (1H, dd, *J*=13.2, 8.1 Hz), 3.11 (1H, dt, *J*=9.5, 8.1 Hz), 3.21 (1H, d, *J*=8.1 Hz), 3.34 (1H, s, OH), 3.69 (3H, s), 3.71 (3H, s), 3.77 (1H, s, OH), 3.86 (3H, s), 4.64 (1H, s), 4.77 (1H, d, *J*=1.1 Hz), 4.82 (1H, d, *J*=1.1 Hz), 5.08 (1H, s), 6.60 (1H, d, *J*=4.0 Hz), and 6.67 (1H, d, *J*=4.0 Hz). ^{13}C NMR δ=20.4, 41.7, 44.4, 52.3, 52.5, 52.6, 52.9, 71.5, 72.3, 79.5, 80.0, 82.5, 84.3, 84.9, 85.3, 137.8, 138.6, 171.3, 171.4, and 173.7. IR ν: 3500, 1725, 1260, and 1215 cm^{-1}].

Dioxolane Formation of 31. A trimethyl orthoformate solution (2 cm^3) of **31** (37 mg) and PPTS (10 mg) was stirred overnight. The mixture was washed with aqueous Na_2CO_3 and extracted with $CHCl_3$. The solvent was evaporated to give **33** [colorless crystals, a 1 : 2.5-mixture of isomers, mp 161—168 °C, 36 mg, 89%. Found: C, 56.73; H, 5.68%. Calcd for $C_{22}H_{26}O_{11}$: C, 56.65; H, 5.62%. ^1H NMR of a major isomer δ=1.35 (3H, s), 1.95 (1H, dd, *J*=14.3, 7.3 Hz), 2.17 (1H, dd, *J*=14.3, 9.9 Hz), 2.93 (1H, ddd, *J*=9.9, 8.1, 7.3 Hz), 3.41 (1H, d, *J*=8.1 Hz), 3.46 (3H, s), 3.68 (6H, s), 3.80 (3H, s), 4.60 (1H, s), 4.75 (2H, s), 4.76 (1H, s), 5.95 (1H, s), and 6.6—6.7 (2H, m) and a minor isomer δ=1.26 (3H, s), 2.00 (1H, dd, *J*=14.3, 7.3 Hz), 2.37 (1H, dd, *J*=14.3, 9.2 Hz), 2.85 (1H, ddd, *J*=9.2, 8.1, 7.3 Hz), 3.43 (3H, s), 3.62 (1H, d, *J*=8.1 Hz), 3.66 (6H, s), 3.78 (3H, s), 4.57 (1H, s), 4.74 (1H, s), 4.78 (1H, s), 5.00 (1H, s), 6.04 (1H, s), and 6.6—6.7 (2H, m)].

Orthoformate Formation of 32. A trimethyl orthoformate solution (2 cm^3) of **32** (22.5 mg) and PPTS (10 mg) gave **34** or **35** [a colorless oil, 22 mg, 83%. ^1H NMR δ=1.42 (1H, dd, *J*=14.4, 9.6 Hz), 1.46 (3H, s), 2.50 (1H, dd, *J*=14.4, 8.0 Hz), 2.96 (1H, ddd, *J*=9.6, 8.0, 5.6 Hz), 3.21 (3H, s), 3.27 (3H, s), 3.66 (1H, d, *J*=5.6 Hz), 3.69 (6H, s), 3.80 (3H, s), 4.59 (1H, s), 4.82 (1H, s), 4.87 (1H, s), 5.03 (1H, s), 5.19 (1H, s), and 6.65 (2H, s)].

Thermolysis of 31. A xylene solution (1.5 cm^3) of **31** (93 mg) was refluxed for 1.5 d to give **37** [a colorless oil, 40 mg; 67%. Found: C, 54.06; H, 5.94%. Calcd for $C_{16}H_{20}O_9$:C, 53.93; H, 5.66%. ^1H NMR δ=1.14 (3H, s), 1.86 (1H, dd, *J*=14.3, 2.9 Hz), 2.38 (1H, dd, *J*=14.3, 9.5 Hz), 2.62 (1H, ddd, *J*=9.5, 7.7, 2.9 Hz), 2.84 (1H, d, *J*=7.7 Hz), 3.8 (1H, s, OH), 3.80 (3H, s), 3.82 (3H, s), 3.88 (3H, s), 4.39 (1H, s, OH), 5.02 (1H, s), and 5.42 (1H, s). ^{13}C NMR δ=22.4, 41.5, 42.4, 51.7, 52.2, 52.5, 52.8, 81.4, 81.9, 83.0, 85.1, 143.5, 144.1, 162.2, 162.4, and 174.1. IR ν: 3475, 3400, 1725, 1640, 1260, and 1220 cm^{-1}. UV (MeOH): 226.6 nm (ε=6200)], **38** [a colorless oil, 2 mg, 7%. Found: *m/z* 172.0736 (M^+). Calcd for $C_8H_{12}O_4$: 172.0736. ^1H NMR δ=1.24 (3H, s), 2.5—2.65 (2H, m), 3.80 (3H, s), 5.63 (1H, dt, *J*=6.2, 1.8 Hz), and 6.13 (1H, dt, *J*=6.2, 2.2 Hz). ^{13}C NMR δ=23.2, 46.4, 53.3, 80.4, 87.7, 130.8, 136.4, and 174.8. IR ν: 3500, 1725, 1250, and 1207 cm^{-1}], and **22** [4.4 mg, 14%], and recovered **32** [23 mg].

Thermolysis of 37. Compound **37** (36 mg) was placed in a tube equipped with a Dry-Ice cold finger and pyrolyzed at 220 °C under reduced pressure (1300 Pa) to give **38** [9.3 mg, 63%], **22** [10 mg: 63%], and recovered **37** [5.4 mg].

HCl-Catalyzed Reaction of 6. a) An EtOH solution (6 cm^3) of **6** (70 mg) and concd HCl (1 drop) was stirred for 30 min at room temperature. The solvent was evaporated and the residue was chromatoraphed on a silica-gel column to give **39** [colorless crystals, mp 139—141 °C, 51 mg; 61%.

Found: C, 62.62; H, 6.40%. Calcd for $C_{24}H_{28}O_9$: C, 62.60; H, 6.13%. ^{1}H NMR δ=1.37 (1H, d, J=9.2 Hz, OH), 1.40 (3H, t, J=7.0 Hz), 1.41 (3H, t, J=7.0 Hz), 3.68 (3H, s), 3.73 (3H, s), 4.02 (4H, q, J=7.0 Hz), 4.23 (1H, d, J=7.0 Hz), 4.50 (1H, dd, J=9.2, 7.0 Hz, H_a), 4.77 (1H, d, J=1.5 Hz), 4.87 (1H, d, J=1.8 Hz), 4.93 (1H, d, J=1.1 Hz), 5.02 (1H, d, J=1.8 Hz), 6.45 (1H, d, J=2.6 Hz), 6.47 (1H, dd, J=8.1, 2.6 Hz), 6.60 (1H, dd, J=5.9, 1.8 Hz), 6.75 (1H, dd, J=5.9, 1.8 Hz), and 7.40 (1H, d, J=8.1 Hz). ^{13}C NMR δ=14.8 (2C), 43.9, 52.5, 52.9, 63.5, 63.9, 71.4, 72.7, 73.3, 79.2, 80.1, 86.3, 88.5, 100.2, 105.0, 117.7, 128.6, 137.0, 139.2, 158.5, 159.4, 171.4, and 171.5. IR ν: 3530, 1740, 1717, 1607, 1575, 1500, 1280, 1255, 1217, 1175, 1115, and 1035 cm^{-1}. UV (MeOH): 208.8 (ε=17200), 228.6 (10100), and 279.2 nm (3000)] and **40a** [colorless crystals, mp 202—203 °C, 10 mg; 13%. Found: C, 57.07; H, 4.56%. Calcd for $C_{20}H_{19}O_8Cl$: C, 56.81; H, 4.53%. ^{1}H NMR δ=2.70 (1H, dd, J=20.4, 2.9 Hz), 2.78 (1H, dd, J=20.4, 2.9 Hz), 2.95 (1H, d, J=5.5 Hz, H_d), 3.70 (3H, s), 3.72 (3H, s), 4.62 (1H, d, J=5.5 Hz, H_a), 4.77 (1H, q, J=2.9 Hz, H_e), 4.80 (1H, d, J=1.8 Hz), 4.84 (1H, s), 4.97 (1H, d, J=1.5 Hz, H_b), 5.35 (1H, d, J=1.5 Hz, H_c), 5.93 (1H, d, J=9.9 Hz), 6.52 (1H, dd, J=9.9, 2.9 Hz, H_f), 6.60 (1H, dd, J=5.9, 1.8 Hz), and 6.67 (1H, dd, J=5.9, 1.8 Hz). ^{13}C NMR δ=37.3, 52.7, 52.8, 55.4, 65.4, 71.4, 72.6, 79.1, 79.8, 82.3, 83.1, 83.8, 88.1, 126.9, 136.9, 138.5, 145.9, 170.6, 170.8, and 194.9. IR ν: 1720, 1685, 1260, and 1225 cm^{-1}. UV (MeOH): 204.6 (ε=11500) and 219.6 nm (12200)].

b) A THF solution (6 cm^3) of **6** (51 mg) and concd HCl (1 drop) was stirred for 3 h at room temperature to give **40a** [12 mg; 22%] and **41** [colorless crystals, mp 158—159 °C, 13.3 mg; 24%. Found: C, 56.97; H, 4.71%. Calcd for $C_{20}H_{19}O_8Cl$: C, 56.81; H, 4.53%. ^{1}H NMR δ=1.38 (1H, d, J=9.2 Hz, OH), 3.68 (3H, s), 3.72 (1H, d, J=7.0 Hz), 3.73 (3H, s), 4.52 (1H, dd, J=9.2, 7.0 Hz), 4.80 (1H, d, J=1.8 Hz), 4.86 (1H, s), 4.92 (1H, s), 4.95 (1H, d, J=1.8 Hz), 5.64 (1H, s), 6.60 (1H, dd, J=5.9, 1.8 Hz), 6.74 (1H, dd, J=5.9, 1.8 Hz), 6.97 (1H, d, J=8.4 Hz), 7.20 (1H, dd, J=8.4, 2.2 Hz), and 7.44 (1H, d, J=2.2 Hz). ^{13}C NMR δ=51.0, 52.7 (2C), 71.4, 72.5, 74.0, 79.3, 80.0, 87.3, 88.2, 116.5, 120.4, 129.6, 129.7, 130.7, 137.0, 139.0, 150.7, 171.0, and 171.1. IR ν: 3600—2800, 1720, 1495, 1430, 1270, and 1220 cm^{-1}. UV (MeOH): 220.6 (ε=9500), 230.6 (7800), and 281.2 nm (2200)].

HCl-Catalyzed Reaction of 11. A THF solution (10 cm^3) of **11** (85 mg) and concd HCl (1 drop) was stirred for 2 h at room temperature to give **42** [colorless crystals, mp 190 °C (decomp), 8 mg, 25%. Found: C, 61.04; H, 4.68%. Calcd for $C_{24}H_{21}O_8Cl$: C, 60.96; H, 4.48%. ^{1}H NMR δ=3.02 (1H, dd, J=18.7, 12.8 Hz), 3.28 (1H, dd, J=18.7, 5.5 Hz), 3.57 (3H, s), 3.60 (1H, d, J=5.1 Hz, H_d), 3.72 (3H, s), 4.24 (1H, s, H_c), 4.48 (1H, dd, J=12.8, 5.5 Hz), 4.77 (1H, d, J=1.8 Hz), 4.89 (1H, d, J=1.8 Hz), 5.10 (1H, s, H_b), 5.34 (1H, d, J=5.1 Hz, H_a), 6.54 (1H, dd, J=5.5, 1.8 Hz), 6.66 (1H, dd, J=5.5, 1.8 Hz), 7.46 (1H, td, J=7.7, 1.1 Hz), 7.68 (1H, ddd, J=7.7, 7.3, 1.5 Hz), 7.91 (1H, dd, J=7.7, 1.5 Hz), and 8.16 (1H, dd, J=7.3, 1.1 Hz). ^{13}C NMR δ=44.0, 45.4, 52.6, 52.8, 61.5, 72.2, 73.0, 79.4, 80.2, 80.7, 82.1, 82.9, 87.9, 126.6, 128.9, 129.9, 130.7, 134.2, 136.9, 138.7, 140.3, 170.5, 170.6, and 193.6. IR ν: 1720, 1690, 1590, 1280, and 1265 cm^{-1}. UV (MeOH): 204.6 (ε=27300), 250.6 (6400), and 293.0 nm (1300)], **43** [colorless crystals, mp 201—202 °C, 15 mg; 48%. Found: C, 63.44; H, 5.13%. Calcd for $C_{24}H_{22}O_9$: C, 63.43; H, 4.88%. ^{1}H NMR δ=2.49 (1H, s, OH), 2.89 (1H, dm, J=18.9 Hz), 2.98 (1H, dd, J=18.9, 2.7 Hz), 3.17 (1H, d, J=4.8 Hz), 3.58 (3H, s), 3.73 (3H, s), 4.41 (1H, s), 4.71 (1H, br s), 4.77 (1H, m), 4.85 (1H, br s), 5.13 (1H, s), 5.17 (1H, d, J=4.8 Hz), 6.54 (1H, dd, J=5.9, 1.8 Hz), 6.65 (1H, dd, J=5.9, 1.8 Hz), 7.43 (1H, t, J=7.7 Hz), 7.65 (1H, dd, J=7.7, 7.3 Hz), 7.97 (1H, d, J=7.7 Hz), and 8.18 (1H, d, J=7.3 Hz). ^{13}C NMR δ=40.0, 47.7, 52.7, 52.9, 72.2, 73.1, 73.9, 79.3, 80.0, 80.2, 80.8, 83.2, 87.0, 126.3, 128.5, 130.9 (2C), 133.8, 137.0, 137.6, 138.7, 170.5, 170.6, and 194.5. IR ν: 3500, 1720, 1680, 1590, 1270, and 1220 cm^{-1}. UV (MeOH): 250.4 (ε=14100) and 292.6 nm (4600)], and recovered **11** [55 mg].

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