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Synthetic Photochemistry. LVII.[1] Facile Photochemical Construction of Hexahydro-*as*-indacene Skeleton, a Carbon Framework of Ikarugamycin, from High-Pressure Diels-Alder Adducts of Tropones-Cyclopentenone

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The high-pressure Diels–Alder reaction of tropones with 2-cyclopenten-1-one afforded isomeric mixtures of adducts. Upon UV irradiation, these adducts isomerized to hexahydro-*as*-indacene, via [1,3] acyl migration, and tetracyclo[7.3.0.0^{3,7}.0^{6,8}]undecene derivatives through a ketene intermediate via a di-π-methane rearrangement. The former tricyclic system corresponds to the carbon skeleton of ikarugamycin. An "*exo* [6+4] adduct" of tropone and 1,4-cyclopentadien-1-ol, an enol form of 2-cyclopentenone, was obtained as a by-product.

Tropones, electron-deficient cyclic trienones, are known to form Diels–Alder adducts with various electron-deficient dienophiles such as maleic anhydride,[2] *N*-phenylmaleimide,[3] and acrylonitrile.[4] Application of a high-pressure technique made even less-reactive dienophiles feasible; recently we examined the reaction of tropones with *p*-benzoquinones.[5] This prompted us to investigate further cycloaddition with an enone such as 2-cyclopenten-1-one, which afforded no product under 1 bar (1 bar=10^5 Pa.).

Since the photoisomerization of dihydrohomobarrelenones to dihydroindenones is well-known,[6] Diels–Alder adducts from a cyclic enone and tropone were expected to form tricyclic analogs.

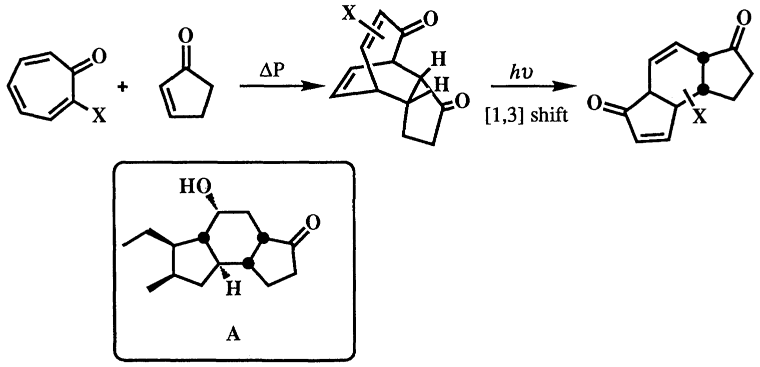
In this paper, we report high-pressure Diels–Alder reactions between tropones and 2-cyclopenten-1-one and the subsequent photoconversion to a tricyclic compound, which has a framework similar to the decahydro-*as*-indacene subunit (A) of ikarugamycin.[7]

Results and Discussion

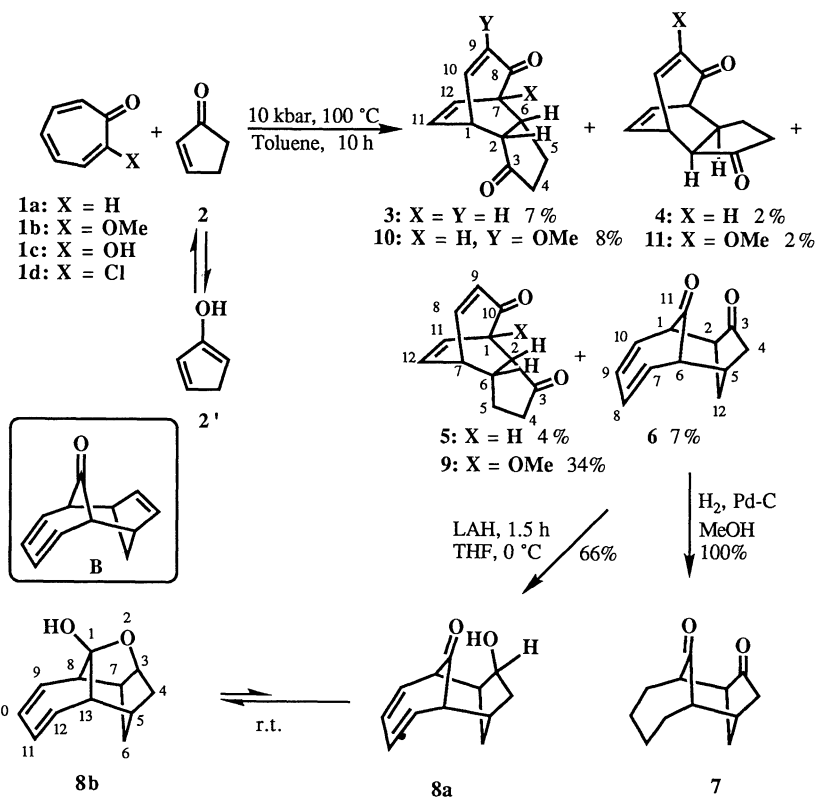
Cycloaddition Reaction. When a toluene solution of tropone (**1**) and 2-cyclopenten-1-one (**2**) was heated at 100 °C for 10 h under 10 kbar, four 1:1-adducts (**3**—**6**) were obtained. The dihydrohomobarrelenone framework for **3**, **4**, and **5** was evident from NMR spectra; e.g., the ^{1}H NMR spectrum of **3** showed the signal of the doublet of doublets at δ=7.12 (J=11.0, 8.4 Hz), ascribable to the β-proton of the α,β-unsaturated ketone. The stereochemistry of the methine protons H-2 and H-6 was determined to be exo by the value ($J_{1,2}$=0 Hz) of the coupling constant. The position of the carbonyl group was found to be at C-3 by analysis of the 2D COSY spectrum, where H-6 showed a correlation with H-12. Therefore, **3** was shown to be tricyclo[5.3.2.0^{2,6}]dodeca-9,11-diene-3,8-dione.

The second product, **4**, was determined to be an *exo* [4+2] adduct from the magnitudes ($J_{1,2}$=5.5 Hz and $J_{6,7}$=8.1 Hz) of the coupling constants of H-1 at δ=3.77 and H-7 at δ=3.71. The third product **5** was another *endo* [4+2] adduct as shown by the coupling constant ($J_{6,7}$=0 Hz), and the position of the carbonyl group was determined to be on C-3.

The spectral data of the remaining product, **6**, was quite different from those of the [4+2] adducts (**3**—**5**); showing no signal lower than δ=6.1 eliminated a [4+2]



Scheme 1.



Scheme 2.

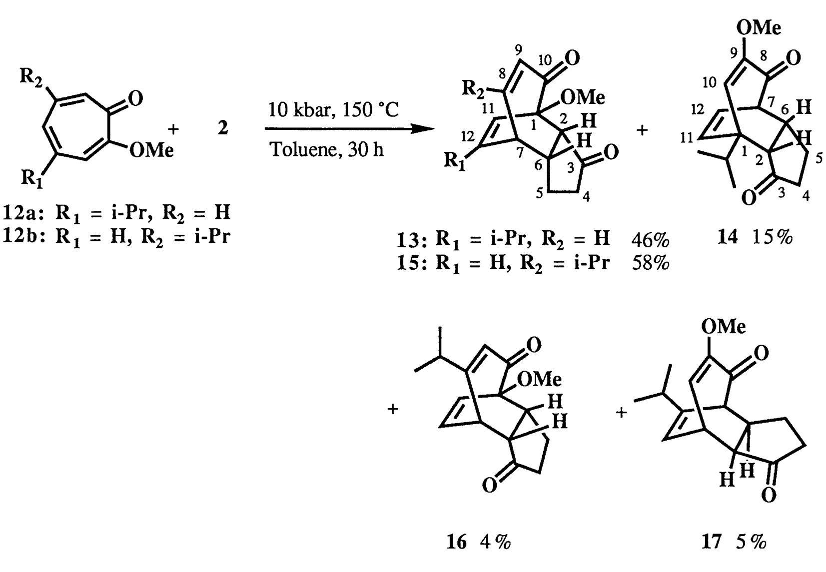
structure. In addition, the ^{1}H NMR spectrum of **6** exhibited four olefinic protons, which also eliminated an [8+2] structure. Its IR spectrum showed two carbonyl absorptions at 1736 and 1713 cm^{-1}; the latter is similar to the absorption (1715 cm^{-1}) of the [6+4] adduct (**B**) between **1a** and cyclopentadiene.8) The UV spectrum of **6** also resembled that of **B**. These observations are consistent with those of tricyclo[4.4.1.1^{2,5}]dodeca-7,9-diene-3,11-dione, which can be derived from **1a** and 1,4-cyclopentadien-1-ol, an enol form of **2**. One of the two sets of methylene proton pairs [δ=1.84 (dt, J=13.0, 4.8 Hz) and 2.66 (dd, J=13.0, 4.0 Hz), and 2.37 (dd, J=19.1, 4.0 Hz) and 2.58 (dd, J=19.1, 7.1 Hz)] revealed a large *gem*-spin coupling constant which indicated the presence of a CO–CH$_2$ group.

In order to determine the stereochemistry, **6** was hydrogenated to a tetrahydro derivative (**7**). However, the signals of the methylene protons overlapped each other in the ^{1}H NMR spectrum. This indicated that the methylene protons at δ=1.84 and 2.26 and the diene part of **6** are in proximity. Furthermore, upon lithium aluminum hydride (LAH) reduction, **6** gave a dihydro derivative, which showed broad signals, indicating an equilibration between the ketol form (**8a**) and the hemiacetal form (**8b**) at room temperature. Thus, **6** was shown to be an *exo*-adduct. We also observed a temperature-dependent equilibrium, i.e., a 14:86 mixture of **8a** and **8b** at 0 °C, while only **8b** was detected at -50 °C. The ^{1}H NMR spectral coupling sequence of **8b** was analyzed by means of decoupled NMR experiments at 0 °C. Two allylic protons signals (H-7 and H-12) appeared at δ=2.94 (dd, J=6.6, 4.0 Hz) and 2.70 (dd, J=7.7, 3.0 Hz), which were coupled with olefinic protons at δ=5.59 (H-8, dd, J=11.7, 7.3 Hz) and 5.61 (H-11, dd, J=11.7, 6.6 Hz), respectively. The absence of spin coupling of these two allylic protons with H-2 at δ=4.59 (m), the proton on the etheral carbon, led us to the conclusion that the structure of **8b** was 2-oxatetracyclo[6.5.0^{3,7}.0^{5,13}]trideca-9,11-dien-1-ol.

The reason why the five-membered carbonyl group was predominantly reduced was speculated as follows: since a five-membered ring has a larger bond-angle strain than a seven-membered ring, the change from an sp^2 carbon to an sp^3 carbon of the five-membered carbonyl group would be accelerated to release the strain.9) Alternatively, the preferential reduction of the five-membered cabonyl group was explained by the Cieplak stereoelectronic effect,10) since the five-membered carbonyl group had a C–H bond antiperiplanar to the incipient σ^* orbital.

Similar explanations would apply to the predominant acetal formation with the confronted hydroxyl group in **8** since the seven-membered carbonyl group in a fused system was more hindered than a monocyclic moiety.

The reaction between 2-methoxytropone (**1b**) and **2** under 10 kbar gave three products (**9**—**11**). The



Scheme 3.

structures were determined by the ^{1}H NMR spectral comparison with those of the [4+2] adducts (**3**—**5**). In this case, no [6+4] adduct was detected. Attempted reactions between tropolone (**1c**) and 2-chlorotropone (**1d**) with **2** were unsuccessful; from **1d**, only a resinous material was obtained, and from **1c**, no product other than the starting material was recovered in 80% yield.

Furthermore, reactions between 4-isopropyl- and 6-isopropyl-2-methoxytropones (**12a** and **12b**) and **2** afforded two adducts (**13** and **14**) from **12a** and three adducts (**15**—**17**) from **12b**, respectively.

The ^{1}H NMR spectrum of the main product **13** from **12a** showed the typical doublet of doublets of a [4+2] adduct at δ=7.11 (J=11.0, 8.4 Hz) and a doublet at δ=3.00 (J=9.2 Hz). Since the latter was assigned to the α-methine proton of the carbonyl group, **13** was deduced to be an *endo* [4+2] adduct. The position of the carbonyl group was deduced from the structure of the photorearrangement product as will be discussed later.

One of the olefinic protons of **14** appeared as a singlet at δ=5.77 and two remaining protons coupled with each other, whose coupling constant (J=8.4 Hz) implied that a methoxyl group was located at C-9 of the bridge and an isopropyl group was at the bridgehead, C-1. Since the α-methine proton of the carbonyl group appeared as a doublet (J=8.8 Hz) at δ=2.90, **14** was another *endo* [4+2] adduct.

From the ^{1}H NMR spectrum, the main product **15** from **12b** was deduced to have an isopropyl group at C-8 from the coupling constants of the olefinic protons, two of which coupled with each other (J=9.2 Hz). Since the bridgehead proton H-7 appeared as a doublet (J=7.3 Hz), being coupled with the olefinic proton at C-12, **15** was an *endo* [4+2] adduct. However, the position of the carbonyl group was not unambiguously determined at this stage.

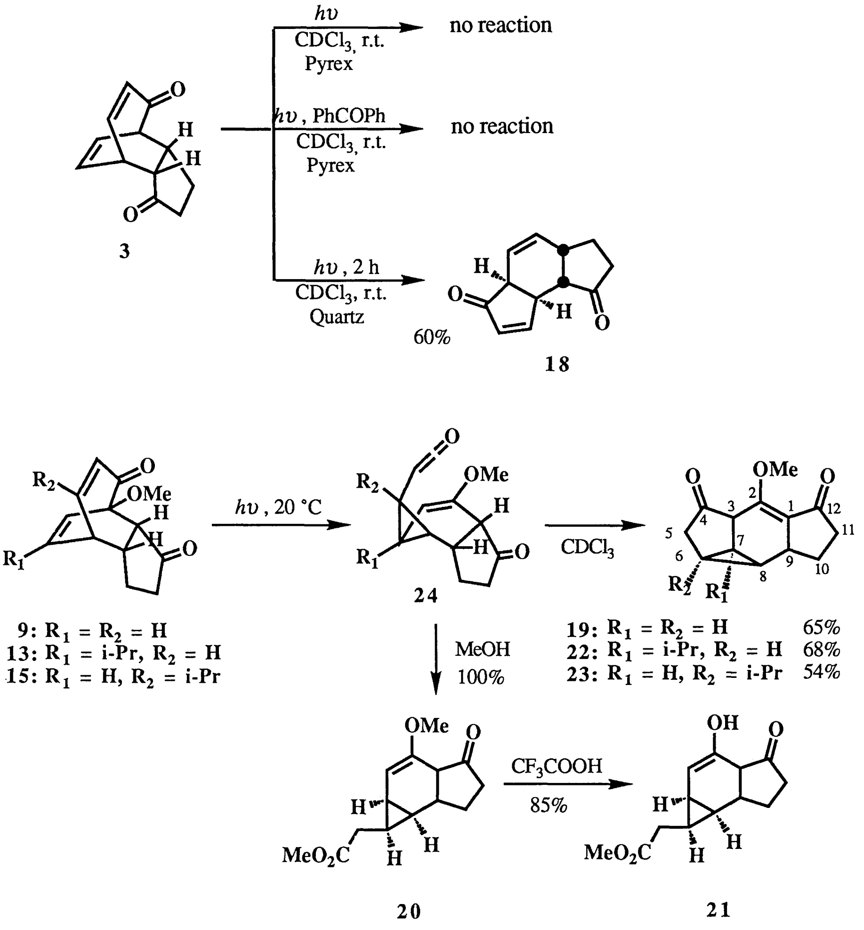
The patterns of three olefinic protons of **16** were similar to those of **15**, indicating a similar type of reaction. Since the signal of H-2 at δ=2.73 was a doublet, which meant $J_{1,2}$=0 Hz, **16** was an *endo* [4+2] adduct. Therefore, **16** was a regioisomer of **15**.

The positions of the methoxyl and isopropyl groups of **17** were deduced by the observation of only two olefinic proton signals in the ^{1}H NMR spectrum. The bridgehead proton, H-1, appeared as a doublet of doublets of doublets (J=9.2, 7.3, 5.5 Hz), which meant that H-1 coupled with the methine proton, H-2, with a coupling constant of 5.5 Hz. Therefore, **17** was an *exo* [4+2] adduct. Since the splitting pattern of H-2, a doublet of doublets, indicated two adjacent protons, the position of the carbonyl group was at C-3.

Thus, tropones reacted with **2** mostly as a 4π-cycloaddend. The regioselectivity of **1b** was parallel to those previously reported.[11] It is quite interesting that **2** behaved as a 4π-component in the reaction with **1a**.[12]

Photochemical Reaction. Upon UV-light irradiation by means of a 400-W high-pressure mercury lamp through a quartz filter in deuteriochloroform ($CDCl_3$), **3** gave a single product, **18**, in 60% yield while no reaction occurred upon irradiation through a Pyrex filter with or without benzophenone, a triplet sensitizer. The ^{1}H NMR spectrum of **18** showed four olefinic protons, in which the signals at δ=7.59 (dd, J=5.6, 2.6 Hz) and 6.19 (dd, J=5.6, 2.4 Hz) indicated the generation of a cyclopentenone moiety. The sequential alignment of four methine protons was determined by the values of the coupling constants. Since the doublet signal (J=7.2 Hz) at δ=2.56 was assigned to be an H-3a proton at the terminal position of the alignment, this indicated the structure of **18** was *cis-transoid-cis*-2,3,3a,5a,8a,8b-hexahydro-*as*-indacene-1,6-dione.

The irradiation of **9** in $CDCl_3$ through a Pyrex filter



Scheme 4.

gave a single product **19**, whose ^{13}C NMR spectrum showed two carbonyl groups at δ=201.8 and 212.8 and two olefinic carbons at δ=114.2 and 160.7, assignable to a vinyl ether. Since no C=C double bonds were observed, **19** was a tetracyclic enedione. A pair of methylene protons at δ=2.03 and 2.78 was assigned to be H-5α and H-5β since the proton at δ=2.78 coupled with H-3 at δ=3.74. Therefore, the double bond was located between C-1 and C-2. Furthermore, H-3 coupled with H-7 at δ=2.00, which further split to a doublet of doublets (J=8.1 and 7.7 Hz) to indicate the presence of a cyclopropane ring. Therefore, **19** was 2-methoxytetracyclo[7.3.0.0^{3,7}.0^{6,8}]undec-1-ene-4,12-dione.

When **9** was irradiated in methanol, a methyl ester, **20**, was obtained. The olefinic proton appeared at δ=4.64 as a doublet (J=4.0 Hz), which coupled with one of three cyclopropane ring protons at δ=1.57 (td, J=8.4 and 4.0 Hz). The coupling constants among protons on the cyclopropane ring showed *cis*-geometry.

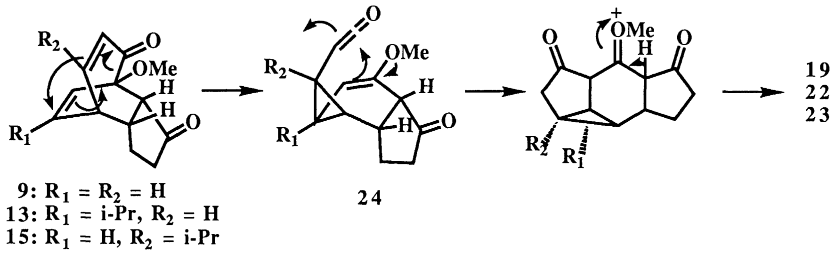
Photoproduct **20** gave a demethylated product, **21**, in 85% yield in trifluoroacetic acid.

Similarly, irradiations of **13** and **15** gave tetracyclic derivatives **22** and **23**, respectively. Their ^{1}H and ^{13}C NMR spectra as well as UV data were similar to those of **19**. Therefore, the positions of the carbonyl groups in the five-membered rings of **13**, **15**, and **16** were determined as shown.

A substituent at the bridgehead affected the photoisomerization course of the [4+2] cycloadducts. Photoreactions of **9**, **13**, and **15**, all of which have a methoxyl group at the bridgehead position, gave tetracyclic derivatives, whereas photoreaction of **3** gave the tricyclic compound **18**. The formation of tetracyclic derivatives was due to the electron-releasing nature of the methoxyl group at the bridgehead.

The formation of a methyl ester, **20**, constitued an intermediacy of a ketene, **24**. In $CDCl_3$, **24** was trapped as **23** via an intramolecular path.

In the photoreaction of **3**, no product formed from either direct irradiation in a Pyrex tube or sensitized irradiation with benzophenone in a Pyrex tube. These data clearly indicate that **3** isomerized to **18** via a π, π^* singlet state, a [1,3] acyl shift. The predominant [1,3] acyl migrations of **3** were similar to those of the dihydrohomobarrelenones$^{6)}$ and benzohomobarrelenone.$^{13)}$



Scheme 5.

Experimental

Elemental analyses were performed by Miss S. Hirashima and Miss T. Mizoguchi, of Institute of Advanced Material Study, Kyushu University. NMR spectra were measured by JEOL FX 100 Model, JEOL GSX 270 H Model, and GSX-500 Model spectrometers in a $CDCl_3$ solution (unless otherwise specified); chemical shifts were expressed in the unit δ. Mass spectra were measured with a JEOL O1SG-2 spectrometer. IR spectra were taken as KBr disks or as a liquid film inserted between NaCl plates using a JASCO IR-A 102 spectrometer. UV spectra were measured by a Hitachi U-3200 spectrophotometer. HPLC separation was performed on a Waters Type 510 system with a UV-detecter and a Microporasil column.

Cycloaddition Reaction of 1a and 2. A toluene solution (4 cm^3) of **1a** (424 mg) and **2** (640 mg) was heated at 100 °C for 10 h under 10000 bar. The solvent was removed under reduced pressure and the residue was purified by SiO_2 column chromatography and HPLC (AcOEt:hexane=1:1) to give 53 mg (7%) of **3**, 14 mg (2%) of **4**, 27 mg (4%) of **5**, and 55 mg (7%) of **6**.

3: Colorless crystals, mp 73—74 °C; ^{1}H NMR δ=1.6—1.8 (1H, m), 2.2—2.4 (2H, m), 2.94 (1H, br d, *J*=10.3 Hz), 3.0—3.1 (1H, m), 3.49 (1H, dm, *J*=7.3 Hz), 3.67 (1H, ddd, *J*=8.4, 7.3, 1.8 Hz), 5.77 (1H, ddd, *J*=11.0, 1.8, 0.7 Hz), 6.14 (1H, ddm, *J*=8.4, 7.3 Hz), 6.47 (1H, dd, *J*=8.4, 7.3 Hz), and 7.12 (1H, dd, *J*=11.0, 8.4 Hz); ^{13}C NMR δ=27.0, 36.8, 37.9, 39.8, 53.7, 59.3, 127.0, 130.4, 138.0, 151.9, 196.3, and 217.0; IR (KBr) 3048, 2956, 1726, 1656, 1626, 1387, 1269, 1248, 1178, 801, and 706 cm^{-1}; UV (MeOH) 224 (ε 5200) and 242 nm (3900 sh); MS *m*/*z* (%) 188 (M^+, 40), 160 (68), 131 (58), 118 (61), 104 (76), 103 (51), 78 (74), 77 (41), 56 (41), 55 (50), 51 (75), 39 (87), 28 (100), and 26 (89).

Found: *m*/*z* 188.0835 (M^+). Calcd for $C_{12}H_{12}O_2$: M, 188.0836.

4: A colorless oil; ^{1}H NMR δ=1.5—1.7 (1H, m), 2.1—2.3 (2H, m), 2.45 (1H, dddd, *J*=19.1, 11.4, 9.9, 1.5 Hz), 2.86 (1H, ddd, *J*=11.4, 5.5, 0.7 Hz), 3.10 (1H, ddd, *J*=11.4, 8.4, 8.1 Hz), 3.71 (1H, ddm, *J*=8.4, 8.1 Hz), 3.77 (1H, dddm, *J*=8.4, 8.1, 5.5 Hz), 5.79 (1H, ddd, *J*=11.0, 1.8, 1.1 Hz), 6.22 (1H, ddd, *J*=8.4, 7.3, 0.7 Hz), 6.56 (1H, ddd, *J*=8.1, 7.3, 0.7 Hz), and 7.04 (1H, dd, *J*=11.0, 8.4 Hz); ^{13}C NMR δ=24.2, 37.7, 38.0, 40.1, 53.8, 58.0, 129.3, 131.2, 137.5, 153.0, 197.4, and 218.0; IR (oil) 3046, 2950, 1738, 1701, 1659, 1628, 1387, 1326, 1240, 1170, 1015, 809, 711, and 675 cm^{-1}; UV (MeOH) 223 nm (ε 3400); MS *m*/*z* (%) 188 (M^+, 52), 160 (87), 132 (40), 131 (87), 118 (44), 117 (55), 104 (100), 103 (47), 91 (47), 78 (8), 77 (60), 51 (68), 39 (59), 28 (53), and 26 (78).

Found: *m*/*z* 188.0835 (M^+). Calcd for $C_{12}H_{12}O_2$: M, 188.0836.

5: A colorless oil; ^{1}H NMR δ=1.50 (1H, m), 2.2—2.5 (3H, m), 2.75 (1H, d, *J*=10.7 Hz), 3.21 (1H, br t, *J*=8.6 Hz), 3.28 (1H, br t, *J*=8.4 Hz), 3.84 (1H, dm, *J*=8.1 Hz), 5.73 (1H, ddd, *J*=11.1, 2.1, 1.6 Hz), 6.12 (1H, ddm, *J*=8.1, 7.2 Hz), 6.50 (1H, ddm, *J*=8.4, 7.2 Hz), and 7.15 (1H, dd, *J*=11.1, 8.4 Hz); ^{13}C NMR δ=26.9, 40.2, 41.6, 42.6, 47.9, 54.1, 127.8, 129.7, 137.5, 152.8, 195.3, and 215.9; IR (oil) 3046, 2960, 1737, 1668, 1629, 1391, 1265, 1116, 797, and 705 cm^{-1}; UV (MeOH) 229 nm (ε 5200); MS *m*/*z* (%) 188 (M^+, 100), 164 (57), 131 (63), 117 (28), 104 (34), 91 (44), 78 (39), 55 (42), 39 (42), and 27 (33).

Found: *m*/*z* 188.0836 (M^+). Calcd for $C_{12}H_{12}O_2$: M, 188.0836.

6: Colorless crystals, mp 163—164 °C; ^{1}H NMR δ=1.84 (1H, dt, *J*=13.0, 4.8 Hz), 2.37 (1H, dd, *J*=19.1, 4.0 Hz), 2.58 (1H, dd, *J*=19.1, 7.1 Hz), 2.66 (1H, dd, *J*=13.0, 4.0 Hz), 2.8—2.9 (1H, m), 3.23 (1H, dt, *J*=7.5, 4.0 Hz), 3.32 (1H, dt, *J*=7.5, 4.0 Hz), 5.60 (1H, dd, *J*=11.5, 7.5 Hz), 5.73 (1H, ddd, *J*=11.5, 7.5, 4.8 Hz), and 6.0—6.05 (2H, m); ^{13}C NMR δ=26.7, 40.1, 47.2, 54.8, 57.6, 59.6, 125.1, 126.5, 127.1, 127.7, 207.0, and 215.4; IR (KBr) 3038, 2956, 1736, 1713, 1397, 1195, 1161, 1021, 862, and 709 cm^{-1}; UV (MeOH) 213 (ε 3100), 222 (2600, sh), 262 (3200), 269 (3100), and 300 nm (260, sh); MS *m*/*z* (%) 188 (M^+, 100), 129 (24), 117 (44), 91 (32), 81 (30), 69 (58), 55 (22), 43 (20), 41 (38), 39 (27), 28 (99), and 26 (23).

Found: C, 76.71; H, 6.43%. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%.

Catalytic Hydrogenation of 6. A MeOH solution (5 cm^3) of **6** (40 mg) was stirred under H_2 atmosphere for 30 min in the presence of Pd/C (10 mg). The catalyst was filtered and the solvent was removed under reduced pressure. The residue was chromatographed on a SiO_2 column (AcOEt:hexane=1:1) to give 40.9 mg (100%) of **7**.

7: A colorless oil; ^{1}H NMR δ=1.6—1.7 (4H, m), 1.75—2.0 (5H, m), 2.07 (1H, dd, *J*=19.1, 3.6 Hz), 2.23 (1H, ddd, *J*=19.1, 6.6, 0.7 Hz), 2.54 (1H, m), 2.65 (1H, m), and 2.7—2.8 (3H, m); ^{13}C NMR δ=26.6, 26.8, 27.7, 28.0, 28.3, 38.2, 44.2, 53.1, 53.4, 55.1, 212.3, and 216.7; IR (oil) 2930, 2866, 1741, 1707, 1478, 1453, 1405, 1208, 1154, 1100, 1017, and 983 cm^{-1}; MS *m*/*z* (%) 192 (M^+, 100), 164 (31), 119 (23), 93 (28), 81 (23), 80 (28), 79 (38), 67 (34), 41 (29), 39 (26), and 26 (23).

Found: *m*/*z* 192.1150 (M^+). Calcd for $C_{12}H_{16}O_2$: M, 192.1151.

Lithium Aluminum Hydride Reduction of 6. A dry THF solution (3 cm^3) of **6** (30 mg) was stirred with LAH (1.7 mg) at 0 °C for 1.5 h. A small portion of sat. NaCl solution was then added. The THF solution was concentrated and the residue was chromatographed on PTLC (20 cm×10 cm, AcOEt:hexane=1:1) to give 20 mg (66%) of **8**.

8: Colorless crystals, mp 103—103.5 °C; ^{1}H NMR at −50 °C, δ=1.25 (1H, ddd, *J*=12.5, 6.6, 3.3 Hz), 1.53 (1H, dt, *J*=12.1, 4.7 Hz), 2.02 (1H, dd, *J*=12.5, 2.9 Hz), 2.10 (1H, dd, *J*=12.1, 2.9 Hz), 2.45 (1H, br s), 2.70 (1H, dd, *J*=7.7, 3.0 Hz), 2.81 (1H, dd, *J*=6.6, 5.5 Hz), 2.94 (1H, dd, *J*=6.6, 4.0 Hz), 4.59 (1H, m), 5.36 (1H, br s), 5.59 (1H, dd, *J*=11.7, 7.3 Hz), 5.61 (1H, dd, *J*=11.7, 6.6 Hz), 5.90 (1H, dd, *J*=11.7, 7.0 Hz), and 6.03 (1H, dd, *J*=11.7, 7.3 Hz); ^{13}C NMR δ=30.4, 44.0, 44.2, 44.6, 50.7, 55.7, 78.1, 99.6, 126.2, 128.2, 128.8, and 130.6; IR (KBr) 3318, 3010, 2942, 1373, 1268, 1158, 1057, 981, 972, 961, 850, and 700 cm^{-1}; MS *m/z* (%) 190 (M$^+$, 100), 145 (40), 130 (86), 129 (46), 128 (53), 124 (44), 117 (55), 107 (65), 105 (59), 91 (83), 79 (99), 78 (49), 77 (63), 67 (44), and 39 (61).

Found: C, 75.77; H, 7.37% and *m/z* 190.0994 (M$^+$). Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42% and 190.0993 (M).

Cycloaddition Reaction of 1b and 2. A toluene solution (2 cm^3) of **1b** (136 mg) and **2** (160 mg) was heated at 120 °C for 12 h under 10000 bar. The solvent was removed under reduced pressure and the residue was purified by SiO_2 column chromatography and HPLC (AcOEt:hexane=1:1) to give 74 mg (34%) of **9**, 18 mg (8%) of **10**, and 5 mg (2%) of **11**.

9: A colorless oil; ^{1}H NMR δ=1.6—1.7 (1H, m), 2.1—2.5 (3H, m), 3.02 (1H, d, *J*=9.5 Hz), 3.05—3.15 (1H, m), 3.36 (1H, ddd, *J*=8.4, 7.3, 1.1 Hz), 3.64 (3H, s), 5.78 (1H, dd, *J*=11.0, 0.7 Hz), 6.11 (1H, dd, *J*=9.2, 0.7 Hz), 6.59 (1H, dd, *J*=9.2, 7.3 Hz), and 7.10 (1H, dd, *J*=11.0, 8.4 Hz); ^{13}C NMR δ=27.0, 40.1, 40.7, 43.2, 50.5, 54.3, 88.5, 128.2, 131.6, 134.9, 151.9, 193.7, and 212.8; IR (oil) 3030, 2944, 1743, 1677, 1638, 1380, 1211, 1153, 1110, 987, 697, and 681 cm^{-1}; MS *m/z* (%) 218 (M$^+$, 70), 189 (22), 161 (25), 147 (95), 121 (43), 108 (100), 91 (45), 78 (40), 65 (61), 56 (39), 51 (33), 44 (39), 40 (76), and 27 (54).

Found: C, 71.23; H, 6.43% and *m/z* 218.0941 (M$^+$). Calcd for $C_{13}H_{12}O_3$: C, 71.54; H, 6.47% and 218.0942 (M).

10: Colorless crystals, mp 87—89 °C; ^{1}H NMR δ=1.65—1.8 (1H, m), 2.2—2.4 (3H, m), 2.89 (1H, dm, *J*=10.3 Hz), 3.0—3.1 (1H, m), 3.55 (3H, s), 3.65 (1H, dm, *J*=7.3 Hz), 3.72 (1H, ddm, *J*=9.5, 7.3 Hz), 6.11 (1H, d, *J*=9.5 Hz), 6.12 (1H, dd, *J*=8.4, 7.3 Hz), and 6.54 (1H, ddd, *J*=8.4, 7.3, 1.1 Hz); ^{13}C NMR δ=26.8, 35.2, 36.6, 39.6, 54.3, 54.9, 58.4, 118.7, 126.5, 139.4, 151.4, 192.0, and 217.4; IR (KBr) 3058, 2950, 1736, 1672, 1631, 1615, 1372, 1228, 1128, 1098, 835, 820, and 772 cm^{-1}; UV (MeOH) 232 (ε 2600) and 278 nm (2300); MS *m/z* (%) 218 (M$^+$, 100), 164 (28), 147 (24), 131 (28), 108 (56), 91 (49), 78 (29), 65 (26), 39 (31), and 26 (24).

Found: *m/z* 218.0942 (M$^+$). Calcd for $C_{13}H_{14}O_3$: M, 218.0942.

11: Colorless crystals, mp 104—105 °C; ^{1}H NMR δ=1.5—1.65 (1H, m), 2.1—2.25 (2H, m), 2.3—2.5 (1H, m), 2.77 (1H, ddd, *J*=11.7, 5.5, 1.1 Hz), 3.0—3.15 (1H, m), 3.50 (3H, s), 3.79 (1H, dddd, *J*=9.2, 7.3, 5.5, 1.1 Hz), 3.87 (1H, dd, *J*=7.3, 6.6 Hz), 5.99 (1H, d, *J*=9.2 Hz), 6.20 (1H, dd, *J*=8.4, 7.3 Hz), and 6.64 (1H, dd, *J*=8.4, 7.3 Hz); ^{13}C NMR δ=24.1, 34.7, 37.8, 40.1, 52.9, 55.1, 56.6, 118.3, 128.5, 139.1, 152.3, 192.8, and 218.2; IR (KBr) 3044, 2924, 1736, 1672, 1616, 1372, 1225, 1118, 824, and 764 cm^{-1}; UV (MeOH) 226 (ε 2400) and 280 nm (3100); MS *m/z* (%) 218 (M$^+$, 100), 175 (20), 174 (35), 131 (31), 130 (46), 105 (22), 91 (40), and 78 (25).

Found: C, 71.49; H, 6.76%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%.

Cycloaddition Reaction of 1c and 2. A toluene solution (2 cm^3) of **1c** (143 mg) and **2** (160 mg) was heated at 100 °C for 10 h under 10000 bar. The solvent was removed under reduced pressure to leave a polymerized material.

Cycloaddition Reaction of 1d and 2. A toluene solution (2 cm^3) of **1d** (122 mg) and **2** (160 mg) was heated at 120 °C for 12 h under 10000 bar. The solvent was removed under reduced pressure and 98 mg (80%) of **1d** was recovered after SiO_2 chromatography (AcOEt:hexane=1:1).

Cycloaddition Reaction of 12a and 2. A toluene solution (4 cm^3) of **12a** (360 mg) and **2** (320 mg) was heated at 120 °C for 50 h under 10000 bar. The solvent was removed under reduced pressure and the residue was purified by SiO_2 column chromatography and HPLC (AcOEt:hexane=1:2) to give 180 mg (46%) of **13**, 60 mg (15%) of **14**, and 87 mg (24%) of **12a**.

13: A colorless oil; ^{1}H NMR δ=1.05 (3H, d, *J*=7.3 Hz), 1.08 (3H, d, *J*=7.3 Hz), 1.5—1.6 (1H, m), 2.0—2.4 (4H, m), 3.00 (1H, d, *J*=9.2 Hz), 3.07 (1H, m), 3.15 (1H, d, *J*=8.4 Hz), 3.65 (3H, s), 5.62 (1H, s), 5.77 (1H, d, *J*=11.0 Hz), and 7.11 (1H, dd, *J*=11.0, 8.4 Hz); ^{13}C NMR δ=20.0, 20.7, 26.5, 34.9, 40.2, 40.4, 46.5, 49.8, 54.3, 88.0, 121.1, 128.6, 151.7, 154.8, 194.1, and 213.1; IR (oil) 2960, 2872, 1744, 1678, 1604, 1463, 1410, 1384, 1229, 1209, 1159, 1107, and 978 cm^{-1}; UV (MeOH) 228 (ε 5600), 281 (2200), 302 (1500), and 313 nm (1200); MS *m/z* (%) 261 (M$^+$+1, 8), 260 (M$^+$, 39), 218 (23), 217 (100), 189 (8), 151 (15), and 83 (6).

Found: *m/z* 260.1412 (M$^+$). Calcd for $C_{16}H_{20}O_3$: M, 260.1412.

14: A colorless oil; ^{1}H NMR δ=1.07 (3H, d, *J*=6.6 Hz), 1.18 (3H, d, *J*=6.6 Hz), 1.8—1.9 (1H, m), 2.2—2.25 (3H, m), 2.58 (1H, sept, *J*=6.6 Hz), 2.90 (1H, d, *J*=8.8 Hz), 3.03 (1H, ddm, *J*=8.8, 7.4 Hz), 3.54 (1H, d, *J*=7.3 Hz), 3.58 (3H, s), 5.77 (1H, s), 6.14 (1H, ddd, *J*=8.4, 7.3, 0.7 Hz), and 6.35 (1H, d, *J*=8.4 Hz); ^{13}C NMR δ=17.5, 18.4, 28.1, 31.4, 38.4, 40.6, 49.2, 53.6, 54.9, 58.7, 119.0, 124.9, 143.6, 150.2, 191.8, and 216.7; IR (oil) 3008, 2962, 2876, 1734, 1689, 1635, 1613, 1462, 1373, 1243, 1208, 1153, 1125, and 754 cm^{-1}; UV (MeOH) 228 (ε 2500) and 278 nm (2500); MS *m/z* (%) 261 (M$^+$+1, 19), 260 (M$^+$, 100), 232 (34), 217 (49), 204 (19), 189 (20), 178 (49), 161 (20), 150 (40), 137 (19), and 135 (40).

Found: *m/z* 260.1411 (M$^+$). Calcd for $C_{16}H_{20}O_3$: M, 260.1412.

Cycloaddition Reaction of 12b and 2. A toluene solution (2 cm^3) of **12b** (180 mg) and **2** (160 mg) was heated at 150 °C for 12 h under 10000 bar. The solvent was removed under reduced pressure and the residue was purified by SiO_2 column chromatography and HPLC (AcOEt:hexane=1:2) to give 153 mg (58%) of **15**, 11 mg (4%) of **16**, 13 mg (5%) of **17**, and 22 mg (12%) of **12b**.

15: A colorless oil; ^{1}H NMR δ=1.13 (3H, d, *J*=7.0 Hz), 1.14 (3H, d, *J*=7.0 Hz), 2.2—2.4 (4H, m), 2.52 (1H, sept, *J*=7.0 Hz), 2.9—3.0 (2H, m), 3.22 (1H, d, *J*=7.3 Hz), 3.63 (3H, s), 5.55 (1H, d, *J*=1.1 Hz), 6.10 (1H, d, *J*=9.2 Hz), and 6.51 (1H, dd, *J*=9.2, 7.3 Hz); ^{13}C NMR δ=20.1, 20.2, 27.6, 37.0, 40.1, 41.4, 47.2, 50.8, 54.1, 87.9, 121.0, 132.3, 134.0, 172.9, 194.1, and 213.1; IR (oil) 2960, 1743, 1669, 1463, 1411, 1385, 1211, 1167, 1113, and 663 cm^{-1}; UV (MeOH) 230 (ε 5900), 258 (3500), and 310 nm (700); MS *m/z* (%) 261 (M$^+$+1, 21), 260 (M$^+$, 100), 217 (31), and 137 (14).

Found: *m/z* 260.1412 (M$^+$). Calcd for $C_{16}H_{20}O_3$: M, 260.1412.

16: A colorless oil; ^{1}H NMR δ=1.13 (6H, d, *J*=6.6 Hz), 2.1—2.4 (4H, m), 2.52 (1H, sept, *J*=6.6 Hz), 2.73 (1H, dm, *J*=10.6 Hz), 3.14 (1H, dddd, *J*=10.6, 8.4, 7.0, 1.5 Hz), 3.57 (3H, s), 3.59 (1H, dm, J=7.0 Hz), 5.63 (1H, t, J=1.5 Hz), 6.11 (1H, ddd, J=9.2, 1.5, 0.7 Hz), and 6.31 (1H, dd, J=9.2, 7.0 Hz); ^{13}C NMR δ=20.0, 20.2, 22.8, 37.1, 38.9, 41.1, 41.5, 53.0, 53.4, 89.0, 122.2, 131.8, 134.0, 172.4, 195.6, and 216.5; IR (oil) 2962, 2874, 1741, 1669, 1629, 1463, 1408, 1385, 1173, 1113, and 665 cm^{-1}; UV (MeOH) 228 (ε 5500), 259 (3400, sh), and 270 nm (2500, sh); MS m/z (%) 260 (M^{+}, 100), 217 (85), 204 (30), 203 (25), 189 (55), 173 (26), 161 (52), 108 (27), 91 (32), 77 (25), 41 (29), and 26 (30).

Found: m/z 260.1414 (M^{+}). Calcd for $C_{16}H_{20}O_3$: M, 260.1412.

17: Colorless crystals, mp 96—98 °C; ^{1}H NMR δ=1.01 (6H, d, J=6.2 Hz), 1.6—1.65 (1H, m), 2.1—2.25 (2H, m), 2.3—2.4 (2H, m), 2.75 (1H, dd, J=11.3, 5.5 Hz), 3.00 (1H, ddt, J=11.3, 8.8, 6.2 Hz), 3.50 (3H, s), 3.72 (1H, ddd, J=9.2, 7.3, 5.5 Hz), 3.82 (1H, dd, J=6.2, 1.5 Hz), 6.02 (1H, d, J=9.2 Hz), and 6.18 (1H, dd, J=7.3, 1.5 Hz); ^{13}C NMR δ=20.7, 20.8, 24.0, 33.8, 34.5, 38.5, 40.1, 53.5, 55.0, 60.2, 119.3, 128.4, 147.8, 152.1, 193.5, and 218.6; IR (KBr) 3052, 2956, 2870, 1738, 1670, 1653, 1614, 1449, 1379, 1246, 1232, 1132, 999, and 881 cm^{-1}; UV (MeOH) 251 (ε 3300) and 277 nm (2400); MS m/z (%) 261 (M^{+}+1, 18), 260 (M^{+}, 100), 232 (11), 217 (14), 178 (11), 164 (30), and 150 (41).

Found: m/z 260.1412 (M^{+}). Calcd for $C_{16}H_{20}O_3$: M, 260.1412.

Irradiation of 3. a) A $CDCl_3$ solution (1 cm^{3}) of **3** (40 mg) was purged with N_2 gas in a Pyrex NMR tube and the solution was irradiated by a 400-W high-pressure mercury lamp for 2 h at room temperature. The solvent was removed under reduced pressure and 38 mg (98%) of **3** was recovered.

b) A $CDCl_3$ solution (1 cm^{3}) of **3** (32 mg) and benzophenone (31 mg) was purged with N_2 gas in a Pyrex NMR tube and the solution was irradiated by a 400-W high-pressure mercury lamp for 3 h at room temperature. The solvent was removed under reduced pressure and 27 mg (84%) of **3** was recovered after SiO_2 chromatography (AcOEt:hexane=1:1).

c) A $CDCl_3$ solution (1 cm^{3}) of **3** (25 mg) was purged with N_2 gas in a quartz NMR tube and the solution was irradiated by a 400-W high-pressure mercury lamp for 2 h at room temperature. The solvent was removed under reduced pressure and the residue was chromatographed on PTLC (20 cm×10 cm, AcOEt:hexane=1:2) to give 15 mg (60%) of **18**.

18: A colorless oil; ^{1}H NMR δ=1.94 (1H, dd, J=12.7, 9.1 Hz), 2.07 (1H, dddd, J=12.7, 11.5, 9.1, 6.4 Hz), 2.16 (1H, ddd, J=19.1, 11.5, 9.1 Hz), 2.28 (1H, dd, J=19.1, 9.1 Hz), 2.56 (1H, br d, J=7.2 Hz), 2.81 (1H, br s, $h_{1/2}$=16 Hz), 2.98 (1H, ddd, J=8.3, 4.8, 2.4 Hz), 3.74 (1H, ddd, J=7.2, 4.8, 2.6 Hz), 5.57 (1H, d, J=9.9 Hz), 5.77 (1H, ddd, J=9.9, 4.4, 2.4 Hz), 6.19 (1H, dd, J=5.6, 2.4 Hz), and 7.59 (1H, dd, J=5.6, 2.6 Hz); ^{13}C NMR δ=26.6, 33.0, 34.0, 39.1, 44.4, 50.2, 126.9, 129.9, 133.7, 166.2, 206.9, and 216.9; MS m/z (%) 188 (M^{+}, 76), 164 (65), 160 (100), 146 (40), 131 (40), 118 (80), 117 (48), 104 (62), and 91 (94).

Found: m/z 188.0834 (M^{+}). Calcd for $C_{12}H_{12}O_2$: M, 188.0836.

Irradiation of 9. a) A $CDCl_3$ solution (1 cm^{3}) of **9** (100 mg) was purged with N_2 gas in a Pyrex NMR tube and the solution was irradiated by a 400-W high-pressure mercury lamp for 120 min at 20 °C. The solvent was removed under reduced pressure and the residue was purified by PTLC (20 cm×10 cm, AcOEt:hexane=1:1) to give 65 mg (65%) of **19**.

19: Colorless crystals, mp 104—104.5 °C; ^{1}H NMR δ=1.30 (1H, td, J=7.7, 1.7 Hz), 1.7—1.8 (2H, m), 2.00 (1H, ddd, J=8.1, 7.7, 6.4 Hz), 2.03 (1H, d, J=20.3 Hz), 2.31 (1H, dd, J=12.2, 5.0 Hz), 2.33 (1H, dd, J=9.0, 2.8 Hz), 2.35—2.45 (2H, m), 2.78 (1H, ddd, J=20.3, 6.5, 2.4 Hz), 3.74 (1H, dd, J=6.4, 2.4 Hz), and 4.04 (3H, s); ^{13}C NMR δ=15.6, 19.4, 21.5, 30.2, 33.8, 37.3, 39.1, 48.4, 59.8, 114.2, 160.7, 201.8, and 212.8; IR (KBr) 2950, 1735, 1708, 1613, 1409, 1291, 1194, and 756 cm^{-1}; UV (MeOH) 282 (ε 9400), 302 (6300), and 310 nm (5500); MS m/z (%) 218 (M^{+}, 100), 190 (34), 175 (48), 158 (43), 147 (27), 116 (36), 109 (84), 91 (40), 77 (31), 44 (25), 41 (31), 39 (30), and 28 (32).

Found: C, 71.81; H, 6.48% and m/z 218.0944 (M^{+}). Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47% and 218.0942 (M).

b) A MeOH solution (1 cm^{3}) of **9** (60 mg) was purged with N_2 gas in a Pyrex NMR tube and the solution was irradiated by a 400-W high-pressure mercury lamp for 40 min at room temperature. The solvent was removed under reduced pressure and the residue was purified by means of PTLC (20 cm×10 cm, AcOEt:hexane=1:1) to give 64.2 mg (100%) of **20** and 4 mg of **9**.

20: A colorless oil; ^{1}H NMR δ=0.99 (1H, td, J=8.4, 2.6 Hz), 1.32 (1H, tt, J=8.4, 7.3 Hz), 1.57 (1H, td, J=8.4, 4.0 Hz), 1.9—2.5 (6H, m), 2.52 (1H, d, J=7.7 Hz), 2.60 (1H, m), 3.59 (3H, s), 3.69 (3H, s), and 4.64 (1H, d, J=4.0 Hz); ^{13}C NMR δ=15.0, 16.2, 19.7, 29.0, 29.3, 33.6, 35.7, 51.7, 52.3, 54.8, 90.1, 153.9, 173.9, and 215.9; IR (oil) 3000, 2950, 1733, 1660, 1438, 1377, 1353, 1313, 1270, 1208, 1173, 1129, 1038, 1009, and 810 cm^{-1}; MS m/z (%) 251 (M^{+}+1, 8), 250 (M^{+}, 37), 163 (49), 149 (23), 121 (100), and 91 (19).

Found: C, 66.90; H, 7.04% and m/z 250.1199 (M^{+}). Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25% and 250.1204 (M).

Demethylation of 20 with CF_3COOH. A $CDCl_3$ solution (1 cm^{3}) of **20** (25 mg) and CF_3COOH (1 drop) was kept in an NMR tube overnight at room temperature. The solvent was removed under reduced pressure and the residue was chromatographed on a SiO_2 column (AcOEt:hexane=1:1) to give 20 mg (85%) of **21**.

21: Colorless crystals, mp 87—88 °C; ^{1}H NMR δ=1.09 (1H, br t, J=8.4 Hz), 1.3—1.35 (2H, m), 1.68 (1H, m), 2.0—2.1 (3H, m), 2.3—2.65 (5H, m), and 3.17 (3H, s); ^{13}C NMR δ=12.2, 14.6, 16.5, 23.4, 29.4, 31.4, 32.3, 37.5, 51.8, 112.0, 168.1, 173.3, and 207.0; IR (KBr) 3244, 2950, 2836, 1735, 1687, 1631, 1439, 1315, 1199, 1170, 1107, 1007, 841, and 753 cm^{-1}; UV (MeOH) 222 nm (ε 8400); MS m/z (%) 236 (M^{+}, 22), 205 (19), 186 (21), 177 (27), 163 (100), 162 (47), 161 (25), 158 (30), 149 (40), 123 (58), 121 (35), 109 (26), 91 (28), 82 (19), and 77 (26).

Found: C, 66.23; H, 6.82%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

Irradiation of 13. A $CDCl_3$ solution (1 cm^{3}) of **13** (50 mg) was purged with N_2 gas in a Pyrex NMR tube and the solution was irradiated by a 400-W high-pressure mercury lamp for 2 h at room temperature. The solvent was removed under reduced pressure and the residue was chromatographed by PTLC (20 cm×10 cm, AcOEt:hexane=1:1) to give 34 mg (68%) of **22**.

22: A colorless oil; ^{1}H NMR δ=0.87 (3H, d, J=6.6 Hz), 0.99 (3H, d, J=6.6 Hz), 1.10 (1H, br d, J=8.1 Hz), 1.5—1.8 (3H, m), 2.12 (1H, d, J=20.5 Hz), 2.3—2.5 (4H, m), 2.80 (1H, ddd, J=20.5, 6.2, 2.2 Hz), 3.52 (1H, s), and 4.06 (3H, s); ^{13}C NMR δ=20.2 (2C) 20.6 (2C), 27.0, 30.5, 33.0, 34.4, 38.7, 39.3, 51.5, 59.4, 114.5, 161.7, 201.7, and 212.5; IR (oil) 2956, 2870, 1741, 1700, 1604, 1462, 1410, 1386, 1305, 1196, 1169, 1147, 1005, 841, and 621 cm^{-1}; UV (MeOH) 282 (ε 7300), 302 (4500), and 311 nm (3600); MS m/z (%) 261 (M^{+}+1, 17), 260 (M^{+}, 100), 232

(7), 218 (31), 189 (13), and 151 (57).

Found: *m*/*z* 260.1412 (M^+). Calcd for $C_{16}H_{20}O_3$: M, 260.1412.

Irradiation of 15. A $CDCl_3$ solution (1 cm^3) of **15** (100 mg) was purged with N_2 gas in a Pyrex NMR tube and the solution was irradiated by a 400-W high-pressure mercury lamp for 110 min at room temperature. The solvent was removed under reduced pressure and the residue was purified by SiO_2 chromatography and HPLC (AcOEt:hexane=1:1) to give 38 mg (54%) of **23** and 30 mg (30%) of **15**.

23: A colorless oil; ^1H NMR δ=0.95 (3H, d, J=6.6 Hz), 1.01 (3H, d, J=6.6 Hz), 1.11 (1H, d, J=8.8 Hz), 1.39 (1H, sept, J=6.6 Hz), 1.74 (1H, m), 1.75 (1H, dd, J=8.8, 6.6 Hz), 1.99 (1H, d, J=20.1 Hz), 2.38 (4H, m), 2.63 (1H, d, J=20.1 Hz), 3.75 (1H, d, J=6.6 Hz), and 4.02 (3H, s); ^{13}C NMR δ=19.5, 19.9, 24.8 (2C), 27.7, 30.5, 33.5, 34.0, 34.6, 39.0, 39.1, 49.6, 58.9, 114.1, 161.1, 201.8, and 211.9; IR (oil) 2956, 2872, 1742, 1702, 1611, 1462, 1416, 1387, 1366, 1199, 1167, 1147, 1004, and 842 cm^{-1}; UV (MeOH) 282 (ε 6200), 302 (4500), and 311 nm (3600); MS *m*/*z* (%) 261 (M^++1, 19), 260 (M^+, 93), 232 (46), 217 (47), 201 (19), 200 (100), 189 (20), 185 (32), 164 (28), 85 (32), and 83 (51).

Found: *m*/*z* 260.1413 (M^+). Calcd for $C_{16}H_{20}O_3$: M, 160.1412.

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