1308 *Bull. Chem. Soc. Jpn. Vol. 81, No. 10, 1308–1314 (2008)*

Highly Stereoselective Intramolecular Diels–Alder Reaction of Decatrienoates Activated by *t*-Butoxycarbonyl, Chloro, and Sulfonyl Groups at the Terminal Position[#]

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Highly stereoselective intramolecular Diels–Alder (IMDA) reaction of decatrienoates has been achieved by using a more sterically hindered ester group, i.e., *t*-butoxycarbonyl, or electron-withdrawing hetero substituents, i.e., chloro and phenylsulfonyl, as terminal activating groups. A remarkable olefin isomerization of the Diels–Alder cycloadduct bearing a phenylsulfonyl group occurred upon heating it for a few hours and it was found that the isomerization can be catalyzed by Brønsted acid.

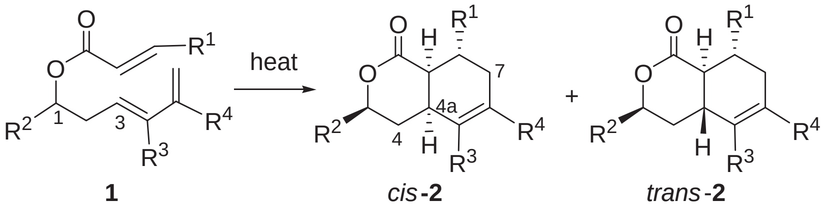
The intramolecular Diels–Alder (IMDA) reaction is a powerful tool for the stereocontrolled construction of polycyclic frameworks from relatively simple precursors.[1] Recently, extensive efforts have been focused upon the stereochemistry of the fused ring junction in IMDA reaction of the ester-tethered deca-1,3,9-trienoate (=3,5-hexadienyl acrylate) derivatives **1**, which can generally give cis fused 3,4,4a,7,8,8a-hexahydro-1*H*-2-benzopyran-1-ones (*cis*-**2**) in good, if not to say satisfactory, stereoselectivity (Scheme 1).[2]

Hence, it has been applied to the synthesis of a variety of complex molecules including natural products such as eleutherobin,[3] lycorine,[2d] and stenine.[4] Although decatrienoates with terminally activated dienophiles are expected to be good substrates in IMDA reactions, expanded examination of their reactivity and selectivity with respect to various activating groups except acetyl[2b,5] or ester[2h] groups are scarce.[6] In view of further transformations in natural product synthesis, heteroatom-containing groups such as sulfonyl and chloro are more attractive activating groups. To explore access to *cis*-**2** in high selectivity we have now examined thoroughly the IMDA reaction of **1** having various dienophile-activating groups.

Results and Discussion

The results of heat-promoted IMDA reaction of **1a**–**1c** combined with literature results are shown in Table 1. Heating acetyl-activated **1a**[5] gave two diastereomeric lactones: *cis*-**2a** predominantly along with *trans*-**2a** in minor amount (Table 1, Entry 1). Cycloaddition of enol silyl ether **1b** and **1c** also yielded two isomeric products (Table 1, Entries 2–4) and the selectivity was slightly improved in DMF (Table 1, Entry 3 vs. Entry 2). These results in hand and in literature indicate that the reaction preferentially proceeds via endo boat-like transition state **A** among the two competing diastereomeric transition states (Scheme 2).[1c,1d,2]

The selectivity for cycloadducts *cis*-**2** increased as the terminal dienophile activating substituent changed along the series COMe < CO_2Et (or CO_2Me) < H < *i*-Pr. Especially, trienoate derivatives with unsaturated electron-withdrawing substituents (e.g., COMe, CO_2Me, and CO_2Et) exhibited lower selectivity than others. In these cases, exo boat-like transition state **B** seems to competitively participate in the reaction due to stabilizing attractive electrostatic and/or secondary orbital interactions between the endo-oriented terminal carbonyl group and the diene unit in the transition state, promoting enhanced formation of the minor trans isomer. Therefore, the



1 *cis*-**2** *trans*-**2**

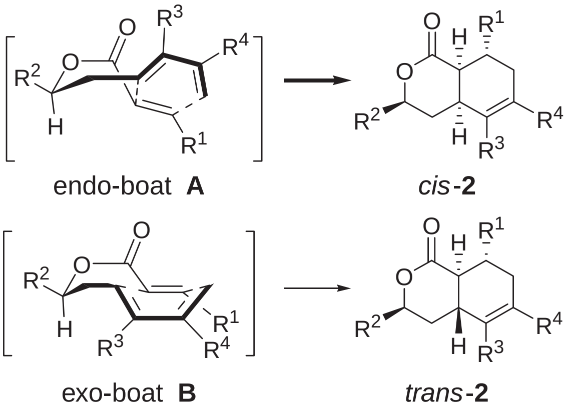
Scheme 1. IMDA reaction of deca-1,3,9-trienoates.

Published on the web October 10, 2008; doi:10.1246/bcsj.81.1308

Table 1. Thermal IMDA Reaction of Activated 1,3,9-Decatrienoates **1a**–**1g**

Entry	**1**	R^1	R^2	R^3	R^4	Temp /°C	Time /h	Yield /%[a]	**2**	cis/trans
1[c]	**1a**[b]	COMe	Me	H	H	135[d]	7	57	**2a**	74:26
2[c]	**1b**	COMe	Me	H	OTIPS	100[d]	21	94	**2b**	70:30
3[c]	**1b**	COMe	Me	H	OTIPS	100[e]	12	88	**2b**	73:27
4[c]	**1c**	CO$_2$Et	Me	H	OTBS	135[d]	16	89	**2c**	80:20
5[f]	**1d**	H	H	H	H	132	47	70	**2d**	92:8
6[f]	**1e**	CO$_2$Me	H	H	H	110	22	82	**2e**	83:17
7[g]	**1f**	COMe	H	Me	H	125	5	52	**2f**	60:40
8[g]	**1g**	i-Pr	H	Me	H	220	20	43	*cis*-**2g**	cis only

a) Isolated yield after purification. b) **1a** is a mixture of E and Z isomers (60:40) at C3 position. c) The reaction was carried out in 0.01–0.1 M (M = mol dm^{-3}) solution for **1a**–**1c**. d) In xylene. e) In *N*,*N*-dimethylformamide. f) Reference 2h. g) Reference 2b.

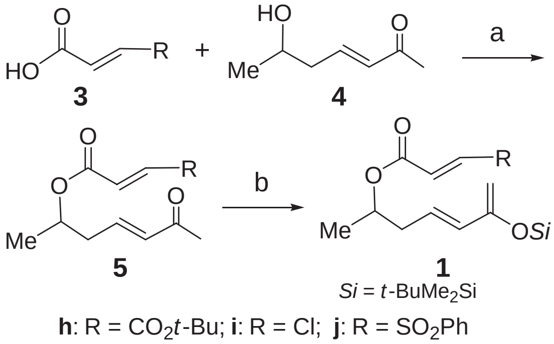


Scheme 2. Transition states for decatrienoates **1**.

selectivity for *cis*-**2** was decreased by increasing the endo stabilizing interactions (i.e., COMe > CO$_2$Et > H).[7] It is also clear from the data of Table 1 that some terminal dienophile substituents certainly play a significant influence in determining the cis stereoselectivity of the IMDA reaction. The decatrienoate **1g** with an isopropyl group (Table 1, Entry 8) cyclizes to give cis fused bicyclic lactones exclusively. As shown in Scheme 2, the exo boat-like transition state **B** apparently has repulsive nonbonded interactions between substituent R^1 and the diene unit, thereby promoting this cyclization to proceed by way of endo boat-like transition state **A**.

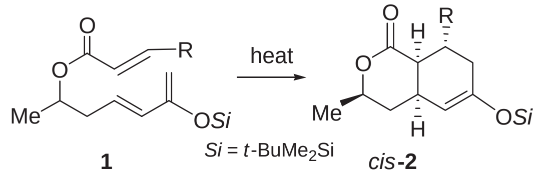
It is anticipated from the above results that a bulky carbonyl-based substituent will enhance cis selective cyclization via transition state **A**. Besides carbonyl-based activating groups for the dienophile moiety, terminal electro-negative and/or bulky hetero substituents will be also promising for cis favored cyclization, and these hetero substituents are important for further manipulation of the C8 position of the cycloadducts.[6b,8]

Then, we turned our attention to the IMDA reaction of *t*-butoxycarbonyl-, chloro-, and phenylsulfonyl-activated triene systems. In Scheme 3 is outlined synthesis of the ester-tethered trienes **1h**,[9a,9b] **1i**,[9c] and **1j**[9d,9e] via ester **5**. Esterification of (*E*)-3-chloroacrylic acid (**3i**) with 6-hydroxyenone **4**[10] was unexpectedly sluggish when using EDC, whereas acid **3h** and **3j** underwent esterification with **4** either using DCC or EDC.



Scheme 3. Syntheses of triene **1h**, **1i**, and **1j**. (a) DCC, DMAP or EDC, DMAP (**5h** 58%, **5i** 54%, **5j** 88%). (b) TBSOTf, Et$_3$N (**1h** 74%, **1i** 78%, **1j** 87%).

Table 2. Thermal IMDA Reaction of Activated 1,3,9-Decatrienoates **1h**–**1j**[a]



Entry	**1**	R	Temp /°C	Time /h	**2**	Yield /%[b]
1	**1h**	CO$_2t$-Bu	115[c]	15	*cis*-**2h**	86
2[d]	**1i**	Cl	175[e]	1.5	*cis*-**2i**	68
3	**1j**	SO$_2$Ph	100[c]	3	*cis*-**2j**	95

a) The reaction was carried out in 0.01–0.1 M solution. b) Isolated yield after purification. c) In toluene. d) Diphenylamine (1.2 equiv) was added as a hydrogen chloride scavenger. e) In 1,2-dichlorobenzene.

The results of thermal cyclization of **1h**–**1j** are summarized in Table 2. As anticipated, *t*-butoxycarbonyl-activated **1h** provided only cycloadduct *cis*-**2h** with the 3-methyl group in anti (equatorial) orientation to the angular hydrogens. The IMDA reactions of chlorotrienoate **1i** also afforded cycloadduct as a single isomer, although higher temperature for complete conversion of the starting triene and addition of amine (as a hydrogen chloride scavenger)[6b] were necessary. Interestingly, phenylsulfonyl-activated **1j** afforded *cis*-**2j** exclusively in high yield in relatively short reaction period. These results suggest that if optically active alcohol **4** is used as one of the starting compounds, enantiomerically pure cycloadducts *cis*-**2** having

Table 3. ^{1}H NMR Data for C8a–H in **2a**–**2c**, and **2h**–**2j** (in $CDCl_3$)

2	δ cis	δ trans
2a	3.16 (dd, $J = 9.2, 3.6$ Hz)	2.83 (dd, $J = 12.2, 10.9$ Hz)
2b	3.16 (dd, $J = 8.5, 3.7$ Hz)	2.71 (dd, $J = 12.2, 11.3$ Hz)
2c	3.19 (dd, $J = 8.8, 3.2$ Hz)	2.69 (dd, $J = 12.2, 11.2$ Hz)
2h	3.15 (dd, $J = 8.6, 3.0$ Hz)	—
2i	2.92 (dd, $J = 8.3, 2.4$ Hz)	—
2j	3.55 (d, $J = 7.8$ Hz)	—

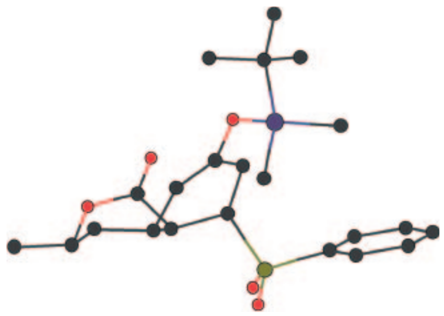


Figure 1. X-ray crystal analysis of **2j**. The H atoms removed for clarity.

four chiral centers can be obtained.

The stereochemistry of the cycloadducts **2a**–**2c** and **2h**–**2j** was assigned primarily on the basis of their 400-MHz ^{1}H NMR spectra, the proton α to the lactone carbonyl (C8a–H) of these compounds being particularly useful for assigning stereochemistry of the ring fusion. As illustrated in Table 3, in the cis fused **2a**–**2c**, **2h**, and **2i**, these signals appear as a doublet of doublets ($J_{8a\text{–}4a} = 8.3\text{–}9.2$ Hz and $J_{8a\text{–}8} = 2.4\text{–}3.7$ Hz), for trans fused **2a**–**2c** those protons also appear as a doublet of doublets with two large coupling constants ($J_{8a\text{–}4a} = 12.2$ Hz and $J_{8a\text{–}8} = 10.9\text{–}11.3$ Hz). In contrast, for cis fused cycloadduct **2j**, this signal appears as a doublet ($J_{8a\text{–}4a} = 7.8$ Hz). It seems likely that the H–C8a–C8–H dihedral angle approaches 90°, simplifying the C8a–H signal to a doublet. These assignments are further corroborated by the COSY and especially NOE experiments; in the latter case, a strong correlation was observed between the proton α to the lactone oxygen and both of the ring juncture protons in cis fused **2** and with only the proton α to the carbonyl in trans fused **2**. Fortunately, **2j** could be crystallized and was submitted to single-crystal X-ray analysis, the result of which is shown in Figure 1.

Experimental results showed that the sterically demanding phenylsulfonyl group in **1j** did not affect the IMDA reactivity affording a single cycloadduct having the same relative stereochemistry as *cis*-**2a**–**2g**. Instead, whilst we were studying the IMDA reaction of **1j**, a rather strange behavior was observed when **1j** was heated in toluene at 100 °C for a prolonged period (9 h). In this case, a single compound, accompanied by trace amounts of unknown by-products,[11] was obtained in 76% yield, which exhibited upfield shift of the olefinic proton on the cyclohexene ring in ^{1}H NMR spectra (4.43 and 4.66 ppm for **6** and *cis*-**2j**, respectively, in $CDCl_3$). We at first anticipated that epimerization should have taken place at C8 or C8a positions as was proposed in the case of **2a**.[5] Extensive 2D NMR experiments, however, allowed us to assign structure **6** for the product (Figure 2). It is quite interesting that neither the proton α to the sulfonyl group nor the proton α to the lactone carbonyl were epimerized under the reaction conditions.

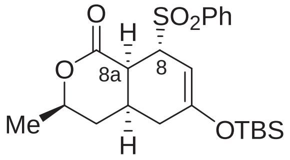
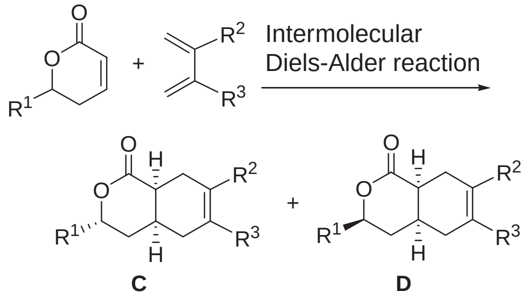


Figure 2. The structure of **6**.

Table 4. Intermolecular Diels–Alder Reaction of Substituted Butadiene and 2-Alken-5-olide



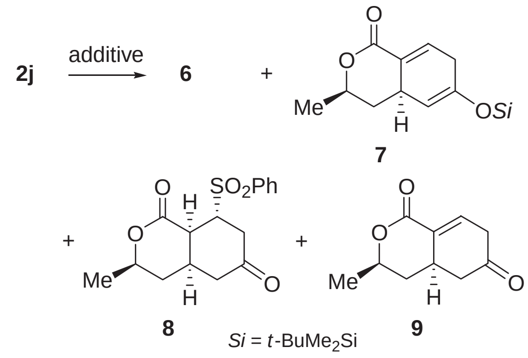
R^1	R^2	R^3	C/D	Yield/%	Ref.
CH_3	H	H	>20:1	42	12a
PhthN($PhCH_2$)CH	CH_2Ph	OTMS	100:0	82	12b

The reaction should have at least two characteristics. At first, the structure of **6** would be thought to be alternatively obtainable from intermolecular Diels–Alder reaction of substituted butadiene and 2-alken-5-olide. However, **6** has trans stereochemistry between the methyl group and the angular hydrogens (Type **D** in Table 4), therefore **6** belongs to type **D** compounds, diastereomers of type **C** compounds which are predominant or exclusive products of intermolecular Diels–Alder reactions, as exemplified in Table 4.[12] Secondly the reaction is quite straightforward and exhibits very clear double-bond isomerization which has not been so often reported in the literature.[13]

We then performed reaction of cycloadduct *cis*-**2j** under close examination under several conditions (Table 5). When heated in toluene at 100 °C for 4 h, *cis*-**2j** afforded the isomer **6** in high yield along with a small amount of **8** and **9** (Table 5, Entry 1). We thought it likely that a trace amount of $PhSO_2H$ generated by splitting off under thermal conditions with formation of **9** might have catalyzed isomerization of *cis*-**2j** to provide **6**. Then *cis*-**2j** was treated with 0.12 equiv of *p*-toluenesulfonic acid for 2 h to produce isomer **6** in 87% yield (Table 5, Entry 2). When *cis*-**2j** was heated in the presence of 6 equiv of triethylamine for 15 h, it was recovered unchanged in 84% yield along with diene **7** in 6% yield (Table 5, Entry 3). It is worth to note that in ^{1}H NMR spectra of **7**, two hydrogens at C7 showed very large long range coupling ($J = 10.5, 7.8$ Hz) between the hydrogen at C4a.[14]

It is quite obvious from the experiments that **6** is thermodynamically a more stable isomer compared to IMDA product *cis*-**2j**. This is in sharp contrast to 5β-3-ketosteroids and 2-decalone, where Δ^3-enol ether (steroid numbering) and 1,2-enol

Table 5. Isomerization of Bicyclic Lactone **2j**[a)]



Entry	Additive	Time /h	Yield/%[b)]				
			6	**7**	**8**	**9**	**2j**
1	—	4	90	—	2[c)]	3[c)]	—
2	*p*-TsOH (0.12 equiv)	2	87	—	0.3[c)]	3[c)]	—
3	Et_3N (6 equiv)	15	—	6	—	—	84

a) The reaction was carried out in 0.01–0.1 M toluene solution at 100 °C. b) Isolated yield after purification except otherwise noted. c) Yields were determined by ^{1}H NMR analysis.

ether (decaline numbering), respectively, were produced predominantly under thermodynamically controlled conditions.[15] Relative stability of double-bond isomers of silyl enol ethers in our system may be influenced by the fused lactone ring which contains oxygen and sp^2-carbon atoms. Inspection of the crystallographic structure indicates that the hydrogen at C5 lies close to the equatorial hydrogen at C4 and that C7 and C8 positions have eclipsed conformation. This conformational strain energy may be released by isomerization from **2j** to **6**. A similar acid-catalyzed thermal isomerization was also observed with *cis*-**2b** and it gave isomerized products possessing the same skeleton as **6** in 32% yield, although concurrent formation of ketone like **8** (17% yield) was observed along with the recovery of *cis*-**2b** in 16%.

In conclusion, we have explored stereoselectivity and reactivity of the IMDA cyclization of variously substituted decatrienoates under thermal conditions and found that, compared to acetyl and ethoxycarbonyl analogues, *t*-butoxycarbonyl- and phenylsulfonyl-activated trienoate **1h** and **1j** exhibited both increased reactivity and exclusive endo boat-like product selectivity and chloro-substituted **1i** showed complete stereoselectivity but moderate reactivity. Unexpectedly, *cis*-**2j** was found to easily undergo isomerization as to the position of the double bond in the presence of a catalytic amount of Brønsted acid. Cycloadducts from the IMDA reaction which appeared in the text seem to be valuable for the synthesis of complex natural products and other functional materials.

Experimental

Solvents were freshly distilled from the appropriate drying agents before use. Reactions were conducted under an atmosphere of dry N_2 unless noted otherwise. Column chromatography was performed using Kieselgel 60 (230–400 mesh) silica gel. All melting points are uncorrected, and were measured on a Büchi 535 micromelting point apparatus. IR spectra were recorded on a Perkin-Elmer Paragon 1000 Fourier transform IR spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-EX 270 (270 MHz) or a JEOL JNM-ALS 400 (400 MHz) spectrometers using internal tetramethylsilane as standard. High-resolution mass spectra were recorded on a JEOL JMS-700 mass spectrometer.

(*E*)-1-Methyl-5-oxo-3-hexen-1-yl (*E*)-4-Oxo-2-pentenoate (5b). To a solution of (*E*)-4-oxo-2-pentenoic acid (2.54 g, 22.1 mmol), *N*,*N*′-dicyclohexylcarbodiimide (DCC, 4.17 g, 20.2 mmol) and 4-(dimethylamino)pyridine (DMAP, 0.17 g, 1.4 mmol) in dichloromethane (120 mL) was added (*E*)-6-hydroxy-3-hepten-2-one (**4**, 2.17 g, 16.9 mmol). The reaction mixture was stirred for 12 h at room temperature and the precipitated *N*,*N*′-dicyclohexylurea was filtered off over celite, the filtrate was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and purification by column chromatography (hexane/AcOEt = 7:3) afforded the title compound (2.36 g, 62%) as a colorless oil. IR (neat, cm^{-1}): 2981, 2936, 1723, 1701, 1681, 1631, 1427, 1362, 1292, 1259, 1182, 982; ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.01 (1H, d, $J = 16.2$ Hz, OOCCH=C*H*), 6.72 (1H, dt, $J = 15.8$, 7.3 Hz, CH_2C*H*=CH), 6.63 (1H, d, $J = 16.2$ Hz, OOCC*H*=CH), 6.14 (1H, d, $J = 15.8$ Hz, CH_2CH=C*H*), 5.17 (1H, app sextet, $J = 6.3$ Hz, C*H*CH_3), 2.56–2.50 (2H, m, C*H*$_2$CH=CH), 2.37 (3H, s, $COCH_3$), 2.25 (3H, s, $COCH_3$), 1.33 (3H, d, $J = 6.3$ Hz, CHC*H*$_3$); ^{13}C NMR (67 MHz, $CDCl_3$): δ 197.6, 197.0 (*C*OCH_3), 164.4 (*C*OO), 141.6, 139.8, 133.4, 131.1 (OOC*C*H=*C*H and CH_2*C*H=*C*H), 70.2 (*C*HCH_3), 38.4 (CH_2), 27.9, 26.8 (CO*C*H$_3$), 19.5 (CH*C*H$_3$); HRMS (FAB+) m/z calcd for $C_{12}H_{17}O_4$ $(M + H)^+$: 225.1127. Found: 225.1129.

By a procedure similar to the preparation of **5b**, esters **5c** and **5i** were prepared from the corresponding acrylic acids **3c** and **3i**, respectively, with **4**.

***t*-Butyl (*E*)-1-Methyl-5-oxo-3-hexen-1-yl (*E*)-2-Butenedioate (5h).** To a solution of *t*-butyl hydrogen fumarate (**3h**, 0.16 g, 0.94 mmol), DMAP (11 mg, 0.09 mol), and *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimide hydrochloride (EDC•HCl, 0.20 g, 1.04 mmol) in dichloromethane (11 mL) was added (*E*)-6-hydroxy-3-hepten-2-one (**4**, 0.11 g, 0.86 mol) at 10 °C. The resulting solution was kept at 10 °C for 3 h. Then, the solvent was removed in vacuo, the concentrate was diluted with AcOEt (40 mL) and made acidic with 0.5 M hydrochloric acid (ca. pH 3). The mixture was washed with 0.5 M $NaHCO_3$ solution, brine, dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. Purification by column chromatography (hexane/AcOEt 6:1 to 1:1) yielded the title compound (0.14 g, 58%) as a colorless oil. IR (neat, cm^{-1}): 2981, 2935, 1716, 1678, 1645, 1428, 1369, 1302, 1261, 1151, 1062, 980, 848; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73–6.63 (3H, m, COOC*H*=C*H*, CH_2C*H*=CH), 6.07 (1H, d, $J = 15.9$ Hz, CH_2CH=C*H*), 5.10 (1H, app sextet, $J = 6.3$ Hz C*H*CH_3), 2.51–2.47 (2H, m, C*H*$_2$CH=CH), 2.20 (3H, s, $COCH_3$), 1.46 (9H, s, *t*-Bu), 1.27 (3H, d, $J = 6.3$ Hz, CHC*H*$_3$); ^{13}C NMR (67 MHz, $CDCl_3$): δ 197.8 (*C*OCH_3), 164.3, 163.7 (OO*C*CH=CH, *C*OO*t*-Bu), 141.8, 135.7, 133.6, 132.2 (OOC*C*H=*C*H and CH_2*C*H=*C*H), 81.9 (O*C*(CH_3)$_3$), 70.1 (*C*HCH_3), 38.6 (*C*H$_2$CH=CH), 27.9 (OC(*C*H$_3$)$_3$), 27.0 (CO*C*H$_3$), 19.7 (CH*C*H$_3$); HRMS (FAB+) m/z calcd for $C_{15}H_{23}O_5$ $(M + H)^+$: 283.1545. Found: 283.1542.

By a procedure similar to the preparation of **5h**, **5j** was prepared from the corresponding acrylic acid **3j** and **4**.

(*E*)-1-Methyl-5-(triisopropylsiloxy)-3,5-hexadien-1-yl (*E*)-4-Oxo-2-pentenoate (1b). To a solution of compound **5b** (0.49 g, 2.2 mmol) and TIPSOTf (0.58 mL, 2.4 mmol) in benzene (25 mL) was added dropwise Et$_3$N (0.35 mL, 2.8 mmol) under Ar atmosphere at 0 °C. The resulting solution was allowed to warm to room temperature and left while stirring for 1 h. The mixture was washed with brine (30 mL) and the organic layers were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. Purification by column chromatography (hexane/AcOEt 9:1, +3% NEt$_3$) yielded the title compound (0.72 g, 86%) as a colorless oil. IR (neat, cm^{-1}): 2945, 2867, 1725, 1704, 1688, 1593, 1464, 1361, 1324, 1290, 1258, 1180, 1026, 884, 681; ^{1}H NMR (270 MHz, CDCl$_3$): δ 6.98 (1H, d, $J = 16.0$ Hz, OOCCH=C*H*), 6.61 (1H, d, $J = 16.0$ Hz, OOCC*H*=CH), 6.06–5.90 (2H, m, CH$_2$C*H*=C*H*), 5.08 (1H, app sextet, $J = 6.3$ Hz, C*H*CH$_3$), 4.27 (1H, s, C=CH*H*), 4.21 (1H, s, C=C*H*H), 2.45–2.37 (2H, m, C*H*$_2$CH=CH), 2.35 (3H, s, COCH$_3$), 1.28 (3H, d, $J = 6.3$ Hz, CHC*H*$_3$), 1.26–1.13 (3H, m, SiC*H*(CH$_3$)$_2$), 1.10–1.05 (18H, m, SiCH(C*H*$_3$)$_2$).

By a procedure similar to the preparation of **1b**, **1c**, and **1h**–**1j** was prepared from the corresponding trienoates.

(3*R,4a*R**,8*R**,8a*R**)-8-Acetyl-3-methyl-6-(triisopropylsiloxy)-3,4,4a,7,8,8a-hexahydro-1*H*-2-benzopyran-1-one (*cis*-2b) and (3*R**,4a*S**,8*R**,8a*R**)-8-Acetyl-3-methyl-6-(triisopropylsiloxy)-3,4,4a,7,8,8a-hexahydro-1*H*-2-benzopyran-1-one (*trans*-2b).** A solution of trienoate **1b** (0.71 g, 1.9 mmol) in DMF (93 mL) was heated at 100 °C for 12 h. Then, the reaction mixture was cooled and brine (120 mL) and ether (120 mL) were added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine and dried over sodium sulfate, filtered and the solvent removed under reduced pressure. Purification by column chromatography (hexane/AcOEt 3:1) gave the title compound *cis*-**2b** (0.46 g, 65%) with compound *trans*-**2b** (0.17 g, 23%) as a colorless oil.

***cis*-2b:** IR (neat, cm^{-1}): 2943, 2866, 1734, 1714, 1676, 1463, 1391, 1371, 1271, 1201, 1173, 1064, 909, 884; ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.54 (1H, br s, H-5), 4.41 (1H, dqd, $J = 12.2$, 6.1, 1.7 Hz, H-3), 3.19 (1H, dt, $J = 6.3$, 3.7 Hz, H-8), 3.16 (1H, dd, $J = 8.5$, 3.7 Hz, H-8a), 2.99–2.93 (1H, m, H-4a), 2.57 (1H, dd, $J = 17.5$, 6.3 Hz, H-7β), 2.27 (1H, dd, $J = 17.5$, 3.7 Hz, H-7α), 2.12 (3H, s, COCH$_3$), 2.08 (1H, ddd, $J = 13.9$, 8.3, 1.7 Hz, H-4β), 1.24 (3H, d, $J = 6.1$ Hz, CHC*H*$_3$), 1.14–1.05 (1H, m, H-4α), 1.05–0.99 (3H, m, SiC*H*(CH$_3$)$_2$), 0.95 (18H, d, $J = 6.3$ Hz, SiCH(C*H*$_3$)$_2$); ^{13}C NMR (67 MHz, CDCl$_3$): δ 208.1 (C=O), 173.3 (C-1), 147.9 (C-6), 105.1 (C-5), 73.1 (C-3), 46.6 (C-8), 37.8, 37.0, 28.4, 28.2 (C-4a, C-8a, C-4, C-7), 27.7 (CO*C*H$_3$), 20.7 (OCH*C*H$_3$), 17.8 (Si*C*H(CH$_3$)$_2$), 12.4 (SiCH(*C*H$_3$)$_2$); HRMS (FAB+) m/z calcd for C$_{21}$H$_{37}$O$_4$Si (M + H)$^+$: 381.2461. Found: 381.2457.

***trans*-2b:** IR (neat, cm^{-1}): 2945, 2867, 1745, 1717, 1667, 1464, 1385, 1353, 1306, 1201, 1123, 1056, 883; ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.72 (1H, br s, H-5), 4.54 (1H, ddq, $J = 9.5$, 6.3, 6.1 Hz, H-3), 2.99 (1H, td, $J = 11.3$, 5.9 Hz, H-8), 2.71 (1H, dd, $J = 12.2$, 11.3 Hz, H-8a), 2.54–2.46 (1H, m, H-4a), 2.33 (3H, s, COCH$_3$), 2.28 (1H, dd, $J = 17.1$, 5.9 Hz, H-7β), 2.07 (1H, dt, $J = 13.4$, 9.5 Hz, H-4β), 1.91 (1H, dd, $J = 17.1$, 11.3 Hz, H-7α), 1.65 (1H, ddd, $J = 13.4$, 9.5, 6.3 Hz, H-4α), 1.34 (3H, d, $J = 6.1$ Hz, CHC*H*$_3$), 1.17–1.07 (3H, m, SiC*H*(CH$_3$)$_2$), 1.03 (18H, d, $J = 6.6$ Hz, SiCH(C*H*$_3$)$_2$); ^{13}C NMR (67 MHz, CDCl$_3$): δ 210.3 (C=O), 174.0 (C-1), 149.0 (C-6), 104.8 (C-5), 72.7 (C-3), 46.4 (C-8), 42.6, 36.5, 32.5, 31.7, 30.3 (C-4a, C-8a, C-4, C-7, CO*C*H$_3$), 21.2 (OCH*C*H$_3$), 17.9 (Si*C*H(CH$_3$)$_2$), 12.6 SiCH(*C*H$_3$)$_2$); HRMS (FAB+) m/z calcd for C$_{21}$H$_{37}$O$_4$Si (M + H)$^+$: 381.2461. Found: 381.2462.

Ethyl (3*R,4a*R**,8*R**,8a*R**)-6-(*t*-Butyldimethylsiloxy)-3-methyl-1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-2-benzopyran-8-carboxylate (*cis*-2c) and Ethyl (3*R**,4a*S**,8*R**,8a*R**)-6-(*t*-Butyldimethylsiloxy)-3-methyl-1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-2-benzopyran-8-carboxylate (*trans*-2c).** ***cis*-2c:** Yield: 71%, colorless oil; IR (neat, cm^{-1}): 2955, 2931, 2858, 1737, 1673, 1472, 1464, 1388, 1369, 1281, 1261, 1198, 1178, 1035, 912, 839; ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.61 (1H, br s, H-5), 4.44 (1H, dqd, $J = 12.2$, 6.1, 2.1 Hz, H-3), 4.41–4.09 (2H, m, OC*H*$_2$CH$_3$), 3.29 (1H, dt, $J = 6.2$, 3.2 Hz, H-8), 3.19 (1H, dd, $J = 8.8$, 3.2 Hz, H-8a), 3.09–2.55 (1H, m, H-4a), 2.52 (1H, dd, $J = 17.2$, 6.2 Hz, H-7β), 2.41 (1H, br d, $J = 17.2$ Hz, H-7α), 2.19 (1H, ddd, $J = 14.1$, 9.0, 2.1 Hz, H-4β), 1.33 (3H, d, $J = 6.1$ Hz, CHC*H*$_3$), 1.28–1.15 (1H, m, H-4α), 1.24 (3H, t, $J = 7.1$ Hz, OCH$_2$C*H*$_3$), 0.88 (9H, s, Si*t*-Bu), 0.09 (3H, s, SiCH$_3$), 0.08 (3H, s, SiCH$_3$); ^{13}C NMR (67 MHz, CDCl$_3$): δ 173.0 (C-1), 172.9 (*C*OOCH$_2$CH$_3$), 148.4 (C-6), 106.4 (C-5), 73.1 (C-3), 61.0 (OCH$_2$), 39.0, 37.9, 37.8, 28.2, 27.9, (C-8, C-8a, C-4a, C-7, C-4), 25.6 (SiC(*C*H$_3$)$_3$), 20.9 (CH*C*H$_3$), 18.0 (Si*C*(CH$_3$)$_3$), 14.2 (CH$_2$*C*H$_3$), −4.3, −4.4 (SiCH$_3$); HRMS (FAB+) calcd for C$_{19}$H$_{33}$O$_5$Si [M + H]$^+$: 369.2097. Found m/z: 369.2099.

***trans*-2c:** Yield: 18%, colorless oil; IR (neat, cm^{-1}): 2955, 2933, 2898, 2858, 1739, 1668, 1364, 1316, 1256, 1196, 1124, 1049, 838, 781; ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.74 (1H, br s, H-5), 4.59 (1H, ddq, $J = 9.7$, 6.3, 6.1 Hz, H-3), 4.25–4.15 (2H, m, OC*H*$_2$CH$_3$), 2.80 (1H, td, $J = 11.2$, 6.1 Hz, H-8), 2.69 (1H, dd, $J = 12.2$, 11.2 Hz, H-8a), 2.60–2.51 (1H, m, H-4a), 2.35 (1H, dd, $J = 17.1$, 6.1 Hz, H-7β), 2.24 (1H, dd, $J = 17.1$, 11.2 Hz, H-7α), 1.95 (1H, dt, $J = 13.4$, 9.7 Hz, H-4β), 1.70 (1H, ddd, $J = 13.4$, 9.3, 6.3 Hz, H-4α), 1.38 (3H, d, $J = 6.1$ Hz, CHC*H*$_3$), 1.28 (3H, t, $J = 7.1$ Hz, OCH$_2$C*H*$_3$), 0.91 (9H, s, Si-*t*-Bu), 0.14 (6H, s, SiCH$_3$); ^{13}C NMR (67 MHz, CDCl$_3$): δ 174.2, 173.5 (C-1 and *C*OOCH$_2$CH$_3$), 148.8 (C-6), 105.8 (C-5), 72.7 (C-3), 60.9 (O*C*H$_2$CH$_3$), 42.0, 40.7 (C-8 and C-8a), 36.6, 33.0, 31.4 (C-4a, C-7, C-4), 25.6 (SiC(*C*H$_3$)$_3$), 21.2 (CH*C*H$_3$), 18.0 (Si*C*(CH$_3$)$_3$), 14.2 (OCH$_2$*C*H$_3$), −4.3, −4.5 (SiCH$_3$); HRMS (FAB+) m/z calcd for C$_{19}$H$_{33}$O$_5$Si, (M + H)$^+$: 369.2097. Found: 369.2093.

***t*-Butyl (3*R**,4a*R**,8*R**,8a*R**)-6-(*t*-Butyldimethylsiloxy)-3-methyl-1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-2-benzopyran-8-carboxylate (*cis*-2h):** Yield: 86%, colorless oil; IR (neat, cm^{-1}): 2956, 2932, 2859, 1731, 1672, 1473, 1369, 1258, 1200, 1176, 867, 841; ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.59 (1H, br s, H-5), 4.43 (1H, dqd, $J = 12.2$, 6.3, 2.3 Hz, H-3), 3.22 (1H, dt, $J = 5.9$, 3.0 Hz, H-8), 3.15 (1H, dd, $J = 8.6$, 3.0 Hz, H-8a), 3.10–3.02 (1H, m, H-4a), 2.49 (1H, dd, $J = 17.4$, 5.9 Hz, H-7β), 2.36 (1H, br d, $J = 17.4$ Hz, H-7α), 2.19 (1H, ddd, $J = 14.2$, 9.2, 2.3 Hz, H-4β), 1.43 (9H, s, O*t*-Bu), 1.33 (3H, d, $J = 6.3$ Hz, CHC*H*$_3$), 1.26–1.16 (1H, m, H-4α), 0.88 (9H, s, Si*t*-Bu), 0.10 (3H, s, SiCH$_3$), 0.09 (3H, s, SiCH$_3$); ^{13}C NMR (67 MHz, CDCl$_3$): δ 173.1 (C-1), 172.1 (*C*OO*t*-Bu), 148.6 (C-6), 106.0 (C-5), 80.9 (O*C*(CH$_3$)$_3$), 72.9 (C-3), 39.7, 38.0, 37.8, 28.1, 27.9 (C-8, C-8a, C-4a, C-7, C-4), 27.8 (OC(*C*H$_3$)$_3$), 25.5 (SiC(*C*H$_3$)$_3$), 20.8 (CH*C*H$_3$), 17.9 (Si*C*(CH$_3$)$_3$), −4.4 (SiCH$_3$), −4.5 (SiCH$_3$); HRMS (FAB+) m/z calcd for C$_{21}$H$_{37}$O$_5$Si (M + H)$^+$: 397.2410. Found: 397.2405.

(3*R,4a*R**,8*R**,8a*R**)-6-(*t*-Butyldimethylsiloxy)-8-chloro-3-methyl-3,4,4a,7,8,8a-hexahydro-1*H*-2-benzopyran-1-one (*cis*-2i).** A solution of **1i** (0.23 g, 0.69 mmol) in 1,2-dichlorobenzene (5 mL) was added dropwise to a solution of diphenylamine (0.14 g, 0.83 mmol) in the same solvent (35 mL) under reflux. The reaction mixture was refluxed and monitored by TLC. After completion of the reaction (1.5 h), the reaction was cooled and the 1,2-dichlorobenzene was removed by short column (hexane/AcOEt 8:1). The resulting oil was purified by column chromatography (hexane/AcOEt 20:1) to give the title compound (0.16 g, 68%) as a light-yellow oil. IR (neat, cm^{-1}): 2931, 2895, 2858, 1738, 1674, 1473, 1379, 1297, 1240, 1194, 1063, 920, 837, 781, 686; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.81 (1H, dt, $J = 4.6$, 2.4 Hz, H-8), 4.71 (1H, br s, H-5), 4.41 (1H, dqd, $J = 12.2$, 6.1, 2.2 Hz, H-3), 3.35–3.31 (1H, m, H-4a), 3.02 (dd, $J = 18.3$, 4.6 Hz, H-7β), 2.92 (1H, dd, $J = 8.3$, 2.4 Hz, H-8a), 2.34 (1H, ddd, $J = 14.2$, 10.0, 2.2 Hz, H-4β), 2.24 (1H, br d, $J = 18.3$ Hz, H-7α), 1.36 (1H, d, $J = 6.1$ Hz, CHCH_3), 1.34–1.25 (1H, m, H-4α), 0.90 (9H, s, Si*t*-Bu), 0.13 (3H, s, $SiCH_3$), 0.12 (3H, s, $SiCH_3$); ^{13}C NMR (67 MHz, $CDCl_3$): δ 171.6 (C-1), 146.0 (C-6), 106.4 (C-5), 72.9 (C-3), 54.1 (C-8), 42.6 (C-4), 37.4 (C-8a), 34.8 (C-4a), 26.5 (C-7), 25.7 (SiC(CH_3)$_3$), 20.7 (CHCH_3), 18.0 (Si*C*(CH_3)$_3$), −4.5 ($SiCH_3$), −4.7 ($SiCH_3$); HRMS (FAB+) m/z calcd for $C_{16}H_{28}O_3ClSi$ $(M + H)^+$: 331.1497. Found: 331.1496.

(3*R,4a*R**,8*R**,8a*R**)-6-(*t*-Butyldimethylsiloxy)-3-methyl-8-phenylsulfonyl-3,4,4a,7,8,8a-hexahydro-1*H*-2-benzopyran-1-one (*cis*-2j):** Yield: 95%, colorless crystals, mp 119.6–120.2 °C; IR (KBr, cm^{-1}): 3055, 2994, 2932, 2859, 1744, 1727, 1682, 1447, 1370, 1309, 1252, 1182, 1143, 1061, 916, 842, 778; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.55 (5H, m, Ph), 4.66 (1H, br s, H-5), 4.51 (1H, dqd, $J = 11.8$, 6.1, 2.3 Hz, H-3), 4.01 (1H, d, $J = 7.9$ Hz, H-8), 3.55 (1H, d, $J = 7.8$ Hz, H-8a), 3.37–3.30 (1H, m, H-4a), 2.55 (1H, dd, $J = 19.0$, 7.9 Hz, H-7β), 2.36 (1H, ddd, $J = 13.0$, 10.2, 2.3 Hz, H-4β), 2.21 (1H, d, $J = 19.0$ Hz, H-7α), 1.37 (3H, d, $J = 6.1$ Hz, CHCH_3), 1.30 (1H, ddd, $J = 13.0$, 11.8, 7.8 Hz, H-4α), 0.89 (9H, s, Si*t*-Bu), 0.14 (3H, s, $SiCH_3$), 0.12 (3H, s, $SiCH_3$); ^{13}C NMR (67 MHz, $CDCl_3$): δ 172.0 (C-1), 145.8 (C-6), 137.7, 134.0, 129.2, 128.3 (Ph), 107.2 (C-5), 73.1 (C-3), 58.6 (C-8), 37.7 (C-4), 34.7 (C-8a), 27.5 (C-4a), 25.5 (SiC(CH_3)$_3$), 25.0 (C-7), 20.6 (CHCH_3), 17.9 (Si*C*(CH_3)$_3$), −4.4 ($SiCH_3$), −4.5 ($SiCH_3$); Anal. Calcd for $C_{22}H_{32}O_5SSi$: C, 60.52; H, 7.39%. Found: C, 60.47; H, 7.56%.

(3*R,4a*R**,8*R**,8a*R**)-6-(*t*-Butyldimethylsiloxy)-3-methyl-8-phenylsulfonyl-3,4,4a,5,8,8a-hexahydro-1*H*-2-benzopyran-1-one (6).** A solution of cycloadduct *cis*-**2j** (0.144 g, 0.33 mmol) in toluene (33 mL) was heated at 100 °C for 4 h. The reaction solvent was removed under reduced pressure and the crude product was purified by column chromatography (hexane/AcOEt 4:1 to 1:1) to give the title compound **6** (0.13 g, 90%) and a mixture of (3*R**,4a*R**,8*R**,8a*R**)-3-methyl-8-phenylsulfonyl-3,4,4a,5,7,8,8a-heptahydro-1*H*-2-benzopyran-1,6-dione (**8**) (2.1 mg, 2%) and (3*R**,4a*R**)-3-methyl-3,4,4a,5,7-pentahydro-1*H*-2-benzopyran-1,6-dione (**9**) (2.0 mg, 3%).

Compound 6: White crystals, mp 135.5–136.5 °C; IR (KBr, cm^{-1}): 3066, 2932, 2859, 1744, 1664, 1447, 1375, 1305, 1256, 1200, 1146, 914, 834, 785; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.57 (5H, m, Ph), 4.61–4.52 (1H, m, H-3), 4.43 (1H, d, $J = 4.7$ Hz, H-7), 4.39 (1H, d, $J = 4.7$ Hz, H-8), 3.57 (1H, d, $J = 6.1$ Hz, H-8a), 3.02–2.91 (1H, m, H-4a), 2.38 (1H, ddd, $J = 14.4$, 10.3, 4.4 Hz, H-4β), 2.17 (1H, dd, $J = 17.7$, 6.1 Hz, H-5β), 1.81 (1H, dd, $J = 17.7$, 12.0 Hz, H-5α), 1.39 (3H, d, $J = 6.1$ Hz, CHCH_3), 1.35–1.26 (1H, m, H-4α), 0.87 (9H, s, Si*t*-Bu), 0.08 (3H, s, $SiCH_3$), 0.05 (3H, s, $SiCH_3$); ^{13}C NMR (67 MHz, $CDCl_3$): δ 171.7 (C-1), 155.9 (C-6), 137.4, 134.0, 129.2, 128.9 (Ph), 93.6 (C-7), 73.3 (C-3), 60.9 (C-8), 36.6, 35.7, 35.6, 25.7 (C-8a, C-4a, C-5, C-4), 25.4 (SiC(CH_3)$_3$), 20.9 (CHCH_3), 17.8 (Si*C*(CH_3)$_3$), −4.5 ($SiCH_3$), −4.7 ($SiCH_3$); HRMS (FAB+) m/z calcd for $C_{22}H_{33}O_5SiS$ $(M + H)^+$: 437.1818. Found: 437.1820.

Compound 8: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.60 (5H, m, Ph), 4.68 (1H, dqd, $J = 11.7$, 6.1, 3.4 Hz, H-3), 4.12 (1H, dt, $J = 6.6$, 3.5 Hz, H-8), 3.89 (1H, br d, $J = 7.6$ Hz, H-8a), 3.37–3.27 (1H, m, H-4a), 2.79 (1H, dd, $J = 16.1$, 6.6 Hz, H-7β), 2.62 (1H, dd, $J = 16.1$, 3.5 Hz, H-7α), 2.50–2.42 (2H, m, H-4β, H-5β), 2.04 (dd, $J = 15.1$, 13.2 Hz, H-5α), 1.60–1.55 (1H, m, H-4α), 1.44 (3H, d, $J = 6.1$ Hz, CHCH_3).

Compound 9: White crystals; IR (KBr, cm^{-1}): 2976, 2934, 1714, 1698, 1643, 1614, 1450, 1392, 1356, 1307, 1258, 1206, 1106, 1039, 1014, 949, 731; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (1H, dt, $J = 5.1$, 2.9 Hz, H-8), 4.54 (1H, dqd, $J = 11.7$, 6.3, 3.9 Hz, H-3), 3.21 (1H, ddd, $J = 23.2$, 5.1, 3.4 Hz, H-7β), 3.03 (1H, dt, $J = 23.2$, 2.9 Hz, H-7α), 2.93–2.84 (1H, m, H-4a), 2.65 (1H, dd, $J = 14.9$, 3.4 Hz, H-5β), 2.26 (1H, dd, $J = 14.9$, 12.4 Hz, H-5α), 2.08 (1H, dd, $J = 13.9$, 3.9 Hz, H-4β), 1.61–1.52 (1H, m, H-4α), 1.44 (3H, d, $J = 6.3$ Hz, CHCH_3).

Table 5, Entry 2. To a solution of cycloadduct **2j** (61 mg, 0.14 mmol) in toluene (14 mL) was added *p*-toluenesulfonic acid (1.9 mg, 0.017 mmol) and the mixture was heated at 100 °C for 2 h. The cooled reaction mixture was washed with saturated $NaHCO_3$ solution followed by brine. The organic layer was dried over magnesium sulfate, filtered and the solvent removed under reduced pressure, then was purified by column chromatography (hexane/AcOEt 4:1 to 1:1) to give white solid **6** (53 mg, 87%) and a mixture of **8** (0.15 mg, 0.3%) and **9** (0.65 mg, 3%).

Table 5, Entry 3. To a solution of cycloadduct **2j** (36 mg, 0.083 mmol) in toluene (8 mL) was added triethylamine (0.069 mL, 0.50 mmol) and the mixture was heated at 100 °C for 15 h. The cooled reaction mixture was washed with saturated NH_4Cl solution followed by brine. The organic layer was dried over magnesium sulfate, filtered and the solvent removed under reduced pressure, then was purified by column chromatography (hexane/AcOEt 5:1 to 4:1) to give **2j** (30 mg, 83%) and (3*R**,4a*R**)-6-(*t*-butyldimethylsiloxy)-3-methyl-3,4,4a,7-tetrahydro-1*H*-2-benzopyran-1-one (**7**) (1.4 mg, 6%) as colorless solids.

Compound 7: White crystals; IR (KBr, cm^{-1}): 2957, 2931, 2859, 1714, 1677, 1472, 1377, 1266, 1218, 1141, 1057, 906, 864, 779; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (1H, dt, $J = 4.9$, 2.3 Hz, H-8), 4.75 (1H, t, $J = 2.3$ Hz, H-5), 4.57 (1H, dqd, $J = 11.9$, 6.3, 3.2 Hz, H-3), 3.32–3.22 (1H, m, H-4a), 2.91 (1H, ddt, $J = 23.2$, 10.5, 2.5 Hz, H-7β), 2.82 (1H, ddd, $J = 23.2$, 7.8, 4.9 Hz, H-7α), 2.01 (1H, dt, $J = 13.4$, 3.2 Hz, H-4β), 1.39 (3H, d, $J = 6.3$ Hz, CHCH_3), 1.32 (1H, ddd, $J = 14.6$, 11.9, 4.6 Hz, H-4α), 0.92 (9H, s, Si*t*-Bu), 0.16 (6H, s, $SiCH_3$); ^{13}C NMR (67 MHz, $CDCl_3$): δ 165.1 (C-1), 148.0 (C-6), 137.0, 127.3 (C-8 and C-8a), 103.6 (C-5), 76.8 (C-3), 39.0, 34.6, 32.1 (C-4a, C-7, C-4), 25.6 (SiC(CH_3)$_3$), 22.0 (CH_3), 18.0 (Si*C*(CH_3)$_3$), −4.4 ($SiCH_3$).

Experimental Procedure for X-ray Crystallography of *cis*-2j. A suitable single crystal *cis*-**2j** was obtained by recrystallization from hexane/AcOEt (5:1). The data were collected at −180 °C on a Rigaku AFC-7R automated four-circle diffractometer by using graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). A summary of the cell parameters, data collection conditions, and refinement results are given in Table 6.

The structures were solved by direct methods and expanded using Fourier techniques.[16] All calculations were performed using the teXsan crystallographic software package.[17] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition number CCDC-656299 for compound *cis*-**2j**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cam-

Table 6. Summary of Crystal Data for Compound *cis*-**2j**

Empirical formula	$C_{22}H_{32}O_5SSi$
Formula weight	436.64
Crystal color, description	colorless, prismatic
Crystal size/mm^3	$0.2 \times 0.2 \times 0.1$
Crystal system	Triclinic
Space group	$P\bar{1}$(#2)
a/Å	14.344(8)
b/Å	17.00(1)
c/Å	10.413(3)
α/deg	102.40(3)
β/deg	92.89(3)
γ/deg	66.53(4)
V/Å^3 $R = 0.04$	2273(1)
Z	4
D_{calcd}/g cm^{-3}	1.276
F_{000}	936.00
μ(Cu Kα)/cm^{-1}	2.017
$2\theta_{\mathrm{max}}$/deg	67.94
No. of measured reflns	8670
Unique relns	6474
Observed reflns	523
R	0.0395
R_w	0.0675
GOF	1.466
Max Shift/error in final cycle	0.0252
Max peak in diff Fourier map/e Å^{-3}	0.38
Min peak in diff Fourier map/e Å^{-3}	−0.39

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We thank Dr. Nobuto Minowa of Meiji Seika Co., Ltd., Japan for X-ray crystallographic analysis of *cis*-**2j**. This work was partly supported by a Sasakawa Scientific Research Grant from The Japan Science Society (to C. Yin), and Cooperative Research Fund from Graduate School of Environment and Information Sciences, Y. N. U.

Supporting Information

Spectroscopic data of **5c**, **5i**, **5j**, **1c**, **1h**, **1i**, and **1j**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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\# This paper is dedicated to the memory of Professor Yoshihiko Ito.

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