Stereoselective Reactions. XVI.[1] Total Synthesis of (−)-β-Bourbonene by Employing Asymmetric (2+2) Photocycloaddition Reaction of Chiral Butenolide

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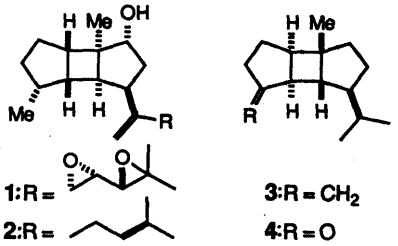
Total synthesis of (−)-β-bourbonene (3) was achieved by employing the (2+2) photocycloaddition reaction of (*S*)-γ-pivaloyloxymethyl-β-methyl-γ-butenolide (5e) with cyclopentenone ethyleneacetal (15). The major photoadduct (16) was readily converted to the *cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]decane system (22) in 70% yield. Further transformation provided the optically pure title compound (3).

Keywords photocycloaddition; β-bourbonene; spatol; tricyclo[5.3.0.0^{2,6}]decane; stereoselectivity; regioselectivity; cytotoxic diterpene; butenolide; asymmetric synthesis; total synthesis

The *cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]decane ring system is found in spatane diterpenes (**1**, **2**)[2] and bourbonene sesquiterpenes (**3**, **4**).[3] Spatol (**1**), a representative of spatane diterpenes isolated from brown marine algae of the family Dictyotaceae, is known to be endowed with remarkable biological properties including a potent inhibition of cell replication.[2c,d] The uniqueness of the carbon framework of these terpenes coupled with their biological activities has attracted much effort aimed at total synthesis of these terpenes.[4,5] For the purpose of total synthesis of spatol and related spatane diterpenes,[6] we have initiated studies on the development of new methodology for the construction of the optically active *cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]decane ring system. We describe here the details of our approach and total syntheses of (−)-β-bourbonene (**3**) and (−)-norbourbonone (**4**), representatives of bourbonene sesquiterpenes.[7]



Synthetic Design The general approach under consideration for the synthesis of the requisite tricyclodecane ring system in optically active form involves the diastereoselective (2+2) photocycloaddition reaction[8,9] of an optically active γ-hydroxymethyl-β-methyl-γ-butenolide (**5b**)[10,11] with a cyclopentenone derivative (Chart 1). It is possible to predict the stereochemistry at the newly created chiral centers of B on the basis of the least hindered approach.[11c] The γ-lactone part of the photoadduct (B) is then converted to the cyclopentenone portion of C. It is noteworthy that A is used not only as a stereocontrolling factor but also as a building block of cyclopentenone, the so-called chiral synthon.

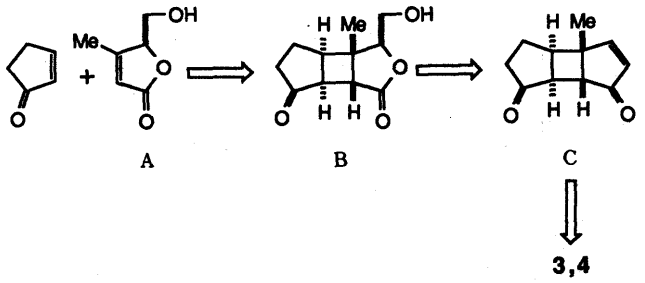
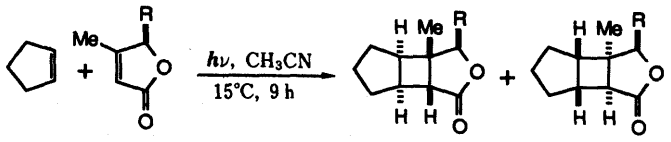


Chart 1

Stereochemistry of the Cycloaddition Photocycloaddition reaction of γ-butylcrotonolactone with 1,1-dimethoxyethylene has been reported by Uda *et al.* to give two diastereomers in an almost non-stereocontrolled manner.[12] Our studies began with irradiation of a solution of **5a** (R = CH_2OCPh_3)[10a] and cyclopentene in acetonitrile using a low pressure mercury lamp at 15 °C under argon. The products were isolated by column chromatography or by recrystallization. The ratio of the two diastereomers was determined by nuclear magnetic resonance (NMR) spectroscopy and by isolation (Table I).

The stereochemistry was assigned based on the NMR characteristics of **6a** and **7a**. The *cis,anti,cis* arrangement of adducts was ascertained by NMR spectroscopy. The coupling constants of the carbonyl α-proton signal appearing at 2.11 (minor) and at 2.30 (major) ppm as a doublet were 4 Hz, corresponding to the desired arrangement.[12,13] Furthermore, the signals of angular methyl carbon of the major and minor products appeared at 12.8 and 19.4 ppm, respectively (Table II). Judging from steric compression

TABLE I. Diastereoface Differentiation in the (2+2) Photoaddition



5 6 7

Run	5	R	Yield (%)[a]	6:7[b]
1[c]	**5a**	$CH_2OC(Ph)_3$	29 (48)	60:40
2	**5b**	CH_2OH	86	56:44[d]
3	**5c**	$CH_2OCH_2OCH_3$	80	50:50[d]
4	**5d**	$CH_2OCOCH(CH_3)_2$	62	62:38
5	**5e**	$CH_2OCO(CH_3)_3$	81	71:29
6[e]	**5e**	$CH_2OCO(CH_3)_3$	30 (95)	79:21
7	**5f**	$CH_2OSi(CH_3)_2C(CH_3)_3$	64	68:32
8	**5g**	$C(CH_3)_2OH$	57	65:35

a) Yields refer to isolated **6** and **7**. Numbers in parentheses are corrected yields based on the consumed **5**. *b*) The ratios were determined based on the isolation of **6** and **7**, except runs 2 and 3. *c*) The reaction was carried out for 16 h. *d*) The ratios were determined by the ^{1}H-NMR spectroscopy (angular methyl proton). *e*) The reaction was carried out at −30 °C.

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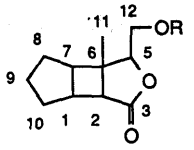
TABLE II. ^{13}C-NMR Spectroscopic Data for **6** and **7**[a]



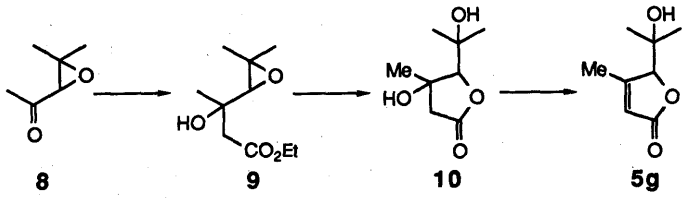
6 and 7

6

7

	6a	7a[b]	6d	7d	6e	7e	6f	7f	6g	7g
C1, C2 and C7	47.57 d	38.70 d	41.33 d	38.75 d	41.47 d	38.74 d	42.01 d	38.70 d	40.26 d	38.84 d
	47.61 d	41.23 d	47.66 d	41.38 d	47.62 d	41.38 d	47.57 d	41.47 d	47.86 d	40.94 d
	48.98 d	48.59 d	48.74 d	48.59 d	48.74 d	48.64 d	49.27 d	48.93 d	50.44 d	50.00 d
C3	179.4 s	179.2 s	178.6 s	179.0 s	178.7 s	179.0 s	179.4 s	179.4 s	178.4 s	173.8 s
C5	89.09 d	87.38 d	87.48 d	87.17 d	87.29 d	86.07 d	89.68 d	88.41 d	95.67 d	94.21 d
C6	41.04 s	40.11 s	41.04 s	40.35 s	40.99 s	40.35 s	41.13 s	40.31 s	42.99 s	40.69 s
C8, C9 and C10	26.07 t	25.83 t	25.98 t	25.88 t	26.03 t	25.88 t	26.37 t	25.98 t	25.78 t	26.27 t
	27.49 t	27.88 t	27.44 t	27.93 t	27.49 t	27.93 t	27.68 t	27.93 t	26.66 t	27.73 t
	32.29 t	32.41 t	32.26 t	32.51 t	32.26 t	32.55 t	32.36 t	32.65 t	31.92 t	32.51 t
C11	12.82 q	19.35 q	13.06 q	19.10 q	13.06 q	19.20 q	12.87 q	19.98 q	14.57 q	21.20 q
C12	62.77 t	62.82 t	63.21 t	63.45 t	63.26 t	63.41 t	62.29 t	61.99 t	71.93 s	71.59 s
C on R	87.14 s	87.09 s	18.86 q	18.91 q	27.10 q	27.15 q	−5.60 q	−5.56 q	25.15 q	23.54 s
	127.1 d		33.92 q	33.87 d	38.70 s	38.74 s	18.03 s	−5.41 q	28.95 q	31.00 q
	127.8 d		176.5 s	176.7 s	177.8 s	179.0 s	25.73 q	18.13 s		
	128.6 d							25.78 q		
	143.5 s									

a) Expressed in ppm relative to internal tetramethylsilane in $CDCl_3$. b) Data obtained from the spectrum of a mixture of **6a** and **7a**.

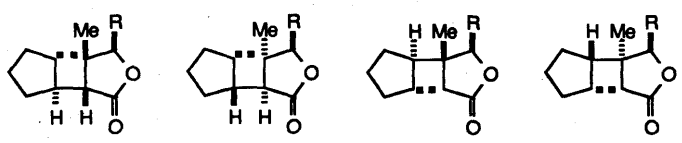


8 9 10 5g

Chart 2

effects, these lead to the assignment of **6a** and **7a** as the major and minor adducts, respectively. It is important to note that the diastereofacial differentiation in photocycloaddition of chiral butenolide (**5a**) is consistent with the least hindered approach, giving **6a** as a major product. However, efficiency was poorer than we had expected.[11c]

Photocycloaddition of several butenolides (**5**) with substituents of various steric sizes was then studied with regard to diastereofacial differentiation (Table I). The ^{13}C-NMR data are summarized in Table II. Chiral butenolides with a variety of side chains were prepared from the corresponding alcohol (**5b**)[14] and from epoxide (**8**) (Chart 2). Efficiency in the diastereofacial differentiation correlates to the bulkiness of the substituents; **5b, c** showed almost no selection and **5e** with the pivaloyl moiety gave the highest ratios of 71 : 29 at 15 °C and 79 : 21 at −30 °C. Compared to a complete stereoselection in the enolate alkylation of **5a**,[11c] the poorer efficiency is probably attributable to the intermediacy of diradical species **11**—**14**.[8] Since **13** and **14** would not be more stable than **11** and **12**, the distribution of



11 12 13 14

products would be governed by the intermediacy of **11** and **12**. Least hindered approach of cyclopentene and **5** would lead to the predominant formation of **11** rather than **12** at the first bond-forming stage. However, the severe steric repulsion between methyl and R groups in the *cis* arrangement would destabilize **11** at the second bond forming stage and **11** would revert to the olefin and **5**, giving rise to formation of both **11** and **12**.

Having established the stereochemistry in (2+2) photocycloaddition of the chiral butenolide (**5**), we turned our attention to the synthesis of β-bourbonene (**3**).

Photocycloaddition of 5e with 15 A (2+2) photocycloaddition of **5e** with **15**[15] under the same conditions described above afforded the four products **16**—**19** in a ratio of 3.1 : 1.3 : 1 : 1. Purification of the crude products by column chromatography afforded an inseparable mixture of **16** and **17** in 44% yield as well as **18** and **19** in 10 and 9.7% yields, respectively. The major product **16** was nicely isolated in 25% yield by recrystallization of the mixture.

The angular methyl carbon signals of these isomers **16**—**19** appeared at 13.5, 15.1, 19.8, and 21.2 ppm, respectively, indicating that **16** and **17** are the products arising from the least-hindered approach as in **6**, and **18** and **19** are those arising from the approach at the opposite face as in **7**. The ^{13}C-NMR data are summarized in Table III.

Furthermore **16** was converted to (−)-β-bourbonene (**3**) of natural configuration *via* the intermediate **22** (*vide infra*), indicating that major photoadduct is **16**. By the same transformation, the three isomers **17**—**19** were converted to **24**, **26**, and **28**, respectively.

These chemical correlations and ^{13}C-NMR spectroscopic analyses allowed the assignment of product structures.

Preferred formation of **16** over **17**, a regioisomer due to ethylene acetal group, is probably attributable to the lower steric congestion caused by interaction with a linear ar-

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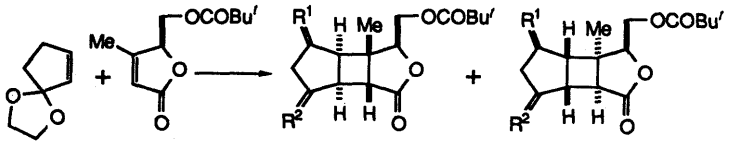
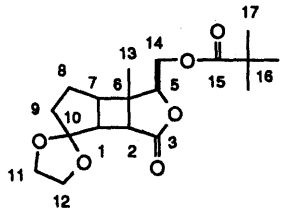
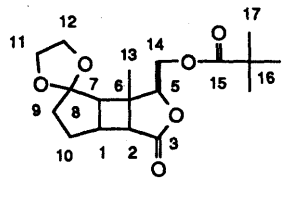


15 5e 16:R^1 = H, R^2 = $O(CH_2)_2O$ 18:R^1 = H, R^2 = $O(CH_2)_2O$
17:R^1 = $O(CH_2)_2O$, R^2 = H 19:R^1 = $O(CH_2)_2O$, R^2 = H
Bu^t = *tert*-butyl

TABLE III. ^{13}C-NMR Spectroscopic Data for 16—19[a]

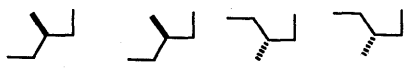


16 and 18

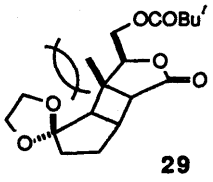


17 and 19

	16	17	18	19
C1, C2 and C7	44.50 d	49.08 d	37.04 d	38.45 d
	45.52 d	52.49 d	44.69 d	44.30 d
			45.32 d	48.98 d
C3, C15	177.4 s	178.2 s	178.0 s	178.0 s
	177.6 s			178.4 s
C5	86.80 d	87.29 d	85.97 d	86.60 d
C6	40.89 s	41.38 s	40.79 s	40.79 s
C8, C9	23.93 t	117.9 s	24.37 t	118.4 s
	34.31 t	29.37 t	34.36 t	29.53 t
C10	117.0 s	34.41 t	117.4 s	34.21 t
C11, C12 and C14	62.92 t	64.33 t	63.16 t	63.06 t
	63.99 t	65.10 t	64.33 t	65.60 t
	64.62 t		64.97 t	
C13	13.45 q	15.06 q	19.84 q	21.15 q
C16	38.40 s	38.40 s	38.79 s	38.75 s
C17	26.80 q	27.10 q	27.15 q	27.10 q



a) Expressed in ppm relative to internal tetramethylsilane in $CDCl_3$.



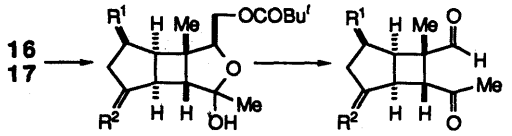
29

rangement of ethyleneacetal, methyl, and pivaloyloxymethyl groups as shown in **29**.

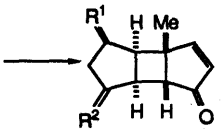
Synthesis of Tricyclo[5.3.0.0^{2,6}]decane Ring The major product **16** was transformed to **22** in a sequence of reactions without any problem. Sequential treatment of **16** with methyl lithium in tetrahydrofuran (THF) (to afford **20**), sodium methoxide in methanol, and sodium metaperiodate in water–ethyl acetate (AcOEt) furnished a keto-aldehyde **21**, which was finally treated with sodium hydroxide in water–ether to afford the desired product **22** in 70% overall yield from **16**.

The other three isomers **17**—**19** were also converted to **24**, **26** and **28** in 52,73, and 58% yields, respectively. Excepting the sign of the optical rotation, **22** and **26**, **24** and **28** were identical with each other in spectroscopic comparisons.

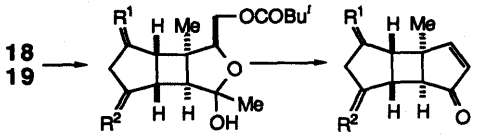
Synthesis of (−)-β-Bourbonene (3) Having accomplished the construction of the desired optically active tricyclo[5.3.0.0^{2,6}]decane system (**22**) according to the our



16 17 → 20:R^1 = H, R^2 = $O(CH_2)_2O$ 21:R^1 = H, R^2 = $O(CH_2)_2O$
23:R^1 = $O(CH_2)_2O$, R^2 = H



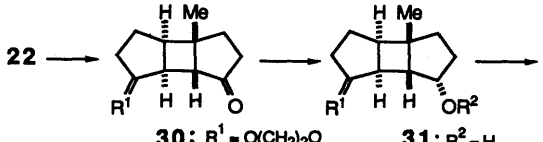
22:R^1 = H, R^2 = $O(CH_2)_2O$
24:R^1 = $O(CH_2)_2O$, R^2 = H



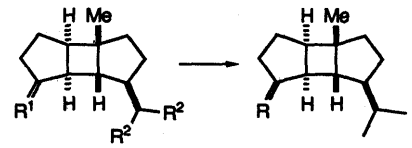
18 19 → 25:R^1 = H, R^2 = $O(CH_2)_2O$ 26:R^1 = H, R^2 = $O(CH_2)_2O$
27:R^1 = $O(CH_2)_2O$, R^2 = H 28:R^1 = $O(CH_2)_2O$, R^2 = H

original design, the remaining steps to **3** were uneventful manipulations. Then **22** was hydrogenated to **30** and reduced with sodium borohydride stereoselectively to give **31** as a single isomer by the attack of hydride from the less hindered side of the carbonyl group in **30**. Tosylation followed by substitution of the tosyloxy group of **32** with sodio diethyl malonate proceeded with inversion of configuration at the carbon atom to give **33**, in which the requisite carbons for the isopropyl group were introduced in the correct stereochemistry. Reduction of the malonic ester moiety to the isopropyl group of **36** and transacetalization gave norbourbonone (**4**)[3a] as a colorless solid. The melting point and specific rotation of synthetic **4** were in good agreement with those reported.[3a]

Finally, methylenation of **4** with methylene triphenyl-



30: R^1 = $O(CH_2)_2O$ 31: R^2 = H
32: R^2 = Ts



33: R^2 = CO_2Et 4: R = O
34: R^2 = CH_2OH 3: R = CH_2
35: R^2 = CH_2OMs
36: R^2 = CH_3

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phosphorane completed the synthesis to give (−)-**3** as an oil. The ^{1}H-NMR, infrared (IR), and mass (MS) spectra data and specific rotation of synthetic (−)-**3** were in good agreement with those reported for natural **3** isolated from *Geranium Bourbon*,[3b] and the IR and MS spectra obtained were superimposable on those of **3** provided by Dr. Yoko Naya.

Conclusion

By (2+2) photocycloaddition of optically active butenolides with cyclopentene as a key step, construction of the optically pure tricyclo[5.3.0.0^{2,6}]decane ring system was accomplished, and this was successfully applied to the first total synthesis of optically pure β-bourbonene. This success, combined with the ready availability of both enantiomers of butenolides (**5**),[14] made it possible to access the optically pure tricyclo[5.3.0.0^{2,6}]decanes in both enantiomers, and was applied to the first total synthesis of optically pure spatane diterpenes (**1**, **2**).[6]

Experimental[16]

(±)-4-Hydroxymethyl-3-methyl-2-buten-4-olide (5b) A solution of (±)-**5a** (2.04 g, 5.5 mmol) in methanol (MeOH) (180 ml) containing 12 N HCl (18 ml) was stirred at room temperature for 3 h. After concentration under reduced pressure, the residue was purified by silica gel column chromatography (ether) to give (±)-**5b** (0.59 g, 84%) as colorless prisms of mp 59—60 °C (from benzene). IR ν_{max}^{KBr} cm^{-1}: 3370 (OH), 1730 (C=O), 1640 (C=C). ^{1}H-NMR ($CDCl_3$) and MS spectra were identical with those of (−)-**5b**.

(±)-4-Methoxymethoxymethyl-3-methyl-2-buten-4-olide (5c) A solution of (±)-**5b** (105 mg, 0.82 mmol), diisopropylethylamine (0.16 ml, 0.92 mmol), and chloromethyl methyl ether (0.07 ml, 0.92 mmol) in CH_2Cl_2 (2 ml) was stirred at room temperature for 5 h and then diluted with CH_2Cl_2 (20 ml). The whole was washed successively with water, 10% HCl, water, and satd. NaCl, then dried over $MgSO_4$. Concentration and purification by silica gel column chromatography (ether) afforded (±)-**5c** (117 mg, 83%) as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1755 (C=O), 1640 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 2.12 (3H, s, CH_3C), 3.34 (3H, s, CH_3O), 3.75 (1H, dd, J=5, 11 Hz, OCH_2CHOCO), 3.90 (1H, dd, J=4, 11 Hz, OCH_2CHOCO), 4.60 (2H, s, OCH_2O), 4.82—4.98 (1H, m), 5.80—5.86 (1H, m, CH_3C=CHCO). MS m/z: Calcd for $C_8H_{12}O_4$ (M^+): 172.0736. Found: 172.0738.

(±)-4-Isobutyryloxymethyl-3-methyl-2-buten-4-olide (5d) A solution of (±)-**5b** (201 mg, 1.57 mmol), isobutyryl chloride (0.25 ml, 2.4 mmol), and pyridine (0.2 ml, 2.5 mmol) in CH_2Cl_2 (5 ml) was stirred at room temperature for 23.5 h. After addition of water (10 ml), the organic layer was washed with 10% HCl, water, satd. $NaHCO_3$, and satd. NaCl successively, then dried over $MgSO_4$. Concentration and purification by silica gel column chromatography (ether) afforded (±)-**5d** as a pale yellow oil (300 mg, 97%). IR ν_{max}^{neat} cm^{-1}: 1760 (lactone C=O), 1740 (ester C=O), 1645 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.15 (6H, d, J=7 Hz, $(CH_3)_2$CH), 2.10 (3H, s, CH_3C), 2.52 (1H, septet, J=7 Hz, $(CH_3)_2$CH), 4.28 (1H, dd, J=5, 12 Hz, OCH_2CHOCO), 4.44 (1H, dd, J=4, 12 Hz, OCH_2CHOCO), 4.89—5.04 (1H, m, OCH$_2$CHOCO), 5.80—5.90 (1H, m, CH_3C=CHCO). MS m/z: Calcd for $C_{10}H_{14}O_4$ (M^+): 198.0890. Found: 198.0870.

(±)-3-Methyl-4-pivaloyloxymethyl-2-buten-4-olid (5e) Prepared according to the procedure described for (−)-**5e**, as a pale yellow oil. IR ν_{max}^{neat} cm^{-1}: 1760 (lactone C=O), 1728 (ester C=O), 1645 (C=C). ^{1}H-NMR ($CDCl_3$) and MS spectra were identical with those of (−)-**5e**.

(±)-4-*tert*-Butyldimethylsilyloxymethyl-3-methyl-2-buten-4-olide (5f) A solution of (±)-**5b** (105 mg, 0.82 mmol), imidazole (168 mg, 2.47 mmol), and *tert*-butyldimethylsilyl chloride (177 mg, 1.18 mmol) in dimethylformamide (DMF) (2 ml) was stirred at room temperature for 6 h. After addition of benzene (20 ml), the whole was washed with water, and satd. NaCl, and then dried over $MgSO_4$. Concentration and purification by silica gel column chromatography (ether) afforded (±)-**5f** (196 mg, 99%) as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1760 (C=O), 1645 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 0.08 (6H, s, $(CH_3)_2$Si), 0.88 (9H, s, $(CH_3)_3$CSi), 2.11 (3H, s, CH_3C), 3.91 (2H, d, J=4, OCH_2CHOCO), 4.72—4.84 (1H, m, OCH$_2$CHOCO), 5.72—5.82 (1H, m, CH_3C=CHCO). MS m/z: Calcd for $C_{12}H_{22}O_3Si$ (M^+): 242.1338. Found: 242.1395.

(±)-4-(2-Hydroxyprop-2-yl)-3-methyl-2-buten-4-olide (5g) *n*-Butyl lithium (*n*-BuLi) (1.43 M in hexane solution, 43.8 ml, 63 mmol) was added to a solution of diisopropylamine (9 ml, 62 mmol) in THF (60 ml) at −78 °C under Ar, then AcOEt (6.1 ml, 62 mmol) was added at −78 °C, and the whole was stirred at −78 °C for 15 min. 3,4-Epoxy-4-methylpentan-2-one[17] (7.15 ml, 63 mmol) was added and the whole was stirred at −78 °C for 30 min, and then satd. NH_4Cl was added. After addition of satd. NaCl, the resultant mixture was extracted with AcOEt (50 ml × 3). The organic layer was washed with satd. NaCl and dried over $MgSO_4$. After concentration, the residue was dissolved in benzene, and the insoluble material was removed by filtration. The filtrate was again concentrated to give (±)-ethyl 4,5-epoxy-3-hydroxy-3,5-dimethylhexanoate (11.1 g, 88%) as a colorless oil. This was used directly without further purification. IR ν_{max}^{neat} cm^{-1}: 3480 (OH), 1730 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.29 (3H, t, J=8 Hz, CH_2CH_3), 1.33 (3H, s, $(CH_3)_2$C), 1.38 (3H, s, $(CH_3)_2$C), 1.54 (3H, s, CH_3COH), 2.63 (2H, s, CH_2CO), 2.80 (1H, s, C(O)CH), 3.35 (1H, s, OH), 4.24 (2H, q, J=8 Hz, CH_2CH_3). MS m/z: 202 (M^+). A solution of the epoxy ester prepared above (9.91 g) and 10% H_2SO_4 (7 ml) in acetone (70 ml) was stirred at room temperature for 2 h, and $NaHCO_3$ (solid) was added to the reaction mixture, then the whole was stirred vigorously. The insoluble material was filtered off, and the filtrate was concentrated *in vacuo*. Crystallization of the residue from AcOEt afforded (±)-3-hydroxy-4-(2-hydroxyprop-2-yl)-3-methylbutan-4-olide (3.4 g, 40%) as colorless needles of mp 125.5—127 °C. IR ν_{max}^{KBr} cm^{-1}: 3350 (OH), 3200 (OH), 1780 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.40 (3H, s, $(CH_3)_2$COH), 1.53 (3H, s, $(CH_3)_2$COH), 1.44 (3H, s, CH_3COH), 2.60 (1H, d, J=18 Hz, CH_2CO), 2.70 (1H, d, J=18 Hz, CH_2CO), 3.99 (1H, s, CHOCO). MS m/z: 156 ($M^+ - H_2O$). *Anal.* Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.07; H, 8.07. A solution of the lactone prepared above (1.84 g, 10.6 mmol) and diazabicycloundecene (DBU) (1.7 ml, 11.3 mmol) in THF (10 ml) was heated under reflux for 5.3 h and cooled. Concentration and purification of the residue by column chromatography (silica gel, benzene–acetone 9:1) afforded (±)-**5g** (525 mg, 32%) as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3440 (OH), 1740 (C=O), 1635 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.10 (3H, s, $(CH_3)_2$COH), 1.38 (3H, s, $(CH_3)_2$COH), 2.20 (3H, s, CH_3C=C), 3.25 (1H, br, OH), 4.69 (1H, s, CHOCO), 5.78—5.92 (1H, m, CH_2C=CHCO). MS m/z: Calcd for $C_8H_{11}O_3$ (M^+−H): 155.0706. Found: 155.0699.

General Procedure for the Photocycloaddition of Butenolides with Cyclopentene A 0.1 M solution of butenolide in acetonitrile containing 10 eq of cyclopentene was internally irradiated with a 10 W low pressure mercury lamp at 15 °C for 9 h. Concentration and purification of the residue as follows gave the purified adducts (Table I).

(±)-(1*R,2*S**,5*R**,6*R**,7*S**)-6-Methyl-5-trityloxymethyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (6a) and (±)-(1*R**,2*S**,5*S**,6*R**,7*S**)-6-Methyl-5-trityloxymethyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (7a)** Purification by column chromatography (silica gel, AcOEt–hexane 1:5) gave a mixture of (±)-**6a** and (±)-**7a** as an oil and recovered (±)-**5a** as a solid. Mixture of (±)-**6a** and (±)-**7a**: IR ν_{max}^{neat} cm^{-1}: 1770 (C=O), 1600 (benzene ring). ^{1}H-NMR ($CDCl_3$) δ: 0.76 (1.8H, s, CH_3C), 1.00 (1.2H, s, CH_3C), 1.05—1.86 (6H, m, $(CH_2)_3$), 2.11 (0.4H, d, J=3 Hz, CHCO of **6a**), 2.22 (0.6H, d, J=4 Hz, CHCO of **7a**), 2.30—2.60 (1H, m), 2.64—2.92 (1H, m), 3.03 (0.6H, dd, J=4, 10 Hz, OCH_2CHOCO of **6a**), 3.20 (0.4H, dd, J=6, 10 Hz, OCH_2CHOCO of **7a**), 3.29 (0.6H, dd, J=4, 10 Hz, OCH_2CHOCO of **6a**), 3.60 (0.4H, dd, J=6, 10 Hz, OCH_2CHOCO of **7a**), 4.26 (0.4H, t, J=6 Hz, OCH$_2$CHOCO of **7a**), 4.43 (0.6H, t, J=4 Hz, OCH$_2$CHOCO of **6a**), 6.90—7.56 (15H, m, PhH). MS m/z: 438 (M^+). Crystallization of the mixture of (±)-**6a** and (±)-**7a** from AcOEt–hexane gave (±)-**6a** as colorless prisms of mp 162—163 °C. IR ν_{max}^{KBr} cm^{-1}: 1760 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 0.84 (3H, s, CH_3C), 1.16—1.84 (6H, m, $(CH_2)_3$), 2.30 (1H, d, J=4 Hz, CHCO), 2.58 (1H, t, J=7 Hz), 2.80—3.00 (1H, m), 3.13 (1H, dd, J=4, 10 Hz, OCH$_2$CHOCO), 3.33 (1H, dd, J=4, 10 Hz, OCH_2CHOCO), 4.57 (1H, t, J=4 Hz, OCH$_2$CHOCO), 7.00—7.56 (15H, m, benzene ring). MS m/z: 438 (M^+). *Anal.* Calcd for $C_{30}H_{30}O_3$: C, 82.16; H, 6.90. Found: C, 81.90; H, 7.15.

(±)-(1*R,2*S**,5*R**,6*R**,7*S**)-5-Hydroxymethyl-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (6b) and (±)-(1*R**,2*S**,5*S**,6*R**,7*S**)-5-Hydroxymethyl-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (7b)** Purification by column chromatography (silica gel, AcOEt–hexane 1:2) gave a mixture of (±)-**6b** and (±)-**7b** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3400 (OH), 1760 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.05 (1.7H, s, CH_3C of **6b**), 1.12 (1.3H, s, CH_3C of **7b**), 1.16—2.00 (6H, m, $(CH_2)_3$), 2.04—2.28 (1H, m), 2.45—3.00 (2H, m), 3.32 (1H, br), 3.64—4.13 (2H, m), 4.31 (0.44H, dd, J=4, 7 Hz, OCH$_2$CHOCO of **6b**), 4.58 (0.56H, t, J=5 Hz, OCH$_2$CHOCO of **7b**). MS m/z: 196 (M^+).

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(±)-(1R*,2S*,5R*,6R*,7S*)-5-Methoxymethoxymethyl-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (6c) and (±)-(1R*,2S*,5S*,6R*,7S*)-5-Methoxymethoxymethyl-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (7c) Purification by column chromatography (silica gel, AcOEt–hexane 1 : 3) gave a mixture of (±)-**6c** and (±)-**7c** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1770 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.06 (1.5H, s, CH_3C), 1.12 (1.5H, s, CH_3C), 1.28—2.10 (6H, m, $(CH_2)_3$), 2.18—2.30 (1H, m), 2.52—3.04 (2H, m), 3.36 (1.5H, s, OCH_3), 3.39 (1.5H, s, CH_3O), 3.64—3.96 (2H, m), 4.33 (1H, t, J=6 Hz, OCH_2HOCO), 4.61 (1H, s, OCH_2O), 4.66 (1H, s, OCH_2O). MS *m/z*: Calcd for $C_{13}H_{20}O_4Si$ (M^+): 240.1361. Found: 240.1371.

(±)-(1R*,2S*,5R*,6R*,7S*)-5-Isobutyryloxymethyl-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (6d) and (±)-(1R*,2S*,5S*,6R*,7S*)-5-Isobutyryloxymethyl-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (7d) Purification by column chromatography (silica gel, ether–hexane 1 : 2) gave (±)-**6d** and (±)-**7d** as colorless oils.

(±)-**6d**: IR ν_{max}^{neat} cm^{-1}: 1770 (lactone C=O), 1735 (ester C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.04 (3H, s, CH_3C), 1.16 (6H, d, J=7 Hz, $(CH_3)_2CH$), 1.28—2.02 (6H, m, $(CH_2)_3$), 2.25 (1H, d, J=4 Hz, CHCO of lactone), 2.32—2.80 (2H, m), 2.80—3.04 (1H, m), 4.11 (1H, dd, J=6, 12 Hz, OCH_2CHOCO), 4.33 (1H, dd, J=4, 12 Hz, OCH_2CHOCO), 4.67 (1H, dd, J=4, 6 Hz, OCH_2CHOCO). MS *m/z*: Calcd for $C_{15}H_{22}O_4Si$ (M^+): 266.1516. Found: 266.1498.

(±)-**7d**: IR ν_{max}^{neat} cm^{-1}: 1775 (lactone C=O), 1740 (ester C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.14 (3H, s, CH_3C), 1.18 (6H, d, J=7 Hz, $(CH_3)_2CH$), 1.28—1.98 (6H, m, $(CH_2)_3$), 2.29 (1H, d, J=3 Hz, CHCO of lactone), 2.40—2.82 (3H, m), 4.36 (3H, s, OCH_2CHOCO). MS *m/z*: Calcd for $C_{15}H_{22}O_4Si$ (M^+): 266.1515. Found: 266.1509.

(±)-(1R*,2S*,5R*,6R*,7S*)-6-Methyl-5-pivaloyloxymethyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (6e) and (±)-(1R*,2S*,5S*,6R*,7S*)-6-Methyl-5-pivaloyloxymethyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (7e) Purification by column chromatography (silica gel, ether–hexane 1 : 2) gave (±)-**6e** and (±)-**7e** as colorless oils.

(±)-**6e**: IR ν_{max}^{neat} cm^{-1}: 1765 (lactone C=O), 1730 (ester C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.04 (3H, s, CH_3C), 1.20 (9H, s, $(CH_3)_3CCO$), 1.40—2.00 (6H, m, $(CH_2)_3$), 2.26 (1H, d, J=4 Hz, OCH_2CHCO), 2.52—2.80 (1H, m), 2.80—3.00 (1H, m), 4.05 (1H, dd, J=4, 12 Hz, OCH_2CHOCO), 4.32 (1H, dd, J=4, 12 Hz, OCH_2CHOCO), 4.65 (1H, t, J=4 Hz, CH_2CHOCO). MS *m/z*: Calcd for $C_{16}H_{24}O_4$ (M^+): 280.1674. Found: 280.1710.

(±)-**7e**: IR ν_{max}^{neat} cm^{-1}: 1770 (lactone C=O), 1725 (ester C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.14 (3H, s, CH_3C), 1.22 (9H, s, $(CH_3)_3CCO$), 1.40—1.96 (6H, m, $(CH_2)_3$), 2.28 (1H, d, J=3 Hz, OCH_2CHCO), 2.68—2.80 (2H, m), 4.33 (3H, s, OCH_2CHOCO). MS *m/z*: Calcd for $C_{16}H_{25}O_4$ (M^++1): 281.1751. Found: 281.1724.

(±)-(1R*,2S*,5R*,6R*,7S*)-5-*tert*-Butyldimethylsilyloxymethyl-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (6f) and (±)-(1R*,2S*,5S*,6R*,7S*)-5-*tert*-Butyldimethylsilyloxymethyl-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (7f) Purification by column chromatography (silica gel, ether–benzene 1 : 20) gave (±)-**6f** and (±)-**7f** as colorless solids.

(±)-**6f**: mp 58—60 °C (colorless prisms from hexane). IR ν_{max}^{KBr} cm^{-1}: 1750 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 0.06 (6H, s, $(CH_3)_2Si$), 0.87 (9H, s, $(CH_3)_3CSi$), 1.13 (3H, s, CH_3C), 1.32—1.96 (6H, m, $(CH_2)_3$), 2.24 (1H, d, J=4 Hz, OCH_2CHCO), 2.58—2.94 (2H, m), 3.78 (1H, dd, J=7, 10 Hz, OCH_2CHOCO), 3.97 (1H, dd, J=5, 10 Hz, OCH_2CHOCO), 4.21 (1H, dd, J=5, 7 Hz, OCH_2CHOCO). MS *m/z*: 295 (M^+-CH_3). *Anal.* Calcd for $C_{17}H_{30}O_3Si$: C, 65.79; H, 9.74. Found: C, 65.84; H, 9.90.

(±)-**7f**: mp 71.5—73 °C (colorless needles from hexane). IR ν_{max}^{KBr} cm^{-1}: 1755 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 0.07 (6H, s, $(CH_3)_2Si$), 0.87 (9H, s, $(CH_3)_3CSi$), 1.13 (3H, s, CH_3C), 1.28—1.97 (6H, m, $(CH_2)_3$), 2.22 (1H, d, J=3 Hz, OCH_2CHCO), 2.65 (1H, t, J=7 Hz), 2.74—2.97 (1H, m), 3.78 (2H, d, J=4 Hz, OCH_2CHOCO), 4.42 (1H, t, J=4 Hz, OCH_2CHOCO). MS *m/z*: 311 (M^++1). *Anal.* Calcd for $C_{17}H_{30}O_3Si$: C, 65.79; H, 9.74. Found: C, 65.62; H, 10.03.

(±)-(1R*,2S*,5R*,6R*,7S*)-5-(2-Hydroxyprop-2-yl)-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (6g) and (±)-(1R*,2S*,5S*,6R*,7S*)-5-(2-Hydroxyprop-2-yl)-6-methyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-one (7g) Purification by column chromatography (silica gel, acetone–benzene 1 : 19) gave (±)-**6g** and (±)-**7g** as a colorless solid and a colorless oil, respectively.

(±)-**6g**: mp 99.5—100 °C (colorless needles from AcOEt–hexane). IR ν_{max}^{KBr} cm^{-1}: 3480 (OH), 1760 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, s, CH_3C), 1.32 (3H, s, CH_3COH), 1.39 (3H, s, CH_3COH), 1.44—2.00 (6H, m, $(CH_2)_3$), 2.10 (1H, br, OH), 2.18 (1H, d, J=5 Hz, $CHCO$), 2.53 (1H, t, J=5 Hz), 2.92—3.17 (1H, m, $CHCHCO$), 4.39 (1H, s, $CHOCO$). MS *m/z*: 207 (M^+−OH). *Anal.* Calcd for $C_{13}H_{20}O_3$: C, 68.61; H, 8.99. Found: C, 68.89; H, 8.98.

(±)-**7g**: IR ν_{max}^{neat} cm^{-1}: 3460 (OH), 1755 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.14 (3H, s, CH_3C), 1.25 (3H, s, CH_3COH), 1.39 (3H, s, CH_3COH), 1.44—2.06 (6H, m, $(CH_2)_3$), 2.26 (1H, br, OH), 2.26 (1H, d, J=4 Hz, $CHCO$), 2.62—2.86 (1H, m), 3.80 (1H, t, J=8 Hz), 3.96 (1H, s, $CHOCO$). MS *m/z*: Calcd for $C_{13}H_{19}O_2$ (M^+−OH): 207.1395. Found: 207.1402.

(−)-4-Hydroxymethyl-3-methyl-2-buten-4-olide (5b) According to the procedure described for (±)-**5b**, (−)-**5b** was prepared from (−)-**5a**[10a] (86%) as colorless needles of mp 60—62.5 °C (from benzene). $[\alpha]_D^{20}$ −27.4° (c=1.05, $CHCl_3$).[18] IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1720 (C=O), 1635 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 2.07 (3H, s, CH_3C), 3.32 (1H, br, OH), 3.68 (1H, dd, J=4, 13 Hz, OCH_2CHOCO), 3.94 (1H, dd, J=3, 13 Hz, OCH_2CHOCO), 4.77 (1H, br, OCH_2CHOCO), 5.60—5.76 (1H, m, $CH_3C=CHCO$). MS *m/z*: 129 (M^++1). *Anal.* Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29. Found: C, 55.97; H, 6.21.

(−)-3-Methyl-4-pivaloyloxymethyl-2-buten-4-olide (5e) A solution of (−)-**5b** (3.3 g, 26 mmol), pivaloyl chloride (4.5 ml, 37 mmol), pyridine (3 ml, 37 mmol), and 4-dimethylaminopyridine (DMAP) (0.5 g, 4 mmol) in CH_2Cl_2 (60 ml) was stirred at room temperature for 23 h. After addition of water (10 ml), the organic layer was washed with 10% HCl, water, stad. $NaHCO_3$, and satd. NaCl, successively, then dried over $MgSO_4$. Concentration afforded (−)-**5e** (3.95 g, 72%) as colorless needles of mp 65—67 °C (from AcOEt–hexane). $[\alpha]_D^{20}$ −69.1° (c=0.90, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1760 (lactone C=O), 1720 (ester C=O), 1640 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.18 (9H, s, $(CH_3)_3CO$), 2.12 (3H, s, CH_3C), 4.36 (1H, dd, J=4, 12 Hz, OCH_2CHOCO), 4.43 (1H, dd, J=3, 12 Hz, OCH_2CHOCO), 5.01 (1H, br, OCH_2CHOCO), 5.82—5.96 (1H, m, $CH_3C=CHCO$). MS *m/z*: 212 (M^+). *Anal.* Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.26; H, 7.60.

Cycloaddition of (−)-5e with 15 A solution of (−)-**5e** (1.74 g, 8.2 mmol) and **15** (90 ml, 80 mmol) in acetonitrile was internally irradiated with a 30 W low pressure mercury lamp at 0 °C for 92 h under Ar. After concentration, the residual oil was separated by medium pressure column chromatography (silica gel, AcOEt–hexane 1 : 4). The first fraction gave (+)-**19** (0.27 g, 9.7%) as colorless prisms of mp 74.5—76 °C (from AcOEt–hexane). $[\alpha]_D^{20}$ +70.8° (c=1.13, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1770 (lactone C=O), 1720 (ester C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.23 (9H, s, $(CH_3)_3CCO$), 1.39 (3H, s, CH_3C), 1.72—2.14 (4H, m, $(CH_2)_2$), 2.40—2.54 (2H, m), 2.60—2.84 (1H, m), 3.78—3.94 (4H, m, $O(CH_2)_2O$), 4.34 (3H, s, OCH_2CHOCO). MS *m/z*: 338 (M^+). *Anal.* Calcd for $C_{18}H_{26}O_6$: C, 63.89; H, 7.74. Found: C, 64.17; H, 7.84. The second fraction gave (+)-**18** (0.29 g, 10%) as colorless needles of mp 110—112 °C (from AcOEt–hexane). $[\alpha]_D^{20}$ +91.2° (c=0.50, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1765 (lactone C=O), 1720 (ester C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.21 (9H, s, $(CH_3)_3CCO$), 1.24 (3H, s, CH_3C), 1.68—2.09 (4H, m, $(CH_2)_2$), 2.47 (1H, dd, J=4, 8 Hz, $CHCHCOO$), 2.75 (1H, d, J=4 Hz, $CHCO$), 2.68—2.86 (1H, m), 3.80—4.02 (4H, m, $O(CH_2)_2O$), 4.34 (3H, s, OCH_2CHOCO). MS *m/z*: 338 (M^+). *Anal.* Calcd for $C_{18}H_{26}O_6$: C, 63.89; H, 7.74. Found: C, 63.69; H, 7.80. The third fraction gave a mixture of (−)-**16** and **17** as a colorless oil (1.67 g). Crystallization of this oil from AcOEt–hexane gave (−)-**16** as colorless needles (0.68 g, 25%) of mp 126—128 °C. $[\alpha]_D^{20}$ −22.5° (c=0.32, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1775 (lactone C=O), 1725 (ester C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.14 (3H, s, CH_3C), 1.20 (9H, s, $(CH_3)_3CCO$), 1.66—2.12 (4H, m, $(CH_2)_2$), 2.52—2.76 (3H, m), 3.76—3.98 (4H, m, $O(CH_2)_2O$), 4.08 (1H, dd, J=4, 12 Hz, OCH_2CHOCO), 4.32 (1H, dd, J=4, 12 Hz, OCH_2CHOCO), 4.61 (1H, t, J=4 Hz, OCH_2CHOCO). MS *m/z*: 338 (M^+). *Anal.* Calcd for $C_{18}H_{26}O_6 \cdot 1/4H_2O$: C, 63.00; H, 7.79. Found: C, 62.98; H, 7.74. The mother liquor (0.74 g) of the third fraction contained (−)-**16** and **17**, but all attempts to separate these compounds were unsuccessful and this mixture was used without further purification.

(−)-(1S,2R,5S,6S,7R)-10-Ethylenedioxy-3,6-dimethyl-5-pivaloyloxymethyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-ol (20) A stirred solution of (−)-**16** (594 mg, 1.75 mmol) in THF (35 ml) was treated with MeLi (1.16 M in ether, 2 ml, 2.32 mmol) at −78 °C under Ar, and the whole mixture was stirred at −78 °C for 50 min, then quenched with satd. NH_4Cl (30 ml). The resultant mixture was extracted with CH_2Cl_2 (50 ml × 3), and the organic layers were combined, washed with satd. NaCl and dried over $MgSO_4$. After evaporation of the solvents, the residue was chromatographed (silica gel, benzene–acetone 40 : 1) to afford epimeric mixture of (−)-**20** (593 mg, 95%) as colorless needles of mp 94.5—95 °C (from AcOEt–hexane). $[\alpha]_D^{20}$ −21.0° (c=1.37, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1720 (ester C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.08—1.32 (12H, m), 1.42 (1.5H, s, $OC(OH)CH_3$), 1.60 (1.5H, s, $OC(OH)CH_3$), 1.68—2.96 (4H, m), 2.11—2.48 (3H, m), 2.69—2.83 (0.5H, m), 3.06 (0.5H, s, OH), 3.64—4.00 (5.5H, m), 4.04 (1H, dd, J=4, 9 Hz, OCH_2CHOCO), 4.74 (0.5H, dd, J=11, 9 Hz,

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CHOC(OH)CH_3). MS *m/z*: 354 (M^+). *Anal.* Calcd for $C_{19}H_{30}O_6$: C, 64.38; H, 8.53. Found: C, 64.42; H, 8.68.

(+)-(1*S*,2*R*,5*S*,6*S*,7*R*)-8-Ethylenedioxy-3,6-dimethyl-5-pivaloyloxymethyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-ol (23) and (−)-(1*S*,2*R*,5*S*,6*S*,7*R*)-10-Ethylenedioxy-3,6-dimethyl-5-pivaloyloxymethyl-4-oxatricyclo-[5.3.0.0^{2,6}]decan-3-ol (20) A stirred solution of (−)-**16** and **17** (obtained as the mother liquor after crystallization of pure (−)-**16**, 737 mg) in THF (50 ml) was treated with MeLi (1.16 M in ether, 2.1 ml, 2.4 mmol) at −78 °C under Ar, and the whole mixture was stirred at −78 °C for 1 h, then treated as described above. The resultant residue was separated by chromatography (silica gel, benzene–acetone 10 : 1). The first fraction gave (+)-**23** (303 mg, 10% from (−)-**5e**) as an oil. $[\alpha]_D^{20}$ +8.82° (*c*=1.52, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440 (OH), 1720 (ester (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.12—1.32 (12H, m), 1.36—1.54 (3H, m), 2.68—2.20 (6H, m), 2.32—2.65 (1H, m), 2.88—3.20 (1H, m), 3.64—4.24 (6.5H, m), 4.73 (0.5H, dd, *J*=9, 11 Hz, CHOC(OH)CH_3). MS *m/z*: Calcd for $C_{19}H_{30}O_6$ (M^+): 354.2039. Found: 354.2017. The second fraction gave (−)-**20** (119 mg, 4.1% from (−)-**5e**) as colorless needles.

(−)-(1*S*,2*R*,6*S*,7*R*)-10-Ethylenedioxy-6-methyltricyclo[5.3.0.0^{2,6}]dec-4-en-3-one (22) Sodium methoxide (3.5 M in MeOH, 0.8 ml, 2.8 mmol) was added to a solution of (−)-**20** (593 mg, 1.68 mmol) in MeOH (40 ml), and the whole was heated under reflux for 30 min and then cooled to room temperature. After addition of water (10 ml) and concentration, the residue was extracted with CH_2Cl_2 (30 ml × 5), and the organic layers were combined and dried over K_2CO_3. Concentration left the crude diol (0.4 g, quant.) as an oil. This oil was dissolved in AcOEt (50 ml), a solution of $NaIO_4$ (0.89 g, 4.2 mmol) in water (35 ml) was added, and the whole was stirred vigorously at room temperature for 1.2 h. AcOEt (100 ml) was added, and the organic layer of the resultant mixture was washed successively with 10% $Na_2S_2O_3$ and satd. NaCl, then dried over $MgSO_4$. Evaporation of the solvent afforded **21** (338 mg) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2620 (C–H of aldehyde), 1720 (C=O of aldehyde and ketone). ^{1}H-NMR ($CDCl_3$) δ: 1.29 (3H, s, CH_3C), 1.72—1.99 (4H, m), 2.07 (3H, s, CH_3CO), 2.58—2.92 (3H, m), 3.60—3.96 (4H, m, O(CH_2)$_2$O), 9.65 (1H, s, CHO). MS *m/z*: 238 (M^+). A solution of 1 N NaOH (2 ml, 2 mmol) was added to a solution of crude **21** (338 mg) in ether (10 ml) and the whole was stirred at room temperature for 1.2 h. After dilution with CH_2Cl_2 (20 ml), the resultant mixture was washed with water (10 ml) and dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatography (silica gel, AcOEt–hexane 1 : 2) afforded (−)-**22** (271 mg, 74% from (−)-**20**) as colorless prisms of mp 49—50.5 °C (from AcOEt–hexane). $[\alpha]_D^{20}$ −179° (*c*=0.40, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1695 (C=O), 1570 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.16 (3H, s, CH_3C), 1.68—2.16 (5H, m), 2.40—2.64 (2H, m), 3.84—4.00 (4H, m, O(CH_2)$_2$O), 6.18 (1H, d, *J*=5 Hz, CH=CHCO), 7.51 (1H, d, *J*=5 Hz, CH=CHCO). MS *m/z*: 220 (M^+). *Anal.* Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.98; H, 7.41.

(−)-(1*R*,2*R*,6*R*,7*R*)-8-Ethylenedioxy-6-methyltricyclo[5.3.0.0^{2,6}]dec-4-en-3-one (24) According to the procedure described for (−)-**22**, (−)-**24** was prepared from **23** as a colorless oil (52%) of $[\alpha]_D^{20}$ −181° (*c*=1.18, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690 (C=O), 1580 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.28 (3H, s, CH_3C), 1.68—2.06 (4H, m, CCH_2CH_2C), 2.08—2.28 (2H, m), 2.32—2.56 (1H, m), 3.70—4.12 (4H, m, O(CH_2)$_2$O), 6.09 (1H, d, *J*=5 Hz, CH=CHCO), 7.47 (1H, d, *J*=5 Hz, CH=CHCO). MS *m/z*: Calcd for $C_{13}H_{16}O_3$ (M^+): 220.1096. Found: 220.1089.

(+)-(1*R*,2*S*,5*S*,6*R*,7*S*)-10-Ethylenedioxy-3,6-dimethyl-5-pivaloyloxymethyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-ol (25) According to the procedure described for (−)-**20**, (−)-**25** was prepared from (+)-**18** as colorless needles (93%) of mp 133.5—135.5 °C (from benzene–hexane). $[\alpha]_D^{20}$ +50.9° (*c*=1.12, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1725 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.18 (3H, s, CH_3C), 1.20 (9H, s, $(CH_3)_3$CO), 1.48 (3H, s, CH_3C(OH)O), 1.52—2.25 (7H, m), 2.31—2.52 (1H, m), 3.63—3.98 (4H, m, O(CH_2)$_2$O), 4.05—4.29 (3H, m, OCH_2CHO). MS *m/z*: 354 (M^+). *Anal.* Calcd for $C_{19}H_{30}O_6$: C, 64.38; H, 8.53. Found: C, 64.29; H, 8.45.

(−)-(1*R*,2*S*,6*R*,7*S*)-10-Ethylenedioxy-6-methyltricyclo[5.3.0.0^{2,6}]dec-4-en-3-one (26) According to the procedure described for (−)-**22**, (−)-**26** was prepared from (+)-**25** as colorless prisms (73%) of mp 50.0—51.0 °C (from AcOEt–hexane). $[\alpha]_D^{20}$ +177° (*c*=1.02, $CHCl_3$). The ^{1}H-NMR and IR spectra were identical with those of (−)-**22**.

(+)-(1*R*,2*S*,5*S*,6*R*,7*S*)-8-Ethylenedioxy-3,6-dimethyl-5-pivaloyloxymethyl-4-oxatricyclo[5.3.0.0^{2,6}]decan-3-ol (27) According to the procedure described for (−)-**20**, (+)-**27** was prepared from (+)-**19** as a colorless oil (quant.) of $[\alpha]_D^{20}$ +16.3° (*c*=0.87, $CHCl_3$). IR ν_{max}^{neat} cm^{-1}: 1730 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.20 (9H, s, $(CH_3)_3$CO), 1.32 (3H, s, CH_3C), 1.48 (3H, s, CH_3C(OH)O), 1.58—2.48 (8H, m), 3.60—3.88 (4H, m, O(CH_2)$_2$O), 3.89—4.08 (1H, m, OCH_2CH), 4.14—4.30 (2H, m, OCH_2CHO). MS *m/z*: Calcd for $C_{19}H_{30}O_6$ (M^+): 354.2042. Found: 354.2047.

(−)-(1*S*,2*S*,6*S*,7*S*)-8-Ethylenedioxy-6-methyltricyclo[5.3.0.0^{2,6}]dec-4-en-3-one (28) According to the procedure described for (−)-**22**, (−)-**28** was prepared from (+)-**27** as a colorless oil (58%) of $[\alpha]_D^{20}$ +186° (*c*=0.88, $CHCl_3$). The IR and ^{1}H-NMR were identical with those of (−)-**24**.

(−)-(1*S*,2*R*,6*S*,7*R*)-10-Ethylenedioxy-6-methyltricyclo[5.3.0.0^{2,6}]decan-3-one (30) A solution of (−)-**22** (271 mg) in AcOEt (30 ml) was hydrogenated over 10% Pd–C (29 mg) under H_2 for 3 h. The catalyst was filtered off and the filtrate was evaporated to give (−)-**30** (263 mg, 96%) as colorless needles of mp 95—96 °C (from hexane). $[\alpha]_D^{20}$ −176° (*c*=0.91, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1720 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.13 (3H, s, CH_3C), 1.60—2.08 (7H, m), 2.12—2.36 (2H, m), 2.38—2.77 (2H, m), 3.68—4.06 (4H, m, O(CH_2)$_2$O). MS *m/z*: 222 (M^+). *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.04; H, 8.21.

(−)-(1*S*,2*R*,3*S*,6*S*,7*R*)-10-Ethylenedioxy-6-methyltricyclo[5.3.0.0^{2,6}]-decan-3-ol (31) $NaBH_4$ (78 mg, 2 mmol) was added to a solution of (−)-**30** (263 mg, 1.18 mmol) in ethanol (EtOH) (10 ml) at −78 °C and the whole was stirred at −78 °C for 2 h and at room temperature for 1.5 h. After evaporation of the solvent, the residue was taken up into satd. NaCl (20 ml), and extracted with CH_2Cl_2 (30 ml × 3), and combined extract was dried over $MgSO_4$. Evaporation of the solvent gave (−)-**31** (279 mg, quant.) as a colorless oil. $[\alpha]_D^{20}$ −35.0° (*c*=1.13, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH). ^{1}H-NMR ($CDCl_3$) δ: 0.98 (3H, s, CH_3C), 1.03—2.39 (12H, m), 3.62—3.95 (4H, m, O(CH_2)$_2$O), 4.32 (1H, dt, *J*=9, 7 Hz, CHOH). MS *m/z*: Calcd for $C_{13}H_{20}O_3$ (M^+): 224.1416. Found: 224.1419.

(−)-(1*S*,2*R*,3*S*,6*S*,7*R*)-10-Ethylenedioxy-6-methyltricyclo[5.3.0.0^{2,6}]dec-an-3-yl *p*-Toluenesulfonate (32) A solution of (−)-**31** (279 mg, 1.18 mmol) and *p*-toluenesulfonyl chloride (1.4 g, 7.3 mmol) in pyridine (10 ml) was stirred at room temperature for 20.5 h. Water (10 ml) was added and resultant mixture was stirred for 30 min, and then extracted with CH_2Cl_2 (30 ml × 3). The combined extracts were washed with water, 10% HCl, water, and satd. $NaHCO_3$, successively, then dried over $MgSO_4$. Concentration gave (−)-**32** (452 mg, quant.) as colorless needles of mp 71—72.5 °C (from hexane). $[\alpha]_D^{20}$ −53.2° (*c*=1.17, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1595, 1360, 1185. ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, s, CH_3C), 1.17—2.30 (11H, m), 2.45 (3H, s, CH_3-aromatic), 3.89—3.91 (4H, m, O(CH_2)$_2$O), 4.75 (1H, dt, *J*=9, 7 Hz, CHOSO$_2$), 7.33 (2H, d, *J*=8 Hz, aromatic), 7.78 (2H, d, *J*=8 Hz, aromatic). MS *m/z*: 223 ($M^+ - CH_3C_6H_4SO_2$). *Anal.* Calcd for $C_{20}H_{26}O_5S$: C, 63.48; H, 6.93. Found: C, 63.40; H, 6.87.

(−)-Diethyl ((1*R*,2*R*,3*R*,6*R*,7*R*)-10-Ethylenedioxy-6-methyltricyclo-[5.3.0.0^{2,6}]decan-3-yl)malonate (33) Diethyl malonate (1.2 ml, 7.9 mmol) was added to a suspension of NaH (247 mg, 55% in oil, 5.9 mmol) in dimethoxyethane (DME) (9 ml) at 0 °C. Then a solution of (−)-**32** (432 mg, 1.14 mmol) in DME (24 ml) was added, the whole was heated under reflux for 19 h and cooled. The reaction mixture was taken up in 10% HCl, and extracted with CH_2Cl_2 (30 ml × 3). The combined extracts were washed successively with water and satd. $NaHCO_3$, and then dried over $MgSO_4$. Evaporation of the solvent and chromatography of the residue (silica gel, benzene–AcOEt 30 : 1) gave (−)-**33** (378 mg, 91%) as a colorless oil. $[\alpha]_D^{20}$ −23.8° (*c*=1.57, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740 (C=O), 1725 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.04 (3H, s, CH_3C), 1.26 (6H, t, *J*=7 Hz, CH_2CH_3), 1.40—2.33 (11H, m), 3.09 (1H, d, *J*=11 Hz, CH(CO_2Et)$_2$), 2.48 (1H, dd, *J*=6, 11 Hz, CHCH(CO_2Et)$_2$), 3.70—4.00 (4H, m, O(CH_2)$_2$O), 4.18 (2H, q, *J*=7 Hz, CH_2CH_3), 4.17 (2H, q, *J*=7 Hz, CH_2CH_3). MS *m/z*: Calcd for $C_{20}H_{30}O_6$ (M^+): 366.2040. Found: 366.2039.

(−)-(1*R*,2*R*,3*R*,6*R*,7*R*)-3-(1,3-Dihydroxyprop-2-yl)-10-ethylenedioxy-6-methyltricyclo[5.3.0.0^{2,6}]decane (34) A solution of (−)-**33** (378 mg, 1.03 mmol) in ether (30 ml) was added to a stirred suspension of lithium aluminum hydride (LAH) (0.16 g, 4.2 mmol) in ether (10 ml) at 0 °C, and the whole was stirred at room temperature for 2 h and then recooled to 0 °C. Water (0.32 ml) and 15% NaOH (0.26 ml) were added successively at 0 °C, and the whole was stirred at room temperature for 2 h. After filtration, the filtrate was concentrated to give **34** (248 mg, 85%) as colorless needles of mp 108—108.5 °C (from AcOEt–hexane). $[\alpha]_D^{20}$ −30.4° (*c*=0.77, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3280 (OH), ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, s, CH_3C), 1.20—2.08 (12H, m), 2.15—2.38 (1H, m), 2.47 (1H, t, *J*=5 Hz), 2.70 (1H, t, *J*=6 Hz), 3.48—4.03 (8H, m). MS *m/z*: 282 (M^+). *Anal.* Calcd for $C_{16}H_{26}O_4 \cdot 1/2H_2O$: C, 65.94; H, 9.34. Found: C, 65.80; H, 9.41.

(−)-Norbourbonone Ethylene Ketal (36) Methanesulfonyl chloride (0.38 ml, 5 mmol) was added to a solution of (−)-**34** (228 mg, 0.81 mmol) in pyridine (1 ml) at 0 °C, and the whole was stirred at room temperature for 36 h. After dilution with CH_2Cl_2 (30 ml), the mixture was washed successively with water, 10% HCl, water, and satd. $NaHCO_3$, then dried

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over $MgSO_4$. Concentration gave dimesylate (**35**) (355 mg, quant.) as a pale yellow oil. A solution of **35** (355 mg, 0.81 mmol) in THF (30 ml) was added to a refluxing suspension of $LiAlH_4$ (0.18 g, 4.7 mmol) in THF (30 ml), and the whole was heated under reflux for 1.8 h and cooled to 0 °C. Water (0.27 ml) and 15% NaOH (0.20 ml) were successively added to the mixture at 0 °C, and the whole was stirred at room temperature for 1 h. After removal of precipitate by filtration, the filtrate was concentrated and chromatographed (silica gel, pentane–ether 20 : 1) to give (−)-**36** (157 mg, 78% from (−)-**34**) as a colorless oil. $[\alpha]_D^{20}$ −23.1° (c=0.78, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1100 (ether). ^{1}H-NMR ($CDCl_3$) δ: 0.85 (3H, d, J=5 Hz, $CH(CH_3)_2$), 0.91 (3H, d, J=5 Hz, $CH(CH_3)_2$), 0.98 (3H, s, CH_3C), 1.06—2.04 (12H, m), 2.06—2.30 (1H, m), 3.60—4.00 (4H, m, $O(CH_2)_2O$). MS m/z: Calcd for $C_{16}H_{26}O_2$ (M^+): 250.1930. Found: 250.1917.

(−)-Norbourbonone (4) A solution of (−)-**36** (146 mg, 0.58 mmol) in acetone (10 ml) containing *p*-toluenesulfonic acid (12 mg) was left standing at room temperature for 23 h. After concentration, the residue was taken up into ether (30 ml), and washed with satd. $NaHCO_3$ and satd. NaCl, successively, then dried over $MgSO_4$. Evaporation of the solvent and column chromatography (silica gel, pentane–ether 10 : 1) gave (−)-**4** (98 mg, 82%) as colorless needles of mp 24.5—25.5 °C (lit.[3b] 23—25 °C). $[\alpha]_D^{22}$ −193° (c=0.38, $CHCl_3$) (lit.[3b] $[\alpha]_D^{22}$ −213° (c=0.39, $CHCl_3$)), $[\alpha]_D^{25}$ −194° (c=0.38, $CHCl_3$) (lit.[4a] $[\alpha]_D^{25}$ −181° (c=0.46, $CHCl_3$)). IR ν_{max}^{neat} cm^{-1}: 1730 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 0.86 (6H, d, J=5 Hz, $CH(CCH_3)_2$), 1.13 (3H, s, CH_3C), 1.00—2.68 (13H, m). MS m/z: Calcd for $C_{14}H_{22}O$ (M^+): 206.1668. Found: 206.1662.

(−)-β-Bourbonene (3) A solution of BuLi (1.56 M in hexane, 0.47 ml, 0.73 mmol) was added to a stirred suspension of methyltriphenylphosphonium bromide (252 mg, 0.71 mmol) in ether (25 ml) at room temperature and the whole was stirred at room temperature for 2 h. A solution of (−)-**4** (71 mg, 0.34 mmol) in ether (3.5 ml) was added at room temperature and the whole was stirred at room temperature for 20 h. After addition of water, the mixture was extracted with pentane (20 ml × 3), and the combined organic layer was dried over $MgSO_4$. Concentration and column chromatography (silica gel, pentane) gave (−)-**3** (69 mg, 98%). $[\alpha]_D^{20}$ −97.0° (neat) (lit.[3a] $[\alpha]_D^{20}$ −91.12° (neat)). IR ν_{max}^{neat} cm^{-1}: 1655 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 0.85 (6H, d, J=5 Hz, $CH(CH_3)_2$), 1.00 (3H, s, CH_3C), 1.04—2.00 (9H, m), 2.08—2.64 (4H, m), 4.71 (2H, br s, C=CH_2). MS m/z: Calcd for $C_{14}H_{24}$ (M^+): 204.1878. Found: 204.1879.

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