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Synthesis of 4-[(*E*)-1-Alkenyl]-2-hydroxybutanolides and (*Z*)-4-Alkylidene-2-butenolides through Cycloadditions Using a Phosphorus-Functionalized Nitrile Oxide

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A sequence of cycloadditions of (diethoxyphosphinyl)acetonitrile oxide with α,β-unsaturated esters, the Raney Ni reduction of the resulting cycloadducts, the Horner–Emmons olefination, and the carbonyl reduction with sodium borohydride leads to 5-[(*E*)-1-alkenyl]-3-hydroxy-4,5-dihydro-2(3*H*)-furanones which can be converted into (*Z*)-5-alkylidene-2(5*H*)-furanones in two steps.

Unsaturated five-membered lactones, butenolides, are often the central skeletons of naturally occurring oxygen heterocycles.[1] Among the numerous reported syntheses of 2-butenolides,[2] the route by dehydration of 2-hydroxybutanolides is not familiar since availability of the starting 2-hydroxybutanolides[3] or their related derivatives[4] is quite narrow.

On the other hand, 2-isoxazoline-5-carboxylates which can be formed as cycloadducts in the cycloadditions of nitrile oxides with conjugated esters are synthetically equivalent to the α-hydroxy-γ-oxo ester functionality by a simple one-step procedure involving reductive N–O bond cleavage and hydrolysis. This cleavage can be conveniently and effectively carried out by the aid of Raney Ni.[5] Application of this sequence to the nitrile oxide bearing a functional group utilizable for olefination would lead to 2-hydroxy-4-oxo-5-alkenoates. These alkene esters must be the promising starting materials in the synthesis of 4-(1-alkenyl)-2-hydroxybutanolides (or 5-(1-alkenyl)-3-hydroxy-4,5-dihydro-2(3*H*)-furanones) and further 4-alkylidene-2-butenolides (or 5-alkylidene-2(5*H*)-furanones).

The present article describes a new synthetic method of butanolides and butenolides through the cycloaddition route using a phosphorus-functionalized nitrile oxide. Hereafter only the nomenclature as well as the compound numbering based on heterocyclic systems is employed in order to avoid confusion.

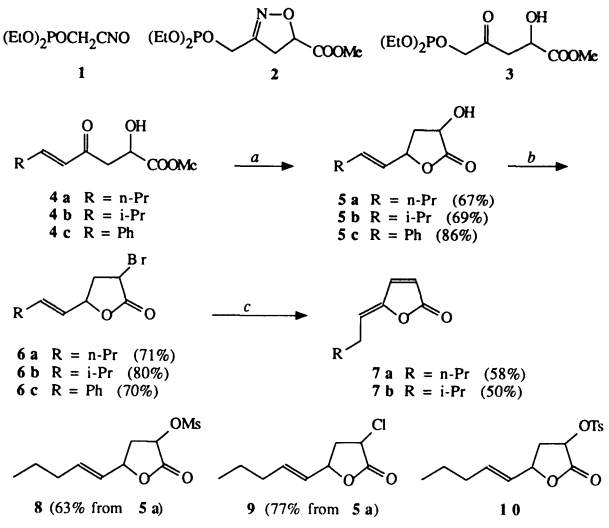
Results and Discussion

We have already reported that (diethoxyphosphinyl)-acetonitrile oxide (**1**) serves as a synthetically useful phosphorus-functionalized nitrile oxide[6,7] which undergoes regioselective cycloaddition with methyl acrylate to produce methyl 3-[(diethoxyphosphinyl)methyl]-2-isoxazoline-5-carboxylate (**2**).[8,9] Methyl 5-(diethoxyphosphinyl)-2-hydroxy-4-oxopentanoate (**3**)[9] can be obtained in a satisfactory yield via the Raney Ni reduction of the cycloadduct **2** in the presence of boric acid.

Though Horner–Emmons olefinations of 4-hydroxy-2-oxoalkylphosphonates are often accompanied by competitive dehydration and/or retro-aldol reaction, use of the combination of triethylamine (or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)) and lithium bromide as a weak base system on the *O*-unprotected substrates was found effective enough to suppress these undesired side reactions.[10]

Under the equivalent conditions (lithium bromide–DBU in dry THF at 0 °C for 24 h), highly functionalized phosphonate **3** was smoothly converted into 2-hydroxy-4-oxo-5-alkenoates **4a—c** (Scheme 1). These olefinations were highly *E*-selective for all the aldehydes employed, no contamination by *Z*-isomers being observed. It should be emphasized that the reactions with aliphatic aldehydes provided the olefins in better yields than that with an aromatic aldehyde (**4a**: 80%; **4b**: 82%; **4c**: 52%).

Reduction of the conjugated carbonyl group at the 4-position of **4** with sodium borohydride was impracticably sluggish in ethanol at 0 °C and that at room



a $NaBH_4$ in MeOH at 0 °C then *p*-TsOH in CH_2Cl_2 at rt
b MsCl / NEt_3 in CH_2Cl_2 at 0 °C then LiBr in THF at rt
c DBU / hydroquinone (cat) in THF under reflux

Scheme 1.

temperature resulted in a complex mixture of many products. However in methanol a smooth reduction took place at 0 °C.[11] The reduction was carefully monitored on thin-layer chromatography (TLC) and as soon as the reduction was complete the crude reaction mixture containing the dihydroxy esters was subjected to lactonization without purification. Treatment of the crude reduction products with a catalytic amount of *p*-toluenesulfonic acid in dichloromethane at room temperature produced 5-(1-alkenyl)-3-hydroxy-4,5-dihydro-2(3*H*)-furanones **5a—c** as about 1:1 mixtures of 3,5-cis and 3,5-trans isomers. Although these two isomers can be separated from each other through careful column chromatography and in the present research their separation was actually carried out for characterization, this separation step may be omitted only for the purpose of synthesizing 2-butenolides.

As direct dehydration of **5a** by the aid of either of dicyclohexylcarbodiimide–copper(I) chloride (reflux in benzene for 5 h)[12] or methyltriphenoxyphosphonium iodide (at 80 °C for 1 h in hexamethylphosphoric triamide (HMPA))[13] ended in the formation of complex mixture, the hydroxyl group was replaced with a more effective leaving group such as mesyl, tosyl, or bromo substituent.

Though *O*-mesylation of **5a** with methanesulfonyl chloride–triethylamine (at 0 °C in dichloromethane) gave the mesylate **8** in a moderate yield, the product obtained on treating **5a** with *p*-toluenesulfonyl chloride–pyridine at room temperature was not the expected tosylate **10** but the chloride **9** (77%). On the other hand, only 18% yield of bromide **6a** was prepared by reacting **5a** with tribromophosphine–pyridine.

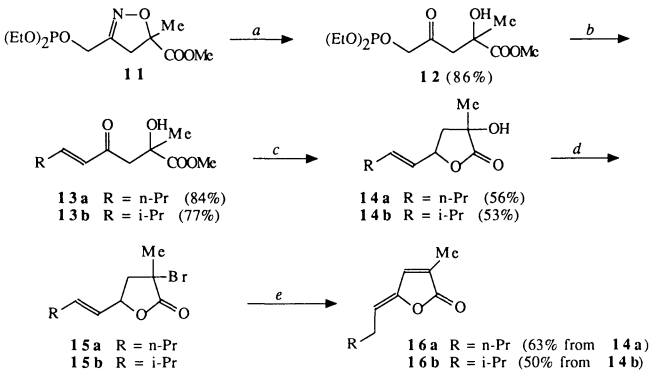
Base-induced dehydrohalogenation of chloride **9** and bromide **6a** was all unsuccessful (with triethylamine under reflux in diethyl ether, dichloromethane, or THF; with pyridine at 80 °C). Only when mesylate **8** was heated with DBU under reflux in THF, a low yield (5%) of the expected 2-butenolide **7a** was obtained. After some efforts, it was found that treating bromide **6a** with DBU under reflux in THF provided 2-butenolide **7a** in 58% yield. The structure of **7a** will be discussed below.

Therefore an effective synthetic route to bromides **6a—c** was searched. The aforementioned high-yield formation of chloride **9** in the attempted tosylation of **5a** indicates a possibility of the ready nucleophilic substitution of the tosylate **10** with a halide nucleophile under the quoted conditions. Accordingly hydroxy lactones **5a—c** were first mesylated and the crude mesylates were allowed to react with lithium bromide in THF at room temperature to give good yields of the expected bromides **6a—c** (Scheme 1). Since the starting hydroxy lactones **5a—c** were all mixtures of 3,5-cis and 3,5-trans isomers, **6a—c** were not stereochemically pure.

Dehydrobromination of bromides **6a—c** was carried out with DBU under reflux in THF where a catalytic amount of hydroquinone was used to inhibit the polymerization of products.[14] Though the 3-bromo-4,5-dihydro-2(3*H*)-furanones **6a—b** underwent smooth dehydrobromination, the phenyl-substituted analog **6c** led to complex mixture under all the employed conditions.

The structures of **7a—b** were assigned as *Z*-isomers of 5-alkylidene-2(5*H*)-furanones on the basis of spectral data where there newly appeared three olefin (3-, 4-, and 1′-Hs) and a pair of methylene (2′-H) protons and disappeared one set of trans-olefin. The *Z*-stereochemistry was confirmed by comparison of the chemical shifts of 1′-H (**7a**: δ=5.32; **7b**: 5.34) with those of *E*- and *Z*-isomers of 5-butylidene-2(5*H*)-furanone (*E*-isomer: 5.70; *Z*-isomer: 5.22),[3b] 5-ethylidene-3-methyl-2(5*H*)-furanone (*E*-isomer: 5.67; *Z*-isomer: 5.20),[15,16] or 3-methyl-5-(2-methylpropylidene)-2(5*H*)-furanone (*E*-isomer: 6.23; *Z*-isomer: 5.43).[17]

One application of the above furanone synthesis using nitrile oxide **1** enables the introduction of a methyl group at the 3-position of 5-alkylidene-2(5*H*)-furanones as shown in Scheme 2.



a Raney Ni / $B(OH)_3$ in aq EtOH at rt
b DBU / LiBr in THF at 0 °C then RCHO at 0 °C
c $NaBH_4$ in MeOH at 0 °C then *p*-TsOH in CH_2Cl_2 at rt
d MsCl / NEt_3 at 0 °C then LiBr in THF under reflux
e DBU / hydroquinone (cat) in THF under reflux

Scheme 2.

Regioselective cycloaddition of nitrile oxide **1** with methyl methacrylate and subsequent Raney Ni reduction of the cycloadduct **11** afforded ester phosphonate **12** (Scheme 2). Horner–Emmons olefination of **12** mediated by lithium bromide–DBU led to (*E*)-olefins **13a,b**. Sodium borohydride reduction of **13** proceeded in a stereoselective fashion to give 3-hydroxy-3-methyl-4,5-dihydro-2(3*H*)-furanones **14a,b** after acid-catalyzed lactonization. Three transformations consisting of mesylation of **14a,b**, bromination of the mesylates with lithium bromide, and the final dehydrobromination of the bromides **15a,b** were carried out in one procedure

without separation of the intermediate products to produce (*Z*)-3-methyl-5-pentylidene-2(5*H*)-furanone (**16a**) and (*Z*)-3-methyl-5-(3-methylbutylidene)-2(5*H*)-furanone (**16b**). No sign of the regioisomeric dehydrobromination leading to 2-methylenebutanolide was even observed.[18]

In conclusion, the cycloaddition route using the phosphorus-functionalized nitrile oxide **1** offers a useful preparation method of 3-hydroxy and 3-halo derivatives of (*E*)-5-(1-alkenylidene)-4,5-dihydro-2(3*H*)-furanones and (*Z*)-5-alkylidene-2(5*H*)-furanones. By a set of appropriate choices of conjugated esters in the cycloaddition step, carbonyl compounds in the olefination step, and nucleophiles in the functional group interconversion of the 3-hydroxyl moiety, this method can be further applied to their families bearing a variety of substitution patterns. Alkylation adjacent to the phosphinyl moiety of 2-isoxazolines **2** and **11** can be also combined.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL GSX-270 instrument (270 MHz), and ^{13}C NMR on a JEOL FX-100 (25.05 MHz) or a JEOL GSX-270 spectrometer (67.94 MHz). Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. High-resolution mass spectra were obtained on the same instrument. Elemental analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck). For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silicagel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

Materials and Solvents. Generation of nitrile oxide **1**, its cycloaddition with methyl acrylate leading to 2-isoxazoline **2**, Raney Ni reduction of **2** furnishing **3**, its Horner–Emmons olefination with benzaldehyde giving **4c** were all previously reported.[8–10] Methyl methacrylate was distilled prior to use. Lithium bromide, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and hydroquinone are commercially available and were used without further purification. Tetrahydrofuran (THF) and dichloromethane were purified immediately before use by distillation from lithium aluminum hydride and calcium hydride, respectively, under nitrogen.

Methyl (*E*)-2-Hydroxy-4-oxo-5-nonenoate (4a). To a solution of lithium bromide (0.377 g, 3.88 mmol) in dry THF (5 ml) was added a solution of **3** (1.095 g, 3.88 mmol) in THF (5 ml). After stirring at room temperature for 10 min under nitrogen, a solution of DBU (0.561 g, 3.69 mmol) in THF (5 ml) was added dropwise at 0 °C. After 1 h at 0 °C, butanal (0.56 g, 7.76 mmol) was added, the mixture was stirred at 0 °C for 24 h, poured into ice water, and then extracted with dichloromethane (25 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane–ethyl acetate (3:1 v/v) to give **4a** (0.624 g, 80%) as a single isomer (by ^{1}H NMR): Colorless liquid; IR (neat) 3480, 1740, 1660, 1620, 1430, 1200, 1100, 1030, and 975 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.95 (3H, t, J=7.3 Hz, *n*-Pr), 1.51 (2H, sx, J=7.3 Hz, *n*-Pr), 2.22 (2H, dt, J=7.3 and 7.0 Hz, *n*-Pr), 3.08 (1H, d, J_{3-2}=10.3 Hz, one of 3-H), 3.09 (1H, d, J_{3-2}=5.5 Hz, the other of 3-H), 3.50 (1H, br s, OH), 3.78 (3H, s, COOMe), 4.57 (1H, dd, J_{2-3}=10.3 and 5.5 Hz, 2-H), 6.11 (1H, d, J_{5-6}=16.1 Hz, 5-H), and 6.89 (1H, dt, J_{6-5}=16.1 and J_{6-7}=7.0 Hz, 6-H); ^{13}C NMR ($CDCl_3$) δ=13.69, 21.30, 34.57 (each *n*-Pr), 43.27 (3-C), 52.49 (COOMe), 67.19 (2-C), 130.42 (5-C), 149.11 (6-C), 174.28 (COOMe), and 197.70 (CO); MS *m/z* (rel intensity, %) 200 (M^+, 11), 141 (16), 97 (base peak), and 55 (57). HRMS Found: *m/z* 200.1050. Calcd for $C_{10}H_{16}O_4$: M, 200.1048.

Methyl (*E*)-2-Hydroxy-7-methyl-4-oxo-5-octenoate (4b). A similar procedure using lithium bromide (0.353 g, 4.06 mmol) in THF (5 ml), **3** (1.147 g, 4.06 mmol) in THF (5 ml), DBU (0.588 g, 3.86 mmol) in THF (5 ml), and 2-methylpropanal (0.586 g, 8.13 mmol) at 0 °C for 1 h after column chromatography on silica gel with hexane–ethyl acetate (3:1 v/v), gave **4b** (0.667 g, 82%) as a single isomer (by ^{1}H NMR): Colorless liquid; IR (neat) 3480, 1740, 1660, 1620, 1440, 1360, 1270, 1210, 1100, 1030, and 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.06 (6H, d, J=7.0 Hz, *i*-Pr), 2.3—2.7 (1H, m, *i*-Pr), 3.0—3.2 (2H, m, 3-H), 3.4—3.5 (1H, m, OH), 3.76 (3H, s, COOMe), 4.55 (1H, dd, J_{2-3}=10.0 and 5.5 Hz, 2-H), 6.04 (1H, dd, J_{5-6}=16.1 and J_{5-3}=1.5 Hz, 5-H), and 6.84 (1H, dd, J_{6-5}=16.0 and J_{6-7}=6.0 Hz, 6-H); ^{13}C NMR ($CDCl_3$) δ=21.18, 31.23 (each *i*-Pr), 43.27 (3-C), 52.50 (COOMe), 67.11 (2-C), 127.45 (5-C), 155.24 (6-C), 174.24 (COOMe), and 198.06 (CO); MS *m/z* (rel intensity, %) 200 (M^+, 5), 141 (14), 97 (base peak), 96 (13), 69 (11), and 41 (22). HRMS Found: *m/z* 200.1048. Calcd for $C_{10}H_{16}O$: M, 200.1048.

3-Hydroxy-5-[(*E*)-1-pentenyl]-4,5-dihydro-2(3*H*)-furanone (5a). To a solution of **4a** (0.787 g, 3.93 mmol) in methanol (10 ml) was added sodium borohydride (0.149 g, 3.93 mmol). After stirring at room temperature for 10 min, acetone (5 ml) was added at 0 °C. The mixture was stirred at 0 °C for 10 min, poured into ice water, and extracted with dichloromethane (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was dissolved in dichloromethane (10 ml) containing *p*-toluenesulfonic acid (0.075 g, 0.393 mmol), the mixture was stirred at room temperature for 3 h, poured into ice water, and then extracted with dichloromethane (20 ml×2). After dried over magnesium sulfate, the combined extracts were evaporated in vacuo and the residue was chromatographed on silica gel with hexane–ethyl acetate (2:1 v/v) to give **5a** (0.447 g, 67%) as a 1:1 mixture of two diastereomers (by ^{1}H NMR) which could be separated from each other by a careful column chromatography.

3,5-*trans*-5a: Colorless liquid; IR (neat) 3400, 1770, 1670, 1450, 1320, 1180, 1120, 970, and 940 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (3H, t, J=7.3 Hz, *n*-Pr), 1.41 (2H, sx, J=7.3 Hz, *n*-Pr), 2.04 (2H, dt, J=7.3 and 7.0 Hz, *n*-Pr), 2.3—2.5 (2H, m, 4-H), 3.6—3.8 (1H, br s, OH), 4.53 (1H, dd, J_{3-4}=7.7 and 7.3 Hz, 3-H), 5.0—5.2 (1H, m, 5-H), 5.48 (1H, dd, $J_{1'-2'}$=15.0 and

$J_{1'-5}$=7.0 Hz, 1'-H), and 5.80 (1H, dt, $J_{2'-1'}$=15.0 and $J_{2'-3'}$=7.0 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=13.59, 21.91, 34.11 (each *n*-Pr), 36.47 (4-C), 67.32 (3-C), 78.74 (5-C), 127.14 (1'-C), 135.52 (2'-C), and 178.06 (2-C); MS (25 eV) *m/z* (rel intensity, %) 170 (M^+, 2), 98 (29), 83 (base peak), 82 (58), 81 (68), 70 (28), and 55 (21).

3,5-*cis*-5a: Colorless liquid; IR (neat) 3400, 1770, 1670, 1450, 1310, 1190, 1120, 960, and 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, J=7.3 Hz, *n*-Pr), 1.43 (2H, sx, J=7.3 Hz, *n*-Pr), 1.9—2.1 (3H, m, *n*-Pr and one of 4-H), 2.06 (1H, ddd, J_{gem}=12.5, J_{4-3}=8.0 Hz, and J_{4-5}=5.4 Hz, the other of 4-H), 3.6—3.8 (1H, br s, OH), 4.55 (1H, m, 3-H), 4.76 (1H, ddd, J_{5-4}=10.8, 5.4, and $J_{5-1'}$=7.7 Hz, 5-H), 5.50 (1H, dd, $J_{1'-2'}$=15.4 and $J_{1'-5}$=7.7 Hz, 1'-H), and 5.86 (1H, dt $J_{2'-1'}$=15.4 and $J_{2'-3'}$=7.0 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=13.95, 21.86, 34.11 (each *n*-Pr), 37.70 (4-C), 68.61 (3-C), 77.79 (5-C), 126.88 (1'-C), 137.27 (2'-C), and 177.88 (2-C); MS (25 eV) *m/z* (rel intensity, %) 170 (M^+, 1), 113 (47), 98 (24), 83 (base peak), 82 (47), 81 (59), and 70 (21).

No satisfactory analytical data were obtained due to hygroscopic nature of the both isomers of **5a**.

3-Hydroxy-5-[(*E*)-3-methyl-1-butenyl]-4,5-dihydro-2(3*H*)-furanone (5b). A similar procedure using **4b** (0.231 g, 1.15 mmol) in methanol (5 ml), sodium borohydride (0.044 g, 1.15 mmol), and *p*-toluenesulfonic acid (0.022 g, 0.115 mmol) in dichloromethane (5 ml) gave **5b** (0.135 g, 69%), after silica-gel column chromatography with hexane–ethyl acetate (5:1 v/v), as a 1:1 mixture of two diastereomers (by ^{1}H NMR). These two isomers could be separated from each other through a careful column chromatography.

3,5-*trans*-5b: Colorless prisms; mp 30—32 °C; IR (KBr) 3400, 1780, 1670, 1470, 1180, 1120, 1030, and 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.00 (6H, d, J=7.7 Hz, *i*-Pr), 2.2—2.5 (1H, m, *i*-Pr), 2.37 (1H, ddd, J_{gem}=13.2, J_{4-3}=7.7, and J_{4-5}=4.4 Hz, one of 4-H), 2.41 (1H, ddd, J_{gem}=13.2, J_{4-5}=7.7, and J_{4-3}=7.3 Hz, the other of 4-H), 4.20 (1H, br s, OH), 4.55 (1H, ddd, J_{3-4}=7.7, 7.3, and J_{3-OH}=3.3 Hz, 3-H), 5.06 (1H, ddd, J_{5-4}=7.7, 4.4, and $J_{5-1'}$=7.0 Hz, 5-H), 5.43 (1H, ddd, $J_{1'-2'}$=15.4, $J_{1'-5}$=7.0, and $J_{1'-3'}$=1.5 Hz, 1'-H), and 5.78 (1H, ddd, $J_{2'-1'}$=15.4, $J_{2'-3'}$=6.6, and $J_{2'-5'}$=1.1 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=21.89, 30.65 (each *i*-Pr), 36.47 (4-C), 67.33 (3-C), 78.80 (5-C), 124.07 (1'-C), 142.41 (2'-C), and 177.98 (2-C); MS *m/z* (rel intensity, %) 142 (M^+—CO, 1), 99 (11), 95 (28), 93 (16), 84 (17), 83 (51), 82 (base peak), 81 (14), 73 (11), and 70 (41).

3,5-*cis*-5b: Colorless prisms; mp 36—38 °C; IR (KBr) 3400, 1780, 1660, 1460, 1320, 1180, 1120, 1030, 930, and 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.01 (6H, d, J=7.0 Hz, *i*-Pr), 2.03 (1H, ddd, J_{gem}=12.8, J_{4-3}=11.4, and J_{4-5}=10.6 Hz, one of 4-H), 2.2—2.5 (1H, m, *i*-Pr), 2.72 (1H, ddd, J_{gem}=12.8, J_{4-3}=8.1, and J_{4-5}=5.1 Hz, the other of 4-H), 4.12 (1H, s, OH), 4.60 (1H, ddd, J_{3-4}=11.4, 8.1, and J_{3-OH}=4.4 Hz, 3-H), 4.75 (1H, ddd, J_{5-4}=10.6, 5.1, and $J_{5-1'}$=7.7 Hz, 5-H), 5.45 (1H, ddd, $J_{1'-2'}$=15.4, $J_{1'-5}$=7.7, and $J_{1'-3'}$=1.5 Hz, 1'-H), and 5.83 (1H, dd, $J_{2'-1'}$=15.4 and $J_{2'-3'}$=6.6 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=21.84, 30.70 (each *i*-Pr), 37.74 (4-C), 68.64 (3-C), 77.91 (5-C), 123.94 (1'-C), 144.11 (2'-C), and 177.91 (2-C); MS *m/z* (rel intensity, %) 170 (M^+, 1), 95 (44), 93 (32), 84 (22), 83 (65), 82 (base peak), 81 (19), 79 (11), 77 (12), 73 (19), and 70 (35).

No satisfactory analytical results were obtained due to hygroscopic nature of the both isomers of **5b**.

3-Hydroxy-5-[(*E*)-2-phenylethenyl]-4,5-dihydro-2(3*H*)-furanone (5c). A similar procedure was applied to **4c** under the following conditions: **4c** (0.171 g, 0.73 mmol) in methanol (5 ml), sodium borohydride (0.028 g, 0.73 mmol), 10 min at 0 °C, acetone (2 ml), 10 min at room temperature, hydrolytic workup and extraction with dichloromethane, *p*-toluenesulfonic acid (0.014 g., 0.073 mmol) in dichloromethane (10 ml), 20 min at room temperature, hydrolytic workup and extraction with dichloromethane, silica-gel column chromatography with hexane–ethyl acetate. A 1:1 mixture (by ^{1}H NMR) of two diastereomers of **5c** (0.128 g, 86%) was obtained. These isomers could be separated through a careful column chromatography.

3,5-*trans*-5c: Colorless prisms (dichloromethane–hexane); mp 100—103 °C; IR (KBr) 3420, 1750, 1310, 1230, 1180, 1120, 930, 800, 750, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.49 (1H, ddd, J_{gem}=13.2, J_{4-3}=8.1, and J_{4-5}=2.2 Hz, one of 4-H), 2.51 (1H, ddd, J_{gem}=13.2, J_{4-3}=8.1, and J_{4-5}=4.8 Hz, the other of 4-H), 3.58 (1H, br s, OH), 4.59 (1H, t, J_{3-4}=8.1 Hz, 3-H), 5.28 (1H, ddd, $J_{5-1'}$=6.2, J_{5-4}=4.8, and 2.2 Hz, 5-H), 6.17 (1H, dd, $J_{1'-2'}$=15.8 and $J_{1'-5}$=6.2 Hz, 1'-H), 6.67 (1H, d, $J_{2'-1'}$=15.8 Hz, 2'-H), and 7.2—7.4 (5H, m, Ph); MS *m/z* (rel intensity, %) 204 (M^+, 9), 131 (12), 129 (12), 128 (16), 117 (15), 115 (30), 105 (17), 104 (base peak), 103 (14), 102 (13), 91 (32), 77 (18), 76 (40), 63 (14), and 51 (26). Found: C, 70.47; H, 5.92%. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92%.

3,5-*cis*-5c: Colorless prisms (dichloromethane–hexane); mp 135—138 °C; IR (KBr) 3450, 1750, 1320, 1200, 1120, 970, 910, 800, 760, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.12 (1H, ddd, J_{gem}=12.5, J_{4-5}=11.0, and J_{4-3}=10.8 Hz, one of 4-H), 2.84 (1H, ddd, J_{gem}=12.5, J_{4-3}=8.1, and J_{4-5}=5.5 Hz, the other of 4-H), 3.22 (1H, br s, OH), 4.61 (1H, dd, J_{3-4}=10.8 and 8.1 Hz, 3-H), 4.98 (1H, ddd, J_{5-4}=11.0, 5.5, and $J_{5-1'}$=7.3 Hz, 5-H), 6.19 (1H, dd, $J_{1'-2'}$=15.8 and $J_{1'-5}$=7.3 Hz, 1'-H), 6.72 (1H, d, $J_{2'-1'}$=15.8 Hz, 2'-H), and 7.2—7.4 (5H, m, Ph); MS *m/z* (rel intensity, %) 204 (M^+, 6), 129 (21), 128 (12), 117 (19), 115 (37), 104 (base peak), 103 (11), 91 (30), 78 (14), 77 (16), and 51 (22). Found: C, 70.47; H, 5.92%. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.91%.

3-Bromo-5-[(*E*)-1-pentenyl]-4,5-dihydro-2(3*H*)-furanone (6a). To a solution of **5a** (0.06 g, 0.35 mmol) in dry dichloromethane (2 ml) were added, at 0 °C under nitrogen, triethylamine (0.043 g, 0.42 mmol) and methanesulfonyl chloride (0.055 g, 0.42 mmol). After stirring at 0 °C for 2 h, the mixture was poured into saturated aqueous ammonium chloride and extracted with dichlomethane (15 ml×2). The combined extracts were washed with saturated aqueous sodium hydrogencarbonate and dried over magnesium sulfate. The residue obtained by evaporation of the dichloromethane in vacuo was dissolved in dry THF (2 ml). After lithium bromide (0.061 g, 0.71 mmol) was added, the mixture was stirred at room temperature for 20 h under nitrogen, poured into water, and extracted with dichloromethane (15 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–ethyl acetate (7:1 v/v) to give **6a** (0.058 g, 71%) as a 1:1 mixture (by ^{1}H NMR) of two diastereomers which could be separated from each other through a careful column chromatography.

3,5-*trans*-6a: Colorless liquid; IR (neat) 1780, 1670, 1460, 1430, 1380, 1320, 1180, 1030, 970, and 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, J=7.3 Hz, *n*-Pr), 1.43 (2H, sx, J=7.3 Hz, *n*-Pr), 2.07 (2H, dt, J=7.3 and 6.6 Hz, *n*-Pr),

2.47 (1H, ddd, J_{gem}=14.7, J_{4-5}=7.3, and J_{4-3}=6.6 Hz, one of 4-H), 2.59 (1H, ddd, J_{gem}=14.7, J_{4-5}=5.5, and J_{4-3}=2.2 Hz, the other of 4-H), 4.44 (1H, dd, J_{3-4}=6.6 and 2.2 Hz, 3-H), 5.14 ((1H, dt, J_{5-4}=$J_{5-1'}$=7.3, and J_{5-4}=5.5 Hz, 5-H), 5.50 (1H, dd, $J_{1'-2'}$=15.4 and $J_{1'-5}$=7.3 Hz, 1'-H), and 5.92 (1H, dt, $J_{2'-1'}$=15.4 and $J_{2'-3'}$=6.6 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=13.58, 21.81, 34.14 (each *n*-Pr), 38.96 (4-C), 40.16 (3-C), 80.31 (5-C), 125.65 (1'-C), 137.71 (2'-C), and 172.42 (2-C); MS *m/z* (rel intensity, %) 234 (M^++2, 18), 232 (M^+, 20), 191 (47), 189 (50), 153 (75), 109 (58), 81 (28), 78 (21), 69 (23), 67 (base peak), and 55. HRMS Found: *m/z* 232.0093. Calcd for $C_9H_{13}O_2Br$: M, 232.0099.

3,5-*cis*-6a: Colorless liquid; IR (Neat) 1780, 1660, 1450, 1320, 1265, 1160, 970, and 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, J=7.3 Hz, *n*-Pr), 1.43 (2H, sx, J=7.3 Hz, *n*-Pr), 2.07 (2H, dt, J=7.3 and 6.6 Hz, *n*-Pr), 2.38 (1H, ddd, J_{gem}=13.9, J_{4-5}=8.6, and J_{4-5}=8.4 Hz, one of 4-H), 3.02 (1H, ddd, J_{gem}=13.9, J_{4-3}=8.4, and J_{4-5}=6.2 Hz, the other of 4-H), 4.56 (1H, t, J_{3-4}=8.4 Hz, 3-H), 4.89 (1H, ddd, J_{5-4}=8.6, 6.2, and $J_{5-1'}$=7.7 Hz, 5-H), 5.60 (1H, dd, $J_{1'-2'}$=15.4 and $J_{1'-5}$=7.7 Hz, 1'-H), and 5.87 (1H, dt, $J_{2'-1'}$=15.4 and $J_{2'-3'}$=6.6 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=13.59, 21.80, 34.10 (each *n*-Pr), 37.91 (4-C), 39.77 (3-C), 79.98 (5-C), 126.49 (1'-C), 137.56 (2'-C), and 172.51 (2-C); MS *m/z* (rel intensity, %) 234 (M^++2, 43), 232 (M^+, 39), 191 (34), 189 (34), 153 (37), 109 (52), 78 (25), 67 (base peak), and 55 (84). HRMS Found: *m/z* 232.0086. Calcd for $C_9H_{13}O_2Br$: M, 232.0099.

3-Bromo-5-[(*E*)-3-methyl-1-butenyl]-4,5-dihydro-2(3*H*)-furanone (6b). A similar procedure was applied to **5b** under the following conditions: **5b** (0.287 g, 1.69 mmol) in dry dichloromethane (3 ml), triethylamine (0.205 g, 2.02 mmol), and methanesulfonyl chloride (0.263 g, 2.02 mmol) at 0 °C for 3 h, hydrolytic workup and extraction with dichloromethane (20 ml×2), lithium bromide (0.293 g, 3.37 mmol) in THF (3 ml), stirring at room temperature for 24 h, hydrolytic workup and extraction with dichloromethane, column chromatography on silica gel with hexane–ethyl acetate (7:1 v/v). A 1:1 mixture of two diastereomers of **6b** (by ^{1}H NMR, 0.315 g, 80%) was obtained by this procedure, which could be separated from each other through a careful column chromatography.

3,5-*trans*-6b: Colorless liquid; IR (neat) 1780, 1670, 1460, 1430, 1320, 1290, 1180, 1030, 970, and 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02 (6H, d, J=7.0 Hz, *i*-Pr), 2.2—2.5 (1H, m, *i*-Pr), 2.49 (1H, ddd, J_{gem}=14.7, J_{4-5}=8.8, and J_{4-3}=6.2 Hz, one of 4-H), 2.59 (1H, ddd, J_{gem}=14.7, J_{4-5}=5.5, and J_{4-3}=1.8 Hz, the other of 4-H), 4.45 (1H, dd, J_{3-4}=6.2 and 1.8 Hz, 3-H), 5.12 (1H, ddd, J_{5-4}=8.8, 5.5, and $J_{5-1'}$=7.3 Hz, 5-H), 5.45 (1H, dd, $J_{1'-2'}$=15.4 and $J_{1'-5}$=7.3 Hz, 1'-H), and 5.90 (1H, dd, $J_{2'-1'}$=15.4 $J_{2'-3'}$=5.5 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=21.79, 30.71 (each *i*-Pr), 38.98 (4-C), 40.16 (3-C), 80.36 (5-C), 122.67 (1'-C), 144.47 (2'-C), and 172.39 (2-C); MS *m/z* (rel intensity, %) 234 (M^++2, 3), 232 (M^+, 3), 191 (38), 189 (41), 153 (53), 109 (96), 81 (27), 69 (92), 67 (51), and 55 (base peak). HRMS Found: *m/z* 232.0081. Calcd for $C_9H_{13}O_2Br$: M, 232.0099.

3,5-*cis*-6b: Colorless liquid; IR (neat) 1780, 1670, 1470, 1325, 1170, 975, and 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02 (6H, d, J=7.0 Hz, *i*-Pr), 2.2—2.5 (1H, m, *i*-Pr), 2.37 (1H, ddd, J_{gem}=13.6, J_{4-3}=9.2, and J_{4-5}=8.8 Hz, one of 4-H), 3.02 (1H, ddd, J_{gem}=13.6, J_{4-3}=8.4, and J_{4-5}=6.2 Hz, the other of 4-H), 4.57 (1H, dd, J_{3-4}=9.2 and 8.4 Hz, 3-H), 4.88 (1H, dd, J_{5-4}=8.8, 6.2, and $J_{5-1'}$=7.3 Hz, 5-H), 5.54 (1H, dd, $J_{1'-2'}$= 15.4 and $J_{1'-5}$=7.3 Hz, 1'-H), and 5.85 (1H, dd, $J_{2'-1'}$=15.4 and $J_{2'-3'}$=6.6 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=21.77, 30.71 (each *i*-Pr), 37.82 (4-C), 39.80 (3-C), 80.04 (5-C), 123.54 (1'-C), 144.32 (2'-C), and 172.43 (2-C); MS *m/z* (rel intensity, %) 234 (M^++2, 2), 232 (M^+, 2), 191 (22), 189 (21), 153 (57), 109 (67), 81 (24), 79 (23), 69 (base peak), 67 (54), 56 (21), and 55 (94). HRMS Found: *m/z* 232.0074. Calcd for $C_9H_{13}O_2Br$: M, 232.0099.

3-Bromo-5-[(*E*)-2-phenylethenyl]-4,5-dihydro-2(3*H*)-furanone (6c). A similar procedure was applied to **5c** under the following conditions: **5c** (0.099 g, 0.048 mmol) in dichloromethane (3 ml), triethylamine (0.054 g, 0.53 mmol), and methanesulfonyl chloride (0.061 g, 0.53 mmol) in dichloromethane (1 ml) at −20 °C, stirring at 0 °C for 2 h, hydrolytic workup and extraction with dichloromethane (20 ml×2), lithium bromide (0.084 g, 0.97 mmol) in THF (2 ml), at room temperature for 24 h, hydrolytic workup and extraction, column chromatography on silica gel with hexane–ethyl acetate (7:1 v/v). A 1:1 mixture (by ^{1}H NMR) of two diastereomers of **6c** (0.09 g, 70%) was obtained, which could be separated from each other through a careful column chromatography.

3,5-*trans*-6c: Colorless liquid; IR (neat) 1770, 1490, 1440, 1370, 1305, 1170, 1030, 970, 920, and 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.5—2.8 (2H, m, 4-H), 4.48 (1H, dd, J_{3-4}=6.6 and 2.2 Hz, 3-H), 5.33 (1H, dt, J_{5-4}=8.8, 7.3, and $J_{5-1'}$=7.3 Hz, 5-H), 6.17 (1H, dd, $J_{1'-2'}$=15.8 and $J_{1'-5}$=7.3 Hz, 1'-H), 6.76 (1H, d, $J_{2'-1'}$=15.8 Hz, 2'-H), and 7.2—7.5 (5H, m, Ph).

3,5-*cis*-6c: Colorless liquid; IR (neat) 1770, 1480, 1440, 1380, 1330, 1165, 970, 920, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.49 (1H, ddd, J_{gem}=13.9, J_{4-3}=8.8, and J_{4-5}=7.7 Hz, one of 4-H), 3.12 (1H, ddd, J_{gem}=13.9, J_{4-3}=8.4, and J_{4-5}=6.6 Hz, the other of 4-H), 4.60 (1H, dd, J_{3-4}=8.8 and 8.4 Hz, 3-H), 5.11 (1H, ddd, J_{5-4}=7.7, 6.6, and $J_{5-1'}$=7.3 Hz, 5-H), 6.28 (1H, dd, $J_{1'-2'}$=15.8 and $J_{1'-5}$=7.3 Hz, 1'-H), 6.73 (1H, d, $J_{2'-1'}$= 15.8 Hz, 2'-H), and 7.2—7.5 (5H, m, Ph).

(*Z*)-5-Pentylidene-2(5*H*)-furanone (7a). To a solution of **6a** (0.276 g, 1.18 mmol) in dry THF (12 ml) were added hydroquinone (0.013 g, 0.118 mmol) and DBU (0.36 g, 2.37 mmol) in THF (8 ml). The mixture was heated under reflux for 2 h, poured into saturated aqueous ammonium chloride, and extracted with diethyl ether (20 ml×2). The combined ethers were washed with saturated aqueous sodium chloride, dried over magnesium sulfate, and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–ethyl acetate (5:1 v/v) to give **7a**[3b] (0.105 g, 58%) as a single isomer (by ^{1}H NMR): Pale yellow liquid; IR (neat) 1780, 1670, 1550, 1460, 1180, 1120, 1100, 1060, 940, 870, and 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, J=7.0 Hz, *n*-Bu), 1.2—1.6 (4H, m, *n*-Bu), 2.41 (2H, dt, J=8.1 and 7.0 Hz, *n*-Bu), 5.32 (1H, t, $J_{1'-2'}$=8.1 Hz, 1'-H), 6.14 (1H, d, J_{3-4}=5.5 Hz, 3-H), and 7.35 (1H, d, J_{4-3}=5.5 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ=13.79, 22.36, 26.18, 31.04 (each *n*-Bu), 117.81 (1'-C), 118.90 (3-C), 143.72 (4-C), 149.74 (5-C), and 170.20 (2-C); MS *m/z* (rel intensity, %) 152 (M^+, 13), 109 (28), 81 (36), 80 (39), 68 (26), 67 (27), 55 (85), and 41 (base peak). HRMS Found: *m/z* 152.0839. Calcd for $C_9H_{12}O_2$: M, 152.0837.

(*Z*)-5-(3-Methylbutylidene)-2(5*H*)-furanone (7b). A similar prodedure was applied to **6a** under the following conditions: **6a** (0.34 g, 1.46 mmol), hydroquinone (0.016 g, 0.146 mmol), and DBU (0.444 g, 2.92 mmol) in dry THF (25 ml), heating under reflux for 2 h, hydrolytic workup and

extraction with diethyl ether (25 ml×2), column chromatography on silica gel with hexane–ethyl acetate (5:1 v/v). A single isomer (by ^{1}H NMR) of **7b** (0.111 g, 50%) was obtained: Pale yellow liquid; IR (neat) 1780, 1670, 1560, 1330, 1210, 1145, 1110, 1080, 950, 890, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.95 (6H, d, J=6.6 Hz, *i*-Bu), 1.7—1.9 (1H, m, *i*-Bu), 2.35 (2H, dd, J=8.1 and 6.6 Hz, *i*-Bu), 5.34 (1H, t, $J_{1'-2'}$=8.1 Hz, 1'-H), 6.15 (1H, d, J_{3-4}=5.5 Hz, 3-H), and 7.37 (1H, d, J_{4-3}=5.5 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ=22.33, 28.57, 35.32 (each *i*-Bu), 116.58 (1'-C), 118.96 (3-C), 143.65 (4-C), 150.22 (5-C), and 170.22 (2-C); MS *m/z* (rel intensity, %) 152 (M^+, 4), 81 (25), 80 (23), 56 (53), 55 (53), and 42 (base peak). HRMS Found: *m/z* 152.0835. Calcd for $C_9H_{12}O_2$: M, 152.0837.

3-(Methylsulfonyloxy)-5-[(*E*)-1-pentenyl]-4,5-dihydro-2(3*H*)-furanone (8). To a solution of **5a** (0.071 g, 0.42 mmol) in dry dichloromethane (2 ml) were added dropwise, at 0 °C under nitrogen, methanesulfonyl chloride (0.057 g, 0.5 mmol), and then triethylamine (0.046 g, 0.46 mmol). After stirring for 2 h at 0 °C, the mixture was poured into saturated aqueous ammonium chloride and extracted with dichloromethane (20 ml×2). The combined extracts were washed with water, dried over magnesium sulfate, and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–ethyl acetate (3:1 v/v) to give **8** (0.066 g, 63%) as a 1:1 mixture of two diastereomers (by ^{1}H NMR) which could be separated from each other through a careful column chromatography.

3,5-*trans*-8: Colorless liquid; IR (neat) 1780, 1670, 1460, 1370, 1170, 970, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, J=7.3 Hz, *n*-Pr), 1.43 (2H, sx, J=7.3 Hz, *n*-Pr), 2.07 (2H, ddt, J=7.3, 6.6, and 1.5 Hz, *n*-Pr), 2.50 (1H, ddd, J_{gem}=13.9, J_{4-3}=8.1, and J_{4-5}=4.8 Hz, one of 4-H), 2.67 (1H, dt, J_{gem}=13.9, J_{4-3}=J_{4-5}=7.0 Hz, the other of 4-H), 3.25 (3H, s, Me), 5.0—5.2 (1H, m, 5-H), 5.29 (1H, dd, J_{3-4}=8.1 and 7.0 Hz, 3-H), 5.48 (1H, ddt, $J_{1'-2'}$=15.4, $J_{1'-5}$=7.0, and $J_{1'-3'}$=1.5 Hz, 1'-H), and 5.86 (dt, $J_{2'-1'}$=15.4 and $J_{2'-3'}$=6.6 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=13.58, 21.79, 34.05 (each *n*-Pr), 35.09 (Me), 39.42 (4-C), 74.09 (3-C), 79.05 (5-C), 126.29 (1'-C), 136.77 (2'-C), and 171.25 (2-C); MS *m/z* (rel intensity, %) 153 (M^+—OMs, 1), 97 (13), 83 (11), 81 (35), 79 (57), 69 (13), 67 (35), and 55 (base peak).

3,5-*cis*-8: Colorless liquid; IR (neat) 1780, 1670, 1460, 1370, 1180, 970, 840, and 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, J=7.3 Hz, *n*-Pr), 1.42 (2H, sx, J=7.3 Hz, *n*-Pr), 2.07 (2H, dt, J=7.3 and 6.6 Hz, *n*-Pr), 2.2—3.0 (2H, m, 4-H), 3.29 (3H, s, Me), 4.83 (1H, ddd, J_{5-4}=10.6, 8.4, and $J_{5-1'}$=7.7 Hz, 5-H), 5.37 (1H, dd, J_{3-4}=10.6 and 8.4 Hz, 3-H), 5.50 (1H, dd, $J_{1'-2'}$=15.4 and $J_{1'-5}$=7.7 Hz, 1'-H), and 5.91 (1H, dt, $J_{2'-1'}$=15.4 and $J_{2'-3'}$=6.6 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=13.56, 21.74, 34.07 (each *n*-Pr), 35.95 (Me), 39.65 (4-C), 74.28 (3-C), 77.82 (5-C), 126.10 (1'-C), 138.25 (2'-C), and 171.23 (2-C); MS *m/z* (rel intensity, %) 153 (M^+—OMs, 1), 152 (19), 109 (10), 108 (10), 107 (25), 97 (25), 95 (57), 83 (15), 81 (57), 80 (14), 79 (47), 69 (22), and 55 (base peak). Found: C, 48.53; H, 6.74%. Calcd for $C_{10}H_{16}O_5S$: C, 48.37; H, 6.50%.

3-Chloro-5-[(*E*)-1-pentenyl]-4,5-dihydro-2(3*H*)-furanone (9). To a solution of **5a** (0.1 g, 0.588 mmol) in pyridine (1 ml) was added *p*-toluenesulfonic acid (0.268 g, 1.41 mmol). The mixture was stirred at 0 °C for 3 h, at room temperature for 23 h, poured into water, and extracted with diethyl ether (15 ml×2). The combined extracts were washed with 1 M hydrochloric acid and then with water, dried over magnesium sulfate, and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–ethyl acetate (7:1 v/v) to give a 1:1 mixture of two diastereomers (by ^{1}H NMR) which could be separated from each other through a careful column chromatography.

3,5-*trans*-9: Colorless liquid; IR (neat) 1780, 1660, 1450, 1370, 1320, 1175, 960, and 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, J=7.3 Hz, *n*-Pr), 1.43 (2H, sx, J=7.3 Hz, *n*-Pr), 2.09 (2H, q, J=7.3 Hz, *n*-Pr), 2.4—2.6 (2H, m, 4-H), 4.44 (1H, dd, J_{3-4}=6.6 and 3.3 Hz, 3-H), 5.15 (1H, q, J_{5-4}=$J_{5-1'}$=7.3 Hz, 5-H), 5.48 (1H, dd, $J_{1'-2'}$=15.4 and $J_{1'-5}$=7.3 Hz, 1'-H), and 5.90 (1H, dt, $J_{2'-1'}$=15.4 and $J_{2'-3'}$=7.3 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=13.58, 21.84, 34.15 (each *n*-Pr), 39.58 (4-C), 51.27 (3-C), 79.84 (5-C), 125.84 (1'-C), 137.45 (2'-C), and 171.96 (2-C); MS *m/z* (rel intensity, %) 188 (M^+, 10), 153 (27), 145 (87), 109 (70), 88 (24), 82 (41), 79 (52), 77 (27), 69 (27), 67 (base peak), 65 (20), and 55 (79). HRMS Found: *m/z* 188.0492. Calcd for $C_9H_{13}O_2Cl$: M, 188.0603.

3,5-*cis*-9: Colorless liquid; IR (neat) 1780, 1670, 1450, 1380, 1320, 1180, 970, and 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, J=7.3 Hz, *n*-Pr), 1.43 (2H, sx, J=7.3 Hz, *n*-Pr), 2.07 (2H, q, J=7.3 Hz, *n*-Pr), 2.26 (1H, m, one of 4-H), 2.96 (1H, m, the other of 4-H), 4.56 (1H, dd, J_{3-4}=10.3 and 8.4 Hz, 3-H), 4.8—4.9 (1H, m, 5-H), 5.54 (1H, dd, $J_{1'-2'}$=15.4 and $J_{1'-5}$=7.3 Hz, 1'-H), and 5.88 (1H, dt, $J_{2'-1'}$=15.4 and $J_{2'-3'}$=7.3 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=13.58, 21.80, 34.11 (each *n*-Pr), 39.55 (4-C), 51.30 (3-C), 78.89 (5-C), 126.40 (1'-C), 137.79 (2'-C), and 172.10; MS *m/z* (rel intensity, %) 188 (M^+, 17), 153 (34), 147 (29), 145 (73), 109 (68), 88 (32), 82 (39), 79 (54), 77 (25), 69 (29), 67 (base peak), 65 (21), and 55 (78). HRMS Found: *m/z* 188.0599. Calcd for $C_9H_{13}O_2Cl$: M, 188.0603.

Methyl 3-[(Diethoxyphosphinyl)methyl]-5-methyl-2-isoxazoline-5-carboxylate (11). To a solution of (diethoxyphosphinyl)acetaldehyde oxime (7.81 g, 40 mmol) in dry DMF (50 ml) was added dropwise at −20 °C a solution of NBS (14.2 g, 80 mmol) in dry DMF (50 ml). After stirring at −20 °C for 1 h and at 0 °C for 30 min, the mixture was diluted with dry diethyl ether (50 ml). A mixture of methyl methacrylate (8.01 g, 80 mmol) and triethylamine (4.05 g, 40 mmol) in diethyl ether (50 ml) was slowly added, the resulting mixture was stirred at room temperature for 18 h, poured into ice water, and extracted with dichloromethane (50 ml×2). The combined extracts were washed with water, dried over magnesium sulfate, and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–ethyl acetate (5:1 v/v) to give **11** (7.62 g, 65%): Pale yellow liquid; IR (neat) 1740, 1670, 1440, 1390, 1340, 1250, 1020, 960, and 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.33 (6H, t, J=7.0 Hz, OEt), 1.60 (3H, s, Me), 2.95 (2H, d, J_{H-P}=22.0 Hz, PCH_2), 3.01, 3.59 (each 1H, dd, J_{gem}=18.0 and J_{H-P}=4.0 Hz, 4-H), 3.76 (3H, s, COOMe), and 4.11 (4H, dq, J=7.0 and J_{H-P}=8.0 Hz, OEt); ^{13}C NMR ($CDCl_3$) δ=16.39 (d, J_{C-P}= 5.9 Hz, OEt), 23.35 (Me), 26.26 (d, J_{C-P}=140.9 Hz, PCH_2), 47.04 (4-C), 52.89 (COOMe), 62.63 (d, J_{C-P}=5.9 Hz, OEt), 85.9 (5-C), 151.44 (d, J_{C-P}=9.8 Hz, 3-C), and 172.31 (COOMe); MS *m/z* (rel intensity, %) 293 (M^+, 1), 234 (base peak), 206 (28), 178 (59), and 160 (16). Satisfactory analytical result was not obtained because of its hygroscopic nature.

Methyl 5-(Diethoxyphosphinyl)-2-hydroxy-2-methyl-4-oxopentanoate (12). To a solution of **11** (7,62 g, 26 mmol) in

aqueous ethanol (17%, 78 ml) were added Raney Ni (W-2, suspension in ethanol, 6 ml) and boric acid (6.43 g, 104 mmol). The mixture was stirred at room temperature under hydrogen (1 atm) for 14 h. After removal of the catalyst by filtration through Celite 545, the filtrate was diluted with water and extracted with dichloromethane (30 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with ethyl acetate to give **12** (6.6 g, 86%): Colorless liquid; IR (neat) 3340, 1740, 1710, 1450, 1390, 1250, 1020, 970, and 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.34 (6H, t, J=7.0 Hz, OEt), 1.41 (3H, s, Me), 3.04 (1H, d, J_{gem}=17.6 one of 3-H), 3.11 (2H, d, J_{H-P}=22.7 Hz, 5-H), 3.28 (1H, d, J_{gem}=17.6 Hz, the other of 3-H), 3.76 (3H, s, COOMe), 3.82 (1H, s, OH), and 4.14 (4H, dq, J=7.0 and J_{H-P}=7.5 Hz, OEt); ^{13}C NMR ($CDCl_3$) δ=16.31 (d, J_{C-P}=6.8 Hz, OEt), 26.26 (Me), 43.18 (d, J_{C-P}=127.2 Hz, PCH_2), 52.71 (COOMe), 52.86 (3-C), 62.72 (d, J_{C-P}=5.9 Hz, OEt), 72.45 (2-C), 176.01 (COOMe), and 200.79 (d, J_{C-P}=5.9 Hz, 4-C); MS m/z (rel intensity, %) 296 (M^+, 0.3), 237 (base peak), 167 (22), 139 (42), 123 (30), 42 (54), and 30 (20). HRMS Found: m/z 296.1023. Calcd for $C_{11}H_{21}O_7P$: M, 296.1023.

Methyl (*E*)-2-Hydroxy-2-methyl-4-oxo-5-nonenoate (13a). Under nitrogen, a solution of **12** (0.727 g, 2.45 mmol) in dry THF (5 ml) was added to a solution of lithium bromide (0.213 g, 2.45 mmol) in THF (2 ml). After stirring at room temperature for 10 min, a solution of DBU (0.355 g, 2.33 mmol) in THF (5 ml) was added at 0 °C, stirring was continued for 1 h, and then butanal (0.354 g, 4.19 mmol) was slowly added. After stirring at 0 °C for 24 h, the reaction mixture was poured into ice water and extracted with dichloromethane (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane–ethyl acetate (3:1 v/v) as an eluent to give **13a** (0.443 g, 84%): Colorless liquid; IR (neat) 3510, 1750, 1670, 1630, 1460, 1380, 1300, 1210, 1120, and 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (3H, t, J=7.3 Hz, n-Pr), 1.43 (3H, s, Me), 1.50 (2H, sx, J=7.3 Hz, n-Pr), 2.21 (2H, dq, J=7.3 and 1.5 Hz, n-Pr), 2.91, 3.26 (each 1H, J_{gem}=17.2 Hz, 3-H), 3.76 (3H, s, COOMe), 4.00 (1H, s, OH), 6.07 (1H, dt, J_{5-6}=15.8 and J_{5-7}=1.5 Hz, 5-H), and 6.88 (1H, dt, J_{6-5}=15.8 and J_{6-7}= 7.3 Hz, 6-H); ^{13}C NMR ($CDCl_3$) δ=13.68, 21.24, 34.54 (each n-Pr), 26.28 (Me), 48.83 (3-C), 52.64 (COOMe), 72.74 (2-C), 130.29 (5-C), 149.24 (6-C), 176.32 (COOMe), and 199.00 (4-C); MS m/z (rel intensity, %) 214 (M^+, 5), 155 (27), 97 (base peak), 55 (62), 43 (51), and 41 (24). HRMS Found: m/z 214.1207. Calcd for $C_{11}H_{18}O_4$: M, 214.1208.

Methyl (*E*)-2-Hydroxy-2,7-dimethyl-4-oxo-5-octenoate (13b). A similar procedure was applied under the following conditions: **12** (1.439 g, 4.86 mmol) in dry THF (9 ml), lithium bromide (0.422 g, 4.86 mmol) in THF (2 ml), 10 min at room temperature, DBU (0.702 g, 4.61 mmol) in THF (9 ml) at 0 °C, stirring at 0 °C for 1 h, 2-methylpropanal (0.701 g, 9.71 mmol), stirring at 0 °C for 24 h, hydrolytic workup and extraction with dichloromethane (20 ml×2), column chromatography on silica gel with hexane–ethyl acetate (3:1 v/v). This procedure gave **13b** (0.805 g, 77%): Colorless liquid; IR (neat) 3500, 1740, 1670, 1630, 1460, 1370, 1200, 1120, and 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.07 (6H, d, J=7.0 Hz, i-Pr), 1.43 (3H, s, Me), 2.3—2.6 (1H, m, i-Pr), 2.92, 3.26 (each 1H, d, J_{gem}=17.2 Hz, 3-H), 3.76 (3H, s, COOMe), 3.99 (1H, s, OH), 6.02 (1H, dd, J_{5-6}=16.1 and J_{5-7}=1.5 Hz, 5-H), and 6.84 (1H, dd, J_{6-5}=16.1 and J_{6-7}=6.6 Hz, 6-H); ^{13}C NMR ($CDCl_3$) δ=21.17, 31.17 (each i-Pr), 26.25 (Me), 48.97 (3-C), 52.50 (COOMe), 72.61 (2-C), 127.45 (5-C), 155.06 (6-C), 176.25 (COOMe), and 199.07 (4-C); MS m/z (rel intensity, %) 214 (M^+, 4), 155 (29), 97 (base peak), 43 (34), and 41 (24). HRMS Found: m/z 214.1212. Calcd for $C_{11}H_{18}O_4$: M, 214.1204.

3-Hydroxy-3-methyl-5-[(*E*)-1-pentenyl]-4,5-dihydro-2(3*H*)-furanone (14a). A single isomer of **14a** (0.347 g, 56%) was obtained by a procedure similar to that employed for the preparation of **5a** from **4a** under the following conditions: **13a** (0.723 g, 3.37 mmol) in methanol (8 ml), sodium borohydride (0.128 g, 3.37 mmol), stirring at 0 °C for 10 min, acetone (4 ml), stirring at 0 °C for 10 min, hydrolytic workup and extraction with dichloromethane (20 ml×2), the crude product and p-toluenesulfonic acid (0.064 g, 0.337 mmol) in dichloromethane (8 ml), stirring at room temperature for 2 h, hydrolytic workup and extraction with dichloromethane (20 ml×2), column chromatography on silica gel with hexane–ethyl acetate (5:1 v/v): Colorless prisms; mp 49—51 °C; IR (KBr) 3400, 1750, 1440, 1380, 1320, 1180, 1120, 960, 920, and 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91 (3H, t, J=7.3 Hz, n-Pr), 1.42 (2H, sx, J=7.3 Hz, n-Pr), 1.49 (3H, s, Me), 1.91 (1H, dd, J_{gem}=13.6 and J_{4-5}=8.4 Hz, one of 4-H), 2.05 (2H, q, J=7.3 Hz, n-Pr), 2.50 (1H, dd, J_{gem}=13.6 and J_{4-5}=6.2 Hz, the other of 4-H), 3.71 (1H, br s, OH), 5.05 (1H, ddd, J_{5-4}=8.4, 6.2, and $J_{5-1'}$=7.3 Hz, 5-H), 5.46 (1H, dd, $J_{1'-2'}$=15.1 and $J_{1'-5}$=7.3 Hz, 1'-H), and 5.84 (1H, dt, $J_{2'-1'}$=15.1 and $J_{2'-3'}$=7.3 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=13.59, 21.91 (each n-Pr), 23.92 (Me), 34.17 (n-Pr), 43.37 (4-C), 73.66 (3-C), 78.64 (5-C), 127.28 (1'-C), 136.22 (2'-C), and 178.54 (COOMe); MS m/z (rel intensity, %) 167 (M^+—OH, 0.4), 97 (20), 81 (34), 71 (26), 67 (19), 58 (17), 55 (18), and 43 (base peak). Found C, 64.92; H, 9.00%. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%.

3-Hydroxy-3-methyl-5-[(*E*)-3-methyl-1-butenyl]-4,5-dihydro-2(3*H*)-furanone (14b). A similar procedure was applied to **13b** under the following conditions: **13b** (0.747 g, 3.49 mmol) in methanol (7 ml), sodium borohydride (0.132 g, 3.49 mmol) stirring at 0 °C for 10 min, acetone (3 ml), stirring at 0 °C for 10 min, hydrolytic workup and extraction with dichloromethane (15 ml×2), the crude product and p-toluenesulfonic acid (0.066 g, 0.349 mmol) in dichloromethane (7 ml), stirring at room temperature for 1 h, hydrolytic workup and extraction with dichloromethane (15 ml×2), silica-gel column chromatography with hexane–ethyl acetate (5:1 v/v). From this procedure was obtained a single isomer of **14b** (0342 g, 53%) which was contaminated by a trace amount of an unidentified product: Colorless prisms; mp 85—87 °C; IR (KBr) 3420, 1750, and 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (6H, d, J=7.0 Hz, i-Pr), 1.50 (3H, s, Me), 1.92 (1H, dd, J_{gem}=13.6 and J_{4-5}=8.4 Hz, one of 4-H), 2.50 (1H, dd, J_{gem}=13.6 and J_{4-5}=6.2 Hz, the other of 4-H), 3.76 (1H, m, OH), 5.05 (1H, ddd, J_{5-4}=8.4, 6.2, and $J_{5-1'}$=7.0 Hz, 5-H), 5.41 (1H, dd, $J_{1'-2'}$=15.4 and $J_{1'-5}$=7.0 Hz, 1'-H), and 5.82 (1H, dd, $J_{2'-1'}$=15.4 and $J_{2'-3'}$=6.2 Hz, 2'-H); ^{13}C NMR ($CDCl_3$) δ=21.89 (i-Pr), 23.99 (Me), 30.71 (i-Pr), 43.34 (4-C), 73.66 (3-C), 78.67 (5-C), 124.26 (1'-C), 143.06 (2'-C), and 178.50 (2-C); MS m/z (rel intensity, %) 167 (M^+—OH, 8), 95 (21), 81 (49), 71 (22), 55 (34), and 43 (base peak).

(*Z*)-3-Methyl-5-pentylidene-2(5*H*)-furanone (16a). To a solution of **14a** (0.23 g, 1.25 mmol) in dry dichloromethane

(5 ml) were added, at 0 °C under nitrogen, triethylamine (0.152 g, 1.5 mmol) and methanesulfonyl chloride (0.171 g, 1.5 mmol). After stirring at 0 °C for 3 h, the mixture was poured into saturated aqueous ammonium chloride and extracted with dichloromethane (15 ml×2). The combined extracts were washed with saturated aqueous sodium hydrogencarbonate, dried over magnesium sulfate, and evaporated in vacuo. The residue was dissolved in dry THF (5 ml) and lithium bromide (0.217 g, 2.5 mmol) was added. The mixture was refluxed under nitrogen for 1 h, poured into water, and extracted with dichloromethane (15 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was filtered through a short column packed by silica gel. The fraction eluted with hexane–ethyl acetate (5:1 v/v) was evaporated in vacuo to give crude **15a** (0.183 g). This product was disolved in dry THF (1 ml) and were added hydroquinone (0.014 g, 0.125 mmol) and DBU (0.38 g, 2.5 mmol). This mixture was refluxed under nitrogen for 1 h, poured into saturated aqueous ammonium chloride, and extracted with diethyl ether. The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane–diethyl ether (5:1 v/v) to afford **16a** (0.131 g, 63%): Colorless luquid; IR (neat) 1780, 1670, 1620, 1460, 1050, 990, 890, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91 (3H, t, J=7.0 Hz, *n*-Bu), 1.2—1.5 (4H, m, *n*-Bu), 1.99 (3H, d, J_{Me-4}=1.5 Hz, Me), 2.37 (2H, dt, J=7.7 and 7.0 Hz, *n*-Bu), 5.17 (1H, t, $J_{1'-2}$=7.7 Hz, 1'-H), and 7.02 (1H, q, J_{4-Me}=1.5 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ=10.47 (Me), 13.81, 22.36, 25.89, 31.26 (each *n*-Bu), 114.81 (1'-C), 128.85 (3-C), 137.91 (4-C), 148.43 (5-C), and 171.27 (2-C); MS *m/z* (rel intensity, %) 166 (M^+, 16), 123 (58), 110 (35), 96 (31), 95 (23), 81 (32), 69 (20), 68 (60), 67 (20), 60 (28), and 55 (base peak). HRMS Found: *m/z* 166.0990. Calcd for $C_{10}H_{14}O_2$: M, 166.0993.

(*Z*)-3-Methyl-5-(3-methylbutylidene)-2(5*H*)-furanone (16b). A similar procedure was performed under the following procedure: **14b** (0.339 g, 1.84 mmol) in dry dichloromethane (7 ml), addition of triethylamine (0.223 g, 2.21 mmol) and methanesulfonyl chloride (0.253 g, 2.21 mmol) at 0 °C, stirring at 0 °C for 3 h under nitrogen, hydrolytic workup and extraction with dichloromethane, the crude product and lithium bromide (0.32 g, 3.68 mmol) in THF (5 ml), heating under reflux for 1 h, hydrolytic workup and extraction with dichloromethane, filtration through a short column, the crude product (0.297 g) and hydroquinone (0.02 g, 0.184 mmol) and DBU (0.56 g, 3.68 mmol) in THF (4 ml), heating under reflux for 1 h, hydrolytic workup and extraction with diethyl ether, a silica-gel chromatography with hexane–diethyl ether (5:1). Thus a single isomer of **16b** (0.153 g, 50%) was obtained: Colorless liquid; IR (neat) 1770, 1680, 1620, 1460, 1060, 1040, 990, 890, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (6H, d, J=6.6 Hz, *i*-Bu), 1.6—1.9 (1H, m, *i*-Bu), 1.99 (3H, d, J_{Me-4}=1.5 Hz, Me), 2.27 (2H, dd, J=8.1 and 7.3 Hz, *i*-Bu), 5.17 (1H, t, $J_{1'-2'}$=8.1 Hz, 1'-H), and 7.01 (1H, q, J_{4-Me}=1.5 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ=10.48 (Me), 22.32, 28.65, 35.06 (each *i*-Bu), 113.57 (1'-C), 128.95 (3-C), 137.76 (4-C), 148.89 (5-C), and 171.30 (2-C); MS *m/z* (rel intensity, %) 166 (M^+, 12), 123 (85), 111 (21), 95 (36), 68 (44), 67 (24), 56 (88), 54 (22), and 40 (base peak). HRMS Found: *m/z* 166.0992. Calcd for $C_{10}H_{14}O_2$: M, 166.0993.

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