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Palladium-Catalyzed Carbonylation of 2-(propargyl)allyl Phosphates Leading to Highly Unsaturated γ-Lactones

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General Information. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JMN-270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, and m = multiplet, br = broad), coupling constant (Hz), integration, and assignment. Infrared spectra (IR) were obtained on a Hitachi 270-50 spectrometer; absorption data are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument using ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Analytical GC was carried out on a Shimadzu GC-14B gas chromatography, equipped with a flame ionization detector. Melting points were determined on a Yamato melting point apparatus and are uncorrected. Recycling Preparative HPLC was performed on a Japan Analytical industry LC-908. Column chromatography was performed using SiO_2 (Merk Silicael 60 (230-400 mesh))

Materials. THF was distilled from sodium benzophenone ketyl. $[Pd(\pi\text{-}C_3H_5)Cl]_2$ was purchased from Strem Chemicals Inc., and used without further purification.

Dicyclohexylmethyl amine was distilled prior to use. All starting materials were prepared as described below.

2-Methylene-4-hexyn-1-yl Diethyl Phosphate (1a). Ethyl 2-methylene-4-hexynoate was prepared, using a modification of the method described by Kirschleger.[1] To a mixture of ethyl benzoylacetate (49 mmol, 9.5 g) and 1-bromo-2-butyne[2] (55 mmol, 7.3 g) was added potassium carbonate (60 mmol, 8.3 g) and sodium iodide (13 mmol, 2.0 g), and the reaction mixture was stirred at room temperature for 12 hours. To the resulting mixture were added potassium carbonate (60 mmol, 8.3 g), paraformaldehyde (60 mmol, 1.8 g) and THF (60 mL), and the resulting suspension refluxed for 12 hours. The contents were dissolved in water (40 mL), and extracted with ether (40 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was distilled under reduced pressure (42-43 °C/1 mmHg) to give ethyl 2-methylene-4-hexynoate (4.3 g, 57 %) as a colorless oil.

To a solution of ethyl 2-methylene-4-hexynoate (32 mmol, 4.9 g) in diethyl ether (30 mL) was added dropwise diisobutylaluminum hydride (1 M in hexane, 60 mmol) at 0 °C over 1 hour, and the mixture was stirred at room temperature for 4 hours. 4N HCl (60 mL) was carefully added to the solution, and the organic layer was separated. The aqueous layer was extracted with ether (40 mL), and the combined ethereal layers were dried over $MgSO_4$. After removal of volatiles, the residue was subjected to a column chromatography on silica gel (eluent; hexane/EtOAc = 1/1, R_f 0.48) to give 2-methylene-4-hexyn-1-ol (2.8 g, 78 %) as a colorless oil.

The desired compound (**1a**) was prepared using a modification of the method described by Murahashi.[3] To a solution of 2-methylene-4-hexyn-1-ol (25 mmol, 2.8 g), pyridine (50 mmol, 4.0 mL) in CH_2Cl_2 (25 mL) was added dropwise diethyl chlorophosphate (29 mmol, 4.2 mL) at 0 °C, and the mixture was stirred at room temperature for 12 hours. Diethyl ether (40 mL) and 1N HCl (30 mL) were added to the resulted suspension, and the organic layer was separated. The ether was washed with 1N HCl (30 mL), and saturated $NaHCO_3$ (30 mL x 2), and dried over $MgSO_4$. After removal of volatiles, the residue was subjected to a column chromatography on silica gel (eluent; hexane/EtOAc = 2/1, R_f 0.07) to give 2-methylene-4-hexyn-1-yl diethyl phosphate (**1a**) (3.5 g, 56 %). Colorless oil; R_f 0.07 (hexane/EtOAc = 2/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.35 (t, ^3J(H,H) = 7.0 Hz, 6H), 1.82 (t, ^5J(H,H) = 2.7 Hz, 3H), 2.97 (brs, 2H), 4.12 (dq, ^3J(H,H) = 7.0 Hz, ^3J(H,P) = 7.0 Hz, 4H), 4.53 (d, ^3J(H,P) = 7.3 Hz, 2H), 5.20 (brs, 1H), 5.29 (brs, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 3.5, 16.0 (d, ^3J(C,P) = 6.7 Hz), 23.0, 63.7 (d, ^2J(C,P) = 6.1 Hz), 69.0 (d, ^2J(C,P) = 5.6 Hz), 74.6, 78.5, 114.2, 139.6 (d, ^3J(C,P) = 7.3 Hz); IR (neat) 2988 m, 2920 w, 1662 w, 1450 m, 1398 m, 1276 s, 1166 m, 1034 s, 890 m, 804 m; MS, m/z (relative intensity, %) 246 (0.4) [M^+], 155 (29), 127 (23), 109 (11), 99 (61), 92 (36), 91 (100), 81 (18), 77 (14), 65 (17), 53 (18), 51 (11); exact mass calcd for $C_{14}H_{25}O_4P$ 246.1021, found 246.1028.

2-Methylene-4-nonyn-1-yl Diethyl Phosphate (1b). 1-Bromo-2-heptyne was prepared by the treatment of 2-heptyn-1-ol[4] with PBr_3 using a modification of the method described by Brandsma.[5] The compound (**1b**) was prepared by a procedure similar to that used for **1a**. Colorless oil; R_f 0.13 (hexane/EtOAc = 2/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.91 (t, ^3J(H,H) = 7.0 Hz, 3H), 1.34 (dt, ^4J(H,P) = 0.8 Hz, ^3J(H,H) = 7.3 Hz, 6H), 1.39-1.54 (m, 4H), 2.15-2.22 (m, 2H), 2.99 (brs, 2H), 4.12 (dq, ^3J(H,P) = 7.0 Hz, ^3J(H,H) =

7.3 Hz, 4H), 4.53 (d, ^3J(H,P) = 7.0 Hz, 2H), 5.20 (brs, 1H), 5.29 (brs, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.4, 16.0 (d, ^3J(C,P) = 6.7 Hz), 18.3, 21.8, 22.9, 30.9, 63.7 (d, ^2J(C,P) = 5.6 Hz), 69.0 (d, ^2J(C,P) = 5.6 Hz), 75.4, 83.3, 114.2, 139.8 (d, ^3J(C,P) = 7.3 Hz); IR (neat) 3476 w, 2936 m, 1660 w, 1462 m, 1394 m, 1270 s, 1164 m, 1030 s, 910 m, 874 m, 802 m, 750 w; MS, *m*/*z* (relative intensity, %) 288 (0.49) [M^+], 155 (69), 127 (41), 119 (15), 105 (32), 99 (76), 93 (10), 92 (52), 91 (100), 81 (20), 79 (23), 78 (11), 77 (24), 65 (27), 55 (14), 53 (14), 52 (13); exact mass calcd for $C_{14}H_{25}O_4P$ 288.1490, found 288.1489.

5-Cyclohexyl-2-methylene-4-pentyn-1-yl Diethyl Phosphate (1c). 3-Cyclohexyl-2-propyn-1-ol was prepared from cyclohexylacetylene[6] using a modification of the method of Denis.[4] 1-Bromo-3-cyclohexyl-2-propyne was prepared by the reaction of the corresponding alcohol with PBr_3 using a modification of the method described by Brandsma.[5] The compound (**1c**) was prepared by a procedure similar to that used for **1a**. Colorless oil; R_f 0.23 (hexane/EtOAc = 1/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.22-1.57 (m, 12H), 1.64-1.81 (m, 4H), 2.34-2.40 (m, 1H), 3.00 (brs, 2H), 4.12 (dq, ^3J(H,P) or ^3J(H,H) = 7.0 Hz, ^3J(H,H) or ^3J(H,P) = 7.3 Hz, 4H), 4.53 (d, ^3J(H,P) = 6.8 Hz, 2H), 5.20 (brs, 1H), 5.31 (brs, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.1 (d, ^3J(C,P) = 6.7 Hz), 23.1, 24.9, 25.9, 29.1, 33.0, 63.8 (d, ^2J(C,P) = 6.1 Hz), 69.1 (d, ^2J(C,P) = 5.6 Hz), 75.4, 87.8, 114.1, 139.8 (d, ^3J(C,P) = 7.3 Hz); IR (neat) 3484 w, 2924 m, 1658 w, 1452 m, 1264 s, 1166 w, 1034 s, 870 w, 680 w; MS, *m*/*z* (relative intensity, %) 314 (0.65) [M^+], 160 (41), 155 (77), 145 (44), 132 (16), 131 (35), 127 (45), 119 (17), 118 (20), 117 (65), 115 (16), 105 (33), 104 (19), 99 (75), 92 (57), 91 (100), 81 (43), 79 (44), 78 (29), 77 (40), 67 (29), 65 (27), 55 (20), 53 (19); exact mass calcd for $C_{16}H_{27}O_4P$ 314.1647, found 314.1654.

6,6-Dimethyl-2-methylene-4-heptyn-1-yl Diethyl Phosphate (1d). 4-Bromo-1,1-dimethyl-2-butyne was prepared by the reaction of 1,1-dimethyl-2-butyn-4-ol[4] with PBr_3 using a modification of the method described by Brandsma.[5] The compound (**1d**) was prepared by a procedure similar to that used for **1a**. Colorless oil; R_f 0.14 (hexane/ether = 2/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.22 (s, 9H), 1.34 (dt, ^4J(H,P) = 0.8 Hz, ^3J(H,H) = 7.3 Hz, 6H), 2.98 (s, 2H), 4.12 (dq, ^3J(H,H) = 7.3 Hz, ^3J(H,P) = 7.8 Hz, 4H), 4.52 (d, ^3J(H,P) = 6.7 Hz, 2H), 5.20 (brs, 1H), 5.31 (brs, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.2 (d, ^3J(C,P) = 6.7 Hz), 23.0, 27.4, 31.2, 63.8 (d, ^2J(C,P) = 5.6 Hz), 69.2 (d, ^2J(C,P) = 5.6 Hz), 74.0, 92.1, 114.1, 139.8 (d, ^3J(C,P) = 7.3 Hz); IR (neat) 3458 w, 2972 s, 1660 w, 1480 m, 1462 m, 1428 m, 1396 m, 1366 m, 1270 s, 1204 w, 1164 m, 1032 s, 912 m, 870 m, 816 m, 754 w; MS, *m*/*z* (relative intensity, %) 288 (3) [M^+], 155 (18), 127 (11), 119 (100), 117 (10), 105 (30), 99 (29), 92 (55), 81 (12), 79 (20), 78 (10), 77 (20), 57 (10), 55 (11), 53 (10); exact mass calcd for $C_{14}H_{25}O_4P$ 288.1491, found 288.1486.

(*E*)-2-(2-Butynyl)-2-heptenyl Diethyl Phosphate (1e). Methyl (*E*)-2-(2-butynyl)-2-heptenoate was prepared, using a modification of the method of Trost.[7] A mixture of methyl (triphenylphosphoranylidene)acetate (40 mmol, 13.2 g), 1-bromo-2-butyne[2] (45 mmol, 6.0 g), potassium carbonate (80 mmol, 11.0 g) and EtOAc (50 mL) was stirred at reflux for 24 hours. After filtration, the filtrate was concentrated *in vacuo*. To the concentrate were added valeraldehyde (60 mmol, 5.2 g) and chloroform (80 mL), and the mixture was stirred at reflux for 3 days. After removal of volatiles, the crude mixture was diluted with ether. The suspension was filtered through Celite, and the filtrate was concentrated under reduced pressure to give crude methyl (*E*)-2-(2-butynyl)-2-heptenoate (9.3 g), which was used without further purification in the next step.

To a solution of methyl (*E*)-2-(2-butynyl)-2-heptenoate (9.3 g) in diethyl ether (40 mL) was added dropwise diisobutylaluminum hydride (1M in hexane, 80 mmol) at 0 °C over 1 hour, and the mixture was stirred at room temperature for 4 hours. 4N HCl (120 mL) was carefully added to the solution, and an organic layer was separated. The aqueous layer was extracted with ether (40 mL), and the combined ether was dried over $MgSO_4$. After removal of volatiles, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 3/1, R_f 0.28) to give (*E*)-2-(2-butynyl)-2-hepten-1-ol (2.2 g, 33 %) as a colorless oil.

To a solution of (*E*)-2-(2-butynyl)-2-hepten-1-ol (13 mmol, 2.2 g), pyridine (26 mmol, 2.1 mL) and CH_2Cl_2 (20 mL) was added dropwise diethyl chlorophosphate (16 mmol, 2.3 mL) at 0 °C, and the mixture was stirred at room temperature for 12 hours. Diethyl ether (40 mL) and 1N HCl (30 mL) were added to the resulted suspension, and the organic layer was separated. The ether was washed with 1N HCl (30 mL), and saturated $NaHCO_3$ (30 mL x 2), and dried over $MgSO_4$. After removal of volatiles, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 2/1, R_f 0.13) to give (*E*)-2-(2-butynyl)-2-hepten-1-yl diethyl phosphate (**1e**) (2.3 g, 59 %). The stereochemistry of **1e** was determined by NOE enhancement. Colorless oil; R_f 0.13 (hexane/EtOAc = 2/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.90 (t, ^3J(H,H) = 7.0 Hz, 3H), 1.25-1.43 (m, 10H), 1.76 (t, ^5J(H,H) = 2.4 Hz, 3H), 2.05-2.13 (m, 2H), 2.97 (brs, 2H), 4.12 (dq, ^3J(H,H) or ^3J(H,P) = 7.0 Hz, ^3J(H,P) or ^3J(H,H) = 8.0 Hz, 4H), 4.55 (dd, ^4J(H,H) = 0.8 Hz, ^3J(H,P) = 7.0 Hz, 2H), 5.58 (t, ^3J(H,H) = 7.0 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 3.6, 14.0, 16.2 (d, ^3J(C,P) = 6.6 Hz), 17.5, 22.4, 27.4, 31.3, 63.6 (d, ^2J(C,P) = 5.6 Hz), 70.7 (d, ^2J(C,P) = 5.6 Hz), 75.7, 75.9, 130.3 (d, ^3J(C,P) = 7.3 Hz), 131.6; IR (neat) 3476 w, 3260 w, 2932 m, 2868 m, 1676 w, 1462 m, 1396 m, 1268 s, 1164 m, 1032 s, 848 w, 818 w, 750 w; MS, *m*/*z* (relative intensity, %) 302 (0.6) [M^+], 155 (100), 148 (13), 133 (33), 127 (67), 119 (42), 107 (10), 106 (37), 105 (36), 99 (71), 93 (12), 92 (14), 91 (48), 81 (12), 79 (20), 77 (15); exact mass calcd for $C_{15}H_{27}O_4P$ 302.1647, found 302.1652.

5-Methylene-2-decyn-6-yl Diethyl Phosphate (1f). 5-Methylene-2-decyn-6-ol was prepared, using a modification of the method described by Gaudemar.[8] To a suspension of zinc powder (100 mmol, 6.5 g) in THF (80 mL) was added dropwise a solution of 1-bromo-2-butyne[2] (105 mmol, 14.0 g) in THF (5 mL) at –15 °C over 20 min, and the mixture was stirred at same temperature for 20 min. A solution of 1-heptyn-3-ol (25 mmol, 2.8 g) in THF (5 mL) was added at 0 °C, the resulting mixture was stirred at room temperature for 24 hours. 3N HCl (80 mL) was added to the mixture at 0 °C, and the organic layer was separated. The aqueous layer was extracted with ether (40 mL), and the combined etheral layers were dried over $MgSO_4$. After removal of volatiles, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 4/1, R_f 0.36) to give 5-Methylene-2-decyn-6-ol (2.0 g, 48 %) as a colorless oil.

To a solution of 5-methylene-2-decyn-6-ol (12 mmol, 2.0 g), pyridine (24 mmol, 1.9 mL) and CH_2Cl_2 (15 mL) was added dropwise diethyl chlorophosphate (13 mmol, 1.9 mL) at 0 °C, and the mixture was stirred at room temperature for 12 hours. Diethyl ether (40 mL) and 1N HCl (30 mL) were added to the resulted suspension, and the organic layer was separated. The ether was washed with 1N HCl (30 mL), and saturated $NaHCO_3$ (30 mL x 2), and dried over $MgSO_4$. After removal of volatiles, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 2/1, R_f 0.19) to give 5-methylene-2-decyn-6-yl diethyl phosphate (**1f**) (2.0 g, 60 %). Colorless oil; R_f 0.19 (hexane/EtOAc = 2/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.89 (t, ^3J(H,H) = 6.8 Hz, 3H), 1.24-1.38 (m, 10H), 1.63-1.78 (m, 2H), 1.83 (t, ^5J(H,H) = 2.7 Hz, 3H), 2.94 (dq, ^5J(H,H) = 1.9 Hz, ^2J(H,H) = 13.0 Hz, 2H), 4.00-4.12 (m, 4H), 4.81 (d, ^3J(H,P) = 7.0 Hz, 2H), 5.19 (bs, 1H), 5.36 (bs, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 3.6, 13.8, 16.0 (d, ^3J(C,P) = 7.3 Hz), 20.6, 22.2, 27.0, 33.7 (d, ^3J(C,P) = 6.2 Hz), 63.5 (d, ^2J(C,P) = 5.6 Hz), 75.0, 78.7, 81.4 (d, ^2J(C,P) = 6.2 Hz), 114.4, 142.7 (d, ^3J(C,P) = 3.5 Hz); IR (neat) 3452 w, 2944 m, 1658 w, 1450 m, 1396 m, 1264 s, 1162 w, 1030 s, 910 m, 802 w; MS, *m*/*z* (relative intensity, %) 302 (0.12) [M^+], 155 (79), 133 (25), 127 (53), 119 (32), 106 (32), 105 (25), 99 (100), 92 (12), 91 (65), 81 (25), 79 (21), 77 (20), 65 (15), 55 (14), 53 (19); exact mass calcd for $C_{15}H_{27}O_4P$ 302.1647, found 302.1653.

2-(2-Butynyl)-cinnamyl Diethyl Phosphate (1g). This compound (**1g**) was prepared by a procedure similar to that used for **1e**. The starting material **1g** was obtained as a 10:1 mixture of *E*- and *Z*-isomers. The ratio of two isomers was determined by ^{1}H NMR analysis, and the stereochemistry was determined by NOE enhancement. Spectral data were obtained from a mixture of *E*- and *Z*-isomers. Yellow oil; R_f 0.20 (hexane/EtOAc = 1/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.32-1.38 (m, 6H), [1.77 (t, ^5J(H,H) = 2.4 Hz, *Z*-isomer), 1.81 (t, ^5J(H,H) = 2.4 Hz, *E*-isomer), 3H], [3.12 (brs, *E*-isomer), 3.24 (brs, *Z*-isomer), 2H], 4.06-4.21 (m, 4H), [4.64 (d, ^3J(H,P) = 6.5 Hz, *Z*-isomer), 4.73 (dd, ^4J(H,H) =

0.8 Hz, ^3J(H,P) = 7.0 Hz, *E*-isomer), 2H], 6.64 (brs, 1H), 7.24-7.39 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ [3.5, (*Z*-isomer), 3.6 (*E*-isomer)], 16.2 (d, ^3J(C,P) = 6.1 Hz), [16.6 (*E*-isomer), 20.3 (*Z*-isomer)], [63.7 (d, ^2J(C,P) = 5.6 Hz, *E*-isomer), 68.2 (d, ^2J(C,P) = 5.0 Hz, *Z*-isomer)], [68.3 (d, ^2J(C,P) = 5.0 Hz, *Z*-isomer), 70.1 (d, ^2J(C,P) = 5.6 Hz, *E*-isomer)], 75.5, 75.7, 76.7, 77.4, 109.2, 127.2, 128.2, 128.6, 129.2, 132.6 (d, ^3J(C,P) = 7.3 Hz), 135.9; IR (neat) 3478 w, 3244 w, 2982 m, 2920 m, 2218 w, 1654 w, 1602 w, 1495 m, 1482 m, 1449 m, 1394 m, 1369 w, 1265 s, 1163 m, 1035 s, 877 m, 817 m, 750 m, 699 m, 643 w; MS, *m*/*z* (relative intensity, %) 322 (0.7) [M^+], 169 (12), 168 (65), 167 (77), 165 (24), 155 (22), 154 (19), 153 (100), 152 (38), 141 (12), 128 (24), 127 (19), 116 (10), 115 (82), 99 (37), 91 (14), 81 (19), 53 (22), 51 (13); exact mass calcd for $C_{17}H_{23}O_4P$ 322.1334, found 322.1328.

2-(1-Methylethylidene)-4-hexyn-1-yl Diethyl Phosphate (1h). Ethyl 2-(1-methylethylidene)-4-hexynoate was prepared, using a modification of the method described by Kraus.[10] To a suspension of NaH (45 mmol, 1.8 g) in THF (12 mL) was added dropwise triethyl phosphonoacetate (45 mmol, 10.2 g) at 0 °C, and the mixture was stirred at room temperature until the evolution of hydrogen gas subsided. A solution of 1-bromo-2-butyne[2] (46 mmol, 6.1 g) in THF (12 mL) was slowly added at 0 °C, and the resulting mixture was stirred at room temperature for 1 hour. After filtration, the filtrate was condensed *in vacuo*, and the residue was diluted in THF (5 mL). To a suspension of NaH (45 mmol, 1.8 g) in THF (40 mL) was added dropwise the above solution, and the reaction mixture was stirred at room temperature for 1 hour. Acetone (90 mmol, 7.0 mL) was added, and the suspension was stirred for 12 hours. The suspension was dissolved in water (60 mL), and extracted with ether (40 mL x 2). The combined organic solution was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 4/1, R_f 0.46) to give ethyl 2-(1-methylethylidene)-4-hexynoate (2.8 g, 36 %) as a colorless oil.

To a suspension of lithium aluminum hydride (16 mmol, 0.6 g) in diethyl ether (25 mL) was added ethyl 2-(1-methylethylidene)-4-hexynoate (16 mmol, 2.8 g) at 0 °C over 1 hour, and the mixture was stirred at room temperature for 12 hours. Water (2.4 mL) was carefully added, and the white suspension filtered through Celite. The filtrate was dried over $MgSO_4$. After removal of volatiles, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 4/1, R_f 0.19) to give 2-(1-methylethylidene)-4-hexyn-1-ol (1.6 g, 70 %) as a colorless oil.

To a solution of 2-(1-methylethylidene)-4-hexyn-1-ol (11 mmol, 1.6 g), pyridine (23 mmol, 1.9 mL) and CH_2Cl_2 (15 mL) was added dropwise diethyl chlorophosphate (13 mmol, 1.9 mL) at 0 °C, and the mixture was stirred at room temperature for 12 hours. Diethyl ether (40 mL) and 1N HCl (30 mL) were added to the resulted suspension, and an organic layer was separated. The ether was washed with 1N HCl (30 mL), and saturated $NaHCO_3$ (30 mL x 2), and dried over $MgSO_4$. After removal of volatiles, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 1/1, R_f 0.24) to give 2-(1-methylethylidene)-4-hexyn-1-yl diethyl phosphate (**1h**) (2.0 g, 68 % yield). Colorless oil; R_f 0.24 (hexane/EtOAc = 1/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.34 (dt, ^4J(H,P) = 1.1 Hz, ^3J(H,H) = 7.0 Hz, 6H), 1.76 (t, ^5J(H,H) = 2.7 Hz, 3H), 1.78 (s, 3H), 1.81 (s, 3H), 2.99 (brs, 2H), 4.12 (dq, ^3J(H,H) = 7.0 Hz, ^3J(H,P) = 7.3 Hz, 4H), 4.67 (d, ^3J(H,P)

= 8.1 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 3.3, 15.9 (d, ^3J(C,P) = 6.7 Hz), 19.5, 20.3, 20.6, 63.4 (d, ^2J(C,P) = 5.6 Hz), 65.6 (d, ^2J(C,P) = 6.1 Hz), 75.3, 75.6, 123.9 (d, ^3J(C,P) = 7.3 Hz), 134.5; IR (neat) 3470 w, 3240 w, 2978 s, 2910 s, 2740 w, 2488 w, 1868 w, 1667 w, 1444 s, 1390 s, 1370 s, 1267 s, 1161 s, 1095 s, 1036 s, 862 m, 798 m, 750 m; MS, *m*/*z* (relative intensity, %) 274 (0.1) [M^+], 155 (66), 127 (41), 120 (17), 105 (63), 99 (100), 91 (26), 81 (15), 79 (16), 77 (17), 65 (10), 53 (14); exact mass calcd for $C_{13}H_{23}O_4P$ 274.1334, found 274.1336.

2-(2-Butynyl)-5,5-dimethyl-cyclohex-2-en-1-yl Diethyl Phosphate (1i). 2-(2-butynyl)-5,5-dimethyl-cyclohex-2-en-1-one was prepared, using a modification of the method described by Mattay.[9] To a mixture of 2-(2-butynyl)-5,5-dimethyl-cyclohex-2-en-1-one (38 mmol, 6.7 g), $CeCl_3 \cdot 7H_2O$ (40 mmol, 15.0 g), and methanol (150 mL) was added portionwise $NaBH_4$ (40 mmol, 1.5 g) at 0 °C, the reaction mixture was stirred at room temperature for 12 hours. 1N HCl (80 mL) was added, and the resulting solution was concentrated *in vacuo*. The concentrate was extracted with ether (80 mL x 2), and the combined organic solution was dried over $MgSO_4$. After removal of volatiles, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 3/1, R_f 0.35) to give 2-(2-butynyl)-5,5-dimethyl-cyclohex-2-en-1-ol (4.0 g, 60 %) as a pale yellow oil.

To a solution of 2-(2-butynyl)-5,5-dimethyl-cyclohex-2-en-1-ol (23 mmol, 4.0 g), pyridine (50 mmol, 4.0 mL) and CH_2Cl_2 (30 mL) was added dropwise diethyl chlorophosphate (30 mmol, 4.6 mL) at 0 °C, and the mixture was stirred at room temperature for 12 hours. Diethyl ether (50 mL) and 1N HCl (40 mL) were added to the resulting suspension, and the organic layer was separated. The ether was washed with 1N HCl (40 mL), and saturated $NaHCO_3$ (40 mL x 2), and dried over $MgSO_4$. After removal of the volatile, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 2/1, R_f 0.13) to give 2-(2-butynyl)-5,5-dimethyl-2-cyclohexyl diethyl phosphate (**1i**) (4.3 g, 59 % yield). Pale yellow oil; R_f 0.13 (hexane/EtOAc = 2/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.94 (s, 3H), 1.01 (s, 3H), 1.34 (td, ^4J(H,P) = 2.7 Hz, ^3J(H,H) = 7.3 Hz, 6H), 1.69-2.00 (m, 4H), 1.83 (t, ^5J(H,H) = 2.4 Hz, 3H), 3.00 (q, ^2J(H,H) = 19.4 Hz, 2H), 4.08-4.19 (m, 4H), 4.88 (q, ^3J(H,P) = 6.7 Hz, 1H), 5.92 (brs, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 3.4, 16.1 (d, ^3J(C,P) = 7.0 Hz), 22.7, 27.2, 29.6, 30.2, 39.0, 42.9, 62.5 (d, ^2J(C,P) = 6.2 Hz), 74.8 (d, ^2J(C,P) = 6.1 Hz), 75.6, 78.5, 126.5, 130.8 (d, ^3J(C,P) = 7.9 Hz); IR (neat) 3478 w, 2954 m, 2832 w, 1636 w, 1457 w, 1391 m, 1367 m, 1260 s, 1164 m, 1097 m, 1033 s, 986 s, 923 m, 884 w, 816 w, 751 w, 604 w; MS, *m*/*z* (relative intensity, %) 314 (0.9) [M^+], 160 (52), 155 (76), 145 (65), 127 (53), 117 (24), 107 (26), 105 (25), 99 (100), 91 (42), 81 (22), 77 (22), 53 (39); exact mass calcd for $C_{16}H_{27}O_4P$ 314.1647, found 314.1653.

[2-(2-Butynyl)-2-methyl-cyclohex-6-en-1-yl]-methyl Diethyl Phosphate (1j). To a solution of ^{t}BuOK (55 mmol, 6.2 g) in ^{t}BuOH (100 mL) was added dropwise 2-methylcyclohexanone (50 mmol, 5.6 g) at 60 °C, the reaction mixture was stirred at the same temperature for 30 min. 1-Bromo-2-butyne[2] (70 mmol, 7.3 g) was added over 10 min. at 50 °C, the resulting mixture was refluxed for 20 hours. H_2O (80 mL) was added, and the resulting solution was concentrated *in vacuo*. The concentrate was extracted with ether (80 mL x 2), and the combined organic solution was dried over $MgSO_4$. After removal of volatiles, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 4/1, R_f 0.44) to give 2-(2-butynyl)-2-methyl-cyclohexanone (3.4 g, 41 %).

1-(2-butynyl)-2-hydroxymethyl-1-methyl-cyclohex-2-en was prepared, using a modification of the method described by and Di Grandi.[11] A mixture of 2-(2-butynyl)-2-methyl-cyclohexanone (15 mmol, 2.4 g), hydrazine monohydrate (250 mmol, 8 mL), triethylamine (21 mmol, 3 mL), and ethanol (150 mL) was stirred at 100 °C for 20 hours. The solvent and excess reagents were removed *in vacuo*, the residue was subjected to column chromatography on silica gel (eluent; ether/triethylamine = 99/1, R_f 0.43) to give hydrazone. To a mixture of hydrazone (13 mmol, 2.3 g), DBN (85 mmol, 10.5 g), and ether (60 mL) was added dropwise a solution of I_2 (26 mmol, 6.6 g) in ether (60 mL), the reaction mixture was stirred at room temperature for 12 hours. The ether was washed with saturated $NaHCO_3$ (60 mL), dried over K_2CO_3, and concentrated *in vacuo*. The concentrate was dissolved in benzene (50 mL), and refluxed in the presence of DBN (3 g) for 12 hours. The mixture was poured into ether (60 mL) and washed with 1N $Na_2S_2O_3$ (100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 20/1, R_f 0.56) to give 1-(2-butynyl)-2-iodo-1-methyl-cyclohex-2-en. To a solution of vinyl iodide (8.7 mmol, 2.4 g) in dry THF (15 mL) was added ^{t}BuLi (1.49 M in pentane, 18 mmol) at -78 °C, the resulting bright yellow suspension was stirred at the same temperature for 20 min. Paraformaldehyde (80 mmol, 2.4 g) was added one portion, the mixture was stirred for 3 hours. 1N HCl (40 mL) was added, and extracted with ether (30 mL x 2) The combined organic solution was dried over $MgSO_4$. After removal of volatiles, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 4/1, R_f 0.21) to give 1-(2-butynyl)–2 -hydroxymethyl-1-methyl-cyclohex-2-en (332 mg, 18 %) as a clear oil.

To a solution of 1-(2-butynyl)-2-hydroxymethyl-1-methyl-cyclohex-2-en (2 mmol, 332 mg), pyridine (4 mmol, 0.3 mL) and CH_2Cl_2 (2 mL) was added diethyl chlorophosphate (3 mmol, 0.4 mL) at 0 °C, and the mixture was stirred at room temperature for 12 hours. Diethyl ether (10 mL) and 1N HCl (10 mL) were added to the resulting suspension, and the organic layer was separated. The ether was washed with 1N HCl (10 mL), and saturated $NaHCO_3$ (10 mL), and dried over $MgSO_4$. After removal of the volatile, the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 3/1, R_f 0.13) to give [2-(2-butynyl)-2-methyl-cyclohex-6-en-1-yl]-methyl diethyl phosphate (**1j**) (252 mg, 42 % yield) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.13 (s, 3H), 1.34 (td, ^4J(H,P) = 1.1 Hz, ^3J(H,H) = 7.0 Hz, 6H), 1.39-1.44 (m, 1H), 1.60-1.68 (m, 2H), 1.78 (t, ^5J(H,H) = 2.4 Hz, 3H), 1.81-1.89 (m, 1H), 2.02-2.09 (m, 2H), 2.27 (q, ^5J(H,H) = 2.4 Hz, 2H), 4.11 (dq, ^3J(H,H) = 7.0 Hz, ^3J(H,P) = 7.6 Hz, 4H), 4.52 (dt, ^4J(H,H) = 1.4 Hz, ^3J(H,P) = 5.9 Hz, 2H), 5.83 (t, ^4J(H,H) = 1.4 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 3.4, 16.1 (d, ^3J(C,P) = 6.7 Hz), 18.4, 25.5, 25.6, 30.1, 35.4, 36.2, 63.6 (d, ^2J(C,P) = 5.6 Hz), 68.7 (d, ^2J(C,P) = 5.6 Hz), 76.3, 77.4, 129.2, 138.0 (d, ^3J(C,P) = 7.3 Hz); IR (neat) 3458 w, 3256 w, 2922 s, 1837 w, 1655 w, 1447 m, 1390 m, 1369 m, 1265 s, 1190 w, 1162 m, 1021 s, 858 w, 803 w, 751 w, 601 w; MS, *m/z* (relative intensity, %) 314 (2) [M^+], 261 (17), 160 (28), 155 (100), 145 (18), 127 (35), 107 (20), 99 (31), 91 (11); exact mass calcd for $C_{16}H_{27}O_4P$ 314.1643, found 314.1645.

Typical Procedure. A 50-mL resealable Schlenk tube was flame-dried under a stream of nitrogen. The flask was charged with 2-methylene-4-hexyn-1-yl diethyl phosphate (**1a**) (0.5 mmol, 123 mg), $[(\pi\text{-}C_3H_5)PdCl]_2$ (0.01 mmol, 3.7 mg), dicyclohexylmethylamine (1.0 mmol, 0.2 mL), and THF (2 mL), and a three-way stopcock, which connected to a vacuum line and a balloon filled with carbon monoxide, was attached to the flask. The system was carefully evacuated and refilled with carbon monoxide four times and then filled with carbon monoxide (1 atm). Finally it was sealed and immersed in an oil bath at 80 °C. After 40 hours had elapsed, the flask was removed from the oil bath and allowed to cool for 1 h, after which the CO was released. The contents were transferred to a 100-mL round-bottomed flask and volatiles were removed *in vacuo*. The residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 20/1) to give 4,5-dihydro-3-methyl-5-methylene-2*H*-cyclopenta[*b*]furan-2-one (**2a**) (54 mg, 73 % yield) as a white solid.

4,5-Dihydro-3-methyl-5-methylene-2*H*-cyclopenta[*b*]furan-2-one (2a). White solid; mp 69-73 °C (hexane); R_f 0.47 (hexane/EtOAc = 3/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.95 (s, 3H), 3.31 (m, 2H), 5.09 (s, 1H), 5.24 (s, 1H), 6.07 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 9.2, 29.3, 108.6, 112.2, 113.7, 148.2, 157.8, 159.8, 173.4; IR (KBr) 3524 w, 2936 w, 1944 w, 1922 w, 1770 s, 1660 s, 1614 s, 1498 w, 1406 m, 1374 m, 1306 m, 1246 w, 1232 m, 1184 m, 1106 w, 1050 w, 972 m, 918 w, 858 s, 748 m, 722 w, 674 w, 660 w, 646 w; MS, *m*/*z* (relative intensity, %) 148 (80) [M^+], 120 (26), 91 (100), 67 (49), 65 (15), 53 (25), 51 (24), 50 (16); Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.72; H, 5.55.

4,5-Dihydro-3-butyl-5-methylene-2*H*-cyclopenta[*b*]furan-2-one (2b). Colorless oil; R_f 0.51 (hexane/EtOAc = 4/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.94 (t, ^3J(H,H) = 7.3 Hz, 3H), 1.29-1.43 (m, 2H), 1.53-1.64 (m, 2H), 2.37 (t, ^3J(H,H) = 7.6 Hz, 2H), 3.35 (brs, 2H), 5.08 (brs, 1H), 5.23 (brs, 1H), 6.07 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 22.4, 24.0, 29.3, 29.7, 108.4, 112.1, 118.4, 148.6,157.4, 160.1, 173.2; IR (neat) 3524 w, 3038 w, 2932 m, 2864 m, 1780 s, 1656 m, 1612 m, 1462 w, 1408 m, 1382 w, 1236 w, 1210 w, 1184 w, 1062 w, 1006 w, 934 w, 868 s, 764 w, 722 w, 650 w, 618 w; MS, *m*/*z* (relative intensity, %) 190 (86) [M^+], 162 (16), 161 (30), 148 (48), 147 (90), 134 (24), 133 (21), 121 (30), 120 (38), 119 (81), 105 (19), 91 (100), 79 (22), 78 (16), 77 (38), 67 (68), 66 (19), 64 (61), 63 (19), 55 (28), 53 (24), 52 (22), 51 (45), 50 (19); exact mass calcd. for $C_{12}H_{14}O_2$ 190.0994, found 190.0992.

4,5-Dihydro-3-cyclohexyl-5-methylene-2*H*-cyclopenta[*b*]furan-2-one (2c). Colorless oil; R_f 0.51 (hexane/EtOAc = 4/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.13-1.44 (m, 5H), 1.70-2.00 (m, 5H), 2.39-2.51 (m, 1H), 3.39 (brs, 2H), 5.06 (brs, 1H), 5.21 (s, 1H), 6.06 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.9, 26.0, 30.4, 31.2, 34.8, 108.2, 112.0, 123.1, 148.9, 156.0, 160.3, 172.7; IR (neat) 3088 w, 2920 s, 2852 m, 1770 s, 1690 w, 1644 s, 1612 s, 1452 m, 1408 m, 1370 m, 1326 w, 1280 w, 1244 w, 1212 m, 1184 m, 1138 w, 1072 w, 1030 w, 978 m, 902 s, 868 s, 798 w, 770 w, 736 w, 654 w; MS, *m*/*z* (relative intensity, %) 216 (100) [M^+], 160 (50), 145 (23), 134 (56), 92 (20), 91 (58), 79 (23), 78 (26), 77 (39), 67 (68), 65 (26), 55 (30), 53 (22), 51 (33); exact mass calcd. for $C_{14}H_{16}O_2$ 216.1150, found 216.1149.

4,5-Dihydro-3-(1,1-dimethylethyl)-5-methylene-2*H*-cyclopenta[*b*]furan-2-one (2d). White solid; mp 74-75 °C (hexane); R_f 0.51 (hexane/EtOAc = 4/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.31 (s, 9H), 3.45 (t, ^4J(H,H) = 1.4 Hz, 2H), 5.06 (brs, 1H), 5.20 (brs, 1H), 6.05 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 28.4, 31.4, 31.8, 108.1, 111.8, 126.4, 148.6, 155.2, 159.7, 171.2; IR (KBr) 3092 w, 2984 m, 1884 w, 1764 s, 1644 s, 1610 s, 1484 w, 1464 w, 1410 m, 1382 w, 1364 m, 1310 m, 1264 w, 1240 w, 1198 m, 982 m, 950 w, 902 s, 878 s, 860 m, 810 w, 774 w, 738 w, 684 w, 662 w; MS, *m*/*z* (relative intensity, %) 190 (55) [M$^+$], 175 (100), 148 (37), 147 (57), 119 (19), 91 (40), 77 (26), 67 (34), 65 (15), 58 (16), 55 (16), 53 (17), 51 (29); exact mass calcd. for $C_{12}H_{14}O_2$ 190.0994, found 190.0994.

4,5-Dihydro-3-methyl-5-pentylidene-2*H*-cyclopenta[*b*]furan-2-one (2e). Reaction of **1e** (or **1f**) gave the same product (**2e**) as a 1:2 mixture of *E*- and *Z*-isomers. The ratio of the two isomers was determined by ^{1}H NMR analysis, and the stereochemistry of **2e** was determined by NOE enhancement. All spectral data were obtained from a mixture of *E*- and *Z*-isomers. Colorless oil; R_f 0.31 (hexane/EtOAc = 10/1); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.89-0.96 (m, 3H), 1.34-1.47 (m, 4H), 1.94 (t, ^5J(H,H) = 1.4 Hz, 3H), [2.17 (q, ^3J(H,H) = 7.3 Hz, *E*-isomer), 2.23 (q, ^3J(H,H) = 7.3 Hz, *Z*-isomer), 2H], 3.24-3.30 (m, 2H), [5.49 (q, ^3J(H,H) = 7.3 Hz, *Z*-isomer), 5.65 (q, ^3J(H,H) = 7.3 Hz, *E*-isomer), 1H], [6.02 (s, *E*-isomer), 6.28 (s, *Z*-isomer), 1H]; ^{13}C NMR (68 MHz, $CDCl_3$) δ 9.2, [13.9 (*Z*-isomer), 14.0 (*E*-isomer)], [22.3 (*Z*-isomer), 22.4 (*E*-isomer)], [31.6 (*E*-isomer), 32.0 (*Z*-isomer)], [29.2 (*Z*-isomer), 29.4 (*E*-isomer)], [29.5 (*Z*-isomer), 26.8 (*E*-isomer)], [108.9 (*E*-isomer), 113.2 (*Z*-isomer)], 112.8, 112.9, [125.4 (*Z*-isomer), 126.3 (*E*-isomer)], 139.7, 141.0, 157.6, 157.7, 157.8, 158.8, [173.8 (*Z*-isomer), 173.9 (*E*-isomer)]; IR (neat) 3528 w, 3092 w, 2928 s, 2860 m, 2736 w, 2248 w, 1932 w, 1768 s, 1660 s, 1612 s, 1498 w, 1462 m, 1412 m, 1380 m, 1298 m, 1234 m, 1192 w, 1092 w, 1042 w, 966 s, 856 s, 746 m, 720 w, 650 w; MS, *m*/*z* (relative intensity, %) 204 (19) [M^+], 162 (12), 161 (100), 148 (15), 133 (33), 105 (23), 103 (10), 91 (13), 79 (19), 77 (23), 65 (11), 55 (13), 53 (18), 51 (15); exact mass calcd. for $C_{14}H_{16}O_2$ 204.1150, found 204.1141.

4,5-Dihydro-5-benzylidene-3-methyl-2*H*-cyclopenta[*b*]furan-2-one (2g). Reaction of **1g** gave the product (**2g**) as a 1:1 mixture of *E*- and *Z*-isomers. The ratio of the two isomers was determined by ^1H NMR analysis, and the stereochemistry of **2g** was determined by NOE enhancement. All spectral data were obtained from a mixture of *E*- and *Z*-isomers. Yellow solid; R_f 0.45 (hexane/EtOAc = 4/1); ^1H NMR (270 MHz, $CDCl_3$, TMS) δ 1.99 (s, 3H), [3.45 (s, *Z*-isomer), 3.60 (s, *E*-isomer), 2H], [6.18 (s, *E*-isomer), 6.62 (s, *Z*-isomer), 1H], [6.58 (s, *E*-isomer), 6.50 (s, *Z*-isomer), 1H], 7.21-7.38 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 9.3, [28.9 (*E*-isomer), 30.6 (*Z*-isomer)], [109.5 (*Z*-isomer), 114.9 (*E*-isomer)], [123.9 (*Z*-isomer), 124.8 (*E*-isomer)], 114.0, 127.2, 128.2, 128.3, 128.6, 128.7, 136.9, 141.4, 142.5, 156.6, 157.7, 158.4, 161.7, 173.8; IR (KBr) 3084 w, 1758 s, 1654 m, 1590 m, 1496 w, 1454 w, 1408 w, 1378 w, 1298 w, 1248 m, 1192 w, 1144 w, 1046 w, 970 m, 918 w, 896 w, 858 m, 748 m, 722 w, 688 w, 658 w; MS, *m*/*z* (relative intensity, %) 224 (100) [M^+], 196 (23), 195 (16), 181 (32), 167 (30), 165 (22), 153 (36), 152 (28), 115 (54), 89 (23), 83 (25), 82 (17), 77 (15), 65 (17), 63 (23), 53 (27), 51 (27); exact mass calcd. for $C_{15}H_{12}O_2$ 224.0837, found 224.0842.

4,5-Dihydro-3-methyl-5-(1-methylethylidene)-2*H*-cyclopenta[*b*]furan-2-one (2h). White solid; mp 147-148 °C (hexane); R_f 0.44 (hexane/EtOAc = 4/1); ^1H NMR (270 MHz,

$CDCl_3$, TMS) δ 1.83 (s, 3H), 1.88 (s, 3H), 1.93 (s, 3H), 3.22 (s, 2H), 6.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 9.0, 20.9, 21.2, 28.0, 110.4, 112.2, 128.2, 135.2, 157.4, 158.0, 174.2; IR (KBr) 3820 w, 3798 w, 3650 w, 3502 w, 3112 w, 2968 w, 2926 m, 2856 w, 1941 w, 1759 s, 1653 s, 1606 s, 1494 m, 1438 m, 1411 m, 1378 m, 1316 m, 1255 s, 1139 w, 1098 w, 1048 w, 971 m, 897 w, 871 m, 863 m, 810 w, 745 m, 722 w, 679 w, 653 m; MS, *m*/*z* (relative intensity, %) 176 (100) [M^+], 161 (62), 133 (66), 105 (57), 91 (26), 79 (20), 77 (27), 67 (23), 65 (23), 58 (16), 53 (31), 52 (21), 51 (48), 50 (20); exact mass calcd. for $C_{11}H_{12}O_2$ 176.0837, found 176.0838.

4,6,7,8-Tetrahydro-7,7-dimethyl-2*H*-indeno[1,2-*b*]furan-2-one (2i). White solid; mp 116-117 °C (hexane); R_f 0.50 (hexane/EtOAc = 3/1); ^1H NMR (270 MHz, $CDCl_3$, TMS) δ 0.99 (s, 6H), 1.93 (s, 3H), 2.09 (d, ^4J(H,H) = 4.3 Hz, 2H), 2.36 (s, 2H), 3.23 (s, 2H), 5.72 (t, ^4J(H,H) = 4.3 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 9.2, 27.5, 28.5, 30.9, 35.6, 39.3, 111.2, 120.0, 123.4, 139.7, 153.1, 158.0, 174.3; IR (KBr) 3034 m, 2958 m, 2870 m, 1937 w, 1761 s, 1661 s, 1642 s, 1495 w, 1473 w, 1458 w, 1435 w, 1413 s, 1387 m, 1378 m, 1364 m, 1338 w, 1285 s, 1259 m, 1195 w, 1183 w, 1152 w, 1121 w, 1089 w, 1019 w, 978 s, 941 m, 929 m, 906 w, 891 w, 868 m, 815 m, 784 m, 745 m, 719 w, 694 w, 671 w, 661 w; MS, *m*/*z* (relative intensity, %) 216 (100) [M^+], 201 (73), 188 (20), 187 (17), 173 (77), 159 (18), 145 (41), 129 (18), 128 (19), 117 (18), 115 (31), 105 (24), 91 (45), 79 (27), 78 (18), 77 (34), 70 (16), 67 (22), 65 (39), 64 (26), 63 (21), 53 (46), 52 (16), 51 (41); Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.61; H, 7.53.

4a,5,6,7,-Tetrahydro-3,4a-dimethyl-naphtho[2,3-*b*]furan-2(4*H*)-one (2j). White solid; mp 102-103 °C (hexane); R_f 0.43 (hexane/EtOAc = 4/1); ^1H NMR (270 MHz, $CDCl_3$, TMS) δ 1.11 (s, 6H), 1.54-1.87 (m, 4H), 1.90 (d, ^5J(H,H) = 1.6 Hz, 3H), 2.18-2.26 (m, 2H), 2.35 (d, ^2J(H,H) = 17 Hz, 1H), 2.60 (d, ^2J(H,H) = 17 Hz, 1H), 5.79 (t, ^4J(H,H) = 3.8 Hz, 1H), 5.93 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 8.4, 17.9, 25.8, 26.0, 34.4, 37.1, 37.2, 109.3, 120.4, 130.6, 138.3, 147.3, 147.8, 171.4; IR (KBr) 2932 m, 1754 s, 1646 m, 1622 m, 1454 w, 1382 w, 1359 w, 1317 w, 1293 w, 1246 w, 1215 m, 1122 w, 1072 w, 1049 w, 1008 m, 991 m, 927 w, 901 w, 882 w, 858 w, 755 w, 629 w; MS, *m*/*z* (relative intensity, %) 216 (100) [M^+], 201 (99), 173 (28), 145 (28), 124 (31), 115 (24), 93 (21), 91 (46), 79 (23), 77 (28), 65 (23), 53 (33), 51 (26); exact mass calcd. for $C_{14}H_{16}O_2$ 216.1150, found 216.1147.

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