## **Supporting Information**

Dienyl Homoallyl Alcohols via Palladium Catalyzed Ene-Type Reaction of

Aldehydes with 1,3-Dienes

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## **Experimental Section**

Reactions employed oven-dried glassware unless otherwise noted. Thin layer

chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck,

Silica gel 60F<sub>254</sub>). Flash chromatography columns were packed with 230-400 mesh silica

gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a

continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data

were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical

shift values were given in ppm downfield from the internal standard. Infrared spectra were

recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra

(HRMS) were measured with a JEOL JMS-DX303.

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## **Solvents and Reagents**

Tetrahydrofuran was dried and distilled from benzophenone and sodium immediately prior to Pd(OAc)<sub>2</sub>, use under nitrogen atmosphere. PPh<sub>3</sub>, dppf [2,2'-bis(diphenylphosphino)diphenyl [1,1'-bis(diphenylphosphino)ferrocene], **DPEphos** Ether], **BINAP** [2,2'-bis(diphenylphosphino)-1,1'-binaphthyl], Xantphos [4,5-bis(diphenylphosphino)-9,9-dimethylxanthene ] (Aldrich), Et<sub>3</sub>B (1.0 M THF solution), n-Bu<sub>3</sub>B (1.0 M THF solution), Ph<sub>3</sub>B (0.25 M THF solution), Et<sub>2</sub>Zn (1.0 M hexane solution) (Aldrich) were purchased and used without further purification. Isoprene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, myrcene, and methyl sorbate (Tokyo Kasei Kogyo Co., Ltd) were purchased and distilled prior to use. Benzaldehyde, p-methoxybenzaldehyde, p-chlororbenzaldehyde, dihydrocinnamaldehyde, isovaleraldehyde, cyclohexanecarbaldehyde (Aldrich) were purchased and distilled prior to use by Kugelrohr apparatus. 2-Hydroxy tetrahydrofuran and 2-hydroxy tetrahydropyran were prepared according to the literature.1

General procedure for the Pd-catalyzed coupling reaction of aldehyde with isoprene (run 6, Table 1): To a solution of  $Pd(OAc)_2$  (22.4 mg, 0.1 mmol) and Xantphos (57.8 mg, 0.1 mmol) in dry THF (5 mL) were successively added benzaldehyde (106 mg, 1 mmol), isoprene (400 mL, 4 mmol), and triethylborane (2 mmol, 1.0 M THF solution) via syringe under nitrogen atmosphere. The mixture was stirred at ambient temperature for 24 h. The mixture was diluted with 30 mL of EtOAc and washed with 2 N HCl, sat. NaHCO<sub>3</sub>, and then brine. The extract was dried (MgSO<sub>4</sub>) and concentrated in vacuo and the residual oil was subjected to column chromatography over silica gel (hexane/EtOAc = 10/1 v/v) to give 1a (173 mg, 99%,  $R_f = 0.47$ ; hexane/ethyl acetate = 4/1 v/v).

**3-Methylene-1-phenylpent-4-en-1-ol (1a)**; IR (neat): 3381 (br), 3030 (m), 2930 (m), 1597 (m), 1495 (w), 1454 (m), 1377 (w), 1194 (w), 1043 (m), 893 (s), 760 (m), 700 (s) cm<sup>-1</sup>;  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.10 (br s, 1 H), 2.58 (dd, J = 14.1, 9.0 Hz, 1 H), 2.67 (dd, J = 14.1, 4.1 Hz, 1 H), 4.83 (dd, J = 9.0, 4.1 Hz, 1 H), 5.09 (s, 1 H), 5.13 (d, J = 10.7 Hz, 1 H), 5.15 (s, 1 H), 5.32 (d, J = 17.6 Hz, 1 H), 6.41 (dd, J = 17.6, 10.7 Hz, 1 H), 7.23-7.39 (m, 5 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  42.2, 72.2, 114.2, 118.7, 125.7, 127.4, 128.3, 138.2, 142.6, 144.0. High-resolution MS, calcd for  $C_{12}H_{14}O$ : 174.1045. Found m/z (relative intensity): 174.0988 (M<sup>+</sup>, 6.9), 188.1178 (100).

**4-Methyl-3-methylene-1-phenylpent-4-en-1-ol** (**1b**); IR (neat): 3381 (br), 3082 (w), 3032 (w), 2947 (m), 1805 (w), 1599 (s), 1495 (m), 1452 (s), 1190 (w), 1041 (s), 895 (s), 760 (m), 700 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.95 (s, 3 H), 2.04 (brs, 1 H), 2.58 (dd, J = 14.1, 9.5 Hz, 1 H), 2.79 (dd, J = 14.1, 3.8 Hz, 1 H), 4.82 (dd, J = 9.5, 3.8 Hz, 1 H), 5.07 (s, 2 H), 5.19 (s, 1 H), 5.24 (s, 1 H), 7.25-7.39 (m, 5 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  21.1, 44.6, 72.5, 113.6, 115.4, 125.7, 127.4, 128.3, 142.2, 144.1, 144.3. High-resolution MS, calcd for  $C_{13}H_{16}O$ : 188.1201. Found m/z (relative intensity): 188.1171 (M<sup>+</sup>, 100).

(*E*)-3-Methylene-1-phenylhex-4-en-1-ol (1c); IR (neat): 3395 (br), 3032 (m), 2910 (m), 2876 (m), 1649 (w), 1605 (m), 1493 (w), 1452 (m), 1051 (w), 966 (w), 756 (m), 700 (s) cm<sup>-1</sup>;  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.80 (d, J = 6.7 Hz, 3 H), 2.07 (d, J = 2.4 Hz, 1 H), 2.51 (dd, J = 14.0, 9.4 Hz, 1 H), 2.69 (dd, J = 14.0, 3.6 Hz, 1 H), 4.82 (ddd, J = 9.4, 3.6, 2.4 Hz, 1 H), 4.95 (s, 1 H), 5.04 (s, 1 H), 5.83 (dq, J = 15.7, 6.7 Hz, 1 H), 6.12 (d, J = 15.7 Hz, 1 H), 7.27-7.39 (m, 5 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  18.4, 43.3, 72.1, 116.0, 125.7, 126.1, 127.4, 128.3, 132.7, 142.5, 144.1. High-resolution MS, calcd for  $C_{13}H_{16}O$ : 188.1201. Found m/z (relative intensity): 188.1171 (M<sup>+</sup>, 100).

**7-Methyl-1-phenyl-3-vinylocta-3,6-dien-1-ol** (**1d**); (Z : E = 3 : 1); IR (neat): 3383 (br), 3086 (w), 2970 (m), 2914 (s), 2856 (m), 1636 (w), 1593 (w), 1495 (m), 1452 (s), 1375 (m), 1026 (m), 905 (m), 756 (m), 700 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> Z isomer)  $\delta$  1.63 (s, 3 H), 1.69 (d, J = 1.2 Hz, 3 H), 2.01 (d, J = 2.2 Hz, 1 H), 2.44 (dd, J = 13.9, 9.5 Hz, 1 H), 2.71 (dd, J = 13.9, 3.9 Hz, 1 H), 2.88 (t, J = 7.2 Hz, 2 H), 4.80 (ddd, J = 9.5, 3.9, 2.2 Hz, 1 H), 5.07 (tq, J = 7.2, 1.2 Hz, 1 H), 5.20 (d, J = 11.0 Hz, 1 H), 5.35 (d, J = 17.6 Hz, 1 H), 5.43 (t, J = 7.2 Hz, 1 H), 6.74 (dd, J = 17.6, 11.0 Hz, 1 H), 7.26-7.38 (m, 5 H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> E isomer)  $\delta$  1.59 (s, 3 H), 1.68 (d, J = 1.2 Hz, 3 H), 1.96 (d, J = 2.4 Hz, 1 H), 2.64 (dd, J = 13.8, 5.0 Hz, 1 H), 2.77 (dd, J = 13.8, 8.7 Hz, 1 H), 2.88 (t, J = 7.2 Hz, 2 H), 4.84 (ddd, J = 8.2, 5.0, 2.4 Hz, 1 H), 4.99 (tq, J = 7.2, 1.2 Hz, 1 H), 5.02 (d, J = 11.0 Hz, 1 H), 5.24 (d, J = 17.9 Hz, 1 H), 5.52 (t, J = 7.2 Hz, 1 H), 6.34 (dd, J = 17.9, 11.0 Hz, 1 H), 7.26-7.38 (m, 5 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, Z isomer) δ 17.8, 25.6, 26.7, 44.2, 72.1, 114.3, 121.8, 125.7, 127.2, 128.2, 132.2, 132.3, 132.4, 132.7, 144.1;  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>, E isomer)  $\delta$  17.7, 25.6, 27.5, 44.2, 72.9, 114.3, 121.6, 125.6, 127.3, 128.2, 132.2, 132.3, 132.4, 132.7, 144.2. High-resolution MS, calcd for  $C_{17}H_{22}O$ : 242.1671. Found m/z (relative intensity): 242.1667  $(M^+, 37.4), 226.1681 (100).$ 

(2*E*,4*E*)-Methyl 2-[hydroxyl(phenyl)methyl]hexa-2,4-dienoate (1e); IR (neat): 3487 (br), 3061 (w), 3032 (w), 2997 (m), 2961 (m), 2918 (m), 1695 (s), 1637 (s), 1602 (m), 1493 (m), 1435 (s), 1304 (m), 1236 (s), 1018 (m), 976 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.91 (dd, J = 7.0, 1.5 Hz, 3 H), 3.69 (s, 3 H), 4.11 (d, J = 8.7 Hz, 1 H), 5.81 (d, J = 8.7 Hz, 1 H), 6.27 (dq, J = 14.6, 7.0 Hz, 1 H), 6.57 (ddq, J = 14.6, 11.6, 1.5 Hz, 1 H), 7.21-7.37 (m, 6 H); <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.37 (dd, J = 6.8, 1.7 Hz, 3 H), 3.19 (s, 3 H), 4.22 (d, J = 10.5 Hz, 1 H), 5.71 (dq, J = 14.8, 6.8 Hz, 1 H), 5.95 (d, J = 10.5 Hz, 1 H), 6.35 (ddq, J = 14.8, 11.5, 1.7 Hz, 1 H), 7.05 (t, J = 7.4 Hz, 2 H), 7.18 (d, J = 7.4 Hz, 1 H), 7.34 (d, J = 11.5 Hz, 1 H), 7.56 (d, J = 7.4 Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  19.0, 51.7, 69.7, 125.2, 126.0, 126.9,

128.1, 128.4, 140.8, 141.6, 142.8, 167.9. High-resolution MS, calcd for  $C_{14}H_{16}O$ : 232.1099. Found m/z (relative intensity): 232.1084 (M<sup>+</sup>, 100).

NOE Increment of irradiation at the bold face proton of compound 1e ( $C_6D_6$ ).

**1-(4-Methoxyphenyl)-3-methylenepent-4-en-1-ol (1f)**; IR (neat): 3406 (br), 3086 (w), 2912 (m), 2835 (m), 1612 (m), 1593 (m), 1514 (s), 1248 (s), 1175 (m), 1036 (m), 901 (m), 831 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.98 (d, J = 2.1 Hz, 1 H), 2.57 (dd, J = 14.1, 9.0 Hz, 1 H), 2.67 (dd, J = 14.1, 4.3 Hz, 1 H), 3.80 (s, 3 H), 4.80 (ddd, J = 9.0, 4.3, 2.1 Hz, 1 H), 5.08 (s, 1 H), 5.13 (d, J = 10.7 Hz, 1 H), 5.16 (s, 1 H), 5.32 (d, J = 17.6 Hz, 1 H), 6.40 (dd, J = 17.6, 10.7 Hz, 1 H), 6.88 (d, J = 8.5 Hz, 2 H), 7.30 (d, J = 8.5 Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  41.5, 54.7, 71.2, 113.1, 113.5, 118.0, 126.3, 135.6, 137.7, 142.1, 158.4. High-resolution MS, calcd for  $C_{13}H_{16}O_2$ : 204.1150. Found m/z (relative intensity): 204.1150 (M<sup>+</sup>, 83.1), 137.0560 (100).

**1-(4-Chlorophenyl)-3-methylenepent-4-en-1-ol** (**1g**); IR (neat): 3369 (br), 3086 (w), 2931 (m), 2330 (w), 1595 (m), 1491 (s), 1090 (s), 1015 (s), 903 (s), 829 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.06 (br s, 1 H), 2.53 (dd, J = 14.1, 9.0 Hz, 1 H), 2.67 (dd, J = 14.1, 4.1 Hz, 1 H), 4.82 (dd, J = 9.0, 4.1 Hz, 1 H), 5.07 (s, 1 H), 5.15 (d, J = 10.8 Hz, 1 H), 5.17 (s, 1 H), 5.30 (d, J = 17.6 Hz, 1 H), 6.41 (dd, J = 17.6, 10.8 Hz, 1 H), 7.25-7.33 (m, 5 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  42.3, 71.5, 114.3, 118.9, 127.0, 128.4, 133.1, 138.0, 142.2, 142.3. High-resolution MS, calcd for  $C_{12}H_{13}ClO$ : 208.0655. Found m/z (relative intensity):

208.0626 (M<sup>+</sup>, 40.6), 193.0404 (100).

**5-Methylene-1-phenylhept-6-en-3-ol (1h)**; IR (neat): 3312 (br), 3050 (w), 3010 (w), 2922 (s), 2851 (m), 1620 (w), 1595 (m), 1508 (s), 1456 (m), 1246 (m), 1037 (m), 897 (m), 698 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.83 (m, 2 H), 2.28 (dd, J = 13.8, 9.0 Hz, 1 H), 2.53 (dd, J = 13.8, 3.8 Hz, 1 H), 2.70 (ddd, J = 13.8, 7.8, 8.6 Hz, 1 H), 2.84 (ddd, J = 13.8, 7.8, 8.6 Hz, 1 H), 3.79 (m, J = 9.0, 3.8 Hz, 1 H), 5.08 (s, 1 H), 5.09 (d, J = 10.8 Hz, 1 H), 5.16 (s, 1 H), 5.21 (d, J = 17.6 Hz, 1 H), 6.37 (dd, J = 17.6, 10.8 Hz, 1 H), 7.16-7.29 (m, 5 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  32.1, 38.8, 40.1, 69.0, 114.2, 118.3, 125.7, 128.3, 138.3, 141.9, 142.9. High-resolition MS, calcd for  $C_{14}H_{18}O$ : 202.1358. Found m/z (relative intensity): 202.1334 (M<sup>+</sup>, 9.9), 184.1227 (100).

**2-Methyl-6-methyleneoct-7-en-4-ol (1i)**; IR (neat): 3358 (br), 3088 (w), 2957 (s), 2931 (s), 2870 (m), 1595 (m), 1468 (m), 1367 (m), 1261 (m), 1022 (m), 991 (m), 897 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.92 (d, J = 6.8 Hz, 3 H), 0.94 (d, J = 6.3 Hz, 3 H), 1.28 (ddd, J = 13.8, 8.6, 4.3 Hz, 1 H), 1.46 (ddd, J = 13.8, 8.7, 5.4 Hz, 1 H), 1.82 (qqdd, J = 6.8, 6.3, 5.4, 4.3 Hz, 1 H), 2.21 (dd, J = 13.9, 8.9 Hz, 1 H), 2.48 (dd, J = 13.9, 3.9 Hz, 1 H), 3.82 (dddd, J = 8.9, 8.7, 8.6, 3.9 Hz, 1 H), 5.09 (s, 1 H), 5.11 (d, J = 10.7 Hz, 1 H), 5.15 (s, 1 H), 5.25 (d, J = 17.6 Hz, 1 H), 6.39 (dd, J = 17.6, 10.7 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  22.2, 23.5, 24.8, 40.7, 46.6, 67.7, 114.1, 118.2, 138.5, 143.2. High-resolution MS, calcd for C<sub>10</sub>H<sub>18</sub>O: 154.1358. Found m/z (relative intensity): 154.1325 (M<sup>+</sup>, 24.5), 135.1141 (100).

**1-Cyclohexyl-3-methylenepent-4-en-1-ol (1j)**; IR (neat): 3414 (br), 3086 (w), 2926 (s), 2852 (s), 1593 (m), 1450 (m), 1394 (w), 1261 (w), 1086 (w), 991 (m), 895 (m) cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.06-1.80 (m, 11 H), 1.90 (br s, 1 H), 2.14 (dd, J = 13.9, 10.0 Hz, 1 H), 2.59 (dd, J = 13.9, 2.7 Hz, 1 H), 3.50 (ddd, J = 10.0, 5.7, 2.7 Hz, 1 H), 5.08 (s, 1 H), 5.09 (d, J =

10.3 Hz, 1 H), 5.15 (s, 1 H), 5.23 (d, J = 17.6, 1 H), 6.38 (dd, J = 17.6, 10.3 Hz, 1 H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  26.7, 28.3, 29.2, 36.9, 43.6, 73.4, 114.1, 118.2, 138.4, 143.6. High-resolution MS, calcd for C<sub>12</sub>H<sub>20</sub>O: 180.1514. Found m/z (relative intensity): 180.1506 (M<sup>+</sup>, 29.5), 162.1354 (100).

**6-Methyleneoct-7-ene-1,4-diol** (**1k**); IR (neat): 3306 (br), 3086 (w), 2935 (s), 2872 (m), 2359 (w), 1703 (w), 1595 (s), 1435 (s), 1404 (s), 1227 (s), 999 (m), 899 (s), 748 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.67-1.83 (m, 4 H), 2.17 (s, 2 H), 2.29 (dd, J = 13.9, 9.0 Hz, 1 H), 2.50 (dd, J = 13.9, 3.8 Hz, 1 H), 3.68 (m, 2 H), 3.80 (ddm, J = 9.0, 3.8 Hz, 1 H), 5.10 (s, 1 H), 5.12 (d, J = 11.1 Hz, 1 H), 5.17 (s, 1 H), 5.26 (d, J = 17.6 Hz, 1 H), 6.39 (dd, J =17.6, 11.1 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  29.3, 34.1, 40.2, 62.9, 69.6, 114.2, 118.3, 138.3, 142.9. High-resolution MS, calcd for  $C_9H_{16}O_2$ : 156.1150. Found m/z (relative intensity): 156.1146 (M<sup>+</sup>, 87.9), 138.1017 (100).

**7-Methylenenon-8-ene-1,5-diol (1l)**; IR (neat): 3331 (br), 3088 (w), 2937 (s), 2864 (m), 1595 (m), 1437 (m), 1404 (m), 1072 (m), 1028 (m), 899 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.49-1.63 (m, 6 H), 2.23 (dd, J = 13.9, 8.9 Hz, 1 H), 2.51 (dd, J = 13.9, 3.8 Hz, 1 H), 3.66 (t, J = 6.2 Hz, 2 H), 3.75 (m, 1 H), 5.09 (s, 1 H), 5.11 (d, J = 10.9 Hz, 1 H), 5.15 (s, 1 H), 5.24 (d, J = 17.6 Hz, 1 H), 6.38 (dd, J = 17.6, 10.9 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  22.0, 32.7, 36.8, 40.2, 62.9, 69.5, 114.2, 118.3, 138.4, 143.1. High-resolution MS, calcd for  $C_{10}H_{18}O_2$ : 170.1307. Found m/z (relative intensity): 170.1304 (M<sup>+</sup>, 94.6), 137.0912 (100).

## Reference

1) S. Kodato, M. Nakagawa, K. Nakayama, T. Hino, Tetrahedron, 1989, 45, 7247.

















































