Supplementary Information

Palladium-catalyzed allylic alkenylation of allylic alcohols with *n*-butyl acrylate

Naofumi Tsukada, Tetsuo Sato and Yoshio Inoue

Materials. Commercially available chemicals were used as received except for *n*-butyl acrylate and the solvents, which were distilled from CaH_2.

General Procedure for the Alkenylation of Allylic Alcohols with *n*-Butyl Acrylate. To a suspension of $Pd_2(dba)_3)\cdot CHCl_3$ (13 mg, 0.0125 mmol), PCy_3 (7.0 mg, 0.025 mmol), and Ts_2O (0.6 mmol, 0.20 g) in *n*-butyl acrylate (4 mL) was added allyl alcohol (0.5 mmol) under nitrogen atmosphere in a pressure vial. After 12 h of heating at 80 °C, the mixture was filtered through a short silica gel column using ether as an eluent. Excess *n*-butyl acrylate was removed under reduced pressure (20 mmHg, 50 °C), and the 1,4-diene was purified by silica gel column chromatography. The isomers were separated, where possible, by preparative GC.

***n*-Butyl 2(*E*),5-hexadienoate 1.** ^{1}H NMR (500 MHz, $CDCl_3$) □ 6.97 (dt, *J* = 15.6, 6.6 Hz, 1H), 5.86 (dt, *J* = 15.6, 1.7 Hz, 1H), 5.82 (ddt, *J* = 17.7, 9.7, 6.6 Hz, 1H), 5.15 (dd, *J* = 9.7, 1.6 Hz, 1H), 5.11 (dd, *J* = 17.7, 1.6 Hz, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.95 (ddd, *J* = 6.6, 6.5, 1.7 Hz, 2H), 1.64 (tt, *J* = 9.6, 6.7 Hz, 2H), 1.40 (tq, *J* = 9.6, 7.5 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) □ 166.6, 146.3, 133.9, 122.2, 117.2, 64.2, 36.1, 30.7, 19.2, 13.7; IR (neat) 3082, 2960, 2874, 1428, 1656, 1466, 1428, 1386, 1326, 1274, 1214, 1173, 1115, 1065, 1029, 984, 919, 840 cm^{-1}; GC-MS m/e (relative intensity) 39 (43), 40 (11), 41 (100), 43 (12), 55 (12), 56 (23), 57 (21), 65 (10), 67 (57), 95 (56), 97 (11), 113 (38), 127 (3), 168 (M^+, 0.2); elemental analysis calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. found : C, 71.13; H, 9.71.

***n*-Butyl 2(*E*),4(*E*)-hexadienoate 2.** ^{1}H NMR (500 MHz, $CDCl_3$) □ 7.25 (dd, *J* = 15.4, 11.4 Hz, 1H), 6.16 (dd, *J* = 15.8, 11.4 Hz, 1H), 6.15 (dq, *J* = 15.8, 7.4 Hz, 1H), 5.77 (d, *J* = 15.4 Hz, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 1.86 (d, *J* = 7.4 Hz, 3H), 1.64 (tt, *J* = 7.0, 6.7 Hz, 2H), 1.40 (tq, *J* = 9.2, 7.0 Hz, 2H), 0.94 (t, *J* = 9.2 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) □ 167.4, 144.8, 139.1, 129.8, 119.1, 64.1, 30.8, 19.2, 18.6, 13.7; IR (neat) 3020,

2960, 2874, 1714, 1646, 1619, 1449, 1384, 1327, 1301, 1244, 1217, 1187, 1139, 1086, 1065, 1000, 930, 869, 800 cm^{-1}; GC-MS m/e (relative intensity) 39 (48), 40 (11), 41 (100), 43 (13), 55 (10), 65 (14), 66 (12), 67 (81), 95 (73), 97 (69), 112 (28), 114 (11), 153 (2), 168 (M^+, 7); elemental analysis calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. found : C, 71.12; H, 9.80.

***n*-Butyl 2(*E*),5(*E*)-nonadienoate 4a.** ^{1}H NMR (500 MHz, $CDCl_3$) □ 6.96 (dt, *J* = 15.6, 6.5 Hz, 1H), 5.82 (dt, *J* = 15.6, 1.7 Hz, 1H), 5.50 (dtt, *J* = 15.3, 6.7, 1.4 Hz, 1H), 5.40 (dtt, *J* = 15.3, 6.4, 1.2 Hz, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.88 (dddd, *J* = 6.5, 6.4, 1.4, 1.7 Hz, 2H), 2.00 (ddt, *J* = 6.7, 1.2, 7.5 Hz, 2H), 1.64 (tt, *J* = 7.5, 6.7 Hz, 2H), 1.39 (tq, *J* = 7.5, 7.4 Hz, 2H), 1.38 (tq, *J* = 7.5, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) □ 166.8, 147.6, 133.4, 125.2, 121.5, 64.1, 35.1, 34.6, 30.7, 22.4, 19.2, 13.7, 13.7; IR (neat) 2959, 2932, 2873, 1723, 1653, 1465, 1381, 1323, 1271, 1200, 1166, 1125, 1088, 1065, 1027, 972, 840 cm^{-1}; GC-MS m/e (relative intensity) 39 (37), 41 (100), 42 (10), 43 (17), 53 (16), 55 (31), 56 (11), 57 (25), 67 (47), 69 (11), 77 (10), 79 (23), 81 (15), 94 (10), 97 (24), 109 (16), 125 (4), 137 (6), 154 (8), 210 (M^+, 3); elemental analysis calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. found : C, 74.13; H, 10.38.

***n*-Butyl 6-phenyl-2(*E*),5(*E*)-hexadienoate 4b.** ^{1}H NMR (500 MHz, $CDCl_3$) □ 7.35 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.30 (ddd, *J* = 7.2, 7.1, 2.1 Hz, 2H), 7.22 (tt, *J* = 7.2, 1.4 Hz, 1H), 7.04 (dt, *J* = 15.7, 6.5 Hz, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 15.9, 6.8 Hz, 1H), 5.90 (dt, *J* = 15.7, 1.7 Hz, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 3.11 (ddd, *J* = 6.8, 6.5, 1.7 Hz, 2H), 1.64 (tt, *J* = 8.7, 6.7 Hz, 2H), 1.40 (tq, *J* = 8.7, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) □ 166.6, 146.4, 137.1, 132.5, 128.6, 127.4, 126.1, 125.4, 122.3, 64.2, 35.2, 30.7, 30.7, 19.2, 13.7; IR (neat) 3082, 3059, 3027, 2959, 2933, 2872, 1719, 1652, 1598, 1496, 1465, 1449, 1417, 1385, 1324, 1306, 1268, 1232, 1199, 1160, 1090, 1069, 1028, 966, 845, 743, 693 cm^{-1}; GC-MS m/e (relative intensity) 39 (52), 40 (11), 41 (100), 43 (14), 51 (20), 55 (21), 56 (18), 57 (34), 57 (25), 63 (13), 65 (26), 71 (18), 77 (18), 84 (51), 89 (10), 91 (37), 97 (99), 105 (24), 115 (60), 116 (16), 127 (11), 128 (83), 129 (17), 141 (44), 142 (56), 143 (60), 169 (15), 188 (11), 207 (17), 244 (M^+, 25); elemental analysis calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. found : C, 78.19; H, 8.30.

***n*-Butyl 6-methyl-2(*E*),5(*E*)-heptadienoate 4c.** Compound **4c** could not be separated from small amounts of isomers. The structure was determined by ^{1}H NMR. ^{1}H NMR

(500 MHz, $CDCl_3$) □ 6.92 (dt, *J* = 15.6, 6.3 Hz, 1H), 5.81 (dt, *J* = 15.6, 1.8 Hz, 1H), 5.15 (m, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.88 (m, 2H), 1.73 (d, *J* = 0.9 Hz, 3H), 1.67-1.60 (m, 2H), 1.62 (s, 3H), 1.45-1.35 (m, 2H), 0.94 (t, *J* = 7.4 Hz); GC-MS m/e (relative intensity) 39 (36), 41 (90), 43 (19), 53 (21), 55 (37), 57 (33), 67 (31), 79 (27), 84 (24), 95 (84), 97 (100), 111 (11), 123 (21), 125 (10), 140 (37), 196 (M^+, 23).

***n*-Butyl 4-methyl-2(*E*),5(*E*)-heptadienoate 4d.** Compound **4d** could not be separated from small amounts of isomers. The structure was determined by ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$) □ 6.91 (dd, *J* = 15.7, 6.8 Hz, 1H), 5.78 (dd, *J* = 15.7, 1.4 Hz, 1H), 5.47 (ddq, *J* = 15.3, 1.1, 6.3 Hz, 1H), 5.36 (ddq, *J* = 15.3, 6.8, 1.5, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 3.02-2.92 (m, 1H), 1.67 (ddd, *J* = 6.3, 1.5, 1.1 Hz, 3H), 1.66-1.61 (m, 2H), 1.44-1.36 (m, 2H), 1.13 (d, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); GC-MS m/e (relative intensity) 39 (22), 41 (57), 43 (13), 53 (13), 55 (24), 67 (22), 79 (19), 95 (100), 111 (51), 123 (8), 125 (14), 139 (5), 140 (10), 167 (4), 196 (M^+, 2).

***n*-Butyl (*E*)-3-(2-cyclohexenyl)acrylate 4e.** ^{1}H NMR (500 MHz, $CDCl_3$) □ 6.12 (dd, *J* = 15.7, 7.0 Hz, 1H), 5.82 (ddt, *J* = 10.0, 2.2, 3.7 Hz, 1H), 5.81 (dd, *J* = 15.7, 1.4 Hz, 1H), 5.55 (ddt, *J* = 10.0, 5.2, 2.3 Hz, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.99-2.91 (m, 1H), 2.04-1.98 (m, 2H), 1.90-1.82 (m, 1H), 1.73-1.64 (m, 1H), 1.64 (tt, *J* = 9.4, 6.7 Hz, 2H), 1.62-1.54 (m, 1H), 1.54-1.46 (m, 1H), 1.40 (tq, *J* = 9.4, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) □ 167.0, 152.2, 129.2, 127.2, 120.5, 64.1, 37.8, 30.7, 27.9, 24.9, 20.2, 19.2, 13.7; IR (neat) 3022, 2958, 2933, 2872, 1721, 1652, 1449, 1434, 1384, 1321, 1308, 1274, 1244, 1169, 1137, 1094, 1065, 1025, 984, 892, 854, 726, 670 cm^{-1}; GC-MS m/e (relative intensity) 39 (42), 41 (90), 43 (10), 51 (13), 53 (26), 54 (10), 55 (46), 56 (10), 57 (31), 65 (15), 67 (23), 73 (13), 74 (11), 77 (30), 78 (20), 79 (93), 80 (34), 81 (10), 91 (39), 92 (41), 93 (18), 105 (15), 106 (12), 107 (60), 133 (12), 134 (15), 135 (24), 151 (10), 152 (100), 153 (11), 208 (M^+, 5).

***n*-Butyl 5-methyl-2(*E*),5-hexadienoate 4f.** ^{1}H NMR (500 MHz, $CDCl_3$) □ 6.96 (dt, *J* = 15.6, 7.1 Hz, 1H), 5.85 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.83 (s, 1H), 4.75 (s, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 2.88 (dd, *J* = 7.1, 1.5 Hz, 2H), 1.74 (s, 3H), 1.64 (tt, *J* = 9.4, 6.7 Hz, 2H), 1.40 (tq, *J* = 9.4, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) □ 166.6, 146.2, 142.2, 122.7, 112.5, 64.2, 40.5, 30.7, 22.5, 19.2, 13.7; IR (neat) 3079, 2961, 2874, 1723, 1651, 1456, 1383, 1326, 1310, 1276, 1200, 1160, 1075, 1027, 984, 894 cm^{-1}; GC-MS m/e (relative intensity) 39(53), 41(77), 53(24), 55(20), 57(18), 78(31), 80(21), 81(100), 109(26), 111(24), 127(15) 167(2), 182(M^+, 0.6); elemental analysis

calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. found : C, 71.85; H, 9.81.

***n*-Butyl 5-methyl-2,4-hexadienoate 5.** ^{1}H NMR (500 MHz, $CDCl_3$) □ 7.56 (dd, *J* = 15.1, 11.6 Hz, 1H), 5.98 (double septet, *J* = 11.6, 0.9 Hz, 1H), 5.76 (d, *J* = 15.1 Hz, 1H), 4.15 (t, *J* = 6.7 Hz, 1H), 1.89 (d, *J* = 0.9 Hz, 3H), 1.88 (d, *J* = 0.9 Hz, 3H), 1.65 (tt, *J* = 9.4, 6.7 Hz, 2H), 1.41 (tq, *J* = 9.4, 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) □ 167.8, 146.2, 140.9, 123.7, 118.6, 64.0, 30.8, 26.5, 19.2, 18.9, 13.7; IR (neat) 2960, 2934, 2873, 1713, 1640, 1612, 1446, 1384, 1353, 1308, 1277, 1212, 1160, 1139, 1065, 1048, 1025, 991, 879, 721 cm^{-1}; GC-MS m/e (relative intensity) 39(37), 41(55), 53(27), 55(13), 57(10), 79(32), 80(24), 81(100), 109(28), 111(70), 126(13) 167(4), 182(M^+, 15); elemental analysis calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. found : C, 71.39; H, 9.79.