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Titanocene-Catalyzed Alkylative Dimerization of Vinyl Grignard Reagent Using Alkyl Halides

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Typical Experimental Procedures and Analytical Data of Products

General

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were recorded with a Perkin-Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass spectra (EI) were obtained using a JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. HPLC separations were performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent. Column chromatography was conducted using Kanto Chemical Co., Inc. silica gel 60 (63-210 μm). Elemental analyses were performed on a Perkin Elmer 240C apparatus. GC yields were determined using octane as an internal standard. Vinyl Grignard reagent, Cp_2TiCl_2 (Kanto Chemical Company), *tert*-butyl Bromide, cyclohexyl bromide (Tokyo Chemical Industry Company), norbornyl bromide, adamanty iodide, 2,3-dimethylbutadiene, dimethylphenylchlorosilane, (Aldrich Chemical Company), *sec*-butyl Bromide, *n*-butyl bromide, *n*-octyl iodide, cyclohexyl iodide, cyclohexyl chloride, 3-pentanone, D_2O (Wako Pure Chemical Industries) were purchased and used as received. 2-Bromo-2-methyloctane was prepared from 2-methyloctane-2-ol and phosphorus tribromide. Cyclopropylmethyl iodide were prepared according to the literature (R. S. Tipson, M. A. Clapp, L. H. Cretcher, *J. Org. Chem*. **1947**, *12*, 133.)

A Typical Procedure

1-Deuterio-5,5-dimethyl-2-undecene (3-*d*$_1$) and

3-Deuterio-5,5-dimethyl-1-undecene (4-*d*$_1$)

To a mixture of 2-bromo-2-methyloctane (102.1 mg, 0.50 mmol), Cp_2TiCl_2 (14.9 mg, 0.06 mmol) and hexane (0.22 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.1 mL, 1.5 mmol) at -20 °C. After stirring for 3 h, D_2O was added to the solution at 25 °C. Aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (hexane) gave 84 mg (92%) of **3-*d*$_1$** and **4-*d*$_1$**. IR(NaCl): 2958, 2928, 1640, 1469, 1364, 908 cm^{-1}; Anal. Calcd for $C_{13}H_{25}D$: C, 85.16; H and D, 14.84. found: C, 85.20; H and D, 14.80; **3-*d*$_1$**: (*E* isomer) δ 5.48-5.34 (m, 2H), 1.84 (d, *J* = 6.1 Hz, 2H), 1.66-1.62 (m, 2H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.3, 126.7, 45.1, 41.9, 33.2, 32.0, 30.3, 27.0, 23.9, 22.7, 17.8 (t, *J* = 19.3 Hz), 14.0; MS (EI) *m*/*z* (relative intensity, %): 183 (M^+, 0.2), 127 (30), 126 (23), 98 (8), 86 (5), 85 (64), 84 (4), 72 (6), 71 (100), 70 (7), 69 (12), 57 (62), 56 (24), 55 (16), 43 (50), 41 (16); HRMS calcd for $C_{13}H_{25}D$: 183.2096, found 183.2088.; (*Z* isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.56-5.48 (m, 2H), 1.92 (d, *J* = 7.3 Hz, 2H), 1.60-1.56 (m, 2H), 1.32-1.10 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.6, 125.0, 42.0, 38.8, 33.7, 32.0, 30.3, 27.0, 24.1, 22.7, 14.0, 12.7 (t, *J* = 19.3 Hz); MS (EI) *m*/*z* (relative intensity, %): 183 (M^+, 1), 128 (3), 127 (31), 126 (14), 125 (24), 112 (6), 99 (13), 98 (100), 97 (13), 85 (46), 84 (12), 83 (10), 82 (23), 71 (69), 70 (18), 69 (24), 57 (46), 56 (70), 55 (62), 43 (45), 41 (22); HRMS calcd for $C_{13}H_{25}D$: 183.2096, found 183.2089.; **4-*d*$_1$**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, *J* = 6.7, 10.2, 17.0 Hz, 1H), 5.02-4.90 (m, 2H), 2.01-1.91 (m, 1H), 1.34-1.12 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 113.6, 42.0, 41.1, 32.6, 32.0, 30.3, 28.3 (t, *J* = 19.0 Hz), 27.2, 24.0, 22.7, 14.1; MS (EI) *m*/*z* (relative intensity, %): 183 (M^+, 0.2), 127 (32), 126 (18), 98 (6), 86 (4), 85 (60), 72 (6), 71 (100), 70 (7), 69 (10), 57 (59), 56 (20), 55 (15), 43 (50), 41 (13); HRMS calcd for $C_{13}H_{25}D$: 183.2096, found 183.2093.

2-(2,2-dimethyl-octyl)-3-butenoic acid (5)

To a mixture of 2-bromo-2-methyloctane (103.6 mg, 0.50 mmol), Cp_2TiCl_2 (14.9 mg, 0.06 mmol) and hexane (0.22 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.1 mL, 1.5 mmol) at -20 °C. After stirring for 3 h, CO_2 was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude

product. Purification by column chromatography on silica gel (hexane/ether = 2/1) gave 82 mg (72%) of **5**. IR(NaCl): 3083, 2957, 2929, 2859, 1708, 1637, 1469, 1416, 1388, 1367, 1286, 1220, 991, 920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.81 (ddd, *J* = 8.3, 10.0, 16.9 Hz, 1H), 5.21-5.09 (m, 2H), 3.13 (ddd, *J* = 8.3, 7.8, 4.4 Hz, 1H), 1.88 (dd, *J* = 7.8, 14.2 Hz, 1H), 1.42 (dd, *J* = 4.4, 14.2 Hz, 1H), 1.30-1.20 (m, 10H), 0.90-0.86 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 116.7, 46.6, 43.6, 42.3, 33.4, 31.9, 30.1, 27.2, 27.1, 23.8, 22.7, 14.1; MS (EI) *m*/*z* (relative intensity, %): 226 (M^+, 0.3), 211 (2), 171 (2), 165 (6), 143 (7), 142 (4), 141 (37), 128 (5), 127 (47), 126 (16), 125 (8), 123 (7), 109 (9), 100 (6), 99 (40), 98 (5), 97 (41), 96 (15), 95 (100), 94 (4), 86 (6), 85 (59), 83 (10), 81 (17), 79 (4), 73 (4), 72 (5), 71 (90), 70 (10), 69 (29), 67 (11), 59 (10), 57 (69), 56 (14), 55 (43), 53 (7), 43 (63), 41 (37); HRMS calcd for $C_{14}H_{26}O_2$ 226.1933, found 226.1928. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. found: C, 74.18; H, 11.41.

5,5-Dimethyl-1-dimethylphenylsilyl-2-undecene (6)

To a mixture of 2-bromo-2-methyloctane (103.6 mg, 0.50 mmol), Cp_2TiCl_2 (14.9 mg, 0.06 mmol) and hexane (0.22 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.1 mL, 1.5 mmol) at -20 °C. After stirring for 3 h, chlorodimethylphenylsilane (126 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (hexane) gave 114 mg (72%, *E*/*Z* = 97/3) of **6**. (*E* isomer) IR(NaCl): 3050, 3018, 2955, 2927, 2858, 1654, 1467, 1427, 1383, 1364, 1248, 1156, 1113, 967, 837, 729, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.50 (m, 2H), 7.35-7.32 (m, 3H), 5.38-5.22 (m, 2H), 1.83 (d, *J* = 6.6 Hz, 2H), 1.68 (d, *J* = 7.3 Hz, 2H), 1.32-1.06 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H), 0.77 (s, 6H), 0.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 133.6, 128.9, 127.7, 127.4, 126.5, 45.4, 41.9, 33.3, 32.0, 30.3, 27.0, 23.9, 22.7, 21.8, 14.2, -3.2. ; MS (EI) *m*/*z* (relative intensity, %): 316 (M^+, 2), 190 (1), 137 (4), 136 (13), 135 (100), 121 (2), 107 (2), 105 (2), 85 (2), 71 (3), 57 (2), 43 (3); HRMS calcd for $C_{21}H_{36}Si$ 316.2586, found 316.2593. Anal. Calcd for $C_{21}H_{36}Si$: C, 79.67; H, 11.46. found: C, 79.40; H, 11.50.

3-Ethyl-4- vinyl-6,6-dimethyl-3-dodecanol (7a)

To a mixture of 2-bromo-2-methyloctane (102 mg, 0.50 mmol), Cp_2TiCl_2 (14.9 mg, 0.06 mmol) and hexane (0.22 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.1 mL, 1.5 mmol) at -20 °C. After stirring for 3 h, 3-pentanone (64.6 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was

added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (hexane/ether = 95/5) gave 116 mg (87%) of **7a**. IR(NaCl): 3491, 2930, 2858, 1636, 1466, 1385, 1365, 1254, 1159, 1006, 952, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.72 (ddd, *J* = 10.0, 10.2, 17.3 Hz, 1H), 5.14-5.07 (m, 2H), 2.32-2.28 (m, 1H), 1.60-1.38 (m, 5H), 1.30-1.19 (m, 12H), 0.89-0.84 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 117.3, 75.3, 47.3, 43.0, 40.5, 33.6, 32.0, 30.2, 28.6, 28.0, 27.9, 23.9, 22.7, 14.1, 7.6, 7.4; MS (CI) *m*/*z* (relative intensity, %): 269 (M+1, 0.2), 252 (5), 251 (26), 249 (3), 195 (3), 181 (7), 167 (10), 153 (5), 141 (4), 139 (6), 128 (10), 127 (100), 126 (5), 125 (32), 113 (3), 111 (6), 97 (4), 87 (28), 85 (9), 71 (7); HRMS (CI) calcd for $C_{18}H_{37}O$ 269.2844, found 268.2837. Anal. Calcd for $C_{18}H_{36}O$: C, 80.53; H, 13.52. found: C, 80.39; H, 13.36.

3-Ethyl-4- vinyl-6,6-dimethyl-3-heptanol (7b)

To a mixture of *t*-butyl bromide (66 mg, 0.48 mmol), Cp_2TiCl_2 (14.9 mg, 0.06 mmol) and hexane (0.22 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.1 mL, 1.5 mmol) at -20 °C. After stirring for 1 h, 3-pentanone (64.6 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (pentane/ether = 95/5) gave 73 mg (77%) of **7b**. IR(NaCl): 3494, 2953, 1636, 1465, 1365, 1244, 1160, 953, 911 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.72 (ddd, *J* = 10.0, 10.0, 17.1 Hz, 1H), 5.16-5.07 (m, 2H), 2.33-2.29 (m, 1H), 1.63-1.41 (m, 5H), 1.28-1.22 (m, 2H), 0.90-0.85 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 117.4, 75.2, 47.7, 42.6, 31.3, 30.4, 28.6, 27.9, 7.6, 7.4; MS (CI) *m*/*z* (relative intensity, %): 199 (M+1, 1), 182 (14), 181 (100), 126 (2), 125 (18), 111 (16), 109 (2), 97 (8), 87 (22), 85 (10), 71 (5); HRMS (CI) calcd for $C_{13}H_{27}O$ 199.2062, found 199.2080. Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. found: C, 78.54; H, 12.92.

3-Ethyl-4- vinyl-6-methyl-3-octanol (7c)

To a mixture of *s*-butyl bromide (66 mg, 0.48 mmol), Cp_2TiCl_2 (14.9 mg, 0.06 mmol) and hexane (0.22 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.1 mL, 1.5 mmol) at -20 °C. After stirring for 3 h, 3-pentanone (64.6 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange

crude product. Purification by column chromatography on silica gel (pentane/ether = 95/5) gave 61 mg (64%) of **7c** as a mixture of diastereomers with ca. 1:1 ratio indicated by ^{1}H, ^{13}C NMR and GC. A 1:1 mixture of diastereomers; IR(NaCl): 3492, 2964, 1636, 1460, 1377, 1260, 911 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70-5.58 (m, 1H), 5.17-5.03 (m, 2H), 2.25-2.20 (m, 1H), 1.58-1.42 (m, 5H), 1.39-1.17 (m, 5H), 0.88-0.81 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 139.2, 117.7, 117.6, 75.3, 75.2, 48.9, 48.8, 35.5, 35.1, 31.9, 31.7, 31.1, 28.50, 28.47, 28.3 (2C), 27.1, 20.5, 18.1, 11.5, 10.8, 7.59, 7.57, 7.4, 7.3; MS (CI) *m*/*z* (relative intensity, %): 199 (M+1, 3), 182 (15), 181 (100), 139 (7), 126 (6), 125 (60), 112 (12), 111 (99), 109 (7), 99 (18), 97 (51), 87 (44), 85 (58), 83 (10), 75 (5), 71 (18); HRMS (CI) calcd for $C_{13}H_{27}O$ 199.2062, found 199.2065. Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. found: C, 78.98; H, 13.15.

3-Ethyl-2-vinyl-1-norbornyl-3-pentanol (7d)

To a mixture of *exo*-2-norbornyl bromide (87 mg, 0.49 mmol), Cp_2TiCl_2 (14.9 mg, 0.06 mmol) and hexane (0.22 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.1 mL, 1.5 mmol) at -20 °C. After stirring for 3 h, 3-pentanone (64.6 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (hexane/ether = 95/5) gave 74 mg (63%) of **7d** as a mixture of diastereomers with ca. 1:1 ratio indicated by ^{1}H, ^{13}C NMR and GC. A 1:1 mixture of diastereomers; IR(NaCl): 3483, 2949, 2869, 1636, 1456, 1379, 1314, 1258, 1167, 1143, 1125, 1005, 948, 910 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71-5.60 (m, 1H), 5.17-5.01 (m, 2H), 2.22-1.85 (m, 4H), 1.60-1.02 (m, 15H), 0.88-0.83 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 139.2, 117.8 (2C), 75.1 (2C), 50.5, 48.6, 42.5, 39.65, 39.57, 39.21, 39.17, 37.3, 36.8, 36.4, 35.8, 35.5, 35.2, 35.0, 30.2, 29.9, 28.8, 28.6, 28.5 (2C), 28.4, 28.3, 7.5 (2C), 7.38, 7.36; MS (CI) *m*/*z* (relative intensity, %): 237 (M+1, 0.8), 220 (17), 219 (100), 217 (6), 177 (5), 163 (12), 150 (5), 149 (26), 137 (12), 136 (4), 135 (31), 123 (13), 121 (5), 109 (11), 97 (3), 95 (11), 87 (21), 69 (2); HRMS (CI) calcd for $C_{16}H_{29}O$ 237.2218, found 237.2211. Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. found: C, 81.08; H, 11.65.

3-Ethyl-4- vinyl-3-nonanol (7e)

To a mixture of *n*-butyl bromide (66 mg, 0.48 mmol), Cp_2TiCl_2 (18.7 mg, 0.075 mmol) and hexane (0.24 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.2 mL, 1.65 mmol) at -20 °C. After stirring for 3 h, 3-pentanone (64.6 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the

product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (pentane/ether = 95/5) gave 47 mg (50%) of **7e**. IR(NaCl): 3485, 2963, 2858, 1636, 1463, 1378, 1259, 1005, 948, 911 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.64 (ddd, *J* = 10.0, 10.0, 17.1 Hz, 1H), 5.16-5.03 (m, 2H), 2.12-2.06 (m, 1H), 1.57-1.43 (m, 5H), 1.31-1.14 (m, 8H), 0.89-0.84 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 117.7, 75.2, 51.5, 31.9, 28.6, 28.4, 28.1, 27.8, 22.6, 14.1, 7.5, 7.4; MS (CI) *m*/*z* (relative intensity, %): 199 (M+1, 1), 182 (14), 139 (4), 125 (11), 111 (16), 97 (13), 87 (16), 85 (3), 83 (4); HRMS (CI) calcd for $C_{13}H_{27}O$ 199.2062, found 199.2051. Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. found: C, 78.52; H, 12.97.

1-(1-Adamantyl)-3-ethyl-2-vinyl-3-pentanol (7f)

To a mixture of 1-adamantyl iodide (130 mg, 0.50 mmol), Cp_2TiCl_2 (14.9 mg, 0.06 mmol) and hexane (0.22 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.1 mL, 1.5 mmol) at -20 °C. After stirring for 1 h, 3-pentanone (64.6 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (hexane/ether = 95/5) gave 78 mg (56%) of **7f**. IR(NaCl): 3490, 2967, 2899, 2846, 1636, 1452, 1362, 1347, 1326, 1257, 1160, 1099, 1005, 951, 909 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.71 (ddd, *J* = 9.8, 9.8, 17.0 Hz, 1H), 5.14-5.07 (m, 2H), 2.39-2.34 (m, 1H), 1.94-1.90 (m, 4H), 1.69-1.38 (m, 17H), 1.29-1.25 (m, 1H), 1.12 (dd, *J* = 9.8, 13.6 Hz, 1H), 0.89-0.82 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 117.1, 75.3, 45.5, 43.6, 43.3, 37.1, 33.2, 28.8, 28.6, 27.9, 7.6, 7.4; MS (CI) *m*/*z* (relative intensity, %): 277 (M+1, 0.3), 275 (5), 260 (11), 259 (52), 257 (9), 190 (3), 189 (6), 136 (11), 135 (100), 123 (6), 87 (22); HRMS (CI) calcd for $C_{19}H_{31}$ (M-H_2O) 259.2428, found 259.2426. Anal. Calcd for $C_{19}H_{32}O$: C, 82.55; H, 11.67. found: C, 82.28; H, 11.39.

3-Ethyl-4-vinyl-3-tridecanol (7g)

To a mixture of *n*-octyl iodide (120 mg, 0.50 mmol), Cp_2TiCl_2 (18.7 mg, 0.075 mmol) and hexane (0.24 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.2 mL, 1.65 mmol) at -20 °C. After stirring for 1 h, 3-pentanone (64.6 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (hexane/ether = 95/5) gave 61 mg (48%) of **7g**. IR(NaCl): 3481, 2926, 2854, 1636, 1459, 1378, 1257,

1160, 948, 911 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.64 (ddd, *J* = 9.8, 9.8, 17.1 Hz, 1H), 5.16-5.03 (m, 2H), 2.11-2.05 (m, 1H), 1.61-1.42 (m, 5H), 1.31-1.23 (m, 16H), 0.90-0.84 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 117.7, 75.2, 51.5, 31.9, 29.7, 29.63, 28.61, 29.3, 28.6, 28.4, 28.14, 28.11, 22.7, 14.1, 7.5, 7.4; MS (CI) *m*/*z* (relative intensity, %): 255 (M+1, 1), 238 (19), 237 (100), 235 (4), 181 (4), 167 (7), 153 (8), 139 (9), 125 (11), 111 (13), 97 (14), 87 (31), 83 (4); HRMS (CI) calcd for $C_{17}H_{35}O$ 255.2688, found 255.2665. Anal. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47. found: C, 79.97; H, 13.49.

1-Cyclohexyl-3-ethyl-2-vinyl-3-pentanol (7h)

To a mixture of cyclohexyl iodide (102 mg, 0.49 mmol), Cp_2TiCl_2 (14.9 mg, 0.06 mmol) and hexane (0.22 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.1 mL, 1.5 mmol) at -20 °C. After stirring for 3 h, 3-pentanone (64.6 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (hexane/ether = 95/5) gave 75 mg (69%) of **7h**. IR(NaCl): 3484, 2967, 2924, 2852, 1636, 1449, 1379, 1167, 1126, 1005, 956, 944, 924, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.64 (ddd, *J* = 9.8, 9.8, 17.1 Hz, 1H), 5.16-5.03 (m, 2H), 2.28-2.22 (m, 1H), 1.82-1.79 (m, 1H), 1.69-1.43 (m, 10H), 1.28-1.10 (m, 7H), 0.85 (d, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 117.7, 75.2, 48.1, 36.0, 35.1, 34.9, 31.8, 28.5, 28.3, 26.7, 26.5, 26.2, 7.6, 7.3; MS (CI) *m*/*z* (relative intensity, %): 225 (M+1, 0.8), 208 (15), 207 (100), 205 (7), 165 (6), 151 (18), 138 (7), 137 (24), 125 (22), 123 (27), 112 (6), 111 (58), 109 (12), 97 (33), 95 (5), 87 (34), 83 (6); HRMS (CI) calcd for $C_{15}H_{29}O$ 225.2218, found 225.2223. Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. found: C, 80.01; H, 12.64.

3-Ethyl-4-vinyl-8-nonene-3-ol (13)

To a mixture of cyclopropylmetyl iodide (91 mg, 0.50 mmol), Cp_2TiCl_2 (18.7 mg, 0.075 mmol) and hexane (0.24 mL) was added vinyl magnesium chloride (1.42 M in THF, 1.2 mL, 1.65 mmol) at -20 °C. After stirring for 1 h, 3-pentanone (64.6 mg, 0.75 mmol) was added to the solution at 25 °C. After stirring for 1 h, aqueous 1N HCl was added and the product was extracted with ether, dried over Na_2SO_4, and evaporated to give an orange crude product. Purification by column chromatography on silica gel (pentane/ether = 95/5) gave 51 mg (51%) of **13**. IR(NaCl): 3483, 3074, 2967, 1639, 1459, 1377, 1159, 1002, 950, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.80 (tdd, *J* = 6.8, 10.3, 17.1 Hz, 1H), 5.65 (ddd, *J* = 10.0, 10.0, 17.1 Hz, 1H), 5.17-4.92 (m, 4H), 2.12-1.98 (m, 3H),

1.59-1.41 (m, 6H), 1.27-1.19 (m, 3H), 0.88-0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 138.9, 117.9, 114.4, 75.3, 51.4, 33.8, 28.6, 28.4, 27.6, 27.4, 7.5, 7.4; MS (CI) *m*/*z* (relative intensity, %): 197 (M+1, 3), 180 (14), 179 (100), 138 (3), 137 (21), 124 (6), 123 (71), 111 (6), 110 (11), 109 (100), 98 (6), 97 (76), 96 (4), 95 (43), 87 (40), 83 (22), 81 (9), 69 (5); HRMS (CI) calcd for $C_{13}H_{25}O$ 197.1905, found 197.1906. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. found: C, 79.29; H, 12.03.