General Methods: Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All manipulations involving air-sensitive materials were performed under nitrogen or argon, with such materials being exposed only to throughly dried and degassed solvents. Anmhydrous ether, THF, and CH_2Cl_2 were purchased from Kanto Kagaku Co., Ltd. And were used as they are.

^1H NMR and ^{13}C NMR spectra were recorded with a Varian Gemini-200 (200 and 50 MHz), a Mercury-300 (300 and 75 MHz), and a VXR-500 (500 MHz: only for ^1H) in $CDCl_3$ unless otherwise noted, respectively. Chemical shifts were recorded in parts per million downfield from internal tetramethylsilane (Me_4Si). ^{19}F NMR spectra were recorded with a Varian Mercury-300 (282 MHz) and a VXR-500 (470 MHz) in $CDCl_3$ unless otherwise noted. Chemical shifts were reported in ppm downfield from internal hexafluorobenzene (C_6F_6). Data were tabulated in the following order: number of proton, multipilicity (s: singlet; d: doublet; t: triplet; q: quartet; quint: quintet; sex: sextet; sep: septet; m: multiplet; br: broad peak), coupling constants (in hertz). Infrared (IR) spectara were obtained on a JASCO FT/IR-500 spectrometer, and all spectra were reported in wave numbers (cm^{-1}) with the reference at the 1601.4 cm^{-1} absorptionof a polystyrene film. Column chromatography was conducted eith silica gel (BW-200, 100-200 mesh) by using mixture of hexanes and ethyl acetate (v/v).

(2*S*,3*R*,6*S*)-3-Benzoyloxy-6-[(*tert*-butyldimethylsilyl)oxy]methyl-5-[difluoro-(methane-sulfonyloxy)metyl]-2-methoxy-3,6-dihydro-2*H*-pyran (3): To a stirred solution of allylic alcohol **1**[1] (0.444 g, 1 mmol) in 10 mL of CH_2Cl_2 was added methanesulfonyl chloride (0.093 g, 1.2 mmol) and Et_3N (0.167 g, 1.2 mmol) at 0 °C. After the mixture was stirred for 1 h at that temperature, the reaction was quenched with aqueous $NaHCO_3$, and the mixture was diluted with CH_2Cl_2 followed by the separation of the resulting organic layer. The aqueous layer was extracted twice with CH_2Cl_2, and the combined CH_2Cl_2 layers were washed with H_2O, dried over $MgSO_4$, and evaporated. Purification by silica gel column chromatography afforded the rearranged product **3** in 91% yield. ^1H NMR δ 0.08 (6 H, s), 0.89 (9 H, s), 3.27 (3 H, s), 3.47 (3 H, s), 3.87 (1 H, dd, *J*=4.6, 10.5 Hz), 3.96 (1 H, dd, *J*=2.0, 11.2 Hz), 4.16 (1 H, br s), 5.24 (1 H, d, *J*=3.7 Hz), 5.50 (1 H, m), 6.47 (1 H, s), 7.5-8.1 (5 H, m). ^{13}C NMR δ -5.62, -5.45, 18.1, 25.5, 41.3, 55.8, 63.3, 66.3, 68.9, 95.2, 119.9 (t, *J*=273.0 Hz), 128.3, 129.0 (t, *J*=3.0 Hz), 129.1, 129.8, 130.3 (t, *J*=28.3 Hz), 133.4, 165.5. ^{19}F NMR δ 93.9 (d, *J*=152.6 Hz), 96.9 (d, *J*=152.6 Hz). IR (neat) ν 2955.1, 2857.4, 1728.0, 1391.1, 1255.9, 1113.8, 1055.2, 837.7, 776.5, 713.3 cm^{-1}.

(2*S*,3*R*,6*S*)-3-Benzoyloxy-6-[(*tert*-butyldimethylsilyl)oxy]methyl-5-(hydroxy-methyl)-2-methoxy-3,6-dihydro-2*H*-pyran (4): To an EtOH solution of **3** was added $NaBH_4$ (0.11 g, 3 mmol) at room temperature. After the reaction mixture was stirred for 1.0 h at that temperature, the reaction was quenched with H_2O, and the mixture was diluted with Et_2O, followed by separation of the resulting organic layer. The aqueous layer was extracted twice with Et_2O, and the combined ethereal layers were washed with brine, dried with $MgSO_4$ and evaporated. Purification by silica gel column chromatography afforded the allylic alcohol **4** in 86% yield. $[\alpha]_D^{18.0}$ +57.1° (*c* 0.16, $CHCl_3$). ^1H NMR δ 0.10 (3 H, s), 0.10 (3 H, s), 0.89 (9 H, s), 2.94 (1 H, t, *J*=6.2 Hz), 3.45 (3 H, s),

3.83 (1 H, dd, *J*=5.1, 11.0 Hz), 3.93 (1 H, dd, *J*=3.7, 11.0 Hz), 4.12 (2 H, m), 4.25 (1 H, m), 5.19 (1 H, d, *J*=4.2 Hz), 5.50 (1 H, m), 5.83 (1 H, s), 7.4-8.1 (5 H, m). ^{13}C NMR δ -4.77, -4.60, 18.9, 26.4, 56.7, 64.0, 65.4, 68.1, 71.3, 96.4, 121.8, 129.1, 130.3, 130.5, 133.9, 141.0. IR(neat) ν 3516.1, 2950.8, 1732.0 cm^{-1}. Anal. Calcd for $C_{21}H_{32}O_6Si$: C, 61.74; H, 7.89. Found: C, 61.31; H, 8.22.

Preparation of *exo*-difluoromethylenated TBS ether 6.

2-{3-[(*tert*-Butyldimethylsilyl)oxy]ethyl}-1,1-difluorohept-1-ene (6b): Dibromodifluoromethane (4.0 g, 18 mmol) was added to 25 mL of THF at -78 °C and, after addition of hexamethylphosphorous triamide (5.4 g, 36 mmol) and **5b** (7.2 mmol) in a successive manner, the mixture was allowed to warm to room temperature. After 30 min stirring and addition of a mixture of H_2O and pentane (20 and 30 mL, respectively), the usual work-up and chromatographic purification by silica gel (*n*-hex/ CH_2Cl_2=8/1) afforded the intermediate **6b** in 83% yield. ^{1}H NMR ($CDCl_3$) δ 0.00 (3 H, s), 0.04 (3 H, s), 0.86 (9 H, s), 0.87 (3 H, t, *J*=6.6 Hz), 1.20 (3 H, d, *J*=6.6 Hz), 1.29 (4 H, m), 1.45 (2 H, m), 1.97 (2 H, m), 4.61 (1 H, qt, *J*=6.4, 1.8 Hz). ^{13}C NMR ($CDCl_3$) δ -5.2, -5.0, 14.0, 18.1, 22.5, 23.1, 29.1 (t, *J*=2.6 Hz), 32.0, 64.5 (d, *J*=6.4 Hz), 94.1 (t, *J*=13.0 Hz), 153.0 (t, *J*=286.4 Hz). ^{19}F NMR ($CDCl_3$, from C_6F_6) δ 66.72 (1 F, d, *J*=54.9 Hz), 68.15 (1 F, d, *J*=56.5 Hz). Because of the intrinsic instability of compounds **6** and **7**, they were confirmed only by NMR and/or IR, and elemental analyses were tried for the final products.

Mesyloxy-group migration of 6.

(*E*)-1,1-Difluoro-2-ethylidenehept-1-yl methanesulfonate (7b): To a THF solution (10 mL) of **6b** (1 mmol) was added tetra-*n*-butylammonium fluoride (1 mmol) in THF at 0 °C. After stirring for 2 h, the reaction was quenched with H_2O and diluted with Et_2O. The usual work-up afforded the crude γ,γ-difluorinated allylic alcohol which, without further purification, was subjected to the next mesylation (1.2 mmol of MsCl and Et_3N in 10 mL of CH_2Cl_2) to furnish **7b** after usual work-up and chromatographic purification (*n*-hex/AcOEt=4/1). ^{1}H NMR δ 0.88 (3 H, t, *J*=7.0 Hz), 1.30 (4 H, m), 1.44 (2 H, m), 1.73 (3 H, dt, *J*=7.1, 2.6 Hz), 2.16 (2 H, m), 3.21 (3 H, s), 6.20 (1 H, qt, *J*=7.0, 1.7 Hz). ^{13}C NMR δ 13.0, 13.8, 22.2, 25.5, 28.3, 31.7, 41.1, 122.9 (t, *J*=273.9 Hz), 129.6 (t, *J*=7.3 Hz), 131.3 (t, *J*=24.9 Hz). ^{19}F NMR δ 92.9 (s).

$NaBH_4$ reduction of 7 to 8.

(*E*)-2-Ethylideneheptanol (8b): 3 mmol of sodium borohydride was added to **7b** (1 mmol) in EtOH (10 mL) at 0 °C. After stirring for 2 h at room temperature, usual work-up and purification by silica gel column chromatography (*n*-hex/AcOEt=4/1) furnished the desired allylic alcohol **8b**. ^{1}H NMR δ 0.87 (3 H, t, *J*=4.5 Hz), 1.2-1.5 (6 H, m), 1.63 (3 H, d, *J*=7.0 Hz), 2.0 (2 H, m), 3.99 (2 H, s), 5.47 (1 H, q, *J*=10.2 Hz). ^{13}C NMR δ 12.9, 14.0, 22.5, 27.5, 27.9, 31.9, 67.1, 120.8, 140.1. IR (neat) ν 3330.7, 2929.1, 2859.9, 1458.1, 1001.6 cm^{-1}. Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 75.72; H, 13.11.

Ester formation from 7 to 9-11.

To a stirred MeOH solution (10 mL) of **7** (1 mmol) was added NaOMe (3 mmol) at room temperature. After the reaction mixture was stirred for 1 h, the usual work-up and purification by silica gel column chromatography afforded the desired methyl ester **9**.

Methyl (*E*)-2-ethylideneheptanoate (9b)[2]: ^{1}H NMR δ 0.85 (3 H, *J*=6.2 Hz), 1.30 (6 H, d, *J*= 7.5 Hz), 2.26 (2 H, t, *J*=7.1 Hz), 3.69 (3 H, s), 6.80 (1 H, q, *J*=7.2 Hz). ^{13}C NMR δ 13.9, 14.1, 22.4, 26.3, 31.6, 51.4, 133.4, 137.1, 168.4. IR(neat) ν 2954.3, 1716.7, 1435.3, 1258.3, 1197.2, 1142.8 cm^{-1}.

Amide formation from 7 to 12-14. To a stirred THF solution (10 mL) of $LiNEt_2$ (3 mmol), prepared from $NHEt_2$ (0.31 mL, 3 mmol) and *n*-BuLi (1.88 mL, (a 1.6 *M* solution in *n*-hexane)), was added the rearranged product **7** at -78 °C. After the reaction mixture was stirred for 2 h at that temperature, the usual work-up and purification by silica gel column chromatography afforded the desired amide **14**.

***N,N*-Diethyl-(*E*)-2-ethylideneheptanmide (14b):** ^{1}H NMR δ 0.86 (3 H, t, *J*=6.0 Hz), 1.19 (6 H, t, *J*=7.1 Hz), 1.27 (6 H, m), 1.94 (3 H, d, *J*=7.1 Hz), 3.24 (4 H, q, *J*=7.2 Hz), 6.95 (1 H, q, *J*=7.0 Hz). ^{13}C NMR δ 14.0, 14.8, 15.3, 22.5, 25.2, 28.3, 31.8, 43.0, 142.7, 143.9, 190.0. IR(neat) ν 2932.1, 2872.3, 1660.4, 1336.3, 1202.6, 1146.6, 1020.7, 940.0, 785.0 cm^{-1}. Anal. Calcd for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63. Found: C, 73.80; H, 11.73; N, 6.75.

(*E*)-2-(2-Phenylethyl)but-2-enoyl fluoride (15e): To a stirring THF solution of **7e** (0.170 g, 0.59 mmol) was added a 1 *M* THF solution of TBAF (177 μL) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was quenched with water. The usual work-up and purification by silica gel column chromatography (*n*-hex/CH_2Cl_2=8/1) afforded the product **15e** (0.095 g, 0.49 mmol) in 84% yield. ^{1}H NMR δ 1.67 (3 H, d, *J*=7.3 Hz), 2.57-2.69 (2 H, m), 2.72-2.83 (2 H, m), 7.07 (1 H, q, *J*=7.3 Hz), 7.15-7.35 (5 H, m). ^{13}C NMR δ 14.6, 28.7, 34.5, 126.1, 128.0 (d, *J*=48.4 Hz), 128.4, 128.6, 140.8, 146.2, 157.8 (d, *J*=347.9 Hz). ^{19}F NMR δ 176.37 (s). IR (neat) ν 2936, 1797, 1015, 727, 699 cm^{-1}. Anal. Calcd for $C_{12}H_{13}FO$: C, 74.98; H, 6.82. Found: C, 75.16; H, 7.21.

(*E*)-3-(2-Phenylethyl)pent-3-en-2-one (16e): MeMgBr (0.68 mmol) was added slowly at –78 °C to a THF (5 ml) solution of **15e** (0.100 g, 0.520 mmol) containing CuI (0.08 mmol). The reaction mixture was stirred for 3 h at -78 to -40 °C and quenched with saturated aqueous NH_4Cl. Usual work-up and purification by silica gel column chromatography (*n*-hex/CH_2Cl_2=8/1) afforded **16e** (0.076 g, 0.404 mmol) in 78% yield. ^{1}H NMR δ 1.69 (3 H, d, *J*=7.1 Hz), 2.30 (3 H, s), 2.54-2.68 (4 H, m), 6.74 (1 H, q, *J*=7.1 Hz), 7.14-7.30 (5 H, m). ^{13}C NMR δ 14.5, 25.6, 27.4, 34.9, 125.6, 128.0, 128.4, 139.3, 141.8, 142.0, 198.9. IR (neat) ν 2932, 1665, 1266 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.94; H, 8.77.

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