Synthesis of Trifluoro- or Difluoromethylated Olefins by Regio- and Stereocontrolled S_N2'

Reactions of *gem*-Difluorinated Vinyloxiranes

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Experimental section

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 argon, with such materials being exposed only to thoroughly dried and degassed solvents. Anhydrous ether, THF and CH₂Cl₂ were purchased and were used without further purification.

¹H NMR spectra were recorded at 300 or 500 MHz and ¹³C NMR spectra were recorded at 75 MHz: in CDCl₃ unless otherwise noted. Chemical shifts were reported in parts per million (ppm) downfield from internal tetramethylsilane (Me₄Si). ¹⁹F NMR spectra were recorded at 282 or 470 MHz in CDCl₃ unless otherwise noted. Chemical shifts were reported in ppm downfield from internal hexafluorobenzene (C₆F₆). Data were tabulated in the following order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sex, sextet; m, multiplet; br, broad peak), number of protons, coupling constants (in hertz). Infrared (IR) spectra were obtained as thin films on NaCl plates, and all spectra were reported in wave numbers (cm⁻¹). Melting points, mp, were measured without correction. Column chromatography was conducted with silica gel by using a mixture of *n*-hexane and AcOEt (v/v), and before starting separation, it is recommended to “wash” silica gel by passing AcOEt for removing the chance of decomposition of epoxy-containing products, which makes the isolation easier.

Elemental analysis of **11** was not carried out because of inherent instability.

General procedure for the fluorination of **1** with HF-Py.

The reaction of **1a** is described as a representative example. HF-Py (0.022 ml, 0.89 mmol) was added to a flask containing **1a** (0.10 g, 0.45 mmol) in 5 ml of CH₂Cl₂ at 0 °C under Ar atmosphere and the reaction mixture was stirred for 1 h. Then, the reaction was quenched with H₂O and the organic layer was extracted with Et₂O three times and dried over MgSO₄ anhydrous. Removal of the solvents and

purification with silica gel column chromatography (*n*-hexane : AcOEt = 4 : 1) furnished the pure desired **2a** in 91%. Other yields are listed in Table 2.

4-Methyl-1-phenyl-5-trifluoromethylhept-4-en-3-ol (2b): IR (neat) ν 698, 748, 934, 1007, 1057, 1111, 1157, 1215, 1254, 1315, 1381, 1454, 1497, 1605, 1651, 2878, 2940, 2974, 3028, 3063, 3082, 3387 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{F}_3\text{O}$: C, 66.16; H, 7.03. Found: C, 65.92; H, 7.39. **E Isomer:** ^1H NMR δ 1.03 (3 H, t, $J = 7.42$ Hz), 1.64-2.10 (2 H, m), 1.82 (3 H, q, $J = 2.47$ Hz), 2.22 (2 H, bq, $J = 7.42$ Hz), 2.55 (1 H, ddd, $J = 13.7, 10.7, 6.04$ Hz), 2.81 (1 H, m), 4.79 (1 H, m), 7.15-7.34 (5 H, m). ^{19}F NMR δ 106.2 (s). ^{13}C NMR δ 12.4, 13.1, 21.7 (q, $J = 3.14$ Hz), 32.3, 36.6, 70.2 (q, $J = 2.57$ Hz), 124.6 (q, $J = 276.0$ Hz), 125.8, 127.8 (q, $J = 27.2$ Hz), 128.2, 128.3, 141.5, 144.8 (q, $J = 3.44$ Hz). **Z Isomer:** ^1H NMR δ 0.94 (3 H, t, $J = 7.42$ Hz), 1.64-2.10 (2 H, m), 1.88 (3 H, q, $J = 2.75$ Hz), 2.11 (2 H, bq, $J = 7.42$ Hz), 2.50-2.70 (1 H, m), 2.75-2.88 (1 H, m), 4.57 (1 H, m), 7.15-7.34 (5 H, m). ^{19}F NMR δ 102.7 (q, $J = 3.01$ Hz). ^{13}C NMR δ 12.7 (q, $J = 2.29$ Hz), 14.4, 20.6 (q, $J = 2.87$ Hz), 32.0, 36.6 (q, $J = 1.14$ Hz), 69.9, 124.8 (q, $J = 276.3$ Hz), 126.0, 127.8 (q, $J = 26.6$ Hz), 128.3, 128.4, 141.1, 143.9 (q, $J = 3.44$ Hz).

(E)-1-Phenyl-3-trifluoromethylbut-2-en-1-ol (2c): ^1H NMR δ 1.87 (3 H, d, $J = 1.38$ Hz), 5.42 (1 H, d, $J = 8.52$ Hz), 6.27 (1 H, m), 7.27-7.41 (5 H, m). ^{19}F NMR δ 91.7 (s). ^{13}C NMR δ 11.2 (q, $J = 1.44$ Hz), 69.9, 123.7 (q, $J = 272.4$ Hz), 125.9, 126.4 (q, $J = 19.8$ Hz), 128.2, 128.8, 132.2 (q, $J = 5.73$ Hz), 141.5 (q, $J = 0.86$ Hz). IR (neat) ν 698, 745, 760, 899, 1011, 1076, 1115, 1177, 1242, 1281, 1327, 1450, 1493, 1686, 1751, 3314 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}$: C, 61.11; H, 5.13. Found: C, 61.59; H, 5.37.

3-Trifluoromethyl-1,5,5-trimethylcyclohex-2-en-1-ol (2d): ^1H NMR δ 1.03 (3 H, s), 1.06 (3 H, s), 1.34 (3 H, s), 1.58 (1 H, d, $J = 14.3$ Hz), 1.72 (1 H, dt, $J = 14.3, 1.37$ Hz), 1.89 (1 H, bd, $J = 17.0$ Hz), 1.99 (1 H, dsex, $J = 17.0, 1.10$ Hz), 6.19 (1 H, m). ^{19}F NMR δ 91.7 (s). ^{13}C NMR δ 27.2, 29.9, 30.5, 30.6 (q, $J = 0.86$ Hz), 35.9 (q, $J = 0.86$ Hz), 49.6, 68.3, 123.6 (q, $J = 271.7$ Hz), 127.7 (q, $J = 30.1$ Hz),

133.5 (q, $J = 5.44$ Hz). IR (neat) ν 690.5, 814.0, 848.7, 906.5, 1034, 1065, 1114, 1165, 1254, 1300, 1373, 1458, 2843, 2874, 2928, 2959, 3368, 3383 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{F}_3\text{O}$: C, 57.68; H, 7.26. Found: C, 57.81; H, 7.73.

(*E*)-1-(4-Nitrophenyl)-3-trifluoromethylbut-2-en-1-ol (2e): ^1H NMR δ 1.98 (3 H, d, $J = 1.37$ Hz), 5.64 (1 H, brd, $J = 8.51$ Hz), 6.21 (1 H, m), 7.50-7.64 (2 H, m), 8.18-8.30 (2 H, m). ^{19}F NMR δ 91.6 (s). ^{13}C NMR δ 11.4 (q, $J = 1.43$ Hz), 68.8, 123.4 (q, $J = 272.8$ Hz), 123.9, 126.6, 127.9 (q, $J = 30.1$ Hz), 132.9 (q, $J = 5.73$ Hz), 147.3, 148.5. IR (KBr) ν 397, 420, 474, 498, 517, 556, 586, 660, 710, 748, 844, 860, 880, 918, 961, 1015, 1038, 1072, 1107, 1130, 1188, 1215, 1242, 1300, 1346, 1389, 1439, 1516, 1601, 1751, 2307, 2345, 2369, 2369, 2851, 2913, 3013, 3067, 3109, 3510 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{NO}_3$: C, 50.58; H, 3.86; N, 5.36. Found: C, 50.80; H, 4.02; N, 5.24. mp 86 $^{\circ}\text{C}$.

2-Benzyl-3-trifluoromethylbut-2-en-1-ol (2g): *E* Isomer: ^1H NMR δ 1.95 (3 H, s), 3.70 (2 H, brs), 4.23 (2 H, brs), 7.13-7.36 (5 H, m). ^{19}F NMR δ 103.6 (quint, $J = 1.73$ Hz). ^{13}C NMR δ 14.2 (q, $J = 3.44$ Hz), 36.1, 60.7 (q, $J = 3.15$ Hz), 124.4 (q, $J = 275.1$ Hz), 124.6 (q, $J = 28.6$ Hz), 126.5, 128.2, 128.6, 137.6 (q, $J = 1.43$ Hz), 144.0 (q, $J = 3.15$ Hz). IR (neat) ν 698, 729, 756, 856, 1011, 1080, 1115, 1146, 1319, 1387, 1454, 1493, 1601, 1655, 1748, 2932, 3028, 3348 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}$: C, 62.60; H, 5.69. Found: C, 62.82; H, 5.85. ***Z* Isomer:** ^1H NMR δ 1.95 (3 H, s), 3.76 (2 H, brs), 4.12 (2 H, brs), 7.16-7.38 (5 H, m). ^{19}F NMR δ 102.8 (quint, $J = 1.72$ Hz). ^{13}C NMR δ 13.5 (q, $J = 3.44$ Hz), 36.7 (q, $J = 2.29$ Hz), 61.7, 124.4 (q, $J = 275.1$ Hz), 124.7 (q, $J = 28.3$ Hz), 126.5, 128.6, 128.7, 137.9, 143.1 (q, $J = 3.43$ Hz). IR (neat) ν 702, 760, 930, 1011, 1034, 1084, 1115, 1153, 1238, 1323, 1454, 1497, 1605, 1655, 1736, 2932, 3028, 3364 cm^{-1} .

(*E*)-1-Phenyl-3-(2-phenylethyl)-5-trifluoromethylhex-4-en-3-ol (2h): ^1H NMR δ 1.96 (4 H, m), 2.06 (3 H, d, $J = 1.64$ Hz), 2.70 (4 H, m), 6.03 (1 H, m), 7.15-7.35 (10 H, m). ^{19}F NMR δ 92.0 (s). ^{13}C NMR δ 11.4 (q, $J = 1.43$ Hz), 30.1, 43.9, 76.2, 125.4 (q, $J = 273.1$ Hz), 126.0, 127.3 (q, $J = 28.6$ Hz), 128.1, 128.5, 135.7 (q, $J = 5.72$ Hz), 141.5. IR (neat) ν 702, 737, 833, 910, 961, 995, 1030, 1065,

1115, 1173, 1304, 1366, 1454, 1497, 1605, 2866, 2932, 3028, 3063, 3449, 3503, 3564 cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{F}_3\text{O}$: C, 72.39; H, 6.65. Found: C, 72.07; H, 6.52.

(E)-5-Phenyl-3-trifluoromethylpent-2-en-1-ol (2i): ^1H NMR δ 2.52 (2 H, dd, $J = 7.42, 7.42$ Hz), 2.79 (2 H, dd, $J = 7.42, 7.41$ Hz), 3.82 (2 H, bs), 6.23 (1 H, tq, $J = 6.59, 1.65$ Hz), 7.15-7.38 (5 H, m). ^{19}F NMR δ 94.8 (dd, $J = 3.88, 2.15$ Hz). ^{13}C NMR δ 28.0, 34.7, 58.0, 124.1 (q, $J = 273.1$ Hz), 126.3, 128.4, 128.7, 129.1 (q, $J = 28.4$ Hz), 133.8 (q, $J = 6.01$ Hz), 140.3. IR (neat) ν 698, 748, 1007, 1115, 1161, 1184, 1219, 1296, 1323, 1454, 1740, 2365, 2870, 2936, 3028, 3063, 3086, 3329 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}$: C, 62.60; H, 5.69. Found: C, 62.27; H, 6.05.

(E)-1,3-Diphenyl-3-trifluoroprop-2-en-1-ol (2k): ^1H NMR δ 5.11 (1 H, d, $J = 9.03$ Hz), 6.60 (1 H, dq, $J = 9.27, 1.47$ Hz), 7.00-7.50 (10 H, m). ^{19}F NMR δ 95.2 (s). ^{13}C NMR δ 70.3, 123.0 (q, $J = 273.1$ Hz), 126.0, 128.2, 128.4, 128.7, 128.9, 129.5, 131.2, 131.9 (q, $J = 30.1$ Hz), 136.4 (q, $J = 5.15$ Hz), 141.3 (q, $J = 1.15$ Hz). IR (neat) ν 610, 679, 702, 752, 826, 914, 941, 1018, 1072, 1123, 1173, 1246, 1273, 1308, 1447, 1493, 1601, 1667, 1721, 1813, 1883, 1956, 2342, 2365, 2677, 2855, 2924, 3032, 3063, 3333 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}$: C, 69.06; H, 4.71. Found: C, 68.96; H, 4.98.

1-[(E)-3,6,6,6-Tetrafluoro-5-methylhex-4-enyl]benzene (3): ^1H NMR δ 1.77 (3 H, m), 1.84 (1 H, ddddd, $J = 28.4, 14.3, 9.34, 7.42, 4.40$ Hz), 2.15 (1 H, m), 2.72 (1 H, ddd, $J = 13.7, 8.79, 7.43$ Hz), 2.81 (1 H, ddd, $J = 13.7, 9.34, 5.77$ Hz), 5.16 (1 H, m), 6.15 (1 H, m), 7.17-7.36 (5 H, m). ^{19}F NMR δ -18.2 (1 F, m), 91.3 (3 F, m). ^{13}C NMR δ 11.2 (m), 30.7 (d, $J = 4.29$ Hz), 36.5 (dq, $J = 23.5, 0.86$ Hz), 87.7 (d, $J = 165.5$ Hz), 123.4 (q, $J = 273.4$ Hz), 126.2, 128.3, 128.5, 128.8 (dq, $J = 29.8, 10.3$ Hz), 130.6 (dq, $J = 23.2, 5.73$ Hz), 140.4. IR (neat) ν 700, 748, 871, 912, 993, 1024, 1122, 1185, 1296, 1340, 1457, 1496, 2346, 2366, 2862, 2953, 3029, 3074 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{F}_4$: C, 63.41; H, 5.73. Found: C, 63.16; H, 5.95.

***trans*-2-Hydroxy-1-(prop-1-en-2-yliden)-1,2,3,4-tetrahydronaphthalen (5):** ^1H NMR δ 1.60 (3 H, dd, $J = 1.37, 0.55$ Hz), 1.78 (1 H, dddd, $J = 12.4, 11.0, 9.89, 7.69$ Hz), 2.24 (1 H, dddd, $J = 12.4, 4.94, 4.12, 3.29$ Hz), 2.90 (1 H, m), 2.92 (1 H, m), 3.27 (1 H, d, $J = 9.06$ Hz), 3.86 (1 H, ddd, $J = 11.0, 9.06, 3.29$ Hz), 5.08 (1 H, m), 5.18 (1 H, dd, $J = 2.75, 1.38$ Hz), 7.07-7.16 (5 H, m). ^{13}C NMR δ 18.2, 28.2, 30.0, 57.6, 68.5, 117.4, 125.9, 126.0, 128.4, 128.4, 135.2, 135.9, 144.5. IR (neat) ν 745, 810, 841, 895, 957, 980, 1007, 1042, 1069, 1111, 1150, 1184, 1207, 1238, 1277, 1323, 1350, 1373, 1396, 1439, 1489, 1578, 1601, 1647, 1809, 1921, 2342, 2365, 2870, 2932, 3017, 3071, 3387 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.94; H, 8.57. Found: C, 82.66; H, 8.55.

Typical procedure for the reduction of 1 with DIBAL-H: The reaction of (*E*)-3,4-epoxy-1,1-difluoro-2-methyl-6-phenylhex-1-ene **1a** in CH_2Cl_2 is described as a representative example. To a solution of **1a** (0.10 g, 0.45 mmol) in 5 mL of dry CH_2Cl_2 , 2.0 equiv of DIBAL-H (0.89 mmol) was added at -78°C under argon. After 1.0 h stirring, the reaction was quenched with 3 *N* HCl aq, and the organic layer was extracted with CH_2Cl_2 three times and dried over anhydrous MgSO_4 . Removal of the solvents and purification with silica gel column chromatography (*n*-hexane:AcOEt = 4:1) afforded the pure *E*-**7a** in 66% yield. For the yields of other products, see Table 5.

Typical procedure for the reduction of 1 with $\text{BH}_3\cdot\text{THF}$: The reaction of (*E*)-3,4-epoxy-1,1-difluoro-2-methyl-6-phenylhex-1-ene **1a** is described as a representative example. To a solution of **1a** (0.10 g, 0.45 mmol) in 5 mL of dry THF, 0.75 equiv of $\text{BH}_3\cdot\text{THF}$ THF solution (0.33 mmol) was added under argon. After 1.0 h stirring at rt, the reaction was quenched with 3 *N* NaOH aq, and the organic layer was extracted with Et_2O three times, washed with brine, and dried over anhydrous MgSO_4 . Removal of the solvents and purification with silica gel column chromatography (*n*-hexane:AcOEt = 4:1) afforded the pure *Z*-**7a** in 95% yield. For the yields of other products, see Table 7.

5-(Difluoromethyl)-4-methyl-1-phenylhept-4-en-3-ol (7b): ^1H NMR δ 0.96 (3 H, dd, $J = 7.69, 7.42$ Hz), 1.56-2.30 (7 H, m), 2.54-2.86 (1 H, m), 2.81 (1 H, ddd, $J = 14.0, 9.59, 5.22$ Hz), 4.61 (1 H, dd, $J = 8.79, 4.67$ Hz), 6.47 (1 H, t, $J = 55.8$ Hz), 7.13-7.35 (5 H, m). ^{19}F NMR δ 44.9 (1 F, m), 46.3 (1 F, m). **Z Isomer:** ^1H NMR δ 1.05 (3 H, dd, $J = 7.69, 7.42$ Hz), 1.70-1.84 (1 H, m), 1.75 (3 H, dd, $J = 4.12, 3.85$ Hz), 1.96 (1 H, dddd, $J = 14.0, 9.34, 7.96, 6.04$ Hz), 2.19 (2 H, m), 2.56 (1 H, ddd, $J = 13.7, 9.34, 6.87$ Hz), 2.69 (1 H, ddd, $J = 13.7, 9.89, 6.05$ Hz), 4.52 (1 H, m), 6.50 (1 H, t, $J = 55.8$ Hz), 7.13-7.35 (5 H, m). ^{19}F NMR δ 47.8 (1 F, ddq, $J = 310.0, 55.6, 3.88$ Hz), 49.1 (1 F, ddq, $J = 311.1, 55.6, 3.88$ Hz). ^{13}C NMR δ 12.6, 13.7, 19.6 (t, $J = 3.15$ Hz), 31.9, 36.8 (t, $J = 1.43$ Hz), 69.5, 112.8 (t, $J = 232.8$ Hz), 125.9, 128.2, 128.3, 131.5 (dd, $J = 21.7, 20.3$ Hz), 141.1, 141.8 (dd, $J = 9.73, 9.47$ Hz). IR (neat) ν 698, 748, 802, 934, 1003, 1069, 1115, 1157, 1160, 1250, 1285, 1339, 1377, 1454, 1497, 1605, 1655, 2878, 2940, 2970, 3028, 3063, 3387 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{F}_2\text{O}$: C, 70.84; H, 7.93. Found: C, 70.63; H, 7.61.

4,4-Difluoro-3-methyl-1-phenylbut-2-en-1-ol (7c): IR (neat) ν 700, 761, 845, 890, 917, 1020, 1091, 1192, 1249, 1340, 1396, 1420, 1437, 1453, 1473, 1493, 2855, 2927, 2957, 2988, 3031, 3064, 3351 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{F}_2\text{O}$: C, 66.66; H, 6.10. Found: C, 66.10; H, 6.12. **E Isomer:** ^1H NMR δ 1.86 (3 H, m), 5.54 (1 H, ddt, $J = 8.43, 3.41, 1.47$ Hz), 5.95 (1 H, t, $J = 55.7$ Hz), 5.96 (1 H, m), 7.31-7.42 (5 H, m). ^{19}F NMR δ 45.8 (1 F, dd, $J = 300.6, 54.9$ Hz), 46.5 (1 F, dd, $J = 300.6, 54.9$ Hz). ^{13}C NMR δ 9.85 (t, $J = 2.15$ Hz), 69.9, 117.0 (t, $J = 237.2$ Hz), 125.8, 128.0, 128.7, 130.9 (t, $J = 21.8$ Hz), 134.7 (t, $J = 9.74$ Hz), 142.0 (t, $J = 1.58$ Hz). **Z Isomer:** ^1H NMR δ 1.83 (3 H, s), 5.54 (1 H, d, $J = 8.79$ Hz), 5.76 (1 H, d, $J = 8.79$ Hz), 6.67 (1 H, t, $J = 55.5$ Hz), 7.25-7.41 (5H, m). ^{19}F NMR δ 44.3 (1 F, dd, $J = 294.3, 56.5$ Hz), 45.4 (1 F, dd, $J = 314.3, 56.5$ Hz). ^{13}C NMR δ 15.9 (t, $J = 3.14$ Hz), 69.5 (m), 112.1 (t, $J = 234.5$ Hz), 125.7, 127.9, 128.7, 130.8 (dd, $J = 22.3, 21.8$ Hz), 135.4 (t, $J = 8.74$ Hz), 142.1 (t, $J = 2.57$ Hz).

3-(Difluoromethyl)-1,5,5-trimethylcyclohex-2-enol (7d): ^1H NMR δ 1.02 (3 H, s), 1.05 (3 H, s), 1.31 (3 H, s), 1.59 (1 H, d, $J = 14.3$ Hz), 1.71 (1 H, dt, $J = 14.3, 1.37$ Hz), 1.85 (1 H, dq, $J = 17.2, 2.20$

Hz), 1.99 (1 H, dq, $J = 17.1, 1.37$ Hz), 5.89 (1 H, m), 5.89 (1 H, t, $J = 56.0$ Hz). ^{19}F NMR δ 44.2 (1 F, ddd, $J = 301.6, 3.88, 2.16$ Hz), 45.6 (1 F, ddd, $J = 301.6, 4.30, 2.58$ Hz). ^{13}C NMR δ 27.4, 29.8, 30.6 (dd, $J = 1.44, 1.43$ Hz), 30.7, 34.9, 50.3, 68.5, 116.3 (t, $J = 235.9$ Hz), 131.9 (t, $J = 22.1$ Hz), 133.9 (t, $J = 9.74$ Hz). IR (neat) ν 694, 814, 880, 907, 937, 1018, 1061, 1107, 1150, 1188, 1261, 1277, 1369, 1458, 2843, 2874, 2928, 2959, 3387 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{F}_2\text{O}$: C, 63.14; H, 8.48. Found: C, 63.39; H, 7.99.

4,4-Difluoro-3-methyl-1-(4-nitrophenyl)but-2-en-1-ol (7e): IR (KBr) ν 702, 748, 837, 856, 899, 1022, 1092, 1188, 1242, 1285, 1350, 1396, 1450, 1520, 1605, 2862, 2928, 2959, 3082, 3113, 3410 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{F}_2\text{NO}_3$: C, 54.32; H, 4.36; N, 5.76. Found: C, 54.81; H, 4.92; N, 5.45. **E Isomer:** ^1H NMR δ 1.93 (3 H, q, $J = 1.10$ Hz), 5.65 (1 H, m), 5.88 (1 H, m), 5.96 (1 H, t, $J = 55.8$ Hz), 7.52-7.60 (2 H, m), 8.21-8.29 (2 H, m). ^{19}F NMR δ 45.6 (m). ^{13}C NMR δ 10.0 (dd, $J = 2.29, 2.00$ Hz), 68.7, 116.5 (dd, $J = 237.6, 237.3$ Hz), 123.7, 126.5, 132.2 (t, $J = 21.8$ Hz), 133.1 (t, $J = 10.0$ Hz), 147.1, 149.1 (dd, $J = 1.72, 1.43$ Hz). **Z Isomer:** ^1H NMR δ 1.86 (3 H, s), 5.71 (2 H, s), 6.66 (1 H, t, $J = 55.5$ Hz), 7.50-7.59 (2 H, m), 8.15-8.24 (2 H, m). ^{19}F NMR δ 44.6 (1 F, dd, $J = 314.4, 55.2$ Hz), 46.7 (1 F, dd, $J = 314.5, 55.6$ Hz). ^{13}C NMR δ 16.3 (dd, $J = 3.72, 3.16$ Hz), 68.4, 112.1 (dd, $J = 235.6, 235.3$ Hz), 123.7, 126.5, 132.2 (dd, $J = 23.3, 21.5$ Hz), 134.1 (dd, $J = 8.31, 8.02$ Hz), 147.1, 149.1 (dd, $J = 1.43, 1.14$ Hz).

4,4-Difluoro-3-methyl-1-(4-methylphenyl)but-2-en-1-ol (7f): IR (neat) ν 505, 721, 764, 814, 891, 945, 1018, 1092, 1246, 1285, 1339, 1396, 1454, 1512, 1612, 1686, 1906, 2739, 2866, 2928, 2955, 2990, 3024, 3094, 3356, 3588 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_2\text{O}$: C, 67.91; H, 6.65. Found: C, 67.60; H, 6.84. **E Isomer:** ^1H NMR δ 1.83 (3 H, dt, $J = 1.37, 1.10$ Hz), 2.34 (3 H, s), 5.46 (1 H, d, $J = 8.52$ Hz), 5.92 (1 H, t, $J = 56.0$ Hz), 5.94 (1 H, m), 7.15-7.22 (4 H, m). ^{19}F NMR δ 46.3 (m). **Z Isomer:** ^1H NMR δ 1.82 (3 H, s), 2.34 (3 H, s), 5.46 (1 H, d, $J = 8.79$ Hz), 5.74 (1 H, m), 6.65 (1 H, t, $J = 55.4$ Hz), 7.13-7.28 (4 H, m). ^{19}F NMR δ 44.2 (1 F, dd, $J = 314.1, 55.6$ Hz), 45.6 (1 F, dd, $J = 314.1, 55.6$ Hz).

^{13}C NMR δ 15.8 (t, $J = 3.15$ Hz), 21.1, 69.3, 112.1 (t, $J = 234.5$ Hz), 125.7, 129.3, 130.4 (dd, $J = 23.1$, 22.0 Hz), 135.7 (t, $J = 8.69$ Hz), 137.6, 139.2 (t, $J = 1.14$ Hz).

2-Benzyl-4,4-difluoro-3-methylbut-2-en-1-ol (7g): IR (neat) ν 513, 702, 737, 783, 880, 937, 1007, 1057, 1096, 1153, 1192, 1285, 1389, 1454, 1493, 1601, 1682, 2928, 3028, 3063, 3368 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_2\text{O}$: C, 67.91; H, 6.65. Found: C, 67.98; H, 6.43. **Z Isomer:** ^1H NMR δ 1.91 (3 H, quint, $J = 0.73$ Hz), 3.61 (2 H, m), 4.16 (2 H, dtq, $J = 5.73$, 1.71, 0.73 Hz), 6.71 (1 H, t, $J = 55.9$ Hz), 7.17-7.33 (5 H, m). ^{19}F NMR δ 46.2 (d, $J = 55.7$ Hz). ^{13}C NMR δ 11.1 (t, $J = 3.58$ Hz), 36.5, 60.1 (t, $J = 1.01$ Hz), 112.8 (t, $J = 233.0$ Hz), 126.4, 128.3, 128.6, 128.9 (t, $J = 22.3$ Hz), 137.8 (t, $J = 2.57$ Hz), 140.8 (t, $J = 9.45$ Hz). **E Isomer:** ^{19}F NMR δ 45.7 (m).

(Z)-3-(Difluoromethyl)-5-phenylpent-2-en-1-ol (7i): Z Isomer: ^1H NMR δ 2.28-2.36 (2 H, m), 2.61-2.68 (2 H, m), 4.09 (2 H, m), 5.60 (1 H, brt, $J = 6.60$ Hz), 6.35 (1 H, t, $J = 55.5$ Hz), 7.00-7.20 (5 H, m). ^{19}F NMR δ 46.2 (ddd, $J = 55.6$, 3.02, 2.58 Hz). ^{13}C NMR δ 27.3 (dd, $J = 2.57$, 2.39 Hz), 30.2, 53.5, 108.0 (t, $J = 235.3$ Hz), 121.3, 123.7, 123.7, 128.5 (t, $J = 8.88$ Hz), 130.0 (t, $J = 21.2$ Hz), 136.4. IR (neat) ν 698, 748, 799, 910, 1022, 1096, 1153, 1184, 1242, 1300, 1342, 1400, 1454, 1496, 1605, 2866, 2932, 3001, 3028, 3063, 3368 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_2\text{O}$: C, 67.91; H, 6.65. Found: C, 67.96; H, 7.15.

4,4-Difluoro-1,3-diphenylbut-2-en-1-ol (7k): IR (neat) ν 509, 702, 760, 806, 841, 903, 1026, 1096, 1123, 1196, 1234, 1281, 1358, 1393, 1450, 1493, 1601, 1732, 1813, 1890, 1956, 2854, 2928, 3028, 3059, 3364 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_2\text{O}$: C, 73.83; H, 5.42. Found: C, 73.78; H, 5.81. **E Isomer:** ^1H NMR δ 5.22 (1 H, dd, $J = 9.10$, 3.36 Hz), 6.21 (1 H, t, $J = 55.7$ Hz), 6.29 (1 H, dt, $J = 9.27$, 2.32 Hz), 7.05-7.50 (10 H, m). ^{19}F NMR δ 49.0 (d, $J = 56.0$ Hz). ^{13}C NMR δ 70.2, 115.6 (t, $J = 222.9$ Hz), 126.0, 128.0, 128.4, 128.4, 128.6, 129.3, 132.3 (t, $J = 1.00$ Hz), 135.9 (t, $J = 20.6$ Hz), 136.0 (t, $J = 9.02$ Hz), 141.9 (t, $J = 1.29$ Hz). **Z Isomer:** ^1H NMR δ 5.82 (1 H, m), 6.19 (1 H, d, $J = 8.52$ Hz), 6.90 (1 H, t, $J = 54.7$ Hz), 7.15-7.60 (10 H, m). ^{19}F NMR δ 50.9 (2F, dd, $J = 54.7$, 6.03 Hz). ^{13}C NMR

δ 69.8, 112.9 (t, $J = 237.6$ Hz), 125.9, 127.5, 128.0, 128.1, 128.3, 128.7, 134.7 (t, $J = 21.0$ Hz), 135.8 (t, $J = 1.71$ Hz), 138.6 (t, $J = 6.87$ Hz), 141.7 (t, $J = 1.43$ Hz).

5-Difluoromethylene-1-phenylhexan-3-ol (8a): ^1H NMR δ 1.59 (3 H, m), 1.76 (1 H, m), 1.80 (1 H, m), 2.08 (1 H, ddt, $J = 14.3, 4.95, 2.47$ Hz), 2.18 (1 H, m), 2.68 (1 H, ddd, $J = 13.7, 9.06, 7.14$), 2.82 (1 H, ddd, $J = 13.7, 9.34, 6.60$ Hz), 3.74 (1 H, ddd, $J = 12.6, 7.97, 4.94$ Hz), 7.15-7.33 (5 H, m). ^{19}F NMR δ 66.6 (1 F, dsex, $J = 54.7, 3.02$ Hz), 67.3 (1 F, dq, $J = 55.1, 3.01$ Hz). ^{13}C NMR δ 12.5 (dd, $J = 2.29, 1.44$ Hz), 32.1, 36.6 (d, $J = 3.29$ Hz), 38.7, 68.9 (dd, $J = 3.44, 2.30$ Hz), 82.0 (dd, $J = 19.2, 18.9$ Hz), 125.8, 128.3, 128.3, 141.6, 153.7 (dd, $J = 283.1, 280.7$ Hz). IR (neat) ν 700, 746, 856, 926, 1030, 1052, 1082, 1119, 1204, 1268, 1454, 1496, 1604, 1758, 1944, 2344, 2362, 2864, 2927, 3028, 3063, 3086, 3374 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{F}_2\text{O}$: C, 69.01; H, 7.13. Found: C, 68.86; H, 6.97.

4-Difluoromethylene-1-phenylbutan-1-ol (8c): ^1H NMR δ 1.59 (3 H, t, $J = 3.17$ Hz), 2.29 (1 H, ddt, $J = 14.2, 5.37, 2.57$ Hz), 2.50 (1 H, dddd, $J = 14.2, 8.55, 1.10, 0.98$ Hz), 4.80 (1 H, m), 7.27-7.38 (5 H, m). ^{19}F NMR δ 66.9 (1 F, dsex, $J = 53.4, 3.05$ Hz), 67.3 (1 F, dq, $J = 53.4, 3.05$ Hz). ^{13}C NMR δ 12.5 (dd, $J = 2.15, 1.56$ Hz), 38.2 (d, $J = 2.58$ Hz), 72.3 (dd, $J = 3.44, 2.29$ Hz), 81.9 (t, $J = 18.9$ Hz), 125.6, 127.7, 128.4, 143.5, 153.7 (dd, $J = 283.1, 282.1$ Hz). IR (neat) ν 513, 702, 741, 760, 833, 872, 914, 968, 1003, 1030, 1053, 1123, 1204, 1219, 1273, 1331, 1389, 1454, 1492, 1755, 2955, 3032, 3063, 3383 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{F}_2\text{O}$: C, 66.66; H, 6.10. Found: C, 66.72; H, 6.57.

5-(Difluoromethylene)-1,3,3-trimethylcyclohexanol (8d): ^1H NMR δ 0.96 (3 H, s), 1.06 (3 H, s), 1.26 (3 H, s), 1.35 (1 H, d, $J = 14.0$ Hz), 1.53 (1 H, dt, $J = 14.3, 1.92$ Hz), 1.64 (1 H, m), 1.90 (1 H, ddd, $J = 14.3, 4.67, 2.75$ Hz), 2.09 (1 H, dq, $J = 13.7, 1.65$ Hz), 2.31 (1 H, dq, $J = 14.0, 1.65$ Hz). ^{19}F NMR δ 64.2 (1 F, m), 65.1 (1 F, m). ^{13}C NMR δ 27.8, 31.5 (d, $J = 0.86$ Hz), 32.2 (d, $J = 0.86$ Hz), 32.2 (dd, $J = 2.58, 1.72$ Hz), 37.5 (d, $J = 2.02$ Hz), 38.0 (d, $J = 2.29$ Hz), 71.2 (dd, $J = 2.29, 1.44$ Hz), 84.1 (dd, $J = 20.3, 18.6$ Hz), 152.8 (dd, $J = 281.4, 281.1$ Hz). IR (neat) ν 818, 872, 903, 1049,

1069, 1107, 1192, 1211, 1265, 1292, 1335, 1373, 1458, 1763, 2843, 2874, 2924, 2955, 3410 cm^{-1} .

Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{F}_2\text{O}$: C, 63.14; H, 8.48. Found: C, 63.44; H, 8.96.

3-(Difluoromethylene)-5-phenylpentan-1-ol (8i): ^1H NMR δ 2.18-2.36 (4 H, m), 2.71 (2 H, m), 3.66 (2 H, dd, $J = 6.86, 6.60$ Hz), 7.14-7.36 (5 H, m). ^{19}F NMR δ 67.5 (1 F, dq, $J = 52.6, 2.15$ Hz), 68.8 (1 F, dq, $J = 52.6, 2.15$ Hz). ^{13}C NMR δ 28.4 (d, $J = 2.29$ Hz), 29.8 (d, $J = 2.58$ Hz), 34.0 (dd, $J = 3.44, 2.29$ Hz), 60.3 (dd, $J = 3.72, 2.58$ Hz), 85.4 (dd, $J = 18.0, 16.9$ Hz), 126.0, 128.2, 128.3, 140.9, 154.1 (dd, $J = 284.6, 284.9$ Hz). IR (neat) ν 698, 748, 845, 926, 1049, 1099, 1157, 1211, 1258, 1350, 1377, 1454, 1497, 1605, 1748, 2866, 2932, 2959, 3028, 3063, 3082, 3368 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_2\text{O}$: C, 67.91; H, 6.65. Found: C, 67.85; H, 7.14.

3,4-Epoxy-1-fluoro-2-methyl-6-phenylhex-1-ene (11): ^1H NMR δ 1.48 (3 H, dd, $J = 3.30, 1.65$ Hz), 1.80-2.00 (2 H, m), 2.73 (1 H, ddd, $J = 14.0, 8.24, 7.97$ Hz), 2.83 (1 H, ddd, $J = 14.0, 8.79, 6.04$ Hz), 2.90-2.97 (2 H, m), 6.61 (1 H, ddd, $J = 83.2, 3.29, 1.37$ Hz), 7.16-7.33 (5 H, m). ^{19}F NMR δ 30.2 (1 F, dq, $J = 83.2, 3.02$ Hz). ^{13}C NMR δ 7.46 (d, $J = 4.87$ Hz), 32.2, 33.7, 56.8 (d, $J = 2.62$ Hz), 57.3 (d, $J = 13.7$ Hz), 115.8 (d, $J = 9.16$ Hz), 126.0, 128.2, 128.4, 140.9, 147.1 (d, $J = 257.1$ Hz). IR (neat) ν 656, 698, 733, 748, 883, 949, 1030, 1053, 1103, 1126, 1389, 1454, 1497, 1601, 1686, 2859, 2928, 2986, 3028, 3063 cm^{-1} .

Table 5. Reduction of **1a** with Various Reducing Reagents.

entry	conditions (equiv)	yield (%)		<i>E/Z</i>	recovery
		7a	8a	of 7a	of 1a (%)
1	NaBH ₄ (0.5), DMSO, rt, 1 d.	<1	<1	–	>99
2	NaBH ₄ (0.5), DMSO, 100 °C, 1 d.	9	24	>99/<1	– ^a
3	LiAlH ₄ (0.5), Et ₂ O, rt, 1 d.	<1	54	–	19
4	LiAlH ₄ (0.5), THF, reflux, 2 h.	<1	78	–	4
5	Zn(BH ₄) ₂ (0.5), THF, rt, 1 d.	28	<1	<1/>99	– ^a
6	Zn(BH ₄) ₂ (0.5), THF, reflux, 5 h.	60	<1	<1/>99	0
7	DIBAL-H (2.0), <i>n</i> -hexane, 0 °C, 2 h.	74	<1	67/23	0
8	BH ₃ ·THF (1.0), THF, rt, 1 h.	72	<1	<1/>99	0
9	Pd/C (0.05), H ₂ MeOH, rt, 3 h.	45	39	>99/<1	0

Yields, ratios, and recoveries were determined by ¹⁹F NMR. ^a Remaining **1a** decomposed during workup.

Table 6. Reaction of **1a** with DIBAL-H.

entry	conditions	yield (%)	<i>E/Z</i>
1	<i>n</i> -Hexane, 0 °C, 1 h	74	67/33
2 ^a		54	73/27
3 ^b		56	73/27
4	Et ₂ O, 0 °C, 1 h	53	60/40
5	CH ₂ Cl ₂ , 0 °C, 1 h	58	84/16
6	Benzene, 0 °C, 1 h	81	75/25
7 ^{c,d}	CH ₂ Cl ₂ , -78 °C, 1 h	77	>99/<1
8 ^c	<i>n</i> -Hexane, -78 °C, 1 h	64	>99/<1

Yields and ratios were determined by ¹⁹F NMR. ^a 1.2 equiv of DIBAL-H was used. ^b 1.0 equiv of DIBAL-H was used. ^c The remaining **1a** decomposed during workup. ^d 14% of **8a** was formed.

Table 7. Reaction of **1a** with $\text{BH}_3\cdot\text{THF}$.

entry	equiv of $\text{BH}_3\cdot\text{THF}$	yield (%)
1	1.50	29
2	1.00	72
3	0.75	94
4 ^a	0.60	90
5 ^b	0.75	43

Yields were determined by ^{19}F NMR. ^a 5% of **1a** was recovered. ^b Et_2O was used as a solvent.

Scheme 6