Supporting Information

1-Trifluoromethylvinylsilane as a $\text{CF}_2=\text{C}^--\text{CH}_2^+$ Synthon: Synthesis of Functionalized

1,1-Difluoro-1-alkenes via Isolable 2,2-Difluorovinylsilanes

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General considerations: NMR spectra were recorded at the indicated field strengths. Chemical shift values were given in ppm relative to internal Me_4Si (for ^1H NMR: δ 0.00), CDCl_3 (for ^{13}C NMR: δ 77.0), and C_6F_6 (for ^{19}F NMR: δ_{F} 0.00). THF was distilled from sodium benzophenone ketyl prior to use. CH_2Cl_2 was distilled from P_2O_5 and then from CaH , and stored over molecular sieves $4\text{\AA}$. Column chromatography and preparative thin-layer chromatography (PTLC) were performed on

silica gel (KANTO CHEMICAL Co. Inc., Silica Gel 60 and Wako Pure Chemical Industries, Ltd., B5-F), respectively.

Dimethylphenyl(1-trifluoromethylvinyl)silane (8). To a suspension of magnesium turnings (292 mg, 12.0 mmol) and chlorodimethylphenylsilane (3.36 mL, 20.0 mmol) in THF (10 mL) was added 2-bromo-3,3,3-trifluoro-1-propene (1.04 mL, 10.0 mmol) over 8 h at $-10\text{ }^{\circ}\text{C}$ under argon. The reaction mixture was stirred at $-10\text{ }^{\circ}\text{C}$ for 5 h and then at room temperature for an additional 12 h. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were extracted with Et_2O (10 mL x 3). The combined extracts were washed with brine and then dried over MgSO_4 . After removal of the solvent under reduced pressure (30 kPa), the residue was purified by column chromatography (pentane) to give **8** (1.84 mg, 80%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.32 (6H, s), 5.32 (1H, s), 5.84 (1H, bs), 7.33–7.41 (3H, m), 7.46–7.51 (2H, m). ^{13}C NMR (126 MHz, CDCl_3) δ -2.9 , 125.7 (q, $J_{\text{CF}} = 274\text{ Hz}$), 128.0, 129.7, 134.0, 134.2 (q, $J_{\text{CF}} = 17\text{ Hz}$), 135.6, 140.9 (q, $J_{\text{CF}} = 30\text{ Hz}$). ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 101.9 (s). IR (neat) 2967, 1614, 1413, 1255, 1120, 975, 836, 811 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{F}_3\text{Si}$: C, 57.37; H, 5.69. Found: C, 57.43; H, 5.53.

(2,2-Difluoro-1-pentylvinyl)dimethylphenylsilane (9b). To a solution of **8** (2.30 g, 10.0 mmol) in THF (50 mL) was added *n*-BuLi (6.56 mL, 1.63 M in hexane, 10.7 mmol) over 20 min at $-78\text{ }^{\circ}\text{C}$ under argon. After the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 min, H_2O was added to quench the reaction. Organic materials were extracted with Et_2O (10 mL x 3). The combined extracts were washed with brine and then dried over MgSO_4 . After removal of the solvent under reduced pressure (30 kPa), the residue was purified by PTLC (pentane) to give **9b** (2.51 g, 93%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.42 (6H, s), 0.81 (3H, t, $J = 6.9\text{ Hz}$), 1.12–1.27 (6H, m), 1.93 (2H, br t, $J = 7.6\text{ Hz}$), 7.32–7.39 (3H, m), 7.48–7.54 (2H, m). ^{13}C NMR (126 MHz, CDCl_3) δ -2.4 , 13.9, 22.3, 25.7 (dd, $J_{\text{CF}} = 5, 5\text{ Hz}$), 29.5, 31.5, 81.1 (br d, $J_{\text{CF}} = 26\text{ Hz}$), 127.8, 129.2, 133.7, 137.5, 156.6 (dd, $J_{\text{CF}} = 306, 306\text{ Hz}$). ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 85.6 (1F, d, $J_{\text{FF}} = 37\text{ Hz}$), 88.6 (1F, d, $J_{\text{FF}} = 37\text{ Hz}$). IR (neat) 3070, 2958, 2931, 1689, 1428, 1251, 1110, 813, 779, 701 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{F}_2\text{Si}$: C, 67.12; H, 8.26. Found: C, 67.37; H, 8.22.

(2,2-Difluoro-1-undecylvinyl)dimethylphenylsilane (9c). To a solution of 1-iododecane (3.02 g, 11.3 mmol) in Et₂O (10 mL) was added *t*-BuLi (15.3 mL, 1.50 M in pentane, 23.0 mmol) over 5 min at –78 °C under argon. After being stirred at room temperature for 1 h, the reaction mixture was added to a solution of **8** (2.31 mg, 10.0 mmol) in THF (50 mL) over 5 min at –78 °C. The reaction mixture was stirred at –78 °C for 1 h, and then H₂O was added to quench the reaction. Organic materials were extracted with ethyl acetate (AcOEt, 50 mL x 3). The combined extracts were washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane) to give **9c** (3.49 g, 99%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 0.41 (6H, s), 0.88 (3H, t, *J* = 7.0 Hz), 1.12–1.28 (18H), 1.93 (2H, t, *J* = 7.6 Hz), 7.35–7.36 (3H, m), 7.62 (2H, dd, *J* = 7.1, 2.3 Hz). ¹³C NMR (126 MHz, CDCl₃) δ –2.4, 14.1, 22.7, 25.7 (dd, *J*_{CF} = 6, 4 Hz), 29.3, 29.4, 29.5, 29.6, 29.9, 29.9, 31.9, 81.0 (dd, *J*_{CF} = 25, 3 Hz), 127.8, 129.2, 133.7, 137.5, 156.6 (dd, *J*_{CF} = 306, 283 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ_F 85.5 (1F, d, *J*_{FF} = 36 Hz), 88.6 (1F, d, *J*_{FF} = 36 Hz). IR (neat) 2924, 2854, 1685, 1221, 1111, 775, 700 cm^{–1}. Anal. Calcd for C₂₁H₃₄F₂Si: C, 71.54; H, 9.72. Found: C, 71.41; H, 9.93.

(1-Benzyl-2,2-difluorovinyl)dimethylphenylsilane (9d). To a solution of **8** (94 mg, 0.41 mmol) and *N,N,N',N'*-tetramethylethylenediamine (62 μL, 0.41 mmol) in THF (4 mL) was added PhLi (0.42 mL, 1.06 M in Et₂O–cyclohexane, 0.45 mmol) over 10 min at –78 °C under argon. After being stirred for 2.5 h, the reaction mixture was warmed up to 0 °C. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were extracted with Et₂O (5 mL x 3). The combined extracts were washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane) to give **9d** (100 mg, 85%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 0.30 (6H, s), 3.32 (2H, s), 7.02 (2H, d, *J* = 7.3 Hz), 7.13–7.17 (1H, m), 7.18–7.22 (2H, m), 7.29–7.32 (2H, m), 7.34–7.39 (3H, m). ¹³C NMR (126 MHz, CDCl₃) δ –2.5, 31.5 (dd, *J*_{CF} = 7, 5 Hz), 80.7 (dd, *J*_{CF} = 28, 4 Hz), 126.1, 127.7, 128.2, 128.3, 129.3, 133.8, 138.2, 157.3 (dd, *J*_{CF} = 307, 284 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ_F 85.7 (1F, d, *J*_{FF} = 33 Hz), 88.9 (1F, d, *J*_{FF} = 33 Hz). IR (neat) 3027, 2958, 1689, 1600, 1427, 1112, 1027, 779, 734, 700 cm^{–1}. Anal. Calcd for C₁₇H₁₈F₂Si: C, 70.80; H, 6.29. Found: C, 70.79; H, 6.48.

[2,2-Difluoro-1-(2-phenyl-1,3-dithian-2-ylmethyl)vinyl]dimethylphenylsilane (9e).

To a solution of 2-phenyl-1,3-dithiane (216 mg, 1.10 mmol) in THF (5 mL) was added *n*-BuLi (0.71 mL, 1.63 M in hexane, 1.2 mmol) at $-30\text{ }^{\circ}\text{C}$ under argon. The reaction mixture was stirred at $-30\text{ }^{\circ}\text{C}$ for 1 h, and **8** (230 mg, 0.998 mmol) in THF (1 mL) was added over 10 min at $-78\text{ }^{\circ}\text{C}$. After being stirred at $-78\text{ }^{\circ}\text{C}$ for 3 h, the reaction mixture was warmed up to $0\text{ }^{\circ}\text{C}$. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were extracted with AcOEt (10 mL x 3). The combined extracts were washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane–AcOEt 50:1) to give **9e** (361 mg, 89%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.35 (6H, s), 1.85–1.89 (2H, m), 2.56–2.66 (4H, m), 2.72 (2H, s), 7.22–7.25 (1H, m), 7.30–7.35 (5H, m), 7.47–7.49 (2H, m), 7.87–7.88 (2H, m). ^{13}C NMR (126 MHz, CDCl_3) δ –2.1, 24.6, 27.7, 41.3 (d, $J_{\text{CF}} = 7\text{ Hz}$), 60.6, 76.5 (dd, $J_{\text{CF}} = 24, 6\text{ Hz}$), 126.9, 127.5, 128.4, 128.9, 129.4, 133.8, 137.7, 140.7, 157.6 (dd, $J_{\text{CF}} = 313, 285\text{ Hz}$). ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 92.1 (1F, d, $J_{\text{FF}} = 20\text{ Hz}$), 98.0 (1F, d, $J_{\text{FF}} = 20\text{ Hz}$). IR (neat) 2904, 1673, 1224, 1111, 906, 812, 729, 698 cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{F}_2\text{S}_2\text{Si}$: C, 62.03; H, 5.95. Found: C, 62.00; H, 5.98.

[1-(1,3-Dithian-2-ylmethyl)-2,2-difluorovinyl]dimethylphenylsilane (9f).

To a solution of 1,3-dithiane (55 mg, 0.44 mmol) in THF (3 mL) was added *n*-BuLi (0.29 mL, 1.55 M in hexane, 0.44 mmol) at $-20\text{ }^{\circ}\text{C}$ under argon. The reaction mixture was stirred at $-20\text{ }^{\circ}\text{C}$ for 1 h and **8** (92 mg, 0.40 mmol) in THF (1 mL) was added over 10 min at $-78\text{ }^{\circ}\text{C}$. After being stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, the reaction mixture was warmed up to room temperature. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were extracted with Et_2O (5 mL x 3). The combined extracts were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane– CHCl_3 1:1) to give **9f** (99 mg, 75%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.47 (3H, s), 0.48 (3H, s), 1.75–1.85 (1H, m), 1.98–2.05 (1H, m), 2.43 (2H, br d, $J = 7.7\text{ Hz}$), 2.62 (2H, ddd, $J = 14.2, 11.4, 2.5\text{ Hz}$), 2.76 (2H, ddd, $J = 14.2, 5.3, 3.0\text{ Hz}$), 3.64 (1H, t, $J = 7.7\text{ Hz}$), 7.36–7.40 (3H, m), 7.56–7.58 (2H, m). ^{13}C NMR (126 MHz, CDCl_3) δ –2.4, 25.7, 29.9, 31.6 (dd, $J_{\text{CF}} = 3, 3\text{ Hz}$), 46.8 (dd, $J_{\text{CF}} = 3, 3\text{ Hz}$), 78.2 (dd, $J_{\text{CF}} = 25, 4\text{ Hz}$), 127.9, 129.4, 133.8, 136.9, 157.2 (dd, $J_{\text{CF}} = 309, 286\text{ Hz}$). ^{19}F NMR (471 MHz, CDCl_3) δ_{F}

88.2 (1F, d, $J_{\text{FF}} = 29$ Hz), 93.6 (1F, d, $J_{\text{FF}} = 29$ Hz). IR (neat) 3367, 2952, 2898, 1691, 1427, 1234, 1110, 813 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{F}_2\text{S}_2\text{Si}$: C, 54.51; H, 6.10; S, 19.40. Found: C, 54.55; H, 5.99; S, 19.68.

2-Benzyl-4-(dimethylphenylsilyl)-5,5-difluoro-*N,N*-dimethyl-4-pentenamide (9g).

To a solution of diisopropylamine (90 μL , 0.64 mmol) in THF (2 mL) was added *n*-BuLi (0.39 mL, 1.56 M in hexane, 0.60 mmol) at -78 $^{\circ}\text{C}$ under argon. The reaction mixture was stirred for 30 min, and *N,N*-dimethyl-3-phenylpropanamide (115 mg, 0.65 mmol) was added. After the mixture was stirred for 30 min, **8** (92 mg, 0.40 mmol) in THF (1 mL) was added. The reaction mixture was stirred at -78 $^{\circ}\text{C}$ for 10 min and stirred at 0 $^{\circ}\text{C}$ for an additional 15 min. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were extracted with Et_2O (5 mL x 3). The combined extracts were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 2:1) to give **9g** (109 mg, 85%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.43 (6H, s), 2.21 (3H, s), 2.27 (1H, dd, $J = 14.7, 5.7$ Hz), 2.35 (1H, dd, $J = 14.7, 8.7$ Hz), 2.55–2.63 (1H, m), 2.68 (3H, s), 2.71–2.79 (2H, m), 6.95 (2H, d, $J = 7.7$ Hz), 7.11–7.15 (1H, m), 7.15–7.21 (2H, m), 7.32–7.41 (3H, m), 7.51–7.56 (2H, m). ^{13}C NMR (126 MHz, CDCl_3) δ –2.6, –2.3, 28.8 (dd, $J_{\text{CF}} = 6, 3$ Hz), 35.3, 36.5, 38.9, 43.2, 79.3 (dd, $J_{\text{CF}} = 27, 4$ Hz), 126.2, 128.0, 128.1, 128.8, 129.4, 133.7, 137.3, 139.5, 157.1 (dd, $J_{\text{CF}} = 309, 285$ Hz), 174.1. ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 88.2 (1F, d, $J_{\text{FF}} = 31$ Hz), 92.4 (1F, d, $J_{\text{FF}} = 31$ Hz). IR (neat) 3461, 1685, 1645, 1236, 816, 702 cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{F}_2\text{NOSi}$: C, 68.18; H, 7.02; N, 3.61. Found: C, 68.30; H, 7.05; N, 3.45.

4-Dimethylphenylsilyl-2-methyl-5,5-difluoro-1-phenyl-4-penten-1-one (9h). To a solution of diisopropylamine (84 μL , 0.60 mmol) in THF (3 mL) was added *n*-BuLi (0.37 mL, 1.63 M in hexane, 0.60 mmol) at -78 $^{\circ}\text{C}$ under argon. After the reaction mixture was stirred for 30 min, 1-phenyl-1-propanone (80 mg, 0.60 mmol) was added at -78 $^{\circ}\text{C}$ over 30 min. After the mixture was stirred at -78 $^{\circ}\text{C}$ for 30 min, **8** (92 mg, 0.40 mmol) in THF (1 mL) was added. The reaction mixture was stirred at -78 $^{\circ}\text{C}$ for 30 min, warmed up to room temperature, and stirred for an additional 1 h. Then, the reaction mixture was heated to reflux for 8 h and cooled down to room temperature. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were

extracted with Et₂O (5 mL x 3). The combined extracts were washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–CHCl₃ 1:1) to give **9h** (81 mg, 59%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 0.42 (3H, s), 0.48 (3H, s), 1.05 (3H, s), 2.19 (1H, dd, *J* = 14.0, 8.8 Hz), 2.38 (1H, dd, *J* = 14.0, 5.7 Hz), 3.26 (1H, m), 7.33–7.39 (5H), 7.49–7.54 (3H, m), 7.62 (2H, d, *J* = 7.4 Hz). ¹³C NMR (126 MHz, CDCl₃) δ –2.5, –2.3, 16.9, 29.1 (dd, *J*_{CF} = 6, 3 Hz), 40.7 (d, *J*_{CF} = 3 Hz), 79.2 (dd, *J*_{CF} = 28, 5 Hz), 128.0, 128.1, 128.5, 129.4, 132.8, 133.8, 136.1, 137.0, 157.1 (dd, *J*_{CF} = 309, 285 Hz), 203.5. ¹⁹F NMR (471 MHz, CDCl₃) δ_F 87.2 (1F, d, *J*_{FF} = 32 Hz), 92.1 (1F, d, *J*_{FF} = 32 Hz). IR (neat) 2970, 1684, 1689, 1448, 1252, 1227, 1205, 1111, 972, 837, 816, 704 cm^{–1}. Anal. Calcd for C₂₀H₂₂F₂OSi: C, 69.73; H, 6.44. Found: C, 69.62; H, 6.53.

Diethyl 2-[2-(dimethylphenylsilyl)-3,3-difluoroallyl]malonate (9i). To a suspension of NaH (36 mg, 60% dispersion in mineral oil, 0.90 mmol) in THF (2 mL) was added diethyl malonate (127 mg, 0.79 mmol) at 0 °C under argon. After the reaction mixture was stirred for 1 h at 0 °C, **8** (92 mg, 0.40 mmol) in THF (1 mL) was added over 10 min at room temperature. After being heated to reflux for 24 h, the reaction mixture was cooled down to room temperature. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were extracted with Et₂O (5 mL x 3). The combined extracts were washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 5:1) to give **9i** (82 mg, 55%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 0.46 (3H, s), 0.46 (3H, s), 1.21 (6H, t, *J* = 7.2 Hz), 2.59 (2H, d, *J* = 7.9 Hz), 3.21 (1H, t, *J* = 7.9 Hz), 4.11 (4H, q, *J* = 7.2 Hz), 7.26–7.39 (3H, m), 7.51–7.54 (2H, m). ¹³C NMR (126 MHz, CDCl₃) δ –2.5, –2.3, 13.9, 25.1 (dd, *J*_{CF} = 7, 4 Hz), 51.5 (dd, *J*_{CF} = 3, 3 Hz), 61.4, 78.1 (dd, *J*_{CF} = 30, 5 Hz), 127.9, 129.5, 133.7, 136.5, 157.1 (dd, *J*_{CF} = 309, 285 Hz), 168.6. ¹⁹F NMR (471 MHz, CDCl₃) δ_F 88.2 (1F, d, *J*_{FF} = 31 Hz), 92.4 (1F, d, *J*_{FF} = 31 Hz). IR (neat) 3433, 1734, 1689, 1232, 816 cm^{–1}. Anal. Calcd for C₁₈H₂₄F₂O₄Si: C, 58.36; H, 6.53. Found: C, 58.15; H, 6.62.

2-[2-(Dimethylphenylsilyl)-3,3-difluoroallyl]diisopropylamine (9j). To a solution of diisopropylamine (170 μL, 1.2 mmol) in THF (4 mL) was added *n*-BuLi (0.77 mL, 1.55 M in hexane, 1.2 mmol) at –78 °C under argon. After the reaction mixture was stirred

for 1 h, **8** (227 mg, 0.98 mmol) in THF (1 mL) was added. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1.5 h and then stirred at $0\text{ }^{\circ}\text{C}$ for an additional 1 h. Saturated aqueous NaHCO_3 was added to quench the reaction, and organic materials were extracted with Et_2O (5 mL x 3). The combined extracts were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 10:1) to give **9j** (262 mg, 86%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.45 (6H, s), 0.86 (12H, d, $J = 6.7$ Hz), 2.93 (2H, hept, $J = 6.7$ Hz), 3.11 (2H, s), 7.32–7.34 (3H, m), 7.52–7.54 (2H, m). ^{13}C NMR (126 MHz, CDCl_3) δ -2.0 , 20.1 , 40.7 (dd, $J_{\text{CF}} = 9$, 4 Hz), 46.0 , 80.6 (dd, $J_{\text{CF}} = 22$, 5 Hz), 127.6 , 129.0 , 133.9 , 138.0 , 157.5 (dd, $J_{\text{CF}} = 306$, 286 Hz). ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 89.0 (1F, d, $J_{\text{FF}} = 33$ Hz), 89.1 (1F, d, $J_{\text{FF}} = 33$ Hz). IR (neat) 3417 , 2966 , 1687 , 1228 , 835 , 815 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{27}\text{F}_2\text{NSi}$: C, 65.55; H, 8.74; N, 4.50. Found: C, 65.27; H, 8.62; N, 4.35.

[2-(Dimethylphenylsilyl)-3,3-difluoroallyl]isobutylamine (9k). To a solution of isobutylamine (120 μL , 1.2 mmol) in THF (4 mL) was added *n*-BuLi (0.77 mL, 1.55 M in hexane, 1.2 mmol) at $-78\text{ }^{\circ}\text{C}$ under argon. After the reaction mixture was stirred for 1 h, **8** (229 mg, 0.99 mmol) in THF (4 mL) was added. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then stirred at $0\text{ }^{\circ}\text{C}$ for an additional 30 min. Saturated aqueous NaHCO_3 was added to quench the reaction, and organic materials were extracted with AcOEt (10 mL x 4). The combined extracts were washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 5:1) to give **9k** (144 mg, 51%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.46 (6H, s), 0.79 (6H, d, $J = 6.7$ Hz), 1.56 (1H, m), 2.22 (2H, d, $J = 6.7$ Hz), 3.19 (2H, s), 7.35–7.36 (3H, m), 7.55–7.57 (2H, m). ^{13}C NMR (126 MHz, CDCl_3) δ -2.8 , -2.5 , 20.6 , 28.3 , 45.5 (dd, $J_{\text{CF}} = 8$, 4 Hz), 57.0 , 81.0 (dd, $J_{\text{CF}} = 24$, 4 Hz), 127.8 , 129.3 , 133.8 , 137.4 , 157.2 (dd, $J_{\text{CF}} = 307$, 286 Hz). ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 86.9 (1F, d, $J_{\text{FF}} = 33$ Hz), 89.5 (1F, d, $J_{\text{FF}} = 33$ Hz). IR (neat) 3070 , 2956 , 2871 , 1689 , 1427 , 1234 , 1217 , 1111 , 837 , 814 , 779 , 733 , 700 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{F}_2\text{NSi}$: C, 63.56; H, 8.18; N, 4.94. Found: C, 63.69; H, 8.35; N, 4.91.

2-(3,3-Difluoroallyl)-2-phenyl-1,3-dithiane (10b). To a solution of 2-phenyl-1,3-

dithiane (106 mg, 0.540 mmol) in THF (2.5 mL) was added *n*-BuLi (0.35 mL, 1.63 M in hexane, 0.57 mmol) at $-20\text{ }^{\circ}\text{C}$ under argon. The reaction mixture was stirred at $-20\text{ }^{\circ}\text{C}$ for 2 h, and **8** (124 mg, 0.540 mmol) in THF (1.5 mL) was added at $-78\text{ }^{\circ}\text{C}$. After the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, *n*-Bu₄NF (0.60 mL, 1.0 M in THF, 0.60 mmol) was added. The resulting mixture was stirred for 5 min, and then stirred at room temperature for an additional 2 h. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were extracted with Et₂O (5 mL x 3). The combined extracts were washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 10:1) to give **10b** (117 mg, 80%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.95 (2H, m), 2.69–2.72 (6H), 4.09 (1H, dtd, $J_{\text{HF}} = 14.7$, $J = 7.9$, $J_{\text{HF}} = 2.3$ Hz), 7.29 (1H, d, $J = 7.3$ Hz), 7.40 (2H, dd, $J = 7.3$, 7.3 Hz), 7.90 (2H, d, $J = 7.3$ Hz). ¹³C NMR (126 MHz, CDCl₃) δ 24.8, 27.5, 37.9 (d, $J_{\text{CF}} = 5$ Hz), 58.2, 73.1 (dd, $J_{\text{CF}} = 26$, 19 Hz), 127.3, 128.5, 128.5, 140.9, 156.9 (dd, $J_{\text{CF}} = 289$, 287 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ_{F} 70.8 (1F, dd, $J_{\text{FF}} = 44$ Hz, $J_{\text{FH}} = 15$ Hz), 77.1 (1F, d, $J_{\text{FF}} = 44$ Hz). IR (neat) 1743, 1290, 1198, 982, 771, 698 cm⁻¹. Anal. Calcd for C₁₃H₁₄F₂S₂: C, 57.32; H, 5.28. Found: C, 57.46; H, 5.18.

2-Benzyl-5,5-difluoro-*N,N*-dimethyl-4-pentenamide (10c). To a solution of diisopropylamine (90 μL , 0.64 mmol) in THF (3 mL) was added *n*-BuLi (0.37 mL, 1.63 M in hexane, 0.60 mmol) at $-78\text{ }^{\circ}\text{C}$ under argon. After the reaction mixture was stirred for 30 min, *N,N*-dimethyl-3-phenylpropanamide (118 mg, 0.663 mmol) was added. The resulting mixture was stirred for 30 min, and then **8** (92 mg, 0.40 mmol) in THF (1 mL) was added. After being stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, the reaction mixture was warmed up to $0\text{ }^{\circ}\text{C}$. To the reaction mixture was added *n*-Bu₄NF (0.44 mL, 1.0 M in THF, 0.44 mmol), and the mixture was stirred for 10 min. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were extracted with AcOEt (5 mL x 3). The combined extracts were washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 2:1) to give **10c** (65 mg, 64%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 2.20 (1H, m), 2.36 (1H, m), 2.62 (3H, s), 2.74 (1H, dd, $J = 12.4$, 4.9 Hz), 2.86 (3H, s), 2.89–2.99 (2H, m), 4.17 (1H, dddd, $J_{\text{HF}} = 25.3$ Hz, $J = 8.6$, 7.4 Hz, $J_{\text{HF}} = 2.3$ Hz), 7.16 (1H, m), 7.20 (2H, m), 7.26 (2H, m). ¹³C NMR (126 MHz, CDCl₃) δ 25.4 (d, J_{CF}

= 5 Hz), 35.5, 36.9, 38.9, 43.5 (dd, $J_{\text{CF}} = 2$ Hz), 75.7 (dd, $J_{\text{CF}} = 23, 20$ Hz), 126.4, 128.3, 128.8, 139.3, 156.5 (dd, $J_{\text{CF}} = 286, 245$ Hz), 173.4. ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 71.9 (1F, dd, $J_{\text{FF}} = 45$ Hz, $J_{\text{FH}} = 25$ Hz), 74.1 (1F, dd, $J_{\text{FF}} = 45$ Hz, $J_{\text{FH}} = 2$ Hz). IR (neat) 3477, 2925, 1747, 1637 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{F}_2\text{NO}$: C, 66.39; H, 6.77; N, 5.53. Found: C, 66.17; H, 6.91; N, 5.44.

3,3-Difluoro-2-pentyl-1-phenyl-2-propen-1-ol (13a). To a solution of **9b** (108 mg, 0.401 mmol) and benzaldehyde (47 mg, 0.44 mmol) in THF (4 mL) was added tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF, 0.44 mL, 1.0 M in THF, 0.44 mmol) at room temperature under argon. The reaction mixture was stirred at 50 °C for 10 h. Phosphate buffer (pH 7) was added to quench the reaction, and organic materials were extracted with AcOEt (10 mL x 3). The combined extracts were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 5:1) to give **13a** (67 mg, 68%) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 0.80 (3H, t, $J = 7.1$ Hz), 1.08–1.23 (5H, m), 1.25–1.34 (1H, m), 1.79–1.86 (1H, m), 1.87 (1H, d, $J = 3.7$ Hz), 1.89–1.97 (1H, m), 5.69 (1H, ddd, $J = 3.7$ Hz, $J_{\text{HF}} = 1.6, 1.6$ Hz), 7.35–7.39 (5H, m). ^{13}C NMR (126 MHz, CDCl_3) δ 13.9, 22.2, 22.8, 28.5 (dd, $J_{\text{CF}} = 2, 2$ Hz), 31.6, 69.5 (dd, $J_{\text{CF}} = 6, 1$ Hz), 93.3 (dd, $J_{\text{CF}} = 16, 11$ Hz), 125.5, 127.5, 128.3, 141.4 (dd, $J_{\text{CF}} = 2, 2$ Hz), 154.5 (dd, $J_{\text{CF}} = 288, 288$ Hz). ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 69.2 (1F, d, $J_{\text{FF}} = 49$ Hz), 69.6 (1F, d, $J_{\text{FF}} = 49$ Hz). IR (neat) 3388, 2956, 2931, 1739, 1452, 1261, 1211, 1130, 1009, 700 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{F}_2\text{O}$: C, 69.98; H, 7.55. Found: C, 70.08; H, 7.51.

3,3-Difluoro-1-(3-methoxyphenyl)-2-pentyl-2-propenyl acetate (14b). To a solution of **9b** (136 mg, 0.507 mmol) and 3-methoxybenzaldehyde (80 μL , 0.58 mmol) in THF (4 mL) was added TASF (0.55 mL, 1.0 M in THF, 0.55 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature for 1.5 h, and then treated with Et_3N (1 mL) and acetic anhydride (52 μL , 0.55 mmol). After the mixture was stirred at room temperature for 1 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with AcOEt (10 mL x 3), and the combined extracts were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt

10:1) to give **14b** (106 mg, 67%) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 0.83 (3H, t, $J = 7.1$ Hz), 1.13–1.36 (6H, m), 1.81–1.87 (1H, m), 1.91–1.94 (1H, m), 2.16 (3H, s), 3.81 (3H, s), 6.60 (1H, br s), 6.81–6.84 (1H, m), 6.83 (1H, s), 6.88 (1H, br d, $J = 7.6$ Hz), 7.27 (1H, ddd, $J = 7.6, 7.6, 0.9$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 13.9, 21.0, 22.2, 23.4, 28.1, 31.4, 55.2, 70.9 (d, $J_{\text{CF}} = 7$ Hz), 90.3 (dd, $J_{\text{CF}} = 19, 12$ Hz), 111.8, 112.7, 118.0, 129.5, 139.7, 154.9 (dd, $J_{\text{CF}} = 291, 289$ Hz), 159.7, 169.5. ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 70.8 (1F, d, $J_{\text{FF}} = 42$ Hz), 72.5 (1F, d, $J_{\text{FF}} = 42$ Hz). IR (neat) 2956, 2933, 1747, 1603, 1045, 1020 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{F}_2\text{O}_3$: C, 65.37; H, 7.10. Found: C, 65.41; H, 7.26.

3,3-Difluoro-1-(1-naphthyl)-2-pentyl-1-2-propenyl acetate (14c). To a solution of **9b** (132 mg, 0.491 mmol) and 1-naphthaldehyde (91.2 mg, 0.59 mmol) in THF (4 mL) was added TASF (0.55 mL, 1.0 M in THF, 0.55 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature for 4.5 h, and then treated with Et_3N (1 mL) and acetic anhydride (61.3 μL , 0.65 mmol). After the mixture was stirred at room temperature for 1 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with AcOEt (10 mL $\times$ 3), and the combined extracts were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane– AcOEt 10:1) to give **14c** (113 mg, 69%) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 0.73 (3H, t, $J = 7.0$ Hz), 0.93–1.19 (6H, m), 1.77–1.82 (1H, m), 1.85–1.97 (1H, m), 2.19 (3H, s), 7.32 (1H, br s), 7.46–7.56 (3H, m), 7.63 (1H, d, $J = 7.2$ Hz), 7.84 (1H, d, $J = 8.2$ Hz), 7.87 (1H, d, $J = 8.1$ Hz), 7.90 (1H, d, $J = 8.4$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 13.8, 21.2, 22.1, 23.5, 27.9, 31.2, 68.8 (d, $J_{\text{CF}} = 7$ Hz), 89.9 (dd, $J_{\text{CF}} = 19, 11$ Hz), 122.5 (d, $J_{\text{CF}} = 2$ Hz), 123.5, 125.0, 125.9, 126.6, 128.7, 128.9, 130.0, 133.0, 133.6, 154.6 (dd, $J_{\text{CF}} = 291, 290$ Hz), 169.4. ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 71.2 (1F, d, $J_{\text{FF}} = 40$ Hz), 74.2 (1F, d, $J_{\text{FF}} = 40$ Hz). IR (neat) 2956, 2931, 2862, 1751, 1736, 1508, 1369, 1265, 1228, 1041, 793, 779 cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{F}_2\text{O}_2$: C, 72.27; H, 6.67. Found: C, 72.49; H, 6.85.

3,3-Difluoro-2-pentyl-1-(2-phenylethyl)-2-propenyl acetate (14d). To a solution of **9b** (270 mg, 1.01 mmol) and 3-phenylpropanal (68 μL , 1.20 mmol) in THF (8 mL) was added TASF (1.20 mL, 1.0 M in THF, 1.20 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature for 5 h, and then treated with Et_3N

(1 mL) and acetic anhydride (142 μ L, 1.50 mmol). After the mixture was stirred at room temperature for 1 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with AcOEt (10 mL x 3), and the combined extracts were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 10:1) to give **14d** (61 mg, 19%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.89 (3H, t, $J = 7.0$ Hz), 1.26–1.46 (7H, m), 1.85–1.91 (1H, m), 1.97–2.06 (2H, m), 2.03 (3H, s), 2.08–2.14 (1H, m), 2.53–2.66 (2H, m), 5.49 (1H, t, $J = 7.2$ Hz), 7.16 (2H, d, $J = 7.9$ Hz), 7.20 (1H, d, $J = 7.4$ Hz), 7.28 (2H, dd, $J = 7.9, 7.4$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 13.9, 21.0, 22.3, 23.3, 28.5, 31.6, 31.8, 34.3, 72.2 (d, $J_{\text{CF}} = 6$ Hz), 89.3 (dd, $J_{\text{CF}} = 19, 12$ Hz), 126.1, 128.2, 128.5, 140.9, 154.6 (dd, $J_{\text{CF}} = 291, 289$ Hz), 170.0. ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 71.3 (1F, d, $J_{\text{FF}} = 43$ Hz), 73.3 (1F, d, $J_{\text{FF}} = 43$ Hz). IR (neat) 2956, 2931, 2862, 1745, 1369, 1228, 1018, 698 cm^{-1} . HRFIMS m/z (M^+): Calcd. for $\text{C}_{18}\text{H}_{24}\text{F}_2\text{O}_2$: 310.1744, Found: 310.1758.

3,3-difluoro-1-phenyl-2-(2-phenyl-1,3-dithian-2-ylmethyl)-2-propenyl acetate (14e): To a solution of 2-phenyl-1,3-dithiane (235 mg, 1.20 mmol) in THF (4 mL) was added *n*-BuLi (0.77 mL, 1.55 M in hexane, 1.20 mmol) at -25 $^{\circ}\text{C}$ under argon. After the reaction mixture was stirred at -25 $^{\circ}\text{C}$ for 1 h, **8** (232 mg, 1.01 mmol) in THF (1 mL) was added at -78 $^{\circ}\text{C}$. After the reaction mixture was stirred for 2 h, benzaldehyde (142 μ L, 1.40 mmol) and TASF (1.5 mL, 1.0 M in THF, 1.5 mmol) were successively added at -78 $^{\circ}\text{C}$. The mixture was warmed up to room temperature and stirred for 2 h. Et_3N (1 mL) and acetic anhydride (71 μ L, 0.75 mmol) were added, and the mixture was stirred at room temperature for 1 h. Saturated aqueous NaHCO_3 was added to quench the reaction, and organic materials were extracted with AcOEt (10 mL x 3). The combined extracts were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 10:1) to give **14e** (307 mg, 72%) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 1.88–1.93 (2H, m), 2.11 (3H, s), 2.64–2.74 (5H, m), 2.82 (1H, dd, $J = 14.9$ Hz, $J_{\text{FH}} = 2.3$ Hz), 6.14 (1H, d, $J_{\text{FH}} = 3.6$ Hz), 7.21 (2H, d, $J = 6.8$ Hz), 7.26–7.31 (4H, m), 7.36 (2H, dd $J = 8.0, 7.7$ Hz), 7.93 (2H, dd $J = 7.4, 1.4$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 21.0, 24.4, 27.6, 27.7, 41.2, 58.9, 65.7, 72.2 (d, $J_{\text{CF}} = 5$ Hz), 87.0 (dd, $J_{\text{CF}} = 18, 12$ Hz), 126.5, 127.2, 127.8, 128.2, 128.9, 137.8, 140.4, 156.1 (dd, $J_{\text{CF}} = 297, 291$ Hz), 169.5. ^{19}F

NMR (471 MHz, CDCl_3) δ_{F} 80.4 (1F, d, $J_{\text{FF}} = 28$ Hz), 80.8 (1F, d, $J_{\text{FF}} = 28$ Hz). IR (neat) 3062, 2906, 2827, 1732, 1227, 1022, 698 cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{F}_2\text{O}_2\text{S}_2$: C, 62.83; H, 5.27. Found: C, 62.65; H, 5.56.

2-(*N,N*-Diisopropylaminomethyl)-3,3-difluoro-1-phenyl-2-propenyl acetate (14f**):**

To a solution of diisopropylamine (168 μL , 1.20 mmol) in THF (4 mL) was added *n*-BuLi (0.77 mL, 1.55 M in hexane, 1.20 mmol) at -78 $^{\circ}\text{C}$ under argon. The reaction mixture was stirred at -78 $^{\circ}\text{C}$ for 30 min, **8** (230 mg, 1.00 mmol) in THF (1 mL) was added at -78 $^{\circ}\text{C}$. After the mixture was stirred for 1 h, benzaldehyde (132 μL , 1.30 mmol) and TASf (1.5 mL, 1.0 M in THF, 1.5 mmol) were successively added at -78 $^{\circ}\text{C}$. The reaction mixture was warmed up to room temperature and stirred for 3 h. Et_3N (1 mL) and acetic anhydride (71.0 μL , 0.75 mmol) were added to the mixture, and the reaction mixture was stirred at room temperature for 1.5 h. Saturated aqueous NaHCO_3 was added to quench the reaction, and organic materials were extracted with AcOEt (10 mL x 3). The combined extracts were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane–AcOEt 10:1) to give **14f** (229 mg, 70%) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 0.91 (6H, d, $J = 6.6$ Hz), 0.94 (6H, d, $J = 6.6$ Hz), 2.13 (3H, s), 2.94 (2H, hept, $J = 6.6$ Hz), 3.06 (1H, br d, $J = 13.9$ Hz), 3.16 (1H, br d, $J = 13.9$ Hz), 6.44 (1H, br s), 7.25–7.38 (5H, m). ^{13}C NMR (126 MHz, CDCl_3) δ 19.6, 20.5, 21.0, 40.0 (d, $J_{\text{CF}} = 5$ Hz), 46.3, 71.5 (d, $J_{\text{CF}} = 5$ Hz), 90.5 (dd, $J_{\text{CF}} = 16, 8$ Hz), 126.5, 127.7, 128.2, 138.6, 155.5 (dd, $J_{\text{CF}} = 294, 289$ Hz), 169.8. ^{19}F NMR (471 MHz, CDCl_3) δ_{F} 71.6 (1F, d, $J_{\text{FF}} = 40$ Hz), 78.2 (1F, d, $J_{\text{FF}} = 40$ Hz). IR (neat) 2966, 1743, 1371, 1230, 1022, 742, 698 cm^{-1} . HRFIMS m/z (M^+): Calcd. for $\text{C}_{18}\text{H}_{25}\text{F}_2\text{NO}_2$: 325.1853, Found: 325.1858.