Phosphonodifluoromethyl and Phosphonothiodifluoromethyl Radicals. Generation and Addition onto Alkenes and Alkynes.

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Supporting information:

Procedure for compound 11a. Analytical data for compounds 18a-18f, 19a-19f, 21a-21b, 28-32 and 34-38. Selected ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra for compounds 31 and 37.

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***O,O*-Diethyl difluoromethylphosphonate (11a).** Sodium wire (3.5 g, 1.5 mol) is added in portions to a solution of diethylphosphite (20 g, 0.145 mol) in anhydrous THF (90 ml). The mixture is stirred at room temperature for 24 h, during which period of time all the sodium dissolved. Chlorodifluoromethane (40 g, 0.26 mol) is then bubbled through the reaction mixture (addition time: 3 h). The solution is stirred under nitrogen for an additional 12 h and filtered on a path made of a 1:1 mixture of silica and celite. The solid is washed with heptane (3×150 mL) and the filtrate is evaporated. Distillation of this material under reduce pressure ($E_{b22} = 89^{\circ}\text{C}$) furnishes (24 g, 88%) **11a** as a colorless liquid (24 g, 88%). ^1H NMR δ 5.92 (dt, 1H, $2J_{\text{H-F}} = 48.6$, $2J_{\text{H-P}} = 26.7$), 4.20 (dt, 4H, $3J_{\text{H-P}} = 8.4$, $2J_{\text{H-H}} = 7.3$), 1.36 (t, 6H, $3J_{\text{H-H}} = 6.9$). ^{31}P NMR δ 5.27 (t, 1P, $J_{\text{F-P}} = 91.5$). ^{19}F NMR δ 27.14 (dd, 2F, $2J_{\text{F-P}} = 88.0$, $2J_{\text{H-F}} = 47.4$). ^{13}C NMR δ 123.4 (dt, 1C), 64.3 (d, 2C, $2J_{\text{C-P}} = 6.4$), 15.6 (d, 2C, $3J_{\text{C-P}} = 5.3$). IR (NaCl) ν cm^{-1} 2988, 1384, 1268, 1067, 1020. Exact mass (EI, 70eV) m/z calcd for $\text{C}_3\text{H}_{11}\text{O}_3\text{F}_2$ 188.1122. Found 188.1131. Anal. Calcd for: $\text{C}_3\text{H}_{11}\text{O}_3\text{F}_2$: C, 31.93; H, 5.89. Found: C, 30.87; H, 5.84.

***O,O*-Diethyl 1-heptyl-1,1-difluoromethylphosphonate (18a).** Chromatography and elution with H/A (4:1) give **18a** as yellow oil (50 mg, 45%) (R_f 0.42). ^1H NMR δ 4.33-4.12 (m, 4H), 2.11-1.87 (m, 2H), 1.60-1.45 (m, 2H), 1.33-0.81 (m, 10H), 0.69 (t, 3H, $^3J_{\text{H-H}} = 6.9$). ^{31}P NMR δ 6.87 (t, 1P, $^2J_{\text{F-P}} = 110.4$). ^{19}F NMR δ 50.64 (dt, 2F, $^2J_{\text{F-P}} = 108.3$, $^3J_{\text{F-H}} = 20.3$). ^{13}C NMR δ 120.5 (dt, 1C), 64.4 (d, 2C, $^2J_{\text{C-P}} = 6.6$), 40.1 (s, 1C), 32.7 (s, 1C), 31.21 (s, 1C), 30.2 (s, 1C), 24.5 (s, 1C), 23.8 (s, 1C), 23.1 (s, 1C), 16.3 (d, 2C, $^3J_{\text{C-P}} = 6.8$), 14.9 (s, 1C). IR (NaCl) ν cm^{-1} 1236 (P=O), 1110 (C-F), 1040 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{13}\text{H}_{27}\text{O}_3\text{PF}_2$ 300.3261. Found 300.3289. Anal. Calcd for $\text{C}_{13}\text{H}_{27}\text{O}_3\text{PF}_2$: C, 51.99; H, 9.06. Found: C, 52.04; H, 9.09.

***O,O*-Diethyl 1-(2-cyclohexyl-1,1-difluoroethyl)phosphonate (18b).** The residue is purified by chromatography. Elution with H/C (75:25) furnishes **18b** as colorless oil (86 mg, 82%) (R_f 0.24).

^1H NMR δ 4.34-4.11 (m, 4H), 2.36 (m, 1H), 1.71-1.62 (m, 5H), 1.45 (t, 6H, $^3J_{\text{H-H}} = 7.2$), 1.11-0.78 (m, 6H). ^{31}P NMR δ 8.23 (t, 1P, $^2J_{\text{F-P}} = 112.2$). ^{19}F NMR δ 50.73 (dt, 2F, $^2J_{\text{F-P}} = 111.9$, $^3J_{\text{F-H}} = 22.5$). ^{13}C NMR δ 123.0 (dt, 1C), 63.6 (d, 2C, $^2J_{\text{C-P}} = 7.1$), 53.5 (m, 1C), 34.3 (d, 2C, $^2J_{\text{C-P}} = 6.3$), 32.7 (m, 1C), 25.3 (d, 3C), 15.8 (d, 2C). IR (NaCl) ν cm^{-1} 1235 (P=O), 1064 (C-F), 1008 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{12}\text{H}_{23}\text{O}_3\text{PF}_2$ 284.2825. Found 284.3023. Anal. Calcd for $\text{C}_{12}\text{H}_{23}\text{O}_3\text{PF}_2$: C, 50.70; H, 8.15. Found: C, 50.69; H, 8.13.

***O,O*-Diethyl 1-cyclopentyl-1,1-difluoromethylphosphonate (18c)**. Chromatography and elution with H/A (7:3) lead to the isolation of **18c** as a yellow oil (10 mg, 10%) (R_f 0.33). ^1H NMR δ 4.17-4.04 (m, 4H), 2.44-2.17 (m, 1H), 1.75-1.41 (m, 4H), 1.38-1.04 (m, 10H). ^{31}P NMR δ 7.38 (t, 1P, $^2J_{\text{F-P}} = 115.3$). ^{19}F NMR 46.51 (dt, 2F, $^2J_{\text{F-P}} = 113.6$, $^3J_{\text{F-H}} = 17.5$). ^{13}C NMR δ 120.4 (dt, 1C), 64.6 (d, 2C, $^2J_{\text{C-F}} = 6.4$), 45.3 (dt, 1C, $^2J_{\text{C-F}} = 19.9$, $^2J_{\text{C-P}} = 15.0$), 26.4 (dt, 2C, $^3J_{\text{C-F}} = 4.9$, $^3J_{\text{C-P}} = 3.6$), 23.1 (s, 2C), 15.8 (d, 2C, $^3J_{\text{C-P}} = 6.6$). IR (NaCl) ν cm^{-1} 1187 (P=O), 1089 (C-F), 1023 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{10}\text{H}_{19}\text{O}_3\text{PF}_2$ 256.2289. Found 256.2356. Anal. Calcd for $\text{C}_{10}\text{H}_{19}\text{O}_3\text{PF}_2$: C, 46.88; H, 7.47. Found: C, 46.54; H, 7.43. The isolated yield is 20% when *n*- Bu_3SnH is replaced with TTMSSH.

***O,O*-Diethyl 3-butoxy-1,1-difluoromethylphosphonate (18d)**. Chromatography and elution with H/A (7.5:2.5) give **18d** as yellow oil (49 mg, 46%) (R_f 0.25). ^1H NMR δ 4.33-4.17 (m, 4H), 3.70 (t, 2H, $^3J_{\text{H-H}} = 6.8$), 3.28 (t, 2H, $^3J_{\text{H-H}} = 5.9$), 2.47-2.21 (m, 2H), 1.77-1.47 (m, 4H), 1.26 (t, 6H, $^3J_{\text{H-H}} = 6.6$), 0.81 (t, 3H, $^3J_{\text{H-H}} = 7.2$). ^{31}P NMR δ 8.23 (t, 1P, $^2J_{\text{F-P}} = 110.5$). ^{19}F NMR 49.56 (dt, 2F, $^2J_{\text{F-P}} = 112.1$, $^3J_{\text{F-H}} = 19.4$). ^{13}C NMR δ 123.5 (dt, 1C), 72.9 (s, 1C), 64.4 (d, 2C, $^2J_{\text{C-P}} = 7.2$), 62.2 (m, 1C), 34.5 (dt, 1C, $^2J_{\text{C-P}} = 15.5$, $^2J_{\text{C-F}} = 18.6$), 31.9 (s, 1C), 22.2 (s, 1C), 14.8 (d, 2C, $^2J_{\text{C-P}} = 5.8$), 13.8 (s, 1C). IR (NaCl) ν cm^{-1} 1203 (P=O), 1132 (C-F), 1022 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{11}\text{H}_{23}\text{O}_4\text{PF}_2$ 288.2709. Found 288.2765. Anal. Calcd for $\text{C}_{11}\text{H}_{23}\text{O}_4\text{PF}_2$: C,

45.83; H, 8.04. Found: C, 45.73; H, 8.10.

***O,O*-Diethyl 1-[difluoro-(3-tetrahydrofuranyl)methyl]phosphonate (18e).** The residue is purified by chromatography. Elution with H/A (8:2) delivers **18e** as colorless oil (65 mg, 68%) (R_f 0.37). ^1H NMR δ 4.58-4.12 (m, 4H), 3.97-3.54 (m, 4H), 2.95-2.69 (m, 1H), 2.13-1.80 (m, 2H), 1.33 (t, 6H, $^3J_{\text{H-H}} = 5.9$). ^{31}P NMR δ 8.63 (t, 1P, $^2J_{\text{F-P}} = 112.3$). ^{19}F NMR δ 52.56 (dt, 2F, $^2J_{\text{F-P}} = 110.7$, $^3J_{\text{F-H}} = 14.6$). ^{13}C NMR 118.5 (dt, 1C), 70.3 (s, 1C), 65.1 (dt, 1C, $^3J_{\text{C-F}} = 5.8$, $^3J_{\text{C-P}} = 4.0$), 64.3 (d, 2C, $^2J_{\text{C-P}} = 6.5$), 41.9 (dt, 1C, $^2J_{\text{C-F}} = 19.1$, $^2J_{\text{C-P}} = 15.3$), 22.4 (dt, 1C, $^3J_{\text{C-F}} = 5.5$, $^3J_{\text{C-P}} = 4.0$), 14.9 (d, 2C). IR (NaCl) ν cm^{-1} 1231 (P=O), 1054 (C-F), 963 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_9\text{H}_{17}\text{O}_4\text{PF}_2$ 258.2015. Found 258.2051. Anal. Calcd for $\text{C}_9\text{H}_{17}\text{O}_4\text{PF}_2$: C, 41.87; H, 6.64. Found: C, 41.85; H, 6.66. The isolated yield is 10% when *n*-Bu₃SnH is replaced with TTMSSH.

***O,O*-Diethyl 1,1-difluoro-3-phenylsulfonylpropylmethylphosphonate (18f).** Chromatography and elution with H/A (7:3) afford **18f** as a yellow oil (16 mg, 12%) (R_f 0.43). ^1H NMR δ 7.62-7.49 (m, 5H), 4.32-4.17 (m, 4H), 3.32 (dt, 1H, $^3J_{\text{H-H}} = 14.3$, $^2J_{\text{H-H}} = 5.0$), 2.86 (dt, 1H, $^3J_{\text{H-H}} = 14.3$, $^2J_{\text{H-H}} = 4.8$), 2.69-2.30 (m, 2H), 1.35 (t, 6H, $^3J_{\text{H-H}} = 6.9$). ^{31}P NMR δ 6.42 (t, 1P, $^2J_{\text{F-P}} = 105.9$). ^{19}F NMR δ 51.02 (dt, 2F, $^2J_{\text{F-P}} = 104.9$, $^3J_{\text{F-H}} = 20.3$). ^{13}C NMR δ 144.3 (s, 1C), 131.4 (s, 2C), 128.9 (s, 2C), 126.6 (s, 1C), 122.4 (dt, 1C), 64.3 (d, 2C, $^2J_{\text{C-P}} = 6.2$), 38.2 (s, 1C), 37.2 (s, 1C), 16.6 (d, 2C, $^3J_{\text{C-P}} = 6.4$). IR (NaCl) ν cm^{-1} 1335 (SO₂), 1248 (P=O), 1051 (C-F), 1033 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{13}\text{H}_{19}\text{O}_5\text{PF}_2\text{S}$ 356.3274. Found 356.3321. Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{O}_5\text{PF}_2\text{S}$: C, 43.82; H, 5.37. Found: C, 43.87; H, 5.40.

***O,O*-Diethyl 1-heptyl-1,1-difluoromethylphosphonothioate (19a).** The residue is purified by chromatography. Elution with H/C (9:1) delivers **19a** as a colorless oil (101 mg, 54%) (R_f 0.48). ^1H NMR δ 4.31-4.15 (m, 4H), 2.11-1.93 (m, 2H), 1.55-1.37 (m, 2H), 1.37-0.87 (m, 10H), 0.74 (t,

3H, $^3J_{\text{H-H}} = 7.1$). ^{31}P NMR δ 77.14 (t, 1P, $^2J_{\text{F-P}} = 113.1$). ^{19}F NMR δ 49.75 (dt, 2F, $^2J_{\text{F-P}} = 111.7$, $^3J_{\text{F-H}} = 16.9$). ^{13}C NMR δ 119.9 (dt, 1C), 64.8 (d, 2C, $^2J_{\text{C-P}} = 6.2$), 39.3 (s, 1C), 32.2 (s, 1C), 30.7 (s, 1C), 29.3 (s, 1C), 23.9 (s, 1C), 23.6 (s, 1C), 23.4 (s, 1C), 16.4 (d, 2C, $^3J_{\text{C-P}} = 6.4$), 15.3 (s, 1C). IR (NaCl) ν cm^{-1} 1079 (C-F), 1055 (P-O), 694 (P=S). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{13}\text{H}_{27}\text{O}_2\text{PF}_2\text{S}$ 316.3927. Found 316.3956. Anal. Calcd for $\text{C}_{13}\text{H}_{27}\text{F}_2\text{O}_2\text{PS}$: C, 49.35; H, 8.60; S, 10.13. Found: C, 49.43; H, 8.65; S, 10.18. Replacing *n*-Bu₃SnH with TTMSSH leads to the isolation of the same product in 87% yield.

***O,O*-Diethyl 1-(2-cyclohexyl-1,1-difluoroethyl)phosphonothioate (19b)**. Purified by chromatography and eluted with H/C (9:1) to furnish **19b** as colorless oil (98 mg, 88%) (R_f 0.24). ^1H NMR δ 4.29-4.13 (m, 4H), 2.28 (m, 1H), 1.69-1.60 (m, 5H), 1.32 (t, 6H, $^3J_{\text{H-H}} = 6.9$), 1.07-0.82 (m, 6H). ^{31}P NMR δ 77.15 (t, 1P, $^2J_{\text{F-P}} = 113.5$). ^{19}F NMR δ 51.98 (dt, 2F, $^2J_{\text{F-P}} = 111.7$, $^3J_{\text{F-H}} = 23.7$). ^{13}C NMR δ 121.3 (dt, 1C), 64.2 (d, 2C, $^2J_{\text{C-P}} = 6.1$), 53.3 (m, 1C), 33.9 (d, 2C, $^2J_{\text{C-P}} = 5.8$), 31.4 (m, 1C), 26.0 (d, 3C), 16.1 (d, 2C). IR (NaCl) ν cm^{-1} 1035 (C-F), 972 (P-O), 829 (P=S). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{12}\text{H}_{23}\text{O}_2\text{PF}_2\text{S}$ 300.3500. Found 300.3544. Anal. Calcd for $\text{C}_{12}\text{H}_{23}\text{O}_2\text{PF}_2\text{S}$: C, 47.99; H, 7.72; S, 10.68. Found: C, 48.05; H, 7.77; S, 10.71.

***O,O*-Diethyl 1-cyclopentyl-1,1-difluoromethylphosphonothioate (19c)**. Chromatography and elution with H/C (9:1) afford **19c** as a yellowish oil (35 mg, 22%) (R_f 0.50). ^1H NMR δ 4.15-4.01 (m, 4H), 2.56-2.21 (m, 1H), 1.80-1.47 (m, 4H), 1.36-1.14 (m, 7H). ^{31}P NMR δ 77.45 (t, 1P, $^2J_{\text{F-P}} = 116.7$). ^{19}F NMR 47.23 (dt, 2F, $^2J_{\text{F-P}} = 115.1$, $^3J_{\text{F-H}} = 16.9$). ^{13}C NMR δ 120.4 (dt, 1C), 64.6 (d, 2C, $^2J_{\text{C-F}} = 6.4$), 45.3 (dt, 1C, $^2J_{\text{C-F}} = 19.9$, $^2J_{\text{C-P}} = 15.0$), 26.4 (dt, 2C, $^3J_{\text{C-F}} = 4.9$, $^3J_{\text{C-P}} = 3.6$), 23.1 (s, 2C), 15.8 (d, 2C, $^3J_{\text{C-P}} = 6.6$). IR (NaCl) ν cm^{-1} 1089 (C-F), 1023 (P-O), 768 (P=S). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{10}\text{H}_{19}\text{O}_2\text{PF}_2\text{S}$ 272.2962. Found 272.2998. Anal. Calcd for $\text{C}_{10}\text{H}_{19}\text{O}_2\text{PF}_2\text{S}$: C, 44.11; H, 7.03; S, 11.78. Found: C, 44.16; H, 7.07; S, 11.82. Replacing *n*-

Bu₃SnH with TTMSSH leads to the isolation of the same product in 35% yield.

***O,O*-Diethyl 3-butyloxy-1,1-difluoromethylphosphonothioate (19d)**. Purified by chromatography and elution with H/C (4:1) to give **19d** as a yellow oil (91 mg, 81%) (*R*_f 0.35). ¹H NMR δ 4.29-4.14 (m, 4H), 3.63 (t, 2H, ³*J*_{H-H} = 7.3), 3.41 (t, 2H, ³*J*_{H-H} = 6.2), 2.54-2.25 (m, 2H), 1.60-1.46 (m, 4H), 1.32 (t, ³*J*_{H-H} = 7.3), 0.89 (t, 3H, ³*J*_{H-H} = 7.3). ³¹P NMR δ 76.04 (t, 1P, ²*J*_{F-P} = 111.1). ¹⁹F NMR 50.80 (dt, 2F, ²*J*_{F-P} = 111.7, ³*J*_{F-H} = 20.5). ¹³C NMR δ 122.1 (dt, 1C), 70.7 (s, 1C), 64.6 (d, 2C, ²*J*_{C-P} = 6.7), 63.8 (m, 1C), 34.7 (dt, 1C, ²*J*_{C-P} = 14.8, ²*J*_{C-F} = 20.2), 32.4 (s, 1C), 20.0 (s, 1C), 16.0 (d, 2C, ²*J*_{C-P} = 5.5), 14.3 (s, 1C). IR (NaCl) ν cm⁻¹ 1132 (C-F), 1022 (P-O), 657 (P=S). Exact mass (EI, 70eV) *m/z* calcd for C₁₁H₂₃O₃PF₂S 304.3384. Found 304.3369. Anal. Calcd for C₁₁H₂₃O₃PF₂S: C, 43.41; H, 7.62; S, 10.54. Found: C, 43.44; H, 7.66; S, 10.59.

***O,O*-Diethyl 1-[difluoro-(3-tetrahydrofuranyl)methyl]phosphonothioate (19e)**. The compound is obtained from chromatography and elution with H/C (9:1) as a colorless oil (79 mg, 78%) (*R*_f 0.42). ¹H NMR δ 4.32-4.00 (m, 4H), 4.00-3.61 (m, 4H), 2.98-2.72 (m, 1H), 2.08-1.89 (m, 2H), 1.28 (t, 6H, ³*J*_{H-H} = 6.1). ³¹P NMR δ 80.02 (t, 1P, ²*J*_{F-P} = 110.0). ¹⁹F NMR δ 54.31 (dt, 2F, ²*J*_{F-P} = 109.9, ³*J*_{F-H} = 15.8). ¹³C NMR 120.3 (dt, 1C), 69.2 (s, 1C), 65.3 (dt, 1C, ³*J*_{C-F} = 5.4, ³*J*_{C-P} = 3.8), 64.7 (d, 2C, ²*J*_{C-P} = 6.1), 42.1 (dt, 1C, ²*J*_{C-F} = 20.4, ²*J*_{C-P} = 14.7), 23.6 (dt, 1C, ³*J*_{C-F} = 4.5, ³*J*_{C-P} = 3.6), 15.2 (d, 2C). IR (NaCl) ν cm⁻¹ 1054 (C-F), 963 (P-O), 824 (P=S). Exact mass (EI, 70eV) *m/z* calcd for C₉H₁₇O₃PF₂S 274.2686. Found 274.2674. Anal. Calcd for C₉H₁₇O₃PF₂S: C, 39.41; H, 6.25; S, 11.69. Found: C, 39.43; H, 6.31; S, 11.73.

***O,O*-Diethyl 1,1-difluoro-3-phenylsulfonylpropylmethylphosphonothioate (19f)**. The crude sample is purified by chromatography. Elution with H/C (9:1) yields **19f** as colorless oil (59 mg, 43%) (*R*_f 0.35). ¹H NMR δ 7.59-7.48 (m, 5H), 4.25-4.03 (m, 4H), 3.29 (dt, 1H, ³*J*_{H-H} = 14.2, ²*J*_{H-H} = 5.1), 2.92 (dt, 1H, ³*J*_{H-H} = 14.2, ²*J*_{H-H} = 5.0), 2.73-2.37 (m, 2H), 1.38 (t, 6H, ³*J*_{H-H} = 7.1). ³¹P

NMR δ 76.28 (t, 1P, $^2J_{\text{F-P}} = 109.5$). ^{19}F NMR δ 51.02 (dt, 2F, $^2J_{\text{F-P}} = 108.3$, $^3J_{\text{F-H}} = 20.3$). ^{13}C NMR δ 142.7 (s, 1C), 133.5 (s, 2C), 127.6 (s, 2C), 125.9 (s, 1C), 122.2 (dt, 1C), 63.8 (d, 2C, $^2J_{\text{C-P}} = 5.9$), 37.6 (s, 1C), 36.8 (s, 1C), 15.5 (d, 2C, $^3J_{\text{C-P}} = 6.2$). IR (NaCl) ν cm^{-1} 1328 (SO_2), 1093 (C-F), 1020 (P-O), 798 (P=S). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{13}\text{H}_{19}\text{O}_4\text{PF}_2\text{S}_2$ 372.3940. Found 372.3955. Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{O}_4\text{PF}_2\text{S}_2$: C, 41.93; H, 5.14; S, 8.61. Found: C, 41.98; H, 5.17; S, 8.65.

***O,O*-Diethyl 1,1-difluoro-1-(4-methyl-1-(toluene-4-sulfonyl)pyrrolidin)methylphosphonate**

(21a). Chromatography and elution with H/C (9:1) afford **21a** as a 7:3 mixture of *cis* and *trans* isomers; a yellow oil (25 mg, 16%) (R_f 0.35). IR (NaCl) ν cm^{-1} 1344 (SO_2), 1213 (P=O), 1131 (N- SO_2), 1063 (C-F), 1017 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{17}\text{H}_{27}\text{O}_5\text{PF}_2\text{SN}$ 426.0384. Found 426.0535. Anal. Calcd for $\text{C}_{17}\text{H}_{27}\text{O}_5\text{PF}_2\text{SN}$: C, 47.93; H, 6.39; S, 7.53; N, 3.29. Found: C, 47.95; H, 6.38; S, 7.53; N, 3.30. Major diastereoisomer: ^1H NMR δ 7.72 (d, 2H, $^3J_{\text{H-H}} = 8.2$), 7.61 (d, 2H, $^3J_{\text{H-H}} = 8.3$), 4.15-4.03 (m, 4H), 3.54-3.47 (m, 1H), 3.41 (dd, 1H, $^1J_{\text{H-H}} = 9.8$, $^3J_{\text{H-H}} = 6.2$), 3.14 (t(dd), 1H, $^1J_{\text{H-H}} = ^3J_{\text{H-H}} = 9.8$), 3.02 (dd, 1H, $^1J_{\text{H-H}} = ^3J_{\text{H-H}} = 10.3$), 2.65-2.46 (m, 4H), 2.24-2.03 (m, 1H), 1.40-1.28 (t, 6H, $^3J_{\text{H-H}} = 7.6$), 0.64 (d, 3H, $^3J_{\text{H-H}} = 6.7$). ^{31}P NMR δ 8.74 (t, 1P, $^2J_{\text{F-P}} = 109.7$). ^{19}F NMR δ 49.82 (dt, 2F, $^2J_{\text{F-P}} = 108.1$, $^3J_{\text{F-H}} = 17.7$). ^{13}C NMR δ 140.2 (s, 1C), 133.6 (s, 1C), 132.1 (s, 2C), 126.3 (s, 2C), 122.5 (dt, 1C), 64.5 (d, 2C, $^2J_{\text{C-P}} = 5.9$), 54.3 (s, 1C), 52.7 (d, 1C, $^3J_{\text{C-P}} = 8.0$), 34.9 (d, 1C, $^2J_{\text{C-P}} = 3.0$), 32.9 (d, 1C, $^3J_{\text{C-P}} = 12.2$), 22.2 (s, 1C), 16.3 (d, 2C, $^3J_{\text{C-P}} = 7.8$), 12.9 (s, 1C). Minor diastereoisomer: ^1H NMR δ 7.70 (d, 2H, $^3J_{\text{H-H}} = 8.2$), 7.43 (d, 2H, $^3J_{\text{H-H}} = 8.4$), 4.43-4.16 (m, 4H), 3.81 (dd, 1H, $^1J_{\text{H-H}} = 10.5$, $^3J_{\text{H-H}} = 7.2$), 3.31-3.15 (m, 1H), 3.01 (dd, 1H, $^1J_{\text{H-H}} = 10.2$, $^3J_{\text{H-H}} = 7.5$), 2.67 (t(dd), 1H, $^1J_{\text{H-H}} = ^3J_{\text{H-H}} = 9.9$), 2.47-2.29 (m, 3H), 2.12 (ddd, 1H, $^2J_{\text{H-H}} = ^1J_{\text{H-H}} = 16.2$, $^3J_{\text{H-H}} = 3.0$), 2.15-1.92 (m, 1H), 1.74-1.55 (m, 2H), 1.42-1.36 (m, 6H), 0.78 (d, 3H, $^1J_{\text{H-H}} = 7.2$). ^{31}P NMR δ 8.32 (t, 1P, $^2J_{\text{F-P}} = 112.3$). ^{19}F NMR δ 50.23 (dt, 2F, $^2J_{\text{F-P}} = 107.7$, $^3J_{\text{F-H}}$

= 19.5). ^{13}C NMR δ 143.2 (s, 1C), 135.3 (s, 1C), 131.3 (s, 2C), 125.6 (s, 2C), 121.8 (dt, 1C), 65.1 (d, 2C, $^2J_{\text{C-P}} = 6.2$), 56.3 (s, 1C), 53.5 (d, 1C, $^3J_{\text{C-P}} = 8.4$), 38.3 (d, 1C, $^2J_{\text{C-P}} = 4.4$), 35.4 (d, 1C, $^3J_{\text{C-P}} = 12.7$), 21.5 (s, 1C), 17.0 (d, 2C, $^3J_{\text{C-P}} = 7.6$), 11.7 (s, 1C).

***O*, *O* - Diethyl 1,1-difluoro-1-(4-methyl-1-(toluene-4-sulfonyl)pyrrolidin)methylphosphonothioate (21b).** Chromatography and elution with H/C (9:1) lead to the isolation of **21b** as a 7:3 mixture of *cis* and *trans* isomers (yellow oil, 83 mg, 51%) (R_f 0.30). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{17}\text{H}_{27}\text{O}_4\text{PF}_2\text{S}_2\text{N}$ 442.1050. Found 442.1743. Anal. Calcd for $\text{C}_{17}\text{H}_{27}\text{O}_4\text{PF}_2\text{S}_2\text{N}$: C, 46.19; H, 6.16; S, 14.51; N, 3.17. Found: C, 46.18; H, 6.17; S, 14.52; N, 3.18. Major diastereoisomer: ^1H NMR δ 7.70 (d, 2H, $^3J_{\text{H-H}} = 8.2$), 7.66 (d, 2H, $^3J_{\text{H-H}} = 8.2$), 4.15-4.03 (m, 4H), 3.52-3.48 (m, 1H), 3.36 (dd, 1H, $^1J_{\text{H-H}} = 9.8$, $^3J_{\text{H-H}} = 6.0$), 3.11 (t(dd), 1H, $^1J_{\text{H-H}} = ^3J_{\text{H-H}} = 9.8$), 3.05 (dd, 1H, $^1J_{\text{H-H}} = ^3J_{\text{H-H}} = 9.8$), 2.55-2.37 (m, 4H), 2.21-2.03 (m, 1H), 1.38-1.30 (t, 6H, $^3J_{\text{H-H}} = 7.1$), 0.74 (d, 3H, $^3J_{\text{H-H}} = 6.6$). ^{31}P NMR δ 77.43 (t, 1P, $^2J_{\text{F-P}} = 109.2$). ^{19}F NMR δ 51.02 (dt, 2F, $^2J_{\text{F-P}} = 107.7$, $^3J_{\text{F-H}} = 19.5$). ^{13}C NMR δ 142.6 (s, 1C), 135.2 (s, 1C), 131.2 (s, 2C), 126.6 (s, 2C), 121.7 (dt, 1C), 63.6 (d, 2C, $^2J_{\text{C-P}} = 5.9$), 53.9 (s, 1C), 52.1 (d, 1C, $^3J_{\text{C-P}} = 8.0$), 36.3 (d, 1C, $^2J_{\text{C-P}} = 3.0$), 35.2 (d, 1C, $^3J_{\text{C-P}} = 12.2$), 22.5 (s, 1C), 15.5 (d, 2C, $^3J_{\text{C-P}} = 7.0$), 12.4 (s, 1C). IR (NaCl) ν cm^{-1} 1344 (SO_2), 1123 (N-SO_2), 1063 (C-F), 1017 (P-O), 813 (P=S). Minor diastereoisomer: ^1H NMR δ 7.70 (d, 2H, $^3J_{\text{H-H}} = 8.2$), 7.61 (d, 2H, $^3J_{\text{H-H}} = 8.2$), 4.15-4.03 (m, 4H), 3.65 (dd, 1H, $^1J_{\text{H-H}} = 10.1$, $^3J_{\text{H-H}} = 7.0$), 3.55-3.37 (m, 1H), 3.03 (dd, 1H, $^1J_{\text{H-H}} = 10.2$, $^3J_{\text{H-H}} = 7.6$), 2.88 (t(dd), 1H, $^1J_{\text{H-H}} = ^3J_{\text{H-H}} = 9.8$), 2.53-2.31 (m, 3H), 2.15 (ddd, 1H, $^2J_{\text{H-H}} = ^1J_{\text{H-H}} = 15.6$, $^3J_{\text{H-H}} = 2.8$), 2.01-1.83 (m, 1H), 1.71-1.56 (m, 2H), 1.38-1.30 (m, 6H), 0.84 (d, 3H, $^1J_{\text{H-H}} = 6.6$). ^{31}P NMR δ 76.84 (t, 1P, $^2J_{\text{F-P}} = 109.1$). ^{19}F NMR δ 50.56 (dt, 2F, $^2J_{\text{F-P}} = 107.5$, $^3J_{\text{F-H}} = 19.5$). ^{13}C NMR δ 142.2 (s, 1C), 134.8 (s, 1C), 131.1 (s, 2C), 125.3 (s, 2C), 120.4 (dt, 1C), 64.0 (d, 2C, $^2J_{\text{C-P}} = 5.9$), 54.6 (s, 1C), 53.22 (d, 1C, $^3J_{\text{C-P}} = 8.0$), 36.7 (d, 1C, $^2J_{\text{C-P}} = 3.2$), 35.2 (d, 1C, $^3J_{\text{C-P}} = 12.1$), 23.5 (s,

1C), 15.8 (d, 2C, $^3J_{C-P} = 7.4$), 12.3 (s, 1C). IR (NaCl) ν cm^{-1} 1322 (SO₂), 1079 (N-SO₂), 1053 (C-F), 1011 (P-O), 856 (P=S).

***O,O*-Diethyl 1,1-difluorooct-2-enylphosphonate (28).** Isolated by chromatography and elution with H/A (4:1) as a yellow oil (58 mg, 55%) (R_f 0.28). ^1H NMR δ 6.26-6.13 (m, 1H), 5.68-5.48 (m, 1H), 4.29-4.22 (m, 4H), 2.37-2.11 (m, 2H), 1.59-1.34 (m, 6H), 1.28 (t, 6H, $^3J_{H-H} = 6.9$), 0.98-0.75 (m, 6H). ^{31}P NMR δ 6.92 (t, 1P, $^2J_{F-P} = 109.5$). ^{19}F NMR δ 57.83 (dd, 2F, $^2J_{F-P} = 115.1$, $^3J_{F-H} = 16.9$), 54.23 (dd, 2F, $^2J_{F-P} = 118.5$, $^3J_{F-H} = 13.5$). ^{13}C NMR δ 142.6 (s, 1C), 134.1 (s, 1C), 121.5 (dt, 1C), 64.2 (d, 2C, $^2J_{C-P} = 6.7$), 33.8 (s, 1C), 29.3 (s, 1C), 29.2 (s, 1C), 29.1 (s, 1C), 16.2 (d, 2C, $^3J_{C-P} = 5.4$), 15.1 (s, 1C). IR (NaCl) ν cm^{-1} 1267 (P=O), 1104 (C-F), 1006 (P-O). Exact mass (EI, 70eV) m/z calcd for C₁₂H₂₃O₃PF₂ 284.2859. Found 284.2864. Anal. Calcd for C₁₂H₂₃O₃PF₂: C, 50.70; H, 8.15. Found: C, 50.72; H, 8.20.

***O,O*-Diethyl 1,1-difluoro-4-butoxybut-2-enylphosphonate (29).** Chromatography and elution with H/A (4:1) give **29** as a yellow oil (33 mg, 30%) (R_f 0.38). ^1H NMR δ 6.69-6.41 (m, 2H), 4.34-4.27 (m, 4H), 3.32-3.21 (m, 2H), 3.06 (t, 2H, $^3J_{H-H} = 6.6$), 2.51-2.29 (m, 4H), 1.35 (t, 6H, $^3J_{H-H} = 7.7$), 0.90 (t, 3H, $^3J_{H-H} = 5.8$). ^{31}P NMR δ 6.32 (t, 1P, $^2J_{F-P} = 110.2$). ^{19}F NMR 51.10 (dd, 2F, $^2J_{F-P} = 111.8$, $^3J_{F-H} = 17.6$), 51.06 (dd, 2F, $^2J_{F-P} = 109.5$, $^3J_{F-H} = 16.2$). ^{13}C NMR δ 143.8 (s, 1C), 139.0 (s, 1C), 121.6 (dt, 1C), 76.0 (s, 1C), 68.2 (s, 1C), 64.0 (d, 2C, $^2J_{C-P} = 6.9$), 34.3 (s, 1C), 20.5 (s, 1C), 17.4 (d, 2C, $^3J_{C-P} = 6.5$), 14.9 (s, 1C). IR (NaCl) ν cm^{-1} 1196 (P=O), 1023 (C-F), 1014 (P-O). Exact mass (EI, 70eV) m/z calcd for C₁₂H₂₁O₄PF₂ 300.2828. Found 300.2865. Anal. Calcd for C₁₂H₂₁O₄PF₂: C, 48.00; H, 7.05. Found: C, 48.05; H, 7.08.

***O,O*-Diethyl 1,1-difluoro-3-phenylprop-2-enylphosphonate (30).** Chromatography and elution with H/A (4:1) furnish **30** as a yellow oil (78 mg, 68%) (R_f 0.52). ^1H NMR δ 7.24-7.01 (m, 5H), 5.87-5.69 (m, 2H), 4.29-4.14 (m, 4H), 1.38 (t, 6H, $^3J_{H-H} = 7.7$). ^{31}P NMR δ 7.06 (t, 1P, $^2J_{F-P} =$

111.3). ^{19}F NMR δ 58.55 (dd, 2F, $^2J_{\text{F-P}} = 111.7$, $^3J_{\text{F-H}} = 16.9$), 53.91 (dd, 2F, $^2J_{\text{F-P}} = 115.1$, $^3J_{\text{F-H}} = 13.5$). ^{13}C NMR δ 151.2 (s, 1C), 143.2 (s, 1C), 132.8 (s, 1C), 129.7 (s, 2C), 124.3 (s, 1C), 121.9 (s, 2C), 120.6 (dt, 1C), 63.9 (d, 2C, $^2J_{\text{C-P}} = 6.3$), 17.3 (d, 2C, $^3J_{\text{C-P}} = 5.6$). IR (NaCl) ν cm^{-1} 1197 (P=O), 1066 (C-F), 1028 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{O}_3\text{PF}_2$ 290.2467. Found 290.2501. Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{O}_3\text{PF}_2$: C, 53.80; H, 5.90. Found: C, 53.84; H, 5.95.

***O,O*-Diethyl 1,1-difluoro-3-trimethylsilylprop-2-enylphosphonate (31).** Chromatography and elution with H/A (3:2) afford **30** as a yellow oil (71 mg, 67%) (R_f 0.45). ^1H NMR δ 6.51-6.35 (m, 1H), 6.28-6.17 (m, 1H), 4.30-4.14 (m, 4H), 1.32 (t, 6H, $^3J_{\text{H-H}} = 7.3$), 0.16-0.04 (m, 9H). ^{31}P NMR δ 7.74 (t, 1P, $^2J_{\text{F-P}} = 116.9$). ^{19}F NMR δ 59.21 (dd, 2F, $^2J_{\text{F-P}} = 116.8$, $^3J_{\text{F-H}} = 15.2$). ^{13}C NMR δ 142.0 (d, 1C, $^3J_{\text{C-F}} = 7.4$), 134.3 (dt, 1C, $^2J_{\text{C-P}} = 36.0$, $^2J_{\text{C-F}} = 4.2$), 120.5 (m, 1C), 64.7 (d, 2C, $^2J_{\text{C-P}} = 6.5$), 16.3 (d, 2C, $^3J_{\text{C-P}} = 6.5$), 0.1 (m, 3C). IR (NaCl) ν cm^{-1} 1274 (P=O), 1134 (C-F), 1067 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{10}\text{H}_{21}\text{O}_3\text{PF}_2\text{Si}$ 286.3310. Found 286.3432. Anal. Calcd for $\text{C}_{10}\text{H}_{21}\text{O}_3\text{PF}_2\text{Si}$: C, 41.95; H, 7.39. Found: C, 42.01; H, 7.43. Replacing *n*-Bu₃SnH with TTMSSH leads to the isolation of the same product in 64% yield.

***O,O*-Diethyl 1,1-difluoro-3-butoxyprop-2-enylphosphonate (32).** Purification was achieved by chromatography and elution with H/A (4:1) to yield **32** as a yellow oil (67 mg, 63%) (R_f 0.35). ^1H NMR δ 6.37-6.22 (m, 2H), 4.35-4.21 (m, 4H), 3.49 (t, 2H, $^3J_{\text{H-H}} = 6.6$), 2.45-2.29 (m, 4H), 1.09 (t, 6H, $^3J_{\text{H-H}} = 7.0$), 0.81 (t, 3H, $^3J_{\text{H-H}} = 7.2$). ^{31}P NMR δ 7.16 (t, 1P, $^2J_{\text{F-P}} = 104.9$). ^{19}F NMR δ 55.54 (dd, 2F, $^2J_{\text{F-P}} = 111.1$, $^3J_{\text{F-H}} = 15.2$), 50.68 (dd, 2F, $^2J_{\text{F-P}} = 111.7$, $^3J_{\text{F-H}} = 16.9$). ^{13}C NMR δ 143.3 (s, 1C), 140.7 (s, 1C), 123.1 (dt, 1C), 69.5 (s, 1C), 64.4 (d, 2C, $^2J_{\text{C-P}} = 6.9$), 33.3 (s, 1C), 21.3 (s, 1C), 16.2 (d, 2C, $^3J_{\text{C-P}} = 6.0$), 14.7 (s, 1C). IR (NaCl) ν cm^{-1} 1256 (P=O), 1082 (C-F), 1032 (P-O). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{11}\text{H}_{19}\text{O}_4\text{PF}_2$ 286.2559. Found 286.2603. Anal. Calcd for $\text{C}_{11}\text{H}_{19}\text{O}_4\text{PF}_2$: C, 46.15; H, 6.69. Found: C, 46.18; H, 6.73.

***O,O*-Diethyl 1,1-difluorooct-2-enylphosphonothioate (34).** The residue is purified by chromatography. Elution with H/C (4:1) furnishes **34** as a colorless oil (55 mg, 50%) (R_f 0.43). ^1H NMR δ 5.92-5.86 (m, 1H), 5.74-5.54 (m, 1H), 4.29-4.13 (m, 4H), 2.38-2.11 (m, 2H), 1.60-1.33 (m, 6H), 1.28 (t, 6H, $^3J_{\text{H-H}} = 6.9$), 0.90-0.72 (m, 6H). ^{31}P NMR δ 76.36 (t, 1P, $^2J_{\text{F-P}} = 108.4$). ^{19}F NMR δ 58.86 (dd, 2F, $^2J_{\text{F-P}} = 111.3$, $^3J_{\text{F-H}} = 15.5$), 54.16 (dd, 2F, $^2J_{\text{F-P}} = 112.4$, $^3J_{\text{F-H}} = 16.9$). ^{13}C NMR δ 140.2 (s, 1C), 135.0 (s, 1C), 121.4 (dt, 1C), 64.4 (d, 2C, $^2J_{\text{C-P}} = 6.5$), 32.7 (s, 1C), 28.5 (s, 1C), 28.3 (s, 1C), 28.3 (s, 1C), 16.3 (d, 2C, $^3J_{\text{C-P}} = 5.2$), 14.8 (s, 1C). IR (NaCl) ν cm^{-1} 1167 (C-F), 1023 (P-O), 820 (P=S). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{12}\text{H}_{23}\text{O}_2\text{PF}_2\text{S}$ 300.3500. Found 300.3521. Anal. Calcd for $\text{C}_{12}\text{H}_{23}\text{O}_2\text{PF}_2\text{S}$: C, 48.00; H, 7.72; S, 10.68. Found: C, 48.03; H, 7.76; S, 10.71.

***O,O*-Diethyl 1,1-difluoro-4-butoxybut-2-enylphosphonothioate (35).** The residue is purified by chromatography. Elution with H/C (9:1) yields **35** as a colorless oil (43 mg, 37%) (R_f 0.29). ^1H NMR δ 6.67-6.37 (m, 2H), 4.30-4.15 (m, 4H), 3.23-3.15 (m, 2H), 3.09 (t, 2H, $^3J_{\text{H-H}} = 6.1$), 2.56-2.32 (m, 4H), 1.33 (t, 6H, $^3J_{\text{H-H}} = 5.9$), 0.93 (t, 3H, $^3J_{\text{H-H}} = 6.2$). ^{31}P NMR δ 77.42 (t, 1P, $^2J_{\text{F-P}} = 109.6$). ^{19}F NMR δ 58.17 (dd, 2F, $^2J_{\text{F-P}} = 110.2$, $^3J_{\text{F-H}} = 17.9$), 57.73 (dd, 2F, $^2J_{\text{F-P}} = 111.6$, $^3J_{\text{F-H}} = 16.2$). ^{13}C NMR δ 144.4 (s, 1C), 138.7 (s, 1C), 122.4 (dt, 1C), 75.1 (s, 1C), 68.9 (s, 1C), 63.2 (d, 2C, $^2J_{\text{C-P}} = 6.5$), 33.1 (s, 1C), 20.7 (s, 1C), 16.4 (d, 2C, $^3J_{\text{C-P}} = 6.2$), 15.2 (s, 1C). IR (NaCl) ν cm^{-1} 1055 (C-F), 1043 (P-O), 796 (P=S). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{12}\text{H}_{21}\text{O}_3\text{PF}_2\text{S}$ 316.3494. Found 316.3521. Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{O}_3\text{PF}_2\text{S}$: C, 45.56; H, 6.69; S, 10.14. Found: C, 45.61; H, 6.73; S, 10.19.

***O,O*-Diethyl 1,1-difluoro-3-phenylprop-2-enylphosphonothioate (36).** Purification of the crude sample by chromatography and elution with H/C (9:1) lead to the isolation of **36** as a colorless oil (102 mg, 77%) (R_f 0.38). ^1H NMR δ 7.43-7.19 (m, 5H), 5.93-5.77 (m, 2H), 4.23-4.17 (m, 4H),

1.28 (t, 6H, $^3J_{\text{H-H}} = 6.9$). ^{31}P NMR δ 76.03 (t, 1P, $^2J_{\text{F-P}} = 118.5$). ^{19}F NMR δ 59.34 (dd, 2F, $^2J_{\text{F-P}} = 118.5$, $^3J_{\text{F-H}} = 16.9$), 53.50 (dd, 2F, $^2J_{\text{F-P}} = 121.9$, $^3J_{\text{F-H}} = 13.5$). ^{13}C NMR δ 149.4 (s, 1C), 142.2 (s, 1C), 132.3 (s, 1C), 128.4 (s, 2C), 124.8 (s, 1C), 120.6 (s, 2C), 119.2 (dt, 1C), 64.1 (d, 2C, $^2J_{\text{C-P}} = 6.7$), 17.0 (d, 2C, $^3J_{\text{C-P}} = 5.8$). IR (NaCl) ν cm^{-1} 1114 (C-F), 1023 (P-O), 788 (P=S). Exact mass (EI, 70eV) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{PF}_2\text{S}$ 306.3133. Found 306.3184. Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{PF}_2\text{S}$: C, 50.97; H, 5.59; S, 10.47. Found: C, 51.00; H, 5.64; S, 10.51.

***O,O*-Diethyl 1,1-difluoro-3-trimethylsilylprop-2-enylphosphonothiate (37).** The residue is purified by chromatography. Elution with H/C (9:1) delivers **36** as colorless oil (89 mg, 80%) (R_f 0.51). ^1H NMR δ 6.50-6.35 (m, 1H), 6.27-6.16 (m, 1H), 4.29-4.13 (m, 4H), 1.31 (t, 6H, $^3J_{\text{H-H}} = 6.9$), 0.20-0.04 (m, 9H). ^{31}P NMR δ 78.11 (t, 1P, $^2J_{\text{F-P}} = 116.9$). ^{19}F NMR δ 60.88 (dd, 2F, $^2J_{\text{F-P}} = 115.1$, $^3J_{\text{F-H}} = 16.9$), 55.06 (dd, 2F, $^2J_{\text{F-P}} = 121.8$, $^3J_{\text{F-H}} = 13.5$). ^{13}C NMR δ 142.0 (d, 1C, $^3J_{\text{C-F}} = 7.4$), 134.5 (dt, 1C, $^2J_{\text{C-F}} = 27.0$, $^2J_{\text{C-P}} = 5.7$), 120.6 (m, 1C), 64.7 (d, 2C, $^2J_{\text{C-P}} = 6.5$), 16.4 (d, 2C, $^3J_{\text{C-P}} = 6.5$), 0.1 (m, 3C). IR (NaCl) ν cm^{-1} 1092 (C-F), 1069 (P-O), 745 (P=S). Exact (EI, 70eV) m/z calcd for $\text{C}_{10}\text{H}_{21}\text{O}_2\text{PF}_2\text{SSi}$ 302.3983. Found 302.3995. Anal. Calcd for $\text{C}_{10}\text{H}_{21}\text{O}_2\text{PF}_2\text{SSi}$: C, 39.72; H, 7.00; S, 10.60. Found: C, 39.75; H, 7.03; S, 10.63. Replacing *n*-Bu₃SnH with TTMSSH leads to the isolation of the same product in 82% yield.

***O,O*-Diethyl 1,1-difluoro-3-butoxyprop-2-enylphosphonothioate (38).** The residue is purified by chromatography. Elution with H/C (9:1) gives **38** as a colorless oil (84 mg, 75%) (R_f 0.24). ^1H NMR δ 6.41-6.31 (m, 2H), 4.42-4.32 (m, 4H), 3.57 (t, 2H, $^3J_{\text{H-H}} = 6.2$), 2.59-2.34 (m, 4H), 1.15 (t, 6H, $^3J_{\text{H-H}} = 6.9$), 0.85 (t, 3H, $^3J_{\text{H-H}} = 6.9$). ^{31}P NMR δ 74.21 (t, 1P, $^2J_{\text{F-P}} = 102.5$). ^{19}F NMR δ 57.68 (dd, 2F, $^2J_{\text{F-P}} = 108.3$, $^3J_{\text{F-H}} = 17.1$), 52.43 (dd, 2F, $^2J_{\text{F-P}} = 108.6$, $^3J_{\text{F-H}} = 17.0$). ^{13}C NMR δ 142.7 (s, 1C), 140.3 (s, 1C), 121.3 (dt, 1C), 69.3 (s, 1C), 64.8 (d, 2C, $^2J_{\text{C-P}} = 6.8$), 32.6 (s, 1C), 20.4 (s, 1C), 16.5 (d, 2C, $^3J_{\text{C-P}} = 6.0$), 13.6 (s, 1C). IR (NaCl) ν cm^{-1} 1042 (C-F), 1028 (P-O), 737 (P=S). Exact

mass (EI, 70eV) m/z calcd for $C_{11}H_{19}O_3PF_2S$ 302.3225. Found 302.3264. Anal. Calcd for $C_{11}H_{19}O_3PF_2S$: C, 43.70; H, 6.33; S, 10.61. Found: C, 43.75; H, 6.37; S, 10.65.

^{19}F NMR
 CDCl_3

59.5616
59.4806
58.9403
58.8593

^{31}P NMR
 CDCl_3

79.5559
78.1116
76.6674