Syntheses of α -Fluoro- α,β -Unsaturated Thioamides and Thiazolines from a Fluoro-phosphonodithioacetate

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Supporting Information

1) Preparation of compounds 4b-4c, 6b-6c, 6e, 8b-8d, 9a-9d, 10b-10c, 11a-11c:

Compound (4b)	S02	Compound (4c)	S02
Compound (6b)	S03	Compound (6c)	S03
Compound (6e)	S03	Compound (8b)	S04
Compound (8c)	S04	Compound (8d)	S05
Compound (9a)	S05	Compound (9b)	S06
Compound (9c)	S06	Compound (9d)	S07
Compound (10b)	S07	Compound (10c)	S07
Compound (11a)	S08	Compound (11b)	S09
Compound (11c)	S09		

2) NMR spectra of compounds 3, 6a-6e, 7, 8a-8d, 9a-9d, 10a-10c, 11a-11c:

^1H NMR of 3	S10	^1H NMR of 6a	S11
^1H NMR of 6d	S12	^{19}F NMR of 6d	S13
^1H NMR of 6e	S14	^1H NMR of 7	S15
^1H NMR of 8a	S16	^1H NMR of 8b	S17
^{13}C NMR of 8c	S18	^{13}C NMR of 8d	S19
^1H NMR of 9a	S20	^1H NMR of 9b	S21

¹ H NMR of 9c	S22	-S2- ¹³ C NMR of 9d	S23
¹ H NMR of 10a	S24	¹ H NMR of 10b	S25
¹ H NMR of 10c	S26	¹ H NMR of 11a	S27
¹⁹ F NMR of 11a	S28	¹ H NMR of 11b-E	S29
¹ H NMR of 11b-Z	S30	¹⁹ F NMR of 11b	S31
¹ H NMR of 11c	S32		

General. All reactions were conducted under nitrogen atmosphere using oven-dried glassware. THF was distilled from sodium benzophenone, methylene chloride and diisopropylamine were distilled from CaH₂. *n*-Butyllithium in hexane was purchased from Aldrich and titrated before each use. ³¹P and ¹⁹F NMR spectral lines are with respect to the internal references (capillary) H₃PO₄ and CFC₃.

Diethyl 1-fluoro-2-(methylsulfanyl)-2-(phenylsulfanyl)vinylphosphonate (4b). (320 mg, 88 %, Eluent : Et₂O / pentane: 60 / 40): ¹H NMR (250 MHz, CDCl₃) δ 1.30 (t, ³J_{HH} = 7.0 Hz, 6H), 2.25 (s, 3H), 4.19 (m, 4H), 7.33 (m, 5H); ¹⁹F NMR (235 MHz, CDCl₃) δ -92.8 (d, ²J_{FP} = 104.0 Hz); ³¹P NMR (101.2 MHz, CDCl₃) δ 4.2 (d, ²J_{PF} = 103.3 Hz); ¹³C NMR (62.9 MHz, CDCl₃) δ 15.5 (d, ⁴J_{CF} = 4.4 Hz), 16.6 (d, ³J_{CP} = 6.6 Hz), 63.9 (d, ²J_{CP} = 6.0 Hz), 127.7, 129.2, 129.6, 130.9 (dd, ²J_{CP} = 18.4 Hz, ²J_{CF} = 29.1 Hz), 152.9 (dd, ¹J_{CP} = 242.9 Hz, ¹J_{CF} = 288.2 Hz); MS (EI, 70 eV) *m/z* (relative intensity) 336 (M⁺ 43), 199 (26), 198 (79), 171 (24), 155 (44), 152 (42), 147 (21), 134 (45), 124 (41), 121 (41), 109 (77), 107 (25), 93 (20), 91 (50), 86 (76), 54 (100), 81 (41), 78 (38). HRMS (EI, 70 eV) *m/z* [M⁺] calcd for C₁₃H₁₈FO₃PS₂ 336.0419, found 336.0422.

Diethyl 1-fluoro-2-(methylsulfanyl)-2-(vinylsulfanyl)vinylphosphonate (4c). (270 mg, 88 %, Eluent : Et₂O / Pentane 55 / 45): ¹H NMR (250 MHz, CDCl₃) δ 1.36 (t, ³J_{HH} = 7.0 Hz, 6H), 2.40 (s, 3H), 4.20 (m, 4H), 5.42 (d, ³J_{HH} = 9.9 Hz, 1H), 5.43 (d, ³J_{HH} = 16.7 Hz, 1H), 6.39 (ddd, *J*_{HF} = 1.7 Hz, ³J_{HH} = 9.5 Hz, ³J_{HH} = 16.8 Hz); ¹⁹F NMR (235 MHz, CDCl₃) δ -93.8 (d, ²J_{FP} = 103.0 Hz); ³¹P NMR (101.2 MHz, CDCl₃) δ 3.8 (d, ²J_{PF} = 102.9 Hz); ¹³C NMR (62.9 MHz, CDCl₃) δ 15.5 (d, ⁴J_{CF} = 4.2 Hz), 16.6 (d, ³J_{CP} = 6.6 Hz), 63.9 (d, ²J_{CP} = 5.8 Hz), 116.3, 129.8, 130.1 (dd, ²J_{CP} = 18.4 Hz, ²J_{CF} = 29.4 Hz), 151.9 (dd, ¹J_{CP} = 240.8 Hz, ¹J_{CF} = 286.7 Hz); MS (EI, 70 eV) *m/z* (relative intensity) 286 (M⁺ 51), 213 (44), 157 (26), 149 (78), 148 (47),

91 (29), 86 (61), 84 (100), 81 (22). HRMS (EI, 70 eV) m/z [M^+] calcd for $C_9H_{16}FO_3PS_2$ 286.0262, found 286.0267.

Diethyl 1-fluoro-2-[(2-hydroxyethyl)amino]-2-thioxoethylphosphonate (6b). Obtained in 87 % (915 mg; ethyl acetate) starting from **3** (1g, 3.84 mmol) and 2-aminoethanol (2.35 mL, 4.25 mmol): 1H NMR (250 MHz, $CDCl_3$) δ 1.30 (t, $^3J_{HH} = 7.0$ Hz, 6H), 3.80 (m, 4H), 4.20 (m, 5H), 5.49 (dd, $^2J_{HP} = 11.0$ Hz, $^2J_{HF} = 47.2$ Hz, 1H), 9.03 (sbr, 1H); ^{19}F NMR (235 MHz, $CDCl_3$) δ -199.9 (ddd, $^4J_{FH} = 4.0$ Hz, $^2J_{FH} = 47.0$ Hz, $^2J_{FP} = 79.0$ Hz); ^{31}P NMR (101.2 MHz, $CDCl_3$) δ 11.5 (d, $^2J_{PF} = 77.4$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 16.6 and 16.7 (d, $^3J_{CP} = 5.93$ Hz, 6H), 48.0, 59.7, 64.8 and 65.9 (d, $^2J_{CP} = 7.0$ Hz), 92.3 (dd, $^1J_{CP} = 161.4$ Hz, $^1J_{CF} = 204.9$ Hz), 191.1 (d, $^2J_{CP} = 13.3$ Hz); MS (EI, 70 eV) m/z (relative intensity) 273 (M^+ 25), 253 (71), 225 (72), 192 (100), 182 (63), 164 (71), 154 (87), 140 (100), 135 (50), 114 (100), 111 (65), 99 (100), 85 (71), 81 (95), 78 (36), 77 (70), 75 (48), 73 (59). HRMS (EI, 70 eV) m/z [M^+] calcd for $C_8H_{17}FNO_4PS$ 273.0599, found 273.0607.

Diethyl 1-fluoro-2-[(2-hydroxy-1-phenylethyl)amino]-2-thioxoethylphosphonate (6c). Obtained as a mixture of two diastereomers (1/1) in 89 % (1.2 g; ethyl acetate / pentane: 7 / 3), starting from **3** (1g, 3.84 mmol) and phenylglycinol (580 mg, 4.25 mmol): 1H NMR (250 MHz, $CDCl_3$) δ 1.31 (m, 12H), 4.12 (m, 14H), 5.56 and 5.59 (dd, $^2J_{HP} = 10.6$ Hz, $^2J_{HF} = 47.0$ Hz, 1H), 5.58 and 5.82 (m, 1H), 7.32 (m, 10H), 9.02 and 9.28 (sbr, 1H); ^{19}F NMR (235 MHz, $CDCl_3$) δ -189.1 and -189.7 (ddd, $^4J_{FH} = 3.0$ Hz, $^2J_{FH} = 47.0$ Hz, $^2J_{FP} = 77.0$ Hz); ^{31}P NMR (101.2 MHz, $CDCl_3$) δ 12.5 and 12.6 (d, $^2J_{PF} = 78.6$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 16.6 and 16.7 (d, $^3J_{CP} = 6.0$ Hz), 60.6 and 60.8, 64.9 (dd, $^4J_{CP} = 5.2$ Hz, $^4J_{CF} = 11.9$ Hz), 65.4 and 66.0 (d, $^2J_{CP} = 7.0$ Hz), 92.2 and 92.5 (dd, $^1J_{CP} = 160.0$ Hz, $^1J_{CF} = 204.4$ Hz), 190.8 (d, $^2J_{CF} = 14.7$ Hz); MS (EI, 70 eV) m/z (relative intensity) 349 (M^+ 4), 331 (50), 319 (28), 312 (30), 267 (37), 230 (21), 219 (28), 182 (20), 148 (25), 134 (27), 91 (23). HRMS (EI, 70 eV) m/z [M^+] calcd for $C_{14}H_{21}FNO_4PS$ 331.0808, found 331.0819.

Methyl N-[2-(diethoxyphosphoryl)-2-fluoroethanethioyl]phenylalaninate (6e). Following the general procedure for the preparation of **6a-c** and starting from **3** (1g, 3.84 mmol) and methyl phenylalanine ester (760 mg, 4.25 mmol), **6e** was isolated as a mixture of two diastereomers in 85 % yield (1.28 g) by flash chromatography (pentane / ethyl acetate: 4 / 6): 1H NMR (250 MHz, $CDCl_3$) δ 1.30

and 1.33 (m, 6H), 3.23 (dd, $^3J_{\text{HH}} = 5.4$ Hz, $^2J_{\text{HH}} = 14.0$ Hz, 1H) and 3.28 (dd, $^3J_{\text{HH}} = 5.4$ Hz, $^2J_{\text{HH}} = 15.0$ Hz, 1H), 3.31 (dd, $^3J_{\text{HH}} = 5.2$ Hz, $^2J_{\text{HH}} = 15.3$ Hz, 1H) and 3.37 (dd, $^3J_{\text{HH}} = 5.4$ Hz, $^2J_{\text{HH}} = 14.0$ Hz, 1H), 3.72 and 3.73 (s, 3H), 4.20 and 4.23 (m, 4H), 5.40 and 5.42 (m, 1H), 5.52 (dd, $^2J_{\text{HP}} = 11.4$ Hz, $^2J_{\text{HF}} = 47.1$ Hz, 1H) and 5.53 (dd, $^2J_{\text{HP}} = 19.9$ Hz, $^2J_{\text{HF}} = 46.9$ Hz, 1H), 7.22 and 7.24 (m, 5H), 8.44 and 8.46 (sbr, 1H); ^{19}F NMR (235 MHz, CDCl_3) δ -190.8 (ddd, $^4J_{\text{FH}} = 5.0$ Hz, $^2J_{\text{FH}} = 47.0$ Hz, $^2J_{\text{FP}} = 76.0$ Hz) and -190.7 (ddd, $^4J_{\text{FH}} = 5.0$ Hz, $^2J_{\text{FH}} = 47.0$ Hz, $^2J_{\text{FP}} = 75.0$ Hz); ^{31}P NMR (101.2 MHz, CDCl_3) δ 10.4 (d, $^2J_{\text{PF}} = 75.3$ Hz) and 10.9 (d, $^2J_{\text{PF}} = 76.2$ Hz); ^{13}C NMR (62.9 MHz, CDCl_3) δ 16.7 (d, $^3J_{\text{CP}} = 6.4$ Hz) and 16.8 (d, $^3J_{\text{CP}} = 6.3$ Hz), 36.6 and 37.2, 52.9 and 53.0, 58.2 and 58.3, 64.7 (d, $^2J_{\text{CP}} = 6.6$ Hz) and 65.0 (d, $^2J_{\text{CP}} = 6.7$ Hz), 64.8 (d, $^2J_{\text{CP}} = 6.6$ Hz) and 65.1 (d, $^2J_{\text{CP}} = 6.8$ Hz), 92.3 (dd, $^1J_{\text{CP}} = 158.9$ Hz, $^1J_{\text{CF}} = 203.9$ Hz) and 92.6 (dd, $^1J_{\text{CP}} = 160.8$ Hz, $^1J_{\text{CF}} = 207.7$ Hz), 127.7, 129.0, 129.8, 127.8, 129.1, 129.6, 135.4, 135.4, 170.6 and 170.7, 191.2 (d, $^2J_{\text{CF}} = 13.2$ Hz) and 191.3 (d, $^2J_{\text{CF}} = 13.9$ Hz); MS (EI, 70 eV) m/z (relative intensity) 391 (M^+ , 10), 371 (91), 313 (20), 312 (100), 209 (24), 195 (22), 162 (54), 131 (52), 121 (26), 91 (34). HRMS (EI, 70 eV) m/z [M^+] calcd for $\text{C}_{16}\text{H}_{23}\text{FNO}_5\text{PS}$ 391.1018, found 391.1007.

(N-propyl-2-fluoro-4-methyl)-pent-2-enethioamide (8b). Isolated in 72 % (100 mg) by distillation (25° C / 6.10^{-2} mbar), starting from **6a** (200 mg, 0.738 mmol) and isobutyraldehyde (75 μL , 0.811 mmol): ^1H NMR (250 MHz, CDCl_3) δ 0.92 (t, $^3J_{\text{HH}} = 7.4$ Hz, 6H), 0.99 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H), 1.65 (m, 4H), 2.73 (m, 1H, *Z*) and 3.92 (m, 1H, *E*), 3.59 (m, 4H), 5.52 (dd, $^3J_{\text{HH}} = 10.4$ Hz, $^3J_{\text{HF}} = 28.6$ Hz, 1H, *E*) and 6.42 (dd, $^3J_{\text{HH}} = 9.8$ Hz, $^3J_{\text{HF}} = 37.0$ Hz, 1H, *Z*), 7.82 (sbr, 2H); ^{19}F NMR (235 MHz, CDCl_3) δ -130.5 (dd, $^3J_{\text{FH}} = 37.0$ Hz, $^4J_{\text{FH}} = 7.0$ Hz, *Z*) and -113.1 (dd, $^3J_{\text{FH}} = 28.6$ Hz, $^4J_{\text{FH}} = 7.0$ Hz, *E*); ^{13}C NMR (62.9 MHz, CDCl_3) δ 10.4 (*Z*) and 10.5 (*E*), 20.2 (*E*) and 20.3 (*Z*), 21.0 (d, $^4J_{\text{CF}} = 1.5$ Hz, *Z*) and 21.3 (d, $^4J_{\text{CF}} = 2.0$ Hz, *E*), 24.4 (d, $^3J_{\text{CF}} = 3.6$ Hz, *Z*) and 25.3 (d, $^3J_{\text{CF}} = 5.6$ Hz, *E*), 45.2 (*Z*) and 46.2 (*E*), 125.8 (d, $^2J_{\text{CF}} = 16.3$ Hz, *Z*) and 127.2 (d, $^2J_{\text{CF}} = 21.3$ Hz, *E*), 149.3 (d, $^1J_{\text{CF}} = 251.0$ Hz, *Z*) and 152.6 (d, $^1J_{\text{CF}} = 260.0$ Hz, *E*), 184.2 (d, $^2J_{\text{CF}} = 22.0$ Hz, *E*) and 185.1 (d, $^2J_{\text{CF}} = 19.0$ Hz, *Z*); MS (EI, 70 eV) m/z (relative intensity) 189 (M^+ , 100), 146 (28), 115 (21), 97 (13). HRMS (EI, 70 eV) m/z [M^+] calcd for $\text{C}_9\text{H}_{16}\text{FNS}$ 189.0987, found 189.1006.

(N-propyl-2-fluoro)-dodec-2-enethioamide (8c). Isolated in 67 % (128 mg) by distillation (50° C / 6.10^{-2} mbar), starting from **6a** (200 mg, 0.738 mmol) and nonanal (146 μL , 0.811 mmol) : ^1H NMR (250

MHz, CDCl₃) δ 0.75 (t, $^3J_{\text{HH}} = 6.0$ Hz, 6H), 0.91 (t, $^3J_{\text{HH}} = 7.3$ Hz, 6H), 1.15-1.30 (m, 24H), 1.64 (m, 4H), 2.15 (m, 2H, Z) and 4.20 (m, 2H, E), 3.65 (m, 4H), 5.75 (dt, $^3J_{\text{HF}} = 28.1$ Hz, $^3J_{\text{HH}} = 7.7$ Hz, 1H E) and 6.55 (dt, $^3J_{\text{HF}} = 36.5$ Hz, $^3J_{\text{HH}} = 7.9$ Hz, 1H, Z), 7.70 and 7.75 (sbr, 2H); ^{19}F NMR (235 MHz, CDCl₃) δ -130.4 (dd, $^3J_{\text{FH}} = 36.0$ Hz, $^4J_{\text{FH}} = 7.0$ Hz, Z) and -112.6 (dd, $^3J_{\text{FH}} = 28.0$ Hz, $^4J_{\text{FH}} = 7.5$ Hz, E); ^{13}C NMR (62.9 MHz, CDCl₃) δ 11.8 and 11.9, 14.4, 21.6, 21.7, 23.0, 25.6 (d, $^3J_{\text{CF}} = 3.6$ Hz, Z) and 28.0 (d, $^3J_{\text{CF}} = 5.1$ Hz, E), 29.7, 32.2, 46.5 (E) and 47.6 (Z), 122.4 (d, $^2J_{\text{CF}} = 23.9$ Hz, E) and 123.1 (d, $^2J_{\text{CF}} = 18.0$ Hz, Z), 151.5 (d, $^1J_{\text{CF}} = 250.4$ Hz, E) and 155.3 (d, $^1J_{\text{CF}} = 259.9$ Hz, Z), 185.6 (d, $^2J_{\text{CF}} = 21.8$ Hz, E) and 186.3 (d, $^2J_{\text{CF}} = 18.4$ Hz, Z); MS (EI, 70 eV) m/z (relative intensity) 259 (M^+ 40), 227 (71), 226 (56), 174 (85), 146 (29), 135 (100), 115 (26), 103 (18), 83 (12). HRMS (EI, 70 eV) m/z [M^+] calcd for C₁₄H₂₆FNS 259.1770, found 259.1751.

(N-propyl-2-fluoro-3-cyclohexyl)-prop-2-enethioamide (8d). Isolated in 72 % (122 mg) by distillation (75° C / 6.10⁻² mbar), starting from **6a** (200 mg, 0.738 mmol) and cyclohexanecarboxaldehyde (100 μL , 0.811 mmol): ^1H NMR (250 MHz, CDCl₃) δ 0.92 (t, $^3J_{\text{HH}} = 7.4$ Hz, 6H), 1.16-1.68 (m, 24H), 2.98 (m, 1H, Z) and 4.07 (m, 1H, E), 3.59 (m, 4H), 5.53 (dd, $^3J_{\text{HH}} = 10.3$ Hz, $^3J_{\text{HF}} = 28.6$ Hz, 1H, E) and 6.44 (dd, $^3J_{\text{HH}} = 9.8$ Hz, $^3J_{\text{HF}} = 37.2$ Hz, 1H, Z), 7.77 (sbr, 2H); ^{19}F NMR (235 MHz, CDCl₃) δ -130.6 (dd, $^3J_{\text{FH}} = 37.2$ Hz, $^4J_{\text{FH}} = 7.0$ Hz, Z) and -113.2 (dd, $^3J_{\text{FH}} = 28.6$ Hz, $^4J_{\text{FH}} = 8.0$ Hz, E); ^{13}C NMR (62.9 MHz, CDCl₃) δ 10.4 (E) and 10.5 (Z), 20.2 (E) and 20.3 (Z), 24.5, 24.9 (E,Z), 31.0 (d, $^4J_{\text{CF}} = 1.5$ Hz, Z) and 31.4 (d, $^4J_{\text{CF}} = 1.9$ Hz, E), 33.9 (d, $^3J_{\text{CF}} = 2.7$ Hz, Z) and 34.5 (d, $^3J_{\text{CF}} = 5.2$ Hz, E), 45.2 (E) and 46.2 (Z), 124.5 (d, $^2J_{\text{CF}} = 16.3$ Hz, Z) and 125.6 (d, $^2J_{\text{CF}} = 21.2$ Hz, E), 149.6 (d, $^1J_{\text{CF}} = 252.0$ Hz, Z) and 152.7 (d, $^1J_{\text{CF}} = 260.0$ Hz, E), 184.3 (d, $^2J_{\text{CF}} = 22.0$ Hz, E) and 185.1 (d, $^2J_{\text{CF}} = 18.0$ Hz, Z); MS (EI, 70 eV) m/z (relative intensity) 229 (M^+ 100), 196 (66), 189 (24), 186 (24), 146 (25), 141 (22), 139 (25), 135 (25), 134 (23), 111 (20), 102 (20), 84 (15). HRMS (EI, 70 eV) m/z [M^+] calcd for C₁₂H₂₀FNS 229.1300, found 229.1320.

2-(1-fluoro-2-phenyl-ethenyl)-thiazoline (9a). Isolated in 92 % (150 mg; Et₂O / pentane 35 / 65), starting from **7** (200 mg, 0.784 mmol) and benzaldehyde (90 μL , 0.862 mmol) : **(E)-9a**: ^1H NMR (250 MHz, CDCl₃) δ 3.25 (t, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 4.34 (t, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 6.75 (d, $^3J_{\text{HF}} = 22.0$ Hz, 1H), 7.43 (m, 5H); ^{19}F NMR (235 MHz, CDCl₃) δ -104.2 (d, $^3J_{\text{FH}} = 22.0$ Hz); ^{13}C NMR (62.9 MHz, CDCl₃) δ 33.9, 64.8, 117.0 (d, $^2J_{\text{CF}} = 27.8$ Hz), 128.5, 128.9, 130.1 (d, $^4J_{\text{CF}} = 2.8$ Hz), 131.6 (d, $^3J_{\text{CF}} = 10.8$ Hz), 151.3 (d,

$^1J_{\text{CF}} = 245.0$ Hz), 161.2 (d, $^2J_{\text{CF}} = 33.5$ Hz); (**Z**)-**9a**: ^1H NMR (250 MHz, CDCl_3) δ 3.33 (t, $^3J_{\text{HH}} = 8.3$ Hz, 2H), 4.37 (t, $^3J_{\text{HH}} = 8.3$ Hz, 2H), 6.39 (d, $^3J_{\text{HF}} = 36.8$ Hz, 1H), 7.34 (m, 5H); ^{19}F NMR (235 MHz, CDCl_3) δ -113.8 (d, $^3J_{\text{FH}} = 36.8$ Hz); MS (EI, 70 eV) m/z (relative intensity) 207 (M^+ 100), 206 (76), 147 (53), 133 (48), 120 (18), 76 (18). HRMS (EI, 70 eV) m/z [M^+] calcd for $\text{C}_{11}\text{H}_{10}\text{FNS}$ 207.0518, found 207.0501.

2-(1-fluoro-3-methyl-prop-1-enyl)-thiazoline (9b). Isolated in 90 % (122 mg) by distillation (30° C / 6.10^{-2} mbar), starting from **7** (200 mg, 0.784 mmol) and isobutyraldehyde (80 μL , 0.862 mmol): ^1H NMR (250 MHz, CDCl_3) δ 1.00 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6H, *E*) and 1.07 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6H, *Z*), 2.81 (m, 1H, *E*) and 2.87 (m, 1H, *Z*), 3.35 (t, $^3J_{\text{HH}} = 8.1$ Hz, 2H, *E*) and 3.40 (t, $^3J_{\text{HH}} = 8.1$ Hz, 2H, *Z*), 4.34 (t, $^3J_{\text{HH}} = 8.3$ Hz, 2H, *E*) and 4.38 (t, $^3J_{\text{HH}} = 8.3$ Hz, 2H, *Z*), 5.59 (dd, $^3J_{\text{HH}} = 9.5$ Hz, $^3J_{\text{HF}} = 23.0$ Hz, 1H, *E*) and 5.65 (dd, $^3J_{\text{HH}} = 9.5$ Hz, $^3J_{\text{HF}} = 35.0$ Hz, 1H, *Z*); ^{19}F NMR (235 MHz, CDCl_3) δ -119.9 (d, $^3J_{\text{FH}} = 35.0$ Hz, *Z*) and -110.8 (d, $^3J_{\text{FH}} = 23.0$ Hz, *E*); ^{13}C NMR (62.9 MHz, CDCl_3) δ 22.6 (d, $^4J_{\text{CF}} = 6.7$ Hz, *Z*) and 23.2 (d, $^4J_{\text{CF}} = 7.5$ Hz, *E*), 25.1 (d, $^3J_{\text{CF}} = 2.8$ Hz, *Z*) and 25.4 (d, $^3J_{\text{CF}} = 6.8$ Hz, *E*), 32.8 (*E*) and 34.0 (*Z*), 65.5 (*E*) and 65.5 (*Z*), 123.9 (d, $^2J_{\text{CF}} = 18.2$ Hz, *E*) and 125.0 (d, $^2J_{\text{CF}} = 13.5$ Hz, *Z*), 149.5 (d, $^1J_{\text{CF}} = 236.2$ Hz, *E*) and 150.2 (d, $^1J_{\text{CF}} = 250.7$ Hz, *Z*), 161.7 (d, $^2J_{\text{CF}} = 40.8$ Hz, *E*) and 162.1 (d, $^2J_{\text{CF}} = 27.8$ Hz, *Z*); MS (EI, 70 eV) m/z (relative intensity) 173 (M^+ 100), 158 (63), 145 (20), 132 (58), 112 (14). HRMS (EI, 70 eV) m/z [M^+] calcd for $\text{C}_8\text{H}_{12}\text{FNS}$ 173.0674, found 173.0688.

2-(1-fluoro-dodec-1-enyl)-thiazoline (9c). Isolated in 91 % (173 mg) by distillation (45° C / 6.10^{-2} mbar), starting from **7** (200 mg, 0.784 mmol) and Nonylaldehyde (150 μL , 0.862 mmol): ^1H NMR (250 MHz, CDCl_3) δ 0.80 (t, $^3J_{\text{HH}} = 6.9$ Hz, 6H), 1.99-1.37 (m, 24H), 2.17 (m, 2H, *E*) and 2.38 (m, 2H, *Z*), 3.22 (t, $^3J_{\text{HH}} = 8.5$ Hz, 2H, *E*) and 3.27 (t, $^3J_{\text{HH}} = 8.3$ Hz, 2H, *Z*), 4.30 (t, $^3J_{\text{HH}} = 8.3$ Hz, 2H, *E*) and 4.32 (t, $^3J_{\text{HH}} = 8.5$ Hz, 2H, *Z*), 5.53 (dt, $^3J_{\text{HF}} = 35.0$ Hz, $^3J_{\text{HH}} = 7.7$ Hz, 1H, *Z*) and 5.55 (dt, $^3J_{\text{HF}} = 22.0$ Hz, $^3J_{\text{HH}} = 8.1$ Hz, 1H, *E*); ^{19}F NMR (235 MHz, CDCl_3) δ -119.6 (d, $^3J_{\text{FH}} = 35.0$ Hz, *Z*) and -108.8 (d, $^3J_{\text{FH}} = 22.0$ Hz, *E*); ^{13}C NMR (62.9 MHz, CDCl_3) δ 14.4, 23.0, 24.7 (d, $^3J_{\text{CF}} = 6.3$ Hz, *E*) and 24.8 (d, $^3J_{\text{CF}} = 2.8$ Hz, *Z*), 29.0, 29.6, 32.2, 34.0, 65.4 (*E*) and 65.5 (*Z*), 117.4 (d, $^2J_{\text{CF}} = 20.2$ Hz, *E*) and 118.6 (d, $^2J_{\text{CF}} = 14.3$ Hz, *Z*), 150.6 (d, $^1J_{\text{CF}} = 235.8$ Hz, *E*) and 151.7 (d, $^1J_{\text{CF}} = 250.8$ Hz, *Z*), 161.9 (d, $^2J_{\text{CF}} = 40.5$ Hz, *E*) and 162.0 (d, $^2J_{\text{CF}} = 27.5$ Hz, *Z*); MS (EI, 70 eV) m/z (relative intensity) 243 (M^+ 51), 196 (28), 158 (100), 145 (24), 132 (52), 128 (36), 114 (18). HRMS (EI, 70 eV) m/z [M^+] calcd for $\text{C}_{13}\text{H}_{22}\text{FNS}$ 243.1457, found 243.1442.

2-(1-fluoro-2-cyclohexyl-ethenyl)-thiazoline (9d). Isolated in 95 % (160 mg) by distillation (45° C / 6.10⁻² mbar), starting from **7** (200 mg, 0.784 mmol) and cyclohexanecarboxaldehyde (100 µL, 0.862 mmol) : ¹H NMR (250 MHz, CDCl₃) δ 1.00-1.68 (m, 10H,), 2.52 (m, 1H, *Z*) and 2.84 (m, 1H, *E*), 3.22 (t, ³*J*_{HH} = 8.5 Hz, 2H, *E*) and 3.26 (t, ³*J*_{HH} = 8.6 Hz, *Z*), 4.30 (t, ³*J*_{HH} = 8.2 Hz, *Z*) and 4.31 (t, ³*J*_{HH} = 8.5 Hz, 2H, *E*), 5.41 (dd, ³*J*_{HH} = 10.3 Hz, ³*J*_{HF} = 35.0 Hz, *Z*) and 5.43 (dd, ³*J*_{HH} = 10.6 Hz, ³*J*_{HF} = 22.7 Hz, *E*); ¹⁹F NMR (235 MHz, CDCl₃) δ -119.6 (d, ³*J*_{FH} = 35.0 Hz, *Z*) and -110.4 (d, ³*J*_{FH} = 22.7 Hz, *E*); ¹³C NMR (62.9 MHz, CDCl₃) δ 25.8 (*E*) and 26.1 (*Z*), 32.6 (d, ⁴*J*_{CF} = 1.3 Hz, *Z*) and 33.3 (d, ⁴*J*_{CF} = 2.2 Hz, *E*), 33.0 (s, *E*) and 34.0 (s, *Z*), 34.5 (d, ³*J*_{CF} = 1.7 Hz, *Z*) and 34.7 (d, ³*J*_{CF} = 6.2 Hz, *E*), 65.3 (s, *E*) and 65.5 (s, *Z*), 122.7 (d, ²*J*_{CF} = 18.2 Hz, *E*) and 123.7 (d, ²*J*_{CF} = 13.5 Hz, *Z*), 149.8 (d, ¹*J*_{CF} = 237.0 Hz, *E*) and 150.4 (d, ¹*J*_{CF} = 250.7 Hz, *CF Z*), 161.5 (d, ²*J*_{CF} = 39.4 Hz, *E*) and 162.3 (d, ²*J*_{CF} = 27.8 Hz, *Z*); MS (EI, 70 eV) *m/z* (relative intensity) 213 (M⁺ 54), 166 (17), 164 (17), 132 (11), 86 (72), 84 (100). HRMS (EI, 70 eV) *m/z* [M⁺] calcd for C₁₁H₁₆FNS 213.0987, found 213.0981.

Methyl N-[4-(2,2-dimethyl-3-tert-butoxycarbonyl-1,3-oxazolidinyl)-2-fluoropropenethioyl]phenylalaninate (10b). Isolated in 78 % (186 mg; Et₂O / pentane: 3 / 7), starting from **6e** (200 mg, 0.511 mmol) and Garner's aldehyde (120 µL, 0.562 mmol): (*E*)-(**10b**): ¹H NMR (250 MHz, CDCl₃) δ 1.42 (s, 12H,), 1.50 (s, 3H), 3.20 (m, 2H), 3.65 (s, 3H), 3.70 (d, ³*J*_{HH} = 9.1 Hz, 1H), 4.02 (m, 1H), 5.10 (m, 1H), 5.20 (m), 5.30 (dd, ³*J*_{HF} = 17.0 Hz, ³*J*_{HH} = 9.1 Hz), 7.20 (m, 5H), 11.38 (m, 1H); ¹⁹F NMR (235 MHz, CDCl₃) δ -128.9 (d, ³*J*_{FH} = 33.0 Hz, *Z*), -100.8 (d, ³*J*_{FH} = 17.0 Hz, *E*); ¹³C NMR (62.9 MHz, CDCl₃) δ 25.0, 28.0, 28.7, 36.6, 52.8, 54.0 (d, ³*J*_{CF} = 9.7 Hz), 59.7, 68.8 (d, ⁴*J*_{CF} = 1.5 Hz), 82.3, 94.3, 108.5 (d, ²*J*_{CF} = 23.7 Hz), 127.4, 128.9, 129.3, 136.6, 153.6, 154.8 (d, ¹*J*_{CF} = 248.3 Hz), 171.4, 188.0 (d, ²*J*_{CF} = 36.6 Hz); MS (EI, 70 eV) *m/z* (relative intensity) 466 (M⁺ 100), 410 (42), 366 (20), 309 (25), 266 (20), 187 (27), 162 (20). HRMS (EI, 70 eV) *m/z* [M⁺] calcd for C₂₃H₃₁FN₂O₅S 466.193, found 466.194.

Methyl N-[3-(1,2:3,4-di-O-isopropylidene-6-deoxy-galacto-pyranosyl)-2-fluoropropenethioyl]phenylalaninate (10c). Isolated in 20 % (51 mg; ethyl acetate / pentane: 3 / 7), starting from **6e** (200 mg, 0.511 mmol) and galactosaldehyde (145 µL, 0.562 mmol) : ¹H NMR (250 MHz, CDCl₃) δ 1.34, 1.50, 1.57, 3.23 (dd, ³*J*_{HH} = 5.3 Hz, ²*J*_{HH} = 13.9 Hz, 1H, *E*) and 3.26 (dd, ³*J*_{HH} = 4.9 Hz, ²*J*_{HH}

= 13.9 Hz, 1H, Z), 3.35 (dd, $^3J_{\text{HH}} = 5.9$ Hz, $^2J_{\text{HH}} = 13.9$ Hz, 1H, *E*) and 3.42 (dd, $^3J_{\text{HH}} = 6.0$ Hz, $^2J_{\text{HH}} = 13.9$ Hz, 1H, Z), 3.74 (s, 3H, *E*) and 3.76 (s, 3H, Z), 4.21 (dd, $^3J_{\text{HH}} = 1.9$ Hz, $^3J_{\text{HH}} = 5.8$ Hz, 2H), 4.34 (dd, $^3J_{\text{HH}} = 2.5$ Hz, $^3J_{\text{HH}} = 4.9$ Hz, 1H) and 4.39 (dd, $^3J_{\text{HH}} = 2.5$ Hz, $^3J_{\text{HH}} = 4.9$ Hz, 1H, *E*), 4.63 (dd, $^3J_{\text{HH}} = 2.4$ Hz, $^3J_{\text{HH}} = 6.0$ Hz, 1H, *E*) and 4.69 (m, 1H, Z), 5.41 (m, 2H), 5.53 (d, $^3J_{\text{HH}} = 5.0$ Hz, 1H, *E*) and 5.56 (d, $^3J_{\text{HH}} = 5.0$ Hz, 1H, Z), 5.81 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 5.92 (dd, $^3J_{\text{HH}} = 8.3$ Hz, $^3J_{\text{HF}} = 25.0$ Hz, *E*) and 6.71 (dd, $^3J_{\text{HH}} = 8.3$ Hz, $^3J_{\text{HF}} = 35.7$ Hz, 1H, Z), 7.28 (m, 10H), 8.30 (sbr, 1H, *E*) and 8.33 (s, 1H, Z); ^{19}F NMR (235 MHz, CDCl_3) δ -123.2 (dd, $^3J_{\text{FH}} = 36.0$ Hz, $^4J_{\text{FH}} = 6.0$ Hz, Z) and -109.5 (dd, $^3J_{\text{FH}} = 24.0$ Hz, $^4J_{\text{FH}} = 6.0$ Hz, *E*); ^{13}C NMR (62.9 MHz, CDCl_3) δ 23.3, 23.9, 24.9, 25.2 (Z) and 23.4, 24.0, 25.0, 25.3 (*E*), 35.1 (*E*) and 35.2 (Z), 51.5 (*E*) and 51.8 (Z), 56.6 (*E*) and 57.2 (Z), 62.2 (d, $^3J_{\text{CF}} = 3.6$ Hz, Z) and 63.7 (d, $^3J_{\text{CF}} = 8.8$ Hz, *E*), 69.2, 69.6 (Z) and 69.0, 70.2 (*E*), 71.4 (d, $^4J_{\text{CF}} = 2.0$ Hz, *E*) and 71.5 (d, $^4J_{\text{CF}} = 1.5$ Hz, Z), 95.3 (Z) and 95.4 (*E*), 107.9, 108.6, 114.3 (d, $^2J_{\text{CF}} = 12.6$ Hz, Z) and 117.9 (d, $^2J_{\text{CF}} = 28.3$ Hz, *E*), 126.3, 127.7, 128.1 (Z) and 126.4, 127.7, 128.1 (*E*), 134.0 (*E*) and 134.1 (Z), 149.7 (d, $^1J_{\text{CF}} = 259.1$ Hz, Z) and 153.3 (d, $^1J_{\text{CF}} = 267.2$ Hz, *E*), 169.4 (*E*) and 169.7 (Z), 183.2 (d, $^2J_{\text{CF}} = 21.0$ Hz, *E*) and 183.7 (d, $^2J_{\text{CF}} = 20.0$ Hz, Z); MS (EI, 70 eV) m/z (relative intensity) 495 (M^+ , 80), 477 (95), 462 (45), 437 (25), 243 (100), 199 (40), 185 (35), 141 (80), 113 (30), 97 (38), 85 (37), 71 (42). HRMS (EI, 70 eV) m/z [M^+] calcd for $\text{C}_{24}\text{H}_{30}\text{FNO}_7\text{S}$ 495.1727, found 495.1715.

Ethyl 3-(4,5-dihydro-1,3-thiazol-2-yl)-3-fluoroacrylate (11a). Isolated in 79 % (126 mg; Et_2O / pentane: 25 / 75), starting from **7** (200 mg, 0.784 mmol) and ethyl glyoxalate (170 μL , 0.862 mmol, 50% in toluene) : (**E**)-(**11a**): ^1H NMR (250 MHz, CDCl_3) δ 1.27 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H), 3.42 (t, $^3J_{\text{HH}} = 8.6$ Hz, 2H), 4.18 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 4.40 (dt, $^5J_{\text{HF}} = 3.1$ Hz, $^3J_{\text{HH}} = 8.6$ Hz, 2H), 5.94 (d, $^3J_{\text{HF}} = 17.2$ Hz, 1H); ^{19}F NMR (235 MHz, CDCl_3) δ -93.8 (dt, $^5J_{\text{HF}} = 3.1$ Hz, $^3J_{\text{FH}} = 17.2$ Hz); ^{13}C NMR (62.9 MHz, CDCl_3) δ 14.3, 34.6, 61.3, 65.3, 106.4 (d, $^2J_{\text{CF}} = 26.5$ Hz), 160.0 (d, $^2J_{\text{CF}} = 33.5$ Hz), 160.0 (d, $^1J_{\text{CF}} = 265.4$ Hz), 164.0 (d, $^3J_{\text{CF}} = 21.0$ Hz). MS (EI, 70 eV) m/z (relative intensity) 203 (M^+ , 100), 158 (81), 128 (20), 98 (12). (**Z**)-**11a**: ^1H NMR (250 MHz, CDCl_3) δ 1.25 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H), 3.35 (t, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 4.18 (q, $^3J_{\text{HH}} = 7.1$ Hz, 2H), 4.31-4.42 (t, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 5.98 (d, $^3J_{\text{HF}} = 31.2$ Hz, 1H); ^{19}F NMR (235 MHz, CDCl_3) δ -96.35 (d, $^3J_{\text{FH}} = 31.2$ Hz); ^{13}C NMR (62.9 MHz, CDCl_3) δ 14.4, 34.3, 61.3, 65.9, 105.2 (d, $^2J_{\text{CF}} =$

4.5 Hz), 162.0 (d, $^2J_{\text{CF}} = 30.1$ Hz), 162.9 (d, $^1J_{\text{CF}} = 265.4$ Hz), 164.0 (d, $^3J_{\text{CF}} = 2.7$ Hz). HRMS (EI, 70 eV) m/z [M^+] calcd for $\text{C}_8\text{H}_{10}\text{FNO}_2\text{S}$ 203.0416, found 203.0465.

***Tert*-butyl 4-[2-(4,5-dihydro-1,3-thiazol-2-yl)-2-fluorovinyl]-2,2-dimethyl-1,3-oxazolidine-3-carboxylate (11b).** Isolated in 83 % (215 mg; Et_2O / pentane: 25 / 75), starting from **7** (200 mg, 0.784 mmol) and Garner's aldehyde (190 μL , 0.862 mmol) : (**E**)-(**11b**): ^1H NMR (250 MHz, CDCl_3) δ 1.32-1.57 (m, 15H), 3.20 (m, 2H), 3.69 (m, 1H), 3.99-4.11 (m, 1H), 4.19-4.41 (m, 2H), 5.21 (m, 1H), 5.60 (dd, $^3J_{\text{HH}} = 9.3$ Hz, 1H); ^{19}F NMR (235 MHz, CDCl_3) δ -109.9 (d, $^3J_{\text{FH}} = 19.4$ Hz, conformer 1), -109.5 (d, $^3J_{\text{FH}} = 19.4$ Hz, conformer 2); ^{13}C NMR (100 MHz, CDCl_3) δ 24.1, 26.9, 28.6, 32.6, 53.6, 65.8, 69.2, 80.1, 94.6, 117.7 (d, $^2J_{\text{CF}} = 20.3$ Hz), 151.2 (d, $^1J_{\text{CF}} = 240.8$ Hz), 152.1, 162.2 (d, $^2J_{\text{CF}} = 44.4$ Hz). (**Z**)-**11b**: ^1H NMR (400 MHz, CDCl_3) δ 1.25-1.60 (m, 15H), 3.30-3.40 (m, 2H), 3.76 (m, 1H), 4.35 (m, 2H), 4.80 (m, 1H), 5.60 (dd, $^3J_{\text{HH}} = 9.3$ Hz, $^3J_{\text{HF}} = 33.0$ Hz, 1H); ^{19}F NMR (235 MHz, CDCl_3) δ -116.5 (d, $^3J_{\text{HF}} = 33.0$ Hz, conformer 1), -117.8 (d, $^3J_{\text{HF}} = 33.0$ Hz, conformer 2); ^{13}C NMR (100 MHz, CDCl_3) δ 24.2, 26.9, 28.8, 34.1, 52.4, 65.6, 68.2, 80.6, 94.6, 117.0 (d, $^2J_{\text{CF}} = 11.1$ Hz), 151.7 (d, $^1J_{\text{CF}} = 256.2$ Hz), 152.0, 161.6 (d, $^2J_{\text{CF}} = 27.7$ Hz); MS (EI, 70 eV) m/z (relative intensity) 330 (M^+ 7), 274 (95), 215 (100), 199 (22), 173 (20). HRMS (EI, 70 eV) m/z [M^+] calcd for $\text{C}_{15}\text{H}_{23}\text{FN}_2\text{O}_3\text{S}$ 330.1413, found 330.1414.

1,2 ;3,4-di-*o*-isopropylidene-6,7-dideoxy-7-(4,5-dihydro-1,3-thiazol-2-yl)-7-fluorohept-6-enopyranose (11c). Isolated in 79 % (223 mg; Et_2O / pentane 3 / 7), starting from **7** (200 mg, 0.784 mmol) and galactosaldehyde (225 mg, 0.862 mmol) : (**E**)-(**11c**): ^1H NMR (250 MHz, CDCl_3) δ 1.25, 1.40, 1.46 (s, 12H), 3.21 (t, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 4.17-4.57 (m, 5H), 5.32 (d, $^3J_{\text{HH}} = 9.0$ Hz, 1H), 5.44 (d, $^3J_{\text{HH}} = 5.0$ Hz, 1H), 5.67 (dd, $^3J_{\text{HH}} = 9.0$ Hz, $^3J_{\text{HF}} = 19.9$ Hz, 1H); ^{19}F NMR (235 MHz, CDCl_3) δ -105.7 (d, $^3J_{\text{FH}} = 20.0$ Hz); ^{13}C NMR (62.9 MHz, CDCl_3) δ 24.7, 25.4, 26.1, 26.3, 32.7, 63.8 (d, $^3J_{\text{CF}} = 10.8$ Hz), 65.8, 70.4, 71.3, 73.4 (d, $^4J_{\text{CF}} = 2.3$ Hz), 96.8, 109.0, 109.5, 113.1 (d, $^2J_{\text{CF}} = 24.0$ Hz), 151.1 (d, $^1J_{\text{CF}} = 242.0$ Hz), 162.4 (d, $^2J_{\text{CF}} = 44.0$ Hz); MS (EI, 70 eV) m/z (relative intensity) 359 (M^+ 58), 344 (75), 301 (32), 198 (23), 172 (80), 161 (100), 143 (31), 113 (83), 100 (25). HRMS (EI, 70 eV) m/z [M^+] calcd for $\text{C}_{16}\text{H}_{22}\text{FNO}_5\text{S}$ 359.1203, found 359.1208.

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Current Data Parameters
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 DE 10.00 usec
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 PL1 -6.00 dB

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 F2P -0.500 ppm
 F2 -125.06 Hz
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Crude 6d

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Current Data Parameters
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 D1 2.00000000 sec
 D11 7.50 usec
 SFO1 250.1318626 MHz
 NUC1 1H
 PL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 250.1300036 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 9.956 ppm
 F1 2490.35 Hz
 F2P -0.809 ppm
 F2 -202.31 Hz
 PPMCM 0.48932 ppm/cm
 HZCM 122.39376 Hz/cm

Current Data Parameters
 NAME ep609f1
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020117
 Time 5:55
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 4990.020 Hz
 FIDRES 0.152283 Hz
 AQ 3.2834036 sec
 RG 128
 LW 100.200 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 P1 7.50 usec
 SF01 250.1318626 MHz
 NUC1 1H
 FL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 250.1300257 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 FIP 10.000 ppm
 F1 2501.30 Hz
 F2P -0.500 ppm
 F2 -125.06 Hz
 PPMCM 0.47727 ppm/cm
 HZCM 119.38023 Hz/cm

1.7032
1.6738
1.4426
1.4130
1.3838
1.3542
1.1784
0.9765
0.9470
0.9171
0.7353
0.7209
0.7057
0.6759
0.0000

3.4831
3.4553
3.4319
3.4264
3.4027

7.5756
7.5440
7.5374
7.5053
7.3482
7.3103
7.2963
7.2867
7.2807
7.2664
7.2598
7.2438
7.2306
7.1924
7.1865
6.4234
6.3483

ppm

Current Data Parameters
 NAME ep7001
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020611
 Time 14.58
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 4990.020 Hz
 FIDRES 0.152283 Hz
 AQ 3.2834036 sec
 RG 64
 DM 100.200 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 P1 7.50 usec
 SFO1 250.1318626 MHz
 NUC1 1H
 PL1 -6.00 dB

F2 - Processing Parameters
 SI 16384
 SF 250.1300193 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 9.956 ppm
 F1 2490.35 Hz
 F2P -0.809 ppm
 F2 -202.31 Hz
 FPCW 0.48932 ppm/cr
 HZCN 122.39377 Hz/cm

Current Data Parameters
 NAME ep703
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20021005
 Time 14.54
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 4096
 DS 0
 SWH 16339.869 Hz
 FIDRES 0.249327 Hz
 AQ 2.0054517 sec
 RG 6502
 DW 30.600 usec
 DE 10.00 usec
 TE 300.0 K
 D11 0.03000000 sec
 PL12 18.00 dB
 CDEPRG2 waltz16
 PCPD2 100.00 usec
 SFO2 250.1312506 MHz
 NUC2 1H
 PL2 -6.00 dB
 D1 2.00000000 sec
 P1 5.00 usec
 SFO1 62.9027614 MHz
 NUC1 13C
 PL1 -6.00 dB

F2 - Processing parameters
 SI 32768
 SF 62.8953008 MHz
 WDW EM
 SSB 0
 LB 0.80 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 22.00 cm
 F1P 230.000 ppm
 F1 14465.92 Hz
 F2P -5.000 ppm
 F2 -314.48 Hz
 PPMCM 10.68182 ppm/c
 HZCM 671.83618 Hz/cm

Current Data Parameters
 NAME ep19f1
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020203
 Time 19.41
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 4990.020 Hz
 FIDRES 0.152283 Hz
 AQ 3.2834036 sec
 RG 256
 DW 100.200 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.0000000 sec
 P1 7.50 usec
 SFO1 250.1318626 MHz
 NUC1 1H
 PL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 250.1300093 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 FIP 10.000 ppm
 F1 2501.30 Hz
 F2P -0.500 ppm
 F2 -125.06 Hz
 PPMCM 0.47727 ppm/cm
 HZCM 119.38022 Hz/cm

Current Data Parameters
 NAME ep67d1
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020513
 Time 17.01
 INSTRUM spect
 PROBD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 4990.020 Hz
 FIDRES 0.152283 Hz
 AQ 3.2834036 sec
 RG 64
 DW 100.200 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 P1 7.50 usec
 SFO1 250.1318626 MHz
 NUC1 1H
 PL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 250.1300132 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 FIP 9.956 ppm
 F1 2490.35 Hz
 F2P -0.809 ppm
 F2 -202.31 Hz
 PPMCM 0.48932 ppm/cm
 HZCM 122.39377 Hz/cm

0.0000
 1.0115
 0.9755
 0.9487

2.7995
 2.8752
 3.1597
 3.1835
 3.1964
 3.2175
 3.2351
 3.2517
 3.2642
 3.2974
 4.2619
 4.2829
 4.2946
 4.3169
 4.3510
 5.3166
 5.3279
 5.3536
 5.3702
 5.4167
 5.4580

ppm

Current Data Parameters
 NAME ep683d1
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020517
 Time 22.00
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 4990.020 Hz
 FIDRES 0.152283 Hz
 AQ 3.2834036 sec
 RG 64
 DW 100.200 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 P1 7.50 usec
 SFO1 250.1318626 MHz
 NUC1 1H
 PL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 250.1300181 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 9.956 ppm
 F1 2490.35 Hz
 F2P -0.809 ppm
 F2 -202.31 Hz
 PPMCM 0.48932 ppm/cm
 HZCM 122.39377 Hz/cm

Current Data Parameters
 NAME ep684dia
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020523
 Time 8.16
 INSTRUM spect
 PROBHD 5 mm BBO BB-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 13410
 DS 2
 SWH 25125.629 Hz
 FIDRES 0.383387 Hz
 AQ 1.3042164 sec
 RG 2298.8
 DW 19.900 usec
 DE 10.00 usec
 TE 300.0 K
 D11 0.03000000 sec
 PL12 16.00 dB
 CPDPRG2 waltz16
 PCPD2 100.00 usec
 SF02 400.1316005 MHz
 NUC2 1H
 PL2 16.00 dB
 D1 2.00000000 sec
 F1 10.00 usec
 SF01 100.6254358 MHz
 NUC1 13C
 PL1 -3.00 dB

F2 - Processing parameters
 SI 32768
 SF 100.6127290 MHz
 EM
 WDW 0
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 22.00 cm
 FIP 173.913 ppm
 F1 17497.87 Hz
 F2P 15.769 ppm
 F2 1586.60 Hz
 PPMCM 7.18835 ppm/cm
 HZCM 723.23956 Hz/cm

Current Data Parameters
 NAME ep66811
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020509
 Time 2.38
 INSTRUM spect
 PROHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 4990.020 Hz
 FIDRES 0.15283 Hz
 AQ 3.2834036 sec
 RG 128
 DW 100.200 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 F1 7.50 usec
 SFO1 250.1318626 MHz
 NUC1 1H
 PL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 250.1300061 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 11.948 ppm
 F1 2988.68 Hz
 F2P -0.729 ppm
 F2 -182.45 Hz
 PPMCM 0.57627 ppm/cm
 HZCM 144.14221 Hz/cm

Current Data Parameters
 NAME ep69311
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020605
 Time 15.54
 INSTRUM spect
 PROBD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 4990.020 Hz
 FIDRES 0.15283 Hz
 AQ 3.2834036 sec
 RG 64
 DW 100.200 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 F1 7.50 usec
 SFO1 250.1318626 MHz
 NUC1 1H
 PL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 250.1300239 MHz
 WDW EN
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 9.956 ppm
 F1 2490.35 Hz
 F2P -0.809 ppm
 F2 -202.31 Hz
 FPCW 0.48932 ppm/cm
 HZCM 122.39577 Hz/cm

Current Data Parameters
 NAME ep643f1
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020308
 Time 9.21
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SMH 4990.020 Hz
 FIDRES 0.152283 Hz
 AQ 3.2834036 sec
 RG 128
 LW 100.200 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 P1 7.50 usec
 SFO1 250.1318626 MHz
 NUC1 1H
 FL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 250.1300234 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 10.000 ppm
 F1 2501.30 Hz
 F2P -0.500 ppm
 F2 -125.06 Hz
 PPMCM 0.47727 ppm/cm
 HZCM 119.38023 Hz/cm

Current Data Parameters
 NAME t1351f13H
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20040114
 Time 8.56
 INSTRUM spect
 PROBHD 5 mm TBI 1H-B
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.250967 Hz
 AQ 1.9923444 sec
 RG 574.7
 DW 60.800 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 F1 10.00 usec
 SF01 400.1324710 MHz
 NUC1 1H
 PL1 0.00 dB

F2 - Processing parameters
 SI 16384
 SF 400.1300090 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 FLIP 10.025 ppm
 F1 4011.38 Hz
 F2P -0.599 ppm
 F2 -239.51 Hz
 PPMCM 0.53119 ppm/cm
 HZCM 212.54449 Hz/cm

0.0134

1.2534
1.2715
1.2895
1.3032
1.4189
1.6842

3.4121
3.4336
3.4552
4.1710
4.1887
4.2065
4.2247
4.3764
4.3841
4.3979
4.4056
4.4194
4.4270
5.9147
5.9577

7.2610

Integral

3.7464

2.1961

2.2096

2.2174

1.0472

ppm

EtO2CCH=CFThiozoly1 BRUT TL351

Current Data Parameters
NAME ep705f1
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020612
Time 15:06
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 4990.020 Hz
FIDRES 0.152283 Hz
AQ 3.2834036 sec
RG 32
DM 100.200 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
PL 7.50 usec
SFO1 250.1318626 MHz
NUC1 1H
PL1 -6.00 dB

F2 - Processing parameters
SI 16384
SF 250.1300072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
FLP 9.956 ppm
F1 2490.35 Hz
F2P -0.909 ppm
F2 -202.31 Hz
PPMCM 0.48932 ppm/cm
HZCM 122.39376 Hz/cm

Current Data Parameters
NAME tlepl1bpur
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040129
Time 8.50
INSTRUM spect
PROBHD 5 mm TBI 1H-B
PULPROG zg30
TD 32768
SOLVENT CD3CN
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 90.5
DM 60.800 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 10.00 usec
SF01 400.1324710 MHz
NUC1 1H
PL1 0.00 dB

F2 - Processing parameters
SI 16384
SF 400.1300090 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
FLP 7.604 ppm
F1 3042.65 Hz
F2P -0.425 ppm
F2 -169.89 Hz
PPMCM 0.40144 ppm/cm
HZCM 160.62733 Hz/cm

Current Data Parameters
 NAME ep705
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020612
 Time 6.19
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 262144
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 70422.539 Hz
 FIDRES 0.268641 Hz
 AQ 1.8612725 sec
 RG 1149.4
 DW 7.100 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 P1 6.50 usec
 SF01 235.3274550 MHz
 NUCL1 19F
 PL1 -6.00 dB

F2 - Processing parameters
 SI 131072
 SF 235.3574550 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P -98.928 ppm
 F1 -23283.55 Hz
 F2P -125.847 ppm
 F2 -239619.03 Hz
 PPMCM 1.22357 ppm/c
 HZCM 287.97632 Hz/cm

Current Data Parameters
 NAME ep637f1
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020301
 Time 12.31
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWE 4990.020 Hz
 FIDRES 0.152283 Hz
 AQ 3.2834036 sec
 RG 32
 DW 100.200 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 P1 7.50 usec
 SF01 250.1318626 MHz
 NUC1 1H
 FL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 250.1300099 MHz
 EX
 WDW 0
 SSB 0.30 Hz
 LB 0
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 10.000 ppm
 F1 2501.30 Hz
 F2P -0.500 ppm
 F2 -125.06 Hz
 PPMCM 0.47727 ppm/cm
 HZCM 119.38022 Hz/cm