Angewandte
Eine Zeitschrift der Gesellschaft Deutscher Chemiker
Chemie

Supporting Information

Direct Access to β-Fluorinated Aldehydes by Nitrite-Modified Wacker Oxidation

*Crystal K. Chu, Daniel T. Ziegler, Brian Carr, Zachary K. Wickens, and Robert H. Grubbs**

anie_201603424_sm_miscellaneous_information.pdf

Supporting Information

Table of Contents

I. General Information

Anhydrous ether and dichloromethane used for substrate syntheses were purified and dried using a solvent-purification system containing activated alumina. All other solvents were purchased anhydrous with Sure/Seal™ septa from Sigma Aldrich and used without further purification. All reagents and standards were purchased from Sigma Aldrich and used without further purification. All metal salts were purchased from Sigma Aldrich or Strem and used without further purification. NMR analysis was performed on the following instruments at ambient temperature: Varian 300 MHz, Varian 400 MHz, Varian 500 MHz, Bruker 400 MHz spectrometers. High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS- 600H High Resolution Mass Spectrometer.

II. Optimization of Reaction Conditions (Figure 1)

For all reactions in Figure 1: Following work up procedure, nitrobenzene (0.1 mmol, 10.3 μL) was added as a standard, and ^{1}H NMR analysis of the crude product was performed to determine yield and selectivity.

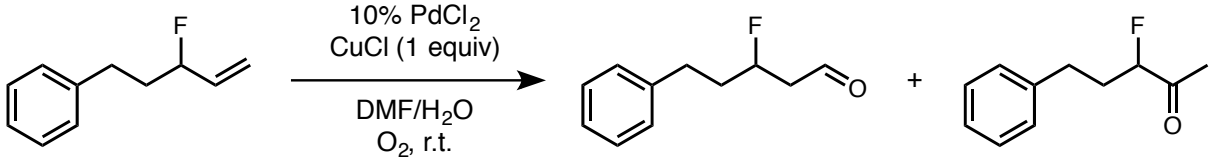


Figure 1a: Tsuji-Wacker conditions. The model substrate (0.1 mmol, 16.4 mg) was reacted using the "Procedure for Tsuji-Wacker oxidations" reported by Grubbs.[1] Oxidation yield: 12%. Selectivity: 0.3:1 (aldehyde/ketone).

[1] Wickens, Z. K.; Skakuj, K.; Morandi, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2014,** *136*, 890-893.

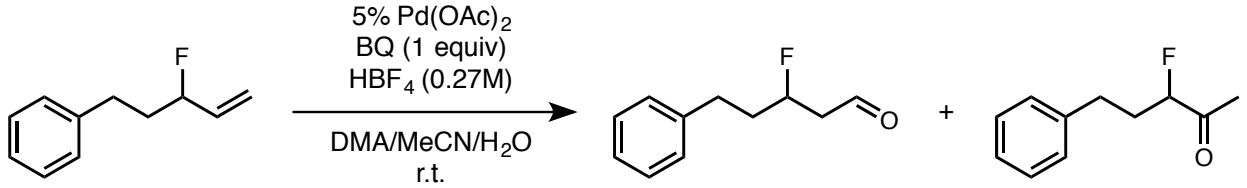


Figure 1b: Grubbs (dicationic) conditions.[2] The model substrate (0.1 mmol, 16.4 mg) was reacted using "General Procedure 2" reported by Grubbs. Following overnight reaction in a 1-dram vial, the work up procedure was followed. Oxidation yield: 48%. Selectivity: 3:1 (aldehyde/ketone).

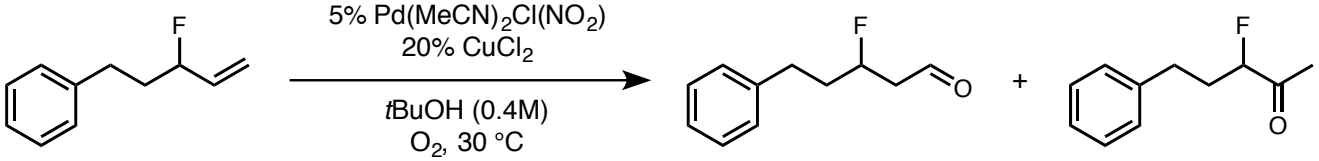


Figure 1c: Feringa conditions.[3] The model substrate (0.1 mmol, 16.4 mg) was reacted using the "General procedure for oxidation reactions with $Pd(MeCN)_2Cl(NO_2)/CuCl_2$" reported by Feringa. Following overnight reaction in a 1-dram vial, the work up procedure was followed. Oxidation yield: 40%. Selectivity: 18:1 (aldehyde/ketone).

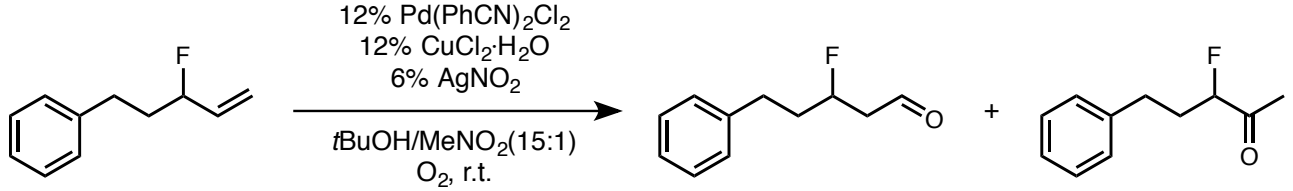


Figure 1d: Grubbs (nitrite) conditions.[4] The model substrate (0.1 mmol, 16.4 mg) was reacted using the "Procedure (C) for small-scale oxidation of alkenes (NMR analysis)" reported by Grubbs. A 1-dram vial was used for the reaction, and, following sparging, the oxygen balloon was removed for the course of the reaction. Oxidation yield: 63%. Selectivity: 26:1 (aldehyde/ketone).

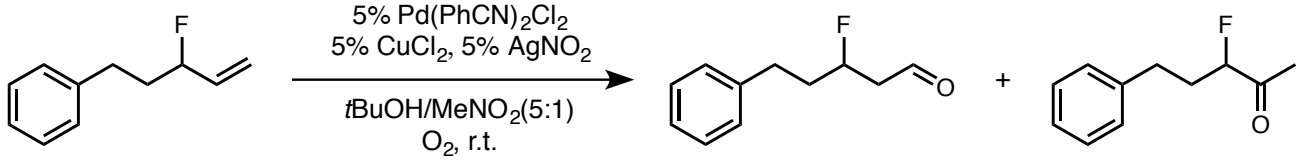


Figure 1e: Optimized conditions. A 1-dram vial equipped with a septum cap and magnetic stir bar was charged with $CuCl_2$ (0.7 mg, 0.005 mmol, 0.05 equiv), $AgNO_2$ (0.8 mg, 0.005 mmol, 0.05 equiv), and $Pd(PhCN)_2Cl_2$ (1.9 mg, 0.005 mmol, 0.05 equiv). The atmosphere was then

[2] Morandi, B.; Wickens, Z. K.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2013,** *52*, 2944-2948.
[3] Weiner, B.; Baeza, A.; Jerphagnon, T.; Feringa, B. L. *J. Am. Chem. Soc.* **2009,** *131*, 9473-9474.
[4] Wickens, Z. K.; Morandi, B.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2013,** *52*, 11257-11260.

purged using an oxygen-filled balloon for ~30 seconds. *Tert*-butanol (0.88 mL) was then added via syringe, followed by nitromethane (0.18 mL). This mixture was sparged using an oxygen-filled balloon for ~60 seconds. (3-fluoropent-4-en-1-yl)benzene (0.1 mmol, 16.4 mg) was injected via glass syringe, the balloon was removed, and the septum cap was greased. The reaction mixture was stirred for 4 hours at room temperature. Upon completion, the solvent was removed via rotary evaporation. The reaction crude was resuspended in dichloromethane and filtered through a glass pipet containing celite, which was washed with dichloromethane. Dichloromethane was removed via rotary evaporation. Oxidation yield: 79%. Selectivity: 36:1 (aldehyde/ketone).

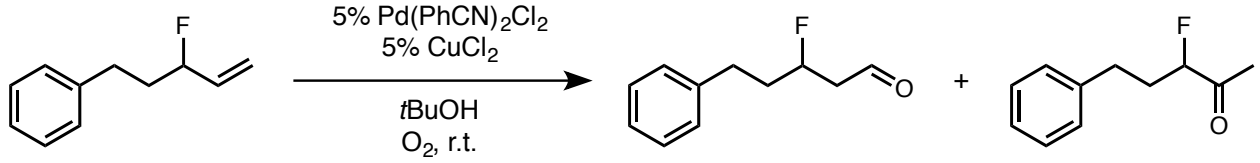


Figure 1f: Wacker conditions in *t*BuOH. A 1-dram vial equipped with a septum cap and magnetic stir bar was charged with $CuCl_2$ (0.7 mg, 0.005 mmol, 0.05 equiv) and $Pd(PhCN)_2Cl_2$ (1.9 mg, 0.005 mmol, 0.05 equiv). The atmosphere was then purged using an oxygen-filled balloon for ~30 seconds. *Tert*-butanol (1.06 mL) was then added via syringe. This mixture was sparged using an oxygen-filled balloon for ~60 seconds. (3-fluoropent-4-en-1-yl)benzene (0.1 mmol, 16.4 mg) was injected via glass syringe, the balloon was removed, and the septum cap was greased. The reaction mixture was stirred overnight at room temperature. Upon completion, the solvent was removed via rotary evaporation. The reaction crude was resuspended in dichloromethane and filtered through a glass pipet containing celite, which was washed with dichloromethane. Dichloromethane was removed via rotary evaporation. Oxidation yield: 8%. Selectivity: 8:1 (aldehyde/ketone).

III. Preparation of Allylic Fluorides

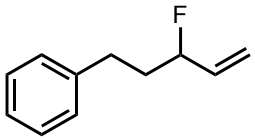
General Procedure A: Synthesis of Allylic Fluorides.[5] $[IrClCOD]_2$ (0.025 equiv) was weighed into a 50 mL polypropylene centrifuge tube equipped with a large stir bar. A first portion of anhydrous ether (30% of the total solvent volume, 0.83 M relative to trichloroacetimidate) was added to the tube, followed by TEA•3HF (3 equiv). The trichloroacetimidate (1.0 equiv) was then dissolved in a second portion of anhydrous ether and added to the reaction vessel, bringing the final concentration of trichloroacetimidate to 0.25 M. The polypropylene tube was closed tightly, and the reaction was stirred vigorously at room temperature for 2 hours. Upon completion, the crude mixture was allowed to separate into two layers. A glass pipette was used to transfer the organic layer to a separatory funnel containing a saturated solution of $NaHCO_3$. Ether was added to the polypropylene tube followed by 2 minutes of vigorous stirring. The organic layer was again transferred to the separatory funnel, and this step was repeated once more. The combined organic layers were separated, and the remaining bicarb solution extracted once with ether. After drying over Na_2SO_4, the solvent was

[5] Topczewski, J. J.; Tewson, T. J.; Nguyen, H. M. *J. Am. Chem. Soc.* **2011,** *133*, 19318-19321. All trichloroacetimidates were synthesized by a general procedure described in this report.

removed by rotary evaporation. The residue was purified by flash chromatography (ether/pentane).

General Procedure B: Fluorinaton of Alcohols. A three-neck round bottom flask was equipped with an addition funnel and two septa. The system was purged with argon, and DAST (0.85 mL, 6.40 mmol, 1 equiv) and anhydrous DCM (6 mL) were added to the flask via syringe. The round-bottom flask was cooled to -78 °C and stirred. The alcohol (1.0 g, 1 equiv) was dissolved in 6 mL anhydrous DCM, transferred to the addition funnel, and added dropwise over 30 minutes. The reaction was allowed to slowly warm to room temperature and stirred overnight. Following reaction completion, the crude mixture was cooled to 0 °C for quenching. One neck previously closed with a septum was opened and saturated $NaHCO_3$ solution was slowly added via addition funnel to bring the mixture to basic pH. The mixture was then stirred for 1 hour at room temperature. The layers were separated, and the organic layer washed with brine. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography.

The yields have not been optimized.



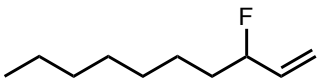
(3-fluoropent-4-en-1-yl)benzene. The fluoride was prepared according to General Procedure A from the corresponding trichloroacetimidate, 5-phenylpent-1-en-3-yl 2,2,2-trichloroacetimidate. The product was purified by flash chromatography (1% ether/pentane). Colorless oil (1.84 g, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.29 (m, 2H), 7.25–7.19 (m, 3H), 6.00–5.86 (m, 1H), 5.40–5.31 (m, 1H), 5.26 (dt, 1H, *J* = 10.7, 1.3 Hz), 4.99–4.82 (m, 1H), 2.86–2.69 (m, 2H), 2.14–1.86 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 136.7 (d, *J* = 20.2 Hz), 128.8, 126.4, 117.4 (d, *J* = 12.6 Hz), 93.0 (d, *J* = 167.6 Hz), 37.2 (d, *J* = 21.4 Hz), 31.3 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -178.86 (ddddd, *J* = 48.5, 28.0, 17.3, 14.2, 3.5 Hz).

MS (EI) *m*/*z* (M^+) calcd for $C_{11}H_{13}F$: 164.1001, found: 164.0982.



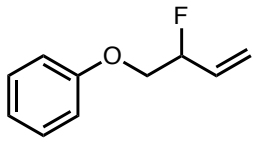
3-fluorodec-1-ene. The fluoride was prepared according to General Procedure A from the corresponding trichloroacetimidate, dec-1-en-3-yl 2,2,2-trichloroacetimidate. The product was purified by flash chromatography (pentane). Colorless oil (250 mg, 32% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (dddd, 1H, *J* = 16.9, 14.0, 10.6, 6.1 Hz), 5.30 (ddt, 1H, *J* = 17.3, 3.6, 1.4 Hz), 5.21 (dt, 1H, *J* = 10.6, 1.3 Hz), 4.94–4.78 (m, 1H), 1.79–1.52 (m, 2H), 1.49–1.21 (m, 10H), 0.92–0.81 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2 (d, *J* = 20.2 Hz), 117.1 (d, *J* = 11.3 Hz), 94.1 (d, *J* = 167.6 Hz), 35.6 (d, *J* = 21.4 Hz), 32.1, 29.7, 29.5, 25.0 (d, *J* = 5.0 Hz), 23.0, 14.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -176.74 (ddddd, *J* = 48.1, 26.2, 17.7, 13.9, 3.6 Hz).

MS (EI) *m*/*z* (M^+–HF) calcd for $C_{10}H_{18}$: 138.1408, found: 138.1430.



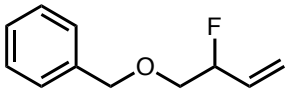
((2-fluorobut-3-en-1-yl)oxy)benzene. The fluoride was prepared according to General Procedure A from the corresponding trichloroacetimidate, 1-phenoxybut-3-en-2-yl 2,2,2-trichloroacetimidate. The product was purified by flash chromatography (5% ether/pentane). Colorless oil (1.20 g, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.02–6.97 (m, 1H), 6.96–6.91 (m, 2H), 6.08–5.96 (m, 1H), 5.53 (ddt, 1H, *J* = 17.3, 3.0, 1.3 Hz), 5.40 (dt, 1H, *J* = 10.8, 1.3 Hz), 5.35–5.18 (m, 1H), 4.20–4.04 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 132.8 (d, *J* = 20.2 Hz), 129.9, 121.6, 119.5 (d, *J* = 11.3 Hz), 115.0, 91.5 (d, *J* = 173.9 Hz), 70.0 (d, *J* = 23.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -185.41 (ddddd, *J* = 48.7, 24.7, 19.8, 14.8, 3.1 Hz).

MS (EI) *m*/*z* (M^+) calcd for $C_{10}H_{11}FO$: 166.0794, found: 166.0788.



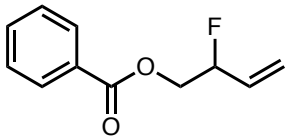
(((2-fluorobut-3-en-1-yl)oxy)methyl)benzene. The fluoride was prepared according to General Procedure A from the corresponding trichloroacetimidate, 1-(benzyloxy)but-3-en-2-yl 2,2,2-trichloroacetimidate. The product was purified by flash chromatography (5% ether/pentane). Colorless oil (144 mg, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.25 (m, 5H), 5.90 (dddd, 1H, *J* = 17.3, 15.1, 10.8, 5.7 Hz), 5.43 (ddt, 1H, *J* = 17.3, 2.9, 1.4 Hz), 5.31 (dt, 1H, *J* = 10.8, 1.3 Hz), 5.18–5.01 (m, 1H), 4.68–4.54 (m, 2H), 3.68–3.54 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.1, 133.3 (d, *J* = 20.2 Hz), 128.8, 128.10, 128.06, 118.8 (d, *J* = 11.3 Hz), 92.6 (d, *J* = 171.4 Hz), 73.8, 72.3 (d, *J* = 22.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -184.63 – -185.09 (m).

MS (EI) *m*/*z* (M^+) calcd for $C_{11}H_{13}FO$: 180.0950, found: 180.0952.



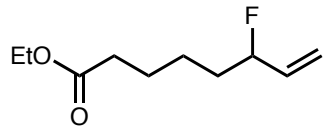
2-fluorobut-3-en-1-yl benzoate. The fluoride was prepared according to General Procedure A from the corresponding trichloroacetimidate, 2-(2,2,2-trichloro-1-iminoethoxy)but-3-en-1-yl benzoate. The product was purified by flash chromatography (10% ether/pentane). Colorless oil (344 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11–8.04 (m, 2H), 7.62–7.54 (m, 1H), 7.49–7.42 (m, 2H), 5.96 (dddd, 1H, *J* = 17.4, 15.1, 10.8, 5.7 Hz), 5.52 (ddt, 1H, *J* = 17.3, 2.8, 1.3 Hz), 5.40 (dt, 1H, *J* = 10.8, 1.2 Hz), 5.32–5.17 (m, 1H), 4.52 (ddd, 1H, *J* = 26.6, 12.4, 3.0 Hz), 4.42 (ddd, 1H, *J* = 20.4, 12.4, 7.0 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 133.6, 132.3 (d, *J* = 20.2 Hz), 130.1, 130.0, 128.8, 119.8 (d, *J* = 11.3 Hz), 91.0 (d, *J* = 173.9 Hz), 66.1 (d, *J* = 22.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -186.05 (ddddd, *J* = 48.7, 26.5, 20.4, 15.0, 3.0 Hz).

MS (EI) *m*/*z* (M^+) calcd for $C_{11}H_{11}FO_2$: 194.0743, found: 194.0721.



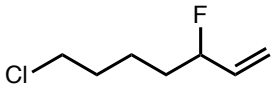
ethyl 6-fluorooct-7-enoate. The fluoride was prepared according to General Procedure A from the corresponding trichloroacetimidate, ethyl 6-(2,2,2-trichloro-1-iminoethoxy)oct-7-enoate. The product was purified by flash chromatography (10% ether/pentane). Colorless oil (124 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dddd, 1H, *J* = 17.3, 14.0, 10.6, 6.1 Hz), 5.30 (ddt, 1H, *J* = 17.3, 3.6, 1.4 Hz), 5.21 (dt, 1H, *J* = 10.6, 1.3 Hz), 4.98–4.73 (m, 1H), 4.12 (q, 2H, *J* = 7.1 Hz), 2.31 (t, 2H, *J* = 7.5 Hz), 1.82–1.33 (m, 6H), 1.25 (t, 3H, *J* = 7.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 136.8 (d, *J* = 20.2 Hz), 117.3 (d, *J* = 12.1 Hz), 93.7 (d, *J* = 167.7 Hz), 60.6, 35.2 (d, *J* = 22.2 Hz), 34.5, 25.0, 24.6 (d, *J* = 5.0 Hz), 14.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -177.17 – -177.57 (m).

MS (EI) *m*/*z* (M^+) calcd for $C_{10}H_{17}FO_2$: 188.1201, found: 188.1185.



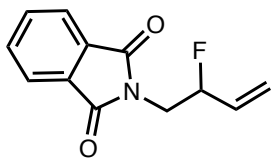
7-chloro-3-fluorohept-1-ene. The fluoride was prepared according to General Procedure A from the corresponding trichloroacetimidate, 7-chlorohept-1-en-3-yl 2,2,2-trichloroacetimidate. The product was purified by flash chromatography (1% ether/pentane). Colorless oil (583 mg, 57% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dddd, 1H, *J* = 17.3, 14.1, 10.6, 6.0 Hz), 5.32 (ddt, 1H, *J* = 17.3, 3.5, 1.4 Hz), 5.23 (dt, 1H, *J* = 10.6, 1.3 Hz), 5.03–4.72 (m, 1H), 3.55 (t, 2H, *J* = 6.6 Hz), 1.93–1.43 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7 (d, *J* = 18.9 Hz), 117.4 (d, *J* = 12.6 Hz), 93.7 (d, *J* = 167.6 Hz), 45.1, 34.7 (d, *J* = 22.7 Hz), 32.6, 22.4 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -177.21 – -177.68 (m).

MS (EI) *m*/*z* (M^+) calcd for $C_7H_{12}ClF$: 150.0612, found: 150.0659.



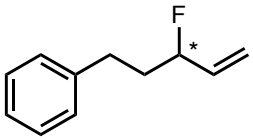
2-(2-fluorobut-3-en-1-yl)isoindoline-1,3-dione. The fluoride was prepared according to General Procedure A from the corresponding trichloroacetimidate, 1-(1,3-dioxoisoindolin-2-yl)but-3-en-2-yl 2,2,2-trichloroacetimidate. The product was purified by flash chromatography (20% Et_2O/pentane). White solid (173 mg, 65% yield).

^1H NMR (500 MHz, $CDCl_3$) δ 7.91–7.80 (m, 2H), 7.78–7.67 (m, 2H), 5.93 (dddd, 1H, *J* = 17.3, 14.5, 10.7, 6.0 Hz), 5.46 (ddt, 1H, *J* = 17.2, 3.3, 1.2 Hz), 5.34 (dt, 1H, *J* = 10.7, 1.2 Hz), 5.29–5.11 (m, 1H), 4.03 (ddd, 1H, *J* = 14.4, 13.7, 8.2 Hz), 3.82 (ddd, 1H, *J* = 26.4, 14.4, 4.0 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 134.5, 133.3 (d, *J* = 17.6 Hz), 132.2, 123.8, 120.0 (d, *J* = 11.3 Hz), 90.4 (d, *J* = 173.9 Hz), 41.8 (d, *J* = 26.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -184.20 – -184.59 (m).

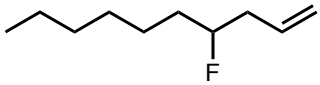
MS (FAB) *m*/*z* (M^++H) calcd for $C_{12}H_{11}FNO_2$: 220.0774, found: 220.0771.



(3-fluoropent-4-en-1-yl)benzene. The fluoride was prepared according to literature procedure[6] from the corresponding trichloroacetimidate, 5-phenylpent-1-en-3-yl 2,2,2-trichloroacetimidate. The commercially available Lin diene ligand investigated by Nguyen (CAS# 940280-80-8, (*S*,*S*)-enantiomer) was used. The product was purified by flash chromatography (1% ether/pentane) followed by purification by preparative HPLC (Daicel CHIRALPAK® IC column, 2.0 cm X 25.0 cm, 0.5% 2-PrOH/hexanes). Colorless oil (37 mg, 30% yield, 90% ee).

HPLC analysis: Daicel CHIRALCEL® OD column; 0.5% 2-PrOH/hexanes; 0.8 mL/min; retention times: 8.5 min (minor), 9.1 min (major).

^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.25–7.18 (m, 3H), 5.92 (dddd, 1H, *J* = 17.3, 14.2, 10.7, 6.0 Hz), 5.34 (ddt, 1H, *J* = 17.2, 3.6, 1.4 Hz), 5.25 (dt, 1H, *J* = 10.6, 1.3 Hz), 5.03–4.77 (m, 1H), 2.88–2.64 (m, 2H), 2.15–1.84 (m, 2H).



4-fluorodec-1-ene. The fluoride was prepared according to General Procedure B from the corresponding alcohol, dec-1-en-4-ol. The product was purified by flash chromatography (pentane). Colorless oil (374 mg, 37% yield).

^1H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, 1H, *J* = 17.2, 10.2, 7.0 Hz), 5.18–5.05 (m, 2H), 4.61–4.43 (m, 1H), 2.46–2.22 (m, 2H), 1.71–1.21 (m, 10H), 0.93–0.85 (m, 3H).

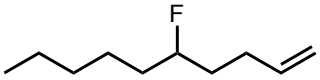
^{13}C NMR (126 MHz, $CDCl_3$) δ 133.8 (d, *J* = 5.0 Hz), 118.0, 93.9 (d, *J* = 168.8 Hz), 39.9 (d, *J* = 21.4 Hz), 35.0 (d, *J* = 21.4 Hz), 32.1, 29.5, 25.3 (d, *J* = 5.0 Hz), 22.9, 14.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -179.49 – -180.17 (m).

MS (EI) *m*/*z* (M^+) calcd for $C_{10}H_{19}F$: 158.1471, found: 158.1478.

---

[6] Zhang, Q.; Stockdale, D. P.; Mixdorf, J. C.; Topczewski, J. J.; Nguyen, H. M. *J. Am. Chem. Soc.* **2015**, *137*, 11912-11915.



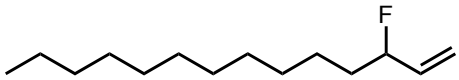
5-fluorodec-1-ene. The fluoride was prepared according to General Procedure B from the corresponding alcohol, dec-1-en-5-ol. The product was purified by flash chromatography (pentane). Colorless oil (495 mg, 49% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (ddt, 1H, *J* = 16.9, 10.2, 6.6 Hz), 5.12–4.90 (m, 2H), 4.63–4.34 (m, 1H), 2.33–2.03 (m, 2H), 1.83–1.17 (m, 10H), 0.94–0.83 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 115.3, 94.1 (d, *J* = 167.6 Hz), 35.5 (d, *J* = 20.2 Hz), 34.7 (d, *J* = 20.2 Hz), 32.04, 29.7 (d, *J* = 5.0 Hz), 25.1 (d, *J* = 5.0 Hz), 22.9, 14.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -180.92 – -181.52 (m).

MS (EI) *m*/*z* (M^+) calcd for $C_{10}H_{19}F$: 158.1471, found: 158.1497.



3-fluorotetradec-1-ene. The fluoride was prepared according to General Procedure A from the corresponding trichloroacetimidate, tetradec-1-en-3-yl 2,2,2-trichloroacetimidate. The product was purified by flash chromatography (pentane). Colorless oil (693 mg, 65% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.96–5.82 (m, 1H), 5.32 (ddt, 1H, *J* = 17.3, 3.6, 1.4 Hz), 5.22 (dt, 1H, *J* = 10.7, 1.3 Hz), 4.97–4.78 (m, 1H), 1.81–1.52 (m, 2H), 1.50–1.18 (m, 18H), 0.97–0.82 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1 (d, *J* = 20.2 Hz), 117.1 (d, *J* = 12.6 Hz), 94.1 (d, *J* = 167.6 Hz), 35.6 (d, *J* = 22.7 Hz), 32.3, 30.00, 29.98, 29.91, 29.86, 29.74, 29.70, 25.0 (d, *J* = 5.0 Hz), 23.0, 14.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -176.52 – -177.01 (m).

MS (EI) *m*/*z* (M^+) calcd for $C_{14}H_{27}F$: 214.2097, found: 214.2095.

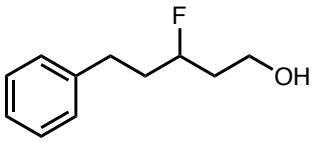
IV. Wacker Oxidations of Allylic Fluorides (Table 1)

General Procedure C: Nitrite-Modified Wacker Oxidations of Allylic Fluorides. A 2-dram vial equipped with a septum cap and magnetic stir bar was charged with $CuCl_2$ (2.7 mg, 0.02 mmol, 0.05 equiv), $AgNO_2$ (3.1 mg, 0.02 mmol, 0.05 equiv), and $Pd(PhCN)_2Cl_2$ (7.7 mg, 0.02 mmol, 0.05 equiv). The atmosphere was then purged using an oxygen-filled balloon for ~30 seconds. *Tert*-butanol (3.5 mL) was then added via syringe, followed by nitromethane (0.7 mL). This mixture was sparged using an oxygen-filled balloon for ~60 seconds, and the balloon was left attached to the vial for the remainder of the reaction. The allylic fluoride (0.4 mmol) was injected via glass syringe, and the reaction mixture was stirred for 4 hours. Upon completion, the solvent was removed via rotary evaporation. The reaction crude was resuspended in ~2 mL dichloromethane and filtered through a glass pipet containing celite washed with dichloromethane into a round-bottom flask. Dichloromethane was removed via rotary evaporation. The crude aldehyde product was subjected to ^{1}H NMR analysis to determine regioselectivity of oxidation prior to reduction.

For solid substrates: The reaction set up was completed as described above, but the allylic fluoride was added as a solution in nitromethane, followed by final sparging with oxygen.

General Procedure D: Reduction of Aldehyde Products and Isolation. The flask containing crude aldehyde product was equipped with a large stir bar, closed with a septum, and purged

using an argon-filled balloon, left attached for the course of the reduction. Dichloromethane (14 mL) and ethanol (10 mL) were added via syringe, and the mixture was stirred and cooled to 0 °C. Sodium borohydride (22.7 mg, 0.6 mmol, 1.5 equiv) was then added and the atmosphere purged again using an argon-filled balloon. This mixture was allowed to warm to room temperature and stirred for 30 minutes. Following reduction of the aldehyde, the reaction mixture was cooled to 0 °C. Saturated NH_4Cl solution (~70 mL) was added slowly (over 5-10 minutes) through the septum via syringe with the argon-filled balloon left intact, followed by vigorous stirring for 30 minutes at 0 °C. The reaction mixture was then transferred to a separatory funnel and extracted 4 times with ether, without further dilution with water. The combined organic layers were washed twice with saturated sodium bicarbonate solution and once with brine, and then dried over Na_2SO_4. The solvent was removed by rotary evaporation and the residue purified by column chromatography (ether/pentane).



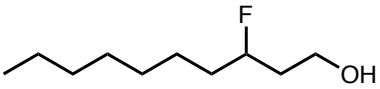
3-fluoro-5-phenylpentan-1-ol (Table 1, Entry 1). The title compound was synthesized according to General Procedures C and D from (3-fluoropent-4-en-1-yl)benzene (65.7 mg, 0.40 mmol). ^{1}H NMR analysis displayed 33:1 aldehyde selectivity. The product was purified by column chromatography on silica gel (40% ether/pentane). Pale yellow oil (60 mg, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.24–7.16 (m, 3H), 4.72 (dtt, 1H, *J* = 49.7, 8.9, 3.4 Hz), 3.88–3.75 (m, 2H), 2.84 (ddd, 1H, *J* = 14.6, 9.9, 5.2 Hz), 2.72 (ddd, 1H, *J* = 13.8, 9.5, 7.0 Hz), 2.12–1.73 (m, 4H), 1.66 (br s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 128.80, 128.77, 126.3, 91.9 (d, *J* = 166.3 Hz), 59.6 (d, *J* = 3.8 Hz), 38.2 (d, *J* = 20.2 Hz), 37.5 (d, *J* = 21.4 Hz), 31.6 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -184.22 (dtd, *J* = 65.9, 33.0, 16.1 Hz).

MS (FAB) *m*/*z* (M^++H) calcd for $C_{11}H_{16}FO$: 183.1185, found: 183.1204.



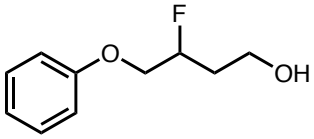
3-fluorodecan-1-ol (Table 1, Entry 2). The title compound was synthesized according to General Procedures C and D from 3-fluorodec-1-ene (63.3 mg, 0.40 mmol). ^{1}H NMR analysis displayed 29:1 aldehyde selectivity. The product was purified by column chromatography on silica gel (40% ether/pentane). Pale yellow solid (62 mg, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.80–4.59 (m, 1H), 3.87–3.75 (m, 2H), 1.94–1.19 (m, 15H), 0.96–0.81 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 93.1 (d, *J* = 166.3 Hz), 59.9 (d, *J* = 3.8 Hz), 38.2 (d, *J* = 20.2 Hz), 35.7 (d, *J* = 21.4 Hz), 32.1, 29.7, 29.5, 25.4 (d, *J* = 3.8 Hz), 22.3, 14.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -182.30 (dddt, *J* = 50.6, 34.2, 29.6, 17.1 Hz).

MS (FAB) *m*/*z* (M^+–F) calcd for $C_{10}H_{21}O$: 157.1592, found: 157.1594.



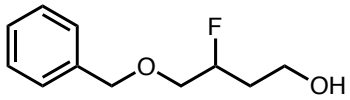
3-fluoro-4-phenoxybutan-1-ol (Table 1, Entry 3). The title compound was synthesized according to General Procedures C and D from ((2-fluorobut-3-en-1-yl)oxy)benzene (66.5 mg, 0.40 mmol). ^{1}H NMR analysis displayed ≥99:1 aldehyde selectivity. The product was purified by column chromatography on silica gel (50% ether/pentane). Pale yellow solid (69 mg, 94% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 6.98 (t, 1H, *J* = 7.4 Hz), 6.93 (d, 2H, *J* = 8.0 Hz), 5.17–4.95 (m, 1H), 4.19–4.09 (m, 2H), 3.92–3.82 (m, 2H), 2.16–1.85 (m, 2H), 1.76 (br s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 129.9, 121.6, 114.9, 90.1 (d, *J* = 172.6 Hz), 69.9 (d, *J* = 23.9 Hz), 59.0 (d, *J* = 5.0 Hz), 34.6 (d, *J* = 20.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -189.32 (ddtd, *J* = 48.3, 31.6, 22.3, 16.3 Hz).

MS (EI) *m*/*z* (M^+) calcd for $C_{10}H_{13}FO_2$: 184.0900, found: 184.0912.



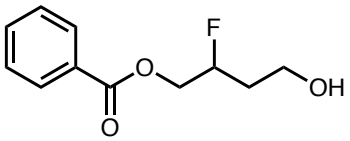
4-(benzyloxy)-3-fluorobutan-1-ol (Table 1, Entry 4). The title compound was synthesized according to General Procedures C and D from (((2-fluorobut-3-en-1-yl)oxy)methyl)benzene (72.1 mg, 0.40 mmol). ^{1}H NMR analysis displayed ≥99:1 aldehyde selectivity. The product was purified by column chromatography on silica gel (50% ether/pentane). Pale yellow oil (74 mg, 93% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5H), 4.98–4.78 (m, 1H), 4.63–4.57 (m, 2H), 3.84–3.76 (m, 2H), 3.70–3.64 (m, 1H), 3.64–3.58 (m, 1H), 2.05–1.81 (m, 2H), 1.68 (br s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 128.8, 128.2, 128.1, 91.2 (d, *J* = 171.4 Hz), 73.8, 72.1 (d, *J* = 22.7 Hz), 59.0 (d, *J* = 5.0 Hz), 34.8 (d, *J* = 21.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.08 – -188.66 (m).

MS (EI) *m*/*z* (M^+) calcd for $C_{11}H_{15}FO_2$: 198.1056, found: 198.1084.



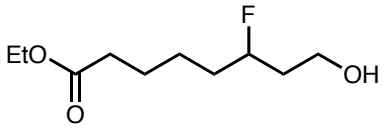
2-fluoro-4-hydroxybutyl benzoate (Table 1, Entry 5). The title compound was synthesized according to General Procedures C and D from 2-fluorobut-3-en-1-yl benzoate (77.7 mg, 0.40 mmol). ^{1}H NMR analysis displayed ≥99:1 aldehyde selectivity. The product was purified by column chromatography on silica gel (60% ether/pentane). White solid (79 mg, 93% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10–8.06 (m, 2H), 7.61–7.55 (m, 1H), 7.49–7.42 (m, 2H), 5.06 (ddddd, 1H, *J* = 49.2, 9.0, 6.4, 3.9, 2.7 Hz), 4.60–4.41 (m, 2H), 3.91–3.86 (m, 2H), 2.14–1.83 (m, 2H), 1.55 (br s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 133.6, 130.1, 129.9, 128.8, 89.6 (d, *J* = 172.6 Hz), 66.6 (d, *J* = 21.4 Hz), 58.8 (d, *J* = 5.0 Hz), 34.4 (d, *J* = 21.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -189.14 – -189.79 (m).

MS (FAB) *m*/*z* (M^++H) calcd for $C_{11}H_{14}FO_3$: 213.0927, found: 213.0938.



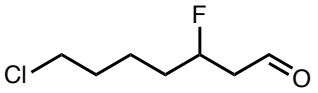
ethyl 6-fluoro-8-hydroxyoctanoate (Table 1, Entry 6). The title compound was synthesized according to General Procedures C and D from ethyl 6-fluorooct-7-enoate (75.3 mg, 0.40 mmol). ^{1}H NMR analysis displayed 29:1 aldehyde selectivity. The product was purified by column chromatography on silica gel (60% ether/pentane). Colorless oil (59 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79–4.59 (m, 1H), 4.11 (q, 2H, *J* = 7.2 Hz), 3.83–3.74 (m, 2H), 2.30 (t, 2H, *J* = 7.4 Hz), 1.93–1.29 (m, 9H), 1.24 (t, 3H, *J* = 7.1 Hz).

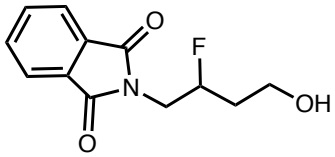
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 92.5 (d, *J* = 166.3 Hz), 60.6, 59.6 (d, *J* = 3.8 Hz), 38.1 (d, *J* = 20.2 Hz), 35.3 (d, *J* = 21.4 Hz), 34.5, 25.0, 24.9 (d, *J* = 3.8 Hz), 14.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -182.90 (dddt, *J* = 50.2, 33.8, 29.7, 16.9 Hz).

MS (FAB) *m*/*z* (M^++H) calcd for $C_{10}H_{20}FO_3$: 207.1396, found: 207.1401.



7-chloro-3-fluoroheptanal (Table 1, Entry 7). The title compound was synthesized according to General Procedure C from 7-chloro-3-fluorohept-1-ene (60.4 mg, 0.40 mmol). Upon completion, nitrobenzene (0.40 mmol) was added as an NMR standard. ^{1}H NMR analysis of an aliquot of the crude reaction mixture (without any rotary evaporation step) displayed 42:1 aldehyde selectivity and 81% yield.



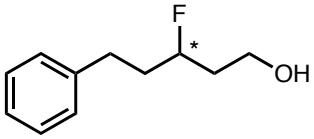
2-(2-fluoro-4-hydroxybutyl)isoindoline-1,3-dione (Table 1, Entry 8). The title compound was synthesized according to General Procedures C and D from 2-(2-fluorobut-3-en-1-yl)isoindoline-1,3-dione (87.7 mg, 0.40 mmol). ^{1}H NMR analysis displayed ≥99:1 aldehyde selectivity. The product was purified by column chromatography on silica gel (1:1:1 ether/DCM/pentane). Light yellow solid (73 mg, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.83 (m, 2H), 7.77–7.70 (m, 2H), 5.10–4.90 (m, 1H), 4.05 (ddd, 1H, *J* = 16.1, 14.5, 7.8 Hz), 3.92–3.78 (m, 3H), 2.02–1.86 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 134.5, 132.2, 123.8, 89.5 (d, *J* = 173.9 Hz), 59.0 (d, *J* = 5.0 Hz), 42.1 (d, *J* = 23.9 Hz), 35.7 (d, *J* = 20.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.23 – -188.74 (m).

MS (EI) *m*/*z* (M^+) calcd for $C_{12}H_{12}FNO_3$: 237.0801, found: 237.0797.



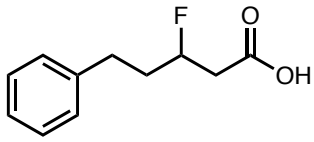
3-fluoro-5-phenylpentan-1-ol (Equation 1). The title compound was synthesized according to General Procedures C and D from (3-fluoropent-4-en-1-yl)benzene (33 mg, 0.20 mmol). ^{1}H NMR analysis displayed 30:1 aldehyde selectivity. The product was purified by column chromatography on silica gel (25→75% ether/pentane). Colorless oil (30 mg, 82% yield, 90% ee).

HPLC analysis: Daicel CHIRALCEL® OD column; 15% 2-PrOH/hexanes; 0.9 mL/min; retention times: 7.3 min (minor), 8.7 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.24–7.16 (m, 3H), 4.72 (dtt, 1H, *J* = 49.7, 8.9, 3.4 Hz), 3.87–3.76 (m, 2H), 2.84 (ddd, 1H, *J* = 14.7, 9.9, 5.2 Hz, 1H), 2.72 (ddd, 1H, *J* = 13.8, 9.5, 7.0 Hz), 2.09–1.74 (m, 4H), 1.55 (br s, 1H).

V. Derivatizations of Beta-Fluorinated Aldehydes (Scheme 2)

All derivatizations were performed on crude aldehydes produced from (3-fluoropent-4-en-1-yl)benzene using General Procedure C. All yields reported over two steps.



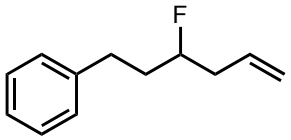
3-fluoro-5-phenylpentanoic acid (Scheme 2a). The title compound was synthesized from 3-fluoro-5-phenylpentanal (produced from 0.40 mmol (3-fluoropent-4-en-1-yl)benzene) using the "General Procedure for Oxidation of Aldehyde to Carboxylic Acid" reported by Borhan.[7] The product was purified by column chromatography on silica gel (5% MeOH/pentane). Clear crystals (71 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (br s, 1H), 7.35–7.27 (m, 2H), 7.24–7.15 (m, 3H), 4.95 (dtt, 1H, *J* = 48.1, 8.3, 4.0 Hz), 2.92–2.50 (m, 4H), 2.17–1.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2 (d, *J* = 6.1 Hz), 141.1, 128.9, 128.8, 126.5, 89.5 (d, *J* = 170.7 Hz), 40.4 (d, *J* = 24.2 Hz), 36.9 (d, *J* = 21.2 Hz), 31.4 (d, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -181.38 – -181.83 (m).

MS (FAB) *m*/*z* (M^++H) calcd for $C_{11}H_{14}O_2F$: 197.0978, found: 197.0980.



(3-fluorohex-5-en-1-yl)benzene (Scheme 2b). A 1-dram vial equipped with a septum cap and stir bar was charged with $MePPh_3Br$ (54 mg, 1.5 equiv, 0.15 mmol). The atmosphere was purged using an argon-filled balloon, and anhydrous THF was added via syringe (0.5 mL). The

[7] Travis, B. R.; Sivakumar, M.; Hollist, G. O.; Borhan, B. *Org. Lett.* **2003**, *5*, 1031-1034.

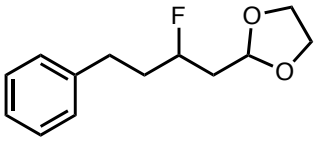
mixture was cooled to 0 °C with stirring, and *n*BuLi (2.5 M in hexanes, 1.4 equiv) was added via glass syringe. The mixture was allowed to stir for 30 minutes at 0 °C. 3-fluoro-5-phenylpentanal (produced from 0.10 mmol (3-fluoropent-4-en-1-yl)benzene) was dissolved in THF (0.2 mL) under argon atmosphere, and the solution was added via microsyringe to the reaction mixture. The reaction was allowed to warm to room temperature and stirred overnight. Saturated NH_4Cl solution was added to the crude mixture and extracted 3 times with ether. Following drying over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by preparative thin-layer chromatography on silica gel (2% ether/pentane). Pale yellow oil (12 mg, 65% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.24 (m, 2H), 7.24–7.15 (m, 3H), 5.91–5.73 (m, 1H), 5.18–5.05 (m, 2H), 4.69–4.39 (m, 1H), 2.83 (ddd, 1H, *J* = 14.9, 9.8, 5.3 Hz), 2.69 (ddd, 1H, *J* = 13.8, 9.4, 7.1 Hz), 2.54–2.24 (m, 2H), 2.08–1.71 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 133.4 (d, *J* = 6.3 Hz), 128.80, 128.79, 126.3, 118.3, 92.8 (d, *J* = 170.1 Hz), 39.9 (d, *J* = 22.7 Hz), 36.8 (d, *J* = 21.4 Hz), 31.6 (d, *J* = 3.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -181.34 – -181.99 (m).

MS (EI) *m*/*z* (M^+) calcd for $C_{12}H_{15}F$: 178.1158, found: 178.1158.



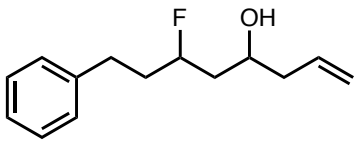
2-(2-fluoro-4-phenylbutyl)-1,3-dioxolane (Scheme 2d). 3-fluoro-5-phenylpentanal (produced from 0.40 mmol (3-fluoropent-4-en-1-yl)benzene) was dissolved in 2 mL ethylene glycol (0.2 M). Molecular sieves (4Å, 130 mg) were then added. *P*-toluenesulfonic acid (76.1 mg, 1 equiv, 0.40 mmol) was added, and the reaction was stirred for 6 hours at room temperature. The reaction was quenched with saturated $NaHCO_3$ solution, and extracted three times with ether. After drying over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (20% Et_2O/pentane). Colorless oil (50 mg, 56% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.23–7.17 (m, 3H), 5.03 (dd, 1H, *J* = 6.4, 3.6 Hz), 4.75 (dtt, 1H, *J* = 49.4, 8.7, 3.6 Hz), 4.03–3.92 (m, 2H), 3.92–3.82 (m, 2H), 2.84 (ddd, 1H, *J* = 13.8, 10.1, 5.2 Hz), 2.71 (ddd, 1H, *J* = 13.9, 9.7, 6.8 Hz), 2.14 (dddd, 1H, *J* = 16.4, 14.5, 8.7, 3.6 Hz), 2.08–1.77 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 128.8, 126.3, 101.9 (d, *J* = 5.0 Hz), 90.5 (d, *J* = 167.6 Hz), 65.3, 65.1, 40.0 (d, *J* = 20.2 Hz), 37.7 (d, *J* = 20.2 Hz), 31.5 (d, *J* = 3.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -183.15 (dtt, *J* = 48.9, 32.5, 16.4 Hz).

MS (FAB) *m*/*z* (M^++H) calcd for $C_{13}H_{18}FO_2$: 225.1291, found: 225.1281.



6-fluoro-8-phenyloct-1-en-4-ol (Scheme 2e). A 20 mL vial containing 3-fluoro-5-phenylpentanal (produced from 0.40 mmol (3-fluoropent-4-en-1-yl)benzene) was purged using

an argon-filled balloon. The aldehyde was dissolved in 3.3 mL anhydrous DCM (0.12 M) and the mixture cooled to -78 °C. Allylboronic acid pinacol ester (75 μL, 0.4 mmol, 1.0 equiv) was then added via glass syringe. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Water was added to the crude mixture and extracted three times with ether. After drying over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (30% Et_2O/pentane). ^1H NMR analysis displayed ~1:1 dr. Colorless oil (72 mg, 81% yield).

^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 2H), 7.24–7.15 (m, 3H), 5.90–5.72 (m, 1H), 5.20–5.08 (m, 2H), 4.96–4.59 (m, 1H), 4.00–3.83 (m, 1H), 2.90–2.77 (m, 1H), 2.76–2.63 (m, 1H), 2.39–2.12 (m, 2H), 2.11–1.46 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 141.6, 134.65, 134.61, 128.80, 128.77, 128.76, 128.75, 126.4, 126.3, 118.9, 118.7, 93.3 (d, *J* = 166.3 Hz), 91.1 (d, *J* = 166.3 Hz), 69.1 (d, *J* = 3.8 Hz), 67.1 (d, *J* = 2.5 Hz), 42.8, 42.4 (d, *J* = 20.2 Hz), 42.1, 41.9 (d, *J* = 18.9 Hz), 37.7 (d, *J* = 21.4 Hz), 37.5 (d, *J* = 20.2 Hz), 31.7 (d, *J* = 5.0 Hz), 31.5 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -181.75 (dtt, *J* = 49.0, 32.5, 15.6 Hz), -183.91 – -184.74 (m).

MS (FAB) *m*/*z* (M^++H) calcd for $C_{14}H_{20}FO$: 223.1498, found: 223.1491.

VI. Mechanistic Studies

General Procedure for Figure 2. A 1-dram vial equipped with a septum cap and magnetic stir bar was charged with $CuCl_2$ (0.7 mg, 0.005 mmol, 0.05 equiv), $AgNO_2$ (0.8 mg, 0.005 mmol, 0.05 equiv), and $Pd(PhCN)_2Cl_2$ (1.9 mg, 0.005 mmol, 0.05 equiv). The atmosphere was then purged using an oxygen-filled balloon for ~30 seconds. *Tert*-butanol (0.88 mL) was then added via syringe, followed by nitromethane (0.18 mL). This mixture was sparged using an oxygen-filled balloon for ~60 seconds. The olefin (0.1 mmol) was injected via glass syringe, the balloon was removed, and the septum cap was greased. The reaction mixture was stirred for 4 hours at room temperature. Upon completion, the solvent was removed via rotary evaporation. The reaction crude was resuspended in dichloromethane and filtered through a glass pipet containing celite, which was washed with dichloromethane. Dichloromethane was removed via rotary evaporation. Nitrobenzene (0.1 mmol, 10.3 μL) was added as a standard, and ^1H NMR analysis of the crude product was performed to determine yield and selectivity.

	Selectivity (%)		Oxidation Yield (%)	
	run 1	**run 2**	**run 1**	**run 2**
n=0	95	96	55	49
n=1	79	80	68	59
n=2	64	69	53	59
1-decene	54	61	54	51

General Procedure for Figure 3a: Individual rate comparison. A 4 mL vial with a stir bar was charged with $CuCl_2$ (2.7 mg, 0.020 mmol), $AgNO_2$ (3.1 mg, 0.020 mmol), and $Pd(PhCN)_2Cl_2$ (7.7 mg, 0.020 mmol). The vial was capped with a septum cap and purged with O_2 using an oxygen-filled balloon. Next, *tert*-BuOH (1.32 mL, anhydrous) and nitromethane (0.36 mL, anhydrous) were added via syringe, and the reaction mixture was stirred. In a separate vial, a solution of olefin (0.20 mmol) and diphenylmethane (16.7 μL, 0.10 mmol; internal standard) in *t*-

BuOH (0.44 mL) was prepared. The olefin solution was added to the catalyst mixture via syringe, and an aliquot (0.3 mL) was immediately collected for a time = 0 data point. The aliquot was quenched with a solution of pyridine (6.0 μL) in DCM (0.2 mL). After quenching, the aliquot was concentrated, diluted with hexanes, and filtered through a plug of celite with hexanes. The filtrate was concentrated and analyzed by ^{1}H NMR. Aliquots were taken at time = 5, 10, 15, and 20 minutes following the same quenching procedure, and conversions were determined by ^{1}H NMR relative to the time = 0 data point.

Tetradecene

Time (min) Conversion (%)

	run 1	**run 2**	**run 3**	**Average**
0	0	0	0	0
5	7.7	6.7	8	7.5
10	12.1	11.9	11.6	11.9
15	17.2	13.7	15.7	15.5
20	19.9	16.9	19.6	18.8

Allylic Fluoride

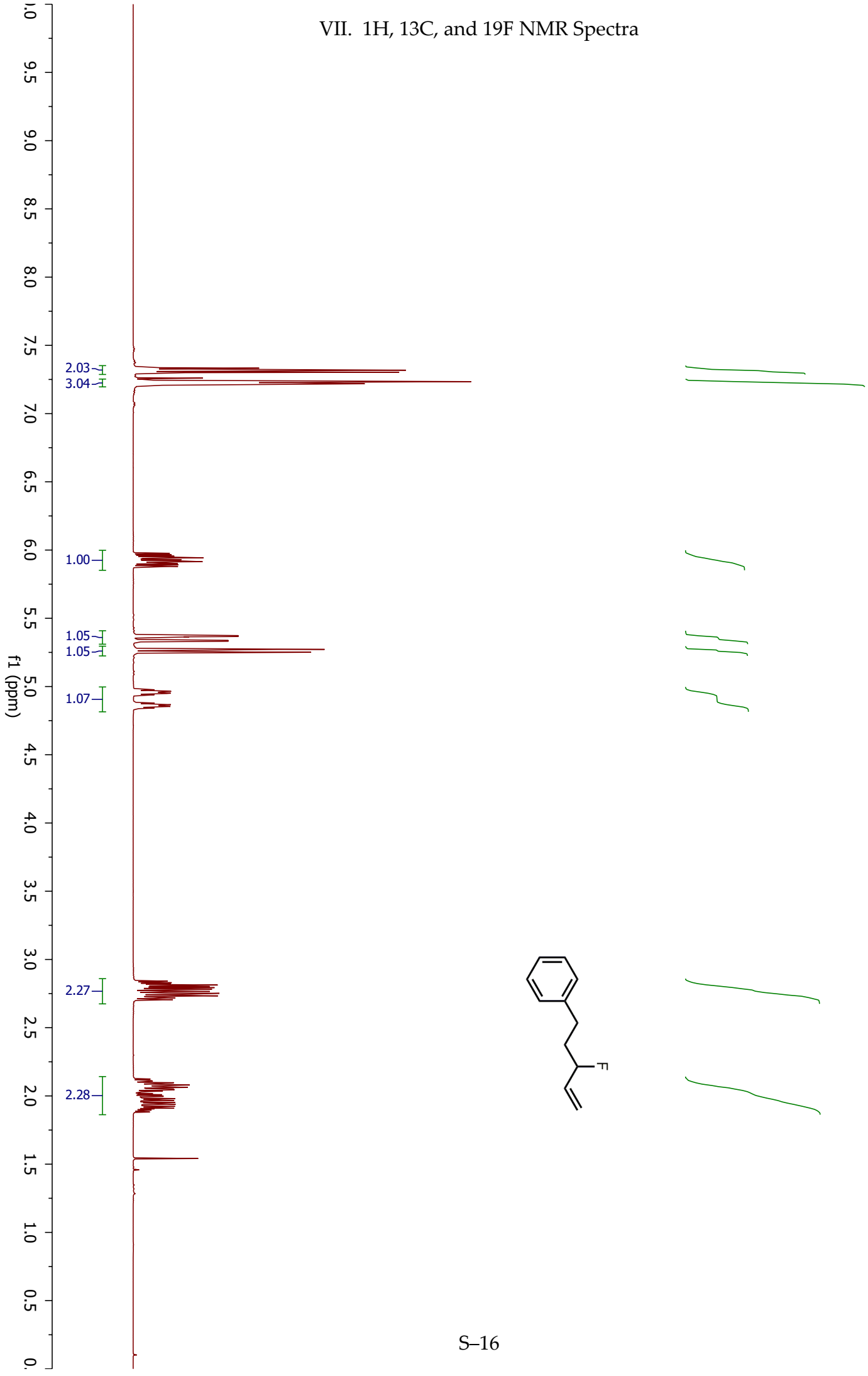
Time (min) Conversion (%)

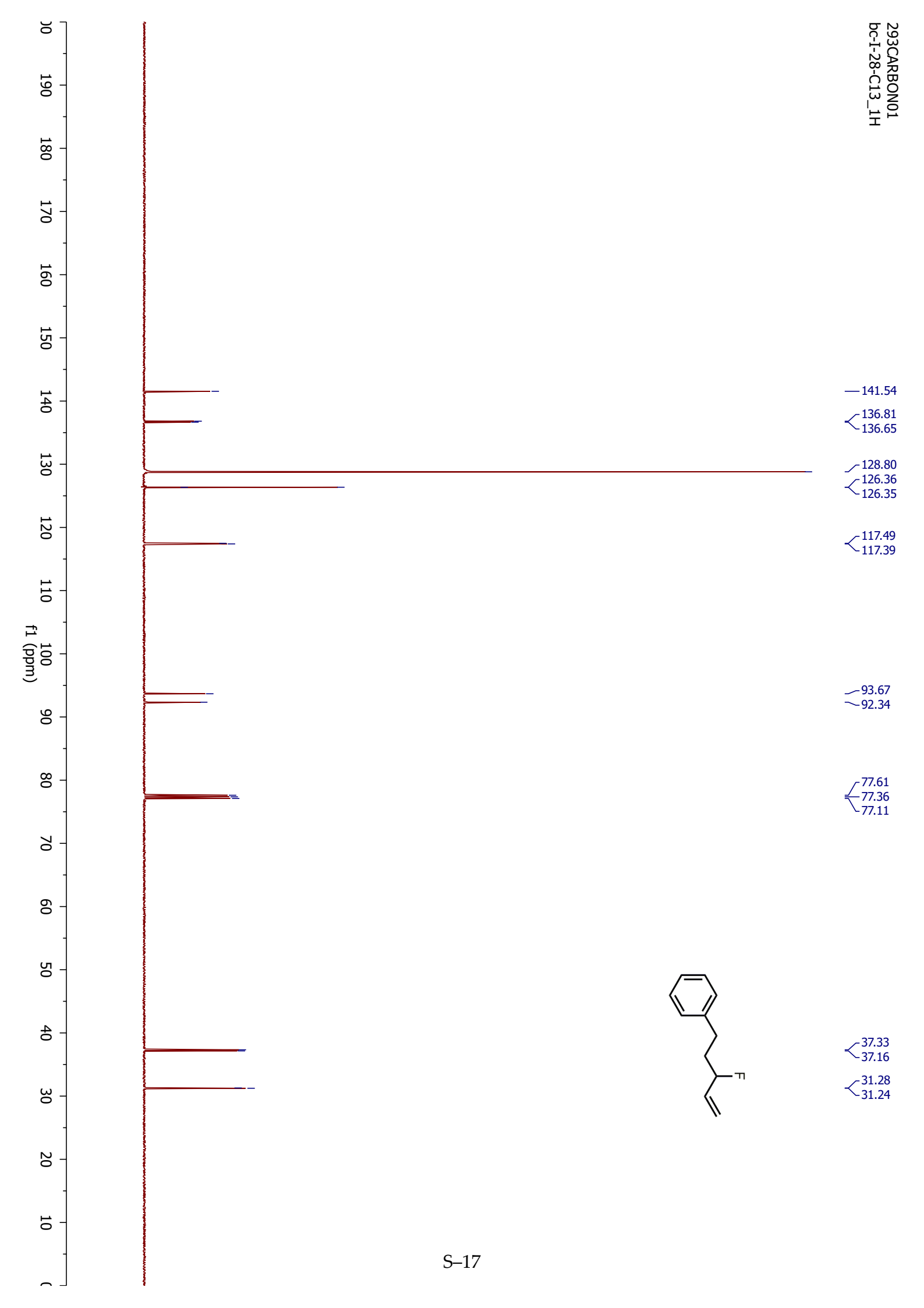
	run 1	**run 2**	**Average**
0	0	0	0
5	9.6	11.2	10.4
10	18.5	20.9	19.7
15	28.4	30.6	29.5
20	36.9	40.5	38.7

General Procedure for Figure 3b: Competition experiment. A 4 mL vial with a stir bar was charged with $CuCl_2$ (2.7 mg, 0.020 mmol), $AgNO_2$ (3.1 mg, 0.020 mmol), and $Pd(PhCN)_2Cl_2$ (7.7 mg, 0.020 mmol). The vial was capped with a septum cap and purged with O_2 using an oxygen-filled balloon. Next, *tert*-BuOH (1.32 mL, anhydrous) and nitromethane (0.36 mL, anhydrous) were added via syringe, and the reaction mixture was stirred. In a separate vial, a solution of tetradecene (19.6 mg, 0.10 mmol), 3-fluorotetradec-1-ene (21.4 mg, 0.10 mmol), and diphenylmethane (16.7 μL, 0.10 mmol; internal standard) in *t*-BuOH (0.44 mL) was prepared. The olefin solution was added to the catalyst mixture via syringe, and an aliquot (0.3 mL) was immediately collected for a time = 0 data point. The aliquot was quenched with a solution of pyridine (6.0 μL) in DCM (0.2 mL). After quenching, the aliquot was concentrated, diluted with hexanes, and filtered through a plug of celite with hexanes. The filtrate was concentrated and analyzed by ^{1}H NMR. A second aliquot was collected at time = 10 minutes following the same quenching procedure, and the conversion of each olefin was determined by ^{1}H NMR relative to the time = 0 data point.

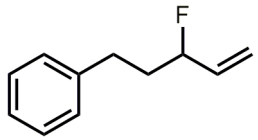
Conversion (%)

	Tetradecene	**Allylic Fluoride**	**Selectivity**
run 1	11.2	5.0	2.2:1
run 2	11.1	4.6	2.4:1


293PROTON01
bc-I-28-C13_1H
2.03
3.04
1.00
1.05
1.05
1.07
2.27
2.28
F
f1 (ppm)

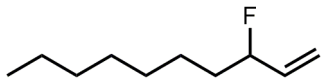

293CARBON01
bc-I-28-C13_1H
141.54
136.81
136.65
128.80
126.36
126.35
117.49
117.39
93.67
92.34
77.61
77.36
77.11
37.33
37.16
31.28
31.24
F
f1 (ppm)

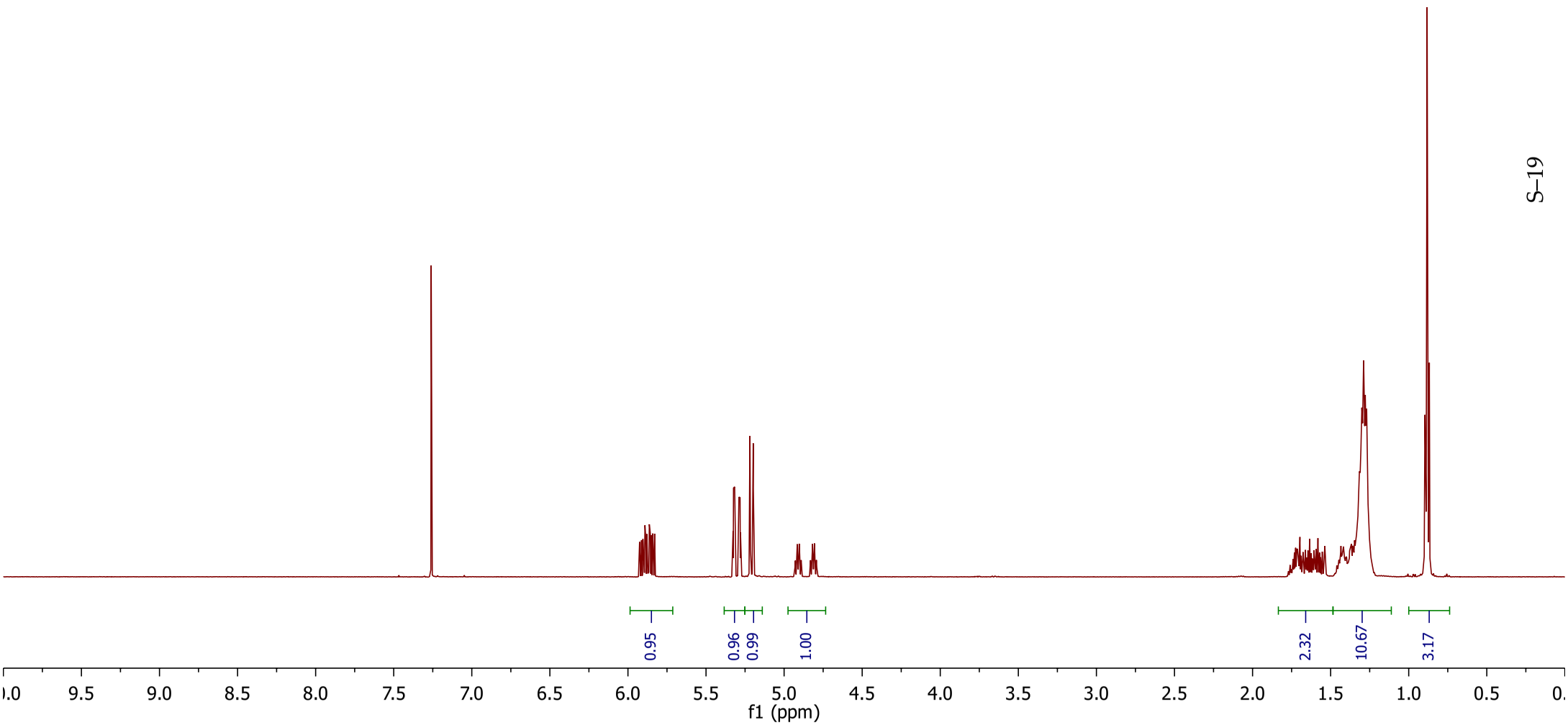
FLUORINE01
CKC0293siena

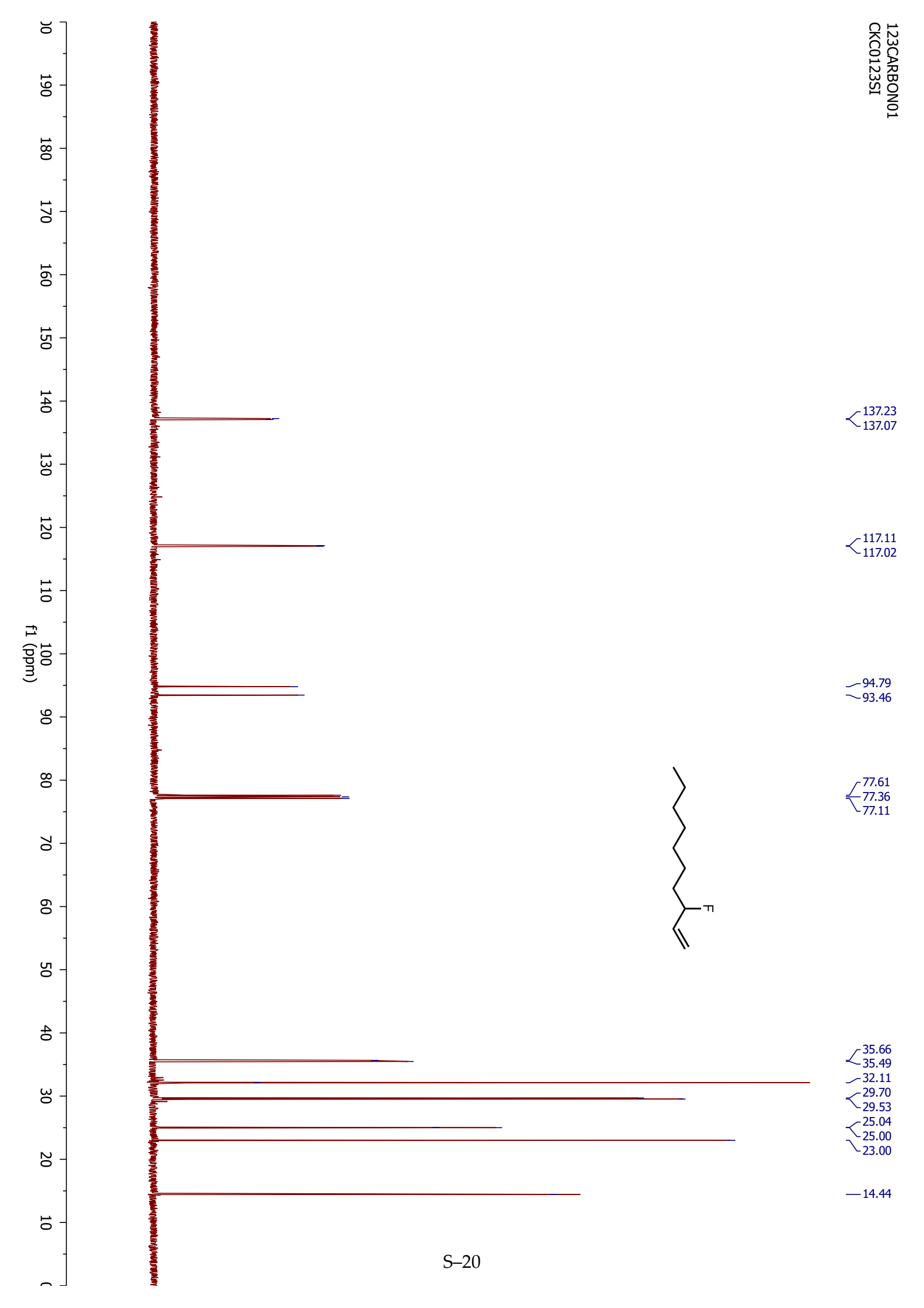


30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

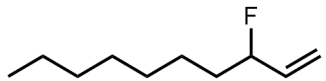
CKC0123SIr
CKC0123SIr



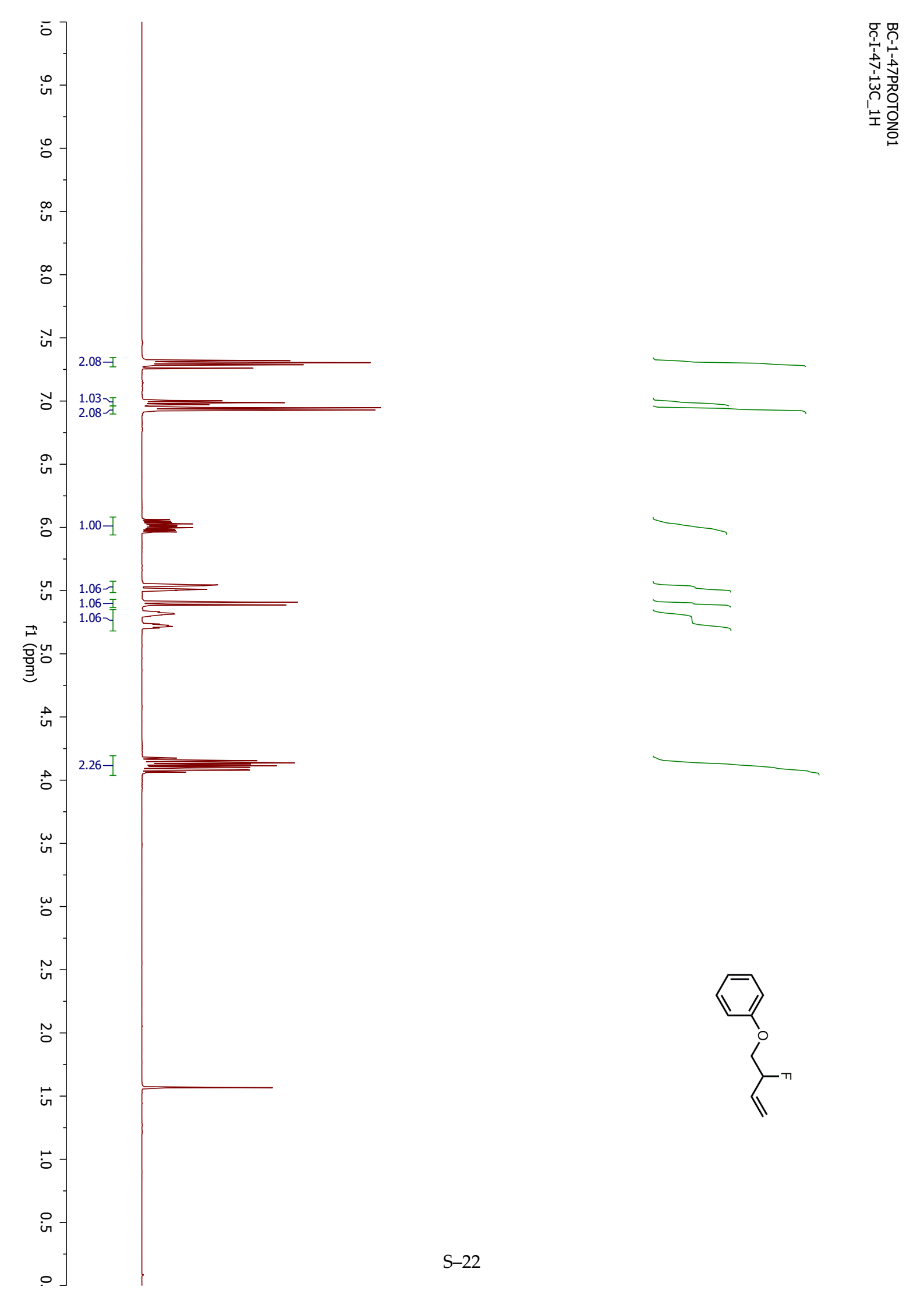


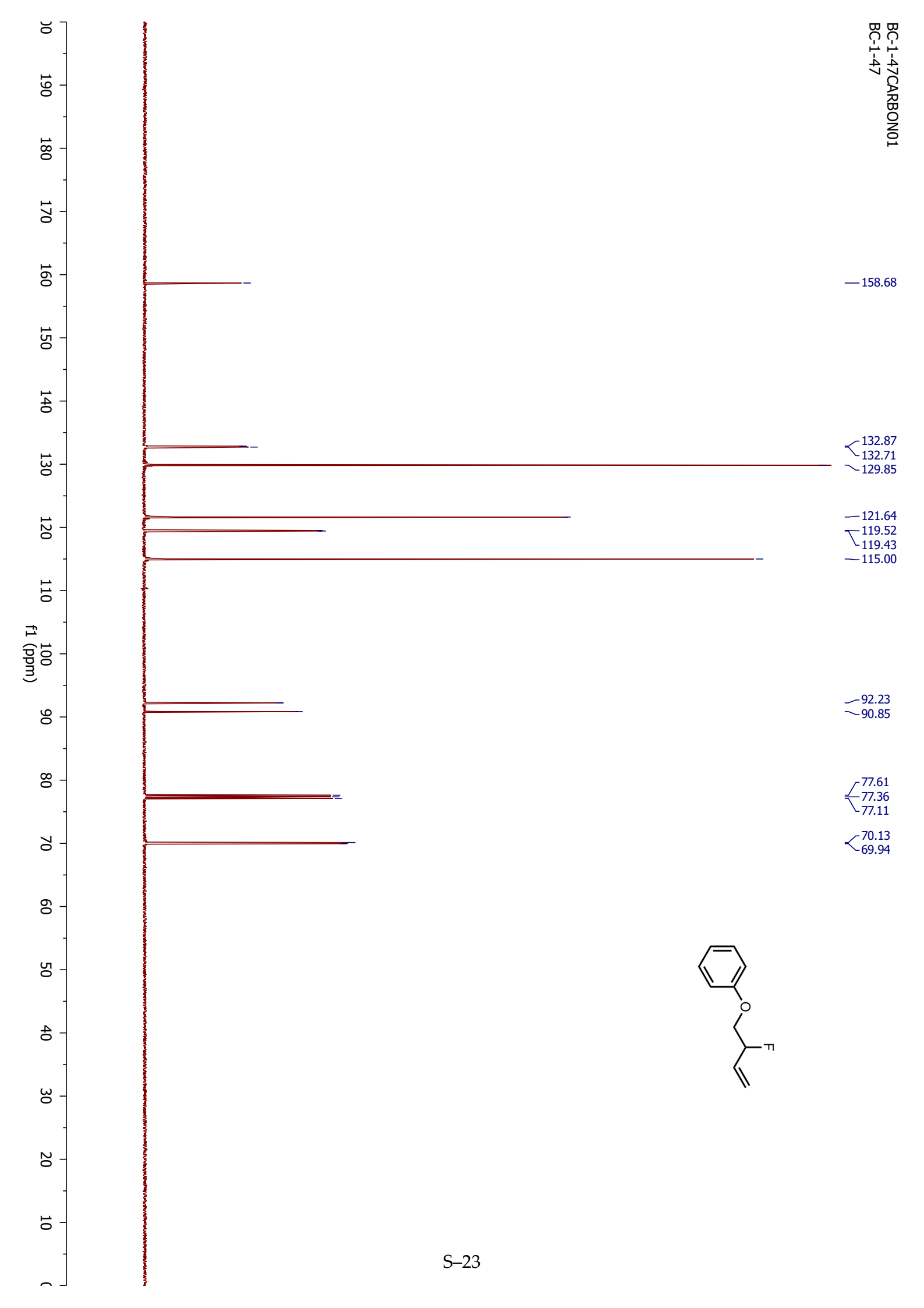

123CARBON01
CKC0123SI
137.23
137.07
117.11
117.02
94.79
93.46
77.61
77.36
77.11
F
35.66
35.49
32.11
29.70
29.53
25.04
25.00
23.00
14.44
f1 (ppm)

FLUORINE01
CKC0123siena

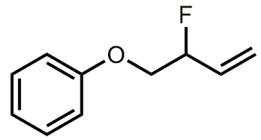


30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

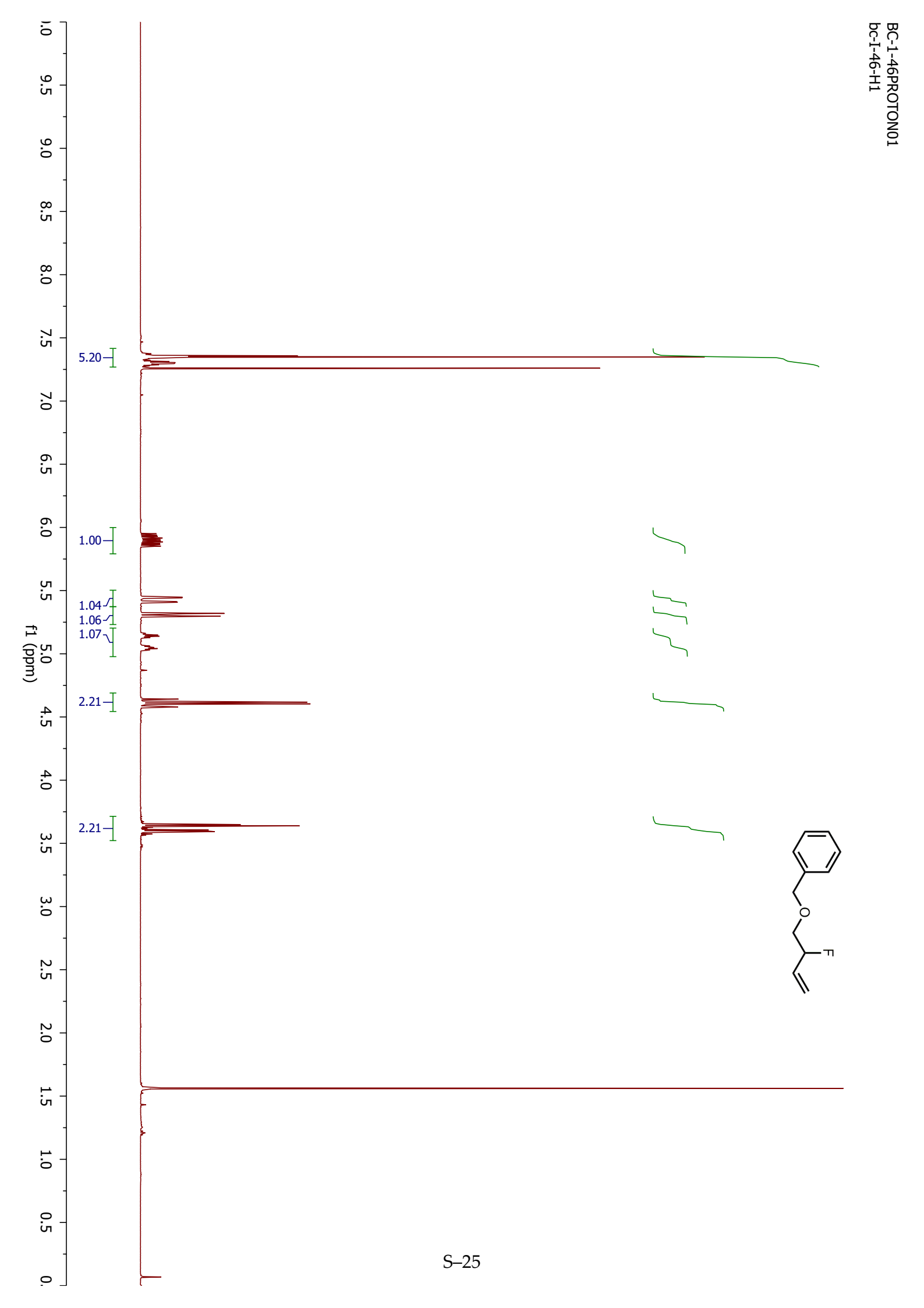

BC-1-47PROTON01
bc-I-47-13C_1H
2.08
1.03
2.08
1.00
1.06
1.06
1.06
2.26
f1 (ppm)
O
F

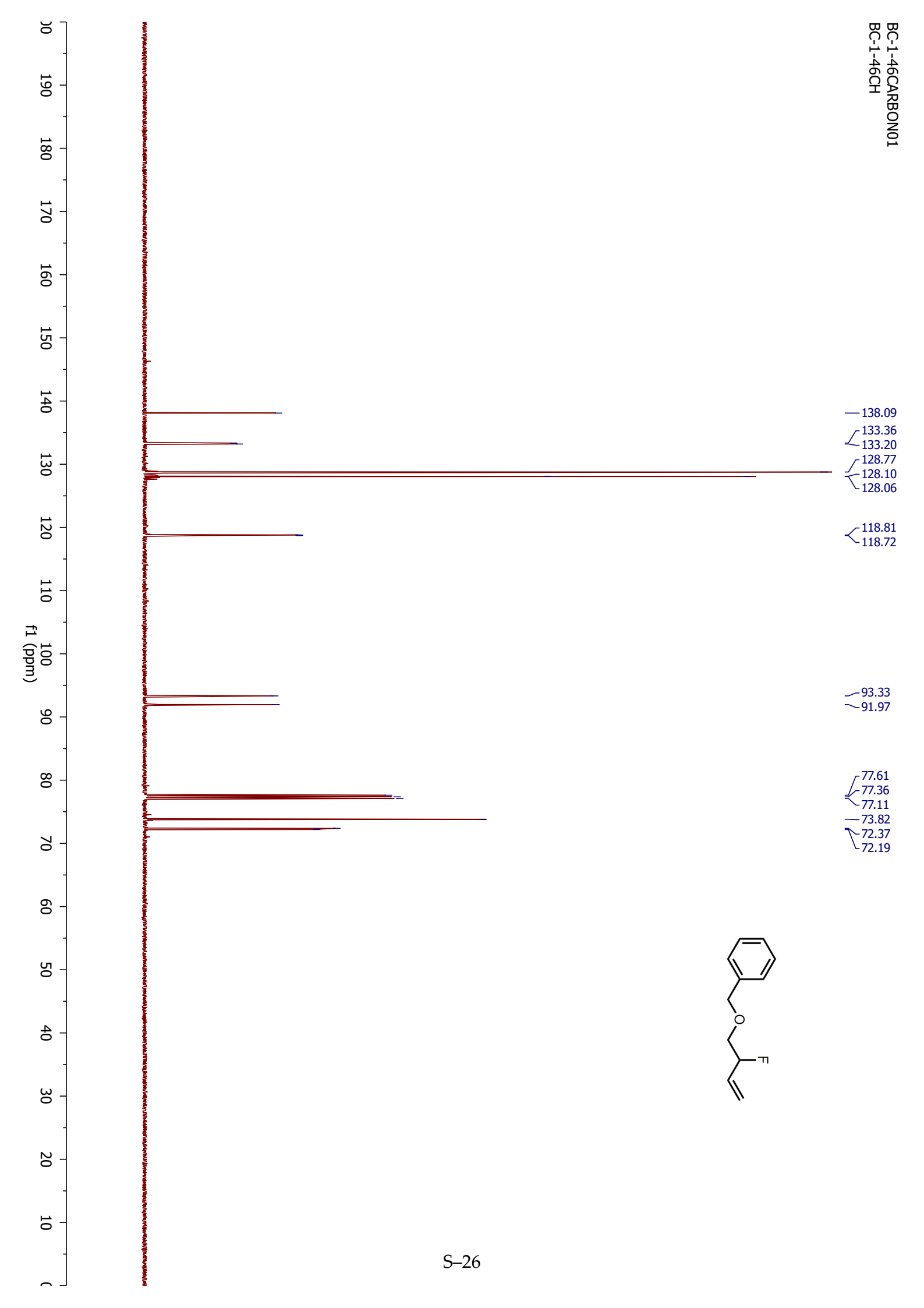

BC-1-47CARBON01
BC-1-47
158.68
132.87
132.71
129.85
121.64
119.52
119.43
115.00
92.23
90.85
77.61
77.36
77.11
70.13
69.94
O
F
f1 (ppm)

FLUORINE01
BC-1-47siena

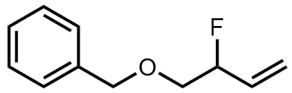


30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

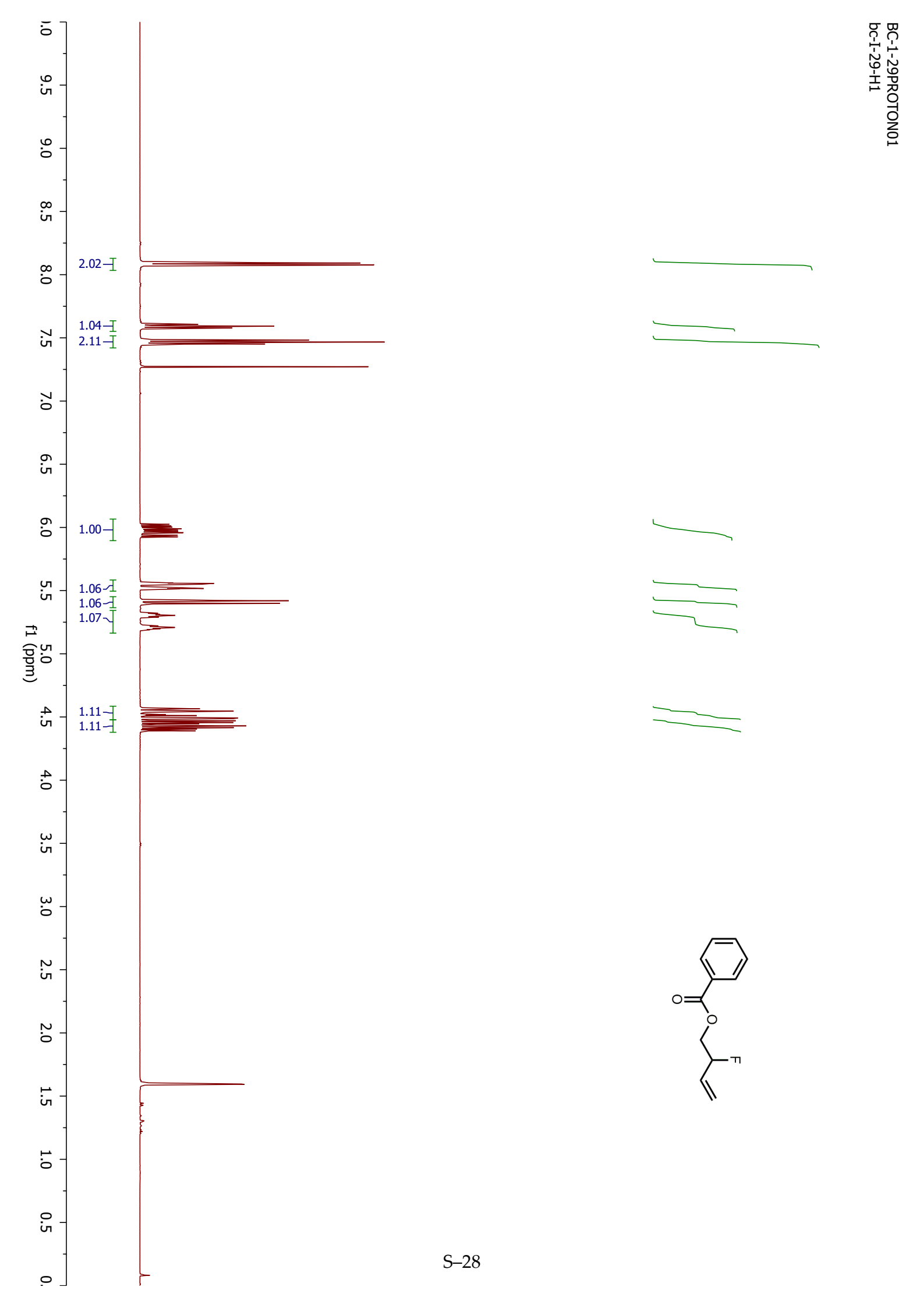

BC-1-46PROTON01
bc-I-46-H1
5.20
1.00
1.04
1.06
1.07
2.21
2.21
f1 (ppm)
O
F

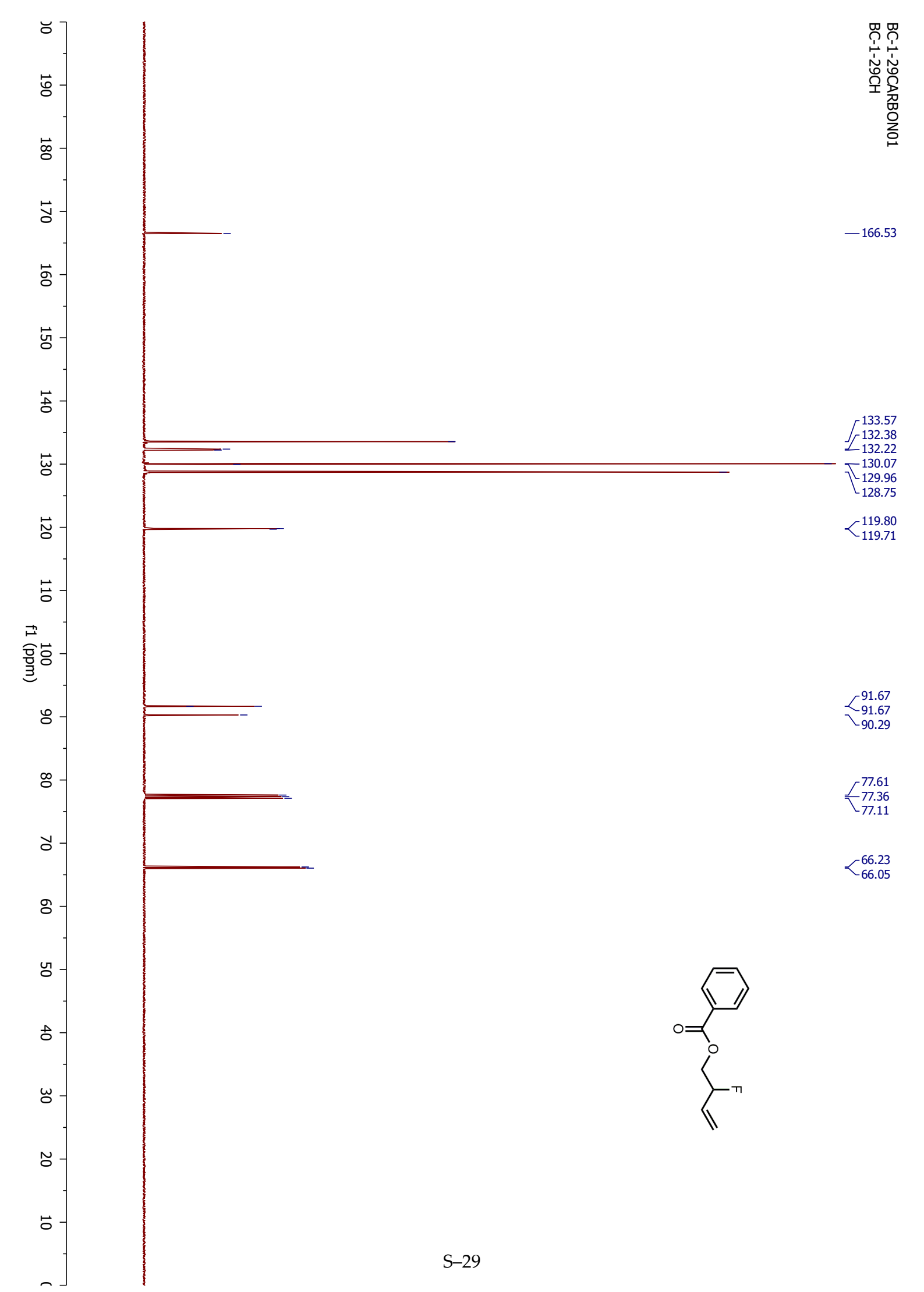

BC-1-46CARBON01
BC-1-46CH
138.09
133.36
133.20
128.77
128.10
128.06
118.81
118.72
93.33
91.97
77.61
77.36
77.11
73.82
72.37
72.19
O
F
f1 (ppm)

FLUORINE01
BC-1-46siena

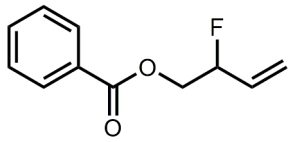


30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


BC-1-29PROTON01
bc-I-29-H1
2.02
1.04
2.11
1.00
1.06
1.06
1.07
1.11
1.11
f1 (ppm)
O
O
F


BC-1-29CARBON01
BC-1-29CH
166.53
133.57
132.38
132.22
130.07
129.96
128.75
119.80
119.71
91.67
91.67
90.29
77.61
77.36
77.11
66.23
66.05
f1 (ppm)
O
O
F

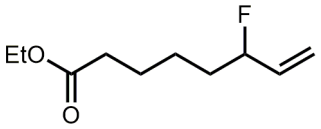
FLUORINE01
BC-1-29siena

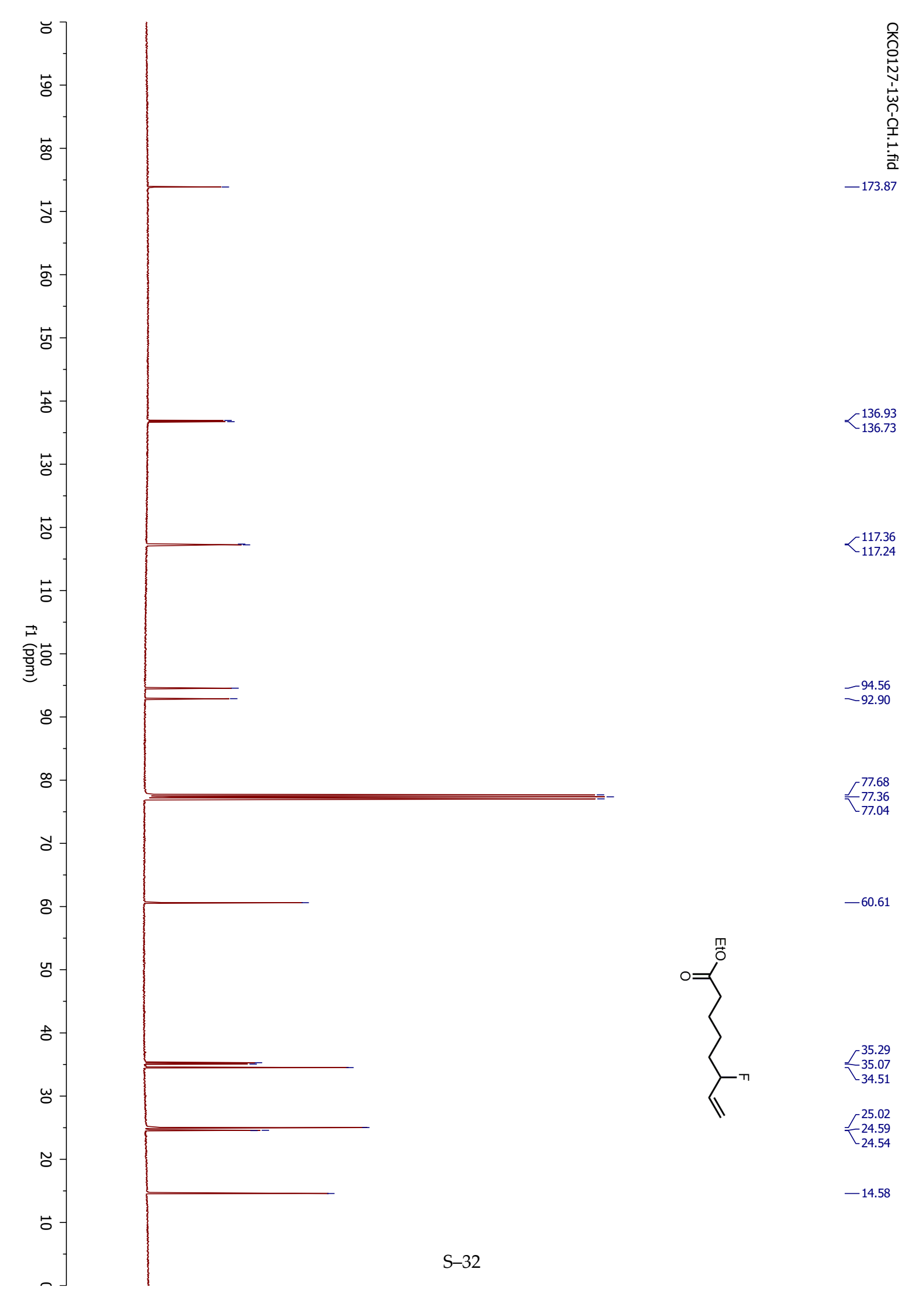


S–30

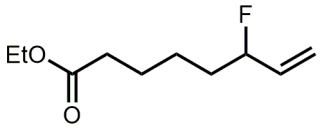
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

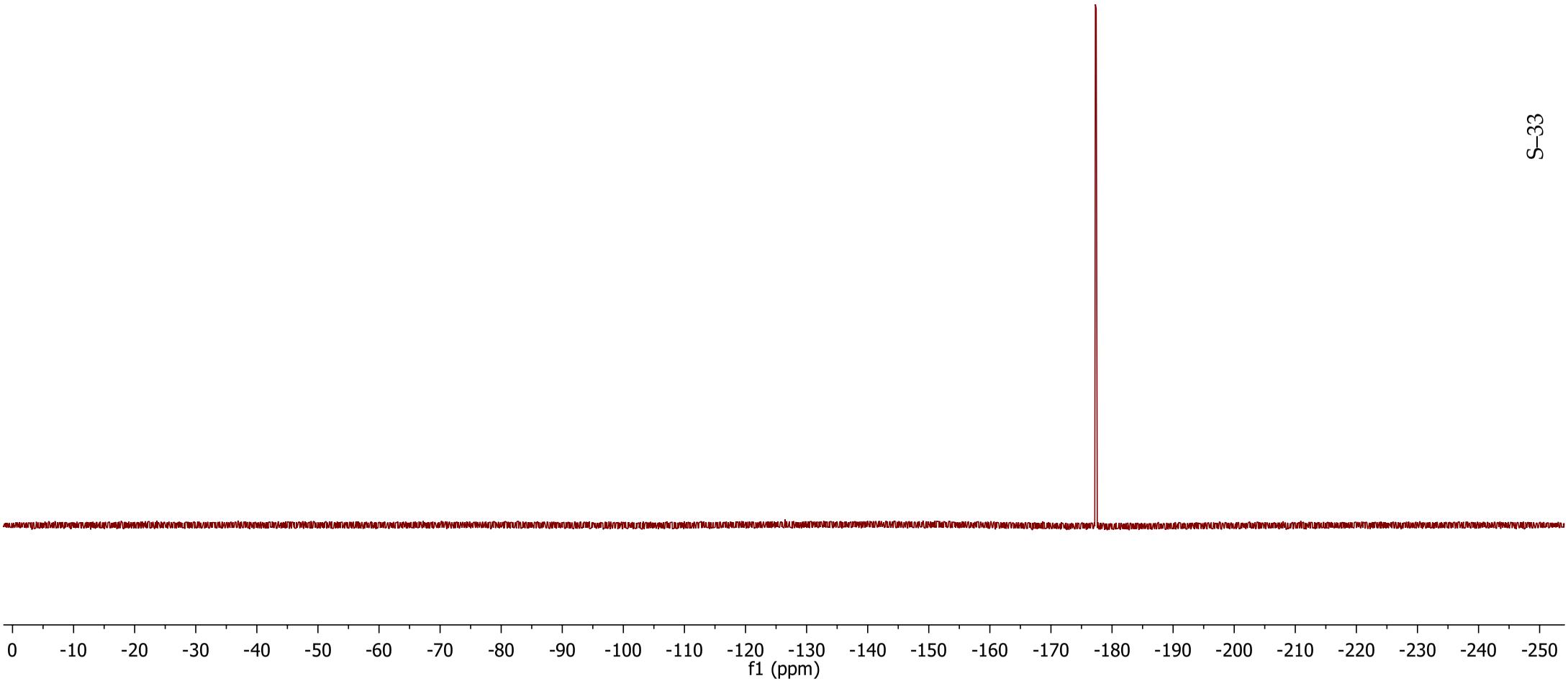
CKC0127-1H-CH.1.fid



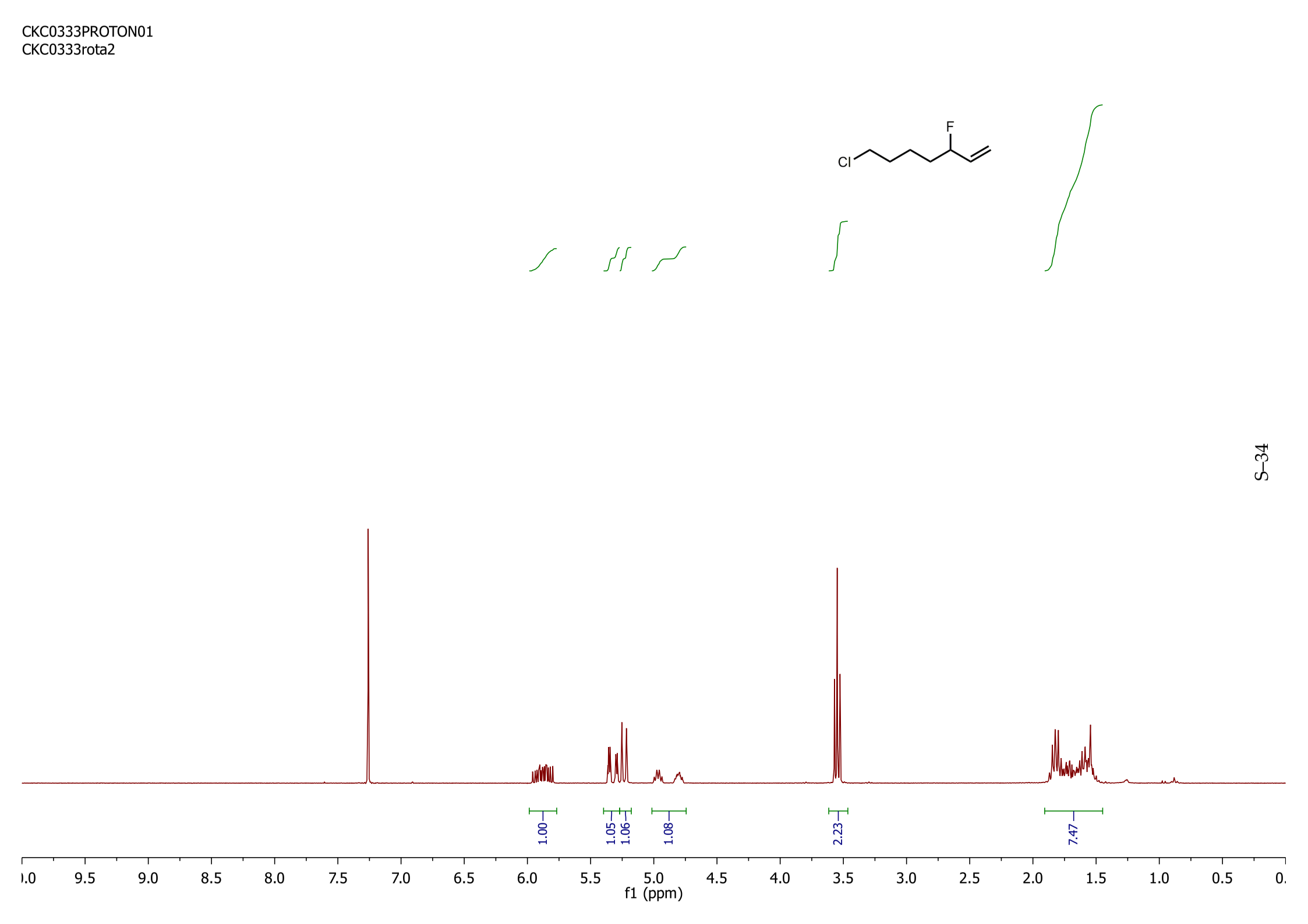

CKC0127-13C-CH.1.fid
173.87
136.93
136.73
117.36
117.24
94.56
92.90
77.68
77.36
77.04
60.61
35.29
35.07
34.51
25.02
24.59
24.54
14.58
f1 (ppm)
EtO
O
F

FLUORINE01
BC-1-29siena



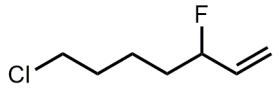


CKC0333PROTON01
CKC0333rota2



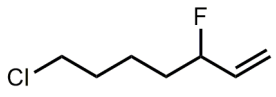
CKC0333CARBON01
CKC0333CH

136.76
136.61
117.45
117.35
94.33
93.00
77.61
77.36
77.11
45.07
34.81
34.63
32.59
22.46
22.42



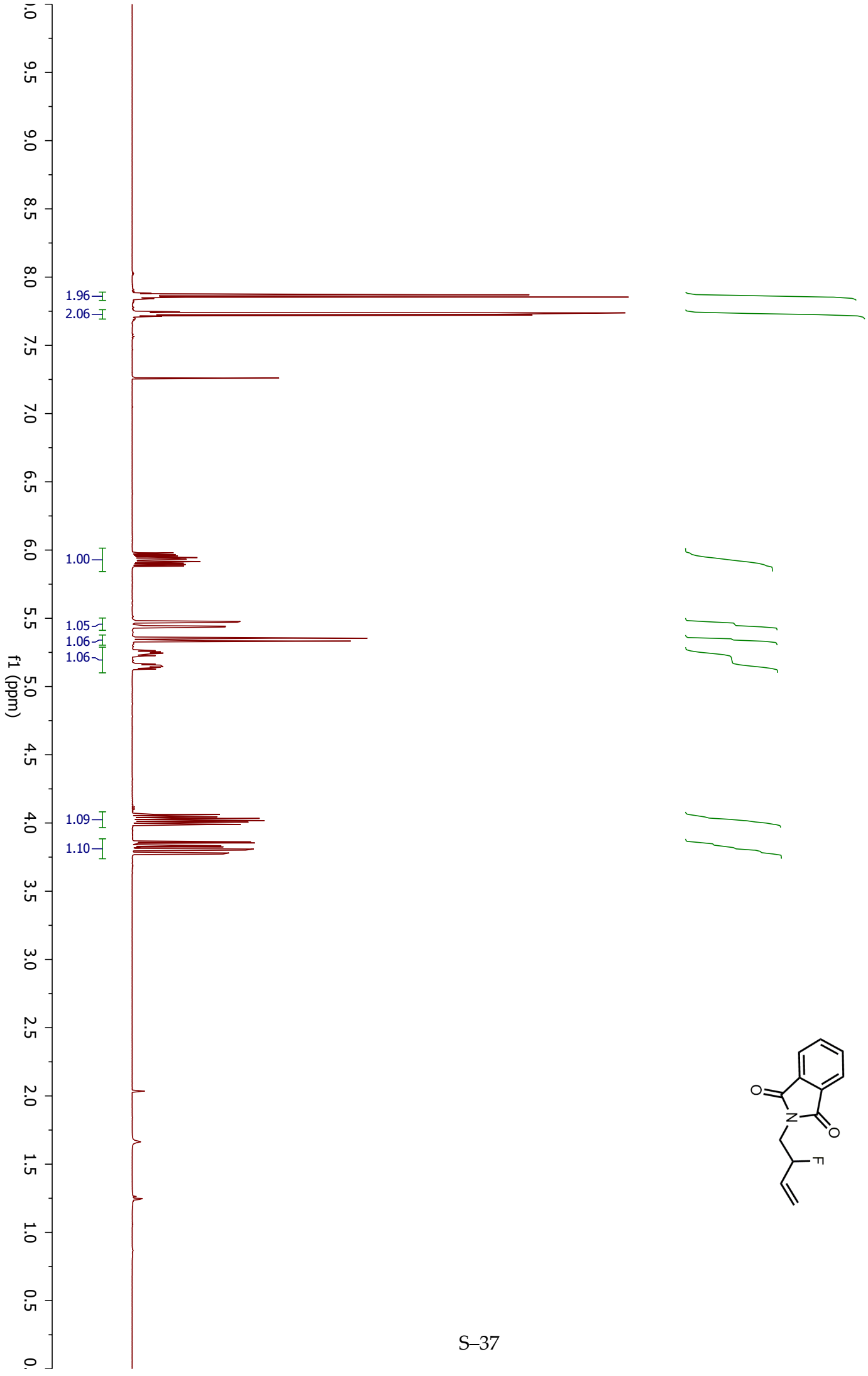
f1 (ppm)

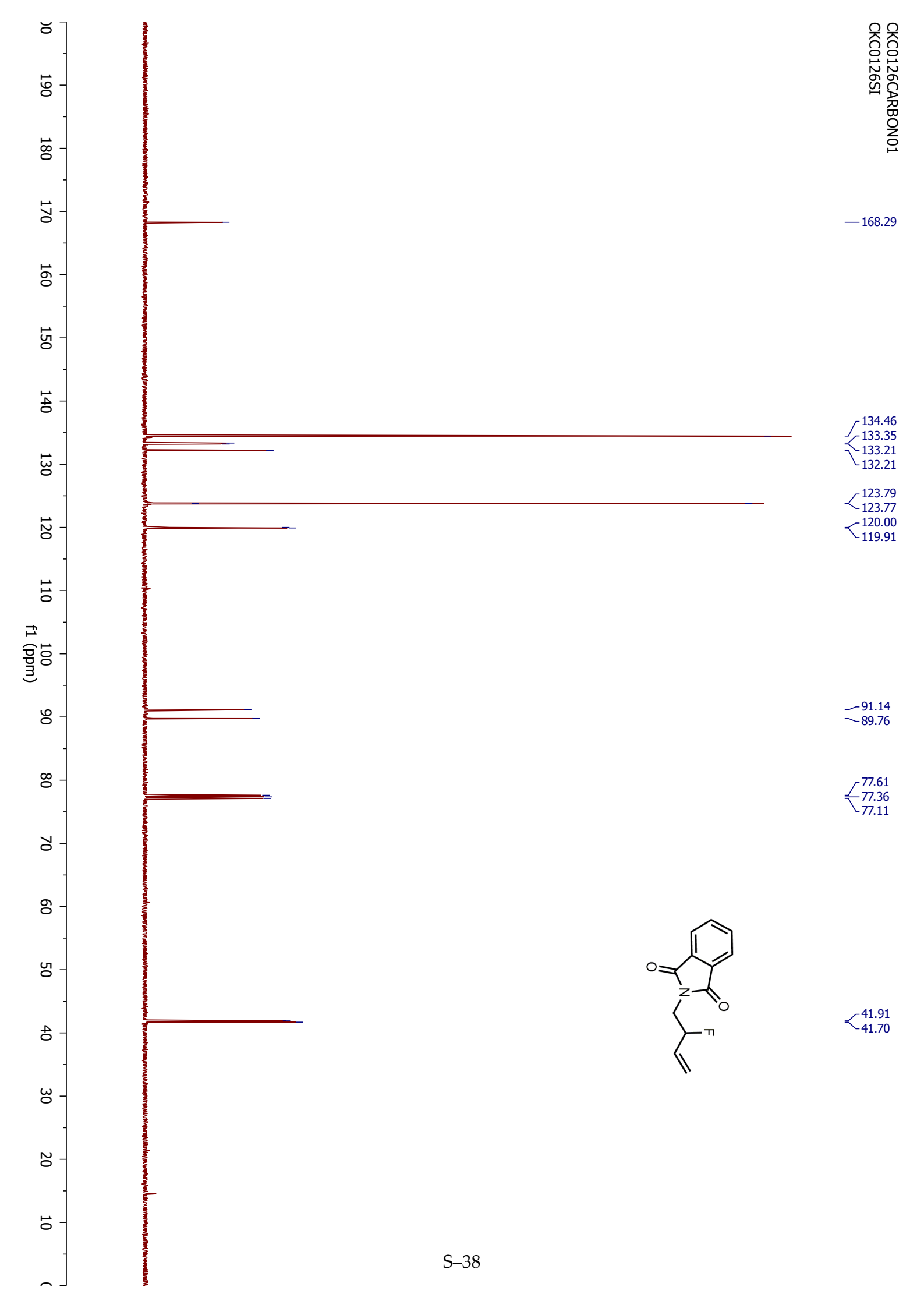
FLUORINE01
CKC0333siena



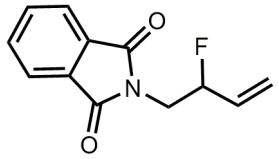
S–36

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


1.96
2.06
1.00
1.05
1.06
1.06
1.09
1.10
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
O
N
O
F

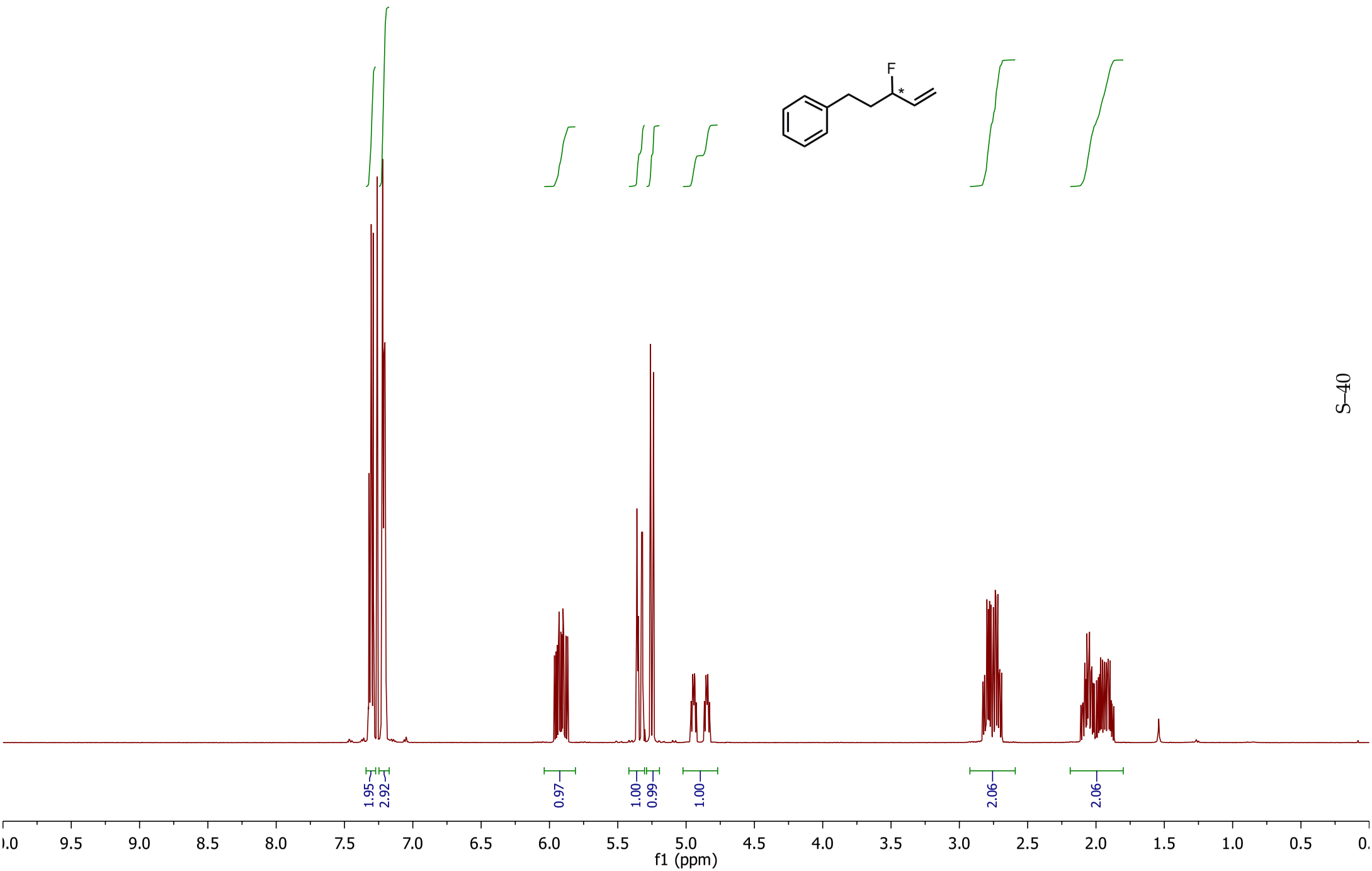

CKC0126CARBON01
CKC0126SI
168.29
134.46
133.35
133.21
132.21
123.79
123.77
120.00
119.91
91.14
89.76
77.61
77.36
77.11
41.91
41.70
f1 (ppm)
O
N
O
F

FLUORINE01
CKC0126siena



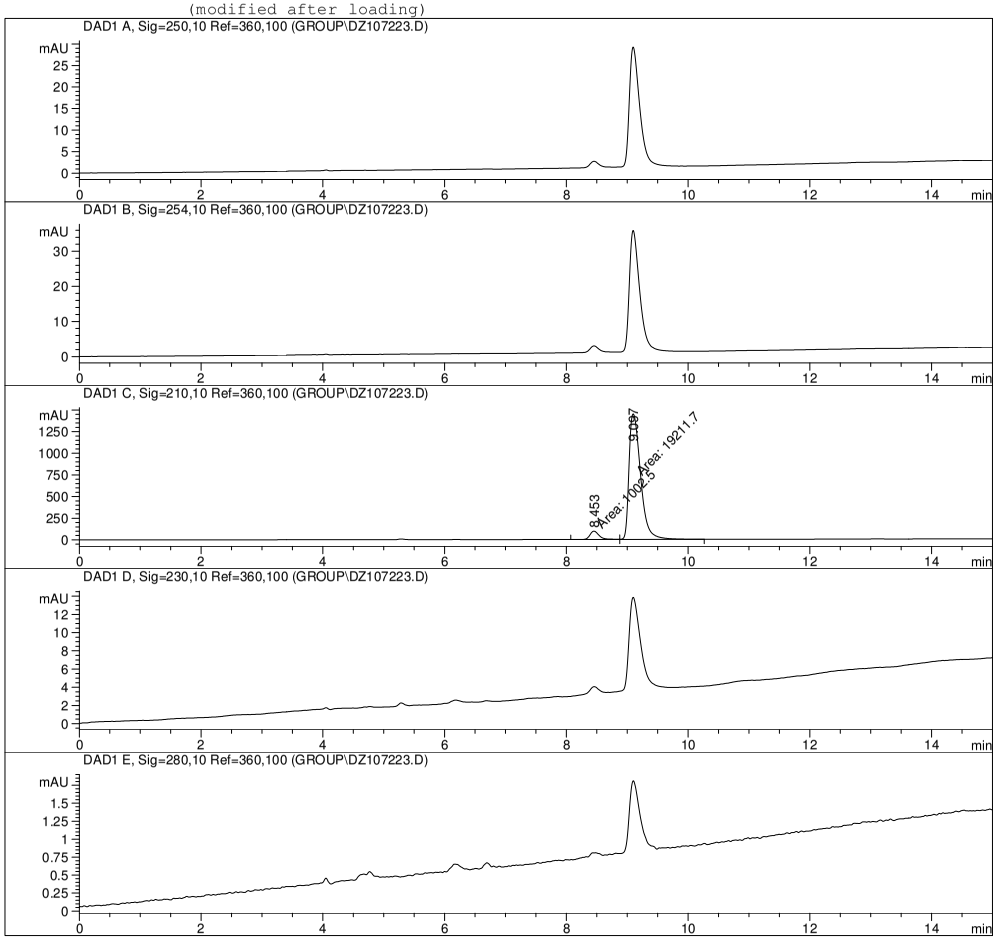
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

PROTON05
DZ-01-072-2-Purified



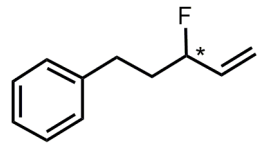
Data File C:\HPCHEM\1\DATA\GROUP\DZ107223.D

```
  ======================================================================
  Injection Date  : 1/28/2016 10:58:48 AM          Seq. Line :   2
  Sample Name     :                                 Location : Vial 28
  Acq. Operator   : XM                                  Inj :   1
  Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
  Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
  Acq. Method     : C:\HPCHEM\1\METHODS\OD-00535.M
  Last changed    : 1/15/2015 9:43:42 AM by SES
  Analysis Method : C:\HPCHEM\1\METHODS\OD-10-20.M
  Last changed    : 1/30/2016 1:16:09 PM by XM
                    (modified after loading)
```



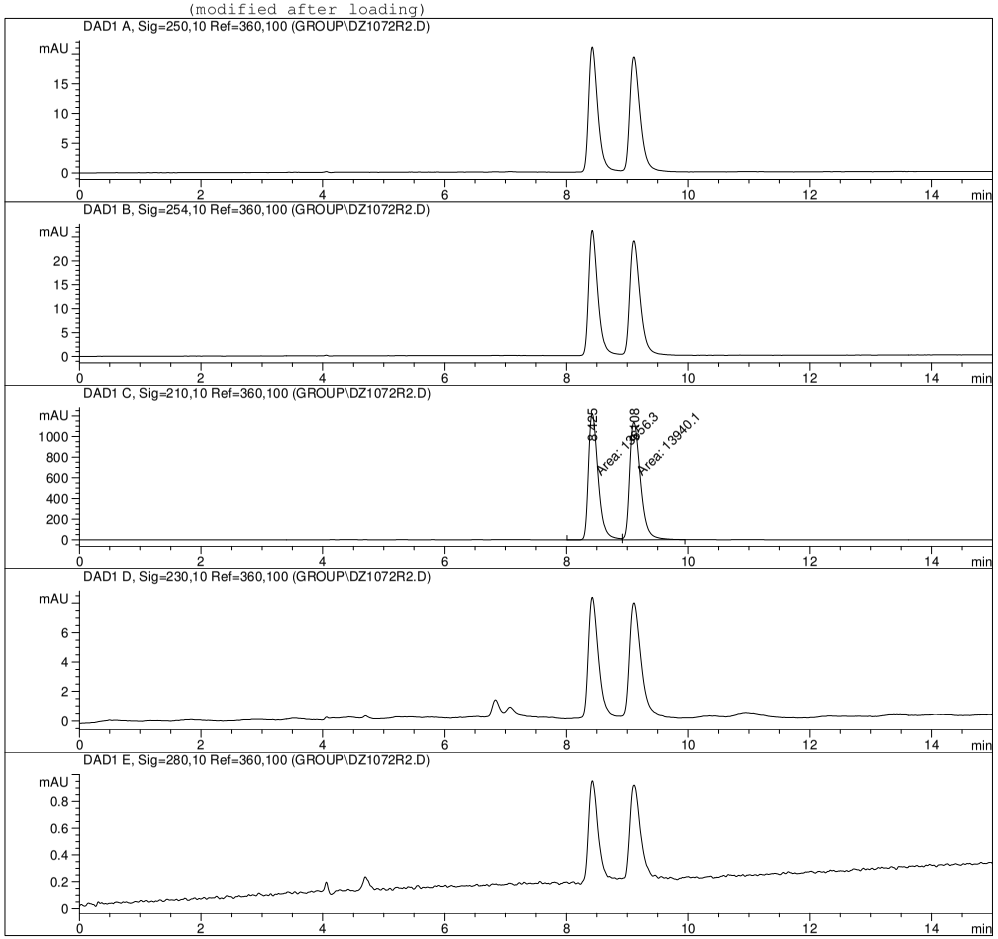
Data File C:\HPCHEM\1\DATA\GROUP\DZ107223.D

```
  ======================================================================
                            Area Percent Report
  ======================================================================

  Sorted By             :      Signal
  Multiplier            :      1.0000
  Dilution              :      1.0000
  Use Multiplier & Dilution Factor with ISTDs


  Signal 1: DAD1 A, Sig=250,10 Ref=360,100


  Signal 2: DAD1 B, Sig=254,10 Ref=360,100


  Signal 3: DAD1 C, Sig=210,10 Ref=360,100

  Peak RetTime Type  Width      Area       Height      Area
    #   [min]        [min]    [mAU*s]      [mAU]        %
  ----|-------|----|-------|----------|----------|--------|
     1   8.453 MF    0.1730 1002.50006   96.58179   4.9594
     2   9.097 FM    0.2206 1.92117e4  1451.21606  95.0406

  Totals :                   2.02142e4  1547.79786

   Results obtained with enhanced integrator!

  Signal 4: DAD1 D, Sig=230,10 Ref=360,100


  Signal 5: DAD1 E, Sig=280,10 Ref=360,100

  ======================================================================
                            *** End of Report ***
```



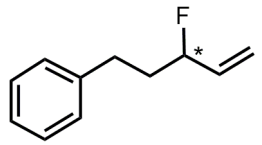
Data File C:\HPCHEM\1\DATA\GROUP\DZ1072R2.D

```
  ====================================================================
  Injection Date  : 1/28/2016 11:35:01 AM          Seq. Line :   3
  Sample Name     :                                 Location : Vial 29
  Acq. Operator   : XM                                  Inj :   1
  Acq. Instrument : Instrument 1                Inj Volume : 15 µl
  Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
  Acq. Method     : C:\HPCHEM\1\METHODS\OD-00535.M
  Last changed    : 1/15/2015 9:43:42 AM by SES
  Analysis Method : C:\HPCHEM\1\METHODS\OD-10-20.M
  Last changed    : 1/30/2016 1:16:09 PM by XM
                    (modified after loading)
```

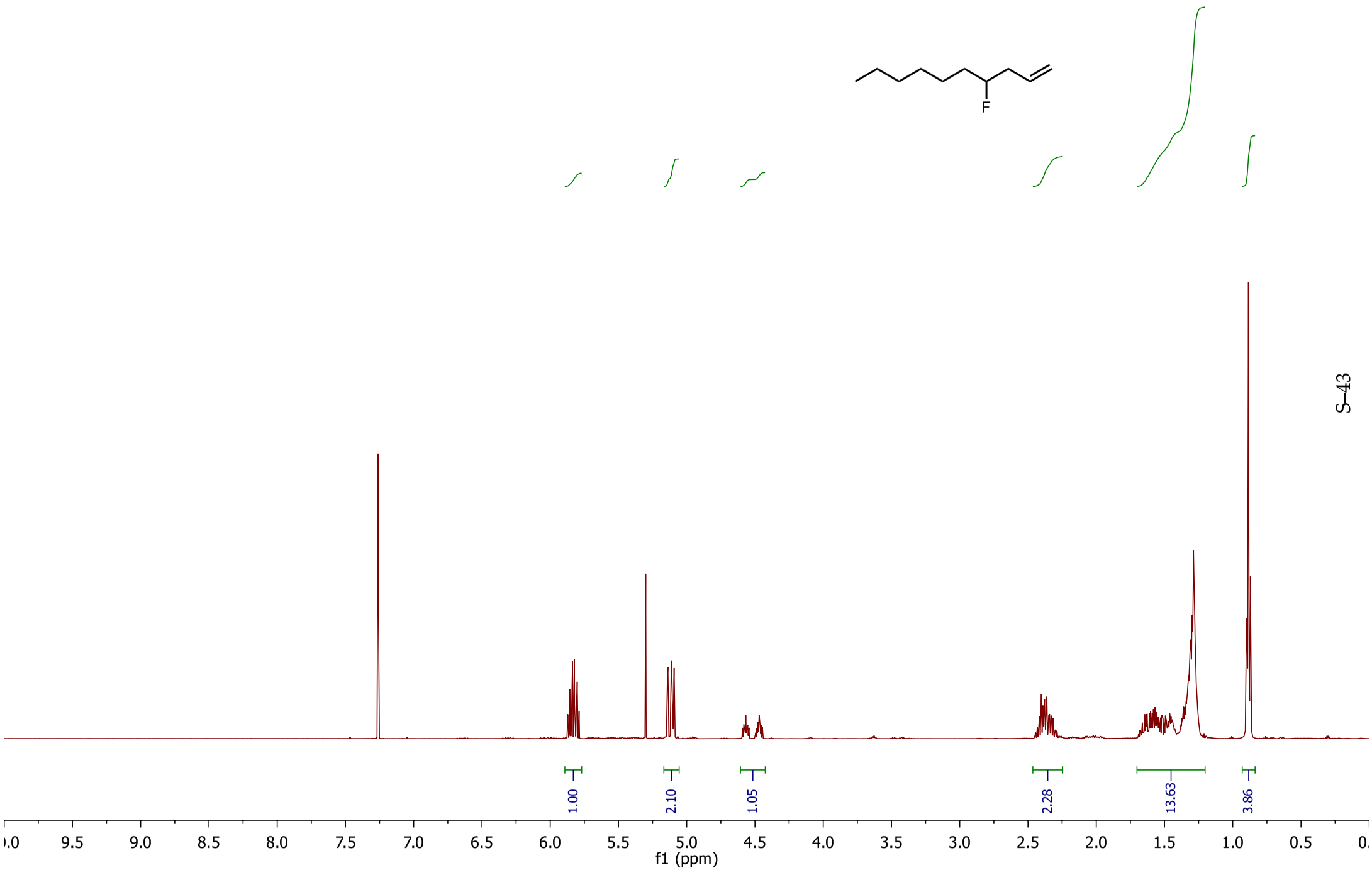


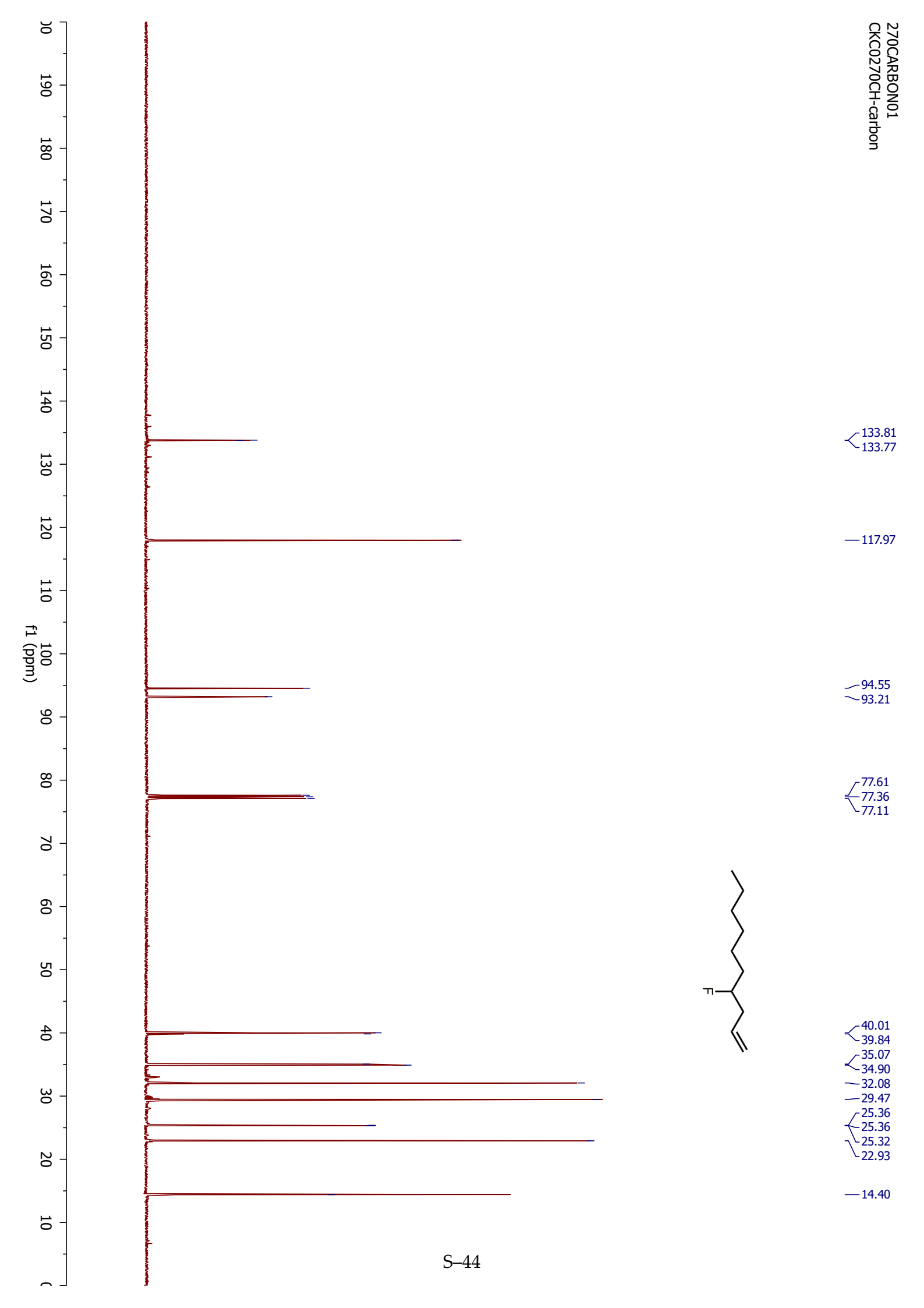
Data File C:\HPCHEM\1\DATA\GROUP\DZ1072R2.D

```
  ====================================================================
                          Area Percent Report
  ====================================================================

  Sorted By             :      Signal
  Multiplier            :      1.0000
  Dilution              :      1.0000
  Use Multiplier & Dilution Factor with ISTDs


  Signal 1: DAD1 A, Sig=250,10 Ref=360,100


  Signal 2: DAD1 B, Sig=254,10 Ref=360,100


  Signal 3: DAD1 C, Sig=210,10 Ref=360,100

  Peak RetTime Type  Width     Area      Height     Area
    #   [min]       [min]   [mAU*s]     [mAU]       %
  ----|-------|----|-------|----------|----------|--------|
     1   8.425 MF    0.1864 1.36563e4  1220.87537  49.4858
     2   9.108 FM    0.2043 1.39401e4  1137.04492  50.5142

  Totals :                   2.75963e4  2357.92029

   Results obtained with enhanced integrator!

  Signal 4: DAD1 D, Sig=230,10 Ref=360,100


  Signal 5: DAD1 E, Sig=280,10 Ref=360,100

  ====================================================================
                          *** End of Report ***
```

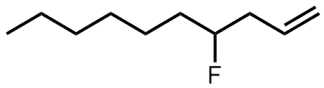


270PROTON01
CKC0270CH-proton



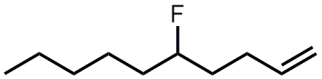

270CARBON01
CKC0270CH-carbon
f1 (ppm)
133.81
133.77
117.97
94.55
93.21
77.61
77.36
77.11
40.01
39.84
35.07
34.90
32.08
29.47
25.36
25.36
25.32
22.93
14.40
F

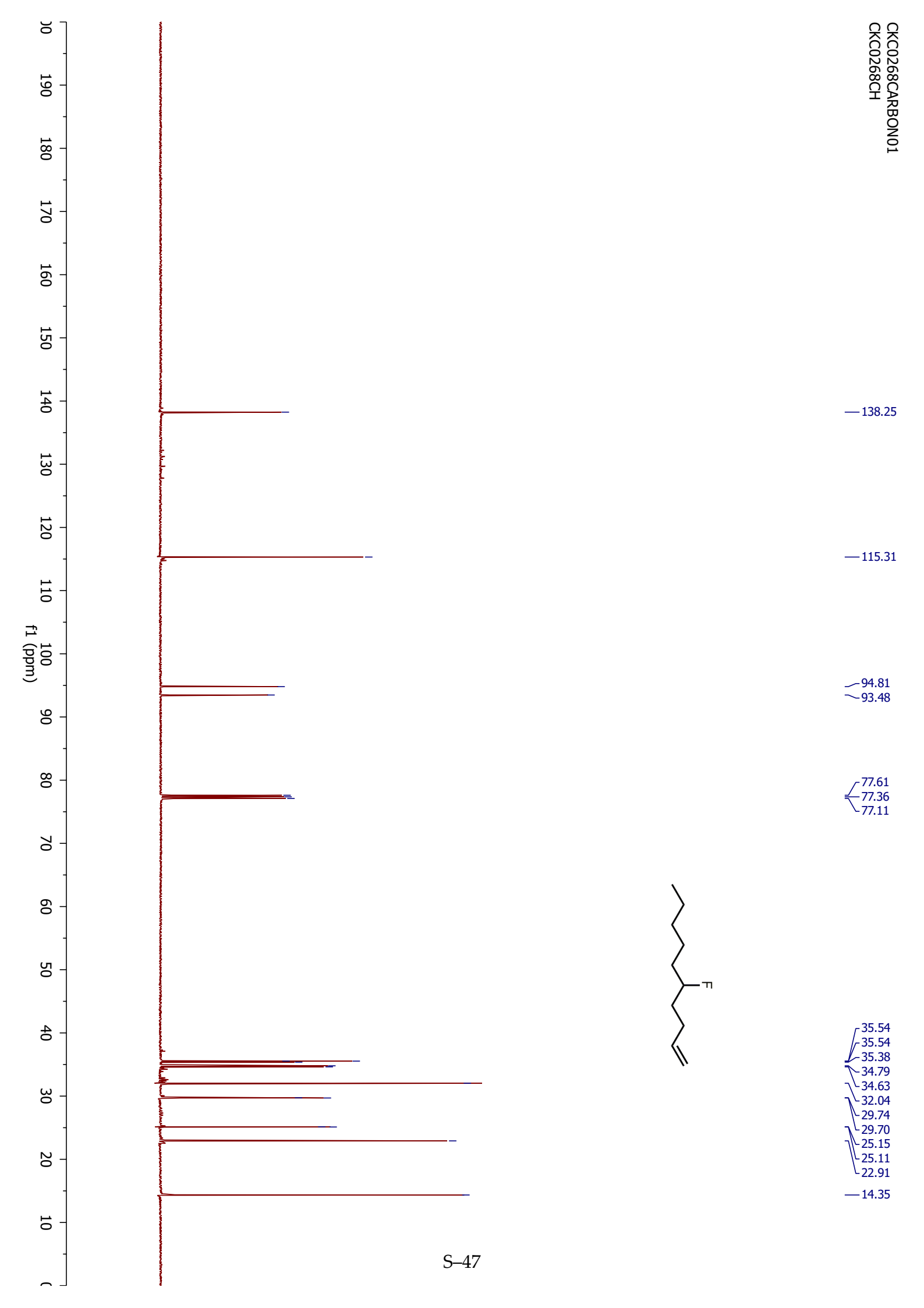
FLUORINE01
CKC0270sienaNo2



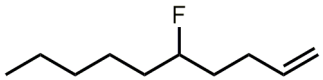
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

CKC0268nosolvent
CKC0268-7-8-15



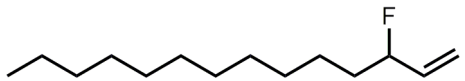

CKC0268CARBON01
CKC0268CH
f1 (ppm)
138.25
115.31
94.81
93.48
77.61
77.36
77.11
35.54
35.54
35.38
34.79
34.63
32.04
29.74
29.70
25.15
25.11
22.91
14.35
F

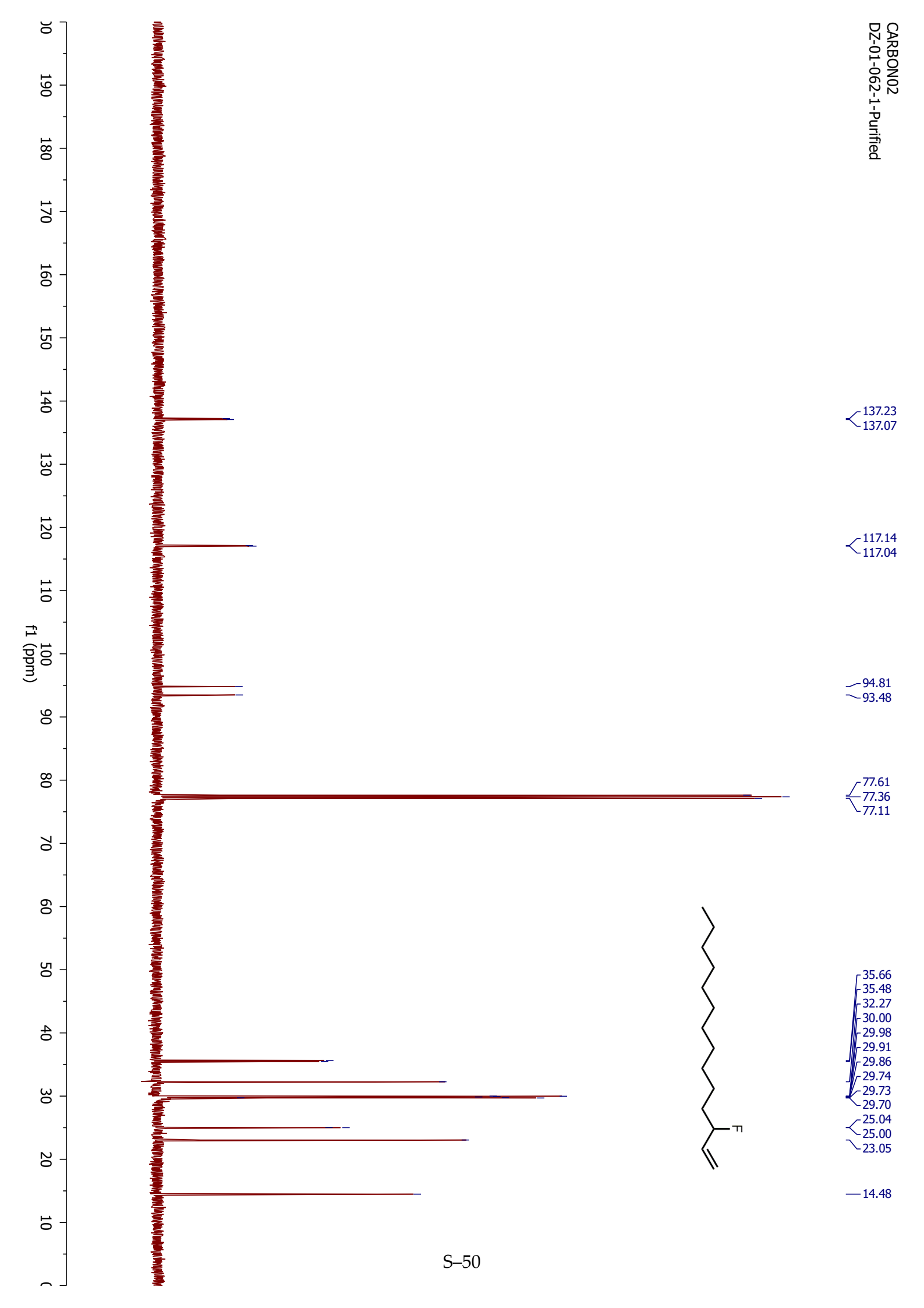
FLUORINE01
CKC0268siena



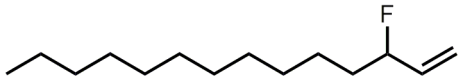
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

PROTON03
DZ-01-062-1-Purified




CARBON02
DZ-01-062-1-Purified
f1 (ppm)
137.23
137.07
117.14
117.04
94.81
93.48
77.61
77.36
77.11
35.66
35.48
32.27
30.00
29.98
29.91
29.86
29.74
29.73
29.70
25.04
25.00
23.05
14.48
F

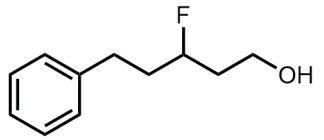
FLUORINE01
BC-1-29siena



0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250

f1 (ppm)

BC-1-60PROTON01
bc-I-60-pure_13C_1H

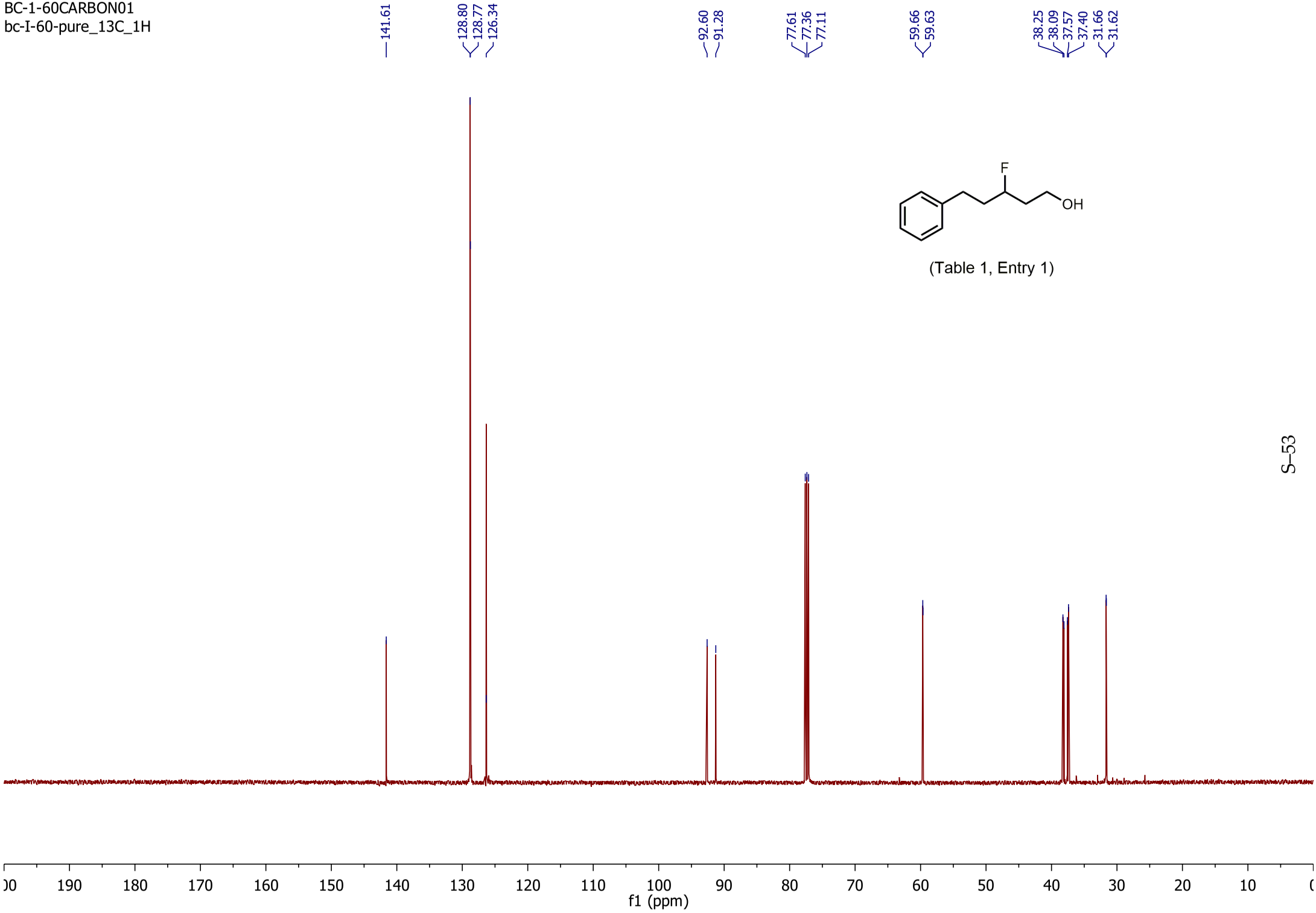


(Table 1, Entry 1)

1.97 3.00 1.00 2.02 1.02 1.03 4.15 1.35

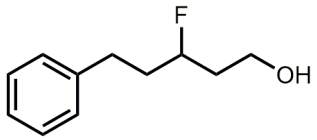
f1 (ppm)

BC-1-60CARBON01
bc-I-60-pure_13C_1H



(Table 1, Entry 1)

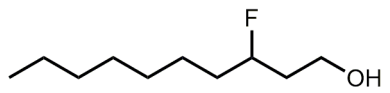
FLUORINE01
CKC0064siena



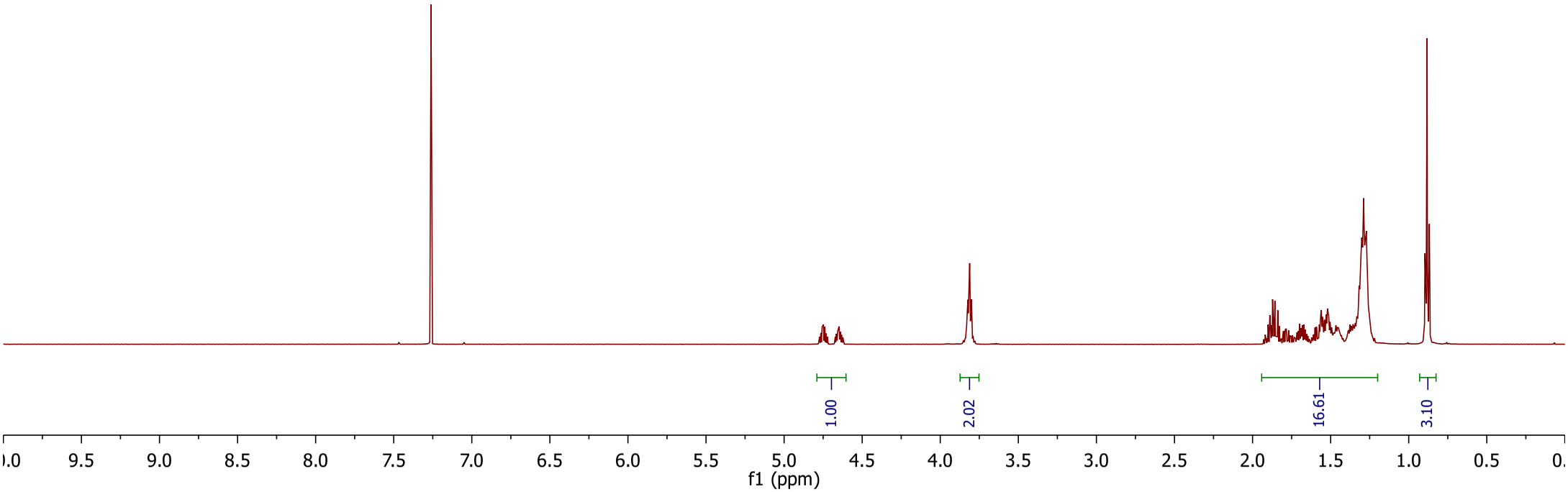
(Table 1, Entry 1)

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

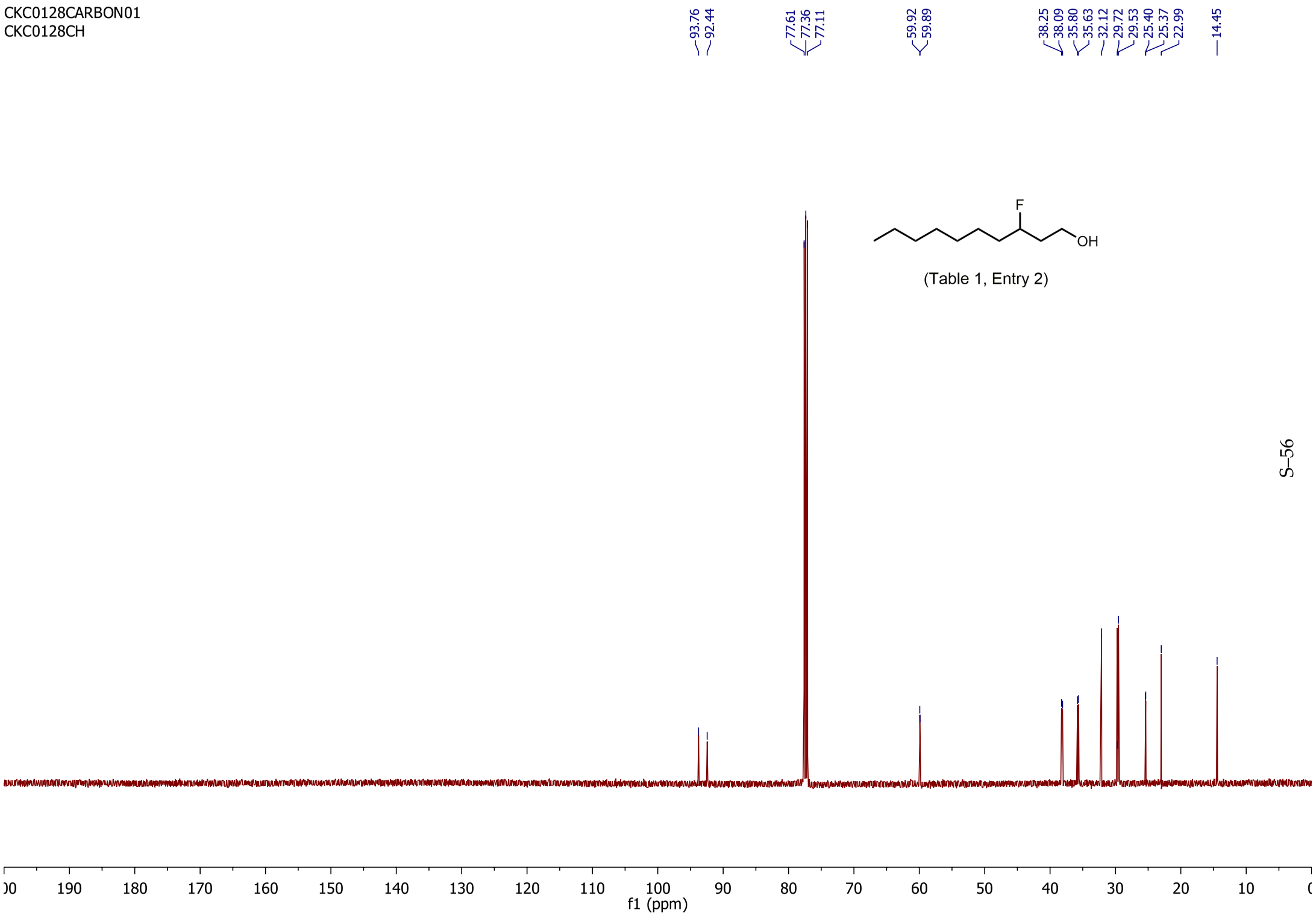
CKC0128PROTON01
CKC0128hivac



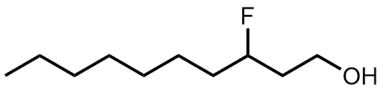
(Table 1, Entry 2)



CKC0128CARBON01
CKC0128CH



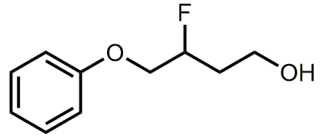
FLUORINE01
CKC0128siena



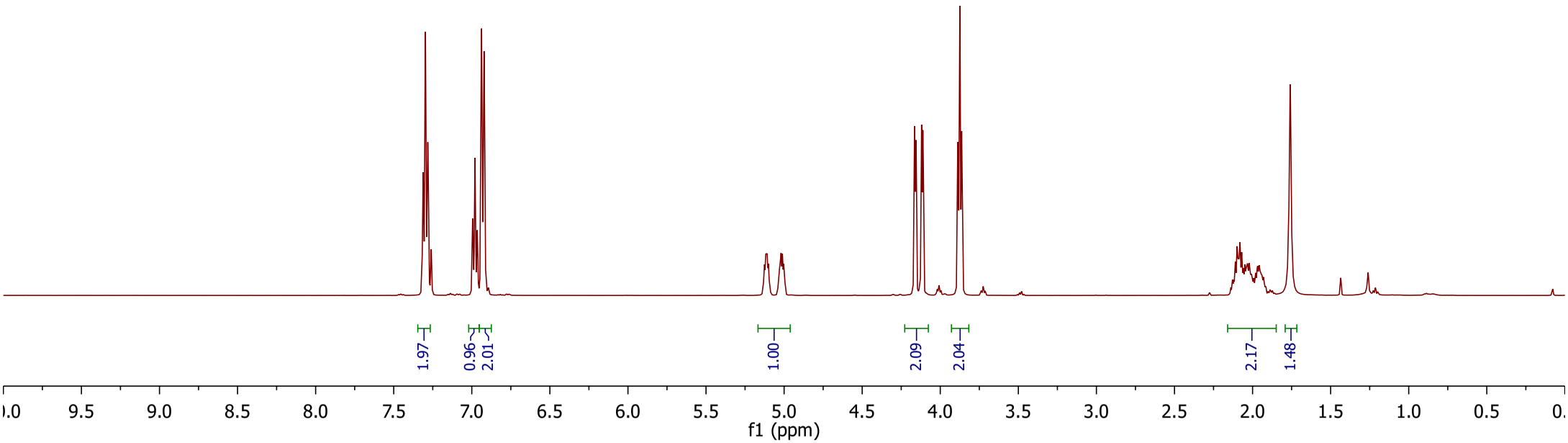
(Table 1, Entry 2)

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

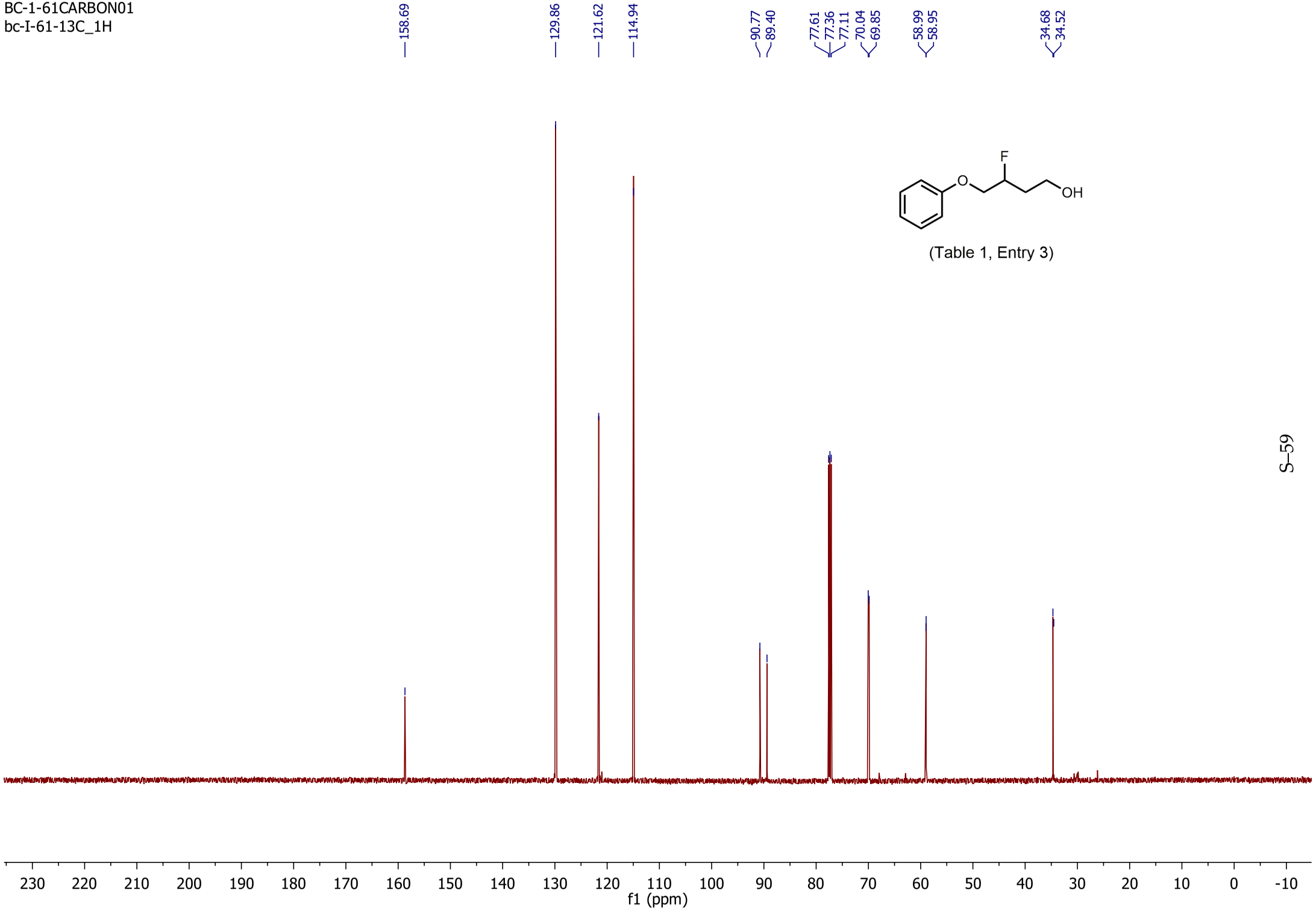
BC-1-61PROTON01
bc-I-61-13C_1H



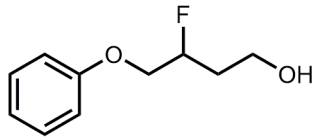
(Table 1, Entry 3)



BC-1-61CARBON01
bc-I-61-13C_1H



FLUORINE01
CKC0103siena

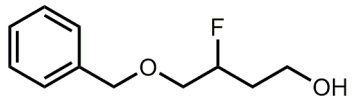


(Table 1, Entry 3)

S–60

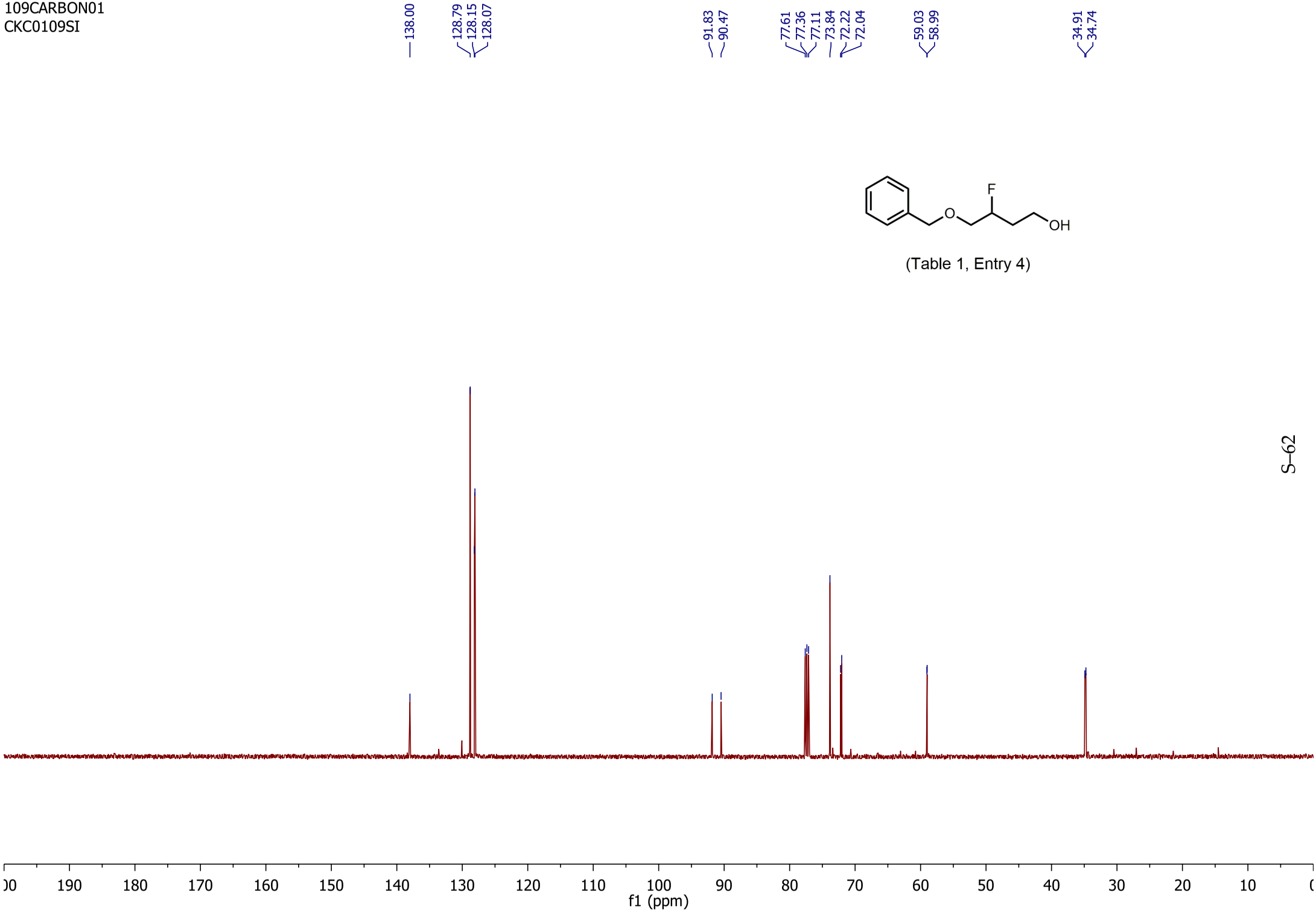
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

CKC0109CH-protonRE
CKC0109CH-protonRE



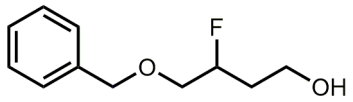
(Table 1, Entry 4)

109CARBON01
CKC0109SI



(Table 1, Entry 4)

FLUORINE01
CKC0109siena

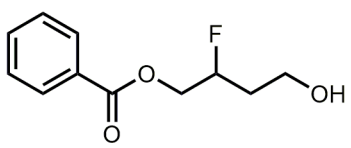


(Table 1, Entry 4)

S–63

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

108PROTON01
CKC0108CH-proton



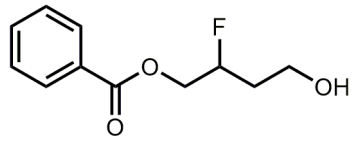
(Table 1, Entry 5)

1.88 1.05 2.20 1.00 2.22 2.07 2.34 1.38

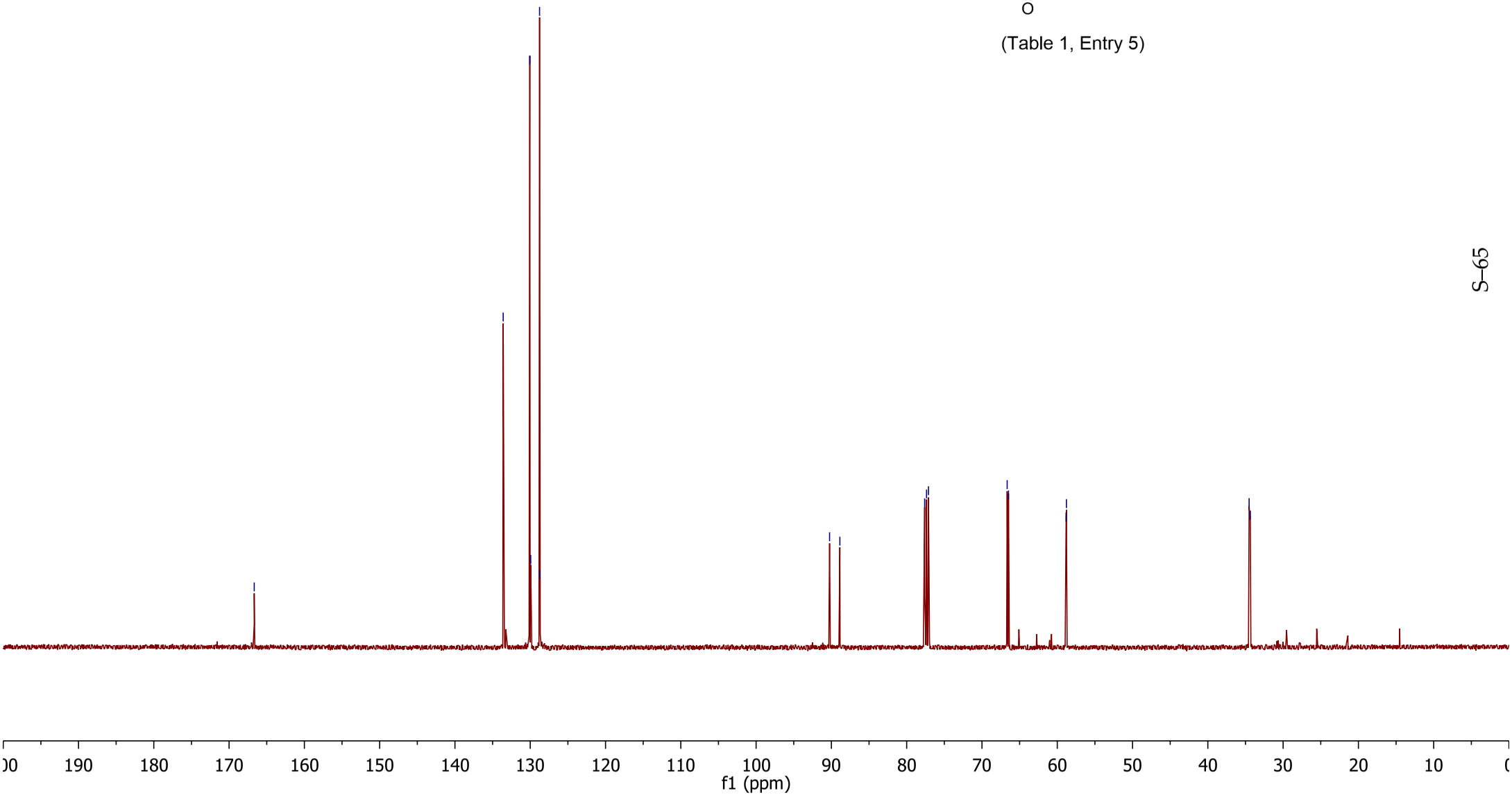
f1 (ppm)

108CARBON01
CKC0108SI

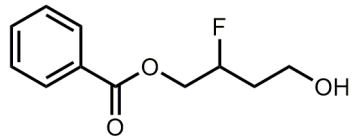
166.66
133.59
130.06
129.94
128.76
128.75
90.24
88.87
77.61
77.36
77.11
66.65
66.48
58.82
58.78
34.52
34.35



(Table 1, Entry 5)



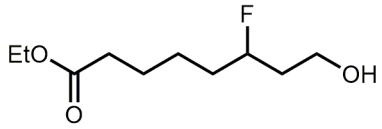
FLUORINE01
CKC0108siena



(Table 1, Entry 5)

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

CKC0154PROTON01
CKC0154hivac

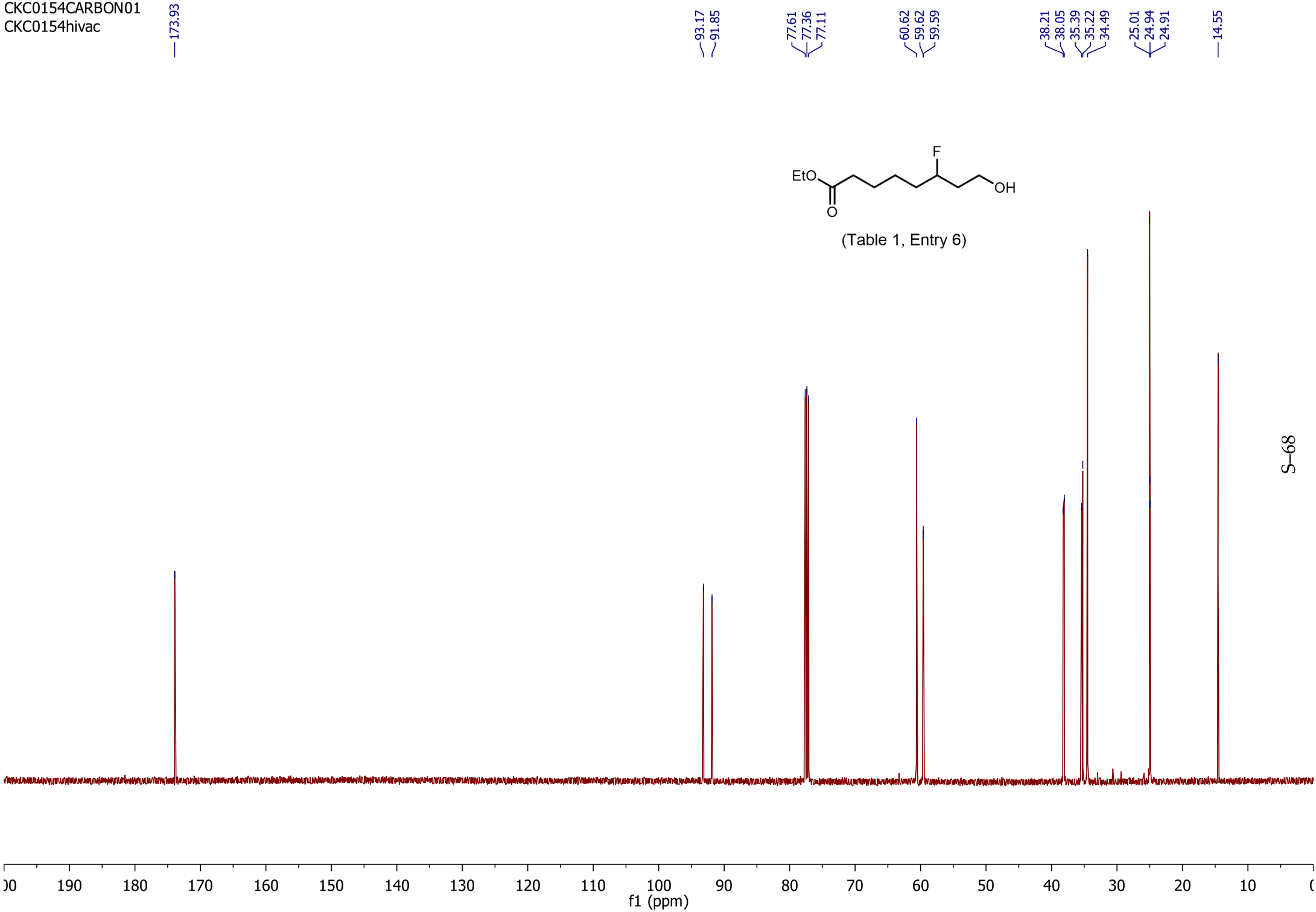


(Table 1, Entry 6)

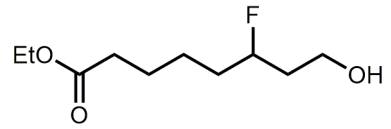
1.00 1.99 2.00 2.06 9.63 3.07

f1 (ppm)

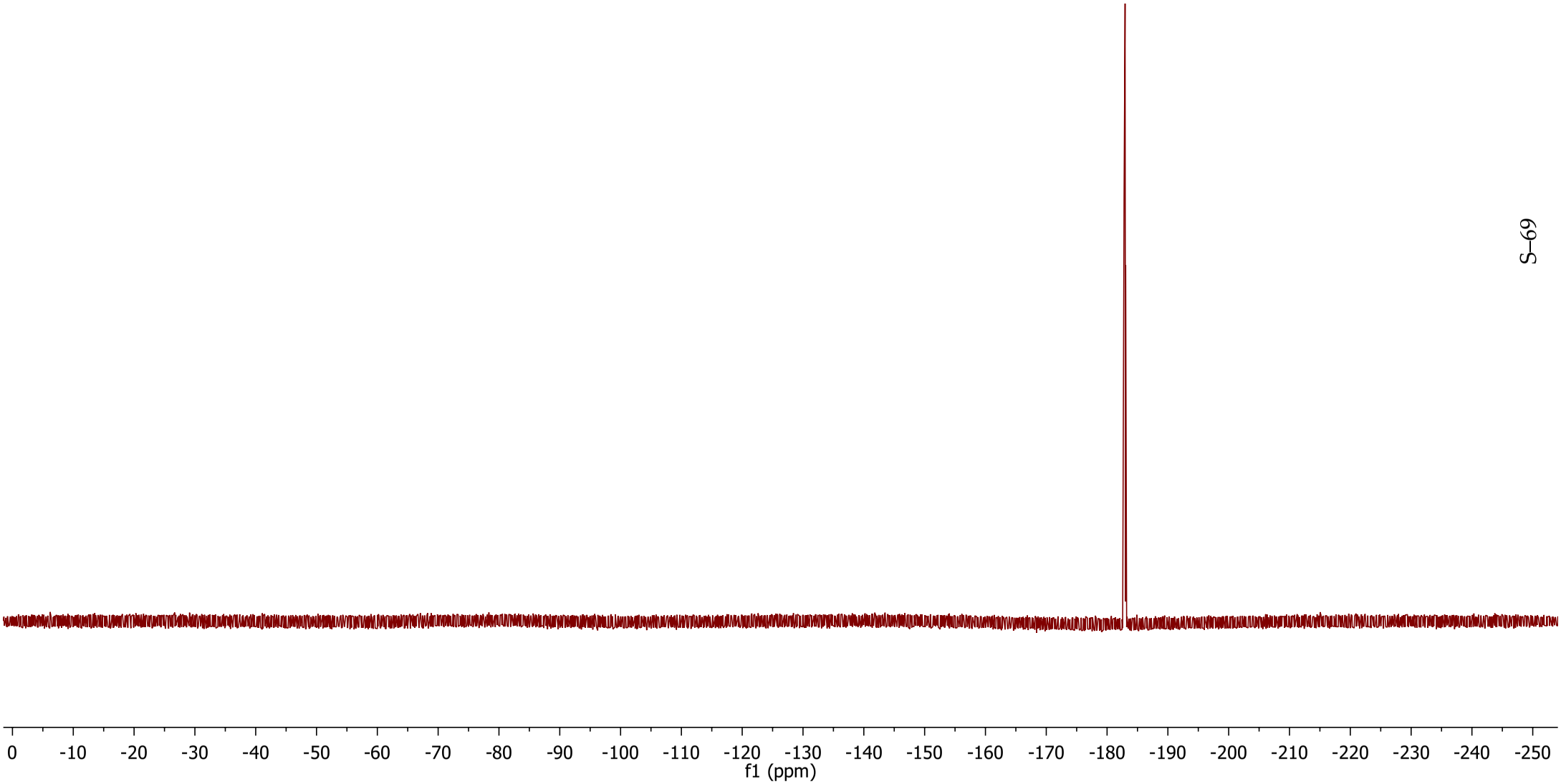
CKC0154CARBON01
CKC0154hivac

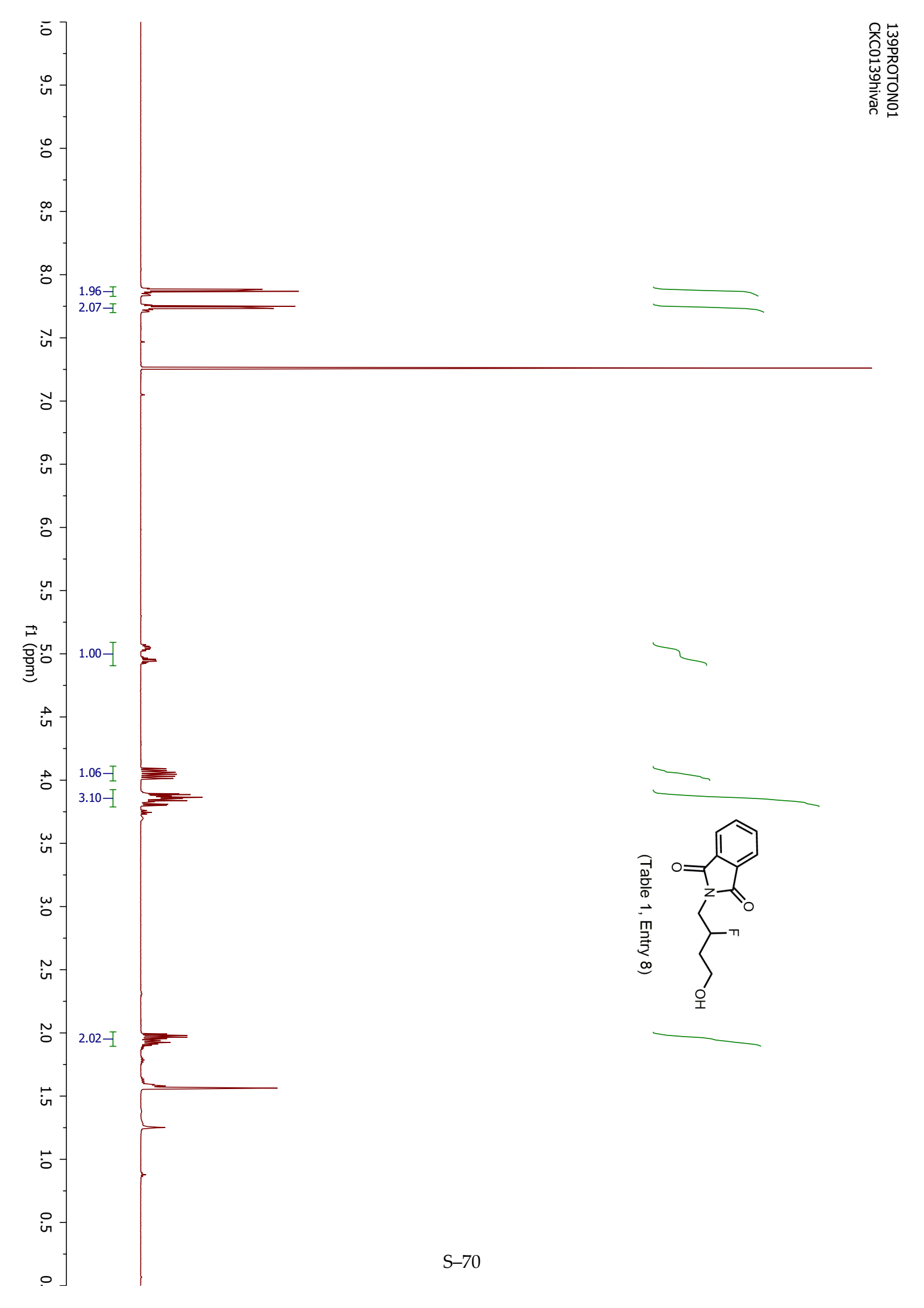


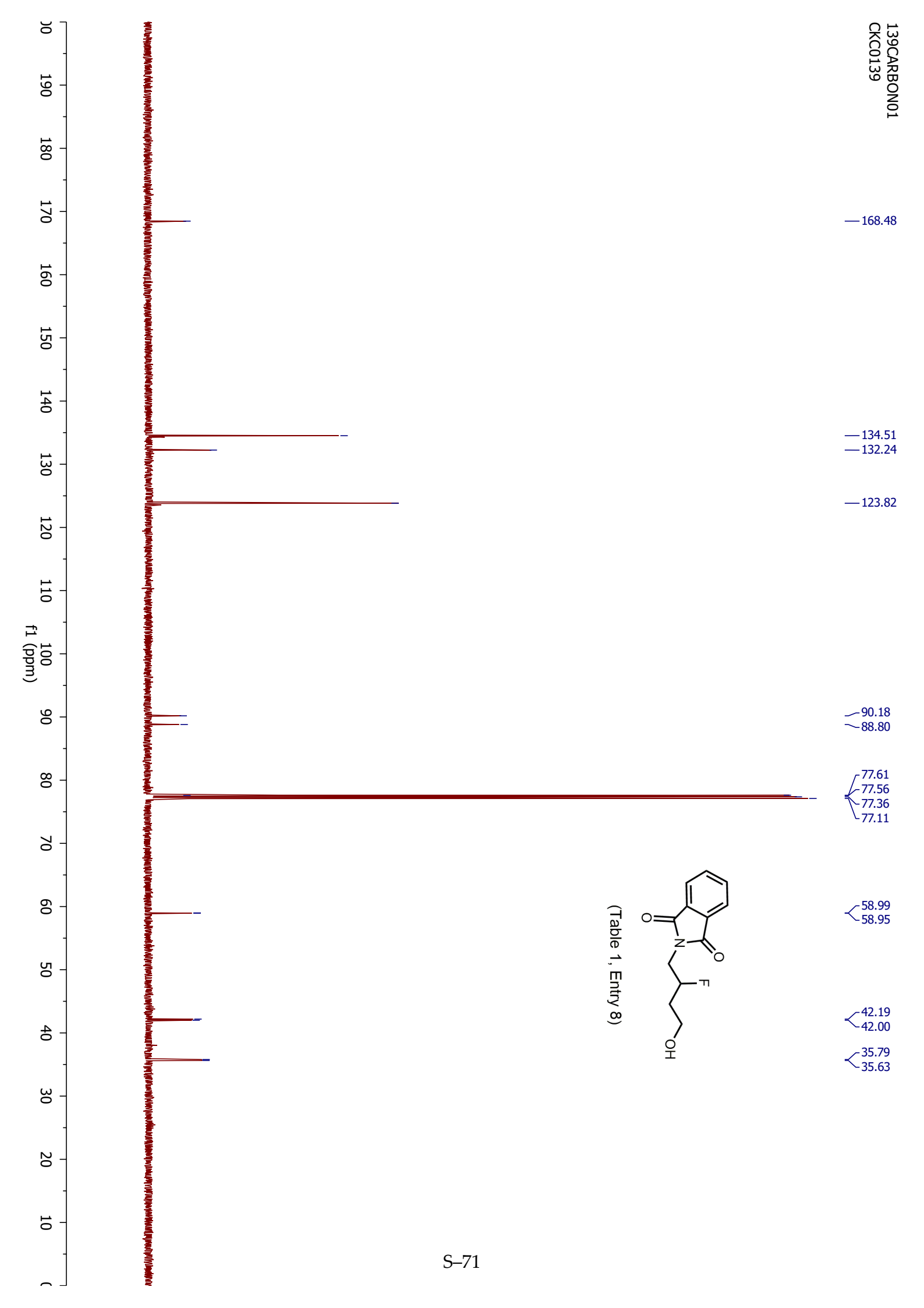
FLUORINE01
BC-1-29siena



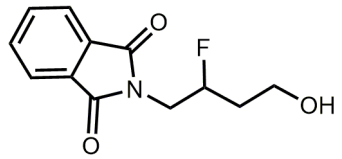
(Table 1, Entry 6)



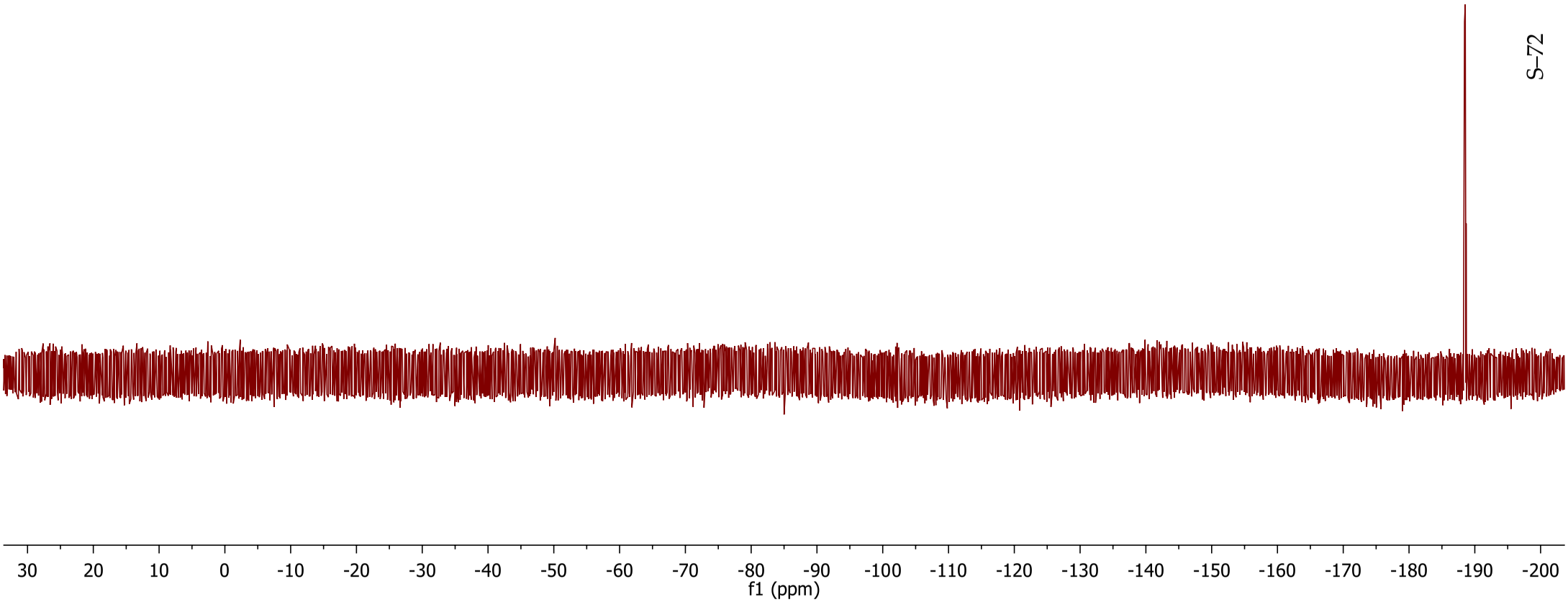

139PROTON01
CKC0139hivac
1.96
2.07
1.00
1.06
3.10
2.02
f1 (ppm)
(Table 1, Entry 8)
O
N
O
F
OH


139CARBON01
CKC0139
168.48
134.51
132.24
123.82
90.18
88.80
77.61
77.56
77.36
77.11
58.99
58.95
42.19
42.00
35.79
35.63
f1 (ppm)
(Table 1, Entry 8)
O
N
O
F
OH

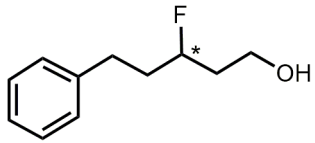
FLUORINE01
CKC0139siena



(Table 1, Entry 8)



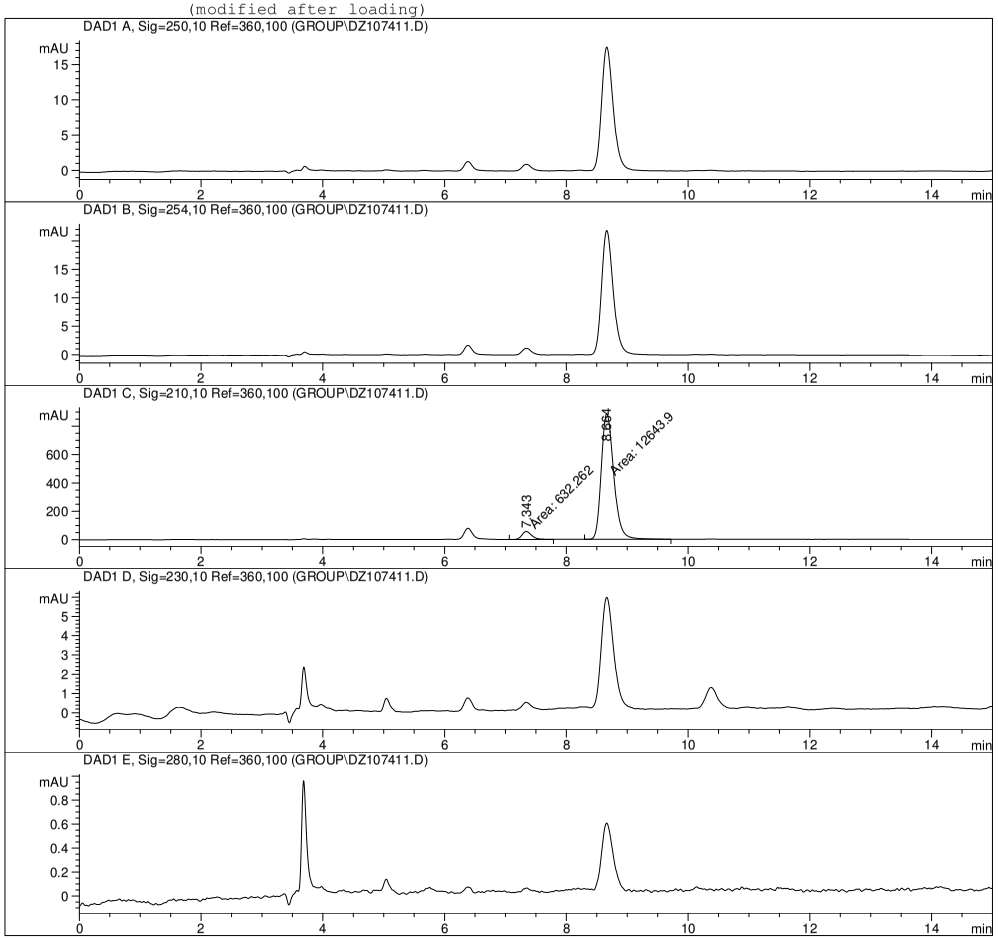
PROTON03
DZ-01-074-1-Purified



(Equation 1)

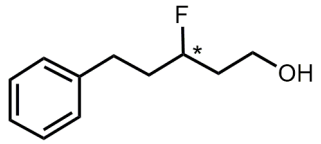
Data File C:\HPCHEM\1\DATA\GROUP\DZ107411.D

```
  ====================================================================
  Injection Date  : 1/30/2016 12:27:33 PM          Seq. Line :   3
  Sample Name     :                                 Location : Vial 2
  Acq. Operator   : XM                                  Inj :   1
  Acq. Instrument : Instrument 1                Inj Volume : 15 µl
  Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
  Acq. Method     : C:\HPCHEM\1\METHODS\OD-15-20.M
  Last changed    : 5/19/2011 9:25:09 PM by NB
  Analysis Method : C:\HPCHEM\1\METHODS\OD-10-20.M
  Last changed    : 1/30/2016 1:16:09 PM by XM
                    (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\DZ107411.D

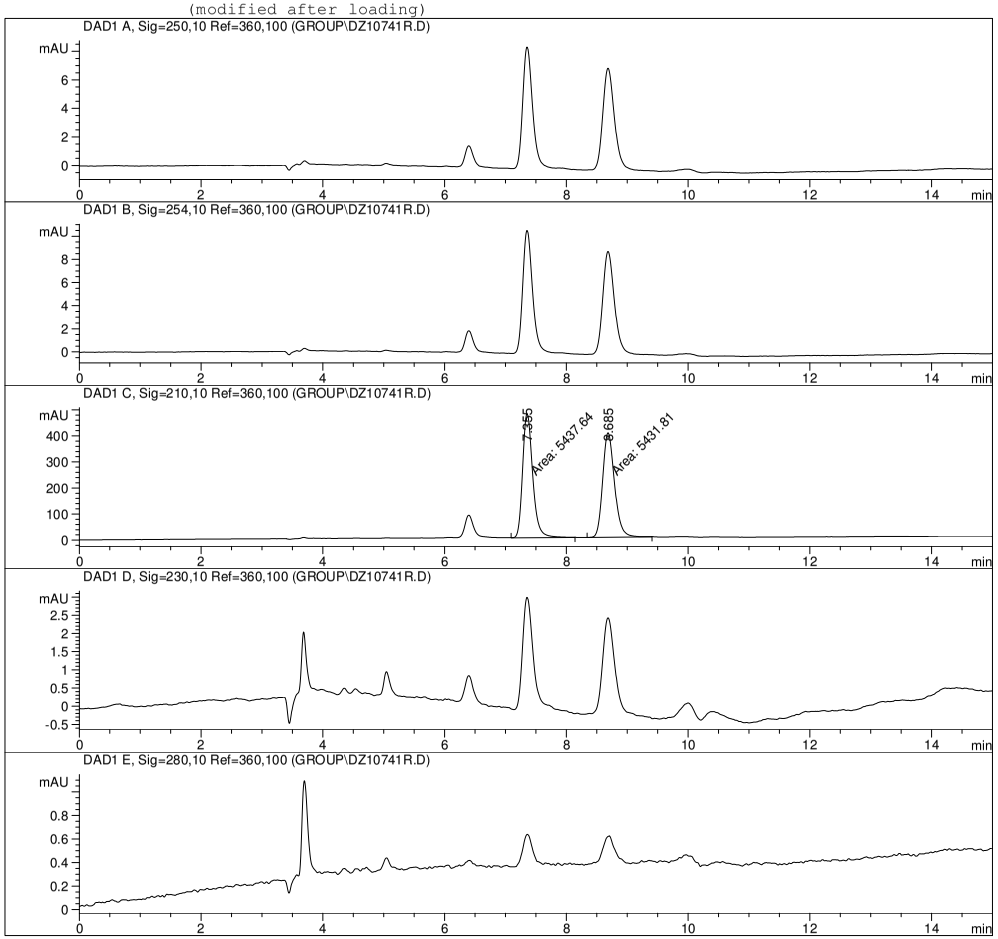
```
  ====================================================================
                          Area Percent Report
  ====================================================================

  Sorted By             :      Signal
  Multiplier            :      1.0000
  Dilution              :      1.0000
  Use Multiplier & Dilution Factor with ISTDs


  Signal 1: DAD1 A, Sig=250,10 Ref=360,100


  Signal 2: DAD1 B, Sig=254,10 Ref=360,100


  Signal 3: DAD1 C, Sig=210,10 Ref=360,100

  Peak RetTime Type  Width     Area      Height     Area
    #   [min]       [min]   [mAU*s]     [mAU]       %
  ----|-------|----|-------|----------|----------|--------|
     1   7.343 MM    0.1888  632.26190   55.80346   4.7624
     2   8.664 MM    0.2383 1.26439e4   884.45312  95.2376

  Totals :                   1.32762e4   940.25658

   Results obtained with enhanced integrator!

  Signal 4: DAD1 D, Sig=230,10 Ref=360,100


  Signal 5: DAD1 E, Sig=280,10 Ref=360,100

  ====================================================================
                          *** End of Report ***
```



(Equation 1)

Data File C:\HPCHEM\1\DATA\GROUP\DZ10741R.D

Injection Date	: 1/30/2016 12:06:19 PM	Seq. Line	: 2
Sample Name	:	Location	: Vial 1
Acq. Operator	: XM	Inj	: 1
Acq. Instrument	: Instrument 1	Inj Volume	: 15 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 2 µl
Acq. Method	: C:\HPCHEM\1\METHODS\OD-15-20.M		
Last changed	: 5/19/2011 9:25:09 PM by NB		
Analysis Method	: C:\HPCHEM\1\METHODS\OD-10-20.M		
Last changed	: 1/30/2016 1:16:09 PM by XM		
	(modified after loading)		



Data File C:\HPCHEM\1\DATA\GROUP\DZ10741R.D

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Signal 2: DAD1 B, Sig=254,10 Ref=360,100

Signal 3: DAD1 C, Sig=210,10 Ref=360,100

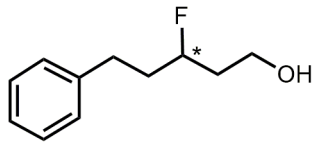
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.355	MM	0.1907	5437.64014	475.33261	50.0268
2	8.685	MM	0.2258	5431.81152	400.93201	49.9732
Totals :				1.08695e4	876.26462	

Results obtained with enhanced integrator!

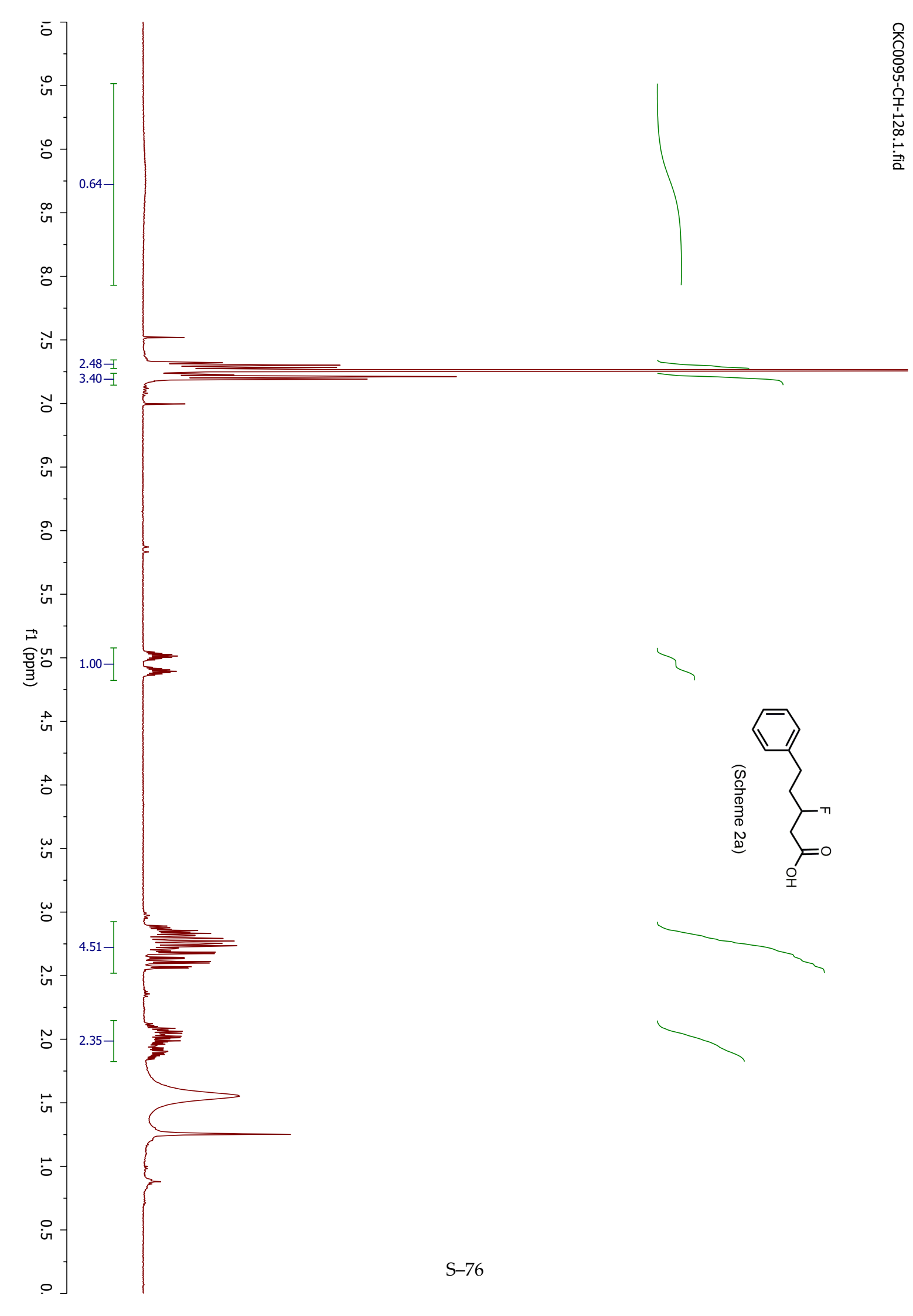
Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Signal 5: DAD1 E, Sig=280,10 Ref=360,100

*** End of Report ***

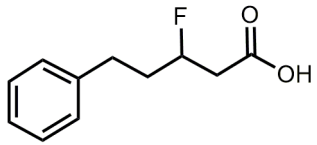


(Equation 1)


CKC0095-CH-128.1.fid
0.64
2.48
3.40
1.00
4.51
2.35
f1 (ppm)
(Scheme 2a)
F
O
OH

CKC0095-repurified-carbon.1.fid

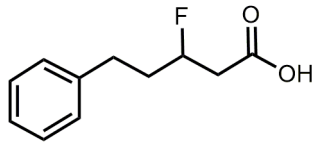
176.21
176.17
141.09
128.89
128.76
126.52
90.34
88.64
77.68
77.56
77.36
77.04
40.55
40.31
36.98
36.78
31.44
31.40



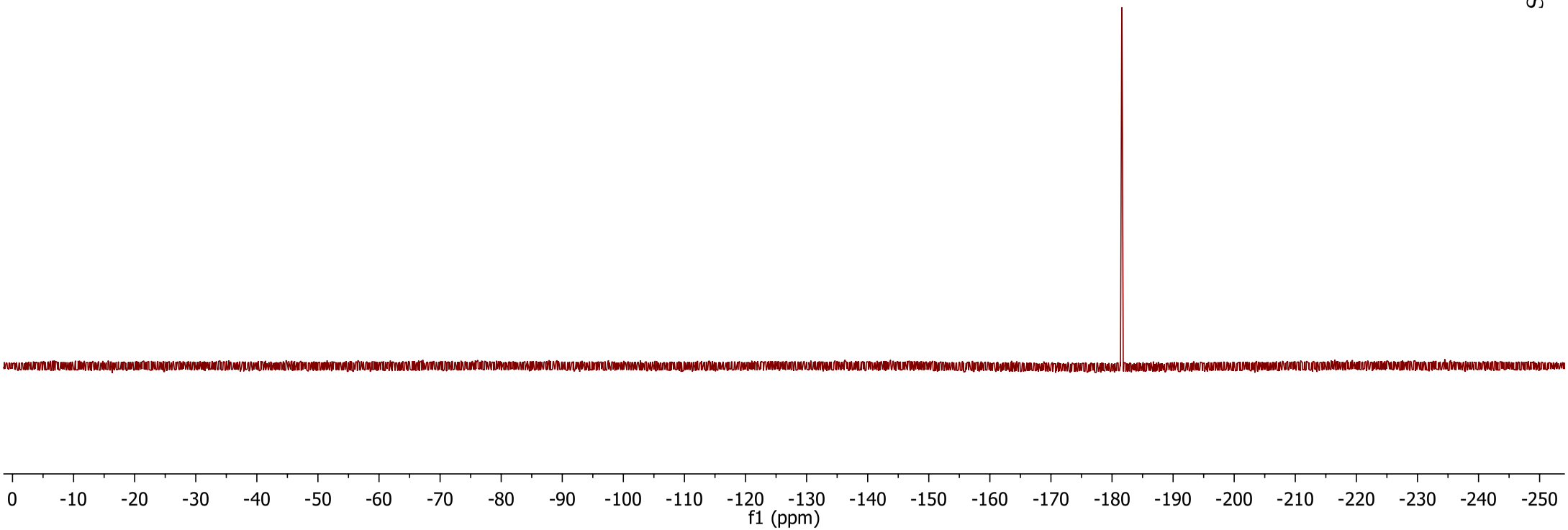
(Scheme 2a)

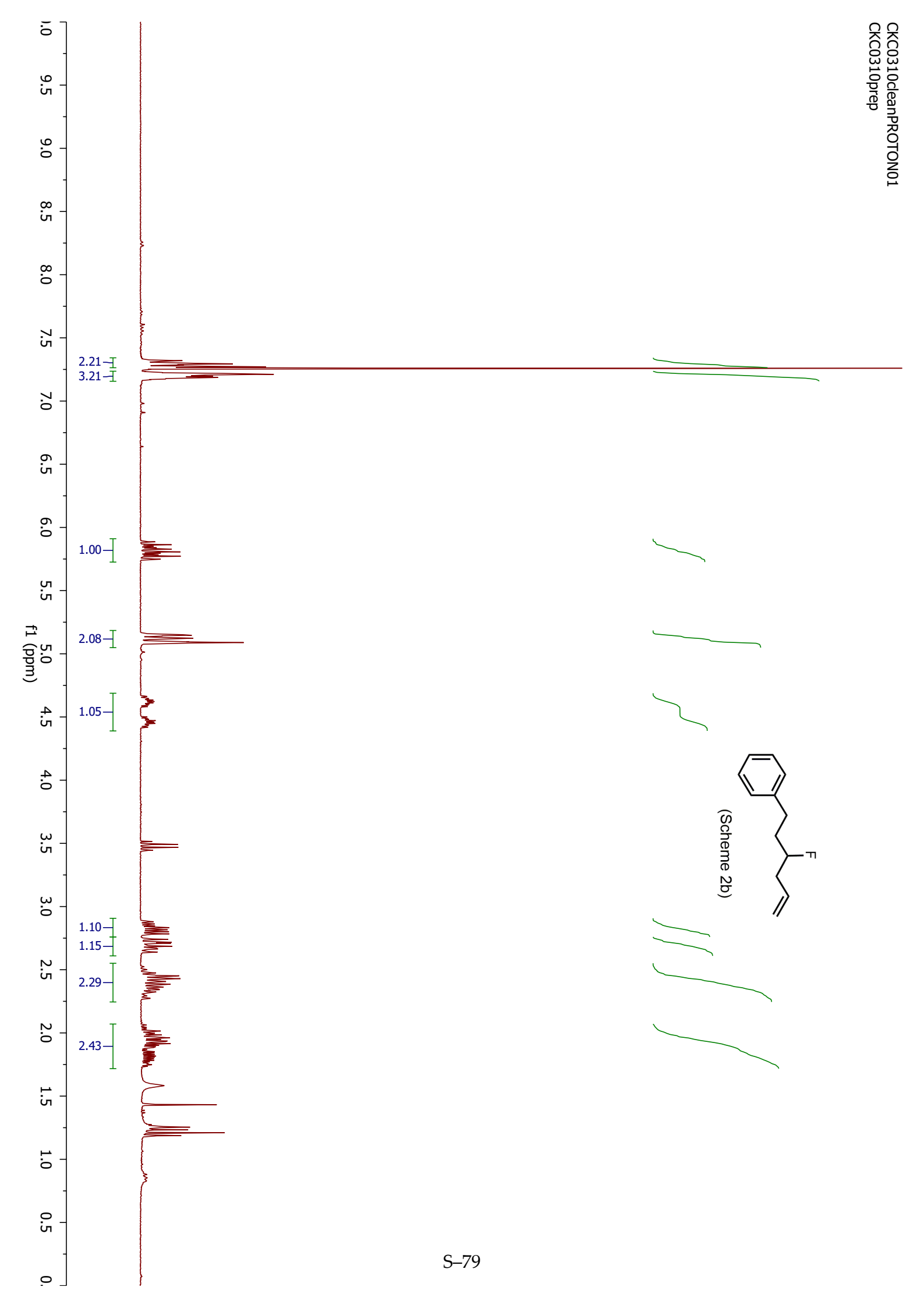
f1 (ppm)

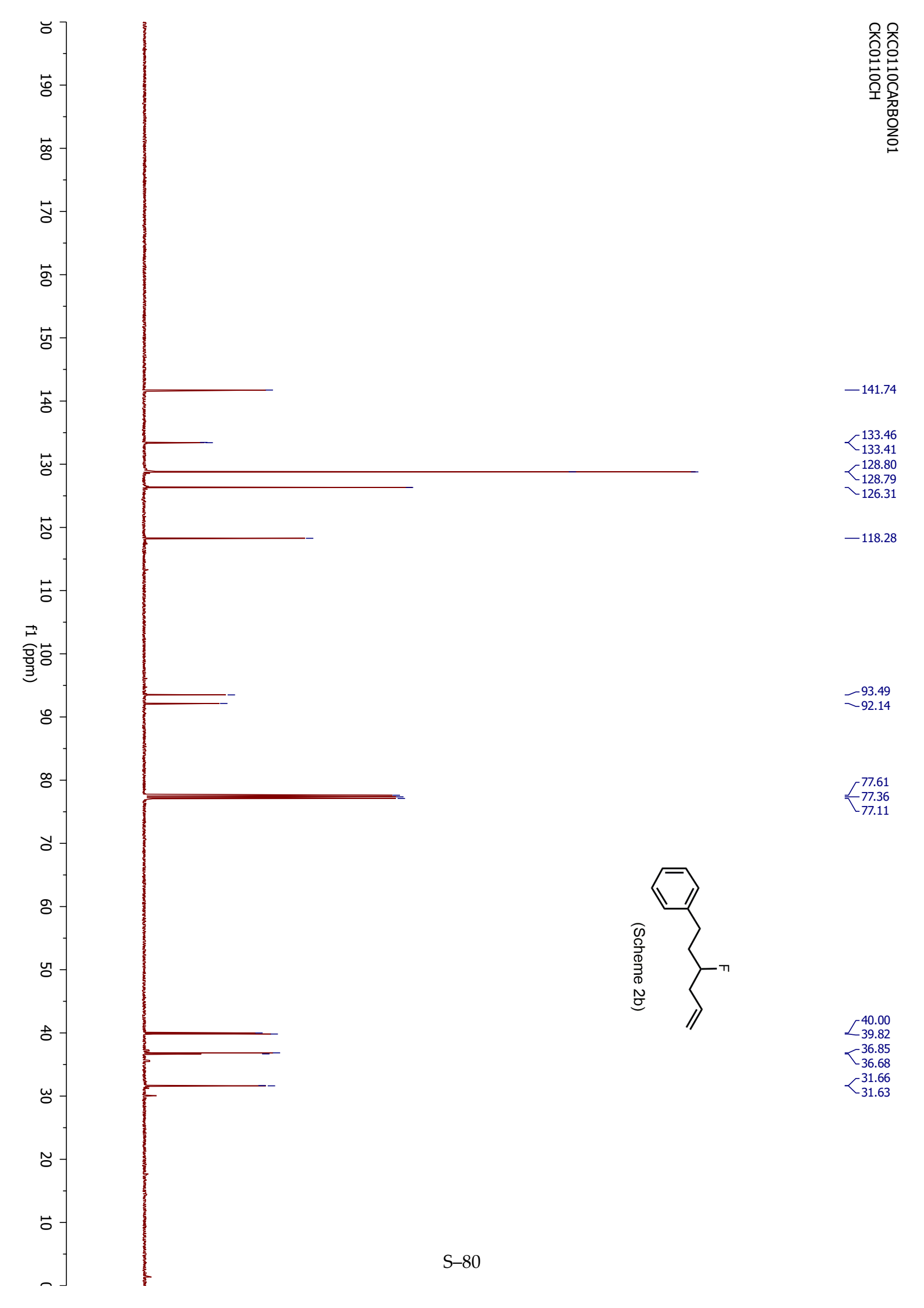
CKC0095FLUORINE
BC-1-29siena



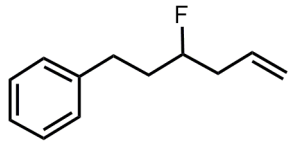
(Scheme 2a)



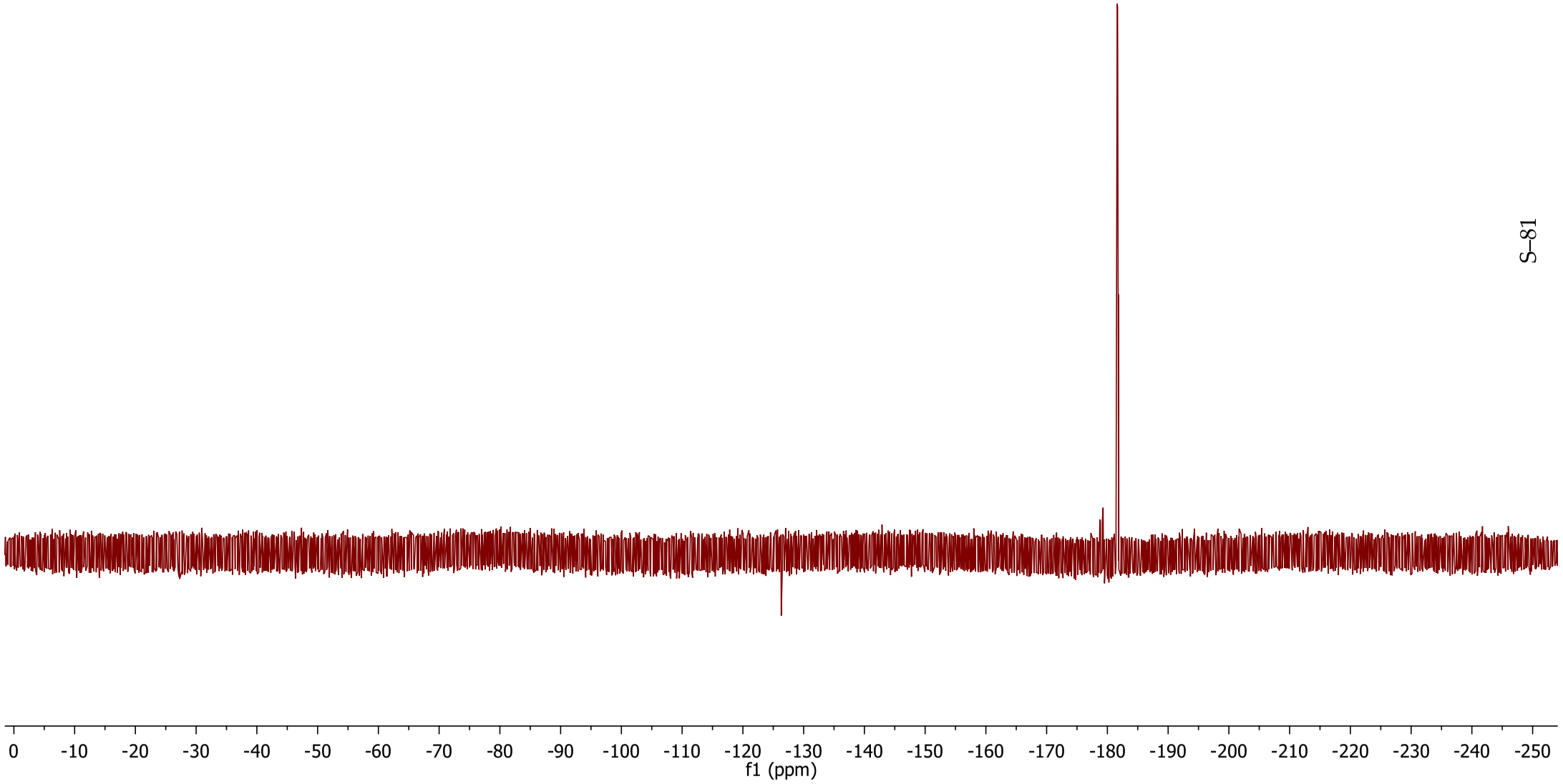

CKC0310cleanPROTON01
CKC0310prep
2.21
3.21
1.00
2.08
1.05
1.10
1.15
2.29
2.43
f1 (ppm)
F
(Scheme 2b)


CKC0110CARBON01
CKC0110CH
141.74
133.46
133.41
128.80
128.79
126.31
118.28
93.49
92.14
77.61
77.36
77.11
40.00
39.82
36.85
36.68
31.66
31.63
F
(Scheme 2b)
f1 (ppm)

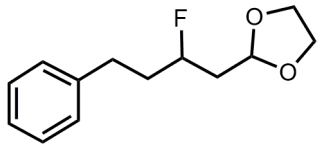
CKC0110FLUORINE01
BC-1-29siena



(Scheme 2b)

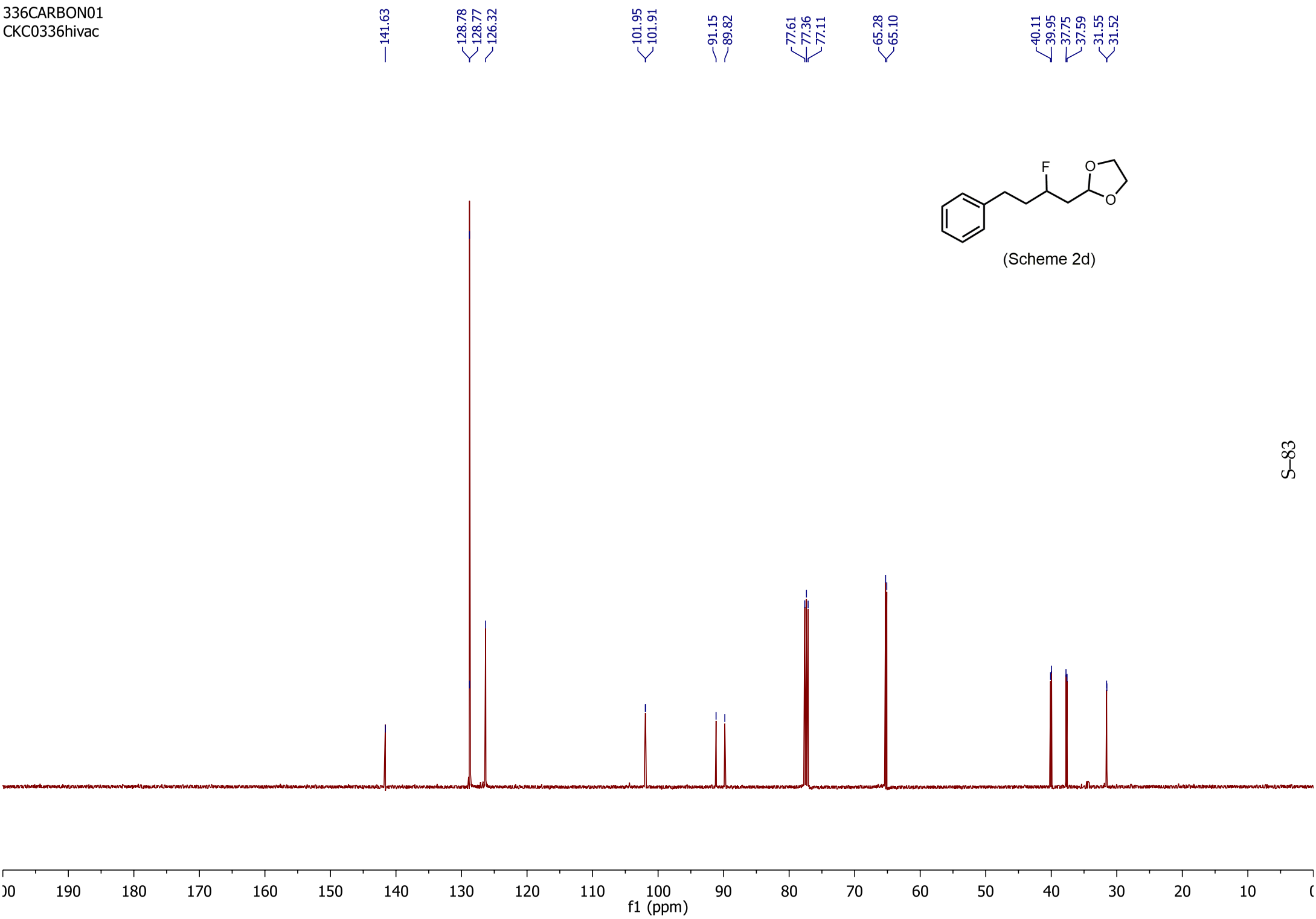


336PROTON01
CKC0336hivac

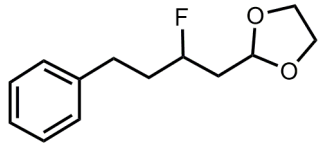


(Scheme 2d)

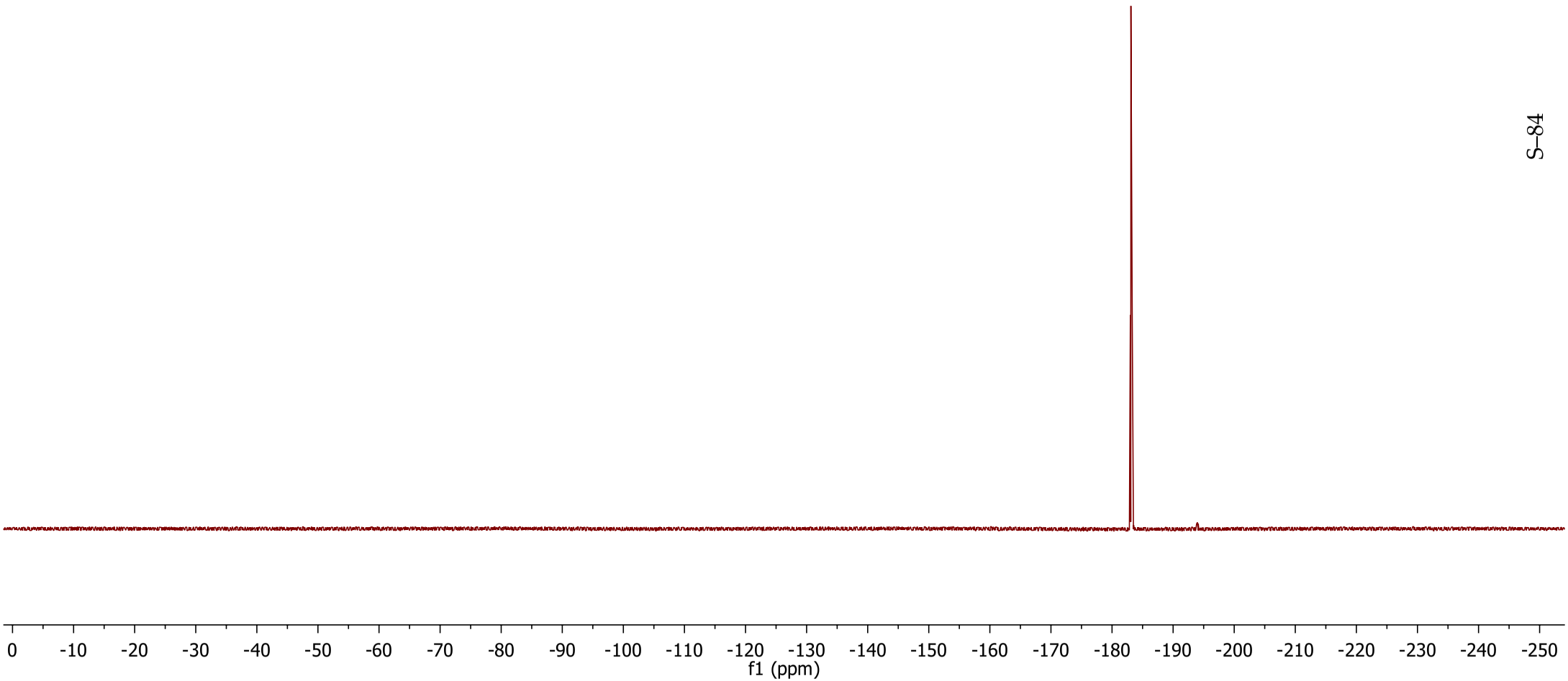
336CARBON01
CKC0336hivac



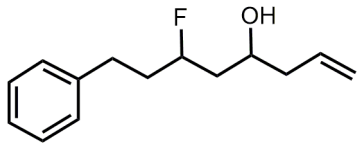
FLUORINE01
BC-1-29siena



(Scheme 2d)



CKC0094pure2
CKC0094pure2



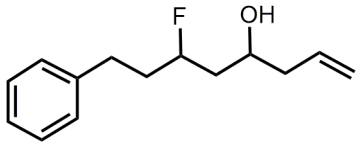
(Scheme 2e)

1.95 2.98 0.94 1.93 0.95 0.93 1.00 1.08 2.18 7.41

f1 (ppm)

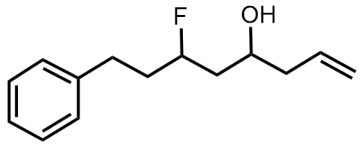
CKC0094CARBON01
CKC0094SI

141.72
141.56
134.65
134.61
128.80
128.77
128.76
128.75
126.36
126.30
118.89
118.73
93.97
92.65
91.75
90.43
77.62
77.36
77.11
69.13
69.10
67.08
67.06
42.76
42.51
42.35
42.07
41.96
41.81
37.80
37.63
37.60
37.44
31.73
31.69
31.54
31.50



(Scheme 2e)

FLUORINE01
CKC0094siena



(Scheme 2e)