Copper Mediated Difluoromethylation of Aryl and Vinyl Iodides

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Supporting Information

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General Experimental Details

All manipulations were conducted under an inert atmosphere with a nitrogen-filled glovebox unless otherwise noted. All reactions were conducted in oven-dried 4-mL or 20-mL vials fitted with a Teflon-lined screw cap under an atmosphere of nitrogen unless otherwise noted.

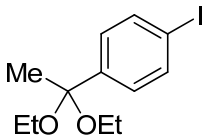
Cesium fluoride was purchased from Sigma-Aldrich and dried at 140°C under vacuum (100 mtorr) for 12 hours prior to use. Trimethyl(trifluoromethyl) silane ($TMSCF_3$, Ruppert's reagent) was purchased from Matrix Scientific. N-Methylpyrrolidone (NMP), 99.5%, Extra Dry over Molecular Sieves, was purchased from Acros and used without further purification. Unless otherwise noted, all other reagents were purchased from commercial suppliers and used as received. Trimethyl(difluoromethyl)silane,[1] 2-((4-iodobenzyl)oxy)tetrahydro-2H-pyran (**1l**)[2] and Z-1-iodo-1-octene (**4a**)[3] were prepared according to literature procedures.

Organic solutions were concentrated by rotary evaporation. Flash column chromatography was performed on Silicylce Siala-P silica gel or on a Teledyne Isco CombiFlash Rf automated chromatography system with 12 g RediSep Rf Gold normal-phase silica columns. The products were visualized by UV light and stained with potassium permanganate ($KMnO_4$).

NMR spectra were acquired on 400 MHz, 500 MHz, or 600 MHz Bruker instruments at the University of California. NMR spectra were processed with MestReNova 5.0 (Mestrelab Research SL). Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^1H and 77.0 ppm for ^{13}C) or to an external standard (1% $CFCl_3$ in $CDCl_3$: 0 ppm for ^{19}F). Coupling constants are reported in hertz.

All GC-MS analyses were conducted with an Agilent 6890N GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μm film) and an Agilent 5973 Mass Selective Detector. The temperature for each run was held at 50 °C for 2 min, ramped from 50 °C to 300 °C at 40 °C/min, and held at 300 °C for 5 min.

Preparation of 1-(1,1-diethoxyethyl)-4-iodobenzene (1h)



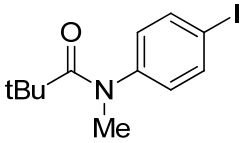
To a 3 mL vial was added 4'-iodoacetophenone (492 mg, 2.0 mmol), tetrabutylammonium tribromide (14 mg, 0.03 mmol) and 2 mL of ethanol. Triethylorthoformate (730 μL, 4.4 mmol) was added and the resulting solution was stirred at room temperature for 10 hours. The reaction was

poured into 5 mL of saturated $NaHCO_3$ and extracted with ethyl acetate. The organic layer was dried with Na_2SO_4 and concentrated to an orange oil (530 mg, 1.7 mmol, 85% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.48 (dq, *J* = 9.3, 7.1 Hz, 2H), 3.40 – 3.29 (m, 2H), 1.53 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.68 (s), 137.07 (s), 128.27 (s), 100.88 (s), 93.18 (s), 56.69 (s), 26.92 (s), 15.31 (s).

Preparation of N-(4-iodophenyl)-N-methylpivalamide (1j)



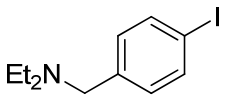
4-iodoaniline (2.19 g, 10 mmol), 4-dimethylaminopyridine (DMAP, 12 mg, 0.1 mmol), and pyridine (1.6 mL, 20 mmol) were dissolved in 20 mL of CH_2Cl_2 and cooled to 0 ^{o}C. Pivaloyl chloride (1.35 mL, 11 mmol) was added dropwise, and the resulting solution was allowed to warm to room temperature and stirred a total of 3 h. The solution was poured into a separatory funnel and washed with 1 x 20 mL of 1 M HCl and 1 x 20 mL of saturated $NaHCO_3$. The organic layer was dried with $MgSO_4$ and concentrated to a white solid (2.90 g, 9.6 mmol).

500 mg of the white solid, N-(4-iodophenyl)pivalamide (1.65 mmol), was dissolved in 2 mL of anhydrous THF and added dropwise to a suspension of 60% NaH (79 mg, 2.0 mmol) in 1 mL of anhydrous THF. The resulting solution was stirred at room temperature for 30 minutes, and methyl iodide (160 µL, 2.5 mmol) was added dropwise. After stirring for 3 h, water was added, and the product was extracted with ether. Drying with $MgSO_4$ and removal of the solvent gave **1j** as a white solid (480 mg, 1.5 mmol, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 6.99 – 6.95 (m, 2H), 3.18 (s, 3H), 1.05 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.93 (s), 145.12 (s), 138.49 (s), 130.70 (s), 92.73 (s), 41.22 (s), 40.80 (s), 29.45 (s).

Preparation of N-ethyl-N-(4-iodobenzyl)ethanamine (1k)



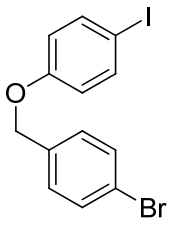
4-iodobenzylbromide (891 mg, 3.0 mmol) was dissolved in 3 mL of CH_2Cl_2 and diethylamine (930 µL, 9.0 mmol) was added at once. After 20 min at room temperature, the reaction was complete, as judged by TLC analysis. The solution was poured into a separatory funnel containing

ethyl acetate and washed with 2 x 10 mL of 3 M KOH and 1 x 10 mL of brine. The organic layer was dried over sodium sulfate and concentrated to give **1k** as a light yellow oil (830 mg, 2.9 mmol, 96% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 3.49 (s, 2H), 2.49 (q, *J* = 7.1 Hz, 4H), 1.02 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.93 (s), 137.14 (s), 130.80 (s), 91.80 (s), 57.00 (s), 46.73 (s), 11.75 (s).

Preparation of 1-bromo-4-((4-iodophenoxy)methyl)benzene (1m)

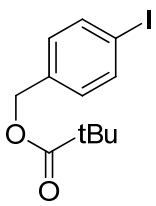


Sodium hydride (60% wt/wt in mineral oil, 132 mg, 3.3 mmol) was suspended in 2 mL of anhydrous THF. 4-Iodophenol (660 mg, 3.0 mmol) in 2 mL of THF was added dropwise to the NaH suspension and stirred at room temperature for 5 min. 4'-Bromo-benzylbromide in 2 mL of THF was added dropwise and stirred at 80 °C for 8 h. The solution was washed with water and extracted with ether. The organic layer was washed with 1 x 10 mL of brine, dried with magnesium sulfate, and concentrated and purified by silica gel chromatography eluting with hexanes (R_f=0.15). White solid (1.01 g, 2.6 mmol, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.53 – 7.49 (m, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.75 – 6.69 (m, 2H), 4.98 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.35 (s), 138.31 (s), 135.54 (s), 131.77 (s), 128.99 (s), 122.03 (s), 117.26 (s), 83.31 (s), 69.32 (s).

Preparation of 4-iodobenzyl pivalate (1n)

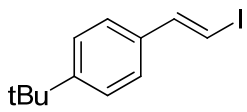


Sodium hydride (60% wt/wt in mineral oil, 132 mg, 3.3 mmol) was suspended in 3 mL of anhydrous THF. 4'-Iodo-benzylalcohol in 2 mL of THF was added dropwise to the NaH suspension and stirred at room temperature for 10 min. Pivaloyl chloride (406 µL, 3.3 mmol) was added dropwise, and the resulting solution was stirred at room temperature for 2 h. The solution was poured into water and extracted with ether. The organic layer was washed with 1 x 10 mL of saturated $NaHCO_3$ and 1 x 10 mL of brine, dried with magnesium sulfate, and concentrated to give **1n** as a light yellow oil (905 mg, 2.8 mmol, 95% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 5.04 (s, 2H), 1.22 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.17 (s), 137.59 (s), 136.09 (s), 129.59 (s), 93.57 (s), 65.30 (s), 38.75 (s), 27.13 (s).

Preparation of (E)-1-(tert-butyl)-4-(2-iodovinyl)benzene (3a)



To 4-(*tert*-butyl)-phenylacetylene (1.27 g, 8.0 mmol) in a small vial was slowly added catecholborane (853 µL, 8.0 mmol). The resulting mixture was heated at 70 °C for 2 h and allowed to cool to room temperature, forming an orange solid. The orange solid was dissolved in 20 mL of THF and 8 mL of 3 M NaOH was added slowly and stirred at room temperature for 10 min. A solution of I_2 (4.06 g, 16 mmol) in 80 mL of THF was added by an addition funnel over 2 h. The dark reaction mixture was filtered thru Celite, diluted with ethyl acetate and washed 2 x 20 mL with saturated sodium thiosulfate and 1 x 10 mL brine. The organic layer was dried with magnesium sulfate and purified by silica gel chromatography eluting with hexanes (R_f = 0.5) to give a light yellow oil that solidified upon standing (1.43 g, 5.0 mmol, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 14.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 14.9 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.54 (s), 144.71 (s), 134.99 (s), 125.70 (s), 125.61 (s), 75.55 (s), 34.67 (s), 31.17 (s).

General Procedure for the Difluoromethylation of Aryl and Vinyl Iodides

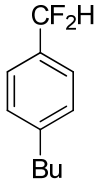
In a nitrogen-filled glove box, aryl or vinyl iodide (0.5 mmol, 1 equiv), copper iodide (0.5 mmol, 1 eq), and cesium fluoride (1.5 mmol, 1 equiv) were combined in a 20 mL vial. To this vial was added 2.5 mL of anhydrous NMP, followed by trimethyl(difluoromethyl)silane (2.5 mmol, 5 equiv). The reaction mixture was heated in a sealed vessel at 120 ºC for 24 h. ***Note:*** *the pressure increases during the reaction due to the formation of volatile fluorotrimethylsilane (Me_3SiF) as a stoichiometric product.* The dark red solution was then cooled to room temperature, and diluted with 15 mL of Et_2O. The mixture was filtered over Celite, washed with an additional 20 mL of Et_2O, and transferred to a separatory funnel. The mixture was washed with 5 x 20 mL of H_2O and 1 x 20 mL of brine, dried with $MgSO_4$, filtered, and concentrated under vacuum. The crude

product was purified by column chromatography on silica gel with pentane or pentane/Et_2O mixtures as the eluent.

Specific Procedures and Characterization of Products

1-butyl-4-(difluoromethyl)benzene (2a)

The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (89 μL **1a**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2a** (83 mg, 90% yield).

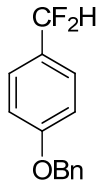


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 6.63 (t, *J* = 56.6 Hz, 1H), 1.67 – 1.56 (m, 2H), 1.37 (dt, *J* = 14.9, 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.82 (t, *J* = 1.9 Hz), 131.77 (t, *J* = 22.4 Hz), 128.68 (s), 125.47 (t, *J* = 6.0 Hz), 114.95 (t, *J* = 238.0 Hz), 35.49 (s), 33.42 (s), 22.28 (s), 13.88 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.06 (d, *J* = 56.6 Hz).

1-(benzyloxy)-4-(difluoromethyl)benzene (2b)



The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (155 mg **1b**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2b** (102 mg, 87% yield).

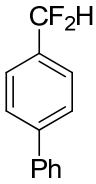
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.31 (m, 7H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.60 (t, *J* = 56.7 Hz, 1H), 5.10 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.51 (t, *J* = 1.6 Hz), 136.46 (s), 128.66 (s), 128.14 (s), 127.43 (s), 127.13 (t, *J* = 5.9 Hz), 127.01 (s), 114.92 (s), 114.83 (t, *J* = 237.5 Hz), 70.09 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.77 (d, *J* = 57.0 Hz).

4-(difluoromethyl)-1,1'-biphenyl (2c)

The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (140 mg **1c**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2c** (90 mg, 88% yield).

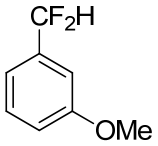


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 6.9 Hz, 1H), 6.70 (t, *J* = 56.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.70 (t, *J* = 2.0 Hz), 140.18 (s), 133.20 (t, *J* = 22.2 Hz), 128.90 (s), 127.89 (s), 127.42 (s), 127.24 (s), 126.01 (t, *J* = 6.0 Hz), 114.73 (t, *J* = 238.5 Hz).

^{19}F NMR (376 MHz, C_6D_6) δ -111.35 (d, *J* = 57.0 Hz).

1-(difluoromethyl)-3-methoxybenzene (2d)



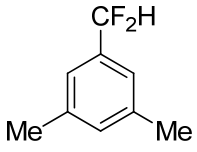
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (59.5 µL **1d**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2d** (64 mg, 81% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.61 (t, *J* = 56.5 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.82 (s), 135.75 (t, *J* = 22.3 Hz), 129.86 (s), 117.82 (t, *J* = 6.3 Hz), 116.59 (t, *J* = 1.8 Hz), 114.55 (t, *J* = 239.0 Hz), 110.66 (t, *J* = 6.1 Hz), 55.36 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.12 (d, *J* = 56.5 Hz).

1-(difluoromethyl)-3,5-dimethylbenzene (2e)



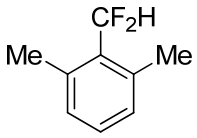
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (72.2 µL **1e**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2e** (58 mg, 74% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (s, 2H), 7.10 (s, 1H), 6.57 (t, *J* = 56.6 Hz, 1H), 2.36 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.44 (s), 134.30 (t, *J* = 21.7 Hz), 132.27 (t, *J* = 1.9 Hz), 123.20 (t, *J* = 6.0 Hz), 114.99 (t, *J* = 238.4 Hz), 21.21 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.61 (d, *J* = 56.7 Hz).

2-(difluoromethyl)-1,3-dimethylbenzene (2f)



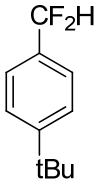
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (116 mg **1f**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2f** (75 mg, 48% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 54.3 Hz, 1H), 2.48 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.05 (t, *J* = 4.0 Hz), 130.31 (t, *J* = 1.5 Hz), 130.00 (t, *J* = 20.3 Hz), 129.18 (s), 114.48 (t, *J* = 236.2 Hz), 19.45 (t, *J* = 1.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.15 (d, *J* = 54.3 Hz).

1-(tert-butyl)-4-(difluoromethyl)benzene (2g)



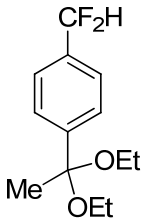
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (130 mg **1g**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2g** (113 mg, 61% yield). A small amount (<10%) of unreacted **1g** was unable to be separated from the product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (q, *J* = 8.5 Hz, 4H), 6.63 (t, *J* = 56.6 Hz, 1H), 1.34 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.00 (t, *J* = 2.0 Hz), 131.54 (t, *J* = 22.4 Hz), 125.61 (s), 125.30 (t, *J* = 6.0 Hz), 114.90 (t, *J* = 238.0 Hz), 34.85 (s), 31.21 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.24 (d, *J* = 56.6 Hz).

1-(1,1-diethoxyethyl)-4-(difluoromethyl)benzene (2h)



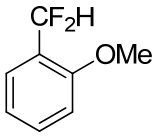
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (160 mg **1h**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2h** (101 mg, 82% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 6.65 (t, *J* = 56.4 Hz, 1H), 3.53 – 3.44 (m, 2H), 3.39 – 3.31 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.74 (s), 133.43 (t, *J* = 22.4 Hz), 126.58 (s), 125.27 (t, *J* = 5.9 Hz), 114.76 (t, *J* = 238.3 Hz), 100.94 (s), 56.77 (s), 27.04 (s), 15.29 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.72 (d, *J* = 56.5 Hz).

1-(difluoromethyl)-2-methoxybenzene (2i)



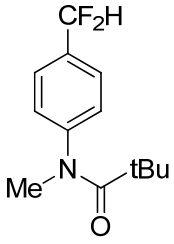
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (117 mg **1i**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2i** (24 mg, 30% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.95 (t, *J* = 47.5 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.27 (t, *J* = 6.0 Hz), 131.94 (t, *J* = 1.9 Hz), 126.22 (t, *J* = 5.8 Hz), 122.71 (t, *J* = 22.0 Hz), 120.59 (s), 113.13 (s), 110.82 (t, *J* = 117.7 Hz), 55.59 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.84 (d, *J* = 55.7 Hz).

N-(4-(difluoromethyl)phenyl)-N-methylpivalamide (2j)



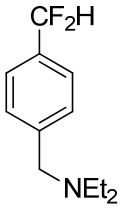
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (159 mg **1j**). The crude mixture was purified by silica gel chromatography (6:1 Hexanes:Ethyl Acetate, R_f=0.13) to give **2j** (63 mg, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.67 (t, *J* = 56.3 Hz, 1H), 3.21 (s, 3H), 1.04 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.01 (s), 147.52 (t, *J* = 2.0 Hz), 133.74 (t, *J* = 22.7 Hz), 129.05 (s), 126.64 (t, *J* = 5.9 Hz), 114.04 (t, *J* = 239.2 Hz), 41.22 (s), 40.82 (s), 29.39 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.24 (d, *J* = 56.3 Hz).

N-(4-(difluoromethyl)benzyl)-N-ethylethanamine (2k)



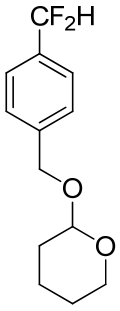
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (145 mg **1k**). The crude mixture was purified by silica gel chromatography (3:1 Hexanes:Ethyl Acetate, R_f=0.2) to give **2k** (63 mg, 59% yield). A small amount (<5%) of unreacted **1k** was unable to be separated from the product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 4H), 6.63 (t, *J* = 56.6 Hz, 1H), 3.59 (s, 2H), 2.52 (q, *J* = 7.1 Hz, 4H), 1.04 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.20 (s), 132.74 (t, *J* = 22.3 Hz), 128.97 (s), 125.37 (t, *J* = 6.0 Hz), 114.86 (t, *J* = 238.1 Hz), 57.23 (s), 46.79 (s), 11.75 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.17 (d, *J* = 56.6 Hz).

2-((4-(difluoromethyl)benzyl)oxy)tetrahydro-2H-pyran (2l)



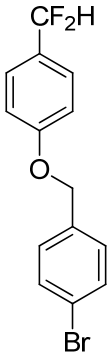
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (159 mg **1l**). The crude mixture was purified by silica gel chromatography (6:1 Hexanes:Ethyl Acetate, R_f=0.49) to give **2l** (85 mg, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 18.5, 8.2 Hz, 4H), 6.64 (t, *J* = 56.5 Hz, 1H), 4.83 (d, *J* = 12.5 Hz, 1H), 4.71 (t, *J* = 3.5 Hz, 1H), 4.55 (d, *J* = 12.5 Hz, 1H), 3.91 (ddd, *J* = 11.4, 8.6, 2.9 Hz, 1H), 3.58 – 3.53 (m, 1H), 1.92 – 1.83 (m, 1H), 1.80 – 1.72 (m, 1H), 1.71 – 1.51 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.23 (t, *J* = 1.9 Hz), 133.49 (t, *J* = 22.4 Hz), 127.78 (s), 125.61 (t, *J* = 6.0 Hz), 114.68 (t, *J* = 238.4 Hz), 97.90 (s), 68.19 (s), 62.16 (s), 30.50 (s), 25.41 (s), 19.29 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.33 (d, *J* = 56.6 Hz).

1-bromo-4-((4-(difluoromethyl)phenoxy)methyl)benzene (2m)



The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (195 mg **1m**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2m** (121 mg, 77% yield). A small amount (<5%) of unreacted **1m** was unable to be separated from the product.

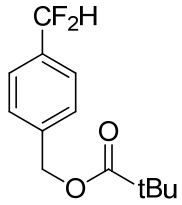
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.60 (t, *J* = 56.7 Hz, 1H), 5.05 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.16 (t, *J* = 1.8 Hz), 135.43 (s), 131.77 (s), 129.51 (s), 129.01 (s), 127.17 (t, *J* = 5.9 Hz), 122.05 (s), 114.84 (s), 114.74 (t, *J* = 237.6 Hz), 69.26 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.86 (d, *J* = 56.7 Hz).

4-(difluoromethyl)benzyl pivalate (2n)

The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (159 mg **1n**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **2n** (63 mg, 52%



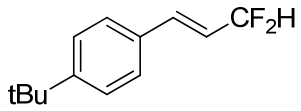
yield). A small amount (<5%) of unreacted **1n** was unable to be separated from the product.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 6.65 (t, *J* = 56.5 Hz, 1H), 5.14 (s, 1H), 1.24 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 178.19 (s), 139.26 (t, *J* = 1.8 Hz), 134.04 (t, *J* = 22.5 Hz), 127.79 (s), 125.78 (t, *J* = 6.0 Hz), 114.50 (t, *J* = 238.8 Hz), 65.35 (s), 38.81 (s), 27.16 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.03 (d, *J* = 56.7 Hz).

(E)-1-(tert-butyl)-4-(3,3-difluoroprop-1-en-1-yl)benzene (4a)



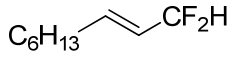
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (143 mg **3a**). The crude mixture was purified by silica gel chromatography (Hexanes, R_f=0.27) to give **4a** (84 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 6.90 – 6.82 (m, 1H), 6.38 – 6.12 (m, 2H), 1.34 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.75 (s), 136.93 (t, *J* = 12.2 Hz), 131.63 (s), 127.01 (s), 125.74 (s), 120.12 (t, *J* = 23.9 Hz), 115.61 (t, *J* = 233.3 Hz), 34.74 (s), 31.18 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.42 – -109.69 (m).

(E)-1,1-difluorononon-2-ene (4b)



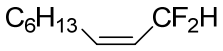
The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (119 mg **3b**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **4b** (74 mg, 91% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.07 (ddd, *J* = 9.8, 7.0, 3.3 Hz, 1H), 6.02 (td, *J* = 56.2, 6.0 Hz, 1H), 5.63 (dt, *J* = 15.4, 7.6 Hz, 1H), 2.17 – 2.08 (m, 2H), 1.45 – 1.38 (m, 2H), 1.34 – 1.25 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.26 (t, *J* = 11.9 Hz), 123.17 (t, *J* = 23.8 Hz), 115.57 (t, *J* = 232.8 Hz), 31.79 (s), 31.59 (s), 28.72 (s), 28.20 (t, *J* = 1.9 Hz), 22.54 (s), 14.02 (s).

^{19}F NMR (376 MHz $CDCl_3$) δ -110.86 – -111.08 (m).

(Z)-1,1-difluorononon-2-ene (4c)



The reaction was performed according to the general procedure for difluoromethylation on a 0.5 mmol scale (119 mg **3b**). The crude mixture was purified by silica gel chromatography (12 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **4b** (34 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (td, *J* = 56.0, 6.9 Hz, 1H), 5.93 – 5.83 (m, 1H), 5.65 – 5.51 (m, 1H), 2.17 (q, *J* = 7.5 Hz, 2H), 1.45 – 1.36 (m, 2H), 1.36 – 1.22 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.04 (t, *J* = 12.1 Hz), 122.75 (t, *J* = 25.1 Hz), 111.91 (t, *J* = 231.0 Hz), 31.55 (s), 29.07 (t, *J* = 1.7 Hz), 28.69 (s), 27.90 (t, *J* = 1.4 Hz), 22.53 (s), 14.01 (s).

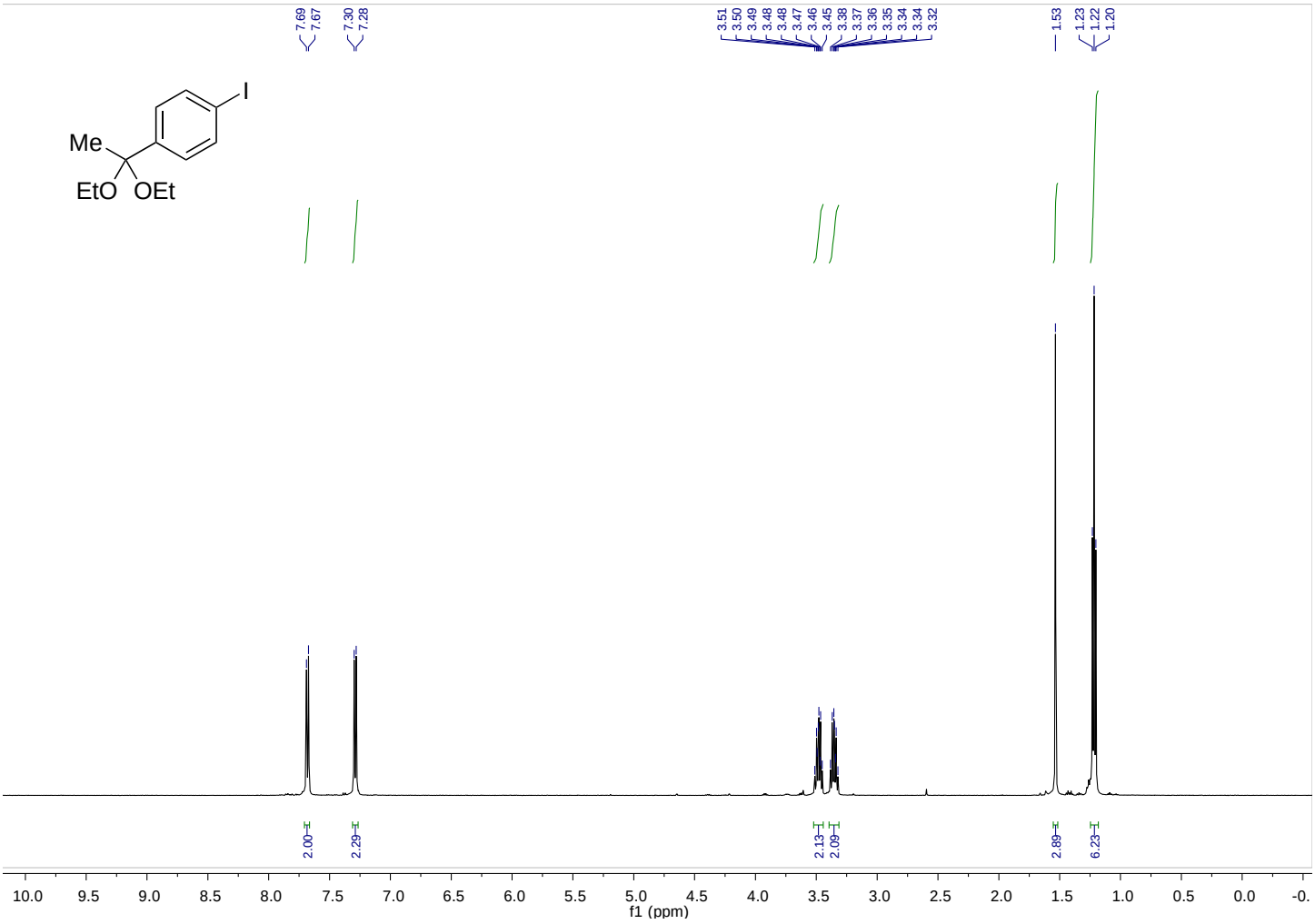
^{19}F NMR (376 MHz, $CDCl_3$) δ -111.16 (d, *J* = 56.0 Hz).

References

(1) Tyutyunov, A. A.; Boyko, V. E.; Igoumnov, S. M. *Fluorine Notes* **2011**, 74, 1; http://notes.fluorine1.ru/public/2011/1_2011/letters/letter2.html.

(2) Mansfeld, U.; Hager, M. D.; Hoogenboom, R.; Ott, C.; Winter, A.; Schubert, U. S. *Chem. Commun.* **2009**, 3386.

(3) Brown, H. C.; Subrahmanyam, C.; Hamaoka, T.; Ravindran, N.; Bowman, D. H.; Misumi, S.; Unni, M. K.; Somayaji, V.; Bhat, N. G. *J. Org. Chem.* **1989**, 54, 6068.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3.36
3.35
3.34
3.34
3.32
1.53
1.23
1.22
1.20
I
Me
EtO
OEt
2.00
2.29
2.13
2.09
2.89
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9.0
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5.5
5.0
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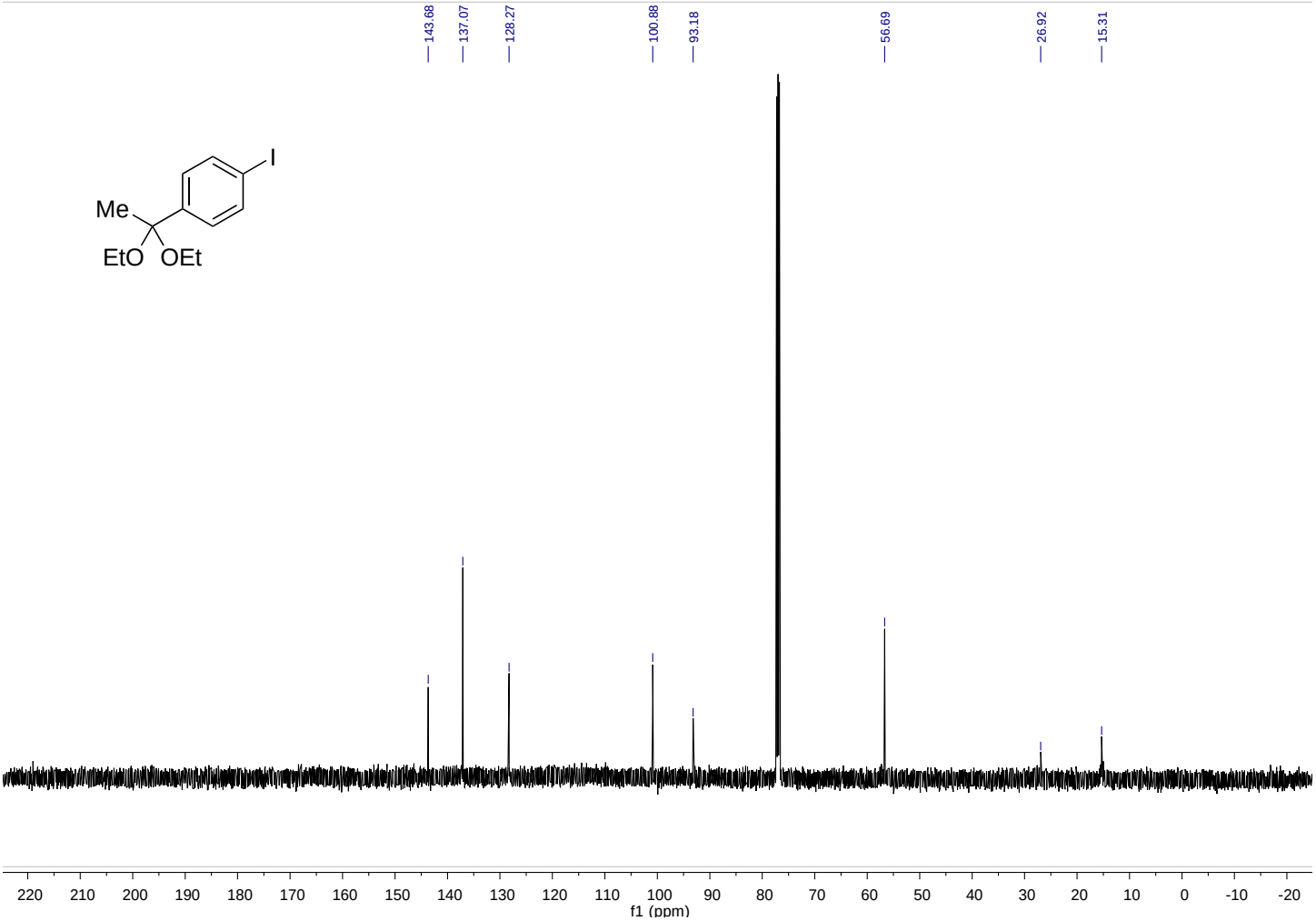
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EtO
OEt
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180
170
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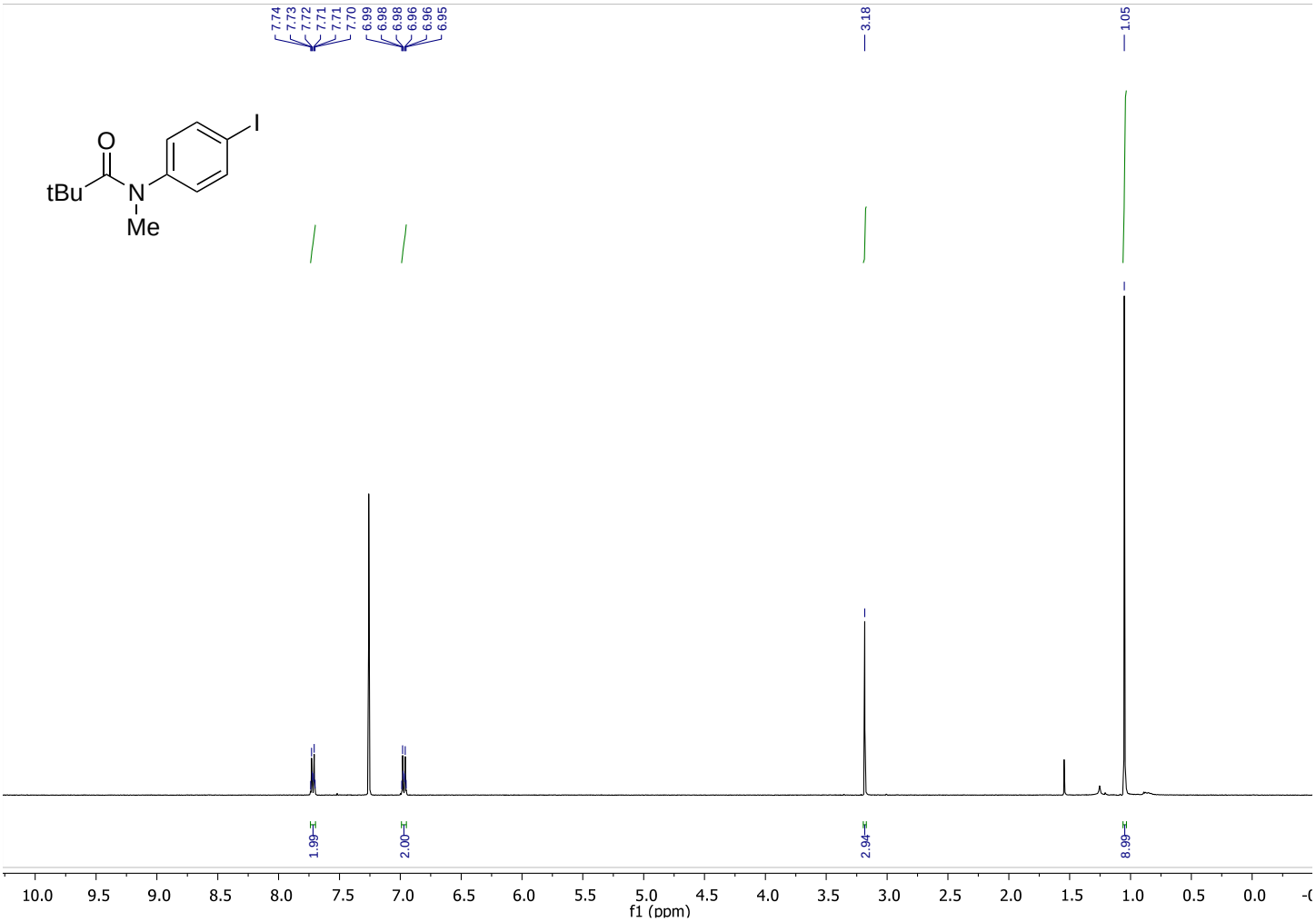
f1 (ppm)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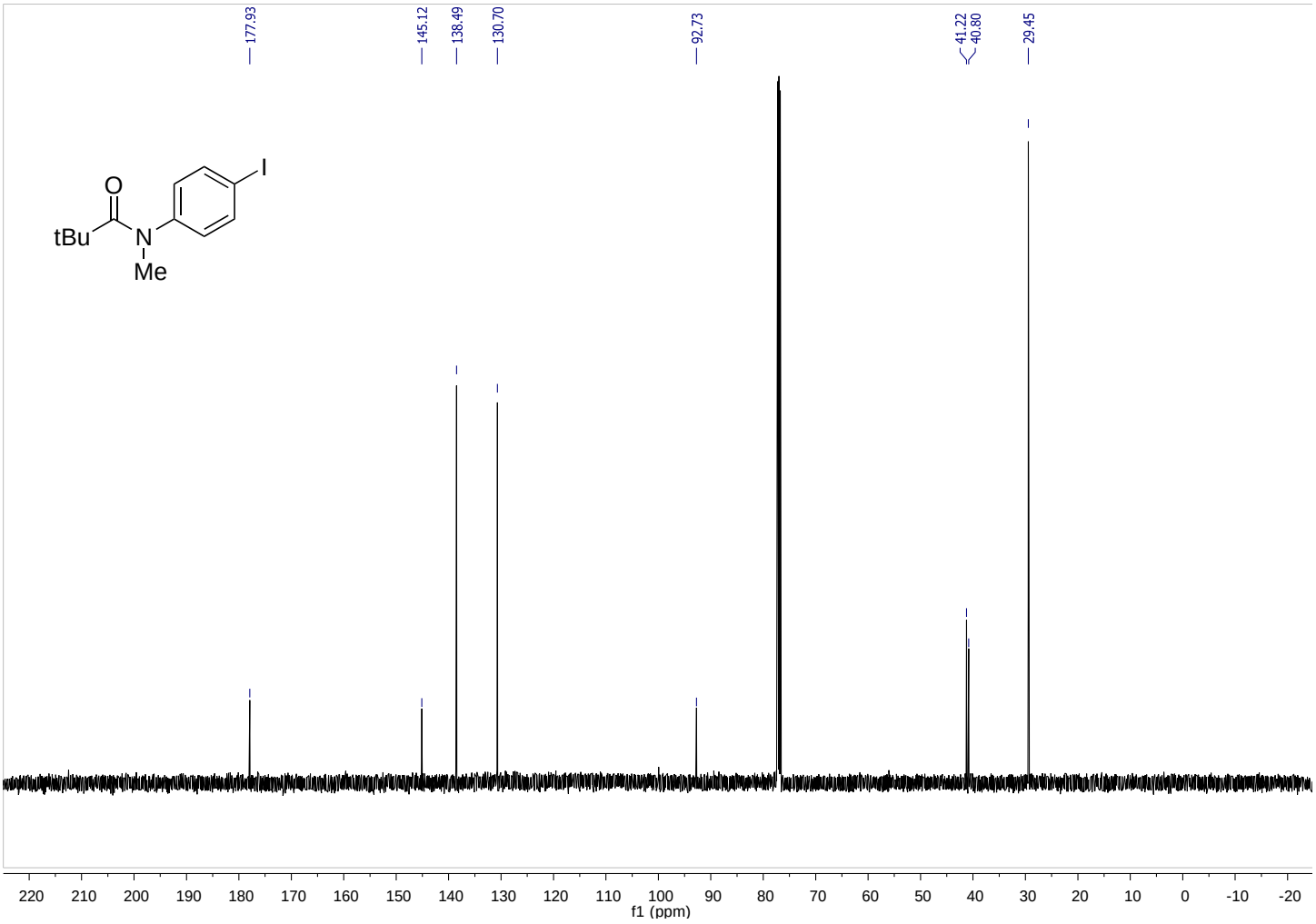
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N
Me
I
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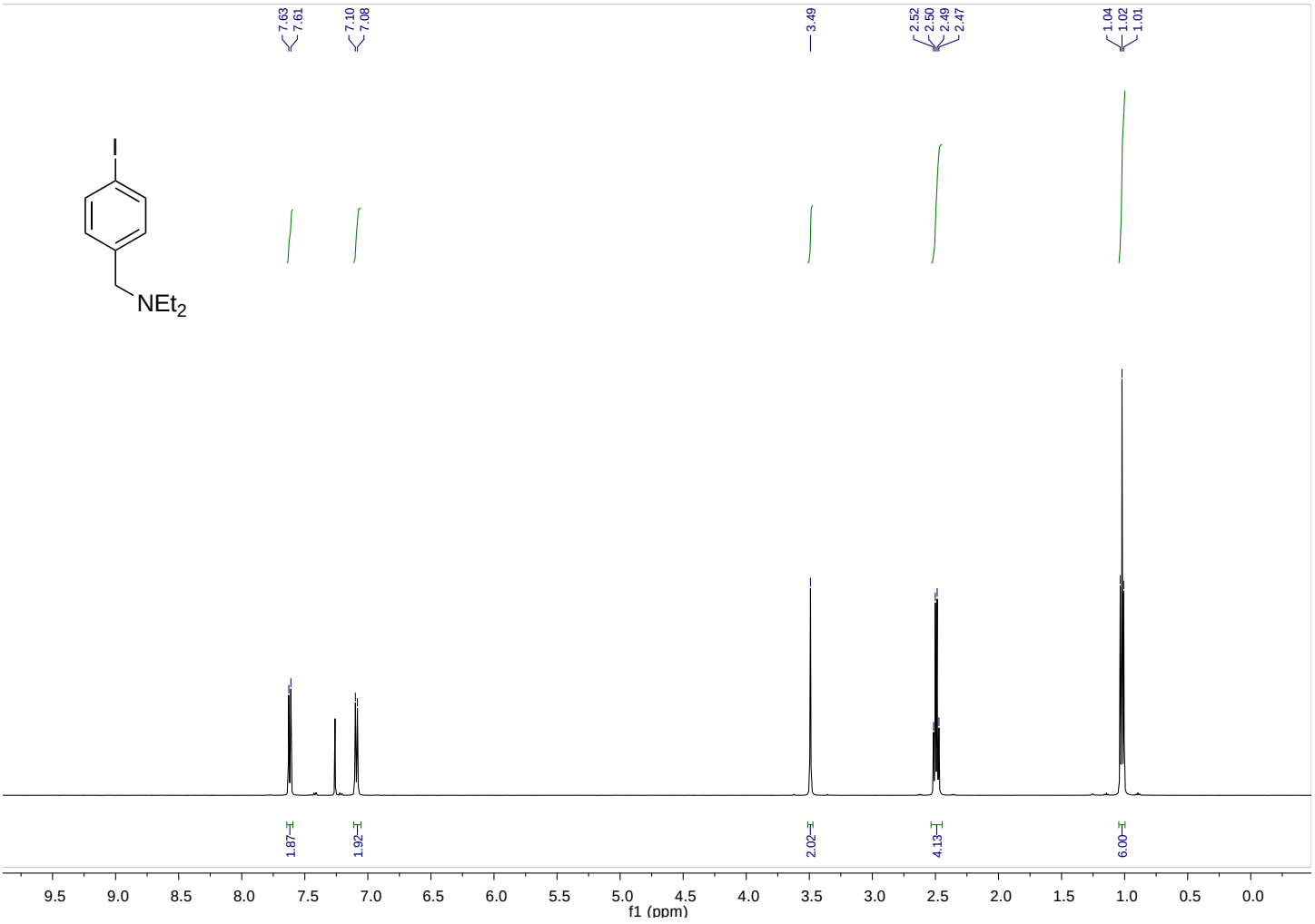
f1 (ppm)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1.02
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NEt2
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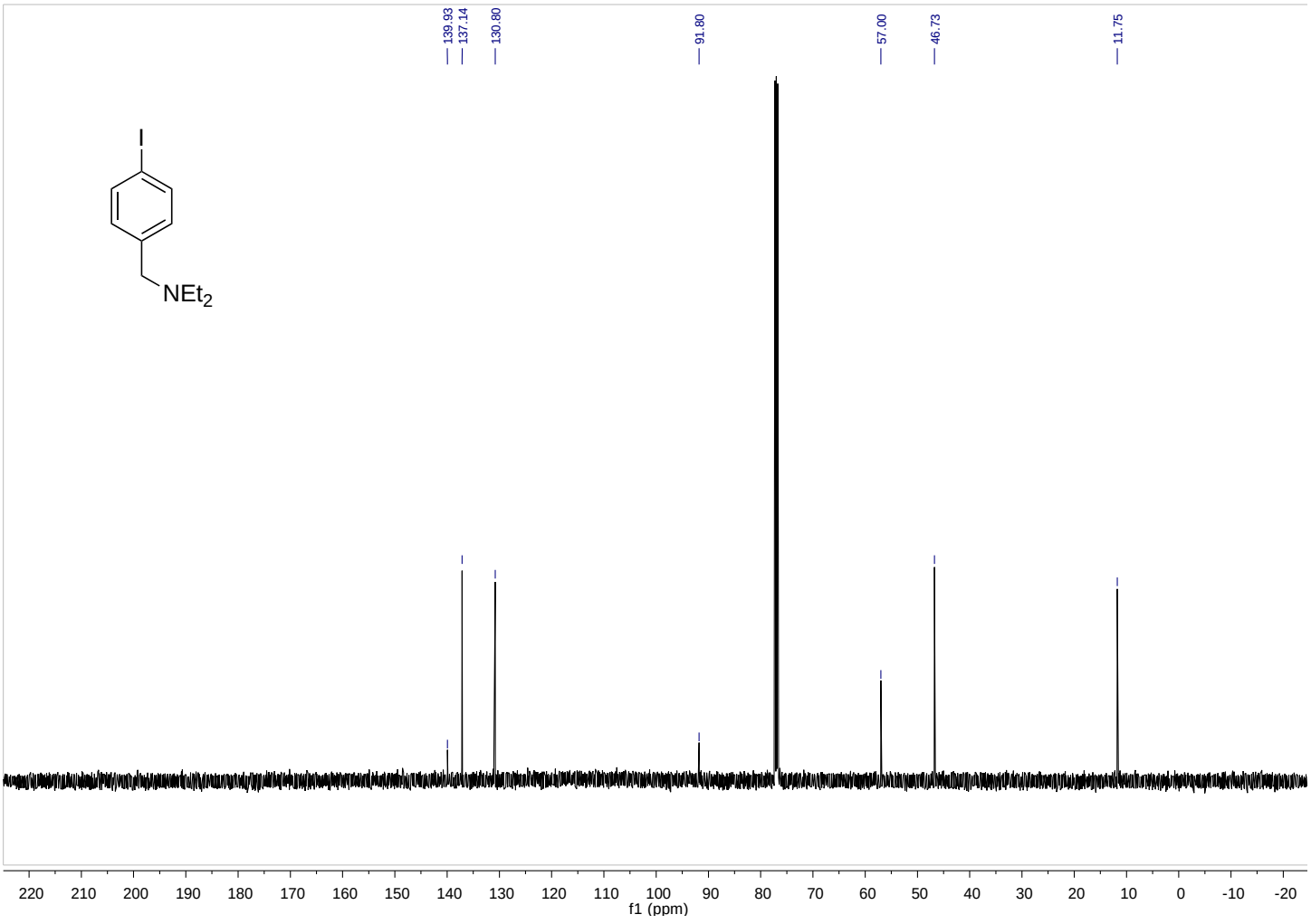
1.92
2.02
4.13
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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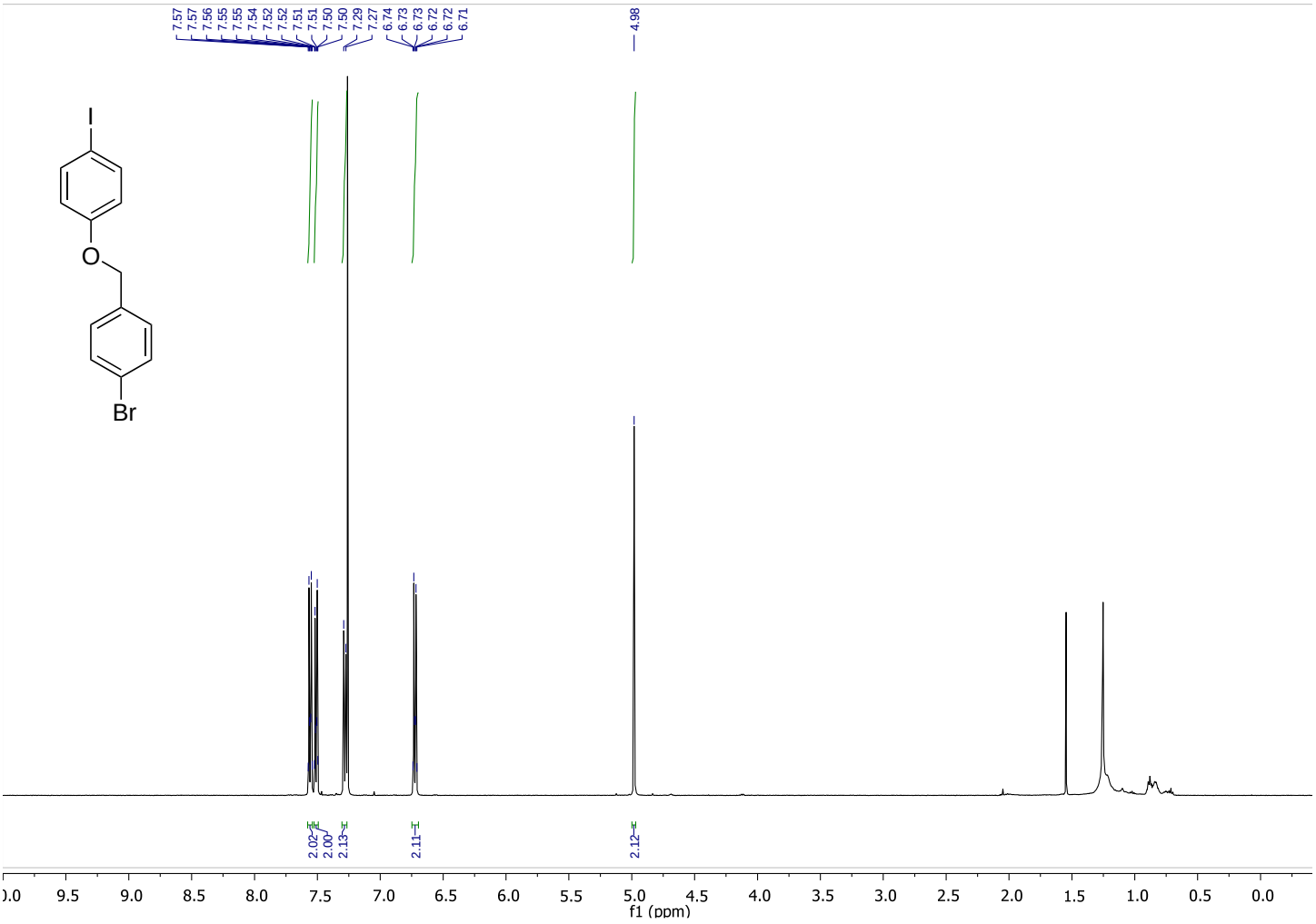
f1 (ppm)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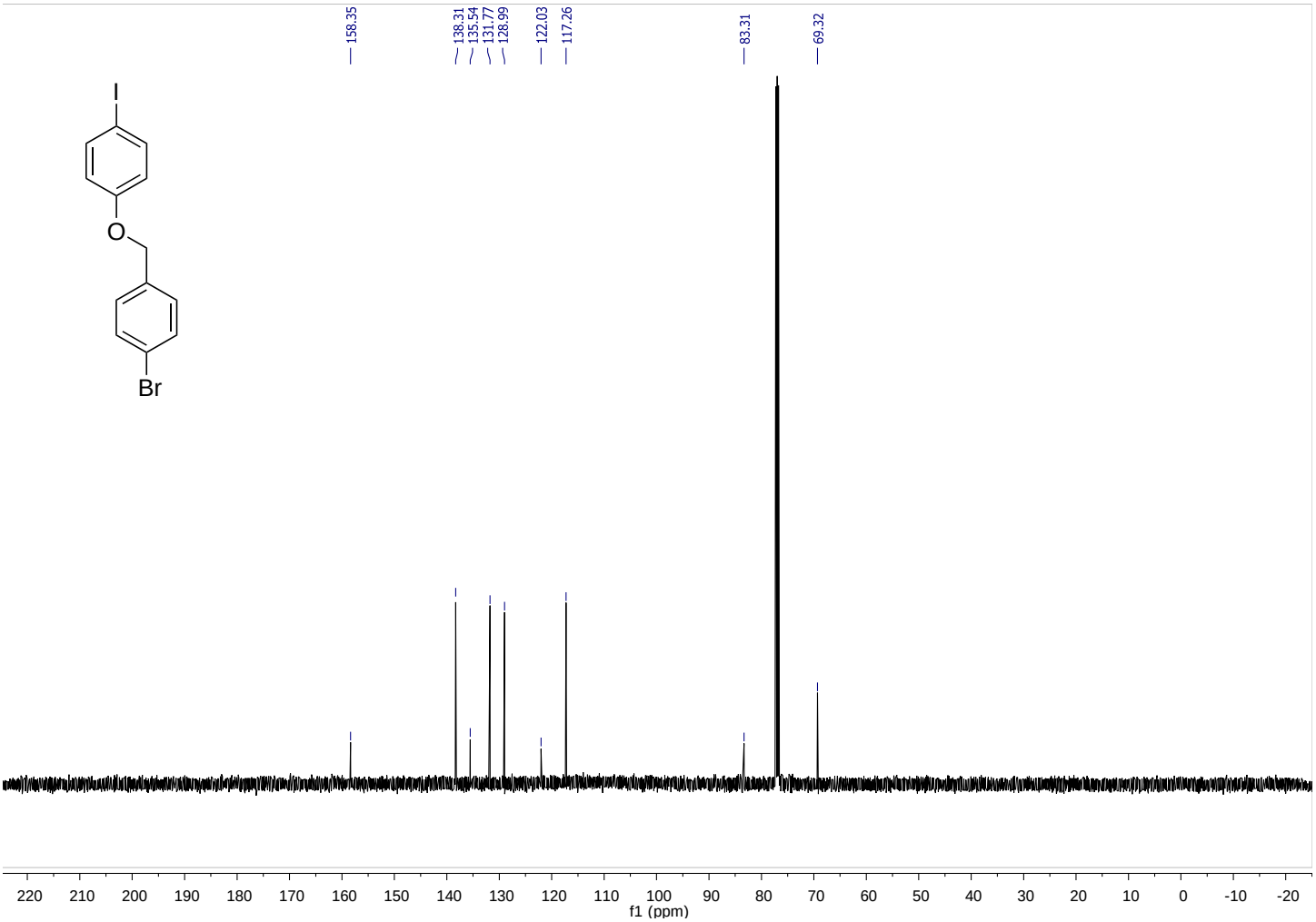
f1 (ppm)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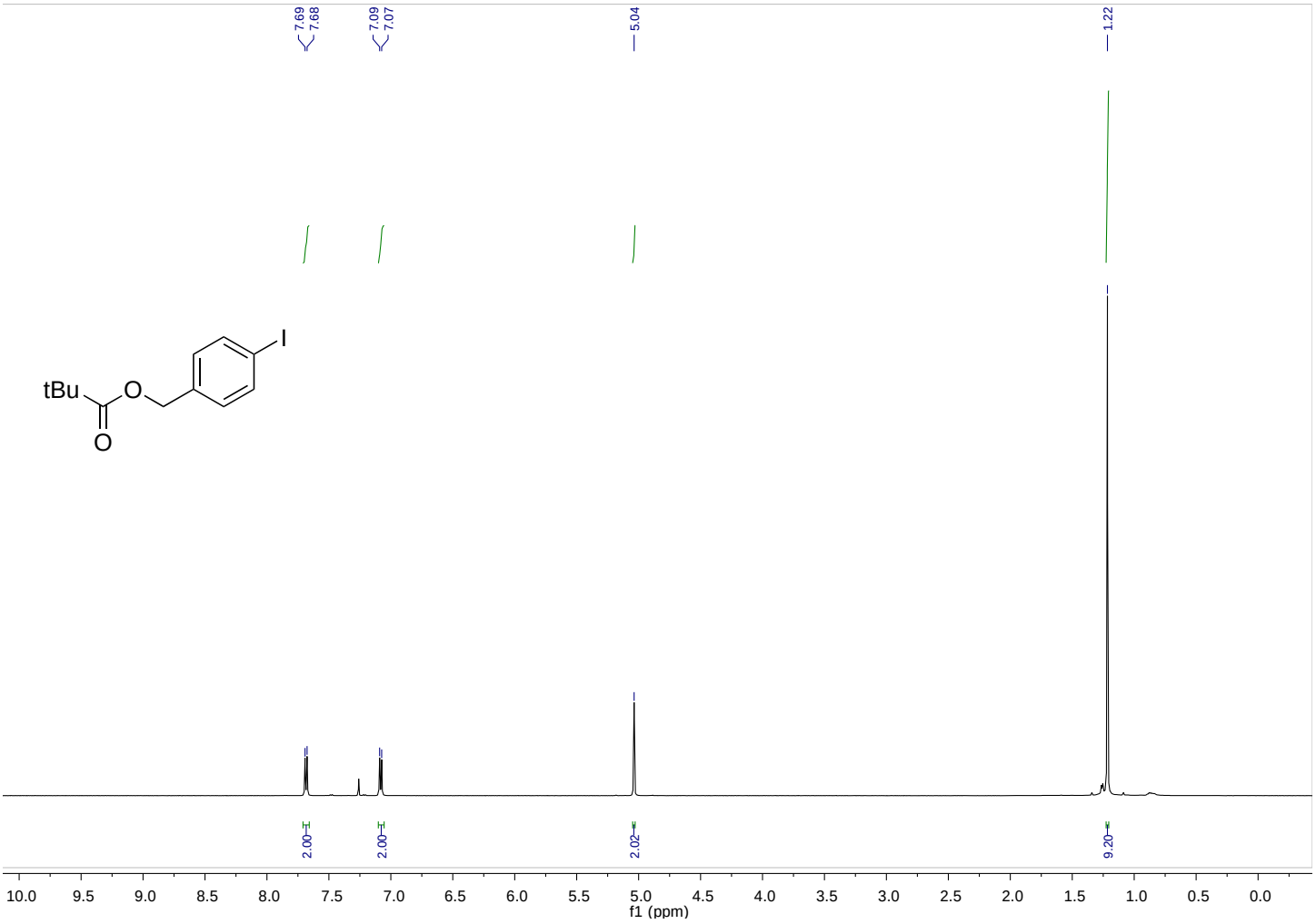
f1 (ppm)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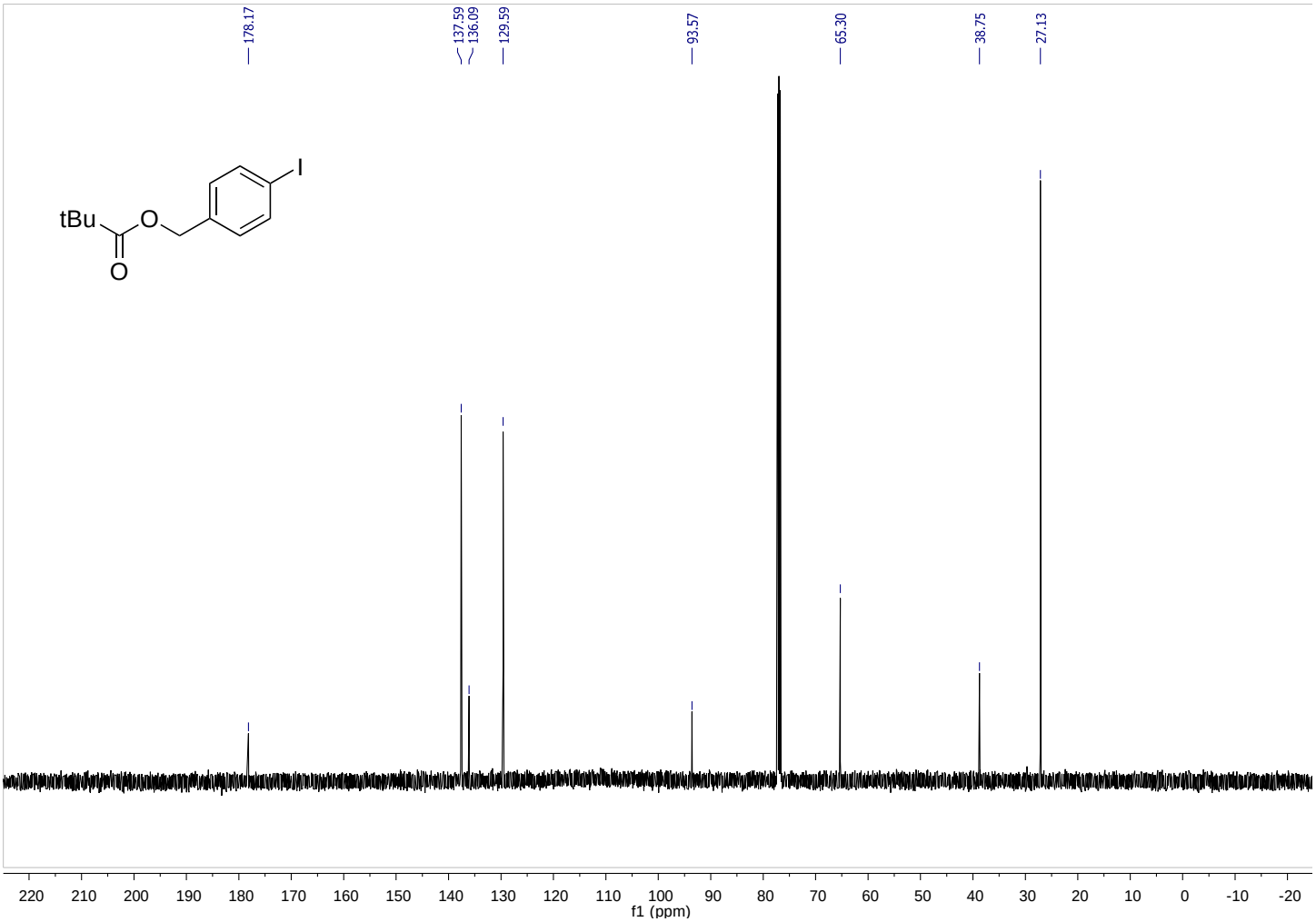
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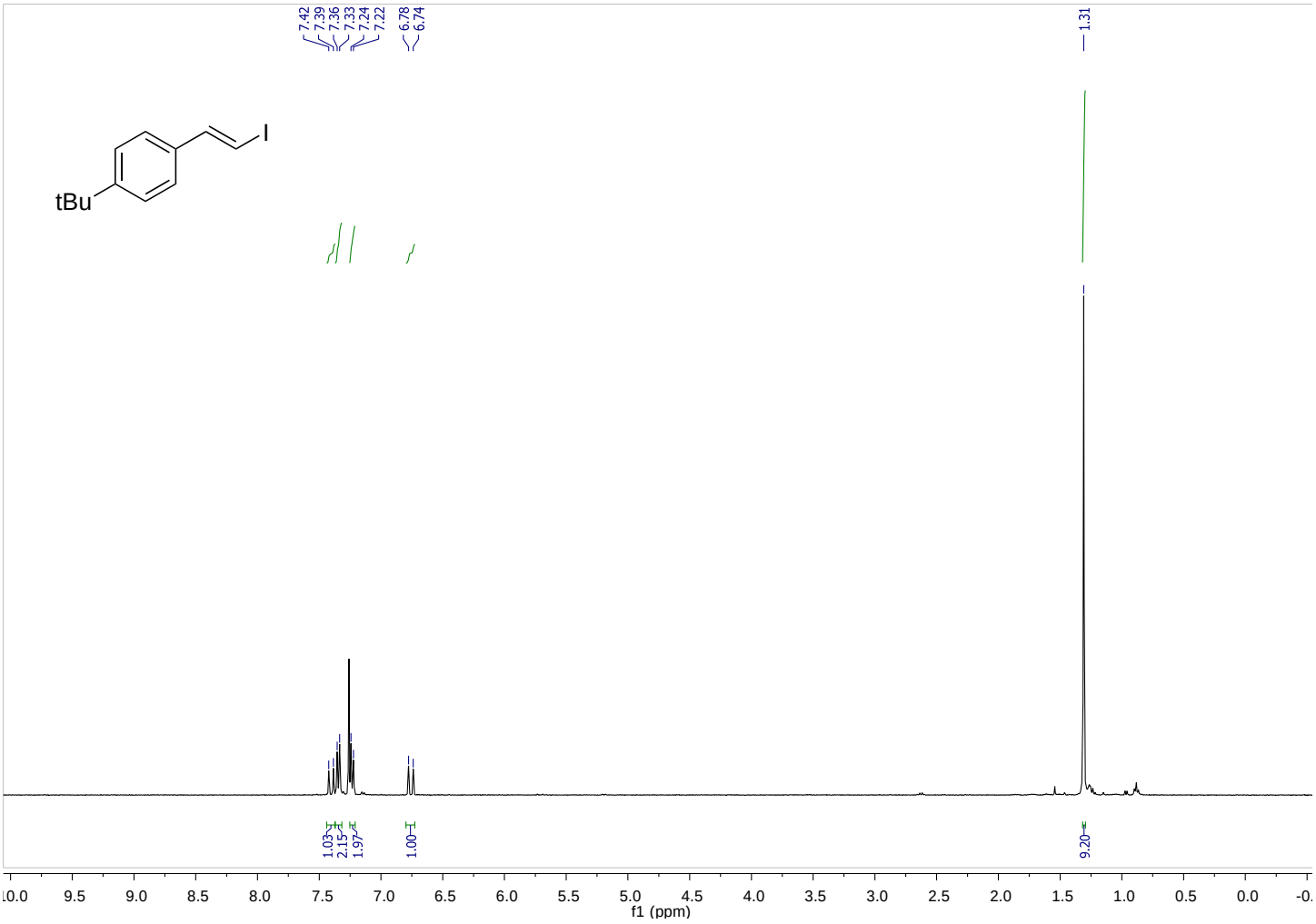
f1 (ppm)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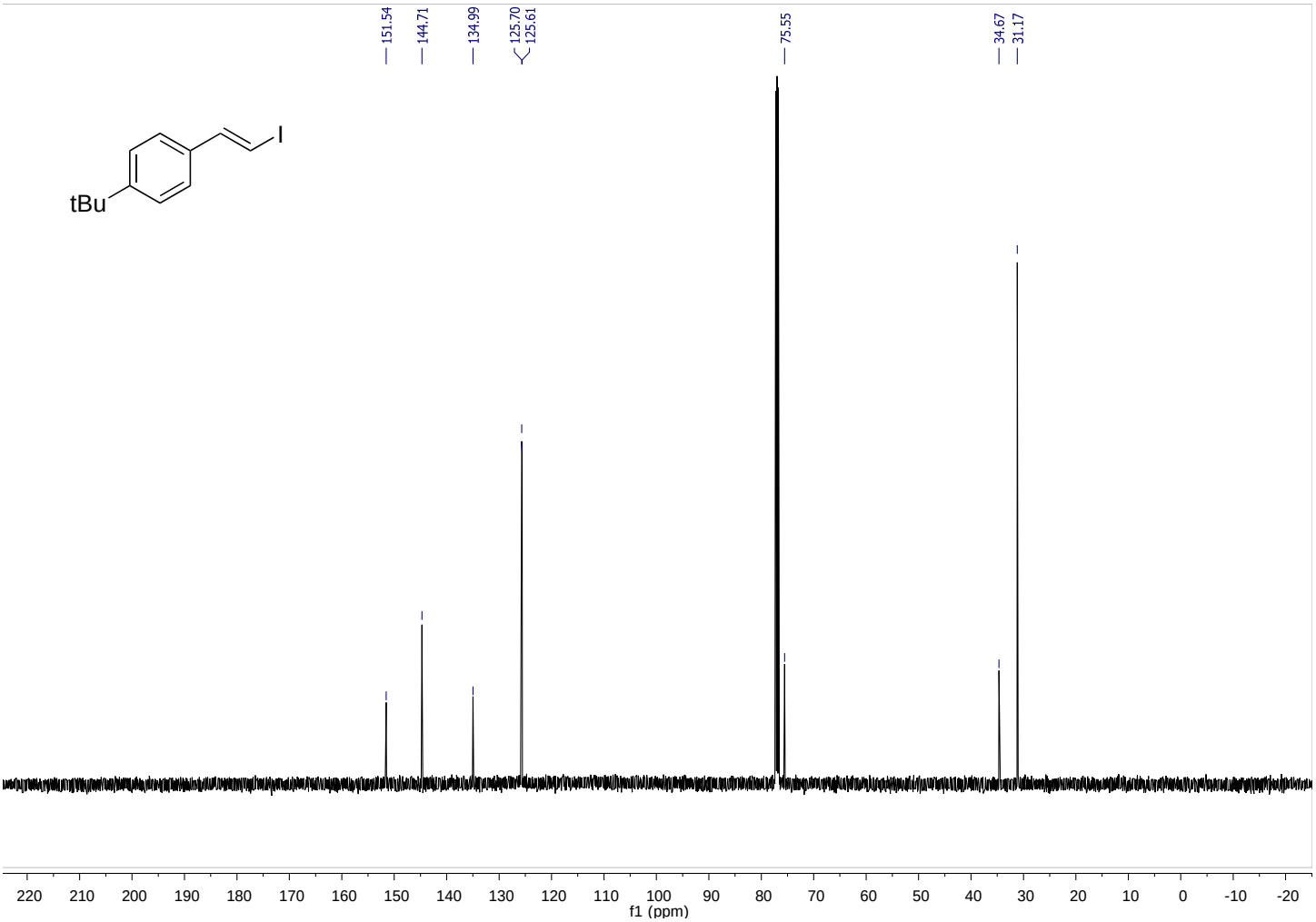
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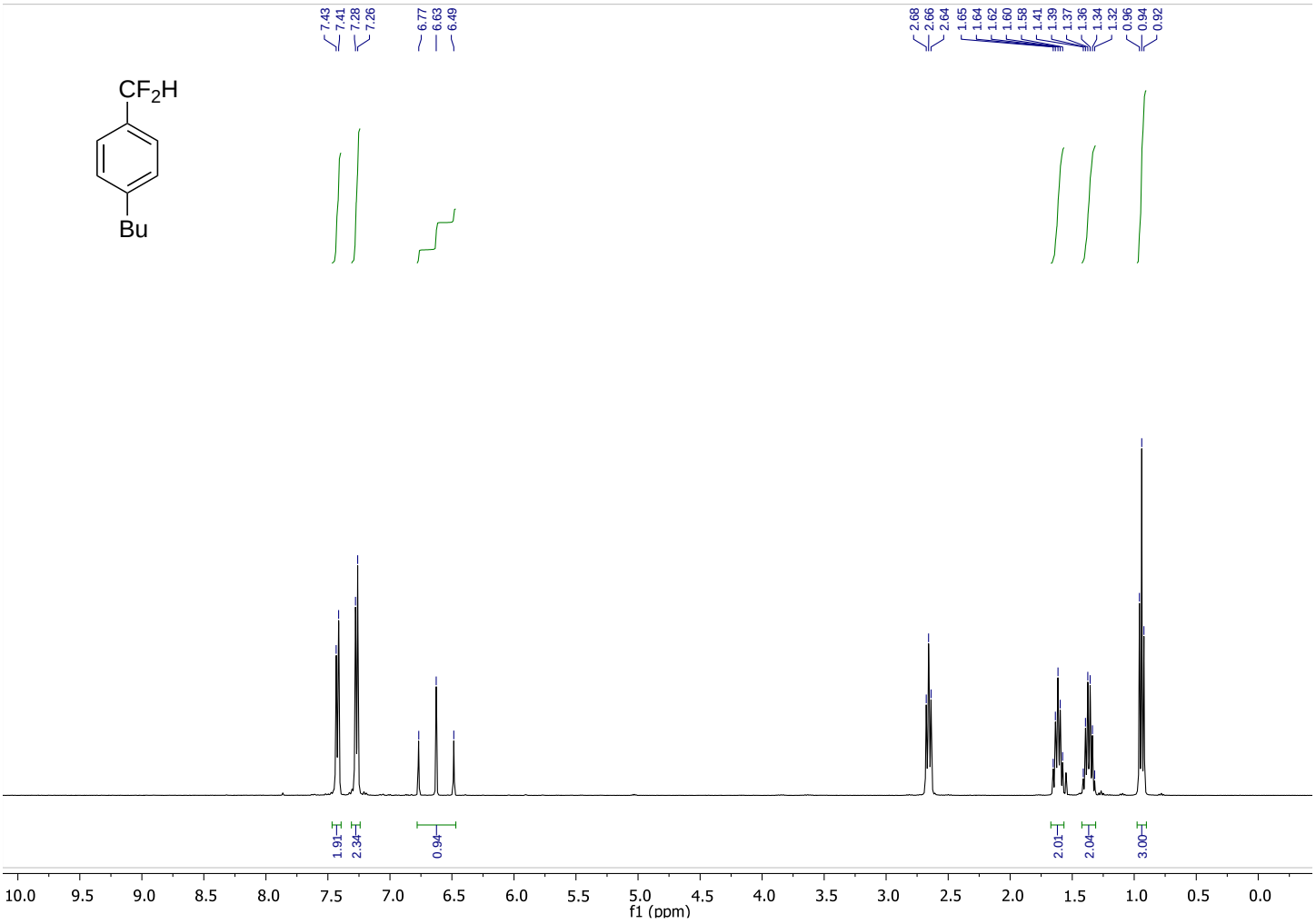
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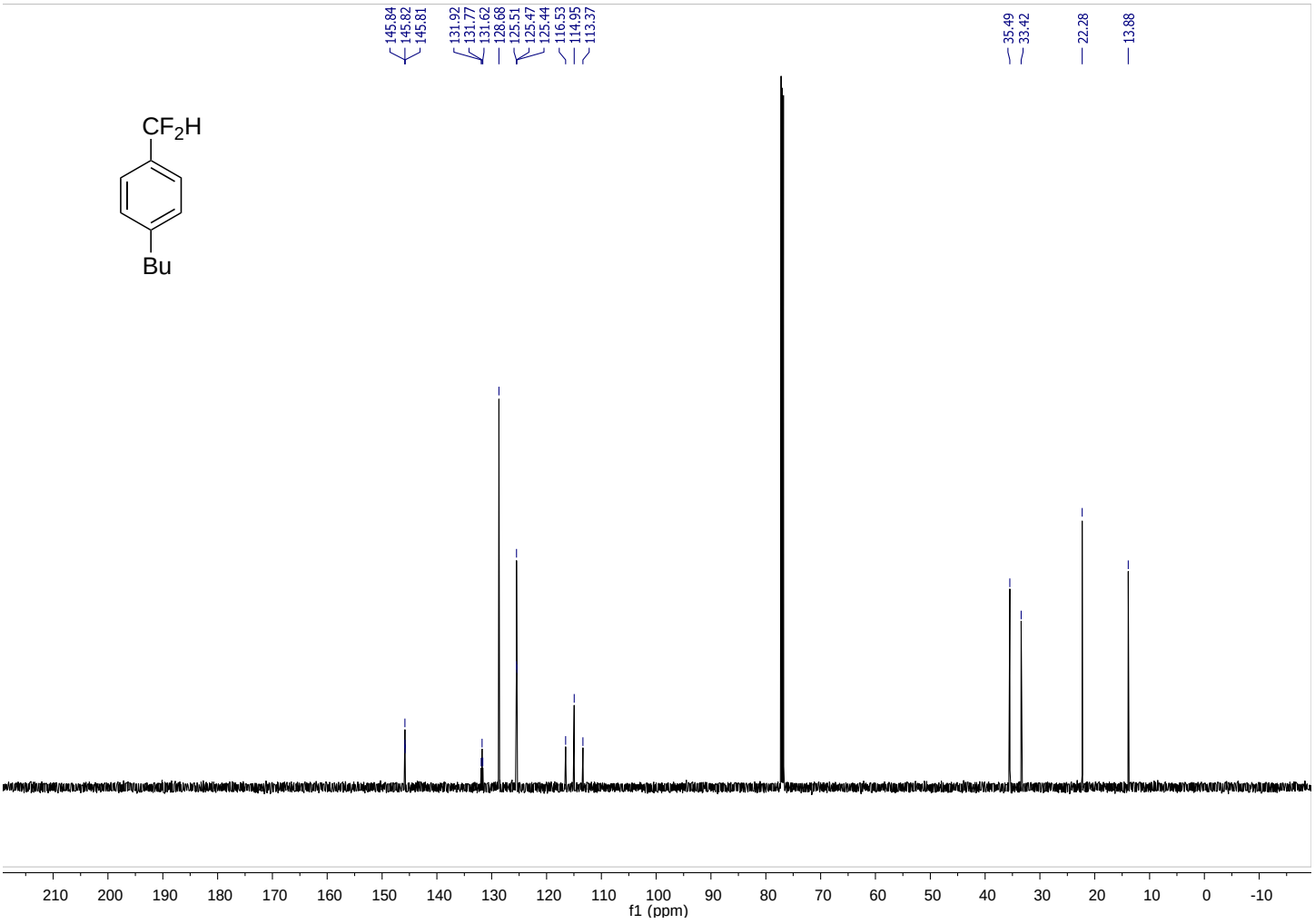
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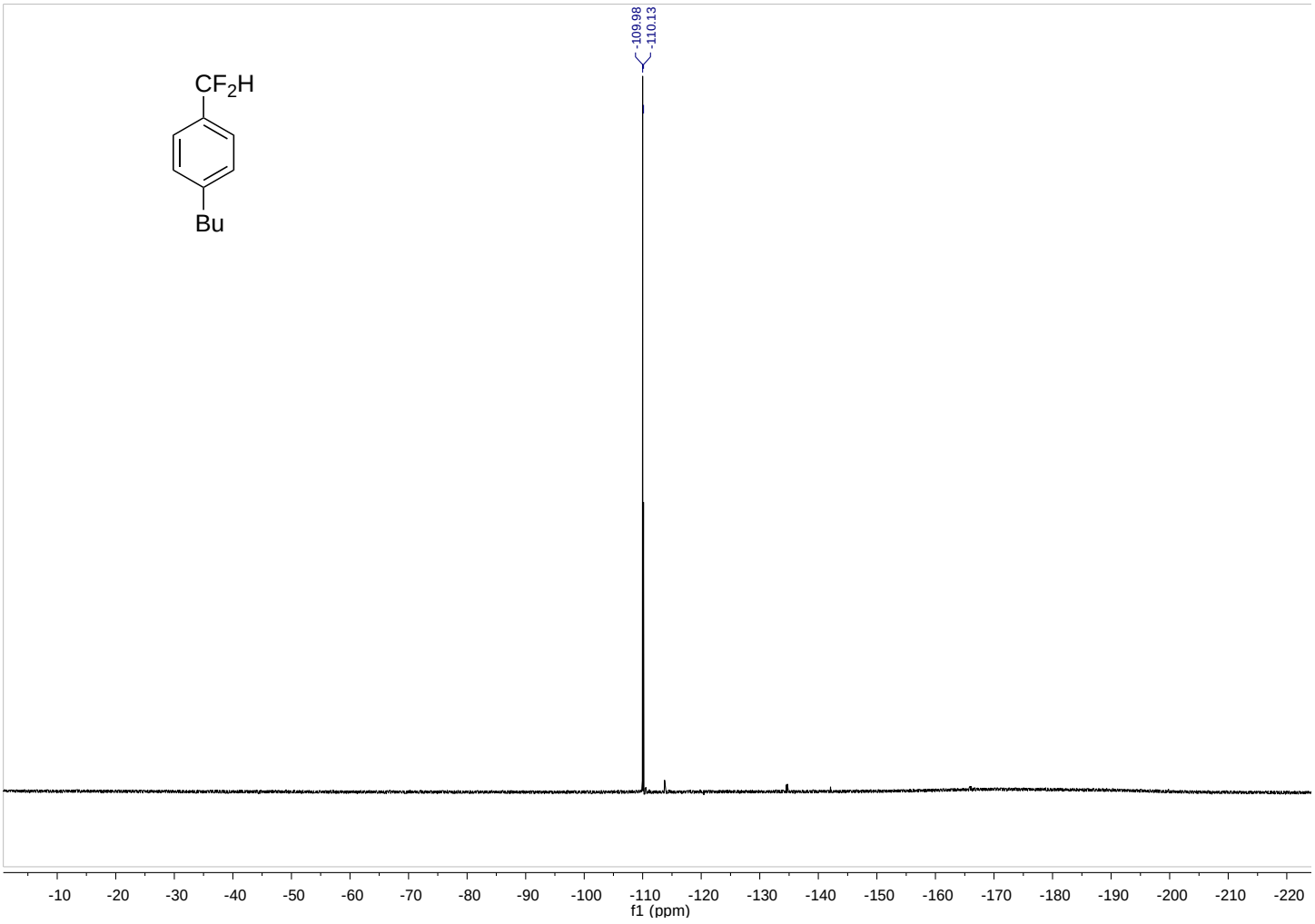
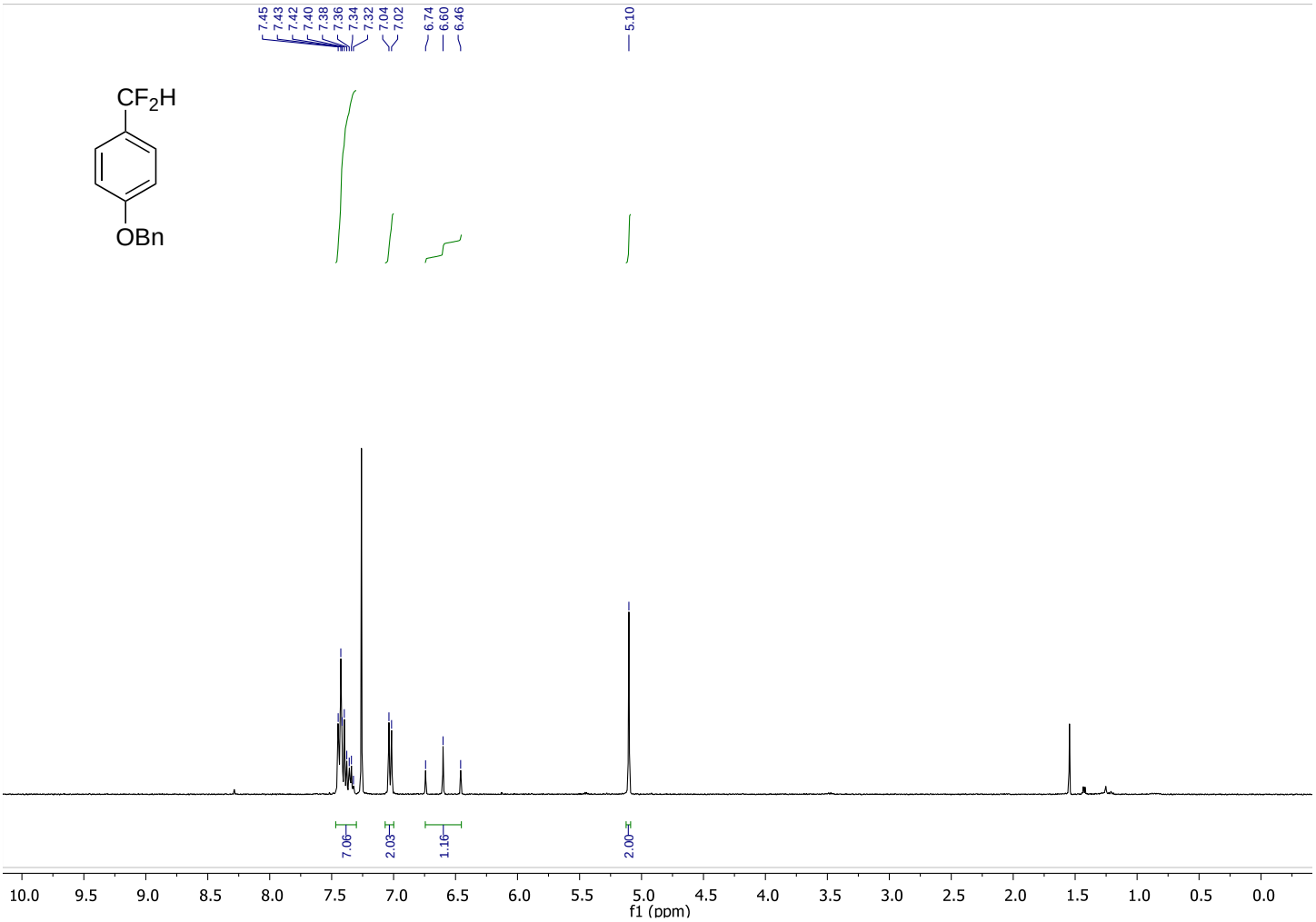
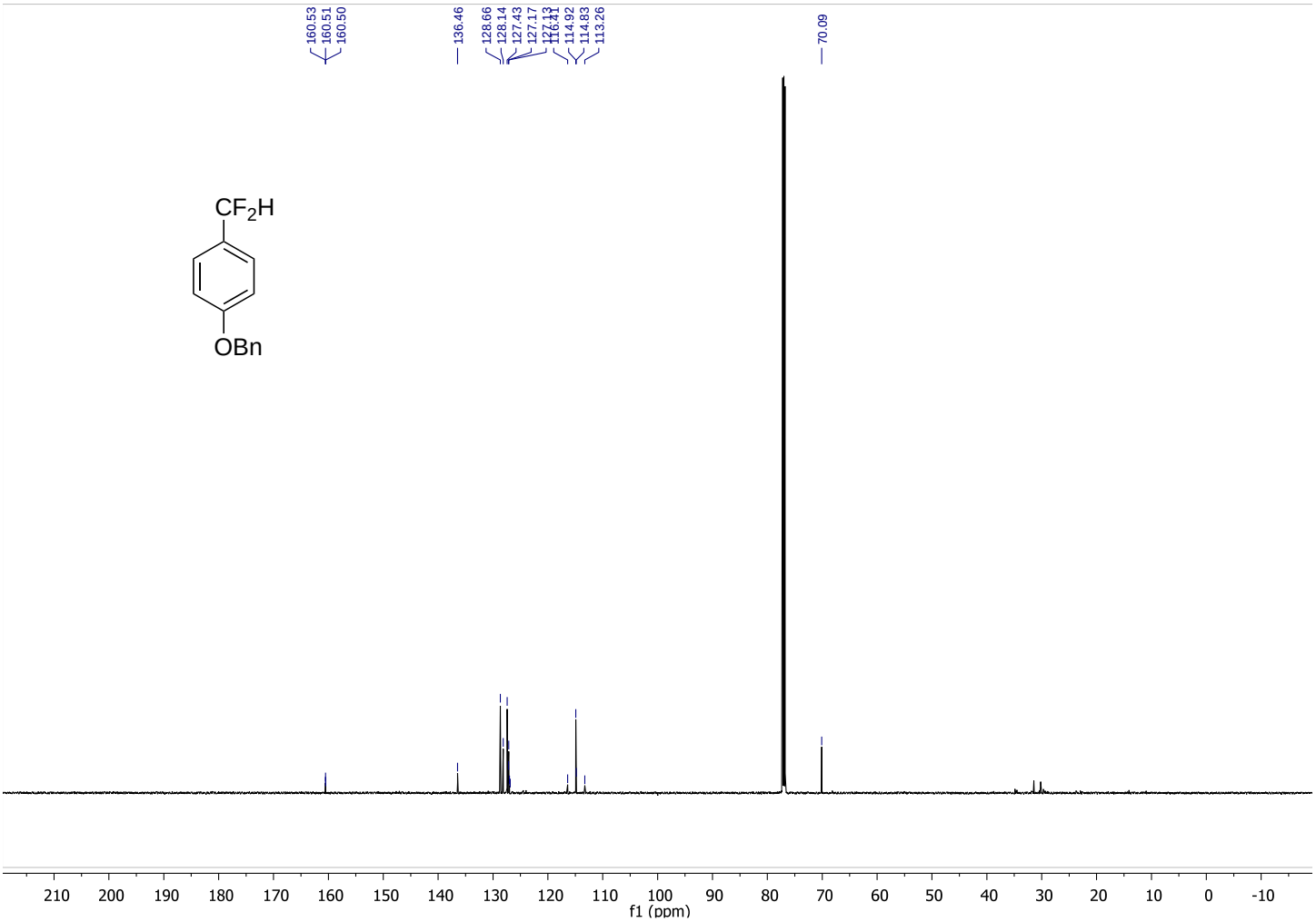
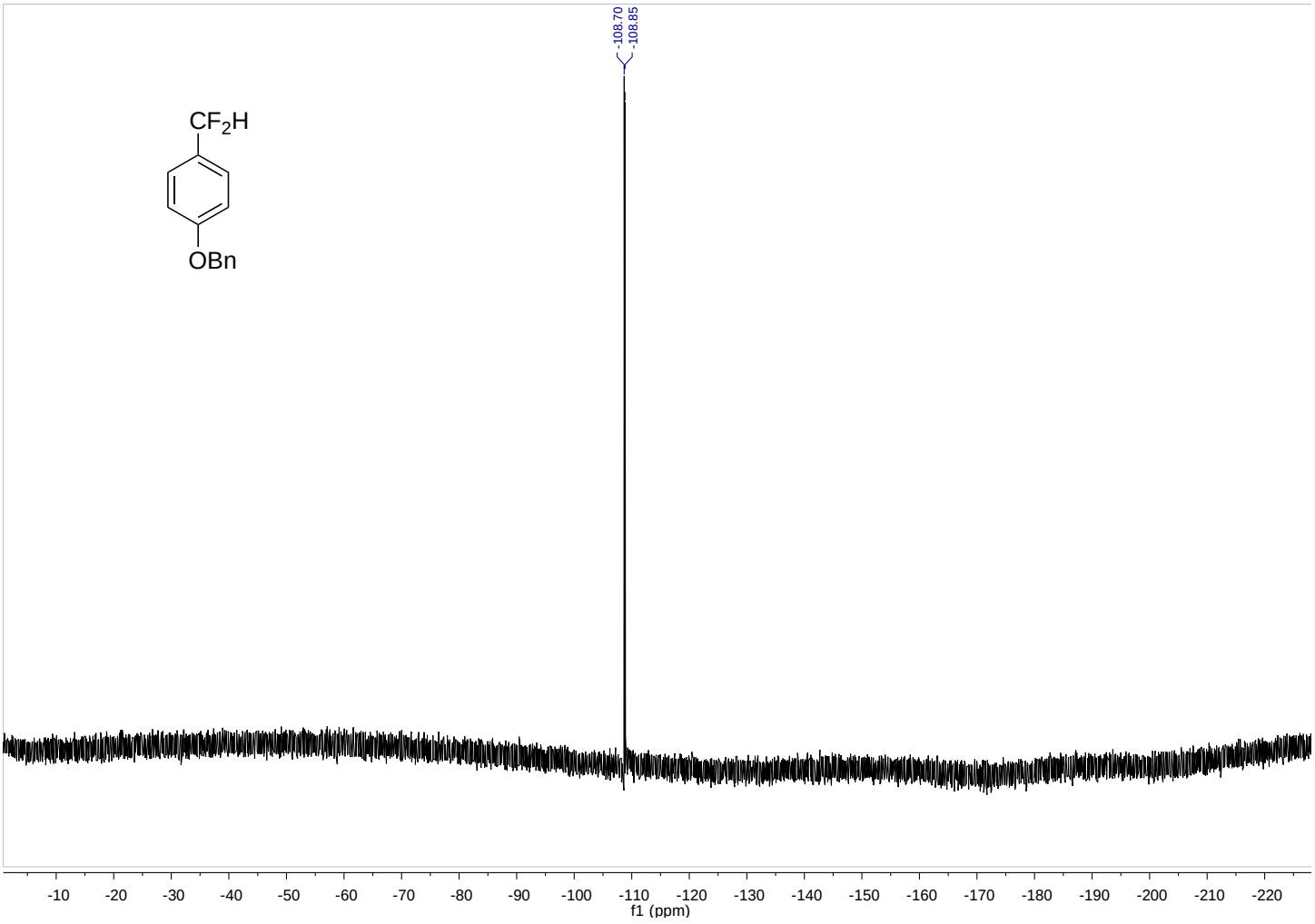
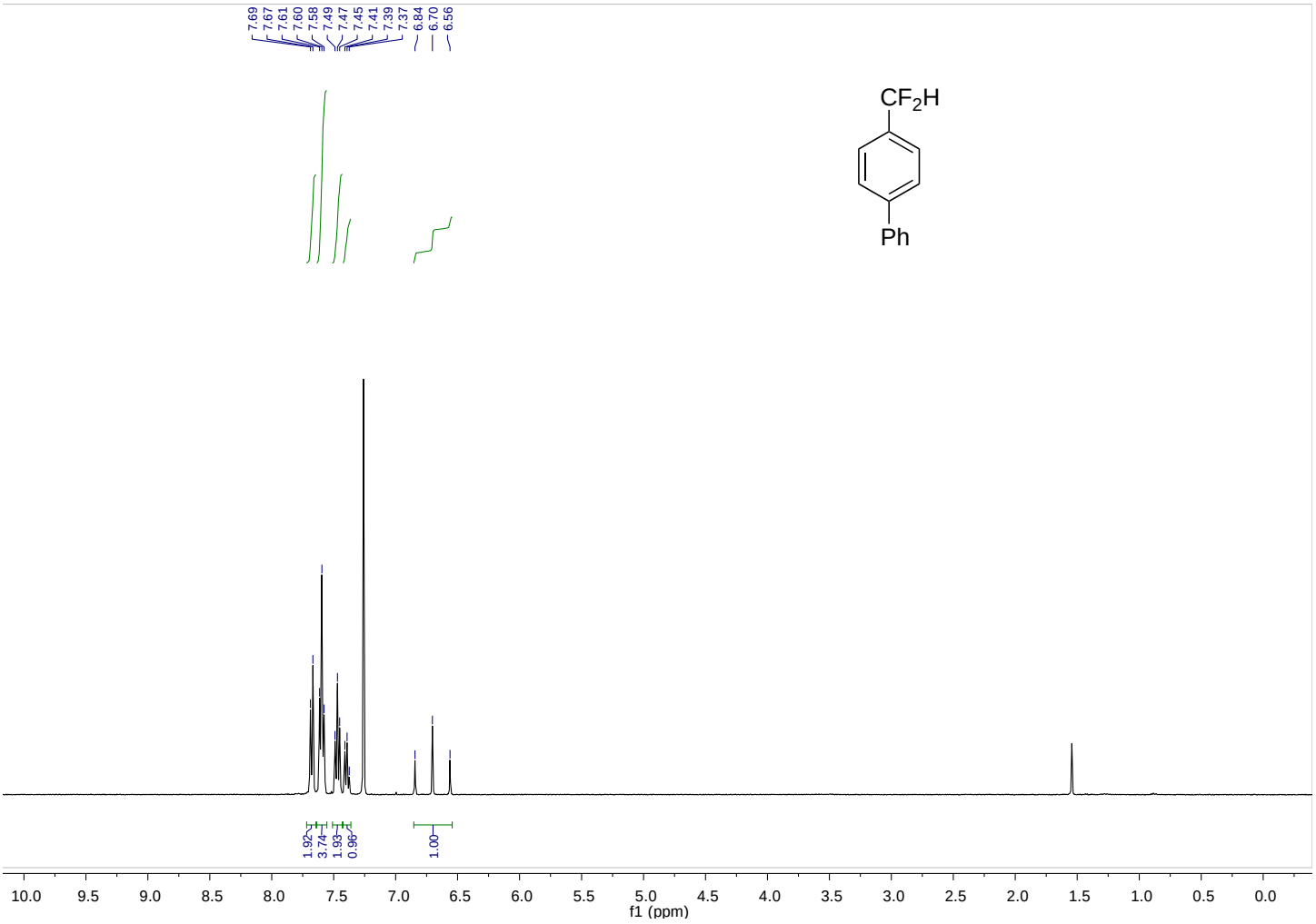
f1 (ppm)

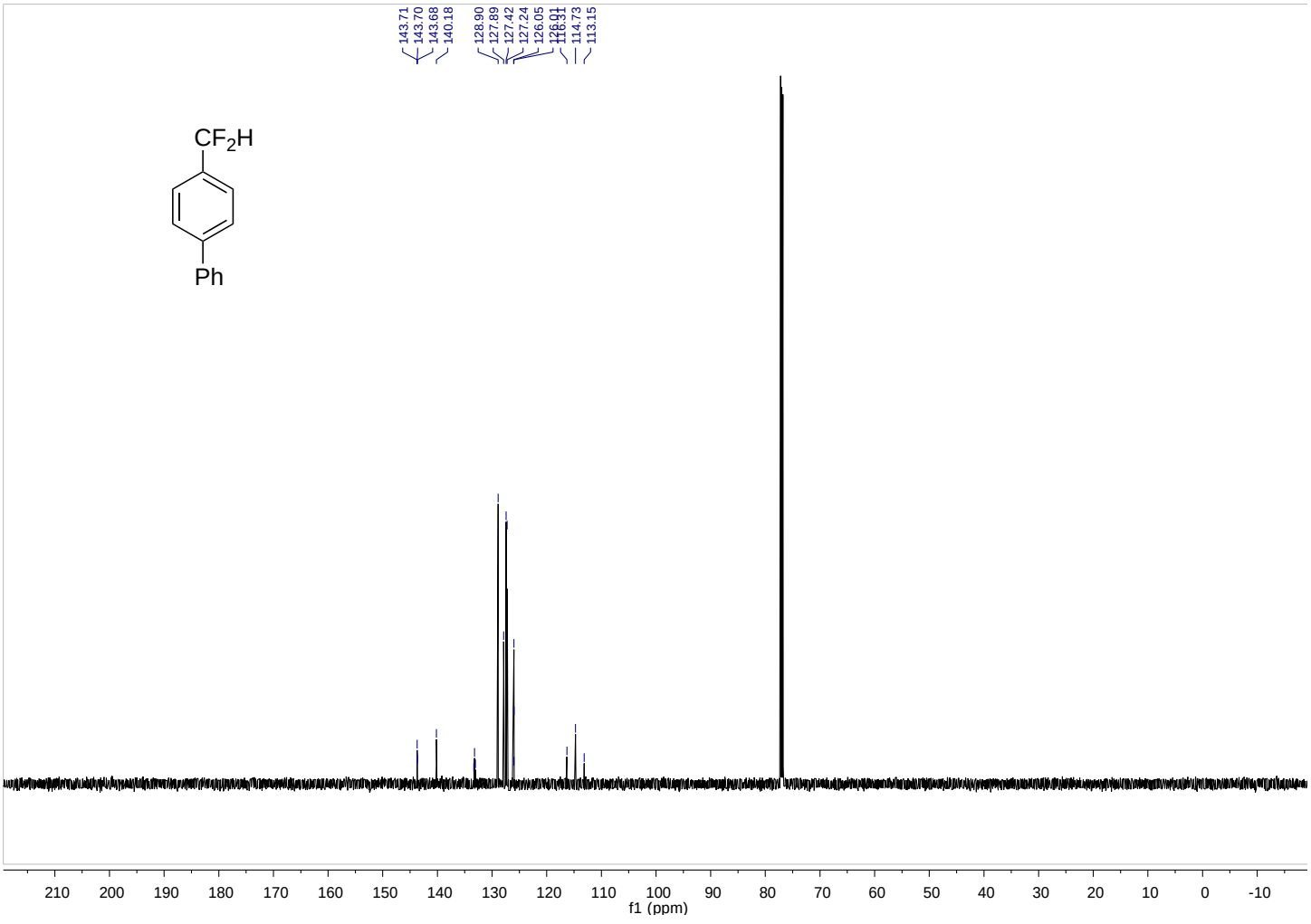

-109.98
-110.13
CF2H
Bu
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

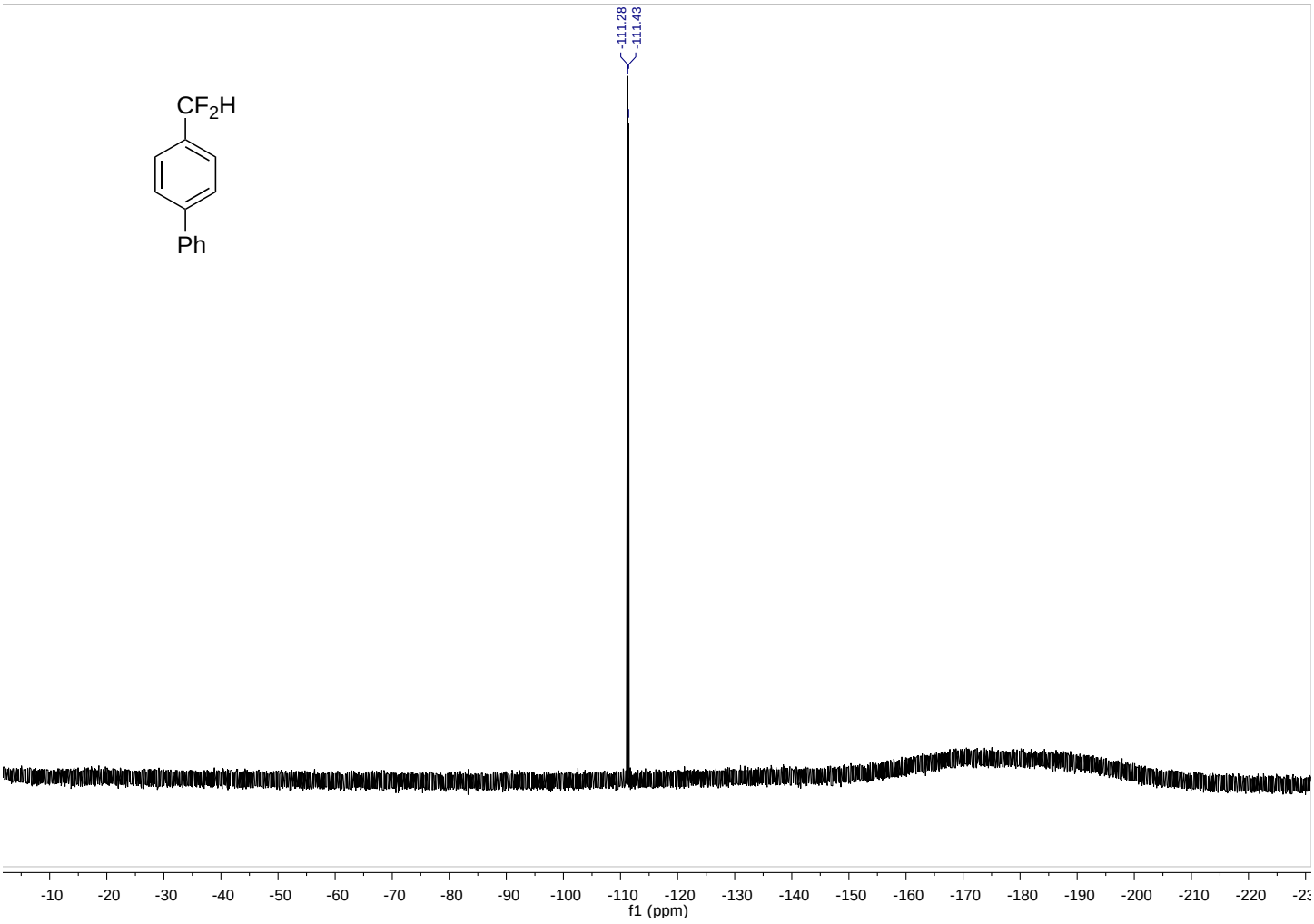

7.45
7.43
7.42
7.40
7.38
7.36
7.34
7.32
7.04
7.02
6.74
6.60
6.46
5.10
CF2H
OBn
7.06
2.03
1.16
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

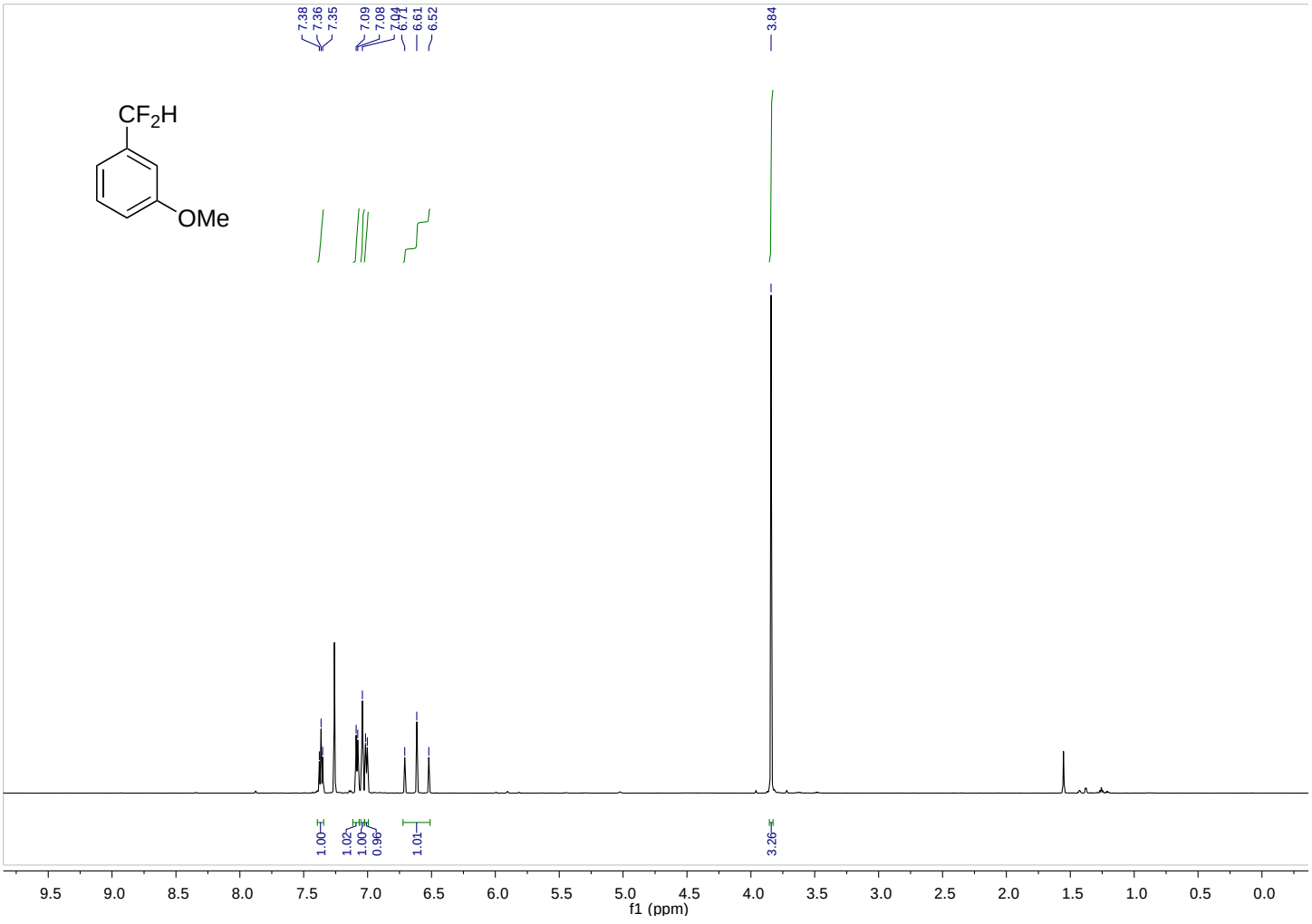

160.53
160.51
160.50
136.46
128.66
128.14
127.43
127.17
114.92
114.83
113.26
70.09
CF2H
OBn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

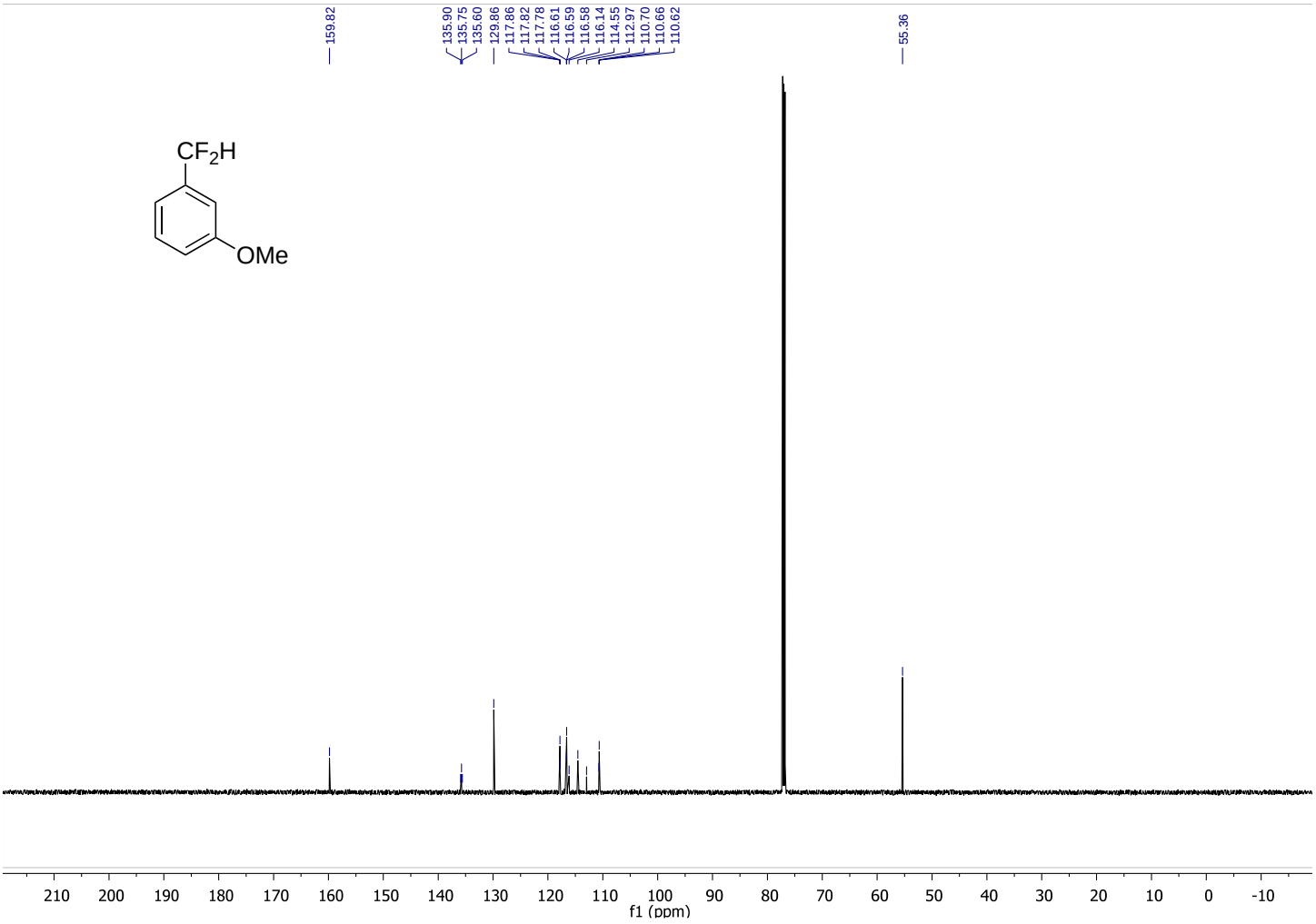

-108.70
-108.85
CF2H
OBn
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

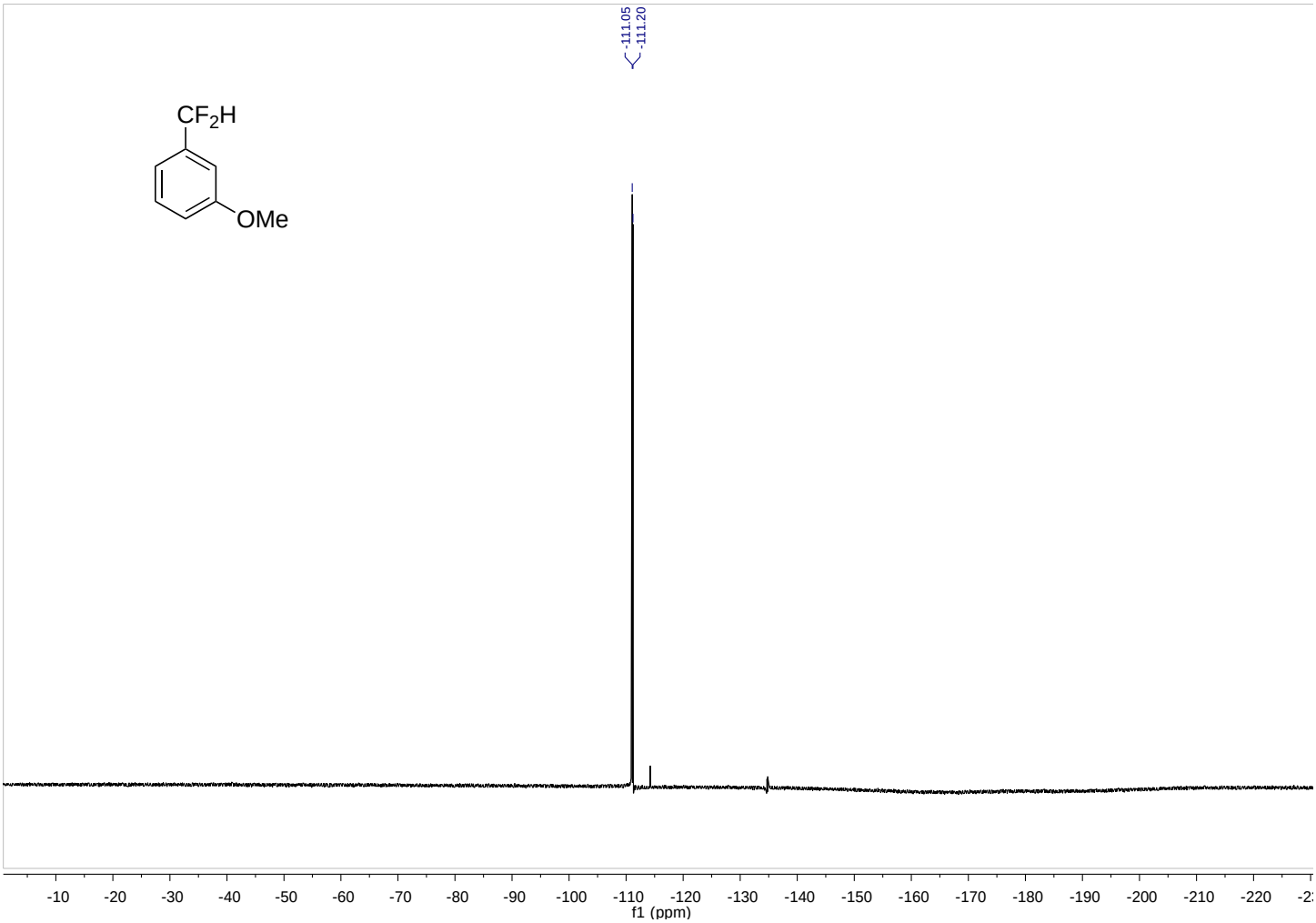

7.69
7.67
7.61
7.60
7.58
7.49
7.47
7.45
7.41
7.39
7.37
6.84
6.70
6.56
CF2H
Ph
1.92
3.74
1.93
0.96
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

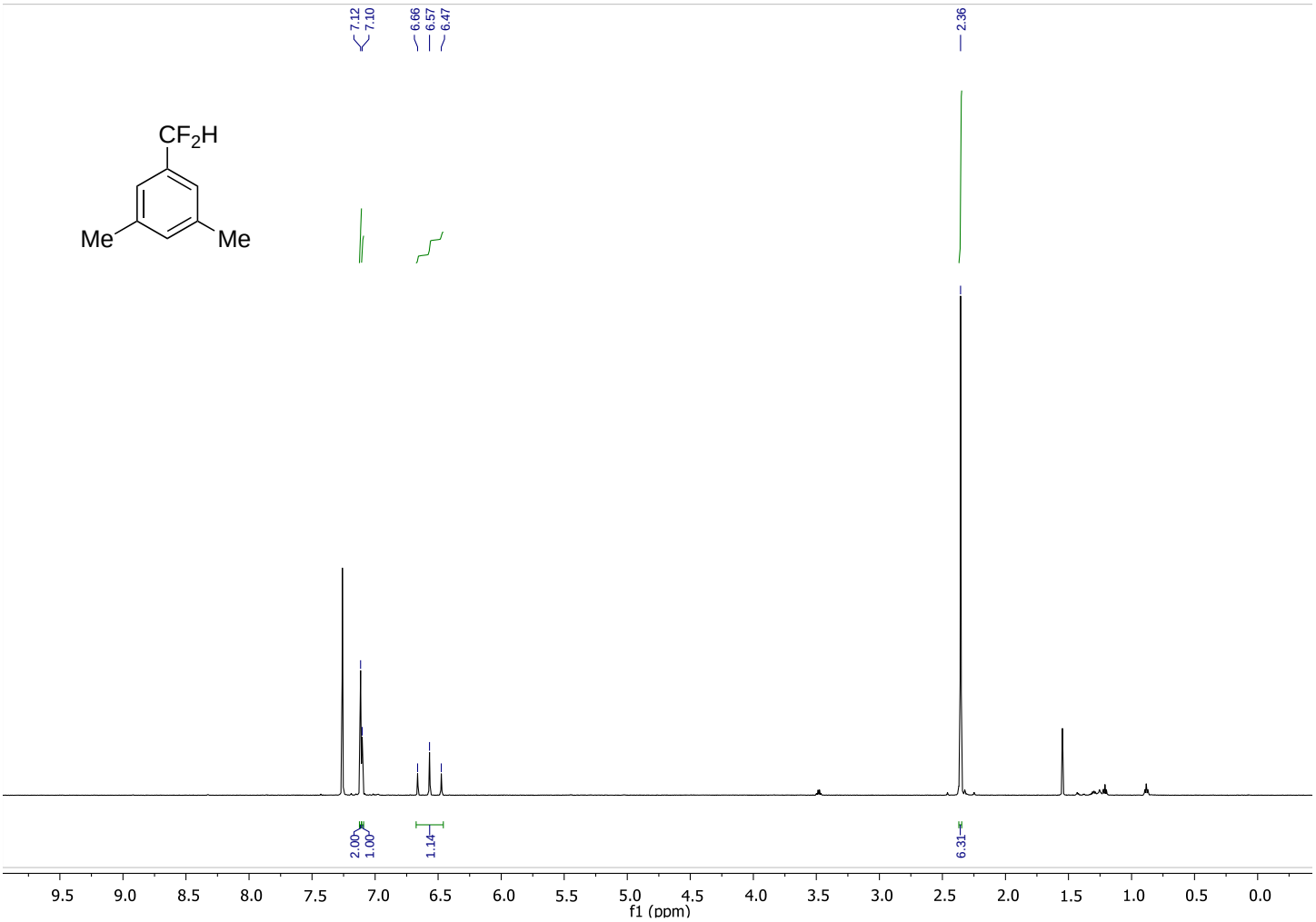

143.71
143.70
143.68
140.18
128.90
127.89
127.42
127.24
126.05
114.73
113.15
CF2H
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

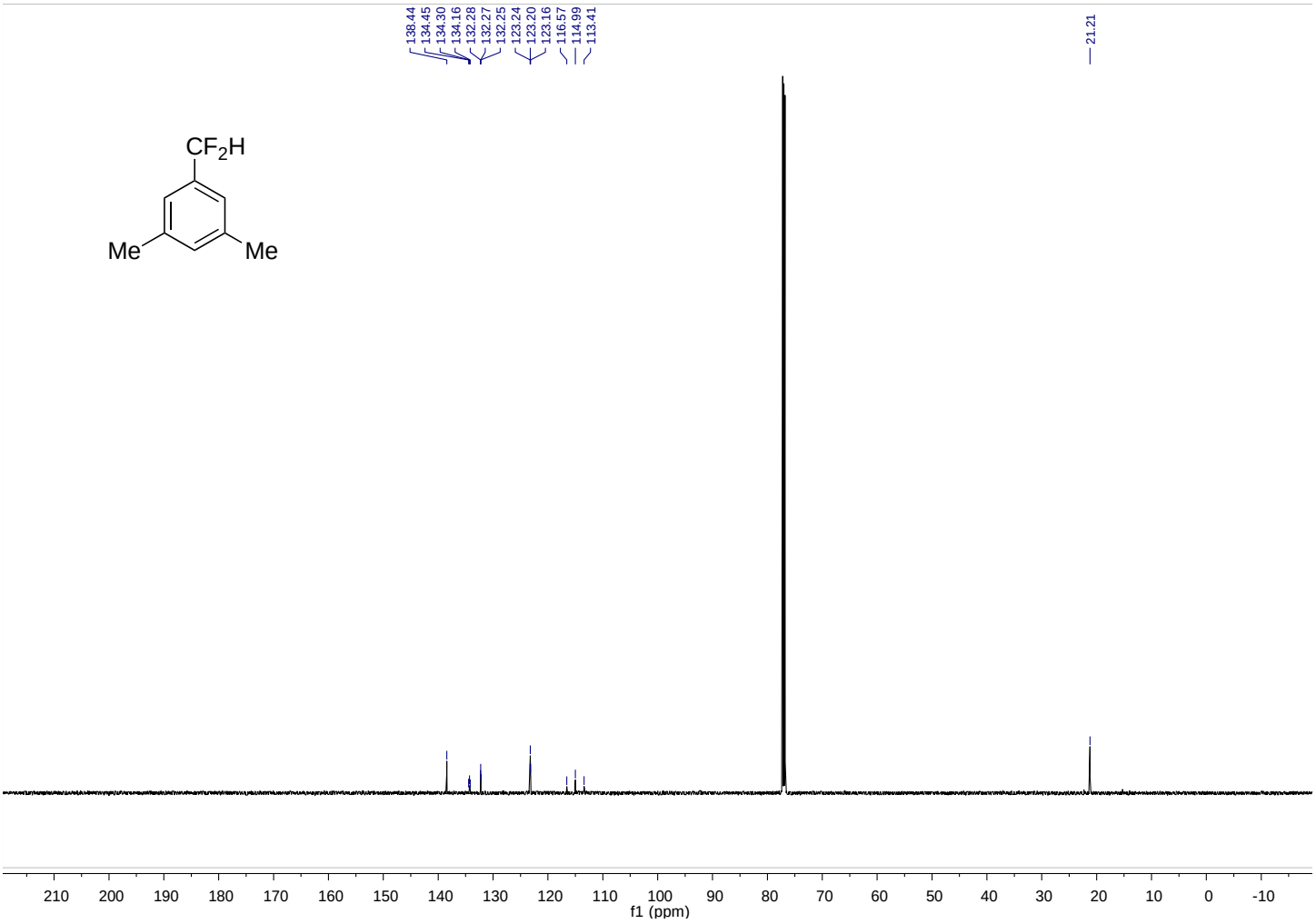

-111.28
-111.43
CF2H
Ph
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

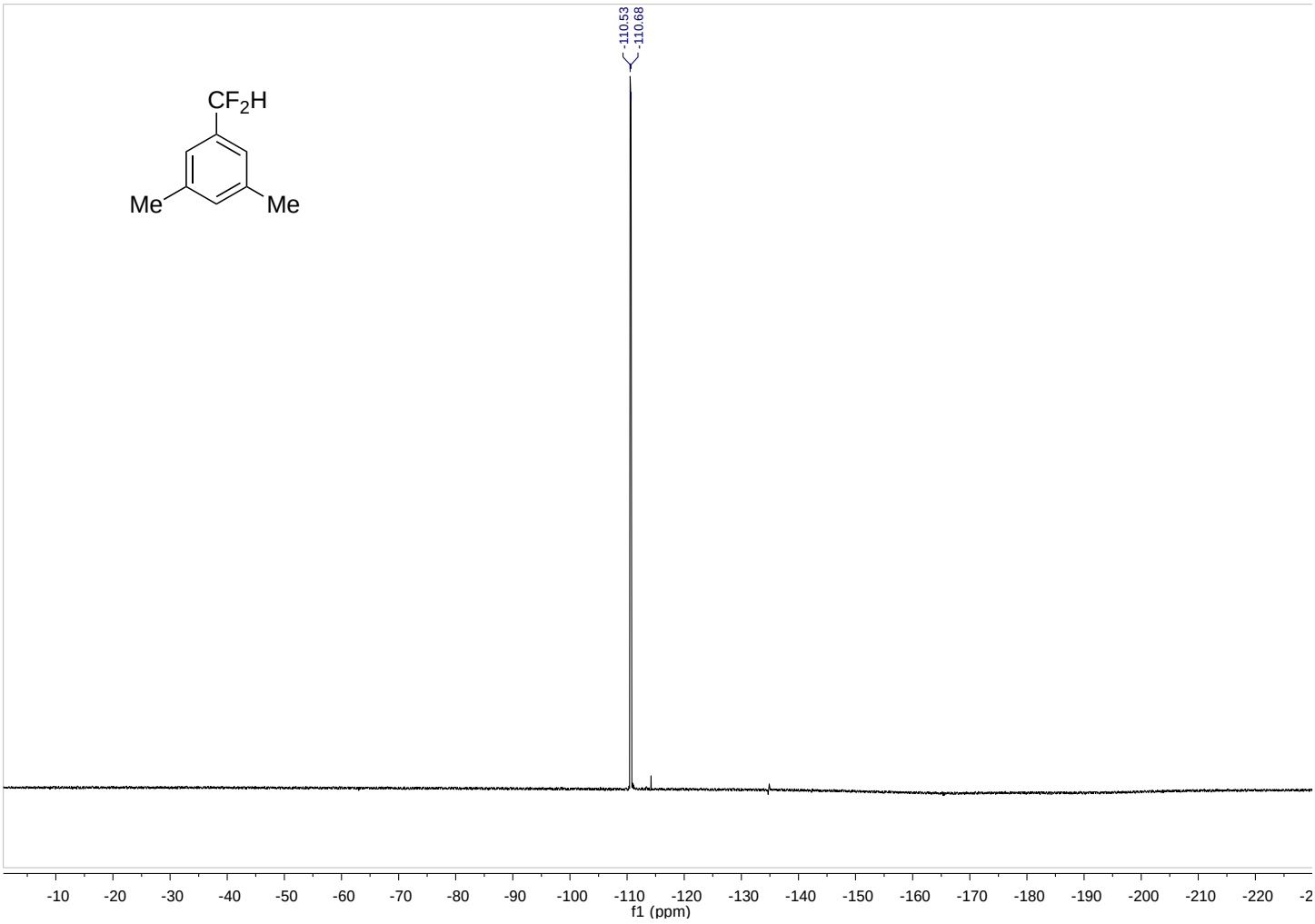

7.38
7.36
7.35
7.09
7.08
7.04
6.71
6.61
6.52
3.84
CF2H
OMe
1.00
1.02
1.00
0.96
1.01
3.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

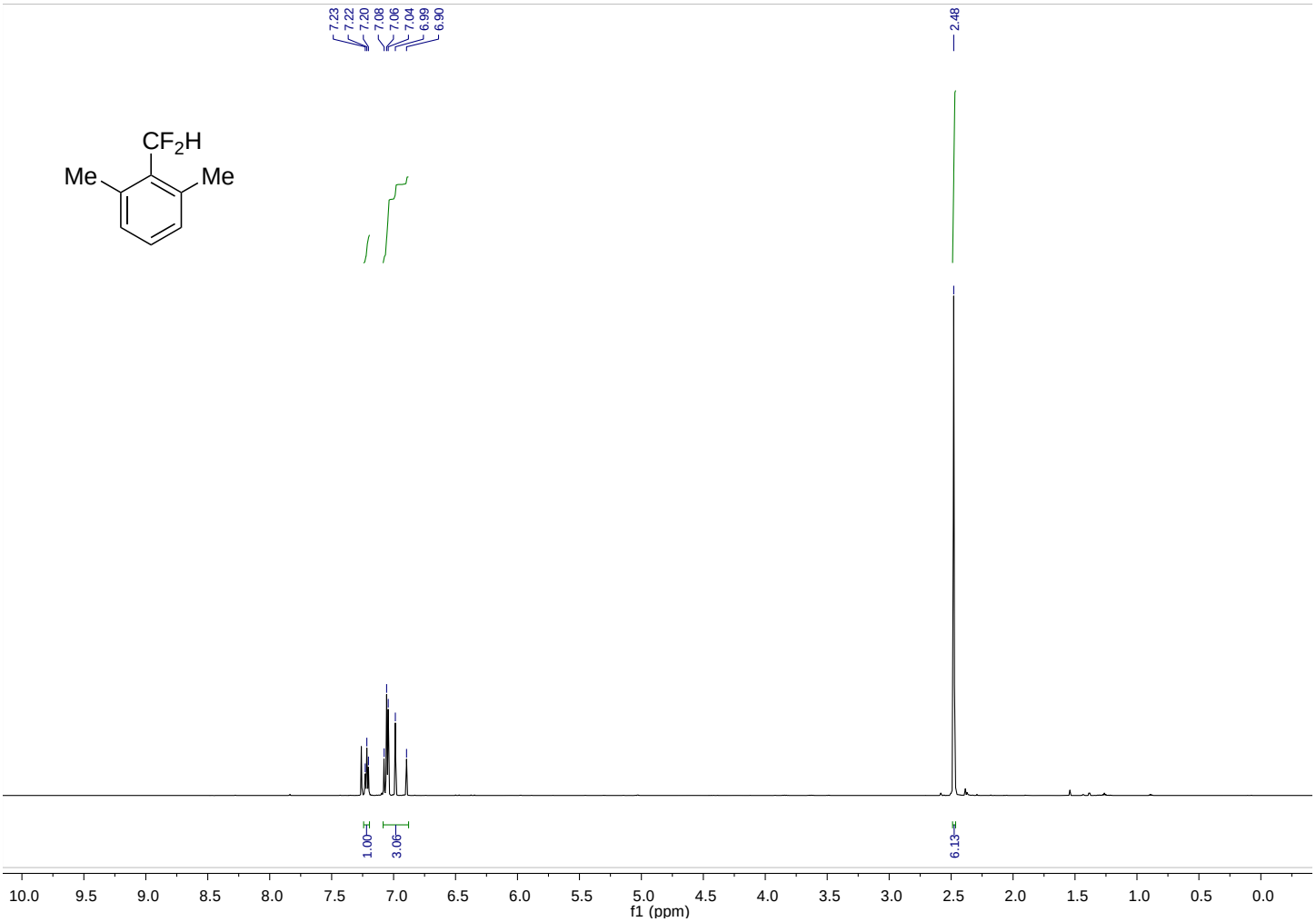

159.82
135.90
135.75
135.60
129.86
117.86
117.82
117.78
116.61
116.59
116.58
116.14
114.55
112.97
110.70
110.66
110.62
55.36
CF2H
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

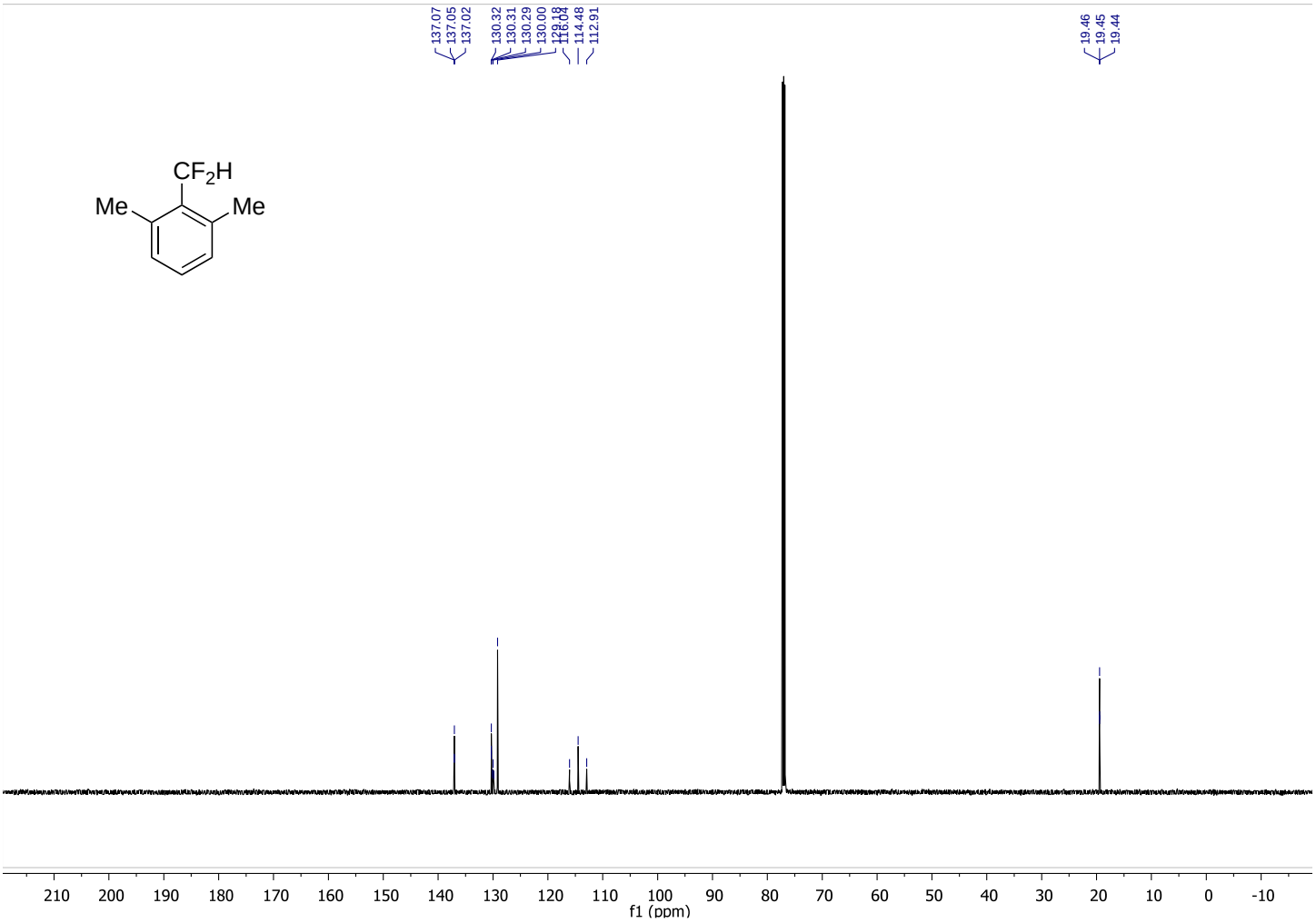

-111.05
-111.20
CF2H
OMe
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

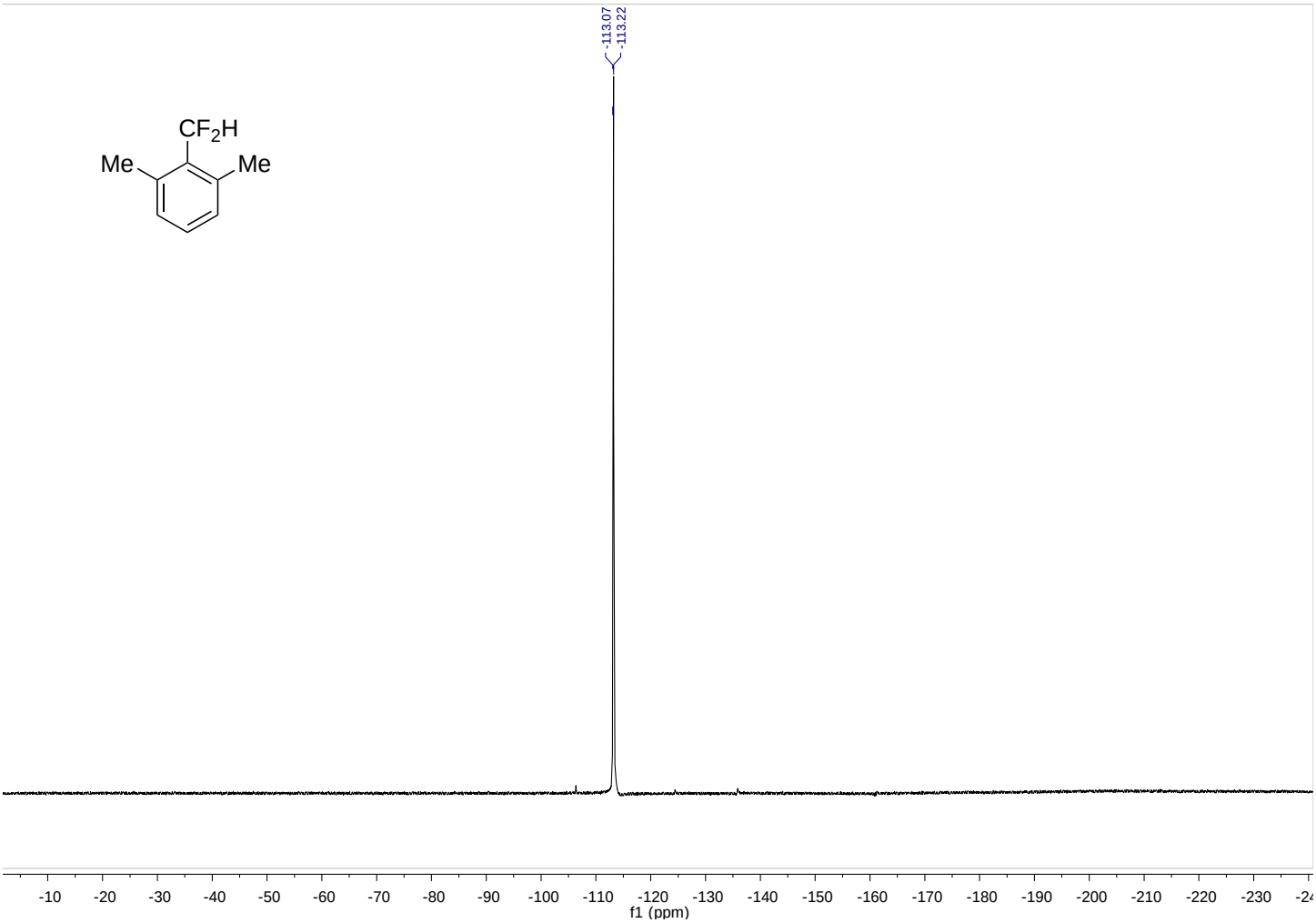

7.12
7.10
6.66
6.57
6.47
2.36
CF2H
Me
Me
2.00
1.00
1.14
6.31
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

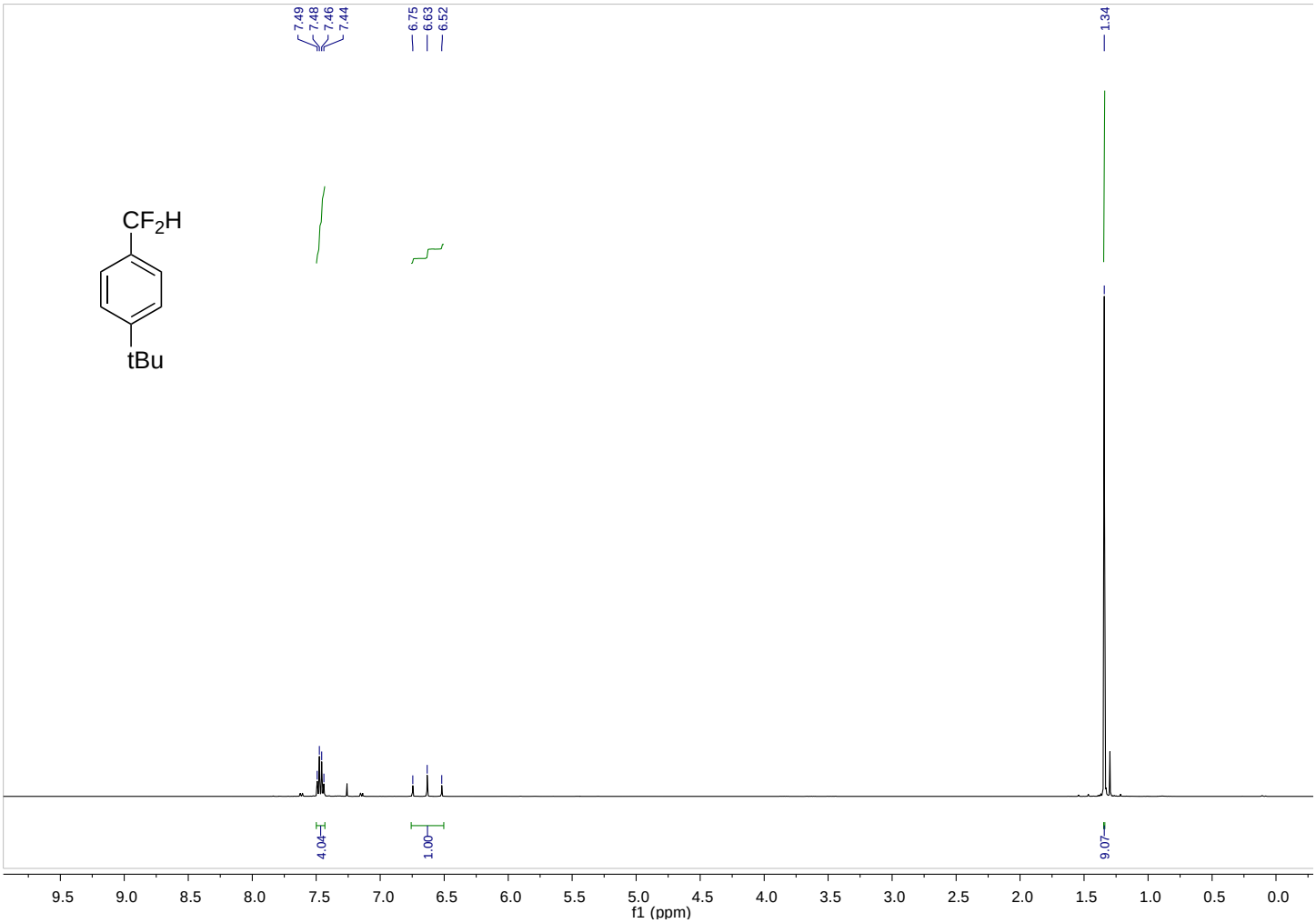

138.44
134.45
134.30
134.16
132.28
132.27
132.25
123.24
123.20
123.16
116.57
114.99
113.41
21.21
CF2H
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

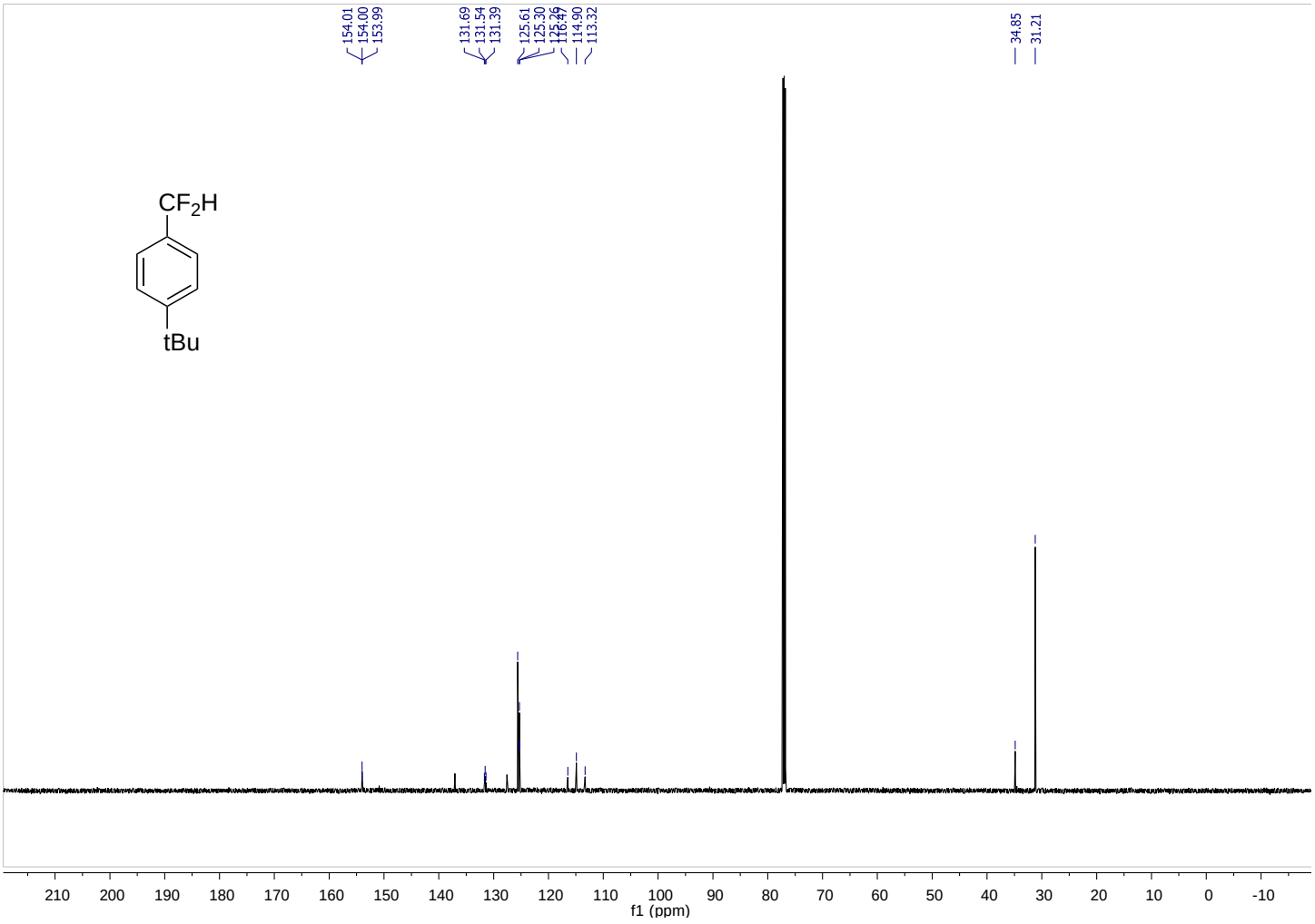

-110.53
-110.68
CF2H
Me
Me
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

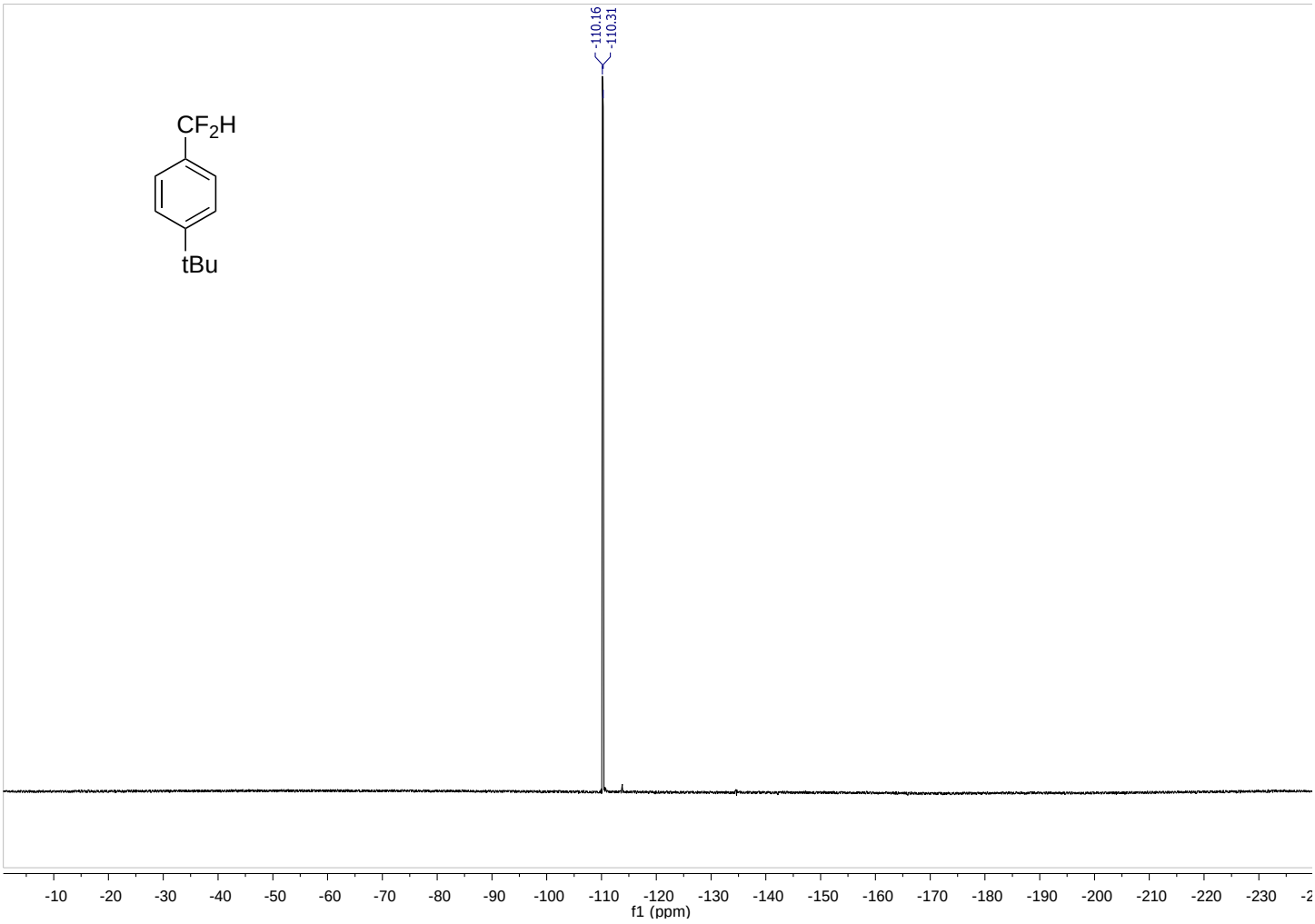

7.23
7.22
7.20
7.08
7.06
7.04
6.99
6.90
2.48
CF2H
Me
Me
1.00
3.06
6.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

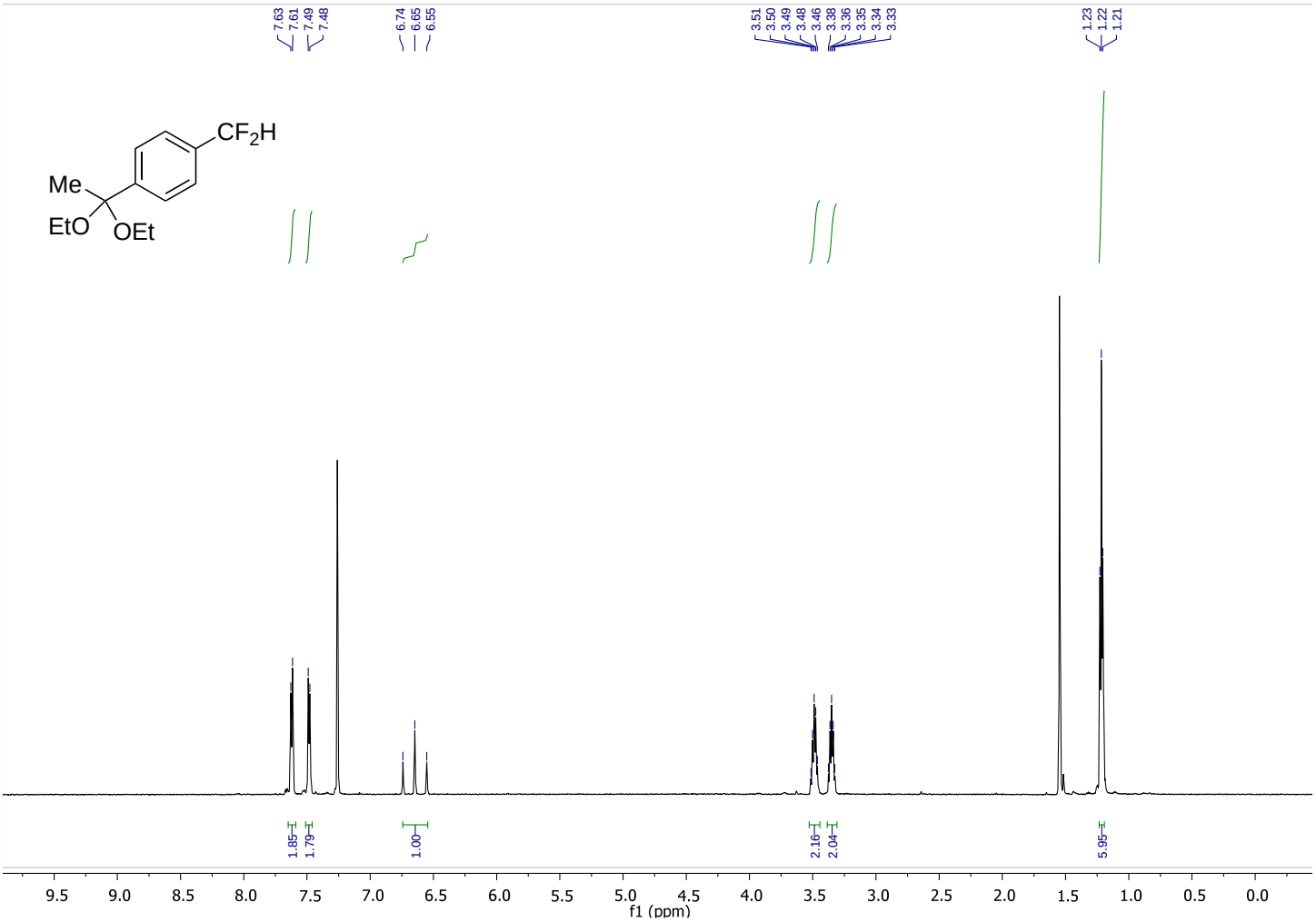

137.07
137.05
137.02
130.32
130.31
130.29
130.00
128.18
116.04
114.48
112.91
19.46
19.45
19.44
CF2H
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

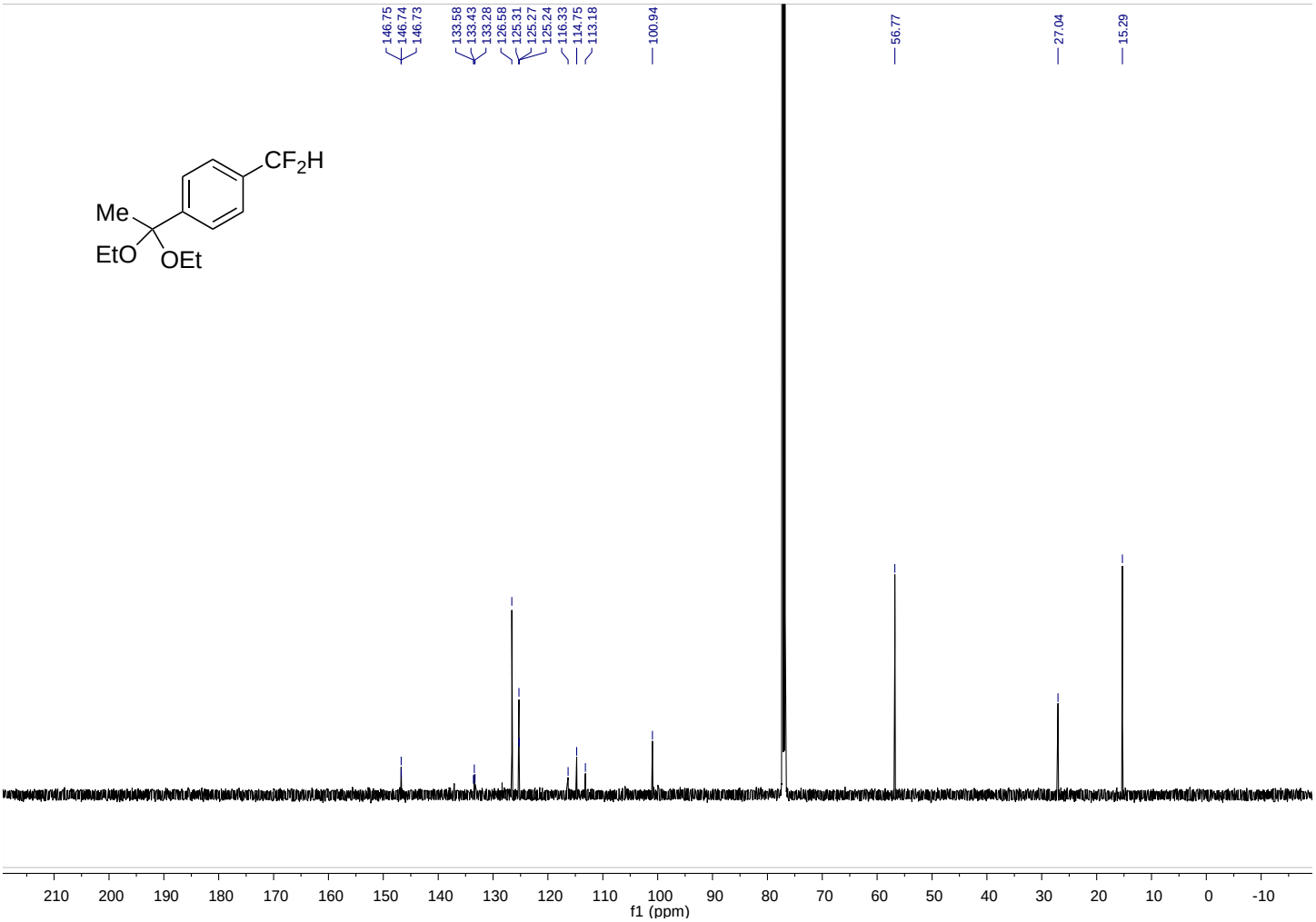

-113.07
-113.22
CF2H
Me
Me
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

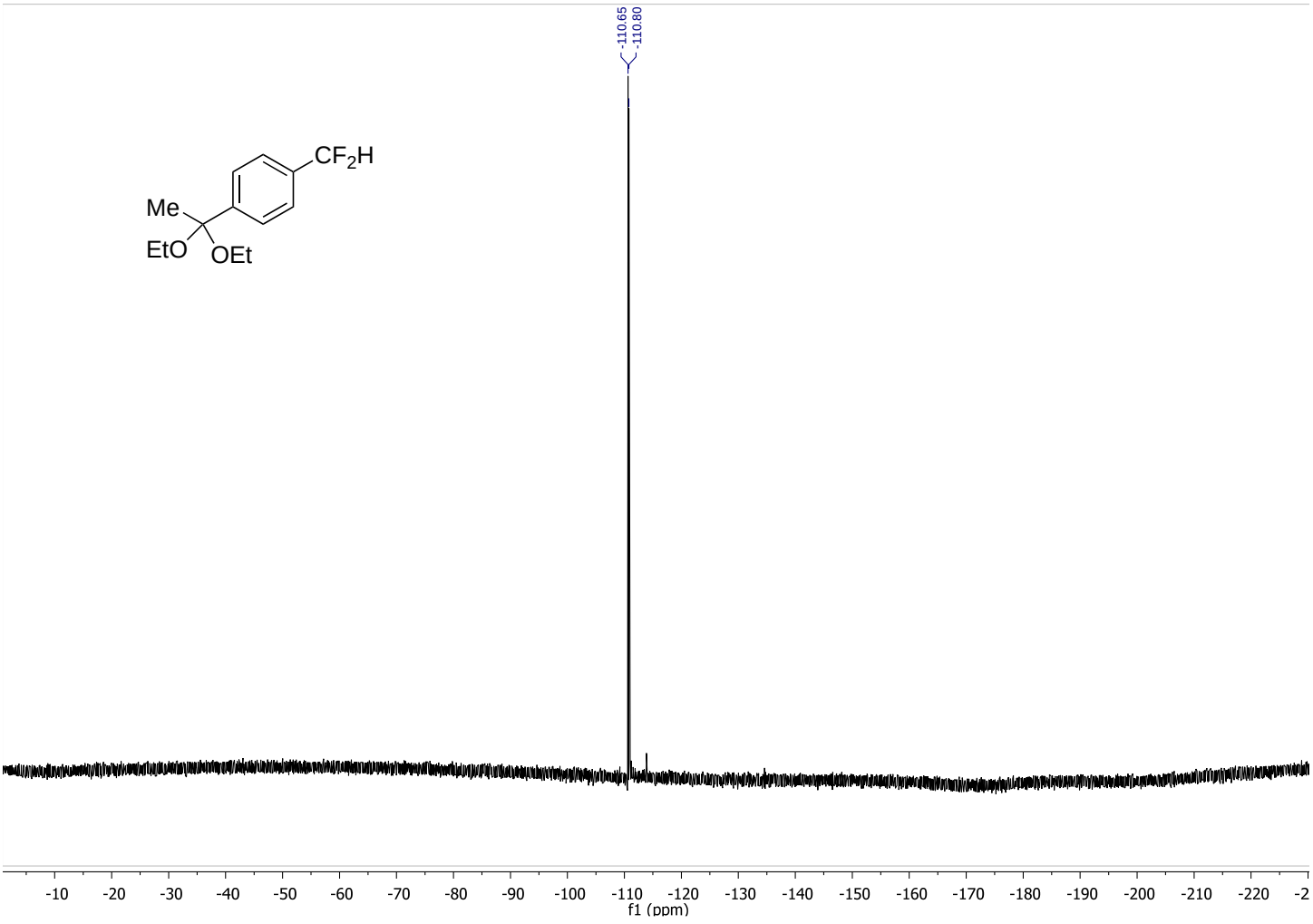

7.49
7.48
7.46
7.44
6.75
6.63
6.52
1.34
CF2H
tBu
4.04
1.00
9.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

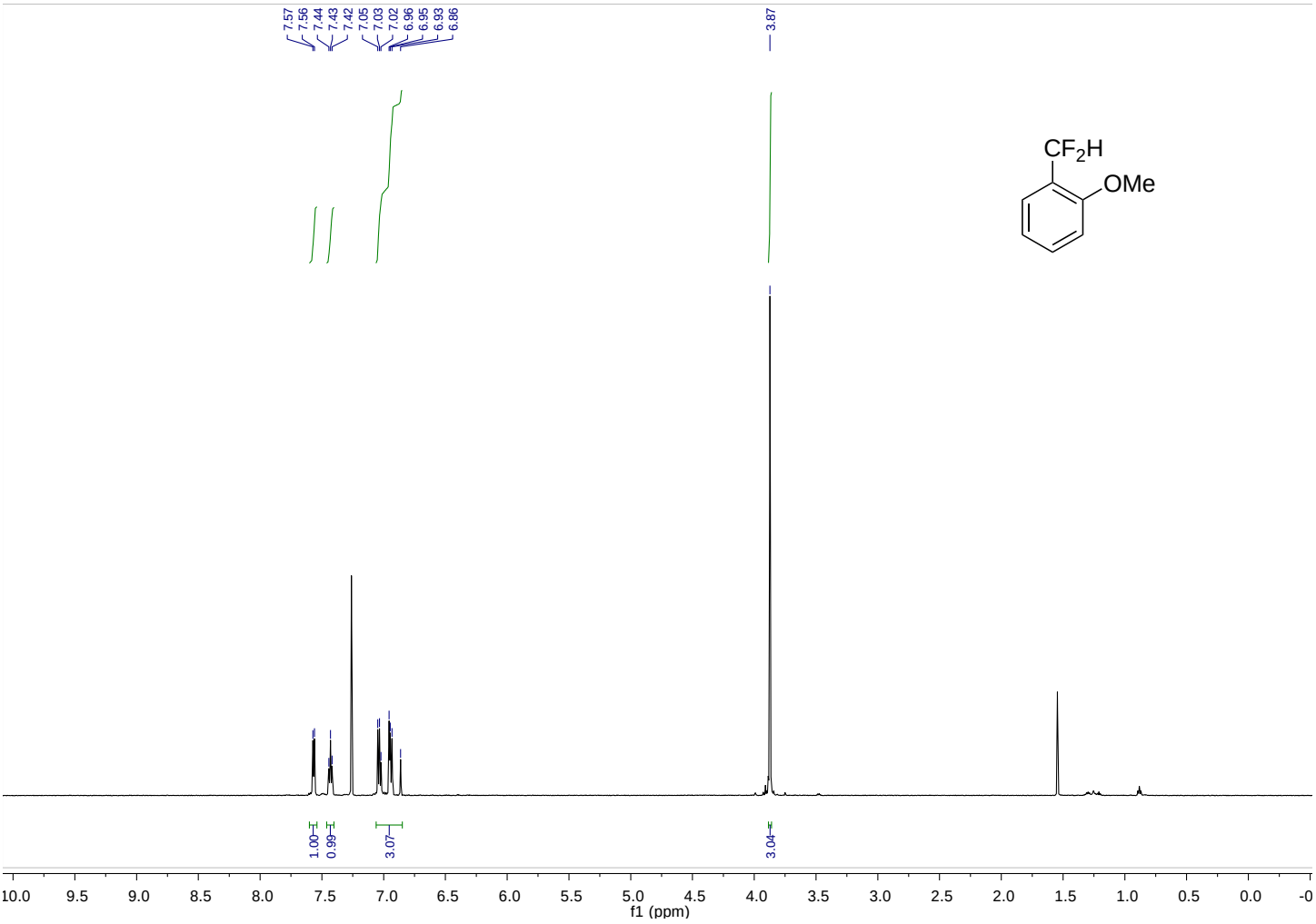

154.01
154.00
153.99
131.69
131.54
131.39
125.61
125.30
114.90
113.32
34.85
31.21
CF2H
tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

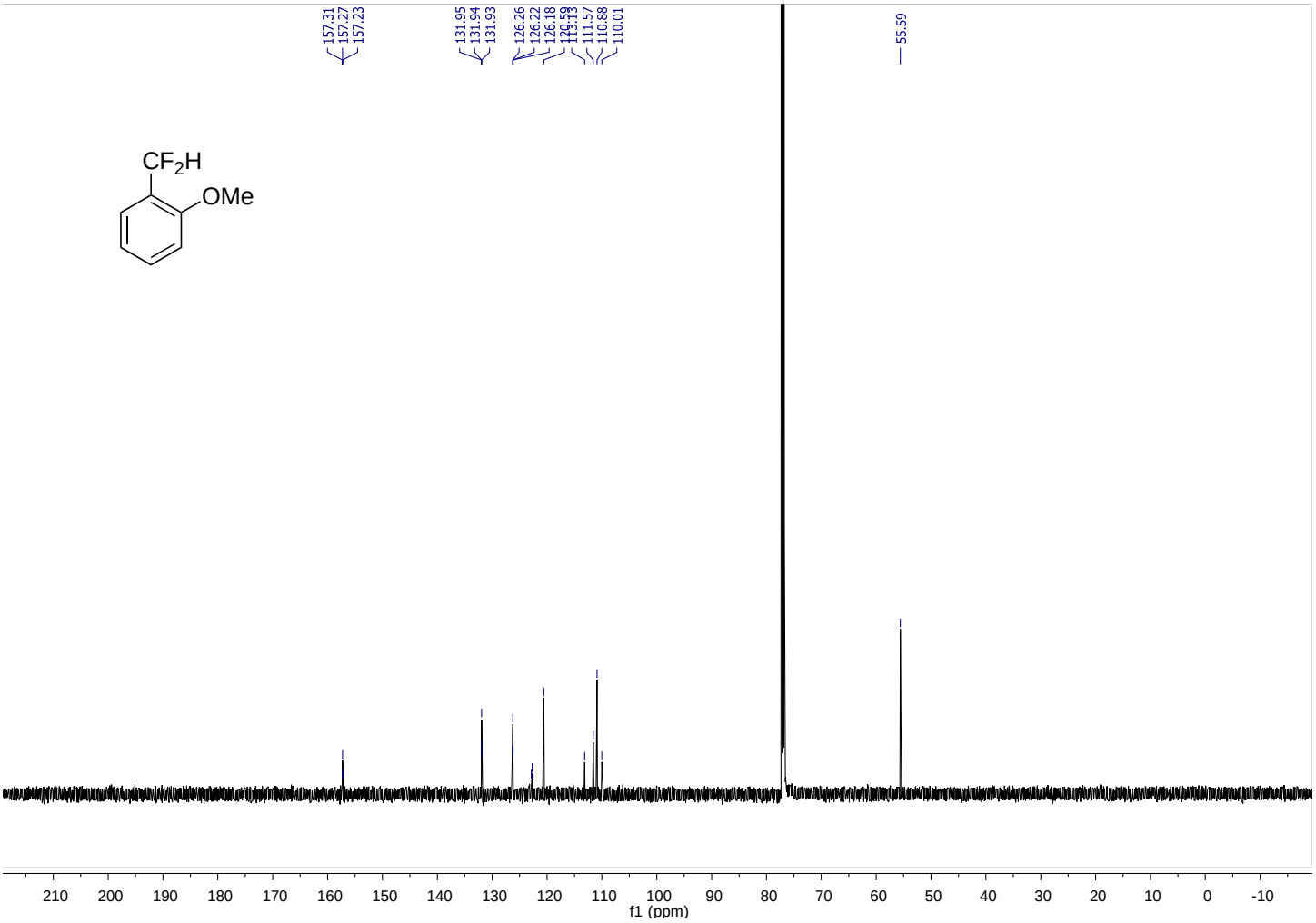

-110.16
-110.31
CF2H
tBu
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

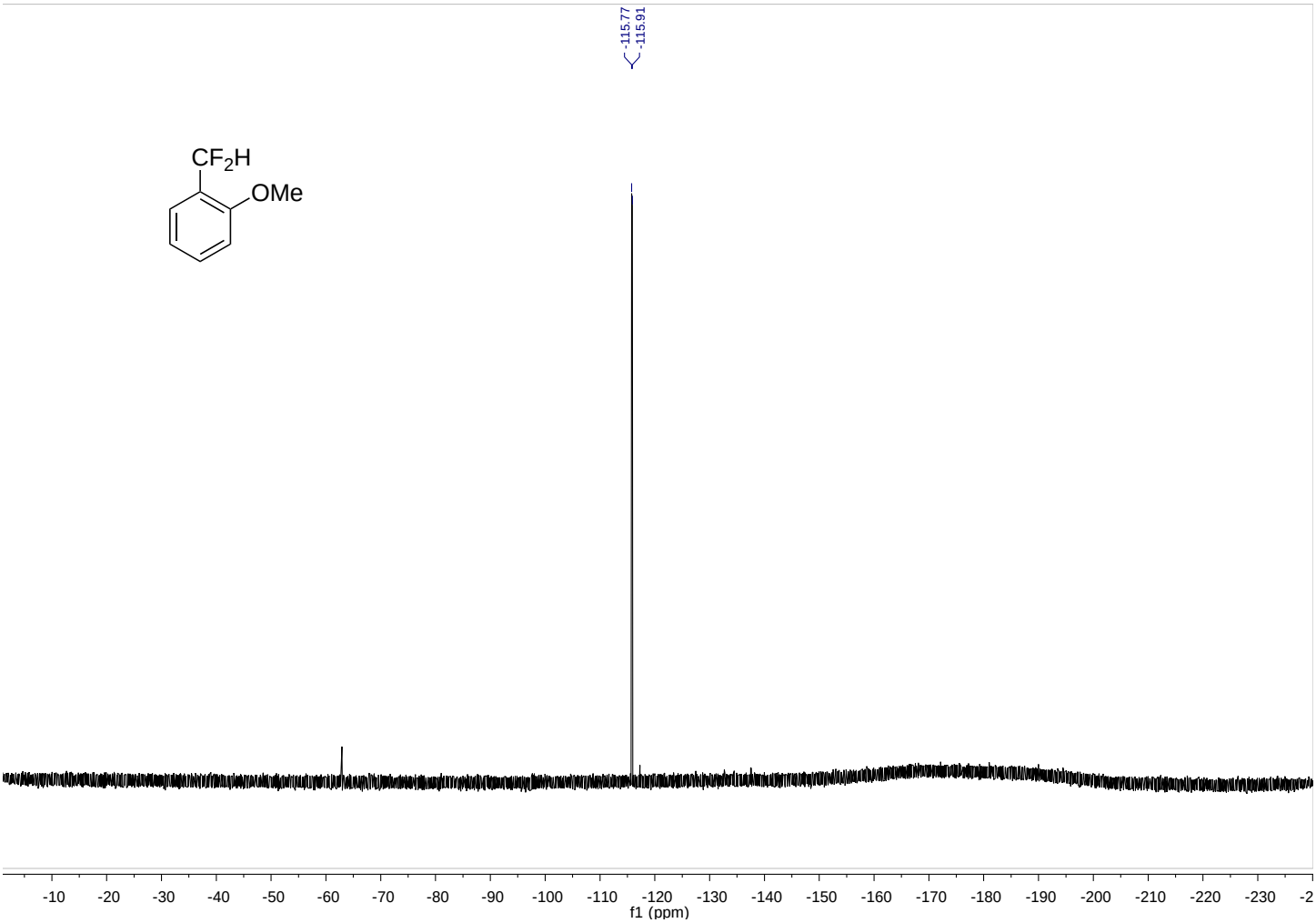

7.63
7.61
7.49
7.48
6.74
6.65
6.55
3.51
3.50
3.49
3.48
3.46
3.38
3.36
3.35
3.34
3.33
1.23
1.22
1.21
CF2H
Me
EtO
OEt
1.85
1.79
1.00
2.16
2.04
5.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

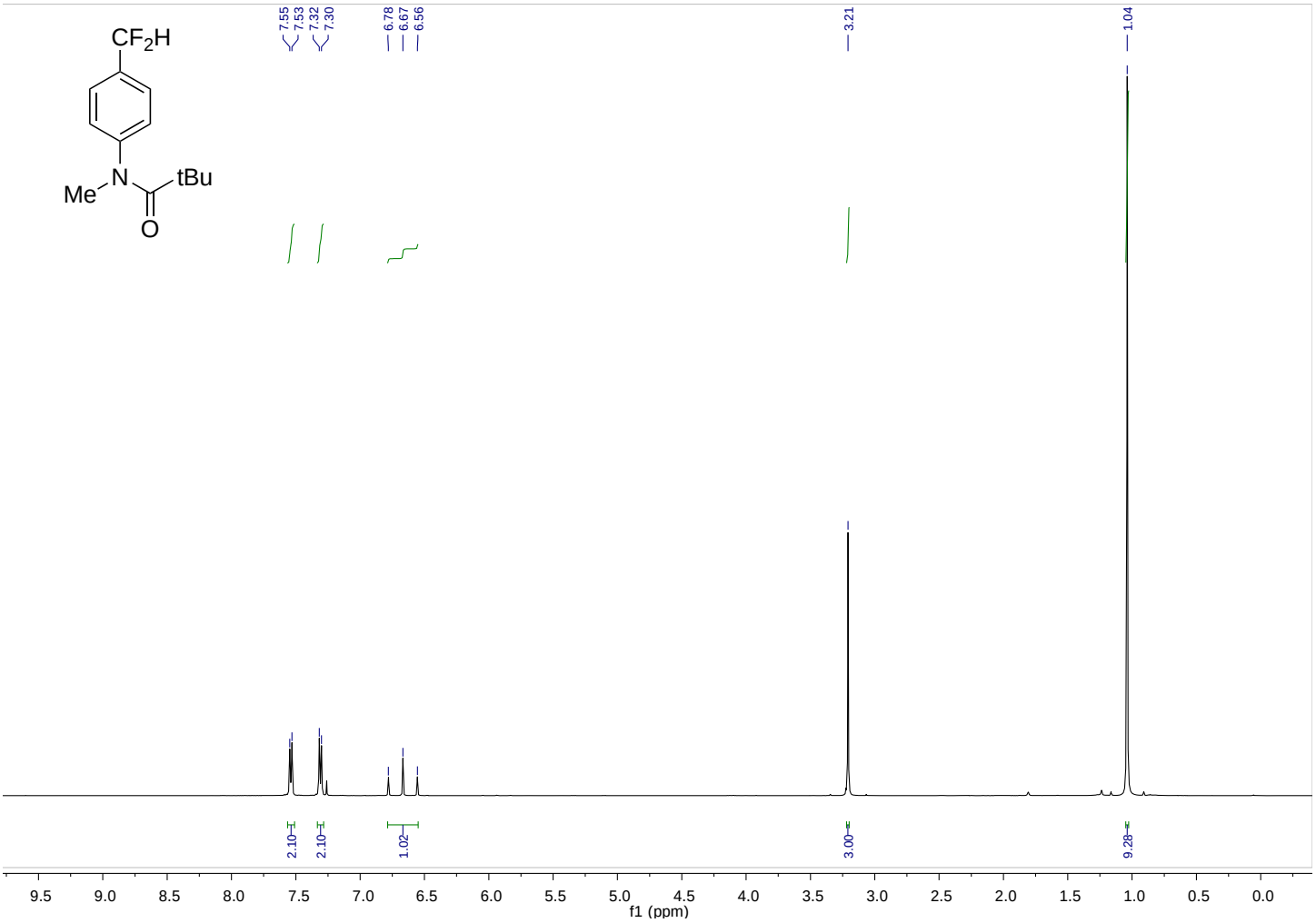

146.75
146.74
146.73
133.58
133.43
133.28
126.58
125.31
125.27
125.24
116.33
114.75
113.18
100.94
56.77
27.04
15.29
CF2H
Me
EtO
OEt
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

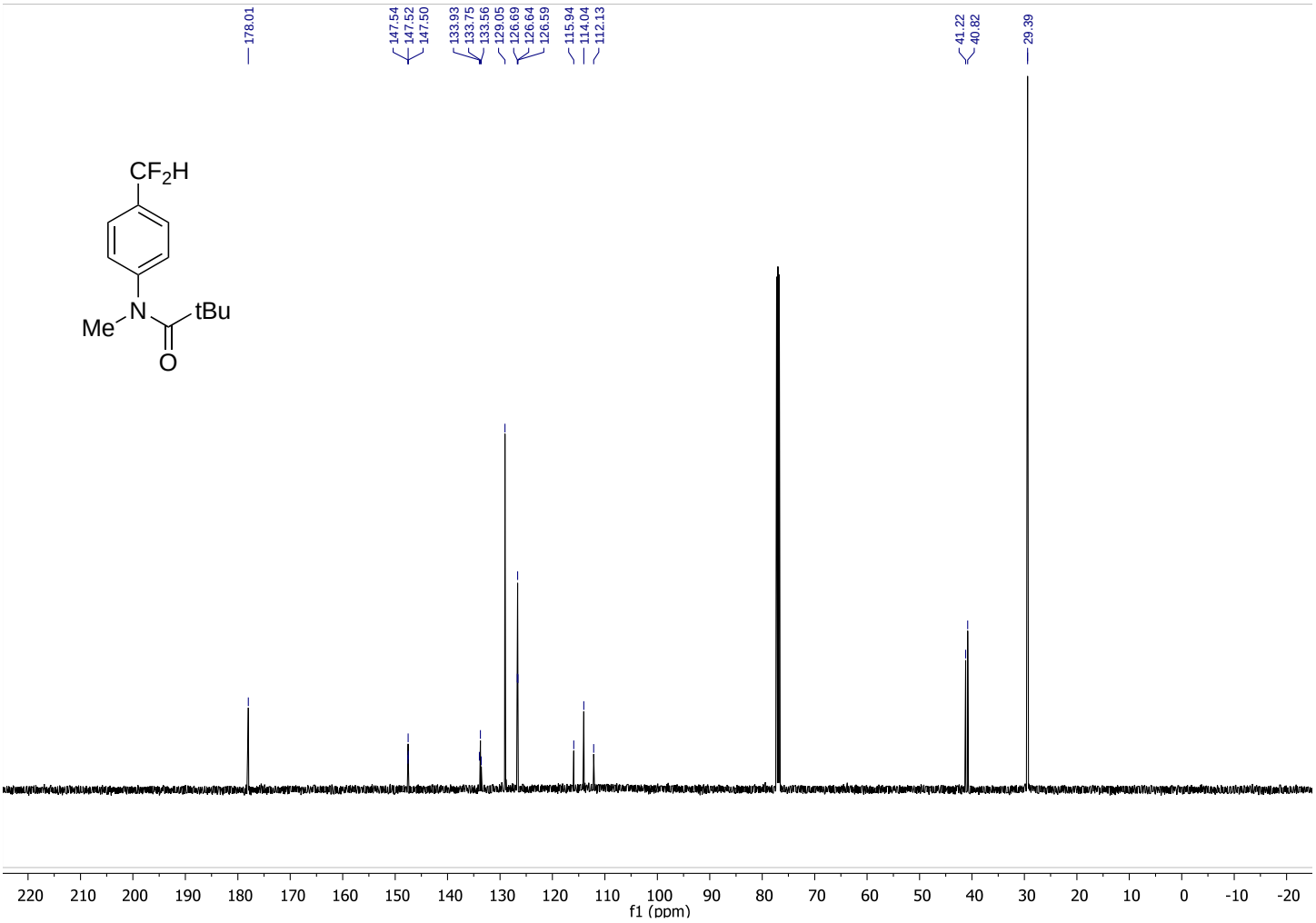

-110.65
-110.80
CF2H
Me
EtO
OEt
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -2
f1 (ppm)

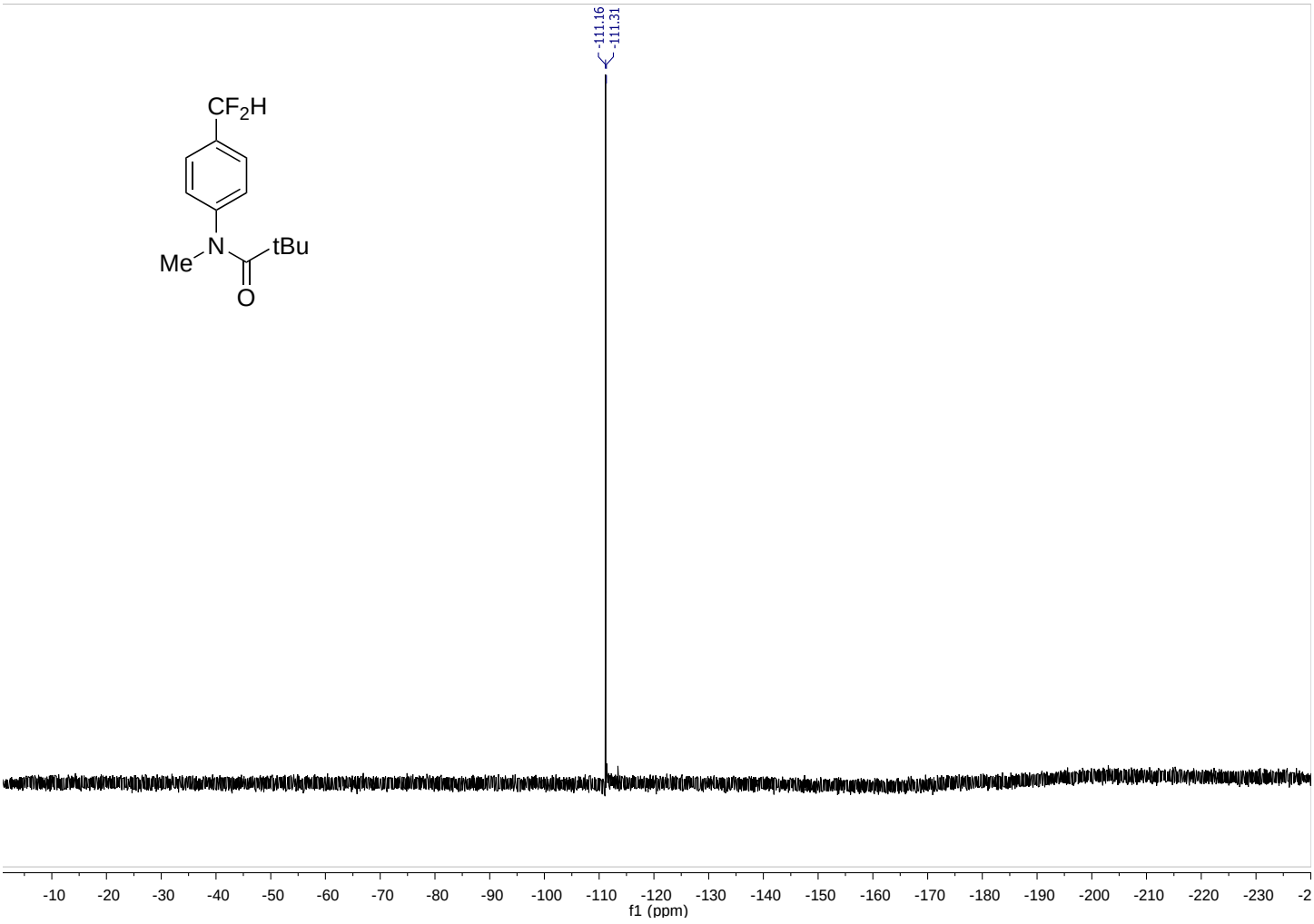

7.57
7.56
7.44
7.43
7.42
7.05
7.03
7.02
6.96
6.95
6.93
6.86
3.87
CF2H
OMe
1.00
0.99
3.07
3.04
f1 (ppm)

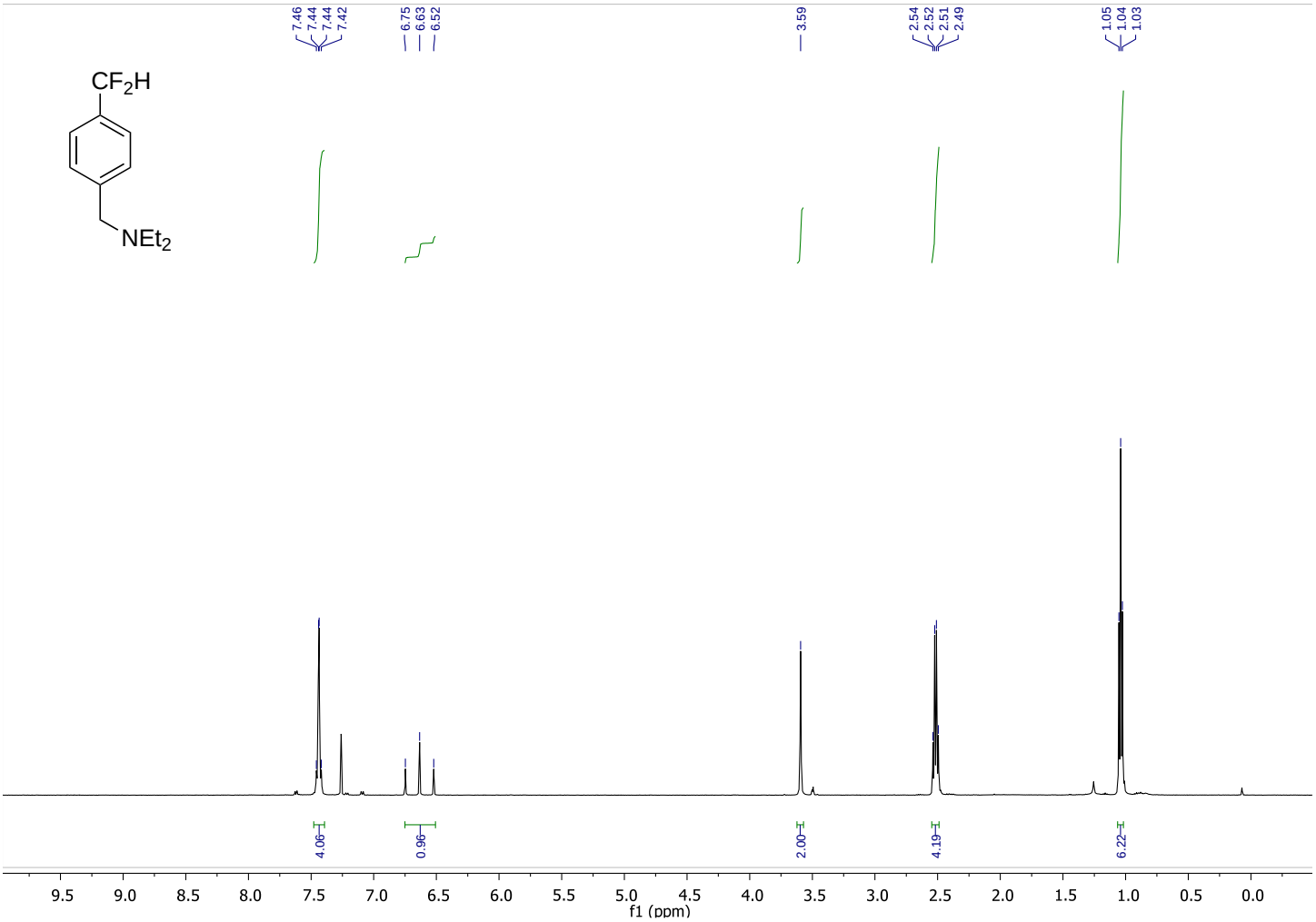

157.31
157.27
157.23
131.95
131.94
131.93
126.26
126.22
126.18
120.59
120.53
111.57
110.88
110.01
55.59
CF2H
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

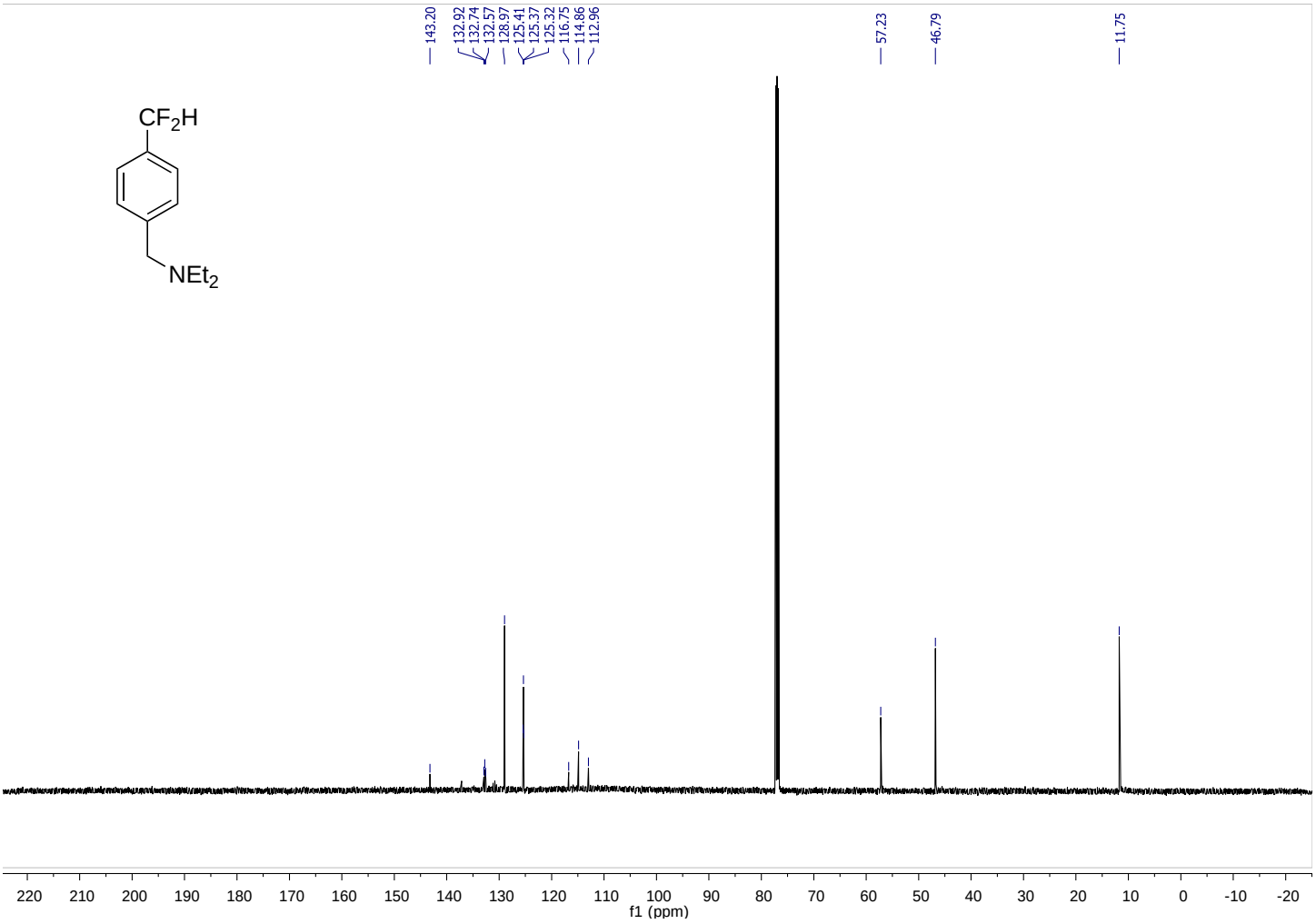

-115.77
-115.91
CF2H
OMe
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -2
f1 (ppm)

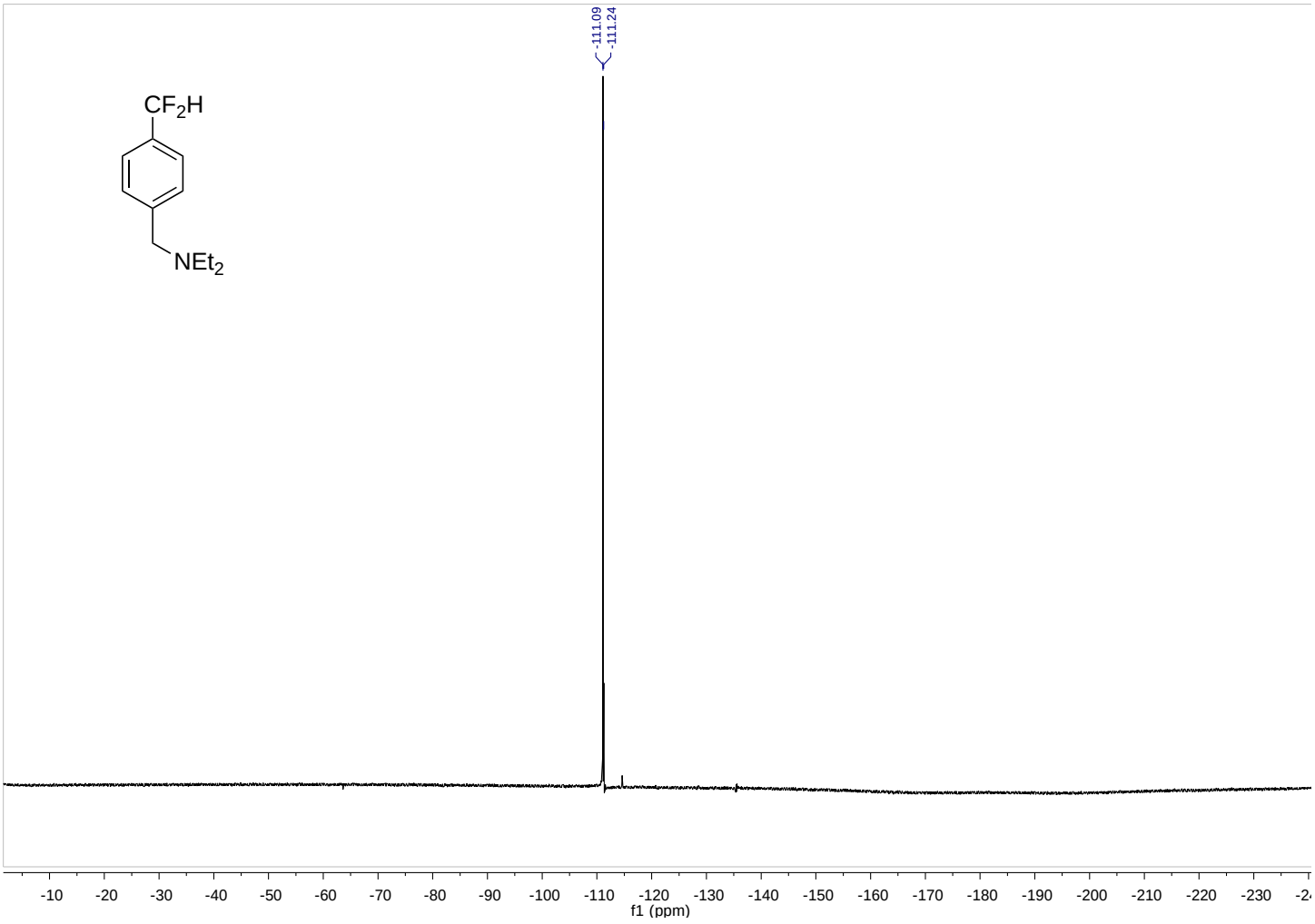

CF2H
Me
N
tBu
O
7.55
7.53
7.32
7.30
6.78
6.67
6.56
3.21
1.04
2.10
2.10
1.02
3.00
9.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

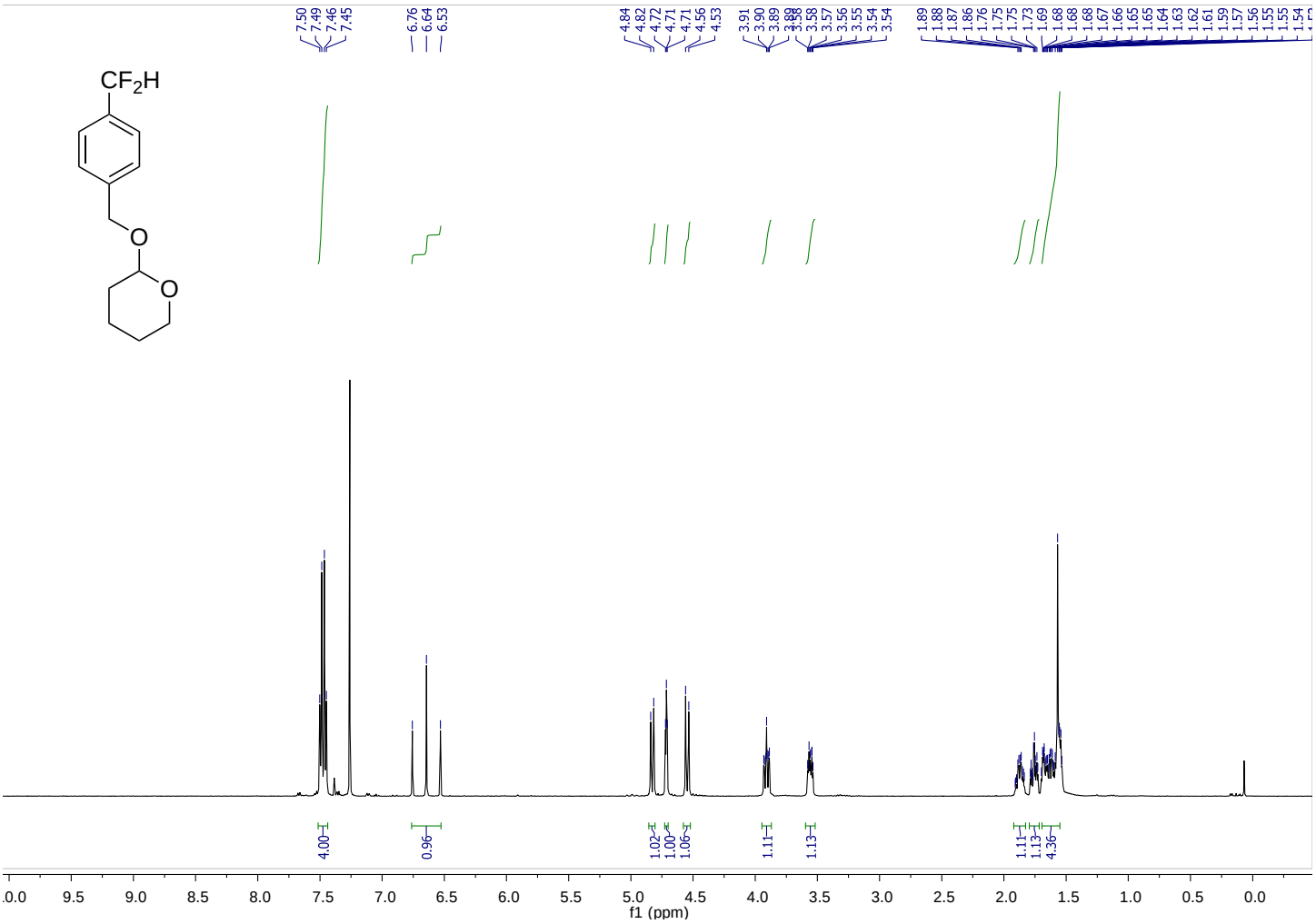

178.01
147.54
147.52
147.50
133.93
133.75
133.56
129.05
126.69
126.64
126.59
115.94
114.04
112.13
41.22
40.82
29.39
CF2H
N
Me
tBu
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

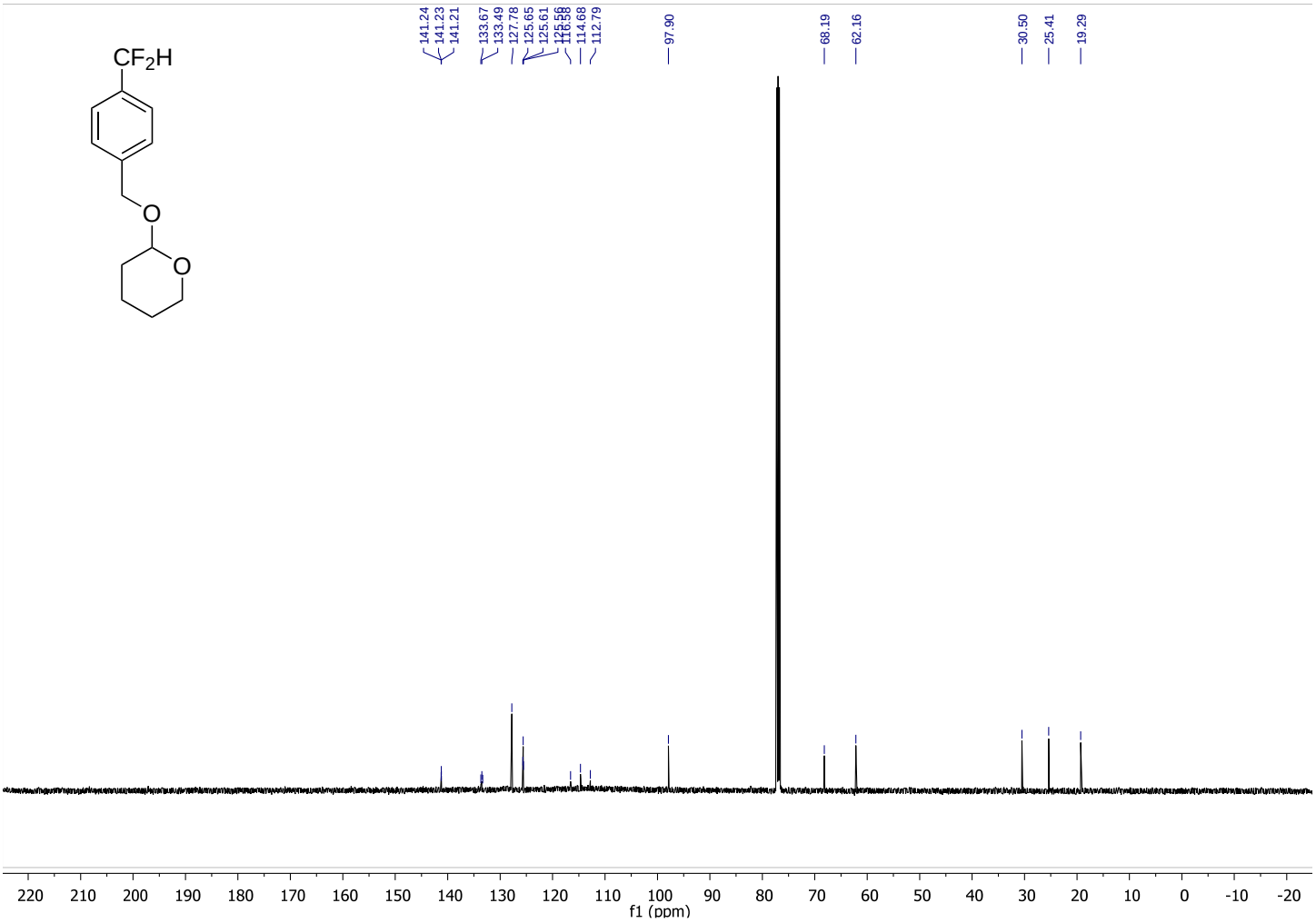

-111.16
-111.31
CF2H
N
Me
tBu
O
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -2
f1 (ppm)

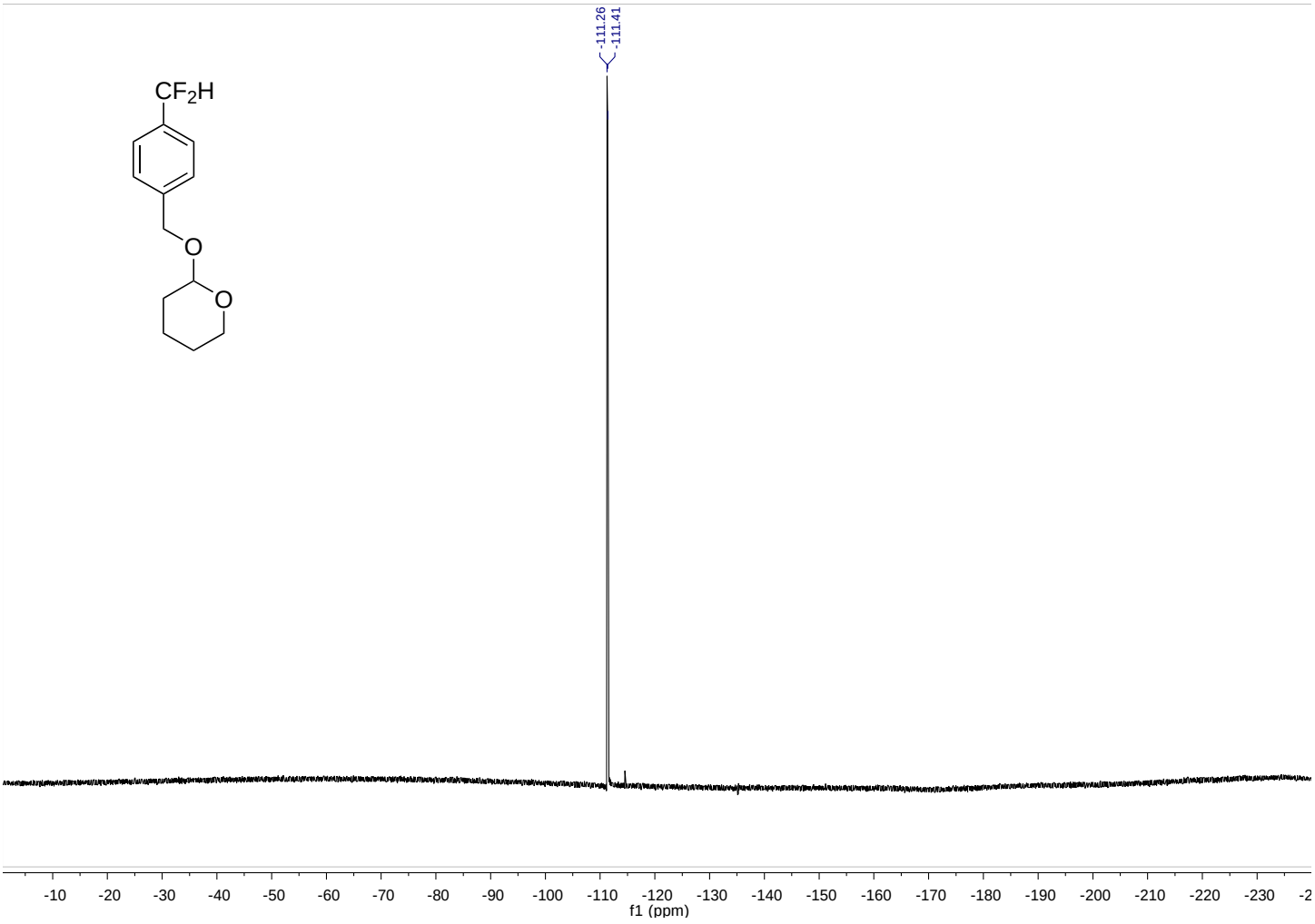

7.46
7.44
7.44
7.42
6.75
6.63
6.52
3.59
2.54
2.52
2.51
2.49
1.05
1.04
1.03
CF2H
NEt2
4.06
0.96
2.00
4.19
6.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

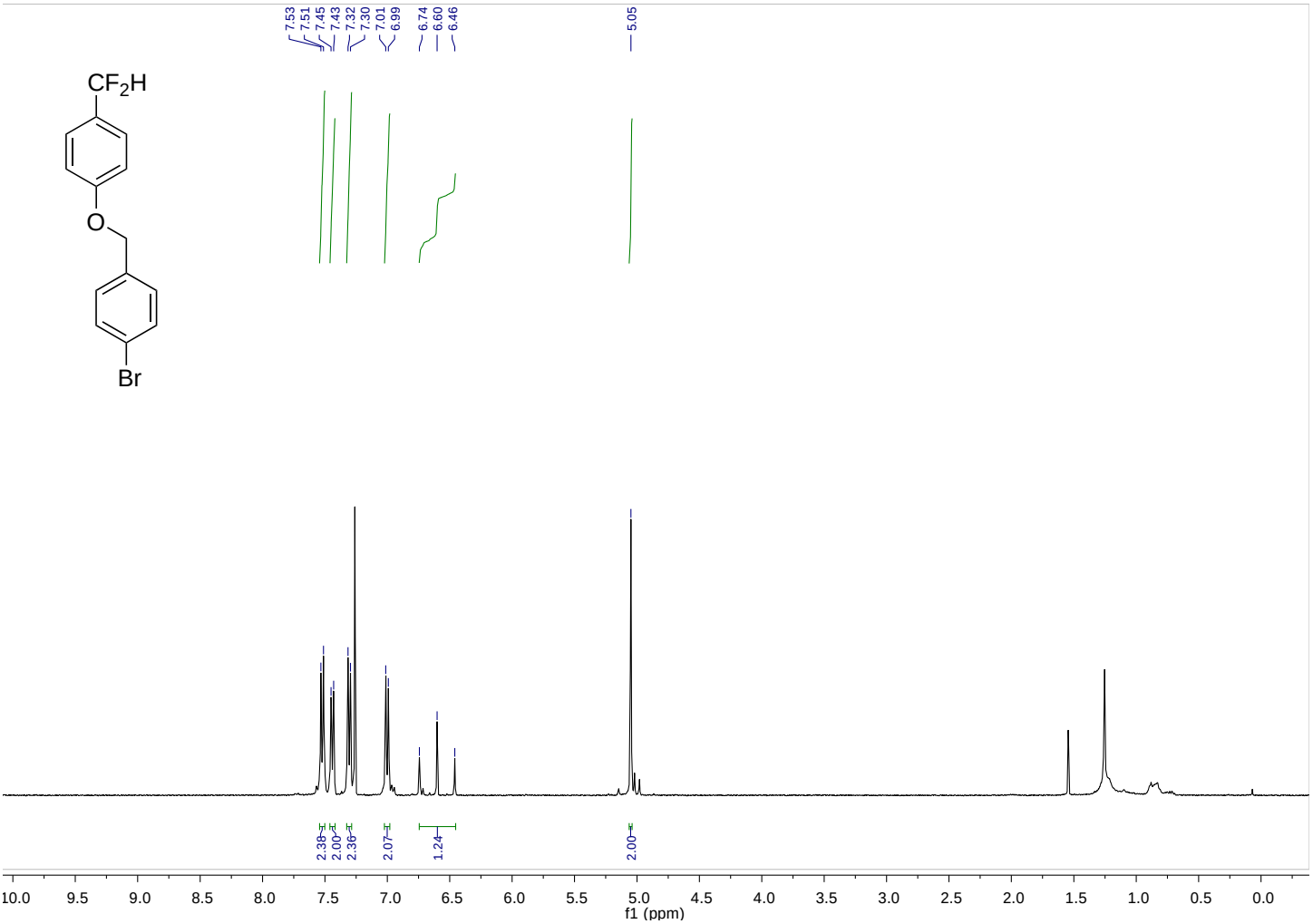

143.20
132.92
132.74
132.57
128.97
125.41
125.37
125.32
116.75
114.86
112.96
57.23
46.79
11.75
CF2H
NEt2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

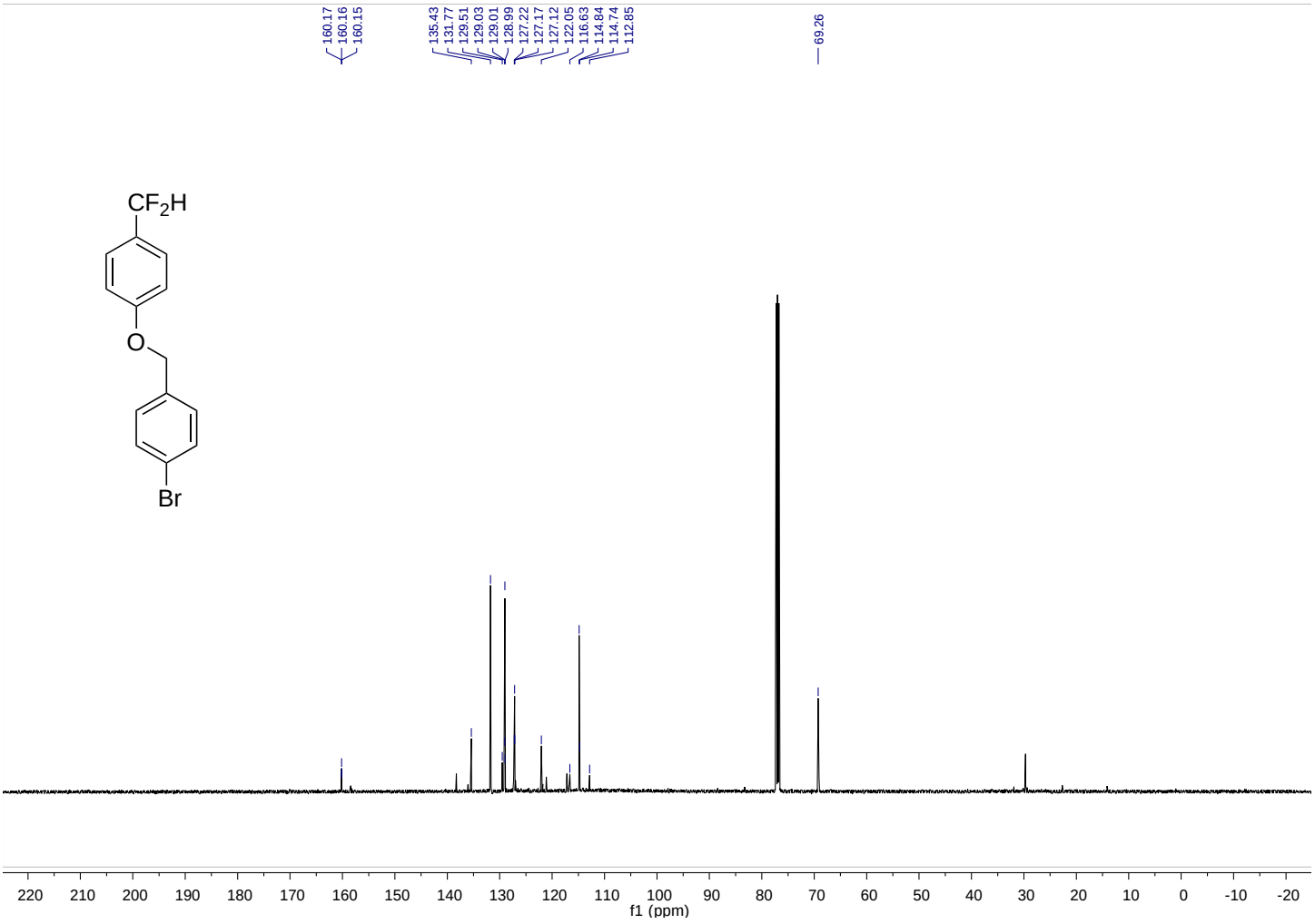

-111.09
-111.24
CF2H
NEt2
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

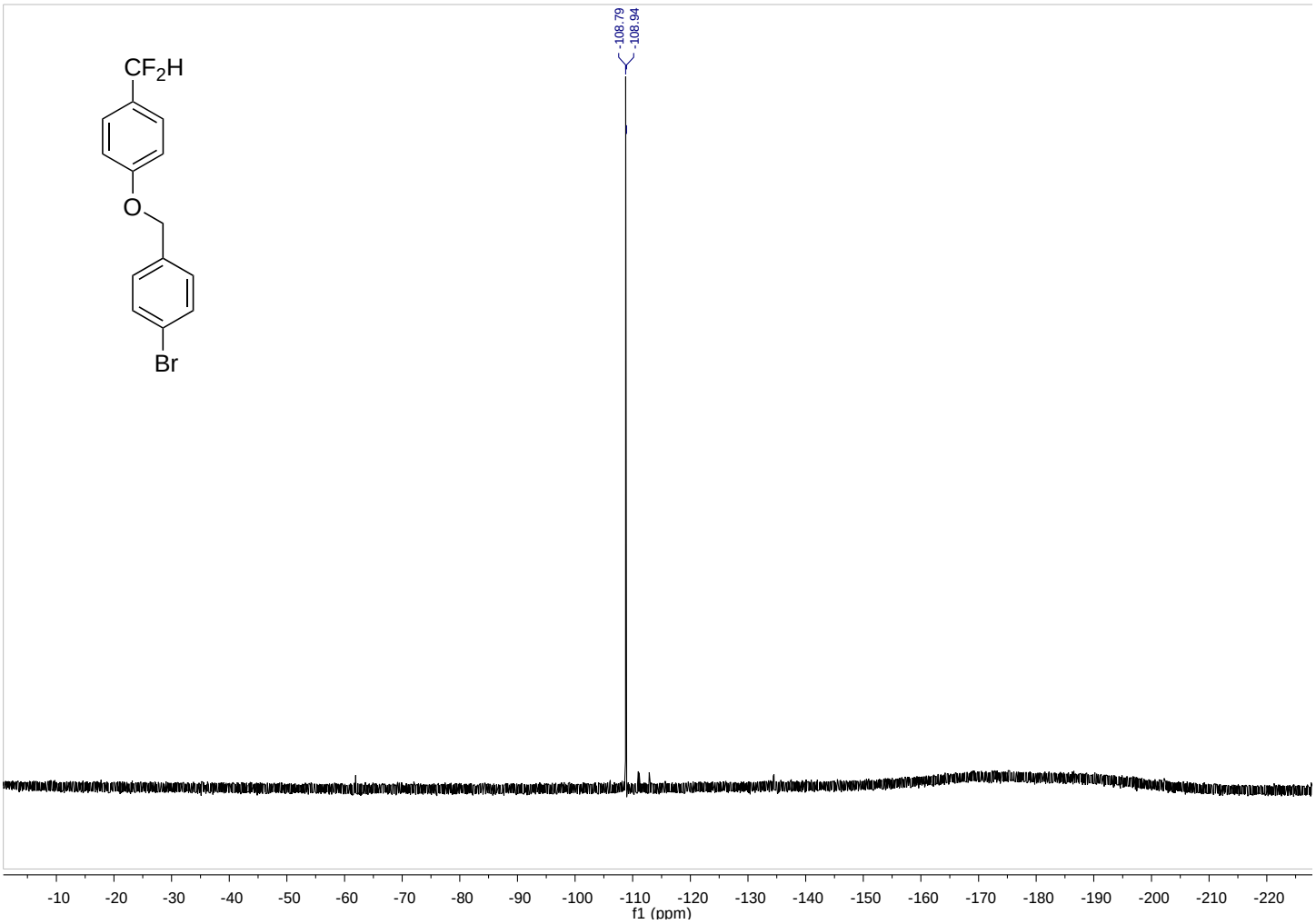

CF2H
O
O
7.50
7.49
7.46
7.45
6.76
6.64
6.53
4.84
4.82
4.72
4.71
4.56
4.53
3.91
3.90
3.89
3.58
3.57
3.56
3.55
3.54
1.89
1.88
1.87
1.86
1.76
1.75
1.73
1.69
1.68
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.59
1.57
1.56
1.55
1.54
4.00
0.96
1.02
1.00
1.06
1.11
1.13
1.11
1.13
4.36
f1 (ppm)

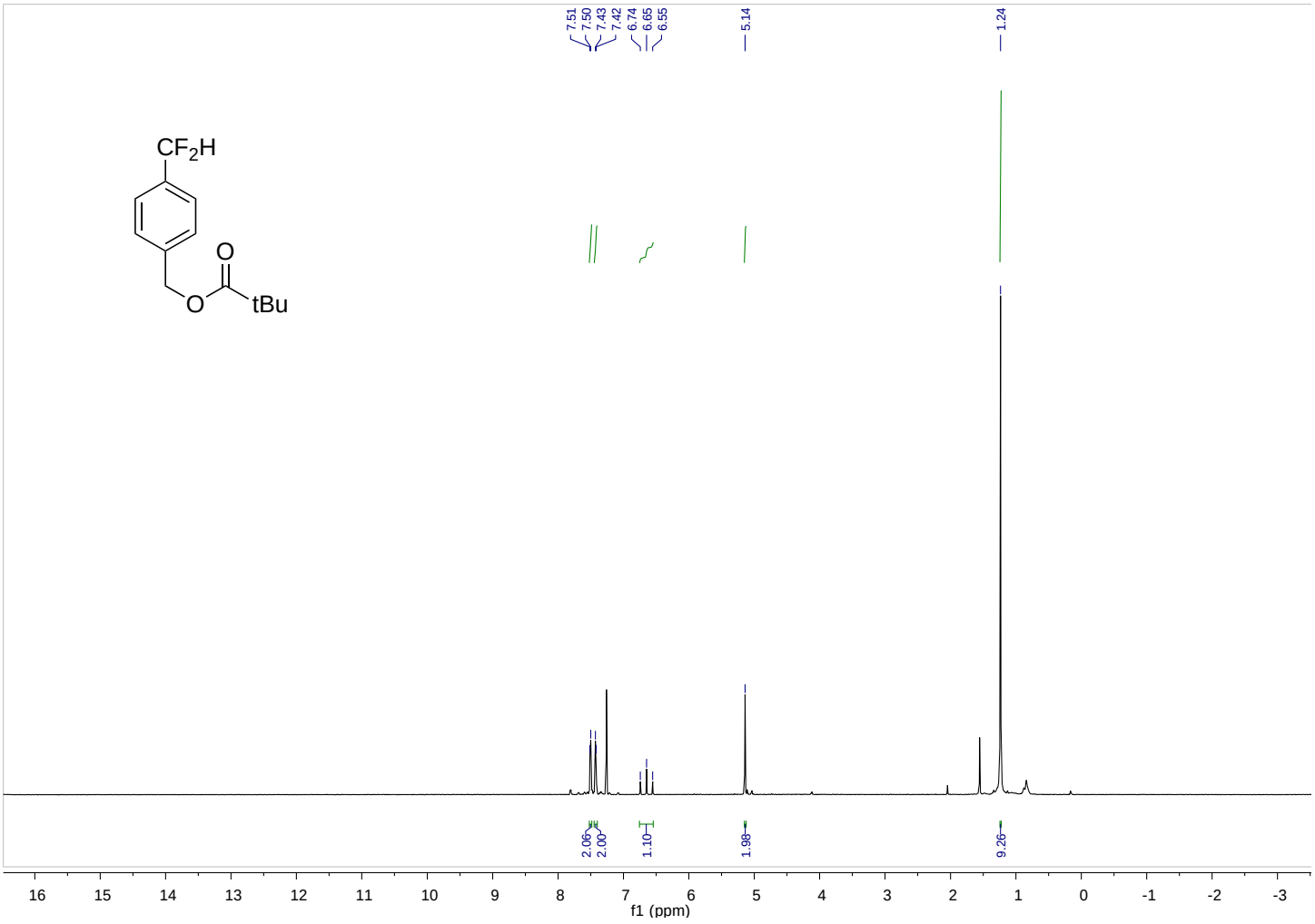

CF2H
O
O
141.24
141.23
141.21
133.67
133.49
127.78
125.65
125.61
125.56
125.53
114.68
112.79
97.90
68.19
62.16
30.50
25.41
19.29
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

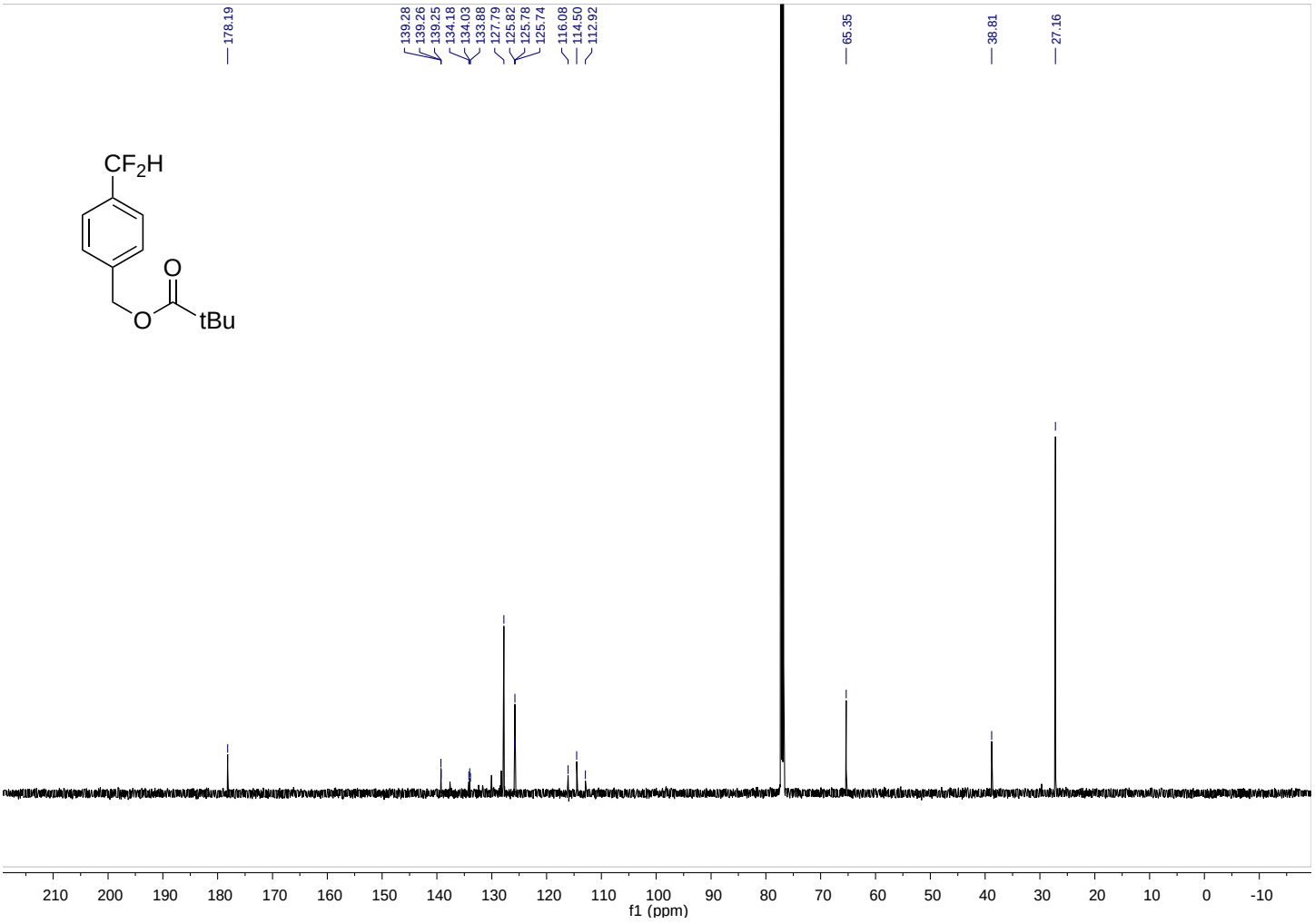

-111.26
-111.41
CF2H
O
O
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

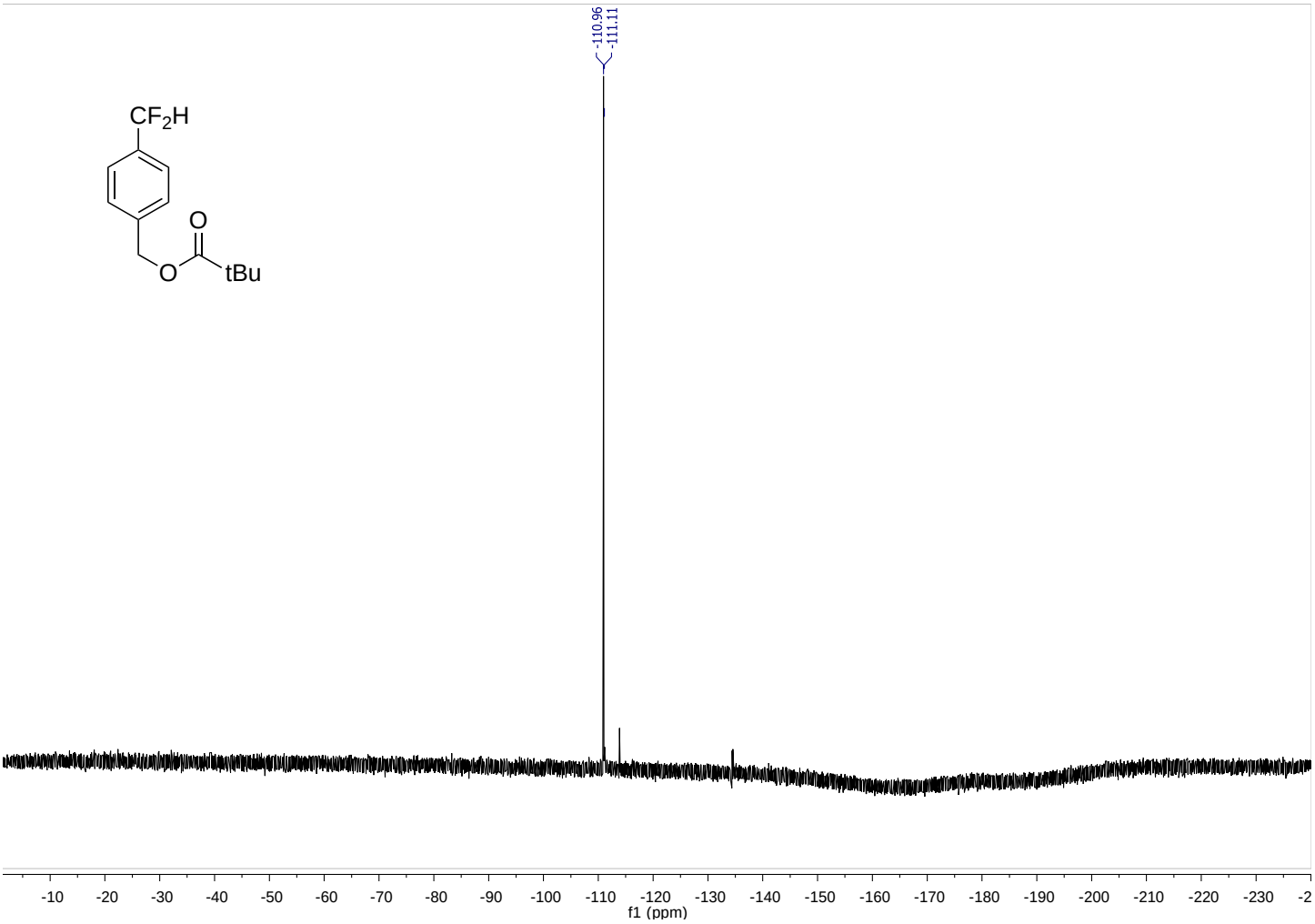

7.53
7.51
7.45
7.43
7.32
7.30
7.01
6.99
6.74
6.60
6.46
5.05
CF2H
O
Br
2.38
2.00
2.36
2.07
1.24
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

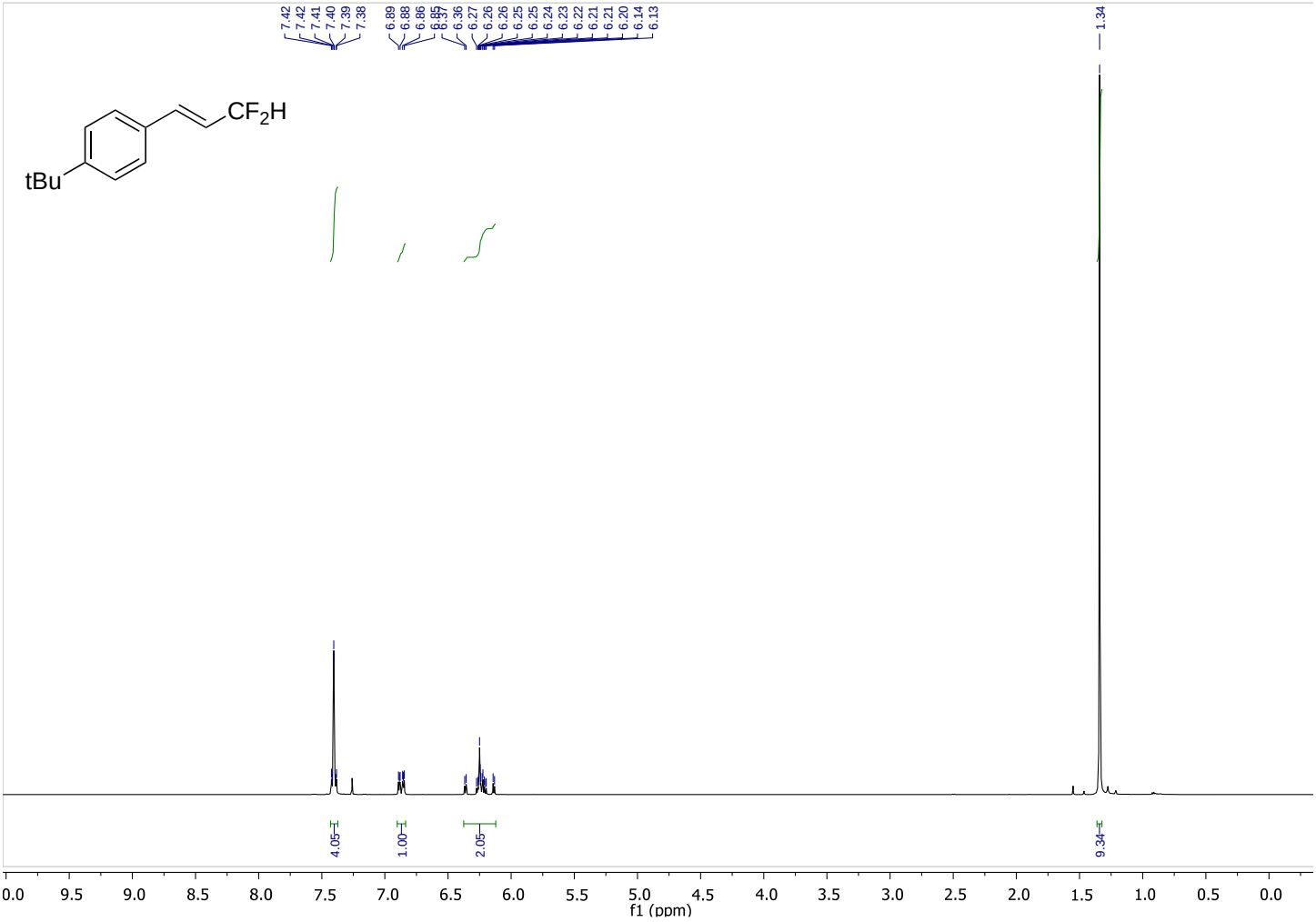

160.17
160.16
160.15
135.43
131.77
129.51
129.03
129.01
128.99
127.22
127.17
127.12
122.05
116.63
114.84
114.74
112.85
69.26
CF2H
O
Br
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

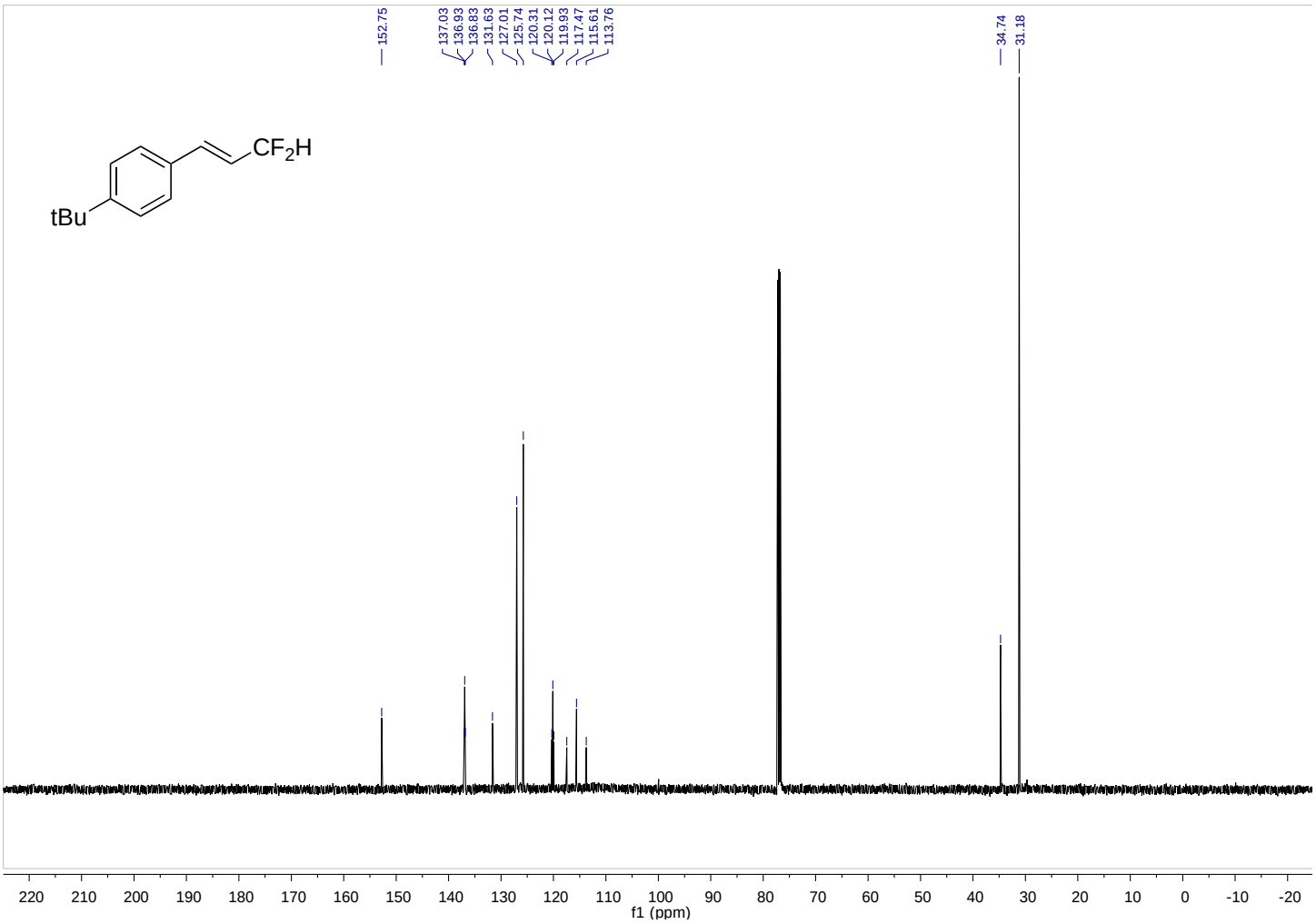

-108.79
-108.94
CF2H
O
Br
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

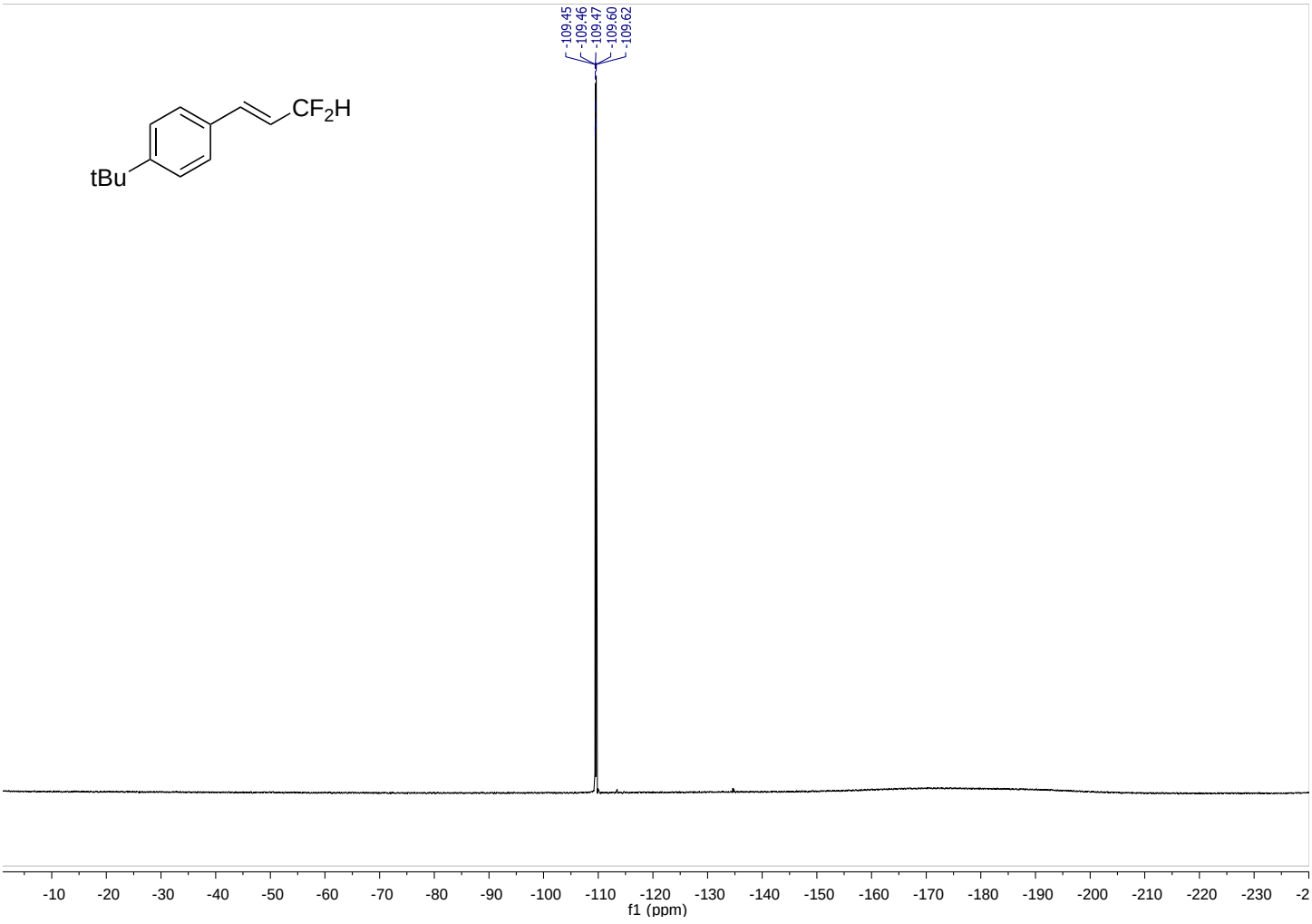

7.51
7.50
7.43
7.42
6.74
6.65
6.55
5.14
1.24
CF2H
O
O
tBu
2.06
2.00
1.10
1.98
9.26
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

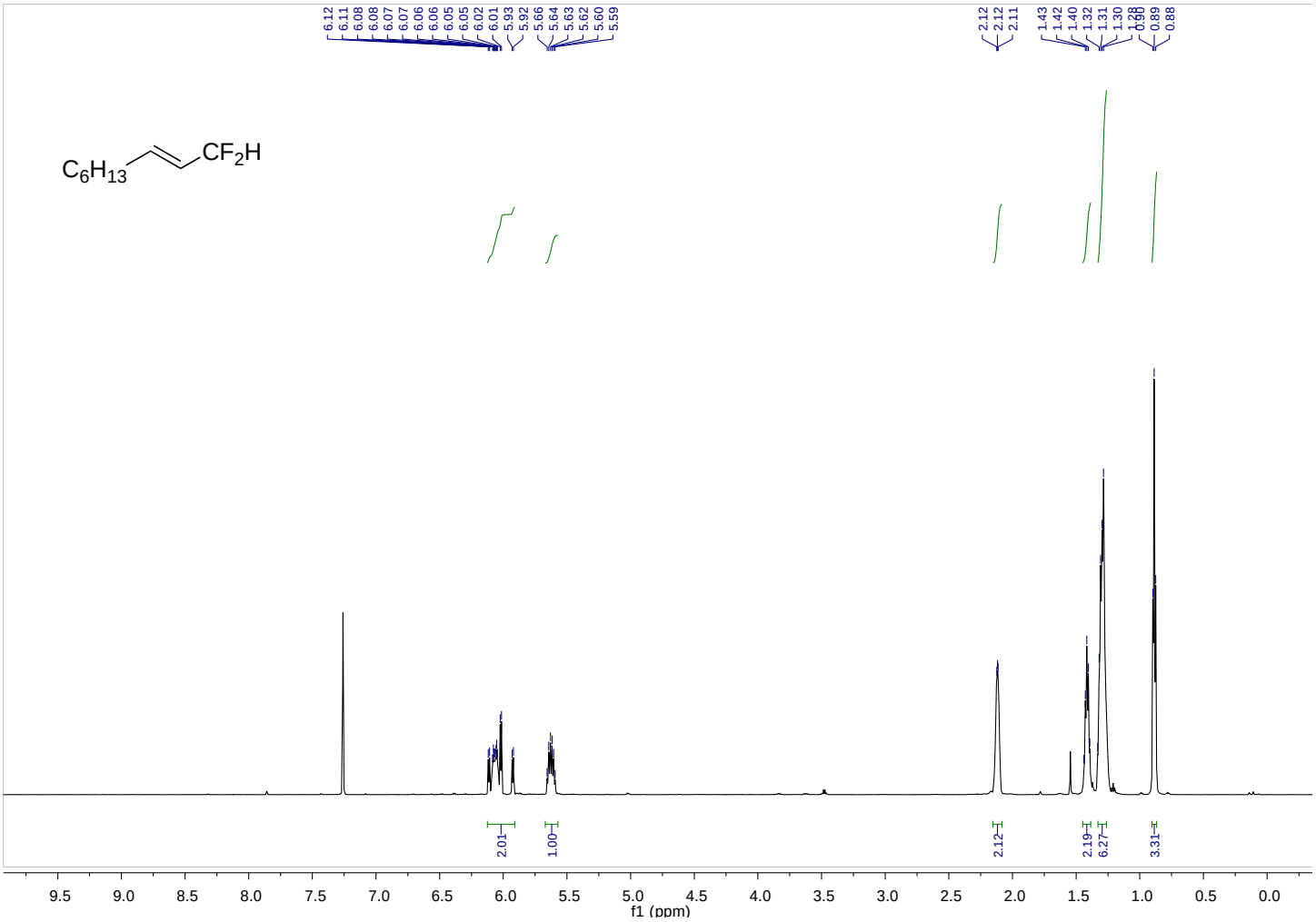

178.19
139.28
139.26
139.25
134.18
134.03
133.88
127.79
125.82
125.78
125.74
116.08
114.50
112.92
65.35
38.81
27.16
CF2H
O
O
tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

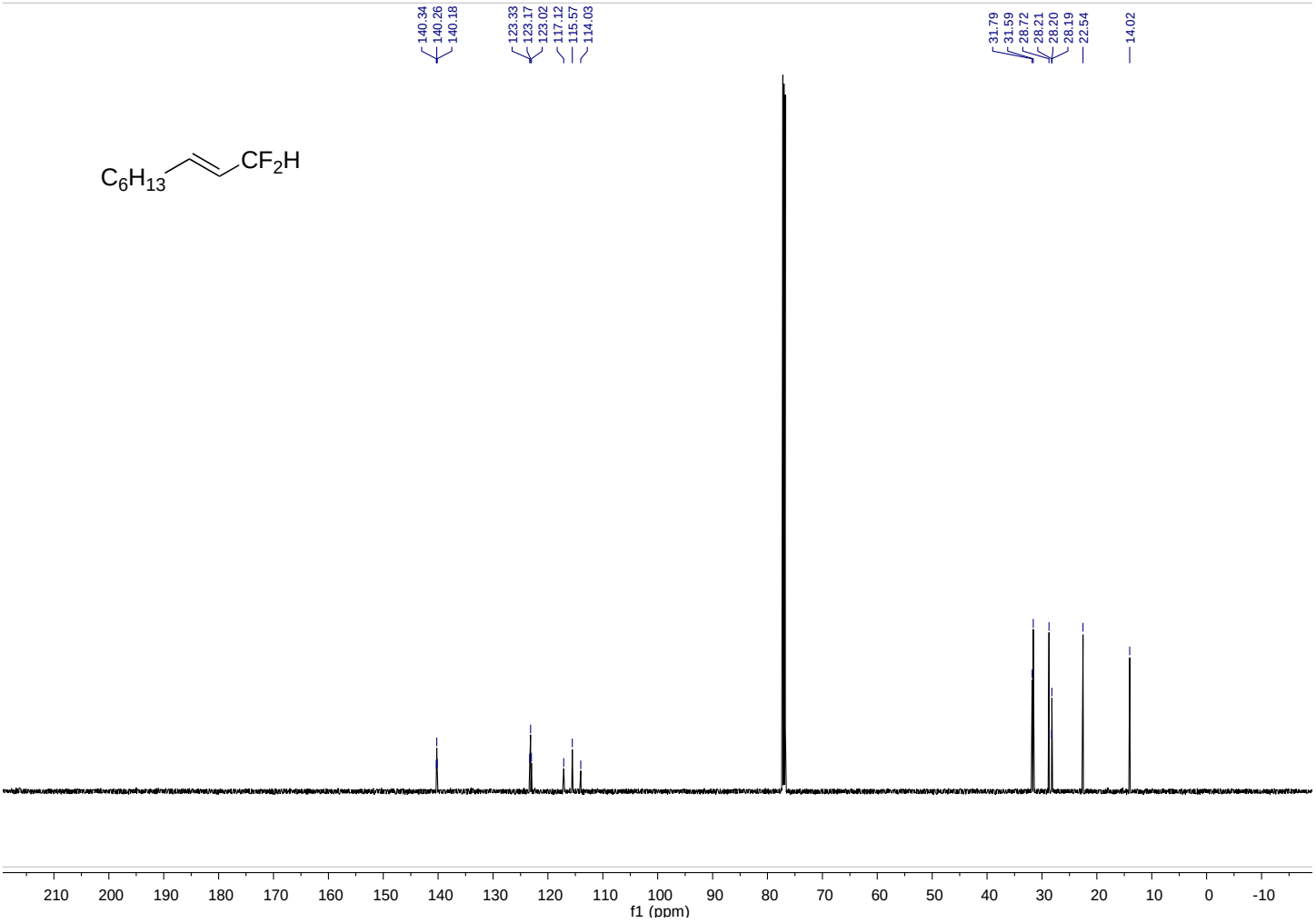

-110.96
-111.11
CF2H
O
O
tBu
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -2
f1 (ppm)

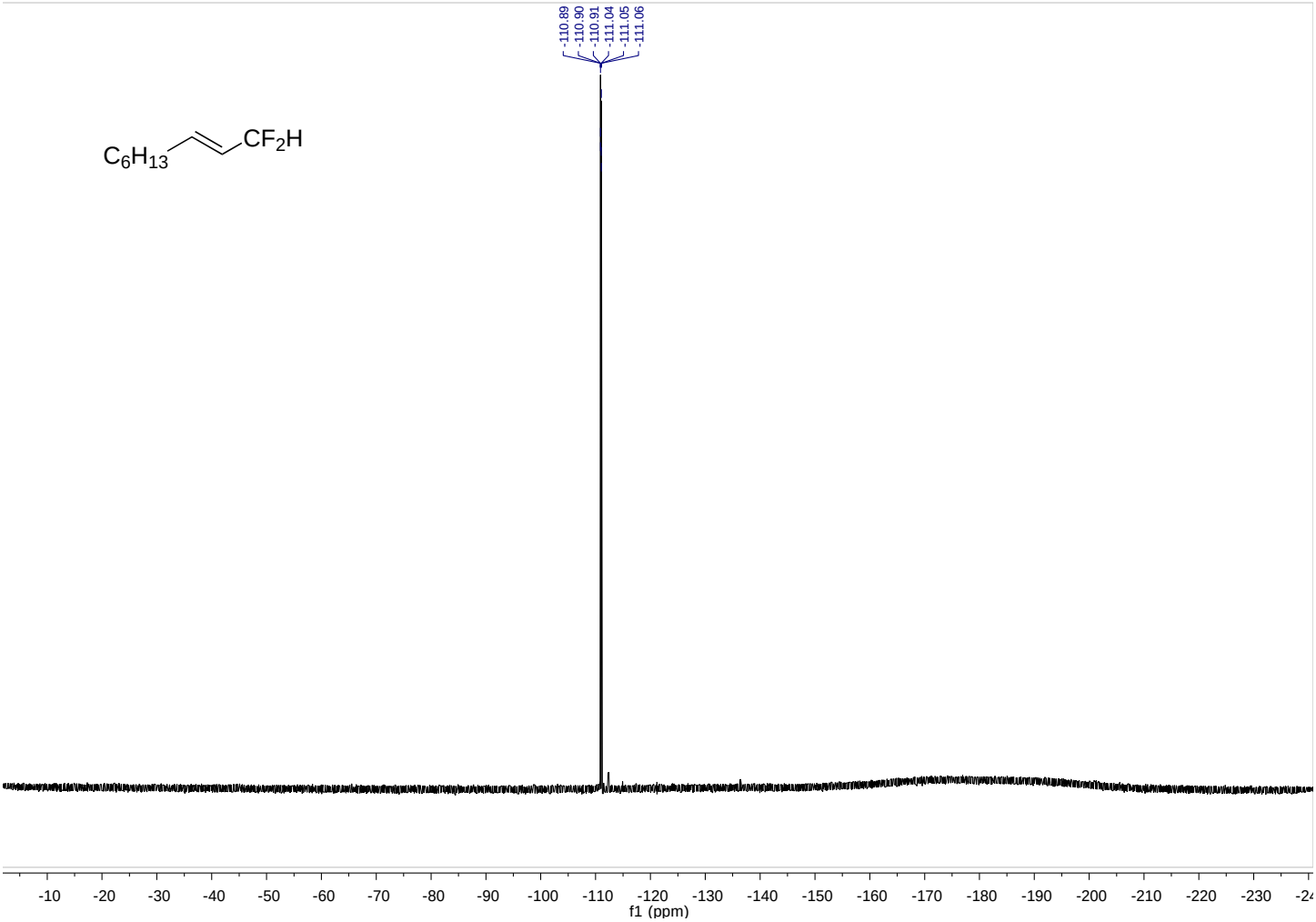

7.42
7.42
7.41
7.40
7.39
7.38
6.89
6.88
6.86
6.85
6.37
6.36
6.27
6.26
6.26
6.25
6.25
6.24
6.23
6.22
6.21
6.21
6.20
6.14
6.13
1.34
CF2H
tBu
4.05
1.00
2.05
9.34
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

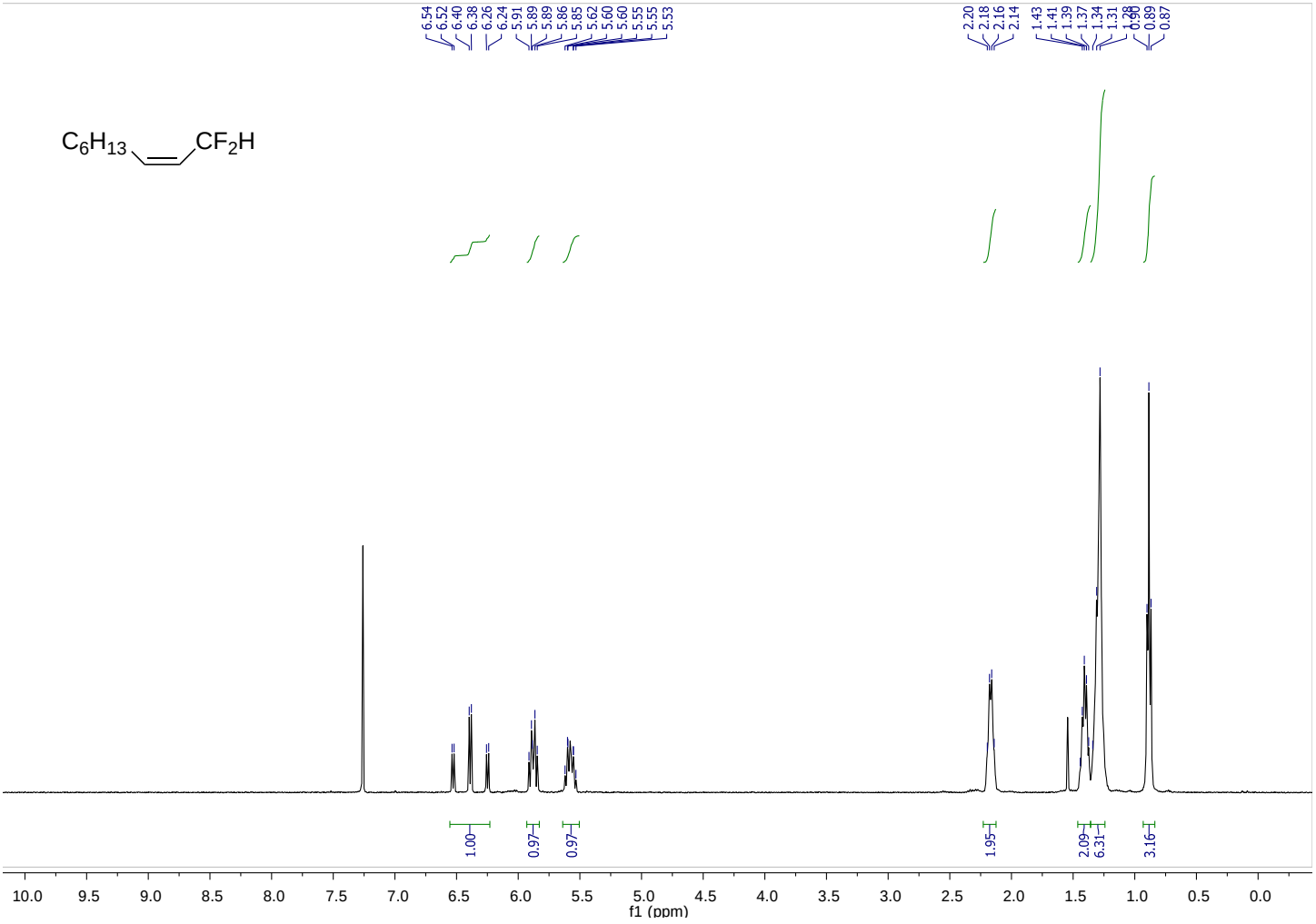

152.75
137.03
136.93
136.83
131.63
127.01
125.74
120.31
120.12
119.93
117.47
115.61
113.76
34.74
31.18
CF2H
tBu
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


-109.45
-109.46
-109.47
-109.60
-109.62
CF2H
tBu
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -2
f1 (ppm)


6.12
6.11
6.08
6.08
6.07
6.07
6.06
6.06
6.05
6.05
6.02
6.01
5.93
5.92
5.66
5.64
5.63
5.62
5.60
5.59
2.12
2.12
2.11
1.43
1.42
1.40
1.32
1.31
1.30
0.90
0.89
0.88
C6H13
CF2H
2.01
1.00
2.12
2.19
6.27
3.31
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
0.0
f1 (ppm)


140.34
140.26
140.18
123.33
123.17
123.02
117.12
115.57
114.03
31.79
31.59
28.72
28.21
28.20
28.19
22.54
14.02
C6H13
CF2H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-110.89
-110.90
-110.91
-111.04
-111.05
-111.06
C6H13
CF2H
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)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6.26
6.24
5.91
5.89
5.89
5.86
5.85
5.62
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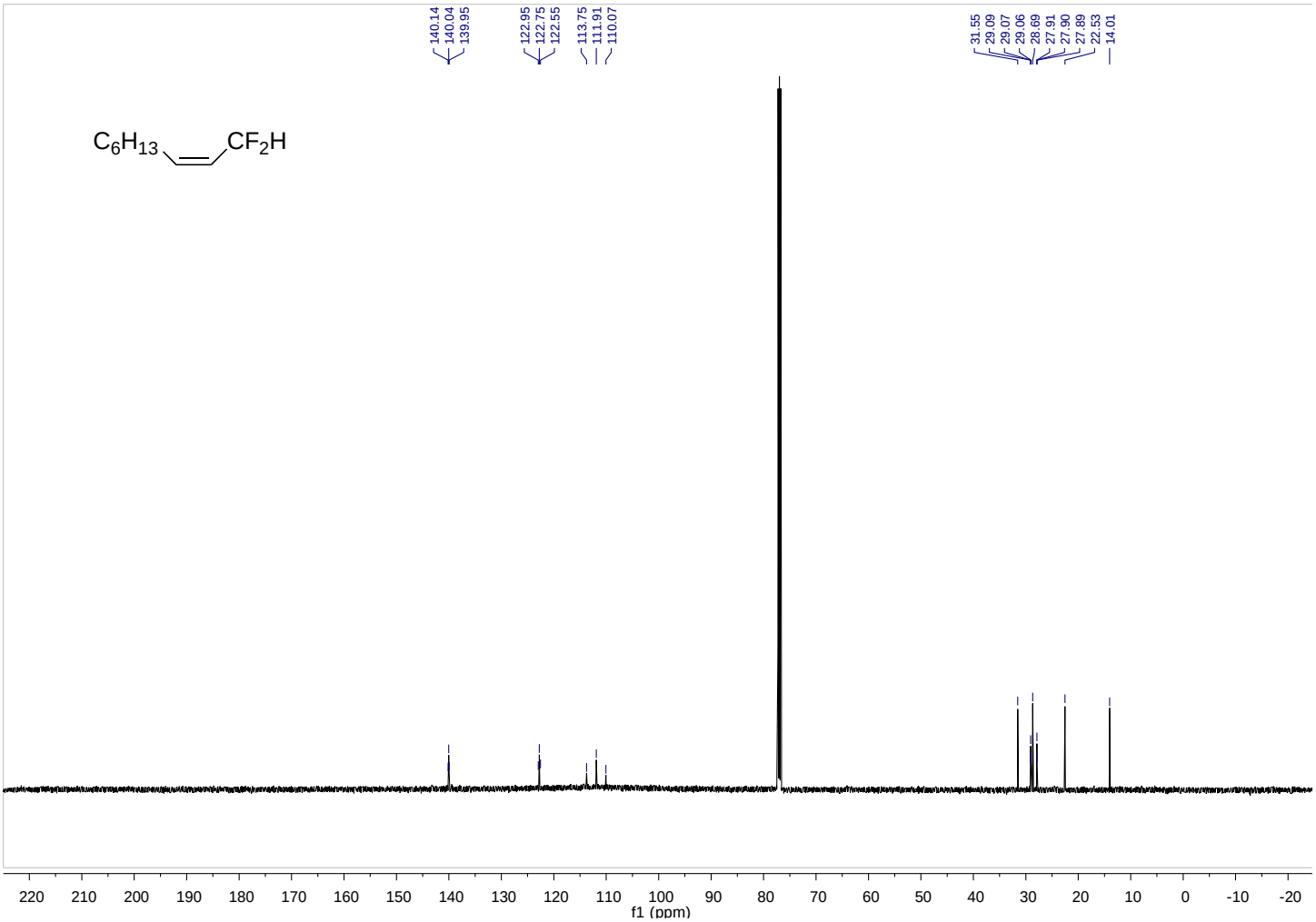
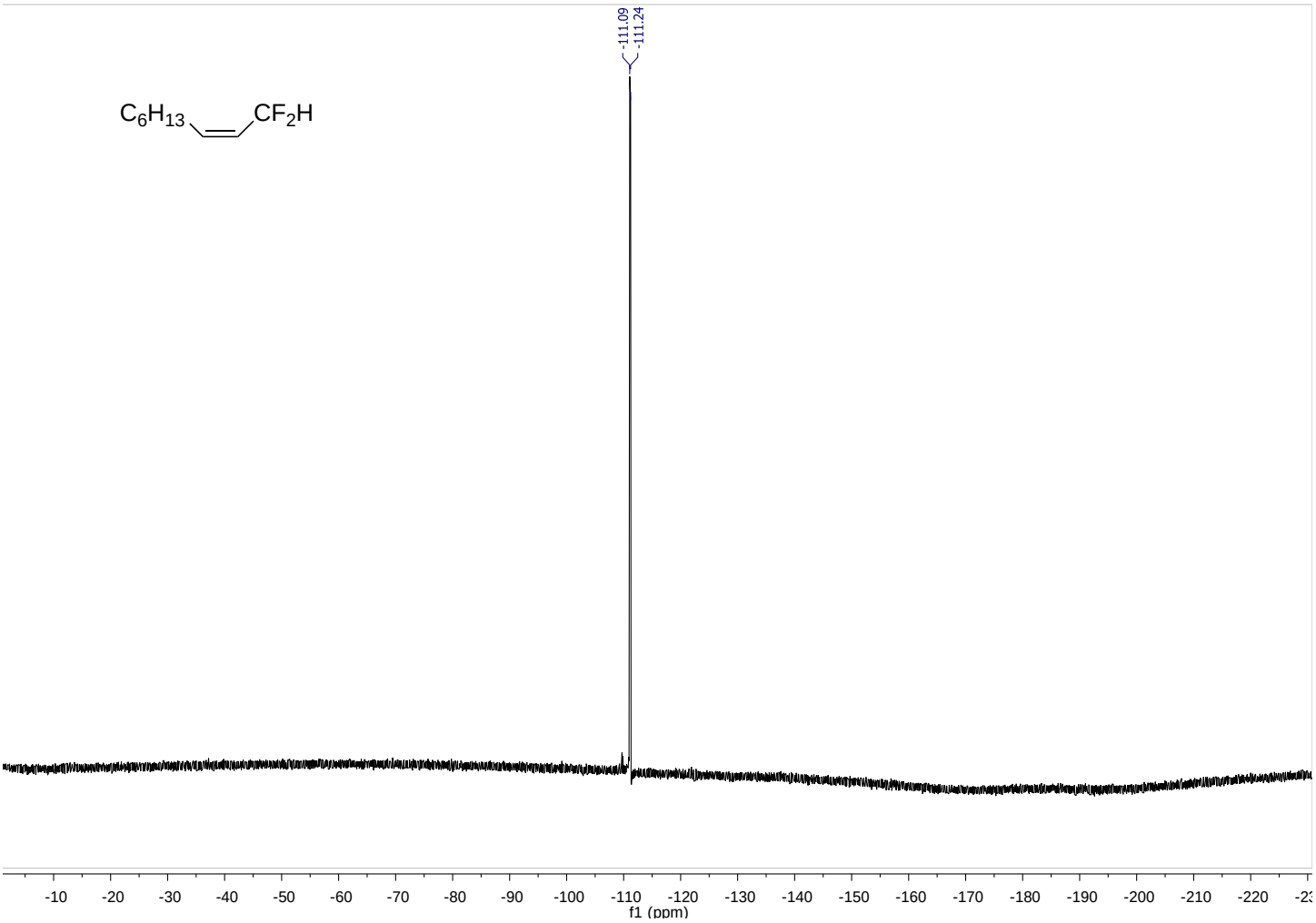
5.60
5.55
5.55
5.53
2.20
2.18
2.16
2.14
1.43
1.41
1.39
1.37
1.34
1.31
0.89
0.87
C6H13
CF2H
1.00
0.97
0.97
1.95
2.09
6.31
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140.14
140.04
139.95
122.95
122.75
122.55
113.75
111.91
110.07
31.55
29.09
29.07
29.06
28.69
27.91
27.90
27.89
22.53
14.01
C6H13
CF2H
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


C6H13
CF2H
-111.09
-111.24
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)