Supporting Information

Metal-Free and User-Friendly Regioselective Hydrofluorination of Olefins

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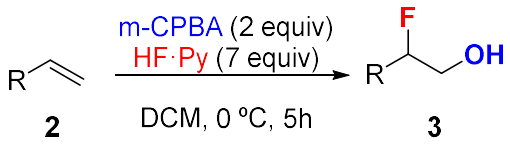
I. General methods:

Reactions were carried out under atmospheric conditions. CH_2Cl_2 was used without further purification. The reactions were monitored with the aid of TLC on 0.25 mm pre-coated silica-gel plates. Visualization was carried out with UV light and aqueous ceric ammonium molybdate solution or potassium permanganate stain. Flash column chromatography was performed with the indicated solvents on silica gel 60 (particle size: 0.040–0.063 mm). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts are given in ppm (δ), referenced to the residual proton resonances of the solvents. Coupling constants (*J*) are given in Hertz (Hz). The letters m, s, d, t, and q stand for multiplet, singlet, doublet, triplet, and quartet, respectively. The letters br indicate that the signal is broad. The abbreviation DCM stands for dichloromethane. HPLC analyses were performed using either a JASCO PU-2089 Plus chromatographer equipped with an MD-2010 detector or an Agilent 1100 series instrument equipped with a refraction index detector using chiral stationary columns from Daicel. IR spectra were recorded in a Thermo Scientific FTIR spectrometer Nicolet iS10.

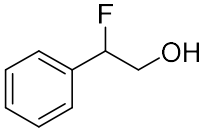
II. General procedure for the 1,2-hydroxyfluorination of olefins



A 5-mL polypropylene vial was charged with *m*-CPBA 77% w/w (90 mg, 0.4 mmol, 2 equiv). DCM (2mL) was added and the resulting suspension was cooled down in an ice bath. Finally, the corresponding olefin (0.2 mmol) was added followed by HF·Py 70% w/w (36µL, 1.4 mmol, 7 equiv).The reaction mixture was stirred 4-5h (TLC), then quenched by the addition of ice and a spatula tip of $KHSO_3$ and stir for 30 additional minutes. The reaction mixture was then extracted with DCM (3 x 5 mL), the combined organic layers dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue thus obtained was purified by flash chromatography using appropriate mixtures of hexanes and ethyl acetate as eluent (for low molecular weight derivatives pentane/diethyl ether mixtures were used due to their high volatility).

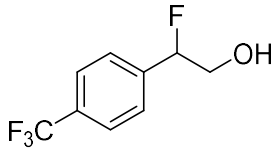
Compounds **3a-g**, **3l-r** and *syn*- and *anti*-**3t** have previously been described and their spectroscopic data were in agreement with those reported in the literature.

2-Fluoro-2-phenylethanol (3a) [1]



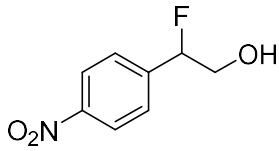
Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded **3a** as a colorless oil (68%, 19 mg). This reaction was also carried out on a 10 mmol scale (1.04 g of styrene) following an otherwise identical procedure, obtaining the title compound in 53 % yield.

2-Fluoro-2-(4-(trifluoromethyl)phenyl)ethanol (3b)



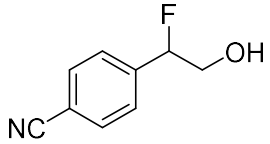
Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded **3b** as a colorless oil (43%, 18 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 5.56 (ddd, *J* = 48.3, 6.2, 3.8 Hz, 1H), 3.95 – 3.74 (m, 2H), 1.96 (dd, *J* = 7.7, 5.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.74 (s, 3F), -189.98 (ddd, 1F, *J* = 48.6, 27.0, 21.8 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 140.3, (d, *J* = 20.0 Hz), 130.9 (q, *J* = 32.3 Hz), 125.9 (d, *J* = 7.5 Hz), 125.6 (q, *J* = 3.6 Hz), 123.9 (q, *J* = 272.2 Hz), 93.9 (d, *J* = 174.0 Hz), 66.3 (d, *J* = 24.1 Hz). HRMS (EI) calcd. for $C_9H_8F_4O$ [M+Na$^+$]: 231,0403, found: 231,0396. IR (neat, ν_{max}, cm^{-1}): 3338, 2360, 1623, 1418, 1323, 1256, 1164, 1113, 1066, 1017, 880, 841, 765, 698.

2-Fluoro-2-(4-nitrophenyl)ethanol (3c) [1]



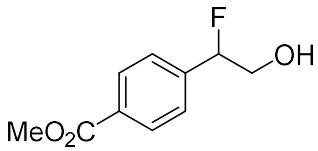
Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded **3c** as a colorless oil (38%, 14 mg).

2-Fluoro-2-(4-cyanophenyl)ethanol (3d)[1]



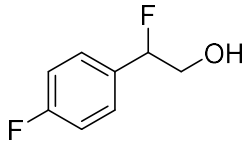
Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded **3d** as a colorless oil (67%, 22 mg).

Methyl 4-(1-fluoro-2-hydroxyethyl)benzoate (3e)[1]



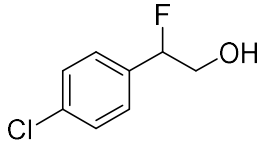
Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded **3e** as a colorless oil (46%, 17 mg).

2-Fluoro-2-(4-fluorophenyl)ethanol (3f)[1]



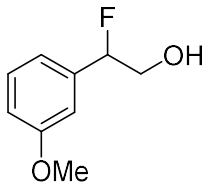
Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded **3f** as a colorless oil (38%, 12 mg).

2-Fluoro-2-(4-chlorophenyl)ethanol (3g)[1]



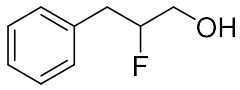
Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded **3g** as a colorless oil (49%, 16 mg).

2-Fluoro-2-(3-methoxyphenyl)ethanol (3k)



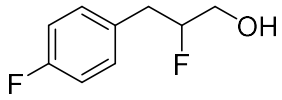
Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded **3k** as a colorless oil (41%, 14 mg). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30 – 7.19 (m, 1H), 6.86 – 6.72 (m, 3H), 5.47 (ddd, *J* = 48.7, 7.5, 3.3 Hz, 1H), 3.93 – 3.77 (m, 2H), 3.75 (s, 3H), 1.92 (br s, OH). ^{19}F NMR (282 MHz, $CDCl_3$) δ -187.89 (ddd, *J* = 48.9, 29.4, 19.5 Hz). ^{13}C NMR (75.5 MHz , $CDCl_3$) δ 159.73, 137.84 (d, *J* = 19.8 Hz), 129.67, 117.80 (d, *J* = 7.1 Hz), 114.17, 111.23 (d, *J* = 7.7 Hz), 94.59 (d, *J* = 172.8 Hz), 66.53 (d, *J* = 24.4 Hz), 55.23. HRMS (EI) calcd. for $C_9H_{11}FO_2$ [M+Na$^+$]: 193.0635, found: 193.0637. IR (neat, ν_{max}, cm^{-1}):3667, 2938, 1587, 1490, 1456, 1435, 12551157854, 780, 735, 696.

2-Fluoro-3-phenylpropanol (3l) [2]



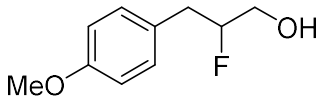
Flash chromatography of the crude reaction product [n-hexane-AcOEt (2:1)] afforded **3l** as a colorless oil (62%, 19 mg). IR (neat, vmax, cm-1): 3370, 3029, 2931, 1719, 1496, 1455, 1257, 1050, 903, 836, 746, 700.

2-Fluoro-3-(4-fluorophenyl)propanol (3m)[2]



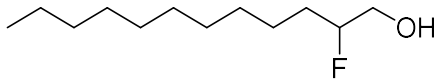
Flash chromatography of the crude reaction product [n-hexane-AcOEt (2:1)] afforded **3m** as a colorless oil (58%, 20 mg). IR (neat, vmax, cm-1): 3369, 2935, 1718, 1602, 1510, 1258, 1222, 1159, 1052, 818, 750.

2-Fluoro-3-(4-methoxyphenyl)propanol (3n)[2]



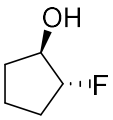
Flash chromatography of the crude reaction product [n-hexane-AcOEt (2:1)] afforded **3n** as a white solid (41%, 15 mg). m. p. = 62-63 ˚C. IR (neat, vmax, cm-1): 3358, 2916, 2838, 1717, 1614, 1587, 1511, 1436, 1302, 1244, 1176, 1111, 1091, 1070, 1023, 886, 809, 749, 717.

2-Fluorododecan-1-ol (3o) [3]



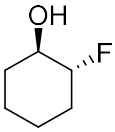
Flash chromatography of the crude reaction product [n-hexane-AcOEt (2:1)] afforded **3o** as a waxy solid (93%, 38 mg). m. p. = 53-54 ˚C (lit. 51-53).[4] HPLC (Chiralcel AY-H, 95:5 hexane/iPrOH, 1 mL min-1, 240 nm) tR(major) = 10,41 min, tR(minor) = 11,27 min. IR (neat, vmax, cm-1): 3461, 2917, 2849, 1456, 1378, 1261, 1101, 965, 860, 827, 719, 628, 622, 616, 611, 605.

***trans*-2-Fluorocyclopentanol (3p)**[5]



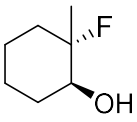
Flash chromatography of the crude reaction product [*n*-pentane-Et_2O (1:1)] afforded **3p** as a colorless oil (72%, 15 mg). IR (neat, ν_{max}, cm^{-1}): 3331, 2963, 1084, 1035, 877. This reaction was also conducted at 2 mmol scale following the next procedure. A 5-mL polypropylene vial was charged with *m*-CPBA 77% w/w (900 mg, 4 mmol, 2 equiv). DCM (20mL) was added and the resulting suspension was cooled down in an ice bath. Finally, cyclopentene (183µL, 2 mmol) was added followed by HF·Py 70% w/w (360µL, 14 mmol, 7 equiv).The reaction mixture was stirred 4-5h (TLC), then quenched by the addition of ice and a spatula of $KHSO_3$ and stir for 30 additional minutes. The reaction mixture was then extracted with DCM (3 x 20 mL), the combined organic layers dried over Na_2SO_4, filtered and concentrated under reduced pressure keeping the rotavap bath at 0ºC. The residue thus obtained was purified by kugelrohr distillation (37-39 ˚C, 15 torr; (lit. 35-38 ˚C, 15 torr)[5]) affording **3p** as a colorless liquid (126 mg, 61%).

***trans*-2-Fluorocyclohexanol (3q)**[3]



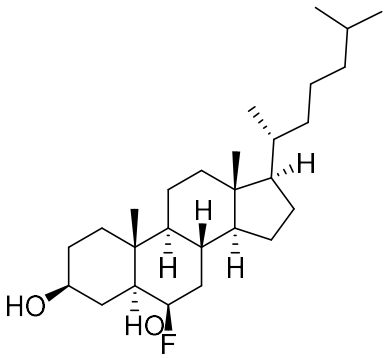
Flash chromatography of the crude reaction product [*n*-pentane-Et_2O (1:1)] afforded **3q** as a colorless oil (63%, 15 mg). IR (ν_{max}, cm^{-1}): 3567, 2934, 2862, 2360, 1734, 1559, 1456, 1099, 1015, 842, 669, 616.

***trans*-Fluoro-2-methylcyclohexanol (3r)**[3]



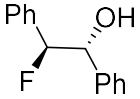
Flash chromatography of the crude reaction product [*n*-pentane-Et_2O (1:1)] afforded **3r** as a colorless oil (19%, 5 mg). IR (neat, ν_{max}, cm^{-1}): 3545, 2929, 2858, 2360, 1716, 1670, 1575, 1448, 1333, 1297, 1262, 1164, 1145, 1092, 1072, 999, 948, 889, 807, 749, 717, 686.

(3S,5R,6R,8S,9S,10R,13R,14S,17R)-6-Fluoro-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-5H-cyclopenta[a]phenanthrene-3,5-diol (3s)



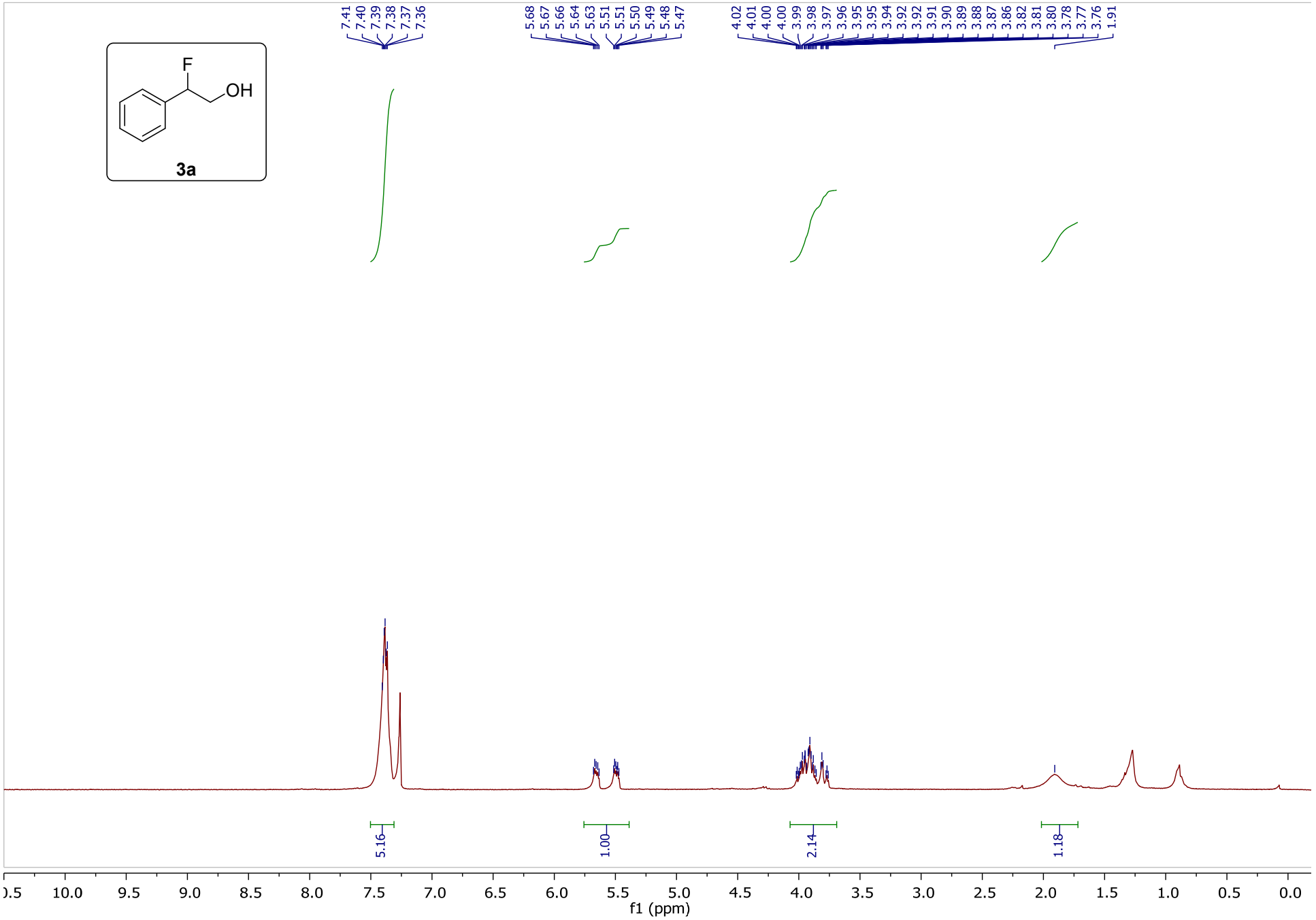
Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded **3s** as a white solid (41%, 14 mg). m.p. =200-203 ˚C ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.18 (dt, *J* = 49.2, 2.8 Hz, 1H), 4.00 (tt, *J* = 10.6, 5.4 Hz, 1H), 2.12 – 1.87 (m, 2H), 1.83 – 0.95 (m, 34H), 0.83 (d, *J* = 6.5 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 95.33 (d, *J* = 178.9 Hz), 74.56 (d, *J* = 21.1 Hz), 67.19 (s), 55.98 (d, *J* = 23.2 Hz), 45.29 (s), 42.69 (s), 40.32 (s), 39.81 (s), 39.43 (s), 38.07 (d, *J* = 2.0 Hz), 36.09 (s), 35.71 (s), 34.82 (s), 31.96 (s), 31.67 (s), 30.66 (s), 30.34 (s), 28.13 (s), 27.94 (s), 23.93 (s), 23.79 (s), 22.75 (s), 22.49 (s), 21.03 (s), 18.59 (s), 15.99 (s), 15.86 (s). ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ -184.8 (m). HRMS (EI) calcd. for $C_{27}H_{47}FO_2$ [M-HF+NH_4^+]: 420.3836, found: 420.3829. IR (neat, ν_{max}, cm^{-1}): 3416, 2936, 2866, 1467, 1375, 1017, 959, 862, 800, 603.

(1R*,2S*)-2-Fluoro-1,2-diphenylethanol (*anti*-3t) [6]



Flash chromatography of the crude reaction product [*n*-hexane-AcOEt (2:1)] afforded ***anti*-3t** as a white solid (76%, 33 mg). m. p. = 97-99 ˚C (lit. 99 ˚C)[7].

[1] Li,Y.; Jiang, X.; Zhao, C.; Fu, X.; Xu, X.; Tang, P. *ACS Catal.* **2017**, *7*, 1606.
[2] Luo, F.; Wang, P.; Gong, Y. *Tetrahedron Lett.* **2010,** *51* (13), 1693-1695.
[3] Yoshino, H.; Nomura, K.; Matsubara, S.; Oshima, K.; Matsumoto, K.; Hagiwara, R.; Ito, Y. *J. Fluorine Chem.* **2004,** *125* (7), 1127-1129.
[4] Nohira, H.; Kamei, M.; Nakamura, S.; Yoshinaga, K; Kai, M.; Katagiri, K. Optically active compound, process for producing same and liquid crystal composition containing same US Patent 4873018, Oct 10, 1989.
[5] Shellhamer, D. F.; Briggs, A. A.; Miller, B. M.; Prince, J. M.; Scott, D. H.; Heasley, V. L. *J. Chem. Soc. Perkin Trans. 2* **1996**, 973-977.
[6] Stavber, G.; Zupan, M.; Jereb, M.; Stavber, S. *Org. Lett.* **2004**, *6*, 4973.
[7] Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672.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OH
3a
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7.40
7.39
7.38
7.37
7.36
5.68
5.67
5.66
5.64
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5.51
5.51
5.50
5.49
5.48
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4.00
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3.95
3.95
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3.92
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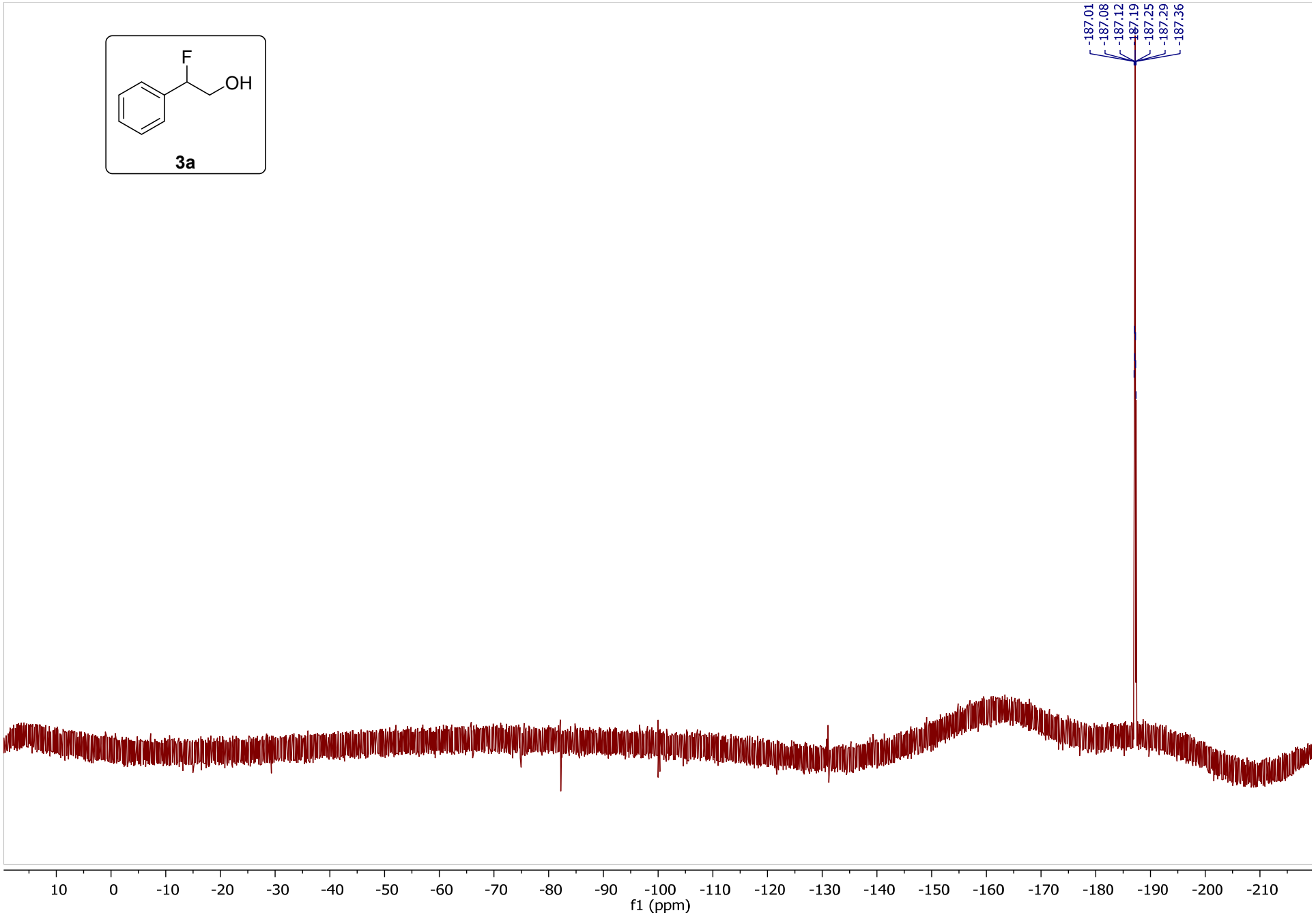
5.16
1.00
2.14
1.18
f1 (ppm)


F
OH
3a
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0
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-20
-30
-40
-50
-60
-70
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-140
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-160
-170
-180
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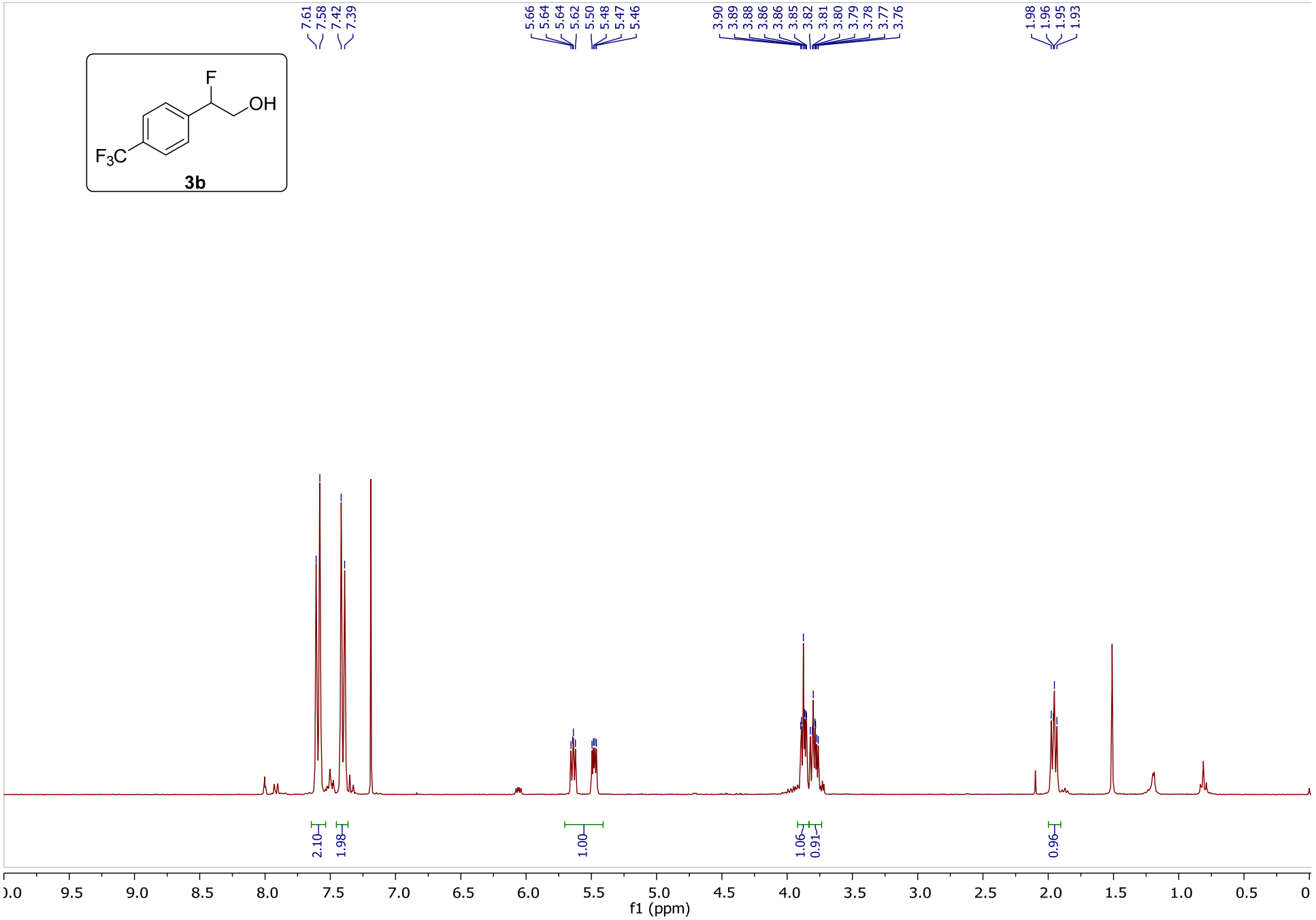
-210
f1 (ppm)


7.61
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5.64
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5.48
5.47
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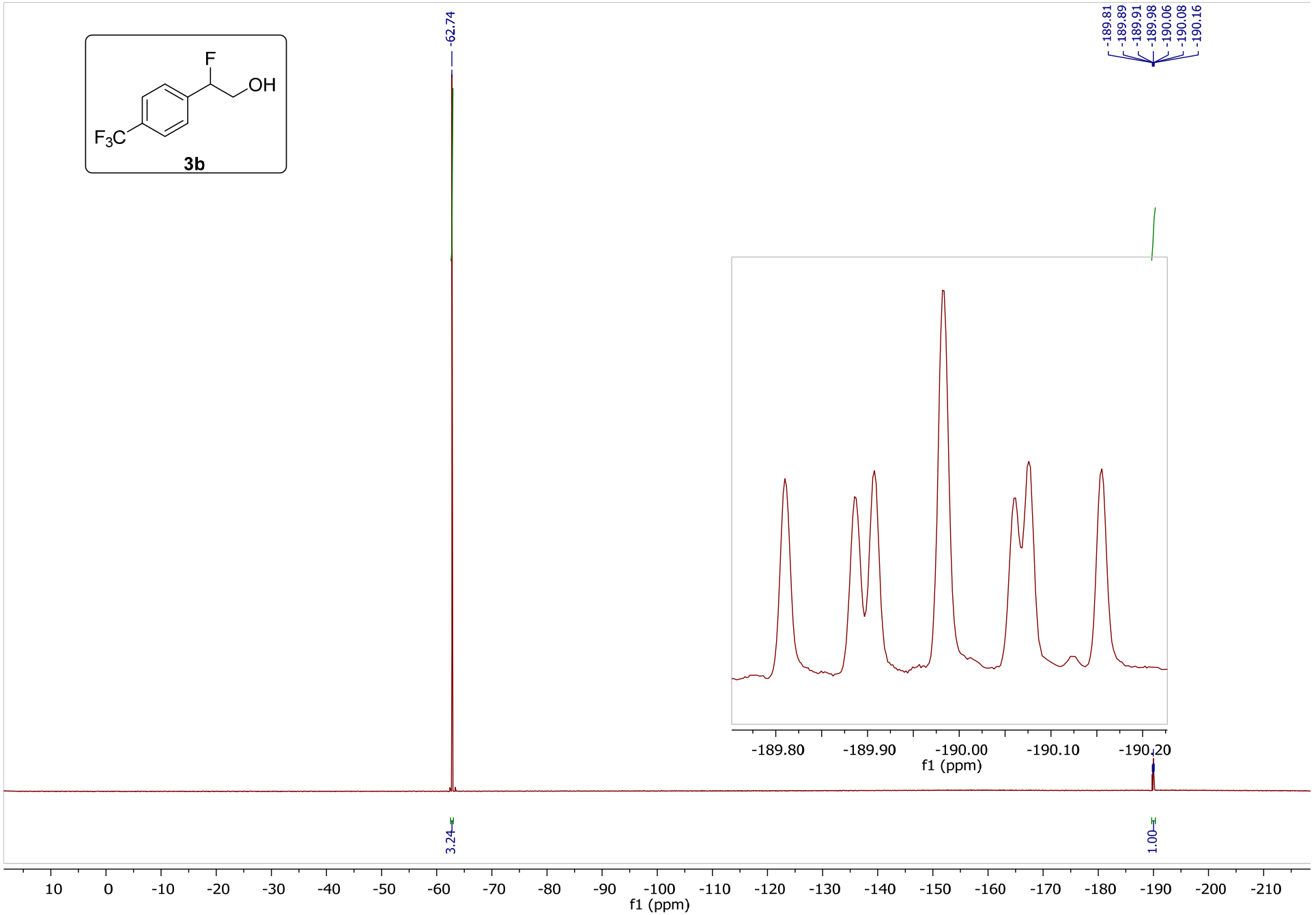
3.76
1.98
1.96
1.95
1.93
F
OH
F3C
3b
2.10
1.98
1.00
1.06
0.91
0.96
f1 (ppm)


F
OH
F3C
3b
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-189.81
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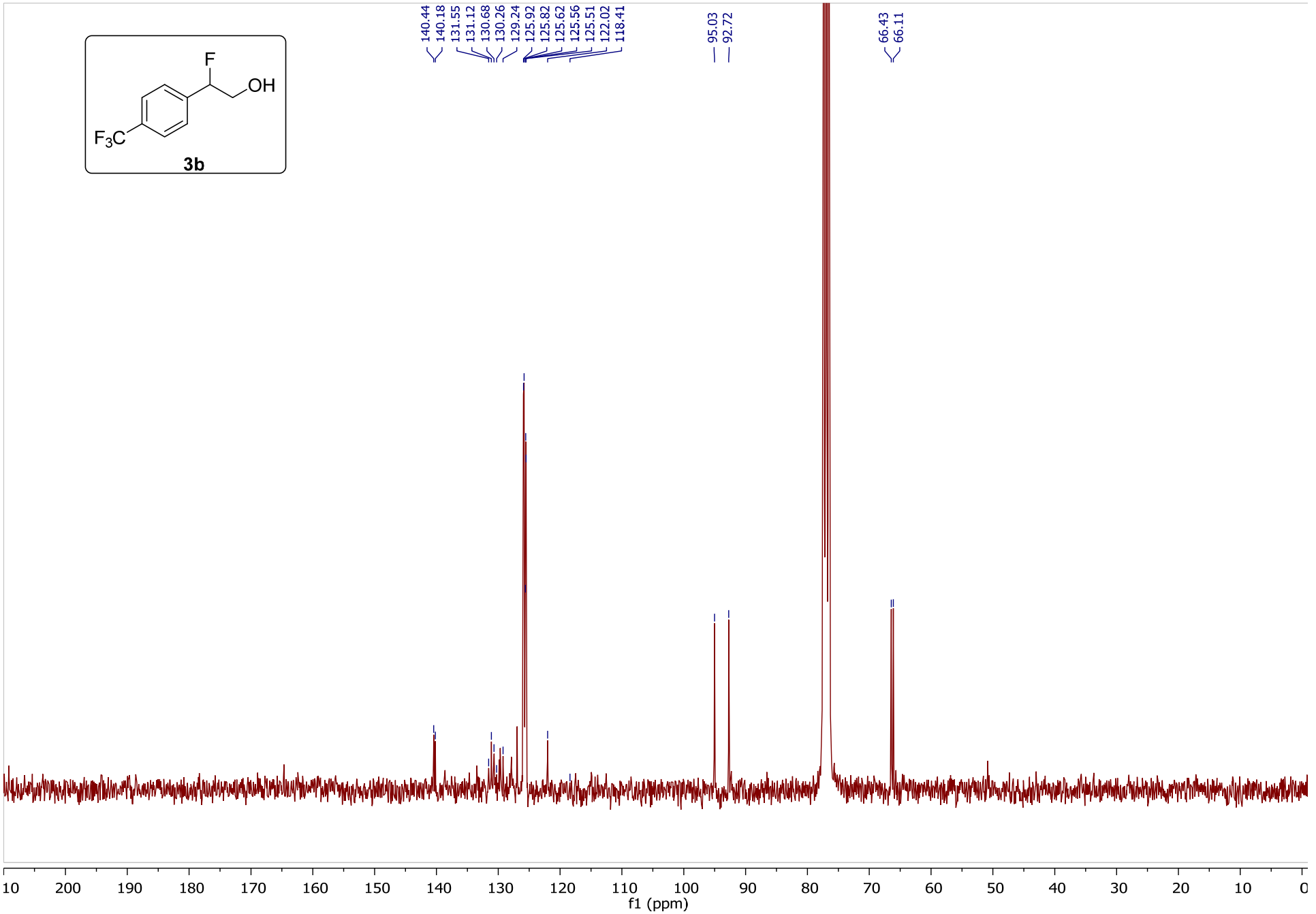
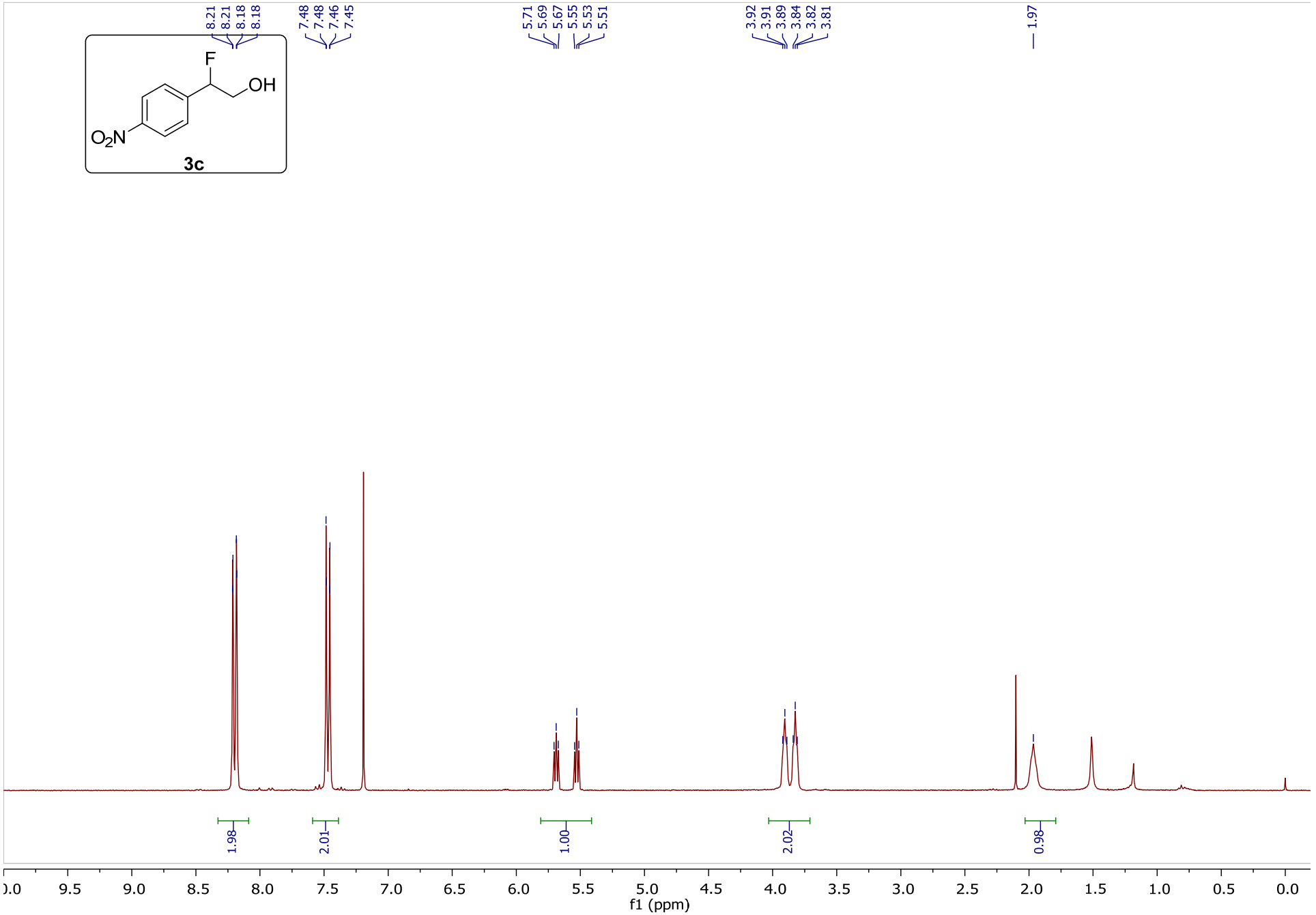
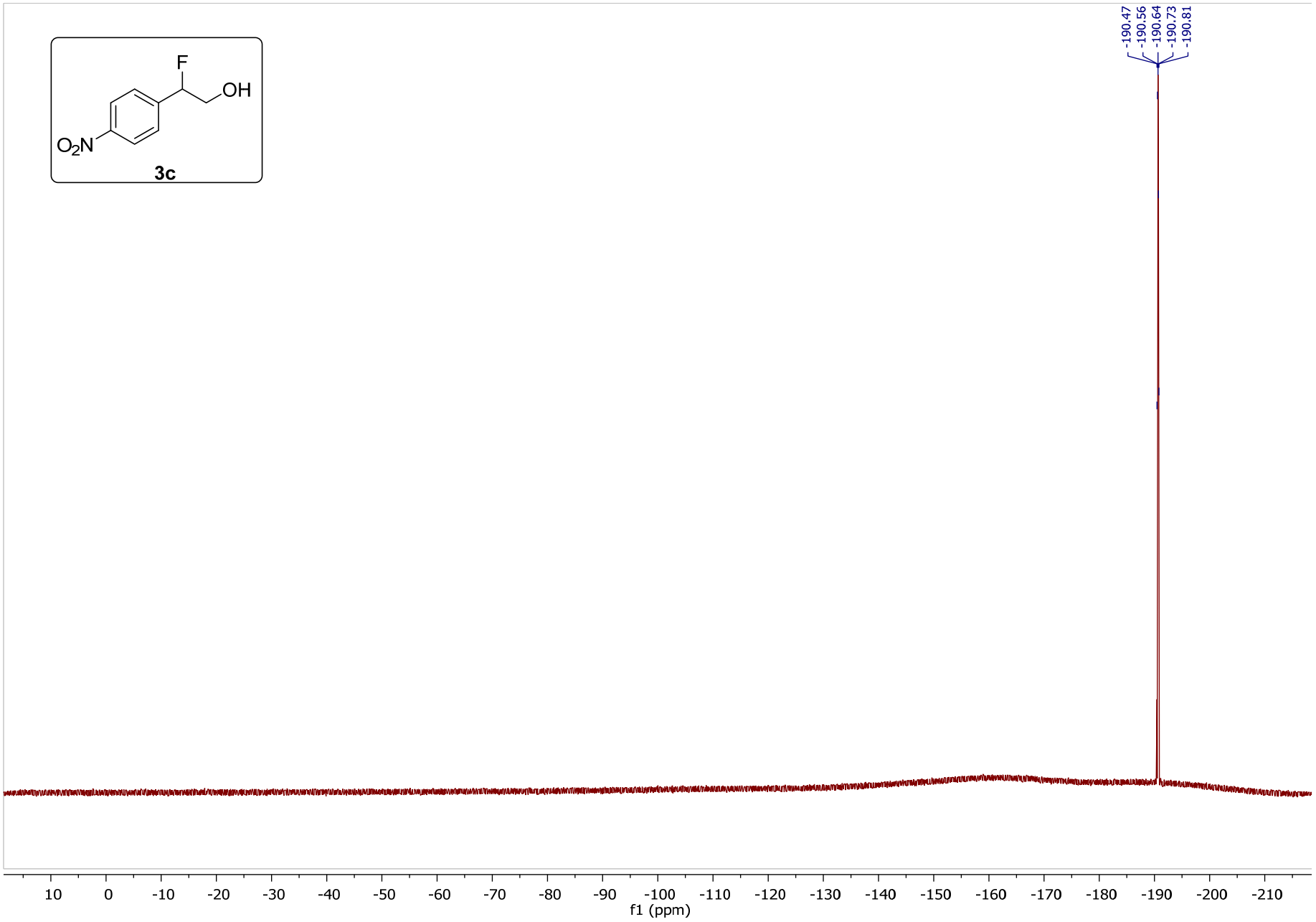
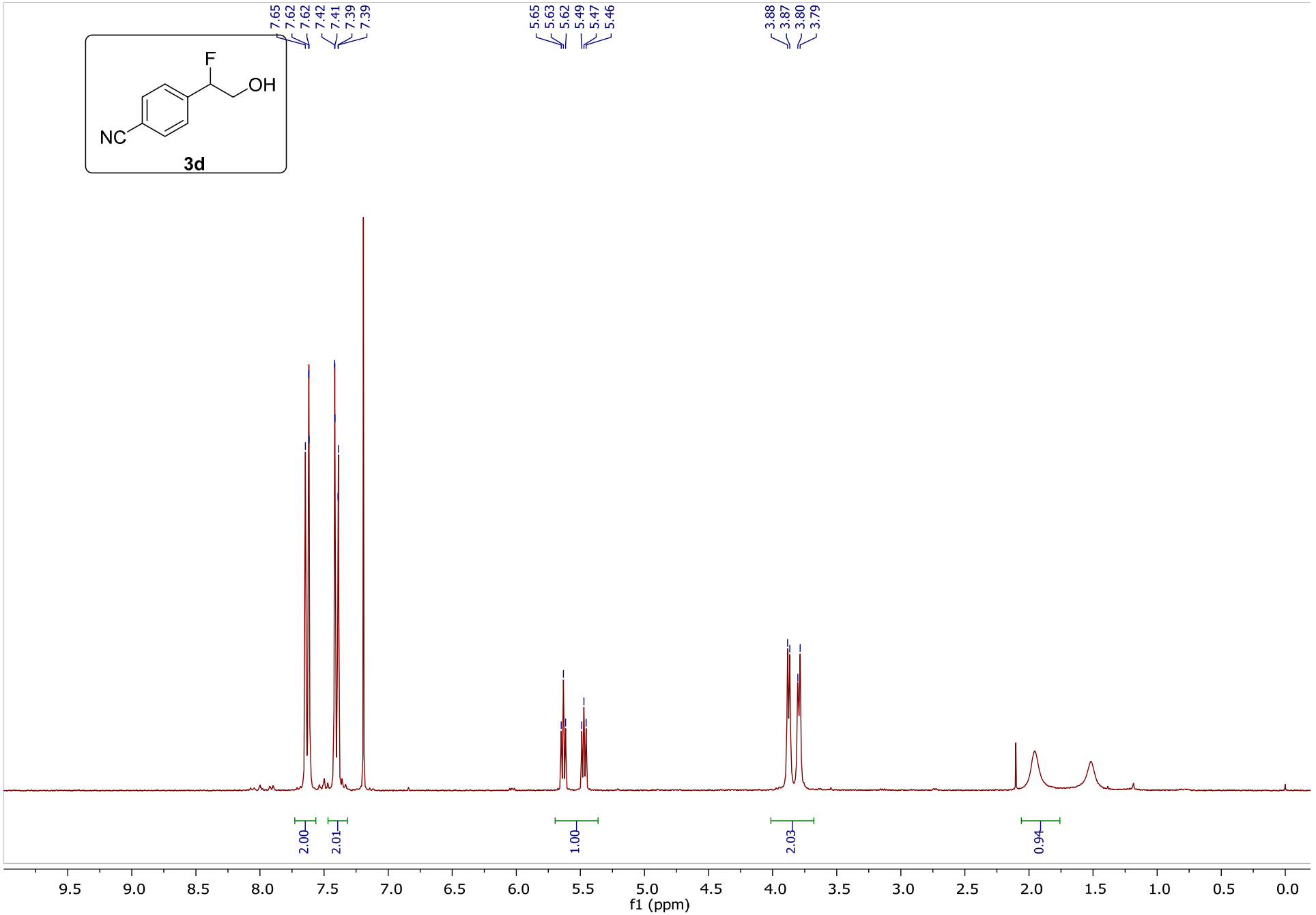
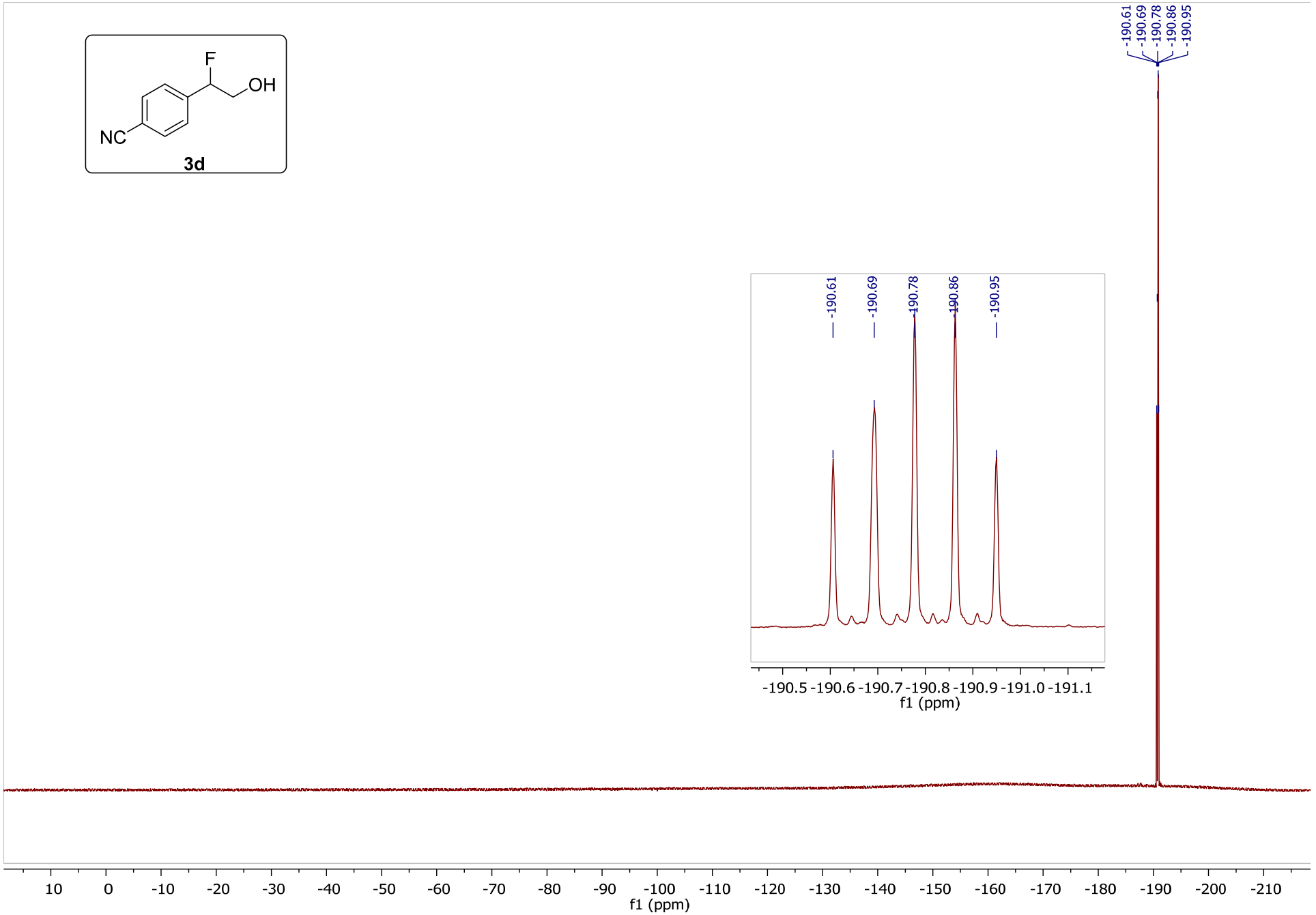
-189.98
-190.06
-190.08
-190.16
-189.80
-189.90
-190.00
-190.10
-190.20
f1 (ppm)
3.24
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

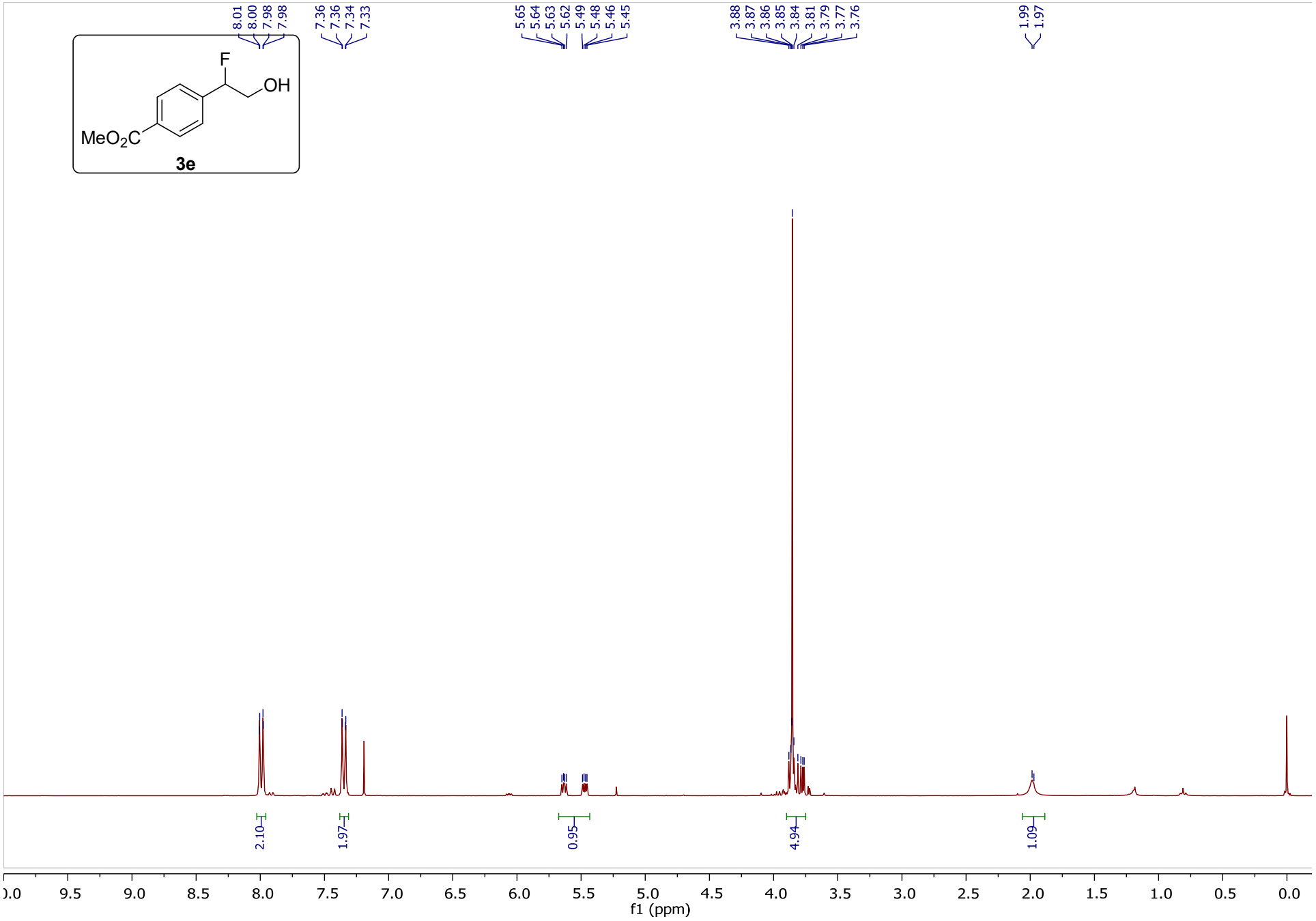

F
OH
F3C
3b
140.44
140.18
131.55
131.12
130.68
130.26
129.24
125.92
125.82
125.62
125.56
125.51
122.02
118.41
95.03
92.72
66.43
66.11
f1 (ppm)

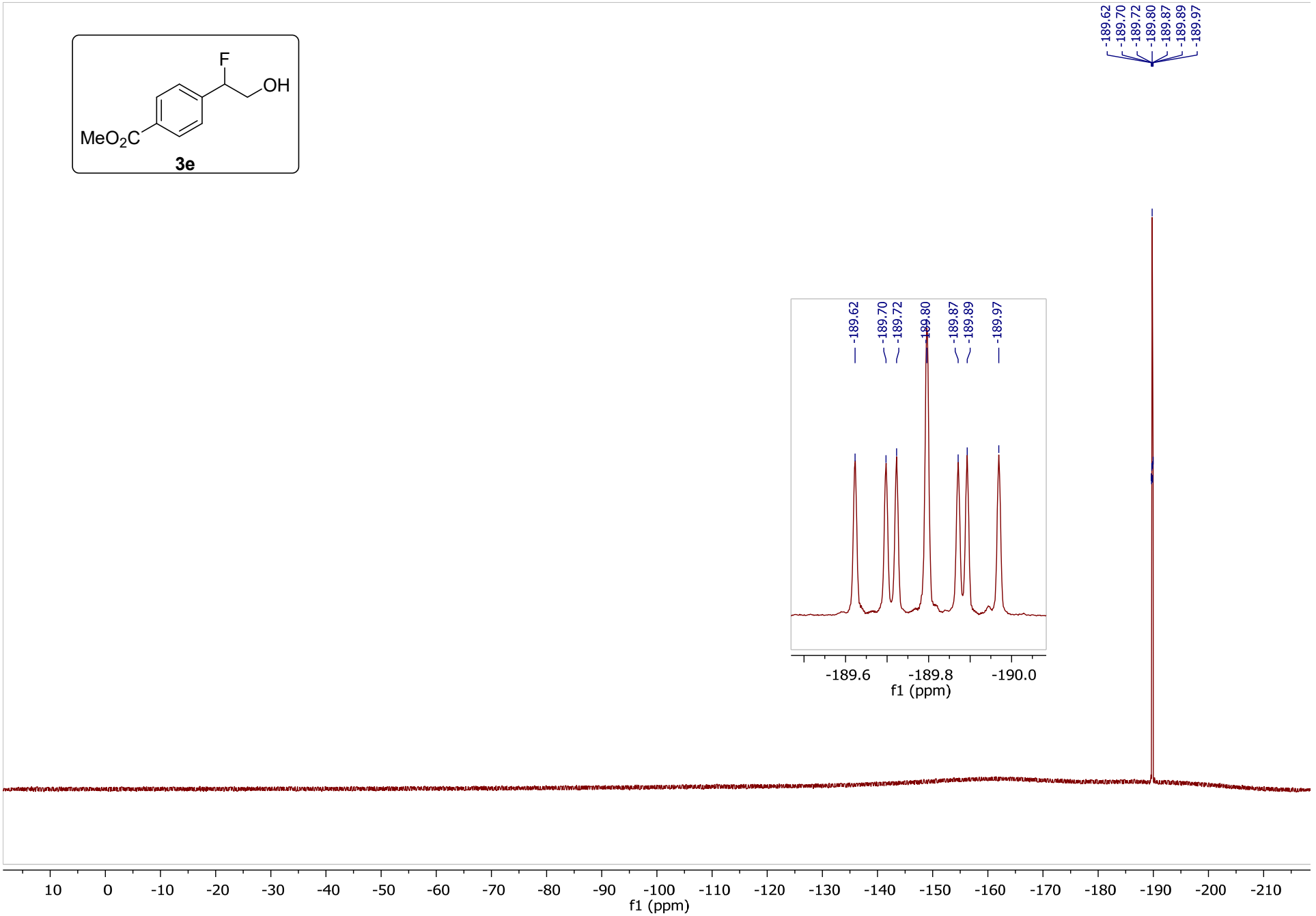

8.21
8.21
8.18
8.18
7.48
7.48
7.46
7.45
5.71
5.69
5.67
5.55
5.53
5.51
3.92
3.91
3.89
3.84
3.82
3.81
1.97
F
OH
O2N
3c
1.98
2.01
1.00
2.02
0.98
f1 (ppm)

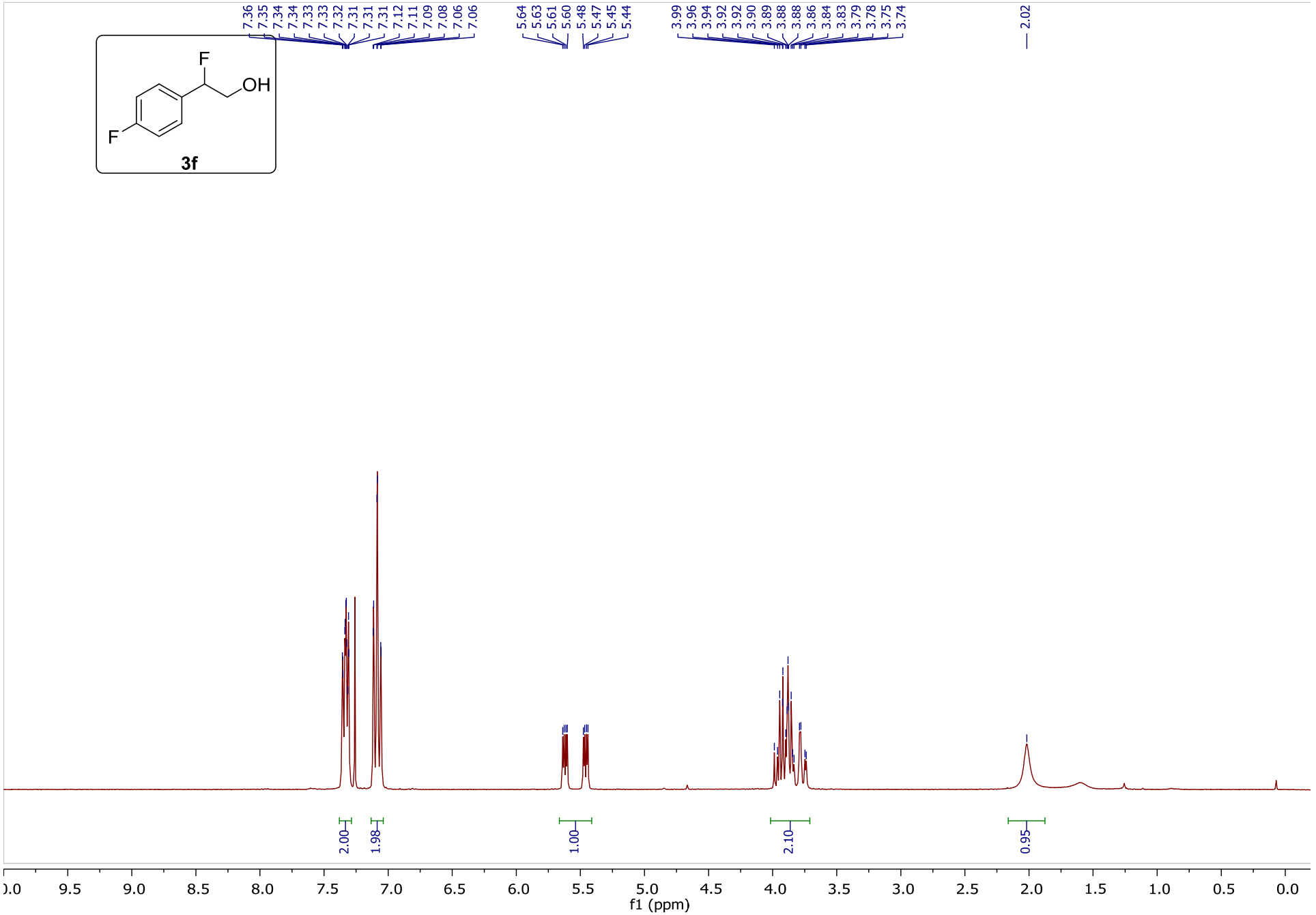

F
OH
O2N
3c
-190.47
-190.56
-190.64
-190.73
-190.81
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

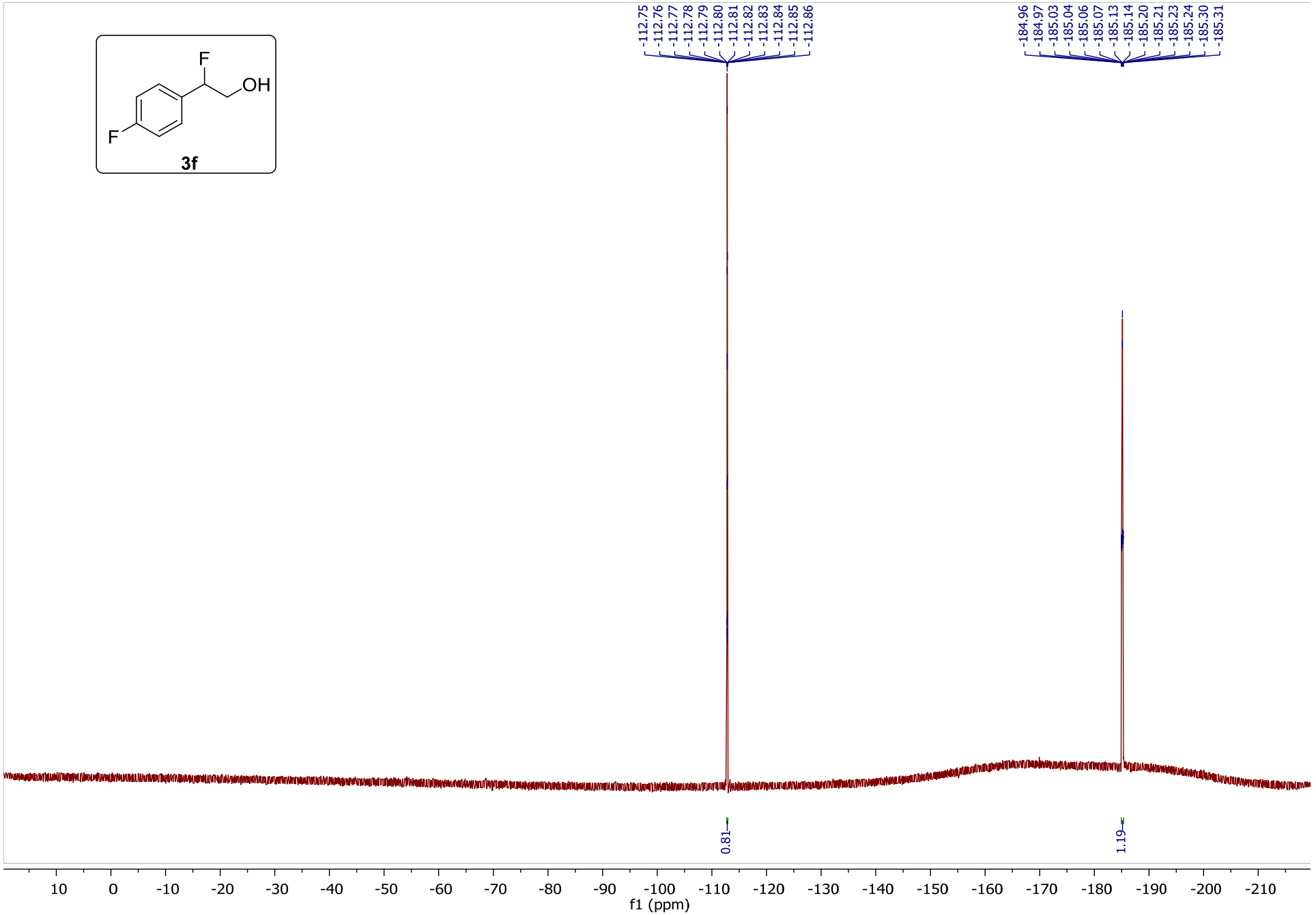

7.65
7.62
7.62
7.42
7.41
7.39
7.39
5.65
5.63
5.62
5.49
5.47
5.46
3.88
3.87
3.80
3.79
F
OH
NC
3d
2.00
2.01
1.00
2.03
0.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

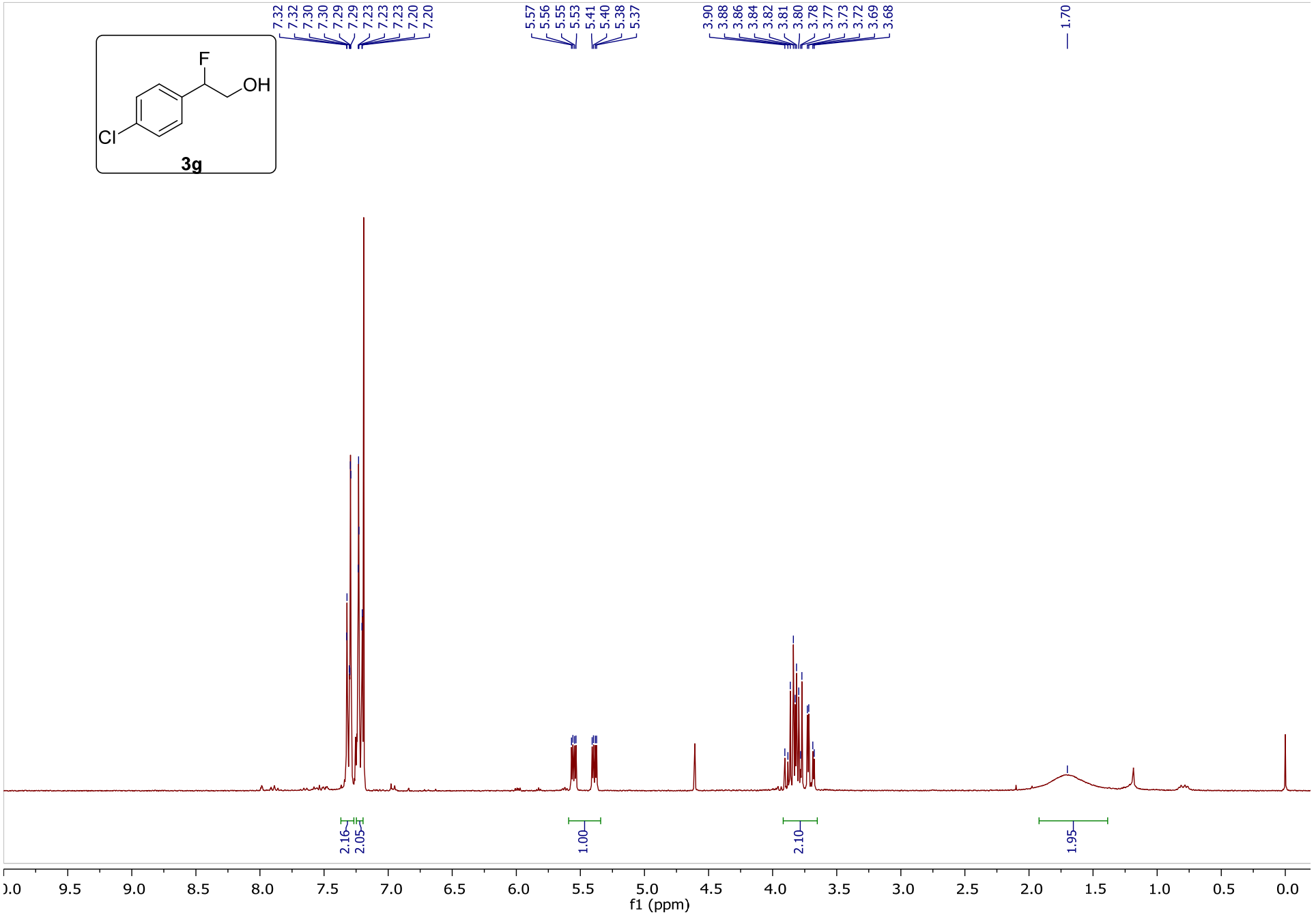

F
OH
NC
3d
-190.61
-190.69
-190.78
-190.86
-190.95
-190.5 -190.6 -190.7 -190.8 -190.9 -191.0 -191.1
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

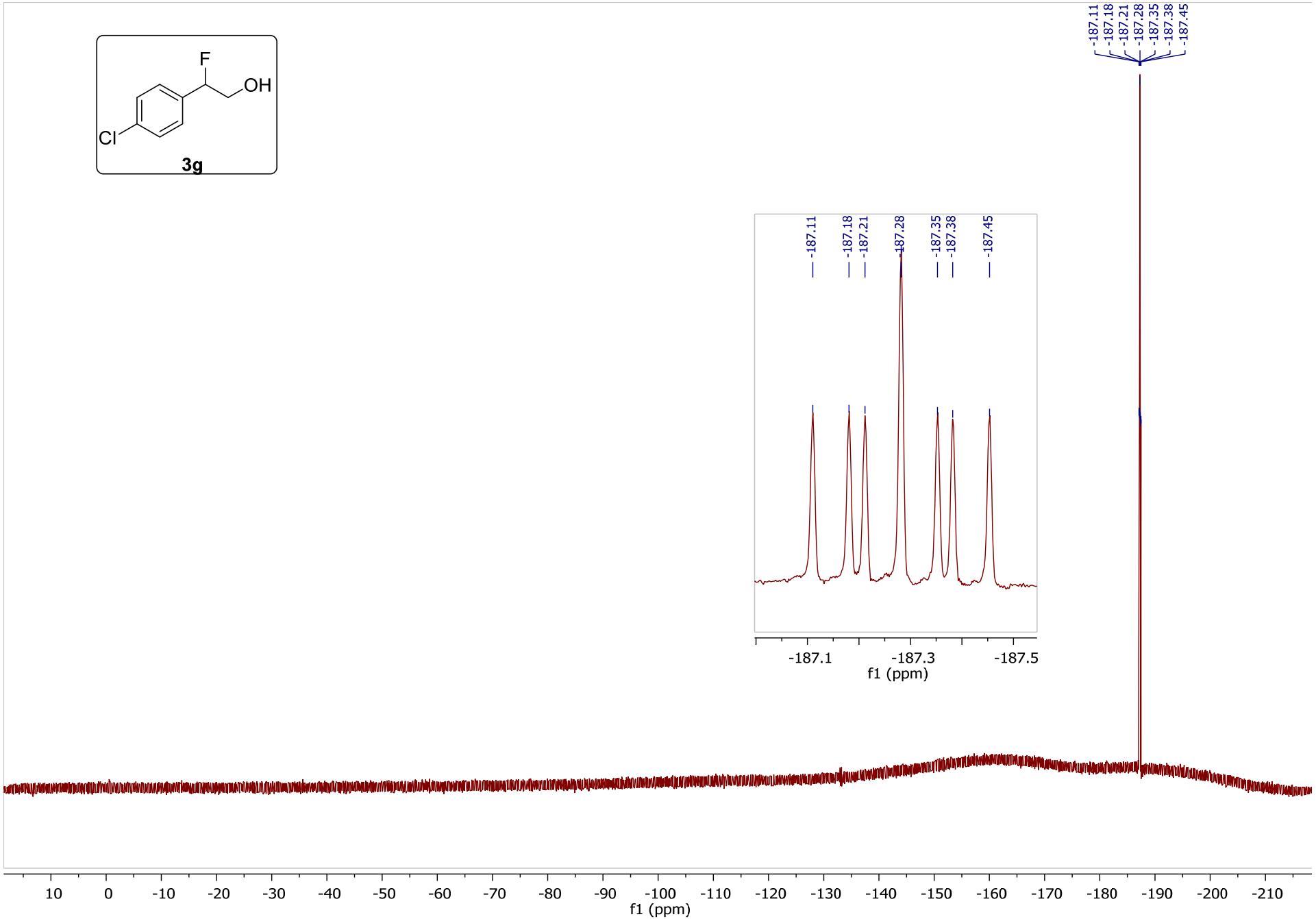

8.01
8.00
7.98
7.98
7.36
7.36
7.34
7.33
5.65
5.64
5.63
5.62
5.49
5.48
5.46
5.45
3.88
3.87
3.86
3.85
3.84
3.81
3.79
3.77
3.76
1.99
1.97
F
OH
MeO2C
3e
2.10
1.97
0.95
4.94
1.09
f1 (ppm)

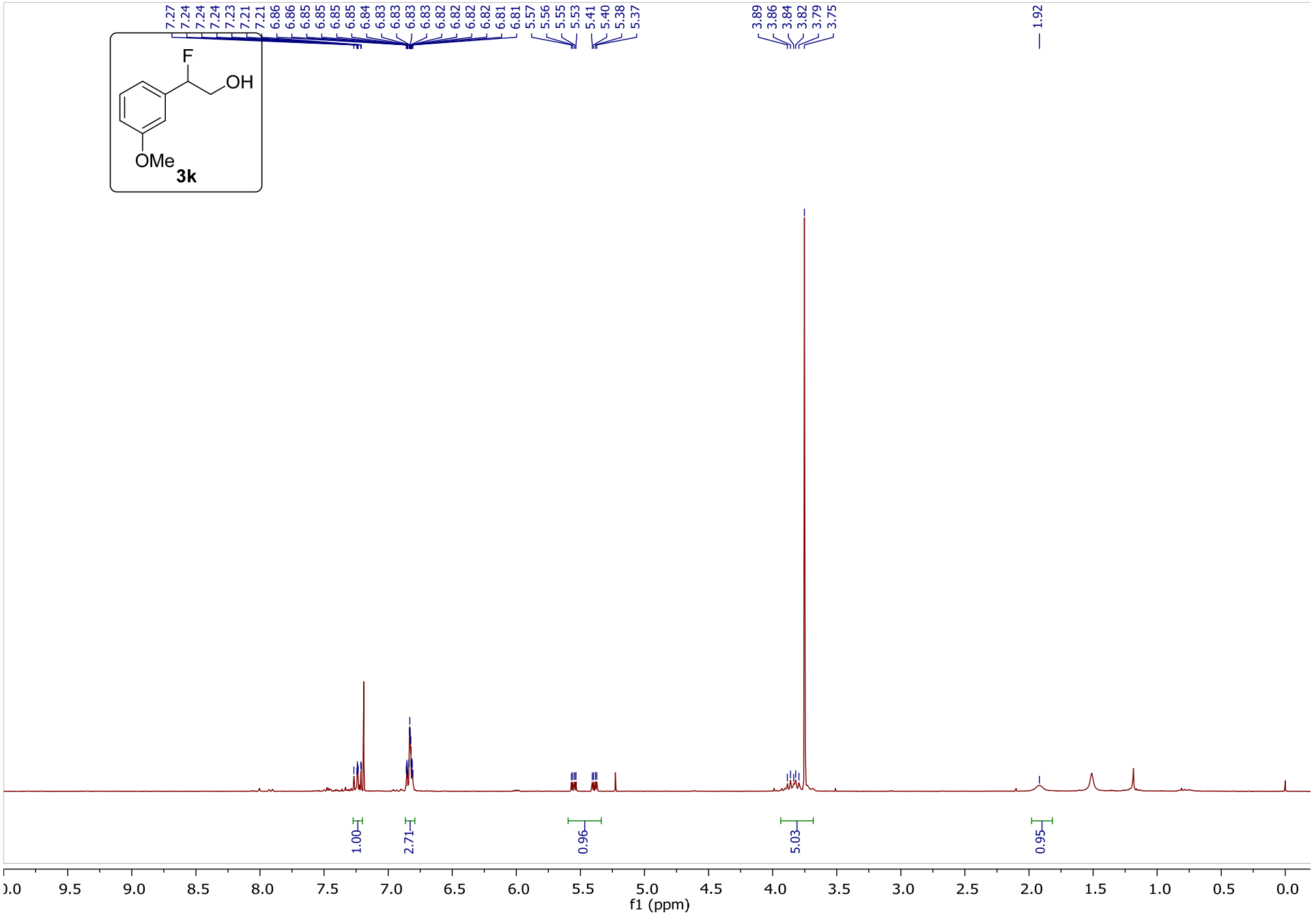

F
OH
MeO2C
3e
-189.62
-189.70
-189.72
-189.80
-189.87
-189.89
-189.97
-189.6
-189.8
-190.0
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

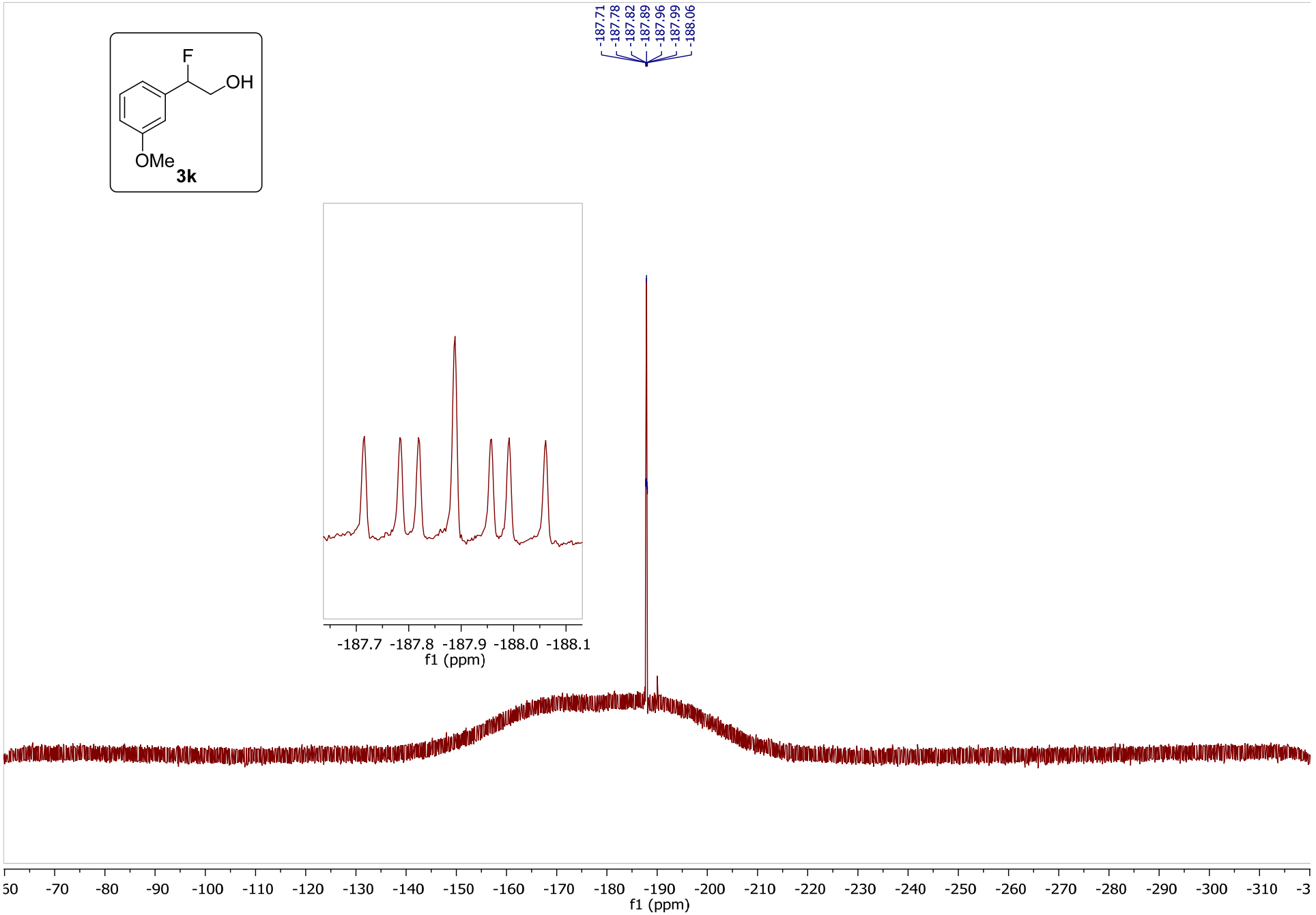

7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.31
7.12
7.11
7.09
7.08
7.06
7.06
5.64
5.63
5.61
5.60
5.48
5.47
5.45
5.44
3.99
3.96
3.94
3.92
3.92
3.90
3.89
3.88
3.88
3.86
3.84
3.83
3.79
3.78
3.75
3.74
2.02
F
OH
F
3f
2.00
1.98
1.00
2.10
0.95
f1 (ppm)

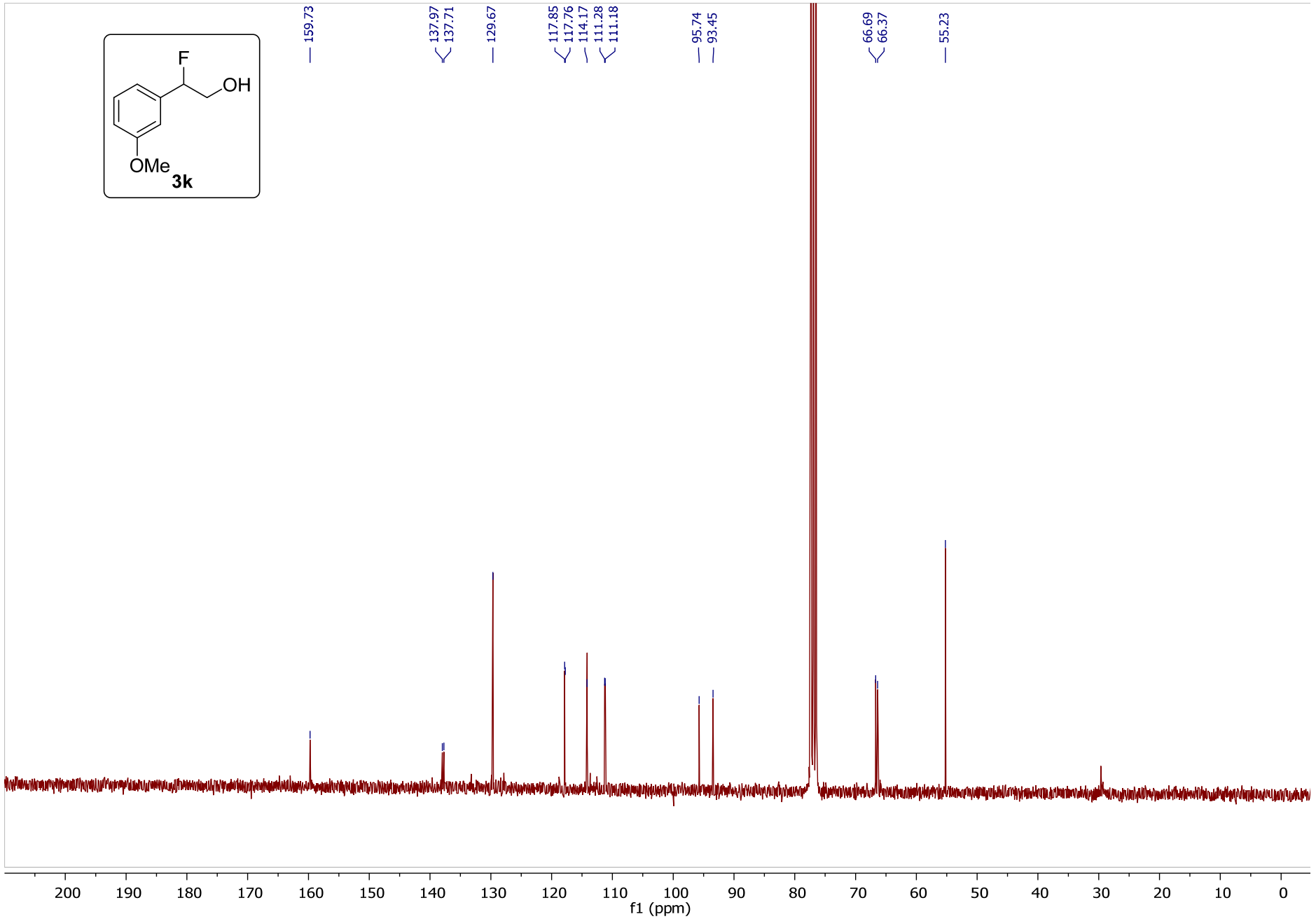

F
OH
F
3f
-112.75
-112.76
-112.77
-112.78
-112.79
-112.80
-112.81
-112.82
-112.83
-112.84
-112.85
-112.86
-184.96
-184.97
-185.03
-185.04
-185.06
-185.07
-185.13
-185.14
-185.20
-185.21
-185.23
-185.24
-185.30
-185.31
0.81
1.19
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

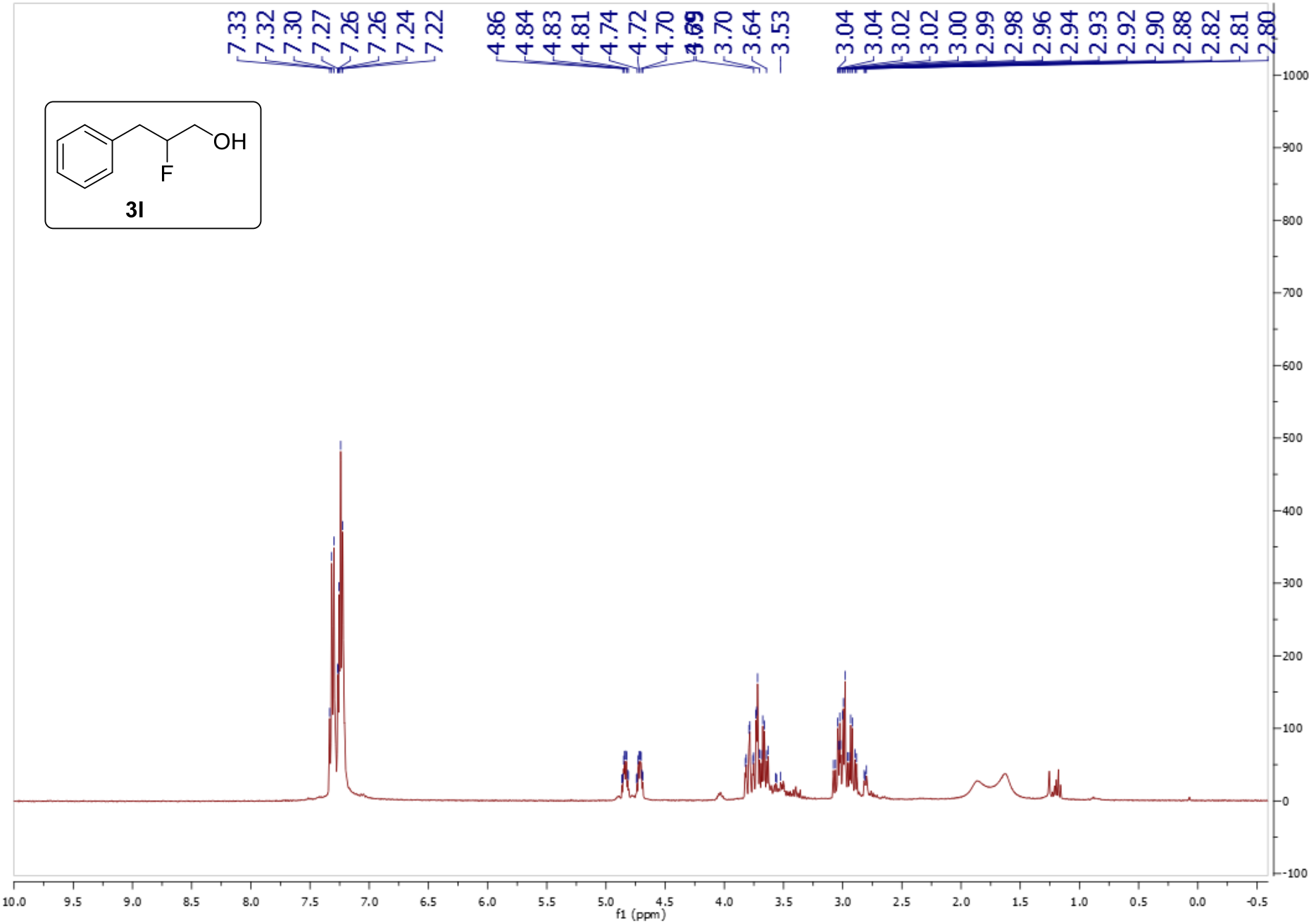

7.32
7.32
7.30
7.30
7.29
7.29
7.23
7.23
7.23
7.20
7.20
5.57
5.56
5.55
5.53
5.41
5.40
5.38
5.37
3.90
3.88
3.86
3.84
3.82
3.81
3.80
3.78
3.77
3.73
3.72
3.69
3.68
1.70
F
OH
Cl
3g
2.16
2.05
1.00
2.10
1.95
f1 (ppm)

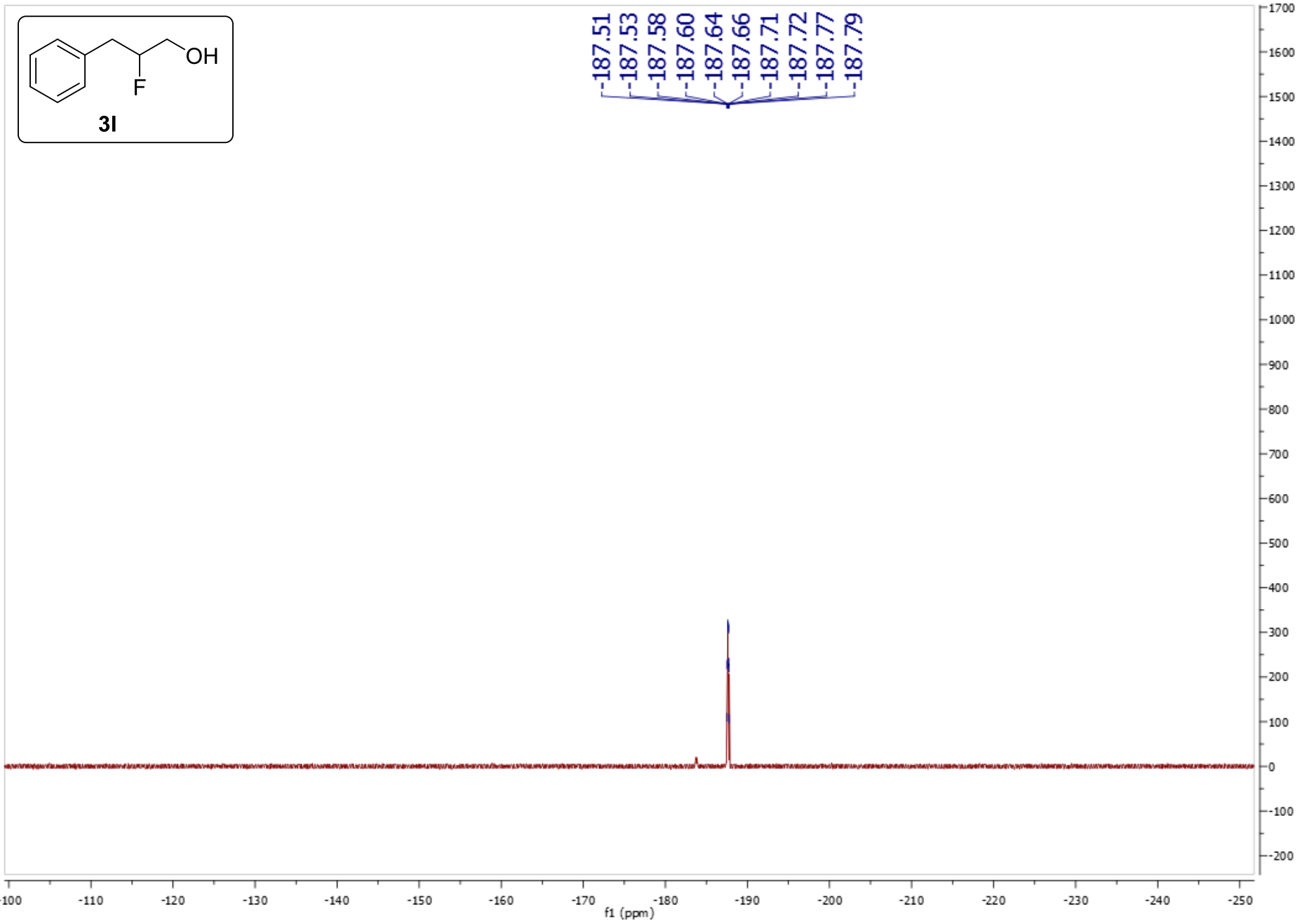

F
OH
Cl
3g
-187.11
-187.18
-187.21
-187.28
-187.35
-187.38
-187.45
-187.1
-187.3
-187.5
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

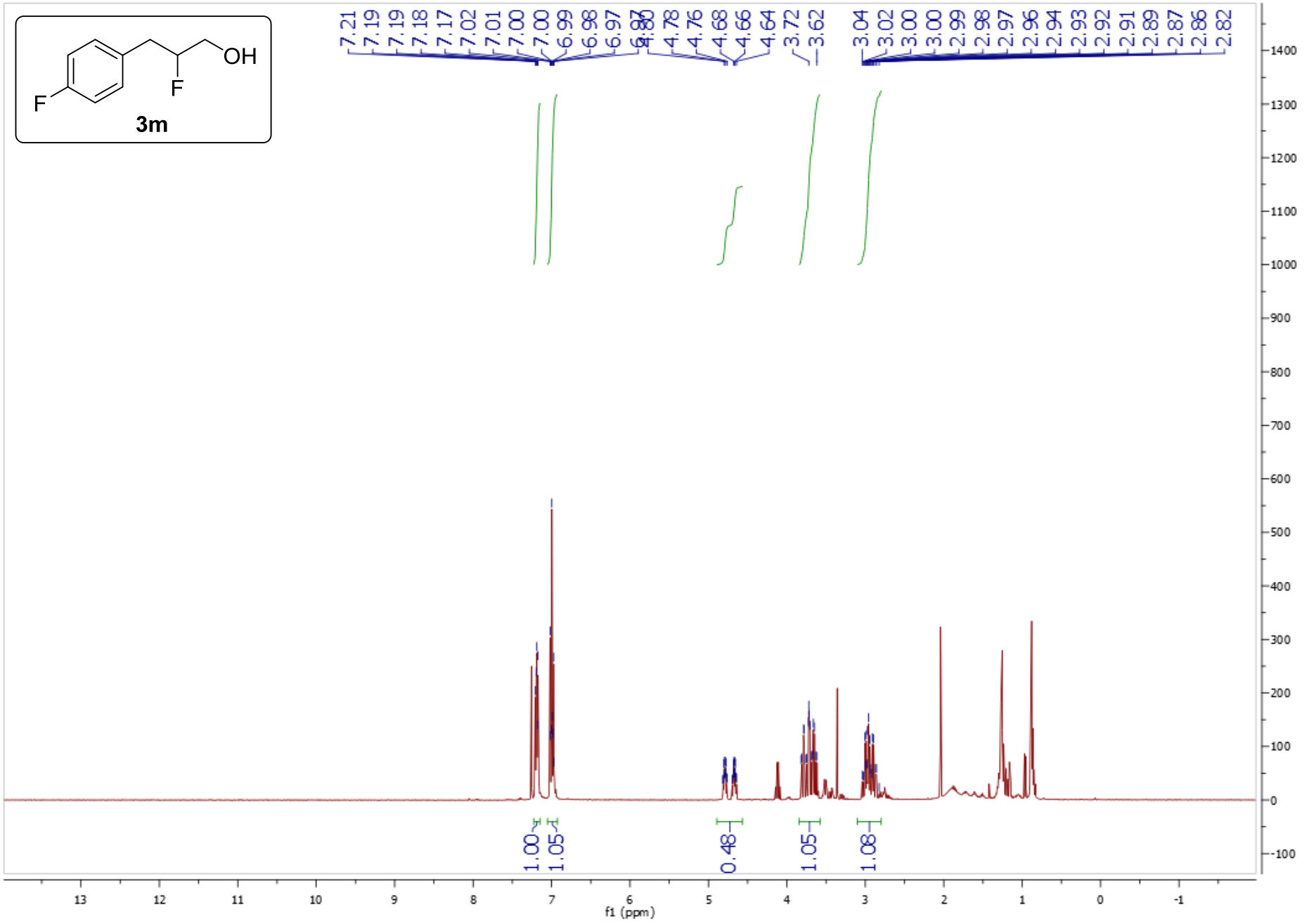

7.27
7.24
7.24
7.24
7.23
7.21
7.21
6.86
6.86
6.85
6.85
6.85
6.85
6.84
6.83
6.83
6.83
6.83
6.82
6.82
6.82
6.82
6.81
6.81
5.57
5.56
5.55
5.53
5.41
5.40
5.38
5.37
3.89
3.86
3.84
3.82
3.79
3.75
1.92
F
OH
OMe
3k
1.00
2.71
0.96
5.03
0.95
f1 (ppm)

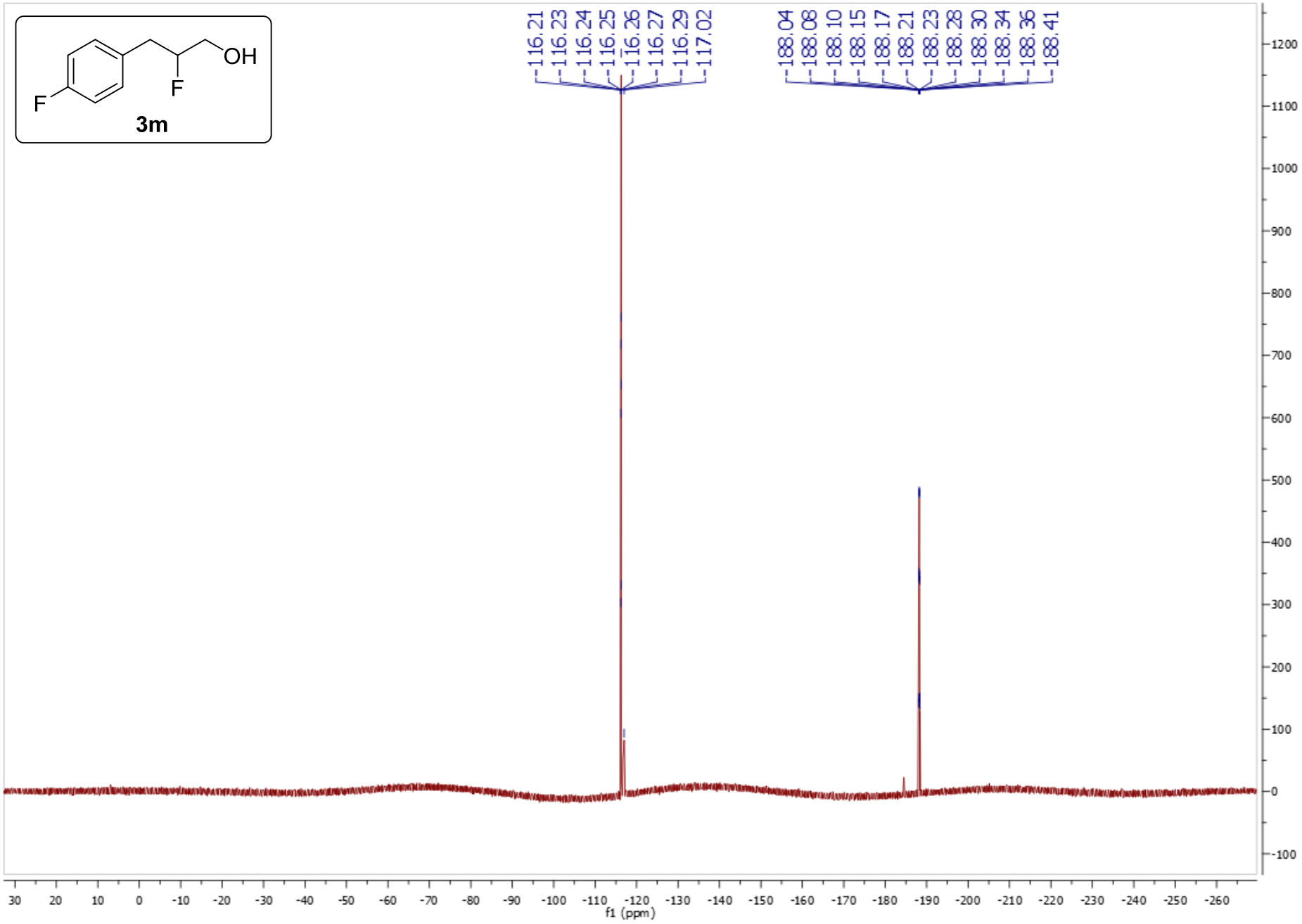

-187.71
-187.78
-187.82
-187.89
-187.96
-187.99
-188.06
F
OH
OMe
3k
-187.7 -187.8 -187.9 -188.0 -188.1
f1 (ppm)
50 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310 -3
f1 (ppm)

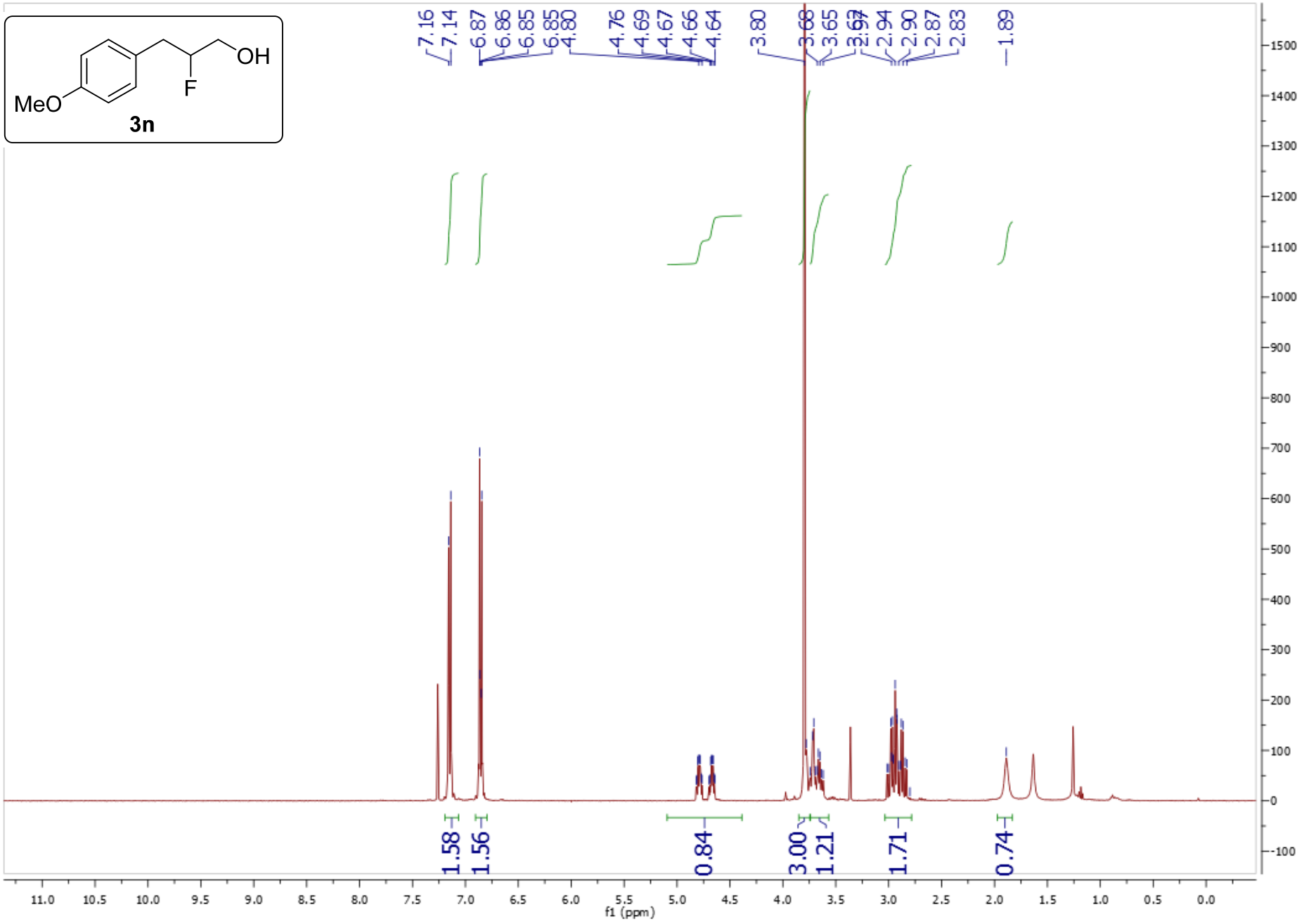

F
OH
OMe
3k
159.73
137.97
137.71
129.67
117.85
117.76
114.17
111.28
111.18
95.74
93.45
66.69
66.37
55.23
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

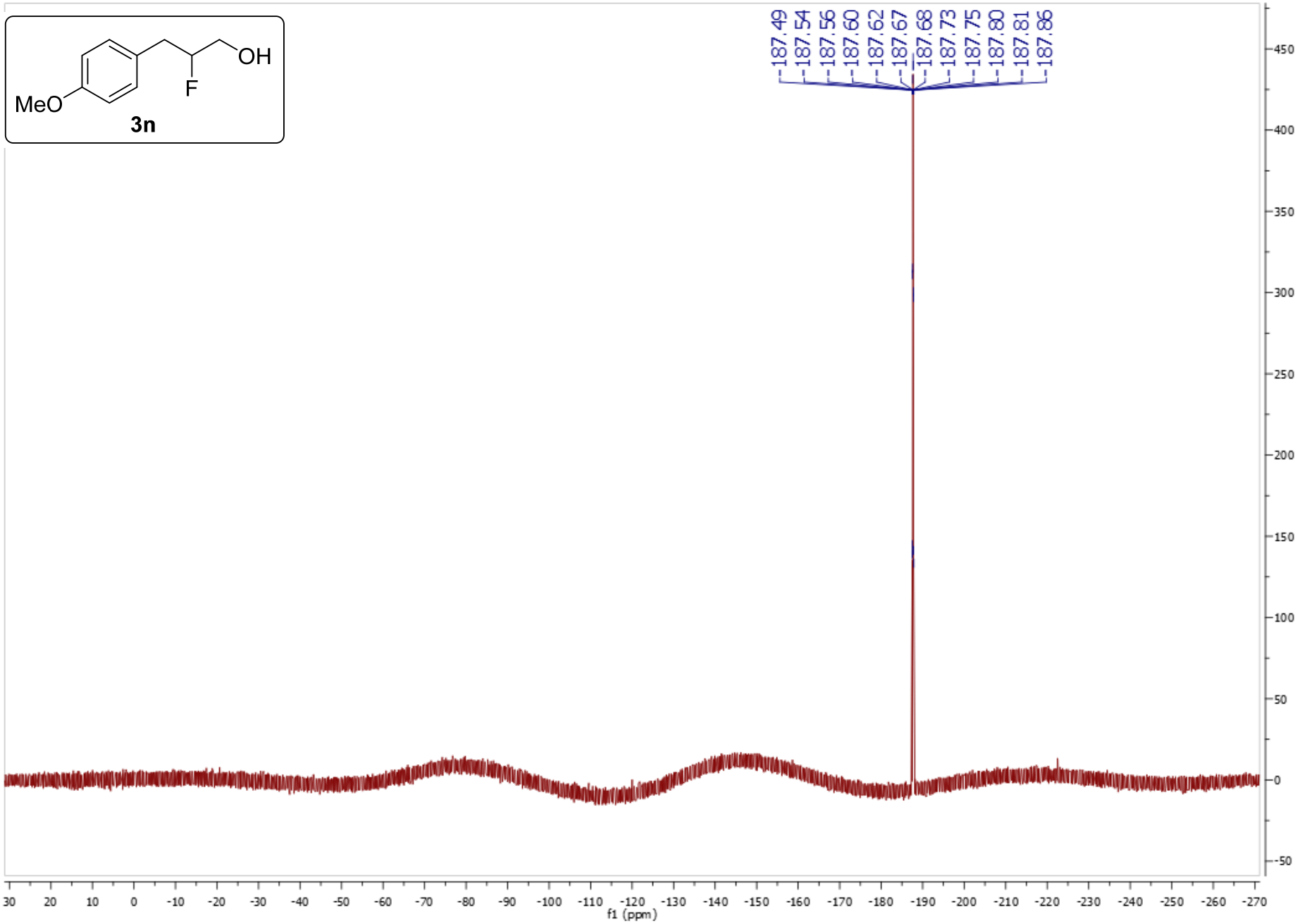

7.33
7.32
7.30
7.27
7.26
7.26
7.24
7.22
4.86
4.84
4.83
4.81
4.74
4.72
4.70
3.70
3.64
3.53
3.04
3.04
3.02
3.02
3.00
2.99
2.98
2.96
2.94
2.93
2.92
2.90
2.88
2.82
2.81
2.80
OH
F
3l
f1 (ppm)

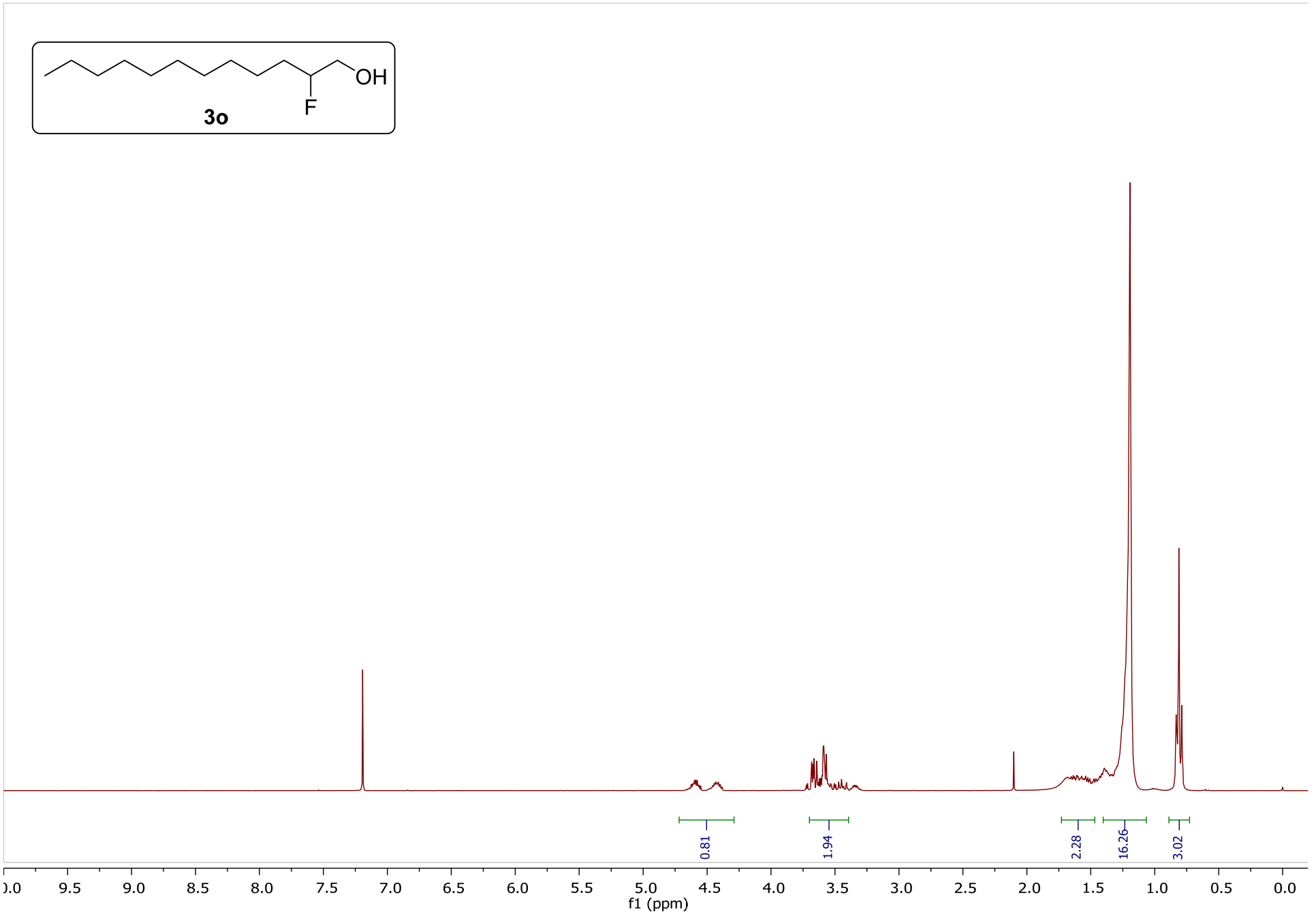

OH
F
3l
-187.51
-187.53
-187.58
-187.60
-187.64
-187.66
-187.71
-187.72
-187.77
-187.79
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

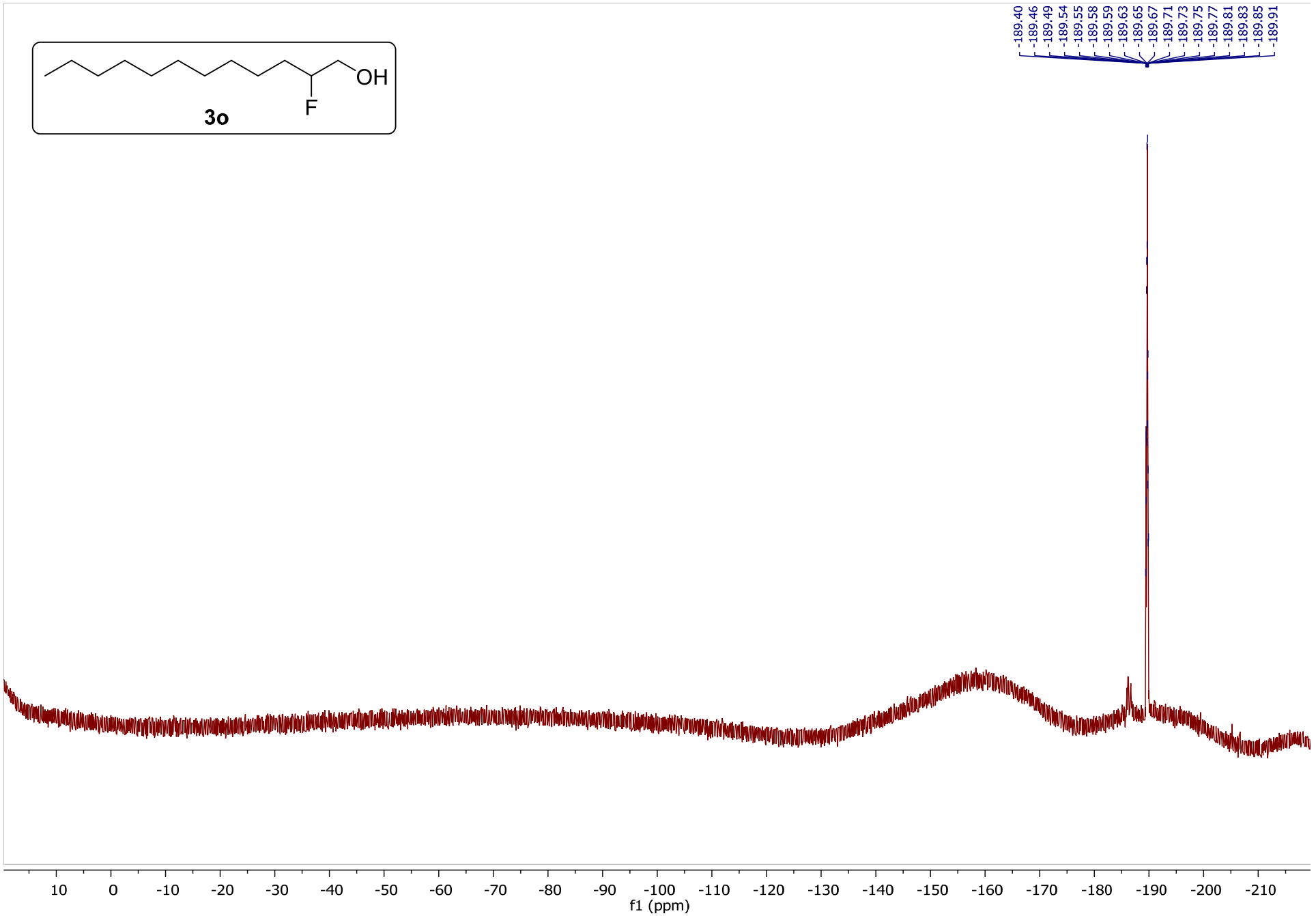

OH
F
F
3m
7.21
7.19
7.19
7.18
7.17
7.02
7.01
7.00
7.00
6.99
6.98
6.97
6.80
4.78
4.76
4.68
4.66
4.64
3.72
3.62
3.04
3.02
3.00
3.00
2.99
2.98
2.97
2.96
2.94
2.93
2.92
2.91
2.89
2.87
2.86
2.82
1.00
1.05
0.48
1.05
1.08
f1 (ppm)

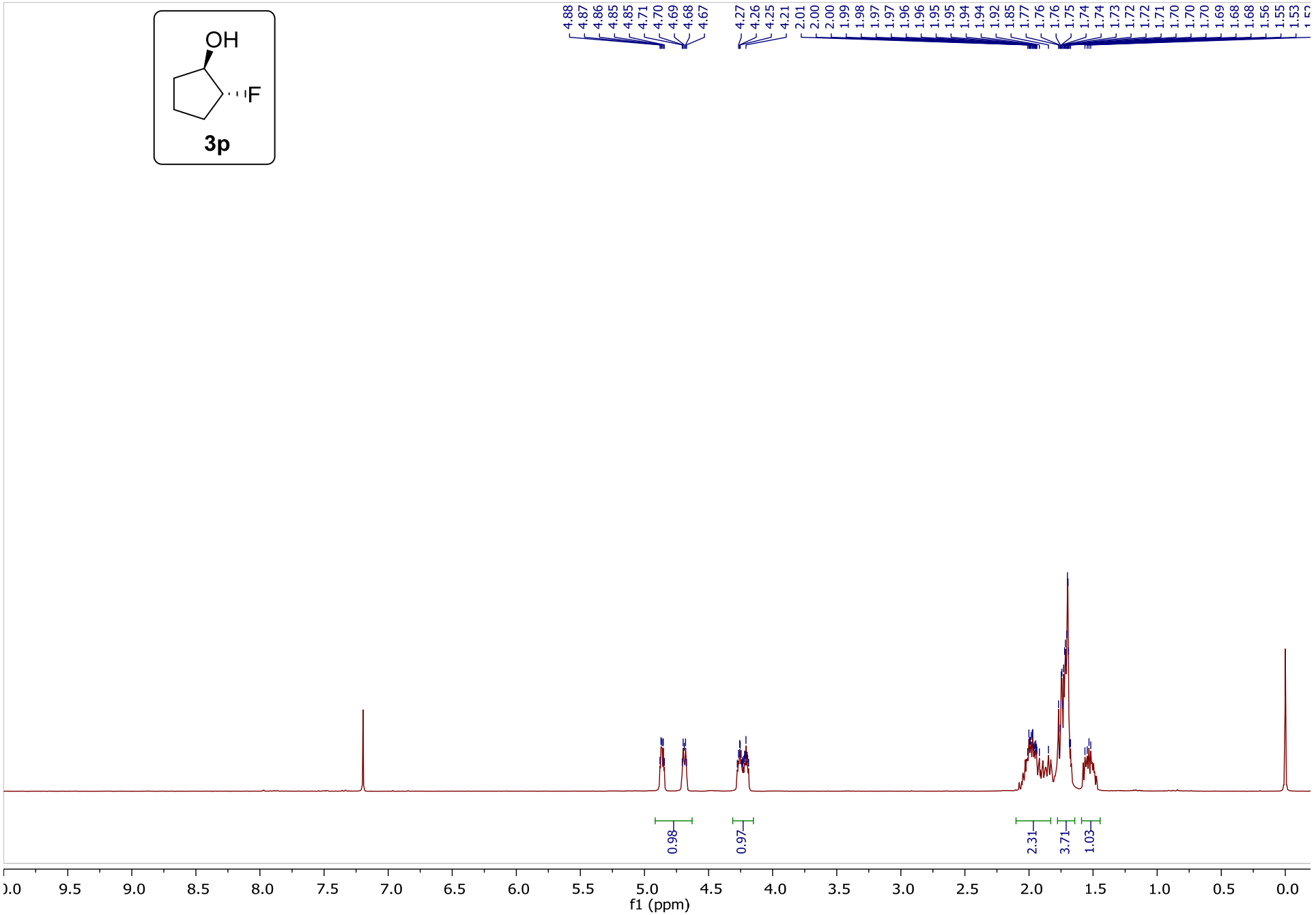

OH
F
F
3m
-116.21
-116.23
-116.24
-116.25
-116.26
-116.27
-116.29
-117.02
-188.04
-188.08
-188.10
-188.15
-188.17
-188.21
-188.23
-188.28
-188.30
-188.34
-188.36
-188.41
f1 (ppm)

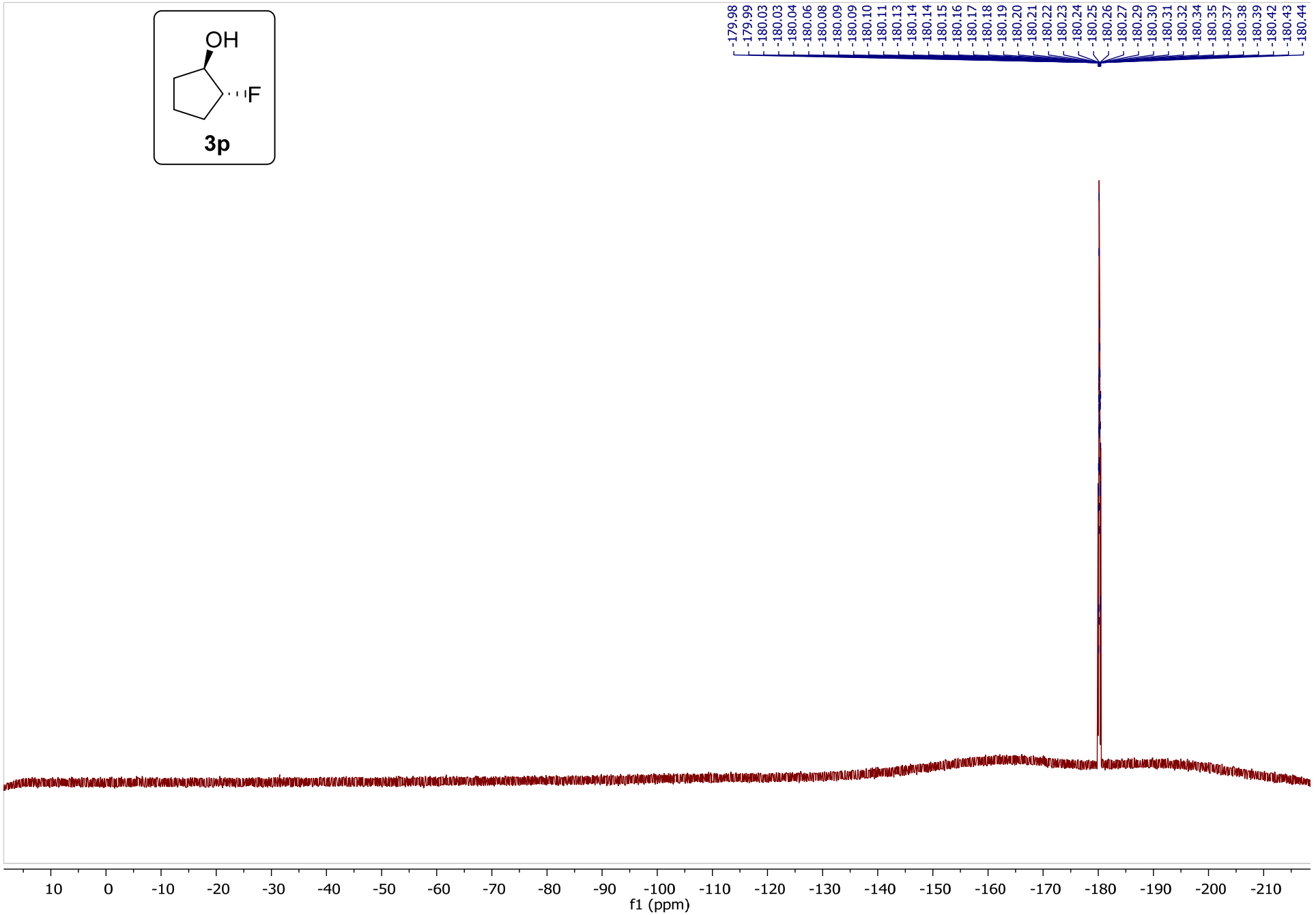

MeO
F
OH
3n
7.16
7.14
6.87
6.86
6.85
6.85
4.80
4.76
4.69
4.67
4.66
4.64
3.80
3.68
3.65
2.94
2.90
2.87
2.83
1.89
1.58
1.56
0.84
3.00
1.21
1.71
0.74
f1 (ppm)

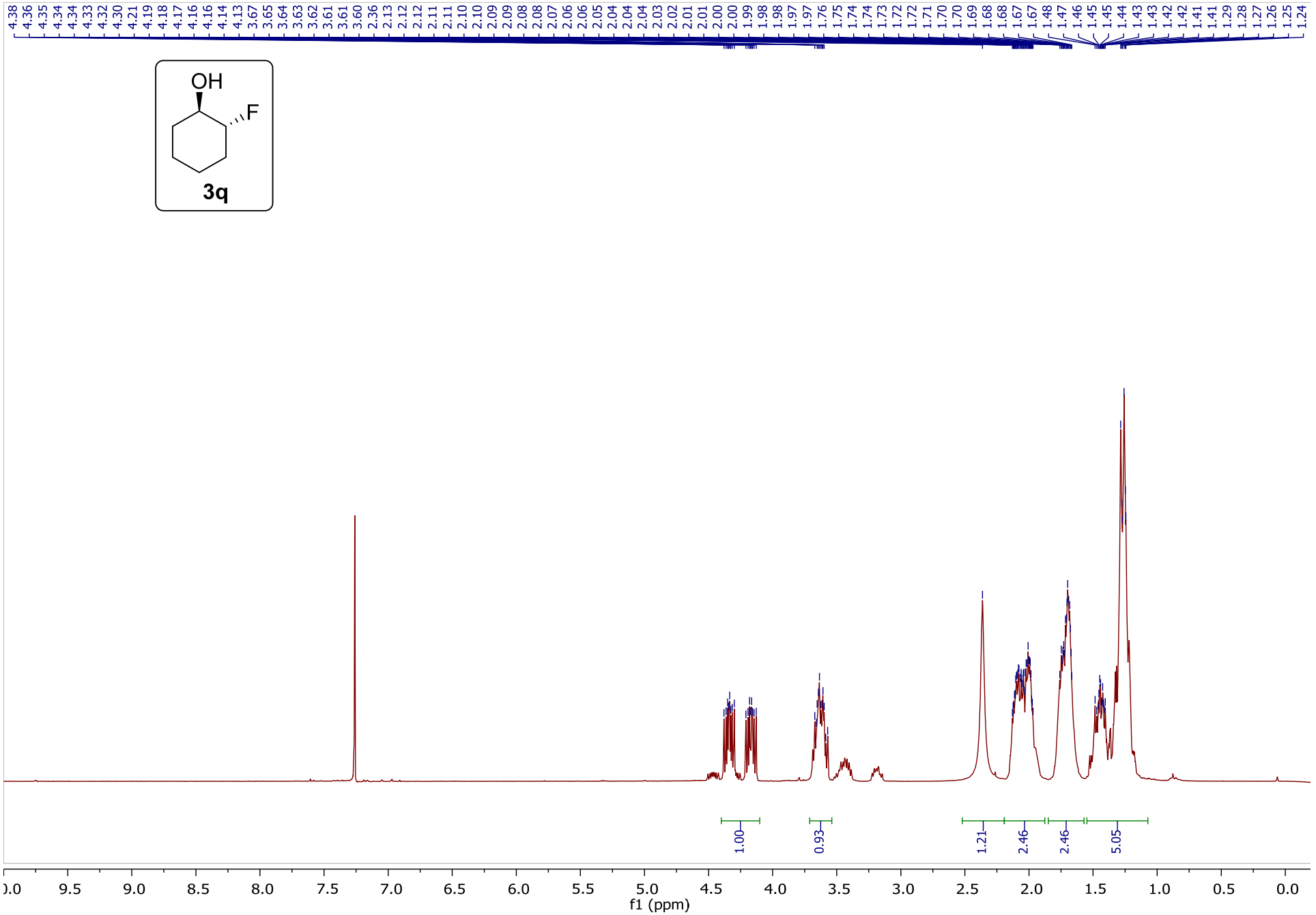

MeO
F
OH
3n
187.49
187.54
187.56
187.60
187.62
187.67
187.68
187.73
187.75
187.80
187.81
187.86
f1 (ppm)


OH
F
3o
0.81
1.94
2.28
16.26
3.02
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)


OH
F
3o
-189.40
-189.46
-189.49
-189.54
-189.55
-189.58
-189.59
-189.63
-189.65
-189.67
-189.71
-189.73
-189.75
-189.77
-189.81
-189.83
-189.85
-189.91
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

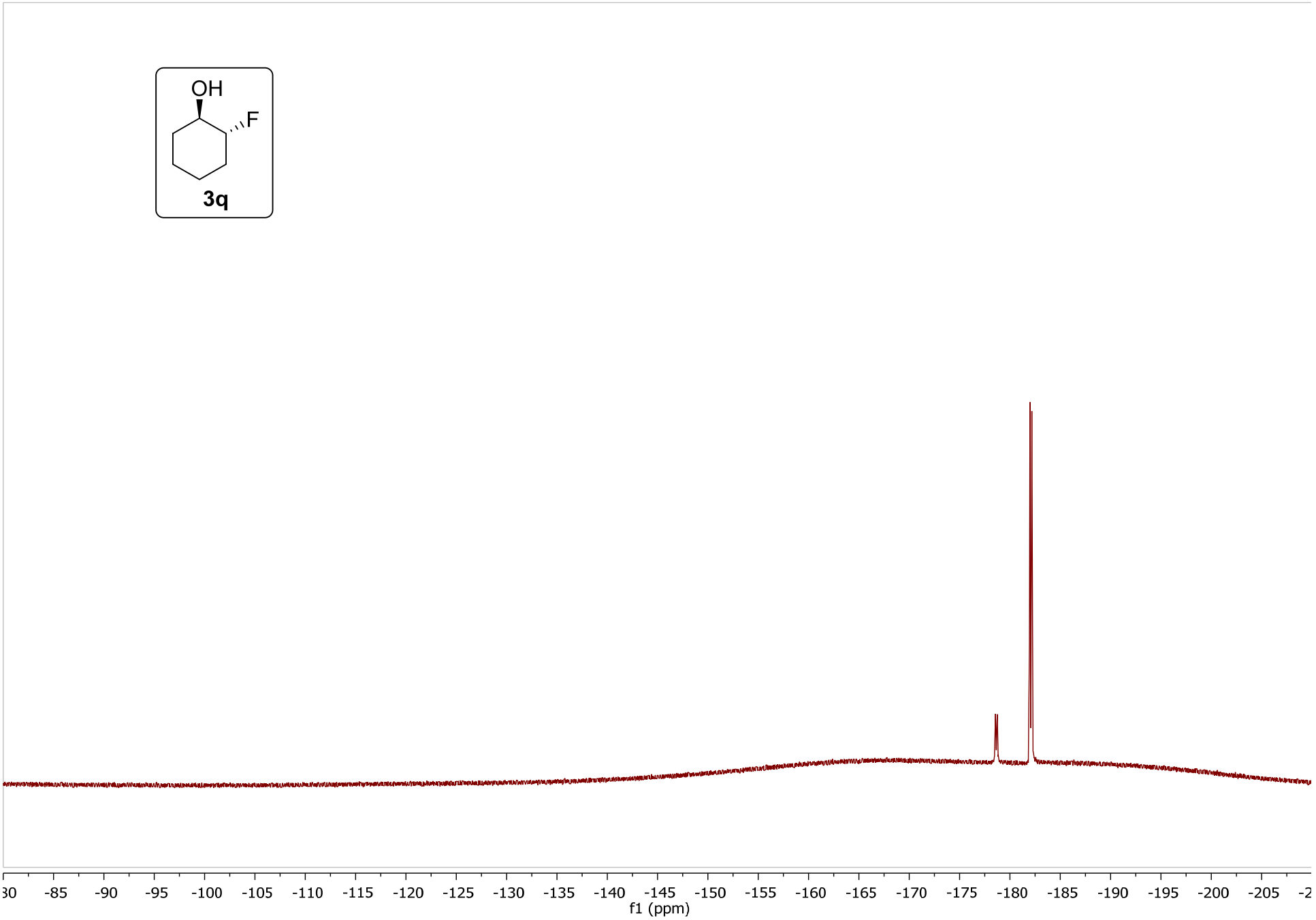

OH
F
3p
4.88
4.87
4.86
4.85
4.85
4.71
4.70
4.69
4.68
4.67
4.27
4.26
4.25
4.21
2.01
2.00
2.00
1.99
1.98
1.97
1.97
1.96
1.96
1.95
1.95
1.94
1.94
1.92
1.85
1.77
1.76
1.76
1.75
1.74
1.74
1.73
1.72
1.72
1.71
1.70
1.70
1.70
1.69
1.68
1.68
1.56
1.55
1.53
0.98
0.97
2.31
3.71
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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)

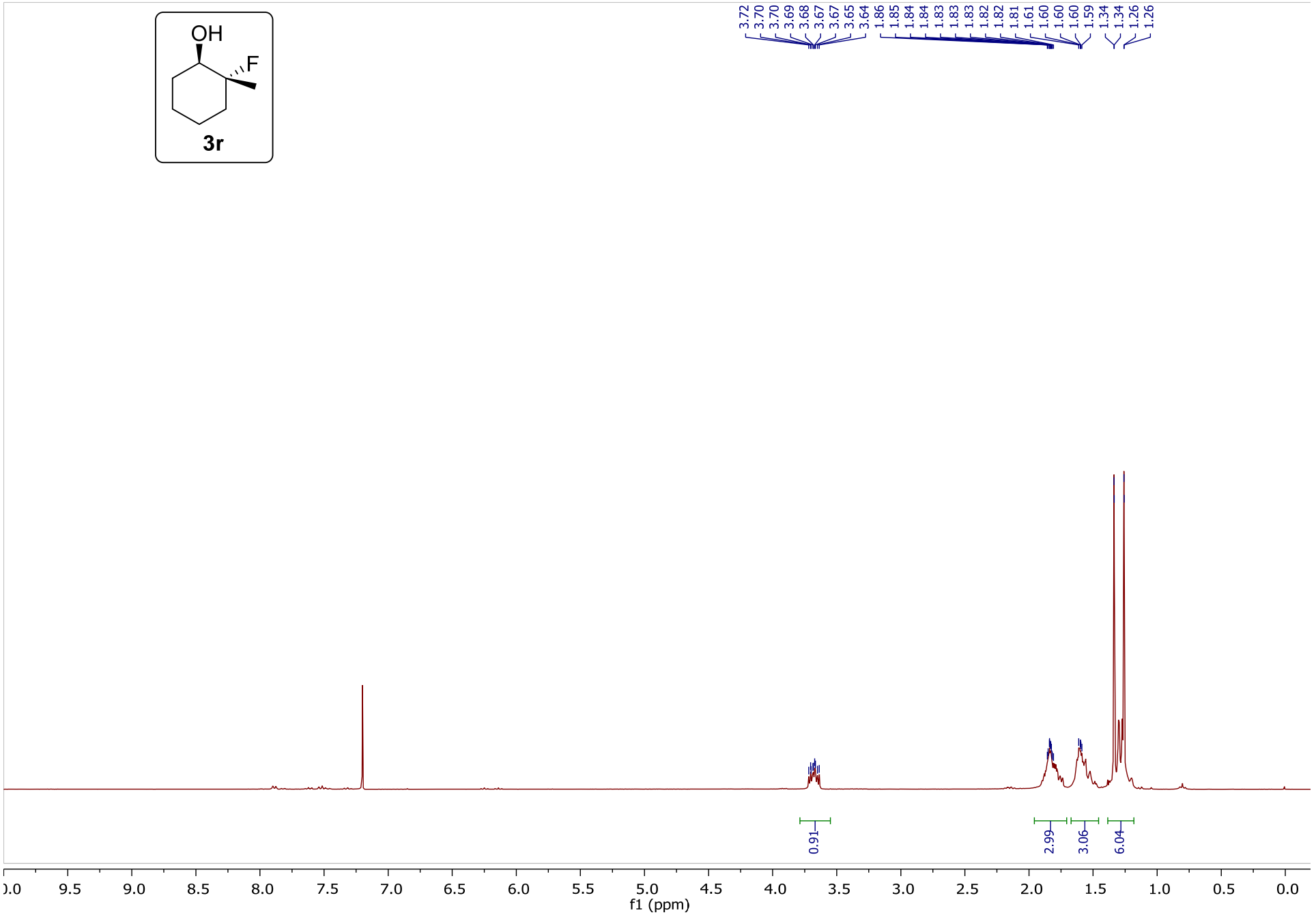

OH
F
3p
-179.98
-179.99
-180.03
-180.03
-180.04
-180.06
-180.08
-180.09
-180.09
-180.10
-180.11
-180.13
-180.14
-180.14
-180.15
-180.16
-180.17
-180.18
-180.19
-180.20
-180.21
-180.22
-180.23
-180.24
-180.25
-180.26
-180.27
-180.29
-180.30
-180.31
-180.32
-180.34
-180.35
-180.37
-180.38
-180.39
-180.42
-180.43
-180.44
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

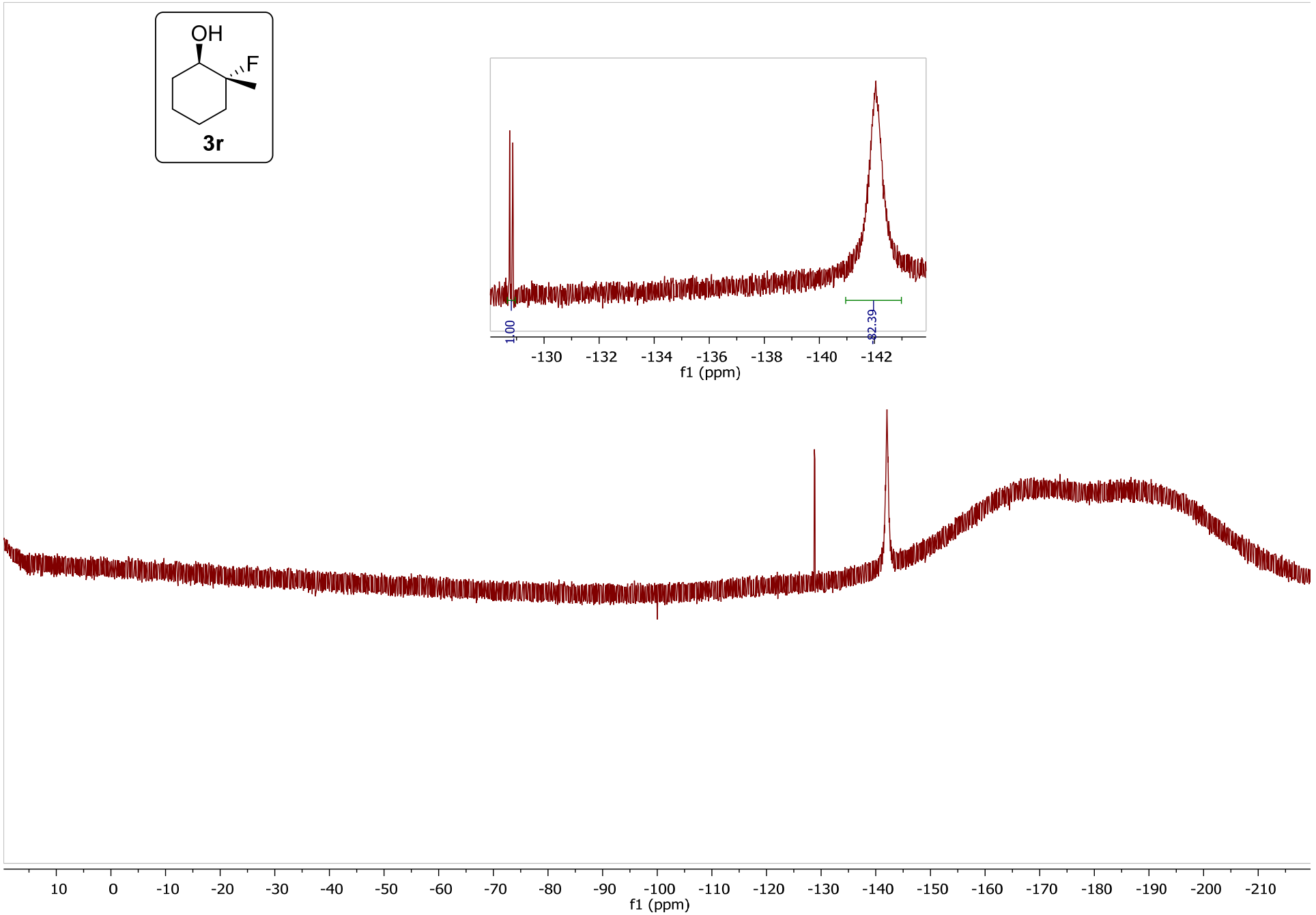

OH
F
3q
f1 (ppm)

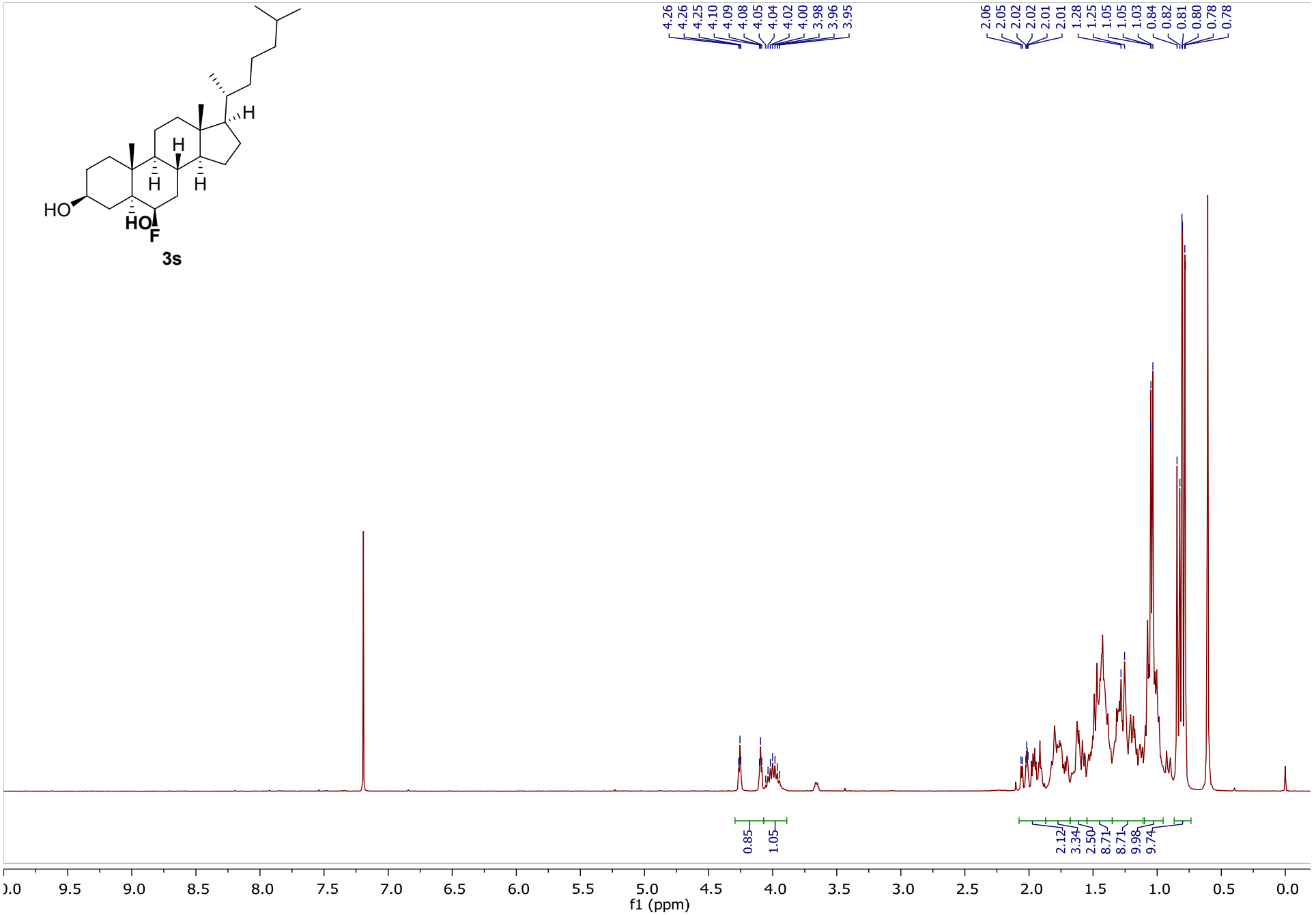
OH
F

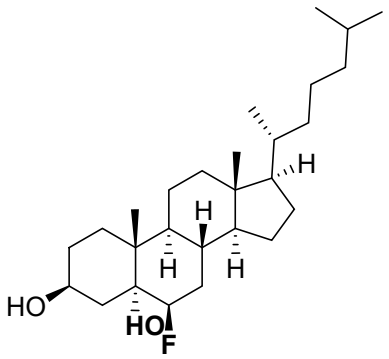
3q


-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
-205
f1 (ppm)


OH
F
3r
3.72
3.70
3.70
3.69
3.68
3.67
3.67
3.65
3.64
1.86
1.85
1.84
1.84
1.83
1.83
1.83
1.82
1.82
1.81
1.61
1.60
1.60
1.60
1.59
1.34
1.34
1.26
1.26
0.91
2.99
3.06
6.04
f1 (ppm)


OH
F
3r
1.00
82.39
-130
-132
-134
-136
-138
-140
-142
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


HO
HO
F
H
H
H
H
3s
4.26
4.26
4.25
4.10
4.09
4.08
4.05
4.04
4.02
4.00
3.98
3.96
3.95
2.06
2.05
2.02
2.02
2.01
2.01
1.28
1.25
1.05
1.05
1.03
0.84
0.82
0.81
0.80
0.78
0.78
0.85
1.05
2.12
3.34
2.50
8.71
9.98
9.74
f1 (ppm)



3s

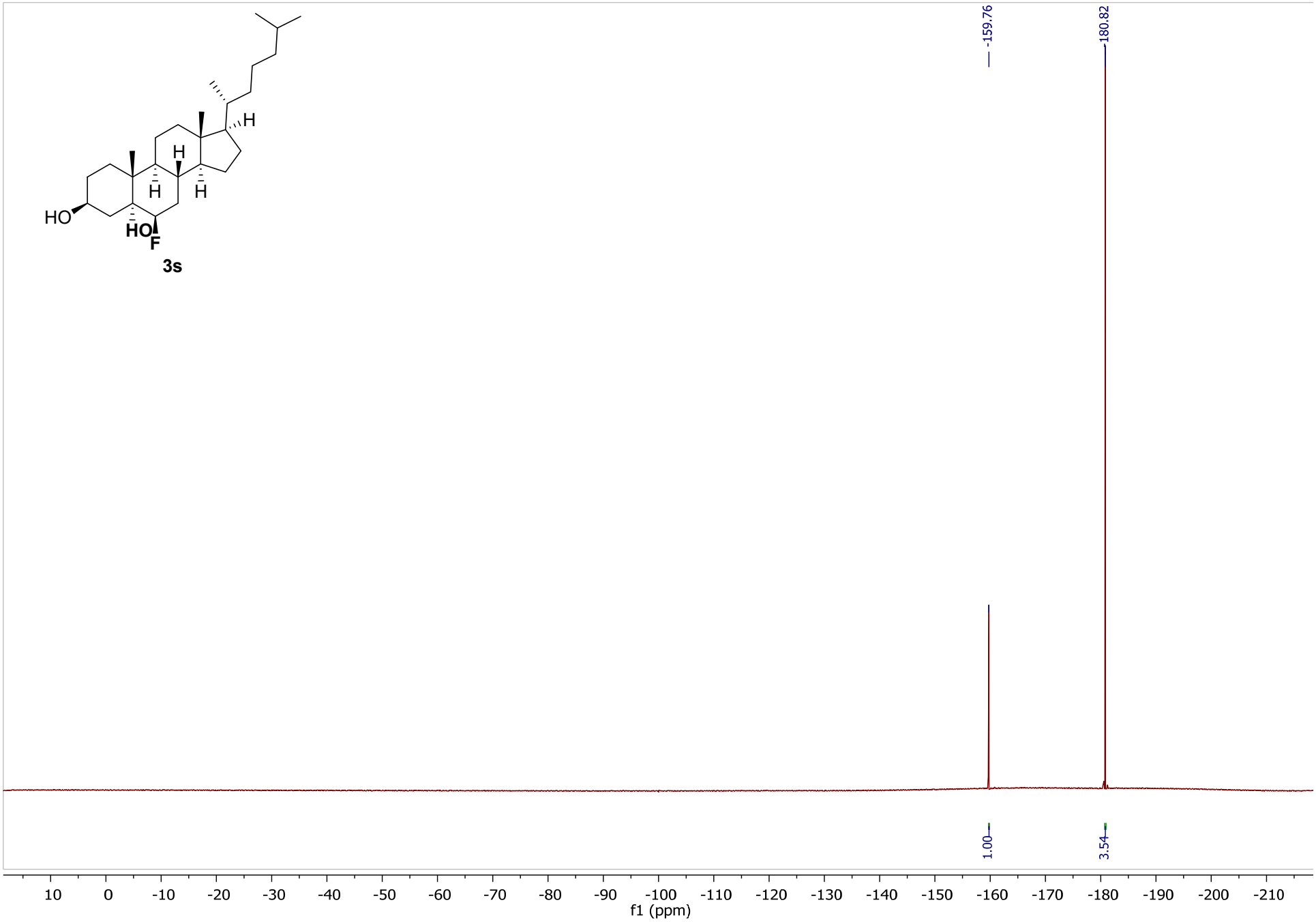
-180.62
-180.64
-180.68
-180.78
-180.79
-180.81
-180.83
-180.85
-180.86
-180.95
-180.97
-180.98
-181.01
-181.02

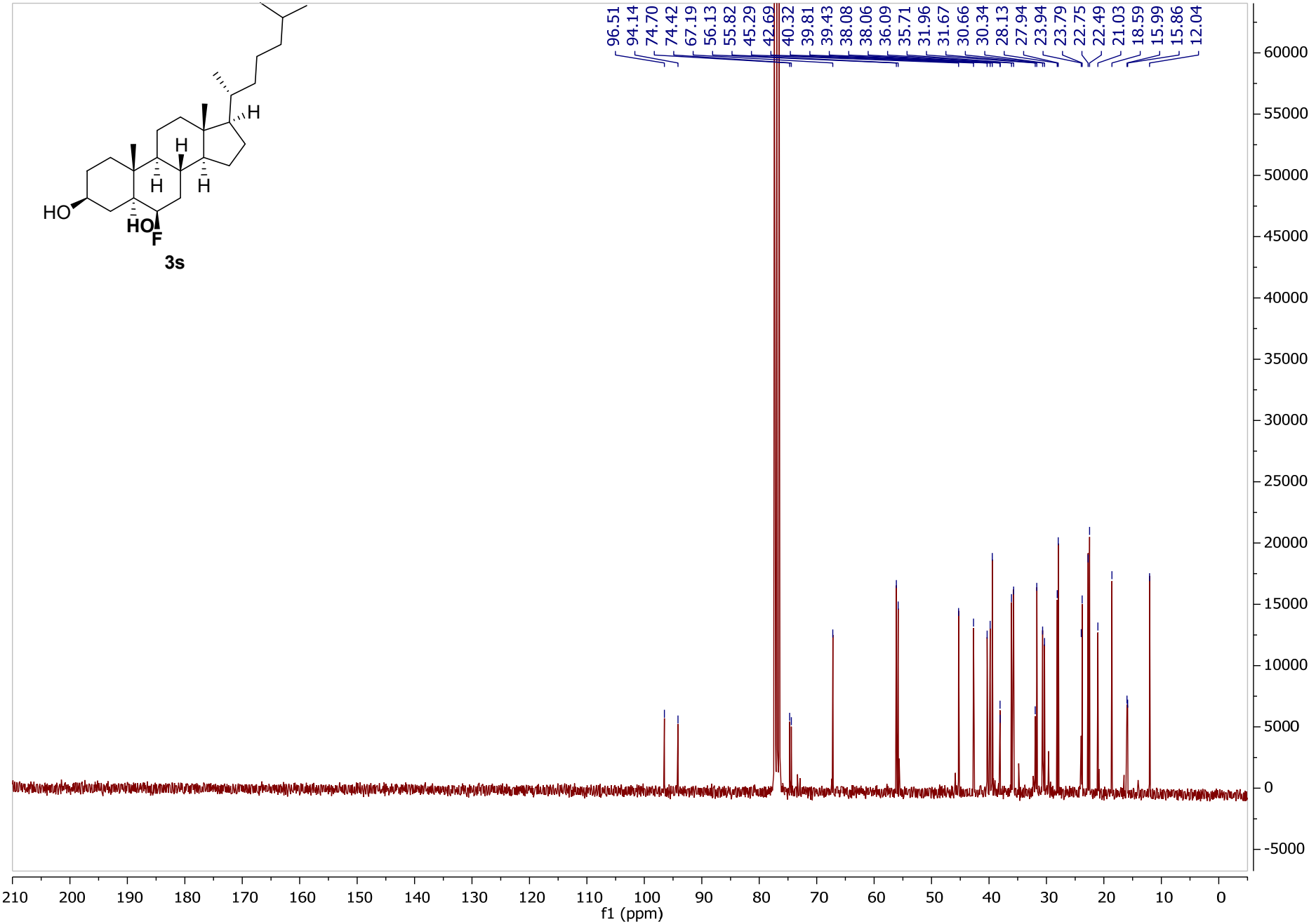
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

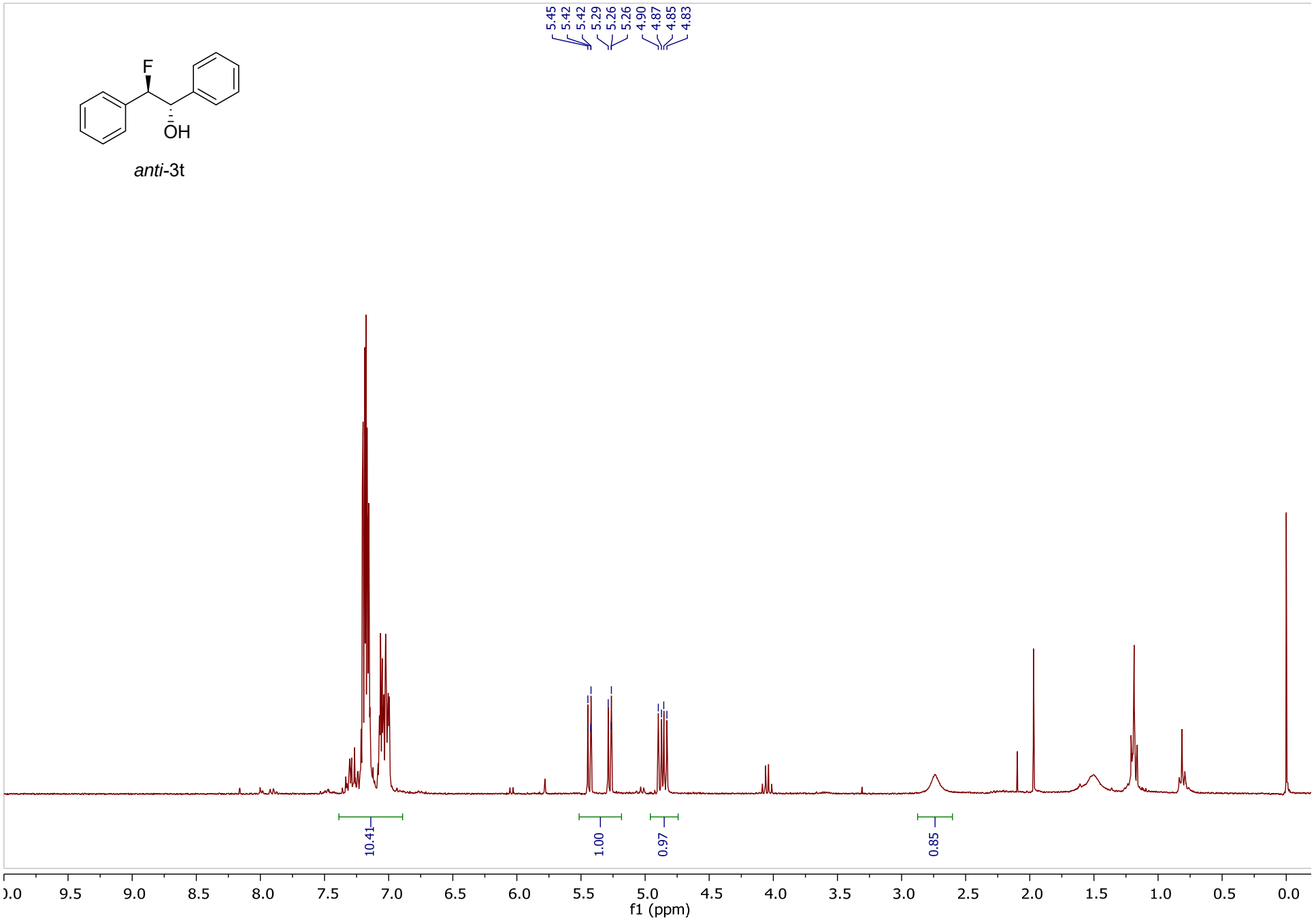
f1 (ppm)

HO
HO
F
H
H
H
H

3s

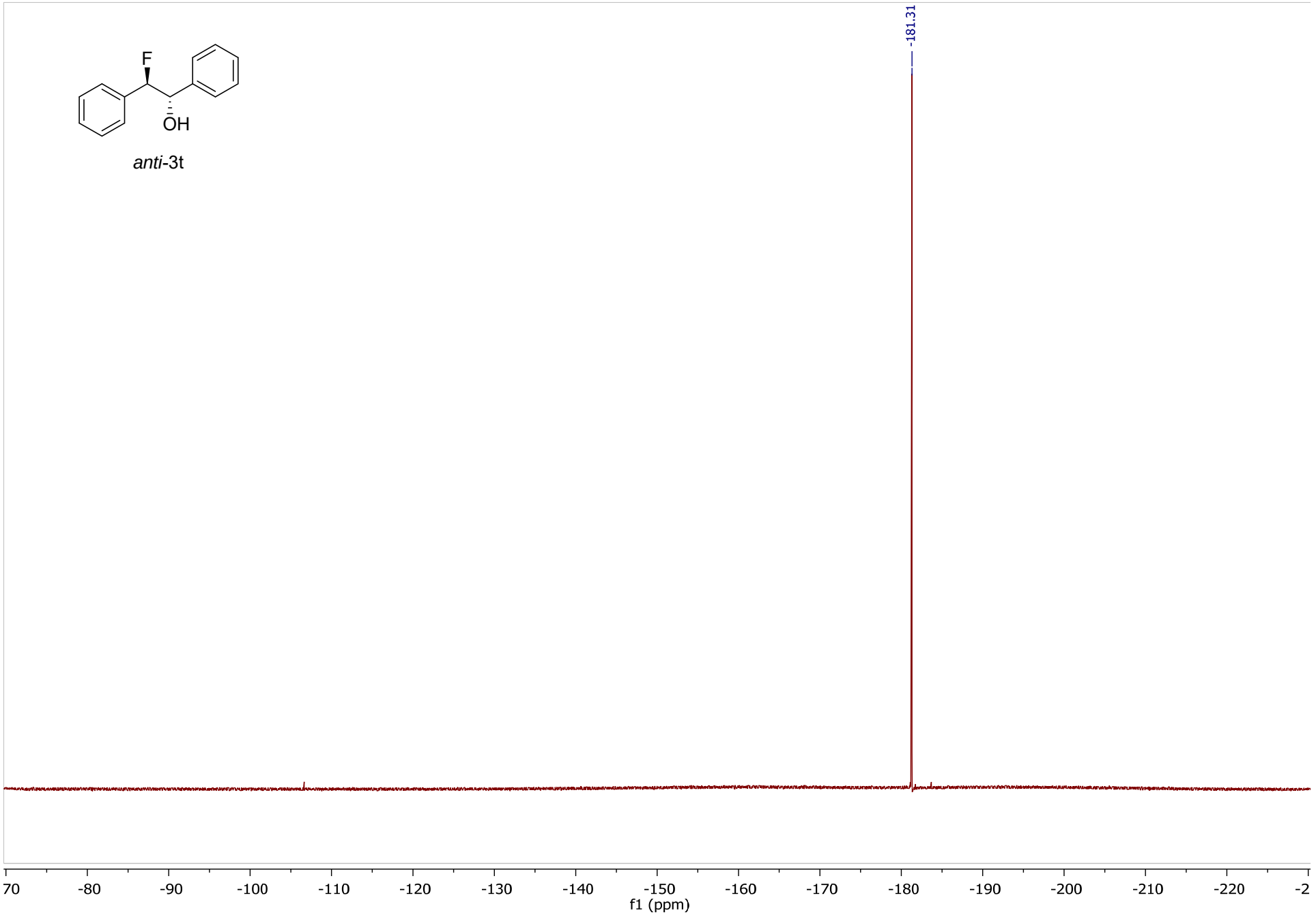

-159.76
180.82
1.00
3.54
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

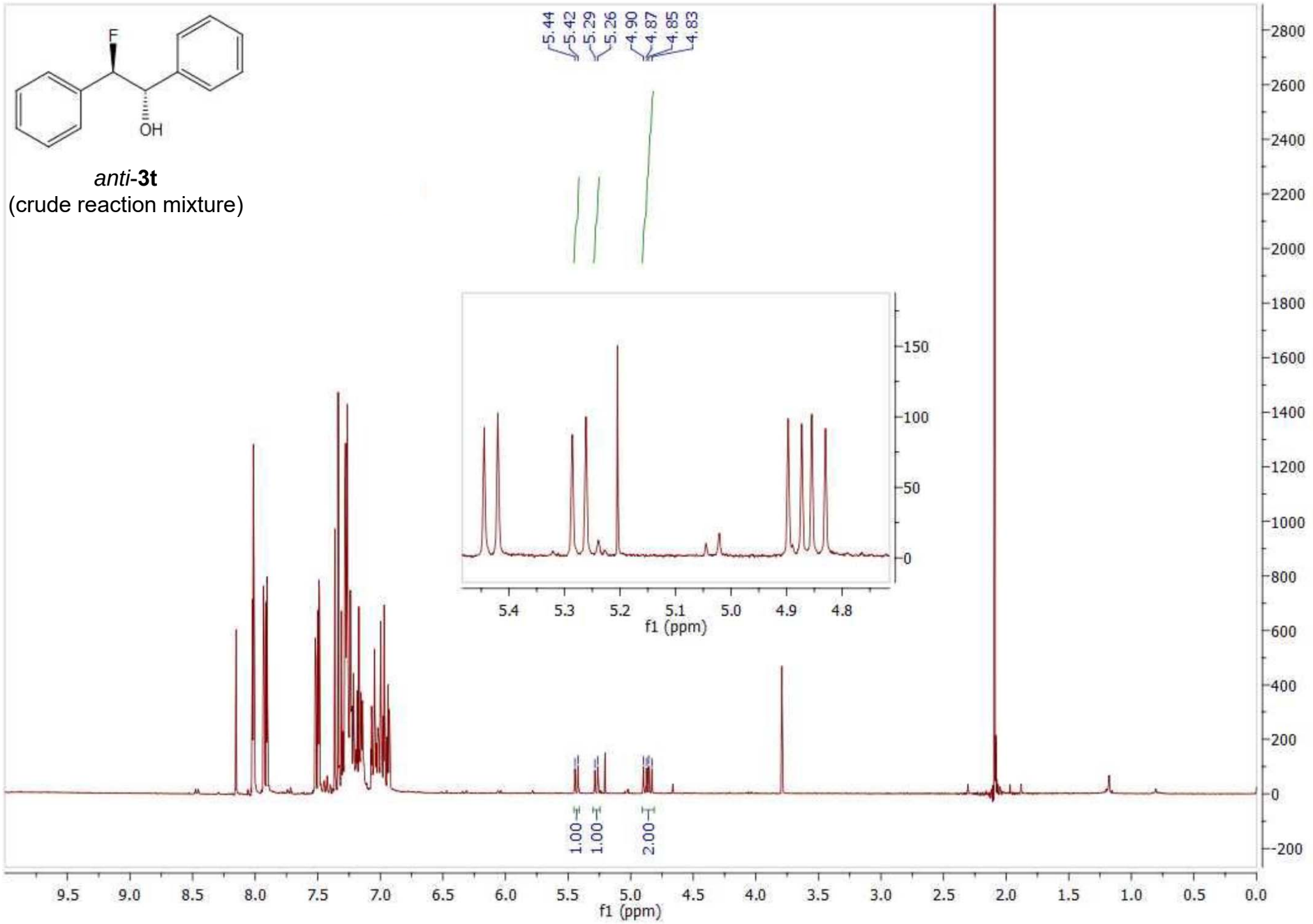

96.51
94.14
74.70
74.42
67.19
56.13
55.82
45.29
42.69
40.32
39.81
39.43
38.08
38.06
36.09
35.71
31.96
31.67
30.66
30.34
28.13
27.94
23.94
23.79
22.75
22.49
21.03
18.59
15.99
15.86
12.04
HO
HO
F
H
H
H
H
3s
f1 (ppm)


5.45
5.42
5.42
5.29
5.26
5.26
4.90
4.87
4.85
4.83
F
OH
anti-3t
10.41
1.00
0.97
0.85
f1 (ppm)

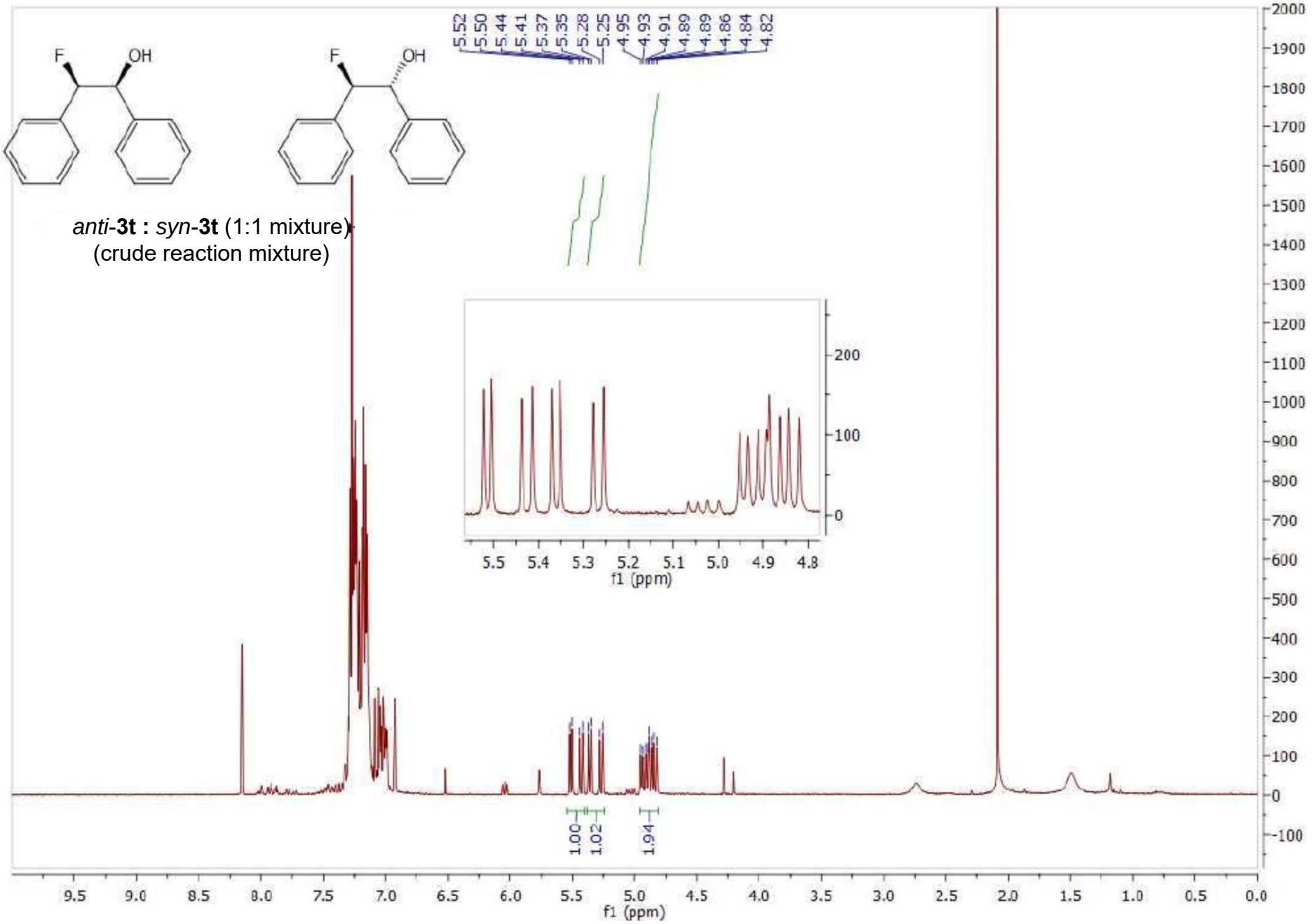
F
OH

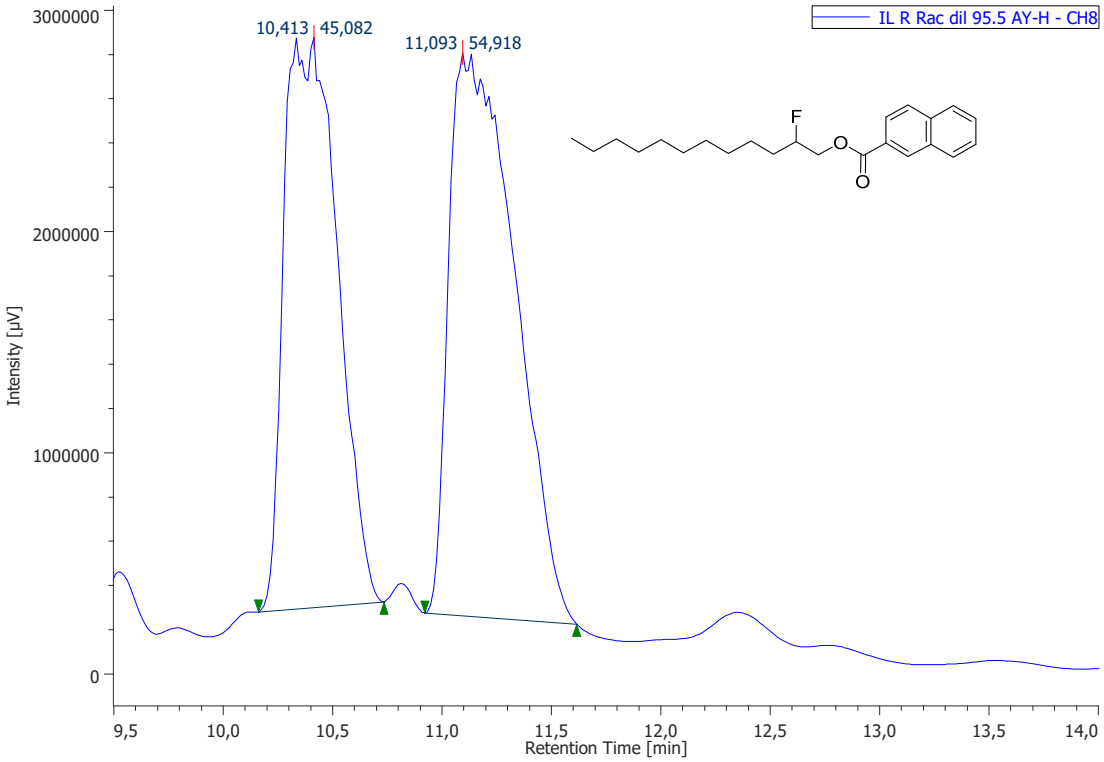
anti-3t

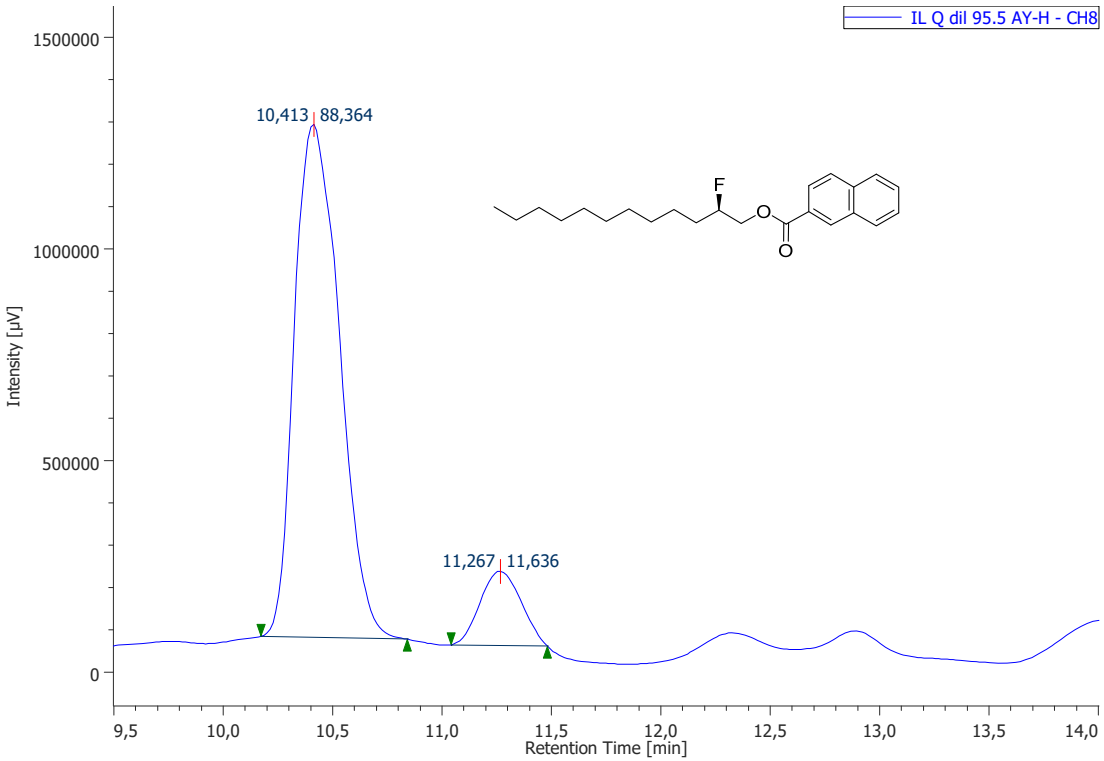

-181.31
70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-2
f1 (ppm)



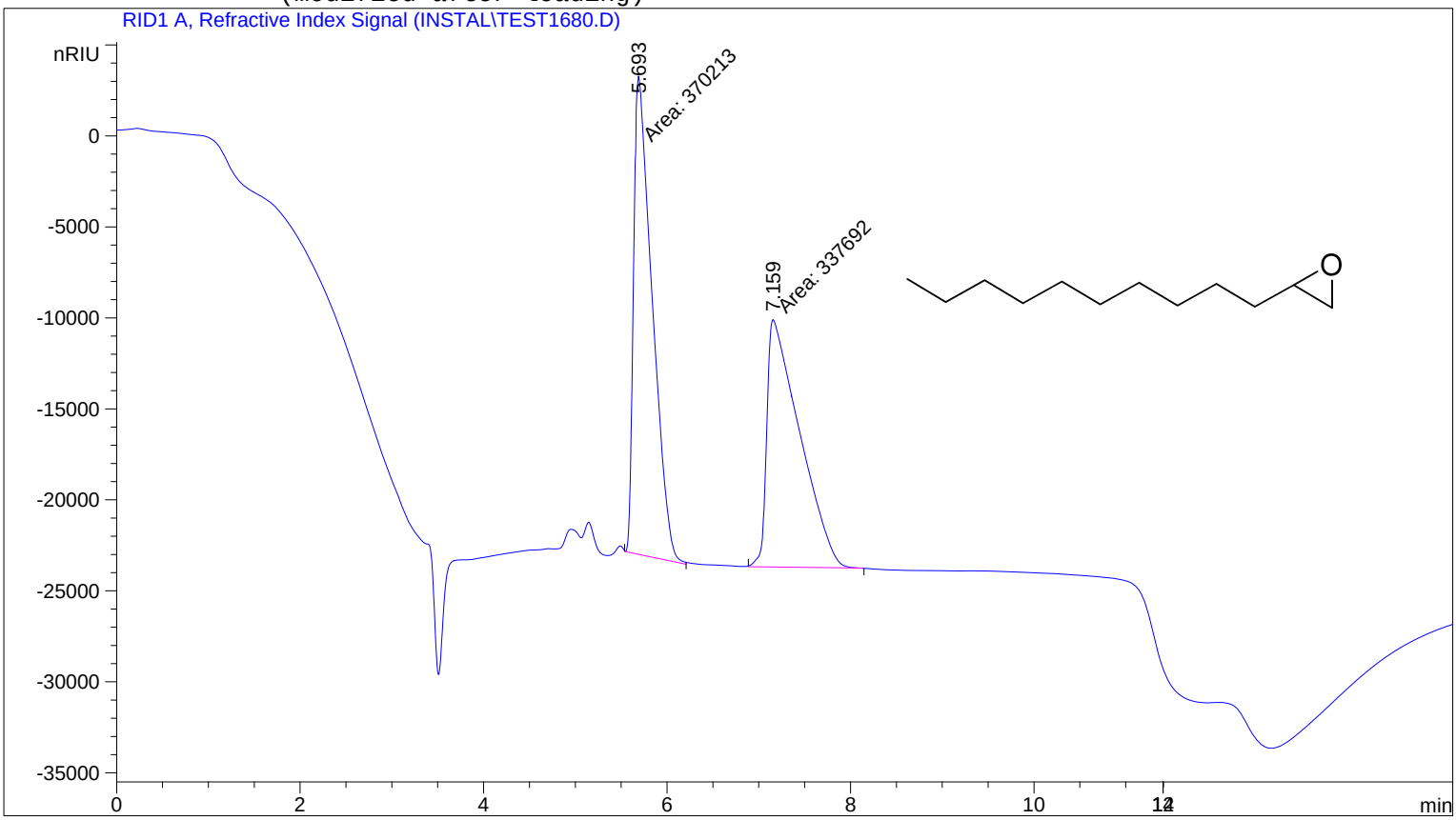
anti-**3t**
(crude reaction mixture)


F
OH
F
OH
5.52
5.50
5.44
5.41
5.37
5.35
5.28
5.25
4.95
4.93
4.91
4.89
4.89
4.86
4.84
4.82
anti-3t : syn-3t (1:1 mixture)
(crude reaction mixture)
f1 (ppm)
1.00
1.02
1.94
f1 (ppm)


IL R Rac dil 95.5 AY-H - CH8
10,413 45,082
11,093 54,918
F
O
O
Intensity [µV]
3000000
2000000
1000000
0
9,5
10,0
10,5
11,0
11,5
12,0
12,5
13,0
13,5
14,0
Retention Time [min]

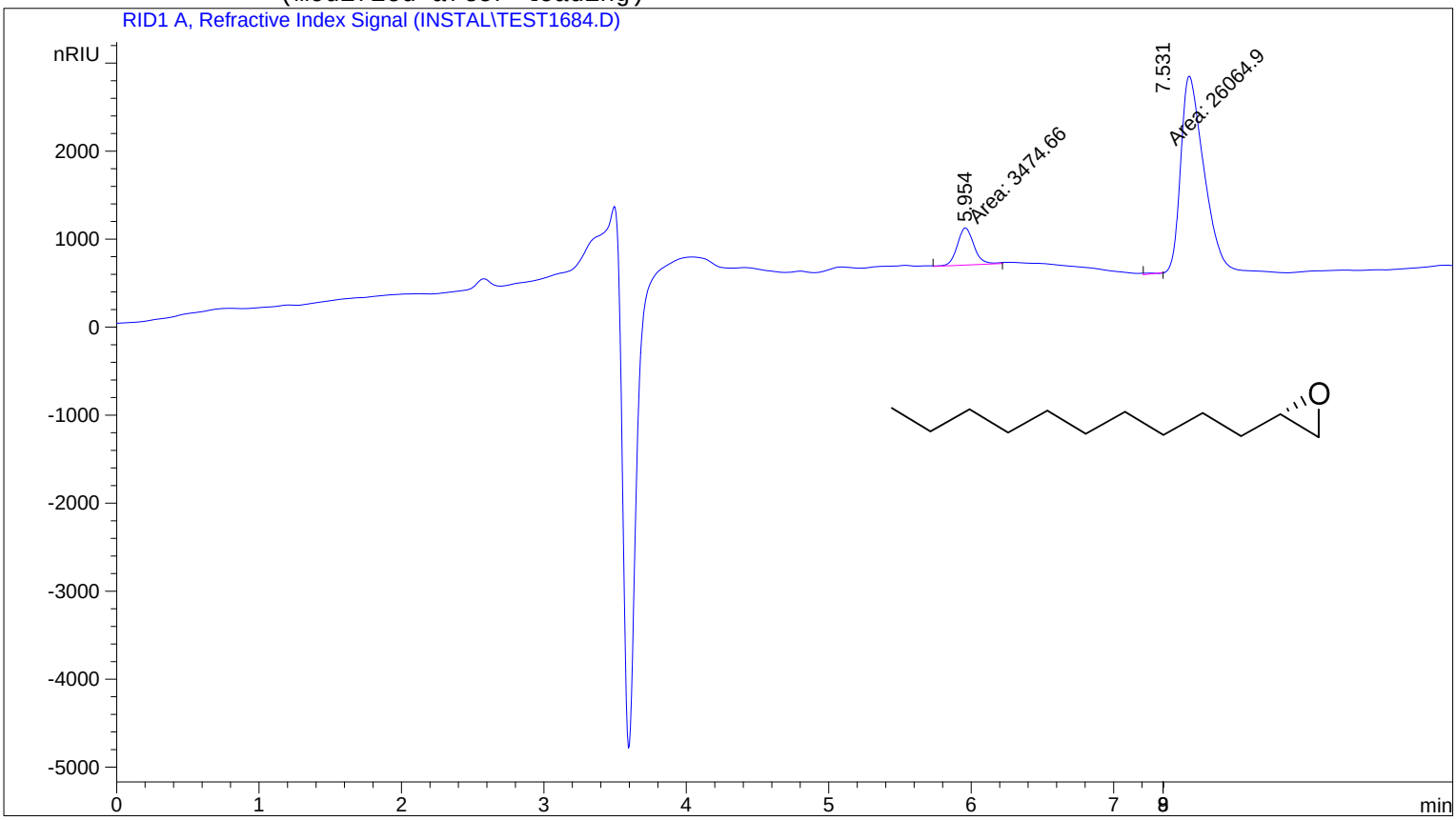

IL Q dil 95.5 AY-H - CH8
10,413 88,364
F
O
O
11,267 11,636
Intensity [µV]
1500000
1000000
500000
0
9,5
10,0
10,5
11,0
11,5
12,0
12,5
13,0
13,5
14,0
Retention Time [min]

```
==========================================================================
Injection Date  : 09/11/2017 17:04:59
Sample Name     : INES1                          Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC1.M
Last changed    : 09/11/2017 17:01:26
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC1.M
Last changed    : 09/11/2017 17:49:53
                  (modified after loading)
```




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

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


Signal 1: RID1 A, Refractive Index Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  [nRIU*s]    [nRIU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.693 MM    0.2326 3.70213e5  2.65251e4   52.2969
   2   7.159 MM    0.4100 3.37692e5  1.37262e4   47.7031

Totals :                  7.07905e5  4.02513e4

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
==========================================================================
Injection Date  : 09/11/2017 18:36:09
Sample Name     : INES1                          Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC1.M
Last changed    : 09/11/2017 18:15:04
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC1.M
Last changed    : 09/11/2017 18:52:07
                  (modified after loading)
```




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

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


Signal 1: RID1 A, Refractive Index Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  [nRIU*s]    [nRIU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.954 MM T  0.1743 3474.66431  421.96310  11.7627
   2   7.531 MM    0.1926 2.60649e4  2255.26758  88.2373

Totals :                  2.95396e4  2677.23068

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```