Electronic Supplementary Information

for

Efficient Direct 2,2,2-Trifluoroethylation of Indoles via C-H Functionalization

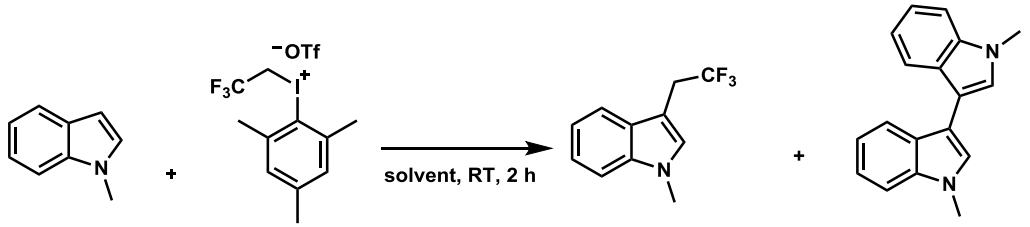
Gergely L. Tolnai, Anna Székely, Zita Makó, Tamás Gáti, János Daru, Tamás Bihari, András Stirling, Zoltán Novák

Content

1. Optimization of trifluoroethylation reaction

1.1. Solvent-optimization using 1-methyl-1-*H*-indole

1-methyl-1*H*-indole (0.1 mmol) was measured into a 4 mL vial, then solvent (0.5 mL) was added. 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (0.1 mmol) was added to the solution, then the reaction was stirred at room temperature for 2 hours. Sample was taken and GC conversion was determined.

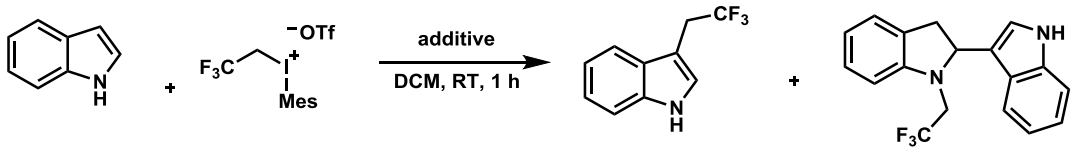


Solvent	GC conversion of SM	Ratio of a:b
acetone	20%	100:1
toluene	84%	1:1
chloroform	90%	3:2
THF	97%	2:1
EtOAc	71%	34:10
DCE	95%	100:1
DCM	100%	100:1

Table 1 *– Optimization of solvents*

1.2. Base-optimization reactions using 1-*H*-indole

1-*H*-indole (0.5 mmol) was measured into a 4 mL vial, then base (1.0 mmol) and dichloromethane (2.5 mL) was added. 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (0.5 mmol) was added to the mixture and the reaction was stirred at room temperature for 1 hour. The reaction was transferred to a separation funnel using ethyl acetate (20 mL) and washed with distilled water (20 mL). The aqueous phase was extracted with ethyl acetate (2×20 mL). The combined organic phases were washed with distilled water (3×20 mL), then dried on $MgSO_4$. The solvent was evaporated under reduced pressure. The mixture was purified by column chromatography using hexanes: ethyl acetate on SiO_2. The ratio of the products was determined by ^{19}F NMR spectra.



117.15
1.0 equiv

478.19
1.0 equiv

199.18
a

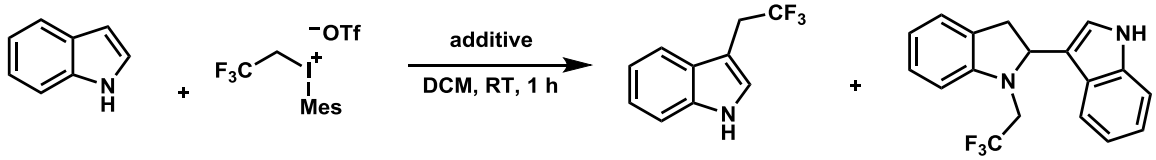
316.32
b

Additive (2 equiv)	Ratio of a:b[a]	Yield
-	2:1	70%
NaH	10:1	70%
Na_2CO_3	10:1	61%
Na_2CO_3, H_2O (5 v/v%)	10:1	73%
pivalic acid	10:4	61%
2,6-di-^{t}Bu-pyridine	100:1	79%

Table 2: *Application of different additives in trifluoroethylation reaction*
[a] determined by ^{19}F NMR

1.3. Effect of inorganic bases on the reaction

1-*H*-indole (0.1 mmol) was measured into a 4 mL vial, then base (0.2 mmol) and dichloromethane (0.5 mL) was added. 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (0.1 mmol) was added to the mixture and the reaction was stirred at room temperature for 1 hour, when the reaction was completed. Sample was taken and ratio of the products was obtained by ^{19}F NMR spectra.



117.15
1.0 equiv

478.19
1.0 equiv

199.18
a

316.32
b

Inorganic base (2 equiv)	Ratio of a:b[a]
NaO^{t}Bu	10:1
Cs_2CO_3	10:4
NaOH	20:1
K_3PO_4	20:1

Table 2: *Further tests for the inorganic bases, [a] determined by ^{19}F NMR*

1.4. Effect of organic bases on the reaction

1-*H*-indole (0.1 mmol) was measured into a 4 mL vial, then base (0.2 mmol) and dichloromethane (0.5 mL) was added. 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (0.1 mmol) was added to the mixture and the reaction was stirred at room temperature for 1 hour. Sample was taken and GC yield was calculated.

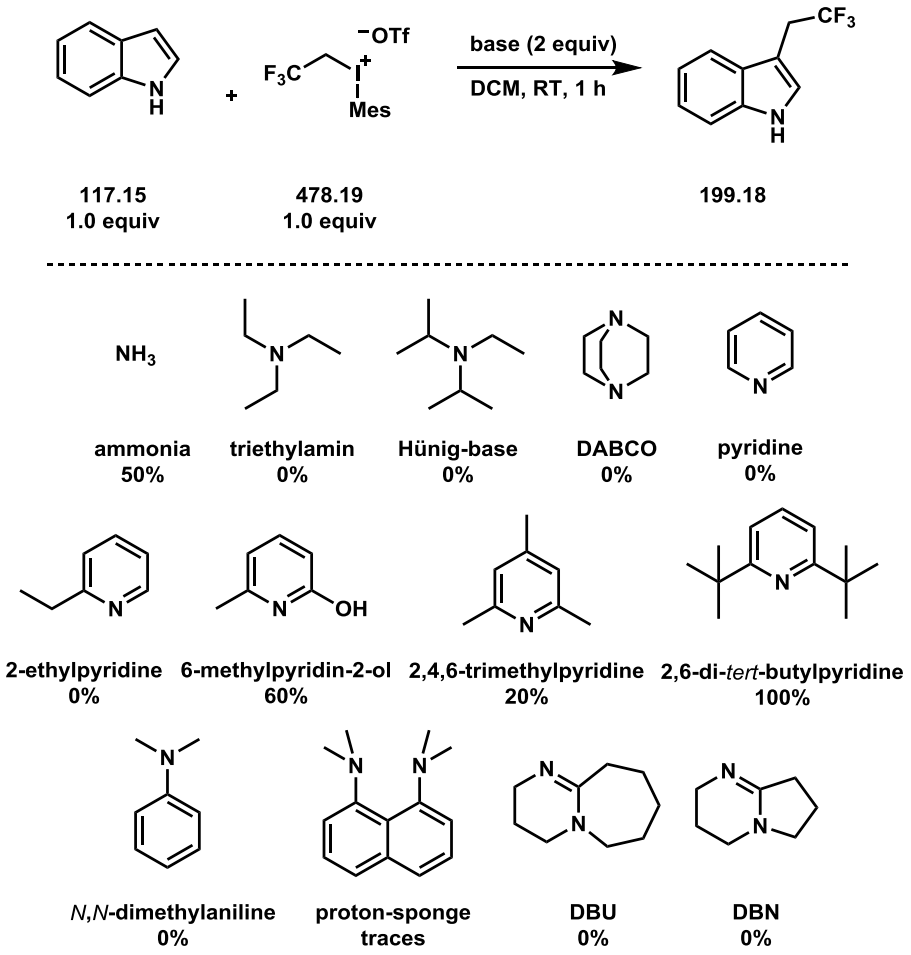
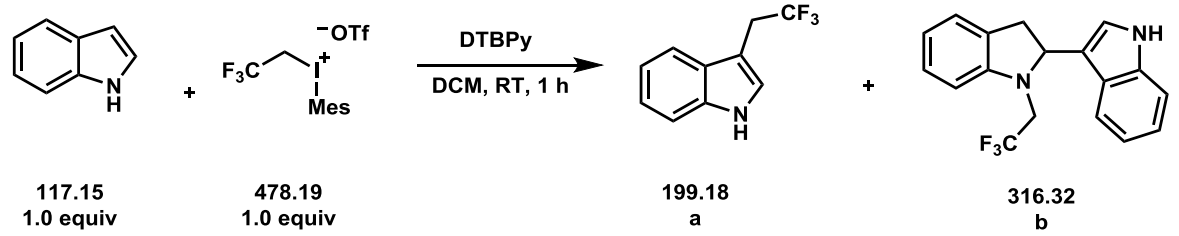


Figure 1 *– Bases and conversion of the reaction*

1.5. Optimizing the quantity of DTBPy

1-*H*-indole (0.1 mmol) was measured into a 4 mL vial, then diterc butylpyridine (x mmol) and dichloromethane (0.5 mL) was added. 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (0.1 mmol) was added to the mixture and the reaction was stirred at room temperature for 1 hour, when the reaction was completed. Sample was taken and GC yield was calculated. The ratio of the products was obtained by ^{19}F NMR spectra.



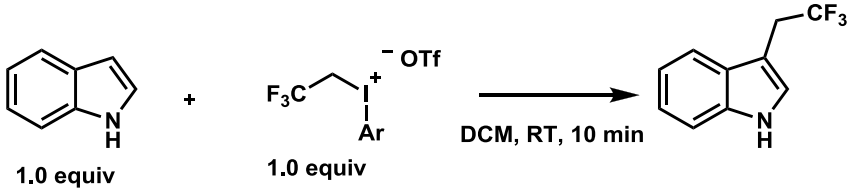
Base (equiv)	Ratio of a:b
1.0	10:1
1.5	10:1
2.0	100:1

Table 4: *Effect of the quantity of DTBPy on the selectivity of the reaction*

After optimizing the quantity of the base, we examined the quantity of the iodonium salt. When 1.0 equivalent of iodonium salt was applied 79% yield was reached. 1.3 equivalent iodonium salt provided the product in 84% yield, so it was accepted as the optimal quantity.

1.6. Study of reactivity of different aryltrifluoroethyliodonium salts

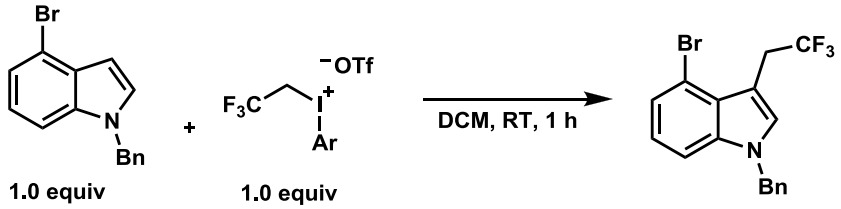
1-*H*-indole (0.1 mmol) was measured into a 4 mL vial and dichloromethane (0.5 mL) was added. 2,2,2-trifluoroethyl(aryl)iodonium trifluoromethanesulfonate (0.1 mmol) was added to the mixture and the reaction was stirred at room temperature for 10 minutes. Sample was taken and GC yield was calculated as well as ^{19}F NMR yield.



-Ar group	Yield	
	GC	^{19}F NMR
-*p*-tolyl	52%	35%
-phenyl	56%	42%
-mesityl	59%	45%

Table 5*: Yield of the reaction using different iodonium salts*

4-bromo-1-benyzlindole (0.1 mmol) was measured into a 4 mL vial and dichloromethane (0.5 mL) was added. 2,2,2-trifluoroethyl(aryl)iodonium trifluoromethanesulfonate (0.1 mmol) was added to the mixture and the reaction was stirred at room temperature for 1 hour. Sample was taken and GC yield was calculated as well as ^{19}F NMR yield.



-Ar group	**Yield**	
	GC	^{19}F NMR
-*p*-tolyl	28%	35%
-phenyl	34%	42%
-mesityl	39%	48%

Table 6: *Conversion of the reaction with different iodonium salts*

2. Computational details

2.1. Applied methods

The calculations have been performed employing the ωB97X-D range-separated hybrid exchange-correlation functional. The combination of the LanL2DZ basis set with additional polarization and diffuse functions from aug-cc-pVDZ-PP for iodine and the 6-31+G* basis set for all other elements (B_1) have been used for all geometry optimizations and frequency calculations. Single point SMD (DCM) solvated electronic energies have been calculated for the optimized structures with basis set B_2: LanL2TZ(f) with additional set of polarization and diffuse functions from the aug-cc-pVTZ-PP for iodine and 6-311++G(3df,3pd) basis set for all but iodine atoms. The ωB97X-D and similar hybrid, dispersion corrected functionals together with the same basis set or other basis sets of similar sizes have been already used successfully to explore reaction mechanisms for various coupling reactions[1]. The optimized intermediates and transition states (TSs) have also been tested by frequency calculations. Additional IRC and normal optimization calculations have also been carried out to prove that the calculated TSs connect the corresponding minima. All solvent-corrected Gibbs free energies have been calculated by the following approach:

$$\Delta G_{solv} = \Delta G_{virt}^{B_1} + E_{SMD}^{B_2} ,$$

where $\Delta G_{virt}^{B_1}$ is the vibrational, rotational, translational thermal correction to Gibbs free energy (harmonic oscillator, rigid rotor, ideal gas approximation) at 25 °C and 1 mol·dm^{-3} concentration using basis set B_1. $E_{SMD}^{B_2}$ is the electronic energy calculated with SMD implicit continuum solvation model, applying Dichloromethane as solvent and basis set B_2. The basis set B_1 was used for all geometry optimizations. The free energy and solvent corrections were computed at the optimal geometries. Ultrafine grid has been employed for all calculations. All calculations have been performed by using the Gaussian 09 package[2].

[1] C. Trujillo, G. Sánchez-Sanz, Karpavičienė, U. Jahn, I. Čikotienė, L. Rulišek, *Chem. Eur. J.* **2014**, *20*, 10360-10370.; P. K. Saith, C. H. Suresh, *Inorg. Chem.*, **2013**, *52*, 6046-6054.; C. Schnaars, M. Hennum, T. Bonge-Hansen, *J. Org. Chem*. **2013**, *78*, 7488-7497. J. Daru, Z. Benda, Á. Póti, Z. Novák, A. Stirling. *Chem. Eur. J.* **2014**, *20*, 15395-15400.

[2] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

2.2. Basis set for geometry optimizations and frequency calculations (B_1)

Basis set for main group elements

For B, C, N, O, F, Si, Cl, Br and H atoms we have used the 6-31+G* basis set.
Basis set for I

```
****
I 0
S   2   1.00
     0.7242000           -2.9731048
     0.4653000            3.4827643
S   1   1.00
     0.1336000            1.0000000
S   1   1.00
     4.200000E-02         1.0000000
P   2   1.00
     1.2900000           -0.2092377
     0.3180000            1.1035347
P   1   1.00
     0.1053000            1.0000000
P   1   1.00
     3.380000E-02         1.0000000
D   1   1.00
     3.000000E-01         1.0000000
D   1   1.00
     1.191000E-01         1.0000000
****
```

The basis set was employed with the LanL2 effective core potential:

```
I 0
I-ECP     3     46
f   potential
  5
0      1.0715702           -0.0747621
1     44.1936028          -30.0811224
2     12.9367609          -75.3722721
2      3.1956412          -22.0563758
2      0.8589806           -1.6979585
s-f potential
  5
0    127.9202670            2.9380036
1     78.6211465           41.2471267
2     36.5146237          287.8680095
2      9.9065681          114.3758506
2      1.9420086           37.6547714
p-f potential
  5
0     13.0035304            2.2222630
1     76.0331404           39.4090831
2     24.1961684          177.4075002
2      6.4053433           77.9889462
```

2 1.5851786 25.7547641
d-f potential
5
0 40.4278108 7.0524360
1 28.9084375 33.3041635
2 15.6268936 186.9453875
2 4.1442856 71.9688361
2 0.9377235 9.3630657

2.3. Basis set employed for single-point energy calculations (B_2)

Basis set for main group elements

For B, C, N, O, F, Si, Cl, Br and H atoms we have used the 6-311++G(3df,3pd) basis set.

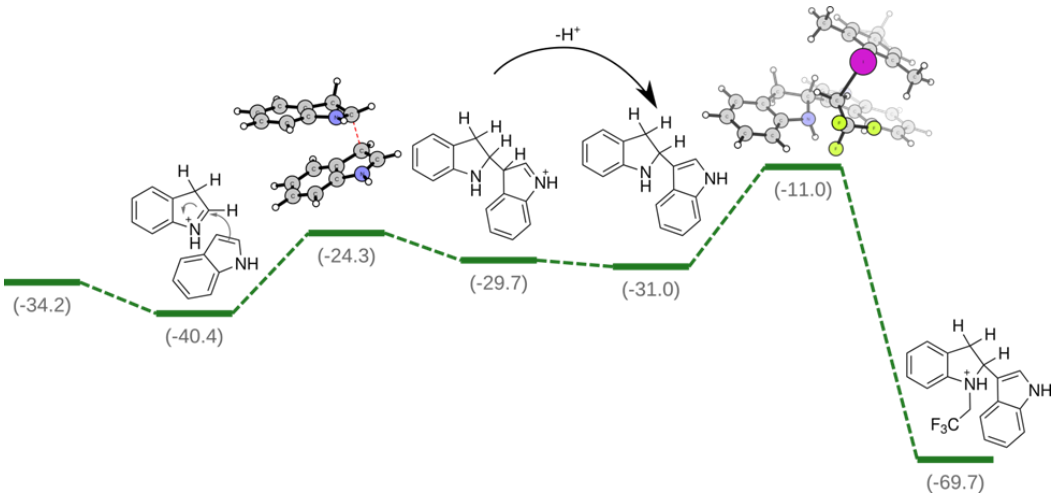
Basis set for I

****
I 0
S 1 1.00
0.7242000 1.0000000
S 1 1.00
0.4653000 1.0000000
S 1 1.00
0.1336000 1.0000000
S 1 1.00
4.120000E-02 1.0000000
P 1 1.00
1.2900000 1.0000000
P 1 1.00
0.3180000 1.0000000
P 1 1.00
0.1053000 1.0000000
P 1 1.00
3.590000E-02 1.0000000
D 1 1.00
1.326620E+02 1.0000000
F 1 1.00
4.064000E-01 1.0000000
F 1 1.00
1.848000E-01 1.0000000
****
The basis set was employed with the LanL2 effective core potential:

I 0
I-ECP 3 46
f potential
5
0 1.0715702 -0.0747621
1 44.1936028 -30.0811224
2 12.9367609 -75.3722721
2 3.1956412 -22.0563758

2 0.8589806 -1.6979585
s-f potential
5
0 127.9202670 2.9380036
1 78.6211465 41.2471267
2 36.5146237 287.8680095
2 9.9065681 114.3758506
2 1.9420086 37.6547714
p-f potential
5
0 13.0035304 2.2222630
1 76.0331404 39.4090831
2 24.1961684 177.4075002
2 6.4053433 77.9889462
2 1.5851786 25.7547641
d-f potential
5
0 40.4278108 7.0524360
1 28.9084375 33.3041635
2 15.6268936 186.9453875
2 4.1442856 71.9688361
2 0.9377235 9.3630657

3. Formation of the side-product



The above free energy profile starts from the σ-complex displayed in Scheme 6 of the article. The profile indicates that the dimerization is more exoenergetic than formation of the product. On the other hand the process is required to surmount higher free energy barrier than the deprotonation of the σ-complex by DTBPy. This explains our experimental observations that in the presence of a suitable base the reaction follows the path leading to product formation, but whithout additional base the indole self-protonation takes place readily.

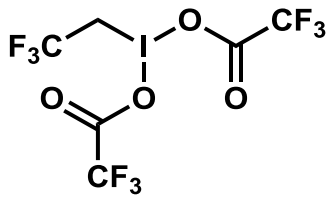
4. Formation of 1- and 2-substituated indoles

Formation of 1-trifluoroethyl-indole requires 30.2 kcal·mol^{-1} activation free energy. All attempts for TS search at C2 position have failed and resulted in 3-trifluoroethyl-indole formation indicating that 2-substitution is highly unfavorable. This hypothesis have been supported by the kinetically prohibited rearrangement of 1 and 3-trifluorethyl sigma-complex to the 2-trifluoroethyl derivative. These routes feature 57.5 and 36.3 kcal·mol^{-1} activation free energies, respectively. We can conclude that formation 2-trifluoroethyl-indole can be safely excluded from the mechanism in agreement with experiment.

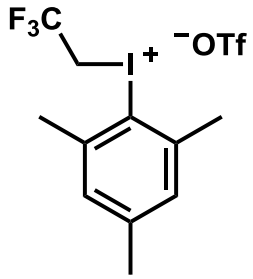
5. Activation Gibbs free energies for trifluoroethylation of different substrates and Gibbs free energies of formation for the corresponding sigma-complexes

Substrate	Activation Gibbs free energy (kcal·mol^{-1})	Gibbs free energy of formation (kcal·mol^{-1})
3a	25.0	-34.2
3b	23.6	-39.3
3c	23.7	-40.1
3d	24.2	-32.6
3e	24.1	-34.9
3f	25.3	-36.9
3g	22.6	-36.6
3h	21.5	-38.4
3i	20.2	-40.7
3j	24.0	-36.1
3k	23.7	-38.7
3l	23.5	-39.5
3m	22.9	-38.7
3n	23.9	-36.3
3o	26.5	-36.0
3p	25.8	-31.8
3q	25.7	-33.3
3r	25.4	-33.0
3s	23.8	-37.4
3t	26.9	-26.9
3u	27.3	-29.2
3v	26.7	-30.5
3w	24.6	-32.6
3x	28.5	-32.4
3y	24.1	-35.9
3z	25.0	-30.3
3aa	26.5	-34.1
3bb	26.2	-34.2
3cc	25.4	-32.3
3dd	23.5	-37.0
3ee	24.6	-33.1
3ff	23.8	-35.7

6. Synthesis of starting materials

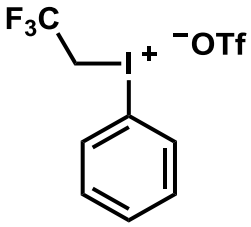


(2,2,2-Trifluoroethyl)-λ^3-iodanediyl bis(2,2,2-trifluoroacetate)[3]: Into a 200 mL round-bottom flask 2,2,2-trifluoroacetic anhydride (72 mL, 520 mmol) and trifluoroacetic acid (620 µL, 10 mol%) was measured and the mixture was cooled to 0 °C. H_2O_2 (8 mL, 50% aqueous solution, 118 mmol) was added dropwise and the mixture was stirred for 5 minutes. 2,2,2-trifluoroiodoethane (8 mL, 80 mmol) was added, then the reaction was allowed to warm up to room temperature and it was stirred for 20 hours. The volatile was evaporated under reduced pressure and white oil was obtained, which crystallized in refrigerator and gave the white solid in quantitative yield. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 4.93 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -63.2, -73.4.

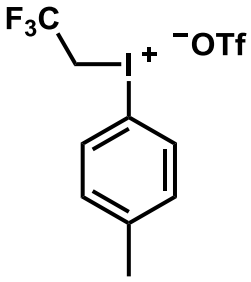


2,2,2-Trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (1a): In a 100 mL round-bottom flask (2,2,2-trifluoroethyl)-λ^3-iodanediyl bis(2,2,2-trifluoroacetate) (7.847 g, 18 mmol) was dissolved in dichloromethane (30 mL), then the solution was cooled to 0 °C and mesitylene (3.88 mL, 28 mmol) was added. Then trifluoromethanesulfonic acid (1.6 mL, 18 mmol) was added dropwise. The reaction mixture turned to a dark red solution and it was kept at 0 °C for 24 hours. The solvent was evaporated under reduced pressure, then diethyl ether was added. White crystals precipitated from the mixture. The product was filtered off and washed with diethyl ether and white solid was obtained (8.15 g, 17 mmol, 92%). M.p. 114 °C. ^{1}H NMR (250 MHz, DMSO) δ = 6.95 (s, 2H), 5.01 (q, *J* = 7.5 Hz, 2H), 2.35 (s, 6H), 2.19 (s, 3H). ^{13}C NMR (63 MHz, DMSO) δ = 141.5, 137.2, 128.0, 104.3, 59.3 (q, *J* = 34.0), 29.2, 20.3. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -61.9, -78.6. IR (ATR) 2036, 1454, 1395, 1279, 1227, 1160, 1130, 1059, 1022, 854, 839 cm^{-1}. HRMS m/z $[M]^+$ Calculated for $C_{11}H_{13}F_3I$: 329.0009; found 329.0014.

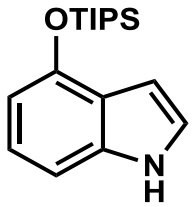
[3] Umemoto, *Bull. Chem. Soc. of Japan*, **1987**, *60*, 3307.



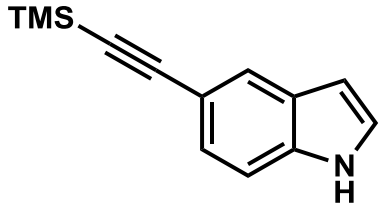
2,2,2-Trifluoroethyl(phenyl)iodonium trifluoromethanesulfonate (1b) [3]**:** In a 20 mL vial (2,2,2-trifluoroethyl)-λ^3-iodanediyl bis(2,2,2-trifluoroacetate) (1.477 g, 4 mmol) was dissolved in dichloromethane (5 mL), then the solution was cooled to 0 °C and benzene (555 µL, 6.2 mmol) was added. Then trifluoromethanesulfonic acid (355 µL, 4 mmol) was added dropwise. The reaction mixture turned to a dark solution and it was kept at 0 °C for 24 hours. The solvent was evaporated, then diethyl ether and chloroform was added and white crystals precipitated from the mixture. The product was filtered off, washed with chloroform and white solid was obtained (1.183 g, 2.7 mmol, 68%). M.p. 115°C. ^{1}H NMR (250 MHz, DMSO) δ = 7.72 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 2H), 4.99 (q, *J* = 7.5 Hz, 1.6H), 3.85 (q, *J* = 10.0 Hz, 0.4H). ^{13}C NMR (63 MHz, DMSO) δ = 137.4, 131.0, 128.0, 95.2, 69.6 (q, *J* = 35.9 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -73.1, -75.3, -77.8, -83.4. IR (ATR) 1223, 1171, 1126, 1063, 1022, 839, 735 cm^{-1}.



2,2,2-Trifluoroethyl(tolyl)iodonium trifluoromethanesulfonate (1c): In a 20 mL vial (2,2,2-trifluoroethyl)-λ^3-iodanediyl bis(2,2,2-trifluoroacetate) (1.477 g, 4 mmol) was dissolved in dichloromethane (5 mL), then the solution was cooled to 0 °C and toluene (660 µL, 6.2 mmol) was added. Then trifluoromethanesulfonic acid (355 µL, 4 mmol) was added dropwise. The reaction mixture turned to a dark solution and it was kept at 0°C for 24 hours. The solvent was evaporated, then chloroform was added and white crystals precipitated from the mixture. The product was filtered off, washed with chloroform and white solid was obtained (1.321 g, 3.0 mmol, 83%). M.p. 109°C. ^{1}H NMR (250 MHz, DMSO) δ = 7.58 (d, *J* = 10.0 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 2H), 5.01 (q, *J* = 7.5 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (63 MHz, DMSO) δ = 137.6, 137.2, 131.8, 91.0, 70.5, 69.1 (q, *J* = 35.9 Hz), 20.9. ^{19}F NMR (235 MHz, DMSO) δ = -73.1, -75.3, -77.8, -83.4**.** IR (ATR) 2976, 1484, 1398, 1238, 1167, 1122, 1063, 1026, 802 cm^{-1}. HRMS m/z $[M]^+$ Calculated for $C_9H_9F_3I$: 300.9701 found 300.9704.



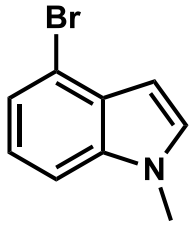
4-((Triisopropylsilyl)oxy)-1*H*-indole[4]: In a 30 mL vial 1*H*-indol-4-ol (266 mg, 2 mmol) was dissolved in dichloromethane (10 mL) and imidazole (300 mg, 4.4 mmol) and triisopropylsilyl chloride (471 μL, 2.2 mmol) was added. The reaction was stirred at room temperature for 7 hours. Reaction mixture was washed into a separation funnel with dichloromethane (10 mL) and it was extracted with distilled water (3×20 mL). Organic phase was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The pure product was obtained as white solid without further purification (571 mg, 1.97 mmol, 99%). M.p. 96-97 °C. R_f = 0.51 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 289 (78%), 246 (100%), 218 (44%), 204 (22%), 190 (33%), 176 (33%), 166 (22%), 144 (40%), 116 (27%), 95 (29%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 6.97 (t, *J* = 2.5 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 2H), 6.56 (t, *J* = 2.5 Hz, 1H), 6.46 (dd, J_1= 5.0 Hz, 2.5 Hz, 1H), 1.34 – 1.19 (m, 3H), 1.06 (d, *J* = 5.0 Hz, 18H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 149.9, 138.2, 123.0, 122.9, 121.9, 108.5, 104.8, 100.8, 18.5, 13.3.



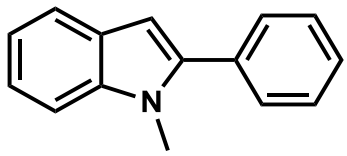
5-((Trimethylsilyl)ethynyl)-1*H*-indole: In a 20 ml vial 5-iodo-1*H*-indole (243 mg, 1.00 mmol) was dissolved in MeCN (2.5 mL), DIPA (0.5 mL) was added, then $Pd(PPh_3)_2Cl_2$ (29.4 mg, 5 mol%) and CuI (4.8 mg, 2.5 mol%) was added. Trimethylsilylacetylene (284 μL, 196 mg, 2.00 mmol) was added, then the vial was flushed with argon. The mixture was stirred for 1 hour at room temperature. The crude mixture was diluted with ethyl acetate (20 mL), extracted with an aqueous solution of HCl (0.25 M), until the pH became acidic. The organic layer was washed with cc. $NaHCO_3$ (25 mL), brine (25 mL), then dried on $MgSO_4$. The solvent was removed under reduced pressure, and the crude was purified by column chromatography (hexanes: ethyl acetate = 5:1) to give the product as a yellow oil (196 mg, 0.92 mmol, 92%). R_f = 0.20 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 213 (35%), 198 (100%), 99 (10%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 7.78 (s, 1H), 7.26 – 7.17 (m, 2H), 7.10 – 7.08 (m, 1H), 6.45 (s, 1H), 0.24 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 135.4, 127.4,

[4] E.J. Corey, *JACS*, **1972**, *94*, 6190-6191.

125.7, 124.9, 114.0, 110.8, 106.9, 102.6, 91.1, 0.0. IR (ATR) 2959, 2147, 1614, 1453, 1414, 1343, 1249, 1145, 940, 841, 760, 721 cm^{-1}.



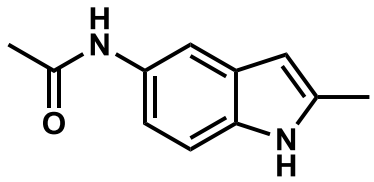
4-Bromo-1-methyl-1*H*-indole[5]: 4-bromo-1*H*-indole (630 µL, 5 mmol) was dissolved in abs. THF (17 mL) in a 50 mL round-bottom flask. The solution was cooled to 0 °C and slowly NaH (180 mg, 60% mineral oil, 7.5 mmol) was added. The solution was stirred at 0 °C for 15 min, then it was stirred at room temperature for 1.5 hours. Then it was cooled to 0 °C again and methyl iodide (405 µL, 6.5 mmol) was added. The reaction was stirred at room temperature for 24 hours. Then it was cooled to 0 °C and water (10 mL) was poured onto it. The aqueous phase was extracted with diethyl ether (3×10 mL) and the combined organic phases were dried on $MgSO_4$. The mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate: 100:1→50:1→ 25:1→ 10:1). The product was obtained as yellow oil (505 mg, 2.4 mmol, 48%). R_f = 0.50 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): 209 (100%), 194 (10,5%), 129 (32%), 115 (21%), 103 (24%), 88 (18%), 74 (18%), 63 (18%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.31 (dd, *J* = 5.0, 7.5 Hz, 2H), 7.11 (dd, *J* = 2.5, 5.0 Hz, 2H), 6.58 (d, *J* = 2.5 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 137.4, 129.8, 129.5, 122.8, 122.6, 115.2, 108.9, 101.7, 33.6.



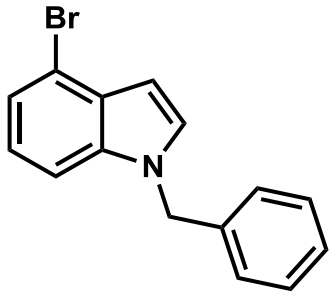
1-Methyl-2-phenyl-1*H*-indole[3]: 1-methyl-2-phenyl-1*H*-indole (290 mg, 1.5 mmol) was dissolved in abs. THF (5 mL) in a 25 mL round-bottom flask. The solution was cooled to 0 °C and slowly NaH (90 mg, 60% mineral oil, 2.25 mmol) was added. The solution was stirred at 0 °C for 15 min, then it was stirred at room temperature for 1.5 hours. Then it was cooled to 0 °C again and methyl iodide (122 µL, 1.95 mmol) was added. The reaction was stirred at room temperature for 24 hours. Then it was cooled to 0 °C and water (15 mL) was poured onto it. The aqueous phase was extracted with diethyl ether (3×20 mL) and the combined organic phases were dried on $MgSO_4$. The mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate: 25:1→ 15:1→ 10:1). The product was obtained as yellow oil (169 mg, 0.82 mmol, 54%). R_f = 0.50 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): 206 (100%), 190 (7%), 178 (22%), 165 (18%), 152 (7%), 139 (7%), 130 (45%),

[5] Tolnai G.L., Ganss,S., Brand J.P. and Waser J., *Org. Lett.*, **2013**, *15*, 112-113.

102 (16%), 89 (11%), 77 (15%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.58 – 7.55 (m, 2H), 7.42 – 7.24 (m, 6H), 6.69 (dd, *J* = 7.5 Hz, 2H), 2.96 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 150.2, 132.5, 131.9, 130.5, 128.8, 128.6, 123.8, 116.7, 109.4, 107.7, 95.4, 86.4, 30.8.



N-(2-Methyl-1*H*-indol-5-yl)acetamide[6]: In a 20 mL vial 2-methyl-1*H*-indol-5-amine (146 mg, 1.00 mmol) was dissolved in pyridine (5 mL) and acetic anhydride (114 μL, 1.2 mmol) was added dropwise. The reaction was stirred at room temperature for 30 minutes. The mixture was poured onto distilled water (25 mL) and ethyl acetate was added (25 mL). The organic phase was washed with 2M HCl solution (3×25 mL). The organic phase was dried on $MgSO_4$, then solvent was evaporated under reduced pressure. The product was obtained as black solid (155 mg, 0.82 mmol, 82%). M.p. 152 °C. R_f = 0.34 (hexanes: ethyl acetate=1:2). MS (EI, 70 eV): *m/z* (%): 188 (45%), 146 (100%), 118 (20%), 91 (8%), 73 (5%), 52 (3%). ^{1}H NMR (250 MHz, CD_3CN) δ = 8.99 (s, 1H), 8.15 (s, 1H), 7.56 (s, 1H), 7.11 (d, *J* = 10.0 Hz, 1H), 7.00 (dd, *J* = 7.5, 2.5 Hz, 1H), 6.00 (s, 1H), 2.28 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (63 MHz, CD_3CN) δ = 168.0, 136.4, 133.0, 130.9, 128.7, 114.0, 110.3, 109.9, 99.3, 22.9, 12.3. IR (ATR) 2961, 2924, 1652, 1566, 1548, 1484, 1372, 1320, 1275, 1014, 873, 791 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{13}N_2O$: 189.1028 found 189.1033.

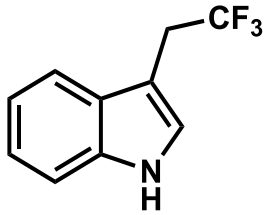


1-Benzyl-4-bromo-1*H*-indole5: 4-bromo-1*H*-indole (627 μL, 5 mmol) was solved in dimethylsulfoxide (50 mL) in a 100 mL round-bottom flask. Potassium hydroxide (1.290 g, 23 mmol) was added to the solution and the reaction was stirred for 30 minutes after which it was a dark brown solution. Then benzyl bromide (713 μL, 6 mmol) was added. The reaction was stirred for 1 hour, then TLC analysis showed complete conversion and the reaction turned into light brown solution. The reaction mixture was poured onto distilled water (50 mL), then it was extracted with ethyl acetate (3×20 mL). The organic phase was dried on $MgSO_4$, then it was evaporated on celite. The product was

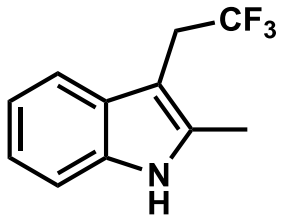
[6] J. DeGraw, L. Goodman, *New Compounds*, **1964**, *7*, 389.

purified by column chromatography. (hexanes: ethyl acetate = 20:1 → 10:1). The product was obtained as pale green solid (1.102 g, 3.9 mmol, 78%). R_f = 0.66 (hexanes: ethyl acetate = 5:1). M.p. 62 °C. MS (EI, 70 eV): *m/z* (%): 285 (18%), 204 (4%), 115 (10%), 91 (100%), 65 (14%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.34 – 7.20 (m, 6H), 7.14 – 7.02 (m, 3H), 6.66 (d, *J* = 2.5 Hz, 1H), 5.32 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 137.4, 137.0, 129.8, 129.3, 129.3, 128.2, 127.2, 123.0, 122.9, 115.4, 109.4, 102.5, 50.9. IR (ATR) 1607, 1559, 1510, 1477, 1432, 1335, 1294, 1264, 1171, 888, 731 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{15}H_{13}BrN$: 286.0226 found 286.0236.

7. Synthesis of 3-trifluoroethylated indoles

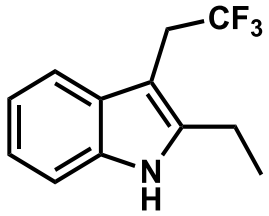


3-(2,2,2-Trifluoroethyl)-1*H*-indole (3a): In a 20 mL vial 1*H*-indole (88 mg, 0.75 mmol) was dissolved in dichloromethane (4 mL) and 2,6-di-*tert*-butylpyridine (340 µL, 1.50 mmol) was added and the mixture was stirred for 5 min, then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (466 mg, 0.975 mmol) was added. The reaction was completed after 1 hour. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 25:1 → 10:1 → 5:1). The product was obtained as pale brown crystals (125 mg, 0.63 mmol, 84%). M.p. 56-57 °C. R_f = 0.40 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): 199 (50%), 180 (9%), 148 (9%), 130 (100%), 102 (14%), 77 (14%), 69 (36%), 51 (12%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 7.27 – 7.07 (m, 3H), 3.46 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 136.4, 127.8, 126.7 (q, *J* = 277.2 Hz), 124.6, 122.9, 120.5, 119.1, 111.7, 105.3 (q, *J* = 3.8 Hz), 30.9 (q, *J* = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2942, 1458, 1424, 1369, 1339, 1260, 1126, 1093, 1011, 910, 820, 738, 668 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{10}H_9F_3N$: 200.0682; found 200.0687.

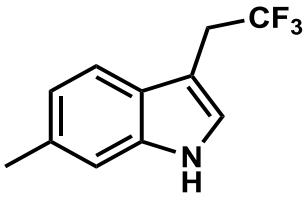


2-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3b): In a 4 mL vial 2-methyl-1*H*-indole (65.5 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00

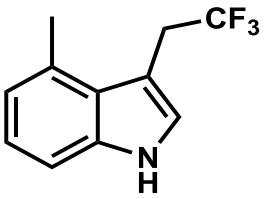
mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 5 minutes. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 10:1 to 5:1) to give the product as white solid (101 mg, 0.48 mmol, 95%). M.p. 112 °C. R_f = 0.30 (hexane: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 213 (40%), 194 (5%). 144 (100%), 115 (8%).^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.73 (s, 1H), 7.44 – 7.41 (m, 1H), 7.18 - 7.03 (m, 3H), 3.37 (q, *J* = 10.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 135.4, 134.6, 129.1, 127.0 (q, *J* = 277.8 Hz), 121.9, 120.3, 118.3, 110.7, 101.3 (q, *J* = 3.2 Hz), 29.9 (q, *J* = 31.5 Hz), 12.0. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.0. IR (ATR) 2924, 1622, 1466, 1425, 1365, 1342, 1275, 1257, 1115, 1093, 832, 750 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{11}F_3N$: 214.0844; found 214.0843.



2-Ethyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3c): In a 4 mL vial 2-ethyl-1*H*-indole (73 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 10 minutes. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1). The product was obtained as white solid (108 mg, 0.48 mmol, 95%). M.p. 106-107 °C. R_f = 0.54 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 227 (49%), 212 (46%), 158 (100%), 143 (54%), 143 (11%), 115 (11%), 77 (10%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.93 (s, 1H), 7.60 – 7.56 (m, 1H), 7.35 – 7.30 (m, 1H), 7.25 – 7.14 (m, 2H), 3.52 (q, *J* = 10.0 Hz, 2H), 2.82 (q, *J* = 7.5 Hz, 2H), 1.33 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 140.0, 135.2, 128.8, 126.6 (q, *J* = 272.8 Hz), 121.7, 120.1, 118.3, 110.6, 100.1 (q, *J* = 3.2 Hz), 29.6 (q, *J* = 31.5 Hz), 19.3, 13.8. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -65.9. IR (ATR) 2991, 2226, 2185, 1462, 1372, 1279, 1264, 1188, 1096, 1063, 832, 750, 656 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{12}H_{13}F_3N$: 228.1000; found 228.0998.

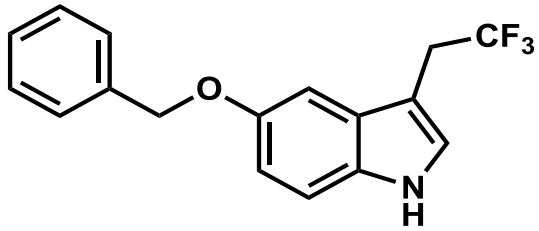


6-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3d): In a 4 mL vial 6-methyl-1*H*-indole (66 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 30 minutes. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1 → 7:1). The product was obtained as brown crystals (66 mg, 0.31 mmol, 62%). M.p. 74-75 °C. R_f = 0.50 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 213 (48%), 144 (100%), 115 (17%), 72 (12%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.94 (s, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.18 (s, 1H), 7.09 – 7.05 (m, 2H), 3.56 (q, *J* = 12.5 Hz, 2H), 2.51 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 136.8, 132.8, 126.7 (q, *J* = 277.2 Hz), 125.6, 124.0, 122.3, 118.8, 111.6, 105.1 (q, *J* = 3.2 Hz), 31.0 (q, *J* = 31.5 Hz), 22.0. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2931, 1622, 1454, 1365, 1264, 1246, 1126, 1093, 1052, 910, 805, 656 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{11}F_3N$: 214.0844; found 214.0843.

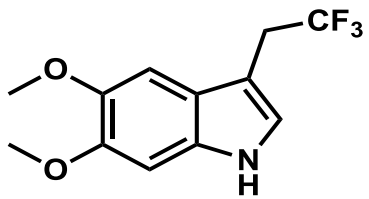


4-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3e): In a 4 mL vial 4-methyl-1*H*-indole (66 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 10 minutes. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1 → 7:1). The product was obtained as orange crystals (85 mg, 0.40 mmol, 80%). M.p. 99-100 °C. R_f = 0.44 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 213 (42%), 144 (100%), 115 (17%), 72 (8%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.09 (s, 1H), 7.26 – 7.22 (m, 1H), 7.16 – 7.10 (m, 2H), 6.93 (d, *J* = 5.0 Hz, 1H), 3.78 (q, *J* = 10.0 Hz, 2H), 2.73 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 136.7, 130.7, 126.5 (q, *J* = 277.2 Hz), 126.0, 125.0, 122.9, 122.4, 109.8, 105.5 (q, *J* = 3.2 Hz), 32.2 (q, *J* = 30.2 Hz), 20.6. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.3. IR (ATR) 2972, 1633, 1365, 1268, 1249, 1134, 1100,

1070, 817, 764, 742, 682 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{11}F_3N$: 214.0844; found 214.0842.

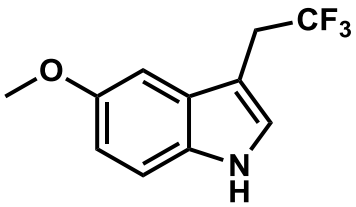


5-(Benzyloxy)-3-(2,2,2-trifluoroethyl)-1*H*-indole (3f): In a 4 mL vial 5-(benzyloxy)-1*H*-indole (112 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 10 minutes. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1 → 7:1). The product was obtained as white crystals (127 mg, 0.42 mmol, 84%). M.p. 95-96 °C. R_f = 0.36 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 305 (25%), 214 (38%), 186 (22%), 117 (10%), 91 (100%), 65 (10%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.04 (s, 1H), 7.54 – 7.25 (m, 6H), 7.18 – 6.98 (m, 3H), 5.15 (s, 2H), 3.52 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.1, 137.9, 131.7, 129.0, 128.3, 128.2, 128.1, 125.5, 120.3 (q, *J* = 536.8 Hz), 113.9, 112.5, 105.0 (q, *J* = 3.2 Hz), 102.7, 71.5, 31.0 (q, *J* = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.0. IR (ATR) 2935, 1626, 1585, 1484, 1454, 1369, 1264, 1197, 1130, 1089, 1014, 943, 798, 735, 697, 668 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{17}H_{15}F_3NO$: 306.1106; found 306.1104.

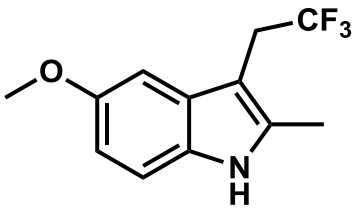


5,6-Dimethoxy-3-(2,2,2-trifluoroethyl)-1*H*-indole (3g): In a 4 mL vial 5,6-dimethoxy-1*H*-indole (89 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 20 minutes. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1 → 7:1→ 5:1→ 4:1). The product was obtained as white crystals (59 mg, 0.23 mmol, 46%). M.p. 97-98 °C. R_f = 0.25 (hexanes: ethyl acetate = 3:1). MS (EI, 70 eV): *m/z* (%): 259 (100%), 244 (43%), 216 (21%), 201 (43%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.13 (s, 1H), 7.03 (s, 2H), 6.85 (s, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 3.51 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ =

147.8, 145.8, 130.7, 126.7 (q, J = 277.2 Hz), 123.2, 120.5, 104.9 (q, J = 3.2 Hz), 100.8, 95.0, 56.7, 56.5, 31.1 (q, J = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2951, 2838, 1488, 1372, 1316, 1249, 1208, 1126, 1085, 988, 910, 843, 746, 649 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{12}H_{13}F_3NO_2$: 260.0898; found 260.0895.

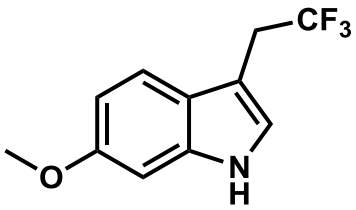


5-Methoxy-3-(2,2,2-trifluoroethyl)-1*H*-indole (3h): In a 4 mL vial 5-methoxy-1*H*-indole (74 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction was stirred at room temperature for 1 hour. Following general procedure the product was purified by column chromatography using gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1 → 7:1). The product was obtained as white solid (103 mg, 0.45 mmol, 90%). M.p. 77-78 °C. R_f = 0.34 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 229 (100%), 214 (61%), 186 (78%), 160 (78%), 145 (22%), 117 (44%), 89 (16%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.08 (s, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.15 (d, J = 2.5 Hz, 1H), 7.07 (s, J = 2.5 Hz, 1H), 6.92 (dd, J = 5.0, 2.5 Hz, 1H), 3.89 (s, 3H), 3.53 (q, J = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.9, 131.5, 128.2, 126.3 (q, J = 321.9 Hz), 125.4, 113.2, 112.5, 105.0 (q, J = 3.2 Hz), 100.8, 56.3, 31.0 (q, J = 30.9 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2757, 2838, 1630, 1585, 1488, 1458, 1443, 1350, 1264, 1238, 1212, 1130, 1085, 1026, 925, 839, 798, 768, 723, 664 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{11}F_3NO$: 230.0787; found 230.0794.

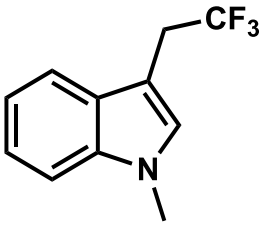


5-Methoxy-2-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3i): In a 4 mL vial 5-methoxy-2-methyl-1*H*-indole (80.5 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 40 minutes. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 10:1 to 5:1) to give the product as white solid (116 mg, 0.48 mmol, 96%). M.p. 122 °C. R_f = 0.25 (hexane: ethyl acetate =

5:1). MS (EI, 70 eV): *m/z* (%): 243 (80%), 228 (20%), 200 (35%), 174 (100%), 159 (30%), 131 (30%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.73 (s, 1H), 7.06 (d, *J* = 10.0 Hz, 1H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.72 (dd, *J* = 5.0, 2.5 Hz, 1H), 3.77 (s, 3H), 3.34 (q, *J* = 10.0 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.8, 135.4, 130.5, 129.6, 127.1 (q, *J* = 277.8 Hz), 111.6, 111.5, 101.1 (q, *J* = 3.2 Hz), 100.8, 56.3, 29.9 (q, *J* = 31.5 Hz), 12.1. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.0. IR (ATR) 2961, 2935, 2838, 1589, 1484, 1454, 1369, 1346, 1260, 1189, 1081, 1014, 966, 839, 802, 735 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{12}H_{13}F_3NO$: 244.0949; found 244.0950.

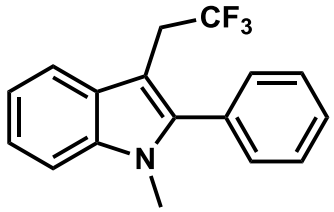


6-Methoxy-3-(2,2,2-trifluoroethyl)-1*H*-indole (3j): In a 4 mL vial 6-methoxy-1*H*-indole (73.5 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 15 minutes. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 10:1 to 4:1) to give the product as white solid (61 mg, 0.27 mmol, 53%). M.p. 139-140 °C. R_f = 0.15 (hexane: ethyl acetate = 5:1). M.p. 140 °C. MS (EI, 70 eV): *m/z* (%): 229 (100%), 214 (90%), 186 (45%), 160 (55%), 145 (25%), 117 (30%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.49 (d, *J* = 10.0 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.85 (dd, *J* = 5, 2.5 Hz, 2H), 3.85 (s, 3H), 3.51 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 157.2, 137.2, 126.6 (q, *J* = 277.2 Hz), 123.4, 122.1, 119.8, 110.6, 105.2 (q, *J* = 3.8 Hz), 95.1, 56.1, 31.0 (q, *J* = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.2. IR (ATR) 2972, 2842, 2178, 1630, 1458, 1365, 1249, 1167, 1130, 1093, 1022, 813, 653 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{11}F_3NO$: 230.0793; found 230.0790.

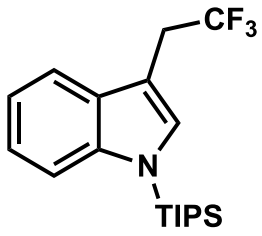


1-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3k): In a 4 mL vial 1-methyl-1*H*-indole (63 μL, 0.500 mmol) was dissolved in dichloromethane (2.5 mL), then 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added and the mixture was stirred at room temperature for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction was completed after 3.5 hours. Following general procedure the product was purified by

column chromatography with gradient elution (hexanes: ethyl acetate, 25:1→ 10). The product was obtained as yellow oil (74 mg, 0.35 mmol, 70%). R_f = 0.48 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 213 (53%), 194 (5%), 144 (100%), 129 (8%), 115 (8%), 102 (8%), 69 (15%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 7.5 Hz, 1H), 7.39 – 7.20 (m, 3H), 7.07 (s, 1H), 3.80 (s, 3H), 3.58 (q, *J* = 12.5 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 137.2, 129.3, 128.3, 126.7 (q, *J* = 277.2 Hz), 122.4, 120.0, 119.2, 109.9, 103.4 (q, *J* = 31.5 Hz), 33.1, 30.8 (q, *J* = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.2. IR (ATR) 2934, 1477, 1384, 1346, 1260, 1126, 1085, 910, 817, 791, 738, 701 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{11}F_3N$: 214.0838; found 214.0845.

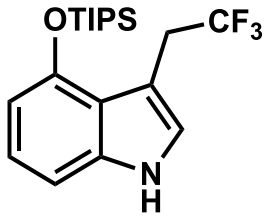


1-Methyl-2-phenyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3l): In a 4 mL vial 1-methyl-2-phenyl-1*H*-indole (104 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction was stirred at room temperature for 2 hours. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1→ 7:1). The product was obtained as an orange oil (98 mg, 0.34 mmol, 68%). R_f = 0.82 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 288 (100%), 220 (60%), 212 (76%), 204 (53%), 178 (22%), 151 (9%), 102 (10%), 89 (7%), 77 (6%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.04 – 6.98 (m, 3H), 6.88 – 6.74 (m, 4H), 6.57 – 6.44 (m, 2H), 3.67 (q, *J* = 7.5 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (62 MHz, $CDCl_3$) δ = 153.1, 135.3, 132.2, 130.3, 129.3, 129.2, 126.6 (q, *J* = 289.8 Hz), 124.2, 122.9, 120.8, 116.3, 95.6 (q, *J* = 25.8 Hz), 88.1, 55.3 (q, *J* = 30.9 Hz), 40.7. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -68.1. IR (ATR) 2953, 1592, 1495, 1484, 1447, 1361, 1260, 1145, 1100, 984, 820, 753, 690, 660 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{17}H_{15}F_3N$: 290.1157; found 290.1158.

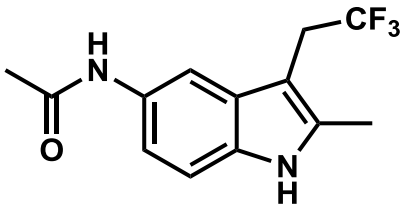


3-(2,2,2-Trifluoroethyl)-1-(triisopropylsilyl)-1*H*-indole (3m): In a 4 mL vial 1-(triisopropylsilyl)-1*H*-indole (137 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-

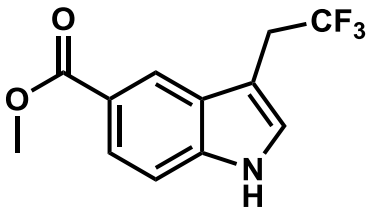
trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 1 hour. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 10:1) to give the product as a white solid (153 mg, 0.43 mmol, 86%). R_f = 0.30 (hexane: ethyl acetate = 5:1). M.p. 77 °C. MS (EI, 70 eV): *m/z* (%): 355 (80%), 336 (5%), 312 (100%), 270 (30%), 248 (35%), 220 (20%), 206 (35%).^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.52 – 7.40 (m, 2H), 7.09 (dd, *J* = 5.0 Hz, 3H), 3.45 (q, *J* = 10.0 Hz, 2H), 1.61 (dt, *J* = 7.5 Hz, 3H), 1.06 (d, *J* = 7.5 Hz, 18H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 141.5, 131.6, 131.1, 126.7 (d, *J* = 277.2 Hz), 122.2, 120.4, 118.9, 114.5, 107.1 (q, *J* = 3.2 Hz), 31.0 (q, *J* = 31.5 Hz), 18.5, 13.2. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.0. IR (ATR) 2950, 2871, 1615, 1451, 1365, 1260, 1130, 1070, 1018, 962, 884, 738, 679 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{19}H_{29}F_3NSi$: 356.2021; found 356.2025.



3-(2,2,2-Trifluoroethyl)-4-((triisopropylsilyl)oxy)-1*H*-indole (3n): In a 4 mL vial 4-((triisopropylsilyl)oxy)-1*H*-indole (145 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 20 minutes. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1). The product was obtained as orange solid (90 mg, 0.24 mmol, 48%). M.p. 100-101 °C. R_f = 0.53 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 371 (21%), 195 (8%), 176 (100%), 148 (58%), 133 (8%), 115 (7%), 77 (21%), 59 (8%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.05 (s, 1H), 7.06 (s, 1H), 6.98 (dd, *J* = 5.0, 7.5 Hz, 2H), 6.53 (dd, *J* = 5.0 Hz, 2.5 Hz, 1H), 3.92 (q, *J* = 10.0 Hz, 2H), 1.50 – 1.36 (m, 3H), 1.19 (d, *J* = 7.5 Hz, 18H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 151.0, 138.4, 126.9 (q, *J* = 276.6 Hz), 123.3, 122.9, 119.4, 108.1, 105.1 (q, *J* = 3.2 Hz), 104.8, 31.4 (q, *J* = 30.9 Hz), 18.4, 13.8. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.3. IR (ATR) 2946, 2871, 1503, 1361, 1264, 1134, 1063, 884, 858, 787, 735, 690 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{19}H_{29}F_3NOSi$: 372.1971; found 372.1977.

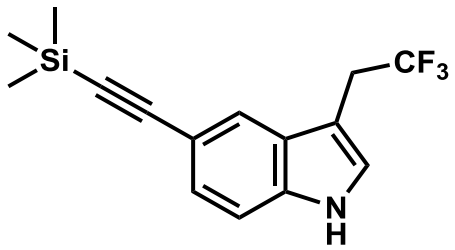


***N*-(2-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indol-5-yl)acetamide (3o):** In a 4 mL vial *N*-(2-methyl-1*H*-indol-5-yl)acetamide (94 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL). 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 min, then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (239 mg, 0.5 mmol) was added. The reaction was stirred at room temperature for 10 minutes. Following general procedure the mixture was purified by column chromatography using hexanes: ethyl acetate (25:1 to 5:1) on SiO_2. The product was obtained as an off-white solid (104 mg, 0.39 mmol, 77%). M.p. 158 °C. R_f = 0.34 (hexane: ethyl acetate = 1:2). MS (EI, 70 eV): *m/z* (%): 270 (56%), 228 (62%), 200 (11%), 159 (100%), 130 (11%), 117 (4%), 89 (3%). ^{1}H NMR (250 MHz, DMSO) δ = 10.97 (s, 1H), 9.71 (s, 1H), 7.71 (s, 1H), 7.19 (s, 2H), 3.57 (q, *J* = 12.5 Hz, 2H), 2.34 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (63 MHz, DMSO) δ = 167.9, 136.0, 132.1, 131.8, 130.0 (q, *J* = 514.1 Hz), 128.5, 114.6, 110.6, 108.6, 99.5 (q, *J* = 3.2 Hz), 28.8 (q, *J* = 33.4), 24.2, 11.5. ^{19}F NMR (235 MHz, DMSO) δ = -64.6. IR (ATR) 2961, 2230, 2163, 1663, 1555, 1484, 1369, 1260, 1122, 1014, 798, 686 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{13}H_{14}F_3N_2O$: 271.1058; found 271.1058.

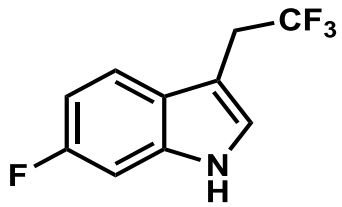


Methyl 3-(2,2,2-trifluoroethyl)-1*H*-indole-5-carboxylate (3p): In a 4 mL vial methyl 1*H*-indole-5-carboxylate (88 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 2.5 hours. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 50:1 to 15:3) to give the product as white solid (95 mg, 0.37 mmol, 74%). M.p. 165 °C. R_f = 0.30 (hexane: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 257 (70%), 226 (100%), 198 (18%), 188 (80%), 148 (70%), 129 (20%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.44 (s, 1H), 8.31 (s, 1H), 7.87 (dd, *J* = 7.5, 2.5 Hz, 1H), 7.32 (d, *J* = 10.0 Hz, 1H), 7.18 (s, 1H), 3.87 (s, 3H), 3.50 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 168.4, 139.0, 131.1, 127.4, 126.5 (q, *J* = 287.3 Hz), 125.9, 124.3, 122.7, 111.4, 106.7 (q, *J* = 2.5 Hz), 52.4, 30.8 (q, *J* = 32.1 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2953, 2226, 2185, 2144,

1689, 1618, 1577, 1439, 1331, 1316, 1287, 1231, 1119, 1074, 1040, 970, 895, 817, 761, 746, 675 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{12}H_{11}F_3NO_2$: 258.0742; found 258.0737.

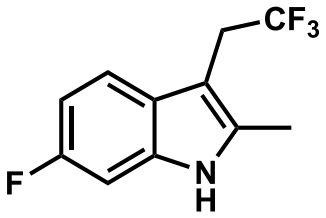


3-(2,2,2-Trifluoroethyl)-5-((trimethylsilyl)ethynyl)-1*H*-indole (3q): In a 4 mL vial 5-((trimethylsilyl)ethynyl)-1*H*-indole (106 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 1.5 hours. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 7:1) to give the product as white solid (124 mg, 0.42 mmol, 84%). R_f = 0.20 (hexanes: ethyl acetate = 5:1). M.p. 84 °C. MS (EI, 70 eV): *m/z* (%): 296 (20 %), 295 (80%), 280 (100 %),230 (50%), 105 (40%), 77 (35%); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.17 (s, 1H), 7.80 (s, 1H), 7.34 – 7.24 (m, 2H), 7.15 (d, *J* = 2.5 Hz, 1H), 3.51 (q, *J* = 10.0 Hz, 2H), 0.31 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 135.6, 127.0, 126.3, 126.0 (q, *J* = 277.8 Hz), 125.0, 122.9, 114.5, 111.2, 106.6, 105.0 (q, *J* =. 3.8 Hz), 91.6, 30.2 (q, *J* = 31.5 Hz), 0.0. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2965, 2931, 2159, 1469, 1428, 1369, 1260, 1134, 1093, 932, 843, 805, 761, 675 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{15}H_{17}F_3NSi$: 296.1082; found 296.1081.

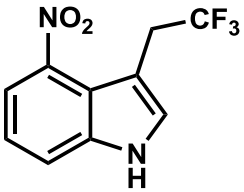


6-Fluoro-3-(2,2,2-trifluoroethyl)-1*H*-indole (3r): In a 4 mL vial 6-fluoro-1*H*-indole (68 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction was stirred at room temperature for 2 hours. Following general procedure the product was purified by column chromatography using gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1 → 7:1). The product was obtained as white solid (80 mg, 0.37 mmol, 74%). M.p. 39-40 °C. R_f = 0.40 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 217 (30%), 148 (100%), 120 (6%), 101 (12%), 74 (7%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.16 (s, 1H), 7.53 (dd, J_1 = 2.5 Hz, 1H), 7.16 (d, *J* =

2.5 Hz, 1H), 7.09 – 6.92 (m, 2H), 3.53 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.5 (d, *J* = 238.8 Hz), 136.3 (d, *J* = 12.6 Hz), 126.5 (q, *J* = 277.2 Hz), 124.9, 124.3, 120.0 (d, *J* = 11.3 Hz), 109.4 (d, *J* = 25.2 Hz), 105.4 (q, *J* = 3.8 Hz), 98.0 (d, *J* = 25.8 Hz), 30.9 (q, *J* = 32.1 Hz).^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.2, -120.7. IR (ATR) 1630, 1562, 1499, 1458, 1369, 1342, 1264, 1246, 1137, 1122, 1093, 951, 910, 839, 805, 735, 653 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{10}H_8F_4N$: 218.0593; found 218.0593.

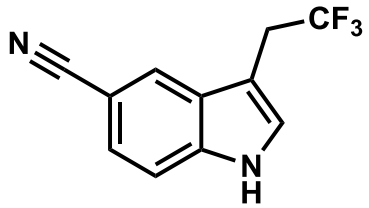


6-Fluoro-2-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3s): In a 4 mL vial 6-fluoro-2-methyl-1*H*-indole (75 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.0 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 10 minutes. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1→ 7:1). The product was obtained as white solid (109 mg, 0.47 mmol, 94%). M.p. 90-91 °C. R_f = 0.34 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 231 (37%), 162 (100%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.87 (s, 1H), 7.42 (dd, $J_1 = J_2$ = 5.0 Hz, 1H), 6.99 – 6.87 (m, 2H), 3.45 (q, *J* = 10.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.0 (d, *J* = 237.5 Hz), 135.3 (d, *J* = 12.0 Hz), 134.9 (d, *J* = 3.2 Hz), 126.9 (q, *J* = 277.8 Hz), 125.6, 119.0 (d, *J* = 9.5 Hz), 108.8 (d, *J* = 24.6 Hz), 101.32 (q, *J* = 3.2 Hz), 97.3 (d, *J* = 26.5 Hz), 29.8 (q, *J* = 31.5 Hz), 11.9. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.0, -121.9. IR (ATR) 2923, 1630, 1499, 1466, 1428, 1361, 1260, 1234, 1130, 1115, 1093, 955, 835, 805, 664 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{10}F_4N$: 232.0749; found 232.0749.

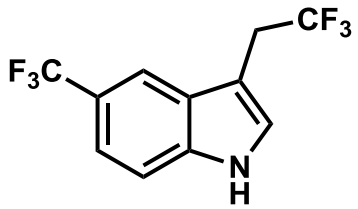


4-Nitro-3-(2,2,2-trifluoroethyl)-1*H*-indole (3t): In a 4 mL vial 4-nitro-1*H*-indole (81 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL), then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction was stirred at room temperature for 4 hours. Following general procedure the product was purified by column chromatography using gradient elution (hexanes: ethyl acetate, 10:1 → 5:1 → 4:1 → 3:1 → 2:1). The

product was obtained as yellow solid (61 mg, 0.25 mmol, 50%). M.p. 153 °C. R_f = 0.27 (hexanes: ethyl acetate = 2:1). MS (EI, 70 eV): *m/z* (%): 244 (60%), 227 (77%), 197 (83%), 166 (27%), 148 (100%), 128 (36%), 101 (27%), 74 (21%). ^{1}H NMR (250 MHz, DMSO) δ = 12.12 (s, 1H), 7.88 – 7.80 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 3.86 (q, J_1 = 12.5 Hz, 2H). ^{13}C NMR (63 MHz, DMSO) δ = 142.3, 139.4, 132.6, 126.9 (q, *J* = 277.2 Hz), 120.8, 119.1, 118.5, 118.0, 102.4 (q, *J* = 4.4 Hz), 31.2 (q, *J* = 29.6 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -61.7. IR (ATR) 2629, 2581, 2189, 1514, 1361, 1320, 1298, 1253, 1141, 1100, 1074, 981, 791, 735 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{10}H_8F_3N_2O_2$: 245.0532; found 245.0541.

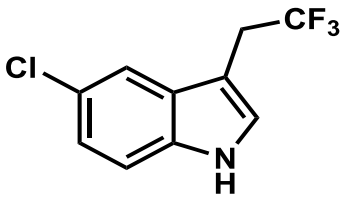


3-(2,2,2-Trifluoroethyl)-1*H*-indole-5-carbonitrile (3u): In a 4 mL vial 1*H*-indole-5-carbonitrile (71 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL). Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 4 hours. Following general procedure the product was purified by column chromatography (4:1 to 2:1) on SiO_2. The product was obtained as white solid (35 mg, 0.16 mmol, 31%). M.p. 192 °C. R_f = 0.43 (hexanes: ethyl acetate = 2:1). MS (EI, 70 eV): *m/z* (%): 224 (17%), 207 (7%), 155 (100%), 128 (7%), 101 (10%), 77 (8%). ^{1}H NMR (250 MHz, DMSO) δ = 11.73 (s, 1H), 8.17 (s, 1H), 7.50 (dd, *J* = 17.5, 7.5 Hz, 3H), 3.80 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, DMSO) δ = 138.1 , 128.8 , 128.6 (q, *J* = 75.6 Hz), 127.4 , 124.8 , 124.3 , 121.0 , 113.3 , 104.7 (q, *J* = 3.8 Hz), 101.5 , 29.2 (q, *J* = 30.2 Hz). ^{19}F NMR (235 MHz, DMSO) δ = -64.9. IR (ATR) 2927, 2853, 2223, 1712, 1618, 1425, 1350, 1324, 1260, 1122, 1081, 1040, 884, 805, 768, 690 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_8F_3N_2$: 225.0634; found 225.0634.

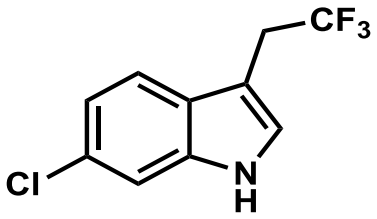


3-(2,2,2-Trifluoroethyl)-5-(trifluoromethyl)-1*H*-indole (3v): In a 4 mL vial 5-trifluoromethyl-1*H*-indole (92.5 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 1.5 hours. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 10:1 to 2:1) to give the

product as white solid (54 mg, 0.20 mmol, 40%). M.p. 92 °C. R_f = 0.10 (hexane: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 267 (40%), 248 (20%), 198 (100%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 7.92 (s, 1H), 7.51 – 7.43 (m, 2H), 7.29 - 7.26 (m, 1H), 3.58 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 137.7 (s), 133.7 (s), 129.0 (q, *J* = 365 Hz), 124.0 (q, *J* = 244 Hz), 123.8 (d, *J* = 47.0 Hz), 123.1 (q, *J* = 31.6 Hz), 119.7 (q, *J* = 3.2 Hz), 116.9 (q, *J* = 4.5 Hz), 112.0, 106.3 (d, *J* = 3.2 Hz), 30.8 (q, *J* = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -60.4, -66.2. IR (ATR) 2946, 2159, 1633, 1436, 1331, 1264, 1242, 1130, 1093, 1063, 914, 891, 809, 686 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_8F_6N$: 268.0561; found 268.0559.

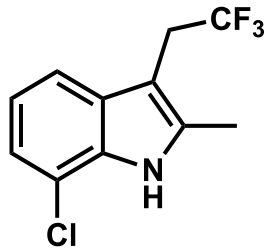


5-Chloro-3-(2,2,2-trifluoroethyl)-1*H*-indole (3w): In a 4 mL vial 5-chloro-1*H*-indole (76 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 1 hour. Following general procedure the mixture was purified by column chromatography using gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1→ 7:1). The product was obtained as white crystals (95 mg, 0.41 mmol, 82%). M.p. 94-95 °C. R_f = 0.41 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 233 (32.2%), 164 (100%), 128 (19.4%), 101 (13.9%), 75 (5.5%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 7.49 (s, 1H), 7.20 – 7.16 (m, 1H), 7.11 – 7.07 (m, 2H), 3.40 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 134.7, 128.8, 126.5 (q, *J* = 277.2 Hz), 126.4, 126.0, 123.3, 118.7, 112.7, 105.1 (q, *J* = 3.2 Hz), 30.8 (q, *J* = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2942, 1652, 1462, 1447, 1372, 1257, 1134, 1093, 1074, 992, 910, 862, 802, 690 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{10}H_8{}^{35}ClF_3N$: 234.0297; found 234.0303.

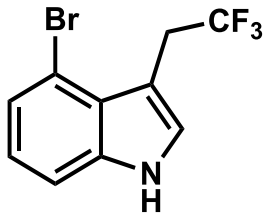


6-Chloro-3-(2,2,2-trifluoroethyl)-1*H*-indole (3x): In a 4 mL vial 6-chloro-1*H*-indole (76 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction was stirred at room

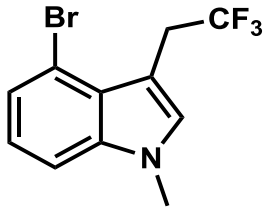
temperature for 4 hours. Following general procedure the product was purified by column chromatography using gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1→ 7:1). The product was obtained as a brown solid (88 mg, 0.38 mmol, 76%). M.p. 62-63 °C. R_f = 0.41 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 233 (49%), 214 (7%), 164 (100%), 148 (7%), 128 (18%), 101 (11%), 75 (7%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.12 (s, 1H), 7.52 (d, *J* = 10 Hz, 1H), 7.37 (s, 1H), 7.18 – 7.13 (m, 2H), 3.52 (q, J_1 = 10.0, 12.5 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 136.7, 128.8, 126.5 (q, *J* = 277.2 Hz), 126.3, 125.3, 121.3, 120.1, 111.6, 105.5 (q, *J* = 3.2 Hz), 30.8 (q, *J* = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2942, 1618, 1454, 1365, 1331, 1260, 1227, 1130, 1093, 906, 847, 805, 738, 694 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{10}H_8{}^{35}ClF_3N$: 234.0297; found 234.0298.



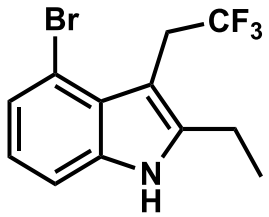
7-Chloro-2-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3y): In a 4 mL vial 7-chloro-2-methyl-1*H*-indole (83 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 3 hours. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1). The product was obtained as white solid (99 mg, 0.40 mmol, 80%). M.p. 79-80 °C. R_f = 0.48 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 247 (25%), 178 (100%), 143 (13%), 115 (13%), 101 (8%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.04 (s, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.15 – 6.93 (m, 2H), 3.35 (q, *J* = 10.0 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 135.5, 132.7, 130.5, 126.8 (q, *J* = 277.8 Hz), 121.3, 121.2, 117.0, 116.3, 102.5 (q, *J* = 3.2 Hz), 30.0 (q, *J* = 31.5 Hz), 12.0. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.0. IR (ATR) 2980, 1626, 1589, 1495, 1458, 1365, 1342, 1257, 1130, 1104, 1003, 891, 835, 776, 735, 720, 675 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{10}{}^{35}ClF_3N$: 248.0454; found 248.0452.



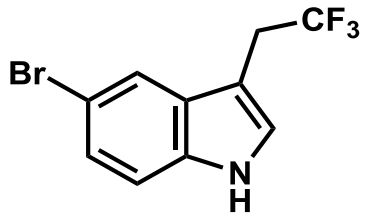
4-Bromo-3-(2,2,2-trifluoroethyl)-1*H*-indole (3z): In a 4 mL vial 4-bromo-1*H*-indole (63 µL, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 1.5 hours. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 10:1 → 7:1). The product was obtained as brown solid (98 mg, 0.35 mmol, 71%). M.p. 125-126 °C. R_f = 0.38 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 277 (46%), 208 (100%), 197 (6%), 148 (22%), 129 (20%), 102 (13%), 69 (33%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.14 (s, 1H), 7.25 – 7.15 (m, 3H), 6.5 (t, *J* = 7.5 Hz, 1H), 3.91 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 137.3, 126.4 (q, *J* = 278.5), 126.2, 125.5, 125.3, 123.7, 114.2, 111.2, 106.0 (q, *J* = 3.8 Hz), 31.0 (q, *J* = 33.4 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.0. IR (ATR) 2953, 2185, 1425, 1365, 1331, 1257, 1122, 1100, 1059, 914, 820, 764, 738, 668 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{10}H_8BrF_3N$: 277.9787; found 277.9791.



4-Bromo-1-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3aa): In a 4 mL vial 4-bromo-1-methylindole (105 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL), then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction was stirred at room temperature for 2 hours. Following general procedure the product was purified by column chromatography using gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 10:1 → 5:1). The product was obtained as green oil (85 mg, 0.29 mmol, 58%). R_f = 0.47 (hexanes: ethyl acetate = 5:1). M.p. 66-67 °C. MS (EI, 70 eV): *m/z* (%): 291 (50%), 272 (10%), 222 (100%), 162 (23%), 143 (40%), 128 (10%), 101 (10%), 69 (20%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.33 – 7.25 (m, 2H), 7.10 – 7.04 (m, 2H), 3.99 (q, *J* = 10.0 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 138.3, 130.8, 126.4 (q, *J* = 277.2 Hz), 125.9, 124.8, 123.1, 114.4, 109.3, 104.1 (q, *J* = 3.8 Hz), 33.5, 30.7 (q, *J* = 30.9 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2949, 1611, 1551, 1480, 1458, 1421, 1357, 1335, 1257, 1126, 1089, 1018, 910, 843, 817, 772, 735, 697 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{10}BrF_3N$: 291.9943; found 291.9955.

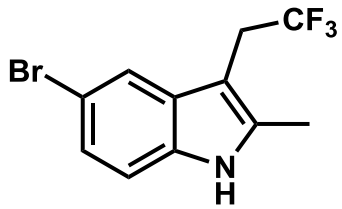


4-Bromo-2-ethyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3bb): In a 4 mL vial 4-bromo-2-ethyl-1*H*-indole (112 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The mixture was stirred at room temperature for 10 minutes. Following general procedure the mixture was purified by column chromatography with gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1→ 7:1). The product was obtained as white solid (137 mg, 0.45 mmol, 90%). M.p. 85-86 °C. R_f = 0.45 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 306 (58%), 292 (24%), 237 (100%), 222 (24%), 176 (18%), 156 (24%), 141 (8%), 128 (10%), 115 (14%), 101 (6%), 74 (8%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.96 (s, 1H), 7.16 (dd, *J* = 5.0 Hz, 7.5 Hz, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 3.82 (q, *J* = 10.0 Hz, 2H), 2.69 (q, *J* = 7.5 Hz, 2H), 1.20 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 142.0, 136.8, 126.7 (q, *J* = 278.5 Hz), 126.5, 125.3, 122.7, 113.6, 110.4, 100.9 (q, *J* = 3.8 Hz), 29.4 (q, *J* = 30.9 Hz), 19.5, 13.6. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -65.4. IR (ATR) 2980, 1555, 1458, 1428, 1365, 1305, 1253, 1126, 1096, 1055, 917, 832, 764, 742, 649 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{12}H_{12}{}^{79}BrF_3N$: 306.0105; found 306.0104.

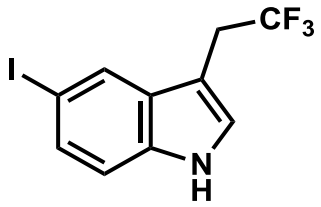


5-Bromo-3-(2,2,2-trifluoroethyl)-1*H*-indole (3cc): In a 4 mL vial 5-bromo-1*H*-indole (98 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 3 hours. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 10:1 to 7:1) to give the product as white solid (117 mg, 0.42 mmol, 84%). M.p. 92 °C. R_f = 0.25 (hexane: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 279 (60%), 277 (60%), 260(5%), 258 (5%), 210 (100%), 208 (100%), 197 (10%), 148 (30%), 129 (55%), 102 (28%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.06 (s, 1H), 7.64 (s, 1H), 7.24 – 7.06 (m, 3H), 3.39 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 135.0, 129.5, 126.4 (q, *J* = 277.2 Hz), 125.9, 125.8, 121.8, 113.9, 113.2, 105.0 (q, *J* = 3.8 Hz), 30.8 (q, *J* = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -

66.1. IR (ATR) 2924, 1648, 1462, 1443, 1369, 1260, 1130, 1093, 1063, 906, 861, 798, 738, 679 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{10}H_8{}^{79}BrF_3N$: 277.9792; found 277.9790.

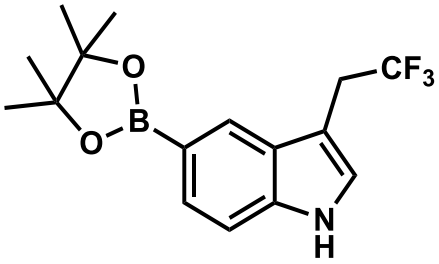


5-Bromo-2-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3dd): In a 4 mL vial 5-bromo-2-methyl-1*H*-indole (105 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 20 minutes. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 10:1 to 4:1) to give the product as white solid (129 mg, 0.44 mmol, 88%). M.p. 100 °C. R_f = 0.15 (hexane: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 293 (60%), 291 (60%), 224 (100%), 222 (100%), 162 (15%), 143 (15%), 115 (15%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.81 (s, 1H), 7.52 (s, 1H), 7.12 (dd, *J* = 7.5, 2.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 3.30 (q, *J* = 10.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 136.1, 134.1, 130.9, 126.8 (q, *J* = 277.8 Hz), 124.7, 120.9, 113.6, 112.2, 101.1 (q, *J* = 3.2 Hz), 29.8 (q, *J* = 31.5 Hz), 12.0. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.0. IR (ATR) 2935, 2185, 1633, 1469, 1432, 1365, 1305, 1260, 1130, 966, 865, 832, 794, 690 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{11}H_{10}{}^{79}BrF_3N$: 291.9949; found 291.9945.



5-Iodo-3-(2,2,2-trifluoroethyl)-1*H*-indole (3ee): In a 4 mL vial 5-iodo-1*H*-indole (122 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 μL, 1.00 mmol) was added. The mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction mixture was stirred at room temperature for 3 hours. Following general procedure the product was purified by column chromatography (hexanes: ethyl acetate = 10:1) to give the product as a white solid (132 mg, 0.41 mmol, 81%). M.p. 74 °C. R_f = 0.35 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 325 (100%), 256 (92%), 207 (30%), 129(55%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.16 (s, 1H), 7.95 (s, 1H), 7.49 (dd, *J* = 7.5 Hz, 2.5 Hz, 1H), 7.17 – 7.14 (m, 2H), 3.49 (q, *J* = 10.0 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 135.4, 131.3, 130.3, 128.1, 126.4 (q, *J* = 277.2 Hz), 125.4, 113.6, 104.7 (q, *J* = 3.2 Hz),

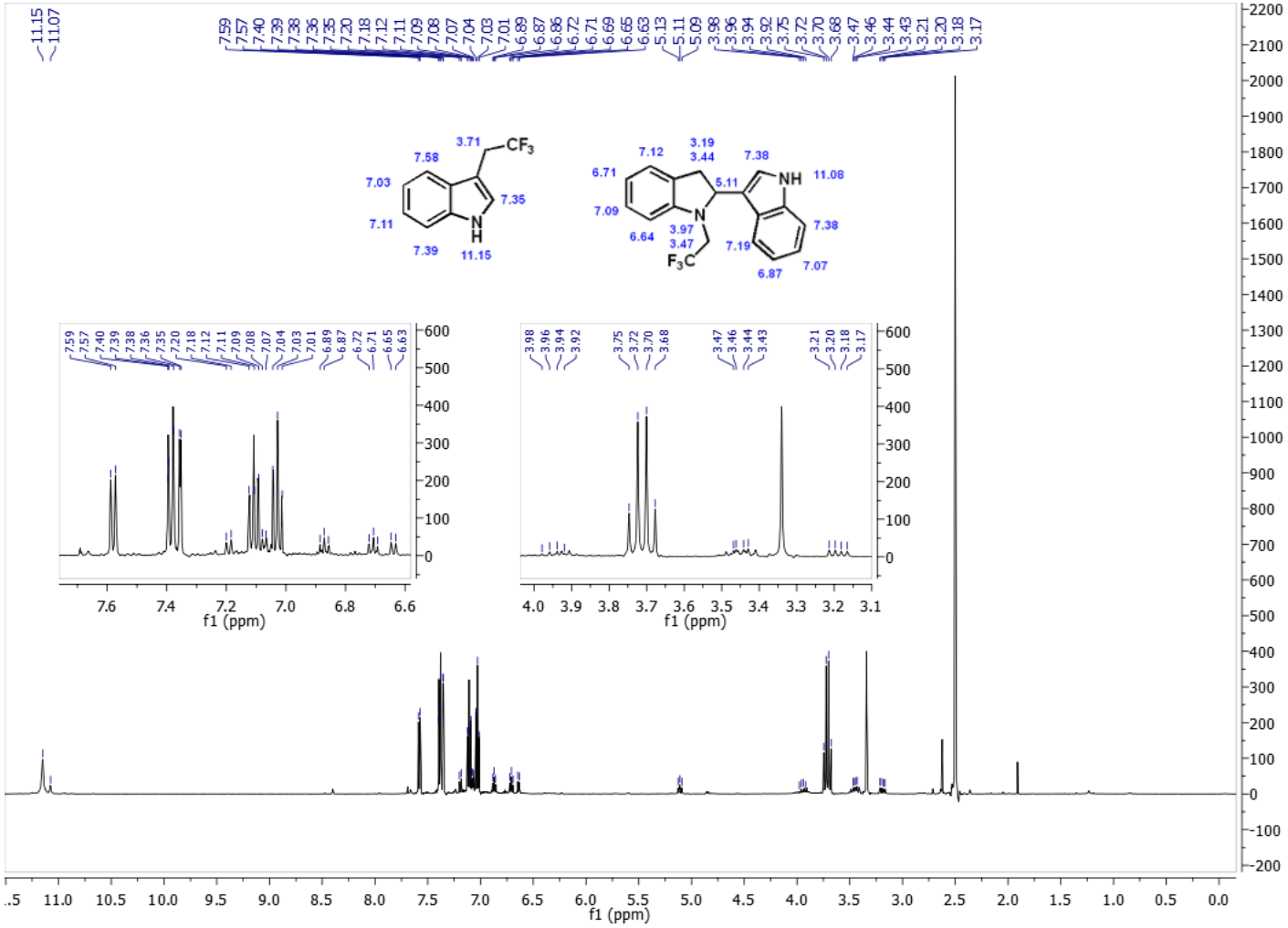
84.0, 30.8 (q, J = 31.5 Hz). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2942, 2920, 1458, 1443, 1425, 1365, 1260, 1242, 1126, 1093, 1055, 910, 869, 798, 783, 679 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{10}H_8F_3IN$: 325.9654; found 325.9649.



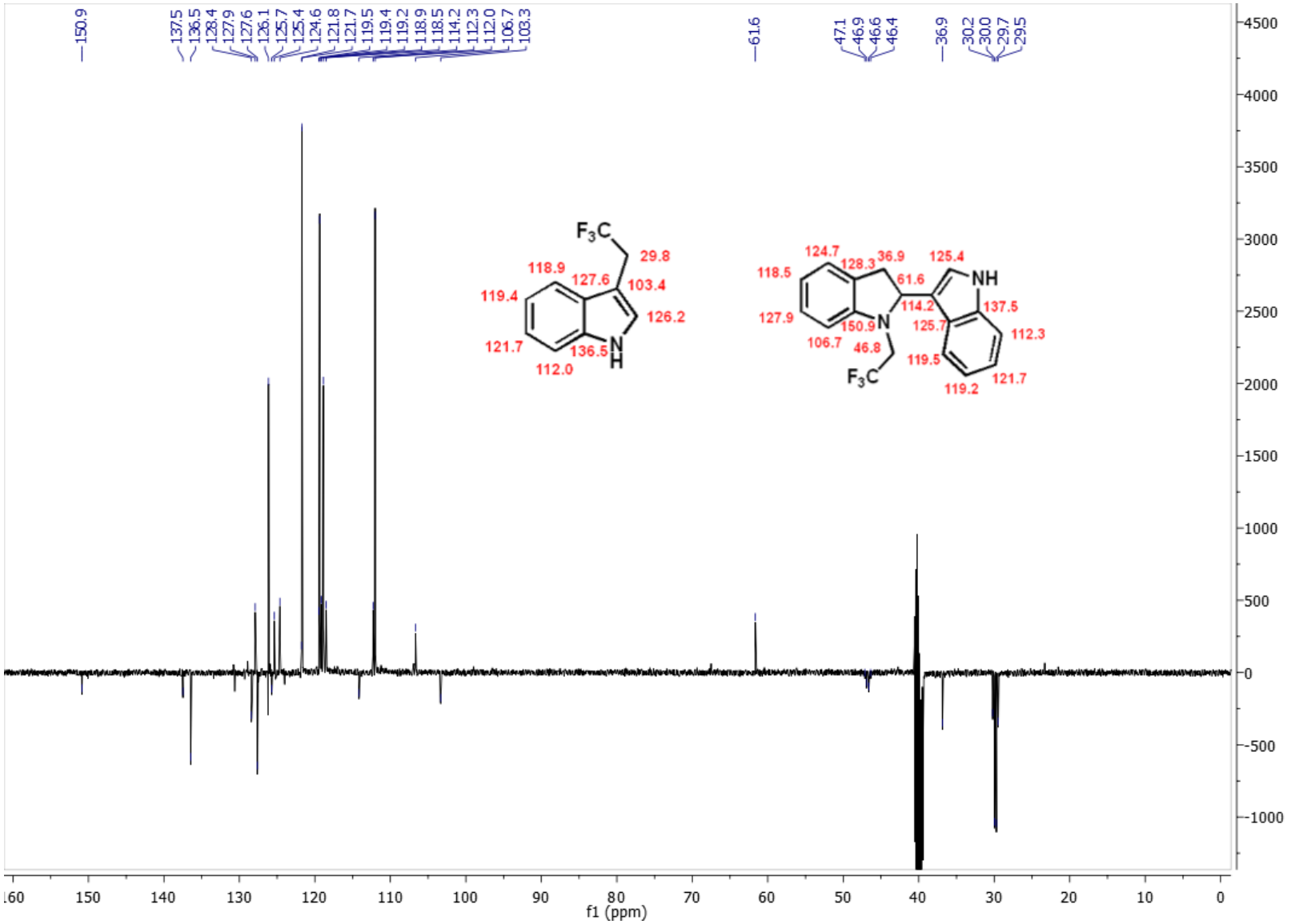
5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(2,2,2-trifluoroethyl)-1*H*-indole (3ff): In a 4 mL vial 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (122 mg, 0.500 mmol) was dissolved in dichloromethane (2.5 mL) and 2,6-di-*tert*-butylpyridine (225 µL, 1.00 mmol) was added and the mixture was stirred for 5 minutes. Then 2,2,2-trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (311 mg, 0.650 mmol) was added. The reaction was stirred at room temperature for 4 hours. Following general procedure the product was purified by column chromatography using gradient elution (hexanes: ethyl acetate, 100:1 → 50:1 → 25:1 → 15:1 → 10:1→ 7:1). The product was obtained as a white solid (135 mg, 0.42 mmol, 83%). M.p. 98-99 °C. R_f = 0.32 (hexanes: ethyl acetate = 5:1). MS (EI, 70 eV): *m/z* (%): 325 (44%), 310 (12%), 239 (38%), 225 (74%), 156 (100%), 130 (12%), 85 (11%), 77 (15%), 57 (12%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.31 (s, 1H), 8.15 (s, 1H), 7.70 (d, J = 10.0 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.16 (s, 1H), 3.57 (q, J = 10.0 Hz, 2H), 1.40 (s, 12H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 138.4, 129.0, 127.5, 126.7, 126.6 (q, J = 276.6 Hz), 124.5, 124.4, 111.1, 105.8 (q, J = 3.2 Hz), 84.0, 30.7 (q, J = 30.9 Hz), 25.3. ^{19}F NMR (235 MHz, $CDCl_3$) δ = -66.1. IR (ATR) 2983, 1618, 1484, 1428, 1354, 1264, 1134, 1100, 1074, 962, 914, 858, 809, 735, 694 cm^{-1}. HRMS m/z $[M+H]^+$ Calculated for $C_{16}H_{20}BF_3NO_2$: 326.1539; found 326.1536.

8. NMR Spectra

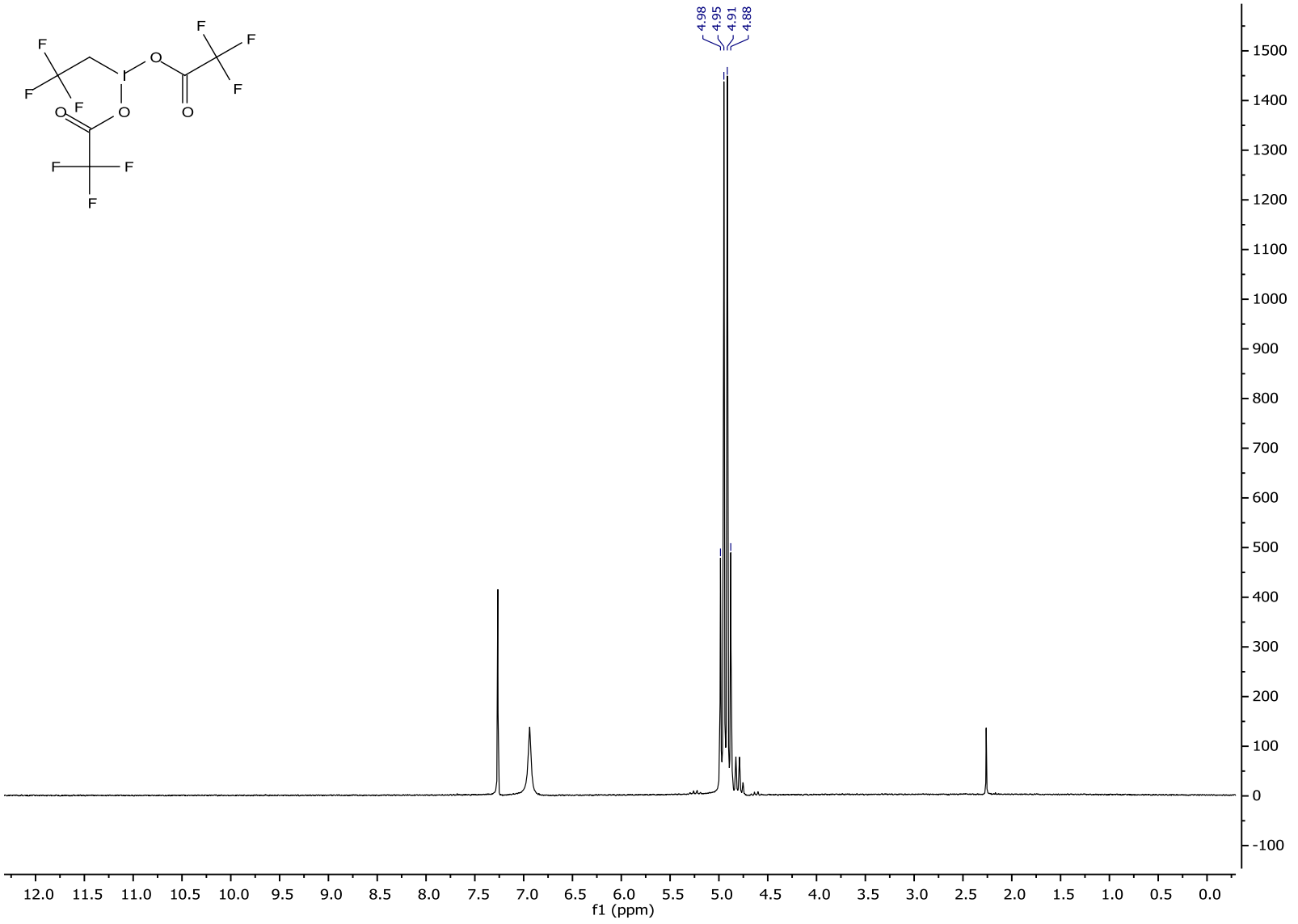
Stucture identification of 3-(2,2,2)-Trifluoroethylated indole and the side-product (^{1}H)

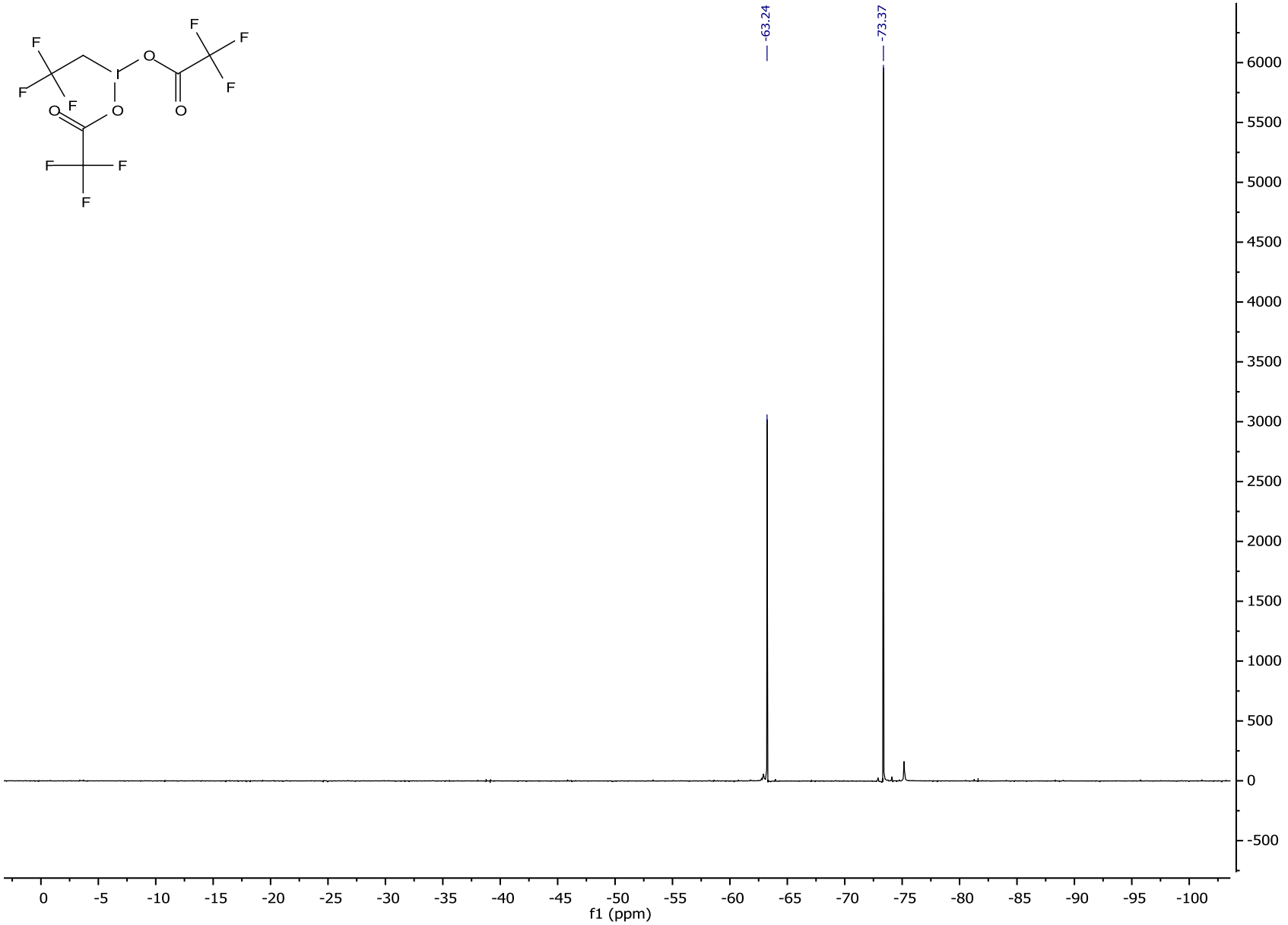


Stucture identification of 3-(2,2,2)-Trifluoroethylated indole and the side-product (^{13}C)

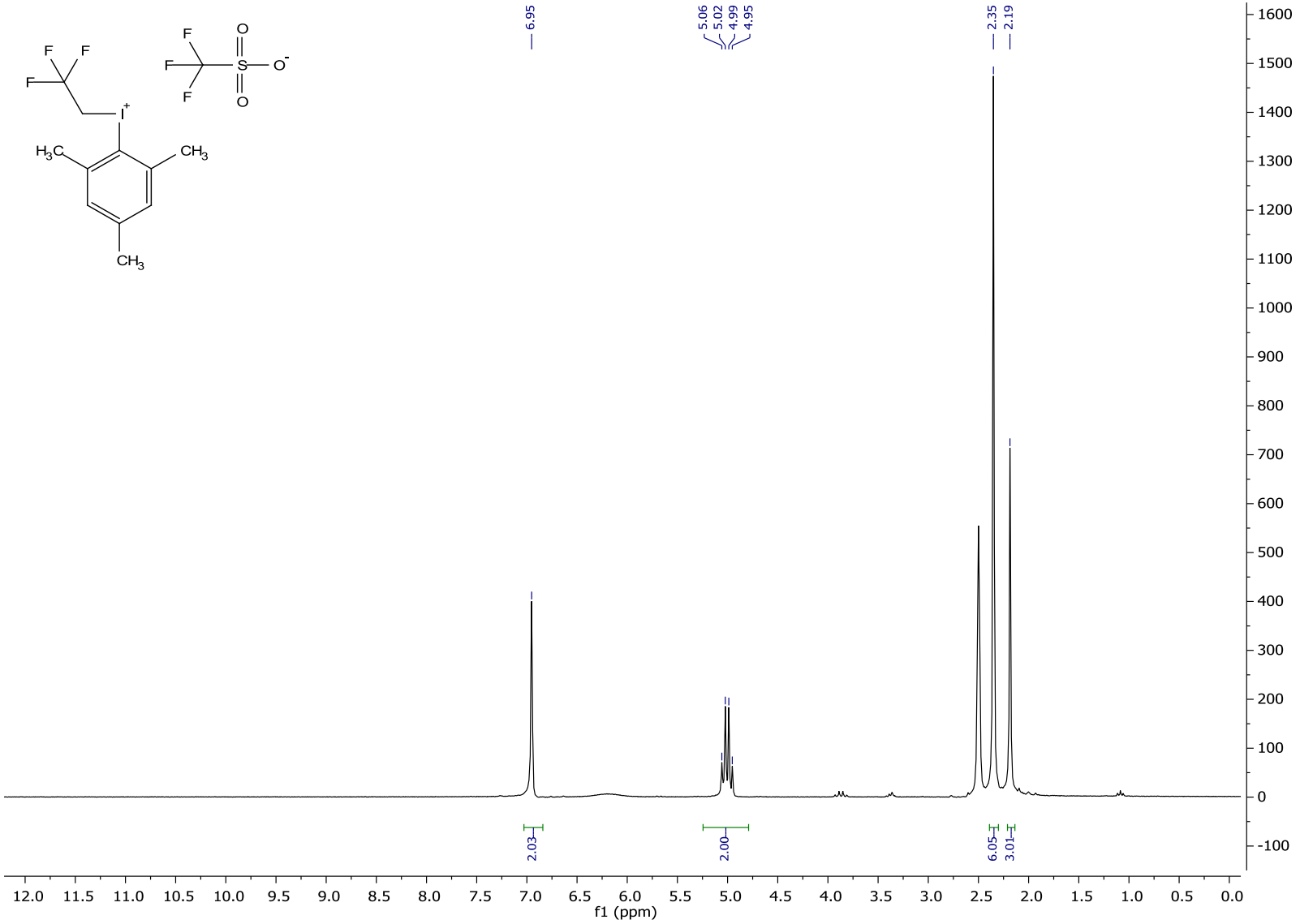


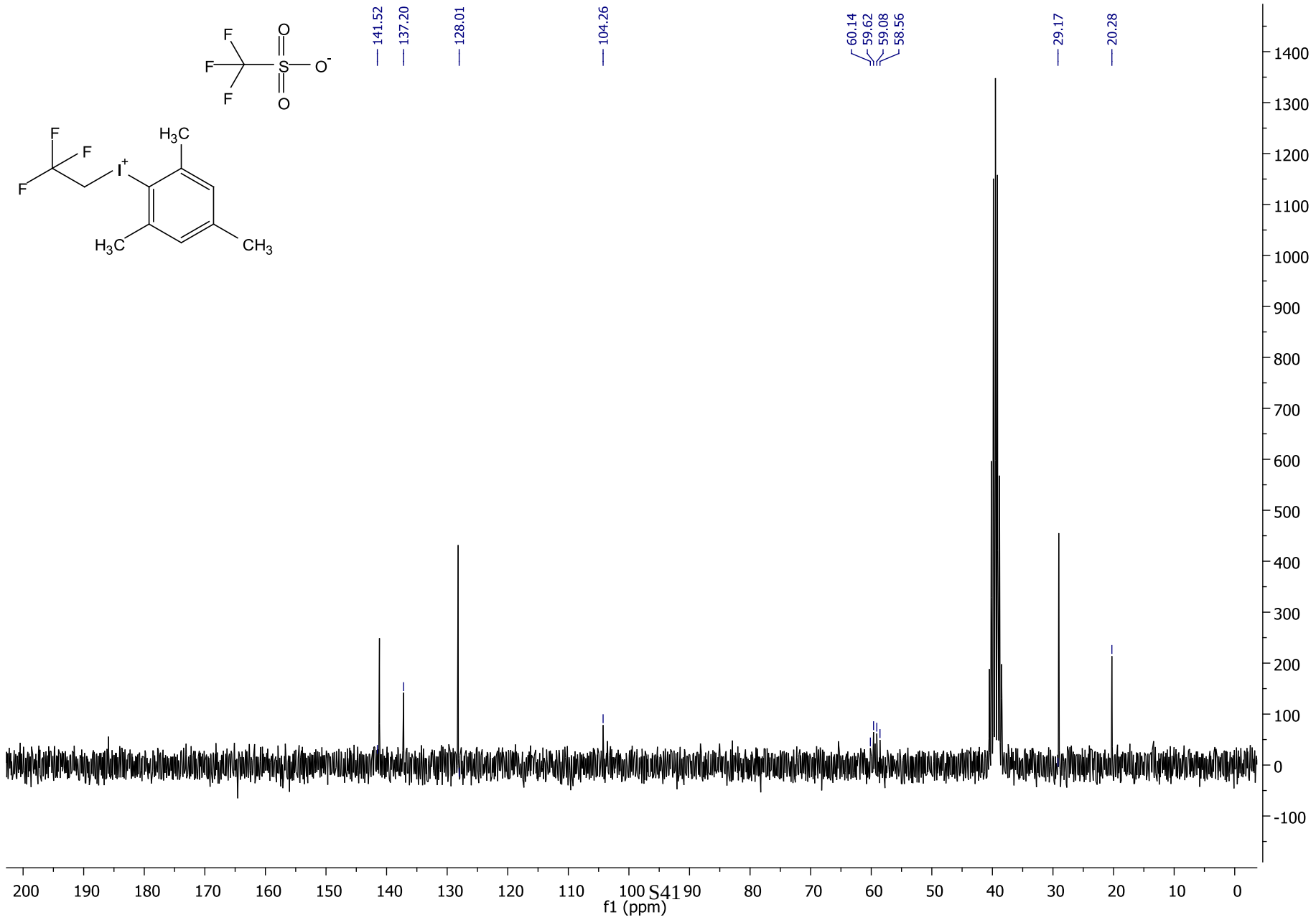
(2,2,2-Trifluoroethyl)-λ^3-iodanediyl bis(2,2,2-trifluoroacetate)

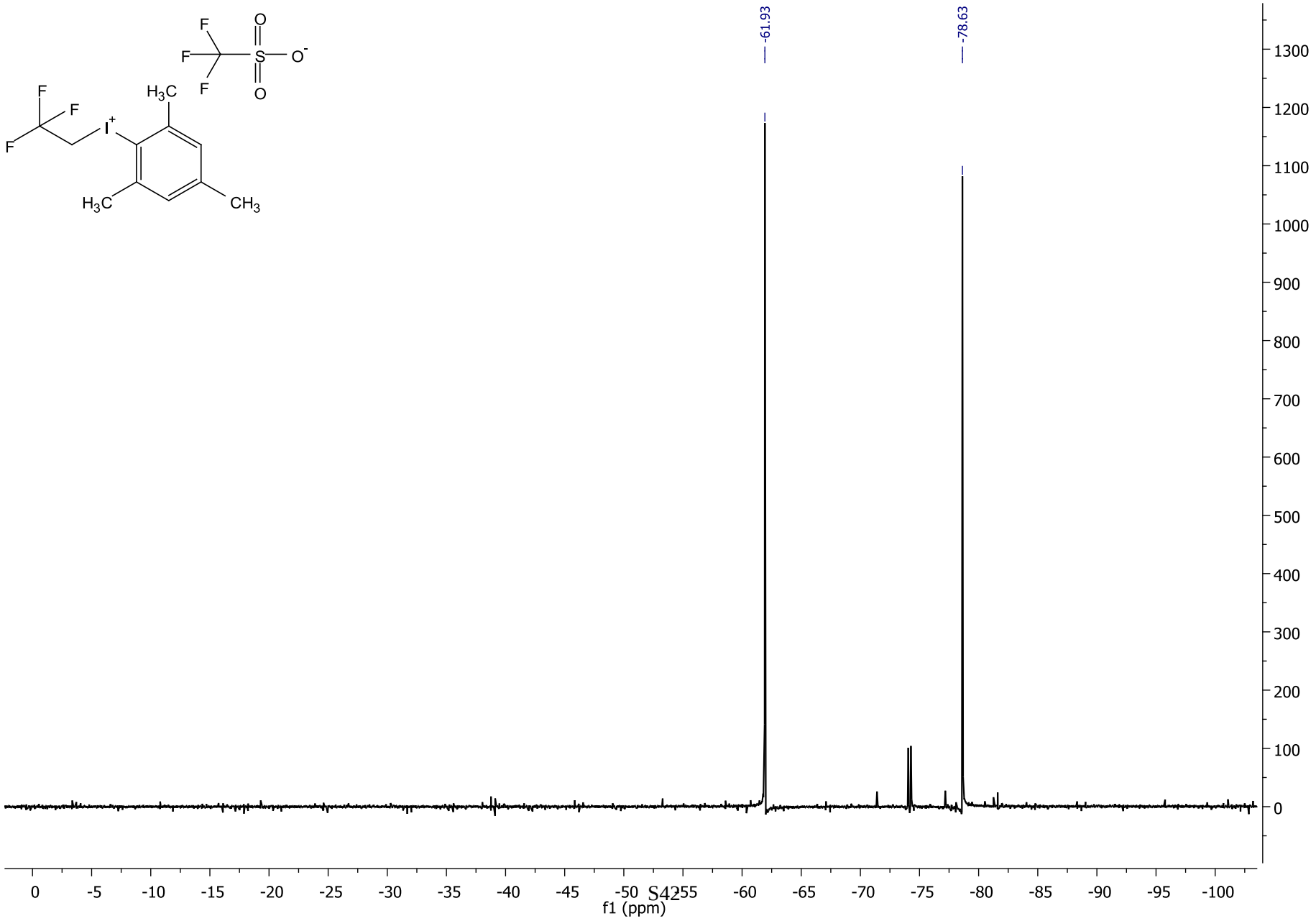



-63.24
-73.37
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

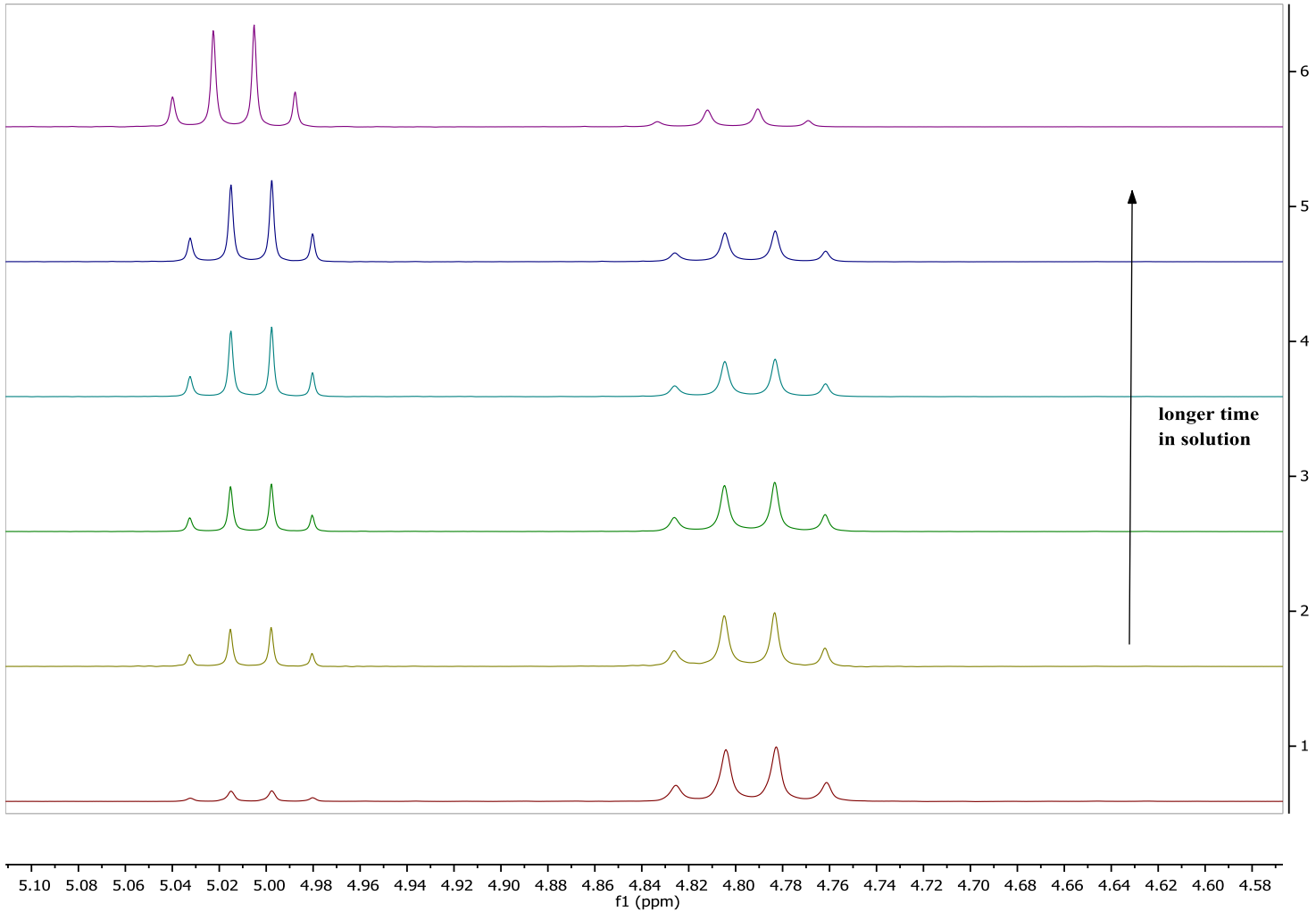
2,2,2-Trifluoroethyl(mesityl)iodonium trifluoromethanesulfonate (1a)



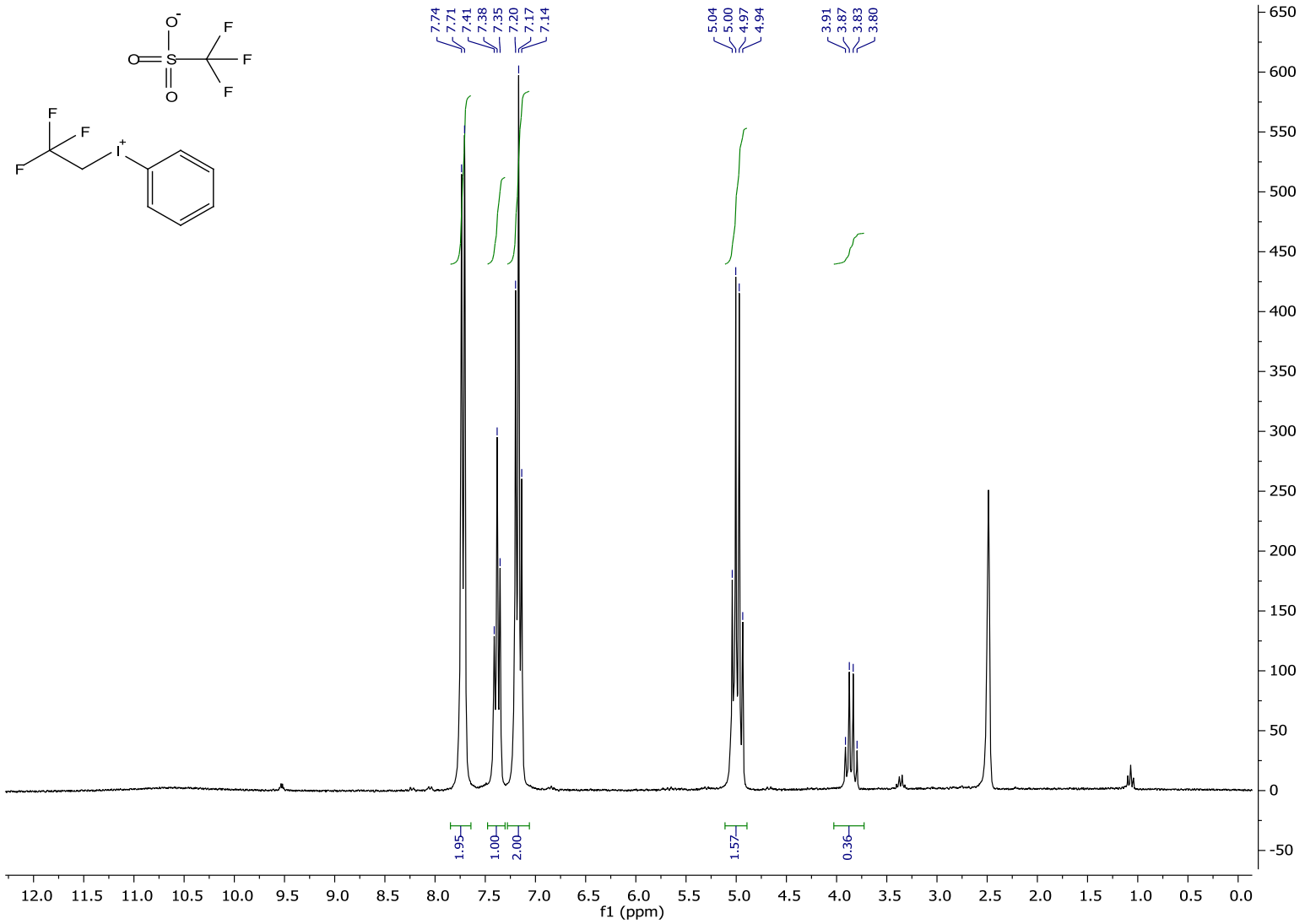

141.52
137.20
128.01
104.26
60.14
59.62
59.08
58.56
29.17
20.28
f1 (ppm)

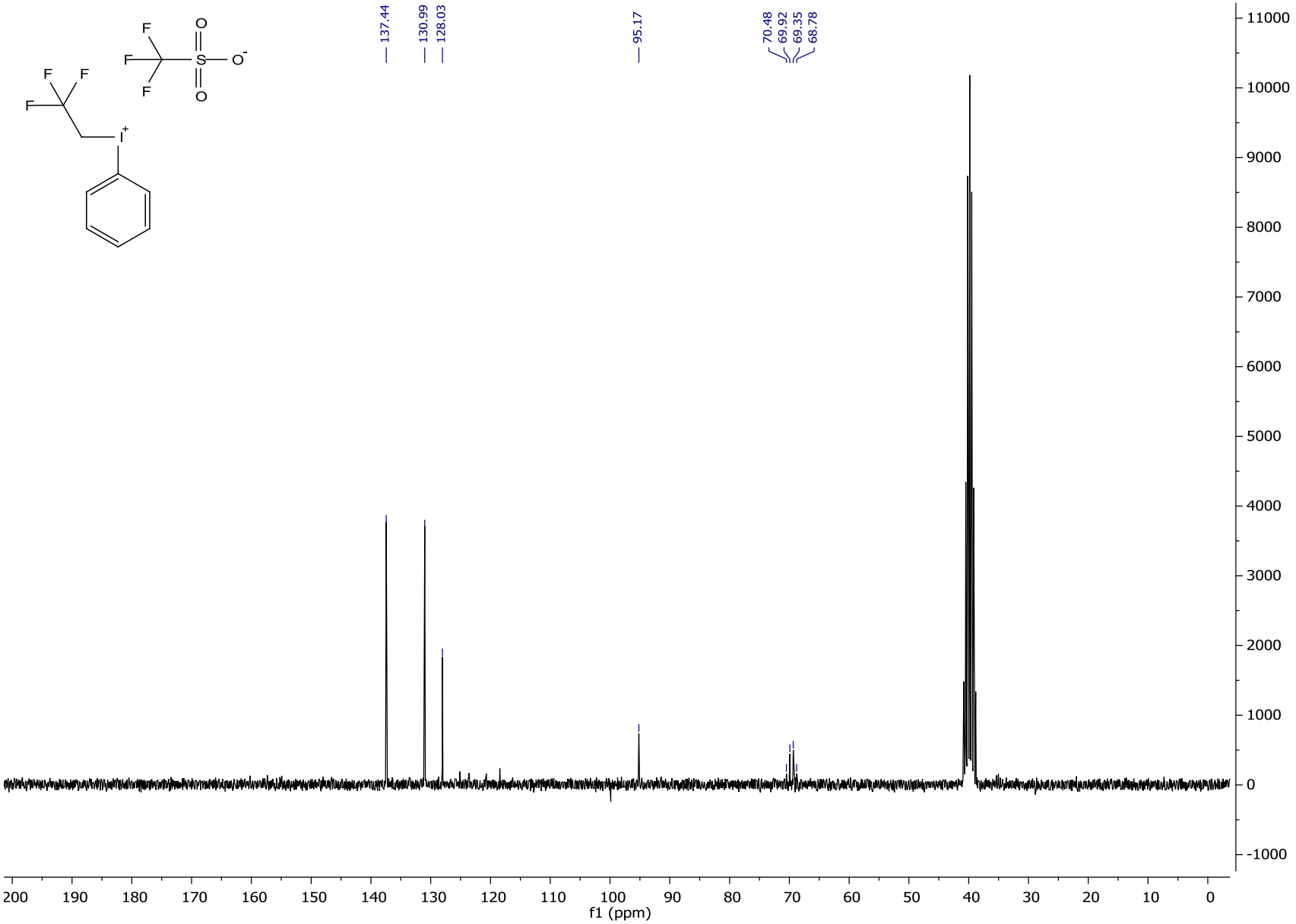

-61.93
-78.63
f1 (ppm)

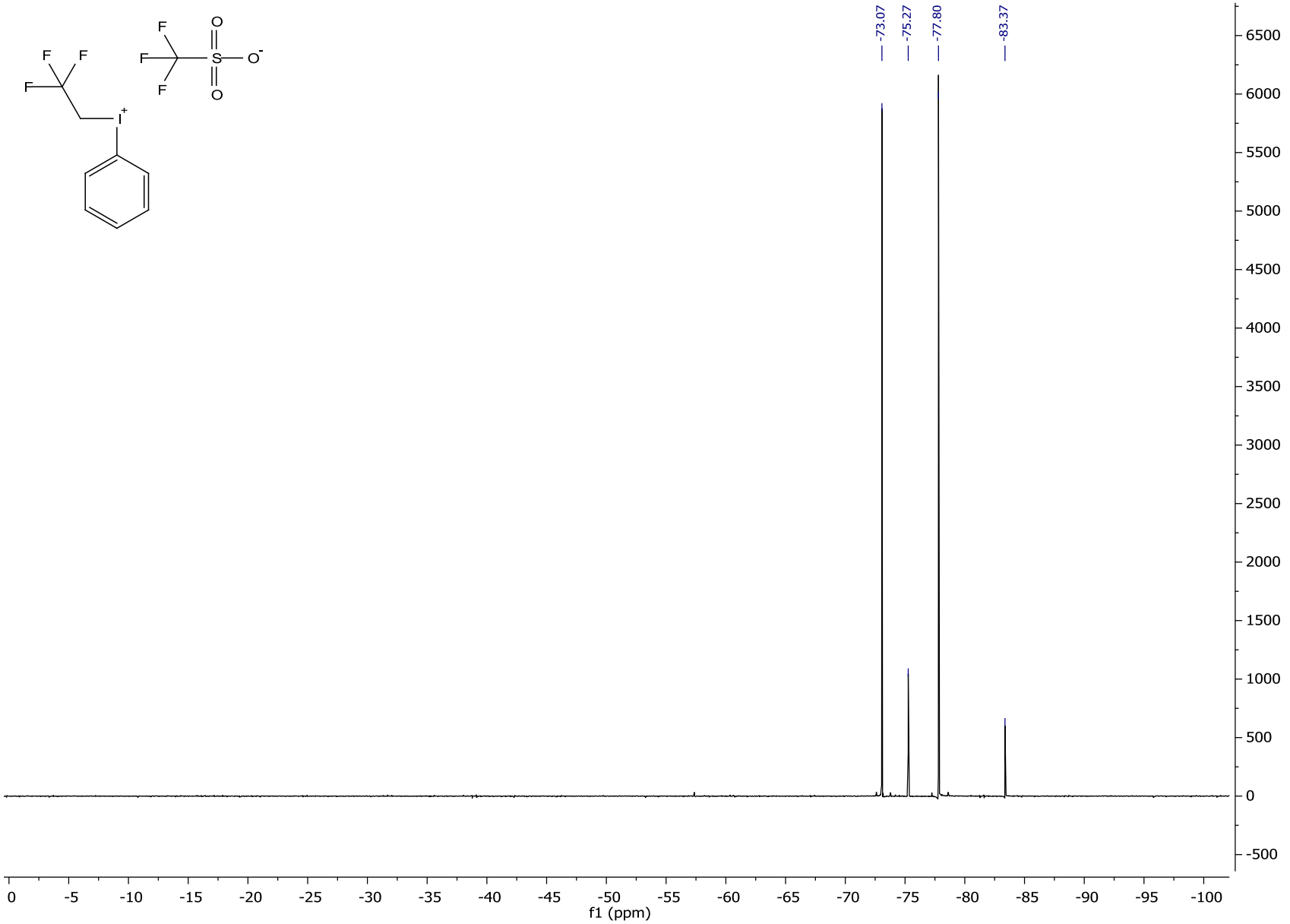
The enhanced reactivity of the iodonium salt is due to their decomposition in solution. The NMR spectra below shows the decomposition with time, which can be observed by the decreasement of the methylene quartet at 4.80 ppm and the enlargement of the quartet at 5.00 ppm. This decomposition leads to a trifluoroethylated derivative, which we could not identify.



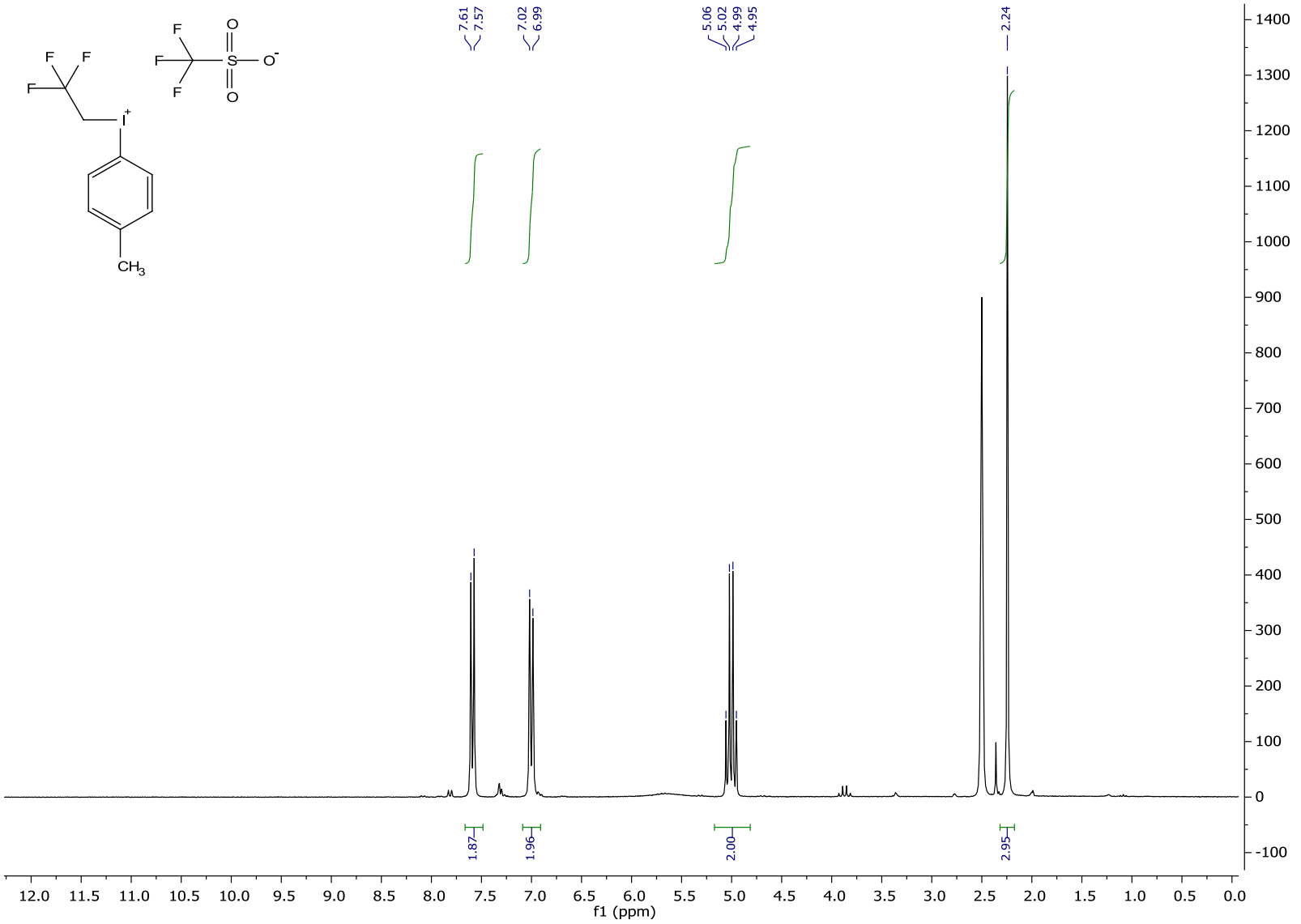
2,2,2-Trifluoroethyl(phenyl)iodonium trifluoromethanesulfonate (1b)

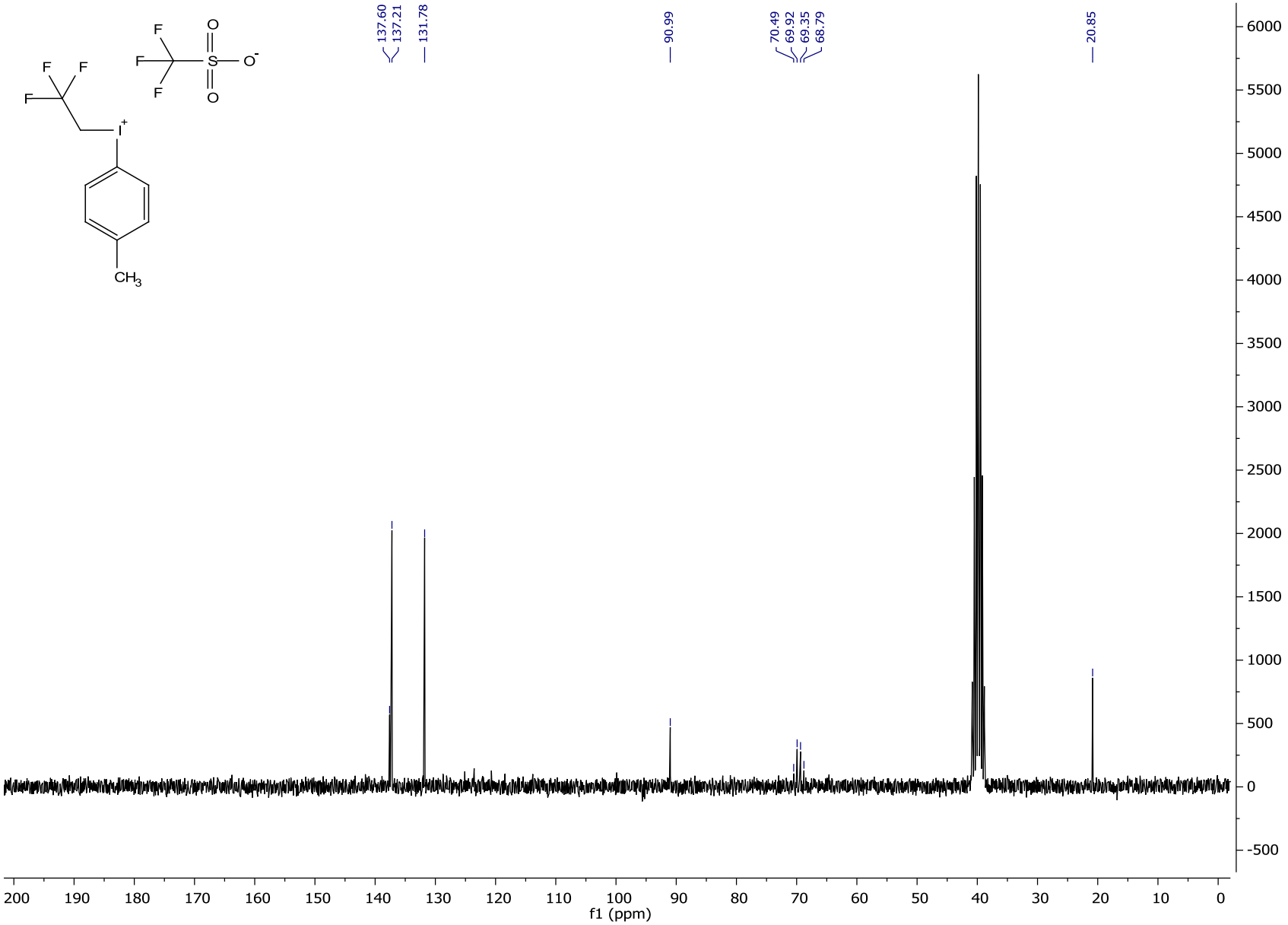


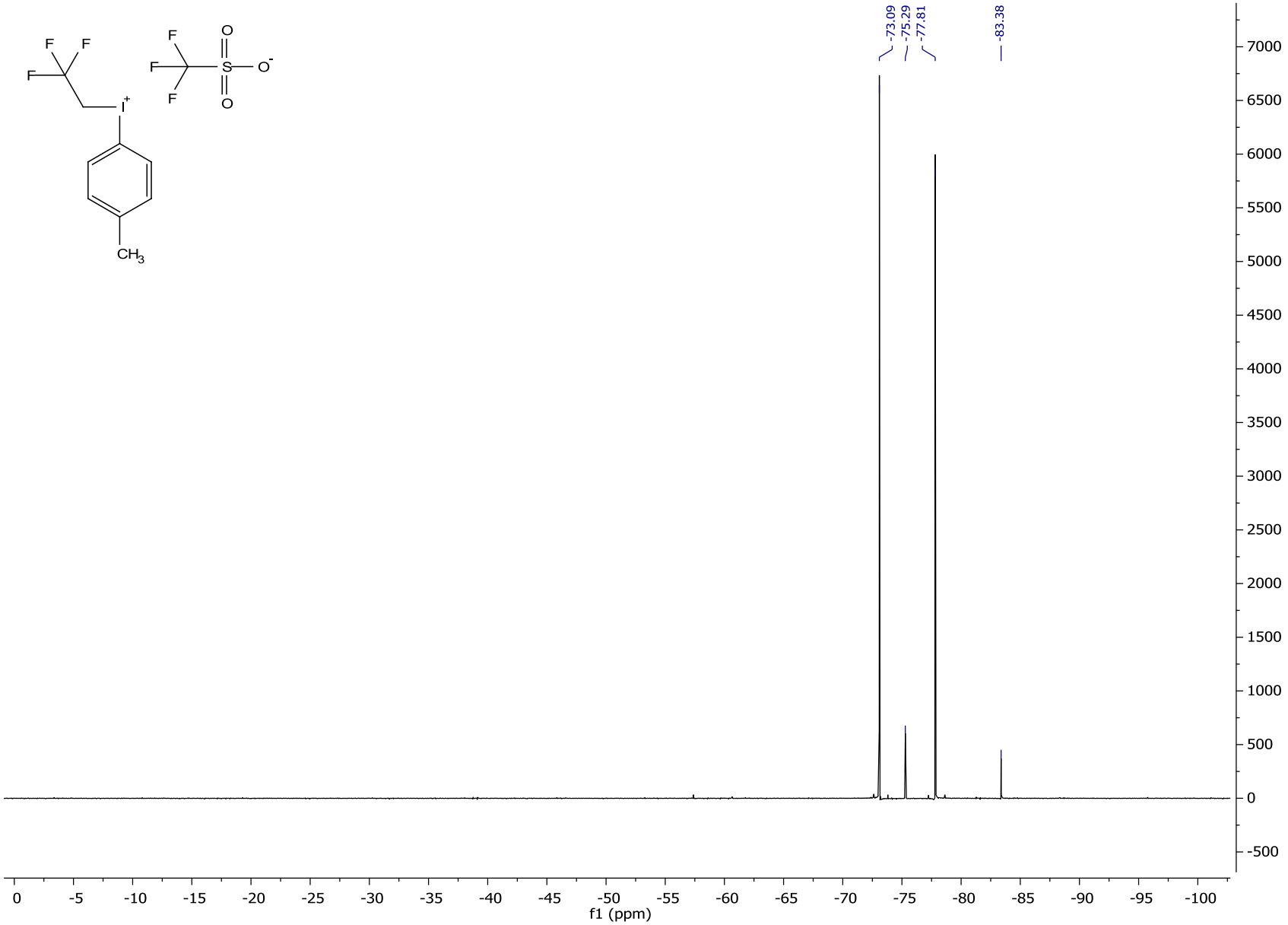

137.44
130.99
128.03
95.17
70.48
69.92
69.35
68.78
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
I+
F
F
F
S
O
O
O-
-73.07
-75.27
-77.80
-83.37
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

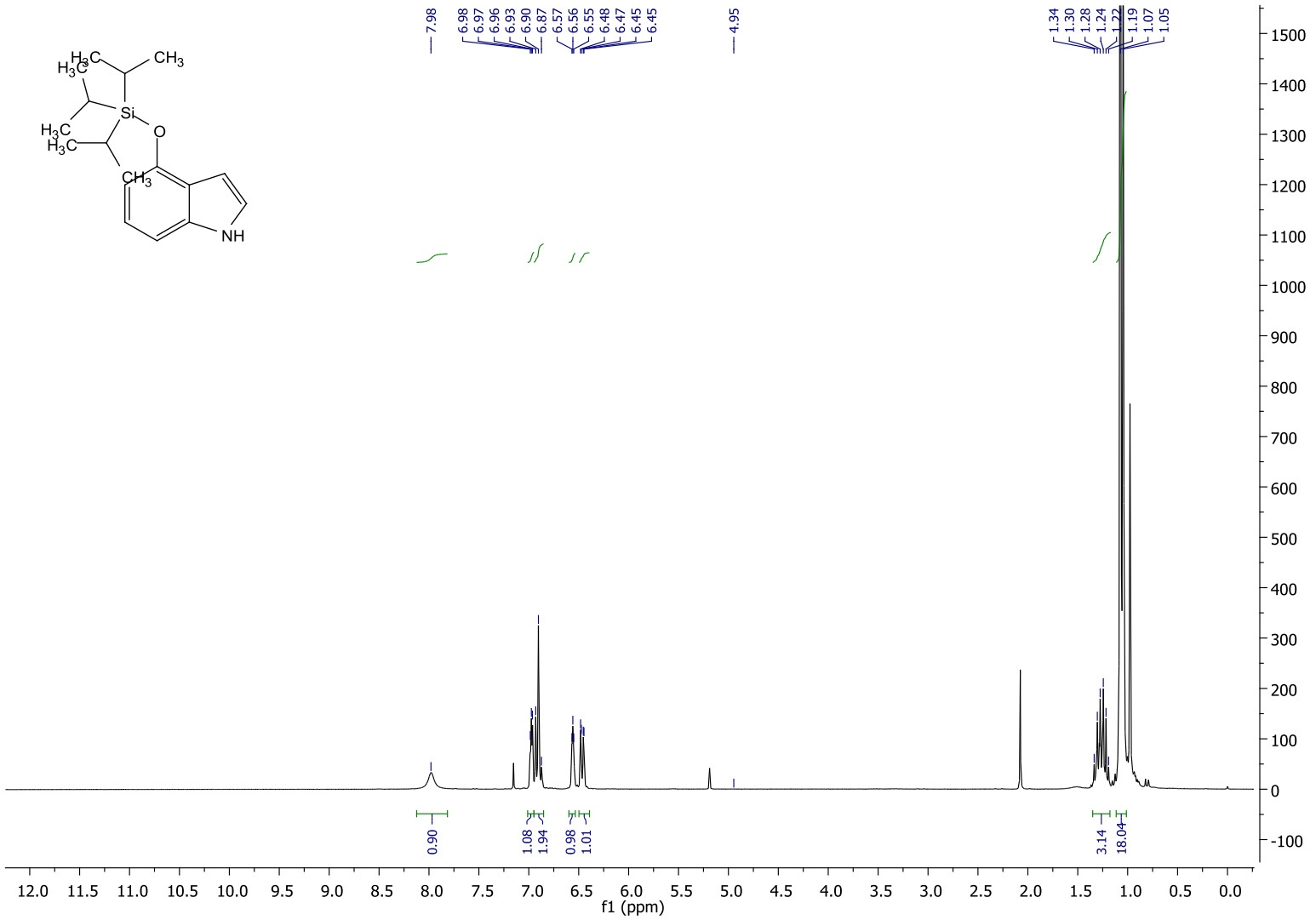
2,2,2-Trifluoroethyl(tollyl)iodonium trifluoromethanesulfonate (1c)

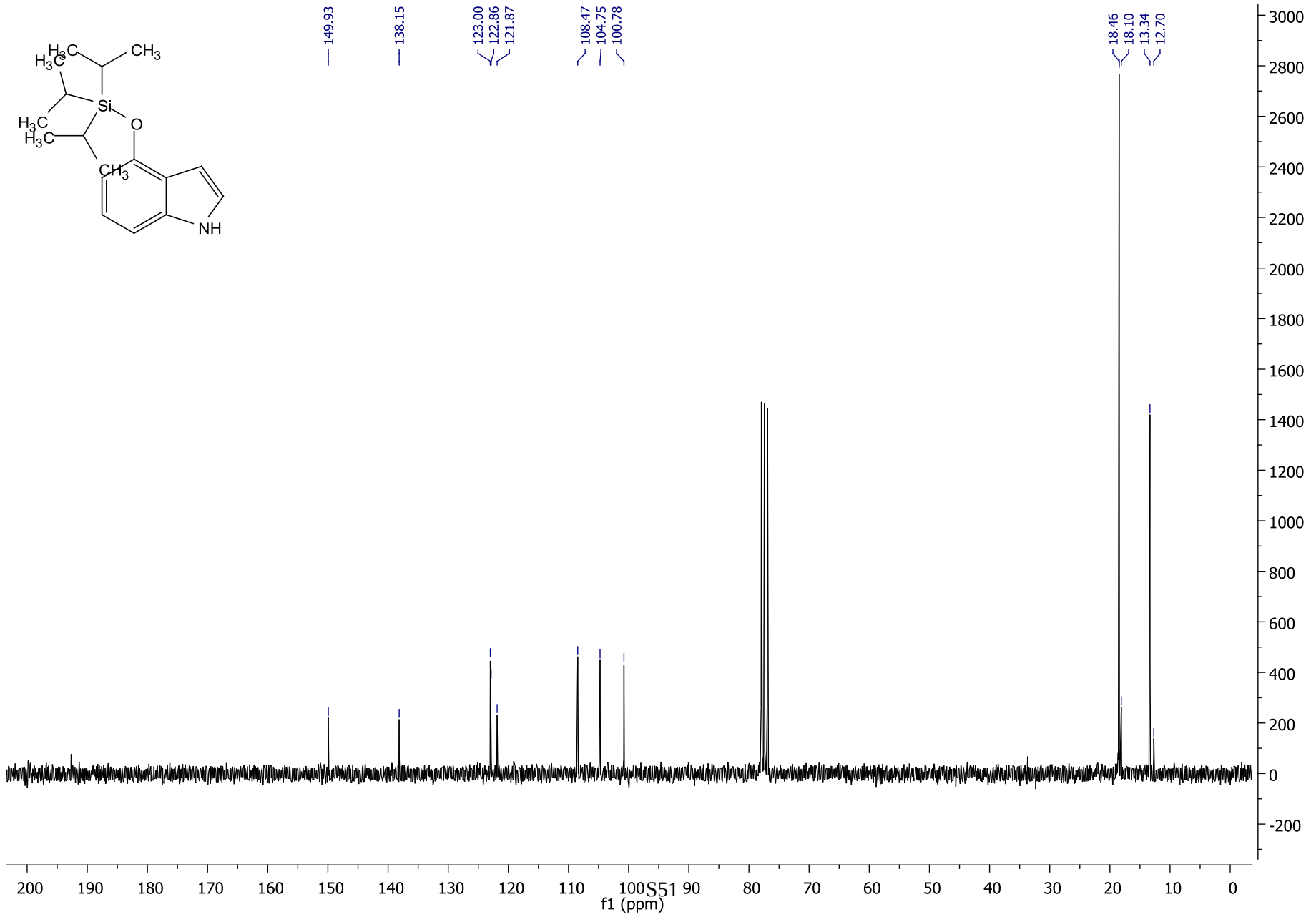



137.60
137.21
131.78
90.99
70.49
69.92
69.35
68.79
20.85
f1 (ppm)

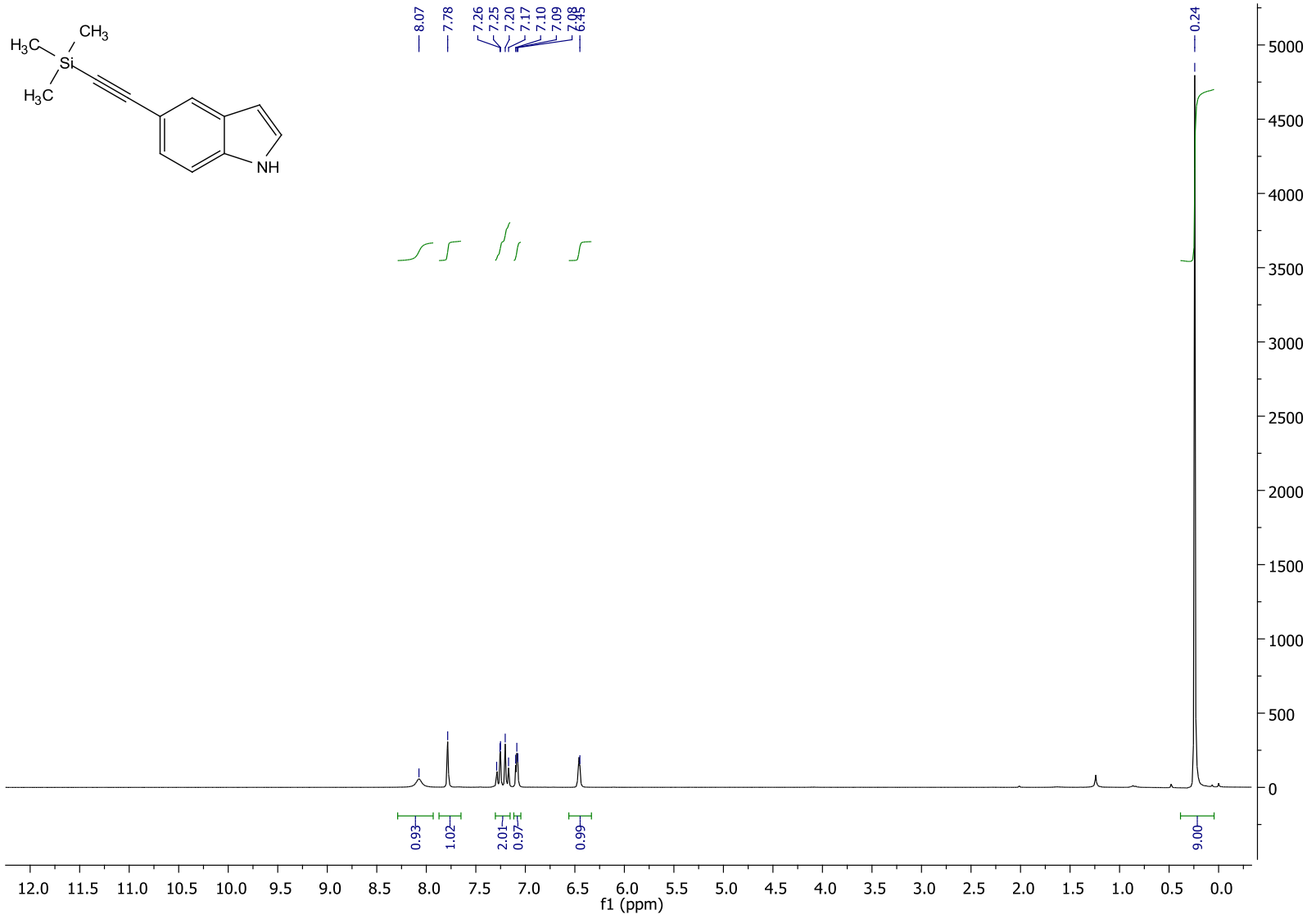

F
F
F
I+
CH3
F
F
F
S
O
O
O-
-73.09
-75.29
-77.81
-83.38
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

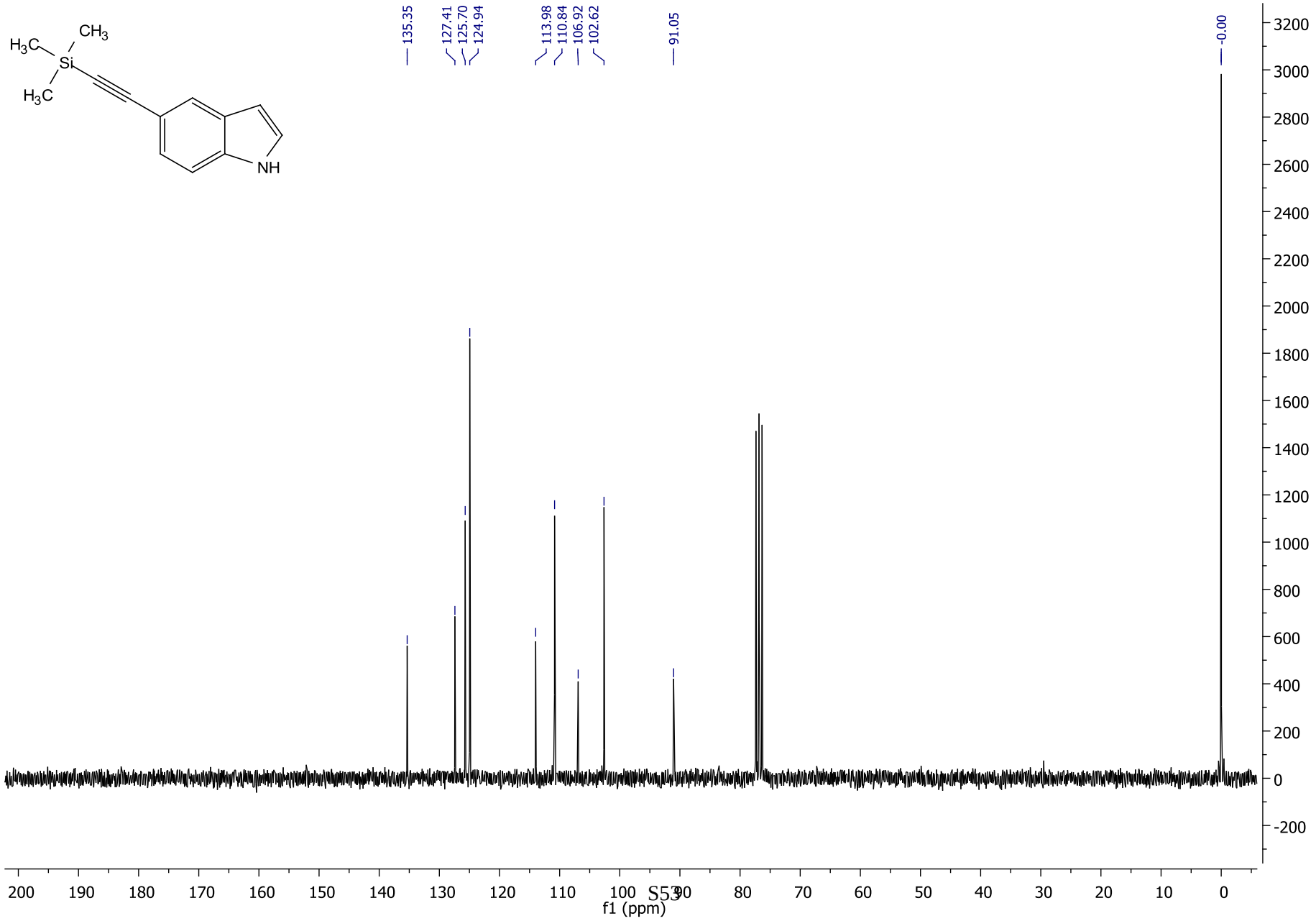
4-((Triisopropylsilyl)oxy)-1*H*-indole



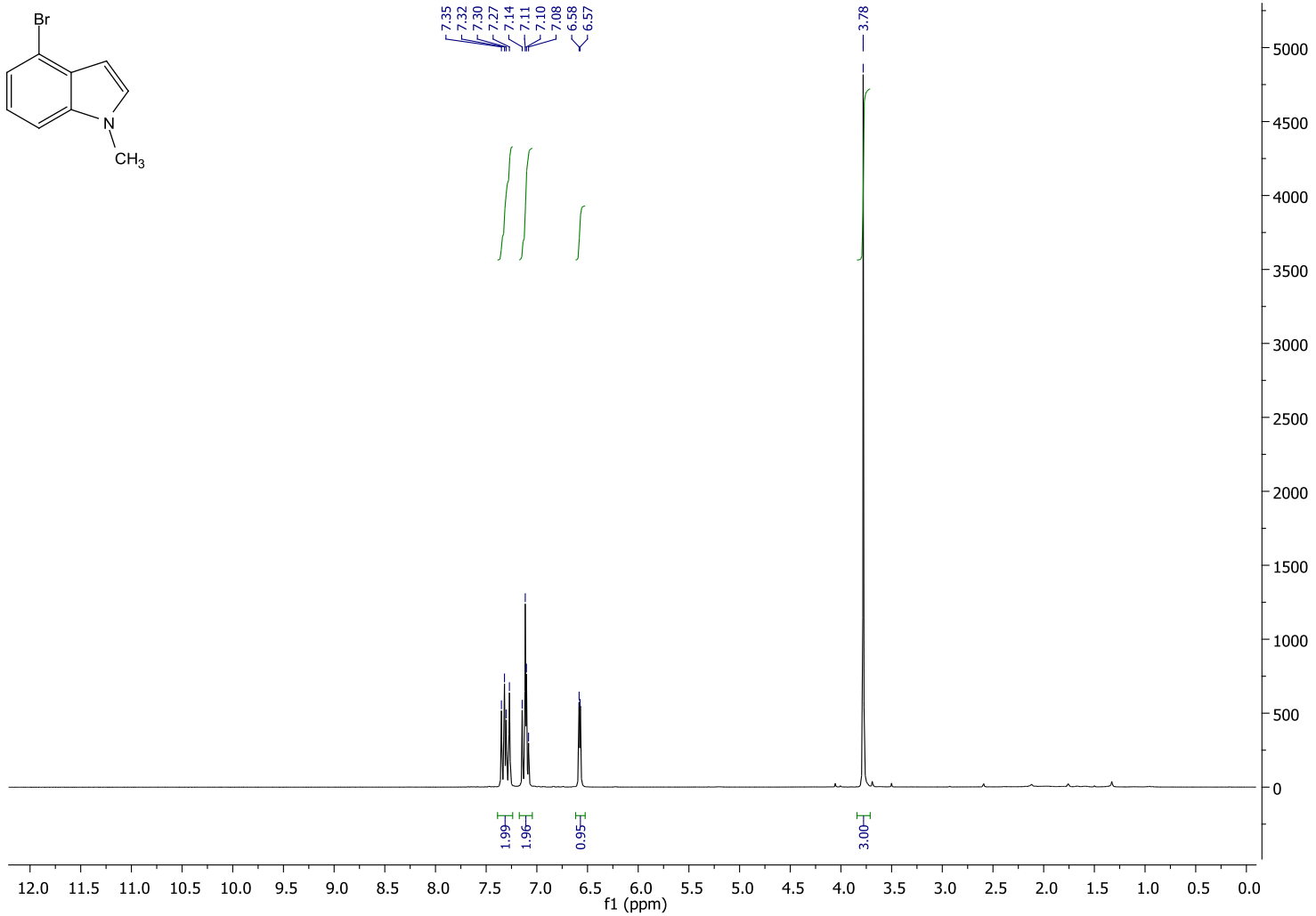

149.93
138.15
123.00
122.86
121.87
108.47
104.75
100.78
18.46
18.10
13.34
12.70
H3C
CH3
H3C
Si
O
H3C
CH3
NH
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

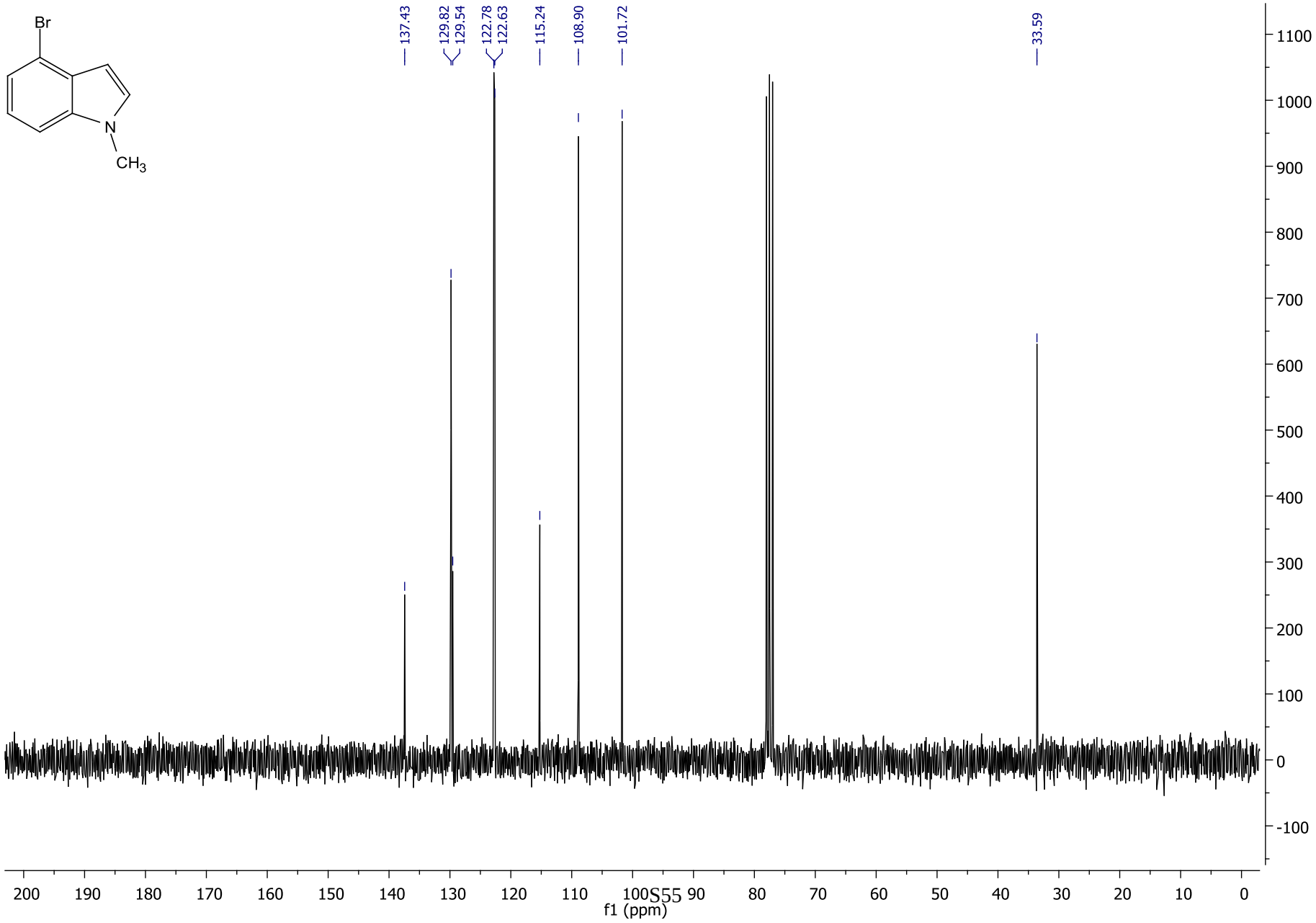
5-((Trimethylsilyl)ethynyl)-1*H*-indole



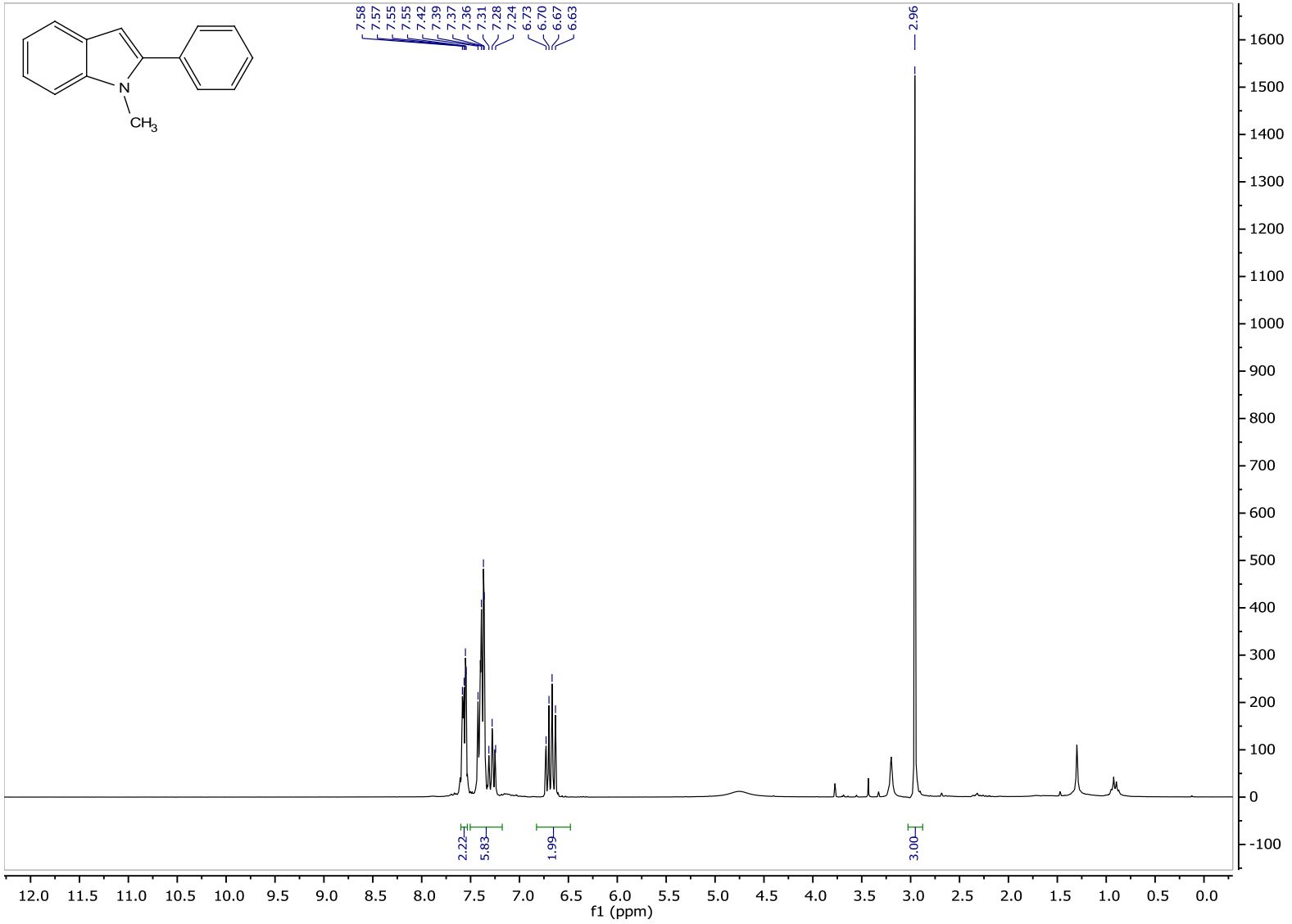

135.35
127.41
125.70
124.94
113.98
110.84
106.92
102.62
91.05
0.00
CH3
H3C
Si
H3C
NH
f1 (ppm)

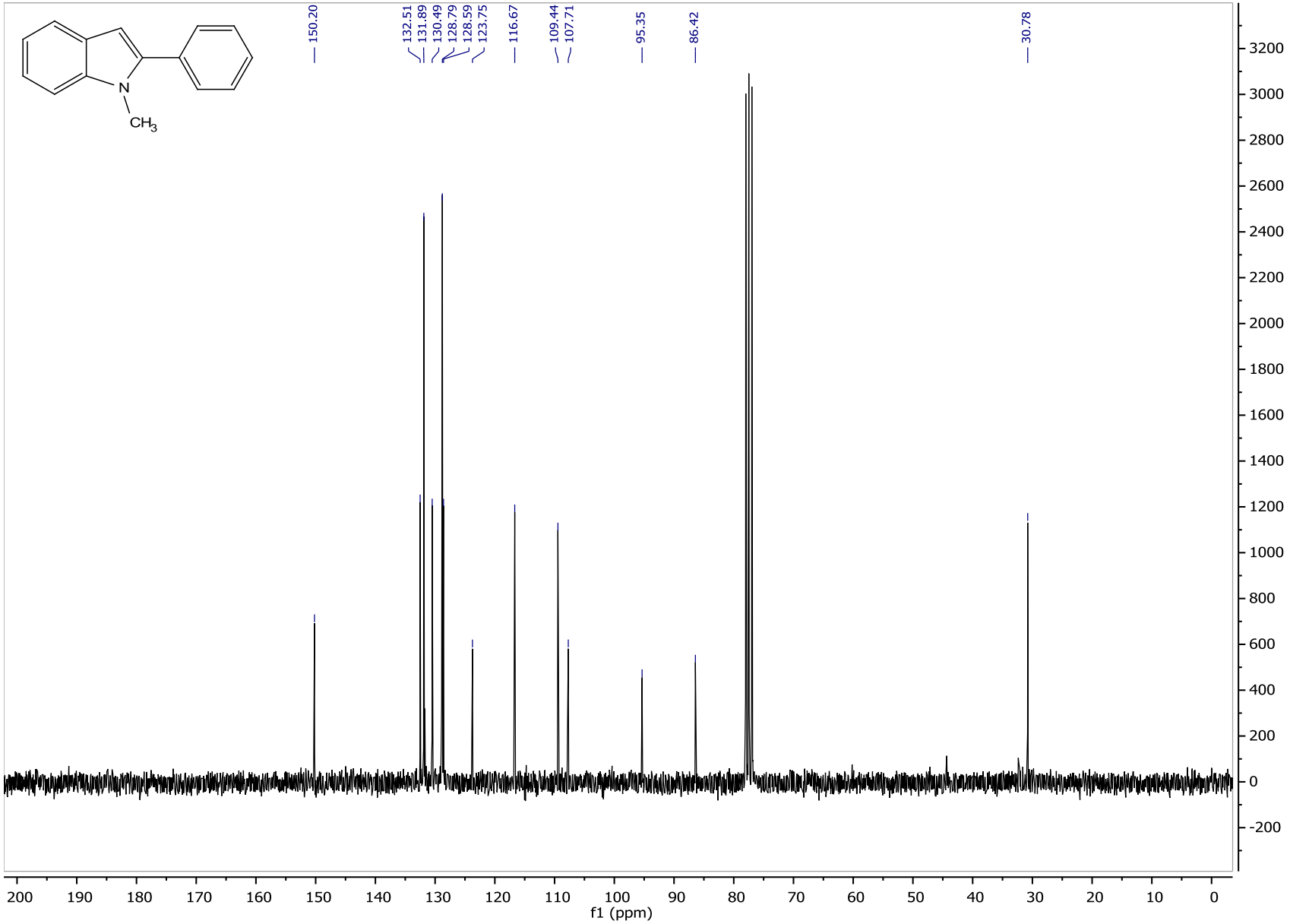
4-Bromo-1-methyl-1*H*-indole



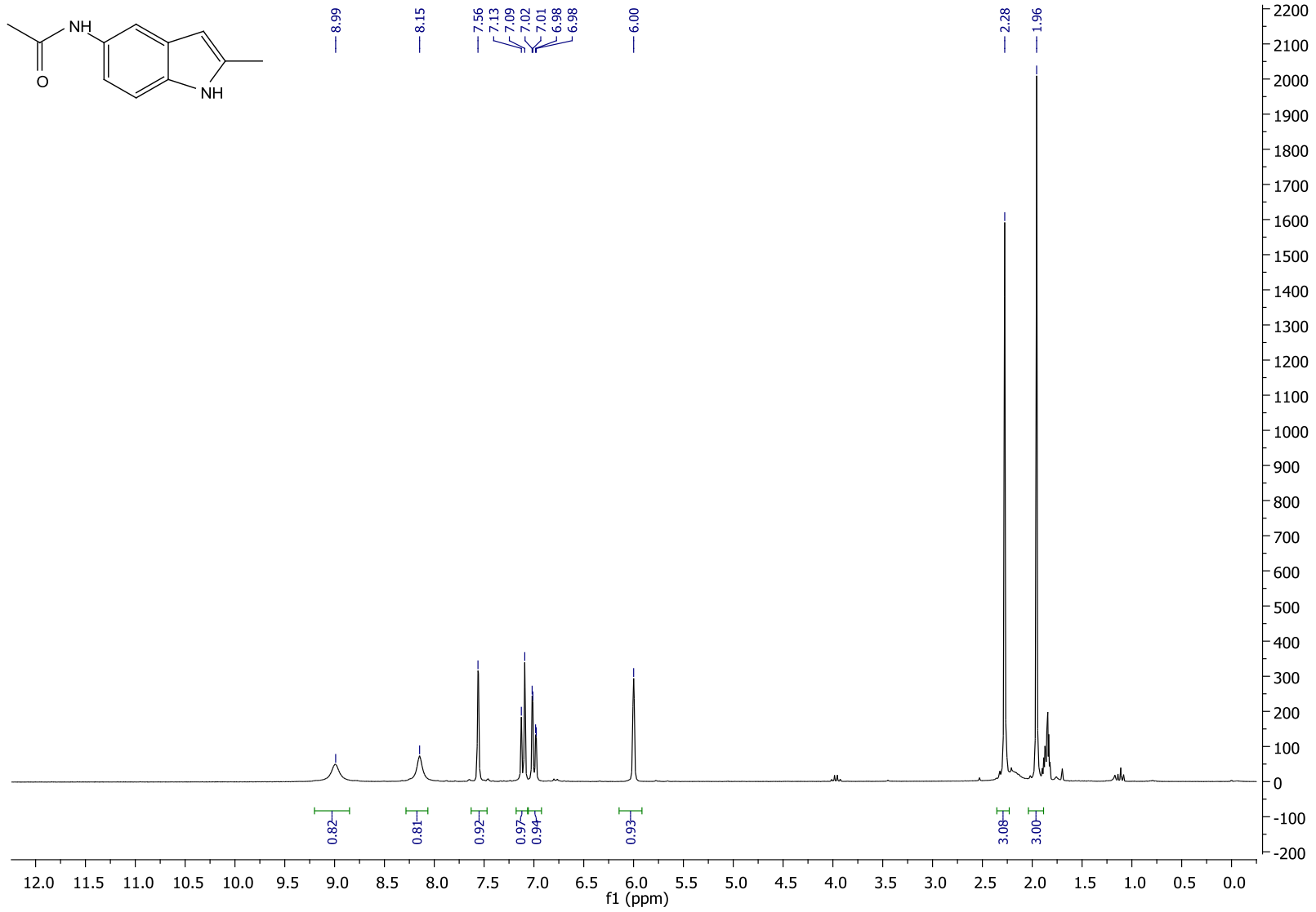

Br
N
CH3
137.43
129.82
129.54
122.78
122.63
115.24
108.90
101.72
33.59
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

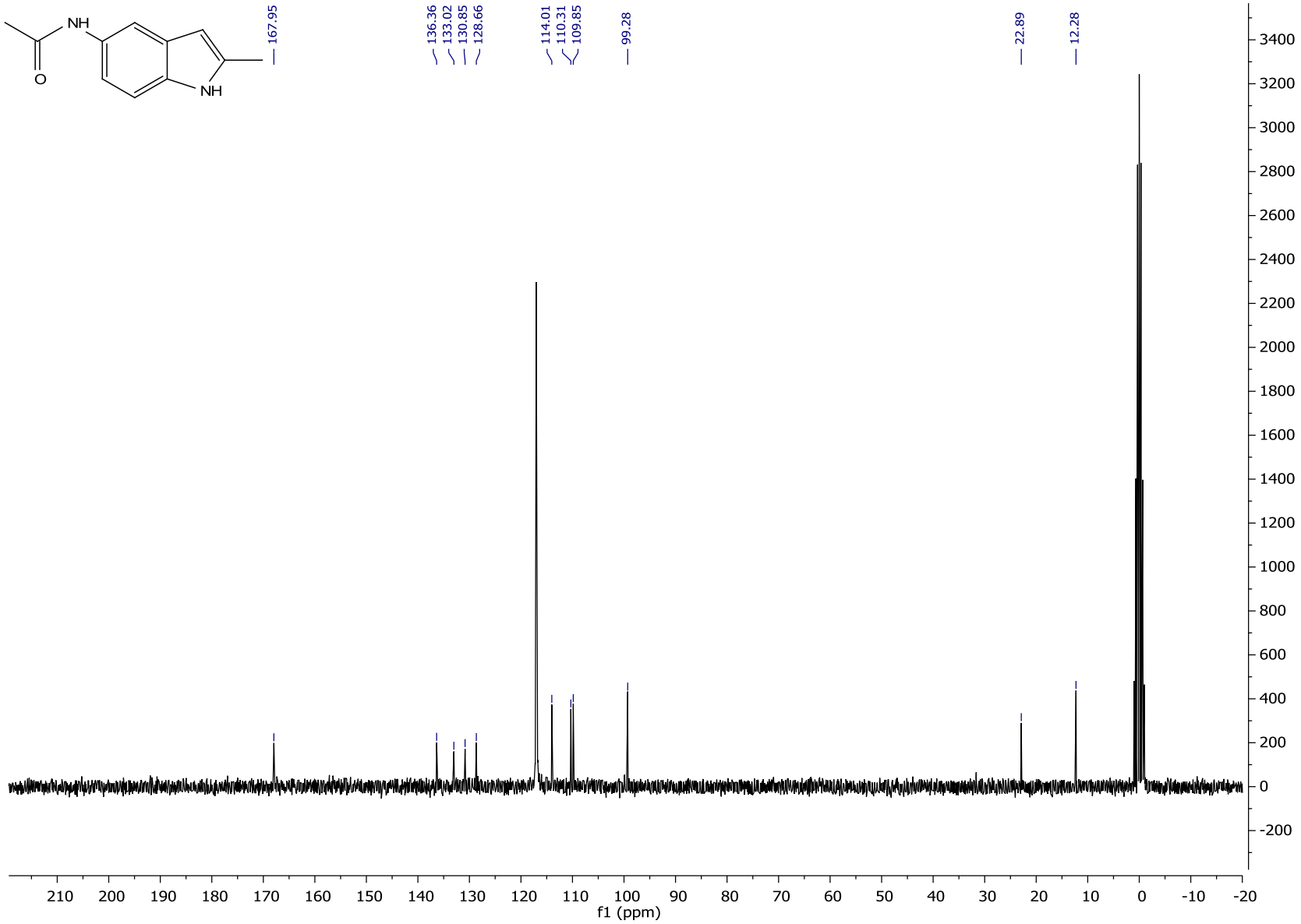
1-Methyl-2-phenyl-1*H*-indole



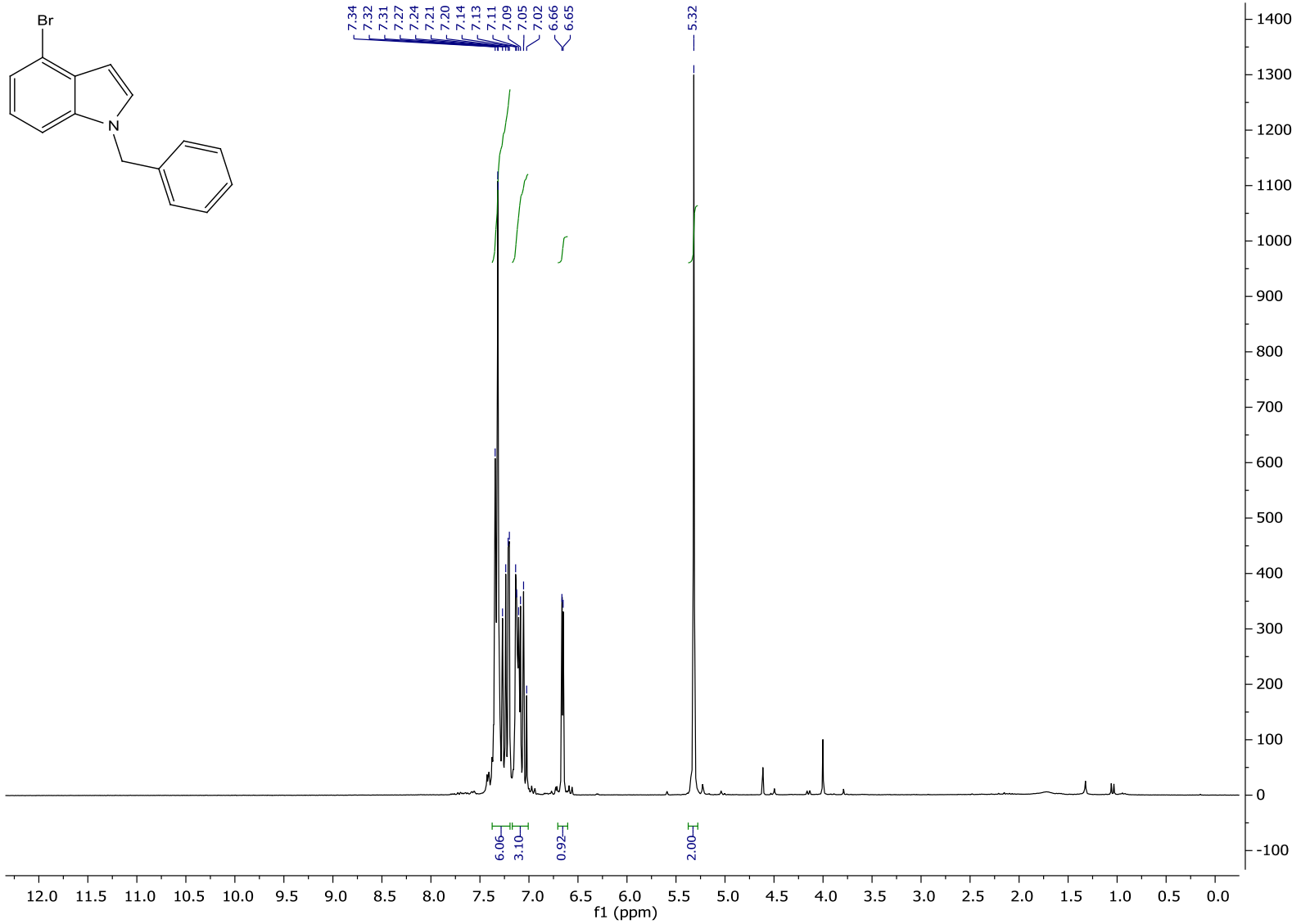

150.20
132.51
131.89
130.49
128.79
128.59
123.75
116.67
109.44
107.71
95.35
86.42
30.78
N
CH3
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

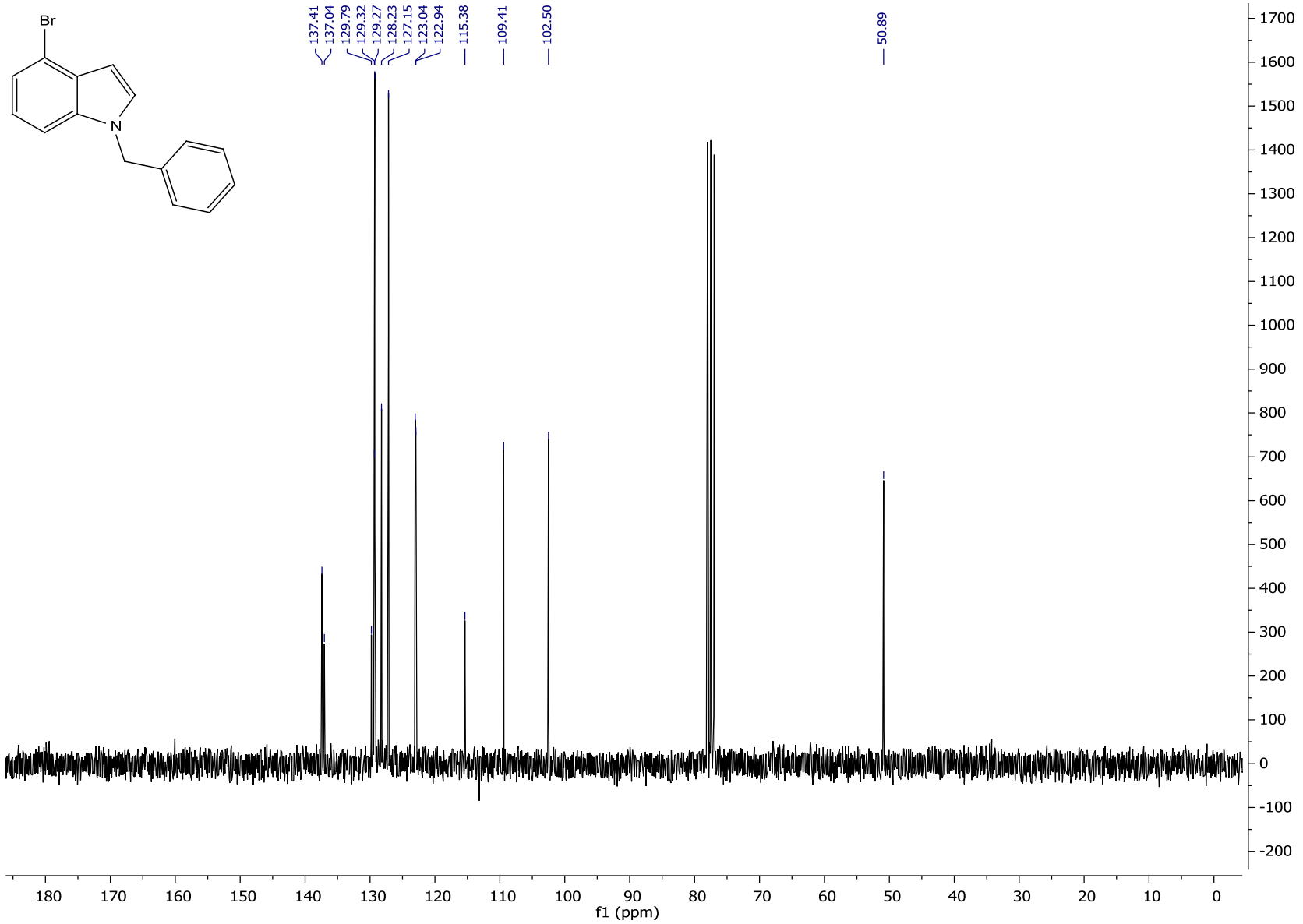
N-(2-Methyl-1*H*-indol-5-yl)acetamide



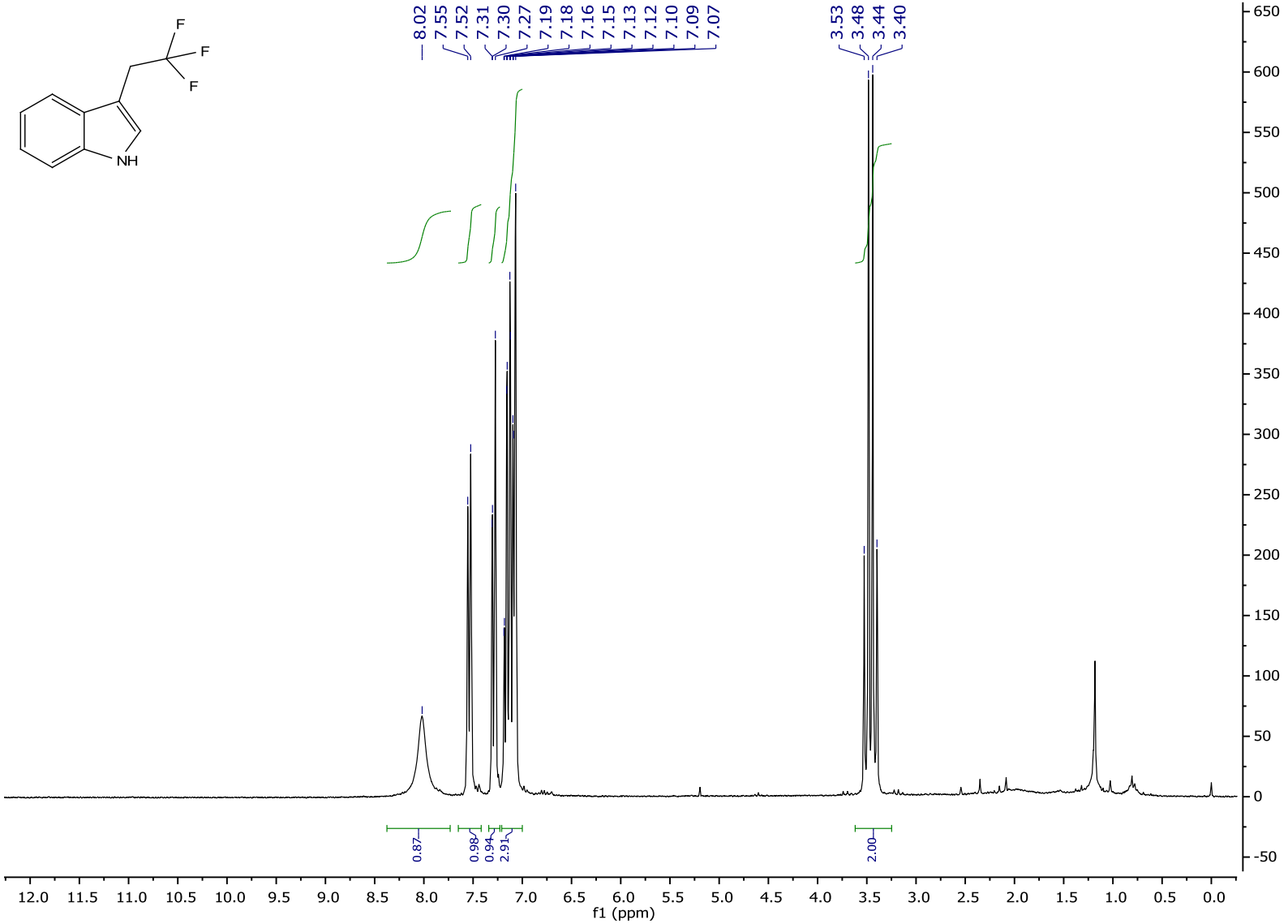

NH
O
NH
167.95
136.36
133.02
130.85
128.66
114.01
110.31
109.85
99.28
22.89
12.28
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

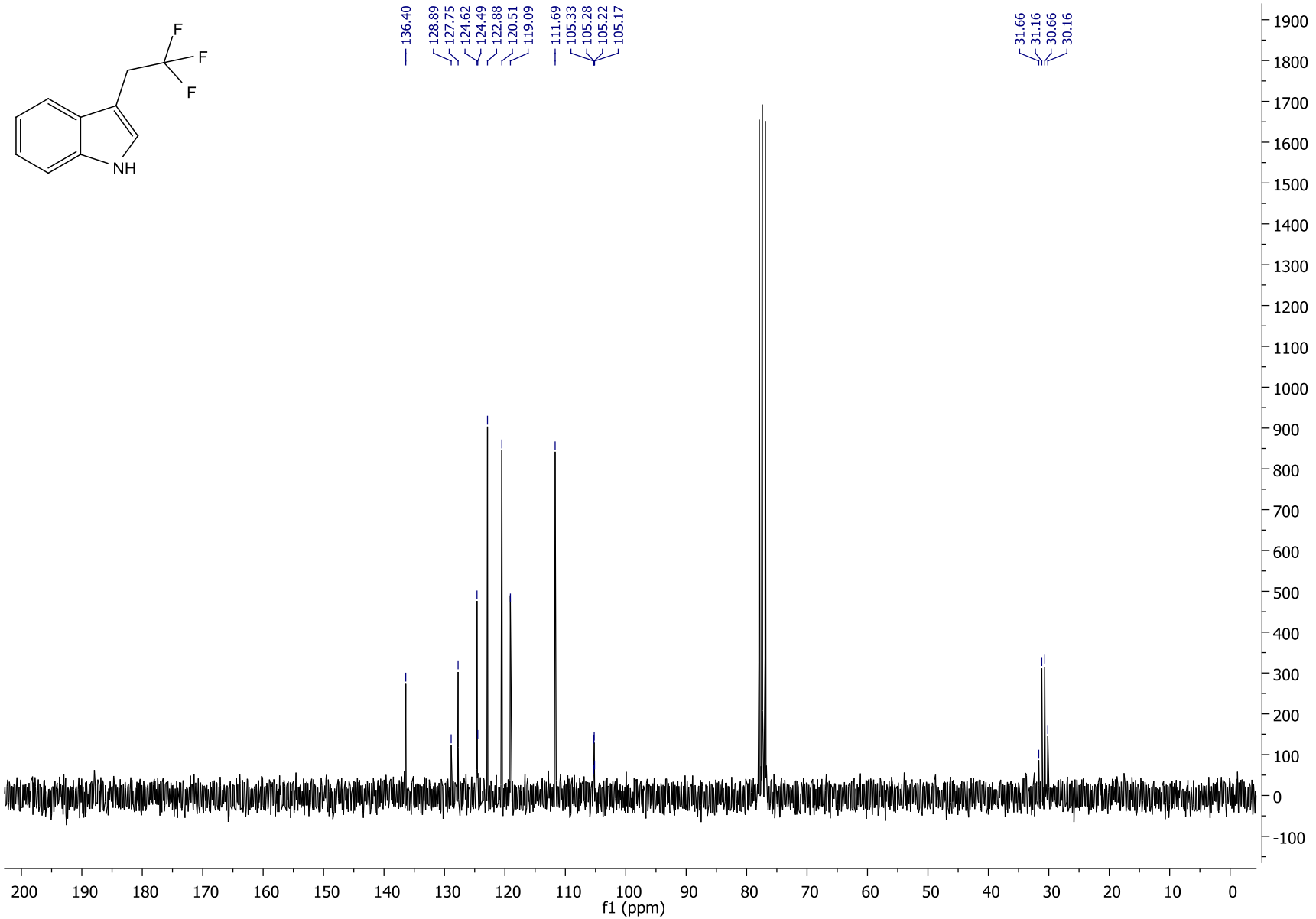
1-Benzyl-4-bromo-1*H*-indole

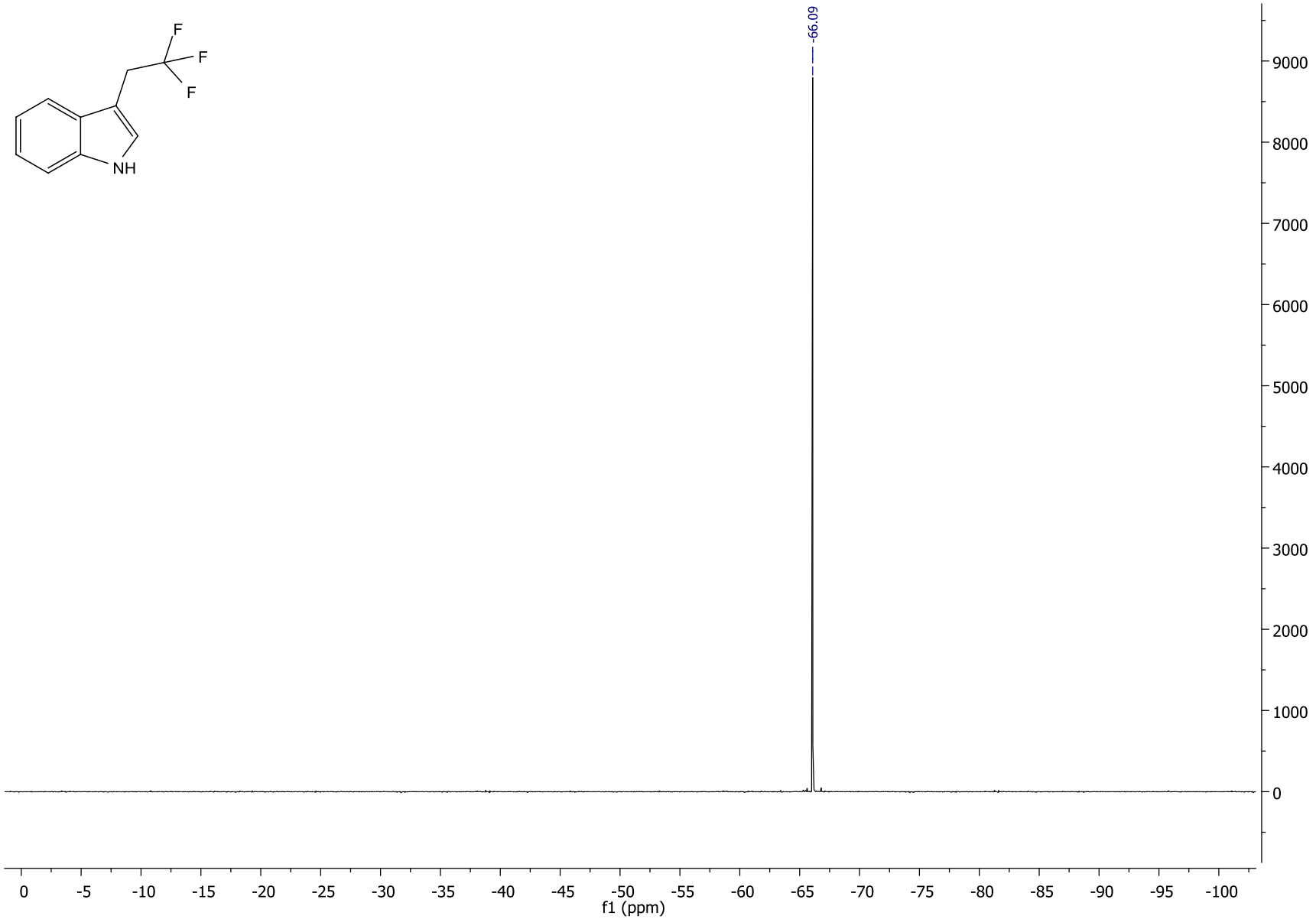

Br
N
7.34
7.32
7.31
7.27
7.24
7.21
7.20
7.14
7.13
7.11
7.09
7.05
7.02
6.66
6.65
5.32
6.06
3.10
0.92
2.00
f1 (ppm)


Br
N
137.41
137.04
129.79
129.32
129.27
128.23
127.15
123.04
122.94
115.38
109.41
102.50
50.89
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

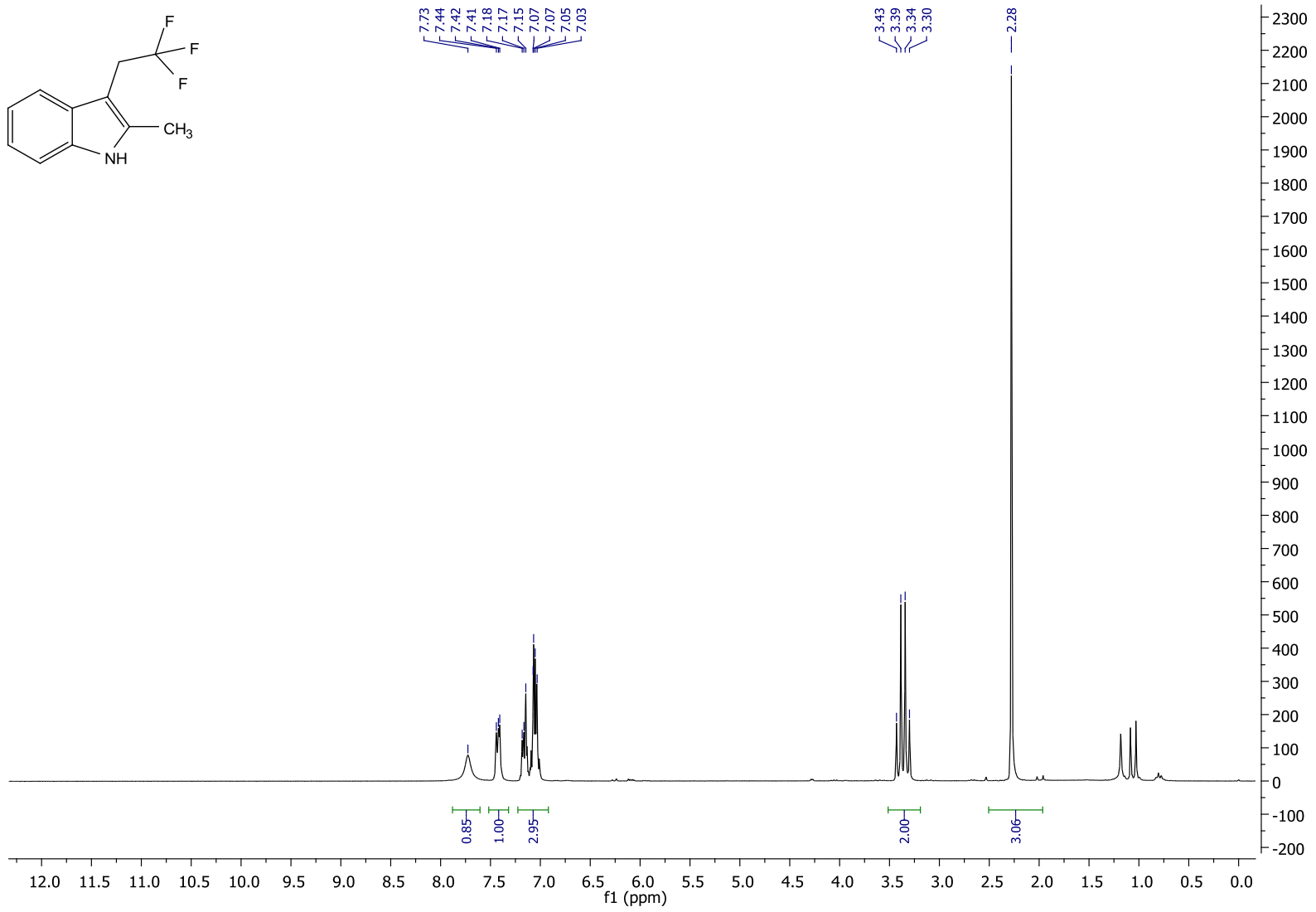
3-(2,2,2-Trifluoroethyl)-1*H*-indole (3a)

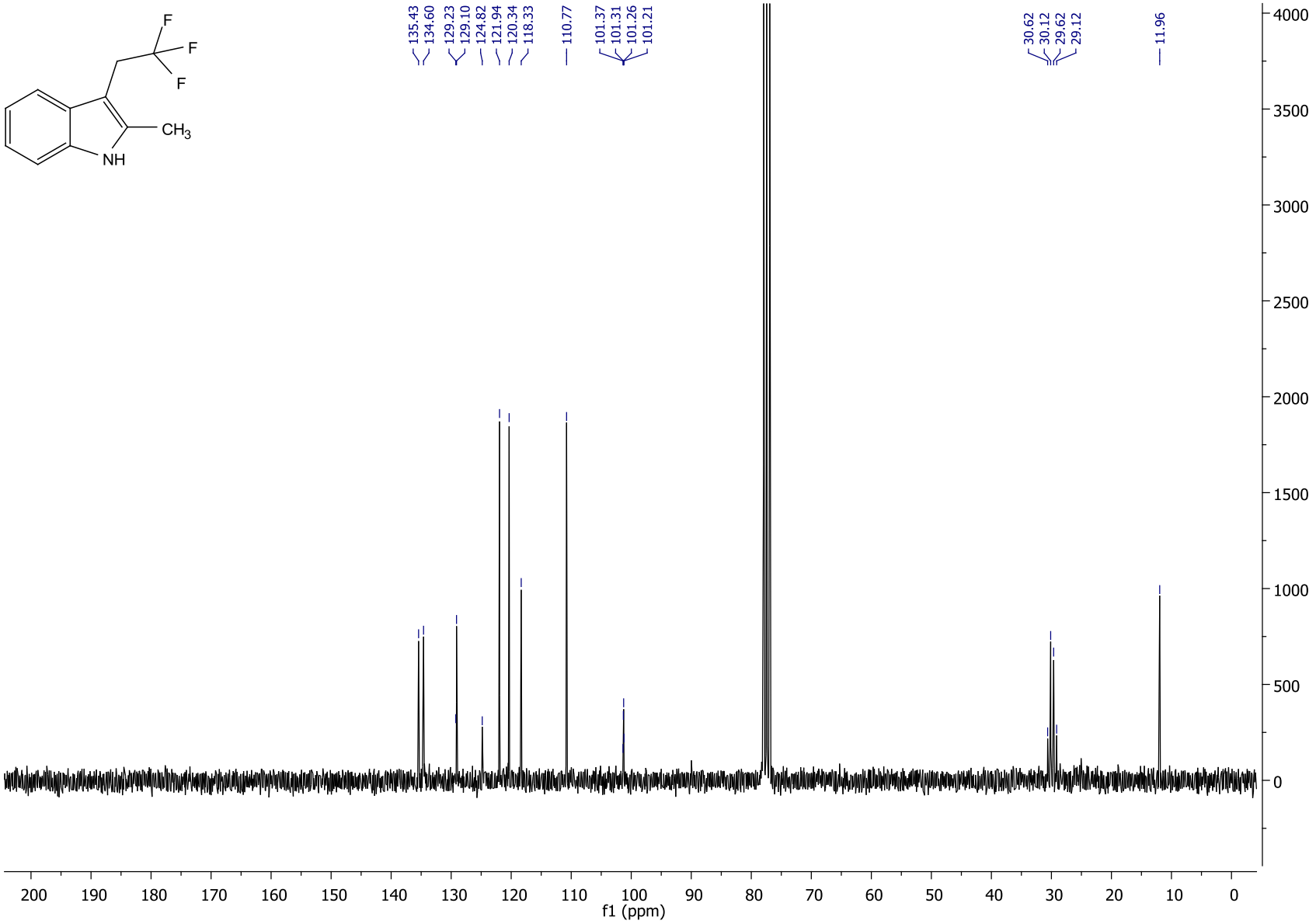


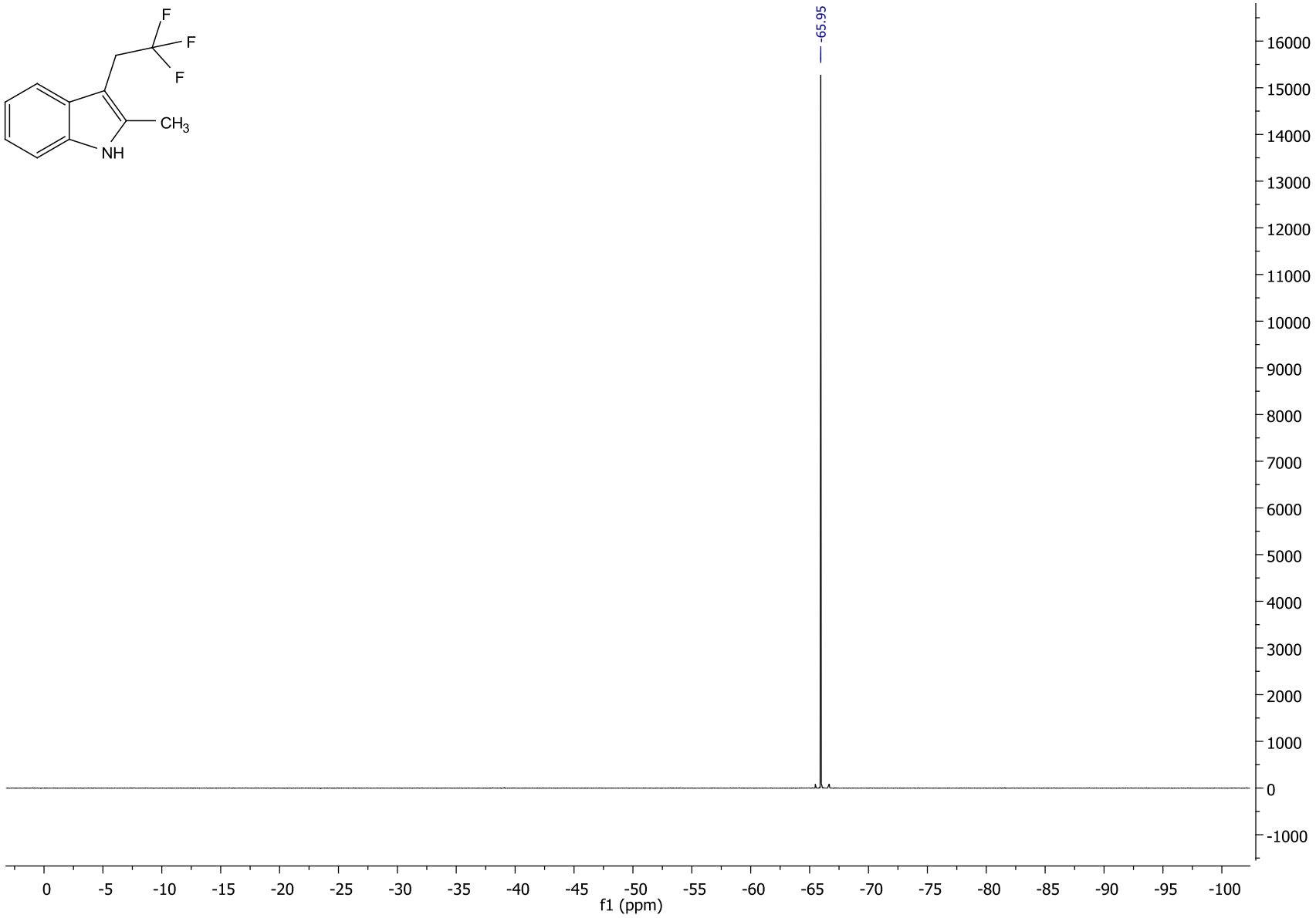

F
F
F
NH
136.40
128.89
127.75
124.62
124.49
122.88
120.51
119.09
111.69
105.33
105.28
105.22
105.17
31.66
31.16
30.66
30.16
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
NH
-66.09
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100
f1 (ppm)

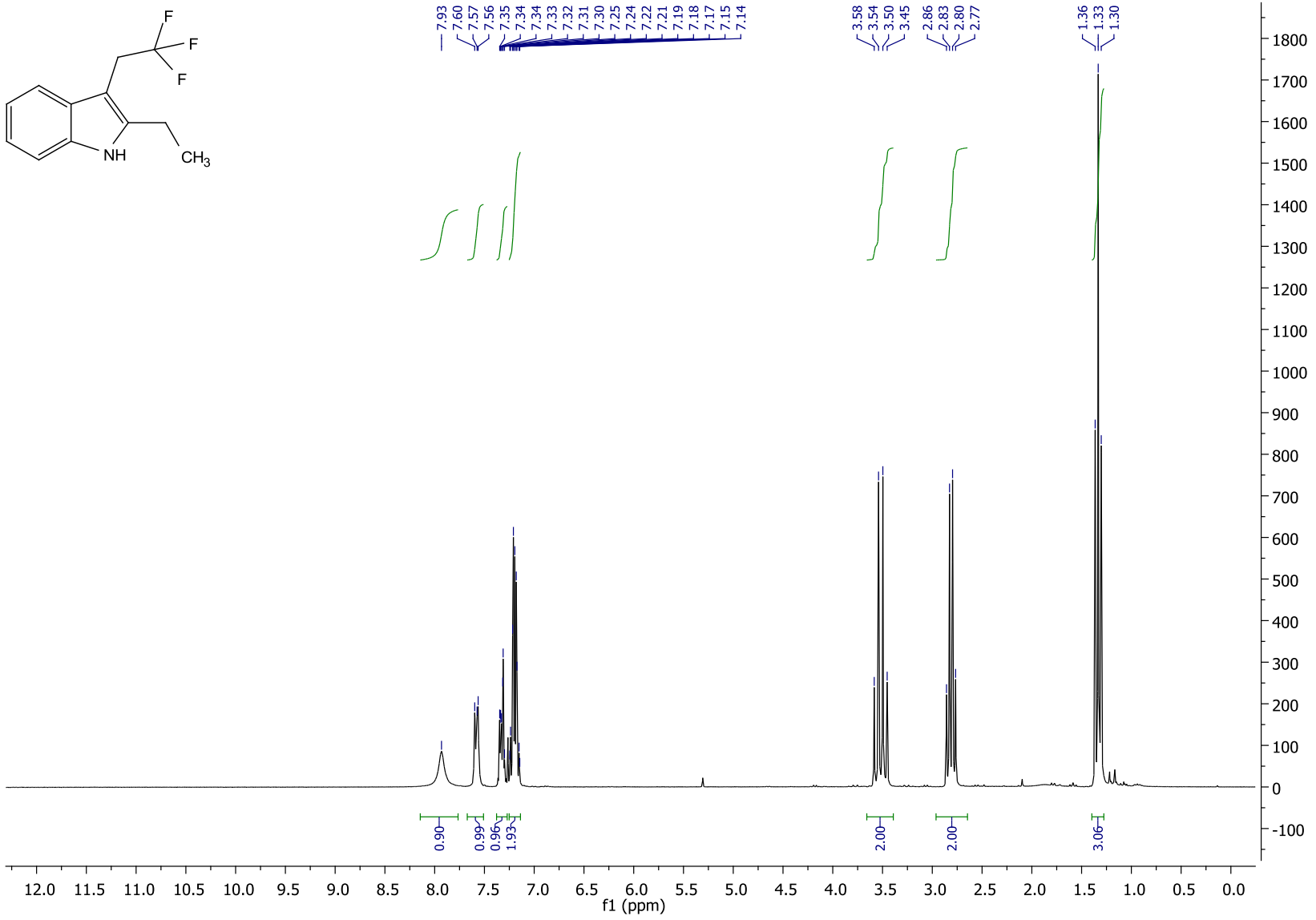
2-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3b)

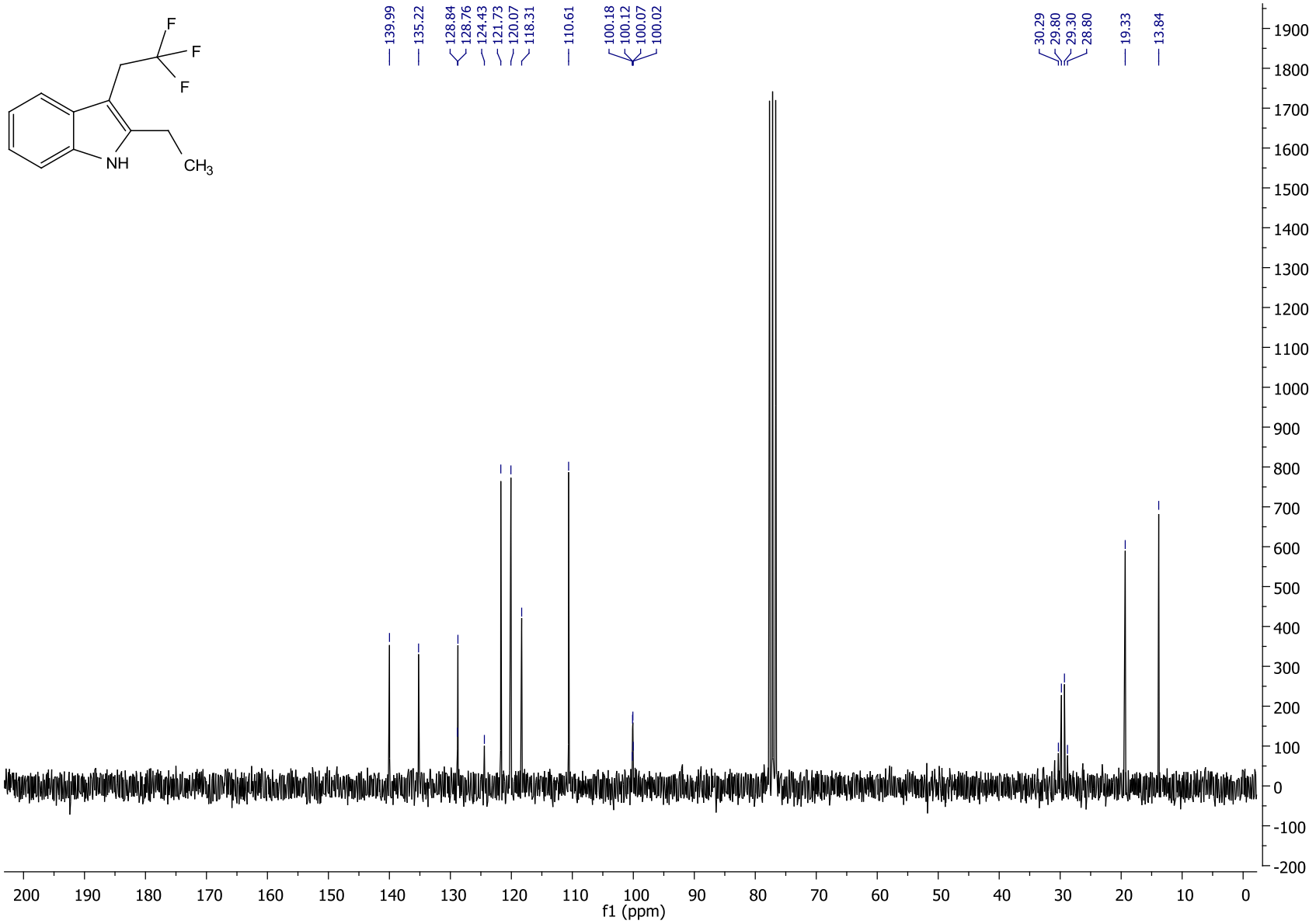


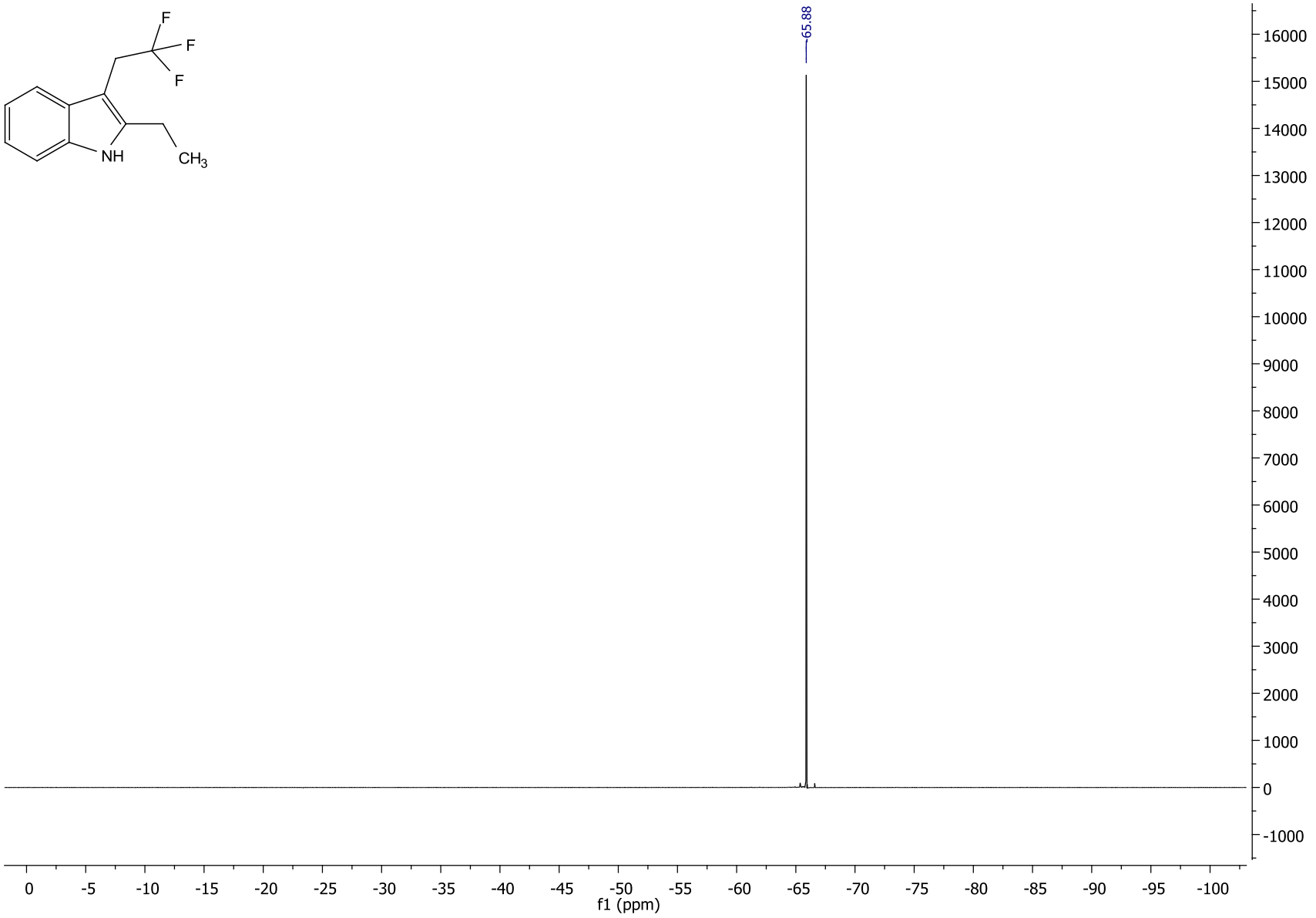

F
F
F
CH3
NH
135.43
134.60
129.23
129.10
124.82
121.94
120.34
118.33
110.77
101.37
101.31
101.26
101.21
30.62
30.12
29.62
29.12
11.96
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
CH3
NH
-65.95
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

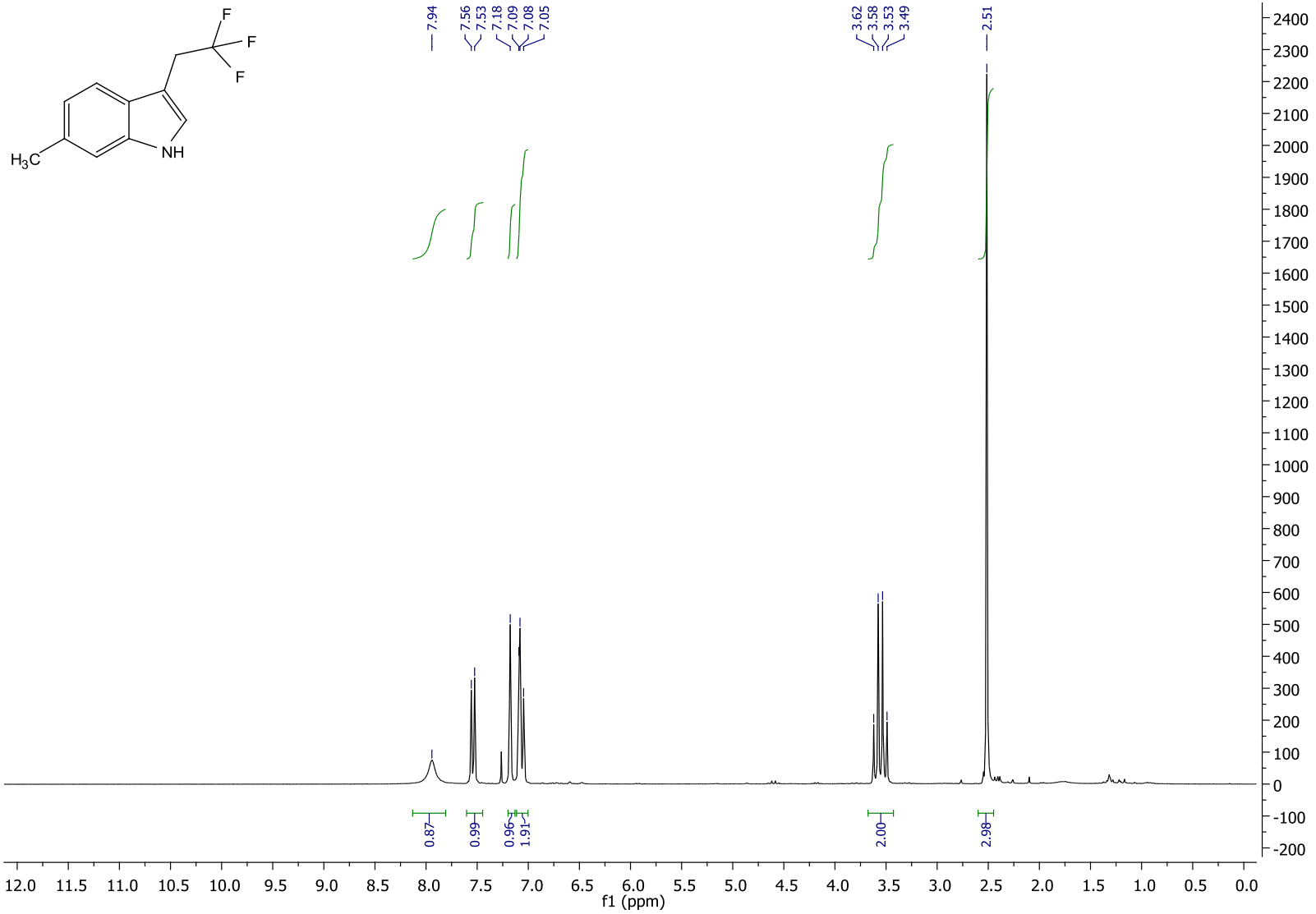
2-Ethyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3c)

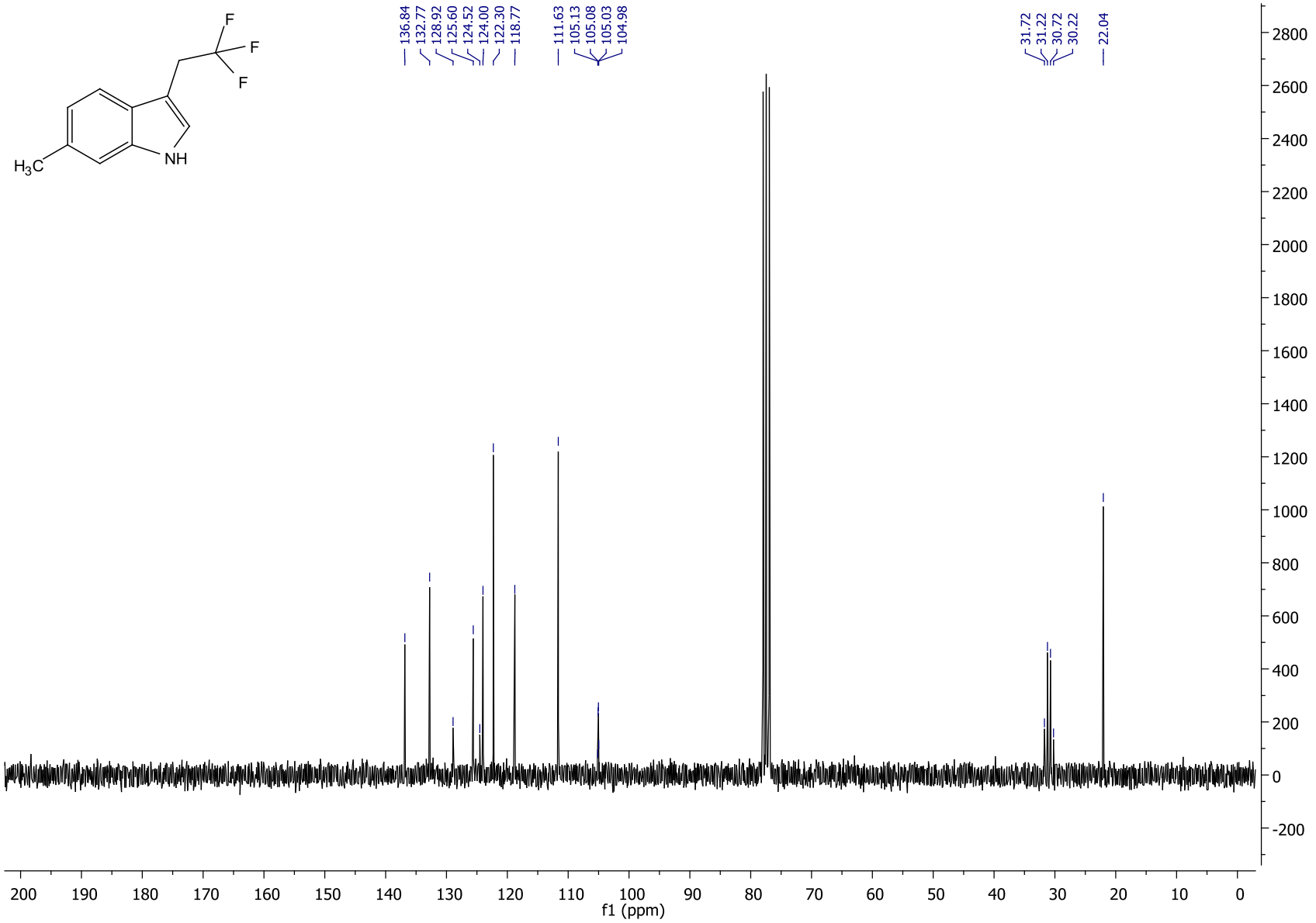


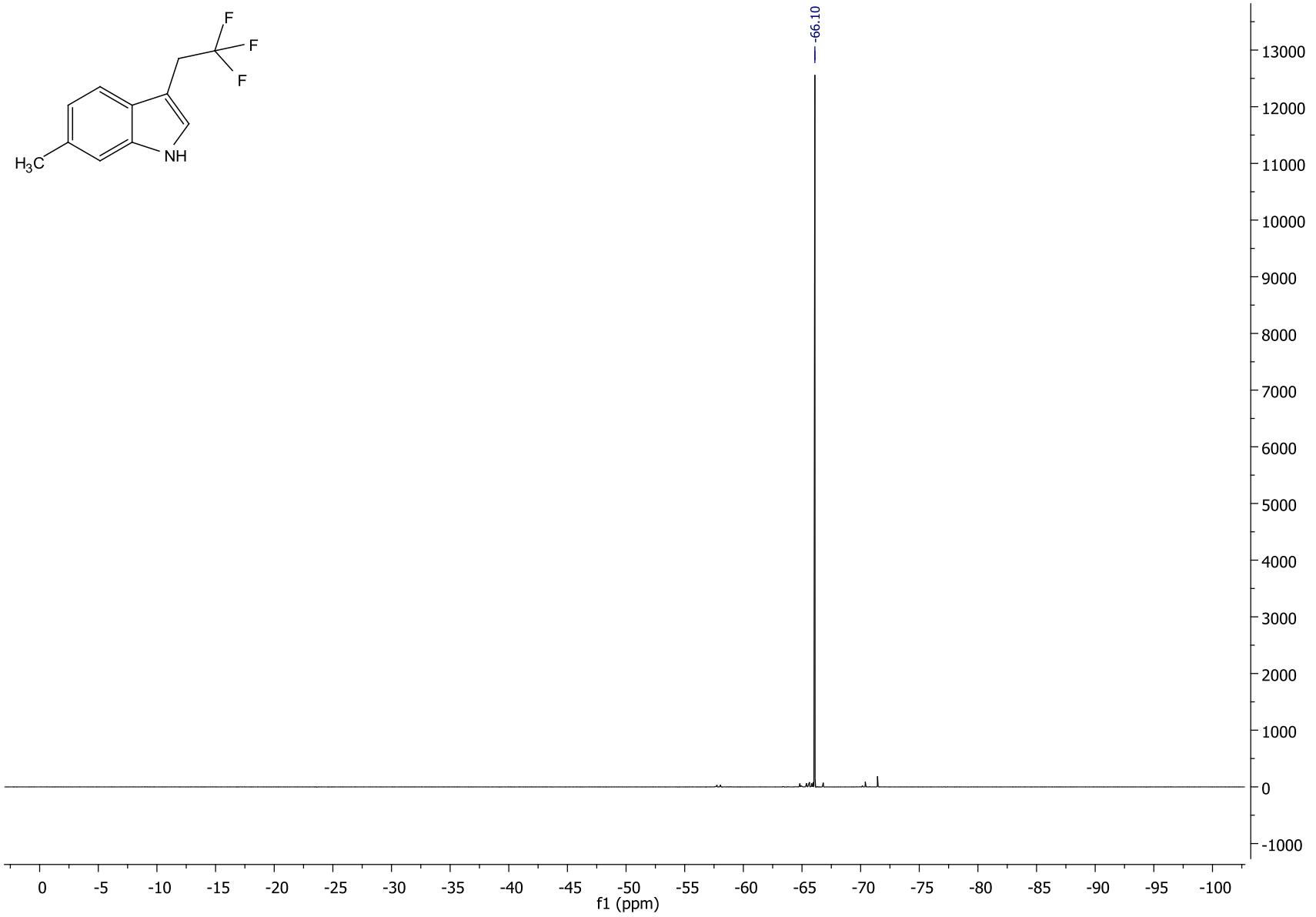

F
F
F
NH
CH3
139.99
135.22
128.84
128.76
124.43
121.73
120.07
118.31
110.61
100.18
100.12
100.07
100.02
30.29
29.80
29.30
28.80
19.33
13.84
f1 (ppm)


F
F
F
NH
CH3
-65.88
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

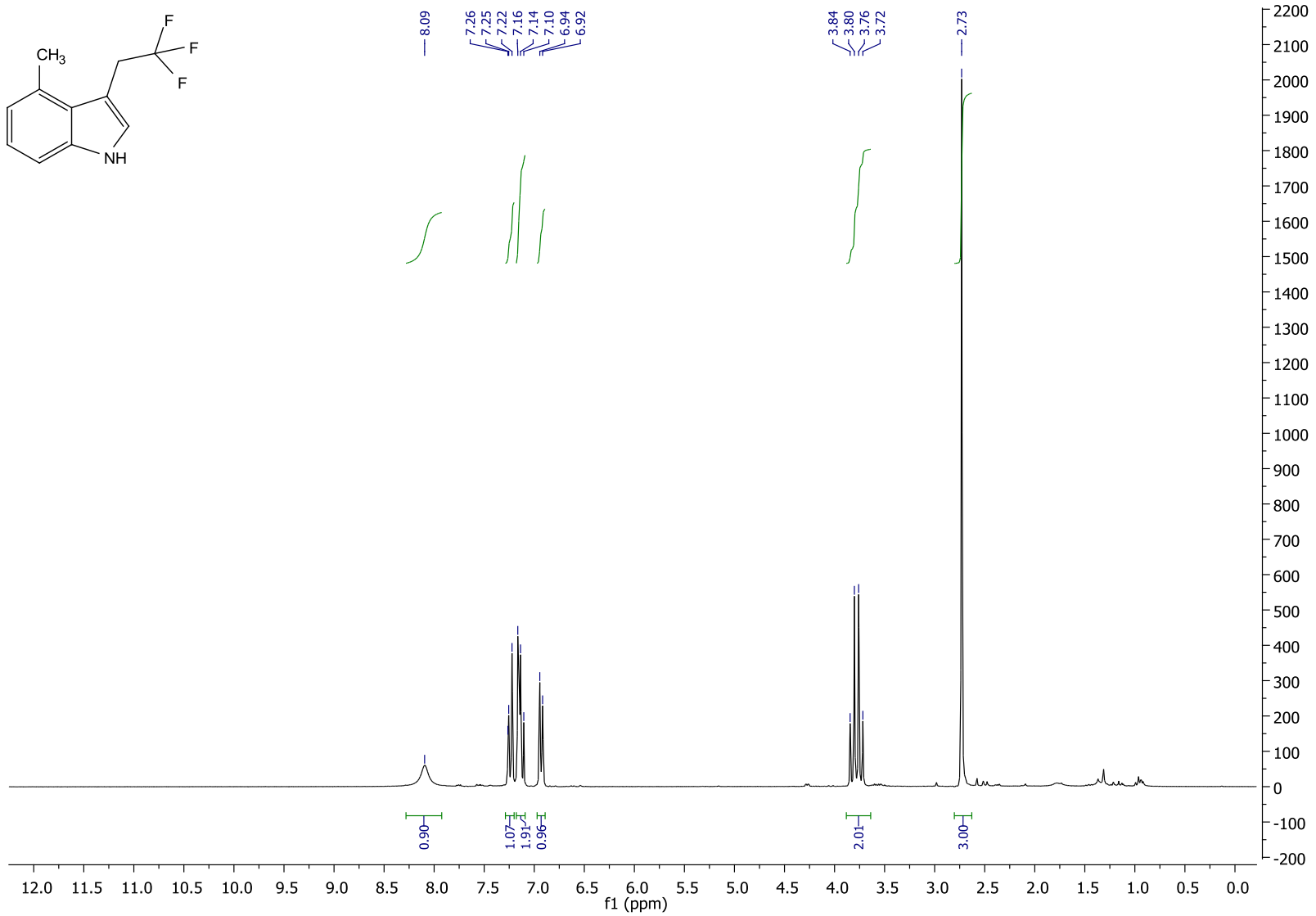
6-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3d)

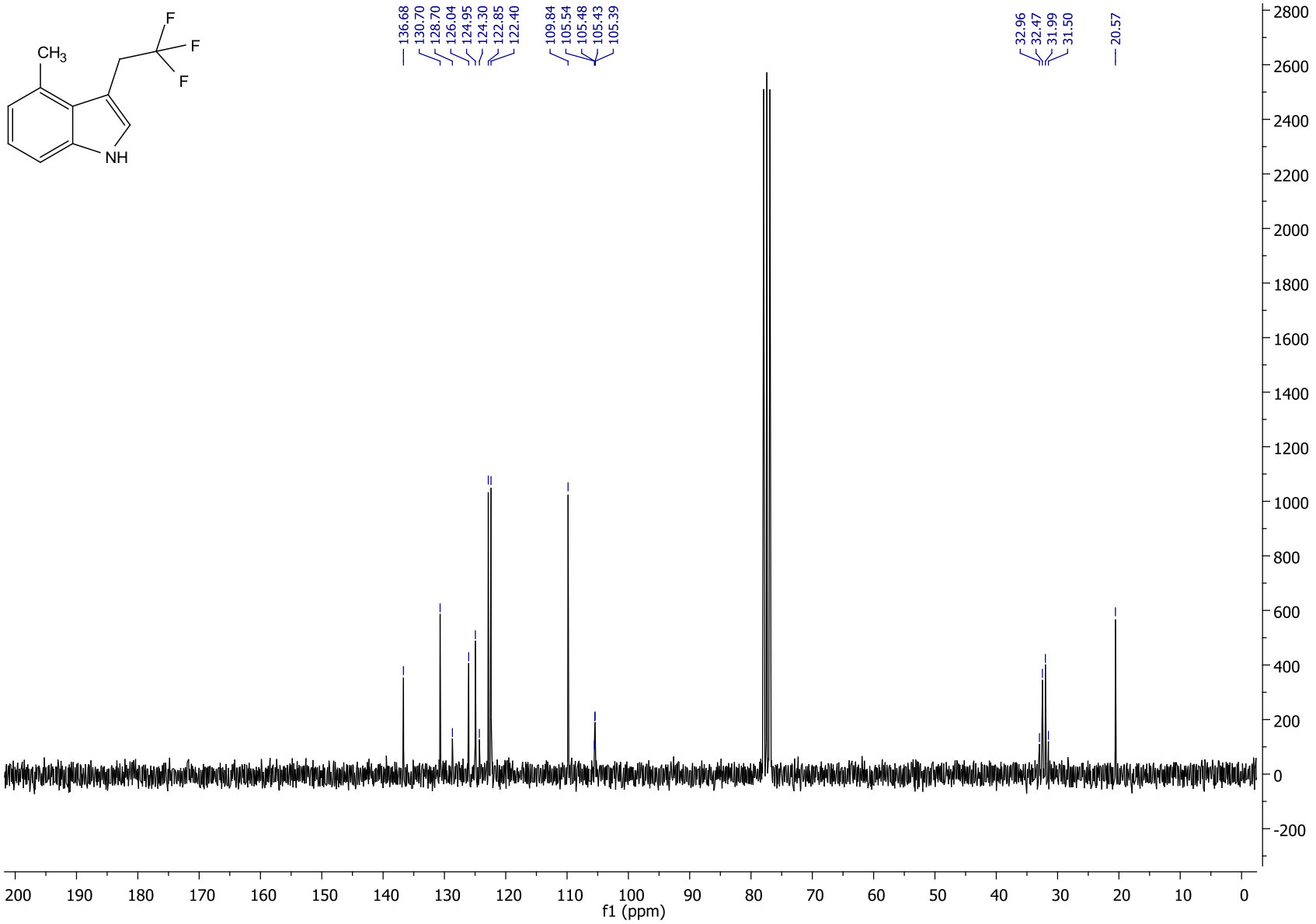


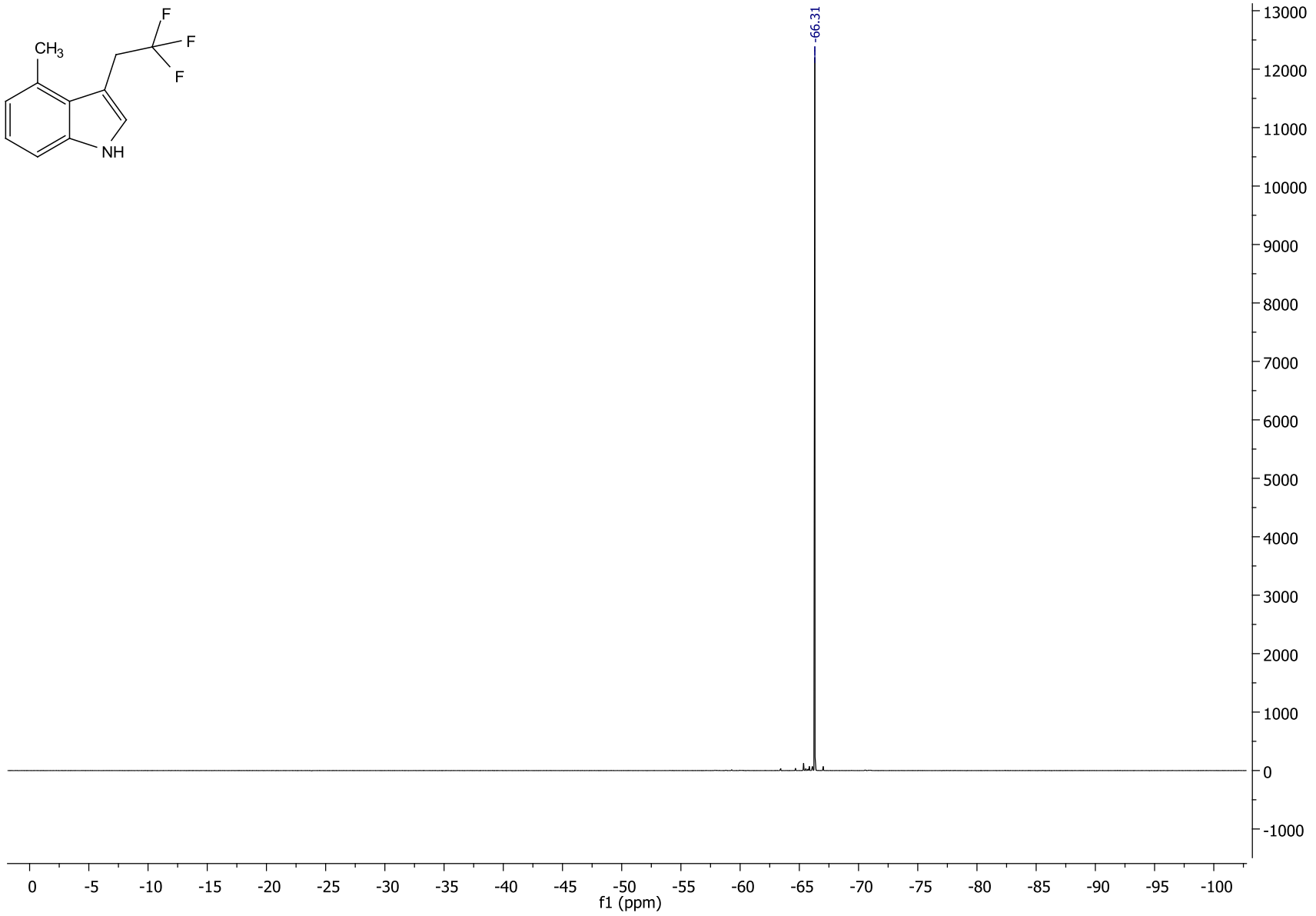

F
F
F
H3C
NH
136.84
132.77
128.92
125.60
124.52
124.00
122.30
118.77
111.63
105.13
105.08
105.03
104.98
31.72
31.22
30.72
30.22
22.04
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
H3C
NH
-66.10
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

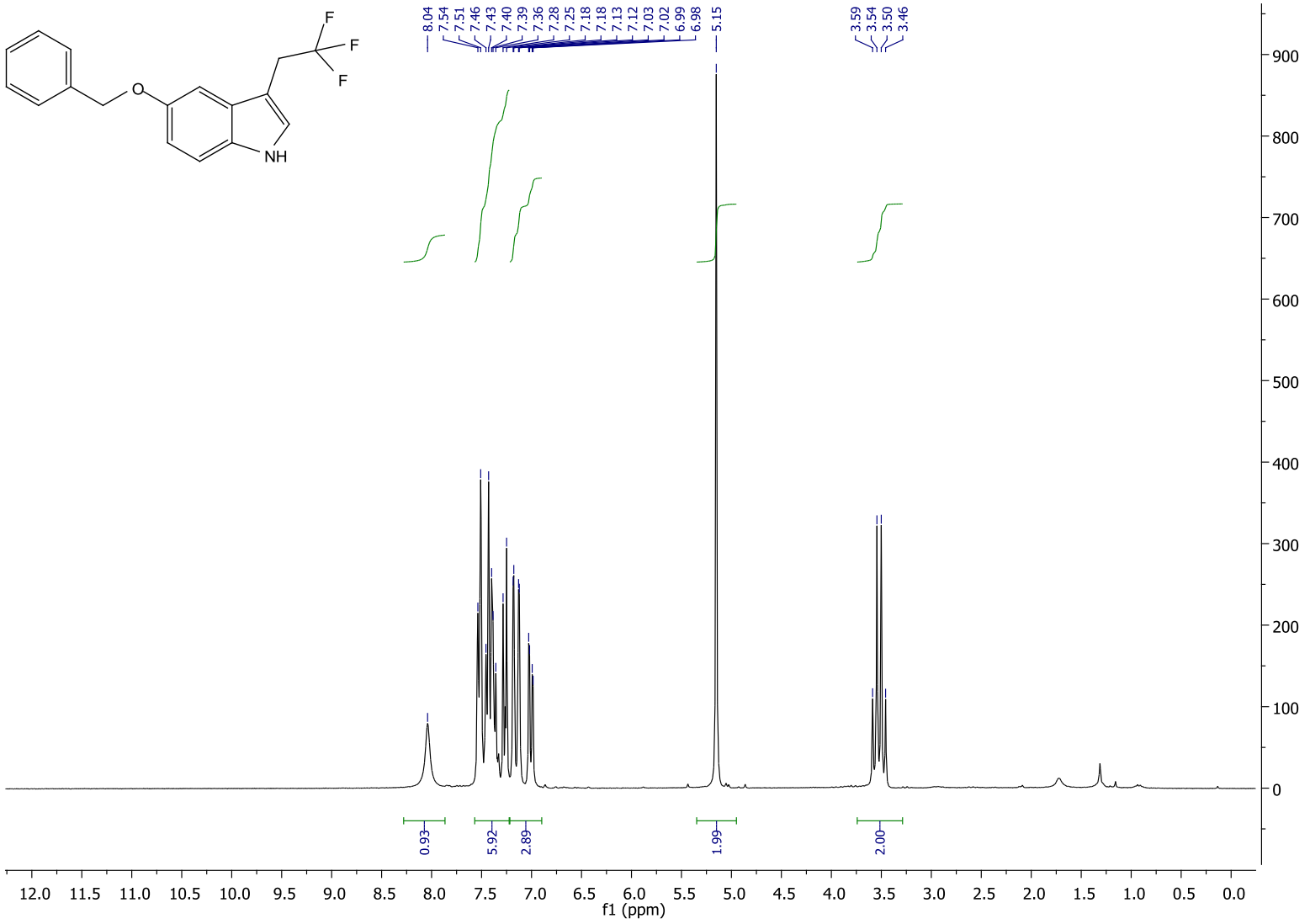
4-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3e)

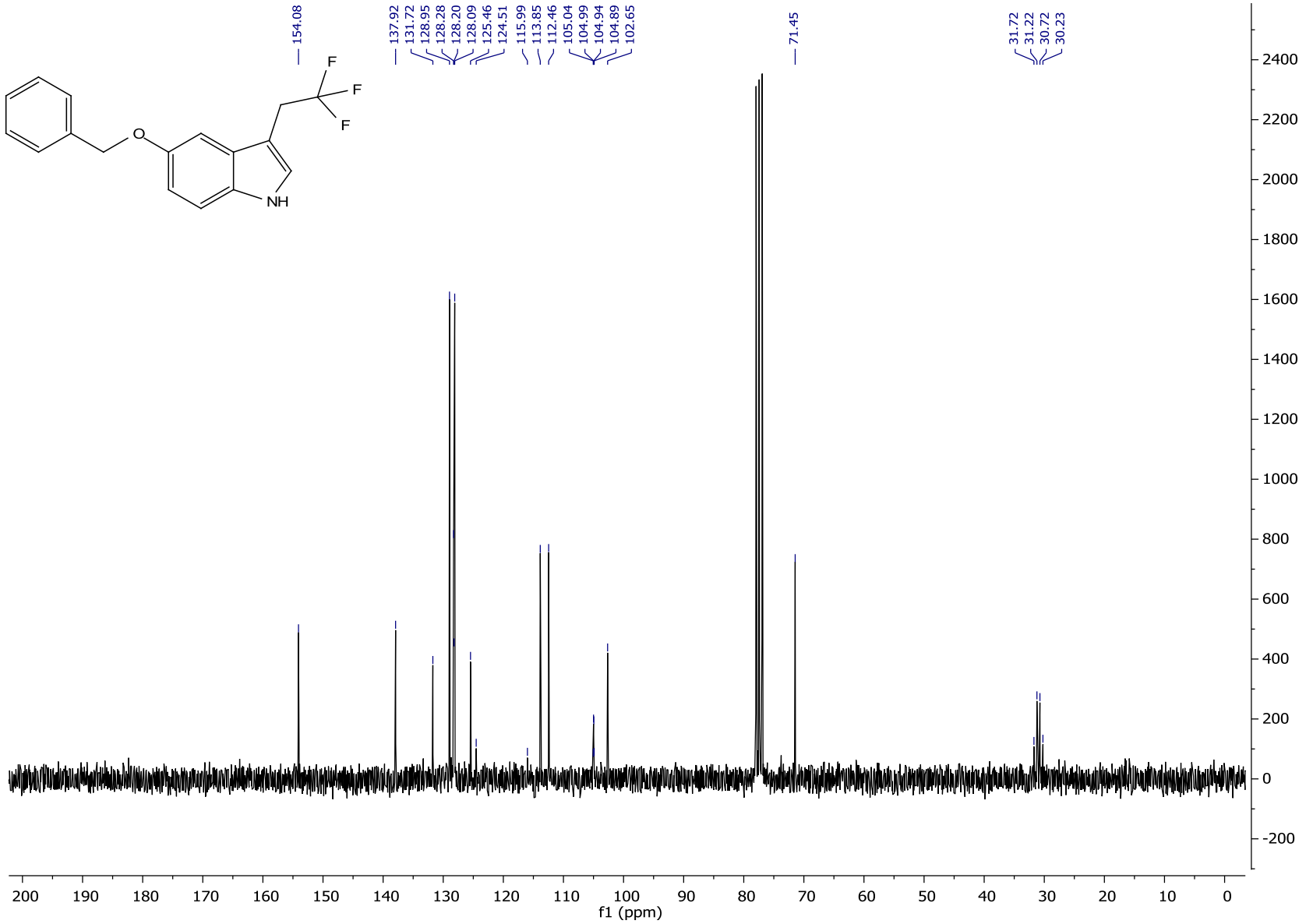


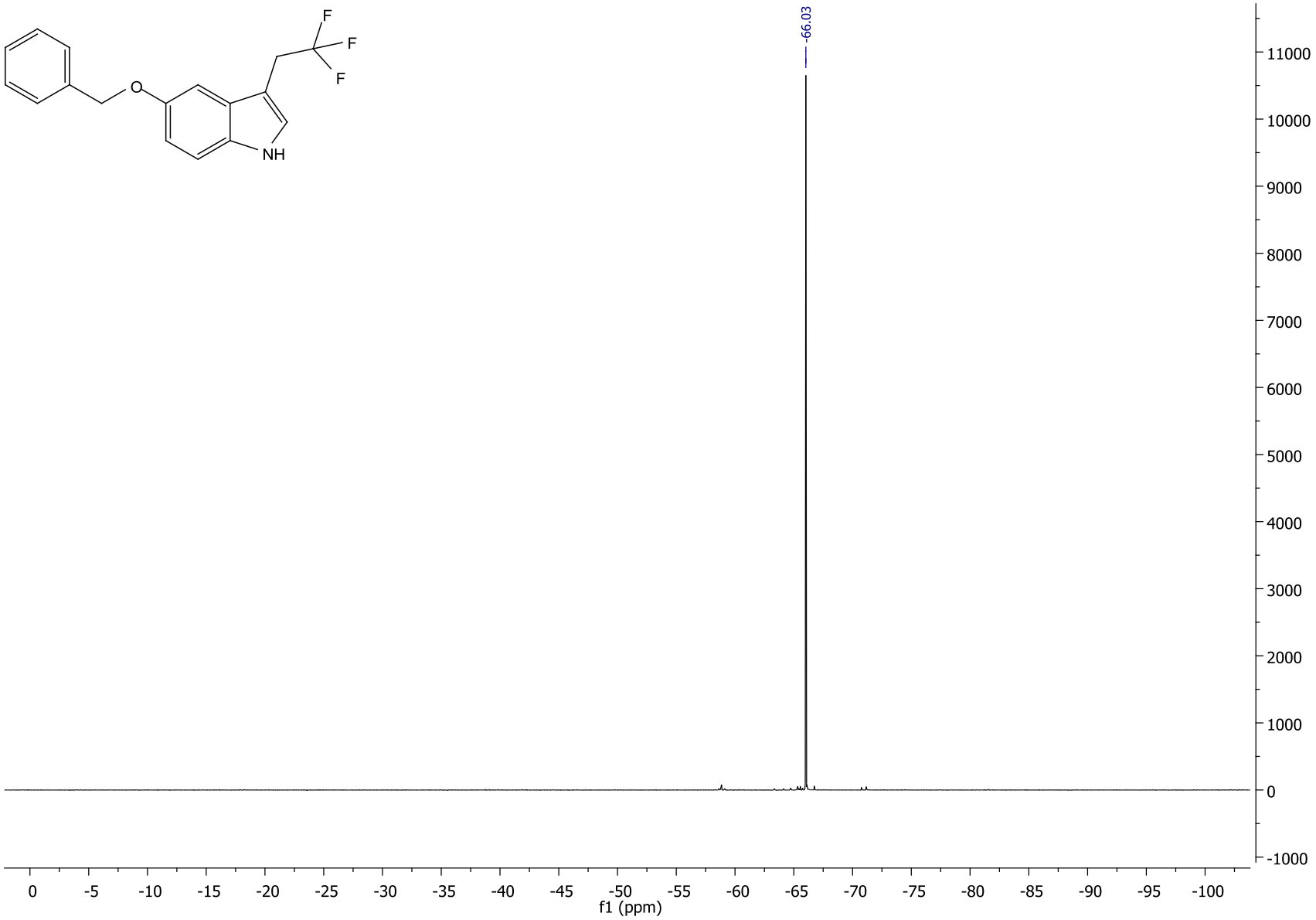

136.68
130.70
128.70
126.04
124.95
124.30
122.85
122.40
109.84
105.54
105.48
105.43
105.39
32.96
32.47
31.99
31.50
20.57
CH3
F
F
F
NH
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
CH3
NH
-66.31
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

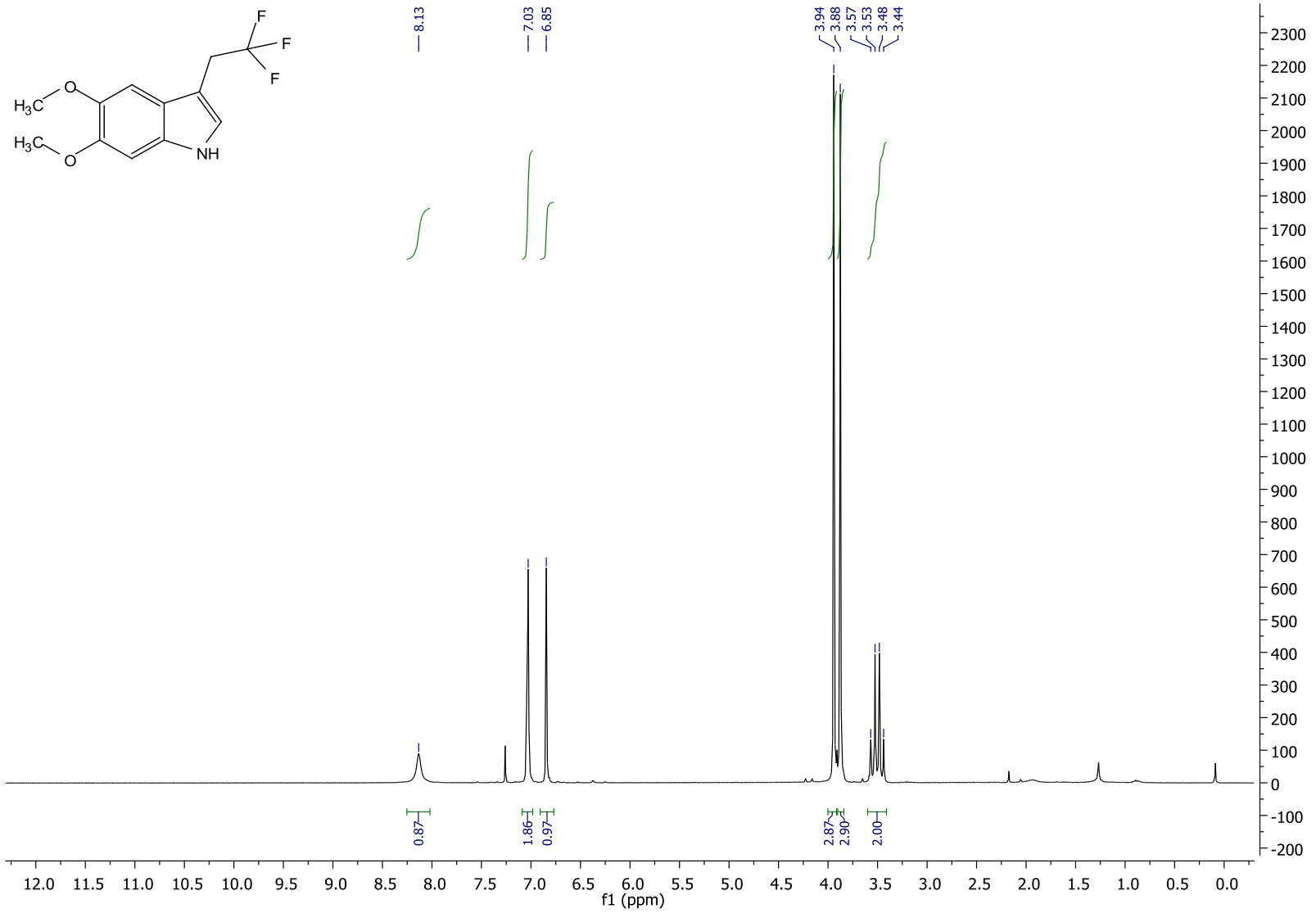
5-(Benzyloxy)-3-(2,2,2-trifluoroethyl)-1*H*-indole (3f)

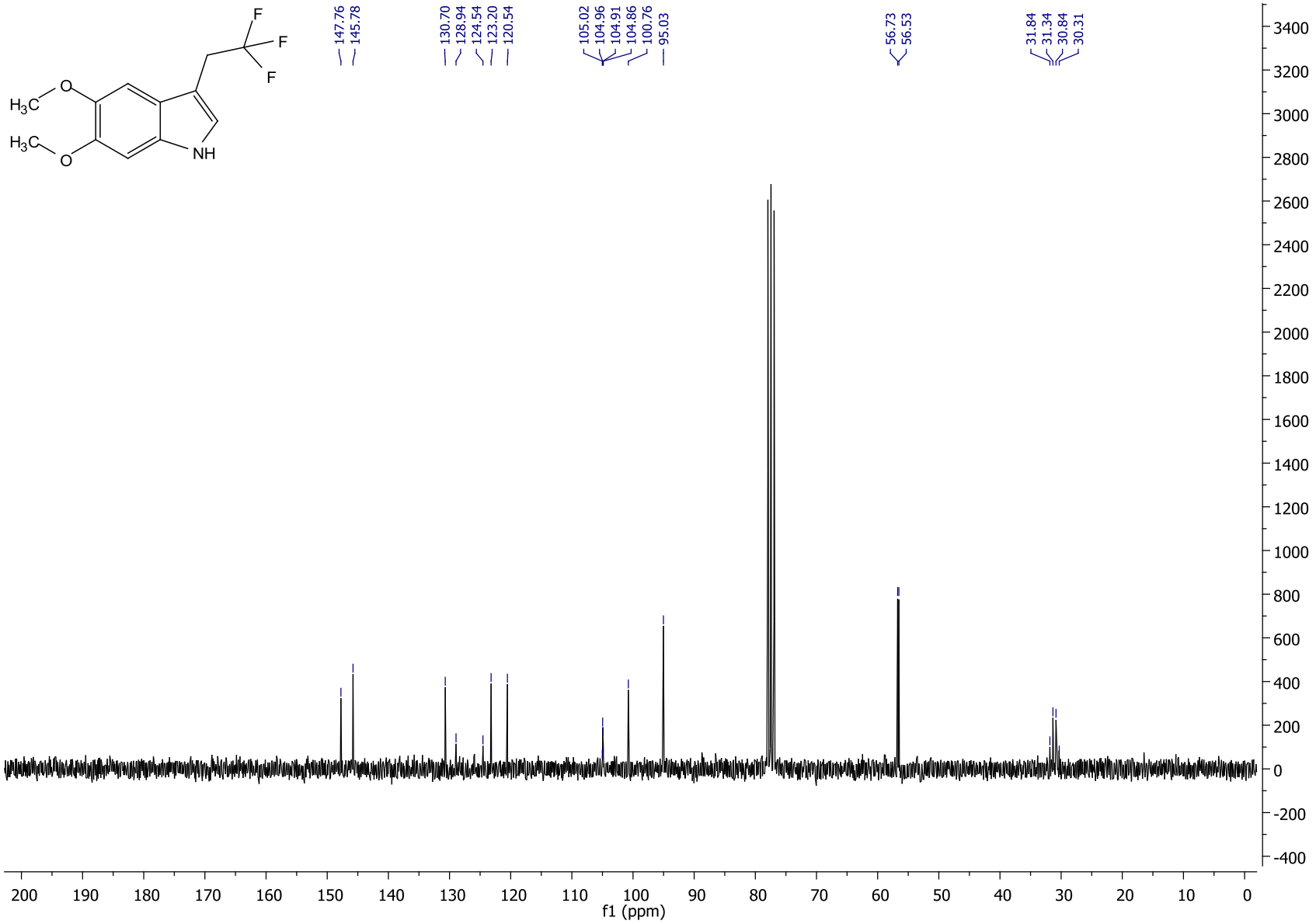


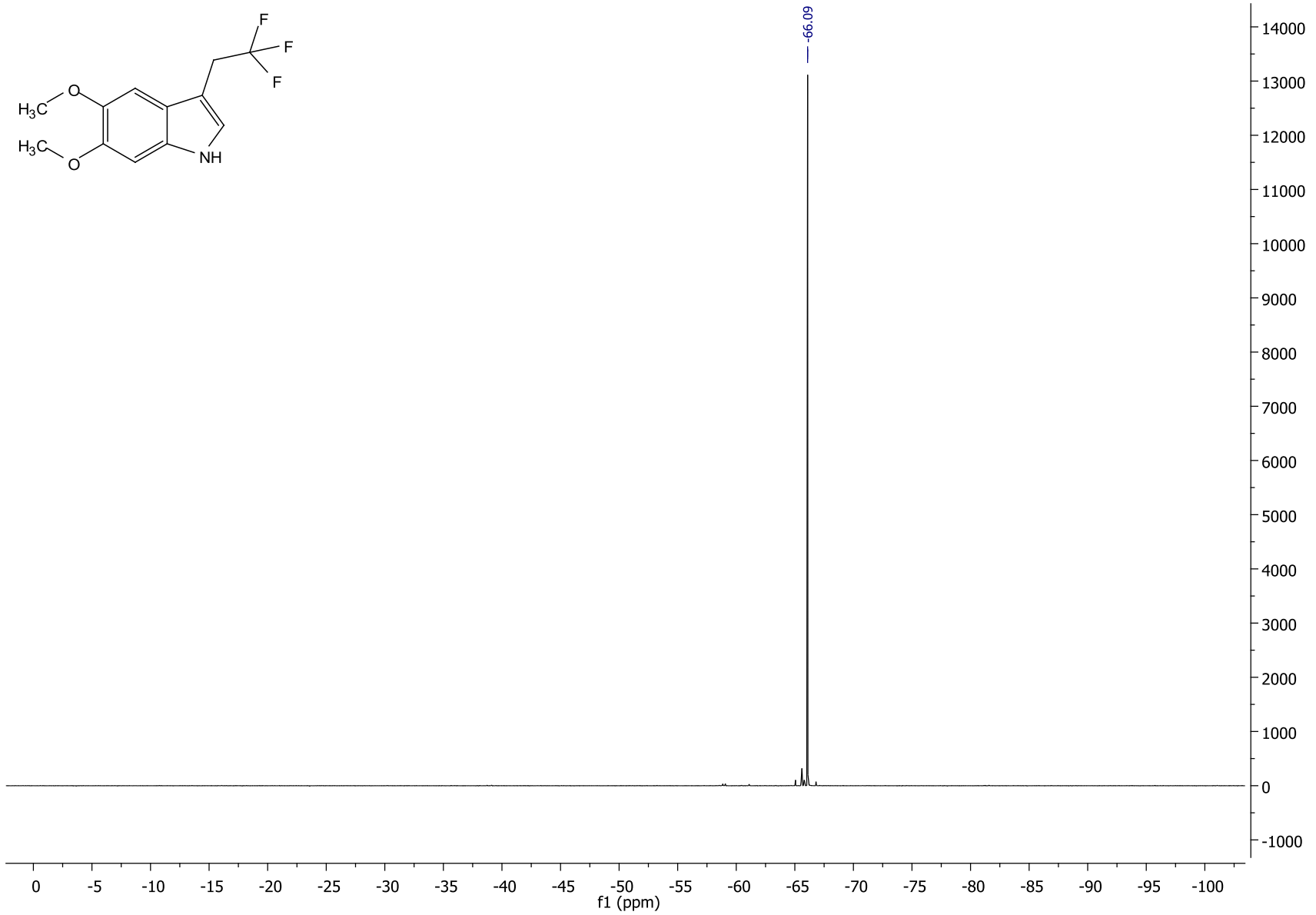

154.08
137.92
131.72
128.95
128.28
128.20
128.09
125.46
124.51
115.99
113.85
112.46
105.04
104.99
104.94
104.89
102.65
71.45
31.72
31.22
30.72
30.23
F
F
F
O
NH
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
O
NH
-66.03
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

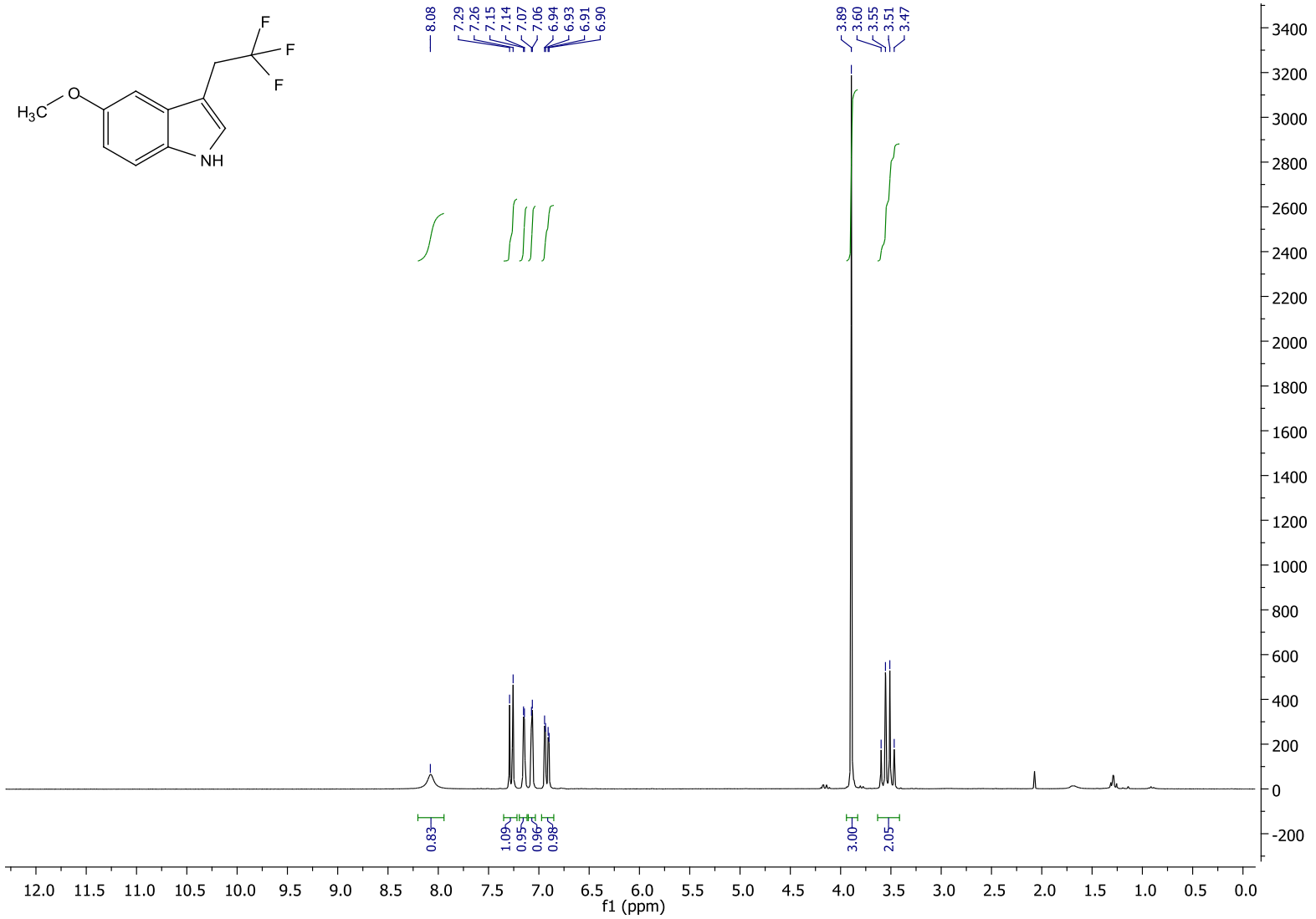
5,6-Dimethoxy-3-(2,2,2-trifluoroethyl)-1*H*-indole (3g)

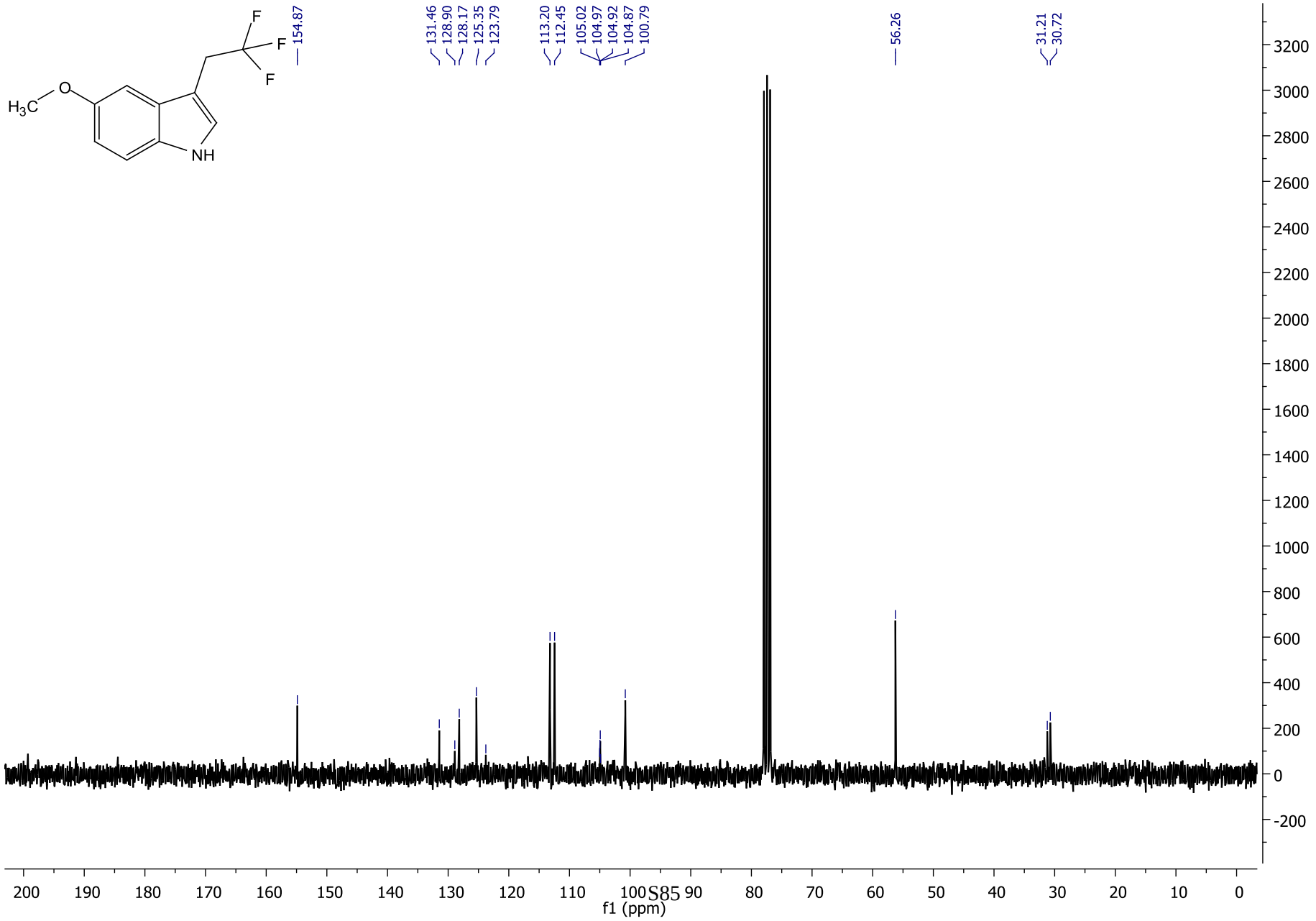


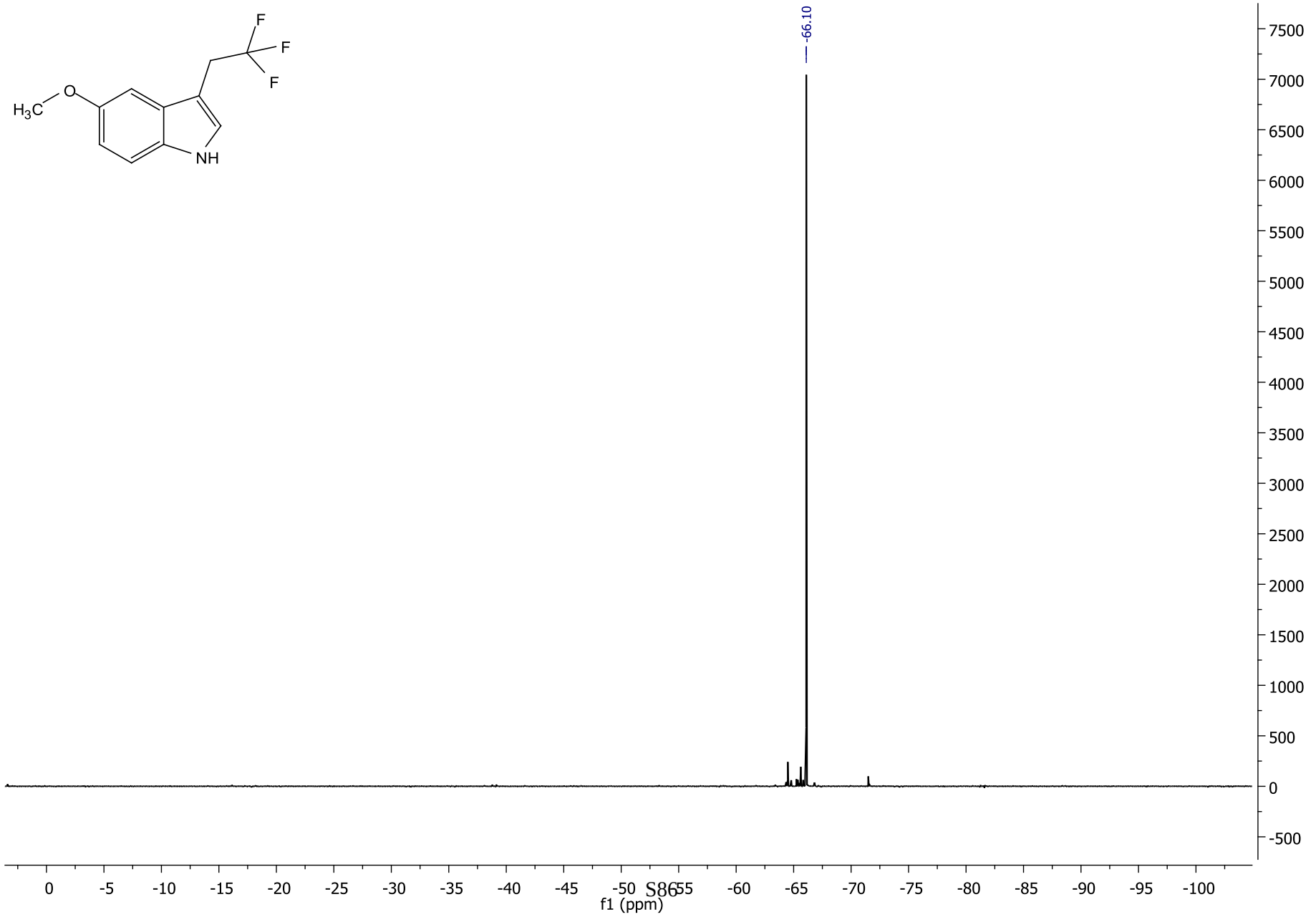

147.76
145.78
130.70
128.94
124.54
123.20
120.54
105.02
104.96
104.91
104.86
100.76
95.03
56.73
56.53
31.84
31.34
30.84
30.31
F
F
F
O
H3C
H3C
O
NH
f1 (ppm)


F
F
F
O
H3C
H3C
O
NH
-66.09
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

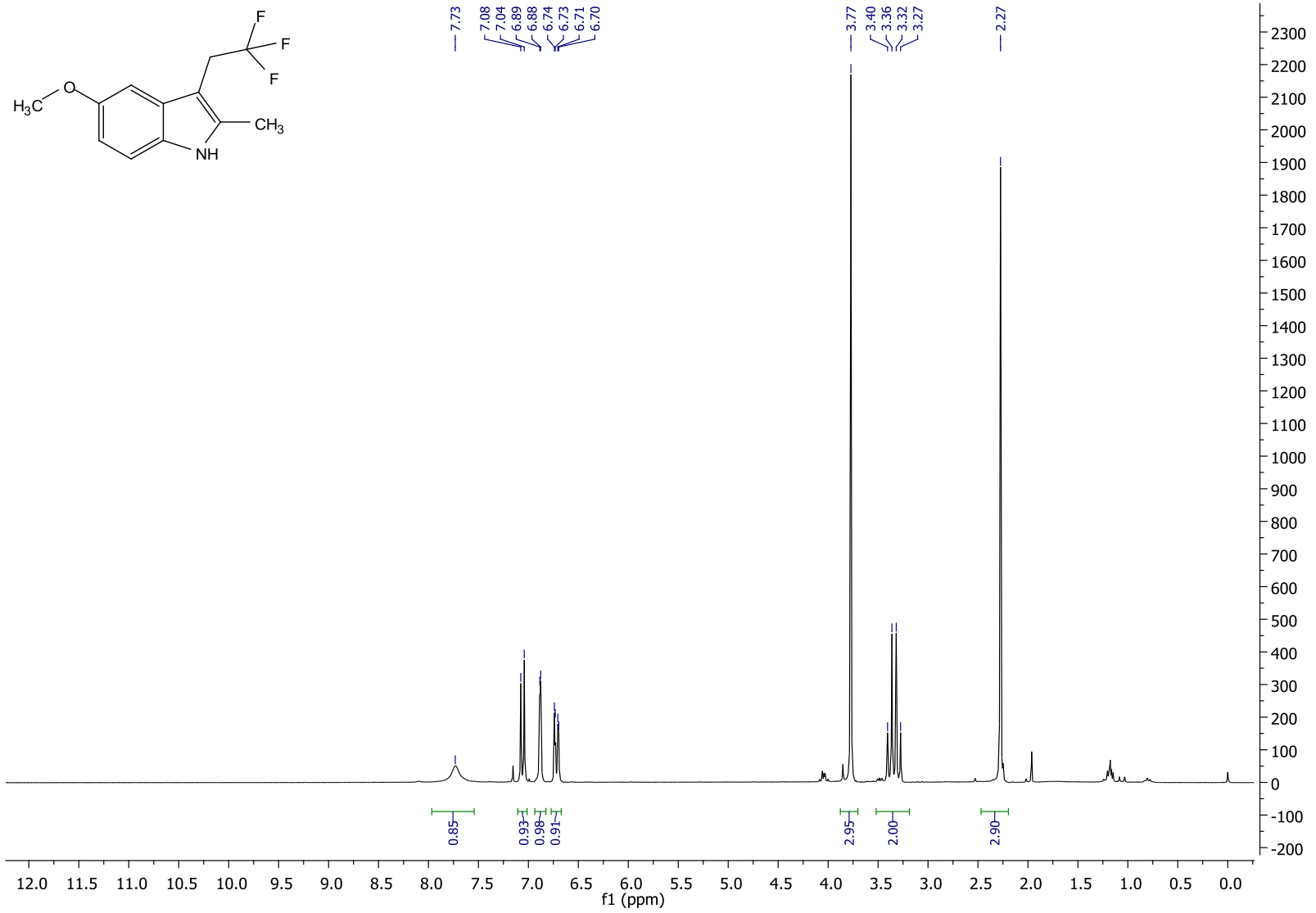
5-Methoxy-3-(2,2,2-trifluoroethyl)-1*H*-indole (3h)

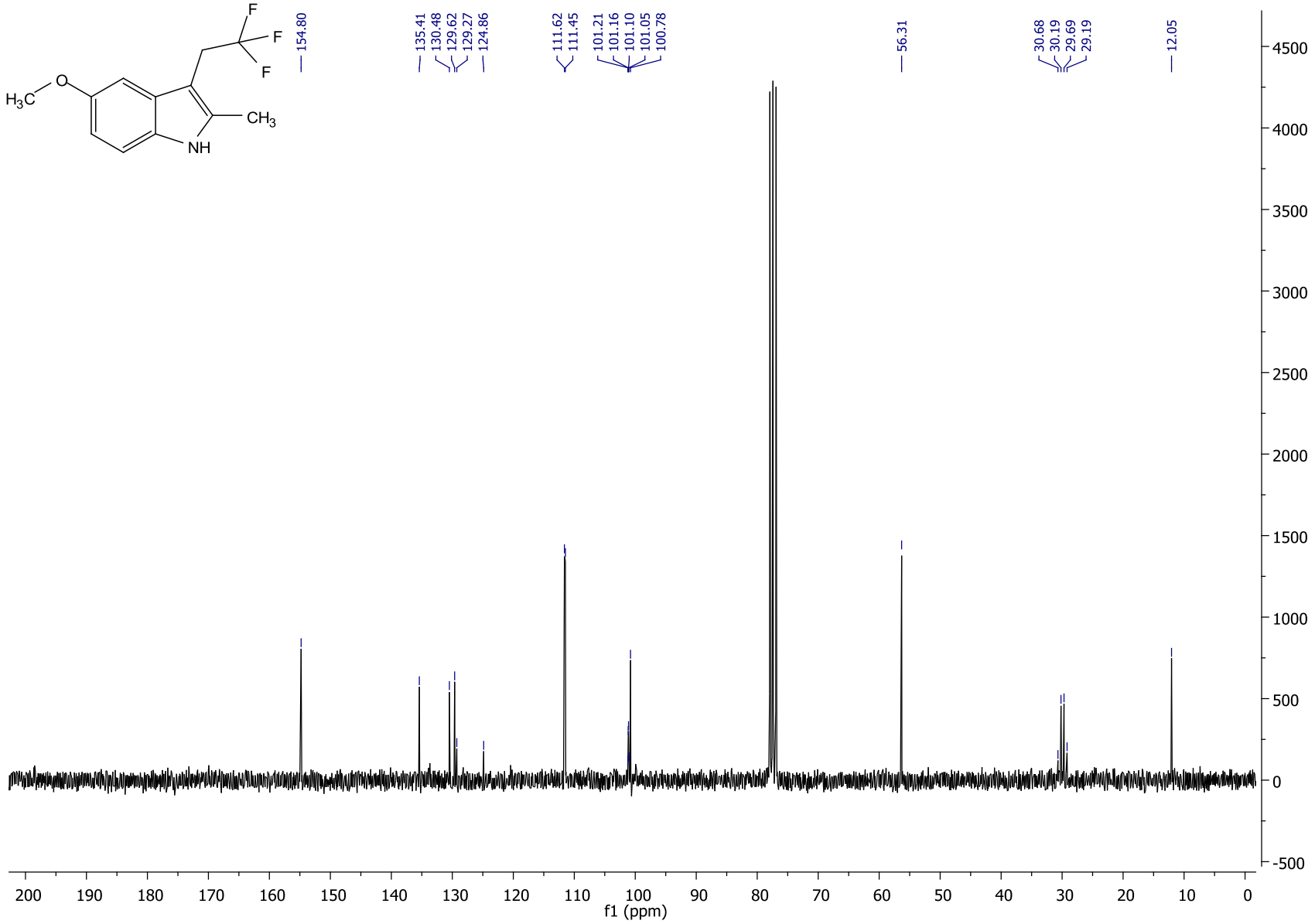


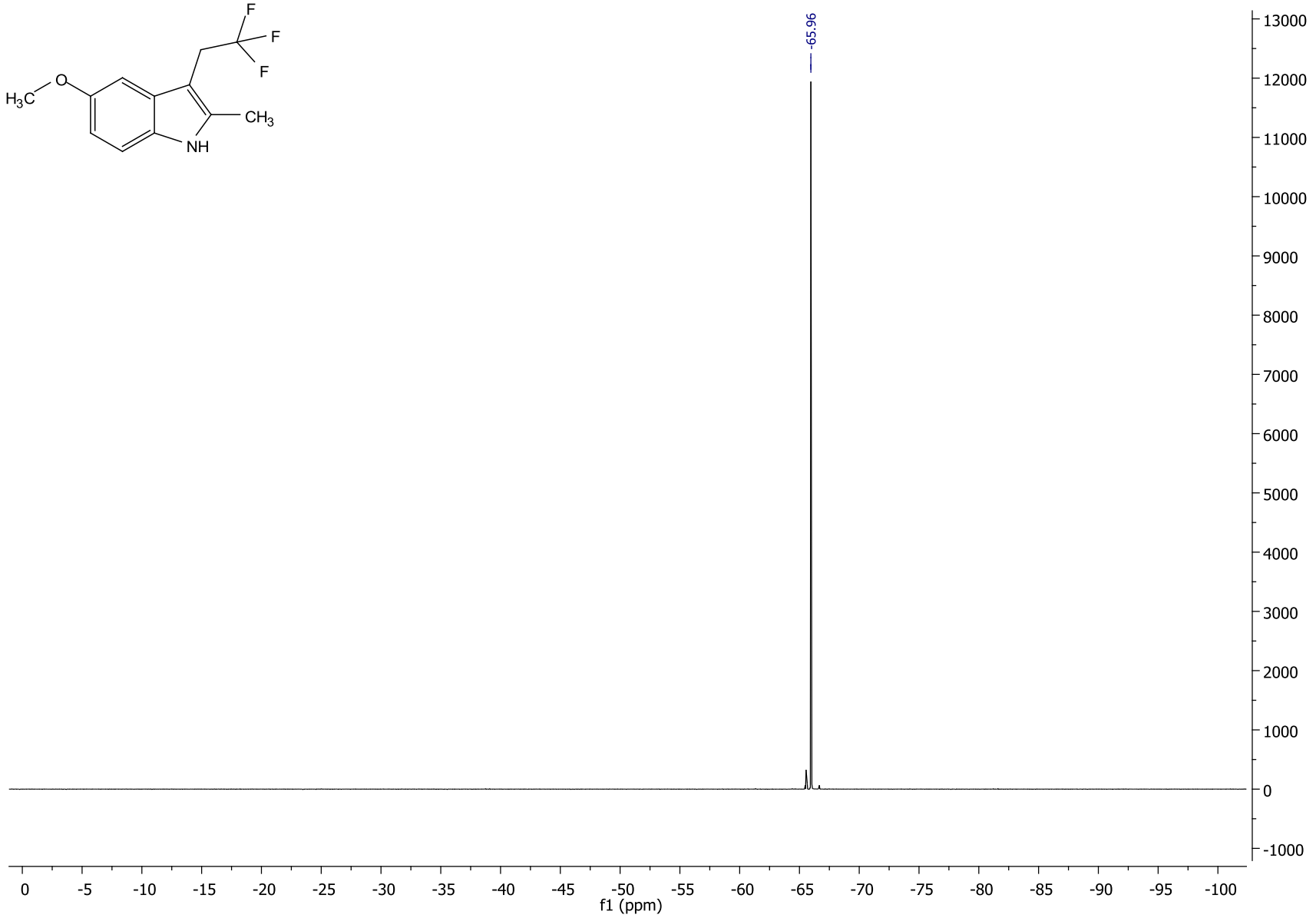

F
F
F
O
H3C
NH
154.87
131.46
128.90
128.17
125.35
123.79
113.20
112.45
105.02
104.97
104.92
104.87
100.79
56.26
31.21
30.72
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
O
H3C
NH
-66.10
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

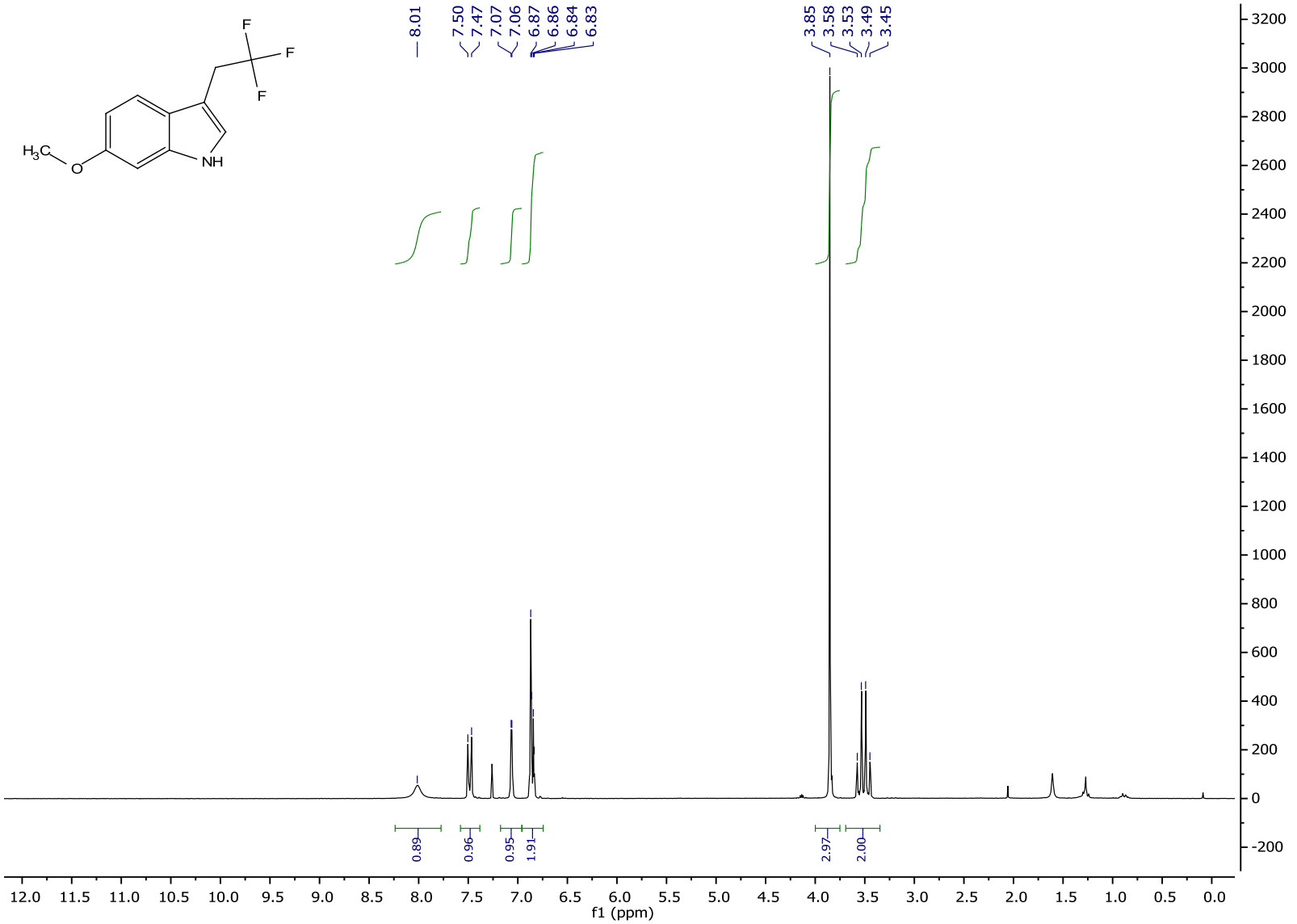
5-Methoxy-2-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3i)

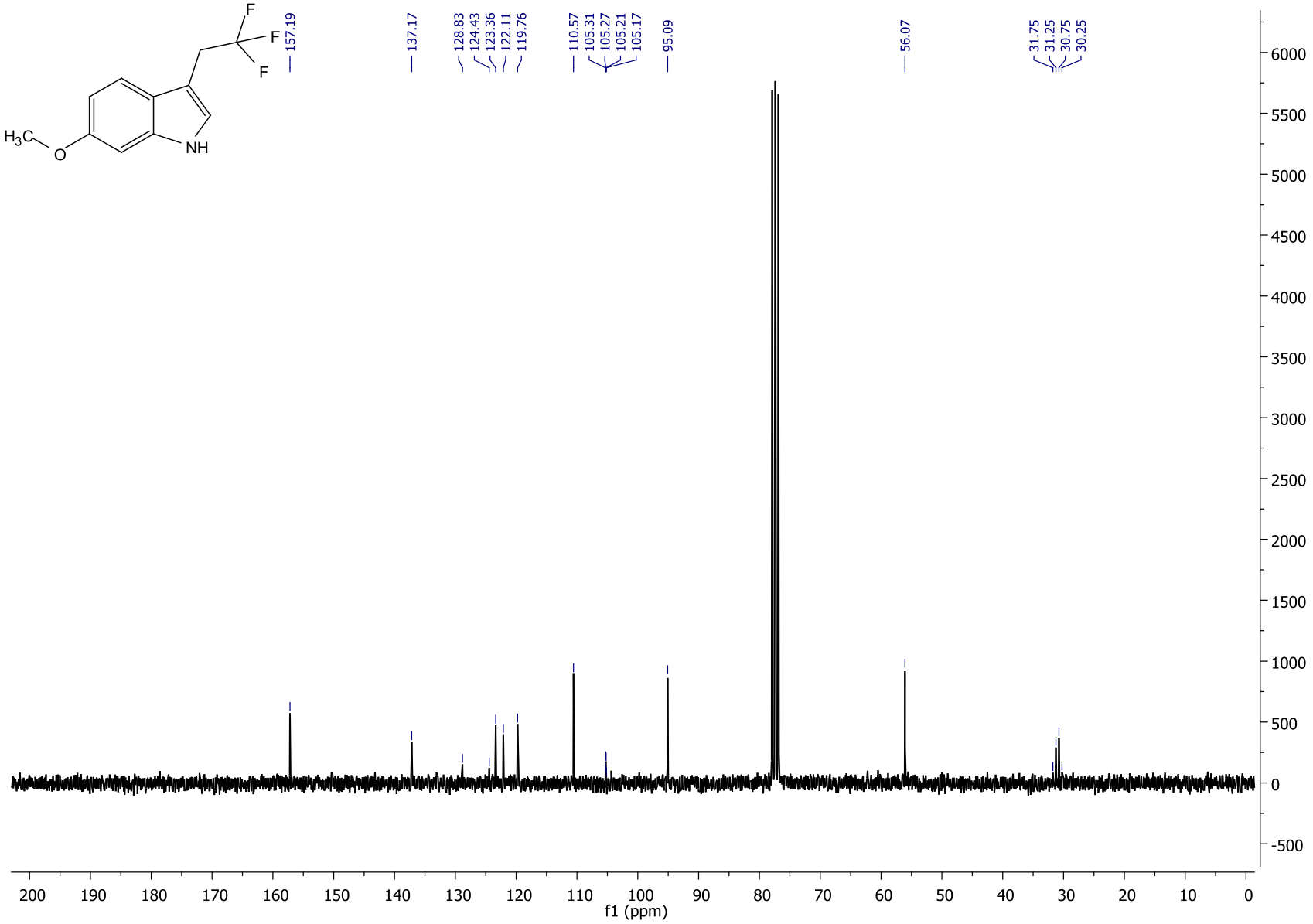


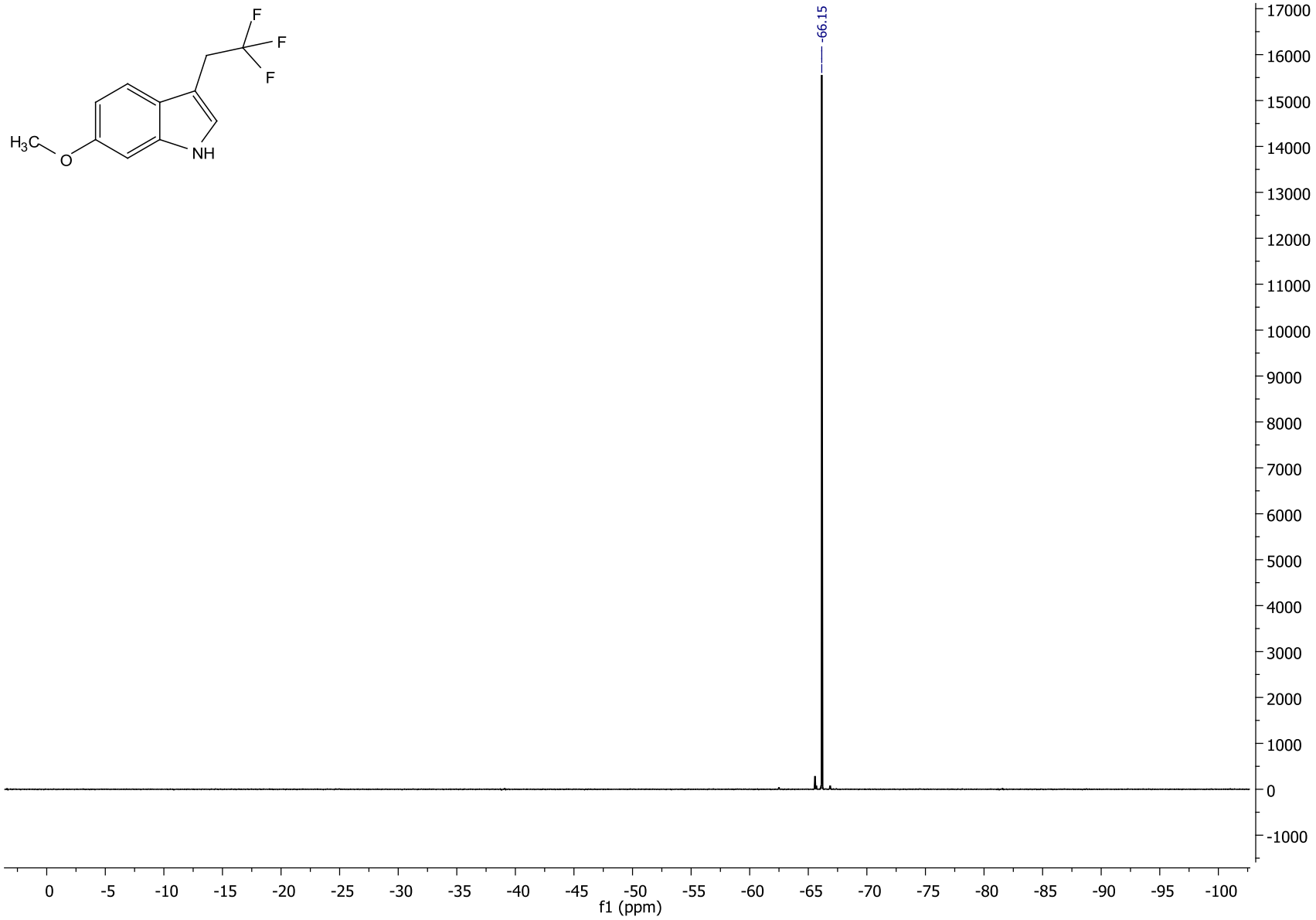

F
F
F
H3C
O
CH3
NH
154.80
135.41
130.48
129.62
129.27
124.86
111.62
111.45
101.21
101.16
101.10
101.05
100.78
56.31
30.68
30.19
29.69
29.19
12.05
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
O
H3C
CH3
NH
-65.96
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

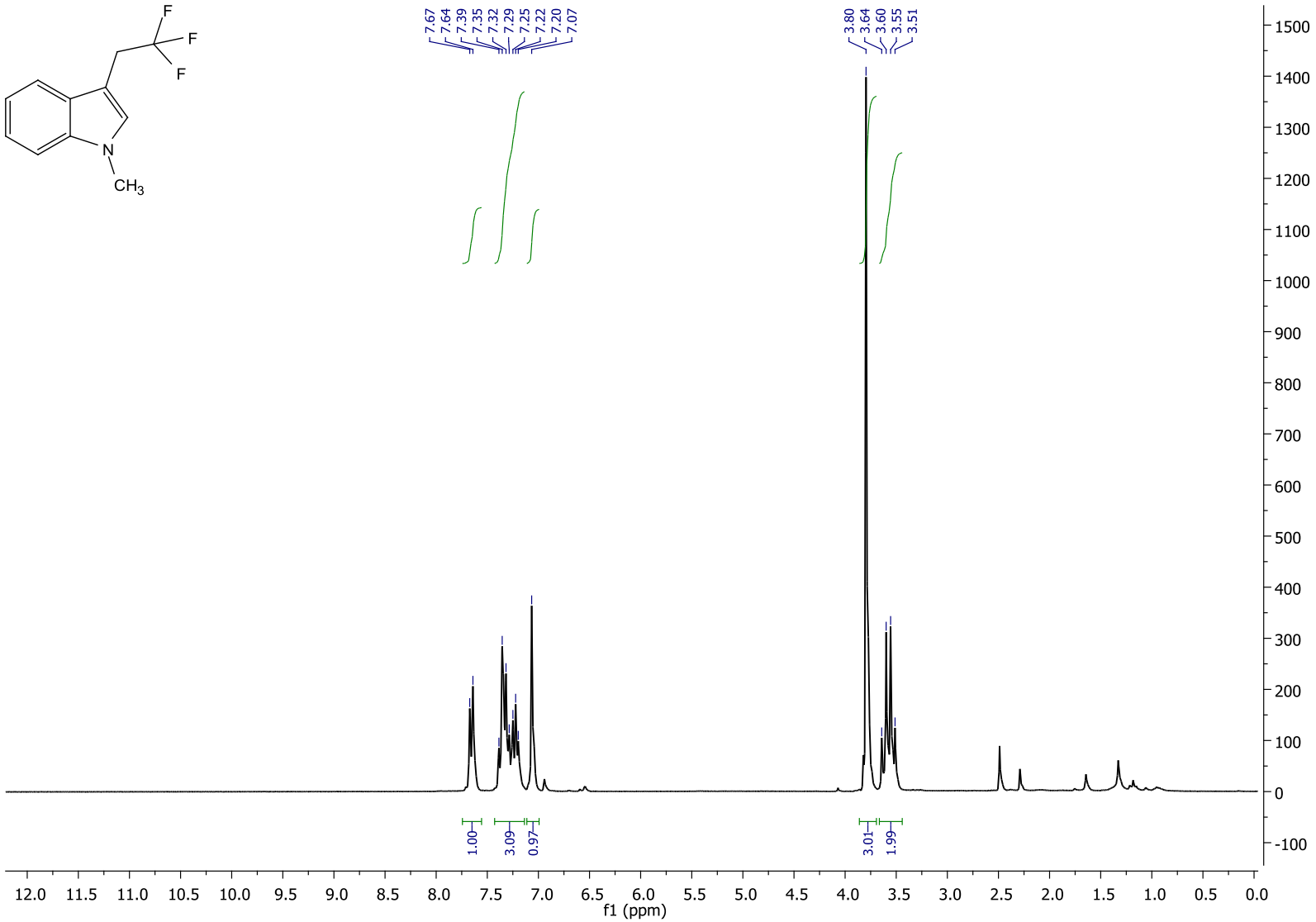
6-Methoxy-3-(2,2,2-trifluoroethyl)-1*H*-indole (3j)

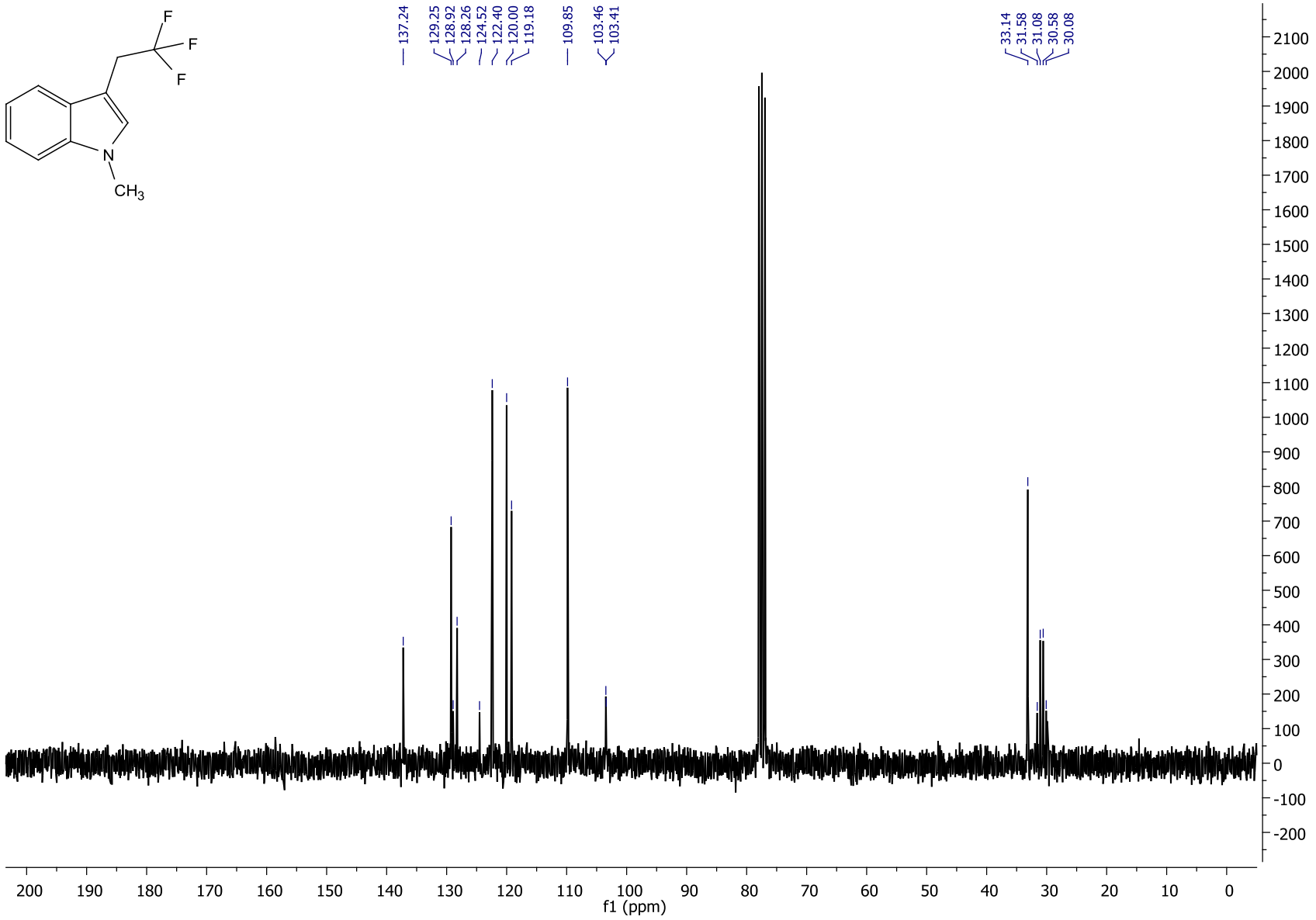


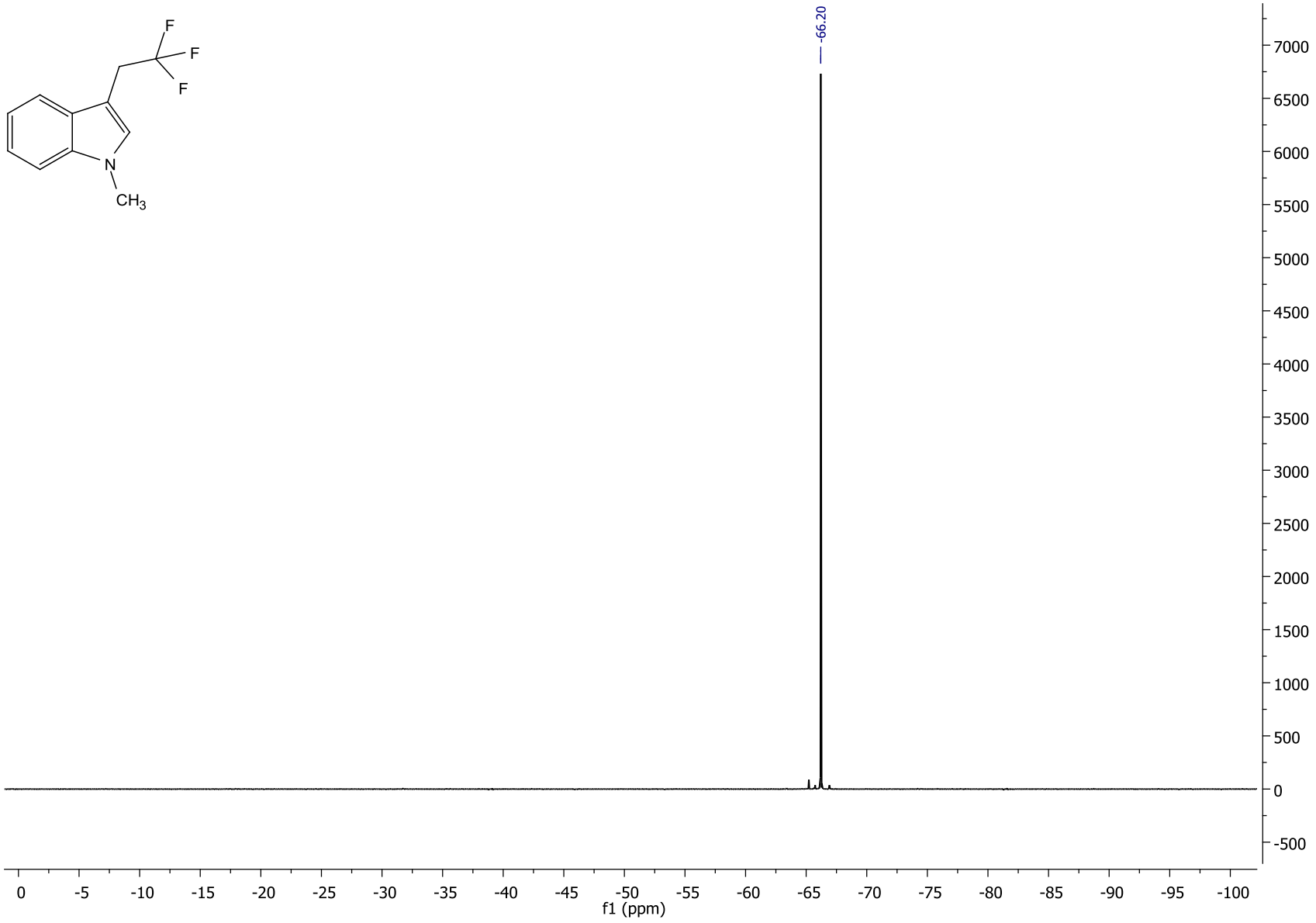

F
F
F
H3C
O
NH
157.19
137.17
128.83
124.43
123.36
122.11
119.76
110.57
105.31
105.27
105.21
105.17
95.09
56.07
31.75
31.25
30.75
30.25
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
H3C
O
NH
-66.15
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

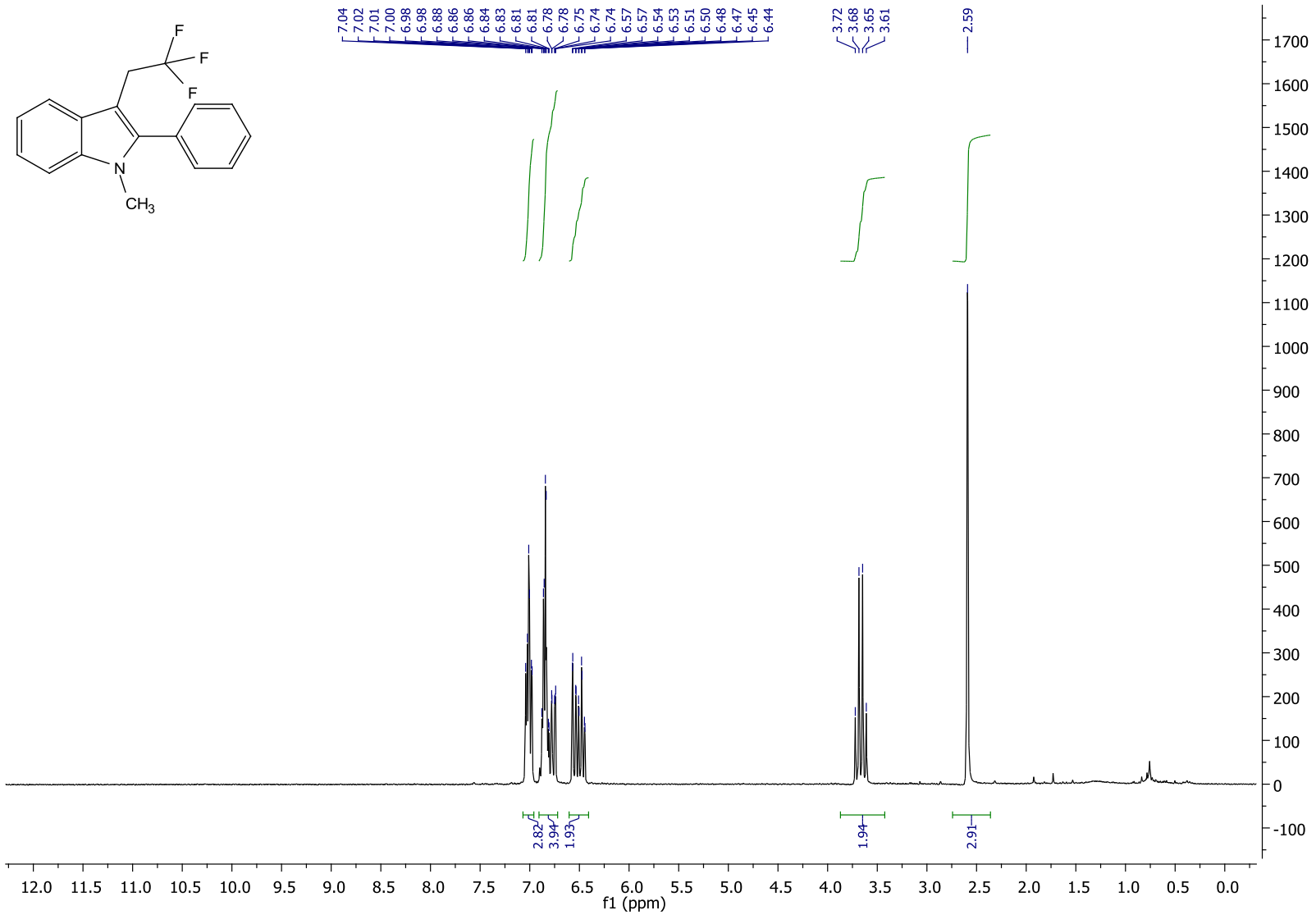
1-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3k)

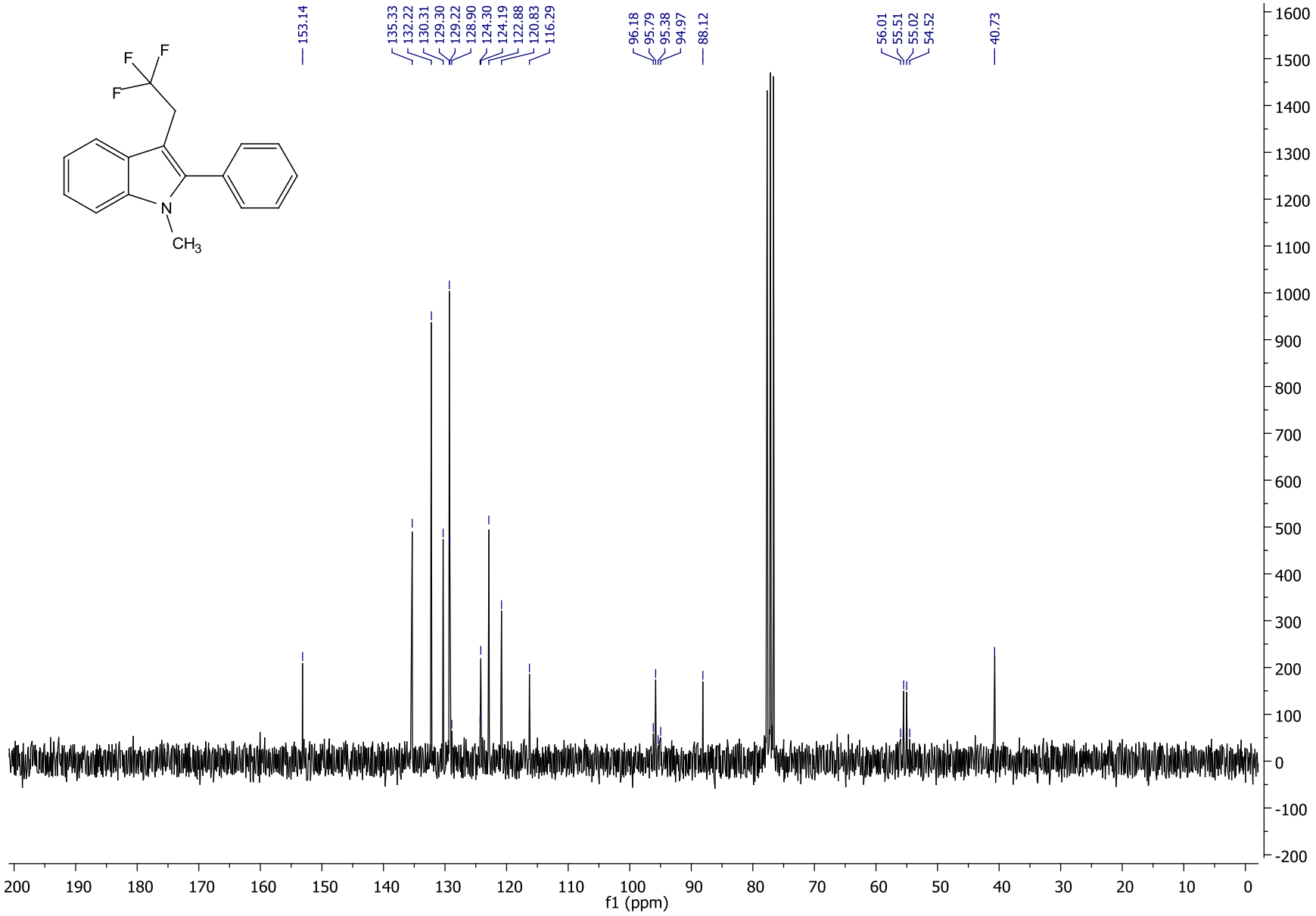


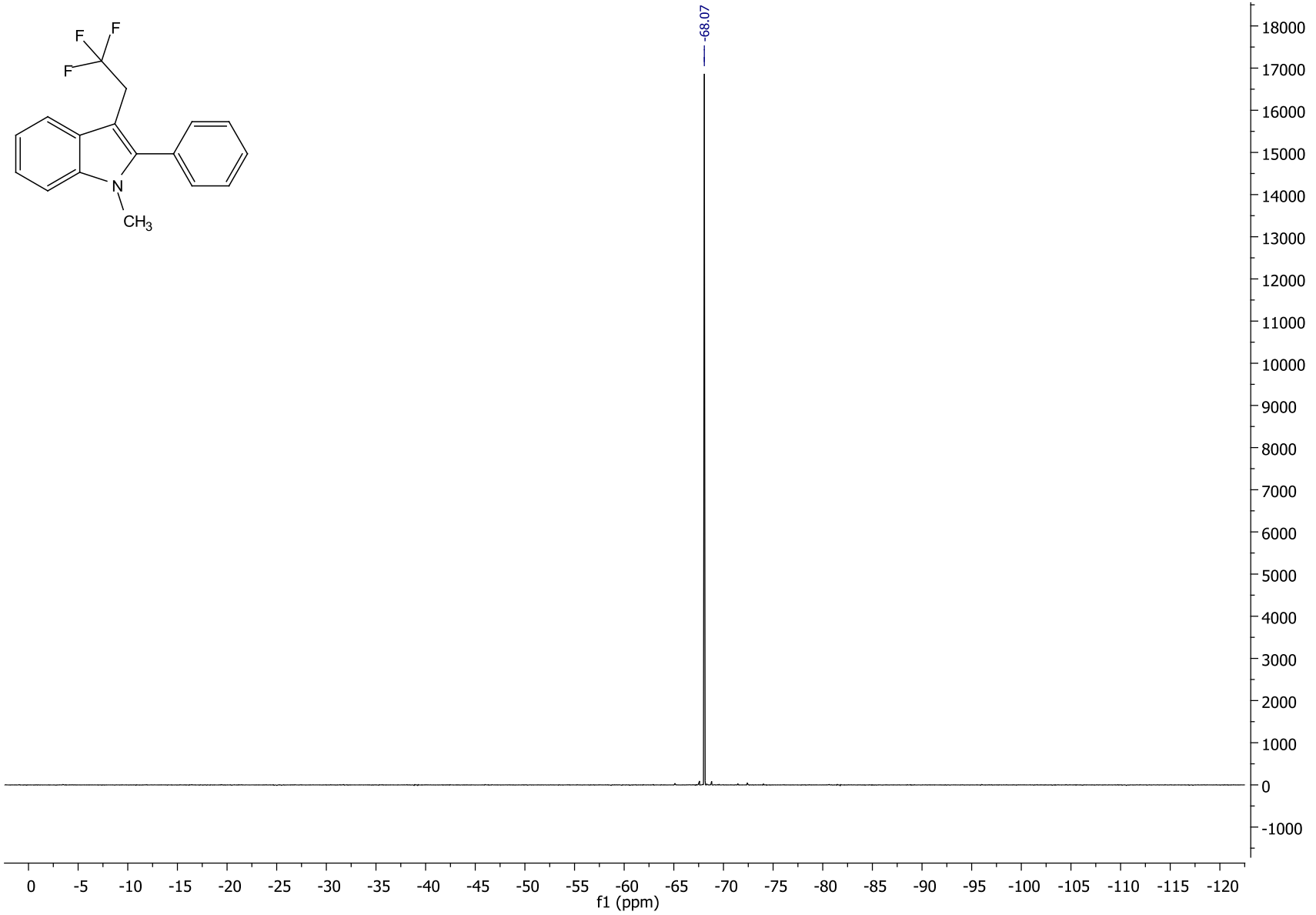

F
F
F
N
CH3
137.24
129.25
128.92
128.26
124.52
122.40
120.00
119.18
109.85
103.46
103.41
33.14
31.58
31.08
30.58
30.08
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
N
CH3
-66.20
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

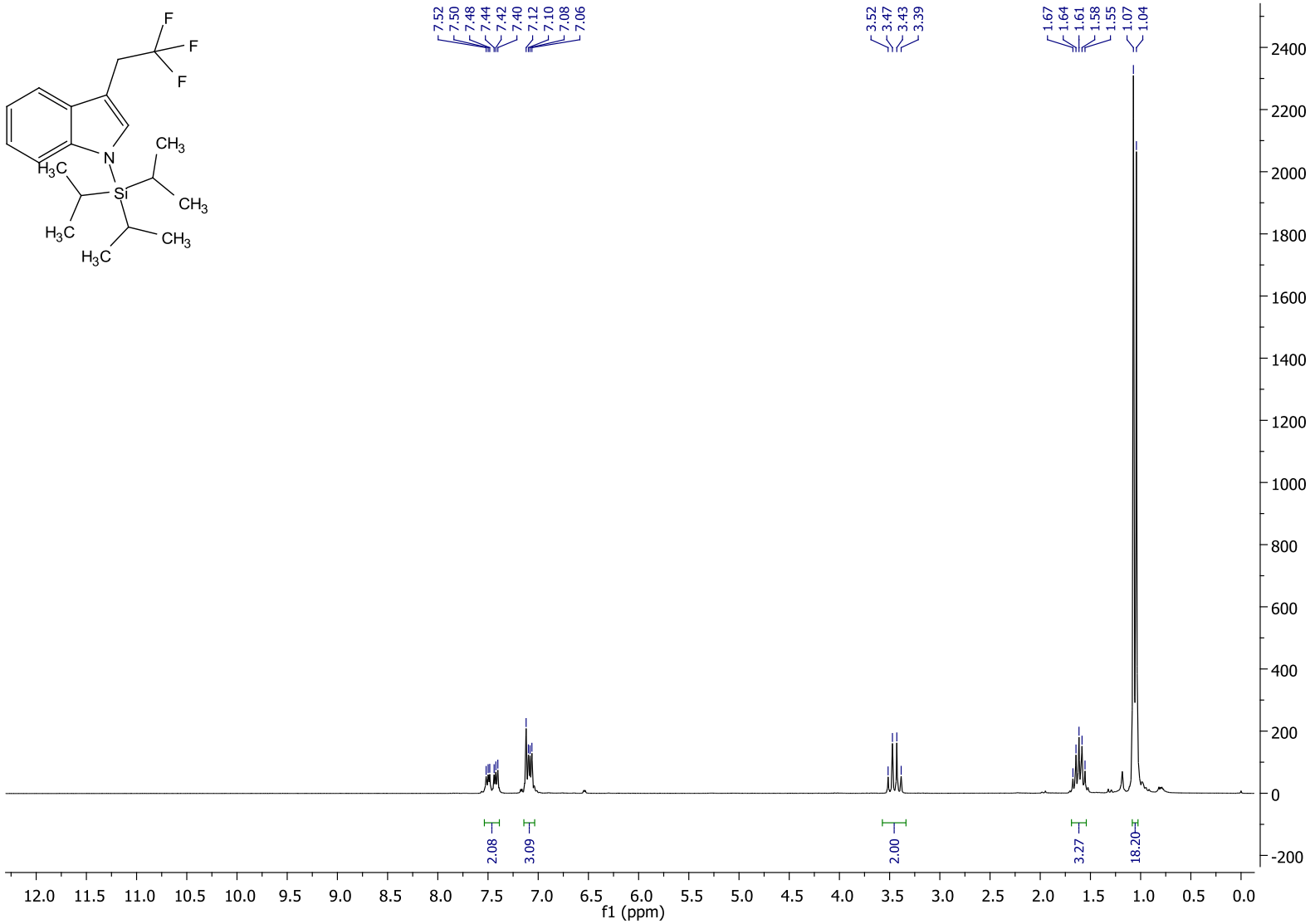
1-Methyl-2-phenyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3l)

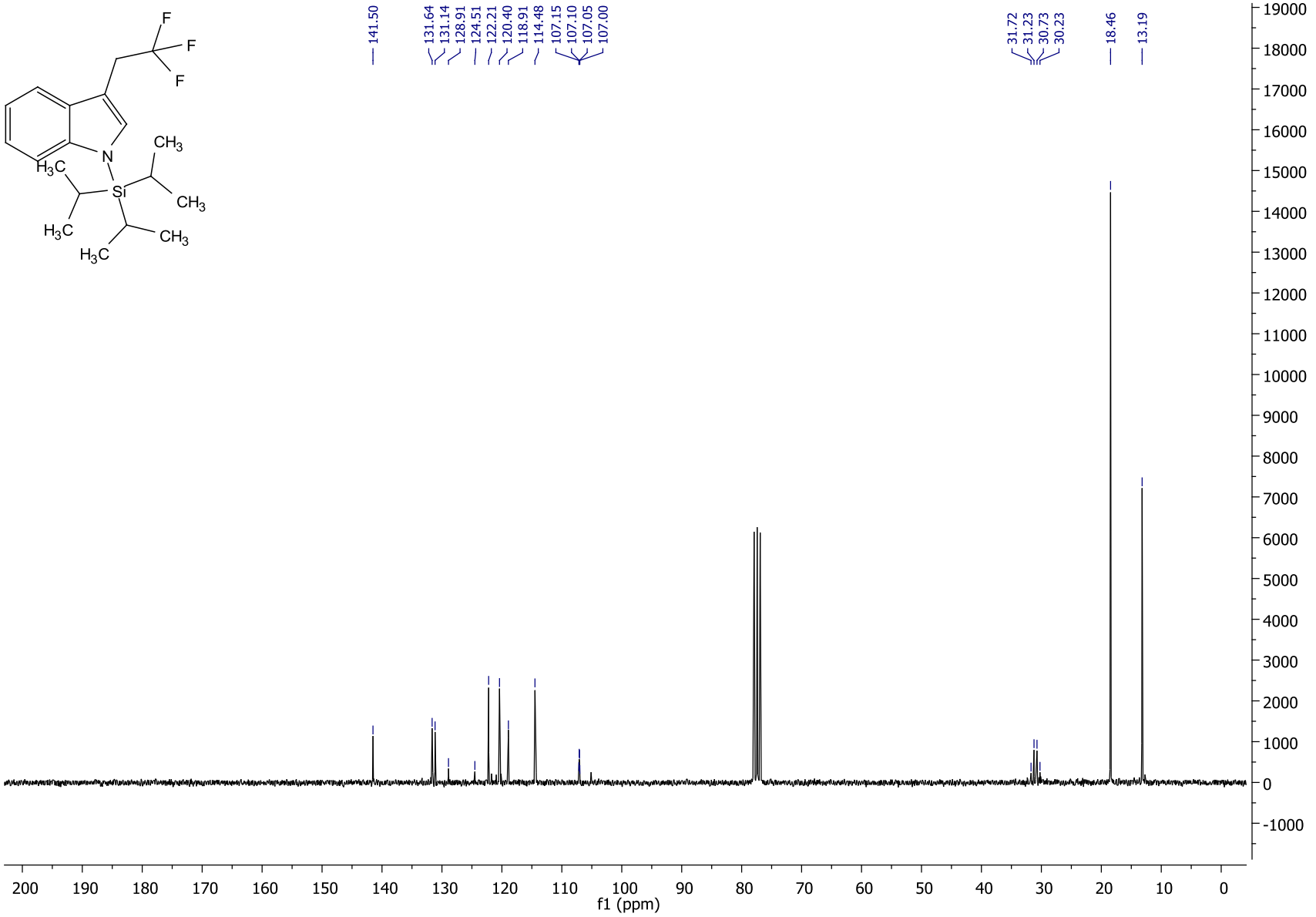


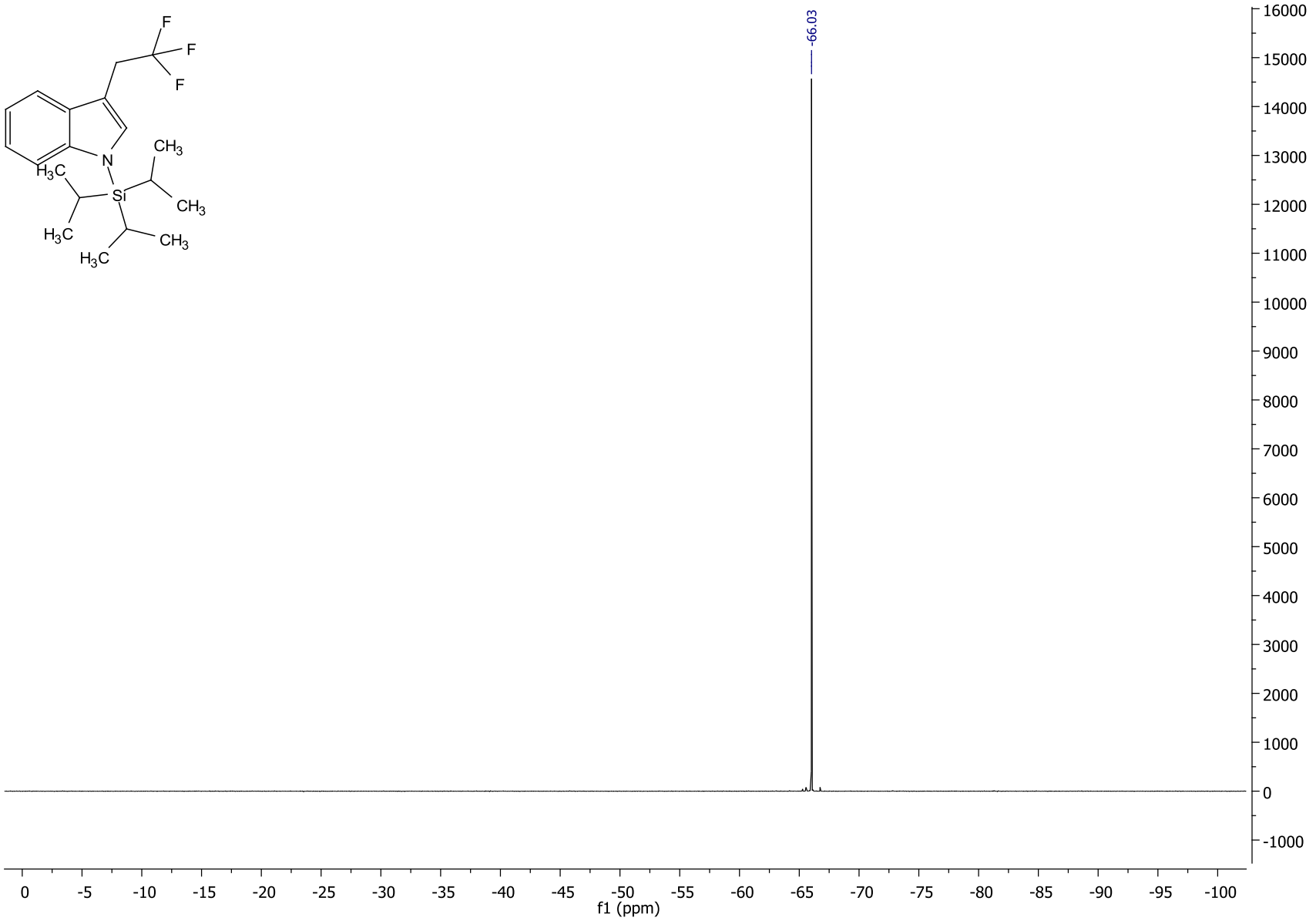

153.14
135.33
132.22
130.31
129.30
129.22
128.90
124.30
124.19
122.88
120.83
116.29
96.18
95.79
95.38
94.97
88.12
56.01
55.51
55.02
54.52
40.73
F
F
F
N
CH3
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
N
CH3
-68.07
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)

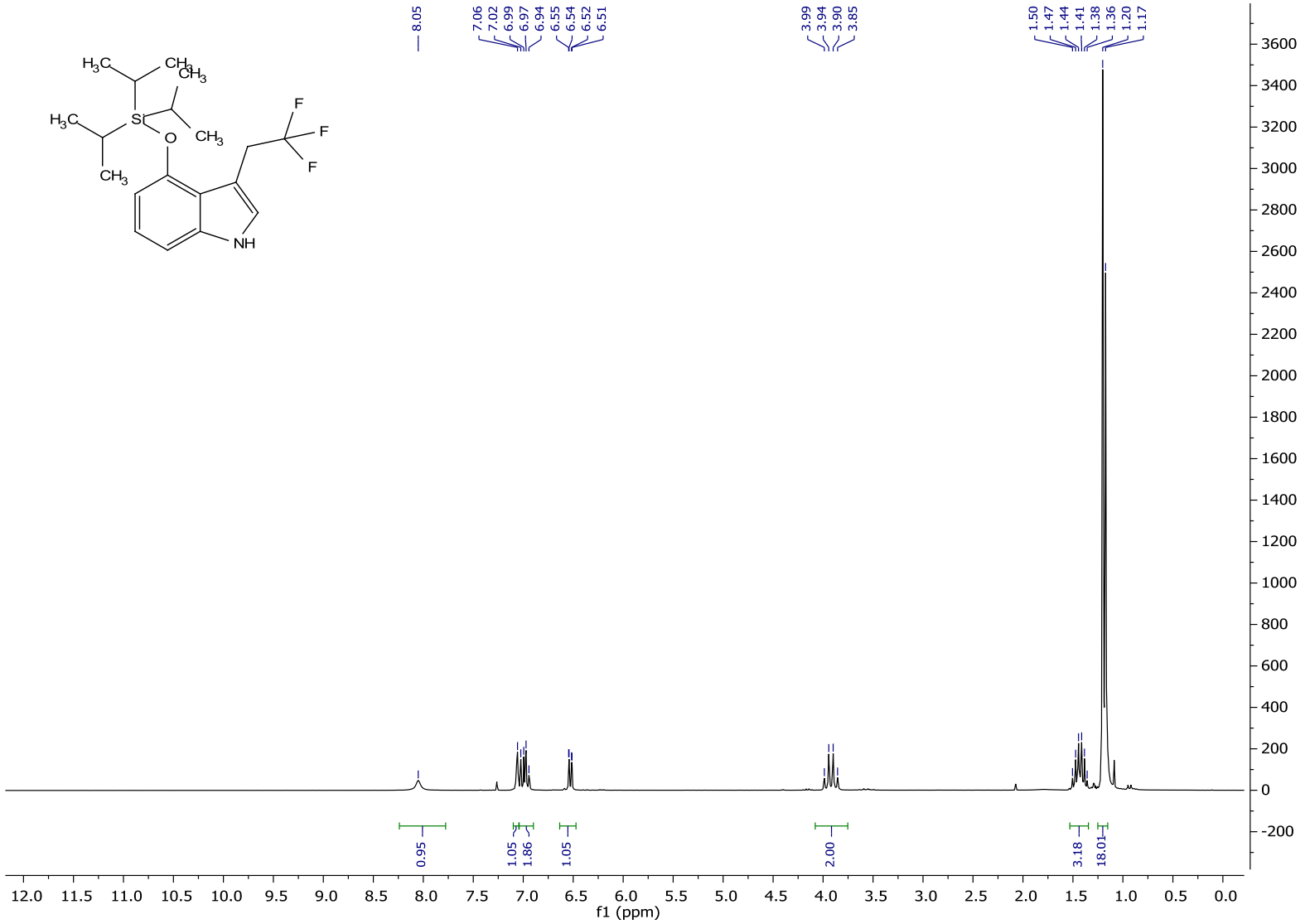
3-(2,2,2-Trifluoroethyl)-1-(triisopropylsilyl)-1*H*-indole (3m)

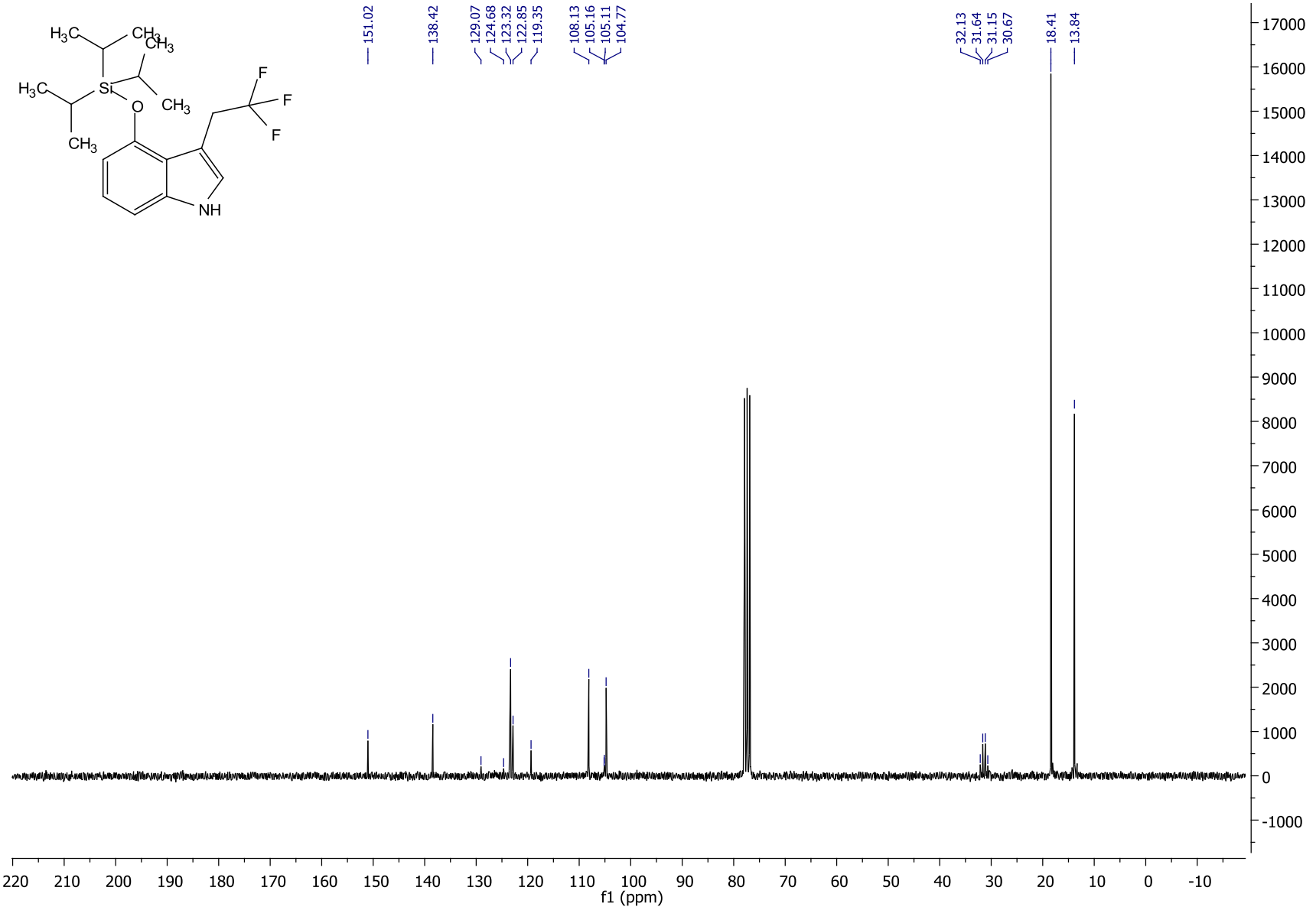


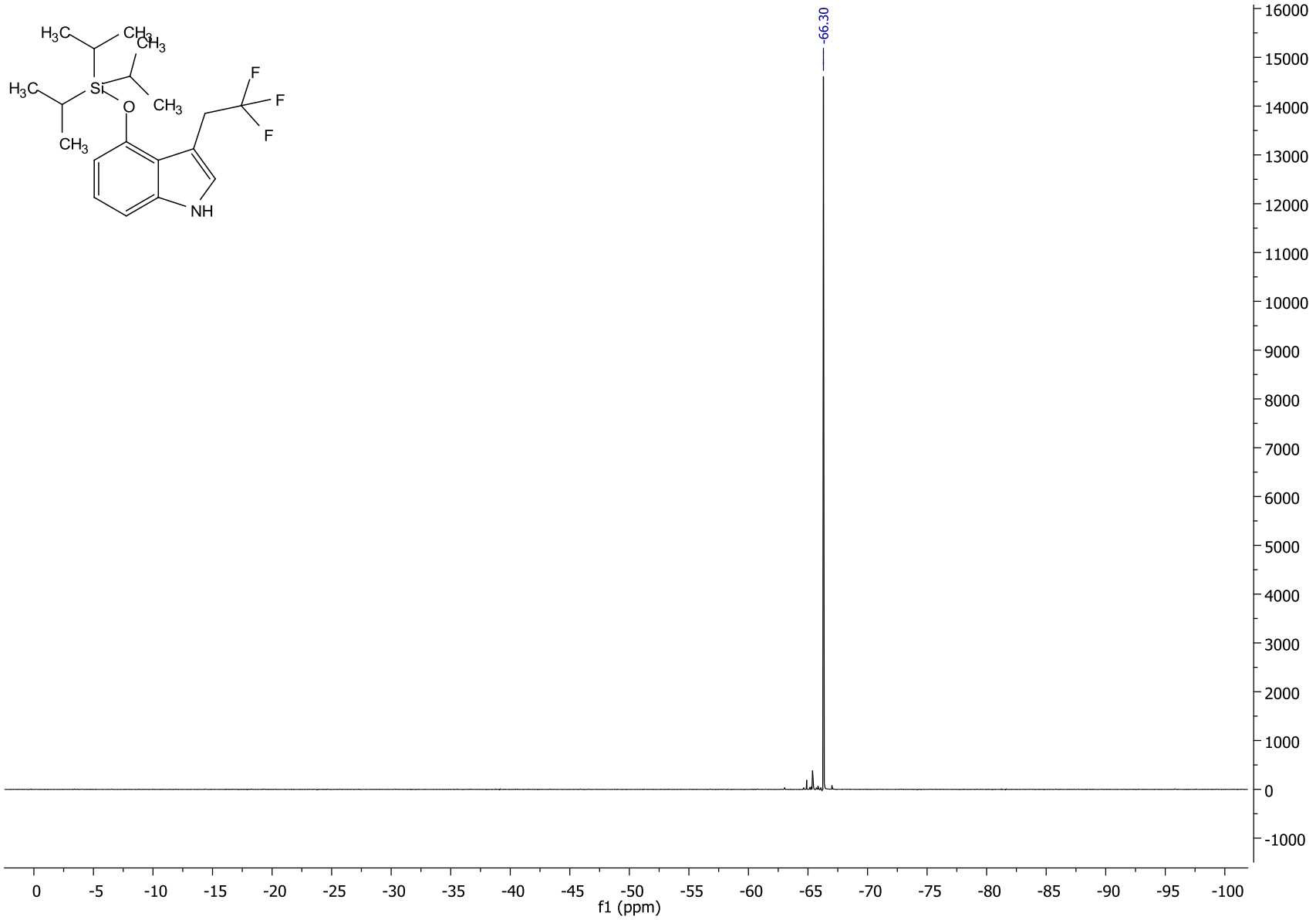

F
F
F
N
Si
CH3
H3C
CH3
H3C
CH3
H3C
141.50
131.64
131.14
128.91
124.51
122.21
120.40
118.91
114.48
107.15
107.10
107.05
107.00
31.72
31.23
30.73
30.23
18.46
13.19
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
N
Si
CH3
H3C
CH3
H3C
CH3
H3C
-66.03
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

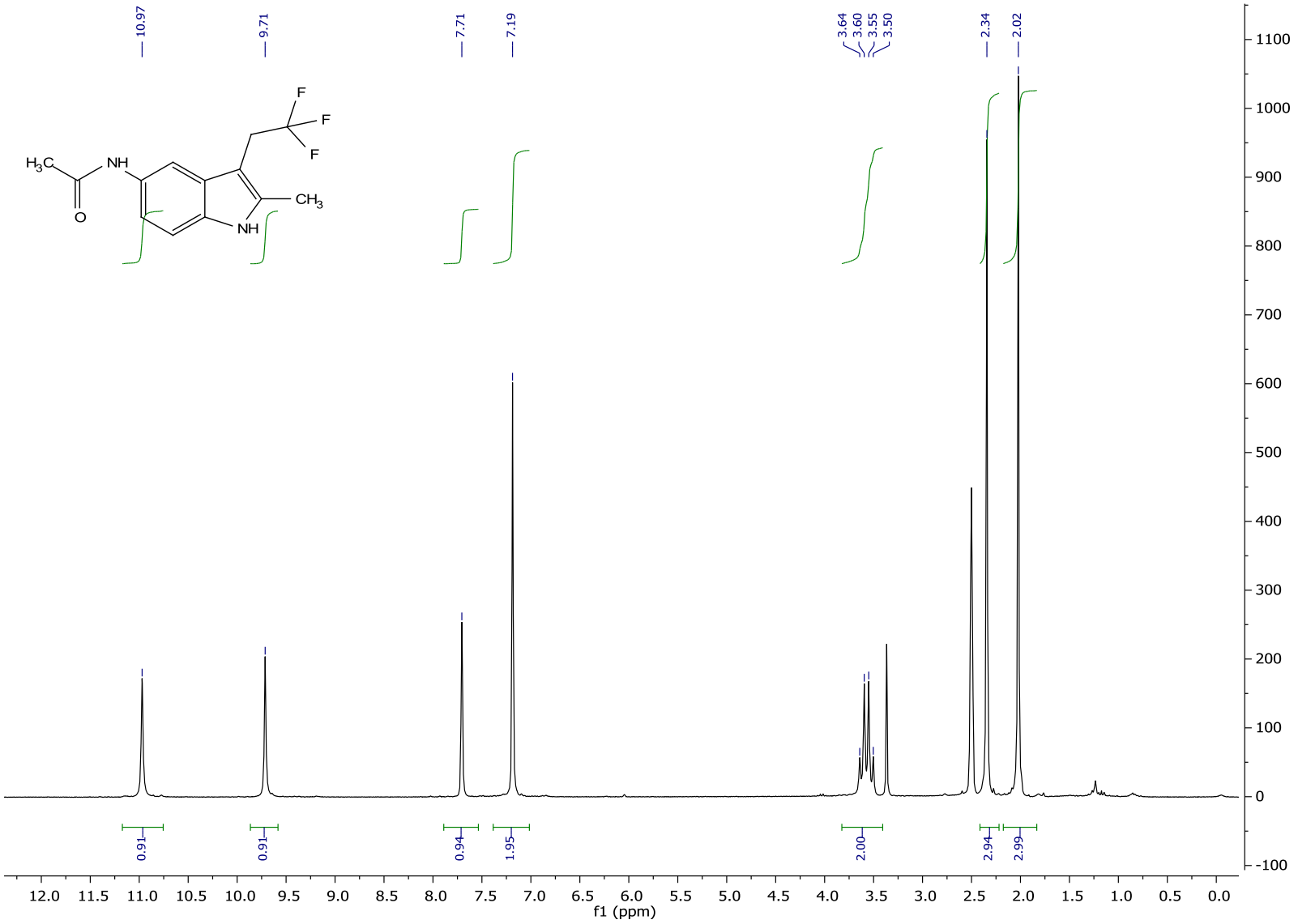
3-(2,2,2-Trifluoroethyl)-4-((triisopropylsilyl)oxy)-1*H*-indole (3n)

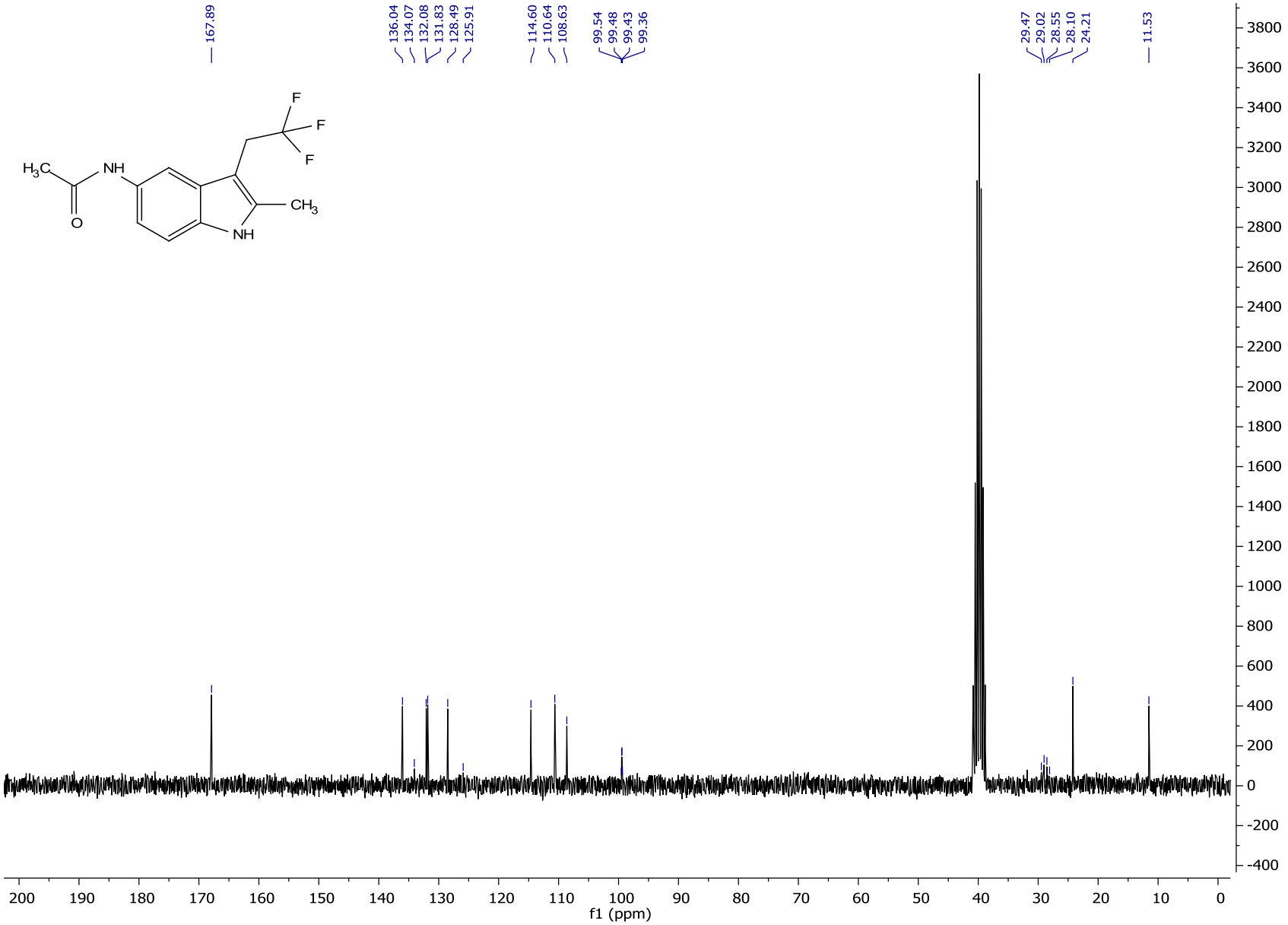


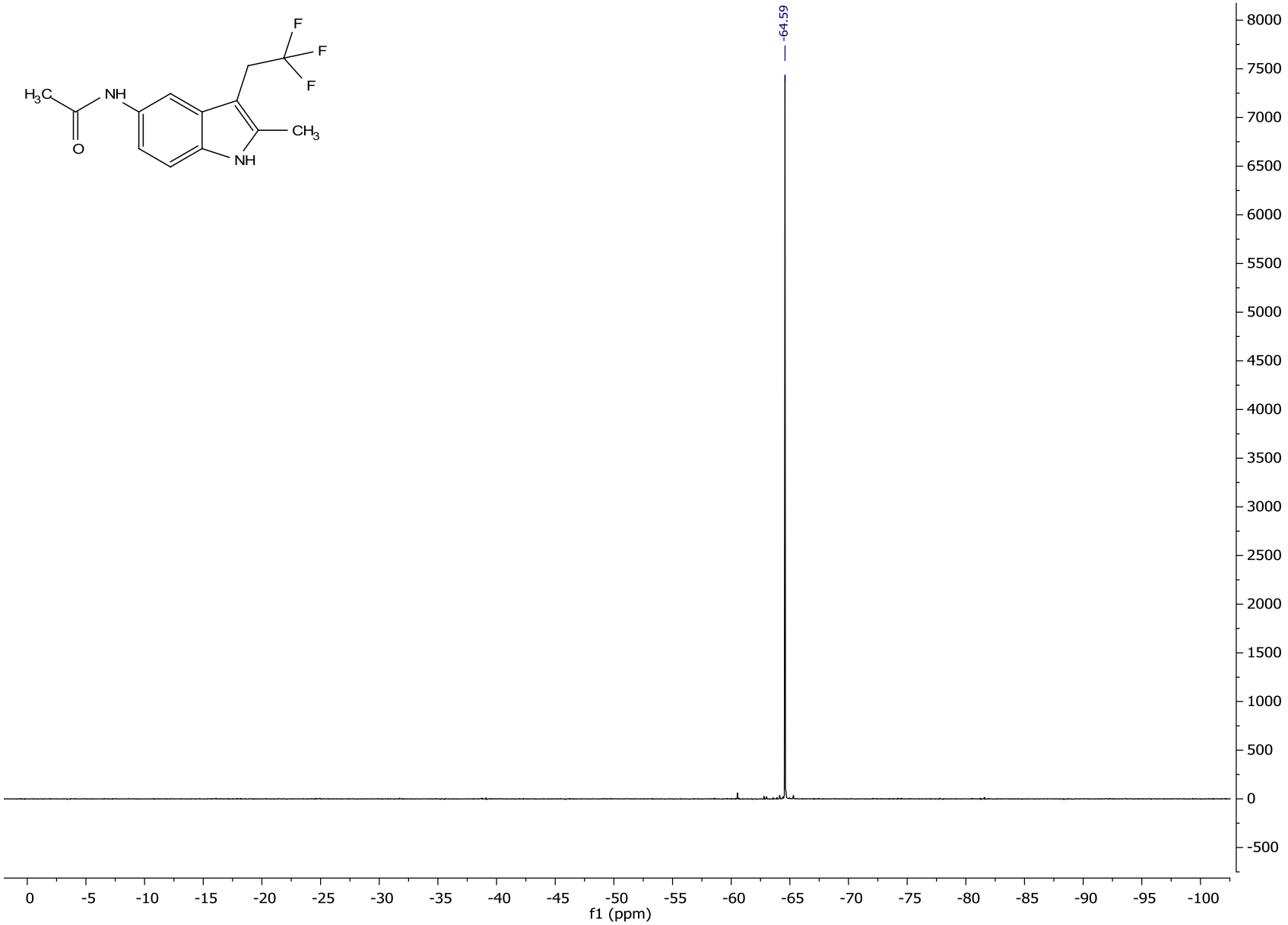

151.02
138.42
129.07
124.68
123.32
122.85
119.35
108.13
105.16
105.11
104.77
32.13
31.64
31.15
30.67
18.41
13.84
f1 (ppm)


H3C
CH3
CH3
H3C
Si
O
CH3
CH3
F
F
F
NH
-66.30
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

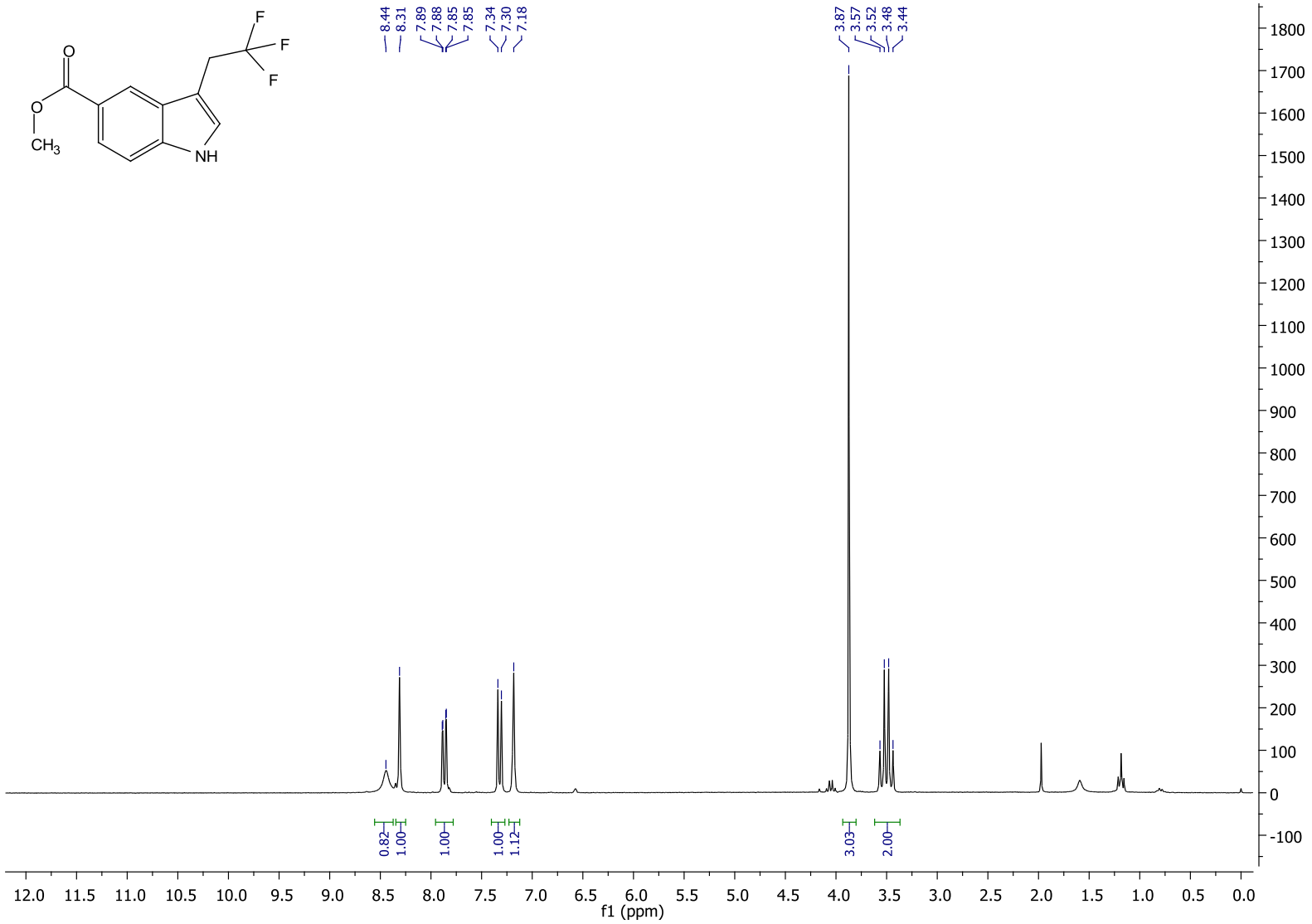
N-(2-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indol-5-yl)acetamide (3o)

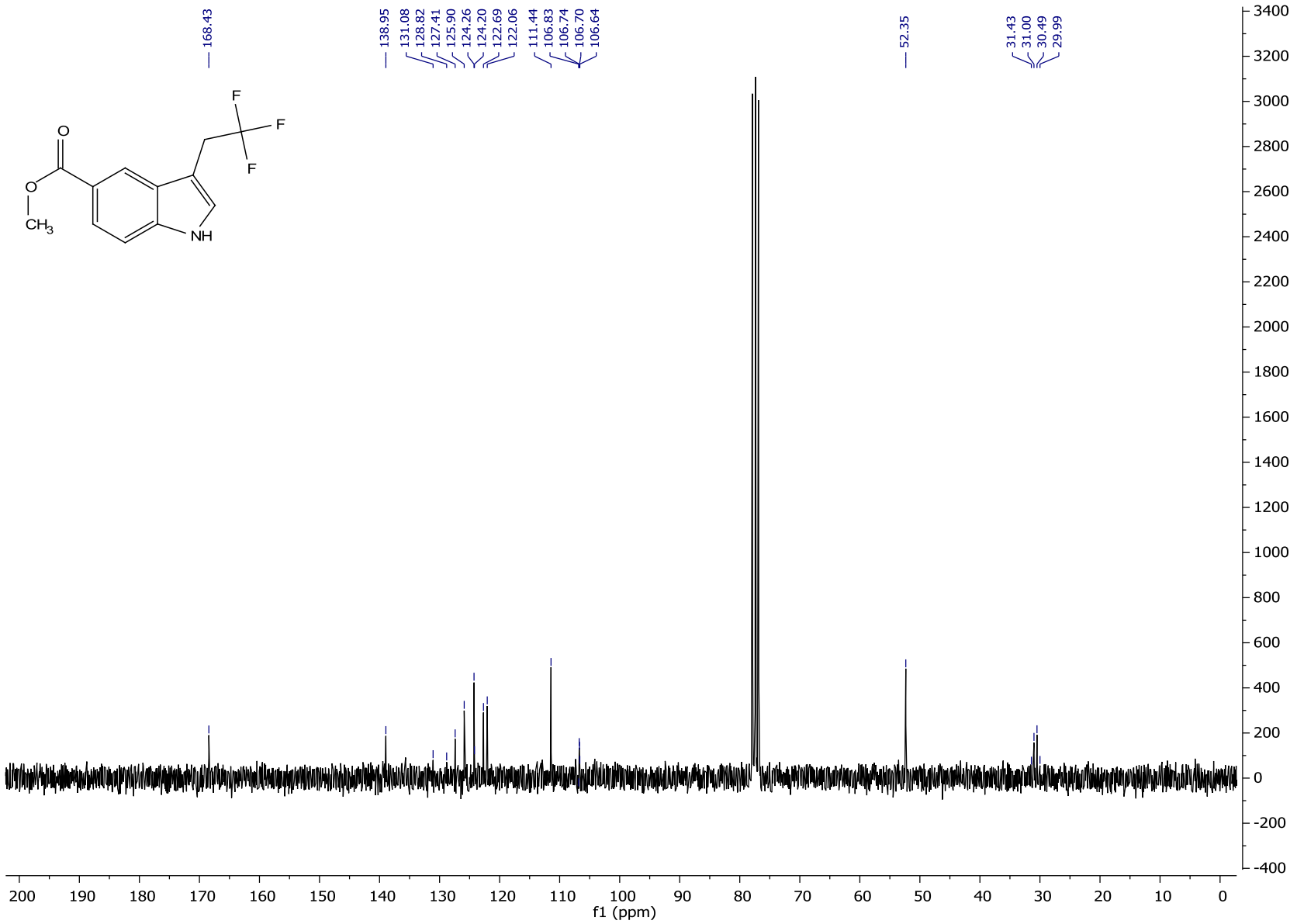



167.89
136.04
134.07
132.08
131.83
128.49
125.91
114.60
110.64
108.63
99.54
99.48
99.43
99.36
29.47
29.02
28.55
28.10
24.21
11.53
F
F
F
H3C
NH
O
CH3
NH
f1 (ppm)

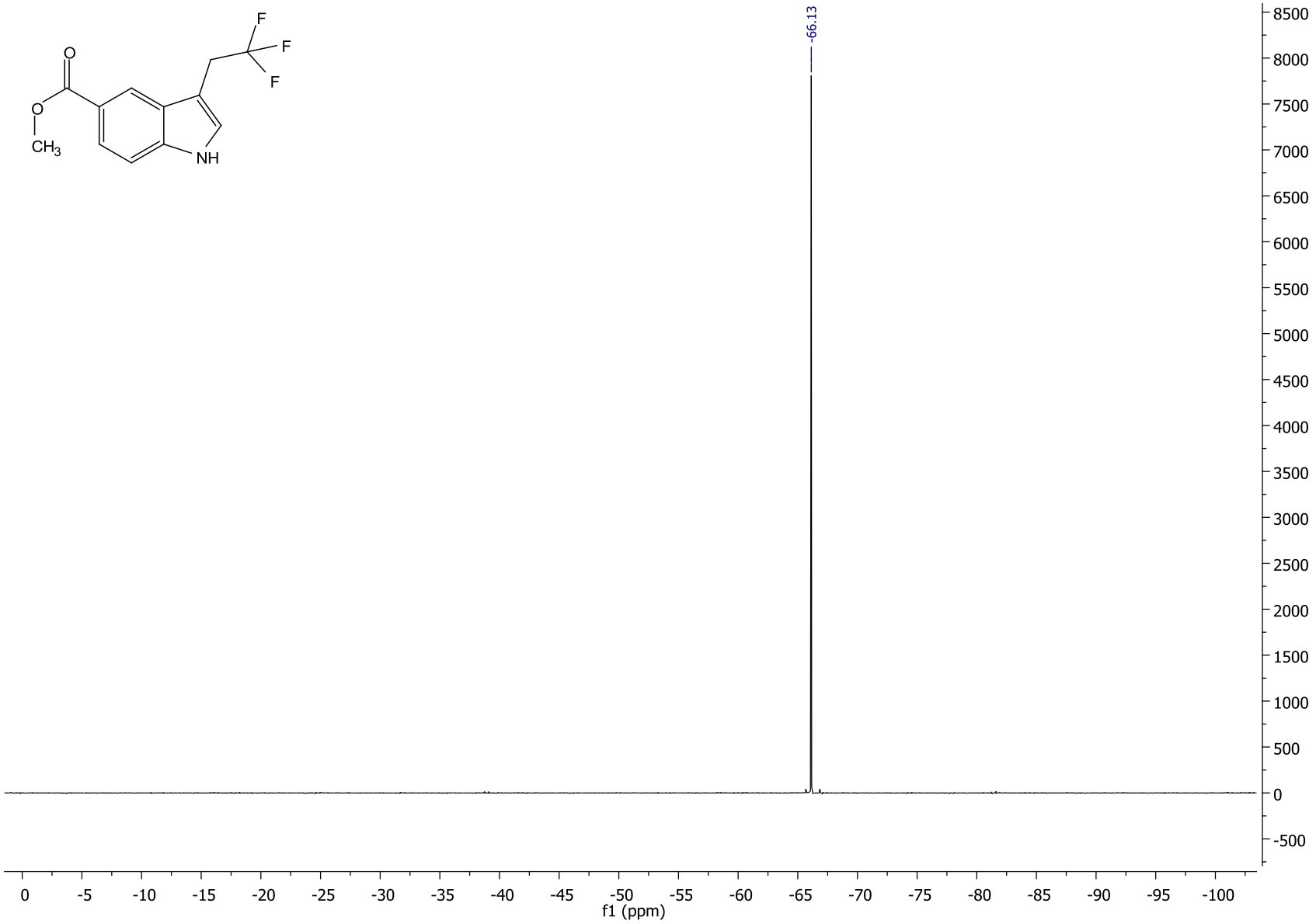

F
F
F
H3C
NH
CH3
O
NH
-64.59
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

Methyl 3-(2,2,2-trifluoroethyl)-1*H*-indole-5-carboxylate (3p)

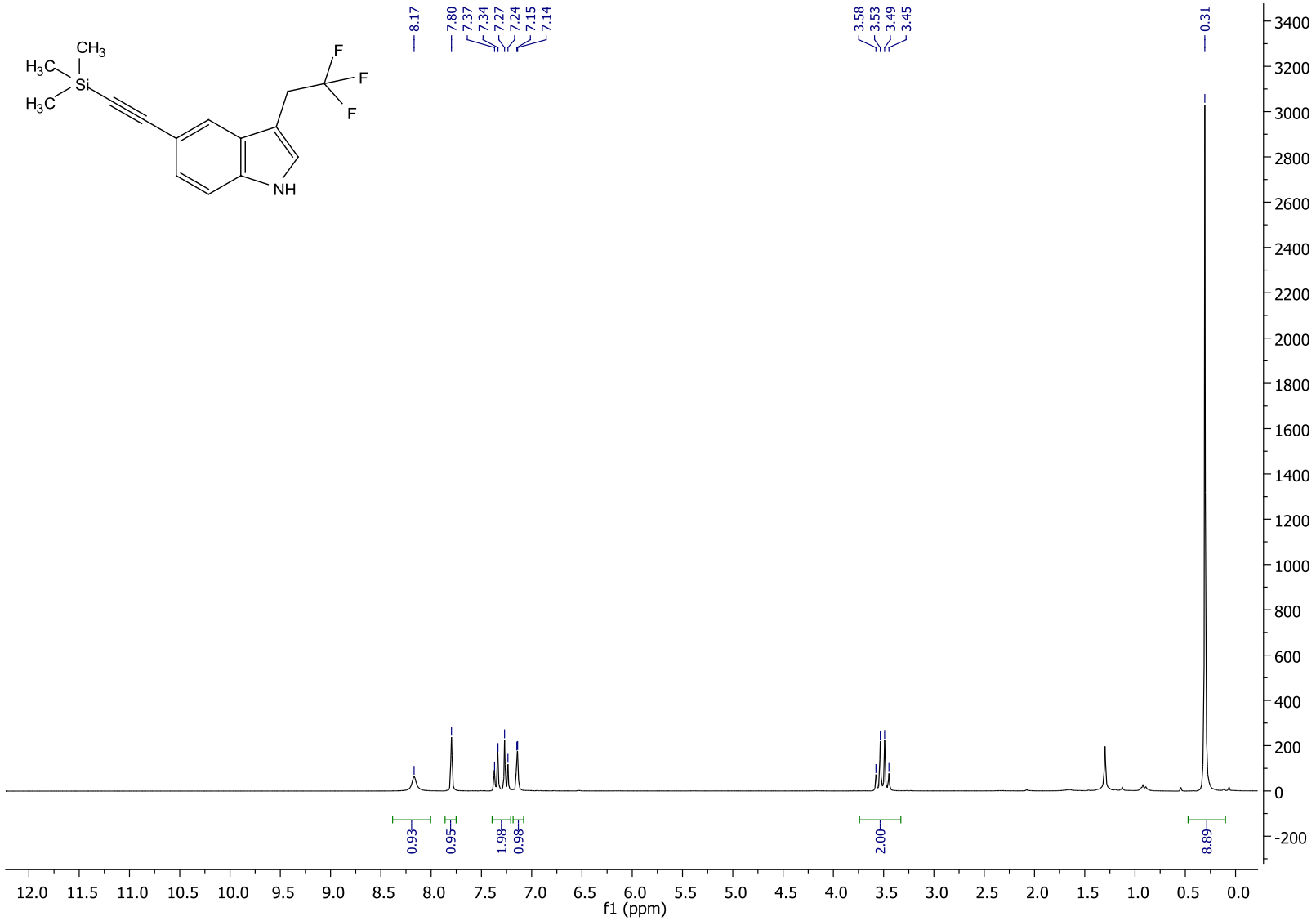


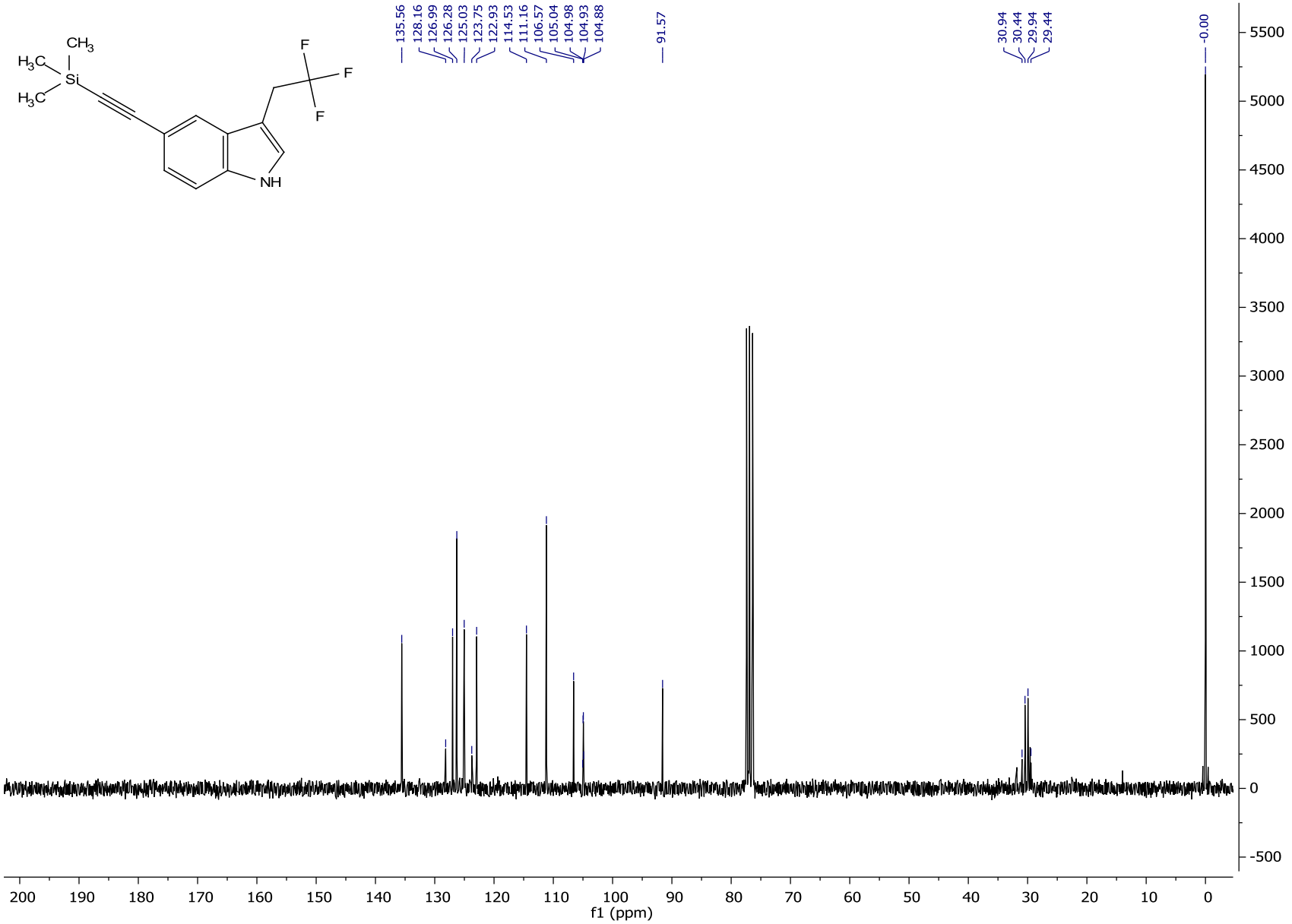

168.43
138.95
131.08
128.82
127.41
125.90
124.26
124.20
122.69
122.06
111.44
106.83
106.74
106.70
106.64
52.35
31.43
31.00
30.49
29.99
F
F
F
O
O
CH3
NH
f1 (ppm)

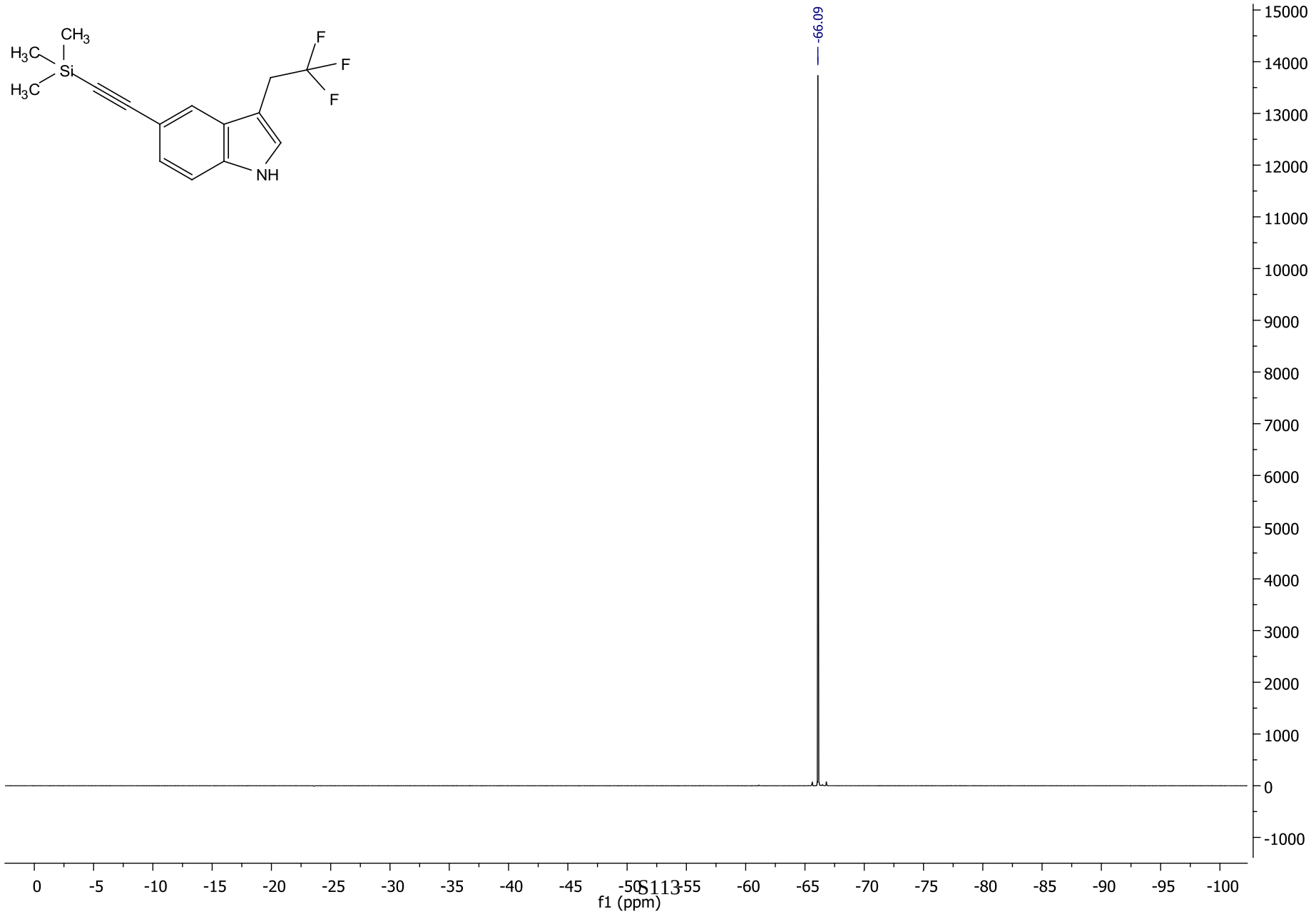
d


F
F
F
O
O
CH3
NH
-66.13
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

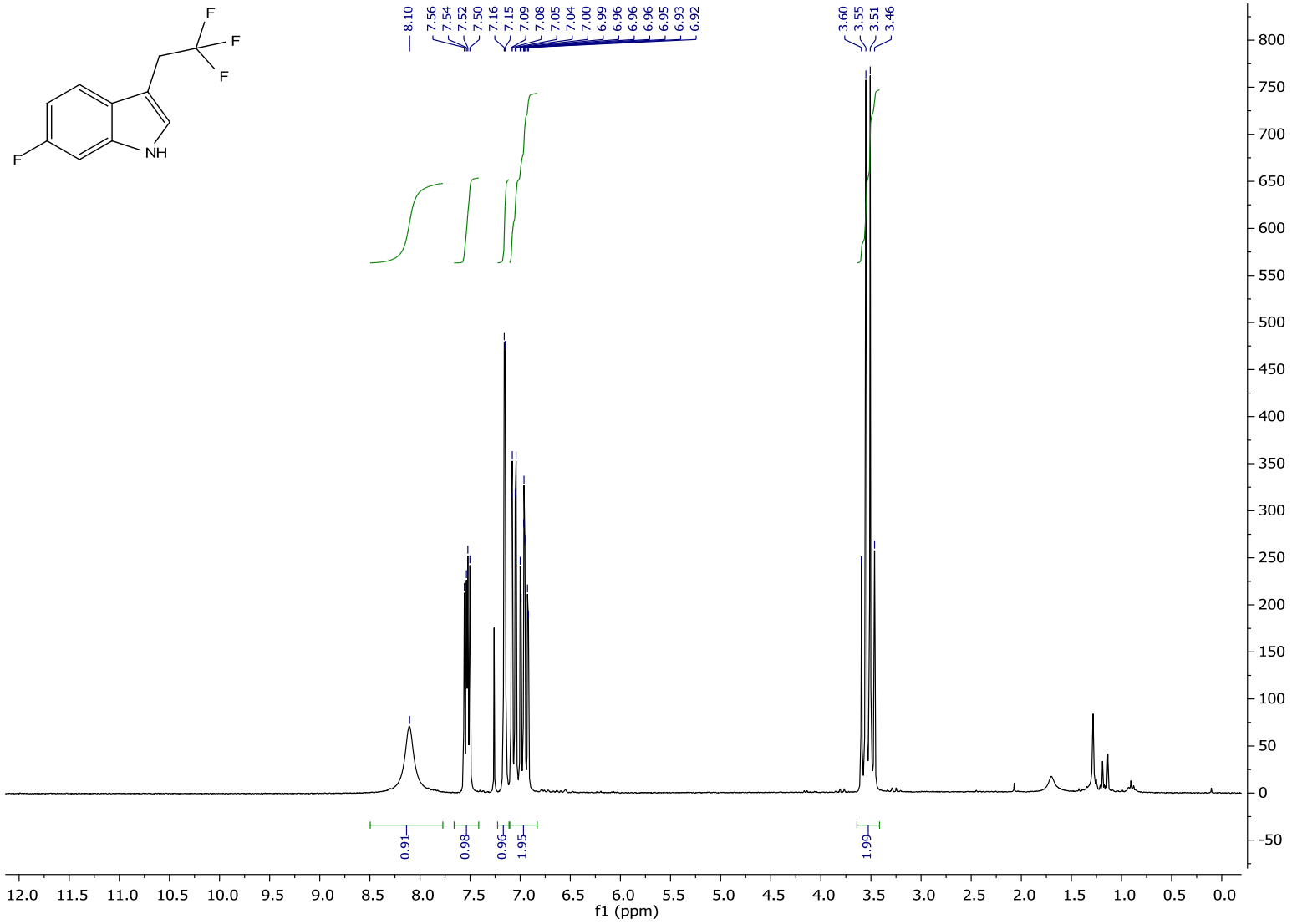
3-(2,2,2-Trifluoroethyl)-5-((trimethylsilyl)ethynyl)-1*H*-indole (3q)

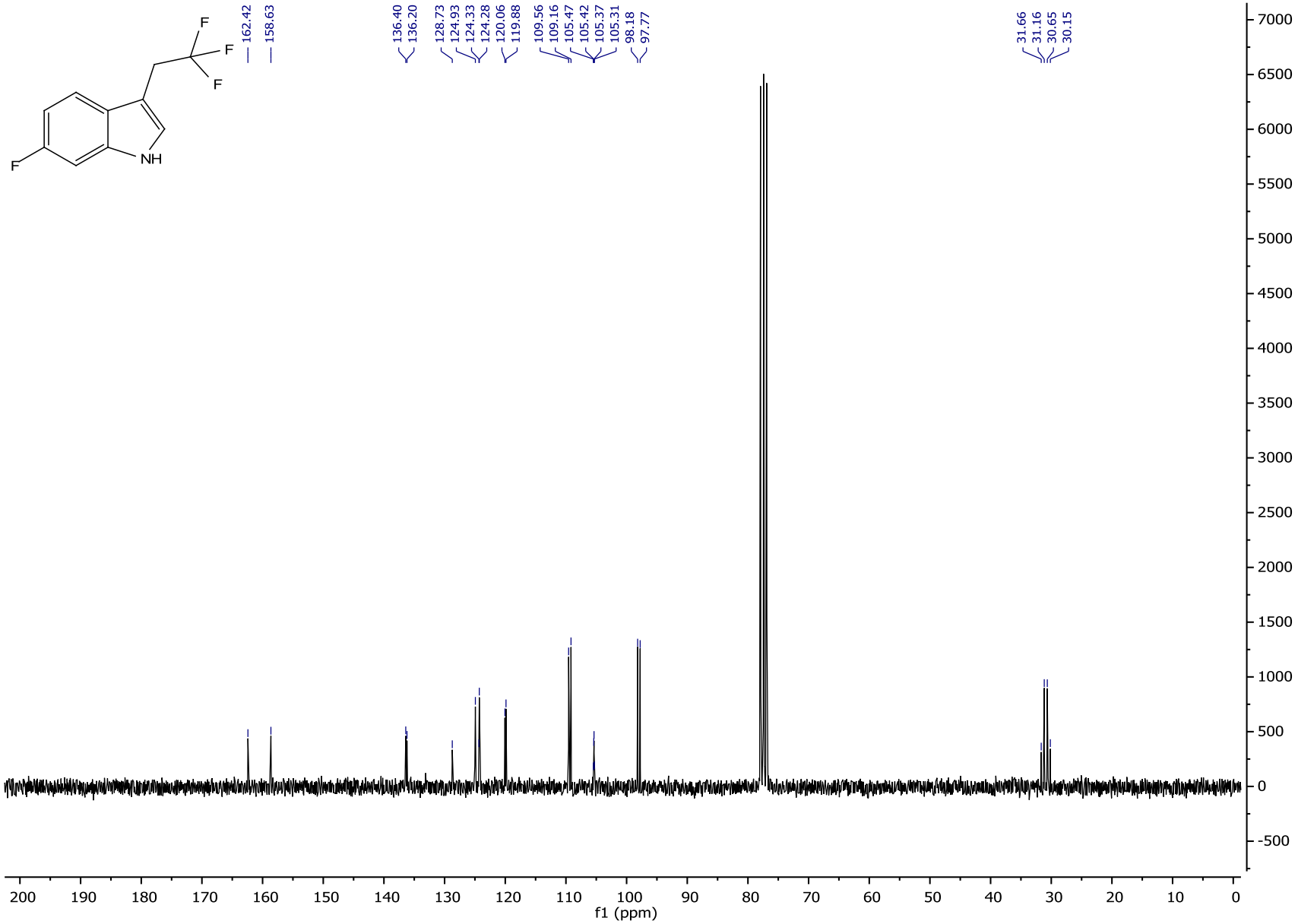


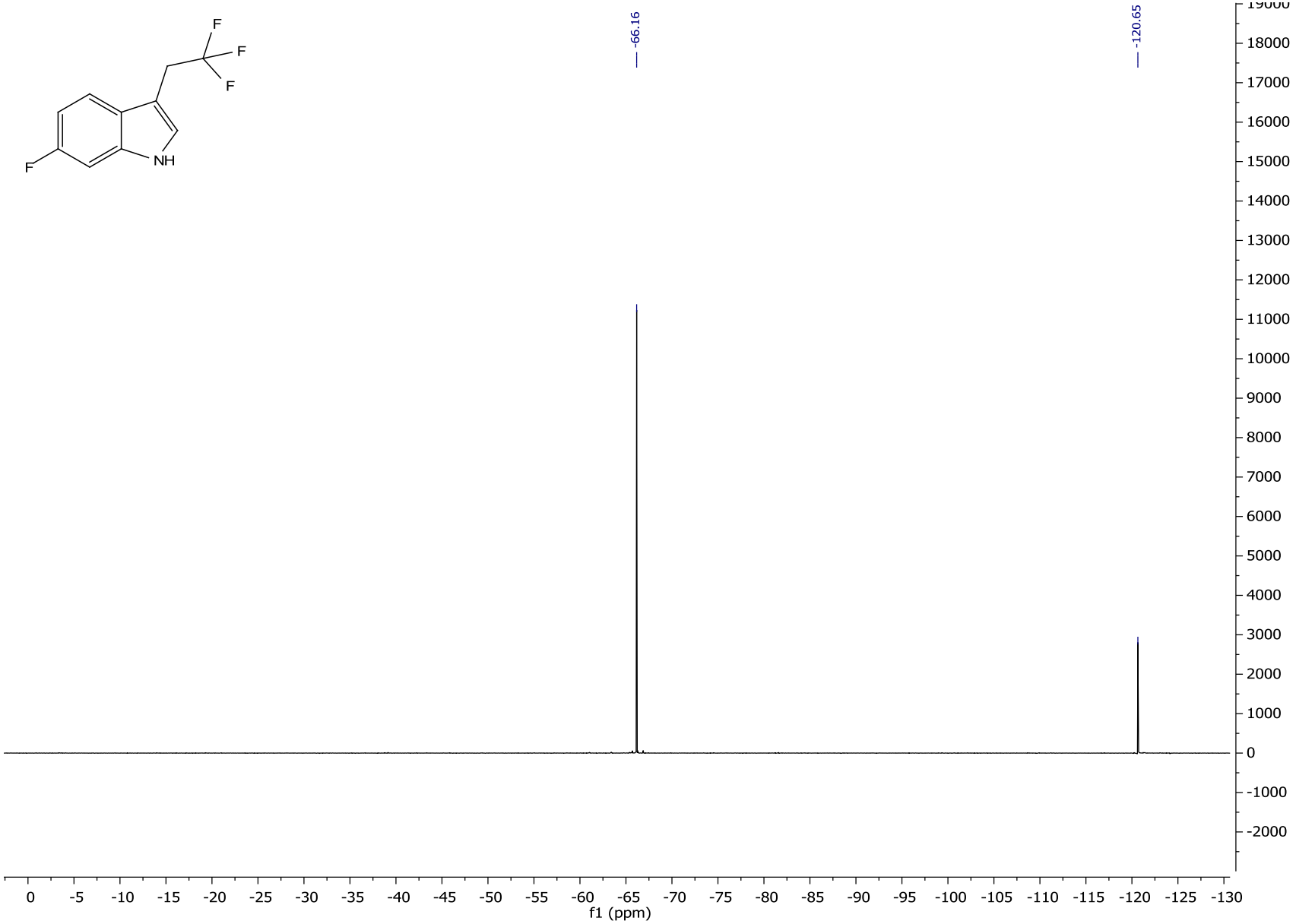

CH3
H3C
Si
H3C
F
F
F
NH
135.56
128.16
126.99
126.28
125.03
123.75
122.93
114.53
111.16
106.57
105.04
104.98
104.93
104.88
91.57
30.94
30.44
29.94
29.44
-0.00
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CH3
H3C
Si
H3C
F
F
F
NH
-66.09
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

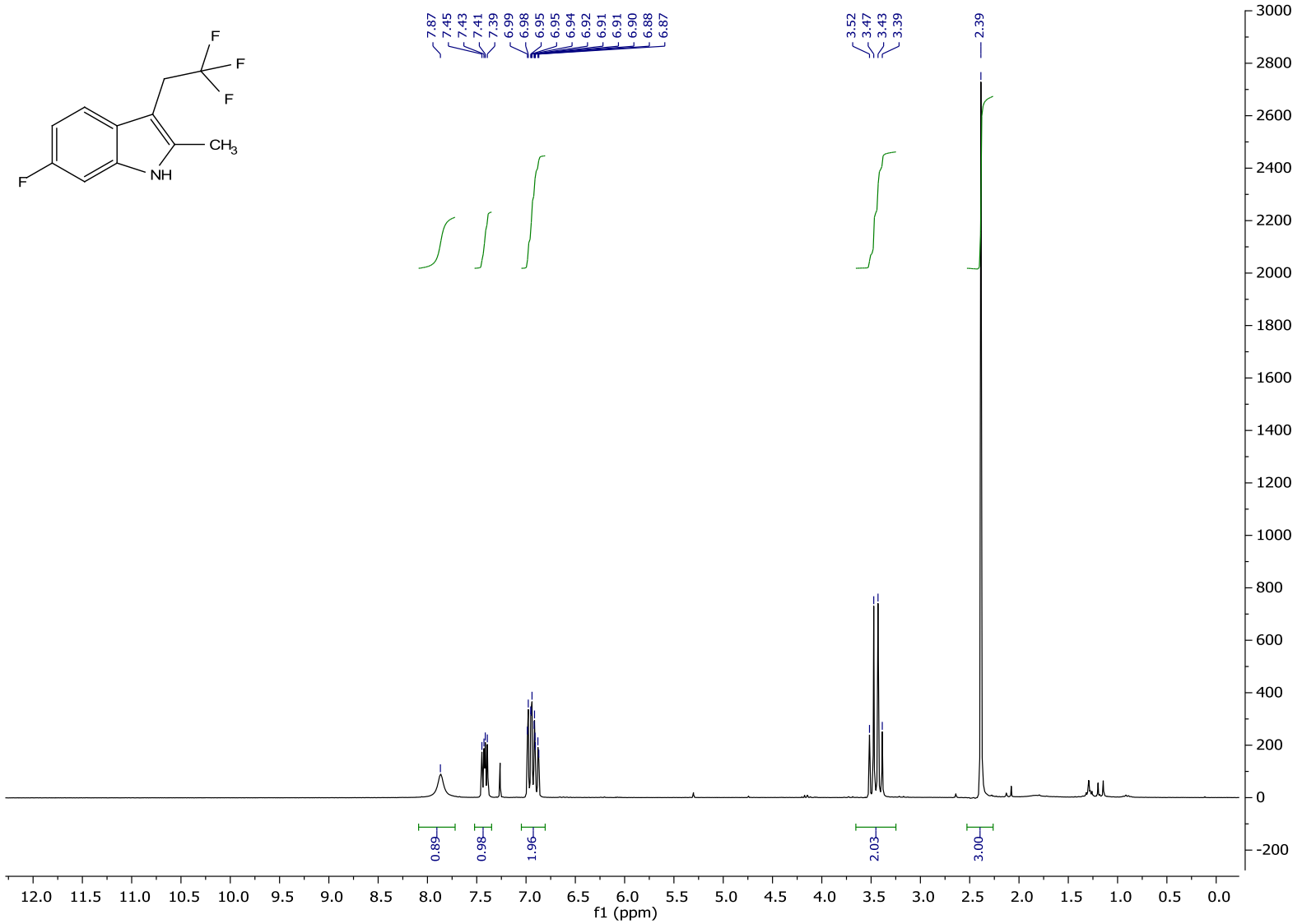
6-Fluoro-3-(2,2,2-trifluoroethyl)-1*H*-indole (3r)

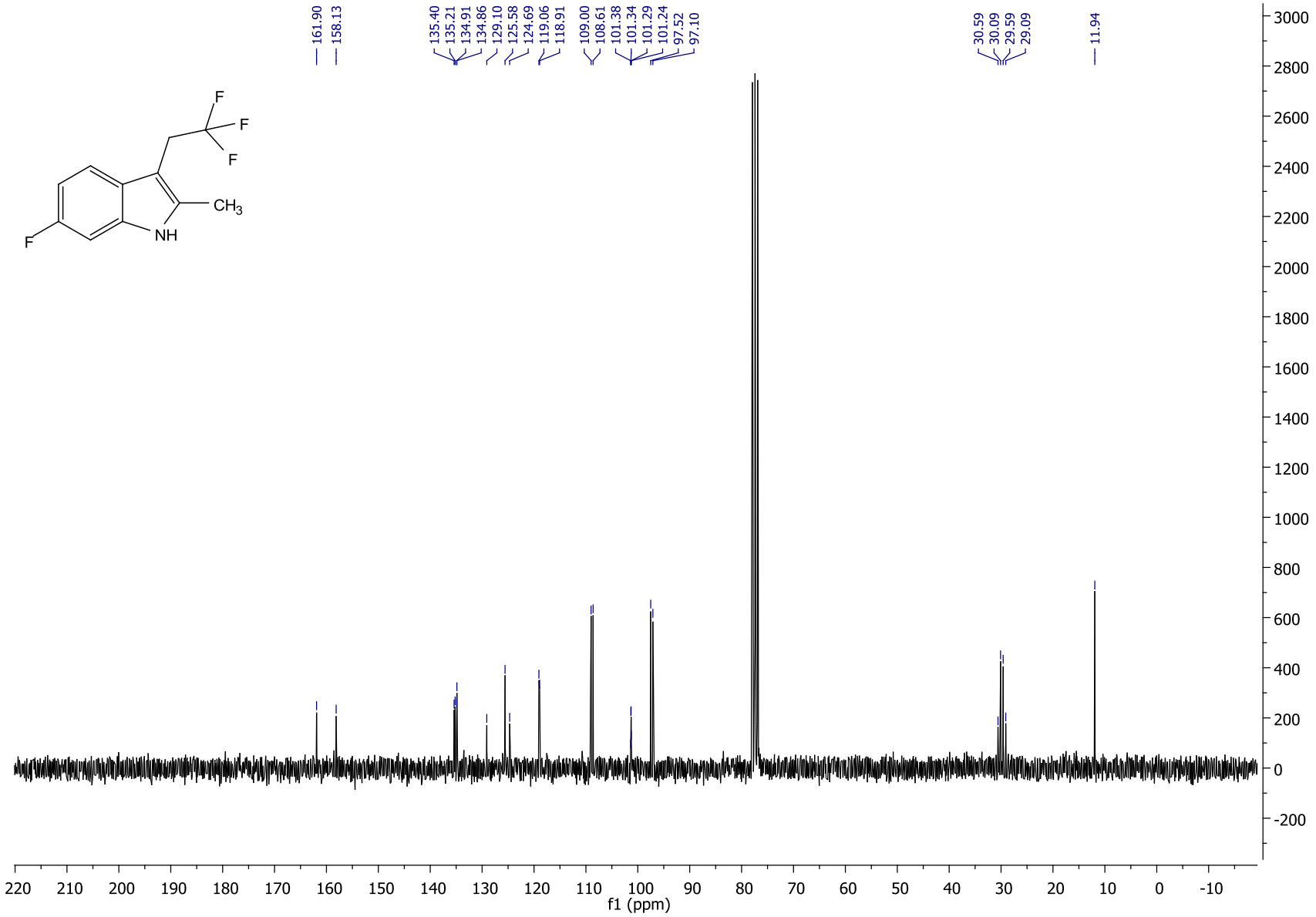


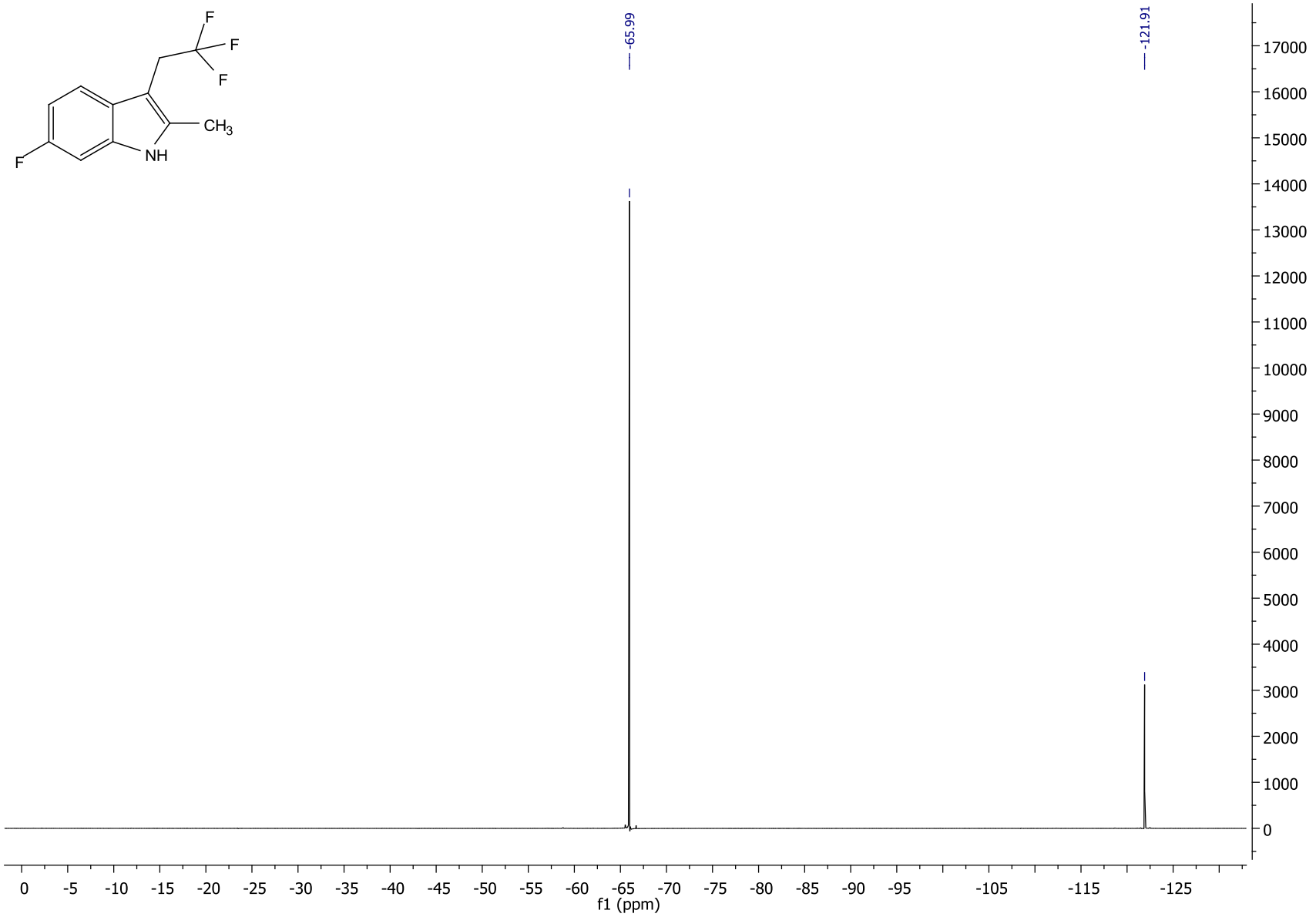

F
F
F
NH
F
162.42
158.63
136.40
136.20
128.73
124.93
124.33
124.28
120.06
119.88
109.56
109.16
105.47
105.42
105.37
105.31
98.18
97.77
31.66
31.16
30.65
30.15
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
NH
F
-66.16
-120.65
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

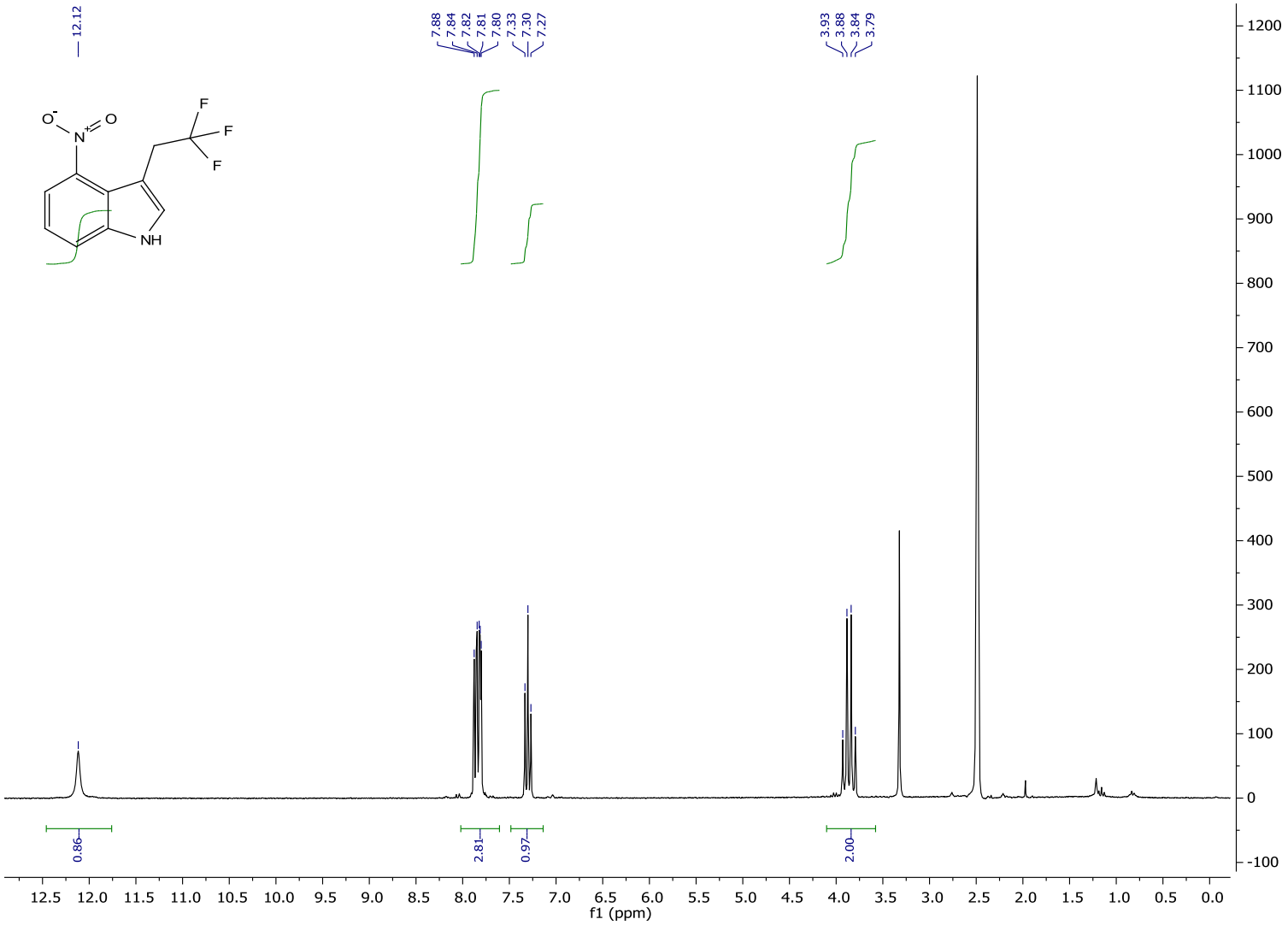
6-Fluoro-2-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3s)

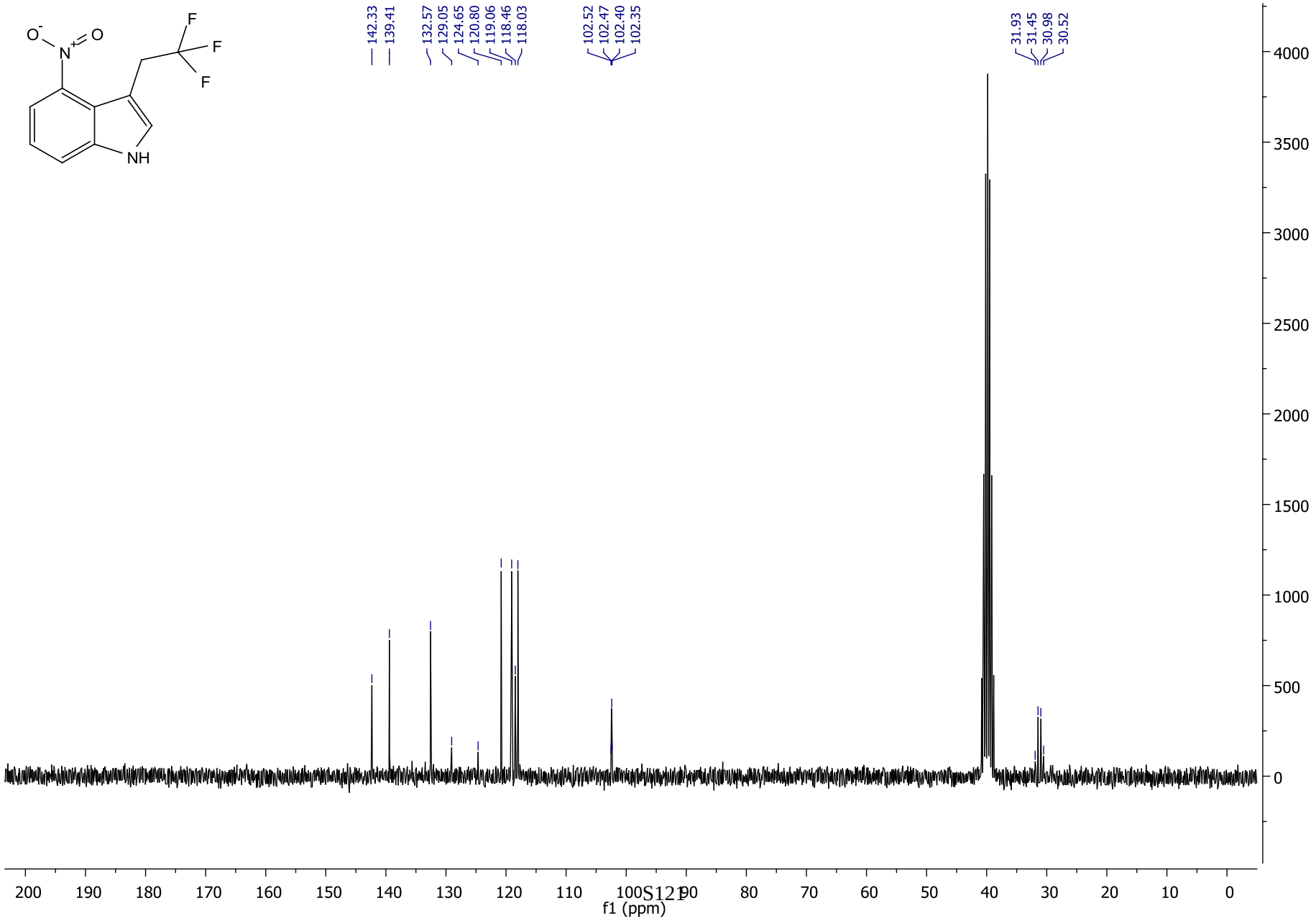


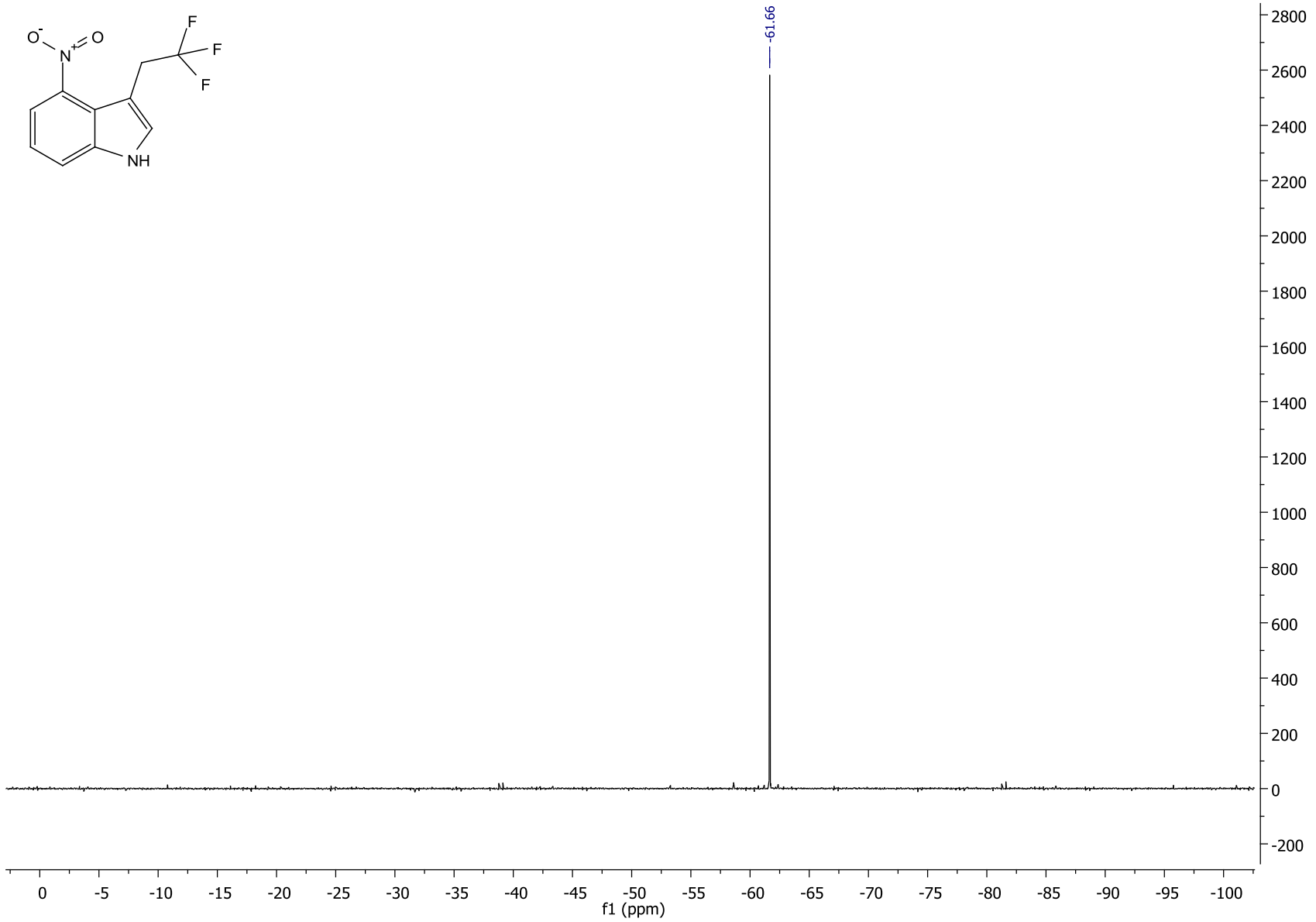

161.90
158.13
135.40
135.21
134.91
134.86
129.10
125.58
124.69
119.06
118.91
109.00
108.61
101.38
101.34
101.29
101.24
97.52
97.10
30.59
30.09
29.59
29.09
11.94
F
F
F
CH3
NH
F
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
F
F
CH3
NH
F
-65.99
-121.91
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)

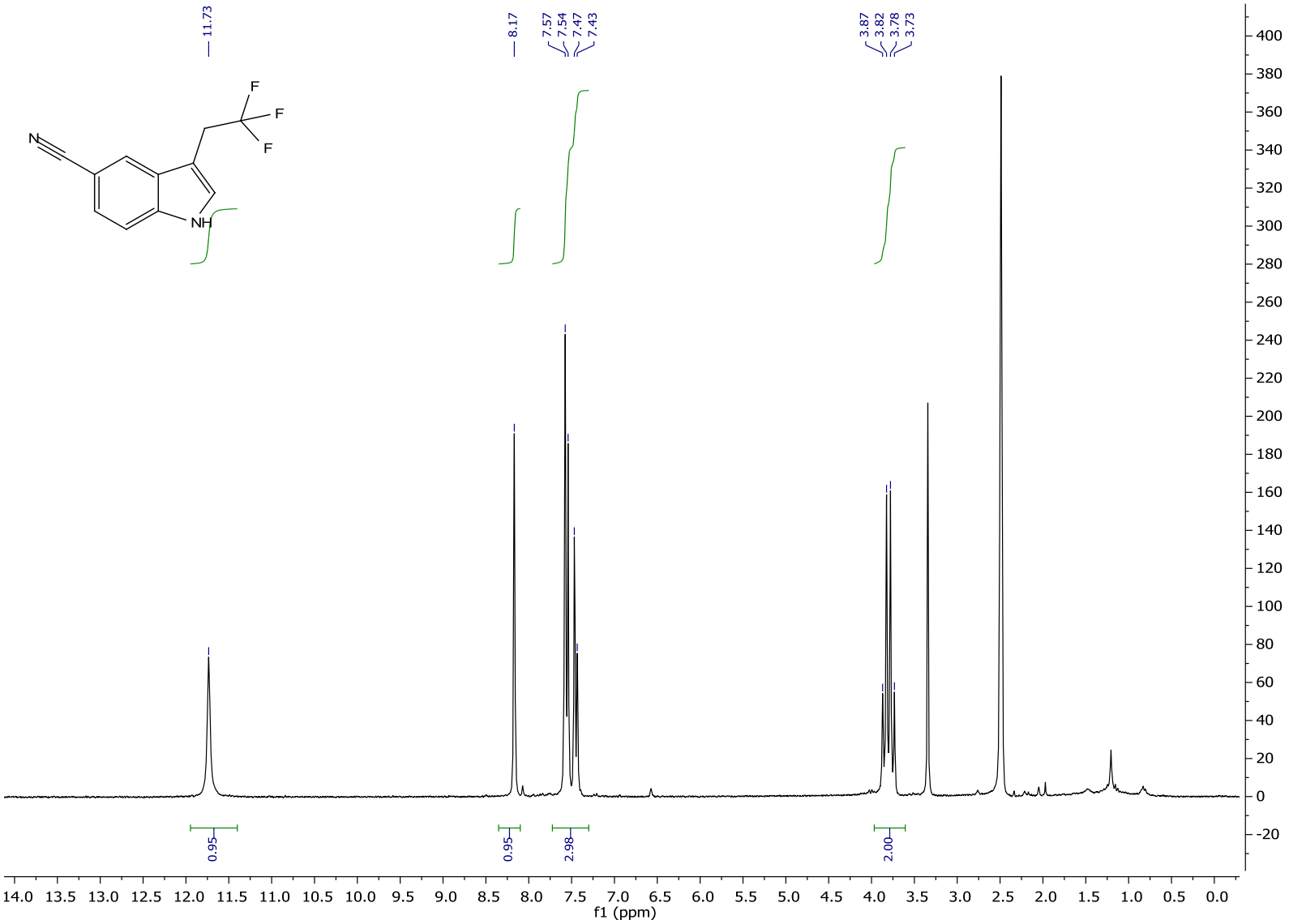
4-Nitro-3-(2,2,2-trifluoroethyl)-1*H*-indole (3t)

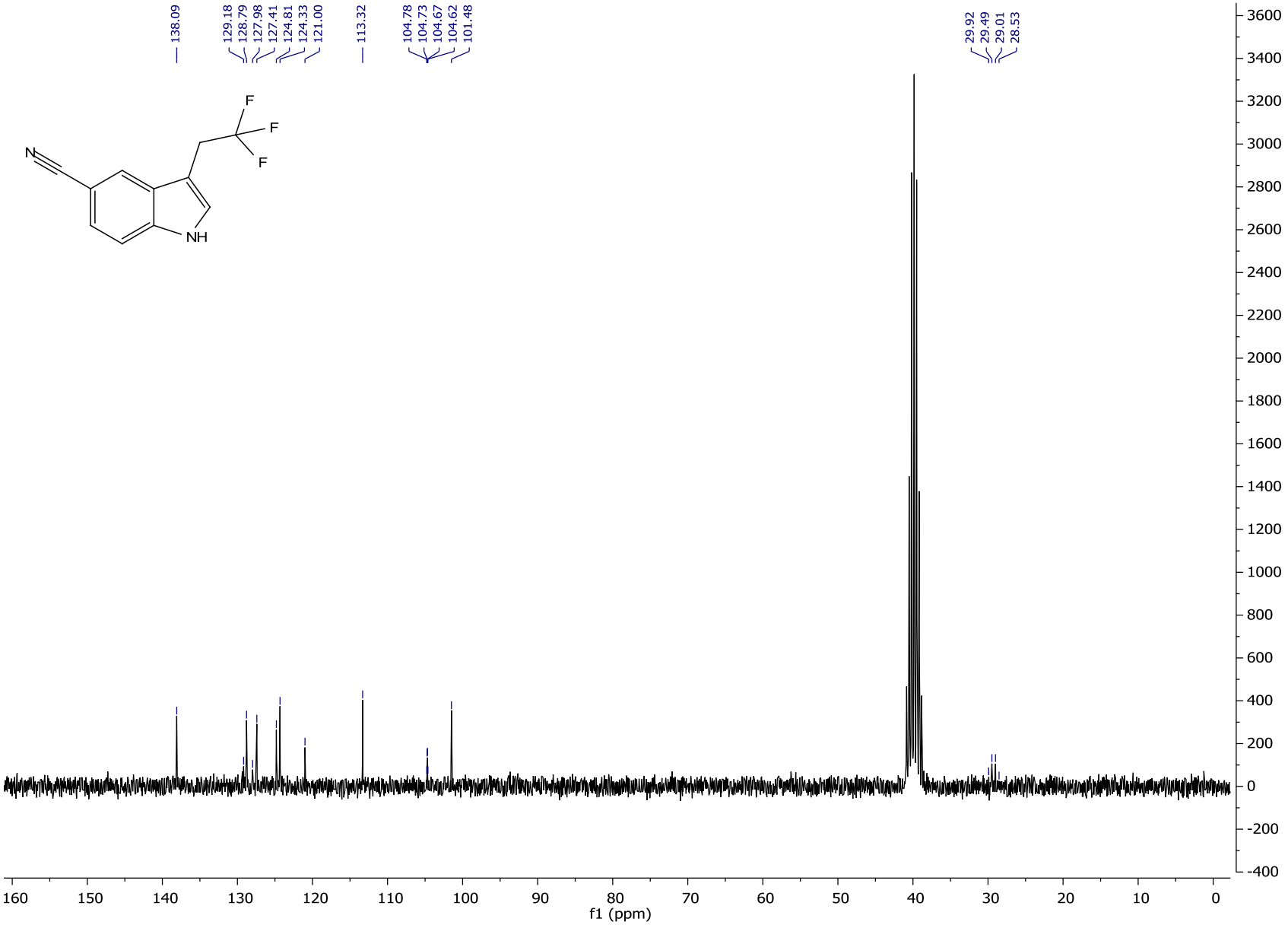


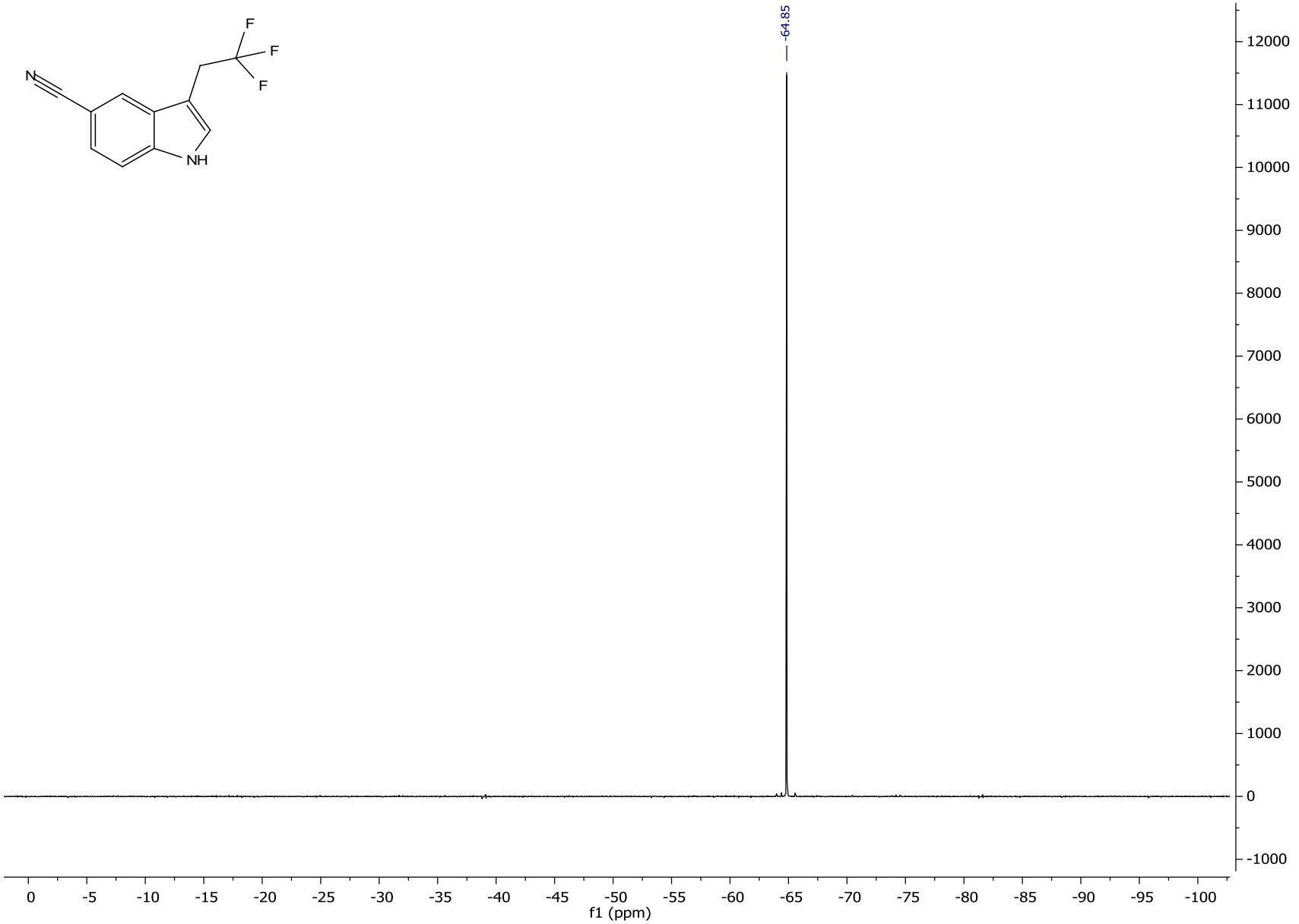

142.33
139.41
132.57
129.05
124.65
120.80
119.06
118.46
118.03
102.52
102.47
102.40
102.35
31.93
31.45
30.98
30.52
F
F
F
O
N
O
NH
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-61.66
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)
F
F
F
O
N
O
NH

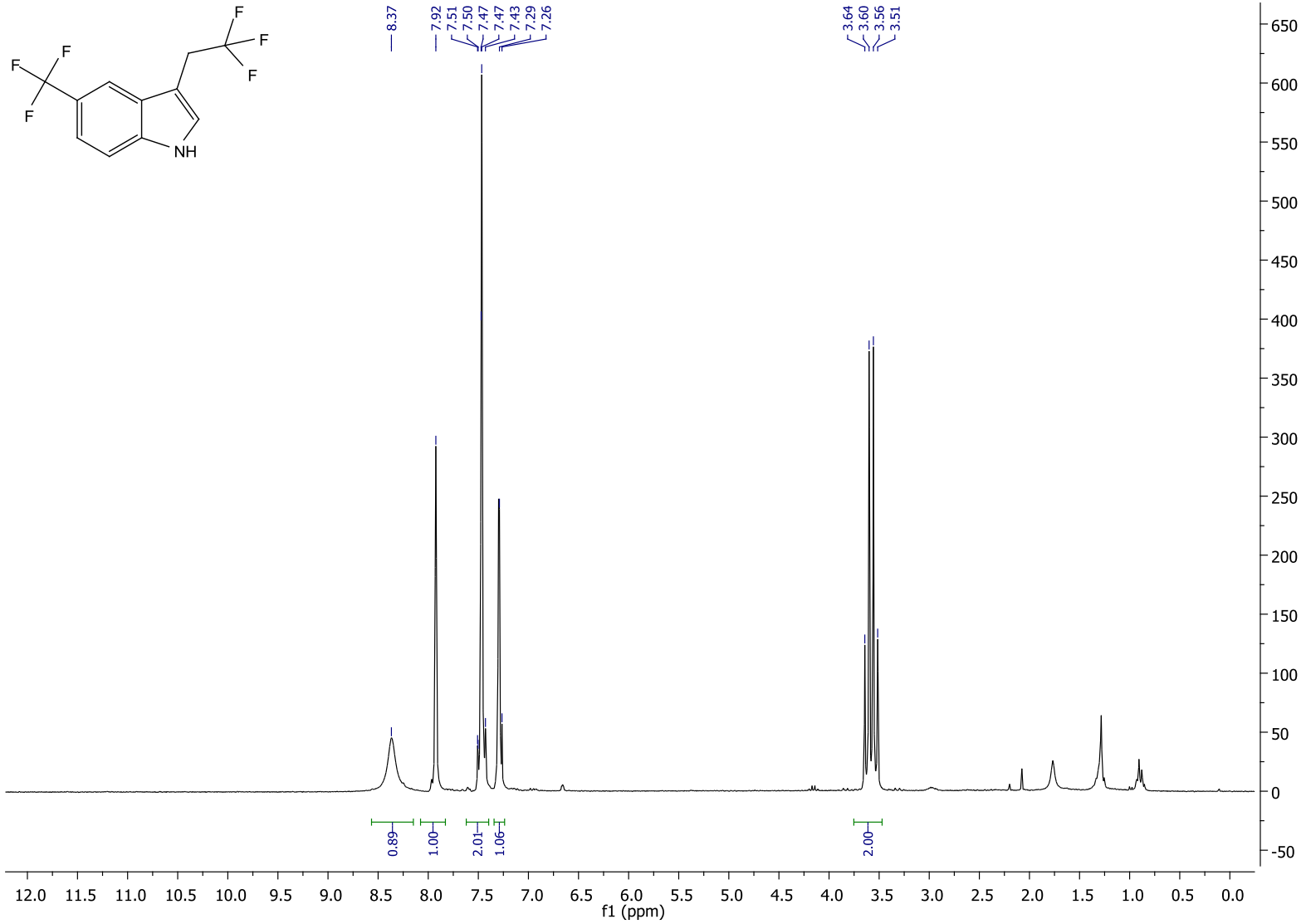
3-(2,2,2-Trifluoroethyl)-1*H*-indole-5-carbonitrile (3u)

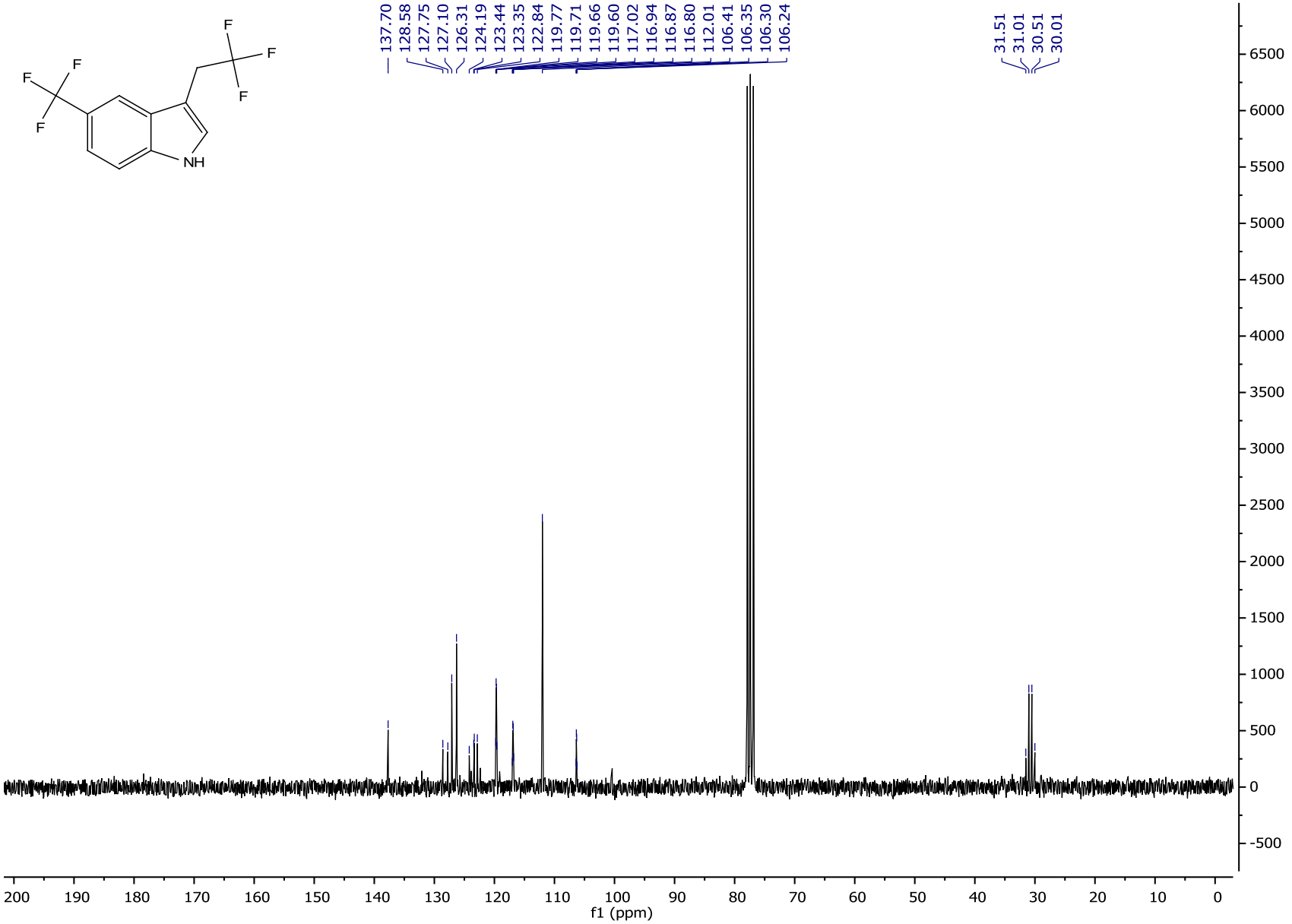


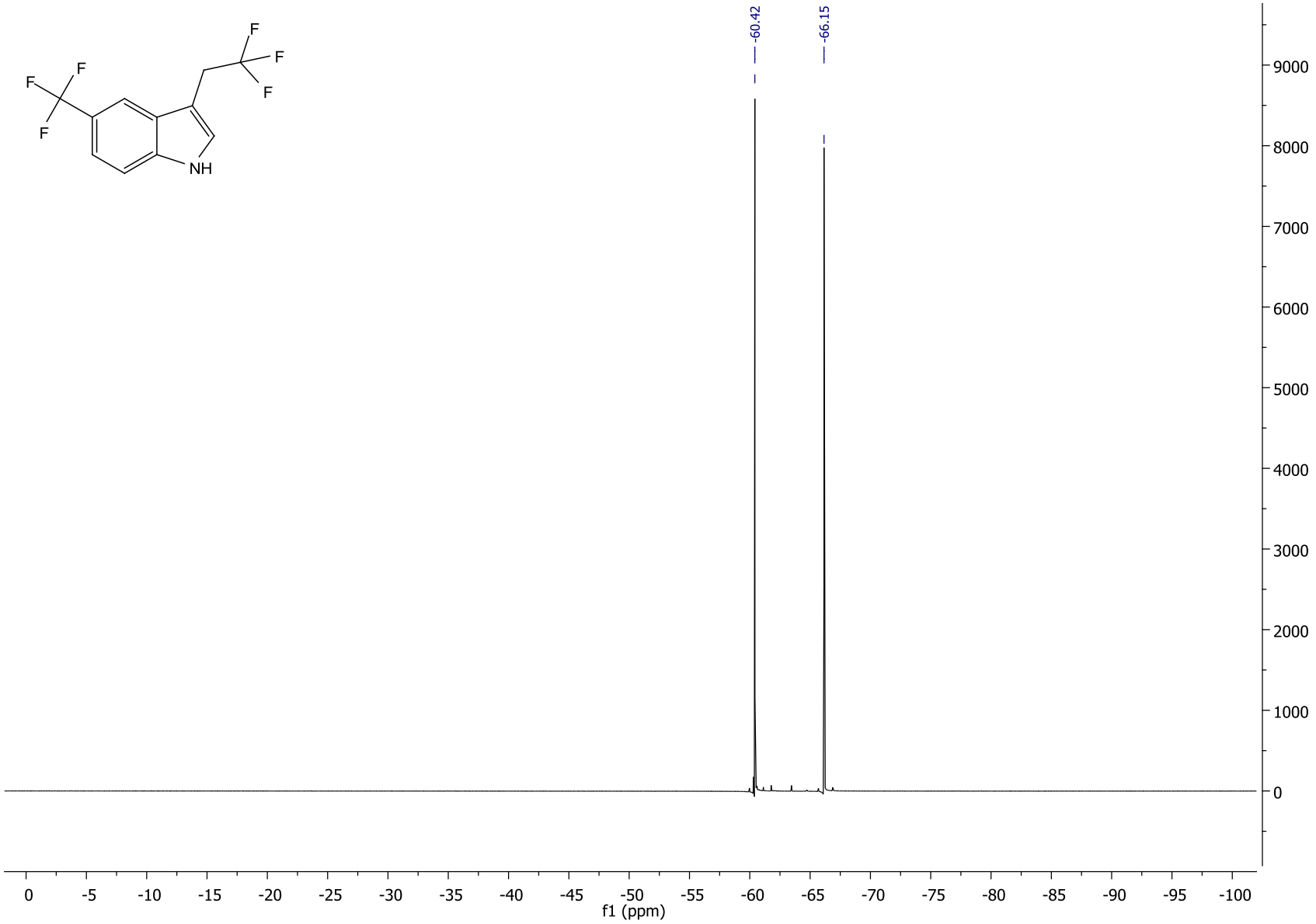

138.09
129.18
128.79
127.98
127.41
124.81
124.33
121.00
113.32
104.78
104.73
104.67
104.62
101.48
29.92
29.49
29.01
28.53
F
F
F
N
NH
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
N
NH
-64.85
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

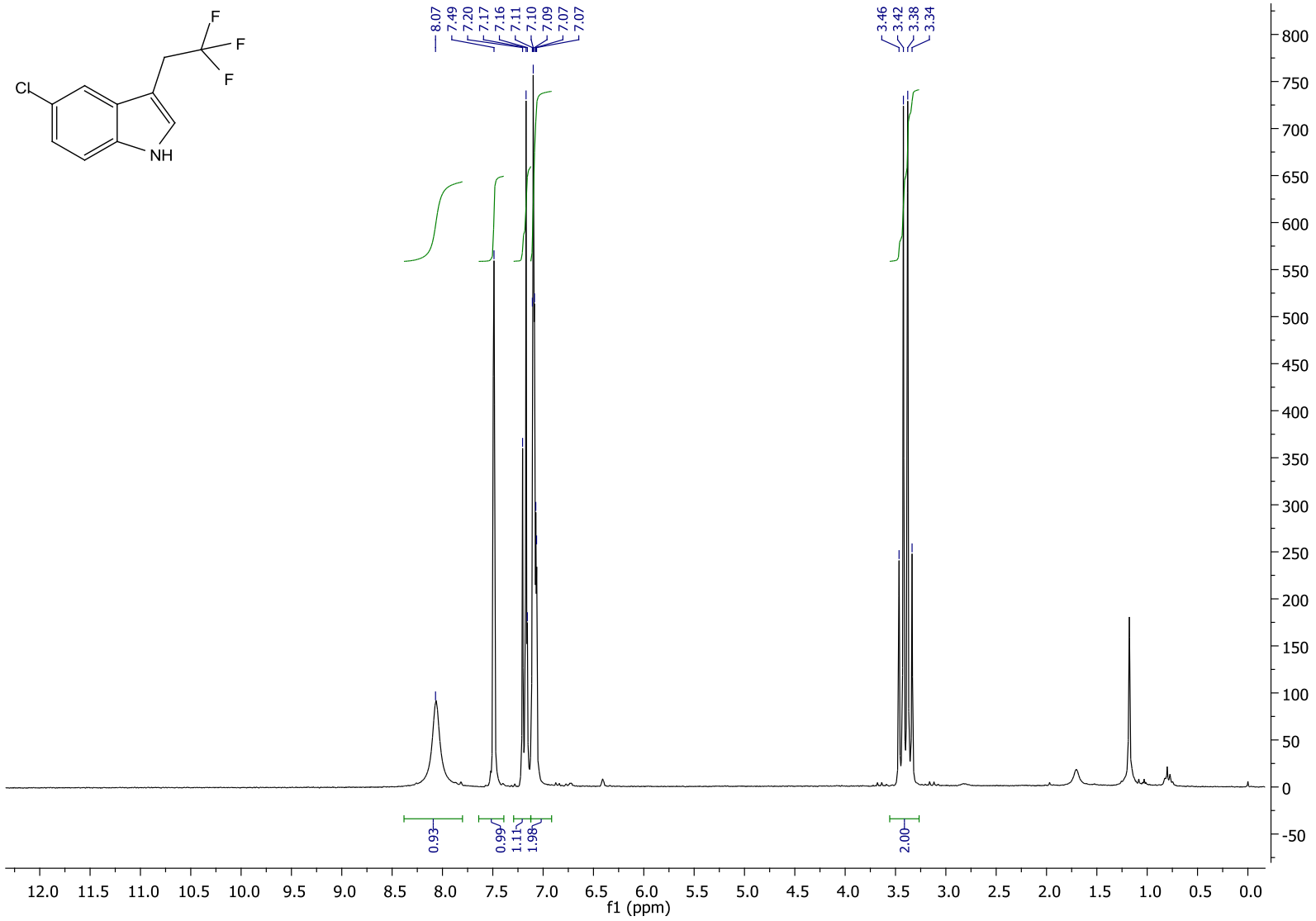
3-(2,2,2-Trifluoroethyl)-5-(trifluoromethyl)-1*H*-indole (3v)

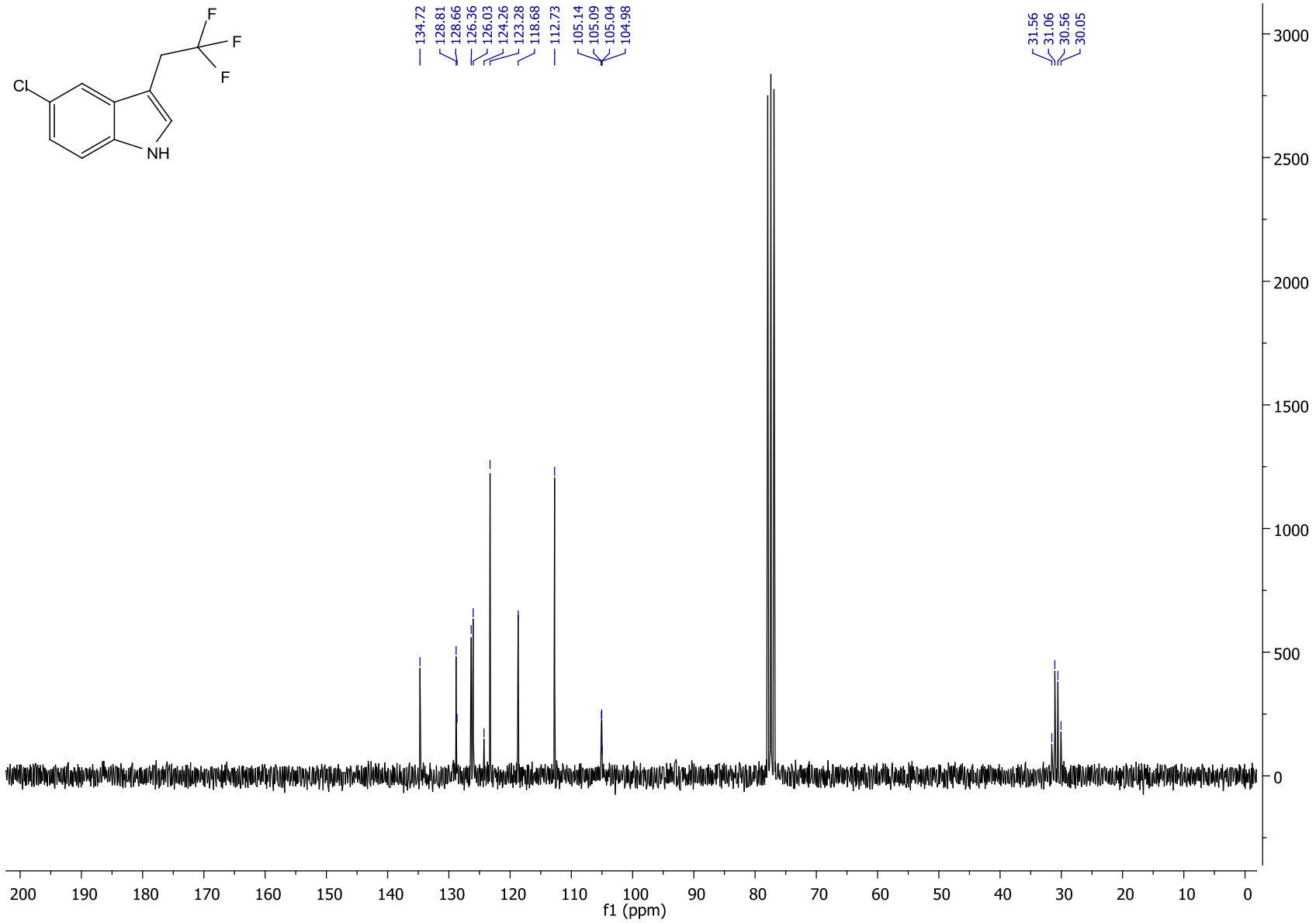


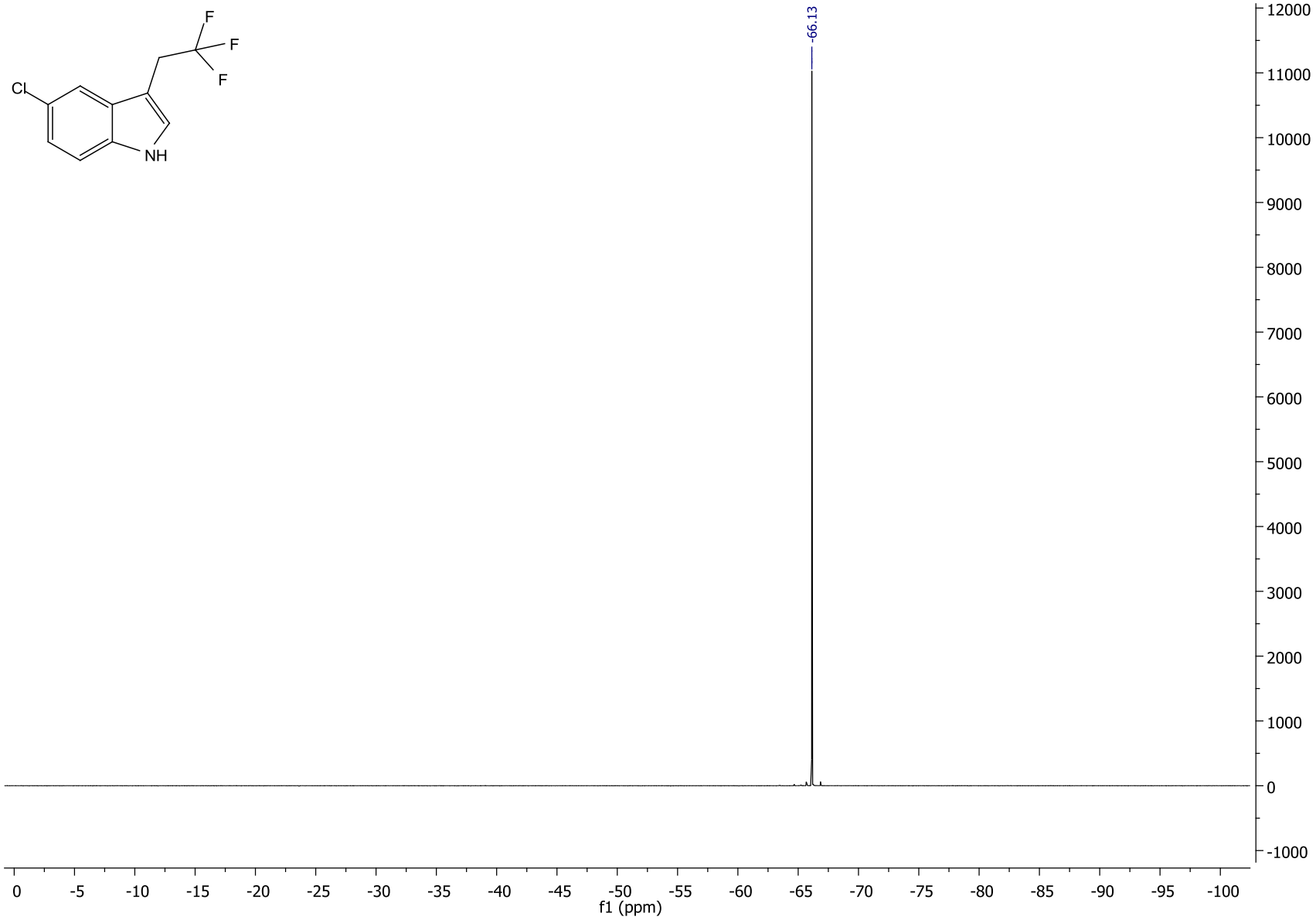

F
F
F
F
F
NH
137.70
128.58
127.75
127.10
126.31
124.19
123.44
123.35
122.84
119.77
119.71
119.66
119.60
117.02
116.94
116.87
116.80
112.01
106.41
106.35
106.30
106.24
31.51
31.01
30.51
30.01
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
F
F
F
NH
-60.42
-66.15
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

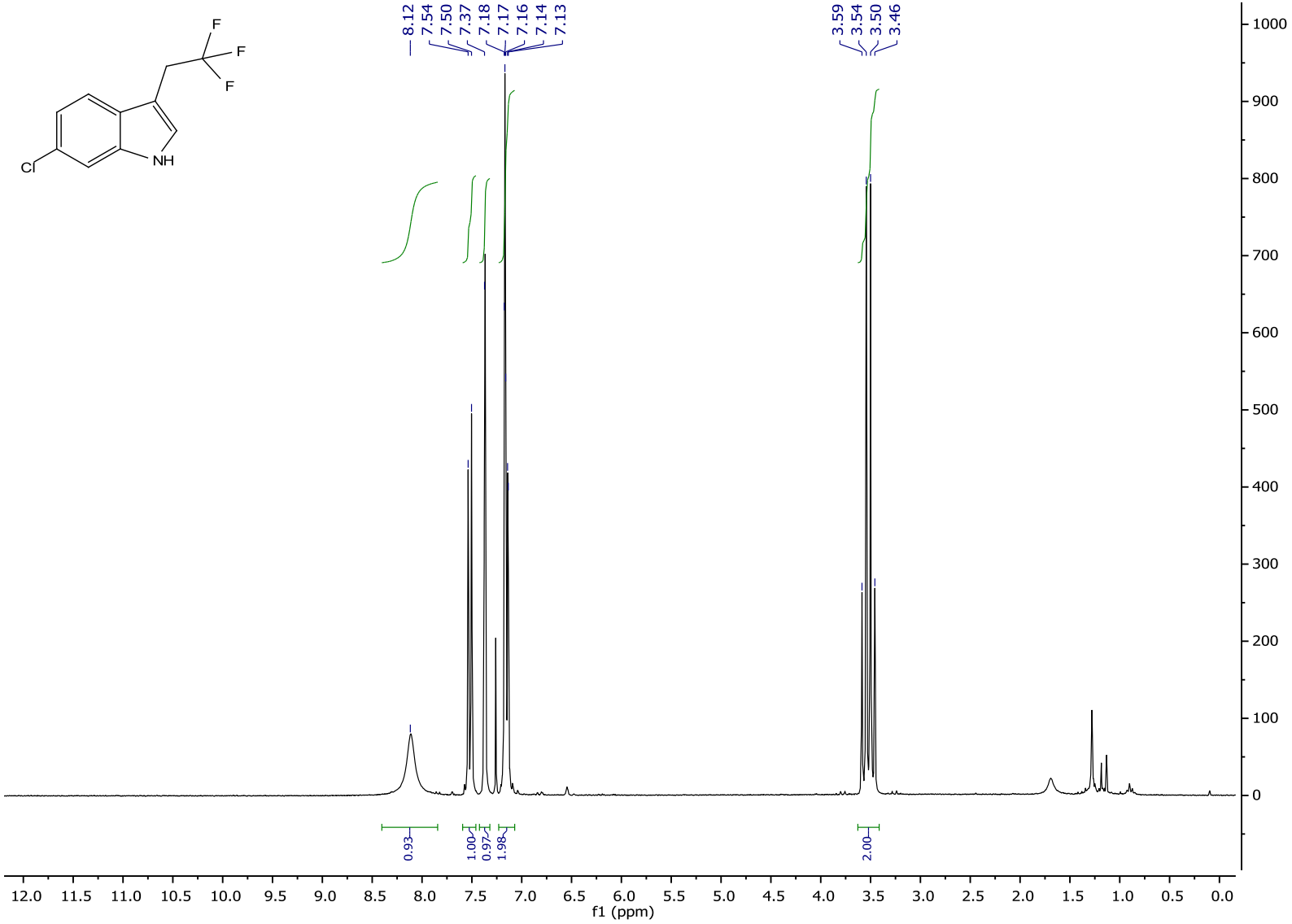
5-Chloro-3-(2,2,2-trifluoroethyl)-1*H*-indole (3w)

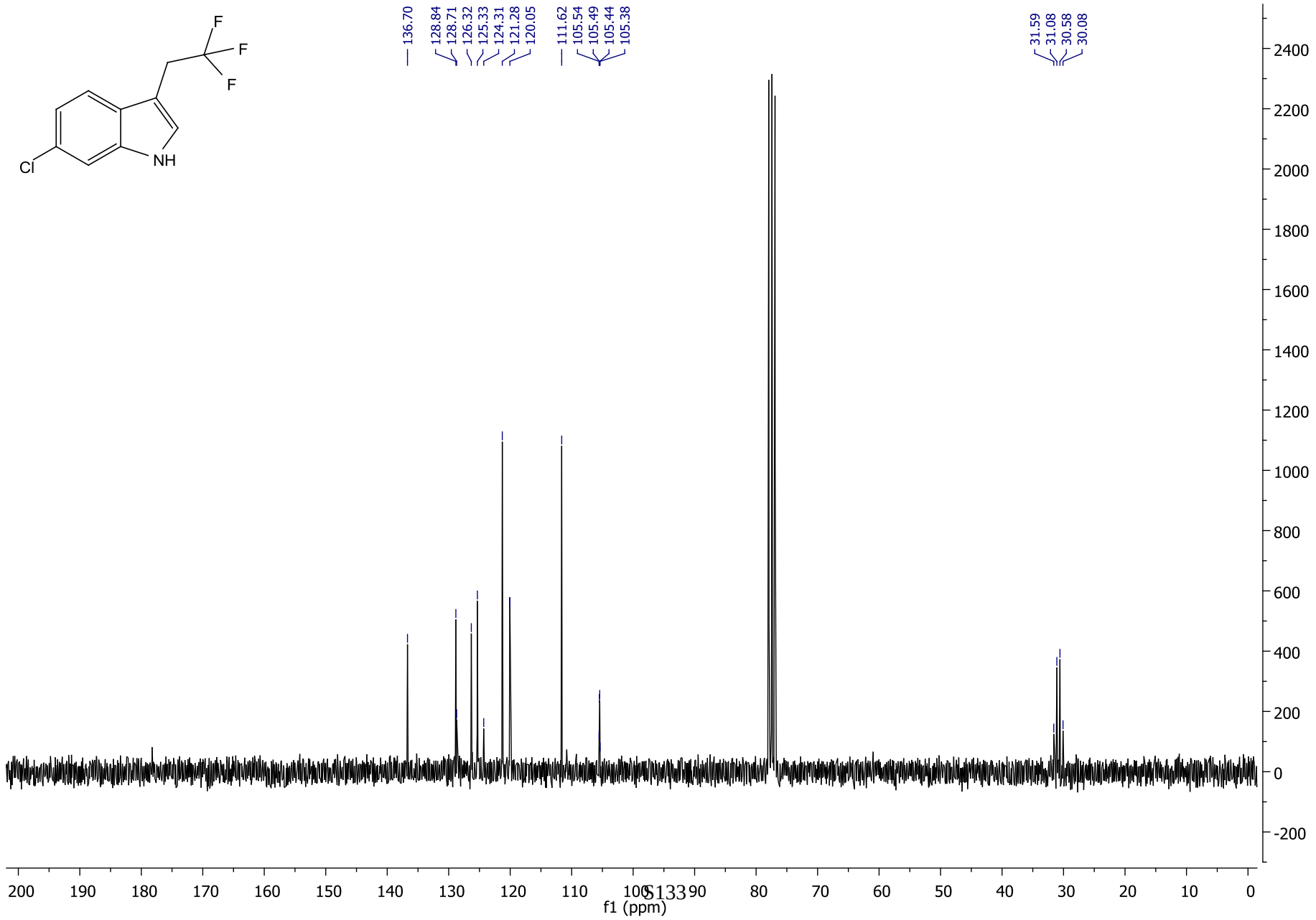


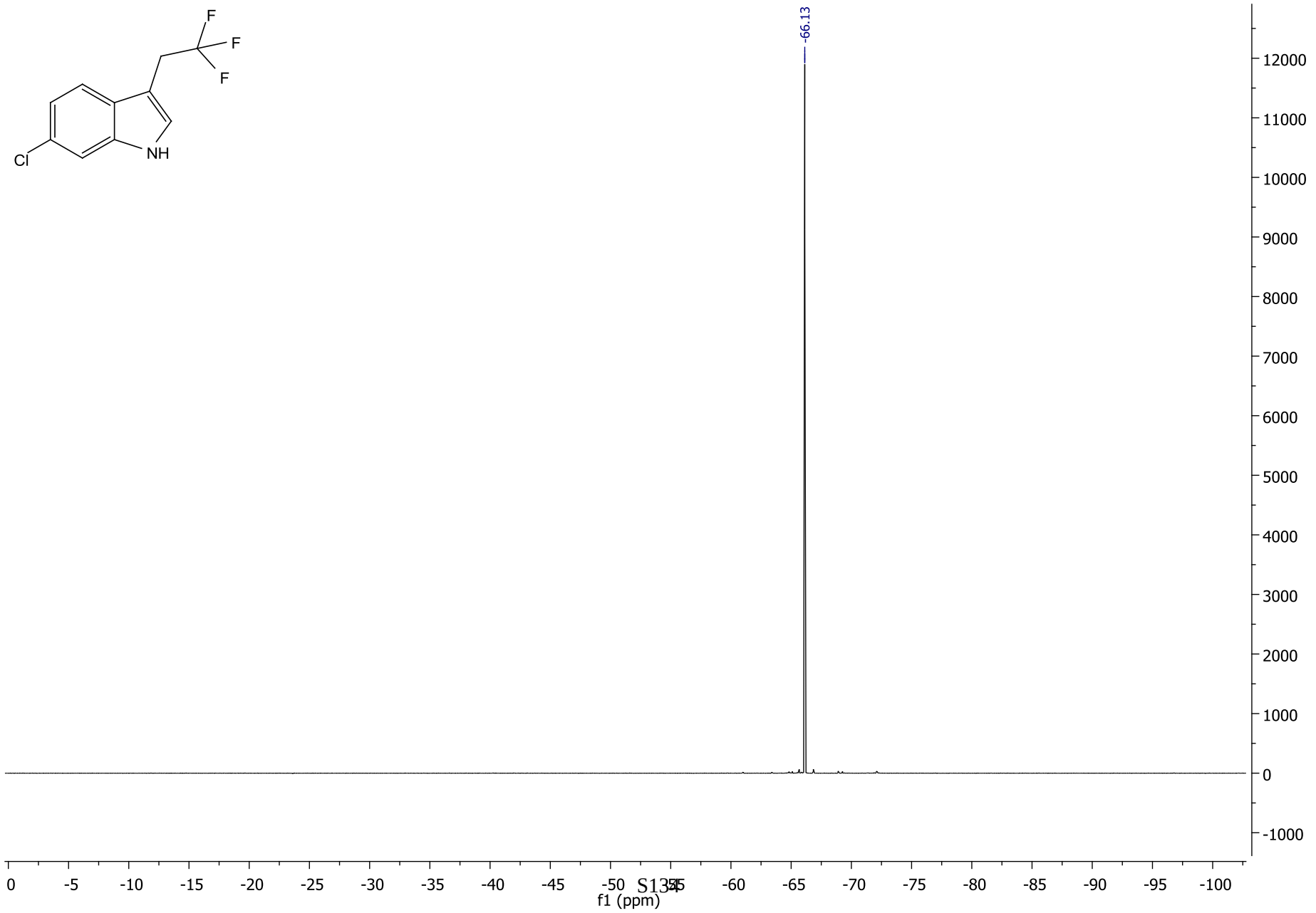

F
F
F
Cl
NH
134.72
128.81
128.66
126.36
126.03
124.26
123.28
118.68
112.73
105.14
105.09
105.04
104.98
31.56
31.06
30.56
30.05
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
Cl
NH
-66.13
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

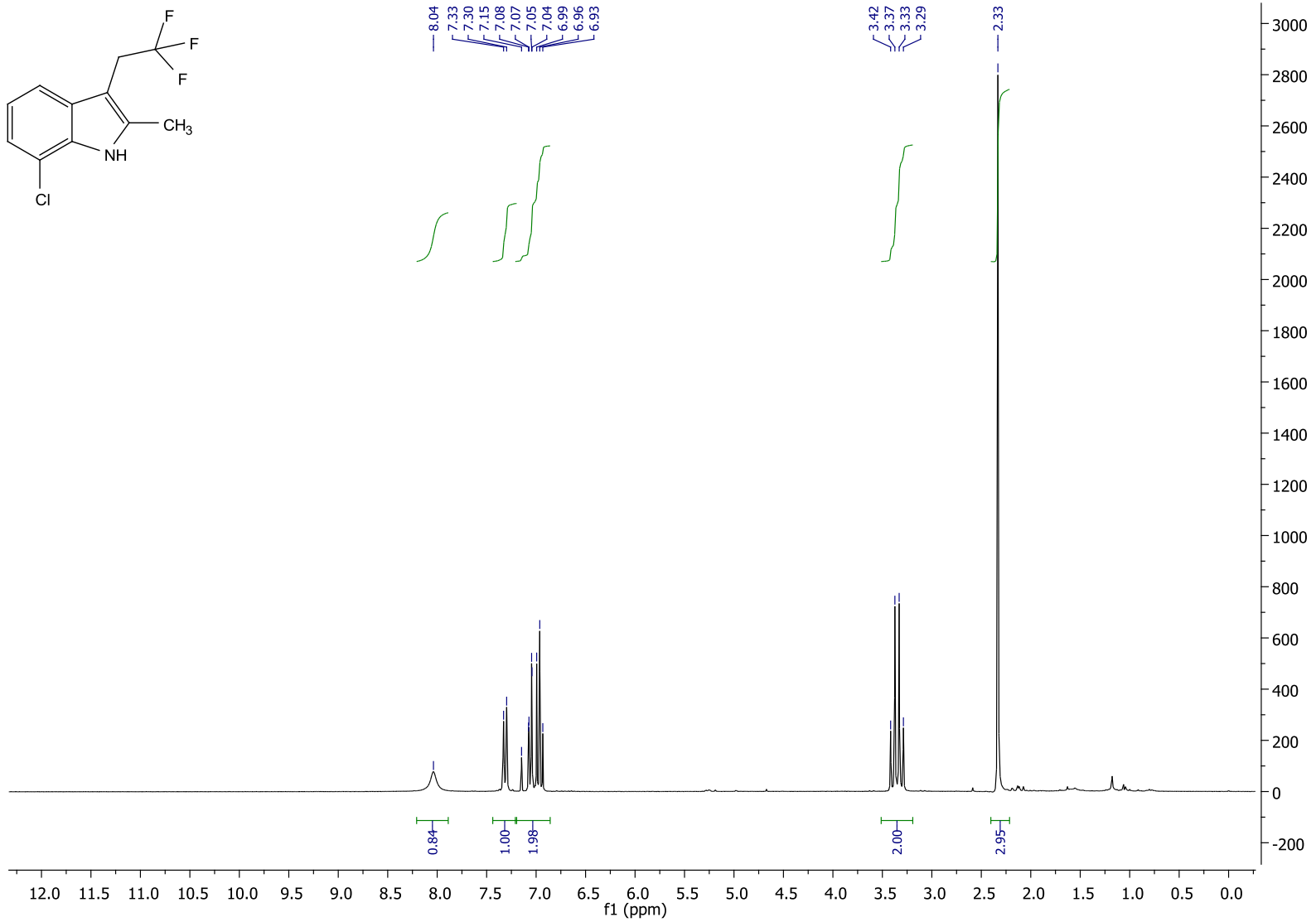
6-Chloro-3-(2,2,2-trifluoroethyl)-1*H*-indole (3x)

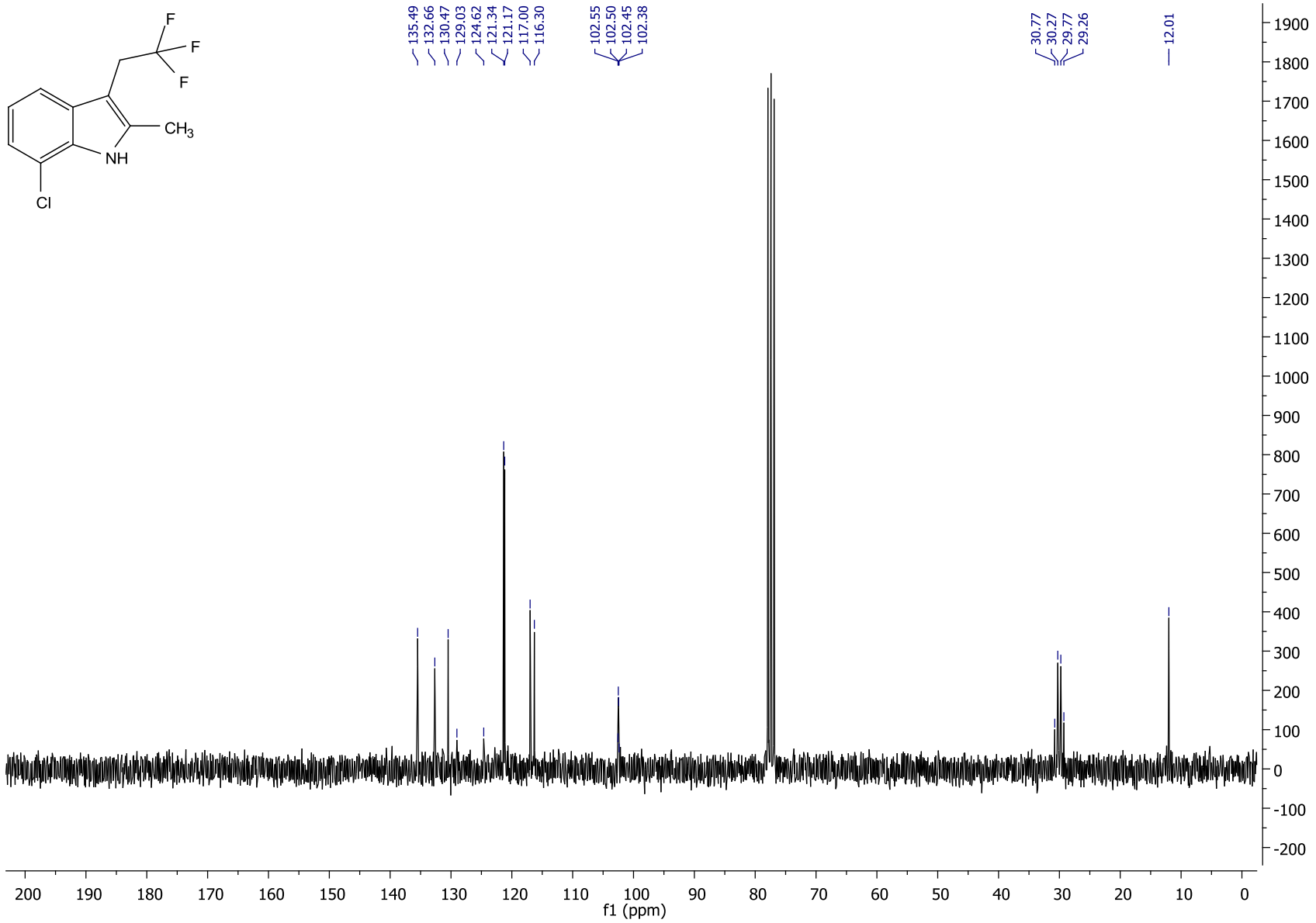


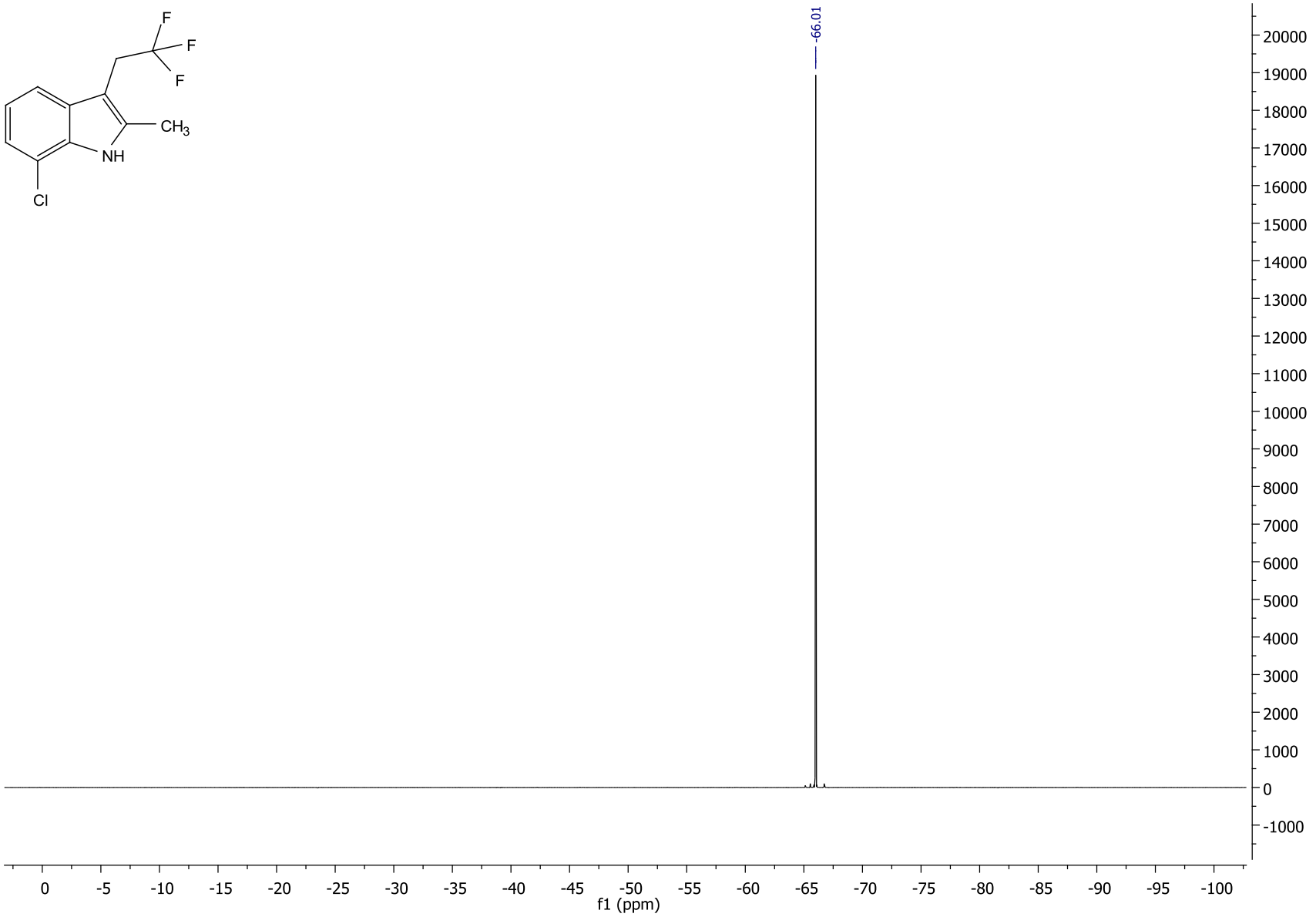

F
F
F
Cl
NH
136.70
128.84
128.71
126.32
125.33
124.31
121.28
120.05
111.62
105.54
105.49
105.44
105.38
31.59
31.08
30.58
30.08
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
Cl
NH
-66.13
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

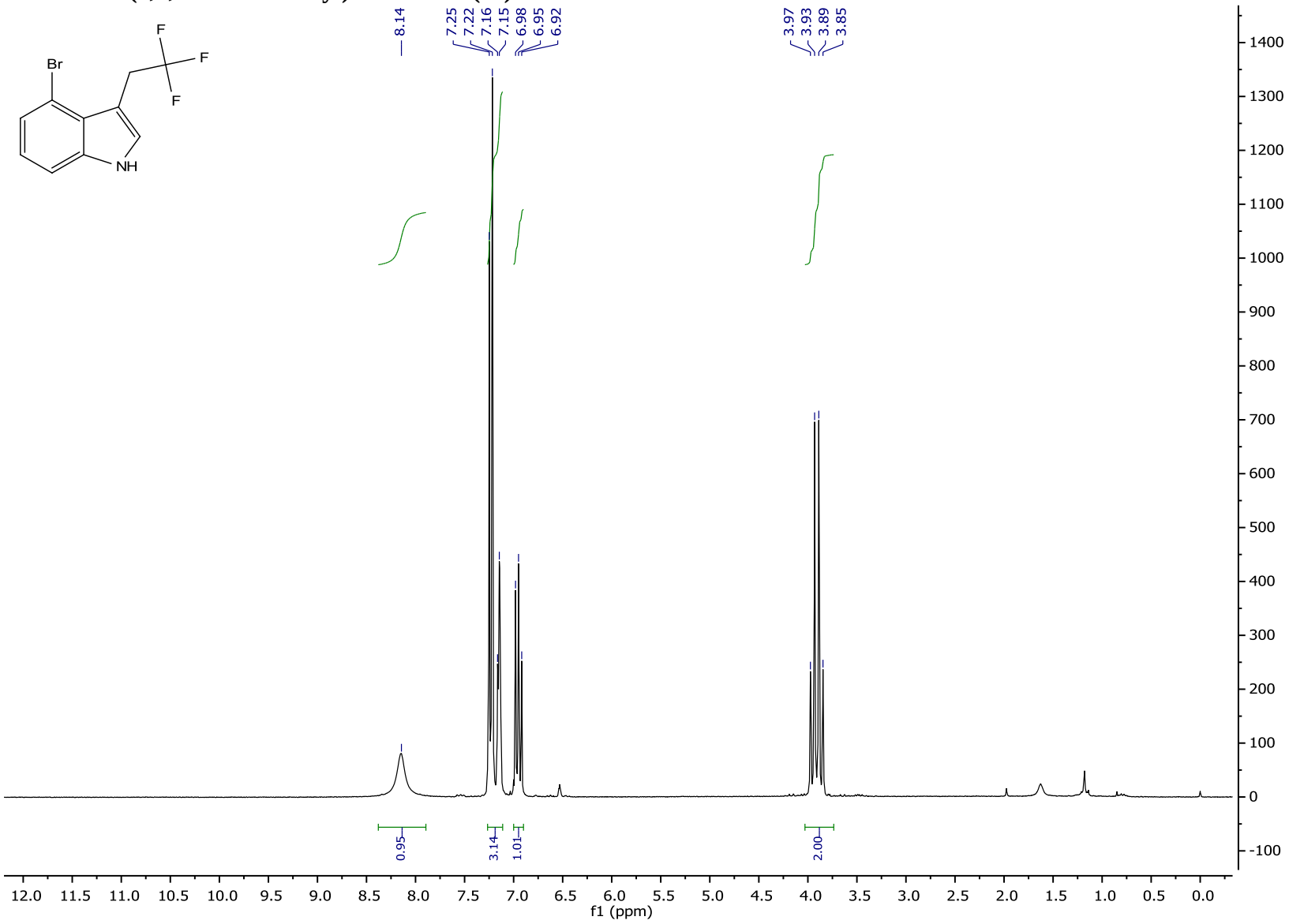
7-Chloro-2-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3y)

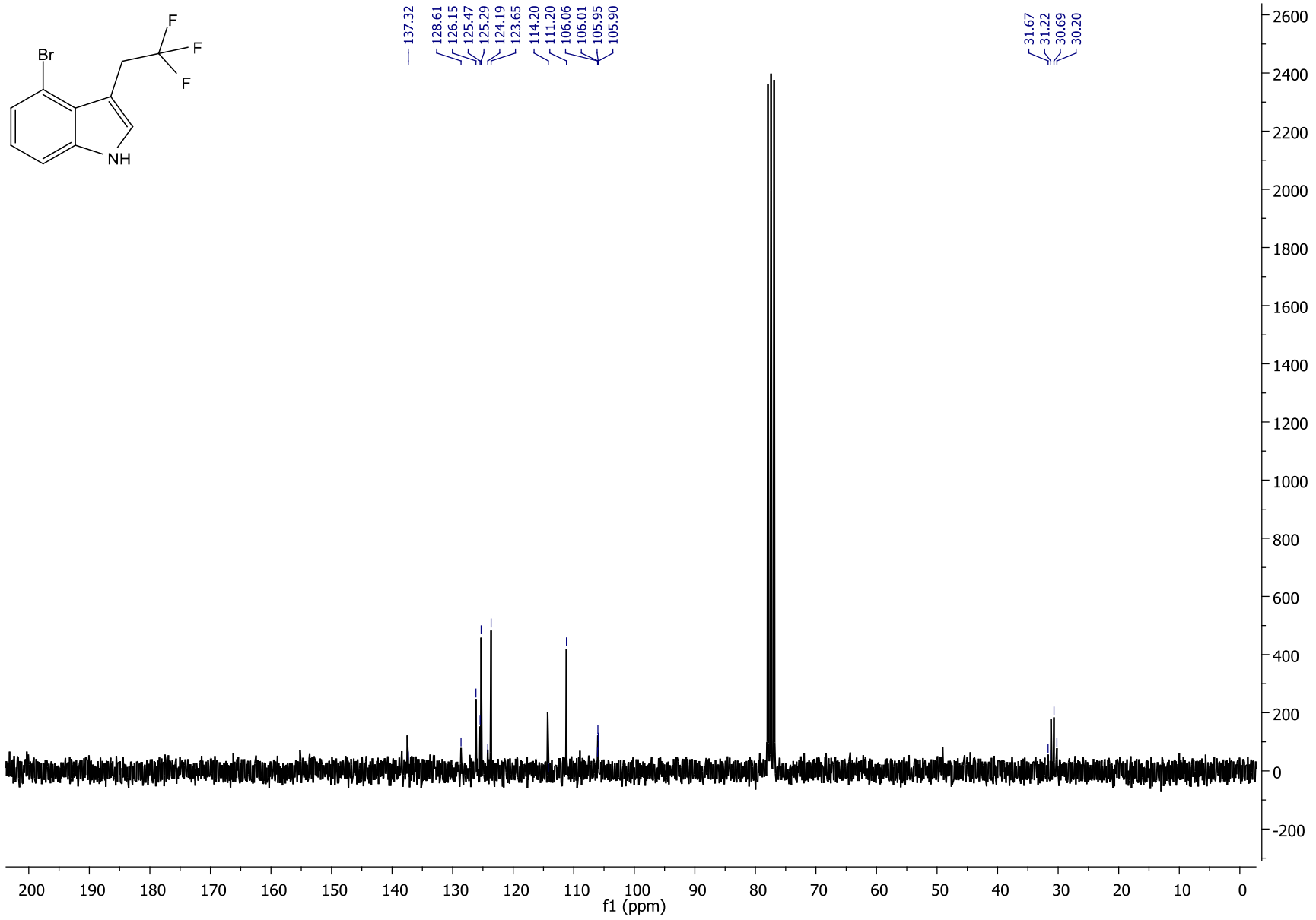


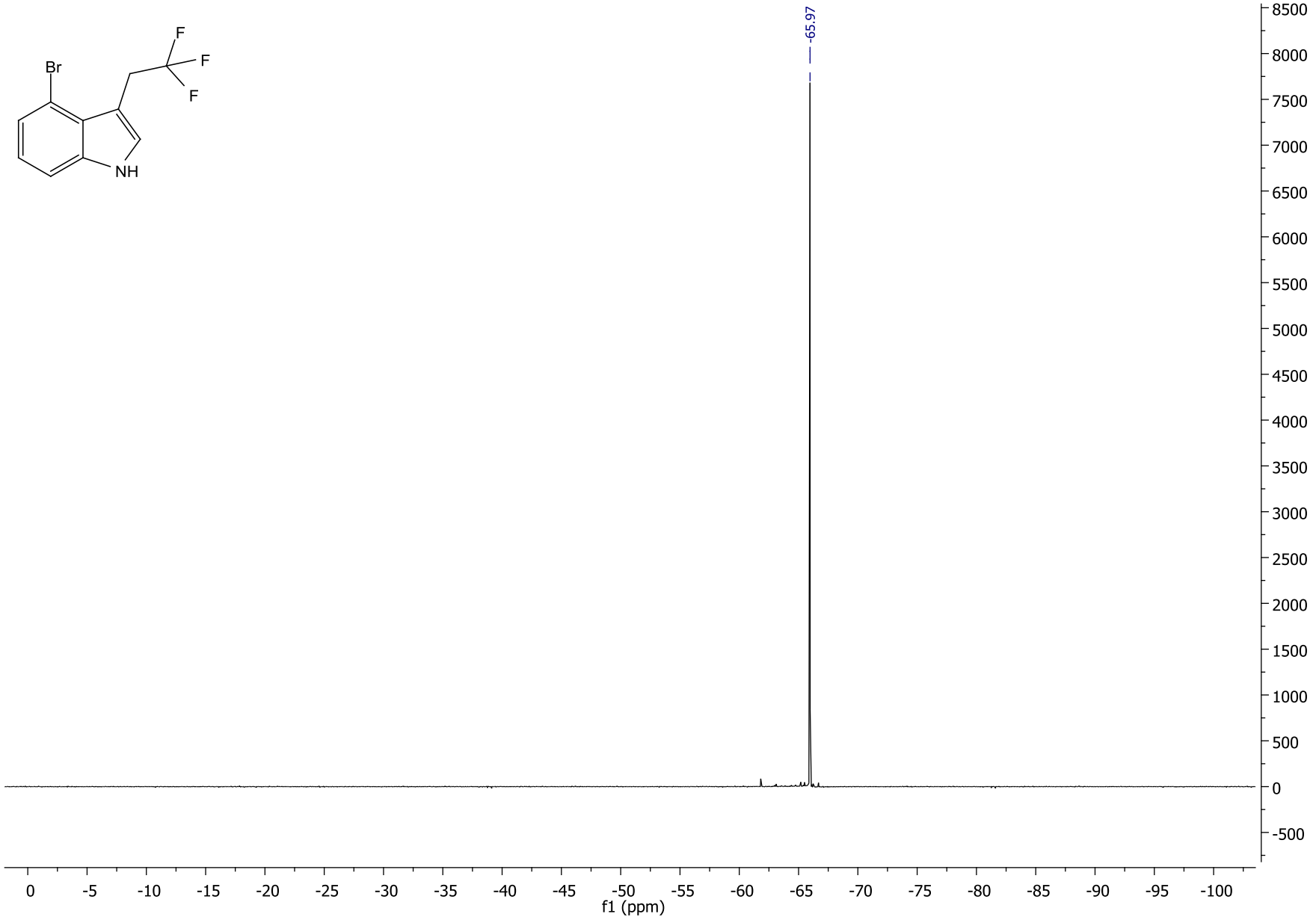

F
F
F
CH3
NH
Cl
135.49
132.66
130.47
129.03
124.62
121.34
121.17
117.00
116.30
102.55
102.50
102.45
102.38
30.77
30.27
29.77
29.26
12.01
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
CH3
NH
Cl
-66.01
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

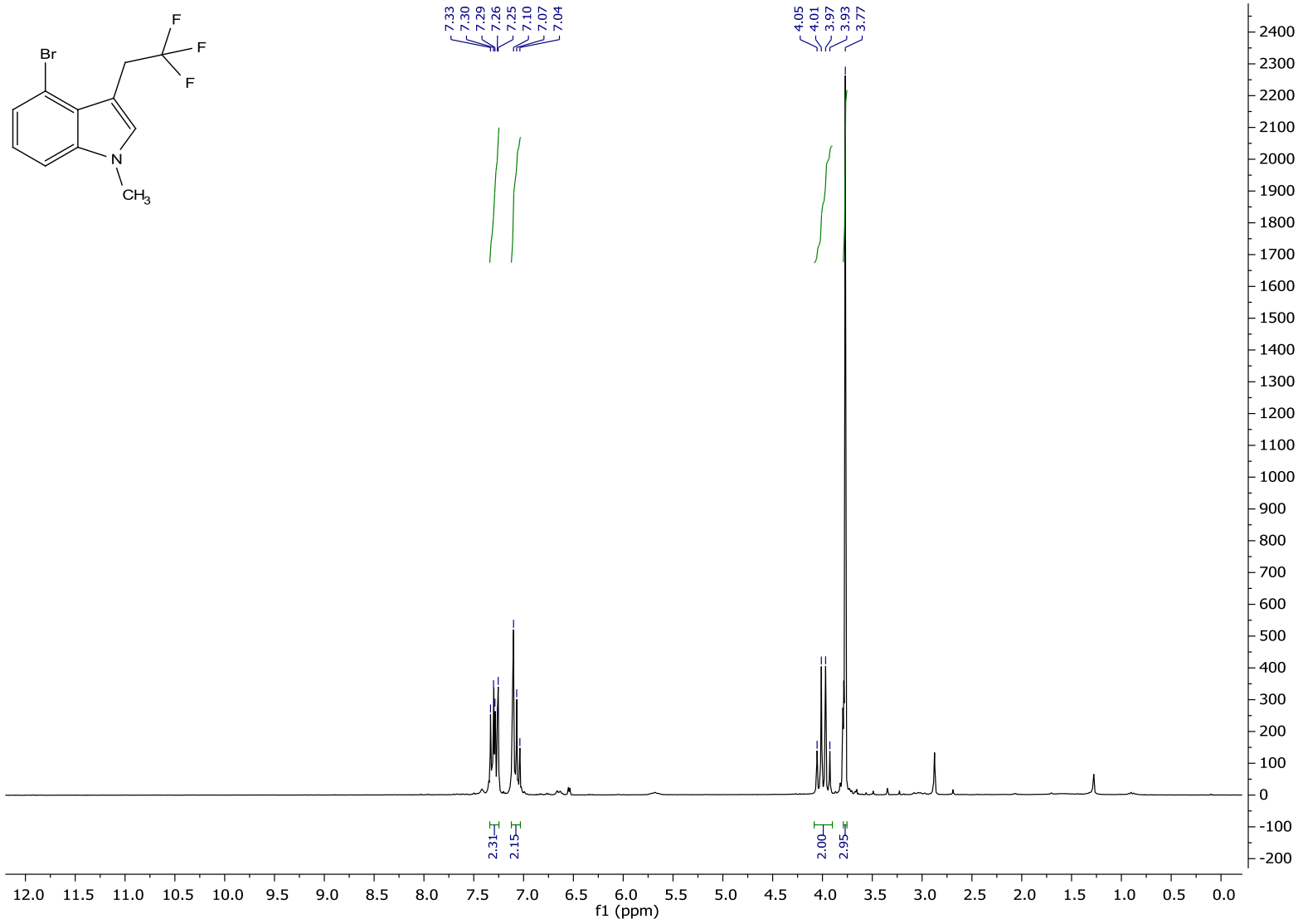
4-Bromo-3-(2,2,2-trifluoroethyl)-1*H*-indole (3z)

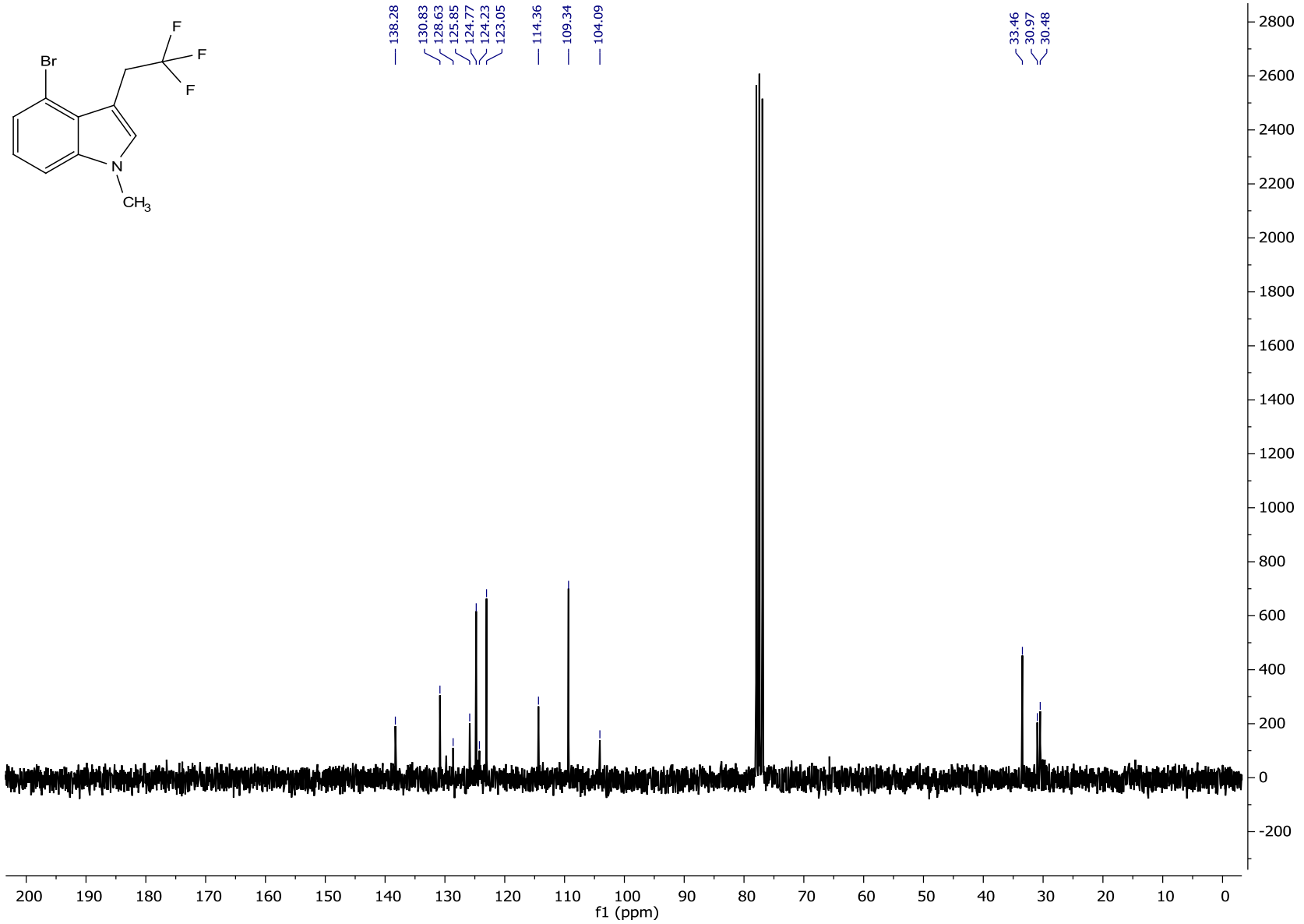


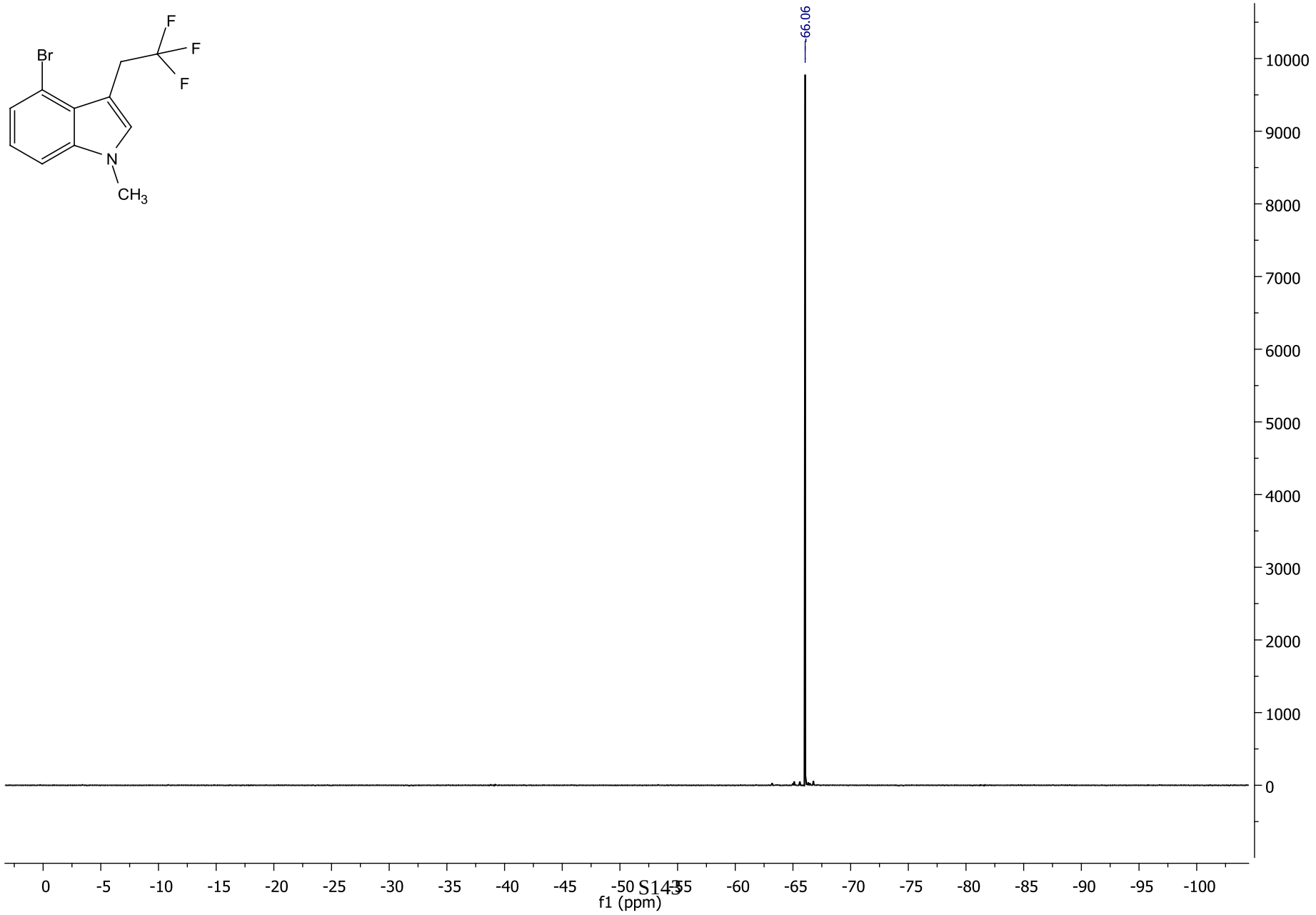

Br
F
F
F
NH
137.32
128.61
126.15
125.47
125.29
124.19
123.65
114.20
111.20
106.06
106.01
105.95
105.90
31.67
31.22
30.69
30.20
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
Br
NH
-65.97
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

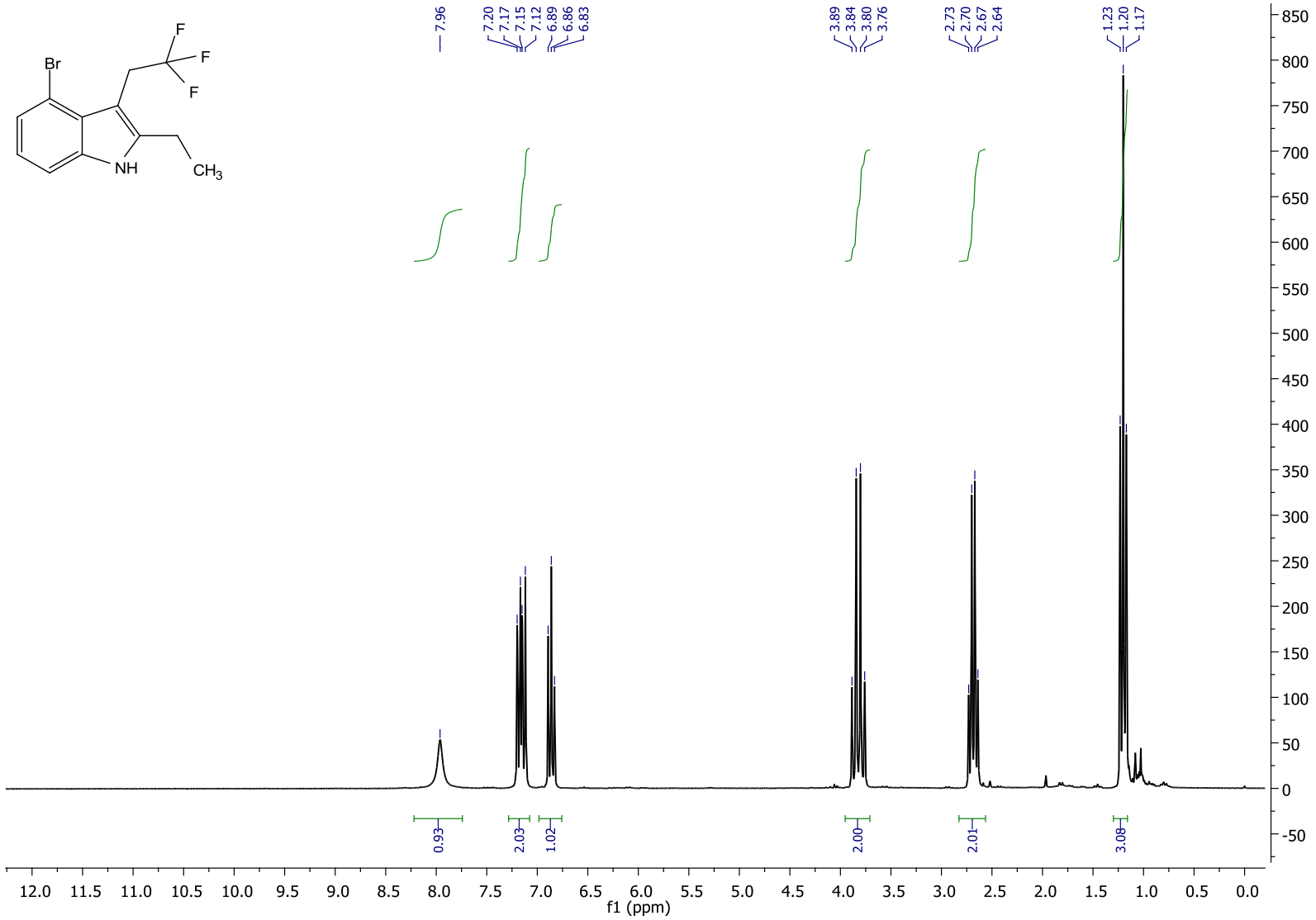
4-Bromo-1-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3aa)

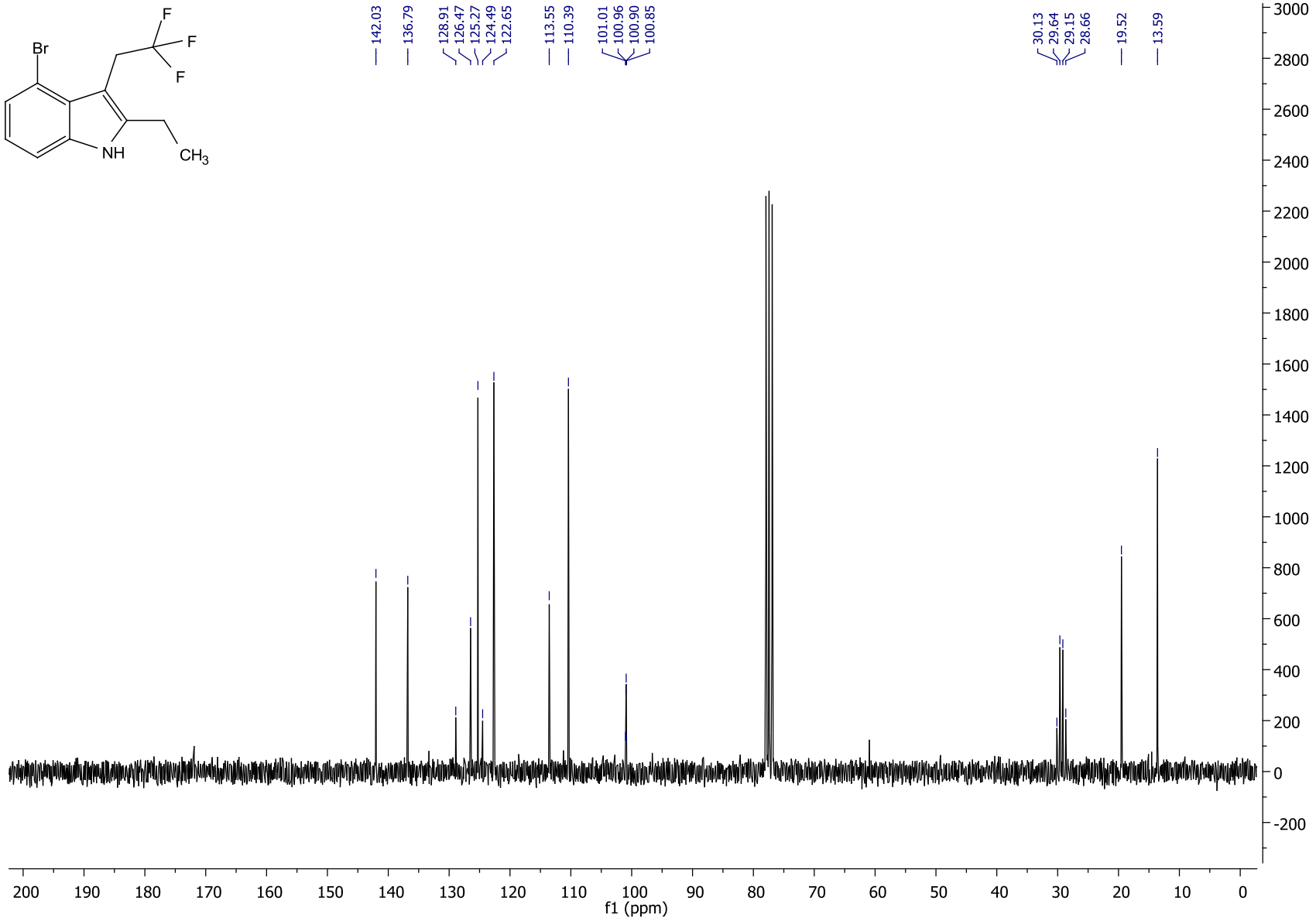


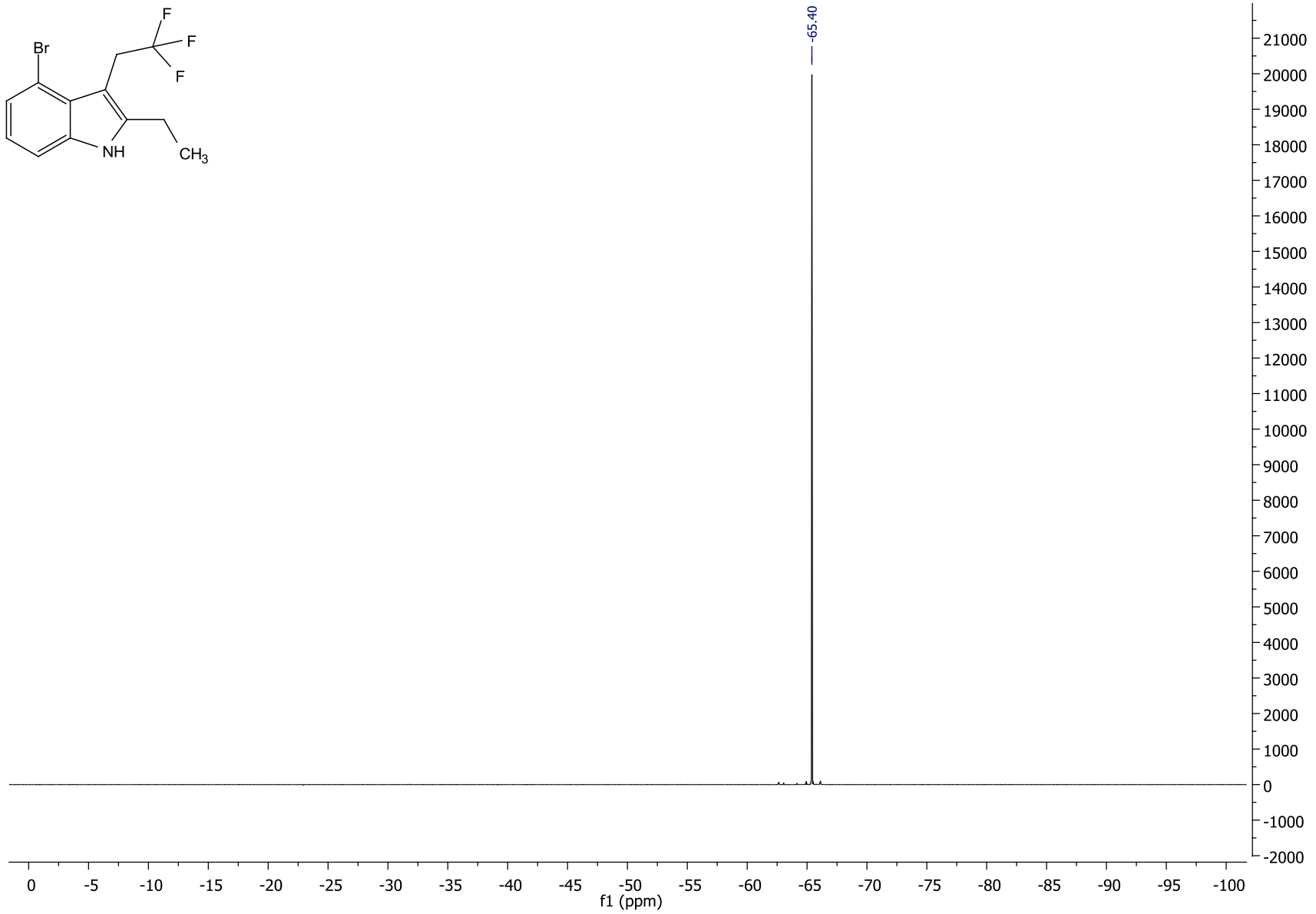

Br
F
F
F
N
CH3
138.28
130.83
128.63
125.85
124.77
124.23
123.05
114.36
109.34
104.09
33.46
30.97
30.48
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
F
F
F
N
CH3
66.06
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

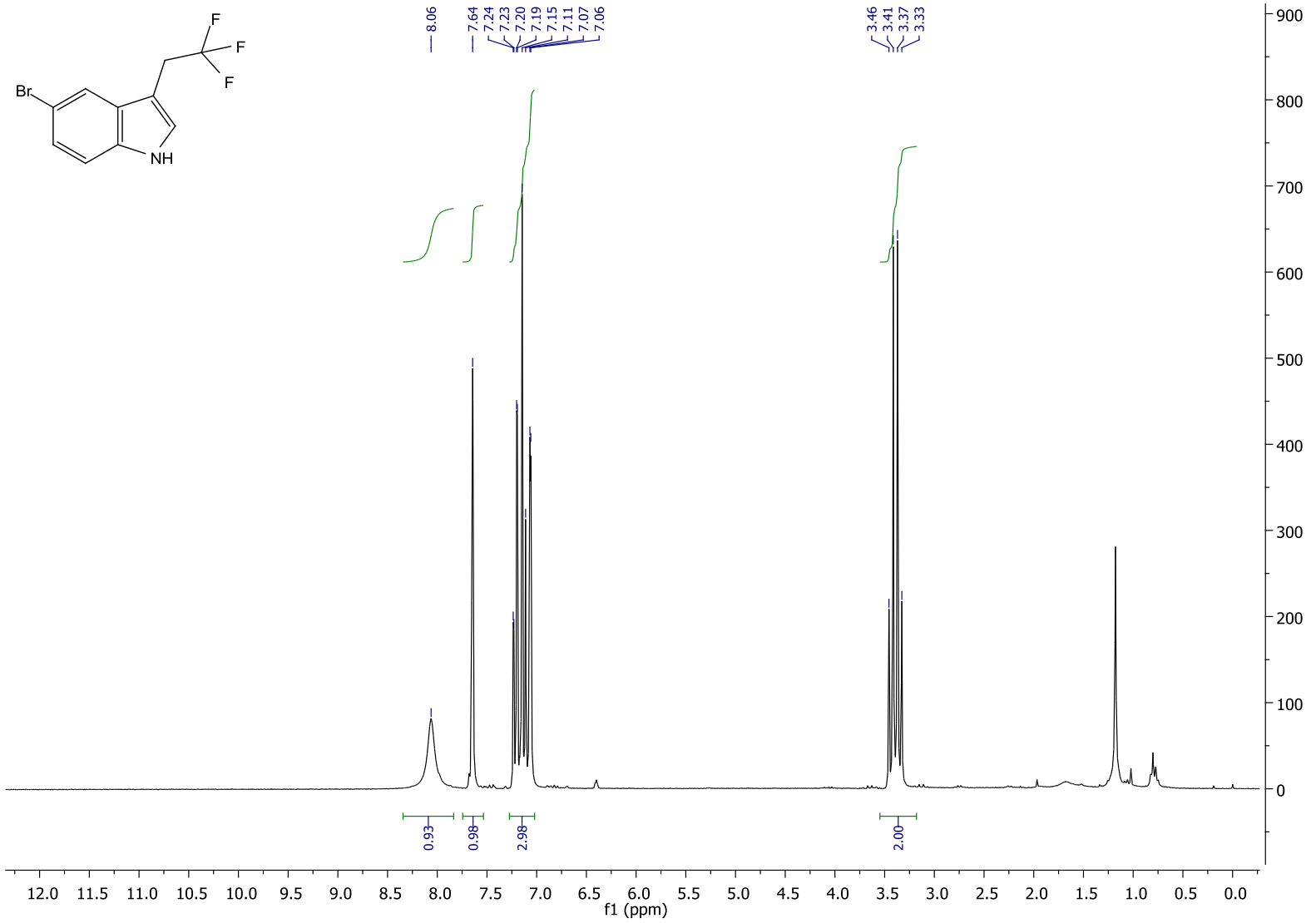
4-Bromo-2-ethyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3bb)

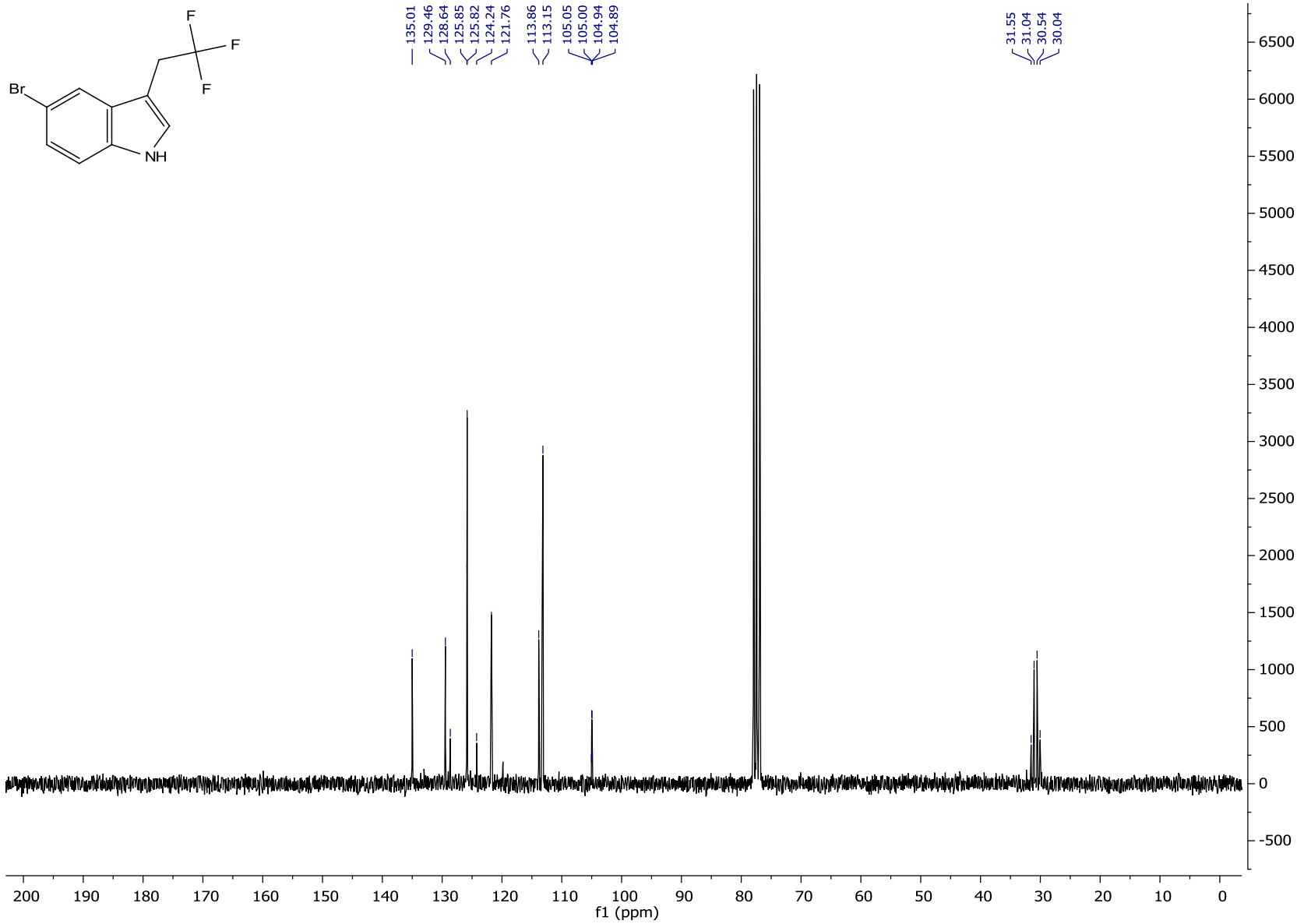


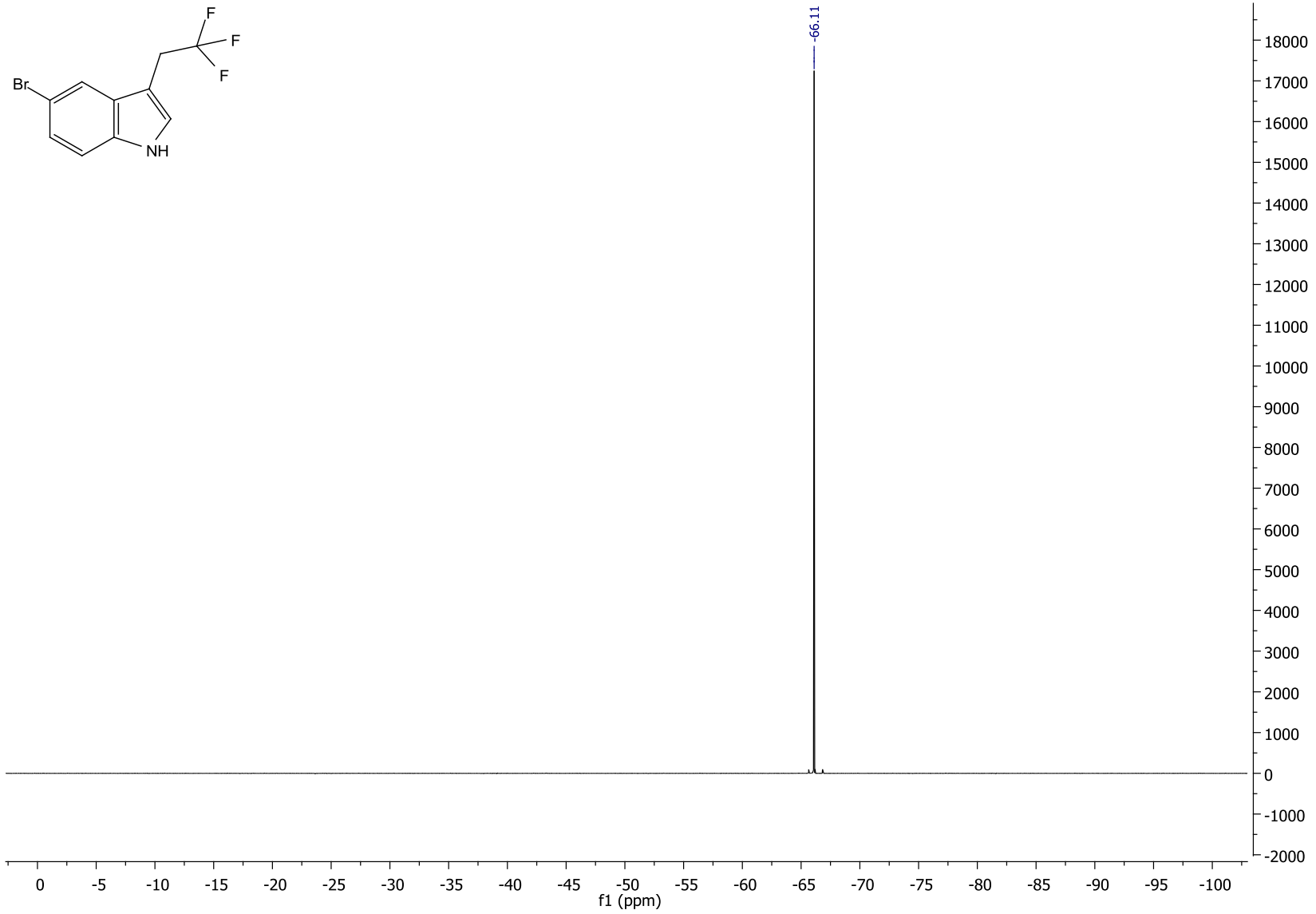

Br
F
F
F
NH
CH3
142.03
136.79
128.91
126.47
125.27
124.49
122.65
113.55
110.39
101.01
100.96
100.90
100.85
30.13
29.64
29.15
28.66
19.52
13.59
f1 (ppm)


F
F
F
Br
NH
CH3
-65.40
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

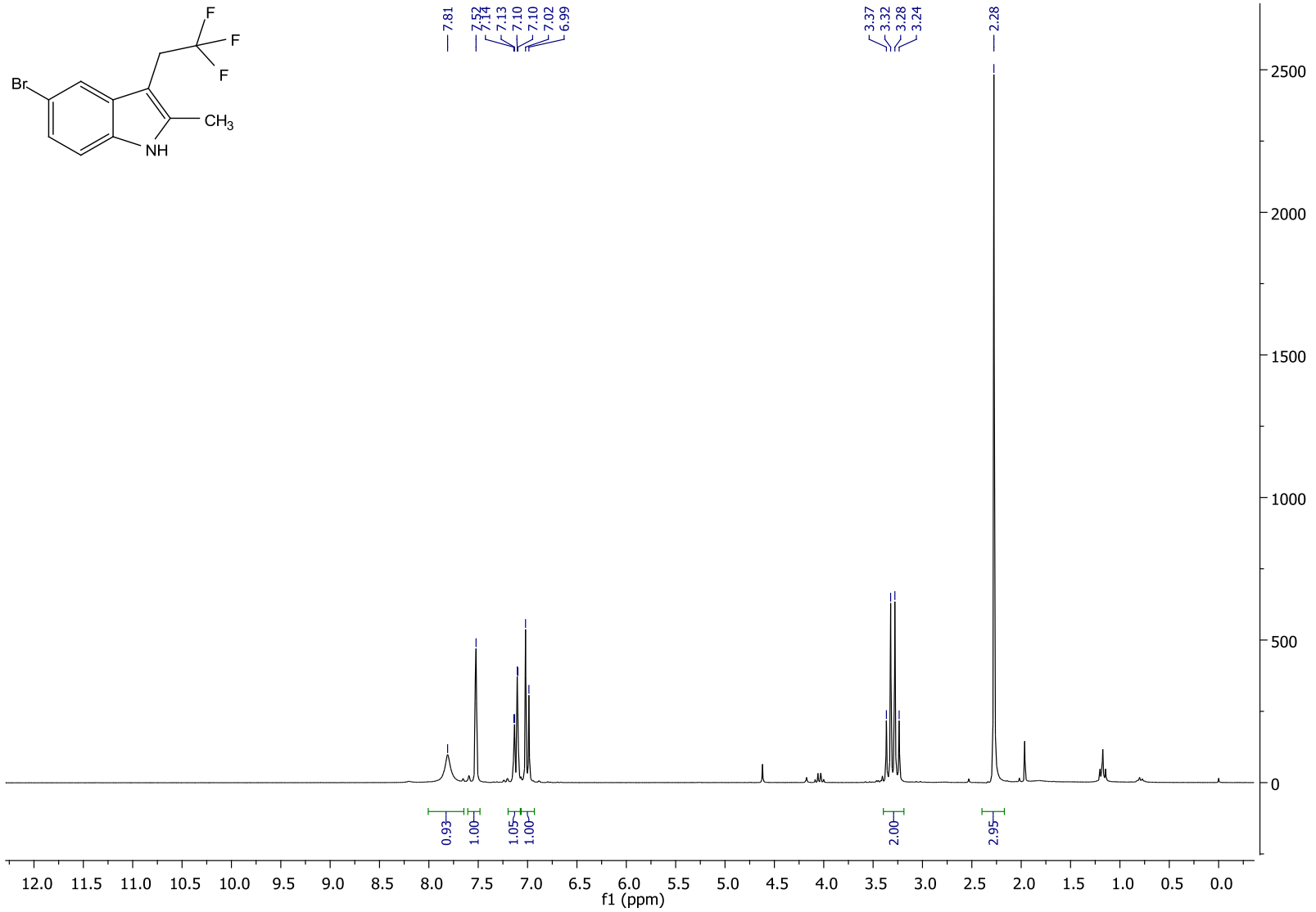
5-Bromo-3-(2,2,2-trifluoroethyl)-1*H*-indole (3cc)

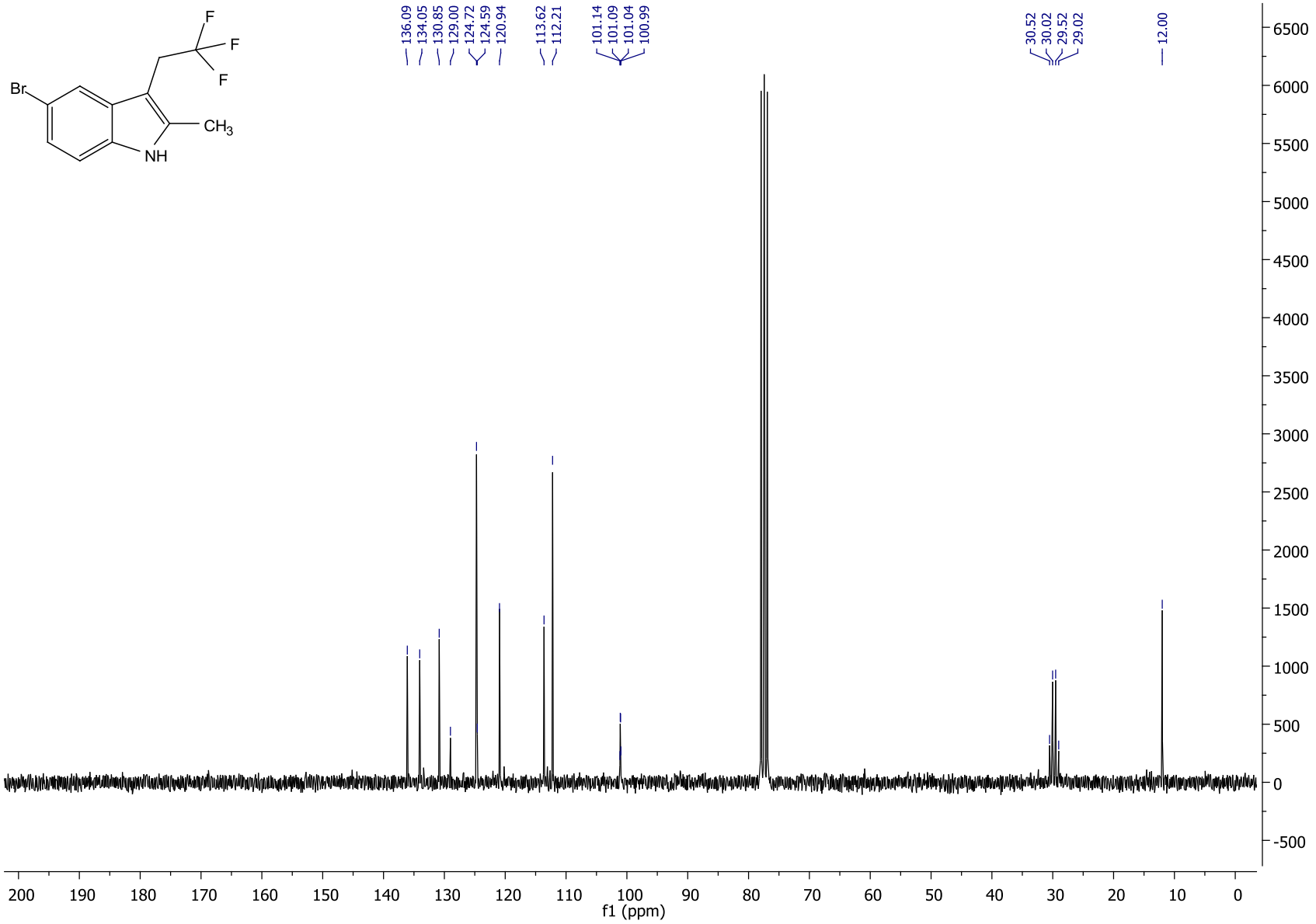


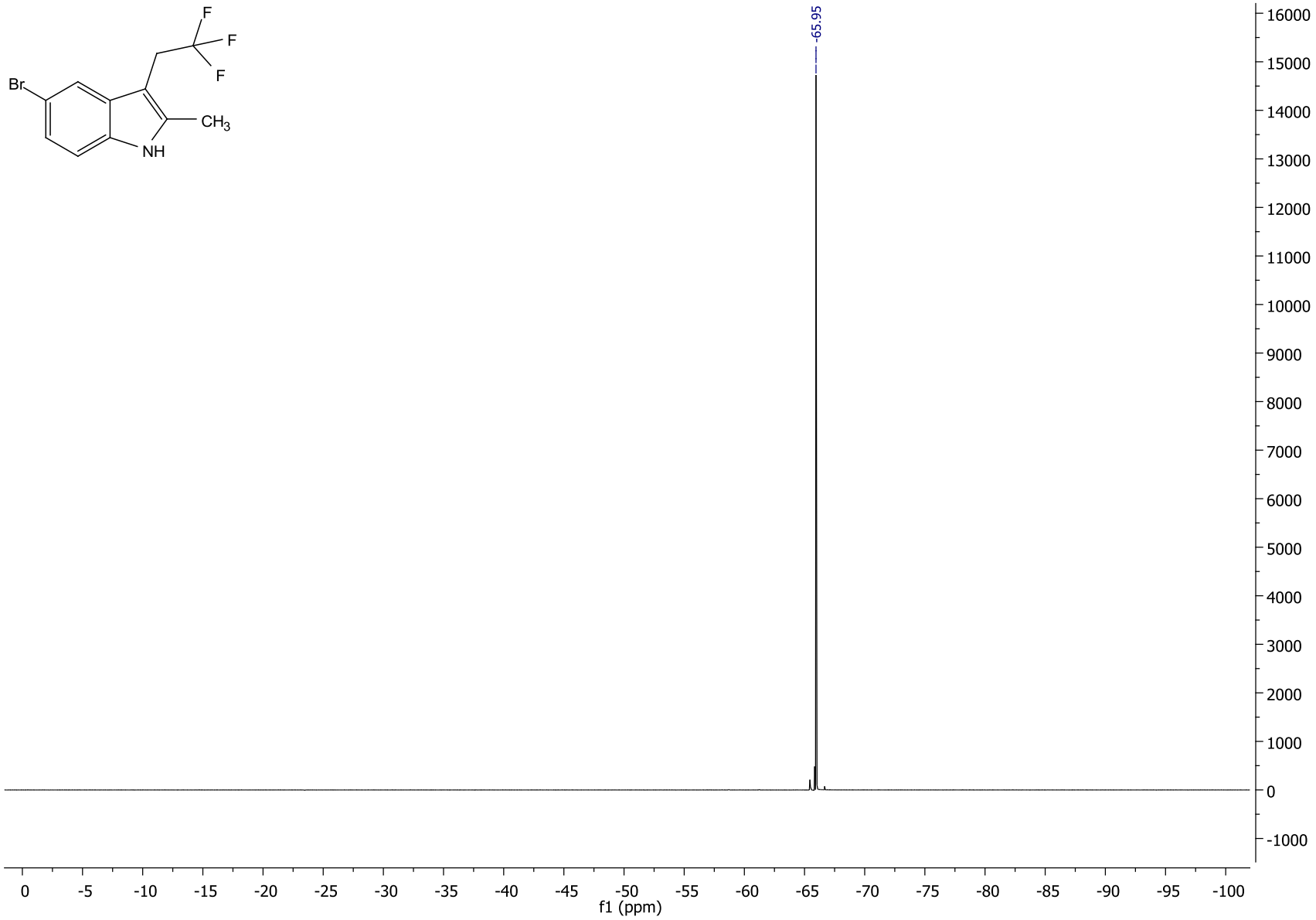

F
F
F
Br
NH
135.01
129.46
128.64
125.85
125.82
124.24
121.76
113.86
113.15
105.05
105.00
104.94
104.89
31.55
31.04
30.54
30.04
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
Br
NH
-66.11
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

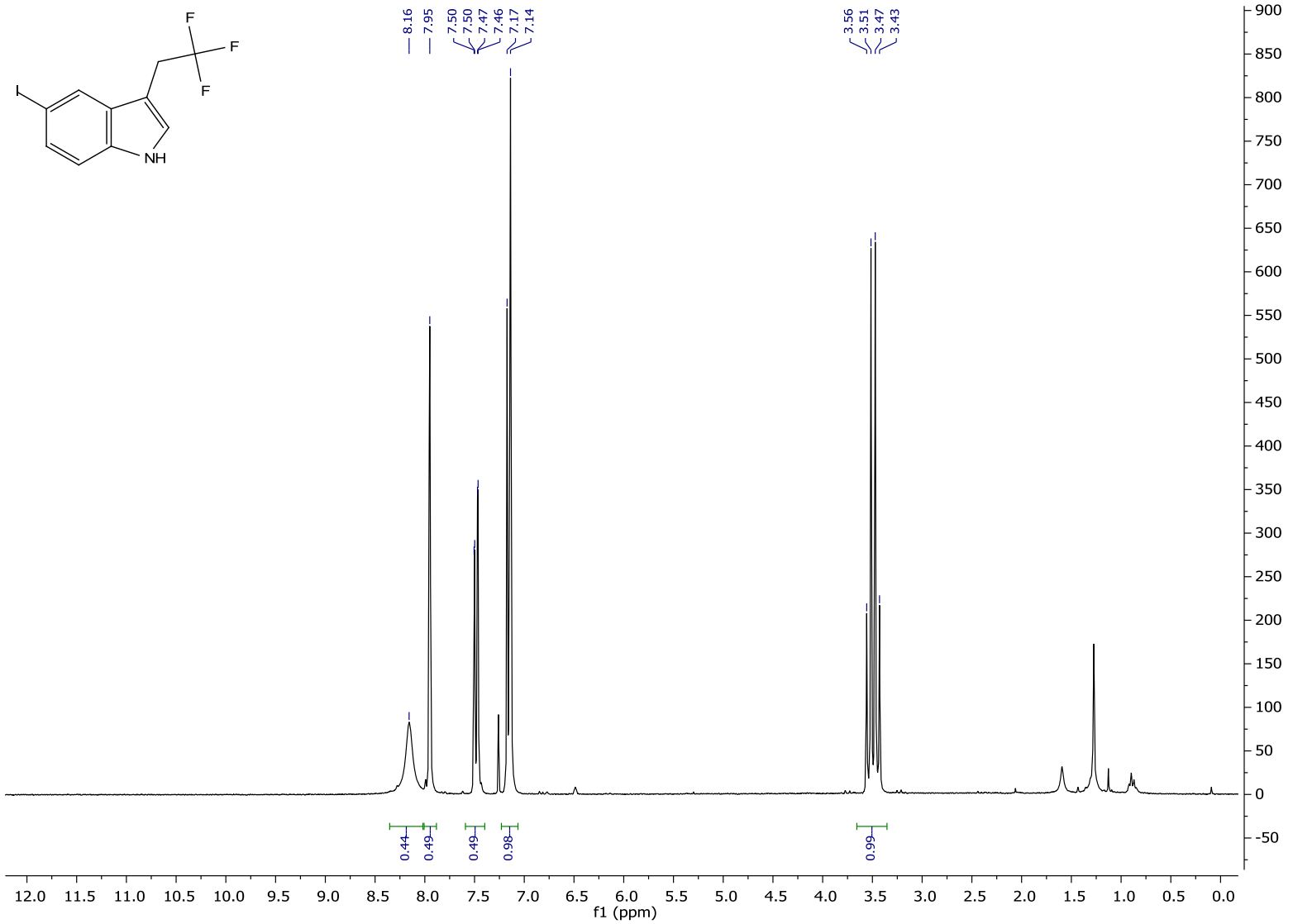
5-Bromo-2-methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (3dd)

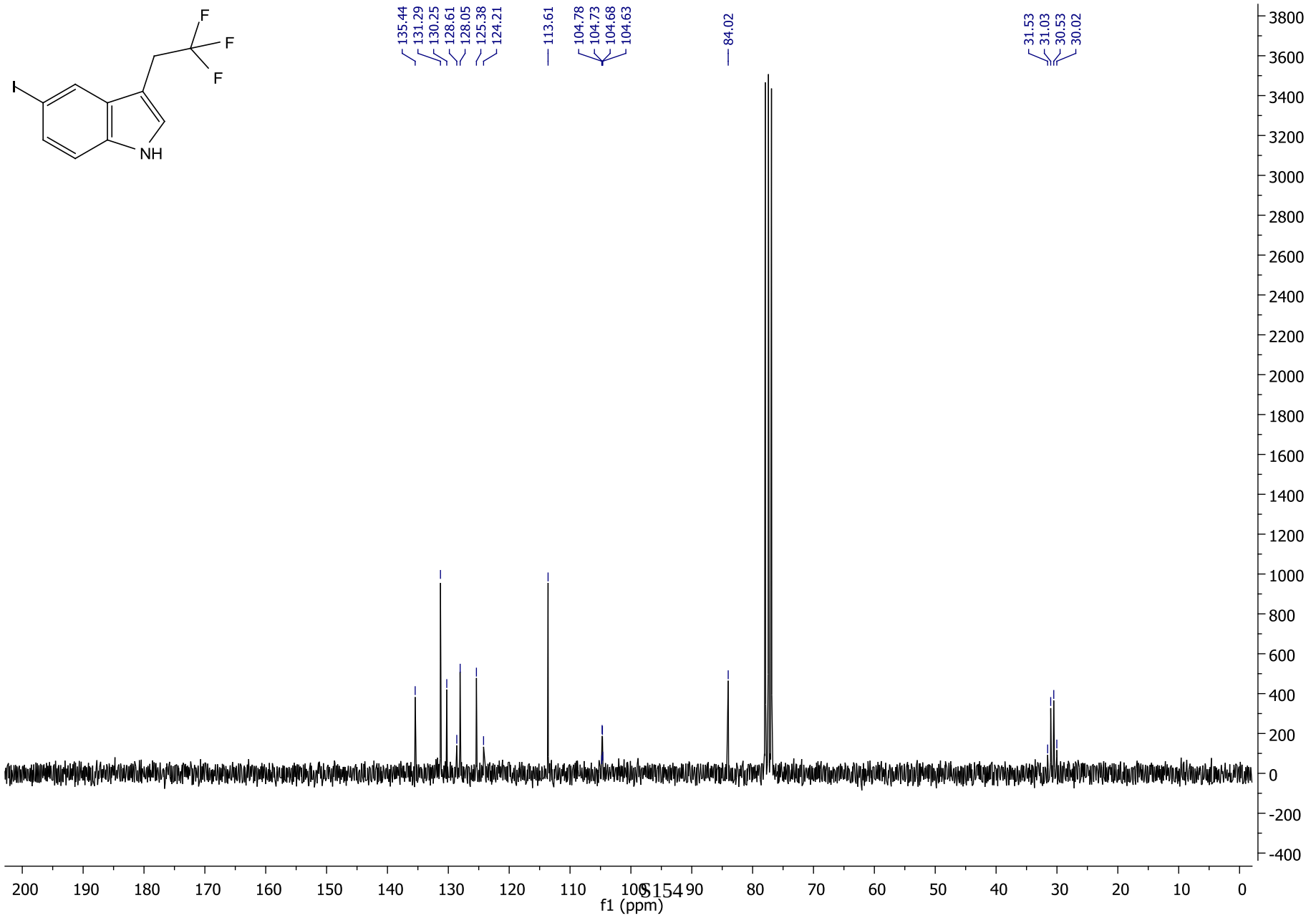


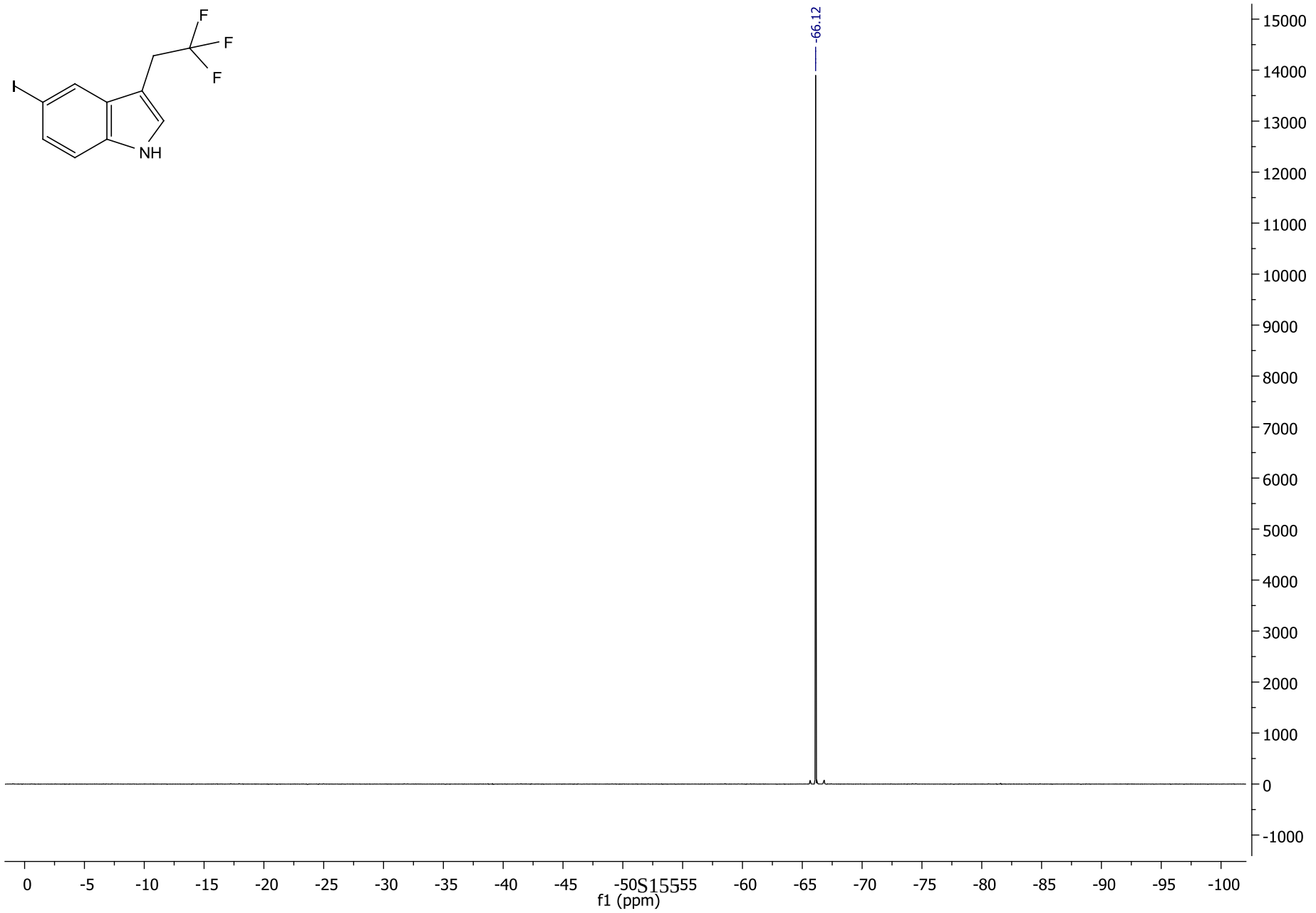

F
F
F
Br
CH3
NH
136.09
134.05
130.85
129.00
124.72
124.59
120.94
113.62
112.21
101.14
101.09
101.04
100.99
30.52
30.02
29.52
29.02
12.00
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
Br
CH3
NH
-65.95
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

5-Iodo-3-(2,2,2-trifluoroethyl)-1*H*-indole (3ee)




F
F
F
NH
135.44
131.29
130.25
128.61
128.05
125.38
124.21
113.61
104.78
104.73
104.68
104.63
84.02
31.53
31.03
30.53
30.02
f1 (ppm)


F
F
F
I
NH
-66.12
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)