Electronic Supplementary Material (ESI) for Green Chemistry.

Micelle-Enabled Clean and Selective Sulfonylation of Polyfluoroarenes in Water Under Mild Conditions

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Supporting Information

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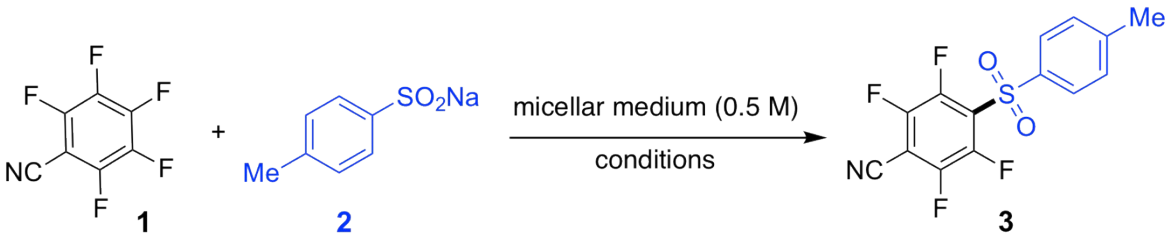
1. General Experimental Details

All manipulations were carried out under air unless otherwise noted. TLC plates (UV 254 indicator, aluminum backed, 175–225 μm thickness, standard grade silica gel, 230–400 mesh) were purchased from Merck. Acetone, ethyl acetate, and hexanes were purchased from Fisher Scientific. NMR solvents were purchased from Cambridge Isotopes Laboratories. Sulfinate salts were either purchased from Sigma-Aldrich or their precursors were obtained as a gift from Novartis Pharma Basil. All compounds were purified either by simple filtration with water washing, by passing through a silica plug, or by flash chromatography using a Teledyne Isco CombiFlash Rf 150. Microwave reaction vials (4 mL volume) were purchased from Biotage. HPLC grade water was used to prepare surfactant solution. GCMS data was recorded using a Thermo Scientific Trace 1300 Gas Chromatograph coupled with a Thermo Scientific ISQ-QD Single Quadrupole Mass Spectrometer. Melting points were determined using a Thomas Hoover melting point apparatus with samples in Kimble Kimex 51 capillaries (1.5–1.8 x 90 mm). NMR spectra were recorded at 23 °C on Varian MR-400, Varian Unity INOVA 500, and Varian VNMRS 700 spectrometers (400, 500 and 700 MHz, respectively). Reported chemical shifts are referenced to residual solvent peaks. IR spectra were acquired on a FTIR Perkin Elmer Spectrum Two: UATR Two spectrometer using 1 cm^{-1} resolution. High resolution mass analyses were obtained either using a 5975C Mass Selective Detector coupled with a 7890A Gas Chromatograph (Agilent Technologies) or orbit-trap. Calibrated MALDI mass measurements were conducted on an Applied Biosystems Voyager System 6032. DLS analyses were performed on Brookhaven 90 Plus Particle Size Analyzer

2. Optimization



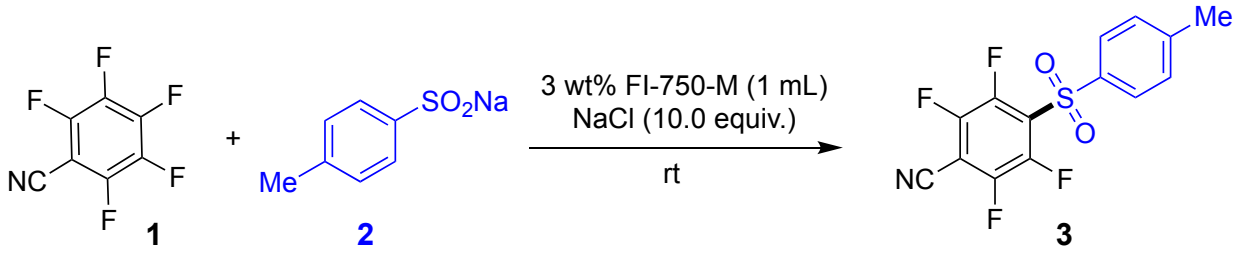
entry	reaction medium	additive	yield (%)[#]
1	acetone	–	52
2	water	–	0
3	3 wt% FI-750-M/acetone (4:1)	–	9
4	water/acetone (4:1)	–	5
5	3 wt% FI-750-M/acetone (4:1)	NaCl (5 equiv.)	58
6	3 wt% FI-750-M/acetone (4:1)	NaCl (10 equiv.)	80
7	water	NaCl (10 equiv.)	0
8	3 wt% FI-750-M	NaCl (10 equiv.)	57
9	3 wt% FI-750-M/THF (4:1)	NaCl (10 equiv.)	57
10	3 wt% FI-750-M/DMSO (4:1)	NaCl (10 equiv.)	70
11	3 wt% FI-750-M/acetone (4:1)	NaF (10 equiv.)	9
12	3 wt% FI-750-M/acetone (4:1)	NaBr (10 equiv.)	38
13	3 wt% TPGS-750-M/acetone (4:1)	NaCl (10 equiv.)	48
14	3 wt% SDS/acetone (4:1)	NaCl (10 equiv.)	1
15	3 wt% Pluronic F-127/acetone (4:1)	NaCl (10 equiv.)	26
16	3 wt% Tween 20/acetone (4:1)	NaCl (10 equiv.)	52
17	water/acetone (4:1)	NaCl (10 equiv.)	18

Conditions: **1** (0.5 mmol), **2** (0.6 mmol), additive (5 mmol), aqueous surfactant (0.8 mL), 0.2 mL acetone, rt (23 ^{o}C), 4 h. [#]Isolated yields.

Method for optimization studies. Sodium *p*-toluenesulfinate salt (0.6 mmol, 1.2 equiv.) and additive were added to an oven-dried 4 mL microwave vial equipped with PTFE-coated magnetic

stir bars. Subsequently, the reaction medium was added, followed by the pentafluorobenzonitrile (0.5 mmol, 1.0 equiv.). The reaction vessel was fitted with a rubber septum which was then wrapped with Teflon tape. The reaction mixture was allowed to stir at room temperature. Reaction progress was monitored at 30 minutes by withdrawing a 20 µL aliquot, passing it through a short silica plug with ethyl acetate, and immediately subjecting the eluted solution to GCMS analysis. After 4 hours had elapsed from the addition of pentafluorobenzonitrile, the septum was removed, and the reaction mixture was extracted with 1 mL portions of ethyl acetate (typically 3 extractions). The combined organic layers were dried over anhydrous $MgSO_4$, diluted with an equal volume of hexanes, and passed through a silica plug using a 1:1 mixture of hexanes and ethyl acetate as eluent. Solvent was removed by rotary evaporation and the containing vessel was placed under high vacuum for 2 hours.

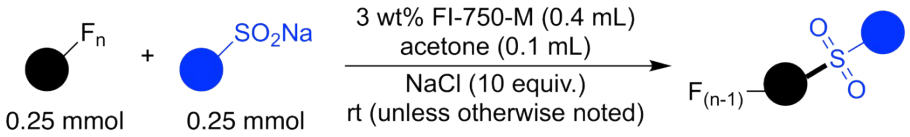
Optimal equivalents of sulfinate salt



entry	**2** (equiv.)	**yield (%)***
1	1.0	81
2	2.0	81
3	3.0	85

Conditions: 1 (0.5 mmol), sodium arylsulfinate **2**, NaCl (10 equiv.), 0.2 mL acetone, 0.8 mL 3 wt% aq. FI-750-M, rt, 14 h; *isolated yield. Product was extracted with ethyl acetate in entries 2 and 3 since it was not appeared as filterable solid.

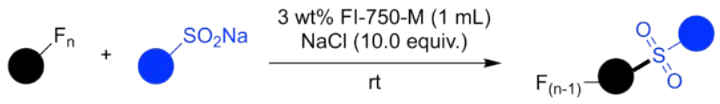
3. Final Optimized General Procedure

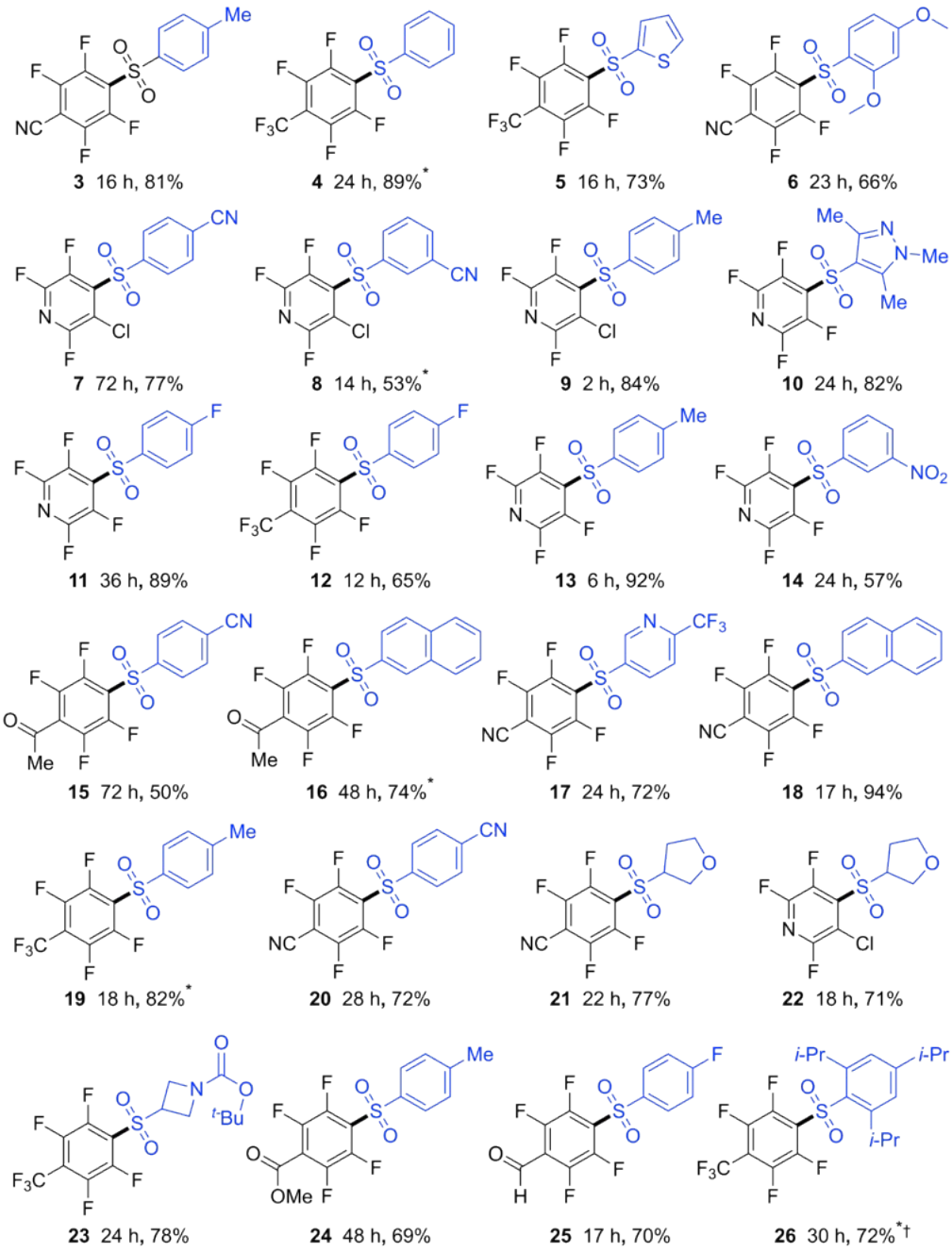


Aryl/heteroarylsulfinate salt (0.25 mmol) and sodium chloride (2.5 mmol) were sequentially added to an oven-dried 4 mL microwave reaction vial equipped with a PTFE-coated magnetic stir bar. Subsequently, 3 wt% aqueous FI-750-M (0.4 mL) and acetone (0.1 mL) were added, followed by addition of the polyfluoroarene (0.25 mmol). The reaction vessel was closed with a rubber septum which was then wrapped with PTFE tape. The reaction mixture was allowed to stir at room temperature. Reaction progress was monitored by TLC and GCMS. Upon reaction completion, most of the products appeared as solids inside the reaction vial. Therefore, 1.0 mL deionized water was added to the reaction mixture and contents were stirred for a minute. Reaction mixture was centrifuged to separate the solid from the liquid layer. Liquid layer was decanted and solid was washed an additional two times with water to obtain pure product. Pure product was dried under reduced pressure before final analyses.

Note: In a few cases (**16**, **26**), the product appeared partly soluble, so the mixture was extracted with ethyl acetate (2 x 0.5 mL), and the contents of the combined organic layers were passed through a hexane-wetted plug of silica gel. Volatiles were evaporated to obtain pure product as a solid.

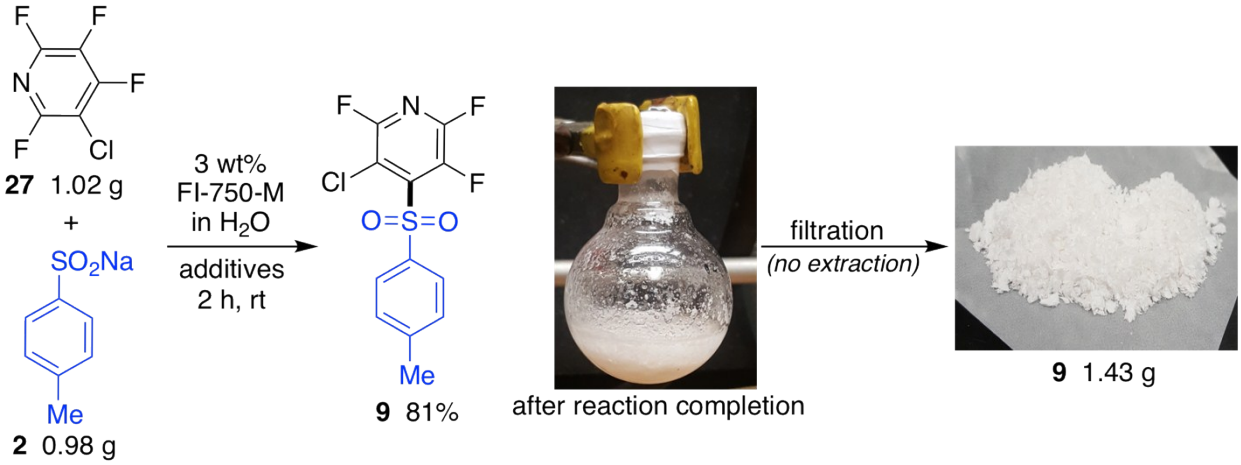
4. Substrate Scope





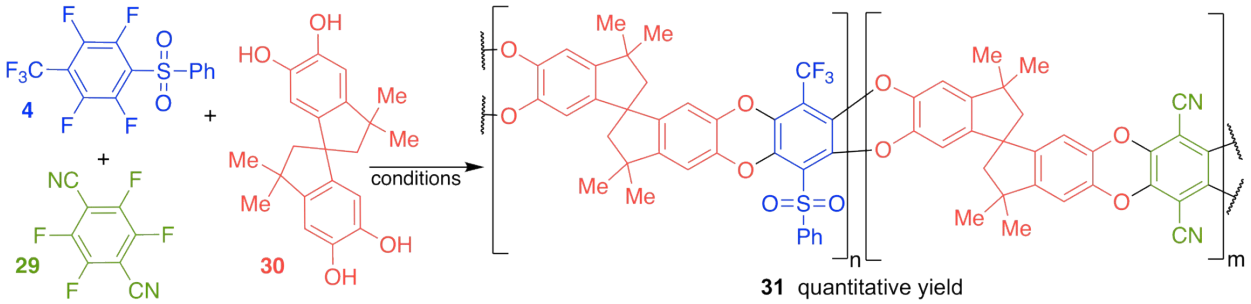
Conditions: polyfluoroaryl (0.25 mmol), sodium arylsulfinate (0.25 mmol), NaCl (10 equiv.), 0.1 mL acetone, 0.4 mL 3 wt% aq. FI-750-M; *yields with reaction temperature 45 °C; †lithium sulfinate salt was used.

5. Gram-Scale Reaction



Sodium *p*-toluenesulfinate **2** (5.5 mmol) and sodium chloride (55 mmol) were added to an oven-dried 25 mL round bottom flask equipped with a PTFE-coated magnetic stirrer bar. Subsequently, 3 wt% aqueous FI-750-M (8 mL) and acetone (2 mL) were added, followed by the addition of polyfluoroarene **27**. The reaction vessel was fitted with a rubber septum which was then wrapped with PTFE tape, and the reaction mixture was allowed to stir at room temperature. Reaction progress was monitored by TLC and GCMS. Upon reaction completion (after 2 h), 10 mL deionized water was added, and the solid material was collected by vacuum filtration with deionized water rinsing (2 x 10 mL). Residual traces of water were removed under high vacuum and the product was obtained as 1.43 g (81%) of white flaky solid. ^{1}H NMR confirmed purity and matched the product obtained from the 0.25 mmol scale reaction as shown in the substrate scope table.

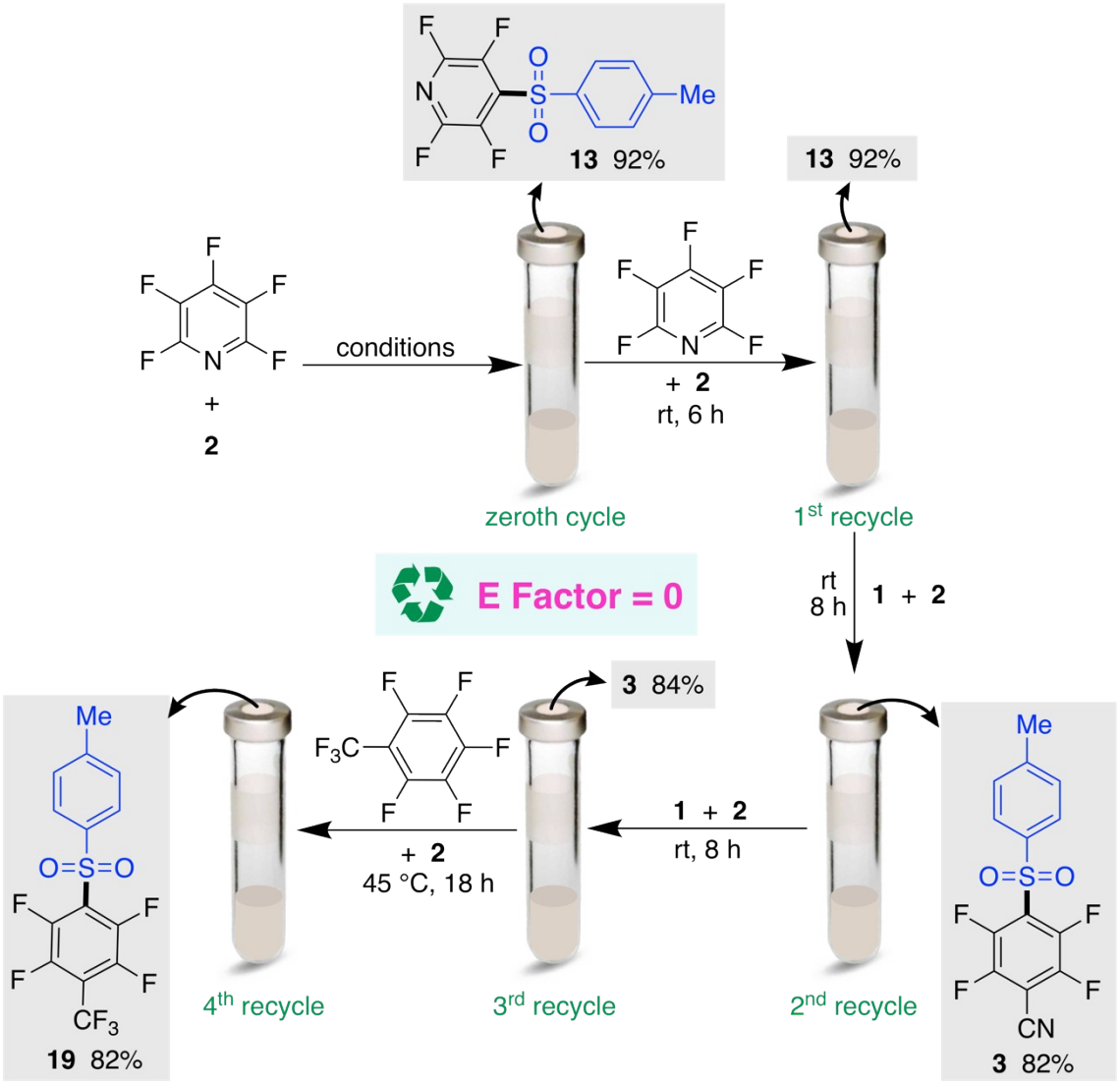
6. Synthesis of Polymer of Intrinsic Miroporosity



Conditions: **4** (0.28 mmol, 1.0 equiv.), **29** (0.56 mmol, 2.0 equiv.), **30** (0.84 mmol, 3.0 equiv.), K_2CO_3 (2.8 mmol, 10 equiv.), 10 mL 3 wt% aqueous FI-750-M, reflux.

1,2,4,5-Tetrafluoro-3-(phenylsulfonyl)-6-(trifluoromethyl)benzene (0.28 mmol, 1.0 equiv.), 2,3,5,6-tetrafluoroterephthalonitrile (0.56 mmol, 2.0 equiv.), 3,3,3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-5,5',6,6'-tetraol (0.84 mmol, 3.0 equiv.), and potassium carbonate (2.8 mmol, 10 equiv.) were added to an oven-dried 50 mL round bottom flask equipped with a PTFE-coated magnetic stir bar, followed by addition of 10 mL 3 wt% aqueous FI-750-M. The reaction vessel was fitted with a water-jacketed reflux condenser and was magnetically stirred in an oil bath pre-heated to 125 °C. Product formation was observed as a yellow precipitate. After 2 h, the reaction vessel was removed from heating and the solid material was collected over a fritted glass funnel by vacuum filtration with subsequent water rinses (3 x 10 mL). The solid material and 20 mL deionized water were added to a 50 mL round bottom flask which was then fitted with a water-jacketed reflux condenser. The suspension was then magnetically stirred in an oil bath pre-heated to 100 °C for 16 hours, at which point the vessel was allowed to cool to room temperature, and the solid material was thereafter collected by vacuum filtration on a fritted glass funnel. Residual traces of water were removed under high vacuum and the product was obtained as 0.33 g (87%) of yellow solid. Analytical data was in accordance with the literature.[1]

7. Recycle Study



Conditions: perfluoroarene (0.25 mmol), aryl sodium sulfinate (0.25 mmol), NaCl (2.5 mmol, only in zeroth cycle), acetone (0.1 mL, only in zeroth cycle), 3 wt% aqueous FI-750-M (0.4 mL, only in zeroth cycle), rt (unless otherwise noted), 6 h (unless otherwise noted).

Zeroth cycle. Sodium *p*-toluenesulfinate salt (0.25 mmol) and sodium chloride (2.5 mmol) were added to an oven-dried stir-bar-equipped 4 mL microwave vial. Subsequently, a mixture of 3 wt% aqueous FI-750-M (0.4 mL) and acetone (0.1 mL) was added (this mixture had been recovered from the gram-scale reaction), followed by addition of pentafluoropyridine (0.25 mmol). The reaction vessel was fitted with a rubber septum which was then wrapped with PTFE tape. The

reaction mixture was allowed to stir at room temperature. Rather than monitoring, the reaction was allowed to run for a set time of 6 hours (based on the reaction completion time of an equivalent reaction set up and monitored previously). Upon reaction completion, the liquid was removed from the precipitate by syringe and transferred to a different vessel that had been prepared for the next iteration in the study. The precipitate was rinsed with water (2 x 0.5 mL), with the water being removed by syringe. Residual traces of water were removed under reduced pressure at 80 °C, and the precipitate was subsequently placed under high vacuum. The pure product **13** was obtained as a white flaky solid (71 mg, 92%), as confirmed by ^{1}H NMR.

First recycle. The aqueous micellar portion recovered from the above reaction (zeroth cycle) mixture was added to an oven-dried stir-bar-equipped 4 mL microwave vial containing sodium *p*-toluenesulfinate salt (0.25 mmol). Pentafluoropyridine (0.25 mmol) was added, and the reaction vessel was fitted with a rubber septum which was then wrapped with PTFE tape. The reaction mixture was allowed to stir at room temperature for 6 hours. Upon reaction completion, the liquid was removed from the precipitate by syringe and transferred to a different vessel that had been prepared for the next iteration in the study. The precipitate was rinsed and dried as in the zeroth cycle. The product was obtained as a white flaky solid (72 mg, 92%), as confirmed by ^{1}H NMR.

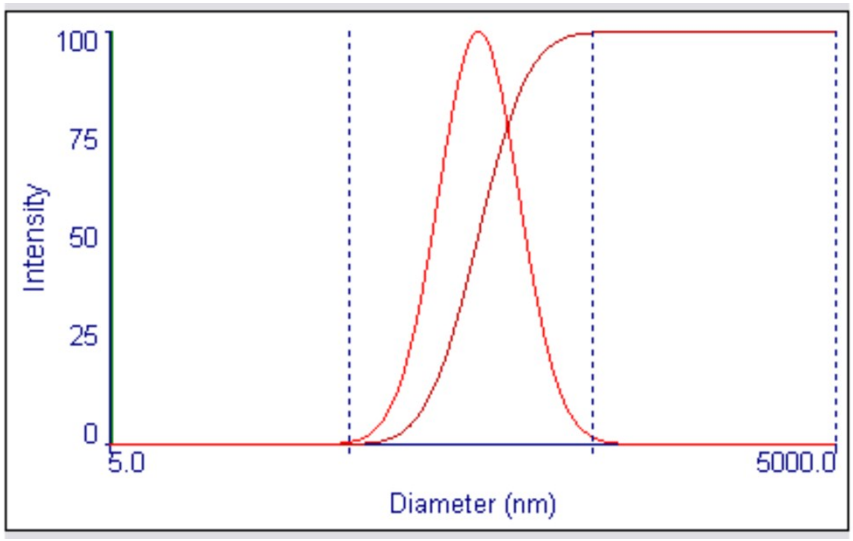
Second recycle The method for the second recycle was identical to that of the first recycle, except that pentafluorobenzonitrile (0.25 mmol) was used in place of pentafluoropyridine, and the reaction was allowed to run for 8 hours. The product was obtained as an off-white flaky solid (67 mg, 82%), as confirmed by ^{1}H NMR.

Third recycle. The method for the third recycle was identical to that of the second recycle. The product was obtained as an off-white flaky solid (69 mg, 84%), as confirmed by ^{1}H NMR. Note: 5.0 equiv. of NaCl was added as additive.

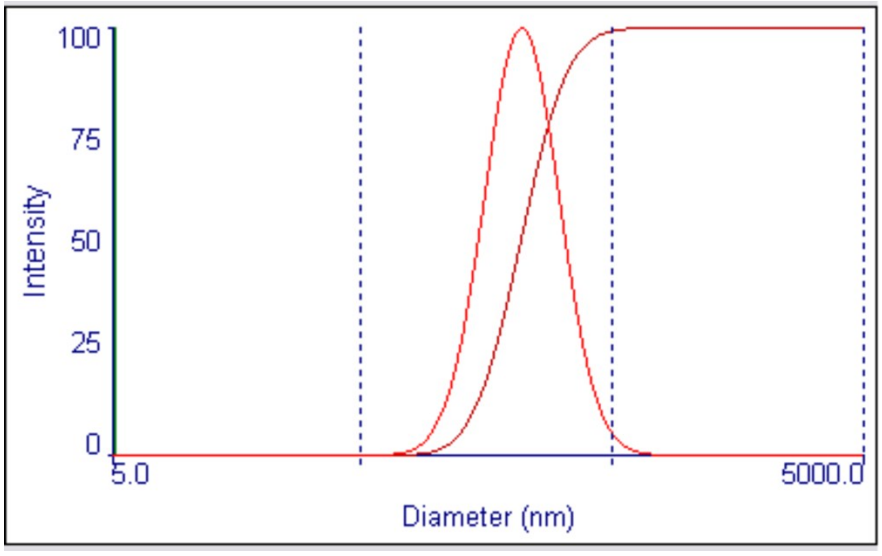
Fourth recycle. The method for the fourth recycle was identical to that of the first recycle, except that octafluorotoluene (0.25 mmol) was used in place of pentafluoropyridine, and the reaction was allowed to run for 18 hours at 45 °C. The product was obtained as an off-white flaky solid (76 mg, 82%), as confirmed by ^{1}H NMR.

8. Dynamic Light Scattering Experiments

Particle size measurements were acquired with a Brookhaven 90 Plus Particle Size Analyzer from Brookhaven Instrument Corporation. A 0.2 wt% aqueous solution of FI-750-M was analyzed for particle size distribution. In a separate experiment, 20% (w/v) of acetone was dissolved in 0.2 wt% aqueous solution of FI-750-M and NaCl was admixed to obtain its 1M concentration. After mixing for 5 minutes, resulting solution was immediately analyzed for particle size determination.



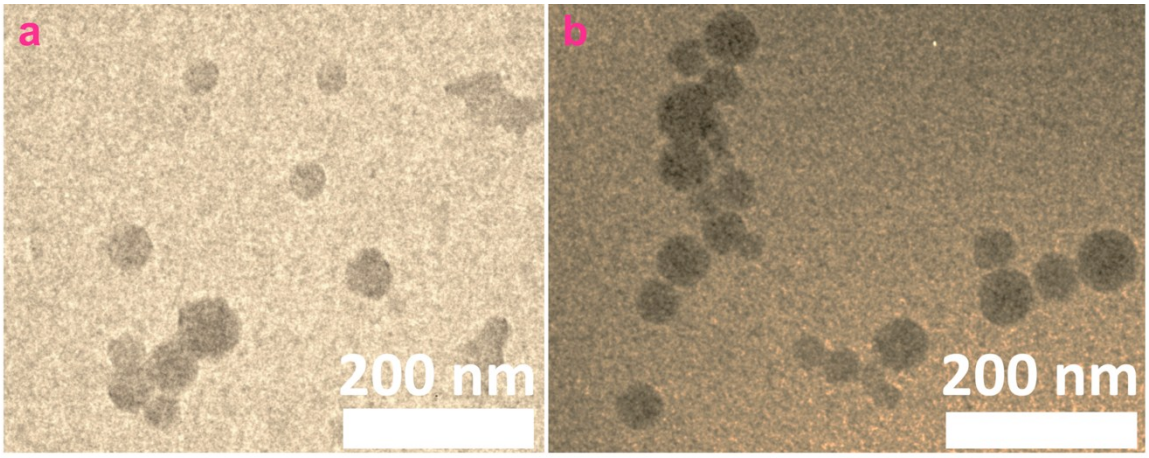
0.2 wt% aqueous FI-750-M – average diameter = 169 nm



0.2 wt% aqueous FI-750-M, 1M NaCl, 20% acetone – average diameter = 169 nm

9. Cryo-TEM

Cryo-TEM analysis was performed in the Facility of High Resolution Microscopy, California Nanoscience Institute, University of California, Santa Barbara. Two different samples were directly analyzed for high resolution images to determine the particle size, shape, and and morphology: a) 3 wt% aqueous FI-750-M and b) 1 M NaCl in 3 wt% aqueous FI-750-M, 20 vol% acetone solution.

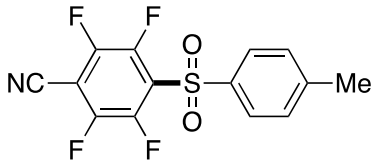


10. Computational Details

The density functional theory calculations were carried out using Turbomole [2], v6.5, with the BP functional[3], the TZVP basis set[4], and the COSMO implicit solvent model[5] with an infinite dielectric constant, which is required for the subsequent COSMO-RS calculations[6]. The COSMO-RS calculations used the BP-TZVP-C1601 parameterization[7] in the COSMOtherm[8] program. Predictions of interfacial tension (IFT) were made using the model by Andersson, et.al[9], using the slightly updated version of the method with geometric averaging of coverages during the IFT iterations[10]. For estimating local solubilities for the different parts of the surfactant, we used the weight factor functionality in COSMOtherm to model the mPEG region, the lipophilic region and the linker region of the FI-750-M and the TPGS-750-M surfactants as different molecules. The non-iterative procedure for calculating solubility was used, because the iterative procedure gave inconsistent results for the perfluoroarene compound. Four different conformers were used for the FI-750-M surfactant with 16 ethylene oxide units to take into account surfactant flexibility and three different conformers were used for the TPGS-750-M surfactant, also with 16 ethylene oxide units. For the interfacial tension model to be reliable, neutral molecules are needed. Therefore, we only modeled the ion pair form of the sodium arylsulfinate **2**. The salts NaF, NaCl and NaBr were also as neutral ion pairs.

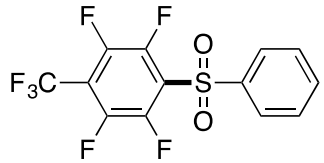
11. Analytical Data

2,3,5,6-tetrafluoro-4-tosylbenzonitrile (3)



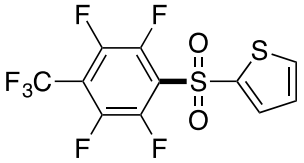
White solid, mp = 156–157 °C, yield 67 mg (81%), R_f 0.38 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.96 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 2.48 (s, 3H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -128.36 – -128.95 (m, 2F), -132.79 – -133.35 (m, 2F); ^{13}C NMR (126 MHz, cdcl$_3$) δ 148.7 – 148.5 (m), 146.5 – 146.4 (m), 145.1 – 145.0 (m), 143.0 – 142.8 (m), 136.9, 130.6, 128.4, 106.3, and 22.0. I.R: ν (cm^{-1}) = 3098 (w), 3067 (w), 2925 (w), 2857 (w), 2248 (m), 1594 (m), 1490 (s). I.R: ν (cm^{-1}) = 3098 (w), 3067 (w), 2925 (w), 2857 (w), 2248 (m), 1594 (m), 1490 (s). HRMS (CI), $[C_{14}H_7F_4NO_2S + H]^+$ calcd. 330.0206, found (*m*/*z*) 330.0215.

1,2,4,5-tetrafluoro-3-(phenylsulfonyl)-6-(trifluoromethyl)benzene[11] (4)



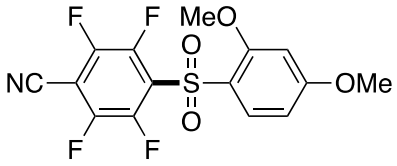
White solid, mp = 135–136 °C, yield 80 mg (89%), R_f 0.40 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl3) δ 8.11 (d, J = 8.0 Hz, 2H), 7.75 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 8.0 Hz, 2H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -56.87 (t, J = 21.9 Hz), -133.88 (dd, J = 20.3, 11.4 Hz), -136.52 (td, J = 22.1, 13.4 Hz); ^{13}C NMR (176 MHz, cdcl$_3$) 145.4 – 145.0 (m), 143.9 – 143.5 (m), 140.0, 135.5, 129.9, 128.3, 125.3 (t, $J_{(C,F)}$ = 14.1 Hz), 120.2 (q, $J_{(C,F)}$ = 276 Hz), 114.3 (qt, $J_{(C,F)}$ = 35.6, 12.7 Hz). I.R: ν(cm^{-1}) = 3103 (w), 3086 (w), 1650 (m), 1585 (m).

2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)sulfonyl)thiophene (5)



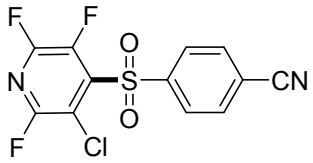
White solid, mp = 134–135 °C, yield 66 mg (73%), R_f 0.23 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, $CdCl_3$) δ 7.95 (d, J = 4.0 Hz, 1H), 7.86 (dd, J = 4.0 and 1.0 Hz, 1H), 7.22 (t, J = 4.0 Hz, 1H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -56.9 (t, $J_{(C,F)}$ = 21.1 Hz, 3F), -133.8 – -133.9 (m, 2F), -136.4 – -136.7 (m, 2F); ^{13}C NMR (126 MHz, $CdCl_3$) δ 145.7 (d, $J_{(C,F)}$ = 16.5 Hz), 145.2 (d, $J_{(C,F)}$ = 16.5 Hz),, 143.4 (d, $J_{(C,F)}$ = 17.1 Hz), 143.2 (d, $J_{(C,F)}$ = 17.1 Hz), 140.7, 136.9, 136.2, 128.7, 125.7 (d, $J_{(C,F)}$ = 13.1 Hz), 120.2 (q, $J_{(C,F)}$ = 272 Hz), 114.4-114.2 ppm. I.R: ν (cm^{-1}) = 3101 (m), 2963 (w), 2923 (m), 2858 (w). HRMS (CI), $[C_{11}H_3F_7O_2S_2 + H]^+$ calcd. 364.9535, found (*m*/*z*) 364.9531.

4-((2,4-dimethoxyphenyl)sulfonyl)-2,3,5,6-tetrafluorobenzonitrile (6)



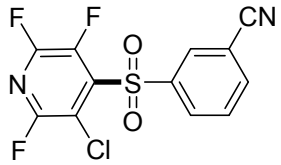
White solid, mp = 145-146 °C, yield 62 mg (66%), R_f 0.14 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.99 (d, J = 8.5 Hz, 1H), 6.63 (dd, J = 8.5 and 2.0 Hz, 1H), 6.44 (d, J = 2.0 Hz, 1H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -130.0 (dt, $J_{(C,F)}$ = 13.2 and 3.3 Hz, 2F), -134.0 (dt, $J_{(C,F)}$ = 13.2 and 3.3 Hz, 2F); ^{13}C NMR (126 MHz, cdcl$_3$) δ 167.2, 159.7, 148.3 (d, J = 16.0 Hz), 146.1 (d, J = 15.8 Hz), 145.7 (d, J = 12.2 Hz), 143.5 (d, J = 12.0 Hz), 132.4 (d, J = 5.5 Hz), 127.5 (t, J = 13.5 Hz), 119.9, 106.6, 105.6, 99.6 (d, J = 13.1 Hz), 98.0 (t, J = 17.2 Hz), 56.7, 55.9. I.R: ν (cm^{-1}) = 3111 (w), 3091 (w), 3025 (m), 2982 (w), 2949 (m), 2922 (m), 2869 (w), 2847 (m), 2248 (m). HRMS (CI), $[C_{15}H_9F_4NO_4S + H]^+$ calcd. 376.0261, found (*m*/*z*) 376.0250.

4-((3-chloro-2,5,6-trifluoropyridin-4-yl)sulfonyl)benzonitrile (7)



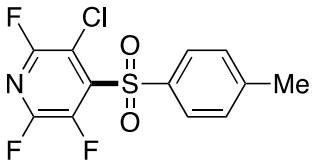
White solid, mp = 192-193 °C, yield 64 mg (77%), R_f 0.51 (1:4, EtOAc/hexanes). ^{1}H NMR (700 MHz, cdcl$_3$) δ 8.22 (d, J = 8.2 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -67.78 (dd, J = 29.6 and 11.3 Hz, 1F), -82.88 (dd, J = 23.0 and 11.3 Hz, 1F), -134.59 (dd, J = 29.6 and 23.0 Hz, 1F); ^{13}C NMR (176 MHz, CdCl$_3$) δ 152.8 – 151.3 (m), 149.3 – 147.6 (m), 142.9, 141.7 – 140 (m), 140.1 (d, $J_{(C,F)}$ = 10.4 Hz), 133.5, 129.3, 119.4, 116.7, and 113.1 – 112.8 (m) ppm. I.R: ν (cm^{-1}) = 3098 (w), 3045 (w), 2959 (w), 2922 (m), 2852 (m), 2237 (m), 1611 (s), 1596 (s). HRMS (CI), $[C_{12}H_4ClF_3N_2O_2S + H]^+$ calcd. 332.9707, found (*m*/*z*) 332.9714.

3-((3-chloro-2,5,6-trifluoropyridin-4-yl)sulfonyl)benzonitrile (8)



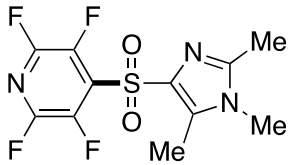
White solid, mp = 118-119 °C, yield 44 mg (53%), R_f 0.28 (1:4, EtOAc/hexanes). ^{1}H NMR (700 MHz, cdcl$_3$) δ 8.42 – 8.23 (m, 2H), 8.03 (d, J = 7.7 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -67.76 (dd, J = 29.9, 11.9 Hz, 1F), -82.83 (dd, J = 23.0, 11.6 Hz, 1F), -134.63 (dd, J = 29.9, 23.0 Hz, 1F); ^{13}C NMR (176 MHz, CdCl$_3$) δ 152.8 – 151.3 (m), 149.3 – 147.6 (m), 141.7 – 140.0 (m), 140.7, 140.1 – 139.9 (m), 138.5, 132.5, 132.2, 131.0, 116.5, 114.8, and 113.1 – 112.8 ppm. I.R: ν (cm^{-1}) = 3057 (w), 2944 (m), 2832 (m), 2238 (w), 1609 (w). HRMS (CI), $[C_{12}H_4ClF_3N_2O_2S]^+$ calcd. 331.9629, found (*m*/*z*) 331.9629.

3-chloro-2,5,6-trifluoro-4-tosylpyridine (9)



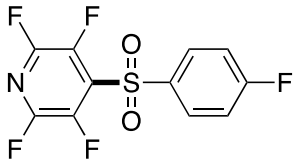
White solid, mp = 181 - 182 °C, yield 68 mg (84%), R_f 0.30 (1.5:8.5, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.98 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 2.48 (s, 3H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -68.98 (dd, J = 29.6, 12.0 Hz), -84.22 (dd, J = 22.6, 12.0 Hz), -135.21 (dd, J = 29.6, 23.1 Hz); ^{13}C NMR (176 MHz, cdcl$_3$) δ 152.6 – 151.2 (m), 149.1 – 147.5 (m), 147.3, 114.8 (d, $J_{(C,F)}$ = 10.2 Hz), 141.6 – 139.8 (m), 136.2, 130.5, 128.7, 112.8 – 112.6 (m), and 22.0 ppm. I.R: ν(cm^{-1})= 3093 (w), 3071 (w), 2961 (m), 2925 (m), 2851 (m). HRMS (CI), $[C_{12}H_7ClF_3NO_2S + H]^+$ calcd. 321.9911, found (*m*/*z*) 321.9904.

2,3,5,6-tetrafluoro-4-((1,2,5-trimethyl-1*H*-imidazol-4-yl)sulfonyl)pyridine (10)



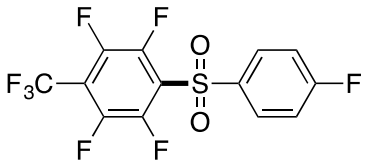
White solid, mp = 157-158 °C, yield 66 mg (82%), R_f 0.11 (2:3, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ ^{1}H NMR (500 MHz, cdcl$_3$) δ 3.75 (s, 1H), 2.53 (s, 1H), 2.36 (s, 1H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -86.4 – -86.5 (m, 2F), -138.4 – -138.6 (m, 2F); ^{13}C NMR (126 MHz, cdcl$_3$) δ 149.5, 145.2 (d, $J_{(C,F)}$ = 17.3 Hz), 145.0, 143.1 (dt, $J_{(C,F)}$ = 17.3 and 7.7 Hz), 139.8 (dd, $J_{(C,F)}$ = 27.8 and 7.7 Hz), 137.7 (dd, $J_{(C,F)}$ = 36.5 and 7.7 Hz), 134.4 (dd, $J_{(C,F)}$ = 17.3 and 7.7 Hz), 115.1, 36.7, 12.9, 10.7 ppm. IR: ν(cm^{-1}) = 2948 (w), 1643 (m), 1526 (w). HRMS (CI), $[C_{11}H_9F_4N_3O_2S + H]^+$ calcd. 324.0424, found (*m*/*z*) 324.0412.

2,3,5,6-tetrafluoro-4-((4-fluorophenyl)sulfonyl)pyridine (11)



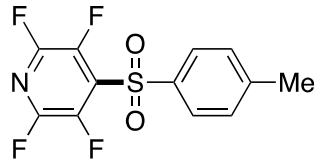
White solid, mp = 171 - 172 °C, yield 69 mg (89%), R_f 0.35 (1:9, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 8.15 (dd, J = 8.5 and 5.5 Hz, 2H), 7.31 (dd, J = 8.5 and 5.5 Hz, 2H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -85.40 – -85.56 (m, 2F), -99.00 – -99.06 (m, 1F), -137.02 – -137.19 (m, 2F); ^{13}C NMR (126 MHz, cdcl$_3$) δ 167.2 (d, $J_{(C,F)}$ = 260 Hz), 145.4 – 143.3 (m), 140.0 – 137.5 (m), 135.3, 131.1 – 131.8 (m), 131.9 (d, $J_{(C,F)}$ = 9.6 Hz), 117.6 (d, $J_{(C,F)}$ = 22.2 Hz). I.R: ν (cm^{-1}) = 3115 (w), 1633 (w), 1590 (m). HRMS (CI), $[C_{11}H_4F_5NO_2S + H]^+$ calcd. 309.9961, found (*m*/*z*) 309.9982.

1,2,4,5-tetrafluoro-3-((4-fluorophenyl)sulfonyl)-6-(trifluoromethyl)benzene (12)



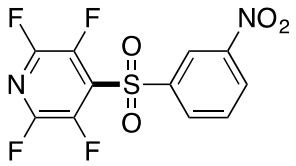
White solid, mp = 132-133 °C, yield 61 mg (65%), R_f 0.56 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 8.13 (dd, J = 8.5 and 5.0 Hz, 2H), 7.30 (dd, J = 8.5 and 0.5 Hz, 2H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -56.8 – -57.0 (m, 3F), -133.9 – -134.0 (m, 2F), -136.3 – -136.4 (m, 2F); ^{13}C NMR (176 MHz, cdcl$_3$) δ 167.7, 166.2, 145.4 -14.4 (m), 136.1, 131.5 (d, $J_{(C,F)}$ = 9.9 Hz), 125.2 (t, $J_{(C,F)}$ = 14.1 Hz), 120.(q, $J_{(C,F)}$ = 275 Hz), 117.4 (d, $J_{(C,F)}$= 23 Hz), 114.8 – 114.3 (m). IR: ν(cm^{-1}) = 3114 (w), 2958 (w), 2922 (m), 2854 (m). HRMS (CI), $[C_{13}H_4F_8O_2S + H]^+$ calcd. 376.9883, found (*m*/*z*) 376.9877.

2,3,5,6-tetrafluoro-4-tosylpyridine (13)



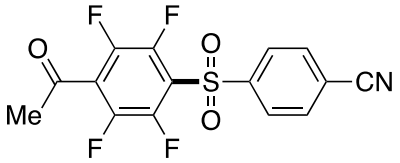
White solid, mp = 183 - 184 °C, yield 70 mg (92%), R_f 0.38 (1:9, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.99 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 2.48 (s, 3H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -85.9 4– -86.03 (m, 2F), -137.10 – -137.25 (m, 2F). ^{13}C NMR (101 MHz, cdcl$_3$) δ 147.5, 145.7 – 144.4 (m), 140.3 – 137.2 (m), 136.4, 133.6 (t, $J_{(C,F)}$ = 17.4 Hz), 130.7, 128.7, and 22.0 ppm. HRMS (CI), $[C_{12}H_7F_4NO_2S + H]^+$ calcd. 306.0212, found (*m*/*z*) 306.0209.

2,3,5,6-tetrafluoro-4-((3-nitrophenyl)sulfonyl)pyridine (14)



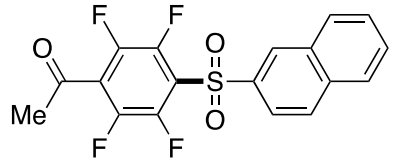
White solid, mp = 127-128 °C, yield 48 mg (57%), R_f 0.19 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 8.92 (s, 1H), 8.62 (d, J = 8.2 Hz, 1H), 8.45 (d, J = 7.8 Hz, 1H), 7.91 (t, J = 8.0 Hz, 1H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -84.4 – -84.6 (m, 2F), -136.3 – -136.5 (m, 2F); ^{13}C NMR (126 MHz, cdcl$_3$) δ 148.8, 145.4 (d, $J_{(C,F)}$ = 13.9 Hz), 143.4 (d, $J_{(C,F)}$= 13.9 Hz), 141.3, 139.7 (d, $J_{(C,F)}$= 36.5 Hz), 137.7 (d, $J_{(C,F)}$= 36.5 Hz),134.1, 131.6, 130.2, and 124.1 ppm. IR: ν(cm^{-1}) = 3096 (m), 3052 (w), 2956 (w), 2926 (m), 2875 (w), 2855 (m), 1542 (s), 1352 (s). HRMS (CI), $[C_{11}H_4F_4N_2O_4S + H]^+$ calcd. 336.9901, found (*m*/*z*) 336.9891.

4-((4-acetyl-2,3,5,6-tetrafluorophenyl)sulfonyl)benzonitrile (15)



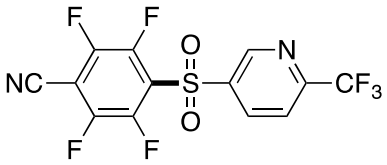
White solid, mp = 184-185 °C, yield 45 mg (50%), R_f 0.44 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H), 2.61 (s, 3H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -130.8 (d, $J_{(C,F)}$ = 9.4 Hz, 2F), -134.8 (d, $J_{(C,F)}$ = 9.4 Hz, 2F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 145.3 (d, $J_{(C,F)}$ = 16.2 Hz), 144.2, 143.2 (d, $J_{(C,F)}$ = 16.2 Hz), 133.5, 129.0, 125.0, 122.1, 118.9, 116.8, and 32.4 ppm. I.R: ν (cm^{-1}) = 3105 (m), 3048 (w), 2958 (w), 2926 (m), 2855 (w), 2236 (m), 1938 (w), 1714 (s). HRMS (CI), $[C_{15}H_7F_4NO_3S + H]^+$ calcd. 358.0156, found (*m*/*z*) 358.0142.

1-(2,3,5,6-tetrafluoro-4-(naphthalen-2-ylsulfonyl)phenyl)ethan-1-one (16)



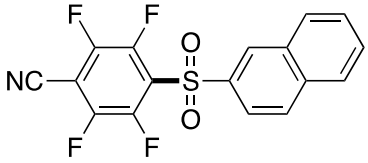
White solid, mp = 145-146 °C, yield 71 mg (74%), R_f 0.42 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 8.69 (s, 1H), 8.05 (d, J = 8.5 Hz, 1H), 8.02 – 8.00 (m, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.72 (dd, J = 8.0 and 0.5 Hz. 1H), 7.67 (dd, J = 8.0 and 0.5 Hz, 1H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -134.4 – -134.6 (m, 2F), -138.8 – -138.9 (m, 2F); ^{13}C NMR (126 MHz, cdcl$_3$) δ 190.8, 145.2 (d, $J_{(C,F)}$ = 15.4 Hz), 144.9 (d, $J_{(C,F)}$ = 15.4 Hz), 143.1 (d, $J_{(C,F)}$ = 18.3 Hz), 142.8 (d, $J_{(C,F)}$ = 15.4 Hz), 137.2, 136.0, 132.2, 130.5, 130.3, 130.2, 129.9, 128.8, 124.0, 123.5, 122.2, and 32.3 ppm. I.R: ν (cm^{-1}) = 3077 (w), 3056 (w), 2962 (w), 2929 (m), 2851 (w), 1714 (s), 1626 (m), 1589 (m). HRMS (CI), $[C_{18}H_{10}F_4O_3S + H]^+$ calcd. 383.0360, found (*m*/*z*) 383.0367.

2,3,5,6-tetrafluoro-4-((6-(trifluoromethyl)pyridin-3-yl)sulfonyl)benzonitrile (17)



White solid, mp = 127-128 °C, yield 69 mg (72%), R_f 0.55 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.58 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -68.4 (s, 3F), -127.2 – -127.3 (m, 2F), -132.4 – -132.5 (m, 2F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8 (q, $J_{(C,F)}$ = 36.3 Hz), 149.7, 148.8 (dd, $J_{(C,F)}$ = 16.4 and 6.0 Hz), 146.7 (dd, $J_{(C,F)}$ = 17.9 and 4.2 Hz), 145.3 (dd, $J_{(C,F)}$ = 17.9 and 4.2 Hz), 143.2 – 143.1 (m), 139.0, 138.3, 125.5 - 125.3 (m), 121.6, 121.5, 119.4, and 100.2 ppm. I.R: ν (cm^{-1}) = 3104 (w), 3058 (w), 3028 (w), 2922 (m), 2844 (w), 2251 (m), 1584 (m), 1572 (m). HRMS (CI), $[C_{13}H_3F_7N_2O_2S + H]^+$ calcd. 384.9876, found (*m*/*z*) 384.9883.

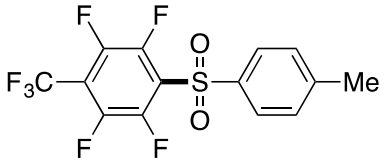
2,3,5,6-tetrafluoro-4-(naphthalen-2-ylsulfonyl)benzonitrile (18)



White solid, mp = 184 - 185 °C, yield 86 mg (94%), R_f 0.48 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 8.70 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H),7.99 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.73 – 7.69 (m, 1H); ^{19}F NMR (470 MHz, cdcl$_3$) δ –128.5 (dd, J = 21.6 and13.2 Hz, 2F), –132.8 (dd, J = 21.6 and13.2 Hz, 2F); ^{13}C NMR (126 MHz, cdcl$_3$) δ 148.6 (d, $J_{(C,F)}$ = 16.2 Hz), 146.5 (d, $J_{(C,F)}$ = 16.2 Hz), 145.2 (d, $J_{(C,F)}$ = 8.9 Hz), 143.1 (d, $J_{(C,F)}$ = 8.9 Hz), 136.5, 136.2, 132.2, 131.0, 130.6, 130.5, 130.0, 128.5, 128.3, 122.1, and

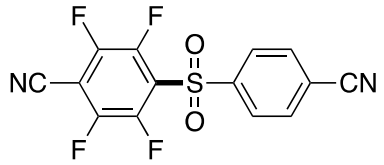
106.3 ppm. I.R: ν (cm^{-1}) = 3171 (w), 2924 (w), 2239 (m), 1619 (m). HRMS (CI), $[C_{17}H_7F_4NO_2S]^+$ calcd. 366.0206, found (*m*/*z*) 366.0191.

1,2,4,5-tetrafluoro-3-tosyl-6-(trifluoromethyl)benzene (19)



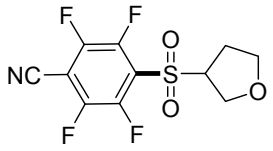
White solid, mp = 159-160 °C, yield 76 mg (82%), R_f 0.44 (1:4, EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.88 (t, *J* = 23.3 Hz, 3F), -134.05 – -134.14 (m, 2F), -136.69 – -136.81 (m, 2F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 145.6-145.5 (m), 143.3-142.8 (m), 137.1, 130.5, 128.4, 125.7 (t, $J_{(C,F)}$ = 14.3 Hz), 120.2 (q, $J_{(C,F)}$ = 277 Hz), 116.0 – 113.4 (m), and 21.9 ppm. HRMS (CI), $[C_{14}H_7F_7O_2S]^+$ calcd. 373.0128, found (*m*/*z*) 373.0114.

4-((4-cyanophenyl)sulfonyl)-2,3,5,6-tetrafluorobenzonitrile (20)



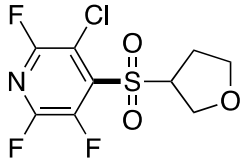
Yellow solid, mp = 229-230 °C, yield 61 mg (72%), R_f 0.47 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, dmso) δ 8.25 (d, *J* = 8.6 Hz, 2H), 8.21 (d, *J* = 8.6 Hz, 2H); ^{19}F NMR (470 MHz, $cdcl_3$) δ -128.65 – -129.06 (m), -133.52 (td, *J* = 13.8, 5.0 Hz); ^{13}C NMR (126 MHz, dmso) δ 148.4 (d, $J_{(C,F)}$ = 16.9 Hz), 146.3 (d, $J_{(C,F)}$ = 20.0 Hz), 144.7 (d, $J_{(C,F)}$ = 14.7 Hz), 142.8, 142.6 (d, $J_{(C,F)}$ = 16.4 Hz), 134.2, 128.6, 117.9, 117.2, and 107.2 ppm. I.R: ν (cm^{-1}) = 3098 (w), 3044 (w), 2960 (w), 2923 (m), 2853 (m), 2237 (m), 1610 (s), 1595 (s). HRMS (CI), $[C_{14}H_4F_4N_2O_2S + H]^+$ calcd. 341.0002, found (*m*/*z*) 341.0011.

2,3,5,6-tetrafluoro-4-((tetrahydrofuran-3-yl)sulfonyl)benzonitrile (21)



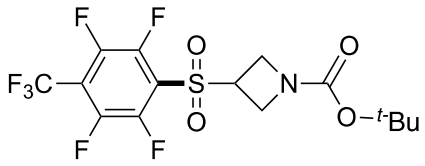
White solid, mp = 133 - 134 °C, yield 60 mg (77%), *R*f 0.38 (1:4, EtOAc/hexanes). ^{1}H NMR (700 MHz, cdcl$_3$) δ 4.39 – 4.28 (m, 1H), 4.03 (ddd, *J* = 23.3, 13.2, 5.6 Hz, 3H), 3.85 (dd, *J* = 14.7, 7.5 Hz, 1H), 2.53 – 2.26 (m, 2H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -127.63 (dq, *J* = 12.2, 7.0 Hz, 2F), -131.93 (dq, *J* = 12.2, 7.0 Hz, 2F); ^{13}C NMR (176 MHz, cdcl$_3$) δ 148.5 – 146.8 (m), 145.6 – 144.0 (m), 124.0 (t, $J_{(C,F)}$ = 16 Hz), 106.1, 99.8 (t, $J_{(C,F)}$ = 16 Hz), 68.4, 66.9, 66.2, and 27.3 ppm. I.R: ν (cm^{-1}) = 2986 (w, 2886 (w), 2247 (w), 1468 (s). HRMS (CI), $[C_{11}H_7F_4NO_3S + Na]^+$ calcd. 331.9975, found (*m*/*z*) 331.9974.

3-chloro-2,5,6-trifluoro-4-((tetrahydrofuran-3-yl)sulfonyl)pyridine (22)



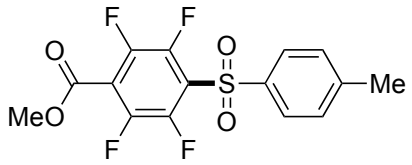
Yellow solid, mp = 128-129 °C, yield 54 mg (71%), R_f 0.14 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 4.33 (dd, *J* = 10.3, 4.7 Hz, 1H), 4.24 – 4.13 (m, 1H), 4.12 – 3.97 (m, 2H), 3.89 (dd, *J* = 14.2, 7.7 Hz, 1H), 2.50 (dt, *J* = 12.8, 5.6 Hz, 1H), 2.28 (ddt, *J* = 13.7, 9.4, 7.0 Hz, 1H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -67.8 (dd, $J_{(C,F)}$ = 29.6 and 11.7 Hz, 1F), -82.9 (dd, $J_{(C,F)}$ = 23.0 and 11.7 Hz, 1F), -135.0 (dd, $J_{(C,F)}$ = 30.0 and 23.0 Hz, 1F); ^{13}C NMR (176 MHz, cdcl$_3$) δ 152.9 – 151.4 (m), 149.3 – 147.7 (m), 142.2 – 140.4 (m), 139.0 (d, $J_{(C,F)}$ = 11 Hz), 113.6 – 113.3 (m), 68.4, 66.8, 64.7, 27.3 ppm. IR: ν(cm^{-1}) = 2966 (m), 2902 (m) 2494 (w), 1715 (m), 1612 (s). HRMS (CI), $[C_9H_7ClF_3NO_3S + H]^+$ calcd. 301.9860, found (*m*/*z*) 301.9861.

***tert*-tutyl 3-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)sulfonyl)azetidine-1-carboxylate (23)**



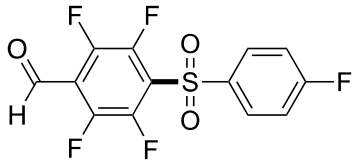
White solid, mp = 152 - 153 °C, yield 85 mg (78%), R_f 0.53 (2:3, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 4.40 – 4.37 (m, 2H), 4.36 – 4.31 (m, 1H), 4.30 – 4.22 (m, 2H), 1.45 (s, 9H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -56.87 (t, J = 21.2 Hz, 3F), -133.26 – -133.33 (m, 2F), -135.07 – -135.23 (m, 2F); ^{13}C NMR (126 MHz, cdcl$_3$) δ 155.6, 145.8 (d, $J_{(C,F)}$ = 14.5 Hz), 143.7 (d, $J_{(C,F)}$ = 15.4 Hz), 121.8 – 121.6 (m), 120.0 (t, $J_{(C,F)}$ = 278 Hz), 115.6 – 115.2 (m), 81.2, 55.4, 49.2, and 28.4 ppm. I.R: ν (cm^{-1}) = 2984 (w), 2895 (w), 1708 (m), 1606 (w). HRMS (CI), [$C_{15}H_{14}F_7NO_4S$ + H - boc]$^+$ calcd. 337.0007, found (*m*/*z*) 336.9998. MALDI-TOF ($C_{15}H_{14}F_7NO_4S$ + Na) calcd. 460.0429, found 460.0459.

1-(2,3,5,6-tetrafluoro-4-tosylphenyl)ethan-1-one (24)



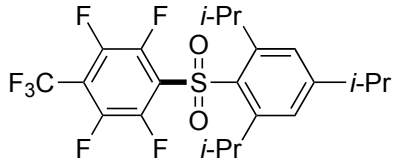
White solid, mp = 141–142 °C, yield 62 mg (69%), R_f 0.40 (1:4, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 3.98 (s, 3H), 2.46 (s, 3H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -135.13 – -135.05 (m, 2F), -136.29 – -136.39 (m, 2F); ^{13}C NMR (176 MHz, cdcl$_3$) δ 159.0, 146.7 – 145.5 (m), 137.6, 130.4 (d, $J_{(C,F)}$ = 40 Hz), 128.4, 126.2, 124.2, 117.1 (t, $J_{(C,F)}$ = 17 Hz), 53.9, and 22.0 ppm. I.R: ν (cm^{-1}) = 3091 (w), 3070 (w), 2964 (m), 2920 (m), 2851 (m), 1741 (s), 1598 (m). HRMS (CI), [$C_{15}H_{10}F_4O_4S$ + Na]$^+$ calcd. 385.0134, found (*m*/*z*) 385.0141.

2,3,5,6-tetrafluoro-4-((4-fluorophenyl)sulfonyl)benzaldehyde (25)



Cream white solid, mp = 111–112 °C, yield 59 mg (70%), R_f 0.28 (3:7, EtOAc/hexanes). ^{1}H NMR (400 MHz, cdcl$_3$) δ 10.28 (s, 1H), 8.13 (dd, J = 7.6 and 5.6 Hz, 2H), 7.30 (t, J = 8.8 Hz); ^{19}F NMR (376 MHz, cdcl$_3$) δ -99.83 (d, J = 5.6 Hz, 1F), -134.98 (m, -134.94 – -135.02, 2F), -141.71 (m, -141.66 – -141.75, 2 F); ^{13}C NMR (176 MHz, cdcl$_3$) δ 181.4, 167.6, 166.1, 147.6-143.3 (m), 136.1 (d, $J_{(C,F)}$ = 4.0 Hz), 131.5 (d, $J_{(C,F)}$ = 10.2 Hz), 126.0 (dd, $J_{(C,F)}$ = 15.0, 4.0 Hz), 118.4 (dd, $J_{(C,F)}$ = 1.7, 1.1 Hz), 117.4 (dd, $J_{(C,F)}$ = 23.2, 1.1 Hz). I.R: ν (cm^{-1}) = 3114 (w), 2957 (w), 2924 (m), 2892 (w), 2875 (w), 2854 (w), 2770 (w), 1910 (w), 1717 (s), 1641 (w), 1589 (s). MALDI-TOF 335.973 (Calcd. m/z 335.983).

1,2,4,5-tetrafluoro-3-(trifluoromethyl)-6-((2,4,6-triisopropylphenyl)sulfonyl)benzene (26)



White solid, yield 87 mg (72%), R_f 0.32 (15:85, EtOAc/hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 6.91 (s, 2H), 3.56 – 3.51 (m, 2H), 2.95 – 2.79 (m, 1H), 1.20-1.19 (m, 6H), 1.11 – 0.99 (m, 12H); ^{19}F NMR (470 MHz, cdcl$_3$) δ -56.03 (dd, J = 21.6 and 6.6 Hz, 3F), -136.32 (d, J = 9.8 Hz, 2F), -141.08 (d, J = 9.8 Hz, 2F). MALDI-TOF 484.133 (Calcd. m/z 484.130).

12. References

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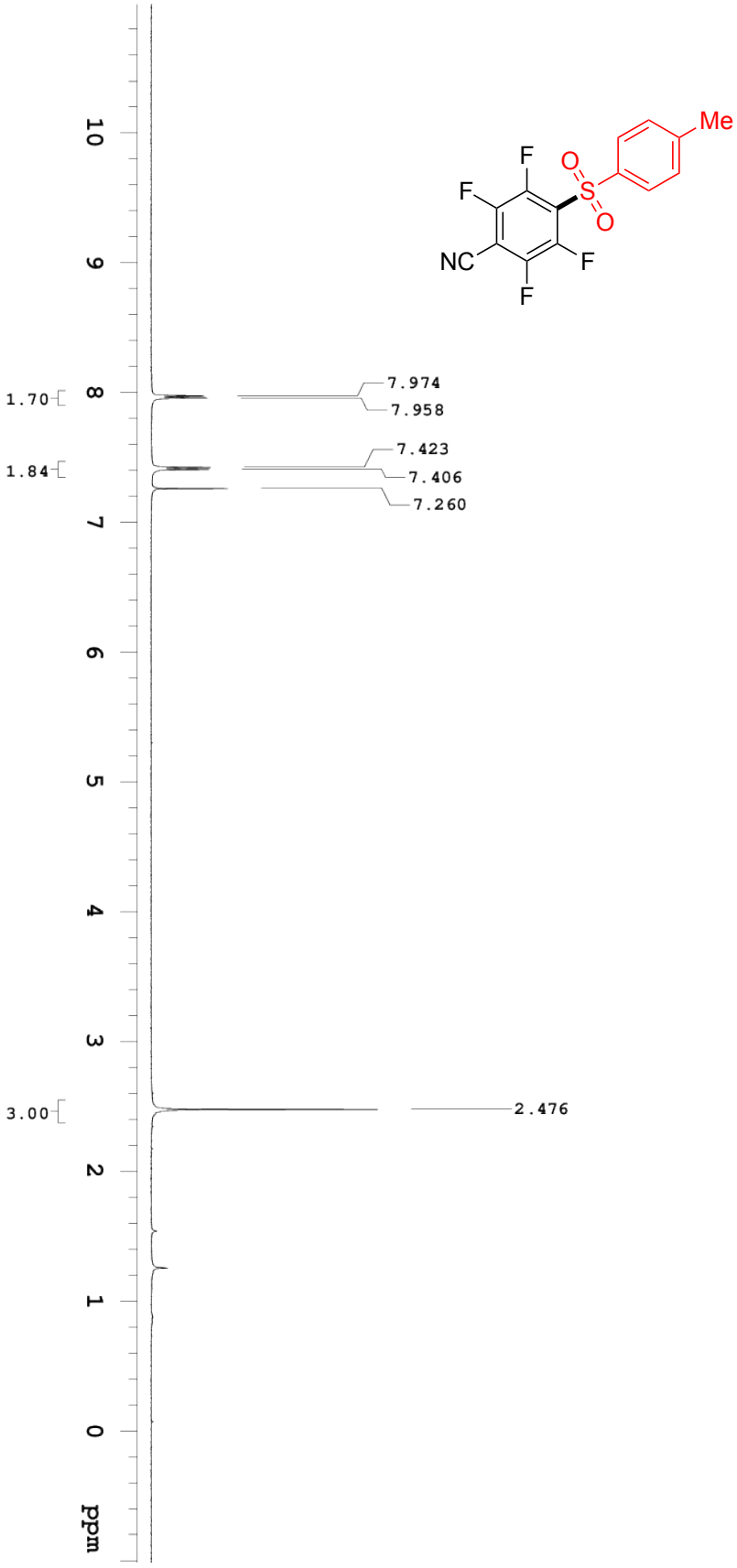
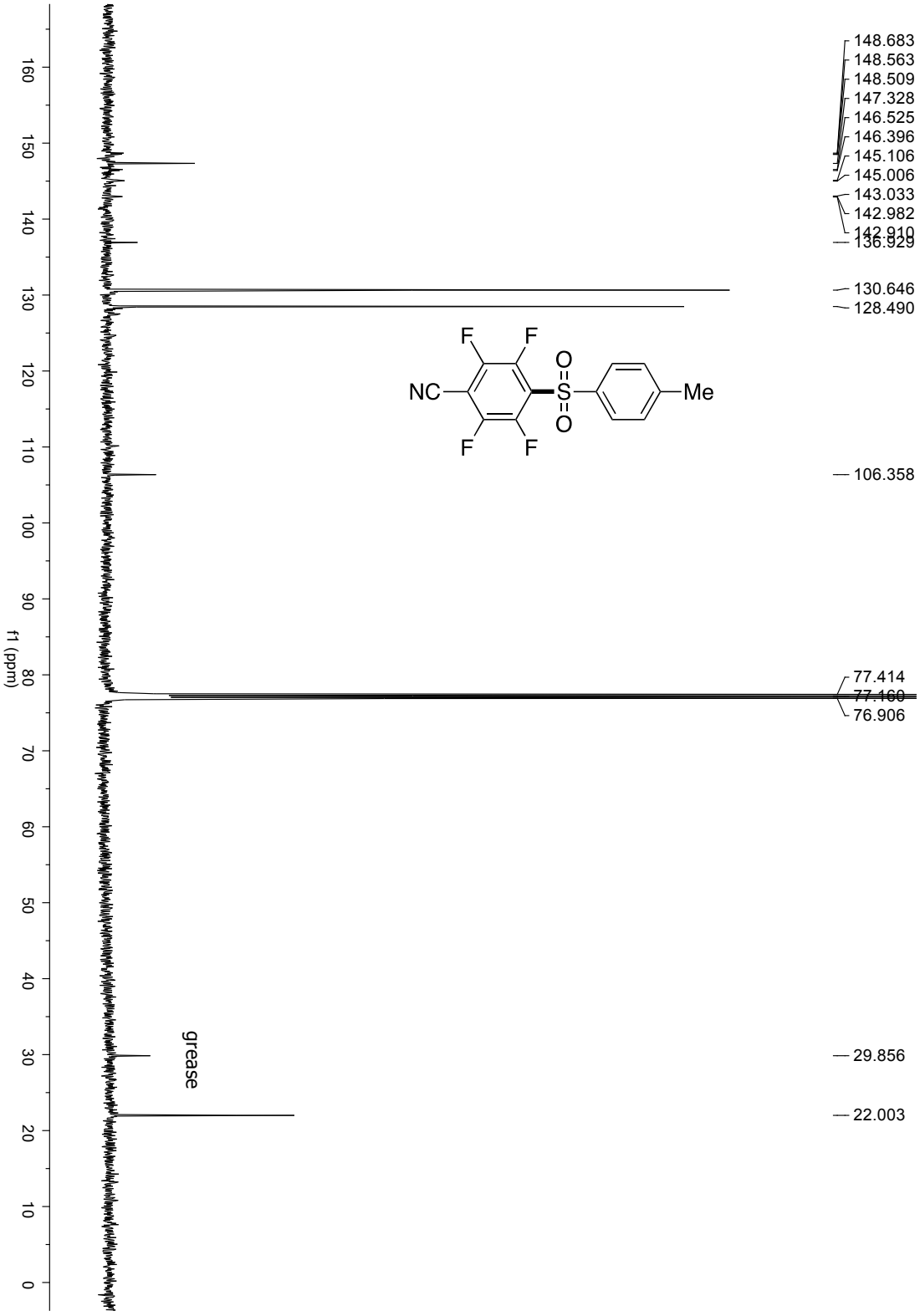
13. ^{1}H, ^{13}C, and ^{19}F NMR Spectra


Me
F
O
S
O
F
NC
F
F
7.974
7.958
7.423
7.406
7.260
2.476
1.70
1.84
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm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148.563
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145.106
145.006
143.033
142.982
142.910
136.929
130.646
128.490
106.358
77.414
77.160
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29.856
22.003
grease
f1 (ppm)
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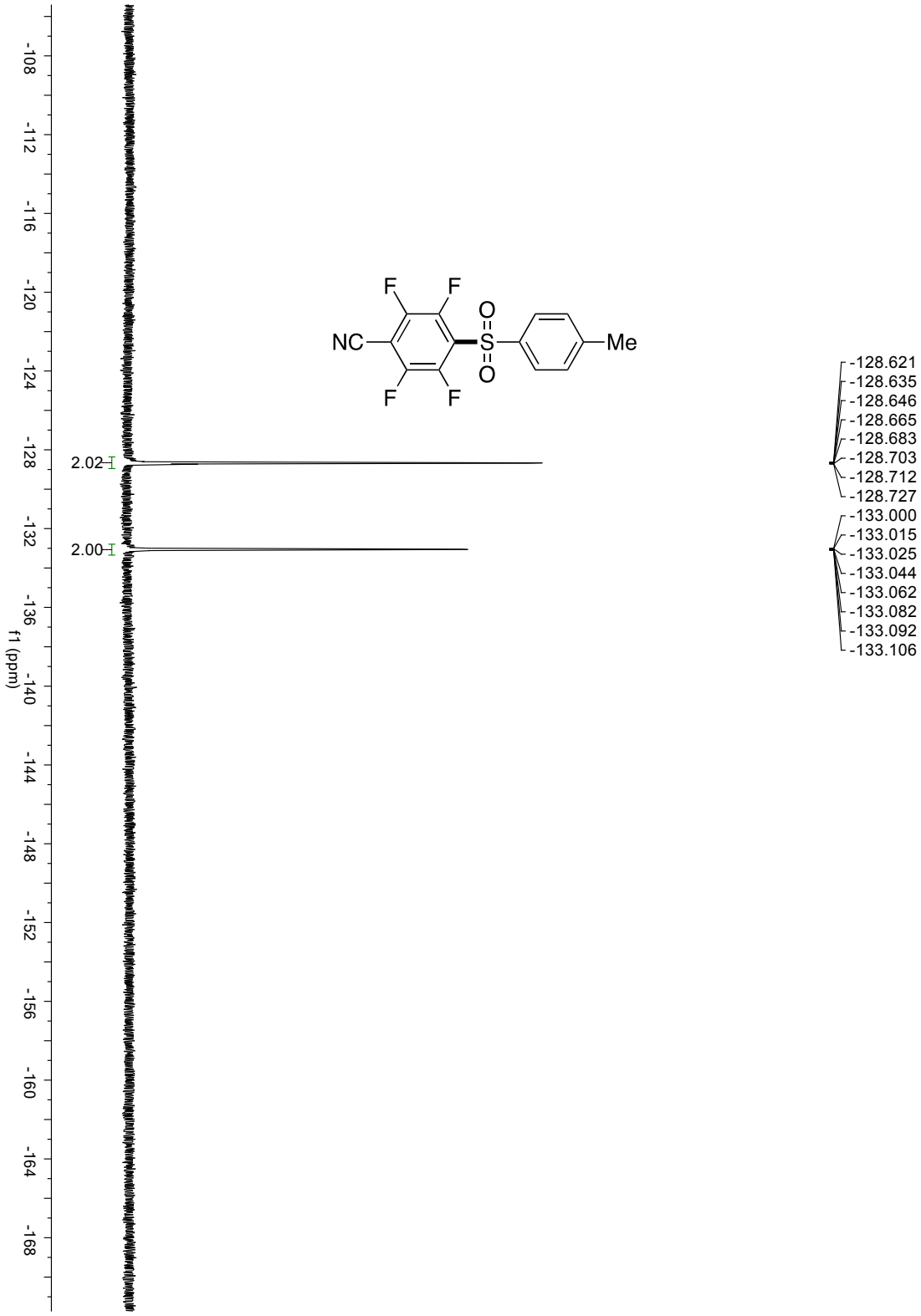
F
O
NC
S
Me
O
F
F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-112
-116
-120
-124
-128
-132
-136
-140
-144
-148
-152
-156
-160
-164
-168
f1 (ppm)
2.02
2.00
F
F
O
NC
S
Me
O
F
F
-128.621
-128.635
-128.646
-128.665
-128.683
-128.703
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-133.025
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-133.062
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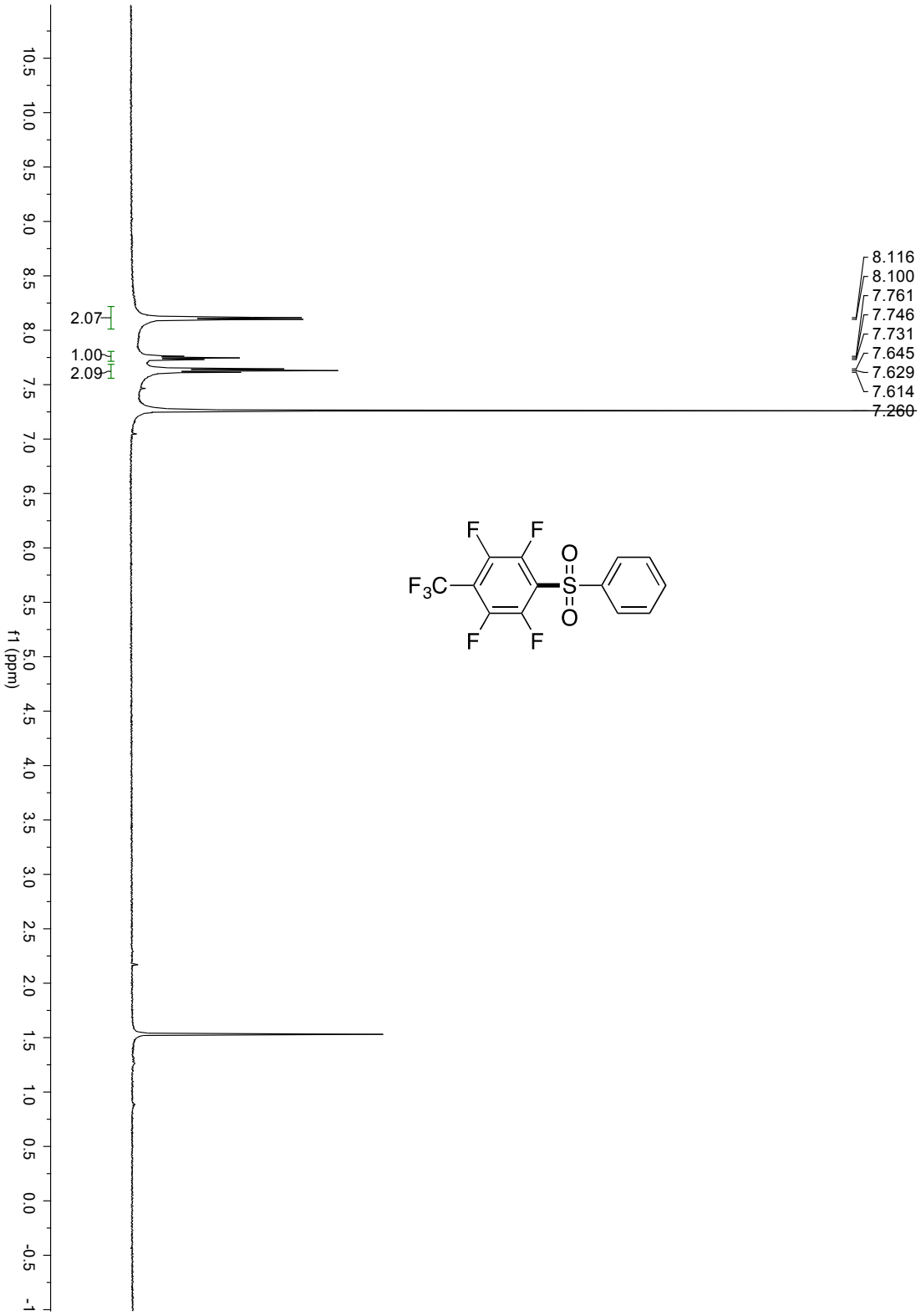
-133.106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8.100
7.761
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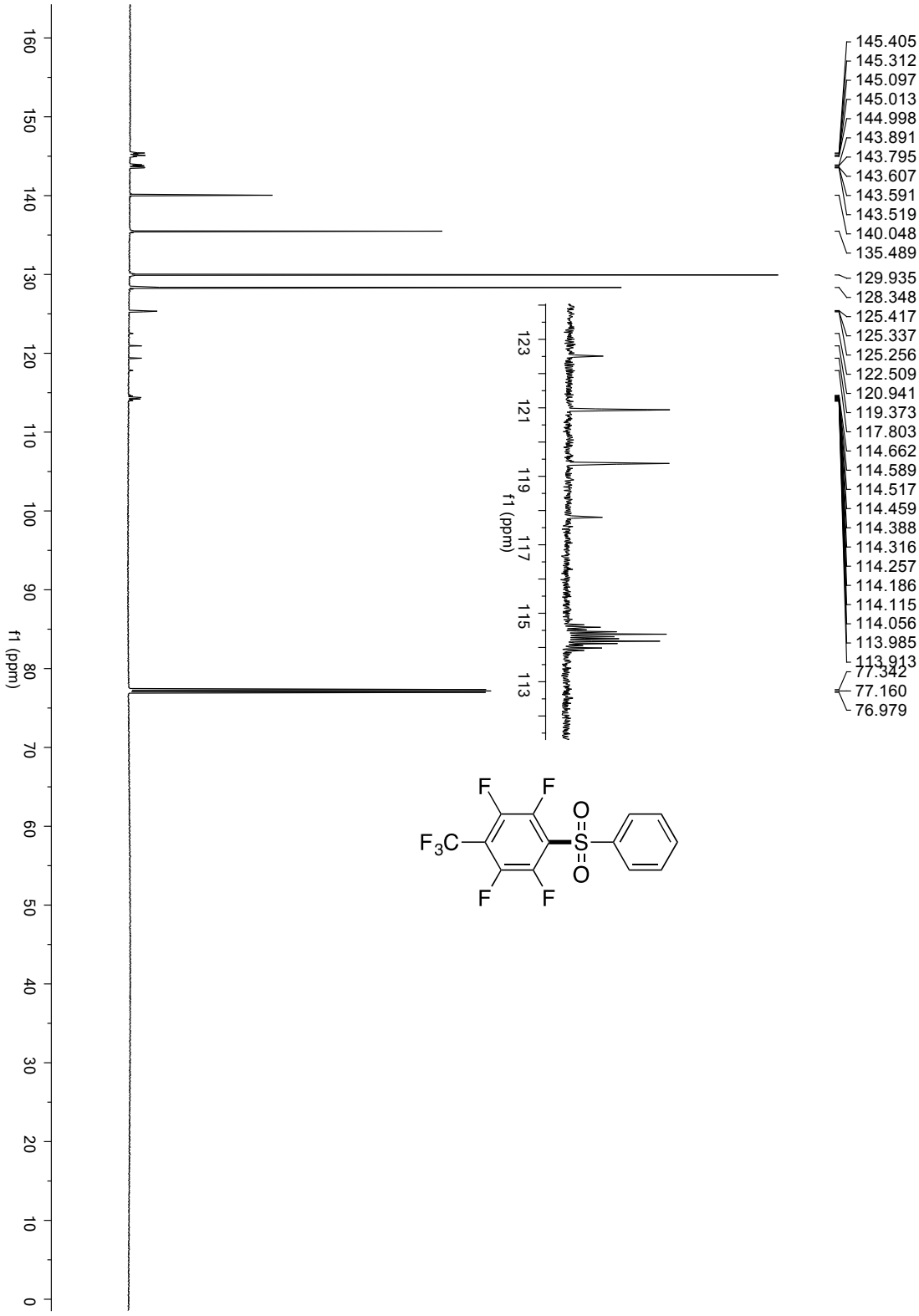
7.731
7.645
7.629
7.614
7.260
2.07
1.00
2.09
F
F
O
S
O
F3C
F
F
f1 (ppm)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145.312
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143.607
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143.519
140.048
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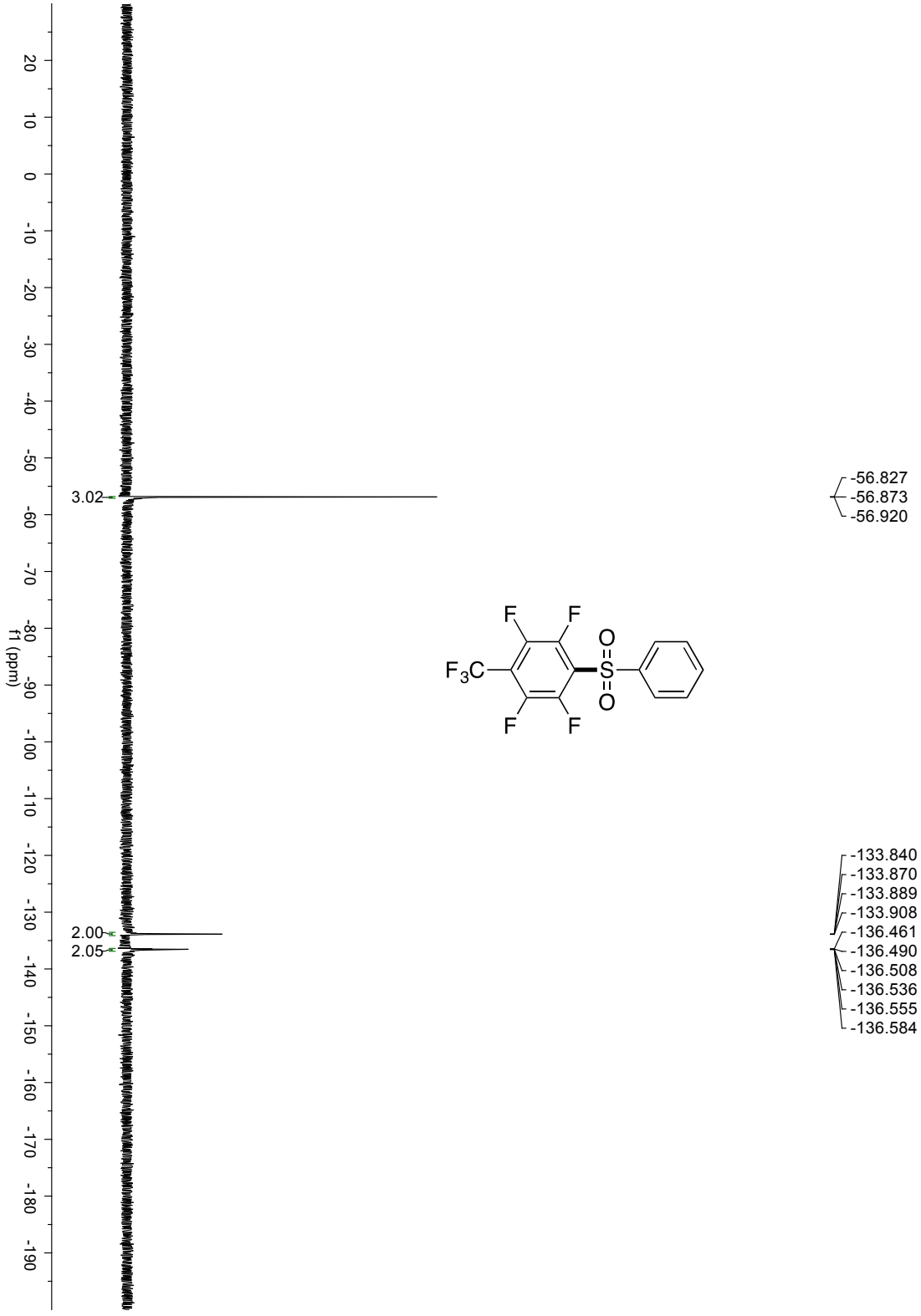
129.935
128.348
125.417
125.337
125.256
122.509
120.941
119.373
117.803
114.662
114.589
114.517
114.459
114.388
114.316
114.257
114.186
114.115
114.056
113.985
113.913
77.342
77.160
76.979
f1 (ppm)
F
F
O
S
O
F3C
F
F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-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)
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2.00
2.05
-56.827
-56.873
-56.920
-133.840
-133.870
-133.889
-133.908
-136.461
-136.490
-136.508
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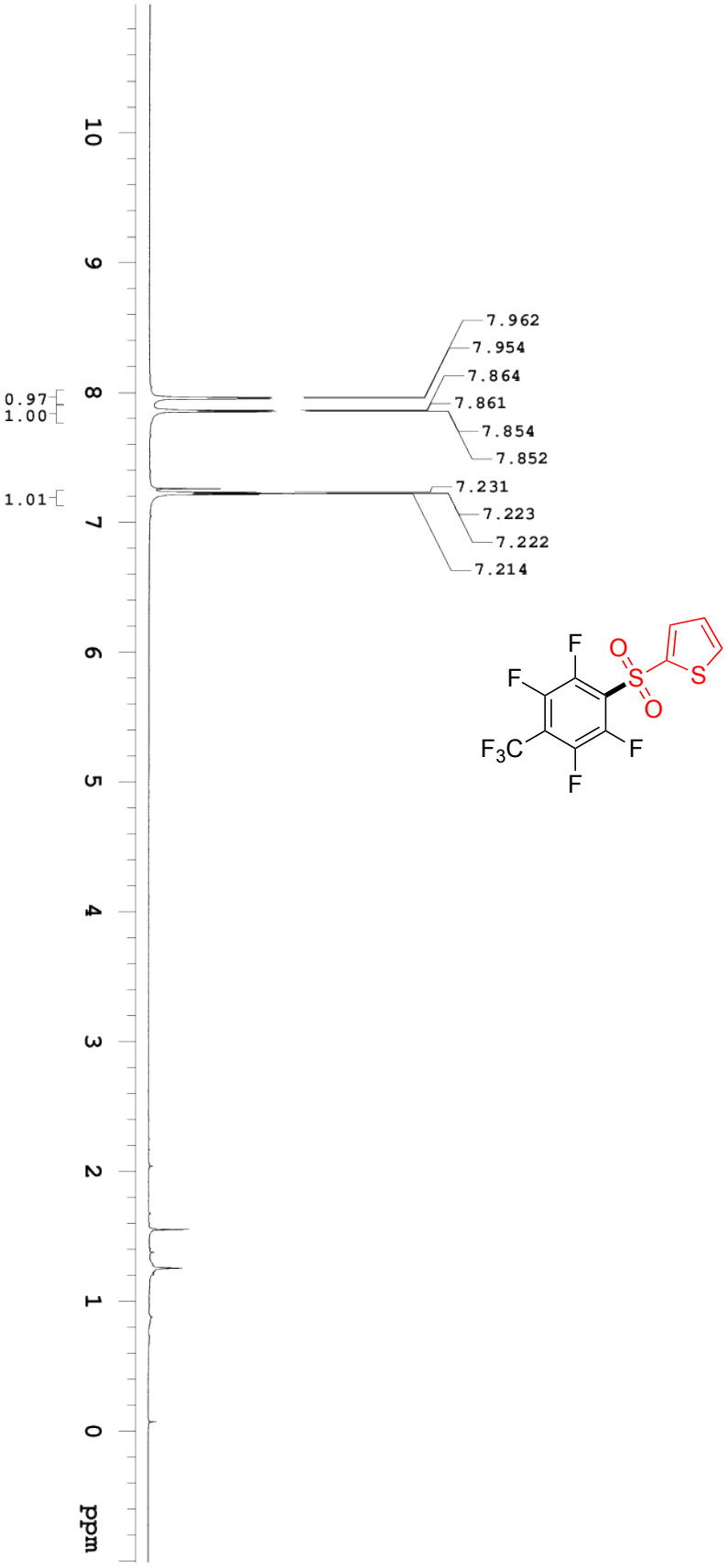
-136.555
-136.584
F
F
F3C
O
S
O
F
F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7.864
7.861
7.854
7.852
7.231
7.223
7.222
7.214
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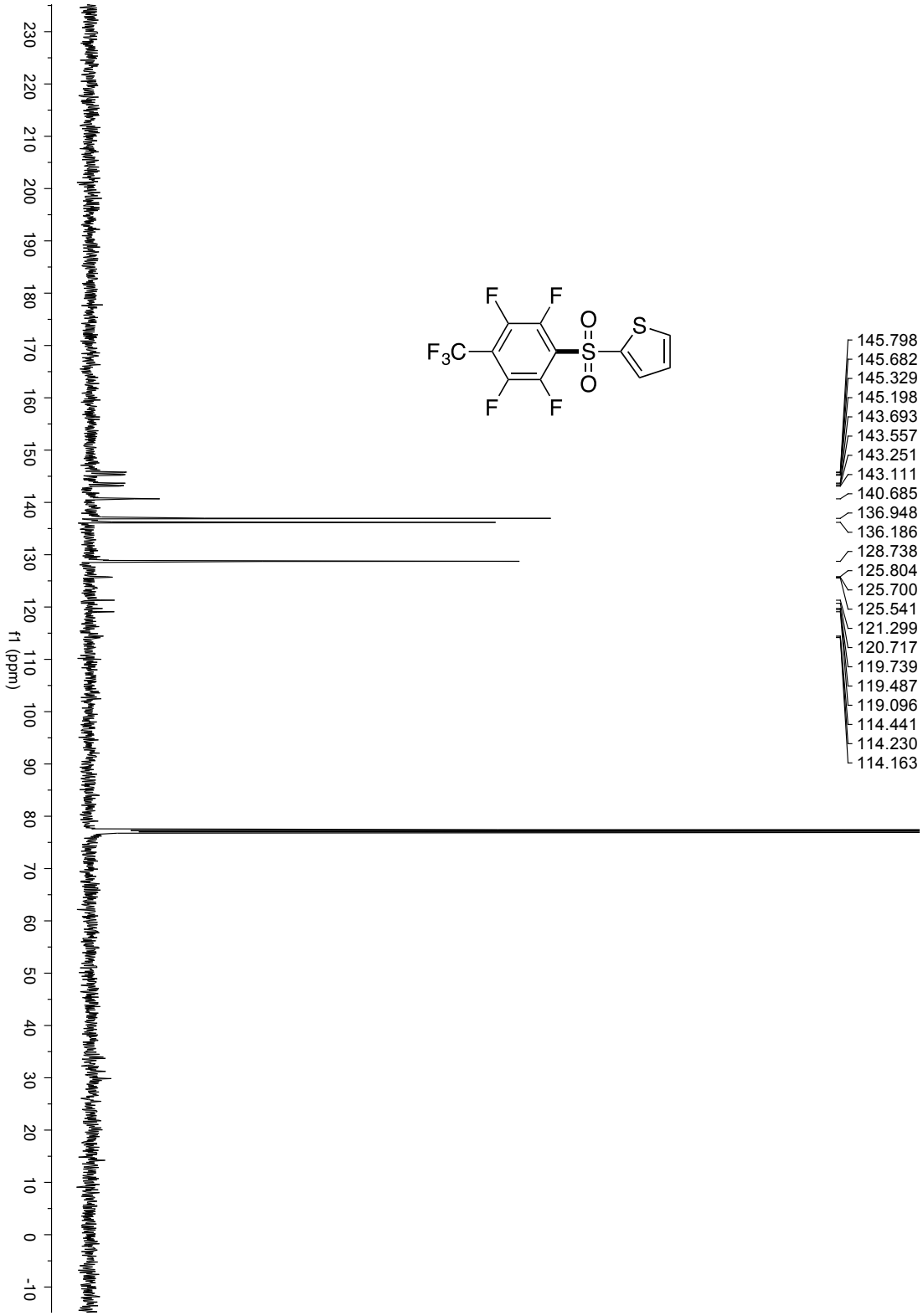
1.00
1.01
10
9
8
7
6
5
4
3
2
1
0
ppm
F
F
O
S
O
S
F3C
F
F


F
F
O
S
S
F3C
O
F
F
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145.198
143.693
143.557
143.251
143.111
140.685
136.948
136.186
128.738
125.804
125.700
125.541
121.299
120.717
119.739
119.487
119.096
114.441
114.230
114.163
f1 (ppm)
230
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210
200
190
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140
130
120
110
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60
50
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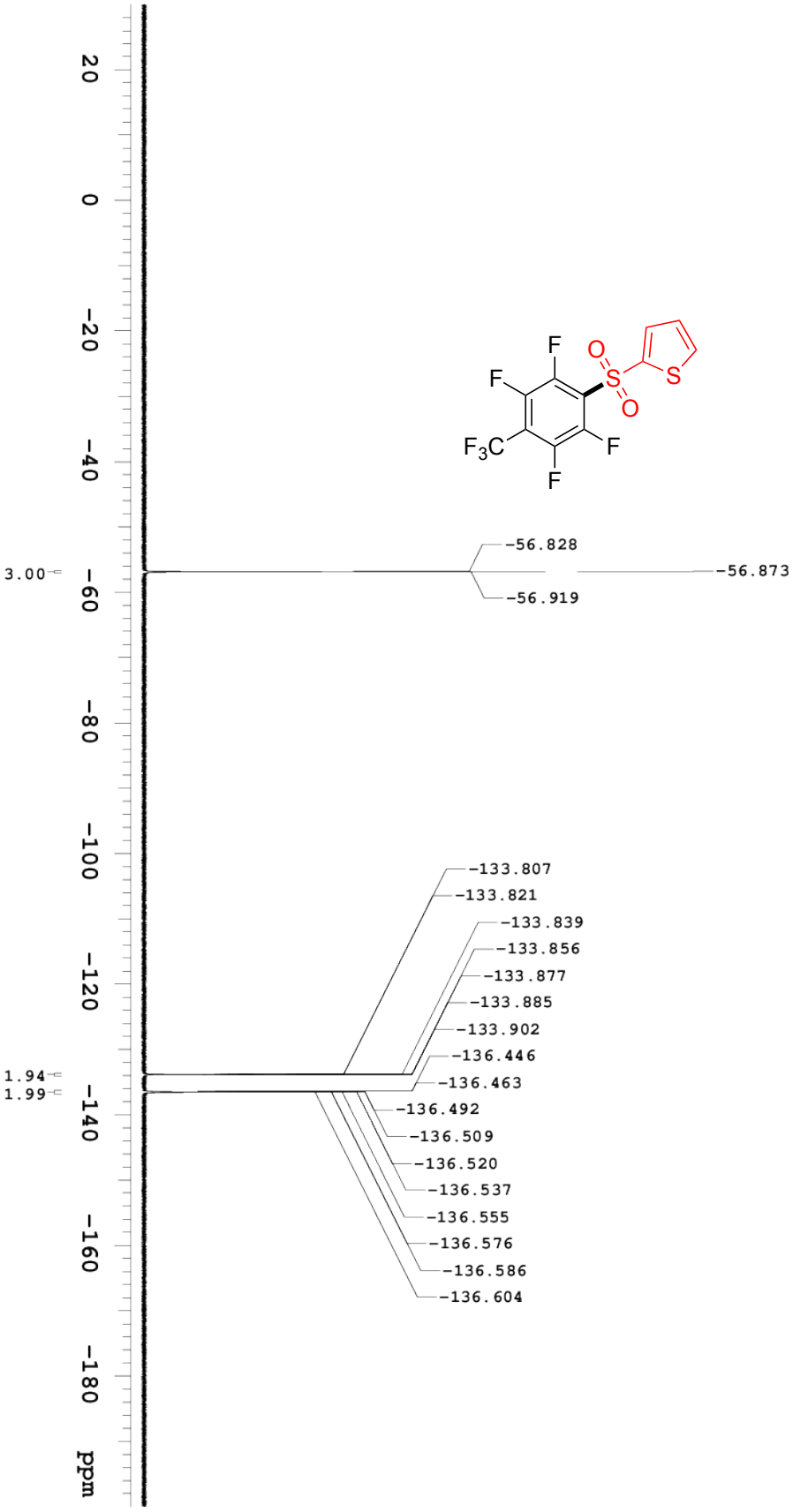
30
20
10
0
-10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F3C
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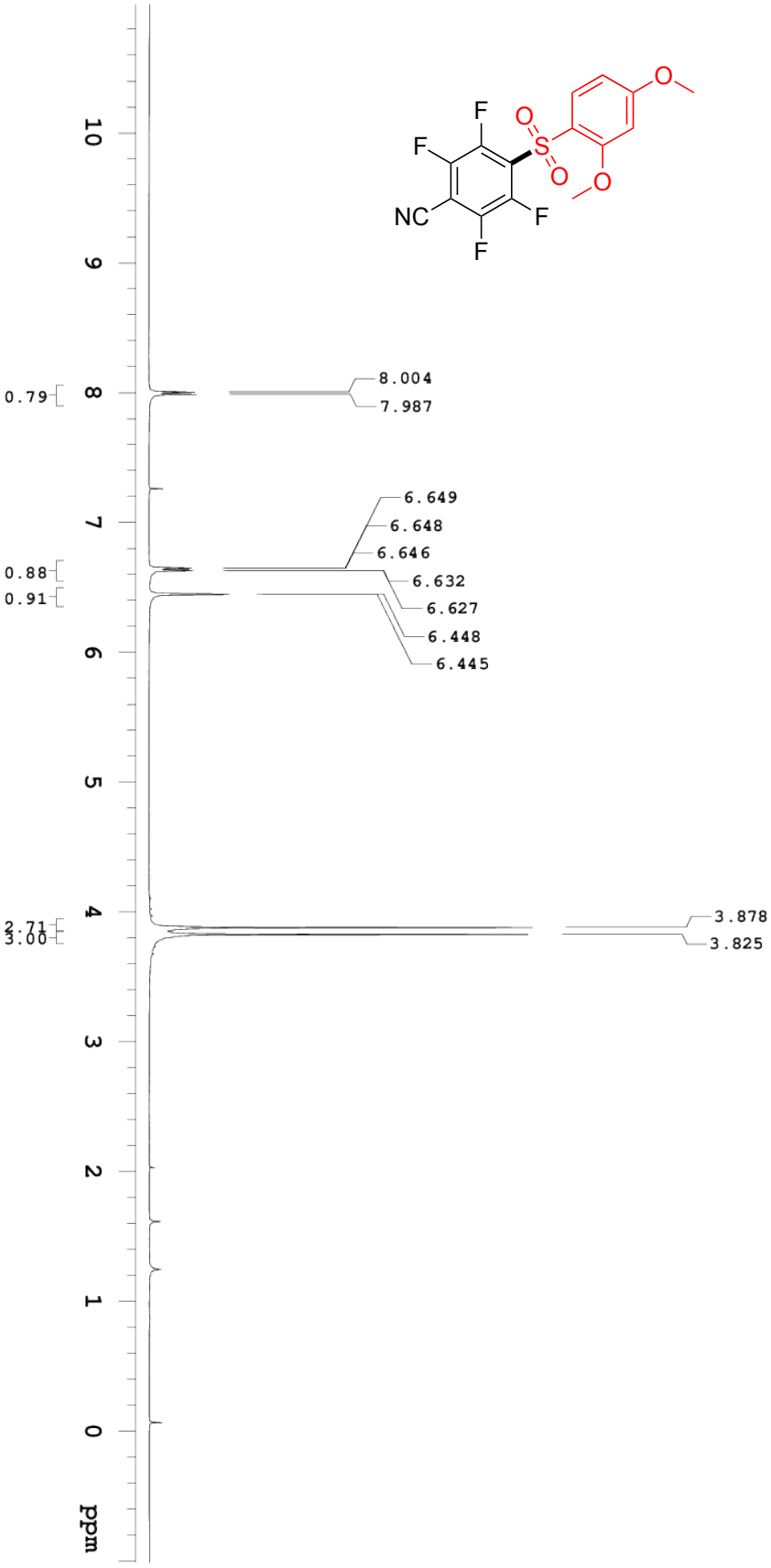
O
S
O
S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F
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O
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O
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6.627
6.448
6.445
3.878
3.825
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10
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6
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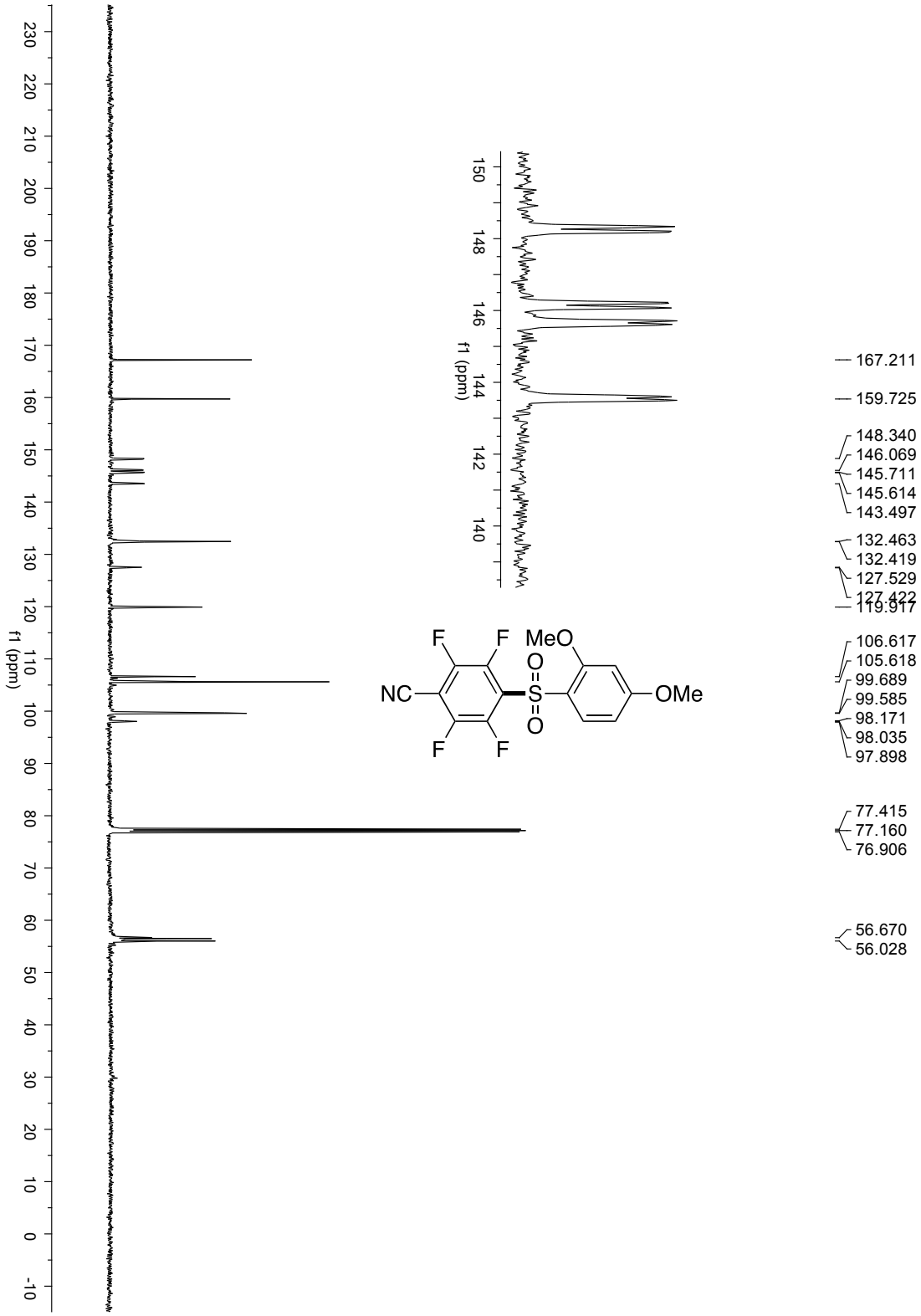
2
1
0
ppm


f1 (ppm)
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220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
150
148
146
144
142
140
f1 (ppm)
F
F
MeO
O
NC
S
OMe
O
F
F
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159.725
148.340
146.069
145.711
145.614
143.497
132.463
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127.422
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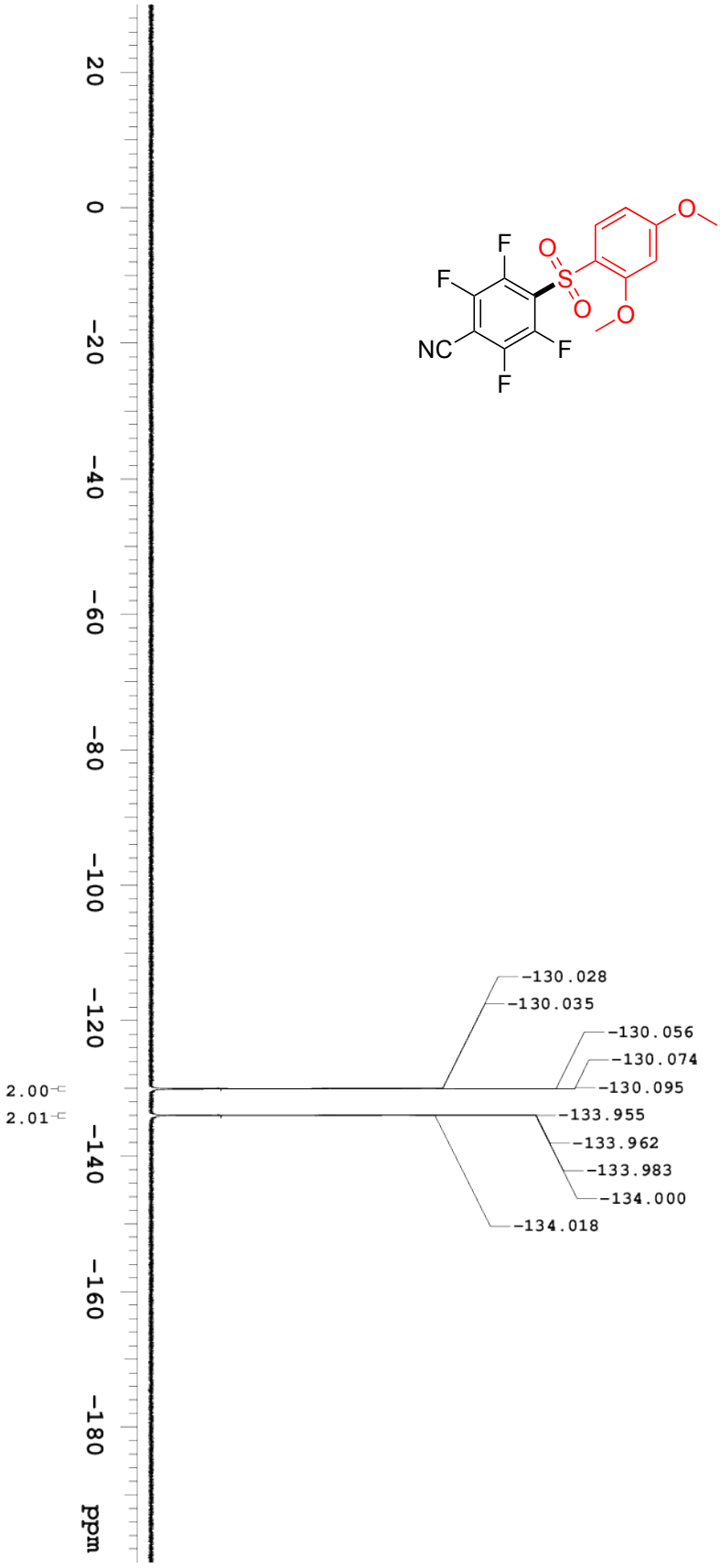
56.028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F
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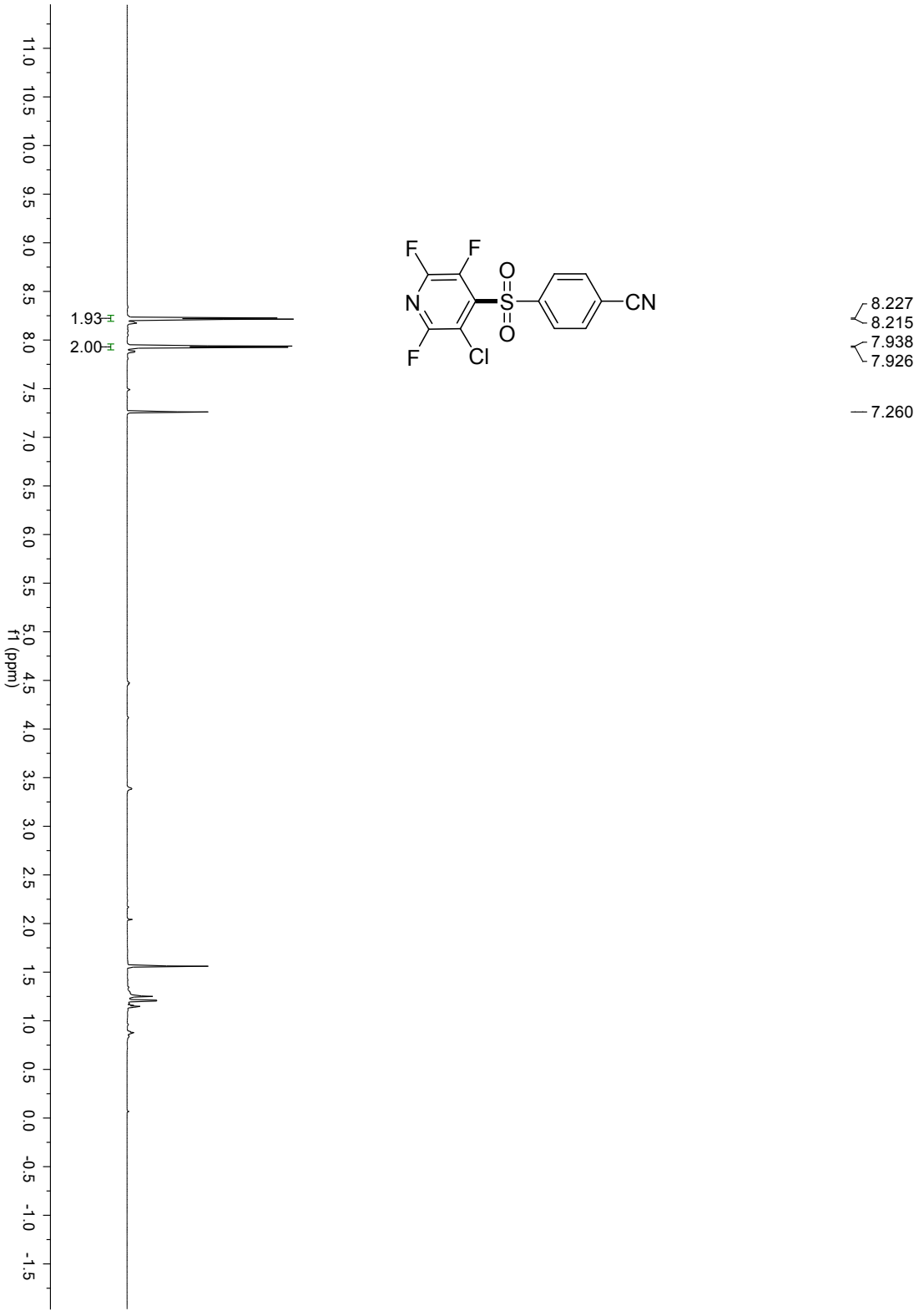
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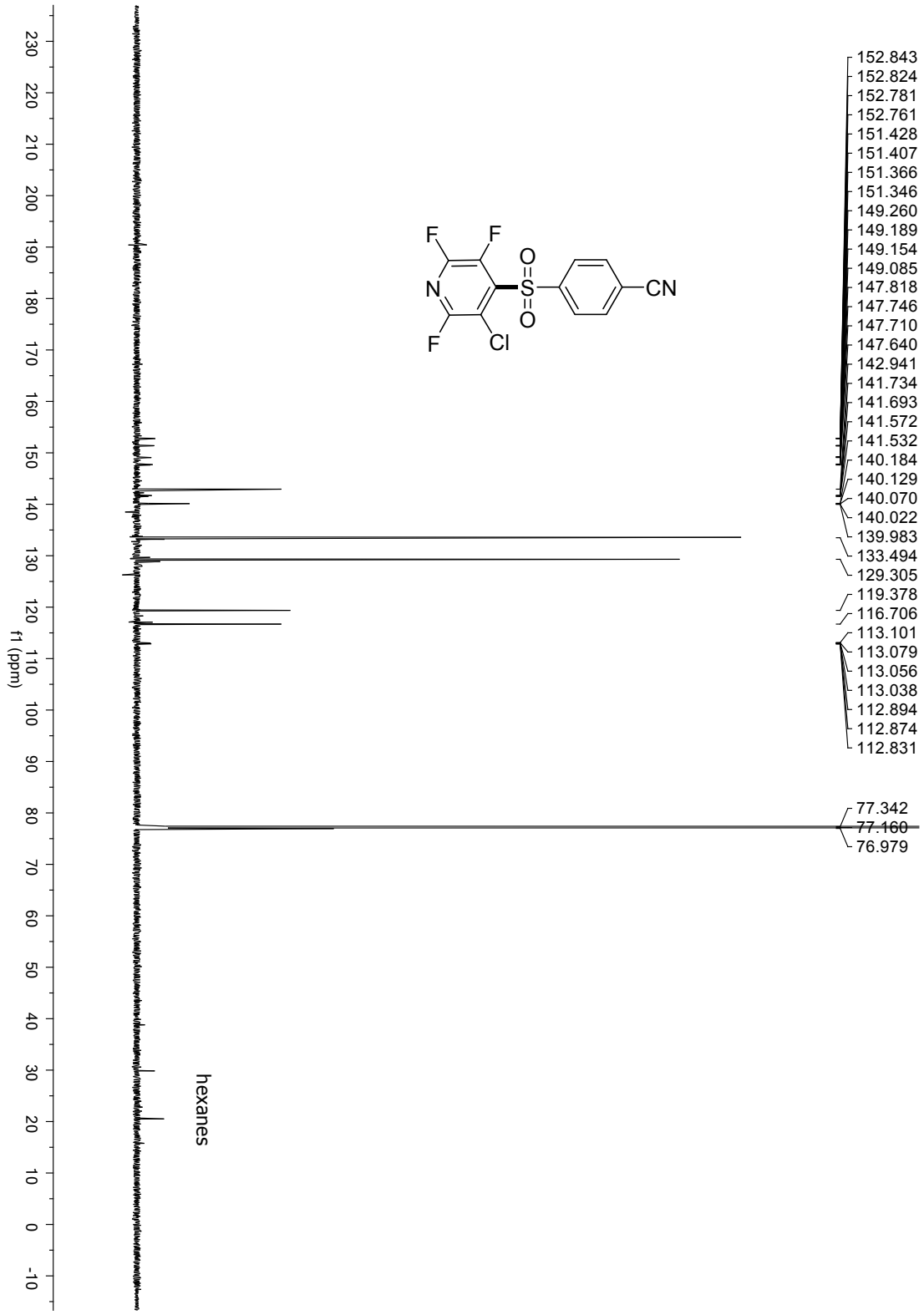
f1 (ppm)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CN
O
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Cl
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147.818
147.746
147.710
147.640
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140.184
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133.494
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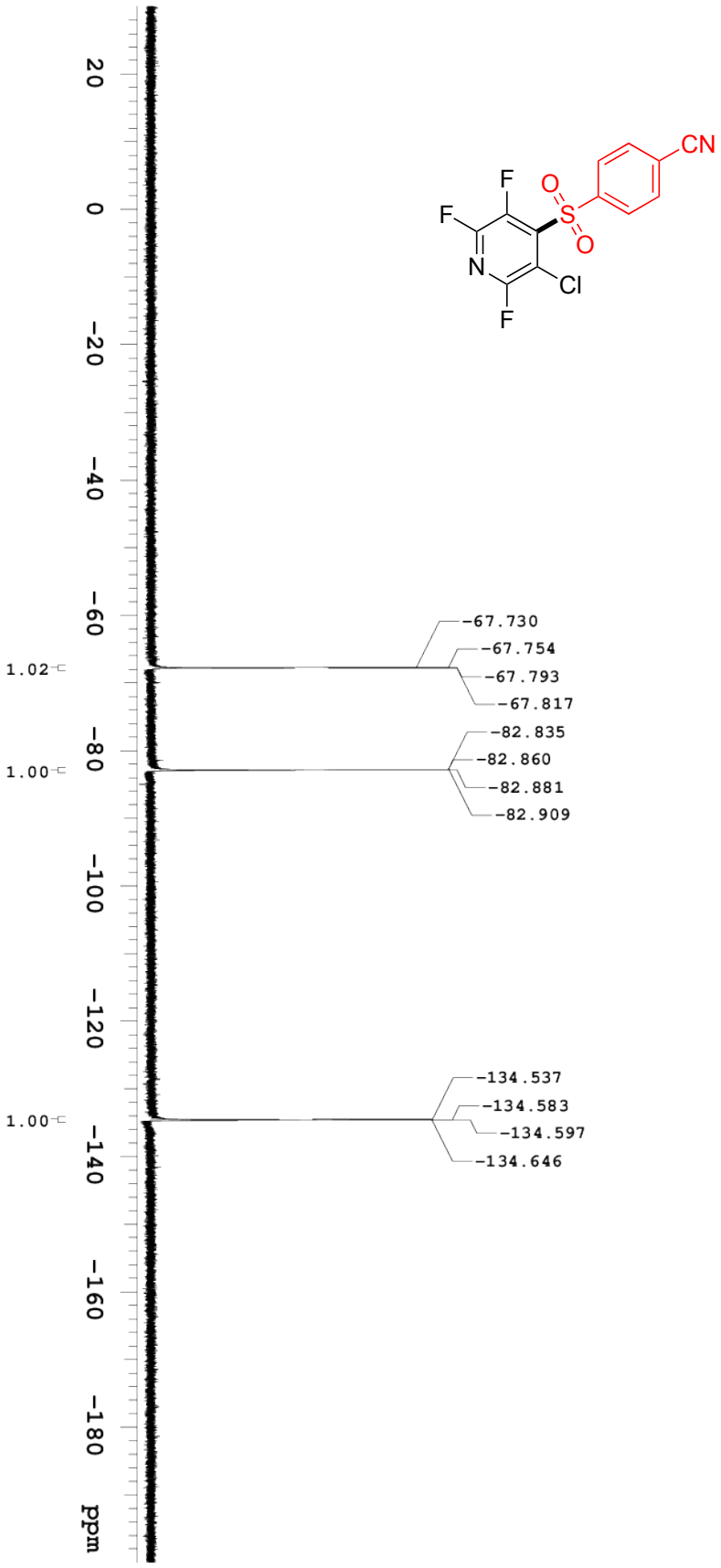
hexanes
f1 (ppm)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-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
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1.00
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-82.881
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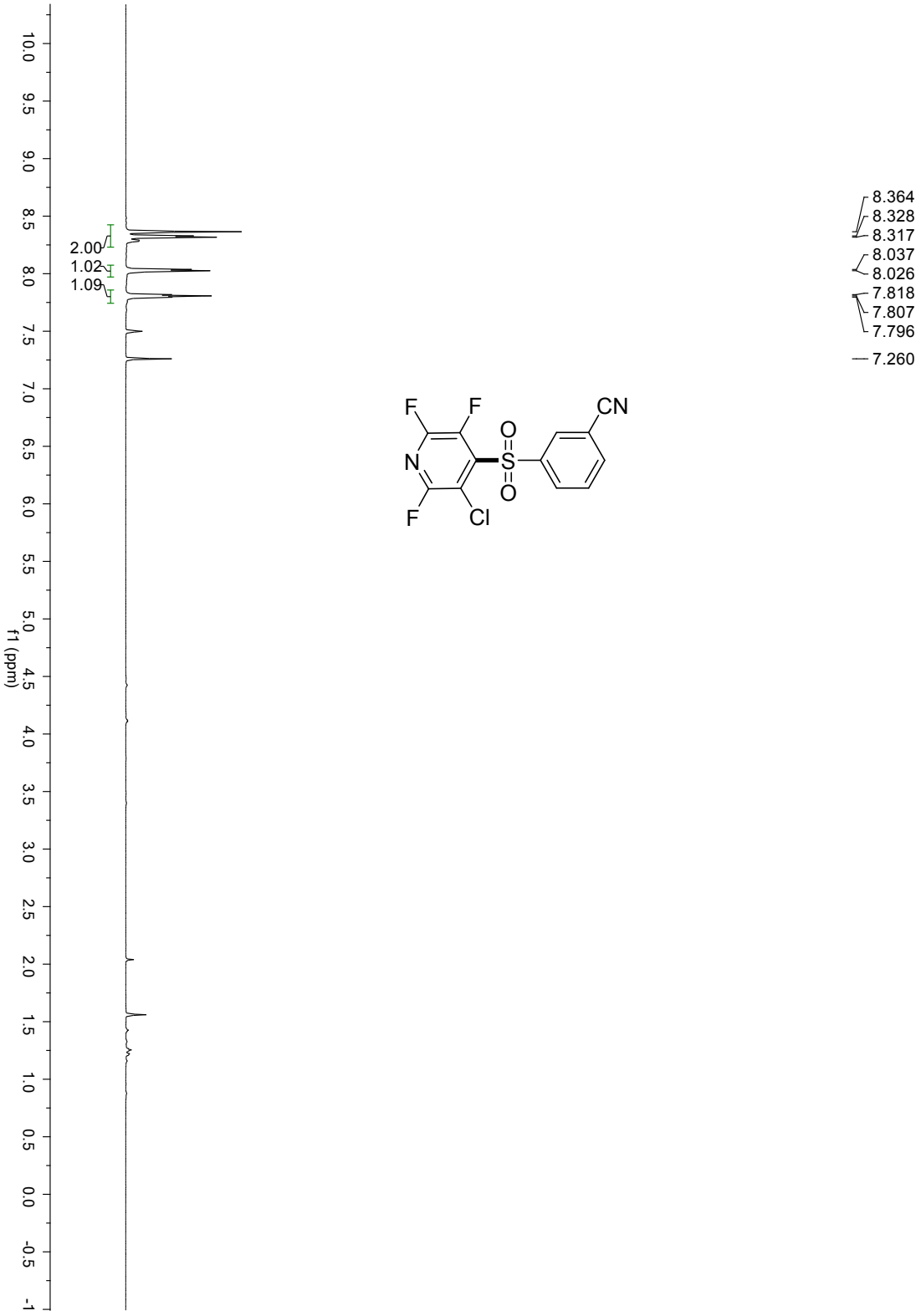
F
N
Cl
F
O
S
O
CN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1.02
1.09
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F
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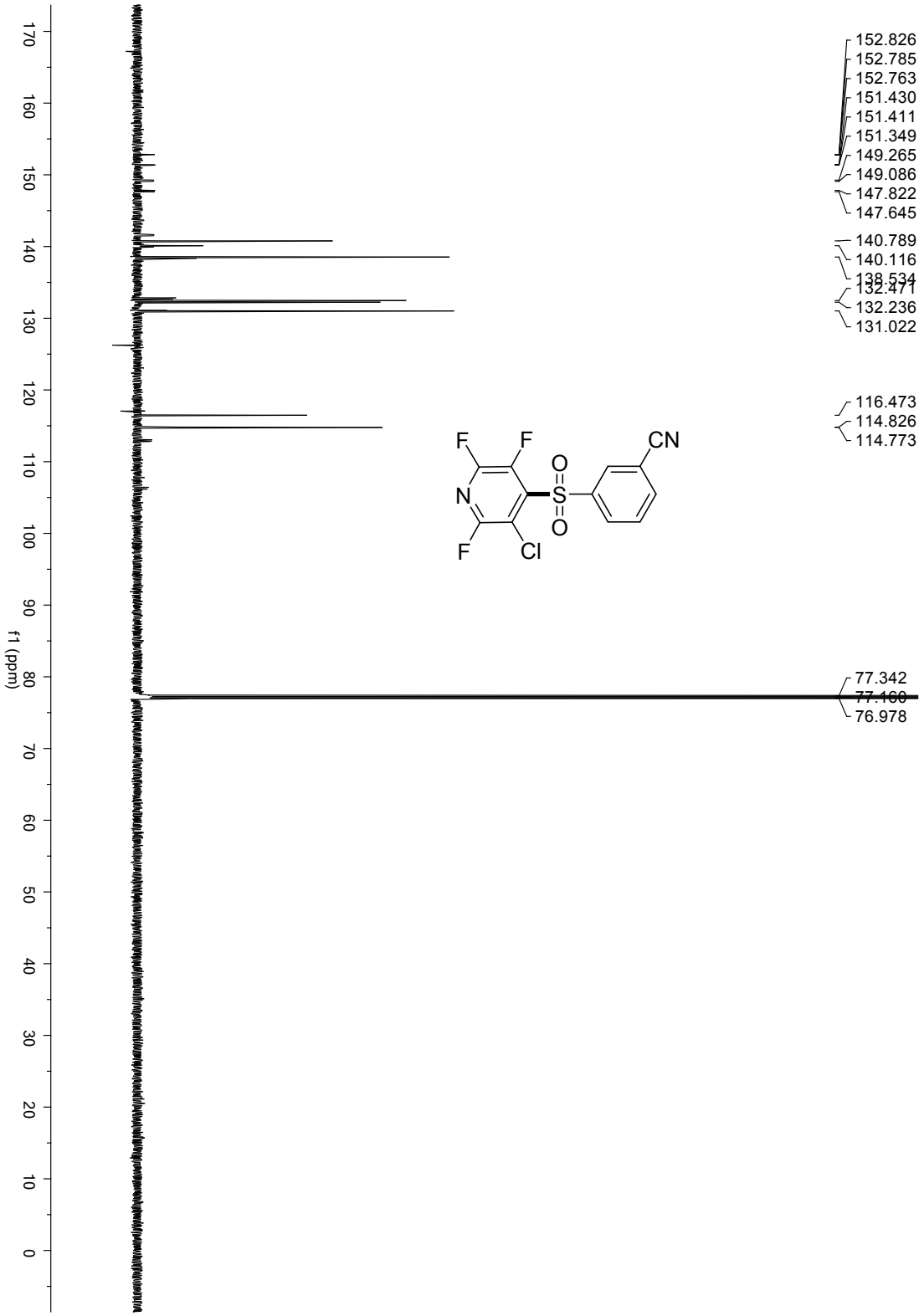
O
N
S
O
F
Cl
f1 (ppm)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140.789
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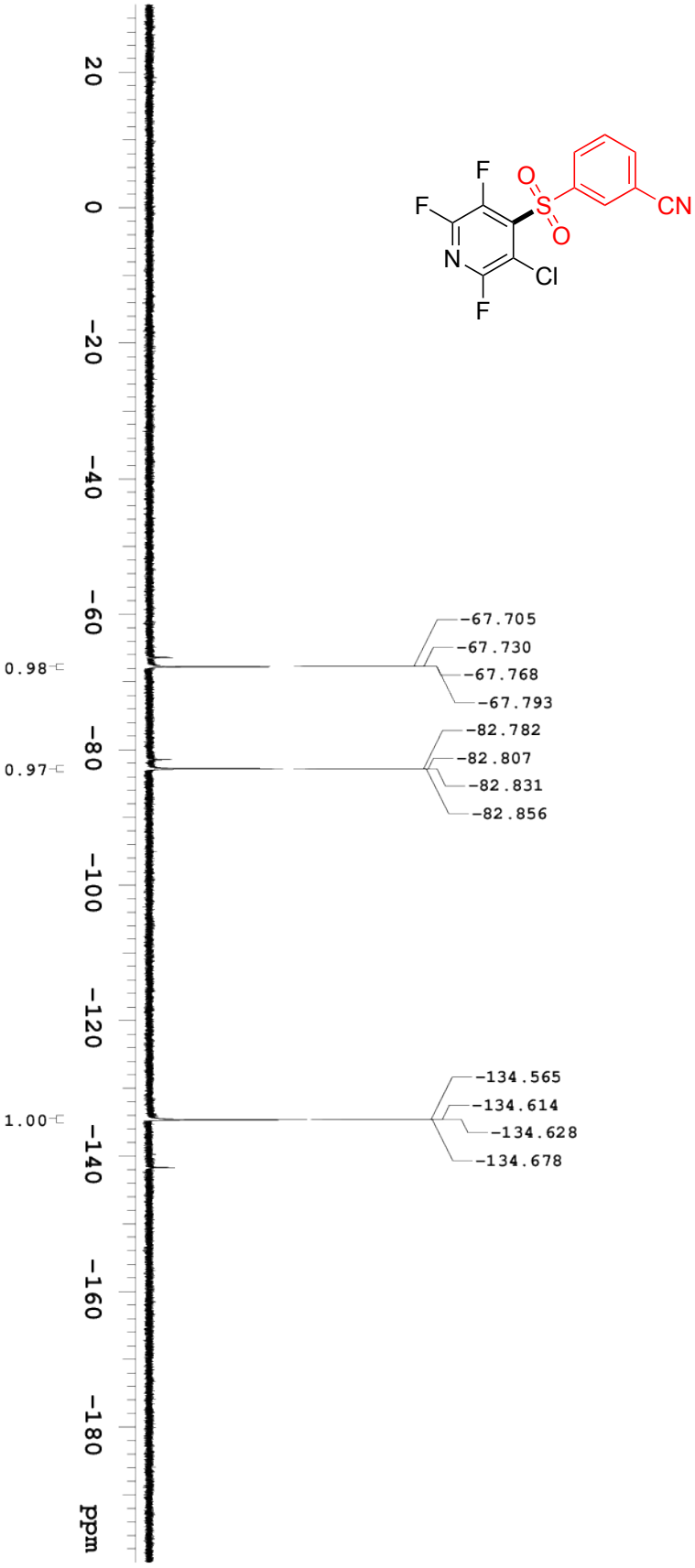
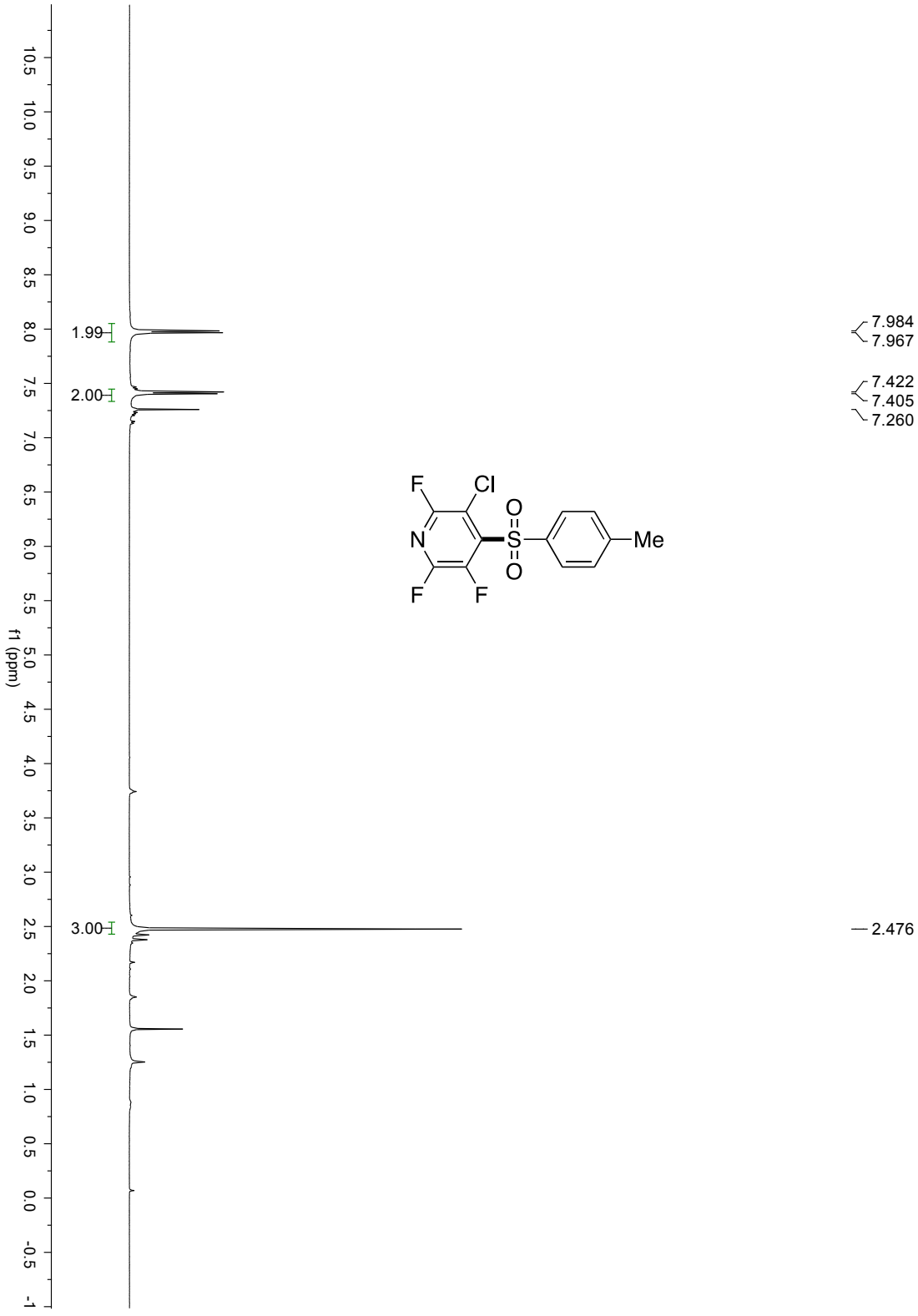
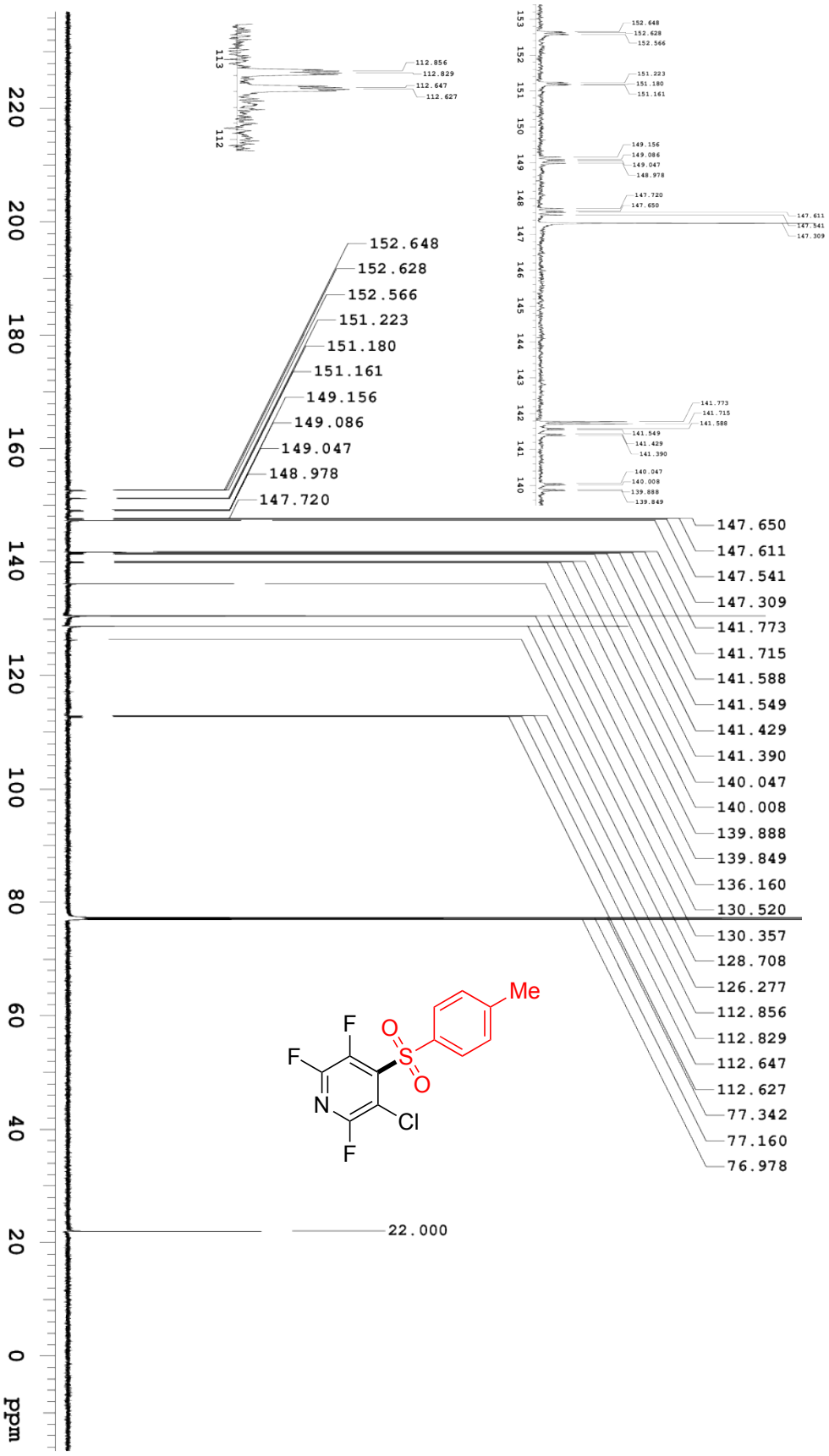
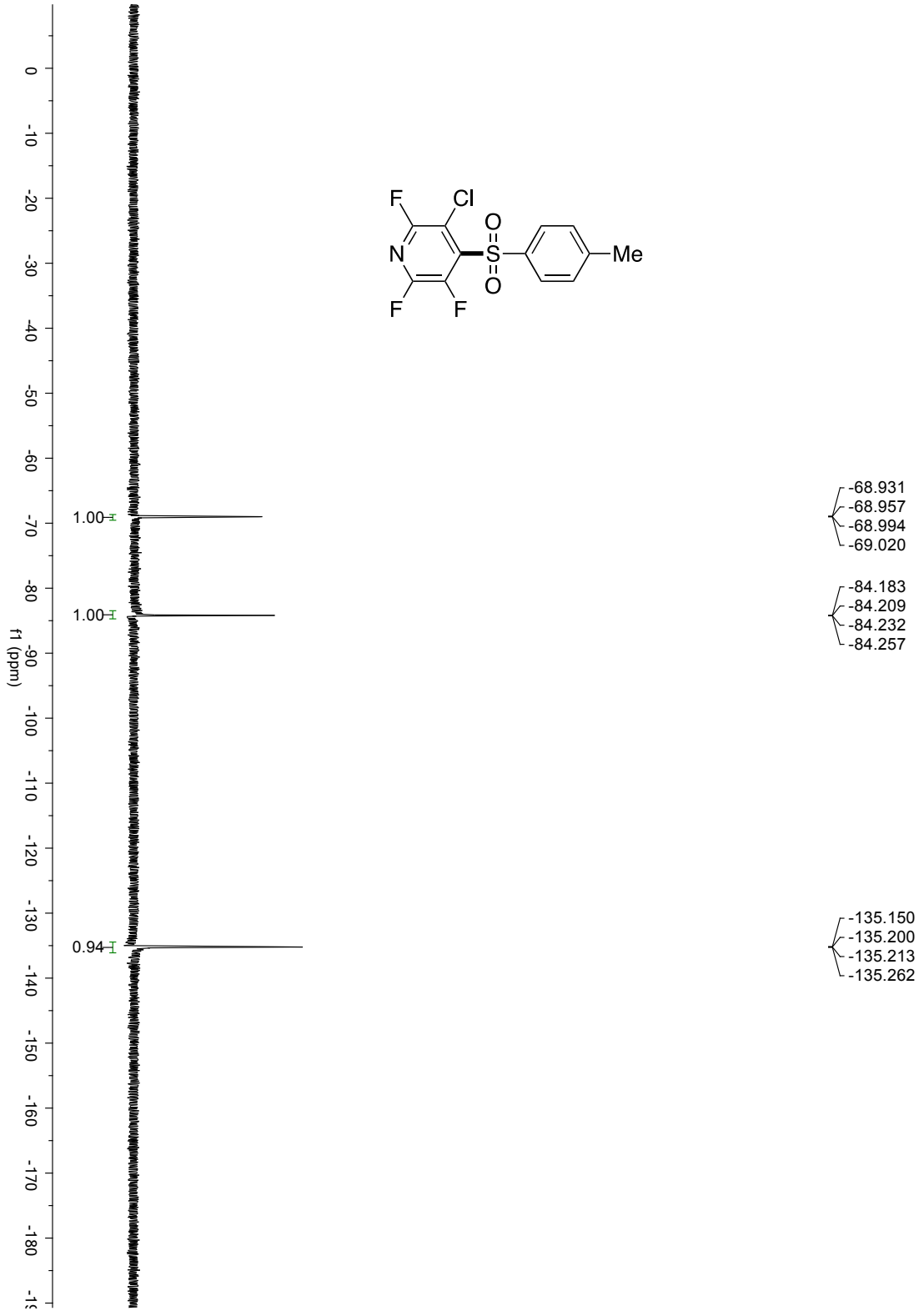
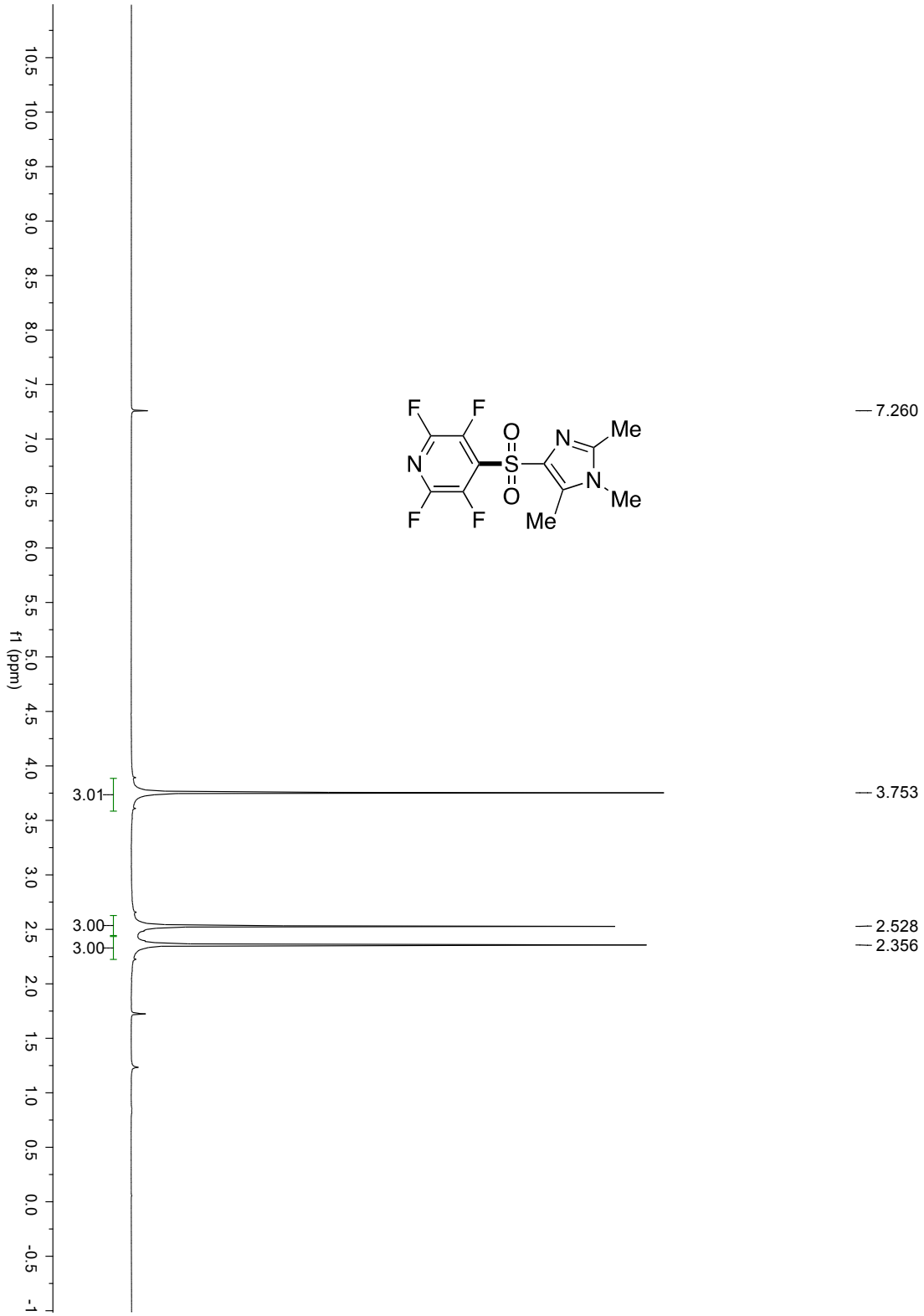
138.534
132.471
132.236
131.022
116.473
114.826
114.773
77.342
77.160
76.978
F
F
CN
O
N
S
O
F
Cl
f1 (ppm)

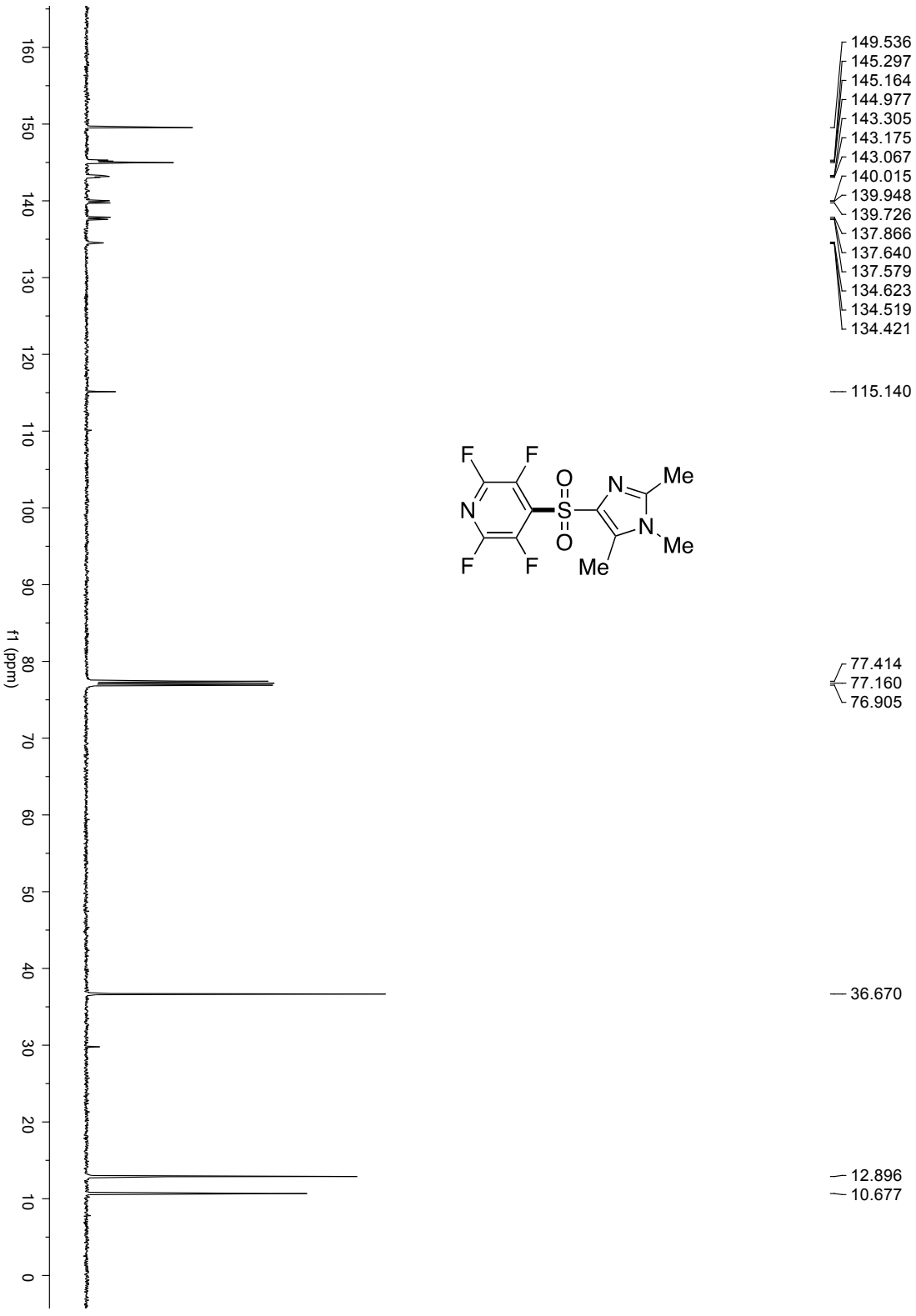

F
F
O
S
O
CN
N
Cl
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
-67.705
-67.730
-67.768
-67.793
-82.782
-82.807
-82.831
-82.856
-134.565
-134.614
-134.628
-134.678
0.98
0.97
1.00

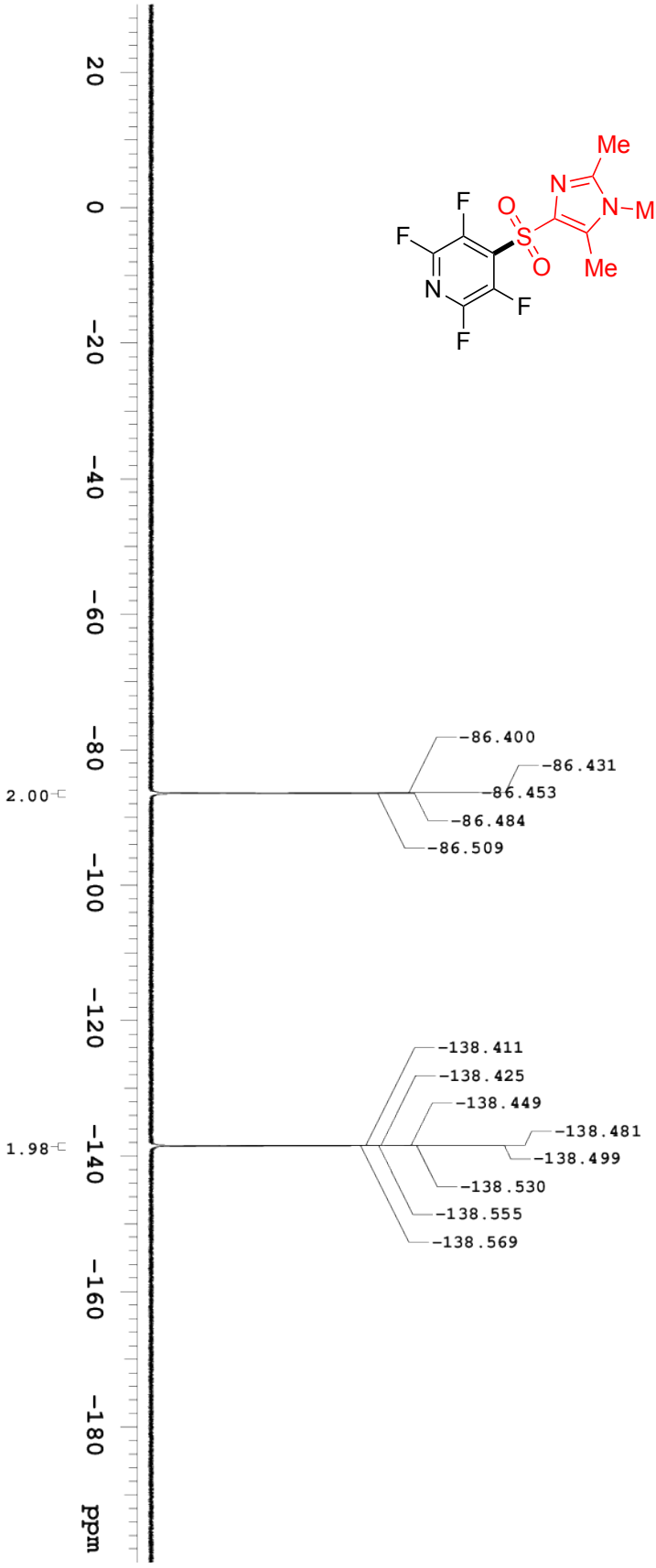

10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
1.99
2.00
3.00
7.984
7.967
7.422
7.405
7.260
2.476
F
Cl
N
O
S
O
Me
F
F

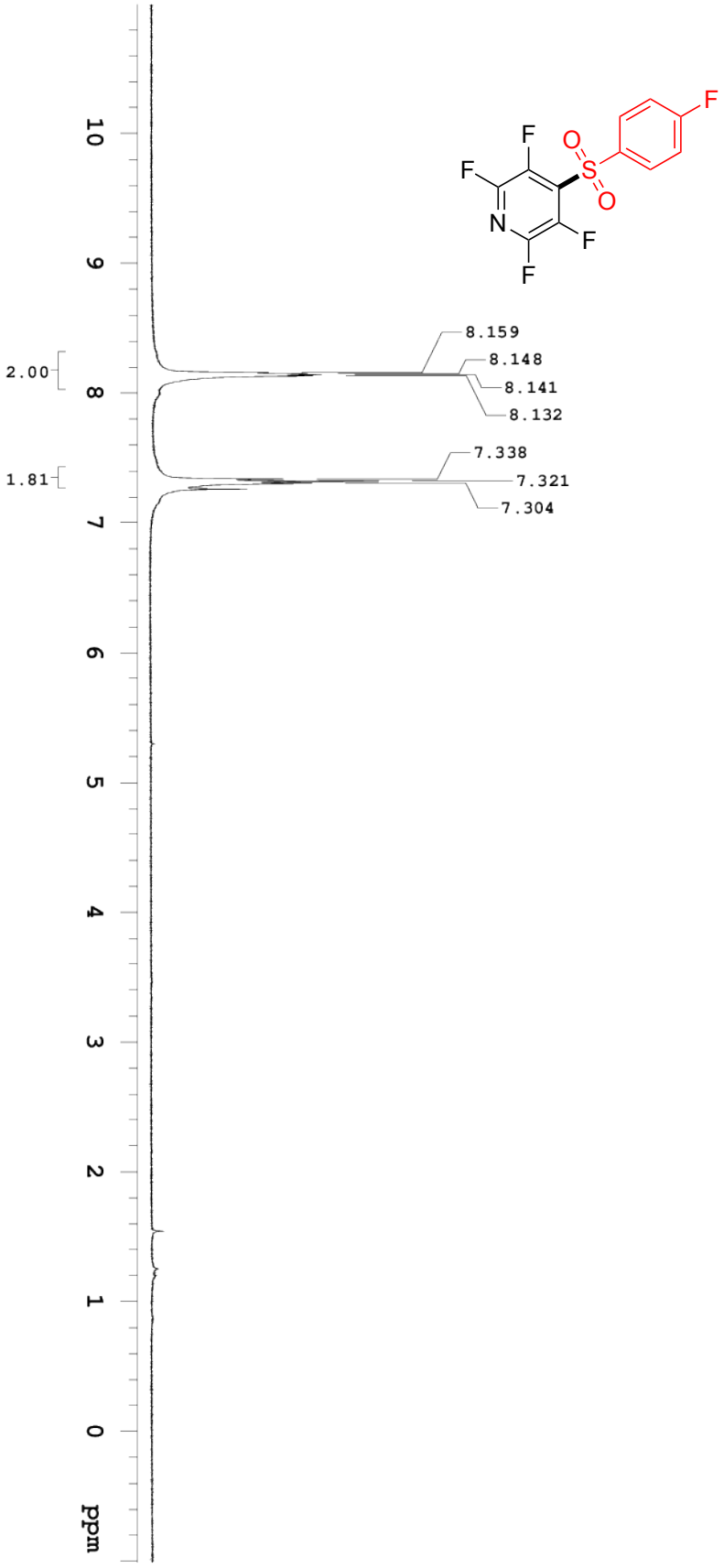

152.648
152.628
152.566
151.223
151.180
151.161
149.156
149.086
149.047
148.978
147.720
147.650
147.611
147.541
147.309
141.773
141.715
141.588
141.549
141.429
141.390
140.047
140.008
139.888
139.849
136.160
130.520
130.357
128.708
126.277
112.856
112.829
112.647
112.627
77.342
77.160
76.978
22.000
Me
F
F
O
S
O
N
Cl
F
ppm

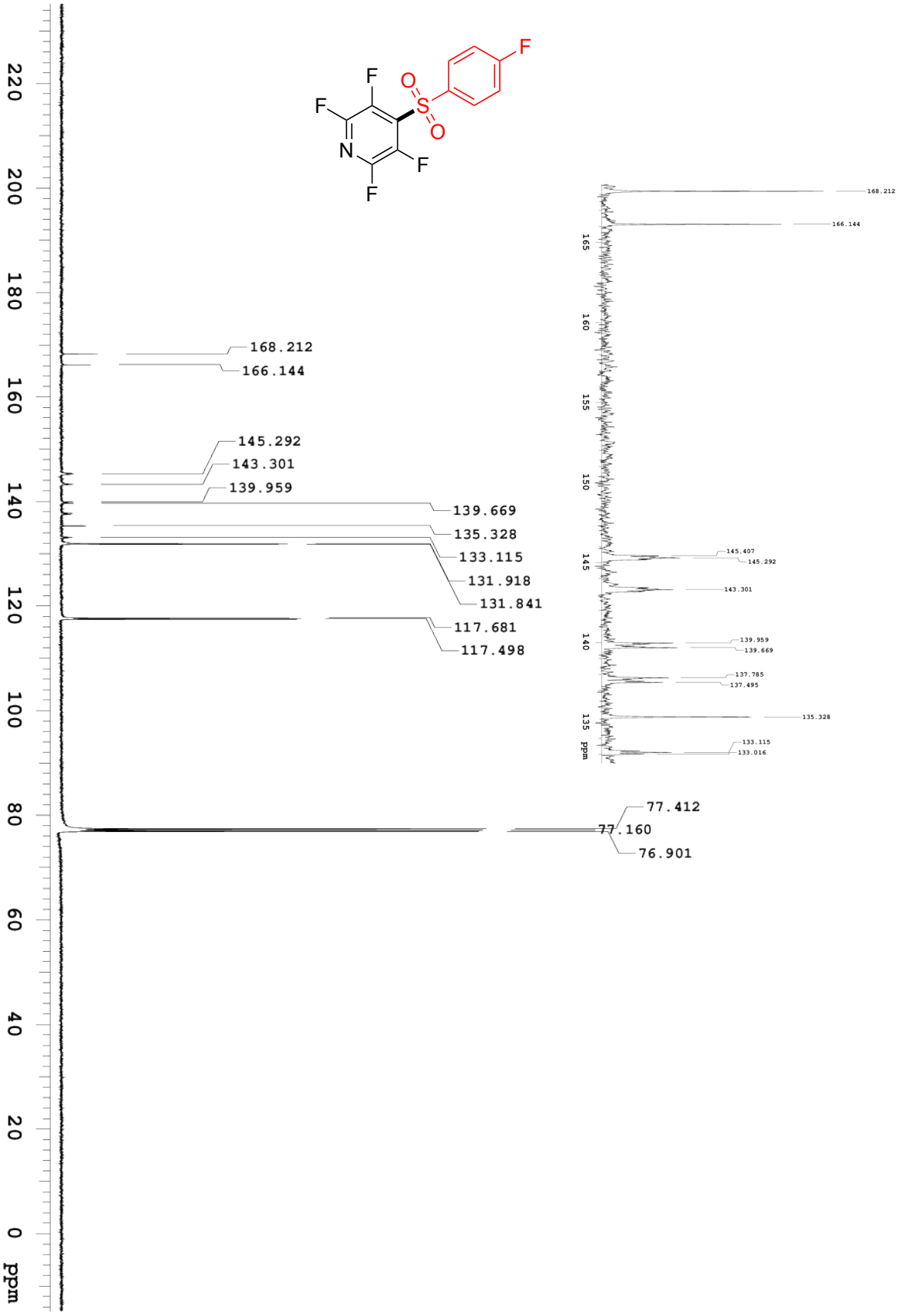

F
Cl
N
O
S
O
Me
F
F
1.00
1.00
0.94
f1 (ppm)
-68.931
-68.957
-68.994
-69.020
-84.183
-84.209
-84.232
-84.257
-135.150
-135.200
-135.213
-135.262

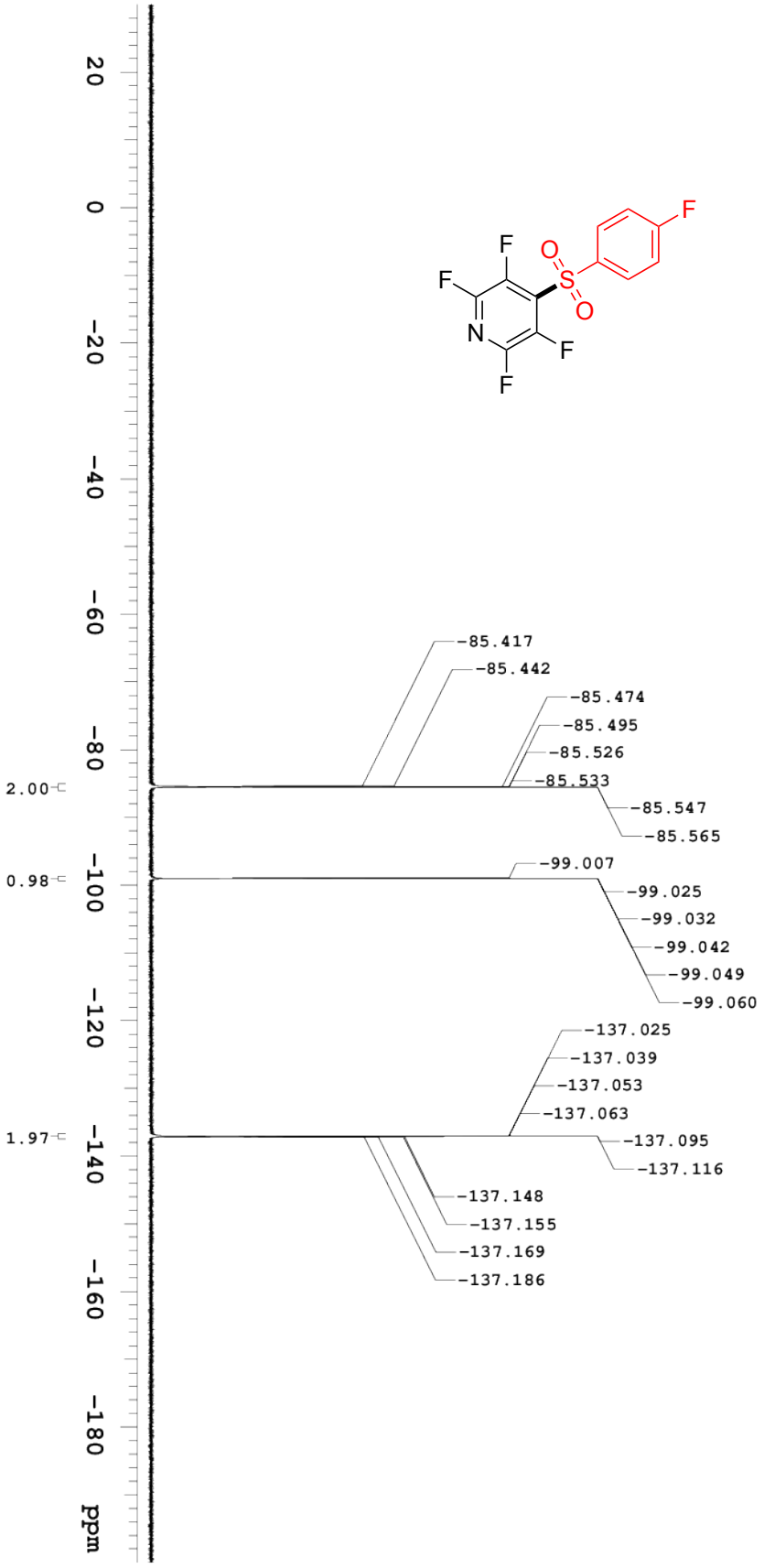

F
F
N
F
F
O
S
O
N
Me
N
Me
Me
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
3.01
3.00
3.00
7.260
3.753
2.528
2.356

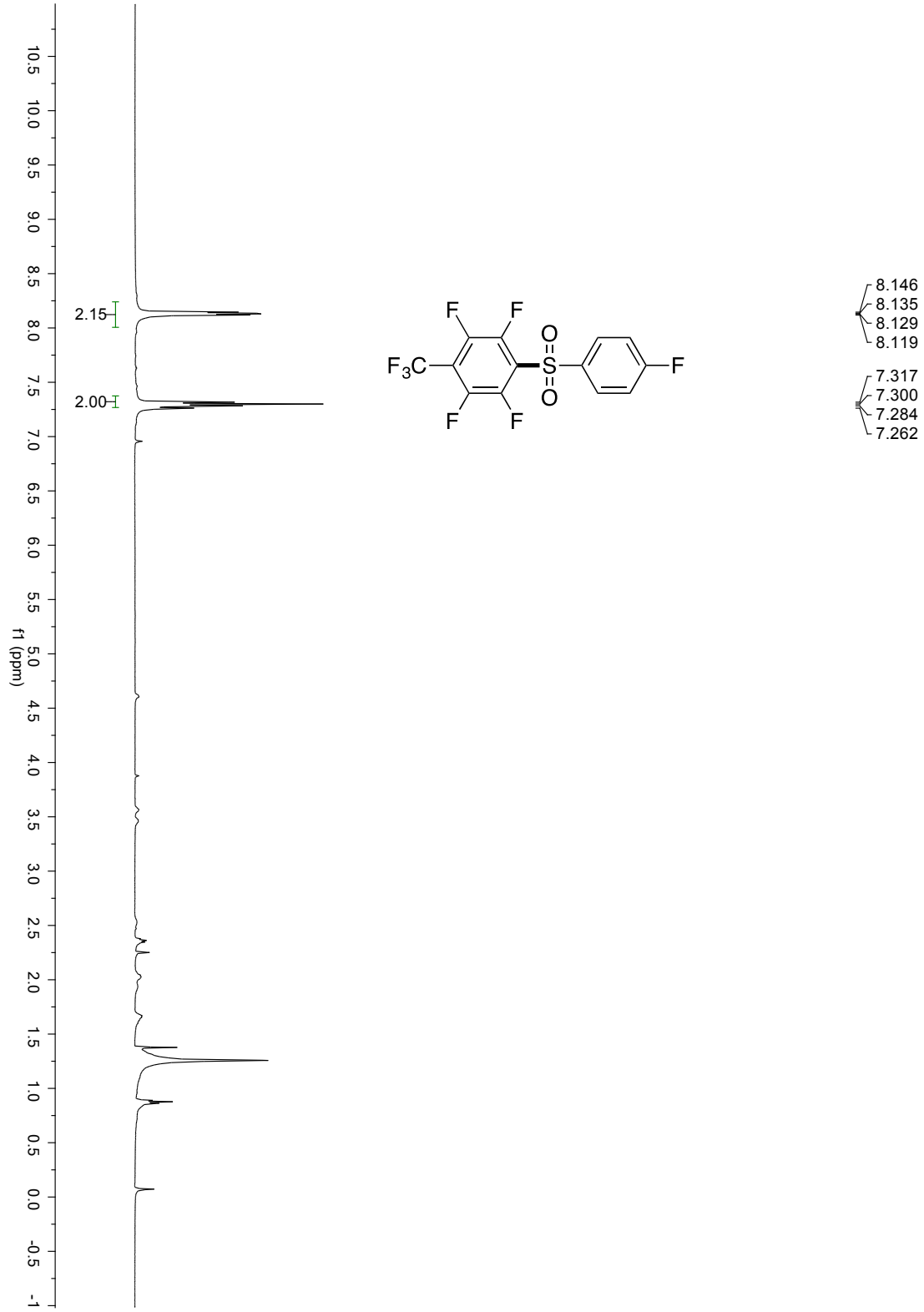

f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
149.536
145.297
145.164
144.977
143.305
143.175
143.067
140.015
139.948
139.726
137.866
137.640
137.579
134.623
134.519
134.421
115.140
77.414
77.160
76.905
36.670
12.896
10.677
F
F
N
F
F
O
S
O
N
Me
N
Me
Me

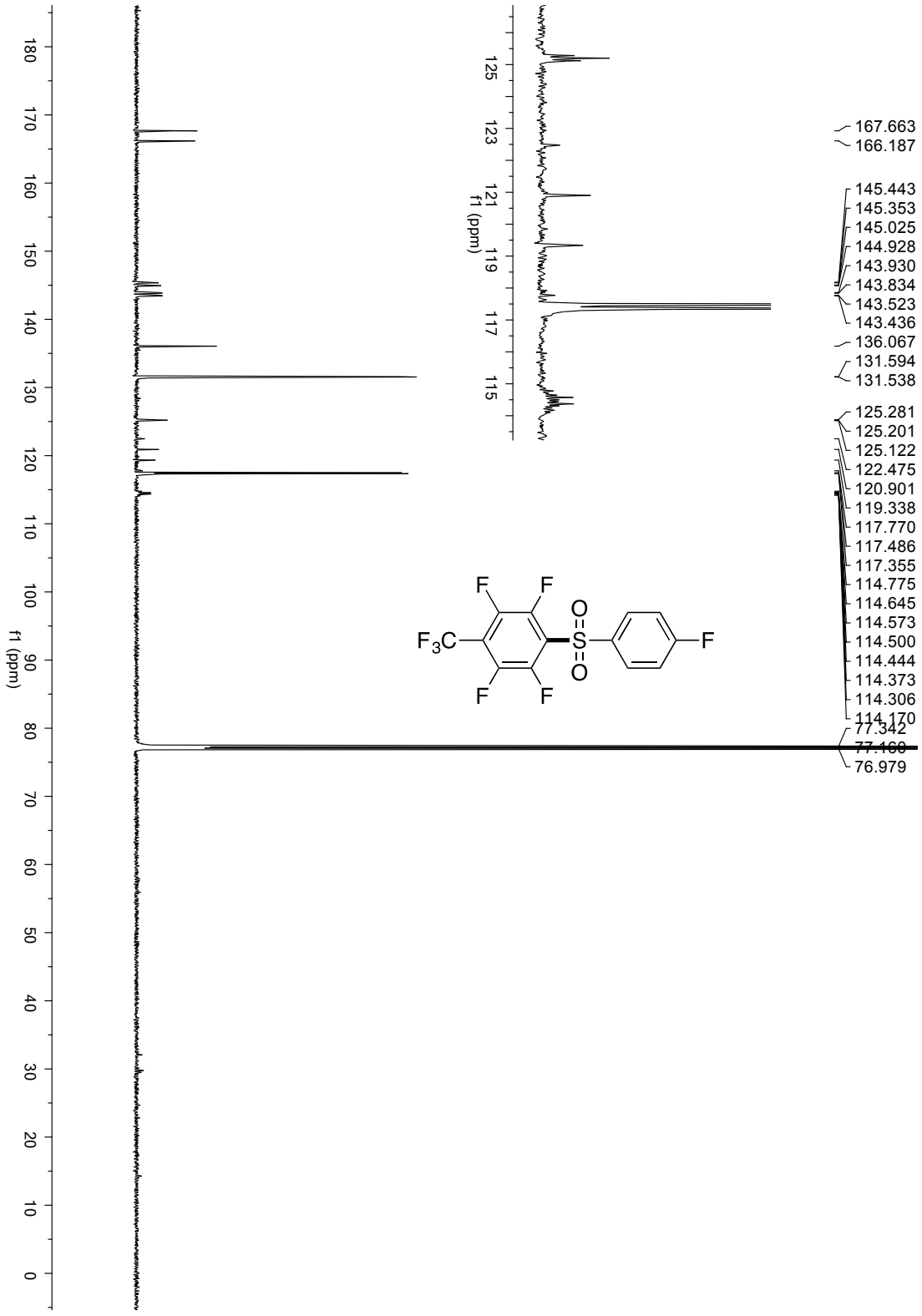

Me
N
N–Me
F
O
S
O
Me
F
N
F
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
2.00
-86.400
-86.431
-86.453
-86.484
-86.509
1.98
-138.411
-138.425
-138.449
-138.481
-138.499
-138.530
-138.555
-138.569

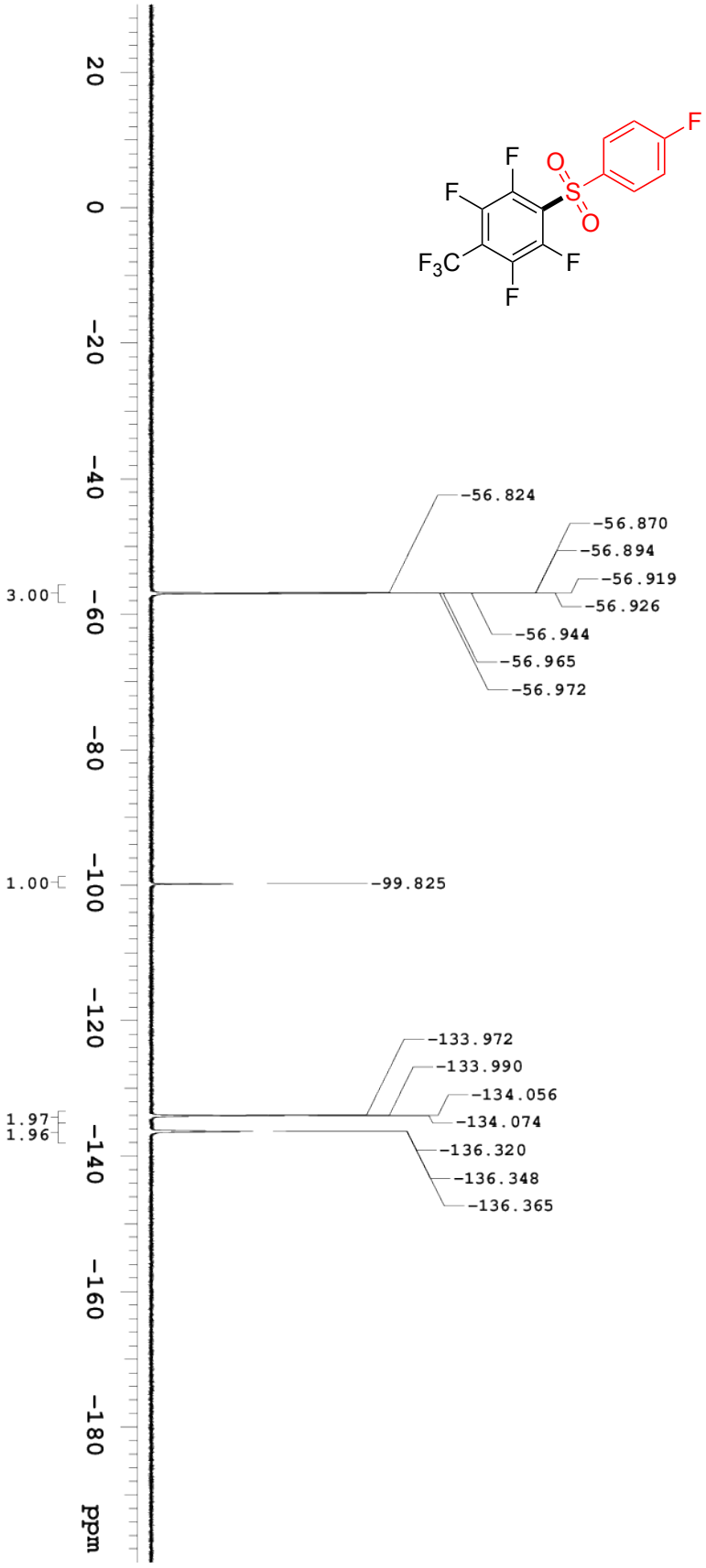

F
F
O
S
O
F
N
F
F
8.159
8.148
8.141
8.132
7.338
7.321
7.304
2.00
1.81
10
9
8
7
6
5
4
3
2
1
0
ppm

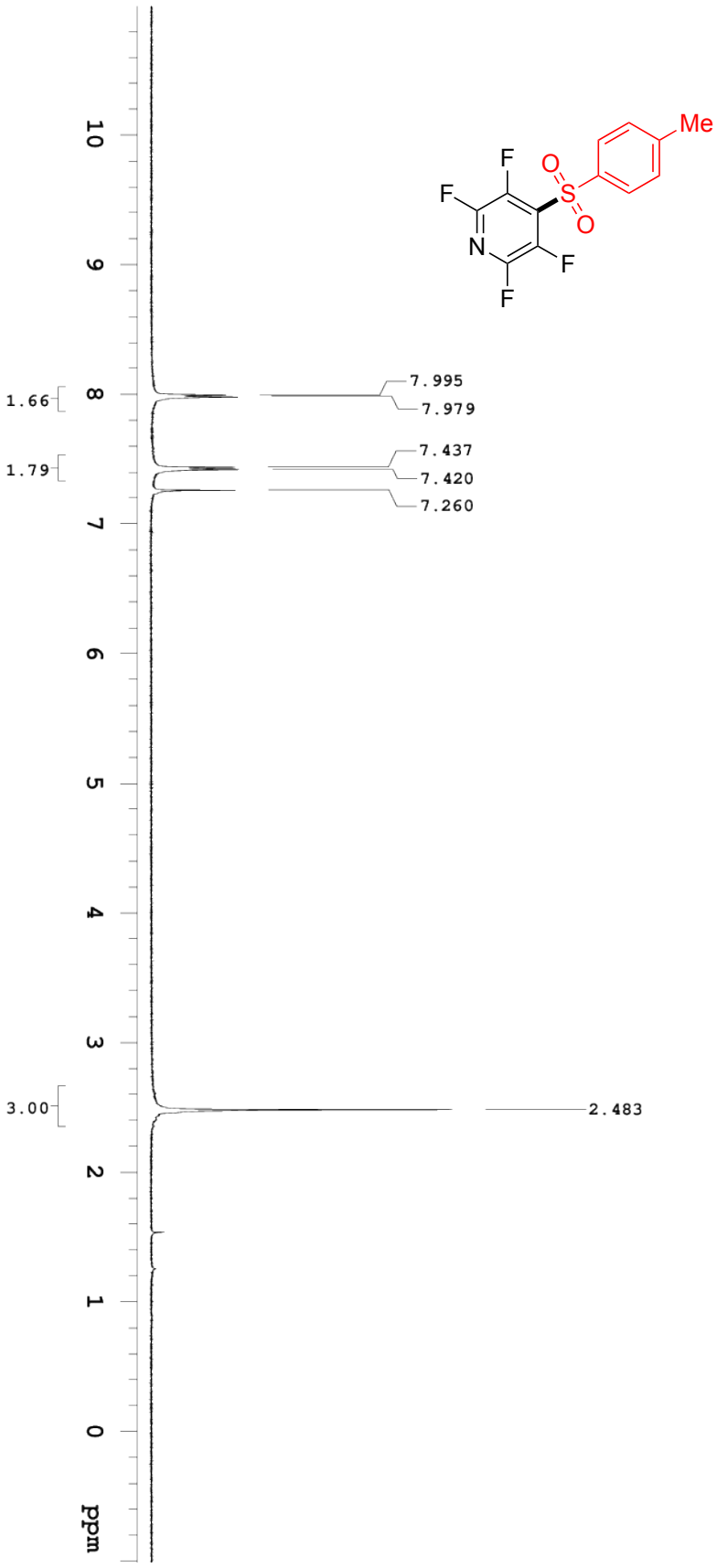

F
F
O
S
O
F
N
F
F
168.212
166.144
145.292
143.301
139.959
139.669
135.328
133.115
131.918
131.841
117.681
117.498
77.412
77.160
76.901
ppm

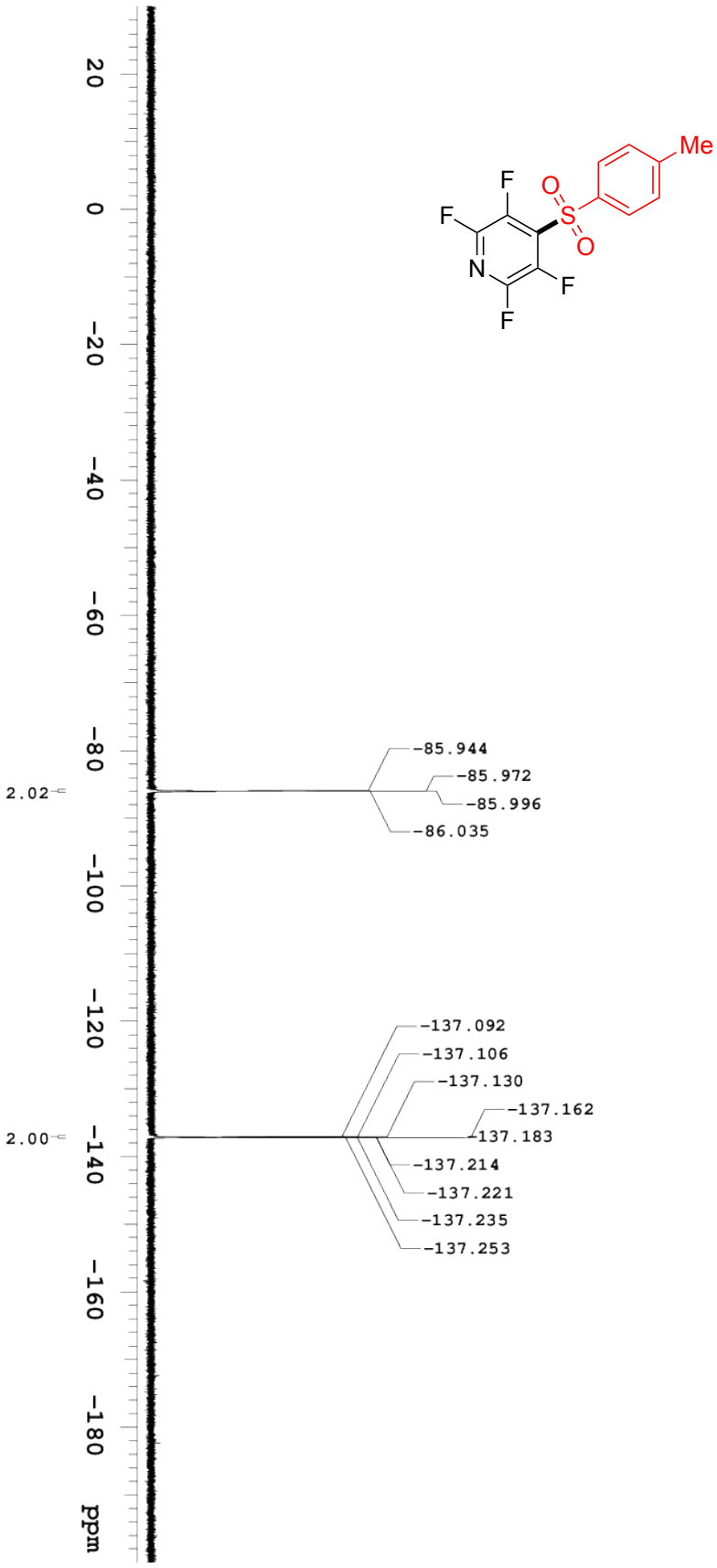

F
F
O
S
O
F
N
F
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
2.00
0.98
1.97
-85.417
-85.442
-85.474
-85.495
-85.526
-85.533
-85.547
-85.565
-99.007
-99.025
-99.032
-99.042
-99.049
-99.060
-137.025
-137.039
-137.053
-137.063
-137.095
-137.116
-137.148
-137.155
-137.169
-137.186

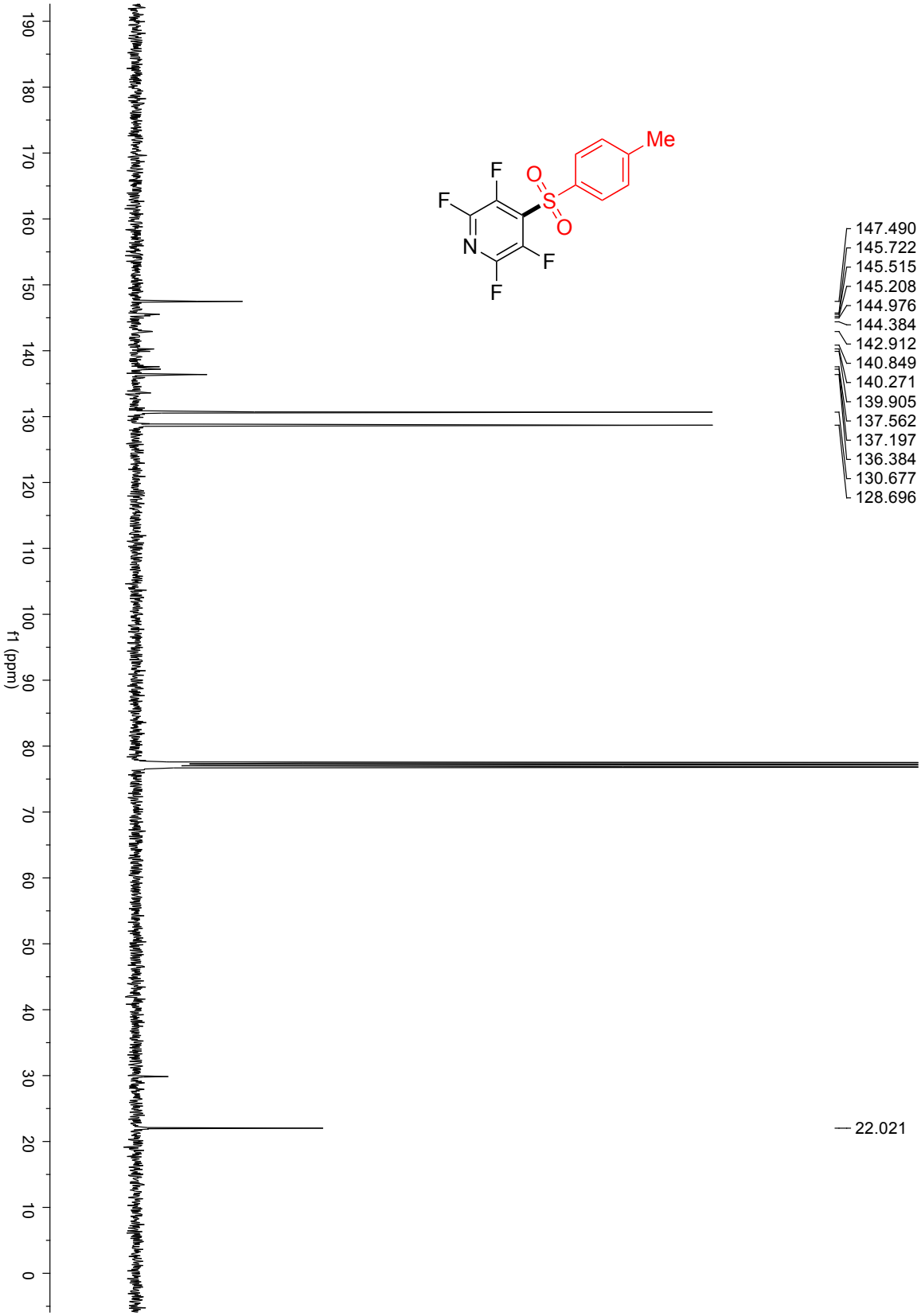

2.15
2.00
F
F
F3C
O
S
O
F
F
F
8.146
8.135
8.129
8.119
7.317
7.300
7.284
7.262
f1 (ppm)

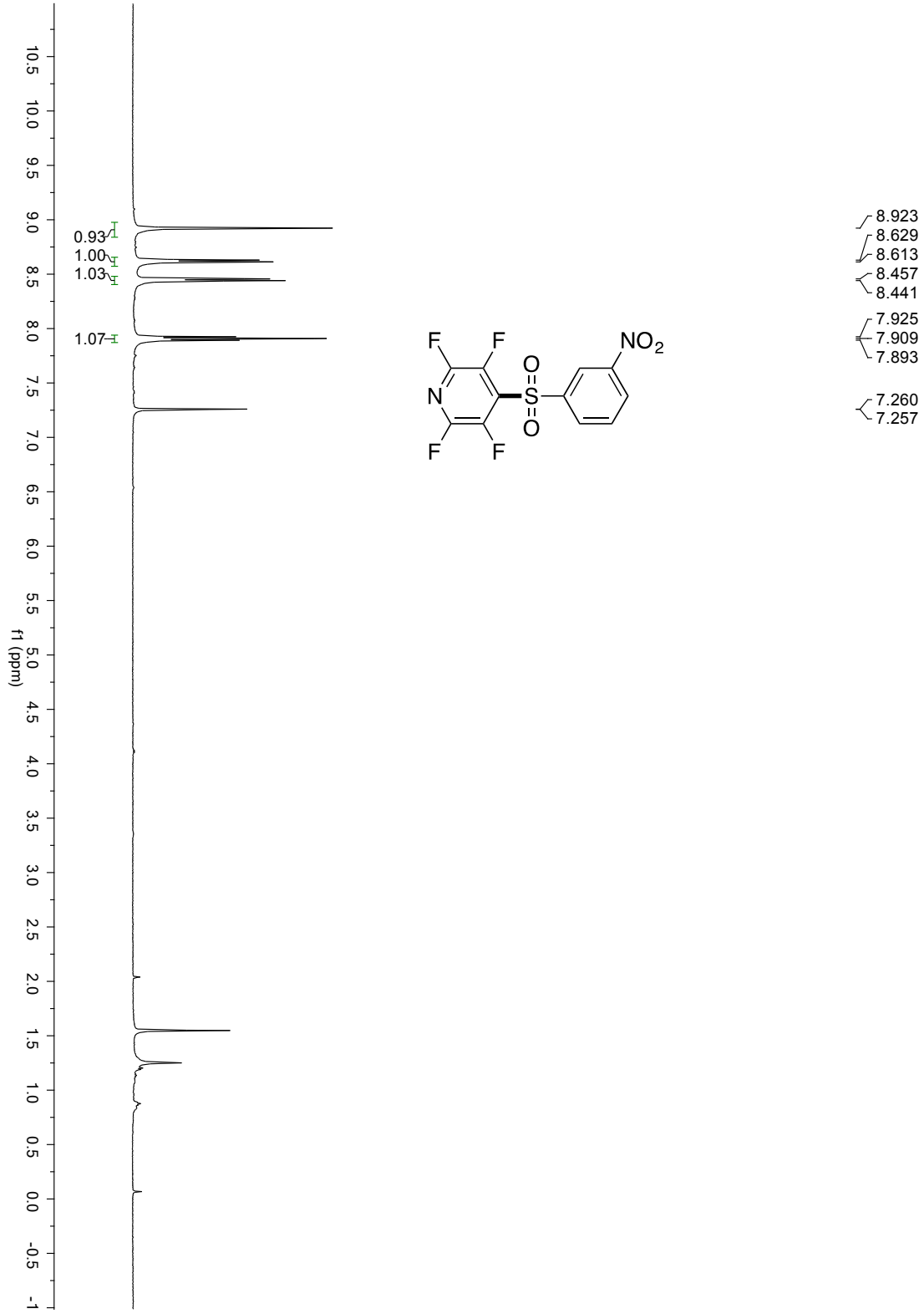

167.663
166.187
145.443
145.353
145.025
144.928
143.930
143.834
143.523
143.436
136.067
131.594
131.538
125.281
125.201
125.122
122.475
120.901
119.338
117.770
117.486
117.355
114.775
114.645
114.573
114.500
114.444
114.373
114.306
114.170
77.342
77.160
76.979
F
F
F3C
O
S
O
F
F
F
f1 (ppm)
f1 (ppm)

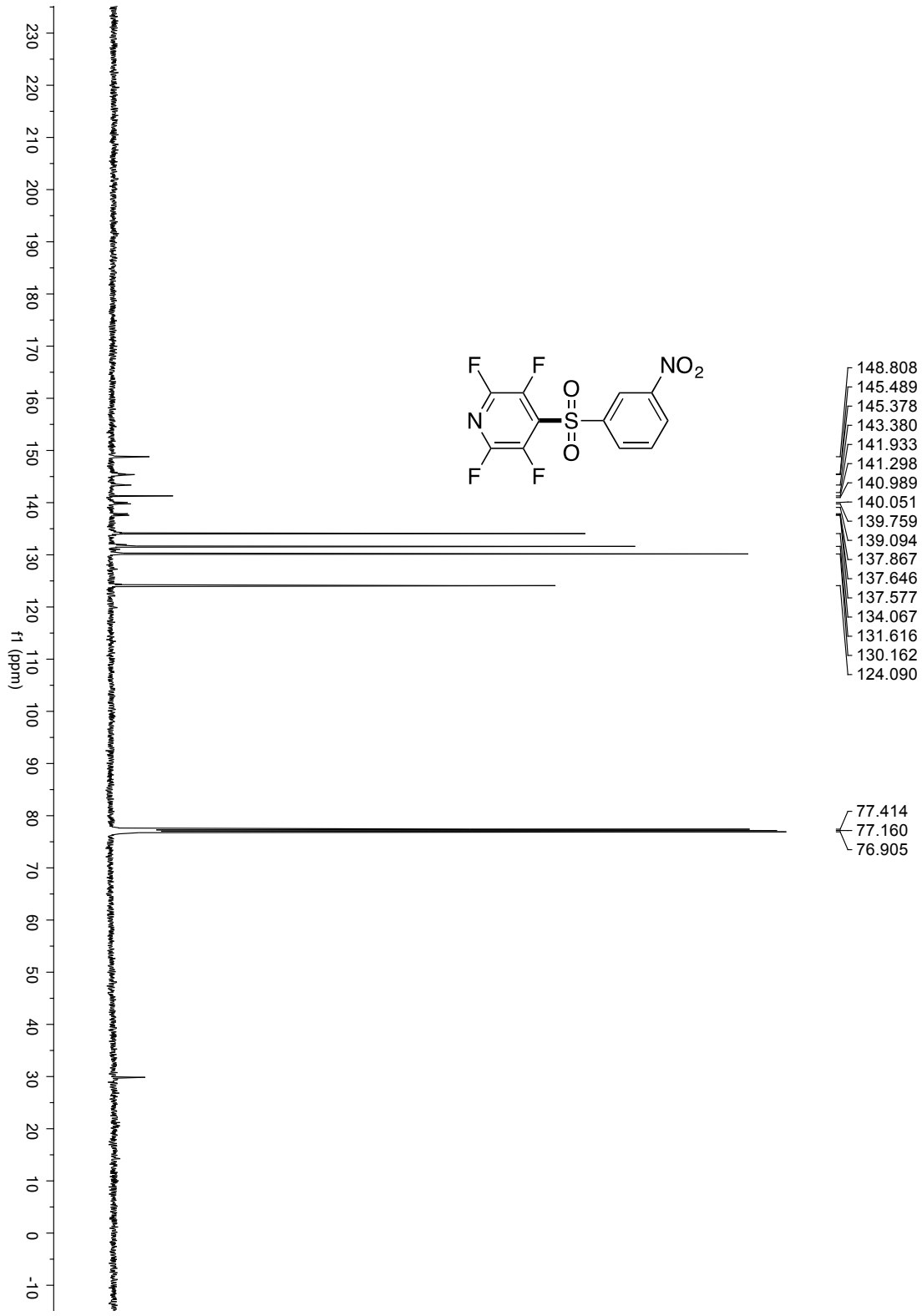

F
F
O
S
O
F
F3C
F
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
3.00
1.00
1.97
1.96
-56.824
-56.870
-56.894
-56.919
-56.926
-56.944
-56.965
-56.972
-99.825
-133.972
-133.990
-134.056
-134.074
-136.320
-136.348
-136.365

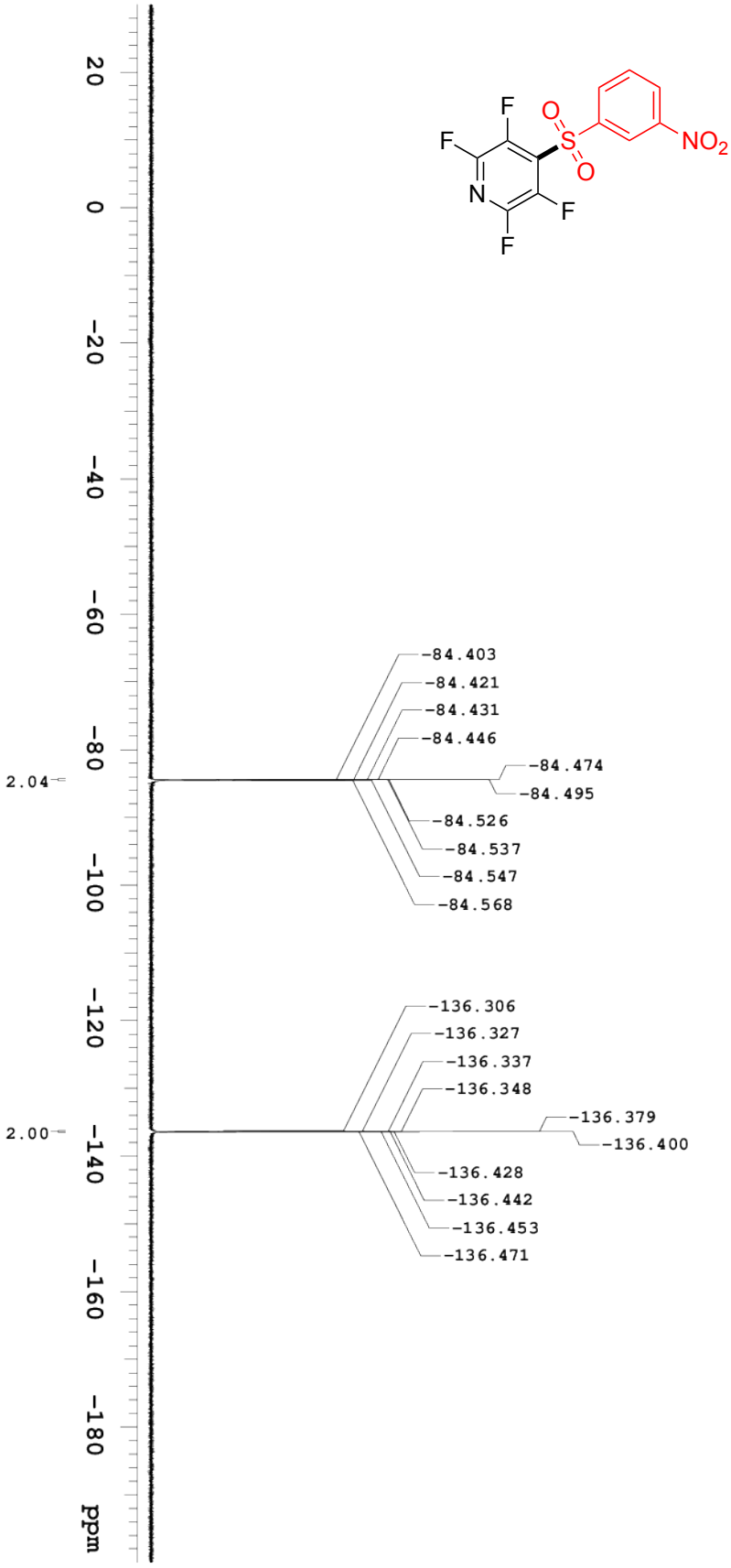

F
F
N
F
F
O
S
O
Me
7.995
7.979
7.437
7.420
7.260
2.483
1.66
1.79
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm

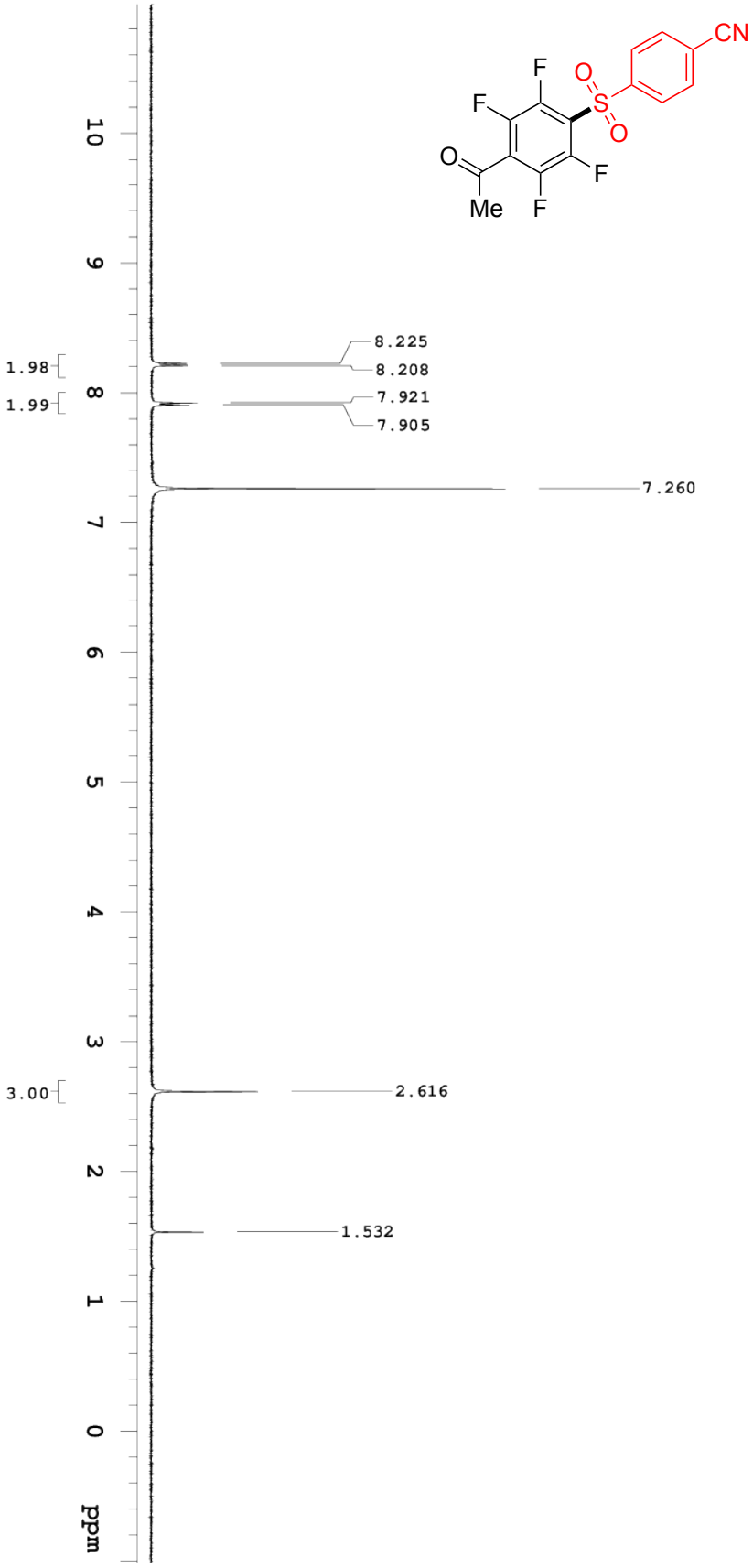

Me
F
F
O
S
O
N
F
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
2.02
-85.944
-85.972
-85.996
-86.035
2.00
-137.092
-137.106
-137.130
-137.162
-137.183
-137.214
-137.221
-137.235
-137.253

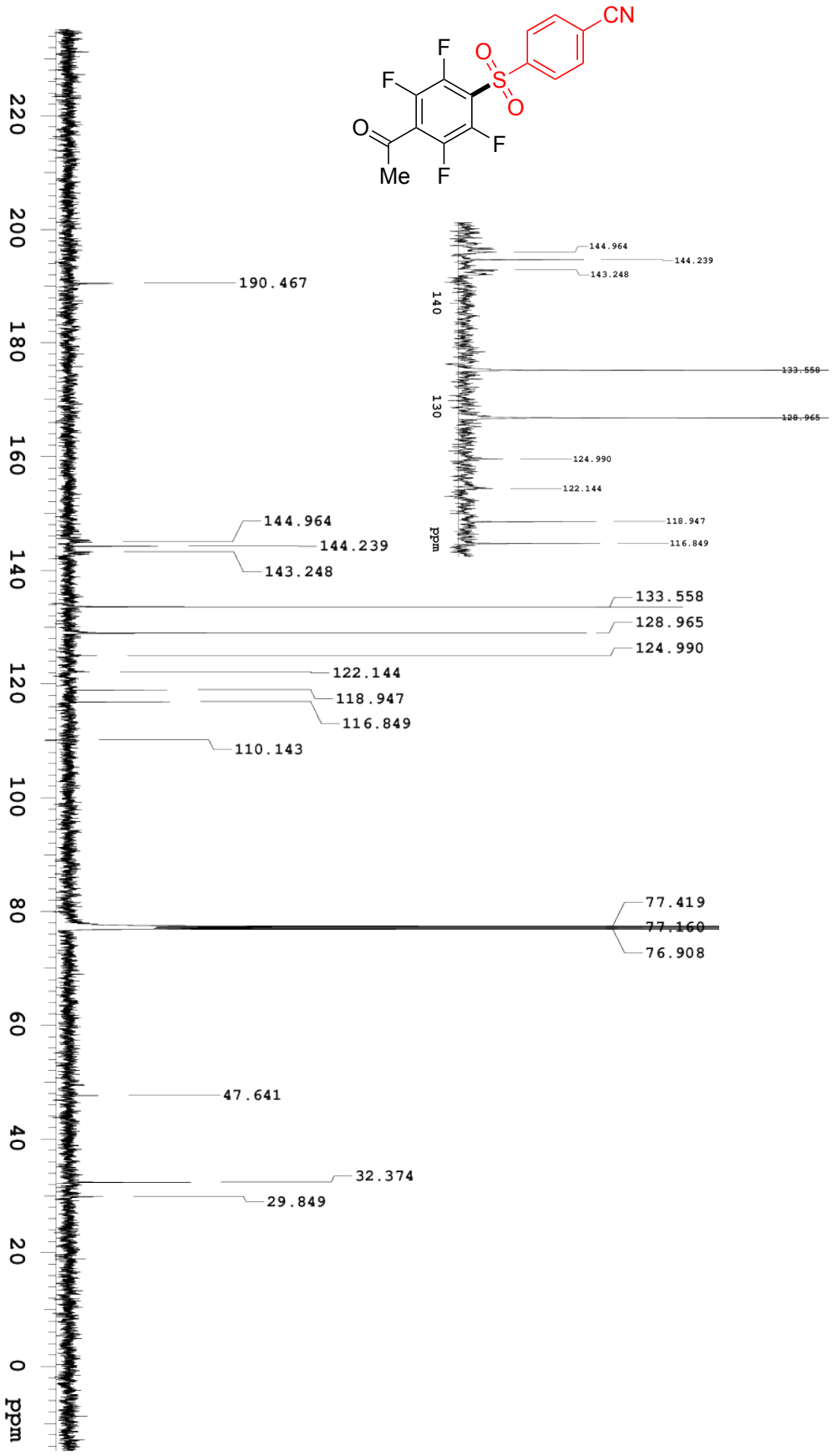

F
F
N
F
F
O
S
O
Me
147.490
145.722
145.515
145.208
144.976
144.384
142.912
140.849
140.271
139.905
137.562
137.197
136.384
130.677
128.696
22.021
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

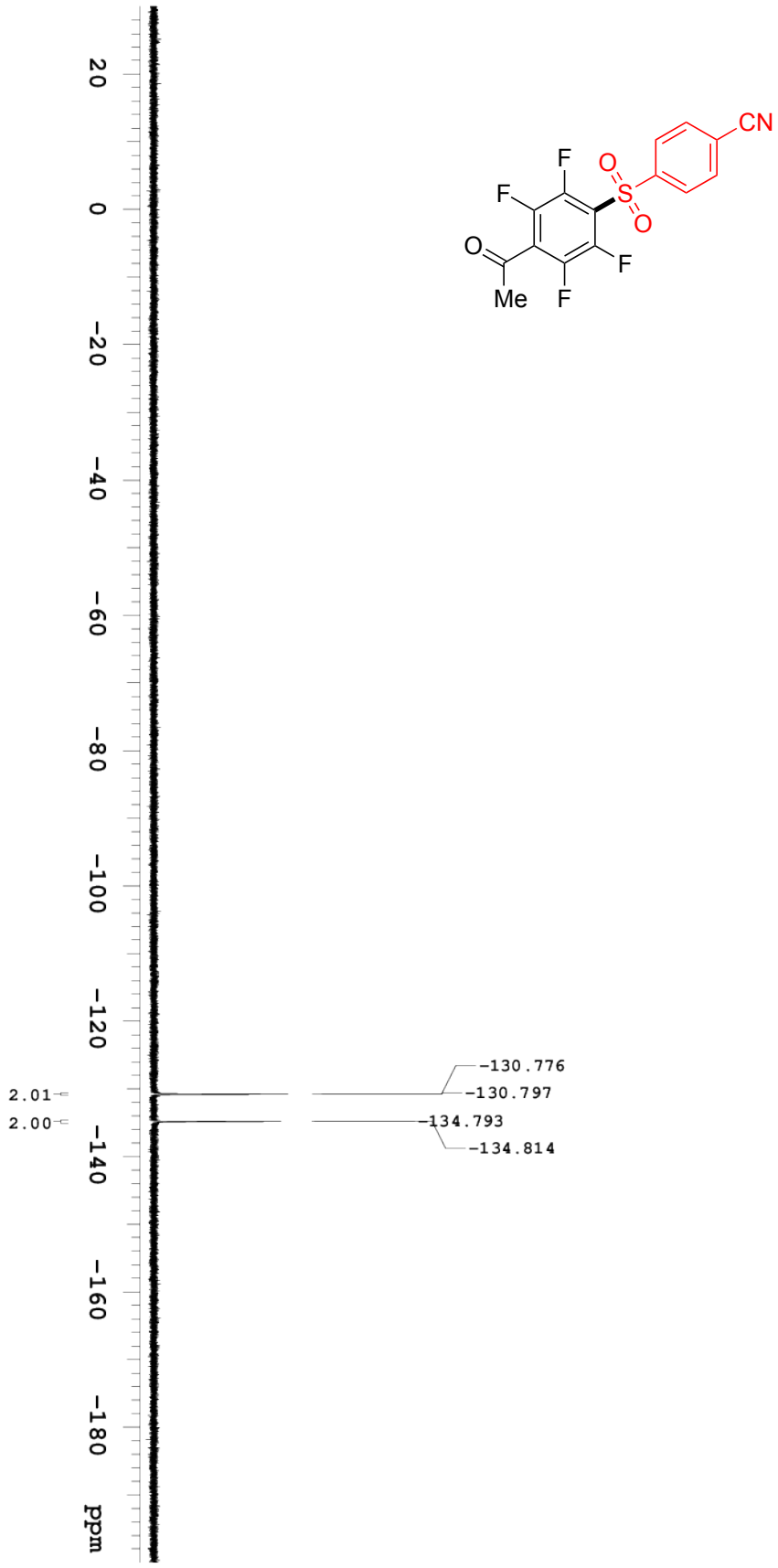

0.93
1.00
1.03
1.07
F
F
N
F
F
O
S
O
NO2
8.923
8.629
8.613
8.457
8.441
7.925
7.909
7.893
7.260
7.257
f1 (ppm)

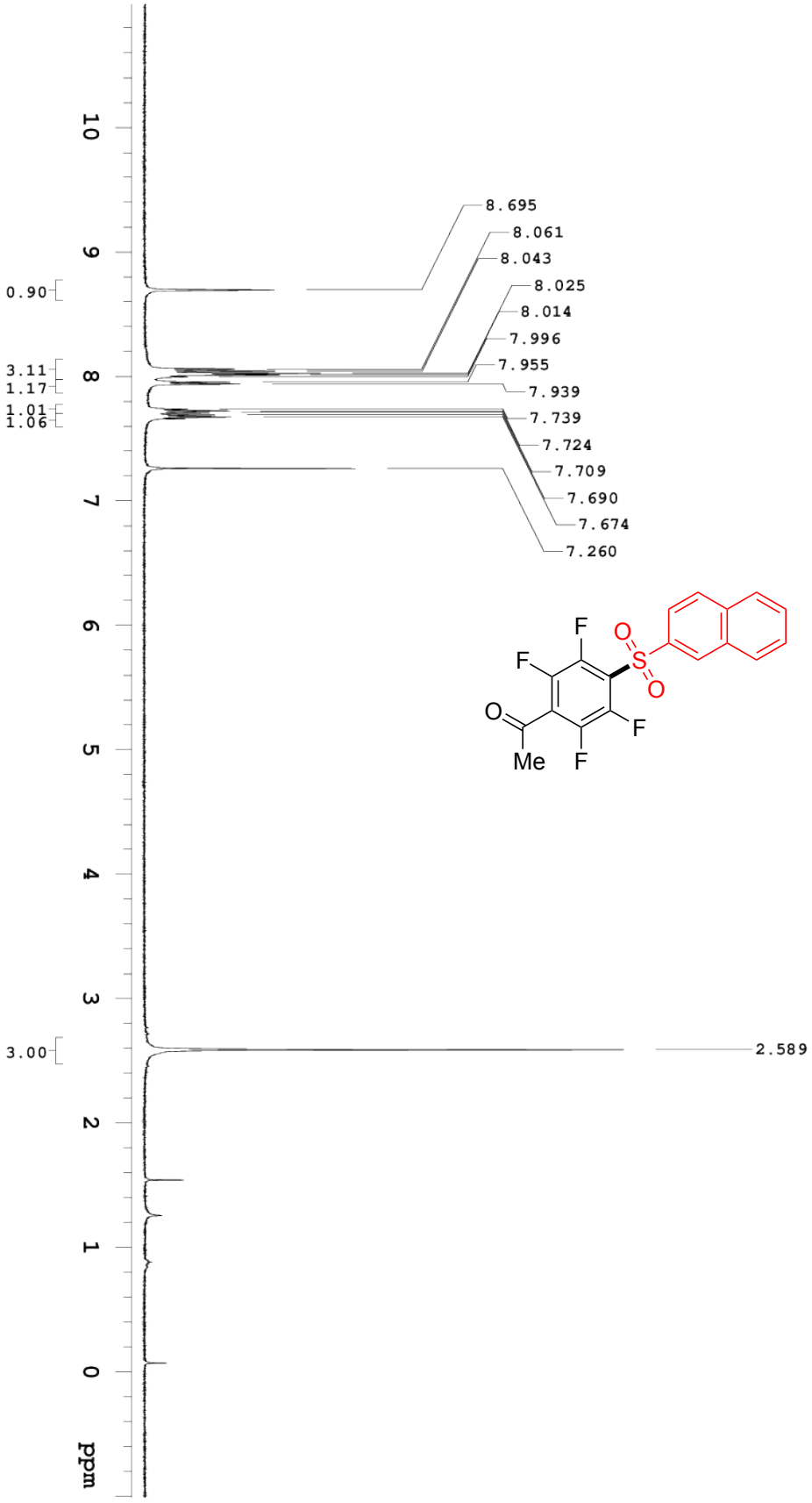

F
F
NO2
O
N
S
O
F
F
148.808
145.489
145.378
143.380
141.933
141.298
140.989
140.051
139.759
139.094
137.867
137.646
137.577
134.067
131.616
130.162
124.090
77.414
77.160
76.905
f1 (ppm)

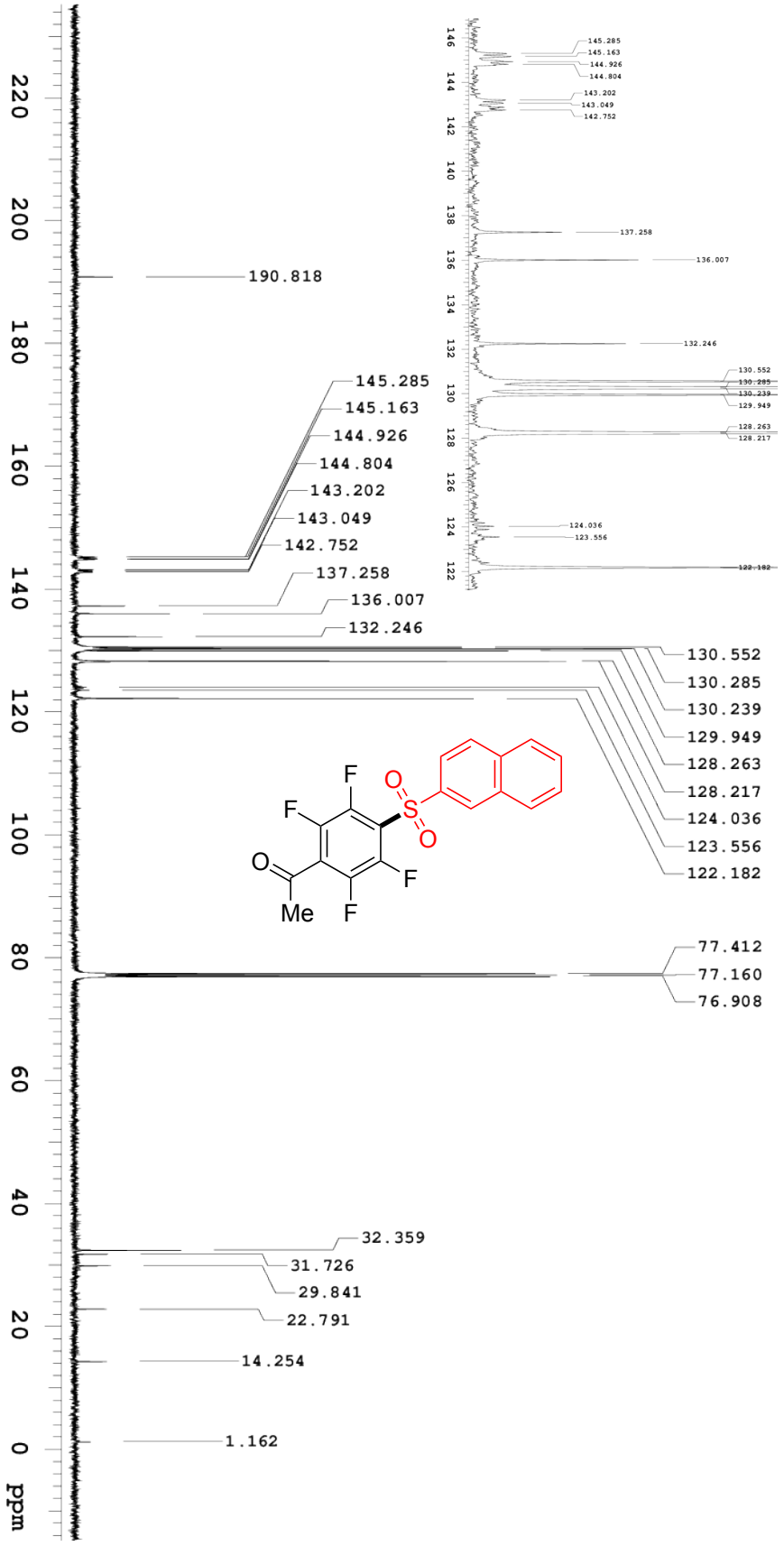

F
F
N
F
F
O
S
O
NO2
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
2.04
-84.403
-84.421
-84.431
-84.446
-84.474
-84.495
-84.526
-84.537
-84.547
-84.568
2.00
-136.306
-136.327
-136.337
-136.348
-136.379
-136.400
-136.428
-136.442
-136.453
-136.471

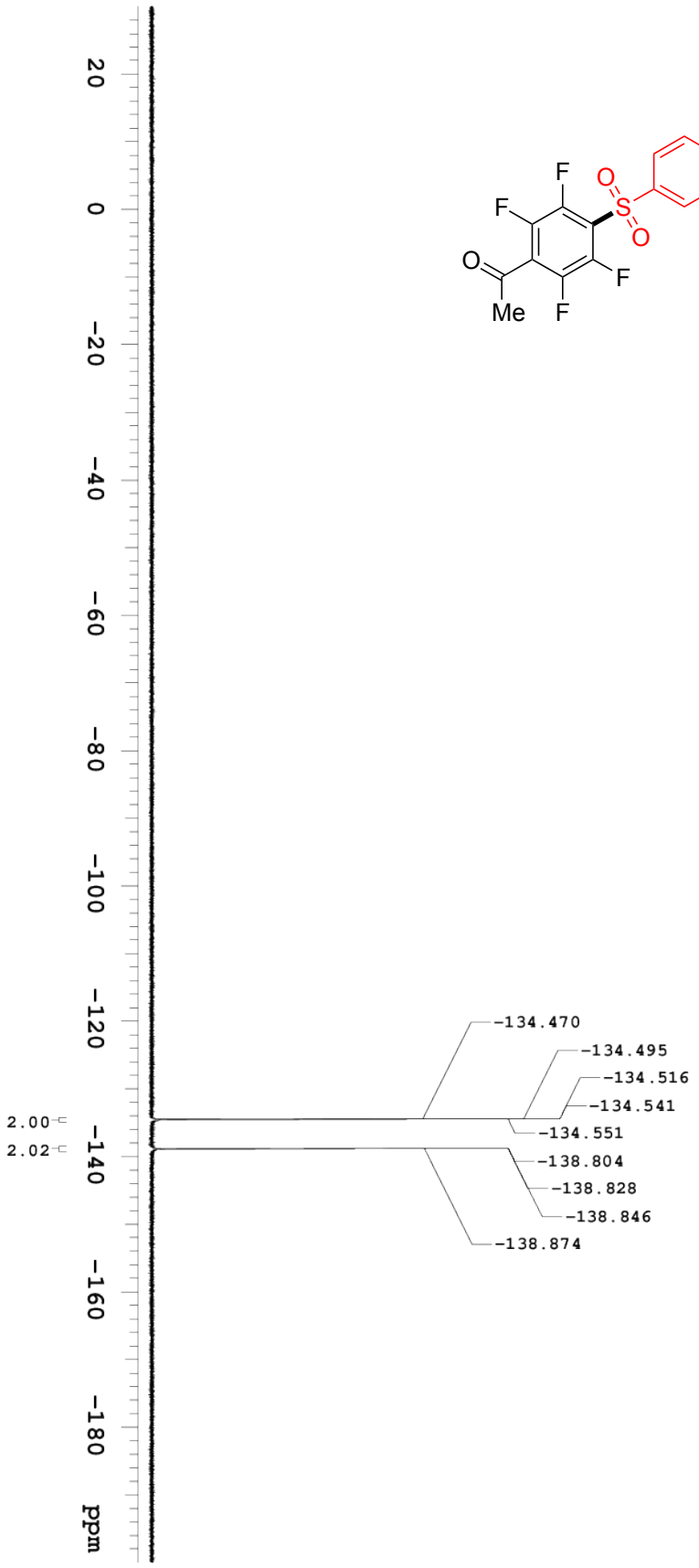

CN
F
O
S
O
F
O
F
Me
F
8.225
8.208
7.921
7.905
7.260
2.616
1.532
1.98
1.99
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm

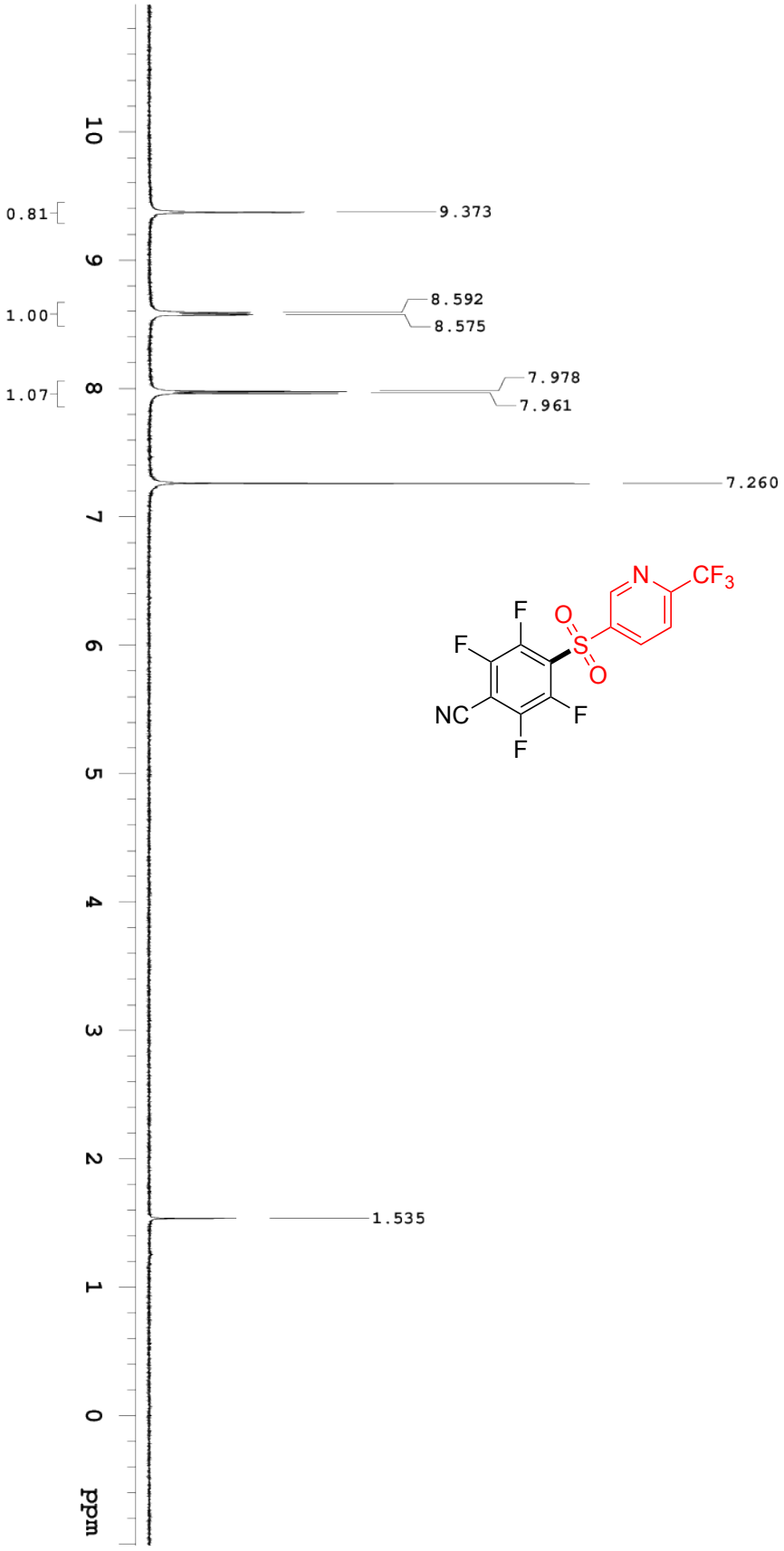

CN
F
F
O
S
O
O
F
Me
F
190.467
144.964
144.239
143.248
133.558
128.965
124.990
122.144
118.947
116.849
110.143
77.419
77.160
76.908
47.641
32.374
29.849
220
200
180
160
140
120
100
80
60
40
20
0
ppm
140
130
ppm

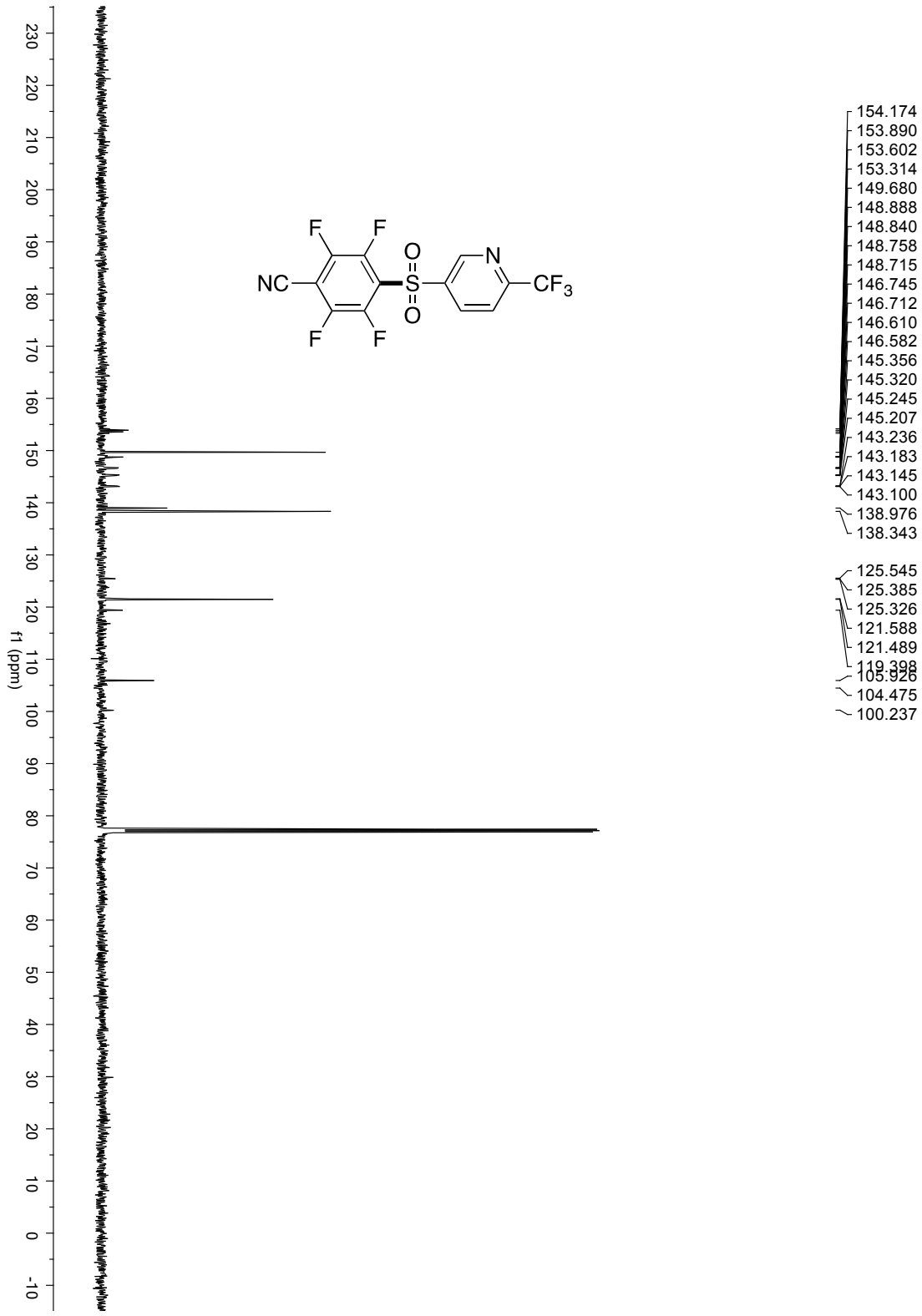

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
2.01
2.00
-130.776
-130.797
-134.793
-134.814
CN
F
F
O
S
O
O
F
Me
F

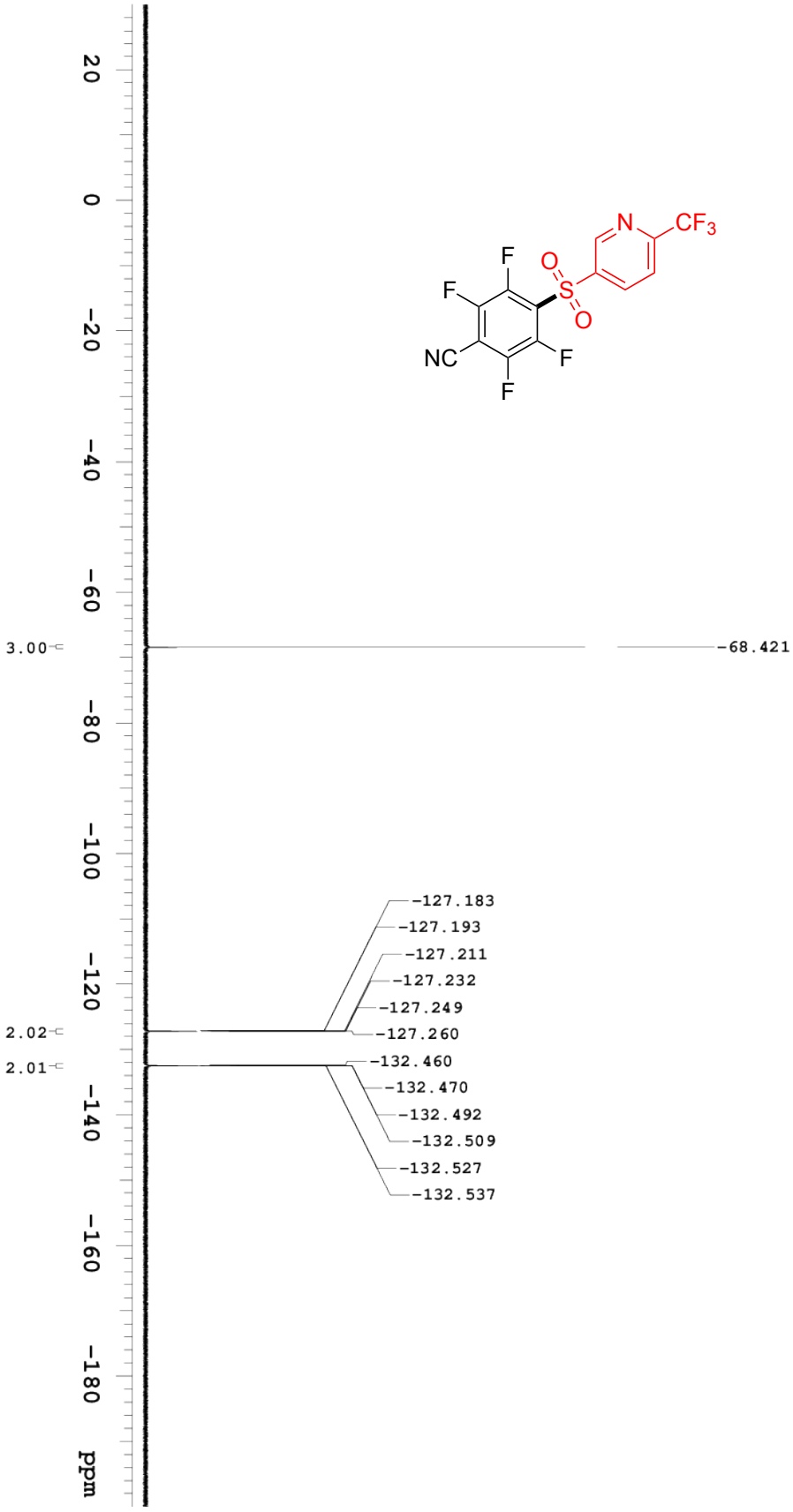

8.695
8.061
8.043
8.025
8.014
7.996
7.955
7.939
7.739
7.724
7.709
7.690
7.674
7.260
2.589
0.90
3.11
1.17
1.01
1.06
3.00
F
F
O
S
O
O
F
Me
F
10
9
8
7
6
5
4
3
2
1
0
ppm

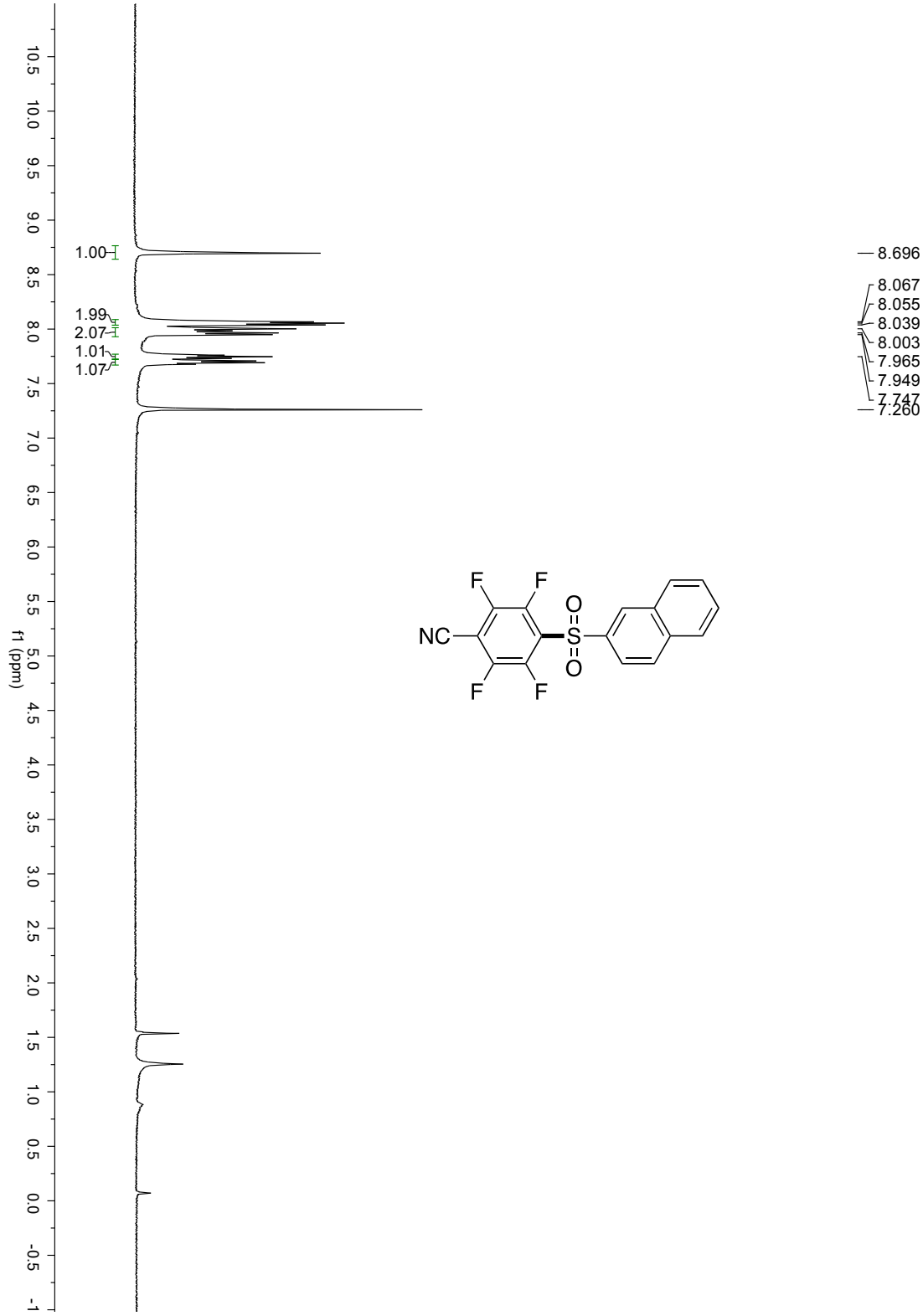

190.818
145.285
145.163
144.926
144.804
143.202
143.049
142.752
137.258
136.007
132.246
130.552
130.285
130.239
129.949
128.263
128.217
124.036
123.556
122.182
77.412
77.160
76.908
32.359
31.726
29.841
22.791
14.254
1.162
ppm
F
F
O
S
O
O
F
F
Me

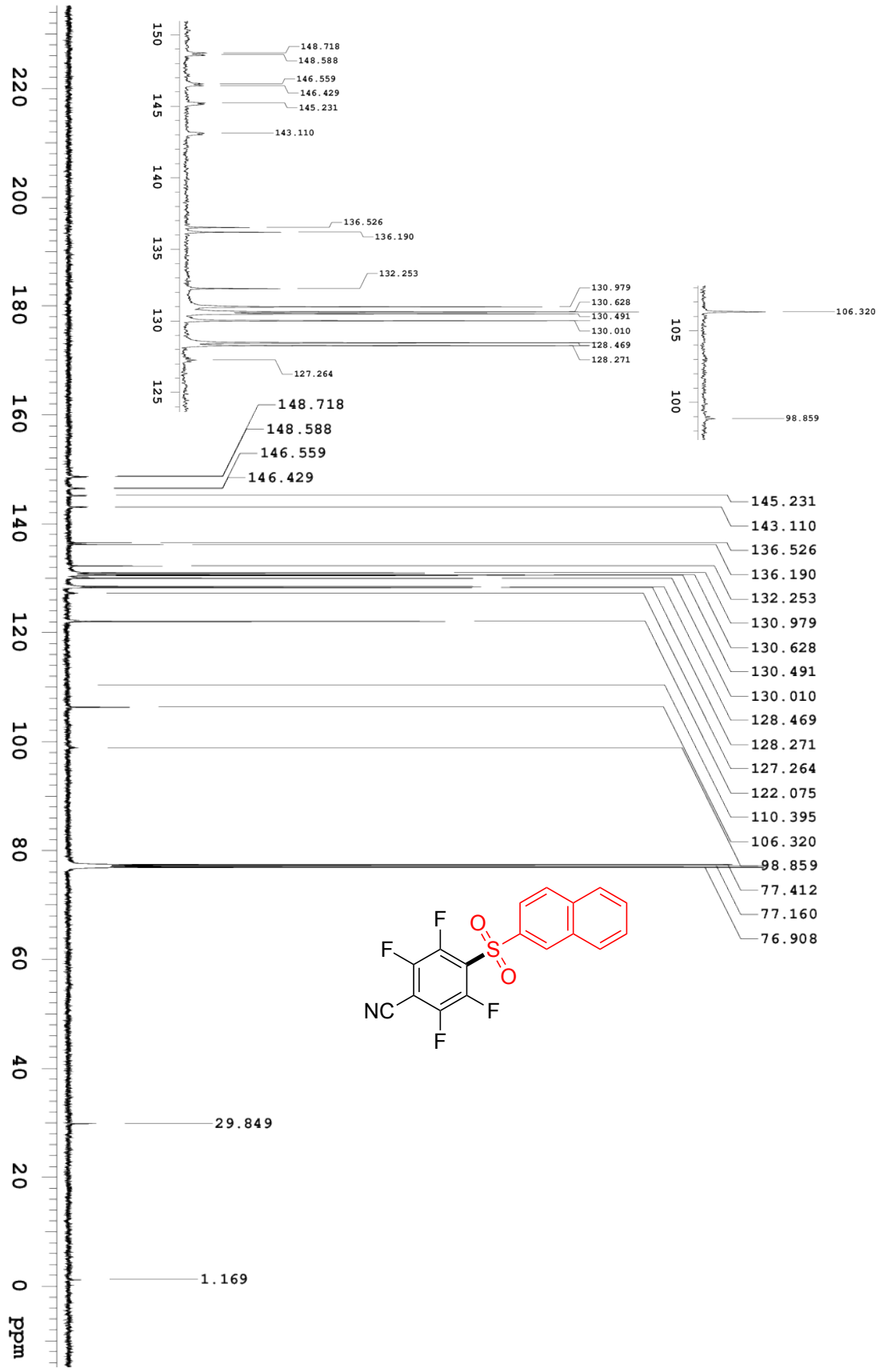

F
O
S
O
F
O
F
Me
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
-134.470
-134.495
-134.516
-134.541
-134.551
-138.804
-138.828
-138.846
-138.874
2.00
2.02


0.81
1.00
1.07
9.373
8.592
8.575
7.978
7.961
7.260
1.535
10
9
8
7
6
5
4
3
2
1
0
ppm
N
CF3
F
O
S
O
F
NC
F
F


F
F
O
N
NC
S
CF3
O
F
F
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
154.174
153.890
153.602
153.314
149.680
148.888
148.840
148.758
148.715
146.745
146.712
146.610
146.582
145.356
145.320
145.245
145.207
143.236
143.183
143.145
143.100
138.976
138.343
125.545
125.385
125.326
121.588
121.489
119.398
105.926
104.475
100.237


F
F
O
S
O
N
CF3
NC
F
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
3.00
-68.421
2.02
2.01
-127.183
-127.193
-127.211
-127.232
-127.249
-127.260
-132.460
-132.470
-132.492
-132.509
-132.527
-132.537


1.00
1.99
2.07
1.01
1.07
8.696
8.067
8.055
8.039
8.003
7.965
7.949
7.747
7.260
F
F
NC
O
S
O
F
F
f1 (ppm)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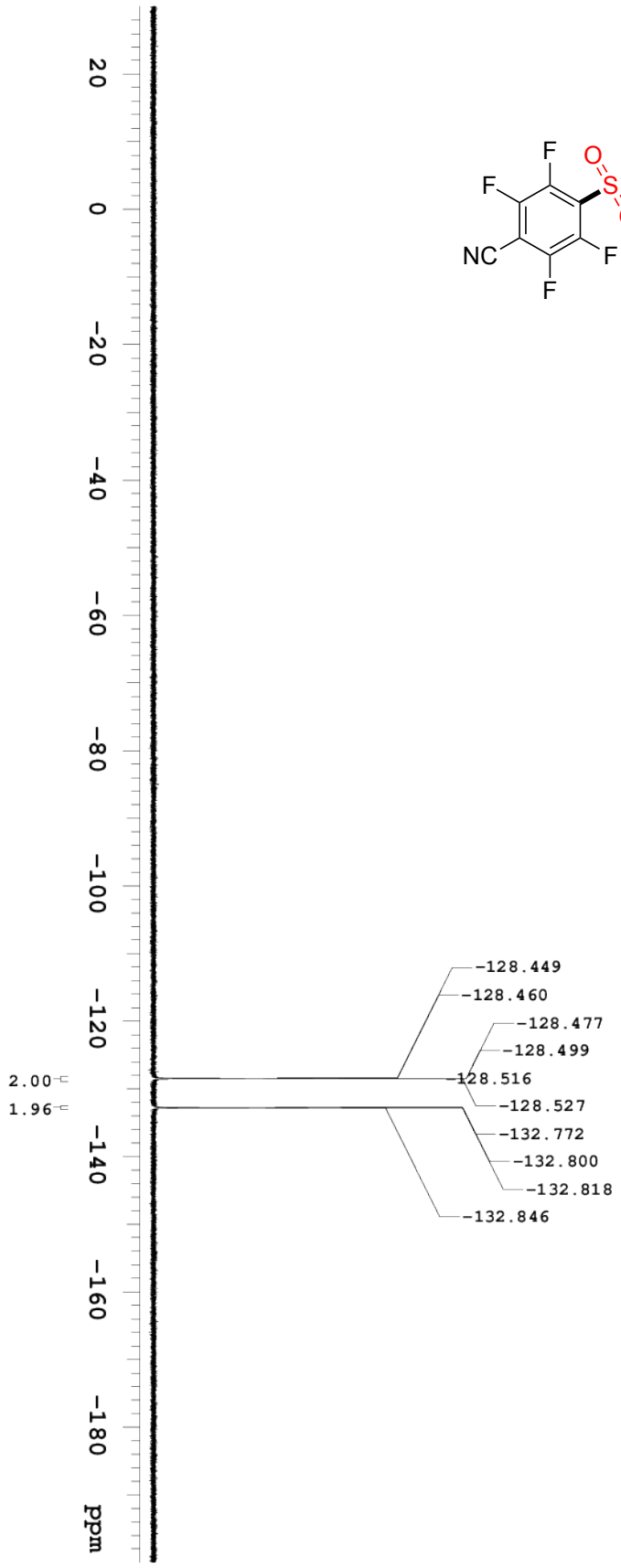
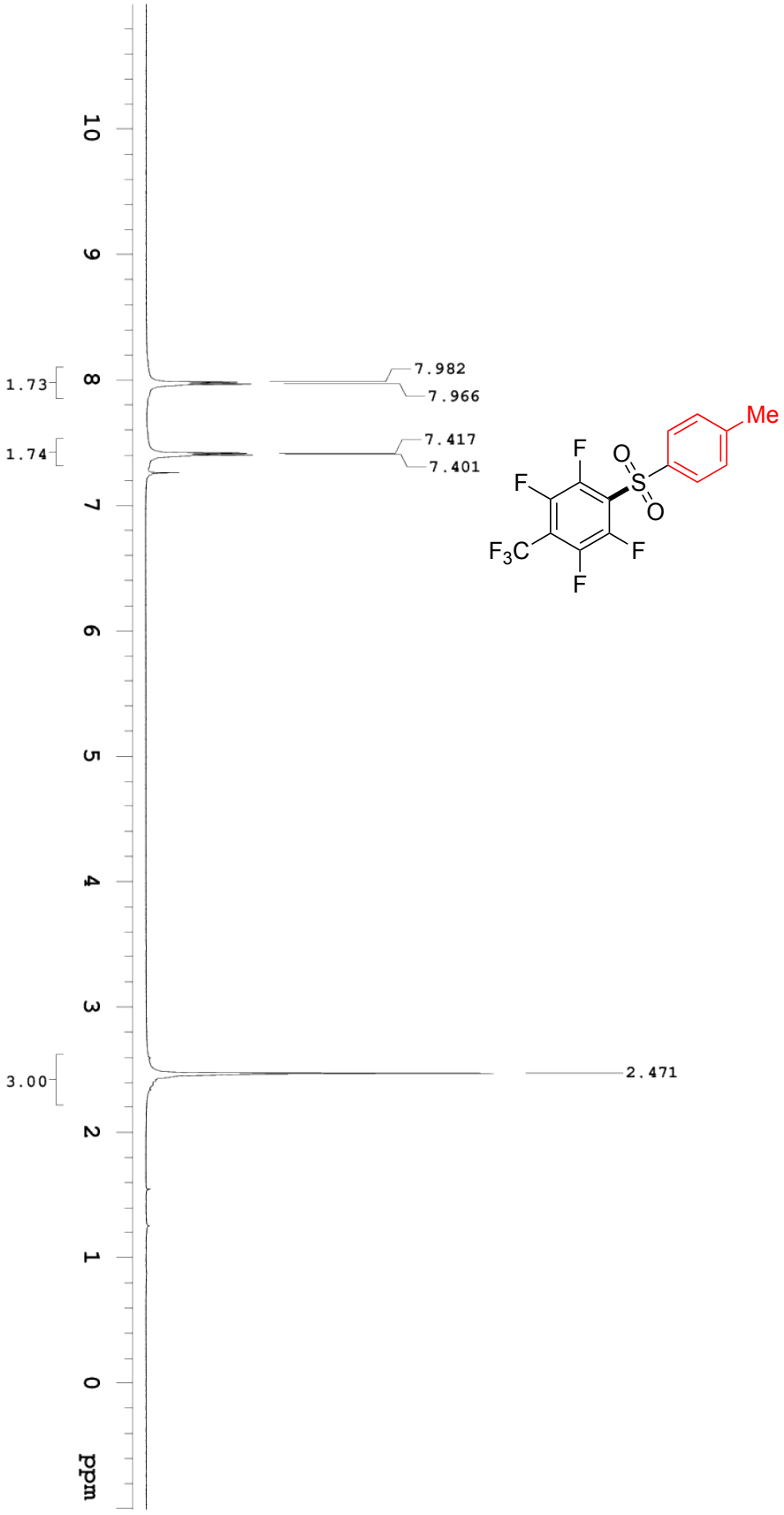
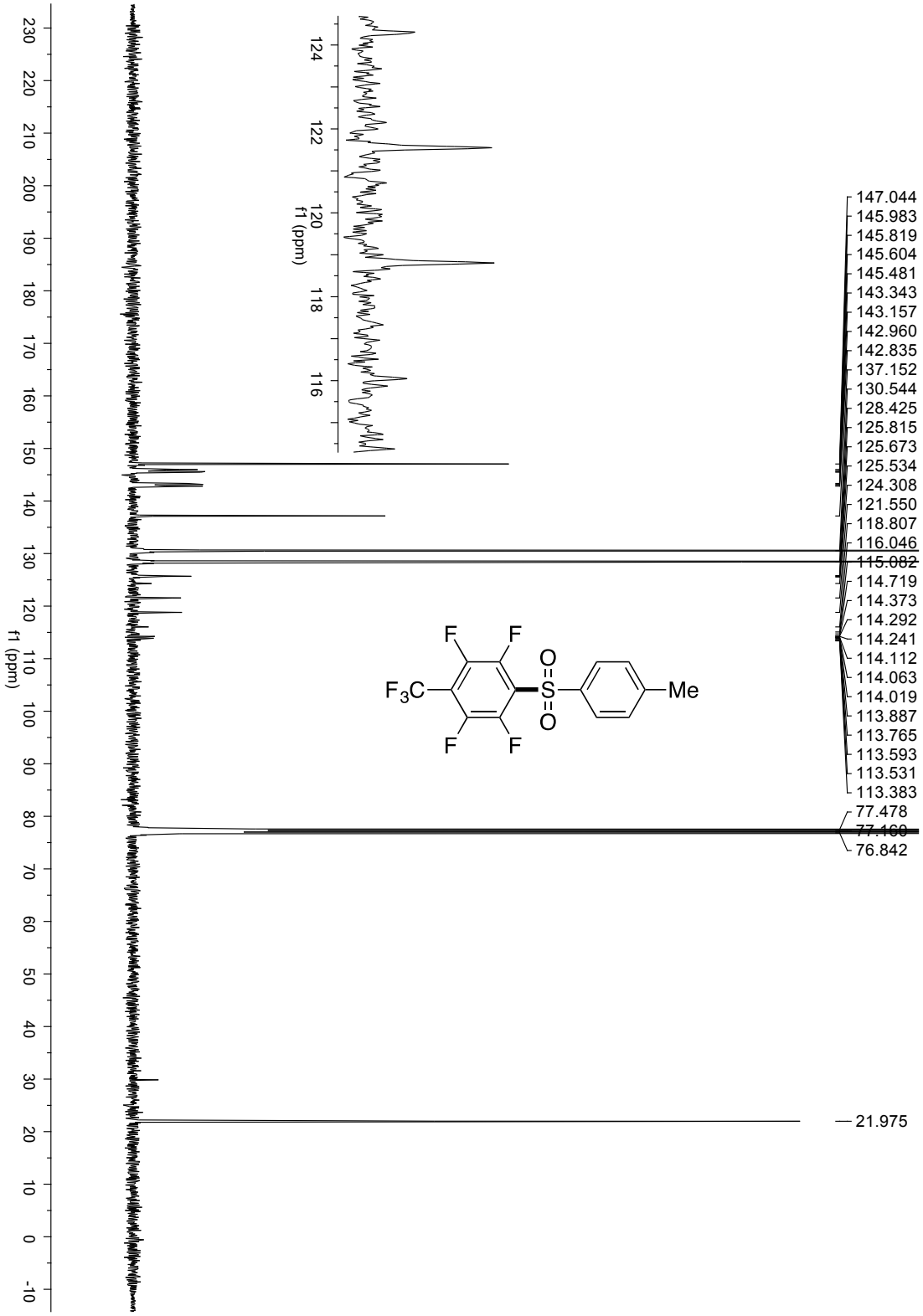
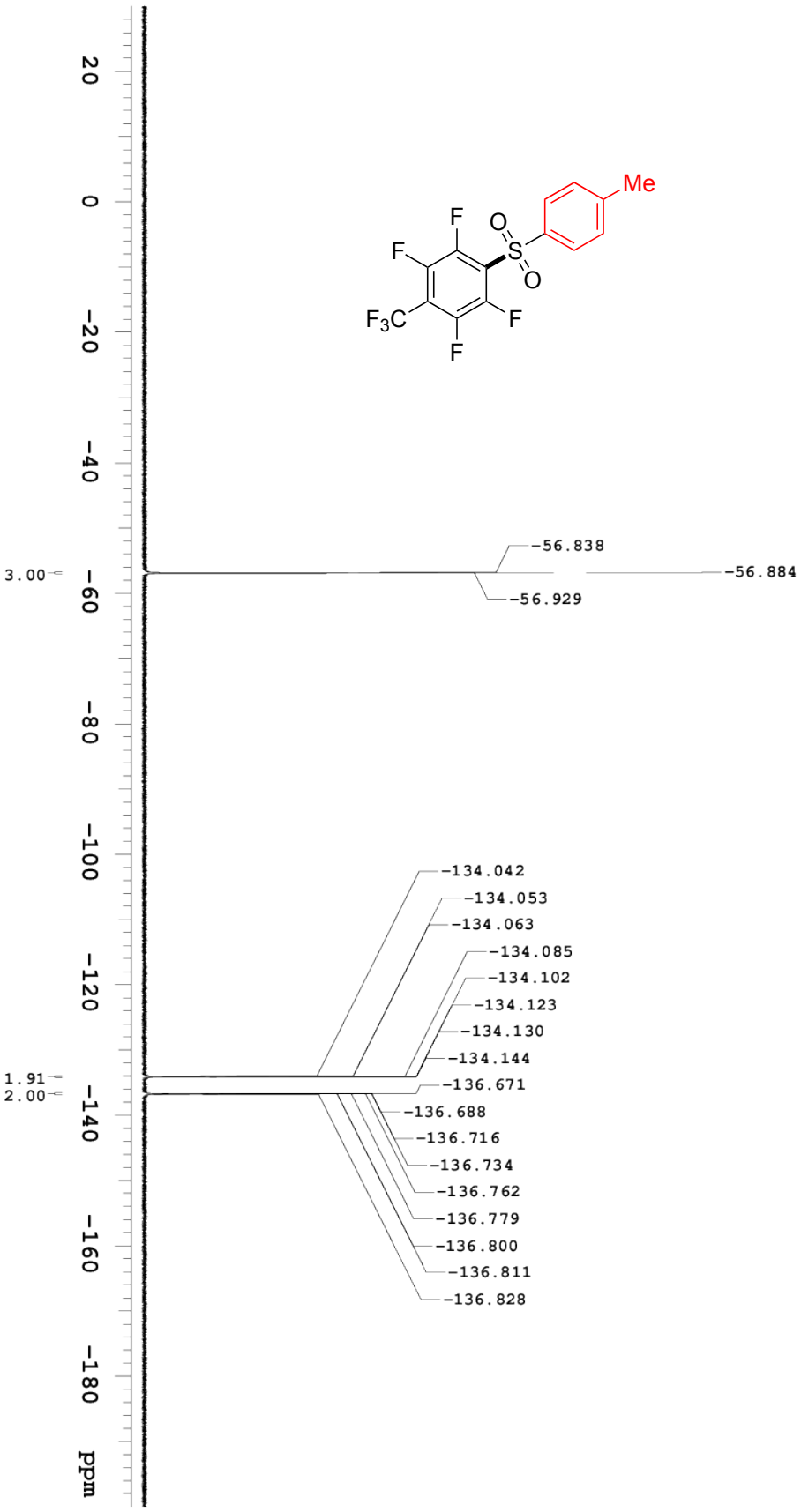
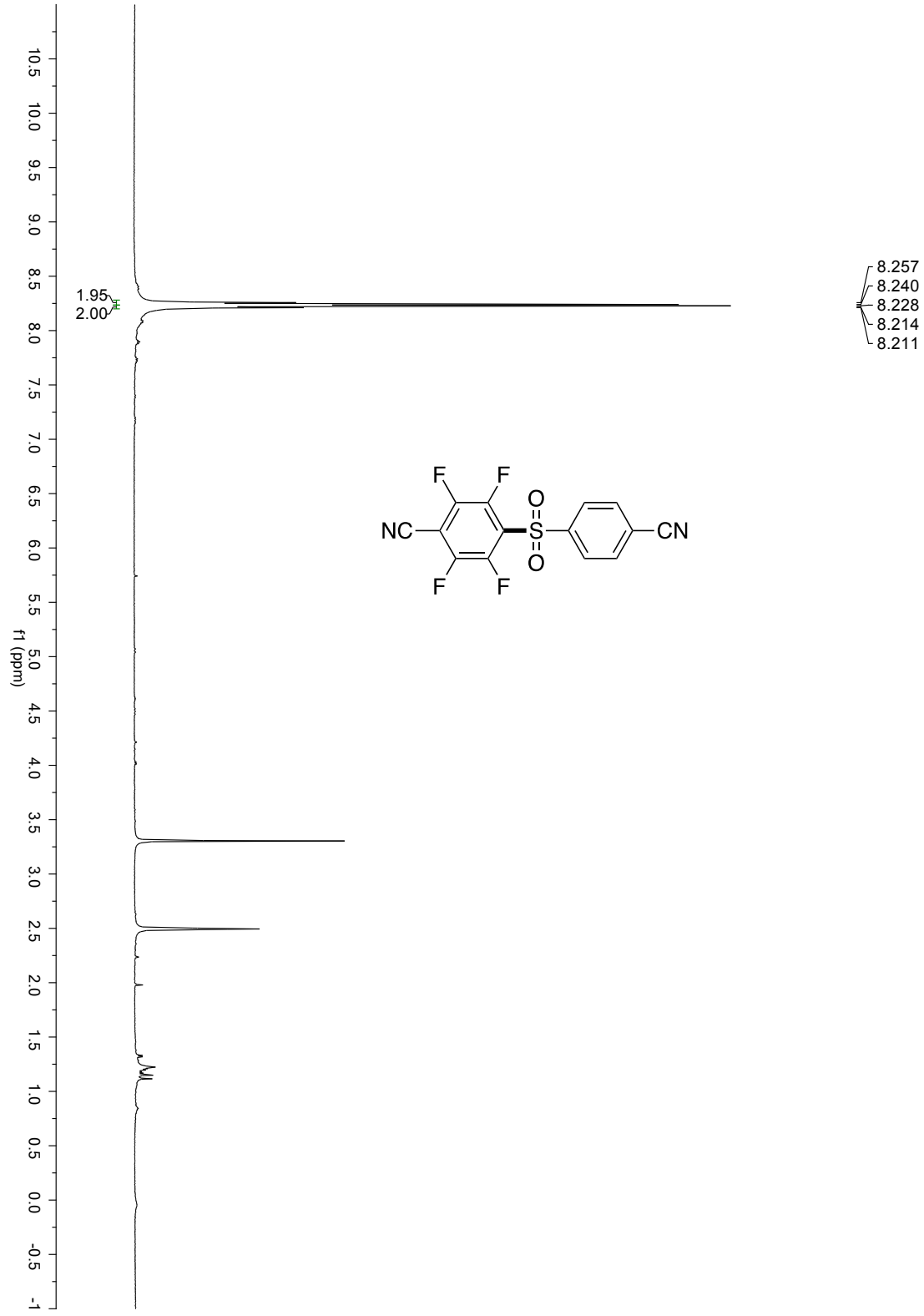
148.588
146.559
146.429
145.231
143.110
136.526
136.190
132.253
130.979
130.628
130.491
130.010
128.469
128.271
127.264
122.075
110.395
106.320
98.859
77.412
77.160
76.908
29.849
1.169
ppm
F
F
O
S
O
NC
F
F

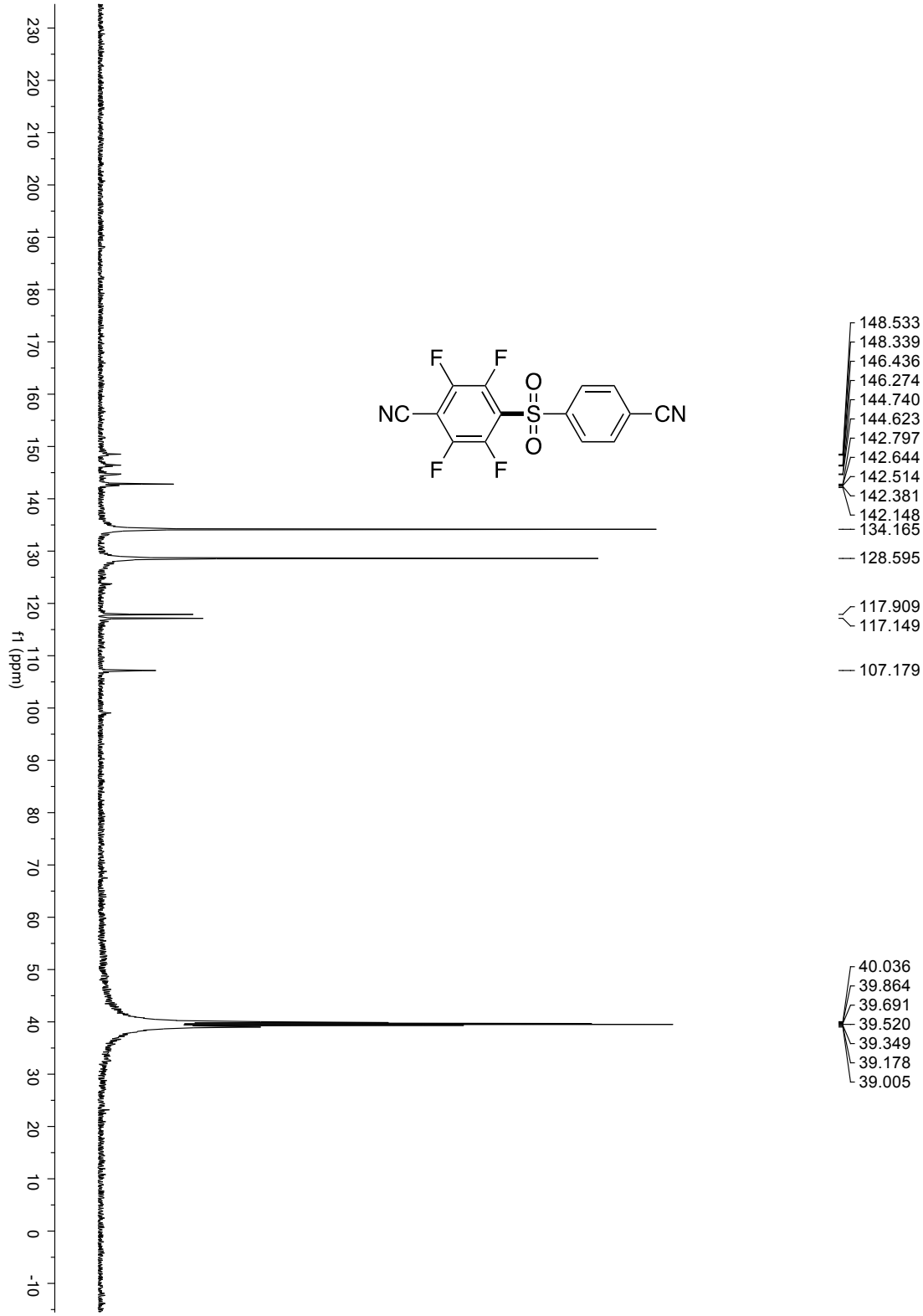

F
F
O
S
O
NC
F
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
-128.449
-128.460
-128.477
-128.499
-128.516
-128.527
-132.772
-132.800
-132.818
-132.846
2.00
1.96

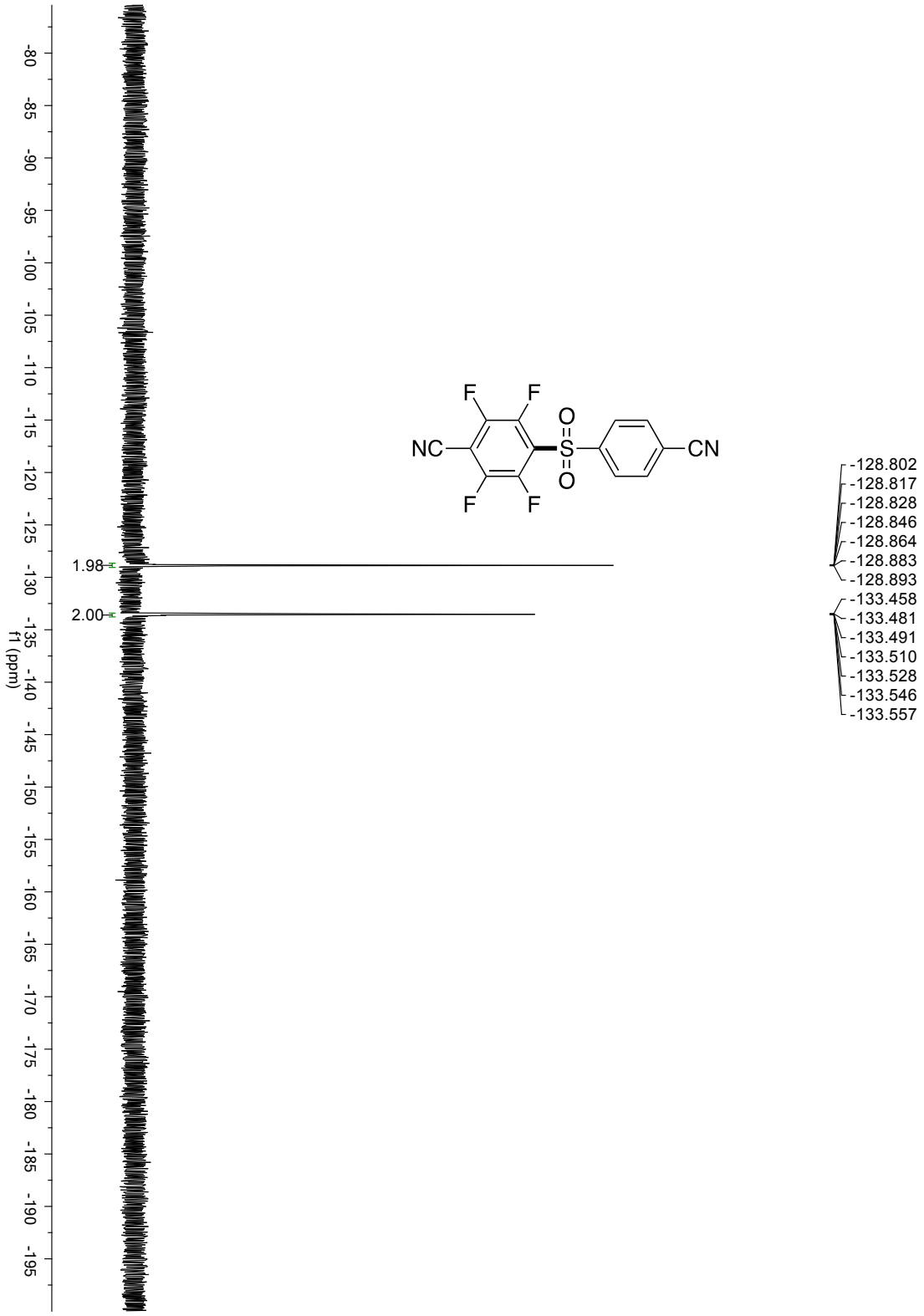

7.982
7.966
7.417
7.401
2.471
1.73
1.74
3.00
Me
F
O
S
O
F
F3C
F
F
10
9
8
7
6
5
4
3
2
1
0
ppm

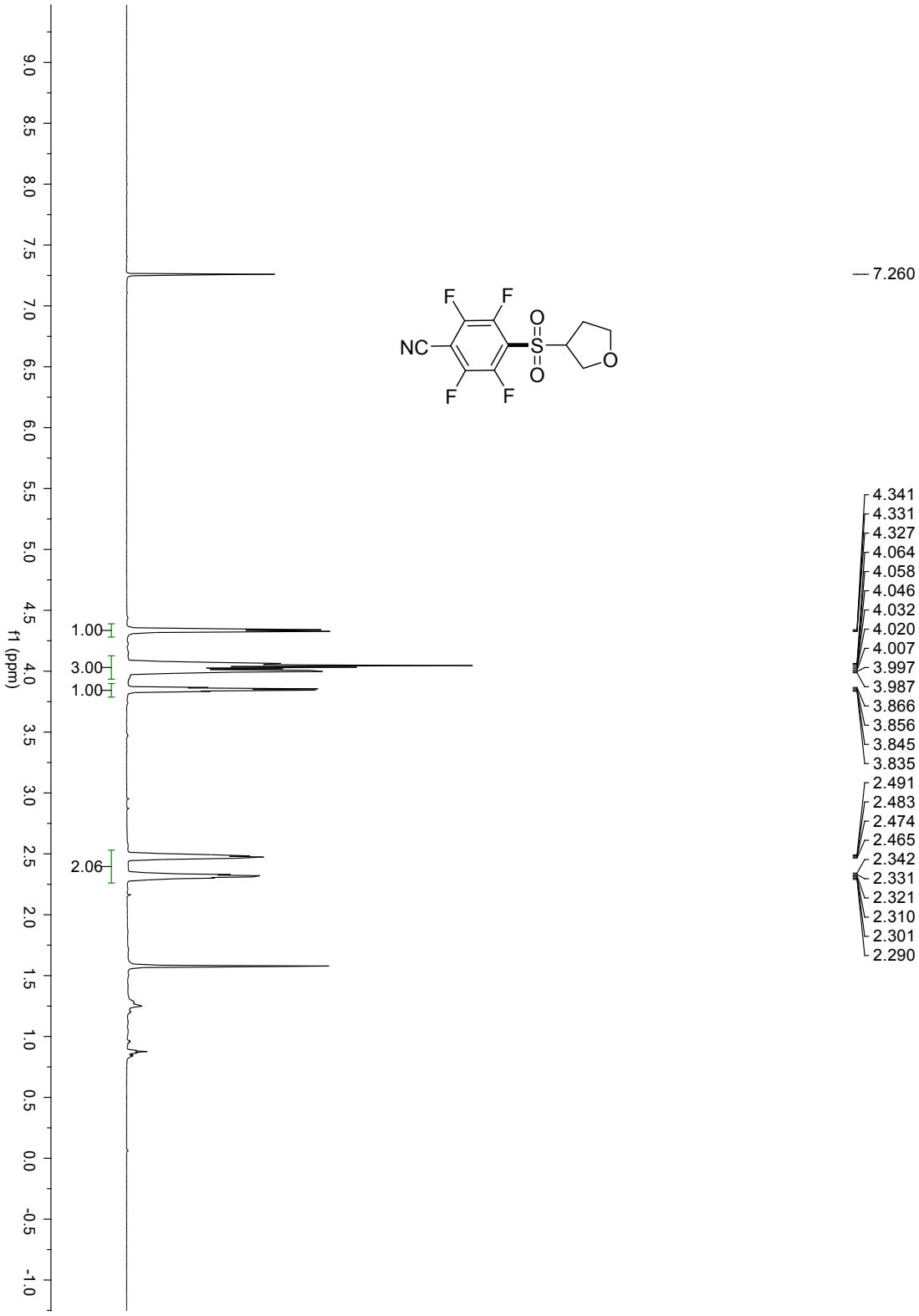

147.044
145.983
145.819
145.604
145.481
143.343
143.157
142.960
142.835
137.152
130.544
128.425
125.815
125.673
125.534
124.308
121.550
118.807
116.046
115.082
114.719
114.373
114.292
114.241
114.112
114.063
114.019
113.887
113.765
113.593
113.531
113.383
77.478
77.160
76.842
21.975
f1 (ppm)
F
F
F3C
O
S
O
Me
F
F

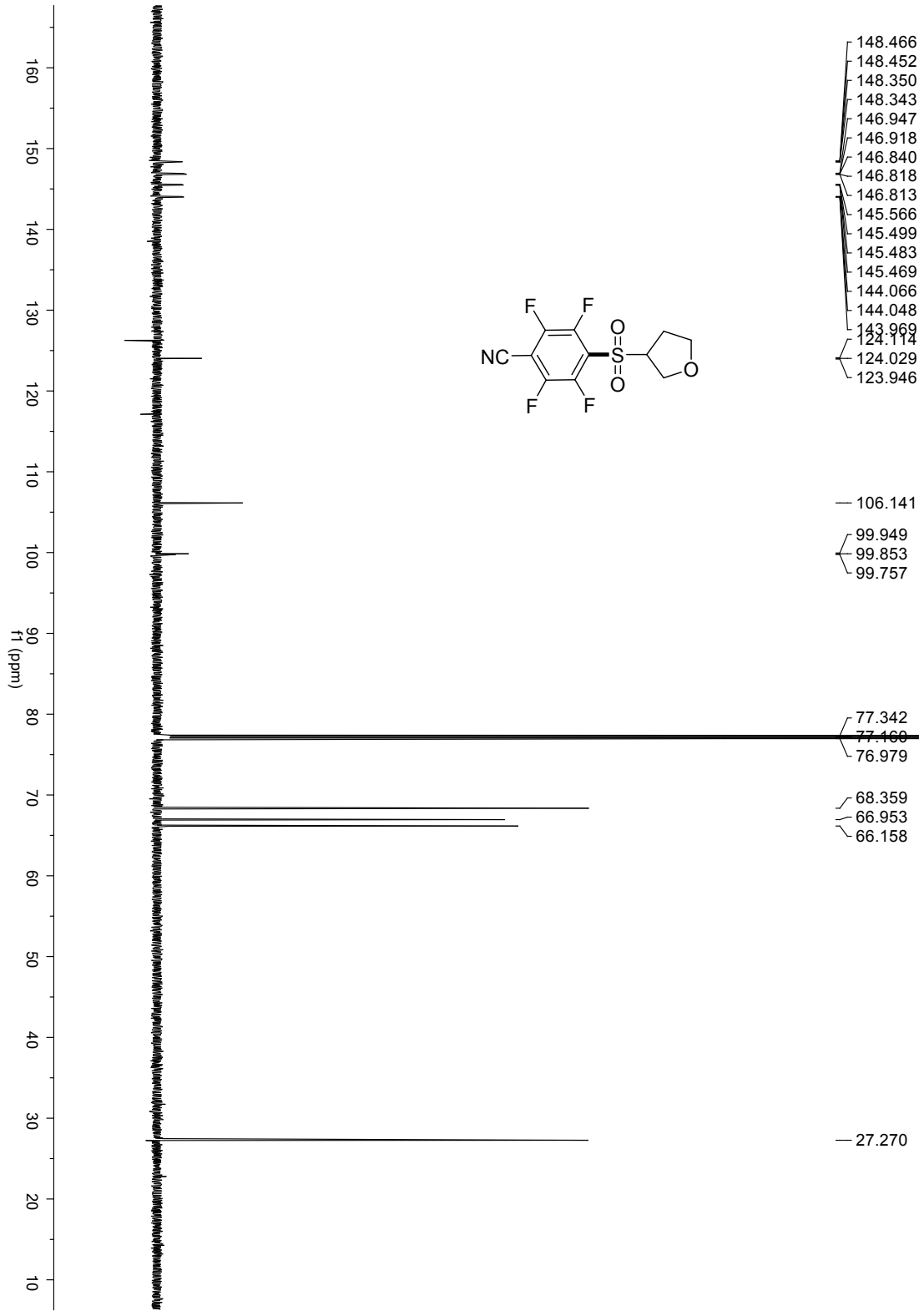

Me
F
O
S
O
F
F3C
F
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
3.00
1.91
2.00
-56.838
-56.884
-56.929
-134.042
-134.053
-134.063
-134.085
-134.102
-134.123
-134.130
-134.144
-136.671
-136.688
-136.716
-136.734
-136.762
-136.779
-136.800
-136.811
-136.828

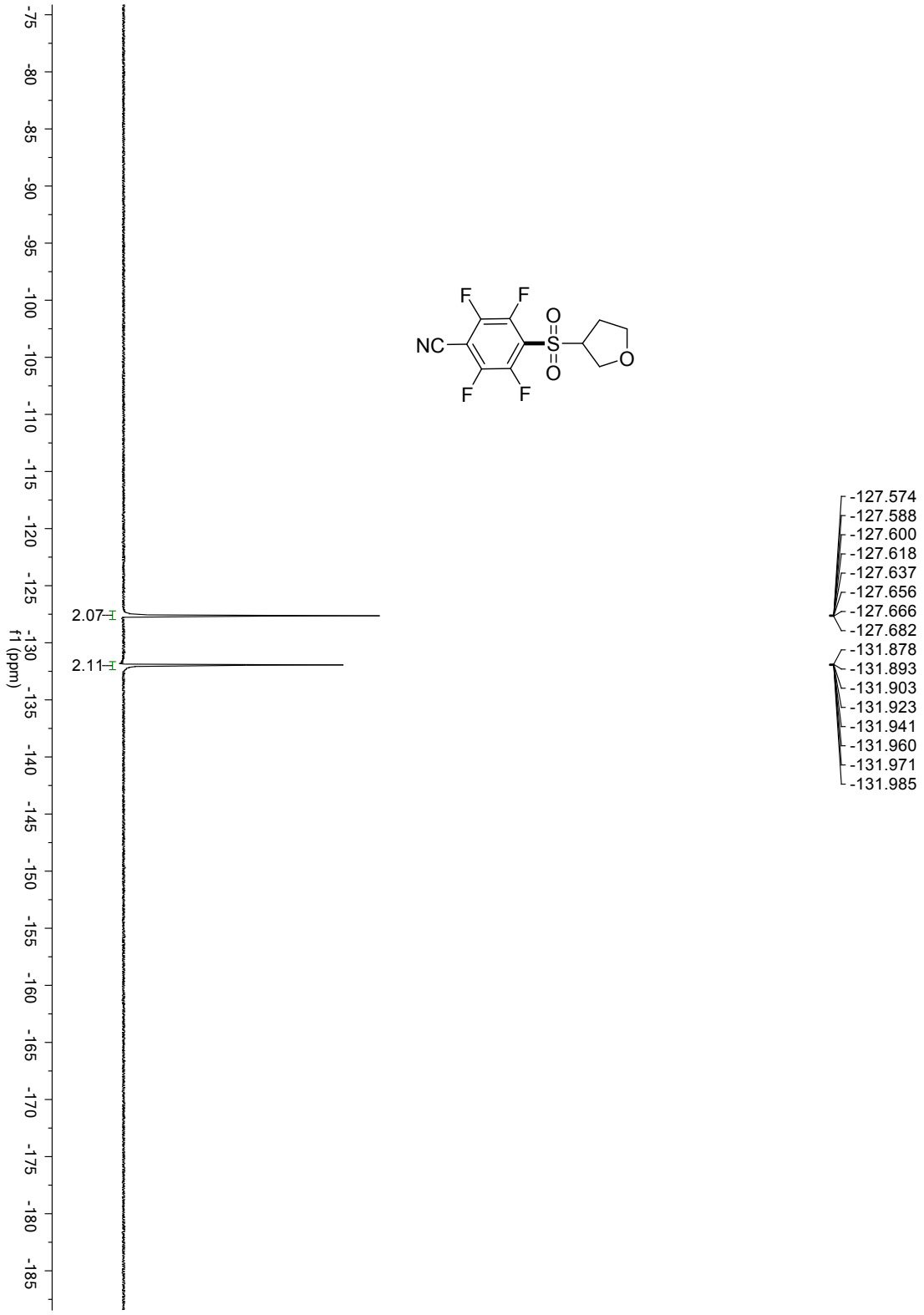

1.95
2.00
8.257
8.240
8.228
8.214
8.211
F
F
O
NC
S
CN
O
F
F
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

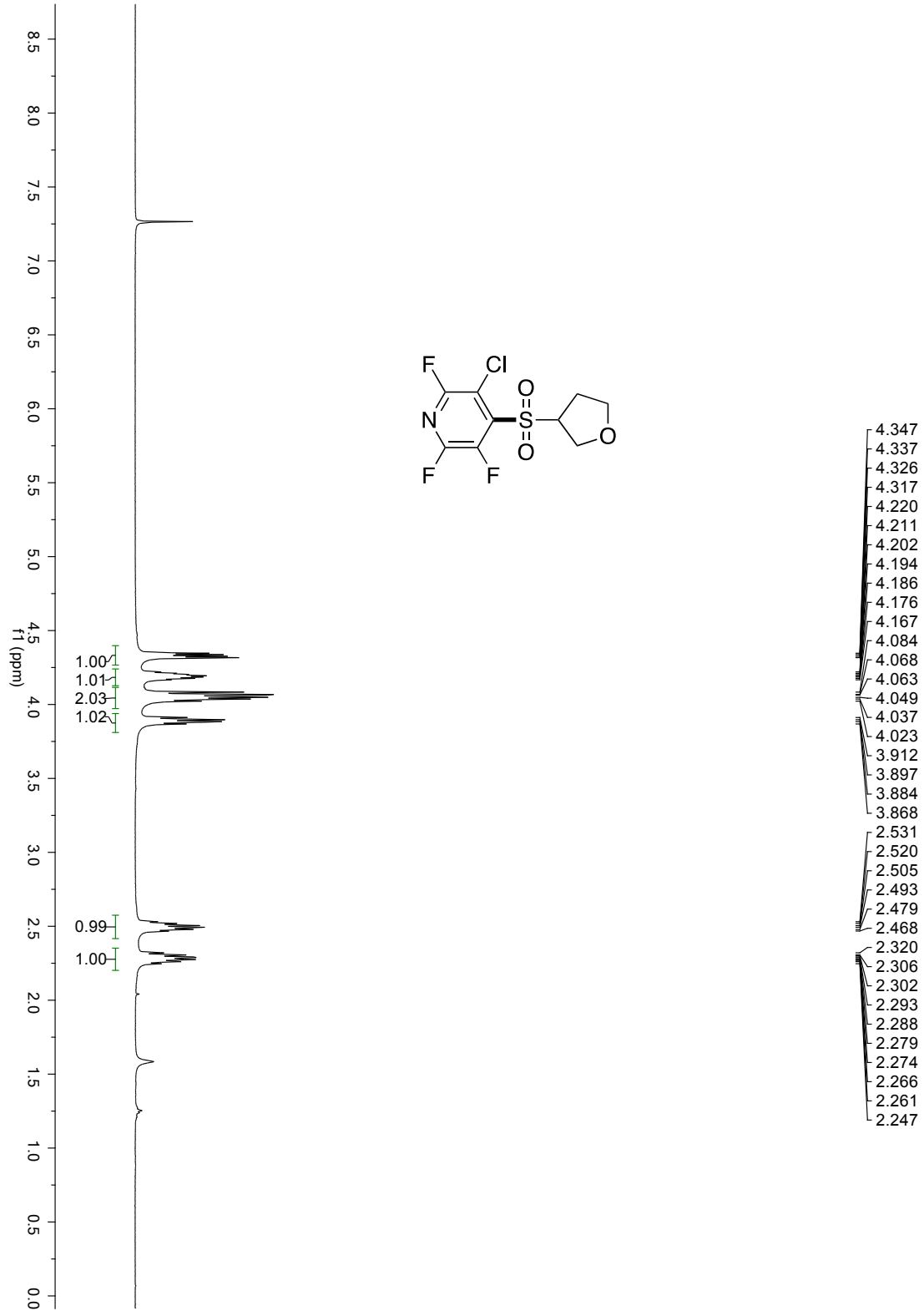

F
F
O
NC
S
CN
O
F
F
148.533
148.339
146.436
146.274
144.740
144.623
142.797
142.644
142.514
142.381
142.148
134.165
128.595
117.909
117.149
107.179
40.036
39.864
39.691
39.520
39.349
39.178
39.005
f1 (ppm)

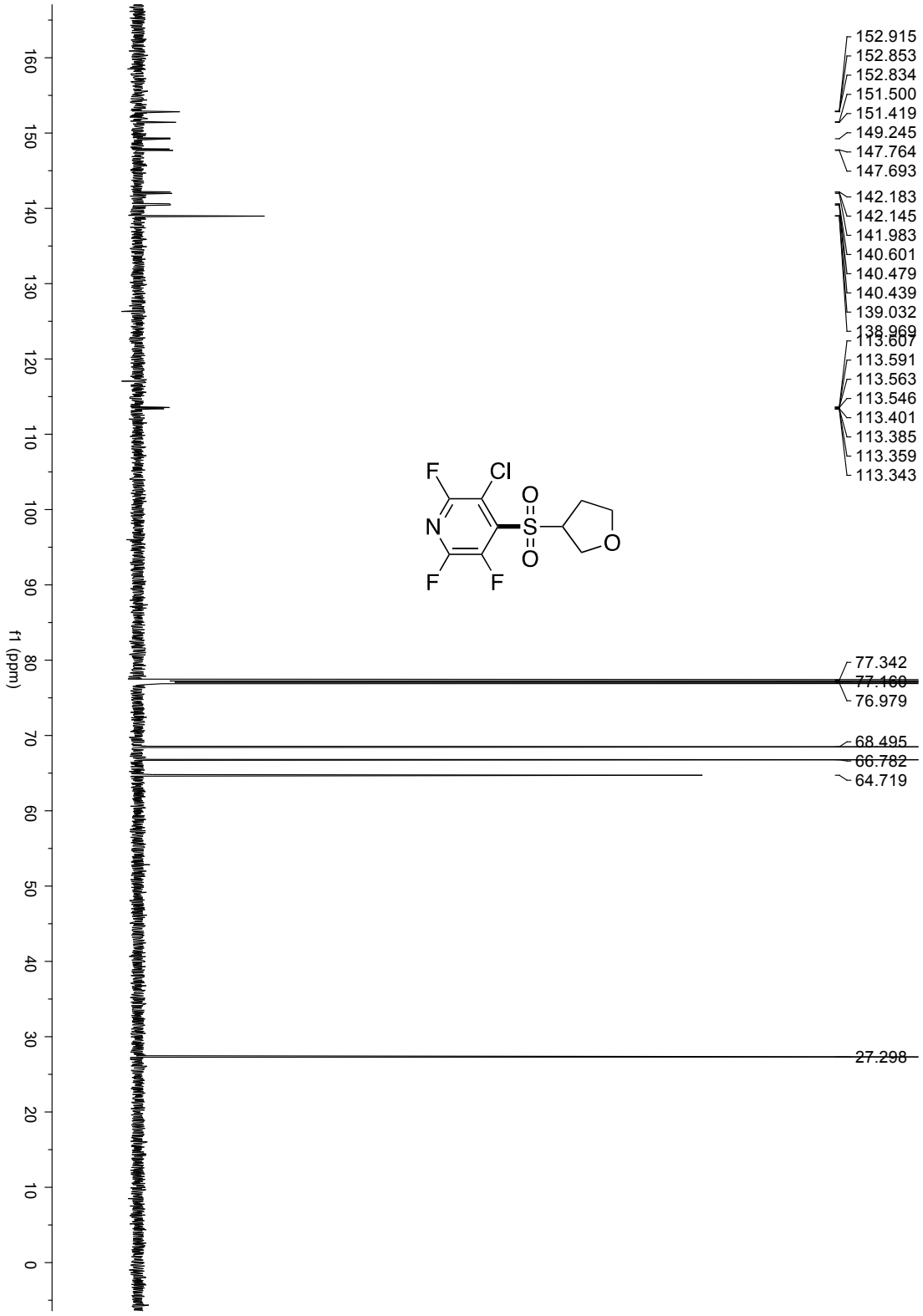

F
F
O
NC
S
CN
O
F
F
-128.802
-128.817
-128.828
-128.846
-128.864
-128.883
-128.893
-133.458
-133.481
-133.491
-133.510
-133.528
-133.546
-133.557
1.98
2.00
f1 (ppm)

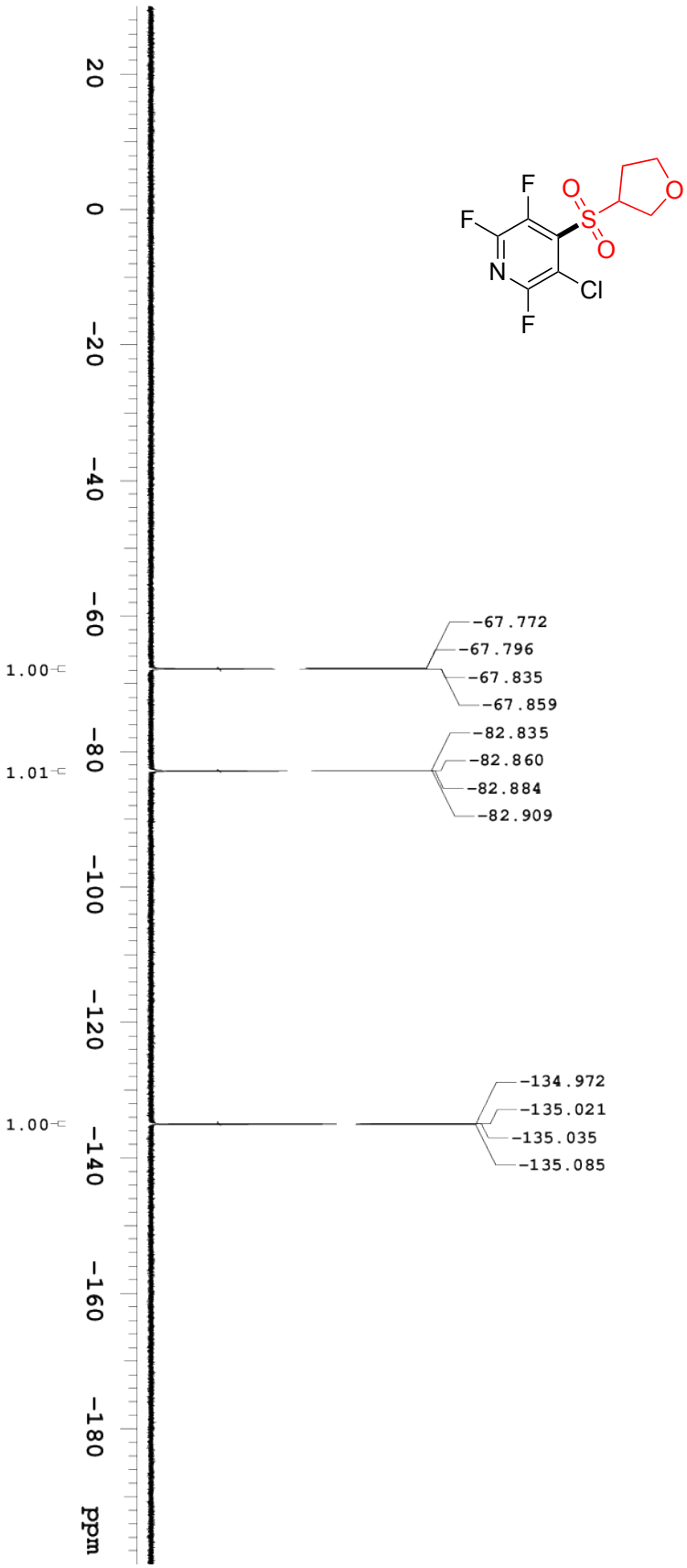

F
F
NC
O
S
O
O
F
F
7.260
4.341
4.331
4.327
4.064
4.058
4.046
4.032
4.020
4.007
3.997
3.987
3.866
3.856
3.845
3.835
2.491
2.483
2.474
2.465
2.342
2.331
2.321
2.310
2.301
2.290
1.00
3.00
1.00
2.06
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

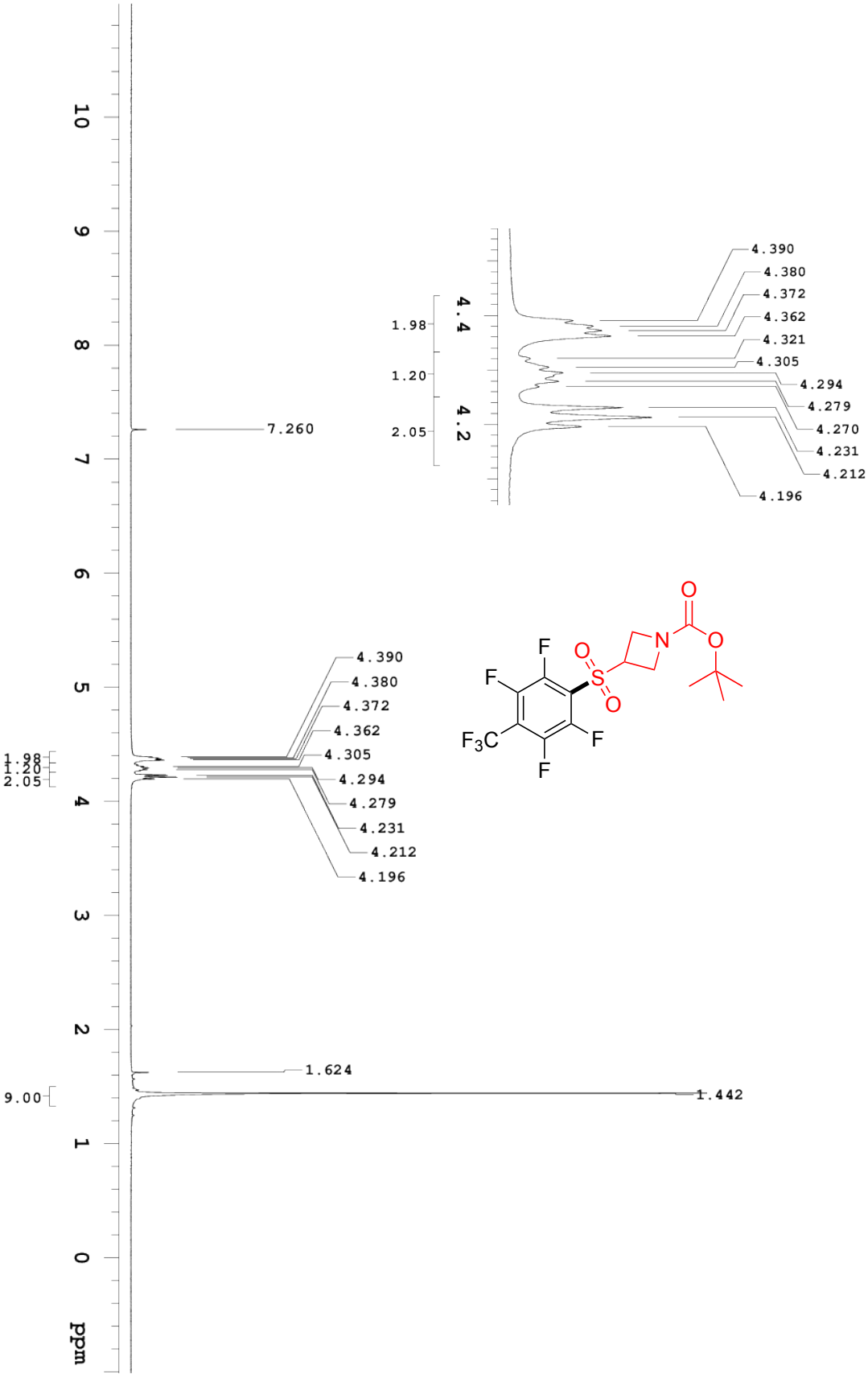

148.466
148.452
148.350
148.343
146.947
146.918
146.840
146.818
146.813
145.566
145.499
145.483
145.469
144.066
144.048
143.969
124.114
124.029
123.946
106.141
99.949
99.853
99.757
77.342
77.160
76.979
68.359
66.953
66.158
27.270
F
F
NC
O
S
O
O
F
F
f1 (ppm)

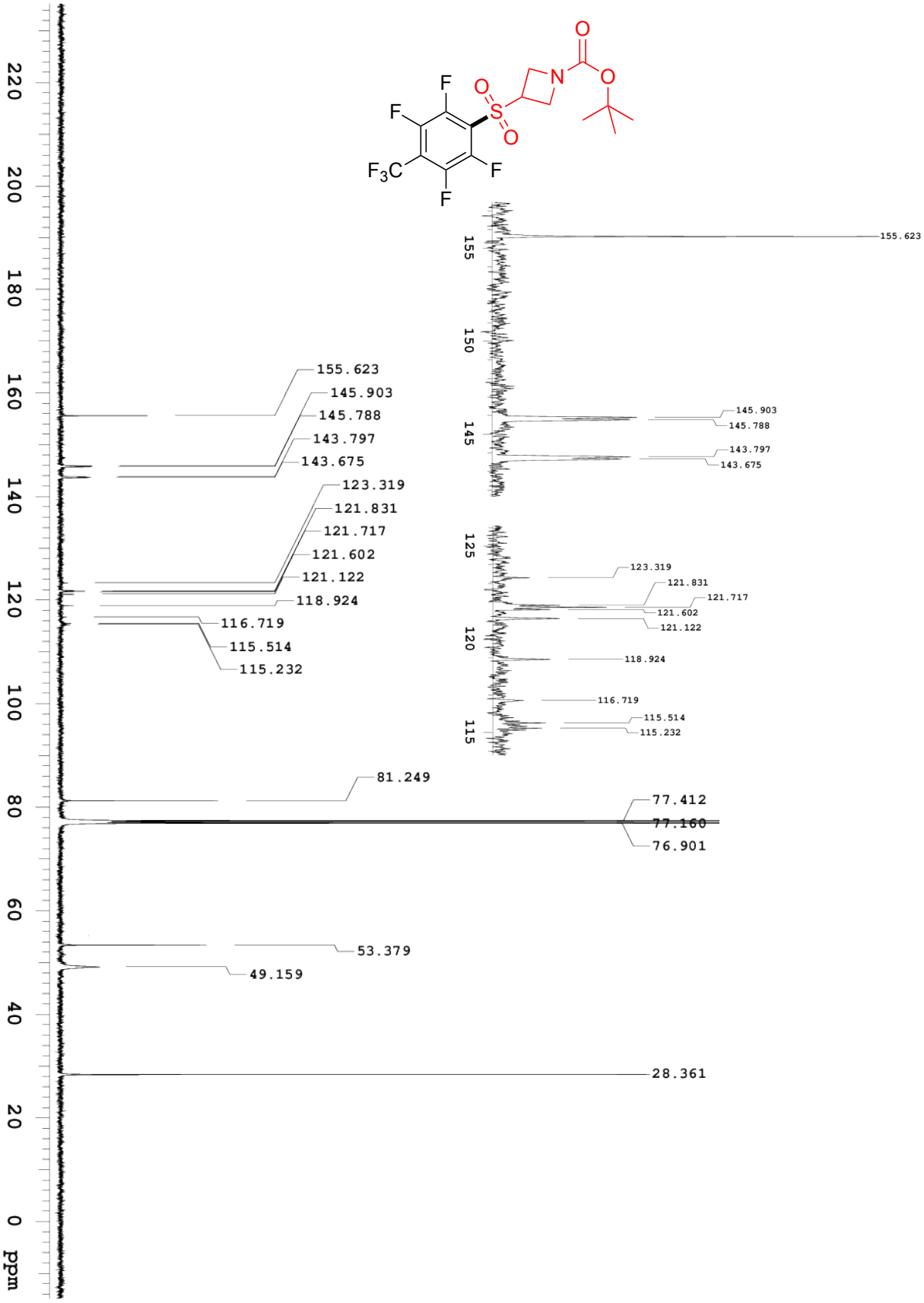

F
F
NC
O
S
O
O
F
F
-127.574
-127.588
-127.600
-127.618
-127.637
-127.656
-127.666
-127.682
-131.878
-131.893
-131.903
-131.923
-131.941
-131.960
-131.971
-131.985
2.07
2.11
f1 (ppm)
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185

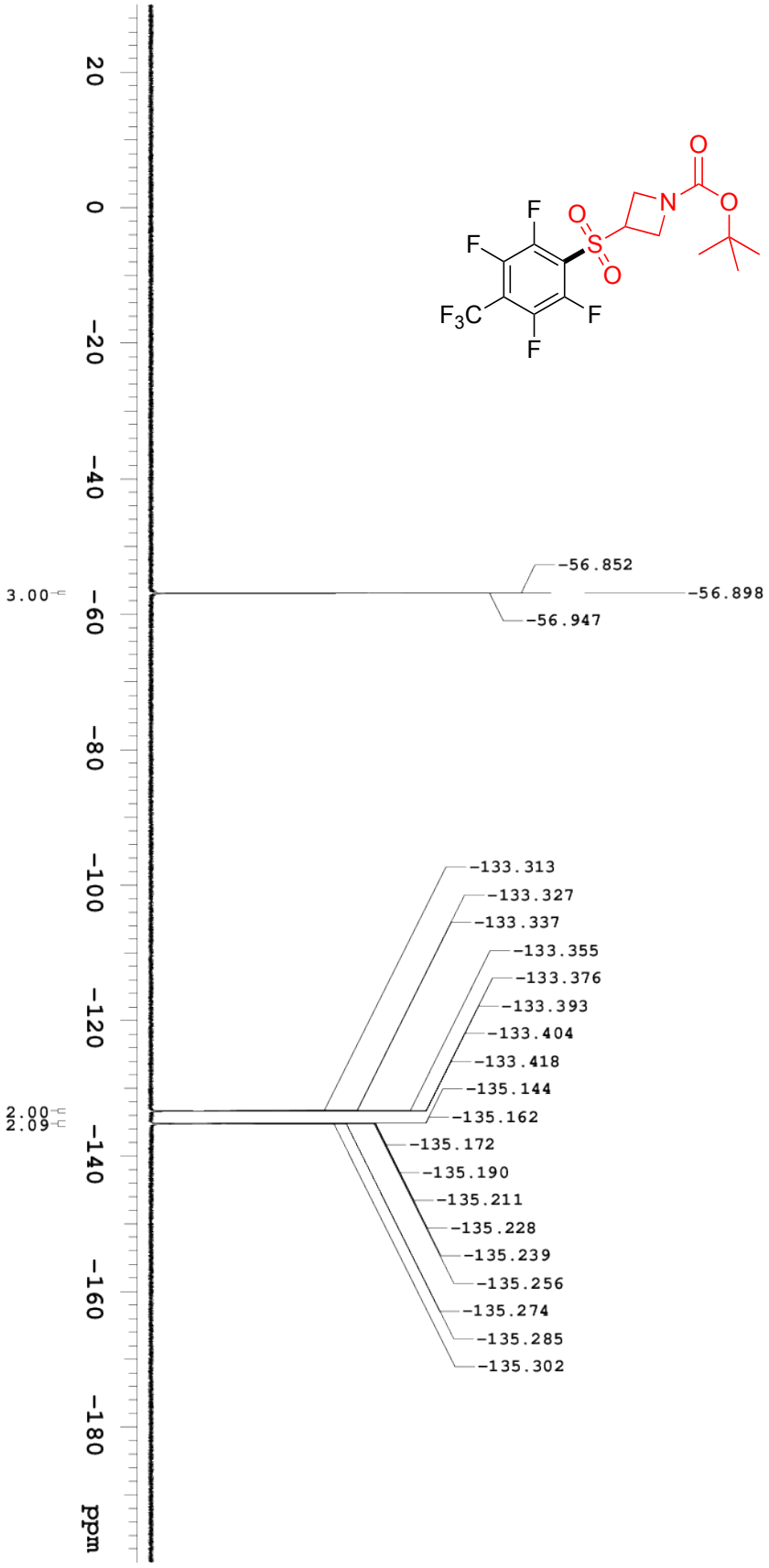

F
Cl
N
O
S
O
O
F
F
4.347
4.337
4.326
4.317
4.220
4.211
4.202
4.194
4.186
4.176
4.167
4.084
4.068
4.063
4.049
4.037
4.023
3.912
3.897
3.884
3.868
2.531
2.520
2.505
2.493
2.479
2.468
2.320
2.306
2.302
2.293
2.288
2.279
2.274
2.266
2.261
2.247
f1 (ppm)
1.00
1.01
2.03
1.02
0.99
1.00

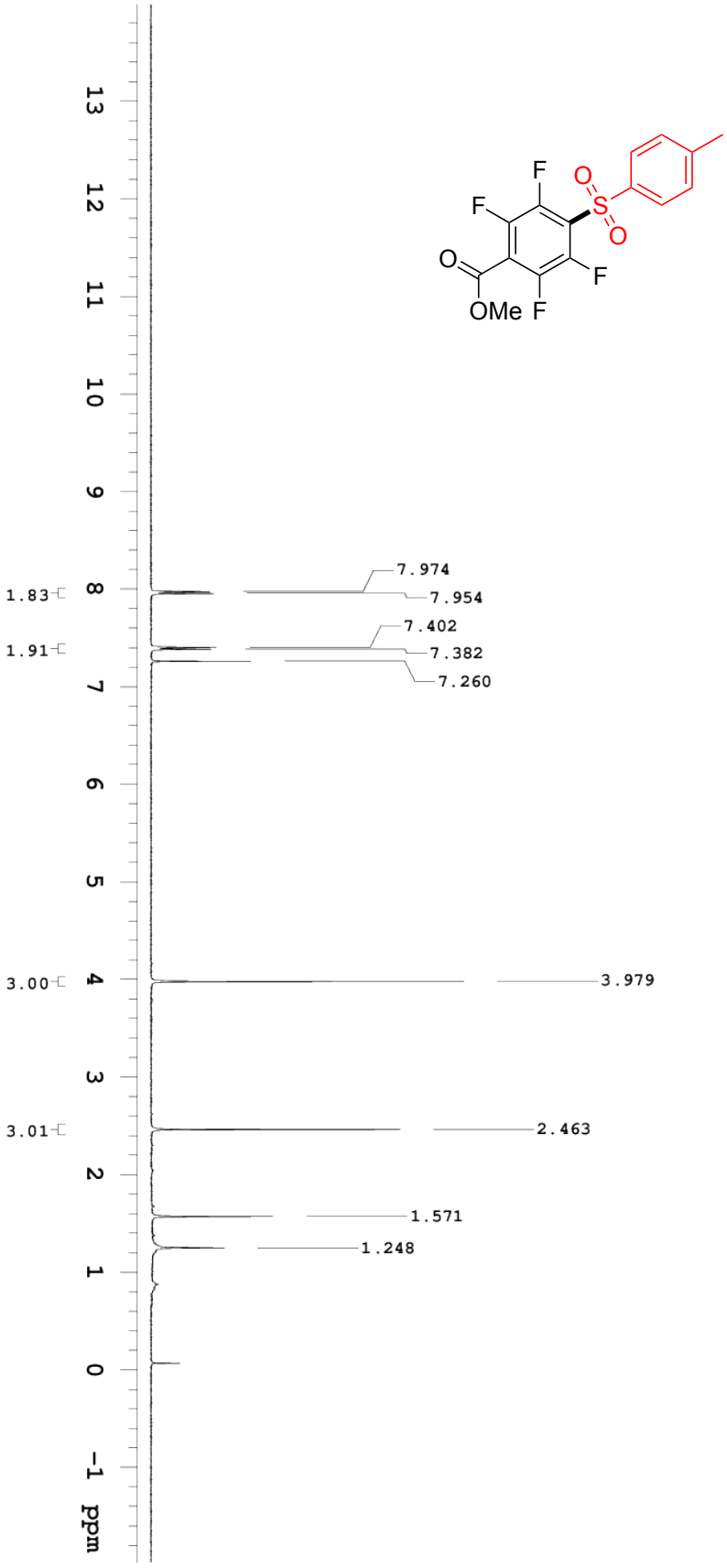

152.915
152.853
152.834
151.500
151.419
149.245
147.764
147.693
142.183
142.145
141.983
140.601
140.479
140.439
139.032
138.969
113.607
113.591
113.563
113.546
113.401
113.385
113.359
113.343
F
Cl
N
O
S
O
O
F
F
77.342
77.160
76.979
68.495
66.782
64.719
27.298
f1 (ppm)

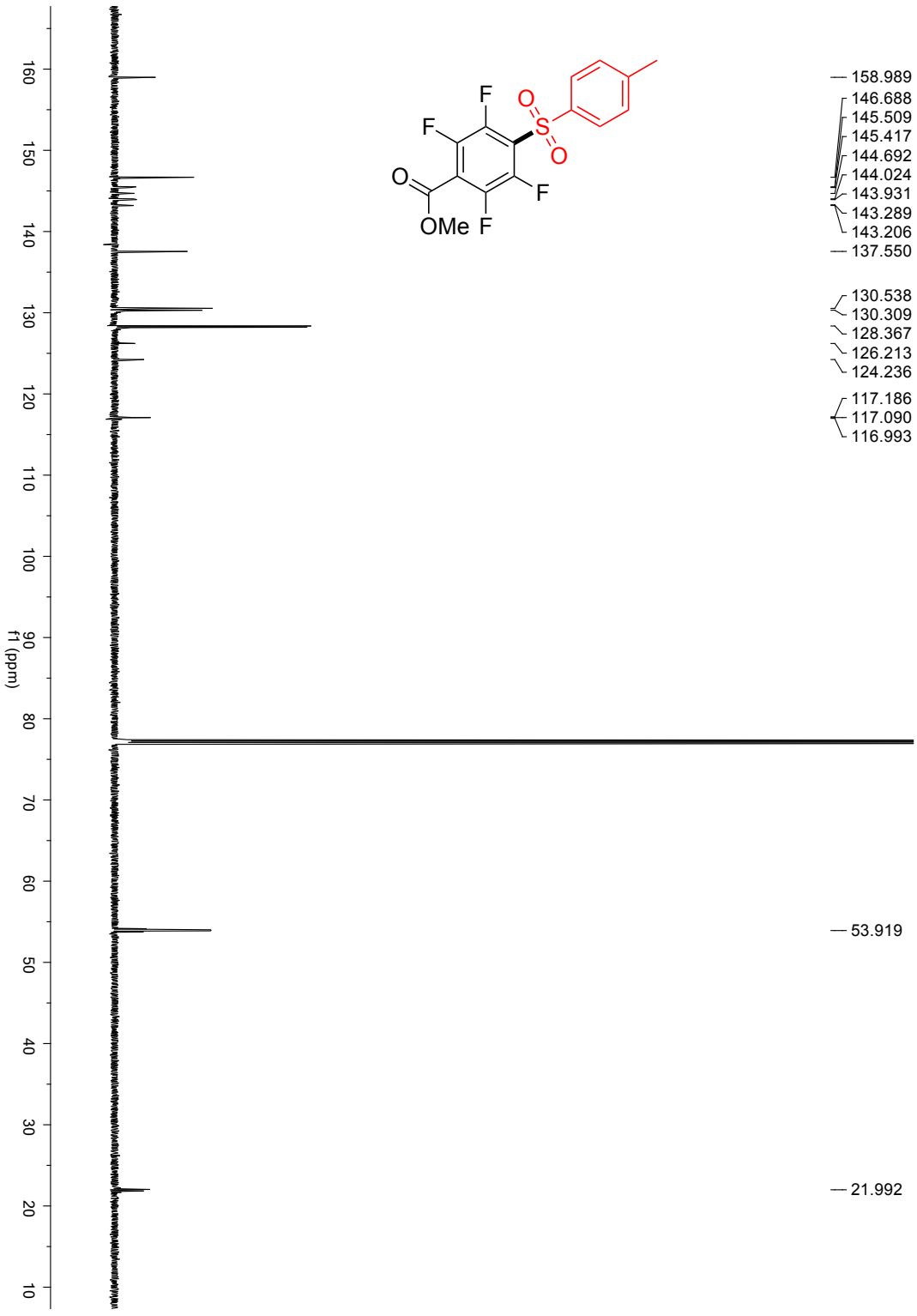

F
F
N
Cl
F
O
S
O
O
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
1.00
1.01
1.00
-67.772
-67.796
-67.835
-67.859
-82.835
-82.860
-82.884
-82.909
-134.972
-135.021
-135.035
-135.085

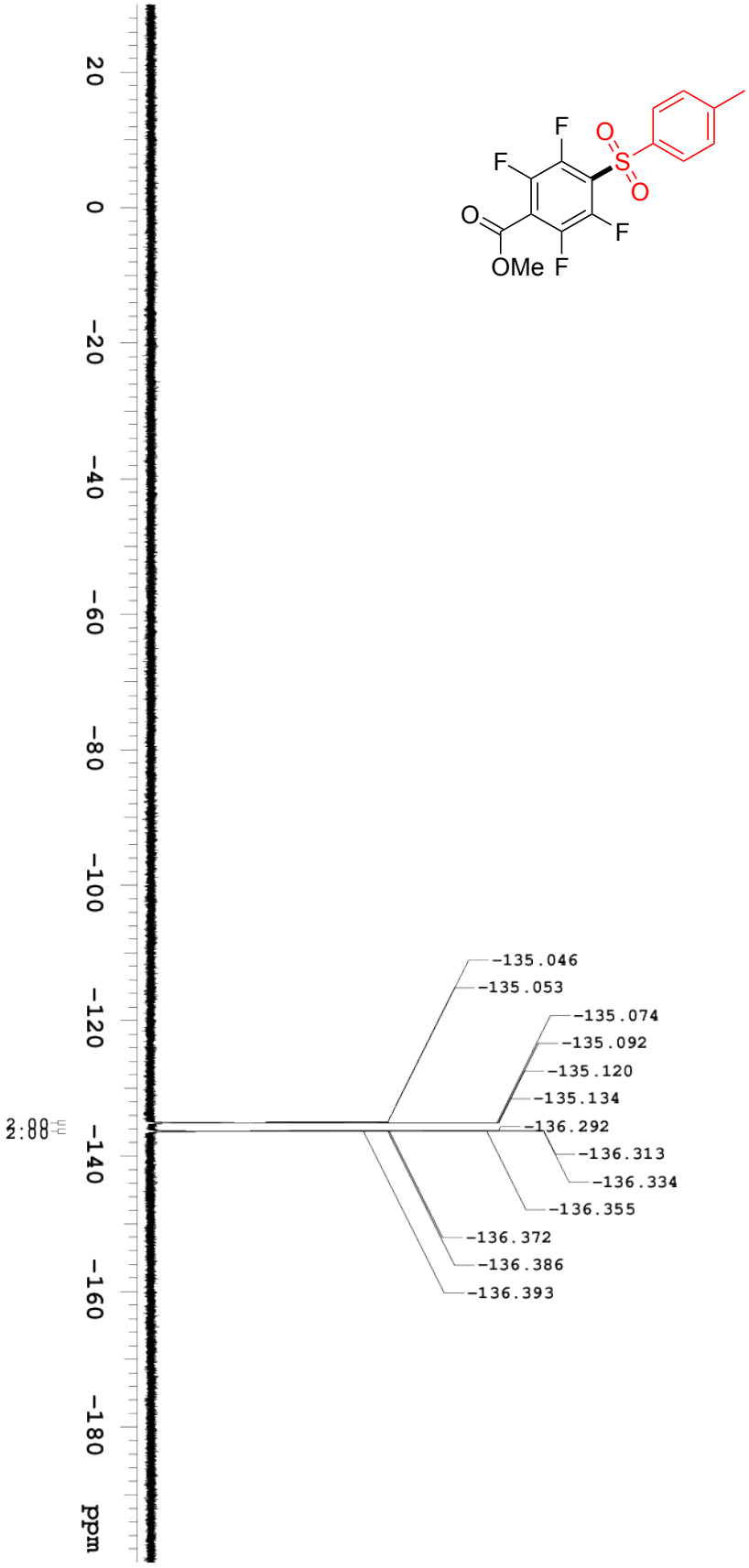

4.390
4.380
4.372
4.362
4.321
4.305
4.294
4.279
4.270
4.231
4.212
4.196
4.4
4.2
1.98
1.20
2.05
7.260
4.390
4.380
4.372
4.362
4.305
4.294
4.279
4.231
4.212
4.196
1.98
1.20
2.05
1.624
1.442
9.00
ppm
F
F
F3C
F
F
O
S
O
N
O
O

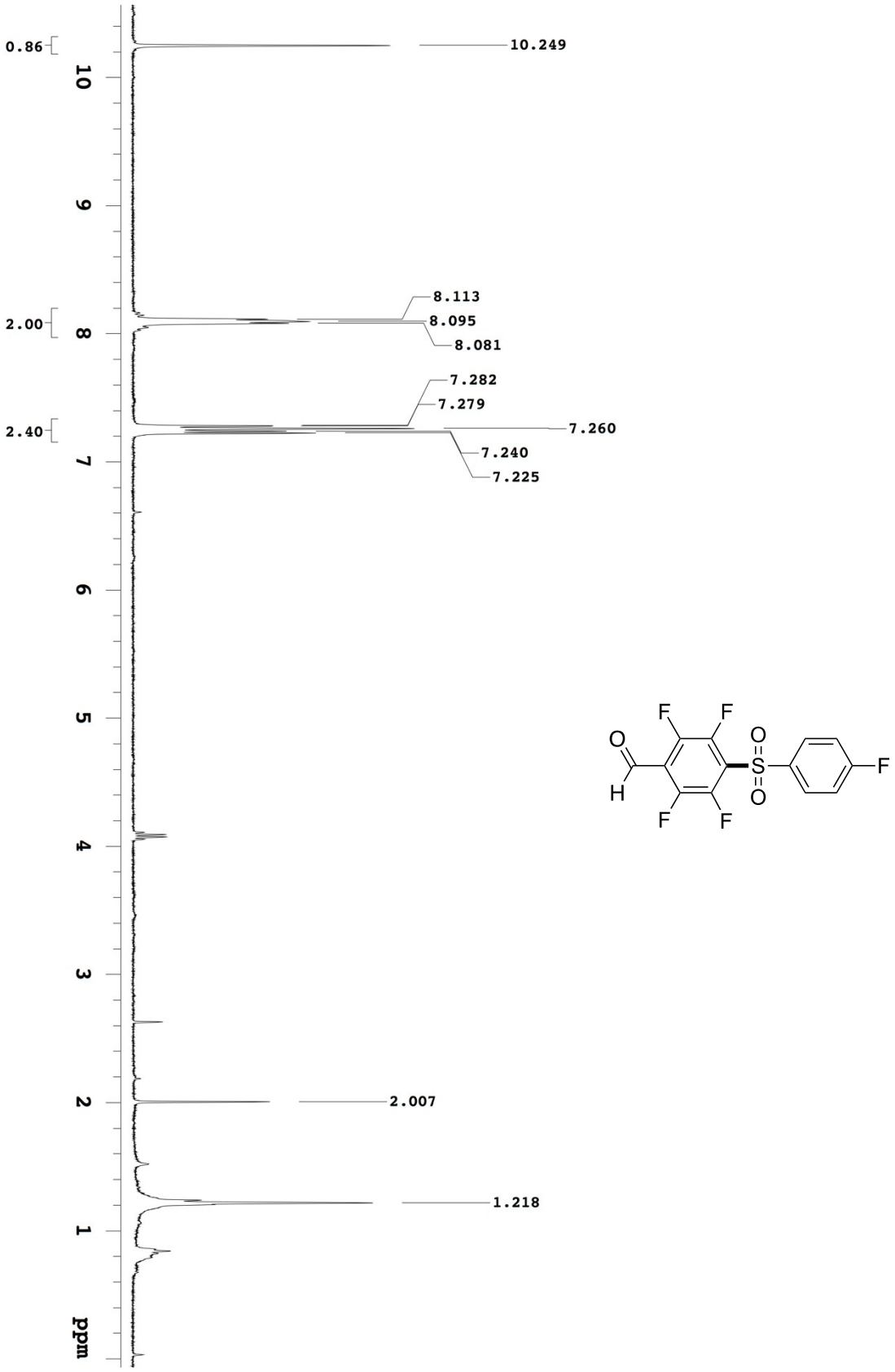

155.623
145.903
145.788
143.797
143.675
123.319
121.831
121.717
121.602
121.122
118.924
116.719
115.514
115.232
81.249
77.412
77.160
76.901
53.379
49.159
28.361
ppm

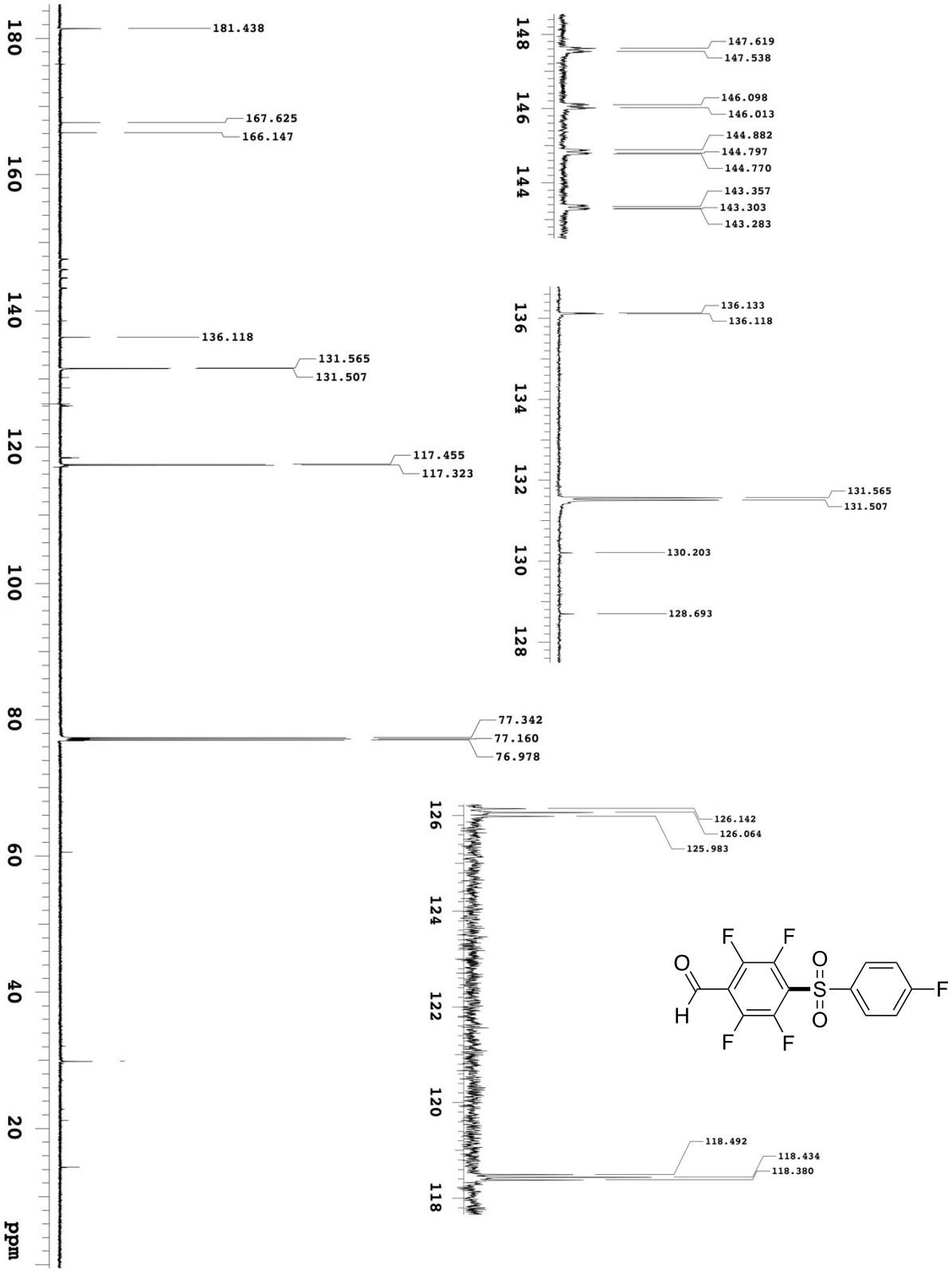

F
F
F3C
F
F
O
S
O
N
O
O
3.00
-56.852
-56.898
-56.947
2.00
2.09
-133.313
-133.327
-133.337
-133.355
-133.376
-133.393
-133.404
-133.418
-135.144
-135.162
-135.172
-135.190
-135.211
-135.228
-135.239
-135.256
-135.274
-135.285
-135.302
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

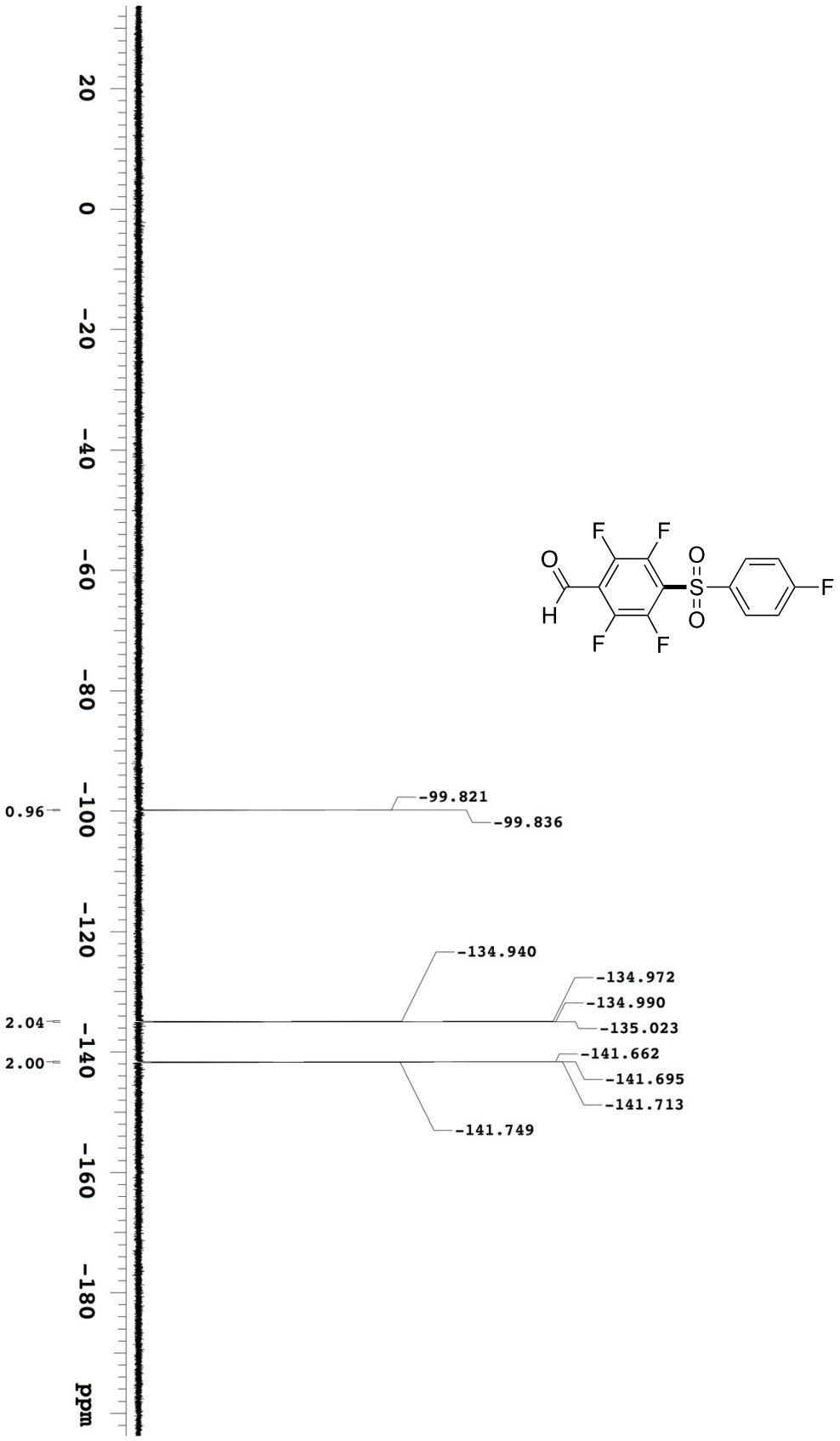

F
O
S
O
F
O
F
OMe F
7.974
7.954
7.402
7.382
7.260
1.83
1.91
3.979
3.00
2.463
3.01
1.571
1.248
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm

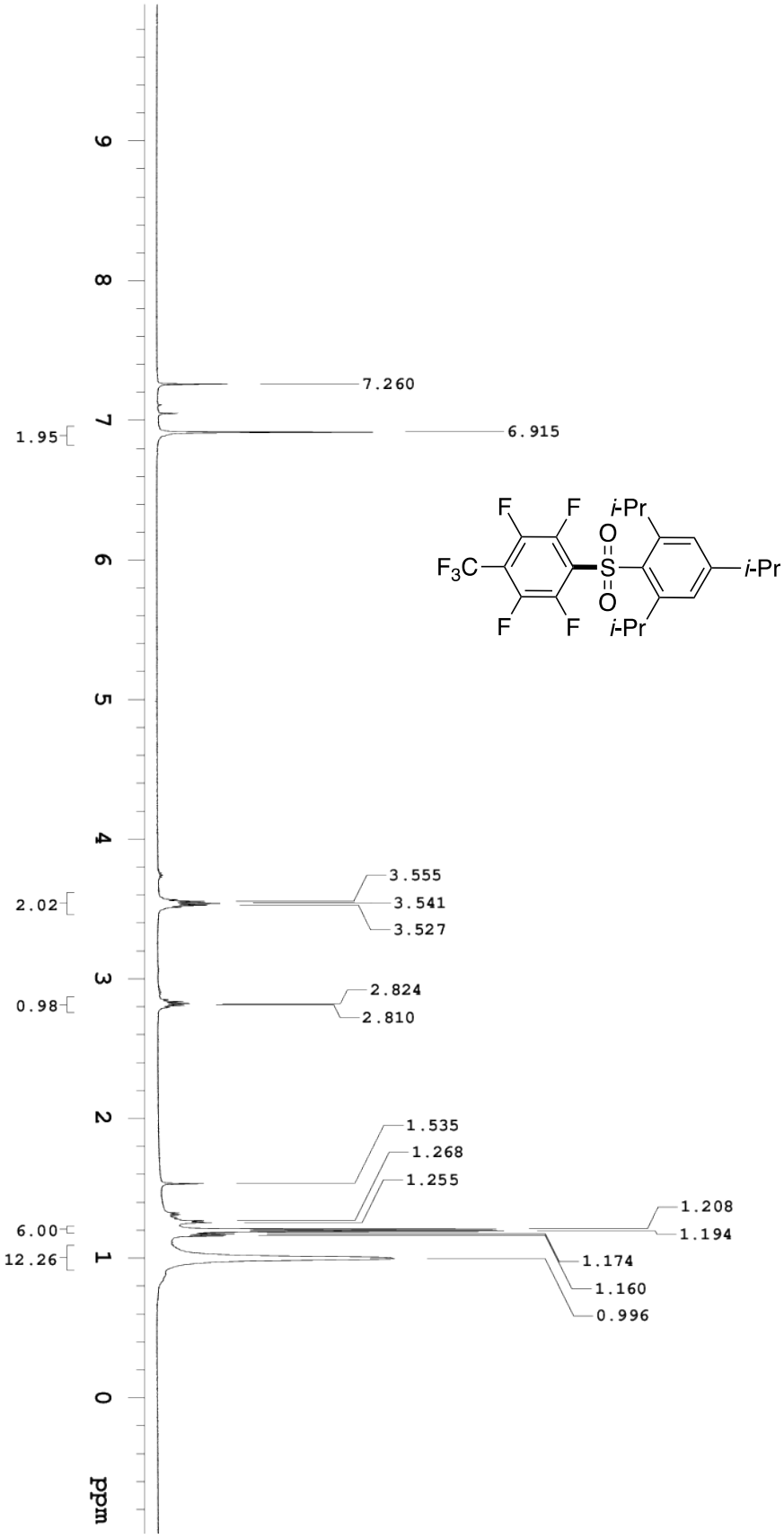

158.989
146.688
145.509
145.417
144.692
144.024
143.931
143.289
143.206
137.550
130.538
130.309
128.367
126.213
124.236
117.186
117.090
116.993
53.919
21.992
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
F
F
O
S
O
O
OMe
F
F

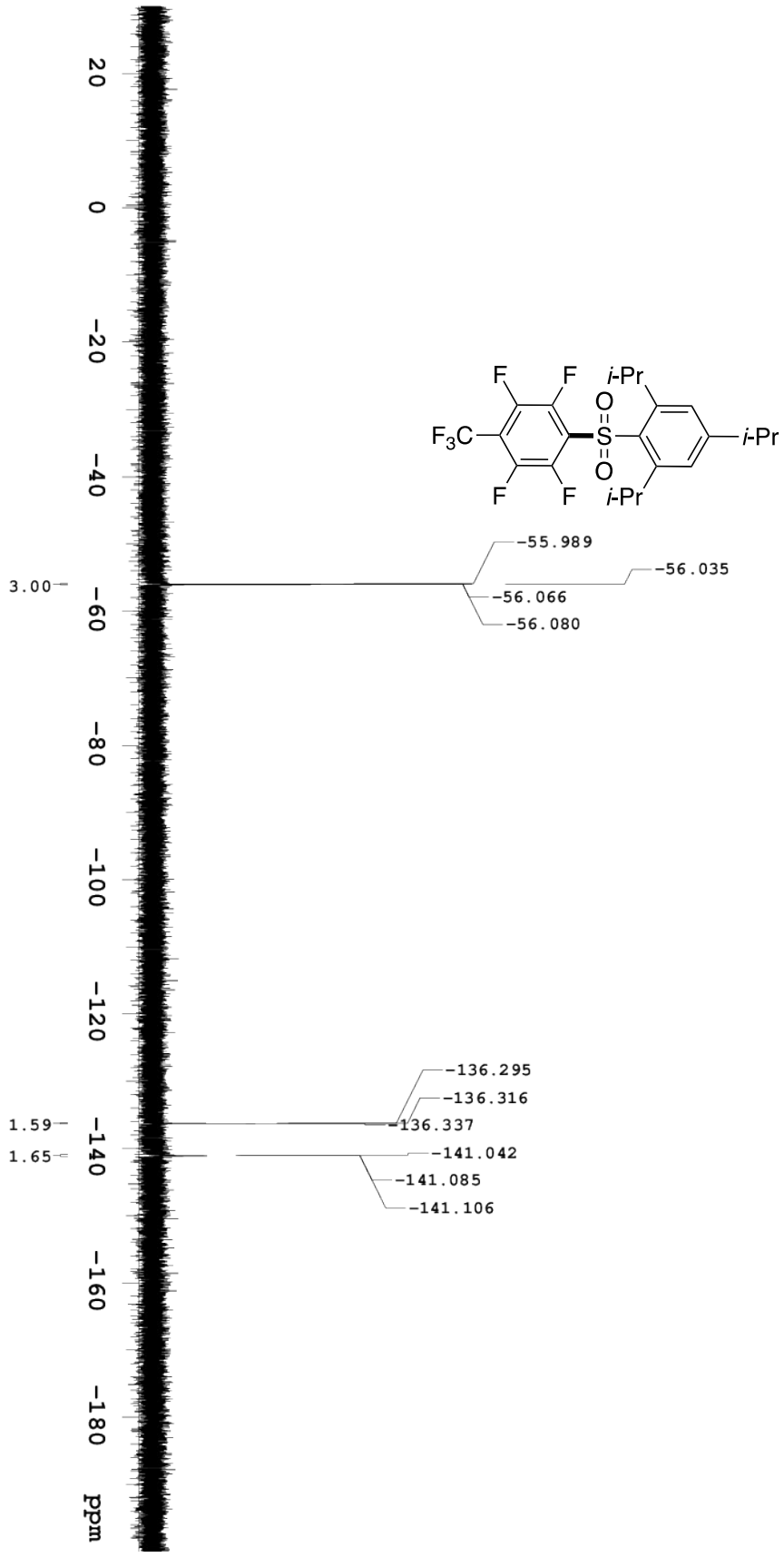

F
F
O
S
O
O
F
OMe
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
2.00
-135.046
-135.053
-135.074
-135.092
-135.120
-135.134
-136.292
-136.313
-136.334
-136.355
-136.372
-136.386
-136.393

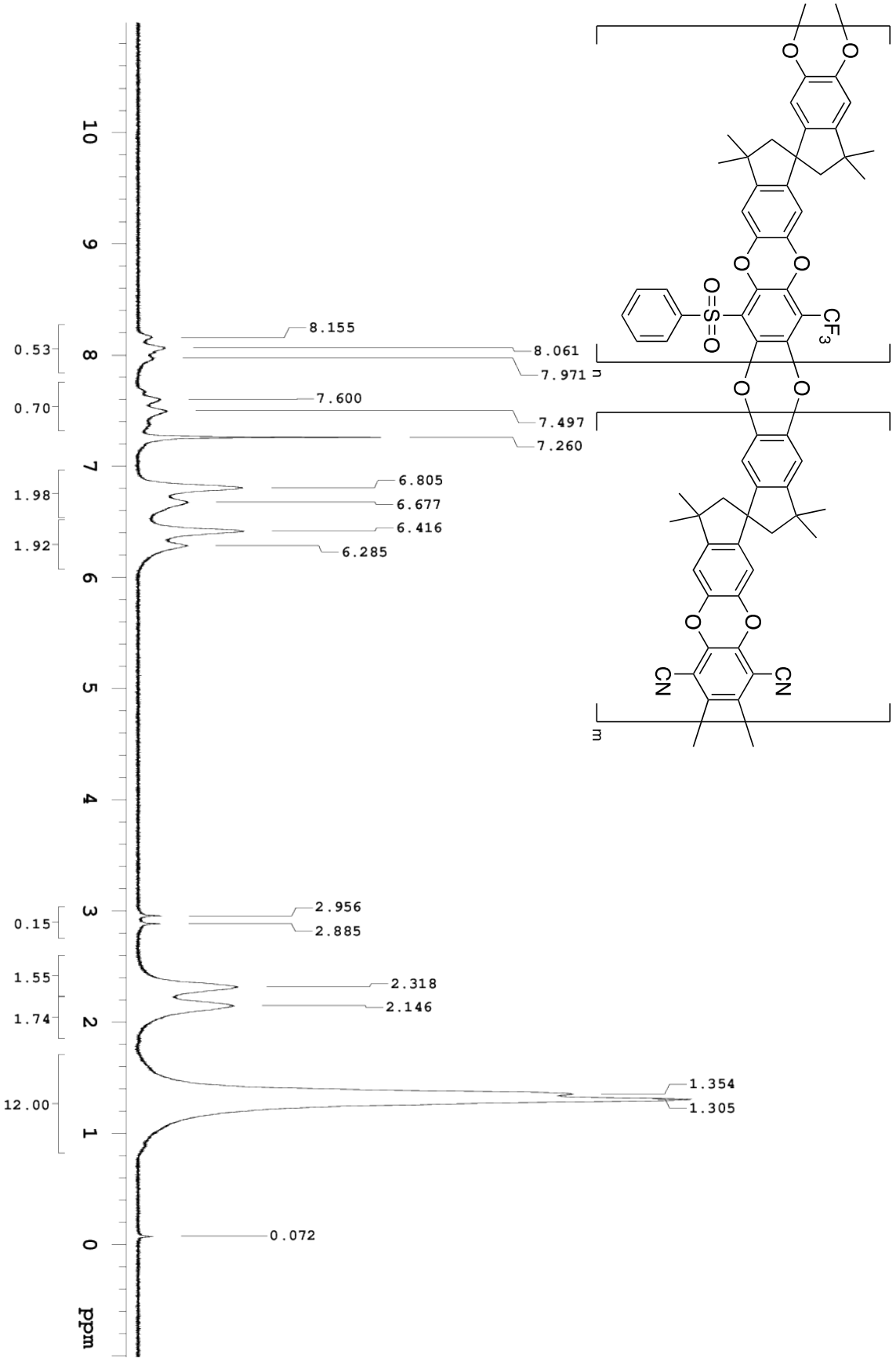

0.86
2.00
2.40
10.249
8.113
8.095
8.081
7.282
7.279
7.260
7.240
7.225
2.007
1.218
ppm
F
F
O
H
O
S
O
F
F
F


181.438
167.625
166.147
136.118
131.565
131.507
117.455
117.323
77.342
77.160
76.978
147.619
147.538
146.098
146.013
144.882
144.797
144.770
143.357
143.303
143.283
136.133
136.118
131.565
131.507
130.203
128.693
126.142
126.064
125.983
118.492
118.434
118.380
ppm
O
H
F
F
F
F
O
S
O
F


20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
0.96
2.04
2.00
-99.821
-99.836
-134.940
-134.972
-134.990
-135.023
-141.662
-141.695
-141.713
-141.749
O
H
F
F
F
F
O
S
O
F


7.260
6.915
1.95
F
F
i-Pr
O
F3C
S
i-Pr
O
F
F
i-Pr
3.555
3.541
3.527
2.02
2.824
2.810
0.98
1.535
1.268
1.255
1.208
1.194
6.00
12.26
1.174
1.160
0.996
9
8
7
6
5
4
3
2
1
0
ppm


20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
F
F
i-Pr
O
F3C
S
i-Pr
O
F
F
i-Pr
-55.989
-56.035
-56.066
-56.080
3.00
-136.295
-136.316
-136.337
1.59
-141.042
1.65
-141.085
-141.106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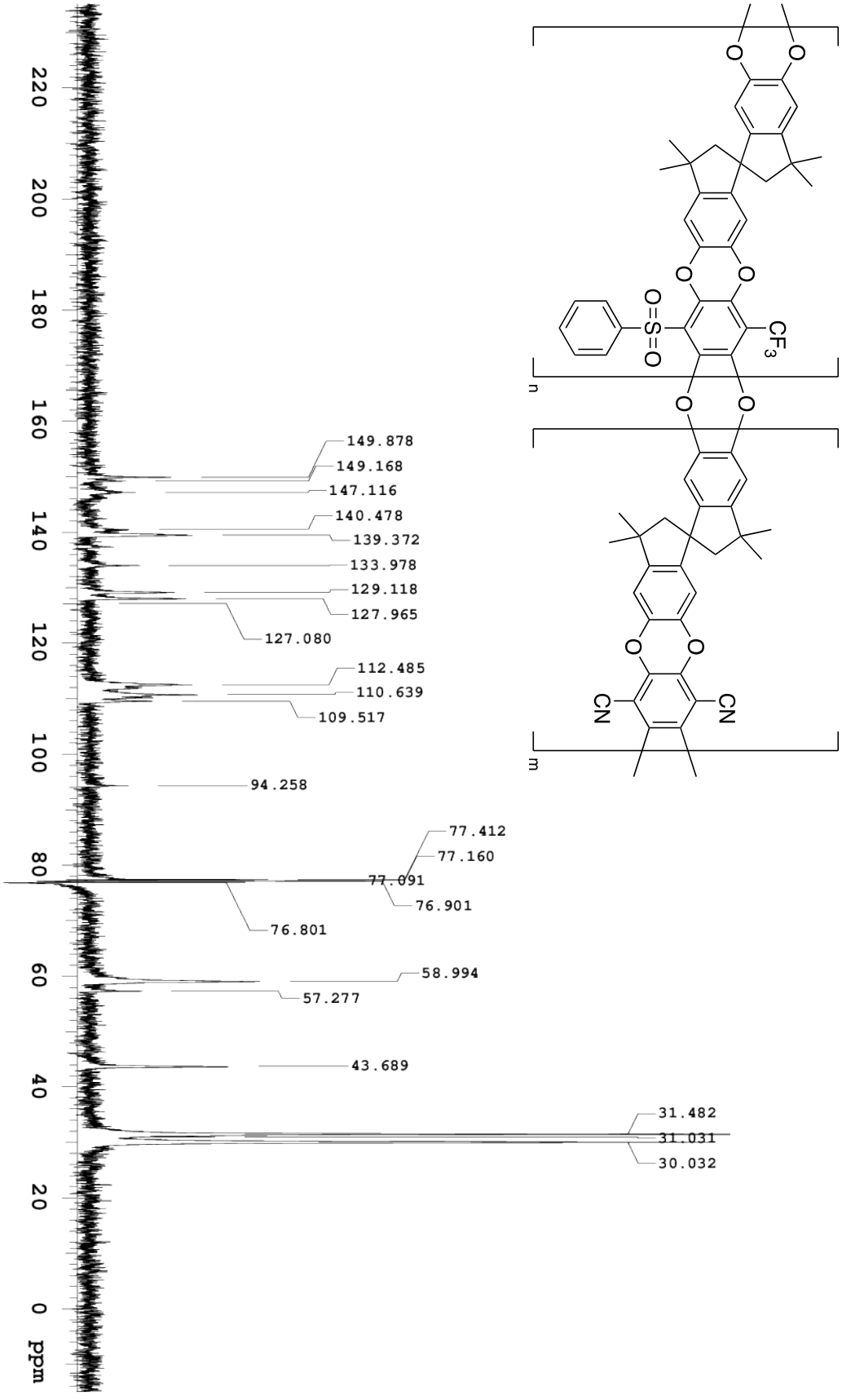
8.061
7.971
7.600
7.497
7.260
6.805
6.677
6.416
6.285
2.956
2.885
2.318
2.146
1.354
1.305
0.072
0.53
0.70
1.98
1.92
0.15
1.55
1.74
12.00
ppm
O=S=O
CF3
CN
CN
n
m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200
180
160
140
120
100
80
60
40
20
0
ppm
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149.168
147.116
140.478
139.372
133.978
129.118
127.965
127.080
112.485
110.639
109.517
94.258
77.412
77.160
77.091
76.901
76.801
58.994
57.277
43.689
31.482
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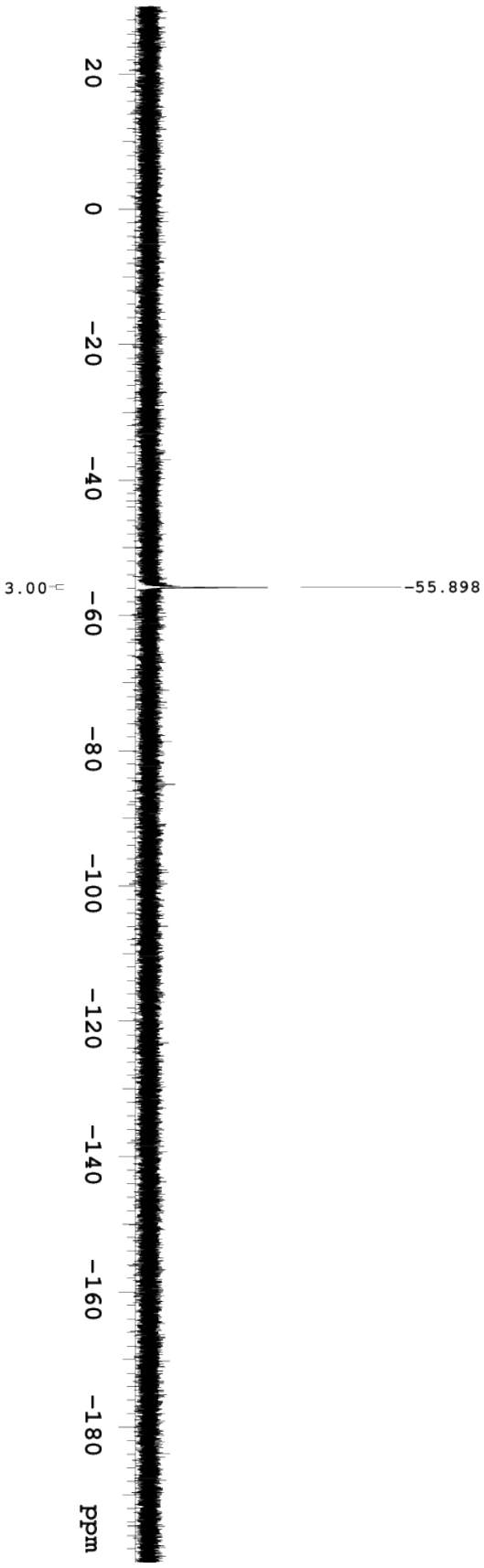
O
O
O
O
O
O
O
O
O
O
O=S=O
CF3
CN
CN
n
m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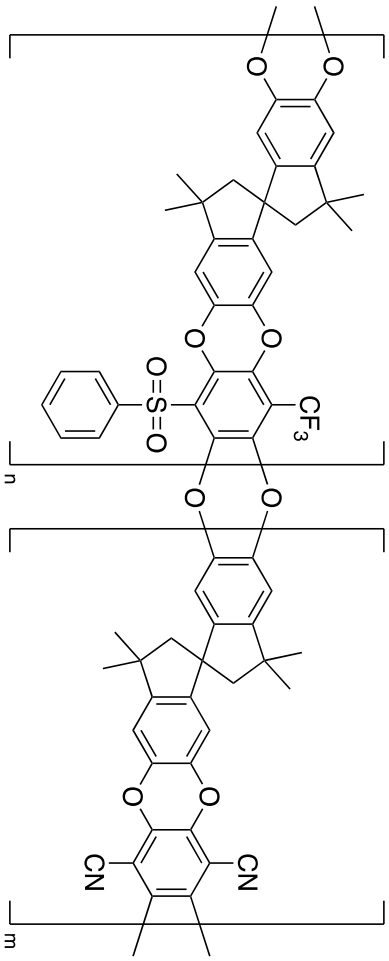
O
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O=S=O
CF3
n
O
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O
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m