Electronic Supplementary Material (ESI) for ChemComm.

Photoredox-catalyzed sulfonylation of difluoroenoxysilanes with the insertion of sulfur dioxide

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Supporting Information

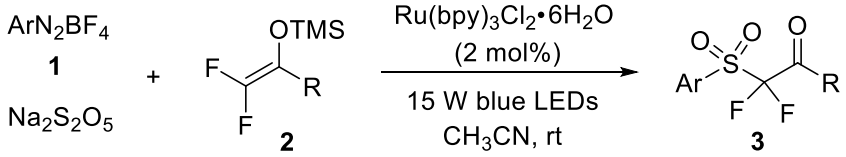
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25-35 °C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

General experimental procedure for the synthesis of difluoroenoxysilanes.[1]

To a mixture of TMSCl (4 equiv) and Mg (4 equiv) in dry THF (0.25 M) was cooled down to 0 ℃ under N_2 atmosphere, then trifluoroacetophenone (1 equiv) was added dropwise. The reaction mixture was stirred for additional 30 min. After evaporation of solvent, hexane was added to the residue, and the resulting salt was filtered. The filtrate was concentrated to give crude difluoroenoxysilane, which could be used directly without further purification.

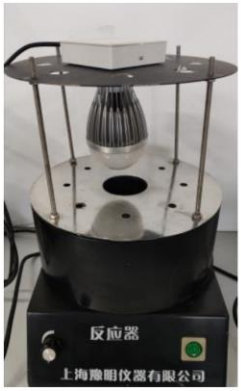
*General experimental procedure for the reaction of aryldiazonium tetrafluoroborates **1**, $Na_2S_2O_5$, and difluoroenoxysilanes **2**.*

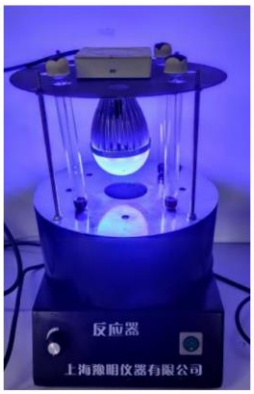


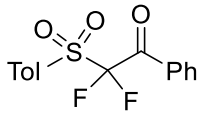
Difluoroenoxysilanes **2** (0.2 mmol) was added to a mixture of $Na_2S_2O_5$ (0.4 mmol), aryldiazonium tetrafluoroborate **1** (0.3 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2 mol%) in CH_3CN

(2.0 mL) under N_2 atmosphere. The mixture was stirred under blue LED irradiation (15 W) for 12 hours. After completion of reaction as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/ethyl acetate = 8:1) to give the corresponding product **3**.

Photoredox set-up:

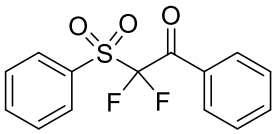






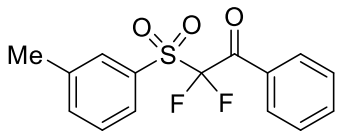
2,2-Difluoro-1-phenyl-2-tosylethan-1-one (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0 (t, *J* = 23.1 Hz), 147.7, 135.3, 132.1, 130.9, 130.8 (t, *J* = 3.1 Hz), 130.2, 129.4, 128.8, 116.5 (t, *J* = 300.7 Hz), 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.7 (s); HRMS (ESI) calcd for $C_{15}H_{12}F_2O_3SNa$ $[M+Na]^+$: 333.0373, found: 333.0373.



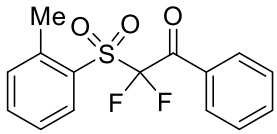
2,2-Difluoro-1-phenyl-2-(phenylsulfonyl)ethan-1-one (**3b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.81 (t, *J* = 7.4 Hz, 1H), 7.73 – 7.62 (m, 3H), 7.54 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7 (t, *J* = 23.2 Hz), 136.0, 135.4, 132.6, 132.0, 130.9, 130.8 (t, *J* = 3.1 Hz), 129.5, 128.9, 116.5 (t, *J* = 301.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.5 (s); HRMS (ESI) calcd for $C_{14}H_{10}F_2O_3SNa$ $[M+Na]^+$: 319.0216, found: 319.0219.



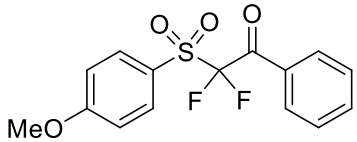
2,2-Difluoro-1-phenyl-2-(*m*-tolylsulfonyl)ethan-1-one (**3c**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.8 Hz, 2H), 7.86 – 7.79 (m, 2H), 7.70 (t, J = 7.3 Hz, 1H), 7.63 – 7.49 (m, 4H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8 (t, *J* = 22.9 Hz), 140.0, 136.8, 135.3, 132.4, 132.0, 131.1, 130.8 (t, *J* = 3.2 Hz), 129.3, 128.8, 128.1, 116.5 (t, *J* = 301.0 Hz), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.5 (s); HRMS (ESI) calcd for $C_{15}H_{12}F_2O_3SNa$ $[M+Na]^+$: 333.0373, found: 333.0371.



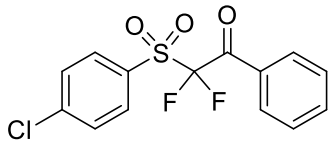
2,2-Difluoro-1-phenyl-2-(*o*-tolylsulfonyl)ethan-1-one (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 6.6 Hz, 2H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8 (t, *J* = 23.0 Hz), 142.0, 135.8, 135.3, 133.3, 133.2, 130.7 (t, *J* = 3.1 Hz), 128.8, 128.6, 128.0, 126.9, 120.2, 117.2, 114.2, 20.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.0 (s); HRMS (ESI) calcd for $C_{15}H_{12}F_2O_3SNa$ $[M+Na]^+$: 333.0373, found: 333.0372.



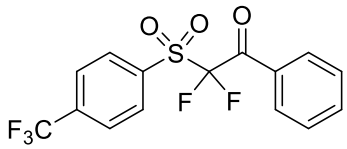
2,2-Difluoro-2-((4-methoxyphenyl)sulfonyl)-1-phenylethan-1-one (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.7 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1 (t, *J* = 23.3 Hz), 165.8, 135.3, 133.3, 132.1, 130.8 (t, *J* = 3.2 Hz), 128.8, 123.3, 116.5 (t, *J* = 300.1 Hz), 114.9, 55.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.9 (s); HRMS (ESI) calcd for $C_{15}H_{12}F_2O_4SNa$ $[M+Na]^+$: 349.0322, found: 349.0323.



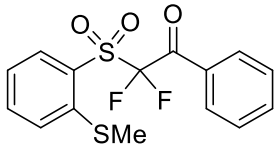
2-((4-Chlorophenyl)sulfonyl)-2,2-difluoro-1-phenylethan-1-one (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6 (t, *J* = 23.0 Hz), 143.3, 135.5, 132.3, 131.9, 131.0, 130.7 (t, *J* = 3.2 Hz), 130.0, 128.9, 116.4 (t, *J* = 301.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.3 (s); HRMS (ESI) calcd for $C_{14}H_9ClF_2O_3SNa$ $[M+Na]^+$: 352.9827, found: 352.9832.



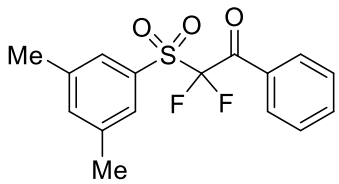
2,2-Difluoro-1-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethan-1-one (**3g**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (t, *J* = 8.5 Hz, 4H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.3 (t, *J* = 22.9 Hz), 137.4 (q, *J* = 33.5 Hz), 136.3, 135.6, 131.8, 131.6, 130.7 (t, *J* = 3.1 Hz), 129.0, 126.6 (q, *J* = 3.6 Hz), 122.8 (q, *J* = 273.6 Hz), 116.4 (t, *J* = 302.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5 (s), -101.0 (s); HRMS (ESI) calcd for $C_{15}H_9F_5O_3SNa$ $[M+Na]^+$: 387.0090, found: 387.0094.



2,2-Difluoro-2-((2-(methylthio)phenyl)sulfonyl)-1-phenylethan-1-one (**3h**)

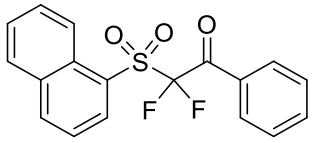
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.61 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7 (t, *J* = 23.1 Hz), 145.1, 135.7, 135.2, 134.3, 132.1, 130.8 (t, *J* = 3.1 Hz), 129.2, 128.8, 126.6, 124.7, 117.4 (t, *J* = 302.8 Hz), 16.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.2 (s); HRMS (ESI) calcd for $C_{15}H_{13}F_2O_3S_2$ $[M+H]^+$: 343.0274, found: 343.0277.



2-((3,5-Dimethylphenyl)sulfonyl)-2,2-difluoro-1-phenylethan-1-one (**3i**)

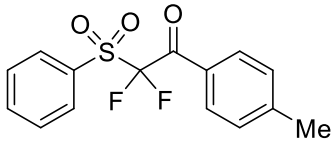
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.9 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.62 (s, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.40 (s, 1H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8 (t,

J = 23.0 Hz), 139.7, 137.8, 135.3, 132.2, 132.1, 130.8 (t, *J* = 3.2 Hz), 128.8, 128.3, 116.6 (t, *J* = 301.0 Hz), 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.5 (s); HRMS (ESI) calcd for $C_{16}H_{14}F_2O_3SNa$ $[M+Na]^+$: 347.0529, found: 347.0531.



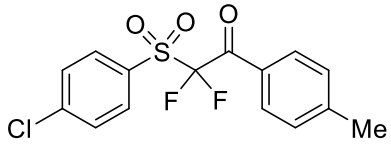
2,2-Difluoro-2-(naphthalen-1-ylsulfonyl)-1-phenylethan-1-one (**3j**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 8.7 Hz, 1H), 8.38 (d, *J* = 7.5 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.73 – 7.62 (m, 3H), 7.55 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7 (t, *J* = 23.0 Hz), 137.8, 135.3, 134.8, 134.2, 132.1, 130.8 (t, *J* = 3.1 Hz), 130.5, 129.4, 129.0, 128.9, 128.6, 127.5, 124.9, 124.3, 117.3 (t, *J* = 302.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.8 (s); HRMS (ESI) calcd for $C_{18}H_{12}F_2O_3SNa$ $[M+Na]^+$: 369.0373, found: 369.0377.



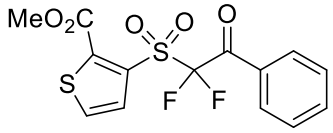
2,2-Difluoro-2-(phenylsulfonyl)-1-(p-tolyl)ethan-1-one (**3k**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 2H), 8.02 (d, *J* = 7.7 Hz, 2H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0 (t, *J* = 22.8 Hz), 146.9, 135.8, 132.5, 130.9, 130.8, 129.5, 129.4, 116.5 (t, *J* = 301.1 Hz), 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.4 (s); HRMS (ESI) calcd for $C_{15}H_{23}F_2O_3S$ $[M+H]^+$: 311.0553, found: 311.0555.



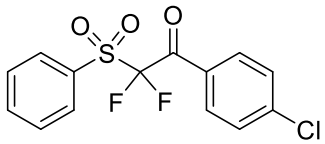
2-((4-Chlorophenyl)sulfonyl)-2,2-difluoro-1-(*p*-tolyl)ethan-1-one (**3l**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.8 (t, *J* = 22.7 Hz), 147.1, 143.1, 132.2, 130.9, 130.8, 129.8, 129.6, 129.3, 116.4 (t, *J* = 301.5 Hz), 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.3 (s); HRMS (ESI) calcd for $C_{15}H_{11}ClF_2O_3SNa$ $[M+Na]^+$: 366.9983, found: 366.9987.



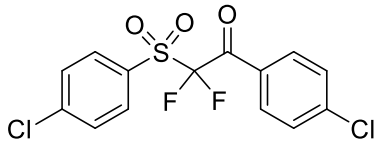
Methyl 3-((1,1-difluoro-2-oxo-2-phenylethyl)sulfonyl)thiophene-2-carboxylate (**3m**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.5 (t, *J* = 23.2 Hz), 159.2, 140.6, 135.3, 134.3, 132.5, 132.0, 130.6 (t, *J* = 3.0 Hz), 129.8, 128.9, 117.1 (t, *J* = 303.9 Hz), 53.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.7 (s); HRMS (ESI) calcd for $C_{14}H_{11}F_2O_5S_2$ $[M+H]^+$: 361.0016, found: 361.0020.



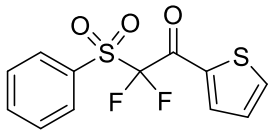
1-(4-Chlorophenyl)-2,2-difluoro-2-(phenylsulfonyl)ethan-1-one (**3n**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 7.9 Hz, 2H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6 (t, *J* = 23.5 Hz), 142.3, 136.1, 132.2, 132.1, 130.8, 130.2, 129.5, 129.2, 116.4 (t, *J* = 300.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.8 (s); HRMS (ESI) calcd for $C_{14}H_9ClF_2O_3SNa$ $[M+Na]^+$: 352.9827, found: 352.9830.



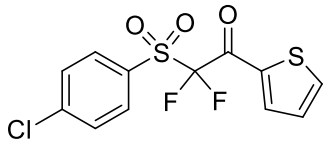
1-(4-Chlorophenyl)-2-((4-chlorophenyl)sulfonyl)-2,2-difluoroethan-1-one (**3o**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5 (t, *J* = 23.3 Hz), 143.5, 142.5, 132.3, 132.1 (t, *J* = 3.2 Hz), 131.6 (t, *J* = 3.1 Hz), 130.0, 129.4, 129.2, 127.2 (t, *J* = 6.0 Hz), 116.3 (t, *J* = 301.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.6 (s); HRMS (ESI) calcd for $C_{14}H_8Cl_2F_2O_3SNa$ $[M+Na]^+$: 386.9437, found: 386.9435.



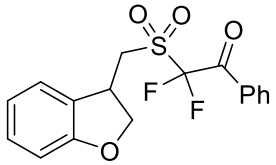
2,2-Difluoro-2-(phenylsulfonyl)-1-(thiophen-2-yl)ethan-1-one (**3p**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 2.1 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 2H), 7.91 (d, *J* = 4.9 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 2H), 7.28 – 7.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6 (t, *J* = 24.3 Hz), 138.4, 138.1 (t, *J* = 4.8 Hz), 136.0, 132.2, 130.8, 129.5, 129.2, 116.0 (t, *J* = 300.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.9 (s); HRMS (ESI) calcd for $C_{12}H_9F_2O_3S_2$ $[M+H]^+$: 302.9961, found: 302.9964.



2-((4-Chlorophenyl)sulfonyl)-2,2-difluoro-1-(thiophen-2-yl)ethan-1-one (**3q**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.12 (m, 1H), 8.00 – 7.91 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5 (t, *J* = 24.4 Hz), 143.4, 138.7, 138.1 (t, *J* = 5.1 Hz), 137.8, 132.3, 130.0, 129.4, 129.1, 115.9 (t, *J* = 300.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.8 (s); HRMS (ESI) calcd for $C_{12}H_7F_2O_3S_2Na$ $[M+Na]^+$: 358.9391, found: 358.9394.

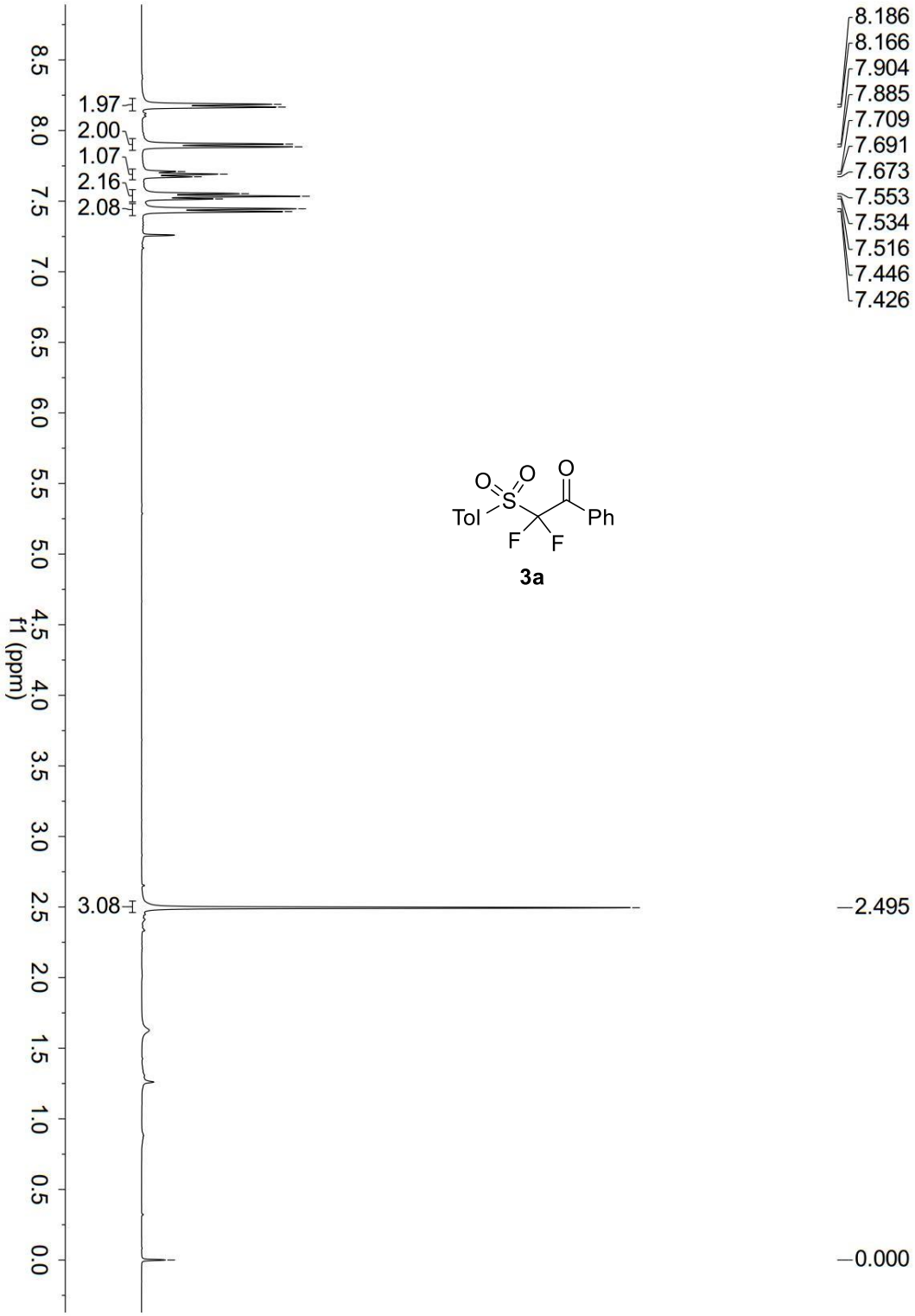


2-(((2,3-Dihydrobenzofuran-3-yl)methyl)sulfonyl)-2,2-difluoro-1-phenylethan-1-one (**6**)

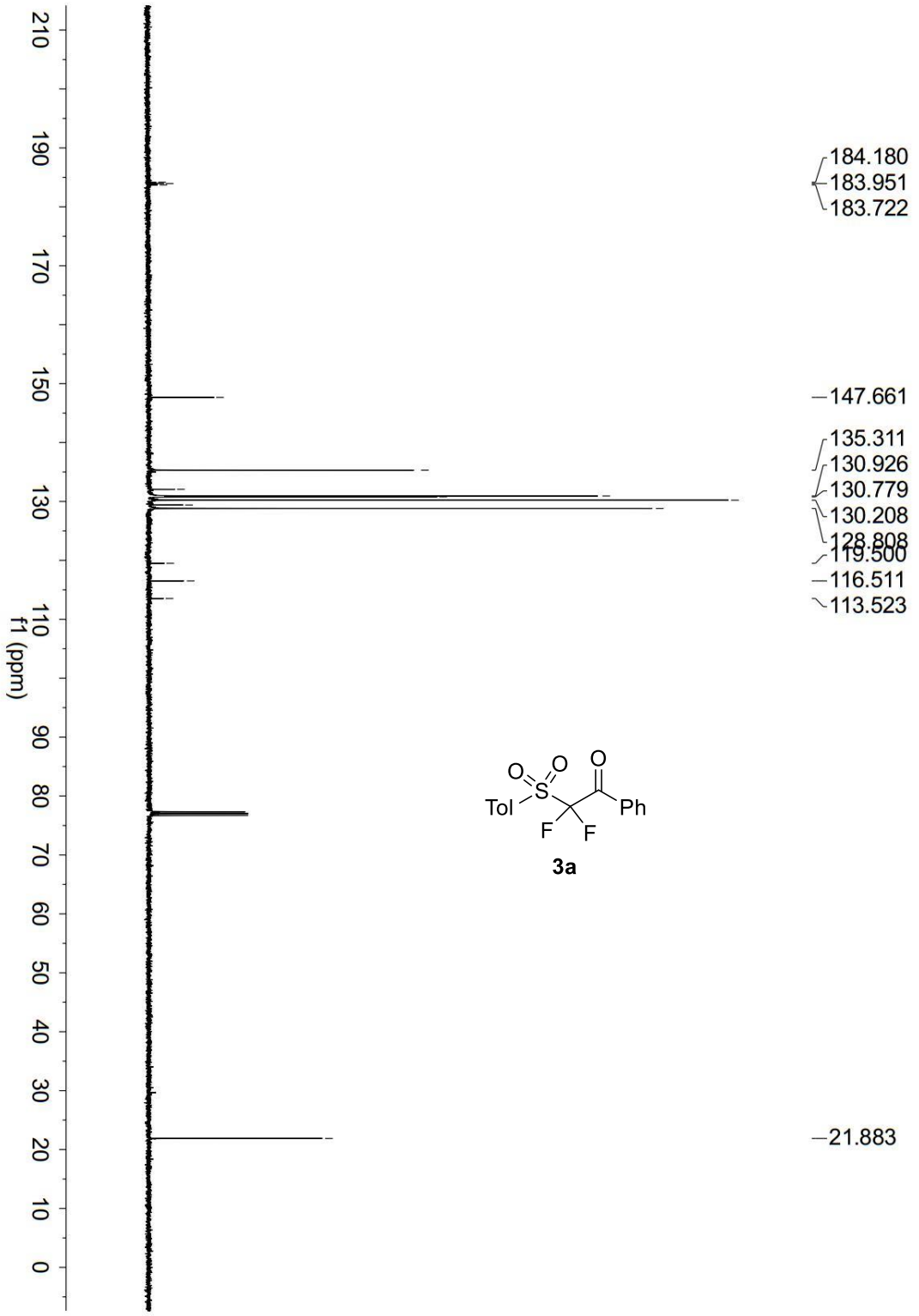
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 5.9 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.76 (t, *J* = 9.2 Hz, 1H), 4.58 (dd, *J* = 9.7, 5.7 Hz, 1H), 4.25 – 4.15 (m, 1H), 3.73 (d, *J* = 14.0 Hz, 1H), 3.60 – 3.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4 (t, *J* = 22.8 Hz), 159.7, 130.6 (t, *J* = 3.2 Hz), 129.8, 129.0, 126.1, 124.4, 121.2, 116.2 (t, *J* = 302.5 Hz), 110.3, 75.5, 54.2, 35.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.6 (d, *J* = 17.2 Hz); HRMS (ESI) calcd for $C_{17}H_{14}F_2O_4SNa$ $[M+Na]^+$: 375.0479, found: 375.0482.

Reference

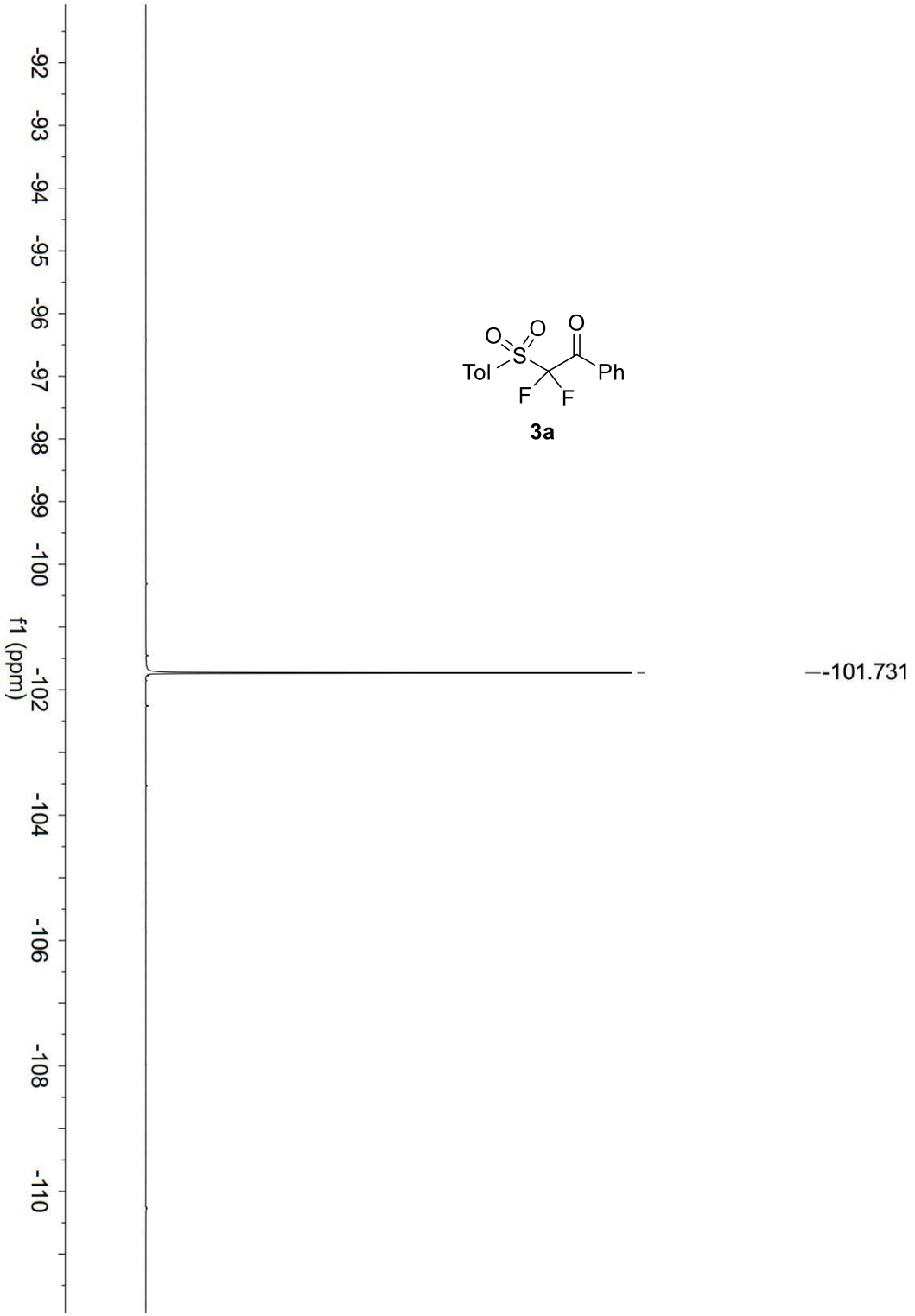
1. (a) Y.-B. Wu, G.-P. Lu, B.-J. Zhou, M.-J. Bu, L. Wan and C. Cai, *Chem. Commun.*, 2016, **52**, 5965; (b) G. K. S. Prakash, J. Hu, M. M. Alauddin, P. S. Conti and G. A. Olah, *J. Fluorine Chem.*, 2003, **121**, 239.


8.186
8.166
7.904
7.885
7.709
7.691
7.673
7.553
7.534
7.516
7.446
7.426
1.97
2.00
1.07
2.16
2.08
3.08
2.495
0.000
f1 (ppm)
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
O
O
O
S
Tol
Ph
F
F

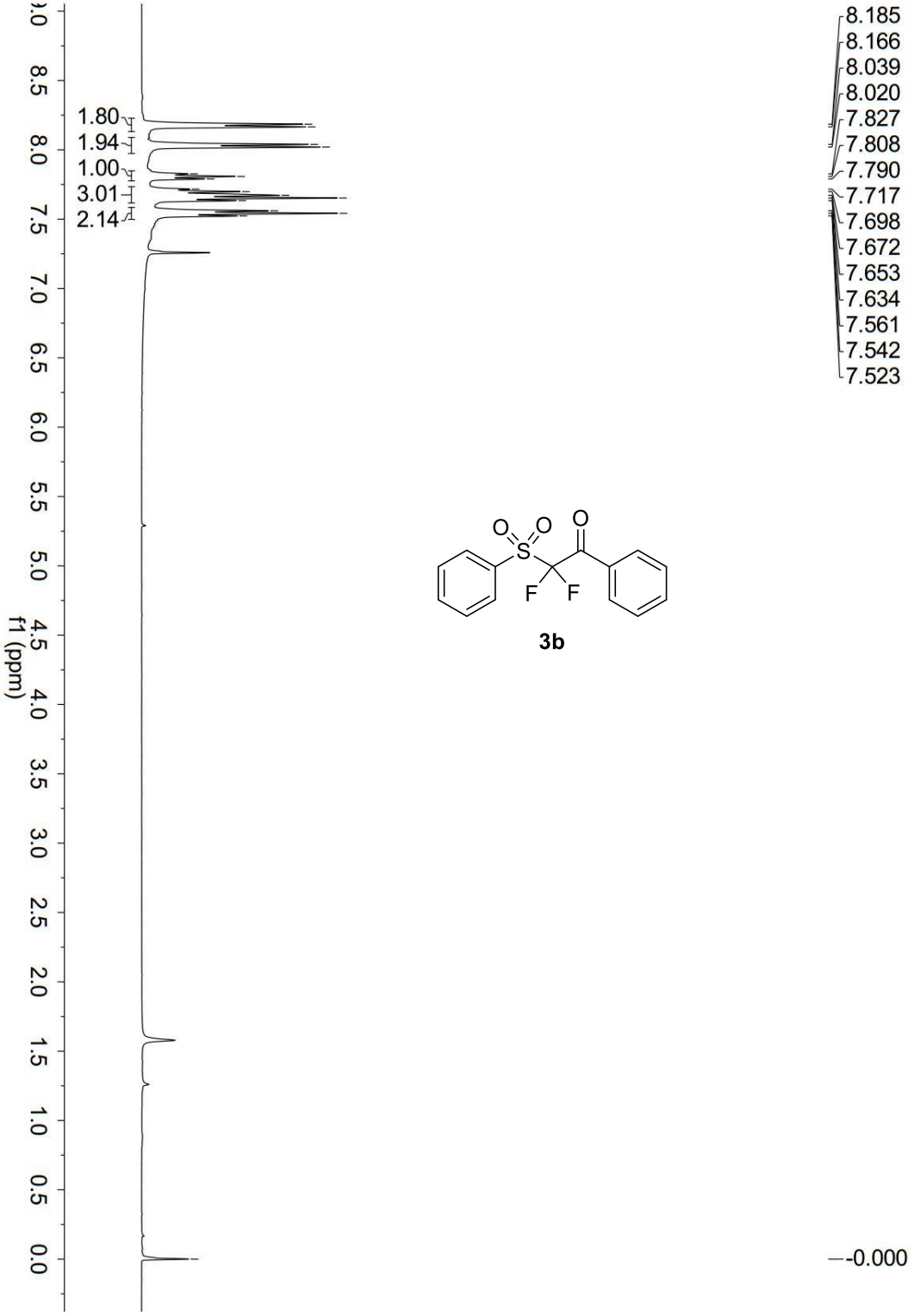
3a


184.180
183.951
183.722
147.661
135.311
130.926
130.779
130.208
128.808
119.500
116.511
113.523
21.883
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
O
O
O
S
Tol
Ph
F
F

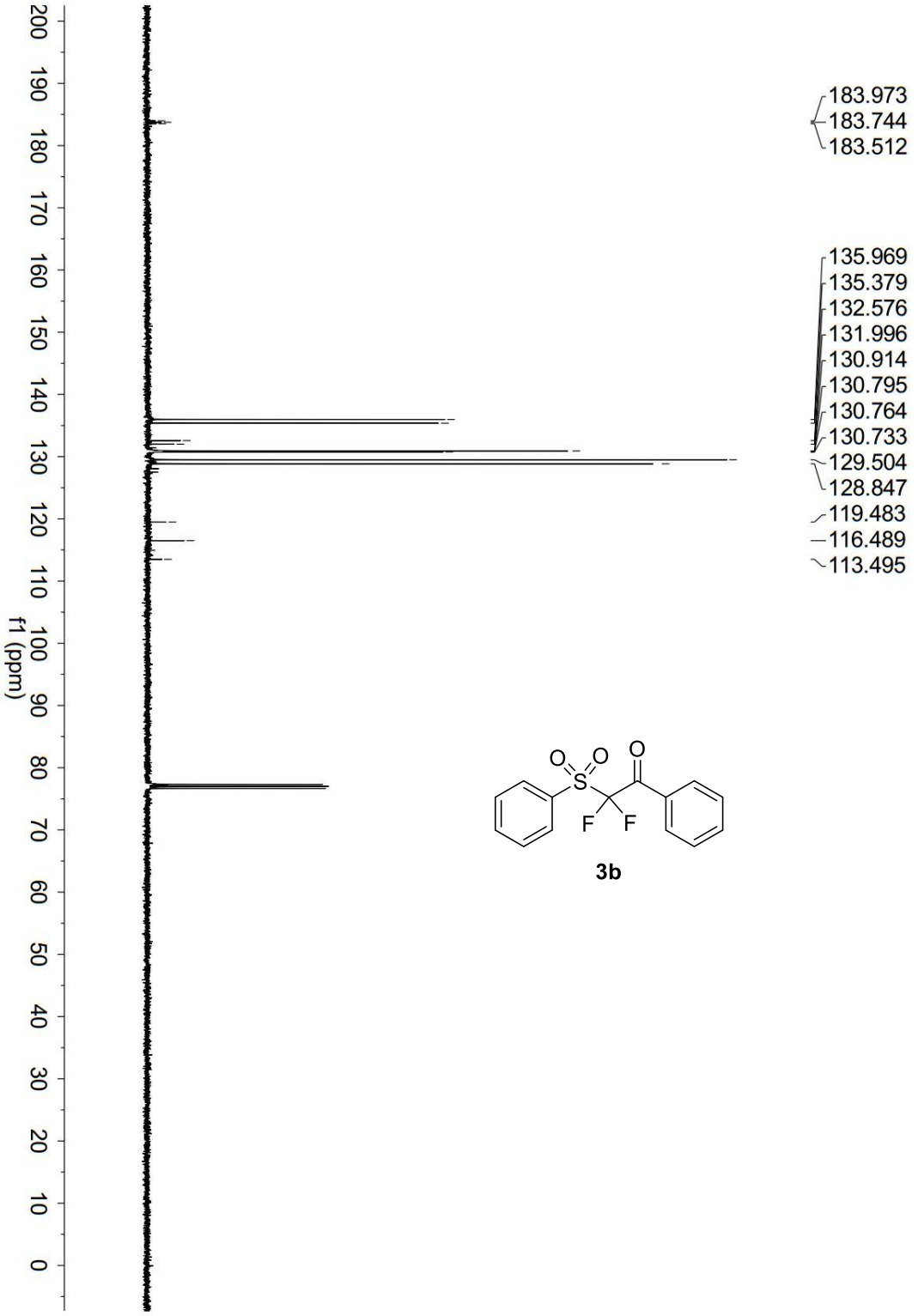
3a


-92
-93
-94
-95
-96
-97
-98
-99
-100
-102
-104
-106
-108
-110
f1 (ppm)
-101.731
O
O
O
S
Tol
Ph
F
F

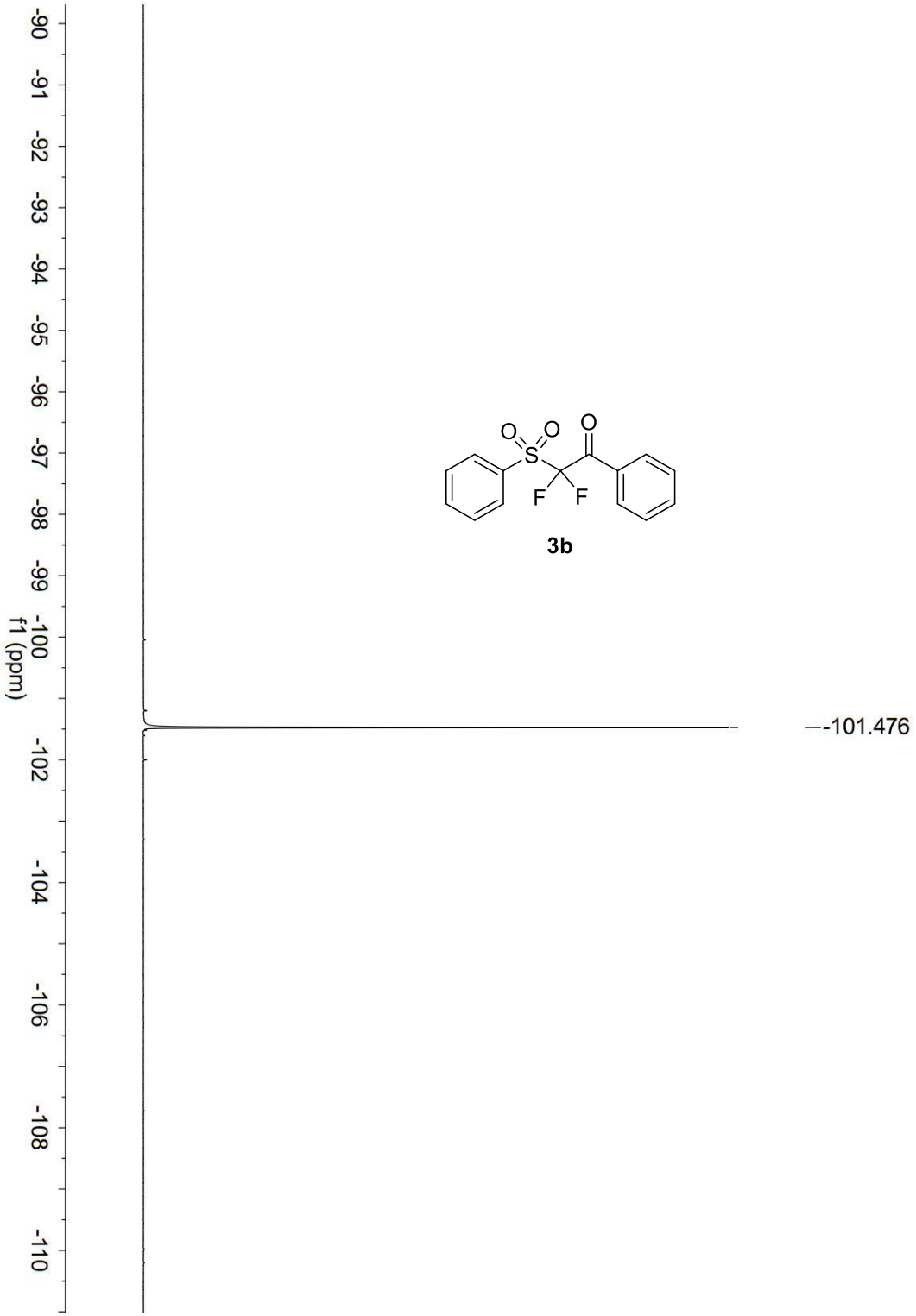
3a


8.185
8.166
8.039
8.020
7.827
7.808
7.790
7.717
7.698
7.672
7.653
7.634
7.561
7.542
7.523
1.80
1.94
1.00
3.01
2.14
-0.000
f1 (ppm)
O
O
O
S
F
F

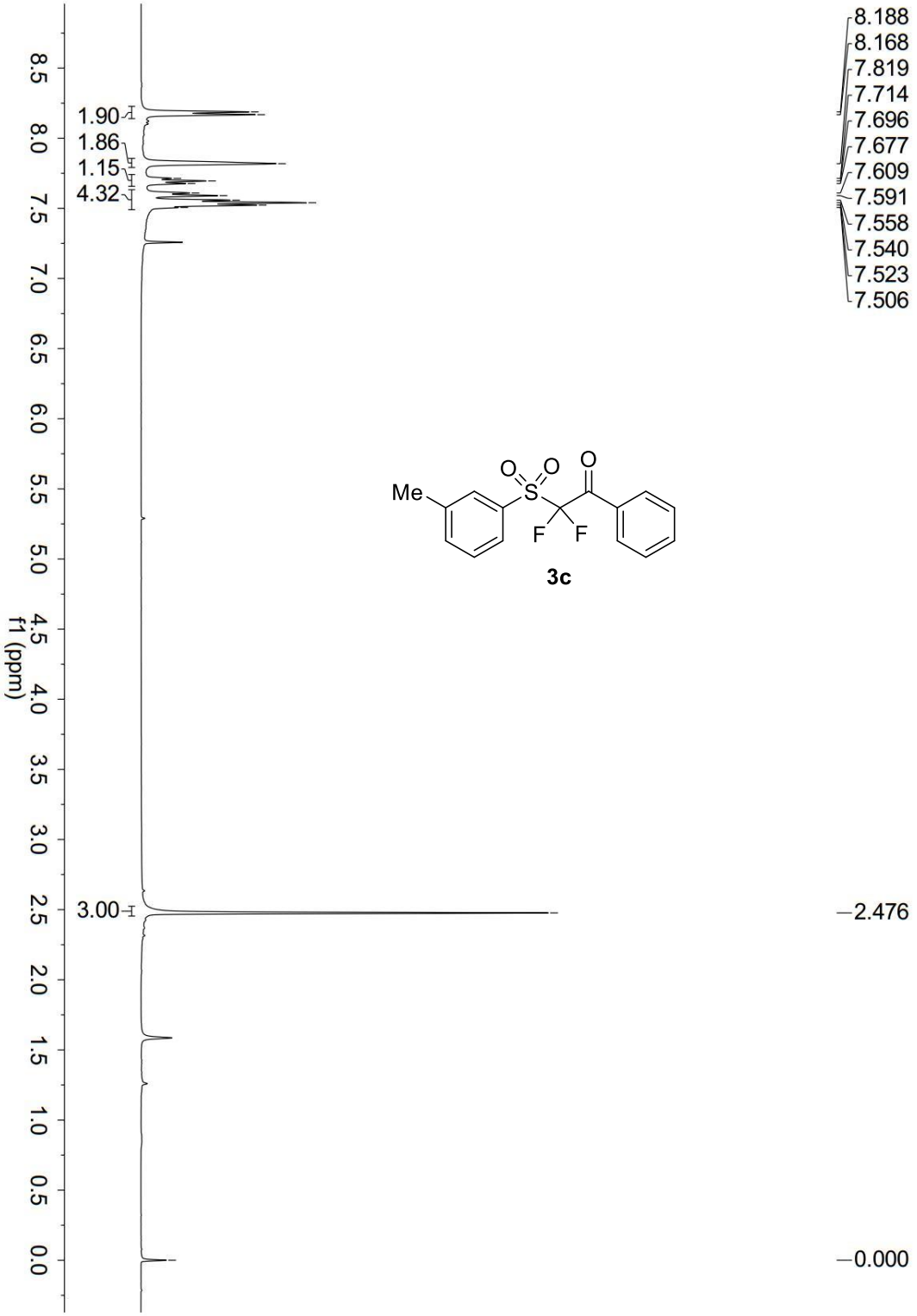
3b

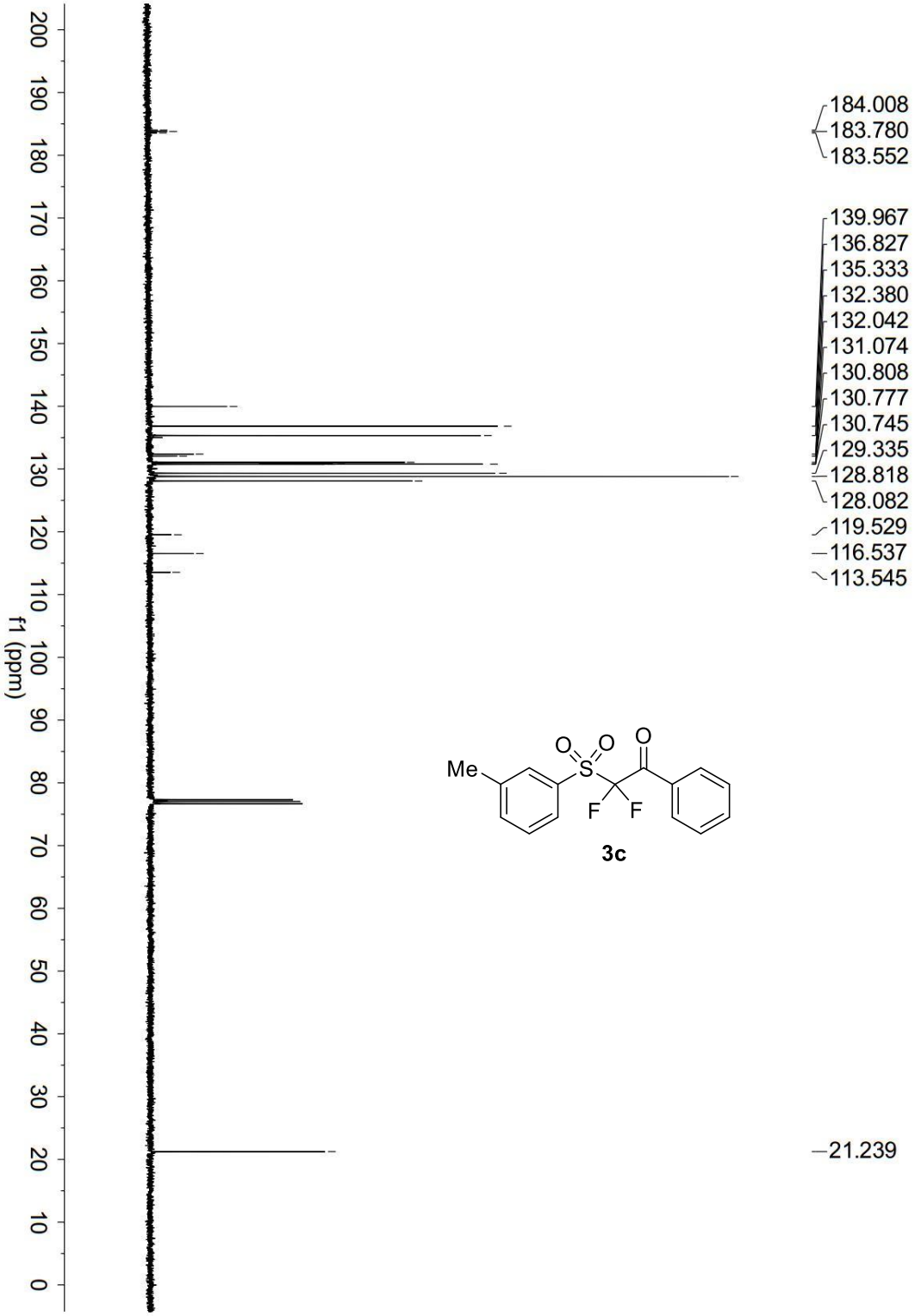

183.973
183.744
183.512
135.969
135.379
132.576
131.996
130.914
130.795
130.764
130.733
129.504
128.847
119.483
116.489
113.495
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
O
S
F
F

3b

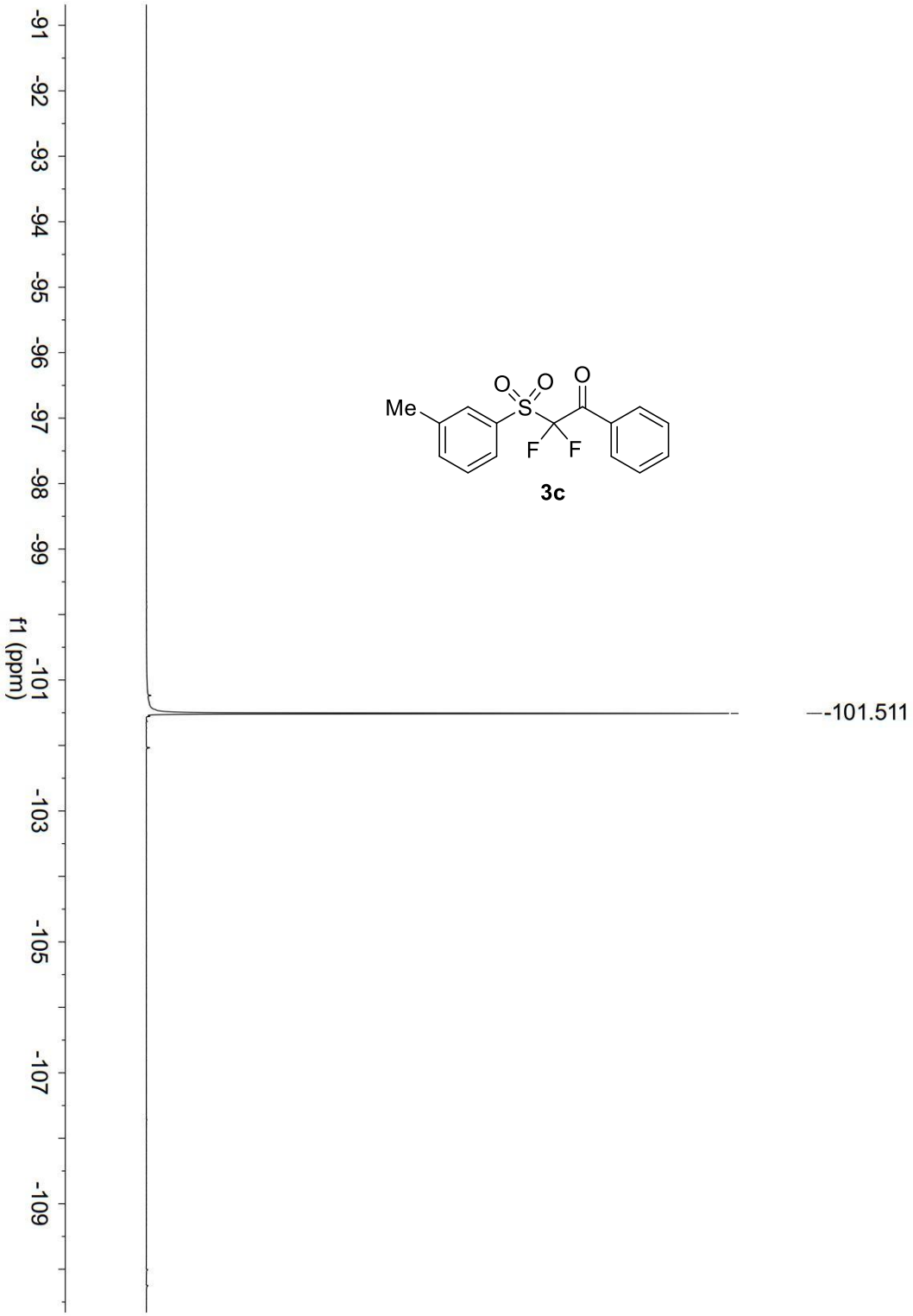

-90
-91
-92
-93
-94
-95
-96
-97
-98
-99
-100
-102
-104
-106
-108
-110
f1 (ppm)
-101.476
O
O
O
S
F
F

3b

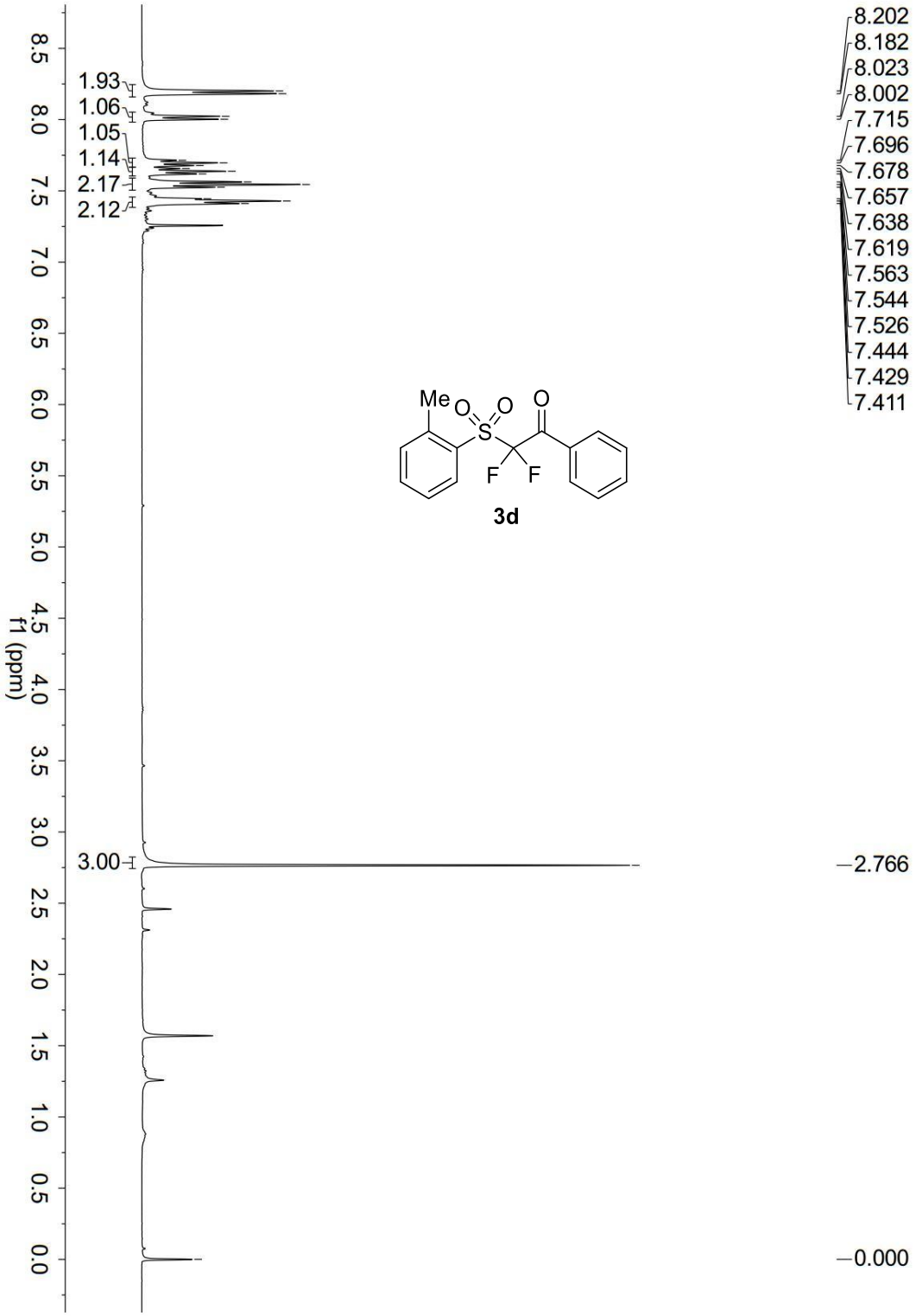

8.188
8.168
7.819
7.714
7.696
7.677
7.609
7.591
7.558
7.540
7.523
7.506
1.90
1.86
1.15
4.32
3.00
2.476
0.000
f1 (ppm)
Me
O
O
S
O
F
F
3c

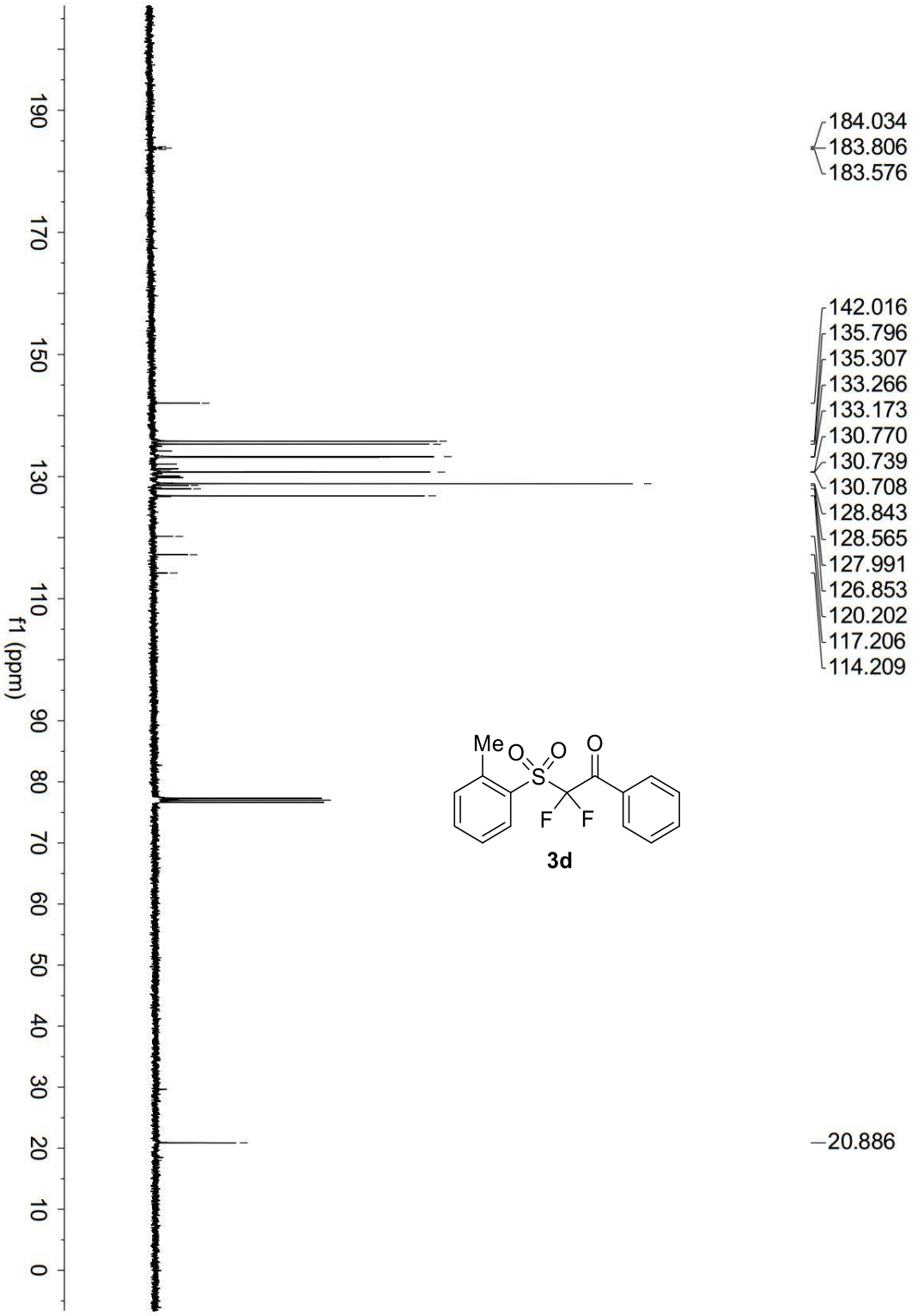

184.008
183.780
183.552
139.967
136.827
135.333
132.380
132.042
131.074
130.808
130.777
130.745
129.335
128.818
128.082
119.529
116.537
113.545
21.239
f1 (ppm)
Me
O
O
S
O
F
F

3c

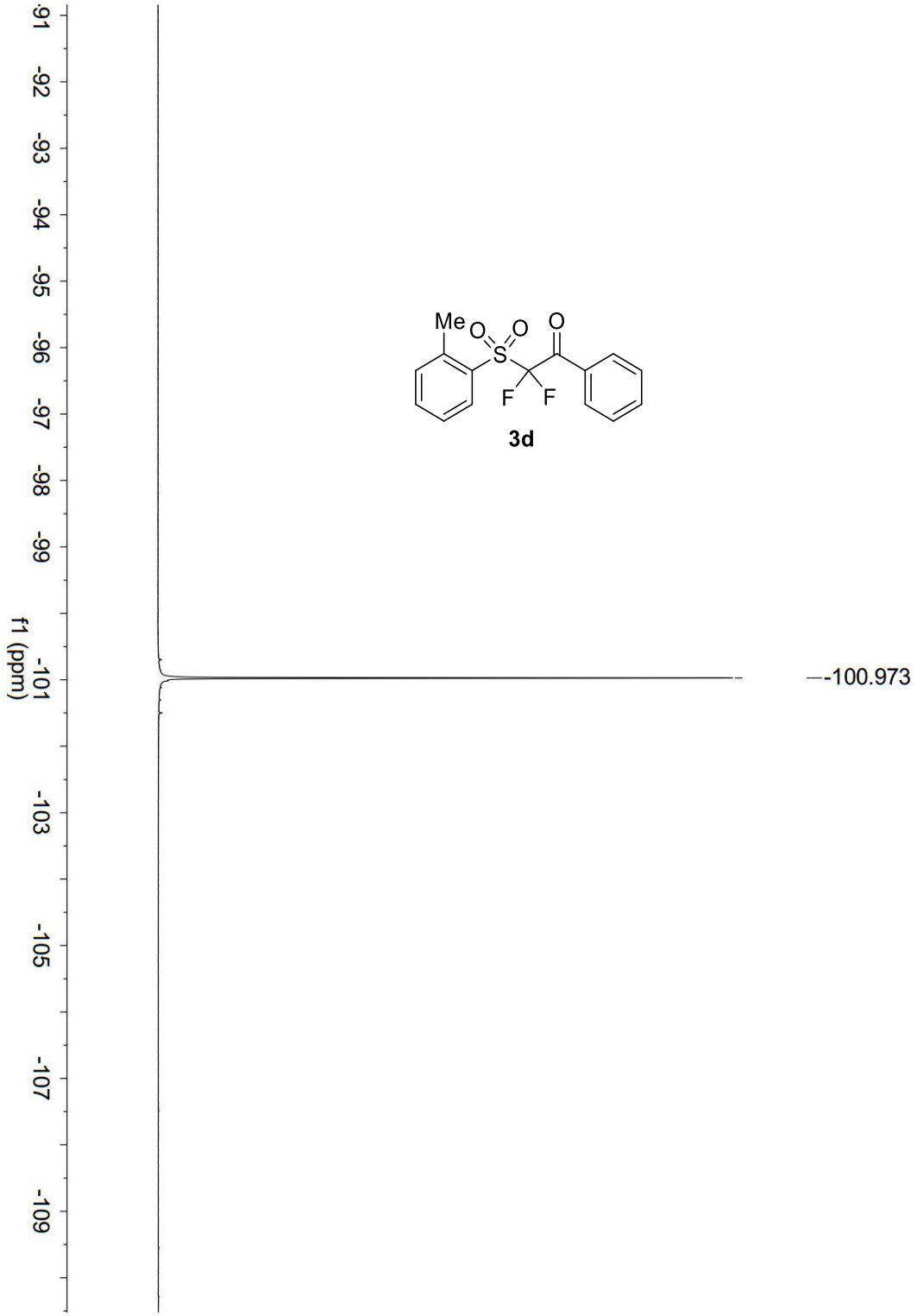

-91
-92
-93
-94
-95
-96
-97
-98
-99
-101
-103
-105
-107
-109
f1 (ppm)
-101.511
Me
O
O
O
S
F
F

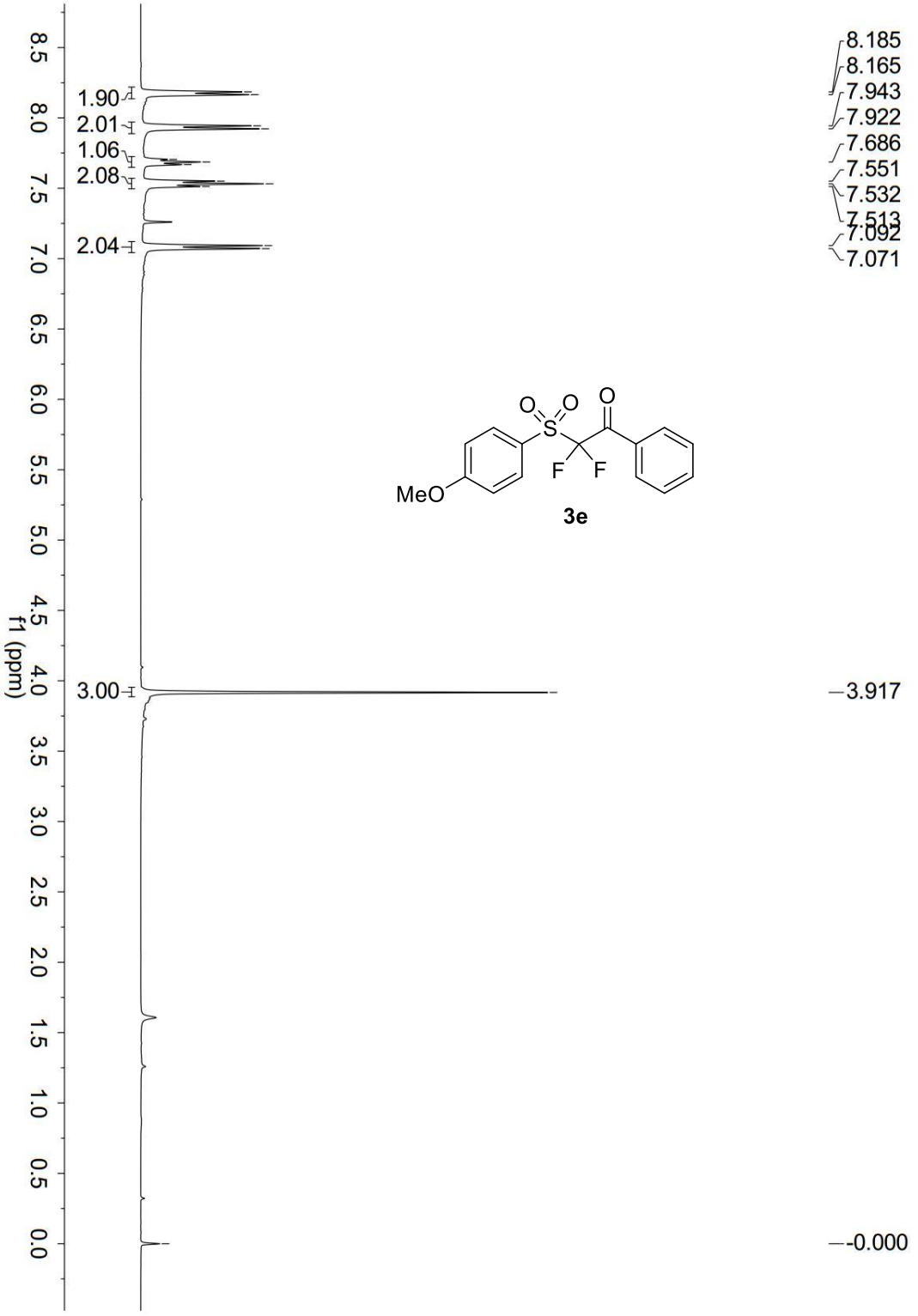
3c


8.202
8.182
8.023
8.002
7.715
7.696
7.678
7.657
7.638
7.619
7.563
7.544
7.526
7.444
7.429
7.411
1.93
1.06
1.05
1.14
2.17
2.12
3.00
2.766
0.000
f1 (ppm)
Me
O
O
S
O
F
F
3d

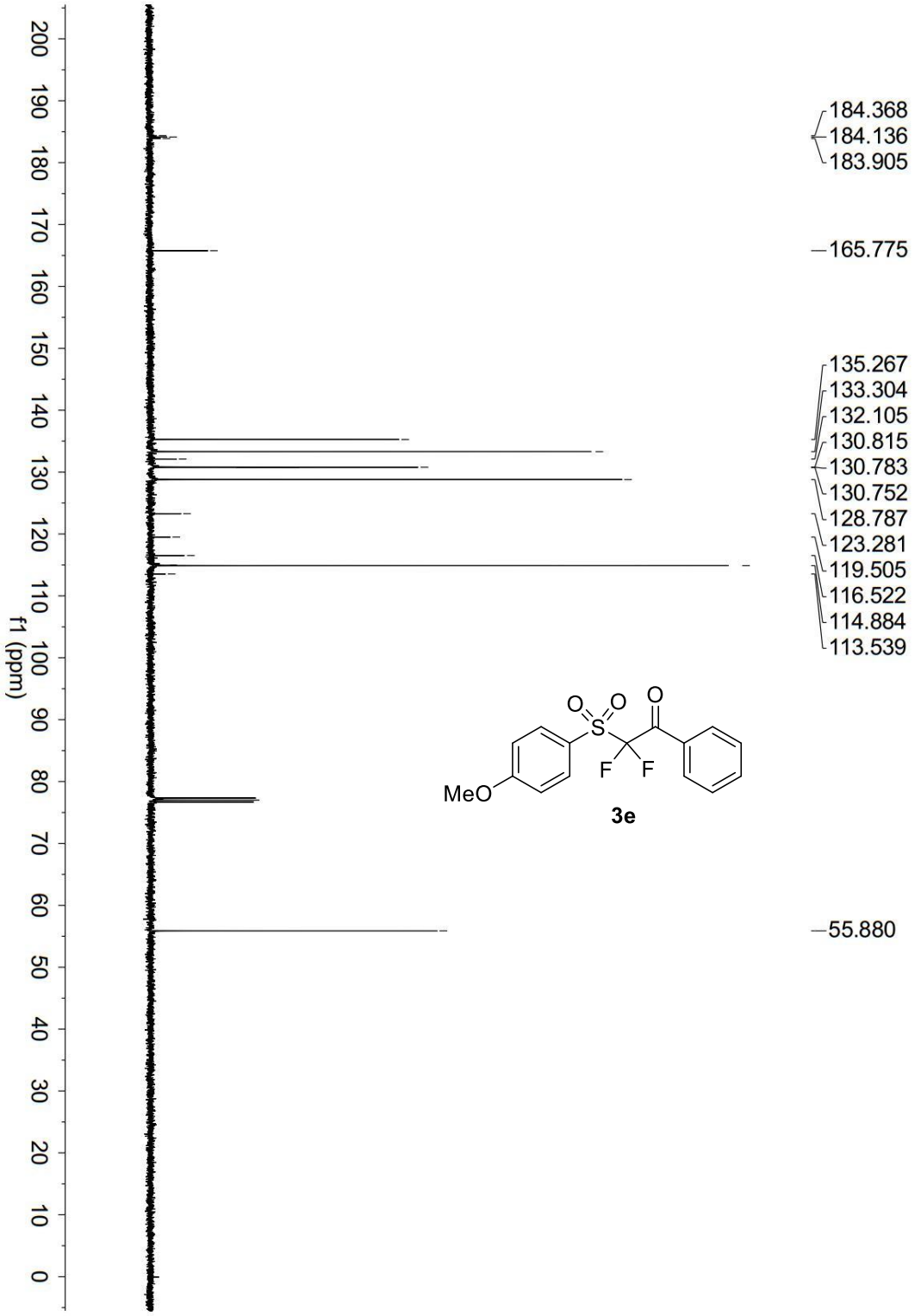

184.034
183.806
183.576
142.016
135.796
135.307
133.266
133.173
130.770
130.739
130.708
128.843
128.565
127.991
126.853
120.202
117.206
114.209
20.886
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Me
O
O
S
O
F
F

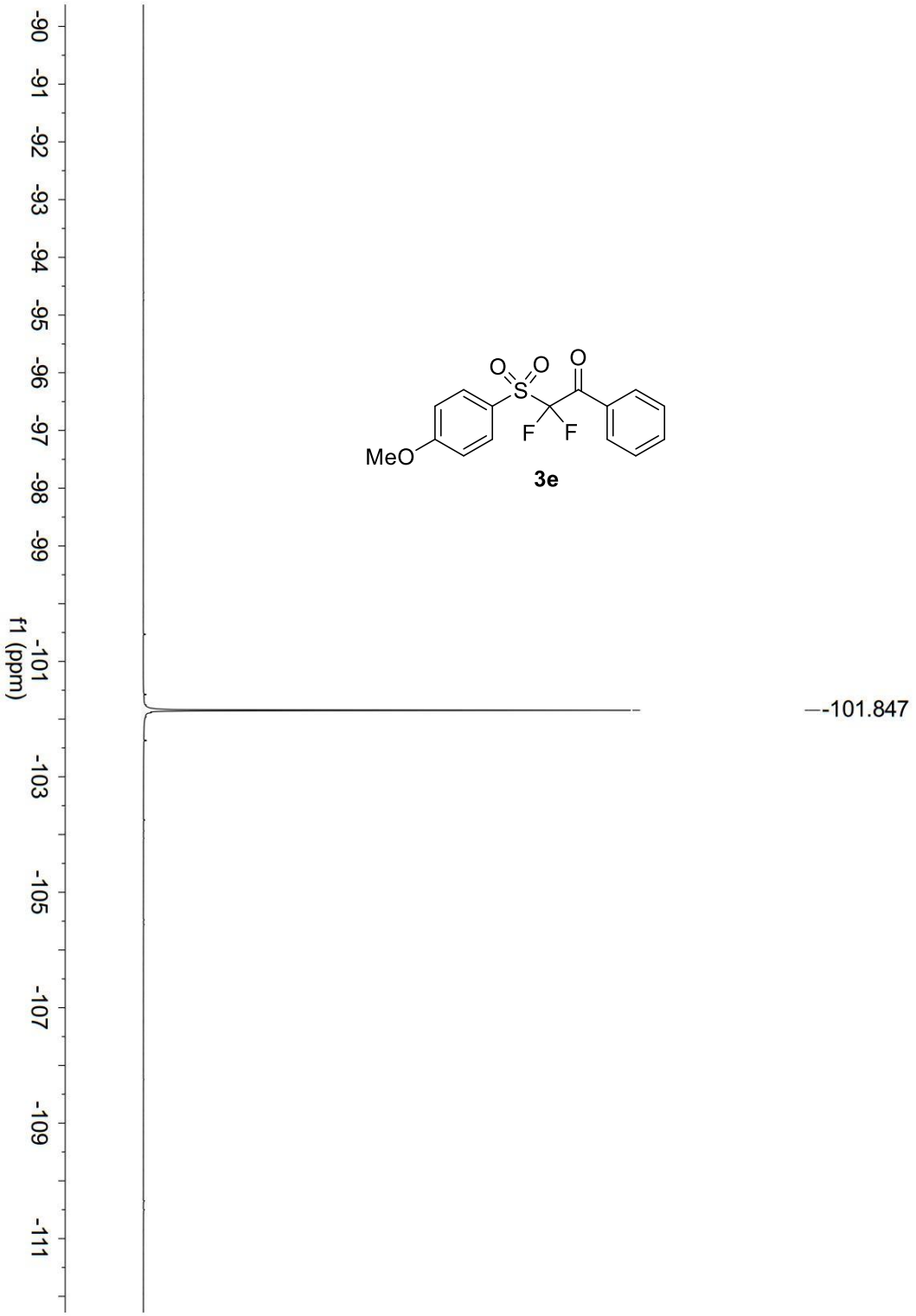
3d


Me
O
O
S
O
F
F
3d
-100.973
-91
-92
-93
-94
-95
-96
-97
-98
-99
-101
-103
-105
-107
-109
f1 (ppm)

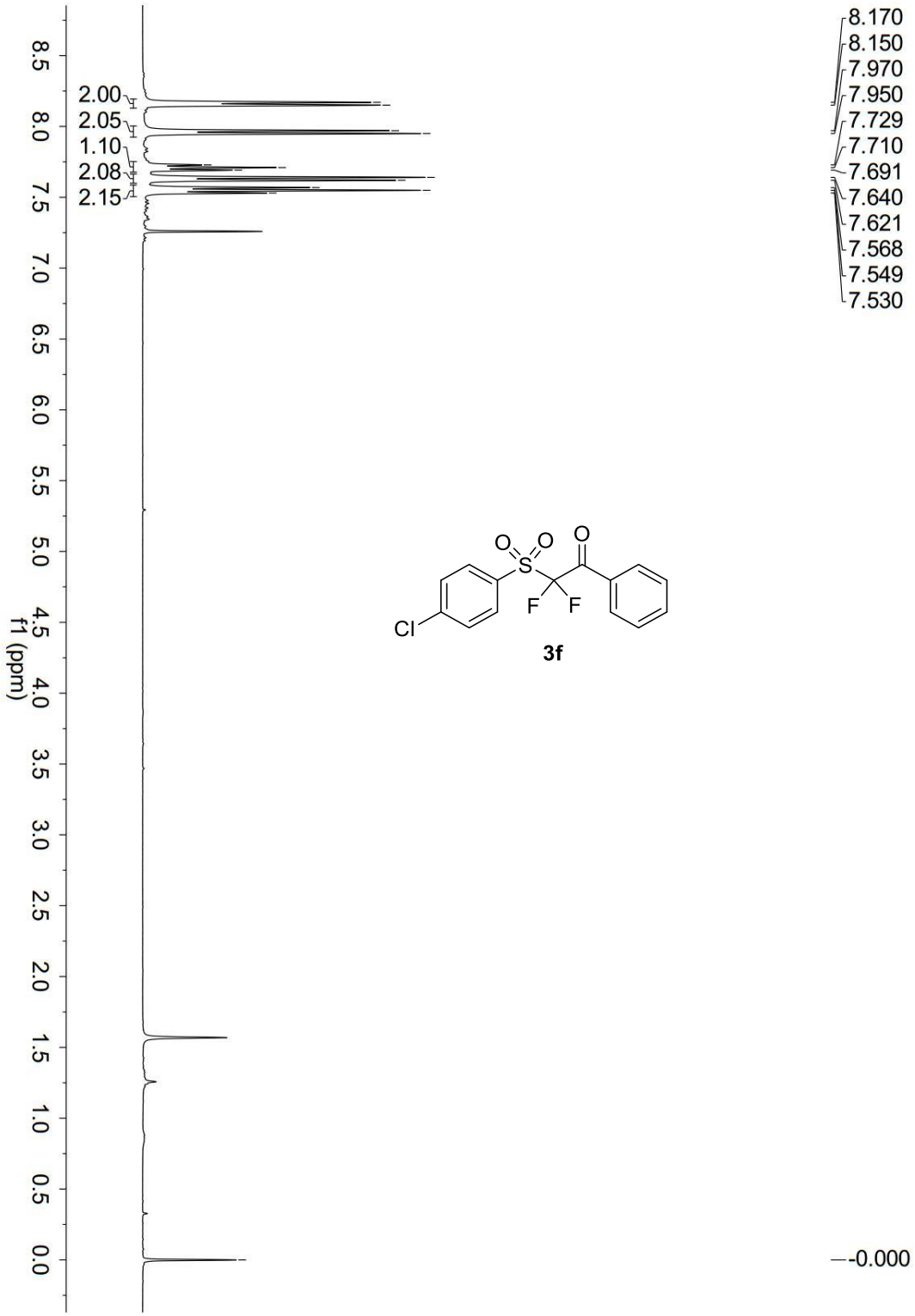

8.185
8.165
7.943
7.922
7.686
7.551
7.532
7.513
7.092
7.071
1.90
2.01
1.06
2.08
2.04
3.00
3.917
-0.000
f1 (ppm)
MeO
F
F
O
O
O
S

3e

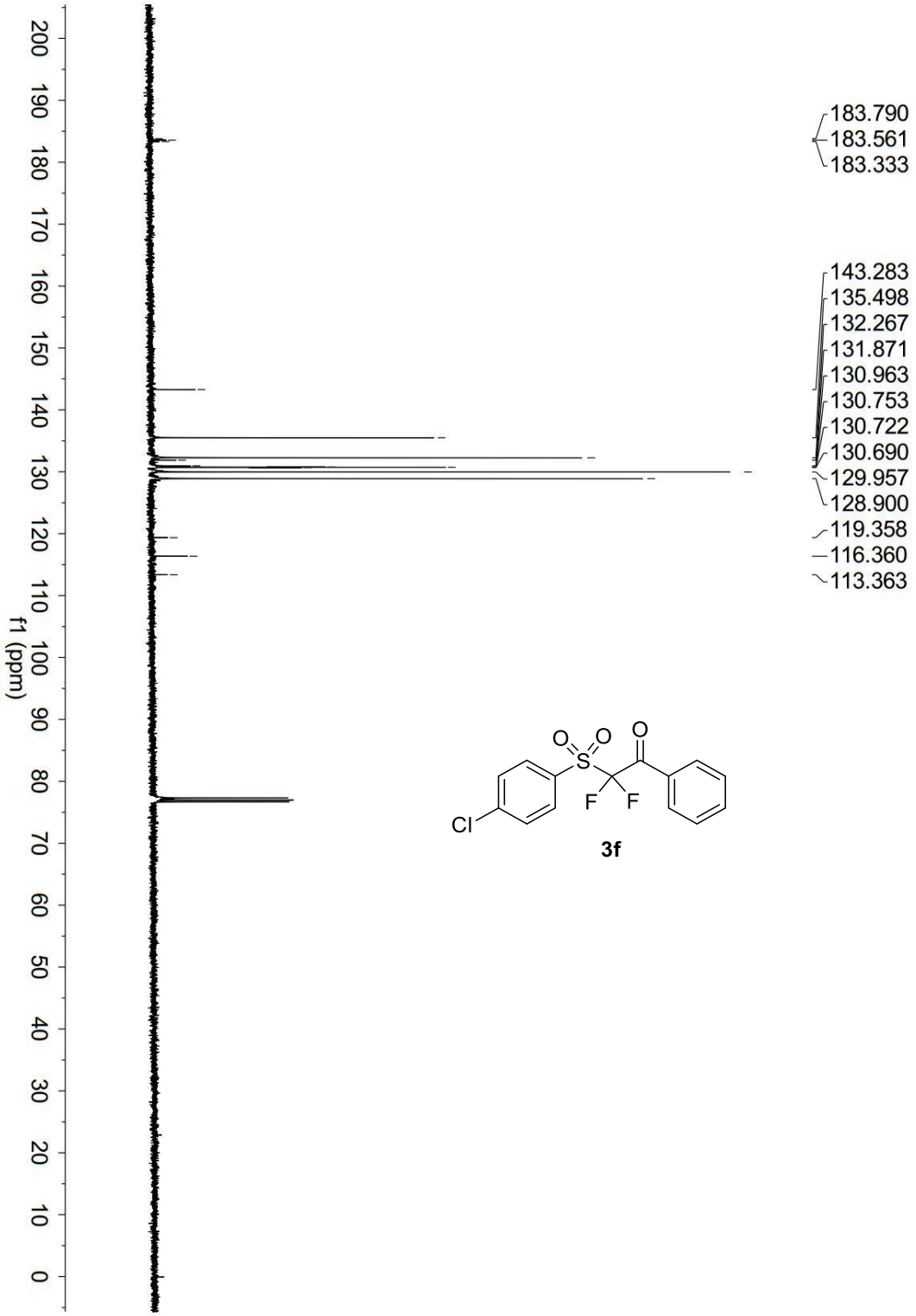

184.368
184.136
183.905
165.775
135.267
133.304
132.105
130.815
130.783
130.752
128.787
123.281
119.505
116.522
114.884
113.539
55.880
f1 (ppm)
MeO
3e


-90
-91
-92
-93
-94
-95
-96
-97
-98
-99
-101
-103
-105
-107
-109
-111
f1 (ppm)
O
O
O
S
F
F
MeO
-101.847

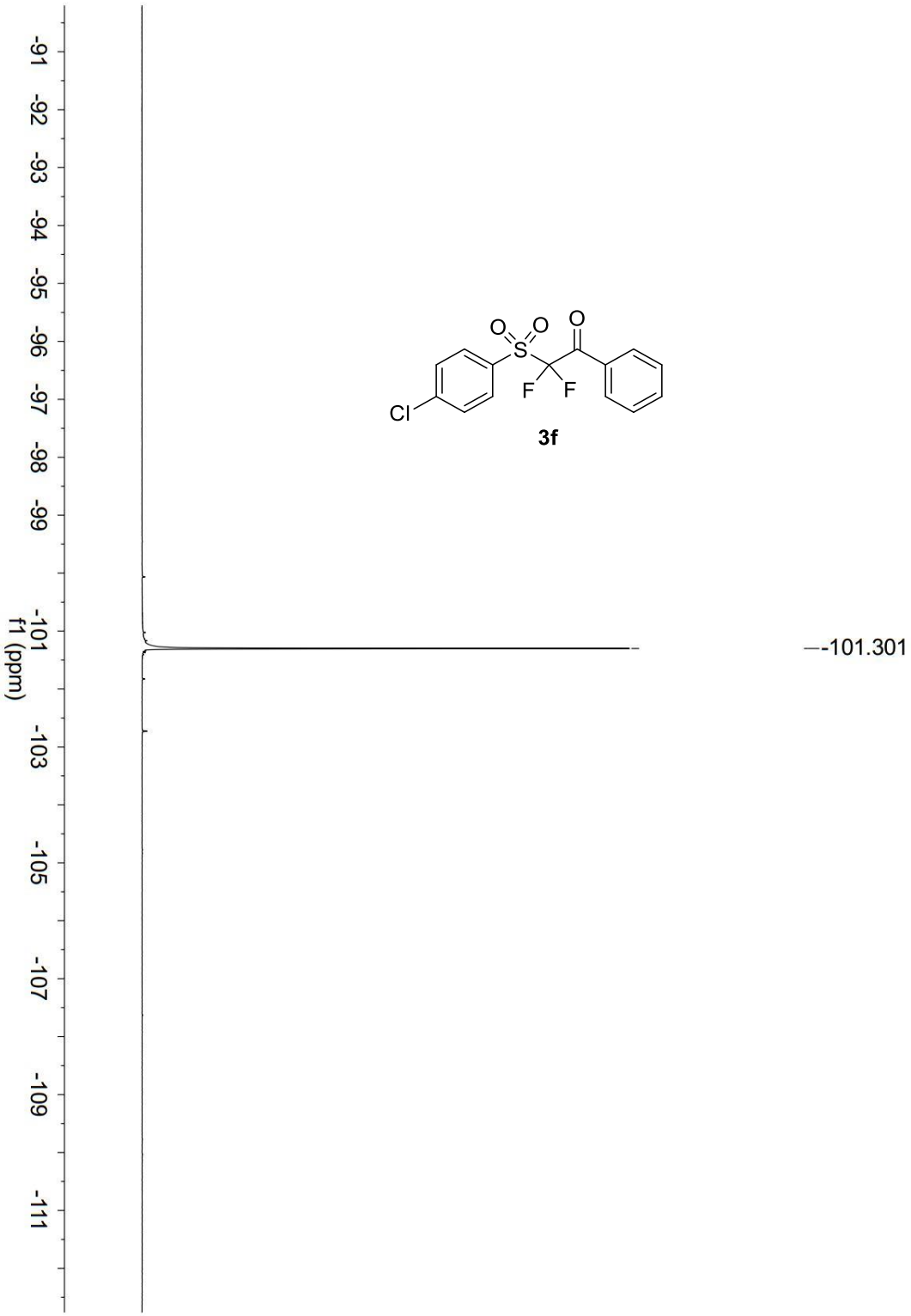
3e


8.170
8.150
7.970
7.950
7.729
7.710
7.691
7.640
7.621
7.568
7.549
7.530
2.00
2.05
1.10
2.08
2.15
-0.000
f1 (ppm)
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
O
O
O
S
F
F
Cl

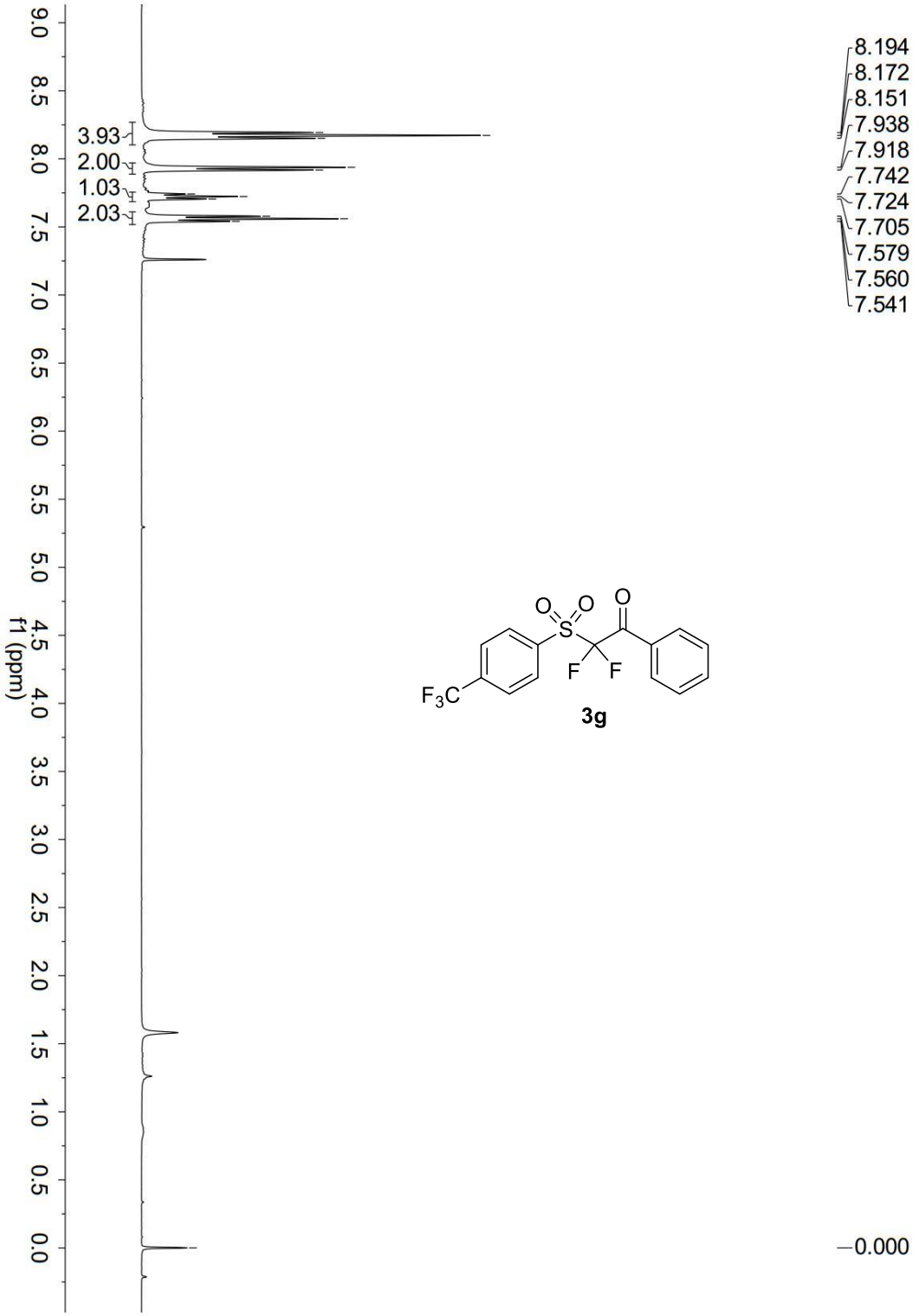
3f


183.790
183.561
183.333
143.283
135.498
132.267
131.871
130.963
130.753
130.722
130.690
129.957
128.900
119.358
116.360
113.363
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
O
S
F
F
Cl

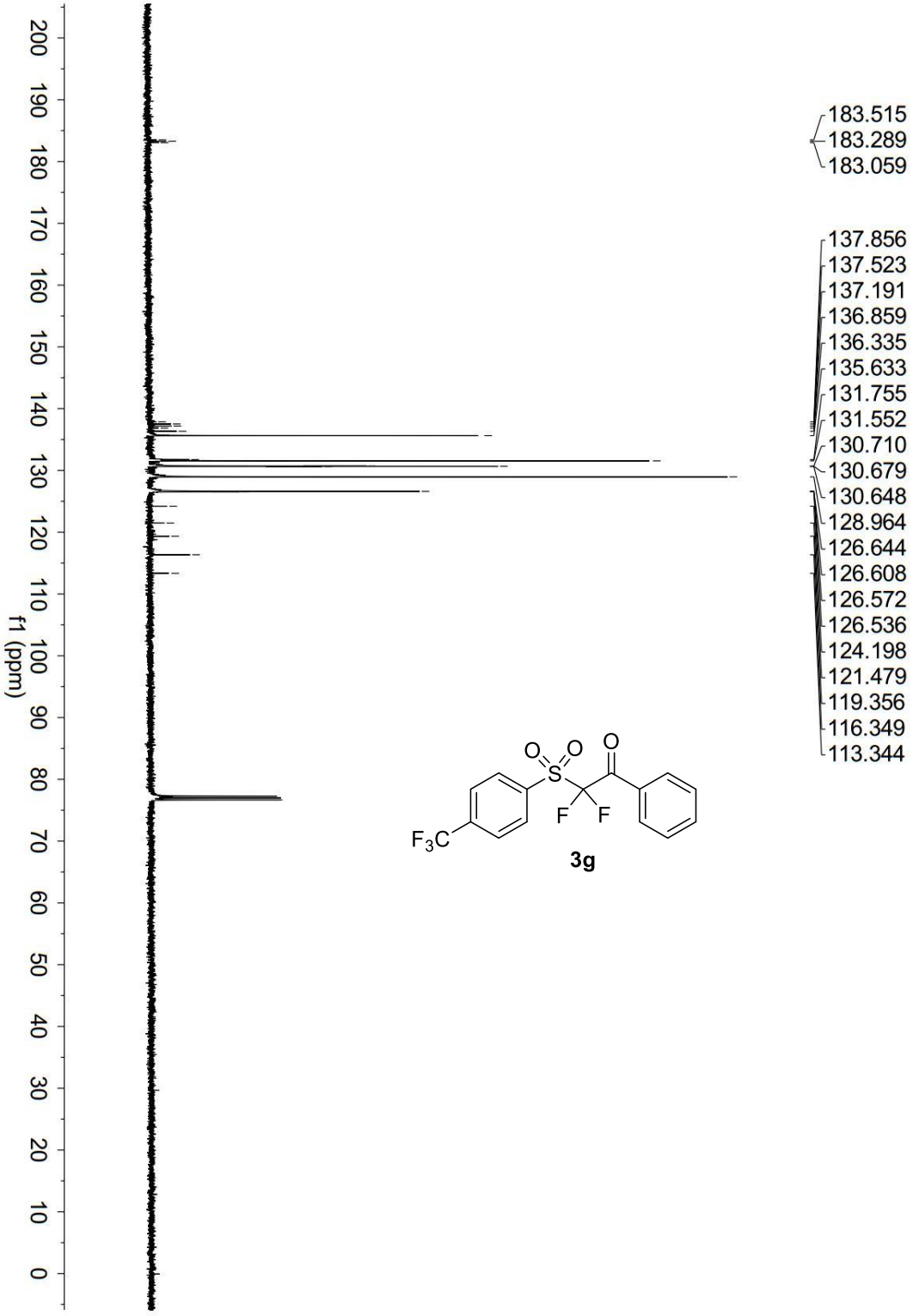
3f


-91
-92
-93
-94
-95
-96
-97
-98
-99
-101
-103
-105
-107
-109
-111
f1 (ppm)
-101.301
O
O
O
S
F
F
Cl

3f


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3.93
2.00
1.03
2.03
8.194
8.172
8.151
7.938
7.918
7.742
7.724
7.705
7.579
7.560
7.541
0.000
O
O
S
O
F
F
F3C

3g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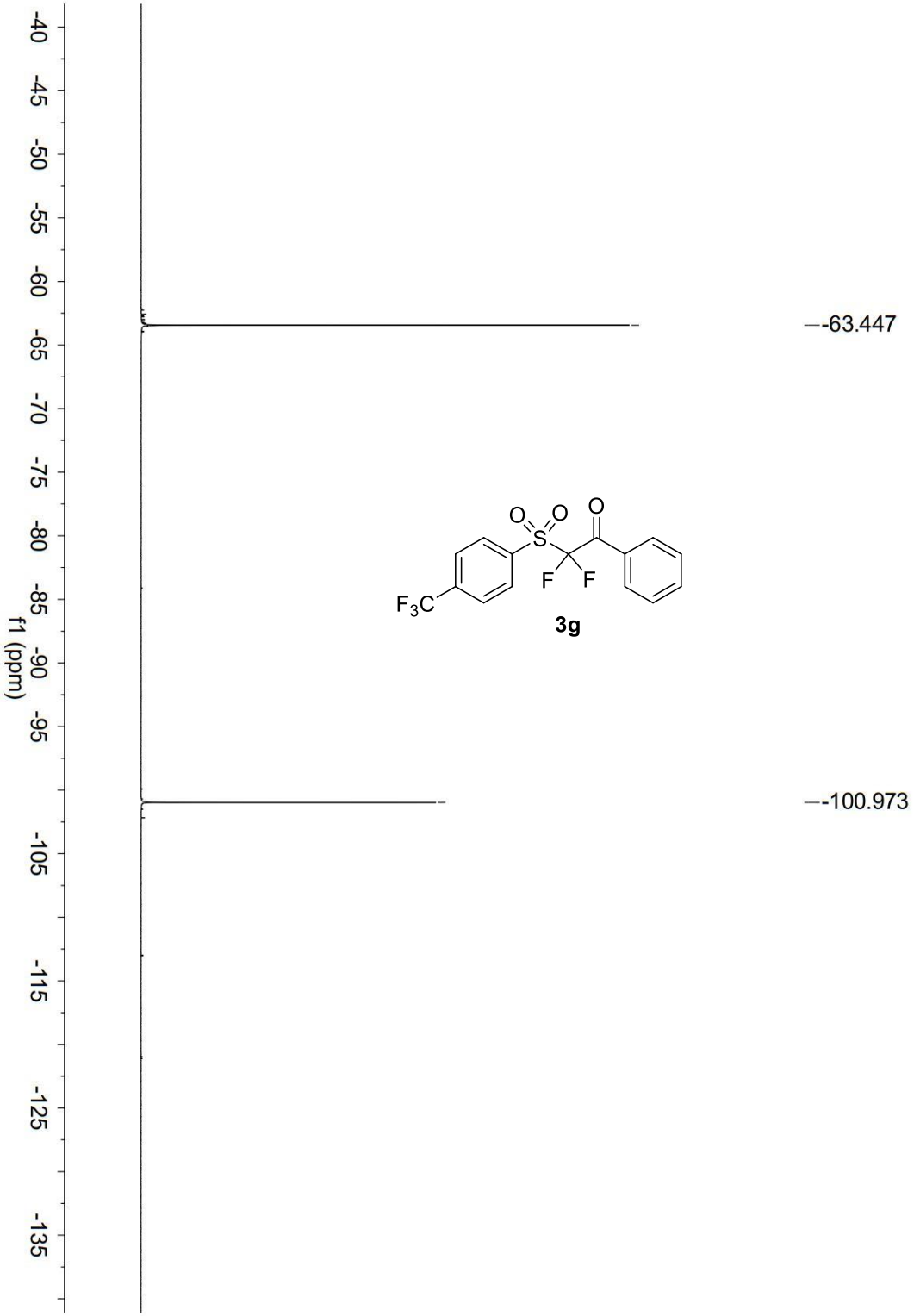
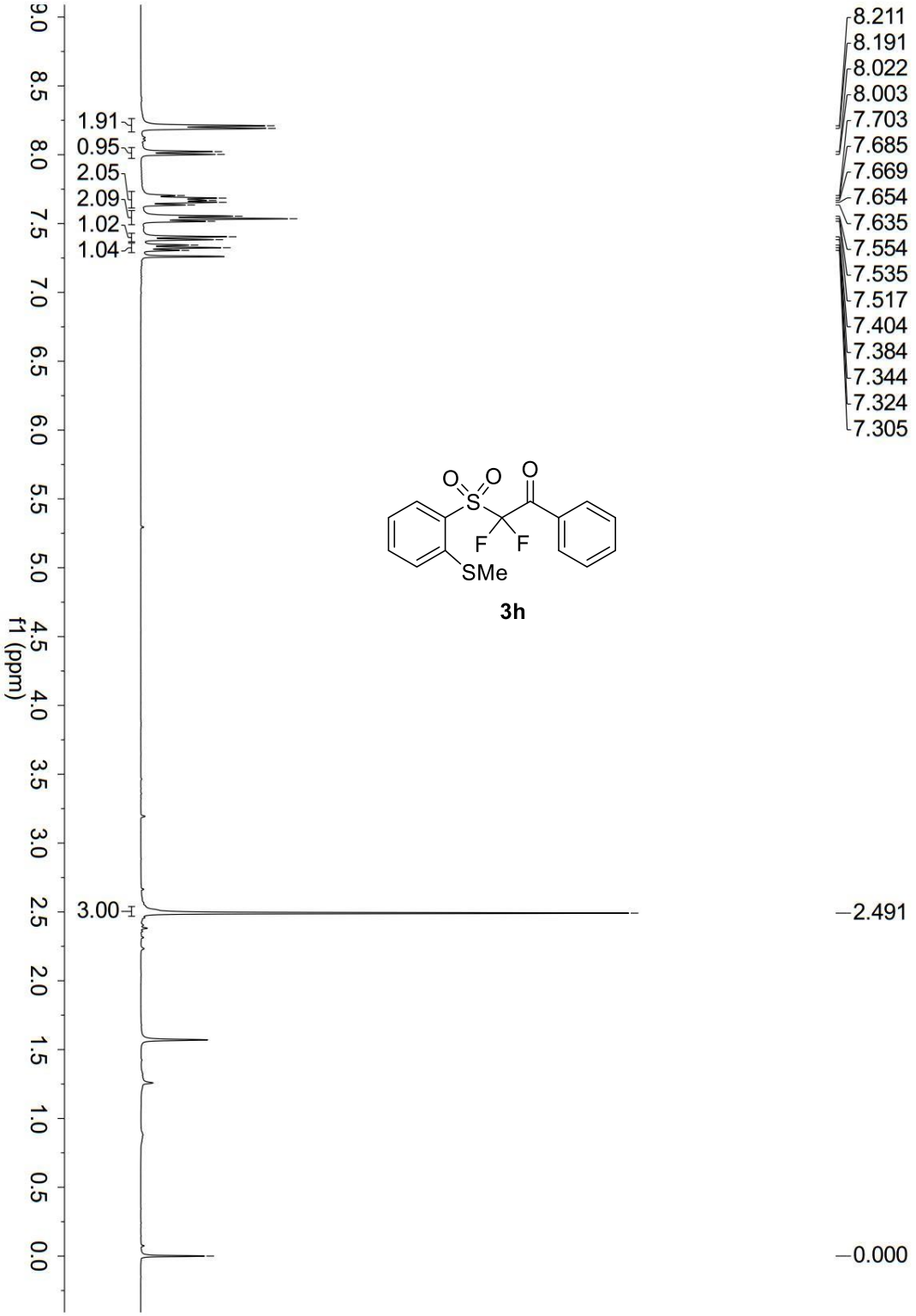
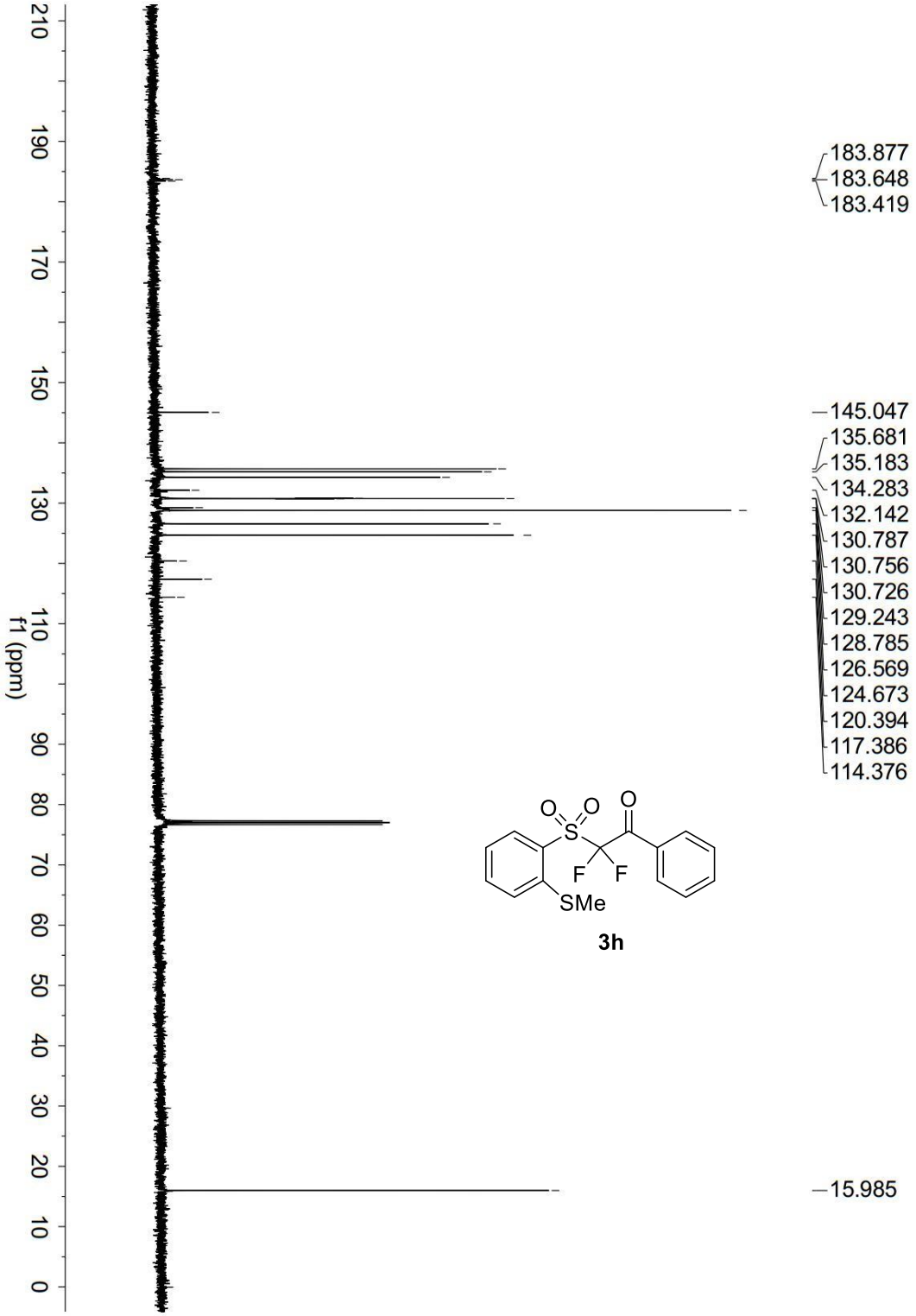
183.289
183.059
137.856
137.523
137.191
136.859
136.335
135.633
131.755
131.552
130.710
130.679
130.648
128.964
126.644
126.608
126.572
126.536
124.198
121.479
119.356
116.349
113.344
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
O
S
F
F
F3C

3g


-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-105
-115
-125
-135
f1 (ppm)
-63.447
-100.973
O
O
O
S
F
F
F3C
3g


8.211
8.191
8.022
8.003
7.703
7.685
7.669
7.654
7.635
7.554
7.535
7.517
7.404
7.384
7.344
7.324
7.305
1.91
0.95
2.05
2.09
1.02
1.04
3.00
2.491
0.000
f1 (ppm)
O
O
O
S
F
F
SMe

3h


183.877
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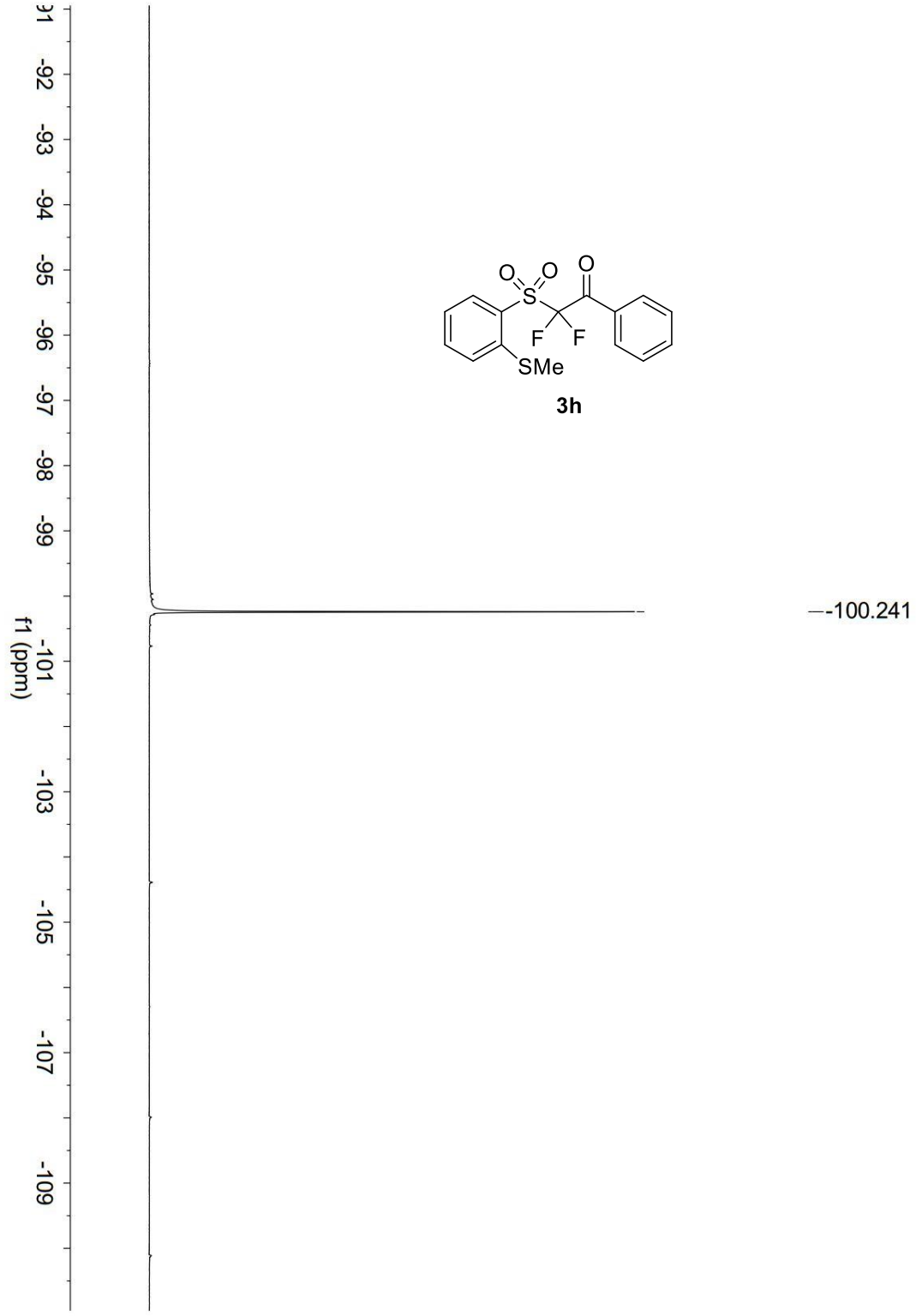
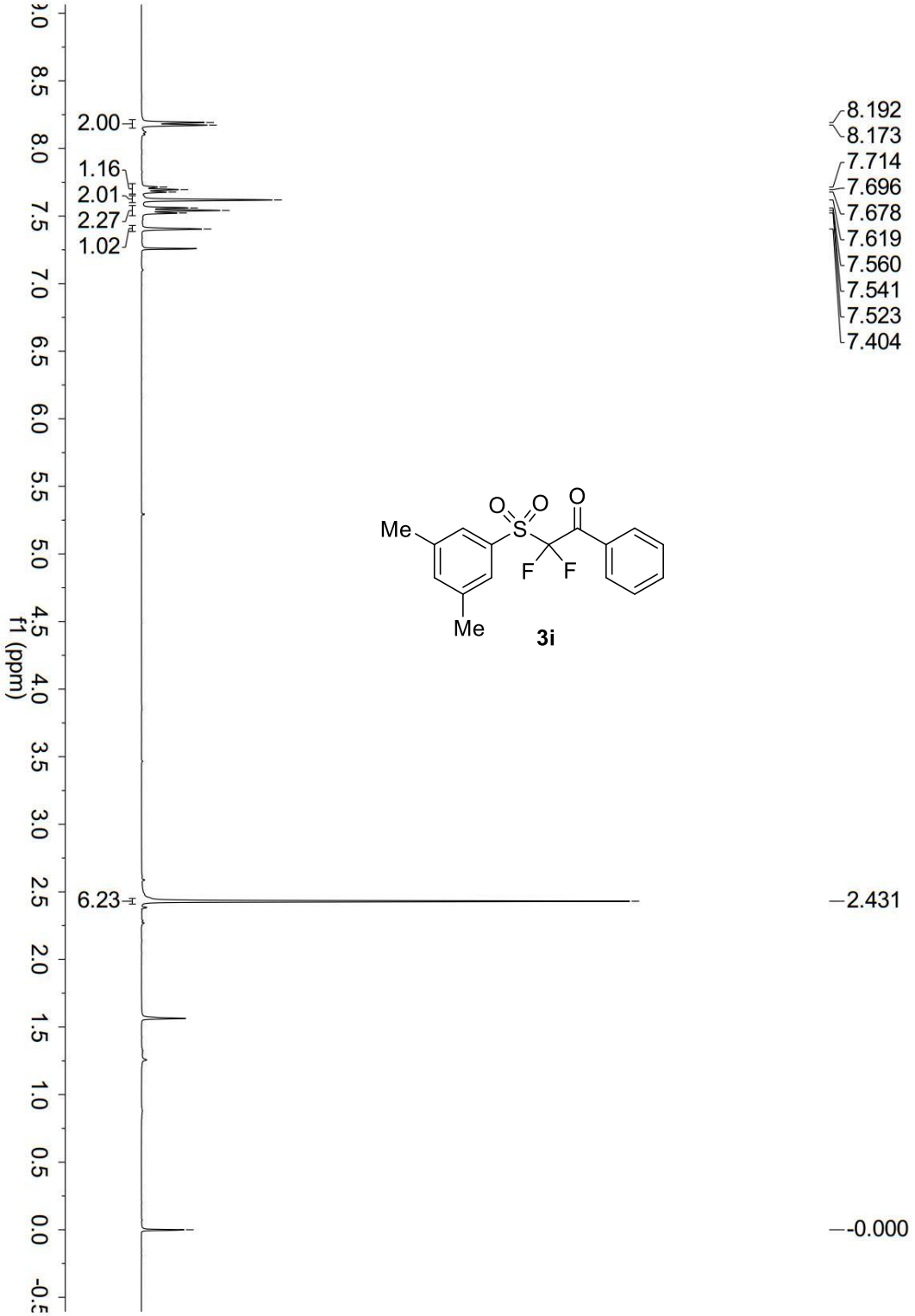
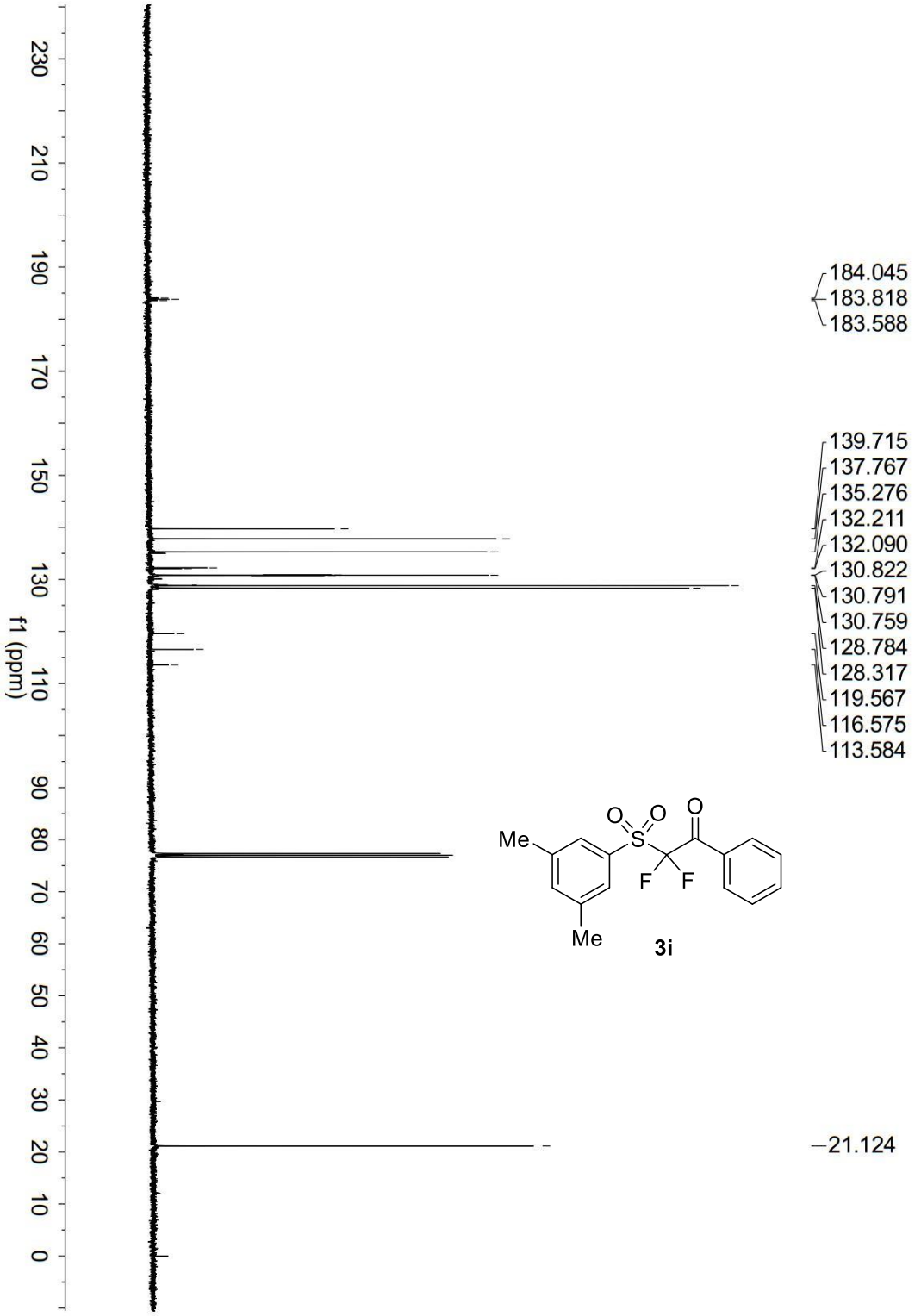
145.047
135.681
135.183
134.283
132.142
130.787
130.756
130.726
129.243
128.785
126.569
124.673
120.394
117.386
114.376
15.985
f1 (ppm)
O
O
O
S
F
F
SMe

3h

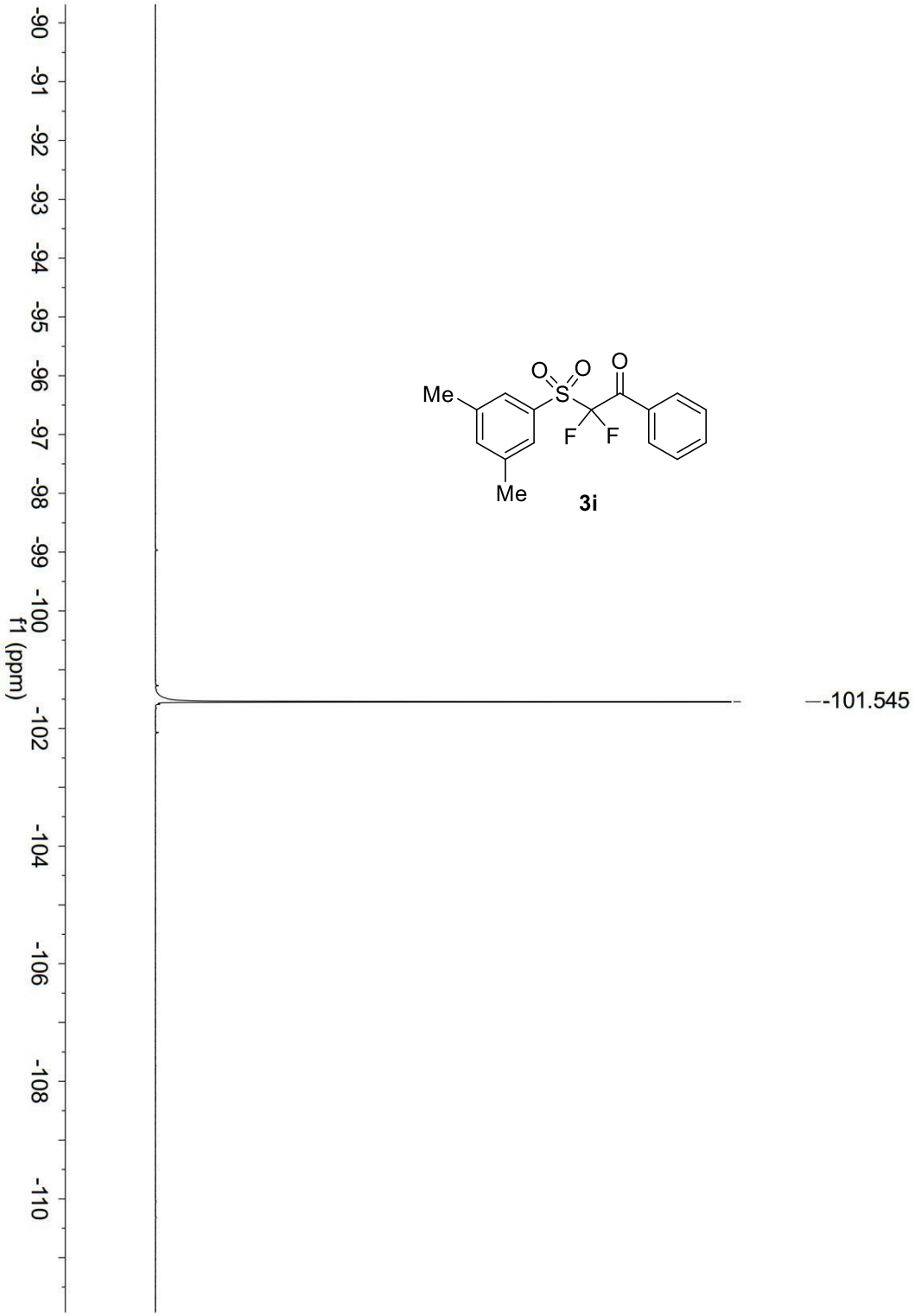

-91
-92
-93
-94
-95
-96
-97
-98
-99
-101
-103
-105
-107
-109
f1 (ppm)
-100.241
O
O
O
S
F
F
SMe

3h

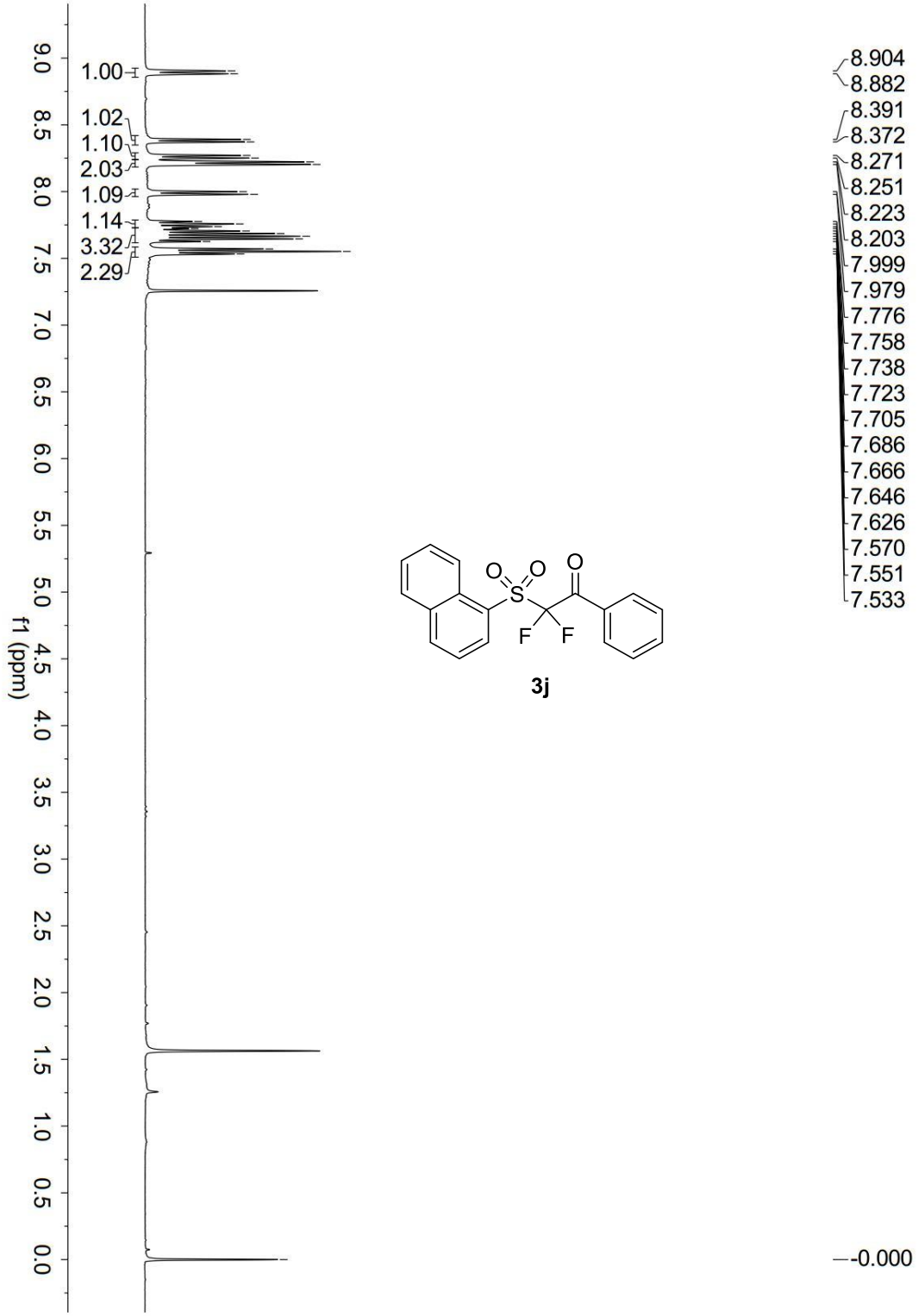

2.00
1.16
2.01
2.27
1.02
6.23
8.192
8.173
7.714
7.696
7.678
7.619
7.560
7.541
7.523
7.404
2.431
-0.000
f1 (ppm)
Me
Me
O
O
S
O
F
F
3i


184.045
183.818
183.588
139.715
137.767
135.276
132.211
132.090
130.822
130.791
130.759
128.784
128.317
119.567
116.575
113.584
21.124
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
O
O
O
S
Me
F
F
Me

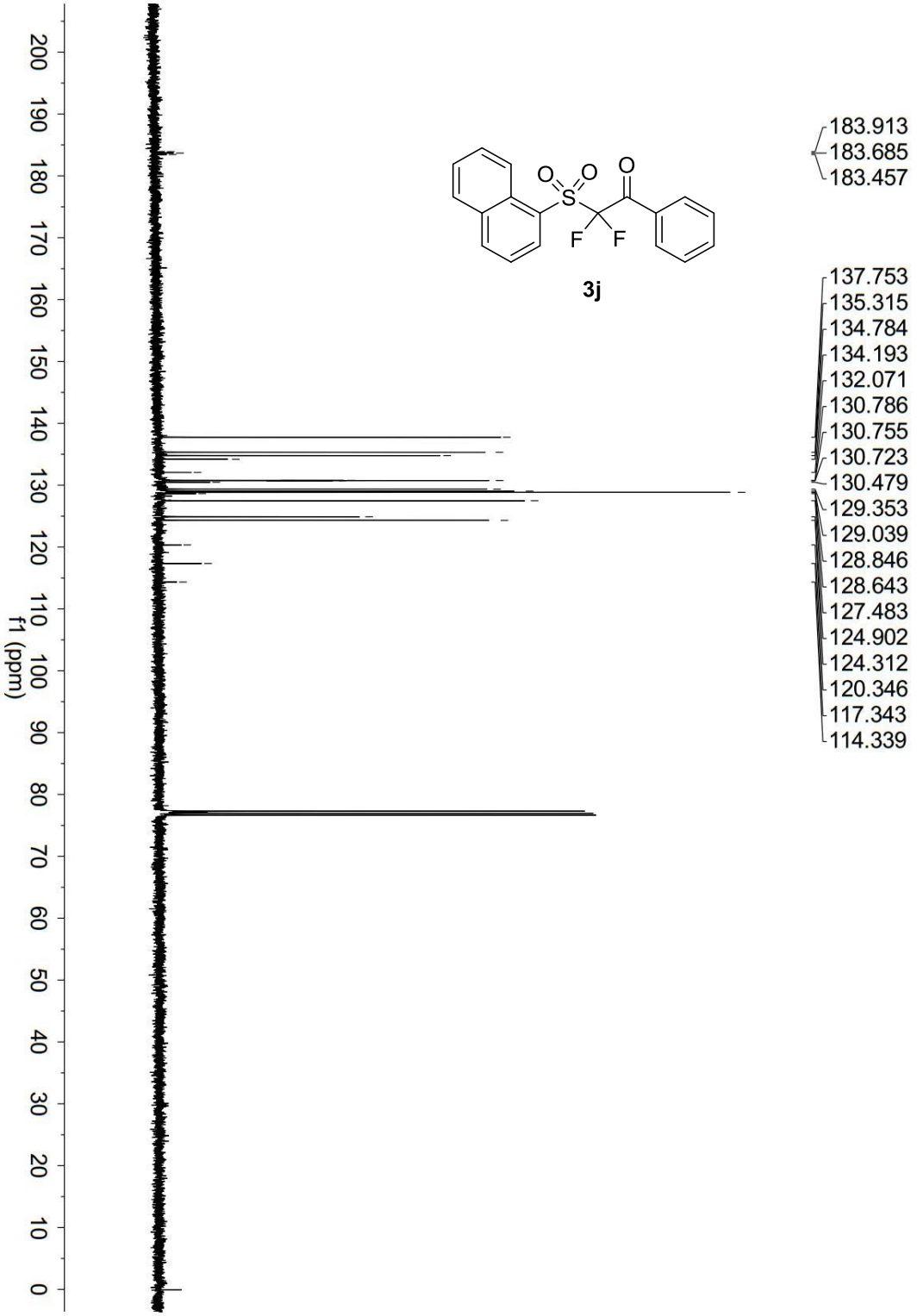
3i

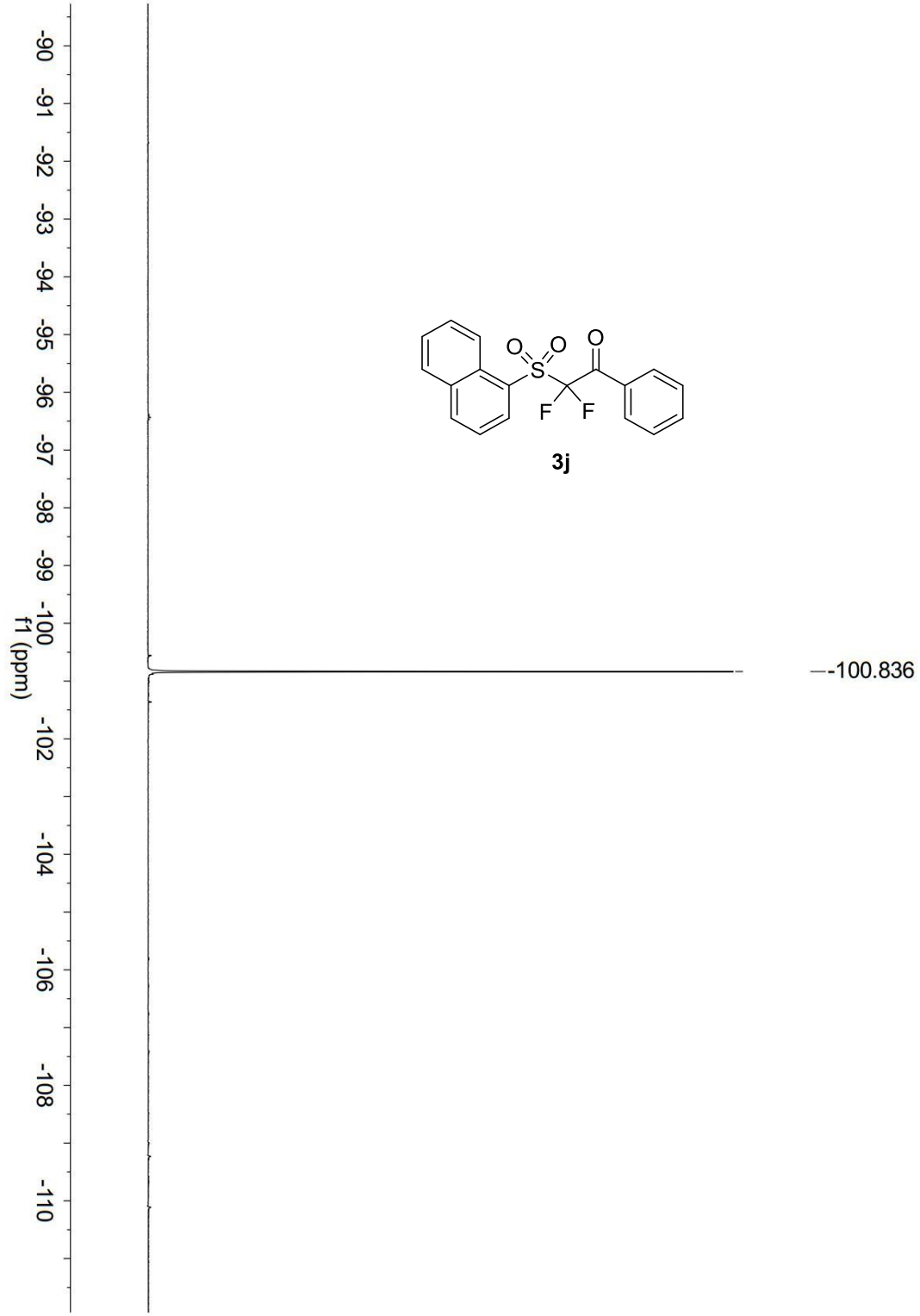

-90
-91
-92
-93
-94
-95
-96
-97
-98
-99
-100
-102
-104
-106
-108
-110
f1 (ppm)
-101.545
Me
Me
O
O
O
S
F
F

3i

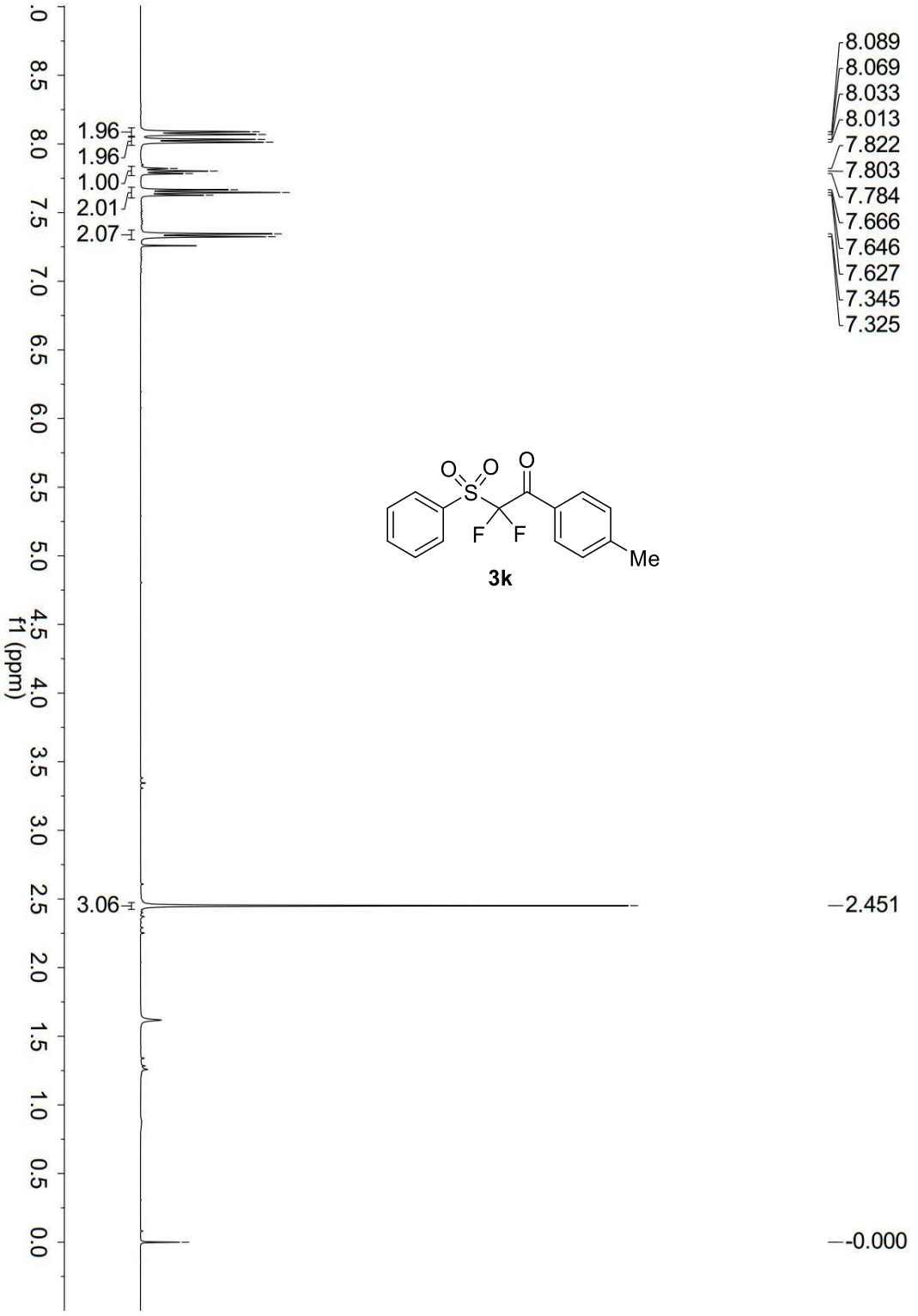

1.00
1.02
1.10
2.03
1.09
1.14
3.32
2.29
f1 (ppm)
8.904
8.882
8.391
8.372
8.271
8.251
8.223
8.203
7.999
7.979
7.776
7.758
7.738
7.723
7.705
7.686
7.666
7.646
7.626
7.570
7.551
7.533
-0.000
O
O
O
S
F
F

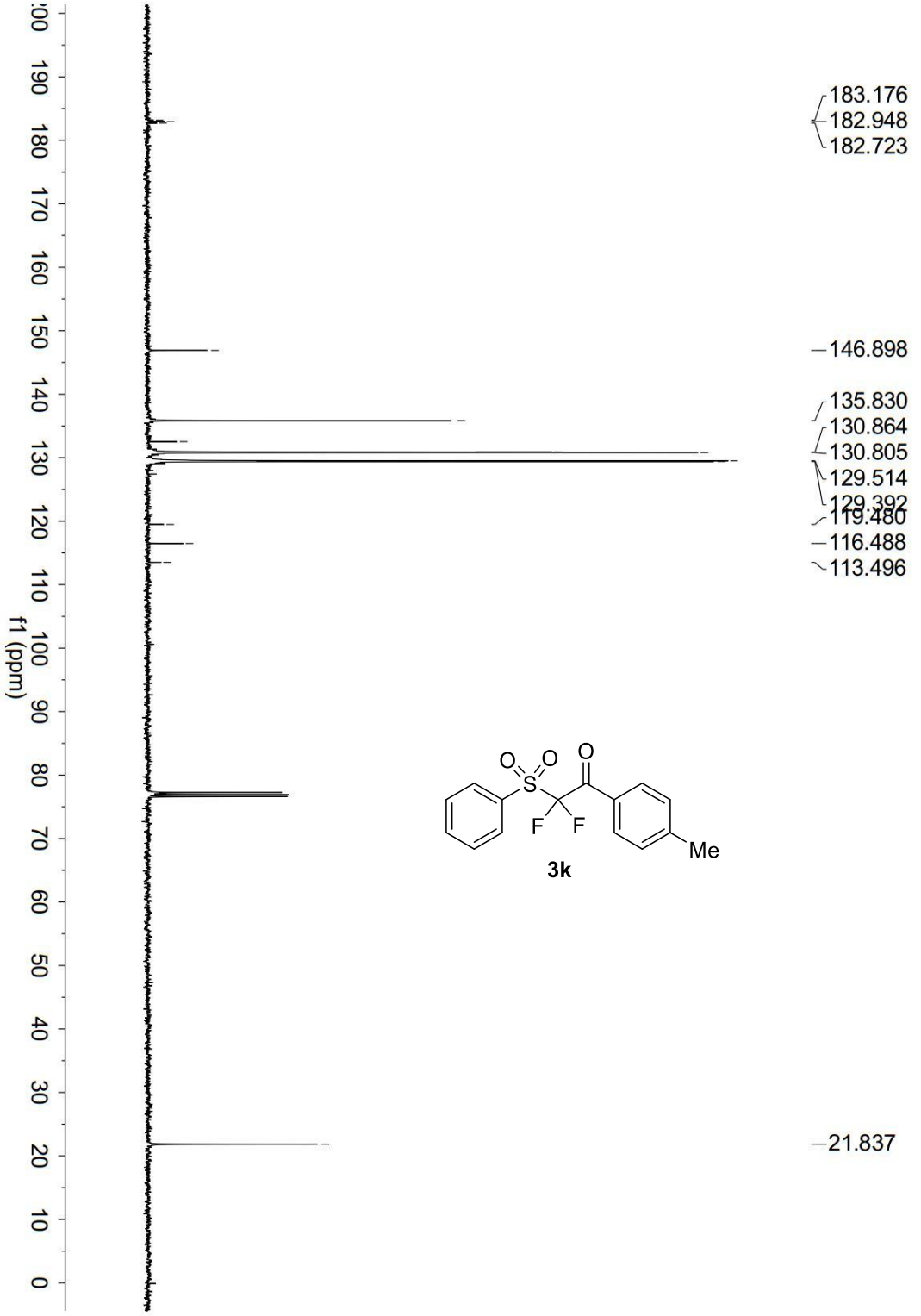
3j


183.913
183.685
183.457
137.753
135.315
134.784
134.193
132.071
130.786
130.755
130.723
130.479
129.353
129.039
128.846
128.643
127.483
124.902
124.312
120.346
117.343
114.339
O
O
O
S
F
F
3j
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

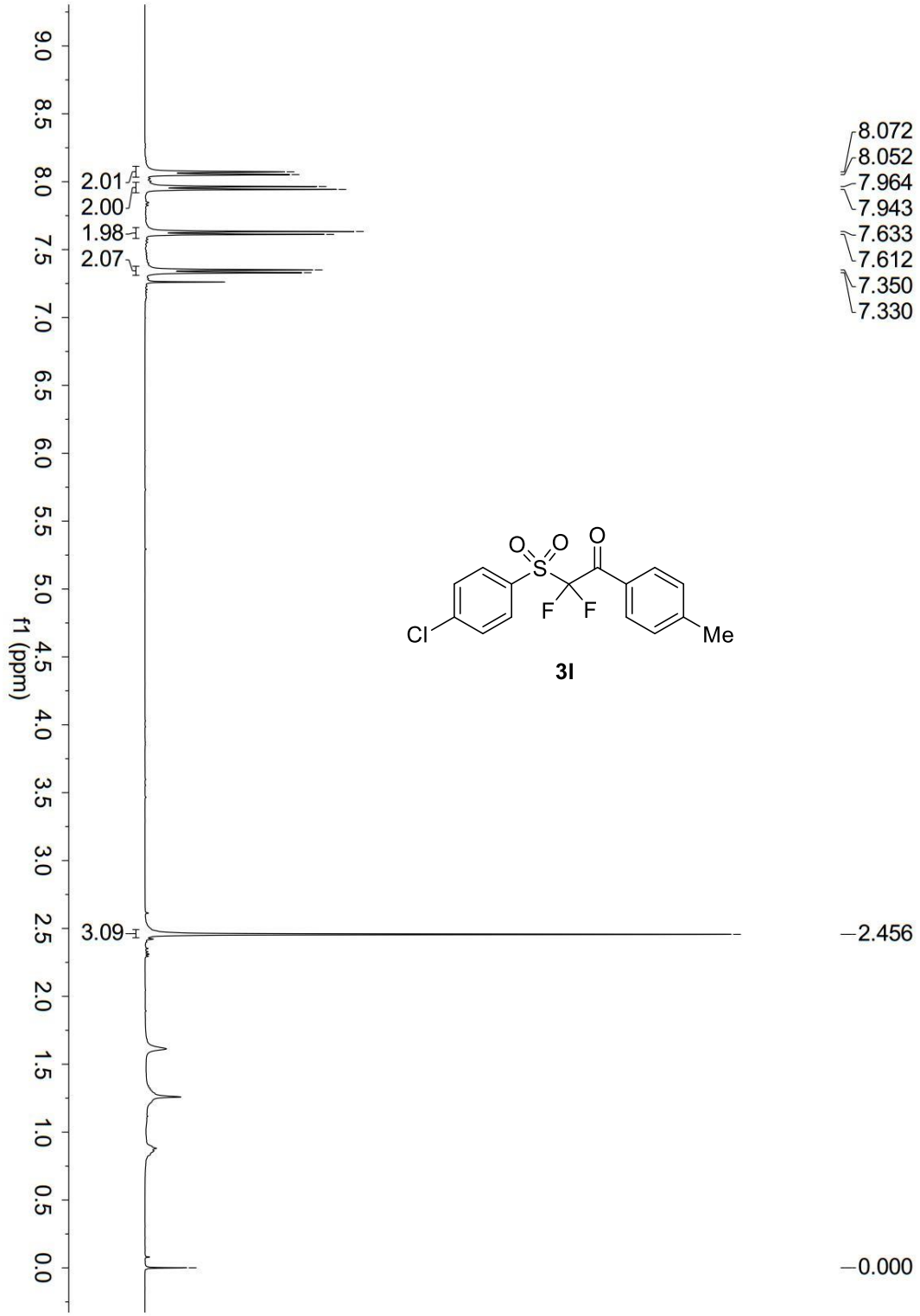

-90
-91
-92
-93
-94
-95
-96
-97
-98
-99
-100
-102
-104
-106
-108
-110
f1 (ppm)
-100.836
O
O
O
S
F
F

3j

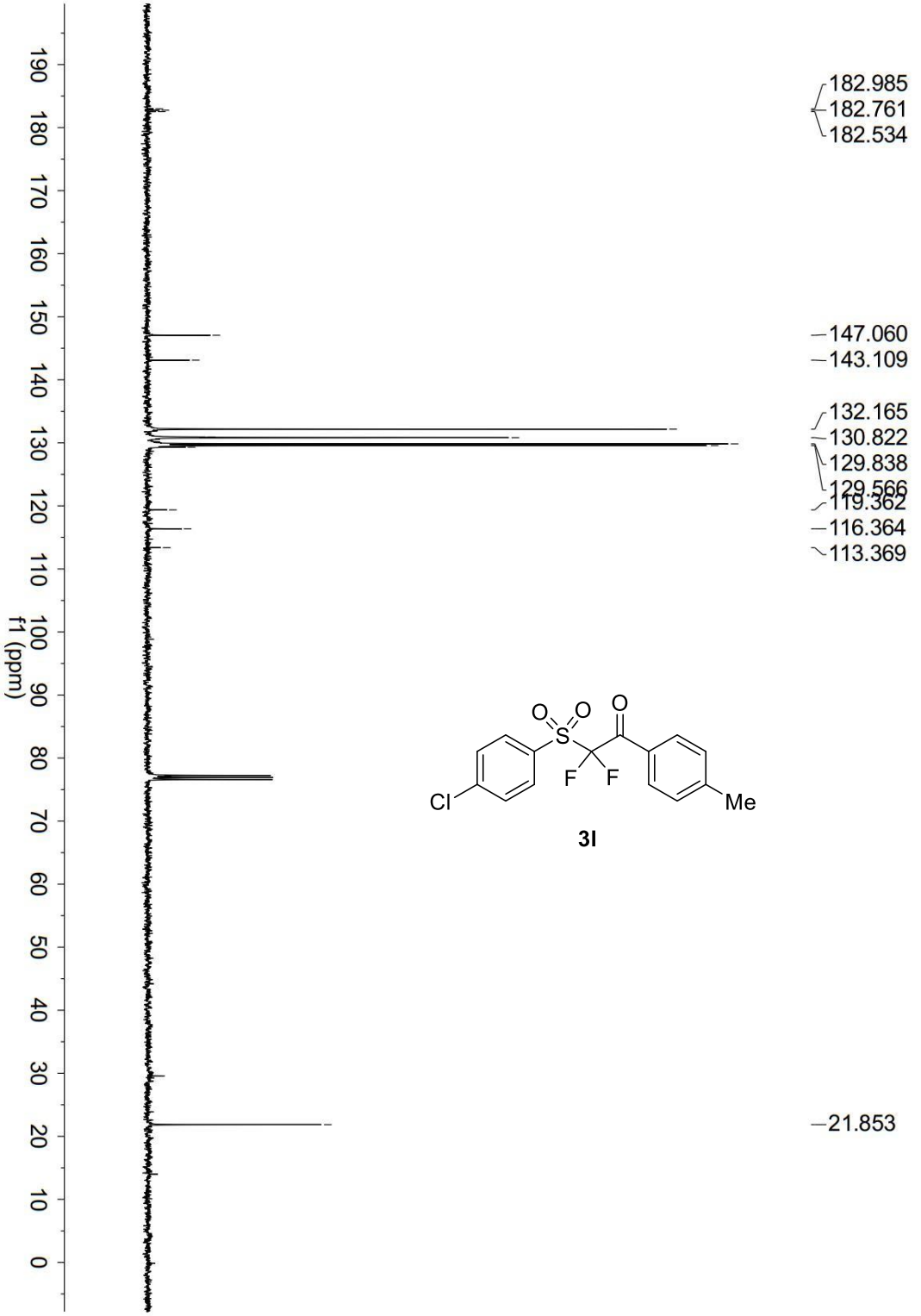

8.089
8.069
8.033
8.013
7.822
7.803
7.784
7.666
7.646
7.627
7.345
7.325
1.96
1.96
1.00
2.01
2.07
3.06
2.451
-0.000
f1 (ppm)
O
O
O
S
F
F
Me
3k


183.176
182.948
182.723
146.898
135.830
130.864
130.805
129.514
129.392
119.480
116.488
113.496
21.837
f1 (ppm)
O
O
O
S
F
F
Me
3k

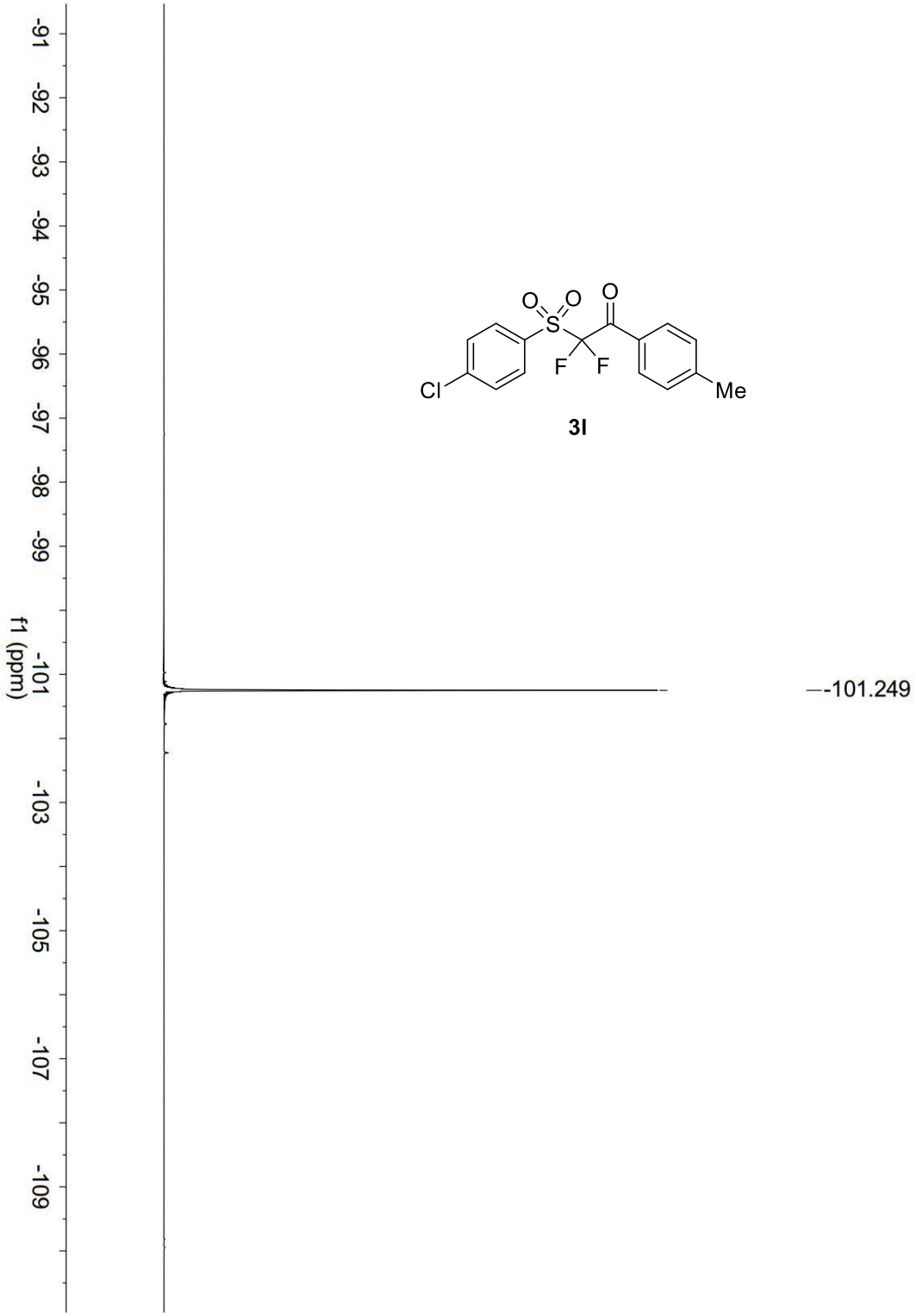

-91
-92
-93
-94
-95
-96
-97
-98
-99
-100
-102
-104
-106
-108
f1 (ppm)
O
O
O
S
F
F
Me
3k
-101.406


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2.01
2.00
1.98
2.07
3.09
8.072
8.052
7.964
7.943
7.633
7.612
7.350
7.330
2.456
0.000
O
O
O
S
F
F
Cl
Me

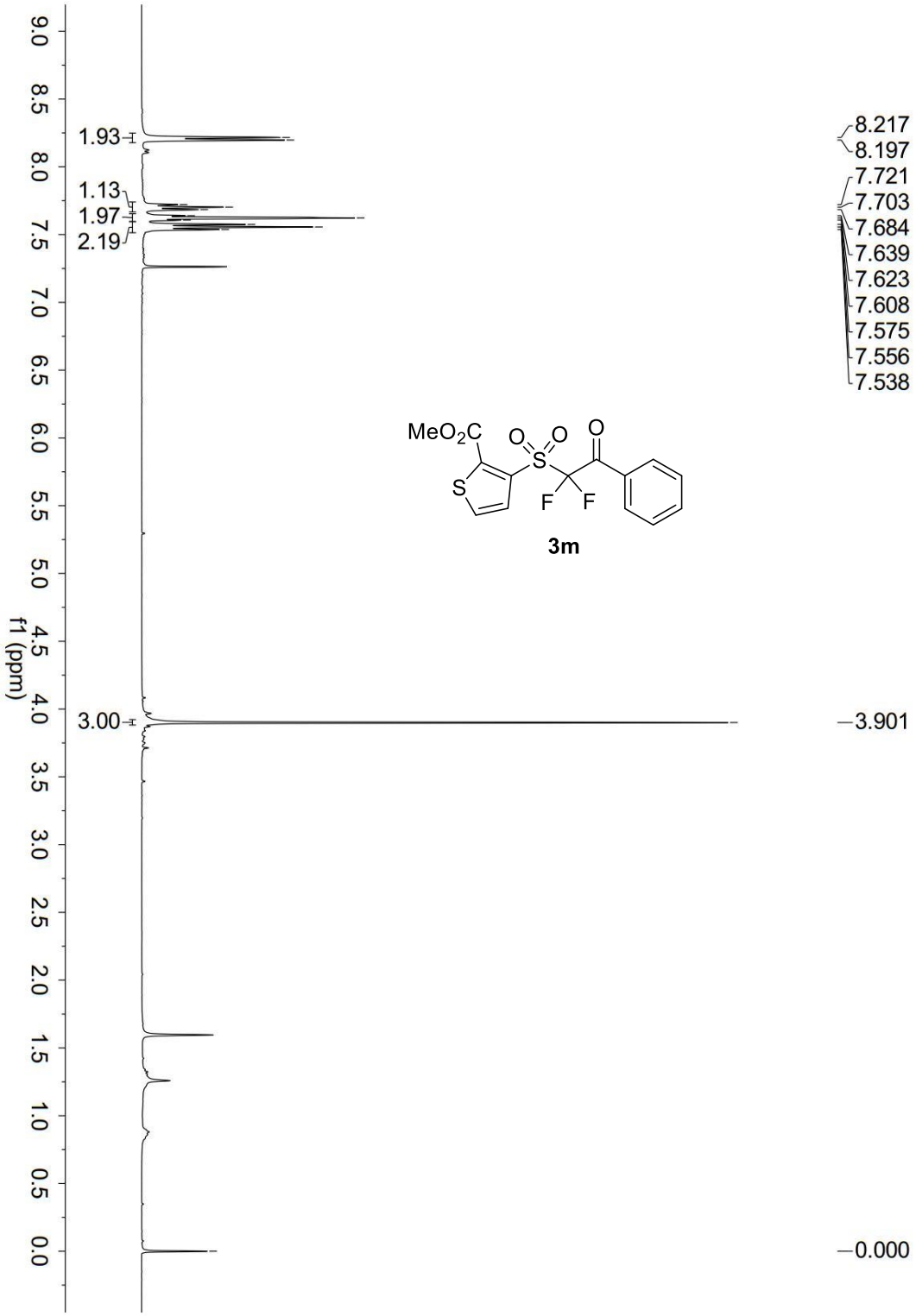
3l


182.985
182.761
182.534
147.060
143.109
132.165
130.822
129.838
129.566
119.362
116.364
113.369
21.853
f1 (ppm)
O
O
O
S
F
F
Cl
Me

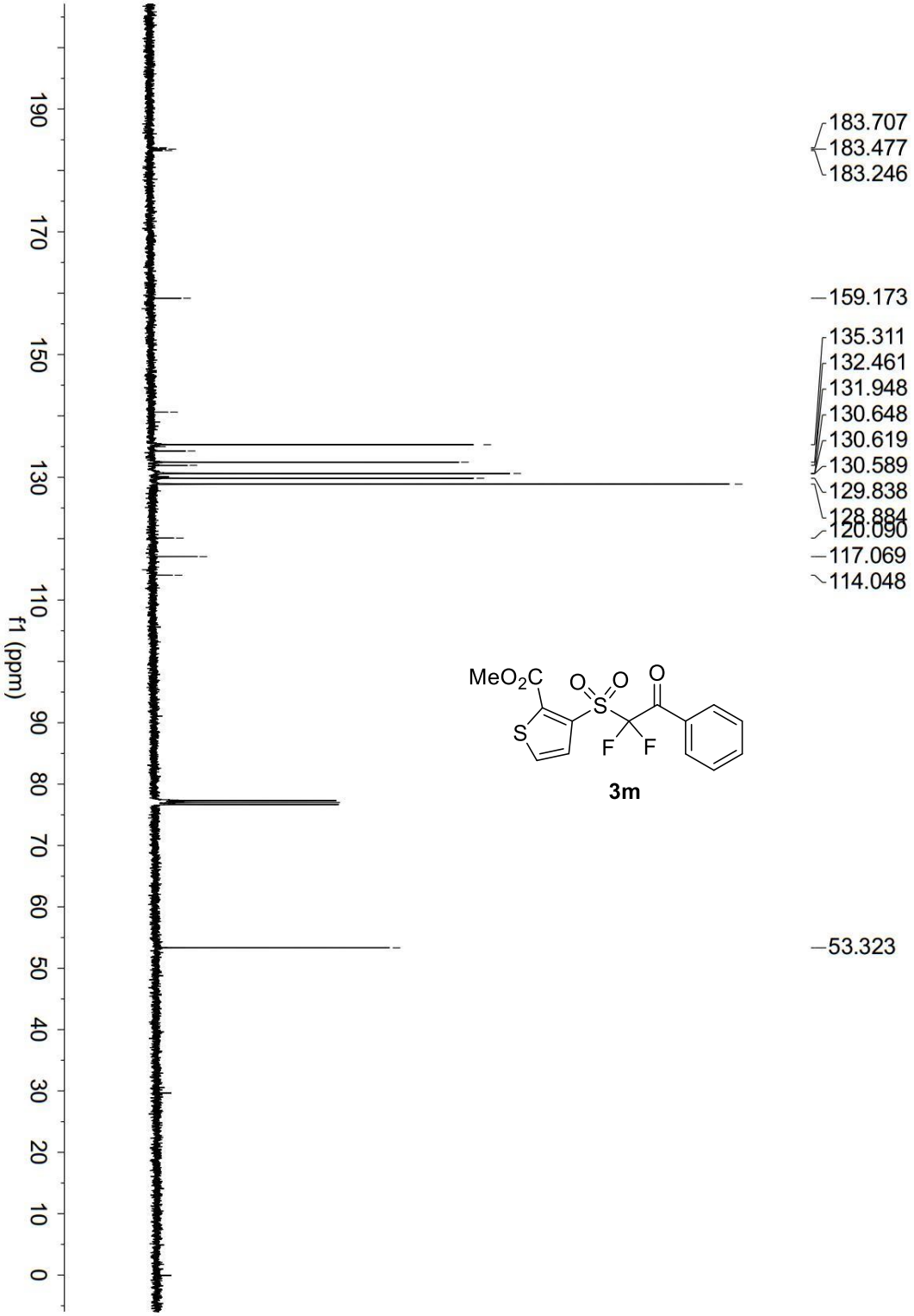
3l


-91
-92
-93
-94
-95
-96
-97
-98
-99
-101
-103
-105
-107
-109
f1 (ppm)
-101.249
O
O
O
S
F
F
Cl
Me

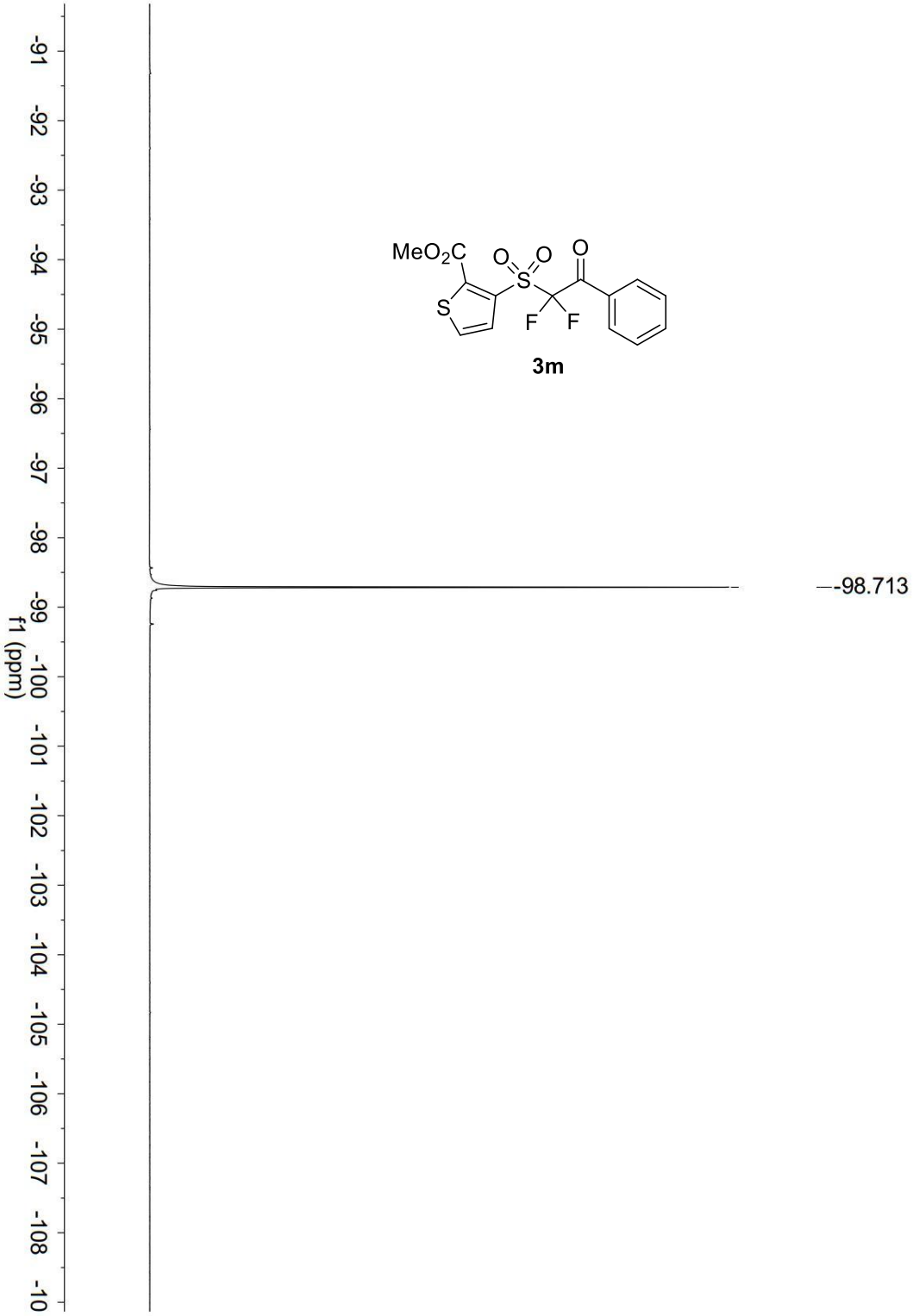
3l

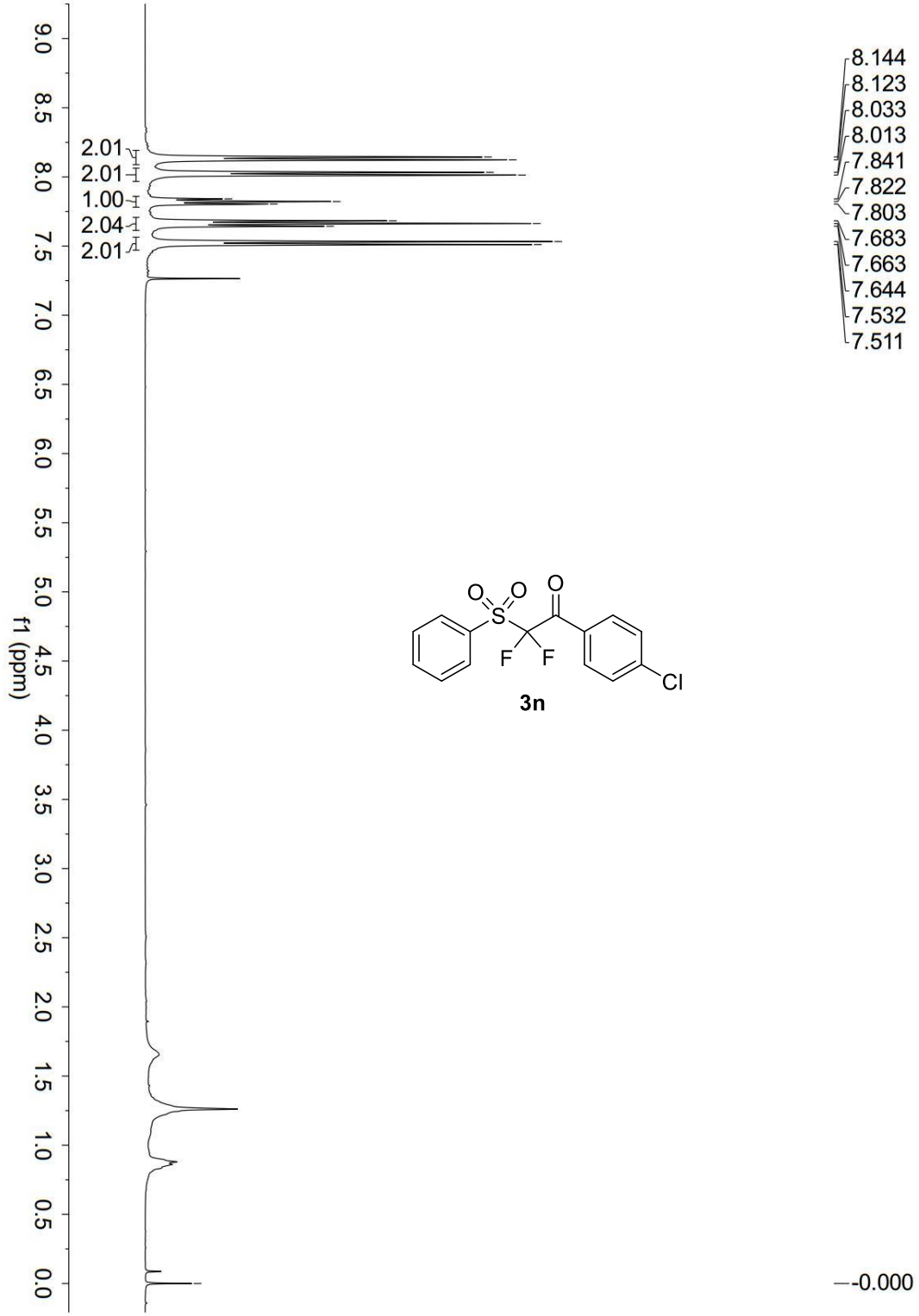

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.93
1.13
1.97
2.19
3.00
8.217
8.197
7.721
7.703
7.684
7.639
7.623
7.608
7.575
7.556
7.538
3.901
0.000
MeO2C
O
O
S
O
S
F
F

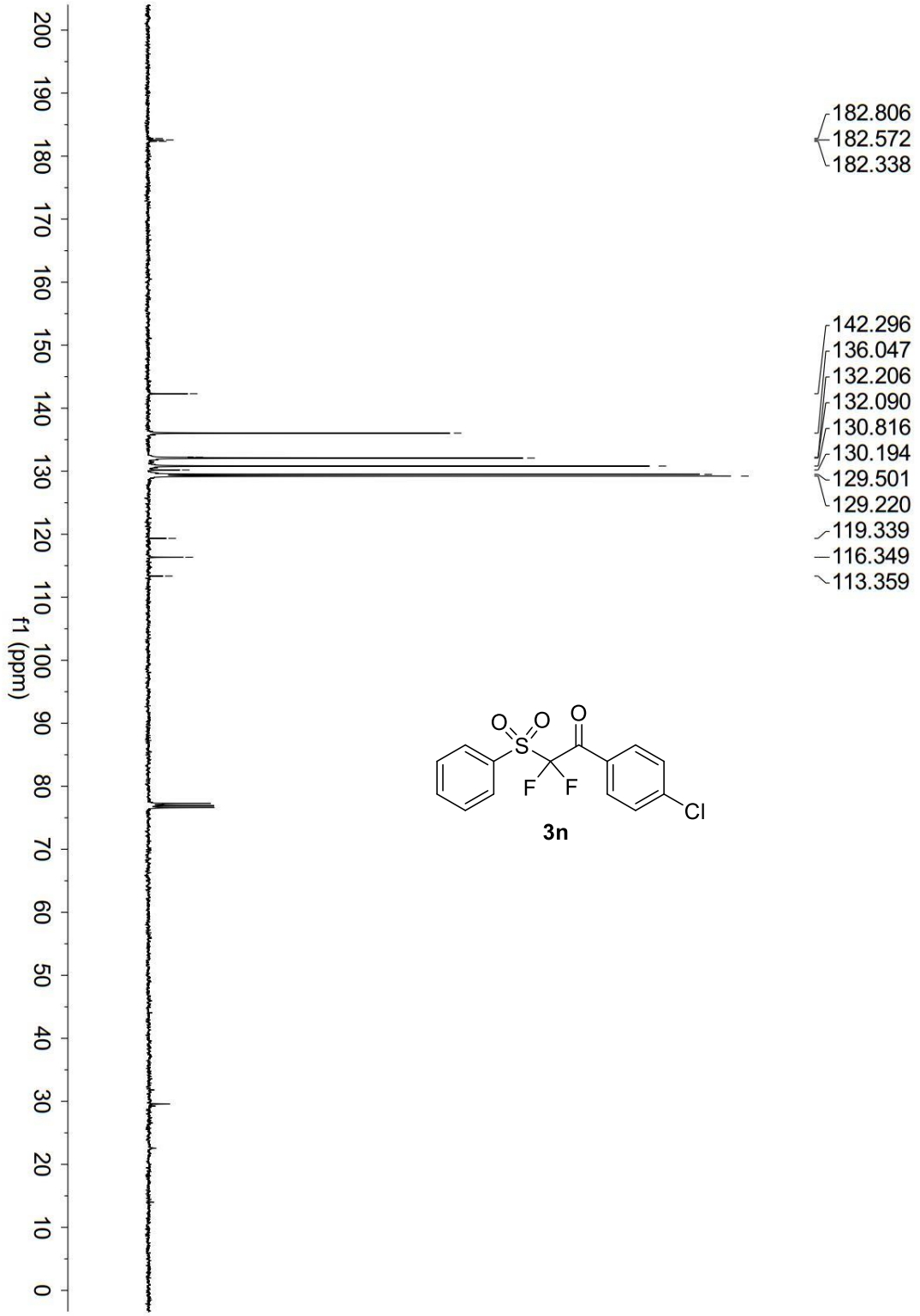
3m


183.707
183.477
183.246
159.173
135.311
132.461
131.948
130.648
130.619
130.589
129.838
128.884
120.090
117.069
114.048
53.323
f1 (ppm)
MeO2C
O
O
O
S
S
F
F

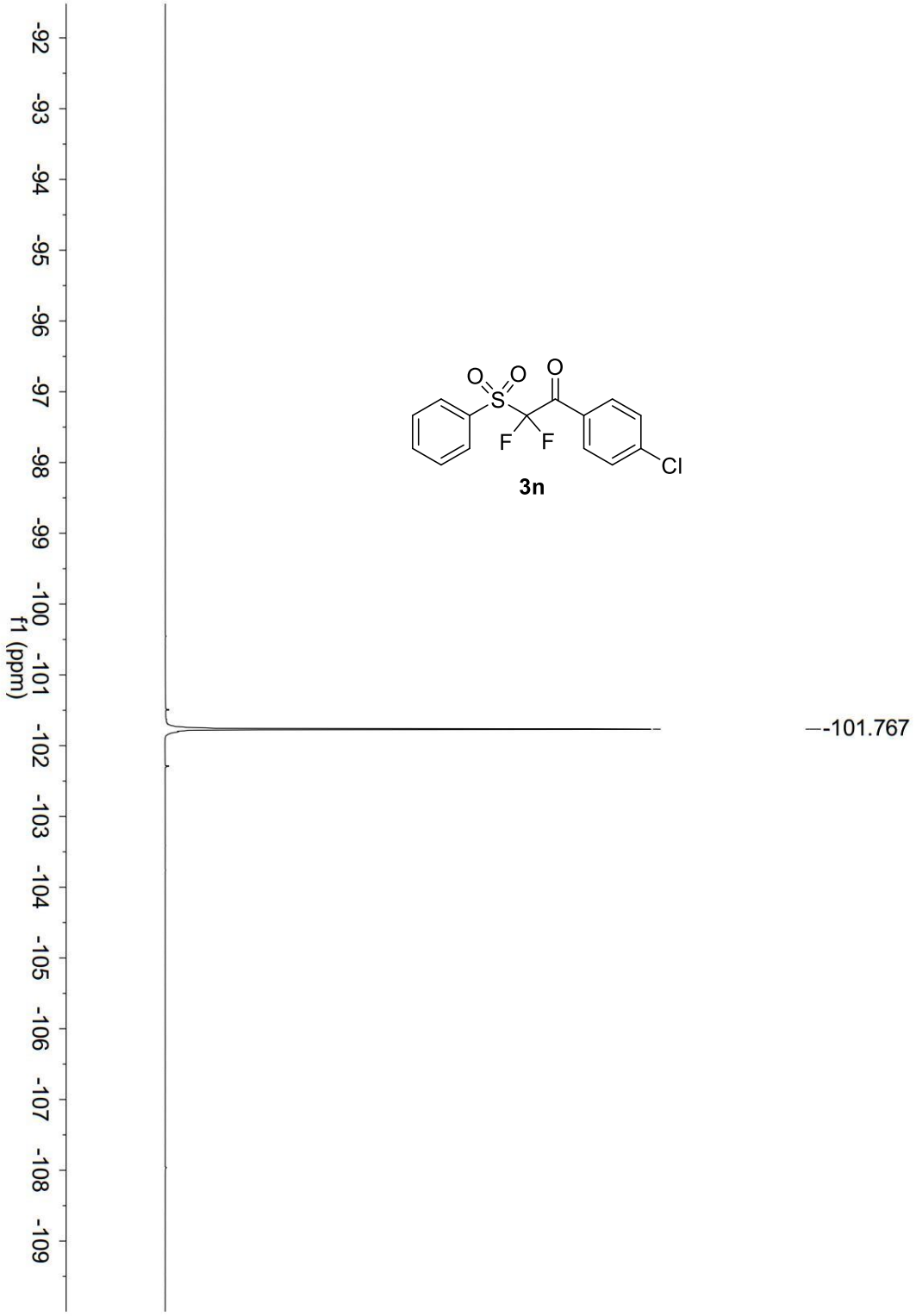
3m

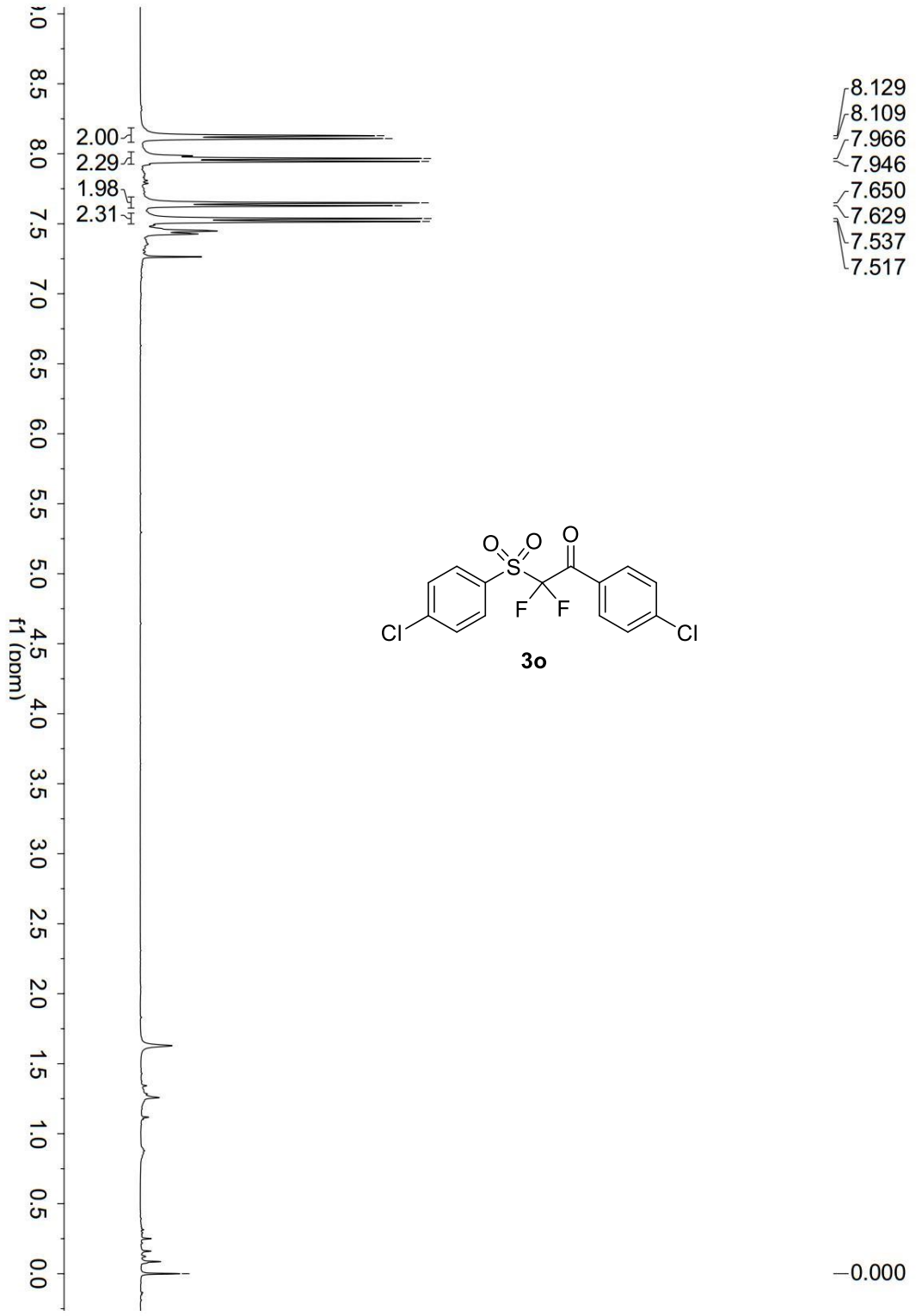

MeO2C
O
O
O
S
S
F
F
3m
-98.713
-91
-92
-93
-94
-95
-96
-97
-98
-99
-100
-101
-102
-103
-104
-105
-106
-107
-108
-10
f1 (ppm)


8.144
8.123
8.033
8.013
7.841
7.822
7.803
7.683
7.663
7.644
7.532
7.511
2.01
2.01
1.00
2.04
2.01
-0.000
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
O
O
S
O
F
F
Cl
3n

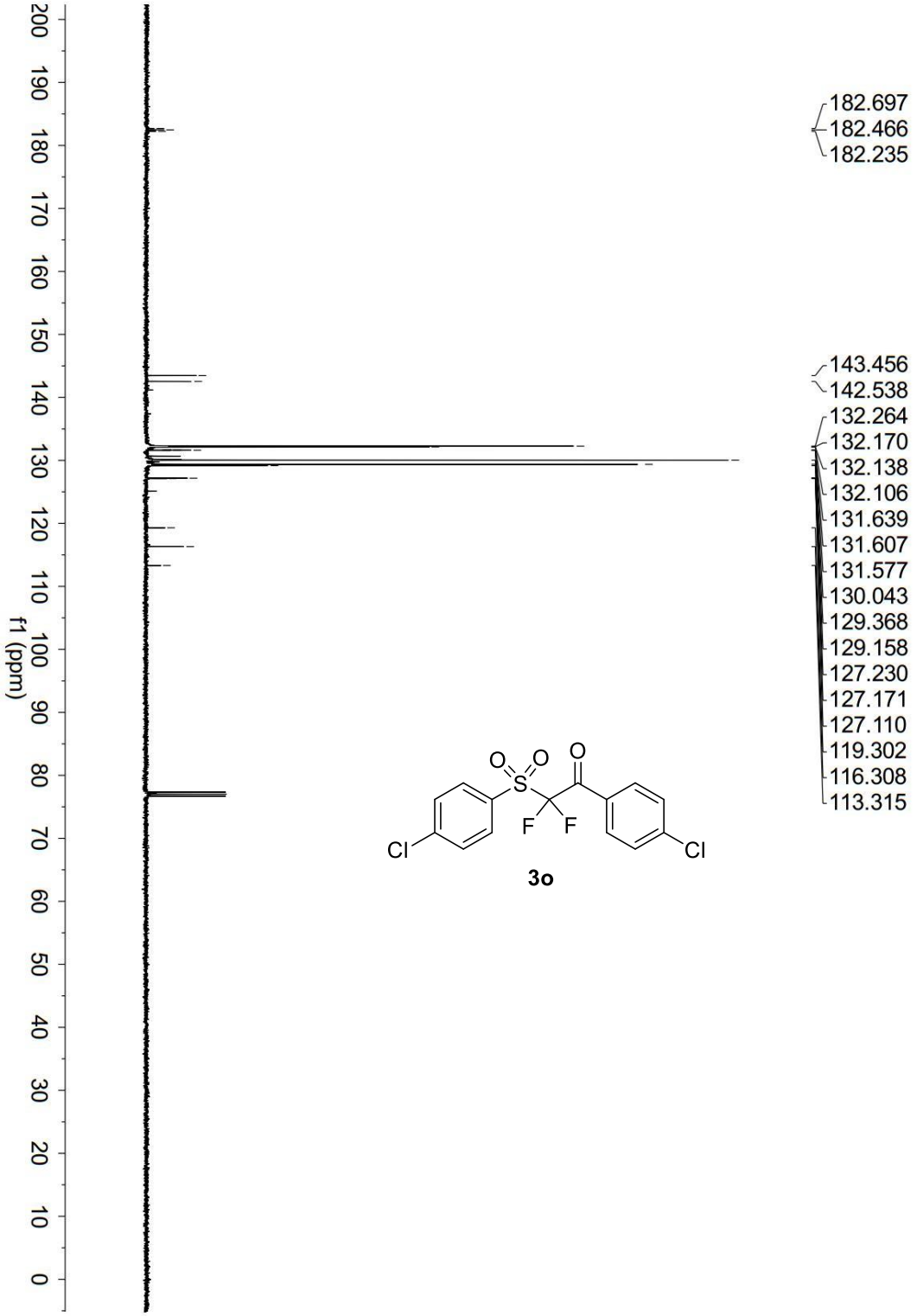

182.806
182.572
182.338
142.296
136.047
132.206
132.090
130.816
130.194
129.501
129.220
119.339
116.349
113.359
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
O
S
F
F
Cl

3n

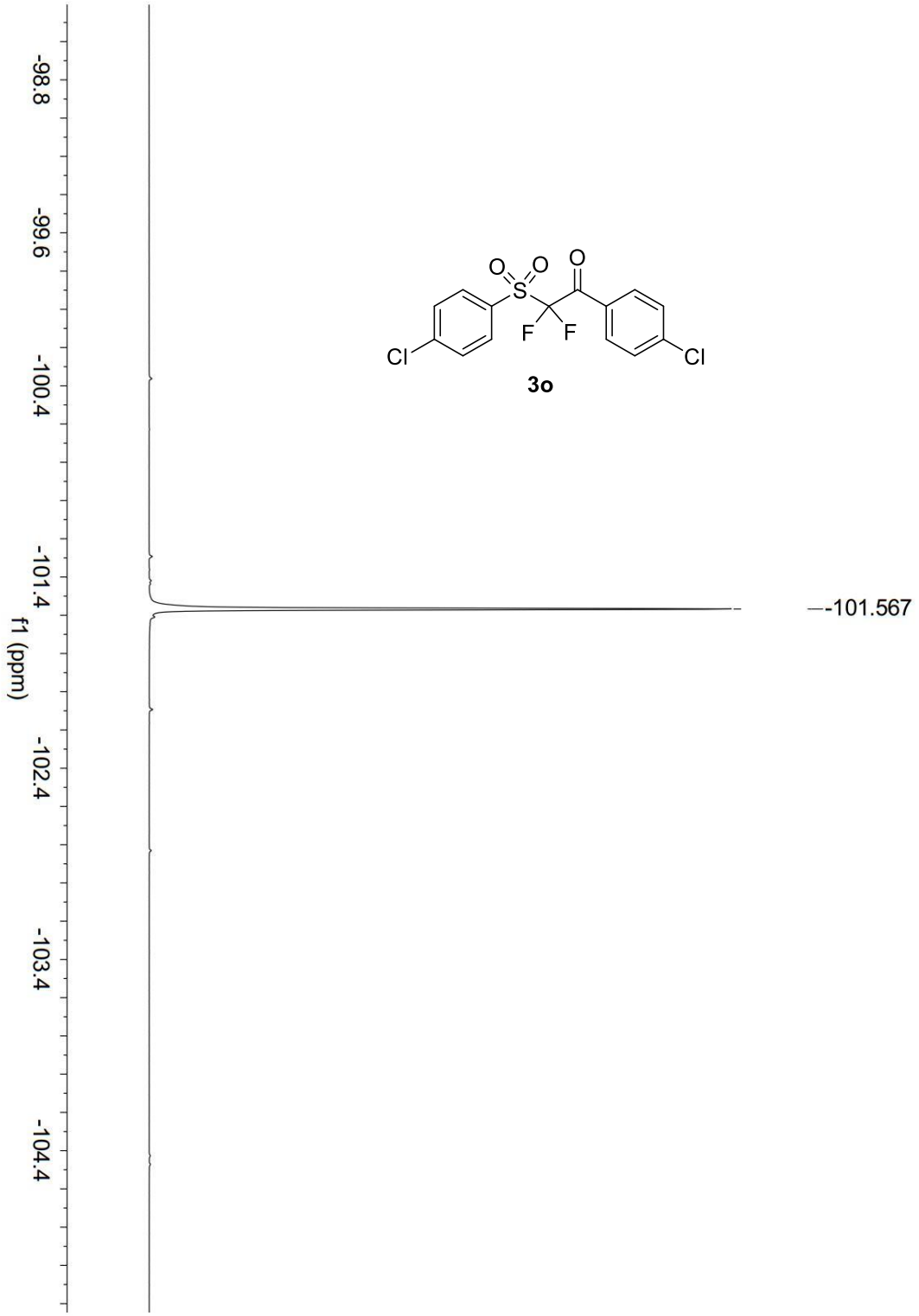

-92
-93
-94
-95
-96
-97
-98
-99
-100
-101
-102
-103
-104
-105
-106
-107
-108
-109
f1 (ppm)
O
O
O
S
F
F
Cl
3n
-101.767

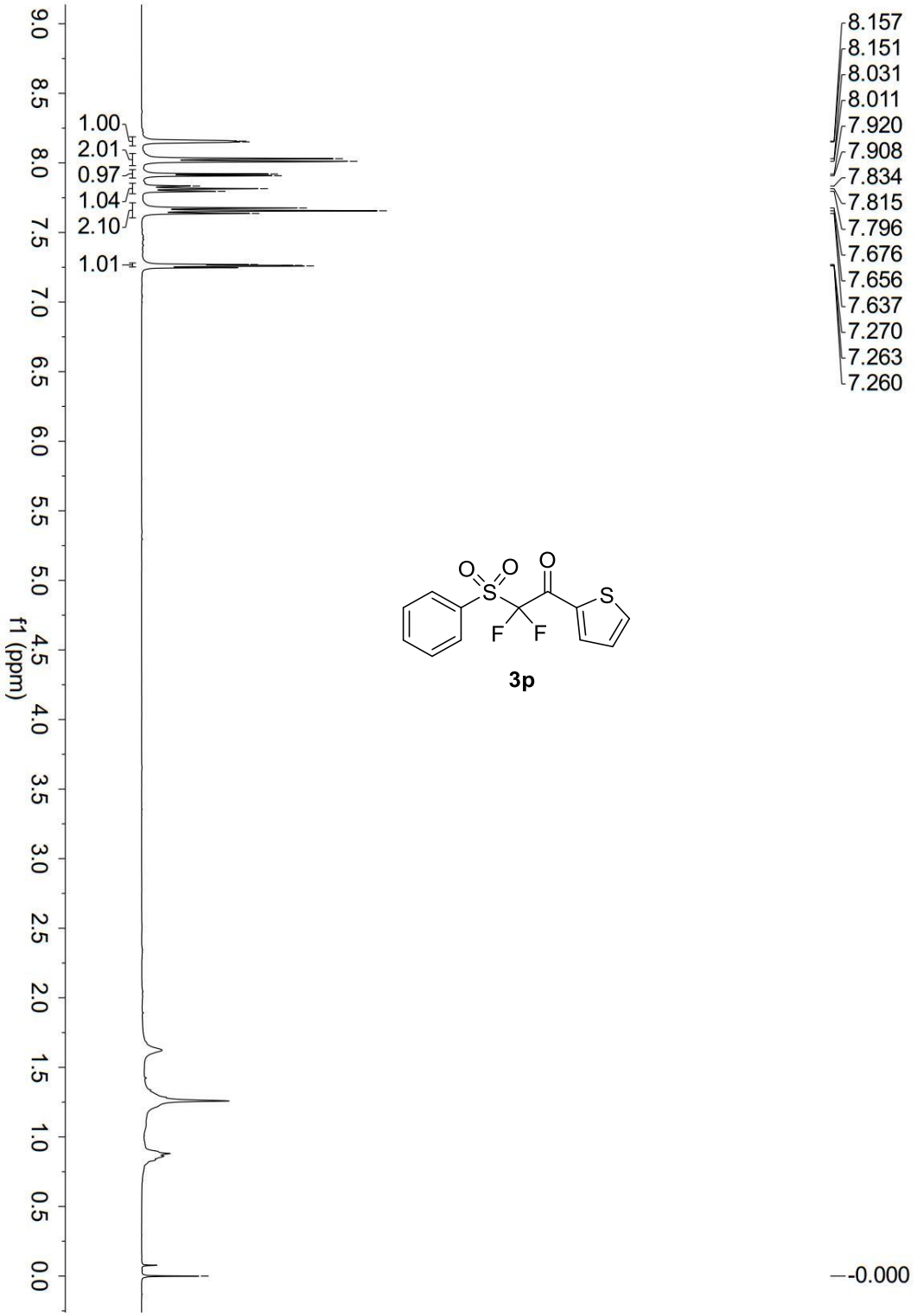

8.129
8.109
7.966
7.946
7.650
7.629
7.537
7.517
2.00
2.29
1.98
2.31
−0.000
f1 (ppm)
O
O
O
S
F
F
Cl
Cl

3o

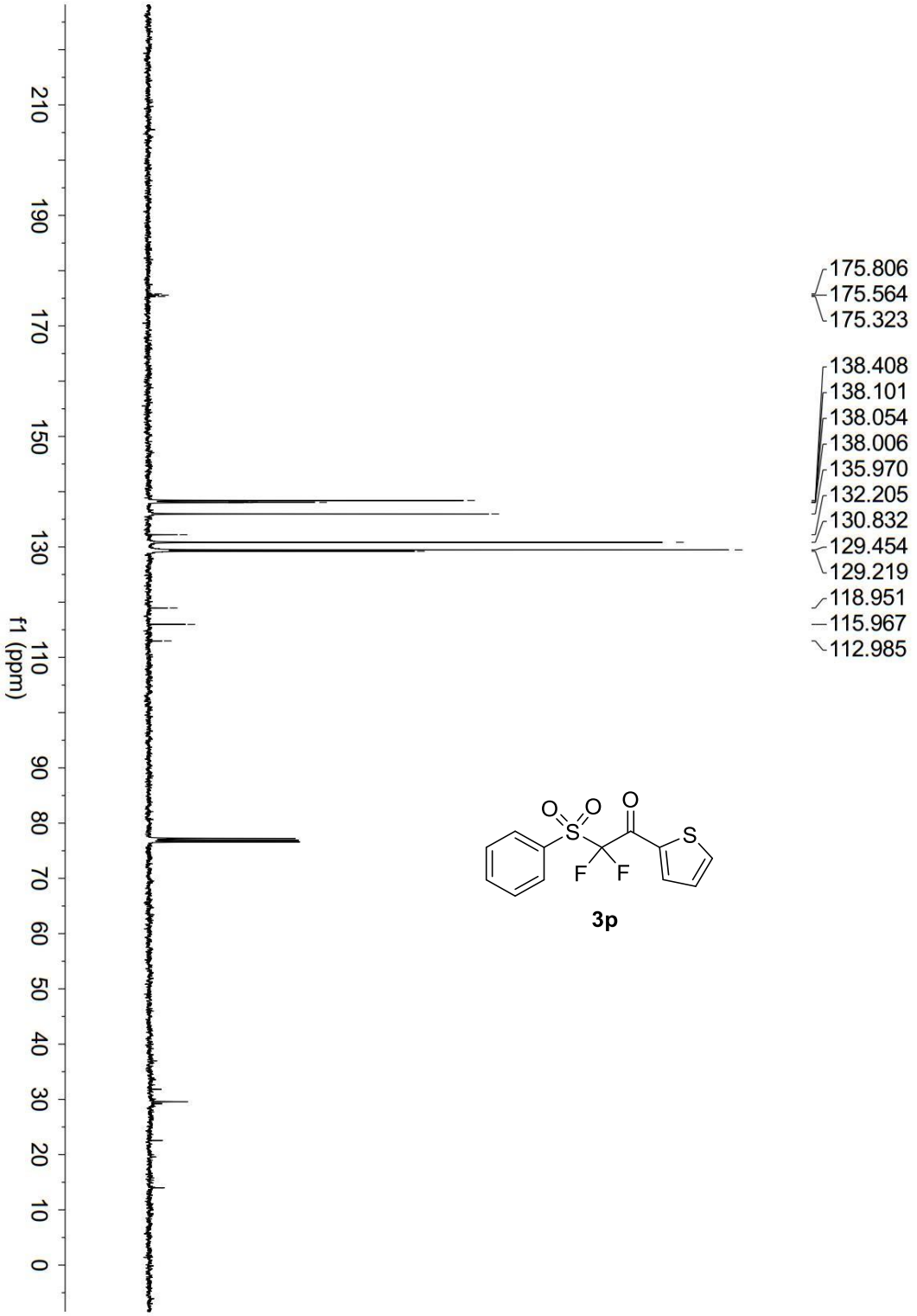

182.697
182.466
182.235
143.456
142.538
132.264
132.170
132.138
132.106
131.639
131.607
131.577
130.043
129.368
129.158
127.230
127.171
127.110
119.302
116.308
113.315
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
O
S
F
F
Cl
Cl

3o

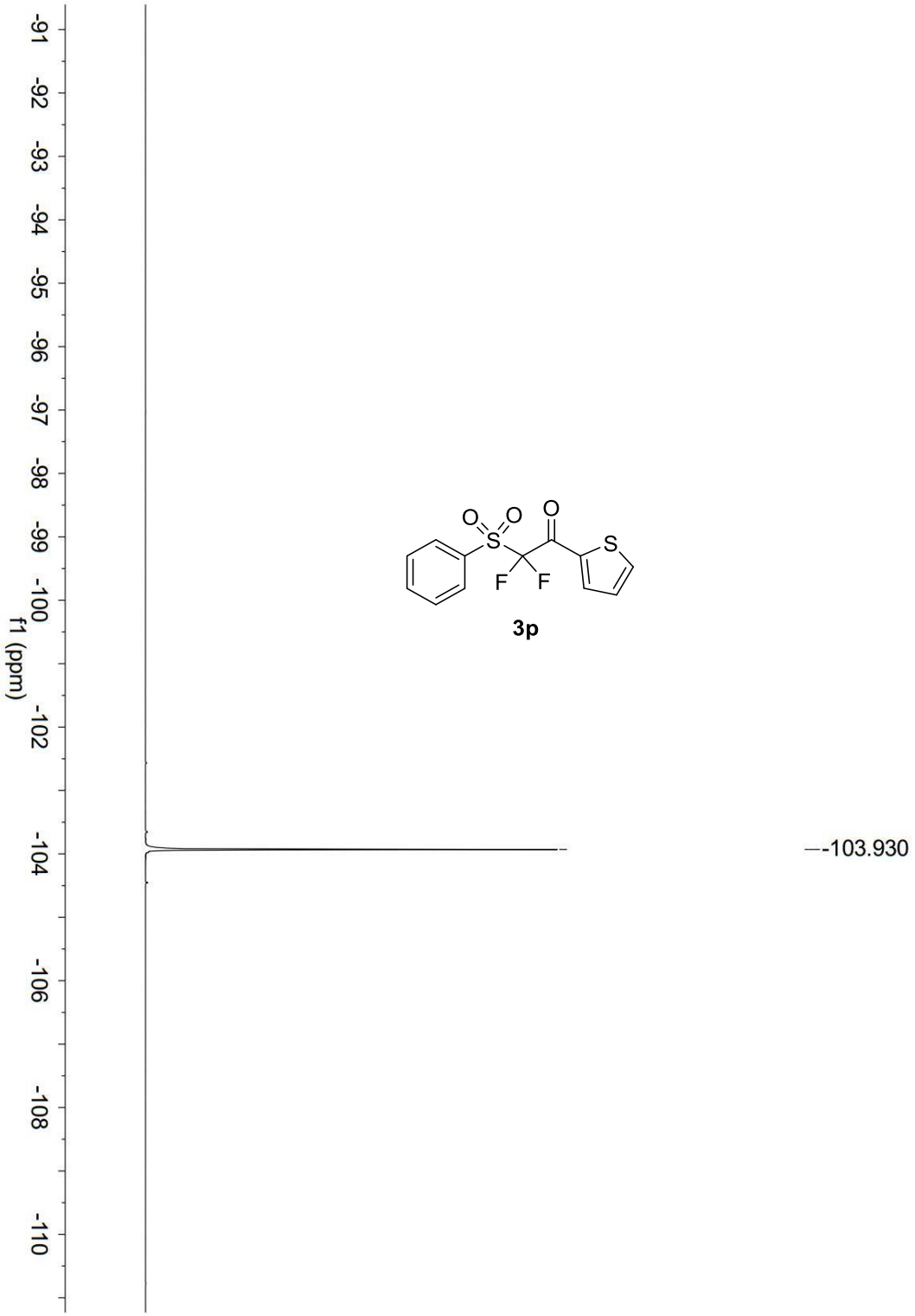

-98.8
-99.6
-100.4
-101.4
-102.4
-103.4
-104.4
f1 (ppm)
-101.567
O
O
O
S
F
F
Cl
Cl
3o

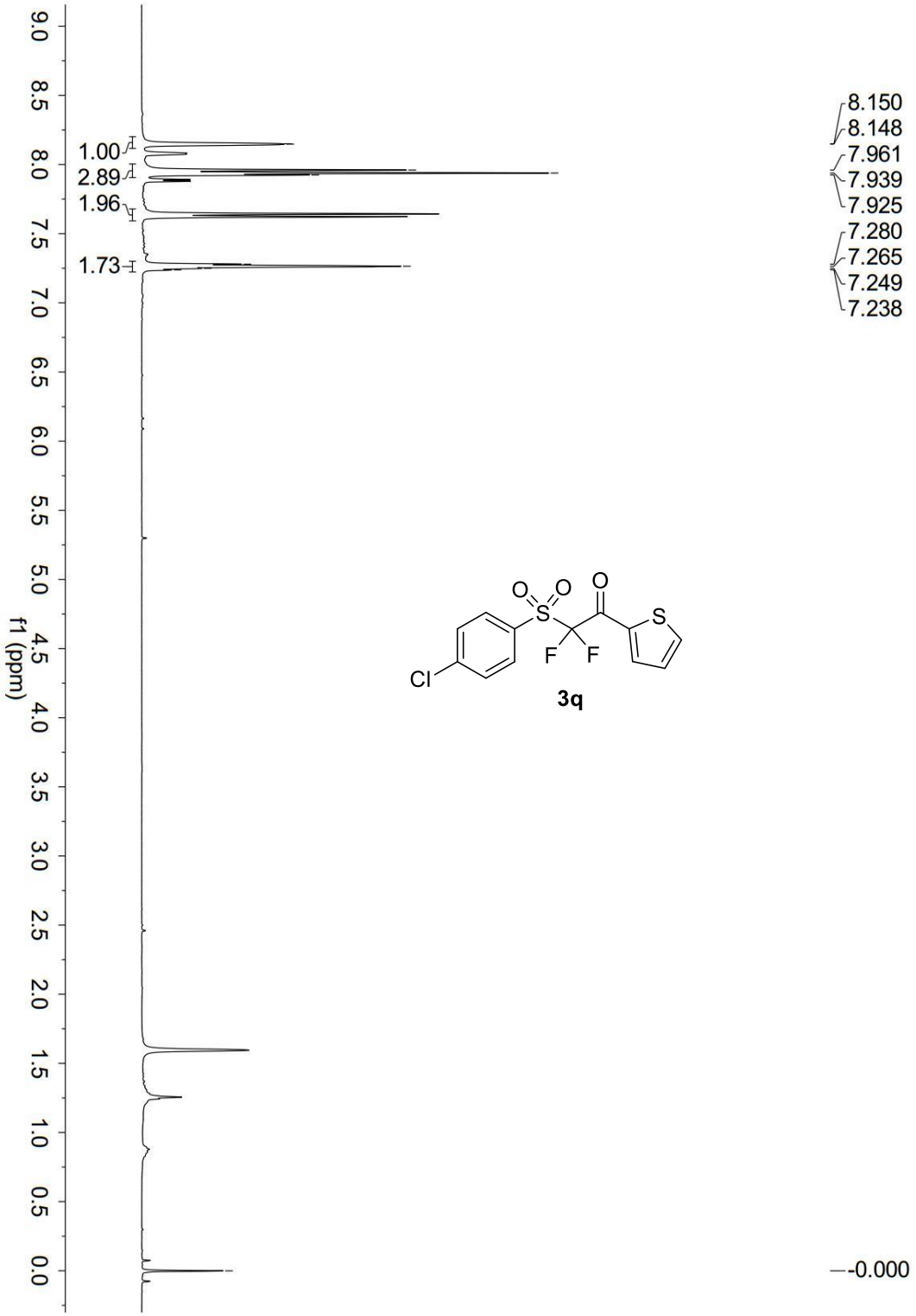

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.00
2.01
0.97
1.04
2.10
1.01
8.157
8.151
8.031
8.011
7.920
7.908
7.834
7.815
7.796
7.676
7.656
7.637
7.270
7.263
7.260
-0.000
O
O
O
S
S
F
F

3p

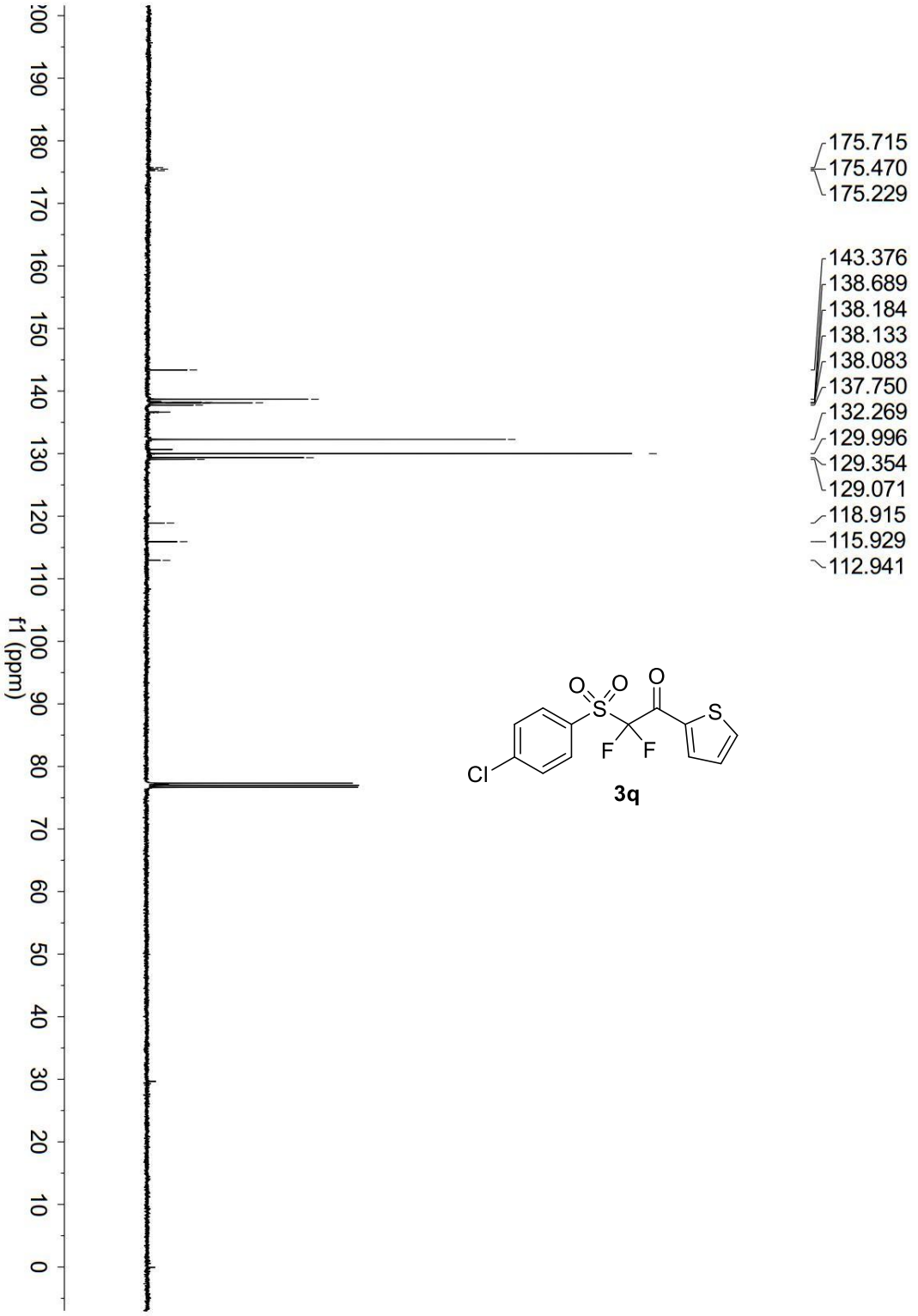

175.806
175.564
175.323
138.408
138.101
138.054
138.006
135.970
132.205
130.832
129.454
129.219
118.951
115.967
112.985
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
O
O
O
S
S
F
F

3p

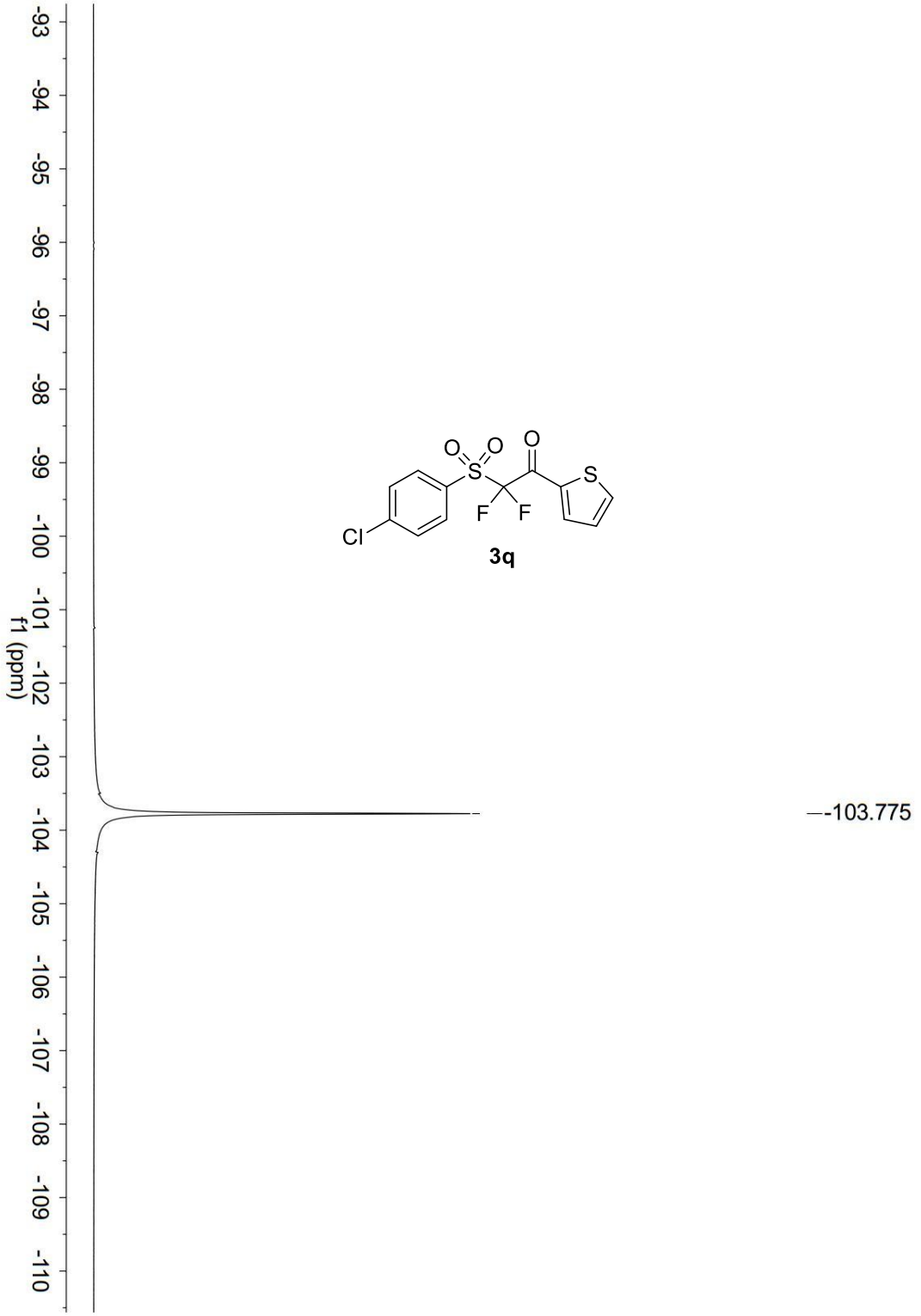

-91
-92
-93
-94
-95
-96
-97
-98
-99
-100
-102
-104
-106
-108
-110
f1 (ppm)
O
O
O
S
F
F
S
3p
-103.930

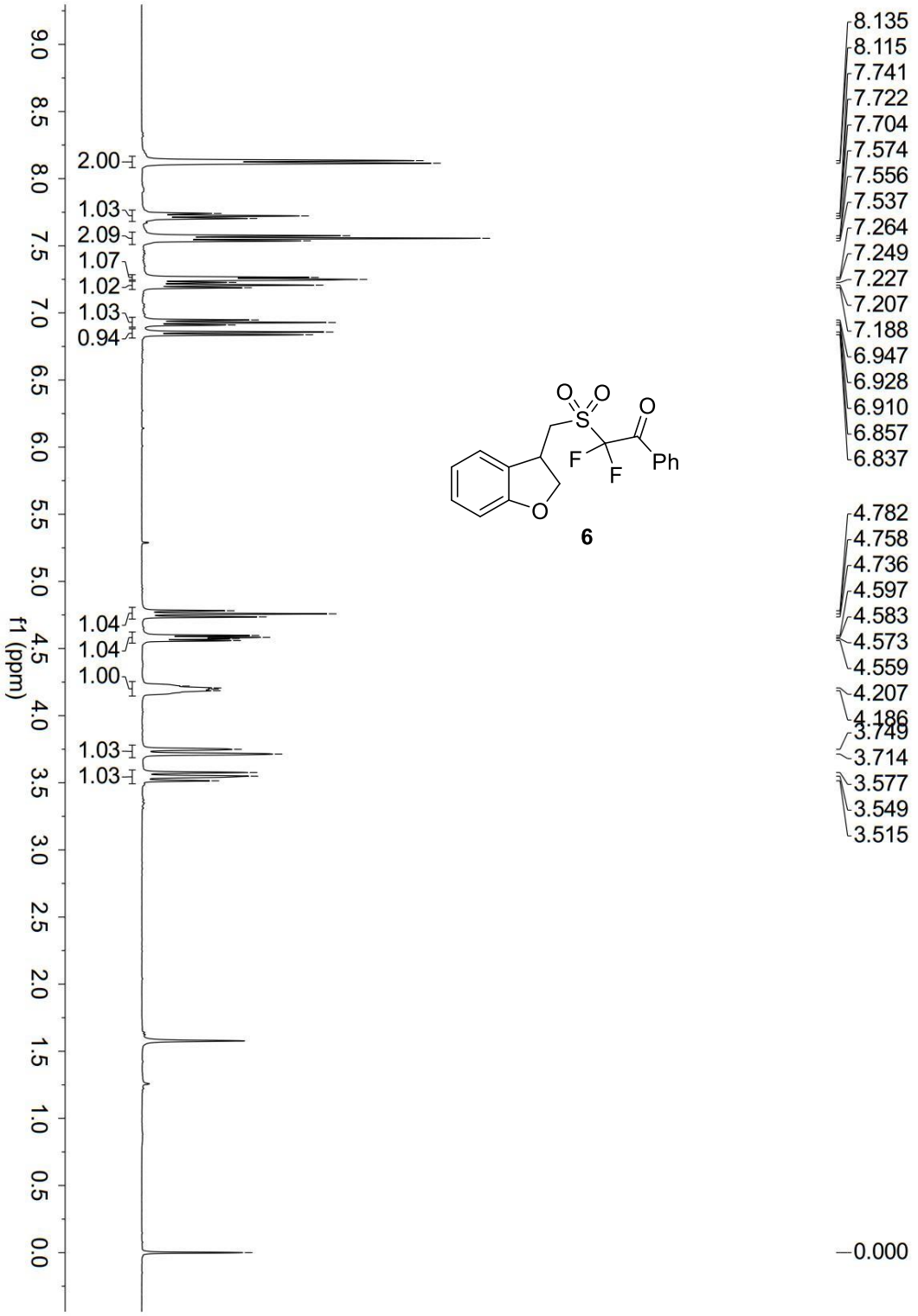

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.00
2.89
1.96
1.73
8.150
8.148
7.961
7.939
7.925
7.280
7.265
7.249
7.238
-0.000
O
O
O
S
S
F
F
Cl

3q

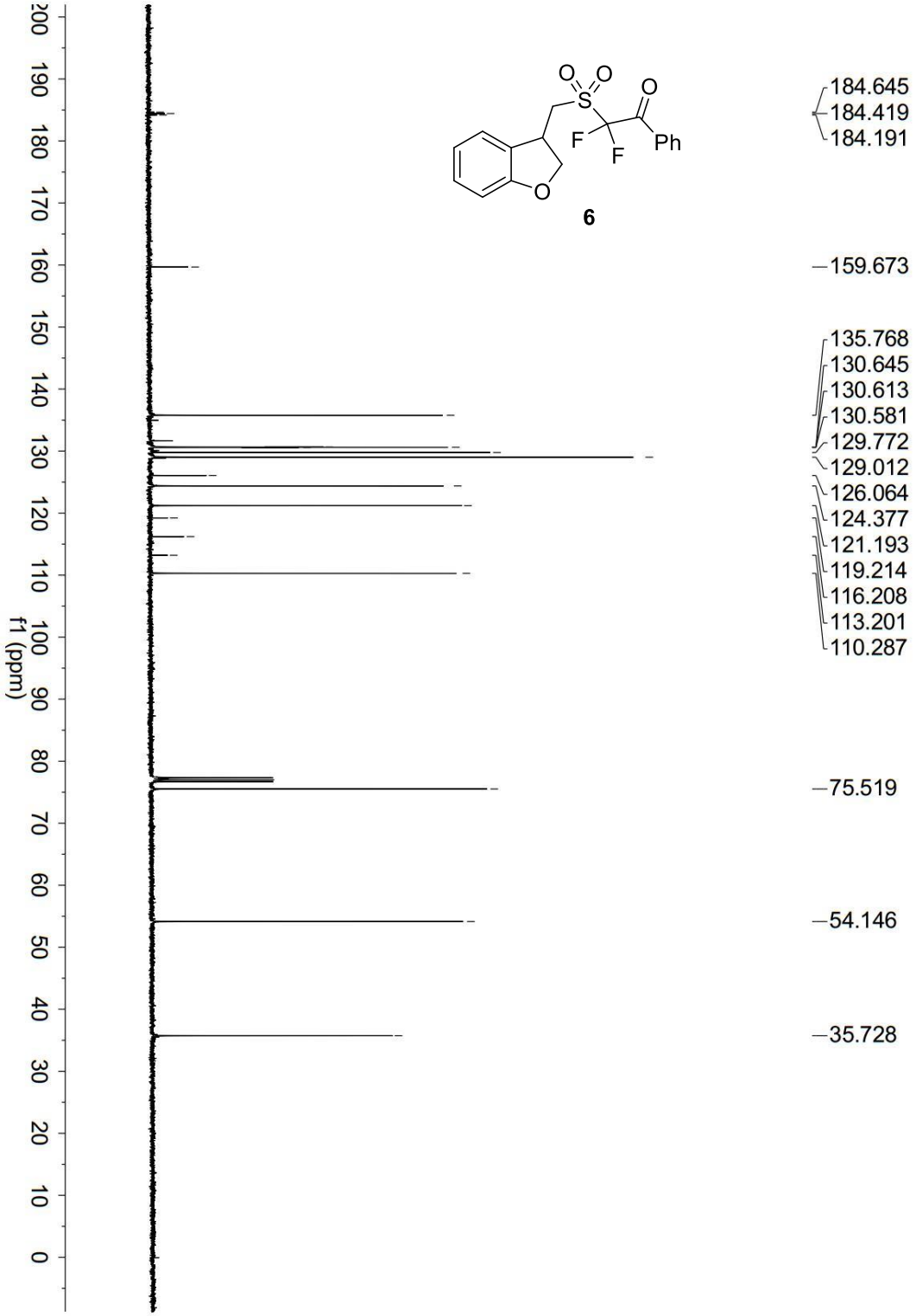

175.715
175.470
175.229
143.376
138.689
138.184
138.133
138.083
137.750
132.269
129.996
129.354
129.071
118.915
115.929
112.941
f1 (ppm)
O
O
O
S
F
F
S
Cl

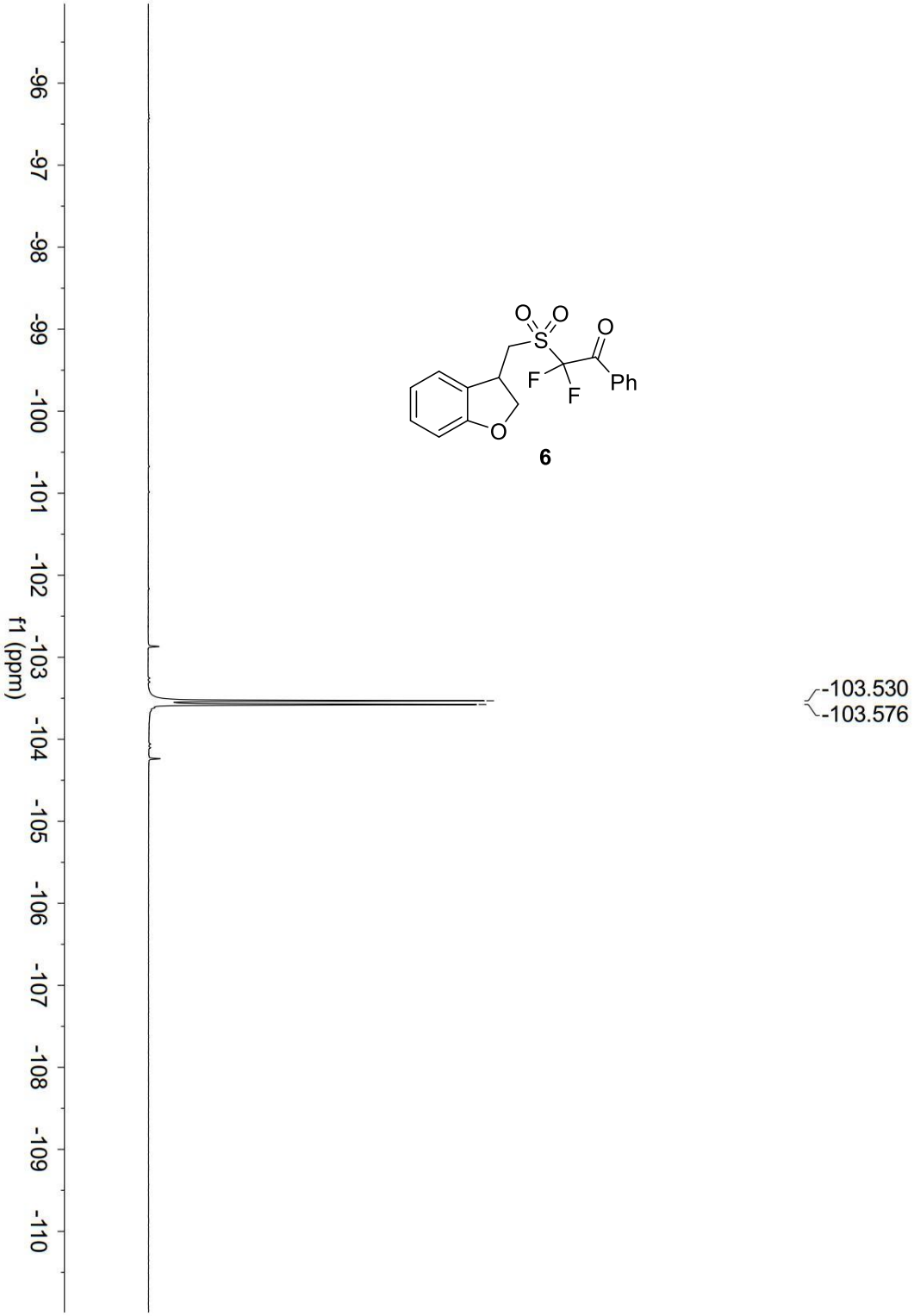
3q


-93
-94
-95
-96
-97
-98
-99
-100
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
f1 (ppm)
O
O
O
S
F
F
S
Cl
3q
-103.775


8.135
8.115
7.741
7.722
7.704
7.574
7.556
7.537
7.264
7.249
7.227
7.207
7.188
6.947
6.928
6.910
6.857
6.837
4.782
4.758
4.736
4.597
4.583
4.573
4.559
4.207
4.186
3.749
3.714
3.577
3.549
3.515
0.000
2.00
1.03
2.09
1.07
1.02
1.03
0.94
1.04
1.04
1.00
1.03
1.03
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
O
O
S
O
F
F
Ph
O

6


f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
S
O
F
F
Ph
O
6
184.645
184.419
184.191
159.673
135.768
130.645
130.613
130.581
129.772
129.012
126.064
124.377
121.193
119.214
116.208
113.201
110.287
75.519
54.146
35.728


-96
-97
-98
-99
-100
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
f1 (ppm)
O
O
S
O
F
F
Ph
O
6
-103.530
-103.576