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Practical and scalable synthesis of bench-stable organofluorosilicate salts

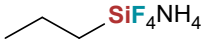
Jarett M. Posz, Stephan R. Harruff, and Ryan Van Hoveln

Department of Chemistry and Physics, Indiana State University, Terre Haute, Indiana, 47809, United States

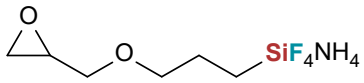
Experimental Section

General Considerations. All reactions were carried out in a plastic beaker unless noted otherwise. ^{1}H NMR ,^{13}C NMR, ^{19}F NMR, and ^{31}P NMR spectra were obtained using an Avance II Bruker-400 NMR Spectrometer or an Avance III HD Bruker-600 NMR Spectrometer. All NMR spectra were acquired at ambient temperature. For ^{1}H NMR, chemical shifts are reported relative to residual protiated solvent peak (δ 2.50 for DMSO-d_6, δ 7.26 for $CDCl_3$, δ 4.79 for D_2O). ^{13}C NMR spectra were measured at 100 MHz or 150 MHz on the same instruments noted above for recording ^{1}H NMR spectra. Chemical shifts were again reported in accordance to the solvent peak (δ 39.52 for DMSO-d_6, δ 77.16 for $CDCl_3$) or were referenced absolutely to the ^{1}H NMR spectrum. ^{19}F NMR spectra were measured at 376 MHz or 564 MHz on the same instruments noted above for recording ^{1}H NMR spectra and the chemical shifts were referenced absolutely to the ^{1}H NMR spectrum. ^{31}P NMR spectra were measured at 162 MHz on the same instrument noted above for recording ^{1}H NMR spectra and the chemical shifts were referenced absolutely to the ^{1}H NMR spectrum. All mass spectra were acquired on a Thermo Scientific Q Exactive Focus using negative polarity. Unless otherwise specified, reagents were used as obtained from the vendor without further purification. Vinyltrimethoxysilane (**1j**), 3-(mercapto)propyltrimethoxysilane (**1g**), n-propyltrimethoxysilane (**1a**), (3-glycidoxypropyl)trimethoxysilane (**1b'**), 3-aminopropyl-trimethoxysilane (**1f**), phenyltrimethoxysilane (**1h**), (3-glycidoxypropyl)triethoxysilane (**1b**), diethylphosphatoethyltriethoxysilane (**1d**), 3-acetoxypropyltrimethoxysilane (**1c**), and 1,2-bis(triethoxysilyl)ethane (**1n**) were purchased from Oakwood Chemical. 3-cyanopropyl-trimethoxysilane (**1e**), *p*-bromophenyltrimethoxysilane (**1i**), (3,3,3-trifluoropropyl)trimethoxy-silane (**1k**), 2-(2-pyridylethyl)trimethoxysilane (**1l**), [2-(3-cylohexenyl)ethyl]trimethoxysilane (**1m**) were purchased from Gelest. Most of the organotetrafluorosilicates did not melt, so sublimation points (s.p.) were measured. Sublimation points were measured by recording the temperature at which material began to deposit in the capillary above the oven of the DigiMelt.

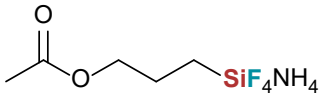
General Procedure for the synthesis of ammonium organotetrafluorosilicates. A solution of NH_4HF_2 (4 M, 1.5 mL, 6.0 mmol, 2.0 equiv) was added to a plastic beaker equipped with a magnetic stir bar and stirred at ambient temperature. Then, the trialkoxysilane was added (3.0 mmol, 1.0 equiv) was added and the reaction was allowed to stir overnight. The next day, the ammonium organotetrafluorosilicate had precipitated and much of the solvent had evaporated. The white powder was transferred to a vial and dried under high vacuum at 40-50 °C overnight. The desired product is formed in sufficiently high purity that no further purification is required.



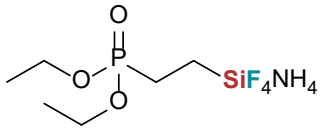
Synthesis of 3a. An additional 2 mL of acetone was added to the reaction. Compound **3a** was isolated as a white solid in 67% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.17 (br s, 4H), 1.30 (h, J = 7.4 Hz, 2H), 0.83 (t, J = 7.3 Hz, 3H), 0.41 (br t, J = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 19.2 (br), 17.7, 17.4. ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.4. HRMS (ESI): m/z calculated for $C_3H_7F_4Si$ $[M - NH_4]^-$ 147.02531, found 147.02481. m.p 100-105 °C.



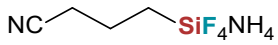
Synthesis of 3b. Compound **3b** was isolated as a white solid in 91% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.86 (br s, 4H), 3.60 (dd, J = 11.5, 2.8 Hz, 1H), 3.33 – 3.26 (m, 2H), 3.18 (dd, J = 11.5, 6.3 Hz, 1H), 3.06 (ddt, J = 5.7, 4.2, 2.8 Hz, 1H), 2.70 (dd, J = 5.2, 4.2 Hz, 1H), 1.50 (p, J = 7.4 Hz, 2H), 0.39 (t, J = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 73.8, 70.9, 50.3, 43.4, 25.2 12.6 (br). ^{19}F NMR (376 MHz, DMSO-d_6) δ -113.1. HRMS (ESI): m/z calculated for $C_6H_{11}F_4O_2Si$ [M - NH_4]$^-$ 219.04644, found 219.04654. mp. 174-176 °C (dec.)



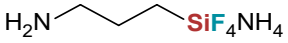
Synthesis of 3c. Compound **3c** was isolated as a white solid in 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.93 (br s, 4H), 3.87 (t, J = 7.2 Hz, 2H), 1.98 (s, 3H), 1.56 (p, J = 7.3 Hz, 2H), 0.42 (dd, J = 9.1, 7.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.5, 67.3, 25.6, 21.2, 13.4 (br). ^{19}F NMR (376 MHz, DMSO) δ -112.7. HRMS (ESI): m/z calculated for $C_5H_9F_4O_2Si$ [M - NH_4]$^-$ 205.03079, found 205.03079. s.p. 166-168 °C.



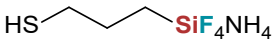
Synthesis of 3d. Compound **3d** was isolated as a white solid in 99% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.07 (br s, 4H), 4.02 – 3.81 (m, 4H), 1.73 – 1.39 (m, 2H), 1.20 (t, J = 7.0 Hz, 6H), 0.72 – 0.43 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 61.0 (d, J = 6.4 Hz), 21.2 (d, J = 136.9 Hz), 16.8 (d, J = 5.6 Hz), 8.4 (br). ^{31}P NMR (162 MHz, DMSO-d_6) δ 35.3. ^{19}F NMR (376 MHz, DMSO-d_6) δ -114.0. HRMS (ESI): m/z calculated for $C_6H_{14}F_4O_3PSi$ [M - NH_4]$^-$ 269.03860, found 269.03925. s.p. 169-187 °C.



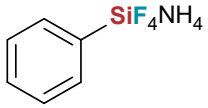
Synthesis of 3e. Compound **3e** was isolated as a white solid in % yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.01 (s, 4H), 2.35 (t, J = 7.1 Hz, 2H), 1.55 (d, J = 7.2 Hz, 2H), 0.56 (d, J = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 121.6, 22.3, 19.6, 16.6. ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.7. HRMS (ESI): m/z calculated for $C_4H_6F_4NSi$ [M - NH_4]$^-$ 172.02056, found 172.02037. s.p. 179-183 °C.



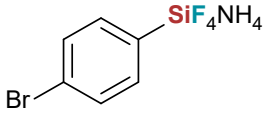
Synthesis of 3f. Compound **3f** was isolated as a white solid in 98% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.33 (br s, 6H), 2.59 (t, J = 7.4 Hz, 2H), 1.49 (p, J = 7.7 Hz, 2H), 0.29 (t, J = 7.8, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 41.4, 23.9, 14.1 (br). ^{19}F NMR (376 MHz, DMSO-d_6) δ -111.7. HRMS (ESI): m/z calculated for $C_3H_8F_4NSi$ [M - NH_4]$^-$ 162.03621, found 162.03595. s.p. 180-183 °C.



Synthesis of 3g. Compound **3g** was isolated as a white solid in 91% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.54 (br s, 5H), 2.38 (t, J = 7.3 Hz, 2H), 1.55 (p, J = 7.7 Hz, 2H), 0.50 (d, J = 8.1 Hz, 2H). ^{13}C NMR (101 MHZ, DMSO-d_6) δ 30.7, 27.8, 16.8 (br). ^{19}F NMR (376 MHZ, DMSO-d_6) δ -112.3. HRMS (ESI): m/z calculated for $C_3H_7F_4SSi$ [M - NH_4]$^-$ 178.99739, found 178.99730. s.p. 111-128 °C.

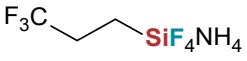


Synthesis of 3h. Compound **3h** was isolated as a white solid in 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76 – 7.70 (m, 2H), 7.26 – 7.21 (m, 1H), 7.21 – 7.15 (m, 2H), 5.23 (br s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.3, 133.3, 128.1, 126.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.0. HRMS (ESI): m/z calculated for $C_6H_5F_4Si$ [M - NH_4]$^-$ 181.00966, found 181.00941. s.p. 128-130 °C.

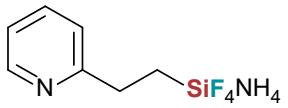


Synthesis of 3i. Compound **3i** was isolated as a white solid in 93% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 5.23 (s, 3H). ^{13}C NMR (101 MHZ, DMSO-d_6) δ 141.7, 140.7, 129.9, 122.7. ^{19}F NMR (376 MHz, DMSO-d_6) δ -117.6. HRMS (ESI): m/z calculated for $C_6H_4BrF_4Si$ [M - NH_4]$^-$ 258.92018, found 258.92123. s.p. 169-171 °C.

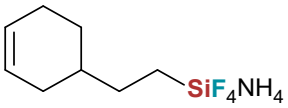
Synthesis of 3j. Compound **3j** was isolated as a white solid in 85% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.86 (dd, J = 17.9, 7.2 Hz, 1H), 5.80 – 5.66 (m, 2H), 5.10 (br s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.0, 136.9 (br). ^{19}F NMR (376 MHz, DMSO) δ -115.7. HRMS (ESI): m/z calculated for $C_2H_3F_4Si$ [M - NH_4]$^-$ 130.99401, found 130.99341. s.p. 98-103 °C.



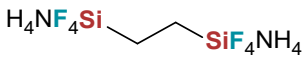
Synthesis of 3k. Compound **3k** was isolated as a white solid in 75% yield.^{1}H NMR (400 MHz, DMSO-d_6) δ 5.88 (br s, 6H), 2.27 – 1.86 (m, 2H), 0.79 – 0.36 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 129.2 (q, J = 276.6 Hz), 30.1 (q, J = 27.7 Hz), 8.6 (br). ^{19}F NMR (376 MHz, DMSO-d_6) δ -67.26 (t, J = 11.6 Hz), -113.58. HRMS (ESI): m/z calculated for $C_3H_4F_7Si$ [M - NH_4]$^-$ 200.99705, found 200.99704. s.p. 127-133 °C.



Synthesis of 3l. Compound **3l** was isolated as a white solid in 85% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.51 (dt, J = 5.3, 1.2 Hz, 1H), 7.77 (td, J = 7.6, 1.8 Hz, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.24 (t, J = 6.4 Hz, 1H), 6.83 (br s, 4H), 2.77 (t, J = 7.9 Hz, 2H), 0.49 (br t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.7, 146.2, 137.6, 123.2, 121.0, 32.1, 16.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.7. HRMS (ESI): m/z calculated for $C_7H_8F_4NSi$ [M - NH_4]$^-$ 210.03621, found 210.03632. m.p. 182-188 °C (s.t.).

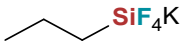


Synthesis of 3m. Compound **3m** was isolated as a white solid in 64% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.37 (br s, 5H), 5.67 – 5.54 (m, 2H), 2.12 – 1.99 (m, 0H), 1.99 – 1.87 (m, 2H), 1.78 – 1.61 (m, 1H), 1.60 – 1.41 (m, 1H), 1.40 – 1.17 (m, 2H), 1.06 (dddd, J = 12.7, 10.7, 9.4, 6.8 Hz, 1H), 0.42 (br t, J = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 128.1, 127.19, 36.9, 33.9, 31.8, 29.9, 25.4, 14.8.^{19}F NMR (376 MHz, DMSO-d_6) δ -112.2. HRMS (ESI): m/z calculated for $C_8H_{13}F_4Si$ [M - NH_4]$^-$ 213.07226, found 213.07259. s.p. 158-161 °C.

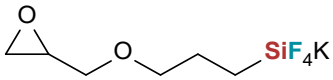


Synthesis of 3n. Compound **3n** was isolated as a white solid in 81% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.67 (br s, 8H), 0.37 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 12.7 (br). ^{19}F NMR (376 MHz, DMSO-d_6) δ -113.6. HRMS (ESI): m/z calculated for $C_2H_4F_7Si_2$ [M - NH_4 - F]$^-$ 216.97398, found 216.97374. s.p. 165-176 °C.

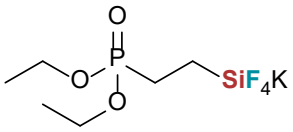
General Procedure for the synthesis of potassium organotetrafluorosilicates. In a plastic beaker equipped with a magnetic stir bar, KHF_2 (0.235 g, 3.0 mmol, 2.0 equiv) was dissolved in 3 mL of water at ambient temperature. Then, the silane was added (1.5 mmol, 1.0 equiv) and then 3 mL of acetone was added. The product begins to precipitate almost immediately. The reaction is allowed to stir for 10 minutes and then filtered and washed with acetone. The white powder is then transferred to vial and dried under high vacuum at 40-50 °C overnight. The desired product is formed in sufficiently high purity that no further purification is required.



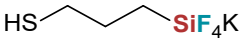
Synthesis of 2a. Compound **2a** was isolated as a white solid in 89% yield. ^{1}H NMR (600 MHz, D_2O) δ 1.4 (h, J = 7.5 Hz, 2H), 0.8 (t, J = 7.4 Hz, 3H), 0.7 (s, 2H). ^{13}C NMR (151 MHz, D_2O) δ 16.5, 15.3, 11.9. ^{19}F NMR (564 MHz, D_2O) δ -136.0. HRMS (ESI): m/z calculated for $C_3H_7F_4Si$ [M - NH_4]$^-$ 147.02531, found 147.02484. Slow decomposition above 340 °C.



Synthesis of 2b. Compound **2b** was isolated as a white solid in 74% yield. ^{1}H NMR (600 MHz, D_2O) δ 3.83 (d, *J* = 9.8 Hz, 1H), 3.49 (tt, *J* = 6.6, 3.4 Hz, 2H), 3.30 – 3.20 (m, 2H), 2.86 (t, *J* = 4.3 Hz, 1H), 2.67 (dd, *J* = 4.4, 2.8 Hz, 1H), 1.65 (p, *J* = 6.9 Hz, 2H), 0.73 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (151 MHz, D_2O) δ 72.9, 70.9, 51.6, 45.0, 21.7, 6.1. ^{19}F NMR (564 MHz, D_2O) δ -135.9. HRMS (ESI): m/z calculated for $C_6H_{11}F_4O_2Si$ $[M - NH_4]^-$ 219.04644, found 219.04666. Slow decomposition above 280 °C.



Synthesis of 2d. Compound **2d** was isolated as a white solid in 77% yield. ^{1}H NMR (600 MHz, D_2O) δ 4.09 – 3.98 (m, 4H), 1.94 – 1.72 (m, 2H), 1.23 (t, J = 7.1 Hz, 6H), 0.69 (br s, 2H). ^{13}C NMR (151 MHz, D_2O) δ 63.4 (d, J = 6.8 Hz), 63.1 (d, J = 3.4 Hz), 15.5 (d, J = 5.8 Hz), 8.2 (br). ^{19}F NMR (564 MHz, D_2O) δ -133.4. HRMS (ESI): m/z calculated for $C_6H_{14}F_4O_3PSi$ $[M - NH_4]^-$ 269.03860, found 269.03952. Slow decomposition above 340 °C.



Synthesis of 2g. Compound **2g** was isolated as a white solid in 96% yield. ^{1}H NMR (600 MHz, D_2O) δ 2.6 (t, *J* = 7.1 Hz, 2H), 1.7 (p, 2H), 0.9 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (151 MHz, D_2O) δ 26.8, 26.4, 8.6 (br). ^{19}F NMR (564 MHz, D_2O) δ -137.2. HRMS (ESI): m/z calculated for $C_3H_7F_4SSi$ $[M - NH_4]^-$ 178.99739, found 178.99712. Slow decomposition above 290 °C.

NOTE ABOUT SPECTRA: Common impurities include hydrolysis (especially the potassium salts) and dehydrosilation, though usually not more than a few percent. The common impurity found in the ^{19}F-NMR is SiF_6^{2-} (-123 ppm in DMSO-d6 and -130 ppm in D_2O). The carbon attached to the silicon tends to be very broad and requires a large number of scans to detect and a line broadening of 5-10 during processing.

NMR and Mass Spectra

Figure S1. ^{1}H-NMR of 3a in DMSO-d6

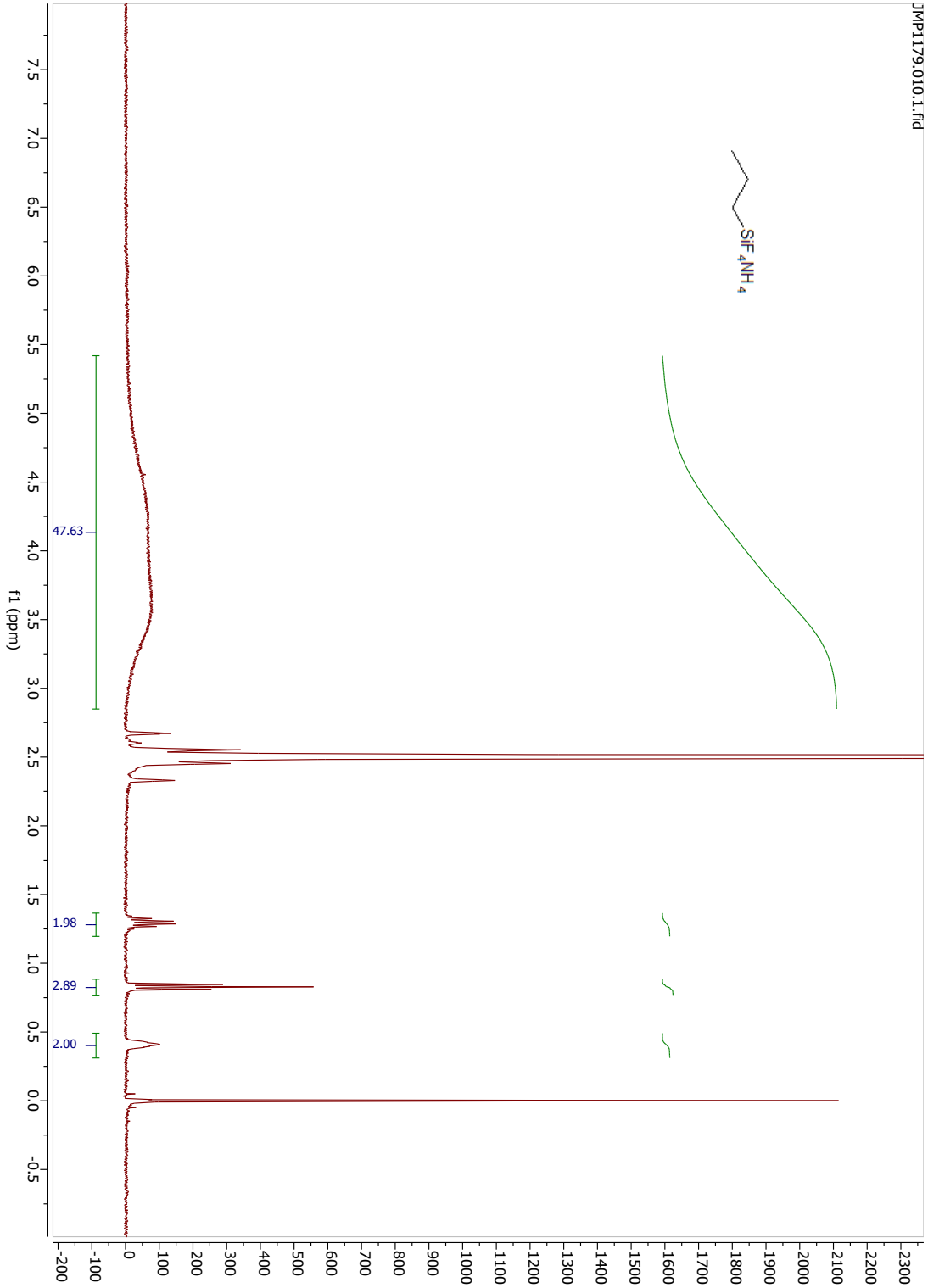


Figure S2. ^{13}C-NMR of 3a in DMSO-d6

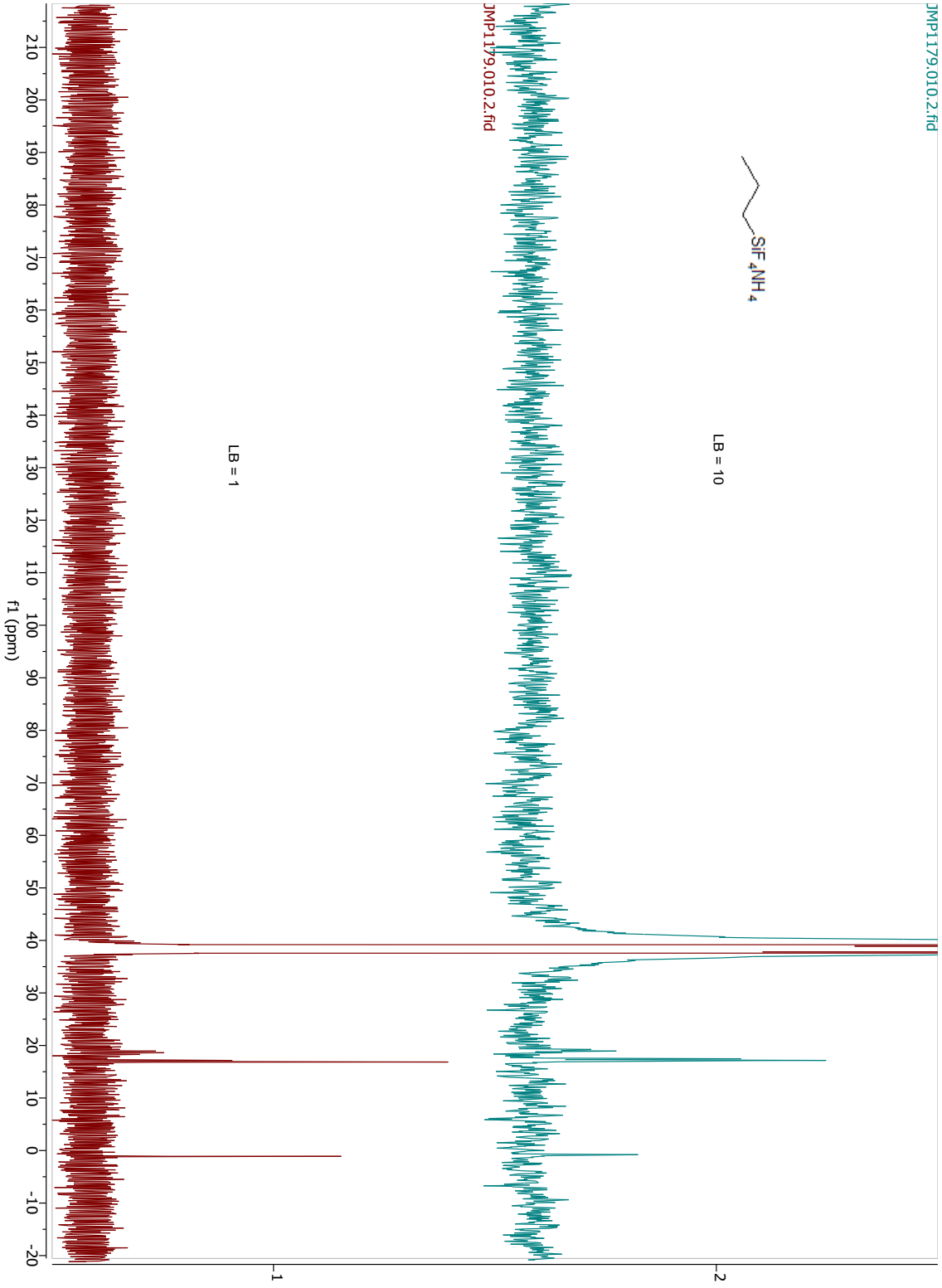


Figure S3. ^{19}F-NMR of 3a in DMSO-d6

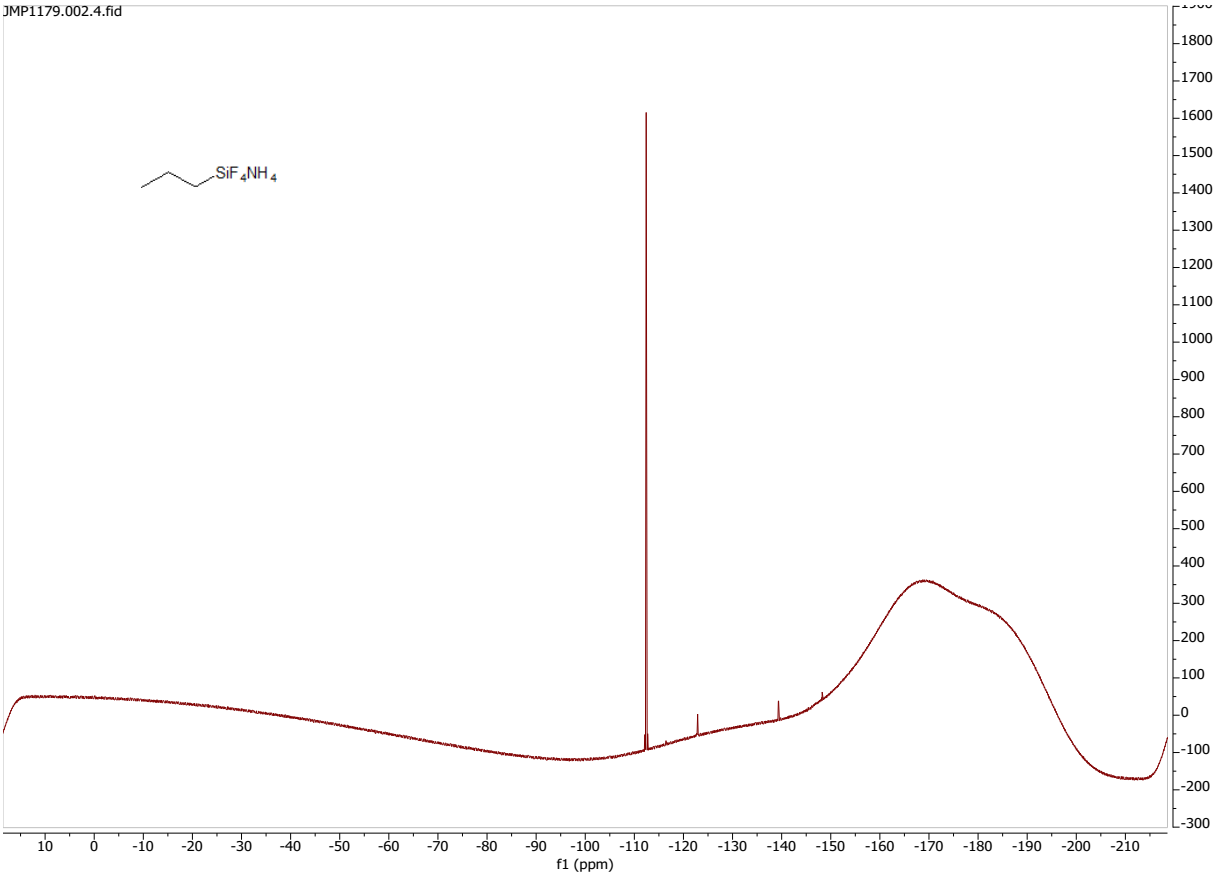


Figure S4. Mass Spectrum of 3a

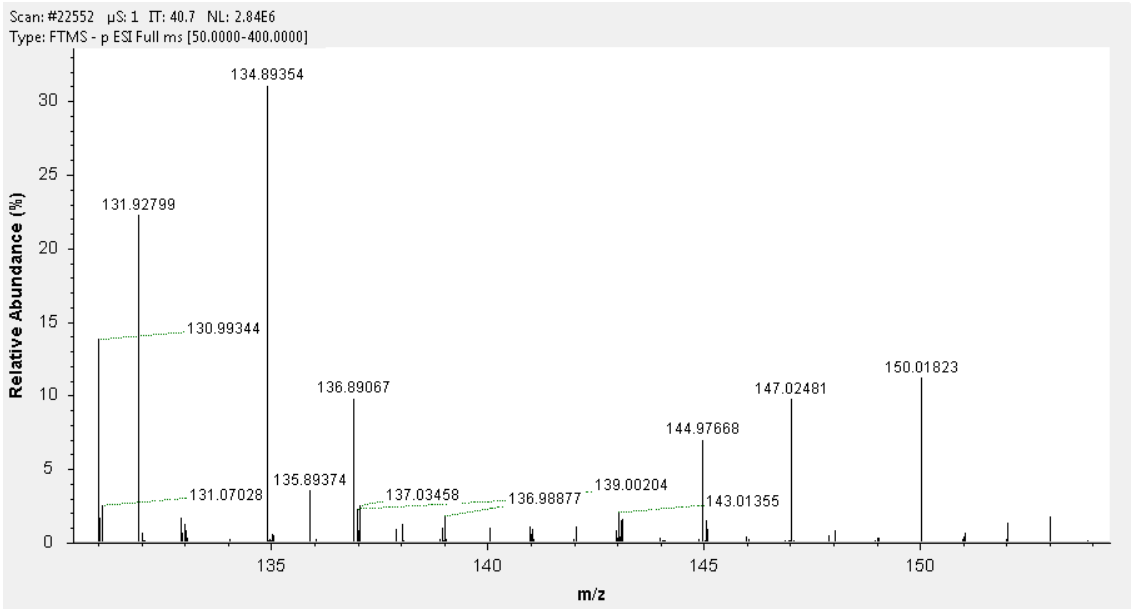


Figure S5. ^{1}H-NMR of 3b in DMSO-d6

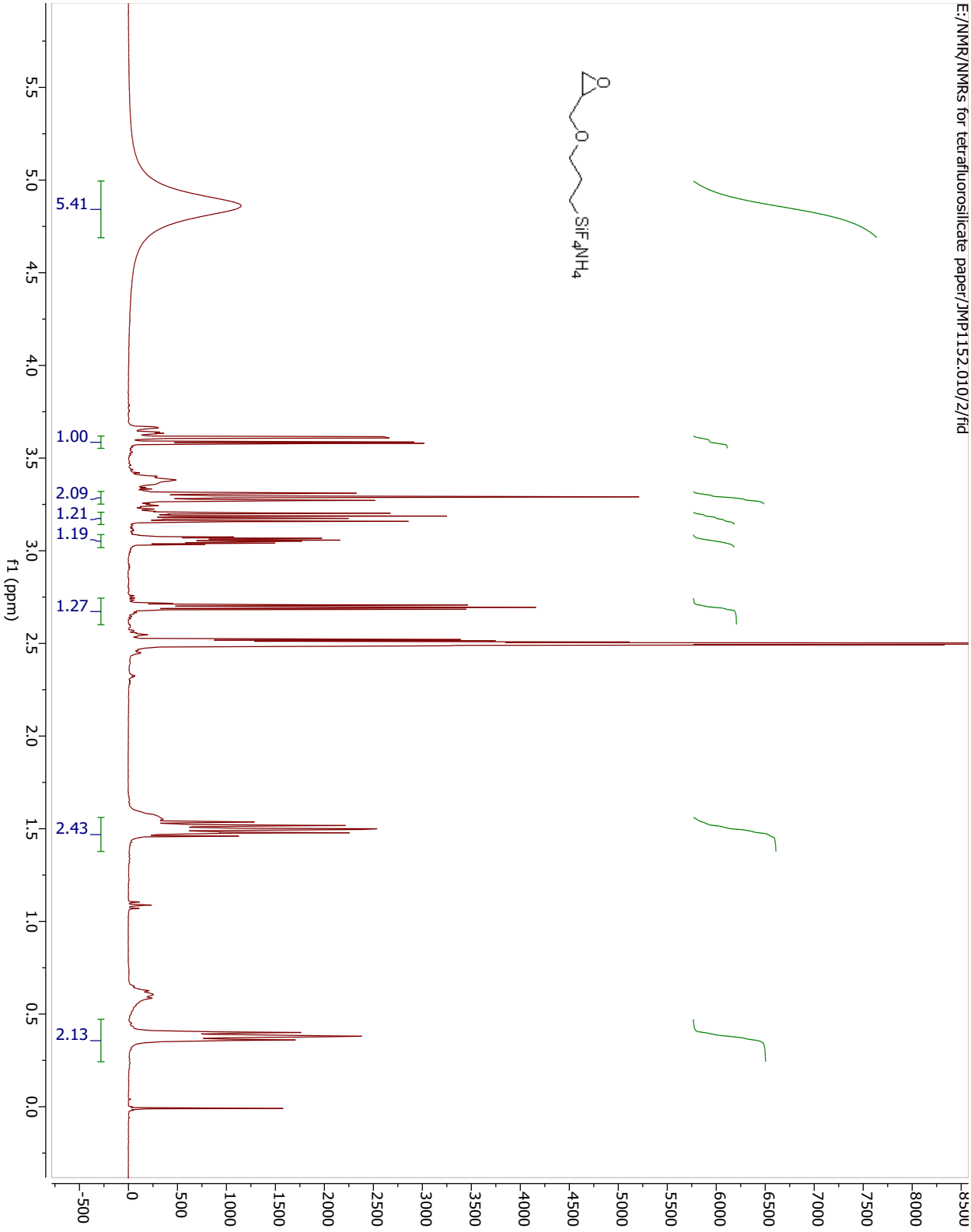


Figure S6. ^{13}C-NMR of 3b in DMSO-d6

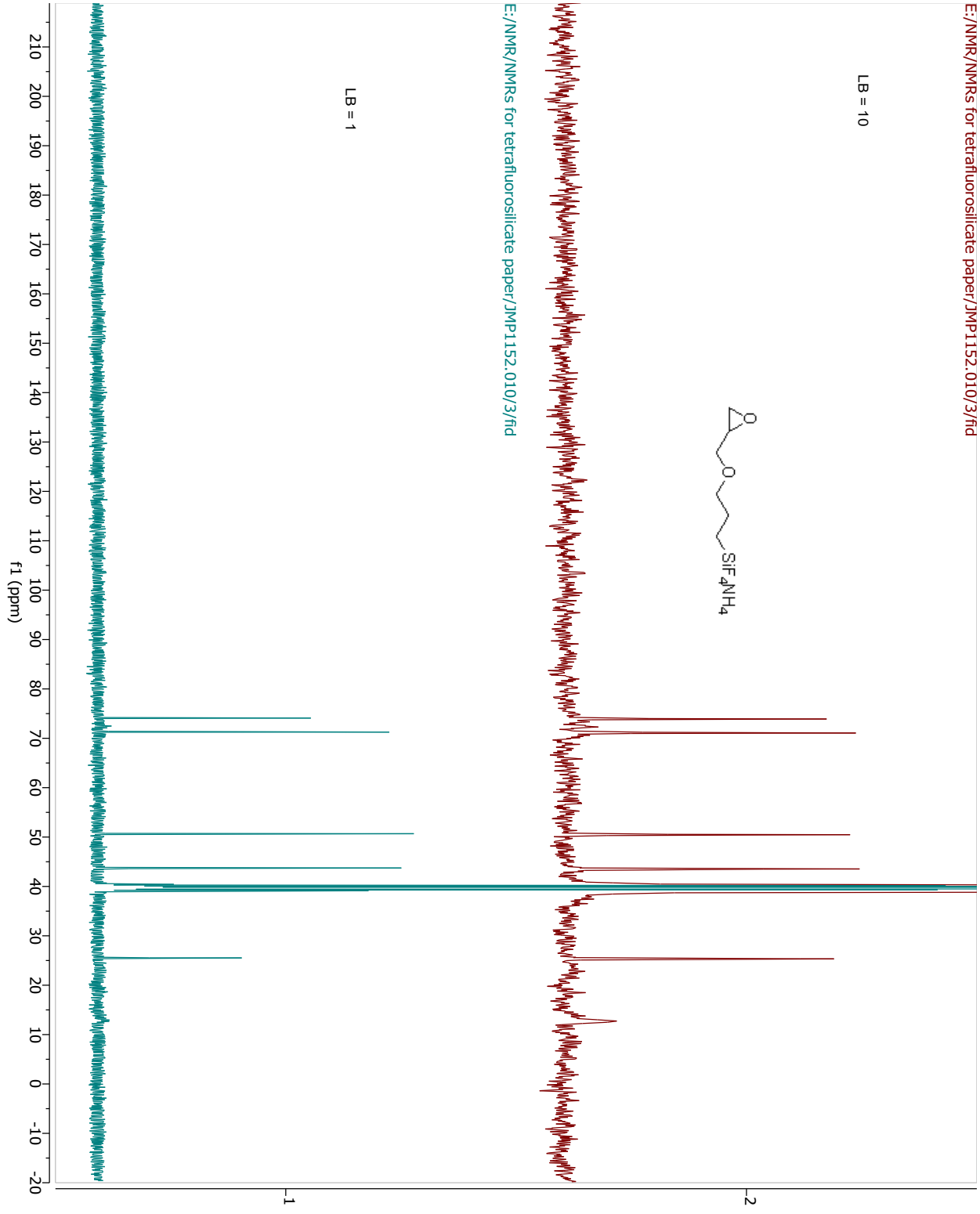


Figure S7. ^{19}F-NMR of 3b in DMSO-d6

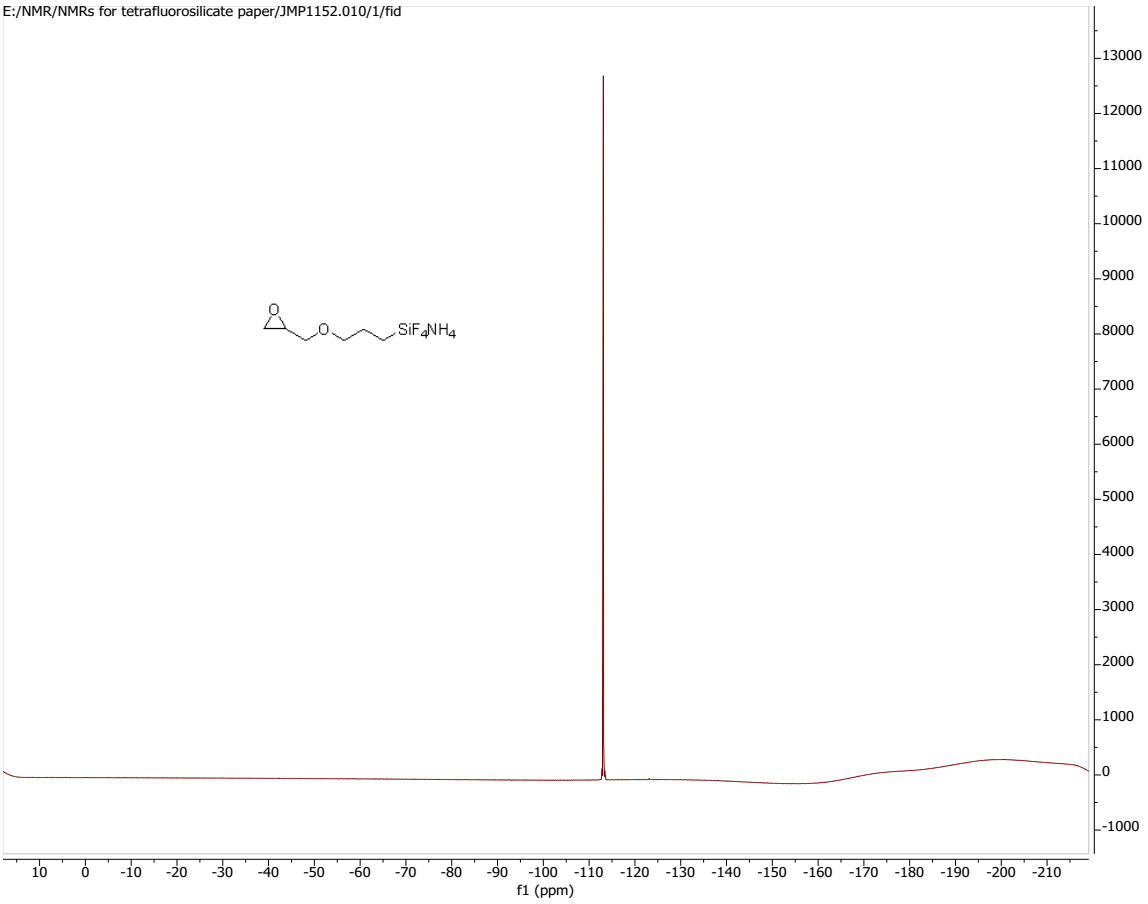


Figure S8. Mass Spectrum of 3b.

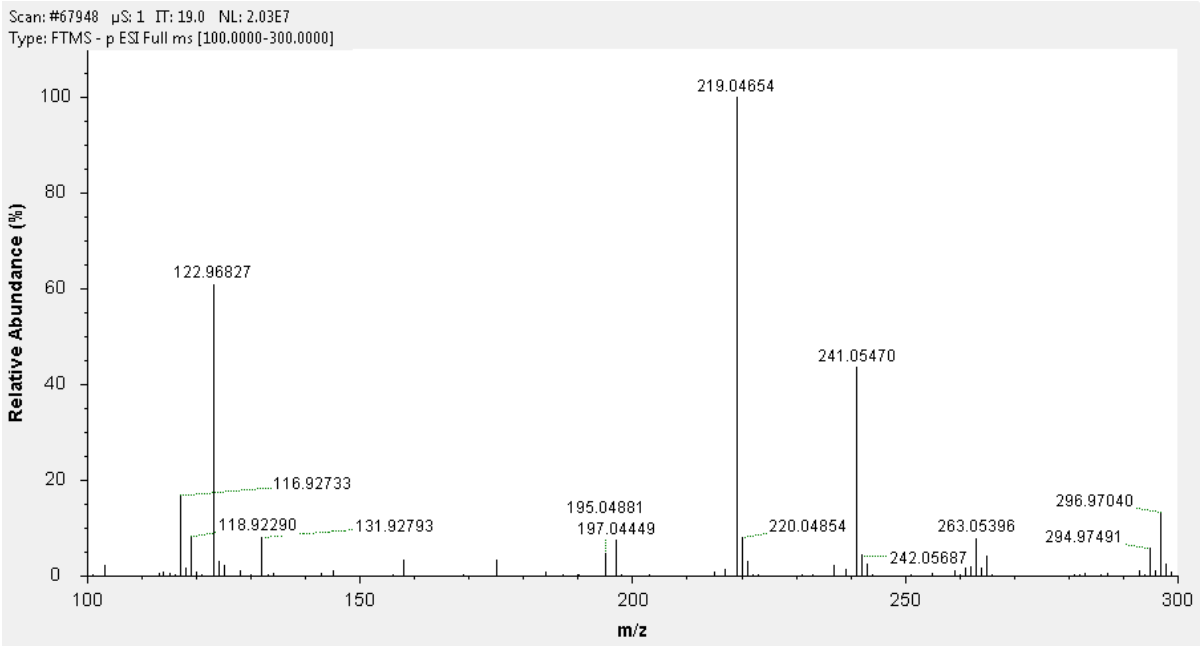


Figure S9. ^{1}H-NMR of 3c in DMSO-d6

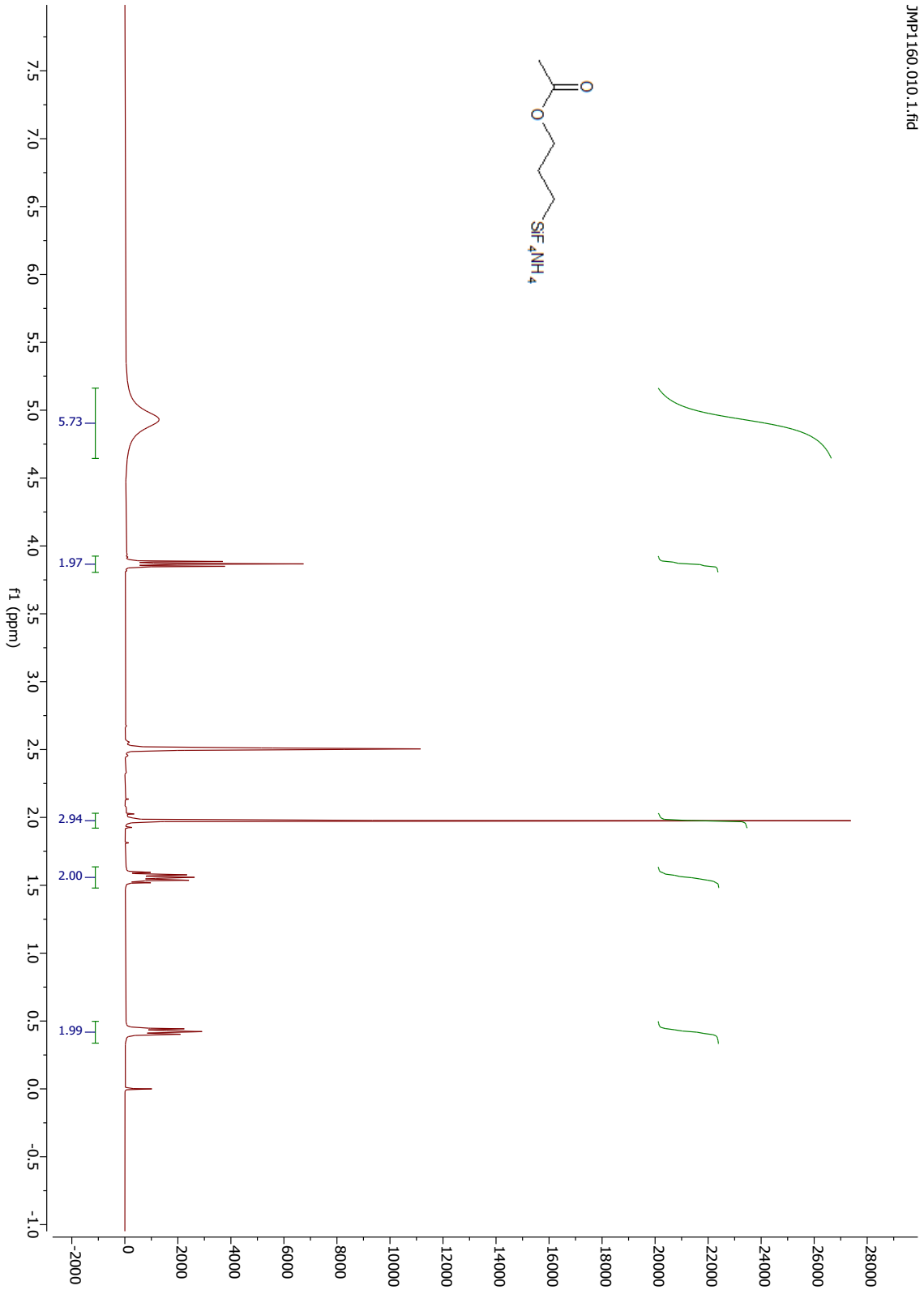


Figure S10. ^{13}C-NMR of 3c in DMSO-d6

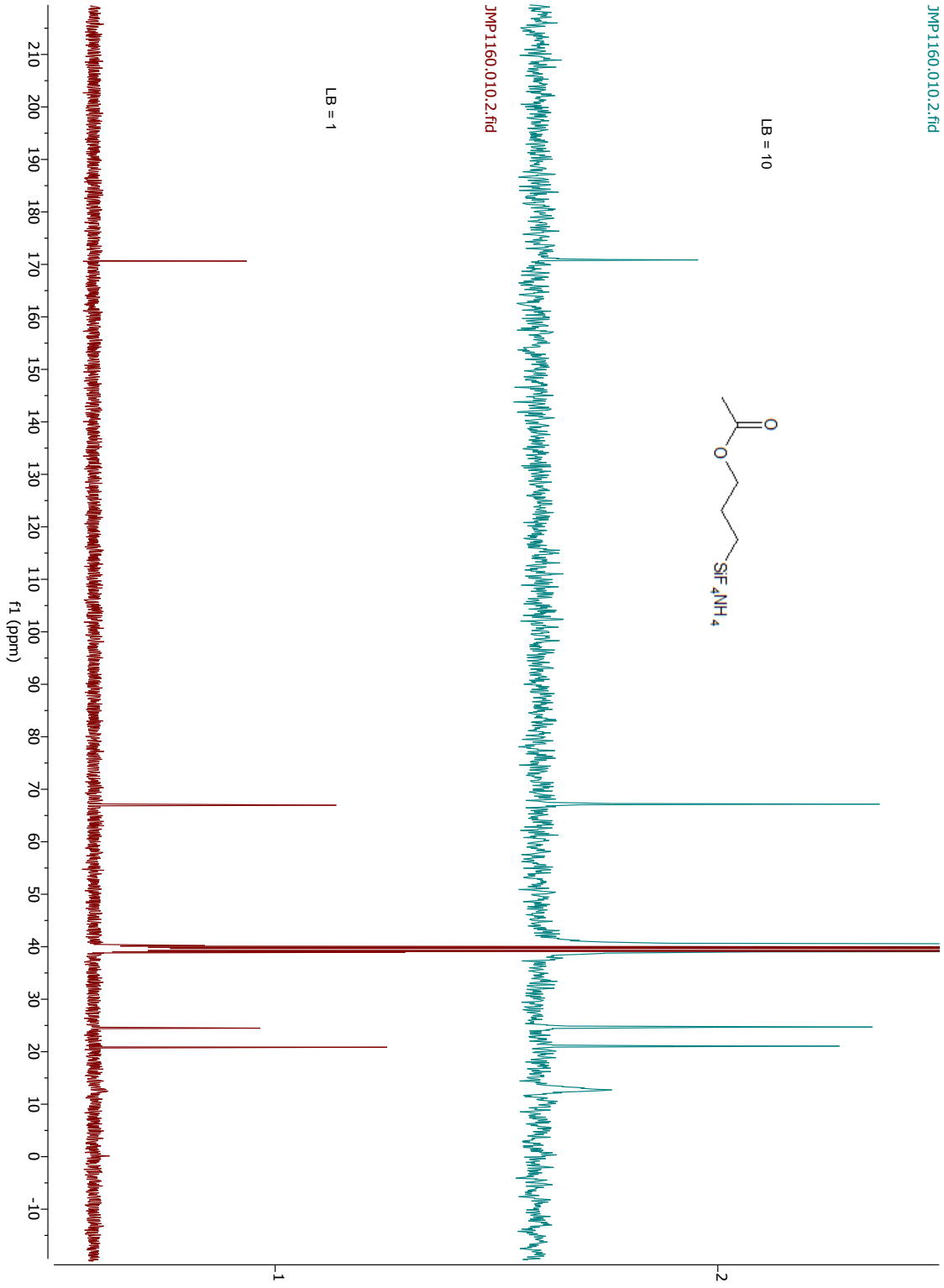


Figure S11. ^{19}F-NMR of 3c in DMSO-d6

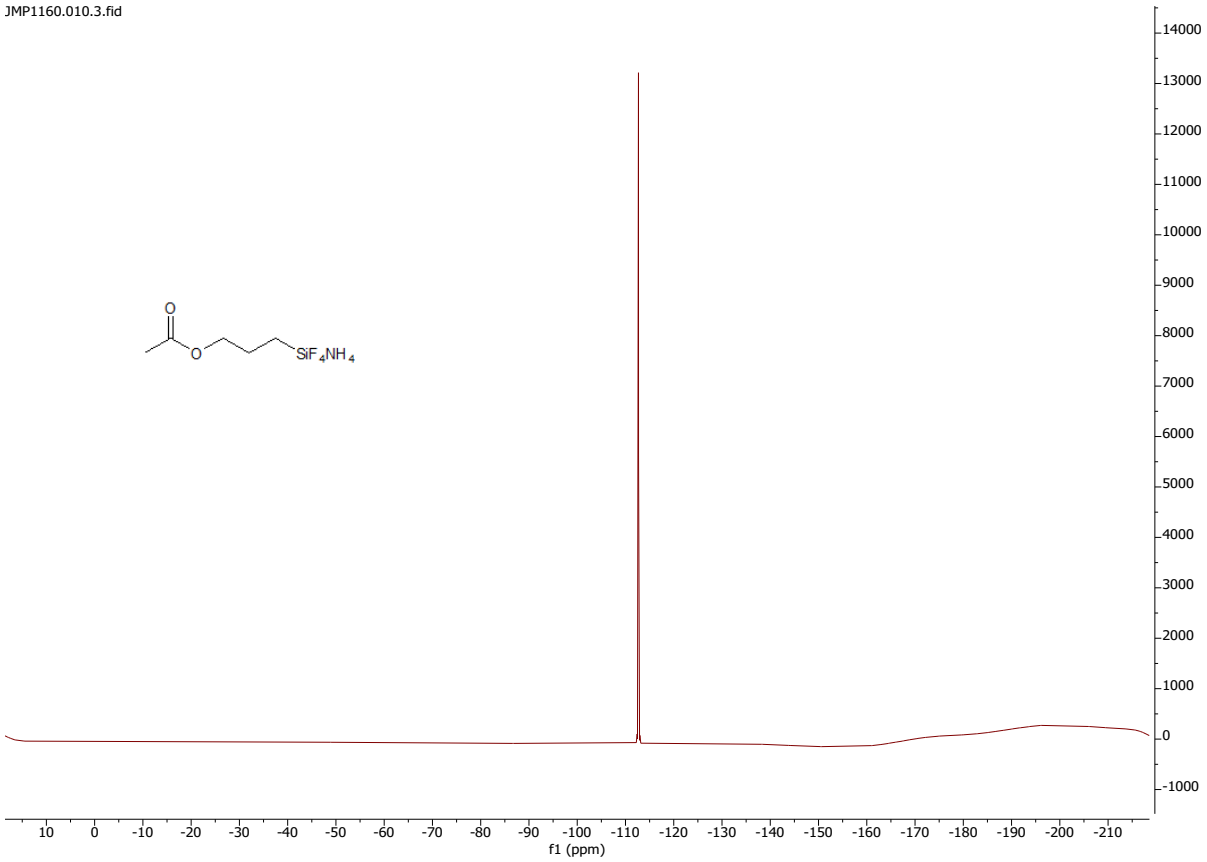


Figure S12. Mass Spectrum of 3c

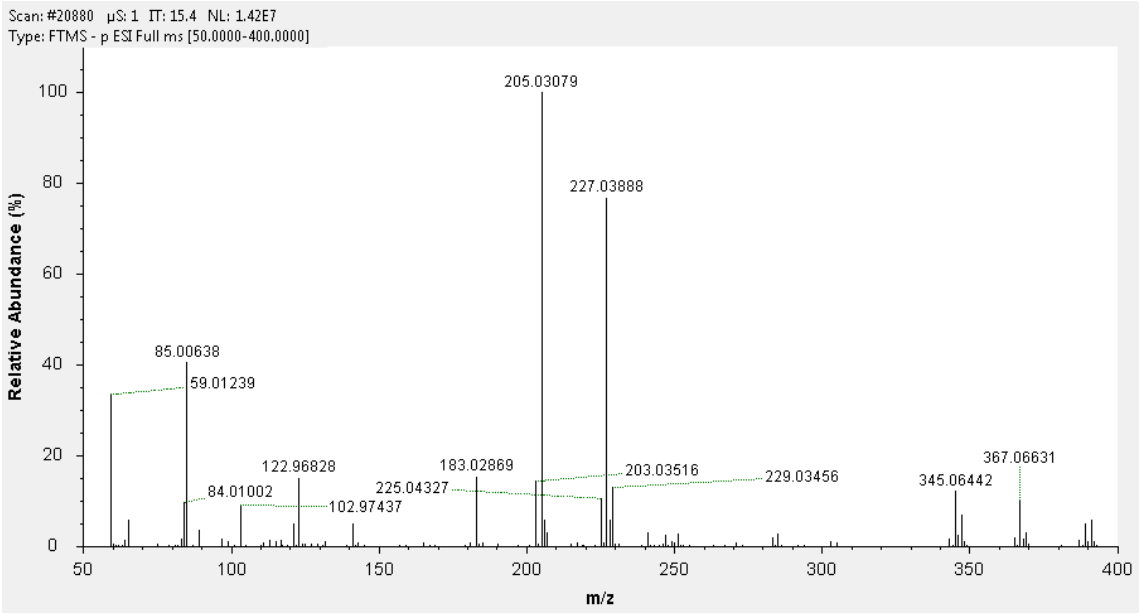


Figure S13. ^{1}H-NMR of 3d in DMSO-d6

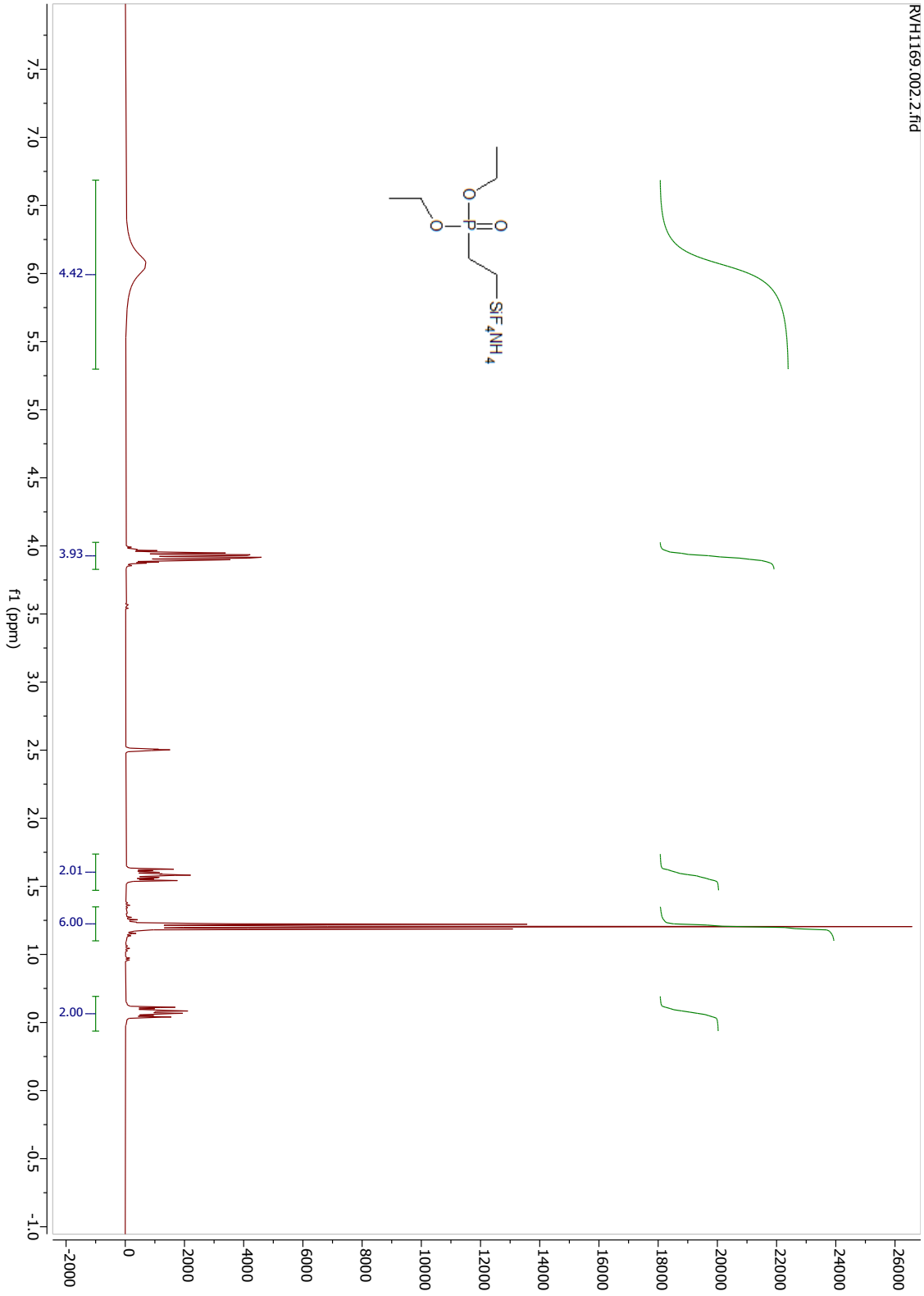


Figure S14. ^{13}C-NMR of 3d in DMSO-d6

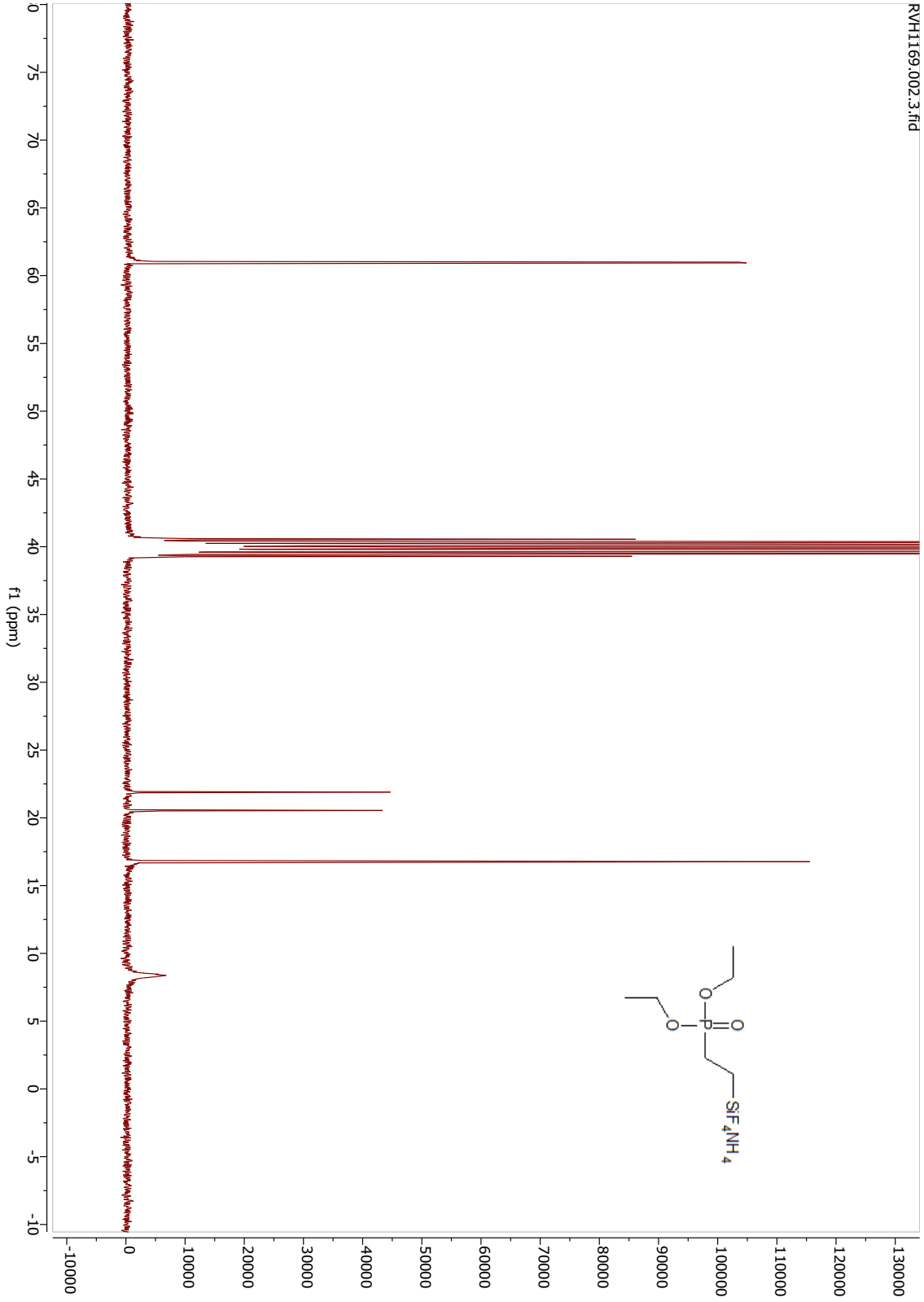


Figure S15. ^{19}F-NMR of 3d in DMSO-d6

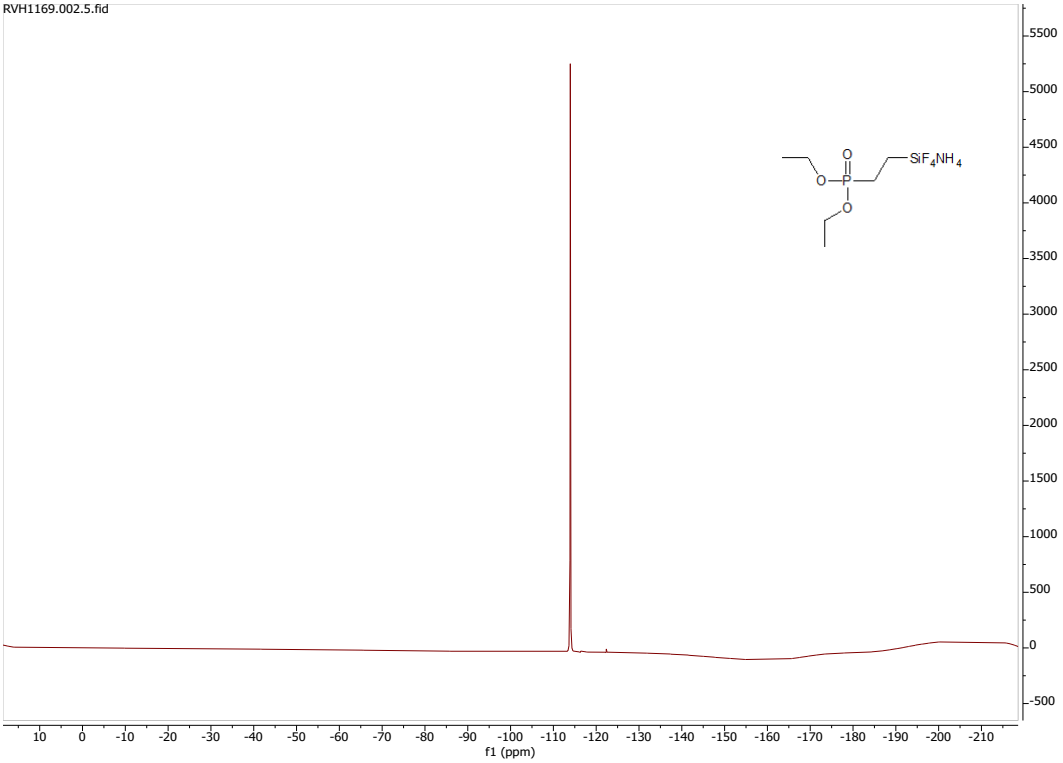


Figure S16. ^{31}P-NMR of 3d in DMSO-d6

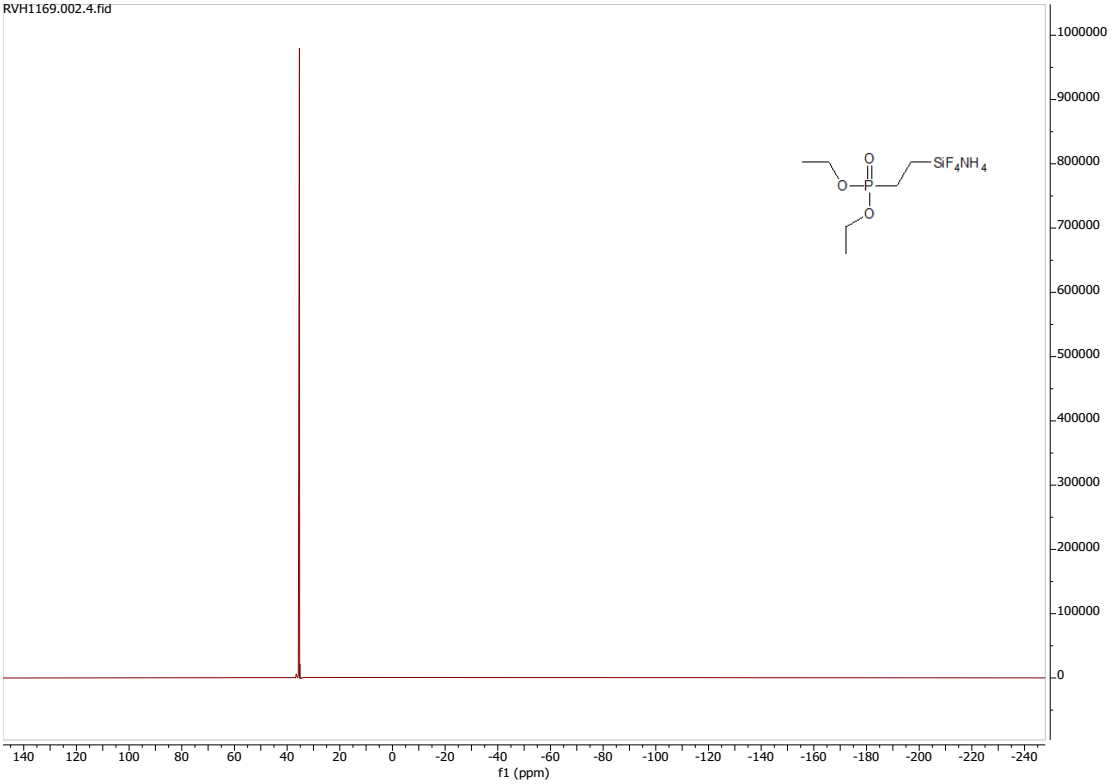


Figure S17. Mass Spectrum of 3d

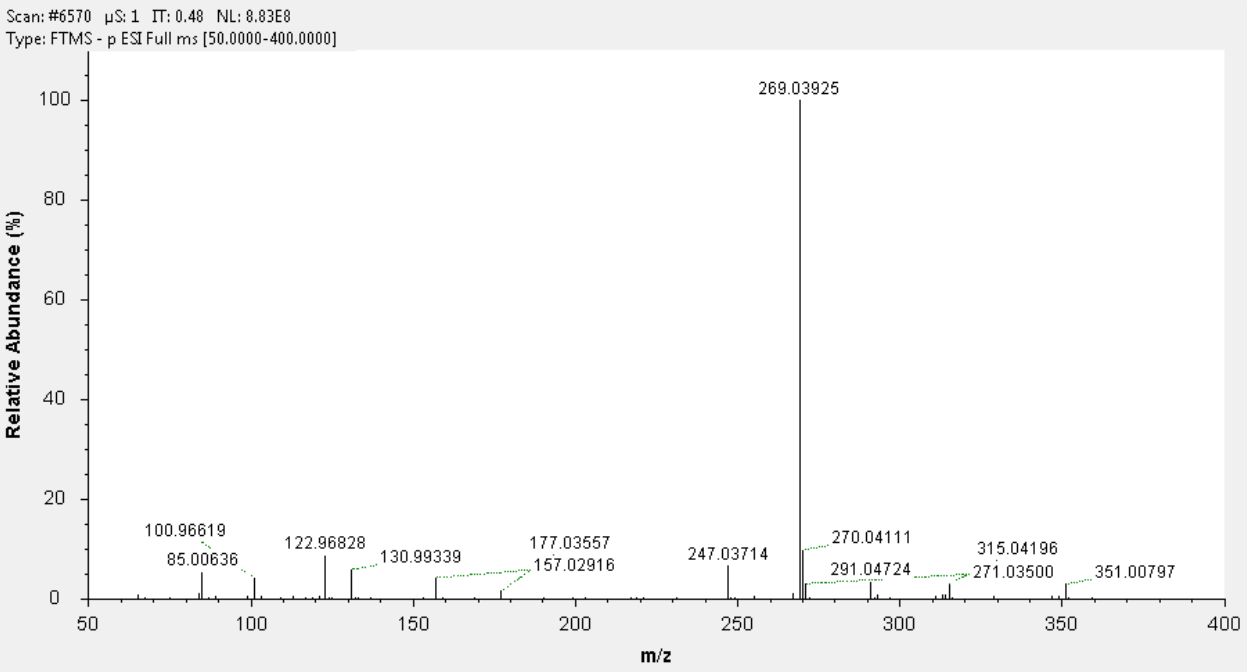


Figure S18. ^{1}H-NMR of 3e in DMSO-d6

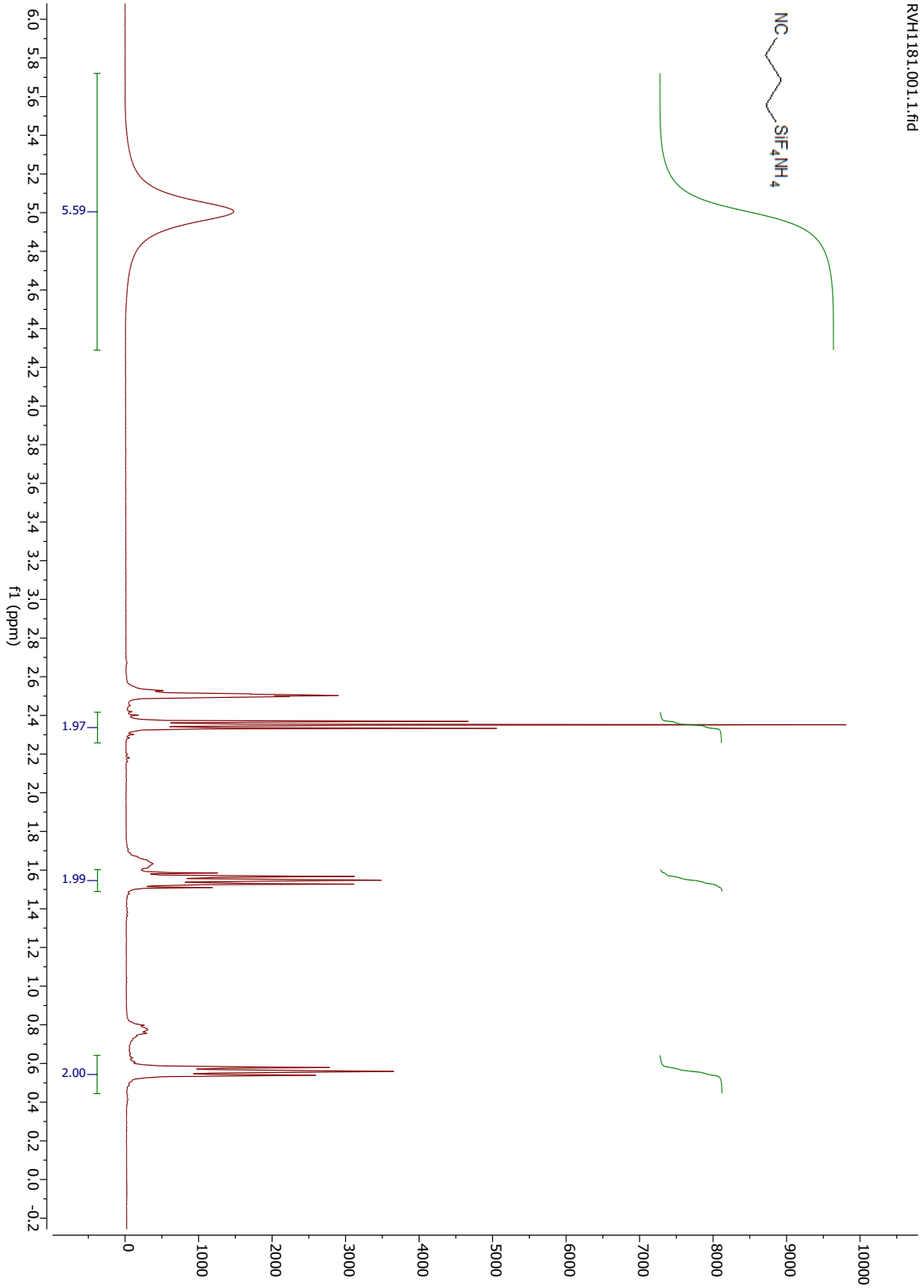


Figure S19. ^{13}C-NMR of 3e in DMSO-d6

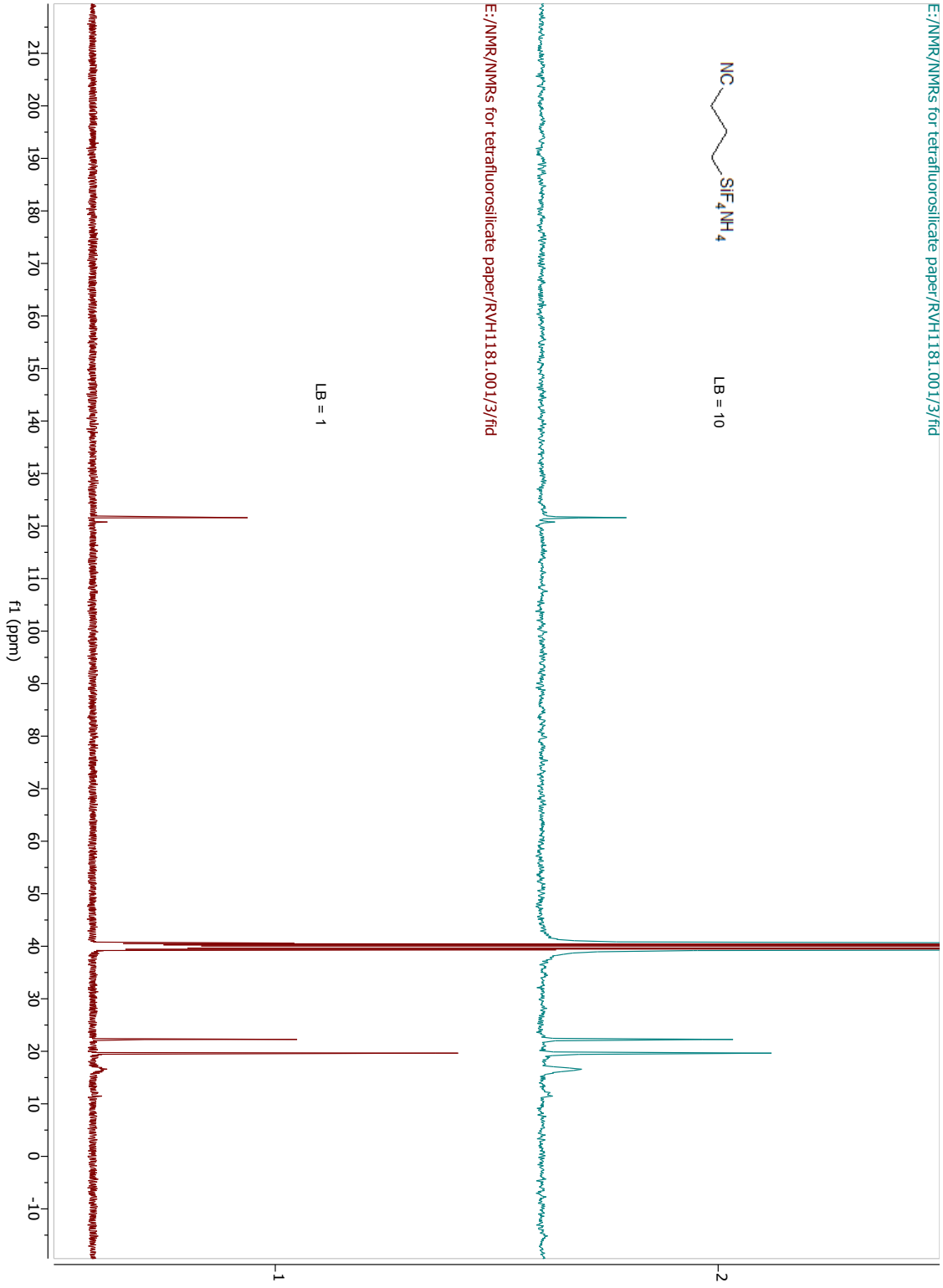


Figure S20. ^{19}F-NMR of 3e in DMSO-d6

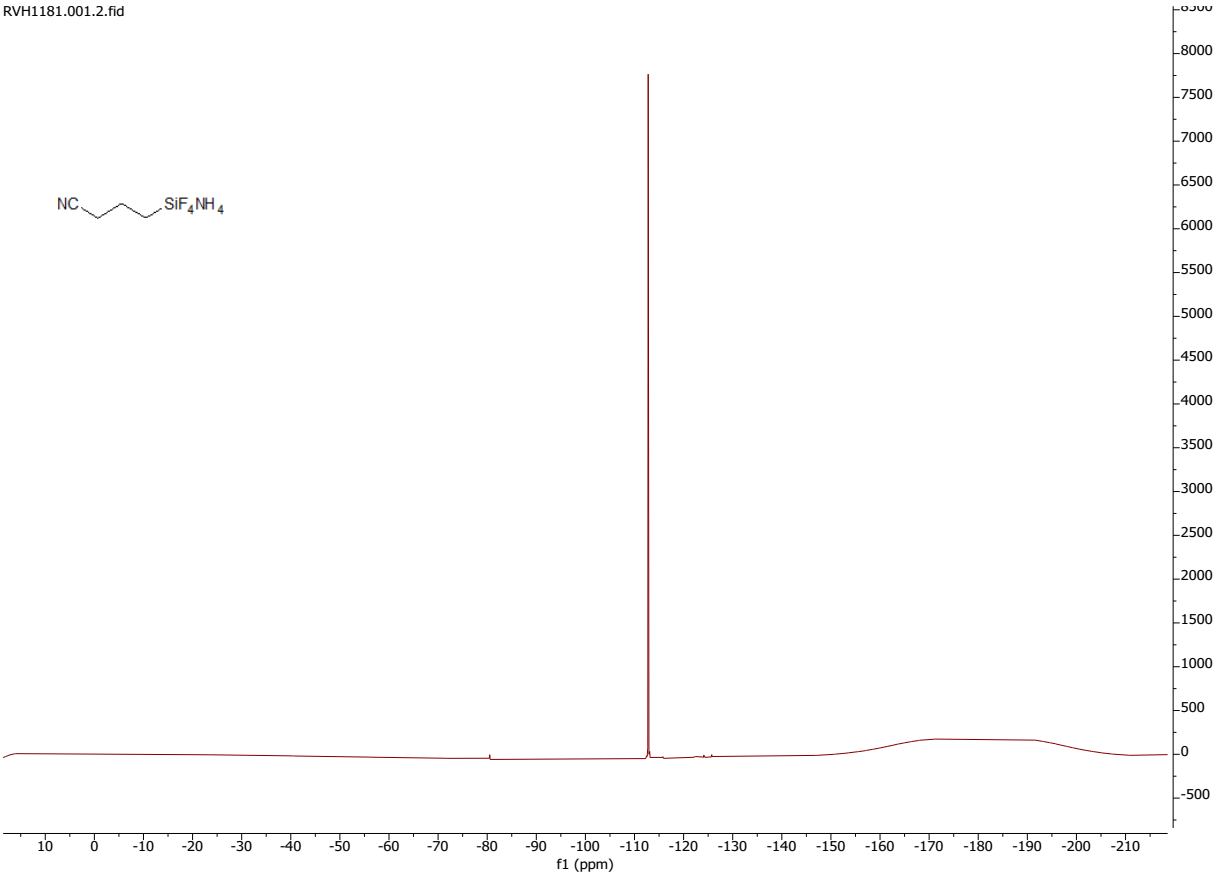


Figure S21. Mass Spectrum of 3e

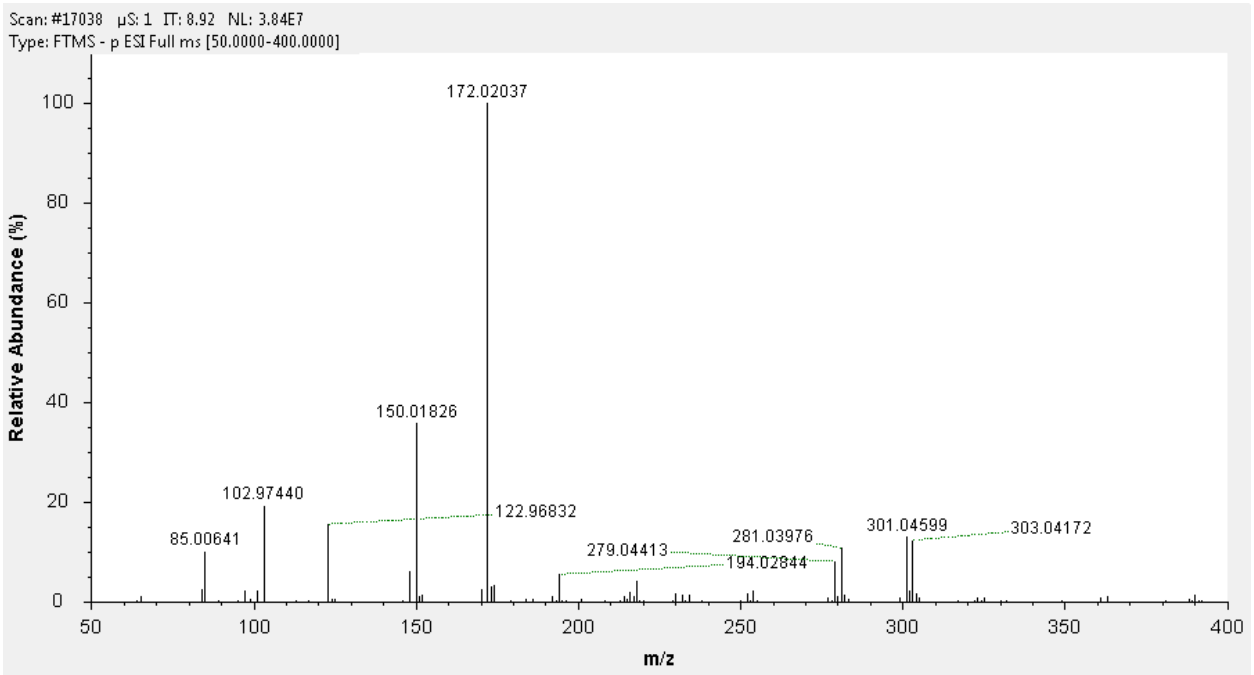


Figure S22. ^{1}H-NMR of 3f in DMSO-d6

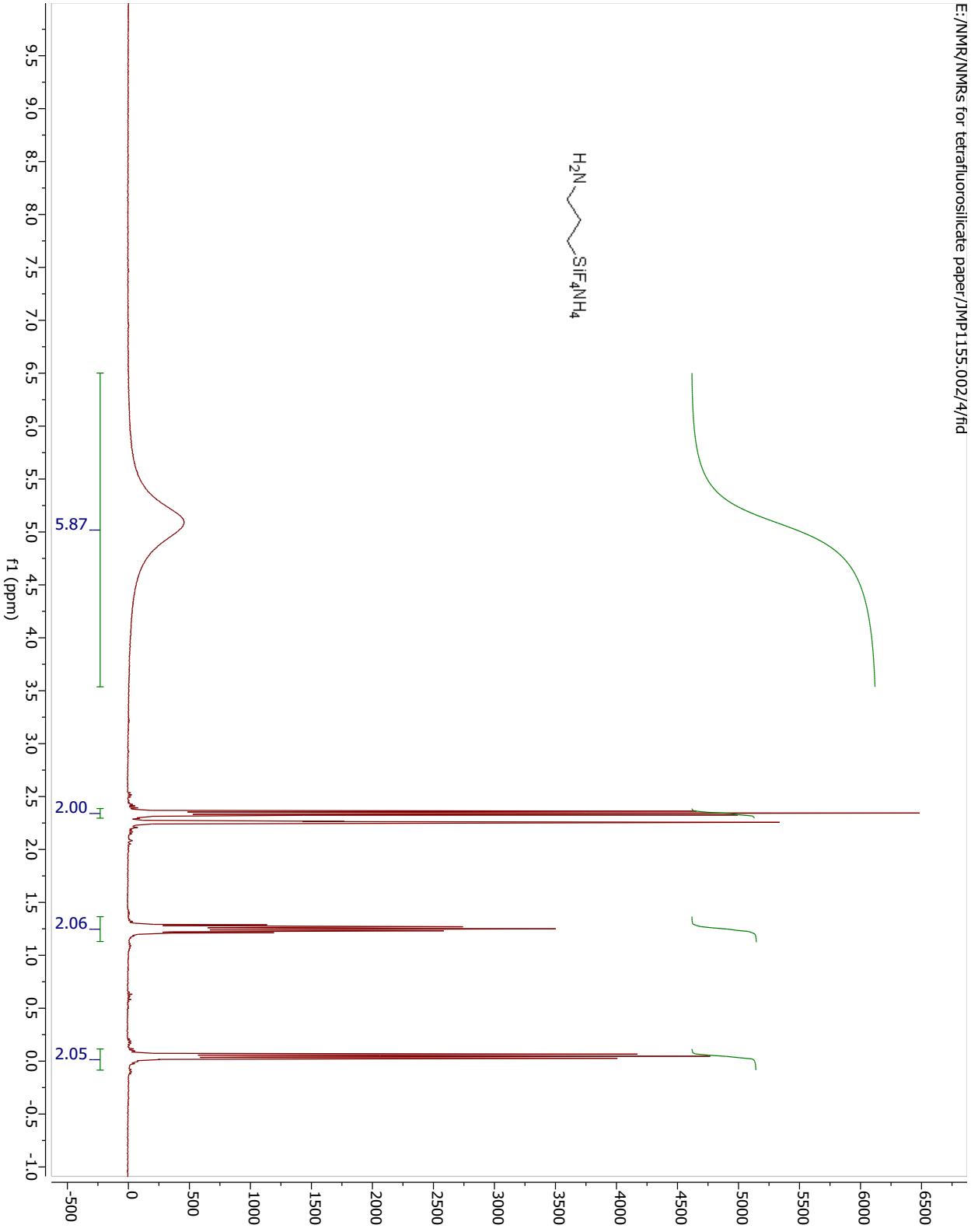


Figure S23. ^{13}C-NMR of 3f in DMSO-d6

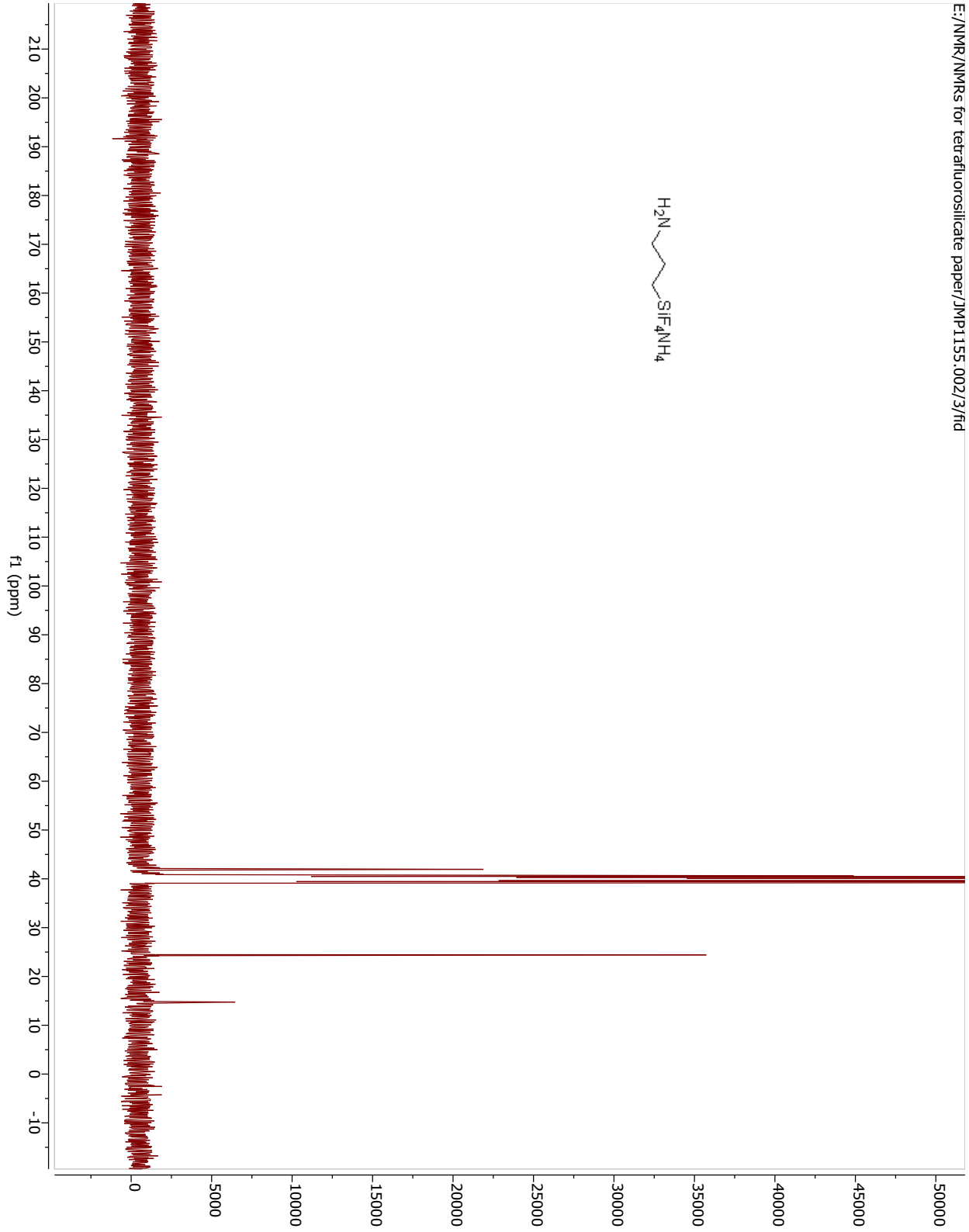


Figure S24. ^{19}F-NMR of 3f in DMSO-d6

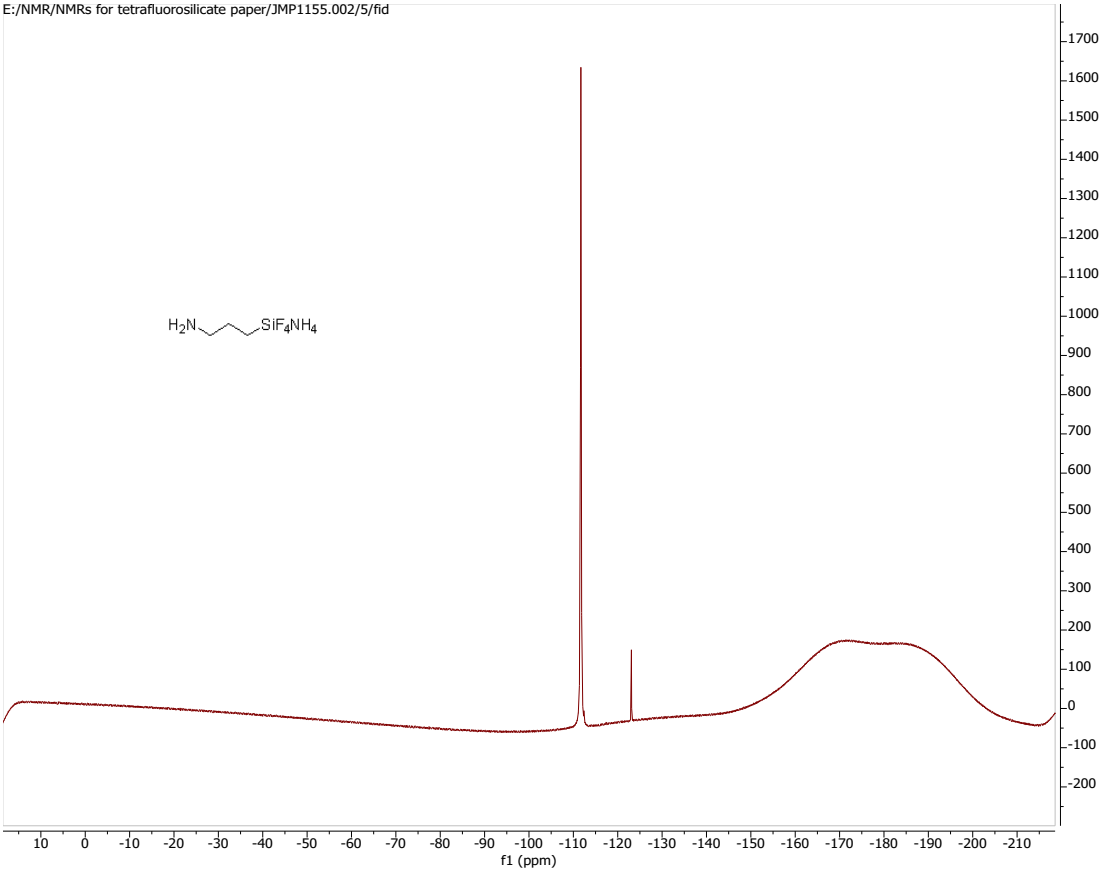


Figure S25. Mass Spectrum of 3f

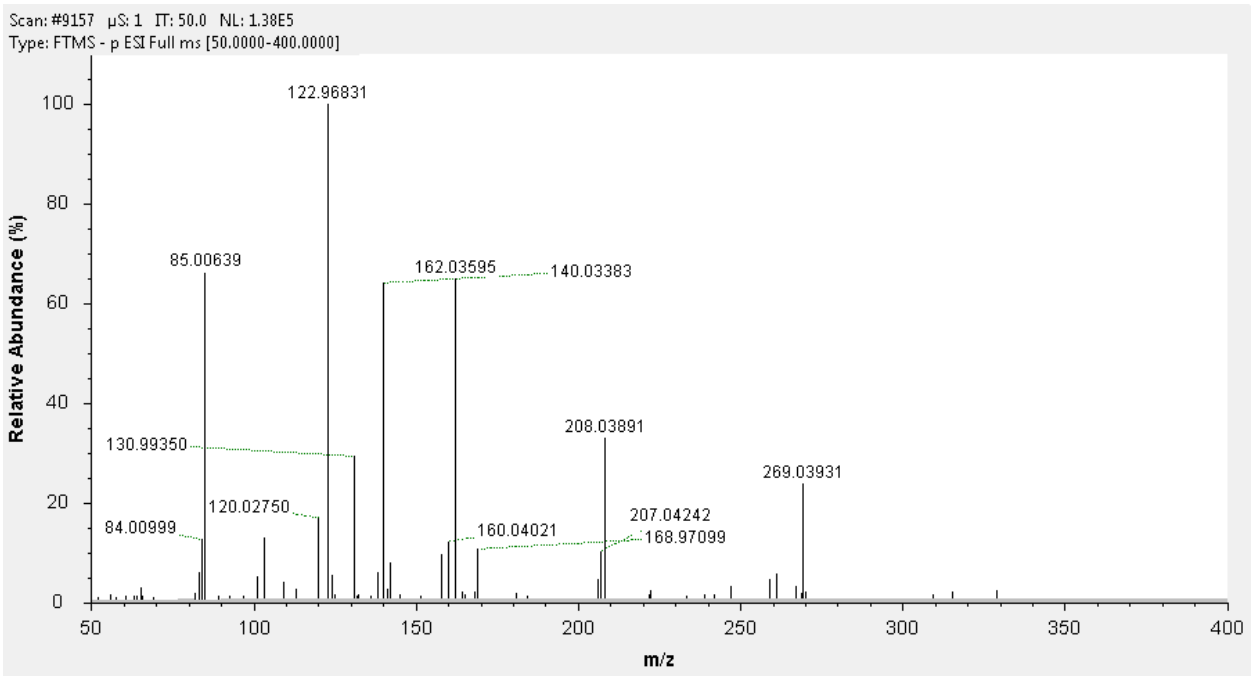


Figure S26. ^{1}H-NMR of 3g in DMSO-d6

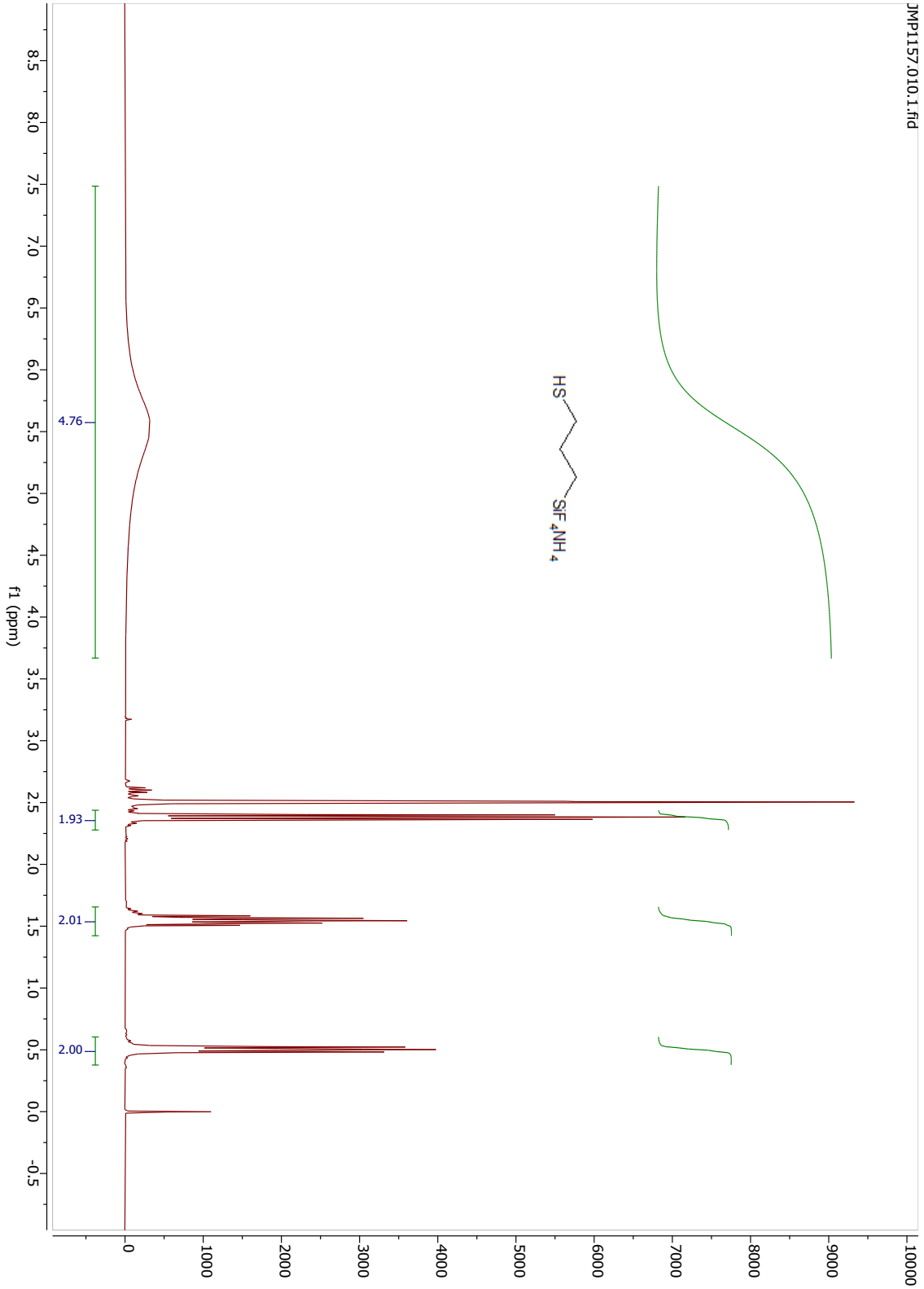


Figure S27. ^{13}C-NMR of 3g in DMSO-d6

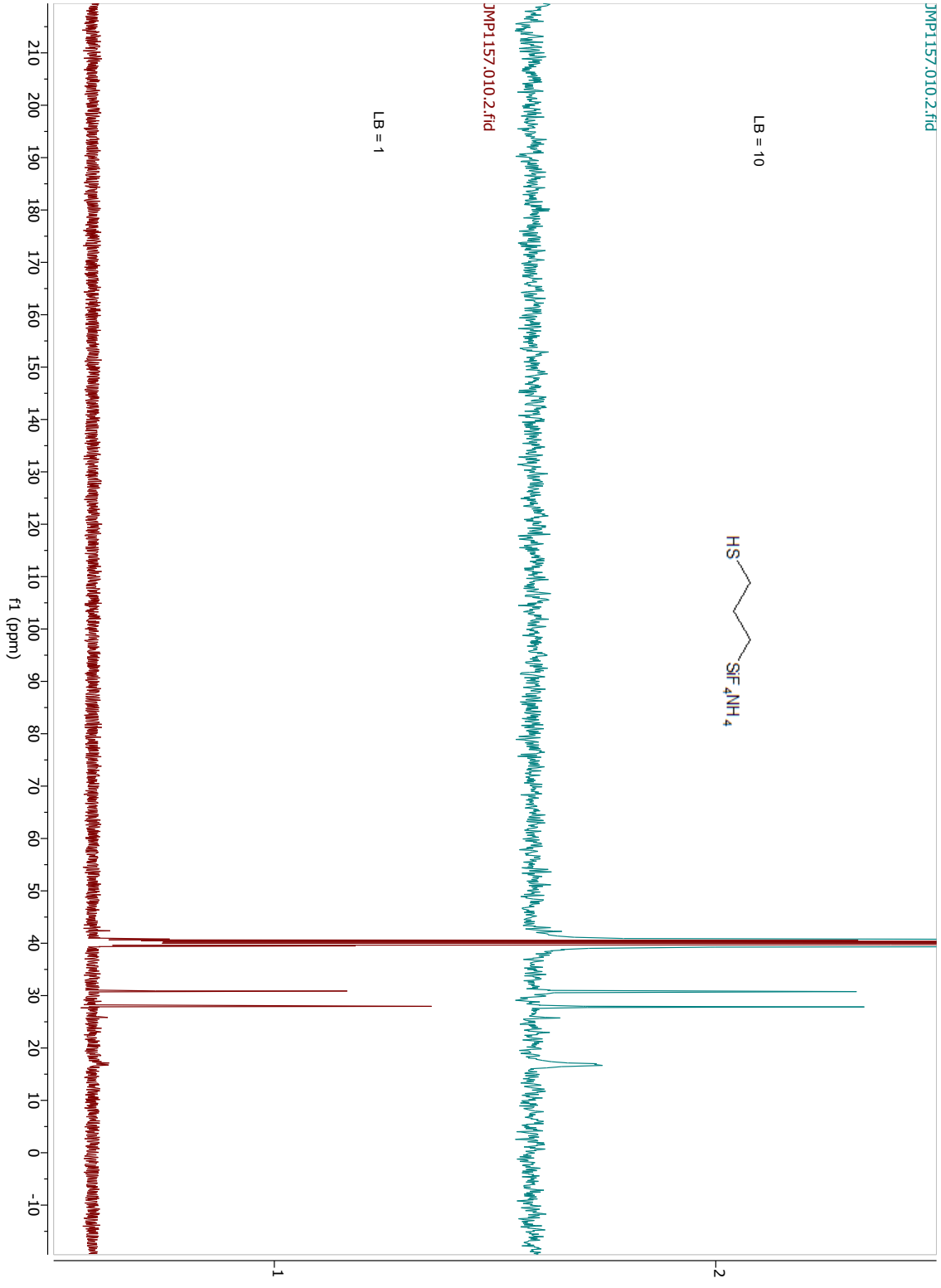


Figure S28. ^{19}F-NMR of 3g in DMSO-d6

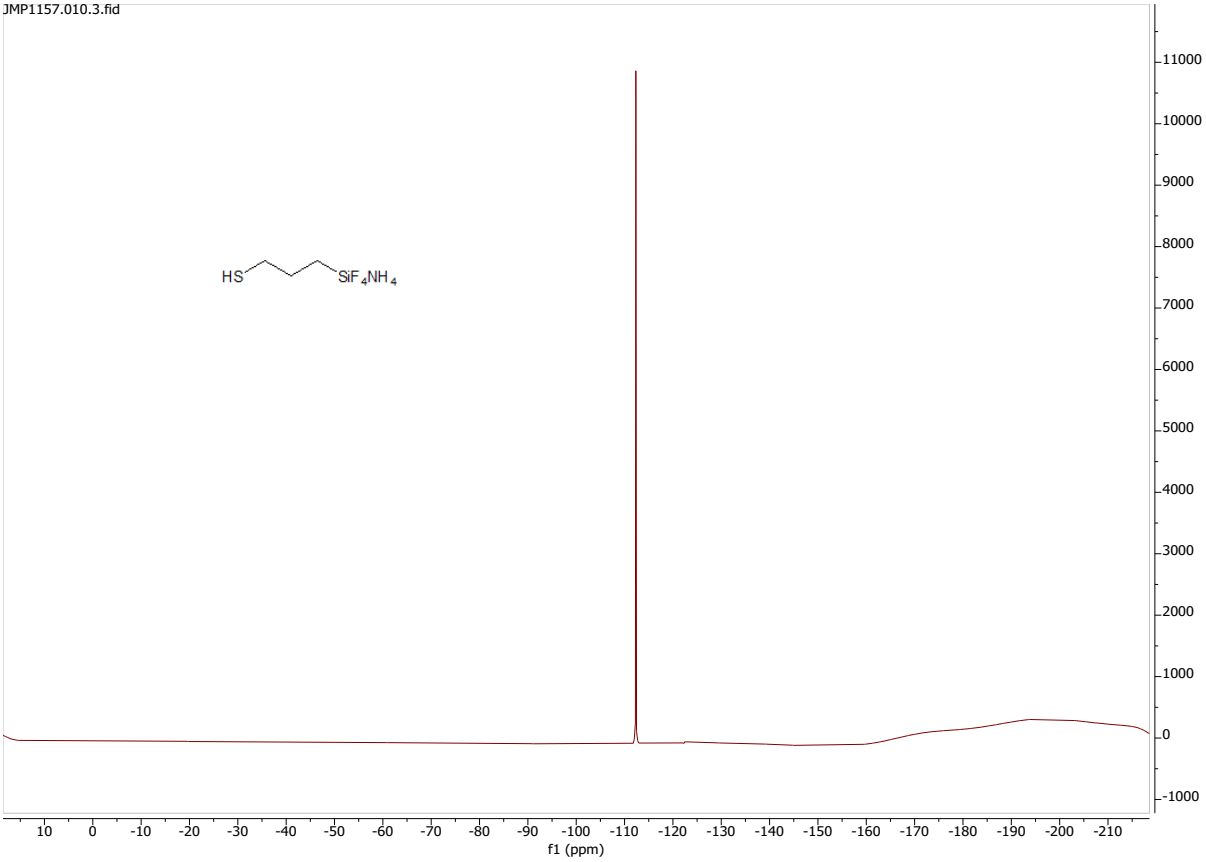


Figure S29. Mass Spectrum of 3g

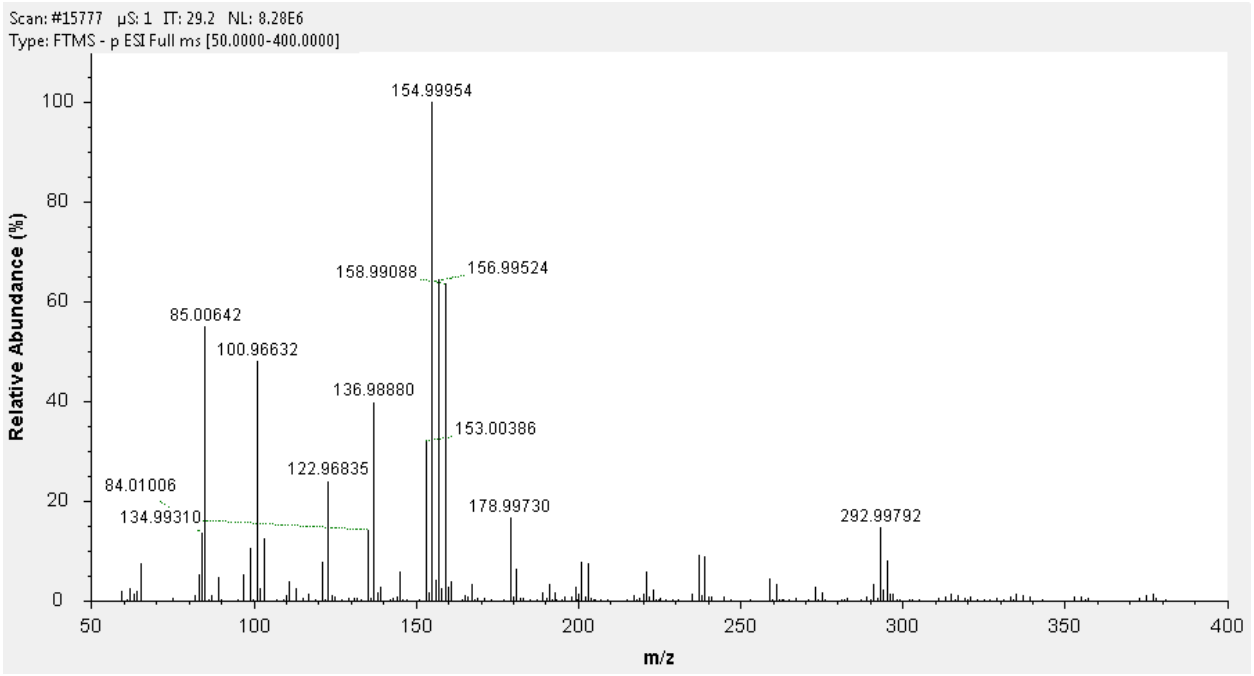


Figure S30. ^{1}H-NMR of 3h in DMSO-d6

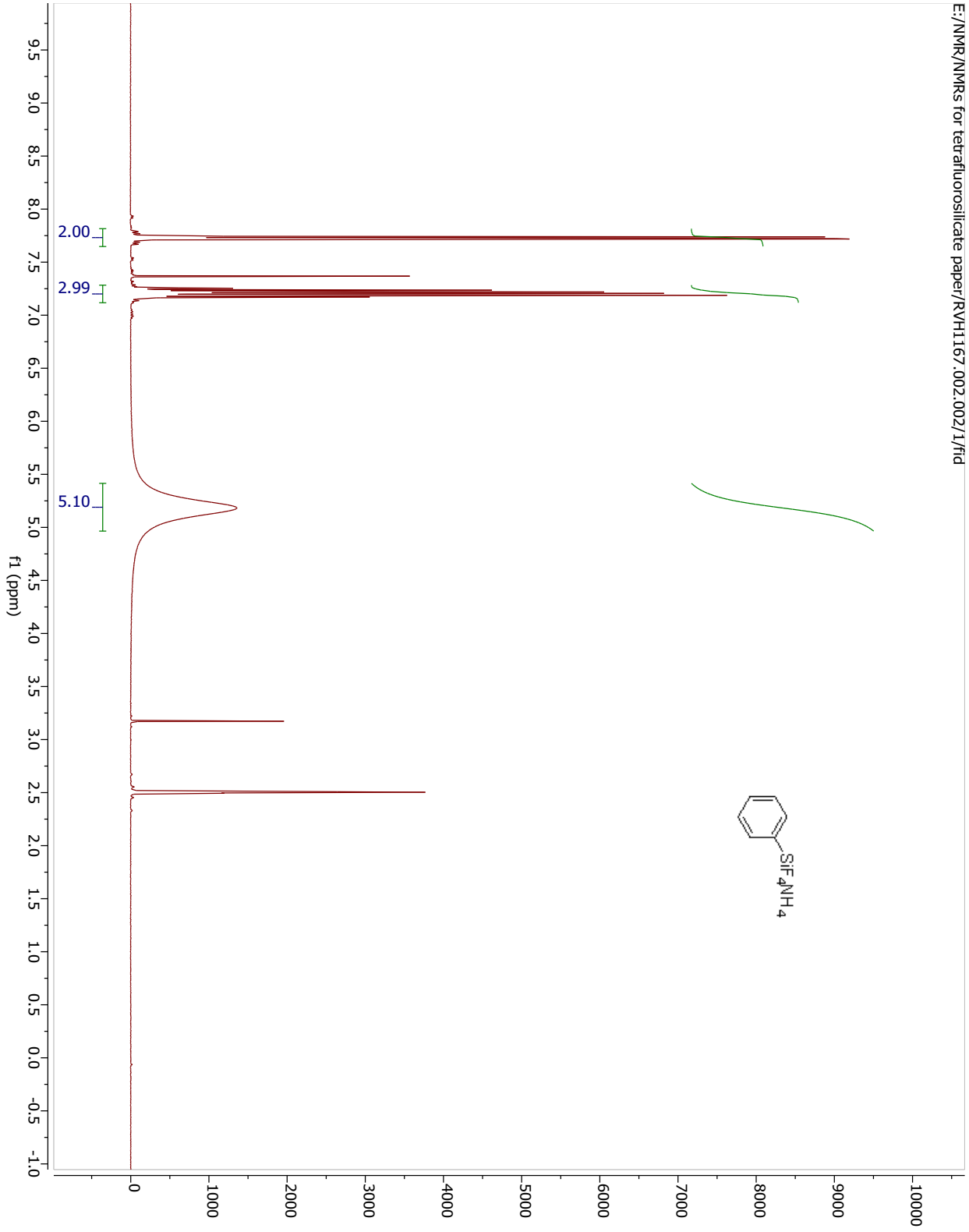


Figure S31. ^{13}C-NMR of 3h in DMSO-d6

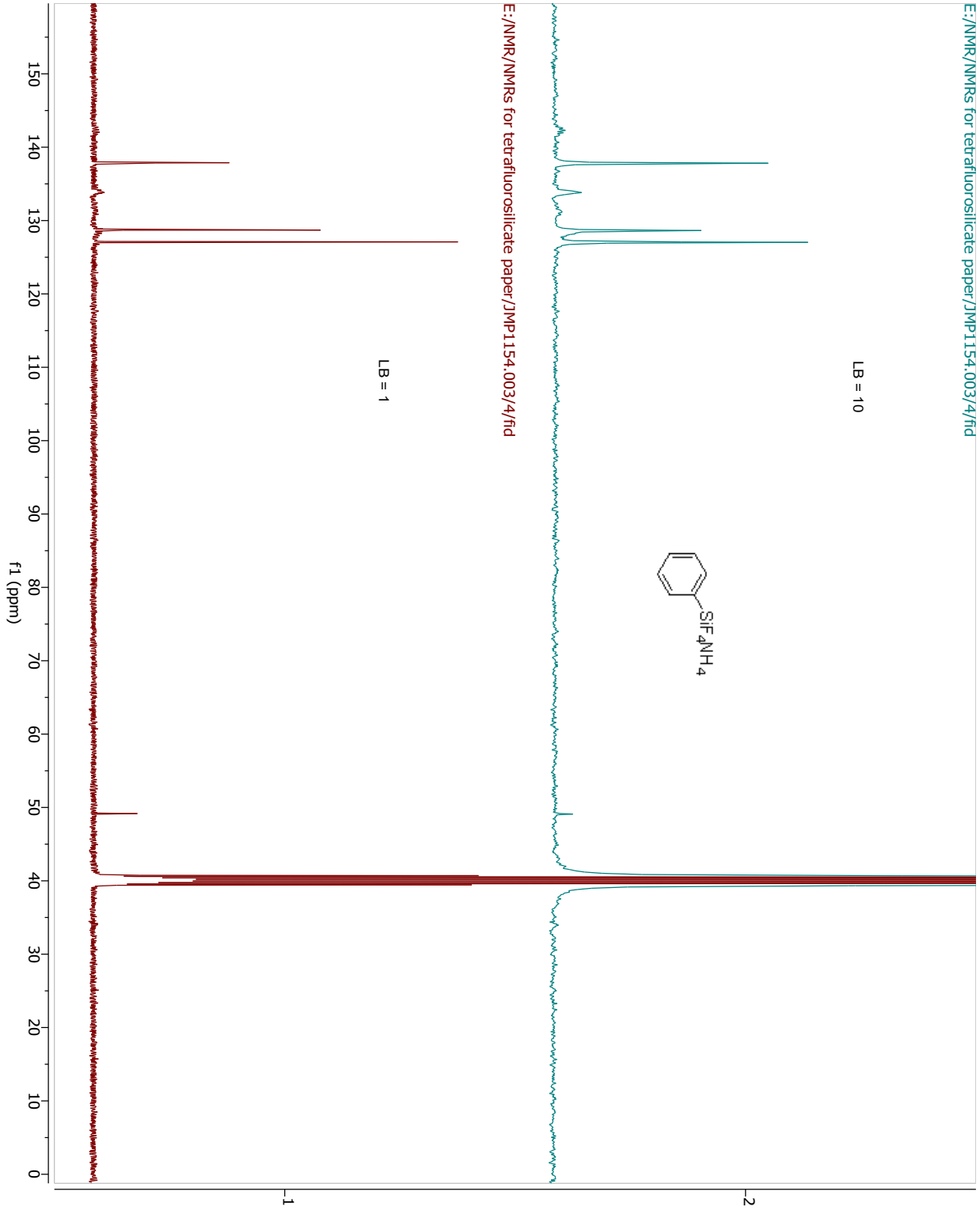


Figure S32. ^{19}F-NMR of 3h in DMSO-d6

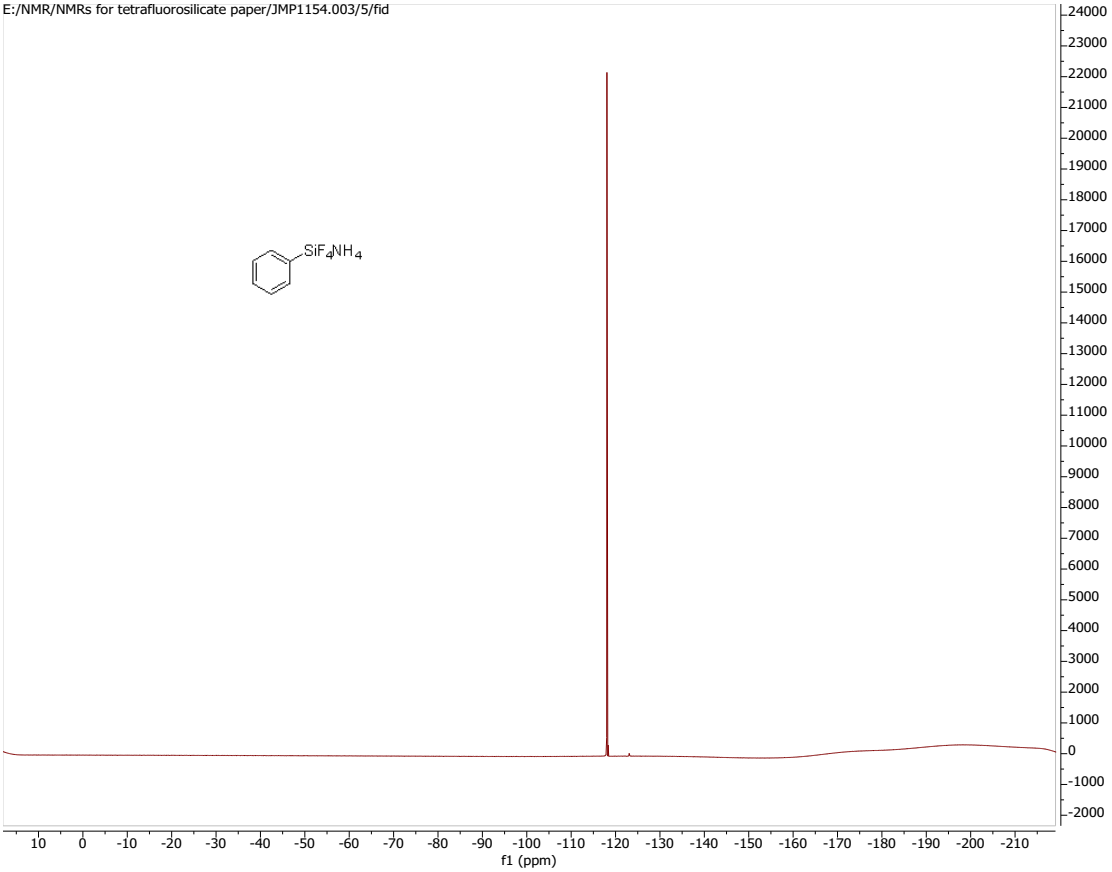


Figure S33. Mass Spectrum of 3h

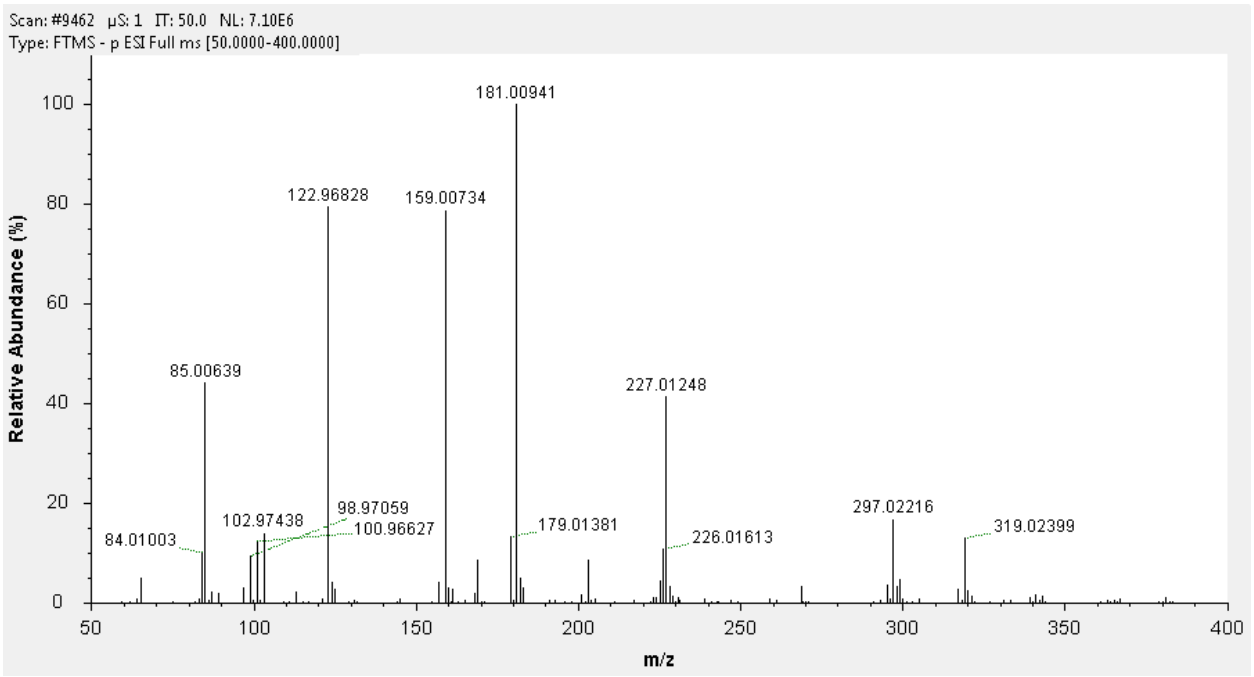


Figure S34. ^{1}H-NMR of 3i in DMSO-d6

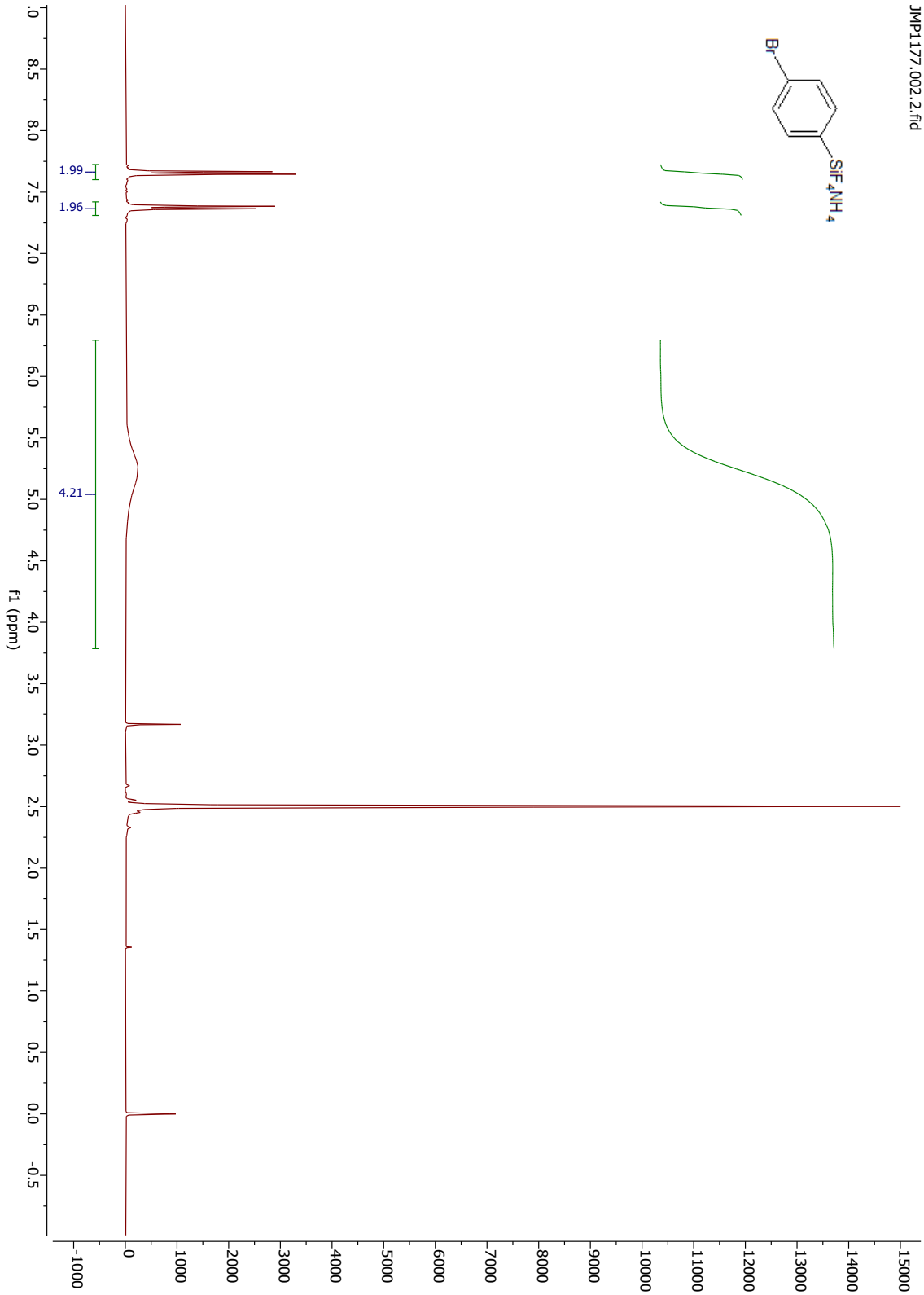


Figure S35. ^{13}C-NMR of 3i in DMSO-d6

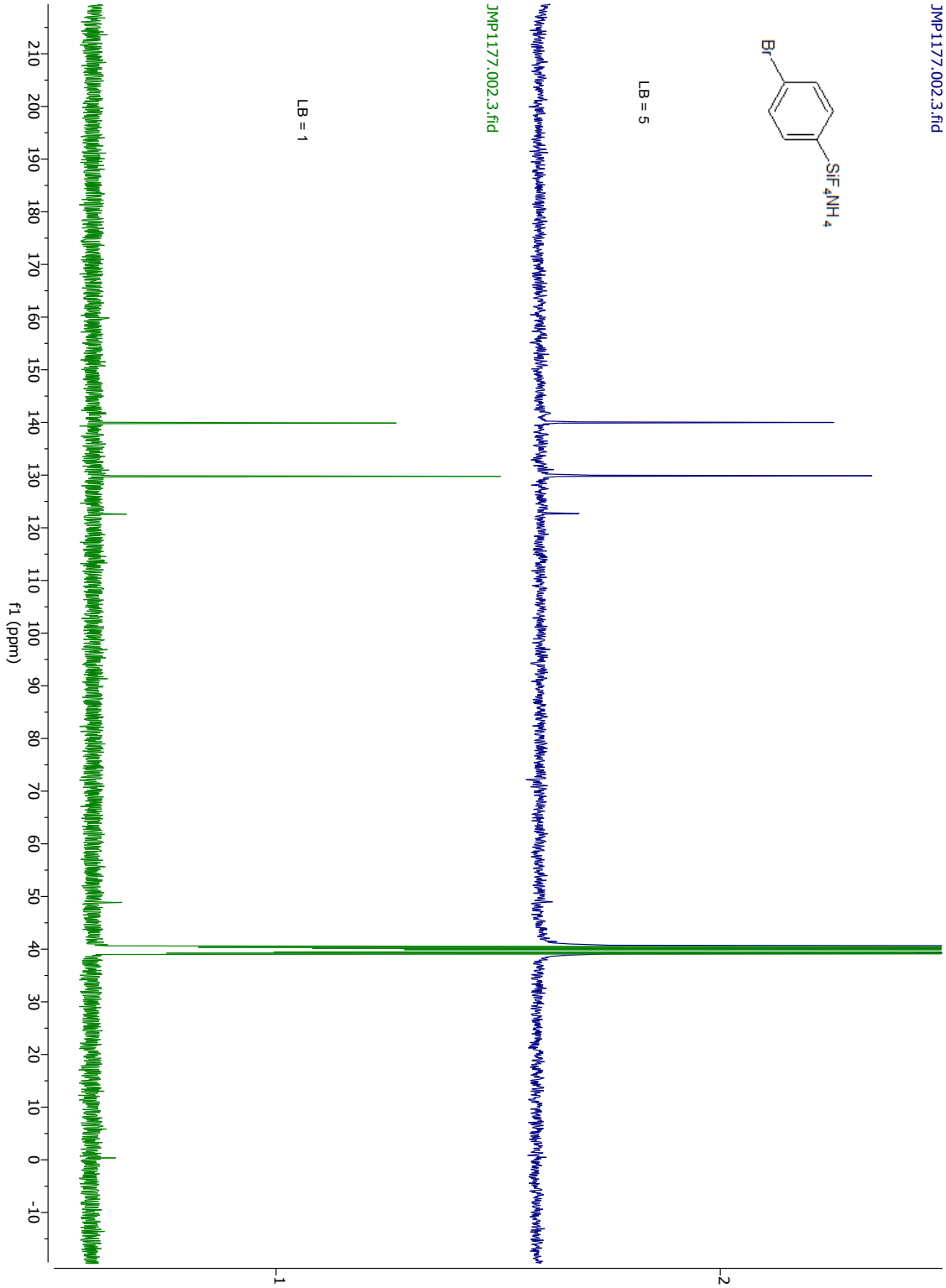


Figure S36. ^{19}F-NMR of 3i in DMSO-d6

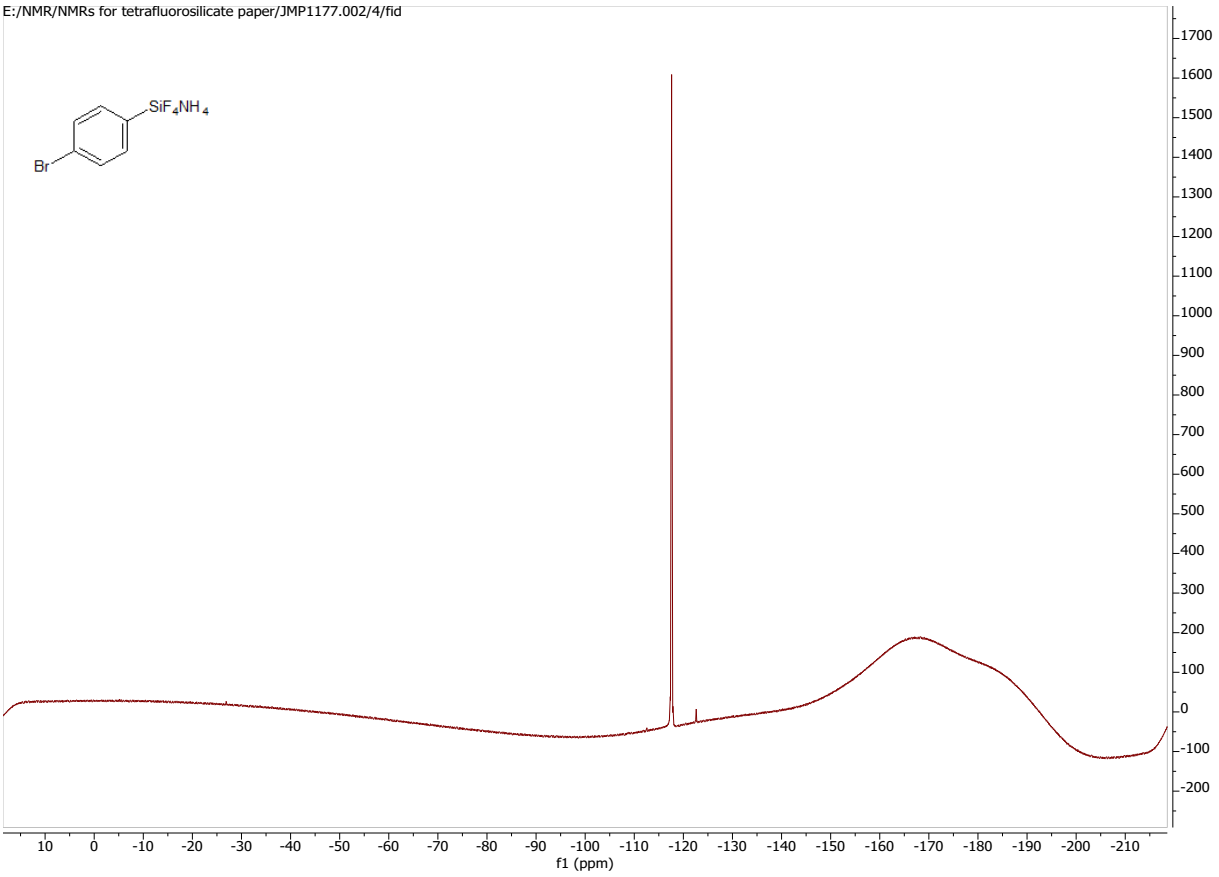


Figure S37. Mass Spectrum of 3i

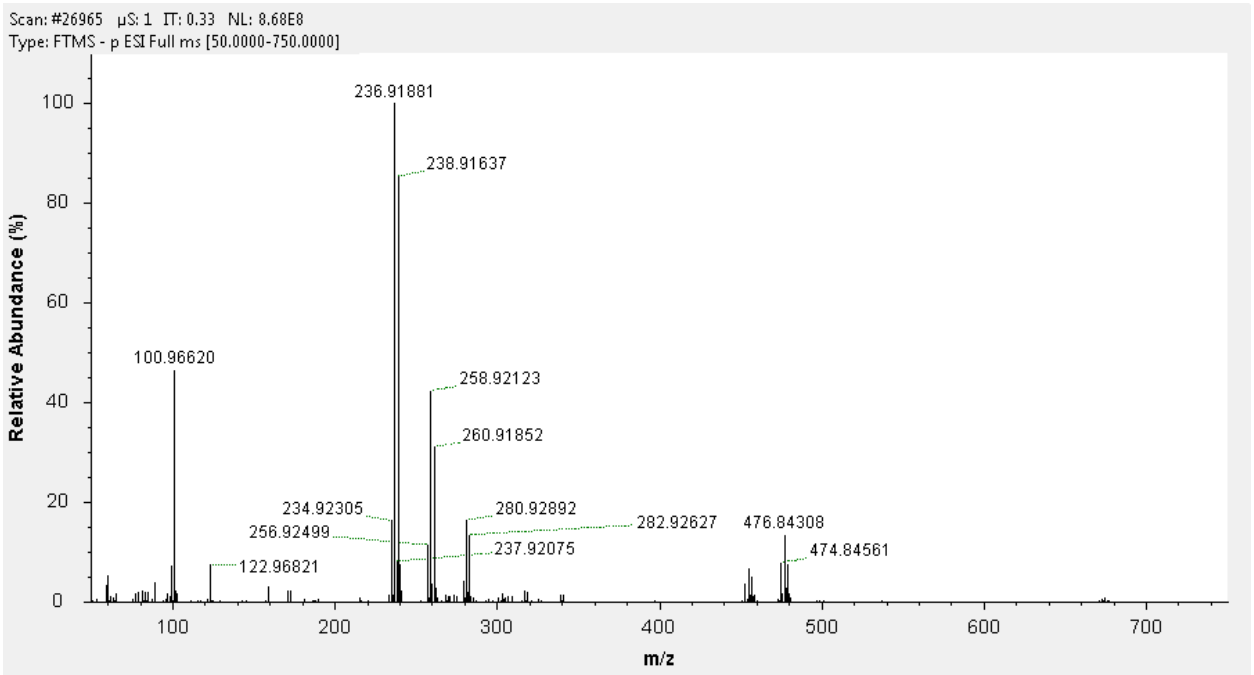


Figure S38. ^{1}H-NMR of 3j in DMSO-d6

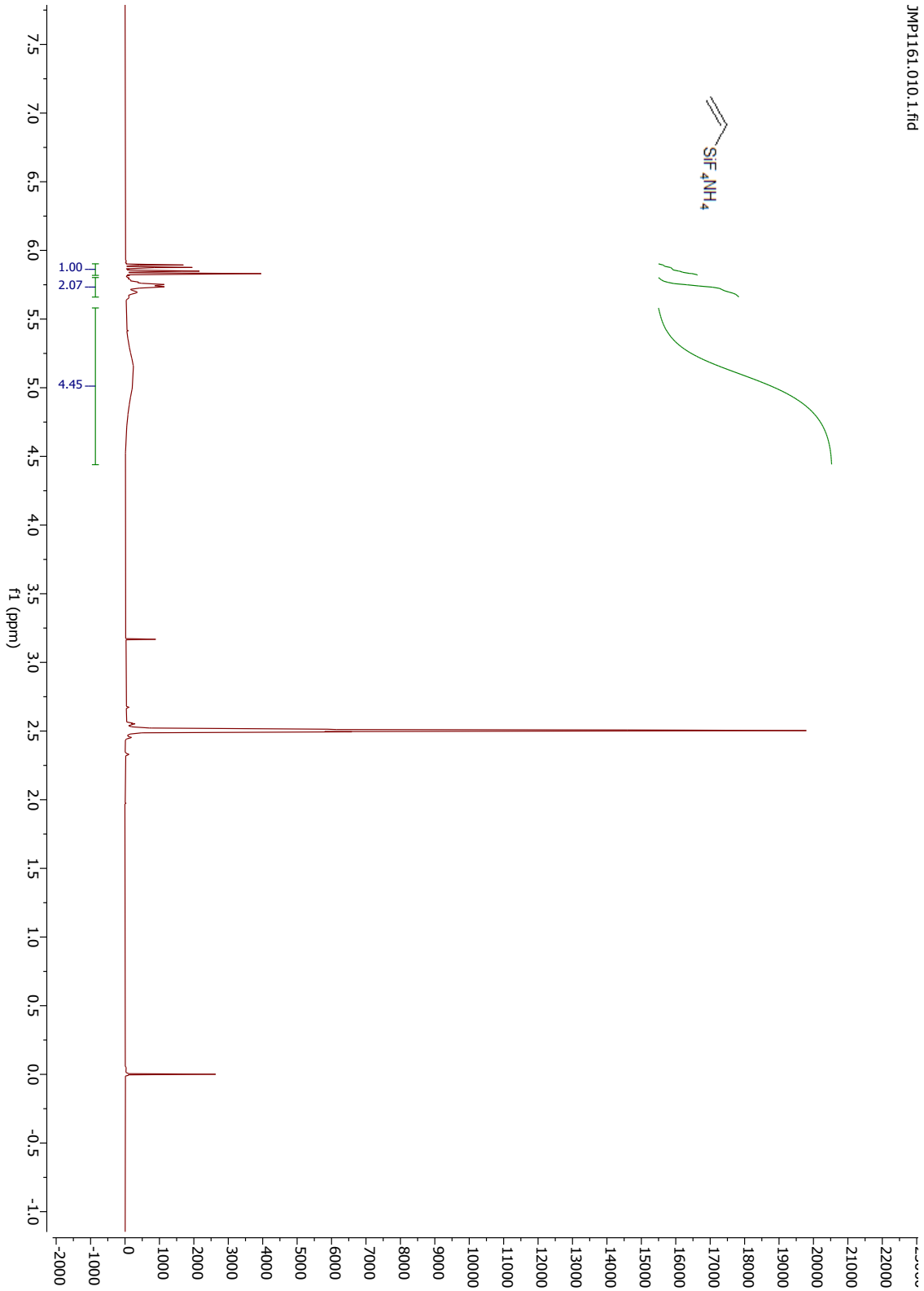


Figure S39. ^{13}C-NMR of 3j in DMSO-d6

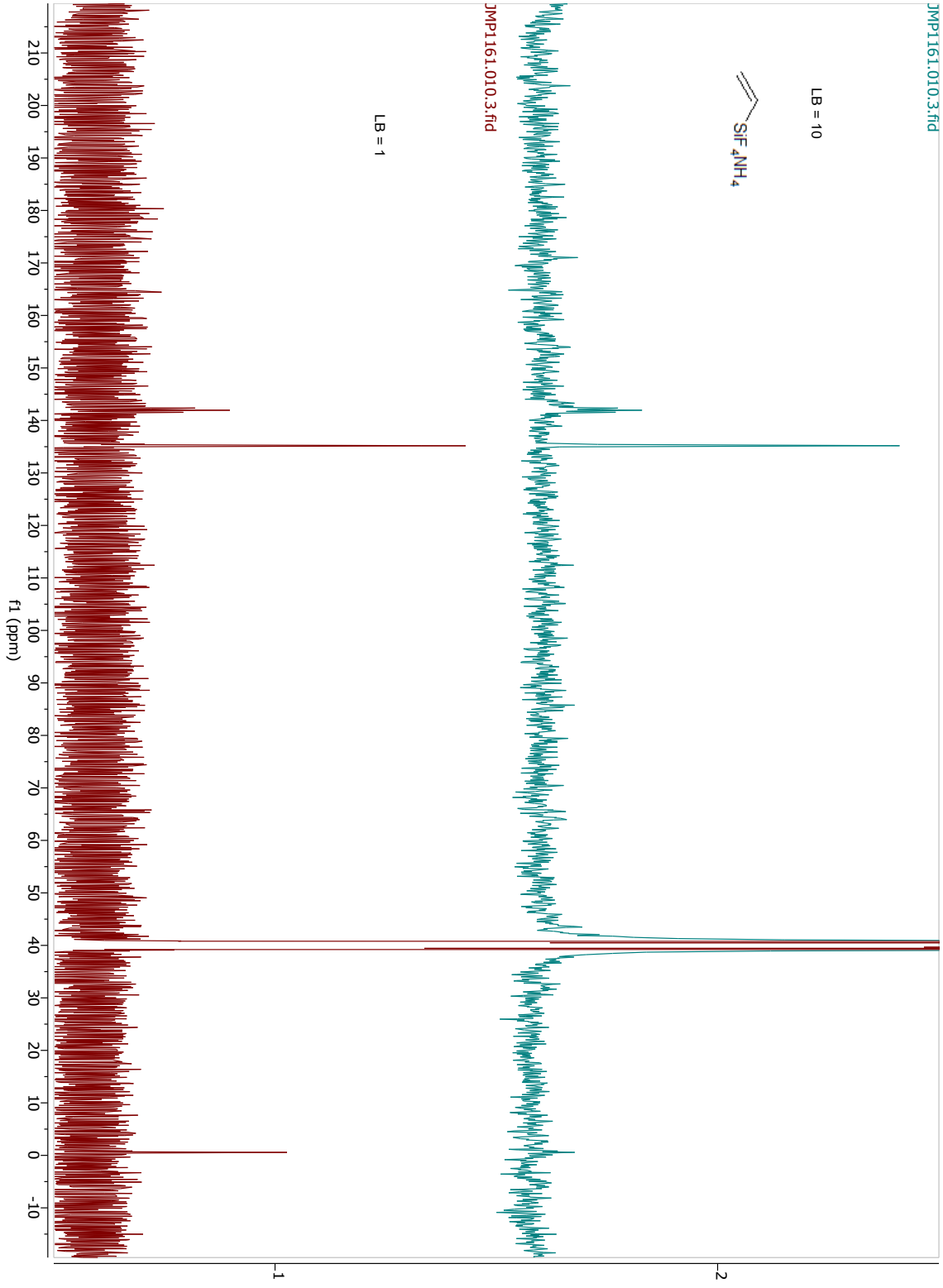


Figure S40. ^{19}F-NMR of 3j in DMSO-d6

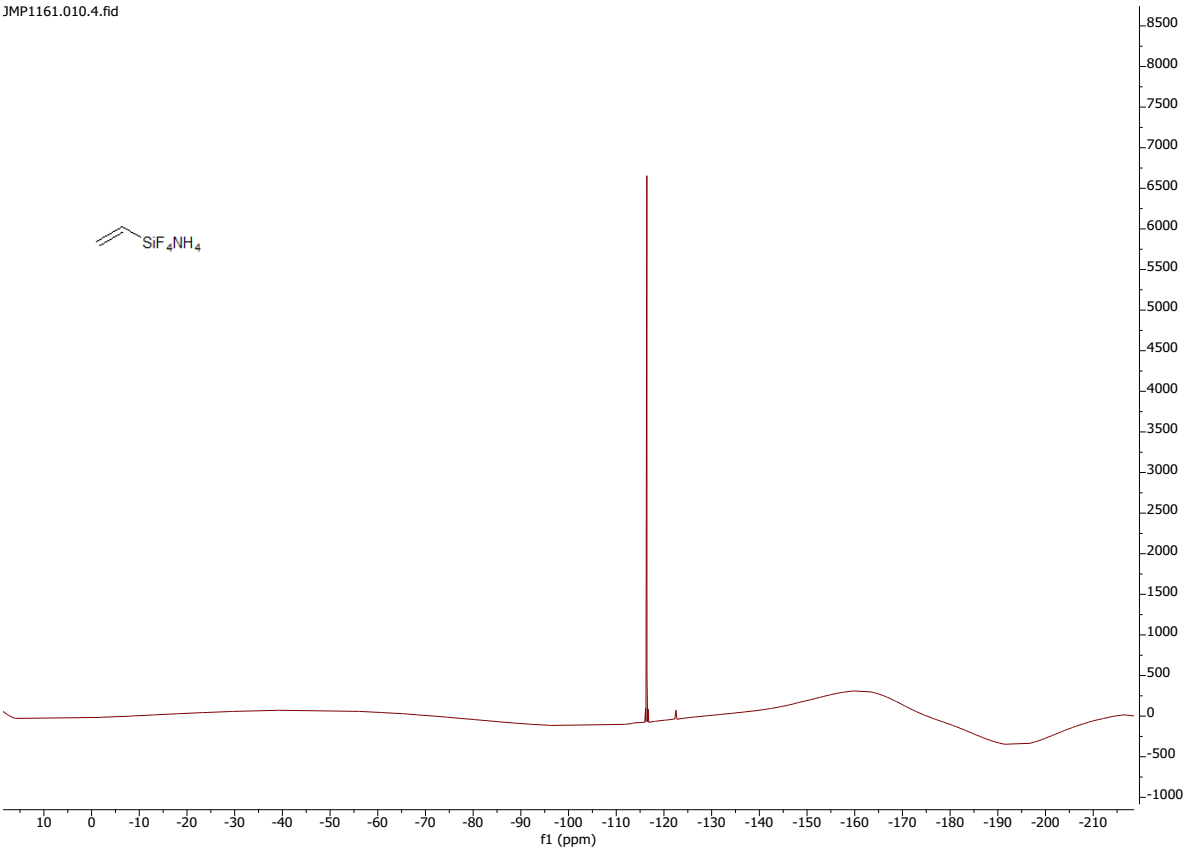


Figure S41. Mass Spectrum of 3j

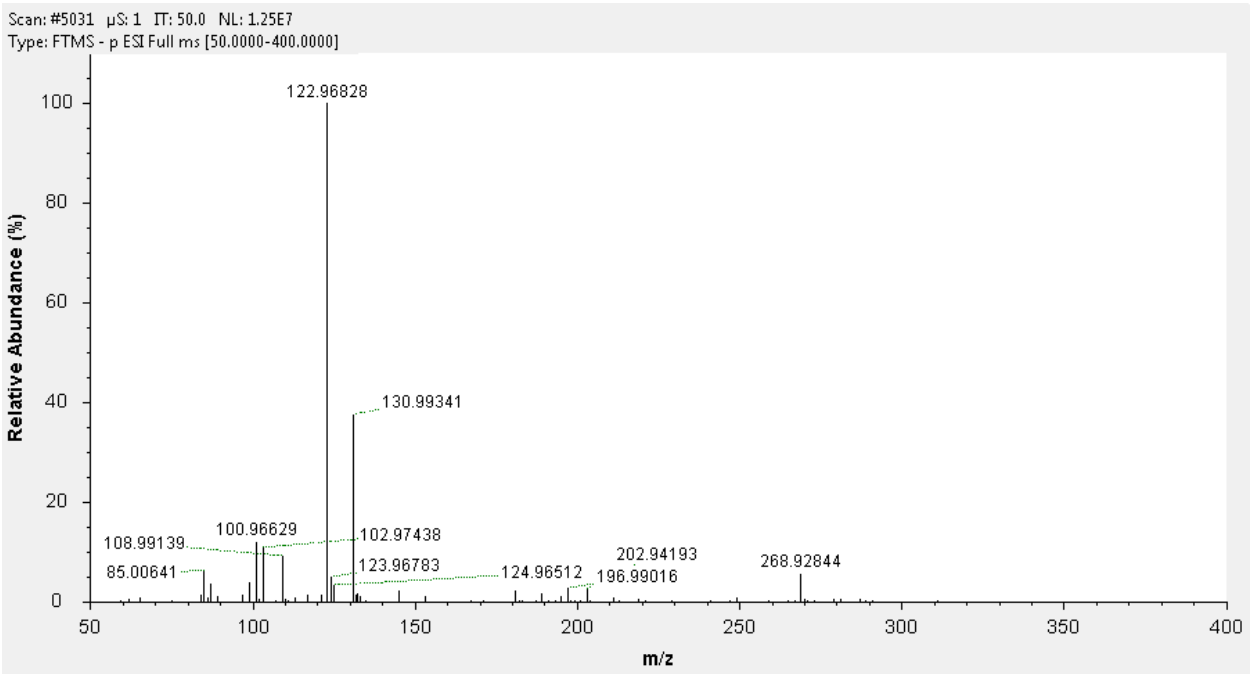


Figure S42. ^{1}H-NMR of 3k in DMSO-d6

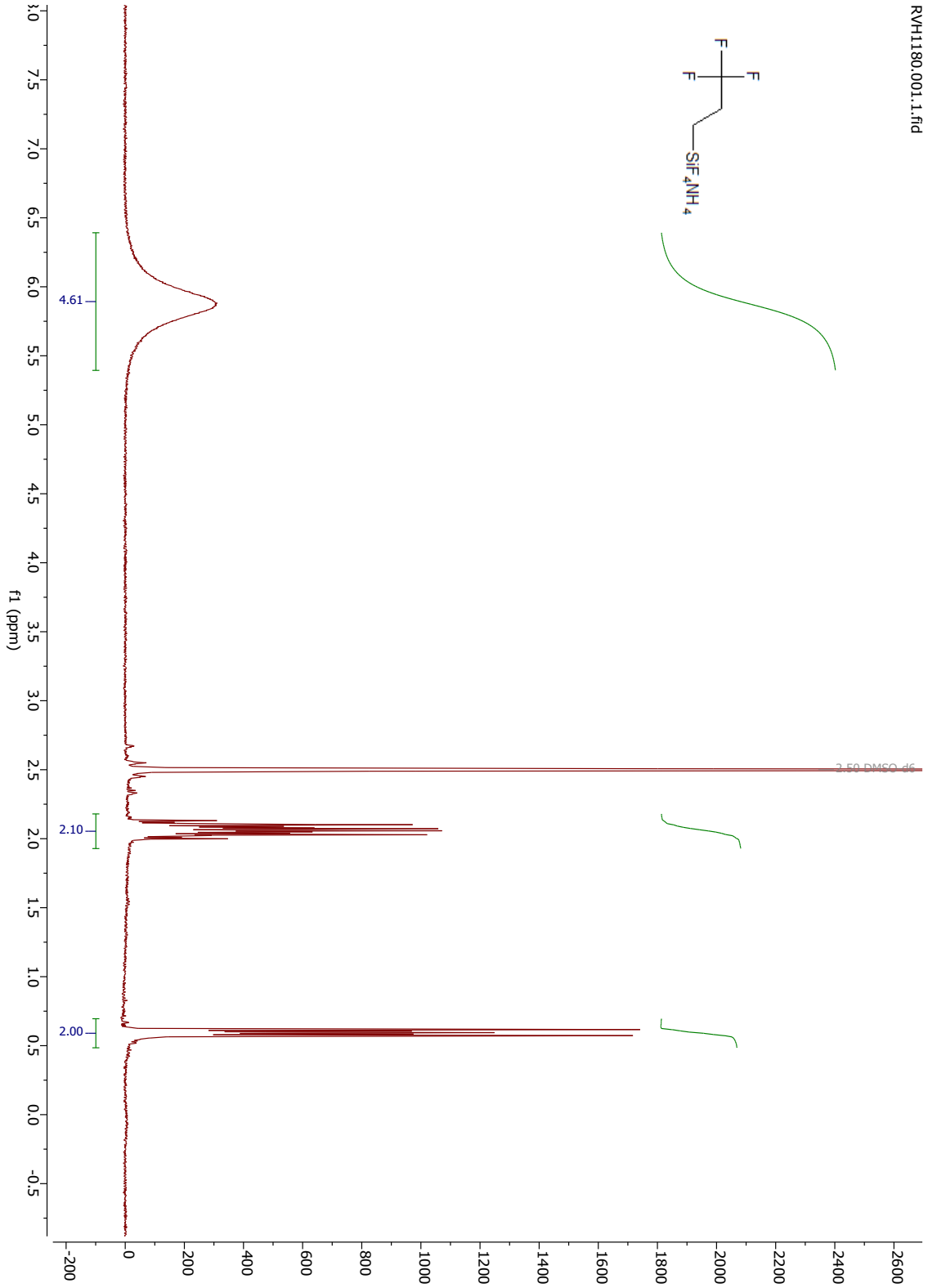


Figure S43. ^{13}C-NMR of 3k in DMSO-d6

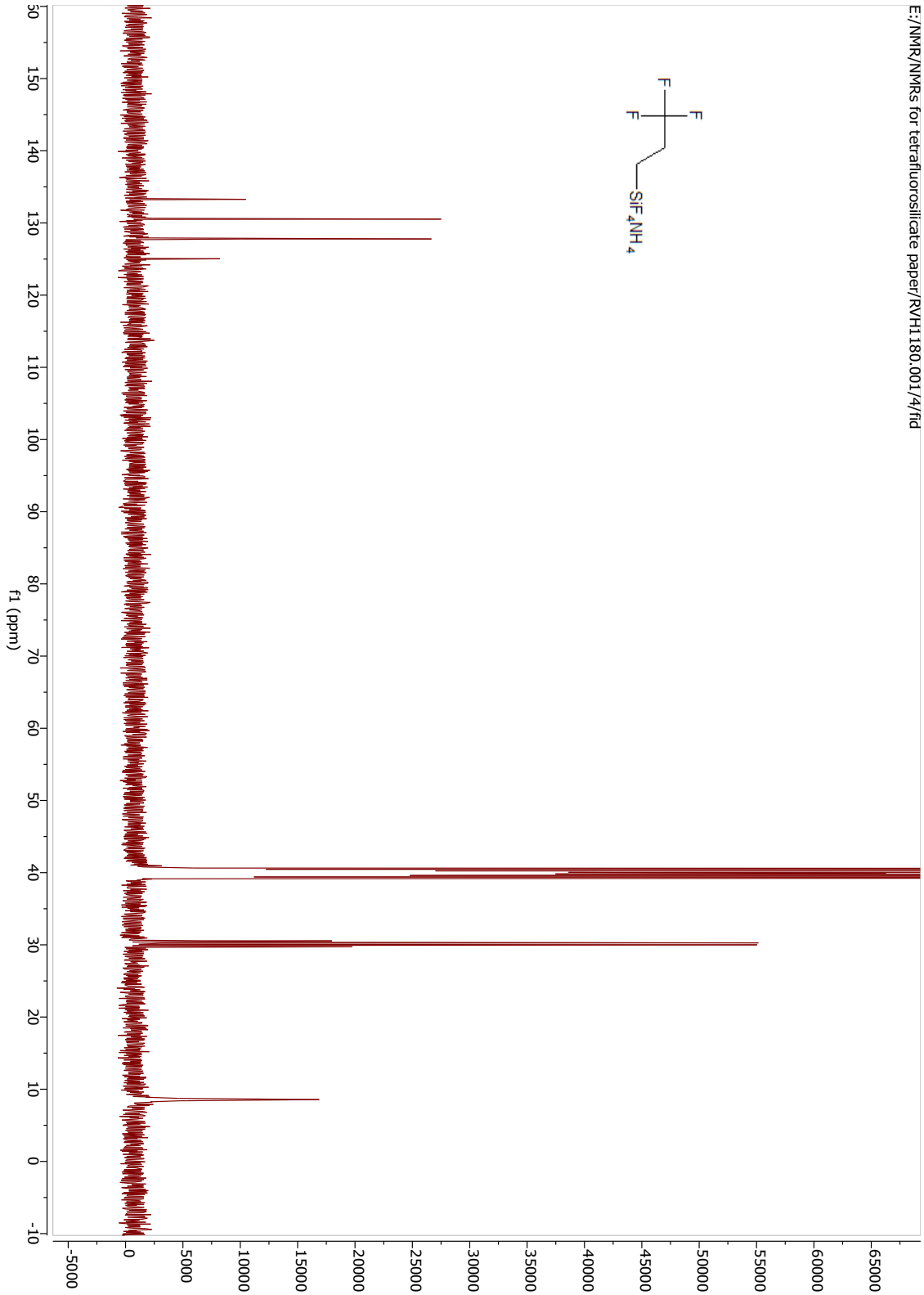


Figure S44. ^{19}F-NMR of 3k in DMSO-d6

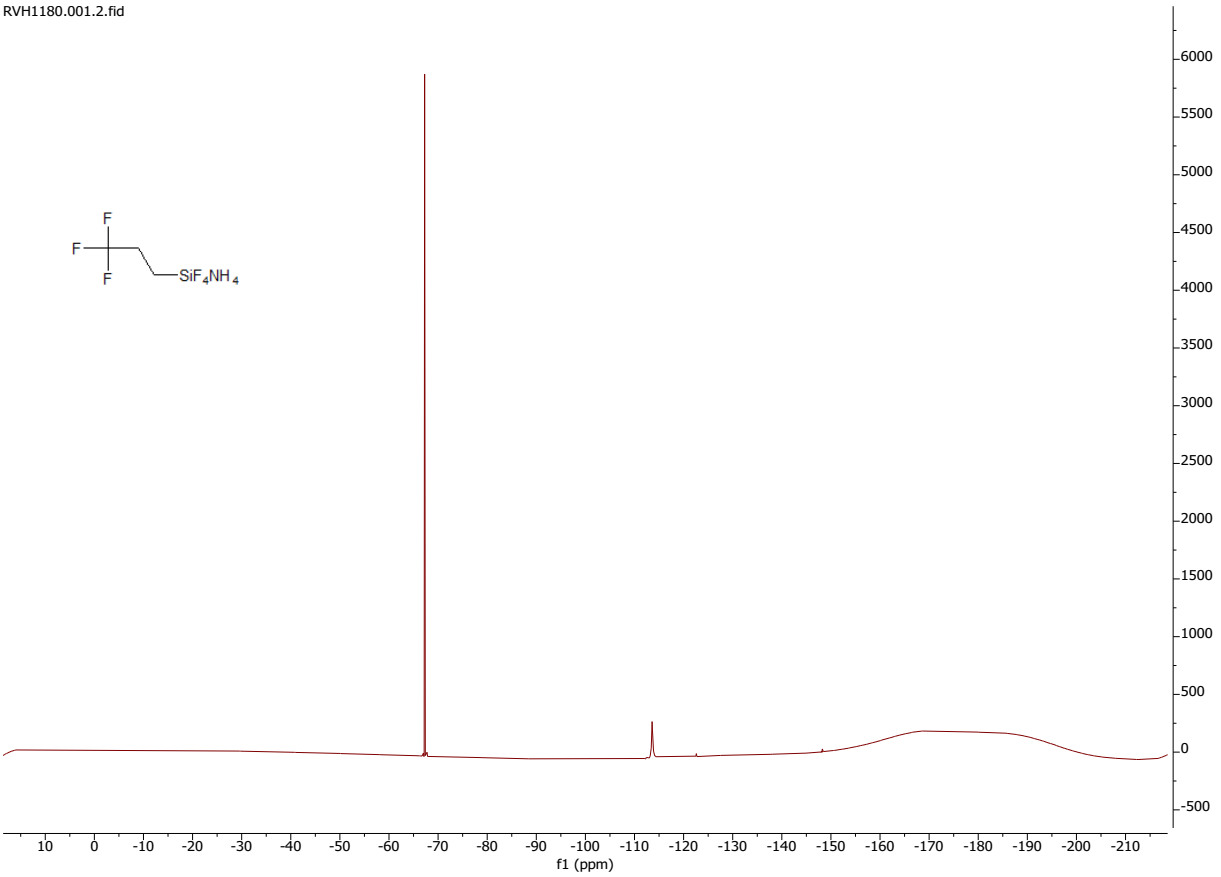


Figure S45. Mass Spectrum of 3k

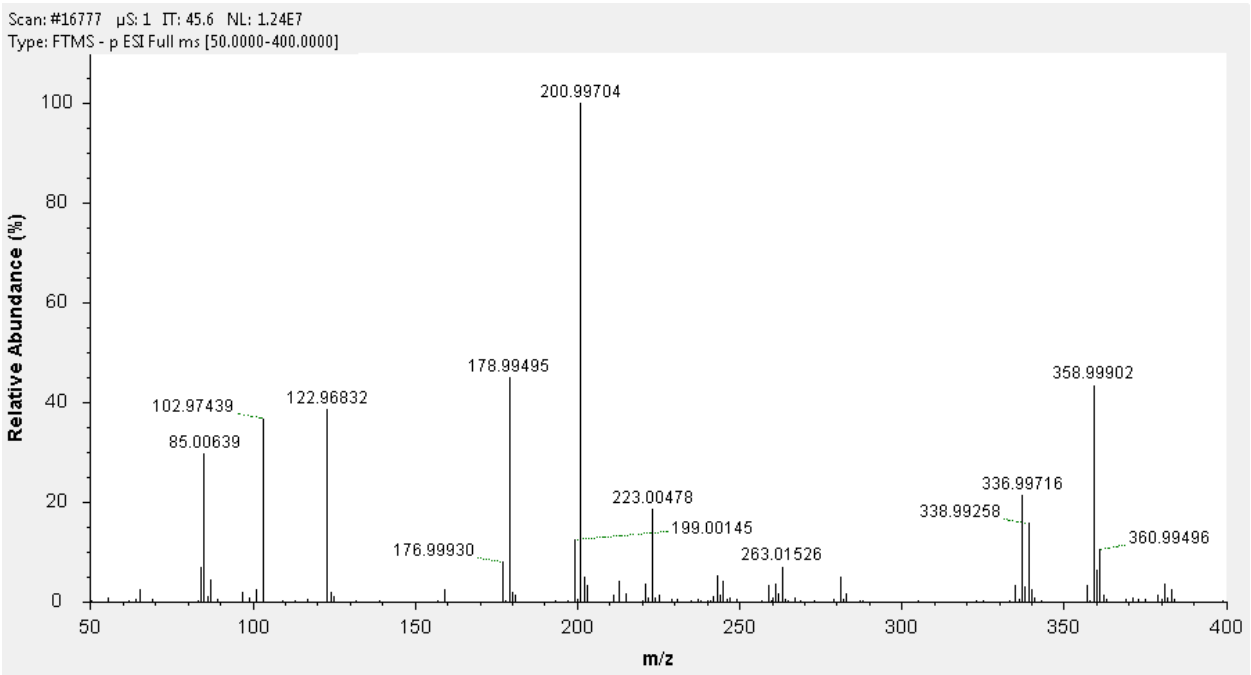


Figure S46. ^{1}H-NMR of 3l in DMSO-d6

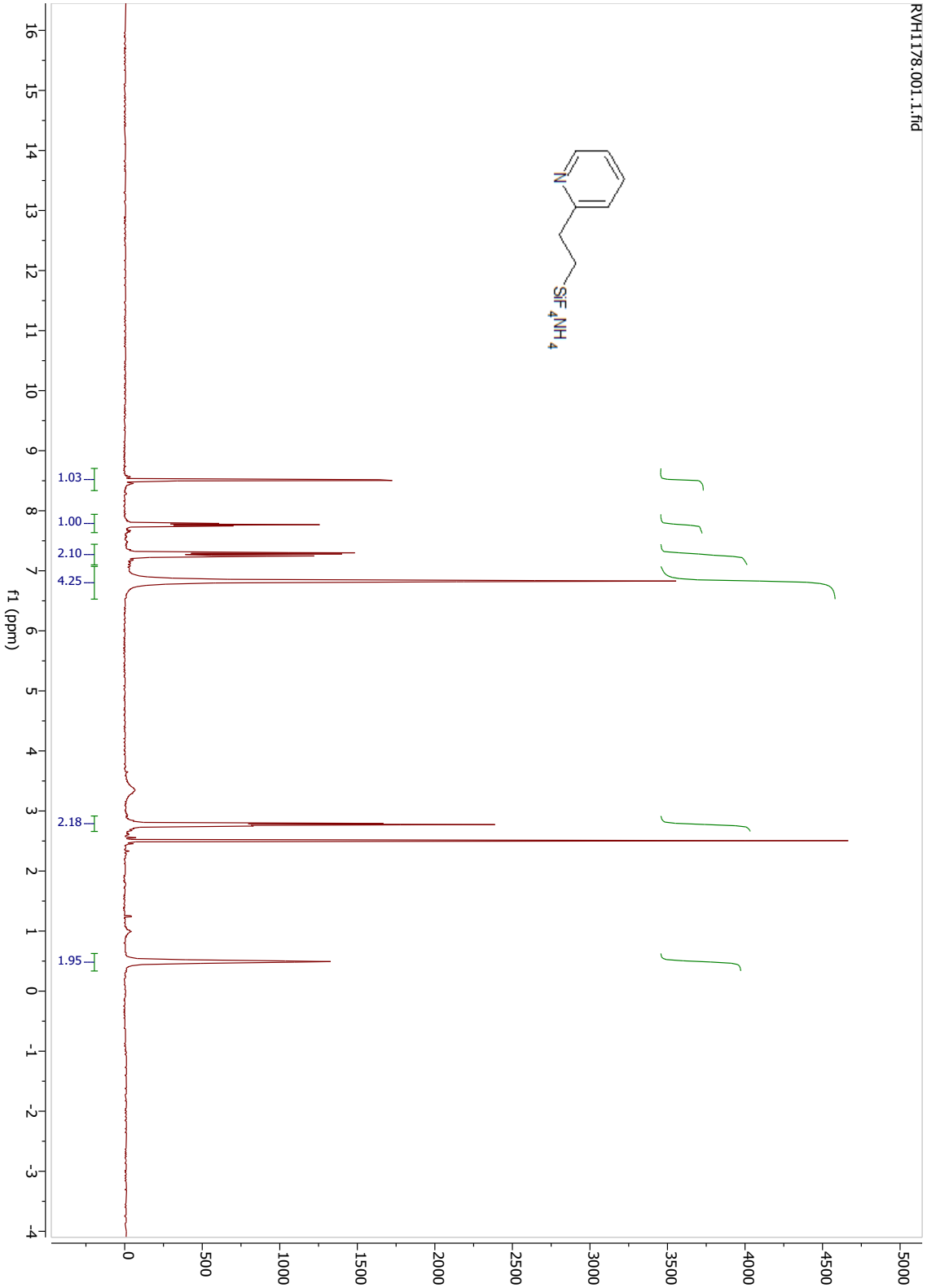


Figure S47. ^{13}C-NMR of 3l in DMSO-d6

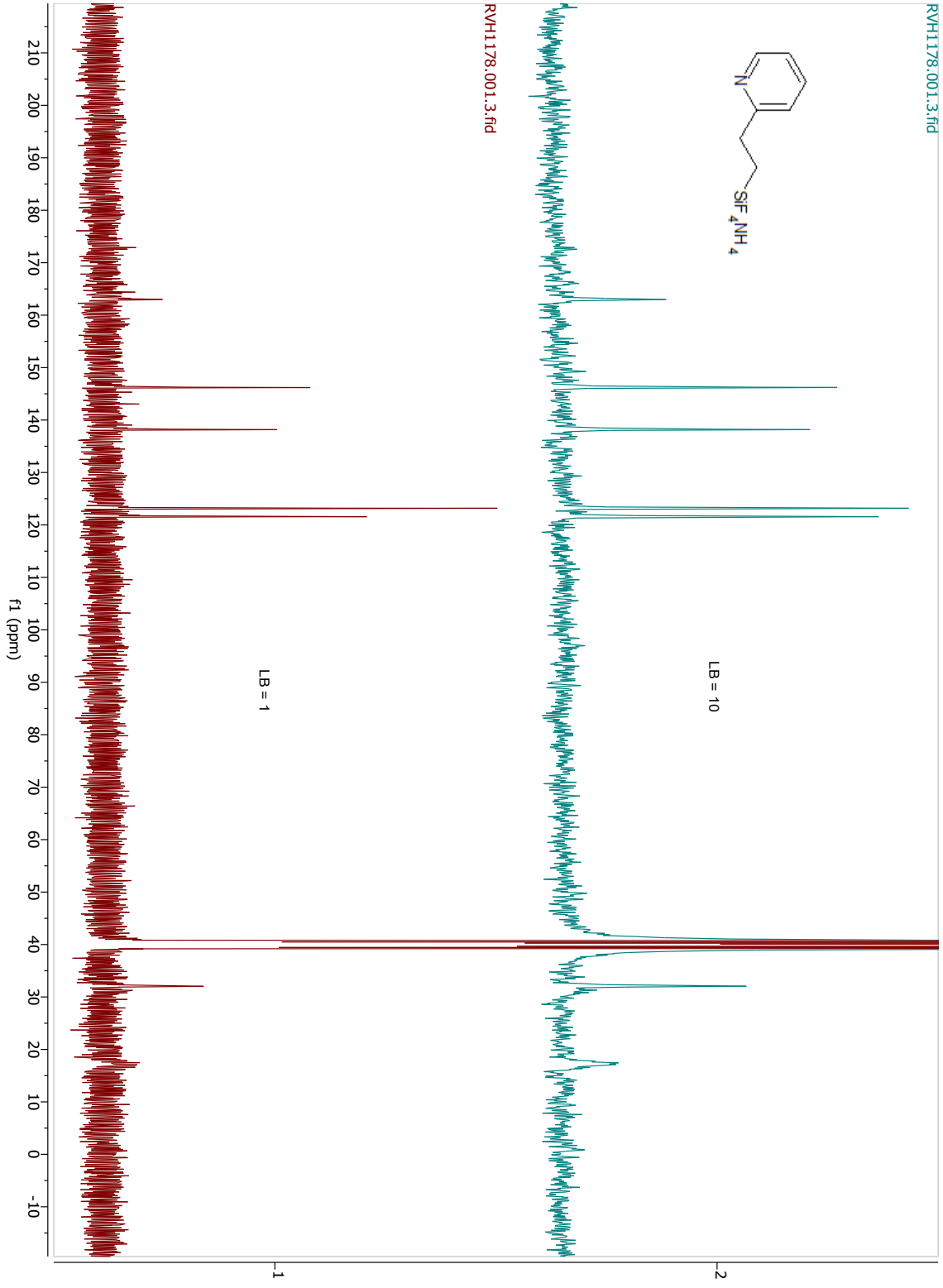


Figure S48. ^{19}F-NMR of 3l in DMSO-d6

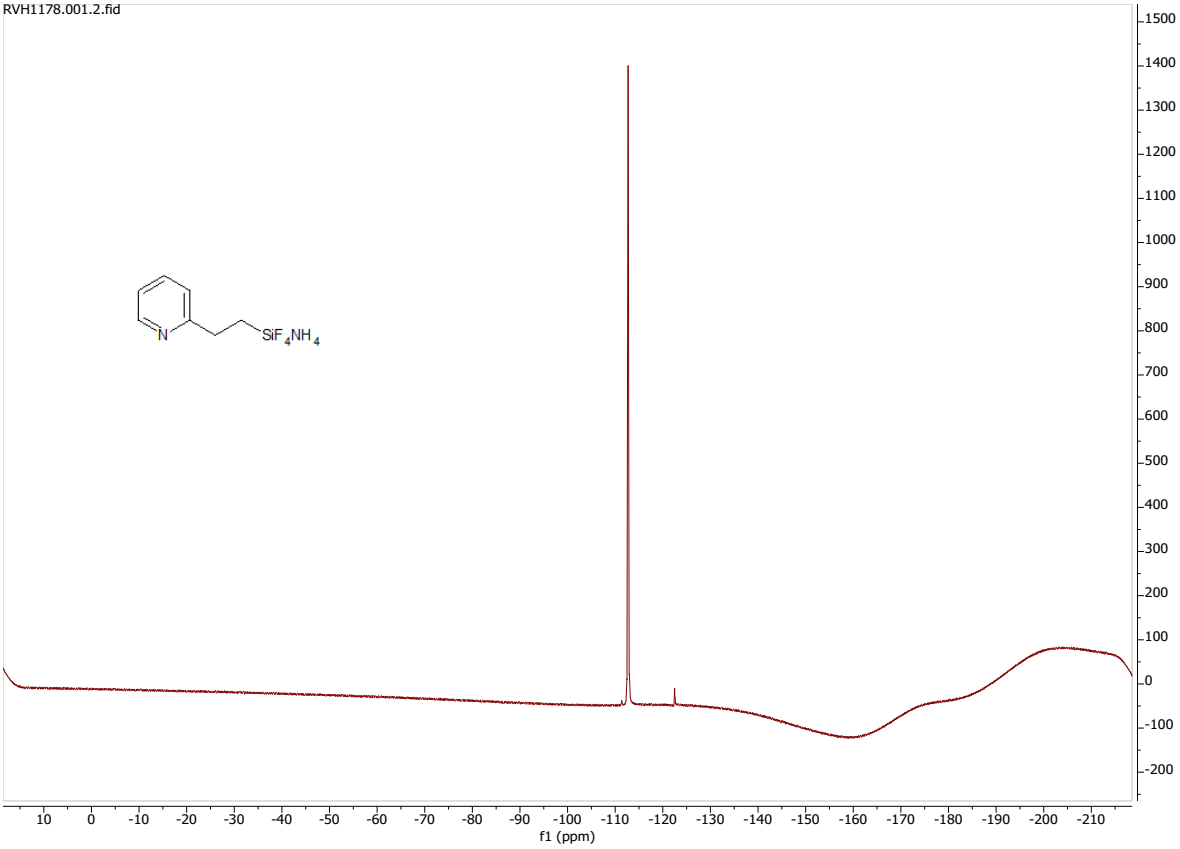


Figure S49. Mass Spectrum of 3l

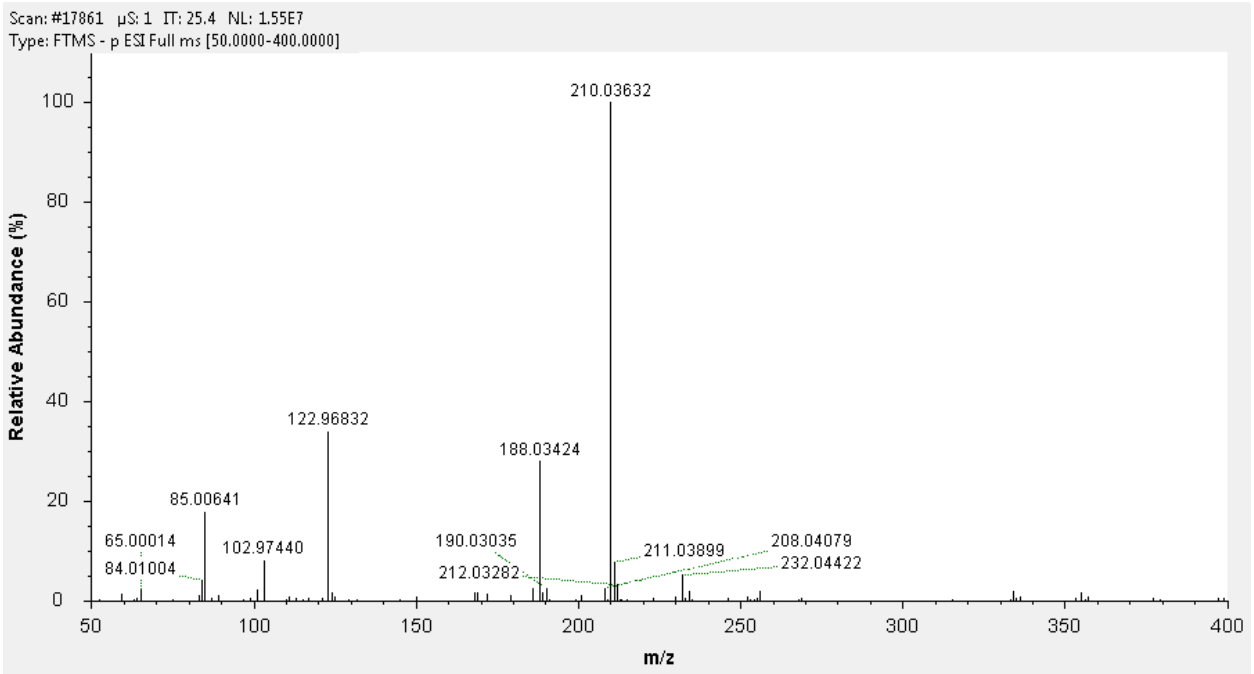


Figure S50. ^{1}H-NMR of 3m in DMSO-d6

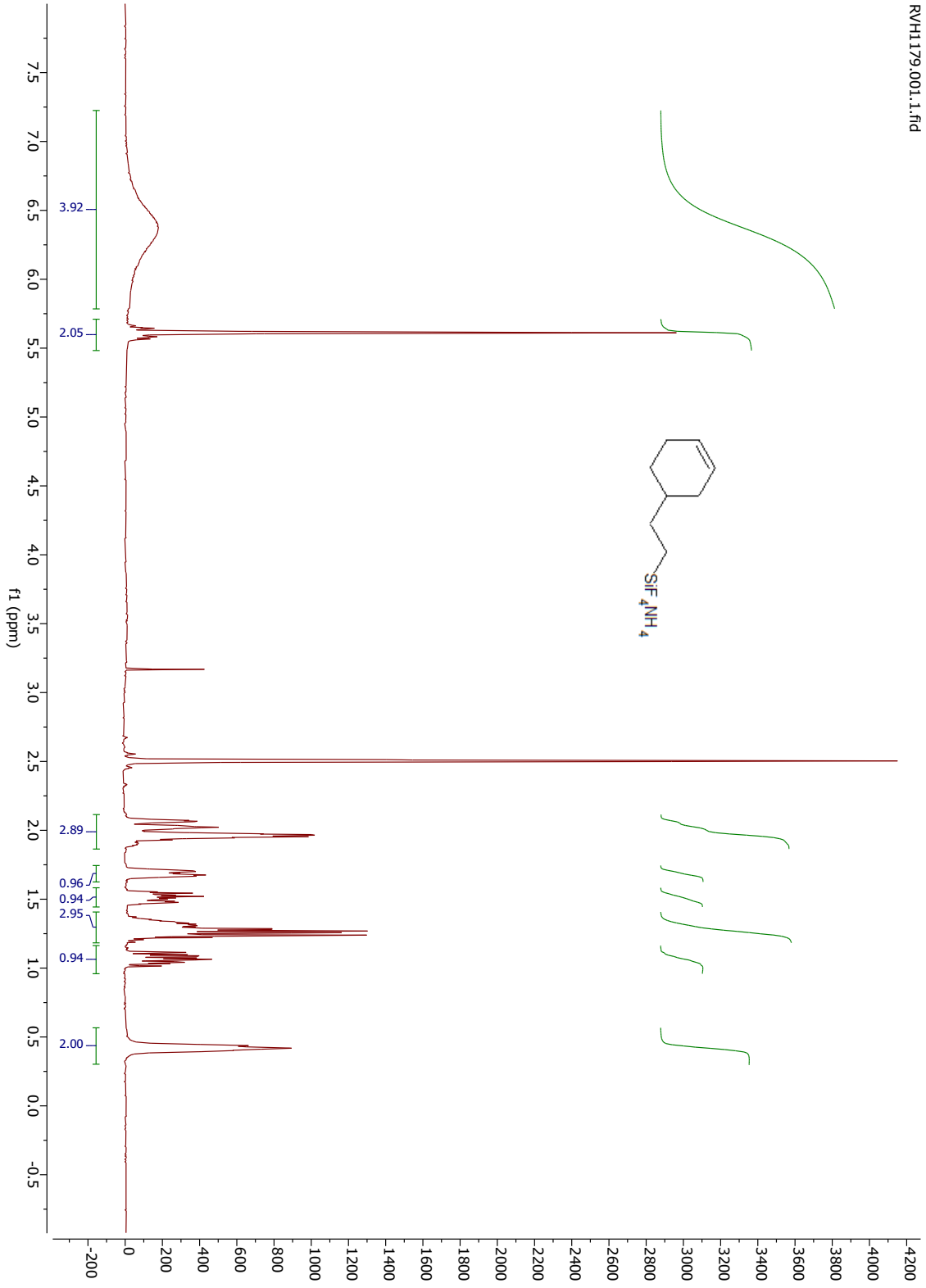


Figure S51. ^{13}C-NMR of 3m in DMSO-d6

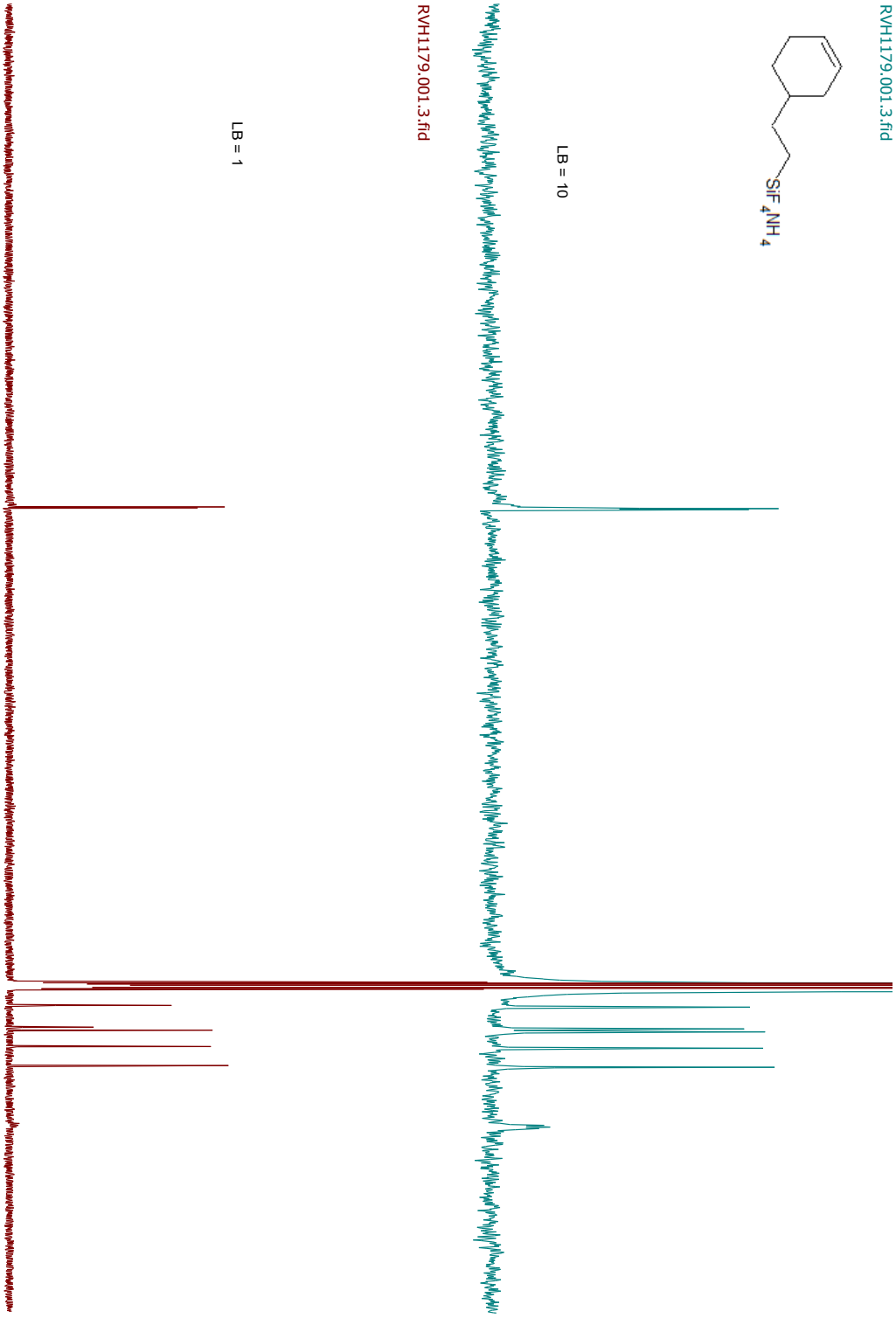


Figure S52. ^{19}F-NMR of 3m in DMSO-d6

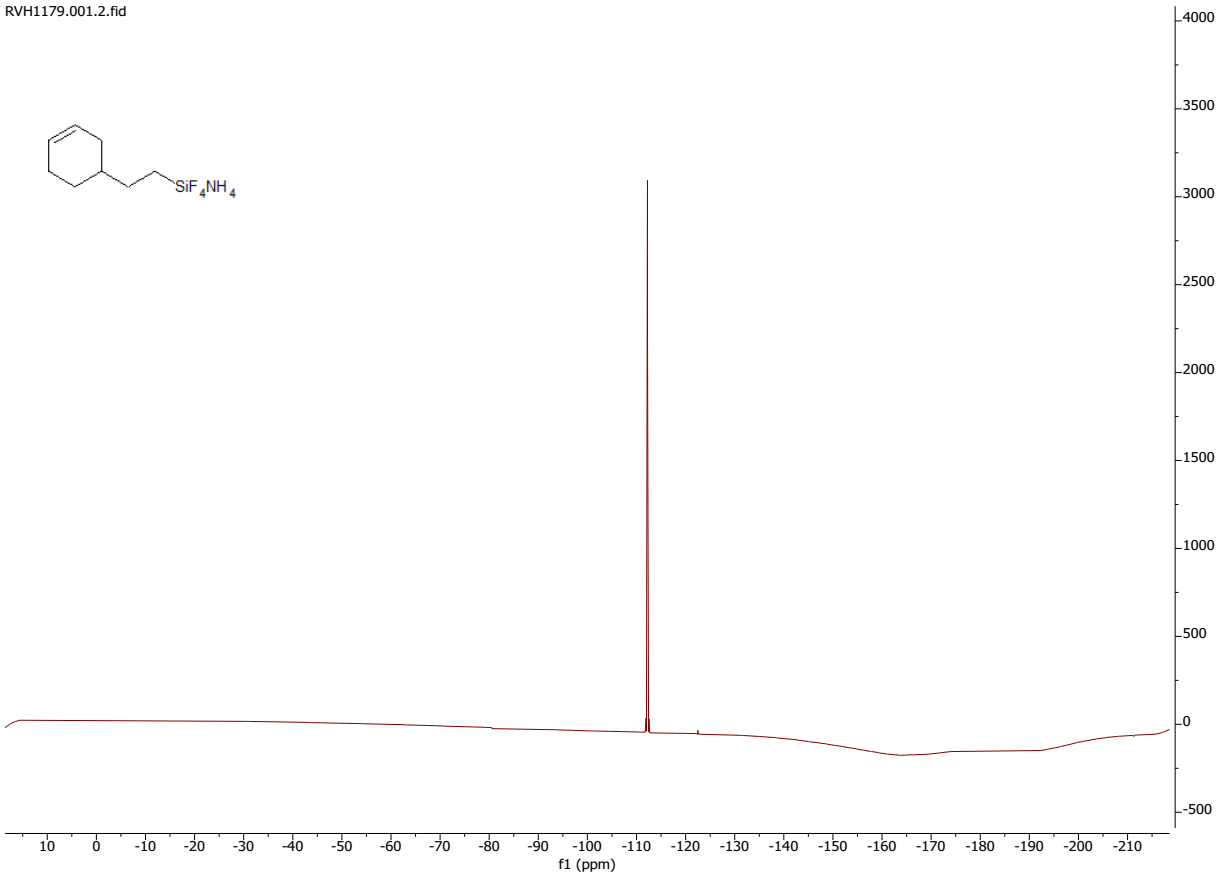


Figure S53. Mass Spectrum of 3m

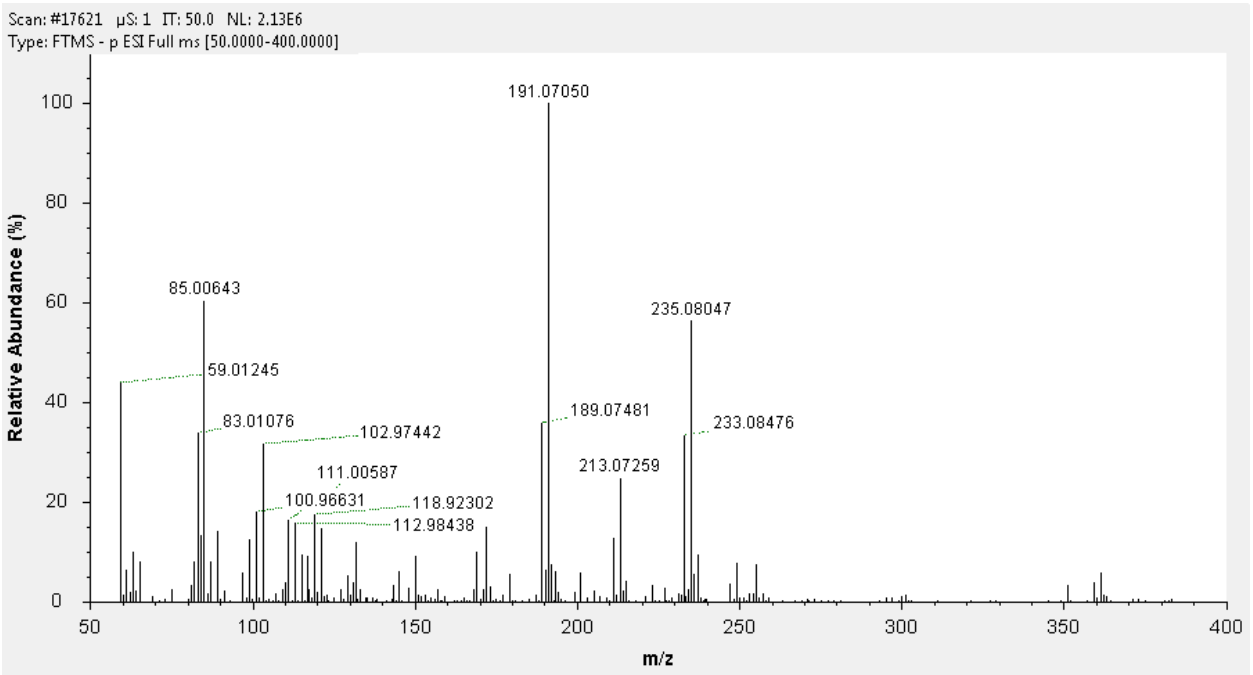


Figure S54. ^{1}H-NMR of 3n in DMSO-d6

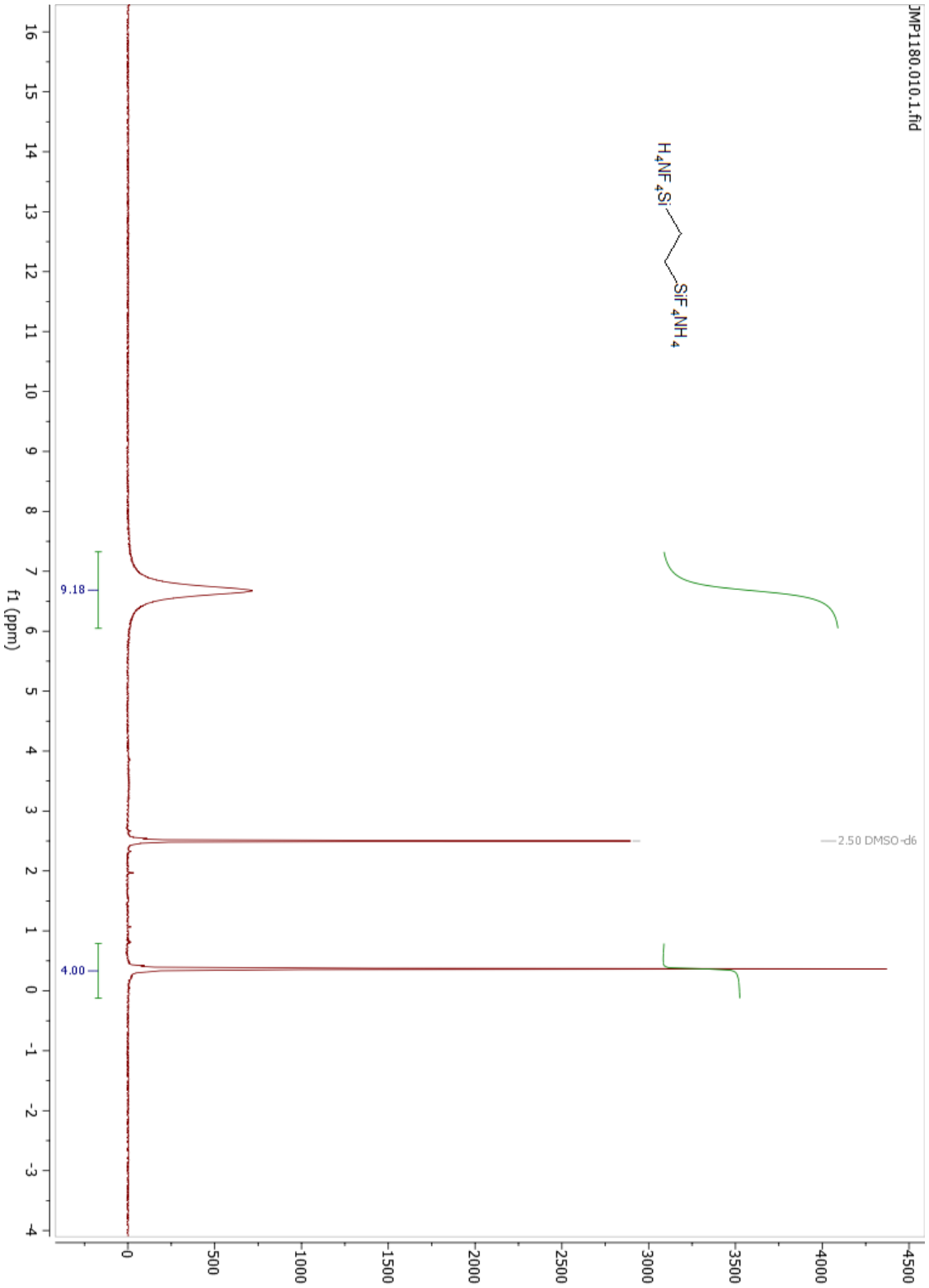


Figure S55. ^{13}C-NMR of 3n in DMSO-d6

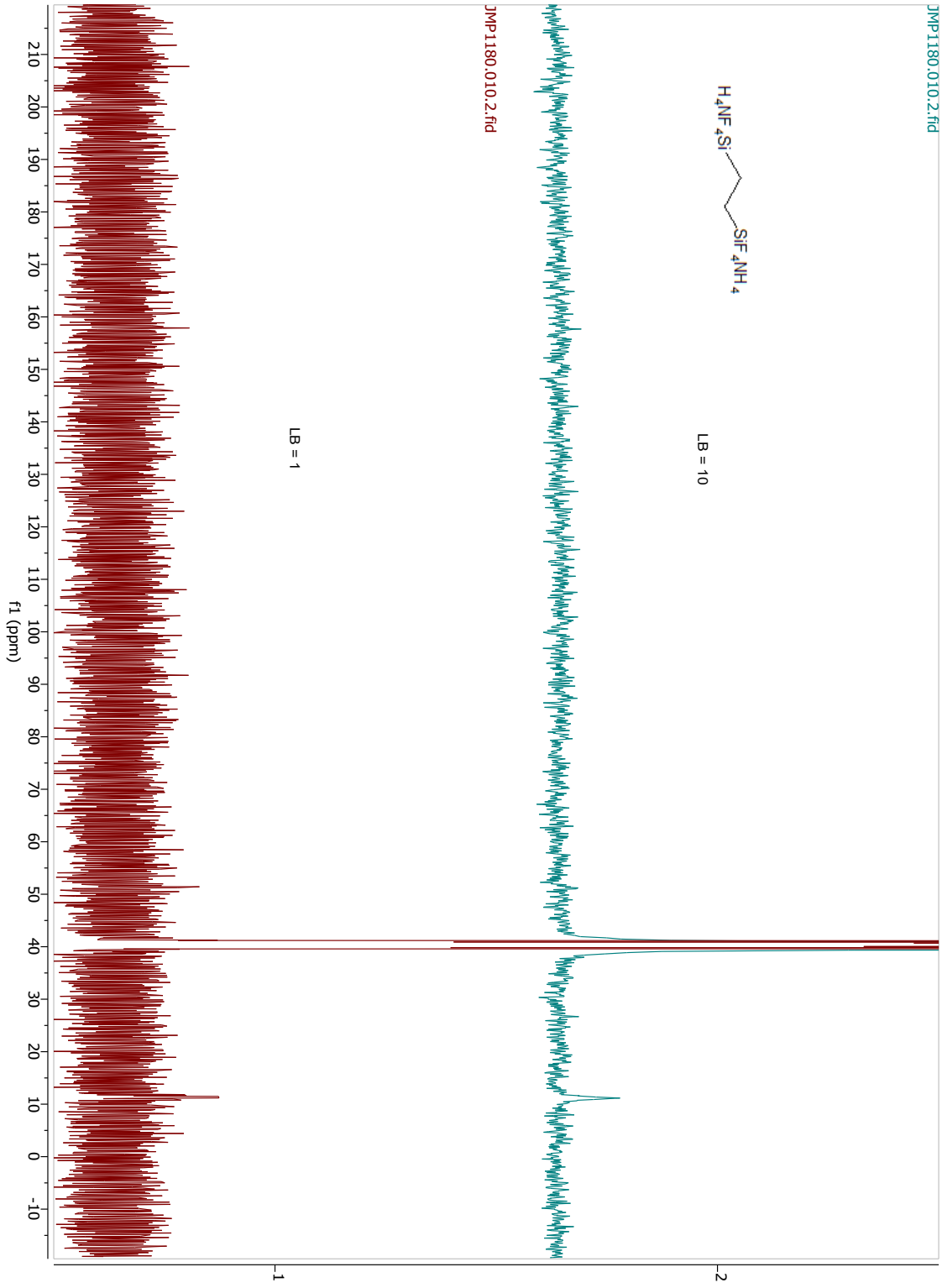


Figure S56. ^{19}F-NMR of 3n in DMSO-d6

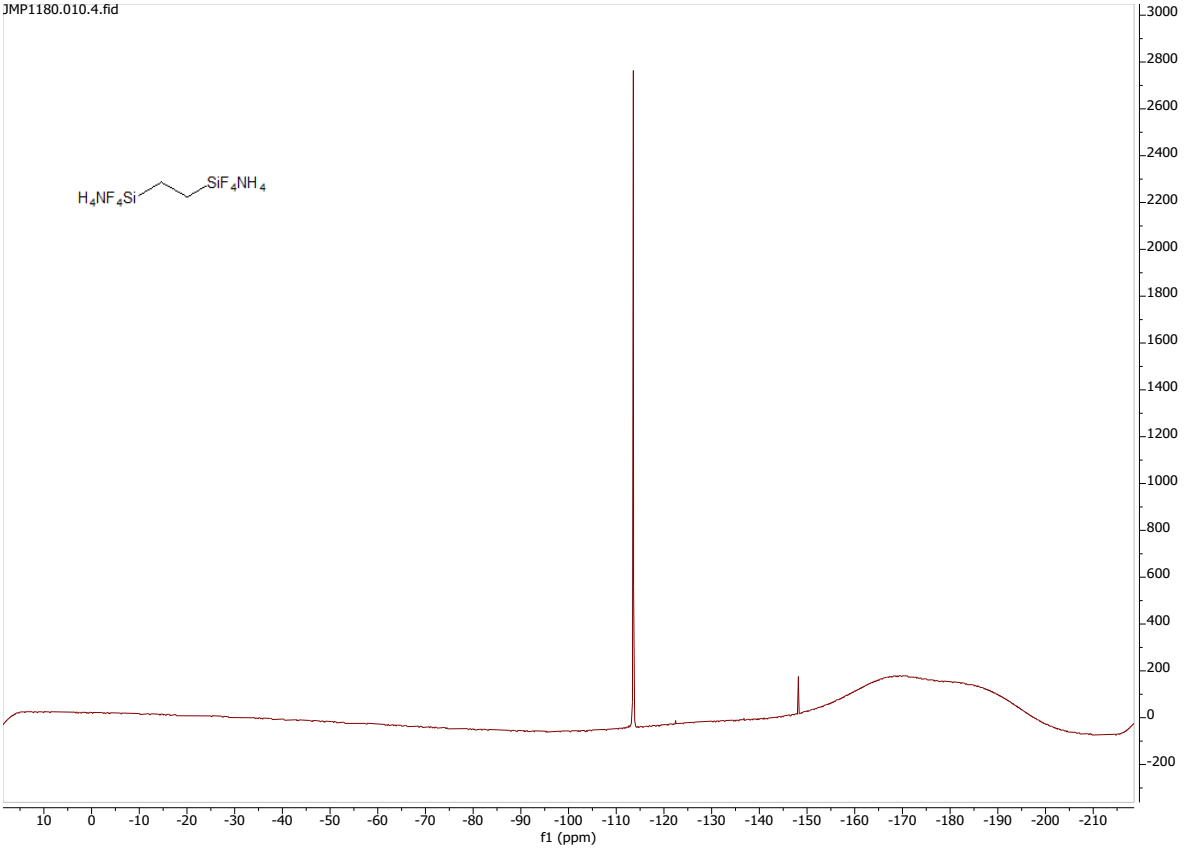


Figure S57. Mass Spectrum of 3n

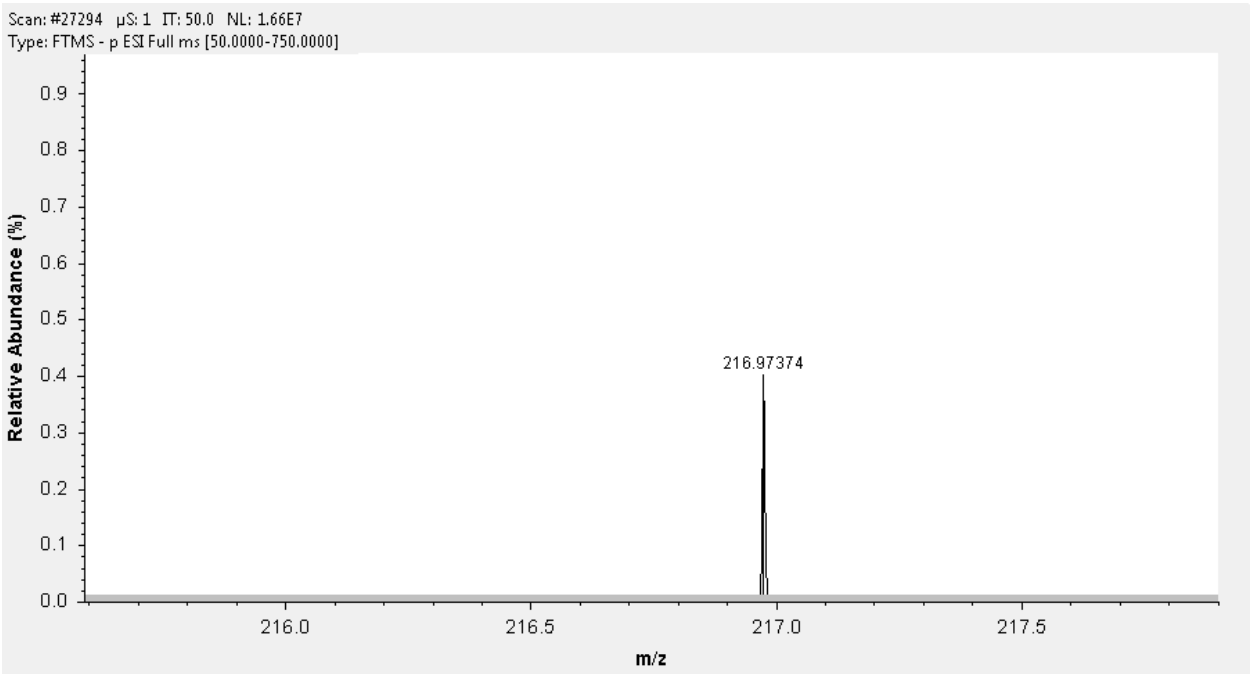


Figure S58. ^{1}H-NMR of 2a in D2O

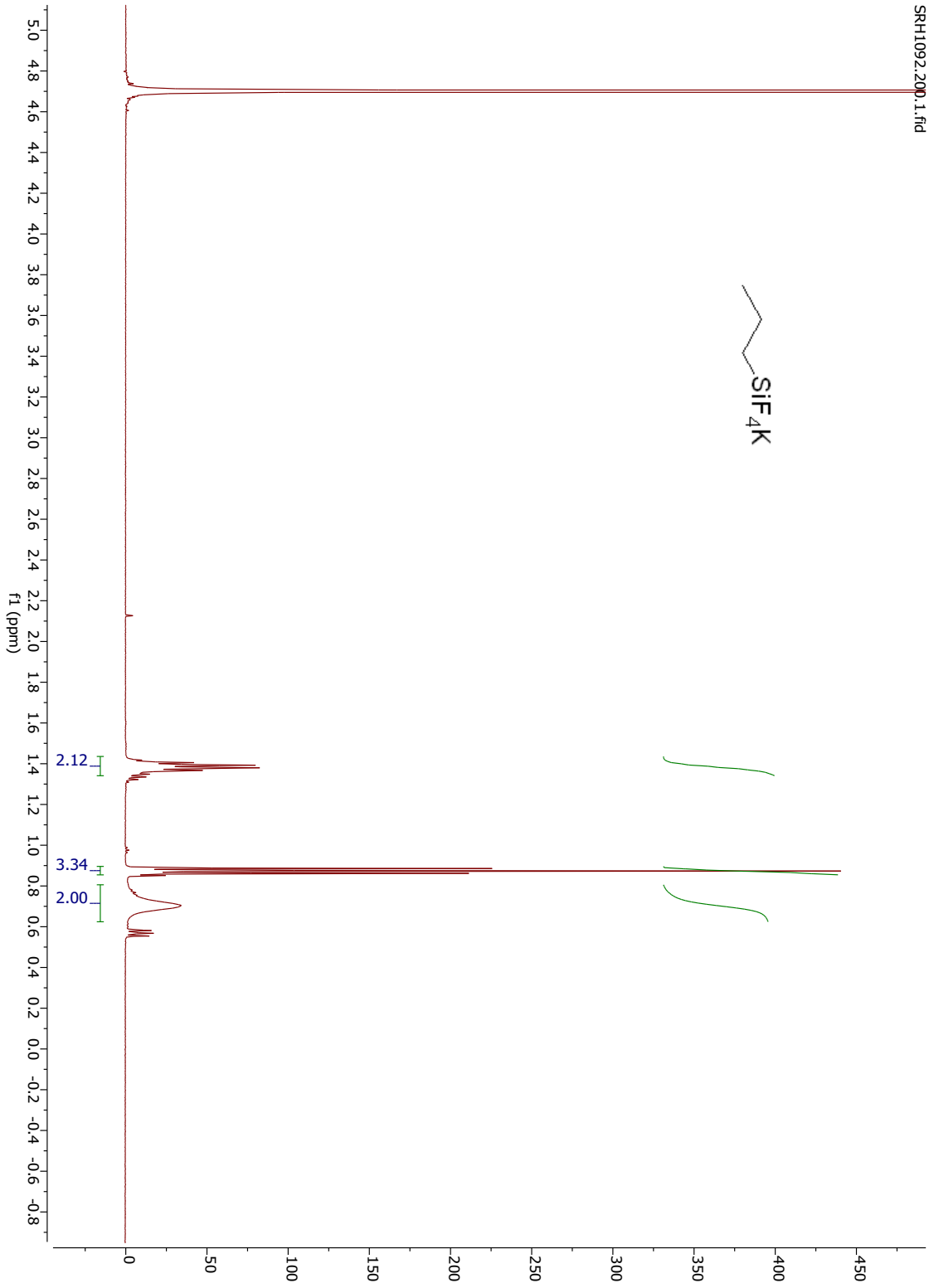


Figure S59. ^{13}C-NMR of 2a in D2O

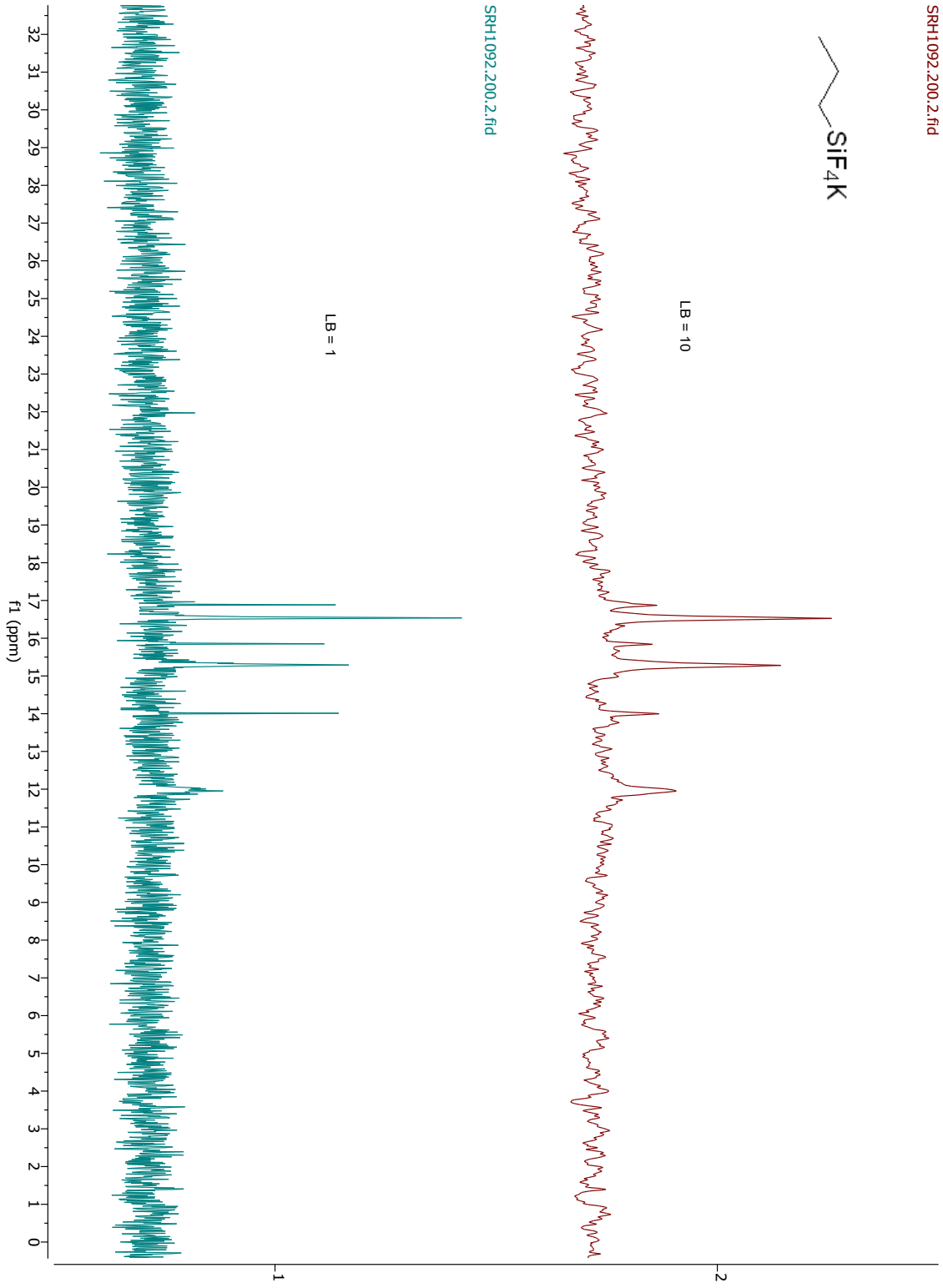


Figure S60. ^{19}F-NMR of 2a in D2O

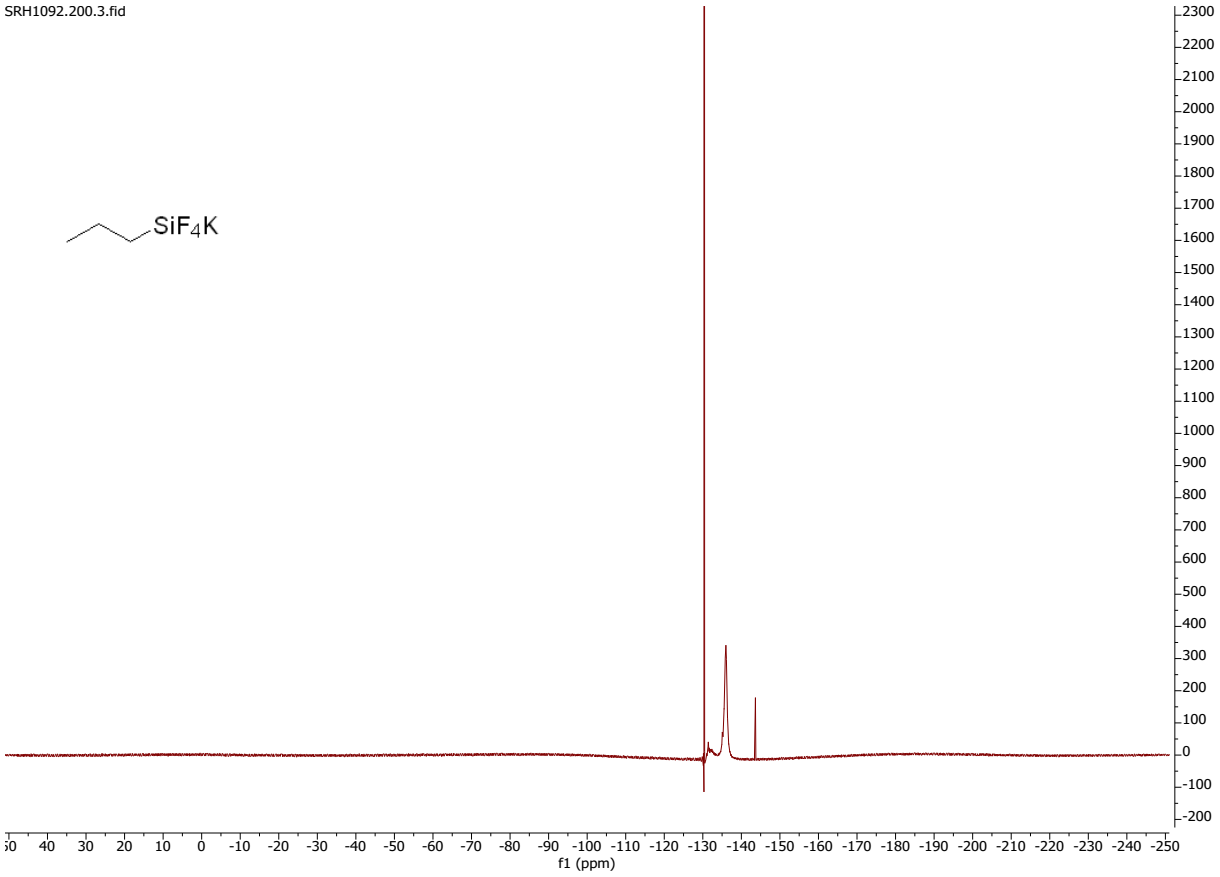


Figure S61. Mass Spectrum of 2a

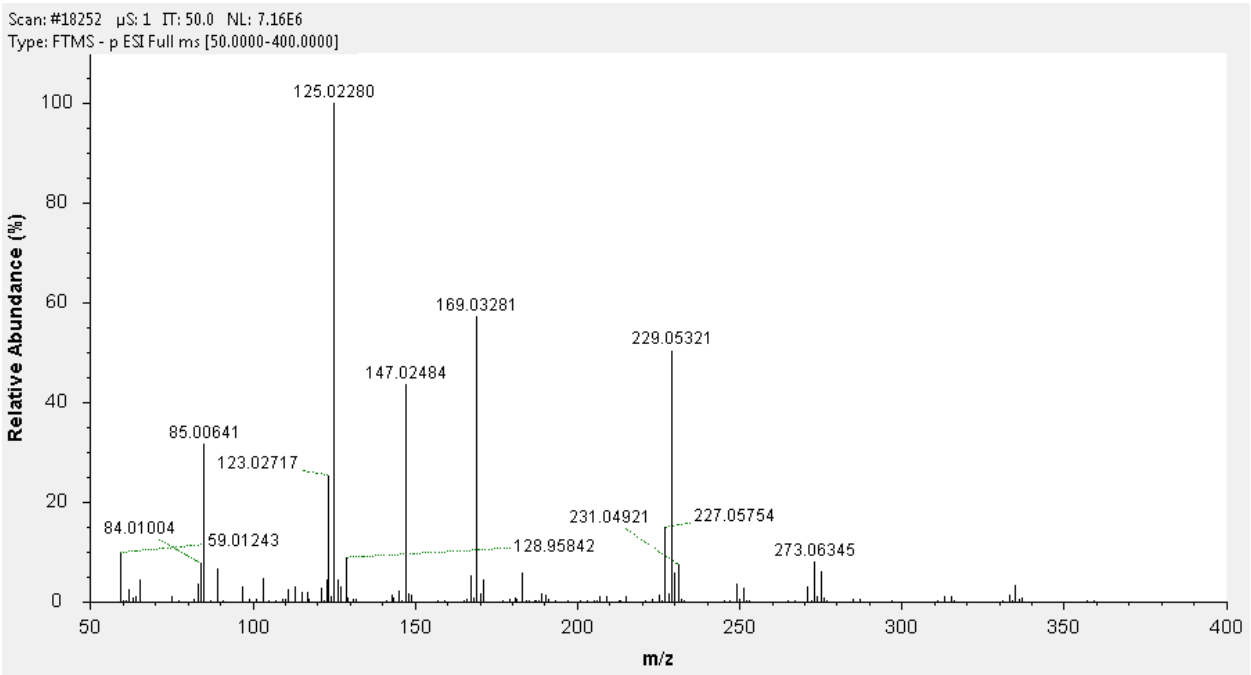


Figure S62. ^{1}H-NMR of 2b in D2O

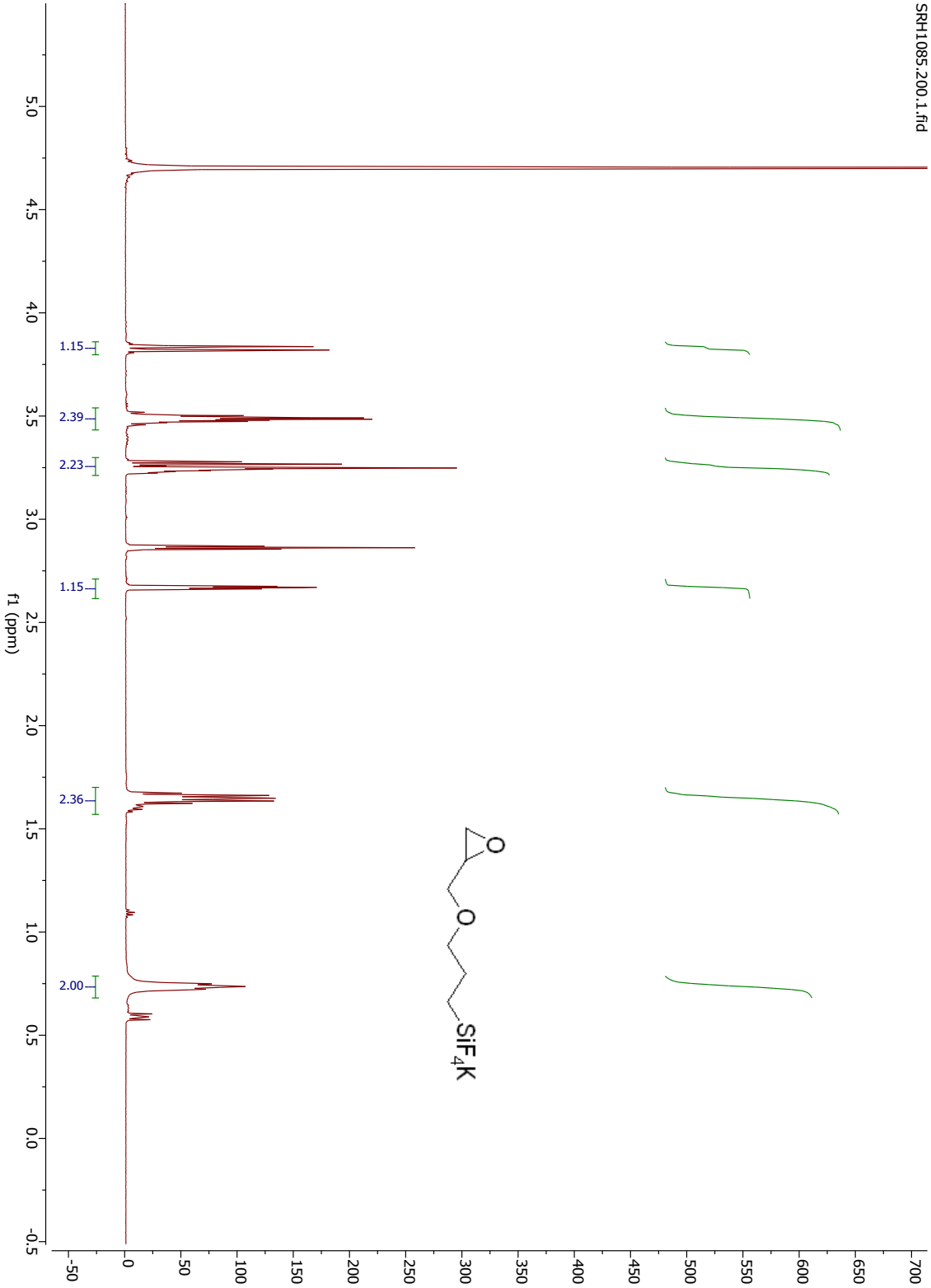


Figure S63. ^{13}C-NMR of 2b in D2O

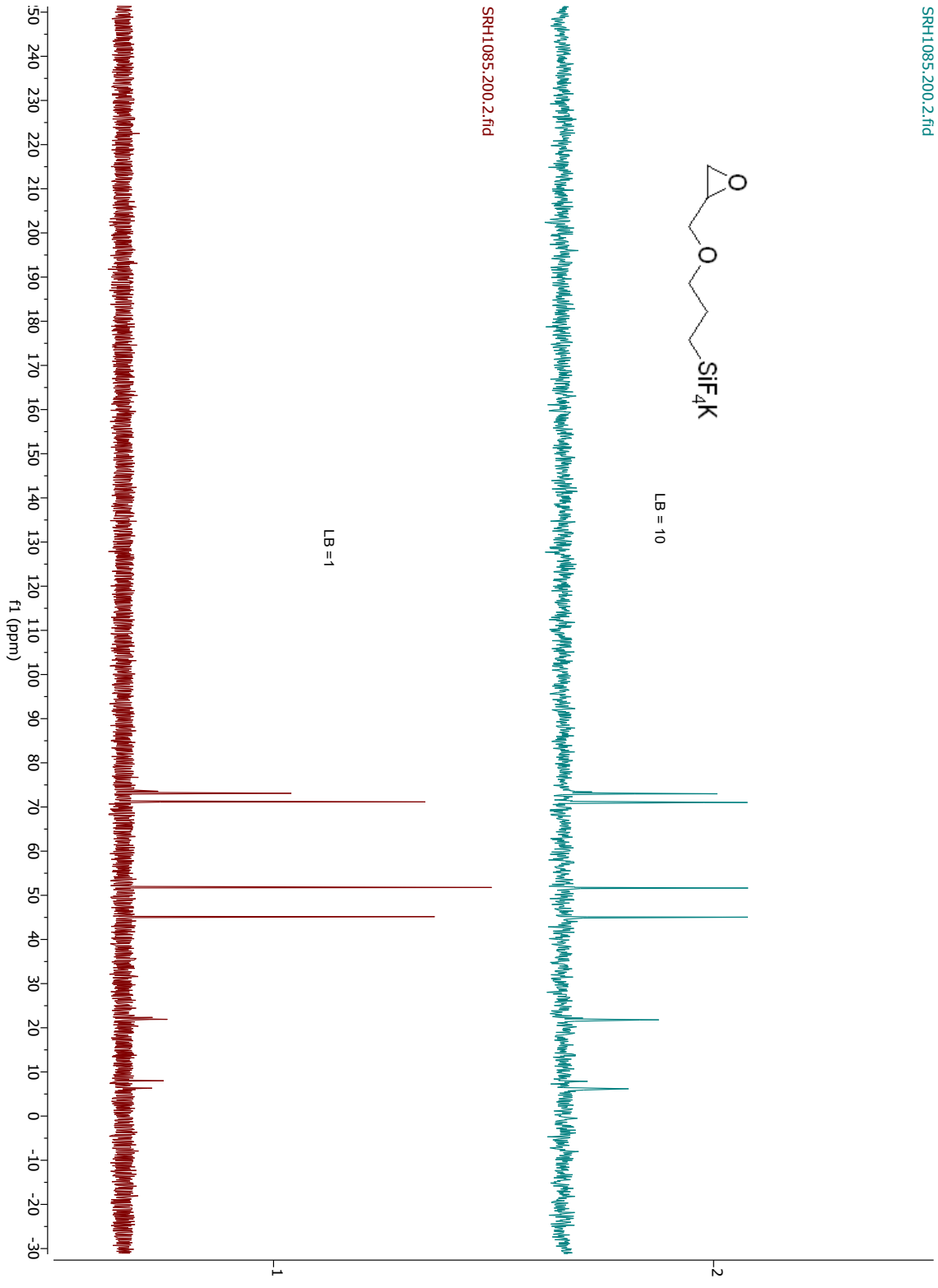


Figure S64. ^{19}F-NMR of 2b in D2O

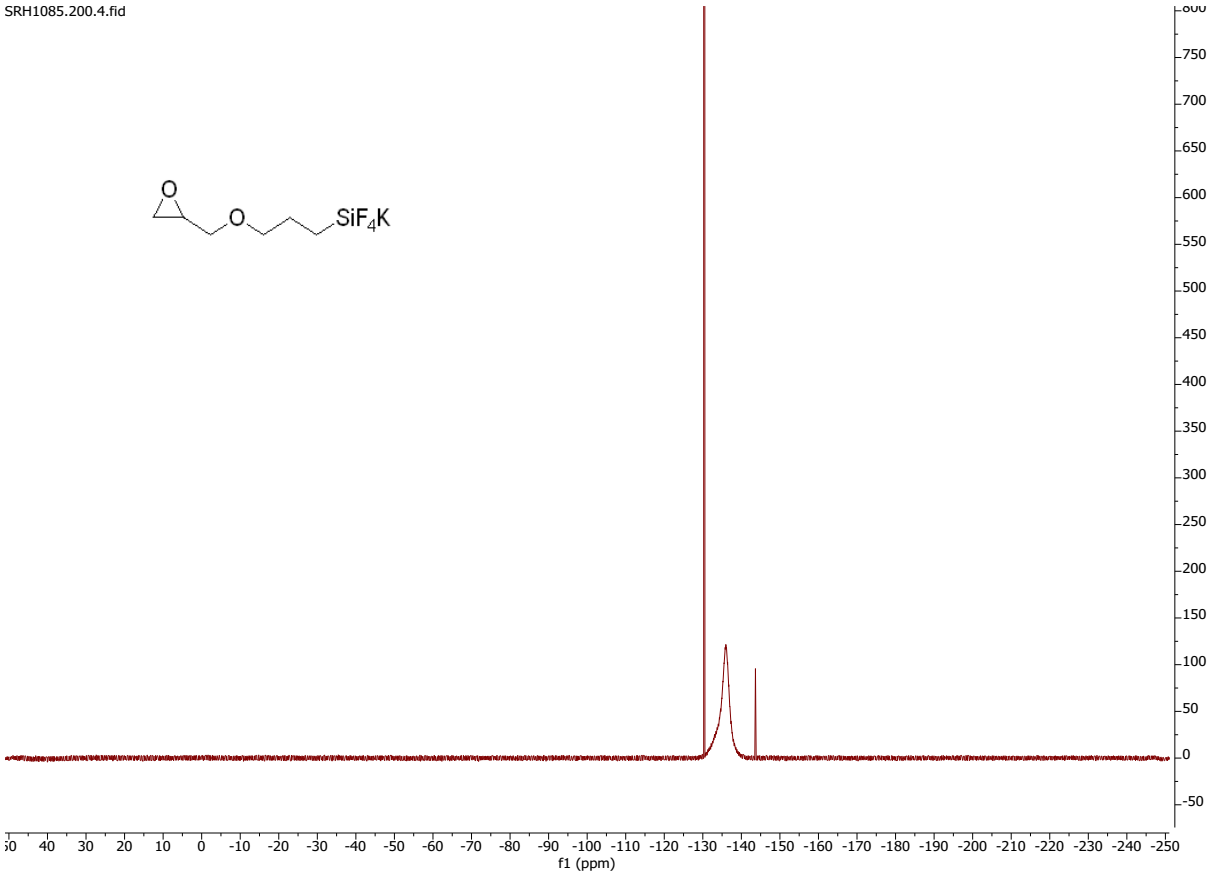


Figure S65. Mass Spectrum of 2b

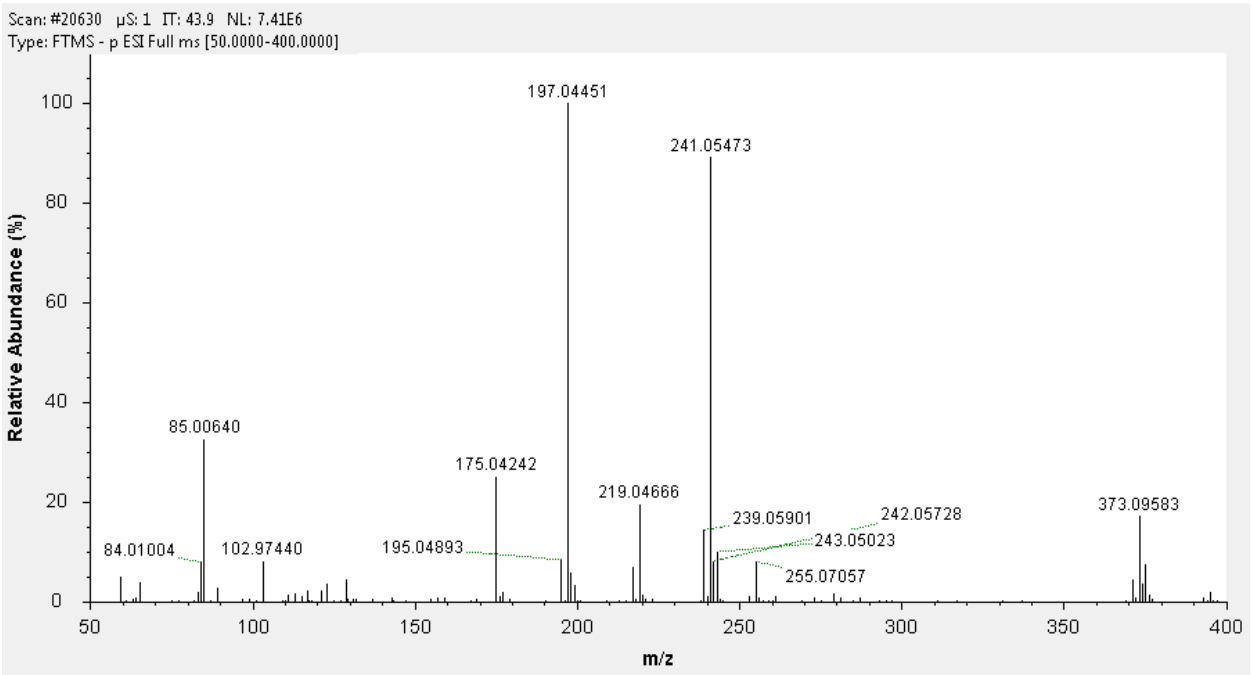


Figure S66. ^{1}H-NMR of 2d in D2O

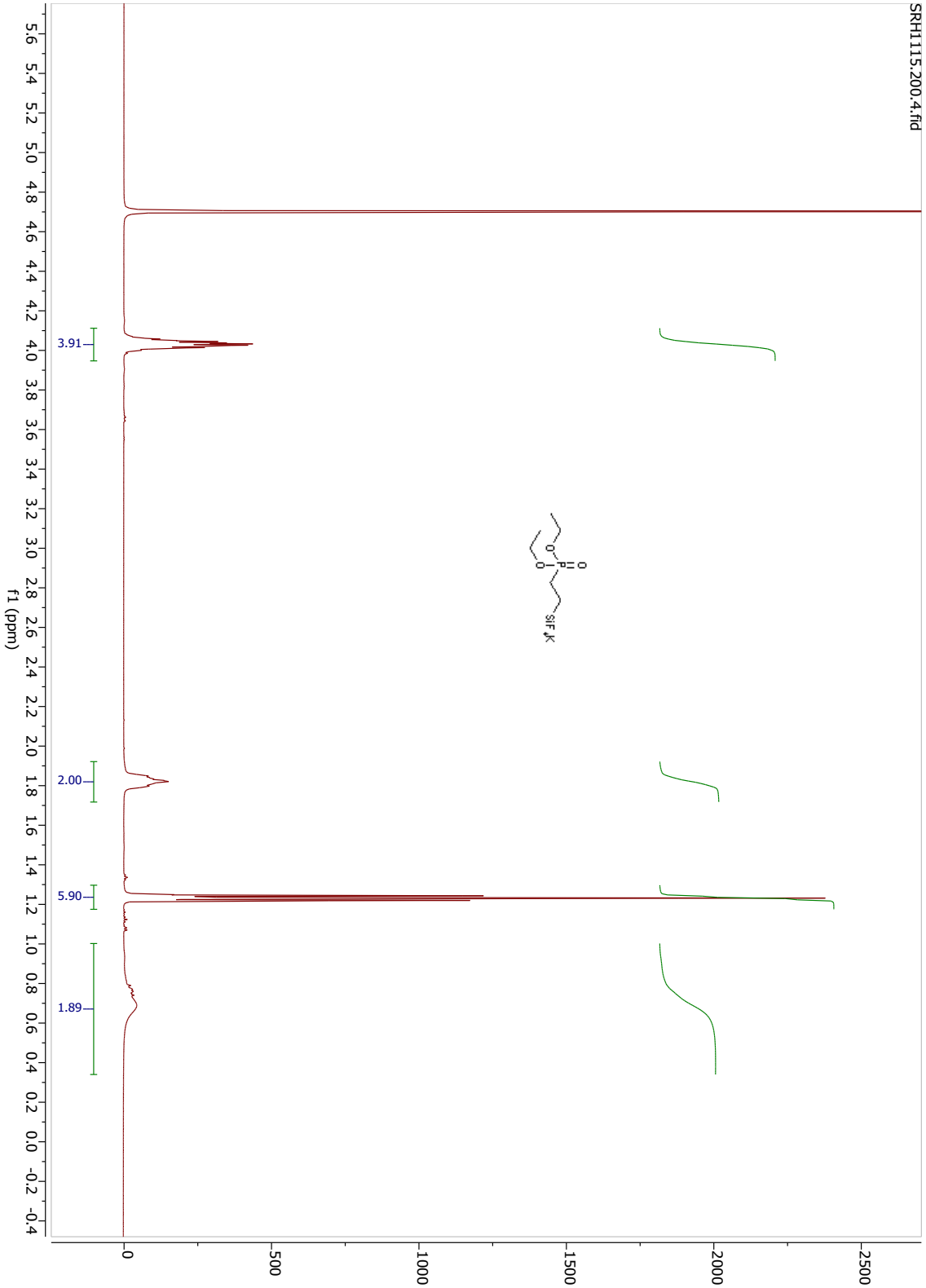


Figure S67. ^{13}C-NMR of 2d in D2O

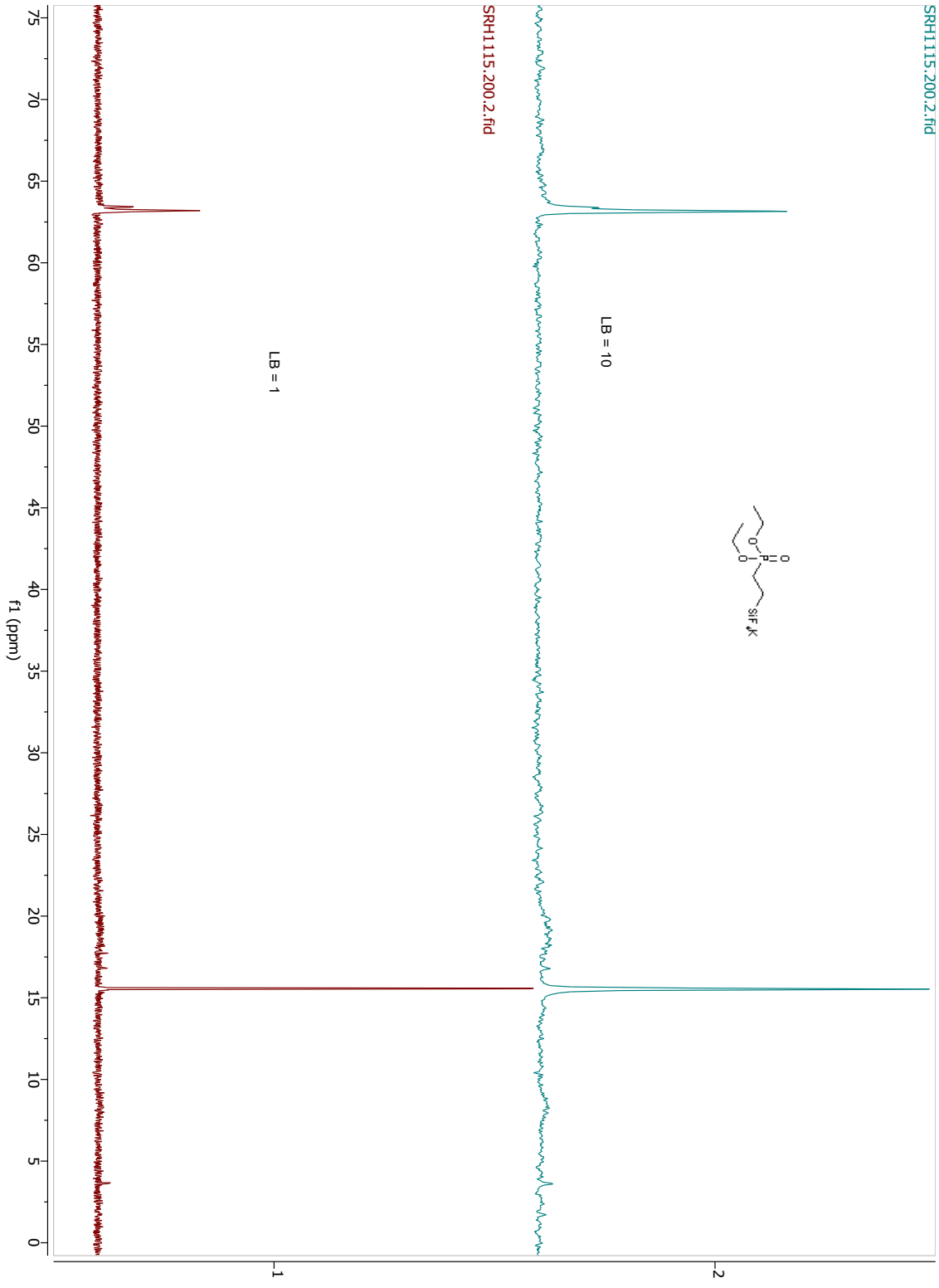


Figure S68. ^{19}F-NMR of 2d in D2O

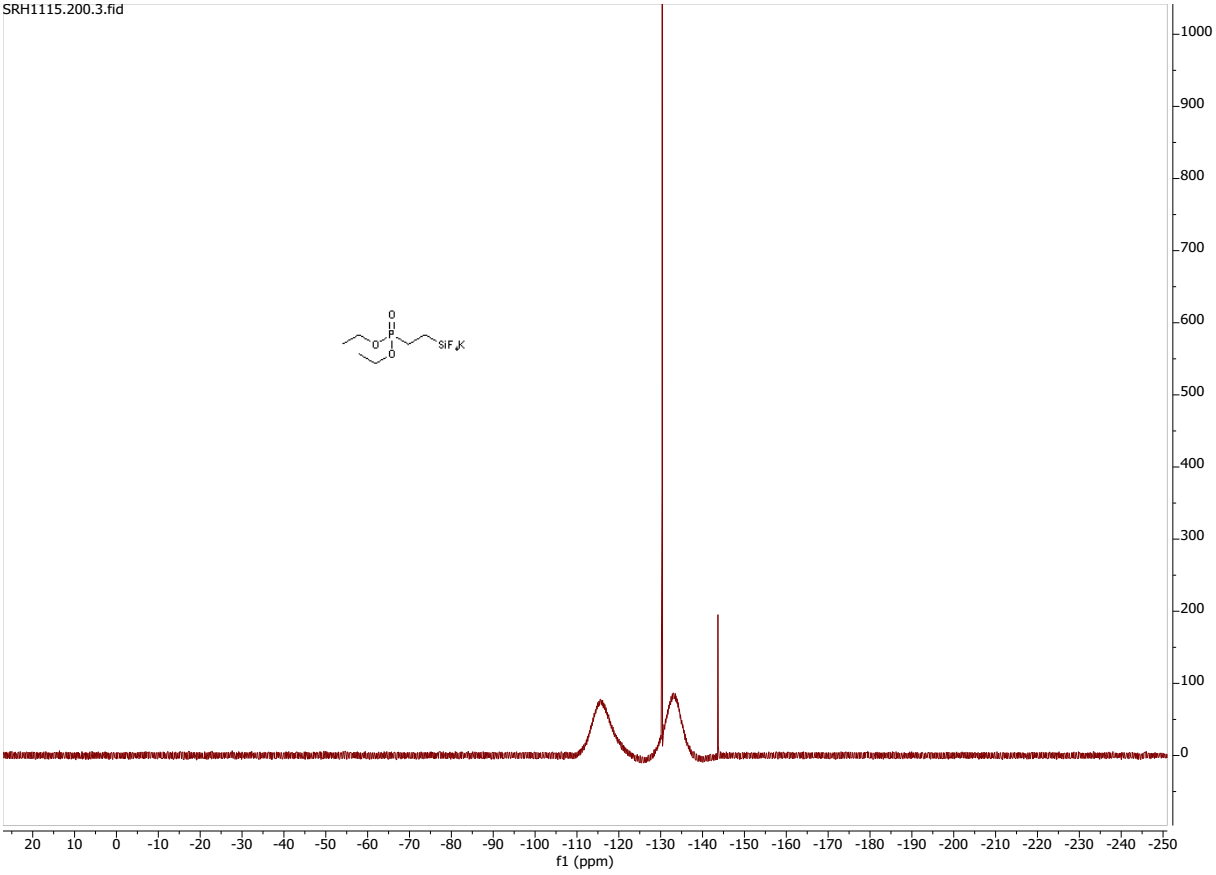


Figure S69. Mass Spectrum of 2d

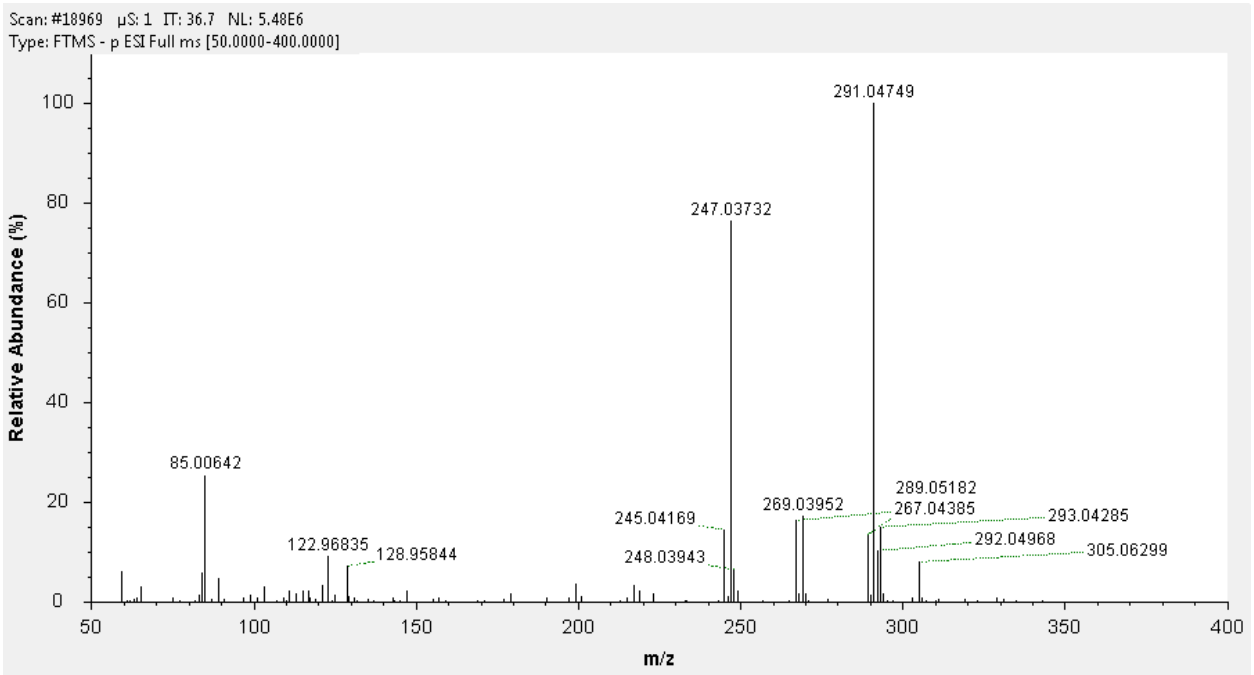


Figure S70. ^{1}H-NMR of 2g in D2O

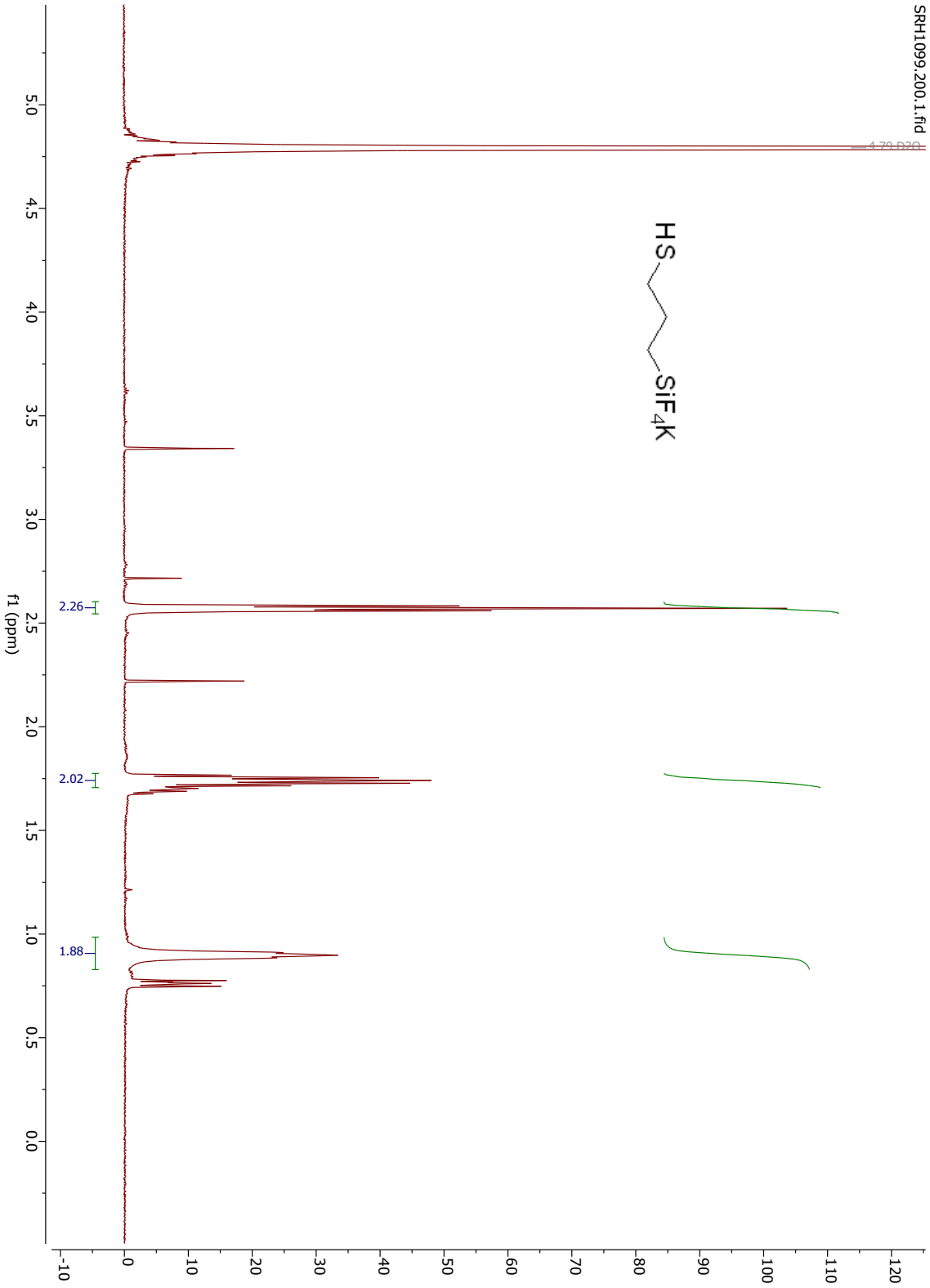


Figure S71. ^{13}C-NMR of 2g in D2O

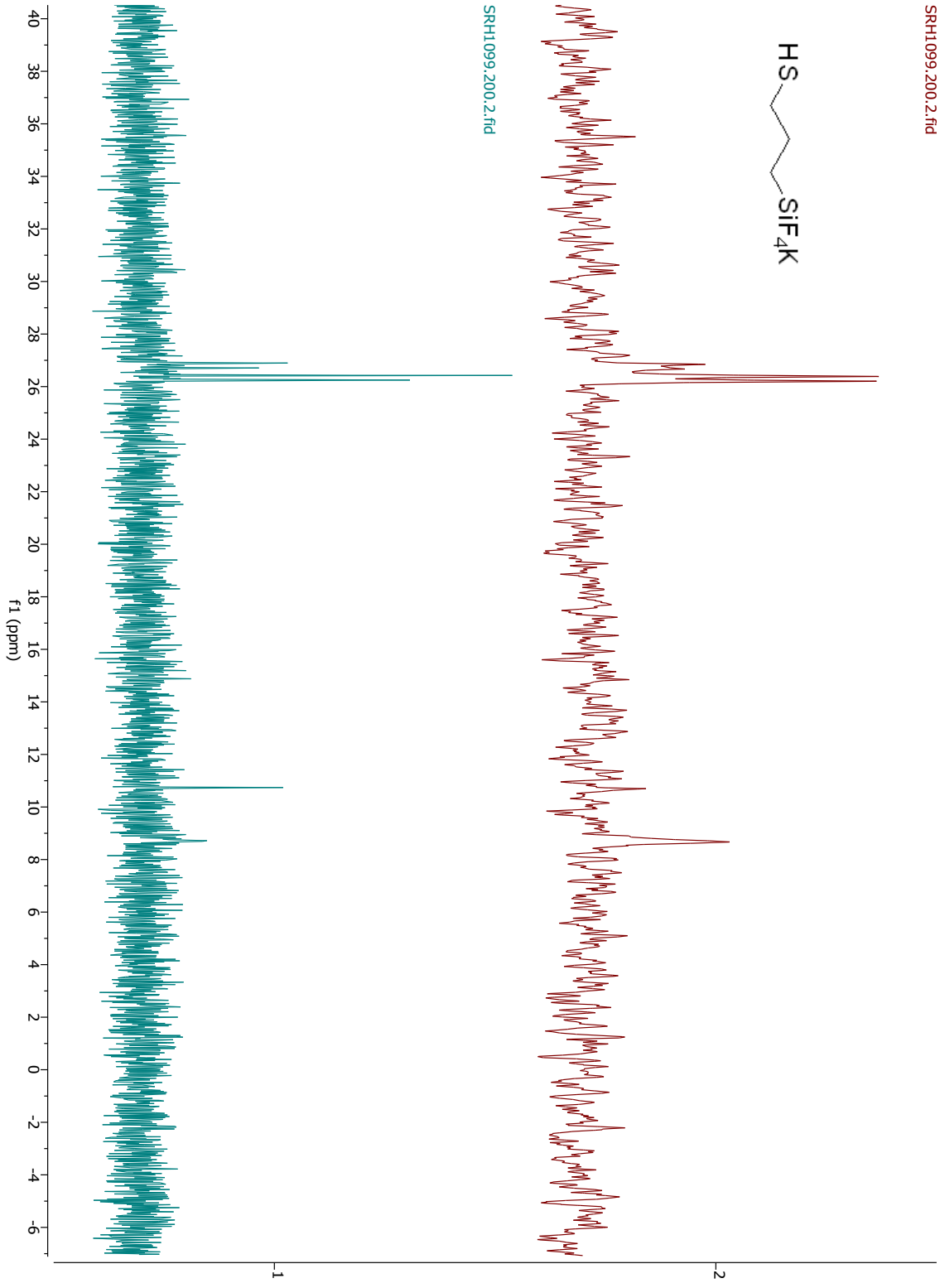


Figure S72. ^{19}F-NMR of 2g in D2O

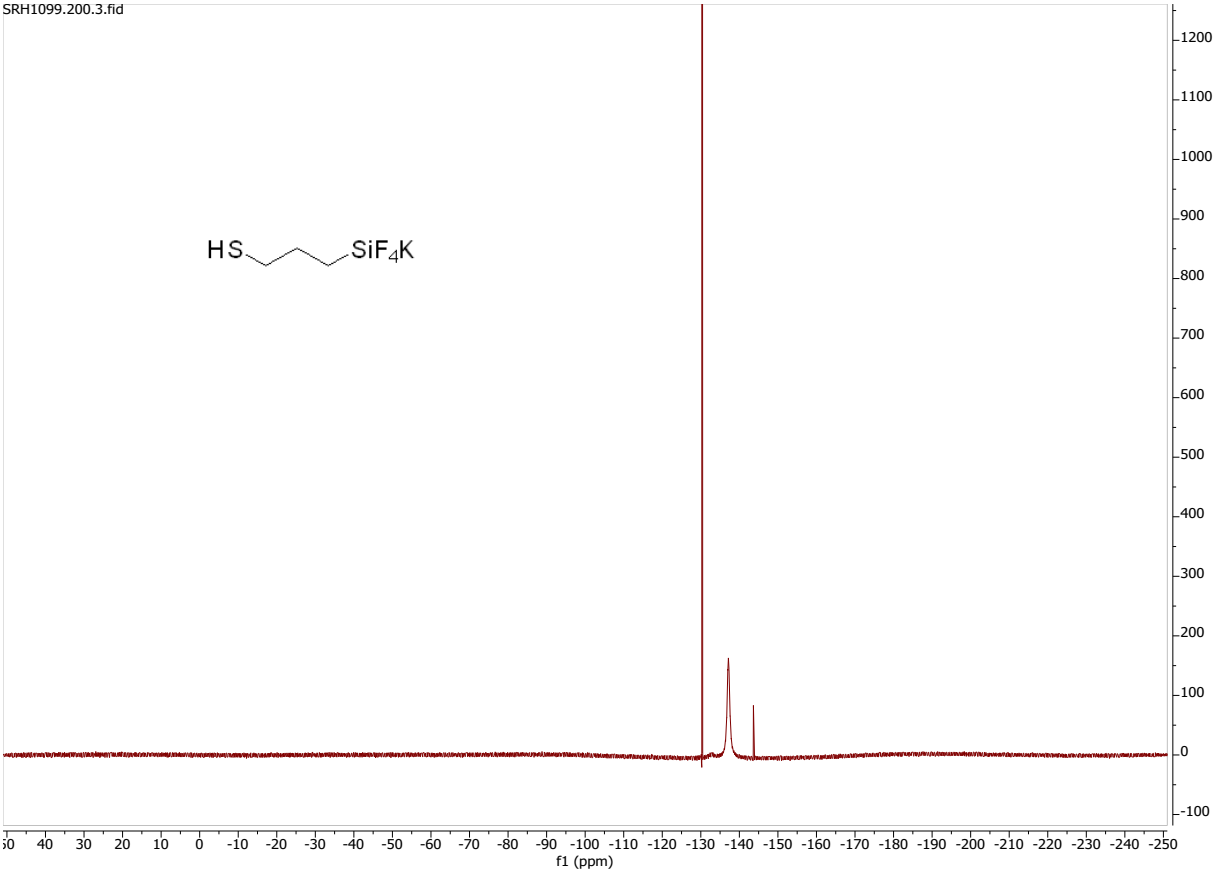
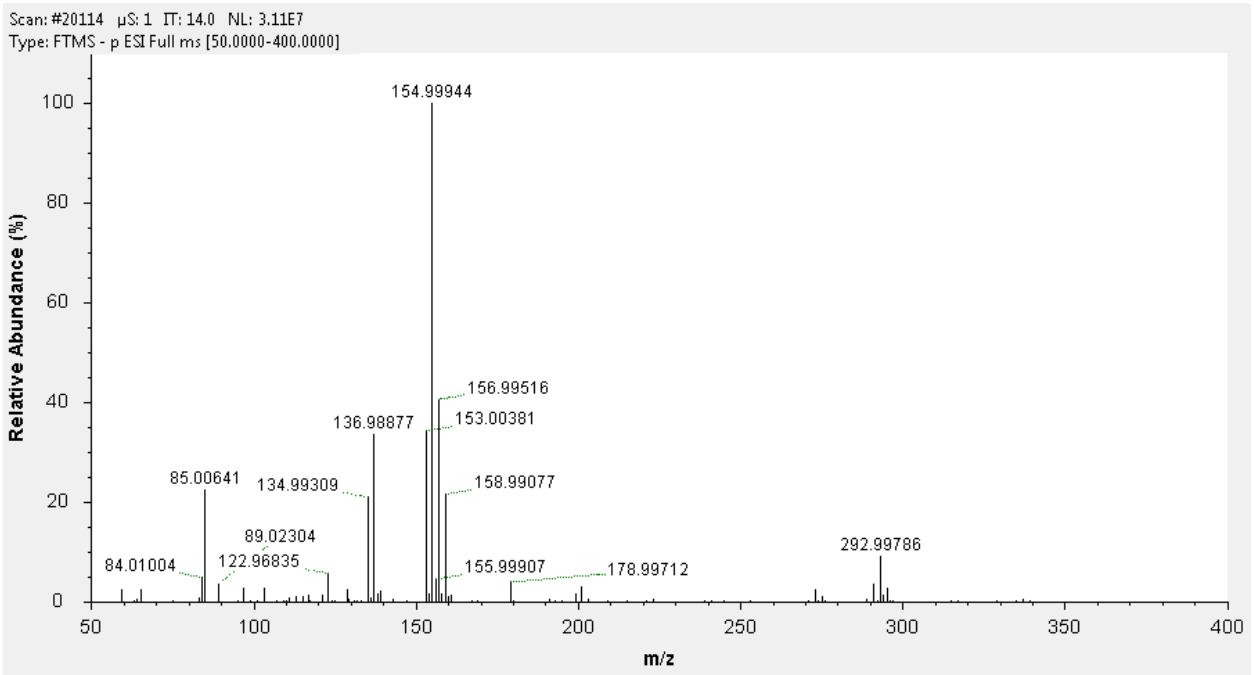


Figure S73. Mass Spectrum of 2g



Scale-Up Experiments

The reactions for larger scales were performed in nearly exactly the same manner with a few exceptions. On smaller scales, the procedure relies on the evaporation of some water to precipitate the product for a good yield. On larger scales, this effect is less dramatic and yields are lowered (Table S1, entry 1). However, increasing the concentration of NH_4HF_2 to 8 M restored the yield, regardless of the scale. On a 1.0 mole scale, the reaction was mechanically stirred rather than stirred with a magnetic stir bar. The NMR spectra for all reaction scales matched those reported above for the 3.0 mmol scale.

Table S1: Synthesis of ammonium phenyltetrafluorosilicate on larger scales.

Entry	Scale	NH_4HF_2 conc.	Yield (g)	Yield (%)
1	15 mmol	4 M	1.7056 g	57%
2	15 mmol	8 M	2.9140 g	98%
3	150 mmol	8 M	24.59 g	82%
4	1.0 mole	8 M	163.57 g	82%

NOTE: Making an 8 M solution of NH_4HF_2 requires gentle warming for the NH_4HF_2 to fully dissolve (usually only a few degrees above room temperature). Additionally, the solution increases in volume during dissolution. This small discrepancy does not seem to affect reactivity. The resulting solution can be stored at room temperature (in a plastic bottle) indefinitely without crystallization of the NH_4HF_2.

Rate of Hydrolysis

Enough material of either 4-bromophenyltrimethoxysilane or ammonium 4-bromophenyltetrafluorosilicate was added to an NMR tube to exceed the saturation limit. Then 0.5 mL of D_2O and 1.0 mL of 1,4-dioxane (as an internal standard) was added to the NMR tube. A ^{1}H-NMR spectrum was acquired every 30 minutes. Notably, the concentration of hydrolysis was set to 0 since the NMR clearly shows no hydrolysis formation (**Figure S74**). Integration of that region produced nothing but noise.

Table S2: Kinetics of Hydrolysis.

	4-bromophenyltrimethoxysilane		Ammonium 4-bromophenyltetrafluorosilicate	
spectrum	Time (min.)	conc. of hydrolysis (mol/L)	Time (min.)	conc. of hydrolysis (mol/L)
1	10	0.001143	20	0
2	40	0.001754	50	0
3	70	0.002024	80	0
4	100	0.003121	110	0
5	130	0.003196	140	0
6	160	0.0038	170	0
7	190	0.004825	200	0
8	220	0.005406	230	0
9	250	0.00586	260	0
10	280	0.006102	290	0
11	310	0.00638	320	0
12	340	0.007182	350	0
13	370	0.007498	380	0
14	400	0.007957	410	0
15	430	0.008139	440	0
16	460	0.00809	470	0
17	490	0.008574	500	0
18	520	0.008594	530	0
19	550	0.009098	560	0
20	580	0.00937	590	0
21	610	0.009936	620	0

Figure S74. Stacked spectra of ammonium p-bromophenyltetrafluorosilicate in D_2O.

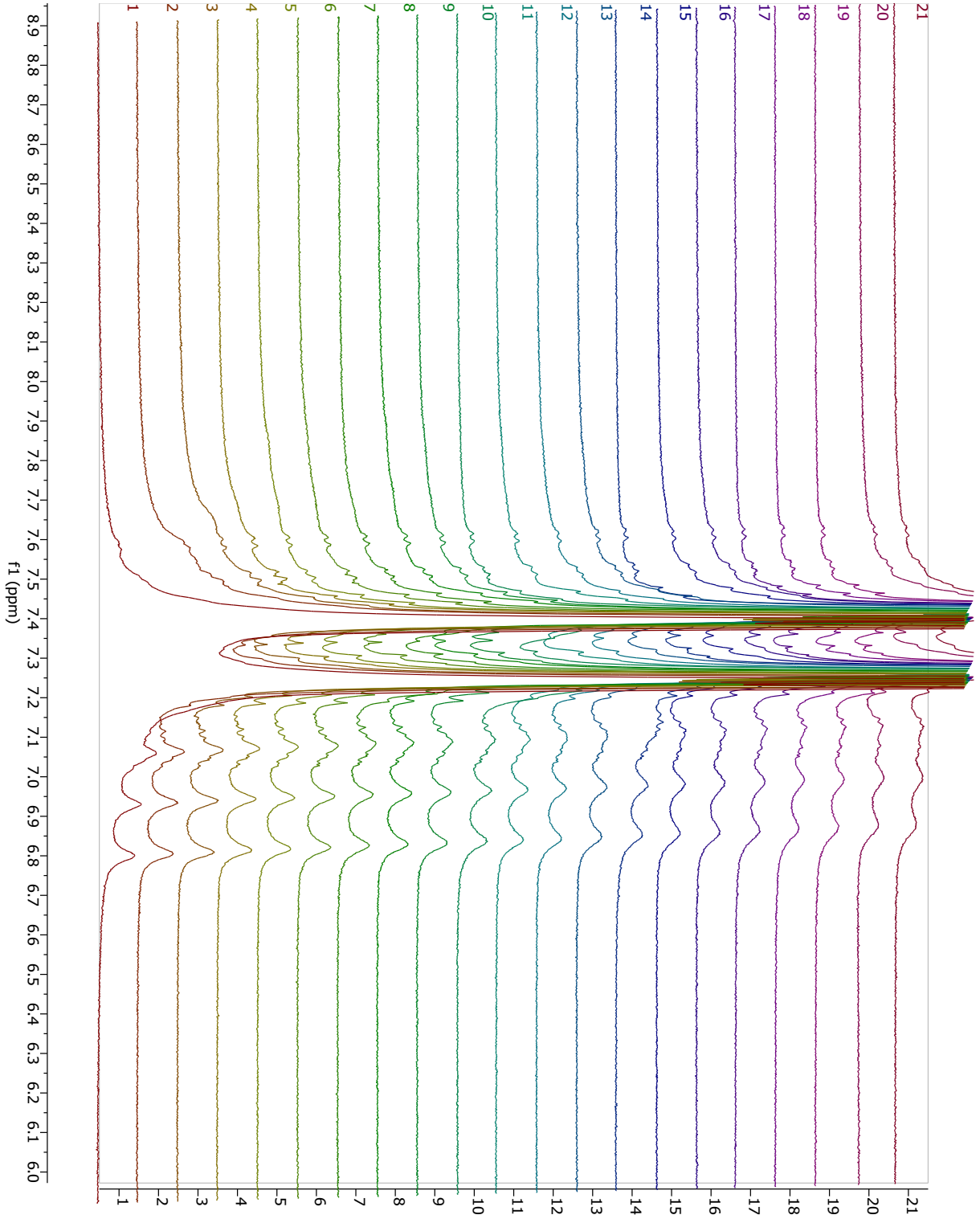
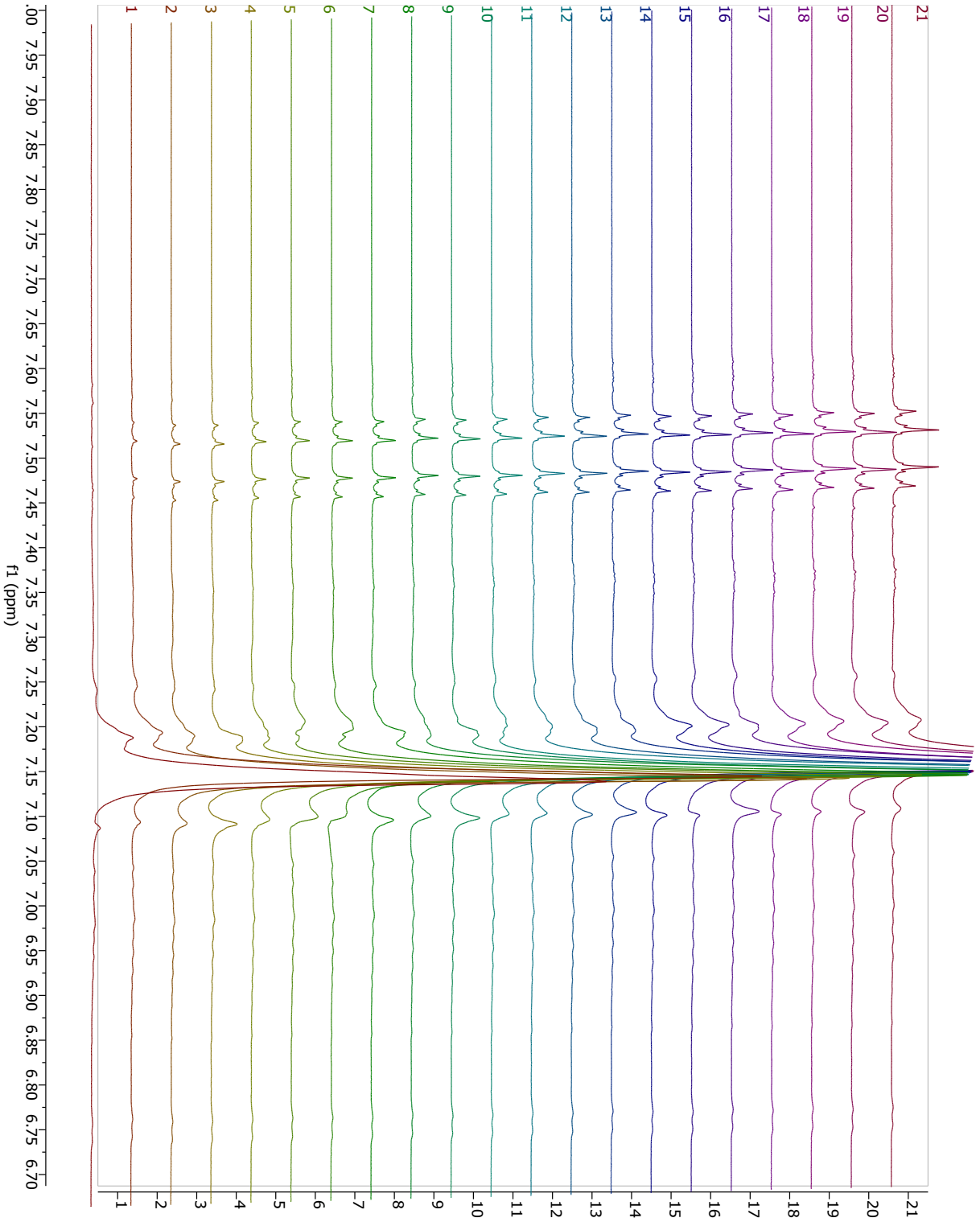


Figure S75. Stacked spectra of p-bromophenyltrimethoxysilane in D_2O.



Comparison of Reactivity

Hiyama coupling procedure. In an argon-filled glovebox, $Pd(PPh_3)_4$ (58 mg, 5%) and ammonium phenyltetrafluorosilicate (299 mg, 1.5 mmol, 1.5 equiv) were weighed into a heavy-walled reaction tube. DMSO (5 mL) and iodobenzene (0.11 mL, 1.0 mmol, 1.0 equiv) added to the tube and then the tube was sealed with a Teflon cap. The reaction was removed from the glovebox, placed into a 150 ºC oil bath, and allowed to stir overnight. The reaction was cooled to ambient temperature, diluted with EtOAc, and filtered through celite. The filtrate was washed with three portions of water, organic layer was dried with Na_2SO_4, and the solvent was removed *in vacuo*. An internal standard (10 mL of 1,1,1,2-tetrachloroethane) was added and the residue was dissolved in $CDCl_3$. The ^{1}H-NMR spectrum matched a commercial sample of biphenyl exactly with 60% yield (**Figure S76**). The same procedure was carried out using phenyltrimethoxysilane instead. The ^{1}H-NMR showed almost no biphenyl.

Fleming-Tamao oxidation procedure. In a plastic beaker, (3-glycidoxypropyl)trimethoxysilane (0.66 mL, 3.0 mmol, 1.0 equiv) was added to 3.0 mL of a 2 M aqueous solution NH_4HF_2 (6.0 mmol, 2.0 equiv). The reaction was allowed to stir for 1 hour at ambient temperature and then 30% aqueous H_2O_2 (3.0 mL, 29.4 mmol, 9.8 equiv) was added. After 4 hours, DMF (0.1 mL) was added as an internal standard and the ^{1}H-NMR showed that the tetrafluorosilicate had completely oxidized to the alcohol in 95% yield (**Figure S77**). The same procedure was carried out using (3-glycidoxypropyl)trimethoxysilane without converting it to the tetrafluorosilicate. The ^{1}H-NMR showed no conversion (**Figure S78**).

Figure S76. ^{1}H-NMR spectra of the Hiyama coupling in $CDCl_3$

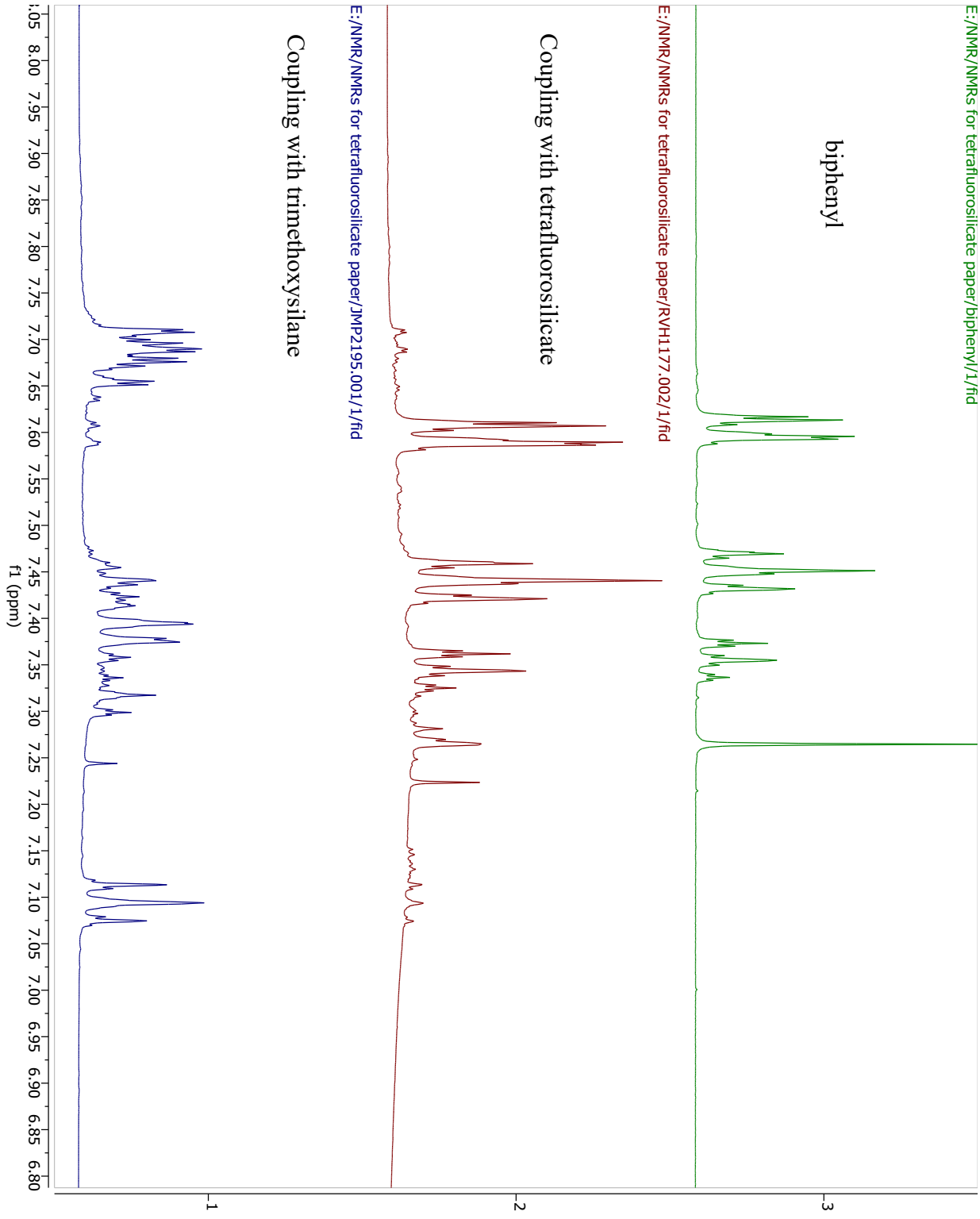


Figure S77. ^{1}H-NMR of Fleming-Tamao with tetrafluorosilicate in H_2O.

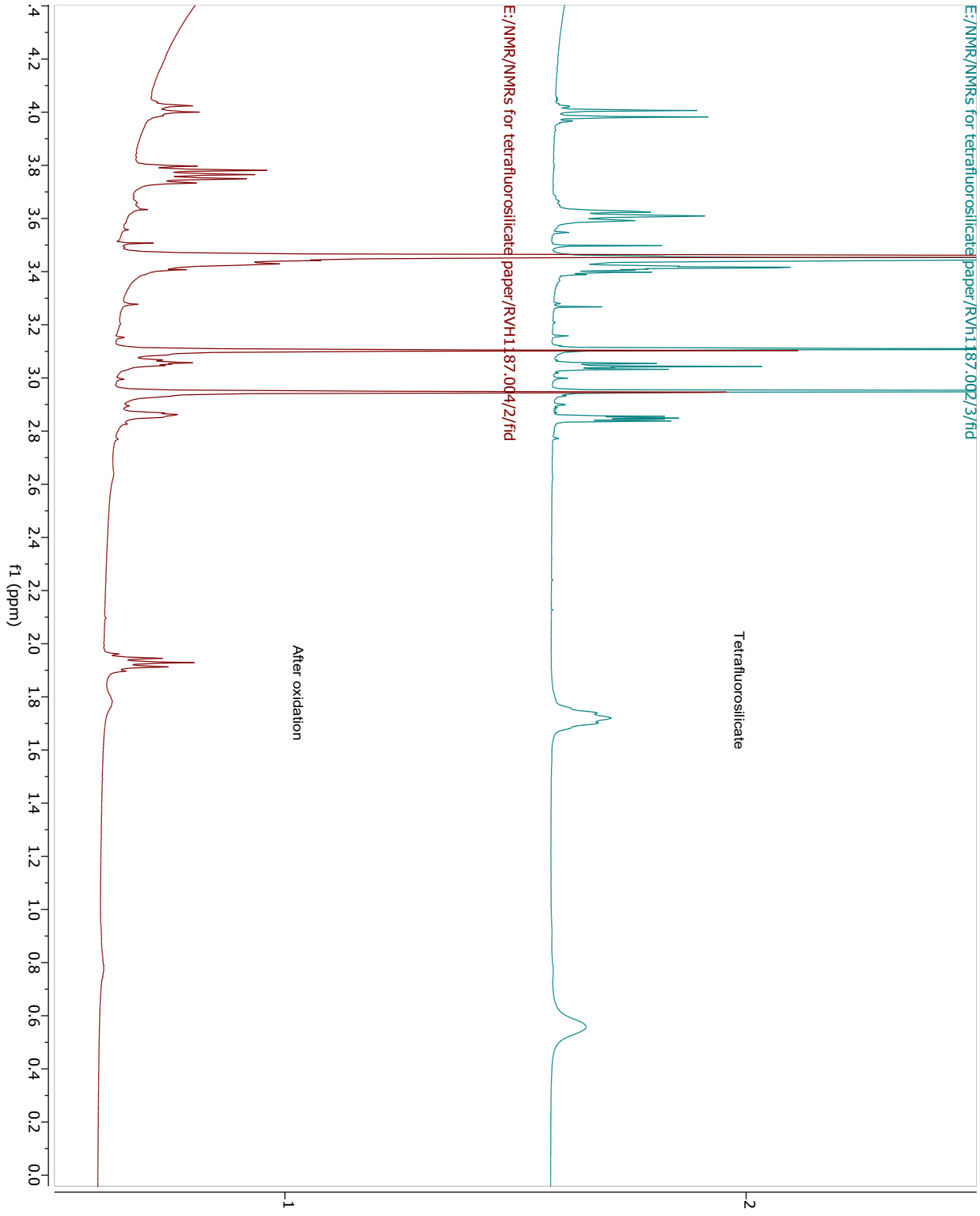


Figure S78. ^{1}H-NMR of Fleming-Tamao with trimethoxysilane in H_2O.