Supporting Information for:

Fluorinated Amine Stereotriads *via* Allene Amination

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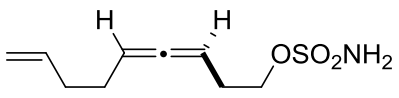
I. General Information. All glassware was either oven-dried overnight at 130 °C or flame-dried under a stream of dry nitrogen prior to use. Unless otherwise specified, reagents were used as obtained from the vendor without further purification. Tetrahydrofuran and diethyl ether were freshly distilled from purple Na/benzophenone ketyl. Dichloromethane, acetonitrile, toluene, and benzene were dried over CaH_2 and freshly distilled prior to use. All other solvents were purified in accordance with "Purification of Laboratory Chemicals".[1] Air- and moisture- sensitive reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen. Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F_{254} plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh) via Still's method.[2] Unless otherwise stated, the mobile phases for column chromatography were mixtures of hexanes/ethyl acetate. Columns were typically run using a gradient method, beginning with 100% hexanes and gradually increasing the polarity using ethyl acetate. Various stains were used to visualize reaction products, including $KMnO_4$ and ceric ammonium molybdate (CAM stain).

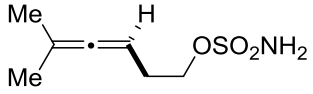
^{1}H NMR and ^{13}C NMR spectra were obtained using either a Bruker-400, Bruker Callisto-500, Bruker Persephone-500, or Bruker Phoebe-600 spectrometers. ^{19}F NMR was obtained using Bruker-400, Bruker Persephone-500, or Bruker Phoebe-600 spectrometers. For ^{1}H NMR, chemical shifts are reported relative to residual protiated solvent peaks (δ 7.26, 7.15 and 7.09 ppm for $CDCl_3$, C_6D_6 and $CD_3C_6D_5$ respectively). ^{13}C NMR spectra were measured at either 151, 126 MHz, or 101 MHz on the same instruments noted above for recording ^{1}H NMR spectra. Chemical shifts were again reported in accordance to residual protiated solvent peaks (δ 77.2, 128.0 and 137.9 ppm for $CDCl_3$, C_6D_6, and $CD_3C_6D_5$, respectively). For ^{19}F NMR, chemical shifts are reported referenced to ^{1}H NMR. Accurate mass measurements were acquired at the

University of Wisconsin, Madison using a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact methods). The NMR and Mass Spectrometry facilities are funded by the NSF (CHE-9974839, CHE-9304546, CHE-9208463, CHE-9629688) and the University of Wisconsin, as well as the NIH (RR08389-01). The Q Exactive Plus mass spectrometer was funded through the NIH (1S10OD020022-1).

II. Preparation of homoallenic sulfamates. General procedure: The following procedure is taken from a literature procedure published by Du Bois.[3] Formic acid (2.2 equiv) was added slowly to a rapidly stirred solution of neat chlorosulfonyl isocyanate (CSI, 2.2 equiv) at 0 ºC. During the addition process, vigorous gas evolution and solidification of the reaction mixture to a white solid were observed. Dry acetonitrile was added to the resulting white solid to make 0.55 M solution of CSI. The reaction mixture was warmed to 23 ºC. After stirring overnight, the mixture was cooled to 0 ºC and a solution of the corresponding homoallenic alcohol (1.0 equiv) in N,N-dimethylacetamide (DMA, same volume as for acetonitrile) was added via syringe. The reaction was warmed to room temperature and stirred until TLC indicated completion of the reaction. The reaction mixture was quenched by adding H_2O, and poured into a separatory funnel containing Et_2O. The aqueous layer was extracted three times with Et_2O and the combined organic layers were washed five times with H_2O, once with brine and dried over Na_2SO_4. The solution was decanted and concentrated by rotary evaporation, yielding a crude product that was purified by silica gel chromatography (Et_2O/hexanes, with gradient) to afford the homoallenic sulfamates.

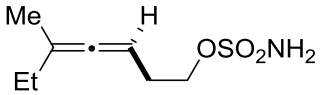


Precursor to compound 13. An oven-dried two-necked round-bottom flask fitted with a stir bar was charged with chlorosulfonyl isocyanate (4.10 g, 29.0 mmol, 2.0 equiv) and cooled to 0 ºC. Formic acid (1.33 g, 28.9 mmol, 2.0 equiv) was added dropwise to the same flask over ca. two minutes, followed by addition of 29 mL distilled CH_3CN. The reaction mixture was warmed to room temperature and stirred for 15 hours. The reaction was then cooled to 0 ºC again and 1.97 g (14.3 mmol, 1.0 equiv) of the alcohol in 29 mL of DMA was added all at once *via* syringe to the reaction. The reaction was warmed to room temperature and stirred for 45 minutes. The reaction mixture was quenched by adding 40 mL H_2O, then poured into a separatory funnel containing an equal volume of Et_2O. The aqueous layer was extracted three times with 30 mL portions of Et_2O and the combined organic layers were washed seven times with 10 mL H_2O for each wash. The organic layer was then washed once with brine and dried over Na_2SO_4. After silica gel chromatography (carried out using a gradient method with initial starting mobile phase consisting of 1:9 Et_2O:hexanes, with a gradual increase to a ratio of 1:1 Et_2O:hexanes in 10% increments; CAM stain), 1.87 g (8.61 mmol, 60% yield) of the sulfamate was obtained as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 1H), 5.20 (qt, *J* = 6.2, 2.9 Hz, 1H), 5.11 (qt, *J* = 6.4, 3.0 Hz, 1H), 5.04 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.01 – 4.97 (m, 1H), 4.84 – 4.72 (m, 2H), 4.26 (t, *J* = 6.8 Hz, 2H), 2.44 (qd, *J* = 6.7, 2.9 Hz, 2H), 2.20 – 2.14 (m, 2H), 2.14 – 2.06 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.9, 138.1, 115.2, 91.9, 86.1, 70.6, 33.2, 28.6, 28.1. HRMS (ESI) m/z calculated for $C_9H_{15}NO_3S$ $[M+NH_4]^+$ 235.1111, found 235.1110.



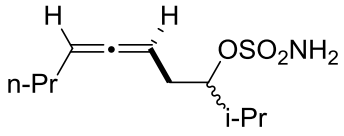
Precursor to compound 16. An oven-dried three-necked round bottom flask fitted with a stir bar was charged with chlorosulfonyl isocyanate (13.8 g, 97.5 mmol, 2.2 equiv) and cooled to 0

ºC. Formic acid (4.50 g, 97.8 mmol, 2.2 equiv) was added dropwise to the same flask over ca. 10 minutes, followed by addition of 81 mL distilled CH_3CN. The reaction mixture was warmed to room temperature and stirred for 12 hours. The reaction was then cooled to 0 ºC and 4.98 g (44.4 mmol, 1.0 equiv) of the alcohol in 81 mL of DMA was added all at once *via* syringe. The mixture was warmed to room temperature and stirred for ca. 2.5 hours. The reaction mixture was quenched by adding 130 mL H_2O, and poured into a separatory funnel containing an equal volume of Et_2O. The aqueous layer was extracted three times with Et_2O and the combined organic layers were washed five times with 45 mL portions of H_2O. The organic layer was then washed once with brine and dried over Na_2SO_4. After silica gel chromatography (carried out using a gradient method with initial starting mobile phase consisting of 0:1 Et_2O:hexanes, with a gradual increase to a ratio of 1:1 in 10% increments; CAM stain), 6.79 g (35.5 mmol, 80% yield) of the sulfamate was yielded as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.95 (qq, *J* = 6.0, 2.9 Hz, 1H), 4.75 (bs, 2H), 4.24 (t, *J* = 6.9 Hz, 2H), 2.40 (q, *J* = 6.8 Hz, 2H), 1.69 (d, *J* = 2.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 96.8, 83.5, 70.8, 28.8, 20.7. HRMS (ESI) m/z calculated for $C_7H_{13}NO_3S$ $[M+Na]^+$ 214.0508, found 214.0508.



Precursor to compound 17. An oven-dried three-necked round bottom flask fitted with a stir bar was charged with chlorosulfonyl isocyanate (18.7 g, 132 mmol, 2.2 equiv) and cooled to 0 ºC. Formic acid (6.10 g, 133 mmol, 2.2 equiv) was added dropwise to the same flask over ca. 15 minutes, followed by addition of 110 mL distilled CH_3CN. The reaction mixture was warmed to room temperature and stirred for 12 hours. The reaction was then cooled to 0 ºC and 7.56 g (59.9 mmol, 1.0 equiv) of the alcohol in 110 mL of DMA was added all at once *via* syringe. The

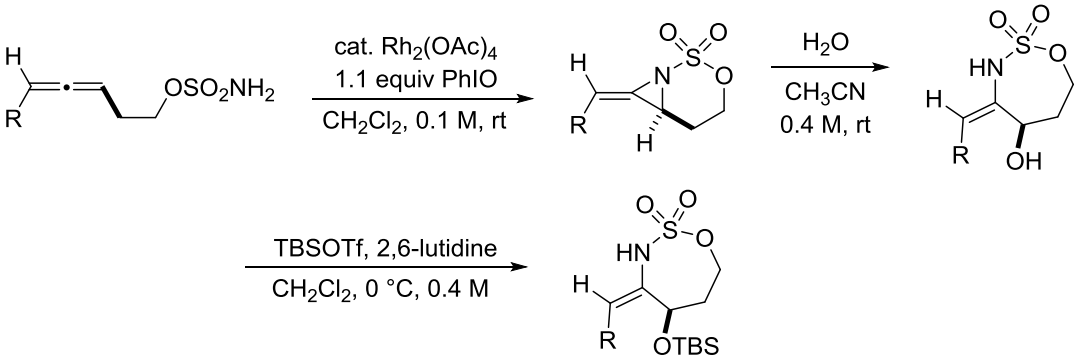
mixture was warmed to room temperature and stirred for 3 hours. The reaction mixture was quenched by adding 180 mL H_2O, and poured into a separatory funnel containing an equal volume of Et_2O. The aqueous layer was extracted three times with Et_2O and the combined organic layers were washed five times with ca. 60 mL portions of H_2O. The organic layer was then washed once with brine and dried over Na_2SO_4. After silica gel chromatography (carried out using a gradient method with initial starting mobile phase consisting of 0:1 Et_2O:hexanes, with a gradual increase to a ratio of 1:1 in 10% increments; CAM stain), 6.51 g of the homoallenic enesulfamate (31.7 mmol, 53%) was obtained as a clear, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.05 (th, *J* = 6.0, 2.9 Hz, 1H), 4.77 (bs, 2H), 4.24 (t, *J* = 6.9 Hz, 2H), 2.41 (q, *J* = 6.8 Hz, 2H), 1.94 (qd, *J* = 7.4, 3.2 Hz, 2H), 1.69 (d, *J* = 2.8 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.0, 103.1, 85.5, 70.9, 29.0, 27.0, 19.2, 12.3. HRMS (ESI) m/z calculated for $C_8H_{15}NO_3S$ $[M-H]^-$ 204.0700, found 204.0702.



Precursor to compound 20. An oven-dried three-necked round bottom flask fitted with a stir bar was charged with chlorosulfonyl isocyanate (1.79 g, 12.7 mmol, 2.4 equiv) and cooled to 0 ºC. Formic acid (0.573 g, 12.5 mmol, 2.3 equiv) was added dropwise to the same flask over ca. 1 minute, followed by addition of 11.4 mL distilled CH_3CN. The reaction mixture was warmed to room temperature and stirred for 12 hours. The reaction was then cooled to 0 ºC and 0.894 g (5.32 mmol, 1.0 equiv) of the alcohol in 11.4 mL of DMA was added all at once *via* syringe. The reaction was warmed to room temperature and stirred for 3 hours. The reaction mixture was quenched by adding 20 mL H_2O, and poured into a separatory funnel containing an equal volume

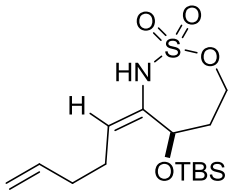
of Et_2O. The aqueous layer was extracted three times with Et_2O and the combined organic layers were washed five times with ca. 6 mL portions of H_2O. The organic layer was washed once with brine and dried over Na_2SO_4. After silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 Et_2O:hexanes, with a gradual increase to a ratio of 1:1 in 10% increments; CAM stain), 0.855 g (3.46 mmol, 65%) of the homoallenic sulfamate was obtained as a diastereomeric mixture with a ratio close to 1:1. The product is a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 – 5.03 (m, 2H), 4.65 (bs, 2H), 4.47 (qd, *J* = 6.1, 1.3 Hz, 1H), 2.48 – 2.43 (m, 2H), 2.17 – 2.05 (m, 1H), 2.01 – 1.94 (m, 2H), 1.43 (h, *J* = 7.3 Hz, 2H), 0.99 (ddd, *J* = 8.7, 6.8, 2.3 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.5, 205.4, 91.6, 91.5, 89.3, 89.2, 85.9, 85.7, 31.7, 31.4, 31.0, 31.0, 30.9, 30.9, 22.5, 22.5, 18.5, 18.4, 17.5, 17.3, 13.8, 13.8. HRMS (ESI) m/z calculated for $C_{11}H_{21}NO_3S$ $[M-H]^-$ 246.1169, found 246.1170.

III. One-pot synthesis of enesulfamates from homoallenic sulfamates.



General procedure: To a flame-dried round bottom flask equipped with a stir bar was added the corresponding homoallenic sulfamate (1.0 equiv) and $Rh_2(OAc)_4$ (0.0075 equiv). Dry CH_2Cl_2 was added to prepare a 0.1 M solution. The mixture was stirred vigorously at room temperature for 5 min to yield a green-blue solution. Iodosylbenzene (1.1 equiv) was added in one portion,

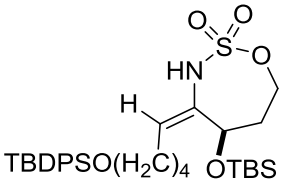
and the resulting mixture was stirred at room temperature for approximately 1 hour (for trisubstituted homoallenic sulfamte, the stirring time was increased to 75 minutes). Upon completion, the solution was concentrated by rotary evaporation. CH_3CN was added to the residue to prepare a 0.4 M solution, followed by the addition of Millipore water (20 equiv). The solution was stirred at room temperature for approximately 1 hour, poured into an Erlenmeyer flask and diluted by a factor of 2-3 with CH_2Cl_2. The solution was dried over Na_2SO_4 until the initially cloudy solution turned clear. The resulting solution was decanted and the residue was washed twice with CH_2Cl_2. The organic portions were combined and concentrated by rotary evaporation. Dry CH_2Cl_2 (0. 4 M) was then added to the residue to prepare a 0.4 M solution, which was cooled to 0 ºC. A single portion of 2,6-lutidine (1.2 equiv) was added, followed by the slow addition of TBSOTf (1.2 equiv). The reaction was stirred at 0 ºC for 30 minutes. The mixture was then quenched by addition of saturated NH_4Cl solution. The aqueous layer was extracted three times with CH_2Cl_2, and the combined organic layers were washed once with brine. The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation to yield a crude oil that is purified by silica gel chromatography to afford the *(E)*-enesulfamate, typically as a clear oil.



Compound 13. To a flame-dried round bottom flask equipped with a stir bar was added the corresponding homoallenic sulfamate (0.503 g, 2.31 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (0.0110 g, 0.0249 mmol, 0.0108 equiv). A portion of 23 mL dry CH_2Cl_2 was added to prepare a 0.1 M

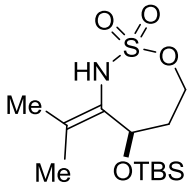
solution. Iodosylbenzene (0.610 g, 2.77 mmol, 1.2 equiv) was added in one portion. After vigorous stirring at room temperature for 25 minutes, 0.680 g of 4 Å MS was added to the reaction mixture. After another 10 minutes, the reaction mixture was filtered through a pad of celite. The celite cake was rinsed with CH_2Cl_2 and CH_2Cl_2 was removed from the combined organics *in vacuo*. To the crude aziridine product was added 5.8 mL CH_3CN, followed by 0.25 mL (0.25 g, 0.0139 mmol, 0.006 equiv) Millipore water. After 2.5 hours of stirring at room temperature, ^{1}H NMR showed the full consumption of the aziridine. The reaction mixture was diluted with ca. 20 mL with CH_2Cl_2 and dried over Na_2SO_4 until the initially cloudy solution turned clear. The resulting solution was decanted and the residue was washed twice with CH_2Cl_2. The organic portions were combined and concentrated by rotary evaporation. A portion of 5.8 mL of dry CH_2Cl_2 was added to the residue to prepare a 0.4 M solution, which was cooled to 0 ºC. A single portion of 2,6-lutidine (0.248 g, 2.32 mmol, 1.0 equiv) was added, followed by dropwise addition of TBSOTf (0.610 g, 2.31 mmol, 1.0 equiv) over ca. 1 minute. The reaction was stirred at 0 ºC for 90 minutes. The mixture was quenched by addition of saturated NH_4Cl solution. The aqueous layer was extracted three times with CH_2Cl_2, and the combined organic layers were washed once with brine. The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation to yield a crude oil that was purified by silica gel chromatography (carried out using a gradient method with the initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 2:23 in 1% increments; $KMnO_4$ stain) to afford 0.375 g (1.08 mmol, 47% yield) of **13** as clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.36 (s, 1H), 5.86 – 5.71 (m, 2H), 5.09 – 5.04 (m, 1H), 5.03 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.80 (t, *J* = 3.2 Hz, 1H), 4.69 (t, *J* = 12.6 Hz, 1H), 4.16 (dt, *J* = 13.0, 3.2 Hz, 1H), 2.24 – 2.16 (m, 4H), 2.12 (ddt, *J* = 15.1, 12.3, 3.0 Hz, 2H), 1.84 (dt, *J* = 15.0, 3.3 Hz, 1H), 0.90 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 131.9, 129.4, 116.2, 64.9, 64.7, 37.9, 33.2, 26.5, 25.8, 18.2, -4.7, -4.9. HRMS (ESI) m/z calculated for $C_{15}H_{29}NO_4SSi$ $[M+NH_4]^+$ 365.1925, found 365.1924.



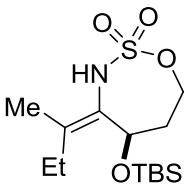
Compound 14. To a flame-dried round bottom flask equipped with a stir bar was added the corresponding homoallenic sulfamate (2.00 g, 4.23 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (0.0198 g, 0.0448 mmol, 0.0075 equiv). 42.2 mL of dry CH_2Cl_2 was added to prepare a 0.1 M solution. The mixture was stirred vigorously at room temperature for 5 minutes to yield a green-blue solution. Iodosylbenzene (1.02 g, 4.65 mmol, 1.1 equiv) was added in one portion, and the resulting mixture was stirred at room temperature for ca. 1 hour. The solution was then concentrated by rotary evaporation. A portion of 42.2 mL of CH_3CN was added to the residue to prepare a 0.4 M solution, followed by addition of Millipore water (3.80 g, 211 mmol, 20.0 equiv). The solution was stirred at room temperature for 1 hour, poured into an Erlenmeyer flask and diluted with 120 mL CH_2Cl_2. The solution was dried over Na_2SO_4 until the initially cloudy solution turned clear. The resulting solution was decanted and the residue was washed twice with CH_2Cl_2. The organic portions were combined and concentrated by rotary evaporation. A 10.5 mL portion of dry CH_2Cl_2 was then added to the residue to prepare a 0.4 M solution, which was cooled to 0 ºC. A single portion of 2,6-lutidine (1.10 g, 10.3 mmol, 2.4 equiv) was added, followed by dropwise addition of TBSOTf (2.30 g, 8.71 mmol, 2.1 equiv) over ca. 5 minutes. The reaction was stirred at 0 ºC for 30 minutes. The mixture was then quenched by addition of saturated NH_4Cl solution. The aqueous layer was extracted three times with CH_2Cl_2, and the combined organic layers were

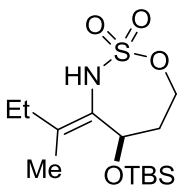
washed once with brine. The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation to yield a crude oil that was purified by silica gel chromatography (carried out using a gradient method with initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 3:17 in 3% increments; $KMnO_4$ stain) to afford 1.09 g (1.80 mmol, 43%) of **14** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 4H), 7.45 – 7.35 (m, 6H), 6.35 (bs, 1H), 5.73 (t, *J* = 7.8 Hz, 1H), 4.78 (t, *J* = 3.1 Hz, 1H), 4.67 (t, *J* = 12.6 Hz, 1H), 4.13 (dt, *J* = 13.0, 3.2 Hz, 1H), 3.66 (t, *J* = 5.8 Hz, 2H), 2.14 – 2.01 (m, 3H), 1.81 (dt, *J* = 15.3, 3.3 Hz, 1H), 1.62 – 1.48 (m, 4H), 1.04 (s, 9H), 0.89 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 134.0, 134.0, 131.5, 130.2, 129.7, 127.8, 64.8, 64.7, 63.6, 37.8, 32.3, 27.0, 26.6, 25.8, 25.6, 19.4, 18.2, -4.8, -4.9. HRMS (ESI) m/z calculated for $C_{31}H_{49}NO_5SSi_2$ $[M+NH_4]^+$ 621.3208, found 621.3204.



Compound 16. To a flame-dried round bottom flask equipped with a stir bar was added the corresponding homoallenic sulfamate (0.102 g, 0.531 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (0.0034 g, 0.0077 mmol, 0.0145 equiv). A 5 mL portion of dry CH_2Cl_2 was added to prepare a 0.1 M solution. The mixture was stirred vigorously at room temperature for 5 minutes to yield a green-blue solution. Iodosylbenzene (0.128 g, 0.583 mmol, 1.1 equiv) was added in one portion, and the resulting mixture was stirred at room temperature for 1 hour. The solution was then concentrated by rotary evaporation. A 2.1 mL portion of CH_3CN was added to the residue to prepare a 0.25 M solution, followed by addition of Millipore water (0.20 g, 11.1 mmol, 21.0 equiv). The solution was stirred at room temperature for 1 hour, poured into an Erlenmeyer flask

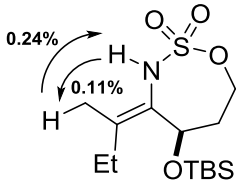
and diluted with 6 mL CH_2Cl_2. The solution was dried over Na_2SO_4 until the initially cloudy solution turned clear. The resulting solution was decanted and the residue was washed twice with CH_2Cl_2. The organic portions were combined and concentrated by rotary evaporation. A 1.3 mL portion of dry CH_2Cl_2 was then added to the residue to prepare a 0.4 M solution, which was cooled to 0 ºC. A single portion of 2,6-lutidine (0.0920 g, 0.859 mmol, 1.6 equiv) was added, followed by dropwise addition of TBSOTf (0.138 g, 0.621 mmol, 1.2 equiv) over ca. 1 minute. The reaction was stirred at 0 ºC for 30 minutes. The mixture was quenched by addition of saturated NH_4Cl solution. The aqueous layer was extracted three times with CH_2Cl_2 and the combined organic layers were washed once with brine. The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation to yield a crude oil that was purified by silica gel chromatography (carried out using a gradient method with initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 3:17 in 3% increments) to yield 53.2 mg of the enesulfamate (0.165 mmol, 31%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.20 (bs, 1H), 4.87 (t, *J* = 3.1 Hz, 1H), 4.70 (t, *J* = 12.5 Hz, 1H), 4.14 (dt, *J* = 12.9, 3.2 Hz, 1H), 2.08 (ddt, *J* = 15.2, 12.3, 3.2 Hz, 1H), 1.92 (s, 3H), 1.81 (dt, *J* = 14.8, 3 Hz, 1H), 1.76 (s, 3H), 0.89 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7, 125.4, 65.8, 64.5, 37.0, 25.8, 20.6, 19.0, 18.2, -4.8, -5.0. HRMS (ESI) m/z calculated for $C_{13}H_{27}NO_4SSi$ [M-H]$^-$ 320.1357, found 320.1358.

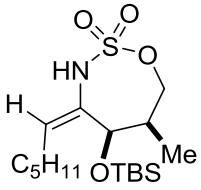




Compound 17. To a flame-dried round bottom flask equipped with a stir bar was added the corresponding homoallenic sulfamate (1.52 g, 7.39 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (0.0274 g, 0.0620 mmol, 0.0084 equiv). A 78 mL portion of dry CH_2Cl_2 was added to prepare a 0.1 M solution. The mixture was stirred vigorously at room temperature for 5 minutes to yield a green-blue solution. Iodosylbenzene (1.78 g, 8.09 mmol, 1.1 equiv) was added in one portion, and the resulting mixture was stirred at room temperature for 1.5 hour. The solution was then concentrated by rotary evaporation. A 18.3 mL portion of CH_3CN was added to the residue to prepare a 0.4 M solution, followed by addition of Millipore water (2.60 g, 144 mmol, 20.0 equiv). The solution was stirred at room temperature for 1 hour, poured into an Erlenmeyer flask and diluted with ca. 60 mL CH_2Cl_2. The solution was dried over Na_2SO_4 until the initially cloudy solution turned clear. The resulting solution was decanted and the residue was washed twice with CH_2Cl_2. The organic portions were combined and concentrated by rotary evaporation. A portion of 18 mL of dry CH_2Cl_2 was then added to the residue to prepare a 0.4 M solution, which was cooled to 0 ºC. A single portion of 2,6-lutidine (0.920 g, 8.59 mmol, 1.2 equiv) was added, followed by dropwise addition of TBSOTf (3.07 g, 11.6 mmol, 1.6 equiv) over ca. 10 minutes. The reaction was stirred at 0 ºC for 30 minutes. The mixture was quenched by addition of saturated NH_4Cl solution. The aqueous layer was extracted three times with CH_2Cl_2 and the combined organic layers were washed once with brine. The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation to yield a crude oil that was purified by silica gel chromatography (carried out using a gradient method with initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 1:19 in 1% increments; $KMnO_4$ stain). The product was obtained as 0.546 g (1.63 mmol, 22%) of enesulfamate **17** isolated as an isomeric mixture (*E:Z* ratio = 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.22 (bs, 0.85H),

6.15 (bs, 0.15H), 4.88 (t, *J* = 3.0 Hz, 0.85H), 4.83 (t, *J* = 3.0 Hz, 0.15H), 4.68 (t, *J* = 12.5 Hz, 1H), 4.13 (dt, *J* = 12.9, 3.3 Hz, 1H), 2.55 (dq, *J* = 14.9, 7.6 Hz, 0.15H), 2.23 (dq, *J* = 14.9, 7.6 Hz, 0.15H), 2.18 – 1.99 (m, 2.7H), 1.90 (s, 2.55H), 1.82 (dt, *J* = 15.0, 3.6 Hz, 1H), 1.73 (s, 0.45H), 1.04 (t, *J* = 7.6 Hz, 2.55H), 0.99 (t, *J* = 7.5 Hz, 0.45H), 0.88 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H). *E* isomer: ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 125.2, 65.6, 64.4, 37.5, 25.9, 25.8, 18.1, 17.7, 12.7, -4.7, -4.9. *Z* isomer: ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 124.9, 65.9, 64.5, 36.9, 26.4, 18.2, 16.1, 11.8, -4.8, -5.0. HRMS (ESI) m/z calculated for $C_{14}H_{29}NO_4SSi$ $[M+Na]^+$ 358.1479, found 358.1476. The identity of the major isomer as *E* was confirmed by NOE experiments:

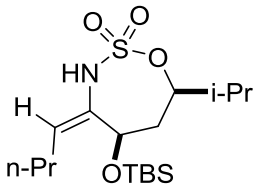




Compound 18. Compound **18** was prepared by a modification of the general procedure. To a flame-dried, round bottom flask equipped with a stir bar was added the corresponding homoallenic sulfamate (2.50 g, 10.7 mmol, 1.0 equiv) and $Rh_2(TPA)_4$ (0.145 g, 0.107 mmol, 0.01 equiv). A 108 mL portion of dry CH_2Cl_2 was added to prepare a 0.1 M solution. The mixture was stirred vigorously at room temperature for 5 minutes to yield a green-blue solution. Iodosylbenzene (2.83 g, 12.9 mmol, 1.2 equiv) was added in one portion, and the resulting mixture was stirred at room temperature for 1.2 hour. The solution was then concentrated by rotary evaporation. A 53 mL portion of CH_3CN was added to the residue to prepare a 0.2 M

solution, followed by addition of Millipore water (4.0 g, 222 mmol, 21.0 equiv). The solution was stirred at room temperature for 1 hour, poured into an Erlenmeyer flask and diluted with 160 mL CH_2Cl_2. The solution was dried over Na_2SO_4 until the initially cloudy solution turned clear. The resulting solution was decanted and the residue was washed twice with CH_2Cl_2. The organic portions were combined and concentrated by rotary evaporation. The crude alcohol (with a *dr* of 3:1) was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 7:18 in 4% increments; $KMnO_4$ stain) to separate the *anti* and *syn* stereoisomers prior to silylation. A 3.5 mL portion of dry CH_2Cl_2 was added to 0.349 g (1.33 mmol, 1.0 equiv) of the *syn*-isomer to prepare a 0.4 M solution, which was cooled to 0 ºC. A single portion of 2,6-lutidine (0.212 g, 1.97 mmol, 1.5 equiv) was added to 0.349 g (1.33 mmol, 1.0 equiv) of the *syn*-isomer, followed by the dropwise addition of TBSOTf (0.702 g, 2.66 mmol, 2.0 equiv) over ca. 1 minute. The reaction was stirred at 0 ºC for 30 minutes. The mixture was quenched by addition of saturated NH_4Cl solution. The aqueous layer was extracted three times with CH_2Cl_2, and the combined organic layers were washed once with brine. The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation to yield a crude oil that was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 1:19 in 1% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain). A 0.215 g (0.571 mmol, 43%) portion of compound **18** was obtained as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 6.46 (bs, 1H), 5.84 (t, *J* = 7.8 Hz, 1H), 4.31 – 4.22 (m, 2H), 3.27 (dd, *J* = 13.0, 2.7 Hz, 1H), 1.81 – 1.65 (m, 3H), 1.24 – 1.09 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.79 (s, 9H), 0.37 (d, *J* = 7.4 Hz, 3H), -0.14 (s, 3H), -0.14 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 132.4, 129.7, 69.5, 68.3, 40.4,

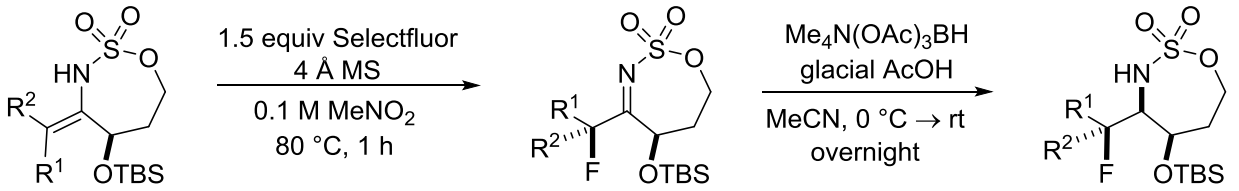
31.7, 29.0, 26.7, 25.7, 22.8, 18.2, 14.2, 13.5, -5.1, -5.2. HRMS (ESI) m/z calculated for $C_{17}H_{35}NO_4SSi$ $[M+NH_4]^+$ 395.2394, found 395.2394.



Compound 20. Compound **20** was prepared by a modification of the general procedure. To a flame-dried, round bottom flask equipped with a stir bar was added the corresponding homoallenic sulfamate (1.00 g, 4.04 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (0.0136 g, 0.0308 mmol, 0.0076 equiv). A 40 mL portion of dry CH_2Cl_2 was added to prepare a 0.1 M solution. The mixture was stirred vigorously at room temperature for 5 min to yield a green-blue solution. Iodosylbenzene (0.980 g, 4.45 mmol, 1.1 equiv) was added in one portion, and the resulting mixture was stirred at room temperature for 1 hour. The solution was concentrated by rotary evaporation and 16 mL of CH_3CN added to the residue to prepare a 0.25 M solution, followed by addition of Millipore water (1.45 g, 80.6mmol, 20.0 equiv). The solution was stirred at room temperature for 1 hour, poured into an Erlenmeyer flask and diluted with ca. 50 mL CH_2Cl_2. The solution was dried over Na_2SO_4 until the initially cloudy solution turned clear. The resulting solution was decanted and the residue was washed twice with CH_2Cl_2. The organic portions were combined and concentrated by rotary evaporation. The crude alcohol was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 2:3 in 5% increments; $KMnO_4$ stain) to yield 0.202 g of the *syn* stereoisomer (0.767 mmol, 19%) prior to silylation. A 2 mL portion of dry CH_2Cl_2 was added to 0.202 g (0.767 mmol, 1.0 equiv) of the *syn*-isomer to

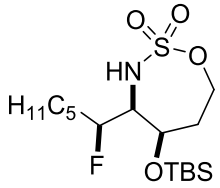
prepare a 0.4 M solution, which was cooled to 0 ºC. A single portion of 2,6-lutidine (0.101 g, 0.944 mmol, 1.2 equiv) was added, followed by dropwise addition of TBSOTf (0.207 g, 0.932 mmol, 1.2 equiv) over ca. 1 minute. The reaction was stirred at 0 ºC for 30 minutes. The mixture was quenched by addition of saturated NH_4Cl solution. The aqueous layer was extracted three times with CH_2Cl_2 and the combined organic layers were washed once with brine. The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation to yield a crude oil that was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 1:17 in 3% increments; $KMnO_4$ stain). A 0.120 g portion of compound **20** (0.318 mmol, 41%) was obtained as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.08 (bs, 1H), 5.86 (t, *J* = 7.8 Hz, 1H), 4.80 (dd, *J* = 7.8, 3.9 Hz, 1H), 4.30 (ddd, *J* = 11.1, 5.4, 2.5 Hz, 1H), 2.20 (ddd, *J* = 15.4, 7.8, 2.5 Hz, 1H), 2.16 – 2.02 (m, 3H), 1.82 (o, *J* = 6.9 Hz, 1H), 1.47 (h, *J* = 7.3 Hz, 2H), 0.98 – 0.93 (m, 9H), 0.90 (s, 9H), 0.11 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.3, 131.8, 85.6, 67.7, 40.8, 33.0, 29.2, 25.9, 22.5, 18.6, 18.2, 17.4, 14.0, -4.6, -4.8. HRMS (ESI) m/z calculated for $C_{17}H_{35}NO_4SSi$ $[M-H]^-$ 376.1983, found 376.1982.

IV. One-pot synthesis of F-N-O triads from enesulfamates.



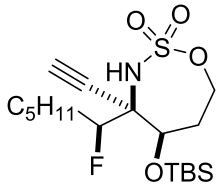
General procedure: To a flame-dried, round bottom flask equipped with a stir bar was added the corresponding enesulfamate (1.0 equiv), Selectfluor (1.5 equiv), and 4 Å MS (same amount as

Selectfluor). Dry CH_3NO_2 was added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for 1 hour. The reaction mixture was then filtered through a pad of celite, and the filtrate concentrated by rotary evaporation. Dry CH_3CN (CH_3CN:CH_3NO_2 = 1:1 v/v) was added to the crude imine, and the reaction mixture was cooled to 0 ºC. Glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (3.0 equiv). The reaction mxiture was warmed to rt and stirred overnight, after which TLC indicated complete consumption of the starting material. The reaction mixture was transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture. The crude product was purified by silica gel chromatography (solvents given for each specific compound below) to give the all-*syn* product as the major diastereomer.



Compound 7a. To a flame-dried, round bottom flask equipped with a stir bar was added the enesulfamate **7** (0.500 g, 1.38 mmol, 1.0 equiv), Selectfluor (0.733 g, 2.07 mmol, 1.5 equiv), and 0.737 g of 4 Å MS. Dry CH_3NO_2 (13.7 mL) was then added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for 1 hour. The reaction mixture was then filtered through a pad of celite. The celite cake was rinsed with CH_2Cl_2. The combined organics were concentrated by rotary evaporation. Dry CH_3CN (13.7 mL) was added to the crude imine and the reaction mixture was cooled to 0 ºC. Glacial AcOH (13.7 mL, AcOH:CH_3CN = 1:1 v/v) was then added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (1.09 g, 4.13 mmol, 3.0 equiv). The

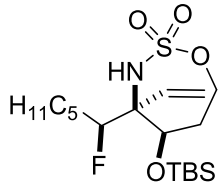
reaction mixture was warmed up to room temperature and stirred for 3 hours. The reaction mixture was transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture, which was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 7:3 in 10% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to give the all-*syn* **7a** as the major diastereomer (0.347 g, 0.906 mmol, 66%) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 5.75 (d, *J* = 10.7 Hz, 1H), 4.63 (t, *J* = 12.4 Hz, 1H), 4.24 (dddd, *J* = 48.2, 9.0, 4.2, 2.3 Hz, 1H), 3.74 (t, *J* = 2.8 Hz, 1H), 3.70 (dt, *J* = 13.0, 3.3 Hz, 1H), 3.30 (ddd, *J* = 25.5, 10.7, 2.3 Hz, 1H), 2.10 – 1.95 (m, 1H), 1.74 – 1.30 (m, 9H), 1.06 (t, *J* = 7.1 Hz, 3H), 1.00 (s, 9H), 0.12 (d, *J* = 1.3 Hz, 3H), 0.00 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 95.0 (d, *J* = 179.1 Hz), 69.5, 63.8, 58.1 (d, *J* = 18.2 Hz), 37.3, 32.3 (d, *J* = 21.0 Hz), 31.9, 25.9, 25.0 (d, *J* = 4.9 Hz), 22.9, 18.0, 14.2, -4.4, -5.1 (d, *J* = 3.2 Hz).^{19}F NMR (471 MHz, C_6D_6) δ -193.61 (dddd, *J* = 47.1, 32.0, 25.5, 13.7 Hz). HRMS (ESI) *m*/*z* calculated for $C_{16}H_{34}FNO_4SSi$ [M + H^+] 384.2035, found 384.2029.



Compound 8a. The enesulfamate **5** (0.400 g, 1.10 mmol, 1.0 equiv) was added to a 25 mL round bottom flask, followed by the addition of Selectfluor (0.589 g, 1.65 mmol, 1.5 equiv) and 0.589 g of 4 Å MS. Distilled CH_3NO_2 (11 mL) was added to make a 0.1 M solution. The reaction was stirred at 80 ºC for 1 hour. Dry CH_2Cl_2 (40 mL) was added to the reaction until no more white

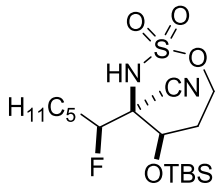
precipitates crashed out. The reaction mixture was then filtered through a pad of celite and concentrated by rotary evaporation to yield the imine. Ethynyl magnesium bromide (6.6 mL, 3.3 mmol, 3.0 equiv) was cooled at 0 ºC for at least 15 min before use. Dry THF (2.2 mL) was added to the imine to make a 0.5 M solution. The imine solution was transferred to the cooled ethynyl magnesium bromide via cannula transfer. An extra 1 mL of dry THF was used to ensure quantitative transfer. The reaction was stirred at 0 ºC for 60 minutes until complete consumption of the starting material was observed by TLC (CH_2Cl_2:hexanes = 1/1, $KMnO_4$ stain). The reaction was quenched by the addition of 20 mL of saturated NH_4Cl solution. The mixture was transferred to a separatory funnel, and the organic layer was extracted three times with EtOAc and washed once with saturated NH_4Cl solution and once with brine, then dried over Na_2SO_4 and concentrated by rotary evaporation to yield the diastereomeric mixture. The product was purified by column chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 1:0 in 10% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to give the all-*syn* **8a** as the major diastereomer (0.314 g, 0.771 mmol, 70%). The product is a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (bs, 1H), 4.63 (t, *J* = 12.2 Hz, 1H), 4.43 (ddd, *J* = 48.4, 10.5, 2.1 Hz, 1H), 4.22 (dd, *J* = 4.9, 1.8 Hz, 1H), 4.17 (dt, *J* = 12.8, 3.4 Hz, 1H), 2.78 (s, 1H), 2.74 (ddt, *J* = 16.0, 11.6, 2.5 Hz, 1H), 1.99 – 1.87 (m, 1H), 1.82 (dt, *J* = 15.9, 4.1 Hz, 1.5 H), 1.78 – 1.70 (m, 0.5H), 1.63 – 1.52 (m, 1H), 1.42 – 1.26 (m, 5H), 0.93 – 0.86 (m, 12H), 0.10 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 95.9 (d, *J* = 188.9 Hz), 80.8 (d, *J* = 1.4 Hz), 76.3 (d, *J* = 6.0 Hz), 73.8, 64.3, 60.9 (d, *J* = 18.9 Hz), 34.5, 31.6, 30.6 (d, *J* = 21.3 Hz), 25.9, 25.0 (d, *J* = 3.2 Hz), 22.6, 18.1, 14.1, -4.1, -4.9 (d, *J* = 2.2 Hz).^{19}F NMR (471 MHz, $CDCl_3$) δ -191.34 (ddd, *J* =

48.8, 41.5, 13.5 Hz). HRMS (ESI) *m*/*z* calculated for $C_{18}H_{34}FNO_4SSi$ [M + NH_4^+] 425.2300, found 425.2299.



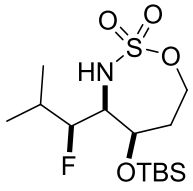
Compound 9a. A 0.351 g (0.965 mmol, 1.0 equiv) portion of the enesulfamate **5** was added to a 25 mL round-bottom flask, followed by sequential addition of Selectfluor (0.513g, 1.44 mmol, 1.5 equiv) and 4 Å MS (0.513 g). A portion of CH_3NO_2 (9.6 mL) was added to make a 0.1 M solution and the reaction mixture was stirred at 80 ºC for 1 hour. Dry CH_2Cl_2 (40 mL) was added until no more white precipitates crashed out. The reaction mixture was then filtered through a pad of celite and concentrated by rotary evaporation to yield the crude imine. Vinyl magnesium bromide (2.9 mL, 2.89 mmol, 3.0 equiv) was cooled at -78 ºC for at least 15 minutes before use. Dry THF (1.9 mL) was added to the imine to make a 0.5 M solution and then transferred to the cooled vinyl magnesium bromide solution via cannula transfer. The reaction mixture was stirred at -78 ºC for 30 minutes until complete consumption of the starting material was observed by TLC (CH_2Cl_2:hexanes = 1:1, $KMnO_4$ stain). A saturated NH_4Cl solution (20 mL) was added to quench the reaction, the mixture transferred to a separatory funnel, and the organic layer extracted three times with EtOAc. The combined organics were washed once with brine, dried over Na_2SO_4 and concentrated by rotary evaporation to yield the crude product as a diastereomeric mixture, which was purified by column chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 1:0 in 10% increments; 1% Et_2O was added to improve separation

among diastereomers; $KMnO_4$ stain) to give the all- *syn* **9a** as the major diastereomer (0.244 g, 0.597 mmol, 61%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.18 (dd, *J* = 18.0, 11.4 Hz, 1H), 5.43 (d, *J* = 11.5 Hz, 1H), 5.30 (d, *J* = 18.0 Hz, 1H), 5.16 (bs, 1H), 4.64 (dd, *J* = 48.0, 11.1 Hz, 1H), 4.52 (dd, *J* = 12.5, 9.1 Hz, 1H), 4.32 (d, *J* = 6.4 Hz, 1H), 4.13 (ddd, *J* = 12.7, 6.8, 2.4 Hz, 1H), 2.31 (dd, *J* = 13.4, 9.2 Hz, 1H), 2.11 (dt, *J* = 14.8, 6.6 Hz, 1H), 1.70 – 1.43 (m, 3H), 1.35 – 1.21 (m, 5H), 0.93 (s, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.11 (s, 3H), 0.11 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1 (d, *J* = 4.4 Hz), 118.2, 96.2 (d, *J* = 185.3 Hz), 74.5, 66.3 (d, *J* = 16.2 Hz), 65.9, 34.6 (d, *J* = 3.5 Hz), 31.6, 29.9 (d, *J* = 21.8 Hz), 26.0, 25.2 (d, *J* = 3.4 Hz), 22.6, 18.1, 14.1, -3.9, -4.8 (d, *J* = 1.5 Hz).^{19}F NMR (471 MHz, $CDCl_3$) δ -191.22 (td, *J* = 46.2, 13.2 Hz). HRMS (ESI) *m*/*z* calculated for $C_{18}H_{36}FNO_4SSi$ [M + H^+] 410.2191, found 410.2187.



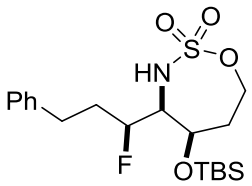
Compound 10a. The enesulfamate **5** (0.150 g, 0.413 mmol, 1.0 equiv) was added to a 10 mL round bottom flask, followed by addition of Selectfluor (0.219 g, 0.618 mmol, 1.5 equiv) and 4 Å MS (0.219 g). CH_3NO_2 (4.1 mL) was added to make a 0.1 M solution and the reaction mixture was stirred at 80 ºC for 1 hour. Dry CH_2Cl_2 (20 mL) was added until no more white precipitate was observed to crash out. The resulting mixture was then filtered through a pad of celite and concentrated by rotary evaporation to yield the crude imine. Dry CH_3CN (4.1 mL) was added to the imine to make a 0.1 M solution, followed by addition of Bu_4NCN (0.223 g, 0.834 mmol, 2.0 equiv). The reaction was stirred at room temperature for 2.6 hour until complete consumption of the starting material was observed by TLC (EtOAc/hexanes = 1/1, $KMnO_4$ stain). The mixture was transferred to a separatory funnel; five times the volume of CH_2Cl_2 was added. The organic

layer was washed once with $NaHCO_3$, once with saturated NH_4Cl, twice with brine, then dried over Na_2SO_4 and concentrated by rotary evaporation to yield the product as a mixture of diastereomers. The product was purified by column chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 1:0 in 10% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to give the all-*syn* **10a** as the major diastereomer (67.2 mg, 0.165 mmol, 40%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (bs, 1H), 4.83 (ddd, *J* = 47.0, 10.7, 2.2 Hz, 1H), 4.56 (dd, *J* = 7.0, 1.7 Hz, 1H), 4.51 (ddd, *J* = 12.6, 8.5, 2.0 Hz, 1H), 4.29 (ddd, *J* = 12.6, 6.9, 2.5 Hz, 1H), 2.38 (ddt, *J* = 16.3, 8.5, 2.2 Hz, 1H), 2.26 (dtd, *J* = 16.2, 7.0, 1.9 Hz, 1H), 2.00 – 1.90 (m, 1H), 1.82 (ddddd, *J* = 41.3, 14.4, 10.2, 5.9, 2.2 Hz, 1H), 1.68 – 1.57 (m, 1H), 1.48 – 1.39 (m, 1H), 1.38 – 1.30 (m, 4H), 0.94 – 0.88 (m, 12H), 0.17 (s, 3H), 0.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 115.5 (d, *J* = 6.5 Hz), 92.9 (d, *J* = 189.6 Hz), 73.9, 66.3, 61.0 (d, *J* = 20.4 Hz), 35.4 (d, *J* = 3.1 Hz), 31.3, 30.9 (d, *J* = 21.1 Hz), 25.8, 24.9 (d, *J* = 3.0 Hz), 22.5, 18.1, 14.0, -4.2, -4.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -192.49 (ddd, *J* = 47.3, 41.5, 14.5 Hz). HRMS (ESI) *m*/*z* calculated for $C_{17}H_{33}FN_2O_4SSi$ [M + NH_4^+] 426.2253, found 426.2245.



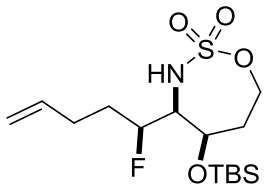
Compound 11a. To a flame-dried, round bottom flask equipped with a stir bar was added the corresponding enesulfamate (102 mg, 0.305 mmol, 1.0 equiv), Selectfluor (160 mg, 0.452 mmol, 1.5 equiv) and 4 Å MS (165 mg). Dry CH_3NO_2 (3 mL) was added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for 1 hour. The reaction mixture was then filtered through a pad

of celite and the filtrate concentrated by rotary evaporation. A 3 mL portion of dry CH_3CN (CH_3CN:CH_3NO_2 = 1:1 v/v) was added to the crude imine, and the reaction mixture was cooled to 0 ºC. 3 mL of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (237 mg, 0.900 mmol, 3.0 equiv). The reaction mxiture was warmed up to room temperature and stirred overnight. The reaction mixture was then transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 2:3 in 8% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to give the all-*syn* product **11a** (20.9 mg, 0.0588 mmol, 19%) as the major diastereomer. The product was a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (d, *J* = 10.8 Hz, 1H), 4.64 (t, *J* = 12.4 Hz, 1H), 4.20 (dd, *J* = 4.1, 2.3 Hz, 1H), 4.15 (dt, *J* = 12.8, 3.2 Hz, 1H), 4.04 (ddd, *J* = 47.3, 8.2, 2.3 Hz, 1H), 3.50 (ddd, *J* = 26.2, 10.8, 2.3 Hz, 1H), 2.19 – 2.06 (m, 2H), 1.85 (dt, *J* = 15.4, 3.8 Hz, 1H), 1.01 (dd, *J* = 6.7, 1.5 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.91 (s, 9H), 0.10 (d, *J* = 1.4 Hz, 3H), 0.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 99.5 (d, *J* = 182.8 Hz), 70.1, 64.3, 55.7 (d, *J* = 17.5 Hz), 37.6, 29.7 (d, *J* = 19.9 Hz), 25.9, 18.4 (d, *J* = 7.5 Hz), 18.1, 17.8 (d, *J* = 6.2 Hz), -4.3, -4.9 (d, *J* = 3.2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -196.82 (ddd, *J* = 47.5, 26.4, 11.9 Hz). HRMS (ESI) m/z calculated for $C_{14}H_{30}FNO_4SSi$ $[M-H]^-$ 354.1576, found 354.1577.



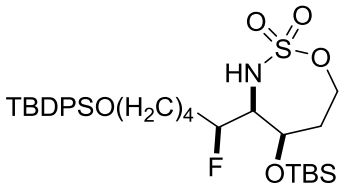
Compound 12a. To a flame-dried, round bottom flask equipped with a stir bar was added the enesulfamate **12** (398 mg, 1.00 mmol, 1.0 equiv), Selectfluor (531 mg, 1.50 mmol, 1.5 equiv), and 4 Å MS (531 mg). Dry CH_3NO_2 (10 mL) was added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for 1.5 hour. The reaction mixture was then filtered through a pad of celite, and the filtrate concentrated by rotary evaporation. A 10 mL portion of dry CH_3CN (CH_3CN:CH_3NO_2 = 1:1 v/v) was added to the crude imine, and the reaction mixture was cooled to 0 ºC. A 10 mL portion of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (790 mg, 3.00 mmol, 3.0 equiv). The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 Et_2O:hexanes, with a gradual increase to a ratio of 3:7 in 6% increments; $KMnO_4$ stain) to yield 283 mg of the all-*syn* stereotriad **12a** (0.678 mmol, 68%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.16 (m, 3H), 5.48 (d, *J* = 10.7 Hz, 1H), 4.59 (t, *J* = 12.5 Hz, 1H), 4.43 (ddt, *J* = 48.3, 9.1, 3.3 Hz, 1H), 4.17 (m, 1H), 4.10 (dt, *J* = 12.8, 2.8 Hz, 1H), 3.34 (ddd, *J* = 23.7, 10.6, 2.6 Hz, 1H), 2.79 (ddd, *J* = 14.0, 9.1, 5.1 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.19 (ttd, *J* = 13.7, 9.1, 5.0 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.93 – 1.75 (m, 2H), 0.89 (s, 9H), 0.06 (s, 3H), 0.05 (s,

3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 128.6, 128.5, 126.2, 93.1 (d, *J* = 179.6 Hz), 69.1, 64.3, 58.0 (d, *J* = 17.7 Hz), 37.2, 33.9 (d, *J* = 21.2 Hz), 30.8 (d, *J* = 5.1 Hz), 25.8, 17.9, -4.4, -5.1 (d, *J* = 2.7 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -195.08 (dddd, *J* = 46.8, 33.2, 24.1, 12.8 Hz). HRMS (ESI) m/z calculated for $C_{19}H_{32}FNO_4SSi$ $[M+H]^+$ 418.1878, found 418.1873.



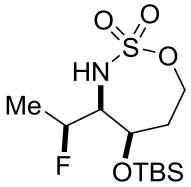
Compound 13a. To a flame-dried, round bottom flask equipped with a stir bar was added the enesulfamate **13** (48.9 mg, 0.141 mmol, 1.0 equiv), Selectfluor (78.0 mg, 0.220 mmol, 1.6 equiv), and 4 Å MS (80.0 mg). Dry CH_3NO_2 (1.5 mL) was added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for 1 hour. The reaction mixture was then filtered through a pad of celite, and the filtrate concentrated by rotary evaporation. A 1.5 mL portion of dry CH_3CN (CH_3CN:CH_3NO_2 = 1:1 v/v) was added to the crude imine and the reaction mixture was cooled to 0 ºC. A 1.5 mL portion of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (119 mg, 0.453 mmol, 3.2 equiv). The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 7:3 in 10% increments; 1% Et_2O was added

to improve separation among diastereomers; $KMnO_4$ stain) to yield 29.8 mg of the all-*syn* stereotriad **13a** (0.0811 mmol, 58%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 17.0, 10.0, 6.7 Hz, 1H), 5.45 (d, *J* = 10.7 Hz, 1H), 5.07 (dd, *J* = 17.2, 1.8 Hz, 1H), 5.02 (d, *J* = 10.2 Hz, 1H), 4.63 (t, *J* = 12.5 Hz, 1H), 4.58 – 4.40 (m, 1H), 4.24 (t, *J* = 2.8 Hz, 1H), 4.16 (dt, *J* = 13.0, 3.3 Hz, 1H), 3.36 (ddd, *J* = 24.4, 10.7, 2.6 Hz, 1H), 2.28 – 2.08 (m, 3H), 1.99 (ttd, *J* = 14.3, 8.6, 5.9 Hz, 1H), 1.86 (dt, *J* = 15.5, 3.7 Hz, 1H), 1.76 – 1.61 (m, 1H), 0.91 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 116.0, 93.7 (d, *J* = 179.6 Hz), 69.4, 64.3, 58.0 (d, *J* = 18.0 Hz), 37.5, 31.4 (d, *J* = 21.3 Hz), 29.0 (d, *J* = 5.3 Hz), 25.9, 18.1, -4.2, -4.9 (d, *J* = 2.9 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -194.62 (dddd, *J* = 46.7, 31.8, 24.1, 13.3 Hz). HRMS (ESI) m/z calculated for $C_{15}H_{30}FNO_4SSi$ $[M-H]^-$ 366.1576, found 366.1575.



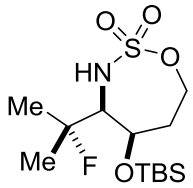
Compound 14a. To a flame-dried, round bottom flask equipped with a stir bar was added the enesulfamate **14** (78.6 mg, 0.130 mmol, 1.0 equiv), Selectfluor (69.7 mg, 0.197 mmol, 1.5 equiv), and 4 Å MS (69.5 mg). Dry CH_3NO_2 (1.3 mL) was added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for 1.5 hour. The reaction mixture was filtered through a pad of celite and the filtrate concentrated by rotary evaporation. A 1.3 mL portion of dry CH_3CN (CH_3CN:CH_3NO_2 = 1:1 v/v) was added to the crude imine and the reaction mixture was cooled to 0 ºC. A 1.3 mL portion of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (105 mg, 0.403 mmol, 3.1 equiv). The reaction mixture was warmed up to room temperature and stirred for 15 hours. The reaction mixture was then

transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 2:3 in 8% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to yield 54.4 mg of the all-*syn* stereotriad **14a** (0.0892 mmol, 69%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 4H), 7.45 – 7.36 (m, 6H), 5.43 (d, *J* = 10.8 Hz, 1H), 4.63 (t, *J* = 12.4 Hz, 1H), 4.44 (ddt, *J* = 47.8, 8.9, 3.3 Hz, 1H), 4.25 – 4.20 (m, 1H), 4.15 (dt, *J* = 13.0, 3.3 Hz, 1H), 3.67 (t, *J* = 6.0 Hz, 2H), 3.33 (ddd, *J* = 23.9, 10.8, 2.7 Hz, 1H), 2.11 (ddt, *J* = 14.9, 12.1, 2.7 Hz, 1H), 1.90 – 1.80 (m, 2H), 1.65 – 1.50 (m, 4H), 1.50 – 1.40 (m, 1H), 1.05 (s, 9H), 0.91 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 134.1, 134.1, 129.5, 127.6, 94.2 (d, *J* = 179.5 Hz), 69.2, 64.3, 63.7, 57.9 (d, *J* = 18.1 Hz), 37.3, 32.1, 31.7 (d, *J* = 21.1 Hz), 26.9, 25.8, 21.2 (d, *J* = 4.9 Hz), 19.2, 17.9, -4.4, -5.0 (d, *J* = 2.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -193.44 – -193.75 (m). HRMS (ESI) m/z calculated for $C_{31}H_{50}FNO_5SSi_2$ $[M+NH_4]^+$ 641.3271, found 641.3270.



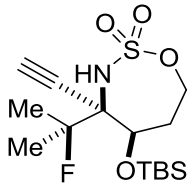
Compound 15a. To a flame-dried, round bottom flask equipped with a stir bar was added the enesulfamate **15** (102 mg, 0.325 mmol, 1.0 equiv), Selectfluor (177 mg, 0.498 mmol, 1.5 equiv), and 4 Å MS (177 mg). Dry CH_3NO_2 (3.3 mL) was added to prepare a 0.1 M solution. The

mixture was stirred at 80 ºC for 1 hour. The reaction mixture was then filtered through a pad of celite, and the filtrate concentrated by rotary evaporation. 3.3 mL of dry CH_3CN (CH_3CN:CH_3NO_2 = 1:1 v/v) was added to the crude imine, and the reaction mixture was cooled to 0 ºC. A 3.3 mL portion of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (266 mg, 1.01 mmol, 3.1 equiv). The reaction mixture was warmed up to room temperature and stirred for 4.5 hours. The reaction mixture was then transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 2:3 in 8% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to yield 73.9 mg of the all-*syn* stereotriad **15a** (0.226 mmol, 69%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 (d, *J* = 10.7 Hz, 1H), 4.66 (dqd, *J* = 47.6, 6.3, 3.0 Hz, 1H), 4.64 (t, 1H), 4.25 (dd, *J* = 3.5, 2.4 Hz, 1H), 4.16 (dt, *J* = 13.0, 3.3 Hz, 1H), 3.31 (ddd, *J* = 22.9, 10.8, 3.0 Hz, 1H), 2.13 (ddt, *J* = 15.4, 12.1, 2.8 Hz, 1H), 1.86 (dt, *J* = 15.6, 3.7 Hz, 1H), 1.43 (dd, *J* = 23.9, 6.3 Hz, 3H), 0.91 (s, 9H), 0.10 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 90.9 (d, *J* = 176.8 Hz), 69.3 (d, *J* = 1.6 Hz), 64.5, 59.4 (d, *J* = 18.1 Hz), 37.7, 26.1, 18.5 (d, *J* = 23.0 Hz), 18.3, -4.0, -4.8 (d, *J* = 2.7 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -186.11 (dp, *J* = 47.4, 23.7 Hz). HRMS (ESI) m/z calculated for $C_{12}H_{26}FNO_4SSi$ $[M+H]^+$ 328.1409, found 328.1405.



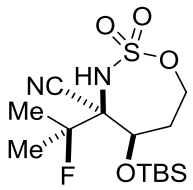
Compound 16a. To a flame-dried, round bottom flask equipped with a stir bar was added the enesulfamate **16** (34.3 mg, 0.107 mmol, 1.0 equiv), Selectfluor (57.4 mg, 0.162 mmol, 1.5 equiv), and 4 Å MS (56.0 mg). Dry CH_3NO_2 (1 mL) was added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for 1 hour. The reaction mixture was then filtered through a pad of celite, and the filtrate concentrated by rotary evaporation. A 1 mL portion of dry CH_3CN (CH_3CN:CH_3NO_2 = 1:1 v/v) was added to the crude imine and the reaction mixture cooled to 0 ºC. A 1 mL portion of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (266 mg, 1.01 mmol, 3.1 equiv). The reaction mixture was warmed to room temperature and stirred for 7 hours. The reaction mixture was transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 1:4 in 4% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to yield 20.3 mg **16a** (0.059 mmol, 56%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (d, *J* = 10.6 Hz, 1H), 4.62 (t, *J* = 12.6 Hz, 1H), 4.58 – 4.54 (m, 1H), 4.17 (dt, *J* = 13.0, 3.2 Hz, 1H), 3.29 (dd, *J* = 14.0, 10.6 Hz, 1H), 2.08 (ddt, *J* = 15.0, 12.1, 2.6 Hz, 1H), 1.90 (dt, *J* = 15.6, 3.8 Hz, 1H), 1.46 (d, *J* = 21.5 Hz, 3H), 1.40 (d, *J* = 21.7 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ

95.4 (d, *J* = 173.4 Hz), 65.5 (d, *J* = 2.9 Hz), 64.4, 61.9 (d, *J* = 26.6 Hz), 37.5, 26.1, 26.0 (d, *J* = 23.5 Hz), 23.7 (d, *J* = 24.3 Hz), 18.2, -3.5, -4.5 (d, *J* = 1.7 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -148.5 – -148.9 (m). HRMS (ESI) m/z calculated for $C_{13}H_{28}FNO_4SSi$ $[M+NH_4]^+$ 359.1831, found 359.1829.



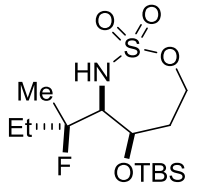
Compound 16b. The enesulfamate **16** (0.150 g, 0.467 mmol, 1.0 equiv) was added to a 10 mL round bottom flask, followed by addition of Selectfluor (0.252 g, 0.711 mmol, 1.5 equiv) and 0.261 g 4 Å MS. Distilled CH_3NO_2 (4.7 mL) was added to make a 0.1 M solution. The reaction was stirred at 80 ºC for 1.5 hour. After 1.5 hour, dry CH_2Cl_2 (40 mL) was added to the reaction until no more white precipitates crashed out. The reaction mixture was filtered through a pad of celite and concentrated by rotary evaporation to yield the imine. A 0.5 M solution of ethynyl magnesium bromide in THF (3.0 mL, 1.50 mmol, 3.2 equiv) was cooled at 0 ºC for at least 15 minutes before use. Dry THF (0.9 mL) was added to the imine to make a 0.5 M solution. The imine solution was then transferred to the cooled ethynyl magnesium bromide. Another 2.1 mL of THF was used to ensure quantitative transfer. The reaction was stirred at 0 ºC for 60 minutes. The reaction was quenched by addition of saturated NH_4Cl solution. The mixture was transferred to a separatory funnel, and the organic layer was extracted three times with EtOAc and washed once with saturated NH_4Cl solution and once with brine, then dried over Na_2SO_4 and concentrated by rotary evaporation to yield the diastereomeric mixture. The product was purified by column chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 7:3 in 14%

increments; $KMnO_4$ stain) to give **16b** as the major diastereomer (0.0891g, 0.244 mmol, 52%), as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.62 (bs, 1H), 4.71 (t, *J* = 12.5 Hz, 1H), 4.54 (dd, *J* = 4.6, 1.7 Hz, 1H), 4.16 (dt, *J* = 12.9, 3.2 Hz, 1H), 2.82 (dddd, *J* = 15.6, 12.1, 2.9, 1.8 Hz, 1H), 2.77 (s, 1H), 1.78 (dt, *J* = 15.9, 4.1 Hz, 1H), 1.65 (d, *J* = 22.0 Hz, 3H), 1.57 (d, *J* = 20.7 Hz, 3H), 0.91 (s, 9H), 0.13 (d, *J* = 1.2 Hz, 3H), 0.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 99.2 (d, *J* = 186.8 Hz), 80.8 (d, *J* = 2.1 Hz), 77.5 (d, *J* = 8.0 Hz), 70.8, 64.0, 62.6 (d, *J* = 21.6 Hz), 34.8, 25.9 (d, *J* = 1.2 Hz), 24.8 (d, *J* = 24.1 Hz), 23.0 (d, *J* = 23.7 Hz), 18.2, -3.6, -4.3 (d, *J* = 2.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -152.30 (hept, *J* = 21.0 Hz). HRMS (ESI) m/z calculated for $C_{15}H_{28}FNO_4SSi$ $[M+Na]^+$ 388.1385, found 388.1382.



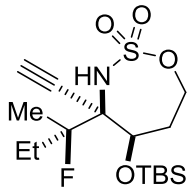
Compound 16c. The enesulfamate **16** (31.7 mg, 0.0986 mmol, 1.0 equiv) was added to a 10 mL round bottom flask, followed by addition of Selectfluor (62.3 mg, 0.176 mmol, 1.8 equiv) and 4 Å MS (58.7 mg). Dry CH_3CN (1.0 mL) was added to make a 0.1 M solution and the reaction mixture was stirred at 40 ºC for 1 day. After 1 day, Bu_4NCN (84.0 mg, 0.313 mmol, 3.2 equiv) was added to the reaction mixture. The color of the solution turned reddish-brown upon addition of Bu_4NCN. The reaction was stirred at room temperature for 3 hours. The mixture was transferred to a separatory funnel and CH_2Cl_2 added to dilute the reaction mixture, followed by the addition of an equal volume of water. The aqueous layer was extracted three times with CH_2Cl_2, the combined organic layers were washed once with brine, dried over Na_2SO_4 and concentrated by rotary evaporation to yield the product as a mixture of diastereomers. The

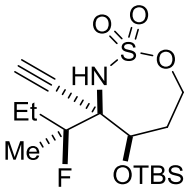
product was purified by column chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increased to a ratio of 7:3 in 14% increments; $KMnO_4$ stain) to give **16c** as the major diastereomer (32.2 mg, 0.0879 mmol, 89%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (bs, 1H), 4.78 – 4.66 (m, 2H), 4.28 (dt, *J* = 13.0, 3.3 Hz, 1H), 2.72 (ddt, *J* = 16.5, 11.8, 2.5 Hz, 1H), 1.97 (dt, *J* = 15.7, 4.0 Hz, 1H), 1.69 (d, *J* = 21.9 Hz, 3H), 1.66 (d, *J* = 20.7 Hz, 3H), 0.92 (s, 9H), 0.17 – 0.13 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 114.9 (d, *J* = 7.1 Hz), 97.8 (d, *J* = 189.8 Hz), 69.4, 64.2, 62.7 (d, *J* = 24.0 Hz), 35.3, 25.9 (d, *J* = 1.0 Hz), 24.6 (d, *J* = 23.8 Hz), 23.4 (d, *J* = 23.5 Hz), 18.1, -3.6, -4.4 (d, *J* = 2.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -151.62 (dt, *J* = 40.3, 18.7 Hz). HRMS (ESI) m/z calculated for $C_{14}H_{27}FN_2O_4SSi$ $[M+NH_4]^+$ 384.1783, found 384.1784.



Compound 17a. To a flame-dried, round bottom flask equipped with a stir bar was added the enesulfamate **17** (0.131 g, 0.391 mmol, 1.0 equiv), followed by the addition of Selectfluor (0.214 g, 0.605 mmol, 1.5 equiv) and 4 Å MS (0.202 g). Dry CH_3CN (3.9 mL) was added to prepare a 0.1 M solution. The mixture was stirred at 40 ºC for 1 day. The reaction mixture was then filtered through a pad of celite, and the filtrate concentrated by rotary evaporation. A 3.9 mL portion of dry CH_3CN was added to the crude imine and the reaction mixture was cooled to 0 ºC. A 3.9 mL portion of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (0.303 g, 1.15 mmol, 2.9 equiv). The reaction mixture was warmed to room temperature and stirred for 2.75 hours. The reaction mixture was transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous

layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4 and concentrated by rotary evaporation to yield the diastereomeric product mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 3:1 in 15% increments; $KMnO_4$ stain) to furnish 37.7 mg **17a** (0.106 mmol, 27%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.55 (d, *J* = 10.6 Hz, 1H), 4.63 (t, *J* = 12.5 Hz, 1H), 4.54 (dd, *J* = 4.2, 2.1 Hz, 1H), 4.16 (dt, *J* = 12.9, 3.3 Hz, 1H), 3.29 (dd, *J* = 18.6, 10.7 Hz, 1H), 2.08 (ddt, *J* = 15.4, 12.1, 2.9 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.67 (ddq, *J* = 27.0, 15.1, 7.5 Hz, 1H), 1.38 (d, *J* = 21.4 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.91 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 97.5 (d, *J* = 176.8 Hz), 65.7 (d, *J* = 2.3 Hz), 64.3, 61.0 (d, *J* = 24.2 Hz), 37.6, 29.1 (d, *J* = 23.4 Hz), 26.0, 21.6 (d, *J* = 24.1 Hz), 18.2, 7.6 (d, *J* = 7.3 Hz), -3.6, -4.5 (d, *J* = 2.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -157.99 (dpd, *J* = 31.3, 21.4, 20.7, 10.1 Hz). HRMS (ESI) m/z calculated for $C_{14}H_{30}FNO_4SSi$ $[M-H]^-$ 354.1576, found 354.1578.

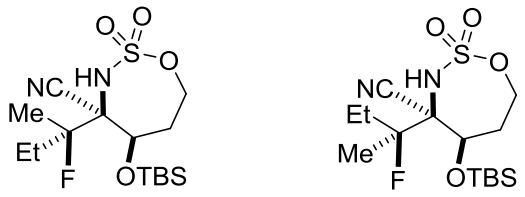




Compound 17b. The enesulfamate **17** (0.120 g, 0.358 mmol, 1.0 equiv) was added to a 10 mL round bottom flask, followed by addition of Selectfluor (0.194 g, 0.548 mmol, 1.5 equiv) and 4 Å MS (0.196 g). Dry CH_3NO_2 (3.6 mL) was added to make a 0.1 M solution and the reaction mixture was stirred at 80 ºC for 1.5 hour. CH_2Cl_2 was added to the reaction until no more white precipitates crashed out. The reaction mixture was then filtered through a pad of celite and concentrated by rotary evaporation to yield the imine. A 0.5 M solution of ethynyl magnesium

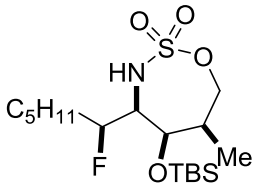
bromide solution in THF (3.2 mL, 1.60 mmol, 4.5 equiv) was cooled at 0 ºC for at least 15 minutes before use. Dry THF (0.7 mL) was added to the imine to make a 0.5 M solution. The imine solution was then transferred to the cooled ethynyl magnesium bromide. Another 2.0 mL of THF was used to ensure quantitative transfer. The reaction was stirred at 0 ºC for 60 minutes. The reaction was quenched by addition of saturated NH_4Cl solution. The mixture was transferred to a separatory funnel, and the organic layer was extracted three times with EtOAc and washed once with brine, then dried over Na_2SO_4 and concentrated by rotary evaporation to yield the diastereomeric mixture. The product was purified by column chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 17:3 in 14% increments; $KMnO_4$ stain) to give an inseparable mixture of diastereomers (38.4 mg, 0.101 mmol, 28%) with **17b** as the major diastereomer. The *dr* of the product oil is 4:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 (bs, 0.20H), 5.59 (bs, 0.80H), 4.70 (t, *J* = 12.5 Hz, 1H), 4.56 (dd, *J* = 4.6, 1.8 Hz, 1H), 4.15 (dt, *J* = 12.9, 3.3 Hz, 1H), 2.83 (dddd, *J* = 15.8, 12.1, 2.9, 1.8 Hz, 0.92H), 2.78 (q, *J* = 1.8 Hz, 0.08H), 2.76 (s, 1H), 2.35 (dp, *J* = 14.8, 7.6 Hz, 1H), 1.93 – 1.80 (m, 1H), 1.80 – 1.74 (m, 1H), 1.57 (d, *J* = 22.1 Hz, 0.6H), 1.47 (dd, *J* = 20.9, 0.8 Hz, 2.4H), 1.05 (t, *J* = 7.4 Hz, 0.6H), 0.97 (t, *J* = 7.5 Hz, 2.4H), 0.91 (s, 7.2H), 0.90 (s, 1.8H), 0.13 (d, *J* = 1.1 Hz, 2.4H), 0.11 (s, 3H), 0.10 (s, 0.6H). ^{13}C NMR (126 MHz, $CDCl_3$) Major diastereomer: δ 100.6 (d, *J* = 191.2 Hz), 81.1 (d, *J* = 2.1 Hz), 71.0, 64.0, 62.9 (d, *J* = 21.6 Hz), 34.7, 29.9, 28.6 (d, *J* = 22.7 Hz), 25.9 (d, *J* = 1.2 Hz), 18.7 (d, *J* = 24.1 Hz), 18.2, 7.4 (d, *J* = 6.6 Hz), -3.6, -4.3 (d, *J* = 2.4 Hz). Minor diastereomer: 101.2 (d, *J* = 189.6 Hz), 81.0 (d, *J* = 2.1 Hz), 70.5, 62.9 (d, *J* = 21.0 Hz), 34.8, 27.6 (d, *J* = 22.7 Hz), 25.9 (d, *J* = 1.1 Hz), 20.1 (d, *J* = 24.4 Hz), 18.1, 7.9 (d, *J* = 3.4 Hz), -3.7, -4.4 (d, *J* = 2.3 Hz).^{19}F NMR (471 MHz, $CDCl_3$) δ -

162.79 (h, *J* = 23.9 Hz), -166.16 – -166.42 (m). HRMS (ESI) m/z calculated for $C_{16}H_{30}FNO_4SSi$ $[M+Na]^+$ 402.1541, found 402.1540.



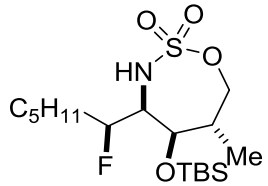
Compound 17c. The enesulfamate **17** (30.6 mg, 0.0913 mmol, 1.0 equiv) was added to a 10 mL round bottom flask, followed by addition of Selectfluor (50.0 mg, 0.141 mmol, 1.5 equiv) and 4 Å MS (49.7 mg). Dry CH_3CN (0.9 mL) was added to make a 0.1 M solution and the reaction mixture was stirred at 40 ºC for 1 day. After 1 day, Bu_4NCN (80.0 mg, 0.298 mmol, 3.3 equiv) was added to the reaction mixture. The color of the solution turned reddish-brown upon addition of Bu_4NCN. The reaction was stirred at room temperature for 3 hours. The mixture was transferred to a separatory funnel, CH_2Cl_2 was added to dilute the reaction mixture. Water (ca. 2 mL) was then added. The aqueous layer was extracted three times with CH_2Cl_2, the combined organic layers washed once with brine, then dried over Na_2SO_4 and concentrated by rotary evaporation to yield the product as a mixture of diastereomers. The product was purified by column chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increased to a ratio of 7:3 in 14% increments; $KMnO_4$ stain) to give **17c** as the major diastereomer as an oil (26.0 mg, 0.0684 mmol, 75%) with a *dr* of 5:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.66 (bs, 0.18H), 5.62 (bs, 0.82H), 4.75 – 4.66 (m, 2H), 4.27 (dt, *J* = 12.9, 3.2 Hz, 1H), 2.78 – 2.70 (m, 1H), 2.37 (dp, *J* = 14.8, 7.4 Hz, 1H), 1.95 (dt, *J* = 16.0, 4.0 Hz, 1H), 1.81 (ddq, *J* = 34.6, 14.8, 7.5 Hz, 1H), 1.63 (d, *J* = 22.0 Hz, 0.54H), 1.57 (d, *J* = 21.0 Hz, 2.46H), 1.10 (t, *J* = 7.4 Hz, 0.54H), 1.03 (t, *J* = 7.5 Hz, 2.46H),

0.92 (s, 9H), 0.16 – 0.13 (m, 6H). Major diastereomer: ^{13}C NMR (126 MHz, $CDCl_3$) δ 114.9 (d, *J* = 7.6 Hz), 99.5 (d, *J* = 193.7 Hz), 69.6, 64.1, 62.9 (d, *J* = 24.1 Hz), 35.2, 28.7 (d, *J* = 22.6 Hz), 25.9 (d, *J* = 3.1 Hz), 19.1 (d, *J* = 23.9 Hz), 18.1, 7.3 (d, *J* = 6.3 Hz), -3.6, -4.4 (d, *J* = 2.4 Hz). Minor diastereomer: ^{13}C NMR (126 MHz, $CDCl_3$) δ 114.9 (d, *J* = 6.8 Hz), 99.9 (d, *J* = 192.7 Hz), 69.2, 64.2, 62.9 (d, *J* = 24.1 Hz), 35.3, 28.3 (d, *J* = 22.8 Hz), 25.9, 20.1 (d, *J* = 24.0 Hz), 7.7 (d, *J* = 3.6 Hz), -3.6, -4.4 (d, *J* = 2.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -161.50 (m), -165.00 (m). HRMS (ESI) m/z calculated for $C_{15}H_{29}FN_2O_4SSi$ $[M-H]^-$ 379.1529, found 379.1532.



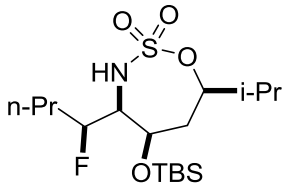
Compound 18a. To a flame-dried, round bottom flask equipped with a stir bar was added the enesulfamate **18** (96.2 mg, 0.255 mmol, 1.0 equiv), Selectfluor (0.148 g, 0.418 mmol, 1.6 equiv) and 4 Å MS (0.147 g). Dry CH_3NO_2 (2.6 mL) was added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for 1 hour. The reaction mixture was then filtered through a pad of celite, and the filtrate concentrated by rotary evaporation. A 2.6 mL portion of dry CH_3CN was added to the crude imine and the reaction mixture was cooled to 0 ºC. A 2.6 mL portion of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (0.210 g, 0.797 mmol, 3.1 equiv). The reaction mxiture was warmed up to room temperature and stirred for ca. 12 hours. The reaction mixture was transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the

diastereomeric mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 2:3 in 8% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to yield 52.1 mg **18a** (0.131 mmol, 51%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.37 (d, *J* = 10.6 Hz, 1H), 4.42 (dddd, *J* = 47.9, 8.4, 4.5, 2.8 Hz, 1H), 4.42 (dd, *J* = 12.7, 10.4 Hz, 1H), 4.04 – 3.97 (m, 1H), 3.81 (dd, *J* = 12.8, 1.6 Hz, 1H), 3.35 (ddd, *J* = 25.3, 10.6, 2.8 Hz, 1H), 2.17 (dqt, *J* = 9.7, 7.3, 2.3 Hz, 1H), 1.91 – 1.77 (m, 1H), 1.69 – 1.55 (m, 1H), 1.51 – 1.27 (m, 6H), 0.96 – 0.92 (m, 12H), 0.90 (t, *J* = 7.2, 3H), 0.11 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 94.2 (d, *J* = 179.3 Hz), 74.7 (d, *J* = 1.4 Hz), 68.7, 59.2 (d, *J* = 17.4 Hz), 41.1, 32.4 (d, *J* = 21.2 Hz), 31.6, 26.4 (d, *J* = 0.9 Hz), 24.5 (d, *J* = 5.2 Hz), 22.6, 18.7, 15.4, 14.1, -2.7, -4.2 (d, *J* = 7.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -190.67 (dtd, *J* = 45.6, 27.7, 14.4 Hz). HRMS (ESI) m/z calculated for $C_{17}H_{36}FNO_4SSi$ $[M+H]^+$ 398.2191, found 398.2191.



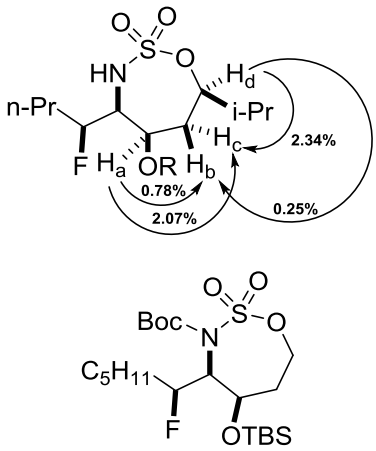
Compound 19a. To a flame-dried, round bottom flask equipped with a stir bar was added the corresponding enesulfamate (88.3 mg, 0.234 mmol, 1.0 equiv), Selectfluor (0.214 g, 0.605 mmol, 2.6 equiv) and 4 Å MS (0.126 g). Dry CH_3NO_2 (2.4 mL) was added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for ca. 7 hours to ensure complete consumption of the starting enesulfamate. The reaction mixture was filtered through a pad of celite and the filtrate concentrated by rotary evaporation. A 2.4 mL portion of dry CH_3CN was added to the crude

imine, and the reaction mixture was cooled to 0 ºC. A 2.4 mL portion of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (0.198 g, 0.751 mmol, 3.2 equiv). The reaction mixture was warmed to room temperature and stirred for 13 hours. The reaction mixture was then transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 3:7 in 6% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to yield 22.2 mg of **19a** (0.0559 mmol, 24%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (d, *J* = 10.7 Hz, 1H), 4.69 (d, *J* = 12.9 Hz, 1H), 4.41 (dddd, *J* = 48.0, 8.8, 4.2, 2.9 Hz, 1H), 3.94 (dd, *J* = 12.9, 2.7 Hz, 1H), 3.84 (d, *J* = 3.2 Hz, 1H), 3.37 (ddd, *J* = 23.8, 10.8, 2.9 Hz, 1H), 1.91 – 1.77 (m, 2H), 1.69 – 1.53 (m, 1H), 1.51 – 1.28 (m, 6H), 1.14 (d, *J* = 7.3 Hz, 3H), 0.93 – 0.87 (overlapping signals, 12H), 0.10 (d, *J* = 1.3 Hz, 3H), 0.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 94.8 (d, *J* = 179.6 Hz), 74.6 (d, *J* = 0.9 Hz), 68.2, 53.7 (d, *J* = 18.3 Hz), 40.0, 32.3 (d, *J* = 21.0 Hz), 31.6, 26.0, 24.6 (d, *J* = 4.8 Hz), 22.6, 18.1, 14.1, 13.5, -4.2, -4.9 (d, *J* = 3.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -192.48 (dddd, *J* = 47.2, 31.5, 23.9, 14.8 Hz). HRMS (ESI) m/z calculated for $C_{17}H_{36}FNO_4SSi$ $[M+H]^+$ 398.2191, found 398.2189.



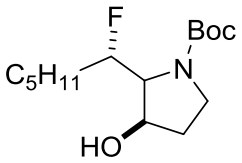
Compound 20a. To a flame-dried, round bottom flask equipped with a stir bar was added a portion of 90.6 mg enesulfamate **20** (0.240 mmol, 1.0 equiv), Selectfluor (0.128 g, 0.361 mmol, 1.5 equiv), and 4 Å MS (0.134 g). Dry CH_3NO_2 (2.4 mL) was added to prepare a 0.1 M solution. The mixture was stirred at 80 ºC for 1 hour. The reaction mixture was then filtered through a pad of celite, and the filtrate concentrated by rotary evaporation. A 2.4 mL portion of dry CH_3CN was added to the crude imine and the reaction mixture was cooled to 0 ºC. A 2.4 mL portion of glacial AcOH (AcOH:CH_3CN = 1:1 v/v) was added to the flask, followed by addition of $Me_4N(OAc)_3BH$ (0.191 g, 0.726 mmol, 3.0 equiv). The reaction mxiture was warmed up to room temperature and stirred for 6 hours. The reaction mixture was transferred to a separatory funnel containing CH_2Cl_2 and washed three times with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to yield the diastereomeric mixture. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 3:7 in 6% increments; 1% Et_2O was added to improve separation among diastereomers; $KMnO_4$ stain) to yield 39.5 mg stereotriad (0.0994 mmol, 41%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04 (d, *J* = 9.5 Hz, 1H), 4.77 (dddd, *J* = 47.2, 8.9, 4.7, 2.3 Hz, 1H), 4.39 – 4.32 (m, 2H), 3.53 (ddt, *J* = 25.3, 9.6, 2.8 Hz, 1H), 2.16 (ddd, *J* = 16.2, 10.7, 5.8 Hz, 1H), 2.03 (ddd, *J* = 15.5, 5.1, 2.8 Hz, 1H), 1.93 – 1.77(m, 2H), 1.64 – 1.34 (m, 2H), 1.00 – 0.94 (m, 9H), 0.91 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 92.8 (d, *J* = 177.3 Hz), 84.9, 70.8, 57.5 (d, *J* = 17.8 Hz), 39.8 (d, *J* = 1.3 Hz), 34.3 (d, *J* = 20.9 Hz), 33.1, 25.9, 18.5, 18.4 (d, *J* = 5.6 Hz), 18.1, 17.6, 13.9, -4.0, -4.9 (d, *J* = 1.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -194.46 (dddd, *J* = 46.3, 30.9, 25.2, 13.9 Hz). HRMS (ESI) m/z calculated for

$C_{17}H_{36}FNO_4SSi$ $[M+NH_4]^+$ 415.2457, found 415.2452. The stereochemistry of the ^{i}Pr group on seven-membered ring was confirmed by NOE experiments:



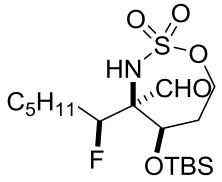
Intermediate for the synthesis of compound 28. A portion of 0.299 g of the stereotriad **7a** (0.779 mmol, 1.0 equiv) was dissolved in 7.5 mL dry CH_2Cl_2 to prepare a 0.1 M solution. A portion of 0.27 mL Boc_2O (0.257g, 1.17 mmol, 1.5 equiv), 0.16 mL NEt_3 (0.116 g, 1.17 mmol, 1.5 equiv) and 0.0117 g DMAP (0.0958 mmol, 0.1 equiv) were added to the flask and the reaction mixture stirred at room temperature for 40 minutes, diluted with CH_2Cl_2 and washed twice with saturated NH_4Cl solution and once with brine. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporation to yield the crude product, which was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 1:1 in 10% increments; $KMnO_4$ stain) to yield 36.3 mg of product as a white solid (0.750 mmol, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.06 (dddd, *J* = 48.7, 10.1, 7.3, 3.2 Hz, 1H), 4.66 – 4.53 (m, 2H), 4.47 (ddd, *J* = 12.5, 4.5, 2.2 Hz, 1H), 4.03 (dq, *J* = 11.2, 3.5 Hz, 1H), 2.33 – 2.20 (m, 1H), 1.89 – 1.63 (m, 3H), 1.55 (s, 9H), 1.44 – 1.27 (m, 6H), 0.92 – 0.87 (m, 12H), 0.15 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 90.7 (d, *J* = 175.8 Hz), 85.7, 72.2 (d, *J* = 4.4 Hz), 69.7,

64.8 (d, *J* = 18.7 Hz), 33.7, 33.1 (d, *J* = 20.6 Hz), 31.7, 28.0, 25.8, 25.0 (d, *J* = 3.8 Hz), 22.7, 18.0, 14.1, -4.7, -5.0.^{19}F NMR (471 MHz, $CDCl_3$) δ -184.27 – -184.72 (m). HRMS (ESI) m/z calculated for $C_{21}H_{42}FNO_6SSi$ $[M+NH_4]^+$ 501.2824, found 501.2826.



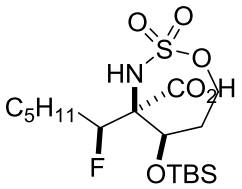
Compound 28. The N-Boc protected stereotriad was converted to the crude pyrrolidine product according to a published procedure[4]. A 51.0 mg (0.105 mmol, 1.0 equiv) portion of the triad was dissolved in 0.52 mL of DMF, followed by addition of 28.0 mg NaI (0.187 mmol, 1.8 equiv). The solution was warmed to 50 ºC and stirred at the same temperature for 15 minutes prior to the addition of NaH (16.6 mg, 0.692 mmol, 6.6 equiv). Upon addition of NaH, the solution turned light yellow. The reaction mixture was then warmed to 68 ºC and stirred at the same temperature for 10.5 hours. The reaction mixture was then cooled down to room temperature and cautiously quenched with H_2O. The mixture was extracted with Et_2O three times. The combined organics were washed once with brine and dried with $MgSO_4$. The mixture was filtered and concentrated *in vacuo*. The crude pyrrolidine was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 2:3 in 7% increments; $KMnO_4$ stain) to yield 22.8 mg (0.0788 mmol, 75%) of **28** as a clear oil. ^{1}H NMR (500 MHz, Tol-d8, 368K) δ 4.81 (dddd, *J* = 47.4, 9.2, 4.1, 2.3 Hz, 1H), 3.92 (q, *J* = 8.2 Hz, 1H), 3.81 (ddd, *J* = 29.3, 7.5, 2.3 Hz, 1H), 3.30 (t, *J* = 7.3 Hz, 2H), 1.90 – 1.78 (m, 1H), 1.78 – 1.60 (m, 3H), 1.53 – 1.36 (m, 11H), 1.32 – 1.20 (m, 5H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Tol-d8, 368K) δ 154.6, 93.0 (d, *J* = 172.6 Hz), 78.7, 71.2, 60.4 (d, *J* = 17.9 Hz), 43.8, 32.4 (d, *J* = 21.1 Hz), 32.4 (d, *J* = 3.6 Hz), 31.6, 28.0, 25.1 (d, *J* = 4.7

Hz), 22.3, 13.4. ^{19}F NMR (471 MHz, Tol-d8, 368K) δ -191.36 – -193.07 (m). HRMS (ESI) m/z calculated for $C_{15}H_{28}FNO_3$ $[M+Na]^+$ 312.1945, found 312.1941.



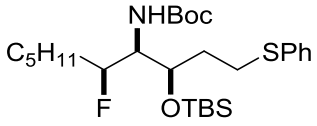
Intermediate for the synthesis of compound 29. A portion of 29.1 mg of the stereotriad **9a** (0.0710 mmol, 1.0 equiv) was subjected to ozonolysis conditions[5] to yield the crude aldehyde product. The **9a** was dissolved in dry CH_2Cl_2 and cooled to -78 ^oC. Ozone was then bubbled into the solution until a persistent blue color was observed. At this point, N_2 was bubbled through the solution in place of the ozone until the blue color went away. A 0.02 mL portion of NEt_3 (14.5 mg, 0.144 mmol, 2.0 equiv) was then added and the solution was warmed to room temperature and allowed to stir for 3.5 hours. After the reaction was complete as indicated by a TLC check (CH_2Cl_2:hexanes = 1:1, $KMnO_4$ stain), the organic solution was diluted with Et_2O, washed once with saturated NH_4Cl solution. After the aqueous layer was extracted three times with Et_2O, the combined organic layers were washed with brine once and dried over Na_2SO_4. The product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 1:1 in 10% increments; $KMnO_4$ stain) to yield 24.5 mg of the aldehyde as clear yellow oil (0.0595 mmol, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (d, *J* = 3.4 Hz, 1H), 5.44 (bs, 1H), 4.80 (ddd, *J* = 46.8, 11.1, 2.0 Hz, 1H), 4.54 – 4.47 (m, 2H), 4.20 (ddd, *J* = 12.2, 6.0, 2.9 Hz, 1H), 2.19 (ddt, *J* = 16.0, 9.2, 2.4 Hz, 1H), 2.10 (dtd, *J* = 15.8, 6.5, 2.1 Hz, 1H), 1.85 – 1.71 (m, 1H), 1.61 – 1.51 (m, 1H), 1.51 – 1.26 (m, 6H), 0.91 (s, 9H), 0.88 (t, *J* = 6.7 Hz, 3H), 0.13 – 0.10 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2 (d, *J* = 4.8 Hz), 94.7 (d, *J* = 185.8 Hz), 72.1, 71.6 (d, *J* = 16.3 Hz), 66.4,

34.4 (d, *J* = 2.2 Hz), 31.4, 30.2 (d, *J* = 21.8 Hz), 25.9, 25.0 (d, *J* = 3.4 Hz), 22.5, 18.1, 14.1, -4.0, -4.9 (d, *J* = 0.71 Hz).[19]F NMR (471 MHz, $CDCl_3$) δ -193.61 (dddd, *J* = 46.6, 42.3, 12.7, 3.4 Hz). HRMS (ESI) m/z calculated for $C_{17}H_{34}FNO_5SSi$ $[M+NH_4]^+$ 429.2249, found 429.2250.



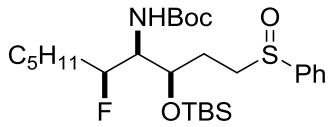
Compound 29. A portion of 60.2 mg (0.146 mmol, 1.0 equiv) of the aldehyde was dissolved in 0.50 mL CH_3CN. An aqueous solution of NaH_2PO_4 (8.7 mg in 0.24 mL H_2O) and 0.1 mL 30% wt% H_2O_2 were added to the dissolved aldehyde and the reaction mixture was cooled to 0 ^oC. Next, an aqueous solution of $NaClO_2$ (15.7 mg in 0.23 mL H_2O) was added and the reaction mixture stirred at room temperature until starting material was consumed after 3 hours. The reaction was quenched with addition of aqueous solution of $NaHSO_3$. After another 30 minutes of stirring, 2 N HCl was added. The reaction mixture was extracted with CH_2Cl_2 three times. The combined organic layers were then washed with 10% NaOH solution twice to ensure deprotonation of the acid. A portion of 2 N HCl was then added to the combined aqueous layers to ensure protonation of the acid. The mixture was then extracted five times with CH_2Cl_2. The combined organic layers were then washed once with brine and dried over Na_2SO_4. A 29.0 mg portion of product **30** (0.0678 mmol, 46%) was obtained as a white solid. The product was clean enough for direct characterization without further purification. [1]H NMR (500 MHz, $CDCl_3$) δ 9.38 – 7.80 (bs, 1H), 5.40 (bs, 1H), 4.91 (dd, *J* = 47.8, 10.2 Hz, 1H), 4.66 (d, *J* = 8.2, 1H), 4.47 (ddd, *J* = 11.3, 8.3, 2.6 Hz, 1H), 4.25 (ddd, *J* = 12.1, 7.3, 2.8 Hz, 1H), 2.34 (dtd, *J* = 15.9, 7.9, 2.5 Hz, 1H), 2.23 (dd, *J* = 16.3, 7.6 Hz, 1H), 1.80 – 1.67 (m, 1H), 1.66 – 1.49 (m, 2H), 1.42 – 1.21 (m, 5H), 0.92 (s, 9H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.12 (s, 3H), 0.12 (s, 3H). [13]C NMR (126 MHz,

$CDCl_3$) δ 171.4, 93.7 (d, *J* = 186.1 Hz), 73.7, 69.3 (d, *J* = 15.7 Hz), 67.2, 35.2 (d, *J* = 2.6 Hz), 31.4, 30.6 (d, *J* = 21.3 Hz), 25.9, 25.4 (d, *J* = 2.8 Hz), 22.6, 18.1, 14.1, -4.1, -4.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -193.69 (td, *J* = 47.1, 46.6, 14.6 Hz). HRMS (ESI) m/z calculated for $C_{17}H_{34}FNO_6SSi$ $[M+NH_4]^+$ 445.2198, found 445.2195.



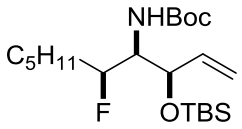
Intermediate for the synthesis of compound 30. The thiophenol ring-opening product was obtained using a published procedure[6] to convert 570 mg Boc-protected enesulfamate (1.18 mmol, 1.0 equiv) to 646 mg (quantitative yield) product as a colorless oil. To a 25 mL round-bottom flask was added the Boc-protected enesulfamate, 0.3 mL PhSH (322 mg, 2.92 mmol, 2.5 equiv), and 13 mL CH_3CN, followed by addition of 332 mg K_2CO_3 (2.40 mmol, 2.0 equiv). The reaction was monitored by TLC (CH_2Cl_2:hexanes = 1:1, $KMnO_4$ stain). After 2 hours, a saturated $NaHCO_3$ solution was added to the reaction mixture and the mixture extracted with EtOAc three times. The combined organic layers were washed once with saturated $NaHCO_3$ and brine, followed by drying with Na_2SO_4. The crude product was concentrated *in vacuo* and purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 1:1 in 10% increments; $KMnO_4$ stain) to give the product. ^{1}H NMR (500 MHz, C_6D_6) δ 7.35 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.92 (tt, *J* = 7.3, 1.3 Hz, 1H), 4.91 (d, *J* = 9.6 Hz, 1H), 4.77 (dddd, *J* = 47.8, 8.5, 5.0, 1.8 Hz, 1H), 4.11 (ddd, *J* = 7.0, 5.3, 3.8 Hz, 1H), 3.98 (dddd, *J* = 28.2, 9.6, 3.9, 1.9 Hz, 1H), 3.04 (dt, *J* = 13.5, 6.9 Hz, 1H), 2.87 (dt, *J* = 12.9, 7.4 Hz, 1H), 1.93 (q, *J* = 7.5 Hz, 2H), 1.79 – 1.64 (m, 1H), 1.57 – 1.46 (m, 1H), 1.43 (s, 9H), 1.39 – 1.29 (m, 2H), 1.24 –

1.10 (m, 4H), 0.90 (s, 9H), 0.83 (t, *J* = 7.0 Hz, 3H), 0.16 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 156.1, 137.2, 129.6, 129.2, 126.1, 92.3 (d, *J* = 172.9 Hz), 79.4, 71.7, 56.1 (d, *J* = 16.5 Hz), 33.0 (d, *J* = 18.2 Hz), 32.9, 31.8, 30.3, 28.4, 26.1, 25.1 (d, *J* = 5.5 Hz), 22.8, 18.1, 14.2, -4.4. ^{19}F NMR (471 MHz, C_6D_6) δ -192.29 (dtd, *J* = 44.5, 28.6, 14.5 Hz). HRMS (ESI) m/z calculated for $C_{27}H_{48}FNO_3SSi$ $[M+H]^+$ 514.3181, found 514.3188.



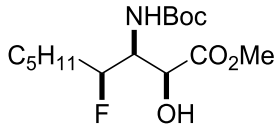
Intermediate for the synthesis of compound 30. A published procedure[6b,7] was used to convert 538 mg of the thiol ring-opening product (1.05 mmol, 1.0 equiv) to 586 mg (quantitative yield) of the sulfoxide product as colorless oil in a *dr* of 1:1. To a 5 mL round-bottom flask was added 1.19 g (12.7 mmol, 12.1 equiv) phenol and the thiol phenol ring-opening product, followed by addition of 30 % by weight H_2O_2 in water (0.83 mL). After 20 minutes, the reaction was quenched by addition of saturated $Na_2S_2O_3$ solution. The reaction mixture was then diluted with H_2O and the aqueous layer was extracted with EtOAc three times. The combined organics were then washed once with saturated K_2CO_3 and once with brine. The organics were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 1:9 in 2% increments to get remove any unreacted phenol; the ratio of the solvent was then gradually increased to 1:3 in 3% increments to afford the product; $KMnO_4$ stain). ^{1}H NMR (500 MHz, C_6D_6) δ 7.55 – 7.50 (m, 2H), 7.08 – 7.01 (m, 2H), 7.01 – 6.94 (m, 1H), 4.95 (dd, *J* = 30.6, 9.6 Hz, 1H), 4.79 – 4.53 (m, overlapping signals, 1H), 4.00 – 3.83 (m, overlapping signals, 2H), 2.83 (dddd, *J* = 21.7, 13.1, 9.9, 5.6 Hz,

1H), 2.64 (dddd, *J* = 13.0, 9.7, 5.4, 2.5 Hz, 1H), 2.22 (ddt, *J* = 15.1, 10.3, 5.4 Hz, 0.5H), 2.14 – 2.05 (m, 0.5H), 1.93 – 1.83 (m, 1H), 1.79 – 1.61 (m, 1H), 1.61 – 1.45 (m, 1H), 1.43 (s, 4.5H), 1.41 (s, 4.5H), 1.38 – 1.08 (m, 6H), 0.87 (s, 4.5H), 0.85 (s, 4.5H), 0.86 – 0.81 (m, overlapping signals, 3H), 0.11 (s, 1.5H), 0.10 (s, 1.5H), 0.02 (s, 1.5H), -0.05 (s, 1.5H). ^{13}C NMR (126 MHz, C_6D_6) δ 156.3, 156.2, 145.7, 145.5, 130.4, 130.4, 129.2, 129.2, 124.2, 124.2, 92.8 (d, *J* = 173.2 Hz), 92.5 (d, *J* = 173.6 Hz), 79.5, 79.4, 72.1, 72.0, 56.1 (d, *J* = 16.7 Hz), 56.0 (d, *J* = 17.1 Hz), 53.1, 52.9, 32.9, 32.8, 31.9, 31.8, 28.4, 26.0, 25.1 (d, *J* = 5.2 Hz), 25.1 (d, *J* = 5.2 Hz), 22.8, 22.8, 18.1, 14.2, 14.2, -4.3, -4.3, -4.5, -4.6. ^{19}F NMR (471 MHz, C_6D_6) δ -192.53 (m). HRMS (ESI) m/z calculated for $C_{27}H_{48}FNO_4SSi$ $[M+H]^+$ 530.3130, found 530.3137.



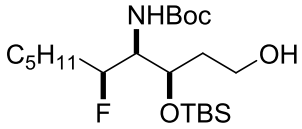
Compound 30. A published procedure[6b,7] was used to convert 20.0 mg sulfoxide (0.0377 mmol, 1.0 equiv) to 12.3 mg (0.0305 mmol, 81%) compound **31** as a white solid. To an oven-dried pressure tube was added the sulfoxide and 1.5 mL of distilled xylenes, followed by addition of 20.0 mg $NaHCO_3$ (0.238 mmol, 6.3 equiv). The reaction mixture was heated at 130 ^{o}C until ^{1}H NMR showed complete consumption of starting material. After 17 hours, the reaction mixture was cooled to room temperature, diluted with H_2O and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed once with brine and dried over Na_2SO_4. After concentration *in vacuo*, the crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 CH_2Cl_2:hexanes, with a gradual increase to a ratio of 1:1 in 5% increments;

$KMnO_4$ stain). ^1H NMR (500 MHz, C_6D_6) δ 5.90 (dddd, *J* = 17.3, 10.2, 7.1, 2.9 Hz, 1H), 5.19 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.01 (dt, *J* = 10.4, 1.3 Hz, 1H), 4.89 (dddd, *J* = 47.8, 7.7, 5.6, 1.4 Hz, 1H), 4.89 (d, *J* = 9.9 Hz, 1H), 4.29 (t, *J* = 6.3 Hz, 1H), 4.00 (dddd, *J* = 29.5, 9.9, 5.6, 1.5 Hz, 1H), 1.86 – 1.72 (m, 1H), 1.65 – 1.51 (m, 1H), 1.45 (s, 9H), 1.40 – 1.28 (m, 2H), 1.24 – 1.12 (m, 4H), 0.96 (s, 9H), 0.83 (t, *J* = 6.9 Hz, 3H), 0.10 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 156.0, 138.5, 116.6, 92.1 (d, *J* = 172.3 Hz), 79.2, 74.9, 57.3 (d, *J* = 16.4 Hz), 32.7 (d, *J* = 20.9 Hz), 31.8, 28.5, 26.0, 25.1 (d, *J* = 5.9 Hz), 22.8, 18.3, 14.2, -4.3, -4.8. ^{19}F NMR (471 MHz, C_6D_6) δ -192.57 – -192.87 (m). HRMS (ESI) m/z calculated for $C_{21}H_{42}FNO_3Si$ $[M+Na]^+$ 426.2810, found 426.2808.



Compound 31. A portion of 9.9 mg of **30** (0.0245 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 and cooled down to -78 °C. Ozone was then bubbled into the solution until a persistent blue color was observed. At this point, the ozone addition was stopped and N_2 was bubbled through the solution until the blue color disappeared. A 0.05 mL portion of NEt_3 was then added and the solution was warmed to room temperature and allowed to stir for 1 hour. The organic solution was diluted with ether and washed once with saturated NH_4Cl solution. After the aqueous layer was extracted three times with ether, the combined organic layers were washed with brine once and dried over Na_2SO_4. The aldehyde was used for the subsequent Pinnick oxidation without further purification. The aldehyde was dissolved in 0.40 mL CH_3CN. An aqueous solution of NaH_2PO_4 (5.2 mg in 0.1 mL H_2O) and 0.1 mL 30% by weight solution of H_2O_2 in water were added to the dissolved aldehyde. The reaction mixture was cooled to 0 °C.

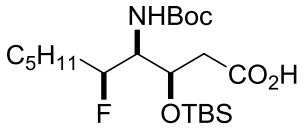
An aqueous solution of $NaClO_2$ (4.8 mg in 0.1 mL H_2O) was added and the solution was stirred at room temp until starting material was consumed (ca. 12 hours). The reaction was then quenched by the addition of an aqueous solution of $NaHSO_3$. After another 30 minutes of stirring, 2 N HCl was added. The reaction mixture was extracted three times with CH_2Cl_2, the combined organics washed once with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude carboxylic acid was dissolved in 0.34 mL MeOH at 0 ^oC. A solution of 0.1 mL $TMSCHN_2$ was added dropwise over 1 minute. After 30 minutes of stirring at 0 ^oC, 0.01 mL AcOH was added and the resulting mixture was concentrated *in vacuo*. A 4.5 mg (0.0140 mmol, 57%) portion of the product **32** was obtained as colorless oil after purification by column chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 1:4 in 3% increments; $KMnO_4$ stain). ^1H NMR (500 MHz, C_6D_6) δ 5.09 (d, *J* = 10.2 Hz, 1H), 4.60 (ddt, *J* = 48.0, 8.5, 3.8 Hz, 1H), 4.34 (ddt, *J* = 23.3, 10.2, 3.4 Hz, 1H), 4.11 (t, *J* = 3.8 Hz, 1H), 3.29 (s, 3H), 3.07 (d, *J* = 4.4 Hz, 1H), 1.70 – 1.58 (m, 1H), 1.41 (s, 9H), 1.30 – 1.03 (m, 7 H), 0.81 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 174.0, 155.8, 92.5 (d, *J* = 173.0 Hz), 79.6, 70.3, 55.7 (d, *J* = 19.4 Hz), 52.4, 32.0 (d, *J* = 20.8 Hz), 31.8, 28.3, 25.0 (d, *J* = 4.4 Hz), 22.8, 14.2. ^{19}F NMR (471 MHz, C_6D_6) δ -193.19 (dddd, *J* = 48.0, 31.9, 23.3, 15.3 Hz). HRMS (ESI) m/z calculated for $C_{15}H_{28}FNO_5$ $[M+Na]^+$ 344.1844, found 344.1840.



Precursor for the synthesis of compound 32. The reaction was repeated three times due to discrepancies in yield on the small scales employed (8.8 mg, 0.0209 mmol, 84%; 37.0 mg,

0.0879 mmol, 42%; 26.7 mg, 0.0634 mmol, 51%). The average of the three reactions was taken as the final yield, which is 59%. The amount of the starting material used for each reaction was 0.0248 mmol, 0.211 mmol, and 0.124 mmol, respectively. The procedure for the reaction carried out on a 0.124 mmol scale involved dissolving compound **31** (49.8 mmg, 0.124 mmol, 1.0 equiv) in THF (1 mL) in a flame-dried, round bottom flask to make a 0.3 M solution, which was then cooled to 0 ^{o}C. The BH_3/THF complex (0.4 mL, 0.400 mmol, 0.83 equiv) was added to the same flask and the reaction mixture stirred at room temperature. After 1 day, H_2O (1.85μL, 0.0019 g, 0.106 mmol, 0.85 equiv) was added to the reaction and stirred continued for another 30 minutes before the addition of a 5 M aqueous solution of NaOH (0.1 mL, 4.2 equiv) and 30% by weight solution of H_2O_2 in water (0.1 mL, 1.02 mmol, 8.2 equiv). The reaction was warmed to room temperature and stirred for 1 hour. A saturated K_2CO_3 solution and H_2O were added to quench the reaction and the resulting solution extracted three times with CH_2Cl_2. The combined organic layers were washed once with brine and dried over Na_2SO_4. After concentration *in vacuo*, the crude product was purified by silica gel chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 1:4 in 3% increments; $KMnO_4$ stain) to yield 26.7 mg alcohol (0.0634 mmol, 51%) as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6) δ 5.08 (d, *J* = 9.6 Hz, 1H), 4.92 – 4.76 (m, 1H), 4.12 – 4.06 (m, 1.5H), 4.03 (ddd, *J* = 10.0, 4.1, 2.0 Hz, 0.5H), 3.61 (dt, *J* = 11.1, 5.6 Hz, 1H), 3.53 (dt, *J* = 11.0, 6.3 Hz, 1H), 1.85 – 1.67 (m, 3H), 1.66 – 1.51 (m, 1H), 1.49 – 1.33 (m, 12H), 1.26 – 1.13 (m, 4H), 0.93 (s, 9H), 0.85 (t, *J* = 6.8 Hz, 3H), 0.16 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 156.4, 92.7 (d, *J* = 172.6 Hz), 79.4, 71.0, 59.4, 56.3 (d, *J* = 16.4 Hz), 36.4 (d, *J* = 2.5 Hz), 33.1 (d, *J* = 21.3 Hz), 31.9, 28.4, 26.1, 25.2 (d, *J* = 5.4 Hz), 22.9, 18.2, 14.2, -4.5, -4.6. ^{19}F NMR

(471 MHz, C_6D_6) δ -192.57 (dtd, *J* = 48.6, 28.3, 14.6 Hz). HRMS (ESI) m/z calculated for $C_{21}H_{44}FNO_4Si$ $[M+H]^+$ 422.3096, found 422.3092.



Compound 32. A portion of 4.0 mg $RuCl_3 \cdot XH_2O$ (0.0024 mmol, 0.1 equiv) was added at 0 °C to a solution of 8.8 mg (0.0209 mmol, 1.0 equiv) alcohol and $NaIO_4$ (20.0 mg, 0.0935 mmol, 4.5 equiv) dissolved in a mixture of 0.3 mL CH_3CN, 0.12 mL CCl_4 and 0.22 mL H_2O. The reaction mixture was warmed to room temperature and stirred for 27 hours. A 1 mL portion of 1 N HCl was added to the reaction mixture and the aqueous layer extracted with EtOAc three times. The combined organics were washed once with brine, dried over Na_2SO_4 and concentrated *in vacuo*. 7.0 mg (0.0161 mmol, 77%) compound **32** was yielded after column chromatography (carried out using a gradient method with an initial starting mobile phase consisting of 0:1 EtOAc:hexanes, with a gradual increase to a ratio of 1:4 in 5% increments; $KMnO_4$ stain) to give the product as a colorless oil. ^{1}H NMR (600 MHz, Tol-d8) δ 4.90 – 4.84 (m, 1.5H), 4.78 (dd, *J* = 7.7, 5.4 Hz, 0.5H), 4.47 (dt, *J* = 8.2, 4.3 Hz, 1H), 4.00 (dddd, *J* = 29.1, 9.6, 3.9, 1.6 Hz, 1H), 2.55 (ddd, *J* = 15.9, 8.0, 2.3 Hz, 1H), 2.46 (dd, *J* = 15.8, 4.6 Hz, 1H), 1.78 – 1.66 (m, 1H), 1.59 – 1.47 (m, 1H), 1.42 (s, 9H), 1.38 – 1.28 (m, 3H), 1.25 – 1.14 (m, 4H), 0.92 (s, 9H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.17 (s, 3H), 0.14 (s, 3H). ^{13}C NMR (151 MHz, Tol-d8) δ 177.1, 156.0, 92.1 (d, *J* = 172.4 Hz), 79.6, 70.3, 56.4 (d, *J* = 16.3 Hz), 38.8 (d, *J* = 3.5 Hz), 32.9 (d, *J* = 21.3 Hz), 31.8, 28.3, 26.0, 25.1 (d, *J* = 5.7 Hz), 22.9, 18.1, 14.1, -4.7, -4.8. ^{19}F NMR (564 MHz, Tol-d8) δ -192.81 (dtd, *J* = 44.0, 28.8, 14.4 Hz). HRMS (ESI) m/z calculated for $C_{21}H_{42}FNO_5Si$ $[M-H]^-$ 434.2744, found 434.2750.

V. References.

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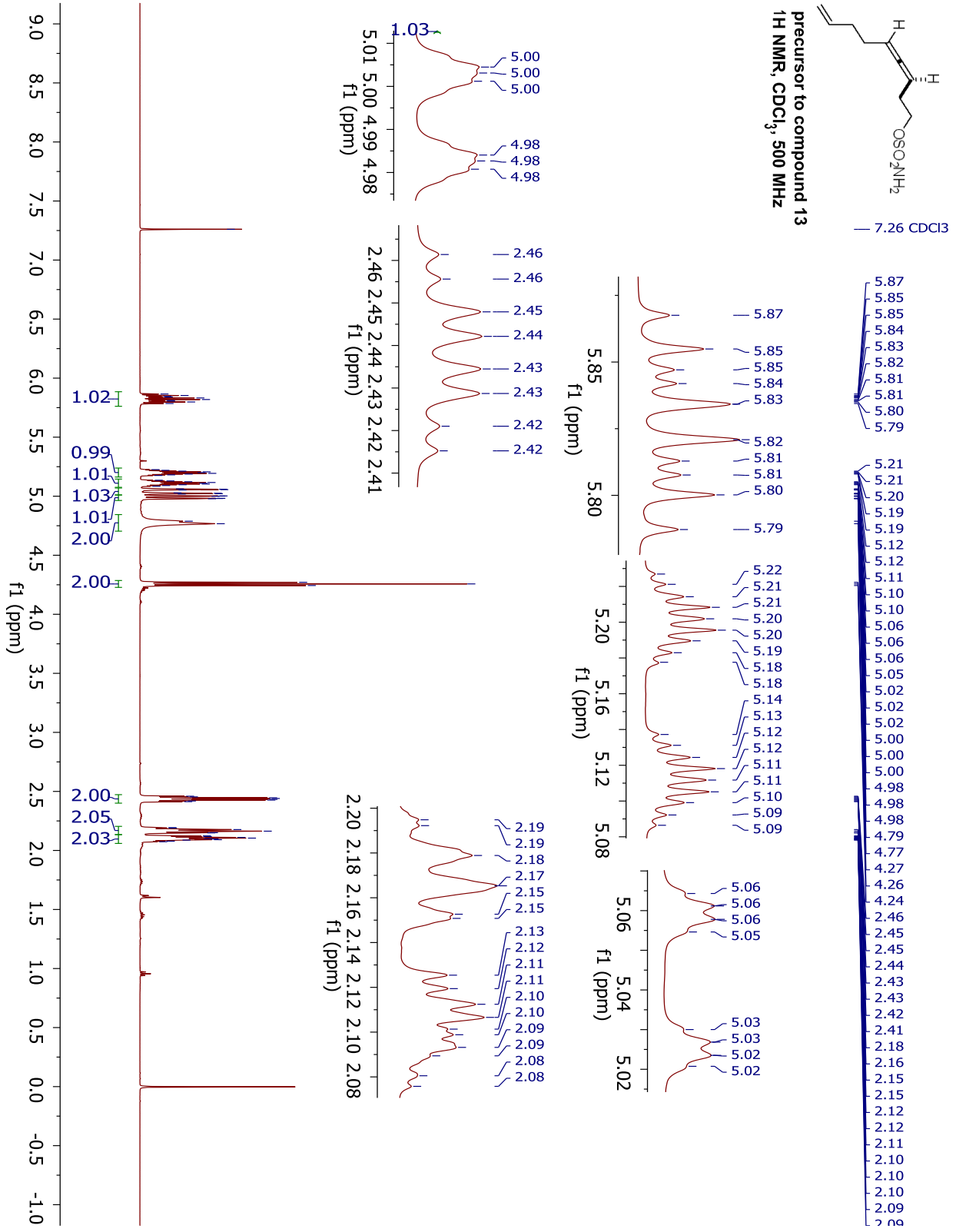
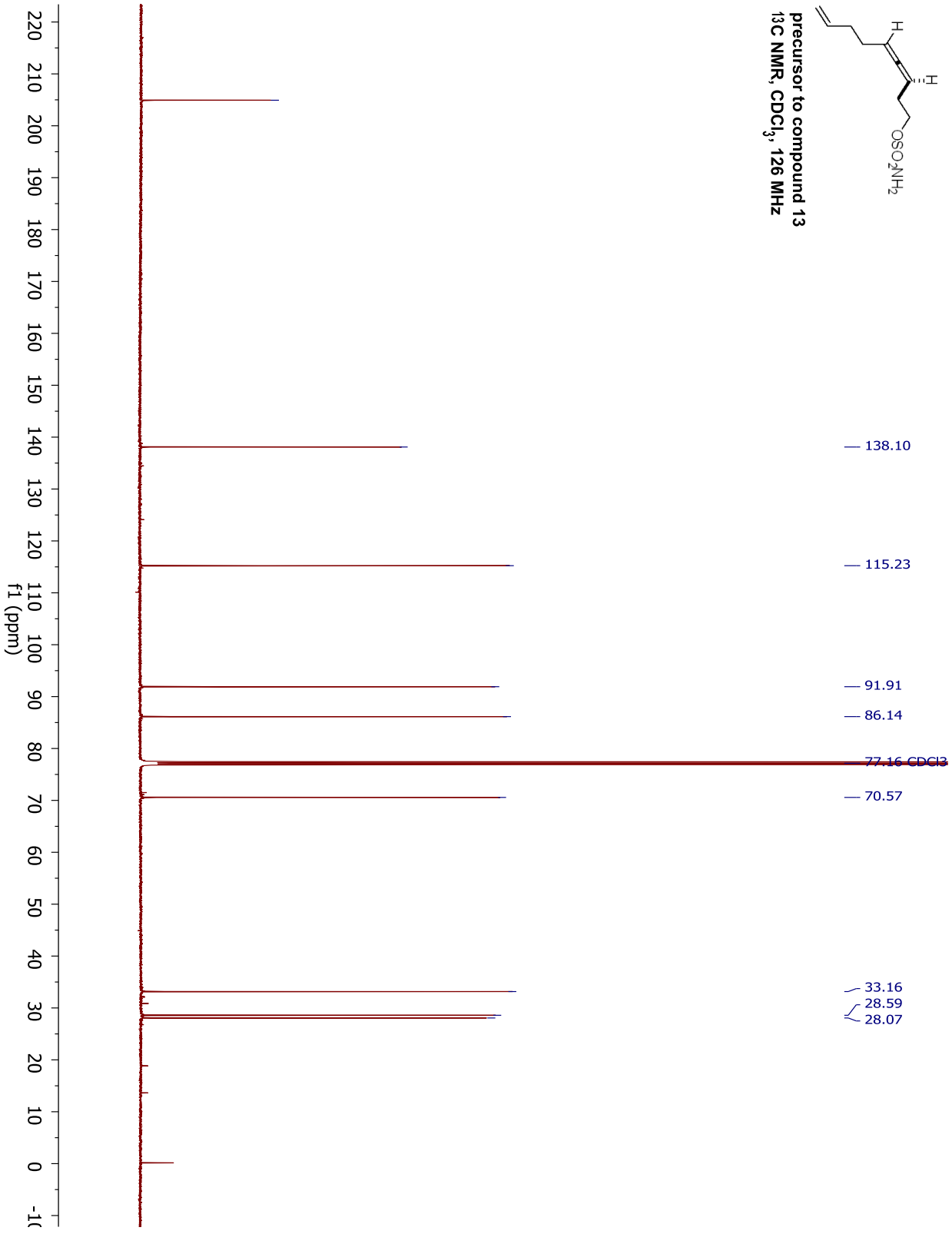
VI. NMR Spectra.

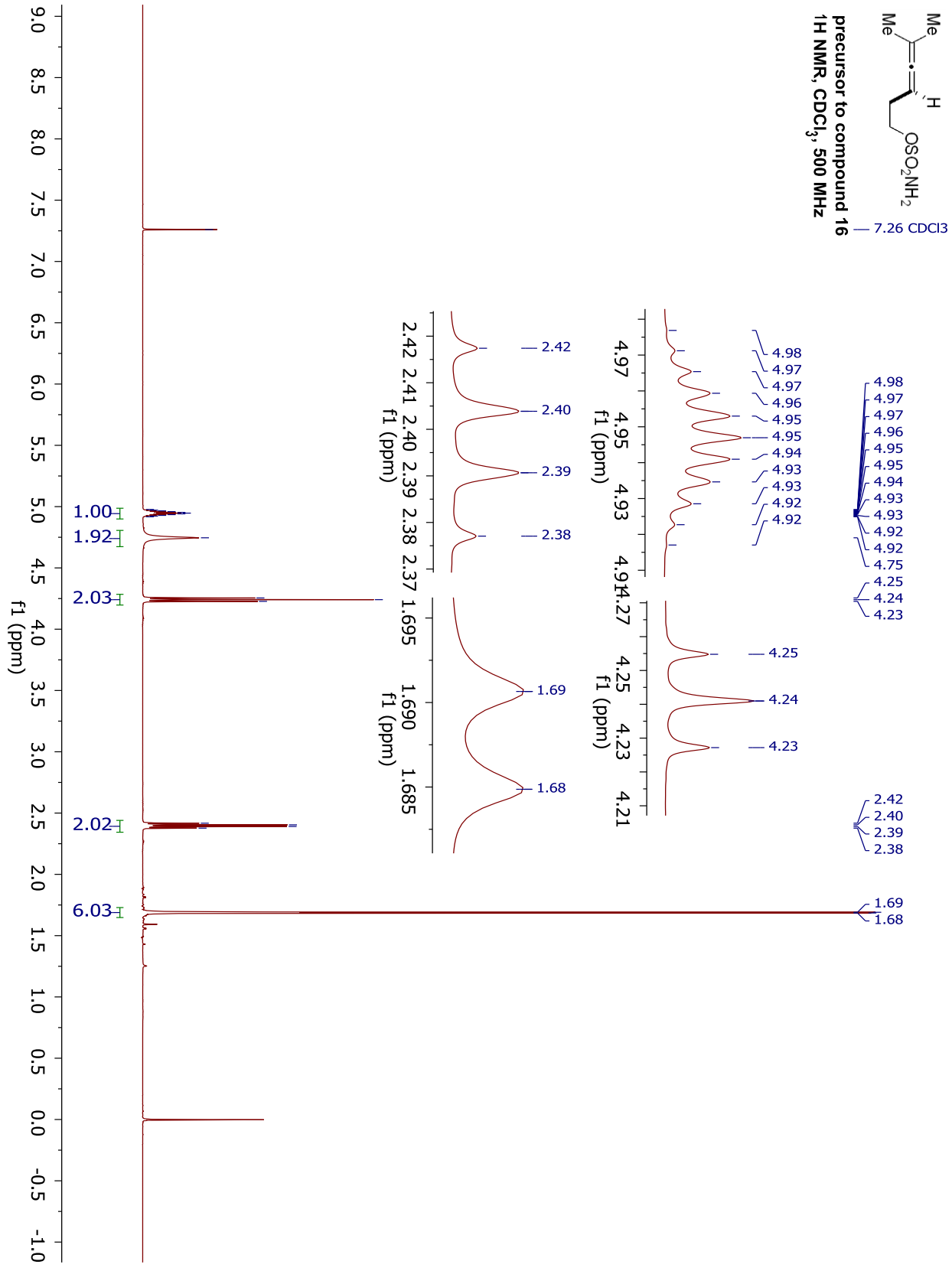
^{1}H NMR for the precursor for compound 13.



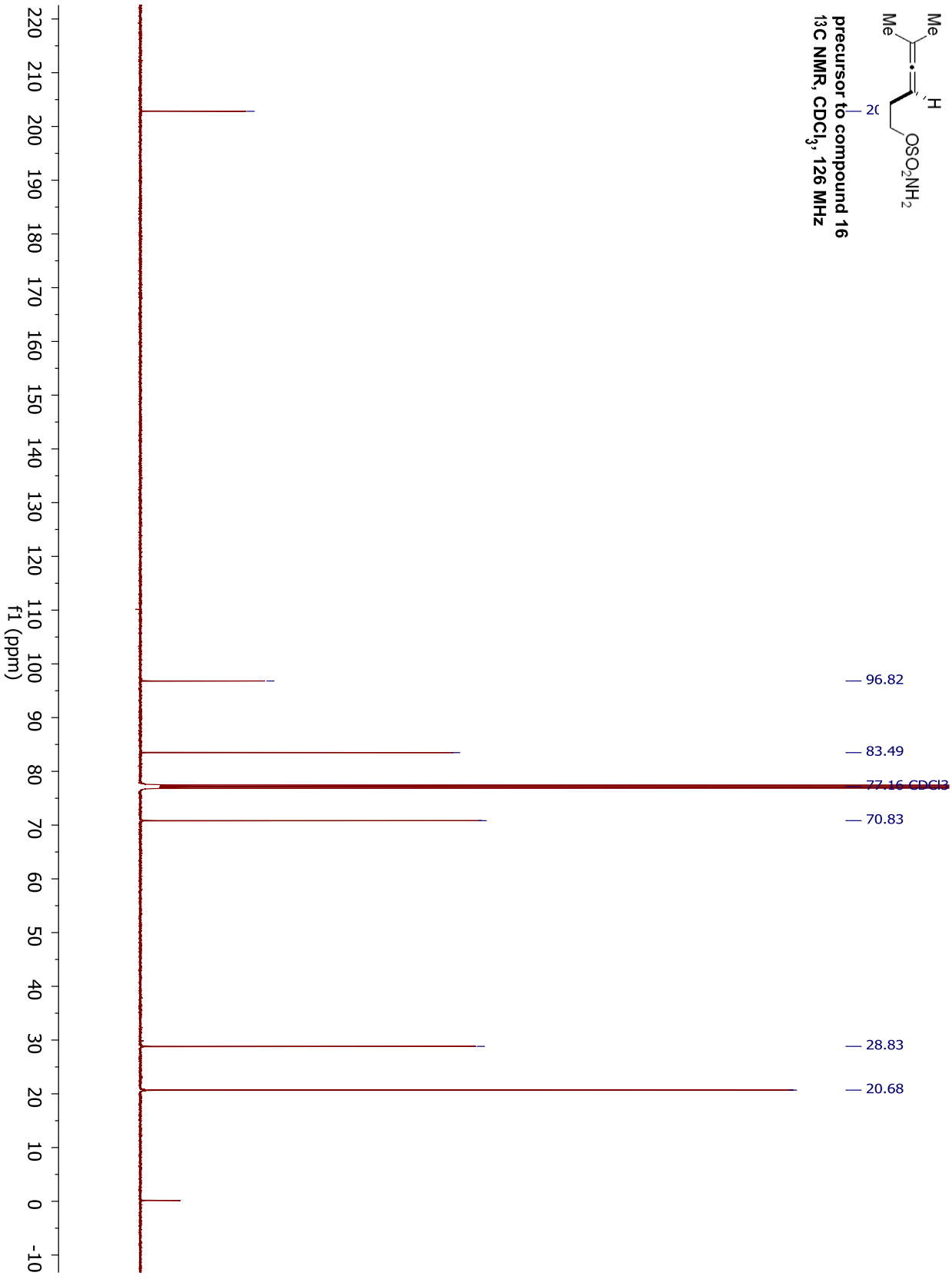
^{13}C NMR for the precursor for compound 13.



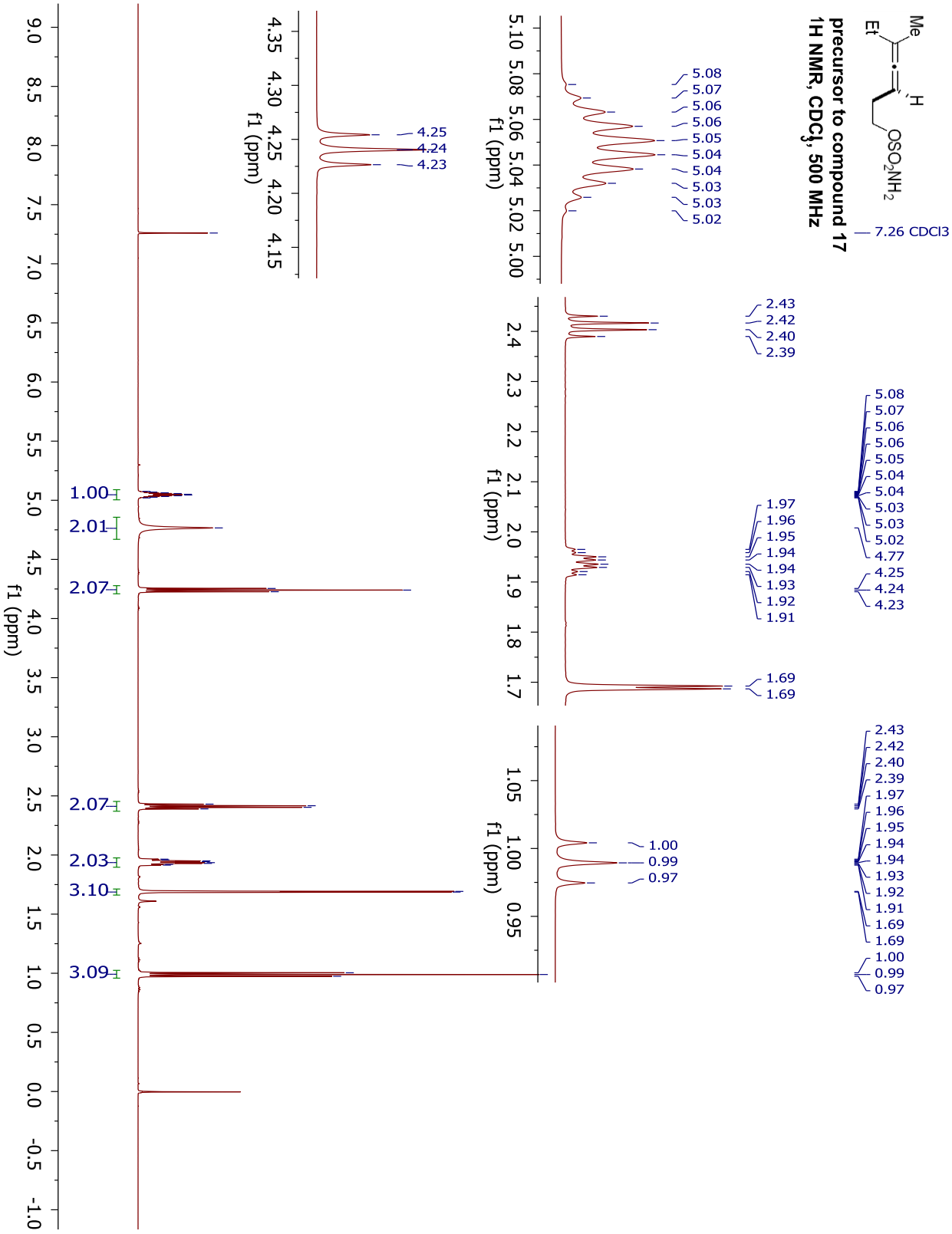
^{1}H NMR for the precursor for compound 16.



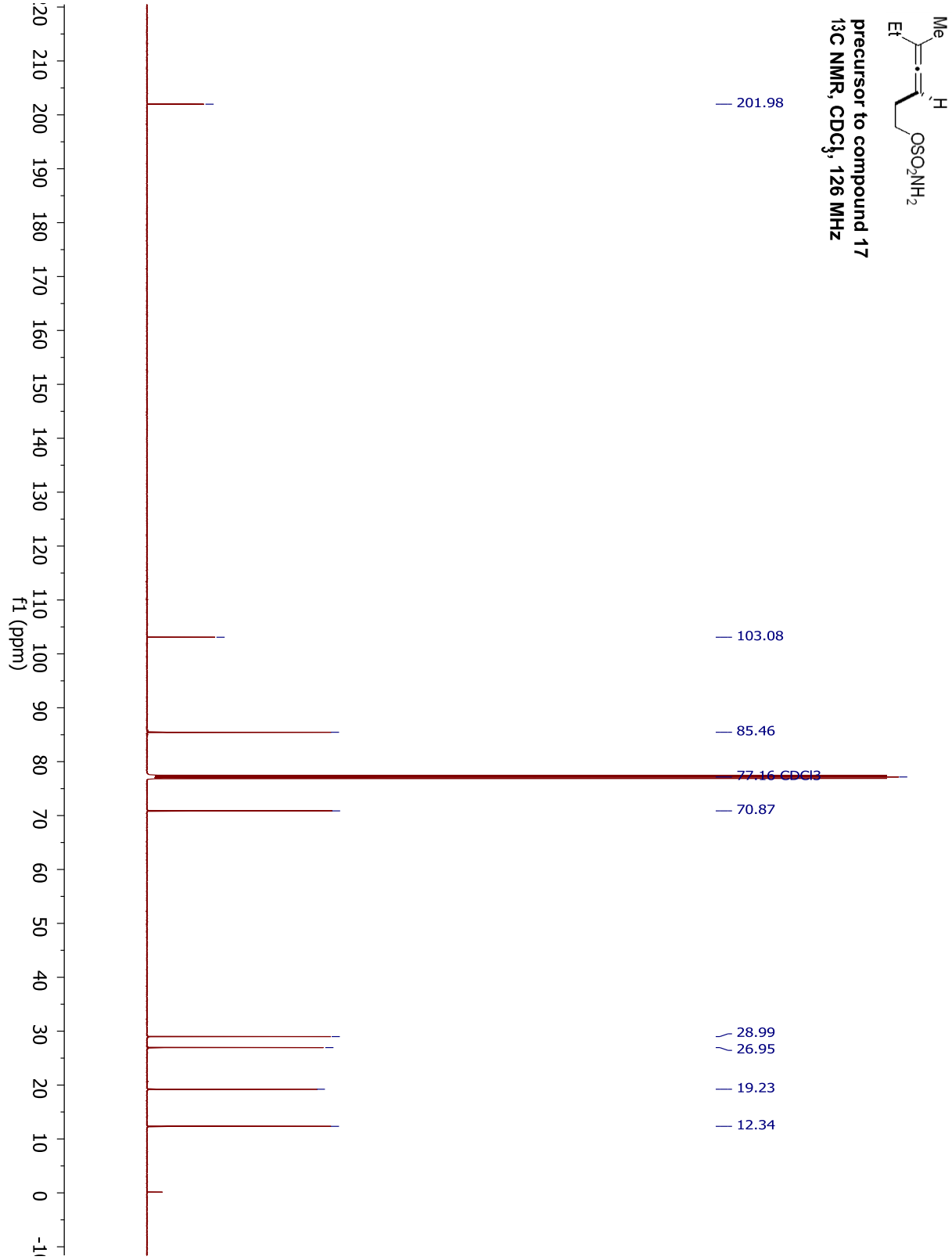
^{13}C NMR for the precursor for compound 16.



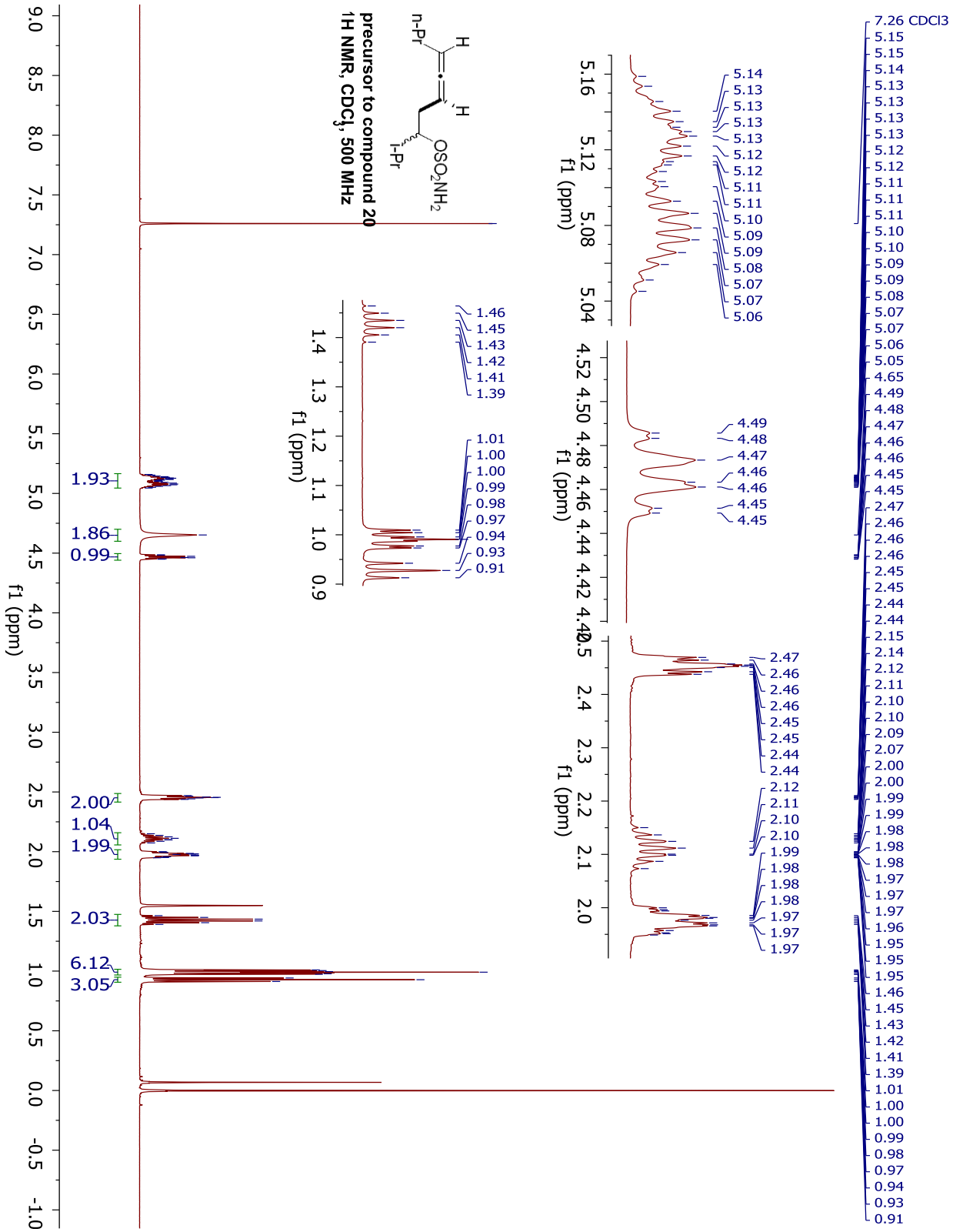
^{1}H NMR for the precursor for compound 17.



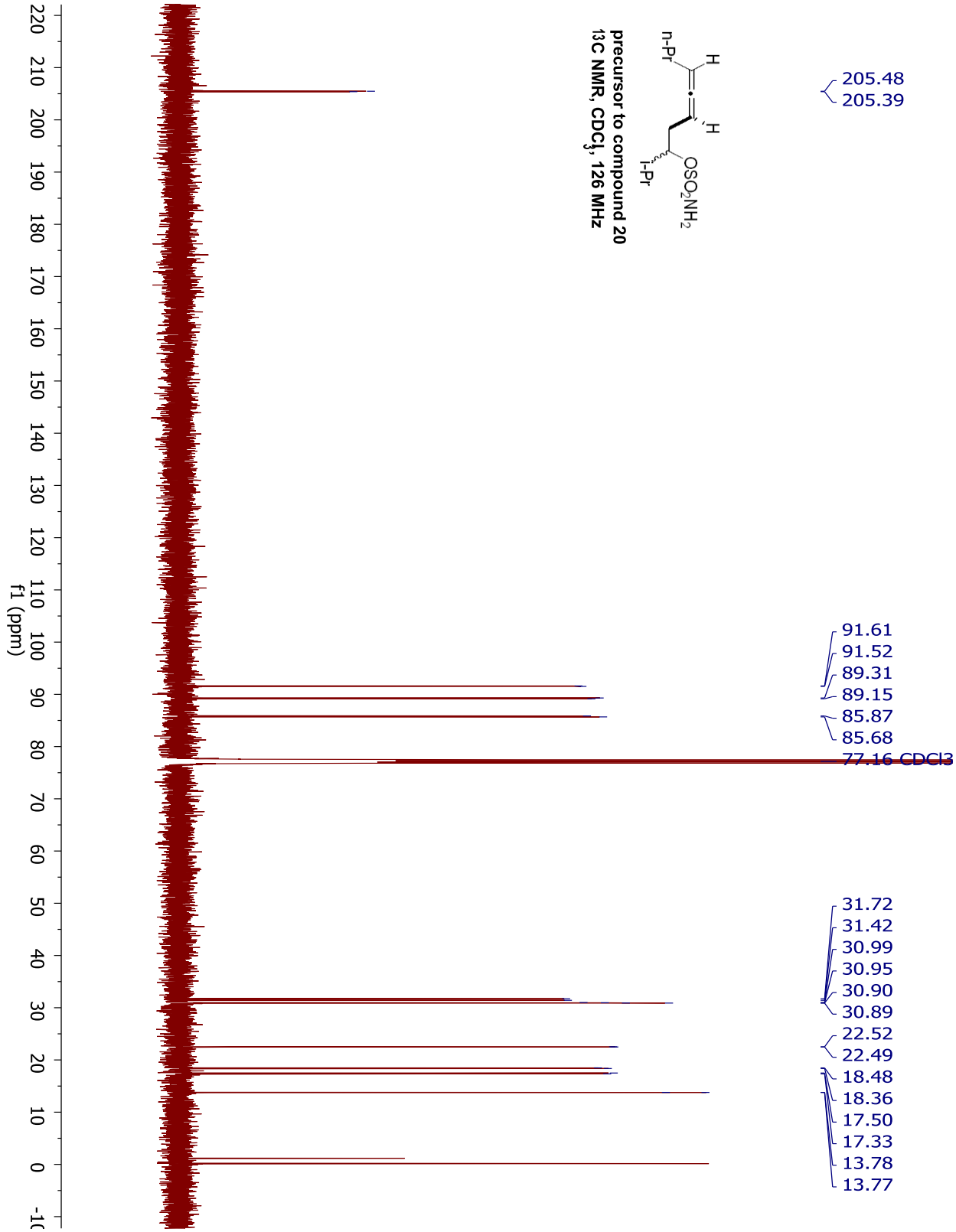
^{13}C NMR for the precursor for compound 17.



^{1}H NMR for the precursor for compound 20.



^{13}C NMR for the precursor for compound 20.



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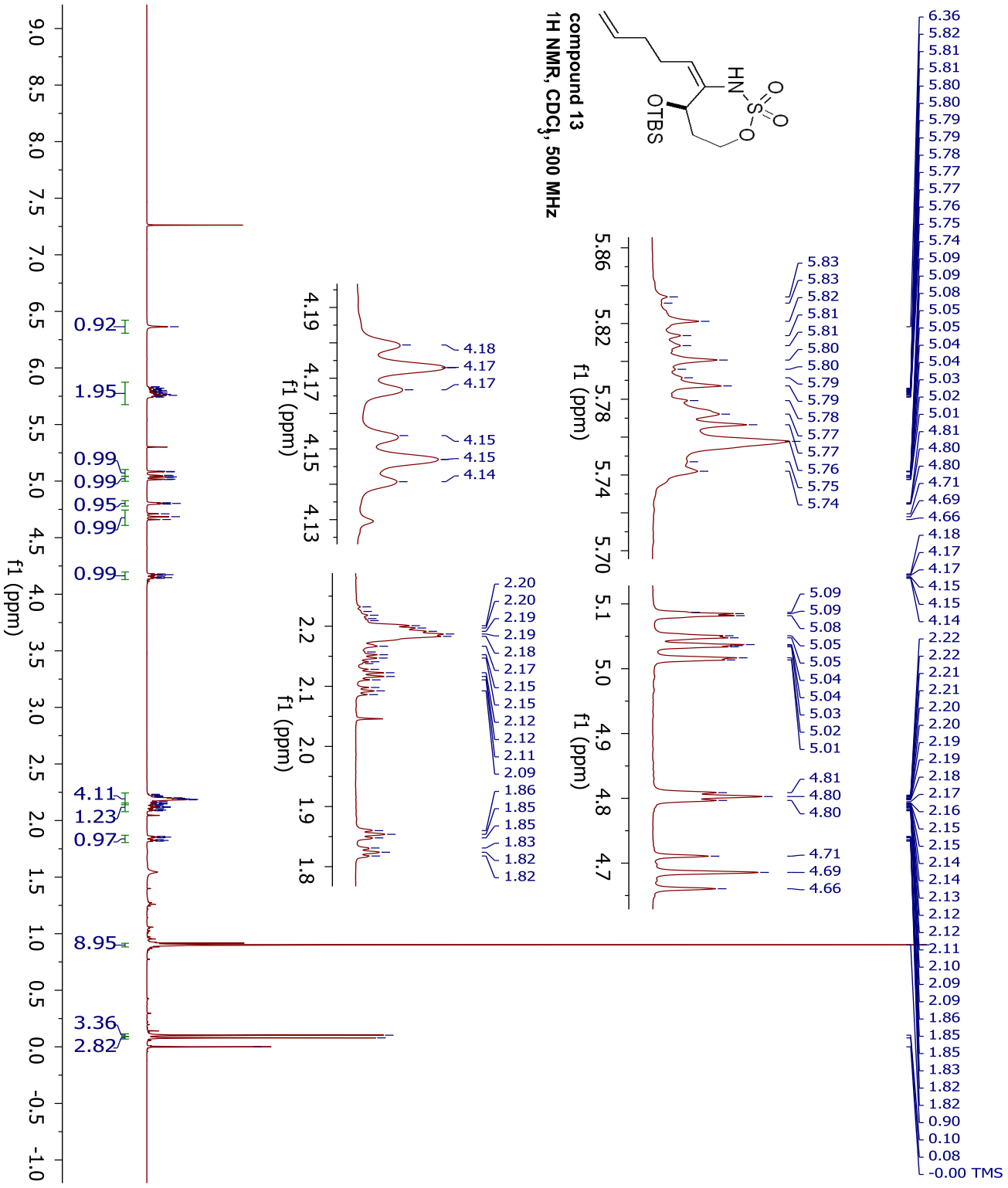

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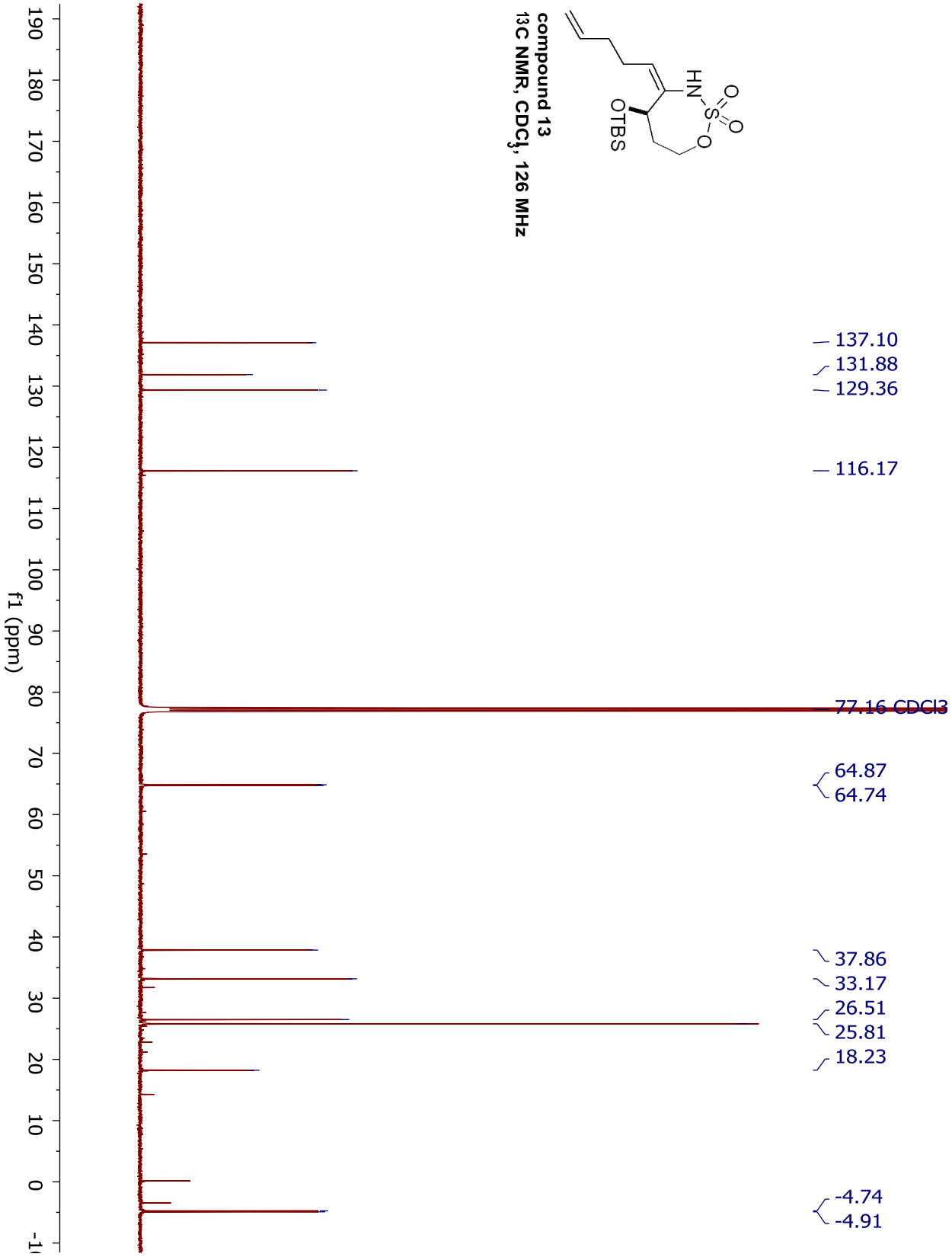
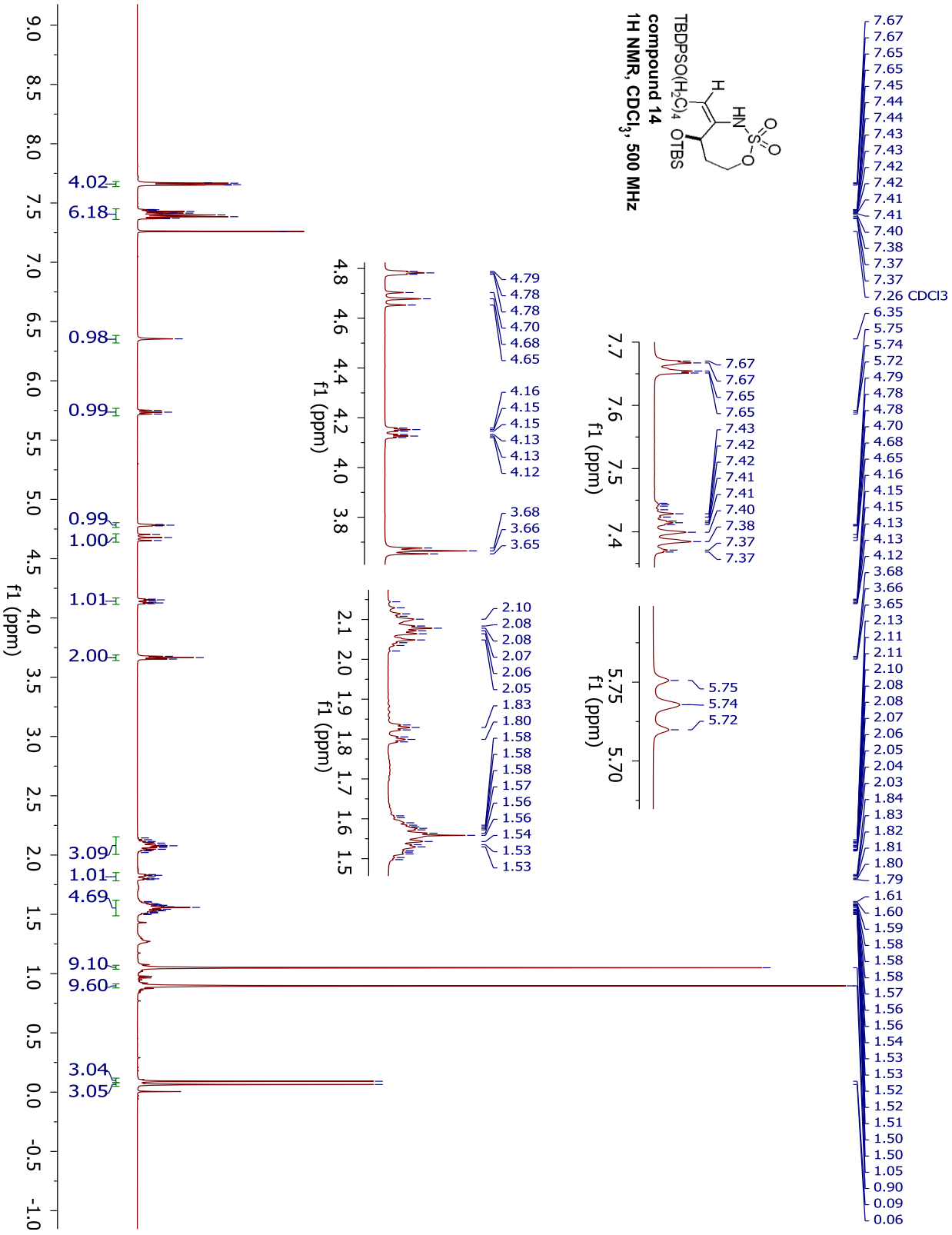
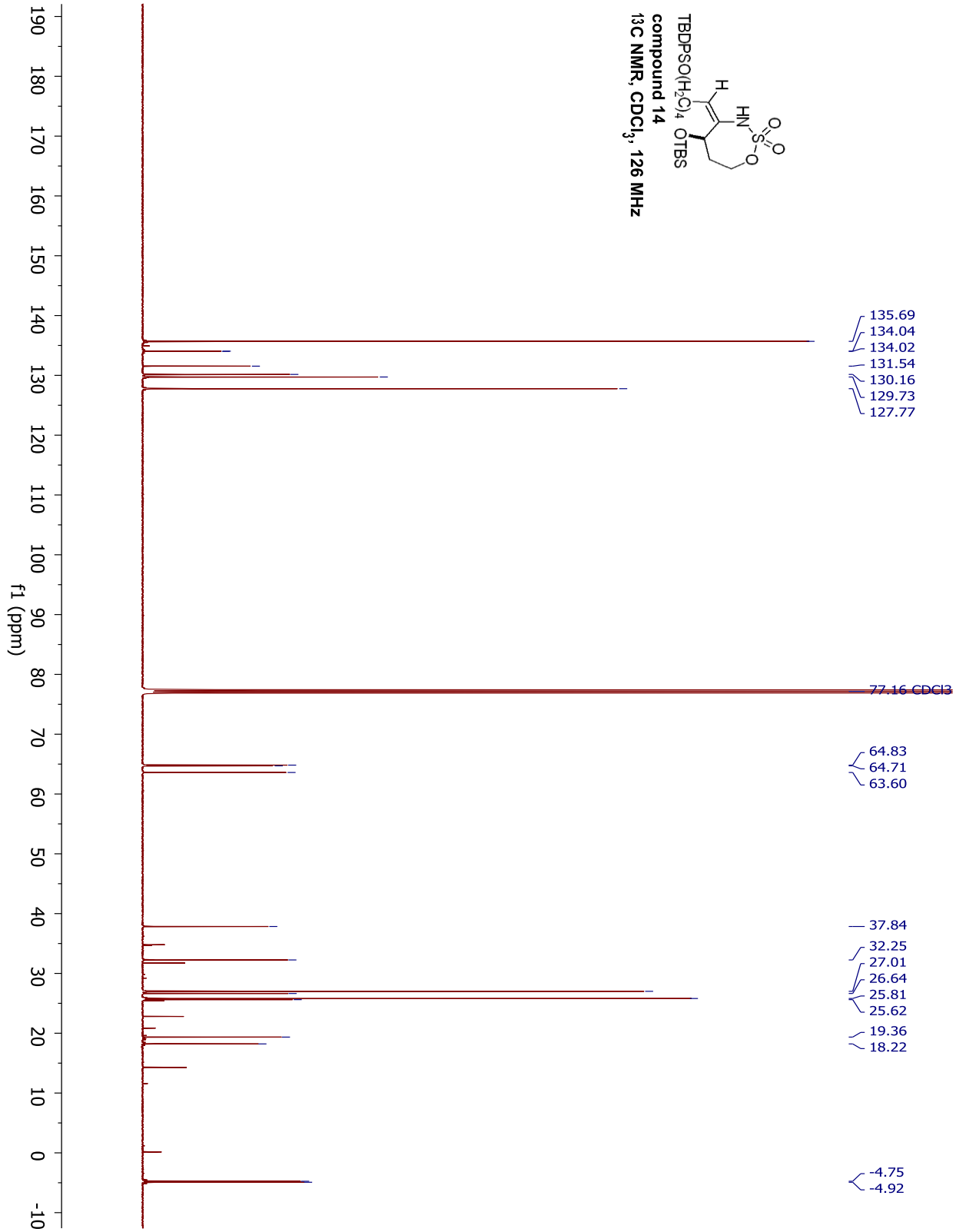


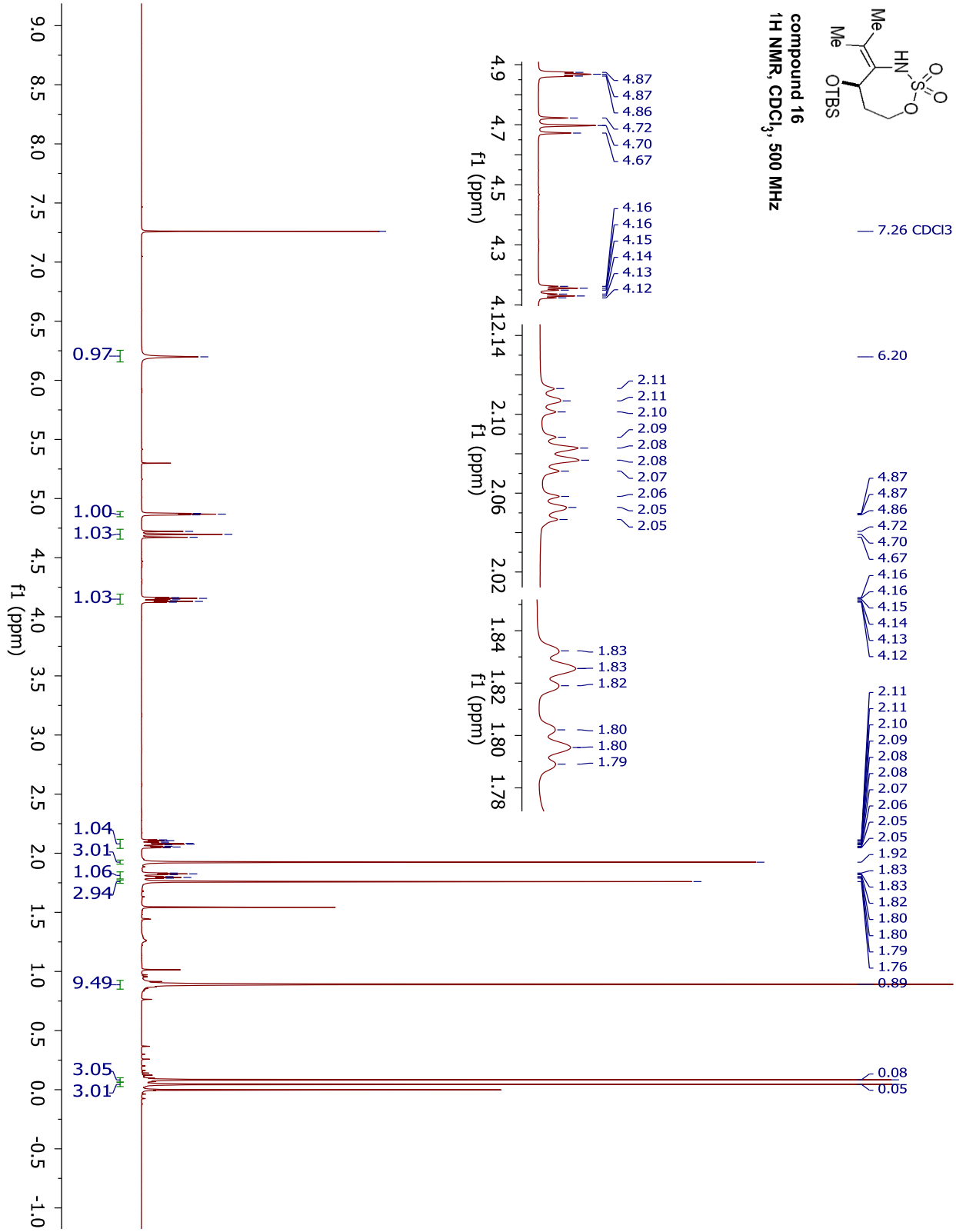
^{1}H NMR for compound 14.



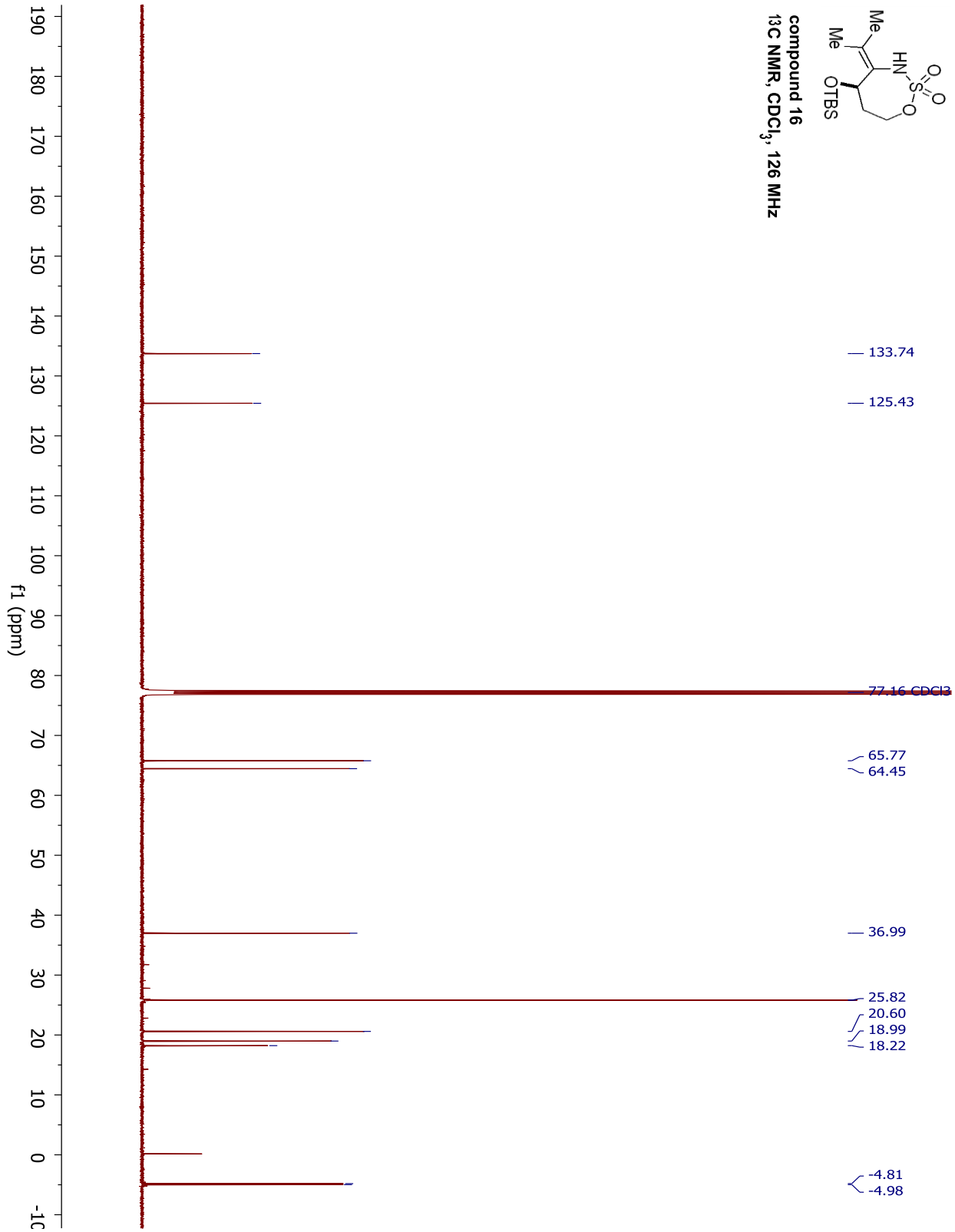
^{13}C NMR for compound 14.



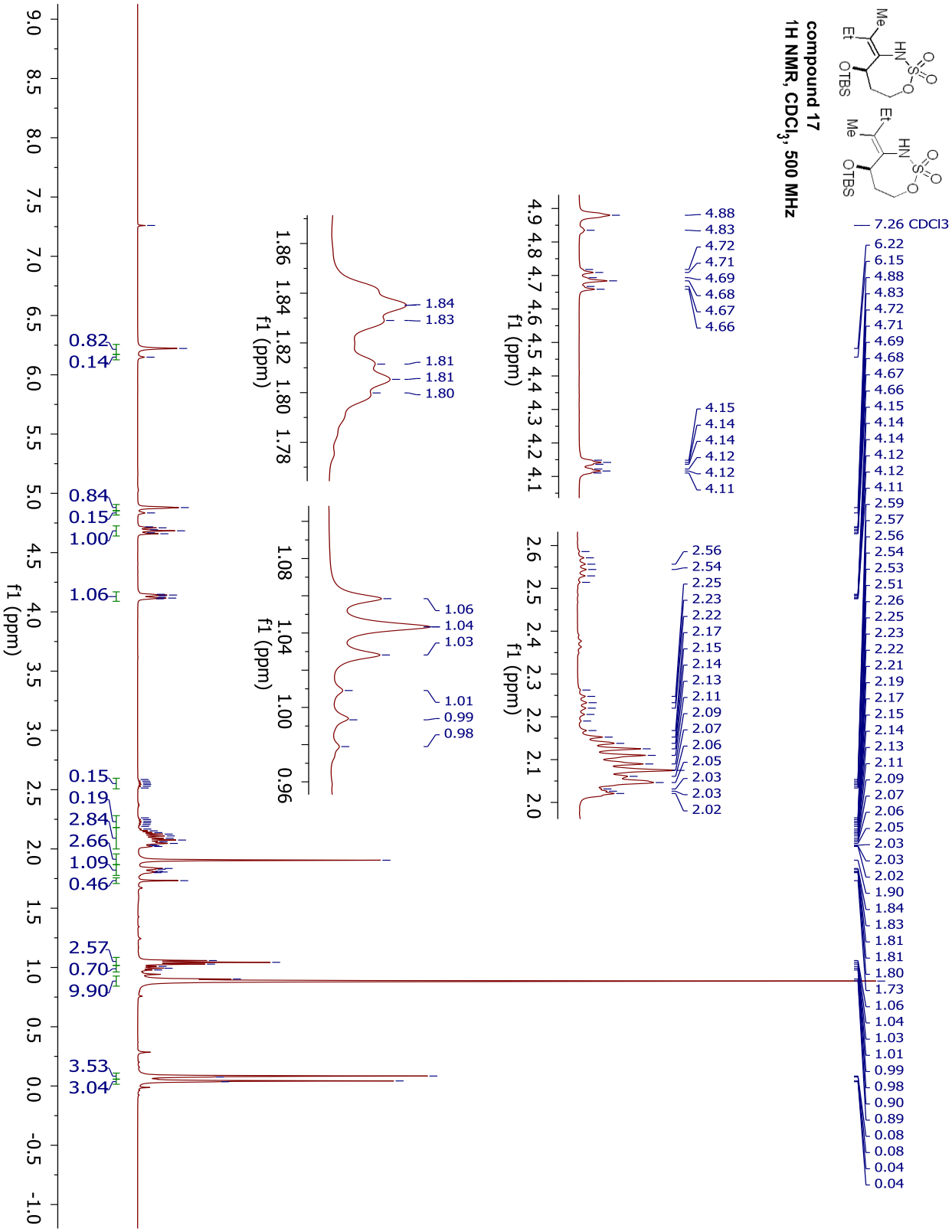
^{1}H NMR for compound 16.



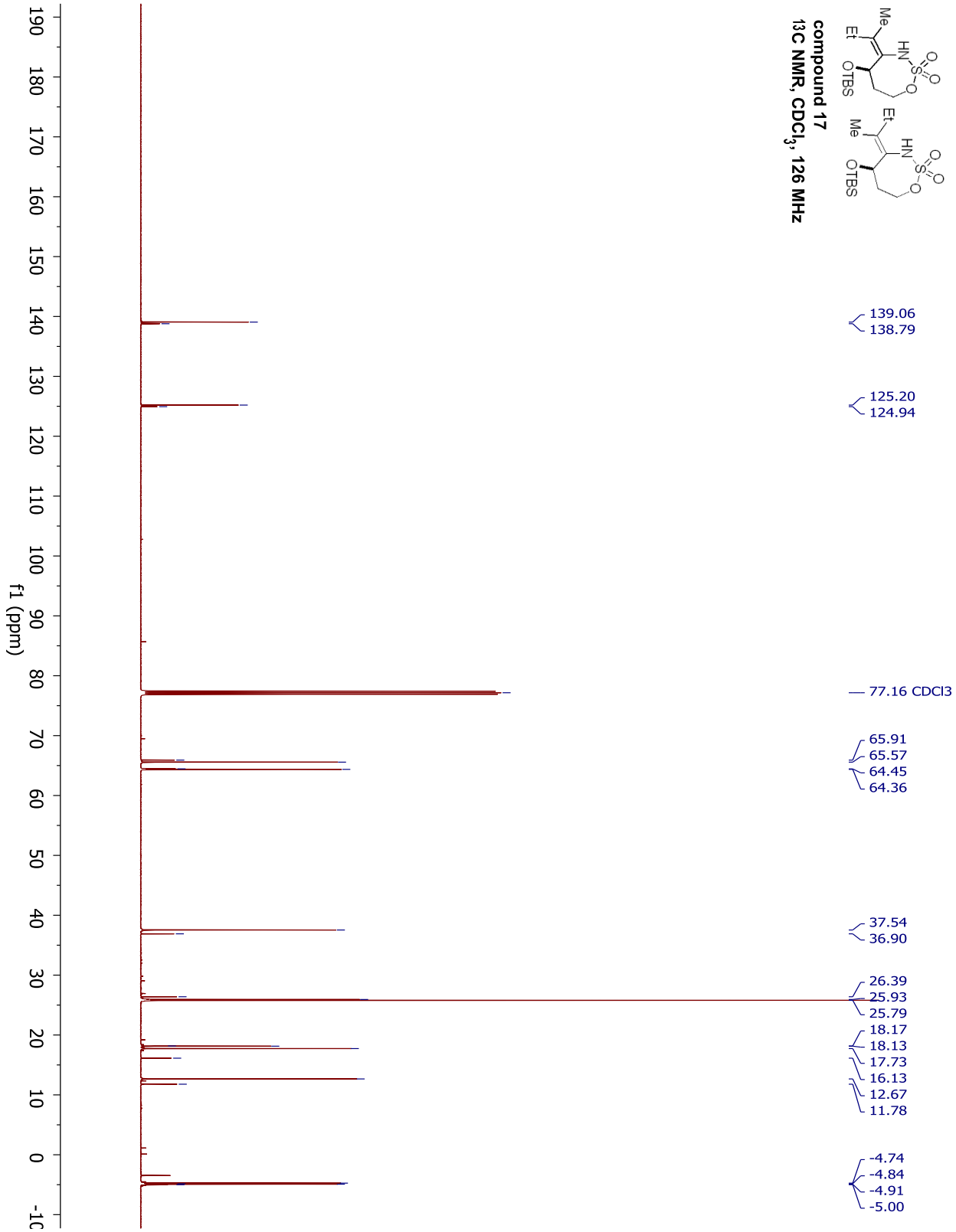
^{13}C NMR for compound 16.



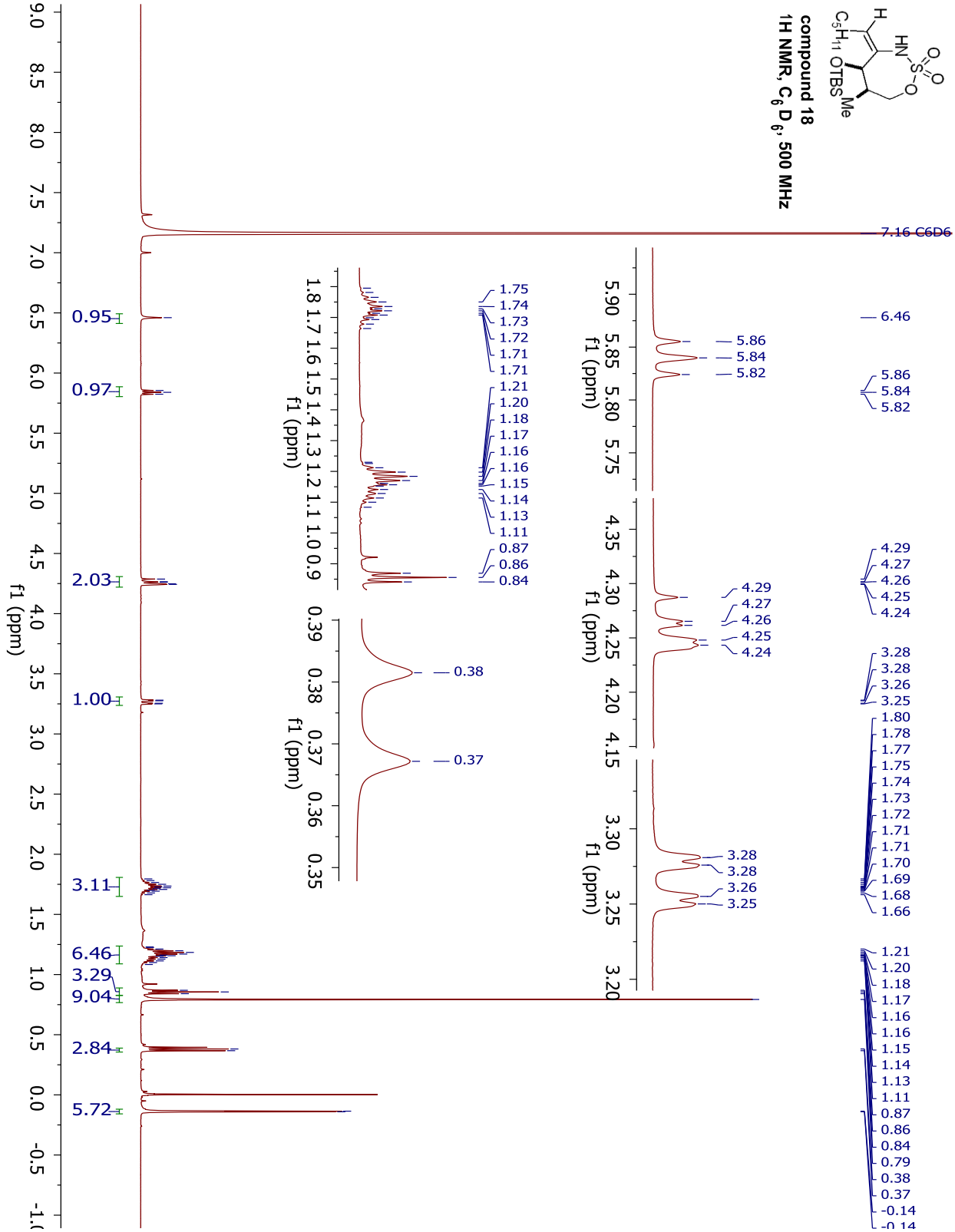
^{1}H NMR for compound 17.



^{13}C NMR for compound 17.



^{1}H NMR for compound 18.



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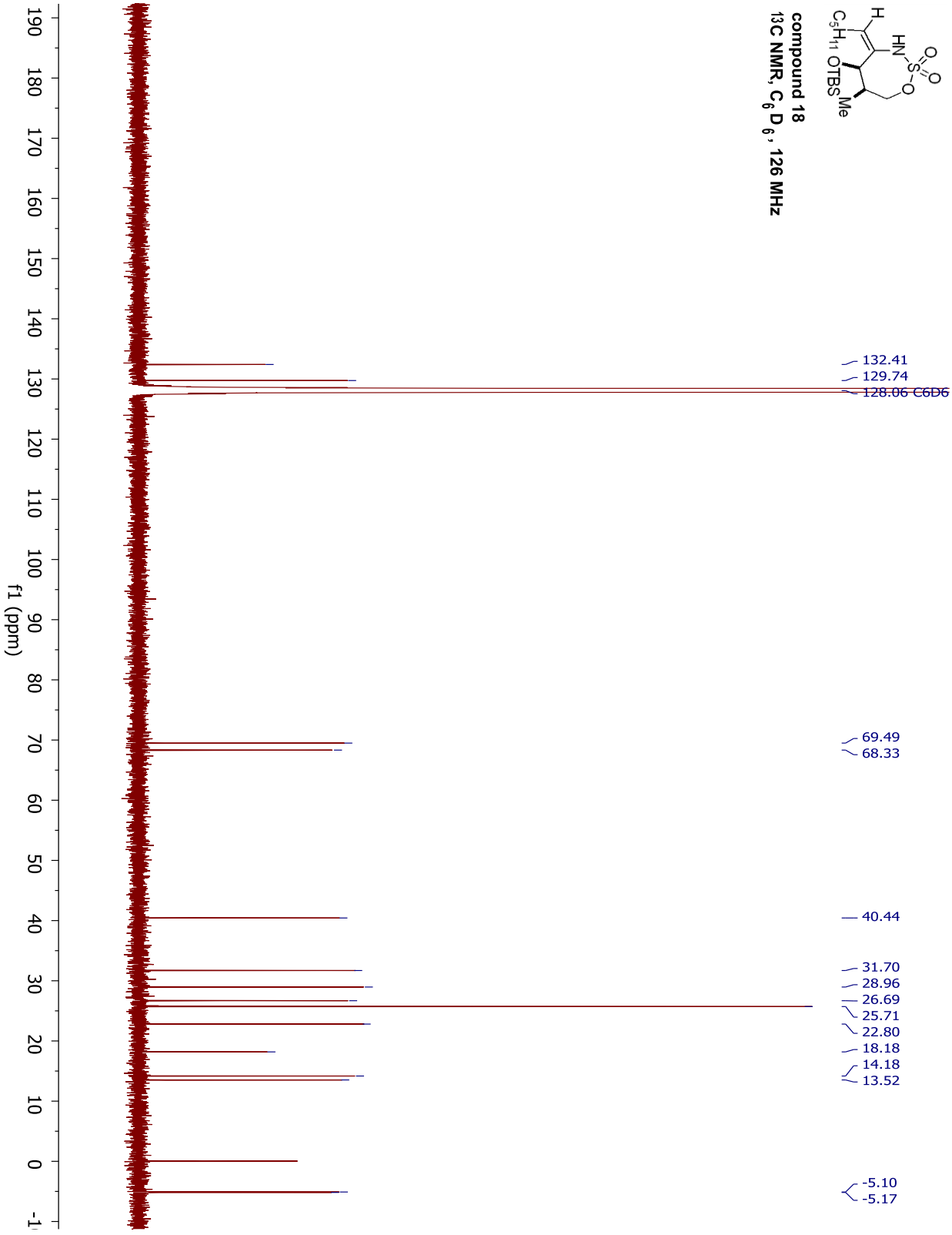
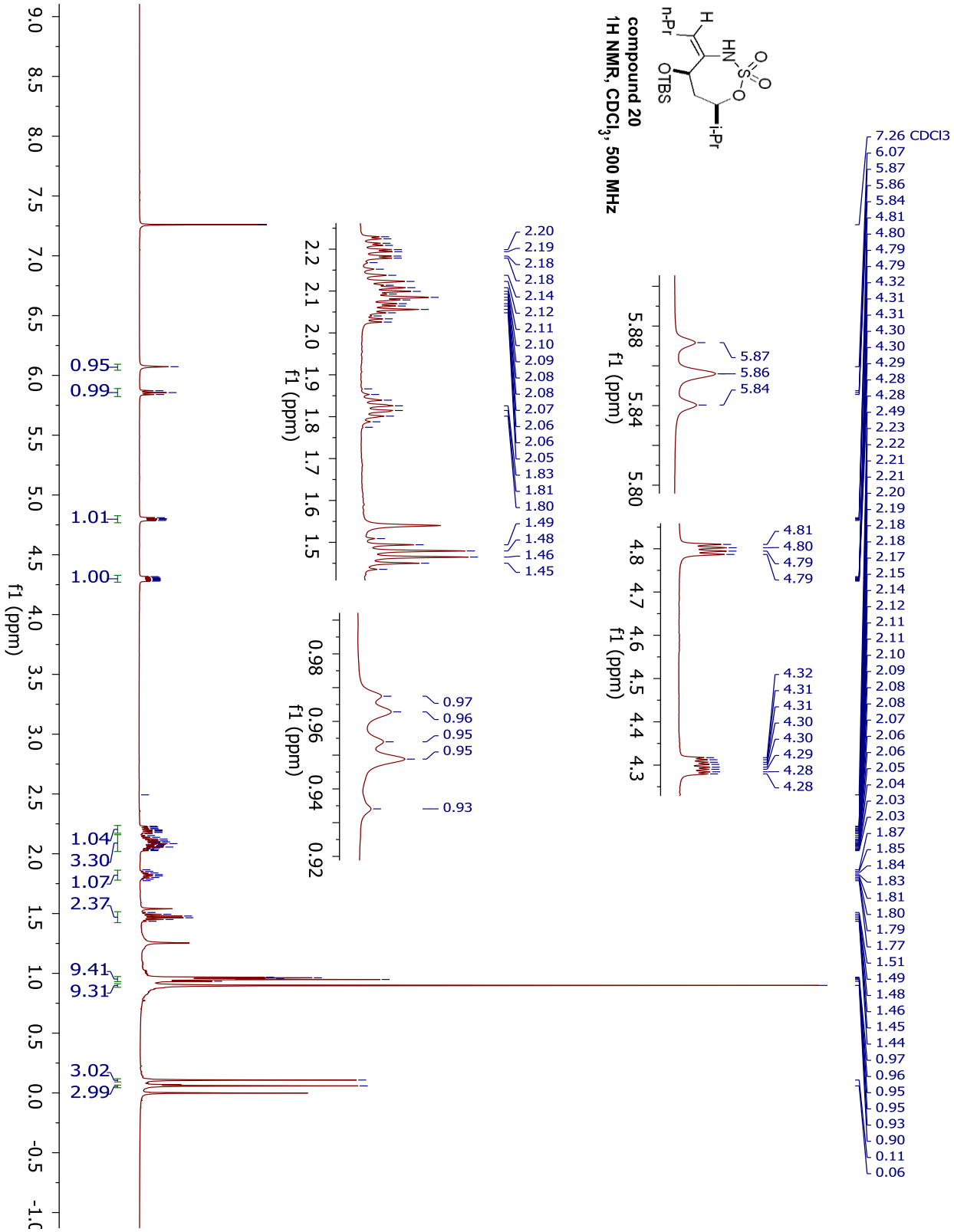


^{1}H NMR for compound 20.



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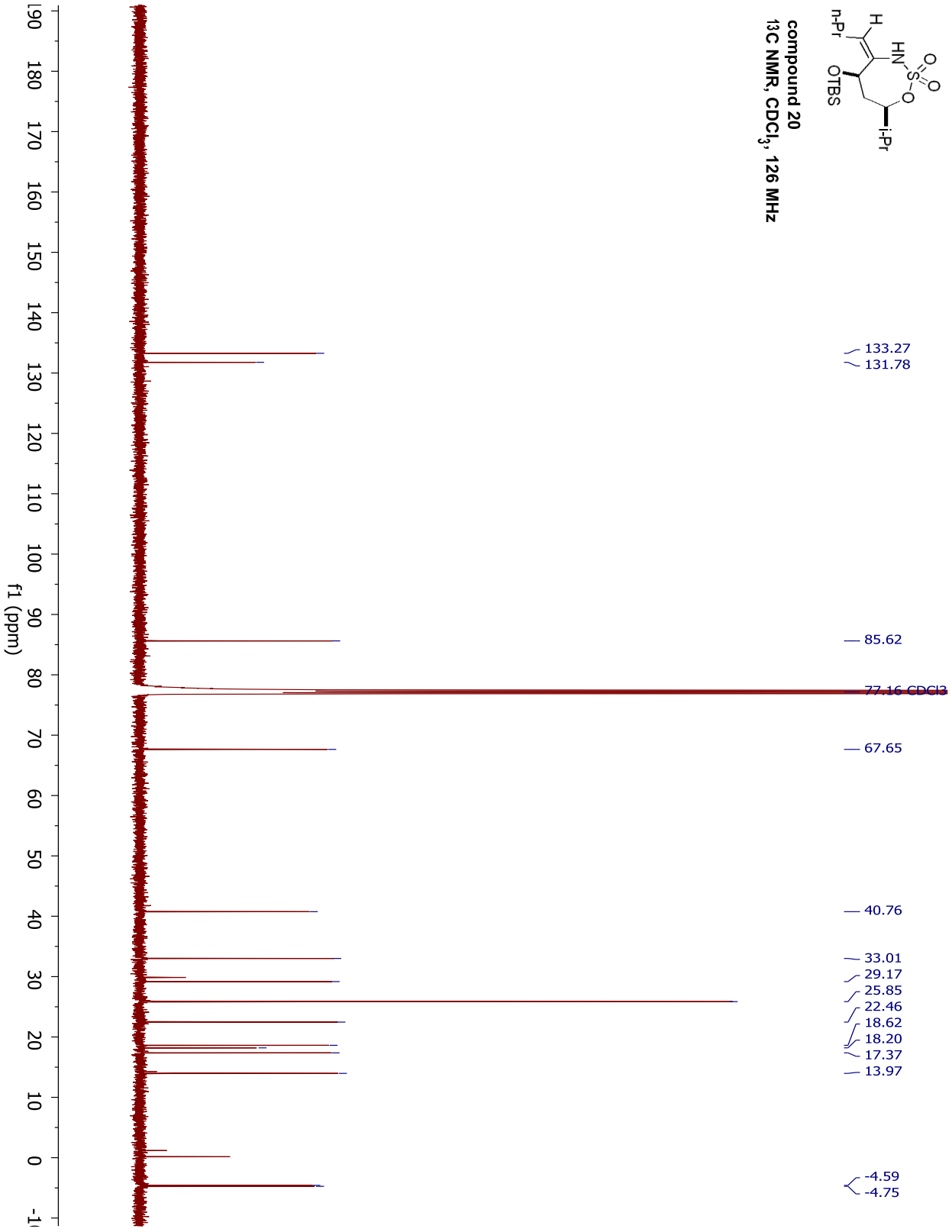
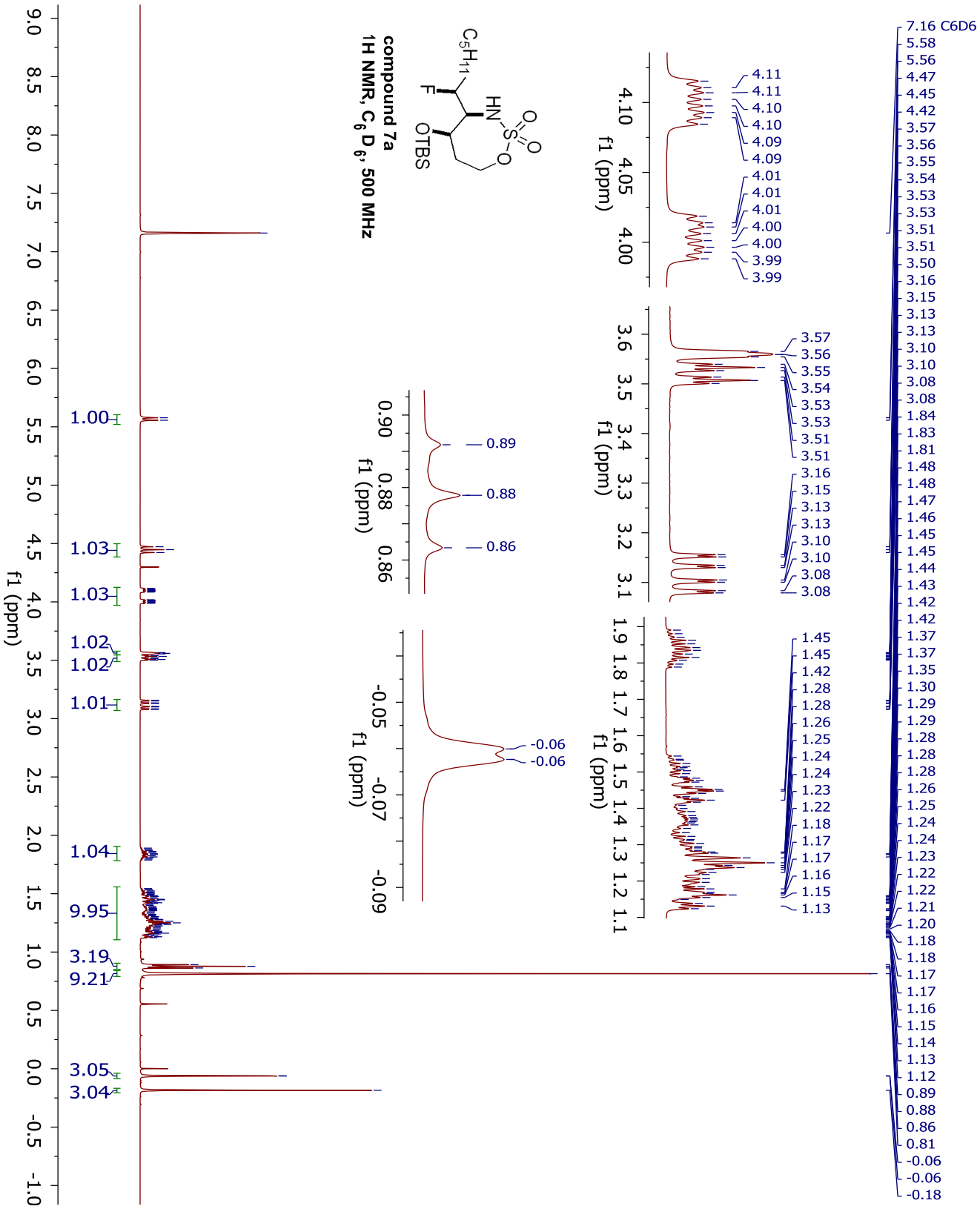


^{1}H NMR for compound 7a.



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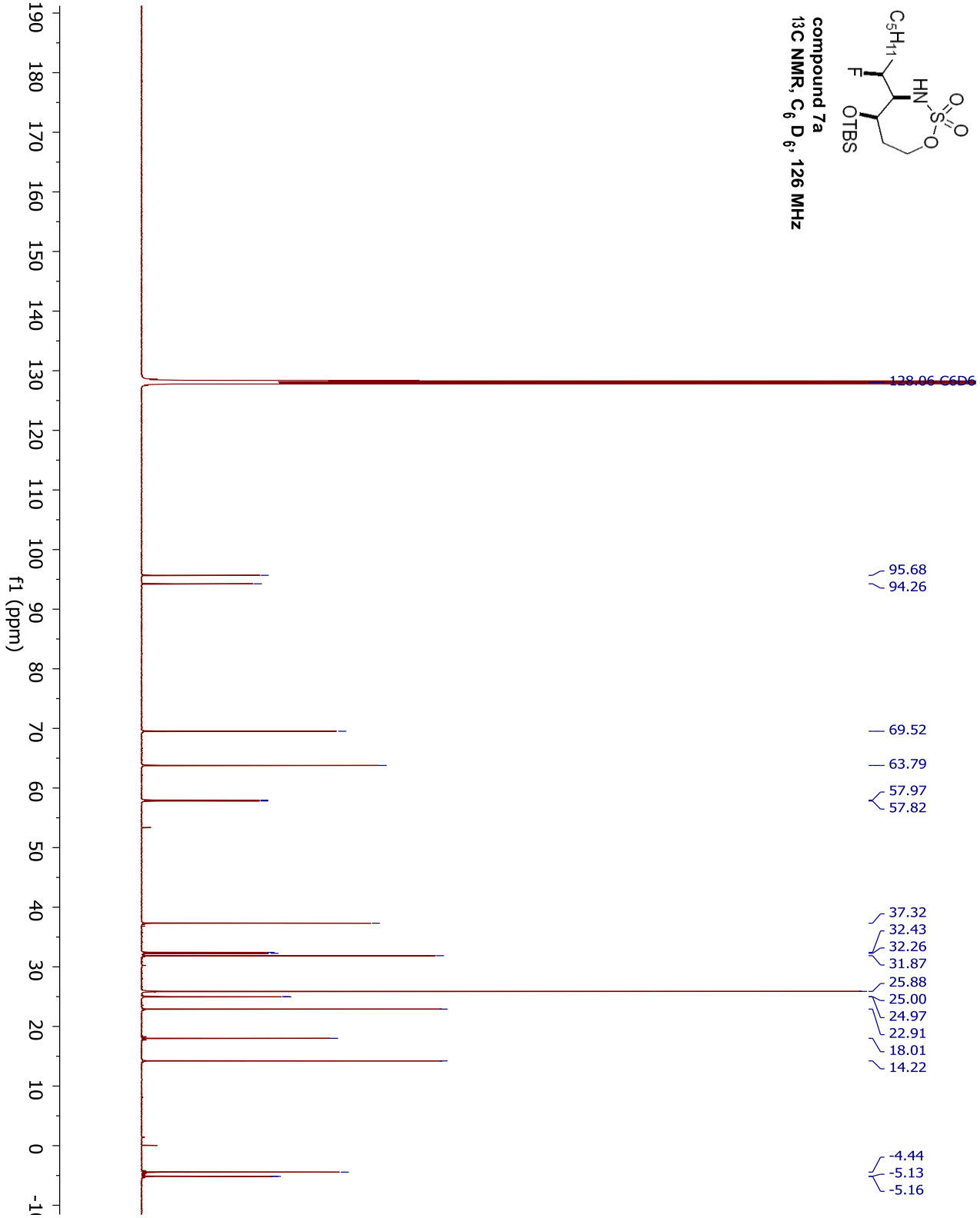
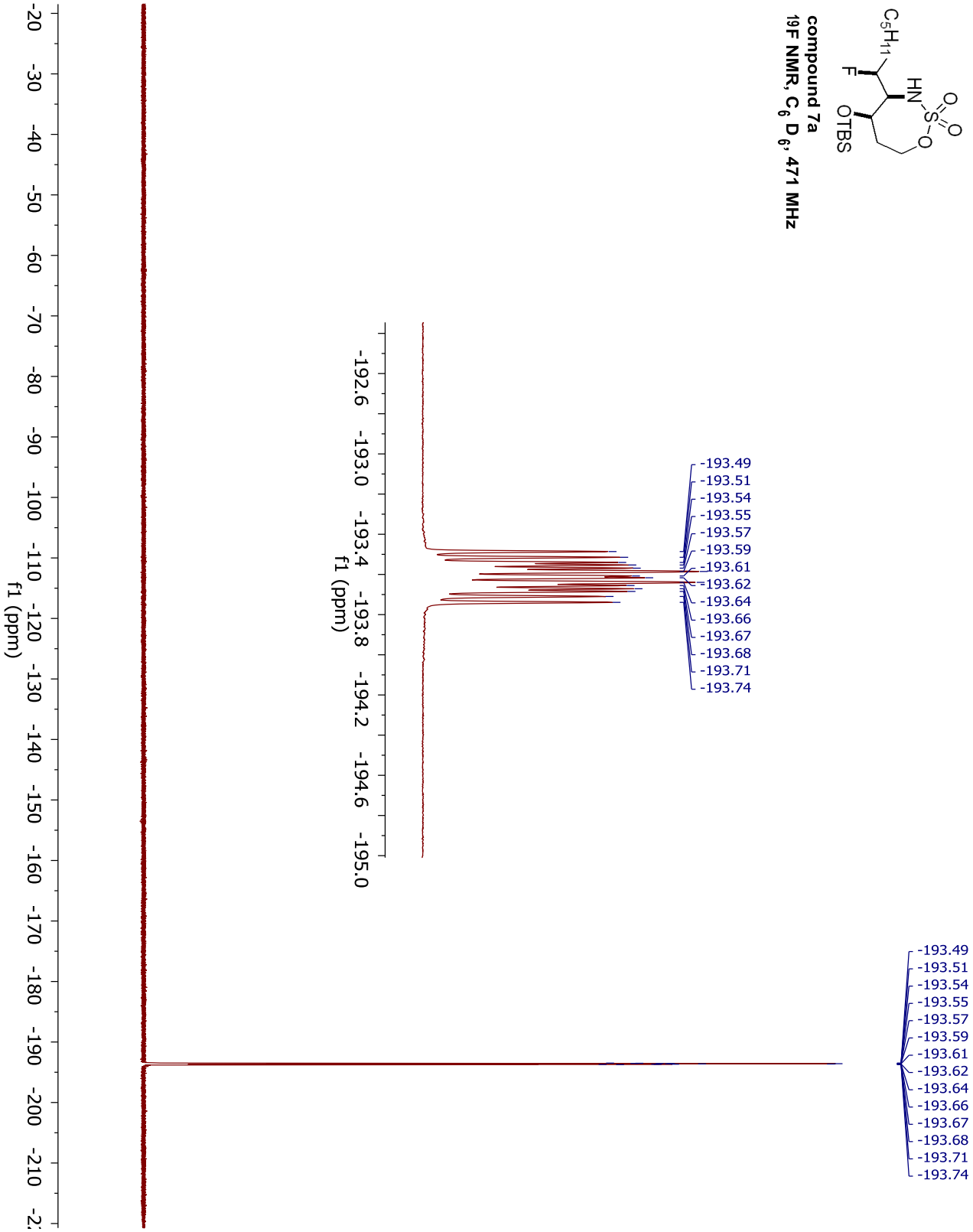
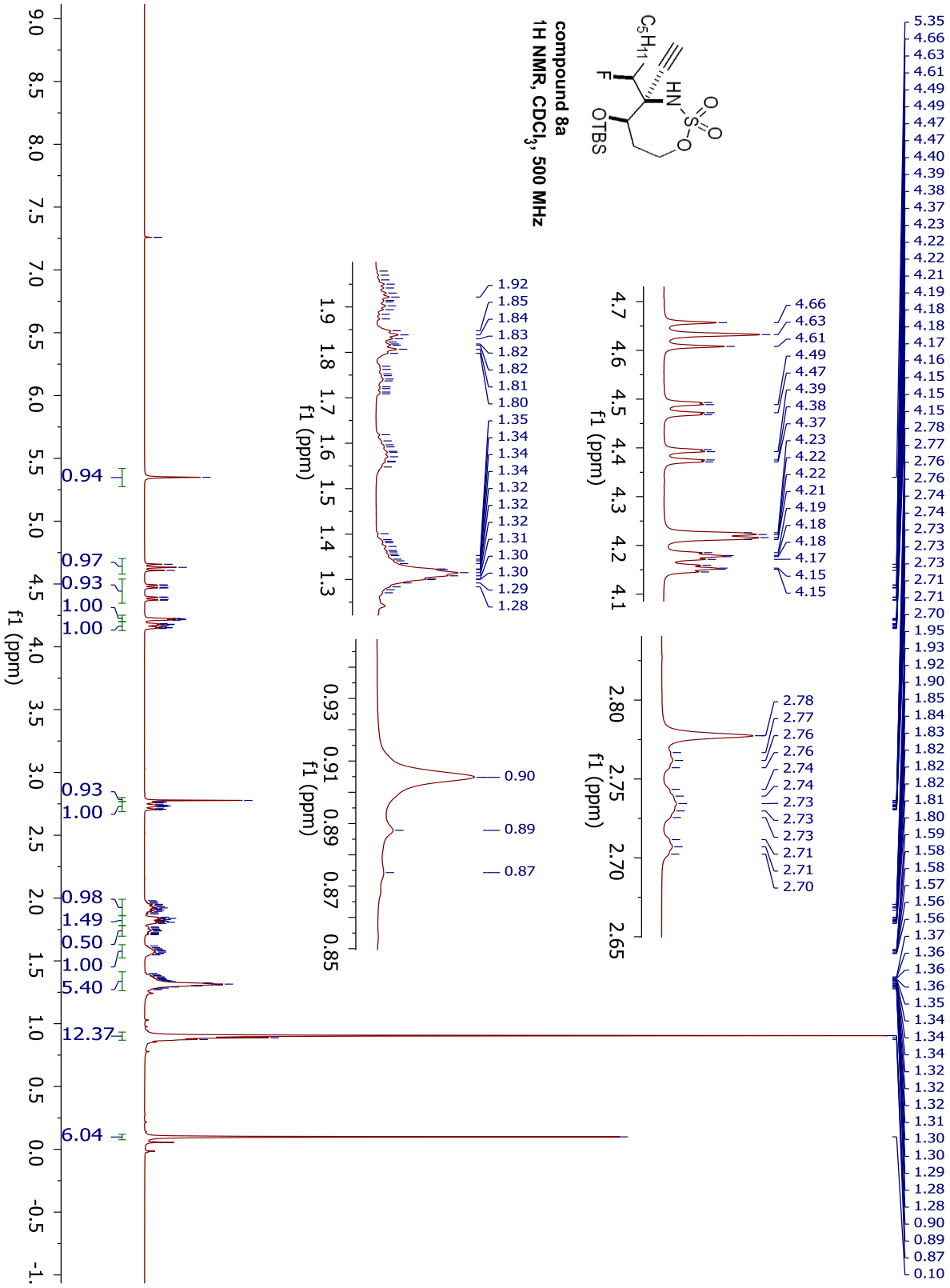


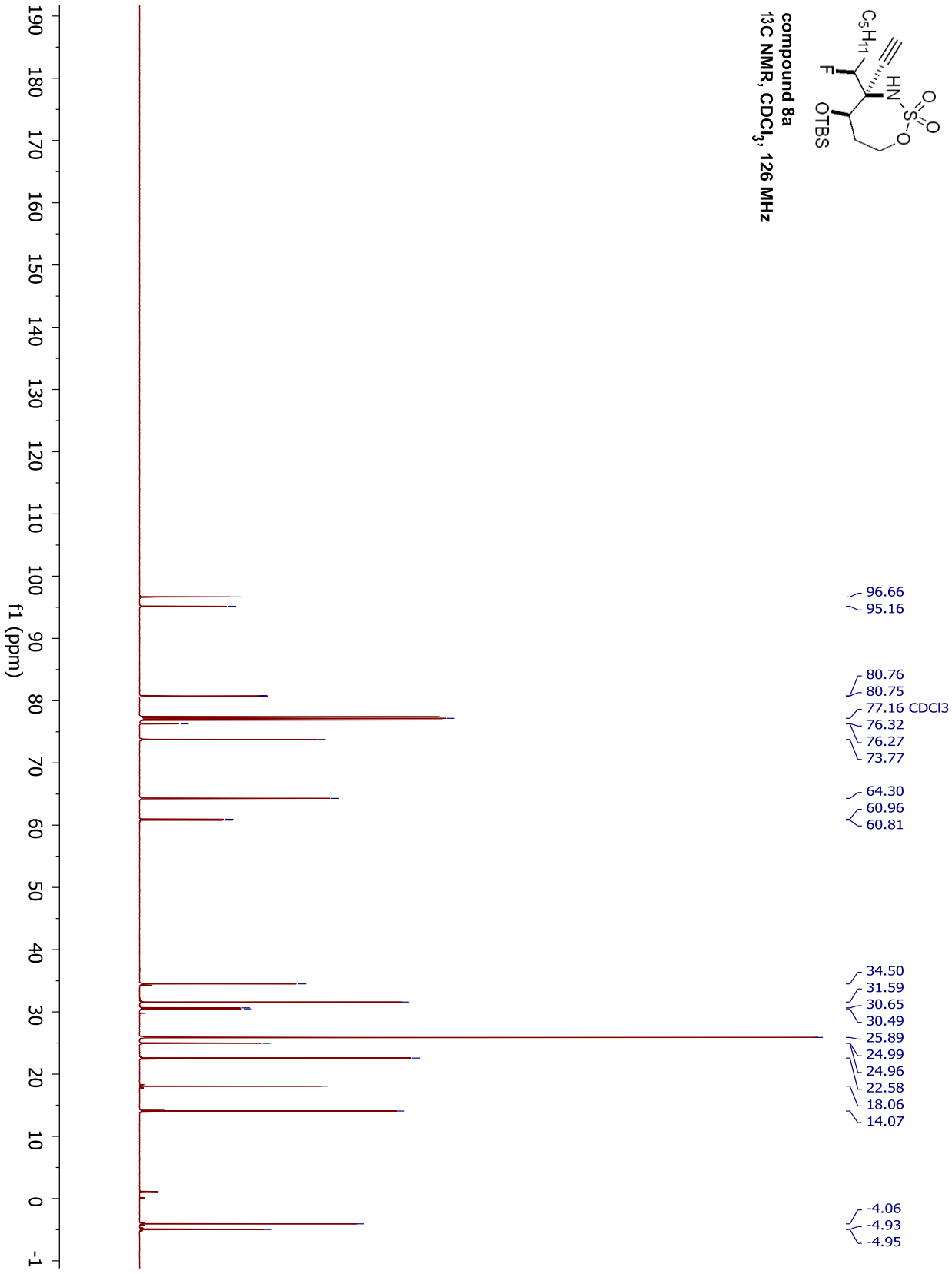
^{19}F NMR for compound 7a.



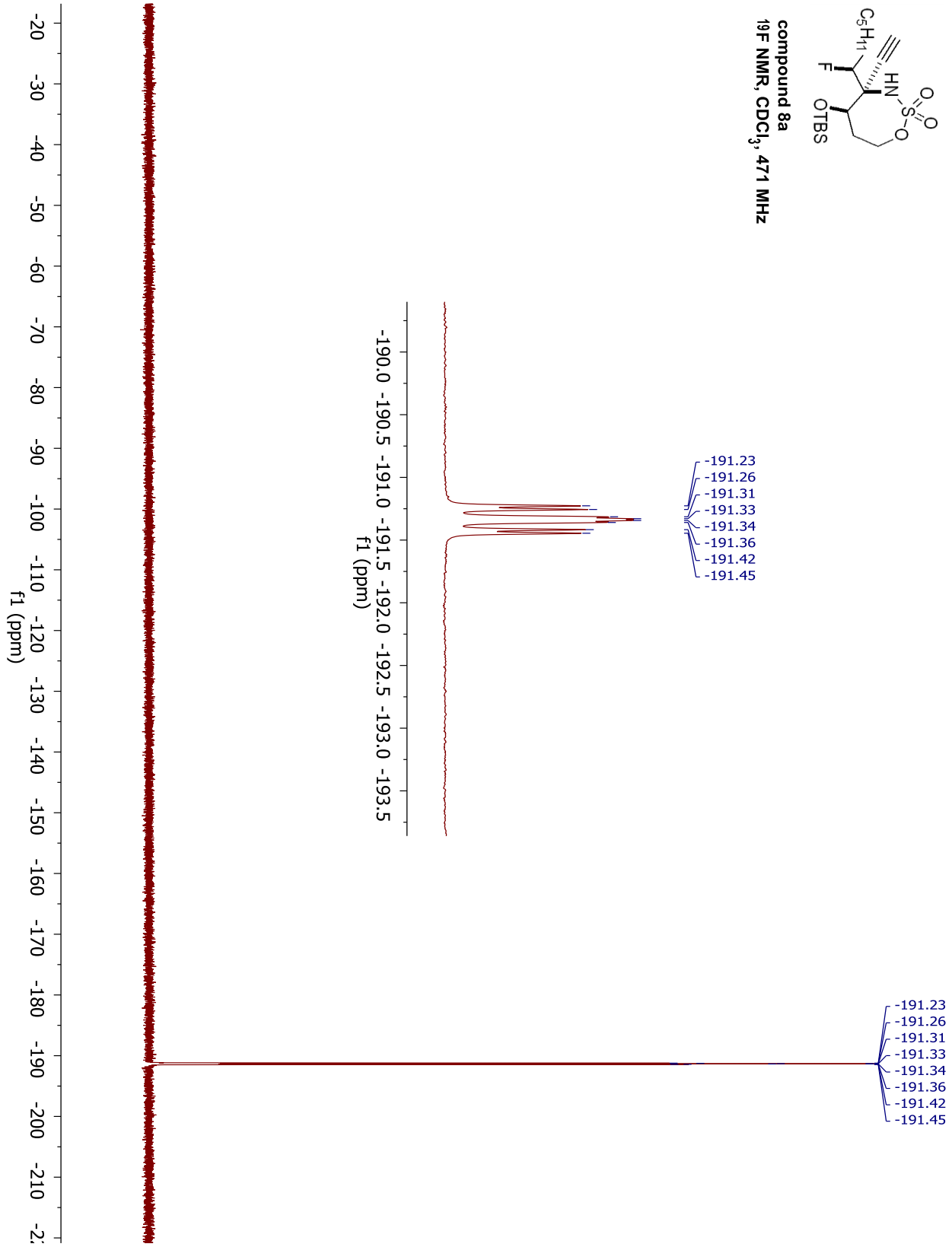
^{1}H NMR for compound 8a.



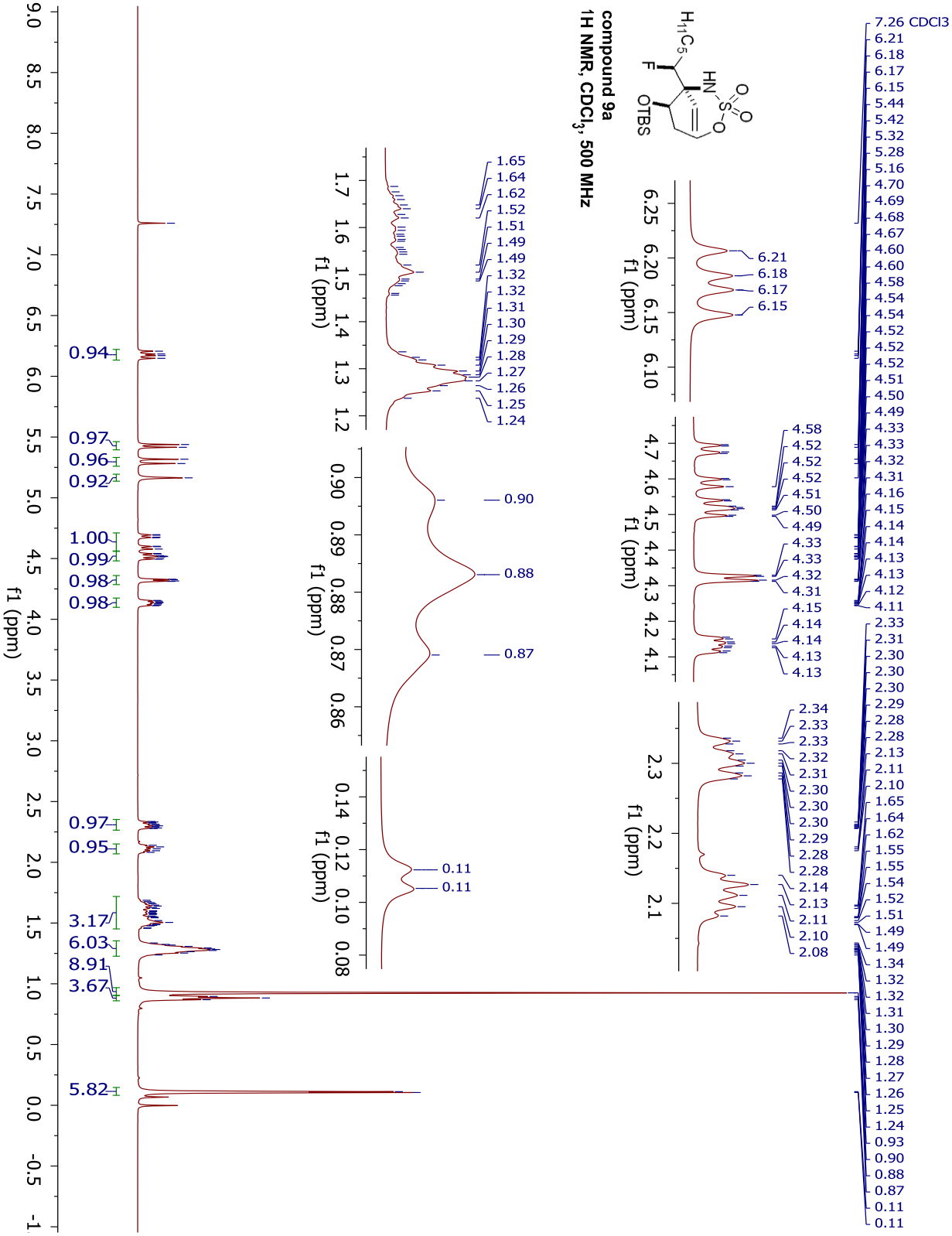
^{13}C NMR for compound 8a.



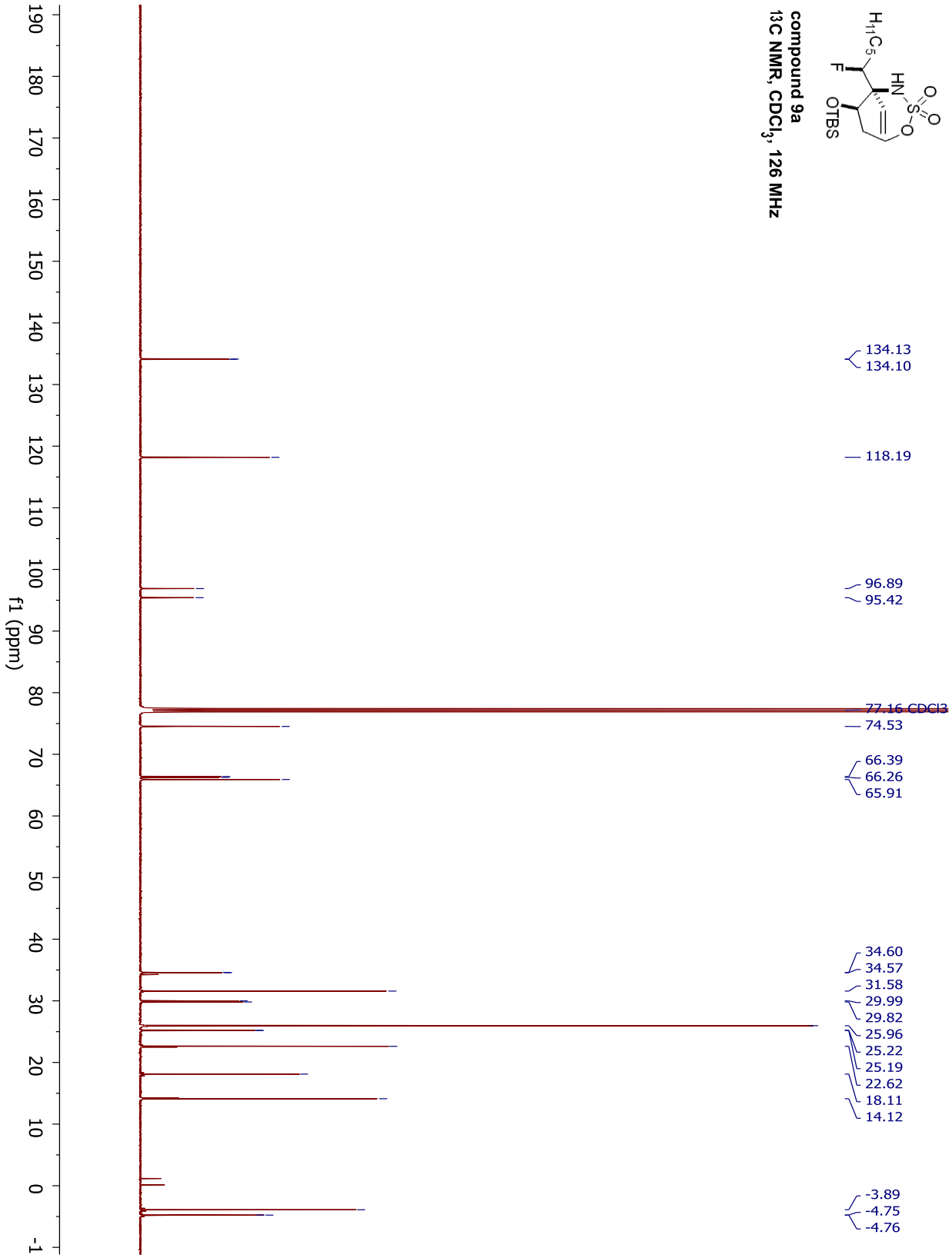
^{19}F NMR for compound 8a.



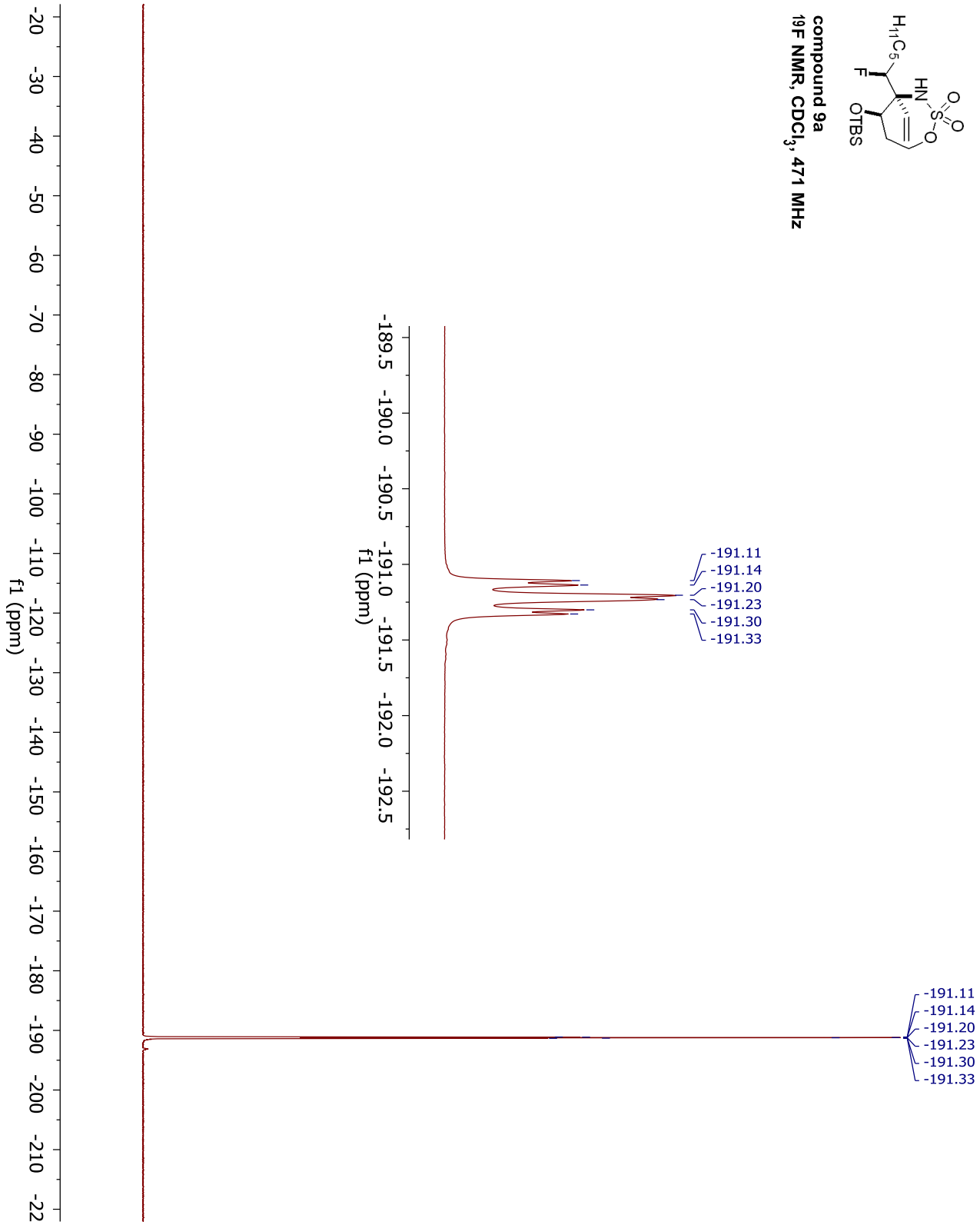
^{1}H NMR for compound 9a.



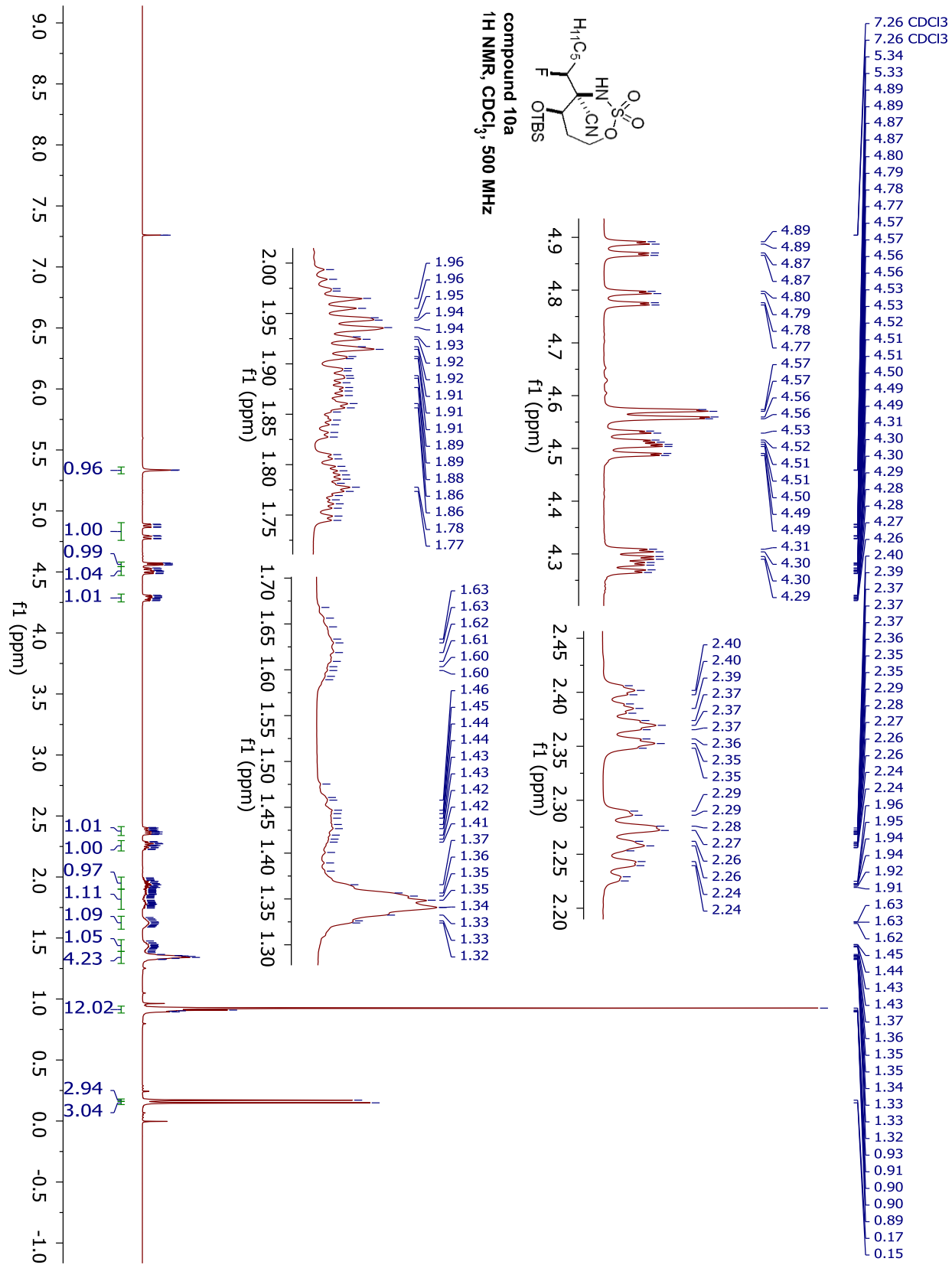
^{13}C NMR for compound 9a.



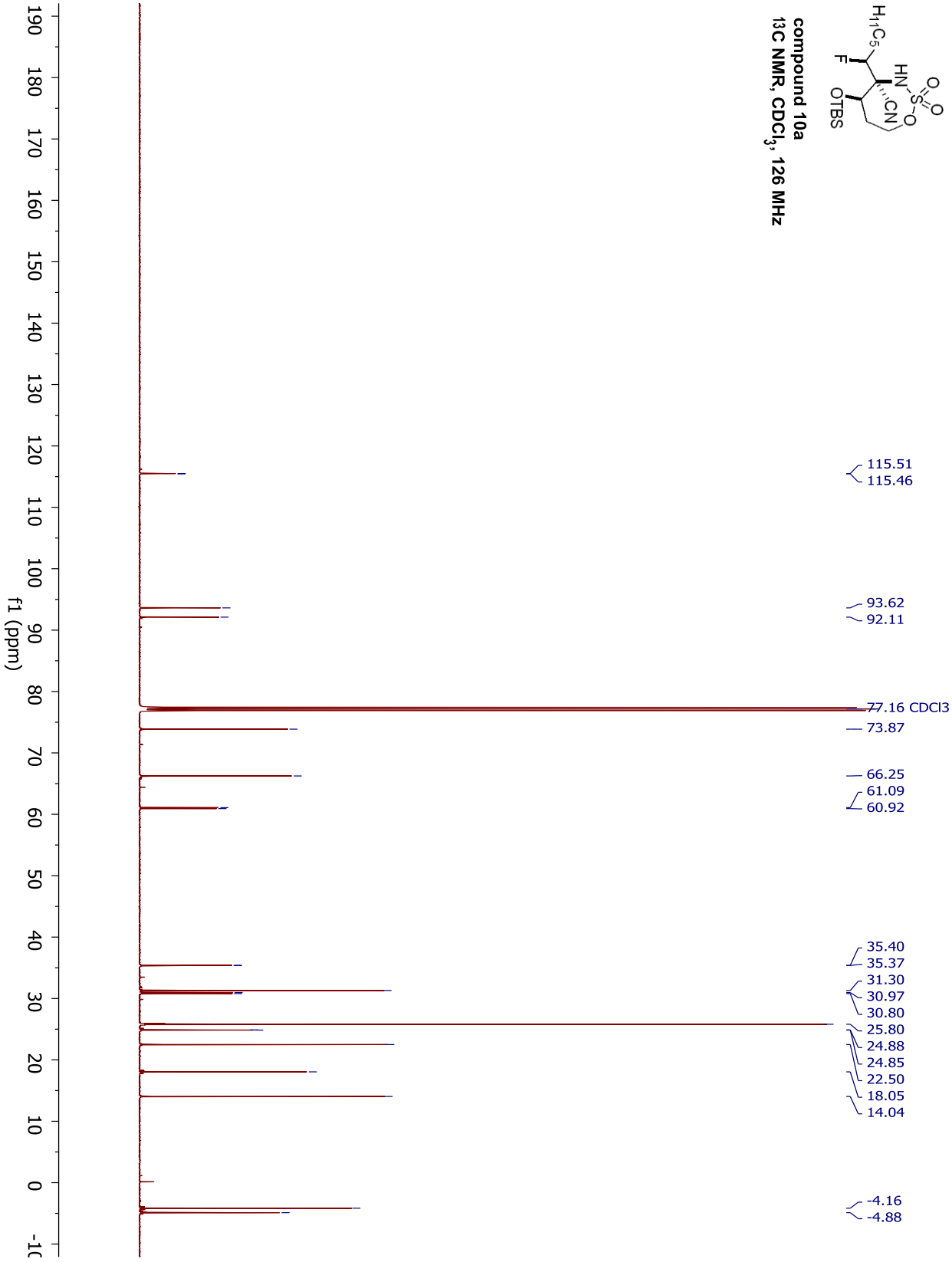
^{19}F NMR for compound 9a.



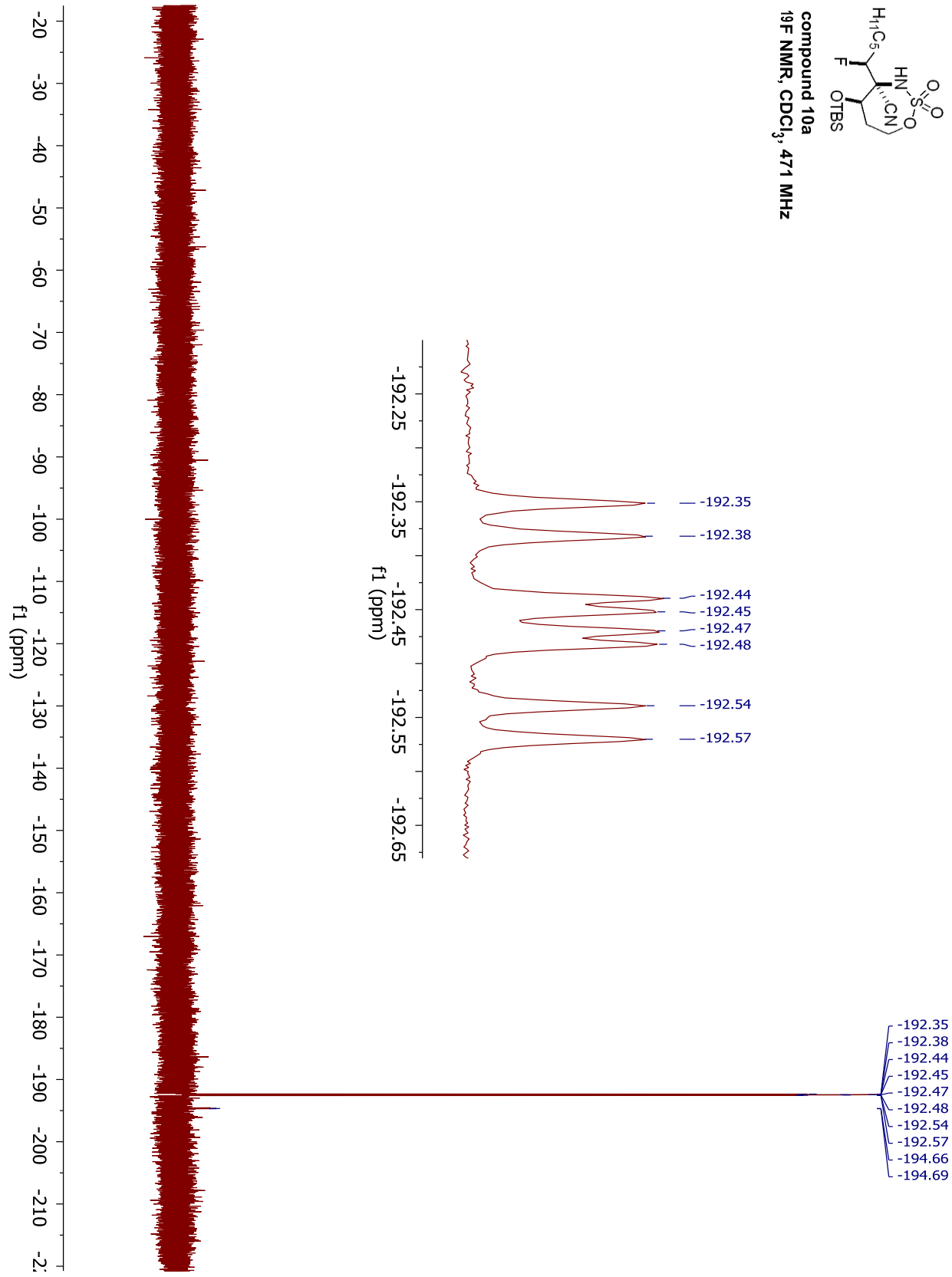
^{1}H NMR for compound 10a.



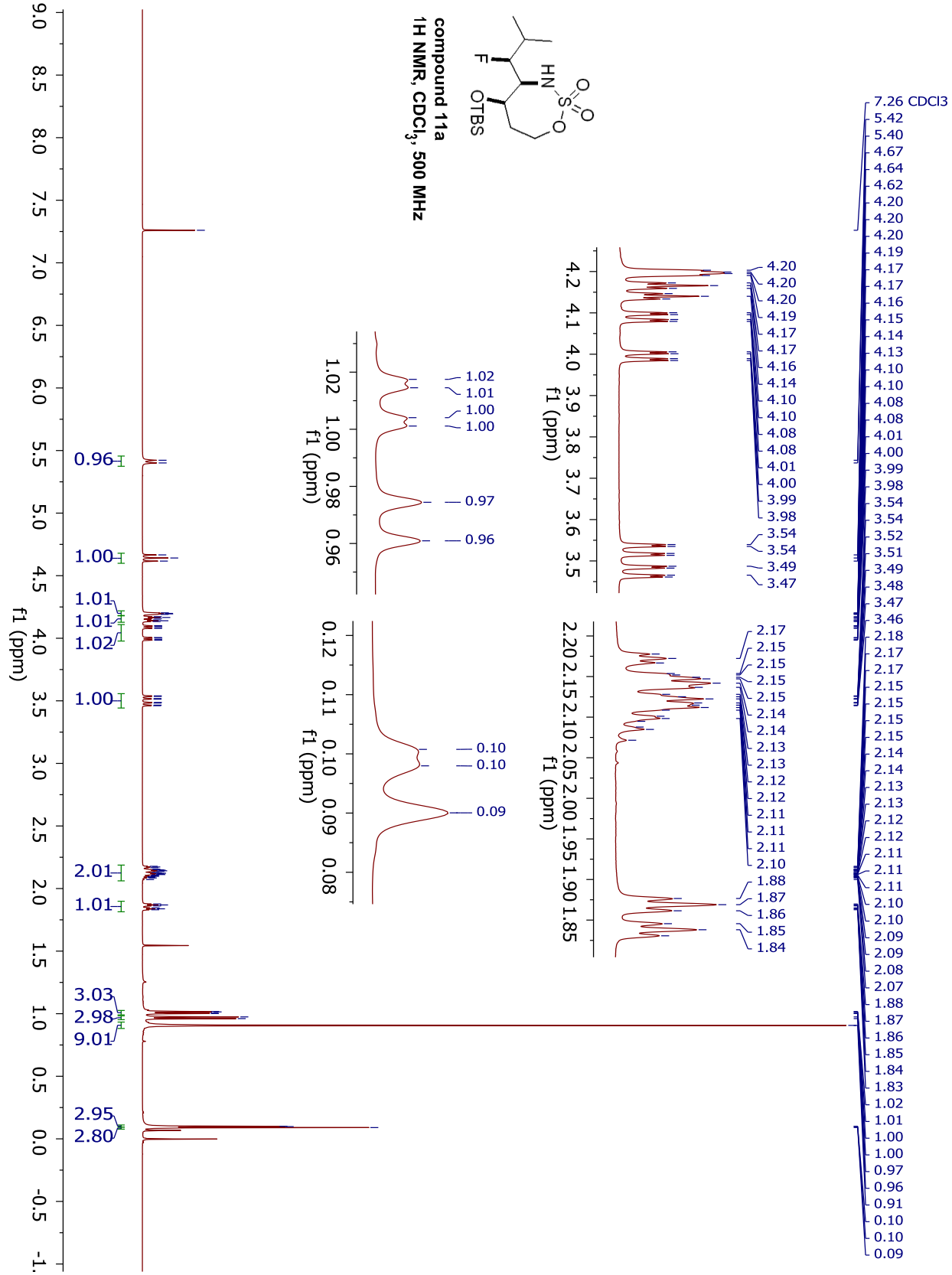
^{13}C NMR for compound 10a.



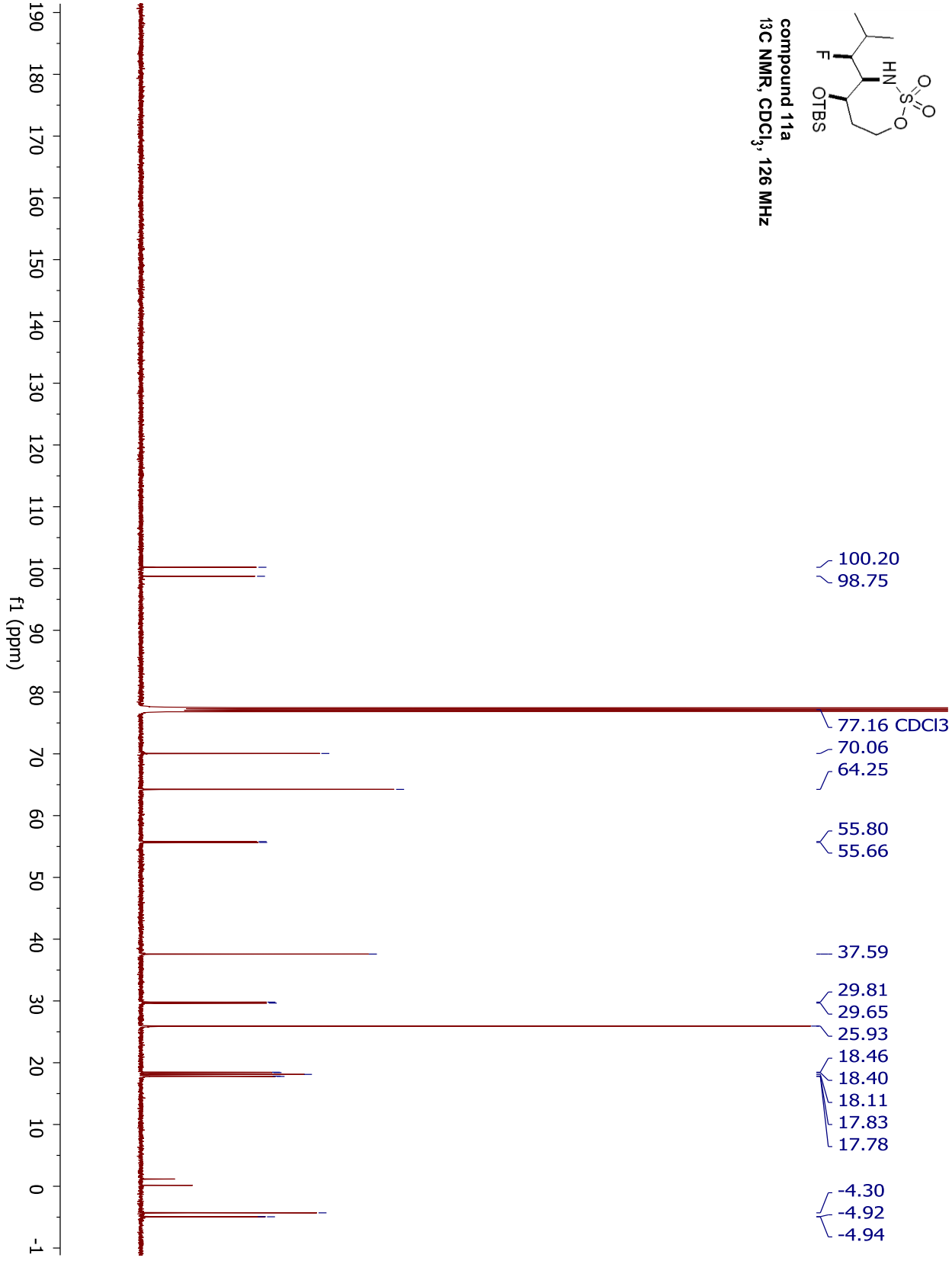
^{19}F NMR for compound 10a.



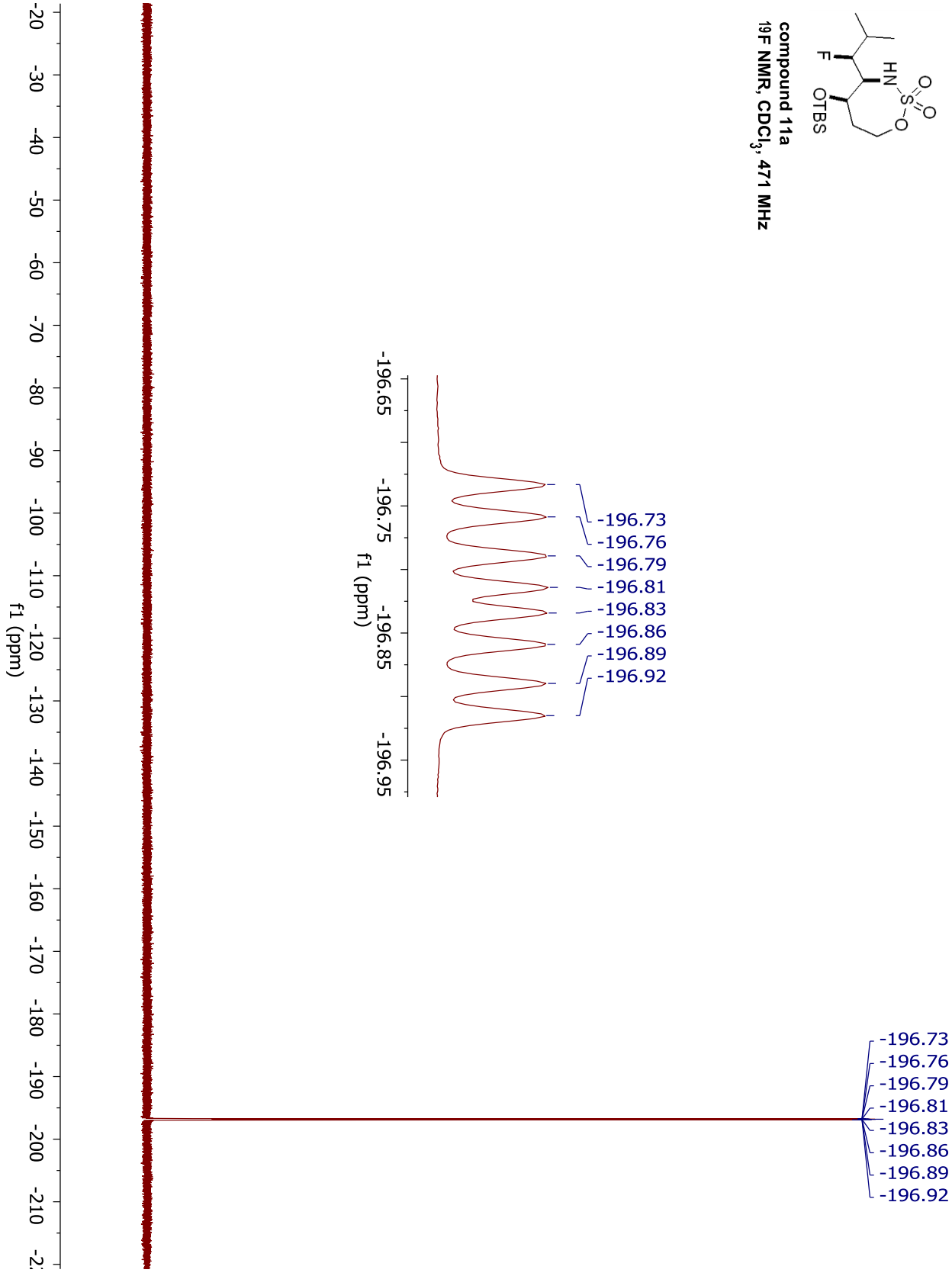
^{1}H NMR for compound 11a.



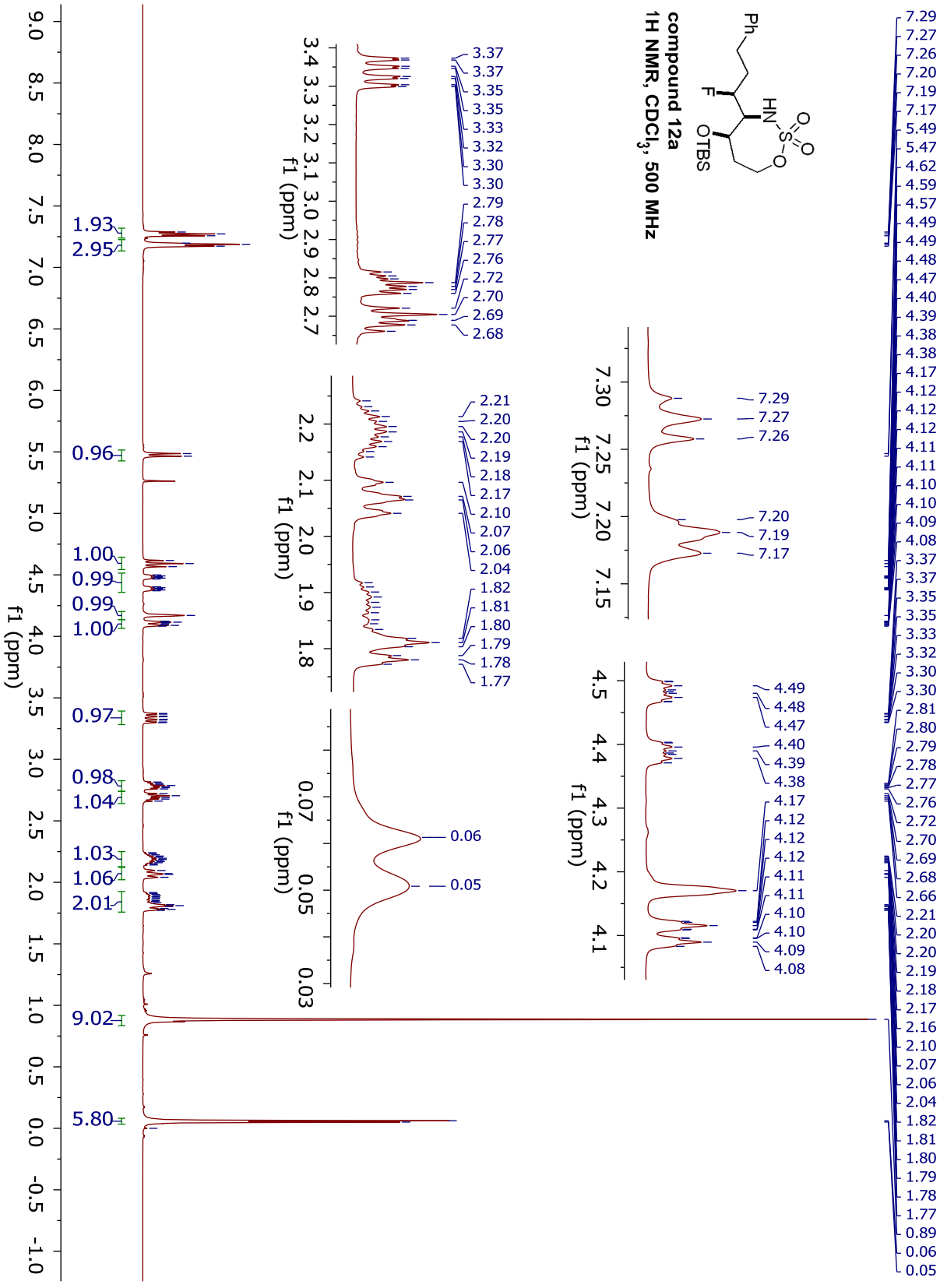
^{13}C NMR for compound 11a.



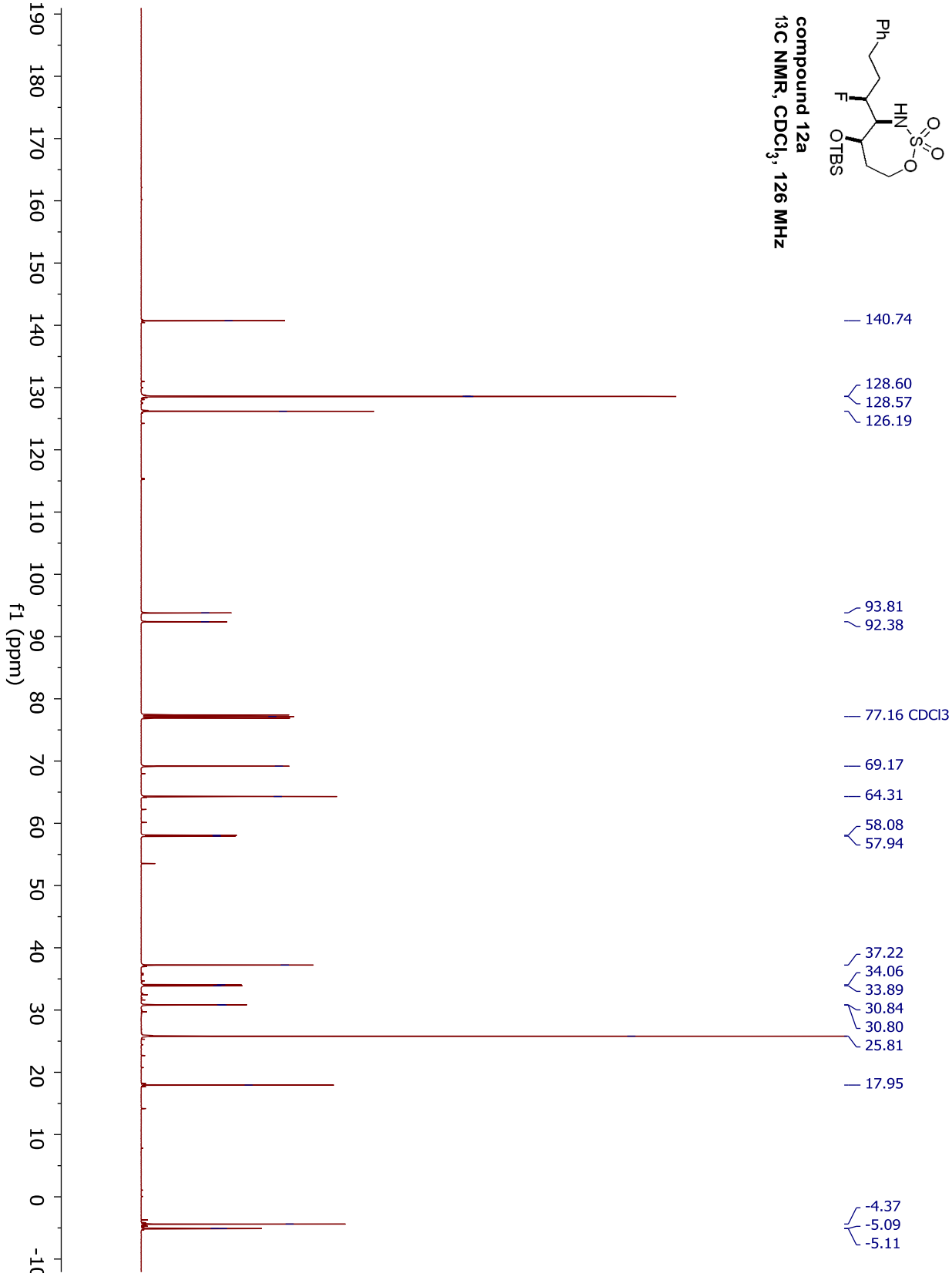
^{19}F NMR for compound 11a.



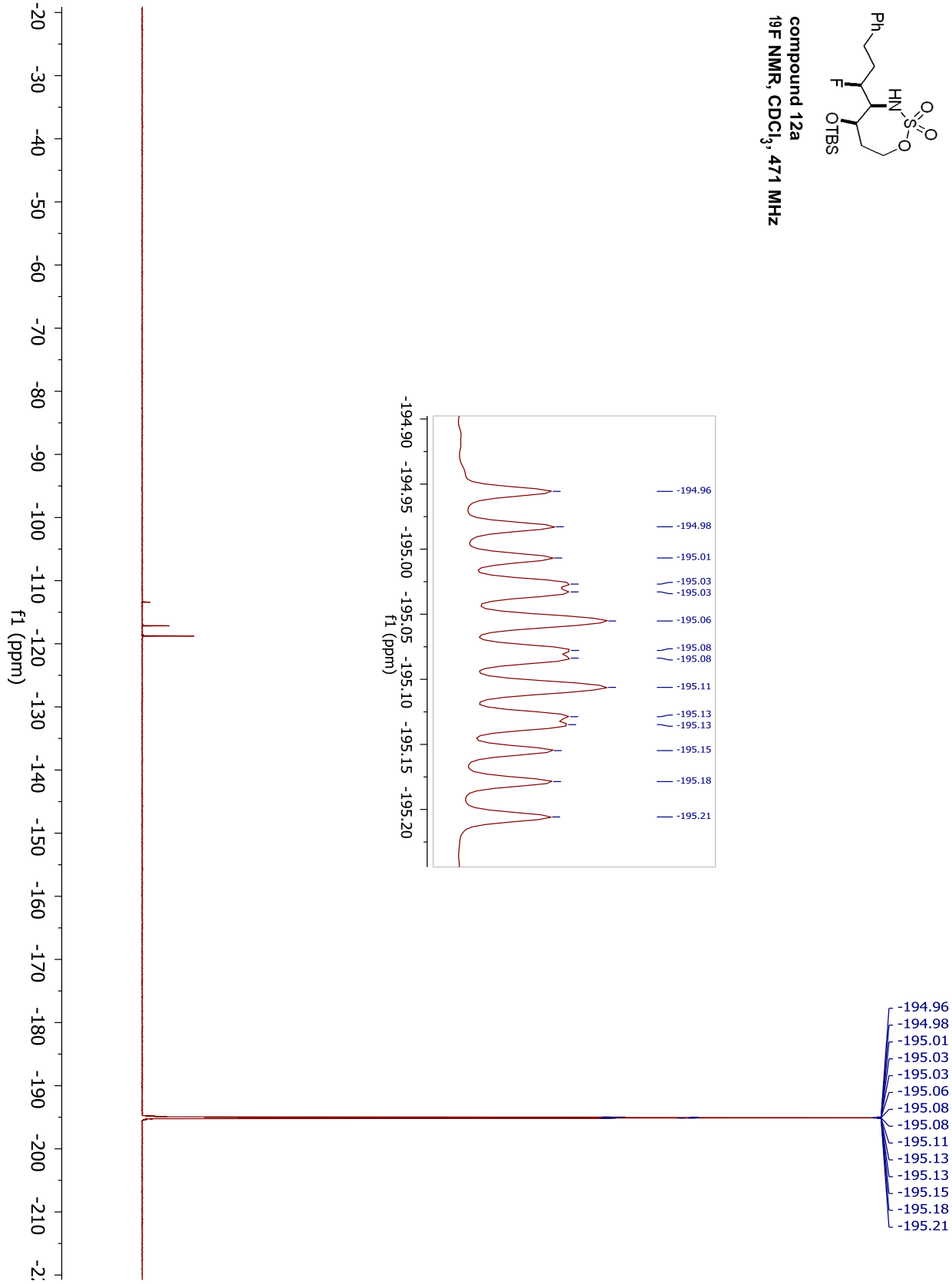
^{1}H NMR for compound 12a.



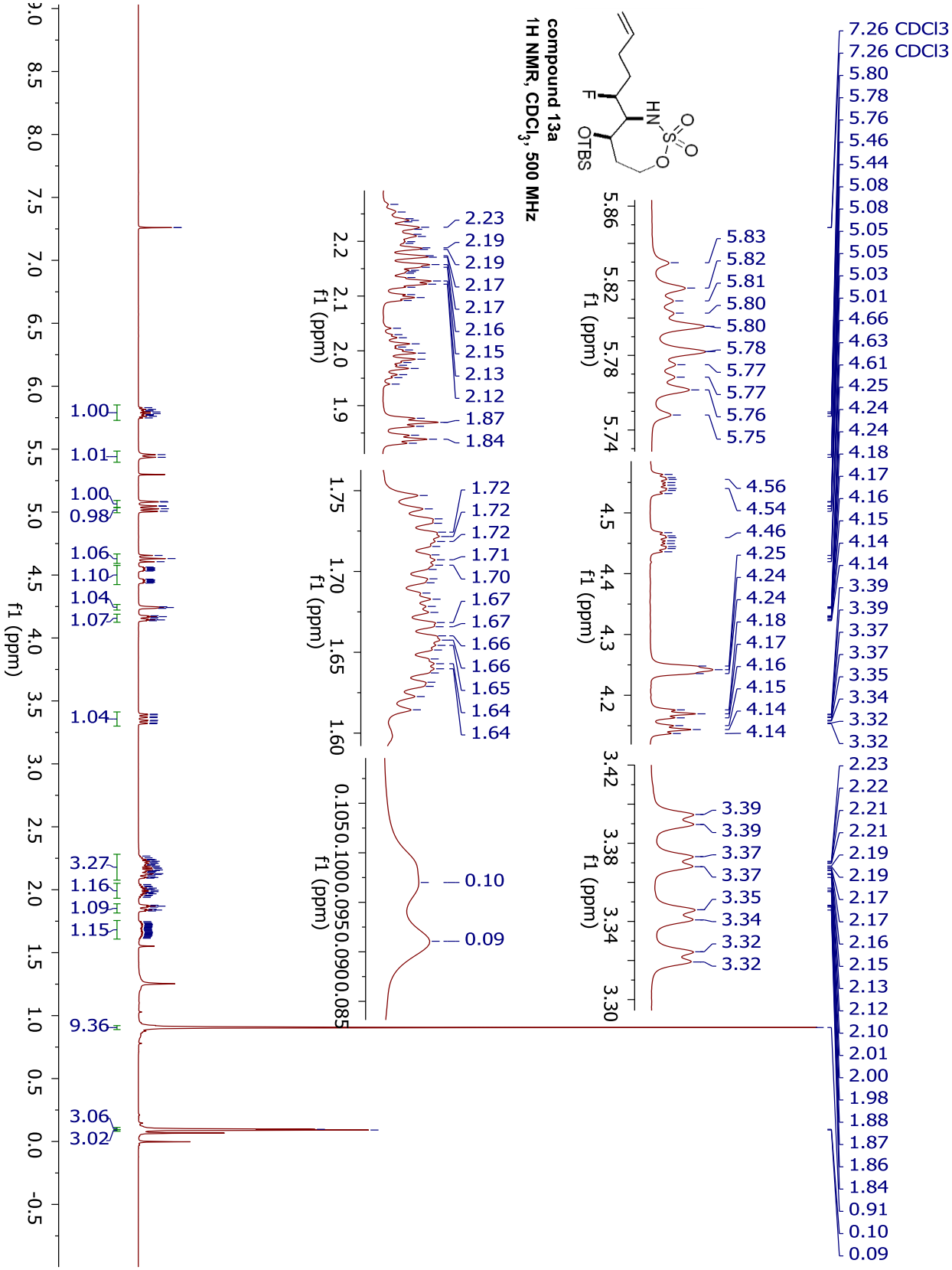
^{13}C NMR for compound 12a.



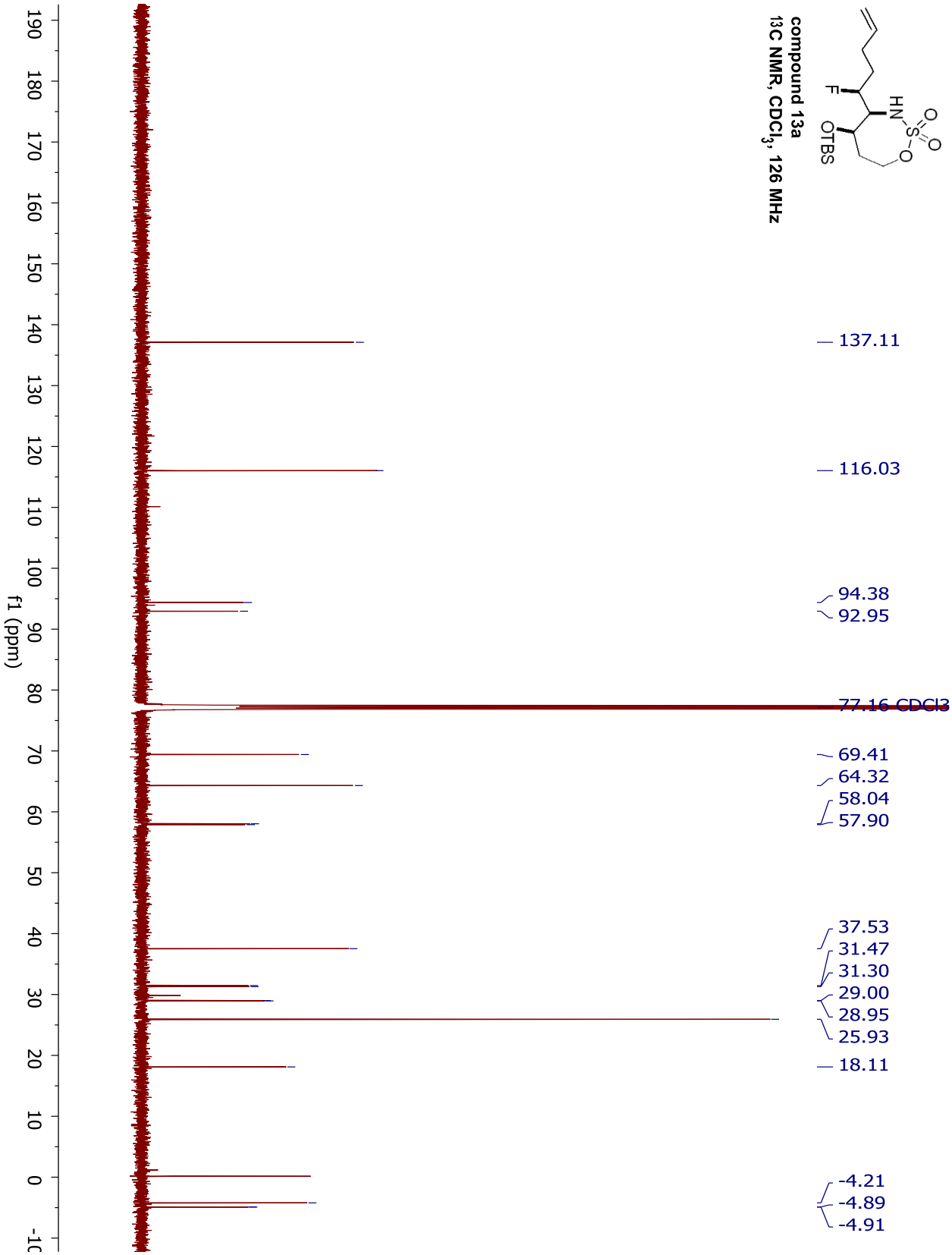
^{19}F NMR for compound 12a.



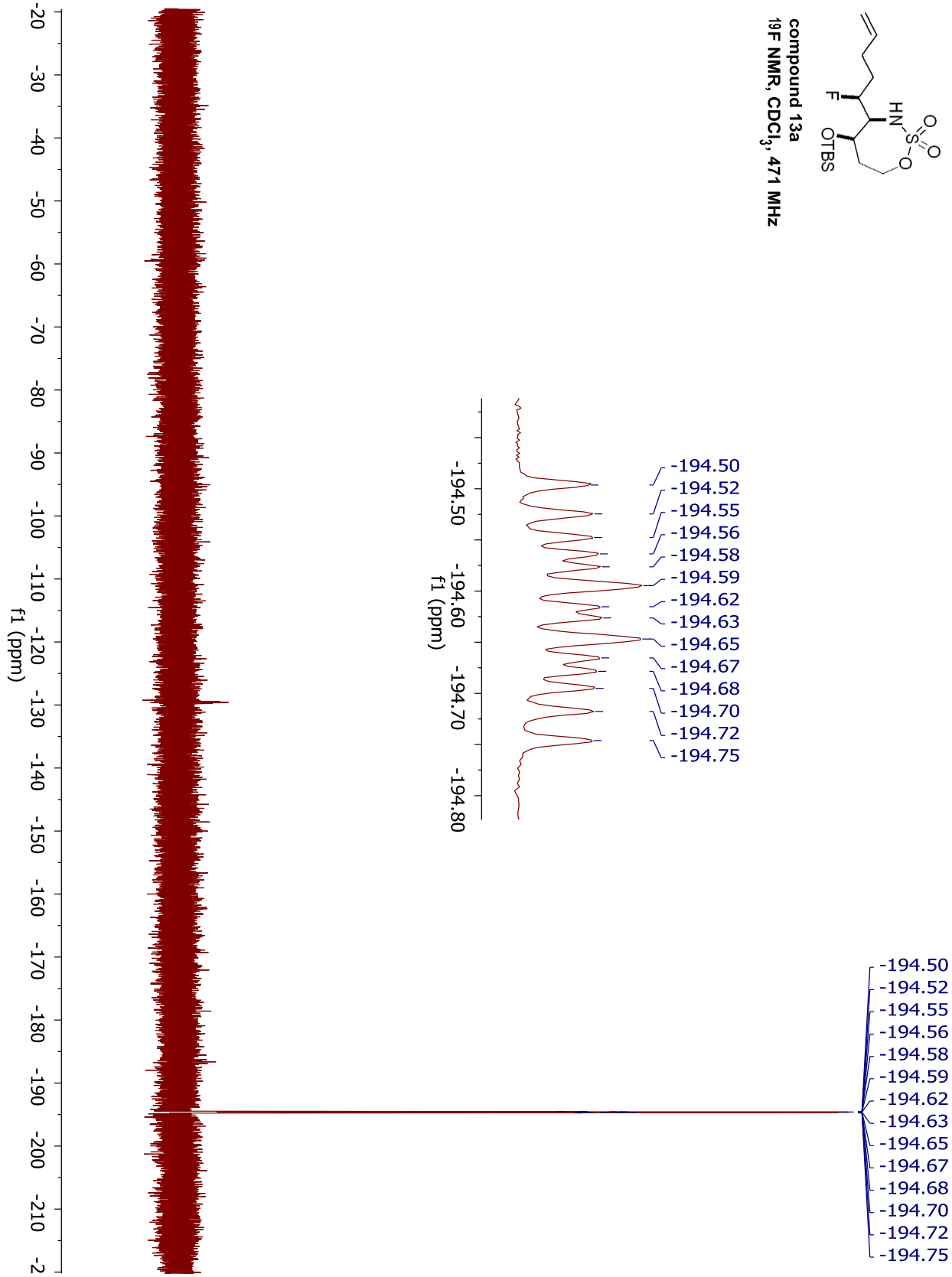
^{1}H NMR for compound 13a.



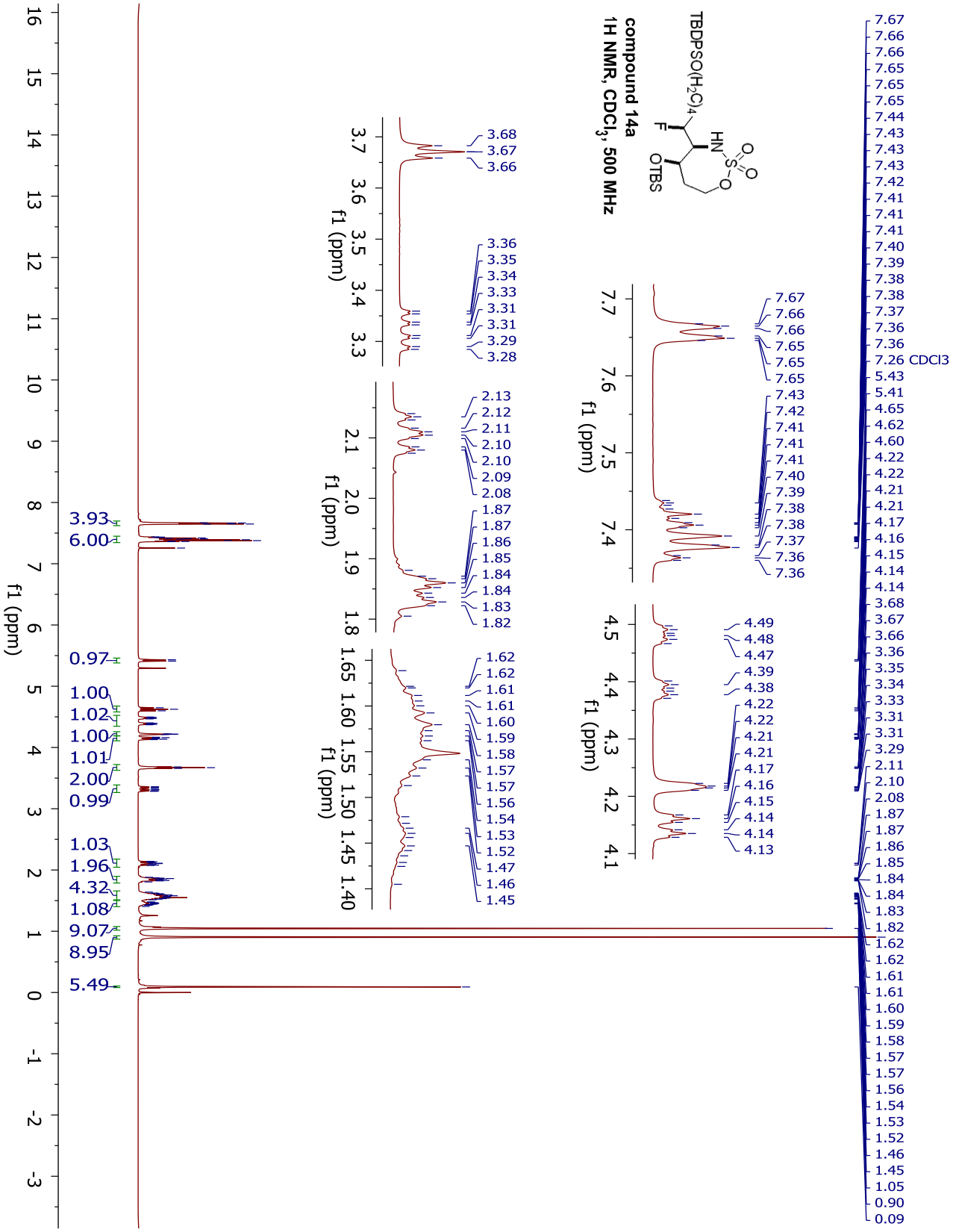
^{13}C NMR for compound 13a.



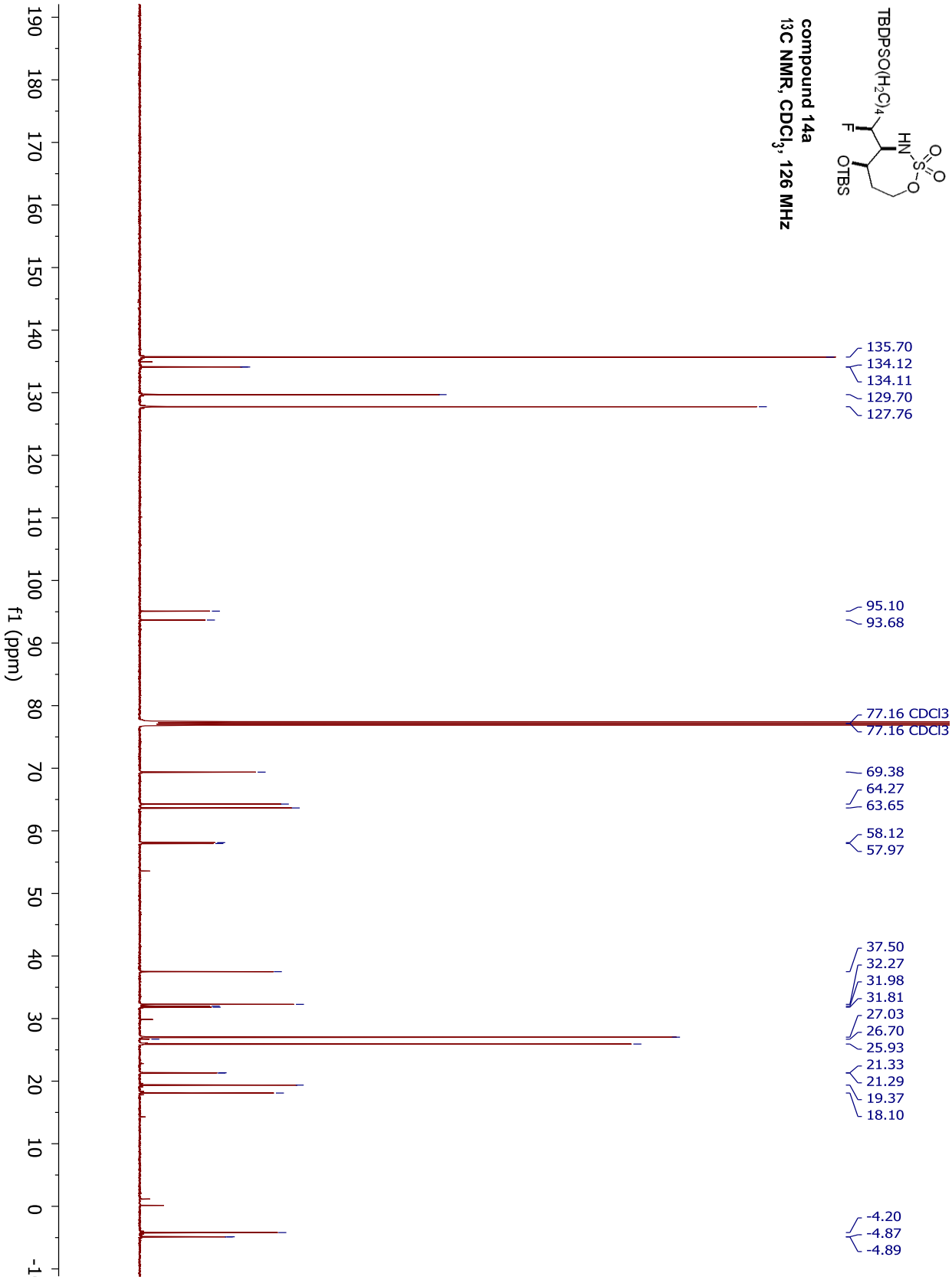
^{19}F NMR for compound 13a.



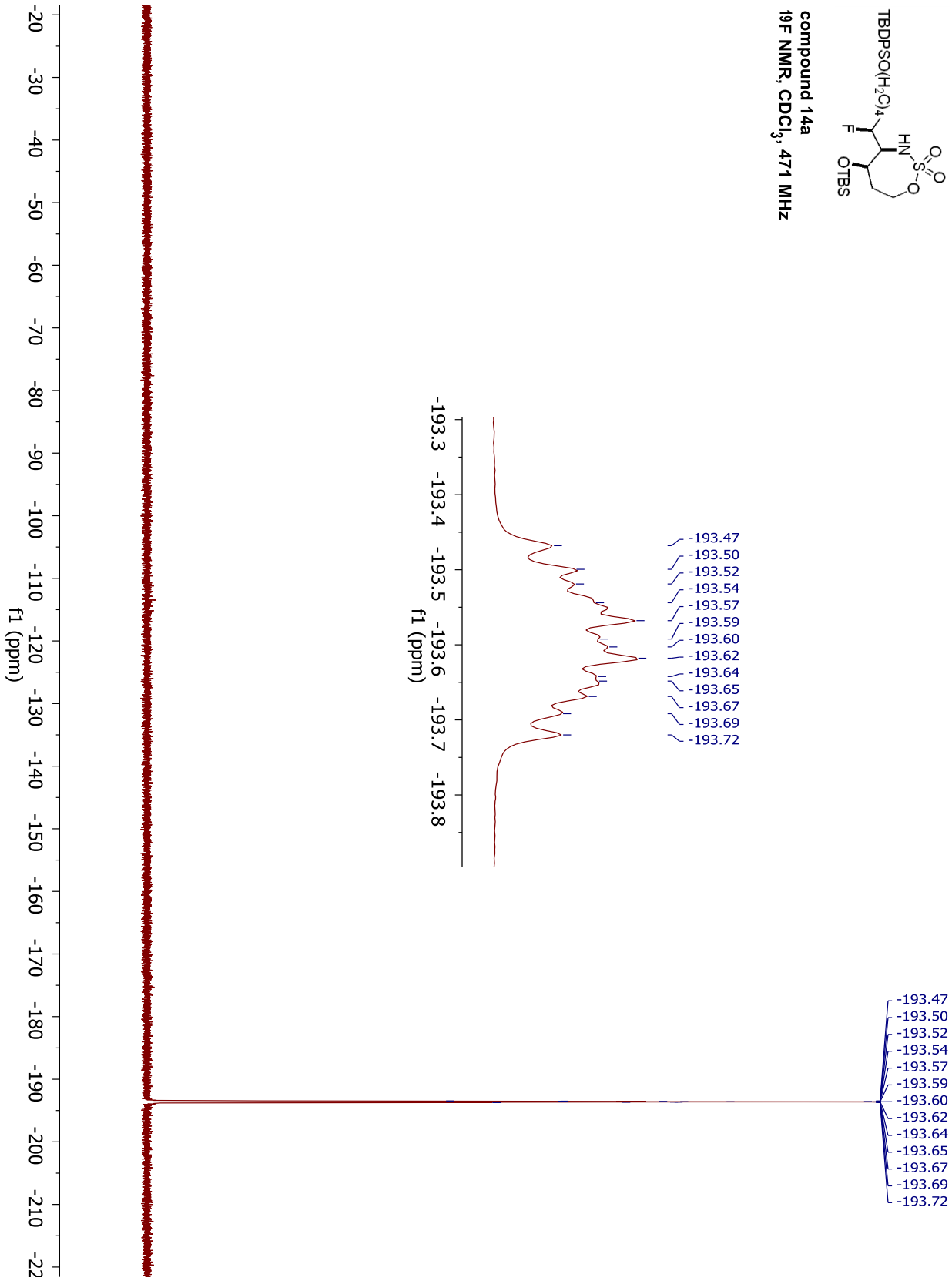
^{1}H NMR for compound 14a.



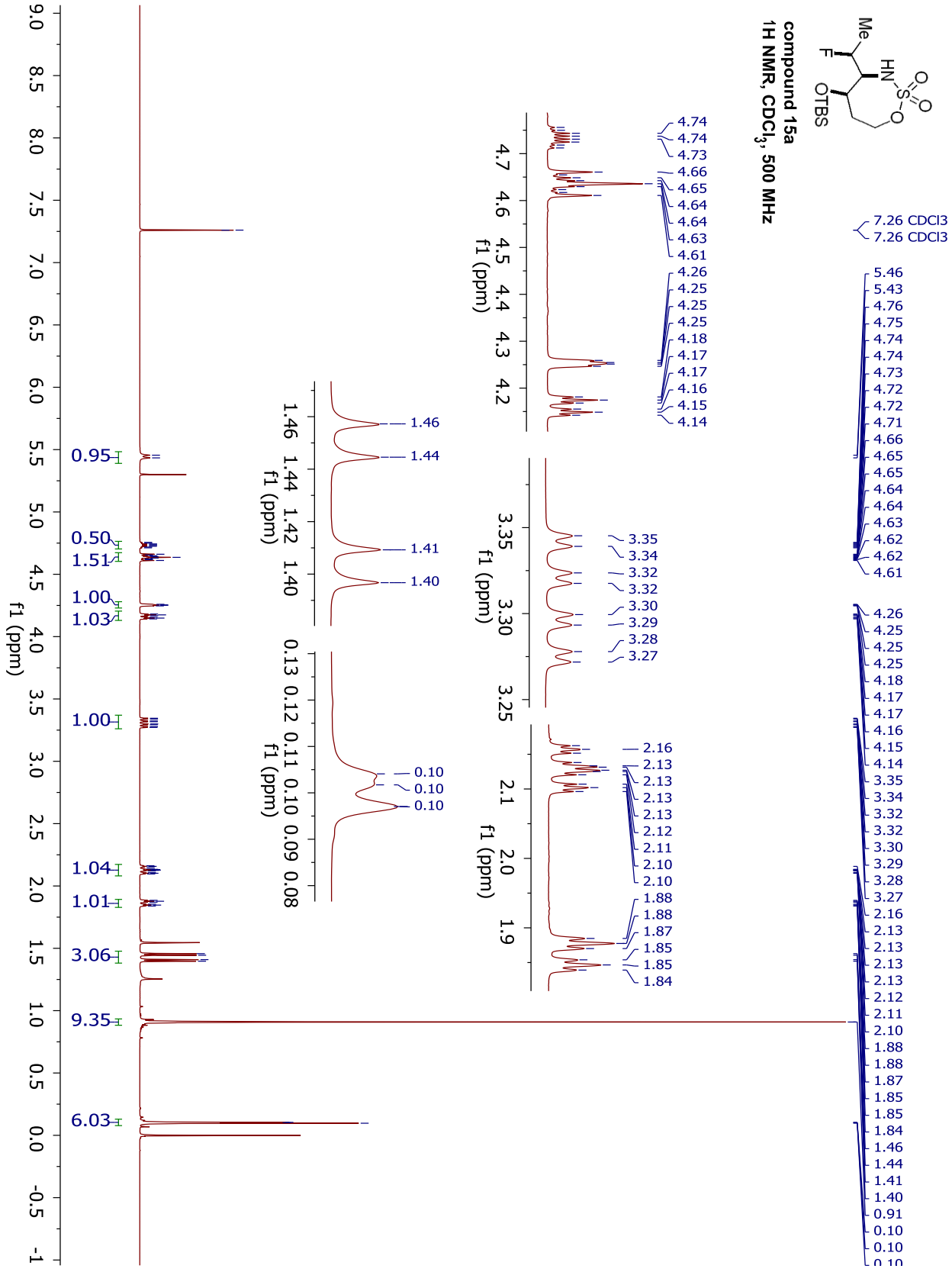
^{13}C NMR for compound 14a.



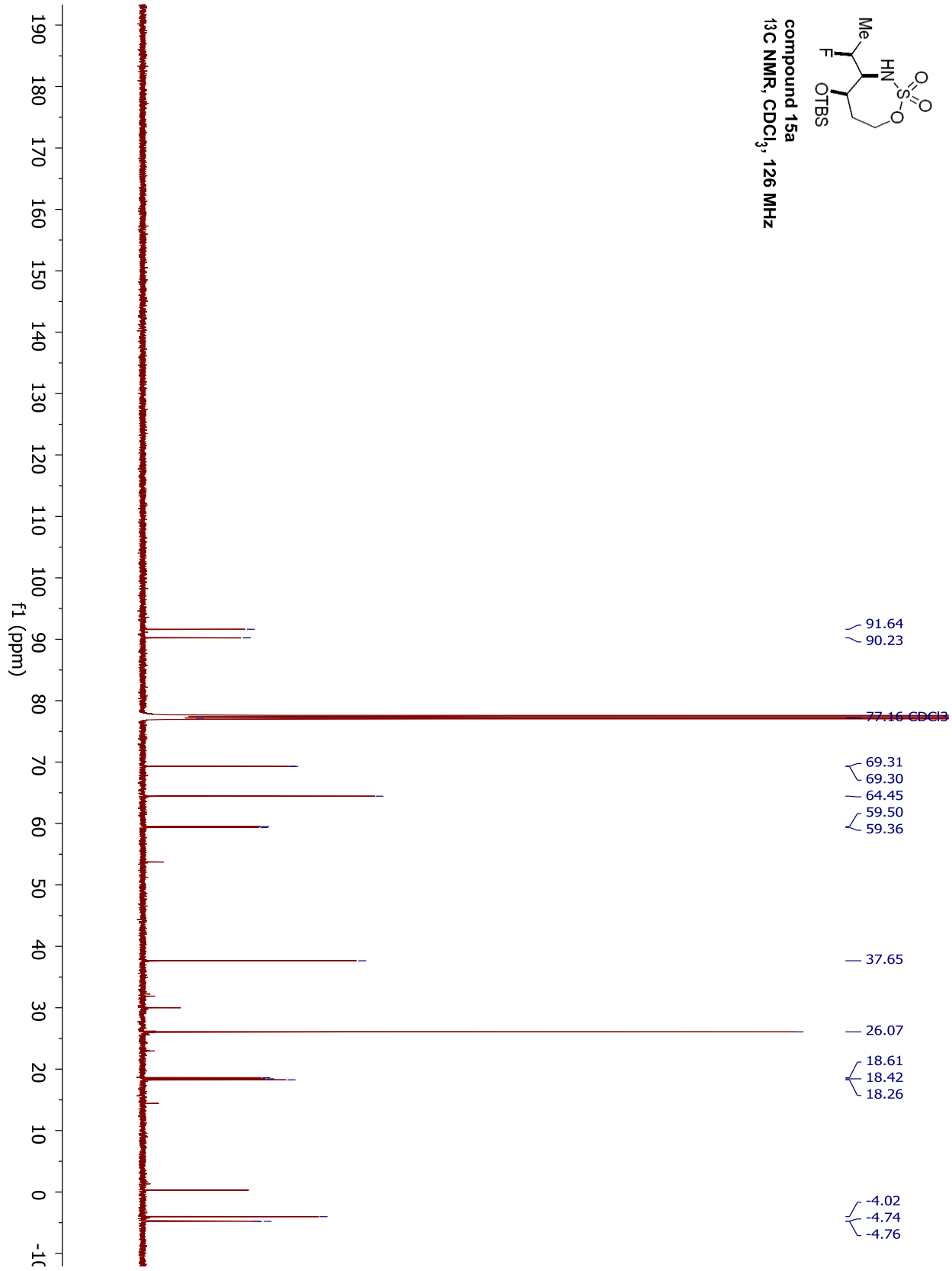
^{19}F NMR for compound 14a.



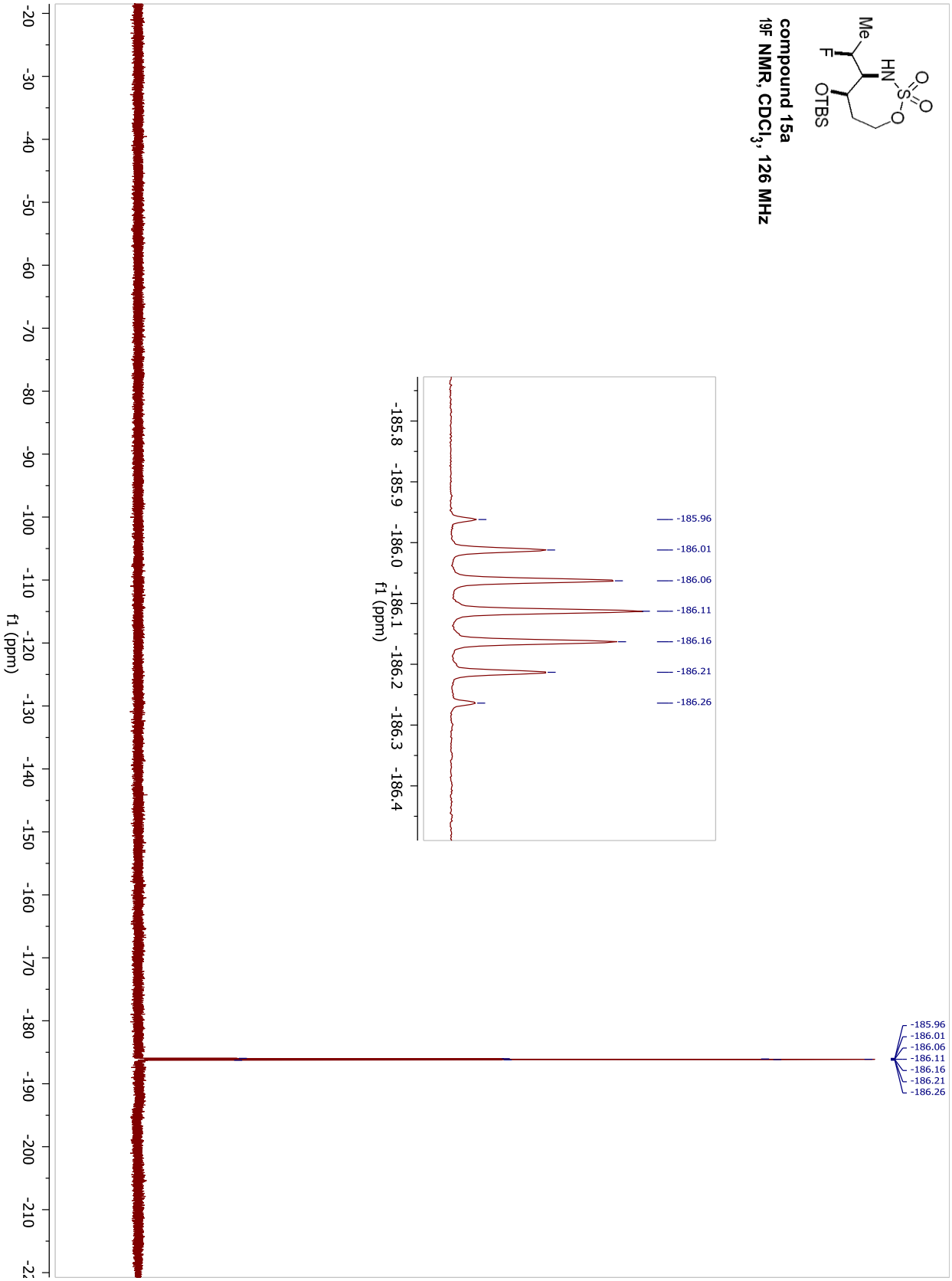
^{1}H NMR for compound 15a.



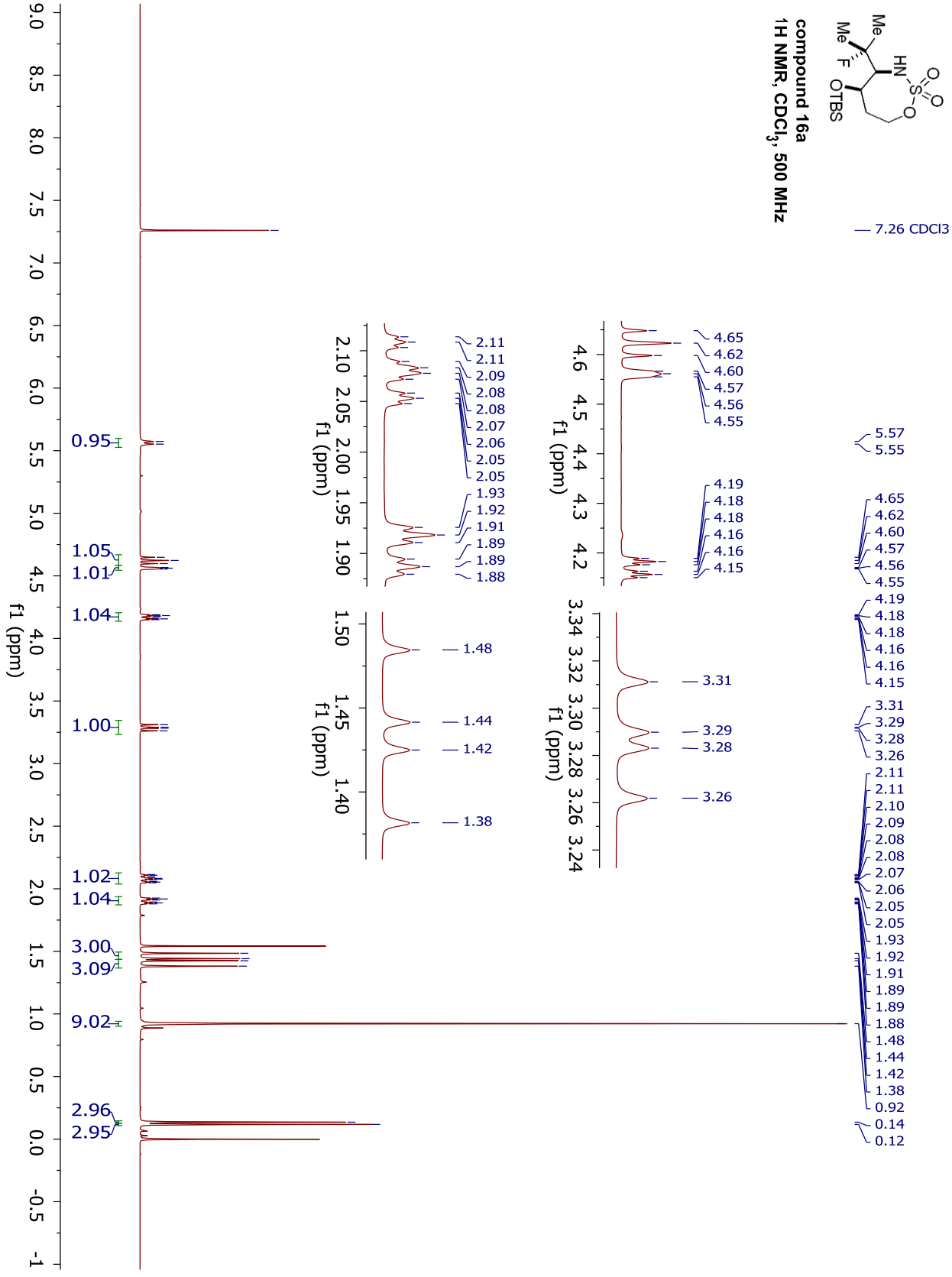
^{13}C NMR for compound 15a.



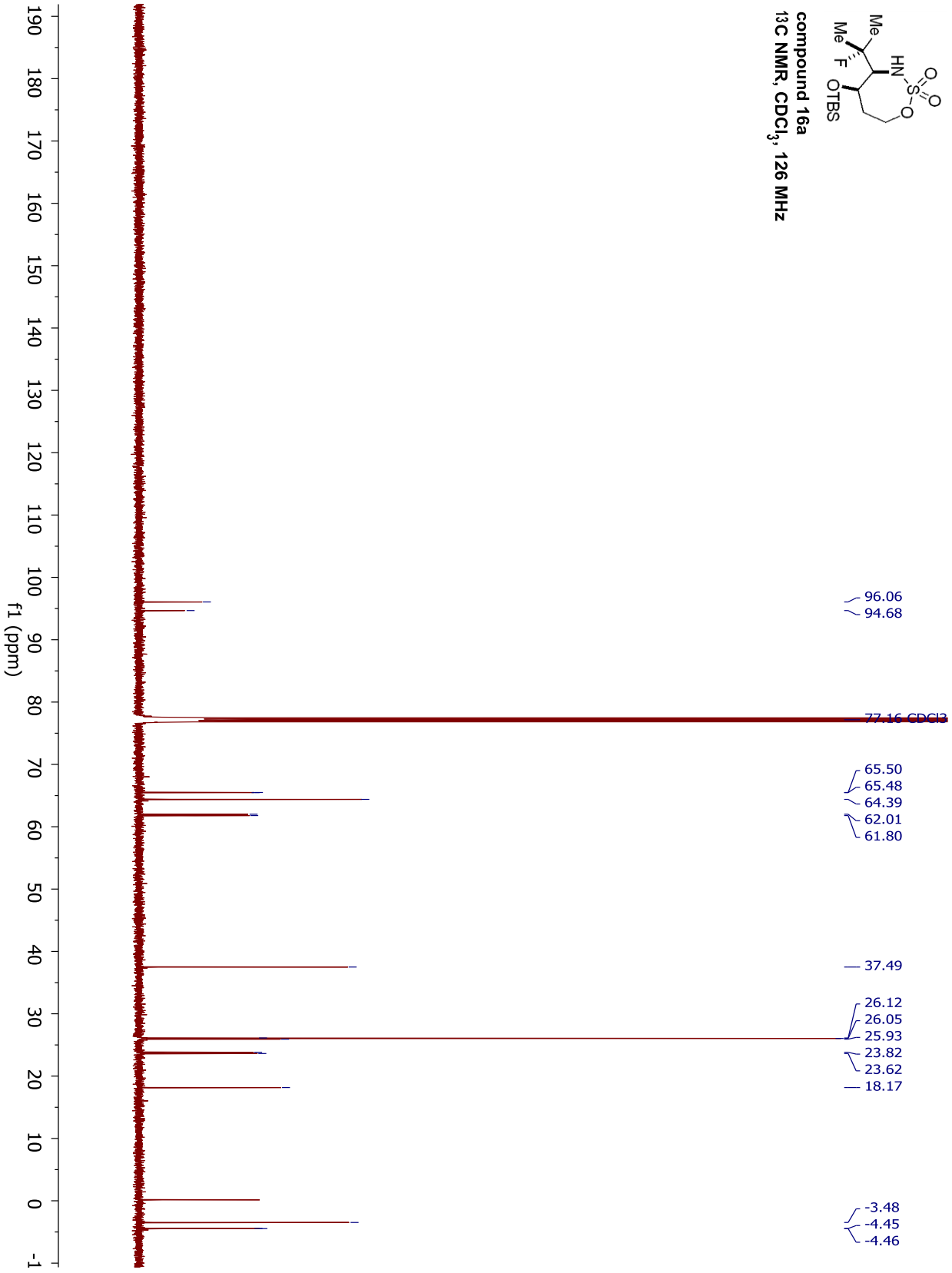
^{19}F NMR for compound 15a.



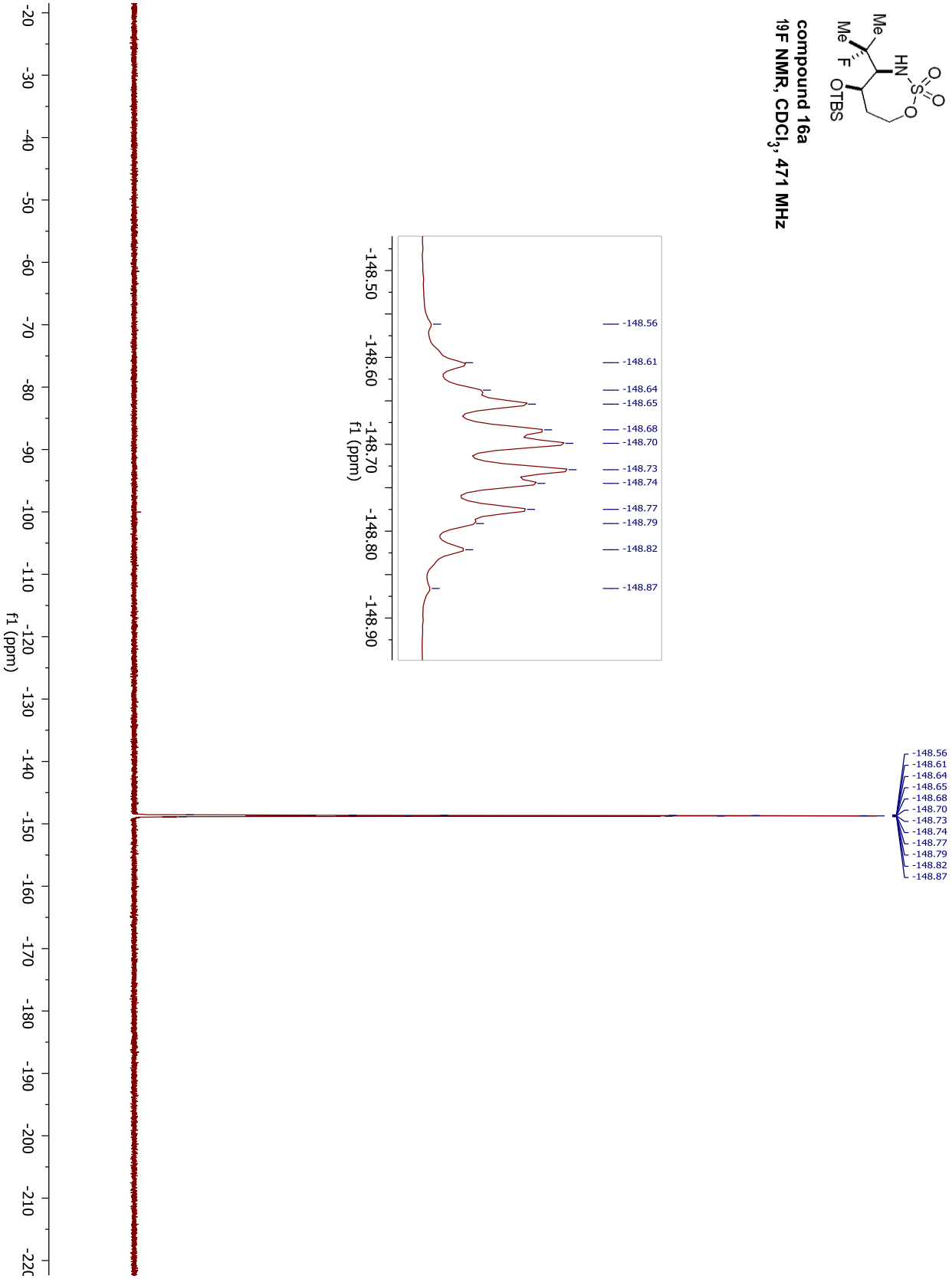
^{1}H NMR for compound 16a.



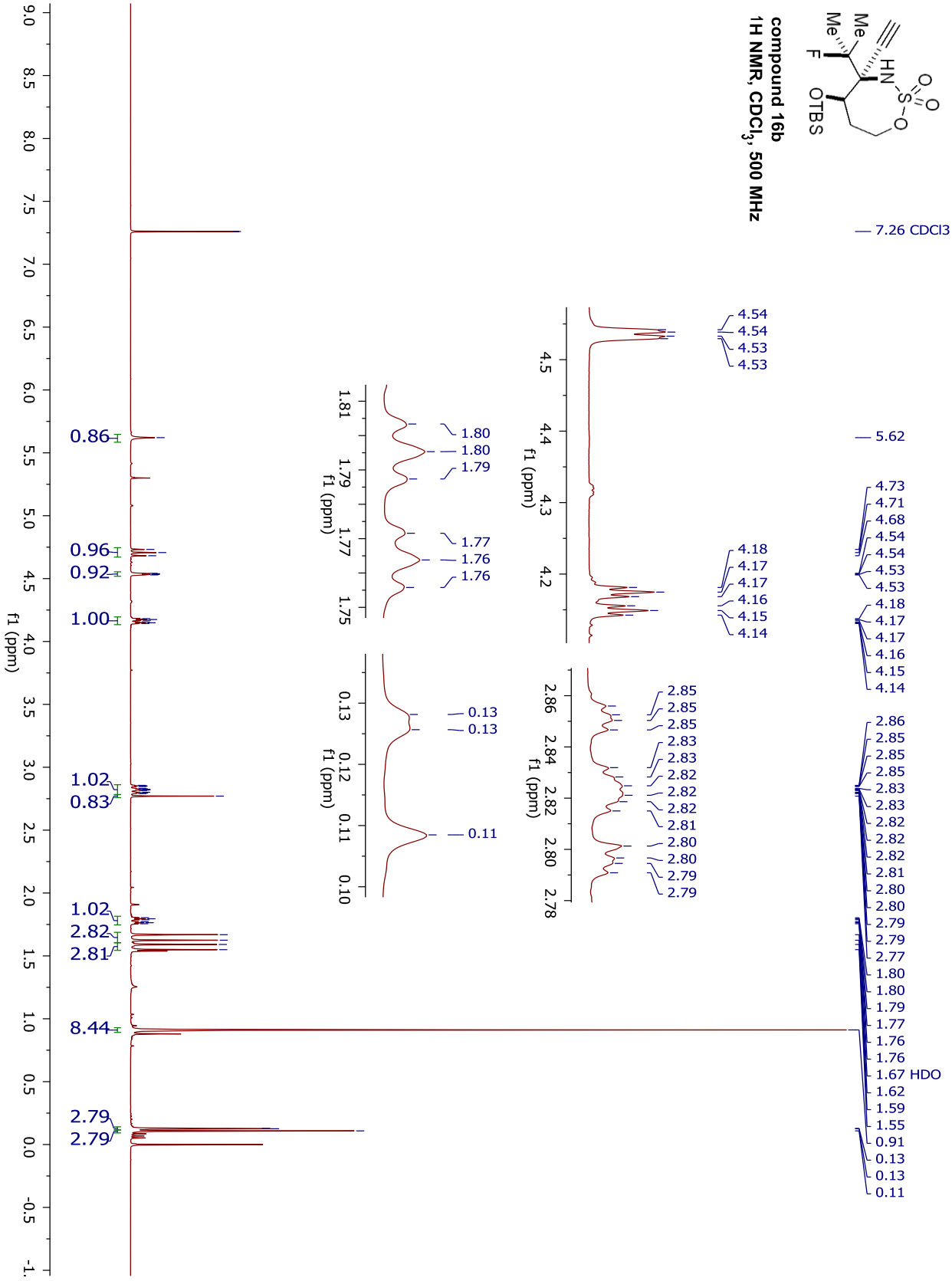
^{13}C NMR for compound 16a.



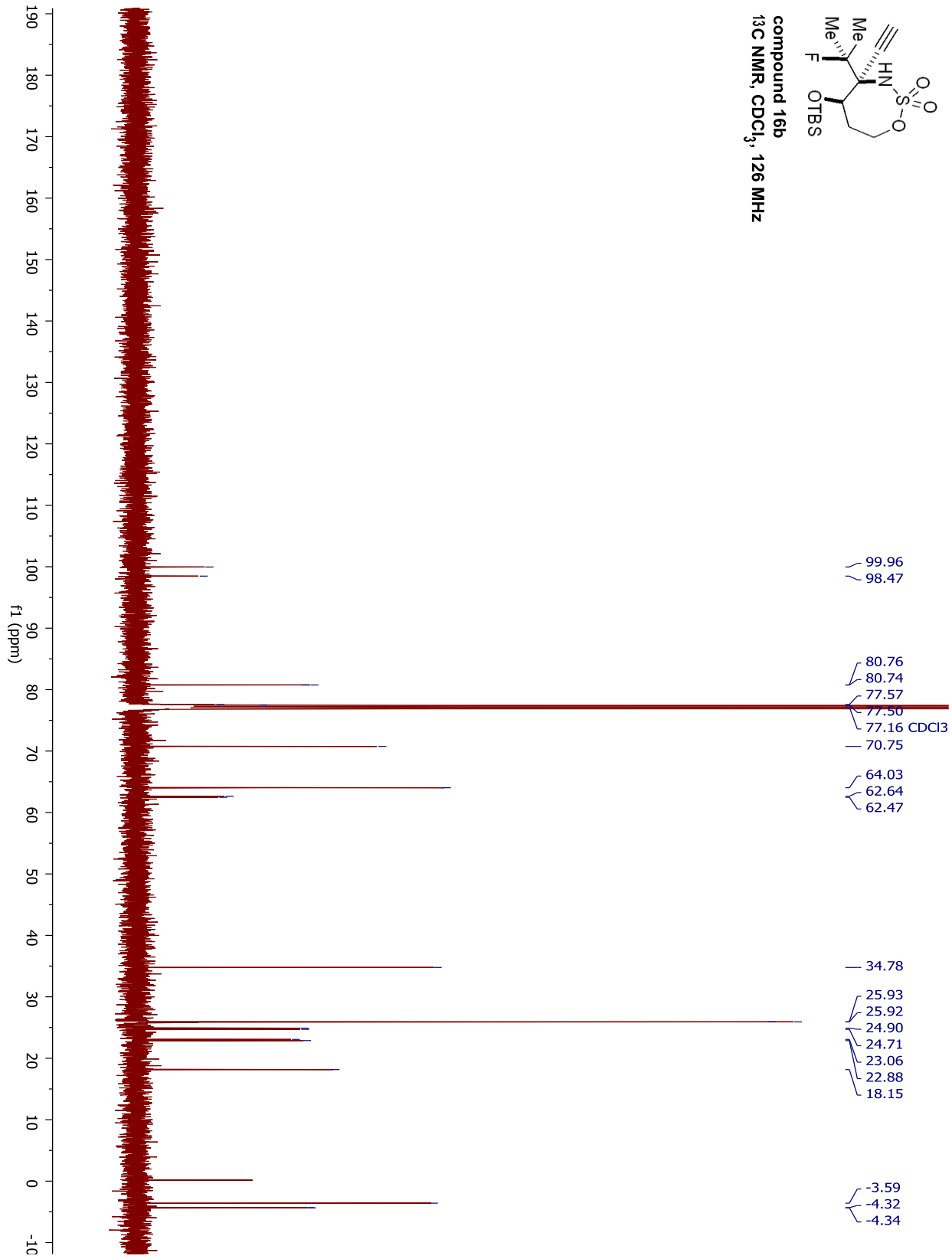
^{19}F NMR for compound 16a.



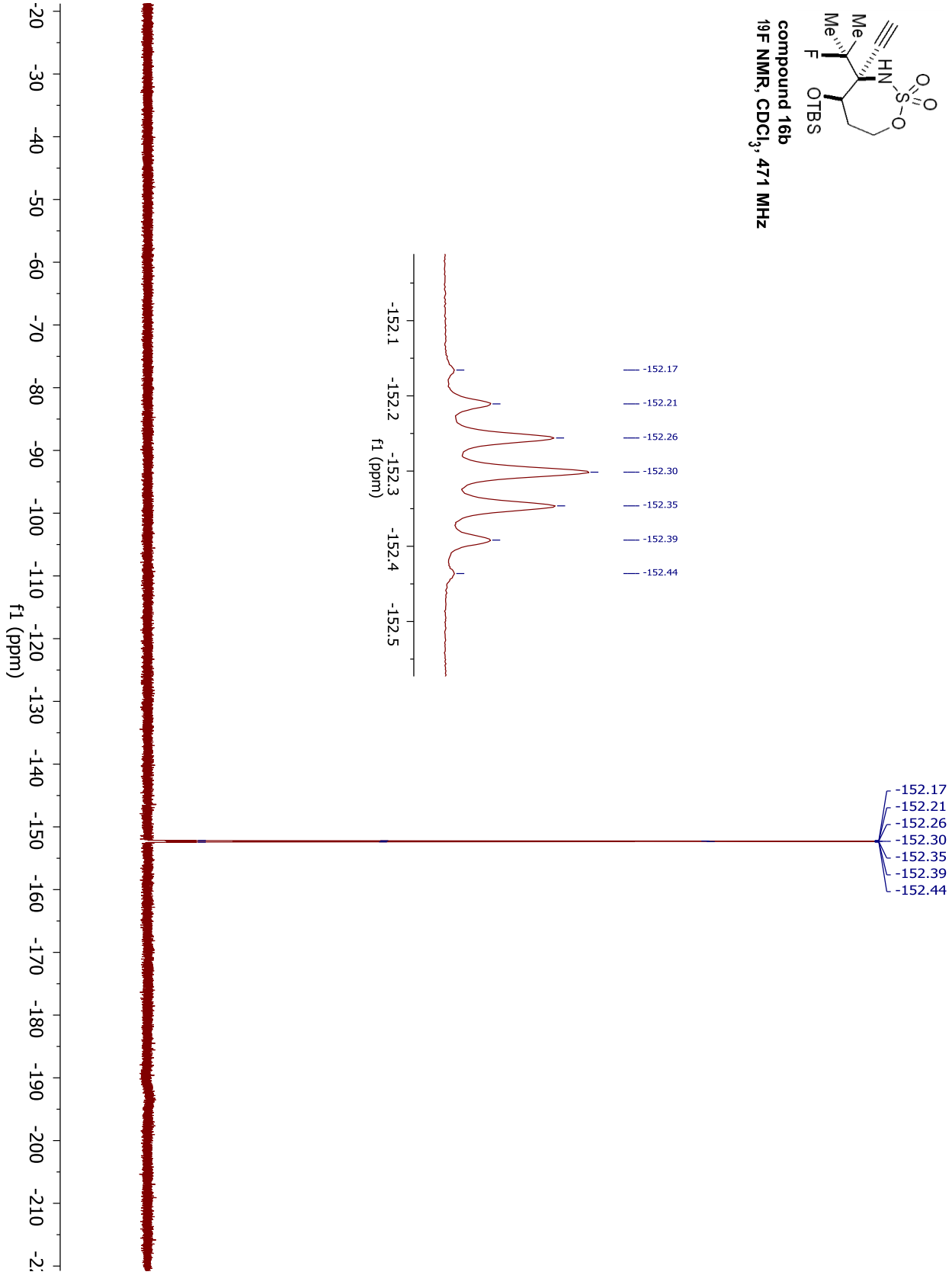
^{1}H NMR for compound 16b.



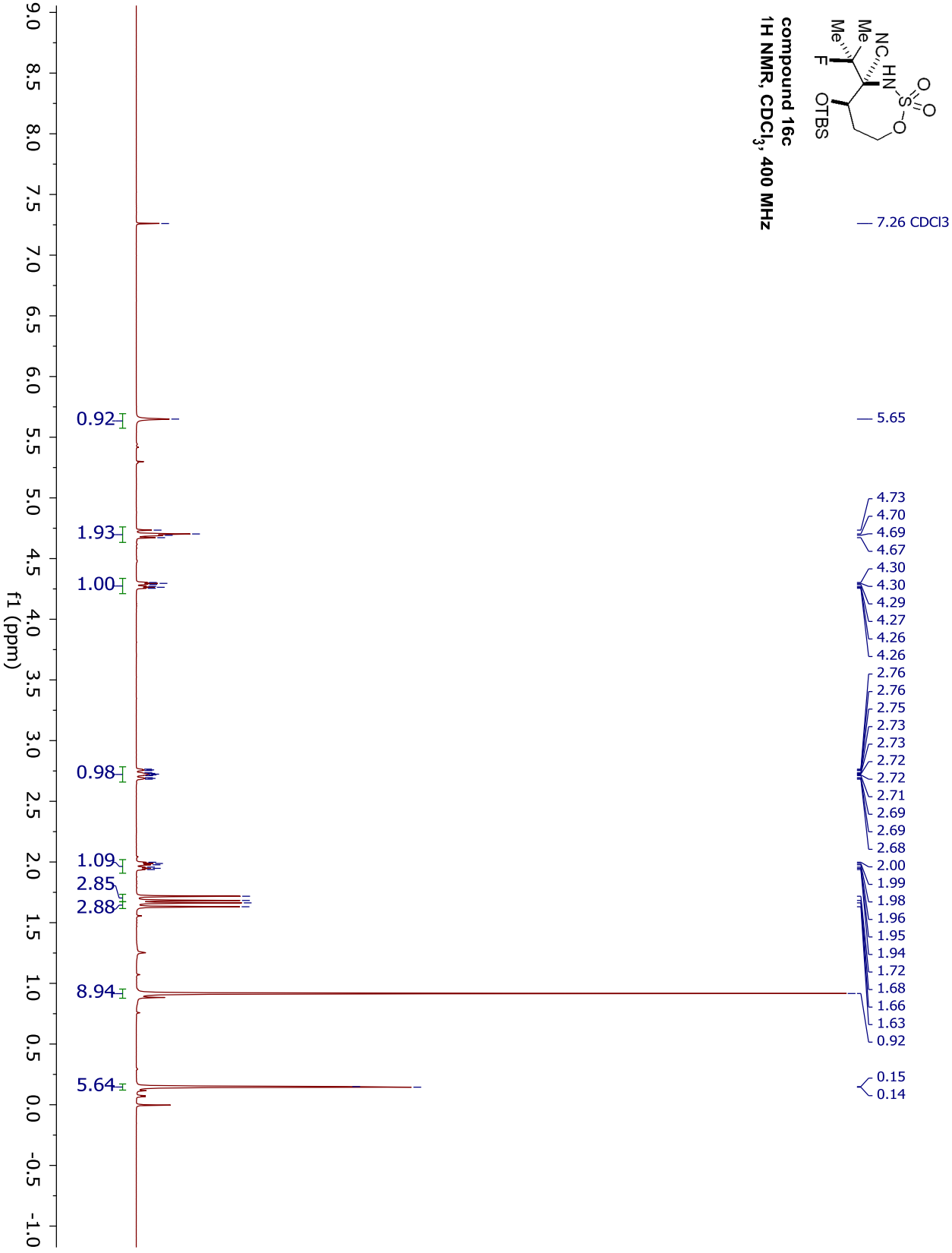
^{13}C NMR for compound 16b.



^{19}F NMR for compound 16b.



^{1}H NMR for compound 16c.



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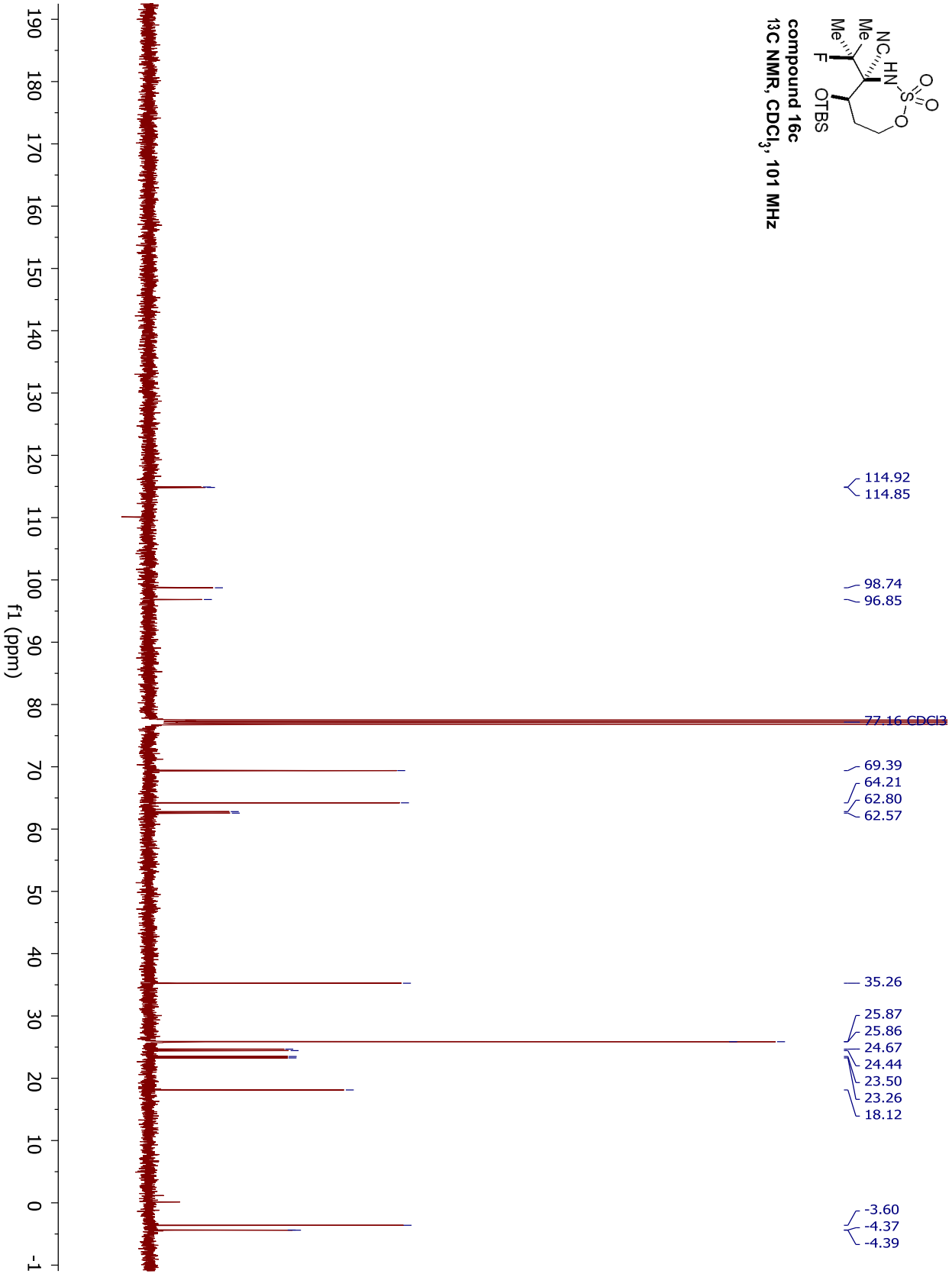
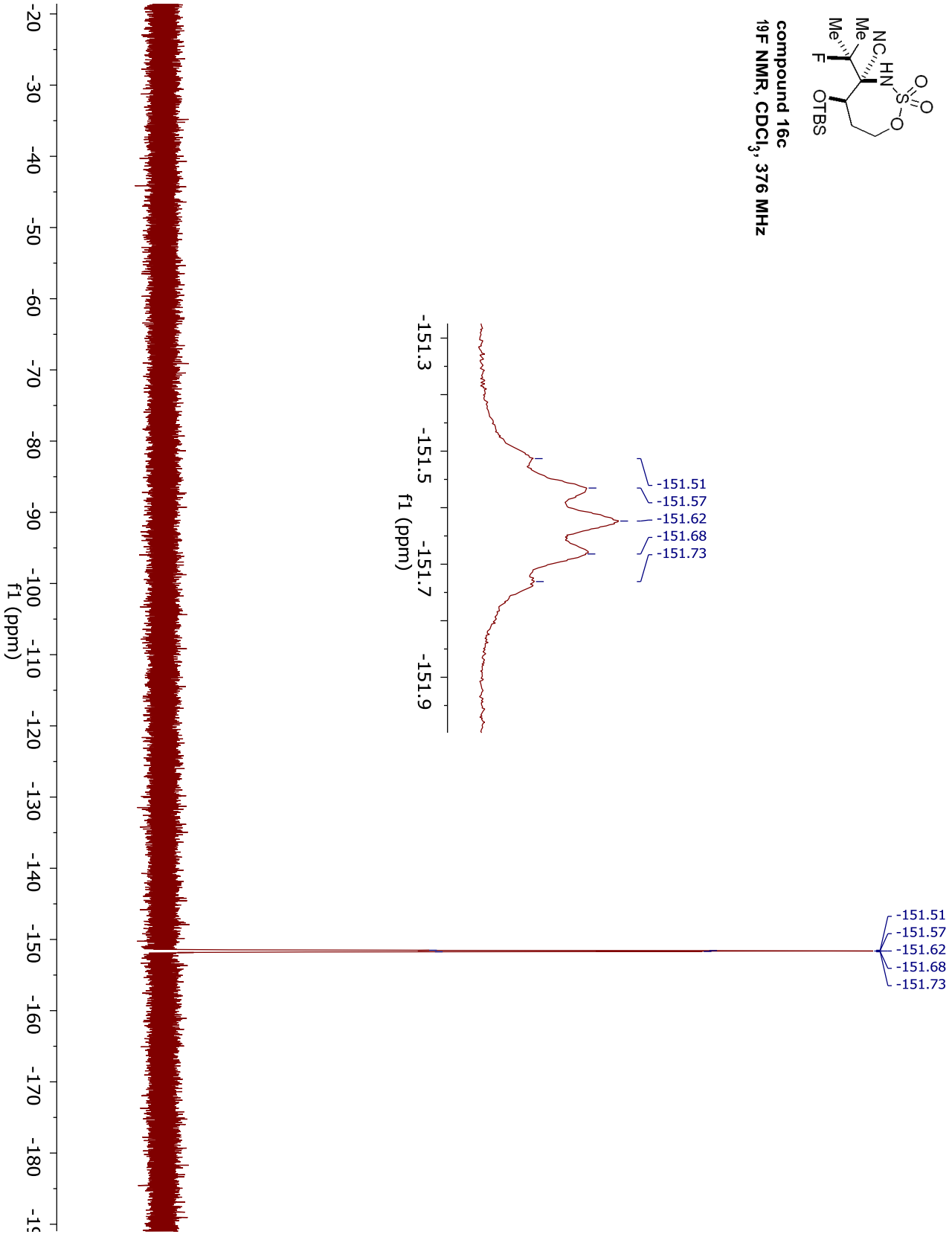
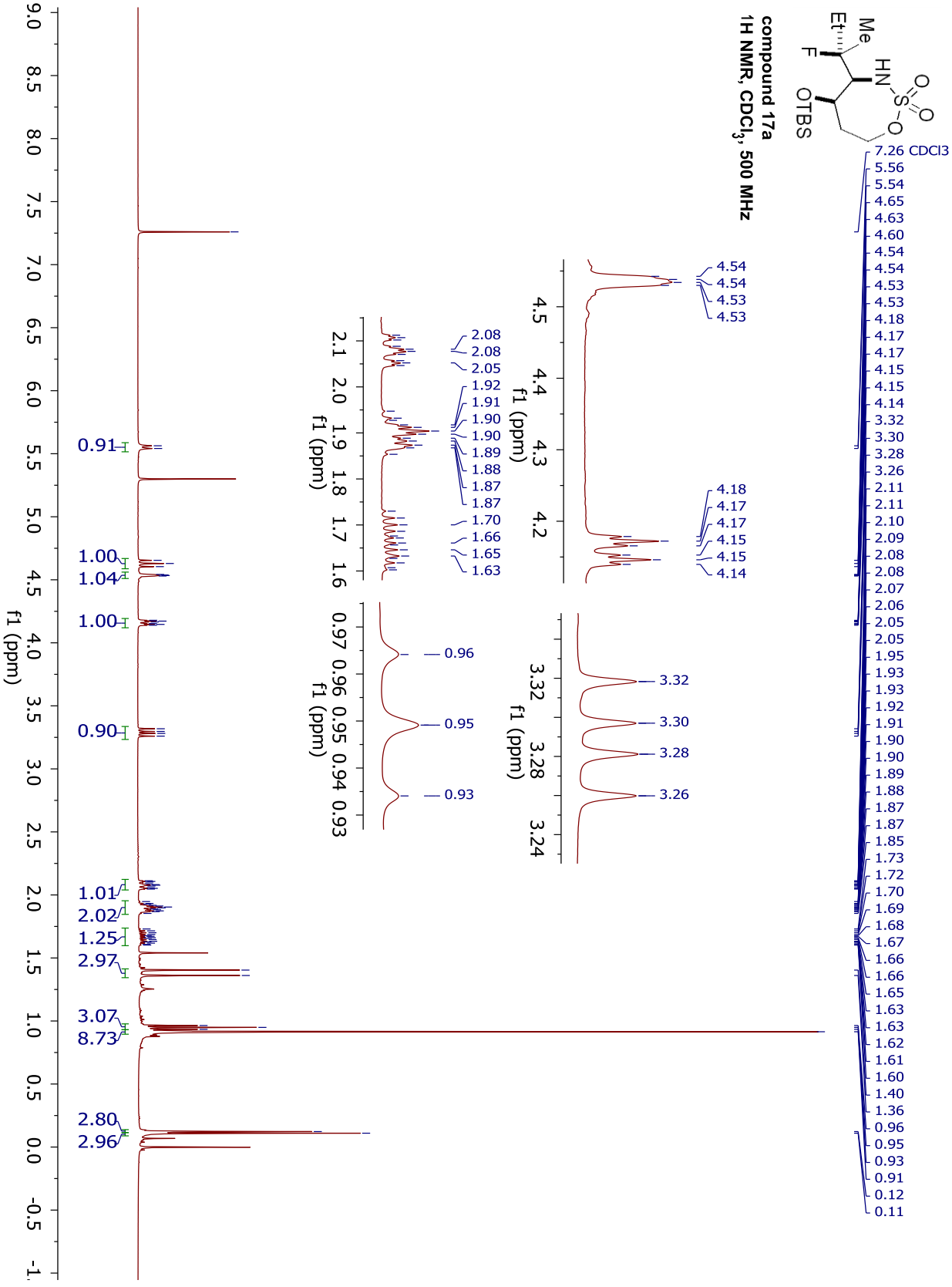


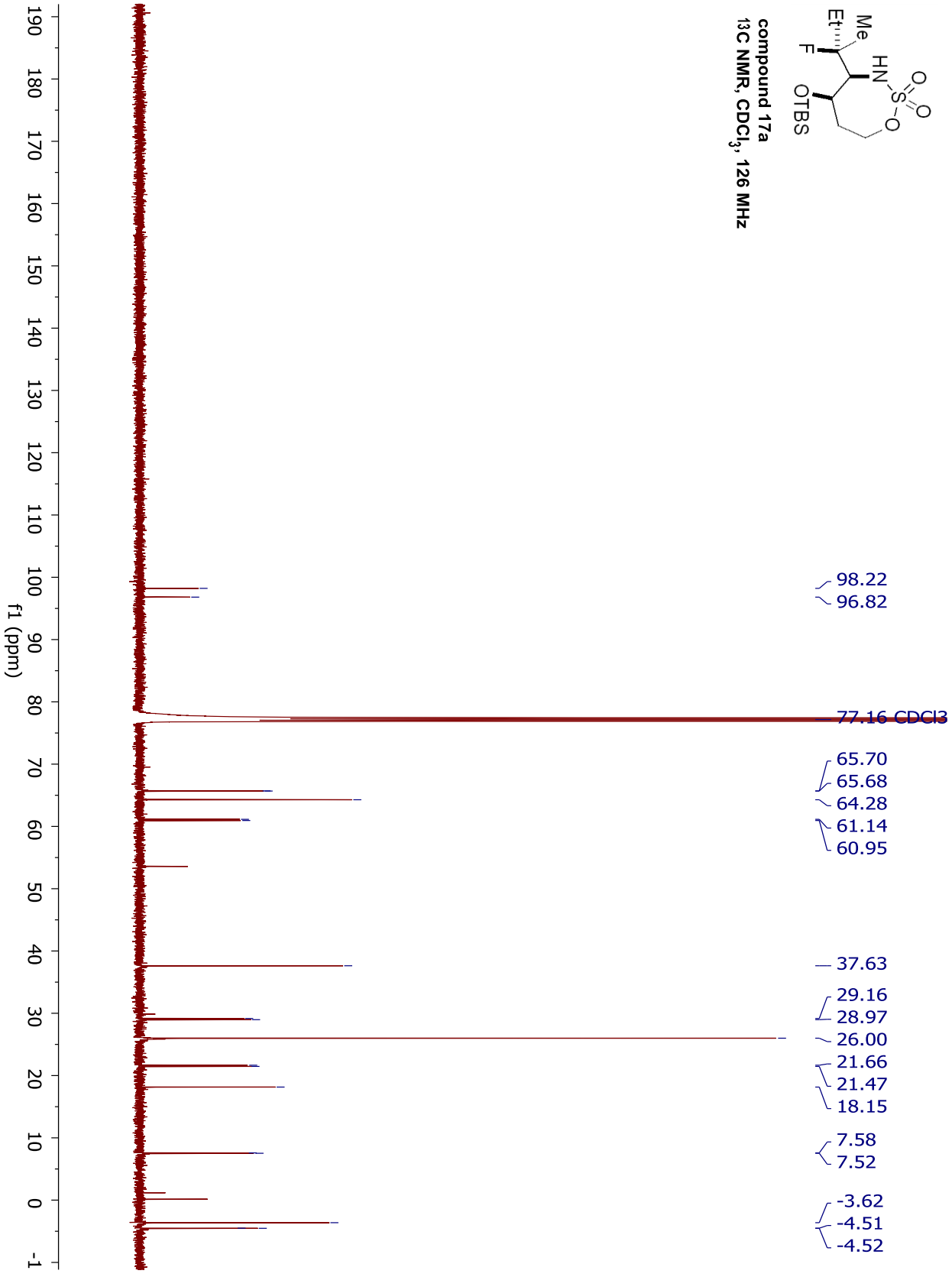
^{19}F NMR for compound 16c.



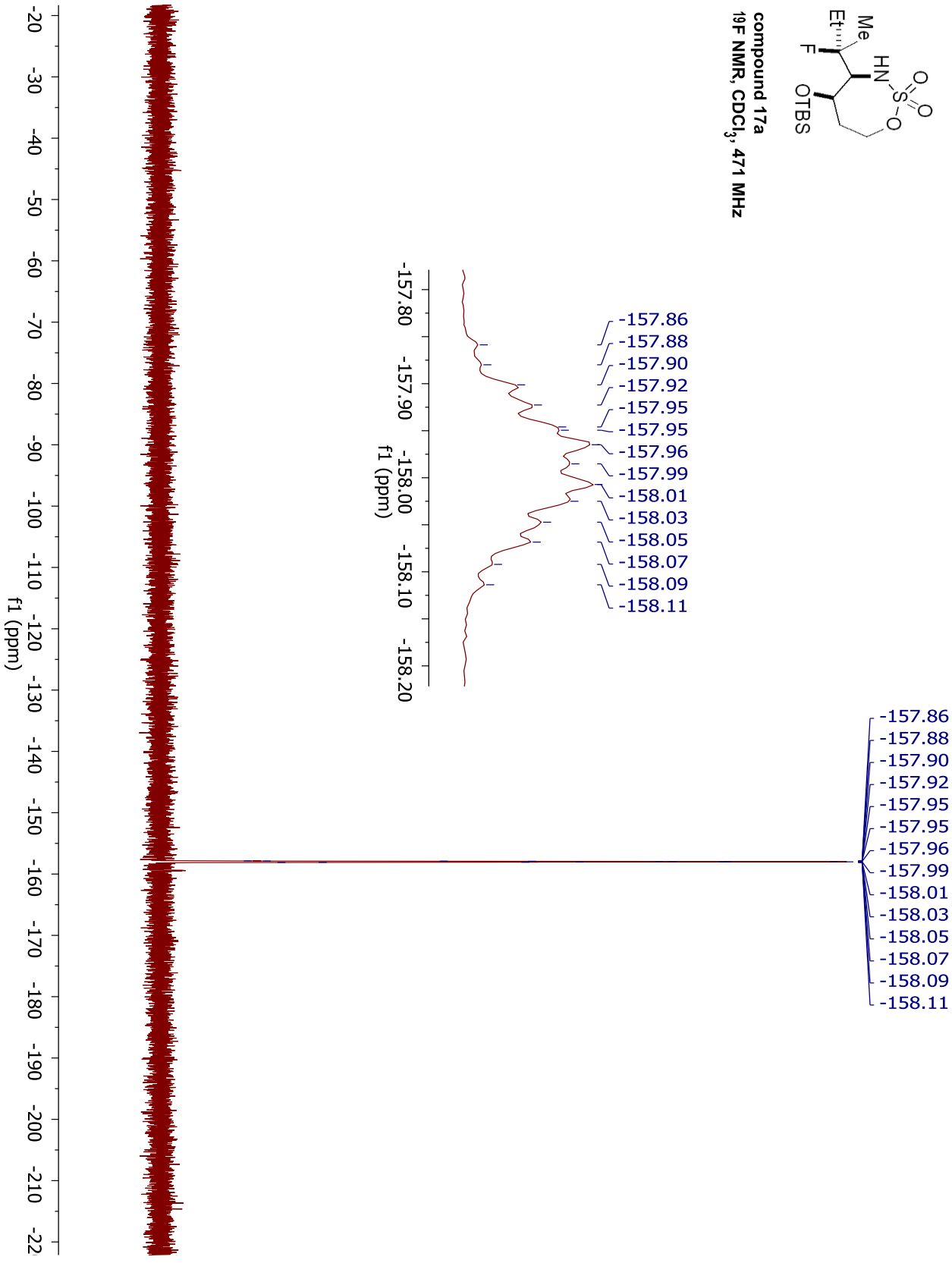
^{1}H NMR for compound 17a.



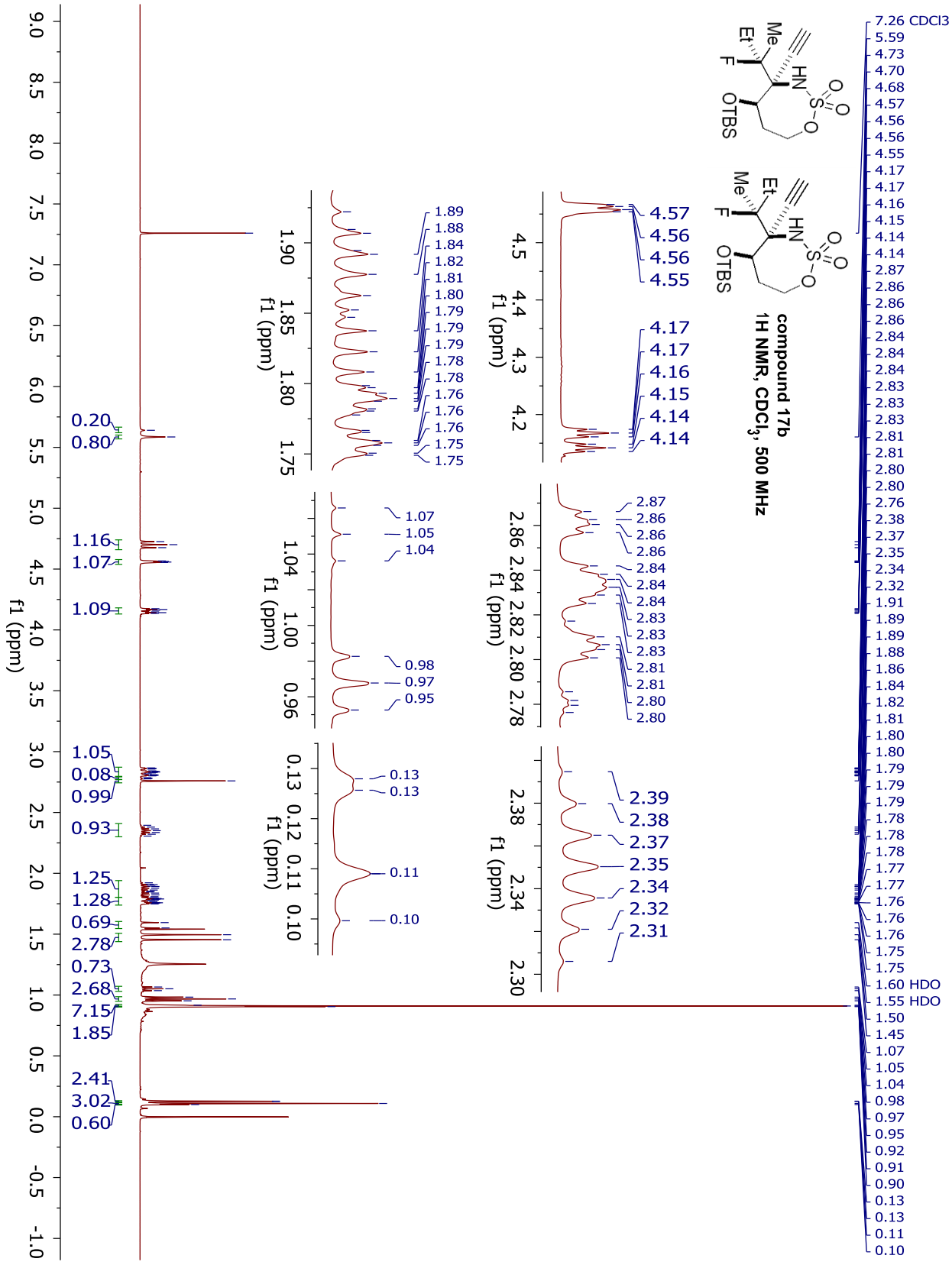
^{13}C NMR for compound 17a.



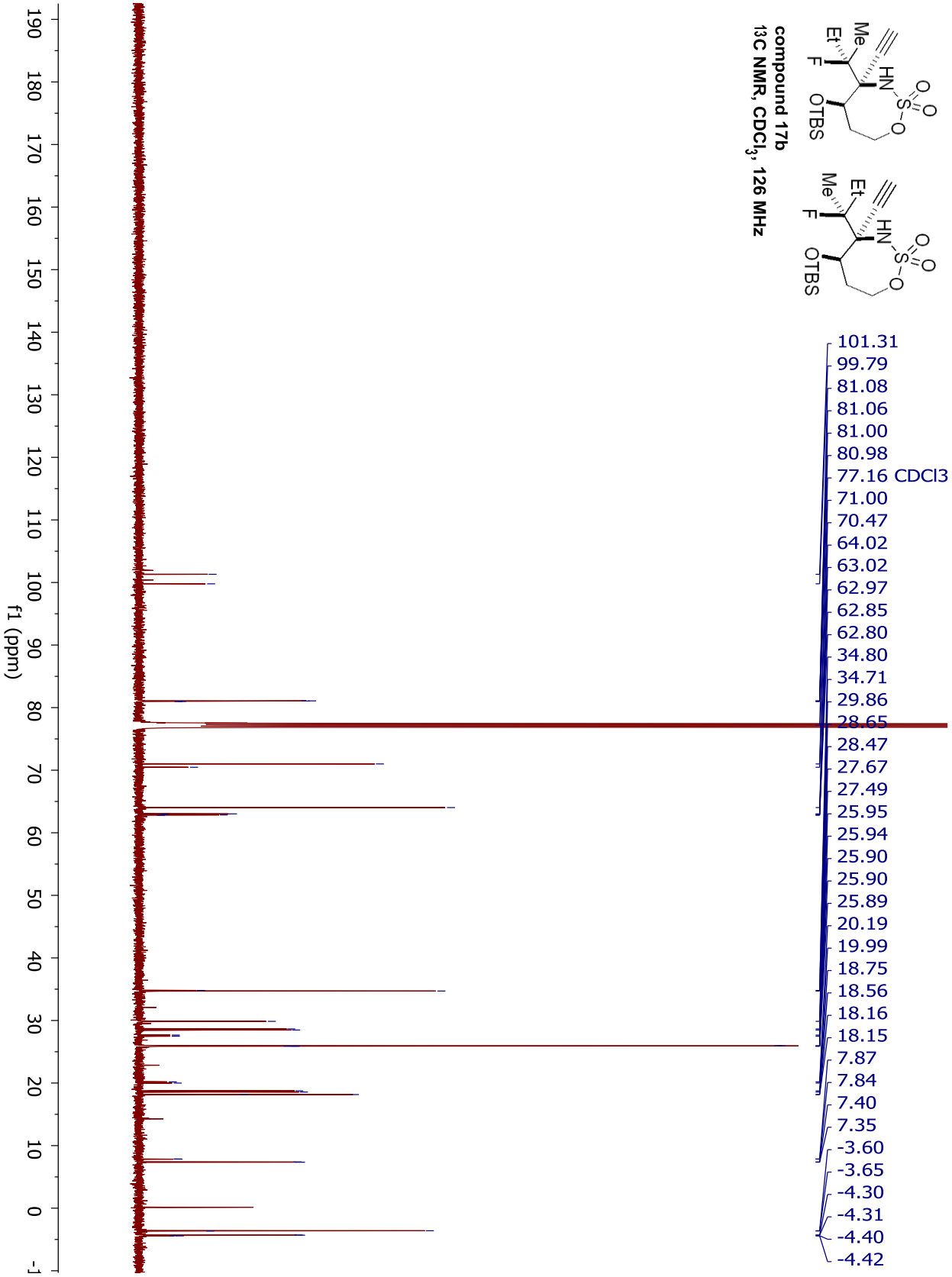
^{19}F NMR for compound 17a.



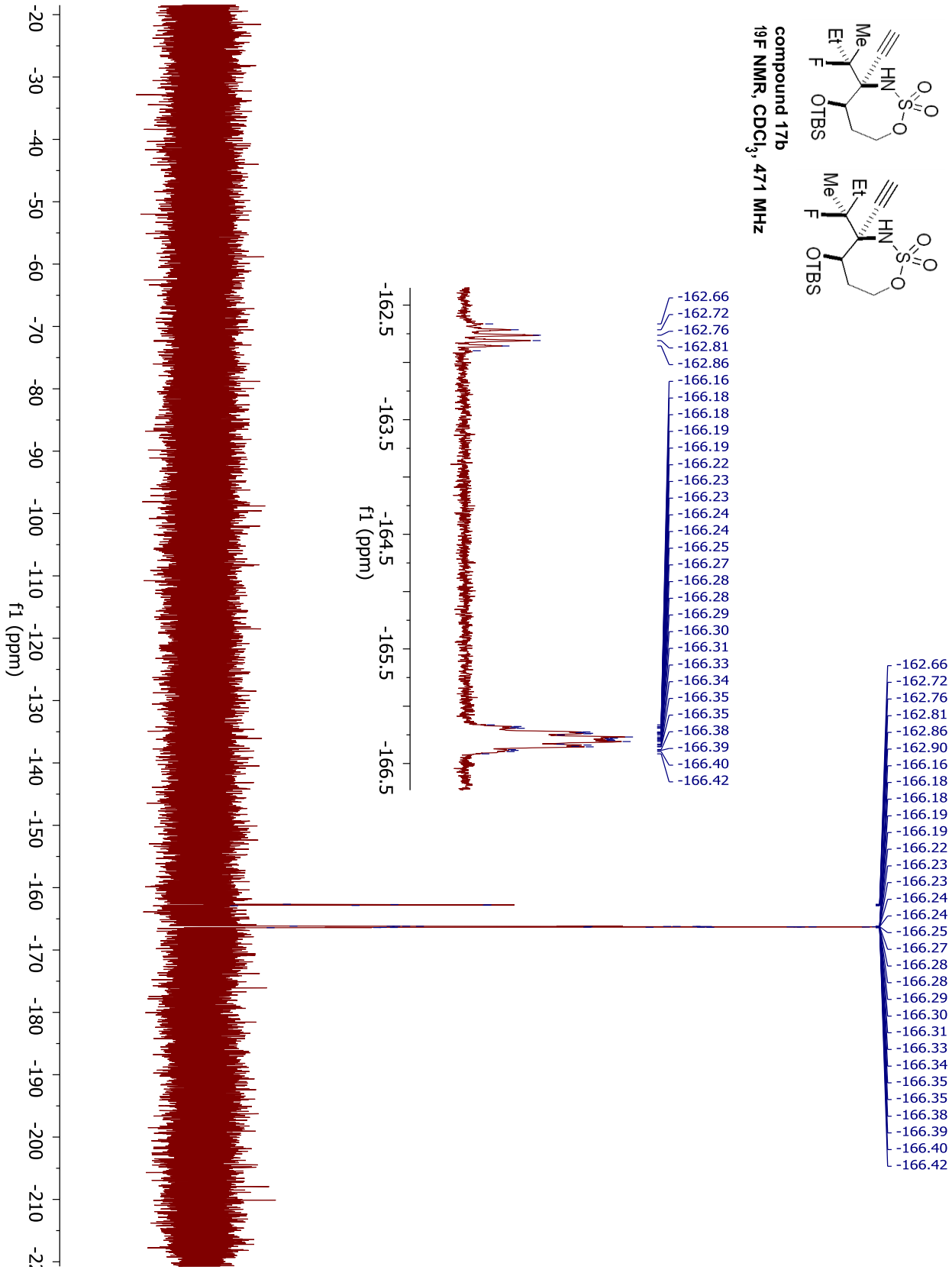
^{1}H NMR for compound 17b.



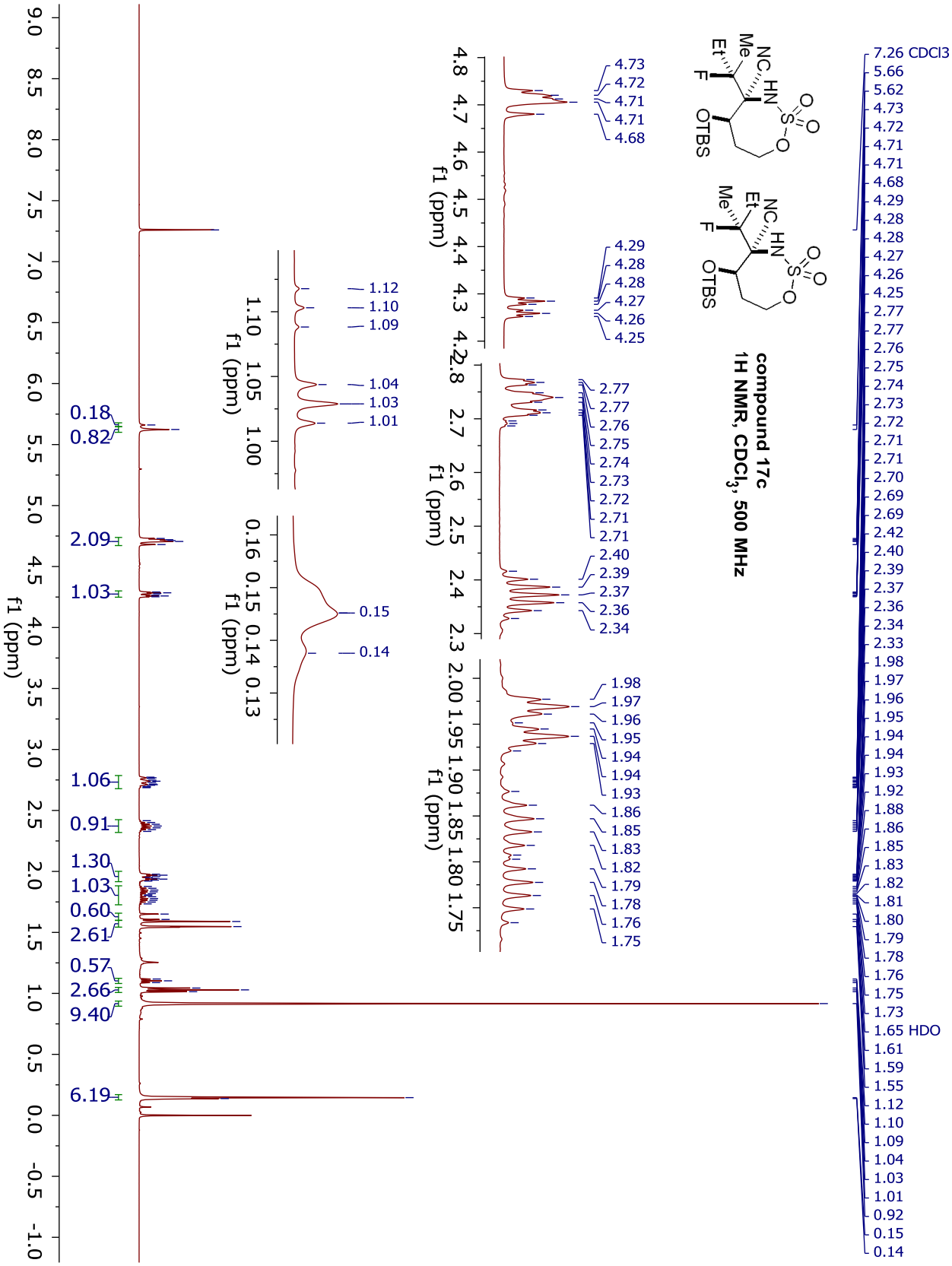
^{13}C NMR for compound 17b.



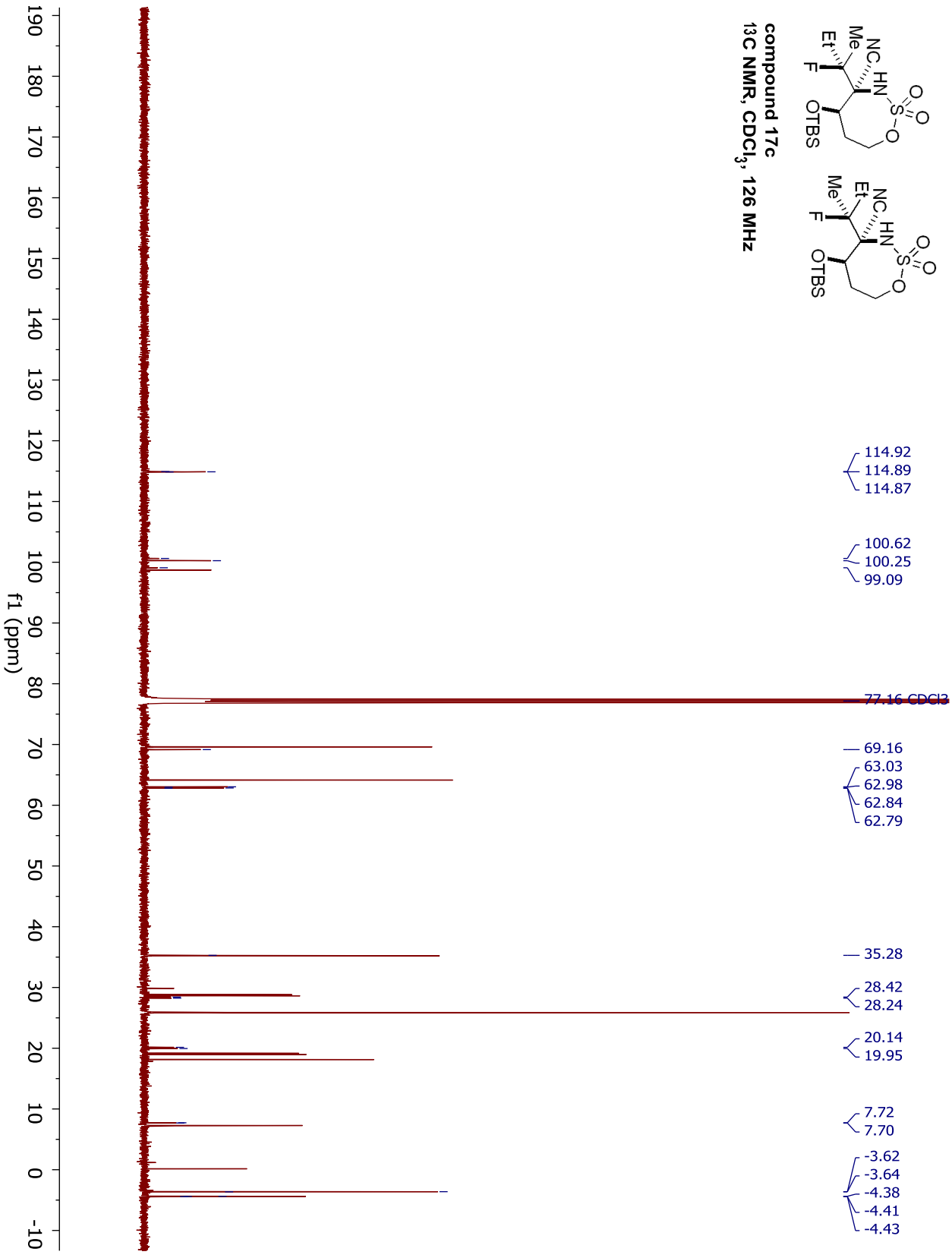
^{19}F NMR for compound 17b.



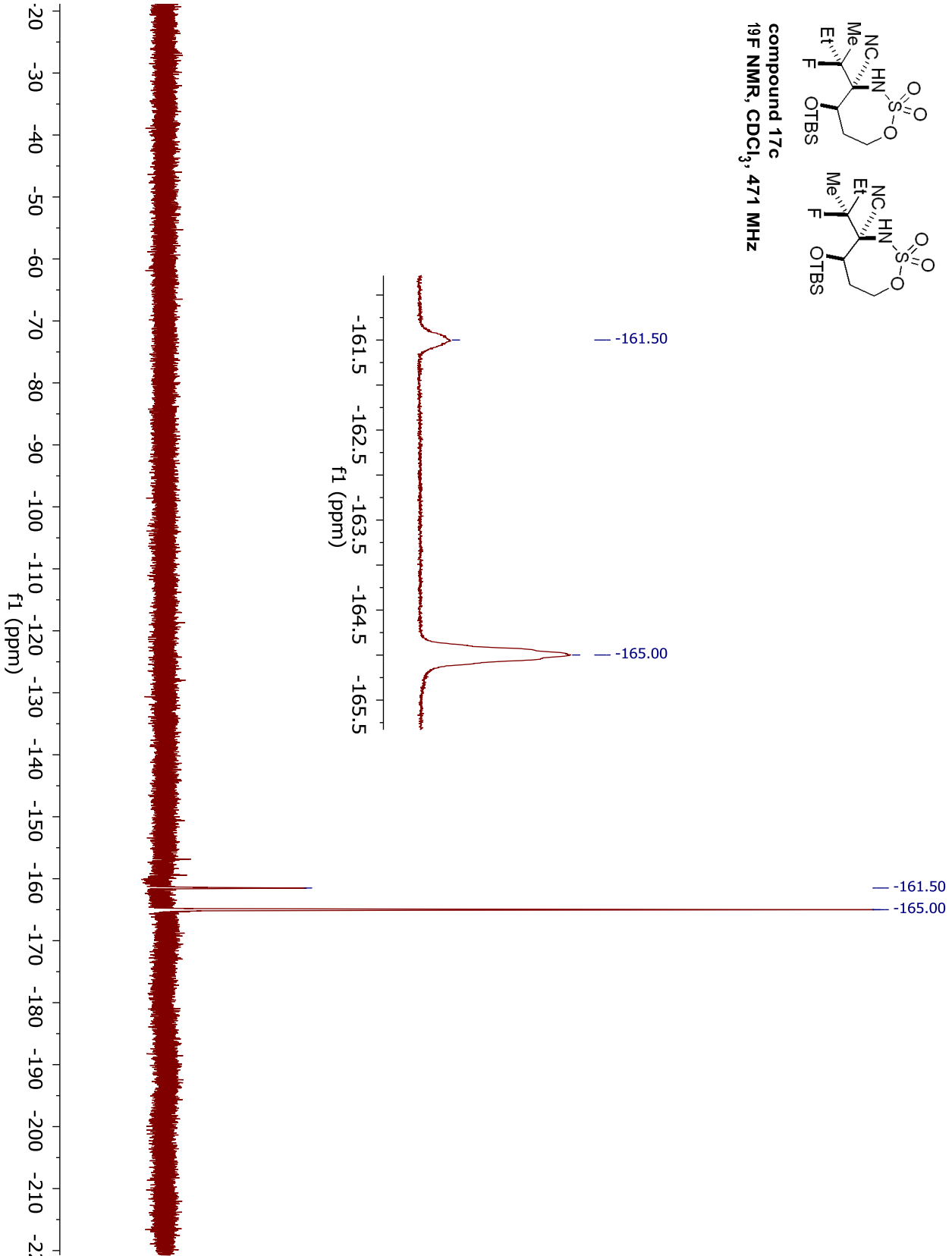
^{1}H NMR for compound 17c.



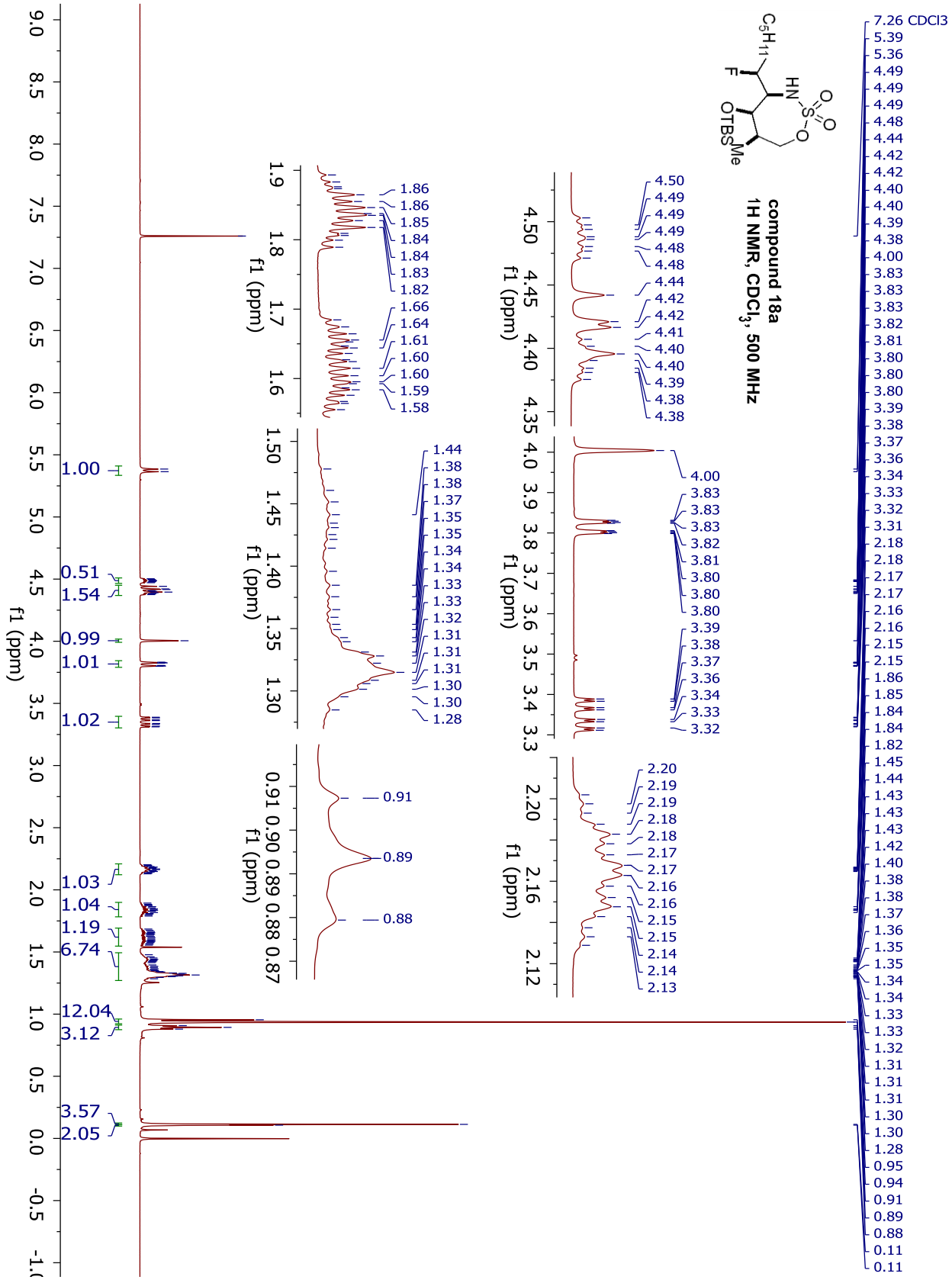
^{13}C NMR for compound 17c.



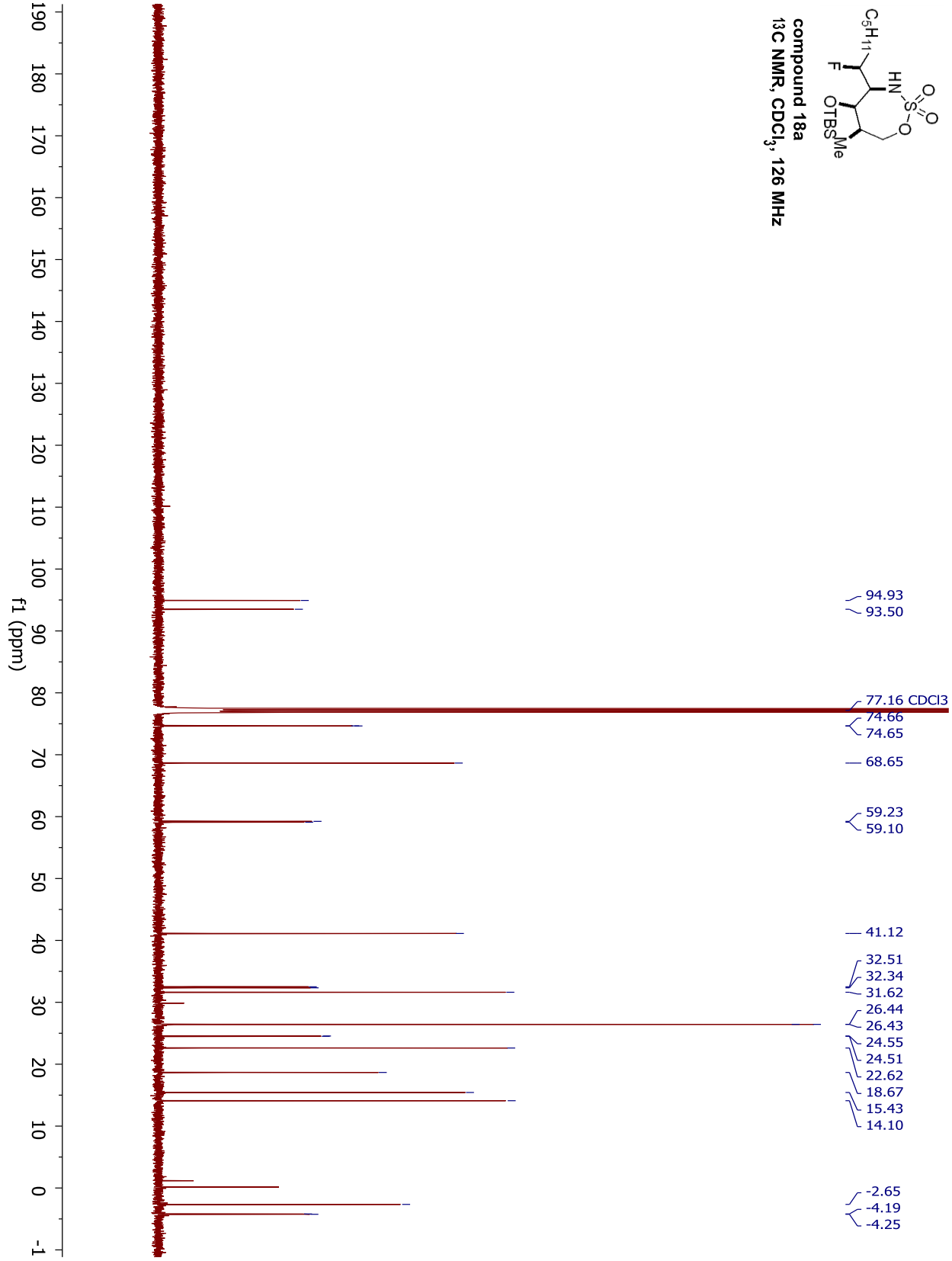
^{19}F NMR for compound 17c.



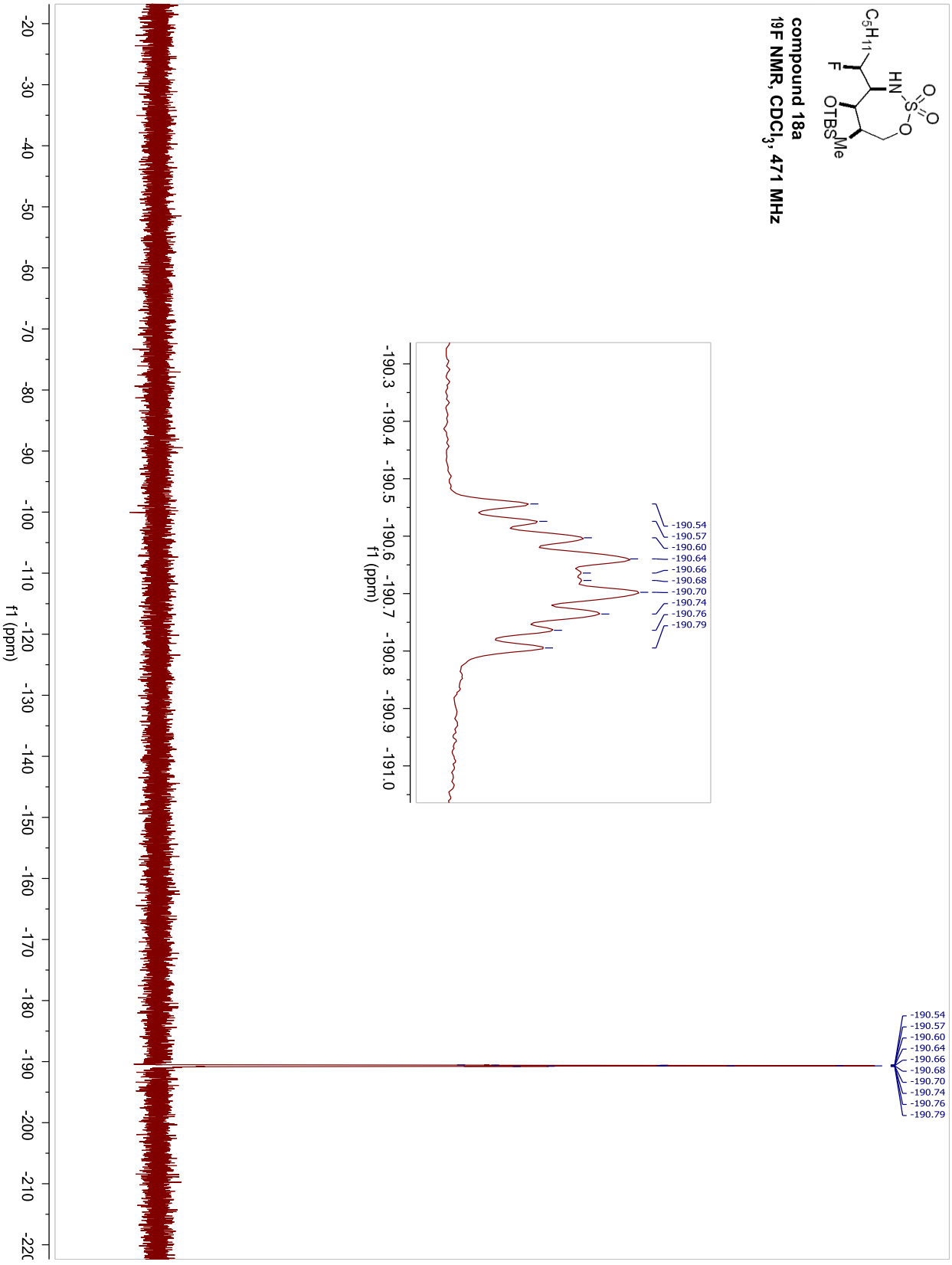
^{1}H NMR for compound 18a.



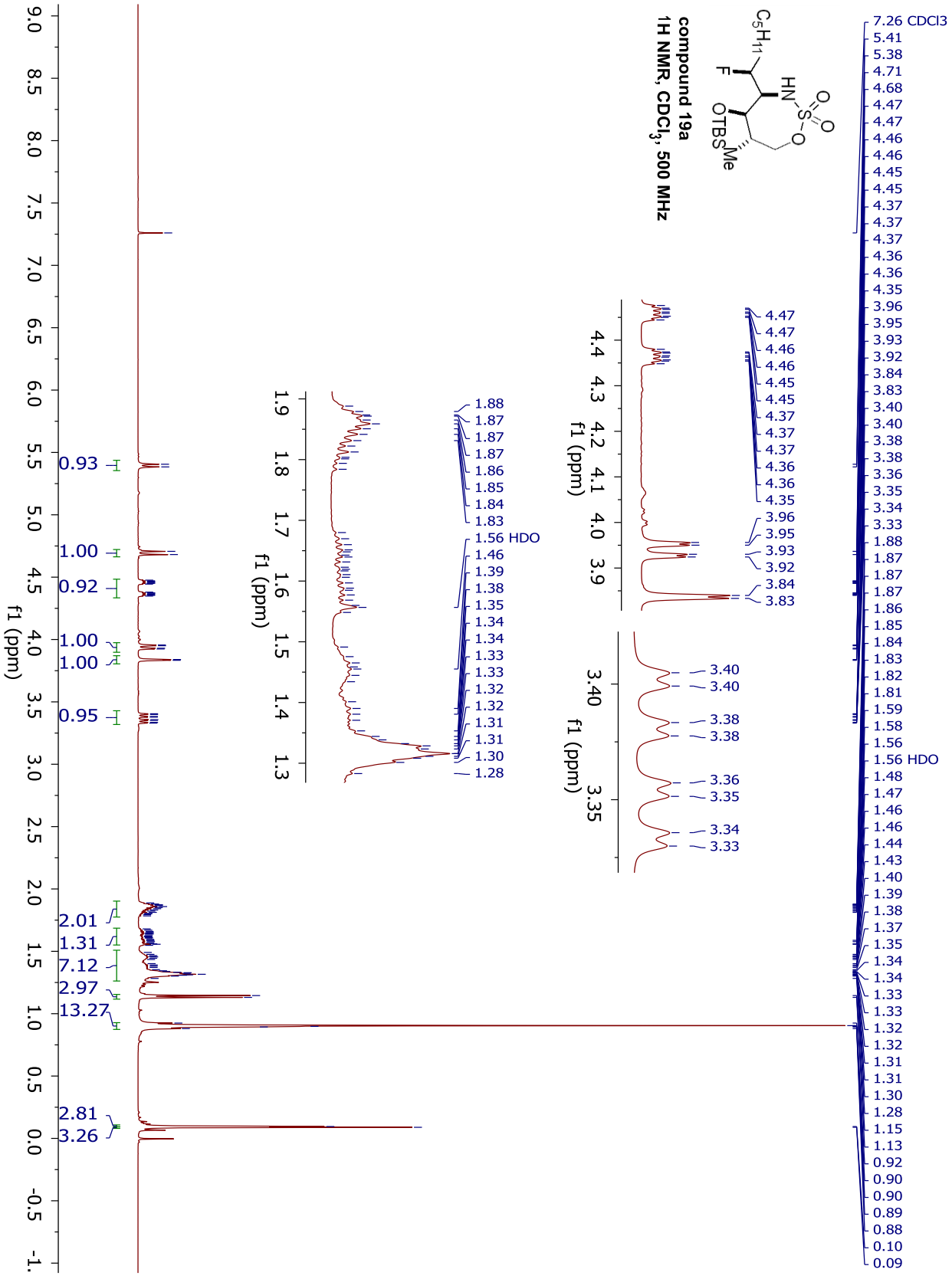
^{13}C NMR for compound 18a.



^{19}F NMR for compound 18a.



^{1}H NMR for compound 19a.



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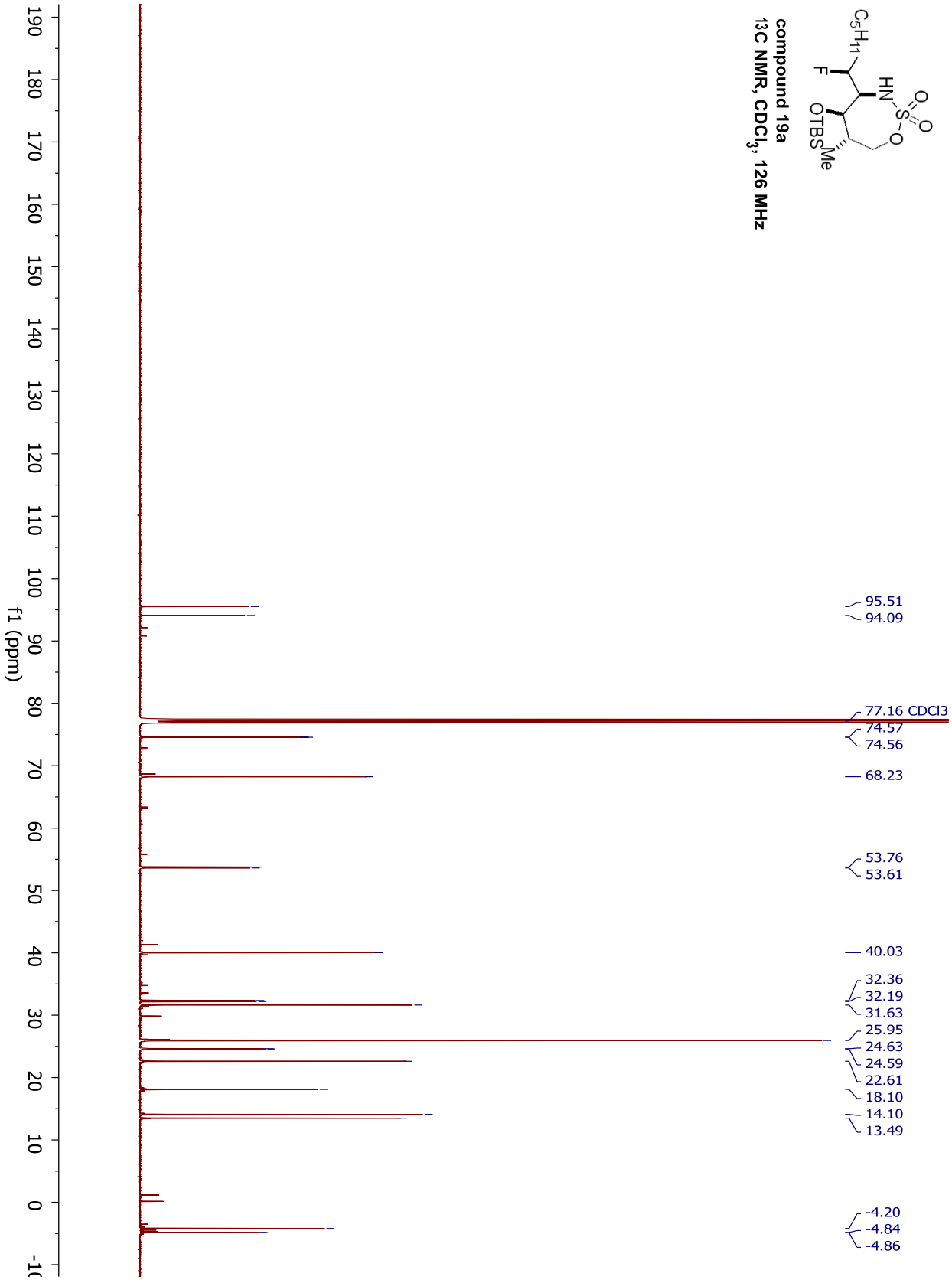

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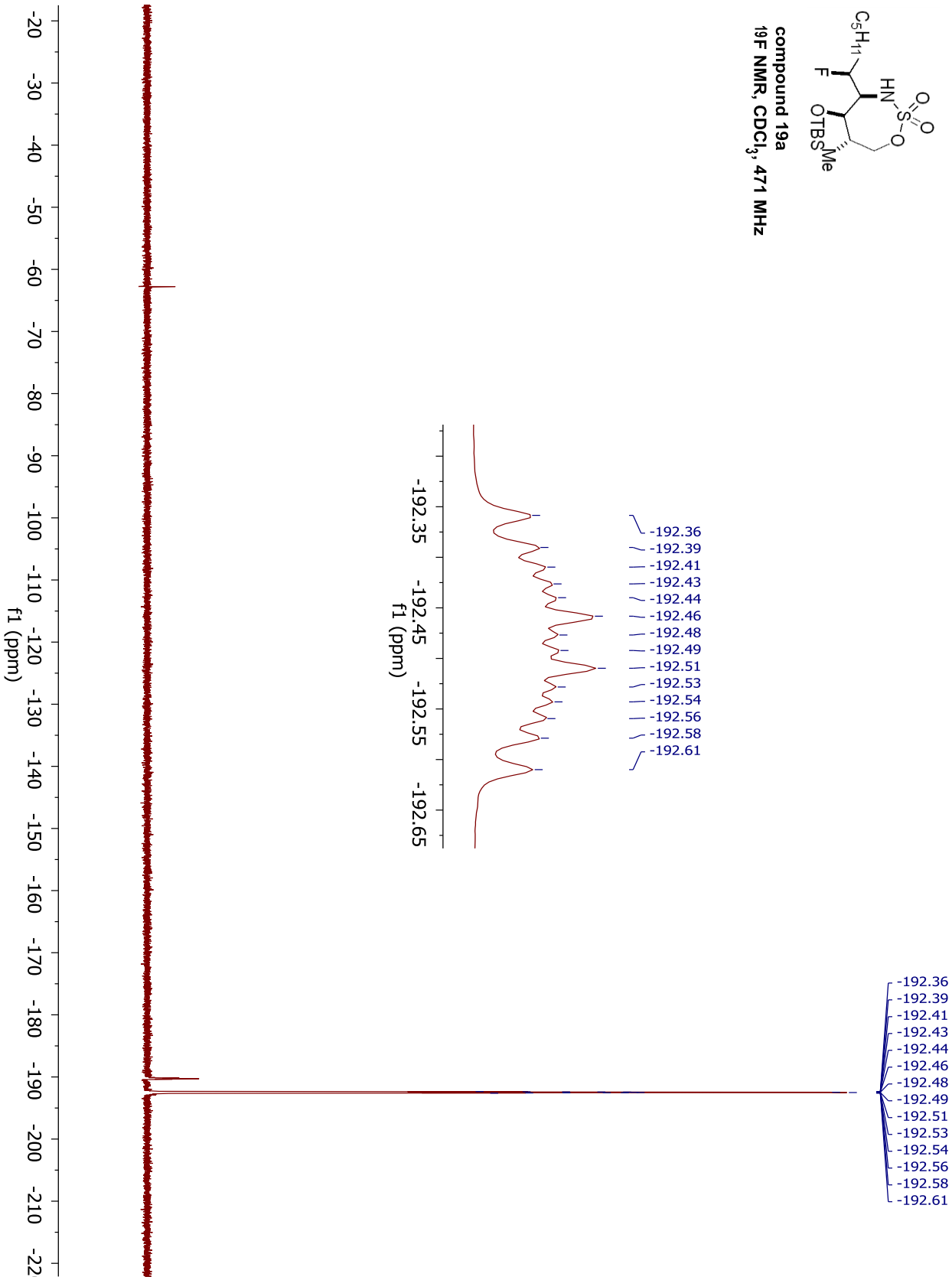
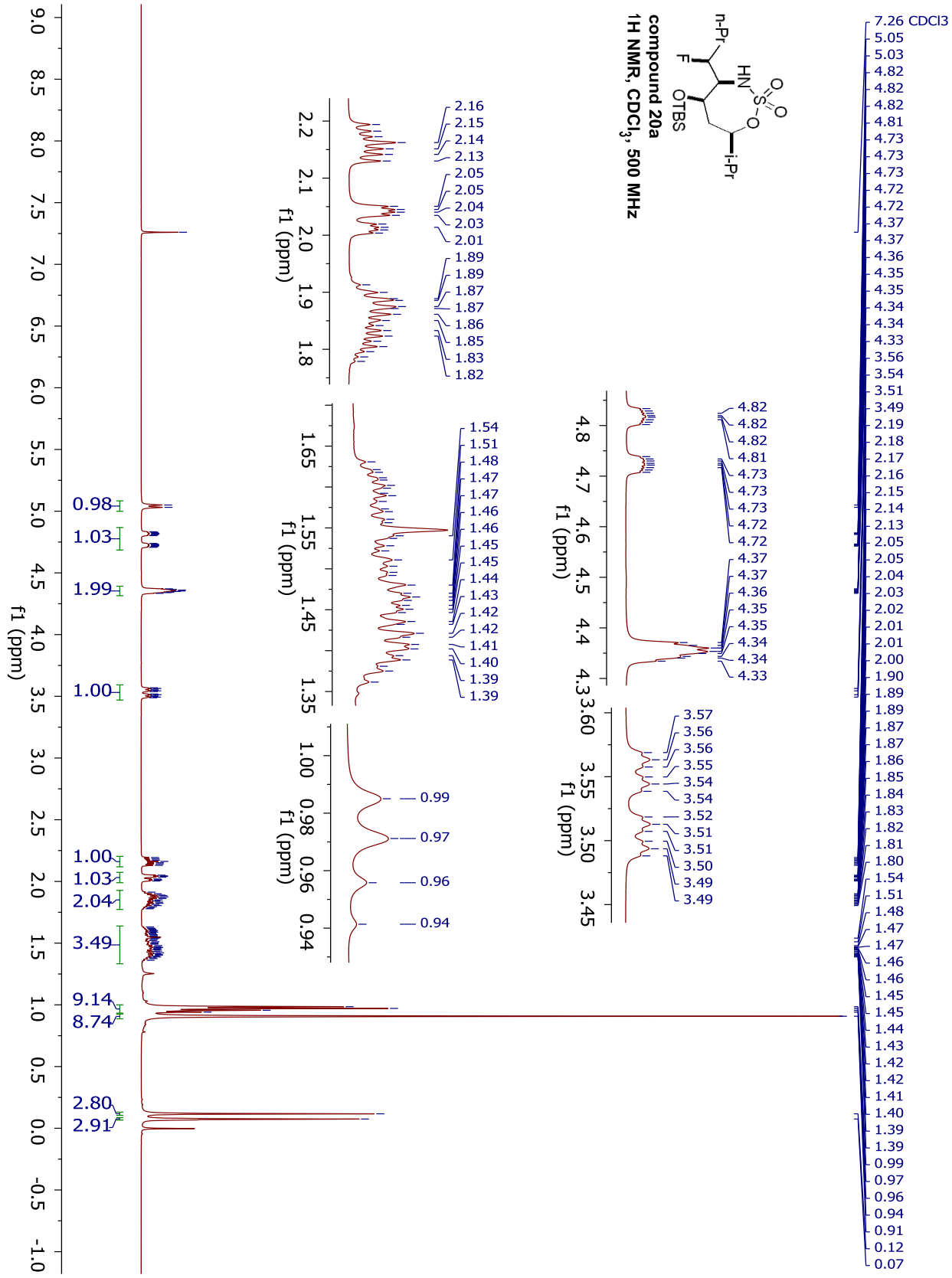
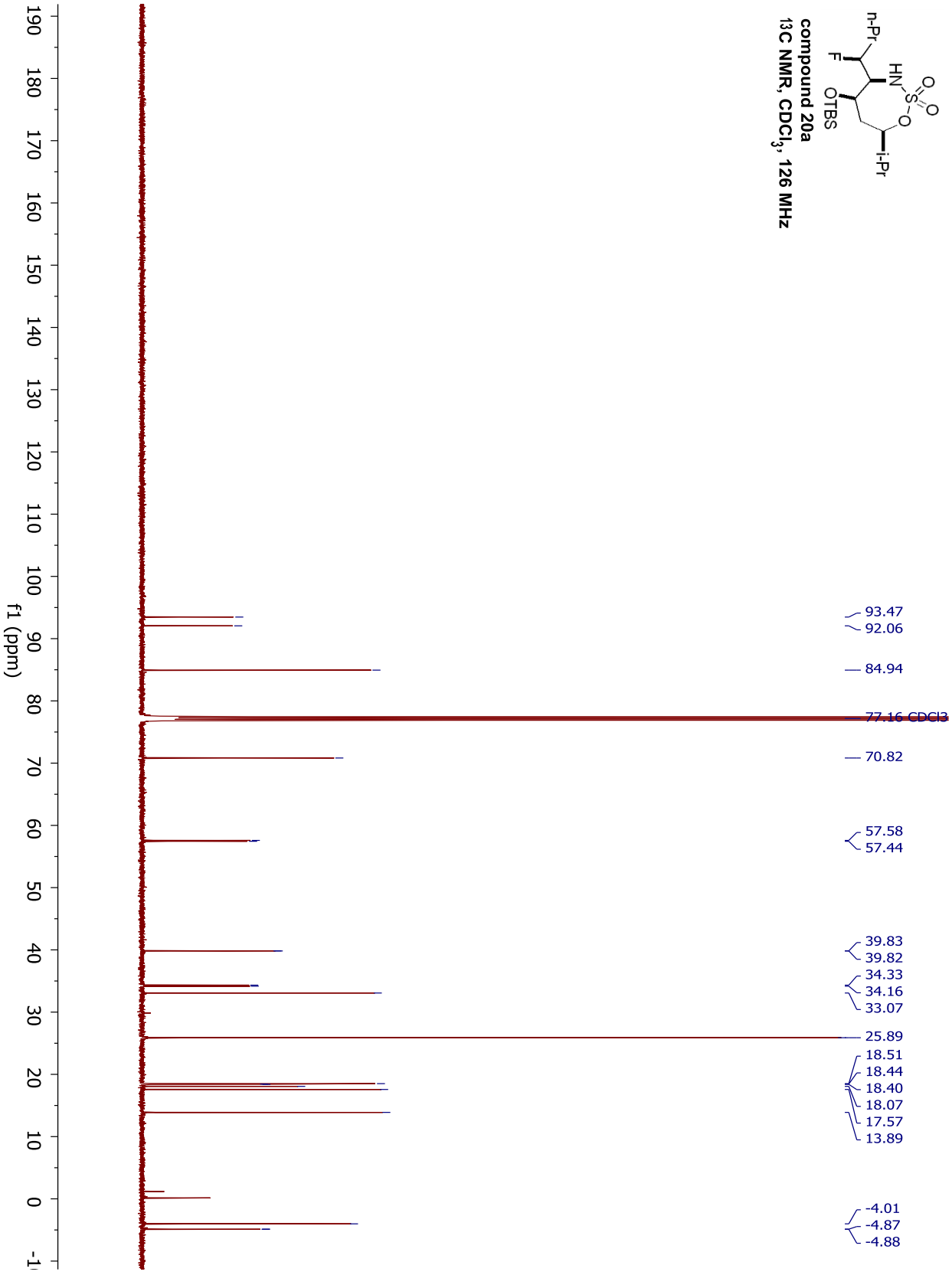


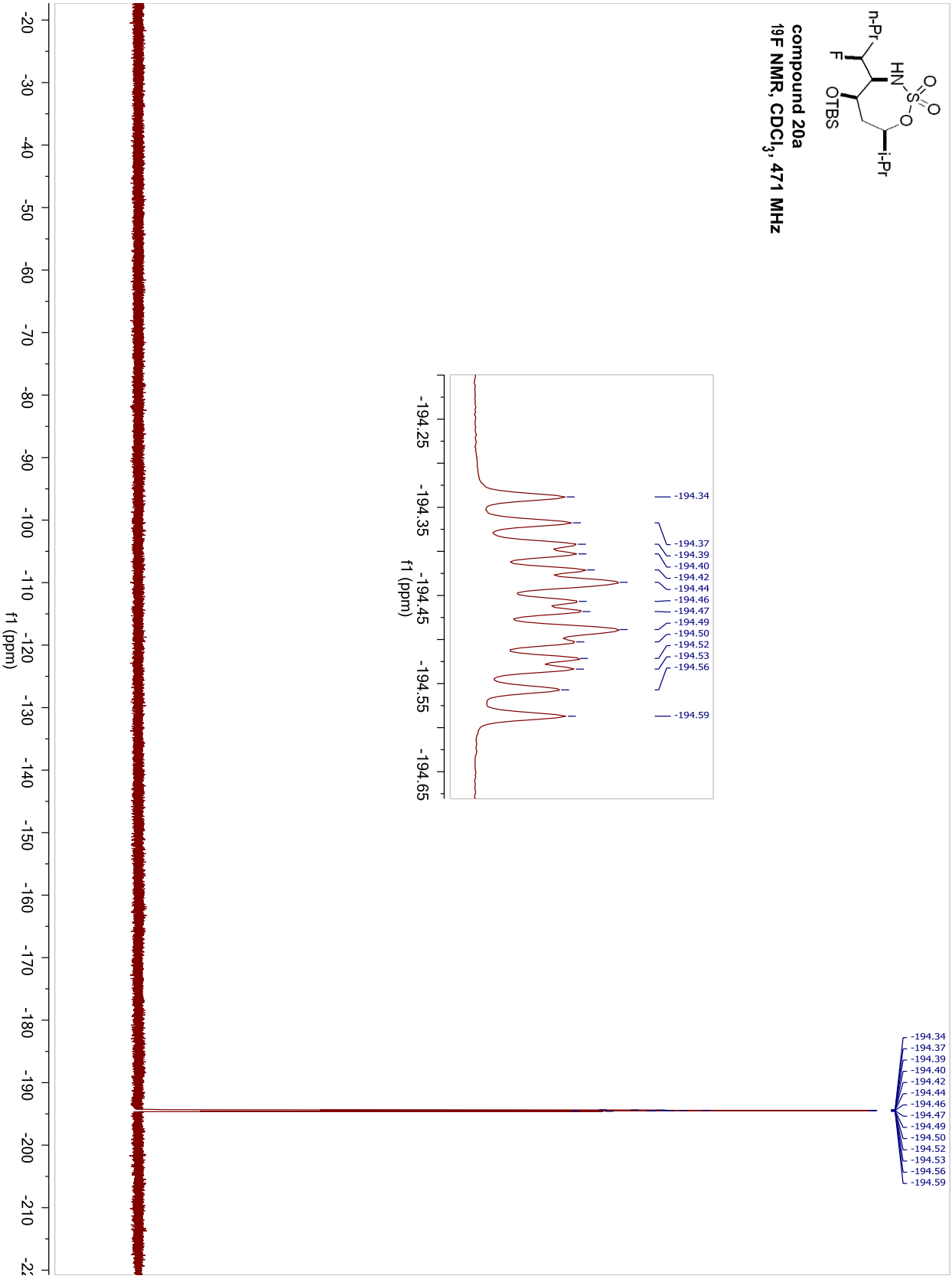
^{1}H NMR for compound 20a.



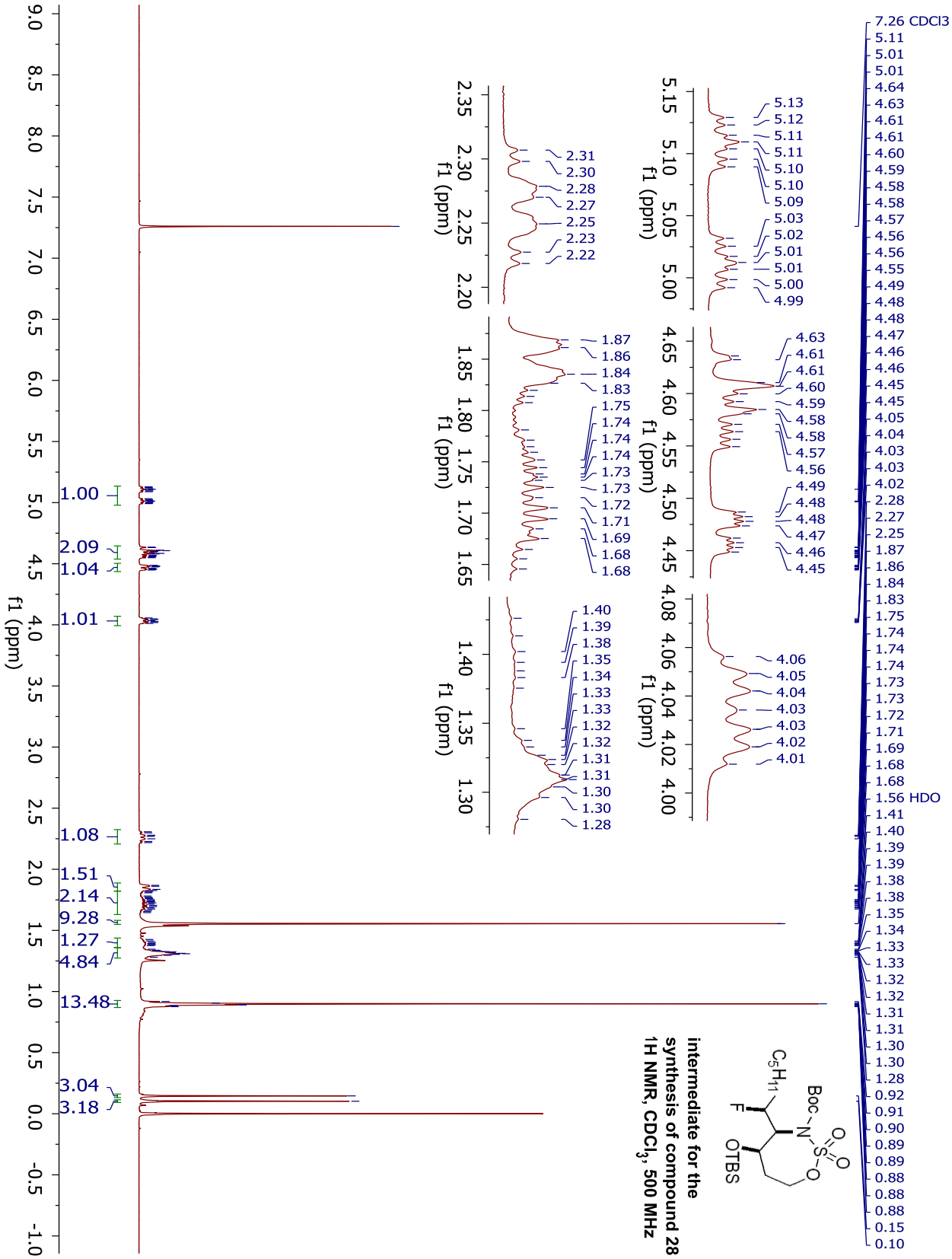
^{13}C NMR for compound 20a.



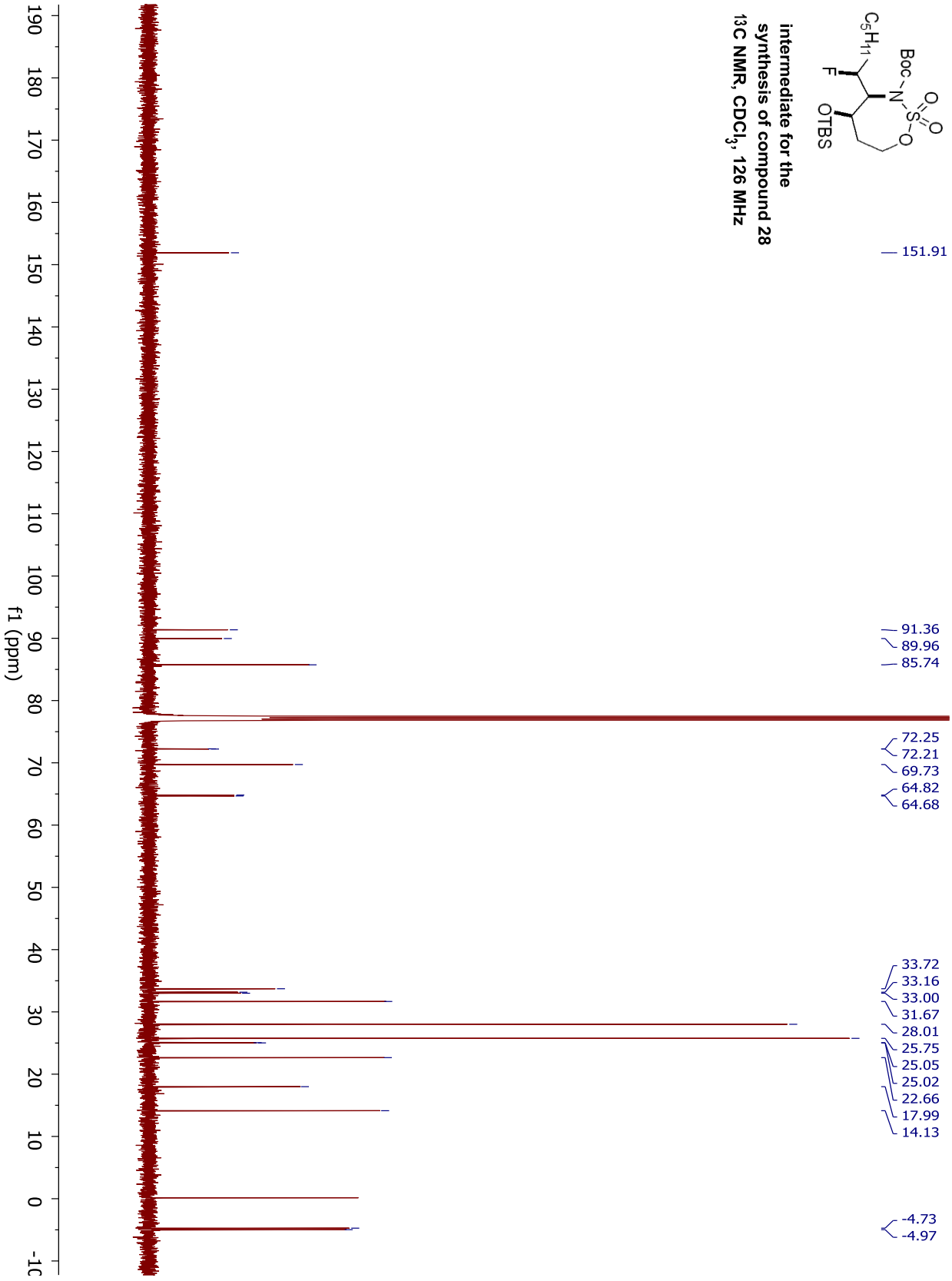
^{19}F NMR for compound 20a.



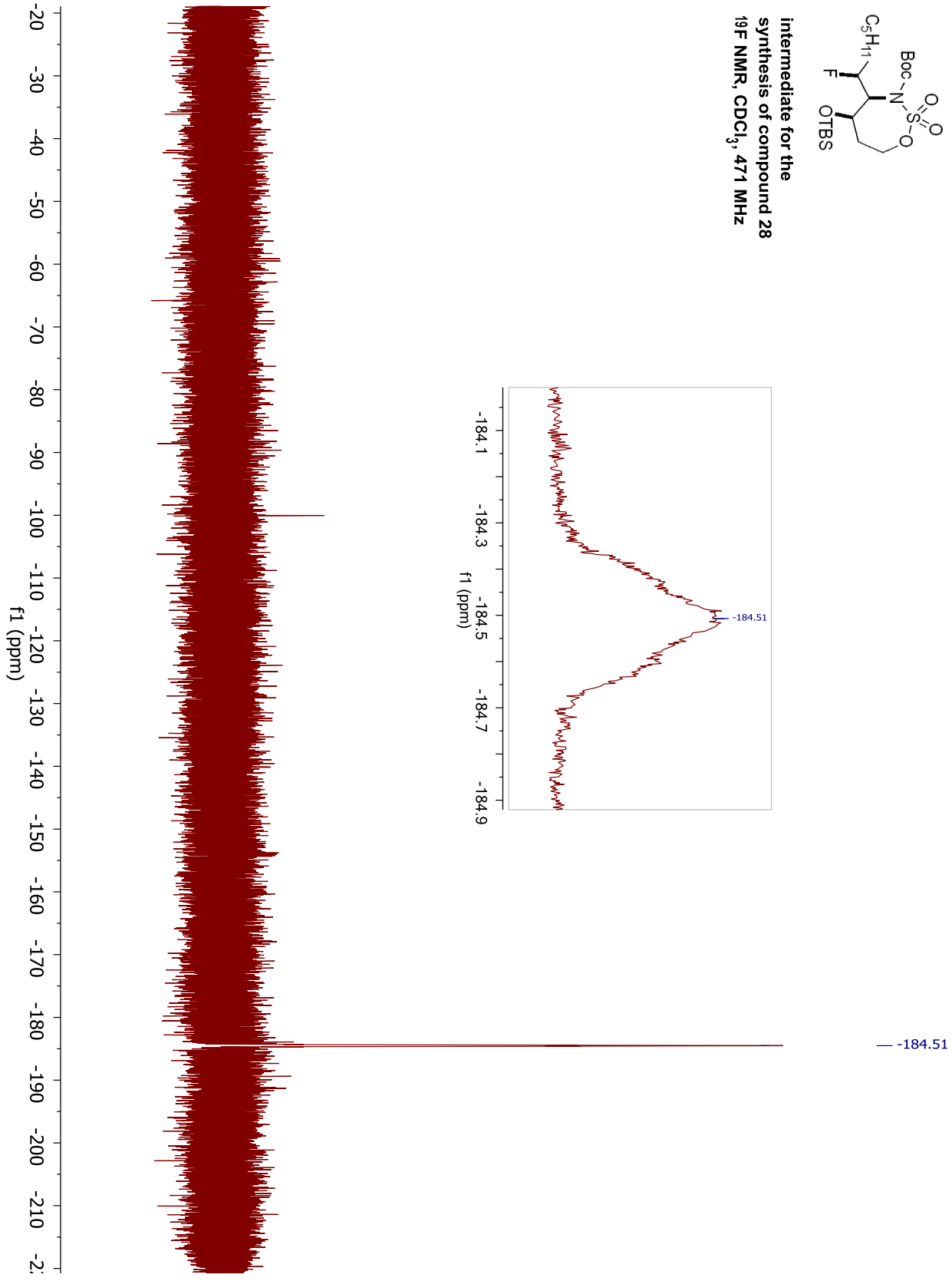
^{1}H NMR for intermediate for the synthesis of compound 28.



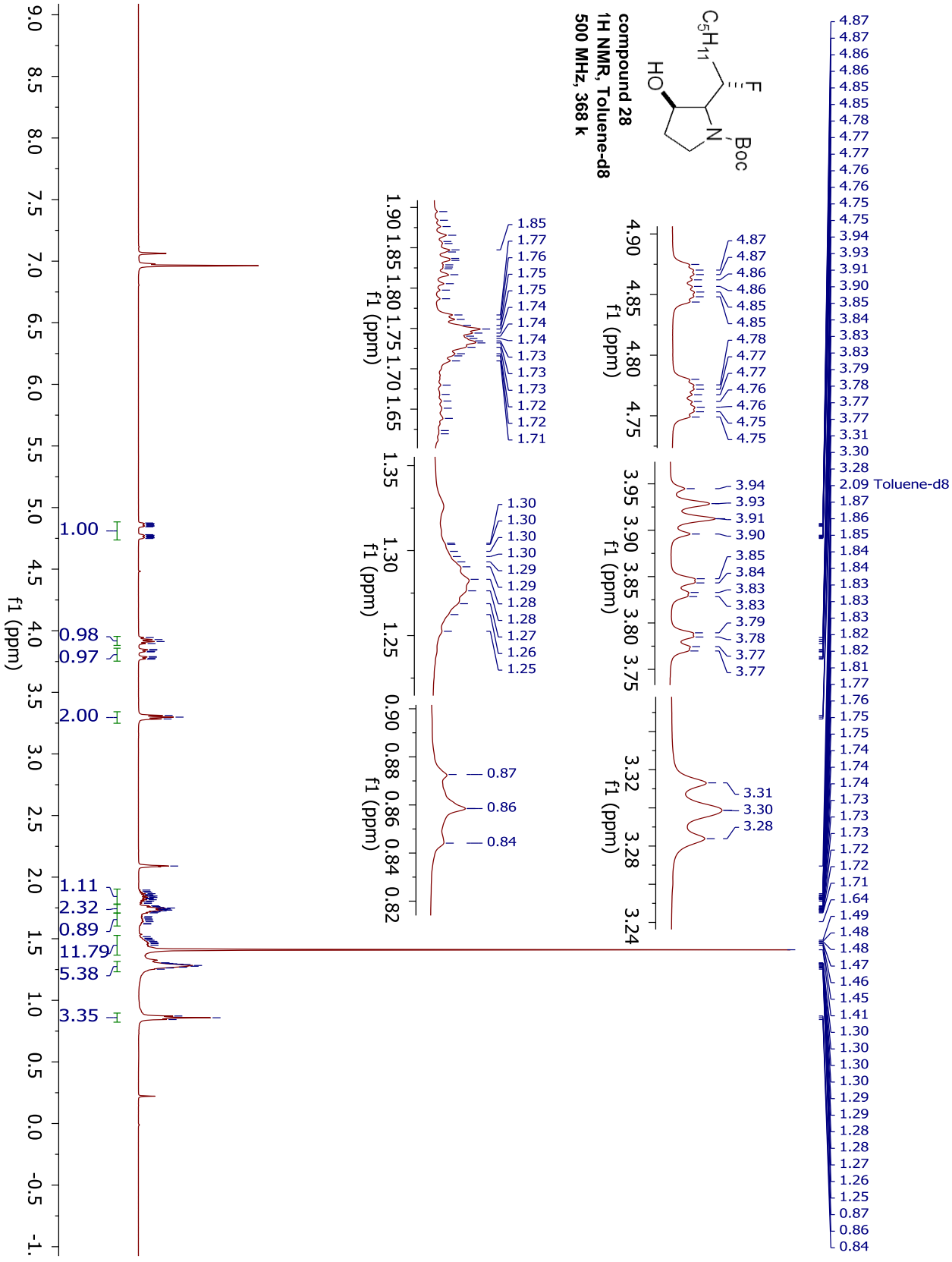
^{13}C NMR for intermediate for the synthesis of compound 28.



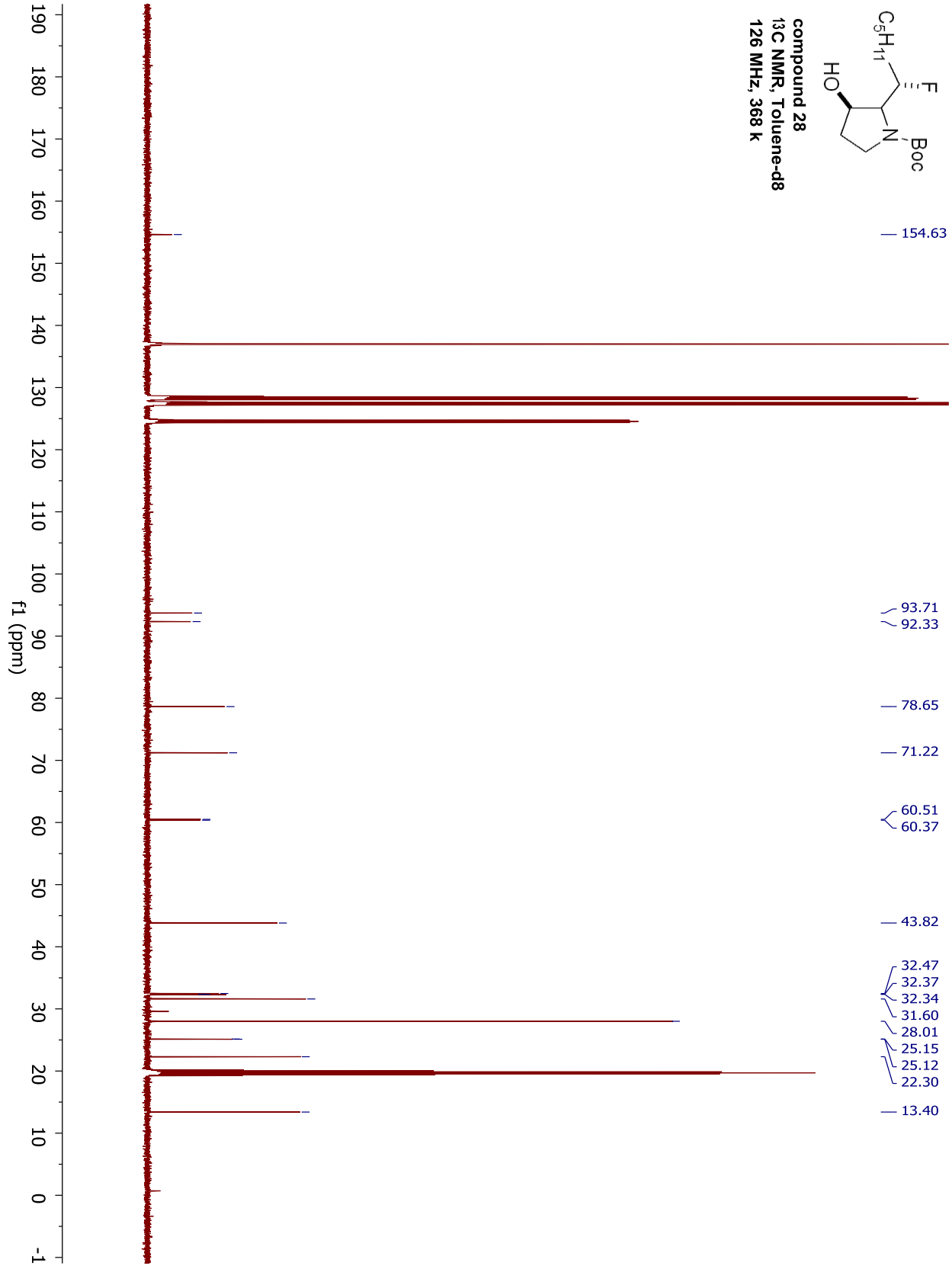
^{19}F NMR for intermediate for the synthesis of compound 28.



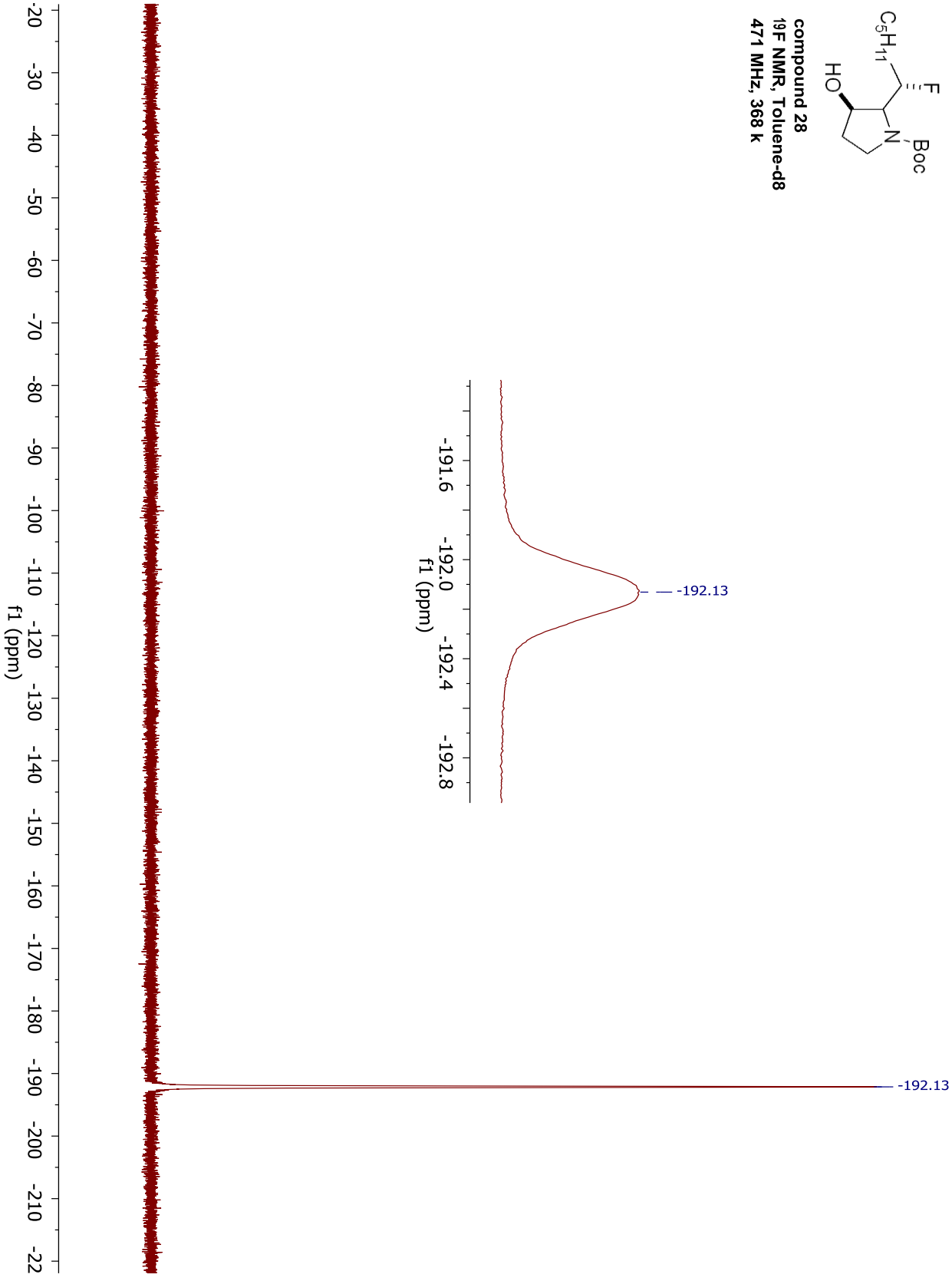
^{1}H NMR for compound 28.



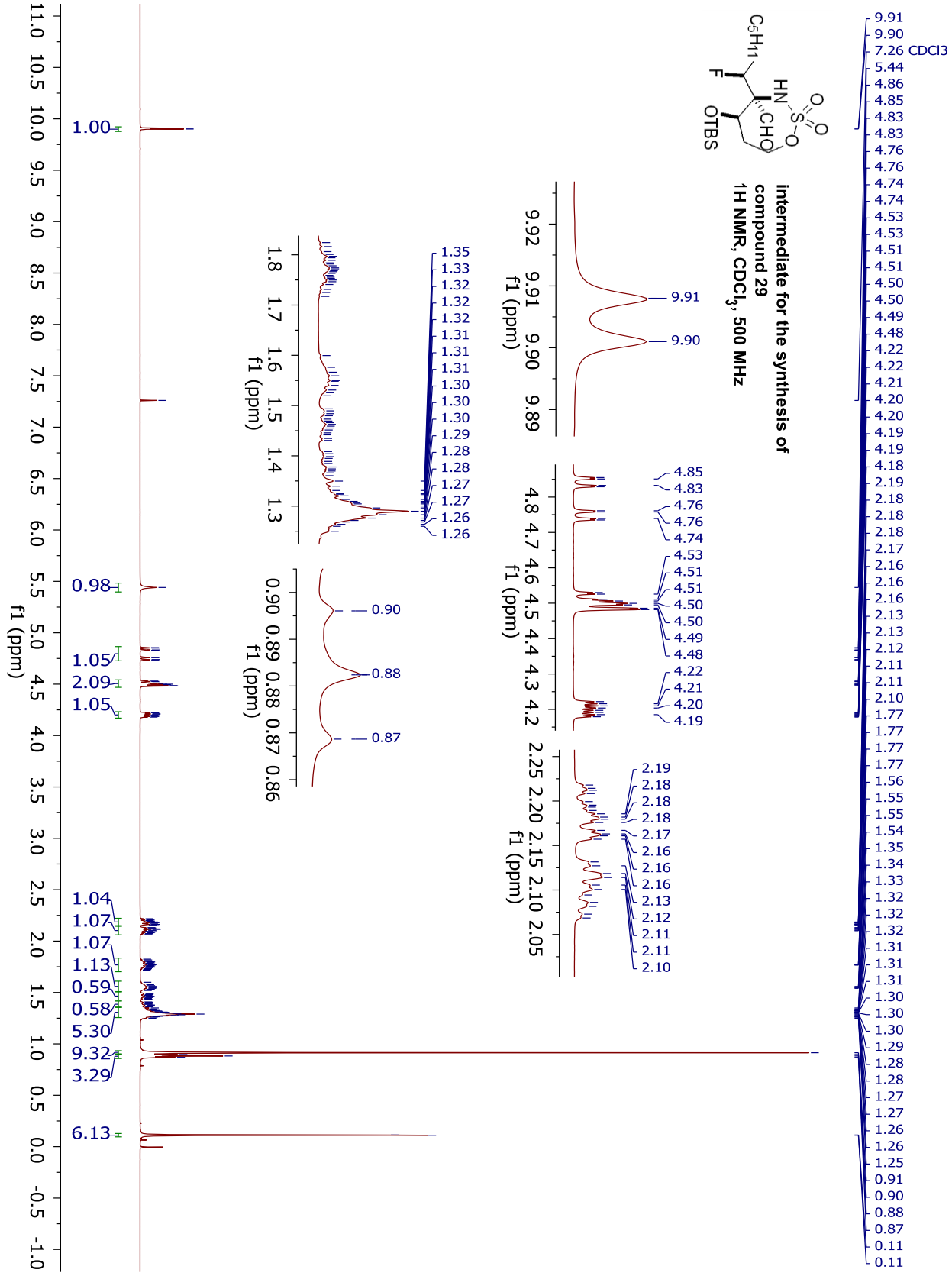
^{13}C NMR for compound 28.



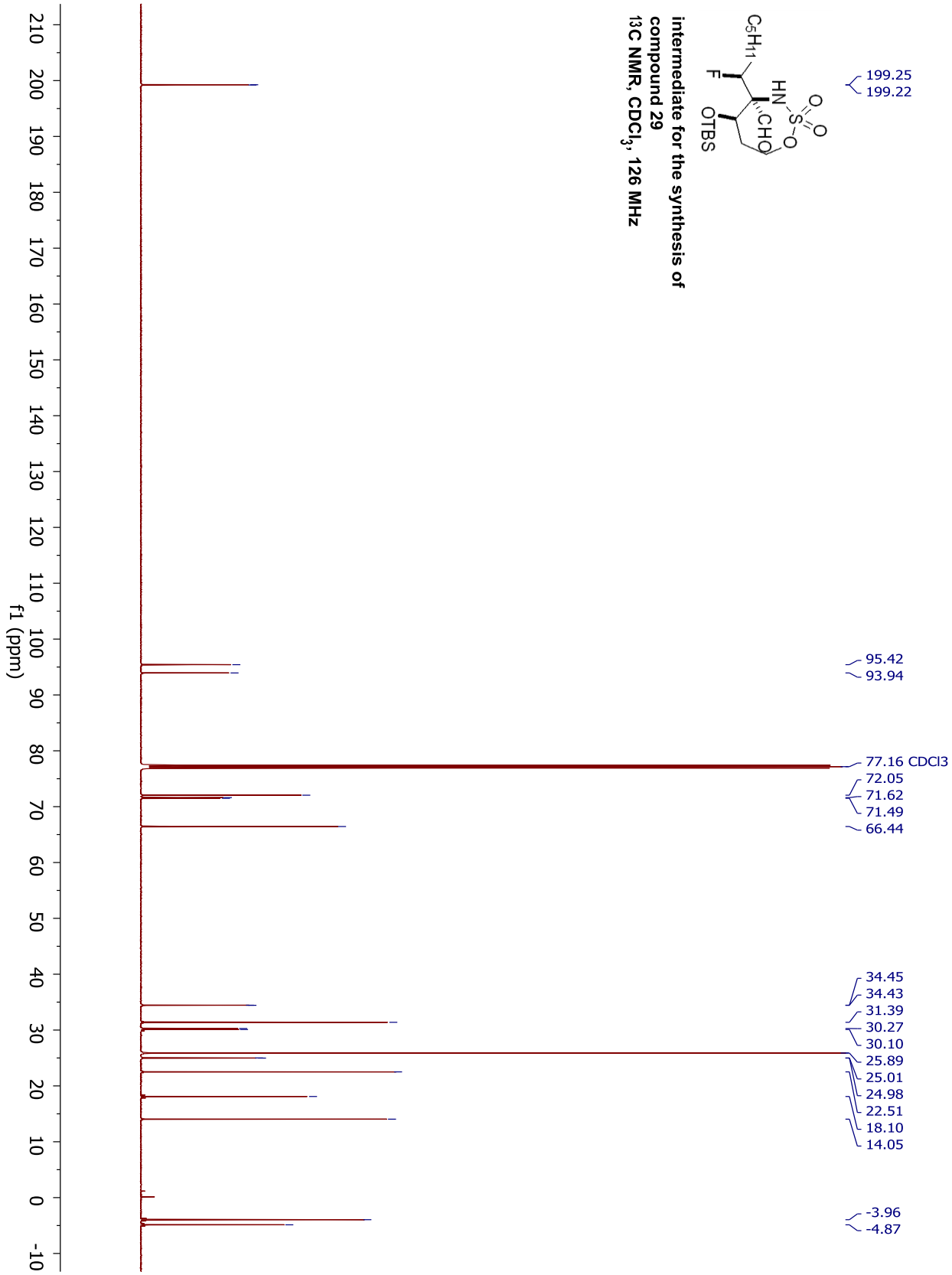
^{19}F NMR for compound 28.



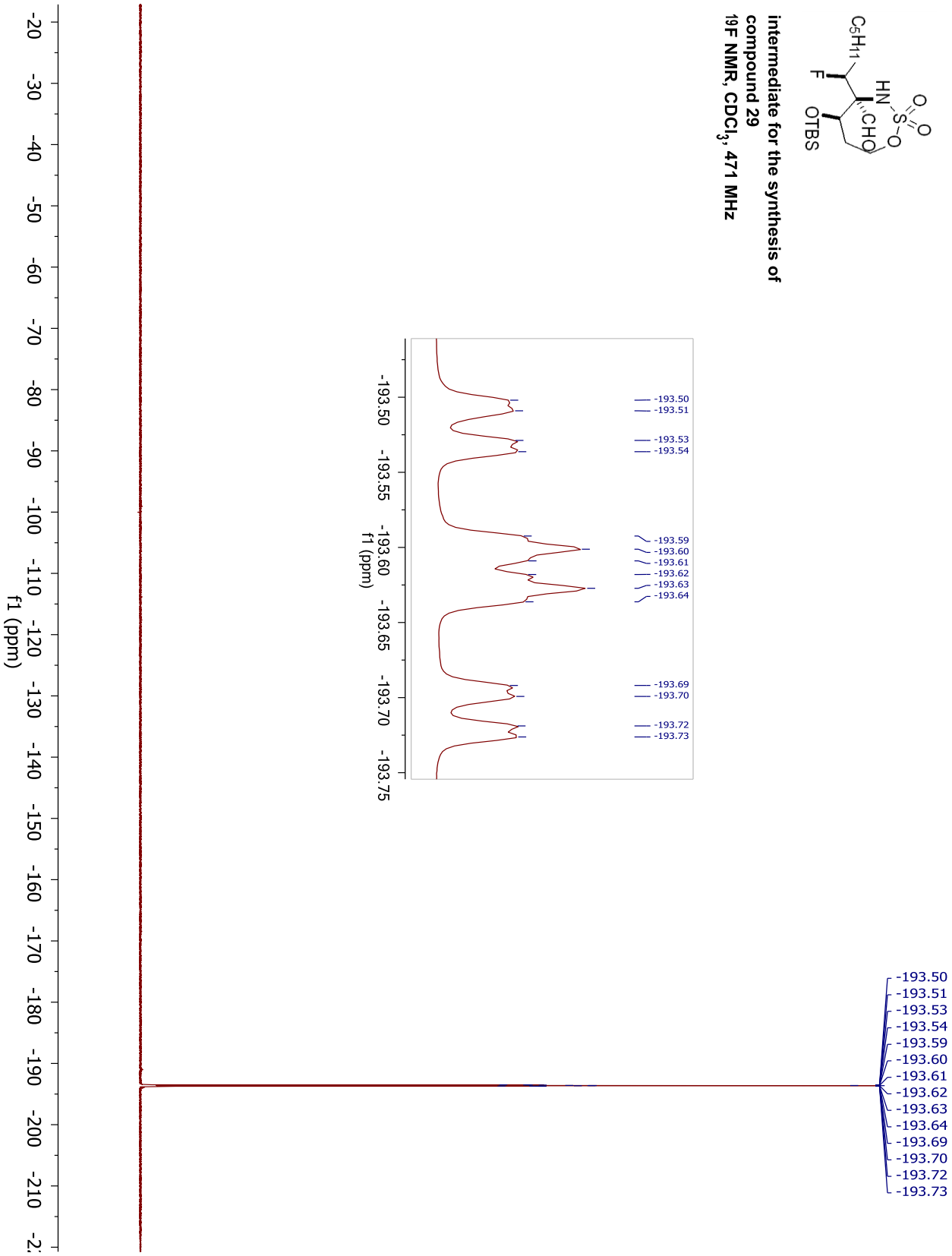
^{1}H NMR for intermediate for the synthesis of compound 29.



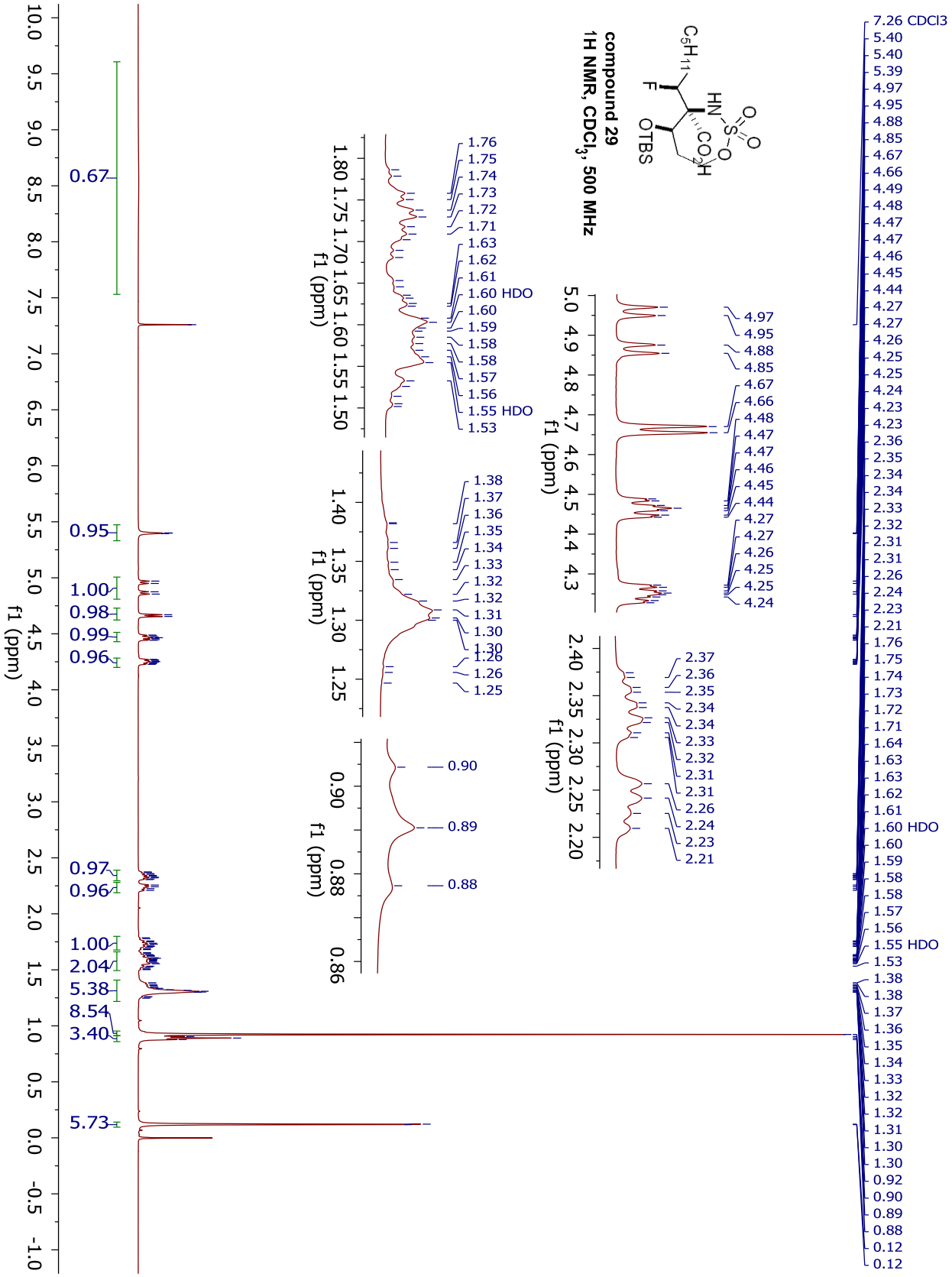
^{13}C NMR for intermediate for the synthesis of compound 29.



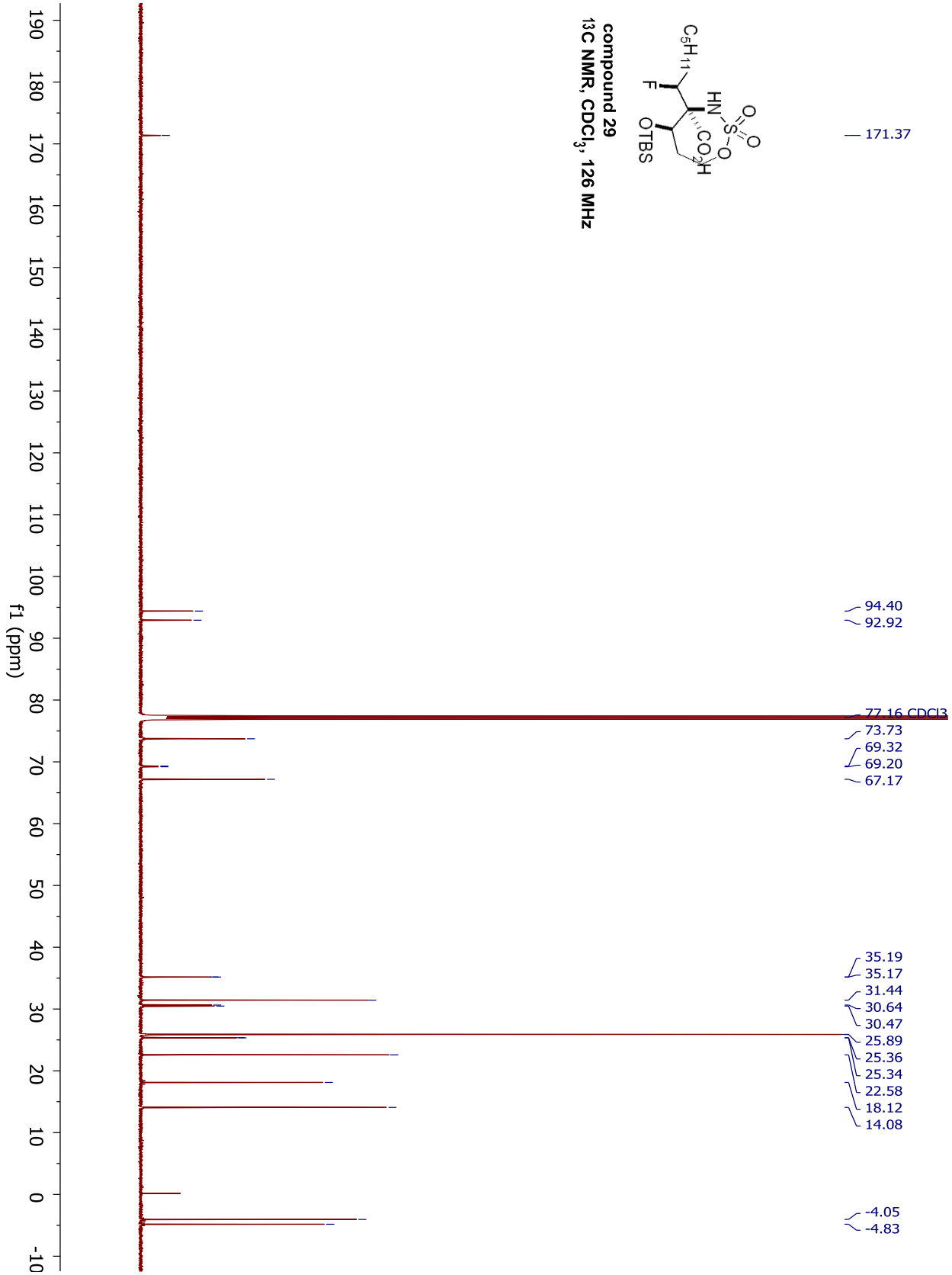
^{19}F NMR for intermediate for the synthesis of compound 29.



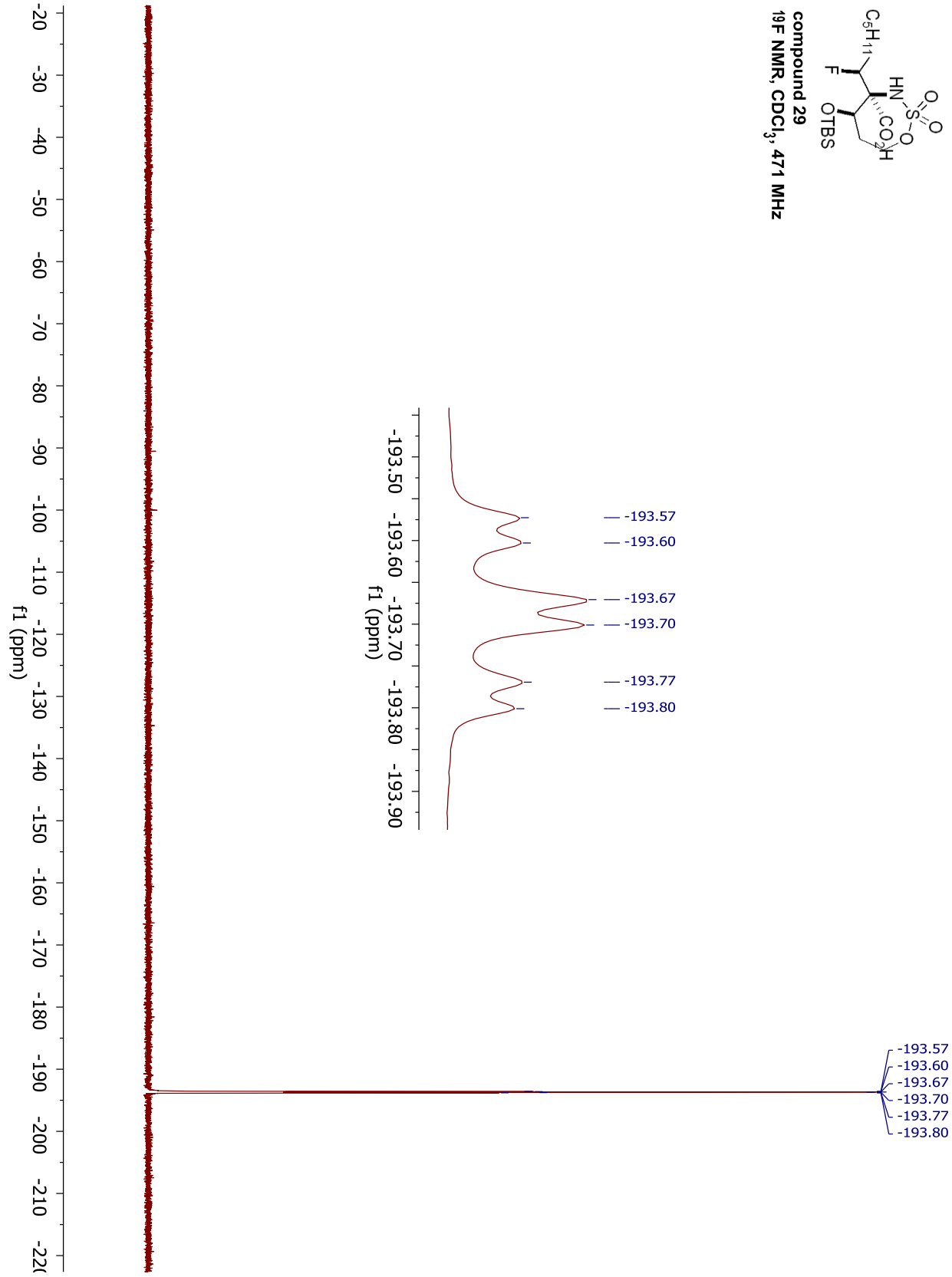
^{1}H NMR for compound 29.



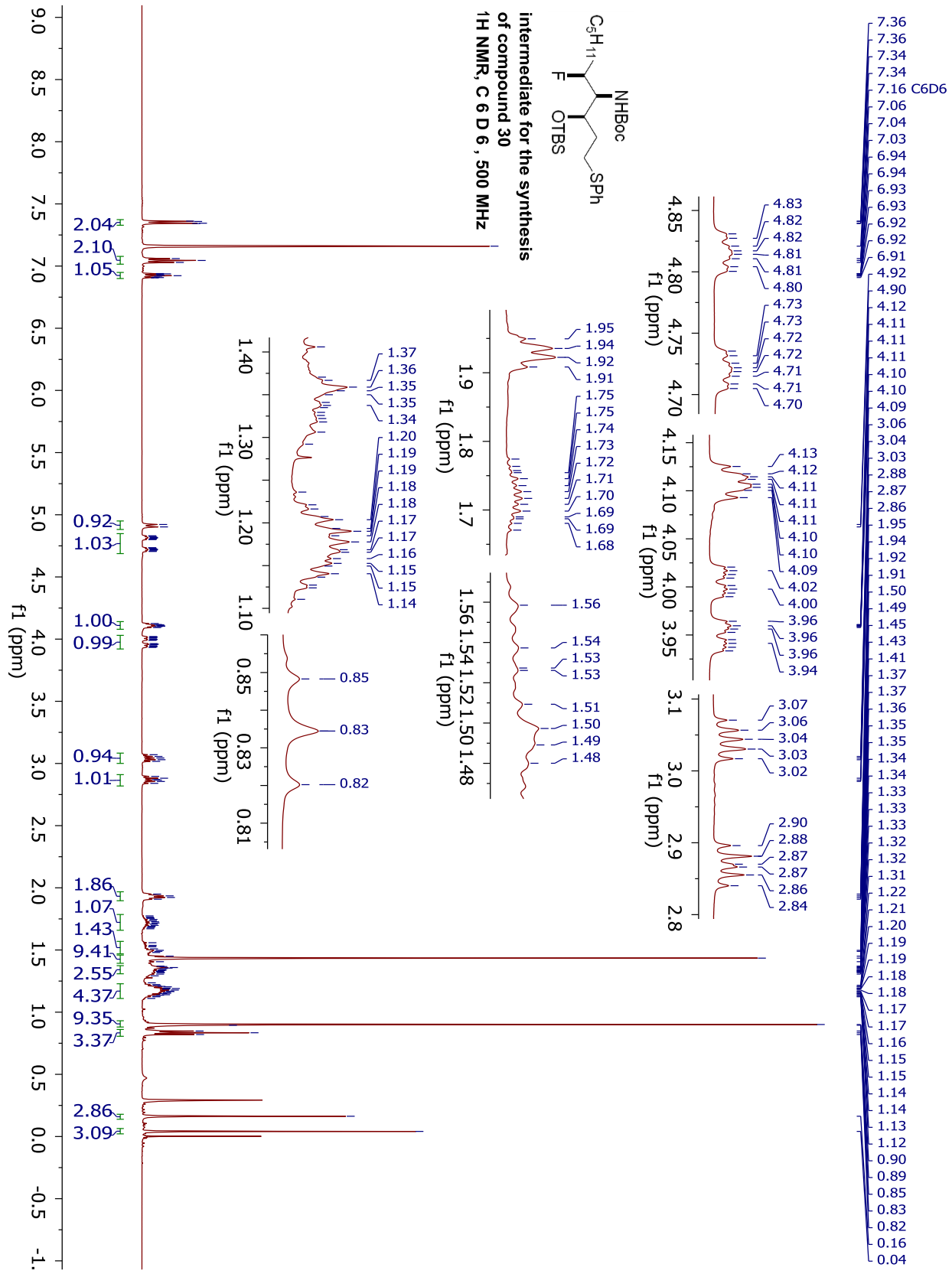
^{13}C NMR for compound 29.

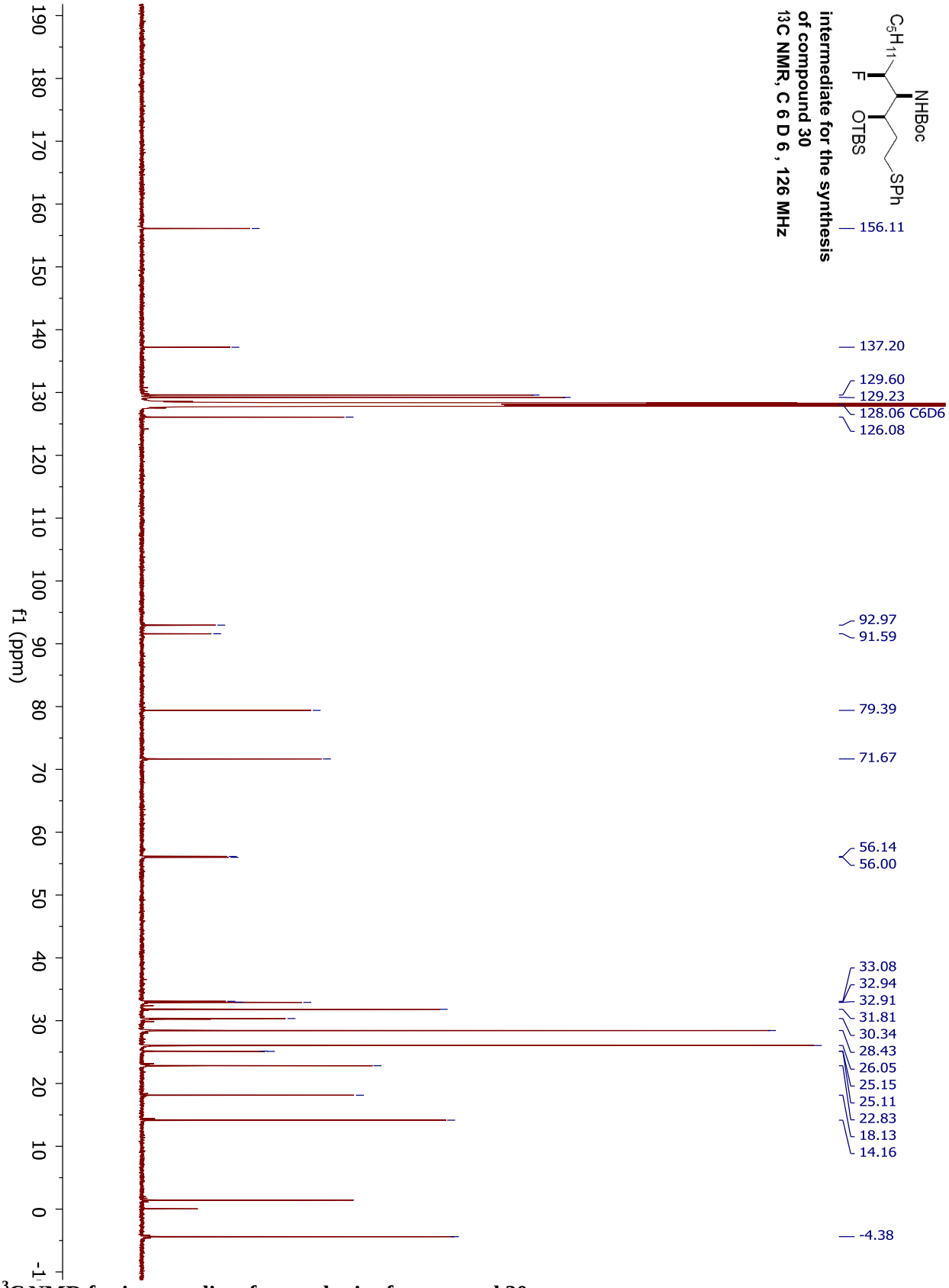


^{19}F NMR for compound 29.



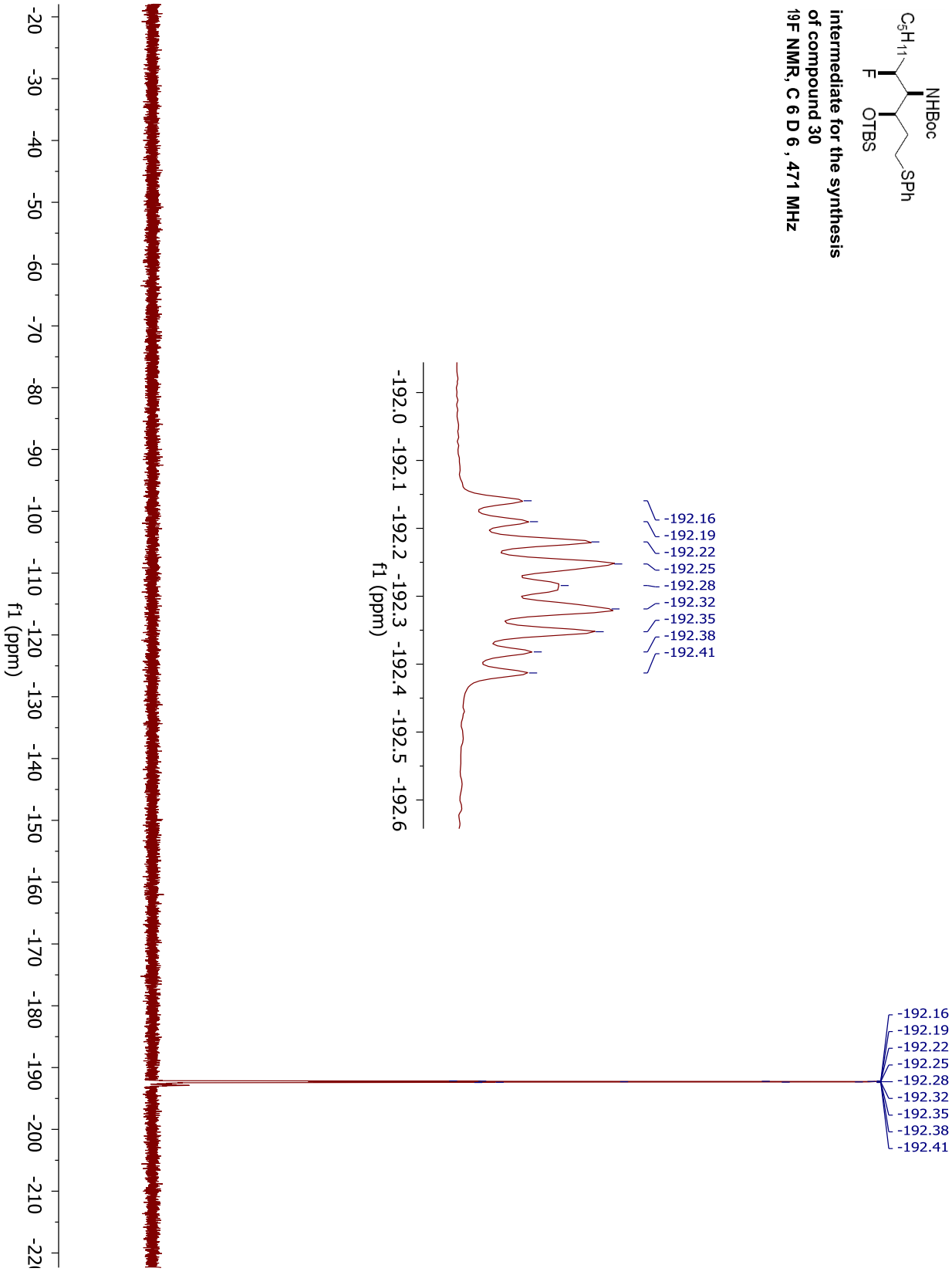
^{1}H NMR for intermediate for synthesis of compound 30.



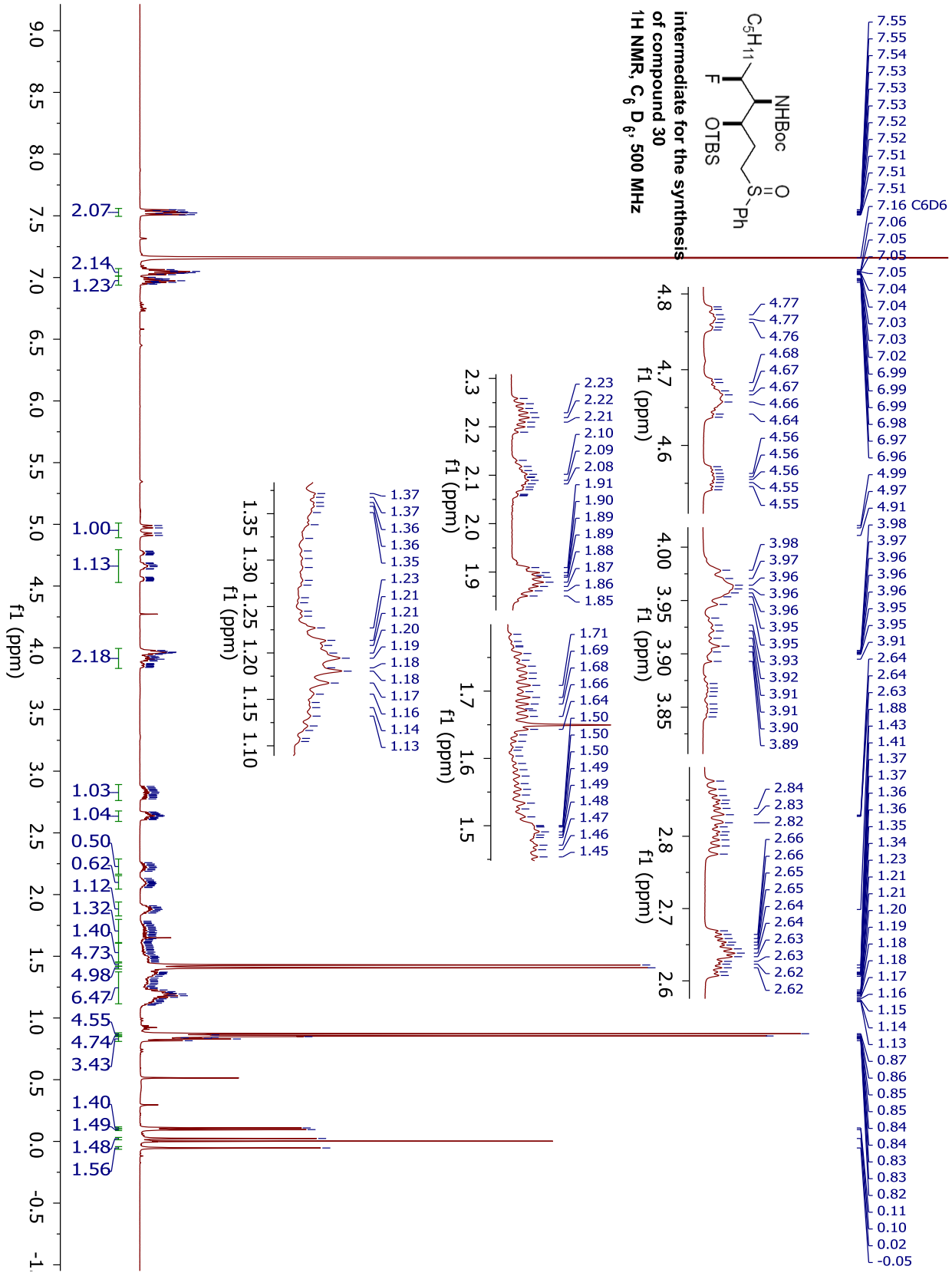


^{13}C NMR for intermediate for synthesis of compound 30.

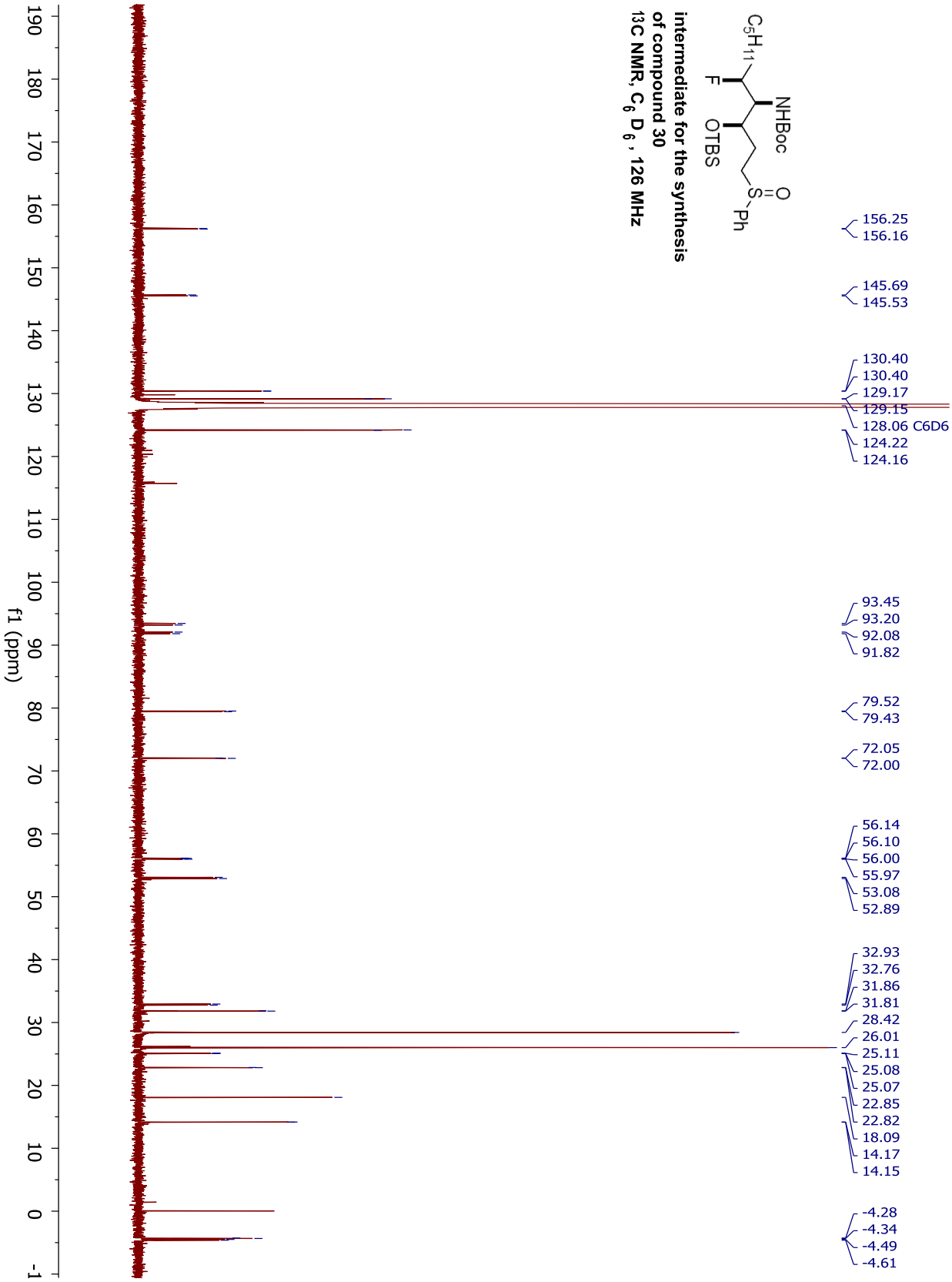
^{19}F NMR for intermediate for synthesis of compound 30.



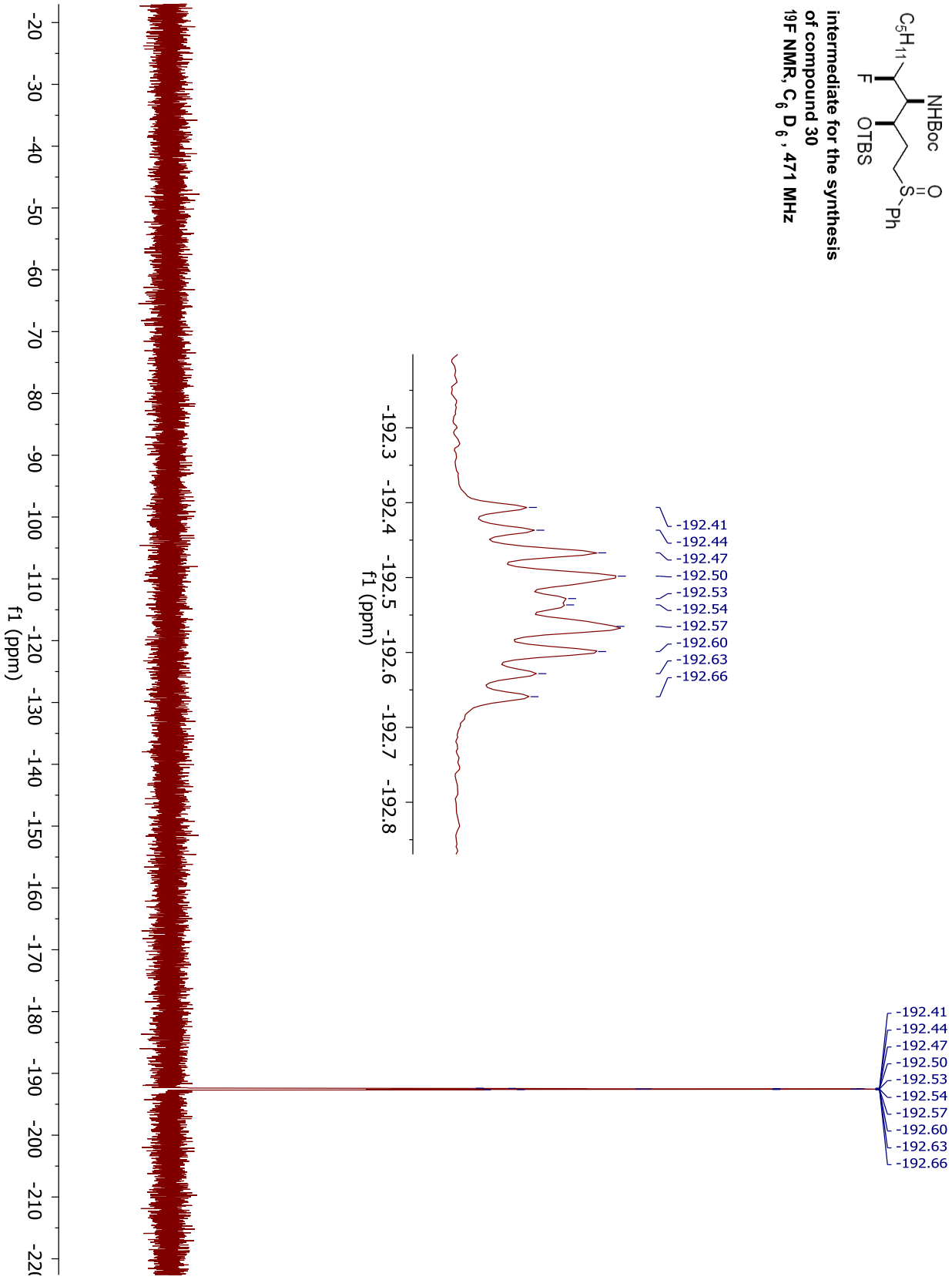
^{1}H NMR for intermediate for synthesis of compound 30.



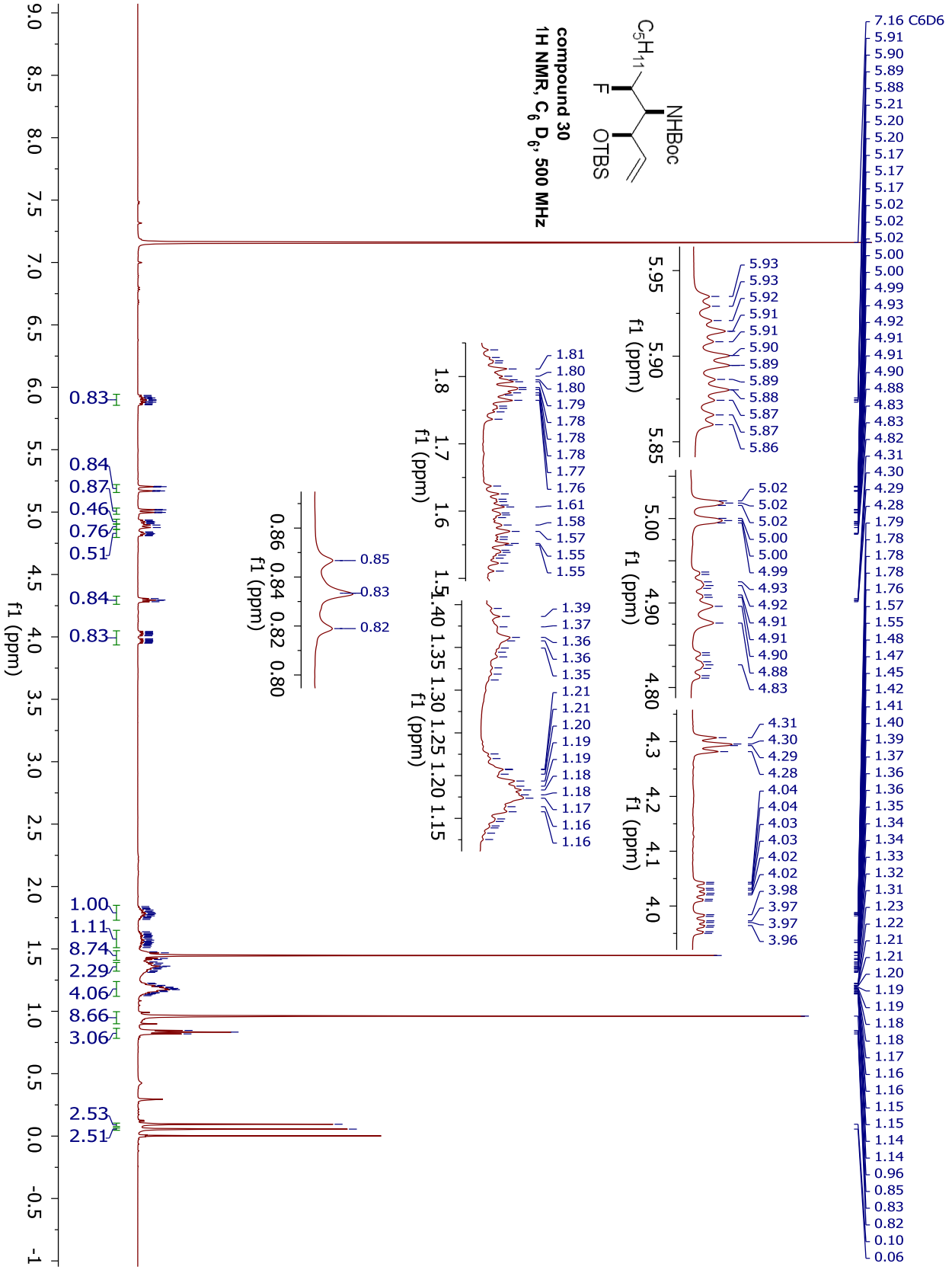
^{13}C NMR for intermediate for synthesis of compound 30.

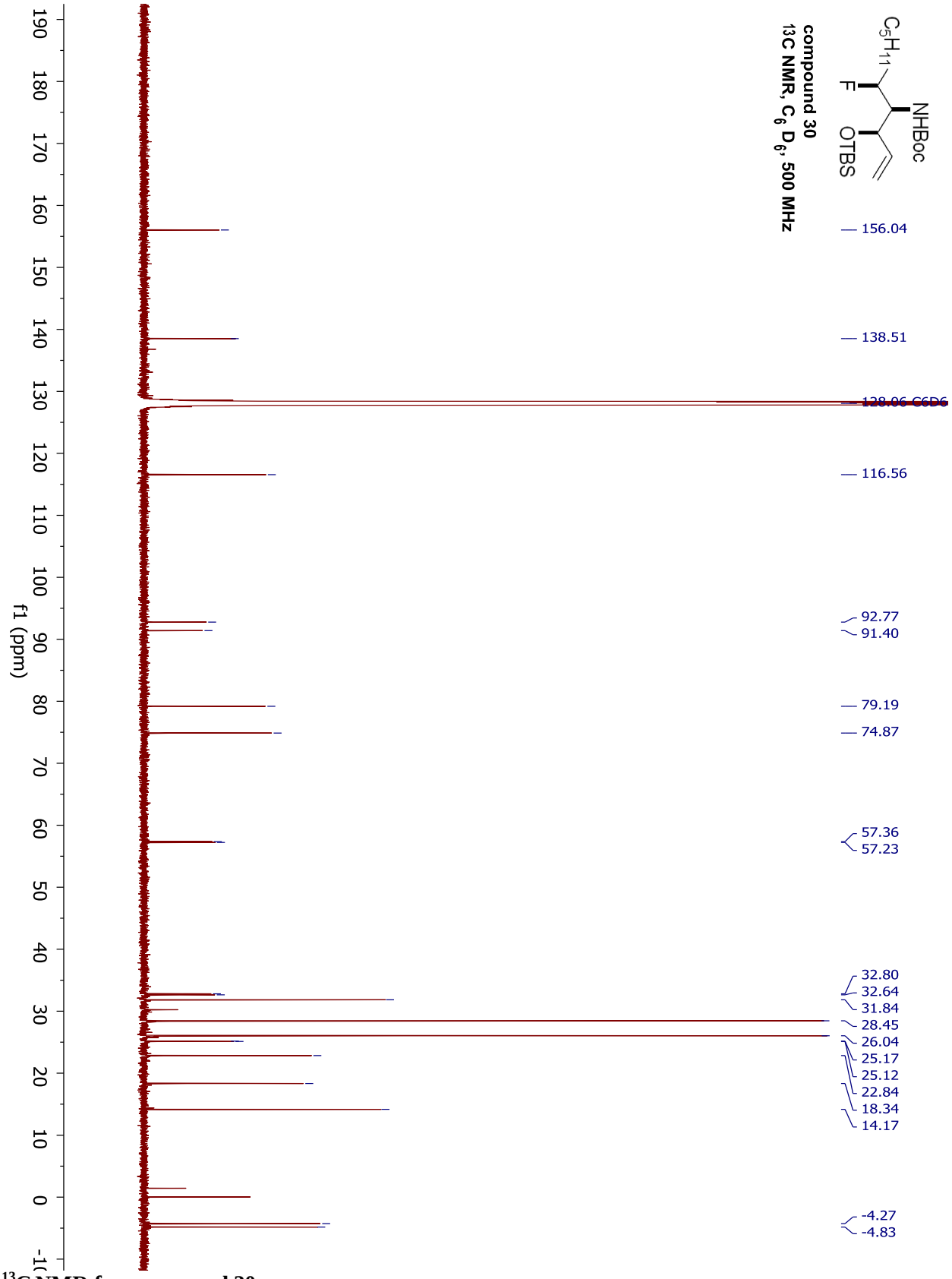


^{19}F NMR for compound intermediate for synthesis of compound 30.



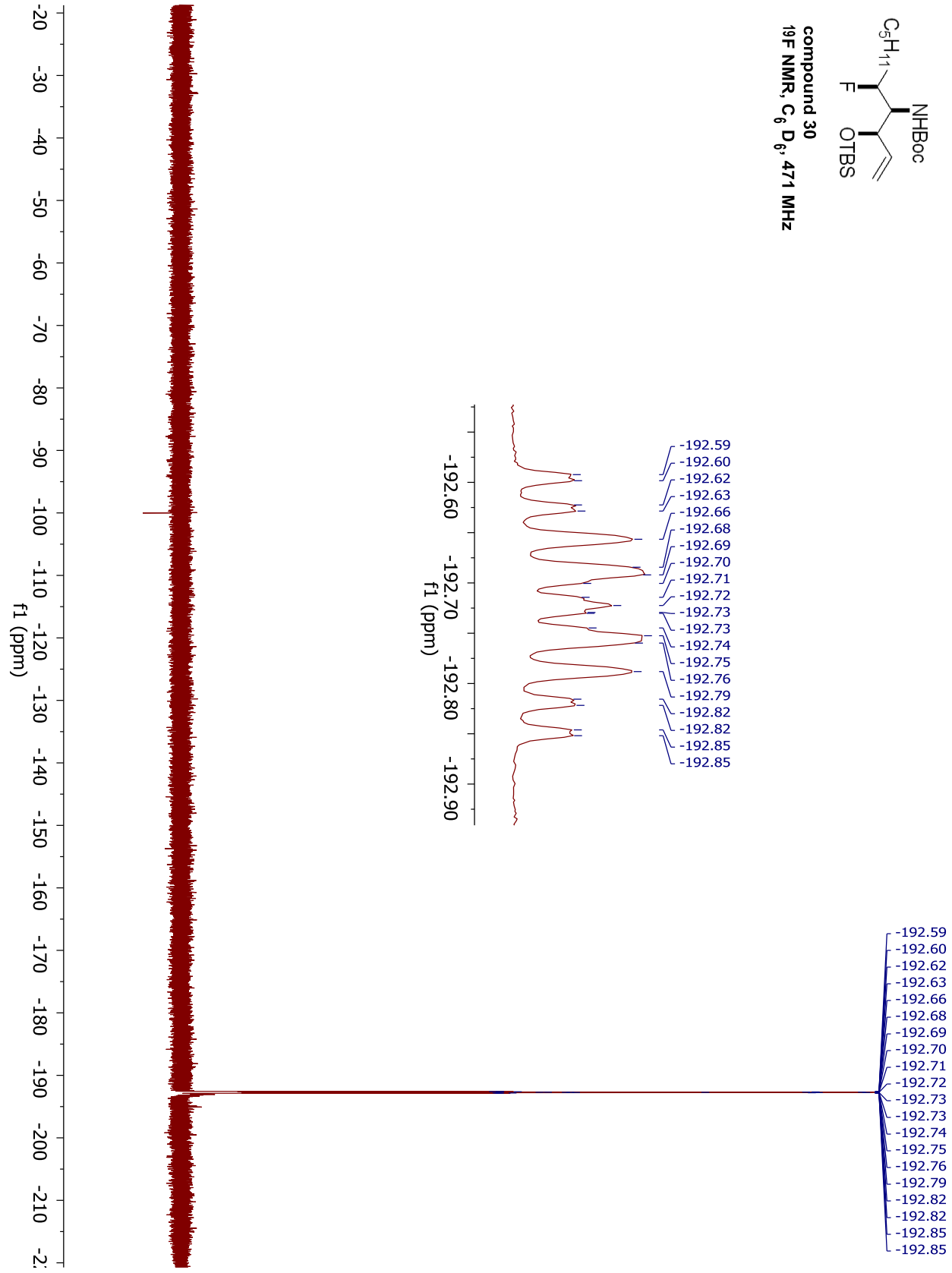
^{1}H NMR for compound 30.

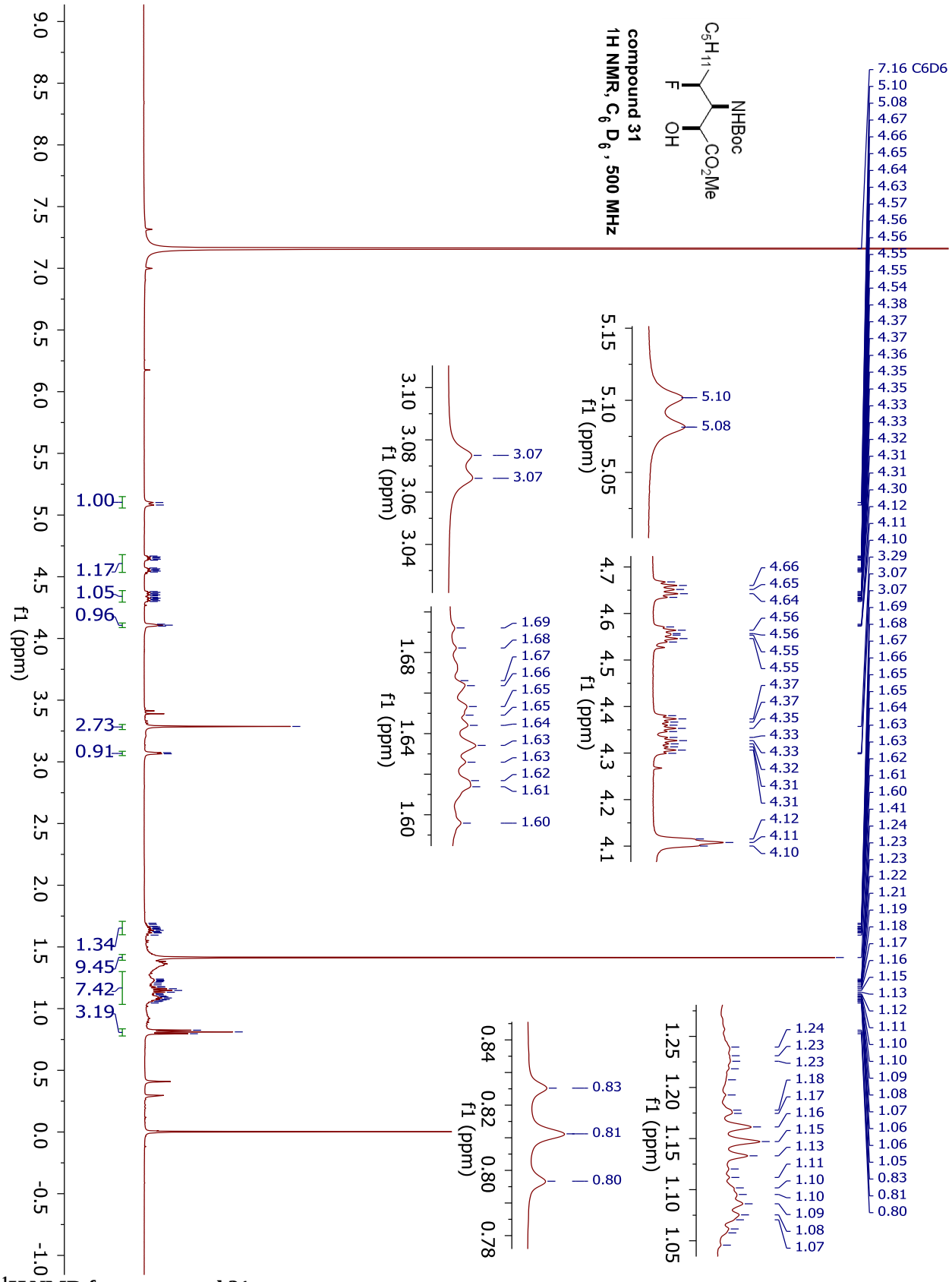




^{13}C NMR for compound 30.

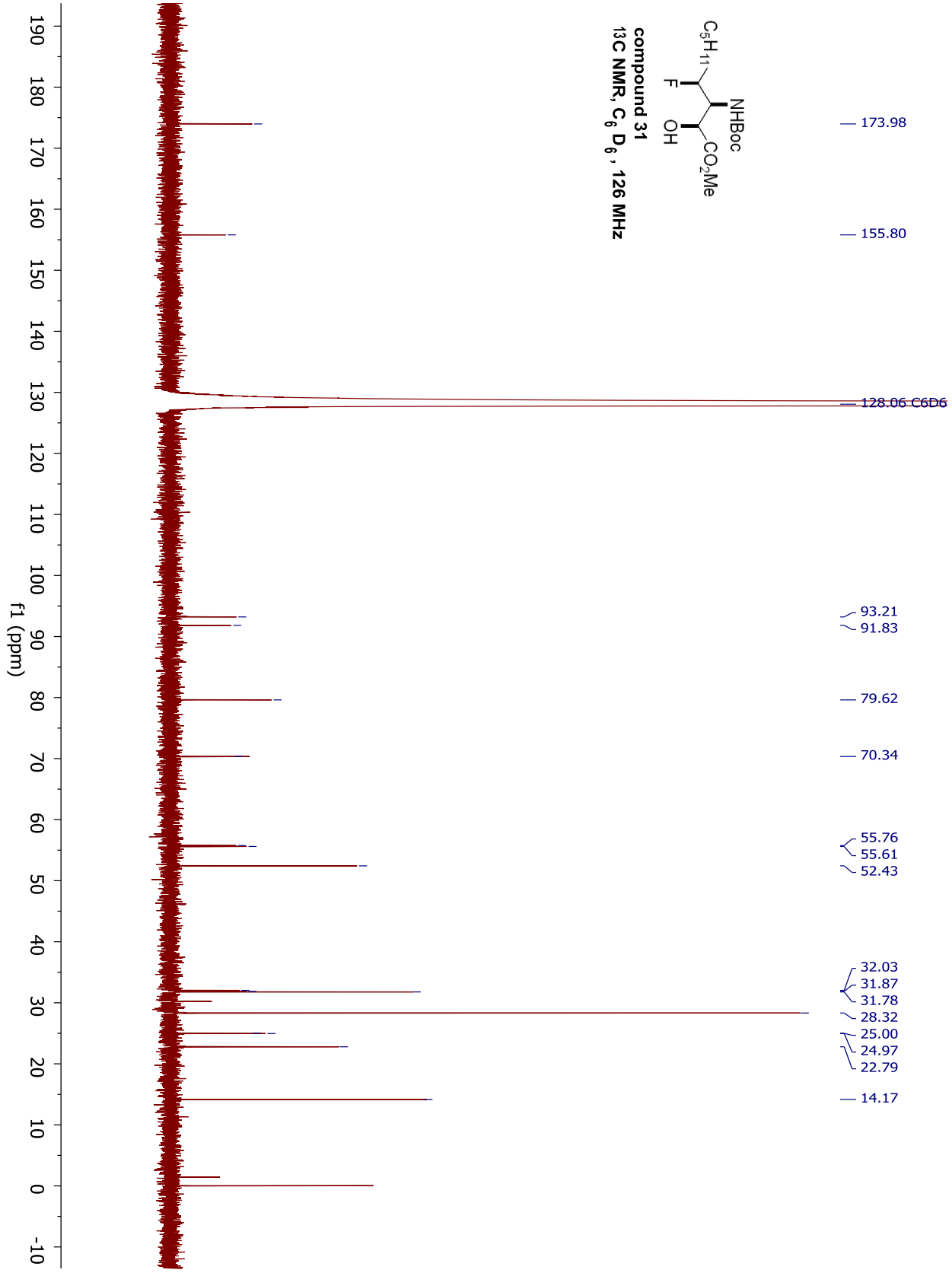
^{19}F NMR for compound 30.

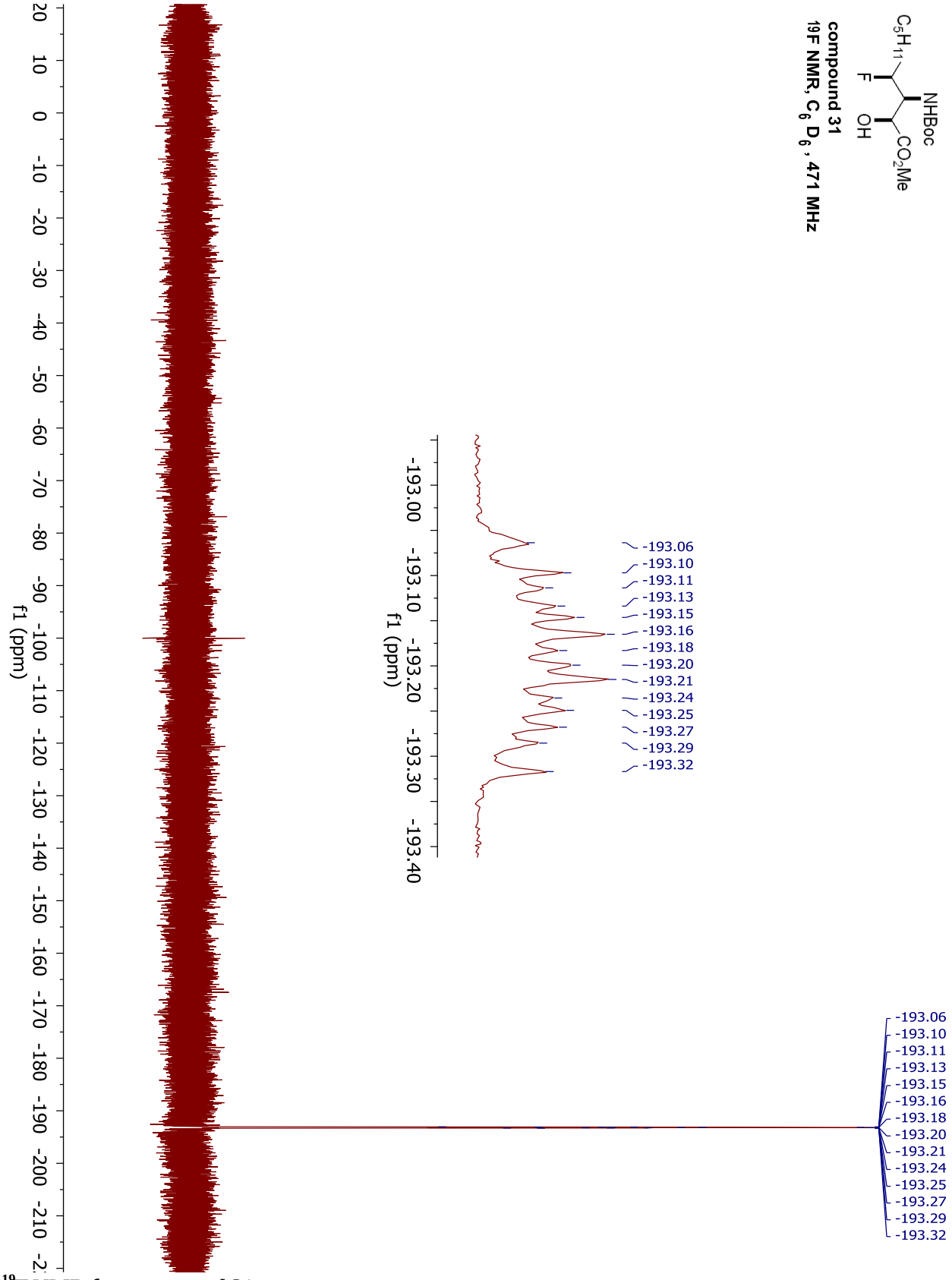




^{1}H NMR for compound 31.

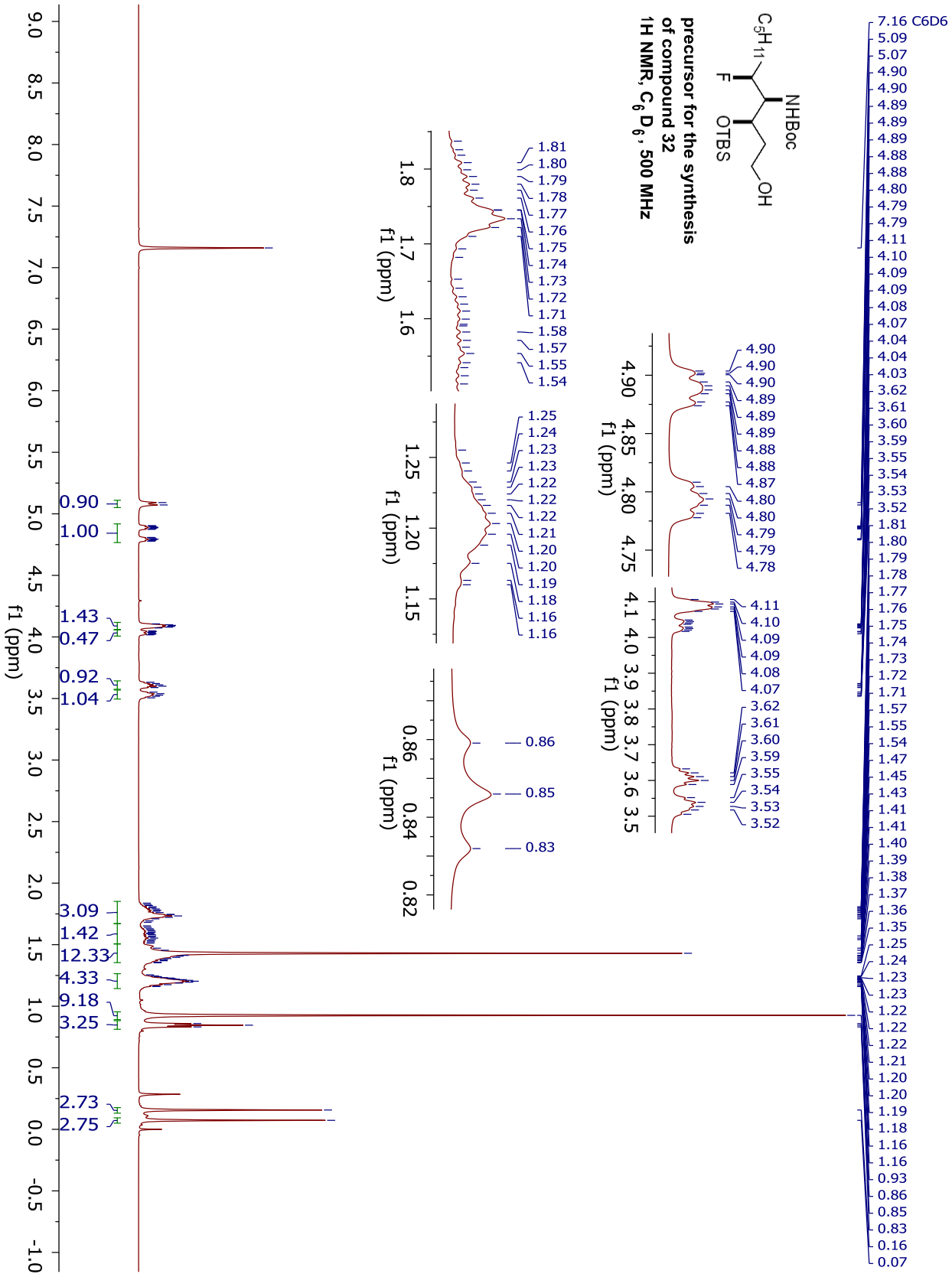
^{13}C NMR for compound 31.



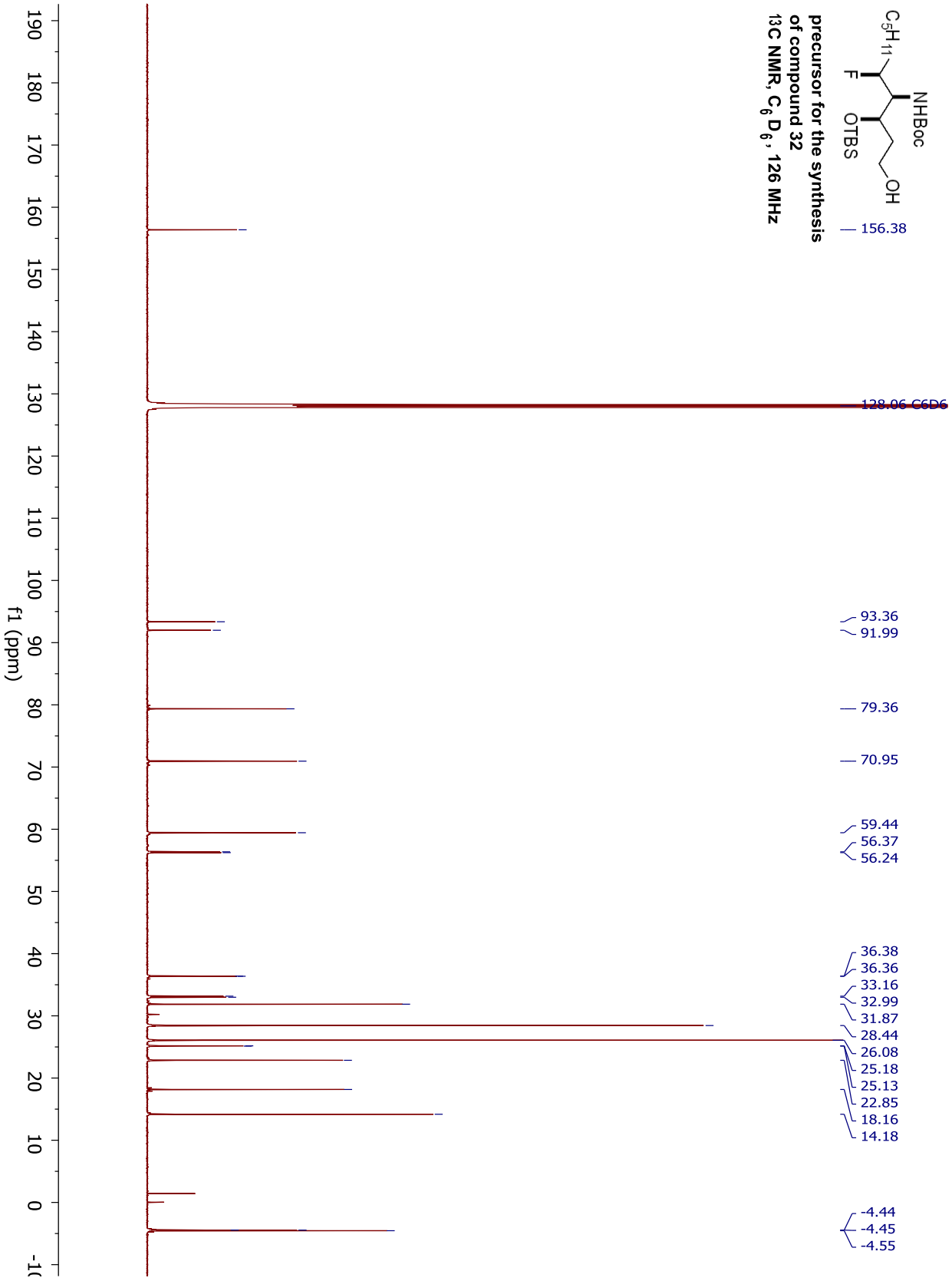


^{19}F NMR for compound 31.

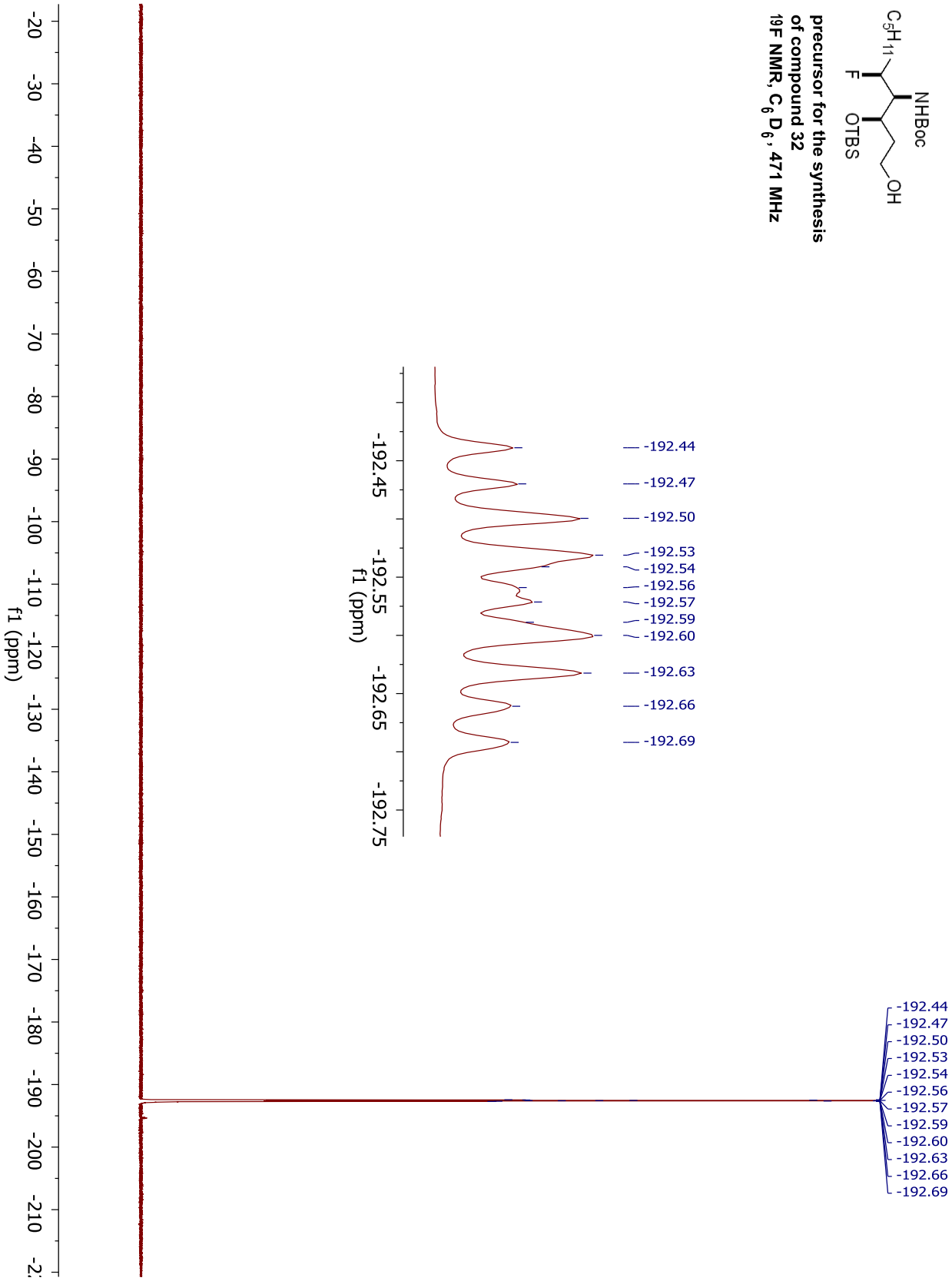
^{1}H NMR for precursor to compound 32.

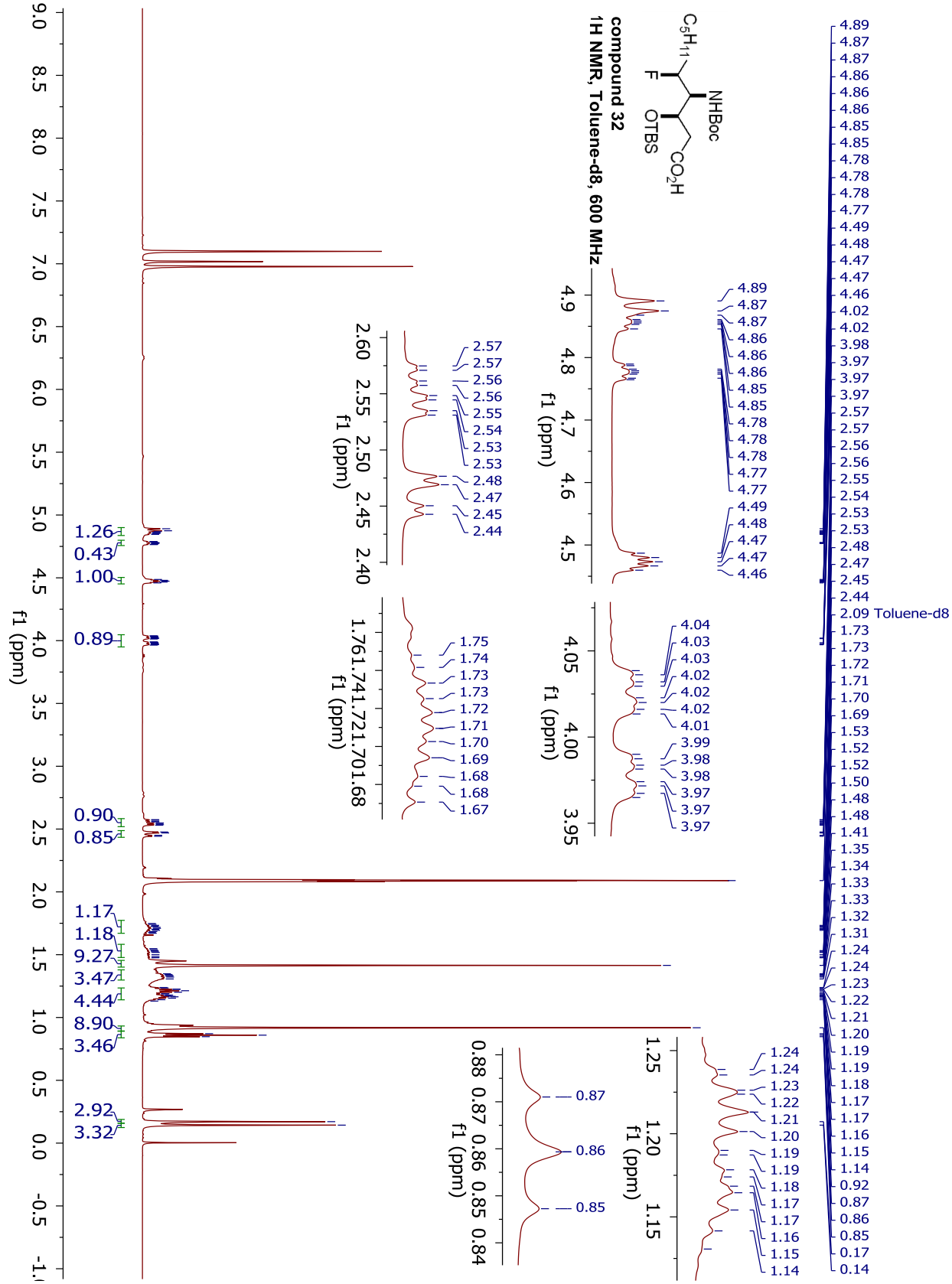


^{13}C NMR for precursor to compound 32.

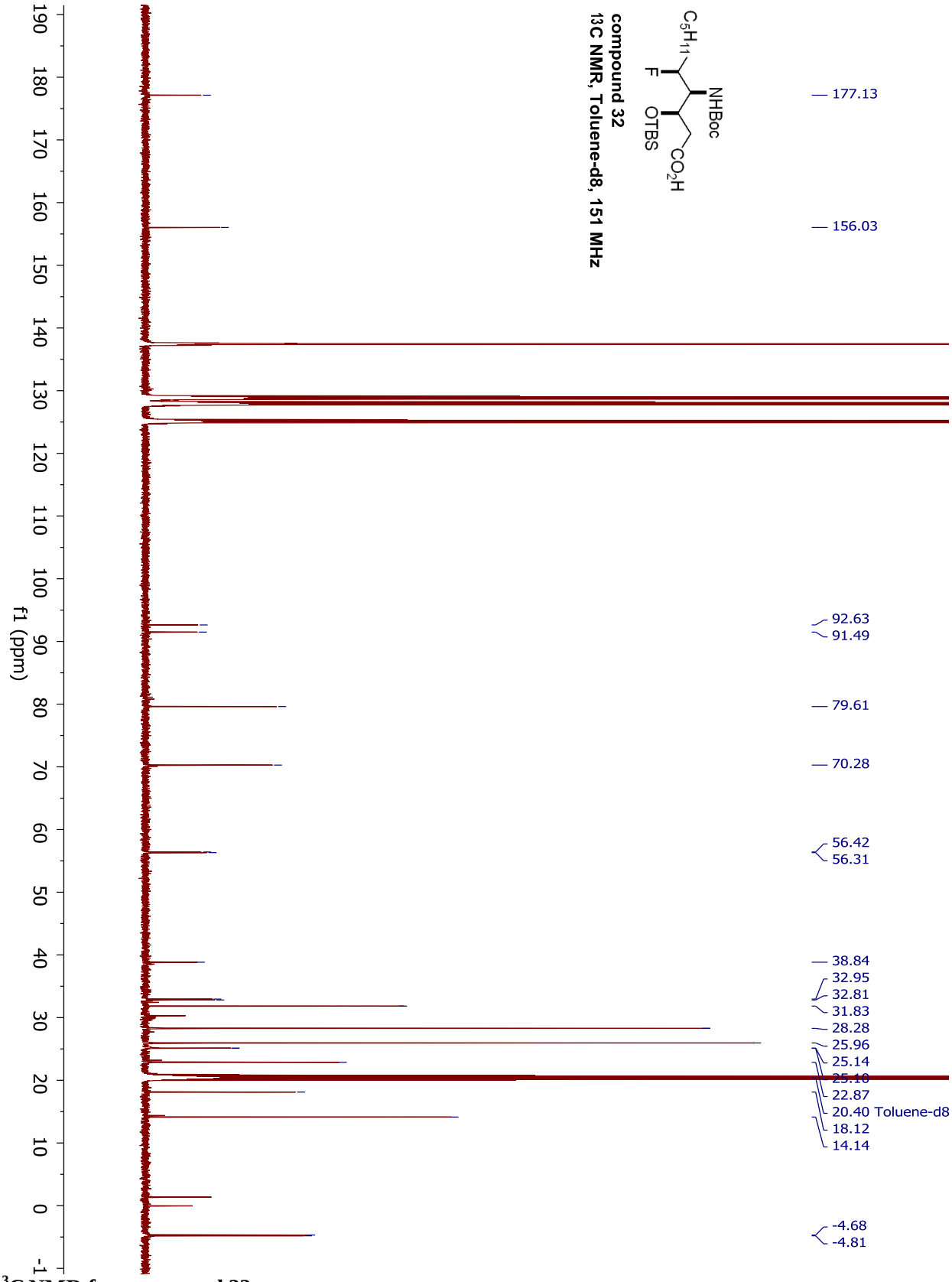


^{19}F NMR for precursor to compound 32.



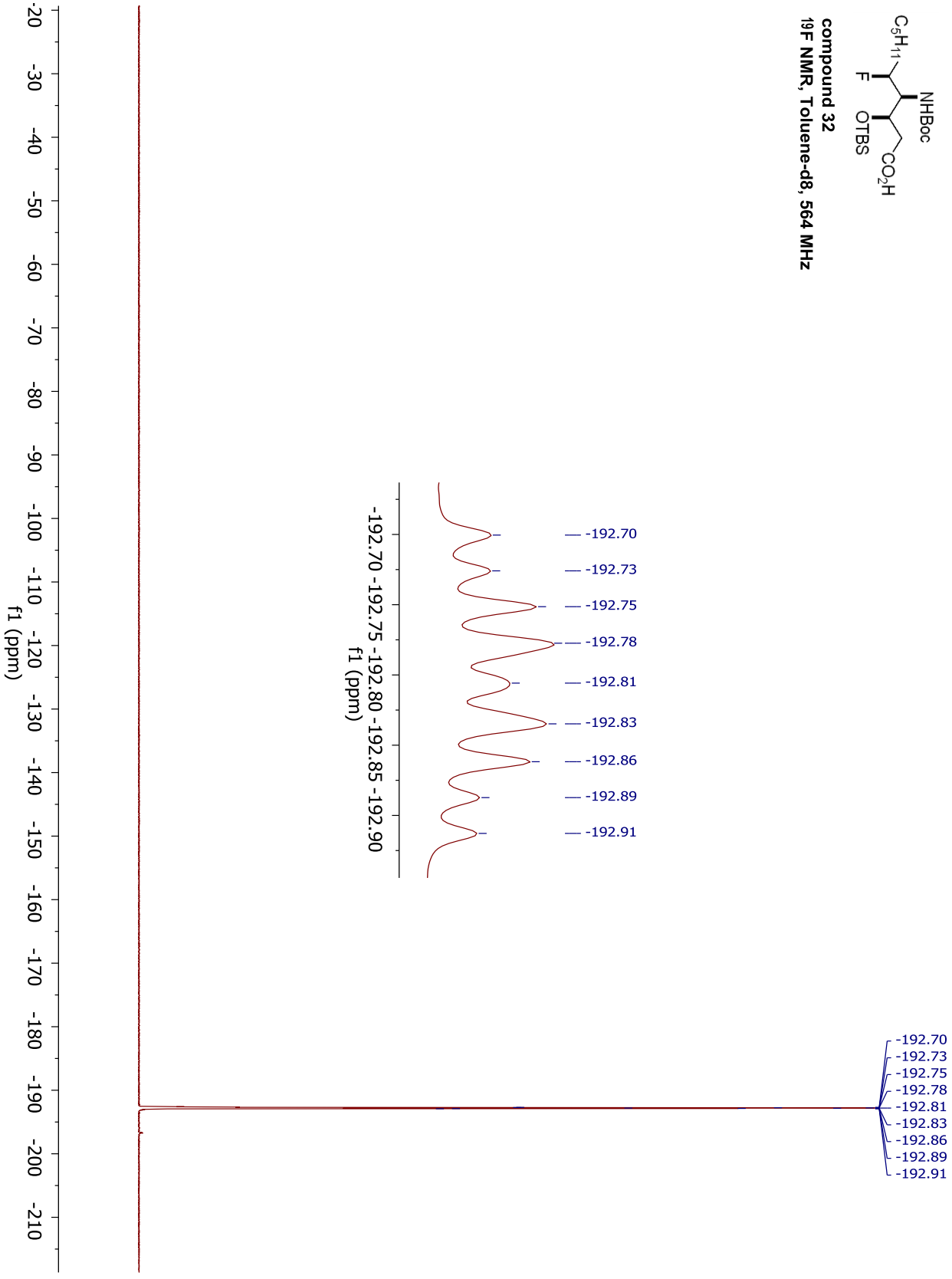


^{1}H NMR for compound 32.



^{13}C NMR for compound 32.

^{19}F NMR for compound 32.



VII. X-ray Crystallographic Data.

Crystallographic Experimental Section for 7a. CCDC number 1548236

Data Collection. A colorless crystal with approximate dimensions 0.40 x 0.30 x 0.20 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.[1]

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about the ω axis. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 9724 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.79 Å. A total of 60494 data were harvested by collecting 4 sets of frames with 0.5º scans in ω and φ with exposure times of 40 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[2]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and *P*1. The *E*-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement.[2-4]

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms (except those attached to N atoms) were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

There are four symmetry-independent diastereomers in the asymmetric unit. The chiral centers C7, C10, and C11 in molecules Si1 and Si1a are *S,R,R,* whereas in molecules Si1b and Si1c/d/e the configurations are *R,S,S.*

There is positional disorder in two parts of molecule Si1c/d/e. The $SiMe_2{}^tBu$ group is disordered over three positions in a 55.9(2) : 32.1(2) : 12.0(2) ratio. The n-butyl section of the 1-fluorohexyl is disordered over two positions with the major component occupancy of 74.5(10)%. The disordered parts were refined with restraints and constraints.

The crystal selected for the single-crystal X-ray diffraction experiment proved to be a non-merohedral twin with a 41.68(9)% second component contribution. The twin components are related by a 180.0° rotation about the a axis.

The final least-squares refinement of 1061 parameters against 17804 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0498 and 0.1337, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{16}H_{34}FNO_4SSi$ (*M* =383.59 g/mol): triclinic, space group P-1 (no. 2), *a* = 14.494(5) Å, *b* = 15.866(5) Å, *c* = 18.793(9) Å, α = 96.478(14)°, β = 90.043(10)°, γ = 90.052(18)°, *V* = 4294(3) $Å^3$, *Z* = 8, *T* = 100.01 K, μ(MoKα) = 0.233 mm^{-1}, *Dcalc* = 1.187 g/cm^3, 60494 reflections measured (2.18° ≤ 2Θ ≤ 53.212°), 17804 unique (R_{int} = 0.0584, R_{sigma} = 0.0680) which were used in all calculations. The final R_1 was 0.0498 (I > 2σ(I)) and wR_2 was 0.1337 (all data).

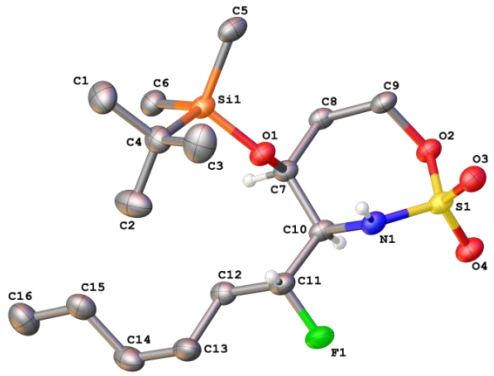


Figure S-1. A molecular drawing of the Si1 diastereomer in **7a** shown with 50% probability ellipsoids. Among the H atoms, only H atoms on the chiral C atoms and N atom are shown.

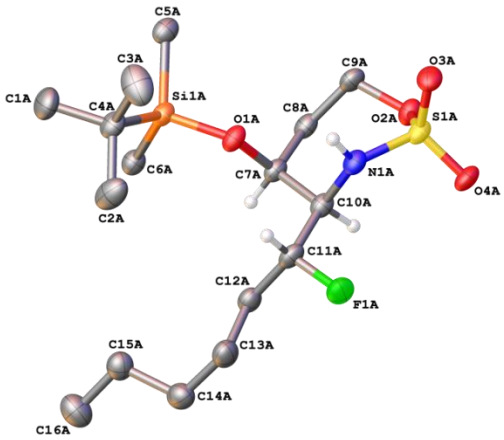


Figure S-2. A molecular drawing of the Si1a diastereomer in **7a** shown with 50% probability ellipsoids. Among the H atoms, only H atoms on the chiral C atoms and N atom are shown.

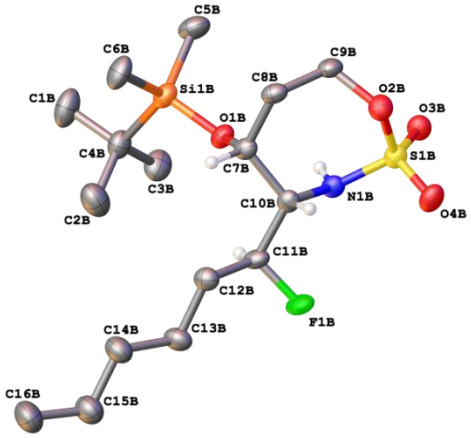


Figure S-3. A molecular drawing of the Si1b diastereomer in **7a** shown with 50% probability ellipsoids. Among the H atoms, only H atoms on the chiral C atoms and N atom are shown.

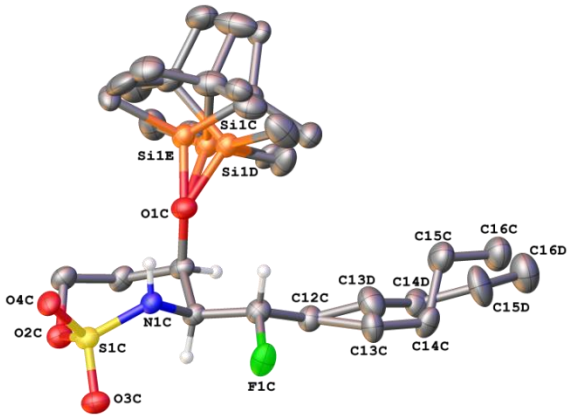


Figure S-4. A molecular drawing of the Si1c/d/e diastereomer in **7a** shown with 50% probability ellipsoids. All positions of the disordered atoms in the $SiMe_2{}^tBu$ group and n-Bu fragments are shown. Among the H atoms, only H atoms on the chiral C atoms and N atom are shown.

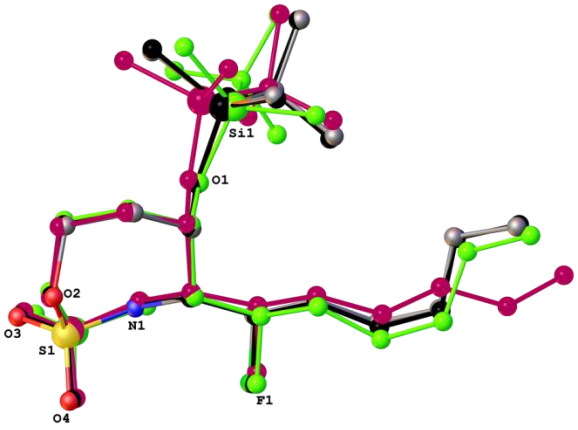


Figure S-5. A molecular drawing showing all diastereomers in **7a** superimposed. For the Si1c/d/e molecule only the major disorder component, Si1a was chosen. Note that molecules Si1b and Si1c/d/e had to be inverted due to their opposite absolute configuration. All H atoms are omitted.

Table S-1. Crystal data and structure refinement for 7a.

Identification code	**7a**
Empirical formula	$C_{16}H_{34}FNO_4SSi$
Formula weight	383.59
Temperature/K	100.01
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	14.494(5)
b/Å	15.866(5)
c/Å	18.793(9)
α/°	96.478(14)
β/°	90.043(10)
γ/°	90.052(18)
Volume/Å^3	4294(3)
Z	8
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	0.233
F(000)	1664.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.18 to 53.212
Index ranges	$-18 \le h \le 18$, $-19 \le k \le 19$, $-23 \le l \le 23$
Reflections collected	60494
Independent reflections	17804 [R_{int} = 0.0584, R_{sigma} = 0.0680]
Data/restraints/parameters	17804/278/1061
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0498, wR_2 = 0.1246
Final R indexes [all data]	R_1 = 0.0690, wR_2 = 0.1337
Largest diff. peak/hole / e Å^{-3}	0.47/-0.65

Table S-2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	10315.4(6)	5623.0(6)	6427.4(4)	26.15(19)
Si1	7780.2(7)	2955.5(6)	6571.4(5)	27.2(2)
O1	8715.6(16)	3524.6(14)	6428.2(11)	27.5(5)
C1	7338(3)	1479(3)	7177(2)	46.5(11)
C2	8834(3)	1468(3)	6546(2)	51.6(12)
C3	8667(4)	2335(3)	7734(2)	54.9(12)

C4	8179(3)	2022(2)	7030.7(19)	35.4(9)
C5	6991(2)	3622(2)	7157.3(18)	34.2(9)
C6	7201(3)	2593(2)	5697.8(18)	33.6(8)
C7	8877(2)	3937(2)	5798.5(16)	24.7(7)
F1	11377.8(14)	3499.9(13)	5522.3(12)	39.2(5)
O2	9386.5(16)	5883.2(15)	6079.7(12)	27.4(5)
O3	10364.0(17)	5960.7(15)	7165.8(12)	31.0(5)
O4	10989.2(17)	5887.6(16)	5949.0(13)	32.4(6)
N1	10264(2)	4617.9(18)	6396.5(14)	25.5(6)
C8	8291(2)	4730(2)	5777.4(17)	24.8(7)
C9	8535(2)	5488(2)	6308.7(18)	28.3(8)
C10	9915(2)	4081(2)	5757.7(17)	24.9(7)
C11	10460(2)	3264(2)	5674.0(19)	30.0(8)
C12	10122(2)	2608(2)	5093.1(18)	29.3(8)
C13	10722(3)	1823(2)	4983(2)	39.2(9)
C14	10371(3)	1189(2)	4370(2)	43(1)
C15	9407(3)	824(2)	4461(2)	37.4(9)
C16	9101(3)	183(3)	3834(2)	53.5(12)
S1A	10378.3(6)	4552.6(6)	8604.5(4)	26.60(19)
Si1A	7732.0(7)	7078.5(6)	8425.8(5)	25.8(2)
F1A	11297.9(14)	6699.1(13)	9620.2(11)	38.4(5)
O1A	8681.7(16)	6546.0(15)	8591.2(12)	27.1(5)
O2A	9450.1(16)	4214.4(15)	8900.8(12)	29.5(6)
O3A	10479.8(18)	4243.1(15)	7869.9(12)	32.8(6)
O4A	11041.7(17)	4321.0(16)	9110.2(13)	30.9(6)
N1A	10268(2)	5557.9(18)	8655.6(15)	27.2(6)
C1A	7279(3)	8539(3)	7795(2)	45.5(10)
C2A	8788(3)	8584(3)	8447(2)	49.8(11)
C3A	8594(4)	7713(3)	7258(2)	57.0(13)
C4A	8116(3)	8016(2)	7965.8(18)	31.6(8)
C5A	6938(3)	6385(2)	7836.7(18)	32.0(8)
C6A	7151(2)	7441(2)	9286.1(18)	30.3(8)
C7A	8827(2)	6125(2)	9214.0(18)	25.6(7)
C8A	8291(3)	5285(2)	9179.1(18)	28.1(8)
C9A	8591(2)	4566(2)	8652.5(19)	29.1(8)
C10A	9879(2)	6032(2)	9293.2(18)	26.5(7)
C11A	10384(2)	6886(2)	9435.5(19)	29.3(8)
C12A	9986(3)	7491(2)	10028.7(19)	30.8(8)
C13A	10557(3)	8293(2)	10213(2)	39.4(9)
C14A	10126(3)	8917(2)	10790(2)	39.4(9)
C15A	9221(3)	9299(2)	10579(2)	38.3(9)
C16A	8847(3)	9946(3)	11153(2)	51.0(11)

S1B	4938.4(6)	4500.5(5)	6301.7(4)	27.34(19)
Si1B	3190.5(7)	7449.9(6)	7134.3(5)	31.6(2)
F1B	6594.4(13)	6347.3(14)	5890.8(12)	38.1(5)
O1B	3955.6(16)	6797.7(15)	6740.7(12)	27.7(5)
O2B	4002.1(17)	4429.7(15)	5872.3(13)	31.2(6)
O3B	4825.6(17)	4160.5(14)	6966.4(12)	30.7(5)
O4B	5581.3(18)	4119.4(16)	5793.0(13)	34.0(6)
N1B	5155(2)	5491.2(18)	6485.4(15)	25.7(6)
C1B	3202(3)	8952(3)	8066(2)	53.7(12)
C2B	4436(3)	8830(3)	7143(2)	55.1(12)
C3B	4533(3)	7998(3)	8183(2)	45.6(10)
C4B	3872(3)	8345(2)	7650.7(19)	36.9(8)
C5B	2499(3)	6864(3)	7747(2)	44.7(10)
C6B	2417(3)	7863(3)	6450(2)	44.9(10)
C7B	4024(2)	6432(2)	6003.6(17)	26.4(8)
C8B	3261(2)	5780(2)	5794.8(18)	28.6(8)
C9B	3255(2)	4978(2)	6160.2(19)	29.8(8)
C10B	4996(2)	6073(2)	5938.4(18)	25.4(7)
C11B	5743(2)	6759(2)	6024.7(19)	29.1(8)
C12B	5652(2)	7437(2)	5524.2(19)	30.5(8)
C13B	6443(3)	8084(2)	5583(2)	35.9(9)
C14B	6211(3)	8867(2)	5227(2)	41.7(9)
C15B	6979(3)	9517(3)	5232(2)	47.3(10)
C16B	6698(4)	10309(3)	4904(3)	62.0(13)
S1C	4824.4(6)	5550.1(5)	8691.7(4)	25.40(19)
Si1C	3221.9(14)	2314.6(12)	8156.4(11)	28.4(4)
O1C	3895.0(17)	3192.0(14)	8348.7(12)	31.5(6)
C1C	2902(8)	1203(5)	6926(5)	66(3)
C2C	3002(6)	2719(5)	6753(4)	47(2)
C3C	4433(5)	1984(5)	7020(4)	48(2)
C4C	3388(4)	2040(4)	7175(3)	45.3(16)
C5C	3662(6)	1466(6)	8665(6)	45(3)
C6C	1976(4)	2496(5)	8379(4)	45.5(18)
C7C	4056(2)	3569(2)	9060.8(16)	27.1(8)
Si1E	3161(4)	2577(4)	7883(4)	28.4(4)
C1E	3160(15)	1015(11)	7030(14)	32(4)
C2E	4360(17)	2038(15)	6755(10)	34(3)
C3E	4513(15)	1305(13)	7859(11)	36(4)
C4E	3835(9)	1693(7)	7363(7)	33(3)
C5E	2364(11)	2134(11)	8510(9)	34(3)
C6E	2484(12)	3185(11)	7257(8)	33(6)
Si1D	3651(2)	2193(2)	7990.3(18)	28.4(4)

C1D	2393(10)	1457(7)	6937(7)	53(3)
C2D	1763(7)	2480(9)	7868(7)	63(3)
C3D	2742(12)	3033(8)	6956(8)	58(4)
C4D	2621(6)	2286(6)	7396(5)	46(2)
C5D	4640(7)	1727(8)	7475(7)	58(3)
C6D	3344(10)	1528(10)	8724(8)	34(3)
F1C	6624.4(14)	3847.0(13)	9051.3(12)	38.9(5)
O2C	3913.1(17)	5574.1(15)	9143.3(12)	28.6(5)
O3C	5473.7(17)	5985.9(15)	9176.2(12)	31.0(6)
O4C	4646.5(18)	5860.6(14)	8021.6(12)	29.0(5)
N1C	5075(2)	4567.8(17)	8518.8(14)	23.3(6)
C8C	3293(2)	4180(2)	9306.6(18)	28.8(8)
C9C	3182(3)	4957(2)	8914.7(19)	30.2(8)
C10C	5021(2)	3991(2)	9078.3(18)	23.2(7)
C11C	5801(2)	3364(2)	8959.3(19)	28.9(8)
C12C	5836(3)	2679(2)	9455.5(19)	30.7(8)
C13C	6739(5)	2180(4)	9389(5)	37.1(19)
C14C	6756(4)	1380(4)	9763(4)	35.4(15)
C15C	6173(4)	654(4)	9402(3)	47.8(17)
C16C	6223(6)	-147(4)	9773(4)	54.9(18)
C13D	6484(16)	1979(12)	9237(14)	47(7)
C14D	6353(14)	1281(11)	9713(11)	37(5)
C15D	6980(13)	549(9)	9507(10)	57(6)
C16D	6754(19)	-235(13)	9857(15)	65(6)

Table S-3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 7a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	22.4(4)	35.7(5)	21.9(4)	9.9(3)	0.3(3)	-2.0(4)
Si1	24.8(5)	34.4(5)	23.5(5)	9.0(4)	1.6(4)	-2.7(4)
O1	25.3(12)	35.5(13)	23.5(12)	11.7(10)	-0.2(10)	-2.4(10)
C1	59(3)	40(2)	42(2)	13.8(19)	9(2)	-6(2)
C2	59(3)	49(3)	52(3)	26(2)	20(2)	20(2)
C3	68(3)	55(3)	47(3)	27(2)	-15(2)	-4(2)
C4	42(2)	33(2)	33(2)	12.1(16)	5.0(18)	-0.1(17)
C5	25.7(19)	51(2)	27.0(19)	7.6(17)	-1.2(15)	-4.9(17)
C6	33(2)	36(2)	33(2)	8.4(16)	2.0(17)	-4.5(17)
C7	23.5(17)	31.7(18)	19.9(17)	8.0(14)	2.2(14)	0.5(14)
F1	24.6(11)	43.0(12)	50.9(13)	9.6(10)	4.2(9)	2.1(9)
O2	23.4(13)	34.0(13)	26.6(13)	11.1(10)	-1.9(10)	-2.1(10)
O3	32.1(13)	39.6(14)	21.7(11)	5.8(10)	-1.3(10)	-2.8(11)
O4	28.2(13)	43.2(14)	27.7(13)	12.2(11)	3.8(10)	-3.6(11)

N1	23.9(14)	34.5(16)	19.7(14)	9.3(12)	-1.7(12)	-2.1(12)
C8	21.2(17)	33.9(18)	20.6(16)	9.2(14)	-1.5(14)	0.6(14)
C9	20.7(18)	38(2)	28.4(19)	12.1(15)	2.3(14)	-1.3(15)
C10	20.6(17)	35.8(19)	19.9(16)	10.4(14)	-0.7(13)	-0.3(14)
C11	25.2(18)	33.6(18)	33.0(19)	11.7(15)	4.4(15)	1.0(15)
C12	30.0(19)	30.9(18)	29.2(18)	12.1(14)	4.3(15)	2.6(15)
C13	32(2)	34(2)	52(2)	9.4(18)	9.1(18)	6.3(16)
C14	48(2)	36(2)	46(2)	11.2(18)	19(2)	9.5(18)
C15	41(2)	35(2)	37(2)	8.9(16)	0.9(17)	11.1(17)
C16	61(3)	40(2)	59(3)	3(2)	-1(2)	10(2)
S1A	24.2(4)	36.8(5)	20.2(4)	9.4(3)	0.0(3)	3.4(4)
Si1A	23.4(5)	32.8(5)	22.9(5)	10.3(4)	0.2(4)	1.1(4)
F1A	26.2(11)	42.5(12)	46.1(13)	3.9(10)	-5.2(9)	-1.6(9)
O1A	22.6(12)	36.8(13)	24.5(12)	15(1)	1.9(10)	1.4(10)
O2A	25.6(13)	34.7(13)	30.2(13)	11.7(11)	1.1(10)	2.5(10)
O3A	41.5(15)	38.9(13)	18.5(11)	5.4(10)	1.6(10)	6.6(11)
O4A	25.1(13)	44.1(15)	25.2(12)	10.8(11)	-4.9(10)	4.9(11)
N1A	28.0(15)	34.0(15)	21.5(14)	11.0(12)	1.2(12)	2.1(13)
C1A	51(3)	42(2)	47(2)	18.3(19)	-6(2)	7(2)
C2A	49(3)	49(3)	56(3)	28(2)	-13(2)	-16(2)
C3A	80(4)	48(3)	47(3)	21(2)	30(3)	6(2)
C4A	32(2)	38(2)	27.3(19)	13.9(15)	0.7(16)	0.2(16)
C5A	27.8(19)	43(2)	26.6(18)	7.4(16)	1.8(15)	2.6(16)
C6A	28.3(19)	33.6(19)	30.2(19)	7.9(15)	-0.7(15)	1.4(16)
C7A	21.0(17)	32.9(18)	23.9(17)	8.2(14)	-1.1(14)	0.5(14)
C8A	24.1(18)	35.6(19)	26.5(17)	12.2(15)	-1.9(15)	0.8(15)
C9A	21.1(18)	36(2)	30.8(19)	7.8(16)	-4.8(15)	-2.9(15)
C10A	22.8(18)	33.8(18)	24.3(17)	9.3(14)	1.3(14)	0.9(14)
C11A	20.1(17)	38.8(19)	30.8(18)	12.0(15)	-4.2(14)	-3.2(15)
C12A	26.2(18)	32.2(19)	34.8(19)	7.1(15)	-4.2(15)	-0.2(15)
C13A	31(2)	39(2)	48(2)	5.3(18)	-5.8(17)	1.2(17)
C14A	45(2)	33(2)	40(2)	5.4(16)	-5.8(18)	-4.2(17)
C15A	34(2)	37(2)	44(2)	6.3(17)	0.6(17)	-0.3(17)
C16A	58(3)	41(2)	54(3)	2(2)	10(2)	-1(2)
S1B	30.2(5)	31.9(5)	20.9(4)	7.5(3)	0.0(4)	3.6(4)
Si1B	29.0(5)	38.0(5)	28.7(5)	8.4(4)	-0.1(4)	9.1(4)
F1B	19.3(10)	50.3(13)	47.9(13)	18.6(10)	-0.3(9)	3.7(9)
O1B	27.2(13)	34.1(13)	22.3(12)	5.2(10)	-0.2(10)	7.1(10)
O2B	34.2(14)	33.0(13)	26.4(13)	3.9(11)	-7.2(11)	0.9(11)
O3B	35.6(14)	33.3(13)	24.1(12)	7.5(10)	1.7(10)	2.4(11)
O4B	38.8(15)	40.1(14)	23.6(13)	5.6(11)	5.3(11)	12.0(12)
N1B	26.7(16)	32.4(15)	19.3(14)	8.4(12)	0.5(12)	2.4(13)

C1B	68(3)	48(2)	43(2)	-2.8(19)	-3(2)	26(2)
C2B	70(3)	41(2)	54(3)	8(2)	6(2)	-6(2)
C3B	46(2)	42(2)	47(2)	-4.8(18)	-11(2)	2.5(19)
C4B	41(2)	35(2)	34.6(19)	2.7(16)	0.7(16)	8.6(17)
C5B	30(2)	61(3)	46(2)	13(2)	7.6(17)	4.1(19)
C6B	46(2)	47(2)	41(2)	5.2(18)	-5.9(18)	21.5(19)
C7B	24.6(18)	32.9(19)	23.4(18)	10.4(15)	-1.4(14)	2.2(15)
C8B	20.8(17)	41(2)	25.1(17)	8.6(15)	0.0(14)	1.0(15)
C9B	19.8(17)	35.4(19)	34.4(19)	4.7(15)	0.7(15)	-1.8(15)
C10B	28.7(18)	30.3(18)	18.6(16)	8.6(13)	1.5(14)	2.6(15)
C11B	18.9(17)	41(2)	29.5(19)	11.5(16)	-1.0(14)	0.4(15)
C12B	29.9(19)	35.6(19)	27.7(18)	10.2(15)	-2.4(14)	-1.0(15)
C13B	33(2)	41(2)	36(2)	14.8(17)	-1.1(16)	-7.0(16)
C14B	41(2)	37(2)	48(2)	11.5(18)	-4.1(19)	-6.9(18)
C15B	47(2)	42(2)	55(3)	14.9(19)	0(2)	-4.2(19)
C16B	61(3)	39(2)	87(4)	16(2)	2(3)	-6(2)
S1C	28.4(5)	28.9(4)	20.0(4)	7.5(3)	0.9(3)	-3.2(4)
Si1C	28.7(11)	28.5(8)	29.3(10)	8.7(7)	-1.8(8)	-1.5(8)
O1C	35.7(14)	32.1(13)	26.6(13)	3.7(10)	-5.0(11)	-4.2(11)
C1C	96(8)	54(5)	45(5)	-2(4)	-8(5)	-33(5)
C2C	57(5)	56(5)	29(4)	9(3)	-5(3)	-11(4)
C3C	57(4)	50(5)	35(4)	-2(4)	1(3)	-6(3)
C4C	53(4)	50(4)	33(3)	6(3)	-2(3)	-15(3)
C5C	42(6)	38(5)	58(5)	23(4)	-12(4)	-6(4)
C6C	33(4)	37(4)	67(5)	5(4)	3(3)	-3(3)
C7C	29.7(19)	29.4(18)	23.3(17)	7.6(14)	-2.9(15)	-5.8(15)
Si1E	28.7(11)	28.5(8)	29.3(10)	8.7(7)	-1.8(8)	-1.5(8)
C1E	39(7)	30(6)	28(8)	10(5)	-7(6)	-1(5)
C2E	42(6)	31(6)	30(5)	2(4)	-1(5)	-6(5)
C3E	40(7)	36(8)	33(7)	5(6)	-4(6)	4(6)
C4E	36(5)	32(4)	32(5)	6(3)	-3(4)	0(4)
C5E	42(6)	31(6)	30(5)	2(4)	-1(5)	-6(5)
C6E	43(10)	34(10)	22(8)	1(7)	2(7)	12(8)
Si1D	28.7(11)	28.5(8)	29.3(10)	8.7(7)	-1.8(8)	-1.5(8)
C1D	55(7)	47(5)	55(6)	3(4)	-22(5)	-10(4)
C2D	55(4)	60(7)	73(6)	1(5)	-16(4)	0(4)
C3D	64(8)	56(6)	58(7)	16(5)	-39(5)	-14(5)
C4D	48(4)	41(4)	48(4)	6(3)	-24(3)	-5(3)
C5D	48(5)	47(7)	77(7)	-6(6)	17(5)	-5(4)
C6D	21(7)	41(7)	40(5)	15(5)	-9(4)	-8(5)
F1C	25.7(11)	43.4(12)	51.6(13)	22.4(10)	4.3(10)	-1.9(9)
O2C	26.1(13)	35.8(14)	24.0(12)	3.8(10)	4.6(10)	-1.6(11)

O3C	32.4(14)	36.0(13)	25.3(12)	6.2(10)	-1.6(11)	-9.6(11)
O4C	37.3(14)	32.0(12)	19.2(11)	8.9(9)	-0.6(10)	2.8(11)
N1C	24.9(15)	25.9(14)	20.2(14)	7.1(12)	0.3(12)	-1.0(12)
C8C	20.7(17)	38.1(19)	29.4(18)	11.6(15)	1.6(14)	-2.8(15)
C9C	23.2(17)	37(2)	30.9(18)	7.8(15)	-1.1(15)	-4.3(16)
C10C	23.0(17)	27.5(17)	20.3(16)	8.1(13)	0.9(13)	-3.7(14)
C11C	29.0(19)	33.4(19)	25.2(18)	7.8(15)	2.9(15)	-1.3(15)
C12C	32.6(19)	33.5(19)	27.1(18)	8.1(15)	2.8(15)	2.1(15)
C13C	38(3)	30(3)	45(4)	12(3)	7(3)	7(3)
C14C	23(3)	43(3)	43(3)	19(2)	1(3)	2(2)
C15C	52(4)	42(3)	52(3)	16(3)	-8(3)	3(3)
C16C	58(4)	43(3)	66(4)	16(3)	-8(4)	3(3)
C13D	63(13)	38(7)	41(10)	4(7)	9(10)	9(8)
C14D	36(11)	41(7)	34(8)	1(6)	7(9)	10(7)
C15D	61(12)	37(7)	72(11)	9(7)	24(9)	19(7)
C16D	70(15)	46(8)	82(15)	16(8)	4(13)	9(9)

Table S-4. Bond Lengths for 7a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.572(2)	O1B	C7B	1.444(4)
S1	O3	1.432(2)	O2B	C9B	1.456(4)
S1	O4	1.423(3)	N1B	C10B	1.475(4)
S1	N1	1.591(3)	C1B	C4B	1.521(5)
Si1	O1	1.667(2)	C2B	C4B	1.527(5)
Si1	C4	1.888(3)	C3B	C4B	1.530(5)
Si1	C5	1.839(4)	C7B	C8B	1.533(5)
Si1	C6	1.875(4)	C7B	C10B	1.521(5)
O1	C7	1.434(3)	C8B	C9B	1.513(5)
C1	C4	1.534(5)	C10B	C11B	1.529(5)
C2	C4	1.525(5)	C11B	C12B	1.513(5)
C3	C4	1.531(5)	C12B	C13B	1.534(5)
C7	C8	1.523(4)	C13B	C14B	1.512(5)
C7	C10	1.524(5)	C14B	C15B	1.516(5)
F1	C11	1.419(4)	C15B	C16B	1.517(5)
O2	C9	1.471(4)	S1C	O2C	1.569(3)
N1	C10	1.481(4)	S1C	O3C	1.431(3)
C8	C9	1.515(5)	S1C	O4C	1.426(2)
C10	C11	1.511(5)	S1C	N1C	1.598(3)
C11	C12	1.503(5)	Si1C	O1C	1.704(3)
C12	C13	1.515(5)	Si1C	C4C	1.862(5)
C13	C14	1.529(6)	Si1C	C5C	1.851(6)
C14	C15	1.529(6)	Si1C	C6C	1.870(6)

C15	C16	1.531(6)	O1C	C7C	1.422(3)
S1A	O2A	1.573(3)	O1C	Si1E	1.629(4)
S1A	O3A	1.420(2)	O1C	Si1D	1.688(4)
S1A	O4A	1.429(2)	C1C	C4C	1.528(7)
S1A	N1A	1.595(3)	C2C	C4C	1.517(7)
Si1A	O1A	1.663(2)	C3C	C4C	1.544(8)
Si1A	C4A	1.887(4)	C7C	C8C	1.510(5)
Si1A	C5A	1.866(4)	C7C	C10C	1.550(5)
Si1A	C6A	1.857(4)	Si1E	C4E	1.890(5)
F1A	C11A	1.409(4)	Si1E	C5E	1.845(6)
O1A	C7A	1.427(4)	Si1E	C6E	1.880(6)
O2A	C9A	1.462(4)	C1E	C4E	1.534(7)
N1A	C10A	1.456(4)	C2E	C4E	1.525(7)
C1A	C4A	1.525(5)	C3E	C4E	1.531(7)
C2A	C4A	1.546(5)	Si1D	C4D	1.880(7)
C3A	C4A	1.529(5)	Si1D	C5D	1.838(7)
C7A	C8A	1.538(5)	Si1D	C6D	1.882(8)
C7A	C10A	1.540(5)	C1D	C4D	1.525(8)
C8A	C9A	1.489(5)	C2D	C4D	1.538(9)
C10A	C11A	1.537(5)	C3D	C4D	1.530(9)
C11A	C12A	1.502(5)	F1C	C11C	1.418(4)
C12A	C13A	1.523(5)	O2C	C9C	1.473(4)
C13A	C14A	1.519(5)	N1C	C10C	1.471(4)
C14A	C15A	1.517(5)	C8C	C9C	1.514(5)
C15A	C16A	1.504(6)	C10C	C11C	1.507(5)
S1B	O2B	1.576(3)	C11C	C12C	1.510(5)
S1B	O3B	1.425(2)	C12C	C13C	1.529(7)
S1B	O4B	1.421(3)	C12C	C13D	1.479(15)
S1B	N1B	1.601(3)	C13C	C14C	1.520(6)
Si1B	O1B	1.636(2)	C14C	C15C	1.524(7)
Si1B	C4B	1.903(4)	C15C	C16C	1.519(8)
Si1B	C5B	1.853(4)	C13D	C14D	1.511(14)
Si1B	C6B	1.879(4)	C14D	C15D	1.491(14)
F1B	C11B	1.406(4)	C15D	C16D	1.508(14)

Table S-5. Bond Angles for 7a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	N1	104.78(14)	C1B	C4B	Si1B	108.8(3)
O3	S1	O2	110.92(14)	C1B	C4B	C2B	109.2(3)
O3	S1	N1	107.55(14)	C1B	C4B	C3B	108.6(3)
O4	S1	O2	102.43(13)	C2B	C4B	Si1B	111.0(3)
O4	S1	O3	118.34(16)	C2B	C4B	C3B	108.5(3)

O4	S1	N1	111.97(16)	C3B	C4B	Si1B	110.7(3)
O1	Si1	C4	106.97(15)	O1B	C7B	C8B	112.5(3)
O1	Si1	C5	108.50(15)	O1B	C7B	C10B	104.4(3)
O1	Si1	C6	109.88(14)	C10B	C7B	C8B	114.3(3)
C5	Si1	C4	110.21(17)	C9B	C8B	C7B	117.7(3)
C5	Si1	C6	110.17(17)	O2B	C9B	C8B	109.0(3)
C6	Si1	C4	111.02(17)	N1B	C10B	C7B	110.3(3)
C7	O1	Si1	124.9(2)	N1B	C10B	C11B	108.0(3)
C1	C4	Si1	108.9(3)	C7B	C10B	C11B	113.1(3)
C2	C4	Si1	110.3(2)	F1B	C11B	C10B	107.0(3)
C2	C4	C1	107.8(3)	F1B	C11B	C12B	108.3(3)
C2	C4	C3	109.7(4)	C12B	C11B	C10B	114.8(3)
C3	C4	Si1	110.0(3)	C11B	C12B	C13B	114.1(3)
C3	C4	C1	110.2(3)	C14B	C13B	C12B	112.2(3)
O1	C7	C8	112.6(3)	C13B	C14B	C15B	115.3(3)
O1	C7	C10	106.7(3)	C14B	C15B	C16B	113.3(4)
C8	C7	C10	114.9(3)	O2C	S1C	N1C	105.42(15)
C9	O2	S1	117.14(19)	O3C	S1C	O2C	103.20(14)
C10	N1	S1	121.9(2)	O3C	S1C	N1C	111.68(15)
C9	C8	C7	116.7(3)	O4C	S1C	O2C	109.63(15)
O2	C9	C8	109.6(3)	O4C	S1C	O3C	119.34(15)
N1	C10	C7	111.8(3)	O4C	S1C	N1C	106.72(14)
N1	C10	C11	108.3(3)	O1C	Si1C	C4C	103.3(2)
C11	C10	C7	113.0(3)	O1C	Si1C	C5C	108.5(4)
F1	C11	C10	105.6(3)	O1C	Si1C	C6C	113.8(3)
F1	C11	C12	109.6(3)	C4C	Si1C	C6C	111.1(3)
C12	C11	C10	114.9(3)	C5C	Si1C	C4C	111.3(4)
C11	C12	C13	113.8(3)	C5C	Si1C	C6C	108.7(4)
C12	C13	C14	111.9(3)	C7C	O1C	Si1C	122.6(2)
C13	C14	C15	116.4(3)	C7C	O1C	Si1E	140.8(3)
C14	C15	C16	113.8(3)	C7C	O1C	Si1D	133.3(2)
O2A	S1A	N1A	105.74(15)	C1C	C4C	Si1C	110.0(5)
O3A	S1A	O2A	109.83(15)	C1C	C4C	C3C	111.3(6)
O3A	S1A	O4A	119.33(15)	C2C	C4C	Si1C	111.7(5)
O3A	S1A	N1A	107.62(15)	C2C	C4C	C1C	108.3(6)
O4A	S1A	O2A	102.49(14)	C2C	C4C	C3C	107.0(6)
O4A	S1A	N1A	110.99(16)	C3C	C4C	Si1C	108.5(4)
O1A	Si1A	C4A	106.54(15)	O1C	C7C	C8C	110.8(3)
O1A	Si1A	C5A	110.04(15)	O1C	C7C	C10C	107.6(3)
O1A	Si1A	C6A	109.13(14)	C8C	C7C	C10C	113.2(3)
C5A	Si1A	C4A	110.63(16)	O1C	Si1E	C4E	107.7(4)
C6A	Si1A	C4A	110.49(17)	O1C	Si1E	C5E	108.3(5)

C6A	Si1A	C5A	109.95(17)
C7A	O1A	Si1A	124.8(2)
C9A	O2A	S1A	117.2(2)
C10A	N1A	S1A	120.6(2)
C1A	C4A	Si1A	109.7(3)
C1A	C4A	C2A	109.1(3)
C1A	C4A	C3A	107.7(3)
C2A	C4A	Si1A	110.8(2)
C3A	C4A	Si1A	110.2(3)
C3A	C4A	C2A	109.2(4)
O1A	C7A	C8A	112.0(3)
O1A	C7A	C10A	106.5(3)
C8A	C7A	C10A	114.3(3)
C9A	C8A	C7A	118.4(3)
O2A	C9A	C8A	109.2(3)
N1A	C10A	C7A	110.6(3)
N1A	C10A	C11A	108.8(3)
C11A	C10A	C7A	113.3(3)
F1A	C11A	C10A	106.5(3)
F1A	C11A	C12A	108.3(3)
C12A	C11A	C10A	115.0(3)
C11A	C12A	C13A	114.0(3)
C14A	C13A	C12A	113.5(3)
C15A	C14A	C13A	114.7(3)
C16A	C15A	C14A	112.7(3)
O2B	S1B	N1B	106.85(15)
O3B	S1B	O2B	109.74(15)
O3B	S1B	N1B	107.03(15)
O4B	S1B	O2B	102.73(15)
O4B	S1B	O3B	119.39(15)
O4B	S1B	N1B	110.47(16)
O1B	Si1B	C4B	106.06(15)
O1B	Si1B	C5B	108.17(16)
O1B	Si1B	C6B	110.31(15)
C5B	Si1B	C4B	111.16(18)
C5B	Si1B	C6B	109.92(19)
C6B	Si1B	C4B	111.12(18)
C7B	O1B	Si1B	130.3(2)
C9B	O2B	S1B	116.5(2)
C10B	N1B	S1B	119.7(2)
O1C	Si1E	C6E	111.0(5)
C5E	Si1E	C4E	109.9(5)
C5E	Si1E	C6E	109.4(5)
C6E	Si1E	C4E	110.5(5)
C1E	C4E	Si1E	109.1(6)
C2E	C4E	Si1E	109.7(6)
C2E	C4E	C1E	107.8(7)
C2E	C4E	C3E	109.8(7)
C3E	C4E	Si1E	110.1(6)
C3E	C4E	C1E	110.3(7)
O1C	Si1D	C4D	105.6(3)
O1C	Si1D	C5D	110.6(4)
O1C	Si1D	C6D	109.6(6)
C4D	Si1D	C6D	109.6(5)
C5D	Si1D	C4D	111.1(5)
C5D	Si1D	C6D	110.2(6)
C1D	C4D	Si1D	112.7(7)
C1D	C4D	C2D	104.9(8)
C1D	C4D	C3D	112.9(8)
C2D	C4D	Si1D	109.0(7)
C3D	C4D	Si1D	110.3(7)
C3D	C4D	C2D	106.7(9)
C9C	O2C	S1C	118.2(2)
C10C	N1C	S1C	120.9(2)
C7C	C8C	C9C	117.4(3)
O2C	C9C	C8C	109.4(3)
N1C	C10C	C7C	109.6(3)
N1C	C10C	C11C	107.9(3)
C11C	C10C	C7C	113.4(3)
F1C	C11C	C10C	105.9(3)
F1C	C11C	C12C	108.3(3)
C10C	C11C	C12C	116.3(3)
C11C	C12C	C13C	112.3(4)
C13D	C12C	C11C	114.9(9)
C14C	C13C	C12C	115.3(5)
C13C	C14C	C15C	114.4(5)
C16C	C15C	C14C	113.5(5)
C12C	C13D	C14D	109.5(14)
C15D	C14D	C13D	111.7(14)
C14D	C15D	C16D	114.3(16)

Table S-6. Hydrogen Bonds for 7a.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O3A	0.870(10)	2.13(2)	2.914(4)	149(4)
N1A	H1AA	O3	0.879(10)	2.098(16)	2.944(4)	162(4)
N1B	H1BA	O4C	0.880(10)	2.109(13)	2.974(4)	167(4)
N1C	H1C	O3B	0.878(10)	2.114(18)	2.938(4)	156(3)

Table S-7. Torsion Angles for 7a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	O2	C9	C8	-96.4(3)	O4B	S1B	O2B	C9B	-162.3(2)
S1	N1	C10	C7	-90.2(3)	O4B	S1B	N1B	C10B	69.3(3)
S1	N1	C10	C11	144.7(2)	N1B	S1B	O2B	C9B	-46.0(3)
Si1	O1	C7	C8	74.2(3)	N1B	C10B	C11B	F1B	62.7(3)
Si1	O1	C7	C10	-158.8(2)	N1B	C10B	C11B	C12B	-177.1(3)
O1	Si1	C4	C1	179.8(2)	C4B	Si1B	O1B	C7B	-130.0(3)
O1	Si1	C4	C2	-62.2(3)	C5B	Si1B	O1B	C7B	110.7(3)
O1	Si1	C4	C3	59.0(3)	C6B	Si1B	O1B	C7B	-9.5(3)
O1	C7	C8	C9	70.4(4)	C7B	C8B	C9B	O2B	-73.7(4)
O1	C7	C10	N1	-59.9(3)	C7B	C10B	C11B	F1B	-175.0(3)
O1	C7	C10	C11	62.6(4)	C7B	C10B	C11B	C12B	-54.8(4)
C4	Si1	O1	C7	141.5(3)	C8B	C7B	C10B	N1B	-68.8(4)
C5	Si1	O1	C7	-99.6(3)	C8B	C7B	C10B	C11B	170.1(3)
C5	Si1	C4	C1	62.0(3)	C10B	C7B	C8B	C9B	53.8(4)
C5	Si1	C4	C2	-180.0(3)	C10B	C11B	C12B	C13B	-176.0(3)
C5	Si1	C4	C3	-58.8(3)	C11B	C12B	C13B	C14B	-165.0(3)
C6	Si1	O1	C7	20.9(3)	C12B	C13B	C14B	C15B	-177.1(3)
C6	Si1	C4	C1	-60.4(3)	C13B	C14B	C15B	C16B	-177.0(4)
C6	Si1	C4	C2	57.7(3)	S1C	O2C	C9C	C8C	93.1(3)
C6	Si1	C4	C3	178.8(3)	S1C	N1C	C10C	C7C	92.6(3)
C7	C8	C9	O2	74.1(3)	S1C	N1C	C10C	C11C	-143.5(3)
C7	C10	C11	F1	170.3(3)	Si1C	O1C	C7C	C8C	-85.3(3)
C7	C10	C11	C12	49.4(4)	Si1C	O1C	C7C	C10C	150.5(2)
F1	C11	C12	C13	56.9(4)	O1C	Si1C	C4C	C1C	174.2(6)
O2	S1	N1	C10	42.0(3)	O1C	Si1C	C4C	C2C	-65.5(5)
O3	S1	O2	C9	-70.3(3)	O1C	Si1C	C4C	C3C	52.2(5)
O3	S1	N1	C10	160.1(2)	O1C	C7C	C8C	C9C	-64.3(4)
O4	S1	O2	C9	162.5(2)	O1C	C7C	C10C	N1C	53.3(3)
O4	S1	N1	C10	-68.3(3)	O1C	C7C	C10C	C11C	-67.3(3)
N1	S1	O2	C9	45.5(3)	O1C	Si1E	C4E	C1E	169.6(11)
N1	C10	C11	F1	-65.3(3)	O1C	Si1E	C4E	C2E	-72.5(11)
N1	C10	C11	C12	173.8(3)	O1C	Si1E	C4E	C3E	48.5(11)
C8	C7	C10	N1	65.7(3)	O1C	Si1D	C4D	C1D	171.1(8)

C8	C7	C10	C11	-171.8(3)
C10	C7	C8	C9	-52.1(4)
C10	C11	C12	C13	175.7(3)
C11	C12	C13	C14	-177.9(3)
C12	C13	C14	C15	-62.0(4)
C13	C14	C15	C16	-179.1(3)
S1A	O2A	C9A	C8A	-94.7(3)
S1A	N1A	C10A	C7A	-91.5(3)
S1A	N1A	C10A	C11A	143.5(2)
Si1A	O1A	C7A	C8A	76.1(3)
Si1A	O1A	C7A	C10A	-158.3(2)
F1A	C11A	C12A	C13A	54.8(4)
O1A	Si1A	C4A	C1A	180.0(3)
O1A	Si1A	C4A	C2A	-59.4(3)
O1A	Si1A	C4A	C3A	61.6(3)
O1A	C7A	C8A	C9A	69.5(4)
O1A	C7A	C10A	N1A	-58.3(4)
O1A	C7A	C10A	C11A	64.1(4)
O2A	S1A	N1A	C10A	43.9(3)
O3A	S1A	O2A	C9A	-70.9(3)
O3A	S1A	N1A	C10A	161.2(3)
O4A	S1A	O2A	C9A	161.3(2)
O4A	S1A	N1A	C10A	-66.5(3)
N1A	S1A	O2A	C9A	45.0(3)
N1A	C10A	C11A	F1A	-66.8(3)
N1A	C10A	C11A	C12A	173.3(3)
C4A	Si1A	O1A	C7A	143.8(3)
C5A	Si1A	O1A	C7A	-96.2(3)
C5A	Si1A	C4A	C1A	60.4(3)
C5A	Si1A	C4A	C2A	-179.0(3)
C5A	Si1A	C4A	C3A	-58.0(3)
C6A	Si1A	O1A	C7A	24.5(3)
C6A	Si1A	C4A	C1A	-61.6(3)
C6A	Si1A	C4A	C2A	59.0(3)
C6A	Si1A	C4A	C3A	180.0(3)
C7A	C8A	C9A	O2A	73.3(4)
C7A	C10A	C11A	F1A	169.8(3)
C7A	C10A	C11A	C12A	49.8(4)
C8A	C7A	C10A	N1A	65.9(4)
C8A	C7A	C10A	C11A	-171.7(3)
C10A	C7A	C8A	C9A	-51.7(4)
C10A	C11A	C12A	C13A	173.8(3)
O1C	Si1D	C4D	C2D	-72.9(7)
O1C	Si1D	C4D	C3D	43.9(8)
C4C	Si1C	O1C	C7C	-173.0(3)
C5C	Si1C	O1C	C7C	-54.7(4)
C5C	Si1C	C4C	C1C	57.9(7)
C5C	Si1C	C4C	C2C	178.2(6)
C5C	Si1C	C4C	C3C	-64.1(6)
C6C	Si1C	O1C	C7C	66.4(4)
C6C	Si1C	C4C	C1C	-63.4(7)
C6C	Si1C	C4C	C2C	56.9(6)
C6C	Si1C	C4C	C3C	174.6(5)
C7C	O1C	Si1E	C4E	-128.5(6)
C7C	O1C	Si1E	C5E	-9.7(8)
C7C	O1C	Si1E	C6E	110.4(8)
C7C	O1C	Si1D	C4D	130.0(4)
C7C	O1C	Si1D	C5D	-109.7(6)
C7C	O1C	Si1D	C6D	12.1(6)
C7C	C8C	C9C	O2C	-75.7(4)
C7C	C10C	C11C	F1C	-175.3(3)
C7C	C10C	C11C	C12C	-55.0(4)
Si1E	O1C	C7C	C8C	-63.5(6)
Si1E	O1C	C7C	C10C	172.3(5)
C5E	Si1E	C4E	C1E	51.8(12)
C5E	Si1E	C4E	C2E	169.7(12)
C5E	Si1E	C4E	C3E	-69.3(12)
C6E	Si1E	C4E	C1E	-69.0(12)
C6E	Si1E	C4E	C2E	48.9(12)
C6E	Si1E	C4E	C3E	169.9(12)
Si1D	O1C	C7C	C8C	-113.2(3)
Si1D	O1C	C7C	C10C	122.6(3)
C5D	Si1D	C4D	C1D	51.1(9)
C5D	Si1D	C4D	C2D	167.1(8)
C5D	Si1D	C4D	C3D	-76.1(9)
C6D	Si1D	C4D	C1D	-70.9(10)
C6D	Si1D	C4D	C2D	45.0(9)
C6D	Si1D	C4D	C3D	161.8(10)
F1C	C11C	C12C	C13C	-50.2(5)
F1C	C11C	C12C	C13D	-72.8(13)
O2C	S1C	N1C	C10C	-44.7(3)
O3C	S1C	O2C	C9C	-160.2(2)
O3C	S1C	N1C	C10C	66.7(3)
O4C	S1C	O2C	C9C	71.6(2)

C11A	C12A	C13A	C14A	177.4(3)	O4C	S1C	N1C	C10C	-161.2(3)
C12A	C13A	C14A	C15A	-65.4(4)	N1C	S1C	O2C	C9C	-42.9(3)
C13A	C14A	C15A	C16A	-177.0(3)	N1C	C10C	C11C	F1C	63.2(3)
S1B	O2B	C9B	C8B	94.6(3)	N1C	C10C	C11C	C12C	-176.6(3)
S1B	N1B	C10B	C7B	91.0(3)	C8C	C7C	C10C	N1C	-69.4(3)
S1B	N1B	C10B	C11B	-145.0(3)	C8C	C7C	C10C	C11C	169.9(3)
Si1B	O1B	C7B	C8B	-69.6(4)	C10C	C7C	C8C	C9C	56.7(4)
Si1B	O1B	C7B	C10B	166.0(2)	C10C	C11C	C12C	C13C	-169.2(4)
F1B	C11B	C12B	C13B	-56.6(4)	C10C	C11C	C12C	C13D	168.2(13)
O1B	C7B	C8B	C9B	-65.0(4)	C11C	C12C	C13C	C14C	-169.0(5)
O1B	C7B	C10B	N1B	54.5(3)	C11C	C12C	C13D	C14D	-171.8(13)
O1B	C7B	C10B	C11B	-66.6(3)	C12C	C13C	C14C	C15C	71.8(8)
O2B	S1B	N1B	C10B	-41.7(3)	C12C	C13D	C14D	C15D	179(2)
O3B	S1B	O2B	C9B	69.7(3)	C13C	C14C	C15C	C16C	178.3(6)
O3B	S1B	N1B	C10B	-159.2(2)	C13D	C14D	C15D	C16D	-168(2)

Table S-8. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7a.

Atom	***x***	***y***	***z***	**U(eq)**
H1A	6879	1834	7452	70
H1B	7531	1020	7452	70
H1D	7067	1237	6721	70
H2A	8515	1258	6101	77
H2B	9036	987	6791	77
H2C	9372	1804	6435	77
H3A	9205	2677	7634	82
H3B	8868	1847	7971	82
H3C	8240	2681	8048	82
H5A	7242	3701	7645	51
H5B	6387	3346	7161	51
H5C	6925	4176	6978	51
H6A	6967	3087	5484	50
H6B	6686	2216	5781	50
H6C	7646	2288	5372	50
H7	8700	3529	5376	30
H1	10120(30)	4420(20)	6796(11)	38
H8A	8331	4906	5289	30
H8B	7640	4577	5858	30
H9A	8025	5905	6337	34
H9B	8624	5303	6790	34
H10	10039	4384	5329	30
H11	10454	3015	6140	36

H12E	10091	2866	4638	35
H12F	9488	2437	5212	35
H13E	10734	1548	5430	47
H13F	11361	1991	4879	47
H14E	10813	711	4301	52
H14F	10374	1471	3926	52
H15E	8958	1296	4518	45
H15F	9395	543	4905	45
H16G	9109	455	3391	80
H16H	8475	-13	3922	80
H16I	9524	-301	3788	80
H1AA	10190(30)	5750(20)	8241(11)	41
H1AB	6861	8187	7477	68
H1AC	7482	9027	7560	68
H1AD	6956	8738	8240	68
H2AA	8498	8751	8912	75
H2AB	8935	9092	8217	75
H2AC	9356	8269	8516	75
H3AA	9127	7362	7350	86
H3AB	8801	8205	7029	86
H3AC	8160	7378	6941	86
H5AA	7199	6286	7354	48
H5AB	6337	6663	7816	48
H5AC	6862	5841	8031	48
H6AA	6999	6949	9536	46
H6AB	6584	7745	9191	46
H6AC	7564	7822	9585	46
H7A	8599	6505	9638	31
H8AA	8313	5090	9661	34
H8AB	7637	5407	9078	34
H9AA	8108	4122	8602	35
H9AB	8689	4768	8178	35
H10A	9997	5704	9708	32
H11A	10391	7166	8985	35
H12G	9928	7195	10463	37
H12H	9359	7655	9889	37
H13G	11176	8131	10376	47
H13H	10640	8576	9774	47
H14G	10021	8624	11221	47
H14H	10570	9382	10922	47
H15G	9314	9571	10135	46
H15H	8761	8840	10475	46

H16J	8259	10166	10995	77
H16K	9289	10414	11246	77
H16L	8750	9680	11593	77
H1BA	4940(30)	5650(20)	6917(10)	39
H1BB	2800	9208	7730	81
H1BC	3548	9399	8354	81
H1BD	2825	8640	8381	81
H2BA	4884	8446	6887	83
H2BB	4762	9299	7420	83
H2BC	4022	9055	6798	83
H3BA	4177	7724	8536	68
H3BB	4895	8465	8428	68
H3BC	4948	7583	7925	68
H5BA	2212	6370	7475	67
H5BB	2019	7237	7973	67
H5BC	2902	6676	8117	67
H6BA	2793	8107	6092	67
H6BB	2010	8301	6687	67
H6BC	2044	7396	6215	67
H7B	3972	6898	5689	32
H8BA	2660	6066	5888	34
H8BB	3302	5613	5272	34
H9BA	3337	5121	6683	36
H9BB	2656	4682	6076	36
H10B	5064	5746	5454	30
H11B	5736	7035	6530	35
H12I	5063	7742	5626	37
H12J	5623	7160	5026	37
H13I	6583	8254	6095	43
H13J	7002	7815	5357	43
H14I	5667	9143	5471	50
H14J	6035	8687	4724	50
H15I	7513	9255	4963	57
H15J	7180	9680	5732	57
H16M	6486	10152	4411	93
H16N	7228	10693	4902	93
H16O	6198	10595	5187	93
H1CA	3138	757	7198	98
H1CB	3021	1048	6415	98
H1CC	2237	1268	7006	98
H2CA	2332	2755	6819	70
H2CB	3141	2574	6243	70

H2CC	3284	3267	6922	70
H3CA	4734	2511	7222	72
H3CB	4534	1900	6501	72
H3CC	4696	1505	7238	72
H5CA	4312	1356	8545	67
H5CB	3302	947	8541	67
H5CC	3606	1646	9180	67
H6CA	1895	2548	8900	68
H6CB	1610	2017	8157	68
H6CC	1769	3019	8197	68
H7C	4068	3108	9383	33
H1EA	2532	1244	7054	48
H1EB	3189	517	7294	48
H1EC	3327	850	6528	48
H2EA	4750	1589	6513	52
H2EB	4747	2515	6950	52
H2EC	3920	2230	6412	52
H3EA	4172	1082	8247	55
H3EB	4947	1741	8062	55
H3EC	4853	843	7586	55
H5EA	2679	2095	8966	52
H5EB	2165	1567	8306	52
H5EC	1824	2504	8590	52
H6EA	1965	3473	7515	50
H6EB	2249	2792	6858	50
H6EC	2885	3607	7071	50
H1DA	2888	1320	6588	79
H1DB	1810	1518	6685	79
H1DC	2337	1000	7244	79
H2DA	1635	2000	8138	94
H2DB	1232	2575	7563	94
H2DC	1875	2990	8202	94
H3DA	3056	3499	7247	87
H3DB	2136	3224	6809	87
H3DC	3113	2853	6530	87
H5DA	4894	2144	7181	87
H5DB	4436	1224	7163	87
H5DC	5115	1565	7804	87
H6DA	3873	1501	9045	50
H6DB	3180	954	8514	50
H6DC	2817	1783	8996	50
H1C	4880(30)	4340(20)	8097(10)	35

H8CA	3395	4375	9820	35
H8CB	2703	3864	9270	35
H9CA	3222	4792	8392	36
H9CB	2569	5216	9022	36
H10C	5108	4331	9555	28
H11C	5773	3089	8454	35
H12A	5313	2284	9345	37
H12B	5764	2942	9956	37
H12C	6011	2942	9940	37
H12D	5209	2438	9489	37
H13A	6869	2022	8874	44
H13B	7244	2558	9585	44
H14A	6535	1521	10261	43
H14B	7403	1184	9788	43
H15A	5522	842	9392	57
H15B	6381	522	8901	57
H16A	5860	-596	9503	82
H16B	5973	-33	10259	82
H16C	6867	-329	9798	82
H13C	7127	2191	9278	57
H13D	6371	1755	8732	57
H14C	6474	1509	10216	45
H14D	5705	1083	9679	45
H15C	7620	724	9633	68
H15D	6953	406	8980	68
H16D	6224	-525	9615	98
H16E	6604	-74	10363	98
H16F	7287	-617	9822	98

Table S-9. Atomic Occupancy for 7a.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
Si1C	0.559(2)	C1C	0.559(2)	H1CA	0.559(2)
H1CB	0.559(2)	H1CC	0.559(2)	C2C	0.559(2)
H2CA	0.559(2)	H2CB	0.559(2)	H2CC	0.559(2)
C3C	0.559(2)	H3CA	0.559(2)	H3CB	0.559(2)
H3CC	0.559(2)	C4C	0.559(2)	C5C	0.559(2)
H5CA	0.559(2)	H5CB	0.559(2)	H5CC	0.559(2)
C6C	0.559(2)	H6CA	0.559(2)	H6CB	0.559(2)
H6CC	0.559(2)	Si1E	0.1203(19)	C1E	0.1203(19)
H1EA	0.1203(19)	H1EB	0.1203(19)	H1EC	0.1203(19)
C2E	0.1203(19)	H2EA	0.1203(19)	H2EB	0.1203(19)
H2EC	0.1203(19)	C3E	0.1203(19)	H3EA	0.1203(19)

H3EB 0.1203(19)	H3EC 0.1203(19)	C4E 0.1203(19)
C5E 0.1203(19)	H5EA 0.1203(19)	H5EB 0.1203(19)
H5EC 0.1203(19)	C6E 0.1203(19)	H6EA 0.1203(19)
H6EB 0.1203(19)	H6EC 0.1203(19)	Si1D 0.3207(19)
C1D 0.3207(19)	H1DA 0.3207(19)	H1DB 0.3207(19)
H1DC 0.3207(19)	C2D 0.3207(19)	H2DA 0.3207(19)
H2DB 0.3207(19)	H2DC 0.3207(19)	C3D 0.3207(19)
H3DA 0.3207(19)	H3DB 0.3207(19)	H3DC 0.3207(19)
C4D 0.3207(19)	C5D 0.3207(19)	H5DA 0.3207(19)
H5DB 0.3207(19)	H5DC 0.3207(19)	C6D 0.3207(19)
H6DA 0.3207(19)	H6DB 0.3207(19)	H6DC 0.3207(19)
H12A 0.745(10)	H12B 0.745(10)	H12C 0.255(10)
H12D 0.255(10)	C13C 0.745(10)	H13A 0.745(10)
H13B 0.745(10)	C14C 0.745(10)	H14A 0.745(10)
H14B 0.745(10)	C15C 0.745(10)	H15A 0.745(10)
H15B 0.745(10)	C16C 0.745(10)	H16A 0.745(10)
H16B 0.745(10)	H16C 0.745(10)	C13D 0.255(10)
H13C 0.255(10)	H13D 0.255(10)	C14D 0.255(10)
H14C 0.255(10)	H14D 0.255(10)	C15D 0.255(10)
H15C 0.255(10)	H15D 0.255(10)	C16D 0.255(10)
H16D 0.255(10)	H16E 0.255(10)	H16F 0.255(10)

Crystallographic Experimental Section for 10a. CCDC number 1548237

Data Collection. A colorless crystal with approximate dimensions 0.158 x 0.106 x 0.043 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.[1]

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an

automated indexing routine built in the APEX3 program suite. The final cell constants were calculated from a set of 6515 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.80 Å. A total of 45920 data were harvested by collecting 3 sets of frames with 0.5º scans in ω with exposure times of 40 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[2]

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/c$ that yielded chemically reasonable and computationally stable results of refinement.[3-8]

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms, except for the amine hydrogen, were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The N1–H1 and N1A–H1A distances were constrained to 0.83Å distance, but the isotropic displacement coefficients on the hydrogen atoms were allowed to refine freely.

Due to the presence of an inversion center, both stereoisomers are present in the crystal structure. There are two chiral molecules in the asymmetric unit. They have the same composition and connectivity, but opposite handedness. The relative configuration is as follows: chiral centers in the Si1 molecules are C3 – *R*, C10 – *S*, and C12 – *S*; the chiral centers on Si1A molecule are C3A – *S*, C10A – *R* and C12A – *R*.

The second molecule exhibited positional disorder in the fluorohexyl chain (atoms C13a–C17a and C13b–C17b)) with the major component contribution of 70.4(4) %. These disordered atoms were refined isotropically.

The final least-squares refinement of 477 parameters against 9093 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0628 and 0.1701, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{17}H_{33}FN_2O_4SSi$ (*M* =408.60 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 13.110(4) Å, *b* = 9.969(4) Å, *c* = 33.818(12) Å, β = 90.959(14)°, *V* = 4419(3) $Å^3$, *Z* = 8, *T* = 100.0 K, μ(MoKα) = 0.231 mm^{-1}, *Dcalc* = 1.228 g/cm^3, 45819 reflections measured (2.408° ≤ 2Θ ≤ 52.882°), 9093 unique (R_{int} = 0.0627, R_{sigma} = 0.0802) which were used in all calculations. The final R_1 was 0.0628 (I > 2σ(I)) and wR_2 was 0.1701 (all data).

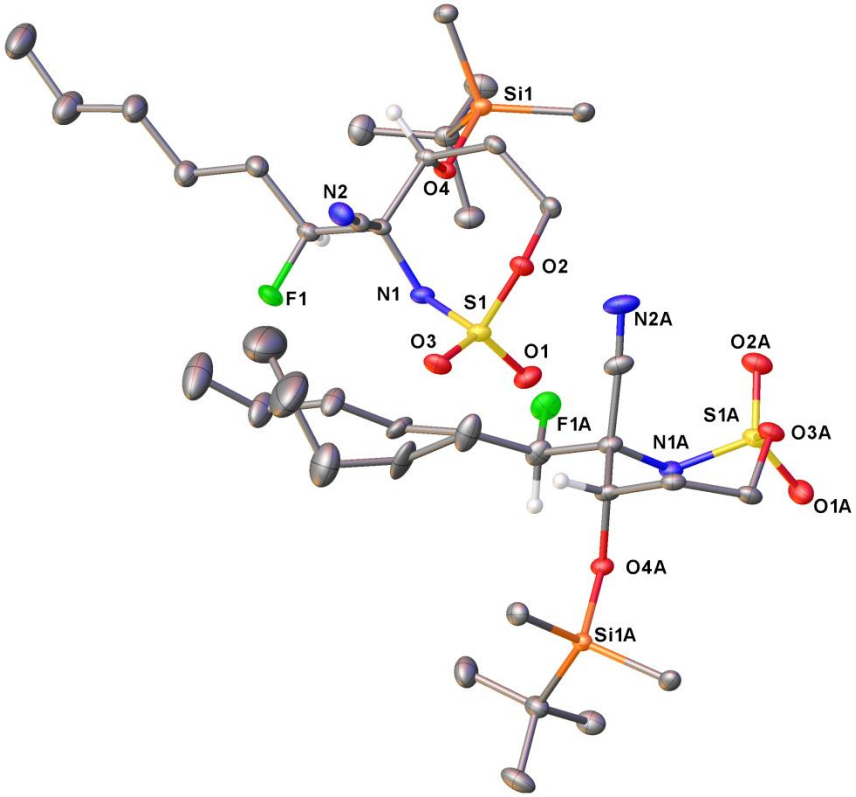


Figure S-6. A molecular drawing of **10a** shown with 50% probability ellipsoids showing the two molecules in the asymmetric unit. All H atoms on non-stereoactive atoms are omitted.

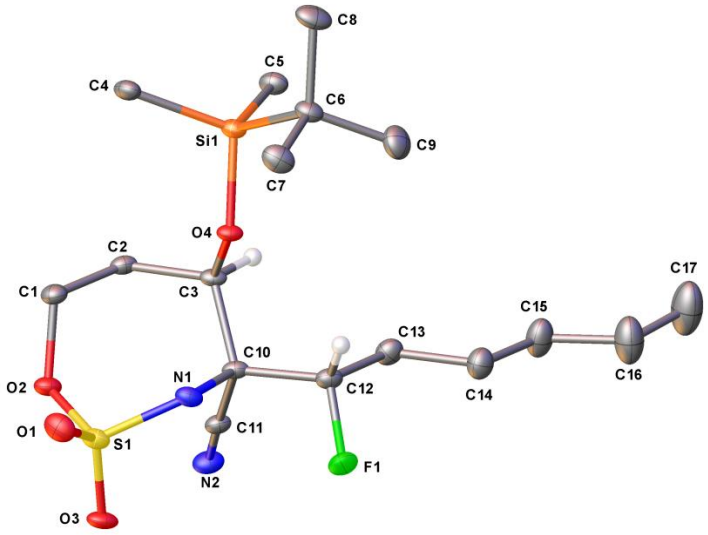


Figure S-7. A molecular drawing of **10a** shown with 50% probability ellipsoids showing the first molecule in the asymmetric unit. All H atoms on non-stereoactive atoms are omitted.

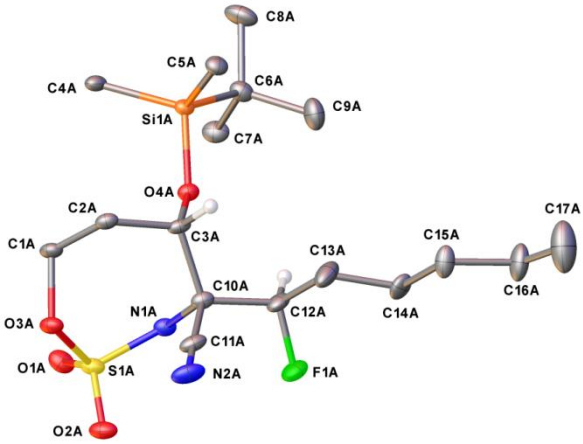


Figure S-8. A molecular drawing of **10a** shown with 50% probability ellipsoids showing the second molecule in the asymmetric unit. The minor disorder component and all H atoms on non-stereoactive atoms are omitted.

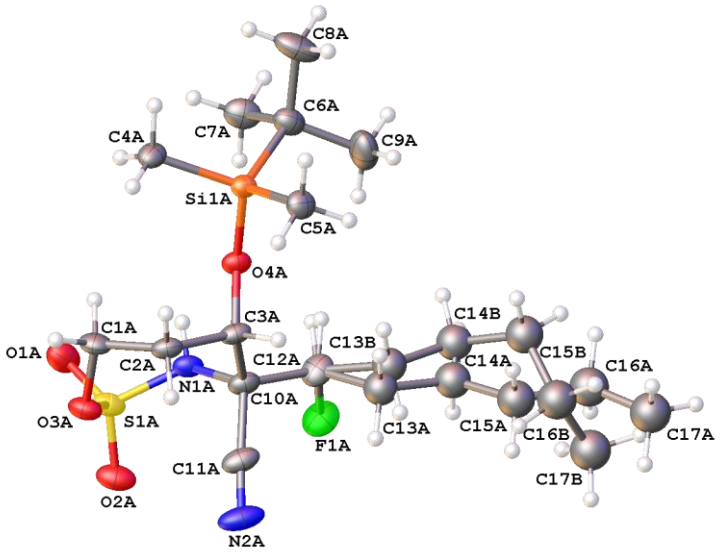


Figure S-9. A molecular drawing of **10a** shown with 50% probability ellipsoids showing the second molecule in the asymmetric unit. Both disorder components are shown.

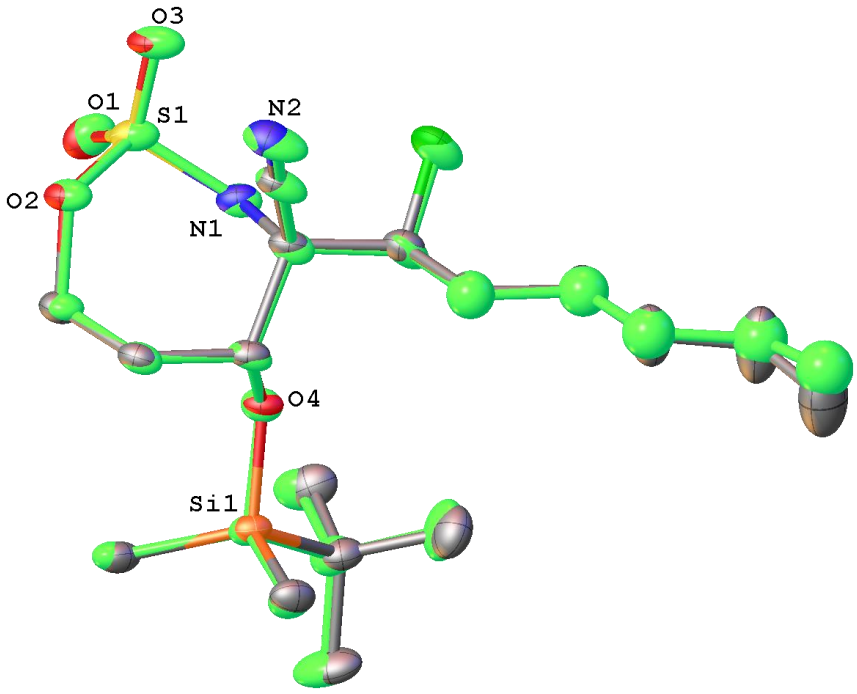


Figure S-10. A molecular drawing of **10a** shown with 50% probability ellipsoids showing the overlay of the two molecules in the asymmetric unit. The minor disorder component of Si1A molecule and all H atoms are omitted.

Table S-10. Crystal data and structure refinement for 10a.

Identification code	Schomaker70b
Empirical formula	$C_{17}H_{33}FN_2O_4SSi$
Formula weight	408.60
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.110(4)
b/Å	9.969(4)
c/Å	33.818(12)
α/°	90
β/°	90.959(14)
γ/°	90
Volume/Å^3	4419(3)
Z	8
ρ_{calc}g/cm^3	1.228
μ/mm^{-1}	0.231
F(000)	1760.0
Crystal size/mm^3	0.158 × 0.106 × 0.043
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.408 to 52.882
Index ranges	$-16 \le h \le 15$, $-12 \le k \le 12$, $-42 \le l \le 42$
Reflections collected	45819
Independent reflections	9093 [R_{int} = 0.0627, R_{sigma} = 0.0802]
Data/restraints/parameters	9093/29/477
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0628, wR_2 = 0.1538
Final R indexes [all data]	R_1 = 0.0933, wR_2 = 0.1701
Largest diff. peak/hole / e Å^{-3}	0.66/-0.88

Table S-11. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 10a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	6457.4(6)	5655.4(7)	6976.5(2)	25.67(19)
Si1	5799.3(6)	10828.2(8)	6555.0(3)	22.7(2)
F1	4723.8(14)	5687.8(18)	5994.4(5)	35.8(5)
O1	7533.2(16)	5778(2)	6959.5(7)	36.2(6)
O2	6030.8(15)	6402(2)	7348.1(6)	26.7(5)
O3	5992.4(17)	4369(2)	6987.8(6)	30.7(5)
O4	5657.1(14)	9161.9(19)	6543.8(6)	21.4(4)

N1	6017.0(19)	6486(2)	6594.0(8)	23.9(5)
N2	3634(2)	5461(3)	6929.5(8)	32.7(6)
C1	6094(2)	7877(3)	7354.6(9)	27.2(7)
C2	5101(2)	8462(3)	7200.9(9)	24.1(6)
C3	4912(2)	8420(3)	6755.2(9)	21.6(6)
C4	6700(2)	11260(3)	6961.5(10)	29.3(7)
C5	4527(2)	11611(3)	6623.2(10)	29.9(7)
C6	6338(2)	11241(3)	6057.2(10)	29.6(7)
C7	7321(3)	10438(4)	5996.0(11)	38.1(8)
C8	6593(3)	12745(3)	6036.3(11)	42.6(9)
C9	5570(3)	10899(4)	5726.3(10)	44.6(9)
C10	4958(2)	6992(3)	6573.7(9)	22.2(6)
C11	4243(2)	6090(3)	6778.0(9)	24.3(6)
C12	4665(2)	7014(3)	6130.6(9)	26.6(7)
C13	3610(2)	7540(3)	6034.8(9)	32.4(7)
C14	3333(3)	7513(4)	5600.7(10)	39.3(8)
C15	2274(3)	8022(5)	5512(1)	51.5(10)
C16	1969(3)	8146(6)	5095.5(12)	70.2(14)
C17	964(4)	8755(6)	5006.4(14)	78.5(16)
S1A	11435.6(6)	8586.8(7)	6978.9(2)	27.81(19)
Si1A	10802.1(6)	3415.7(8)	6555.0(2)	21.99(19)
F1A	9750.8(15)	8561(2)	5981.4(6)	42.1(5)
O1A	12509.3(17)	8466(2)	6971.7(7)	36.6(6)
O2A	10971.3(18)	9863(2)	6987.5(7)	36.3(6)
O3A	10986.3(16)	7848(2)	7346.7(6)	29.0(5)
O4A	10660.0(14)	5092(2)	6539.4(6)	24.1(5)
N1A	11014.3(18)	7762(3)	6594.3(8)	24.8(5)
N2A	8623(2)	8788(3)	6907.6(10)	45.4(8)
C1A	11038(2)	6369(3)	7355.2(10)	28.3(7)
C2A	10061(2)	5786(3)	7190.3(9)	25.0(6)
C3A	9901(2)	5822(3)	6742.8(9)	24.0(6)
C4A	11667(2)	2986(3)	6972.7(9)	28.3(7)
C5A	9525(2)	2630(3)	6605.5(10)	30.1(7)
C6A	11389(2)	3009(3)	6065.1(10)	33.0(7)
C7A	12399(3)	3779(3)	6026.8(11)	37.5(8)
C8A	11611(3)	1500(4)	6041.1(12)	50.2(10)
C9A	10671(3)	3421(5)	5725(1)	49.3(10)
C10A	9964(2)	7252(3)	6560.7(9)	26.0(7)
C11A	9231(2)	8155(3)	6759.4(10)	33.1(8)
C12A	9699(2)	7231(3)	6113.8(10)	33.4(8)
C13B	8786(8)	6487(13)	5936(3)	43.4(5)
C14B	8727(8)	6431(14)	5487(3)	47.7(6)

C15B	7848(7)	5656(12)	5314(4)	52.0(7)
C16B	6801(8)	6156(13)	5380(4)	56.4(7)
C17B	6534(11)	7376(13)	5139(4)	60.7(8)
C13A	8616(4)	6762(6)	6035.6(15)	43.4(5)
C14A	8333(4)	6832(6)	5597.6(15)	47.7(6)
C15A	7255(4)	6396(6)	5514.7(16)	52.0(7)
C16A	6954(4)	6341(7)	5084.3(17)	56.4(7)
C17A	5873(4)	6057(7)	5005.9(19)	60.7(8)

Table S-12. Anisotropic Displacement Parameters ($Å^2×10^3$) for 10a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	24.7(4)	19.2(4)	33.4(4)	1.9(3)	6.4(3)	2.2(3)
Si1	20.8(4)	16.4(4)	31.1(5)	1.6(3)	2.7(3)	0.2(3)
F1	45.3(11)	27.7(10)	34.6(11)	-11.4(8)	2.3(9)	3.8(8)
O1	23.9(11)	37.1(14)	47.9(14)	7.2(11)	4.7(10)	3.6(9)
O2	31.9(12)	16.4(11)	31.9(12)	-0.4(9)	4.7(9)	-0.5(8)
O3	40.4(13)	13.8(10)	38.1(13)	2.3(9)	9.8(10)	-1.4(9)
O4	23(1)	13(1)	28.6(11)	-0.1(8)	6.9(8)	-2.5(8)
N1	22.6(13)	18.1(13)	31.4(14)	2.0(11)	8.8(11)	0.8(10)
N2	31.3(15)	27.1(14)	40.0(16)	-3.0(12)	8.7(12)	-7.9(12)
C1	28.4(16)	19.8(15)	33.5(17)	-2.3(13)	0.6(13)	-3.5(12)
C2	27.1(15)	17.5(14)	27.9(16)	-3.8(12)	6.5(12)	-2.6(11)
C3	20.9(14)	14.0(13)	30.2(16)	-0.1(12)	8.4(12)	-2.4(11)
C4	27.5(16)	19.0(15)	41.2(19)	0.7(13)	-3.0(13)	2.1(12)
C5	24.6(16)	23.5(16)	41.5(19)	-1.1(14)	2.1(13)	2.8(12)
C6	30.9(17)	20.8(16)	37.2(18)	4.5(14)	5.4(13)	-1.0(12)
C7	36.1(19)	38(2)	41(2)	4.9(16)	12.4(15)	4.1(15)
C8	52(2)	26.2(18)	50(2)	11.5(16)	17.7(18)	-1.1(15)
C9	48(2)	53(2)	32(2)	10.7(17)	0.0(16)	-3.5(18)
C10	21.2(14)	15.7(14)	30.0(16)	-2.7(12)	6.7(12)	-1.0(11)
C11	26.3(15)	18.3(14)	28.5(16)	-4.3(12)	4.1(12)	-2.5(12)
C12	29.0(16)	20.7(15)	30.2(17)	-2.9(13)	5.7(13)	-0.6(12)
C13	30.8(17)	32.5(18)	34.1(18)	-8.6(14)	2.5(14)	2.5(13)
C14	39.4(19)	47(2)	31.8(18)	-3.0(16)	0.0(15)	0.4(16)
C15	45(2)	74(3)	36(2)	-9(2)	-4.1(17)	12(2)
C16	54(3)	114(4)	43(2)	-4(3)	-7(2)	20(3)
C17	58(3)	122(5)	55(3)	-13(3)	-12(2)	26(3)
S1A	29.6(4)	19.2(4)	35.0(4)	-1.5(3)	11.1(3)	-1.1(3)
Si1A	19.6(4)	18.0(4)	28.3(4)	-1.1(3)	1.9(3)	-1.7(3)

F1A	46.1(12)	33.2(11)	47.1(12)	18.9(9)	1.8(9)	-2.7(9)
O1A	29.0(12)	37.5(14)	43.7(14)	-8.1(11)	8.9(10)	-6.9(10)
O2A	45.1(14)	21.0(12)	43.2(14)	0.8(10)	17.2(11)	-0.3(10)
O3A	38.2(12)	19.2(11)	30.1(12)	-1.4(9)	10.3(9)	2.4(9)
O4A	20.5(10)	22.1(11)	29.8(11)	1.3(9)	6.9(8)	1.1(8)
N1A	21.8(13)	21.7(13)	31.2(14)	0.0(11)	8.9(11)	1.7(10)
N2A	36.6(17)	27.6(16)	73(2)	13.1(15)	19.8(15)	11.7(13)
C1A	36.4(17)	15.5(15)	33.1(17)	-0.2(13)	6.4(14)	3.7(12)
C2A	23.7(15)	19.7(15)	31.7(17)	4.0(13)	8.5(12)	4.6(11)
C3A	21.0(15)	16.4(14)	34.9(17)	6.8(12)	7.0(12)	3.1(11)
C4A	27.7(16)	17.2(14)	39.9(18)	1.2(13)	-3.2(13)	-0.9(12)
C5A	26.7(16)	26.3(16)	37.4(18)	-0.8(14)	1.3(13)	-5.8(13)
C6A	30.7(17)	31.0(18)	37.7(19)	-5.8(15)	6.3(14)	-1.8(14)
C7A	37.3(19)	33.1(19)	42(2)	1.4(16)	14.9(15)	-3.7(15)
C8A	63(3)	29(2)	60(3)	-15.1(18)	25(2)	-6.7(17)
C9A	46(2)	72(3)	30(2)	-10.1(19)	-1.1(16)	-1.3(19)
C10A	22.2(15)	22.6(15)	33.5(17)	4.4(13)	8.2(12)	3.2(12)
C11A	28.0(17)	24.2(17)	47(2)	13.6(15)	10.3(15)	5.1(13)
C12A	36.2(18)	26.6(17)	37.5(19)	14.9(14)	0.4(14)	-3.6(14)

Table S-13. Bond Lengths for 10a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.418(2)	S1A	N1A	1.628(3)
S1	O2	1.571(2)	Si1A	O4A	1.682(2)
S1	O3	1.421(2)	Si1A	C4A	1.847(3)
S1	N1	1.633(3)	Si1A	C5A	1.859(3)
Si1	O4	1.672(2)	Si1A	C6A	1.883(3)
Si1	C4	1.848(3)	F1A	C12A	1.402(3)
Si1	C5	1.860(3)	O3A	C1A	1.476(3)
Si1	C6	1.882(3)	O4A	C3A	1.419(3)
F1	C12	1.403(3)	N1A	C10A	1.470(4)
O2	C1	1.474(3)	N2A	C11A	1.140(4)
O4	C3	1.427(3)	C1A	C2A	1.505(4)
N1	C10	1.477(4)	C2A	C3A	1.525(4)
N2	C11	1.143(4)	C3A	C10A	1.556(4)
C1	C2	1.511(4)	C6A	C7A	1.538(4)
C2	C3	1.524(4)	C6A	C8A	1.535(5)
C3	C10	1.553(4)	C6A	C9A	1.530(5)
C6	C7	1.535(4)	C10A	C11A	1.485(4)
C6	C8	1.538(4)	C10A	C12A	1.545(4)

C6	C9	1.531(5)	C12A	C13B	1.523(7)
C10	C11	1.479(4)	C12A	C13A	1.515(5)
C10	C12	1.541(4)	C13B	C14B	1.522(8)
C12	C13	1.509(4)	C14B	C15B	1.499(8)
C13	C14	1.507(4)	C15B	C16B	1.482(9)
C14	C15	1.504(5)	C16B	C17B	1.502(9)
C15	C16	1.463(5)	C13A	C14A	1.522(6)
C16	C17	1.478(5)	C14A	C15A	1.501(6)
S1A	O1A	1.413(2)	C15A	C16A	1.503(6)
S1A	O2A	1.411(2)	C16A	C17A	1.465(7)
S1A	O3A	1.569(2)			

Table S-14. Bond Angles for 10a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	111.05(14)	O2A	S1A	O3A	103.85(13)
O1	S1	O3	120.45(14)	O2A	S1A	N1A	109.34(15)
O1	S1	N1	105.23(14)	O3A	S1A	N1A	105.63(13)
O2	S1	N1	105.52(12)	O4A	Si1A	C4A	108.71(12)
O3	S1	O2	104.32(12)	O4A	Si1A	C5A	108.78(13)
O3	S1	N1	109.43(14)	O4A	Si1A	C6A	103.47(13)
O4	Si1	C4	108.54(12)	C4A	Si1A	C5A	111.99(15)
O4	Si1	C5	108.66(13)	C4A	Si1A	C6A	111.61(15)
O4	Si1	C6	103.91(12)	C5A	Si1A	C6A	111.86(15)
C4	Si1	C5	111.91(15)	C1A	O3A	S1A	117.83(18)
C4	Si1	C6	111.72(15)	C3A	O4A	Si1A	124.89(17)
C5	Si1	C6	111.70(15)	C10A	N1A	S1A	122.8(2)
C1	O2	S1	117.65(18)	O3A	C1A	C2A	109.9(2)
C3	O4	Si1	125.48(17)	C1A	C2A	C3A	117.5(2)
C10	N1	S1	121.95(19)	O4A	C3A	C2A	112.5(2)
O2	C1	C2	109.4(2)	O4A	C3A	C10A	103.6(2)
C1	C2	C3	117.0(2)	C2A	C3A	C10A	114.0(3)
O4	C3	C2	112.3(2)	C7A	C6A	Si1A	109.4(2)
O4	C3	C10	104.2(2)	C8A	C6A	Si1A	109.8(2)
C2	C3	C10	114.2(2)	C8A	C6A	C7A	108.7(3)
C7	C6	Si1	109.6(2)	C9A	C6A	Si1A	110.4(2)
C7	C6	C8	108.6(3)	C9A	C6A	C7A	108.8(3)
C8	C6	Si1	109.9(2)	C9A	C6A	C8A	109.8(3)
C9	C6	Si1	110.7(2)	N1A	C10A	C3A	110.0(2)
C9	C6	C7	109.2(3)	N1A	C10A	C11A	111.6(3)
C9	C6	C8	108.9(3)	N1A	C10A	C12A	106.0(2)

N1	C10	C3	109.7(2)	C11A	C10A	C3A	109.7(2)
N1	C10	C11	111.9(2)	C11A	C10A	C12A	108.3(3)
N1	C10	C12	105.6(2)	C12A	C10A	C3A	111.2(3)
C11	C10	C3	110.1(2)	N2A	C11A	C10A	175.7(4)
C11	C10	C12	108.2(2)	F1A	C12A	C10A	106.7(3)
C12	C10	C3	111.1(2)	F1A	C12A	C13B	112.1(6)
N2	C11	C10	174.9(3)	F1A	C12A	C13A	106.7(3)
F1	C12	C10	106.9(2)	C13B	C12A	C10A	123.7(5)
F1	C12	C13	108.2(2)	C13A	C12A	C10A	111.7(3)
C13	C12	C10	115.3(2)	C14B	C13B	C12A	115.9(7)
C14	C13	C12	114.1(3)	C15B	C14B	C13B	115.7(8)
C15	C14	C13	113.3(3)	C16B	C15B	C14B	118.4(9)
C16	C15	C14	117.2(3)	C15B	C16B	C17B	113.5(9)
C15	C16	C17	117.3(4)	C12A	C13A	C14A	111.6(4)
O1A	S1A	O3A	111.16(14)	C15A	C14A	C13A	112.4(4)
O1A	S1A	N1A	105.54(13)	C14A	C15A	C16A	115.0(5)
O2A	S1A	O1A	120.49(14)	C17A	C16A	C15A	114.8(5)

Table S-15. Torsion Angles for 10a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	O2	C1	C2	94.8(3)	Si1A	O4A	C3A	C2A	67.7(3)
S1	N1	C10	C3	89.2(3)	Si1A	O4A	C3A	C10A	−168.63(18)
S1	N1	C10	C11	-33.3(3)	F1A	C12A	C13B	C14B	57.5(12)
S1	N1	C10	C12	-150.9(2)	F1A	C12A	C13A	C14A	59.9(5)
Si1	O4	C3	C2	-67.6(3)	O1A	S1A	O3A	C1A	-68.8(2)
Si1	O4	C3	C10	168.25(18)	O1A	S1A	N1A	C10A	158.9(2)
F1	C12	C13	C14	-58.7(4)	O2A	S1A	O3A	C1A	160.3(2)
O1	S1	O2	C1	68.1(2)	O2A	S1A	N1A	C10A	-70.1(3)
O1	S1	N1	C10	-159.0(2)	O3A	S1A	N1A	C10A	41.1(3)
O2	S1	N1	C10	-41.5(3)	O3A	C1A	C2A	C3A	75.8(3)
O2	C1	C2	C3	-76.1(3)	O4A	Si1A	C6A	C7A	58.4(3)
O3	S1	O2	C1	-160.7(2)	O4A	Si1A	C6A	C8A	177.6(2)
O3	S1	N1	C10	70.3(3)	O4A	Si1A	C6A	C9A	-61.3(3)
O4	Si1	C6	C7	-56.2(3)	O4A	C3A	C10A	N1A	-54.6(3)
O4	Si1	C6	C8	-175.4(2)	O4A	C3A	C10A	C11A	-177.7(3)
O4	Si1	C6	C9	64.2(3)	O4A	C3A	C10A	C12A	62.5(3)
O4	C3	C10	N1	54.2(3)	N1A	S1A	O3A	C1A	45.2(2)
O4	C3	C10	C11	177.8(2)	N1A	C10A	C12A	F1A	-62.0(3)
O4	C3	C10	C12	-62.2(3)	N1A	C10A	C12A	C13B	165.7(7)

N1	S1	O2	C1	-45.4(2)	N1A	C10A	C12A	C13A	-178.2(3)
N1	C10	C12	F1	61.3(3)	C1A	C2A	C3A	O4A	60.9(3)
N1	C10	C12	C13	-178.3(2)	C1A	C2A	C3A	C10A	-56.7(3)
C1	C2	C3	O4	-61.5(3)	C2A	C3A	C10A	N1A	68.1(3)
C1	C2	C3	C10	56.9(3)	C2A	C3A	C10A	C11A	-55.0(3)
C2	C3	C10	N1	-68.7(3)	C2A	C3A	C10A	C12A	-174.8(2)
C2	C3	C10	C11	54.9(3)	C3A	C10A	C12A	F1A	178.5(2)
C2	C3	C10	C12	174.9(2)	C3A	C10A	C12A	C13B	46.2(8)
C3	C10	C12	F1	-179.7(2)	C3A	C10A	C12A	C13A	62.2(4)
C3	C10	C12	C13	-59.4(3)	C4A	Si1A	O4A	C3A	-89.3(2)
C4	Si1	O4	C3	89.8(2)	C4A	Si1A	C6A	C7A	-58.3(3)
C4	Si1	C6	C7	60.6(3)	C4A	Si1A	C6A	C8A	60.9(3)
C4	Si1	C6	C8	-58.6(3)	C4A	Si1A	C6A	C9A	-178.0(2)
C4	Si1	C6	C9	-178.9(2)	C5A	Si1A	O4A	C3A	32.9(3)
C5	Si1	O4	C3	-32.1(3)	C5A	Si1A	C6A	C7A	175.3(2)
C5	Si1	C6	C7	-173.2(2)	C5A	Si1A	C6A	C8A	-65.5(3)
C5	Si1	C6	C8	67.6(3)	C5A	Si1A	C6A	C9A	55.6(3)
C5	Si1	C6	C9	-52.7(3)	C6A	Si1A	O4A	C3A	151.9(2)
C6	Si1	O4	C3	-151.1(2)	C10A	C12A	C13B	C14B	-172.3(8)
C10	C12	C13	C14	-178.4(3)	C10A	C12A	C13A	C14A	176.2(4)
C11	C10	C12	F1	-58.7(3)	C11A	C10A	C12A	F1A	57.8(3)
C11	C10	C12	C13	61.6(3)	C11A	C10A	C12A	C13B	-74.5(7)
C12	C13	C14	C15	179.2(3)	C11A	C10A	C12A	C13A	-58.4(4)
C13	C14	C15	C16	174.7(4)	C12A	C13B	C14B	C15B	177.8(10)
C14	C15	C16	C17	-174.8(5)	C12A	C13A	C14A	C15A	-178.9(5)
S1A	O3A	C1A	C2A	-94.0(3)	C13B	C14B	C15B	C16B	64.7(16)
S1A	N1A	C10A	C3A	-88.6(3)	C14B	C15B	C16B	C17B	73.8(16)
S1A	N1A	C10A	C11A	33.4(3)	C13A	C14A	C15A	C16A	-175.5(5)
S1A	N1A	C10A	C12A	151.0(2)	C14A	C15A	C16A	C17A	-173.7(6)

Table S-16. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 10a.

Atom	*x*	*y*	*z*	U(eq)
H1	6430(20)	7090(30)	6565(10)	35(10)
H1B	6662.2	8180.17	7187.53	33
H1C	6228.1	8191.02	7628.24	33
H2A	5067.32	9410.35	7286.92	29
H2B	4534.81	7980.87	7329.22	29
H3	4224.03	8811.94	6695.6	26
H4A	6385.4	11062.01	7215.88	44

H4B	6866.46	12217.06	6948.39	44
H4C	7324.66	10730.04	6935.94	44
H5A	4081.77	11393.48	6396.44	45
H5B	4603.68	12586.6	6643.35	45
H5C	4223.64	11265.69	6865.86	45
H7A	7820.45	10667.69	6204.07	57
H7B	7602.05	10656.01	5737.09	57
H7C	7169.5	9476.05	6007.83	57
H8A	5965.61	13270.57	6062.31	64
H8B	6904.83	12945.64	5781.66	64
H8C	7070.41	12978.13	6251.48	64
H9A	5399.63	9943.03	5738.56	67
H9B	5869.71	11101.97	5469.56	67
H9C	4949.64	11433.2	5758.91	67
H12	5174.75	7569.33	5987.16	32
H13E	3105.97	6997.67	6179.86	39
H13F	3560.79	8474.67	6131.14	39
H14E	3828.74	8067.55	5455.41	47
H14F	3389.68	6580.59	5502.76	47
H15E	1783.67	7415.03	5641.54	62
H15F	2204.47	8915.16	5636.7	62
H16E	1976.85	7237.78	4976.97	84
H16F	2494.55	8683.02	4960.64	84
H17G	888.04	8889.99	4720.34	118
H17H	914.19	9621.49	5141.61	118
H17I	423.07	8158.24	5098.01	118
H1A	11420(20)	7160(30)	6549(10)	38(10)
H1AA	11147.67	6057.84	7630.66	34
H1AB	11620.04	6058.64	7196.27	34
H2AA	9486.04	6268.74	7311.94	30
H2AB	10021.11	4839.1	7276.74	30
H3A	9217.97	5428.92	6676.18	29
H4AA	12263.87	3577.62	6969.92	42
H4AB	11888.51	2051.59	6947.6	42
H4AC	11307.49	3101.25	7222.16	42
H5AA	9210.18	2949.04	6848.96	45
H5AB	9599.36	1652.76	6616.63	45
H5AC	9092.38	2874.86	6377.69	45
H7AA	12262.15	4745.62	6025.19	56
H7AB	12727.61	3524.21	5779.73	56
H7AC	12851.35	3558.76	6251.2	56
H8AA	12062.88	1238.12	6261.6	75

H8AB	11941.57	1298.42	5790.28	75
H8AC	10969.35	998.99	6056.24	75
H9AA	10013	2968.98	5753.8	74
H9AB	10971.47	3164.23	5472.63	74
H9AC	10569.43	4394.98	5730.82	74
H12B	10301.43	6787.82	5991.73	40
H12A	10193.33	6655.78	5968.7	40
H13A	8794.88	5556.39	6038.47	52
H13B	8155.99	6918.95	6032.06	52
H14A	8690.87	7361.51	5385	57
H14B	9368.23	6031.18	5390.57	57
H15A	7945.99	5598.31	5024.55	62
H15B	7888.69	4730.12	5418.87	62
H16A	6728.87	6373.93	5663.55	68
H16B	6308.45	5433.25	5314.29	68
H17A	7141	7939.55	5111.17	91
H17B	6000.36	7887	5271.76	91
H17C	6285.37	7098.9	4876.42	91
H13C	8139.8	7329.18	6186.5	52
H13D	8542.42	5826.27	6129.04	52
H14C	8422.34	7764.28	5503.61	57
H14D	8803.21	6251.9	5447.99	57
H15C	6789.25	7020.36	5650.27	62
H15D	7156.2	5494.65	5630.9	62
H16C	7124.97	7211.16	4960.97	68
H16D	7366.58	5641.08	4954.51	68
H17D	5737.49	6075.83	4720.07	91
H17E	5453.97	6737.85	5135.09	91
H17F	5703.55	5169.06	5110.12	91

Table S-17. Atomic Occupancy for 10a.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
H12B	0.296(4)	H12A	0.704(4)	C13B	0.296(4)
H13A	0.296(4)	H13B	0.296(4)	C14B	0.296(4)
H14A	0.296(4)	H14B	0.296(4)	C15B	0.296(4)
H15A	0.296(4)	H15B	0.296(4)	C16B	0.296(4)
H16A	0.296(4)	H16B	0.296(4)	C17B	0.296(4)
H17A	0.296(4)	H17B	0.296(4)	H17C	0.296(4)
C13A	0.704(4)	H13C	0.704(4)	H13D	0.704(4)
C14A	0.704(4)	H14C	0.704(4)	H14D	0.704(4)

C15A	0.704(4)	H15C	0.704(4)	H15D	0.704(4)		
C16A	0.704(4)	H16C	0.704(4)	H16D	0.704(4)		
C17A	0.704(4)	H17D	0.704(4)	H17E	0.704(4)		
H17F	0.704(4)						

VIII. References for X-ray.

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