Acid Mediated Formation of Trifluoromethyl Sulfonic Acid Esters from Sulfonic Acids and a Hypervalent Iodine Trifluoromethylating Agent

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Supporting Information

Experimental Procedures

General. Reactions were carried out under an argon atmosphere using Schlenk techniques. 1H, 19F, 13C NMR spectra were recorded on Bruker Avance spectrometers AC 200, DPX 250. DPX 300, DPX 400 and DPX500. ^{1}H positive chemical shifts in ppm are downfield from tetramethylsilane. ^{19}F NMR spectra were referenced to external $CFCl_3$. Mass spectra were measured by the MS service of the Laboratorium für organische Chemie (ETH Zürich).

General Method for the Trifluoromethylation of Sulfonic Acids:
Sulfonic acid (3, 1 mmol, 1 eq) and reagent (1, 1.1 mmol, 1.1 eq) were placed in a Schlenk under an atmosphere of argon, then $CHCl_3$ (5 ml) was added. The resulting white suspension was stirred over night at rt. The suspension was concentrated at reduced pressure and purified by FCC.

Trifluoromethyl naphthalene-2-sulfonate (5a)
Purified by FCC (Pentane/Et_2O 20:1) to give 76% of white solid.
mp 49.5°C; δ_H(500MHz; $CDCl_3$; Me_4Si) 7.73 (1 H, dt, *J* = 1.0 and 7.5, $C_{Ar}H$), 7.80 (1 H, dt, *J* = 1.0 and 7.5, C_{ArH}), 7.97 (1 H, dd, *J* = 8.5 and 1.5, $C_{Ar}H$), 8.01 (1 H, d, *J* = 8.0, C_{ArH}), 8.07-8.11 (2 H, m, $C_{Ar}H$), 8.65 (1H, s, $C_{Ar}H$); δ_C(75MHz; $CDCl_3$; Me_4Si) 118.5 (q, *J* = 266.0, CF_3), 122.2 (s,C_{Ar}), 128.1 (s, C_{Ar}), 128.3 (s, C_{Ar}), 129.7 (s, C_{Ar}), 130.1 (s, C_{Ar}), 130.5 (s, C_{Ar}), 131.1 (s, C_{Ar}), 131.8 (s, C_{Ar}), 131.9 (q, *J* = 0.8, *C*SO_3CF_3), 136.0 (s, C_{Ar}); δ_F(188MHz $CDCl_3$; $CFCl_3$) -53.8 (s); m/z (EI) 276.0063 (M+, 55%), 191 (1, M –OCF_3), 127 (100, M –SO_3CF_3); HRMS (EI) calcd for $C_{11}H_7F_3O_3S$: 276.0063, found 276.0063

Trifluoromethyl (7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (5b)
Purified by FCC (cHex/EtOAc 1:1) to give 62% of a white solid.
mp 61°C; δ_H (500MHz; $CDCl_3$; Me_4Si) 0.95 (3 H, s, CH_3), 1.16 (3 H, s, CH_3), 1.49 – 1.54 (1 H, m), 1.74 – 1.79 (1H, m), 2.02 (1 H, d, *J* = 19.0), 2.10 – 2.15 (1 H, m), 2.20 – 2.21 (1 H, m), 2.39 – 2.48 (2 H, m), 3.36 (1 H, d, *J* = 15.0, $CH_2SO_3CF_3$), 3.95 (1 H, d, *J* = 15.0, $CH_2SO_3CF_3$); δ_C(75MHz; $CDCl_3$; Me_4Si) 19.4 (s, CH_3), 19.5 (s, CH_3), 25.2, 26.7, 42.2, 42.8, 48.0, 51.7 (q, *J* = 1.4, *C*SO_3CF_3), 58.1, 118.4 (q, *J* = 265.9, CF_3), 212.8 (s, C=O); δ_F(282MHz, $CDCl_3$, CFCl3) -53.9; m/z (EI) 300.0636 (M+, 1%), 231 (0.3, M –CF_3), 151 (8, M –SO_3CF_3), 123 (7, M –SO_3CF_3 –$(CH_2)_2$), 109 (100, M –SO_3CF_3 – CH_2CO); HRMS (EI) calcd for $C_{11}H_{15}F_3O_4S$: 300.0638, found 300.0636

Trifluoromethyl 4-chlorobenzenesulfonate (5d)
Purified by FCC (cHex/DCM 20:1) to give 51% of a clear colorless oil.
δ_H(300MHz; $CDCl_3$; Me_4Si) 7.63 (2 H, d, *J* = 8.7, $C_{Ar}H$), 7.98 (2H, d, *J* = 8.7, $C_{Ar}H$): δ_C(75MHz; $CDCl_3$; Me_4Si) 118.4 (q, *J* = 266.6, CF_3), 129.9 (s, C_{Ar}), 130.1 (s, C_{Ar}), 133.6 (q, *J* = 1.0, *C*SO_3CF_3), 142.7 (s, $C_{Ar}Cl$); δ_F(282MHz; $CDCl_3$; $CFCl_3$) -53.9 (s); m/z (EI) 259.9516 (M+, 80%), 175 (78, M –OCF_3), 111 (100, M –SO_3CF_3), HRMS (EI) calcd for $C_7H_4ClF_3O_3S$: 259.9517, found 259.9516

Trifluoromethyl benzenesulfonate (5e)
Purified by FCC (cHex/Et_2O 10:1) to give 42% of a clear colorless oil.
δ_H(300MHz; $CDCl_3$; Me_4Si) 7.65 (2 H, t, J = 7.5, m.-H), 7.80 (1 H, t, J = 7.5, p.-H), 8.04 (2 H, d, J = 7.5, o.-H); δ_C(75MHz; $CDCl_3$; Me_4Si) 118.4 (q, J = 266.0, CF_3), 128.5 (s, C_{Ar}), 129.7 (s, C_{Ar}), 135.2 (q, J = 0.8, $\mathit{C}SO_3CF_3$), 135.7 (s, C_{Ar}); δ_F(282MHz; $CDCl_3$; $CFCl_3$) -54.0 (s); m/z (EI) 225.9905 (M+, 31%), 141 (M –OCF_3), 77 (M –SO_3CF_3); HRMS (EI) calcd for $C_7H_5F_3O_3S$: 225.9906, found 225.9905

Trifluoromethyl 4-methylbenzenesulfonate (5f)
Purified by FCC (cHex/EtOAc 1:1) to give 39% of a clear slightly yellow oil.
δ_H(300MHz; $CDCl_3$; Me_4Si) 2.51 (3 H, s, CH_3), 7.44 (2 H, d, J = 8.1, $C_{Ar}H$), 7.91 (2H, d, J = 8.4, $C_{Ar}H$): δ_C(75MHz; $CDCl_3$; Me_4Si) 21.7 (s, CH_3), 118.4 (q, J = 265.7, CF_3), 128.6 (s, C_{Ar}), 130.3 (s, C_{Ar}), 132.2 (q, J = 0.8,$\mathit{C}SO_3CF_3$), 147.3 (s, C_{Ar}-CH_3); δ_F(188MHz $CDCl_3$; $CFCl_3$) -54.0 (s); m/z (EI) 240.0061 (M+, 39%), 155 (34, M -OCF_3), 91 (100, M -SO_3CF_3); HRMS (EI) calcd for $C_8H_7F_3O_3S$: 240.0063, found) 240.0061

Trifluoromethyl 4-ethylbenzenesulfonate (5g)
Purified by FCC (cHex/EtOAc 20:1) to give 32% of a clear colorless oil.
δ_H(300MHz; $CDCl_3$; Me_4Si) 1.31 (3H. t, J = 7.6, $CH_2\mathit{CH_3}$), 2.81 (2H, q, J = 7.6, $\mathit{CH_2}CH_3$), 7.47 (2H, d, J = 8.7, $C_{Ar}H$), 7.94 (2H, d, J = 8.4, $C_{Ar}H$): δ_C(63MHz; $CDCl_3$; Me_4Si) 14.8 (s, $CH_2\mathit{C}H_3$), 29.0 (s, $\mathit{C}H_2CH_3$), 118.4 (q, J = 267.8 CF_3), 128.7 (s, C_{Ar}), 129.2 (s, C_{Ar}), 132.3 (q, J = 0.9, $\mathit{C}SO_3CF_3$), 153.3 (s, $\mathit{C}_{Ar}CH_2CH_3$); δ_F(282MHz; $CDCl_3$; $CFCl_3$) -54.0 (s); m/z (EI) 254.0223 (M+, 28%), 239 (19, M –CH_3), 169 (7, M –OCF_3) 105 (100, M –SO_3CF_3); HRMS (EI) calcd for $C_9H_9F_3O_3S$: 254.0218, found 254.0223

Trifluoromethyl 4-hydroxybenzenesulfonate (5h)
Purified by FCC (cHex/EtOAc 1:1) to give 39% of a clear slightly yellow oil.
δ_H(300MHz; $CDCl_3$; Me_4Si) 7.05 (2 H, d, J = 9.0, $C_{Ar}H$), 7.91 (2H, d, J = 9.0, $C_{Ar}H$): δ_C(63MHz; $CDCl_3$; Me_4Si) 116.6 (s, C_{Ar}), 118.4 (q, J = 267.9 CF_3), 125.7 (q, J = 0.7, $\mathit{C}SO_3CF_3$), 131.4 (s, C_{Ar}), 162.5 (s, $\mathit{C}_{Ar}OH$); δ_F(282MHz; $CDCl_3$; $CFCl_3$) -54.1 (s); m/z (EI) 241.9860 (M+, 56%), 157 (100, M –OCF_3), 93 (41, M –SO_3CF_3); HRMS (EI) calcd for $C_7H_5F_3O_4S$: 241.9856, found 241.9860

Rate Studies:

Reagents and solvents:

Toluenesulfonic acid monohydrate was purchased from Fluka and used as supplied (99%), (+/-)-10-Camphorsulfonic acid was purchased from ABCR-Chemicals and used as supplied (98%), **1** was synthesized as described in reference 5 and stored under ambient conditions, Chloroform-*d* was purchased from ARMAR Chemicals (99.8%) and stored over molecular sieves, *tert*-butanol was acquired from the ETH stock room and used as supplied.

General procedure for rate studies:

All reactions were monitored by ^{19}F-NMR spectroscopy using a Bruker AVANCE DPX 400 MHz NMR spectrometer operating at 376 MHz. Experimental temperatures were maintained using a Bruker BVT3000 temperature control unit calibrated with a digital thermometer fit to a 5mm NMR tube. Initially, the temperature in the spectrometer was equilibrated on a “standard” sample containing the non-limiting reagent(s) and internal standard ($PhCF_3$) at reaction run concentration and the shim was optimized. A second tube charged with correct amount of the non-limiting reagent and the appropriate amount of limiting reagent was added. The tube was shaken vigorously for 10 – 15 seconds after which it was exchanged with the standard in the spectrometer and the acquisition program was started.

Acquisition program:

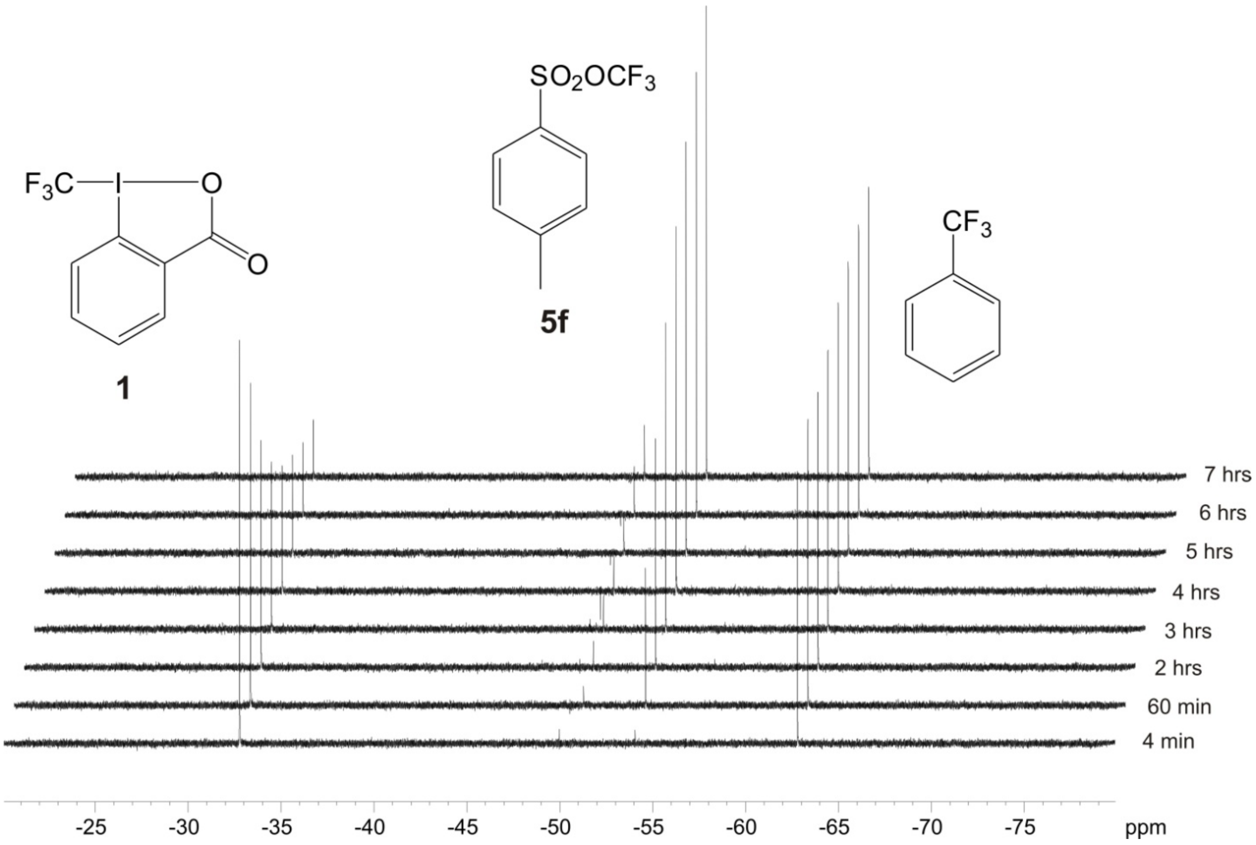
A pseudo 2D NMR experiment designed for kinetic measurements was utilized to monitor reaction progress for all rate experiments. The time interval between individual acquisitions (d1), number of acquisitions averaged (one data point was often obtained as the average of 2 or 4 individual acquisitions) and total number of data points could be varied to effect the frequency of acquisition, signal to noise ratio and experiment duration, respectively.

Data Processing:

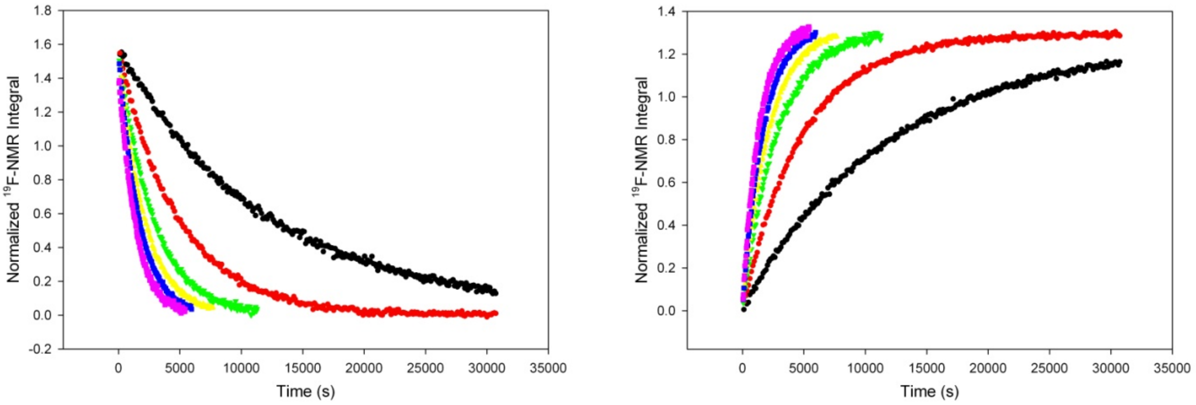
For each data point, integrals corresponding to the ^{19}F-NMR resonances of the trifluoromethyl group of **1**, the trifluoromethyl group of the **5** formed and $PhCF_3$ internal standard were extracted using Bruker’s XWinNMR 3.5 software package. The resulting data were exported as tables of integral values for each signal over all data points measured. The ^{19}F-NMR integration data were then imported into SigmaPlot10 and the data point numbers transformed into time values by multiplying by the correct acquisition duration (d1 + 3s) and number of acquisitions averaged per data point. The time vs. ^{19}F-NMR integration data thus generated were fit to $[\mathbf{1}]=y_0+a\cdot\exp(-kt)$ for exponential decay of **1** and $[\mathbf{5}]=y_0+a\cdot(1-\exp(-kt))$ for exponential increase to maximum concentration of **5** in order to extract observed pseudo first-order rate constants (k_{obs}). A plot of the ^{19}F-NMR integration of the internal standard over time was also generated to confirm that the ratio of ^{19}F-NMR integral to concentration remained constant over the duration of the experiment. Plots of observed rate constants for different non-limiting reagent concentrations were could thus be generated.

Role of 3:

Six runs were carried out in which the reaction of 0.005M **1** with 0.05M, 0.10M, 0.15M, 0.20M, 0.25M and 0.3 M **3f** in 5:1 $CDCl_3$:^{t}BuOH at 298 K was monitored as described above. Integration data for signals at ~-33 ppm, -54.1 ppm and -62.8 ppm (See SI Figure 1) corresponding to the concentrations of **1**, **5f** and $PhCF_3$ were extracted. Overlaid plots of these data after normalization to the average integral of the internal standard of known concentration are shown in SI Figure 2. The observed rate constants derived by the above mentioned curve fitting are summarized in SI Table 1. Experimental uncertainties were left untreated.



SI Figure 1. Stacked plot of selected NMR spectra acquired by monitoring the reaction of 0.005M **1** with 0.05M **3f** in 5:1 $CDCl_3$:^{t}BuOH at 298 K

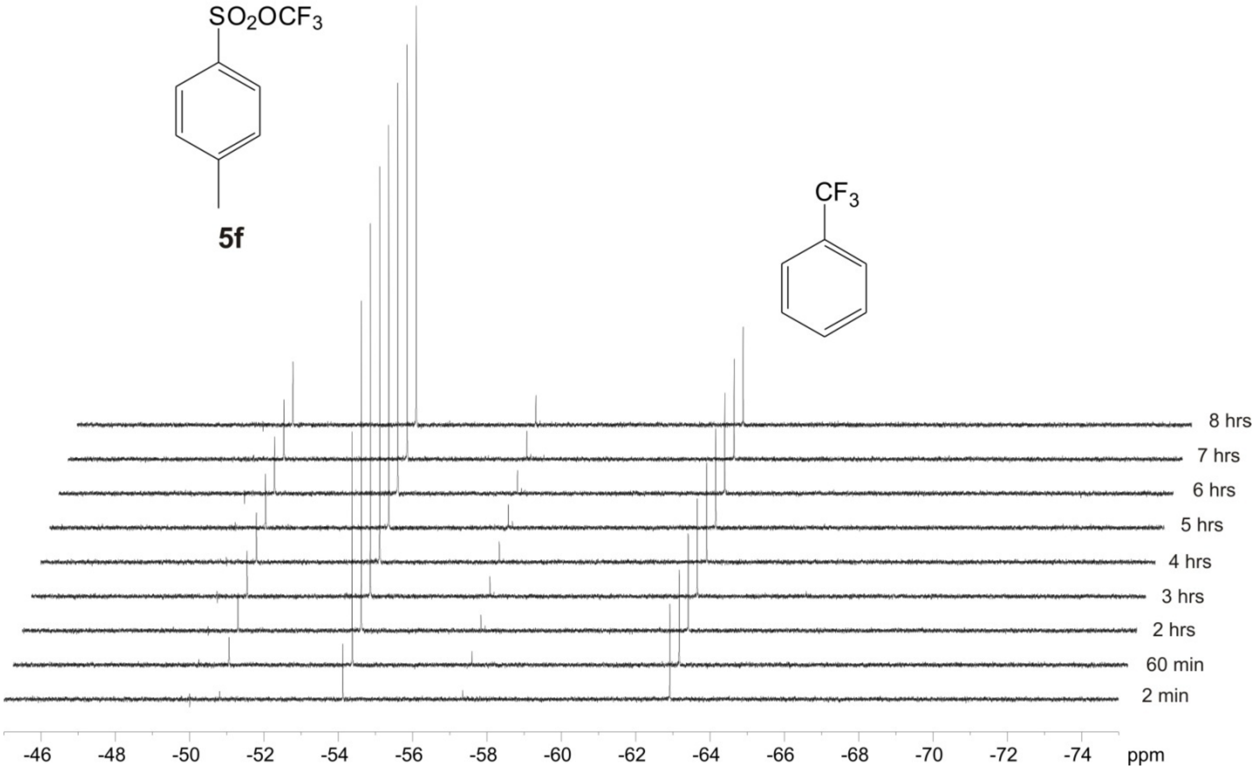


SI Figure 2. Plots of normalized ^{19}F-NMR Integrals versus time showing decay of **1** (left) and formation of **5f** (right) for the reaction of 0.005M **1** with 0.05M (black), 0.10M (red), 0.15M (green), 0.20M (yellow), 0.25M (blue) and 0.3 M (pink) **3f** in 5:1 $CDCl_3$:^{t}BuOH at 298 K.

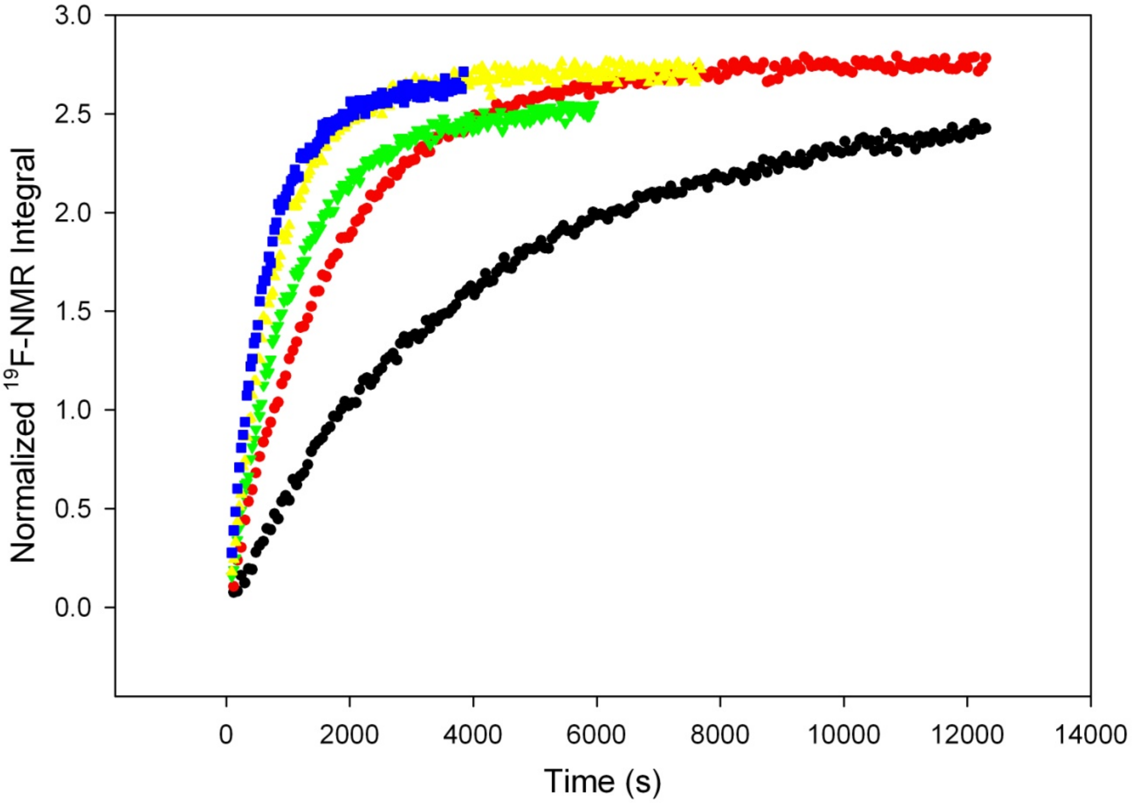
SI Table 1. Observed rate constants (k_{obs}) derived by un-weighted least-squares fitting of ^{19}F-NMR integration data recorded by monitoring the formation of **5f** by reaction of 0.005M **1** with varying concentrations of **3f** as described above.

[**3f**] (mol/L)	k_{obs} (s^{-1})
0.05	$8.43 \cdot 10^{-5}$
0.10	$2.06 \cdot 10^{-4}$
0.15	$3.56 \cdot 10^{-4}$
0.20	$4.75 \cdot 10^{-4}$
0.25	$6.01 \cdot 10^{-4}$
0.30	$7.54 \cdot 10^{-4}$

Role of **1**:
Five runs were carried out in which the reaction of 0.003M **3f** with 0.03M, 0.06M, 0.09M, 0.12M and 0.15M **1** in 5:1 $CDCl_3$:^{t}BuOH at 313 K was monitored as described above. Integration data for signals at -54.1 ppm and -62.8 ppm (See SI Figure 3) corresponding to the concentrations of **5f** and $PhCF_3$ were extracted. Overlaid plots of these data after normalization to the average integral of the internal standard of known concentration are shown in SI Figure 4. The observed rate constants derived by the above-mentioned curve fitting are summarized in SI Table 2. Experimental uncertainties were left untreated.



SI Figure 3. Stacked plot of selected NMR spectra acquired by monitoring the reaction of 0.003M **3f** with 0.03M **1** in 5:1 $CDCl_3$:^{t}BuOH at 313 K.

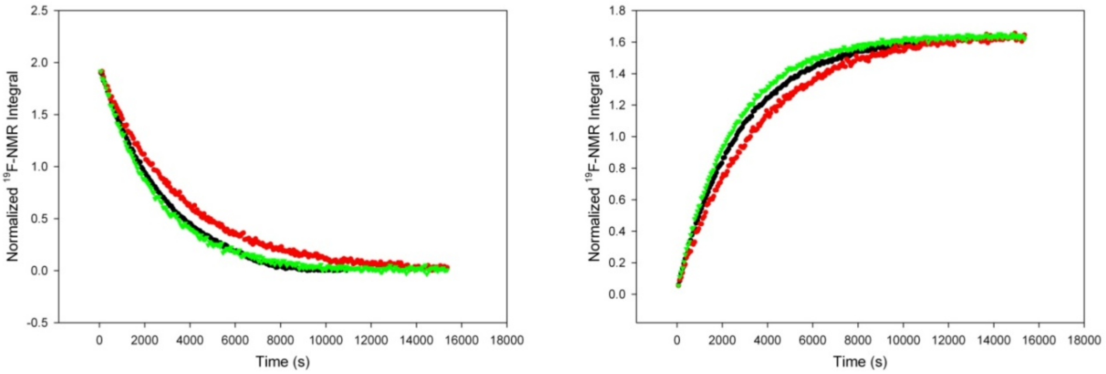


SI Figure 4. Plots of normalized ^{19}F-NMR Integrals versus time showing formation of **5f** for the reaction of 0.003M **3f** with 0.03M (black), 0.06M (red), 0.09M (green), 0.12M (yellow) and 0.15M (blue) **1** in 5:1 $CDCl_3$:^{t}BuOH at 313 K.

SI Table 2. Observed rate constants (k_{obs}) derived by un-weighted least-squares fitting of ^{19}F-NMR integration data recorded by monitoring the formation of **5f** by reaction of 0.003M **3f** with varying concentrations of **1** as described above.

[**1**] (mol/L)	k_{obs} (s^{-1})
0.03	$2.35 \cdot 10^{-4}$
0.06	$5.88 \cdot 10^{-4}$
0.09	$1.00 \cdot 10^{-3}$
0.12	$1.28 \cdot 10^{-3}$
0.15	$1.65 \cdot 10^{-3}$

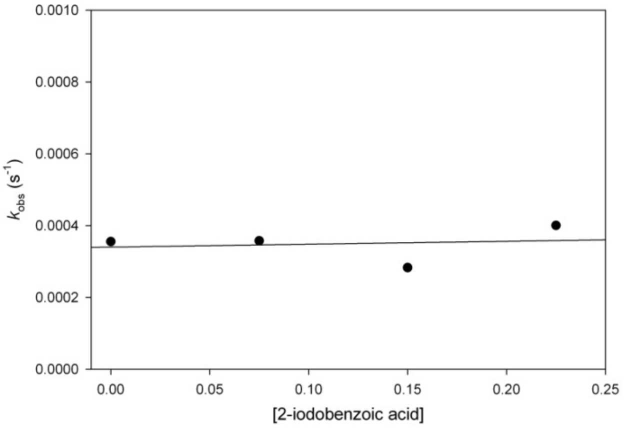
Role of 2-iodobenzoic acid:
Three runs were carried out in which the reaction of 0.005M **1** with 0.15M **3f** in the presence of 0.075M, 0.15M and 0.225M of additional 2-iodobenzoic acid in 5:1 $CDCl_3$:*ᵗ*BuOH at 313 K was monitored as described above. Integration data for signals at ~-33 ppm, -54.1 ppm and -62.8 ppm (See SI Figure 1) corresponding to the concentrations of **1**, **5f** and $PhCF_3$ were extracted. Overlaid plots of these data after normalization to the average integral of the internal standard of known concentration are shown in SI Figure 5. The observed rate constants derived by the above-mentioned curve fitting protocol and are summarized in SI Table 3. Experimental uncertainties were left untreated.



SI Figure 5. Plots of normalized ^{19}F-NMR Integrals versus time showing decay of **1** (left) and formation of **5f** (right) for the reaction of 0.005M **1** with 0.15M **3f** in the presence of 0.075M (black), 0.15M (red) and 0.225M (green) 2-iodobenzoic acid in 5:1 $CDCl_3$:*ᵗ*BuOH at 298 K.

SI Table 3. Observed rate constants (k_{obs}) derived by un-weighted least-squares fitting of ^{19}F-NMR integration data recorded by monitoring the formation of **5f** by reaction of 0.005M **1** 0.15M **3f** in the presence of varying concentrations of 2-iodobenzoic acid as described above.

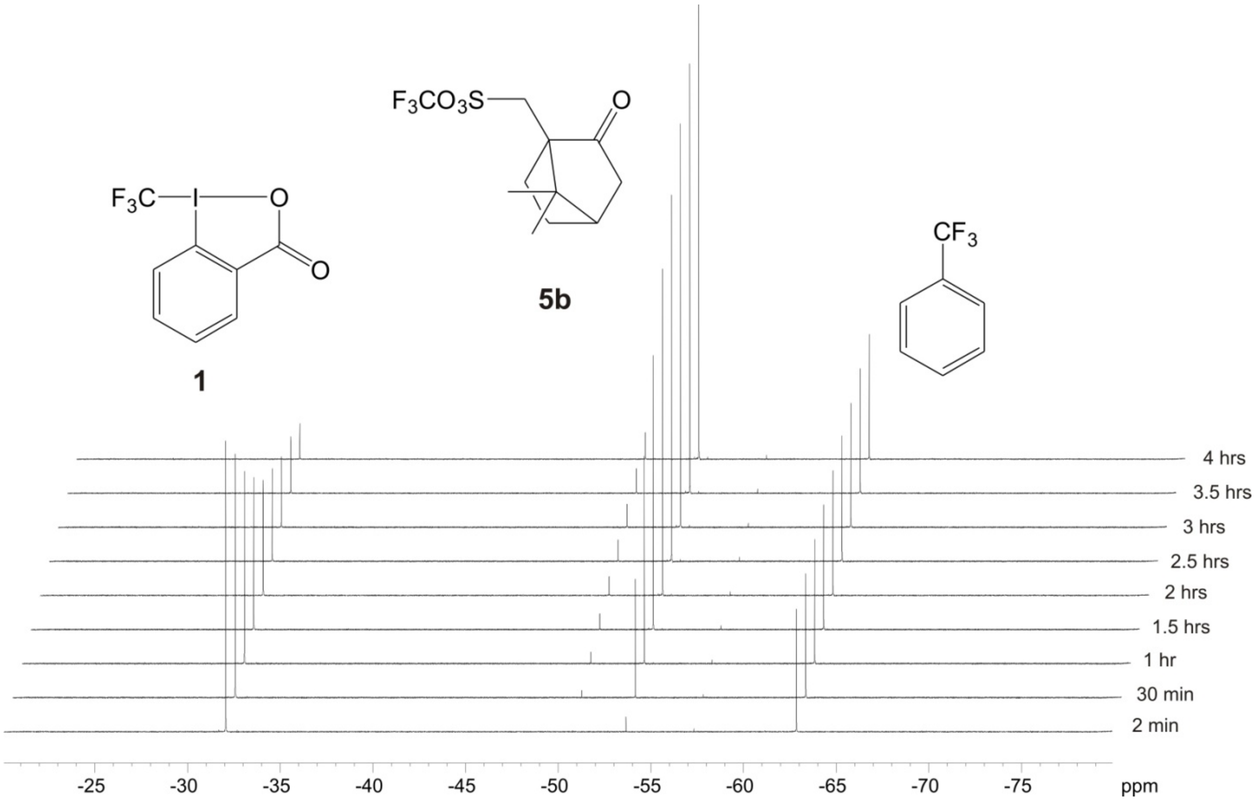
[2-iododbenzoic acid] (mol/L)	k_{obs} (s^{-1})
0.00	$3.56 \cdot 10^{-4}$
0.075	$3.58 \cdot 10^{-4}$
0.15	$2.83 \cdot 10^{-4}$
0.225	$4.01 \cdot 10^{-4}$



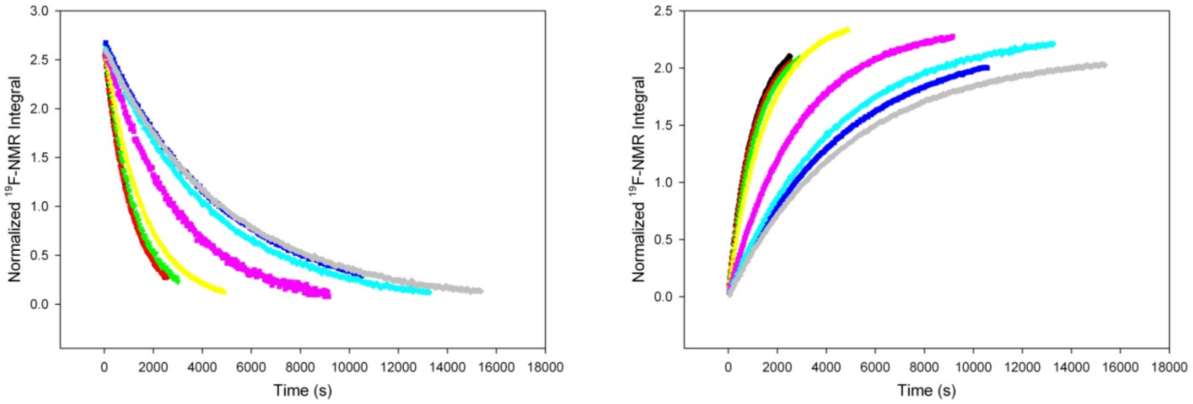
SI Figure 6. Plot of k_{obs} versus [2-iodobenzoic acid] for the trifluoromethylation **3f** (0.15M) with **1** (0.005M) in a 5:1 mixture of $CDCl_3$ and ^{t}BuOH in the presence of varying amounts of 2-iodobenzoic acid at 298 K. The line is the result of an unweighted linear least-squares fit to $k_{obs} = y_0 + m$[2-iodobenzoic acid] where $y_0 = (3.4 \pm 0.5) \times 10^{-4}$ and $m = (1 \pm 4) \times 10^{-4}$.

Role of *tert*-butanol:

Eight runs were carried out in which the reaction of 0.005M **1** with 0.15M **3b** in the presence of 0.00M, 0.005M, 0.05M, 0.5M, 1.1M, 1.7M, 2.4M and 3.7M of additional *tert*-butanol was monitored as described above. Integration data for signals at ~-32 ppm, -53.7 ppm and -62.8 ppm (See SI Figure 7) corresponding to the concentrations of **1**, **5b** and $PhCF_3$ were extracted. Overlaid plots of these data normalized to average internal standard integral are shown in SI Figure 8. The observed rate constants derived by the above mentioned curve fitting protocol and summarized in SI Table 4. Experimental uncertainties were left untreated.



SI Figure 7. Stacked plot of selected NMR spectra acquired by monitoring the reaction of 0.005M **1** with 0.15M **3b** in $CDCl_3$ in the presence of 2.43M ^tBuOH at 300 K.



SI Figure 8. Plots of normalized ^{19}F-NMR Integrals versus time showing decay of **1** (left) and formation of **5b** (right) for the reaction of 0.005M **1** with 0.15M **3b** in $CDCl_3$ in the presence of 0.0M(black), 0.005M (red), 0.05M (green), 0.5M (yellow), 1.1M (pink) and 1.7 M (light blue), 2.4M (blue) and 3.7M (grey) ^{t}BuOH at 300 K.

SI Table 4. Observed rate constants (k_{obs}) derived by un-weighted least-squares fitting of ^{19}F-NMR integration data recorded by monitoring the formation of **5b** by reaction of 0.005M **1** with 0.15M **3b** in $CDCl_3$ in the presence of varying concentrations of ^{t}BuOH as described above.

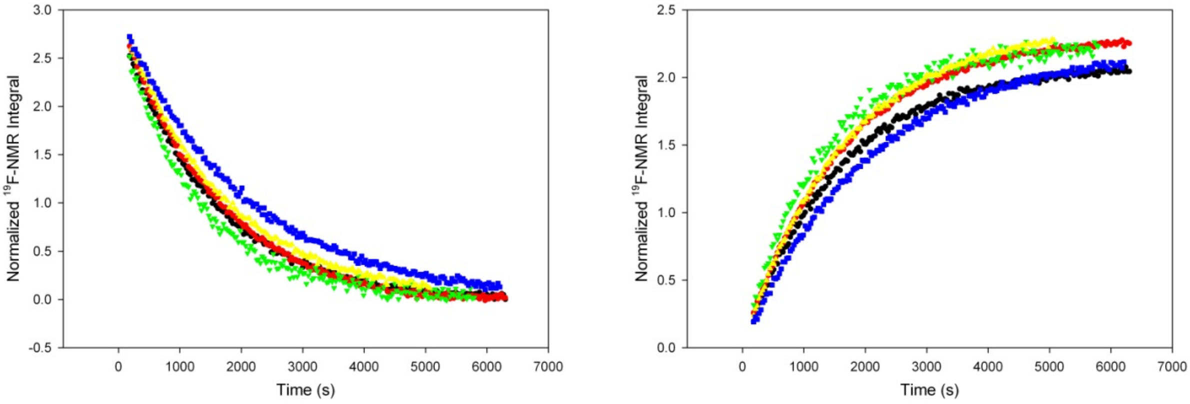
[^{t}BuOH] (mol/L)	k_{obs} (s^{-1})
0.00	$1.01 \cdot 10^{-3}$
0.005	$9.95 \cdot 10^{-4}$
0.05	$8.88 \cdot 10^{-4}$
0.5	$6.49 \cdot 10^{-4}$
1.1	$3.49 \cdot 10^{-4}$
1.7	$2.34 \cdot 10^{-4}$
2.4	$2.14 \cdot 10^{-4}$
3.7	$2.05 \cdot 10^{-4}$

Competition Studies:

Experimental

4-methoxybenzenesulfonic acid was synthesized from 4-methoxybenzenesulfonyl chloride (Fluka >98%) by refluxing in 1 – 2M HCl for 30 mins. After removal of the solvent, the remaining colorless oil was dissolved in a fixed amount of of 5:1 $CDCl_3$:^{t}BuOH and the concentration of 4-methoxybenzenesulfonic acid was determined relative to that of ^{t}BuOH by ^{1}H-NMR spectroscopy (an undetermined amount of water remained in the material). This process was used to obtain solutions of known concentrations for 4-fluorobenzenesulfonic acid and 4-trifluoromethylbenzenesulfonic acid from 4-fluorobenzenesulfonyl chloride (Fluka >98%) and 4-trifluoromethylbenzenesulfonyl chloride (Aldrich 97%). Solutions of known concentrations of toluenesulfonic acid monohydrate, benzenesulfonic acid monohydrate (TCI Deutschland 98%) and 4-nitrobenzenesulfonic acid hydrate (TCI Deutschland 98%) were prepared and the concentrations checked by ^{1}H-NMR spectroscopy. 1:1 mixtures of 0.07M of each 4-substituted benzenesulfonic acid with unsubstituted acid were prepared by mixing the correct amounts of the above mentioned solutions in NMR tubes. For each substrate pair (substituted plus unsubstituted benzenesulfonic acid) two NMR tubes were prepared. An equivalent amount of **1** was added to each of the 10 reaction tubes and one set of five samples was heated on an oil bath to 323 K and the other was allowed to stand at 298 K overnight. The ^{19}F-NMR spectra of all 10 samples were recorded the following day, the ratios of substituted to unsubstituted trifluoromethylester were calculated on the basis of signal integration and the logarithms thereof tabulated (See SI Table 6). In addition, to check the validity of the competition study and verify that reaction of substituted and unsubstituted acid did not interfere with one another a series of pseudo first-order rate studies were carried out on the reaction of 0.15M **3c**, **3d**, **3e**, **3f** and **3i** with 0.01M **1** in 5:1 $CDCl_3$:^{t}BuOH at 303 K (See SI Figure 9). The observed rate constants derived as described in the rate studies section are summarized in SI Table 5. Ratios of rate constants and logarithms thereof determined by this method are shown in SI Table 7 along with σ values taken from reference 12.

Lastly, it is important to clarify that for linear least-squares regressions with the formula $y = a + bx$ the correlation r is defined in terms of the slope of the best fit line as $b = r(s_y / s_x)$ in which s_y and s_x are the standard deviations of the x and y data collected. In the case that $b \approx 0$ then $s_y \approx 0$, therefore the correlation is undefined. Since the slope of the best fit lines in figure 4 are within the uncertainty of the fits 0, it follows that the values for r calculated from the fit ($r = 0.60$ at 298 K and $r = 0.31$ at 323K) do not give any information about the linearity of the data.



SI Figure 9. Plots of normalized ^{19}F-NMR Integrals versus time showing decay of **1** (left) and formation of **5** (right) for the reaction of 0.01M **1** with 0.15M **3c** (black), **3d** (green), **3e** (red), **3f** (yellow)and **3i** (blue) in 5:1 $CDCl_3$:^{t}BuOH at 303 K.

SI Table 5. Observed rate constants (k_{obs}) derived by un-weighted least-squares fitting of ^{19}F-NMR integration data recorded by monitoring the formation of **5** by reaction of 0.01M **1** with 0.15M **3** as described above.

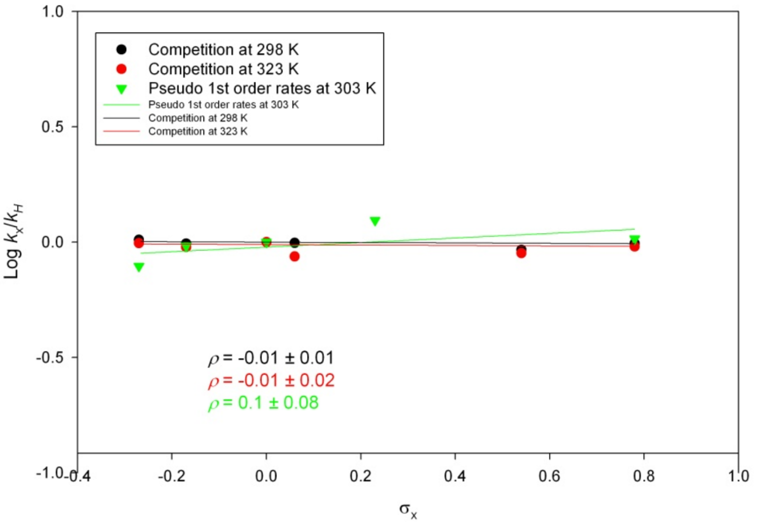
3	k_{obs} (s^{-1})
c	$6.56 \cdot 10^{-4}$
d	$7.88 \cdot 10^{-4}$
e	$6.35 \cdot 10^{-4}$
f	$6.10 \cdot 10^{-4}$
i	$5.00 \cdot 10^{-4}$

SI Table 6. Substituent effect data from ^{19}F-NMR competitions studies at 298 K and 323 K.

	Data from competition experiments		Data from rate experiments	
	$[P_X]$ / $[P_H]$ (298 K)	Log $[P_X]$ / $[P_H]$ (298 K)	$[P_X]$ / $[P_H]$ (323 K)	Log $[P_X]$ / $[P_H]$ (323 K)
$-NO_2$	0.9870	-0.006	0.9554	-0.020
$-CF_3$	0.9258	-0.034	0.8950	-0.048
–Cl	–	–	–	–
–F	0.9912	-0.004	0.8658	-0.063
–H	1	0	1	0
$-CH_3$	0.9840	-0.007	0.9513	-0.022
$-OCH_3$	1.0225	0.010	0.9896	-0.005

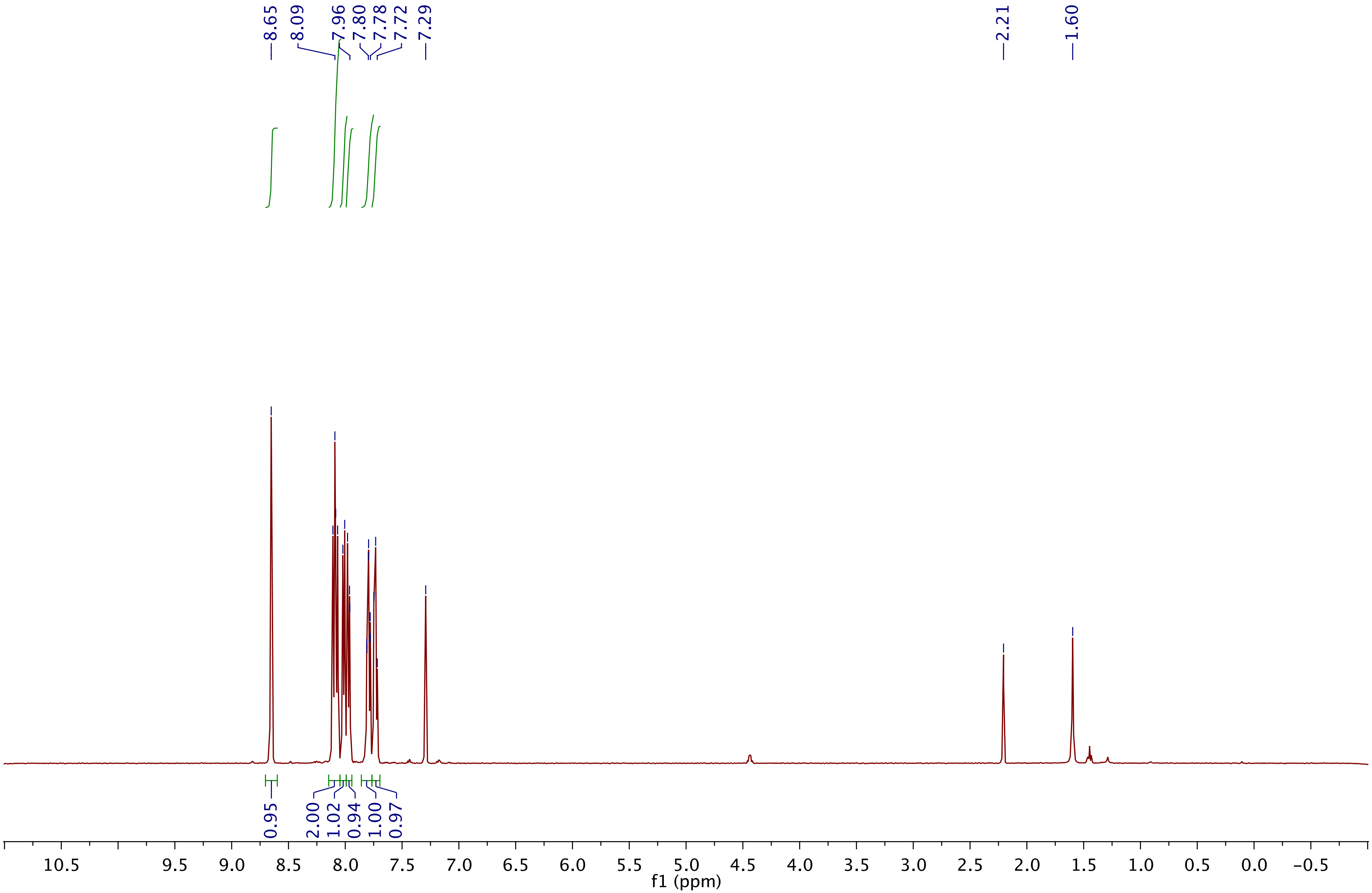
SI Table 7. Substituent effect data from ^{19}F-NMR rate studies at 303 K.

	Hammett σ values[12]	Data from rate experiments	
		k_X / k_H (303 K)	Log k_X / k_H (303 K)
$-NO_2$	0.7800	1.0331	0.014
$-CF_3$	0.5400	–	–
–Cl	0.2300	1.2409	0.094
–F	0.0600	–	–
–H	0.0000	1	0
$-CH_3$	-0.1700	0.9606	-0.017
$-OCH_3$	-0.2700	0.7874	-0.104

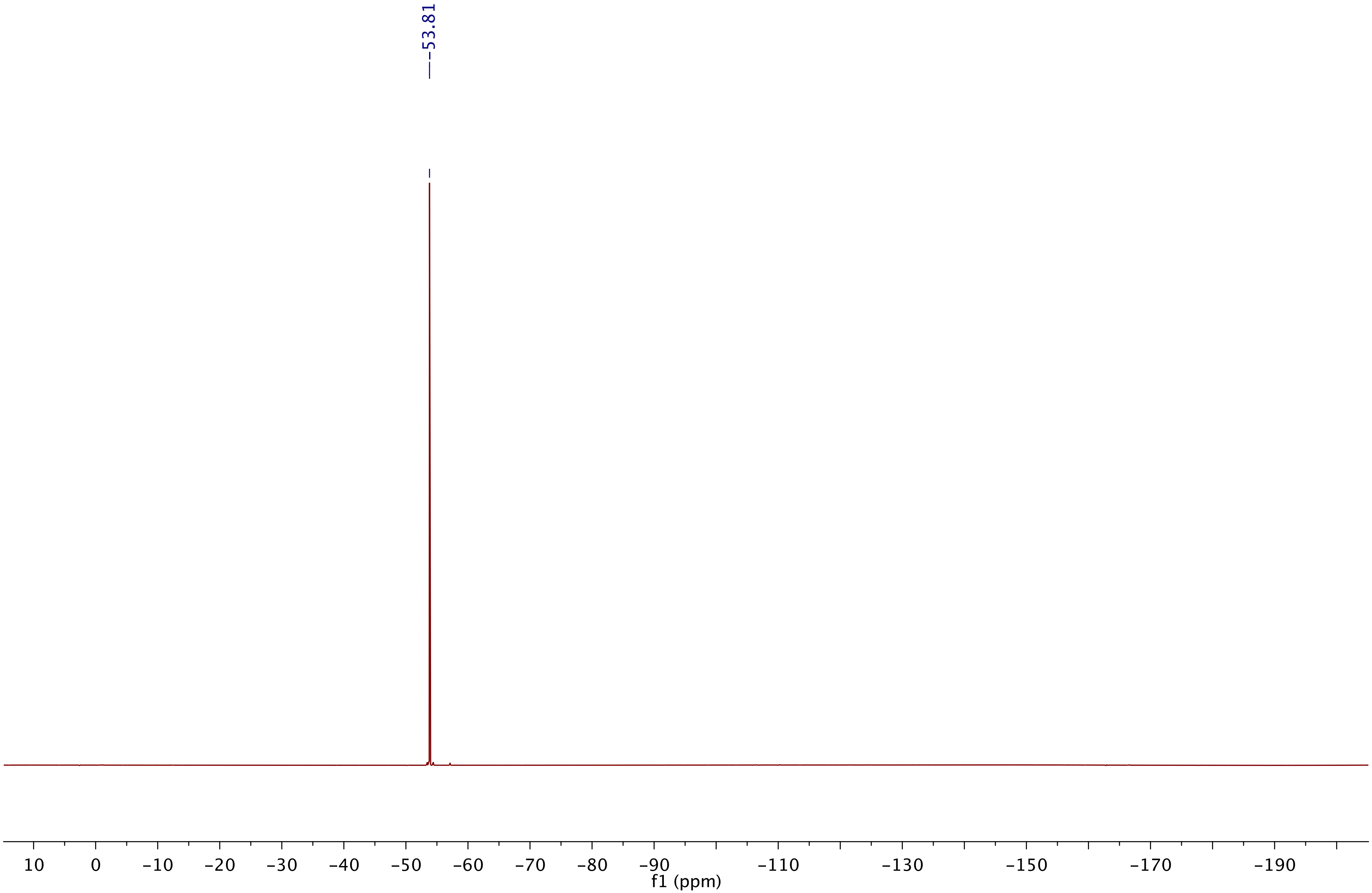


SI Figure 10. Figure 4 including a plot of of log k_X/k_H (where log k_X/k_H has been determined by ^{19}F-NMR rate studies at 303 K) versus σ for various para substituted benzenesulfonic acids. σ values taken from reference, [11] p. 144. ρ values were determined by linear least-squares regression to log log $k_X/k_H = \rho\sigma + b$.

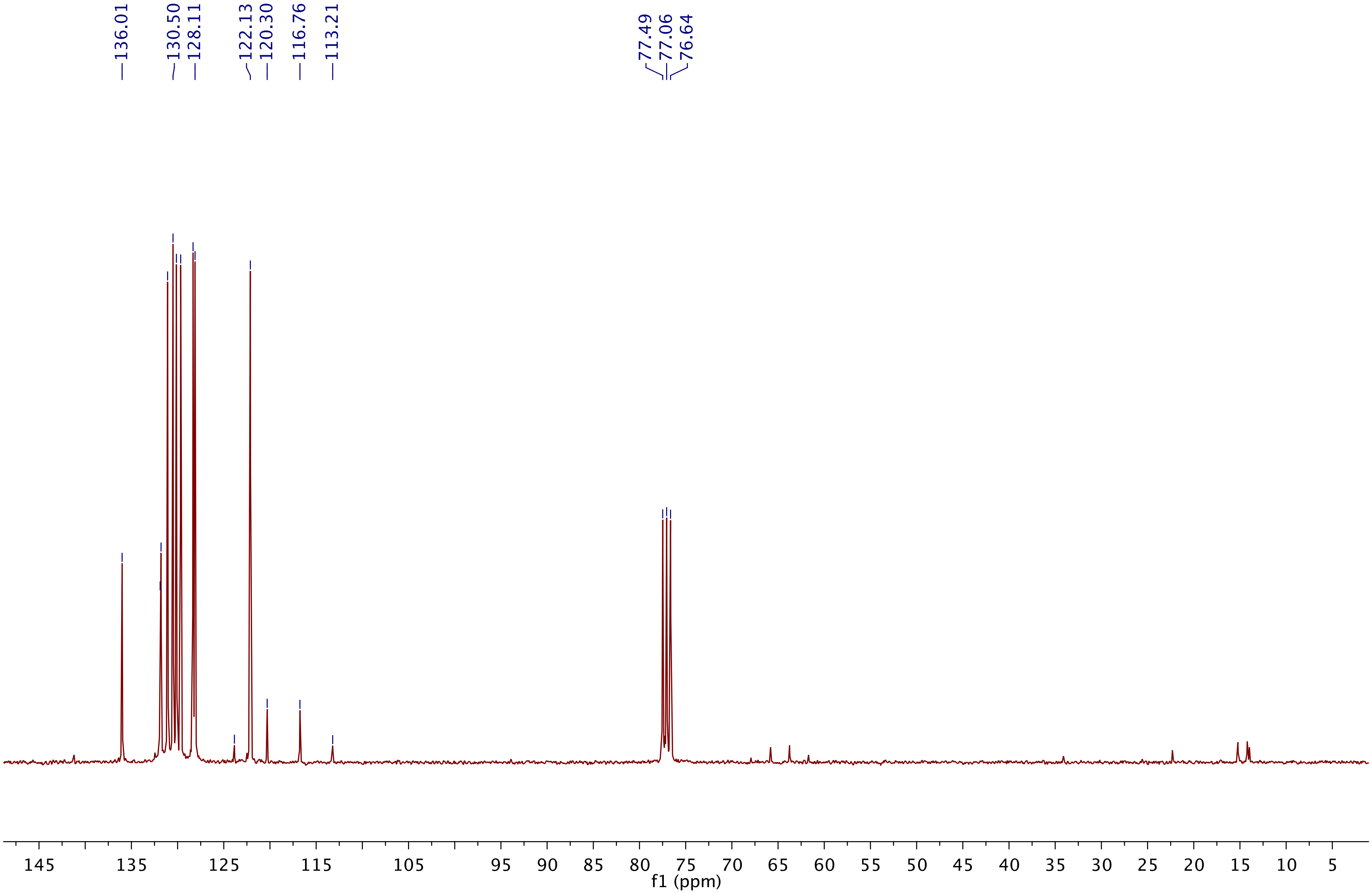
500 MHz 1H-NMR of Trifluoromethyl naphthalene-2-sulfonate (**5a**)



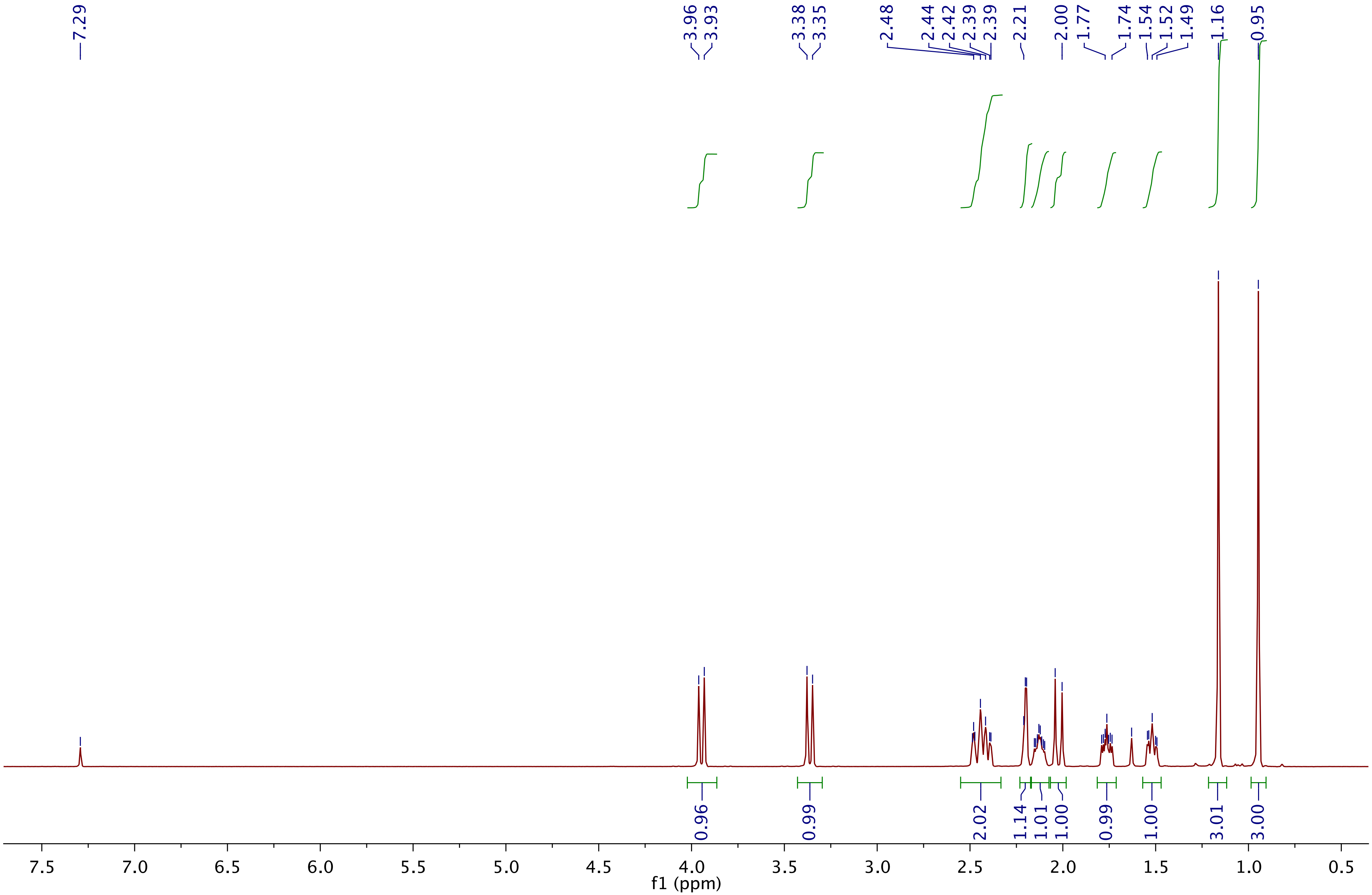
282 MHz 19F-NMR of Trifluoromethyl naphthalene-2-sulfonate (**5a**)



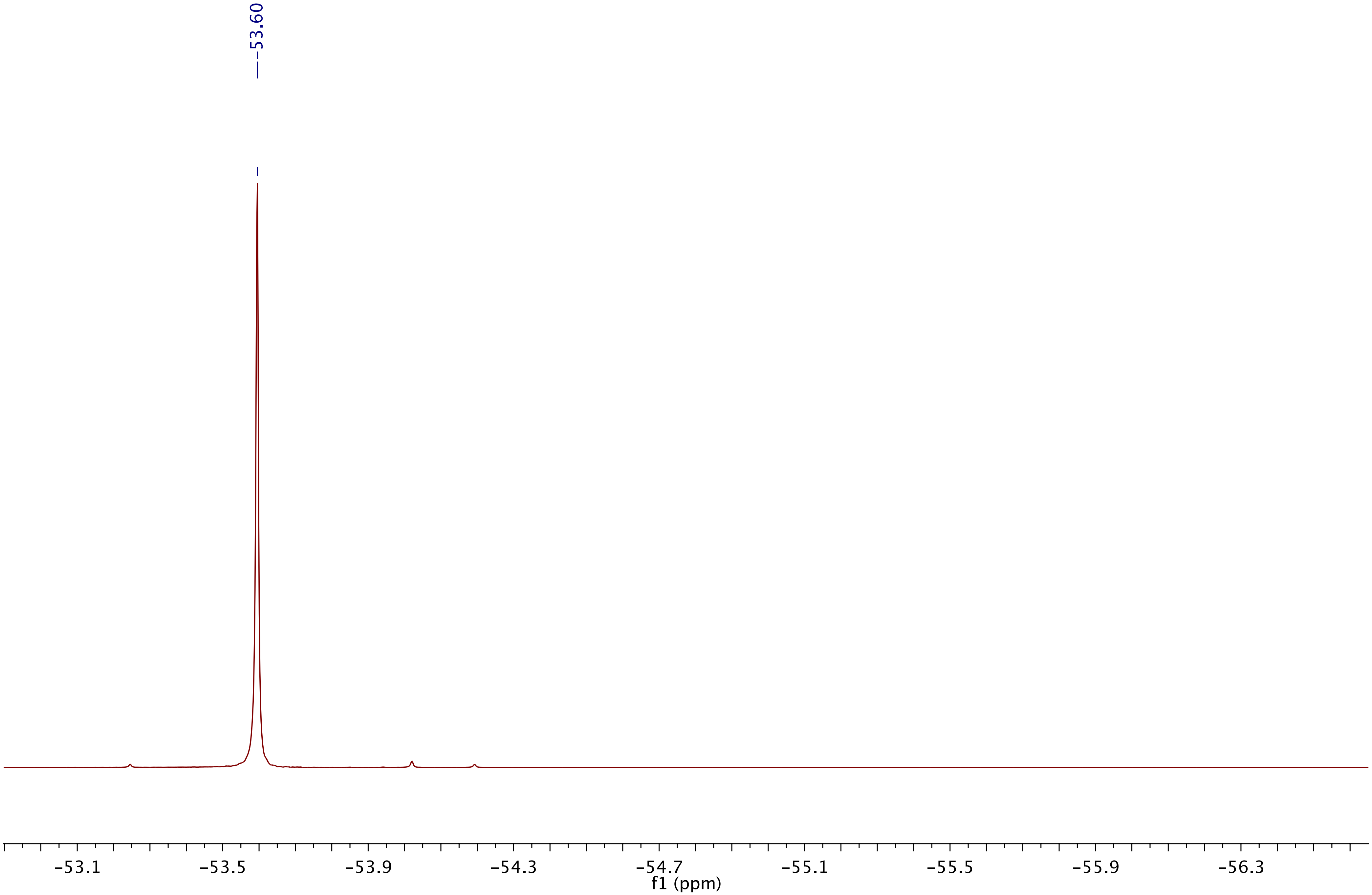
75 MHz 13C-NMR of Trifluoromethyl naphthalene-2-sulfonate (**5a**)



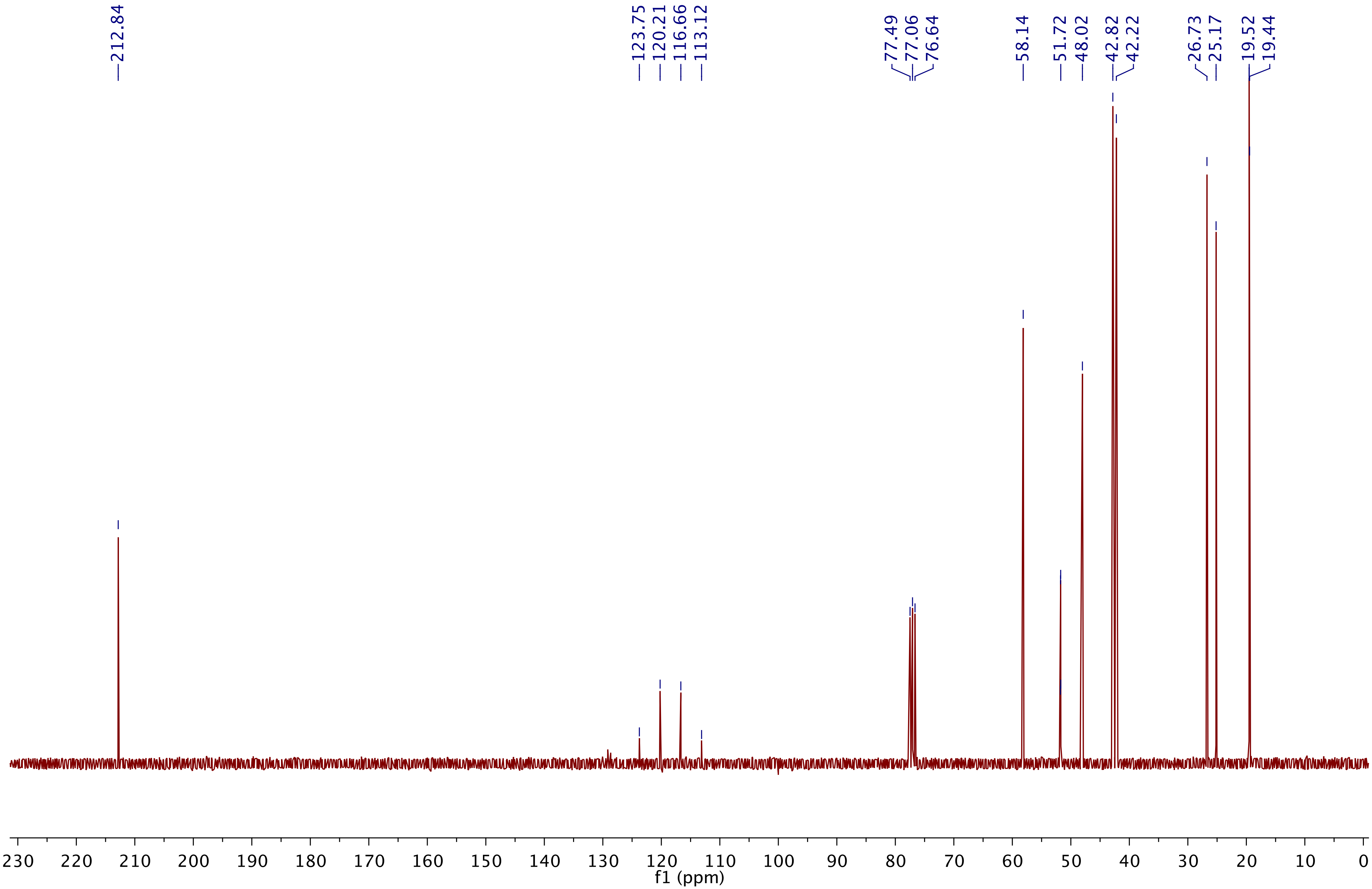
500 MHz 1H-NMR of Trifluoromethyl (7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (**5b**)



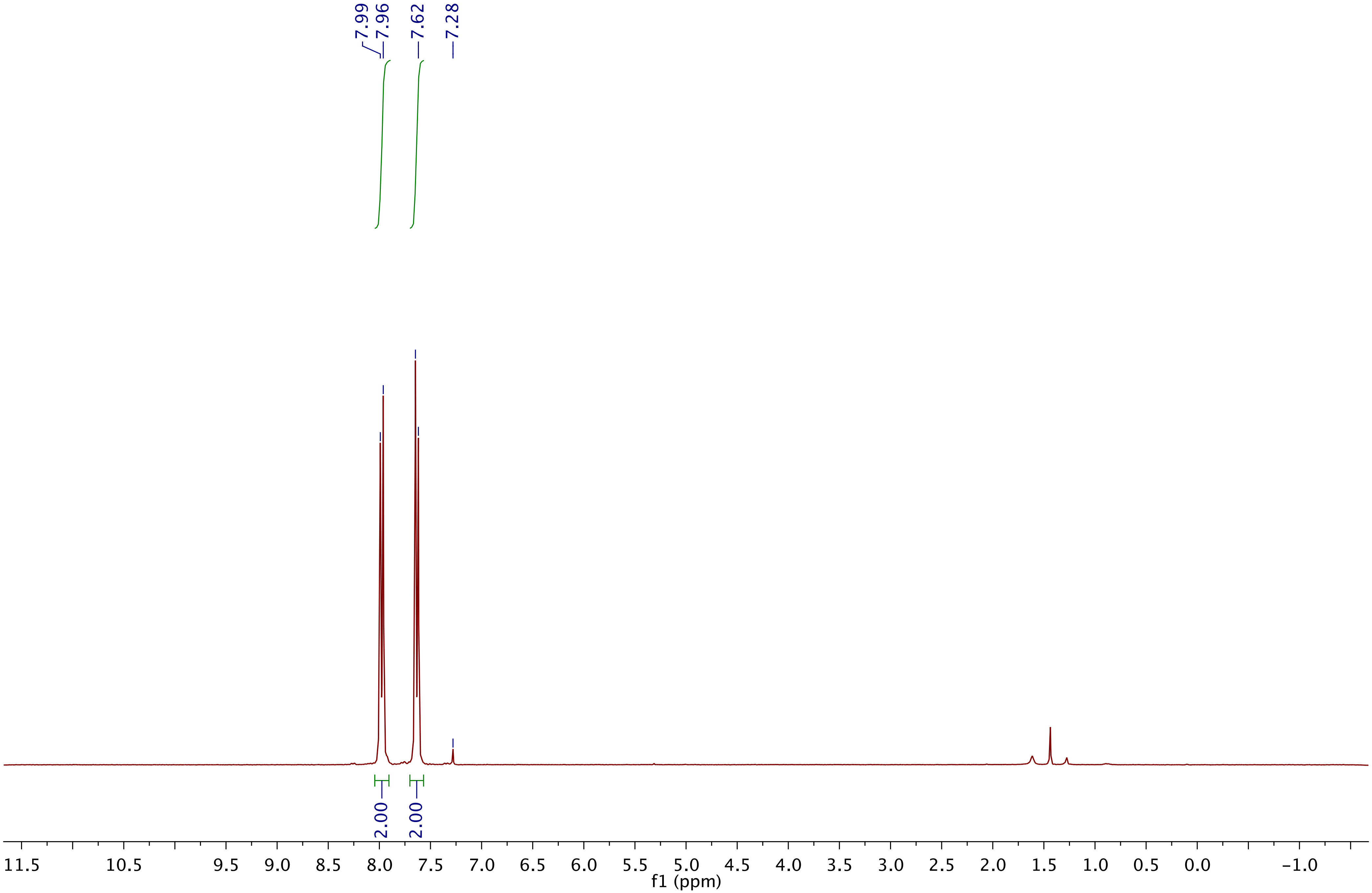
282 MHz 19F-NMR of Trifluoromethyl (7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (**5b**)



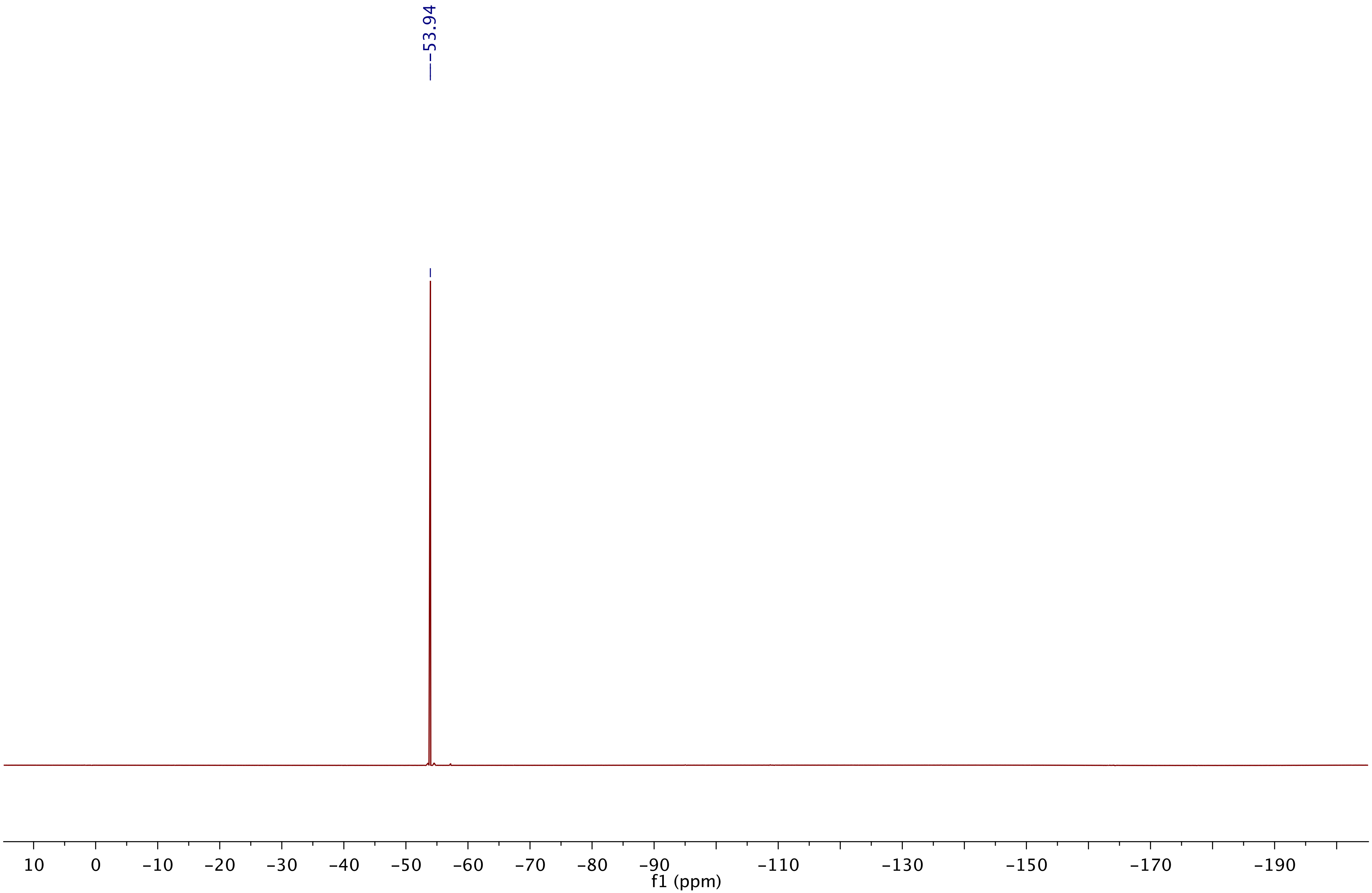
75 MHz 13C-NMR of Trifluoromethyl (7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (**5b**)



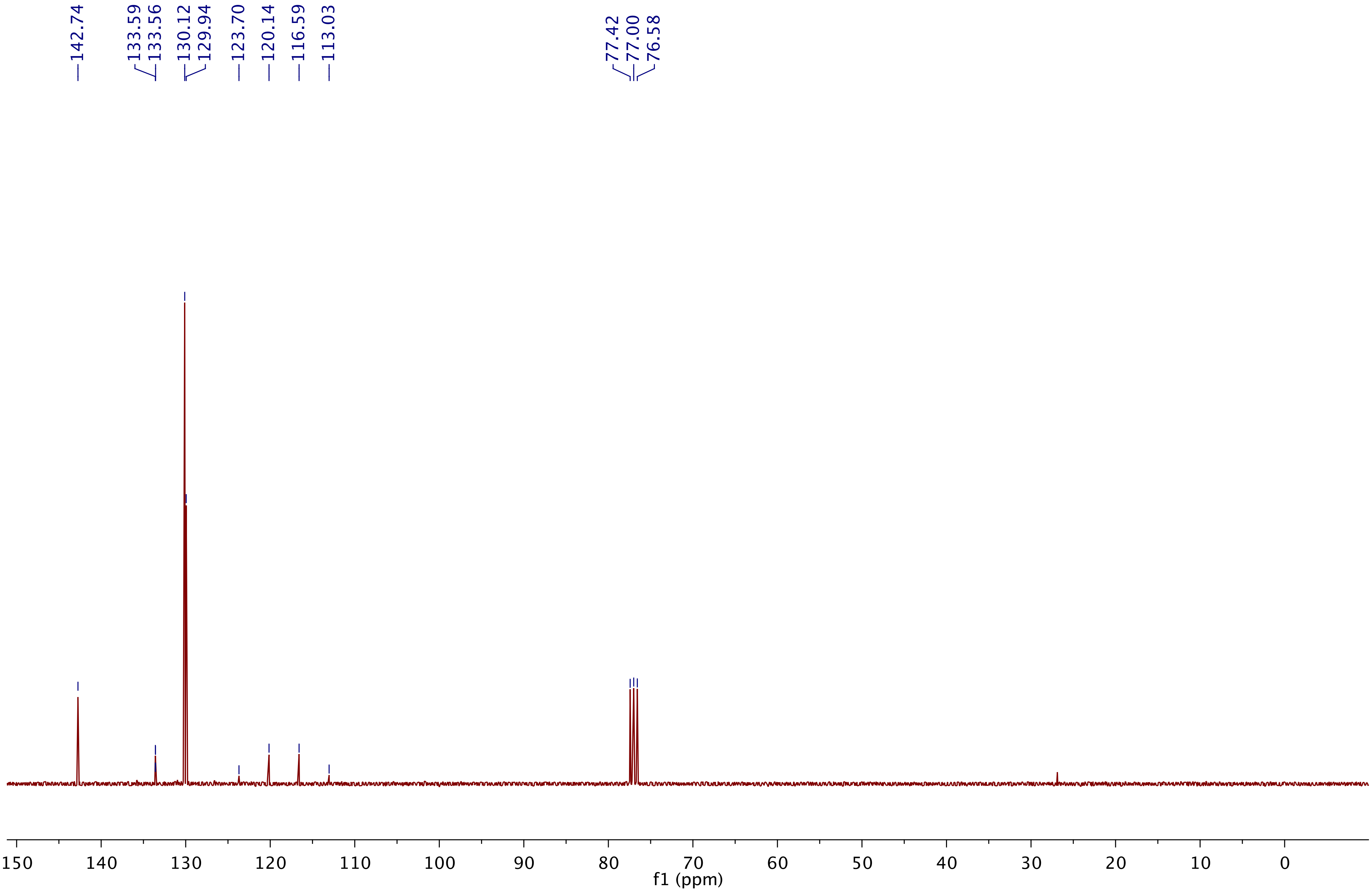
300 MHz 1H-NMR of Trifluoromethyl 4-chlorobenzenesulfonate (**5d**)



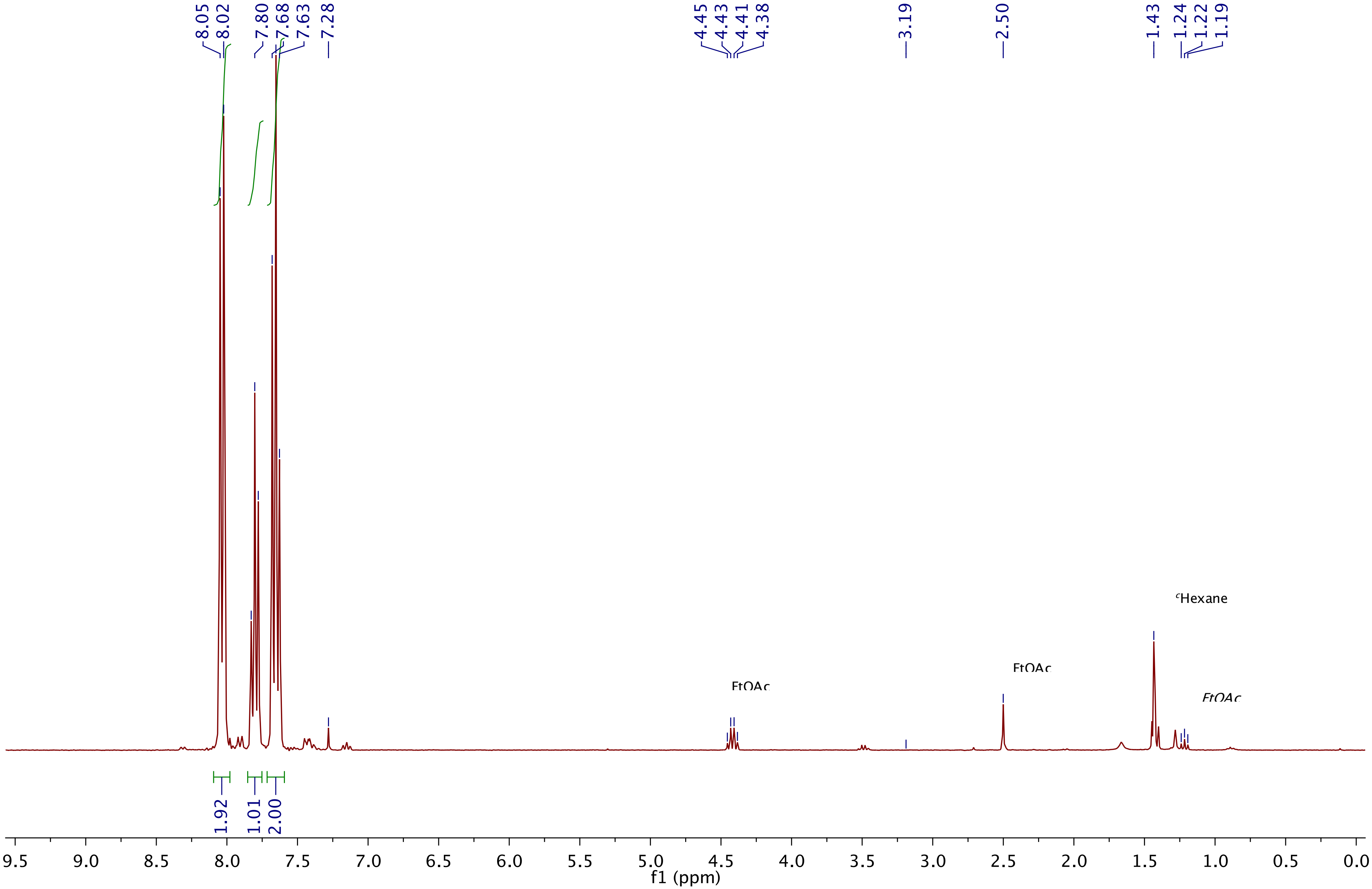
282 MHz 19F-NMR of Trifluoromethyl 4-chlorobenzenesulfonate (**5d**)



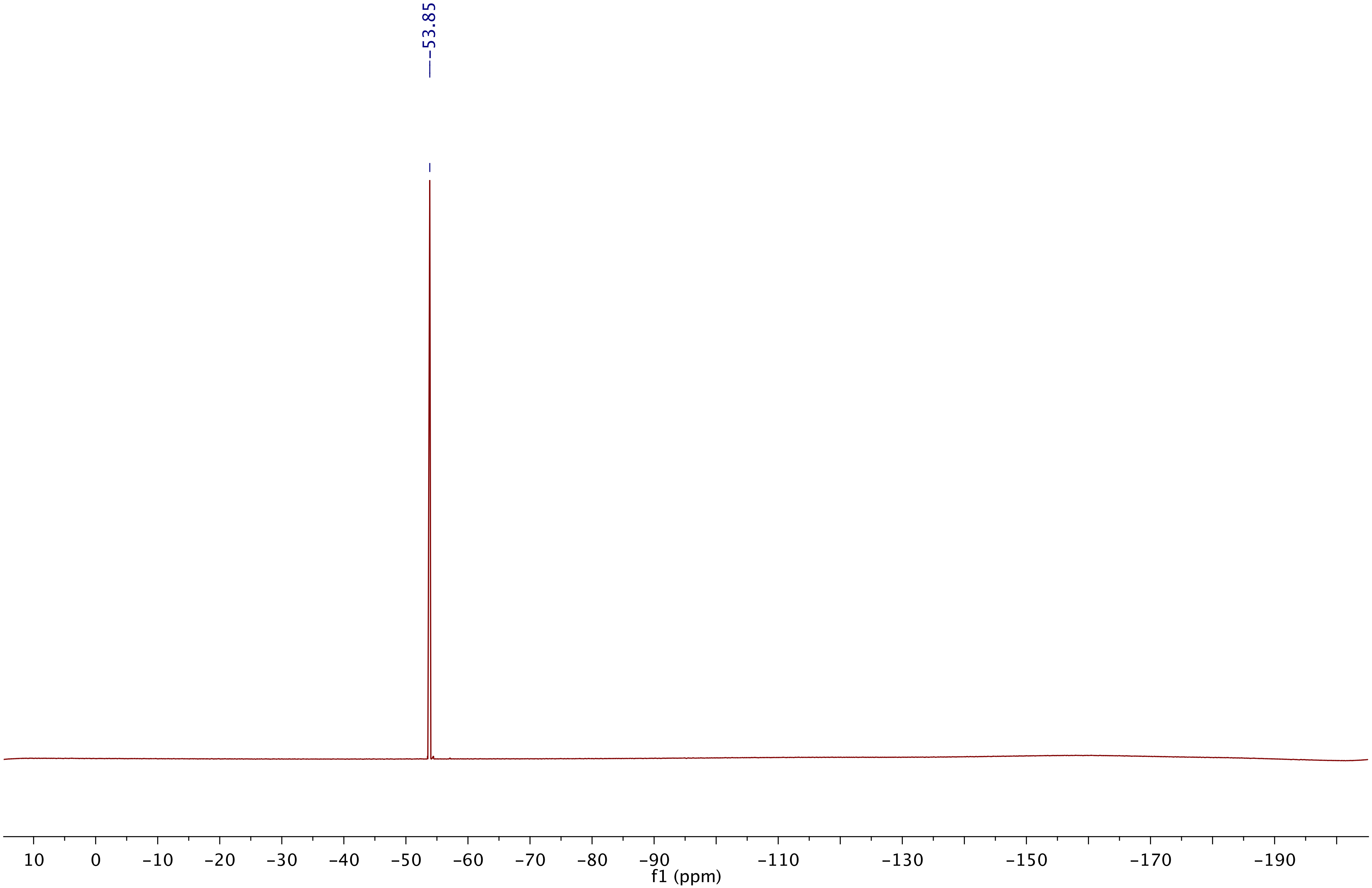
75 MHz 13C-NMR of Trifluoromethyl 4-chlorobenzenesulfonate (**5d**)



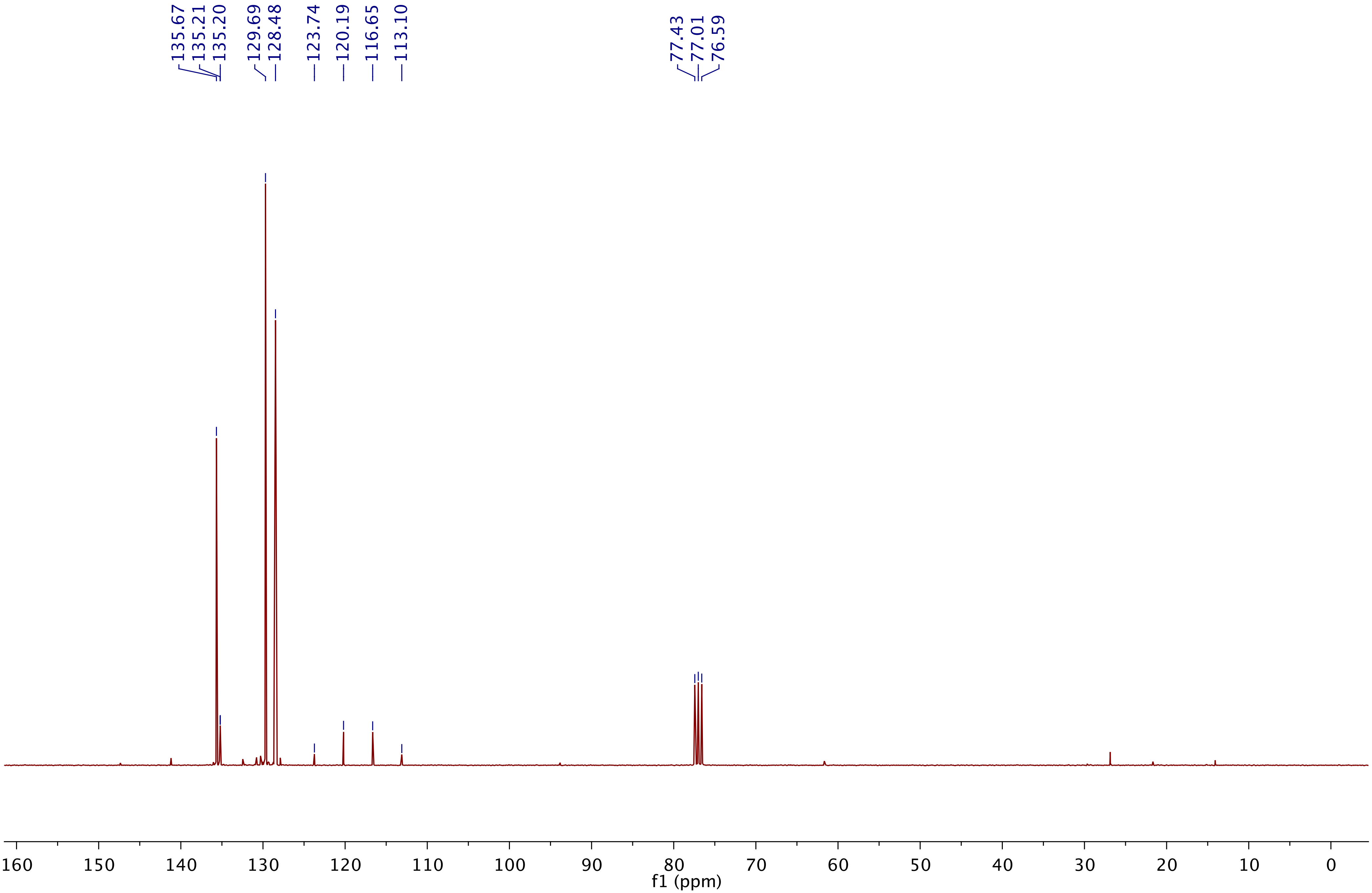
300 MHz 1H-NMR of Trifluoromethyl benzenesulfonate (**5e**)



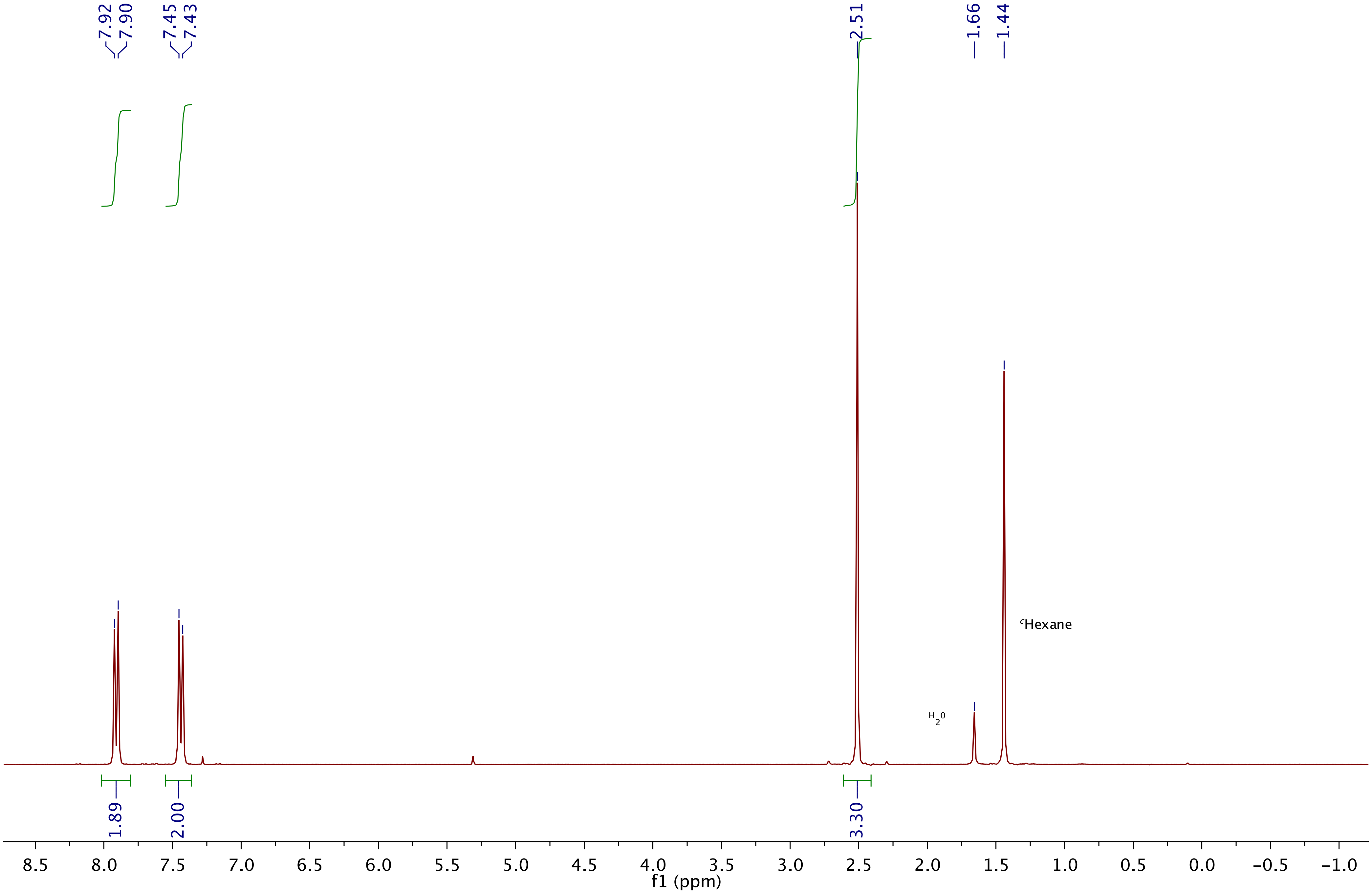
282 MHz 19F-NMR of Trifluoromethyl benzenesulfonate (**5e**)



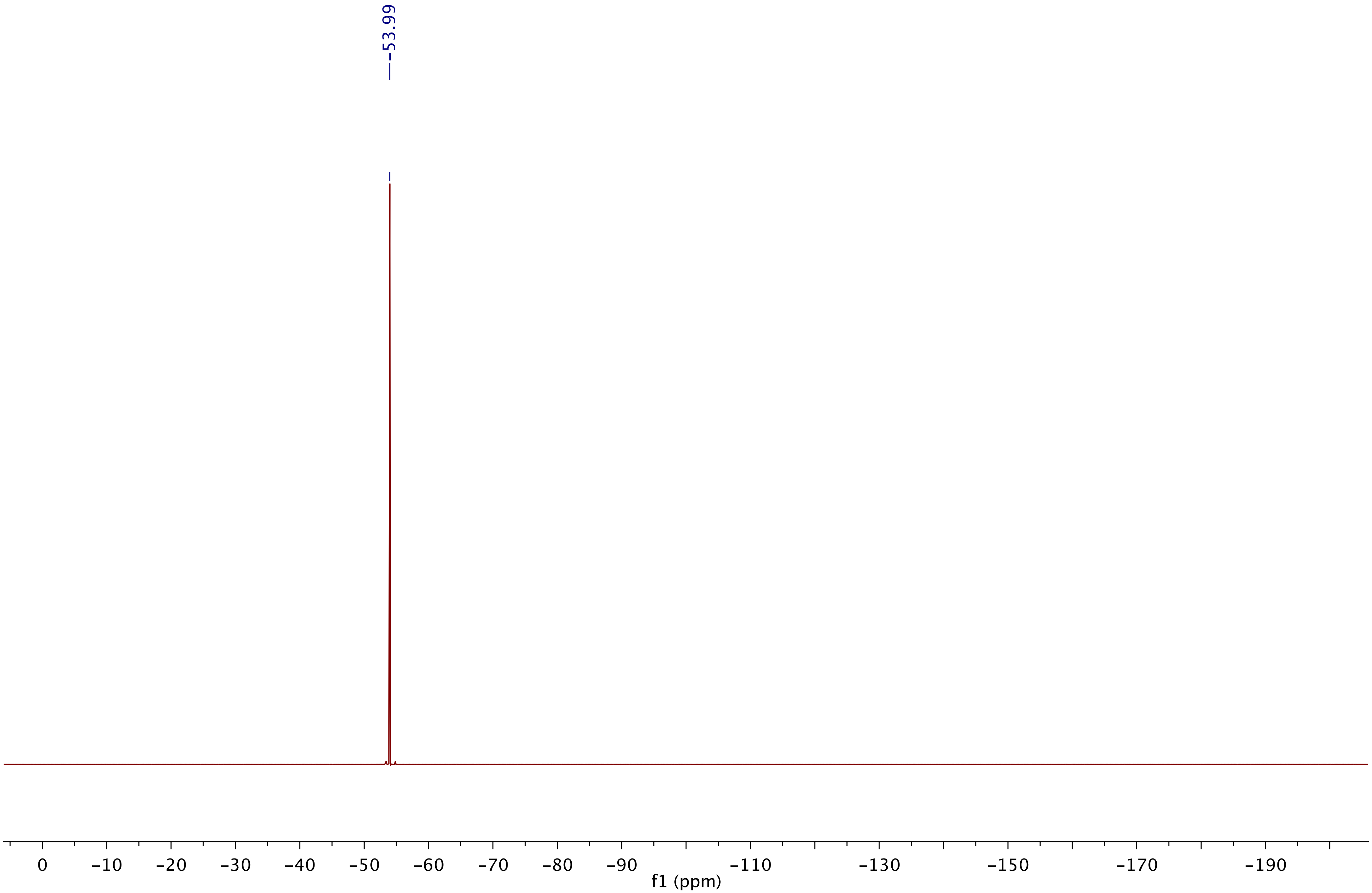
75 MHz 13C-NMR of Trifluoromethyl benzenesulfonate (**5e**)



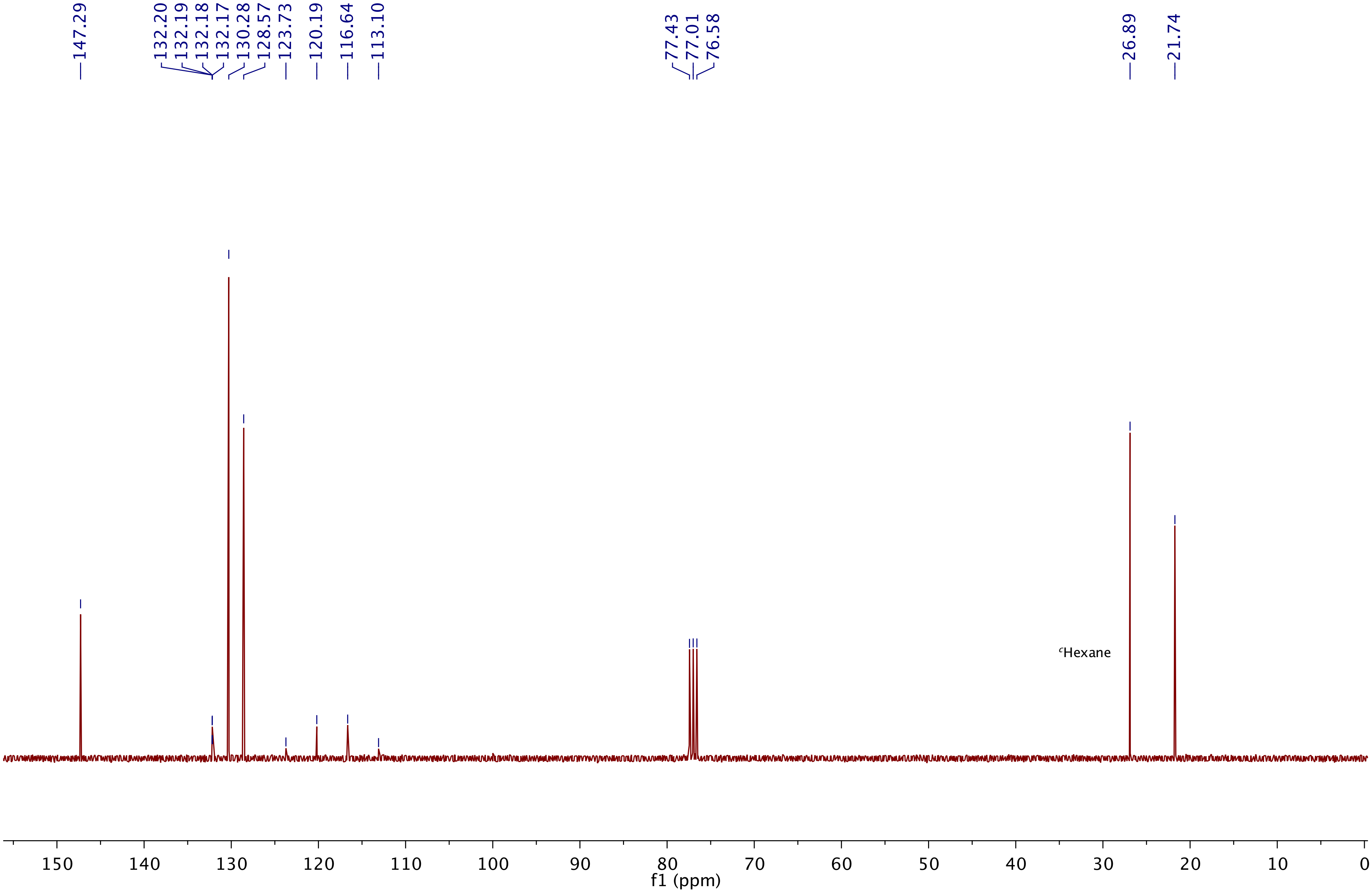
300 MHz 1H-NMR of Trifluoromethyl 4-methylbenzenesulfonate (**5f**)



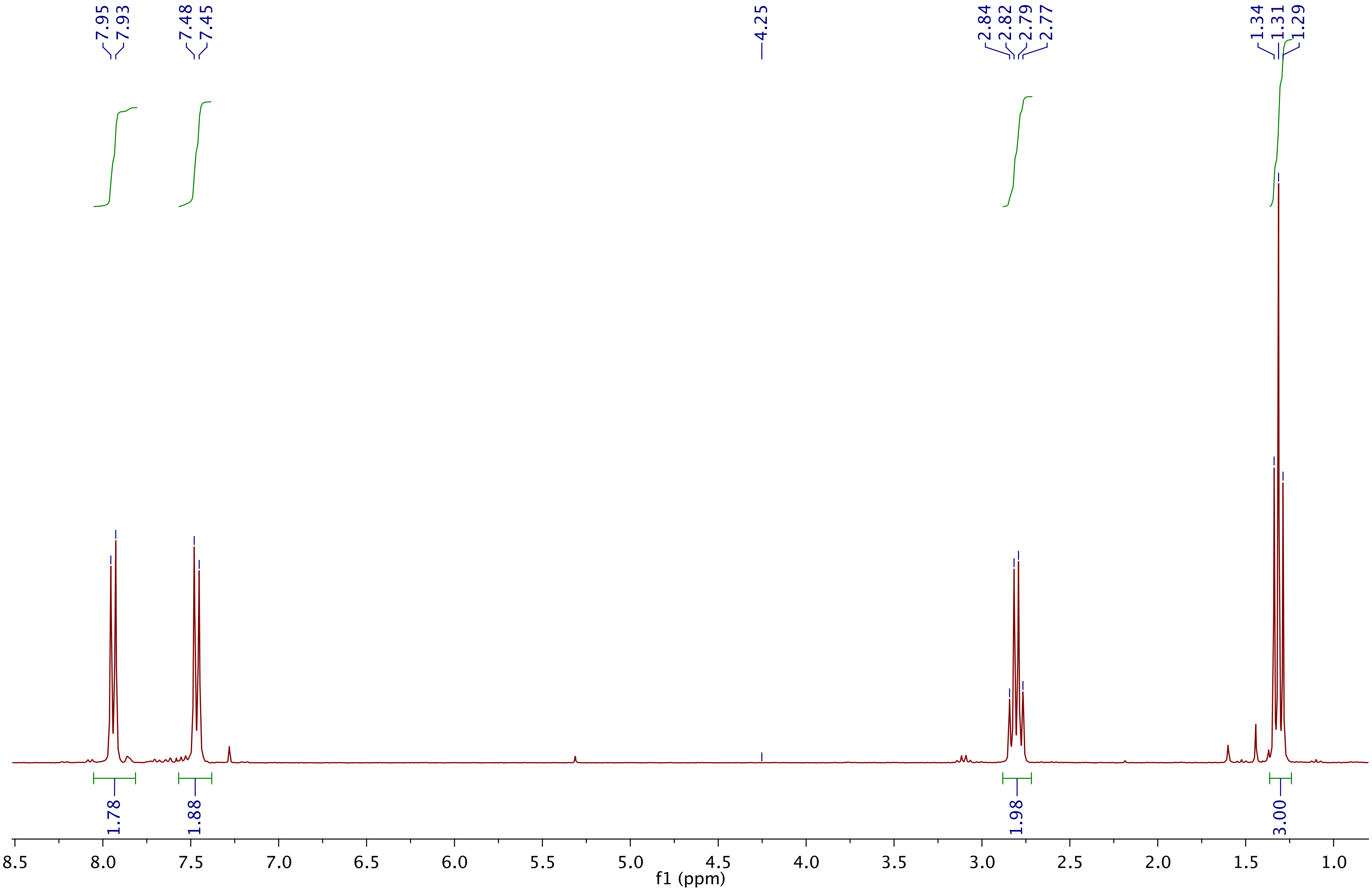
188 MHz 19F–NMR of Trifluoromethyl 4–methylbenzenesulfonate (**5f**)



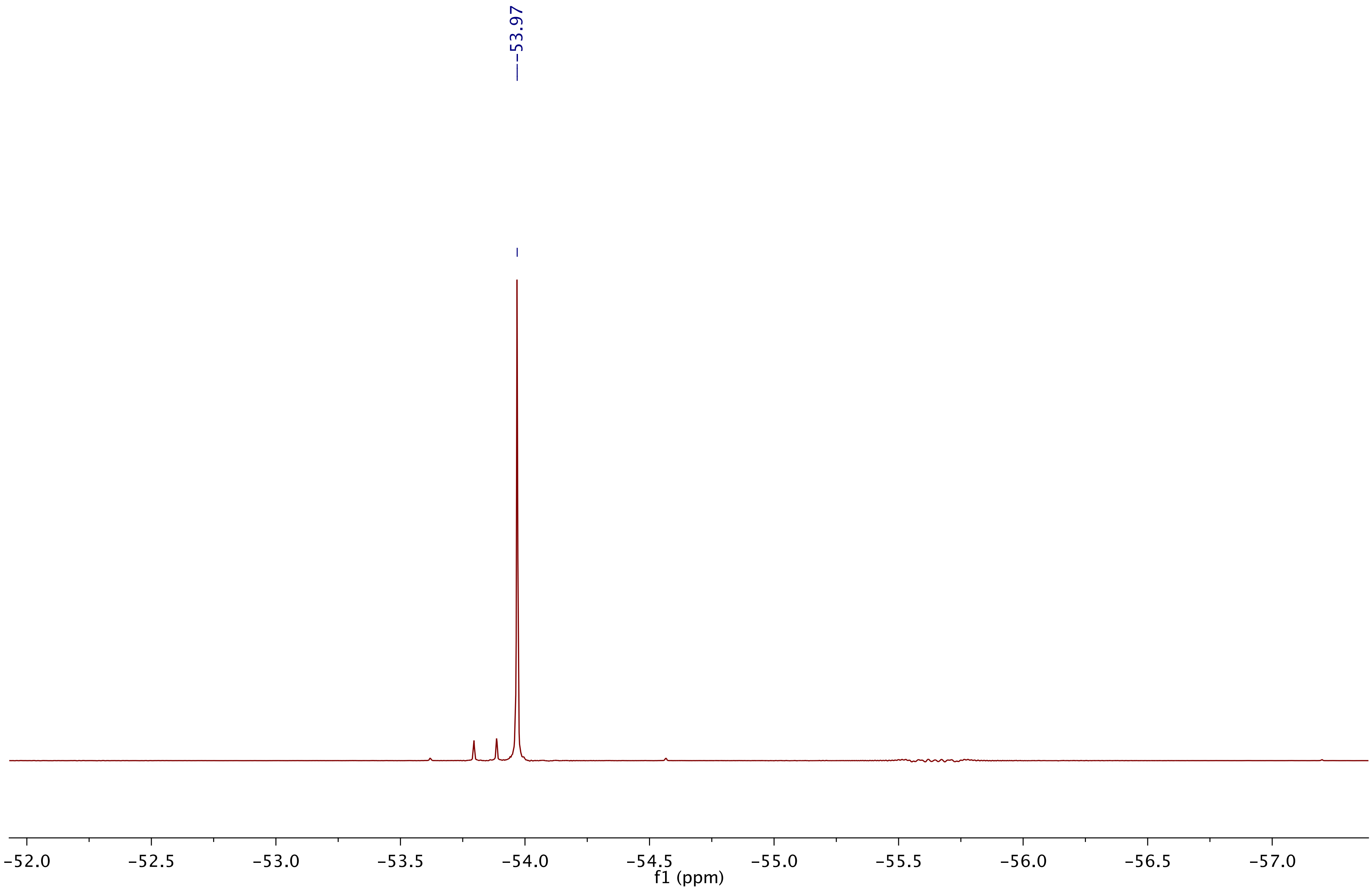
75 MHz 13C-NMR of Trifluoromethyl 4-methylbenzenesulfonate (**5f**)



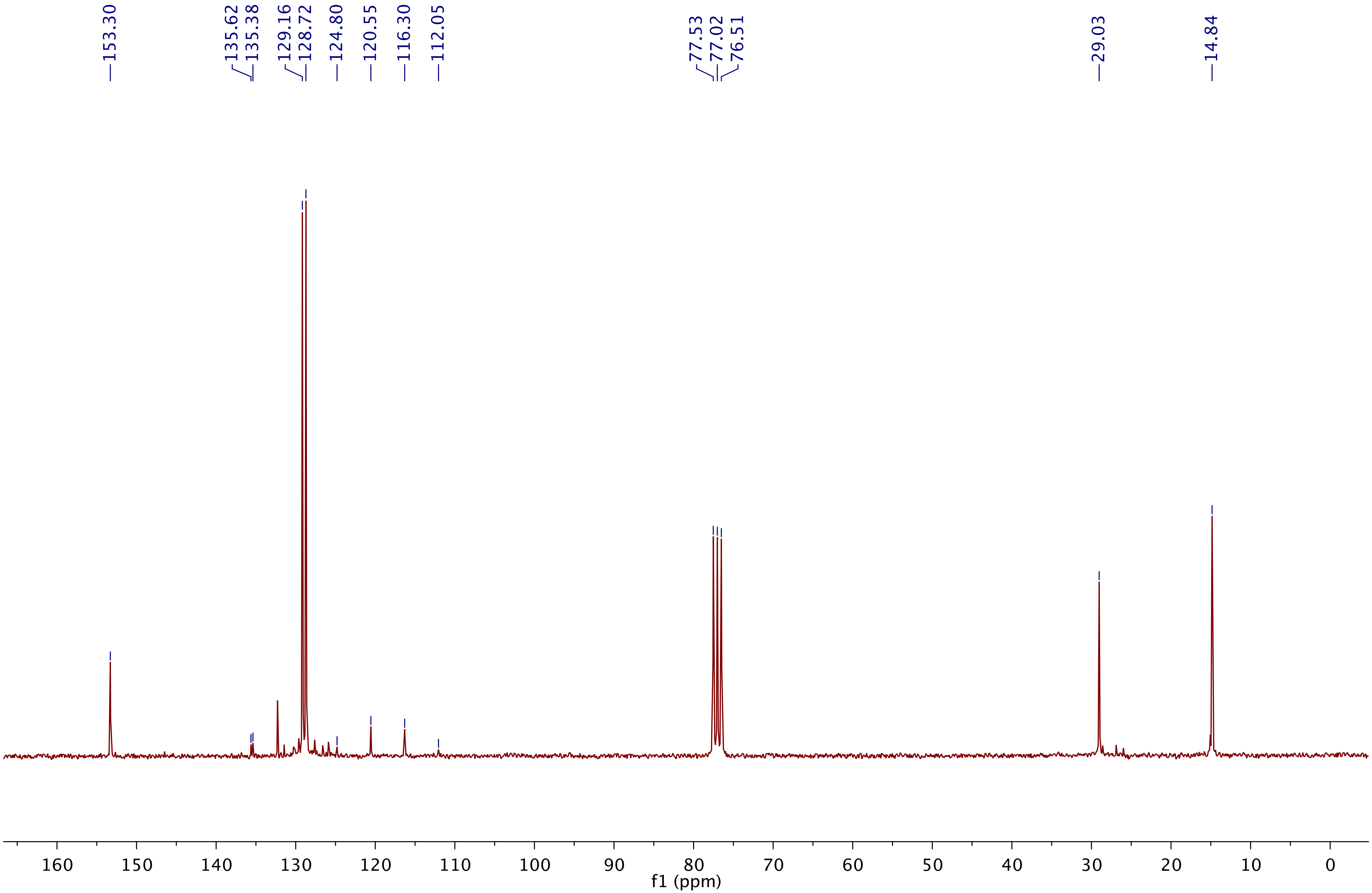
300 MHz 1H-NMR of Trifluoromethyl 4-ethylbenzenesulfonate (**5g**)



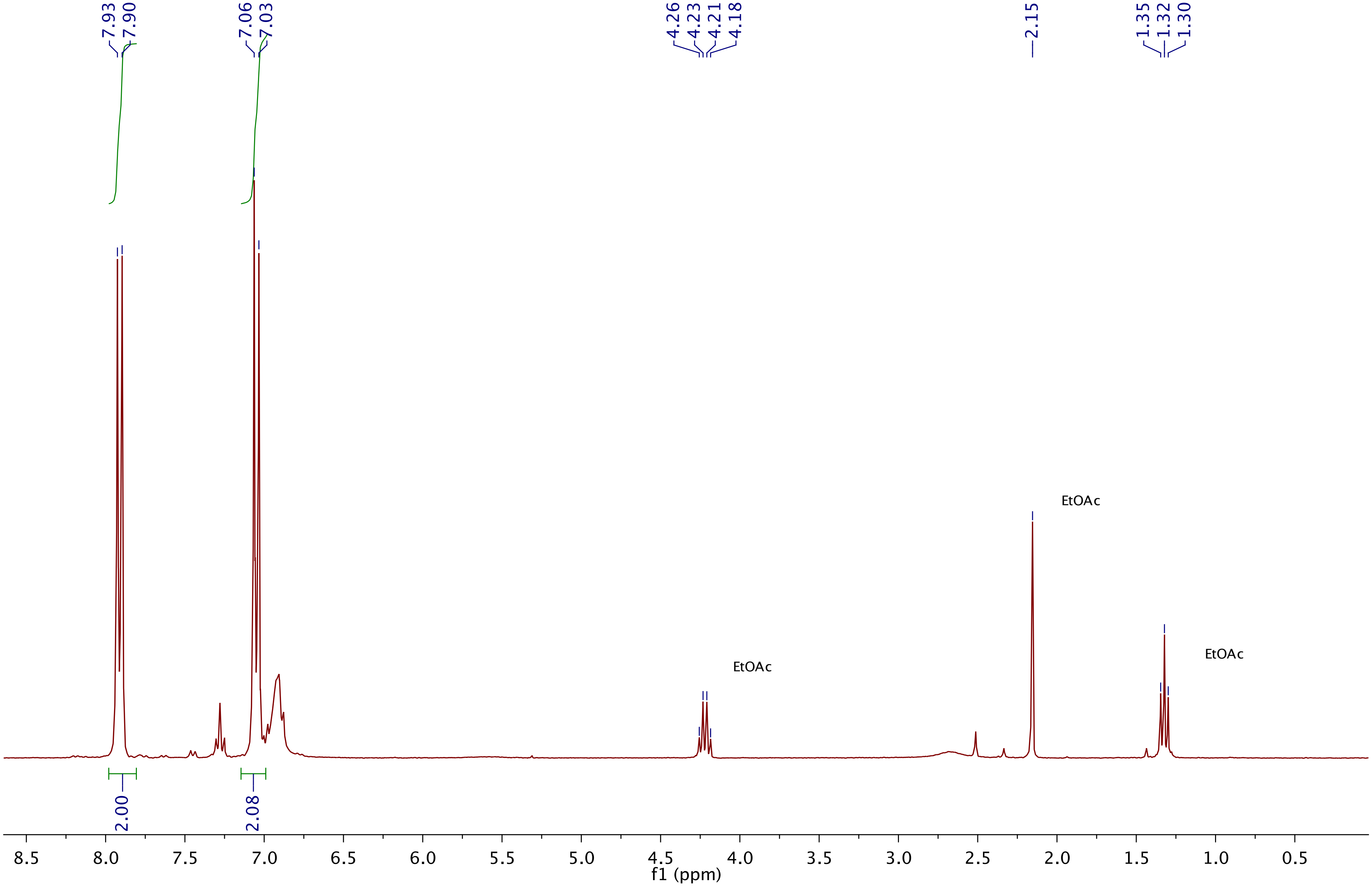
288 MHz 19F-NMR of Trifluoromethyl 4-ethylbenzenesulfonate (**5g**)



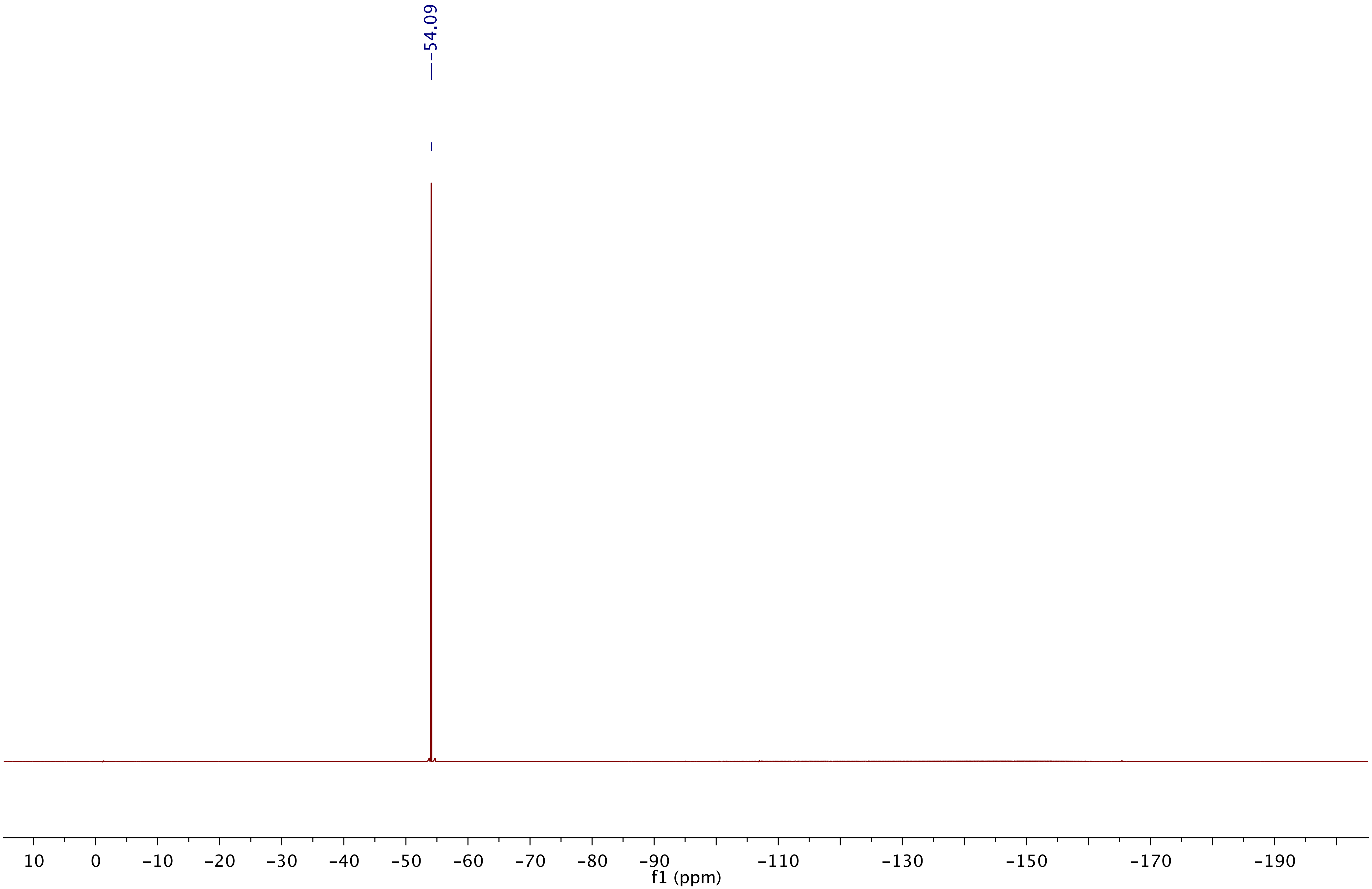
63 MHz 13C-NMR of Trifluoromethyl 4-ethylbenzenesulfonate (**5g**)



300 MHz 1H-NMR of Trifluoromethyl 4-hydroxybenzenesulfonate (**5h**)



282 MHz 19F-NMR of Trifluoromethyl 4-hydroxybenzenesulfonate (**5h**)



63 MHz 13C-NMR of Trifluoromethyl 4-hydroxybenzenesulfonate (**5h**)