

Supplementary Information

Rapid Access to Sulfinyl Fluorides for the Preparation of Sulfonimidoyl Fluorides

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General Information and Instrumentation

All chemicals were acquired commercially from either Sigma-Aldrich, TCI, AK Scientific, or Alfa Aesar. Disposable scintillation 20 mL glass vials equipped with PTFE/Silicone septa were purchased from ChemGlass Life Sciences LLC. Polyethylene tubing was (I.D. 1.67 mm) was purchased from Becton Dickinson. Disposable 1 mL syringes (I.D. 4.69 mm), 3 mL Syringes (I.D. 9.65 mm), 5 mL Syringes (I.D. 12.45 mm), 10 mL Syringes (I.D. 15.90 mm), and 30 mL Syringes (I.D. 22.90 mm) were purchased from Norm-Ject and Henk-Ject. Disposable needles 16G x 1 ½ (1.6 mm x 40 mm) and 21G x 2 (0.8 mm x 5 mm) were purchased from BD PrecisionGlide™. Hypodermic Needles (22G x 4") were purchased from Air-Tite™. White sleeve stoppers (24 x 40 mm) were purchased from VWR®, white sleeve stoppers (OD 14mm) were purchased from Kimble®, and red Suba-Seal® septa were purchased from Chemglass.

Column chromatography was performed using SiliaFlash F60 (40-64 µm) silica from Silicycle. Thin layer chromatography (TLC) was run on Merck Silica gel 60 F254 TLC aluminum sheets and visualized with 254 nm light and KMnO₄ followed by heating with a heat gun.

Low resolution gas chromatography/mass spectrometry (LRMS) spectra were acquired using an Agilent 5977A MSD coupled to 7890B GC. Infrared (IR) spectral data were obtained using a Perkin Elmer Frontier FT-IR. High resolution mass spectra (HRMS) were acquired using a Jeol AccuTOF-GCy 4G spectrometer equipped with a field desorption/ionization ion source.

Proton (¹H), carbon (¹³C), and fluorine (¹⁹F) nuclear magnetic resonance spectra were acquired on either a Bruker AV-300 or Bruker Av-400 spectrometer. ¹H and ¹³C chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak (CDCl₃: ¹H: δ = 7.26 ppm, ¹³C δ = 77.16 ppm). ¹⁹F chemical shifts are reported in ppm relative to an internal standard (PhCF₃: ¹⁹F δ = -63.72, PhF: ¹⁹F δ = -113.15).

Sulfinic acids were prepared by the reduction of sulfonyl chlorides following a literature procedure.¹ Anhydrous chloramine-T was prepared by heating chloramine-T trihydrate in a dry Schlenk tube at 80 °C under vacuum overnight. Anhydrous chloramine-T was stored at room temperature under inert gas.

Example Procedure for Yield Determination by Quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR Spectroscopy

To the reaction solution was added a known quantity of either trifluorotoluene or fluorobenzene. The solution was stirred for 30 seconds before an aliquot was removed via syringe and dissolved in CDCl_3 . A $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum was acquired over 4 scans with a relaxation time of 40 seconds and the spectrum center set between the substrate and standard chemical shifts. The amount of substrate present in the reaction solution was determined by the following equation:

$$\text{mmol of standard} \times \frac{(\# \text{ of F atoms in standard})}{(\# \text{ of F atoms in substrate})} \times \frac{(\int \text{ substrate})}{(\int \text{ standard})} = \text{mmol of substrate}$$

Method for SOF₂ Generation in Acetonitrile (60 mL scale)

Safety Note: SOF₂ is a toxic gas that releases HF. It should only be generated and utilized in a functioning fume-hood. Proper PPE should be worn in addition to a face shield and reaction shield. If in contact with skin, immediately wash with water and apply calcium gluconate gel to the affected area.

Protocol: A 30 mL vial was filled with ground imidazole (21 g) and was fitted with a septum, connected to a 20 mL vial containing KHF₂ (7.029 g, 90 mmol, 3 equiv.) by a polyethylene tube (with the tube encased in the lightly packed imidazole), and to a 100 mL round bottom flask equipped with a stir bar containing 60 mL of acetonitrile by another polyethylene tube. To the 20 mL vial was added thionyl chloride (2.2 mL, 30 mmol, 1.0 equiv.) in one portion using a 3 mL syringe, which was then left inserted in the vial to monitor the buildup of pressure during the reaction. Bubbling of SOF₂ was observed in the round bottom flask. Once the septum on the round bottom flask or the syringe in the vial indicated high pressure within the system, a balloon was inserted with caution to release the pressure. After the bubbling stopped, the tubing was removed from the round bottom flask to afford a solution of SOF₂ in acetonitrile. The concentration is determined by ¹⁹F{¹H} NMR spectroscopy using PhCF₃ as the internal standard.

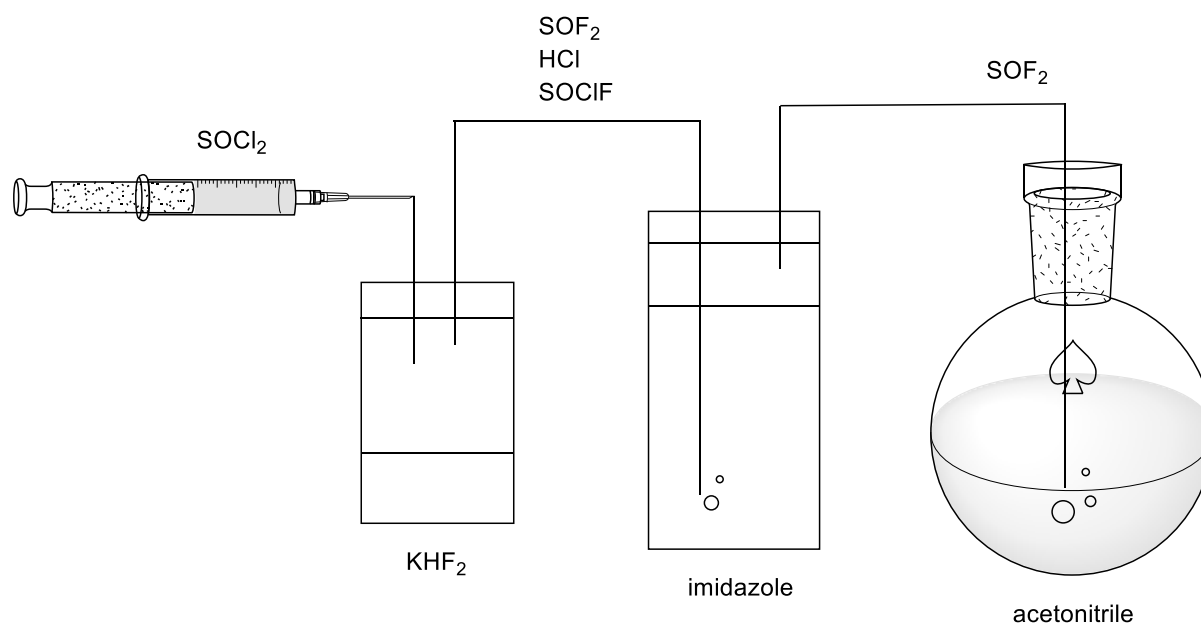


Figure S.1: SOF₂ generation setup schematic.

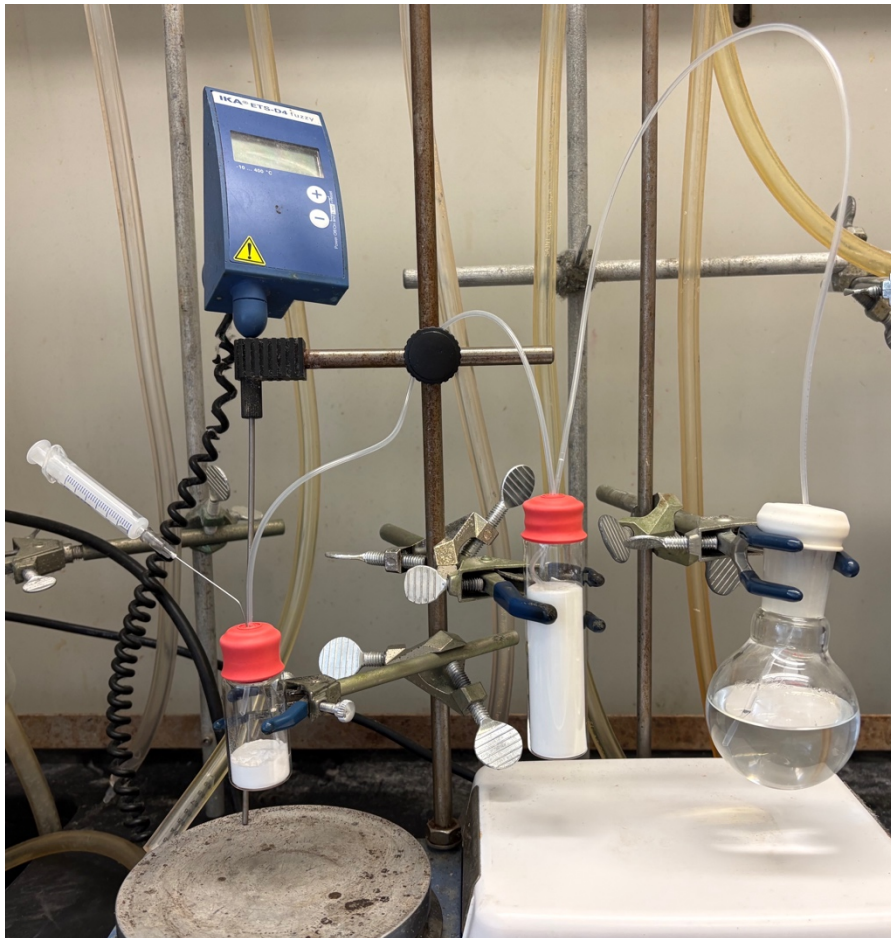
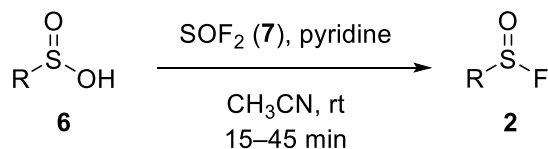


Figure S.2: SOF₂ generation setup. Note: when pressure buildup is observed, a balloon equipped with a needle is inserted carefully into septum of round bottom flask.

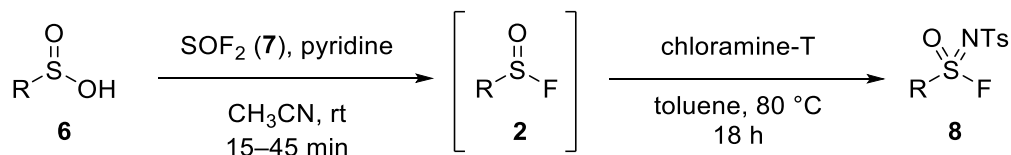
General Method A: Sulfinyl fluoride synthesis from sulfinic acids



To a 20 mL screwcap vial with a septum lid equipped with a stir bar was charged the sulfinic acid (0.25 mmol) before being purged with argon. Pyridine (0.25 mmol) was added to a solution of 0.2^a M SOF₂ dissolved in acetonitrile (0.75 mmol, 3.75 mL), before being added to the 20 mL vial via syringe. The solution was vigorously stirred for 15–45 minutes at room temperature, yielding the corresponding sulfinyl fluoride in situ. The sulfinyl fluoride was immediately used for subsequent reactions without purification. NMR yields were determined by quantitative ¹⁹F{¹H} NMR spectroscopy.

^a molarity of SOF₂ solutions ranged from 0.13–0.28 M.

General Method B: One-pot synthesis of sulfonimidoyl fluorides from sulfinic acids



To a 20 mL vial equipped with a stir bar was added a solution of 0.18^a M SOF₂ in acetonitrile (2.0 mmol, 11 mL) and pyridine (1.0 mmol). The solution was stirred at room temperature for 10 minutes. To a 50 mL round bottom flask equipped with a stir bar and septum was added sulfinic acid (1.0 mmol) before being purged with argon. The SOF₂/pyridine solution was then added to the round bottom flask via syringe, and the reaction was stirred at room temperature for 45 minutes. The reaction was then sparged with argon or nitrogen^b to displace residual SOF₂. To the round bottom flask were then added dry toluene (8 mL), and anhydrous chloramine-T (3.0 mmol). The round bottom flask was equipped with a reflux condenser and purged again with argon. The reaction was stirred at 80 °C overnight before being brought to room temperature. The solution was filtered through a fine-porosity glass frit to remove suspended NaCl. Acetonitrile (8 mL) was added to form an azeotrope with toluene and the reaction mixture was concentrated under reduced pressure. The sulfonimidoyl fluorides were isolated following purification by flash column chromatography.

^a molarity of SOF₂ solutions ranged from 0.13–0.28 M. ^b excessive sparging can result in sulfinyl fluoride decomposition; 5 min is sufficient for this scale.

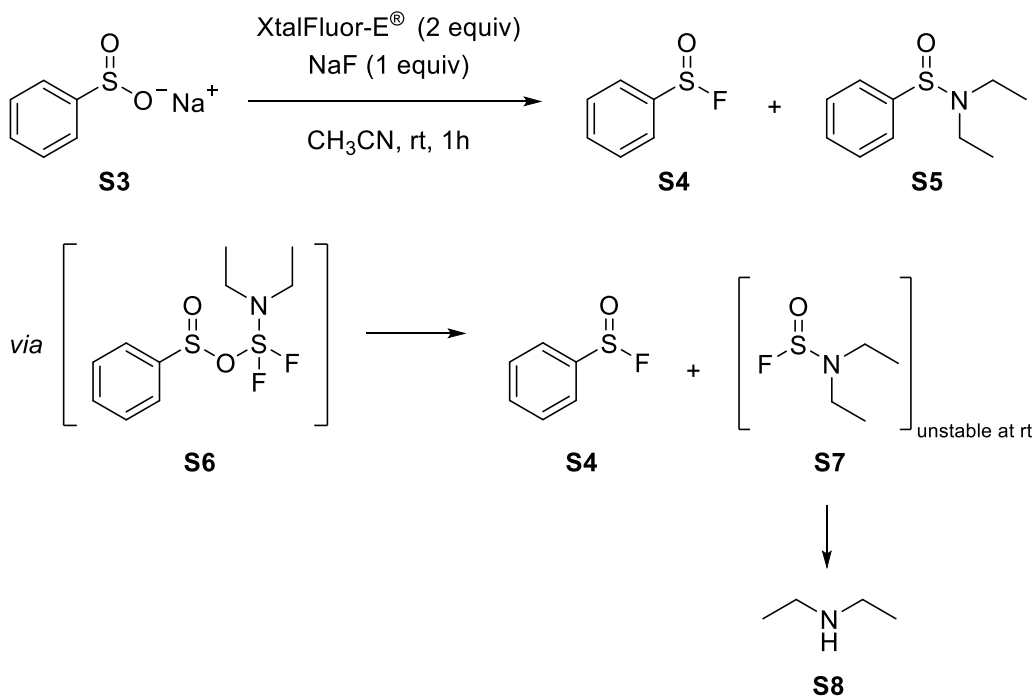
Optimization Experiments for the Synthesis of Sulfinyl Fluoride **S2**

Table S.1. Optimization for the deoxyfluorination of sulfinate salt **S1**

entry	X	sulfur fluoride reagent	additive	solvent	¹⁹ F NMR yield of S2 (%)
1	Pyr	SO ₂ F ₂ (2 equiv)	-	CH ₃ CN	<5%
2	Na	DAST (2 equiv)	-	CH ₃ CN	<5%
3	Na	Xtalfluor-E [®] (2 equiv)	NaF	CH ₃ CN	50%
4	Na	SOF ₂ (2 equiv)	BF ₃ •OEt ₂	DMF	<5%
5	Na	SOF ₂ (1 equiv)	-	DCM	<5%

Sulfinyl fluorides were synthesized based on general method **A** at a 0.25 mmol scale. ¹⁹F{¹H} NMR spectroscopic yields were determined using trifluorotoluene as the internal standard.

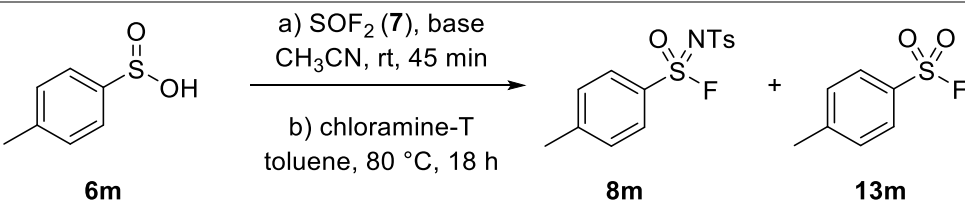
Note: Although Xtalfluor-E[®] in the presence of NaF (entry 3) afforded the highest yield, sulfenamide **S5** was also identified as a remaining side-product. The formation of **S5** occurred from the room temperature decomposition of **S7** to release dimethylamine **S8**. **S8** could react with **S6** or **S4** to form sulfenamide **S5**. **S5** was not readily separable from the desired products, and Xtalfluor-E[®] is therefore not ideal for our one-pot process.



Scheme S.1: Sulfinamide byproducts in XtalFluor-mediated activation of sulfenic acids.

Development of Sulfonimidoyl Fluoride Synthesis

Table S.2. Optimization of one-pot SOF₂-mediated synthesis of sulfonimidoyl fluorides



Reaction scheme: 6m (4-methylbenzenesulfonamide) reacts with SOF₂ (7) and base in CH₃CN at rt for 45 min, followed by chloramine-T in toluene at 80 °C for 18 h, to yield 8m (4-methylbenzenesulfonimidoyl fluoride) and 13m (4-methylbenzenesulfonamide fluoride).

a. base optimization				
entry	base	equiv	¹⁹ F NMR yield of 8m (%)	¹⁹ F NMR yield of 13m (%)
1	pyridine	2.0	28	39
2	NEt ₃	2.0	25	43
3	DIPEA	2.0	43	7
4	DBU	2.0	14	41
5	pyridine	0.9	85	10
6	pyridine	1.0	88	9
7	pyridine	1.1	51	22

b. chloramine-T optimization				
entry	chloramine-T equiv		¹⁹ F NMR yield of 8m (%)	¹⁹ F NMR yield of 13m (%)
1	1.0		38	7
2	2.0		67	19
3	3.0		88	9
4	4.0		36	6

c. toluene volume optimization				
entry	toluene volume (mL)		¹⁹ F NMR yield of 8m (%)	¹⁹ F NMR yield of 13m (%)
1	0		27	22
2	1		51	15
3	2		88	9
4	3		67	15
5	4		55	18

d. temperature optimization				
entry	temperature (°C)		¹⁹ F NMR yield of 8m (%)	¹⁹ F NMR yield of 13m (%)
1	rt		43	8
2	40		66	8
3	60		69	7
4	80		88	9

e. examination of moisture sensitivity				
Entry	toluene	glassware	¹⁹ F NMR yield of 8m (%)	¹⁹ F NMR yield of 13m (%)
1	non-dried	non-dried	41	25
2	anhydrous	non-dried	63	12
3	anhydrous	flame-dried	88	9

Sulfonimidoyl fluorides were synthesized based on general method **B** at a 0.25 mmol scale. ¹⁹F{¹H} NMR spectroscopic yields were determined using fluorobenzene as the internal standard.

Mechanistic Study into Decomposition of Sulfinyl Fluorides

4-Fluorobenzenesulfinyl fluoride (**2a**) was prepared following general method **A** without isolation. To the 20 mL vial was added a known quantity of PhCF₃. The solution was sparged with argon for 10 minutes, where every 2 minutes an aliquot was removed via syringe and diluted with CDCl₃. Quantitative ¹⁹F{¹H} NMR spectra of these samples were used to plot the amount of sulfinyl fluoride decomposition intermediates with respect to time, as shown in Figure **S.2**.

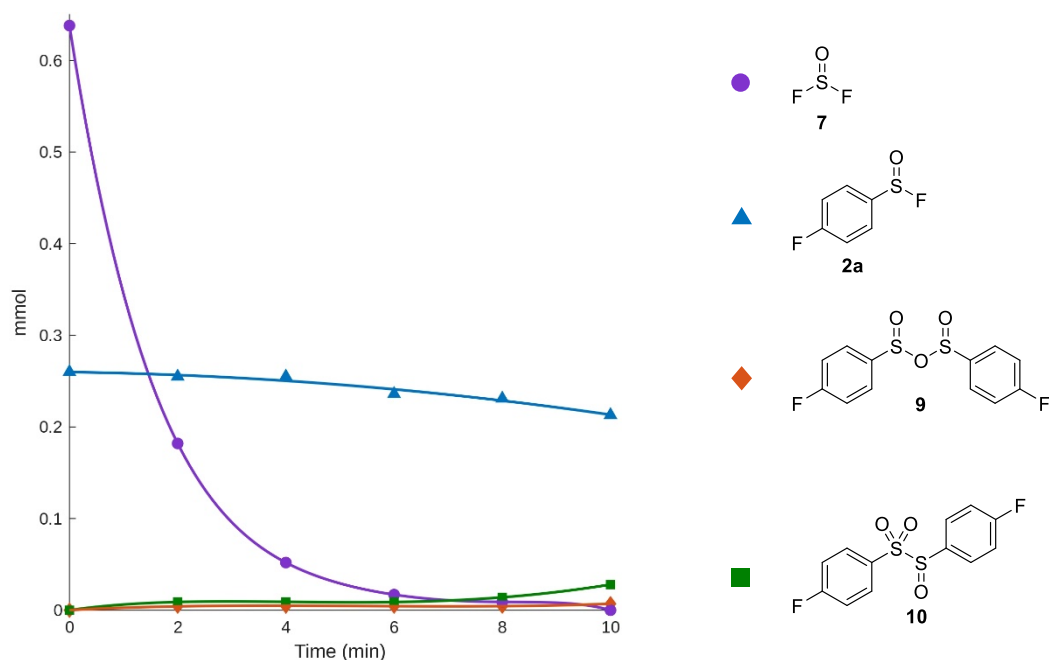
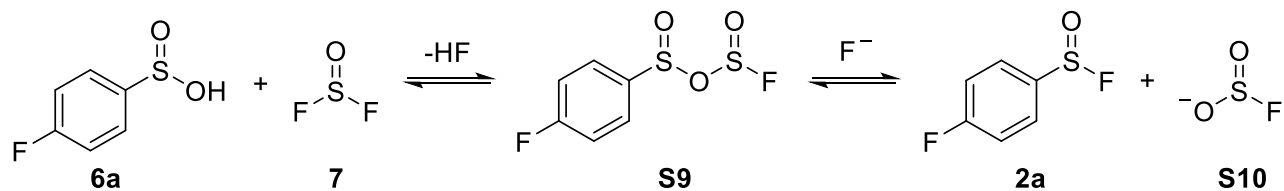


Figure S.2: Decomposition of 4-fluorobenzenesulfinyl fluoride (**2a**) upon degassing of thionyl fluoride (**9**).

Proposed role of thionyl fluoride in sulfinyl fluoride decomposition



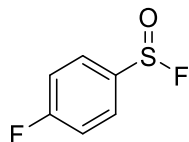
Scheme S.2: Equilibrium between sulfinic acid **6a** and sulfinyl fluoride **2a**.

Initially, the above equilibrium favours formation of sulfinyl fluoride **2a** due to the presence of excess thionyl fluoride (**7**). Upon removal of thionyl fluoride (**7**), we propose that the minor regeneration of sulfinic acid **6a** initiates the sulfinyl fluoride decomposition pathway. This decomposition pathway and observed byproducts are consistent with previous literature reports.^{2,3}

Characterization

$^{19}\text{F}\{^1\text{H}\}$ NMR Spectroscopic Analysis of Crude Sulfinyl Fluorides

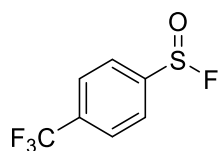
4-Fluorobenzenesulfinyl fluoride (2a)



Following general method **A** using 4-fluorobenzenesulfinic acid, **2a** was obtained in situ in 97% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using trifluorotoluene as the internal standard. The characterization data matched the previously reported data.⁴

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ +7.7 (d, J = 8.3 Hz), -104.0 (d, J = 7.9 Hz).

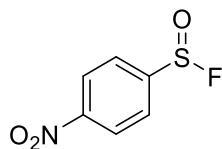
4-(trifluoromethyl)benzenesulfinyl fluoride (2b)



Following general method **A** using 4-(trifluoromethyl)benzenesulfinic acid, **2b** was obtained in situ in 85% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using trifluorotoluene as the internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ +3.4 (q, J = 2.0 Hz), -64.2 (d, J = 1.9 Hz).

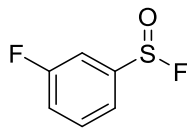
4-Nitrobenzenesulfinyl fluoride (2c)



Following general method **A** using 4-nitrobenzenesulfinic acid, **2c** was obtained in situ in 77% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using trifluorotoluene as the internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ +2.9.

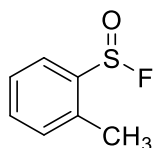
3-Fluorobenzenesulfinyl fluoride (2d)



Following general method **A** using 3-fluorobenzenesulfinic acid, **2d** was obtained in situ in 96% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using trifluorotoluene as the internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ +5.1 (d, J = 1.9 Hz), -110.2 (d, J = 1.5 Hz).

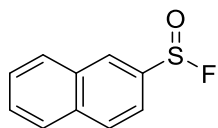
2-Methylbenzenesulfinyl fluoride (2e)



Following general method **A** using 2-methylbenzenesulfinic acid, **2e** was obtained in situ in 81% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using fluorobenzene as the internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ +1.0.

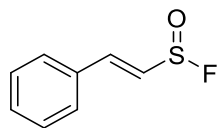
Naphthalene-2-sulfinyl fluoride (2f)



Following general method **A** using naphthalene-2-sulfinic acid, **2f** was obtained in situ in 89% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using trifluorotoluene as the internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ +6.3.

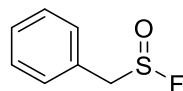
(*E*)-2-phenylethene-1-sulfinyl fluoride (2g)



Following general method **A** using (*E*)-2-phenylethene-1-sulfinic acid, **2g** was obtained in situ in 62% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using trifluorotoluene as the internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ +2.7.

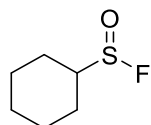
Phenylmethanesulfinyl fluoride (2h)



Following general method **A** using phenylmethanesulfinic acid, **2h** was obtained in situ in 94% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using trifluorotoluene as the internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ -18.0.

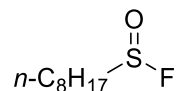
Cyclohexanesulfinyl fluoride (2i)



Following general method **A** using cyclohexanesulfinic acid, **2i** was obtained in situ in 88% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using trifluorotoluene as the internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ -31.4.

Octane-1-sulfinyl fluoride (2j)

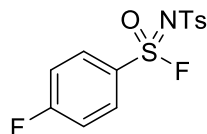


Following general method **A** using octane-1-sulfinic acid, **2j** was obtained in situ in 91% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy using trifluorotoluene as the internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ -20.8.

Analysis of Sulfonimidoyl Fluorides

4-Fluoro-*N*-tosylbenzenesulfonimidoyl fluoride (8a)



Following general method **B** using 4-fluoro-benzenesulfinic acid, **8a** was obtained as a white powder (275 mg, 80% yield).

^1H NMR: (300 MHz, Chloroform-*d*) δ 8.14 – 8.01 (m, 2H), 7.99 – 7.88 (m, 2H), 7.39 – 7.26 (m, 4H), 2.44 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR: (75 MHz, Chloroform-*d*) δ 167.3 (d, $J = 261.5$ Hz), 144.6, 138.8, 131.4 (d, $J = 10.3$ Hz), 129.8, 129.0 (dd, $J = 21.6, 3.3$ Hz), 127.2, 117.5 (d, $J = 23.4$ Hz), 21.8.

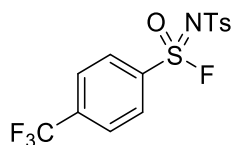
^{19}F NMR: (282 MHz, Chloroform-*d*) δ +75.0, -97.6.

IR (cm^{-1}): 3106, 3064, 2930, 1927, 1590, 1491, 1410, 1334, 1241, 1166, 1124, 1082, 1012.

HRMS (FD) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{11}\text{F}_2\text{N}_1\text{O}_3\text{S}_2$ $[\text{M}]^+$ 331.0148 found 331.0159.

Melting point: 60–62 °C

***N*-Tosyl-4-(trifluoromethyl)benzenesulfonimidoyl fluoride (8b)**



Following general method **B** using 4-(trifluoromethyl)benzenesulfinic acid, **8b** was obtained as a pale-yellow oil (249 mg, 65% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.3 Hz, 2H), 7.98 – 7.82 (m, 4H), 7.35 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H).

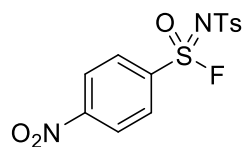
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 144.9, 138.6, 137.9, 137.5, 137.0, 136.8, 129.9, 128.9, 127.3, 127.1 (q, *J* = 3.7 Hz), 124.5, 120.9, 21.8.

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.1, -63.5.

IR (cm⁻¹): 3106, 3060, 1600, 1407, 1319, 1134, 1111, 1062, 1015.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₄H₁₁F₄N₁O₃S₂ [M]⁺ 381.0116 found 381.0133.

4-Nitro-*N*-tosylbenzenesulfonimidoyl fluoride (8c)



Following general method **B** using 4-nitro-benzenesulfinic acid, **8c** was obtained as an off-white powder (227 mg, 63%). The characterization data matched the previously reported data.⁵

¹H NMR: (300 MHz, Chloroform-*d*) δ 8.49 – 8.40 (m, 2H), 8.31 – 8.20 (m, 2H), 7.98 – 7.87 (m, 2H), 7.40 – 7.30 (m, 2H), 2.45 (s, 3H).

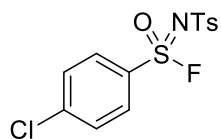
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 152.1, 145.1, 138.8 (d, *J* = 23.3 Hz), 138.4, 130.0, 129.8, 127.3, 125.0, 21.8.

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.1.

IR (cm⁻¹): 3115, 2924, 2857, 1600, 1527, 1356, 1303, 1140, 1086, 1010.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₃H₁₁F₁N₂O₅S₂ [M]⁺ 358.0093 found 358.0083.

4-Chloro-*N*-tosylbenzenesulfonimidoyl fluoride (**8k**)



Following general method **B** using 4-chlorobenzenesulfinic acid, **8k** was obtained as a white powder (281 mg, 80% yield). The characterization data matched the previously reported data.⁵

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H).

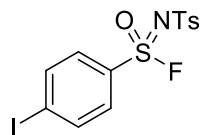
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 144.6, 143.5, 138.8, 131.6 (d, *J* = 21.8 Hz), 130.3, 129.9, 129.6, 127.3, 21.8.

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.2.

IR (cm⁻¹): 3099, 3089, 2924, 1595, 1574, 1477, 1397, 1335, 1287, 1183, 1163, 1126, 1082, 1011.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₃H₁₁ClF₁N₁O₃S₂ [M]⁺ 346.9853 found 346.9847.

4-Iodo-*N*-tosylbenzenesulfonimidoyl fluoride (**8l**)



Following general method **B** using 4-iodo-benzenesulfinic acid, **8l** was obtained as a white solid (351 mg, 79% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 144.6, 139.3, 138.7, 132.8 (d, *J* = 21.7 Hz), 129.8, 129.1, 127.2, 105.1, 21.8.

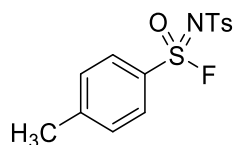
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.2.

IR (cm⁻¹): 3357, 3261, 3094, 2922, 2853, 1595, 1564, 1389, 1335, 1320, 1191, 1136, 1090, 1053, 1004.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₃H₁₁F₁I₁N₁O₃S₂ [M]⁺ 438.9209 found 438.9190.

Melting point: 80–82 °C

4-Methyl-*N*-tosylbenzenesulfonimidoyl fluoride (**8m**)



Following general method **B** using 4-methylbenzenesulfonic acid, **8m** was obtained as a white powder (282 mg, 85% yield). The characterization data matched the previously reported data.⁶

¹H NMR: ¹H NMR (300 MHz, Chloroform-*d*) δ 8.01 – 7.88 (m, 4H), 7.40 (dd, *J* = 8.5, 3.5 Hz, 2H), 7.34 (dd, *J* = 8.2, 3.9 Hz, 2H), 2.48 (s, 3H), 2.44 (s, 3H).

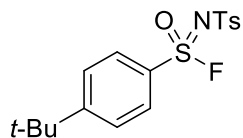
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 148.1, 144.4, 139.0, 130.5, 130.2, 129.9, 129.8, 128.2, 127.2, 22.0, 21.8.

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.1.

IR (cm⁻¹): 3363, 3264, 3086, 2923, 1592, 1335, 1279, 1184, 1162, 1119, 1083, 1069, 1012.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₄H₁₄F₁N₁O₃S₂ [M]⁺ 327.0399 found 327.0408.

4-(*tert*-butyl)-*N*-tosylbenzenesulfonimidoyl fluoride (**8n**)



Following general method **B** using 4-(*tert*-butyl)-benzenesulfonic acid, **8n** was obtained as a white solid (169 mg, 85% yield). The characterization data matched the previously reported data.⁶

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.5, 4.8 Hz, 4H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 2.43 (s, 3H), 1.34 (s, 9H).

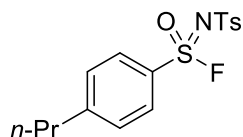
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 161.0, 144.3, 139.13, 130.1, 129.9, 129.8, 128.2, 127.25, 127.0, 35.8, 31.0, 21.8.

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +73.9.

IR (cm⁻¹): 2960, 2925, 2872, 1590, 1340, 1326, 1297, 1166, 1137, 1105, 1083, 1009.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₇H₂₀F₁N₁O₃S₂ [M]⁺ 369.0869 found 369.0851.

4-Propyl-*N*-tosylbenzenesulfonimidoyl fluoride (**8o**)



Following general method **B** using 4-propylbenzenesulfonic acid, **8o** was obtained as a pale-yellow oil (199 mg, 56% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.4, 5.6 Hz, 4H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 2.69 (dd, *J* = 8.5, 6.7 Hz, 2H), 2.43 (s, 3H), 1.66 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

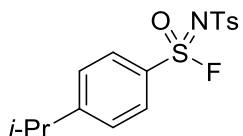
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 152.1, 144.5, 140.0, 138.6, 129.8 (d, *J* = 9.6 Hz), 128.2, 127.3 (d, *J* = 39.8 Hz), 127.2, 38.1, 24.1, 21.8, 13.8.

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.1.

IR (cm⁻¹): 2962, 2931, 2872, 1590, 1410, 1340, 1285, 1163, 1109, 1086, 1012.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₆H₁₈F₁N₁O₃S₂ [M]⁺ 355.0712 found 355.0712.

4-Isopropyl-*N*-tosylbenzenesulfonimidoyl fluoride (**8p**)



Following general method **B** using 4-isopropyl-benzenesulfonic acid, **8p** was obtained as a yellow oil (258 mg, 71% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.4, 3.3 Hz, 4H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 3.02 (hept, *J* = 6.9 Hz, 1H), 2.43 (3, 1H), 1.27 (d, *J* = 6.9 Hz, 6H).

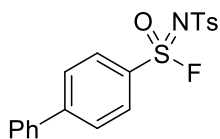
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 158.7, 144.3, 139.1, 130.4, 130.1, 129.8, 128.5, 128.0, 127.3, 34.6, 23.6, 21.8.

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.0.

IR (cm⁻¹): 2965, 2929, 2874, 1594, 1490, 1463, 1415, 1339, 1322, 1164, 1132, 1087, 1054, 1014.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₆H₁₈F₁N₁O₃S₂ [M]⁺ 355.0712 found 355.0719.

***N*-Tosyl-[1,1'-biphenyl]-4-sulfonimidoyl fluoride (8q)**



Following general method **B** using [1,1'-biphenyl]-benzenesulfinic acid, **8q** was obtained as a white powder (282 mg, 72% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.55 – 7.42 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 149.4, 144.4, 139.0, 138.3, 131.4 (d, *J* = 20.7 Hz), 129.8, 129.5, 129.4, 128.8, 128.3, 127.6, 127.3, 21.8.

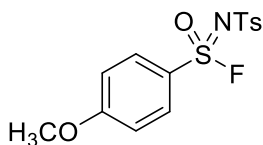
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.4.

IR (cm⁻¹): 3064, 2924, 2854, 1589, 1478, 1449, 1402, 1338, 1315, 1164, 1157, 1129, 1084, 1006.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₉H₁₆F₁N₁O₃S₂ [M]⁺ 389.0556 found 389.0537.

Melting point: 92–94 °C

4-Methoxy-*N*-tosylbenzenesulfonimidoyl fluoride (8r)



Following general method **B** using 4-methoxy-benzenesulfinic acid, **8r** was obtained as a white solid (158 mg, 92%). The characterization data matched the previously reported data.⁷

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.94 (t, *J* = 8.7 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.08 – 6.99 (m, 2H), 3.90 (s, 3H), 2.43 (s, 3H).

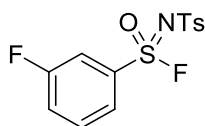
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 165.9, 144.3, 139.1, 130.8, 129.7, 127.2, 123.7 (d, *J* = 20.7 Hz), 115.1, 56.2, 21.7.

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +75.3.

IR (cm⁻¹): 2924, 2852, 1592, 1576, 1496, 1332, 1302, 1270, 1131, 1119, 1087, 1025.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₄H₁₄F₁N₁O₄S₂ [M]⁺ 343.0348 found 343.0332.

3-Fluoro-*N*-tosylbenzenesulfonimidoyl fluoride (**8d**)



Following general method **A** using 3-fluorobenzenesulfonic acid, **8d** was obtained as a white solid (194 mg, 57% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.83 (dd, *J* = 14.7, 8.1 Hz, 1H), 7.74 (dt, *J* = 7.6, 2.2 Hz, 1H), 7.68 – 7.58 (m, 1H), 7.49 (td, *J* = 8.1, 2.4 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H).

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 254.7 Hz), 144.7, 138.7, 134.9 (dd, *J* = 21.9, 7.8 Hz), 131.9 (d, *J* = 7.9 Hz), 129.9, 127.3, 124.1 (d, *J* = 3.7 Hz), 123.8 (d, *J* = 21.0 Hz), 115.7 (d, *J* = 26.2 Hz), 21.8.

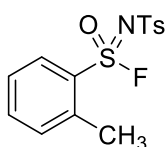
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.2, -106.9 (td, *J* = 7.8, 5.1 Hz).

IR (cm⁻¹): 3085, 2923, 2852, 1593, 1480, 1344, 1306, 1231, 1164, 1131, 1084.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₃H₁₁F₂N₁O₃S₂ [M]⁺ 331.0148 found 331.0155.

Melting point: 62–64 °C

2-Methyl-*N*-tosylbenzenesulfonimidoyl fluoride (**8e**)



Following general method **B** using 2-methylbenzenesulfonic acid, **8e** was obtained as a white powder (275 mg, 84% yield). The characterization data matched the previously reported data.⁸

¹H NMR: (300 MHz, Chloroform-*d*) δ 8.07 – 8.02 (m, 1H), 7.99 – 7.90 (m, 2H), 7.64 (td, *J* = 7.6, 1.4 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 2.68 – 2.62 (m, 3H), 2.45 (s, 3H).

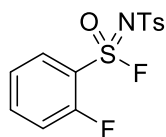
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 144.3, 139.0 (d, *J* = 8.6 Hz), 135.8, 135.6, 133.9, 133.24, 132.5, 132.2, 129.7, 129.6, 129.6 (d, *J* = 1.7 Hz), 128.5, 127.47, 127.1, 126.9, 126.8, 21.61, 20.1 (d, *J* = 1.9 Hz).

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +65.8.

IR (cm⁻¹): 3096, 2927, 2856, 1597, 1470, 1336, 1322, 1287, 1149, 1108, 1085.

HRMS (FD) m/z: $[M]^+$ Calcd for $C_{14}H_{14}F_1N_1O_3S_2$ $[M]^+$ 327.0399 found 327.0407.

2-Fluoro-*N*-tosylbenzenesulfonimidoyl fluoride (**8s**)



Following general method **B** using 2-fluorobenzenesulfinic acid, **8s** was obtained as a white powder (258 mg, 78% yield).

1H NMR: (300 MHz, Chloroform-*d*) δ 8.00 (ddd, $J = 8.3, 6.7, 1.8$ Hz, 1H), 7.95 – 7.88 (m, 2H), 7.83 – 7.73 (m, 1H), 7.42 – 7.27 (m, 4H), 2.44 (s, 3H).

$^{13}C\{^1H\}$ NMR: (75 MHz, Chloroform-*d*) δ 159.5 (dd, $J = 264.1, 1.3$ Hz), 144.6, 138.8 (d, $J = 8.8$ Hz), 130.8, 129.8, 127.2, 125.1 (d, $J = 4.1$ Hz), 122.2 (dd, $J = 23.0, 12.8$ Hz), 118.2 (d, $J = 19.9$ Hz), 21.8.

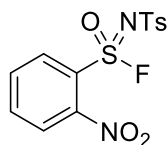
^{19}F NMR: (282 MHz, Chloroform-*d*) δ +70.6 (d, $J = 14.8$ Hz), -105.0 – -105.2 (m).

IR (cm $^{-1}$): 3110, 2935, 1595, 1590, 1474, 1451, 1346, 1319, 1268, 1161, 1141, 1084, 1074.

HRMS (FD) m/z: $[M]^+$ Calcd for $C_{13}H_{11}F_2N_1O_3S_2$ $[M]^+$ 331.0148 found 331.0163.

Melting point: 59–61 °C

2-Nitro-*N*-tosylbenzenesulfonimidoyl fluoride (**8t**)



Following general method **B** using 2-nitrobenzenesulfinic acid, **8t** was obtained as an off-white solid (292 mg, 82%).

1H NMR: (300 MHz, Chloroform-*d*) δ 8.29 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.03 (dd, $J = 8.2, 1.5$ Hz, 1H), 7.96 (td, $J = 7.7, 1.5$ Hz, 1H), 7.92 – 7.84 (m, 3H), 7.38 – 7.31 (m, 2H), 2.45 (s, 3H).

$^{13}C\{^1H\}$ NMR: (75 MHz, Chloroform-*d*) δ 144.9, 138.0, 137.1, 133.5, 131.4 (d, $J = 2.5$ Hz), 129.8, 127.7 (d, $J = 25.1$ Hz), 127.3, 126.4, 126.4, 21.8.

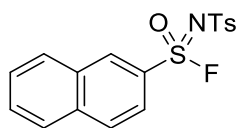
^{19}F NMR: (282 MHz, Chloroform-*d*) δ +71.7.

IR (cm $^{-1}$): 3079, 3032, 1543, 1335, 1326, 1146, 1115, 1085.

HRMS (FD) m/z: $[M]^+$ Calcd for $C_{13}H_{11}F_1N_2O_5S_2$ $[M]^+$ 358.0093 found 358.0093.

Melting point: 63–65 °C

***N*-Tosyl naphthalene-2-sulfonimidoyl fluoride (**8f**)**



Following general method **B** using naphthalene-2-sulfonic acid, **8f** was obtained as an off-white powder (177 mg, 92%). The characterization data matched the previously reported data.⁷

¹H NMR: (300 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 2.0 Hz, 1H), 8.09 – 7.89 (m, 6H), 7.73 (dddd, *J* = 20.6, 8.1, 6.9, 1.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H).

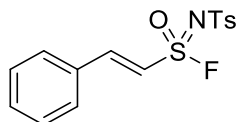
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 144.5, 139.1, 136.3, 131.7, 131.0, 131.0, 130.39, 129.9, 129.8, 128.7, 128.3, 127.3, 121.6, 21.8.

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +74.4.

IR (cm⁻¹): 3057, 2924, 1596, 1317, 1164, 1143, 1130, 1087.

HRMS (FD) m/z: [M]⁺ Calcd for C₁₇H₁₄F₁N₁O₃S₂ [M]⁺ 363.0399 found 363.0406.

***(E)*-2-phenyl-*N*-tosylethene-1-sulfonimidoyl fluoride (**8g**)**



Following general method **B** using (*E*)-2-phenylethene-1-sulfonic acid, **8g** was obtained as a white powder (197 mg, 58% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 15.4 Hz, 1H), 7.60–7.42 (m, 5H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 15.4 Hz, 2.1 Hz, 1H), 2.44 (s, 3H).

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 149.3, 144.3, 138.8, 133.2, 130.5, 129.7, 129.5, 129.4, 127.1, 118.5, 118.2, 21.6.

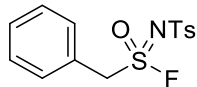
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ +71.0.

IR (cm⁻¹): 3067, 1607, 1576, 1496, 1450, 1335, 1301, 1165, 1125, 1085.

HRMS (FD) m/z: See note.⁸

Melting point: 49–51 °C

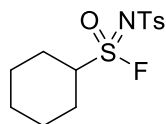
1-Phenyl-*N*-tosylmethanesulfonyl fluoride (**8h**)



Following general method **B** using phenylmethanesulfinic acid, **8h** was obtained in 10% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy of the crude reaction mixture against a fluorobenzene internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR: (282 MHz, Chloroform-*d*) δ +74.1.

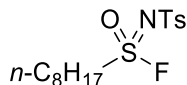
N-Tosylcyclohexanesulfonyl fluoride (**8i**)



Following general method **B** using cyclohexanesulfinic acid, **8i** was obtained in 24% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy of the crude reaction mixture against a fluorobenzene internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) δ +75.7.

N-Tosyl-octane-1-sulfonyl fluoride (**8j**)



Following general method **B** using octane-1-sulfinic acid, **8j** was obtained in 14% yield determined by quantitative $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy of the crude reaction mixture against a fluorobenzene internal standard.

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) δ +67.8.

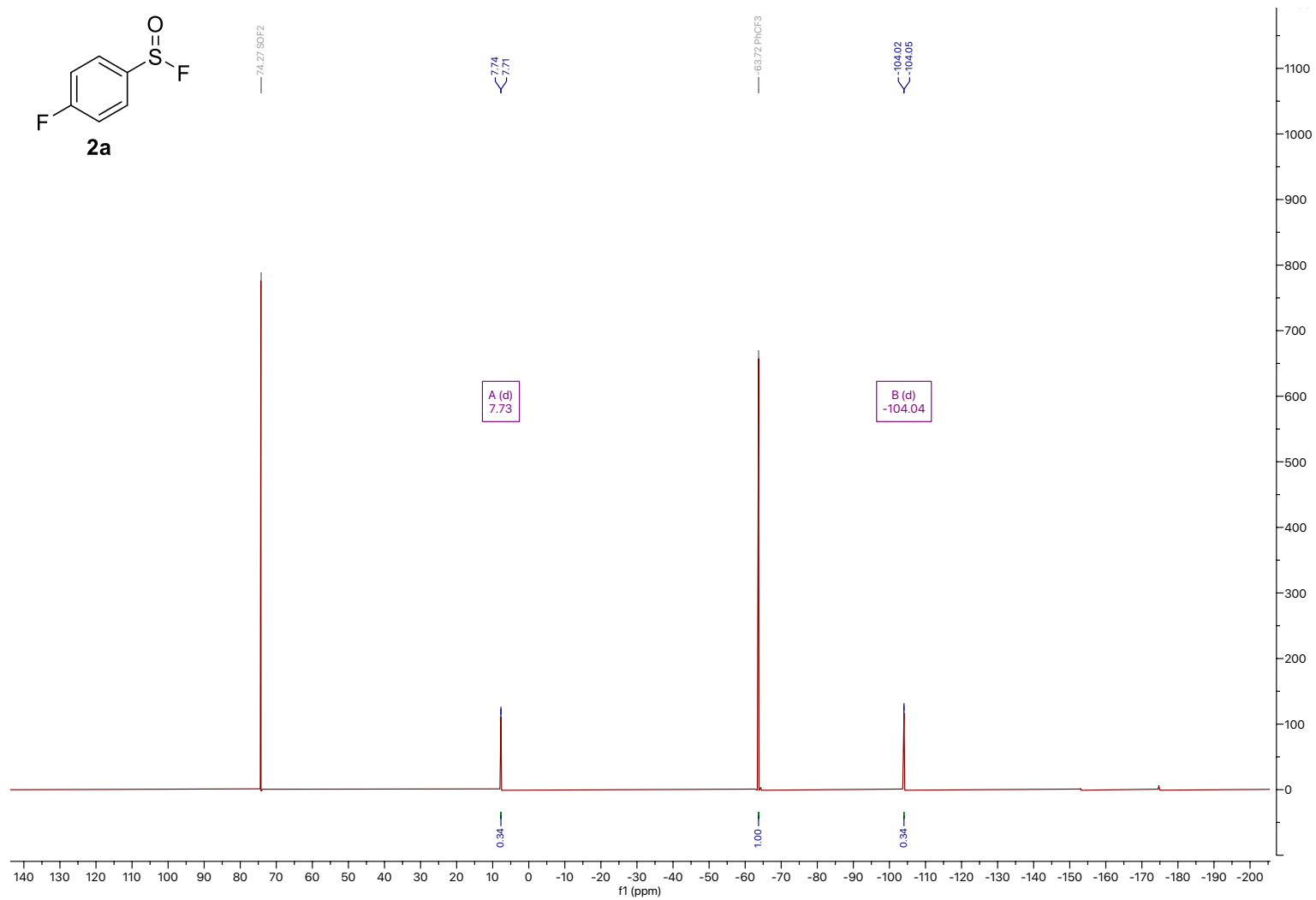
Supplementary References and Notes

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9. This compound failed to ionize under FD, EI, and ESI methods.

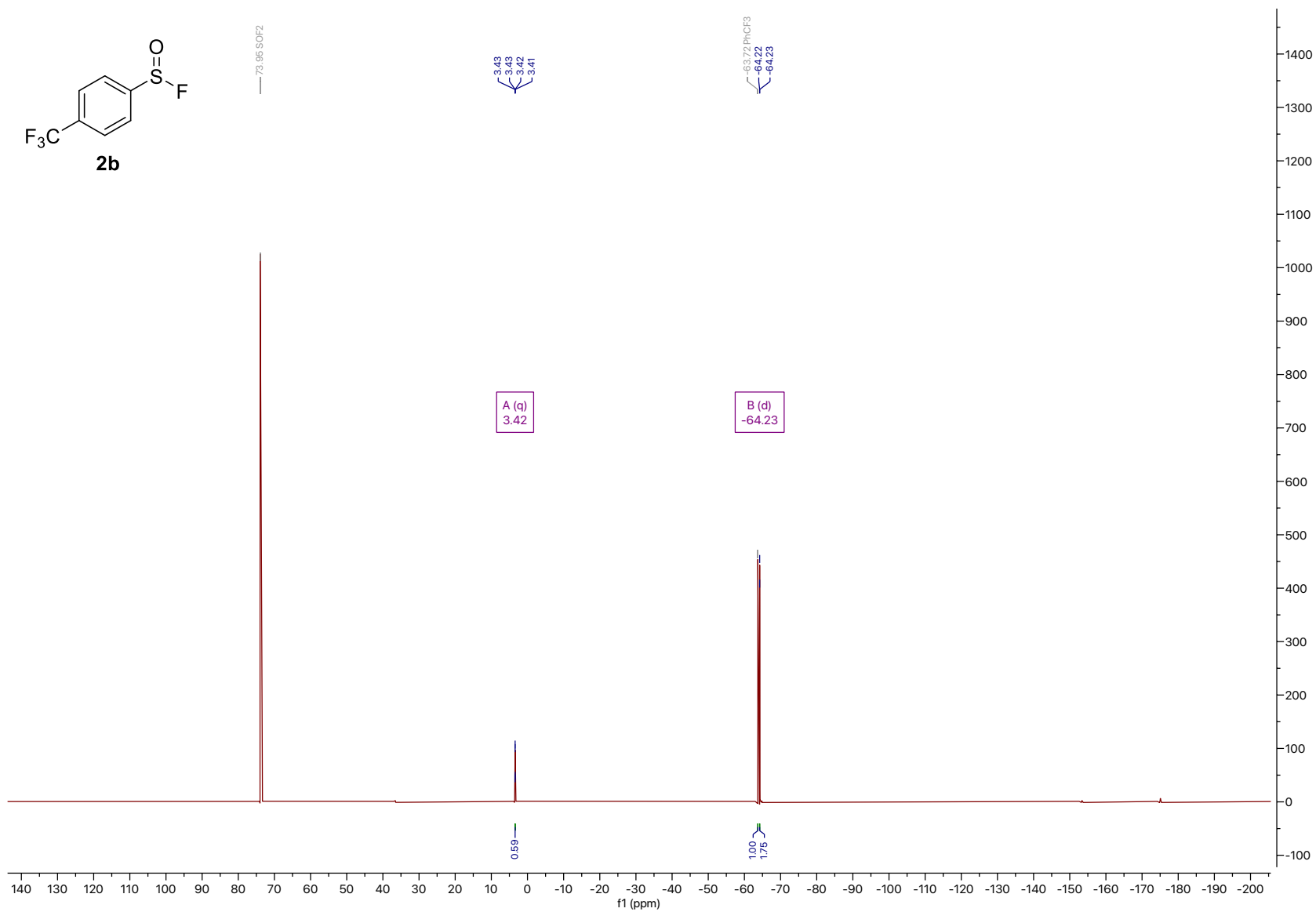
NMR Spectra

Crude Sulfinyl Fluorides

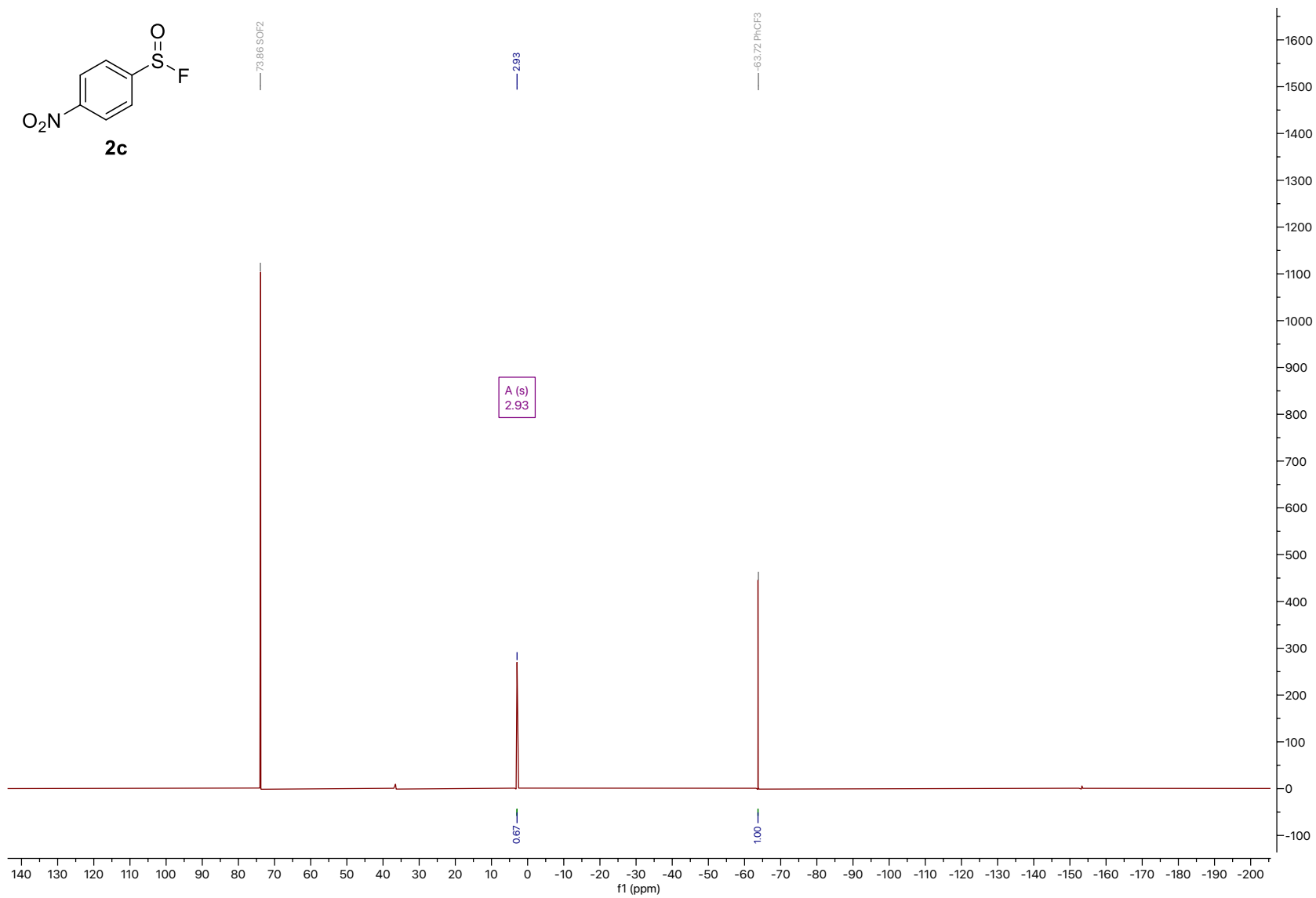
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of 4-fluorobenzenesulfinyl fluoride (2a)



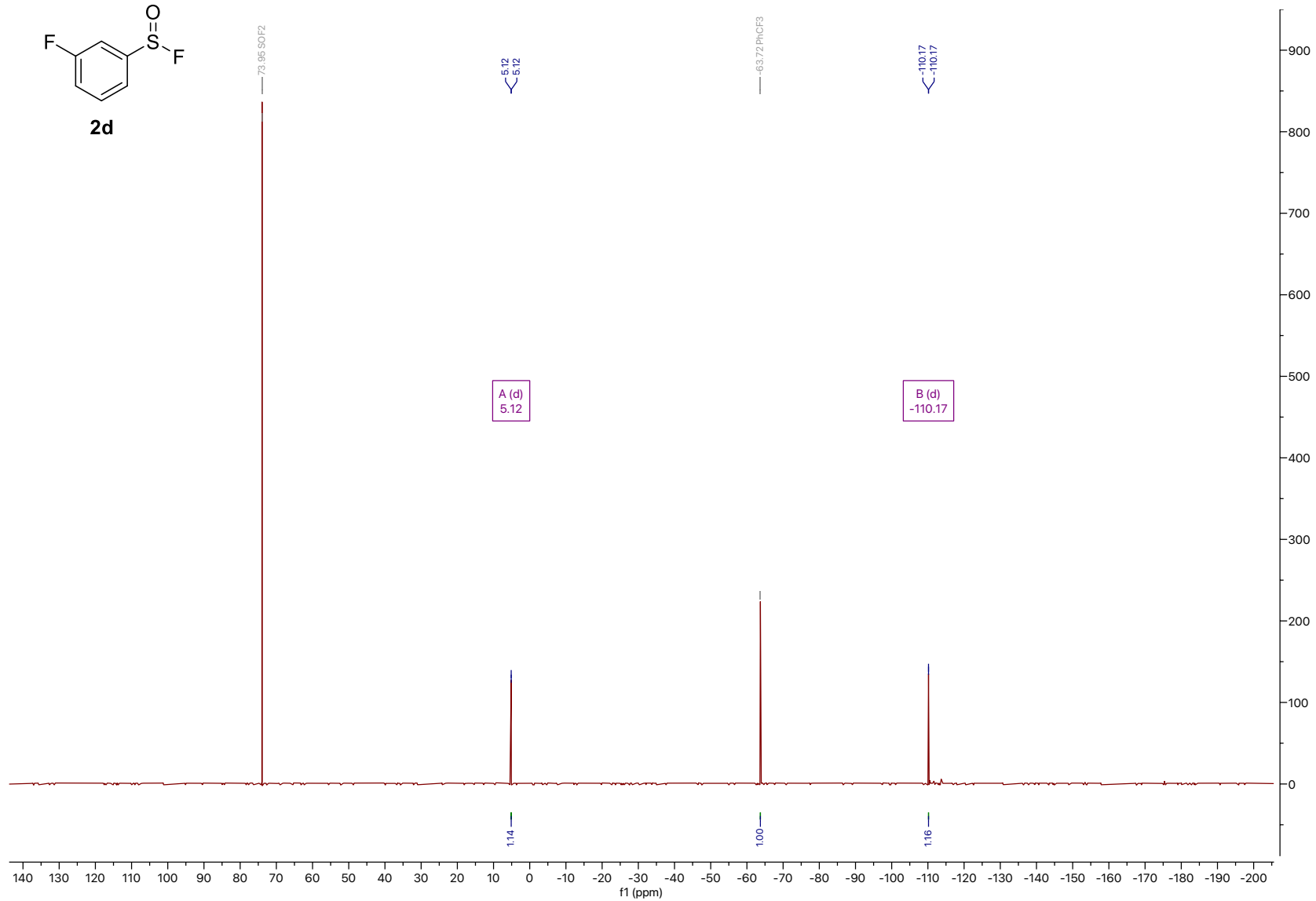
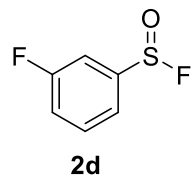
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of 4-(trifluoromethyl)benzenesulfinyl fluoride (2b)



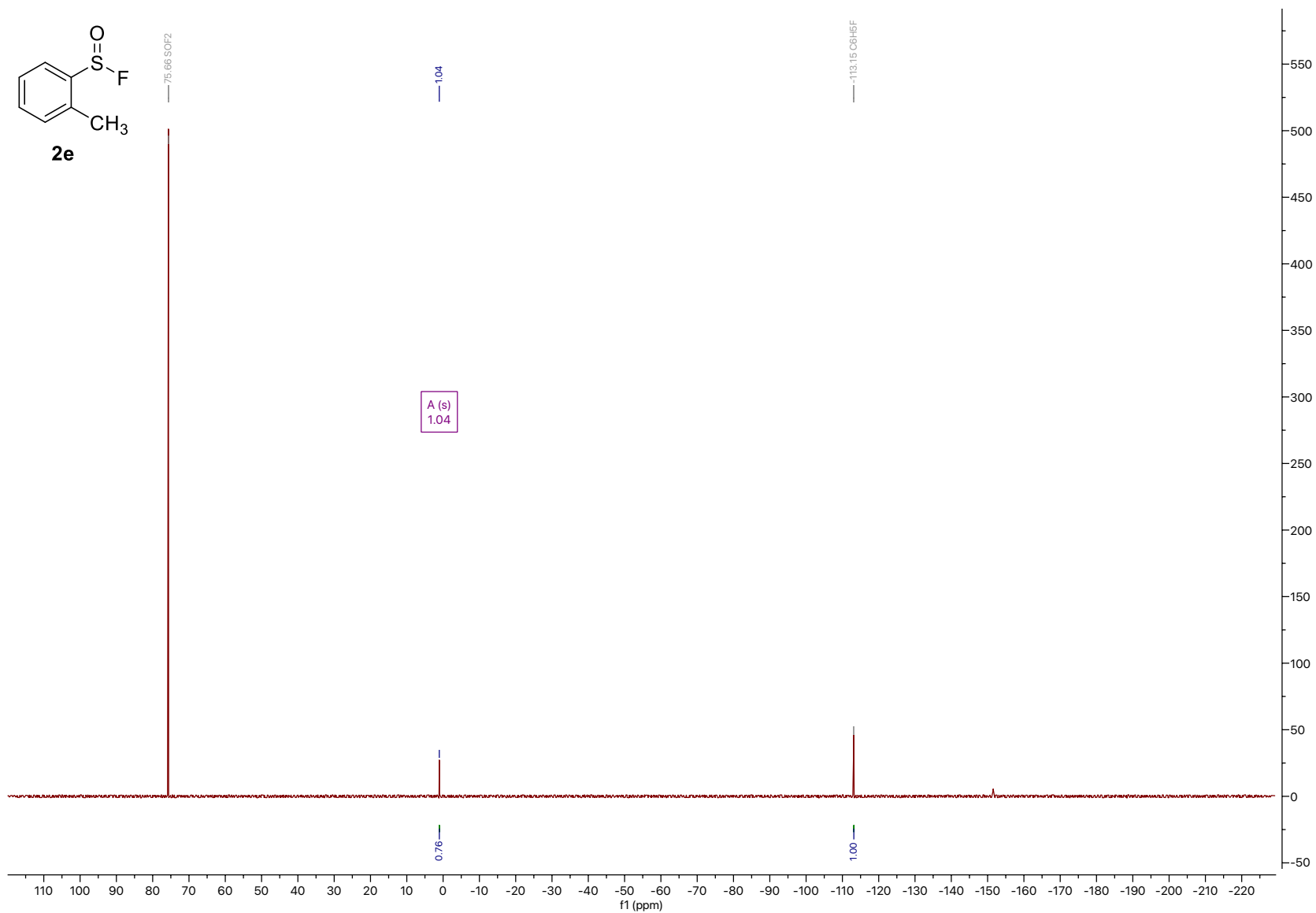
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of 4-nitrobenzenesulfinyl fluoride (2c)



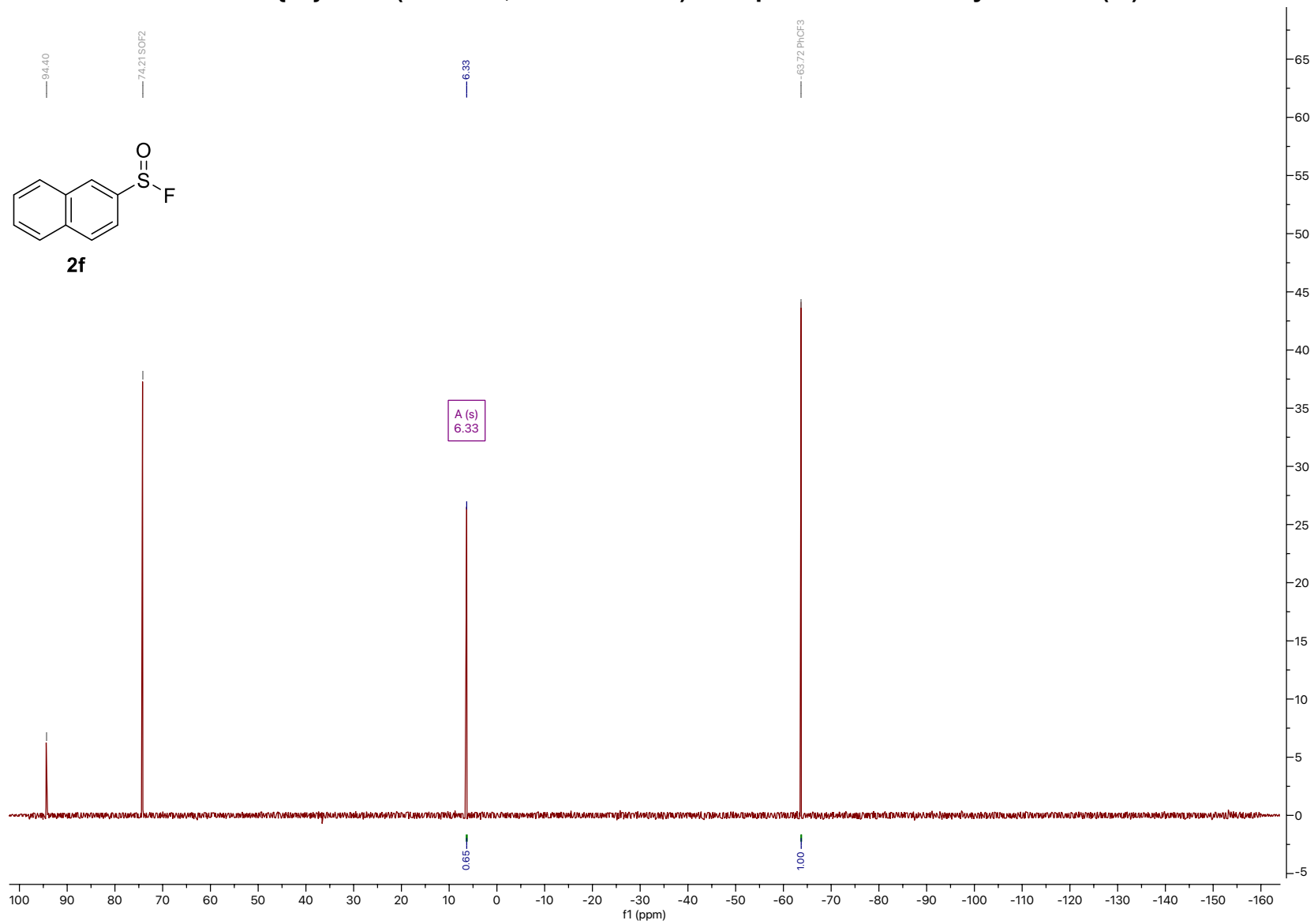
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of 3-fluorobenzenesulfinyl fluoride (2d)



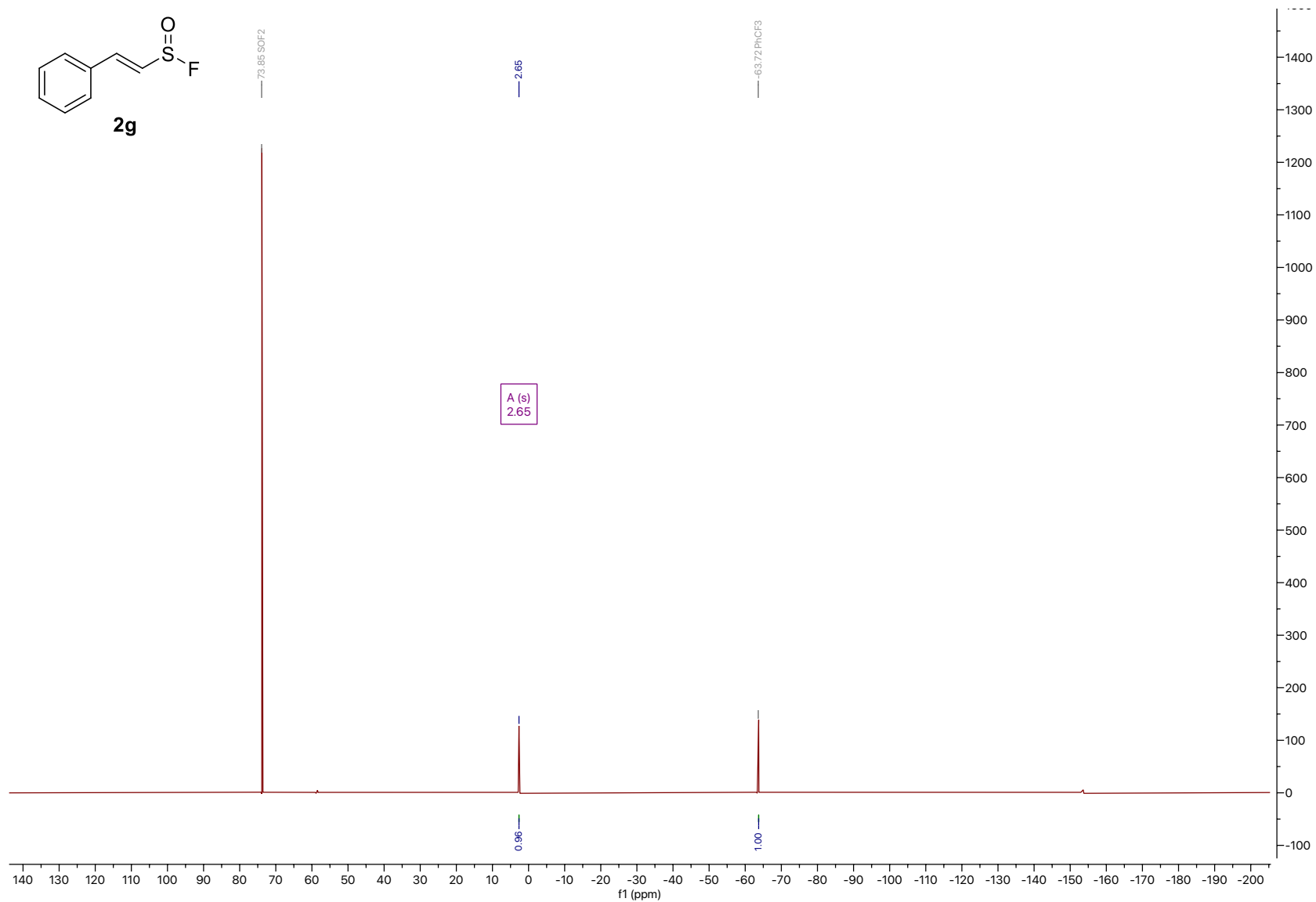
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of 2-methylbenzenesulfinyl fluoride (2e)



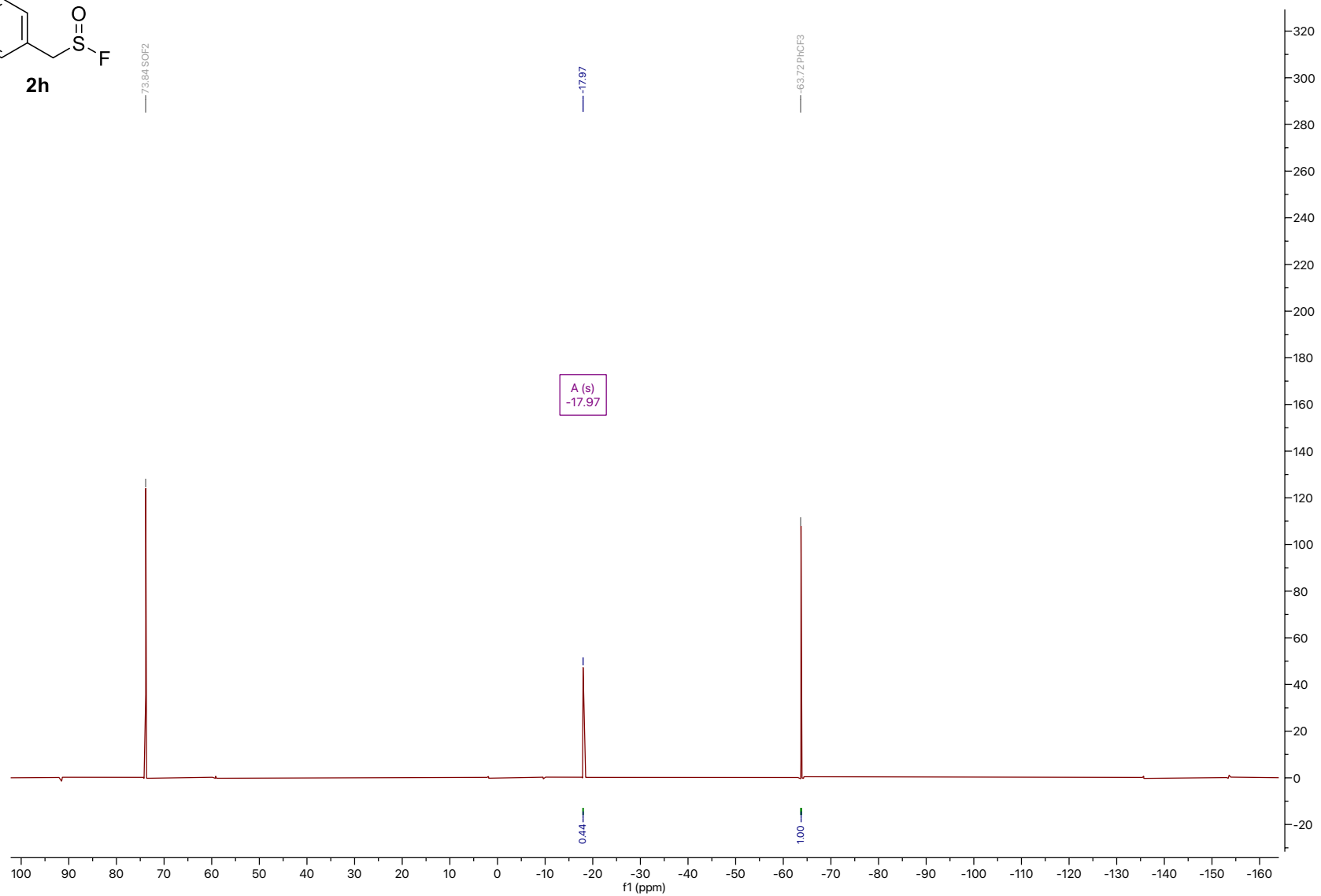
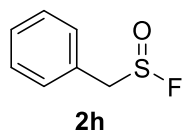
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of naphthalene-2-sulfinyl fluoride (2f)



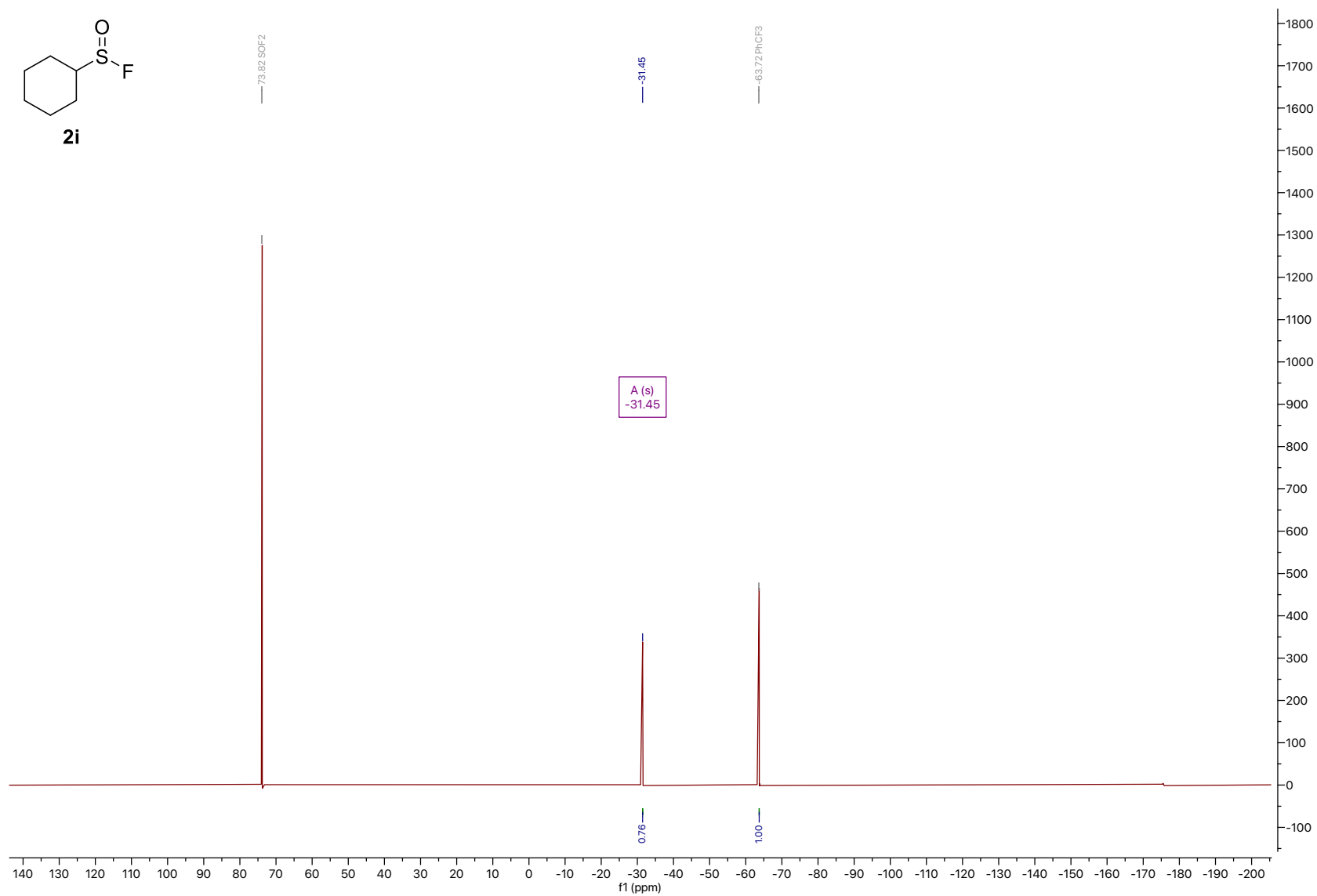
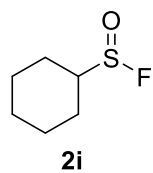
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of (*E*)-2-phenylethene-1-sulfinyl fluoride (2g)



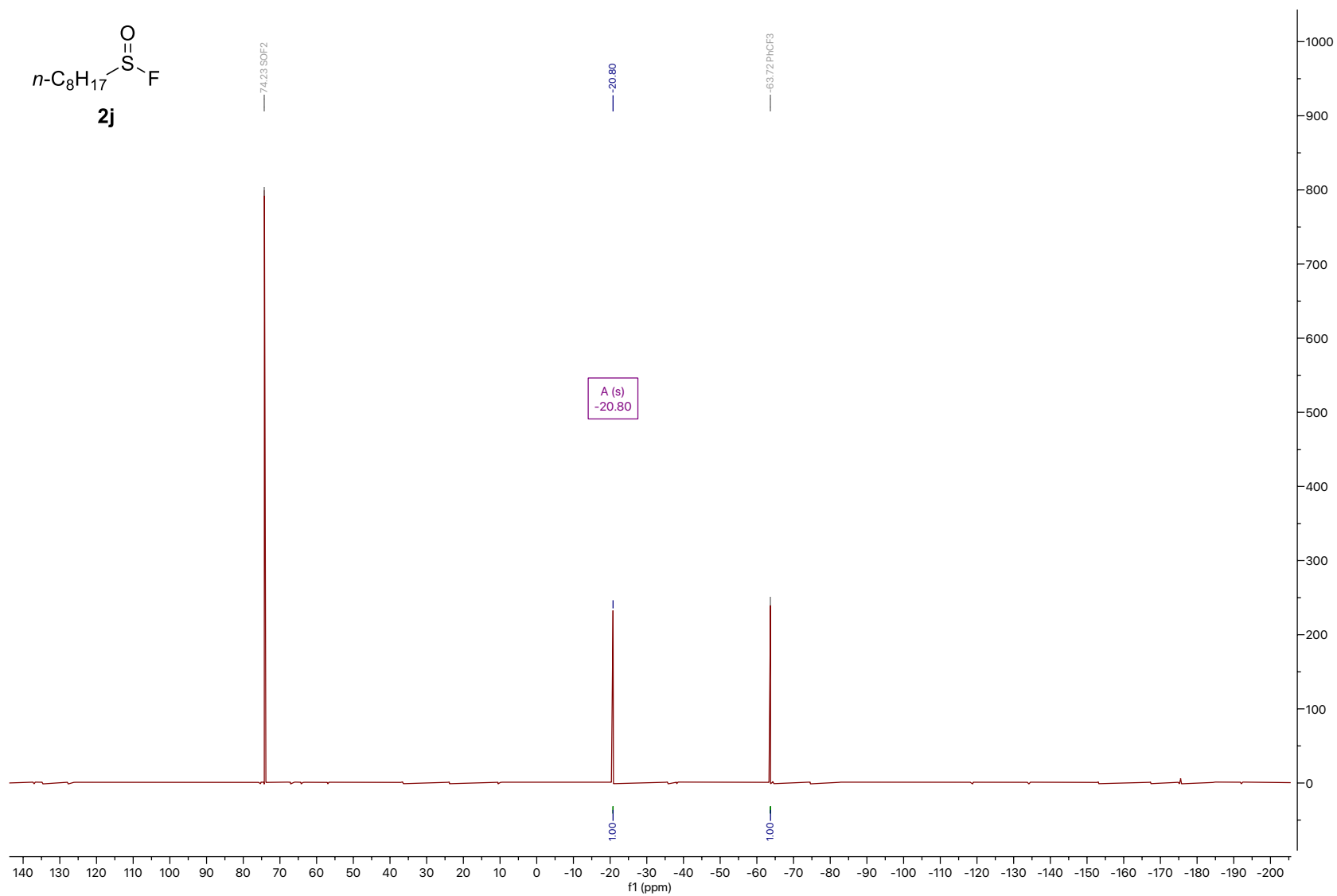
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of phenylmethanesulfonyl fluoride (2h)



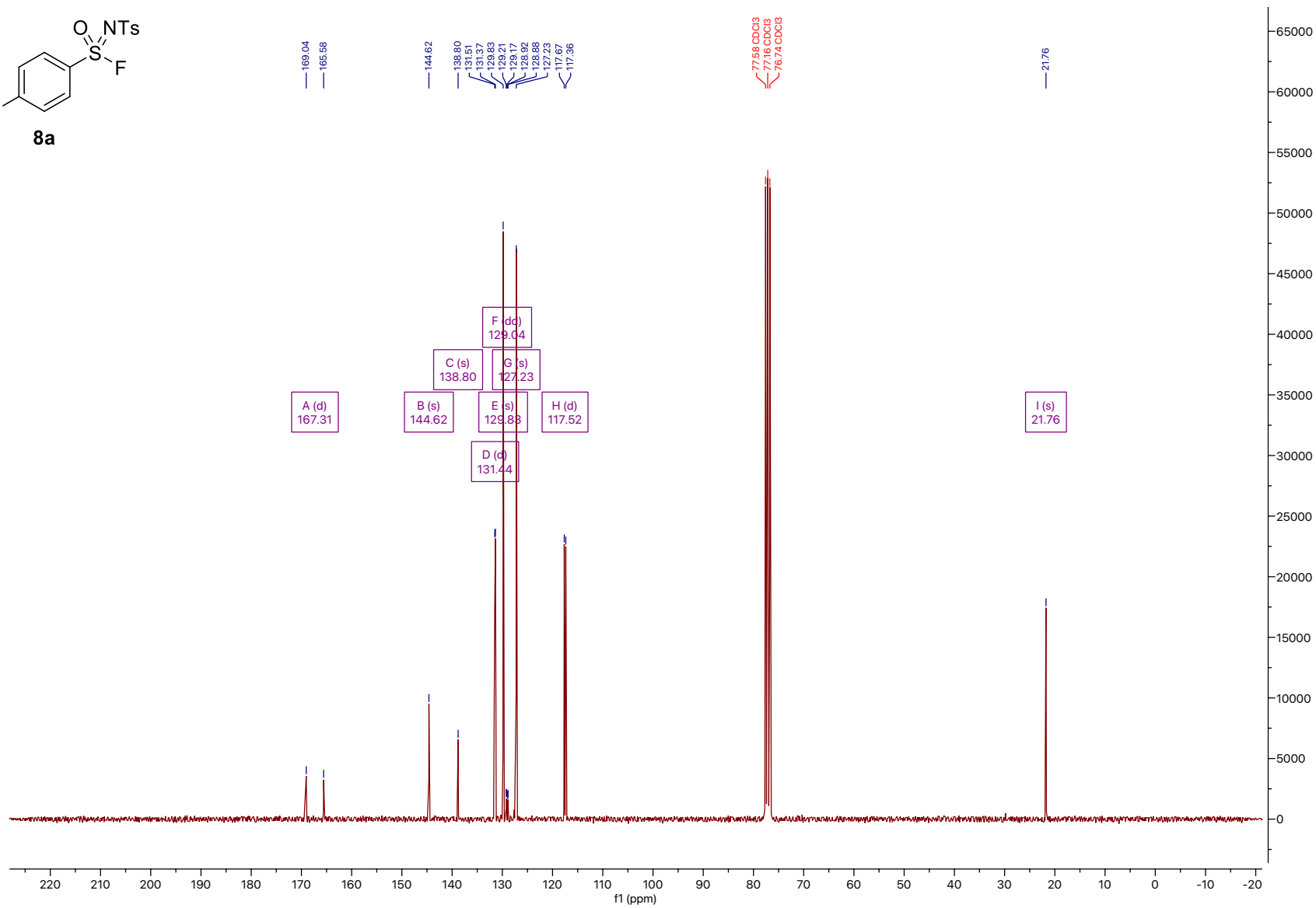
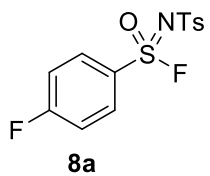
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of cyclohexanesulfinyl fluoride (2i)



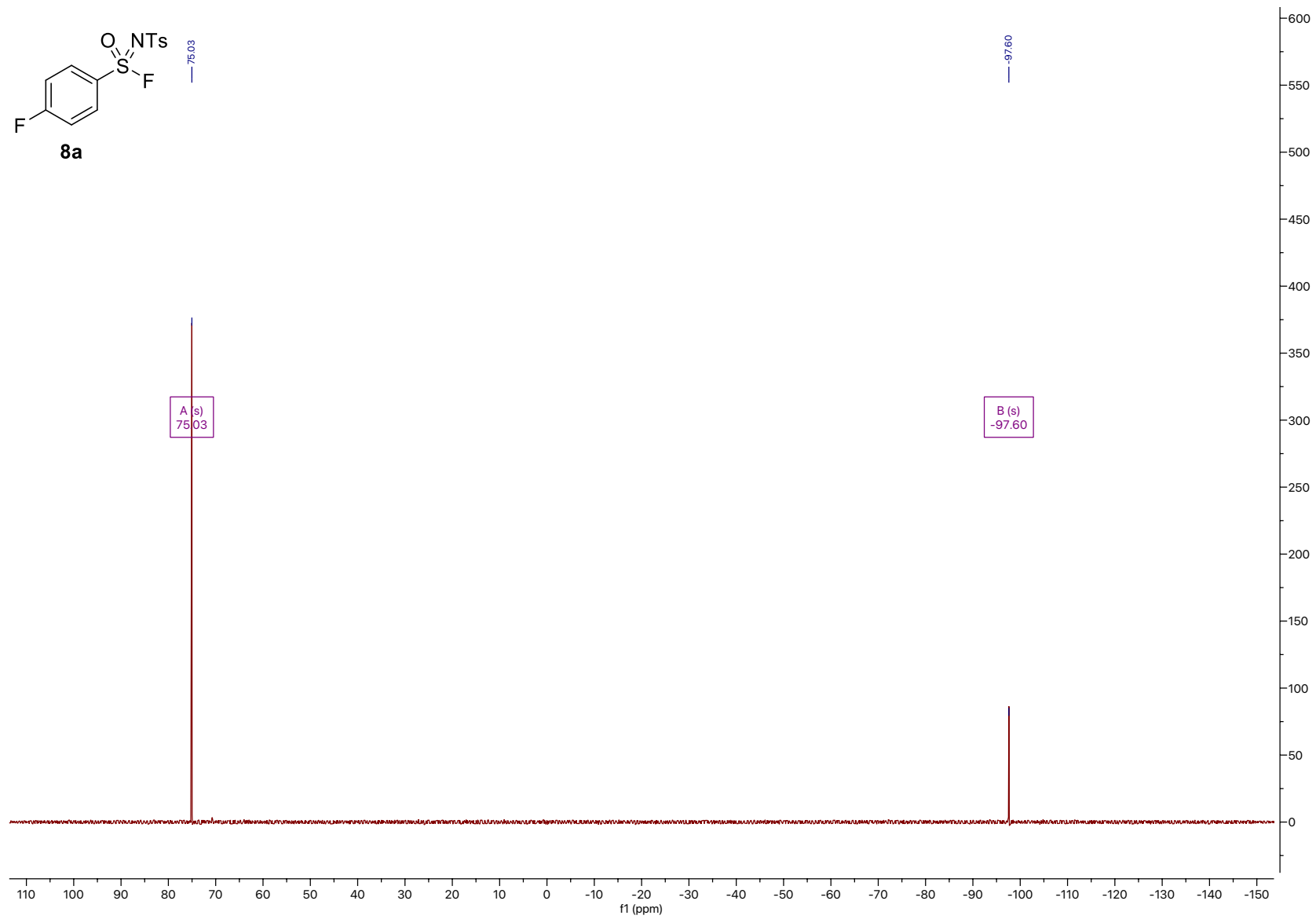
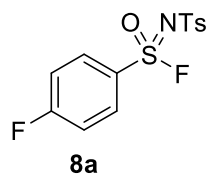
$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of octane-1-sulfinyl fluoride (2j)



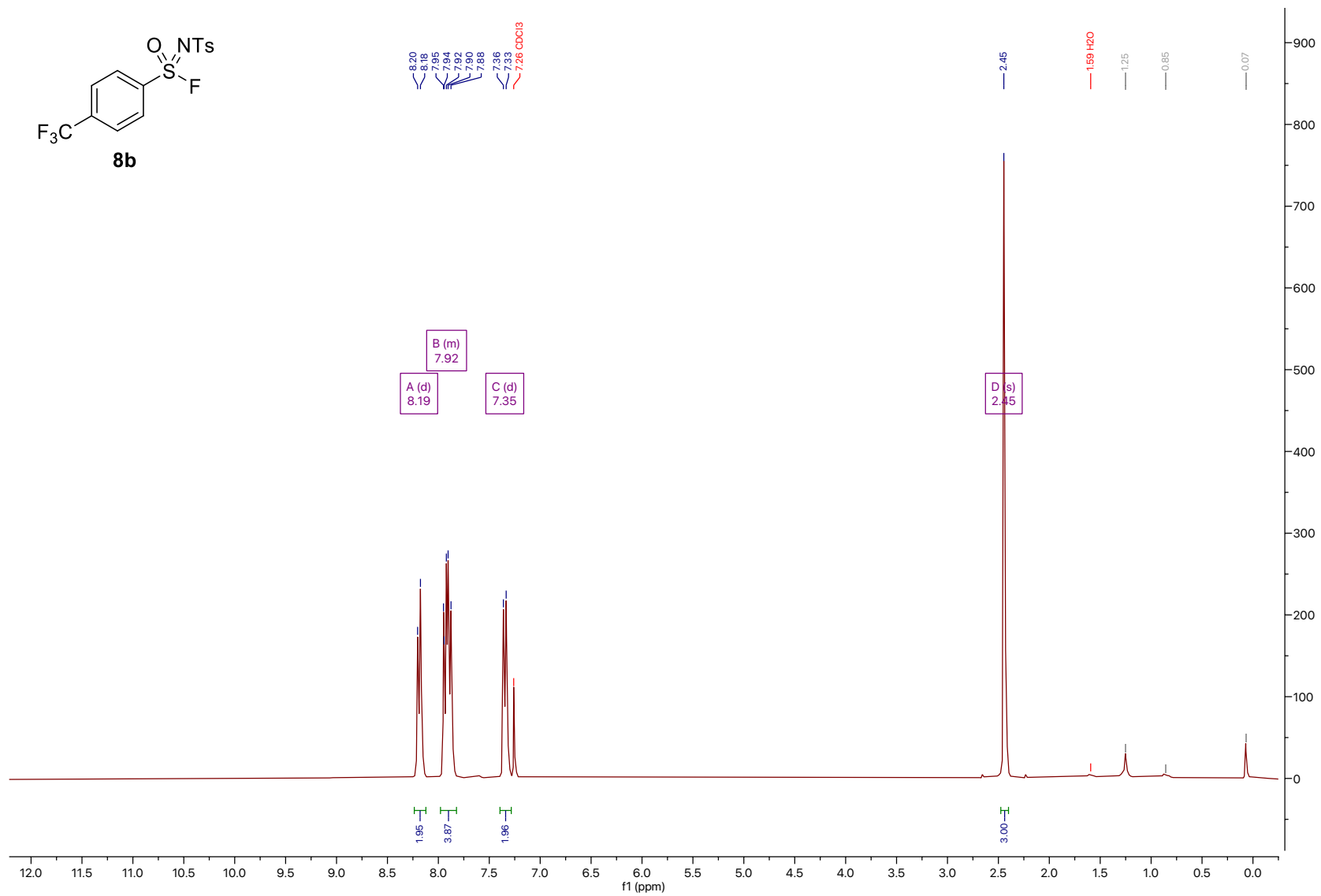
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 4-fluoro-*N*-tosylbenzenesulfonimidoyl fluoride (8a)



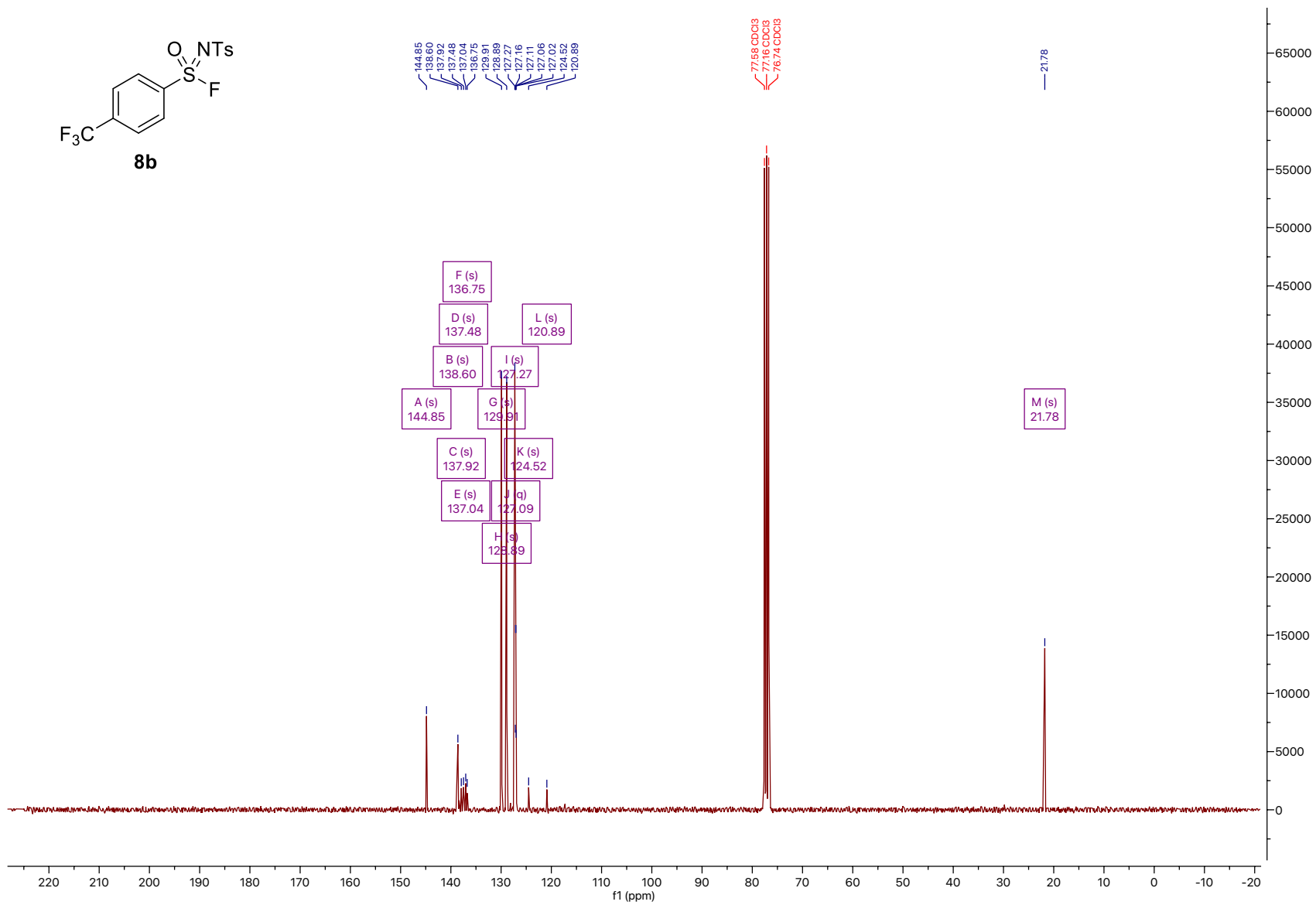
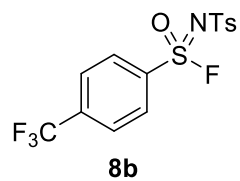
^{19}F NMR (282 MHz, Chloroform-*d*) of 4-fluoro-*N*-tosylbenzenesulfonimidoyl fluoride (8a)



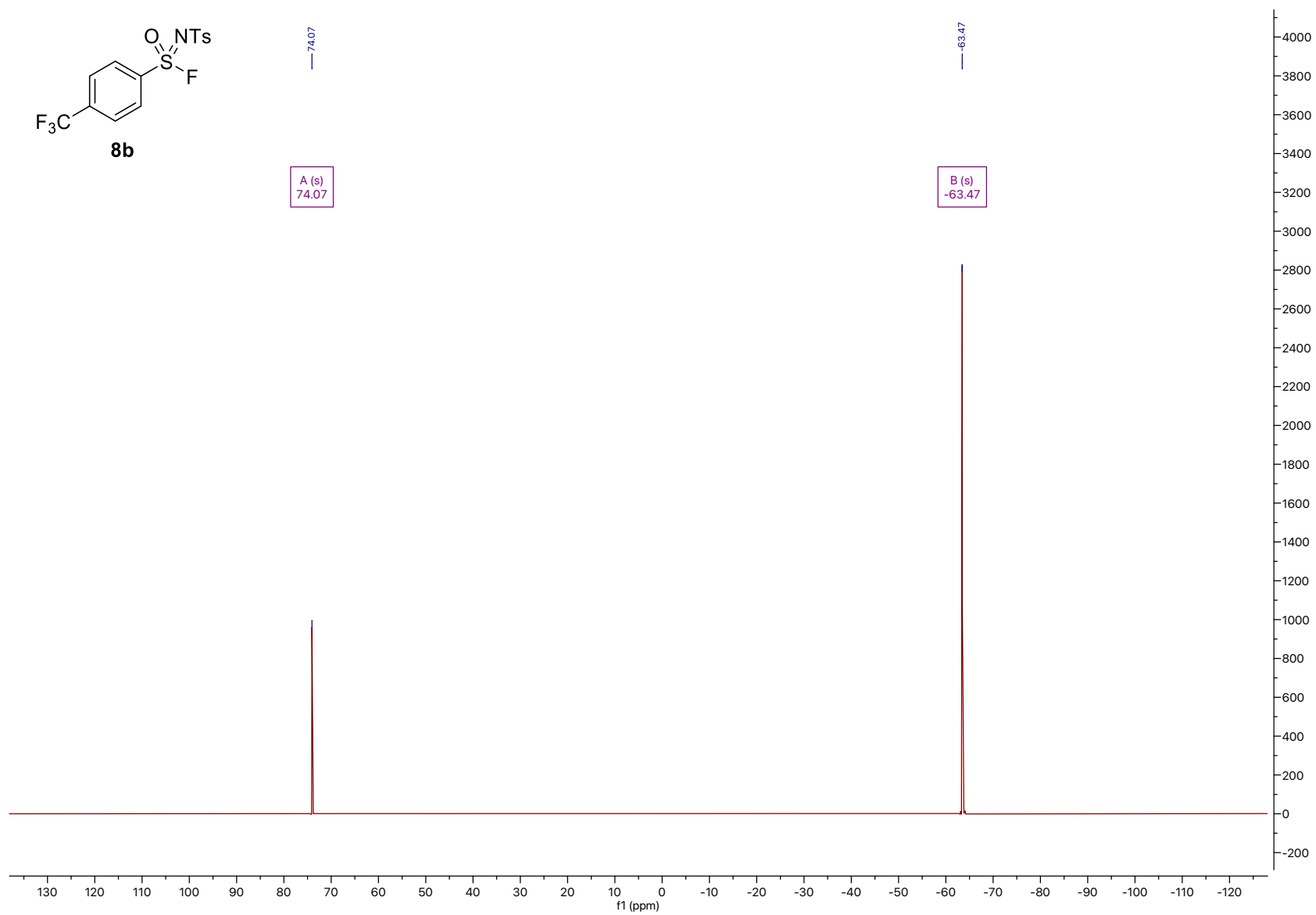
¹H NMR (300 MHz, Chloroform-*d*) of *N*-tosyl-4-(trifluoromethyl)benzenesulfonimidoyl fluoride (8b)



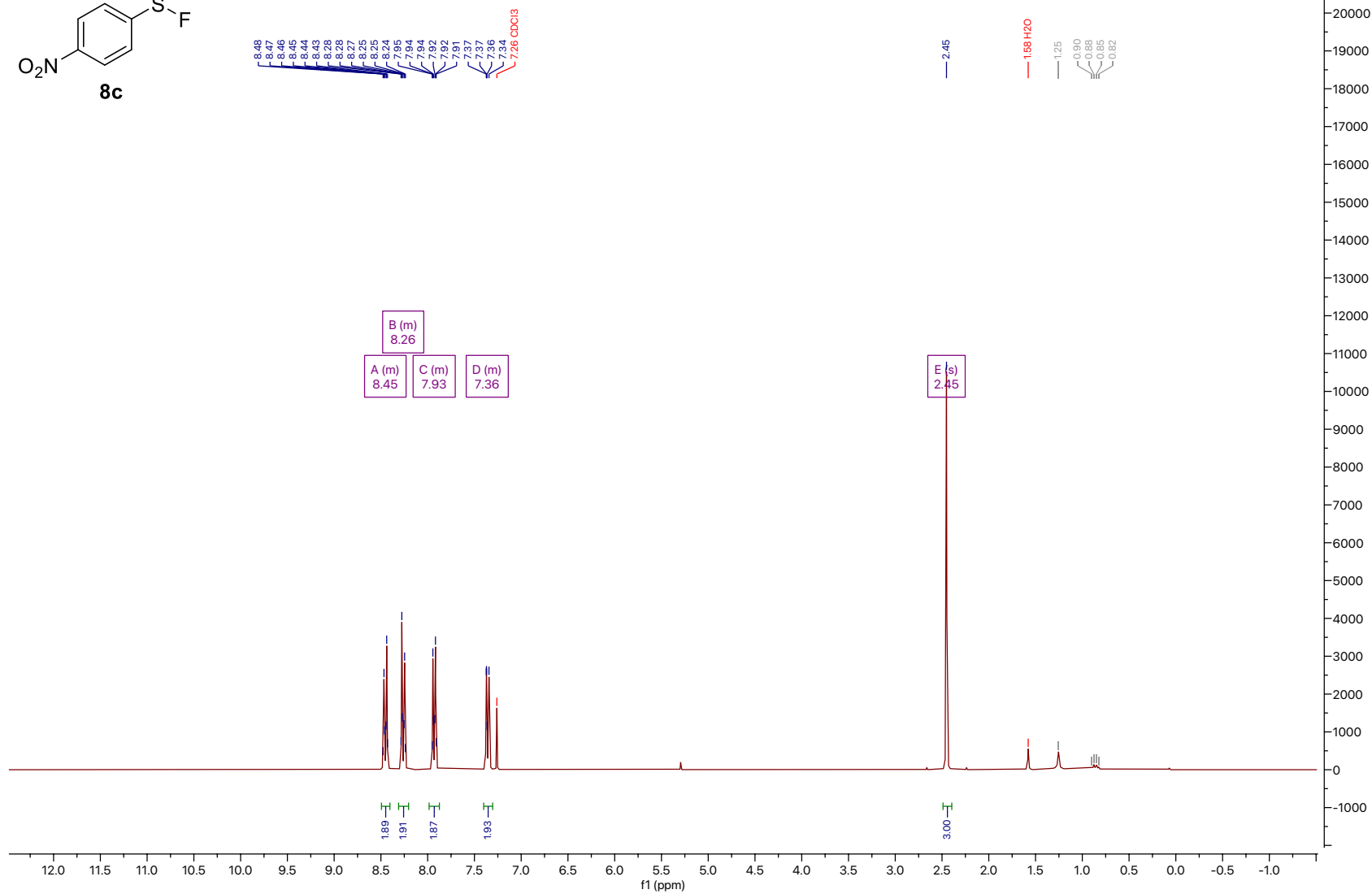
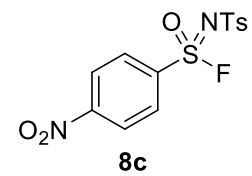
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of *N*-tosyl-4-(trifluoromethyl)benzenesulfonimidoyl fluoride (8b)



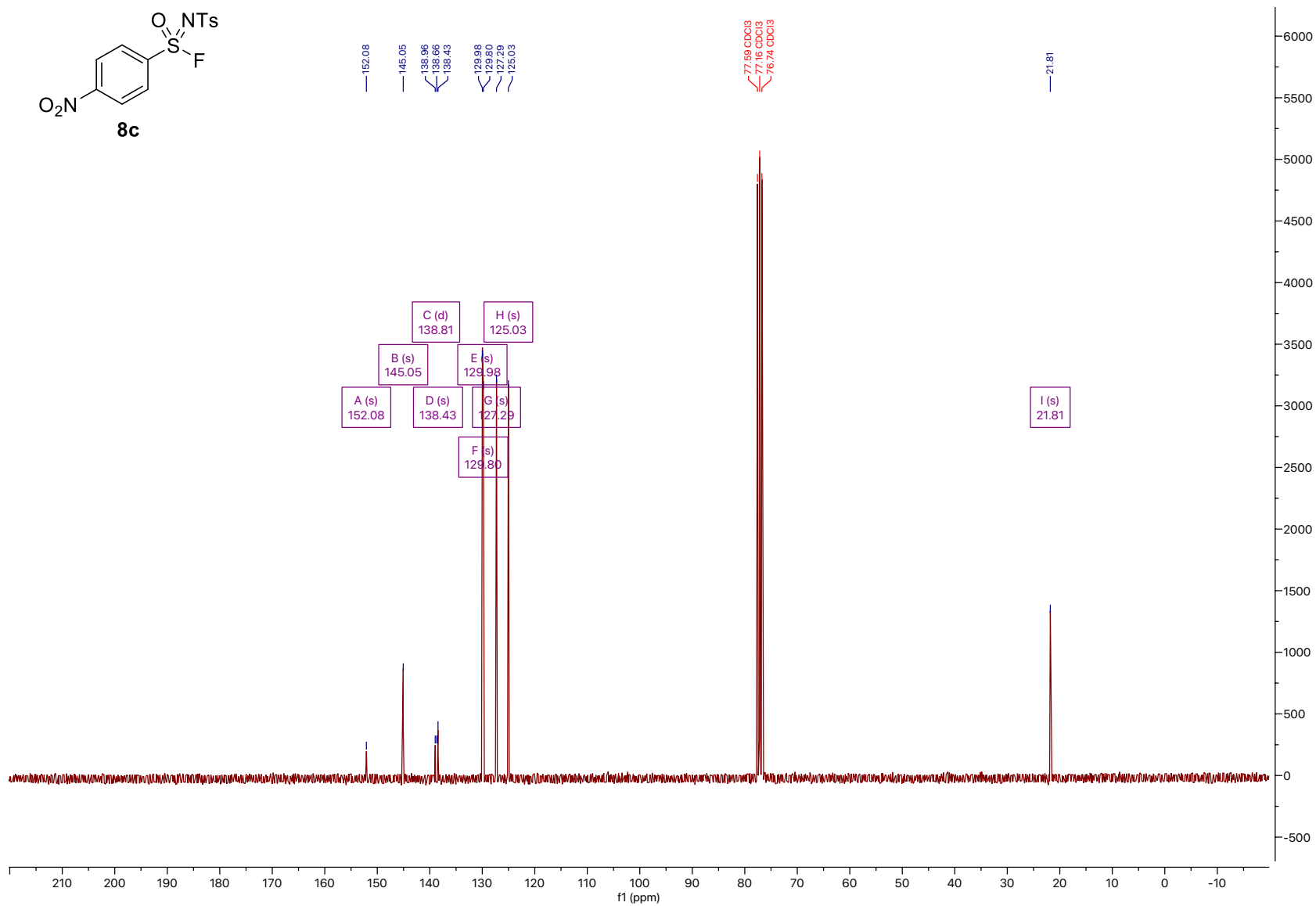
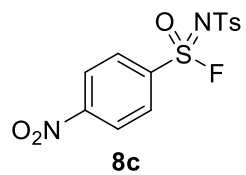
^{19}F NMR (282 MHz, Chloroform-*d*) of *N*-tosyl-4-(trifluoromethyl)benzenesulfonimidoyl fluoride (8b)



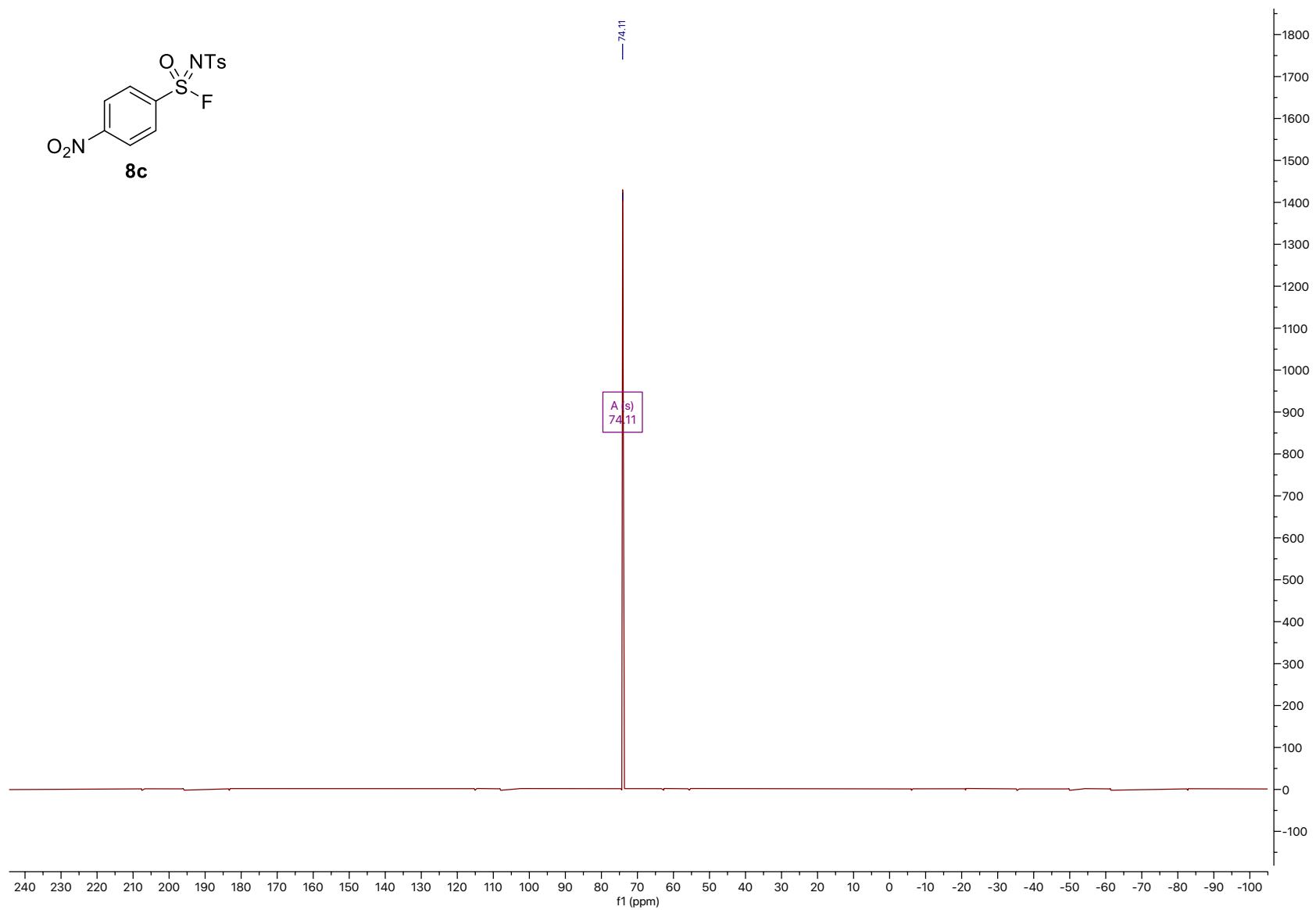
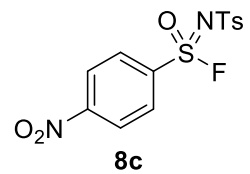
¹H NMR (300 MHz, Chloroform-d) of 4-nitro-N-tosylbenzenesulfonimidoyl fluoride (8c)



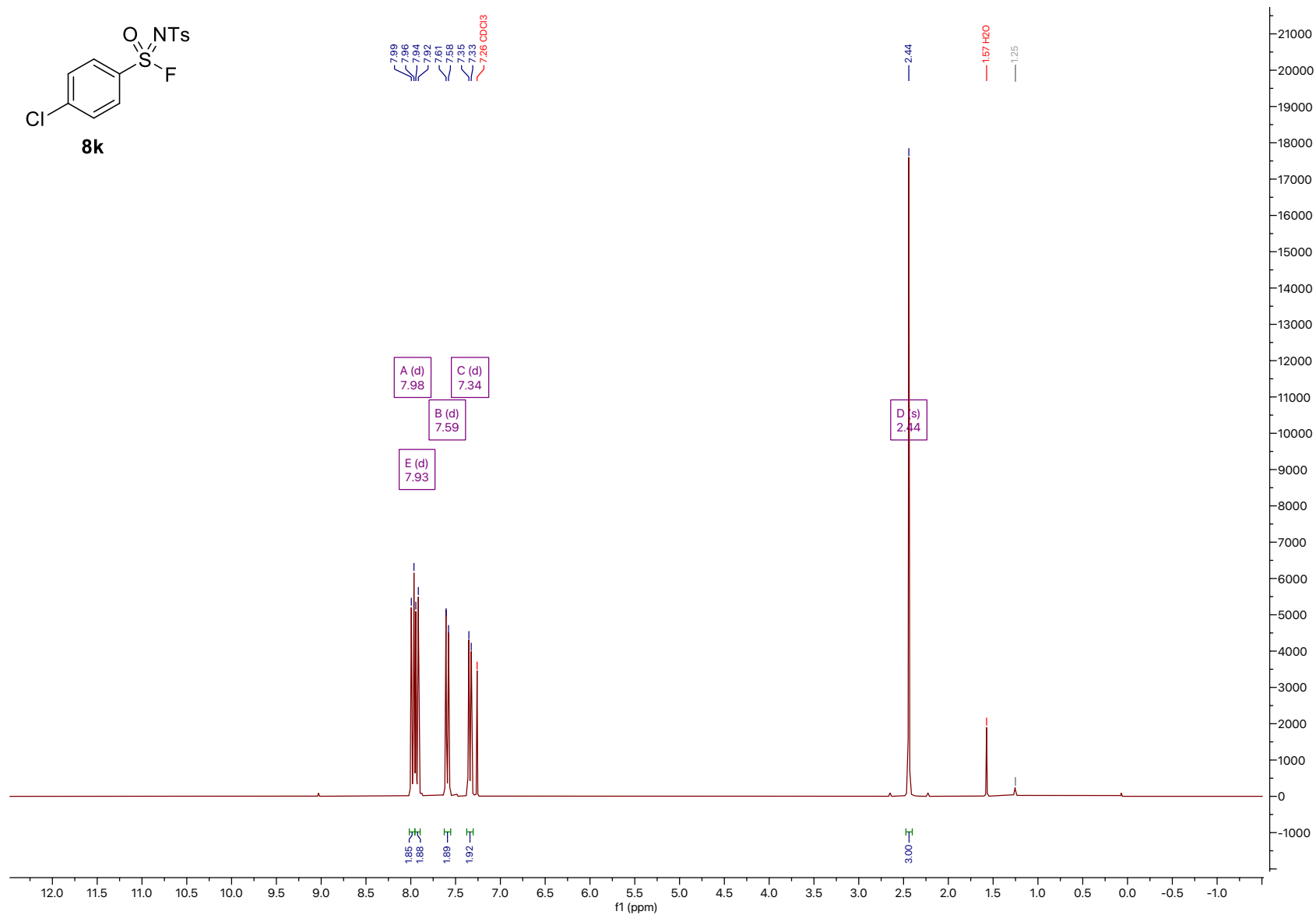
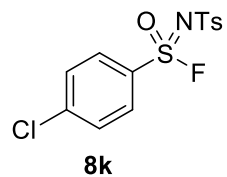
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 4-nitro-*N*-tosylbenzenesulfonimidoyl fluoride (8c)



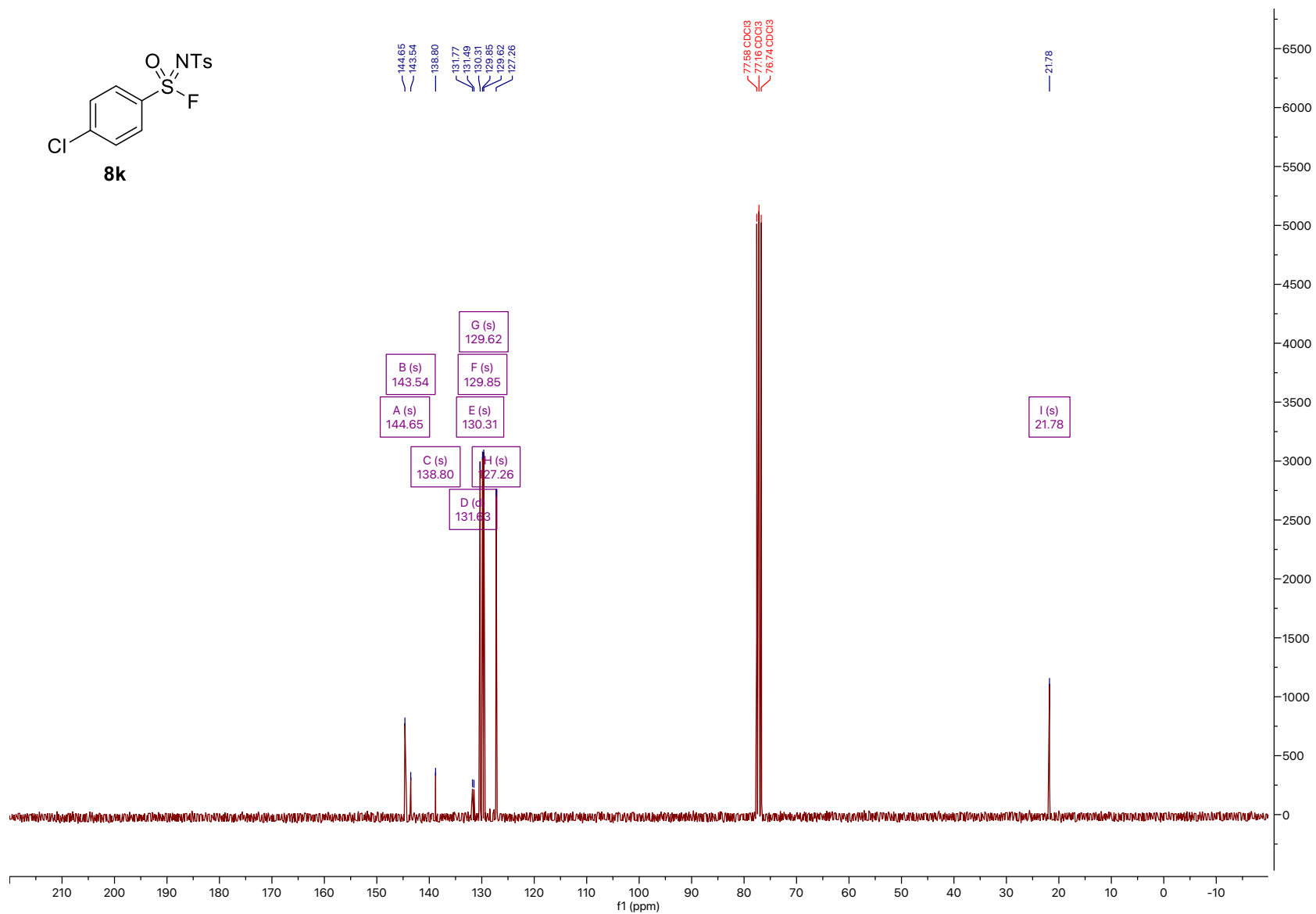
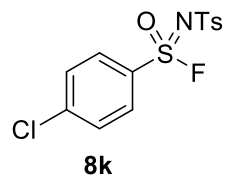
^{19}F NMR (282 MHz, Chloroform-*d*) of 4-nitro-*N*-tosylbenzenesulfonimidoyl fluoride (8c)



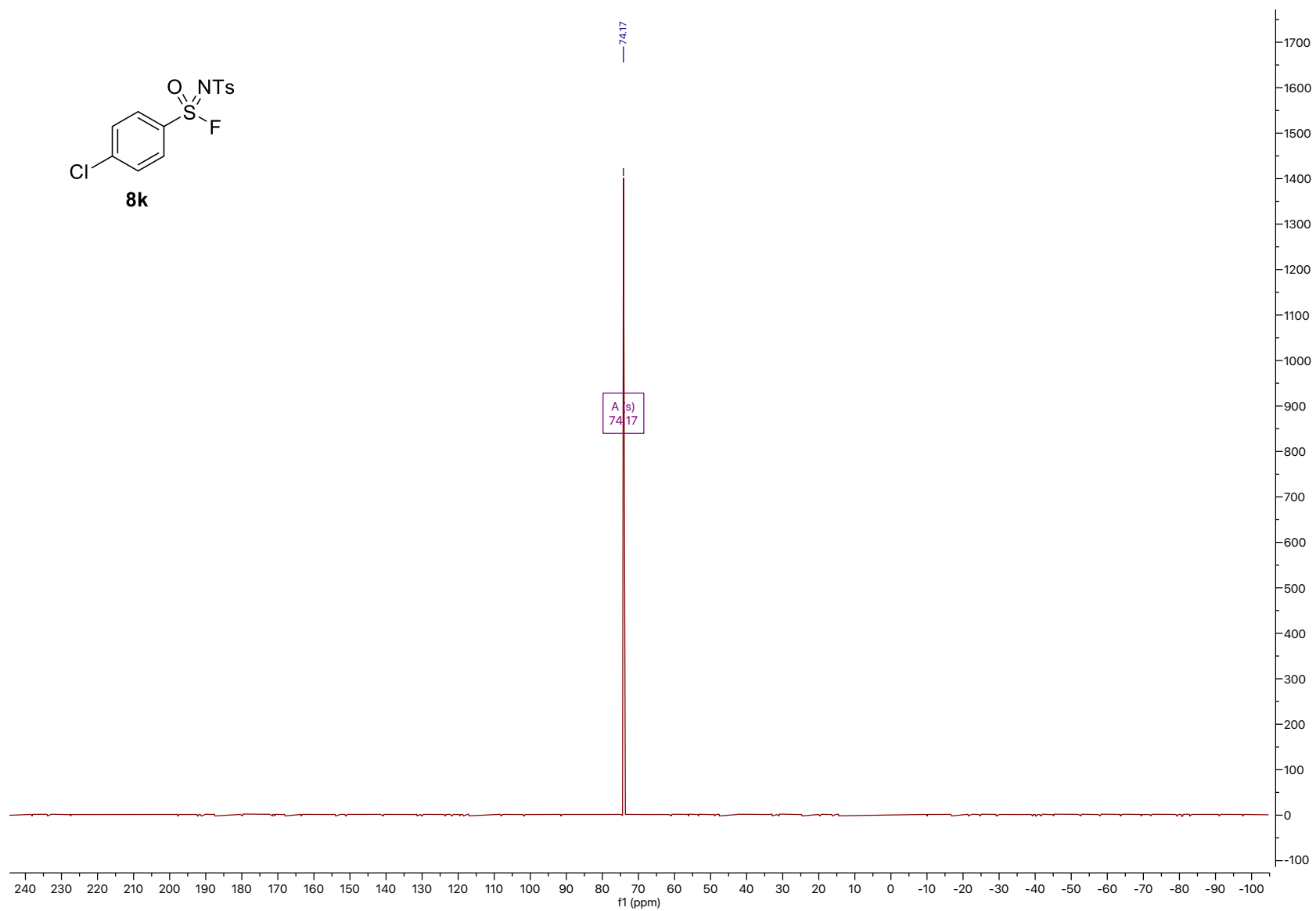
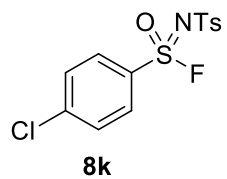
¹H NMR (300 MHz, Chloroform-d) of 4-chloro-N-tosylbenzenesulfonimidoyl fluoride (8k)



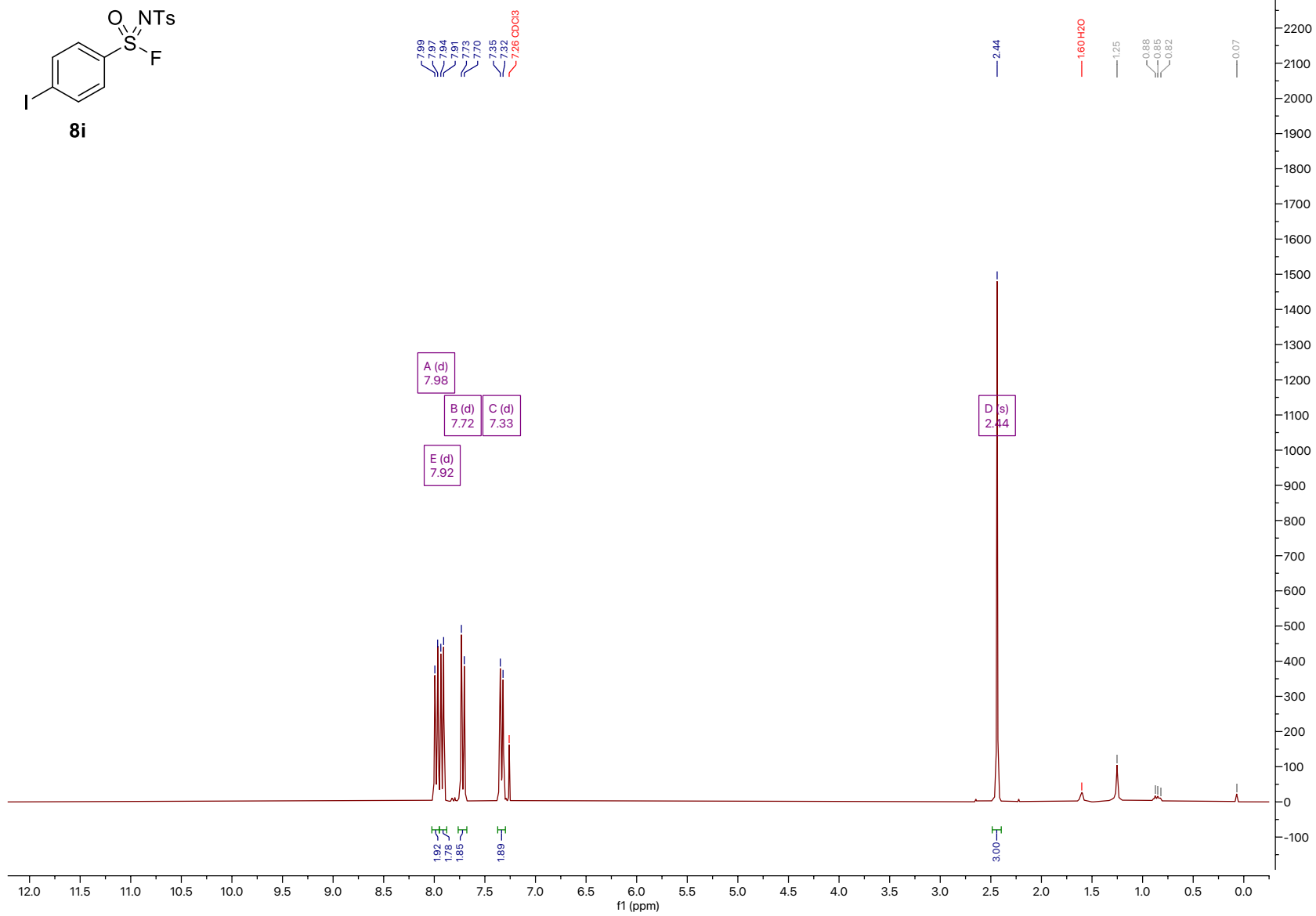
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 4-chloro-*N*-tosylbenzenesulfonimidoyl fluoride (8k)



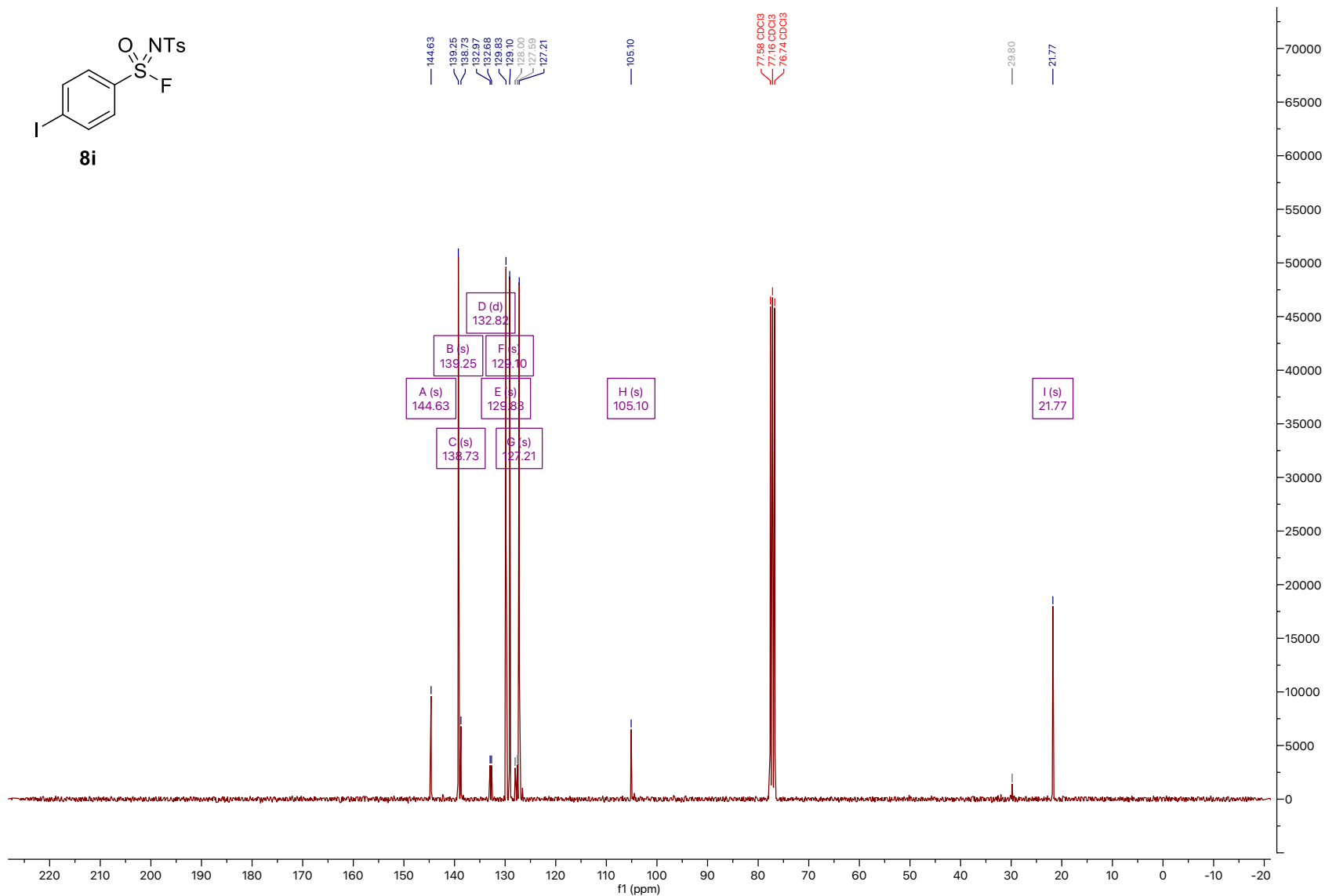
^{19}F NMR (282 MHz, Chloroform-*d*) of 4-chloro-*N*-tosylbenzenesulfonimidoyl fluoride (8k)



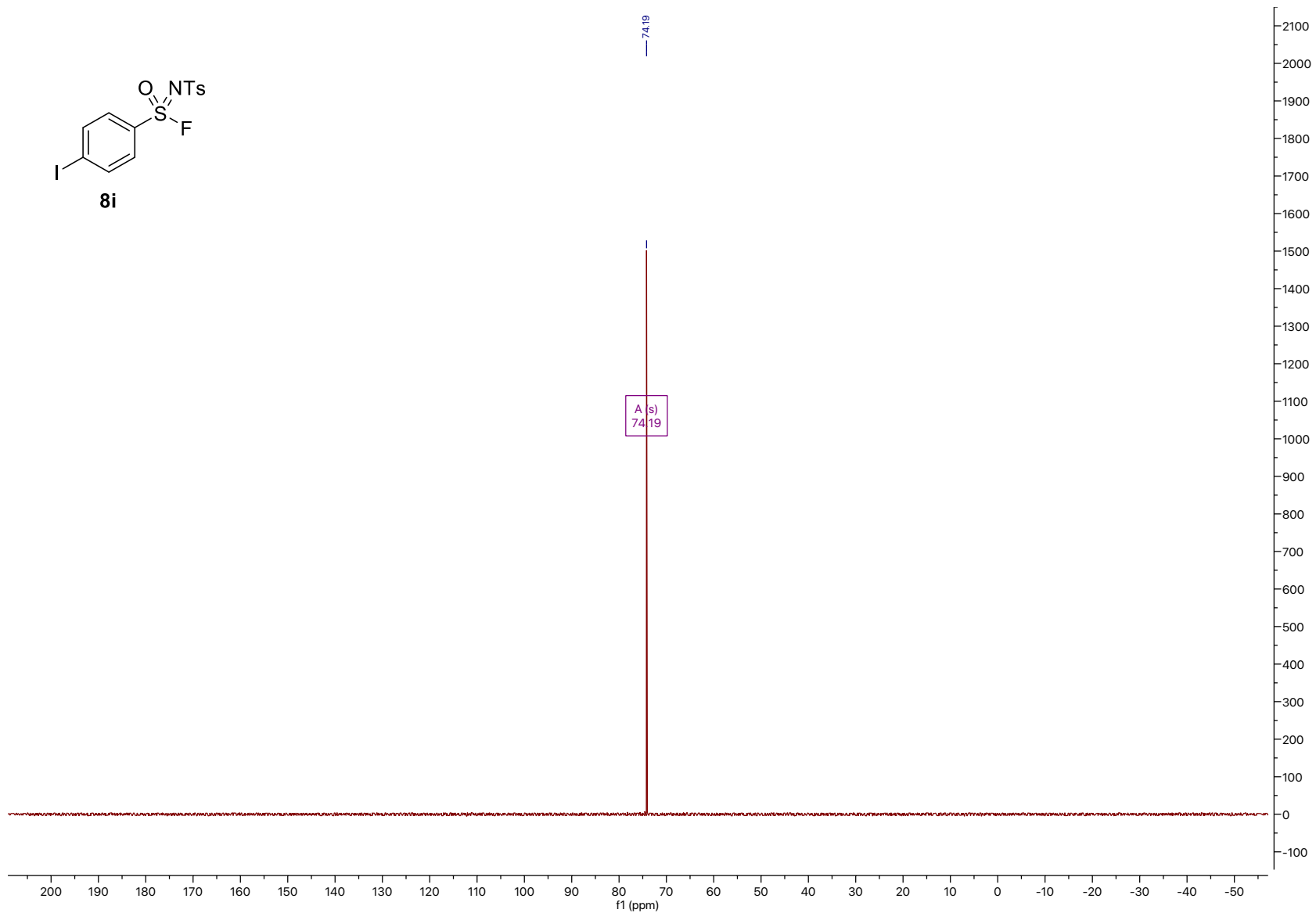
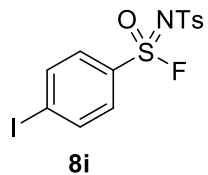
¹H NMR (300 MHz, Chloroform-*d*) of 4-iodo-*N*-tosylbenzenesulfonimidoyl fluoride (8i)



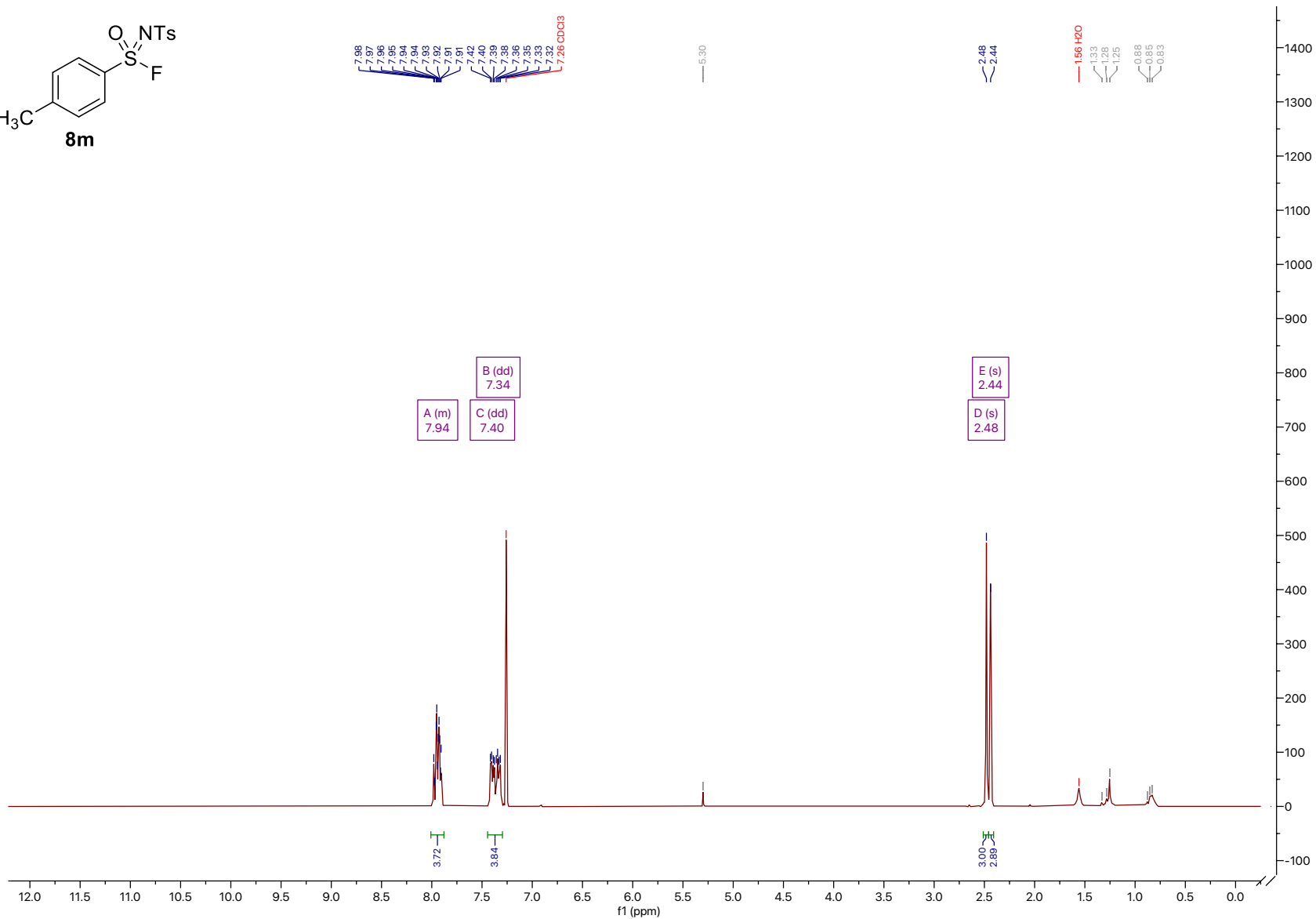
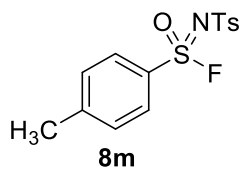
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 4-Iodo-*N*-tosylbenzenesulfonimidoyl fluoride (8i)



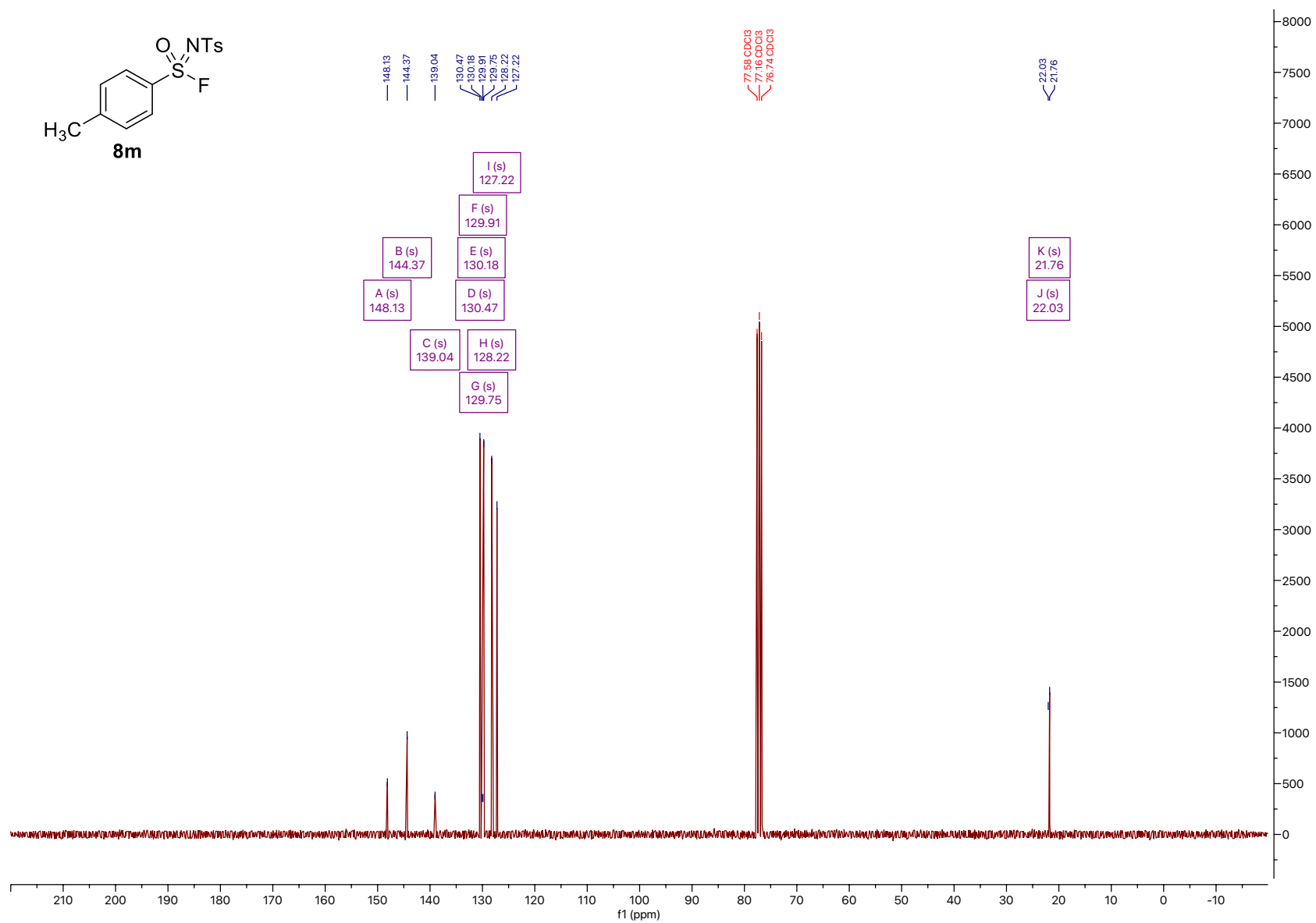
¹⁹F NMR (282 MHz, Chloroform-*d*) of 4-iodo-*N*-tosylbenzenesulfonimidoyl fluoride (8I)



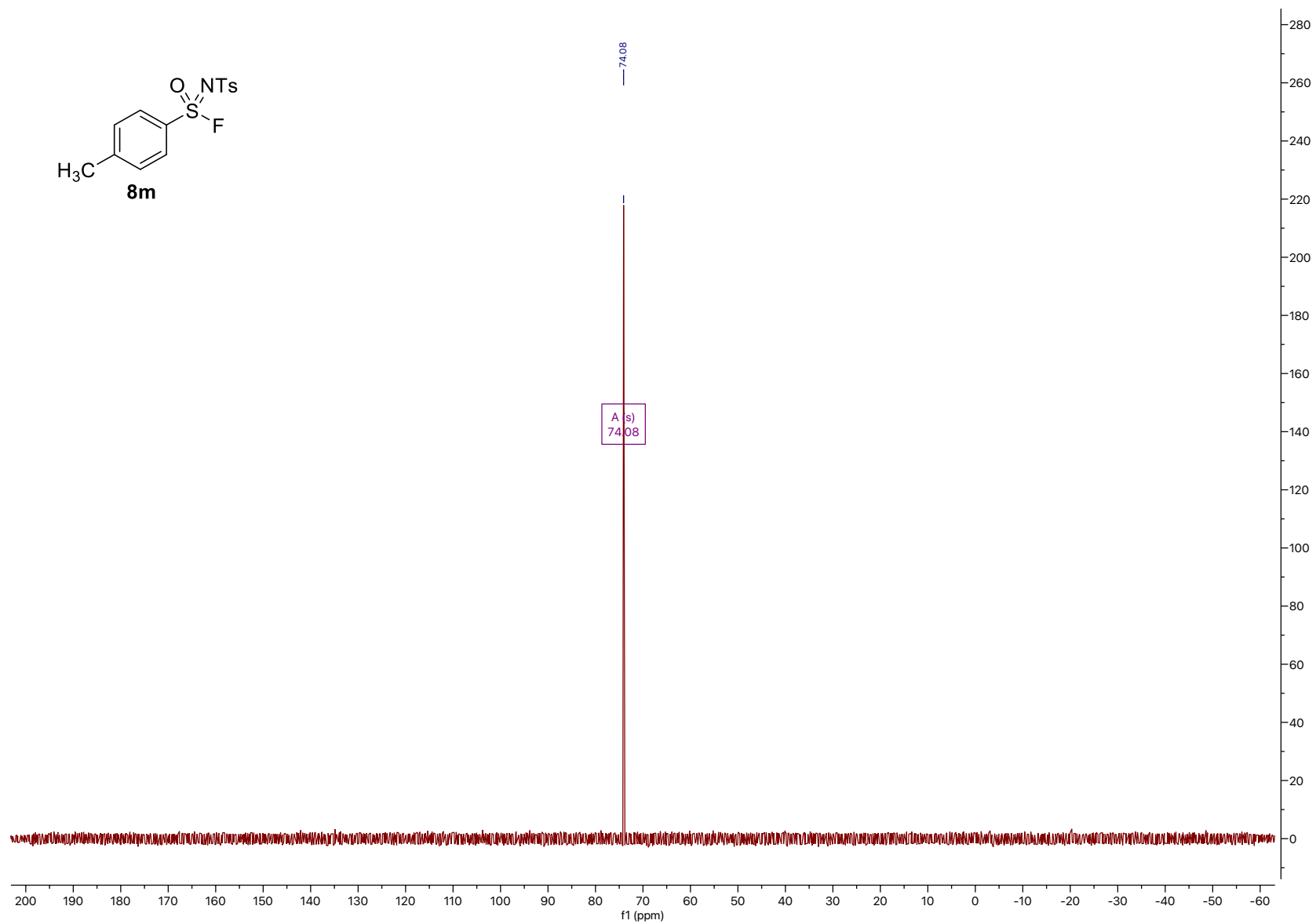
¹H NMR (300 MHz, Chloroform-*d*) of 4-methyl-*N*-tosylbenzenesulfonimidoyl fluoride (8m)



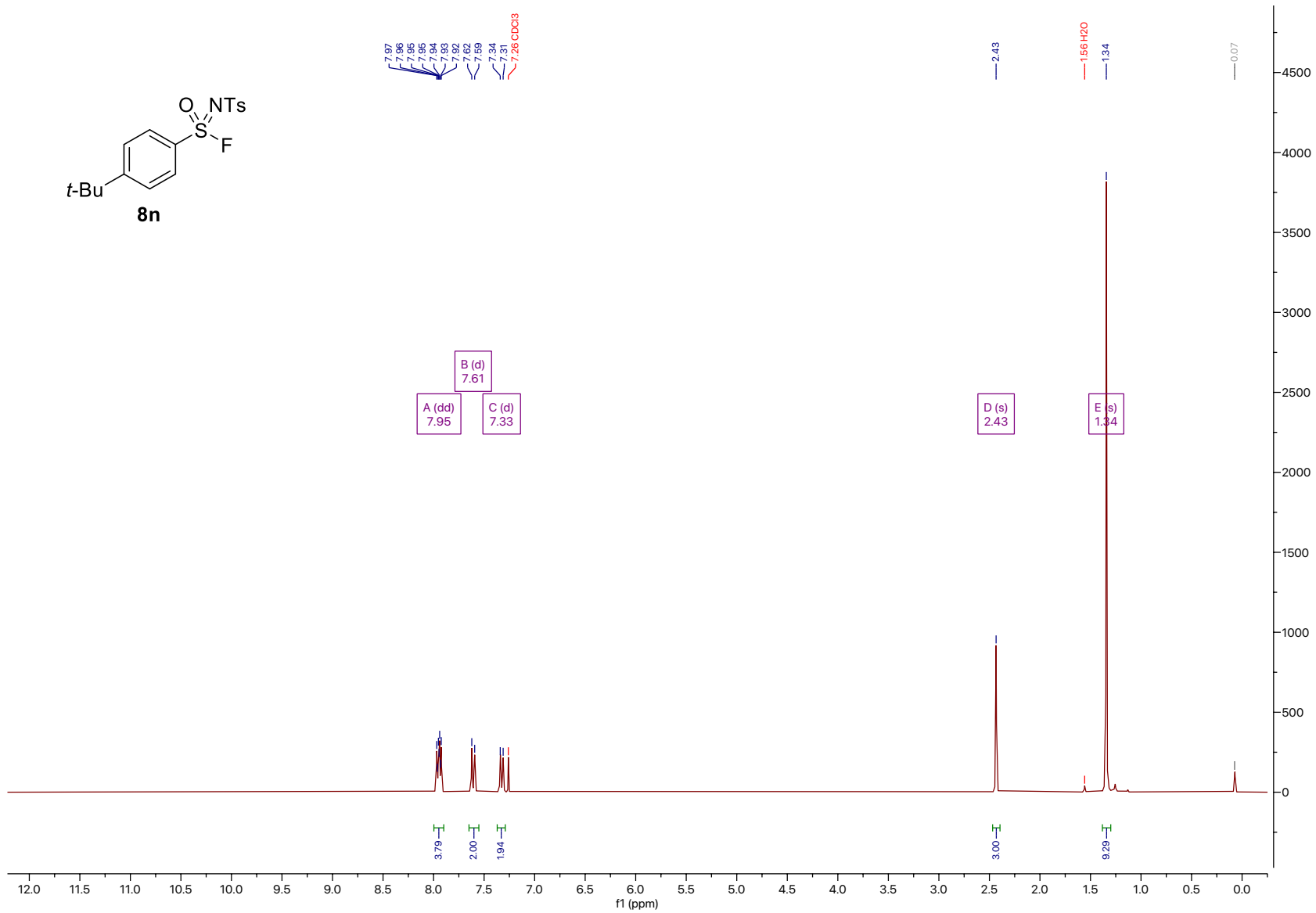
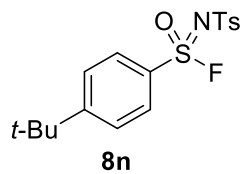
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 4-methyl-*N*-tosylbenzenesulfonimidoyl fluoride (8m)



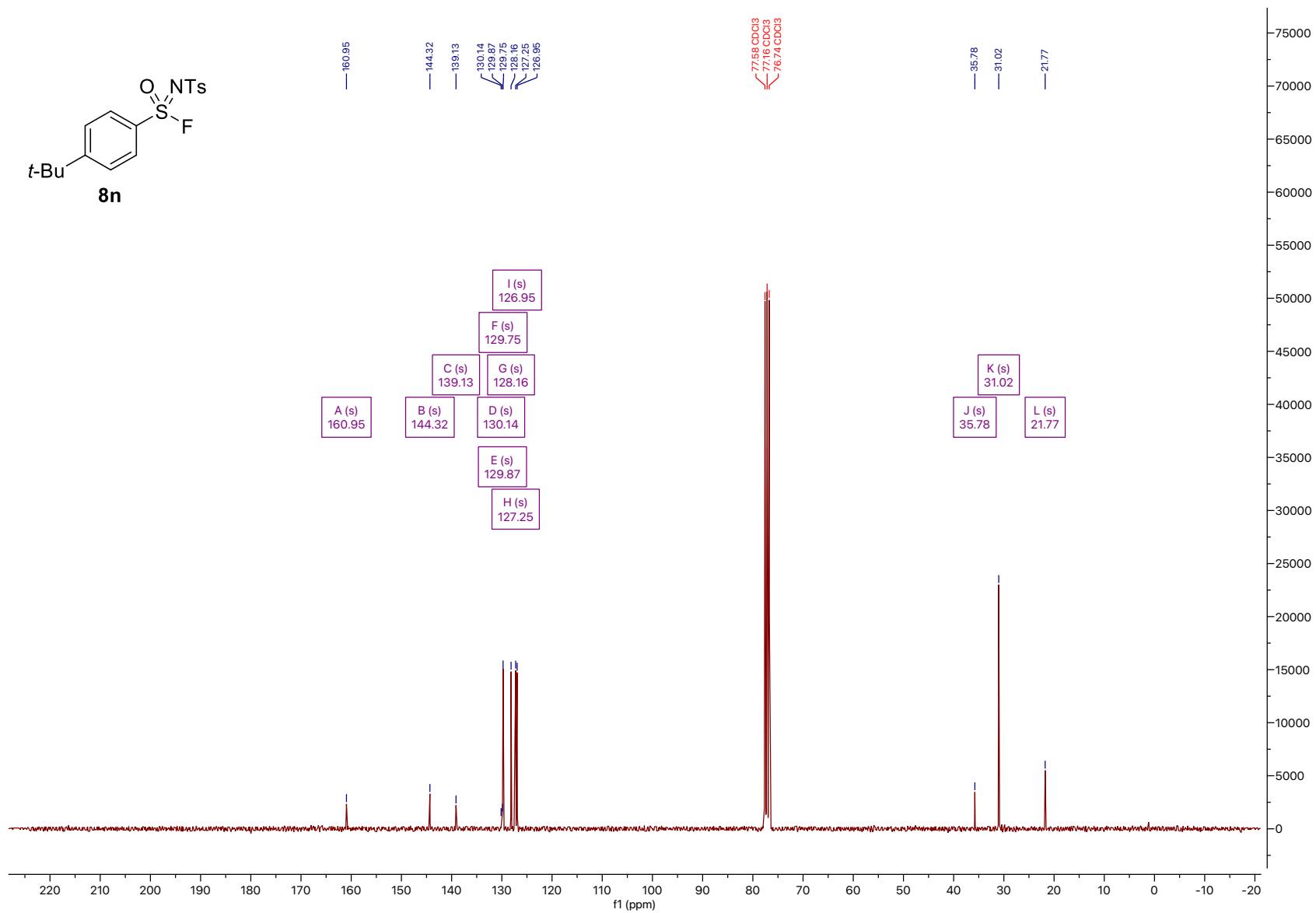
^{19}F NMR (282 MHz, Chloroform-*d*) of 4-methyl-*N*-tosylbenzenesulfonimidoyl fluoride (8m)



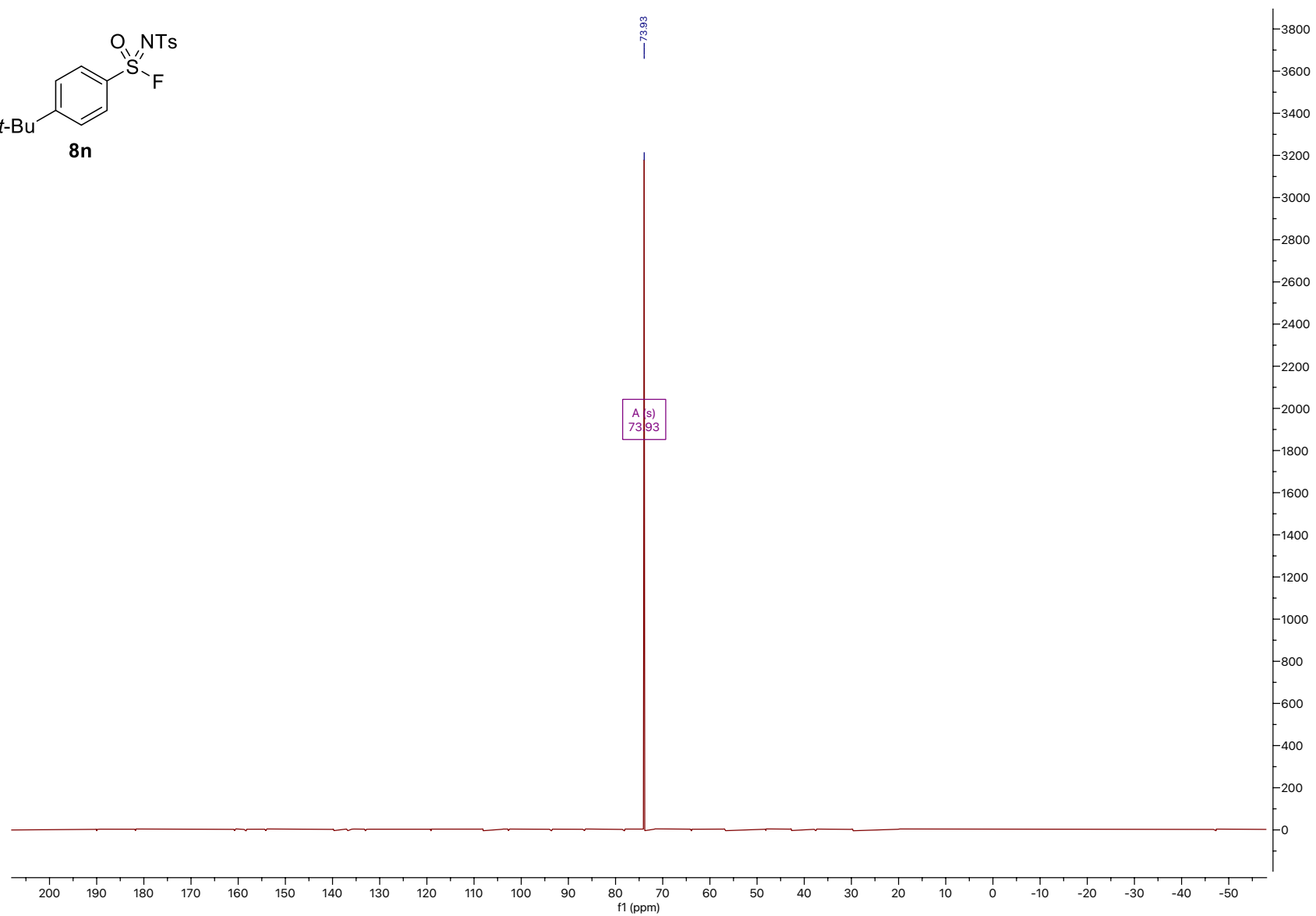
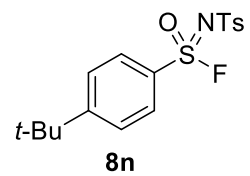
¹H NMR (300 MHz, Chloroform-*d*) of 4-(*tert*-butyl)-*N*-tosylbenzenesulfonimidoyl fluoride (8n)



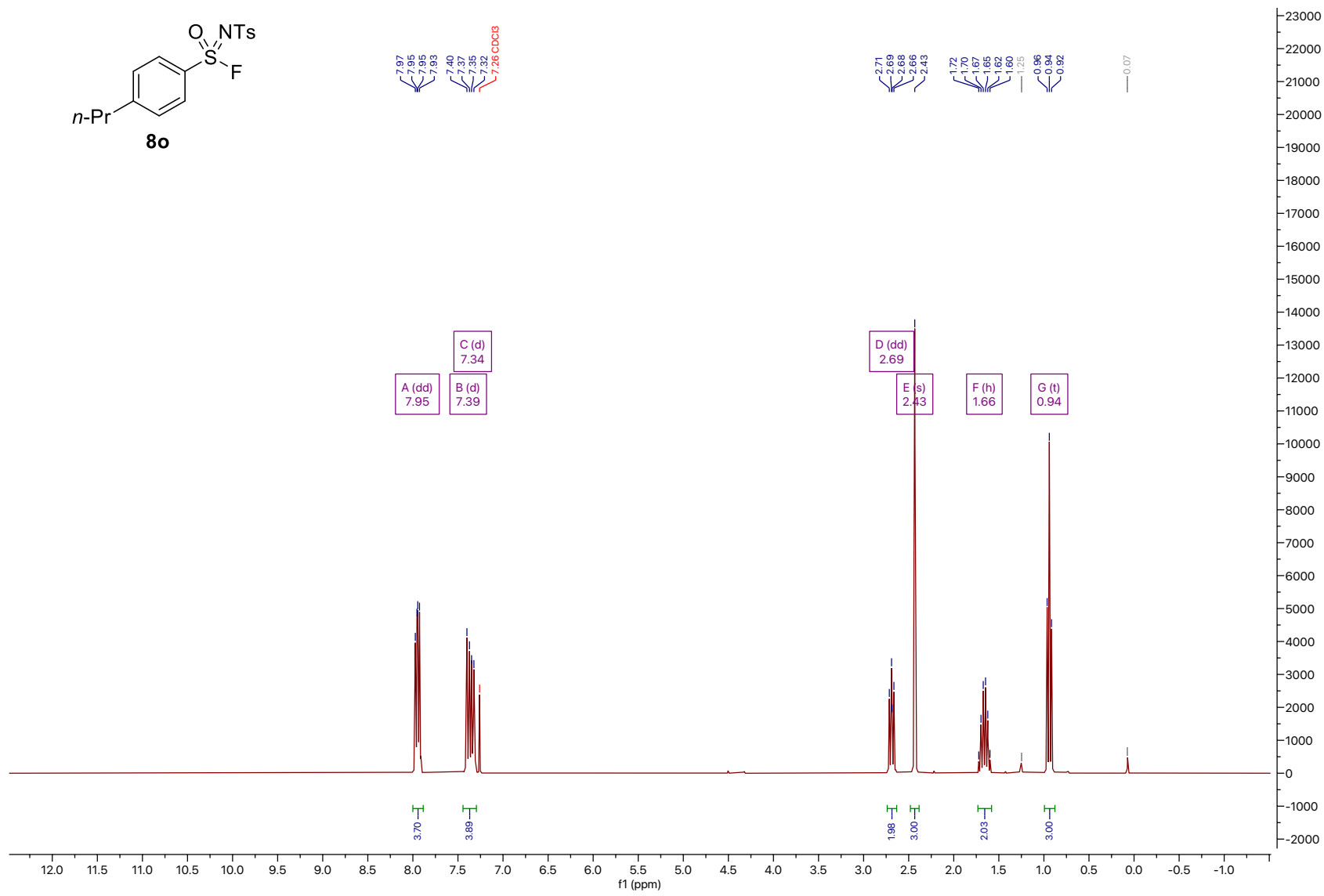
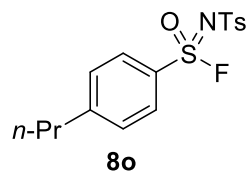
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 4-(*tert*-butyl)-*N*-tosylbenzenesulfonimidoyl fluoride (8n)



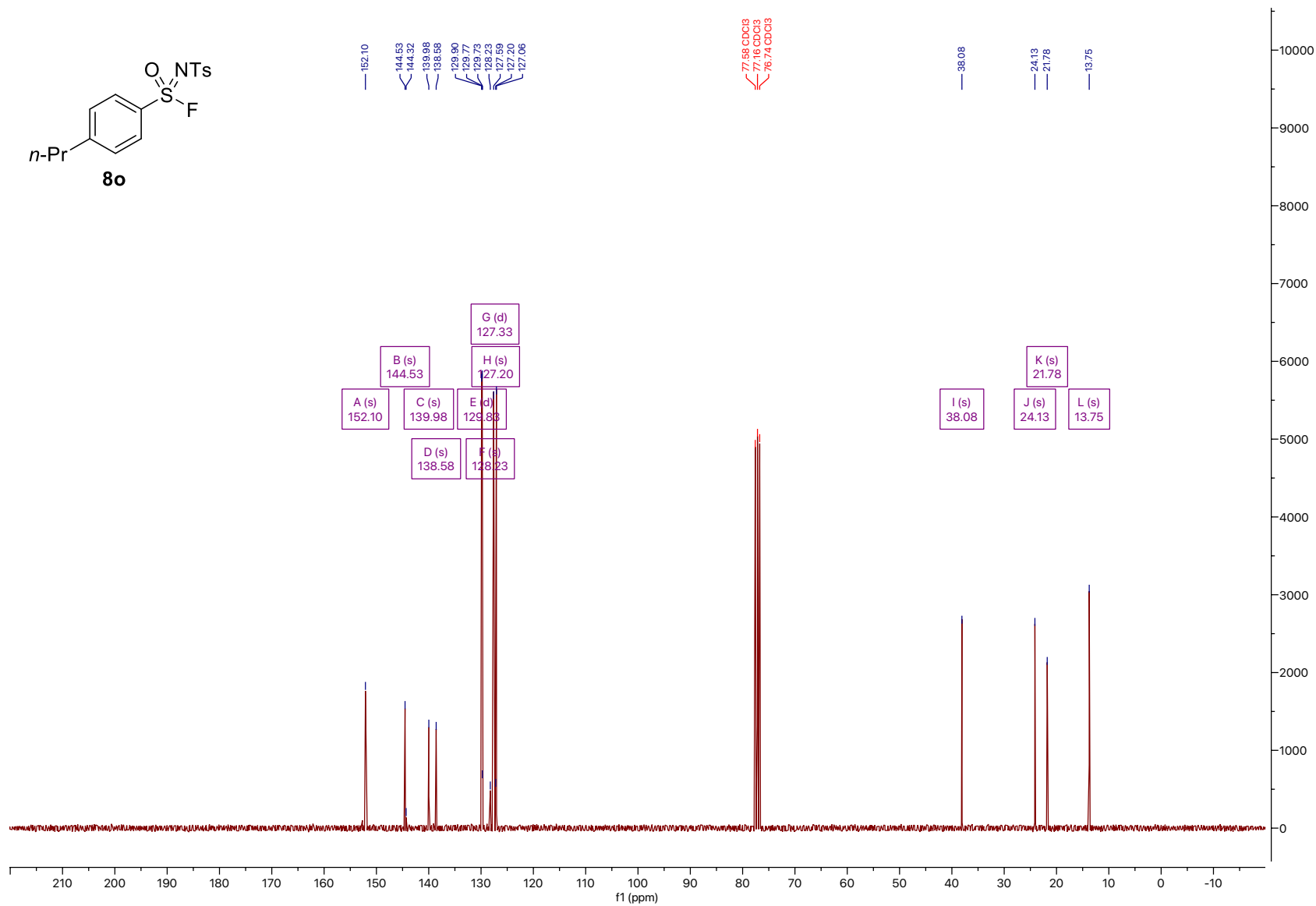
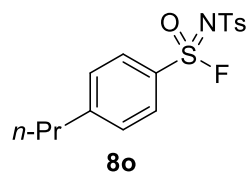
^{19}F NMR (282 MHz, Chloroform-*d*) of 4-(*tert*-butyl)-*N*-tosylbenzenesulfonimidoyl fluoride (8n)



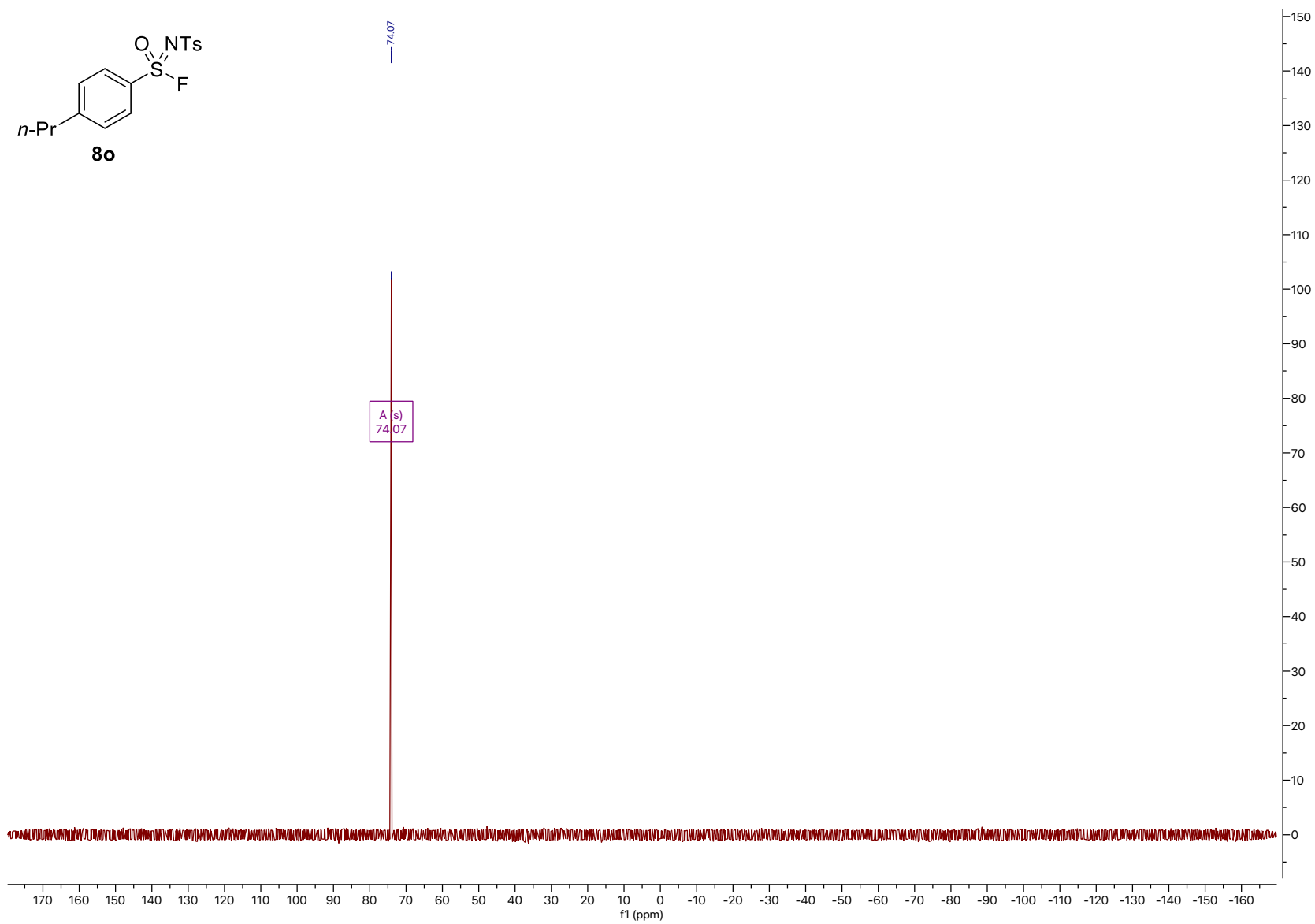
¹H NMR (300 MHz, Chloroform-*d*) of 4-propyl-*N*-tosylbenzenesulfonimidoyl fluoride (8o)



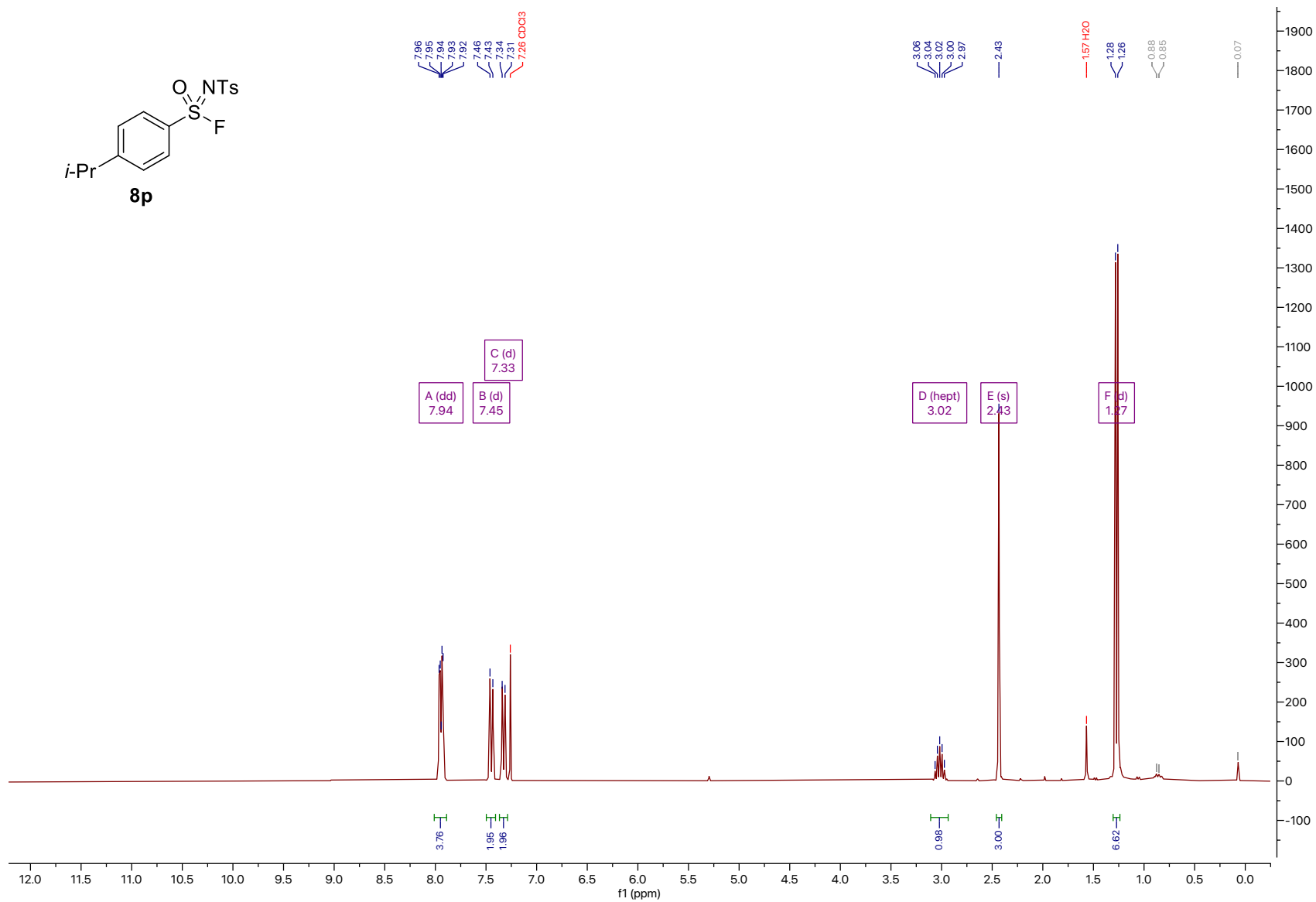
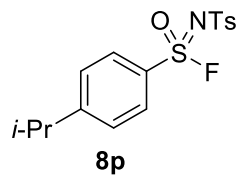
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 4-propyl-*N*-tosylbenzenesulfonimidoyl fluoride (8o)



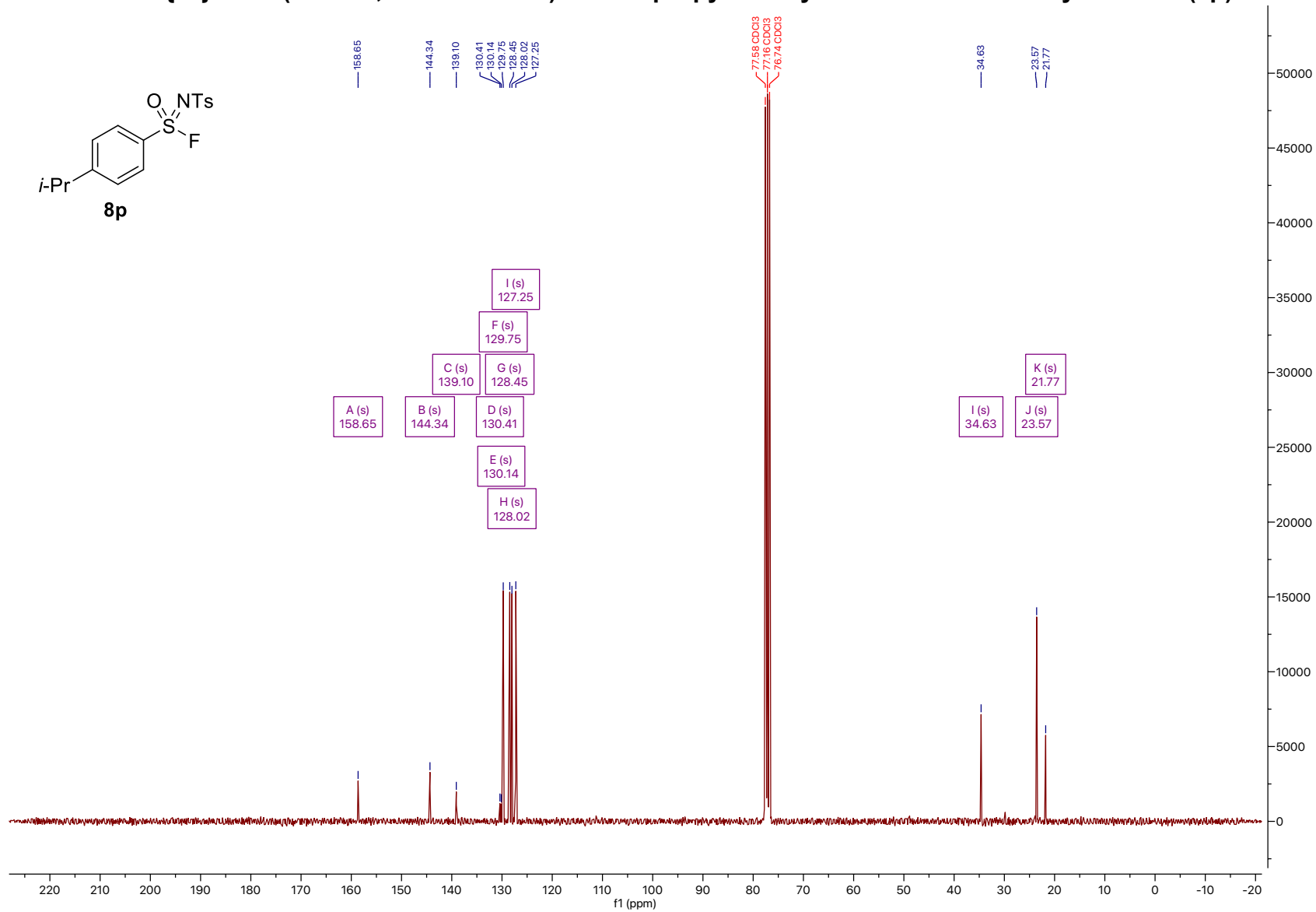
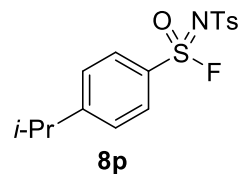
^{19}F NMR (282 MHz, Chloroform-*d*) of 4-propyl-*N*-tosylbenzenesulfonimidoyl fluoride (8o)



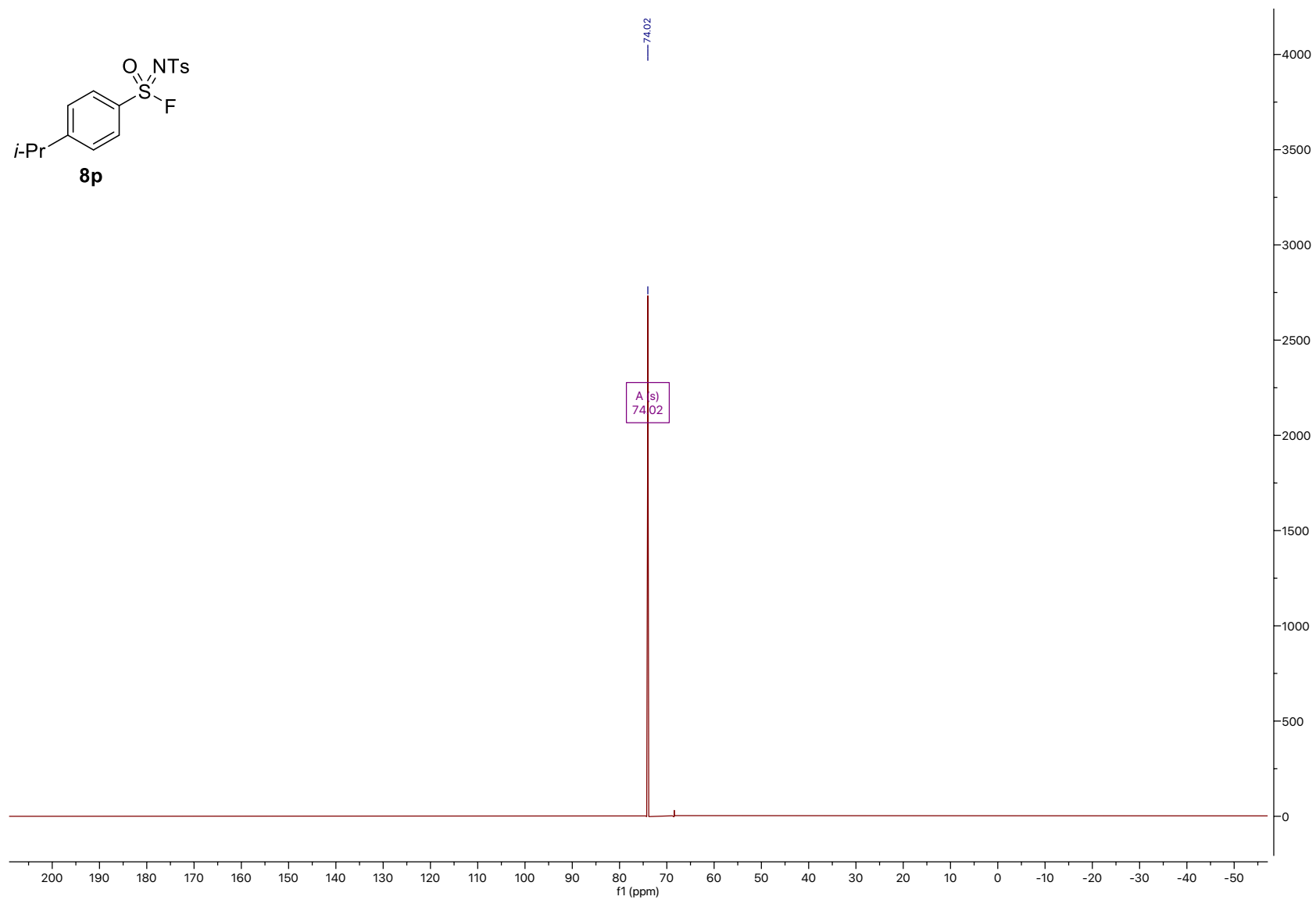
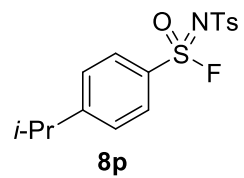
¹H NMR (300 MHz, Chloroform-*d*) of 4-isopropyl-*N*-tosylbenzenesulfonimidoyl fluoride (8p)



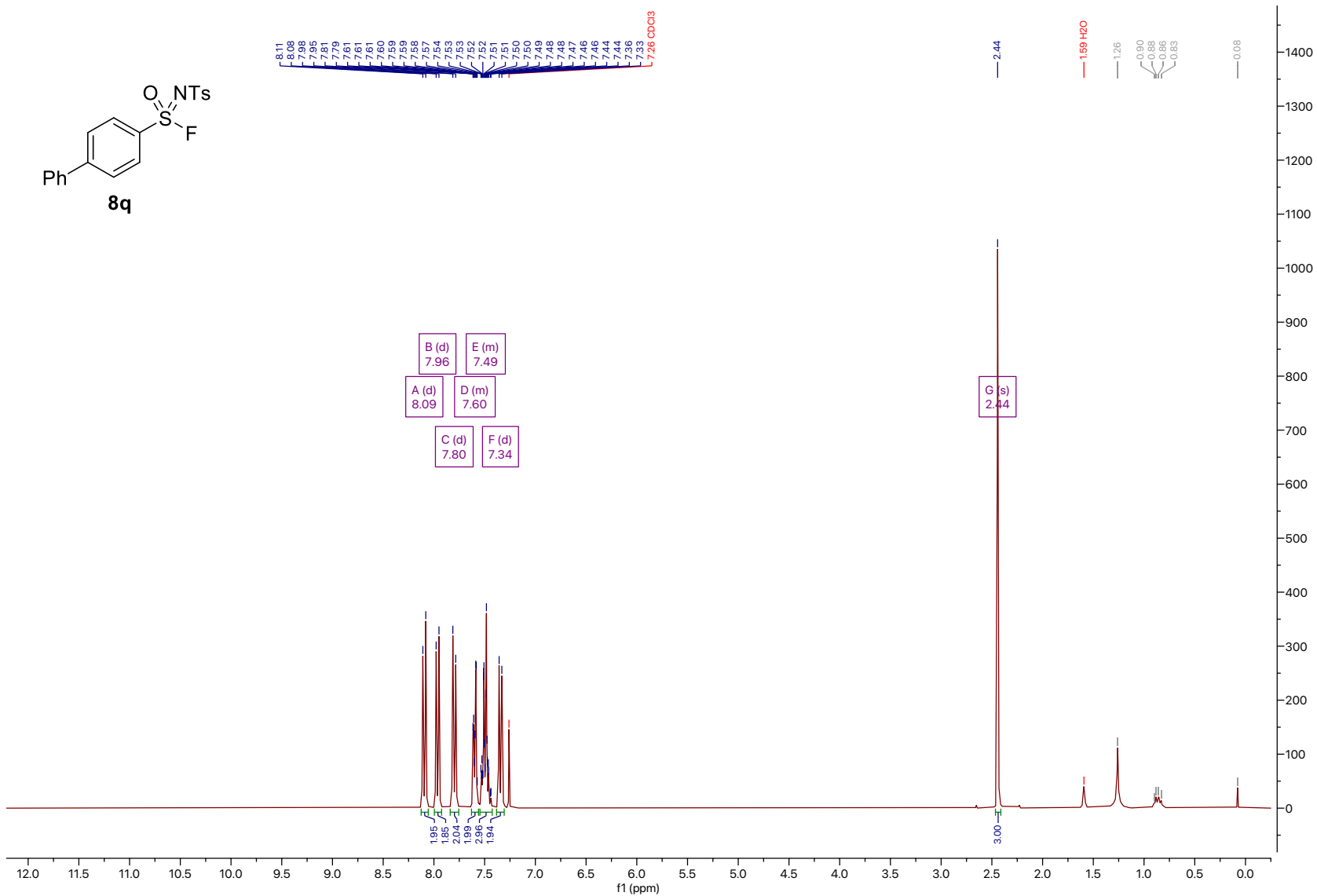
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 4-isopropyl-*N*-tosylbenzenesulfonimidoyl fluoride (8p)



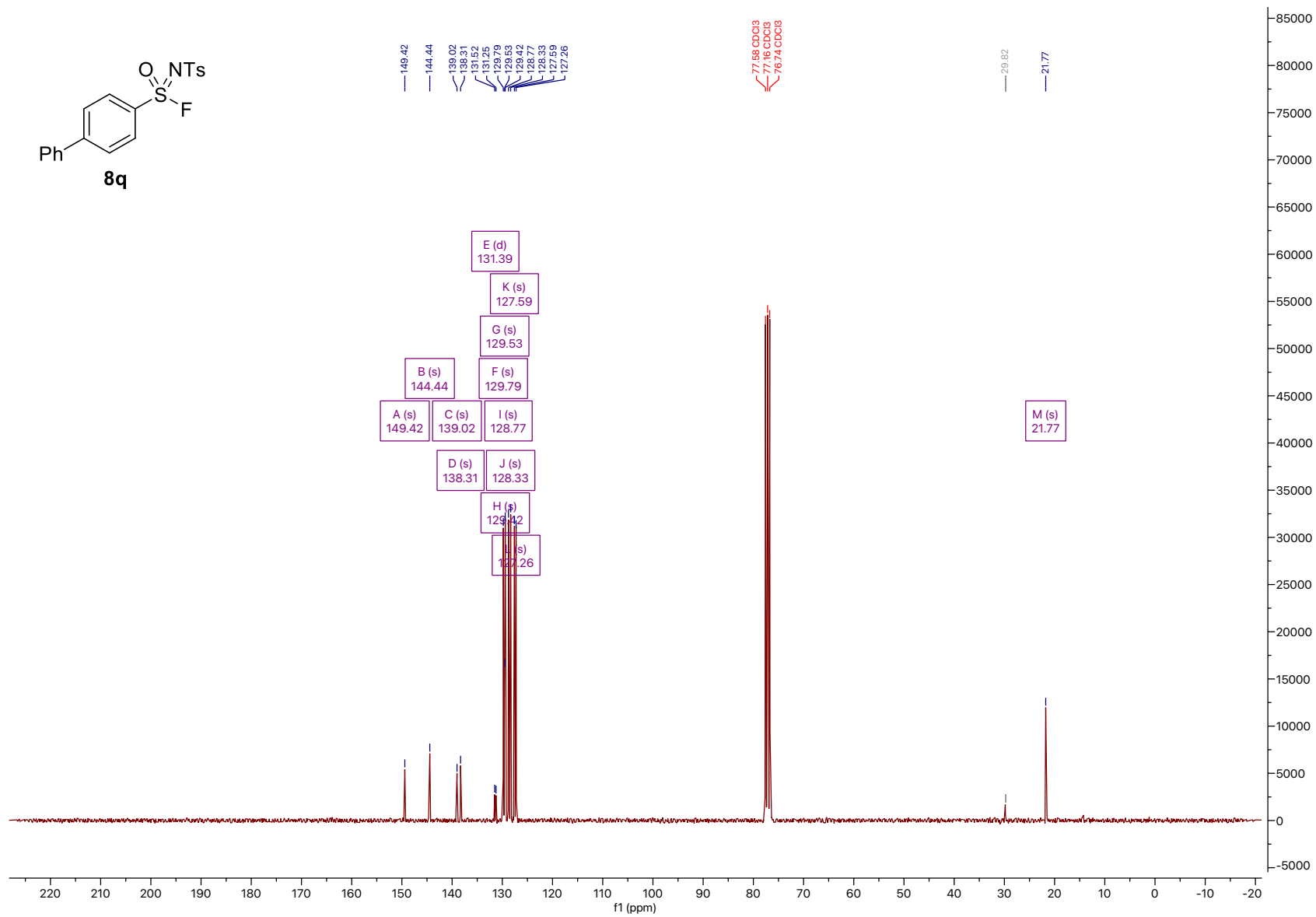
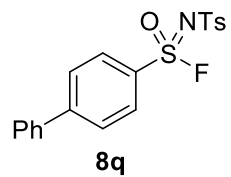
¹⁹F NMR (282 MHz, Chloroform-*d*) of 4-isopropyl-*N*-tosylbenzenesulfonimidoyl fluoride (8p)



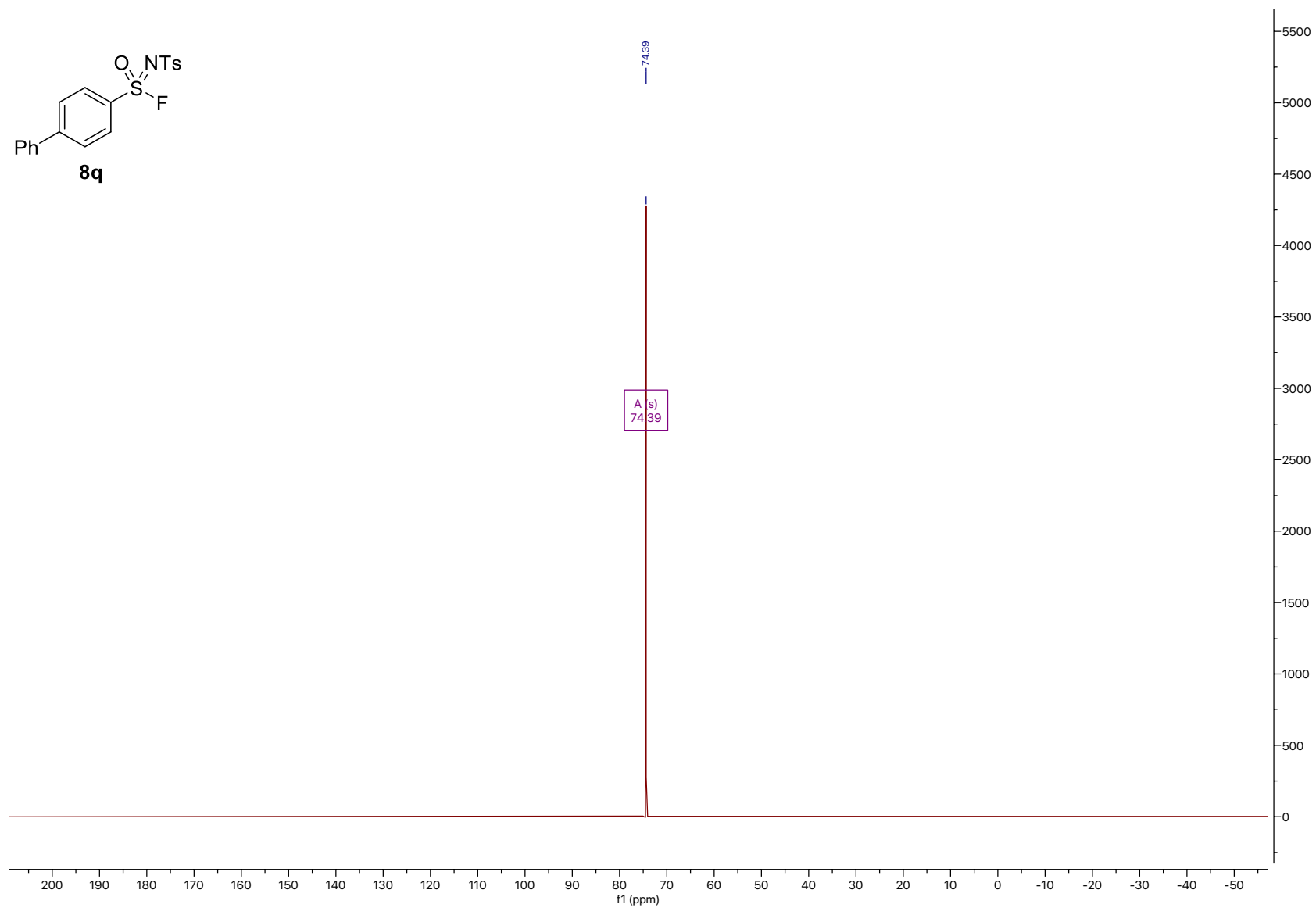
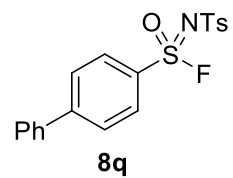
¹H NMR (300 MHz, Chloroform-d) of *N*-tosyl-[1,1'-biphenyl]-4-sulfonimidoyl fluoride (8q)



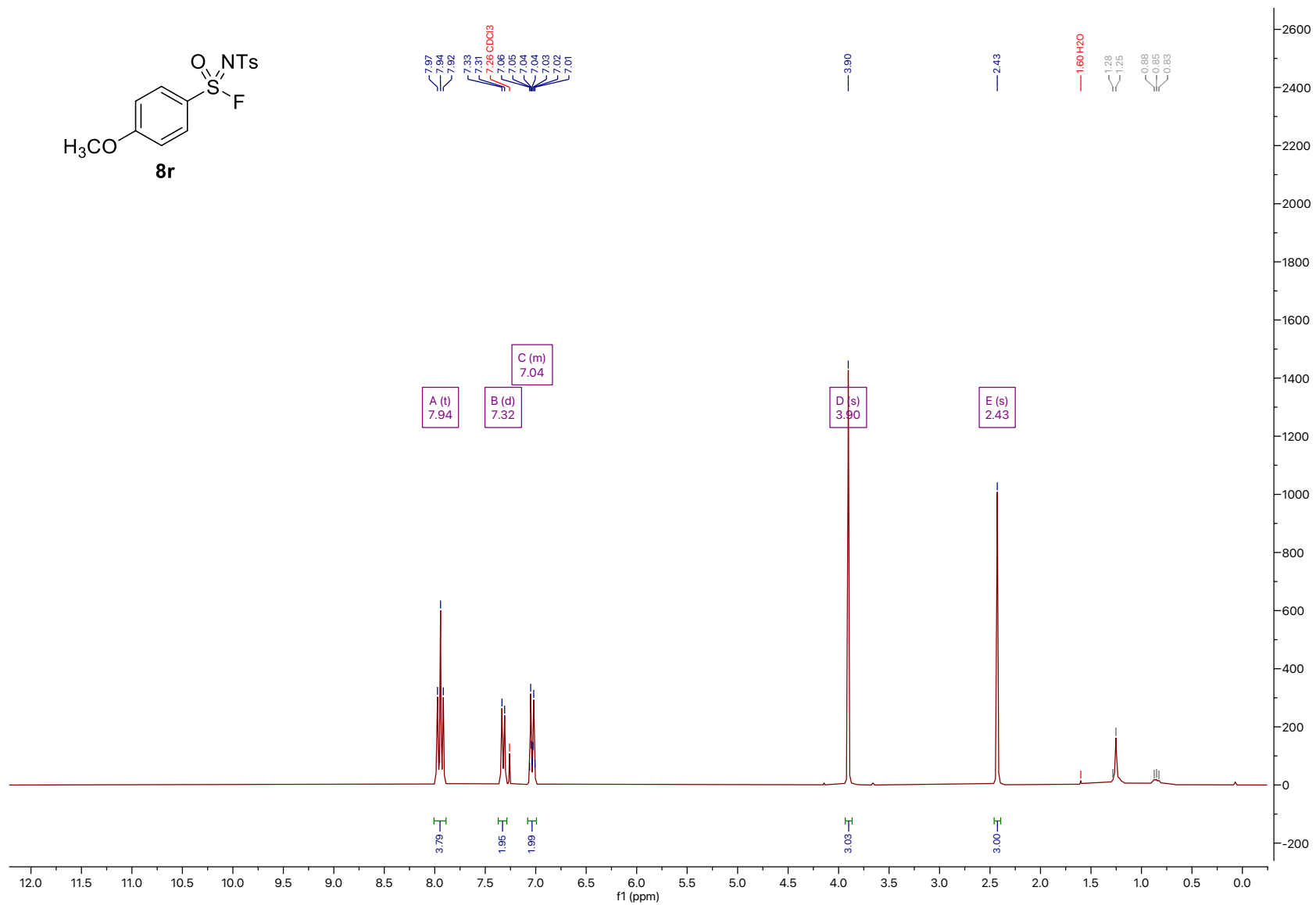
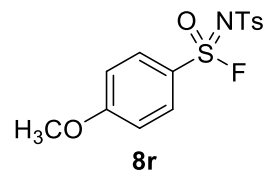
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform- d) of *N*-tosyl-[1,1'-biphenyl]-4-sulfonimidoyl fluoride (8q)



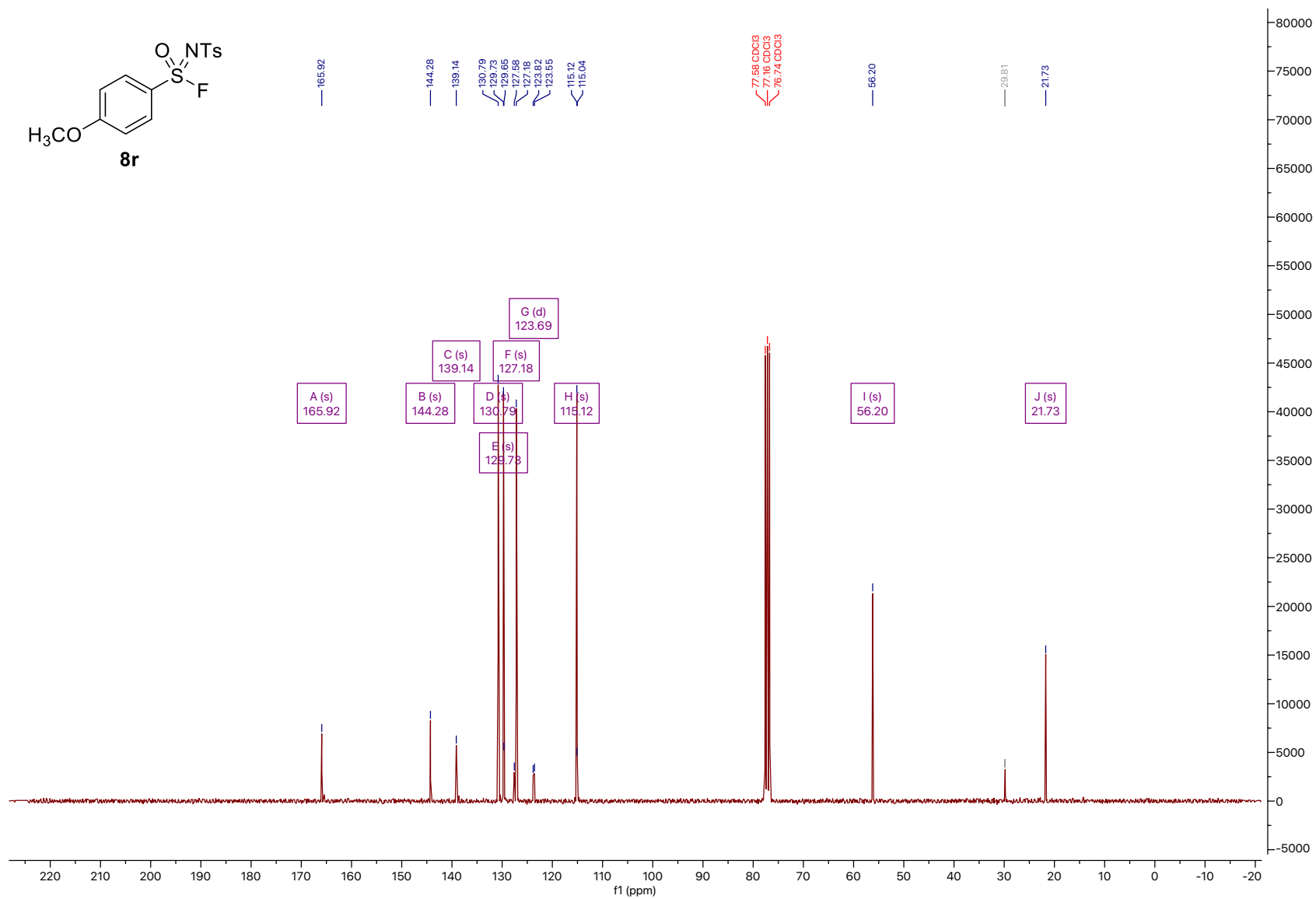
^{19}F NMR (282 MHz, Chloroform-*d*) of *N*-tosyl-[1,1'-biphenyl]-4-sulfonimidoyl fluoride (8q)



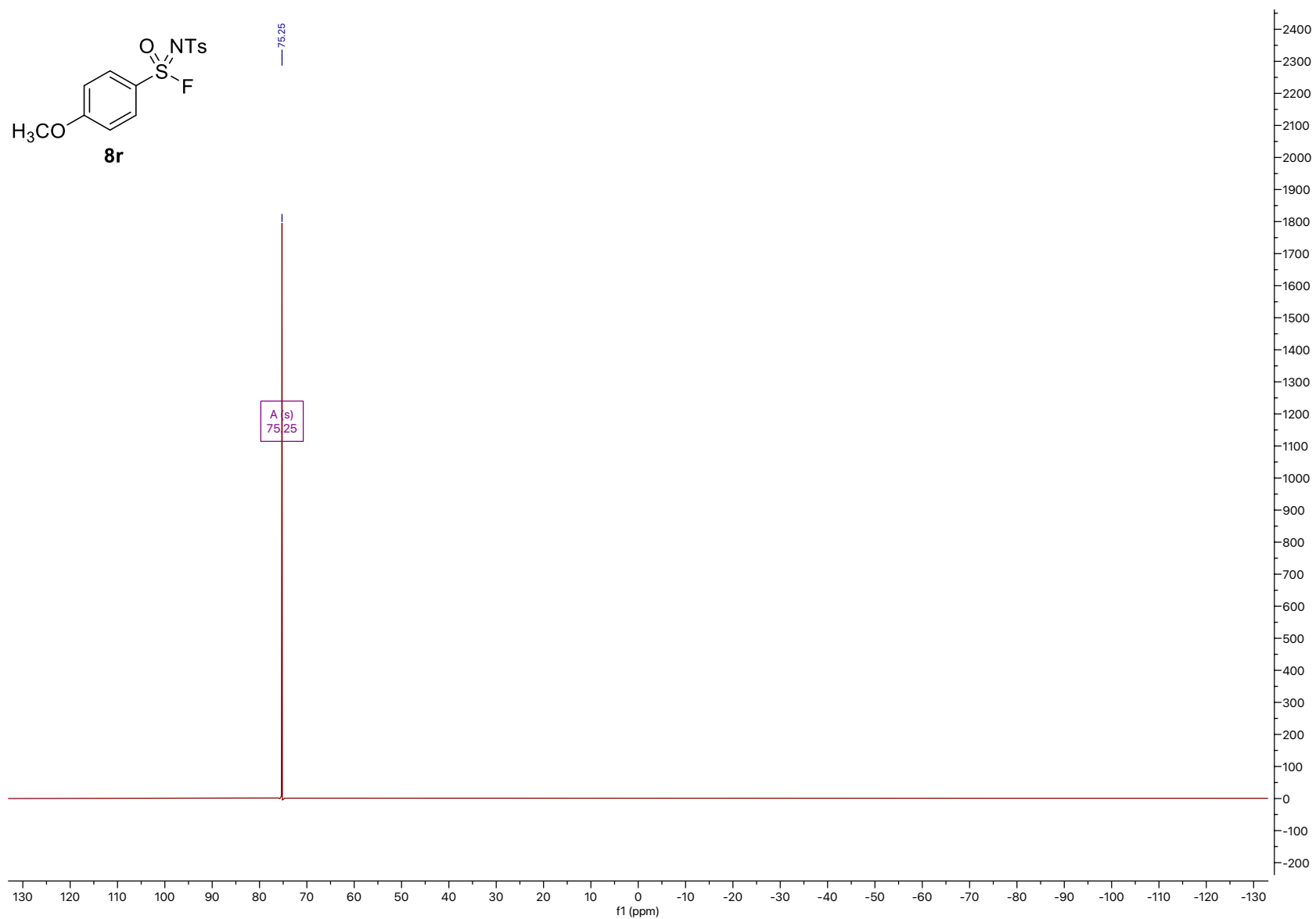
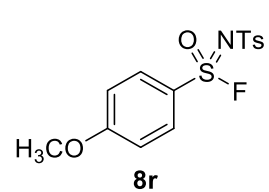
¹H NMR (300 MHz, Chloroform-*d*) of 4-methoxy-*N*-tosylbenzenesulfonimidoyl fluoride (8r)



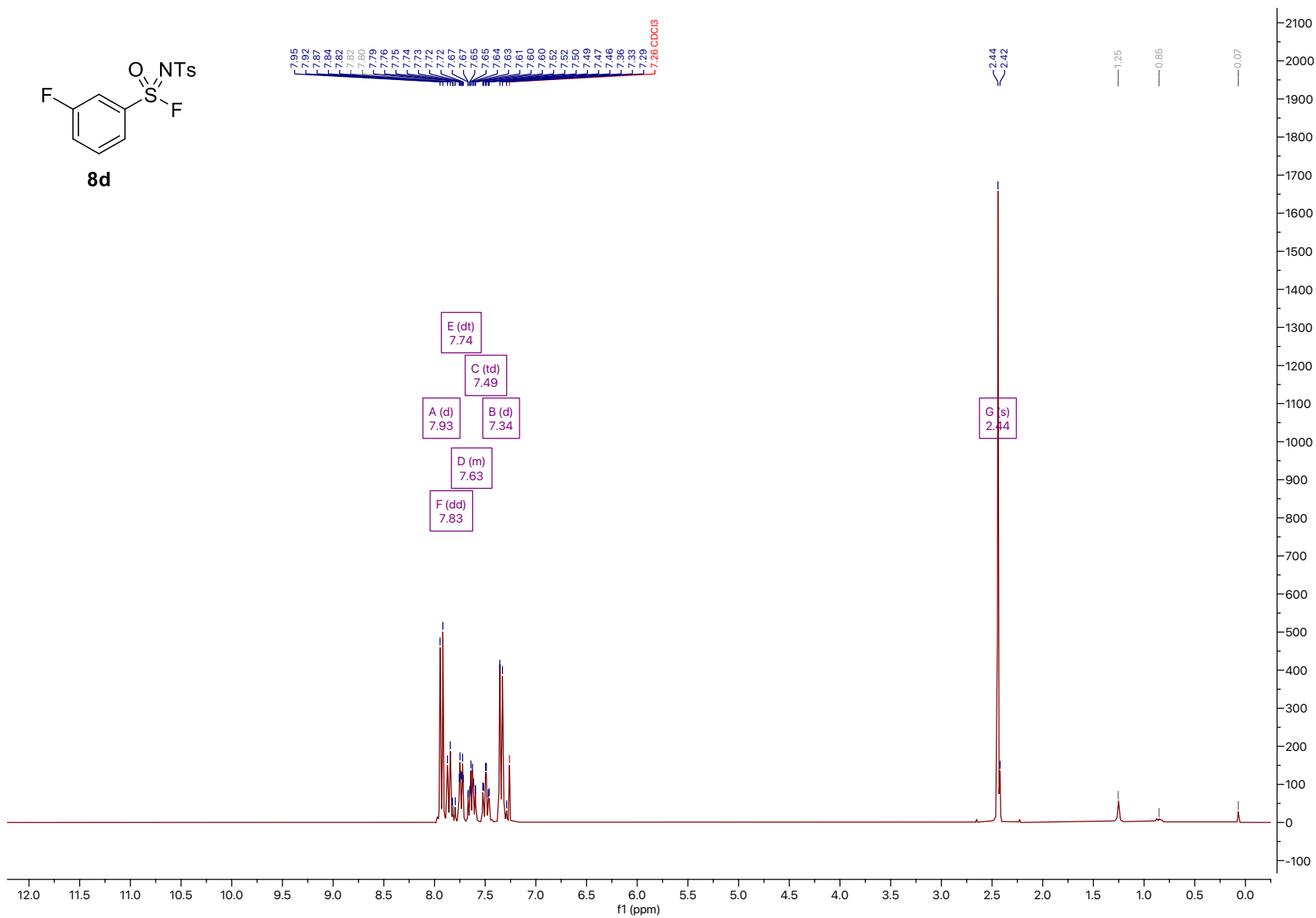
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 4-methoxy-*N*-tosylbenzenesulfonimidoyl fluoride (8r)



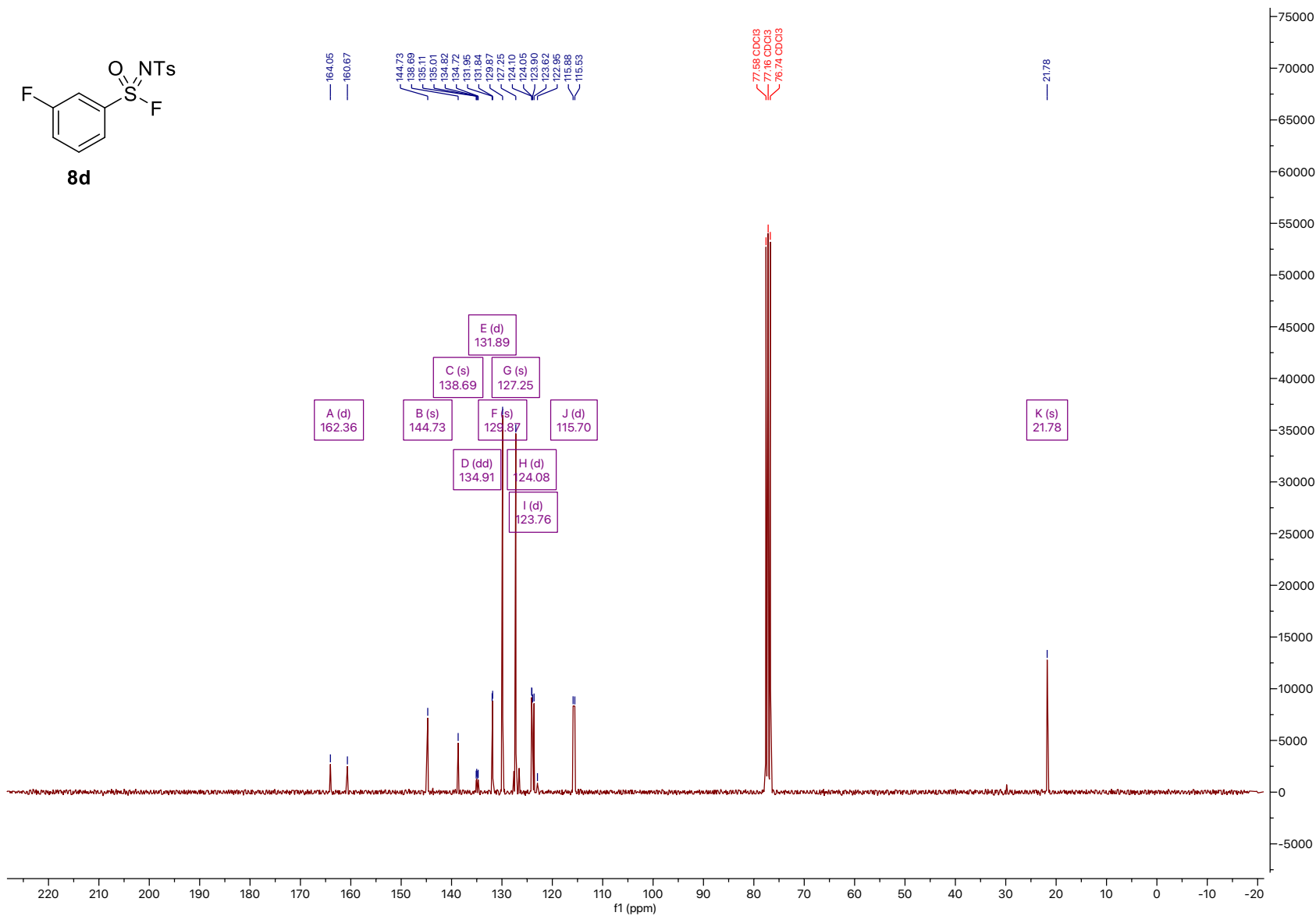
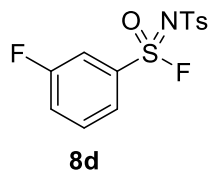
¹⁹F NMR (282 MHz, Chloroform-*d*) of 4-Methoxy-*N*-tosylbenzenesulfonimidoyl fluoride (8r)



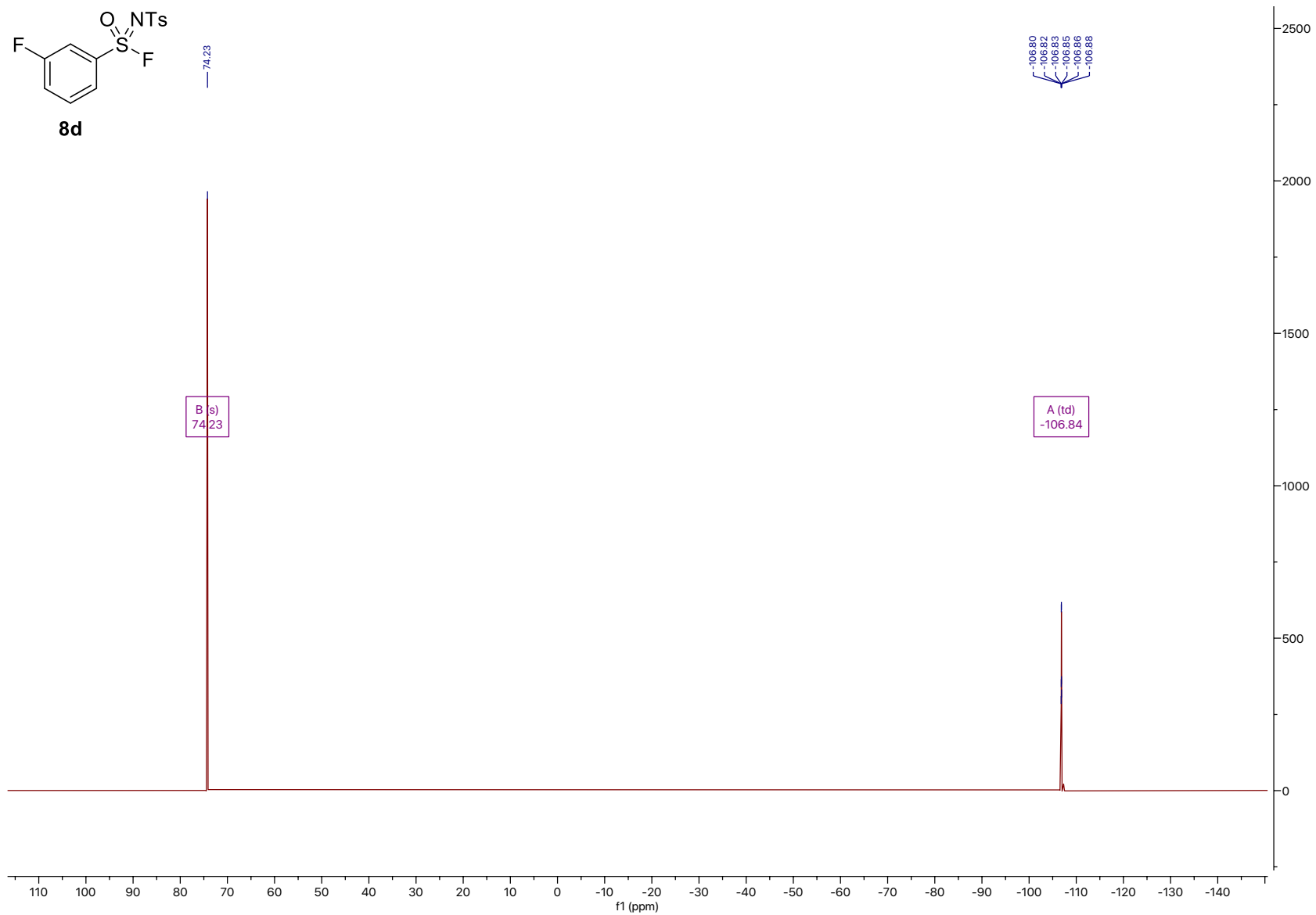
¹H NMR (300 MHz, Chloroform-d) of 3-fluoro-N-tosylbenzenesulfonimidoyl fluoride (8d)



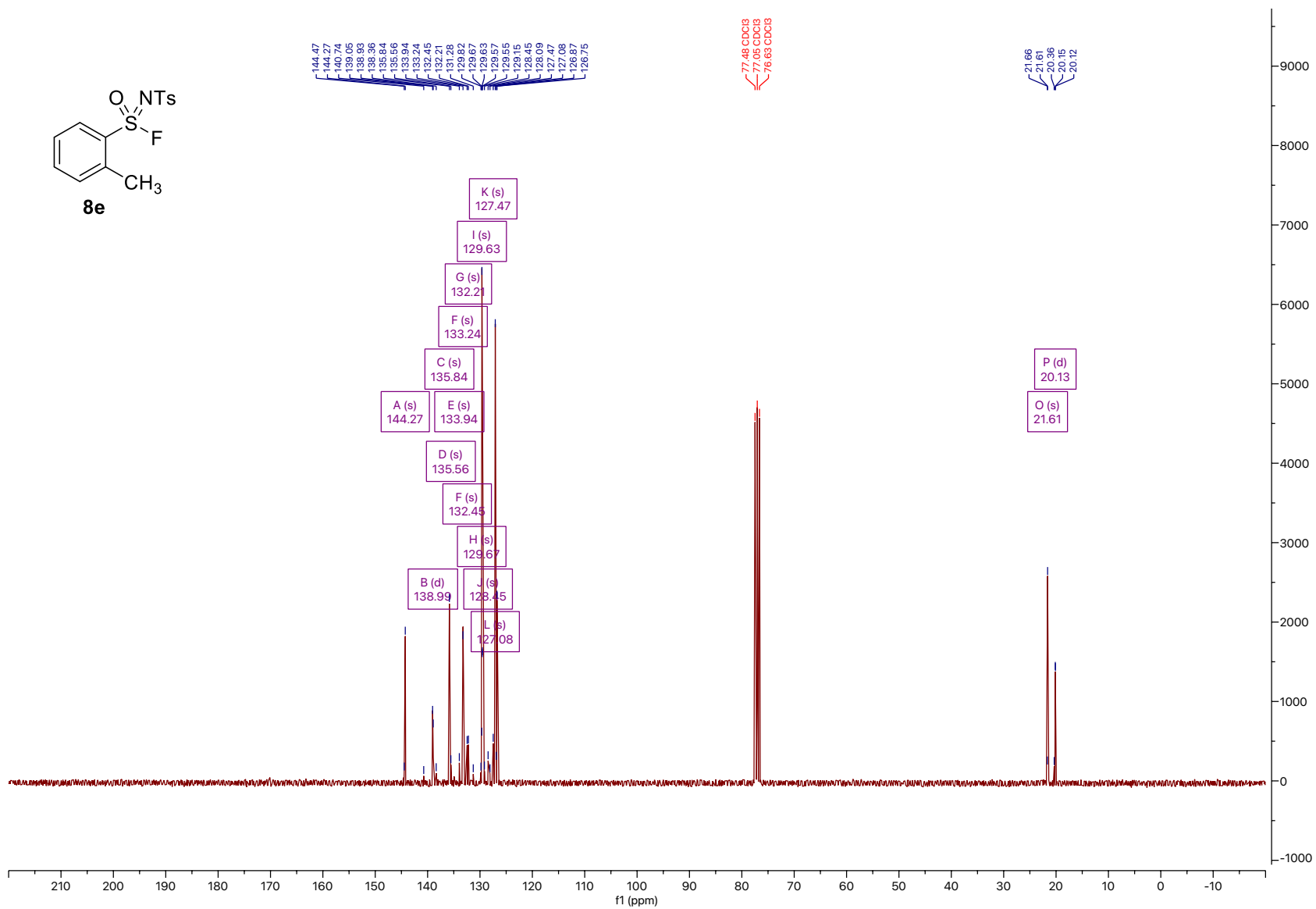
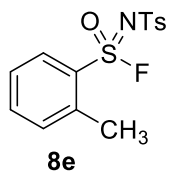
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 3-fluoro-*N*-tosylbenzenesulfonimidoyl fluoride (8d)



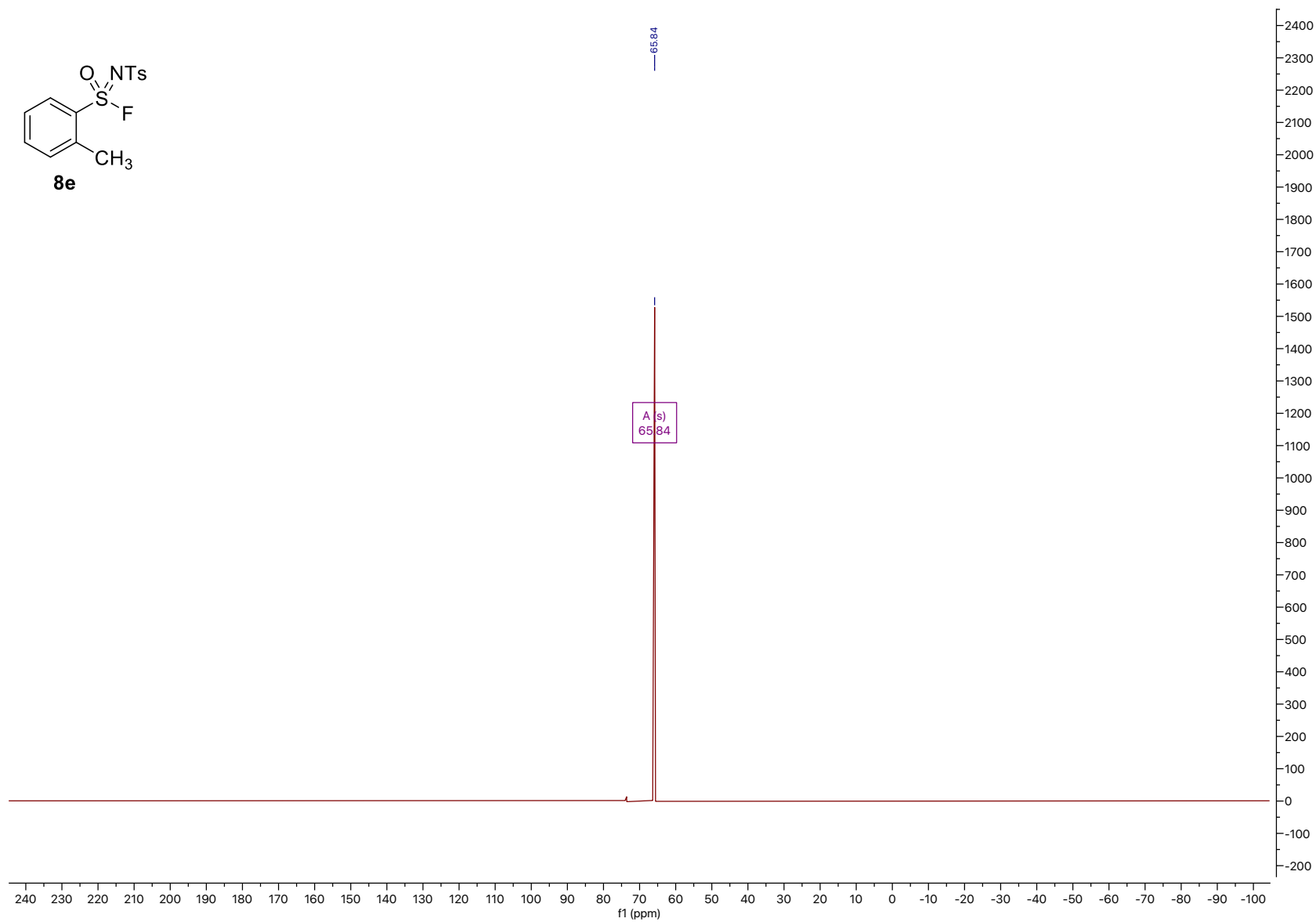
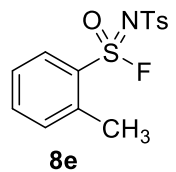
^{19}F NMR (282 MHz, Chloroform-*d*) of 3-fluoro-*N*-tosylbenzenesulfonimidoyl fluoride (8d)



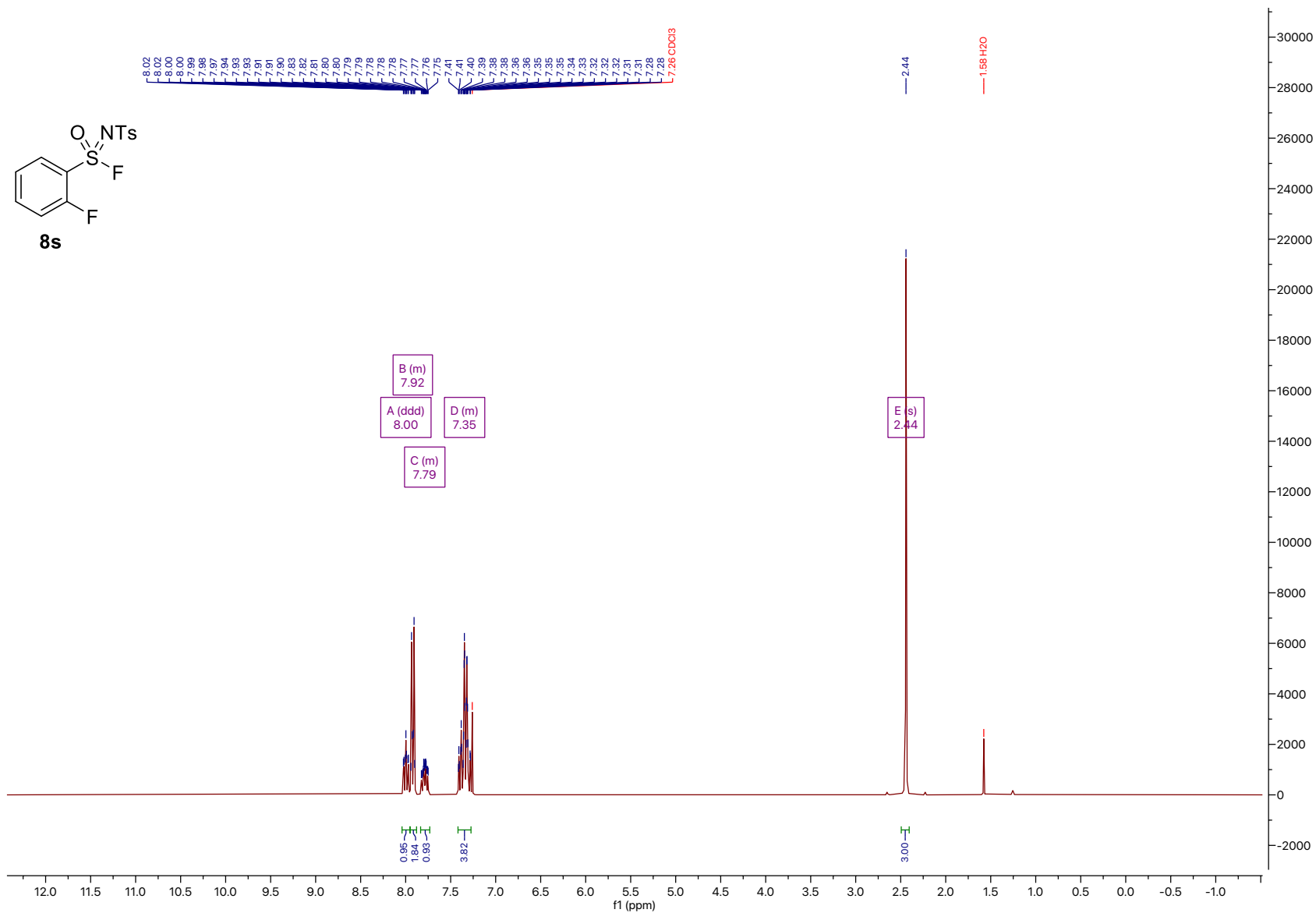
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 2-methyl-*N*-tosylbenzenesulfonimidoyl fluoride (8e)



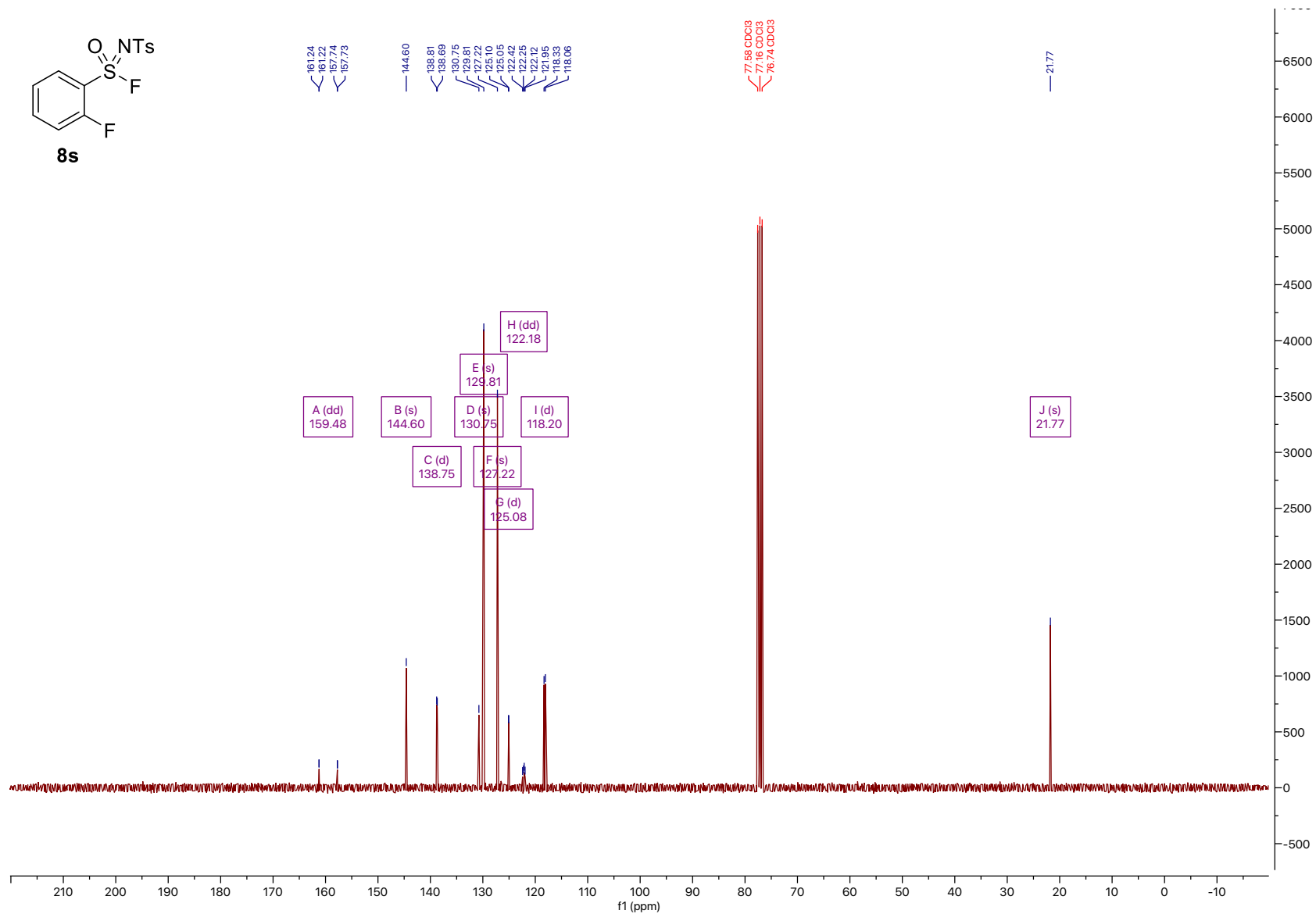
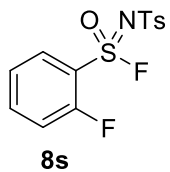
¹⁹F NMR (282 MHz, Chloroform-*d*) of 2-methyl-*N*-tosylbenzenesulfonimidoyl fluoride (8e)



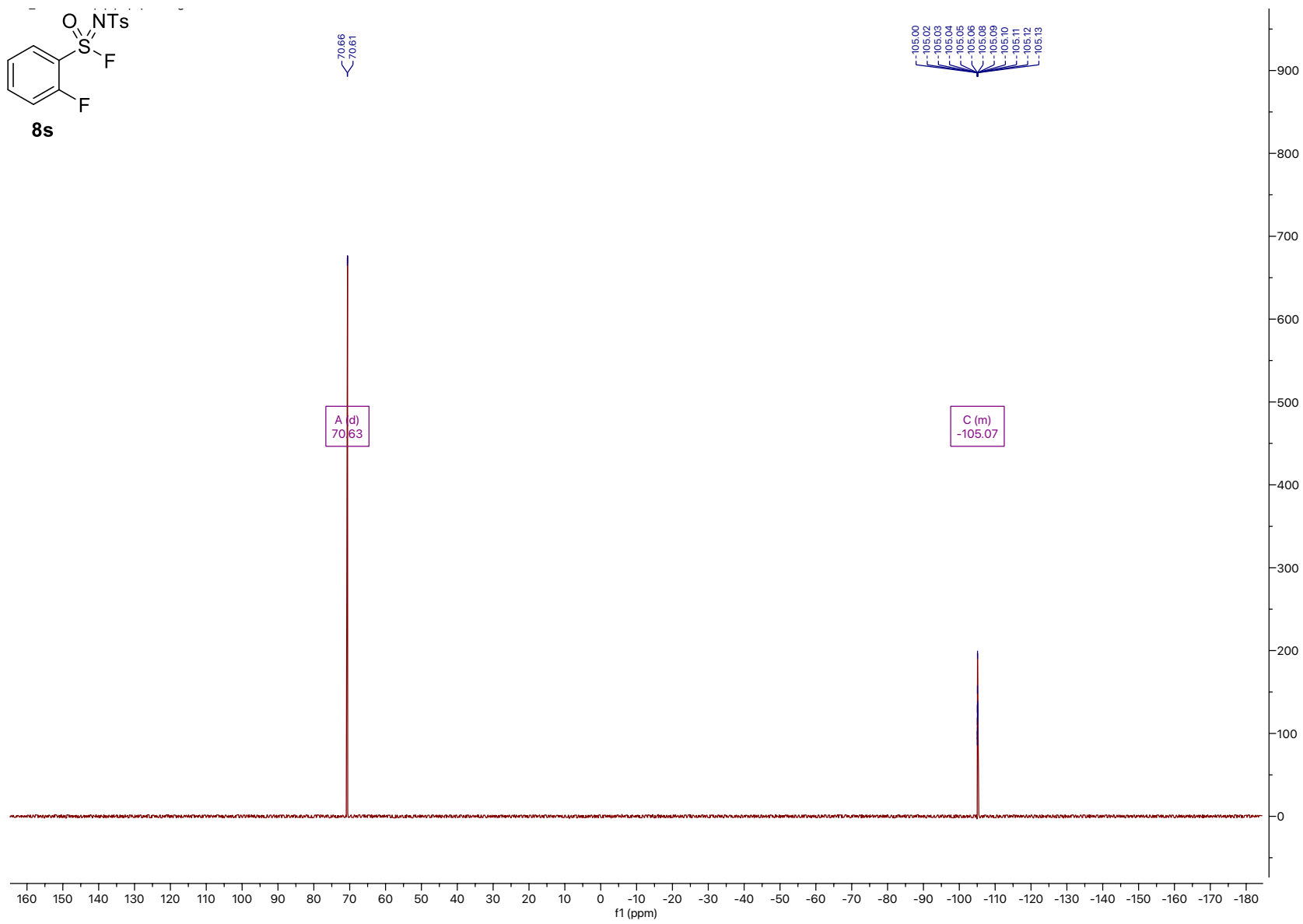
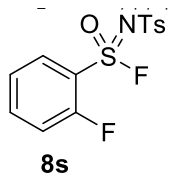
¹H NMR (300 MHz, Chloroform-d) of 2-fluoro-N-tosylbenzenesulfonyl fluoride (8s)



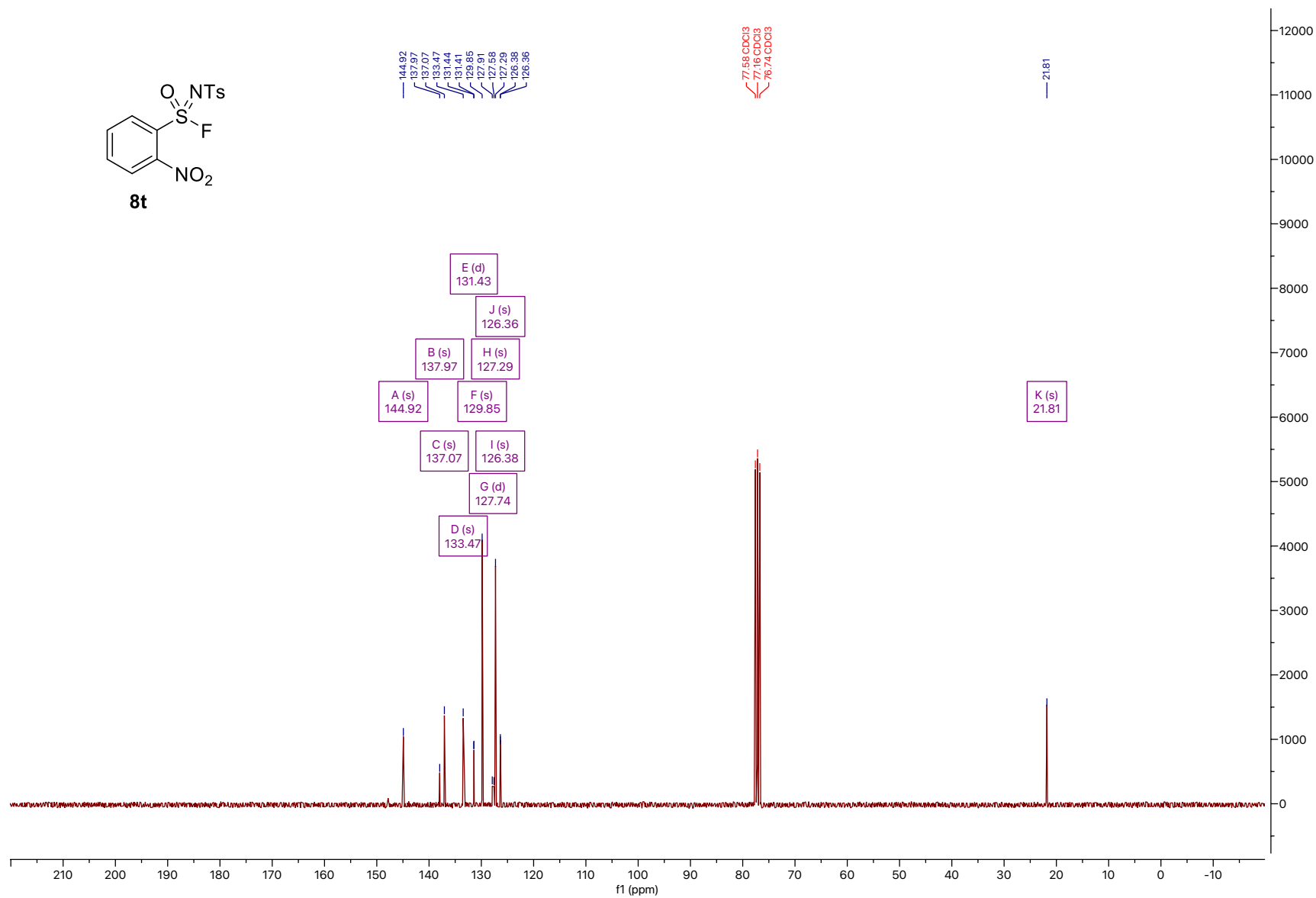
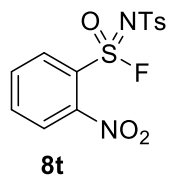
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 2-fluoro-*N*-tosylbenzenesulfonyl fluoride (8s)



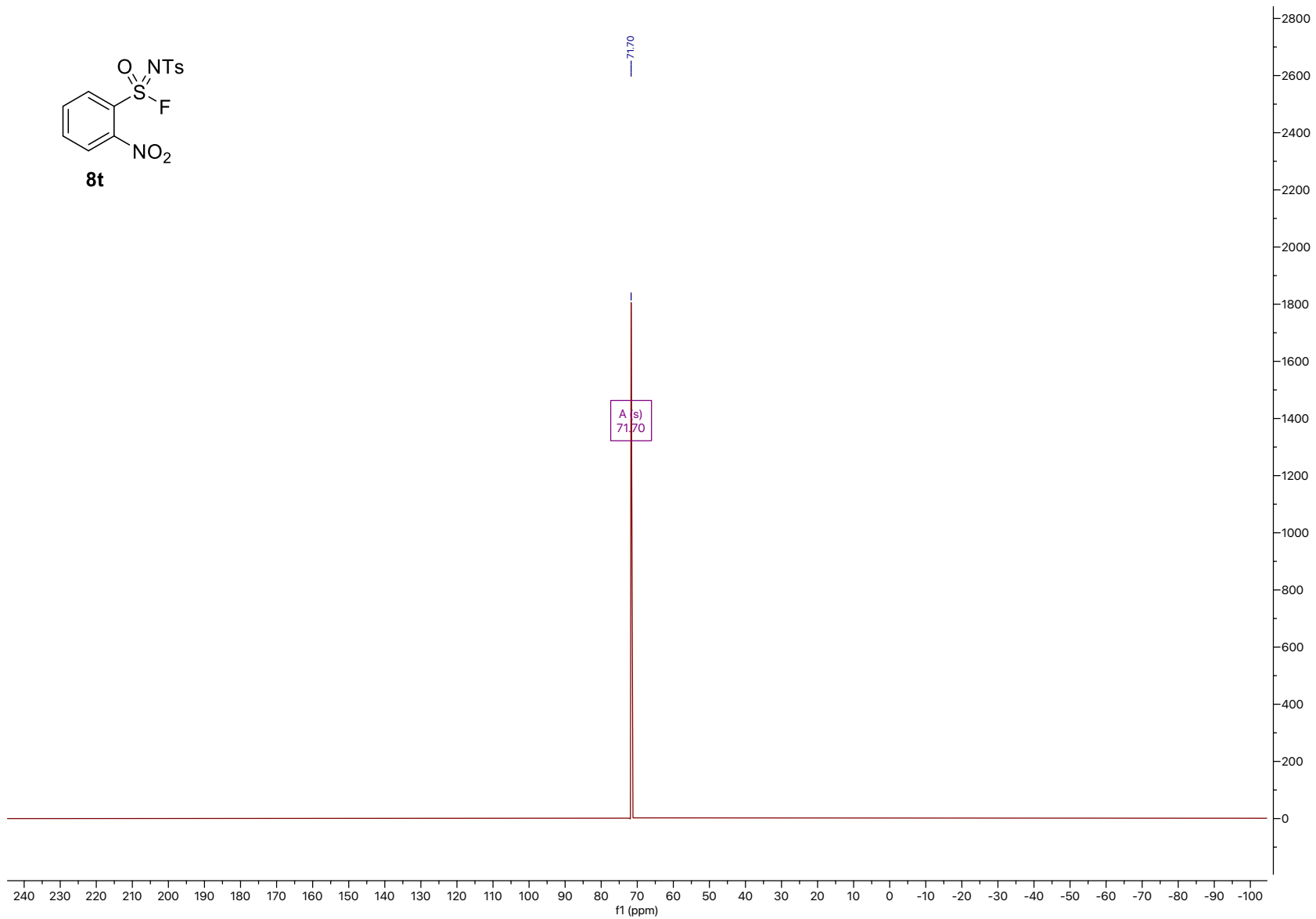
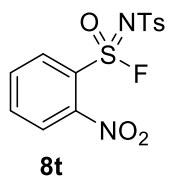
¹⁹F NMR (282 MHz, Chloroform-*d*) of 2-fluoro-*N*-tosylbenzenesulfonimidoyl fluoride (8s)



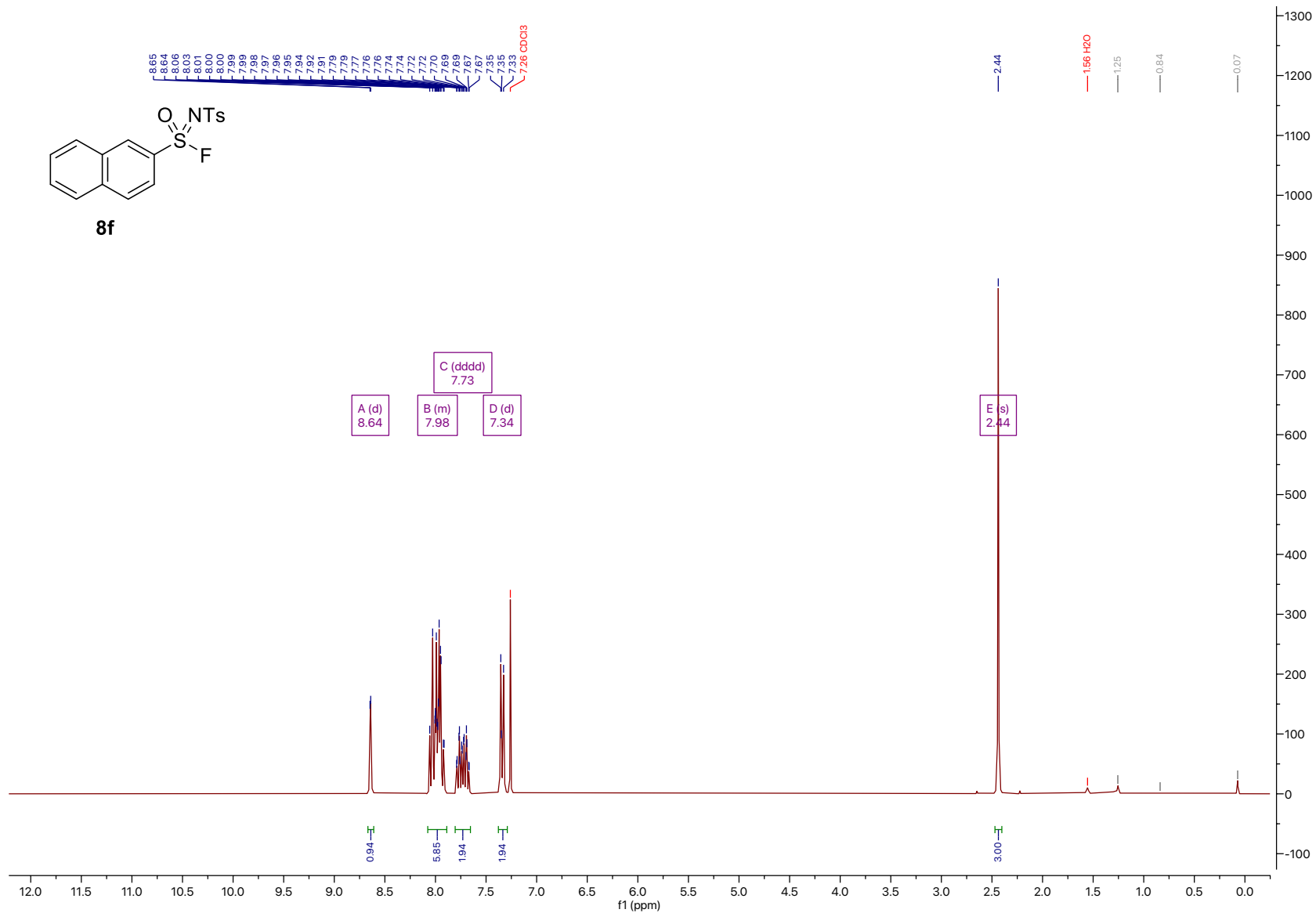
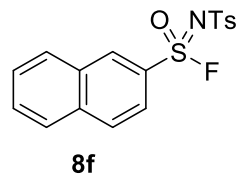
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of 2-nitro-*N*-tosylbenzenesulfonimidoyl fluoride (8t)



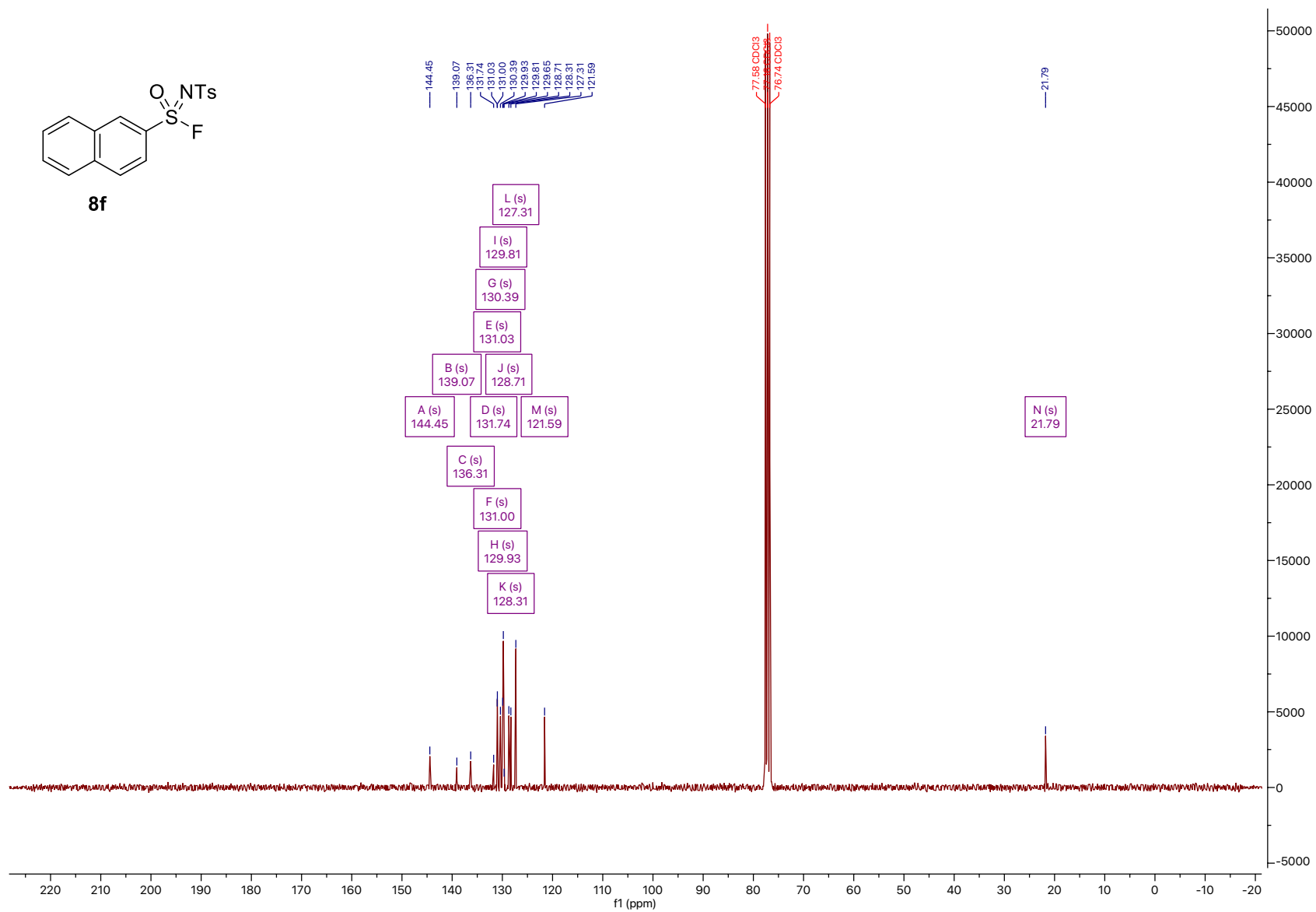
¹⁹F NMR (282 MHz, Chloroform-*d*) of 2-nitro-*N*-tosylbenzenesulfonimidoyl fluoride (8t)



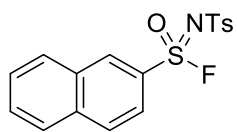
¹H NMR (300 MHz, Chloroform-d) of *N*-tosylnaphthalene-2-sulfonimidoyl fluoride (8f)



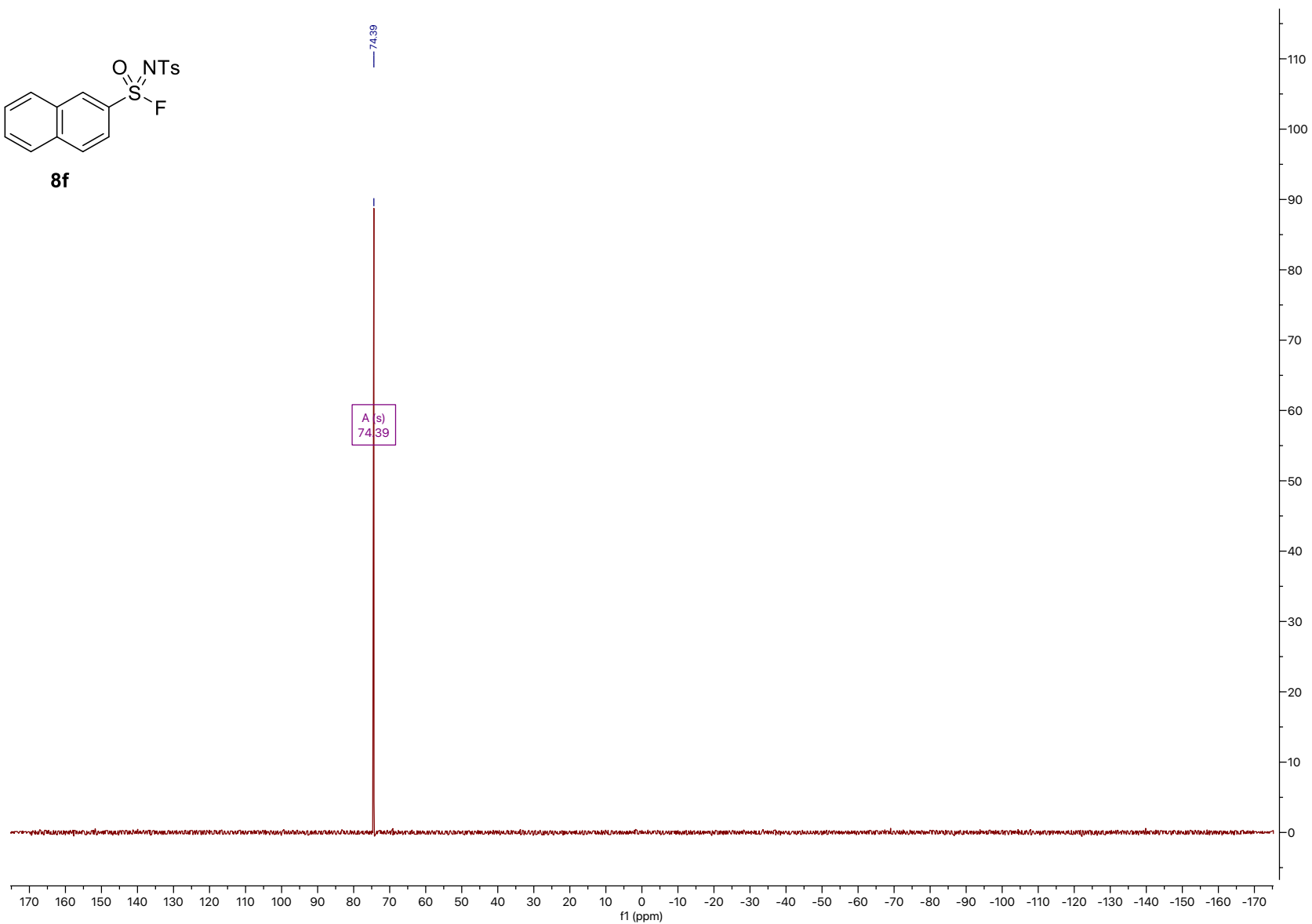
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of *N*-tosyl naphthalene-2-sulfonimidoyl fluoride (8f)



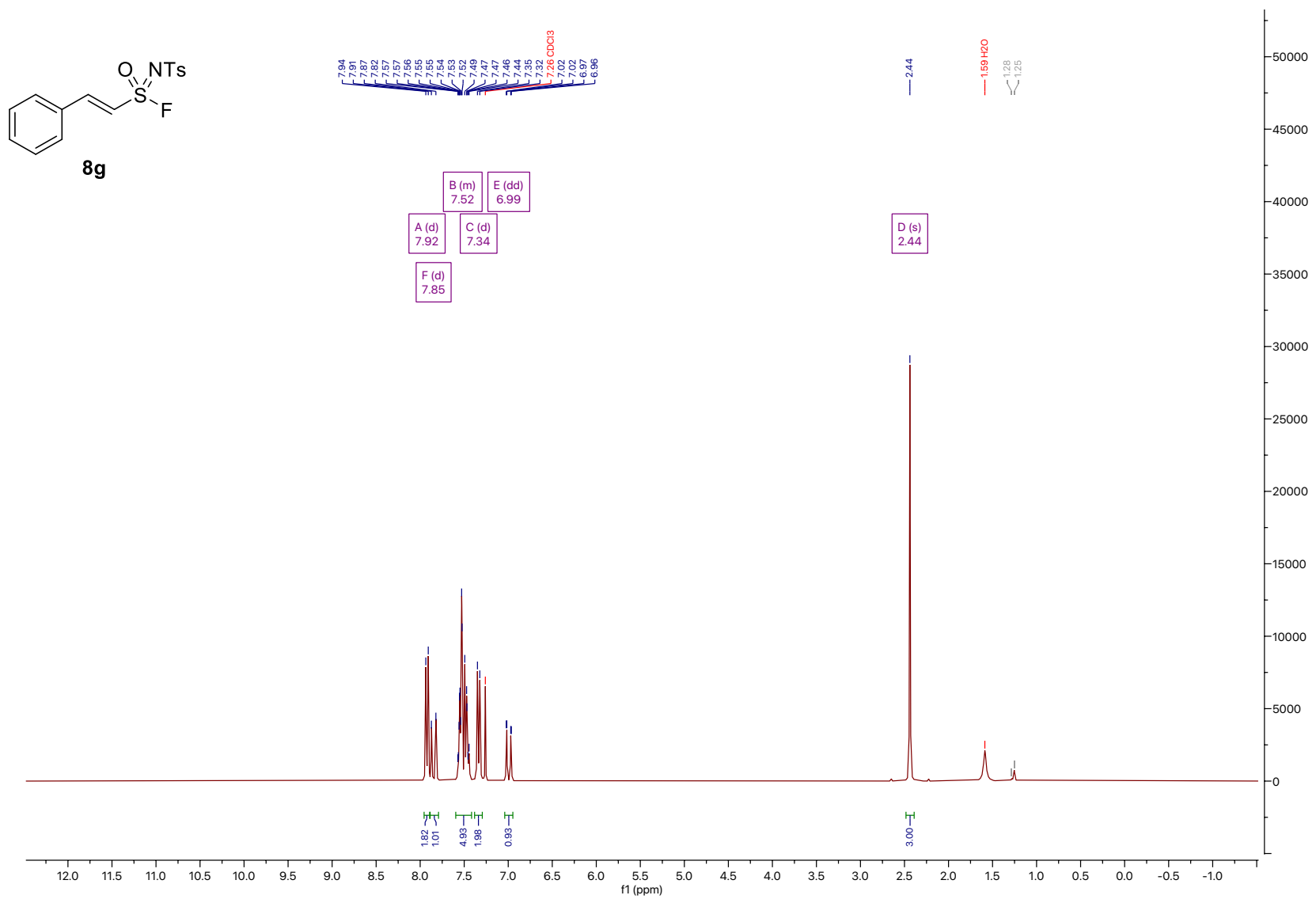
^{19}F NMR (282 MHz, Chloroform-*d*) of *N*-tosyl naphthalene-2-sulfonimidoyl fluoride (8f)



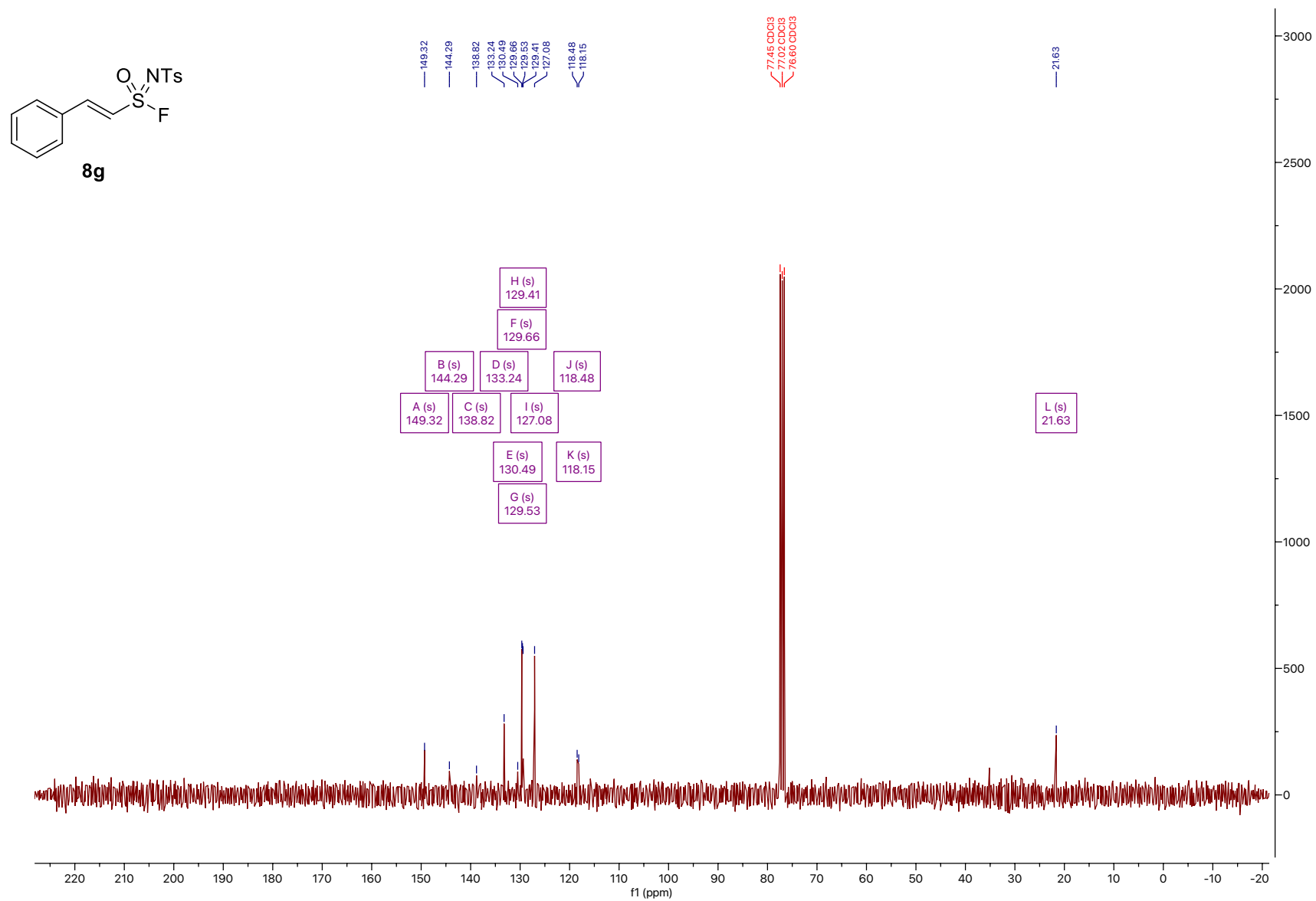
8f



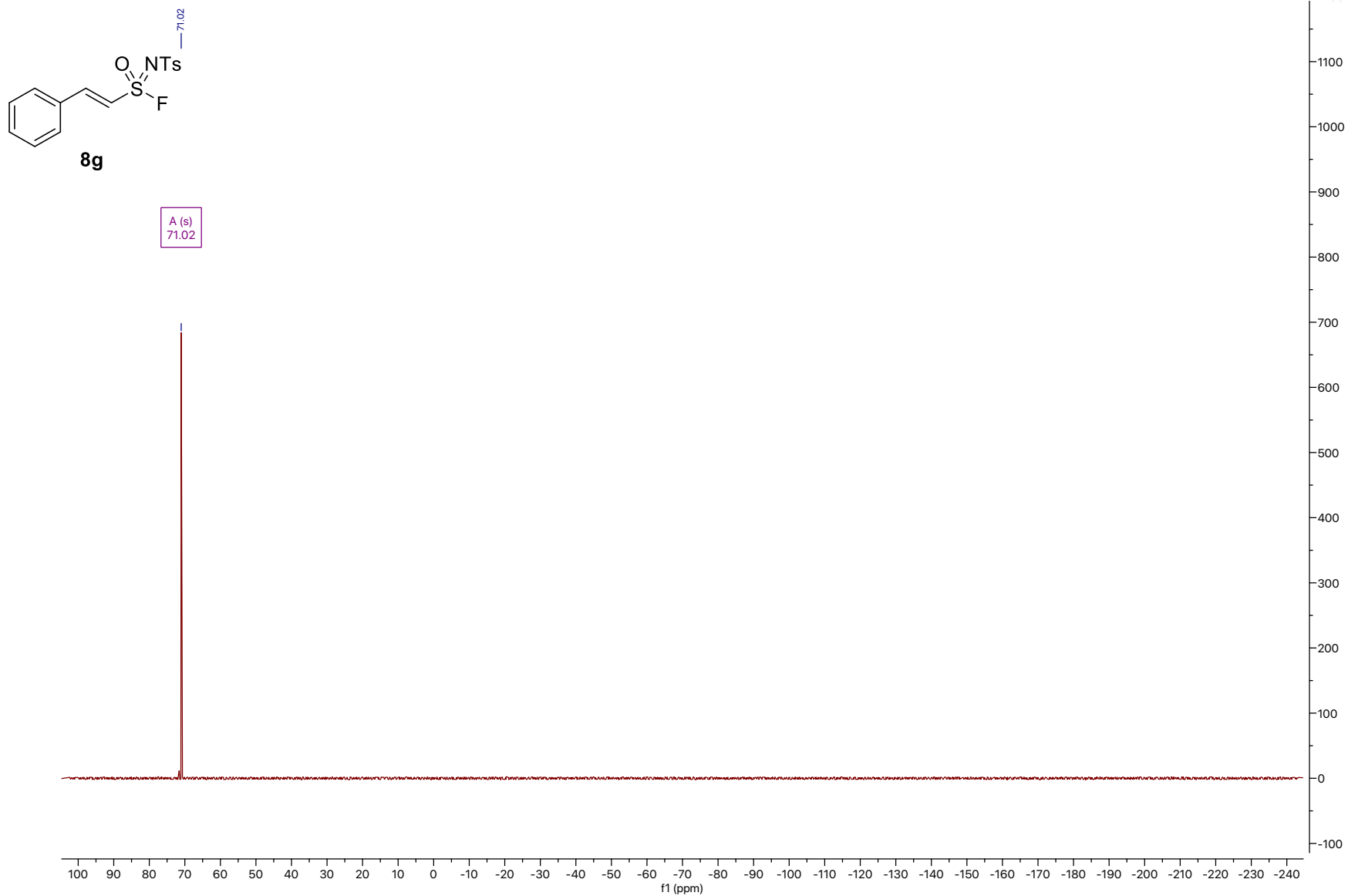
¹H NMR (300 MHz, Chloroform-d) of (E)-2-phenyl-N-tosylethene-1-sulfonimidoyl fluoride (8g)



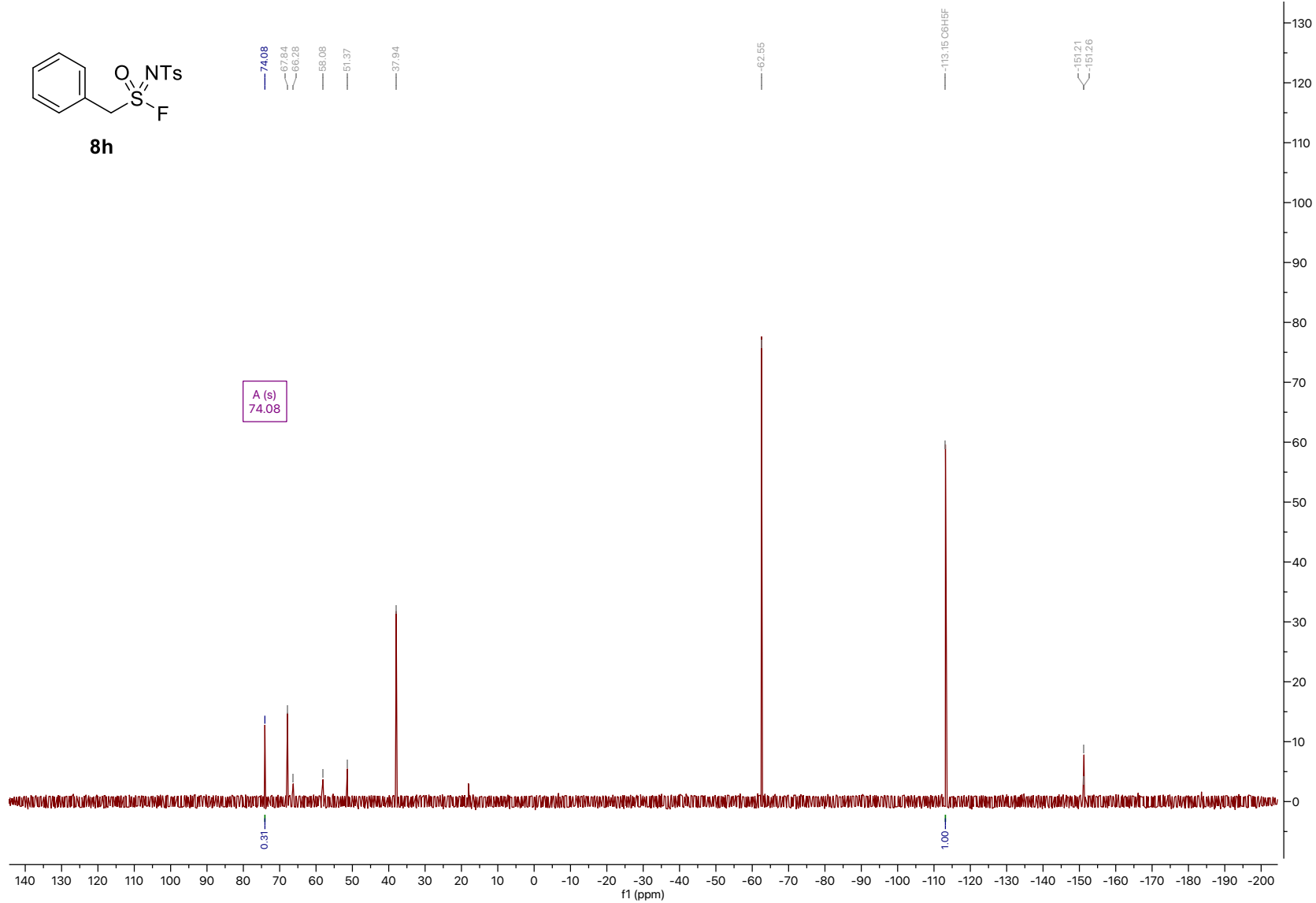
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*) of (*E*)-2-phenyl-*N*-tosylethene-1-sulfonimidoyl fluoride (8g)



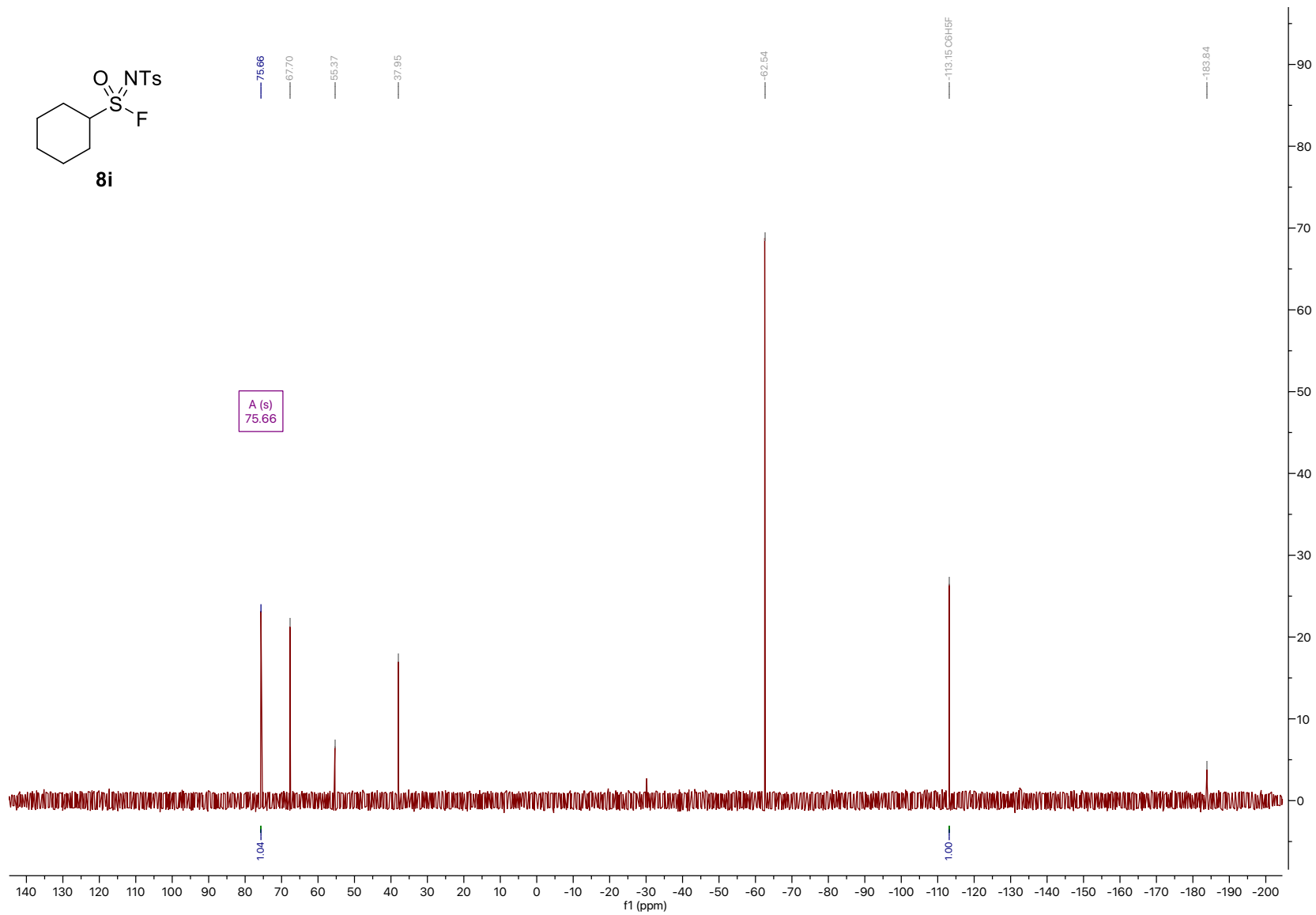
¹⁹F NMR (282 MHz, Chloroform-*d*) of (*E*)-2-phenyl-*N*-tosylethene-1-sulfonimidoyl fluoride (8g)



Crude $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of 1-phenyl-*N*-tosylmethanesulfonyl fluoride (8h)



Crude $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform- d) of *N*-tosylcyclohexanesulfonyl fluoride (8i)



Crude $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*) of *N*-tosyloctane-1-sulfonimidoyl fluoride (**8j**)

