Supporting Information

for the manuscript entitled

Synthesis of *N*-substituted sulfamate esters from sulfamic acid salts by activation with triphenylphosphine ditriflate

J. Miles Blackburn,[‡] Melanie A. Short,[‡] Thomas Castanheiro, Suraj K. Ayer, Tobias D. Muellers, Jennifer L. Roizen*

Department of Chemistry, Duke University, Durham, NC 27708-0354

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General Considerations.

Reagents.
All reagents and chemicals were obtained commercially and used without further purification unless otherwise noted.

Acros	benzylamine, benzyl bromide, diethyl malonate, oxalyl chloride, 3-phenyl-1-propanol, sulfur trioxide pyridine complex, acetonitrile (anhydrous), *tert*-butylamine
Alfa Aesar	(–)-borneol dibenzylamine, ethylamine solution (70% aq), methylamine solution (2 M in THF), phosphorous oxychloride, phosphorous pentachloride, triethylamine, triphenylphospine
BDH	ammonium hydroxide solution (28% NH_3 in H_2O), diethyl ether
Chem Impex	(L)-valinol, *N*-ethyl-*N*'(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl)
Fisher Scientific	*n*-amyl alcohol (*n*-pentanol), magnesium sulfate, *n*-propyl alcohol, toluene (wet), dichloromethane (wet), acetonitrile (wet)
Gelest	*tert*-butyldimethylsilyl chloride
Oakwook Chemical	8-aminoquinoline, cerium(III) chloride, chlorosulfonyl isocyanate, 2-cyanopyridine, diisopropyl azodicarboxylate (DIAD), 4-hydroxybenzonitrile, pentane-1,5-diol, sulfur trioxide trimethylamine complex, 4-(*tert*-butyl)aniline, trichlorotriazine, triethylamine, 2,2,2-trifluoroethyl amine, trifluoromethanesulfonic anhydride, 4-(trifluoromethyl)aniline, triphenylphosphine oxide
Sigma-Aldrich	anisole, 5α-cholestan-3β-ol, 3,7-dimethyl-1-octanol, ethyl acetate, hydrochloric acid (concentrated), hexanes, 2-hydroxypyridine, methyllithium solution (1.6 M in Et_2O), phthalic anhydride, sodium hydride (60% dispersion in mineral oil), *tert*-butanol, thionyl chloride, α, α, α-(trifluoro)toluene, (*S*)-α-methyl benzylamine, (*R*)-α-methyl benzylamine, diethylamine
TCI	acetophenone, (–)-menthol, 3-methylbutan-1-ol
Soap Goods	sodium bicarbonate

Methylene chloride (CH_2Cl_2), and tetrahydrofuran (THF) were obtained from Sigma Aldrich and were purified, dried, and degassed by passage through two columns of neutral, activated alumina under N_2 using an Innovative Technologies solvent purification system. Toluene was obtained from Sigma Aldrich and was purified, dried, and degassed by passage through a column containing copper followed by a column of neutral, activated alumina under N_2 using an Innovative Technologies solvent purification system. Triethylamine (Et_3N) was distilled from CaH_2 and stored in a Schlenk flask for future use. Trifluormethanesulfonic anhydride was stored in a nitrogen-filled glovebox.

Preparation of Known Reagents.

2-(Pyridin-2-yl)propan-2-amine[1] was prepared according to the literature and distilled before use. 5-((Tert-butyldimethylsilyl)oxy)pentan-1-ol,[2] 5-(benzyloxy)pentan-1-ol,[3] and (*S*)-2-(1-hydroxy-3-methylbutan-2-yl)isoindoline-1,3-dione[4] were prepared according to the literature and stored at –20 °C.

Procedures.

Moisture-sensitive reactions were performed using flame-dried glassware under an atmosphere of dry nitrogen (N_2). Air- and water-sensitive reactions, where noted, were performed in an MBraun MB200 glove box held under an atmosphere of nitrogen gas (working pressure 2–6 mbar). Flame-dried equipment was stored in a 130 °C oven before use and either allowed to cool in a cabinet dessicator or assembled hot and allowed to cool under an inert atmosphere. Air- and moisture-sensitive liquids and solutions were transferred *via* plastic or glass syringe or by stainless steel cannula. Chromatographic purification of products was accomplished by flash column chromatography using Silicycle Silica flash F60 (particle size 40–63 μm, 230–400 mesh). Thin layer chromatography was performed on EMD Millipore silica gel 60 F254 glass-backed plates (layer thickness 250 μm, particle size 10–12 μm, impregnated with a fluorescent indicator). Visualization of the developed chromatogram was accomplished by fluorescence quenching under shortwave UV light and/or by staining with *p*-anisaldehyde, or $KMnO_4$ stains. Room temperature is 22 °C.

Instrumentation.

NMR Spectrometry
NMR spectra were obtained on Varian iNOVA spectrometers operating at 400 or 500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR, and 376 MHZ for ^{19}F NMR, and are reported as chemical shifts (δ) in parts per million (ppm). Spectra were referenced internally according to residual solvent signals (^{1}H: $CDCl_3$, 7.26 ppm; CD_3CN, 1.94 ppm; ^{13}C: $CDCl_3$, 77.0 ppm, CD_3CN: 118.3 ppm, d_6-DMSO: 39.5 ppm). Data for NMR spectra use the following abbreviations to describe multiplicity: s, singlet; br s, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; td, triplet of doublets; tt, triplet of triplets; ddd, doublet of doublet of doublets; ddt, doublet of doublet of triplets; app dd, apparent doublet of doublets; m, multiplet. Coupling constant (*J*) are reported in units of Hertz (Hz).

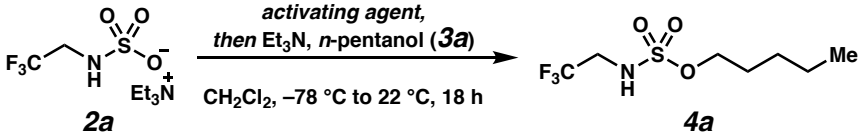
IR spectroscopy
IR spectra were obtained on a Nicolet 6700 FT-IR system. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 0–33% T); m (medium, 34–66% T); w (weak, 67–95% T); and br (broad).

Mass Spectrometry
High resolution mass spectra (HRMS, m/z) were recorded on an Agilent LCMS-TOF-DART spectrometer using electrospray ionization (ESI, Duke University Department of Chemistry Instrumentation Center).

High Pressure Liquid Chromatography (HPLC)
Enantiomeric ratios were determined by HPLC PhenomenexTM Lux® Cellulose I by generating standards in each enantiomeric series and analyzing these standards on a Shimadzu Prominence Modular HPLC.

Optimization of Sulfamate Ester Preparation.

Table S1. Optimization of sulfamate salt activation.



entry[a]	activating agent (equiv)	yield (%)[b]
1	PCl_5 (2.0 equiv)	41
2	$POCl_3$ (2.0 equiv)	44
3	$SOCl_2$ (2.0 equiv)	<5
4	$(COCl)_2$ (10.0 equiv)	nd[c]
5	trichlorotriazine (1.0 equiv)	<5%
6	DIAD, PPh_3	50
7	Tf_2O (1.0 equiv), Ph_3PO (2.1 equiv)	56
8	**Tf_2O (1.5 equiv), Ph_3PO (3.15 equiv)**	**71[d]**

[a]General reaction conditions: reactions performed on 2.0 mmol scale with 1.0 equiv *n*-amyl alcohol, 1.0 equiv sulfamate **2a**, 2.0 equiv Et_3N, CH_2Cl_2 (0.08 M), –78 °C → 22 °C. [b]Isolated yield. [c]Not detected. [d]1.5 equiv sulfamate **2a**.

Procedures for optimization of sulfamic acid salt activation.

Entry 1. A flame-dried flask equipped with magnetic stir bar was charged with PCl_5 (833 mg, 4.0 mmol, 2.0 equiv) and fitted with a reflux condenser and rubber septum with nitrogen inlet. The flask was evacuated and backfilled with nitrogen. Anhydrous toluene (14 mL) and sulfamate salt **2a** (561 mg, 2.0 mmol, 1.0 equiv) were added to the reaction flask sequentially. The resulting yellow solution was heated in an oil bath set at 110 °C for 2 h. After 2 h, the reaction was removed from heat and allowed to cool to room temperature. While cooling, a white/yellow precipitate began to form. The solid was removed by vacuum filtration, rinsing the flask with toluene to achieve quantitative transfer. The filtrate was then concentrated under reduced pressure and the resulting crude sulfamoyl chloride was used without further purification or analysis.

A second flask equipped with magnetic stir bar was then charged with Et_3N (4.0 mmol, 2.0 equiv) and CH_2Cl_2 (8 mL, 0.25 M) and the mixture was cooled at –78 °C in an ^{i}PrOH/dry ice bath. The crude sulfamoyl chloride was transferred dropwise to the Et_3N solution via cannula (during which time a yellow to intense red color often developed), the flask was rinsed with an additional 2 mL of CH_2Cl_2 to achieve quantitative transfer. The resultant solution was stirred at –78 °C for 15 minutes. The alcohol (R^2–OH, 2.0 mmol, 1.0 equiv) was then added as a solution in CH_2Cl_2 (2.0 mL, 1.0 M) to the

triethylamine solution via cannula. The alcohol-containing flask was rinsed with an additional 0.5 mL CH_2Cl_2 to achieve quantitative transfer. Without removing the cooling bath, the reaction was then stirred for 18 h, during which time no additional dry ice was added and the mixture warmed to room temperature.

After 18 h, the reaction was diluted with 1 M HCl (20 mL) and H_2O (10 mL). The biphasic mixture was transferred to a separatory funnel, rinsing the flask with CH_2Cl_2 to achieve quanitative transfer. The organic phase was separated and the aqueous was extracted twice more with CH_2Cl_2 (2 x 25 mL). The combined organic phases were dried with $MgSO_4$, filtered, and concentrated. The crude reaction mixtures were then purified by silica gel flash chromatography by dry loading the samples and eluting with a hexanes:EtOAc solvent system as noted below.

Entries 2–3. A flame-dried flask equipped with magnetic stir bar and fitted with a reflux condenser and rubber septum with nitrogen inlet was charged with sulfamate salt **2a** (561 mg, 2.0 mmol, 1.0 equiv). Chlorinating agent ($POCl_3$ or $SOCl_2$, 2.0 equiv) was then added via syringe. The resulting yellow solution was heated in an oil bath set at 80 °C for 2 h. After 2 h, the reaction was removed from heat and allowed to cool to room temperature. Once cool, the reaction was concentrated under reduced pressure to remove any excess chlorinating agent and furnish the crude sulfamoyl chloride.

A second flask equipped with magnetic stir bar was then charged with Et_3N (4.0 mmol, 2.0 equiv) and CH_2Cl_2 (8 mL, 0.25 M) and the mixture was cooled at –78 °C in an ^{i}PrOH/dry ice bath. The crude sulfamoyl chloride was transferred dropwise to the Et_3N solution via cannula (during which time a yellow to intense red color often developed), the flask was rinsed with an additional 2 mL of CH_2Cl_2 to achieve quantitative transfer. The resultant solution was stirred at –78 °C for 15 minutes. The alcohol (R^2–OH, 2.0 mmol, 1.0 equiv) was then added as a solution in CH_2Cl_2 (2.0 mL, 1.0 M) to the triethylamine solution via cannula. The alcohol-containing flask was rinsed with an additional 0.5 mL CH_2Cl_2 to achieve quantitative transfer. Without removing the cooling bath, the reaction was then stirred for 18 h, during which time no additional dry ice was added and the mixture warmed to room temperature.

After 18 h, the reaction was diluted with 1 M HCl (20 mL) and H_2O (10 mL). The biphasic mixture was transferred to a separatory funnel, rinsing the flask with CH_2Cl_2 to achieve quanitative transfer. The organic phase was separated and the aqueous was extracted twice more with CH_2Cl_2 (2 x 25 mL). The combined organic phases were dried with $MgSO_4$, filtered, and concentrated. The crude reaction mixtures were then purified by silica gel flash chromatography by dry loading the samples and eluting with a hexanes:EtOAc solvent system as noted below.

Entry 4. A flame-dried flask equipped with magnetic stir bar was charged with sulfamate salt **2a** (561 mg, 2.0 mmol, 1.0 equiv) and the flask was evacuated and backfilled with nitrogen. Anhydrous CH_2Cl_2 (25 mL) was added followed by oxalyl chloride (1.7 mL, 20.0 mmol, 10.0 equiv) and DMF (8 µL, 0.1 mmol, 0.05 equiv). Upon complete addition of oxalyl chloride, bubbling was observed. The clear solution was stirred at 22 °C for 1 h

until no further bubbling was observed. The solution was then concentrated under reduced pressure to give the crude sulfamoyl chloride.

A second flask equipped with magnetic stir bar was then charged with Et_3N (4.0 mmol, 2.0 equiv) and CH_2Cl_2 (8 mL, 0.25 M) and the mixture was cooled at –78 °C in an ^{i}PrOH/dry ice bath. The crude sulfamoyl chloride was transferred dropwise to the Et_3N solution via cannula (during which time a yellow to intense red color often developed), the flask was rinsed with an additional 2 mL of CH_2Cl_2 to achieve quantitative transfer. The resultant solution was stirred at –78 °C for 15 minutes. The alcohol (R^2–OH, 2.0 mmol, 1.0 equiv) was then added as a solution in CH_2Cl_2 (2.0 mL, 1.0 M) to the triethylamine solution via cannula. The alcohol-containing flask was rinsed with an additional 0.5 mL CH_2Cl_2 to achieve quantitative transfer. Without removing the cooling bath, the reaction was then stirred for 18 h, during which time no additional dry ice was added and the mixture warmed to room temperature.

After 18 h, the reaction was diluted with 1 M HCl (20 mL) and H_2O (10 mL). The biphasic mixture was transferred to a separatory funnel, rinsing the flask with CH_2Cl_2 to achieve quanitative transfer. The organic phase was separated and the aqueous was extracted twice more with CH_2Cl_2 (2 x 25 mL). The combined organic phases were dried with $MgSO_4$, filtered, and concentrated. The crude reaction mixtures were then purified by silica gel flash chromatography by dry loading the samples and eluting with a hexanes:EtOAc solvent system as noted below.

Entry 5. A flame-dried flask equipped with magnetic stir bar and fitted with a reflux condenser was charged with sulfamate salt **2a** (561 mg, 2.0 mmol, 1.0 equiv) and trichlortriazine (387 mg, 2.0 mmol, 1.0 equiv) and the flask was evacuated and backfilled with nitrogen. Anhydrous acetonitrile (8.0 mL) was added and the reaction flask was heated in an oil bath set at 85 °C for 2 h. After 2 h, the reaction solution was concentrated under reduced pressure to give the crude sulfamoyl chloride.

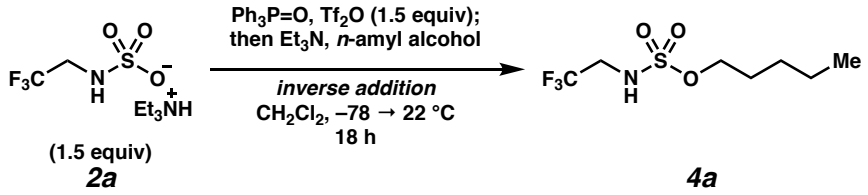
A second flask equipped with magnetic stir bar was then charged with Et_3N (4.0 mmol, 2.0 equiv) and CH_2Cl_2 (8 mL, 0.25 M) and the mixture was cooled at –78 °C in an ^{i}PrOH/dry ice bath. The crude sulfamoyl chloride was transferred dropwise to the Et_3N solution via cannula (during which time a yellow to intense red color often developed), the flask was rinsed with an additional 2 mL of CH_2Cl_2 to achieve quantitative transfer. The resultant solution was stirred at –78 °C for 15 minutes. The alcohol (R^2–OH, 2.0 mmol, 1.0 equiv) was then added as a solution in CH_2Cl_2 (2.0 mL, 1.0 M) to the triethylamine solution via cannula. The alcohol-containing flask was rinsed with an additional 0.5 mL CH_2Cl_2 to achieve quantitative transfer. Without removing the cooling bath, the reaction was then stirred for 18 h, during which time no additional dry ice was added and the mixture warmed to room temperature.

After 18 h, the reaction was diluted with 1 M HCl (20 mL) and H_2O (10 mL). The biphasic mixture was transferred to a separatory funnel, rinsing the flask with CH_2Cl_2 to achieve quanitative transfer. The organic phase was separated and the aqueous was extracted twice more with CH_2Cl_2 (2 x 25 mL). The combined organic phases were dried

with $MgSO_4$, filtered, and concentrated. The crude reaction mixtures were then purified by silica gel flash chromatography by dry loading the samples and eluting with a hexanes:EtOAc solvent system as noted below.

Entry 6. A flame-dried flask equipped with magnetic stir bar was charged with sulfamate salt **2a** (561 mg, 2.0 mmol, 1.0 equiv) and PPh_3 (656 mg, 2.5 mmol, 1.25 equiv) and the flask was evacuated and backfilled with nitrogen. Anhydrous toluene (5.0 mL) was added followed by dropwise addition of diisopryopyl azodicarboxylate (DIAD, 0.55 mL, 2.8 mmol, 1.4 equiv). A separate flame-dried flask was charged with *n*-amyl alcohol which was taken up in PhMe (1.0 mL). The alcohol solution was transferred to the activated suspension dropwise via syringe. The reaction flask was heated in an oil bath set at 65 °C for 18 h. After 18 h, the reaction was worked-up and purified as described in entries 1–5.

Table S2. Optimization of reaction conditions.

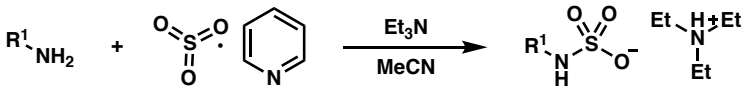


entry[a]	Ph_3P=O (equiv)	Et_3N (equiv)	concentration (M)	yield (%)[b]
1	3.15	2.0	0.04	70
2[c]	3.15	2.0	0.04	46
3	3.15	2.0	0.08	71
4	3.15	2.0	0.16	44
5	1.50	2.0	0.08	67
6	1.65	2.0	0.08	79
7[d]	1.65	2.0	0.08	40
8	1.65	–	0.08	<5
9	1.65	1.0	0.08	5
10	**1.65**	**3.0**	**0.08**	**95**

[a]General reaction conditions: reactions performed on 2.0 mmol scale with 1.0 equiv *n*-amyl alcohol, 1.5 equiv sulfamate **2a**, 1.5 equiv Tf_2O, CH_2Cl_2, –78 °C → 22 °C. [b]Isolated yield. [c]Run by pre-cooling activated sulfamate solution to –78 °C before transfer to Et_3N. [d]Run by pre-cooling Et_3N to 0 °C instead of –78 °C.

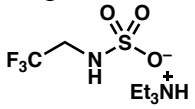
Experimental Procedures.

General Procedure A: Preparation of triethylammonium sulfamate salts.



A round bottom flask equipped with magnetic stir bar was charged with sulfur trioxide pyridine complex (SO_3•pyr, 1.0 equiv). Acetonitrile (0.33 M) was then added in a single portion without taking any precautions to exclude air or moisture. The suspension was stirred at 22 °C until all of the SO_3•pyr had dissolved. Upon complete dissolution, the reaction flask was cooled at 0 °C in an ice water bath and capped with a rubber septum containing a nitrogen inlet. Amine (R^1–NH_2, 1.0 equiv) was then added dropwise via syringe. Following complete addition of amine, Et_3N (1.5 equiv) was added dropwise. The reaction was removed from the ice bath and stirred for 0.5 h. Upon completion, the solvent was removed under reduced pressure to give a triethylammonium sulfamate salt, which was used without further purification.

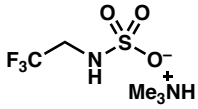
Triethylammonium (2,2,2-trifluoroethyl)sulfamate (2a)



Prepared from sulfur trioxide pyridine complex (3.18 g, 20.0 mmol) and 2,2,2-trifluoroethylamine (1.6 mL, 20.0 mmol) following general procedure A. The product was obtained as a viscous yellow oil (5.6 g, >98% yield) following removal of solvent under reduced pressure.

^{1}H NMR (400 MHz, CD_3CN) δ 9.29 (br s, 1H), 4.26 (br s, 1H), 3.52 (q, J = 9.8 Hz, 2H), 3.10 (q, J = 7.3 Hz, 6H), 1.25 (t, J = 7.3 Hz, 9H).
^{13}C NMR (126 MHz, CD_3CN) δ 126.4 (q, J = 276.8 Hz), 47.1, 45.9 (q, J = 33 Hz), 8.9.
^{19}F NMR (376 MHz, CD_3CN) δ –72.37 (t, J = 9.2 Hz).
IR (neat) ν 3224 (br), 2991 (w), 2950 (w), 2708 (w), 2511 (w), 1637 (w), 1477 (w), 1451 (w), 1394 (w), 1299 (m), 1276 (m), 1233 (m), 1138 (s), 1106 (m), 1032 (s), 963 (m), 898 (w), 838 (m), 792 (m), 734 (m), 661 (w), 578 (s), 536 (m) cm^{-1}.
HRMS (ESI) m/z: $[M – HN^+Et_3]^–$ Calcd for $C_2H_3F_3NO_3S^–$ 177.9791; Found 177.9792.

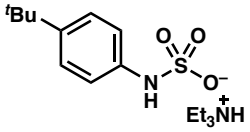
Trimethylammonium (2,2,2-trifluoroethyl)sulfamate (2b)



A round bottom flask equipped with magnetic stir bar was charged with sulfur trioxide trimethylamine complex (SO_3•Me_3, 2.78 g, 20.0 mmol, 1.0 equiv). Acetonitrile (0.33 M) was then added in a single portion without taking any precautions to exclude air or moisture. The suspension was stirred at 22 °C until all of the SO_3•Me_3 had dissolved. Upon complete dissolution, the reaction flask was cooled at 0 °C in an ice water bath and capped with a rubber septum containing a nitrogen inlet. 2,2,2-trifluoroethylamine (1.6 mL, 20.0 mmol, 1.0 equiv) was then added dropwise via syringe. Following complete addition of amine, the reaction was removed from the ice bath and stirred for 0.5 h. The product was obtained as a white solid (4.11 g, 86% yield) following recrystallization by liquid–liquid diffusion with diethyl ether layered on top of the crude reaction mixture.

^{1}H NMR (400 MHz, CD_3CN) δ 3.54 (q, J = 9.8 Hz, 2H), 2.80 (s, 9H).
^{13}C NMR (126 MHz, d_6-DMSO) δ 125.6 (q, J = 278.0 Hz), 44.8 (q, J = 32.8 Hz), 44.2.
^{19}F NMR (376 MHz, CD_3CN) δ –67.59 (dt, J = 11.3, 3.8 Hz)
IR (neat) ν 3261 (br), 3048 (w), 2945 (w), 2759 (br), 1650 (w), 1486 (w), 1454 (w), 1428 (w), 1395 (w), 1295 (w), 1246 (w), 1143 (m), 1107 (m), 1063 (w), 1028 (m), 980 (m), 966 (m), 834 (w), 731 (w), 660 (w), 579 (m), 535 (m) cm^{-1}.
HRMS (ESI) m/z: $[M – HN^+Me_3]^–$ Calcd for $C_2H_3F_3NO_3S^–$ 177.9791; Found 177.9791

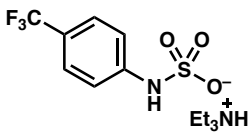
Trimethylammonium (4-*tert*-butyl)phenyl)sulfamate (2c)



Prepared from sulfur trioxide pyridine complex (3.18 g, 20.0 mmol) and 4-(*tert*-butyl)aniline (2.98 g, 20.0 mmol) following general procedure A. The product was obtained as a white solid (6.19 g, 94% yield) following removal of solvent under reduced pressure.

^{1}H NMR (400 MHz, CD_3CN) δ 8.64 (br s, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 3.05 (q, J = 6.8 Hz, 6H), 1.27 (s, 9H), 1.21 (t, J = 7.3 Hz, 9H).
^{13}C NMR (126 MHz, CD_3CN) δ 144.5, 141.0, 126.3, 118.7, 47.2, 34.6, 31.7, 9.0.
IR (neat) ν 3245 (m), 2964 (w), 2867 (w), 2703 (w), 1613 (w), 1513 (m), 1463 (m), 1401 (m), 1364 (w), 1288 (w), 1269 (w), 1252 (m), 1232 (s), 1187 (m), 1165 (s), 1028 (s) 896 (m), 821 (m), 790 (m), 732 (w), 646 (s), 618 (s), 552 (s) cm^{-1}.
HRMS (ESI) m/z: $[M – HN^+Et_3]^–$ Calcd for $C_{10}H_{14}NO_3S^–$ 228.0700; Found 228.0700

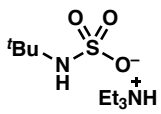
Triethylammonium (4-(trifluoromethyl)phenyl)sulfamate (2d)



Prepared from sulfur trioxide pyridine complex (3.18 g, 20.0 mmol) and 4-(trifluoromethyl)aniline (3.22 g, 20.0 mmol) following general procedure A. The product was obtained as a white solid (6.45 g, 94% yield) following removal of solvent under reduced pressure.

^{1}H NMR (400 MHz, CD_3CN) δ 8.79 (br s, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 3.11–3.04 (m, 6H), 2.28 (br s, 1H), 1.25 (t, J = 7.3 Hz, 9H).
^{13}C NMR (126 MHz, CD_3CN) δ 147.0, 126.7, 123.7 (q, J = 270.2 Hz), 121.5 (q, J = 32.3 Hz), 117.0, 47.3, 8.9
^{19}F NMR (376 MHz, CD_3CN) δ – 61.79
IR (neat) ν 3233 (br), 3005 (w), 2706 (w), 1611 (w), 1519 (m), 1475 (m), 1398 (w), 1310 (m), 1238 (s), 1189 (m), 1156 (m), 1098 (s), 1067 (m) 1032 (s), 951 (w), 894 (m), 857 (m), 733 (w), 666 (m), 634 (m), 612 (s), 562 (m), 530 (m) cm^{-1}.
HRMS (ESI) m/z: $[M – HN^+Et_3]^–$ Calcd for $C_7H_5F_3NO_3S^–$ 239.9948; Found 239.9955

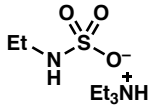
Triethylammonium *tert*-butylsulfamate (2e)



Prepared from sulfur trioxide pyridine complex (7.96 g, 50.0 mmol) and *tert*-butylamine (5.25 mL, 50.0 mmol) following general procedure A. The product was obtained as an off-white solid (12.64 g, >98% yield) following removal of solvent under reduced pressure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (br s, 1H), 7.52 (br s, 1H), 3.16 (q, J = 7.3 Hz, 6H), 1.39–1.33 (m, 18H).
^{13}C NMR (126 MHz, CD_3CN) δ 53.0, 47.1, 30.0, 9.0.
IR (neat) ν 3299 (br), 2956 (w), 2928 (w), 2871 (w), 2636 (w), 1545 (w), 1467 (w), 1360 (m), 1296 (w), 1277 (m), 1153 (s), 1032 (m), 947 (s), 895 (m), 853 (m), 836 (m), 760 (w), 665 (m), 631 (w), 617 (m), 600 (m), 561 (m) cm^{-1}.
HRMS (ESI) m/z: $[M - NEt_3]^-$ Calcd for $C_4H_{10}NO_3S^-$ 152.0387; Found 152.0387.

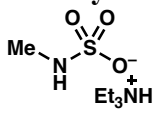
Triethylammonium ethylsulfamate (2f)



Prepared from sulfur trioxide pyridine complex (3.18 g, 20.0 mmol) and ethylamine solution (70% aq, 1.7 mL, 20.0 mmol) following general procedure A. The product was obtained as a brown oil (4.46 g, >98% yield) following removal of solvent under reduced pressure.

^{1}H NMR (400 MHz, CD_3CN) δ 9.34 (br s, 1H), 4.28 (br s, 1H), 3.09 (q, J = 7.3 Hz, 6H), 2.95 (9, J = 7.3 Hz, 2H), 1.26 (t, J = 7.3 Hz, 9H), 1.10 (t, J = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, CD_3CN) δ 46.9, 39.5, 14.9, 8.9.
IR (neat) ν 3404 (br), 2988 (w), 2712 (w), 1644 (w), 1476 (w), 1399 (w), 1280 (w), 1163 (m), 1059 (m), 1033 (s), 930 (w), 838 (w), 540 (m) cm^{-1}.
HRMS (ESI) m/z: $[M - HN^+Et_3]^-$ Calcd for $C_2H_6NO_3S^-$ 124.0074; Found 124.0073

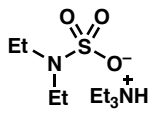
Triethylammonium methylsulfamate (2g)



Prepared from sulfur trioxide pyridine complex (3.18 g, 20.0 mmol) and methylamine (2.0 M solution in THF, 10 mL, 20.0 mmol) following general procedure A. The product was obtained as a viscous yellow oil (4.24 g, >98% yield) following removal of solvent under reduced pressure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (br s, 1H), 4.12 (br s, 1H), 3.16 (q, J = 7.0 Hz, 6H), 2.74 (s, 3H), 1.34 (t, J = 7.4 Hz, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 47.0, 30.6, 8.9.
IR (neat) ν 3270 (br), 2985 (w), 2703 (w), 2507 (w), 1644 (w), 1474 (w), 1397 (w), 1219 (m), 1159 (s), 1057 (m), 1030 (s), 838 (m), 808 (m), 705 (m), 673 (m), 594 (s), 541 (m) cm^{-1}.
HRMS (ESI) m/z: $[M - HN^+Et_3]^-$ Calcd for $CH_5NO_3S^-$ 109.9917; Found 109.9920.

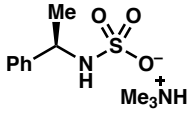
Triethylammonium diethylsulfamate (2h)



Prepared from sulfur trioxide pyridine complex (7.95 g, 50.0 mmol) and diethylamine (5.17 mL, 50 mmol) following general procedure A. The product was obtained as a brown-yellow oil (12.62 g, >98% yield) following removal of solvent under reduced pressure.

^{1}H NMR (400 MHz, CD_3CN) δ 9.52 (br s, 1H), 3.09 (q, J = 7.3 Hz, 4H), 3.04 (q, J = 7.2 Hz, 6H), 1.26 (t, J = 7.2 Hz, 9H), 1.08 (t, J = 7.3 Hz, 6H).
^{13}C NMR (126 MHz, CD_3CN) δ 45.2, 41.1, 12.1, 7.1
IR (neat) ν 3281 (br), 2954 (w), 2930 (w), 2870 (w), 2847 (w), 1463 (m), 1431 (w), 1409 (w), 1383 (w), 1347 (m), 1297 (w), 1276 (m), 1155 (s), 1116 (m), 1061 (w), 1034 (w), 964 (m), 938 (s), 901 (m), 879 (m), 855 (m), 834 (m), 766 (m), 736 (w), 665 (m), 559 (m), 530 (m) cm^{-1}.
HRMS (ESI) m/z: $[M - HN^+Et_3]^-$ Calcd for $C_4H_{10}NO_3S^-$ 152.0387; Found 152.0385.

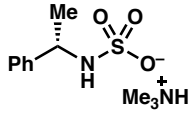
Triethylammonium (*R*)-(1-phenylethyl)sulfamate (2i)



A round bottom flask equipped with magnetic stir bar was charged with sulfur trioxide trimethylamine complex (SO_3•Me_3, 2.78 g, 20.0 mmol, 1.0 equiv). Acetonitrile (0.33 M) was then added in a single portion without taking any precautions to exclude air or moisture. The suspension was stirred at 22 °C until all of the SO_3•Me_3 had dissolved. Upon complete dissolution,, the reaction flask was cooled at 0 °C in an ice water bath and capped with a rubber septum containing a nitrogen inlet. (*R*)-α-Methylbenzylamine (2.59 mL, 20.0 mmol, 1.0 equiv) was then added dropwise via syringe. Following complete addition of amine, the reaction was removed from the ice bath and stirred for 0.5 h. The product was obtained as a low melting white solid (3.62 g, 60% yield) following recrystallization by liquid–liquid diffusion with diethyl ether layered on top of the crude reaction mixture.

^{1}H NMR (400 MHz, CD_3CN) δ 7.42–7.34 (m, 2H), 7.33–7.26 (m, 2H), 7.24–7.16 (m, 1H), 4.40 (q, J = 6.8 Hz, 1H), 2.70 (s, 9H), 2.34 (br s, 1H), 1.41 (d, J = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, CD_3CN) δ 147.0, 128.9, 127.2, 127.1, 54.2, 45.2, 24.6.
IR (neat) ν 3278 (br), 3035 (w), 2966 (w), 2759 (w), 1603 (w), 1483 (m), 1460 (m), 1447 (m), 1427 (m), 1365 (w), 1275 (w), 1203 (s), 1166 (s), 1128 (m), 1084 (m), 1064 (m), 1023 (s), 981 (s), 938 (m), 858 (m), 776 (m), 756 (m), 699 (s), 625 (m), 573 (m), 558 (s), 237 (s) cm^{-1}.
HRMS (ESI) m/z: $[M - HN^+Me_3]^-$ Calcd for $C_8H_{10}NO_3S^-$ 200.0387; Found 200.0387

Triethylammonium (*S*)-(1-phenylethyl)sulfamate (S2a)

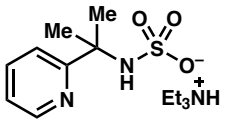


A round bottom flask equipped with magnetic stir bar was charged with sulfur trioxide trimethylamine complex (SO_3•Me_3, 2.78 g, 20.0 mmol, 1.0 equiv). Acetonitrile (0.33 M) was then added in a single portion without taking any precautions to exclude air or moisture. The suspension was stirred at 22 °C until all of the SO_3•Me_3 had dissolved. Upon complete dissolution, the reaction flask was cooled at 0 °C in an ice water bath and capped with a rubber septum containing a nitrogen inlet. (*S*)-α-Methylbenzyl amine (2.59 mL, 20.0 mmol, 1.0 equiv) was then added dropwise via syringe. Following complete addition of amine, the reaction was removed from the ice bath and stirred for 0.5 h. The product was obtained as a low melting white solid (4.01 g, 66% yield) following recrystallization by liquid–liquid diffusion with diethyl ether layered on top of the crude reaction mixture.

^{1}H NMR (400 MHz, CD_3CN) δ 7.37 (d, J = 7.6 Hz, 2H), 7.32–7.28 (m, 2H), 7.22–7.18 (m, 1H), 4.40 (q, J = 6.8 Hz, 1H), 2.69 (s, 9H), 1.40 (d, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 147.2, 129.0, 127.3, 127.3, 54.4, 45.4, 24.7.
IR (neat) ν 3425 (br), 3033 (w), 2748 (w), 1640 (w), 1479 (m), 1460 (m), 1372 (w), 1277 (m), 1167 (m), 1026 (s), 983 (m), 970 (m), 940 (m), 854 (w), 763 (m), 701 (m), 634 (m), 557 (s) cm^{-1}.
HRMS (ESI) m/z: $[M - HN^+Me_3]^-$ Calcd for $C_8H_{10}NO_3S^-$ 200.0387; Found 200.0386

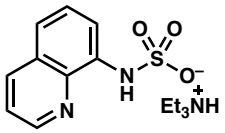
Triethylammonium 2-(pyridin-2-yl)propan-2-yl)sulfamate (2j)



Prepared from sulfur trioxide pyridine complex (1.30 g, 8.15 mmol) and 2-(pyridin-2-yl)propan-2-amine (1.11 g, 8.15 mmol) following general procedure A. The product was obtained as a brown oil (2.51 g, 97% yield) in >90% purity following removal of solvent under reduced pressure. The product was used without any purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (br s, 1H), 8.66 (dd, *J* = 5.3, 1.1 Hz, 1H), 7.83 (td, *J* = 7.8, 1.8 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 7.5, 5.4 Hz) 5.54 (br s, 1H), 3.13 (q, *J* = 7.3 Hz, 6H), 1.74 (s, 6H), 1.31 (t, *J* = 7.3 Hz, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 145.9, 139.3, 122.2, 120.9, 57.1, 46.1, 28.4, 8.5.
IR (neat) ν 3374 (br), 2973 (w), 2359 (w), 2125 (w), 1626 (w), 1592 (w), 1475 (w), 1396 (w), 1157 (m), 1085 (m), 1033 (s), 879 (w), 838 (w), 788 (m), 752 (m), 572 (m) cm^{-1}.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{27}N_3O_3S$ 318.1846; Found 318.1846.

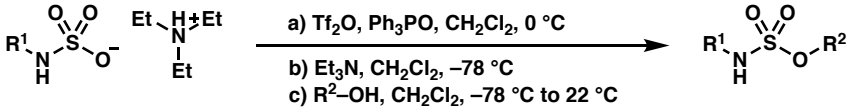
Triethylammonium quinolin-8-ylsulfamate (2k)



Prepared from sulfur trioxide pyridine complex (3.18 g, 20.0 mmol) and 8-aminoquinoline (2.88 g, 20.0 mmol) following general procedure A. The product was obtained as a red-brown solid (6.2 g, 95% yield) following removal of solvent under reduced pressure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (br s, 1H), 8.73 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.63 (br s, 1H), 8.08 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.46 (t, *J* = 8.0, Hz, 1H), 7.36 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.30 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.13 (q, *J* = 7.2 Hz, 6H), 1.33 (t, *J* = 7.3 Hz, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 138.3, 138.1, 136.0, 128.2, 127.4, 121.2, 118.4, 112.9, 46.3, 8.6.
IR (neat) ν 3360 (br), 2989 (w) 2706 (w), 1613 (w), 1578 (m), 1503 (s), 1471 (m), 1412 (m), 1377 (m), 1343 (m), 1327 (m), 1284 (w) 1231 (m), 1190 (s), 1167 (s), 1088 (m), 1029 (s), 903 (m), 823 (s), 793 (s), 644 (m), 594 (s), 548 (s) cm^{-1}.
HRMS (ESI) m/z: $[M - HN^+Et_3]^-$ Calcd for $C_9H_7N_2O_3S^-$ 223.0183; Found 223.0186.

General Procedure B: Preparation of sulfamate esters.

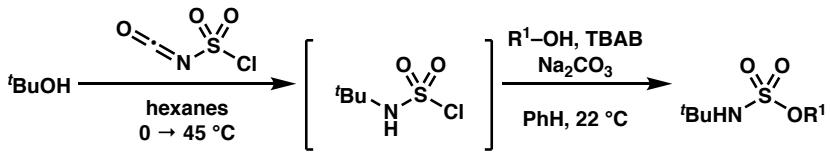


Reactions performed on 2.0 mmol scale unless otherwise noted.

A flame-dried round bottom flask equipped with magnetic stir bar was charged with triphenylphosphine oxide (3.3 mmol, 1.65 equiv) and fitted with a rubber septum. The flask was evacuated and backfilled with N_2. Anhydrous CH_2Cl_2 (10 mL, 0.2 M) was added and the flask was cooled at 0 °C in an ice water bath. Trifluoromethanesulfonic anhydride (3.0 mmol, 1.5 equiv) that had been freshly removed from the glovebox was then added to the cooled solution dropwise via syringe. The reaction was allowed to stir at 0 °C in an ice water bath for 15 minutes. A solution of sulfamate salt (3.0 mmol, 1.5 equiv) in CH_2Cl_2 (2.0 mL, 1.0 M) was added to the activated Ph_3PO via cannula transfer. The flask was rinsed with an additional 0.5 mL CH_2Cl_2 to achieve quantitative transfer. The resulting colorless to pale yellow solution was stirred for 15 minutes at 0 °C. During this time, a clean, flame-dried round bottom flask equipped with stir bar was fitted with a rubber septum and subsequently evacuated and backfilled with N_2. This process was repeated two more times. The flask was then charged with Et_3N (6.0 mmol, 3.0 equiv) and CH_2Cl_2 (8 mL, 0.25 M) and the mixture was cooled at –78 °C in an ^{i}PrOH/dry ice bath. The sulfamate salt solution was transferred dropwise to the Et_3N solution via cannula (during which time a yellow to intense red color often developed), rinsing the flask with an additional 2 mL of CH_2Cl_2 to achieve quantitative transfer. The resultant solution was stirred at –78 °C for 15 minutes. The alcohol (R^2–OH, 2.0 mmol, 1.0 equiv) was then added as a solution in CH_2Cl_2 (2.0 mL, 1.0 M) to the triethylamine solution via canula. The alcohol-containing flask was rinsed with an additional 0.5 mL CH_2Cl_2 to achieve quantitative transfer. Without removing the cooling bath, the reaction was then stirred for 18 h, during which time no additional dry ice was added and the mixture warmed to room temperature.

After 18 h, the reaction was diluted with 1 M HCl (20 mL) and H_2O (10 mL). The biphasic mixture was transferred to a separatory funnel, rinsing the flask with CH_2Cl_2 to achieve quanitative transfer. The organic phase was separated and the aqueous was extracted twice more with CH_2Cl_2 (2 x 25 mL). The combined organic phases were dried with $MgSO_4$, filtered, and concentrated. The crude reaction mixtures were then purified by silica gel flash chromatography by dry loading the samples and eluting with a hexanes:EtOAc solvent system as noted below.

General Procedure C. Alternative preparation of *tert*-butylsulfamate esters.

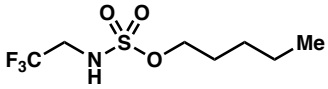


To a flame-dried round bottom flask equipped with magnetic stir bar and fitted with a rubber septum and nitrogen inlet was added hexanes (45 mL, 0.67 M). The reaction flask was then cooled at 0 °C in an ice water bath. *Tert*-butanol (4.3 mL, 45.0 mmol, 1.5 equiv) and chlorosulfonyl isocyanate (3.9 mL, 45.0 mmol, 1.5 equiv) were then sequentially added dropwise via syringe. Upon complete addition, the ice water bath was removed and replaced with an oil bath. The oil bath was heated to 45 °C and the reaction was stirred for 3 h. After 3 h, the reaction was removed from heat and allowed to cool to room

temperature. The suspension was then concentrated under reduced pressure to remove all volatile materials. The crude material was then taken up in anhydrous benzene (50 mL, 0.60 M) and *tetra*-butylammonium bromide (967 mg, 3.0 mmol, 0.1 equiv), alcohol (30 mmol, 1.0 equiv), and sodium carbonate (9.54 g, 90.0 mmol, 3.0 equiv) were added sequentially. Following addition, the reaction was left to stir at 22 °C for 18 h.

After 18 h, the reaction was quenchd by dropwise addition of 1 M HCl until the aqueous phase reached a pH = 1.0. The biphasic solution was then transferred to a separatory funnel rinsing the flask with EtOAc (50 mL) to achieve quantitative transfer. The organic phase was separated and the aqueous was extracted twice more with EtOAc (2 x 50 mL). The combined organic layers were washed once with brine (50 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixtures were then purified by silica gel flash chromatography by dry loading the samples and eluting with a hexanes:EtOAc solvent system.

Pentyl (2,2,2-trifluoroethyl)sulfamate (4a).

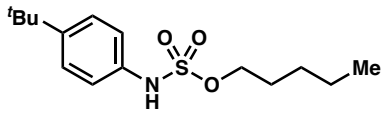


Prepared from salt **2a** or **2b** and *n*-amyl alcohol following general procedure B. The product was obtained as a white solid after silica gel column chromatography using hexanes:EtOAc (8:1).

The product was obtained in 95% yield (473 mg) from salt **2a**.
The product was obtained in 95% yield (2.363 g) from salt **2a** on 10 mmol scale.
The product was obtained in 94% yield (469 mg) from salt **2b**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (br s, 1H), 4.18 (t, *J* = 6.7 Hz, 2 H), 3.79–3.70 (m, 2H), 1.78–1.71 (m, 1H), 1.38–1.36 (m, 4H), 0.92 (t, *J* = 6.9 Hz).
^{13}C NMR (126 MHz, $CDCl_3$) δ 123.4 (q, *J* = 278.9 Hz), 72.0, 44.9 (q, *J* = 35.9 Hz), 28.3, 27.4, 22.1, 13.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ –72.73 (t, *J* = 8.7 Hz).
IR (neat) ν 3291 (br), 2960 (w), 2877 (w), 1463 (w), 1432 (w), 1406 (w), 1350 (m), 1276 (m), 1154 (s), 1115 (s), 1053 (w), 1014 (w), 954 (s), 921 (m), 899 (m), 862 (m), 834 (m), 813 (m), 731 (m), 664 (m), 559 (s) cm^{-1}.
TLC R_f = 0.17 in 8:1 hexane:EtOAc
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}F_3NO_3S$•Na 272.0539; Found 272.0538.

Pentyl (4-(*tert*-butyl)phenyl)sulfamate (4c)

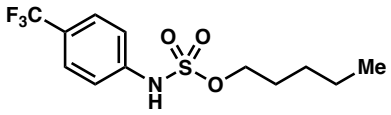


Prepared from salt **2c** and *n*-amyl alcohol following general procedure B. The product was obtained as a yellow oil (442 mg, 74% yield) after silica gel column chromatography using hexanes:EtOAc (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.42 (s, 1H), 4.18 (t, *J* = 6.5 Hz, 2H), 1.73–1.66 (m, 2H), 1.30 (s, 13H), 0.85 (t, *J* = 8.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 133.6, 126.2, 119.6, 71.9, 34.3, 31.2, 28.3, 27.4, 22.0, 13.8.

IR (neat) ν 3282 (br) 2957 (m) 2868 (w), 1613 (w), 1515 (m), 1456 (m), 1404 (m), 1365 (m), 1309 (w), 1285 (w), 1233 (w), 1169 (s), 1017 (m), 918 (s), 853 (m), 830 (m), 724 (m), 697 (w), 640 (m), 602 (m), 537 (m) cm^{-1}.
TLC R_f = 0.25 in 9:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{25}NO_3S$ 300.1628; Found 300.1629.

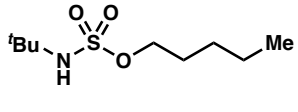
Pentyl (4-(trifluoromethyl)phenyl)sulfamate (4d)



Prepared from salt **2d** and *n*-amyl alcohol following general procedure B. The product was obtained as a yellow oil (561 mg, 90% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 1H), 6.81 (br s, 1H), 4.22 (t, *J* = 6.5 Hz, 2H), 1.74–1.67 (m, 2H), 1.33–1.25 (m, 4H), 0.86 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, CD_3CN) δ 141.9, 127.6, 126.5 (q, *J* = 32.7 Hz), 125.4 (q, *J* = 271.2 Hz), 119.2, 73.1, 29.0, 28.3, 22.7, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ – 62.29
IR (neat) ν 3280 (br), 2960 (w), 2874 (w), 1618 (m), 1521 (m), 1467 (m), 1409 (m), 1358 (m), 1323 (s), 1297 (m), 1236 (w), 1164 (s), 1114 (s), 1070 (s), 1015 (m), 920 (s), 836 (s), 762 (m), 729 (m), 662 (m), 633 (w), 590 (s) cm^{-1}.
TLC R_f = 0.24 in 8:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}F_3NO_3S$•Na 334.0695; Found 334.0693

Pentyl *tert*-butylsulfamate (4e)



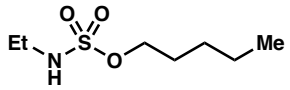
Prepared from salt **2e** and *n*-amyl alcohol following general procedure B. The product was obtained as a colorless oil (264 mg, 59% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

The product was prepared from *n*-amyl alcohol (3.3 mL, 30.0 mmol) in 36% yield (2.4 g) following general procedure C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (br s, 1H), 4.10 (t, *J* = 6.7, 2H), 1.76–1.69 (m, 2H), 1.36–1.35 (m, 4H), 1.35 (s, 1H), 0.91 (t, *J* = 6.9, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 70.1, 54.3, 29.4, 28.3, 27.5, 22.0, 13.7.
IR (neat) ν 3297 (br), 2959 (w), 2934 (w), 2873 (w), 1468 (w), 1430 (w), 1394 (m), 1341 (m), 1231 (w), 1158 (s), 1042 (w), 1001 (m), 963 (s), 912 (m), 873 (m), 810 (m), 767 (w), 724 (m), 615 (m), 584 (m) cm^{-1}.

TLC R_f = 0.20 in 8:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{21}NO_3S$•Na 246.1134; Found 246.1139.

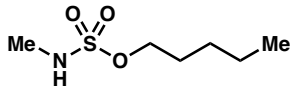
Pentyl ethylsulfamate (4f)



Prepared from salt **2f** and *n*-amyl alcohol following general procedure B. The product was obtained as a colorless oil (183 mg, 47% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (br s, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 3.24–3.17 (m, 2H), 1.77–1.70 (m, 2H), 1.40–1.33 (m, 2H), 1.23 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 70.7, 38.7, 28.5, 27.6, 22.1, 14.9, 13.8.
IR (neat) ν 3300 (br), 2958 (w), 2873 (w), 1429 (w), 1340 (m), 1169 (S), 1107 (w), 1066 (w), 1042 (m), 949 (m), 912 (m), 870 (m), 810 (m), 758 (m), 723 (m), 578 (m) cm^{-1}.
TLC R_f = 0.19 in 8:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_7H_{17}NO_3S$•Na 218.1580; Found 289.1582

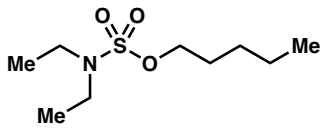
Pentyl methylsulfamate (4g)



Prepared from salt **2g** and *n*-amyl alcohol following general procedure B. The product was obtained as a colorless oil (173 mg, 53% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (br s, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 2.81 (d, *J* = 2.8 Hz, 3H), 1.77–1.70 (m, 2H), 1.41–1.33 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 70.9, 29.7, 28.5, 27.6, 22.1, 13.9.
IR (neat) ν 3311 (br), 2957 (w), 2932 (w), 2872 (w), 1467 (w), 1413 (w), 1340 (m), 1170 (s), 1138 (m), 1075 (m), 1041 (w), 961 (m), 913 (m), 858 (m), 806 (m), 757 (m), 724 (m), 574 (m) cm^{-1}.
TLC R_f = 0.46 in 2:1 hexanes:EtOAc.
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_6H_{15}NO_3S$•Na 204.0665; Found 204.0664.

Pentyl diethylsulfamate (4h)



Prepared from salt **2h** and *n*-amyl alcohol following general procedure B. The product was obtained as a pale yellow oil (75 mg, 17% yield) after silica gel column chromatography using hexanes:EtOAc (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (t, *J* = 6.6, 2H), 3.31 (q, *J* = 7.1, 2H), 1.74–1.66 (m, 2H), 1.40–1.30 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 6H), 0.90 (t, *J* = 6.9, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 70.0, 42.6, 28.7, 27.7, 22.1, 13.9, 13.0.
IR (neat) ν 2959 (w), 2935 (w), 2874 (w), 1467 (w), 1357 (m), 1299 (w), 1204 (m), 1162 (s), 1070 (w), 1021 (m), 966 (m), 938 (m), 902 (m), 787 (m), 760 (m), 717 (m), 689 (m), 580 (m), 537 (m) cm^{-1}.

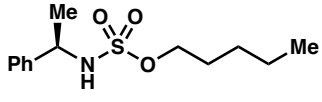
TLC R_f = 0.58 in 4:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{21}NO_3S$•Na 246.1134; Found 246.1136.

Alternative procedure using sodium pentoxide in place of triethylamine and n-amyl alcohol.
A flame-dried round bottom flask equipped with magnetic stir bar was charged with triphenylphosphine oxide (3.3 mmol, 1.65 equiv) and fitted with a rubber septum. The flask was evacuated and backfilled with N_2. Anhydrous CH_2Cl_2 (10 mL, 0.2 M) was added and the flask was cooled at 0 °C in an ice water bath. Trifluoromethanesulfonic anhydride (3.0 mmol, 1.5 equiv) that had been freshly removed from the glovebox was then added to the cooled solution dropwise via syringe. The reaction was allowed to stir at 0 °C in an ice water bath for 15 minutes. A solution of sulfamate salt (3.0 mmol, 1.5 equiv) in CH_2Cl_2 (2.0 mL, 1.0 M) was added to the activated Ph_3PO via cannula transfer. The flask was rinsed with an additional 0.5 mL CH_2Cl_2 to achieve quantitative transfer. The resulting colorless to pale yellow solution was stirred for 15 minutes at 0 °C. During this time, a clean, flame-dried round bottom flask equipped with stir bar was fitted with a rubber septum and subsequently evacuated and backfilled with N_2. This process was repeated two more times. Dichloromethane (10 mL, 0.2 M) and *n*-amyl alcohol (0.22 mL, 2.0 mmol, 1.0 equiv) were then added by syringe and the mixture was cooled at 0 °C in an ice bath. The rubber septum was then quickly removed in order to add sodium hydride (60% dispersion in mineral oil, 80 mg, 2.0 mmol, 1.0 equiv) as a solid before the rubber septum was replaced. This mixture was allowed to stir for 15 minutes at 0 °C. The sodium pentoxide solution was then transferred dropwise to the sulfamate solution via cannula (during which time the solution turned yellow in color), rinsing the flask with an additional 2 mL of CH_2Cl_2 to achieve quantitative transfer. The resultant solution was stirred without removing the cooling bath for 18 h, during which time no additional ice was added and the mixture warmed to room temperature.

After 18 h, the reaction was diluted with 1 M HCl (20 mL) and H_2O (10 mL). The biphasic mixture was transferred to a separatory funnel, rinsing the flask with CH_2Cl_2 to achieve quanitative transfer. The organic phase was separated and the aqueous was extracted twice more with CH_2Cl_2 (2 x 25 mL). The combined organic phases were dried with $MgSO_4$, filtered, and concentrated. The crude reaction mixtures were then purified by silica gel flash chromatography by dry loading the samples and eluting with hexanes:EtOAc (9:1). The product was obtained as a pale yellow oil (302 mg, 68% yield) after silica gel column chromatography.

The characterization data matched that reported above.

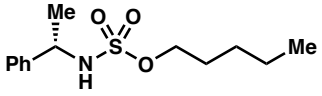
Pentyl (*R*)-(1-phenylethyl)sulfamate (4i)



Prepared from salt **2i** and *n*-amyl alcohol following general procedure B. The product was obtained as a yellow oil (412 mg, 76% yield) after silica gel column chromatography using hexanes:EtOAc (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.28 (m, 5H), 4.62 (q, *J* = 5.8 Hz, 1H), 3.99 (dt, *J* = 9.0, 6.6 Hz, 1H), 3.86 (dt, *J* = 9.0, 6.5 Hz, 1H), 1.57 (d, *J* = 6.5 Hz, 3H), 1.54–1.48 (m, 3H), 1.34–1.05 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 128.6, 127.7, 126.1, 70.5, 54.2, 28.1, 27.3, 23.1, 22.0, 13.7.
IR (neat) ν 3289 (br), 3031 (m), 2957 (m), 2931 (m), 2872 (m), 1604 (m), 1495 (m), 1455 (w), 1431 (w), 1340 (m), 1208 (w), 1170 (s), 1120 (m), 1085 (m), 1021 (m), 956 (s), 912 (m), 879 (m), 810 (m), 760 (m), 742 (m), 698 (s), 619 (m), 551 (s) cm^{-1}.
TLC R_f = 0.34 in 8:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{13}H_{21}NO_3S•NH_4$ 289.1580; Found 289.1583

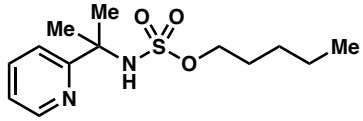
Pentyl (*S*)-(1-phenylethyl)sulfamate (S4a)



Prepared from salt **S2a** and *n*-amyl alcohol following general procedure B. The product was obtained as a yellow oil (405 mg, 75% yield) after silica gel column chromatography using hexanes:EtOAc (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.28 (m, 5H), 4.62 (q, *J* = 5.8 Hz, 1H), 3.99 (dt, *J* = 9.1, 6.6 Hz, 1H), 3.86 (dt, *J* = 9.0, 6.5 Hz, 1H), 1.57 (d, *J* = 6.5 Hz, 3H), 1.54–1.48 (m, 2H), 1.34–1.05 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 128.8, 127.7, 126.1, 70.5, 54.2, 28.1, 27.3, 23.1, 22.0, 13.7.
IR (neat) ν 3290 (br), 3031 (w), 2957 (w), 2931 (w), 2872 (w), 1604 (w), 1495 (w), 1455 (w), 1431 (w), 1340 (m), 1208 (w), 1170 (s), 1120 (m), 1085 (m), 1021 (w), 955 (s), 912 (m), 879 (m), 810 (m), 760 (m), 724 (w), 698 (s), 619 (w), 551 (s) cm^{-1}.
TLC R_f = 0.33 in 8:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{21}NO_3S•Na$ 294.1134; Found 294.1141

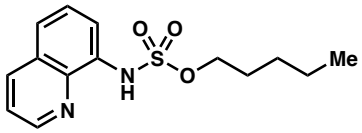
Pentyl (2-pyridin-2-yl)propan-2-yl)sulfamate (4j)



Prepared from salt **2j** and *n*-amyl alcohol following general procedure B. The product was obtained as a yellow oil (172 mg, 28% yield) after silica gel column chromatography using hexanes:EtOAc (8:1 to 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (dt, *J* = 4.7, 1.2 Hz, 1H), 7.73 (td, *J* = 7.8, 1.8 Hz, 1H), 7.39 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.23 (ddd, *J* = 7.6, 4.9, 0.8 Hz, 1H), 7.12 (br s, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 1.73 (s, 6H), 1.68–1.62 (m, 2H), 1.31–1.29 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 147.8, 137.3, 122.3, 118.8, 70.1, 58.8, 28.4, 28.3, 27.1, 22.1, 13.8.
IR (neat) ν 3249 (br), 2957 (w), 2932 (w), 2872 (w), 1592 (w), 1573 (w), 1468 (w), 1433 (m), 1402 (w), 1380 (m), 1340 (m), 1236 (w), 1202 (w), 1171 (m), 1122 (w), 1096 (w), 1019 (w), 995 (m), 953 (m), 914 (m), 830 (m), 788 (m), 750 (m), 726 (w), 655 (w), 623 (w), 592 (w), 565 (m) cm^{-1}.
TLC R_f =0.25 in 4:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{22}N_2O_3S$ 287.1424; Found 287.1434.

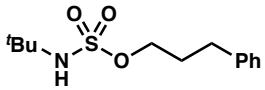
Pentyl quinolin-8-ylsulfamate (4k)



Prepared from salt **2k** and *n*-amyl alcohol following general procedure B. The product was obtained as a yellow oil (178 mg, 30% yield) after silica gel column chromatography using hexanes:EtOAc (3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (br s, 1H), 8.82 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.76 (dd, *J* = 6.2, 2.7 Hz, 1H), 7.56–7.53 (m, 2H), 7.49 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.19 (t, *J* = 6.5 Hz, 2H), 1.65–1.58 (m, 2H), 1.19–1.14 (m, 4H), 0.74 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 137.9, 136.3, 133.4, 128.1, 126.9, 122.1, 121.9, 114.4, 71.9, 28.2, 27.4, 21.9, 13.7.
IR (neat) ν 3278 (br), 2956 (w), 2930 (w), 2860 (w), 1622 (w), 1579 (w), 1504 (s), 1472 (m), 1414 (m), 1376 (s), 1340 (m), 1315 (m), 1236 (w), 1178 (s), 1087 (m), 1059 (w), 960 (m), 923 (s), 859 (s), 289 (s), 755 (s), 724 (m), 633 (m), 575 (s) cm^{-1}.
TLC R_f =0.13 in 4:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}N_2O_3S$ 295.1111; Found 295.1118.

3-Phenylpropyl *tert*-butylsulfamate (4l)

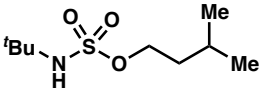


Prepared from salt **2e** and 3-phenyl-1-propanol following general procedure B. The product was obtained as a white solid (336.1 mg, 62% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

The product was prepared from 3-phenyl-1-propanol (4.1 mL, 30.0 mmol) in 38% yield (3.13 g) following general procedure C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 2H), 7.23–7.19 (m, 3H), 4.41 (br s, 1H), 4.13 (t, *J* = 6.5 Hz, 2H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.09–2.02 (m, 2H), 1.36 (s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 128.5, 128.4, 126.1, 69.4, 54.6, 31.7, 30.5, 29.6.
IR (neat) ν 3279 (br), 3026 (w), 2971 (w), 1601 (w), 1497 (w), 1469 (w), 1438 (w), 1394 (m), 1369 (w), 1344 (m), 1231 (w), 1155 (s), 1091 (w), 1044 (w), 992 (m), 922 (s), 873 (m), 827 (m), 801 (m), 744 (m), 730 (m), 698 (s), 615 (m), 573 (m) cm^{-1}.
TLC R_f = 0.17 in hexanes:EtOAc 8:1
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{21}NO_3S$•Na 294.1134; Found 294.1138.

3-Methylpentyl *tert*-butylsulfamate (4m)

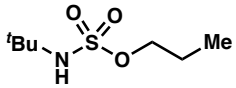


Prepared from salt **2e** and 3-methylbutan-1-ol following general procedure B. The product was obtained as a colorless oil (294.8 mg, 65% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (br, s, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 1.81–1.71 (m, 1H), 1.63–1.57 (m, 2H), 1.36 (s, 9H), 0.94 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 68.8, 54.5, 37.4, 29.6, 24.6, 22.3.
IR (neat) ν 3298 (br), 2960 (w), 2872 (w), 1467 (w), 1429 (w), 1393 (m), 1340 (m), 1231 (w), 1158 (s), 1040 (w), 1001 (m), 949 (s), 881 (m), 786 (m), 747 (m), 615 (m), 587 (m), 530 (w) cm^{-1}.
TLC R_f = 0.23 in hexanes:EtOAc 8:1
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{21}NO_3S$•Na 246.1134 ; Found 246.1138.

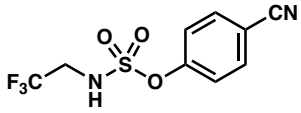
Propyl *tert*-butylsulfamate (4n)



Prepared from salt **2e** and *n*-propanol following general procedure B. The product was obtained as a colorless oil (238.6 mg, 61% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (br s, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 1.76 (h, J = 7.1 Hz, 1H), 1.36 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 71.8, 54.5, 29.6, 22.2, 10.2.
IR (neat) ν 3296 (br), 2973 (w), 1473 (w), 1430 (w), 1394 (m), 1338 (m), 1231 (w), 1157 (s), 1053 (w), 949 (s), 872 (m), 811 (m), 734 (m), 614 (m), 580 (m) cm^{-1}.
TLC R_f = 0.17 in hexanes:EtOAc 8:1
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_7H_{17}NO_3S$•Na 228.0821; Found 228.0823.

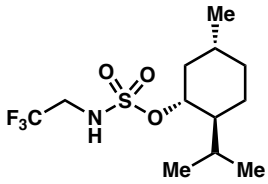
4-Cyanophenyl (2,2,2-trifluoroethyl)sulfamate (4o)



Prepared from salt **2a** and 4-hydroxybenzonitrile general procedure B. The product was obtained as a white powder (521.4 mg, 93% yield) after silica gel column chromatography using hexanes:EtOAc (8 :2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 5.31 (br s, 1H), 3.88 (q, *J* = 8.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 134.2, 123.1 (q, *J* = 276.8 Hz), 122.8, 117.7, 111.1, 45.5 (q, *J* = 36.2 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ –72.32 (t, *J* = 8.5 Hz).
IR (neat) ν 3157 (br), 2248 (w), 1599 (w), 1494 (w), 1476 (w), 1409 (w), 1377 (w), 1304 (w), 1275 (w), 1204 (w), 1154 (m), 1118 (m), 1105 (w), 1019 (w), 969 (w), 867 (m), 849 (w), 835 (w), 815 (w), 781 (w), 680 (w), 646 (w), 576 (m), 555 (m), 542 (m) cm^{-1}.
Rf = 0.57 in hexanes:EtOAc 7:3
HRMS (ESI) m/z: $[M + H]^+$ HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_8F_3N_2O_3S$ 281.0202 ; Found 281.0220.

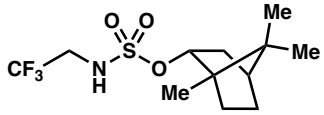
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (2,2,2-trifluoroethyl)sulfamate (4p)



Prepared from salt **2a** and (–)-menthol following general procedure B. The product was obtained as a white powder (449.3 mg, 71% yield) after silica gel column chromatography using hexanes:EtOAc (9:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (t, *J* = 7.2 Hz, 1H), 4.45 (td, *J* = 10.9, 4.6 Hz, 1H), 3.73 (q, *J* = 8 Hz, 2H), 2.34–2.29 (m, 1H), 2.12–2.04 (m, 1H), 1.74–1.66 (m, 2H), 1.47–1.38 (m, 2H), 1.22 (q, *J* = 11.9 Hz, 1H), 1.05 (qd, *J* = 14.1, 13.6, 3.8 Hz, 1H), 0.94 (t, *J* = 7.0 Hz, 6H), 0.89–0.85 (m, 1H), 0.83 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 123.3 (q, *J* = 277.7 Hz), 85.3, 47.6, 45.2 (q, *J* = 37.3 Hz), 41.3, 33.7, 31.6, 25.6, 23.0, 21.8, 20.8, 15.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ –72.48 (t, *J* = 8.6 Hz).
IR (neat) ν 3300 (br), 2944 (w), 2926 (w), 2870 (w), 2848 (w), 1455 (w), 1405 (w), 1356 (w), 1297 (w), 1272 (w), 1151 (m), 1116 (m), 970 (w), 942 (w), 887 (m), 876 (m), 853 2 (w), 837 (w), 819 (w), 801 (w), 665 (w), 595 (w), 581 (m), 560 (m) cm^{-1}.
R_f = 0.32 in hexanes:EtOAc 8:1
HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{12}H_{23}F_3NO_3S$ 316.1272; Found 316.1199.

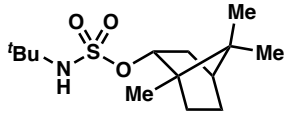
(1*R*,2*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl (2,2,2)-trifluoroethylsulfamate (4q)



Prepared from salt **2a** and (–)borneol following general procedure B. The product was obtained as a white solid (584 mg, 93% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (br s, 1H), 4.71 (ddd, *J* = 9.9, 3.2, 2.2 Hz, 1H), 3.77–3.69 (m, 2H), 2.39–2.31 (m, 1H), 1.90–1.83 (m, 1H), 1.80–1.72 (m, 1H), 1.39–1.25 (m, 4H), 0.91 (s, 3H), 0.89 (s, 3H), 0.88 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 123.3 (q, *J* = 277.5 Hz), 89.7, 49.6, 47.8, 45.2 (q, *J* = 35.7 Hz), 44.6, 36.0, 27.8, 26.4, 19.7, 18.7, 13.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ –72.48 (t, *J* = 8.5 Hz)
IR (neat) ν 3314 (br), 2986 (w), 2957 (w), 1454 (w), 1437 (w), 1409 (w), 1362 (m), 1301 (w), 1274 (m), 1181 (m), 1154 (m), 1100 (m), 1043 (w), 1005 (w), 971 (m), 960 (m), 944 (m), 919 (m), 894 (m), 878 (m), 837 (m), 780 (w), 743 (w), 667 (m), 585 (m), 561 (m), 531 (m) cm^{-1}.
TLC R_f = 0.51 in 4:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{12}H_{20}F_3NO_3S^-$ 314.1043; Found 314.1036.

(1*R*,2*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl *tert*-butylsulfamate (S4b)

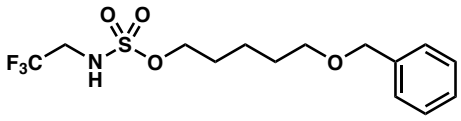


Prepared from salt **2e** and (–)-borneol following general procedure B. The product was obtained as a white solid (298 mg, 51% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71–4.67 (m, 1H), 4.26 (br s, 1H), 2.37–2.29 (m, 1H), 1.92–1.85 (m, 1H), 1.76–1.70 (m, 2H), 1.44–1.25 (m, 12H), 0.93 (s, 3H), 0.88 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 87.5, 54.7, 49.4, 47.6, 44.7, 36.1, 29.9, 27.9, 26.7, 19.7, 18.8, 13.4.

IR (neat) ν 3303 (br) 2961 (m), 2874 (w), 1731 (w), 1462 (w), 1435 (w), 1394 (m), 1380 (w), 1365 (w), 1348 (m), 1305(w), 1230 (w), 1155 (m), 1112 (w), 1081 (w), 1043 (w), 1015 (w), 1000 (m), 985 (m), 968 (m), 938 (m), 919 (w), 870 (m), 855 (m), 837 (w), 799 (m), 782 (m), 741 (w), 656 (m), 617 (m), 595 (w), 569 (m), 553 (m) cm^{-1}.
TLC R_f = 0.62 in 4:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{27}NO_3S$•Na 312.1604; Found 312.1607.

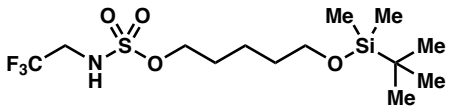
5-(Benzyloxy)pentyl (2,2,2-trifluoroethyl)sulfamate (4r)



Prepared from salt **2a** and 5-(benzyloxy)oentan-1-ol following general procedure B. The product was obtained as a colorless oil (617 mg, 87% yield) after silica gel column chromatography using hexanes:EtOAc (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5H), 4.99 (br s, 1H), 4.50 (s, 2H), 4.18 (t, *J* = 6.5 Hz, 2H), 3.74–3.66 (m, 2H), 3.48 (td, *J* = 6.3, 0.8 Hz, 2H), 1.80–1.72 (m, 2H), 1.69–1.62 (m, 2H), 1.54–1.46 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 128.4, 127.7, 123.4 (q, *J* = 278.0 Hz), 72.9, 71.7, 69.9, 45.0 (q, *J* = 35.4 Hz), 29.0, 28.4, 22.2.
^{19}F NMR (376 MHz) δ –72.70 (t, *J* = 8.7 Hz).
IR (neat) ν 3298 (br), 2940 (w), 2866 (w), 1454 (w), 1359 (m), 1274 (m), 1150 (s), 1116 (m), 1028 (m), 956 (s), 915 (m), 856 (m), 735 (m), 698 (m), 664 (m), 560 (s) cm^{-1}.
TLC R_f = 0.36 in 4:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}F_3NO_4S$ 356.1138; Found 356.1139.

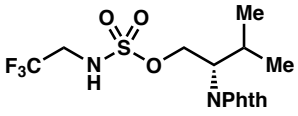
5-((*tert*-Butyldimethylsilyl)oxy)pentyl (2,2,2-trifluoroethyl)sulfamate (4s)



Prepared from salt **2a** and 5-((tert-butyldimethylsilyl)oxy)pentan-1-ol following general procedure B. The product was obtained as a colorless oil (571 mg, 75% yield) after silica gel column chromatography using hexanes:EtOAc (19:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (br s, 1H), 4.17 (t, *J* = 6.5 Hz, 2H), 3.77–3.67 (m, 2H), 3.61 (t, *J* = 6.2 Hz, 2H), 1.80–1.71 (m, 2H), 1.58–1.51 (m, 2H), 1.49–1.39 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 123.5 (q, *J* = 278.0 Hz), 71.9, 62.7, 45.0 (q, *J* = 35.9 Hz), 32.0, 28.4, 25.9, 21.8, 18.3, –5.4.
^{19}F NMR (376 MHz) δ –72.70 (t, *J* = 8.7 Hz).
IR (neat) ν 2954 (m), 2928 (m), 2885 (w), 2856 (m), 1471 (w), 1388 (w), 1361 (w), 1320 (w), 1252 (m) 1218 (w), 1186 (w), 1047 (s), 1003 (m), 939 (w), 832 (s), 775 (s), 696 (w), 669 (m), 573 (w) cm^{-1}.
TLC R_f = 0.18 in 9:1 hexanes:EtOAc
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{28}F_3NO_4SSi$ 380.1533; Found 380.1539.

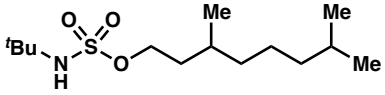
(*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-methylbutyl (2,2,2-trifluoroethyl)sulfamate (4t)



Prepared from salt **2a** and (*S*)-2-(1-hydroxy-3-methylbutan-2-yl)isoindoline-1,3-dione following general procedure B. The product was obtained as a white solid (590 mg, 75% yield) after silica gel column chromatography using hexanes:EtOAc (5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.38 (br s, 1H), 4.82 (t, *J* = 10.4 Hz, 1H), 4.50 (dd, *J* = 10.4, 4.1 Hz, 1H), 4.22 (td, *J* = 10.2, 4.1 Hz, 1H), 3.70–3.61 (m, 2H), 2.47–2.38 (m, 1H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 134.3, 131.4, 123.4, 123.2 (q, *J* = 276.6 Hz), 68.7, 56.5, 45.0 (q, *J* = 35.0 Hz), 27.7, 20.0, 19.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ –72.78 (t, *J* = 8.9 Hz).
IR (neat) ν 3293 (br), 2972 (w), 2080 (w), 1770 (w), 1697 (s), 1613 (w), 1464 (m), 1438 (w), 1387 (s), 1362 (s), 1291 (m), 1265 (s), 1173 (s), 1148 (s), 1114 (s), 1089 (m), 1061 (m), 1028 (m), 1010 (w), 982 (s), 960 (s), 868 (s), 848 (m), 831 (m), 796 (m), 784 (s), 721 (s), 699 (m), 659 (m), 613 (m), 579 (m), 561 (s), 526 (s) cm^{-1}.
TLC R_f = 0.30 in 3:1 hexanes:EtOAc.
HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{15}H_{16}F_3N_2O_5S$ 3920810 ; Found 393.0729.

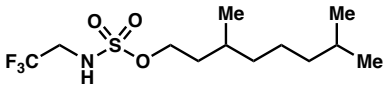
3,7-Dimethyloctyl *tert*-butylsulfamate (4u)



Prepared from salt **2e** and 3,7-dimethyloctan-1-ol following general procedure B. The product was obtained as a yellow oil (366.5 mg, 62% yield) after silica gel column chromatography using hexanes:EtOAc (8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (br s, 1H), 4.19–4.10 (m, 2H), 1.80–1.71 (m, 1H), 1.62–1.58 (m, 1H), 1.56–1.48 (m, 2H), 1.36 (s, 9H), 1.32–1.20 (m, 4H), 1.16–1.13 (m, 2H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 68.8, 54.5, 39.1, 37.0, 35.7, 29.6, 29.3, 27.9, 24.5, 22.6, 22.5, 19.3.
IR (neat) ν 3296 (br), 2954 (m), 2926 (m), 2869 (w), 1467 (w), 1430 (w), 1393 (w), 1343 (m), 1230 (w), 1159 (s), 1000 (m), 950 (m), 885 (m), 770 (w), 616 (m), 588 (w) cm^{-1}.
R_f = 0.22 in 8:1 hexanes:EtOAc.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{32}NO_3S$ 294.2097 ; Found 294.2098.

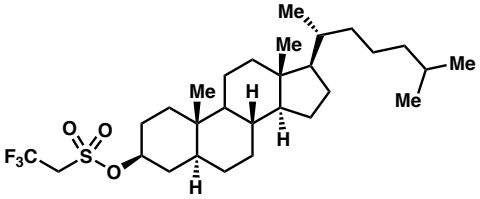
3,7-Dimethyloctyl (2,2,2-trifluoroethyl)sulfamate (4v)



Prepared from salt **2a** and 3,7-dimethyloctan-1-ol following general procedure B. The product was obtained as a yellow oil (616 mg, 96% yield) after silica gel column chromatography using hexanes:EtOAc (19:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (br s, 1H), 4.26–4.16 (m, 2H), 3.79–3.68 (m, 2H), 1.82–1.72 (m, 1H), 1.63–1.46 (m, 3H), 1.33–1.20 (m, 3H), 1.19–1.08 (m, 3H), 0.91 (t, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 123.4 (q, *J* = 278.3 Hz), 70.5, 45.1 (q, *J* = 36.5 Hz), 39.1, 36.9, 35.5, 29.3, 27.9, 24.5, 22.6, 22.5, 19.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ –72.74 (t, *J* = 8.7 Hz).
IR (neat) ν 3281 (br), 2954 (w), 2930 (w), 2870 (w), 2847 (w), 1463 (m), 1431 (w), 1409 (w), 1383 (w), 1347 (m), 1276 (m), 1155 (s), 1116 (m), 1061 (w), 1034 (w), 964 (m), 938 (s), 901 (m), 879 (m), 855 (m), 834 (m), 766 (m), 736 (w), 664 (m), 559 (m), 530 (m) cm^{-1}.
R_f = 0.57 in 4:1 hexanes:EtOAc.
HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{12}H_{24}F_3NO_3S$ 318.1356; Found 318.1351.

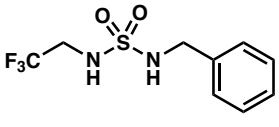
(3*S*,5*S*,8*R*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (2,2,2-trifluoroethyl)sulfamate (4W)



Prepared from salt **2a** and 5α-cholestan-3β-ol following general procedure B. The product was obtained as a white solid (793 mg, 72% yield) after silica gel column chromatography using hexanes:EtOAc (9 : 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (t, *J* = 7.0 Hz, 1H), 4.55–4.47 (m, 1H), 3.77–3.69 (m, 2H), 2.02–1.94 (m, 2H), 1.83–1.75 (m, 3H), 1.69-1.64 (m, 2H), 1.60–1.51 (m, 3H), 1.50-1.44 (m, 1H), 1.36–1.22 (m, 9H), 1.17–1.06 (m, 6H), 1.04–0.96 (m, 4H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.82 (s, 3H), 0.66-0.69 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 123.4 (q, *J* = 277.2 Hz), 84.2, 56.4, 56.3, 54.1, 45.2 (q, *J* = 25.2 Hz), 44.8, 42.6, 39.9, 39.5, 36.8, 36.1, 35.8, 35.4, 35.3, 34.6, 31.9, 28.5, 28.2, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.2, 18.7, 12.2, 12.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ –72.43 (t, *J* = 8.7 Hz).
IR (neat) ν 3283 (br), 2930 (m), 2867 (m), 1461 (w), 1412 (w), 1346 (m), 1297 (w), 1275 (m), 1151 (s), 1119 (m), 973 (m), 938 (s), 905 (m), 880 (m), 836 (m), 733 (w), 667 (w), 605 (m), 569 (m), 529 (m) cm^{-1}.
HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{29}H_{49}F_3NO_3S$ 548.3463 ; Found 548.3370.

***N*-(Benzyl)-*N*'-(2,2,2-trifluoroethyl)sulfamide (6a)**

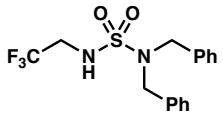


Prepared from salt **2a** and *N*-benzylamine following general procedure B. The product was obtained as a white powder (461 mg, 86% yield) after silica gel column chromatography using hexanes:EtOAc (4:1).

^{1}H NMR (400 MHz, CD_3CN) δ 7.39–7.35 (m, 4H), 7.34–7.28 (m, 1H), 5.88 (t, *J* = 7.0 Hz, 1H), 5.75 (br s, 1H), 4.15 (d, *J* = 6.3 Hz, 2H), 3.65–3.57 (m, 2H).

^{13}C NMR (126 MHz, CDCN) δ 138.5, 129.5, 128.9, 128.5, 125.4 (q, *J* = 277.4 Hz), 47.4, 44.8 9 (q, *J* = 34.5 Hz).
^{19}F NMR (376 MHz, CD_3CN) δ –73.18 (t, *J* = 9.3 Hz).
IR (neat) ν 3291 (br), 1463 (w), 1416 (w), 1352 (w), 1321 (m), 1292 (m), 1267 (m), 1211 (w), 1143 (m), 1109 (m), 1083 (m), 1062 (m), 1027 (m), 1000 (w), 981 (w), 962 (m), 921 (w), 906 (m), 887 (m), 836 (m), 753 (w), 732 (m), 697 (m), 667 (m), 560 (m) cm^{-1}.
Rf = 0.43 in hexanes:EtOAc 7:3
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{11}F_3N_2O_2S$•Na 291.0386 ; Found 291.0391.

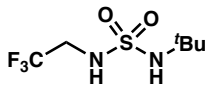
_N,N_-Dibenzyl-_N'_-(2,2,2-trifluoroethyl)sulfamide (6b)



Prepared from salt **2a** and *N,N*-dibenzylamine following general procedure B. The product was obtained as a white solid (588.5 mg, 82% yield) after silica gel column chromatography using hexanes:EtOAc (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.29 (m, 10H), 4.33 (s, 4H), 4.27 (br s, 1H), 3.54–3.46 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 128.8, 128.7, 128.1, 123.6 (q, *J* = 280.0 Hz), 50.9, 44.7 (q, *J* = 35.1 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ –72.50 (t, *J* = 8.7 Hz).
IR (neat) ν 3289 (br), 1494 (w), 1455 (w), 1397 (w), 1372 (w), 1351 (w), 1335 (w), 1291 (w), 1272 (w), 1207 (w), 1140 (m), 1120 (m), 1091 (w), 1076 (w), 1050 (w), 1026 (w), 961 (w), 938 (w), 927 (w), 914 (w), 891 (w), 834 (w), 811 (w), 776 (w), 746 (w), 721 (w), 702 (w), 694 (m), 664 (w), 605 (), 595 (w), 555 (w), 535 (w) cm^{-1}.
R_f = 0.60 in 7:3 hexanes:EtOAc.
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{17}F_3N_2O_2S$•Na 381.0855 ; Found 381.0862.

_N_-(_t_-Butyl)-_N'_-(2,2,2-trifluoroethyl)-sulfamide (6c)

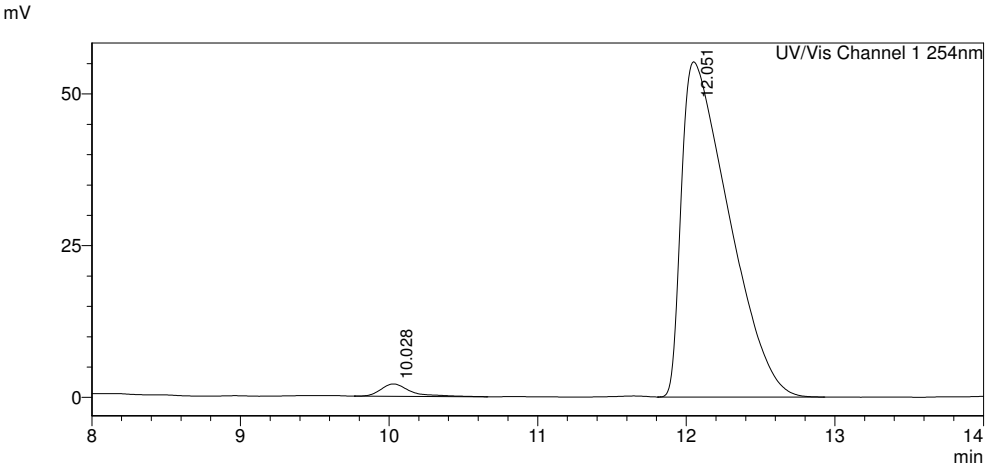


Prepared from salt **2a** and *t*-Butylamine following general procedure B. The product was obtained as a white solid (402.5 mg, 86% yield) after silica gel column chromatography using hexanes:EtOAc (8 : 2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 (br s, 1H), 4.18 (br s, 1H), 3.71–3.62 (m, 2H), 1.37 (s, 9H).
^{13}C NMR (126 MHz, CDCN) δ 125.5 (q, *J* = 277.7 Hz), 54.7, 44.9 (q, *J* = 34.4 Hz), 29.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ –71.87 (t, *J* = 8.9 Hz).
IR (neat) ν 3302 (br), 2986 (w), 1478 (w), 1467 (w), 1426 (w), 1396 (w), 1372 (w), 1322 (m), 1294 (m), 1272 (m), 1232 (w), 1154 (m), 1130 (m), 1109 (m), 1037 (w), 990 (m), 960 (m), 929 (w), 866 (m), 833 (m), 818 (w), 663 (m), 624 (m), 553 (m) cm^{-1}.
R_f = 0.27 in hexane : EtOAc 8 : 2
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_6H_{13}F_3N_2O_2S$•Na 257.0542; Found 257.0548.

Compound 4i: HPLC: Column: Cellulose II (3 µm, 4.6 mm X 250 mm). Mobile phase: 90:10 hexanes:isopropanol, 1.0 mL/min. Detection wavelength: 254 nm. e.r. = 2:98

<Chromatogram>



<Peak Table>

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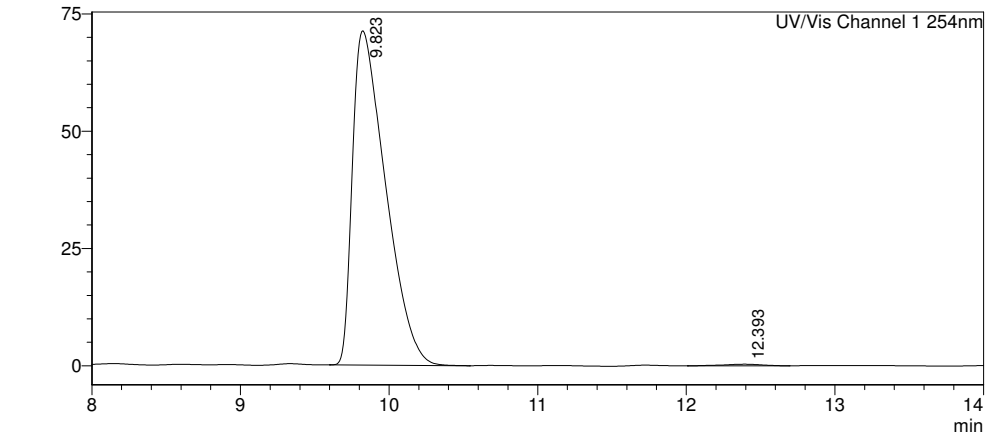
Total		1253237	57277		100.000

Compound S4a: HPLC: Column: Cellulose II (3 µm, 4.6 mm X 250 mm). Mobile phase: 90:10 hexanes:isopropanol, 1.0 mL/min. Detection wavelength: 254 nm. e.r. = 99:1

<Chromatogram>



<Peak Table>

UV/Vis Channel 1 254nm

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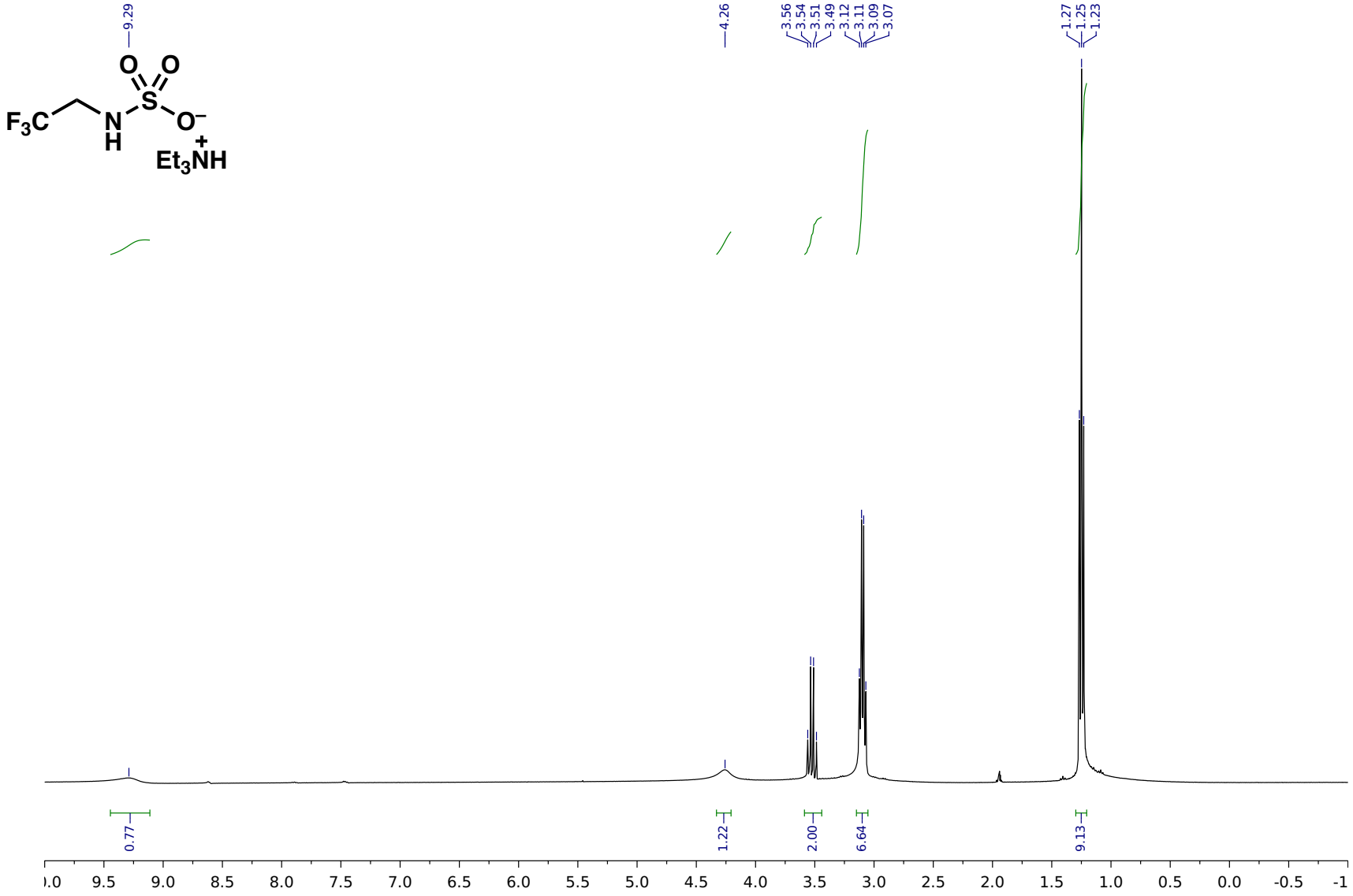
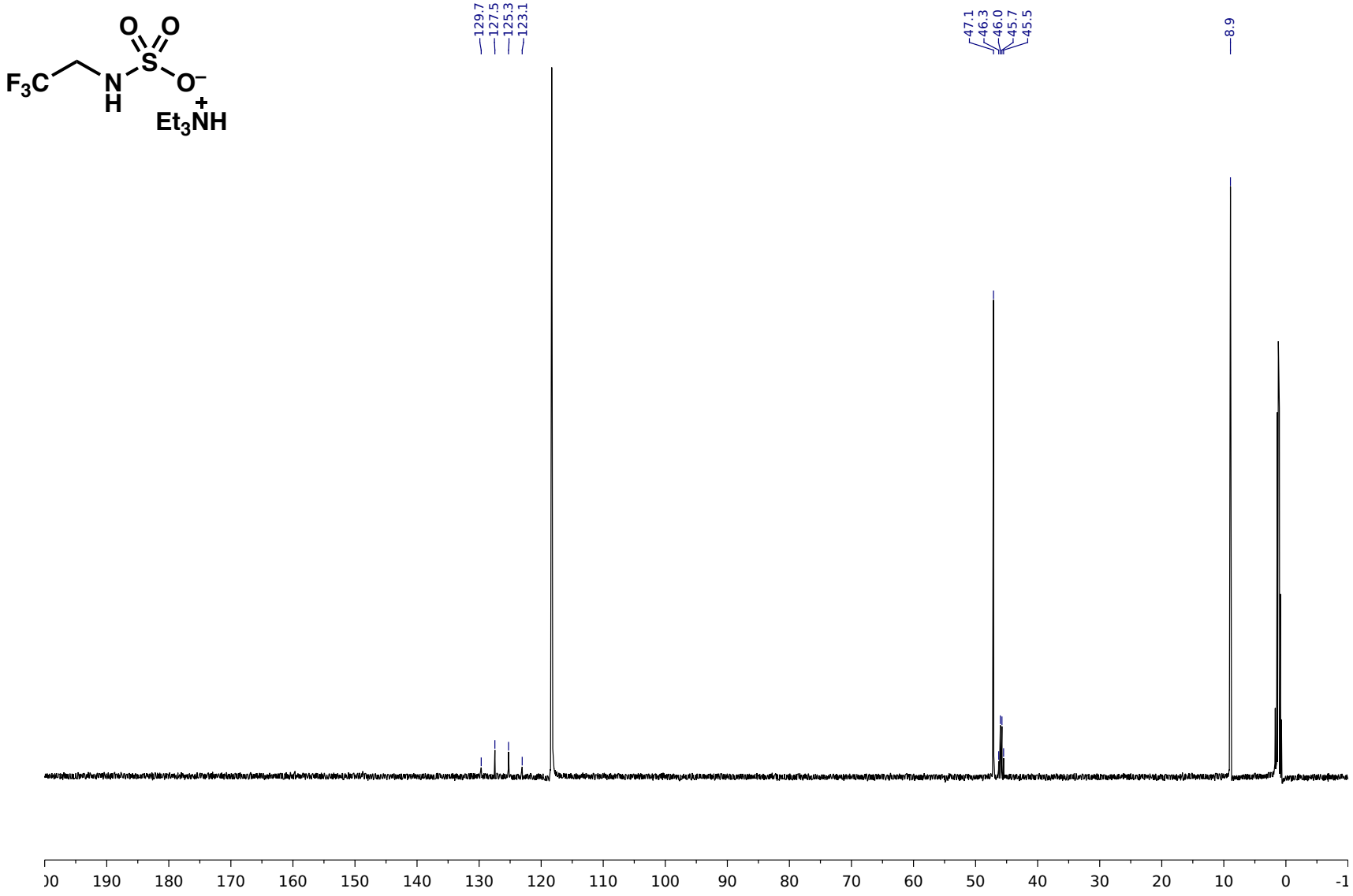
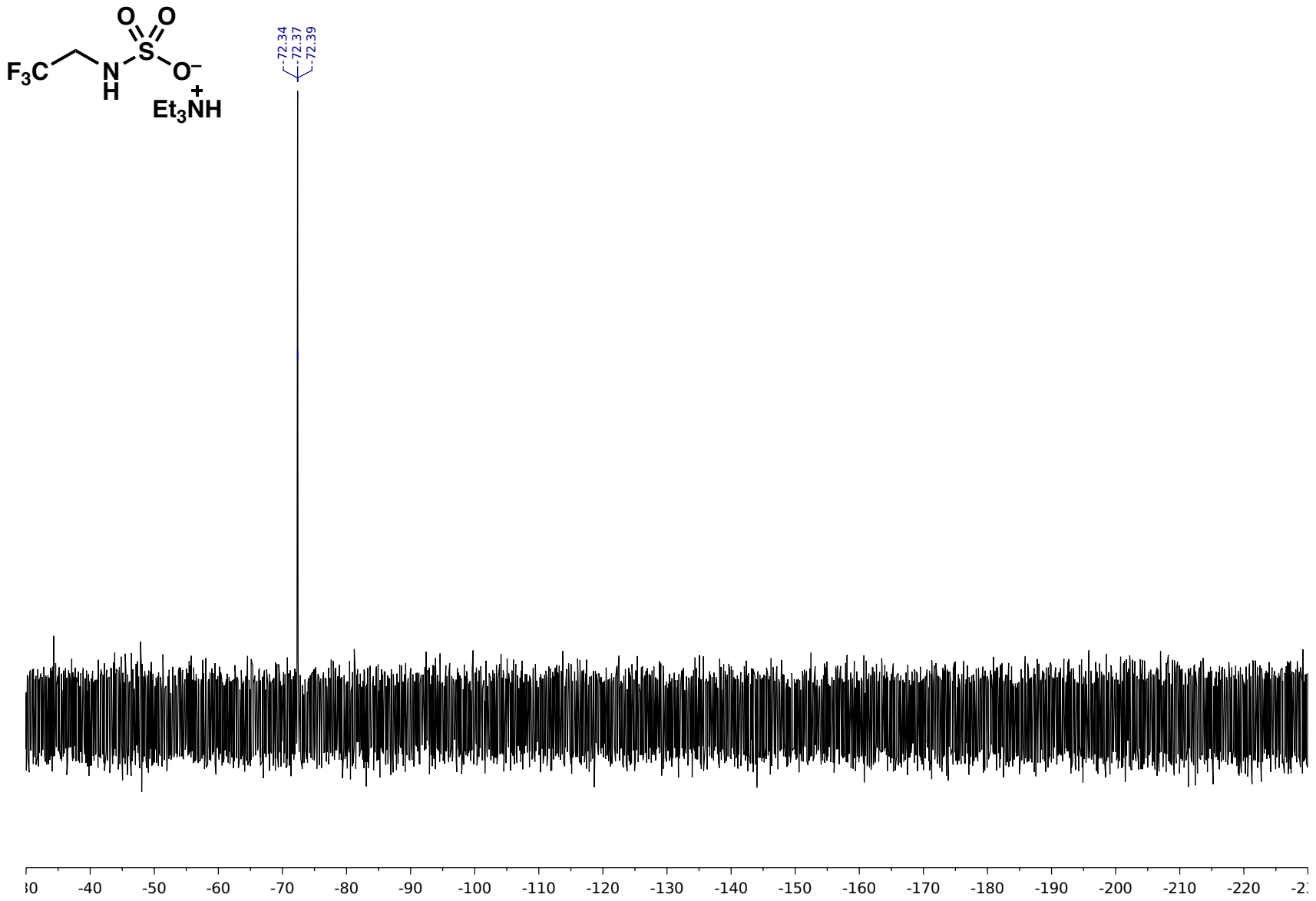
Total		1113750	71611		100.000



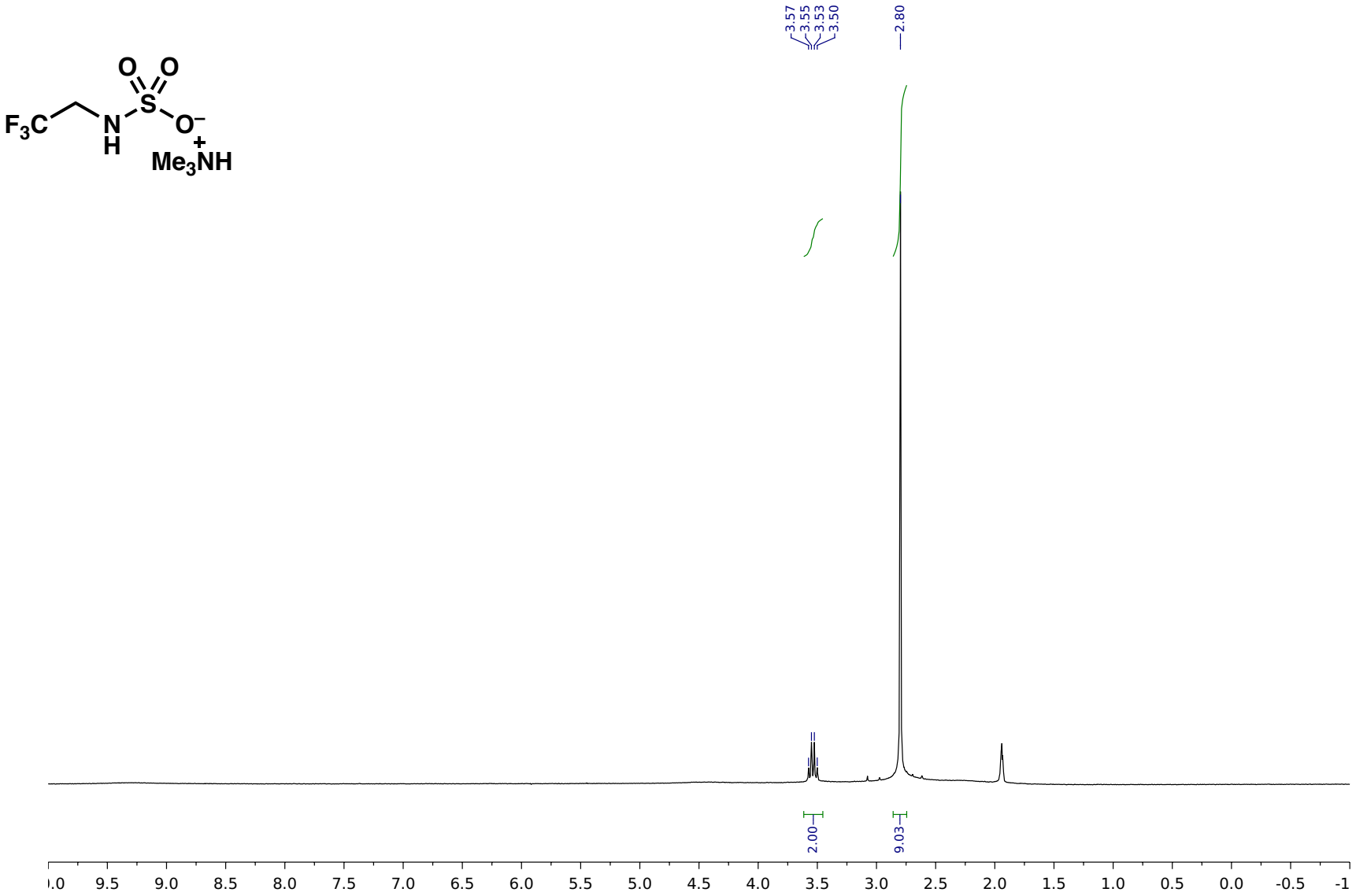
^{1}H NMR (400 MHz, CD_3CN) of triethylammonium (2,2,2-trifluoroethyl)sulfamate (**2a**)



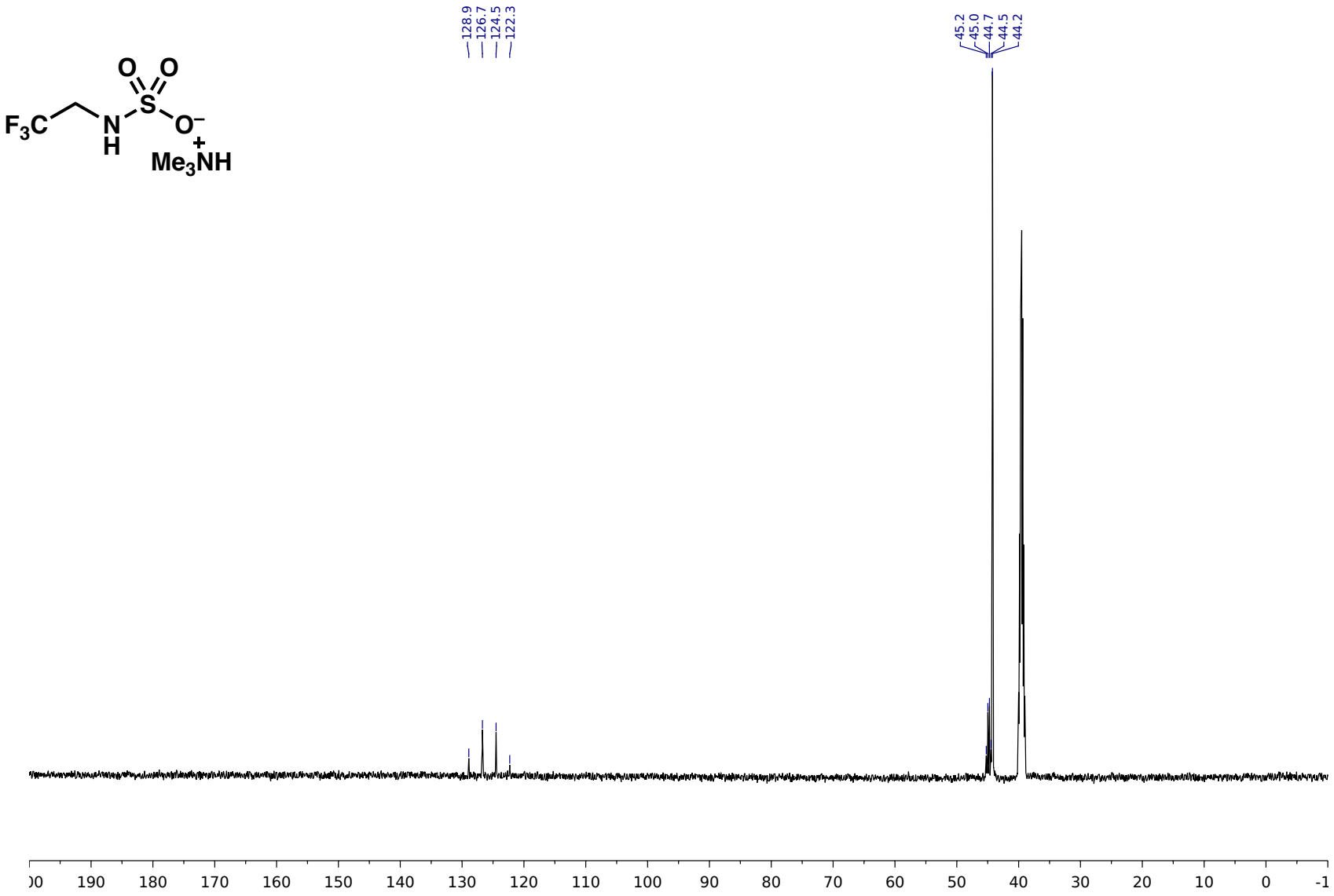
^{13}C NMR (126 MHz, CD_3CN) of triethylammonium (2,2,2-trifluoroethyl)sulfamate (**2a**)



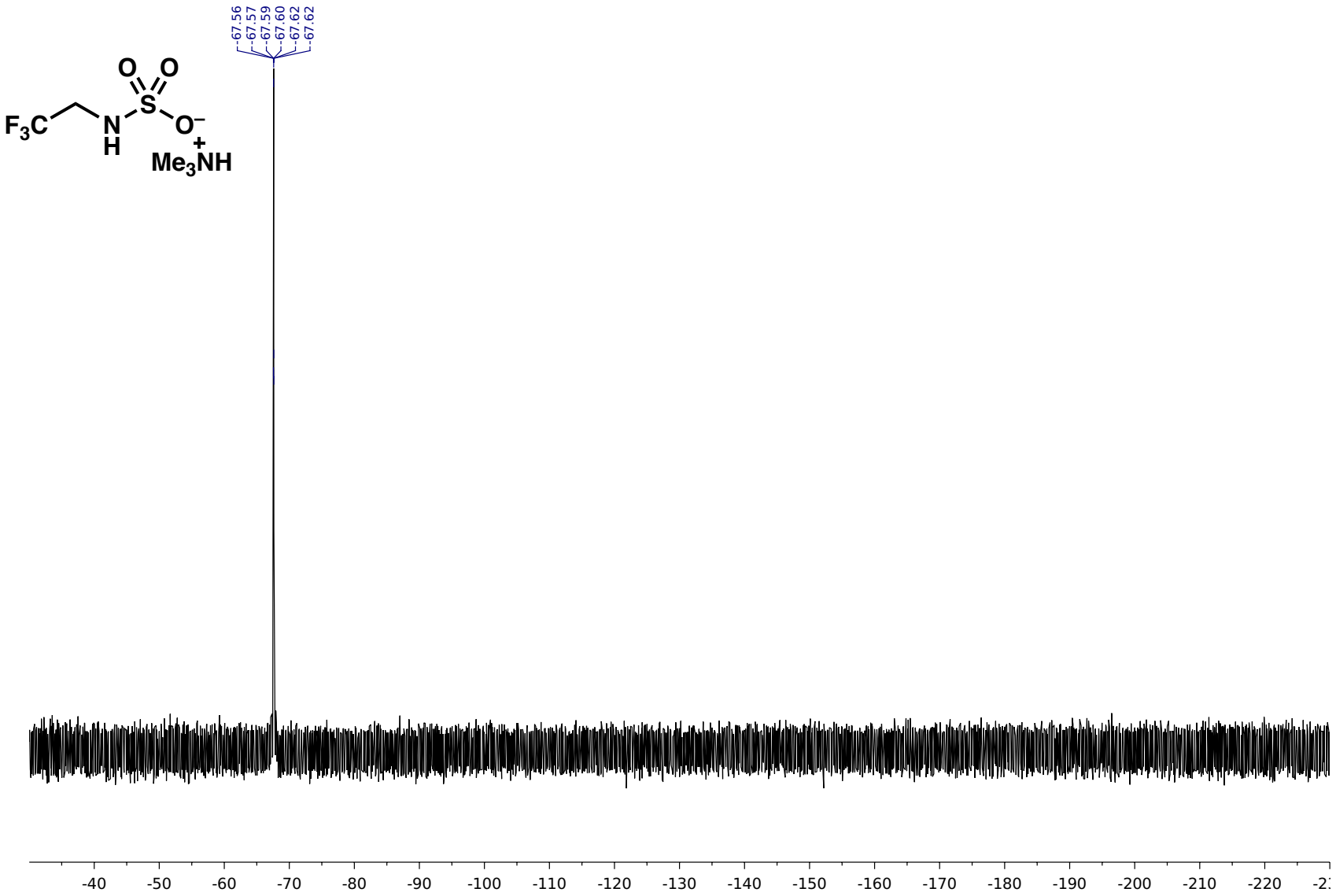
^{19}F NMR (376 MHz, $CDCl_3$) of triethylammonium (2,2,2-trifluoroethyl)sulfamate (**2a**)



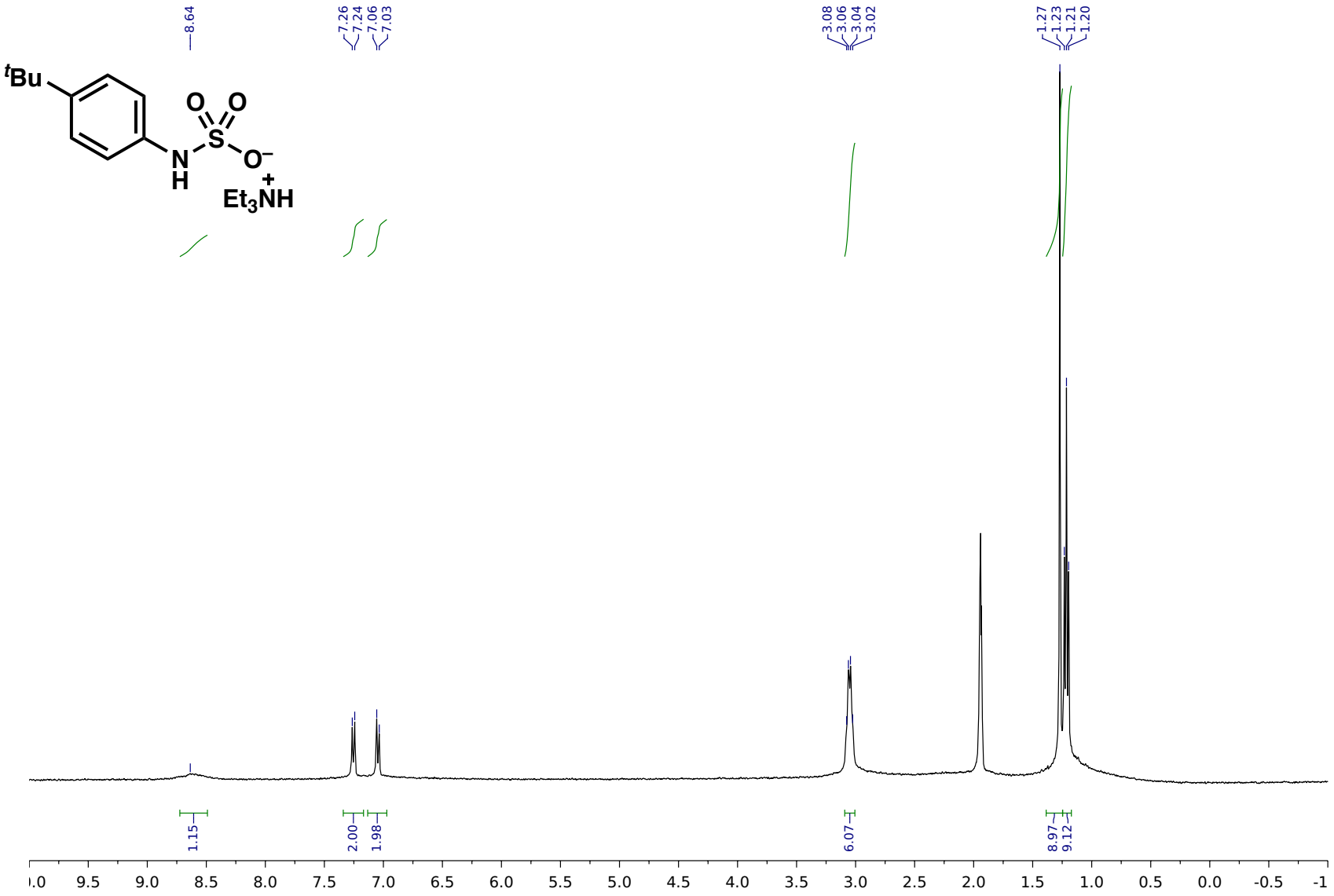
^{1}H NMR (400 MHz, CD_3CN) of trimethylammonium (2,2,2-trifluoroethyl)sulfamate (**2b**)



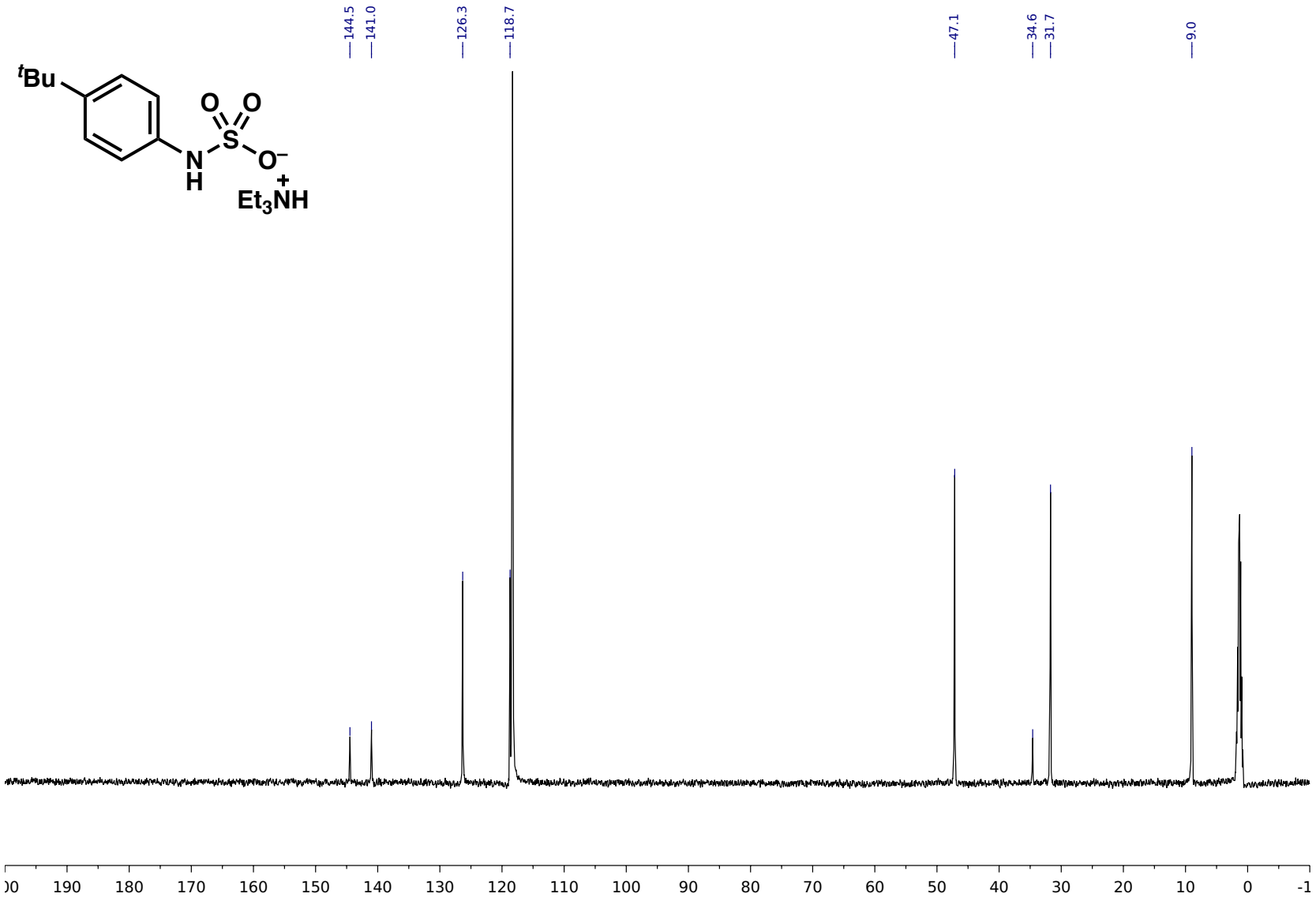
^{13}C NMR (126 MHz, d_6 DMSO) of trimethylammonium (2,2,2-trifluoroethyl)sulfamate (**2b**)



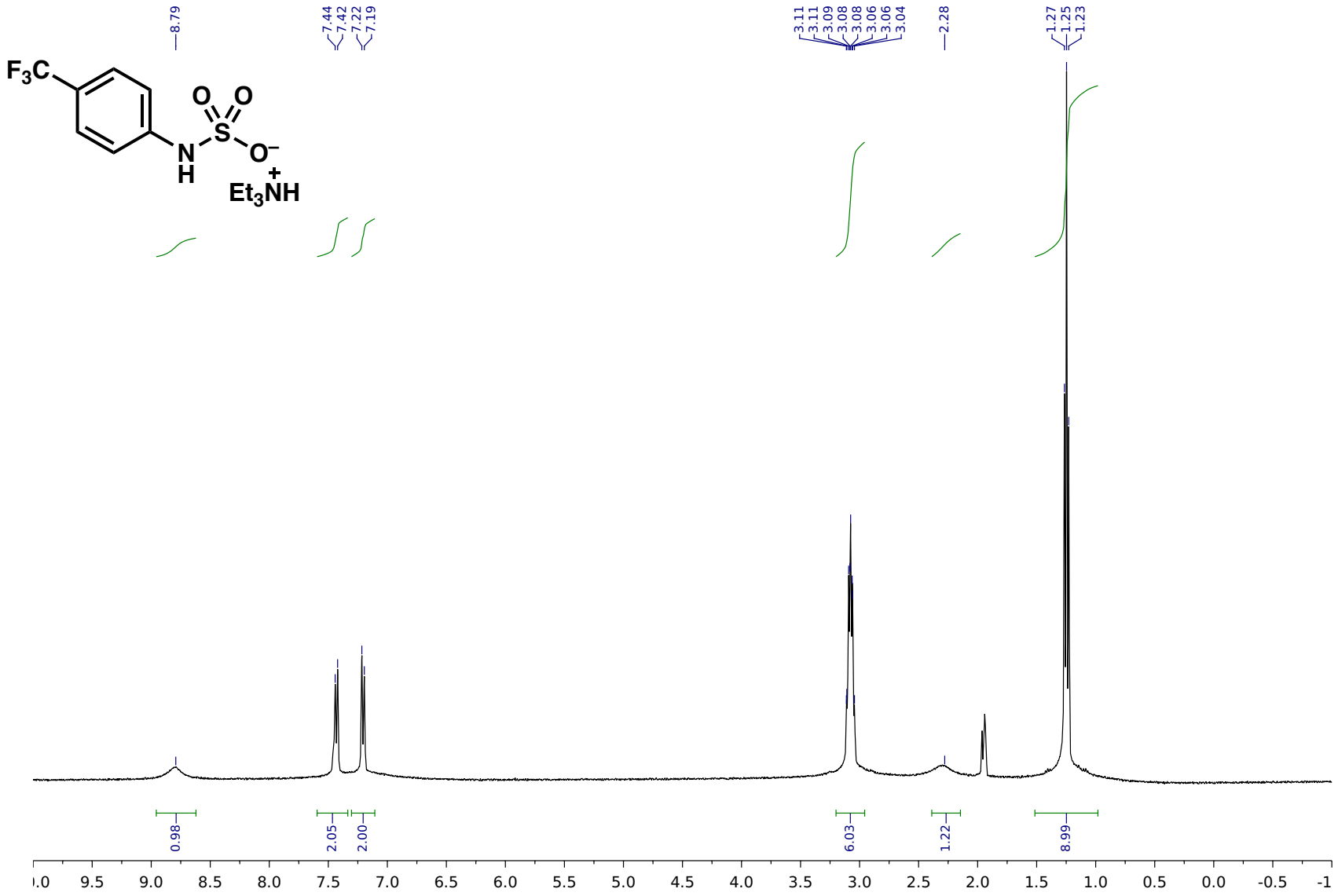
^{19}F NMR (376 MHz, CD_3CN) of trimethylammonium (2,2,2-trifluoroethyl)sulfamate (**2b**)



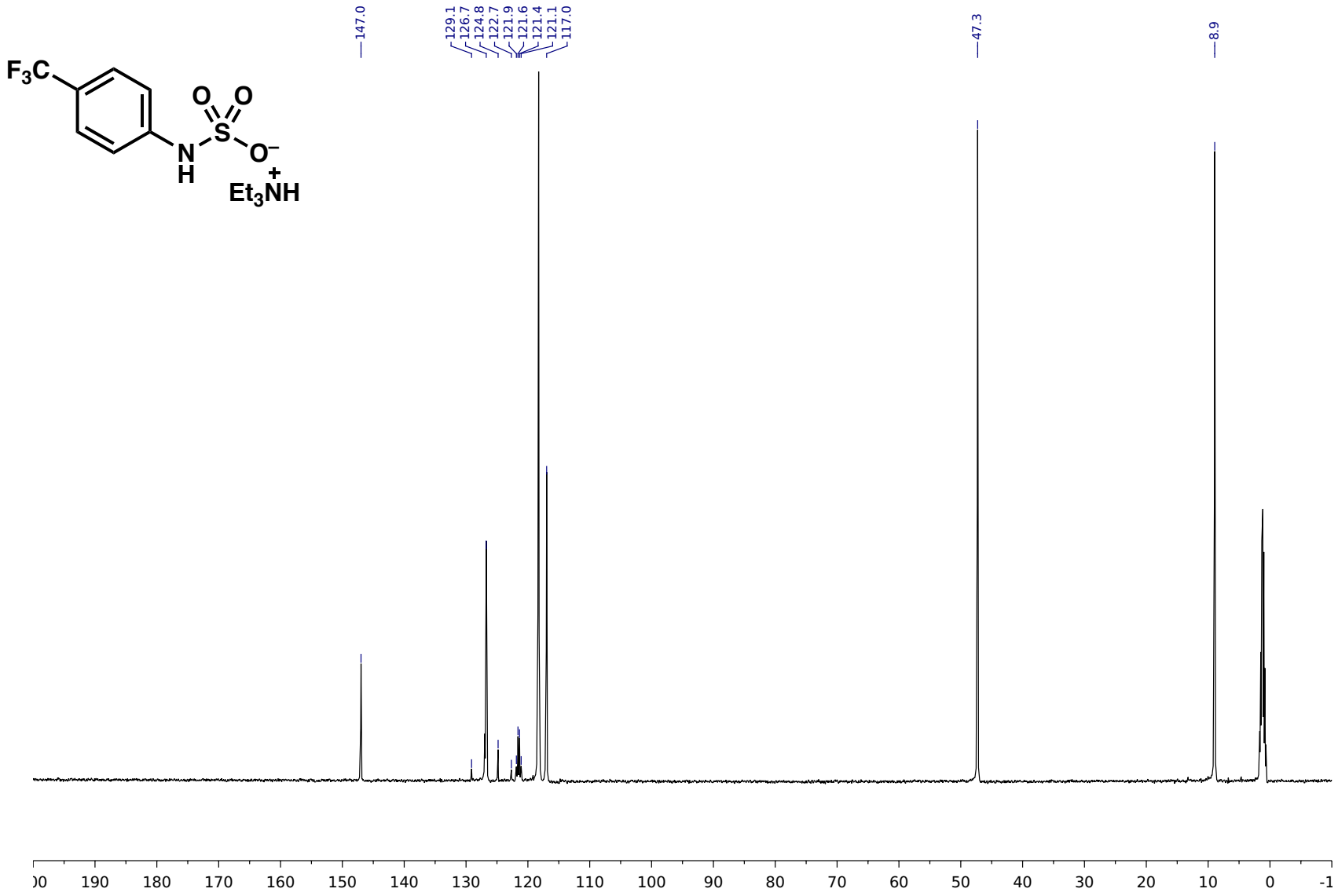
^{1}H NMR (400 MHz, CD_3CN) of triethylammonium (4-*tert*-butyl)phenyl)sulfamate (**2c**)



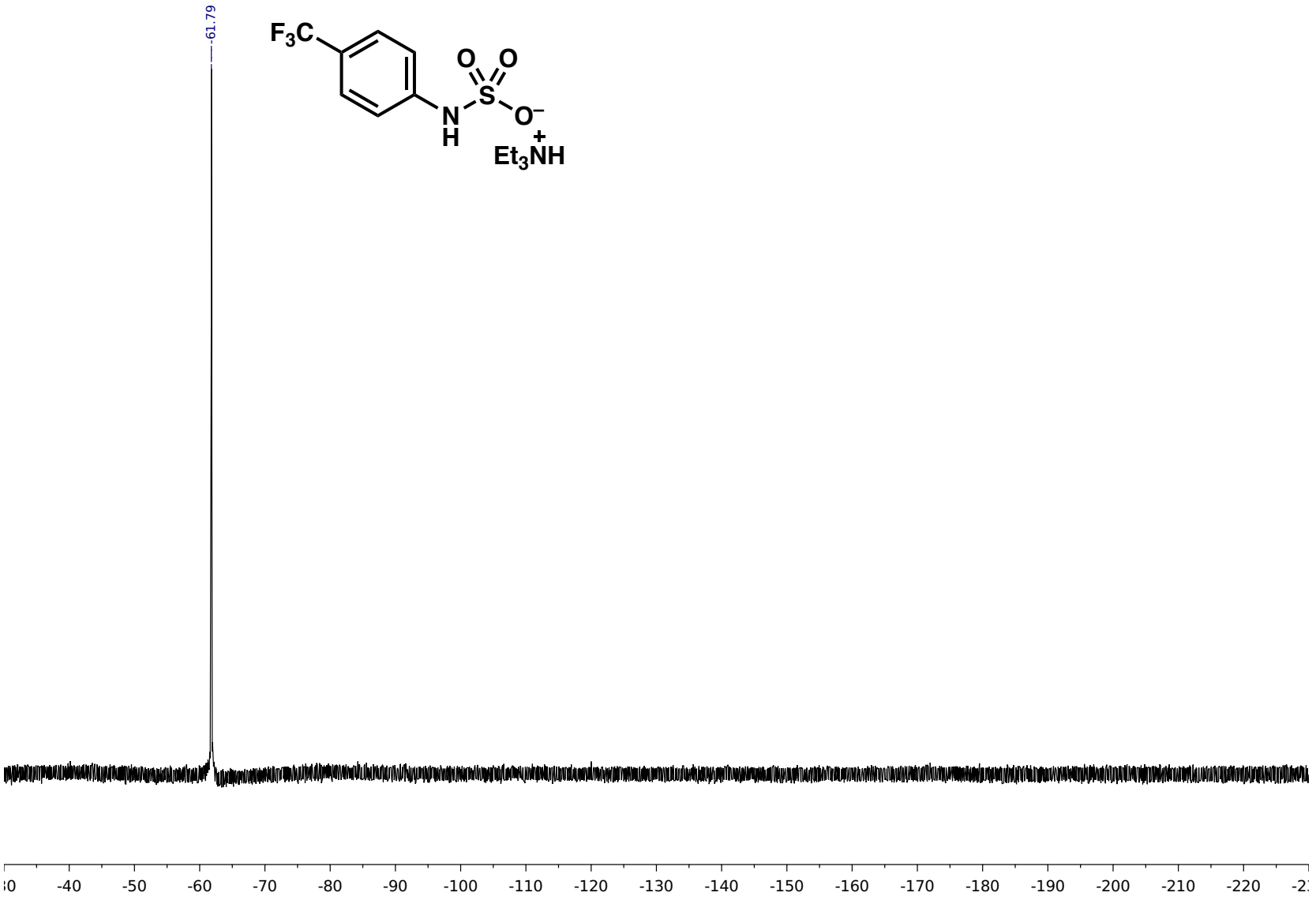
^{13}C NMR (500 MHz, CD_3CN) of triethylammonium (4-*tert*-butyl)phenylsulfamate (**2c**)



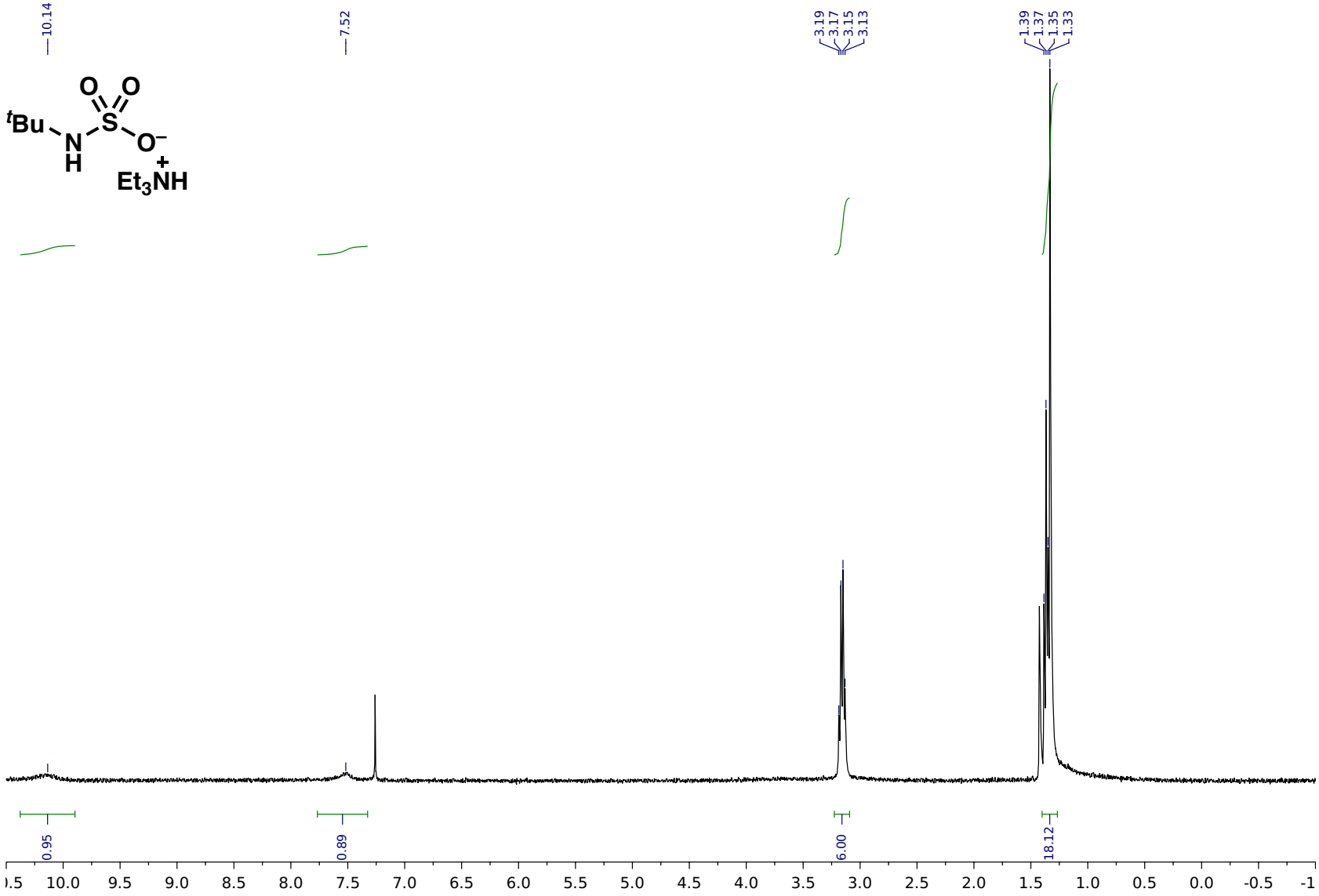
^{1}H NMR (400 MHz, CD_3CN) of triethylammonium (4-(trifluoromethyl))phenylsulfamate (**2d**)



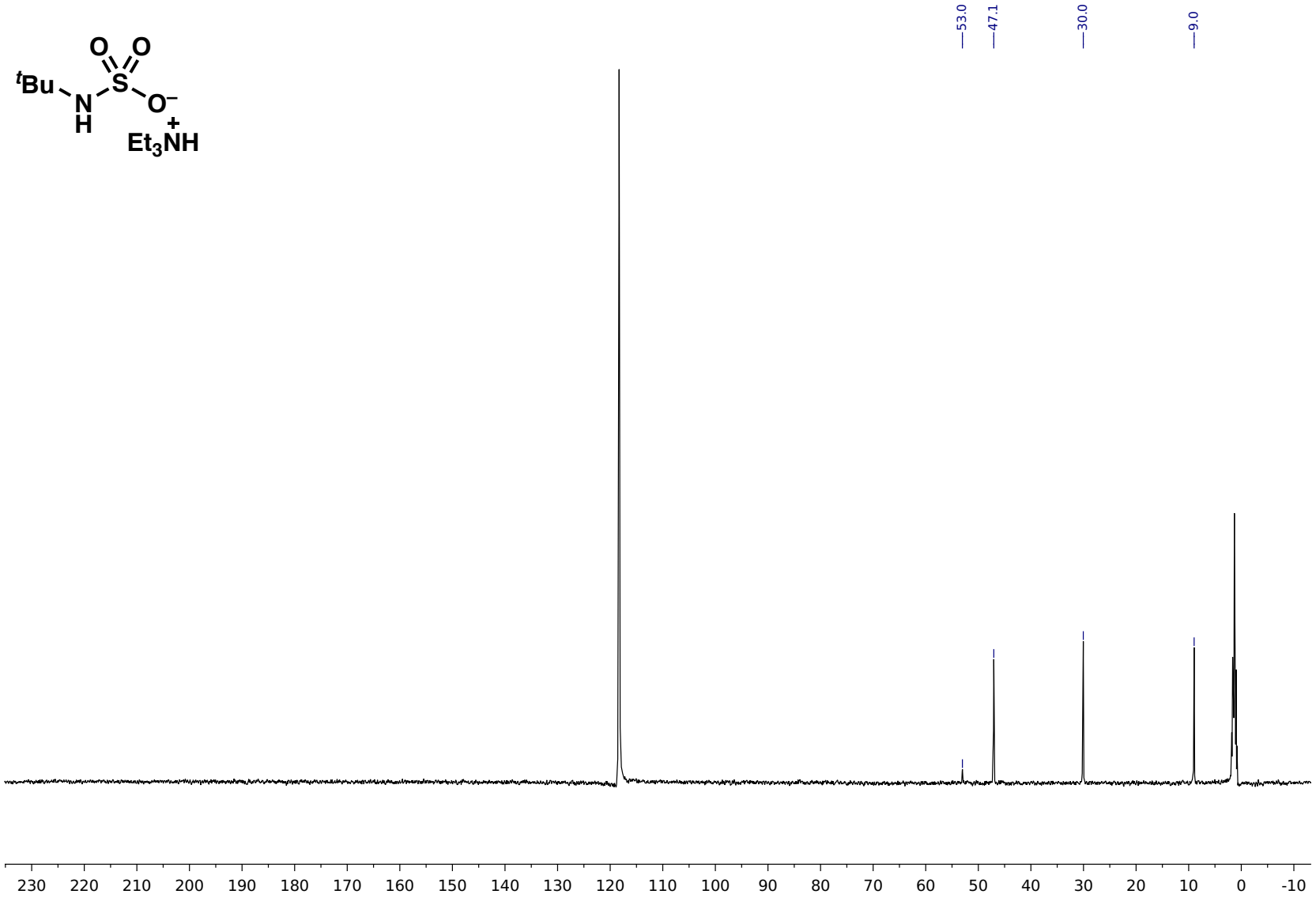
^{13}C NMR (500 MHz, CD_3CN) of trimethylammonium (4-(trifluoromethyl))phenylsulfamate (**2d**)



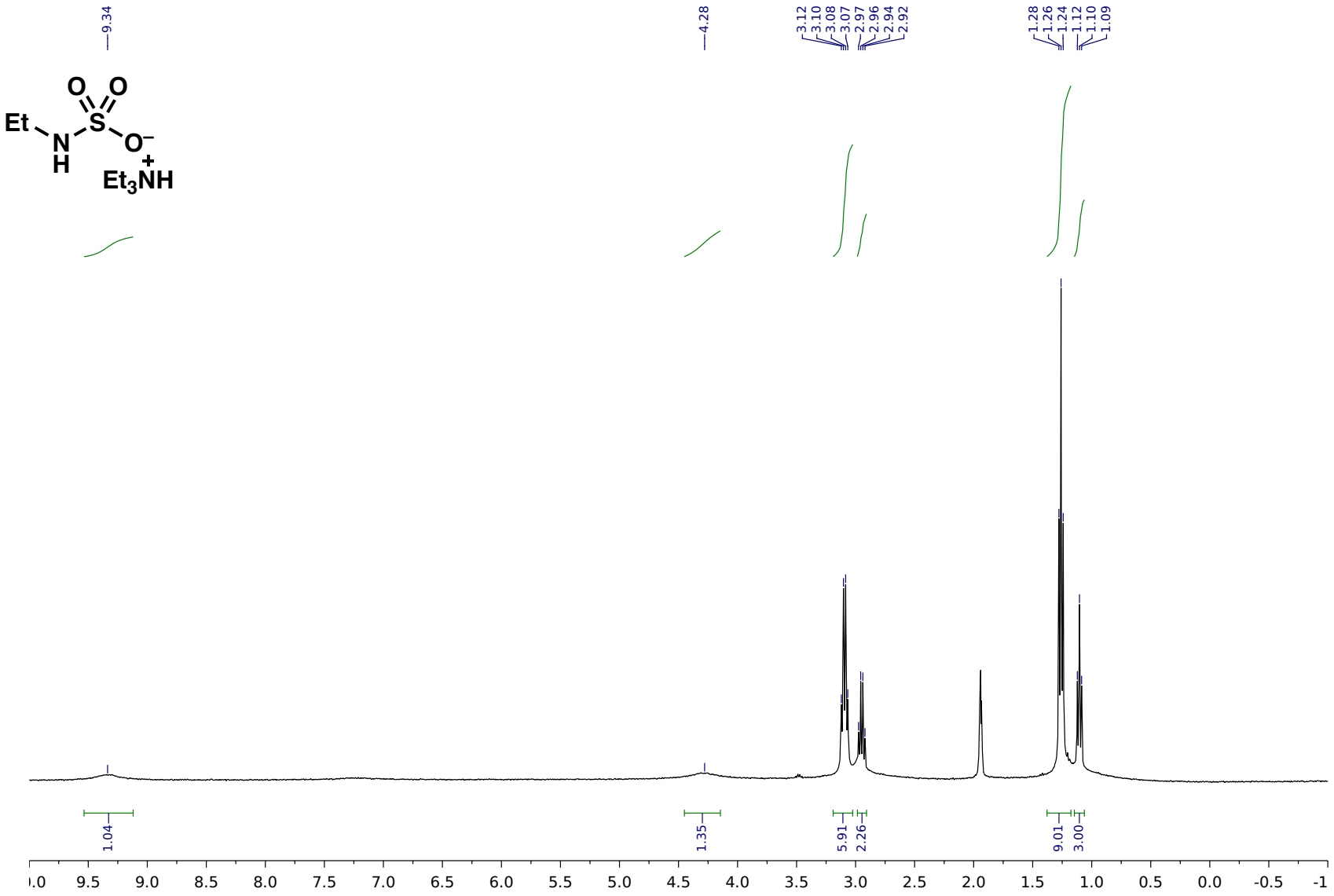
^{19}F NMR (376 MHz, CD_3CN) of triethylammonium (4-(trifluoromethyl))phenylsulfamate (**2d**)



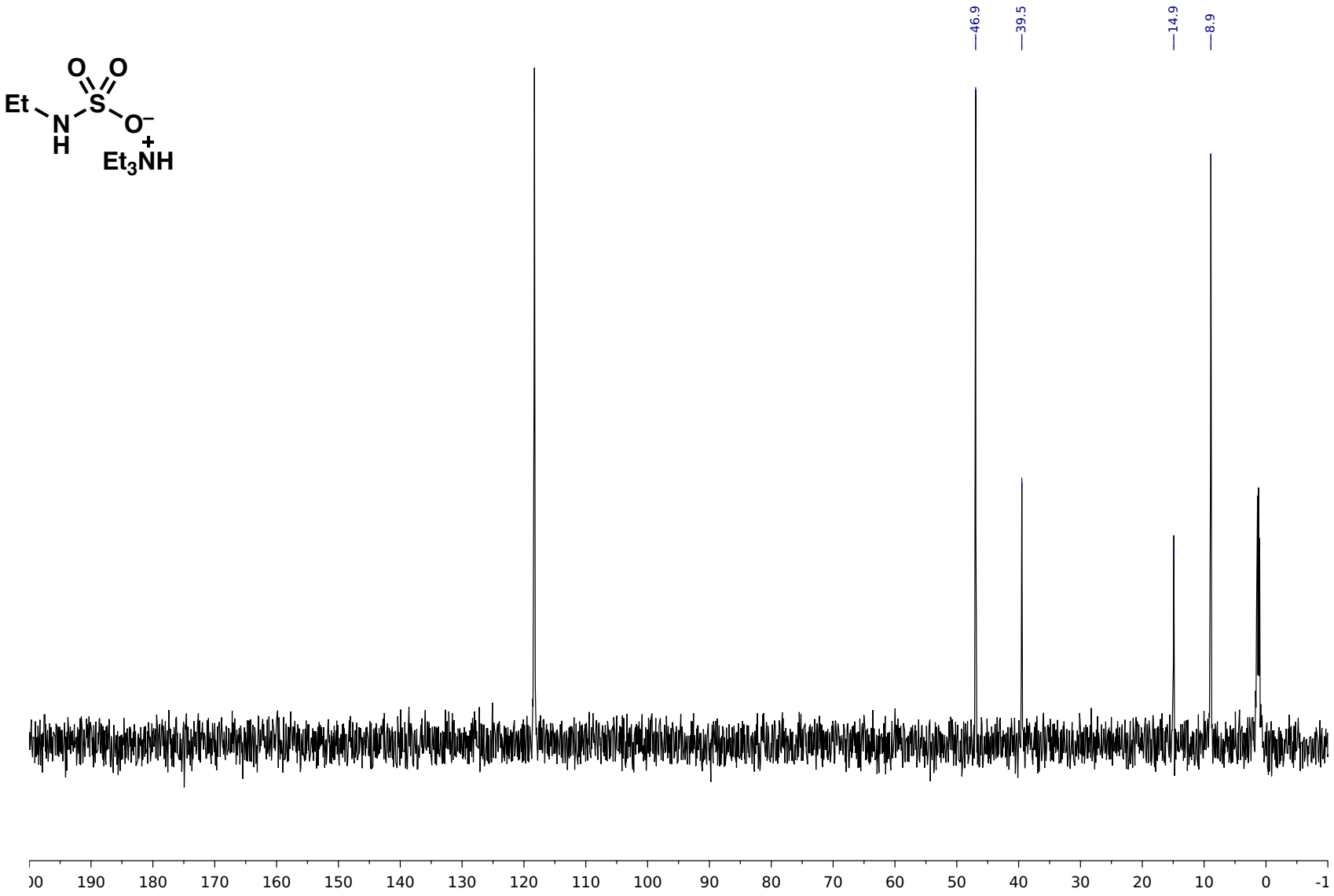
^{1}H NMR (400 MHz, $CDCl_3$) of triethylammonium *tert*-butylsulfamate (**2e**)



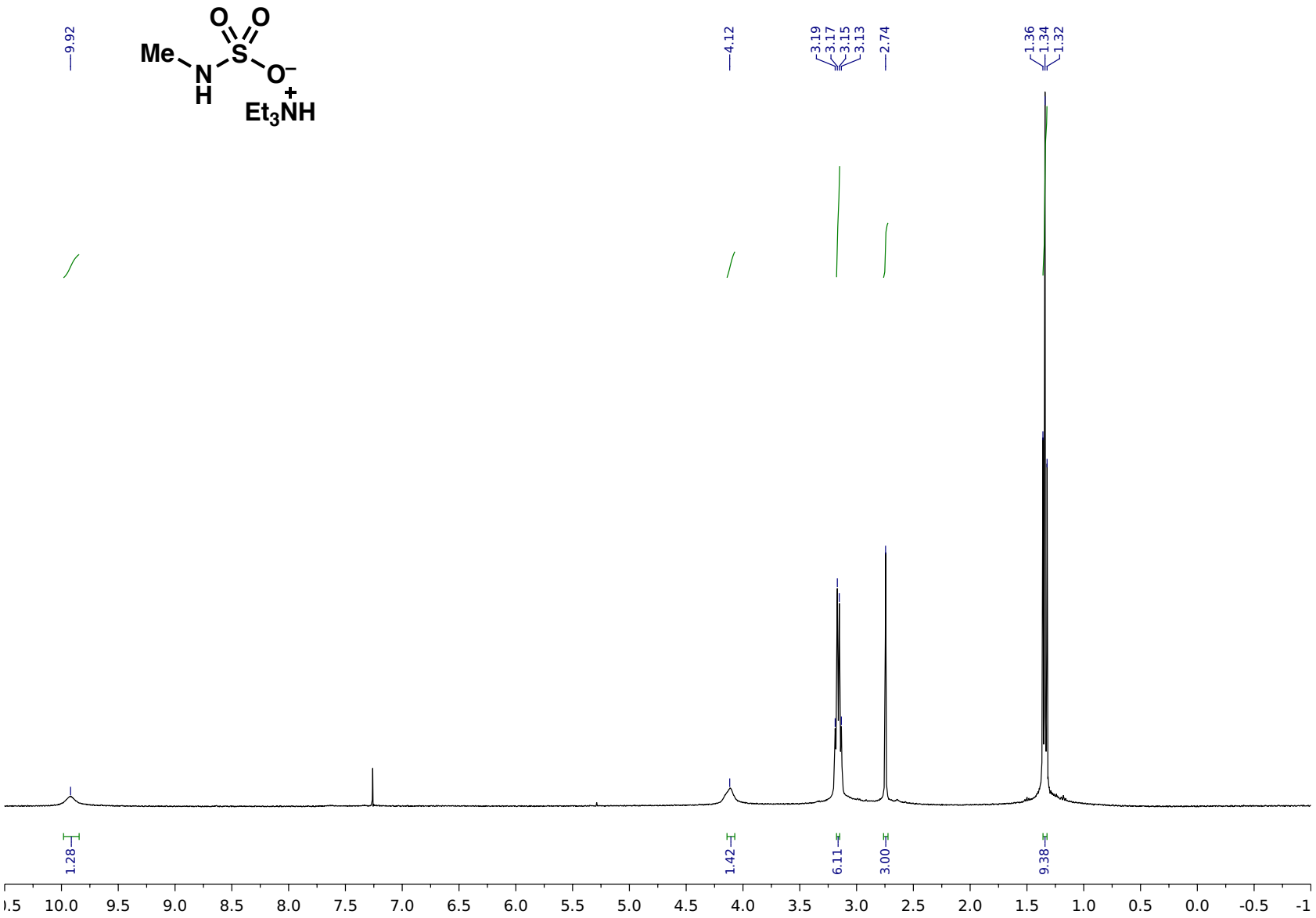
^{13}C NMR (126 MHz, CD_3CN) of triethylammonium *tert*-butylsulfamate (**2e**)



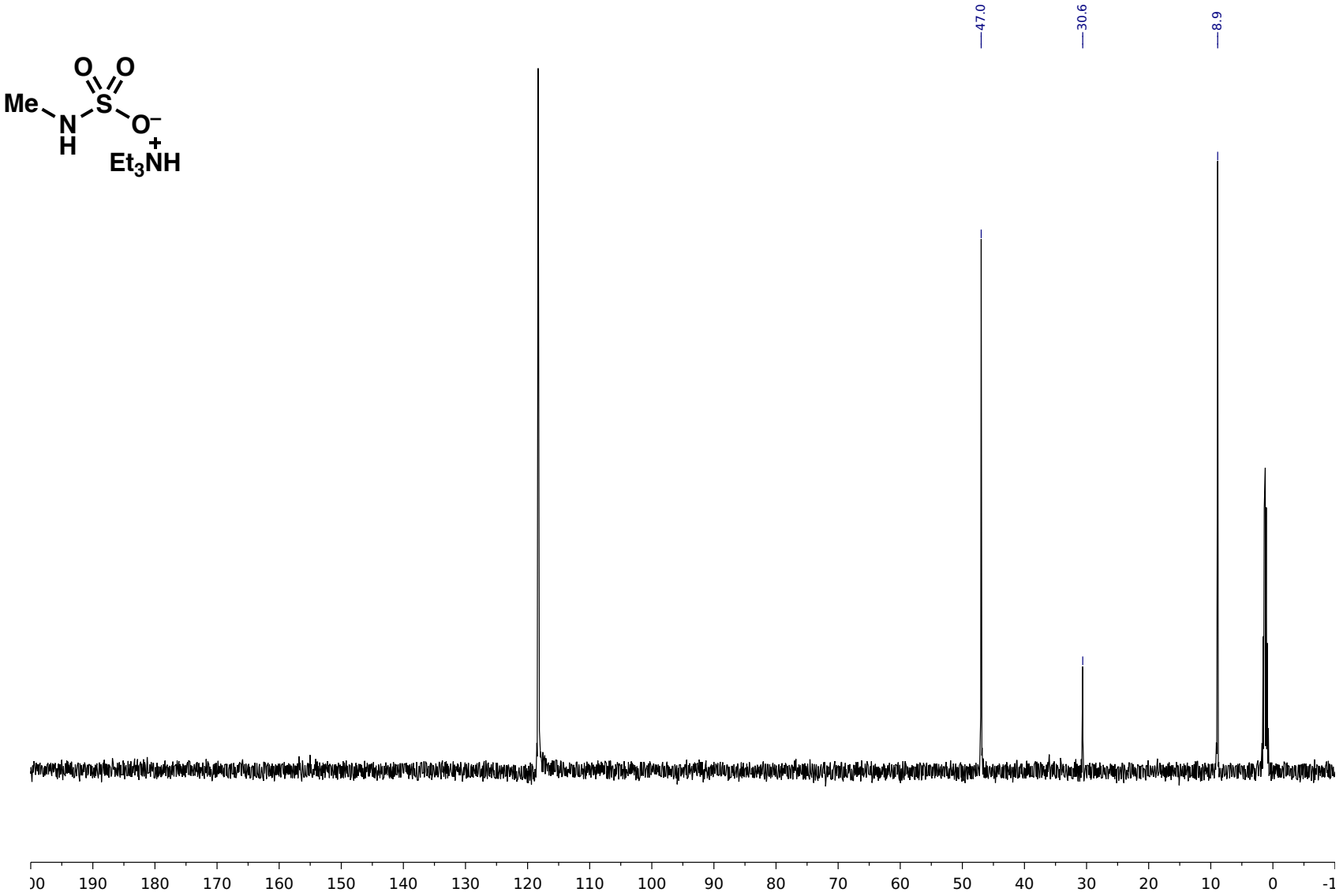
^{1}H NMR (400 MHz, CD_3CN) of triethylammonium ethylsulfamate (**2f**)



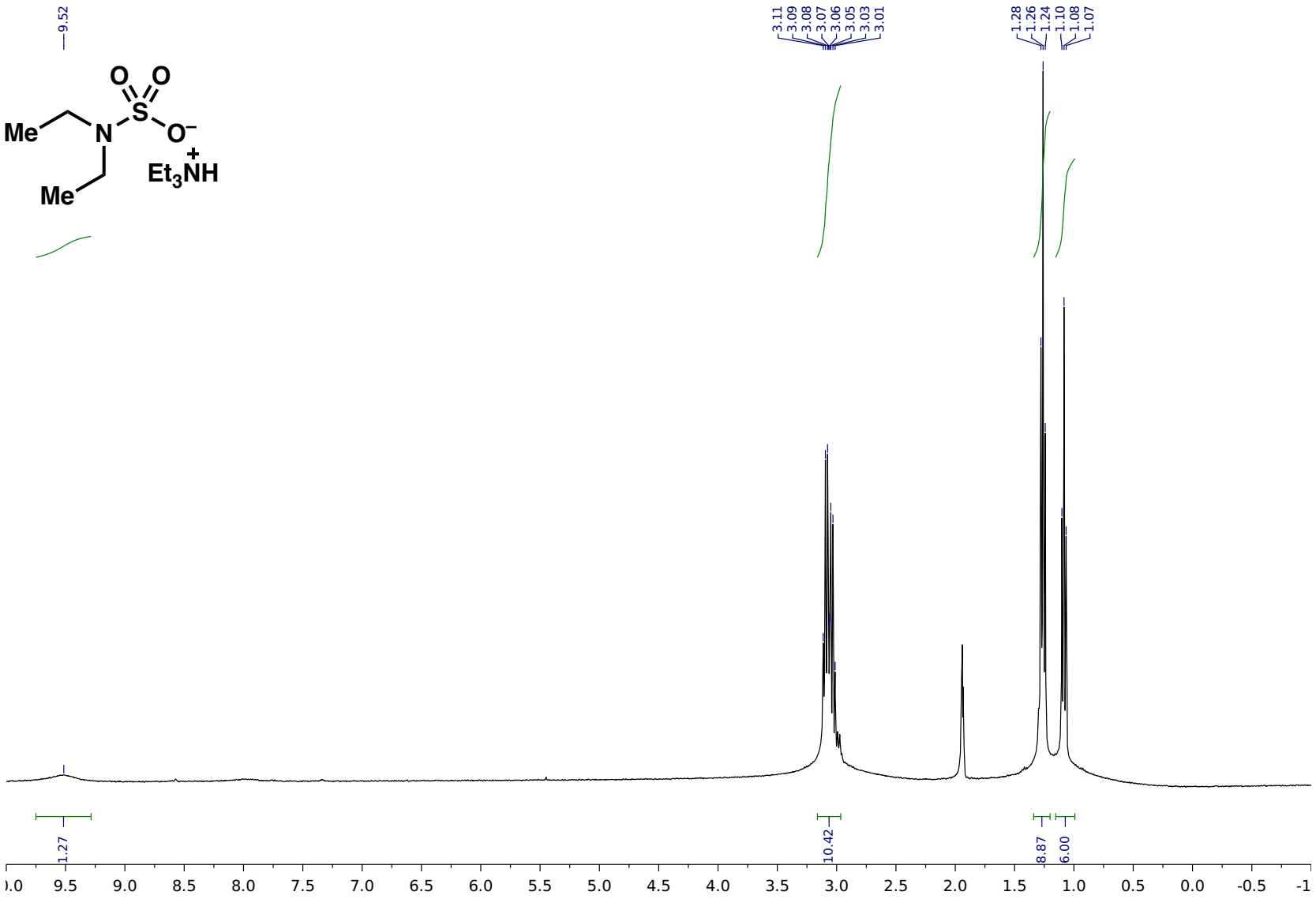
^{13}C NMR (400 MHz, CD_3CN) of triethylammonium ethylsulfamate (**2f**)



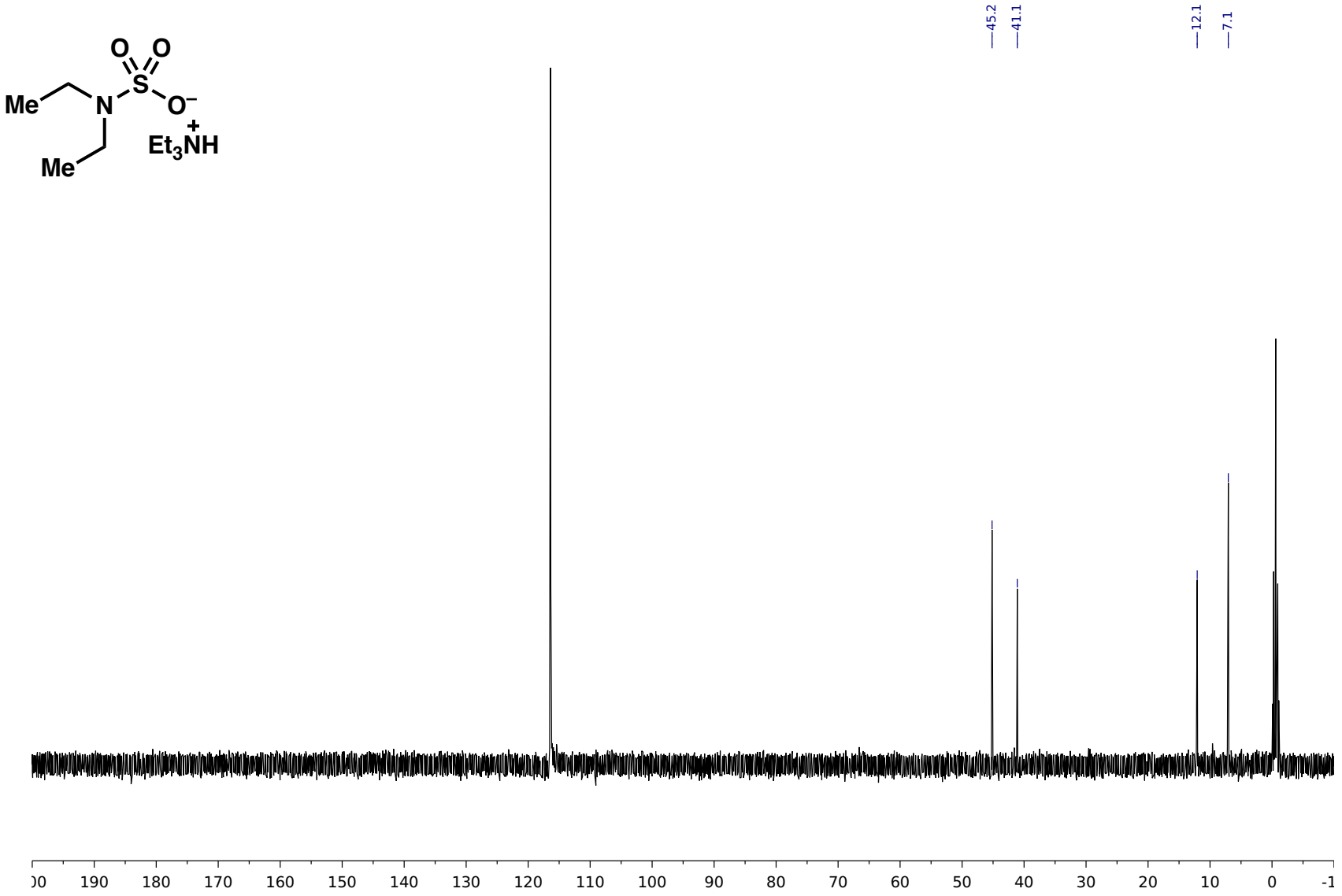
^{1}H NMR (400 MHz, $CDCl_3$) of triethylammonium methylsulfamate (**2g**)



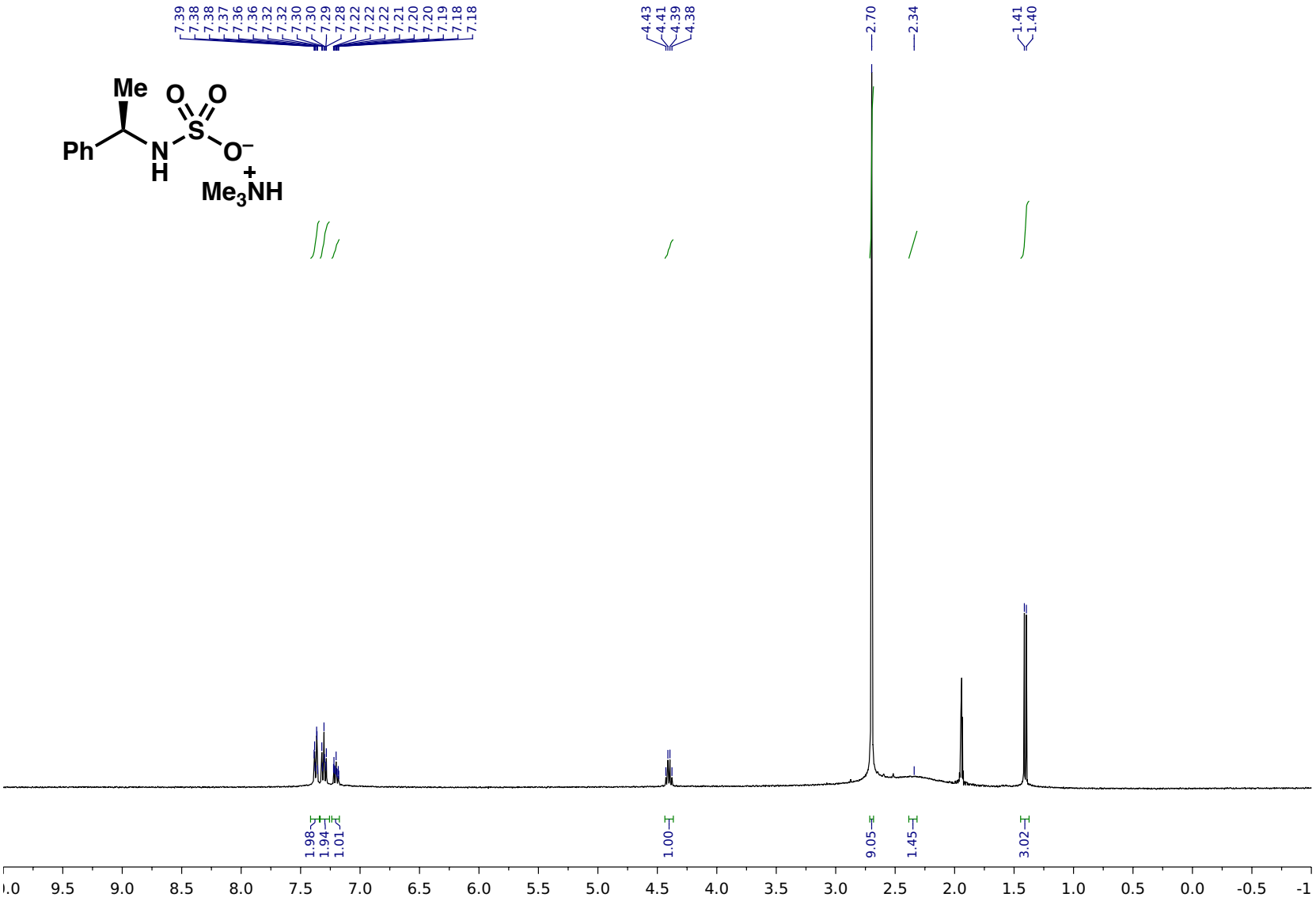
^{13}C NMR (126 MHz, CD_3CN) of triethylammonium methylsulfamate (**2g**)



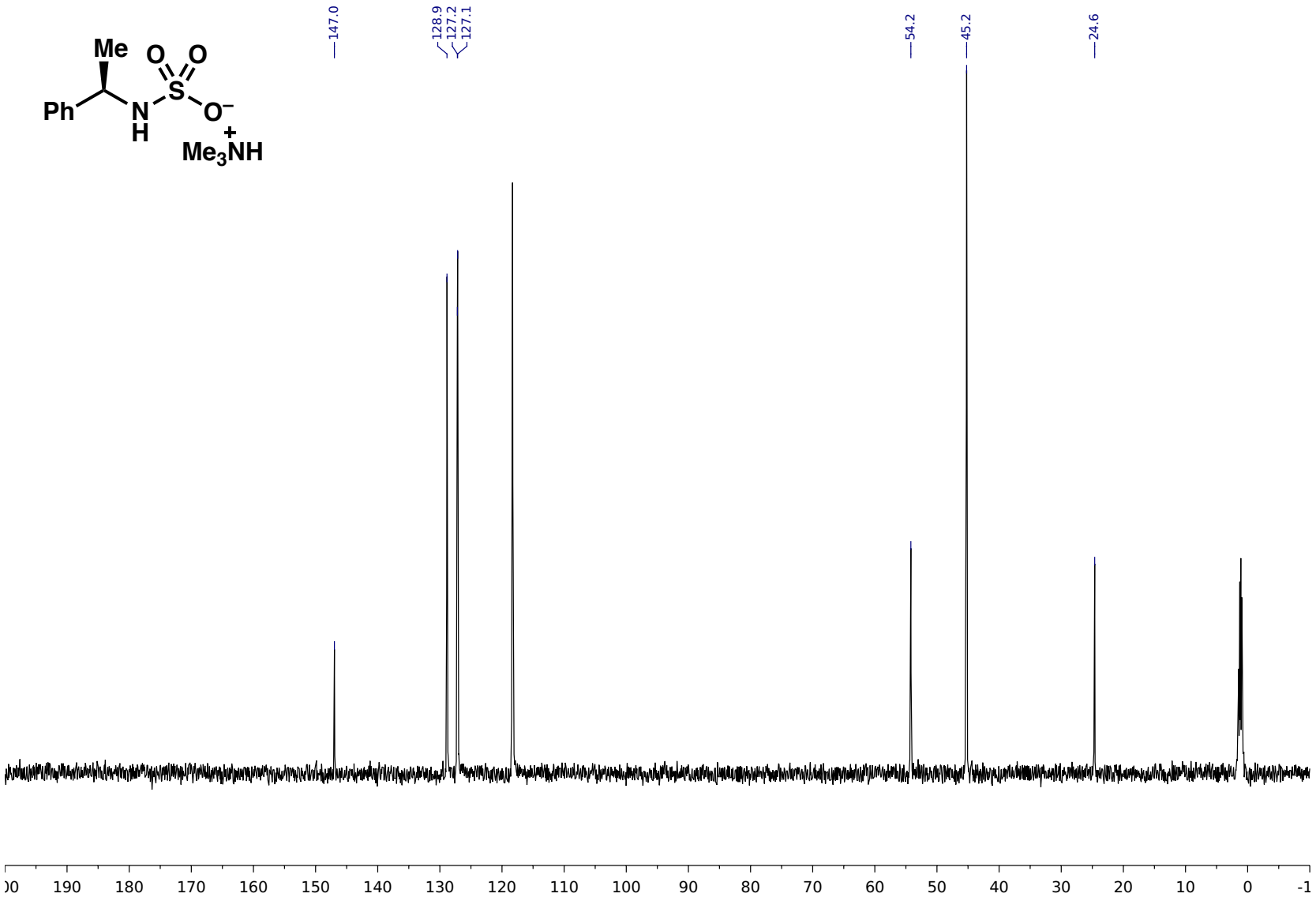
^{1}H NMR (400 MHz, CD_3CN) of triethylammonium diethylsulfamate (**2h**)



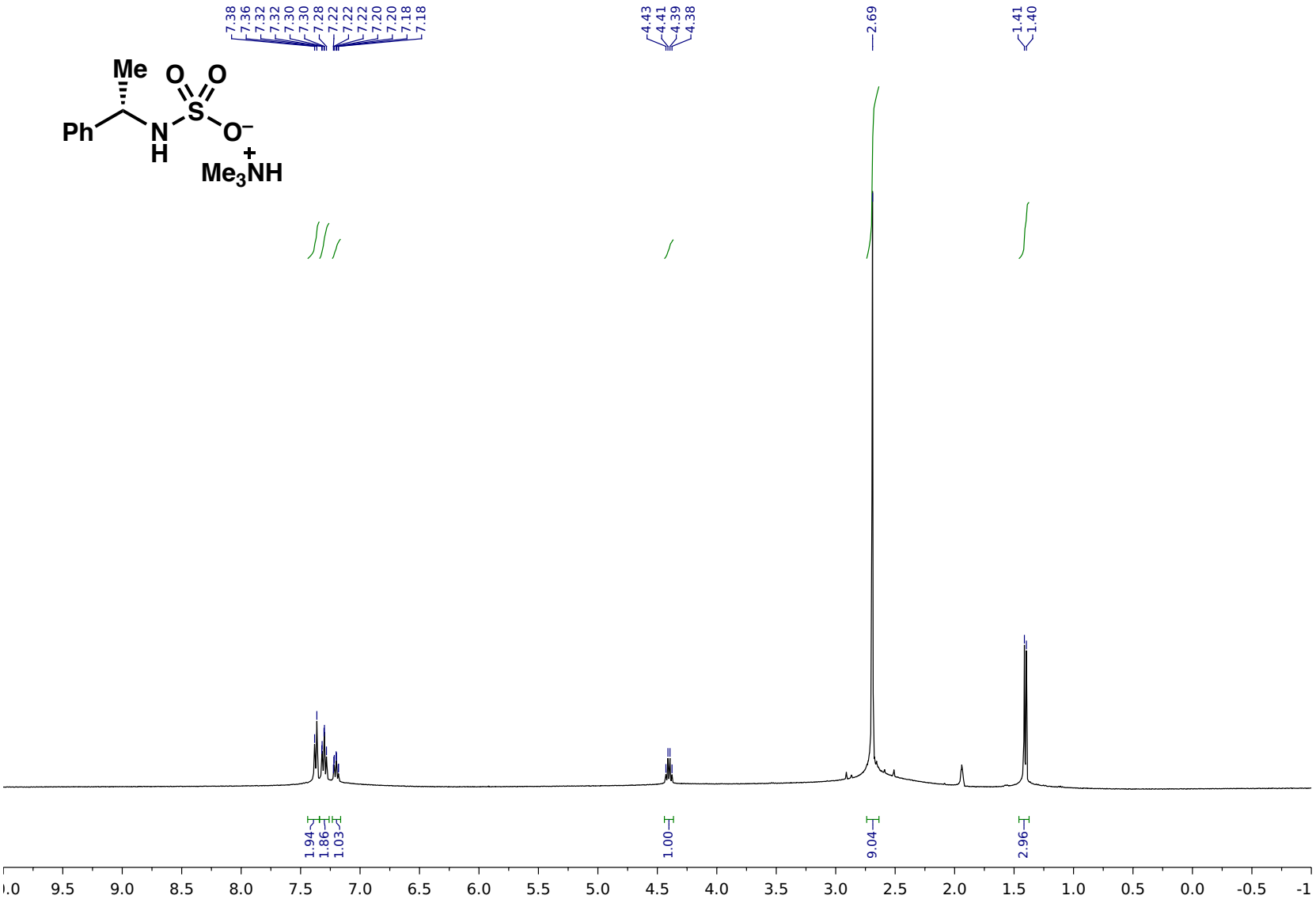
^{13}C NMR (126 MHz, CD_3CN) of triethylammonium diethylsulfamate (**2h**)



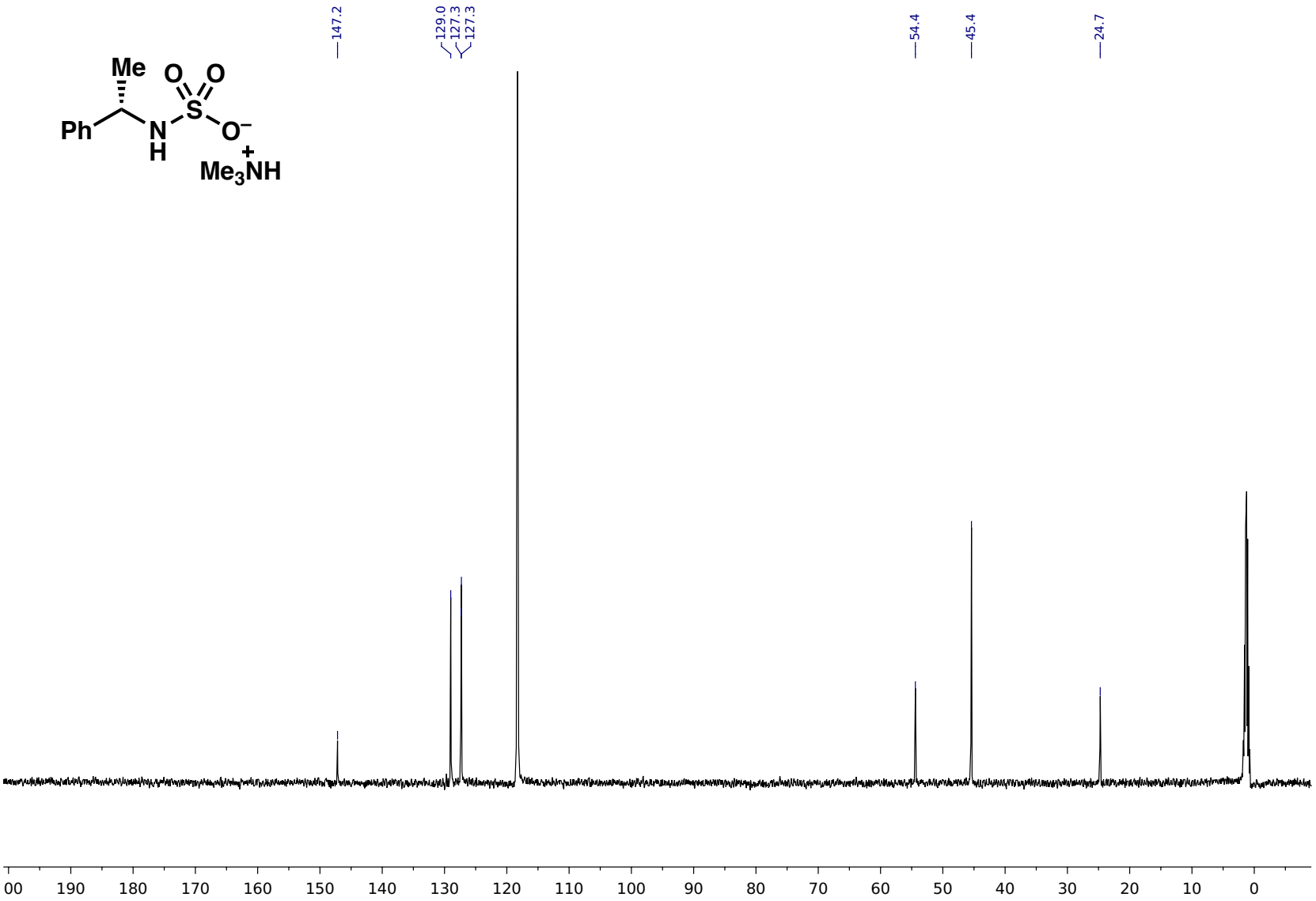
^{1}H NMR (400 MHz, CD_3CN) of triethylammonium (*R*)-(1-phenylethyl)sulfamate (**2i**)



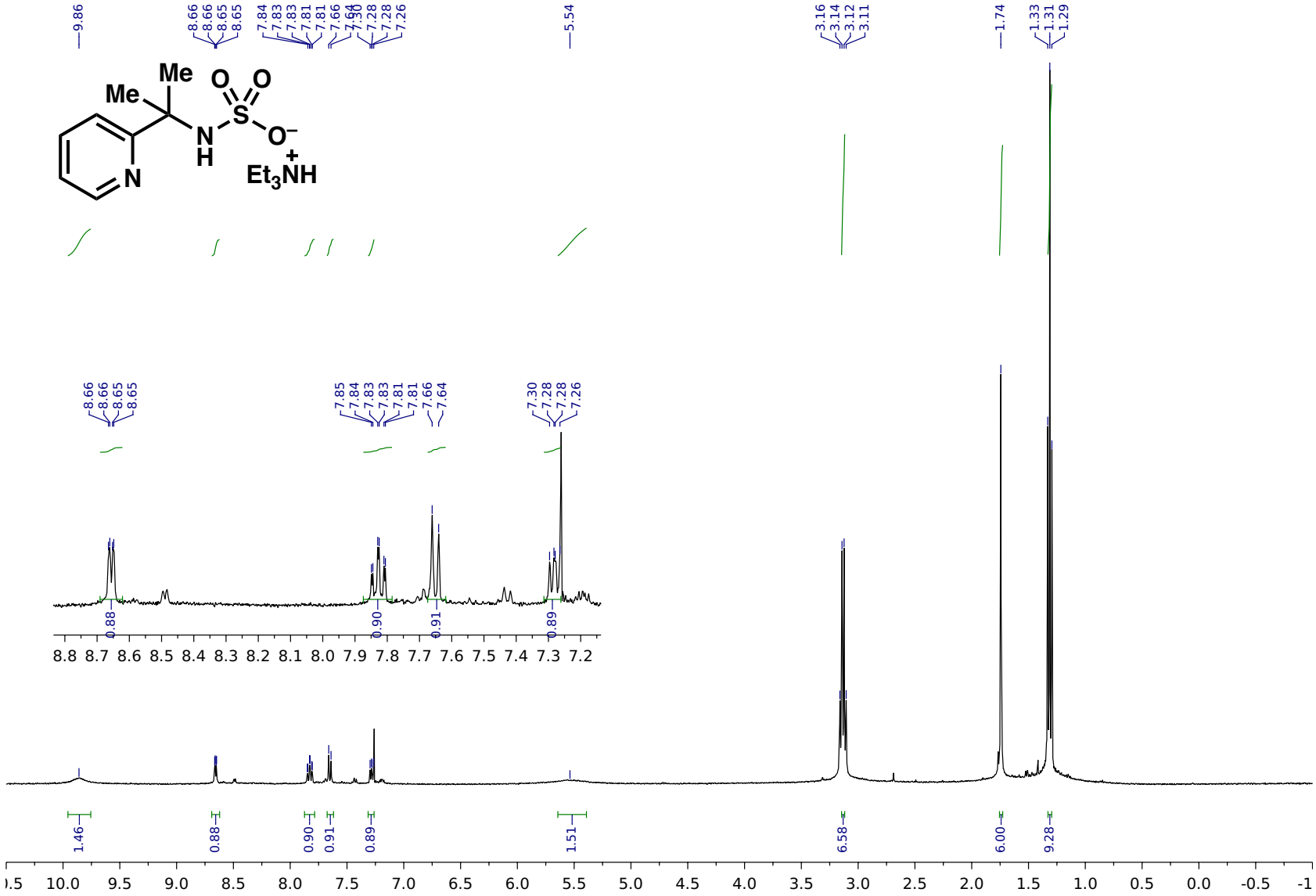
^{13}C NMR (500 MHz, CD_3CN) of triethylammonium (*R*)-(1-phenylethyl)sulfamate (**2i**)



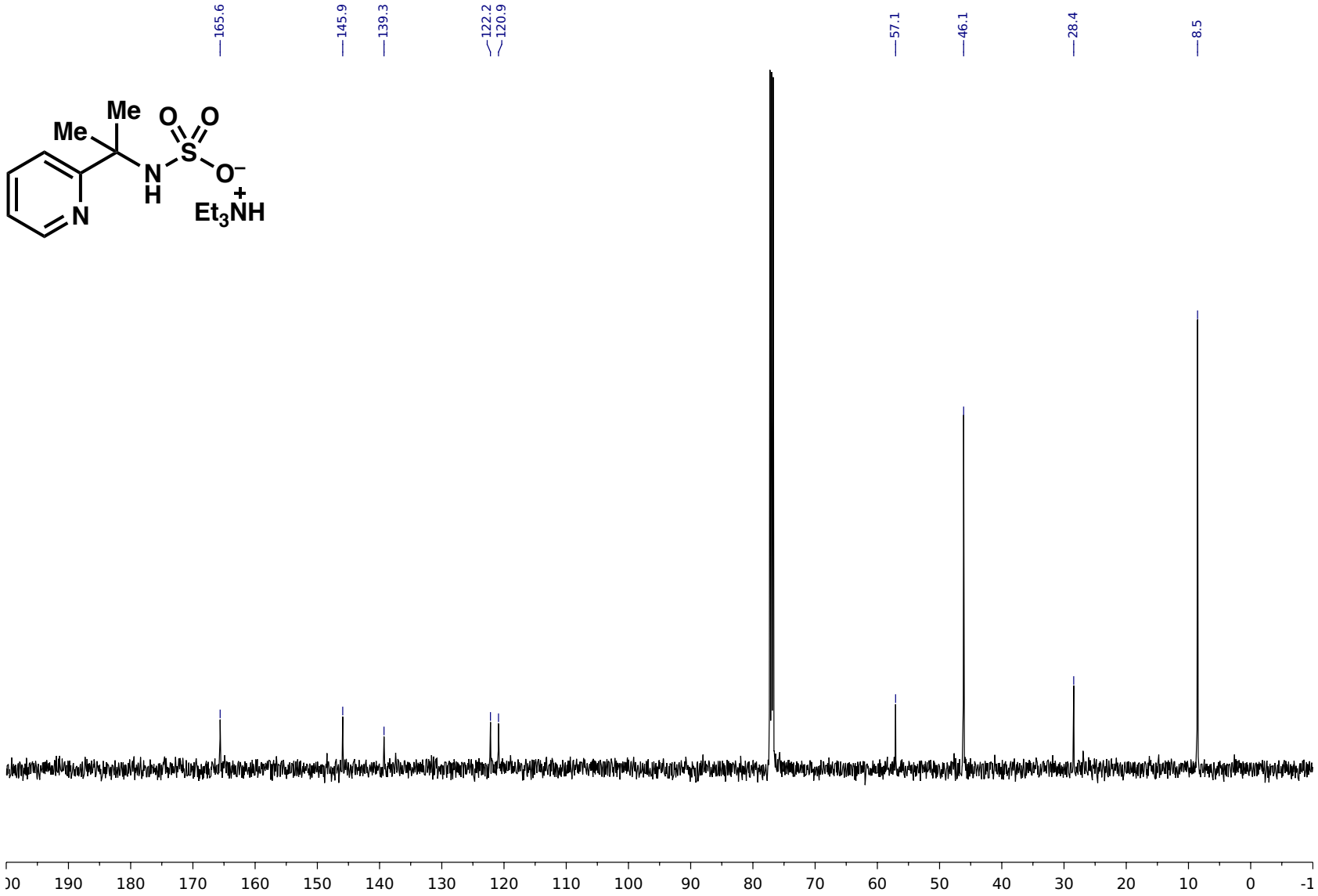
^{1}H NMR (400 MHz, CD_3CN) of triethylammonium (*S*)-(1-phenylethyl)sulfamate (**S2a**)



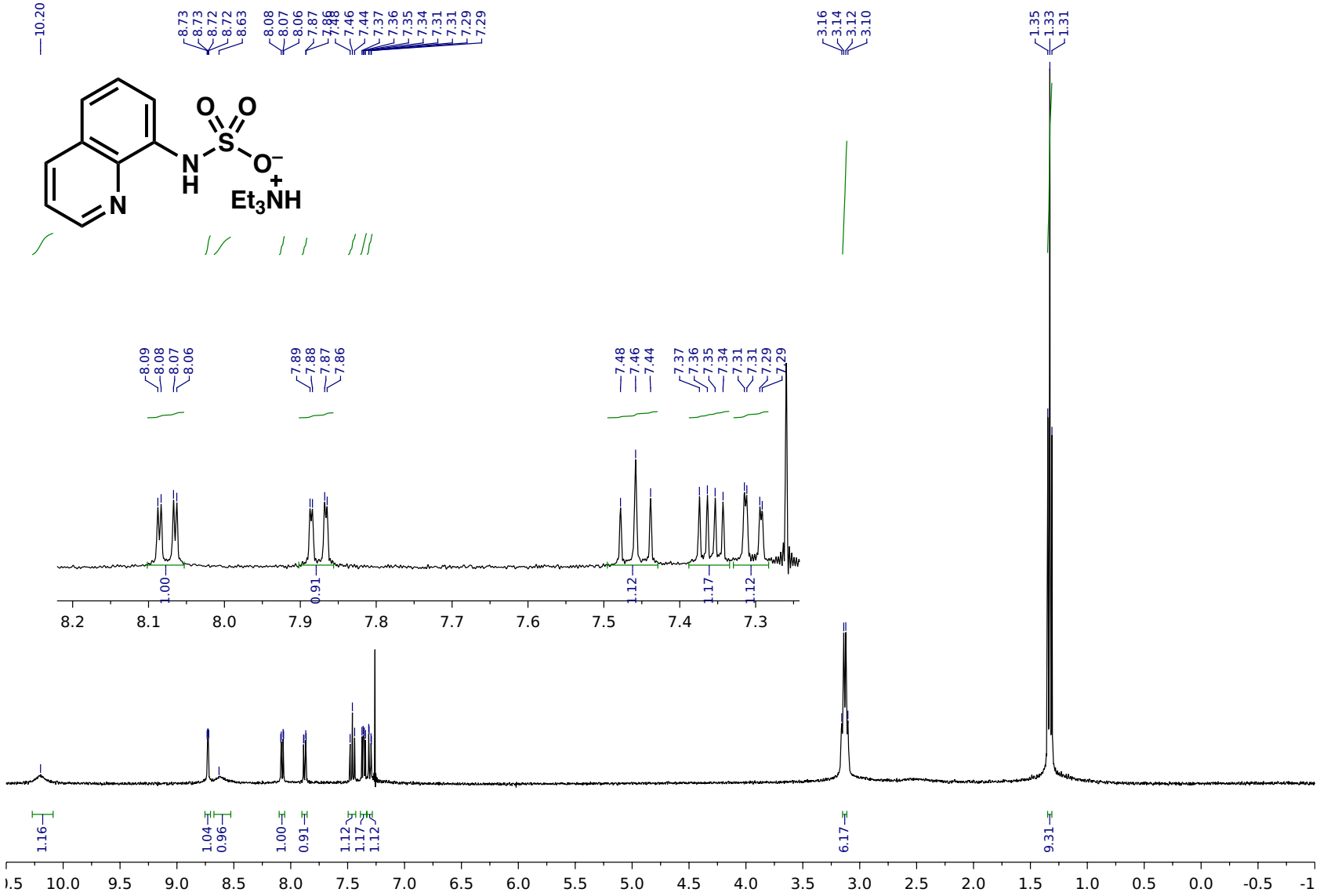
^{13}C NMR (500 MHz, CD_3CN) of triethylammonium (*S*)-(1-phenylethyl)sulfamate (**S2a**)



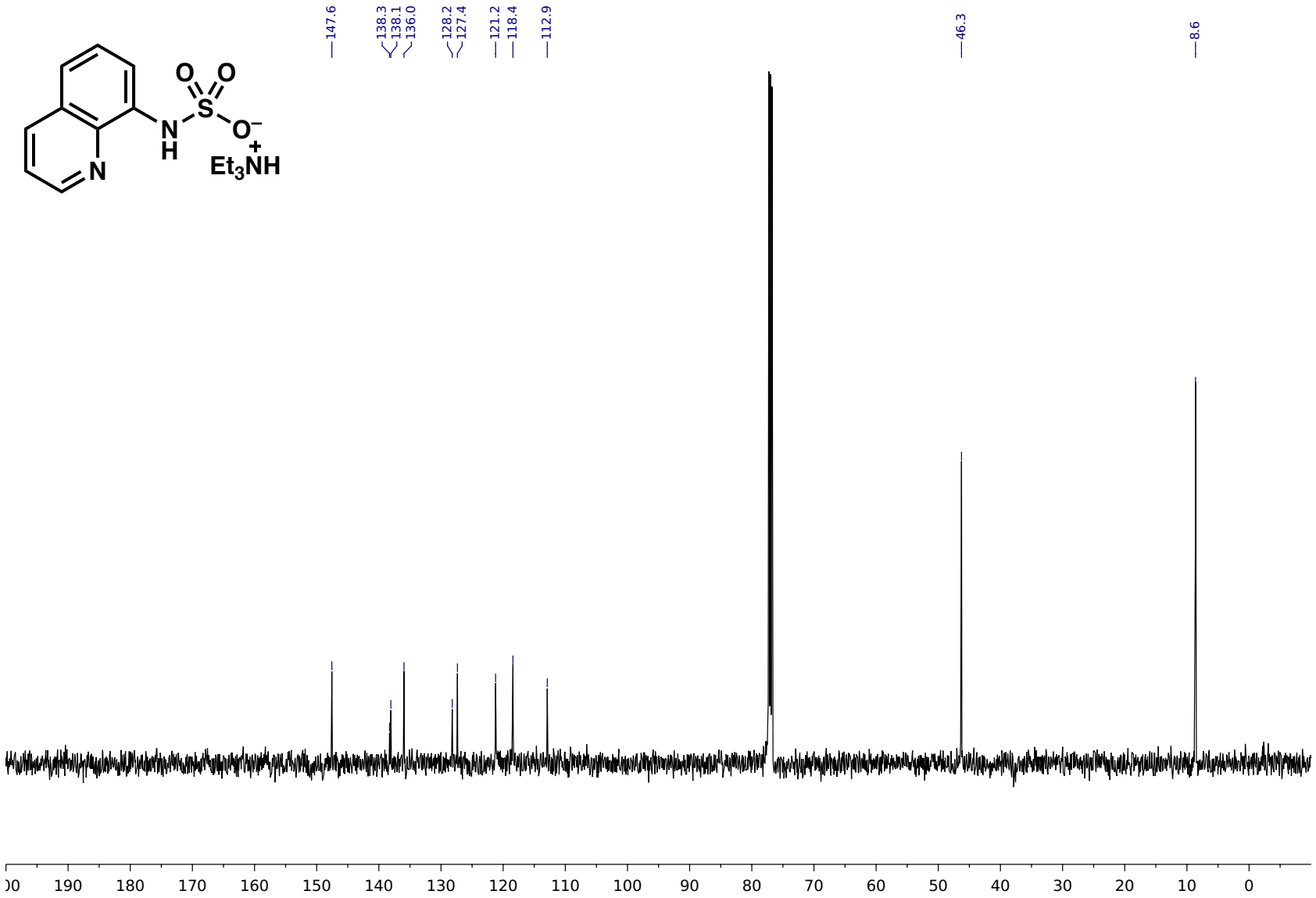
^{1}H NMR (400 MHz, $CDCl_3$) of triethylammonium 2-((pyridin-2-yl)propan-2-yl)sulfamte (**2j**)



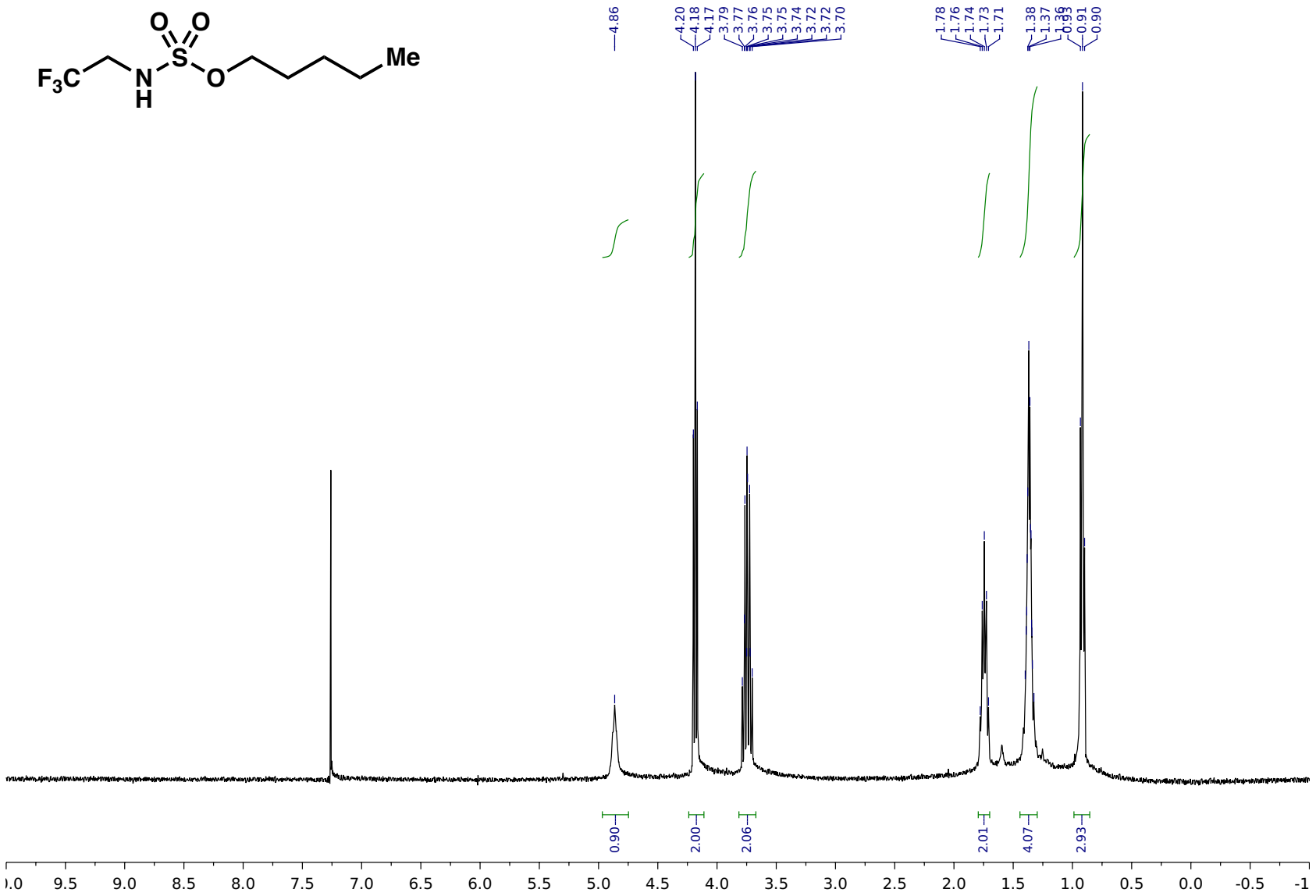
^{13}C NMR (126 MHz, $CDCl_3$) of triethylammonium 2-((pyridin-2-yl)propan-2-yl)sulfamte (**2j**)



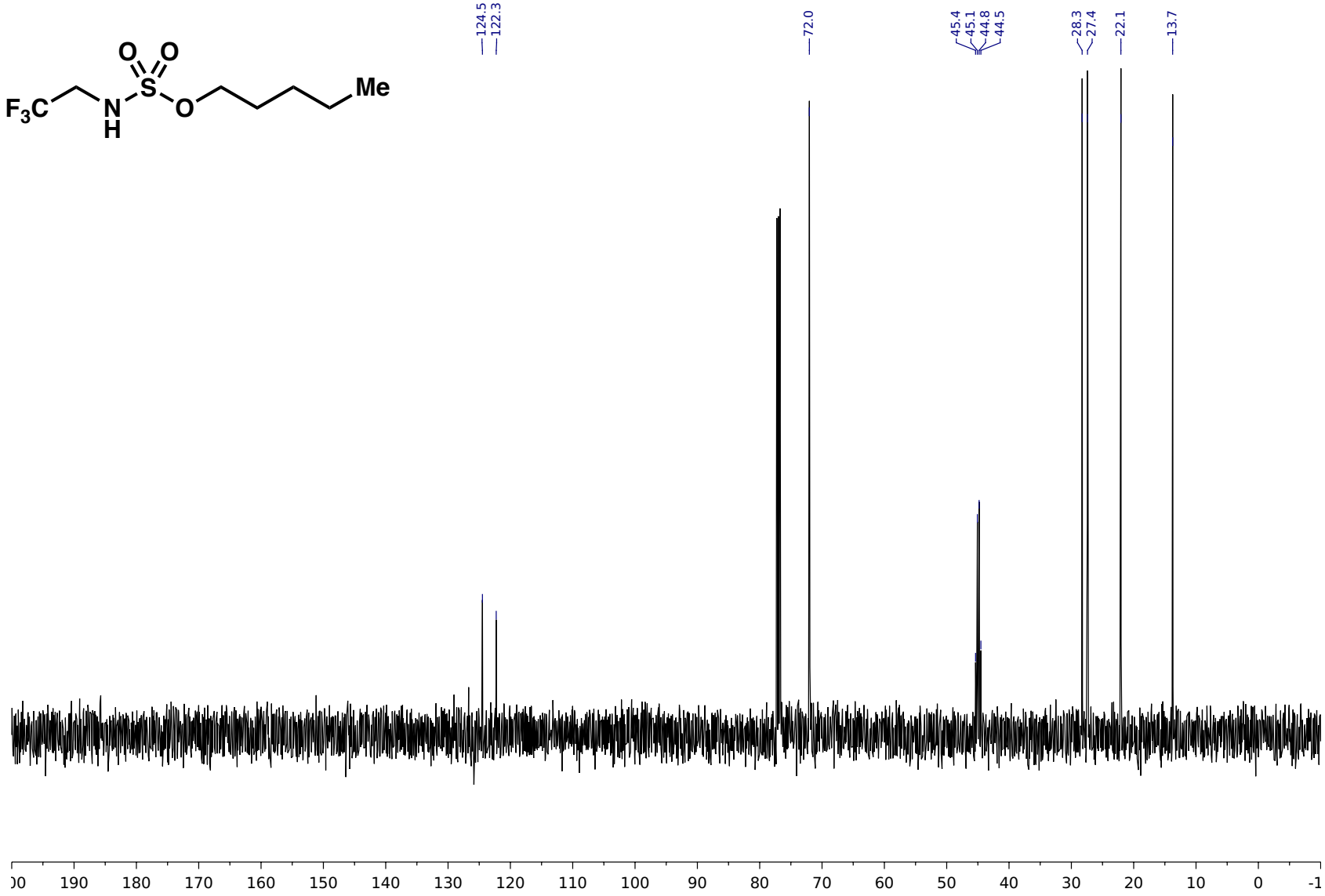
^{1}H NMR (400 MHz, $CDCl_3$) of triethylammonium quinolin-8-ylsulfamate (**2k**)



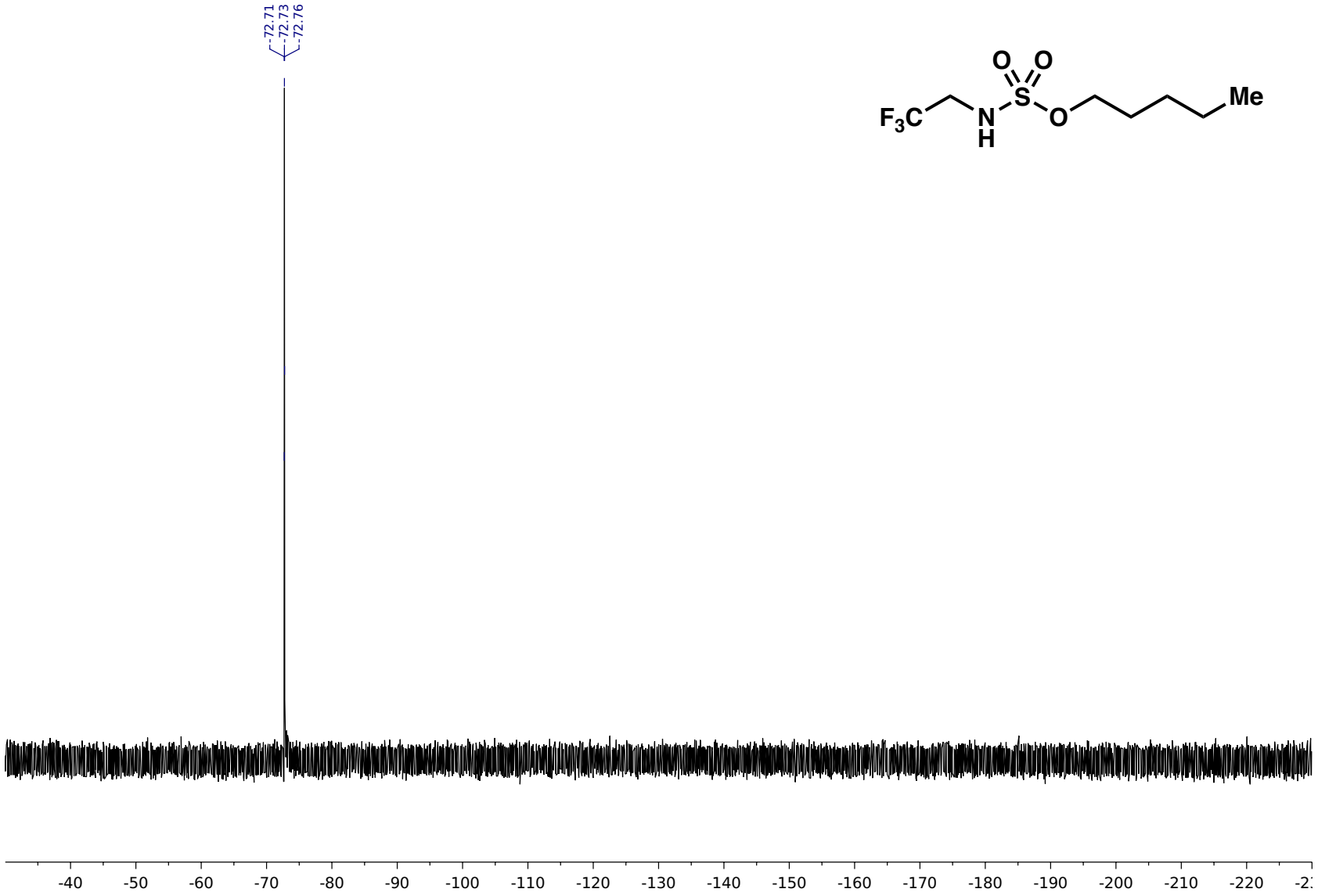
^{13}C (126 MHz, $CDCl_3$) of triethylammonium quinolin-8-ylsulfamate (**2k**)



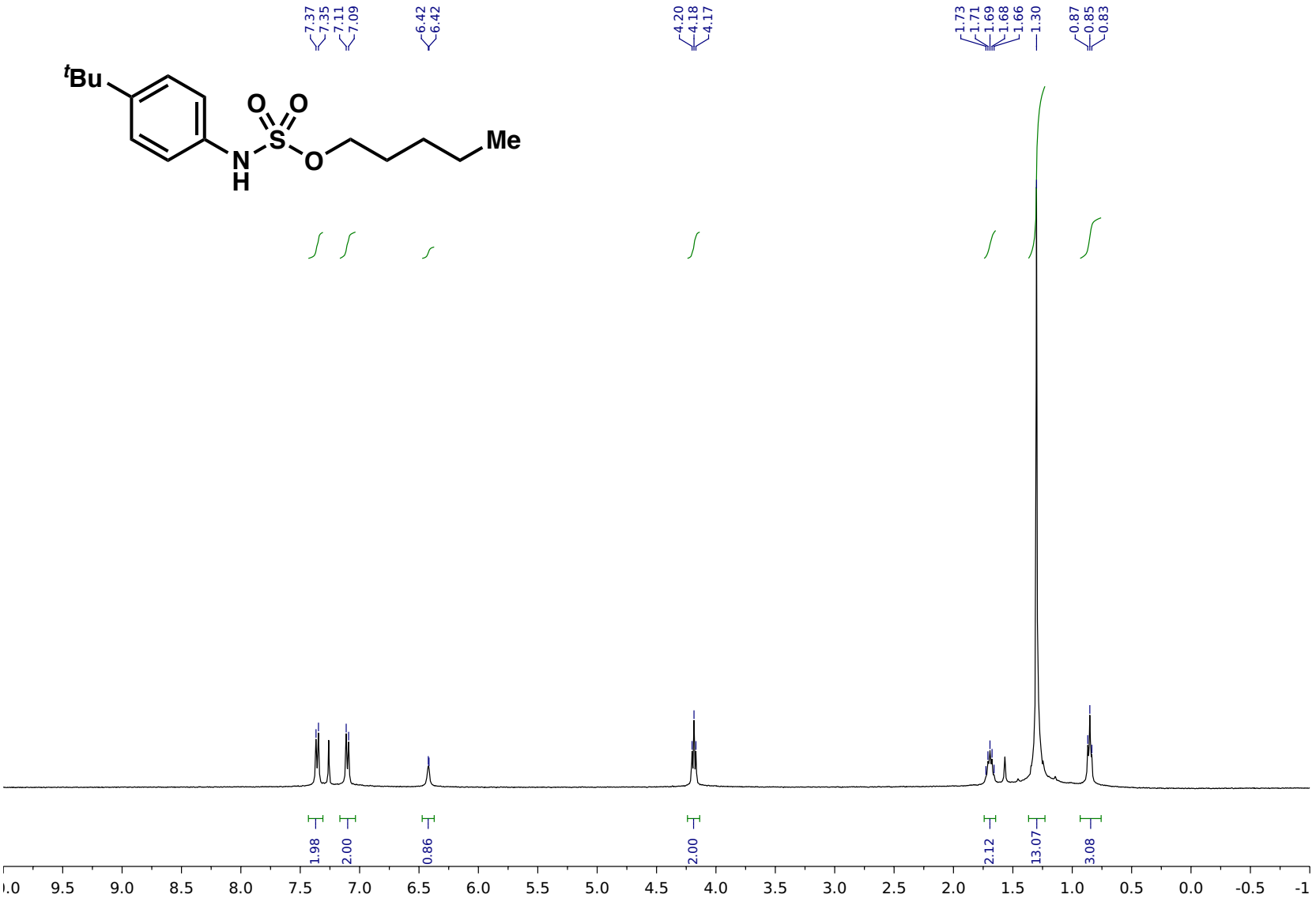
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl (2,2,2-trifluoroethyl)sulfamate (**4a**)



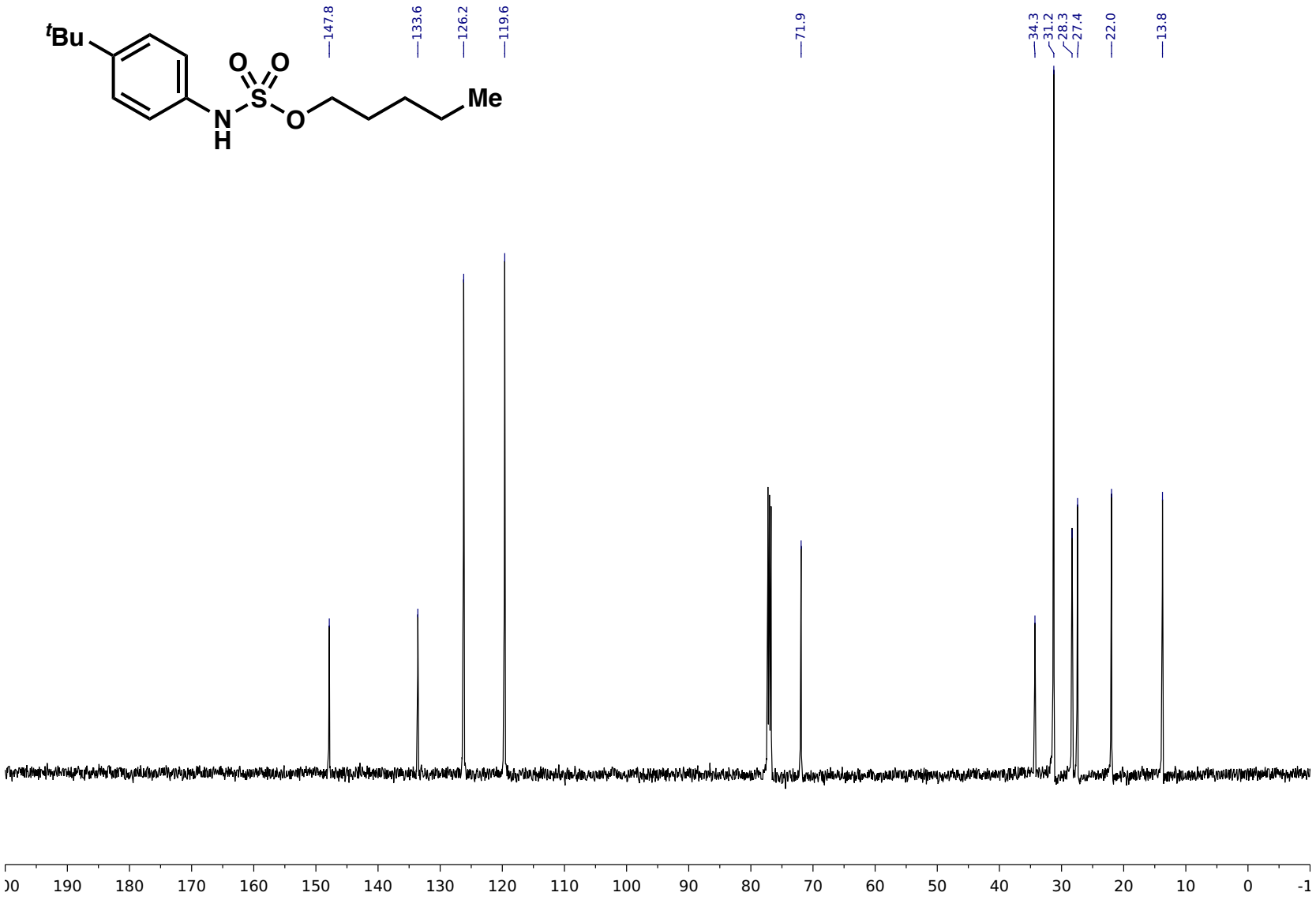
^{13}C NMR (126 MHz, $CDCl_3$) of pentyl (2,2,2-trifluoroethyl)sulfamate (**4a**)



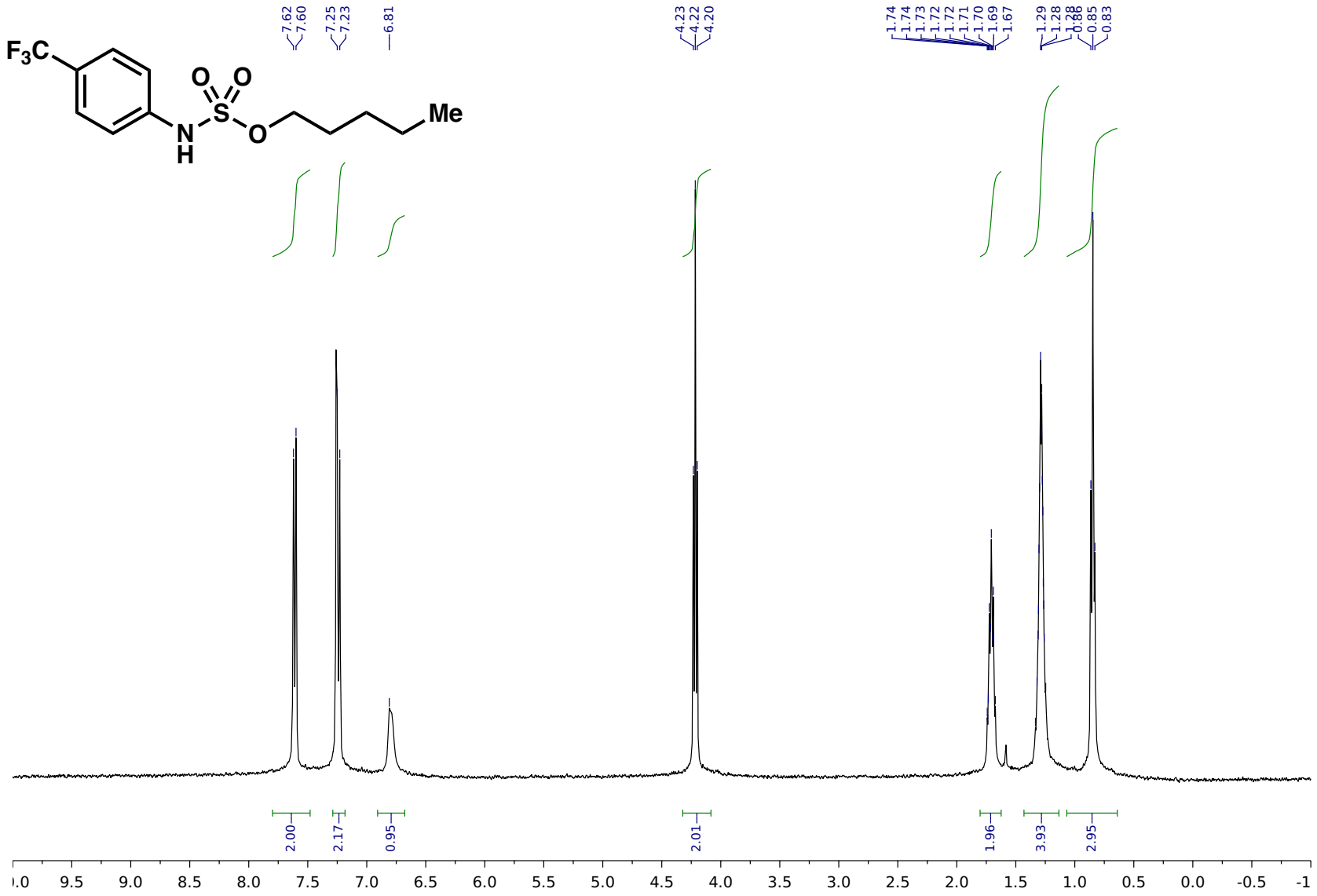
^{19}F NMR (376 MHz, $CDCl_3$) of pentyl (2,2,2-trifluoroethyl)sulfamate (**4a**)



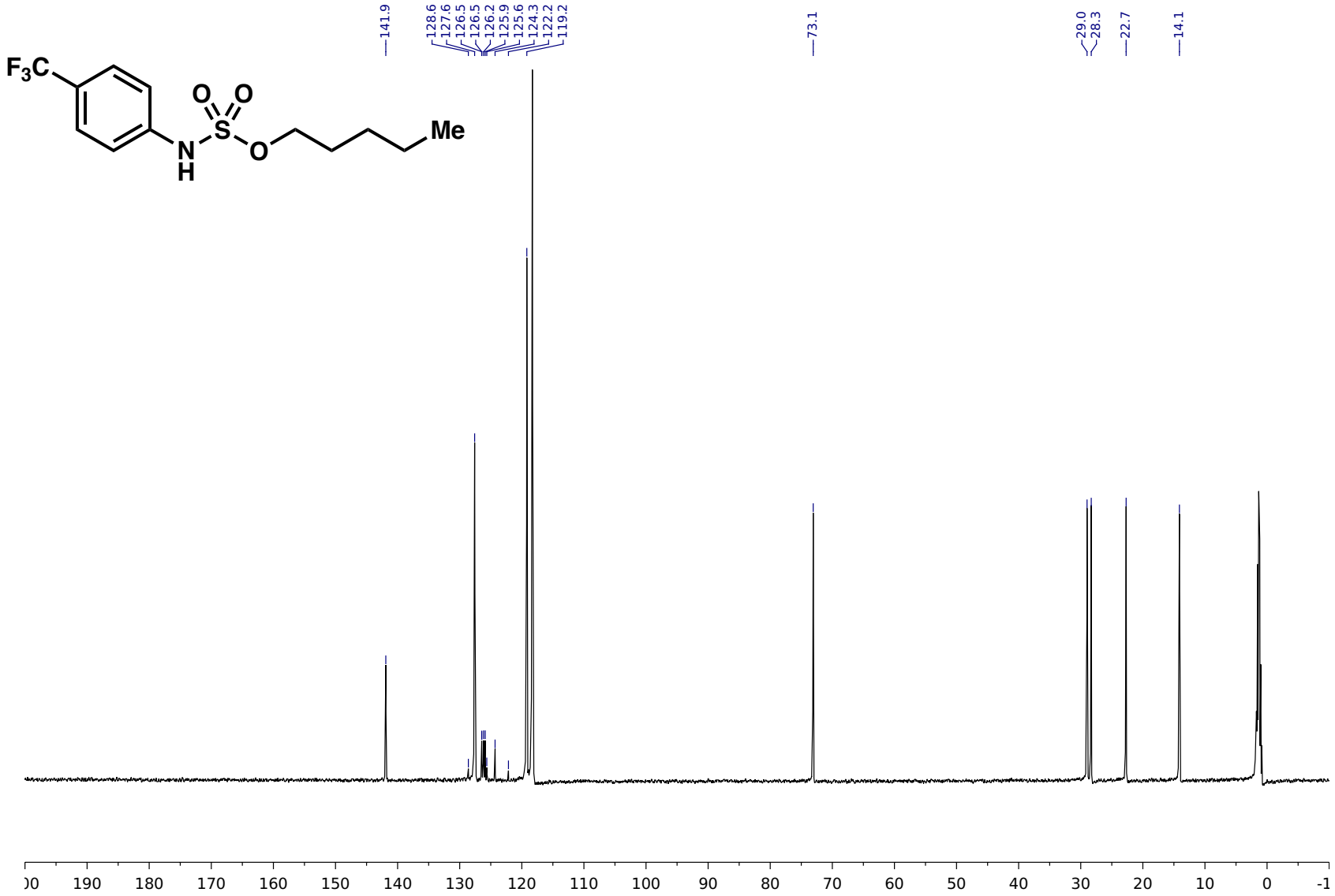
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl (4-*tert*-butyl)phenyl)sulfamate (**4c**)



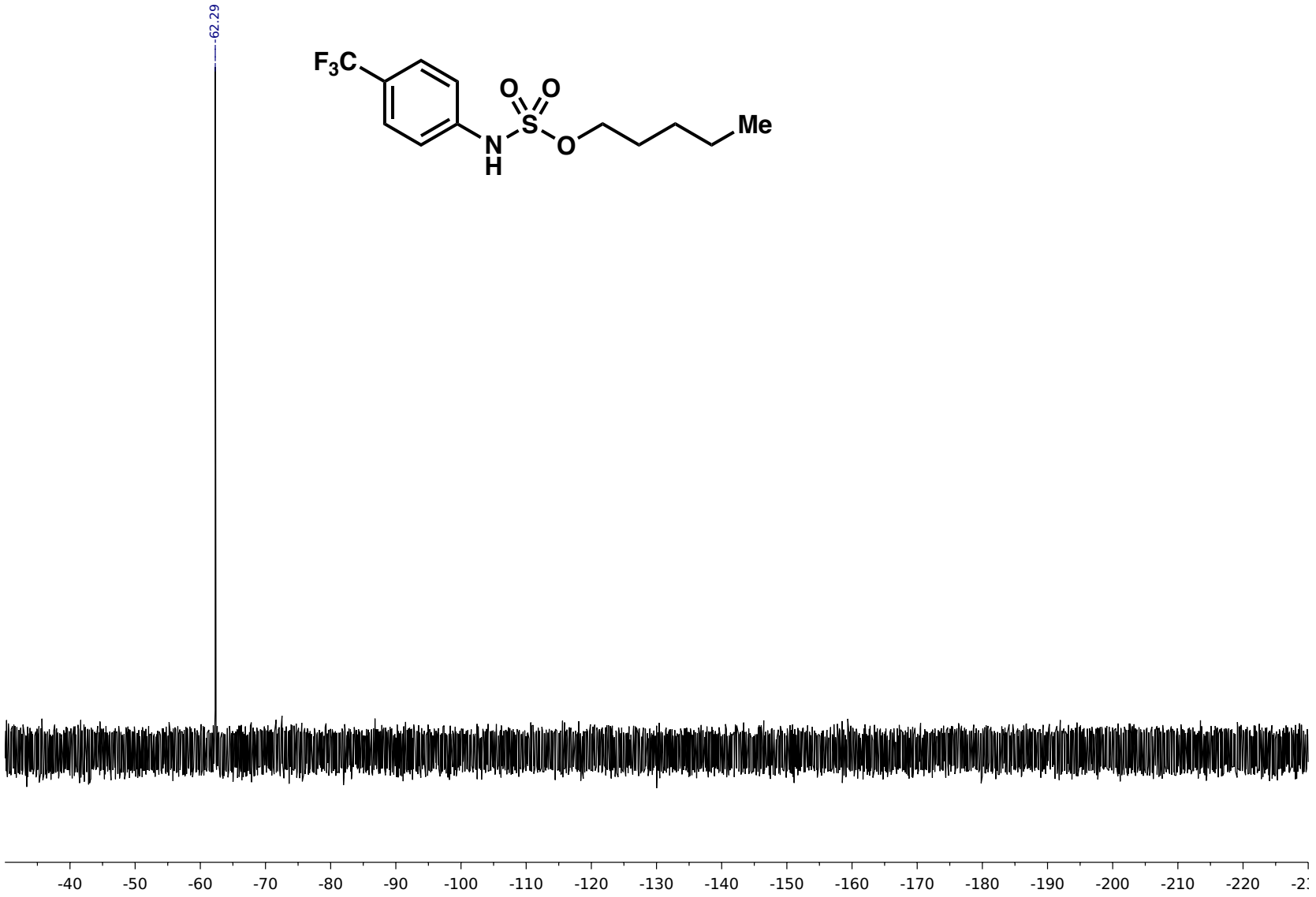
^{13}C NMR (500 MHz, $CDCl_3$) of pentyl (4-*tert*-butyl)phenyl)sulfamate (**4c**)



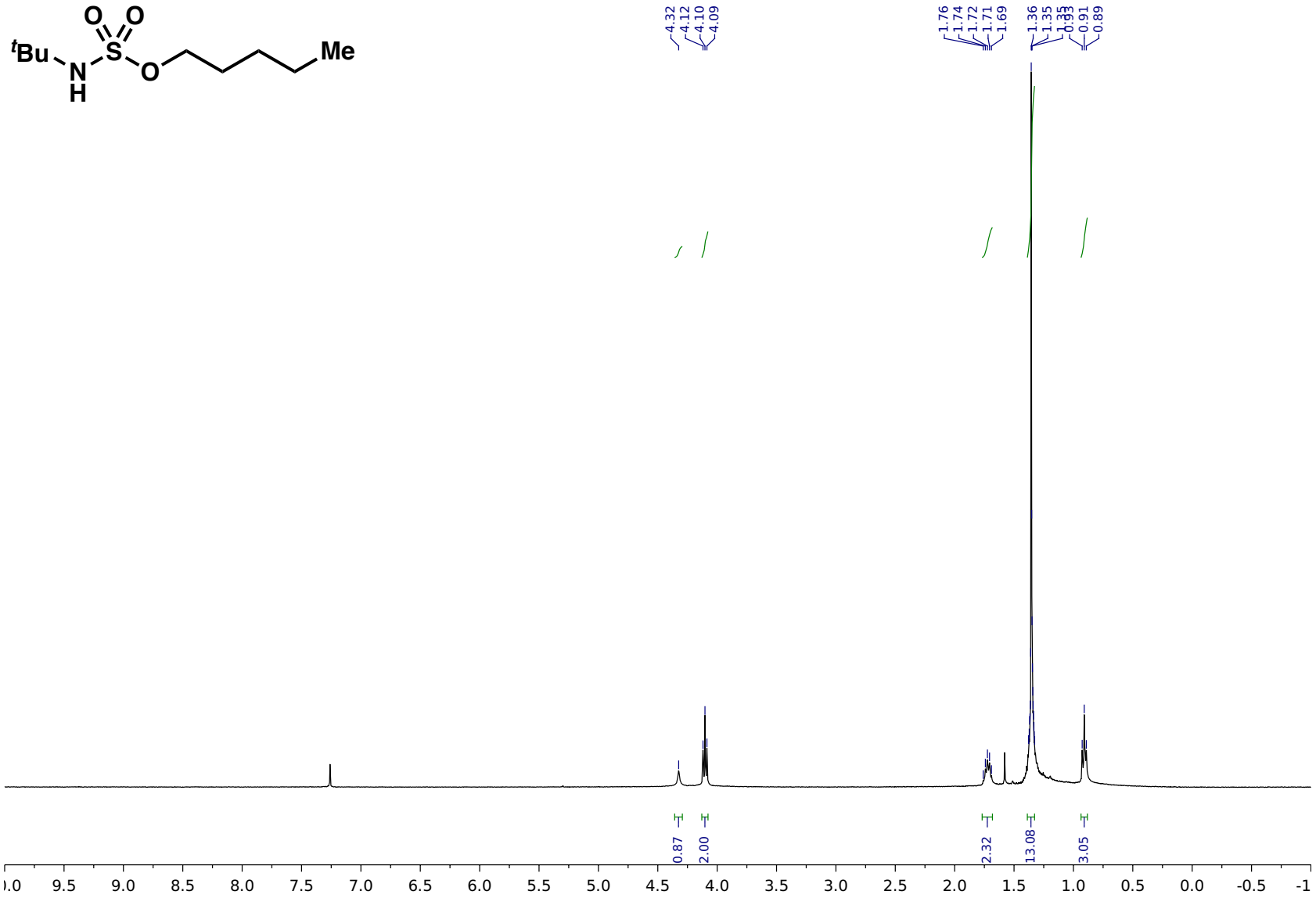
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl (4-(trifluoromethyl)phenyl)sulfamate (**4d**)



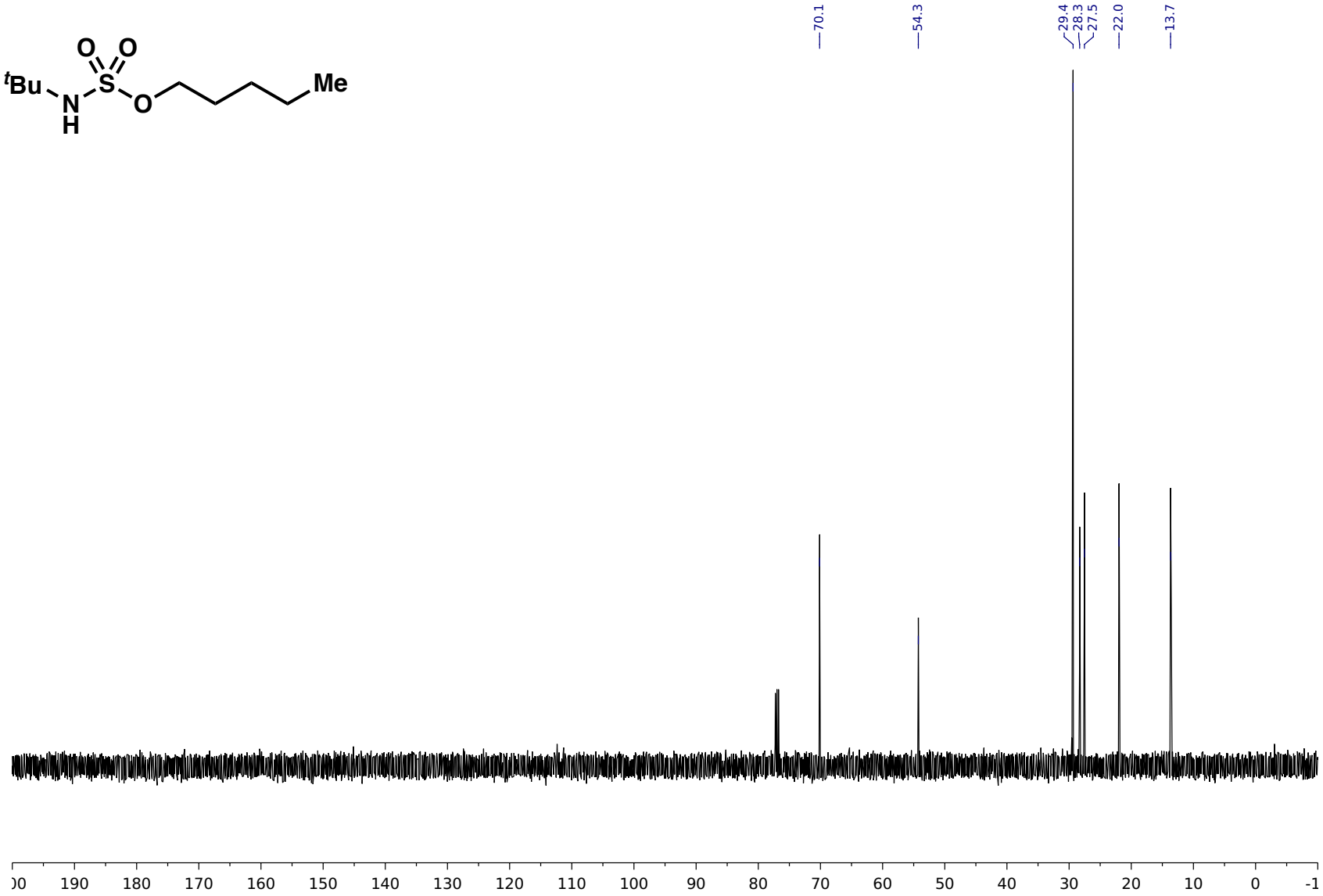
^{13}C NMR (126 MHz, $CDCl_3$) of pentyl (4-(trifluoromethyl)phenyl)sulfamate (**4d**)



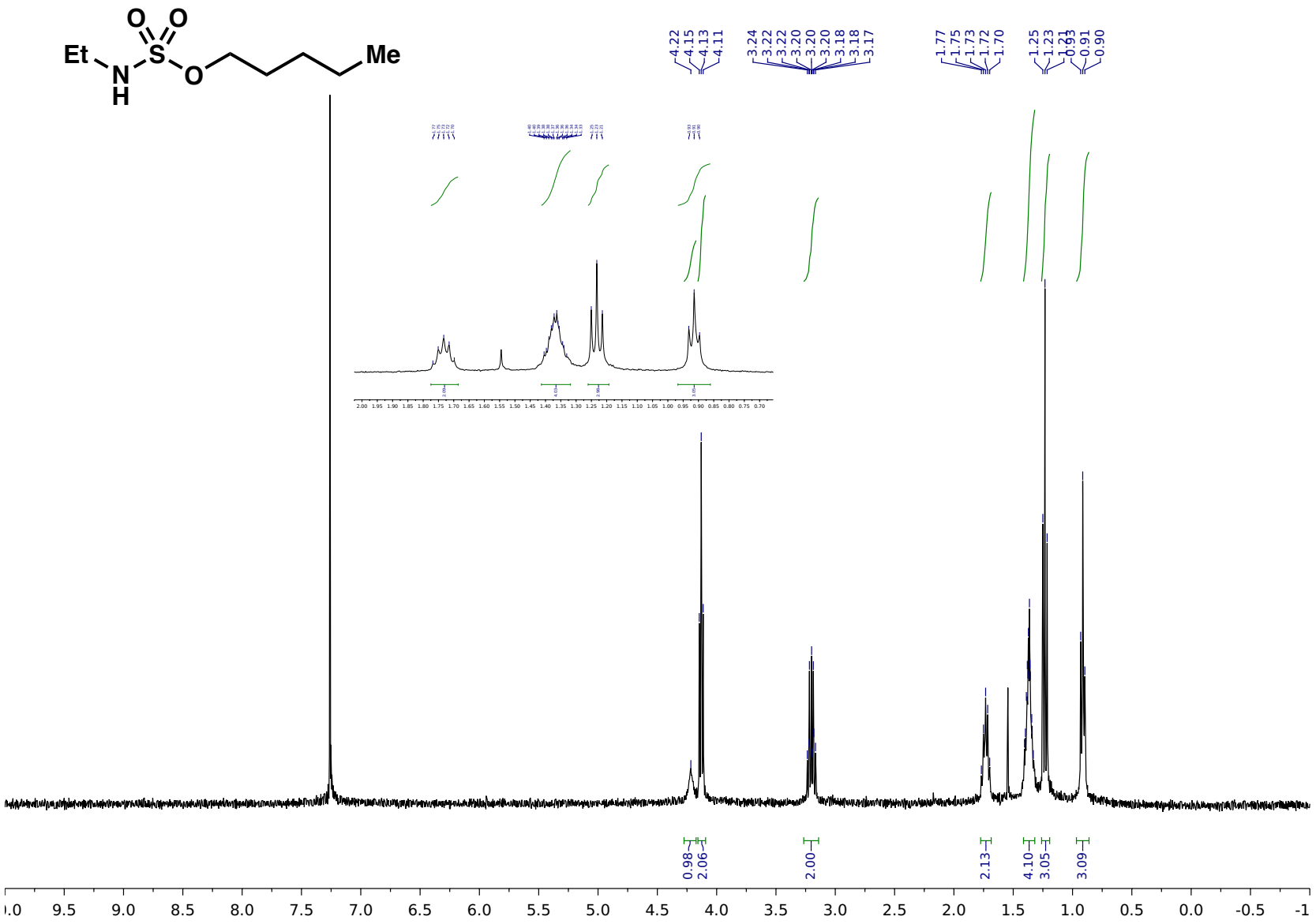
^{19}F NMR (376 MHz, $CDCl_3$) of pentyl (4-(trifluoromethyl)phenyl)sulfamate (**4d**)



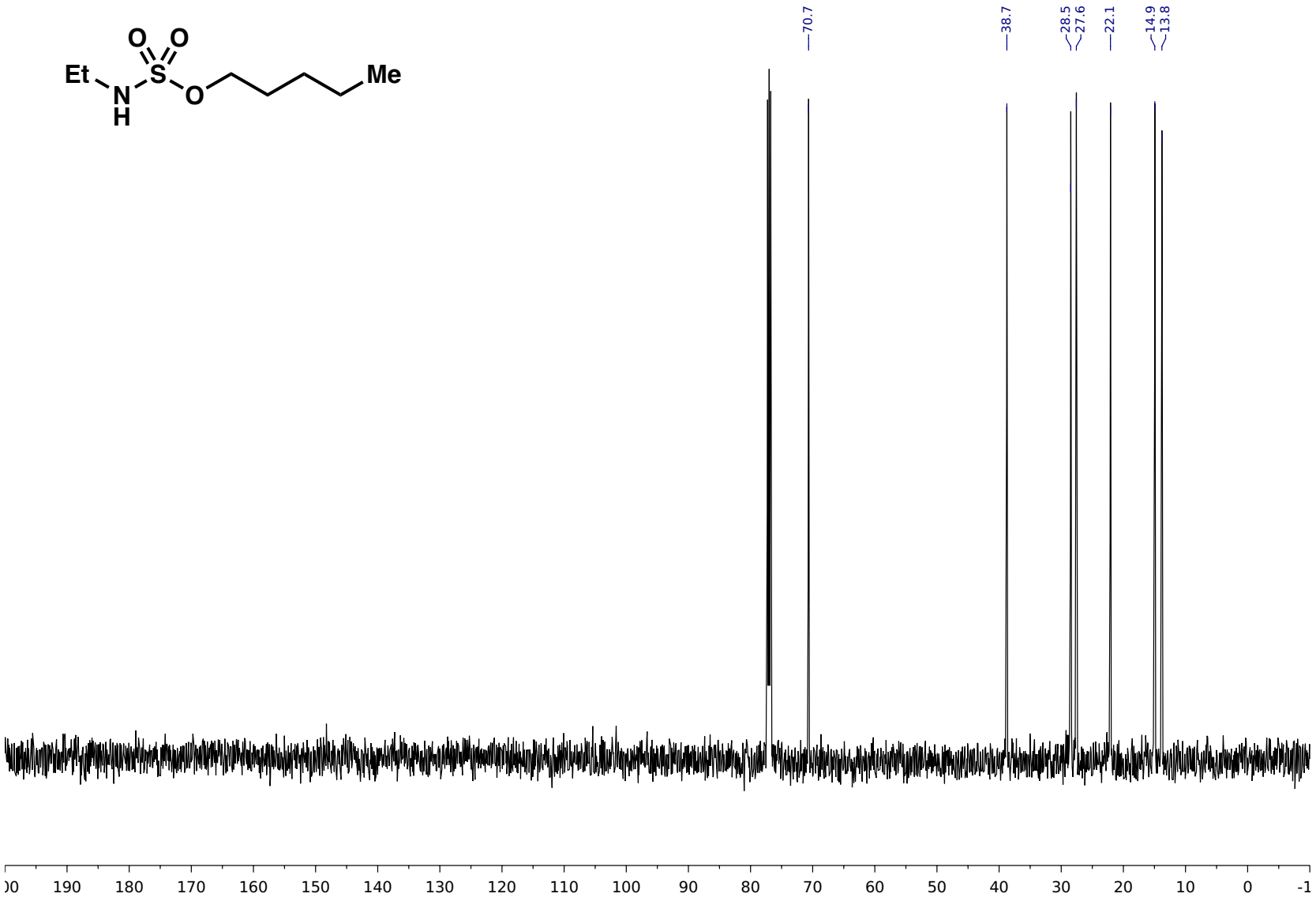
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl *tert*-butylsulfamate (**4e**)



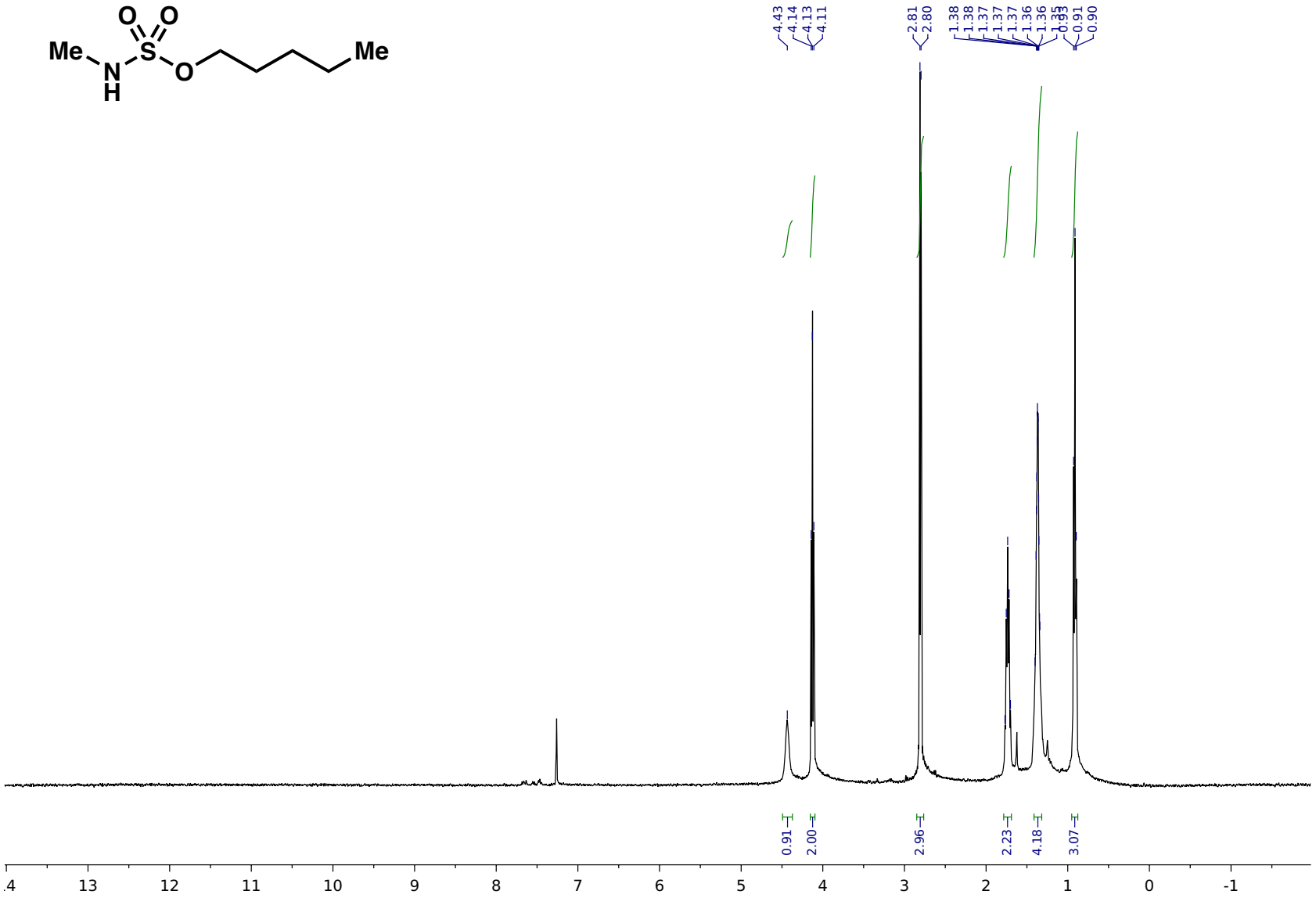
^{13}C NMR (126 MHz, $CDCl_3$) of pentyl *tert*-butylsulfamate (**4e**)



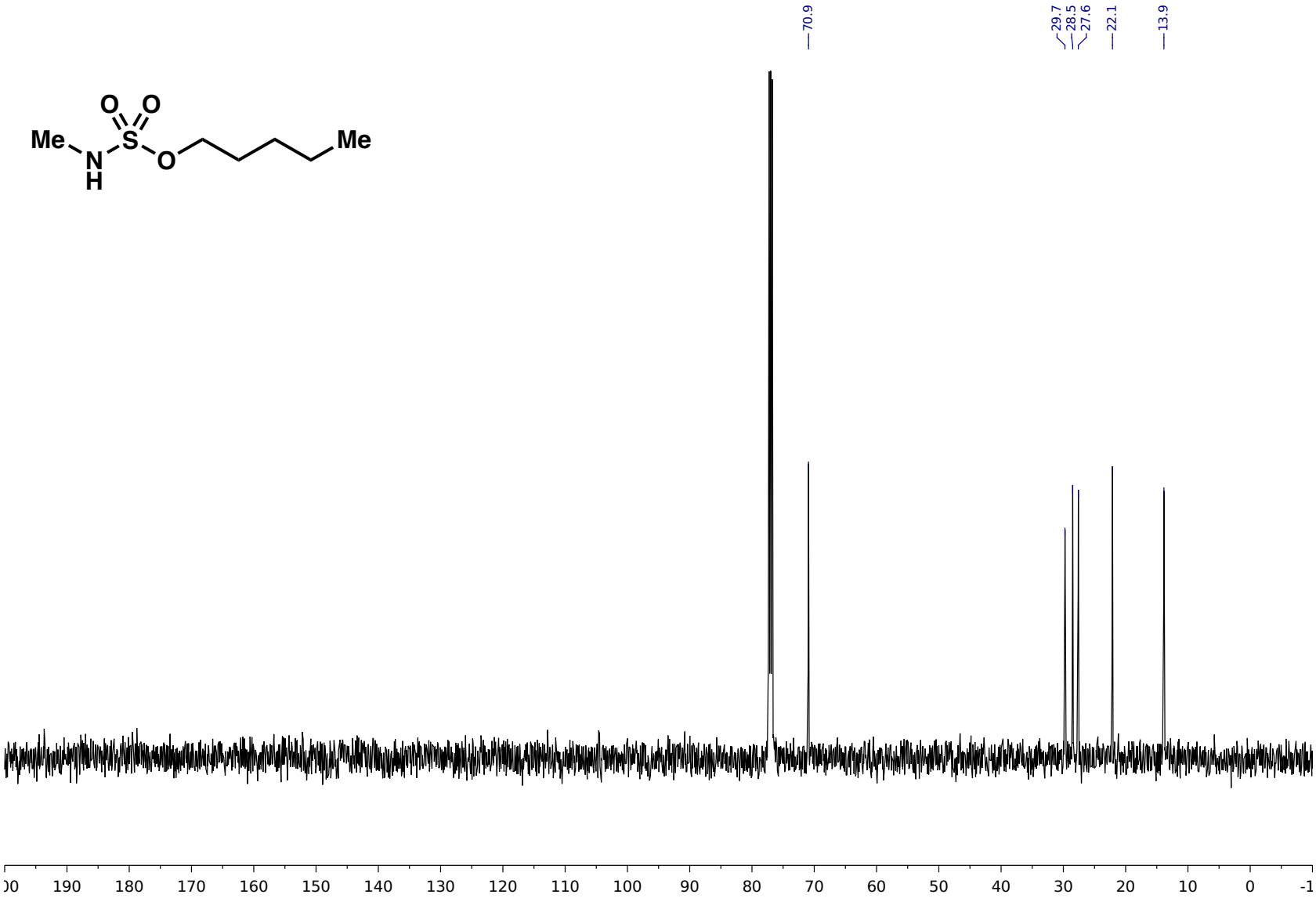
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl ethylsulfamate (**4f**)



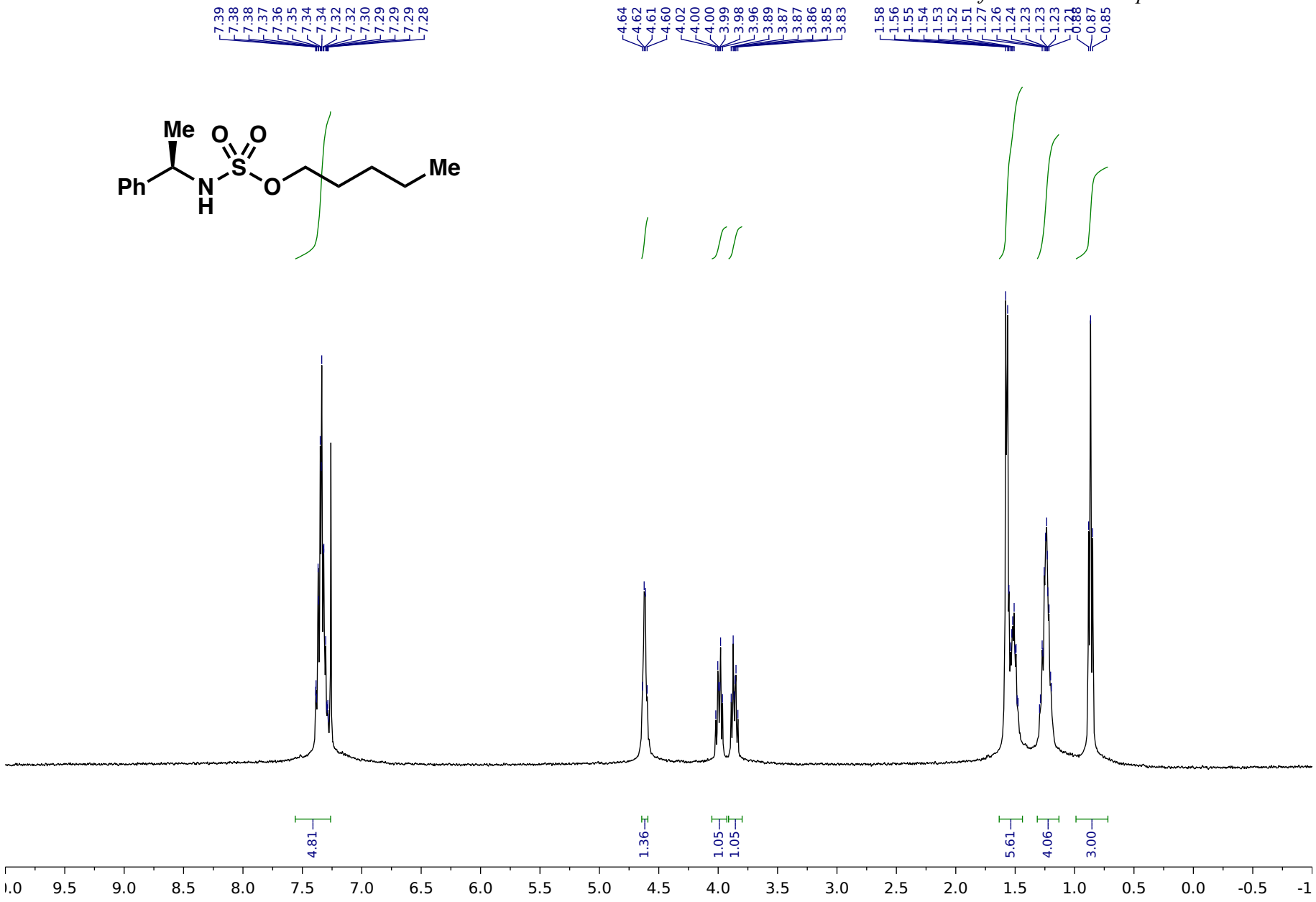
^{13}C NMR (500 MHz, $CDCl_3$) of pentyl ethylsulfamate (**4f**)



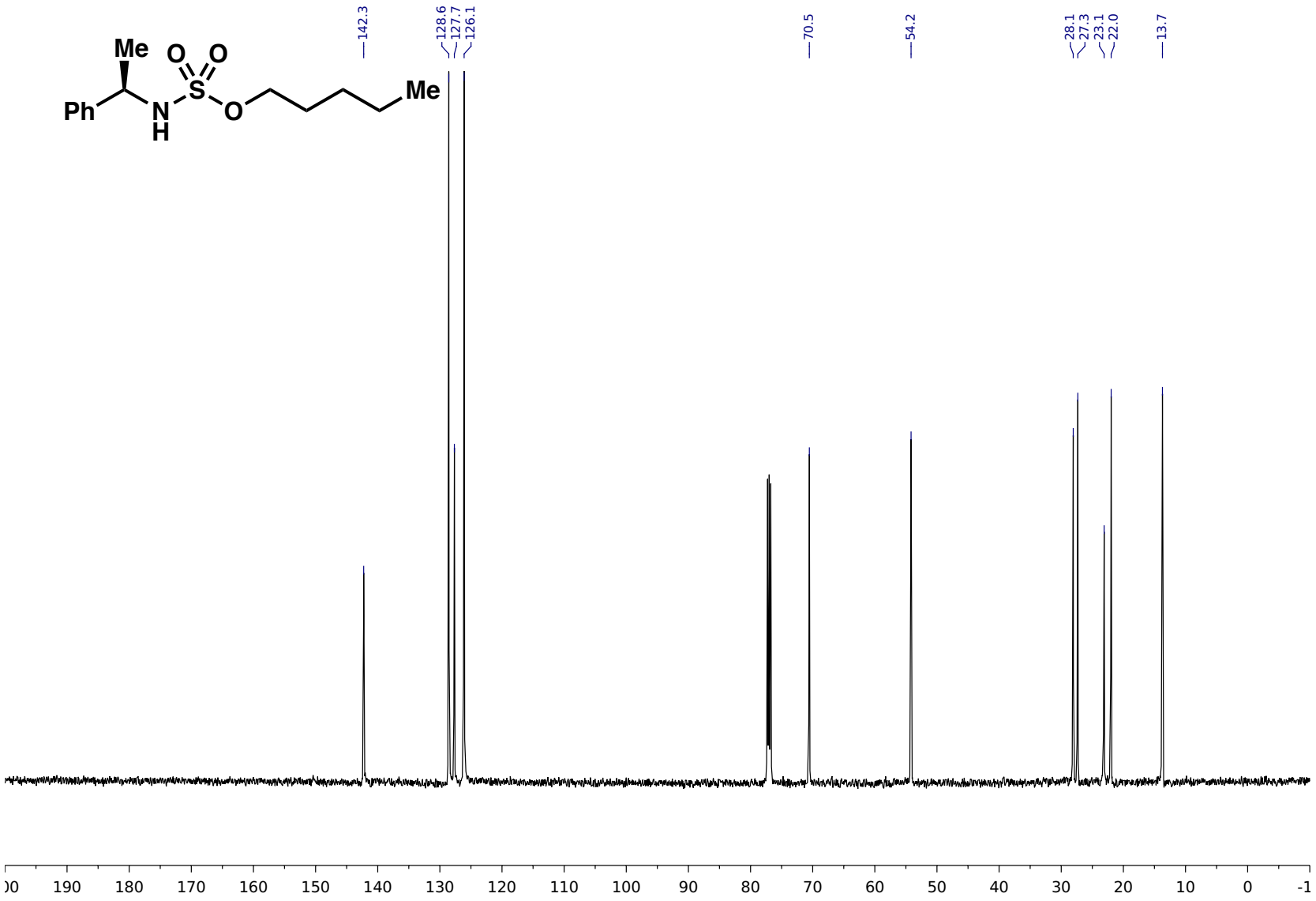
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl methylsulfamate (**4g**)



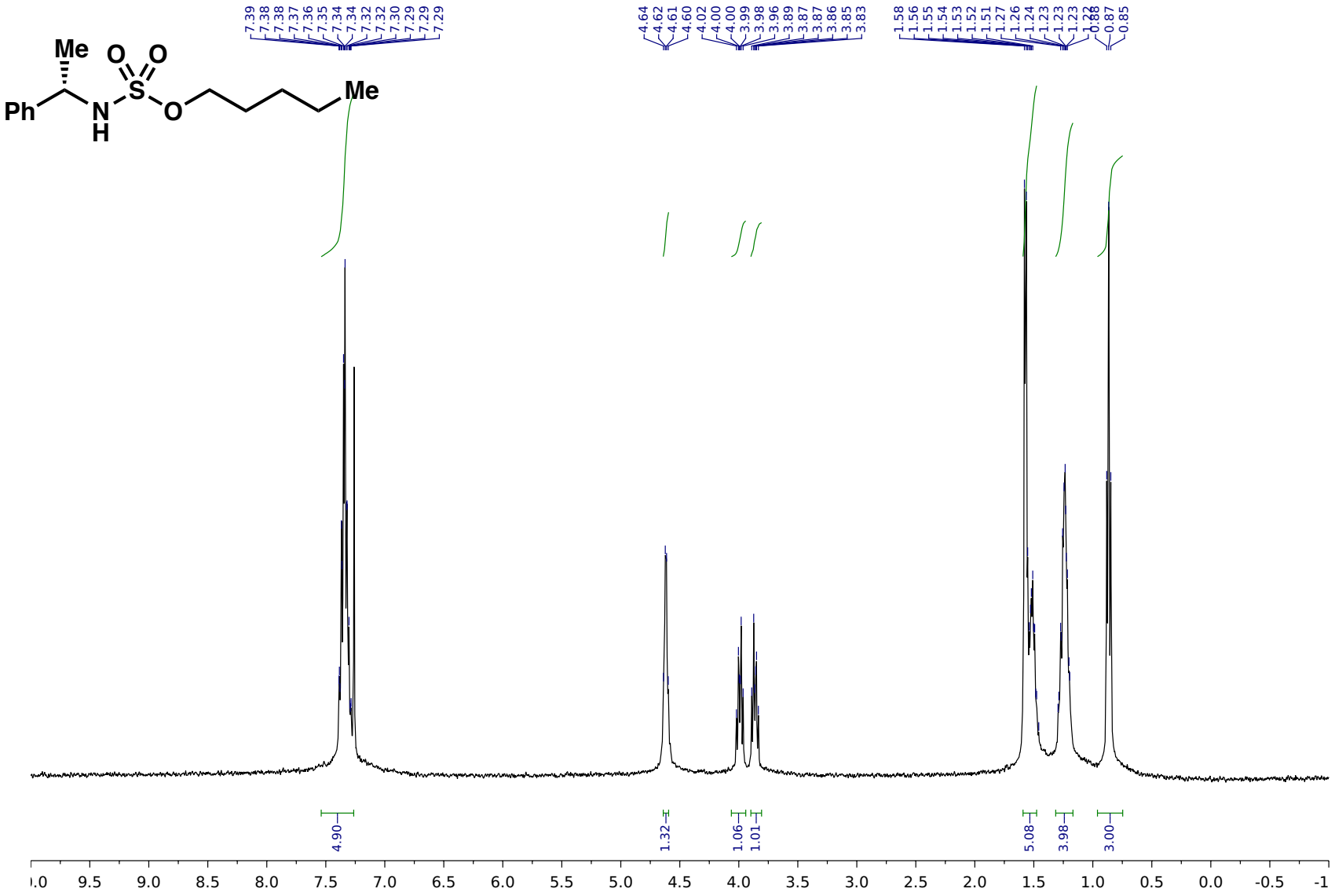
^{13}C NMR (126 MHz, $CDCl_3$) of pentyl methylsulfamate (**4g**)



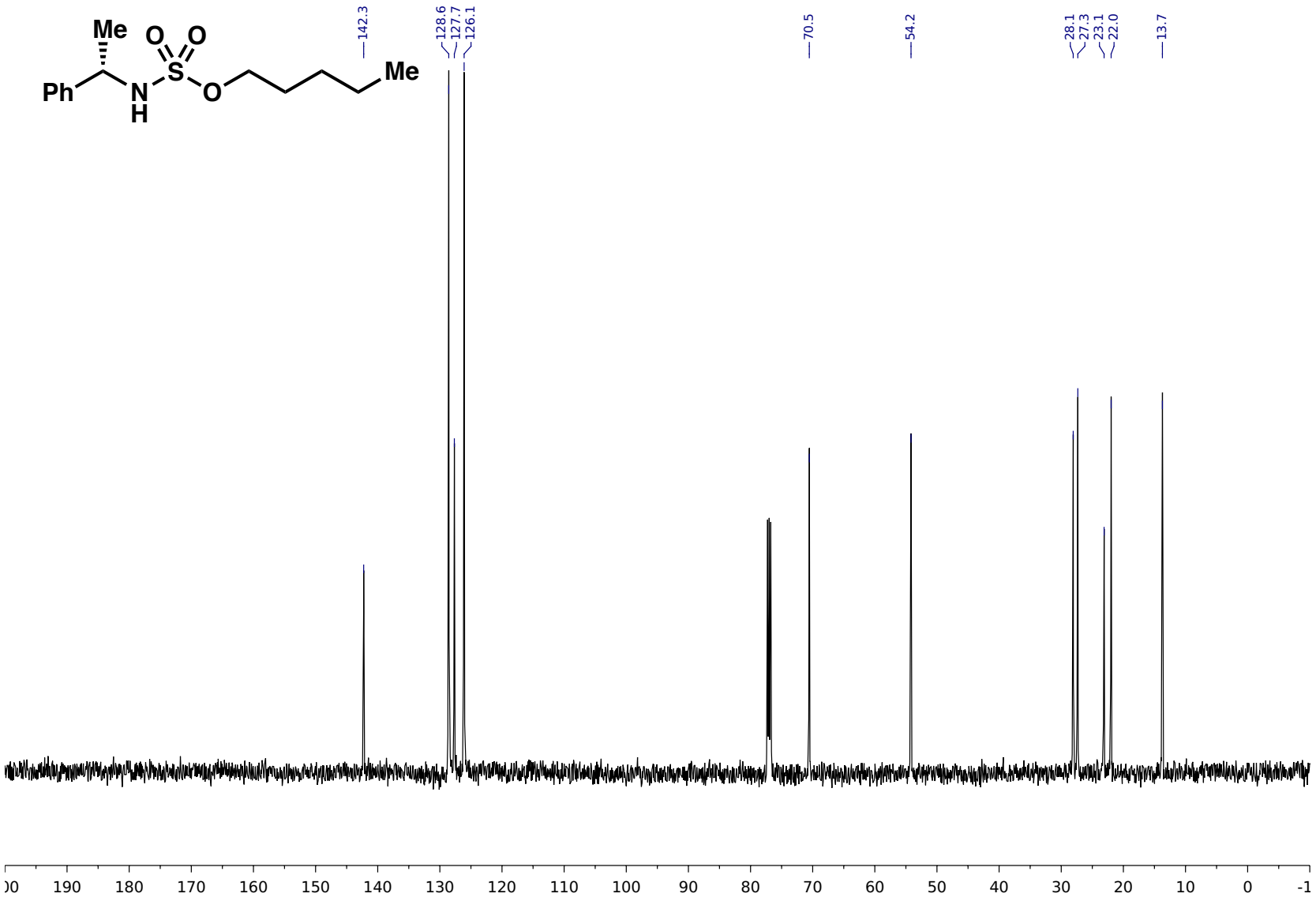
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl (*R*)-(1-phenylethyl)sulfamate (**4i**)



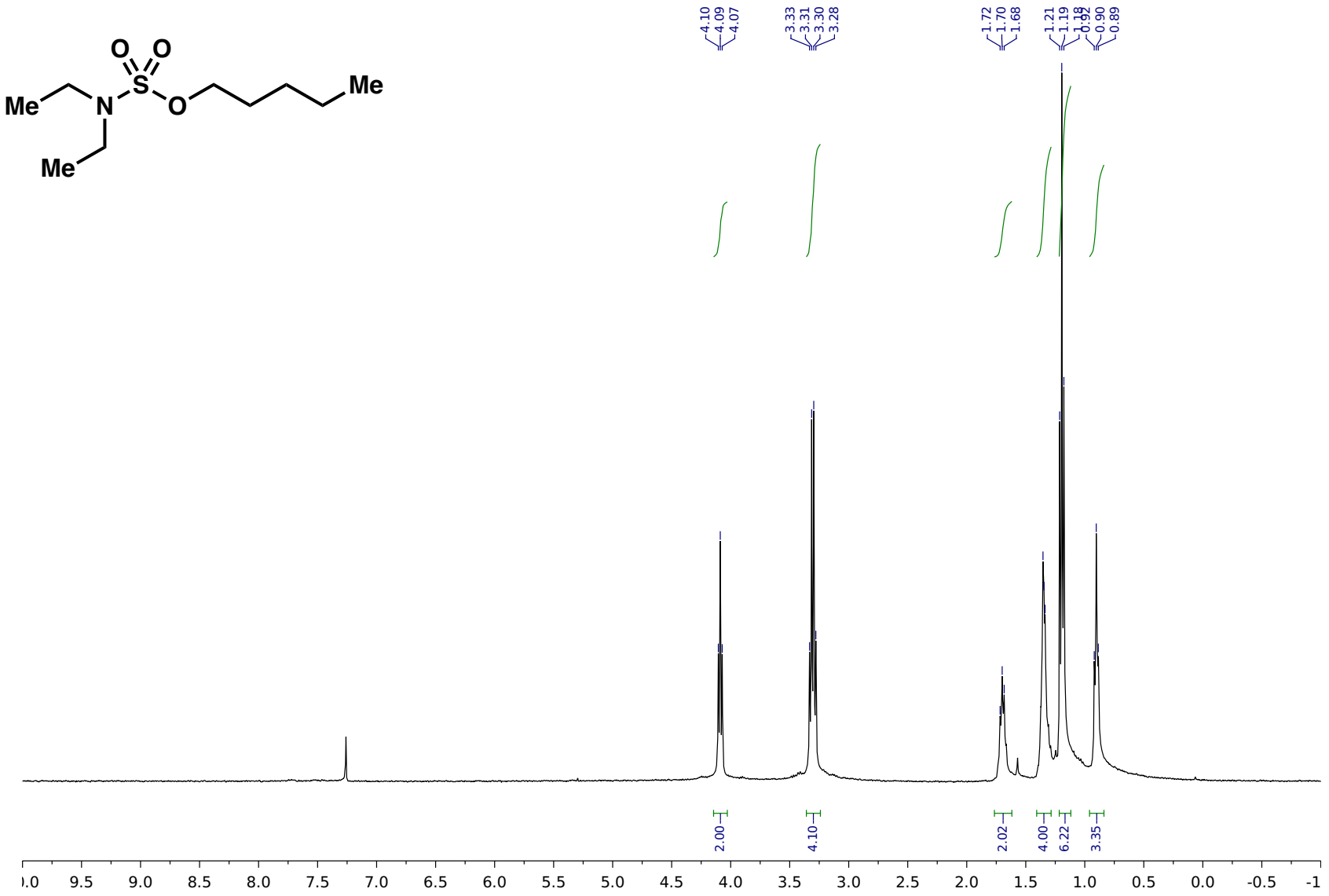
^{13}C NMR (500 MHz, $CDCl_3$) of pentyl (*R*)-(1-phenylethyl)sulfamate (**4i**)



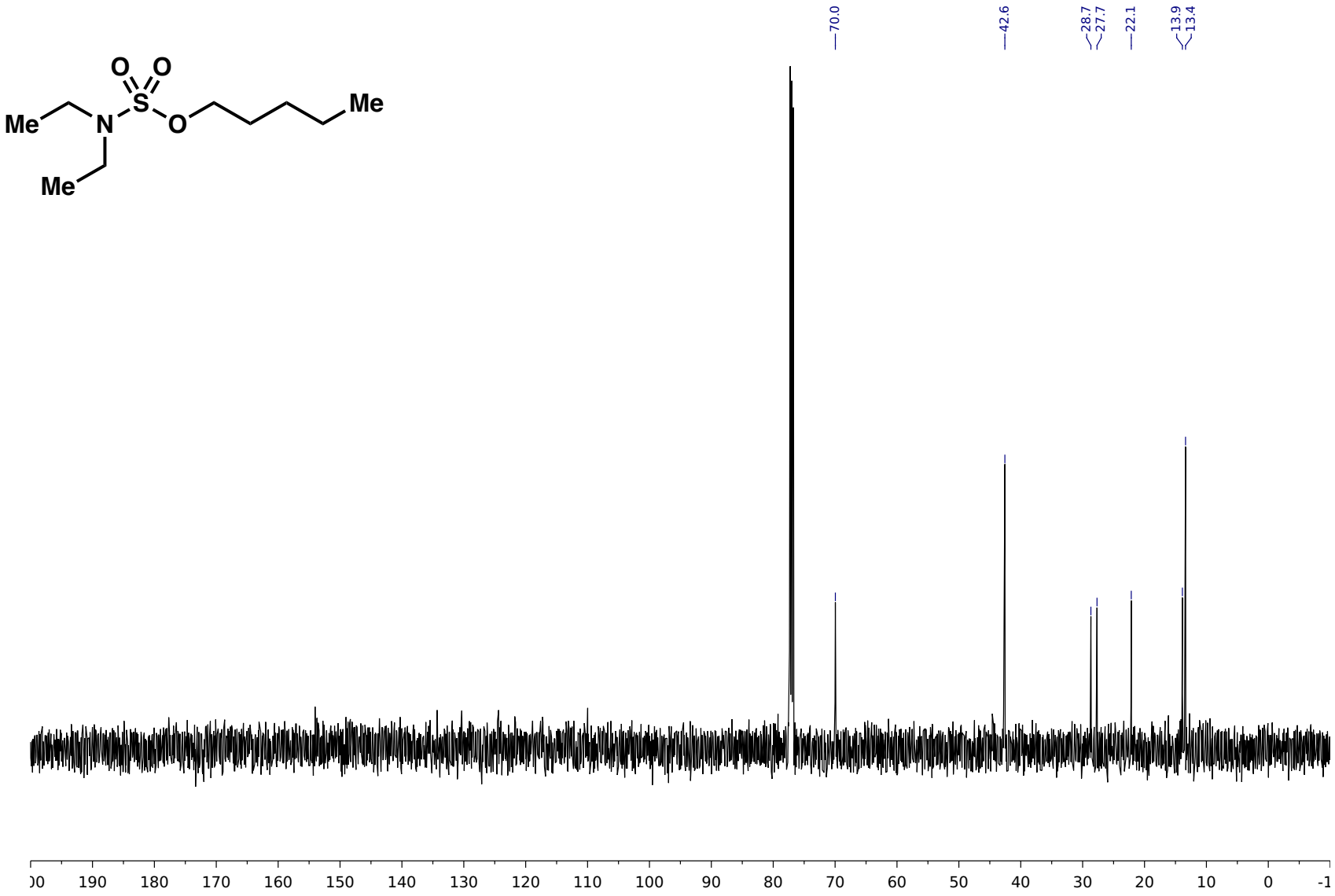
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl (*S*)-(1-phenylethyl)sulfamate (**S4a**)



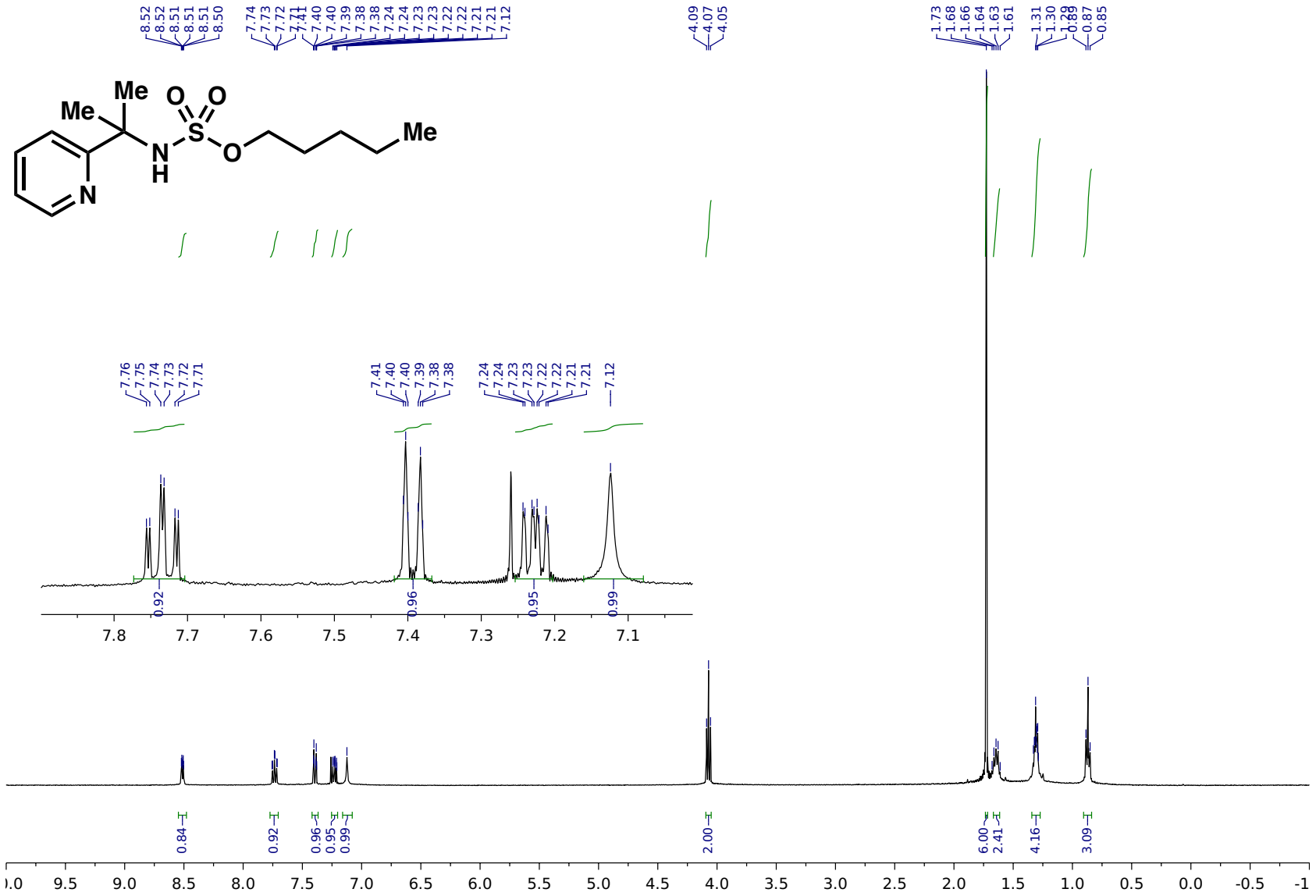
^{13}C NMR (400 MHz, $CDCl_3$) of pentyl (*S*)-(1-phenylethyl)sulfamate (**S4a**)



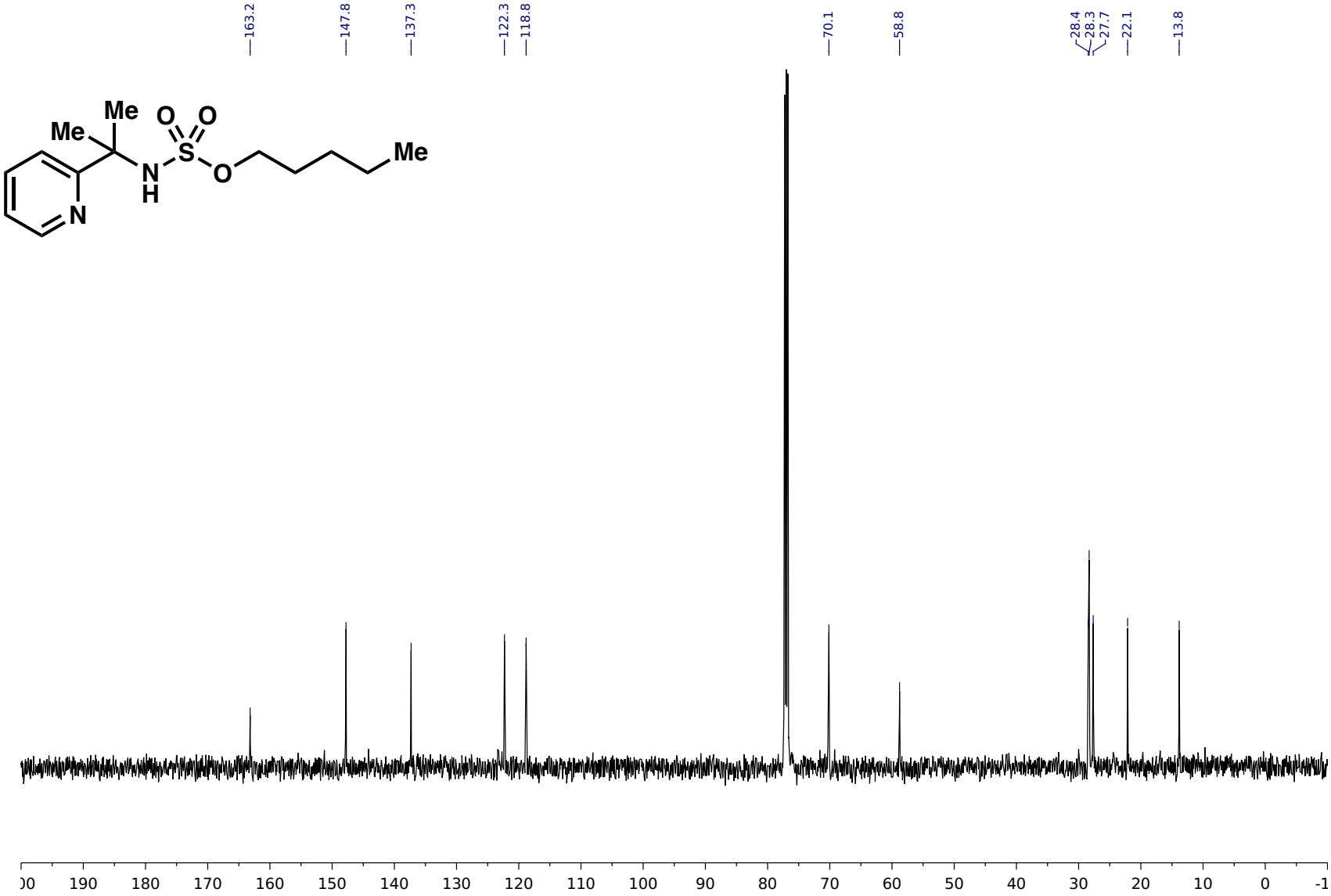
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl diethylsulfamate (**4h**)



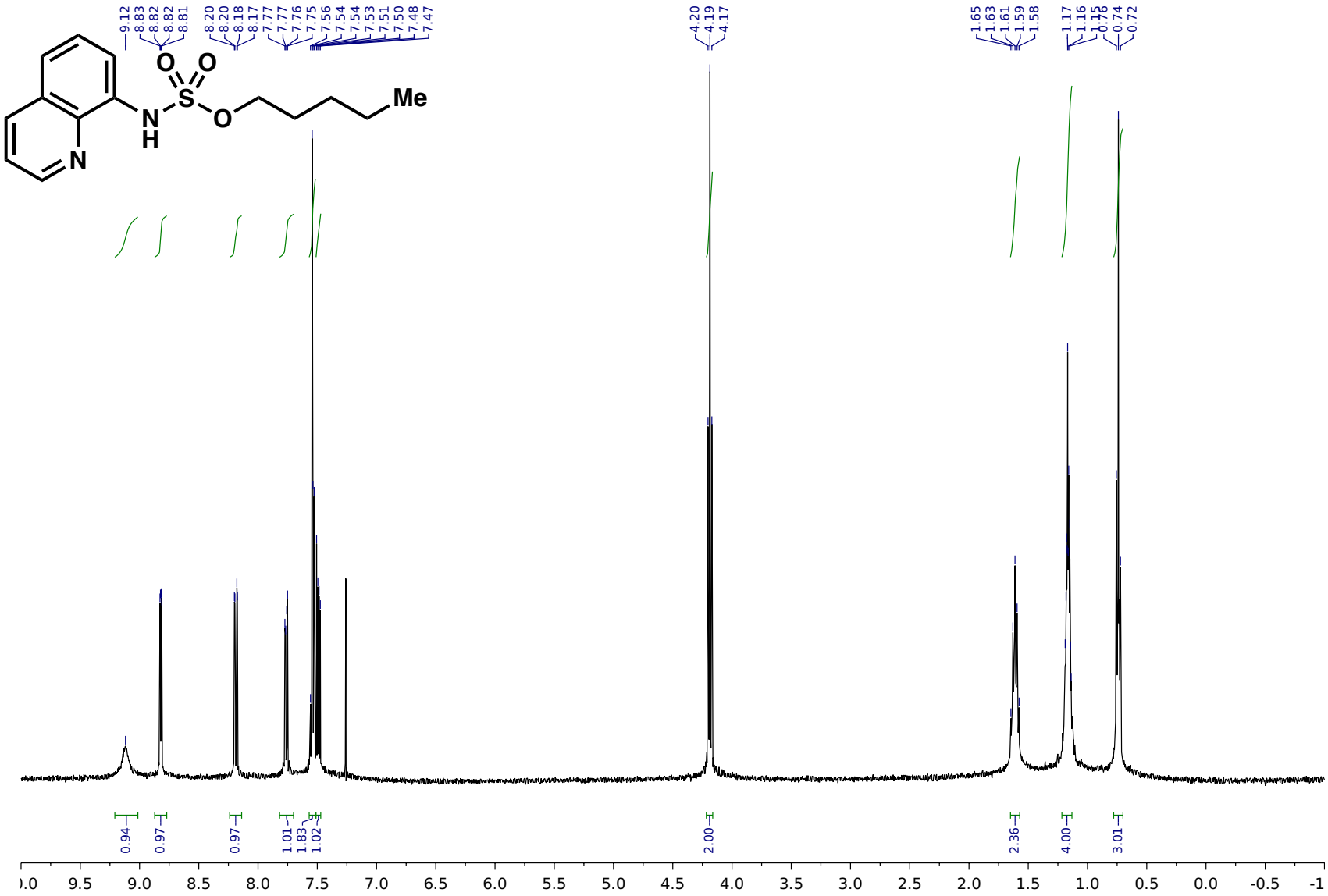
^{13}C NMR (126 MHz, $CDCl_3$) of pentyl diethyllsulfamate (**4h**)



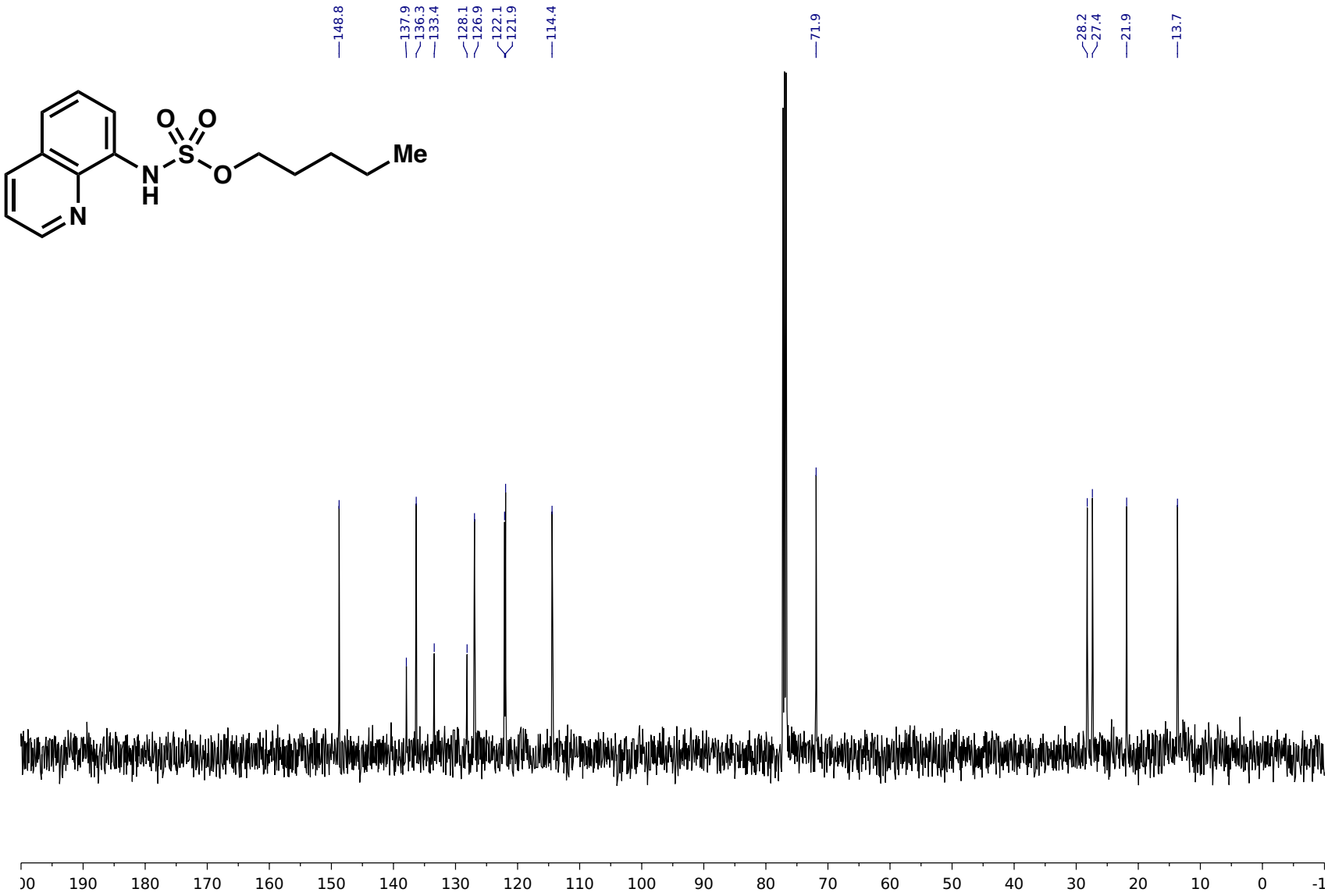
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl (2-pyridin-2-yl)propan-2-yl)sulfamate (**4j**)



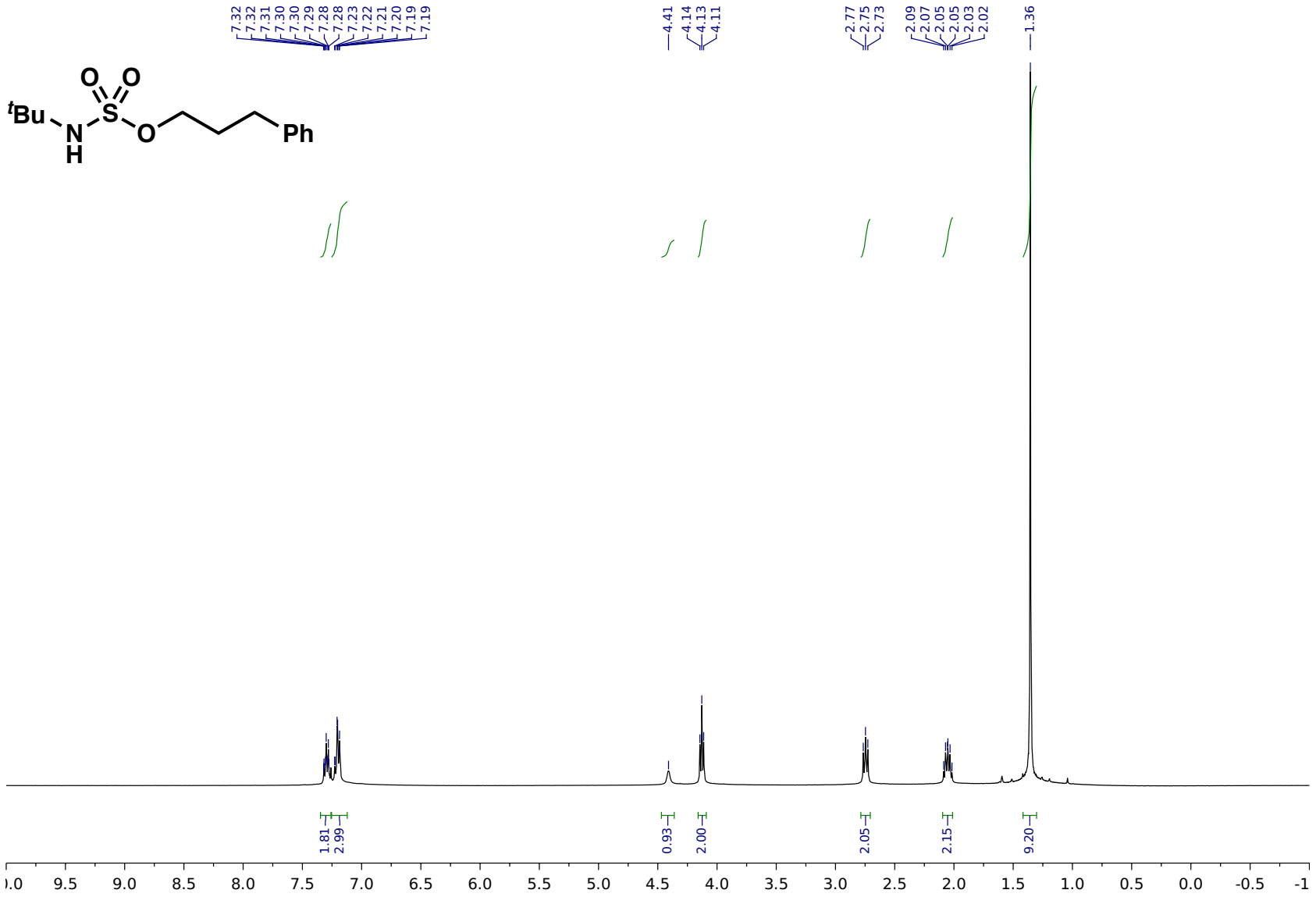
^{13}C NMR (126 MHz, $CDCl_3$) of pentyl (2-pyridin-2-yl)propan-2-yl)sulfamate (**4j**)



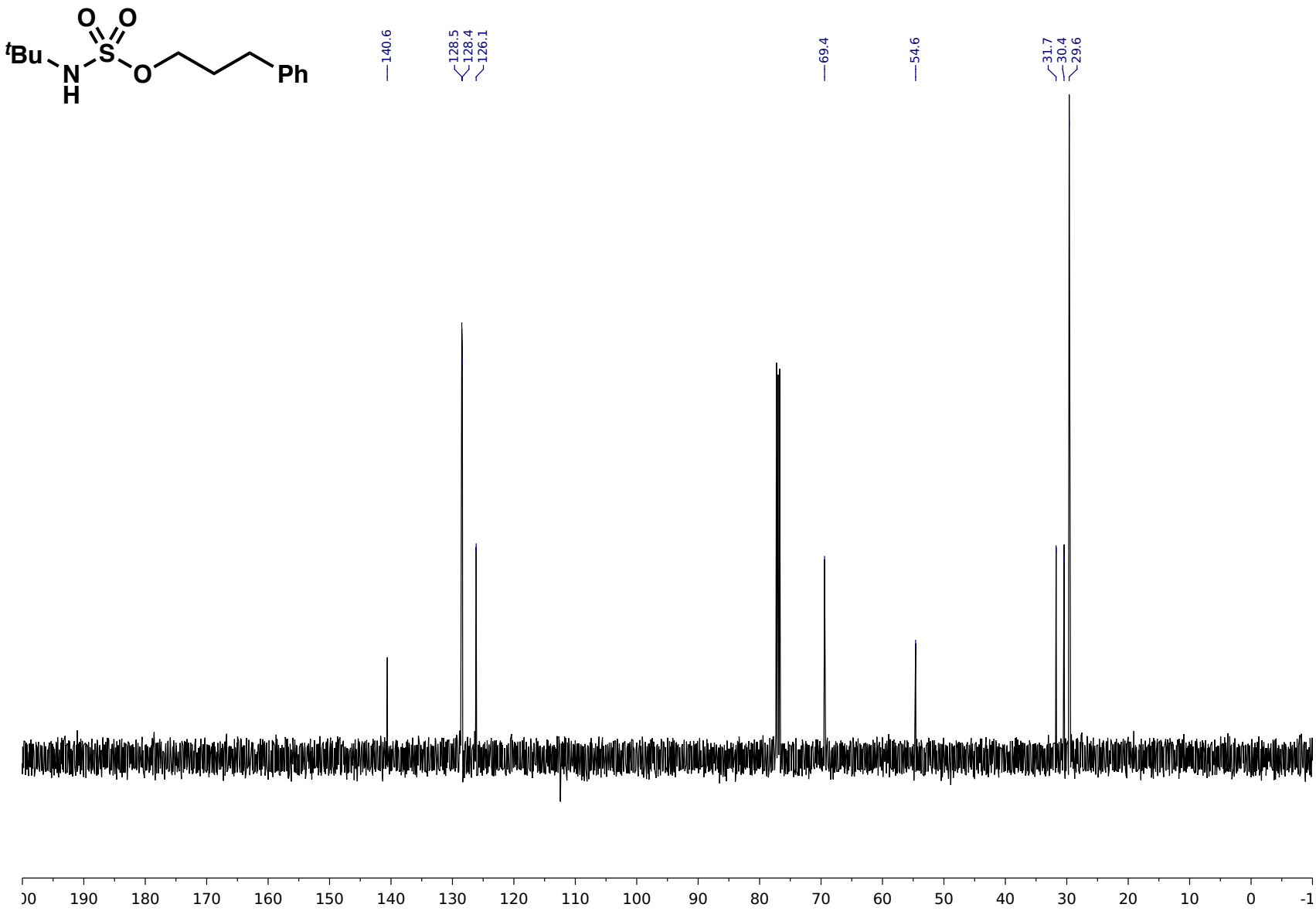
^{1}H NMR (400 MHz, $CDCl_3$) of pentyl quinolin-8-ylsulfamate (**4k**)



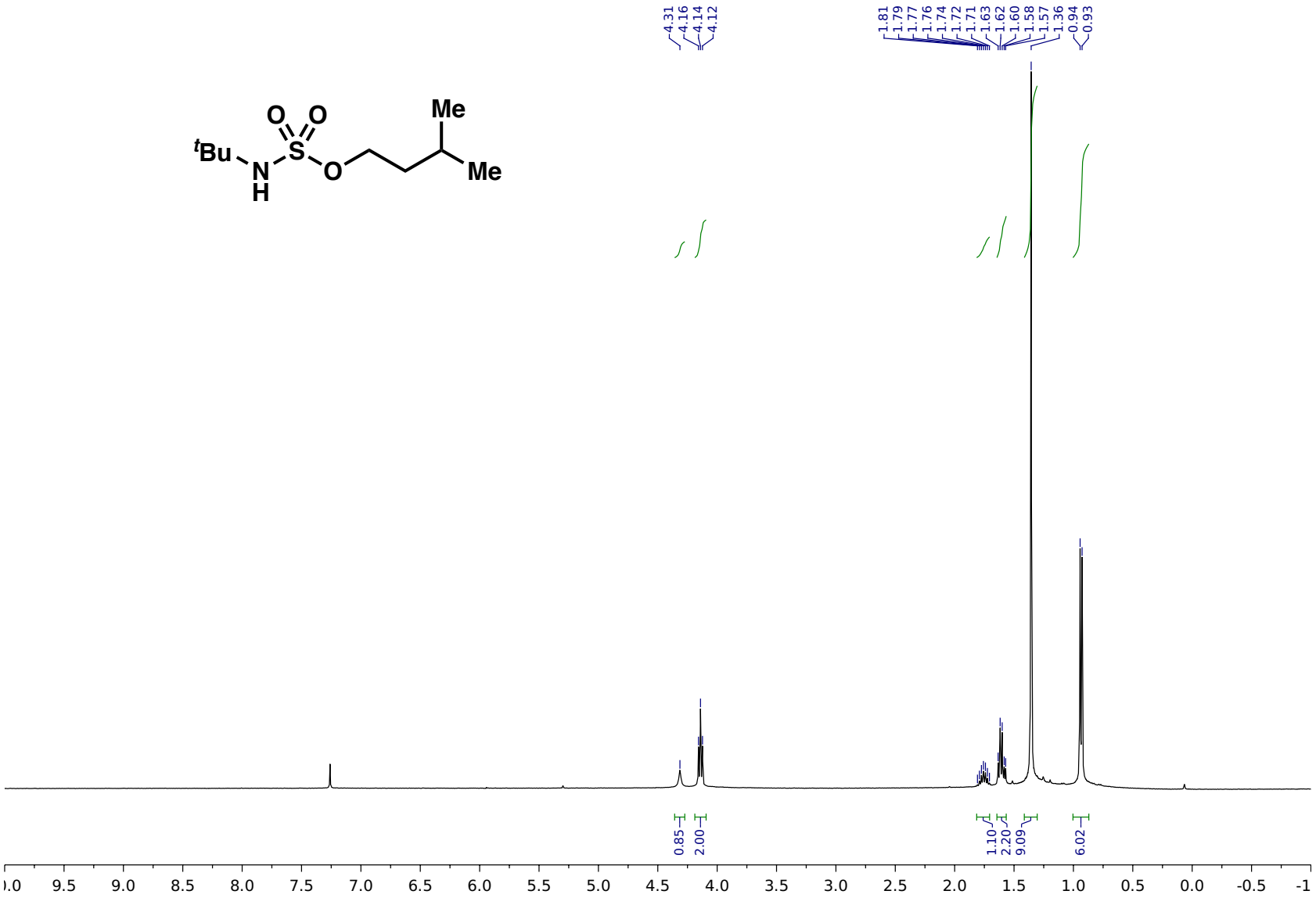
^{13}C NMR (126 MHz, $CDCl_3$) of pentyl quinolin-8-ylsulfamate (**4k**)



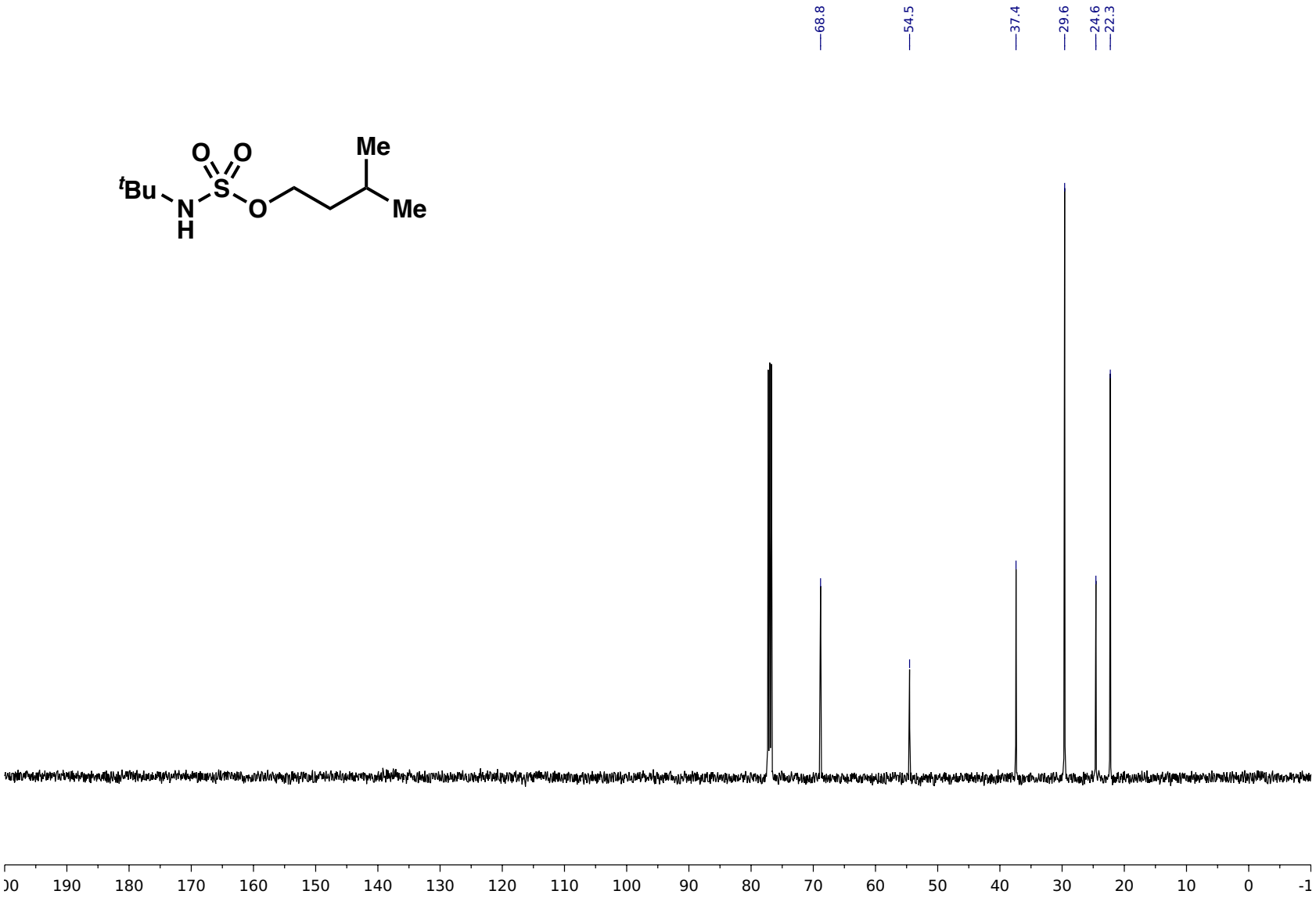
^{1}H NMR (400 MHz, $CDCl_3$) of 3-phenylpropyl *tert*-butylsulfamate (**4l**)



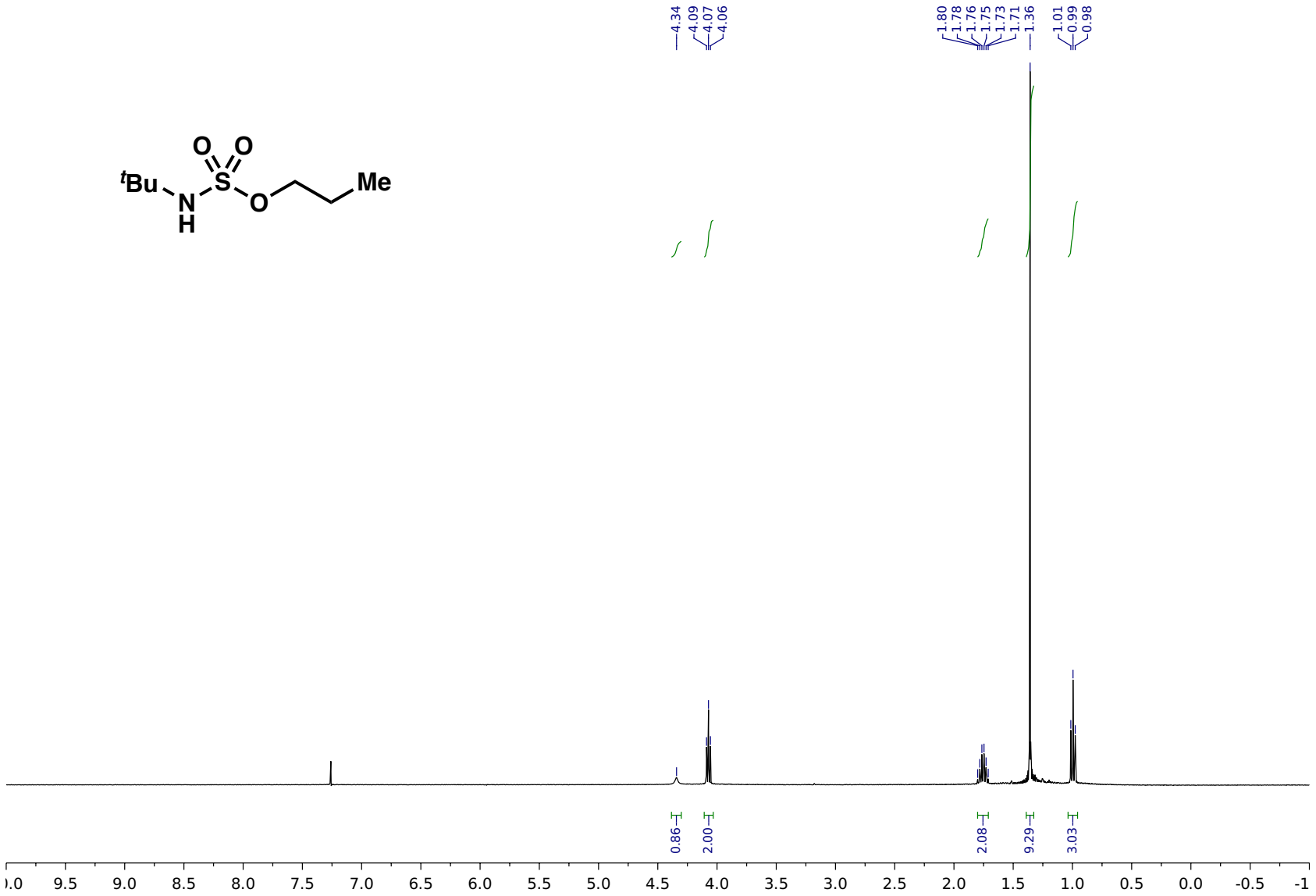
^{13}C NMR (126 MHz, $CDCl_3$) of 3-phenylpropyl *tert*-butylsulfamate (**4l**)



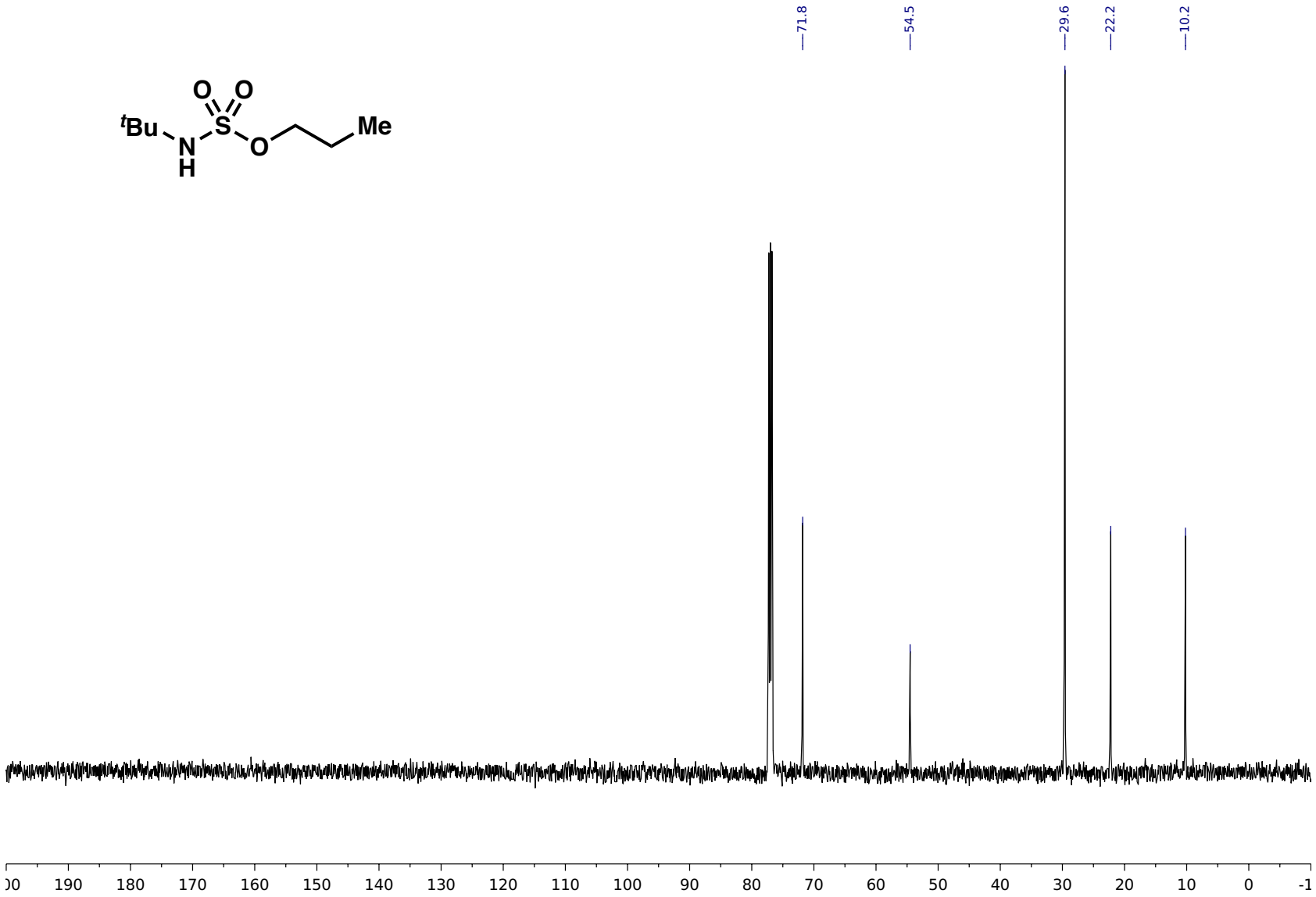
^{1}H NMR (400 MHz, $CDCl_3$) of 3-Methylpentyl *tert*-butylsulfamate (**4m**)



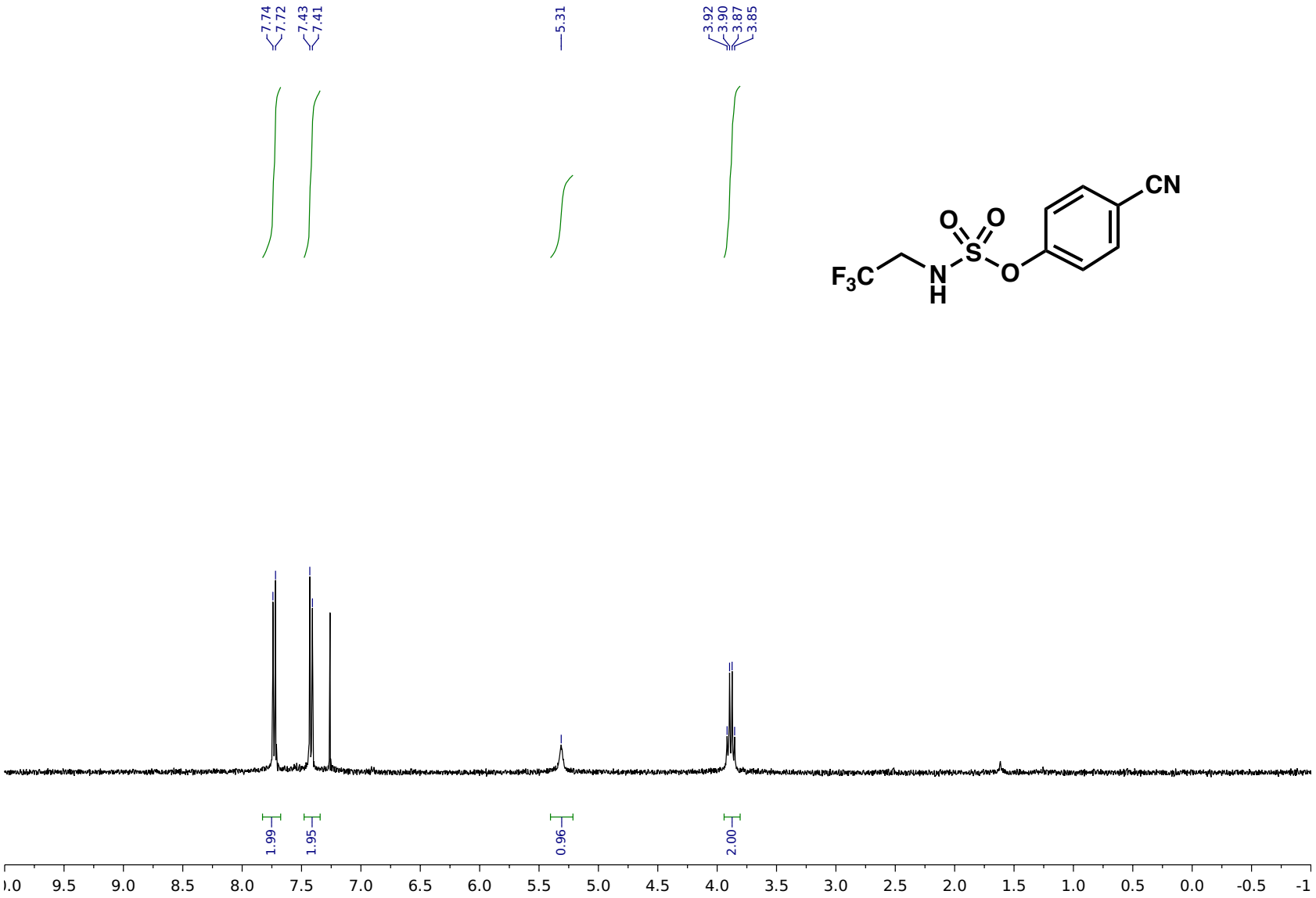
^{13}C NMR (126 MHz, $CDCl_3$) of 3-Methylpentyl *tert*-butylsulfamate (**4m**)



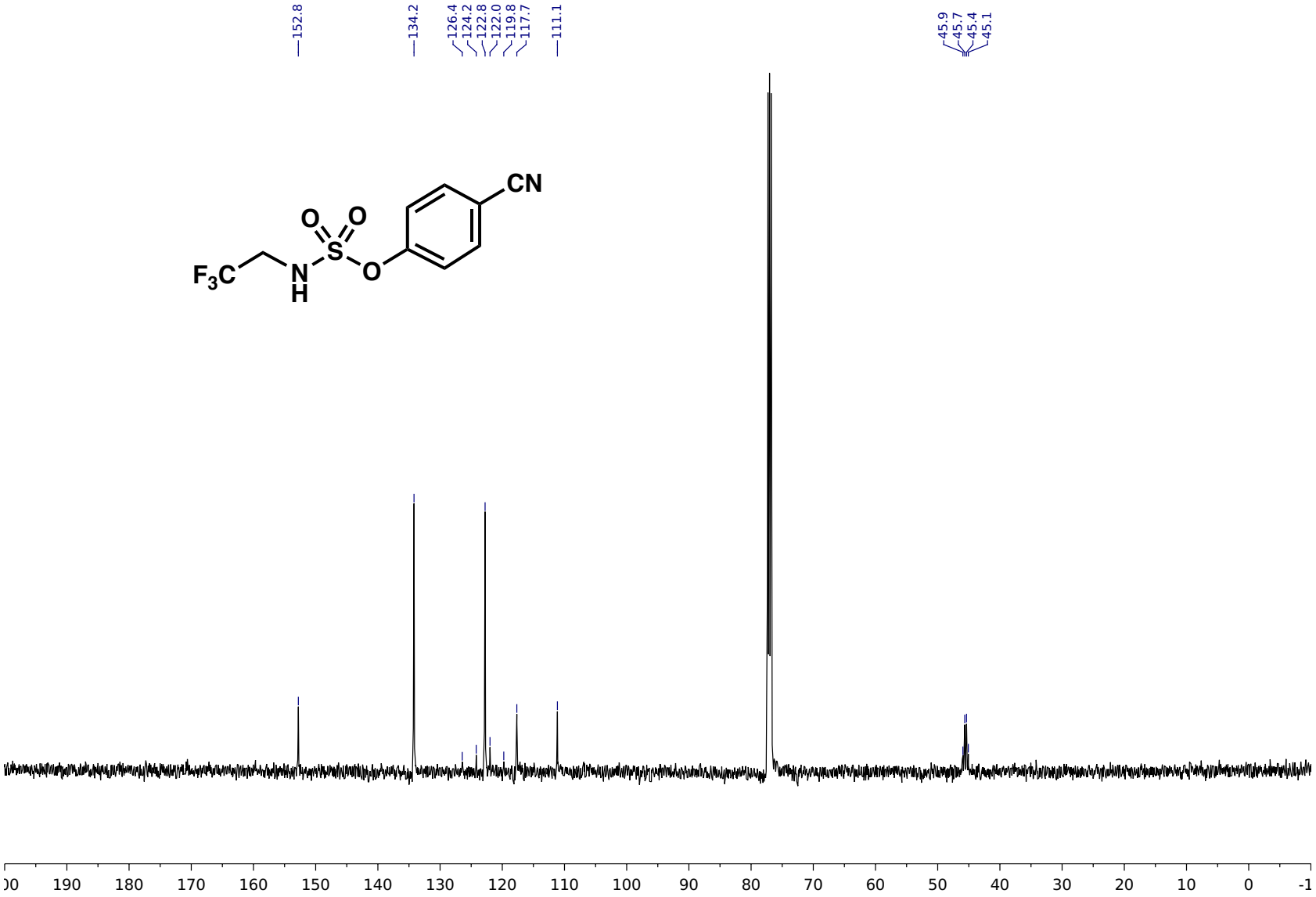
^{1}H NMR (400 MHz, $CDCl_3$) of Propyl *tert*-butylsulfamate (**4n**)



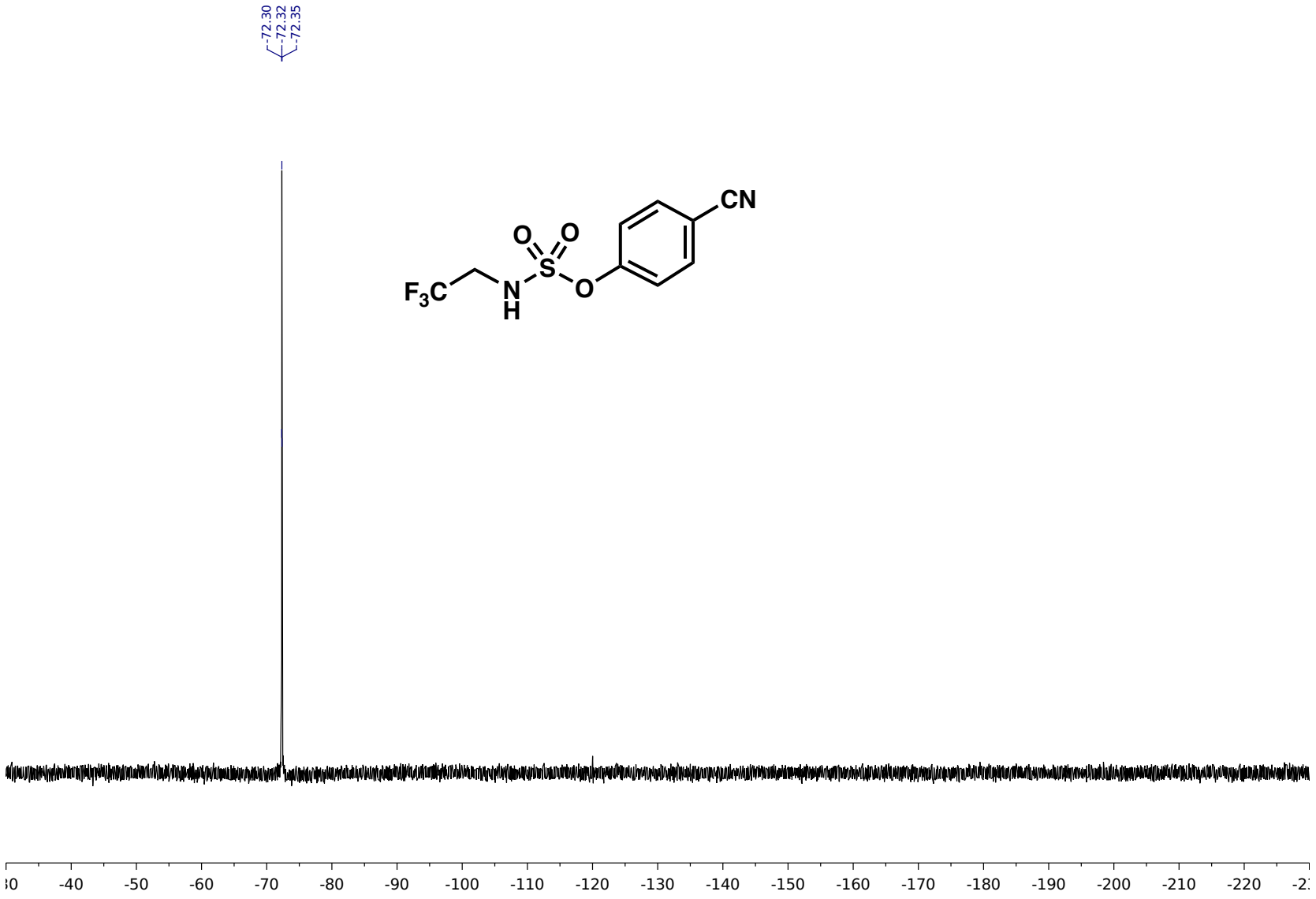
^{13}C NMR (126 MHz, $CDCl_3$) of Propyl *tert*-butylsulfamate (**4n**)



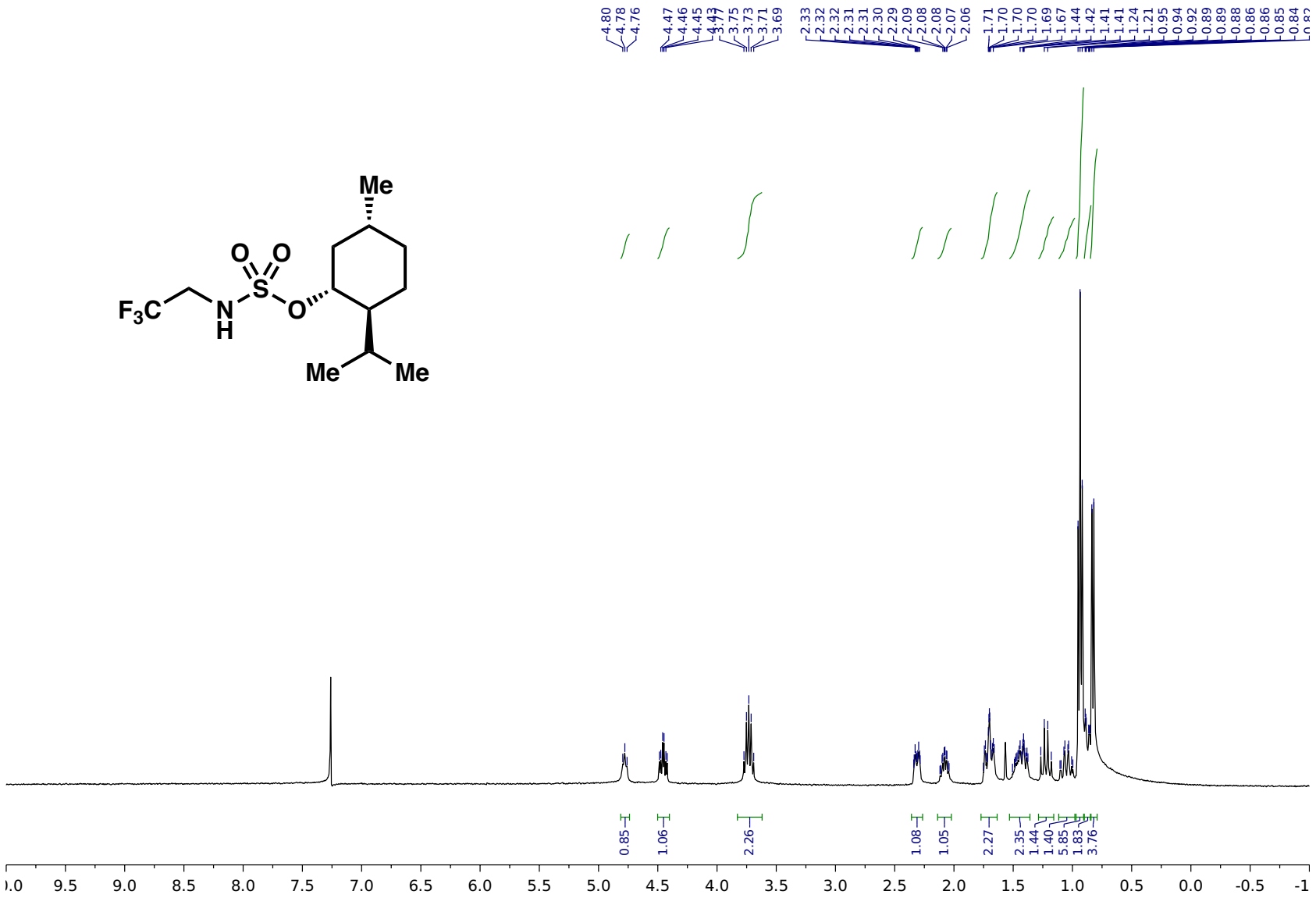
^{1}H NMR (400 MHz, $CDCl_3$) of 4-Cyanophenyl (2,2,2-trifluoroethyl)sulfamate (**4o**)



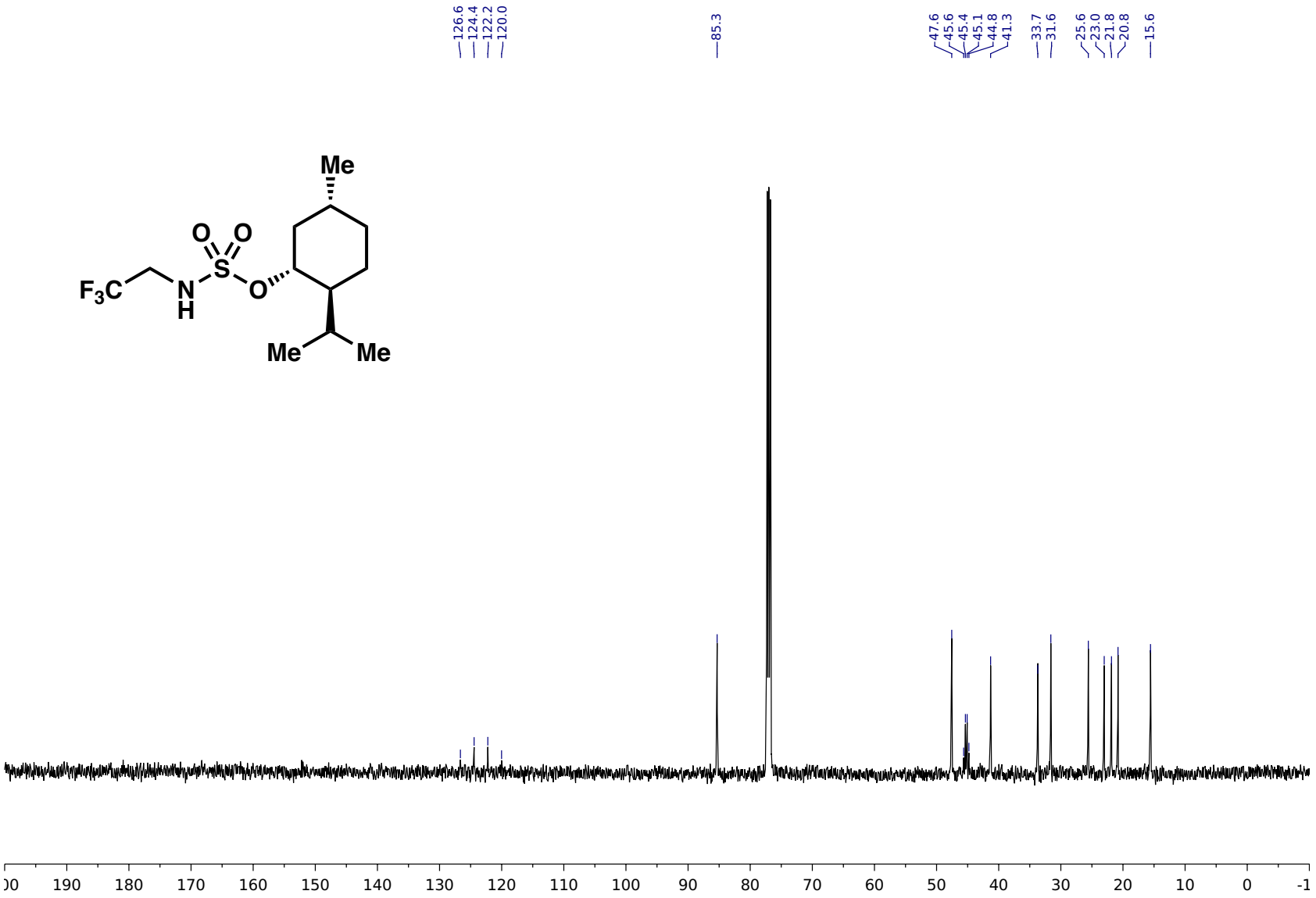
^{13}C NMR (126 MHz, $CDCl_3$) of 4-Cyanophenyl (2,2,2-trifluoroethyl)sulfamate (**4o**)



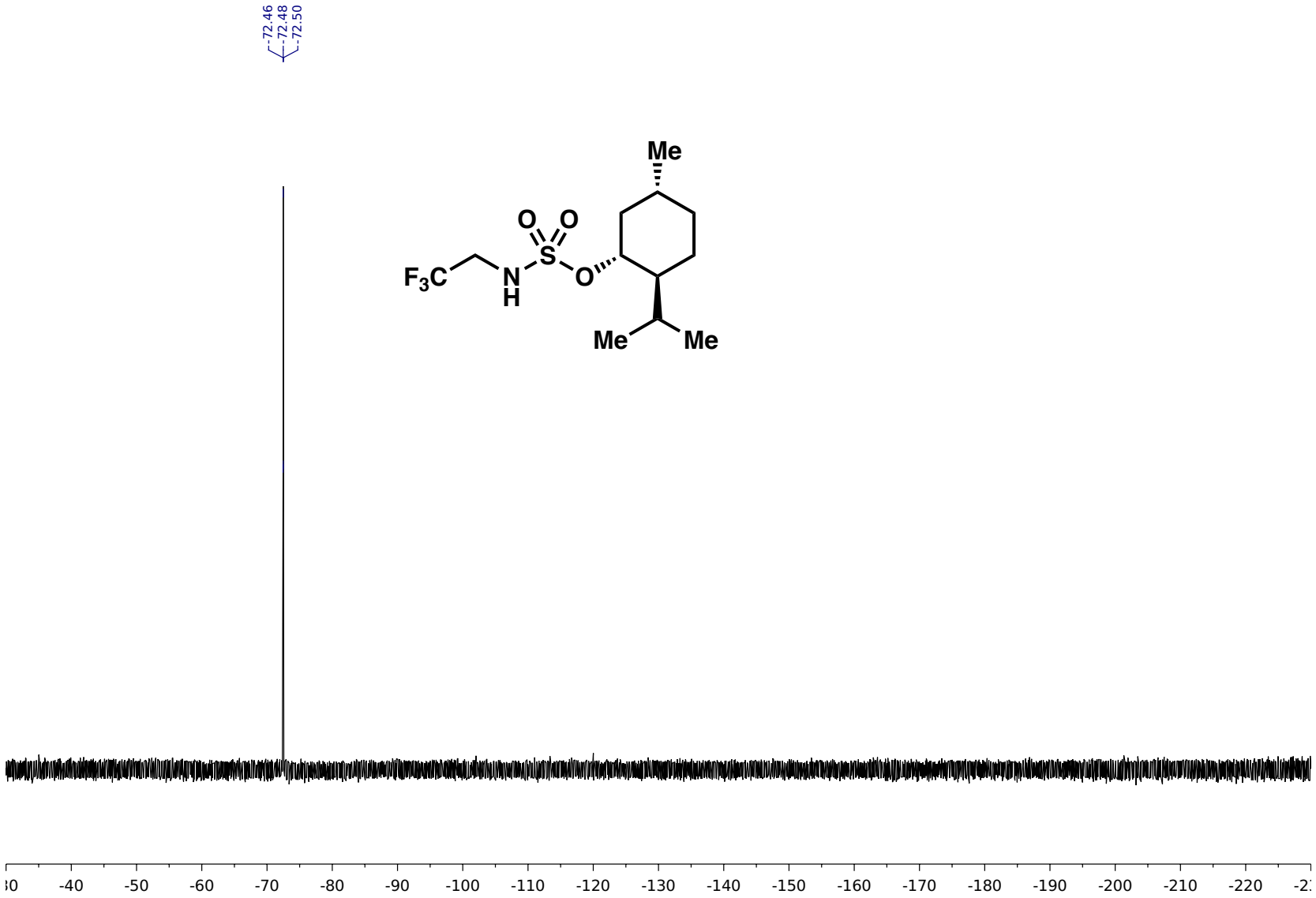
^{19}F NMR (376 MHz, $CDCl_3$) of 4-Cyanophenyl (2,2,2-trifluoroethyl)sulfamate (**4o**)



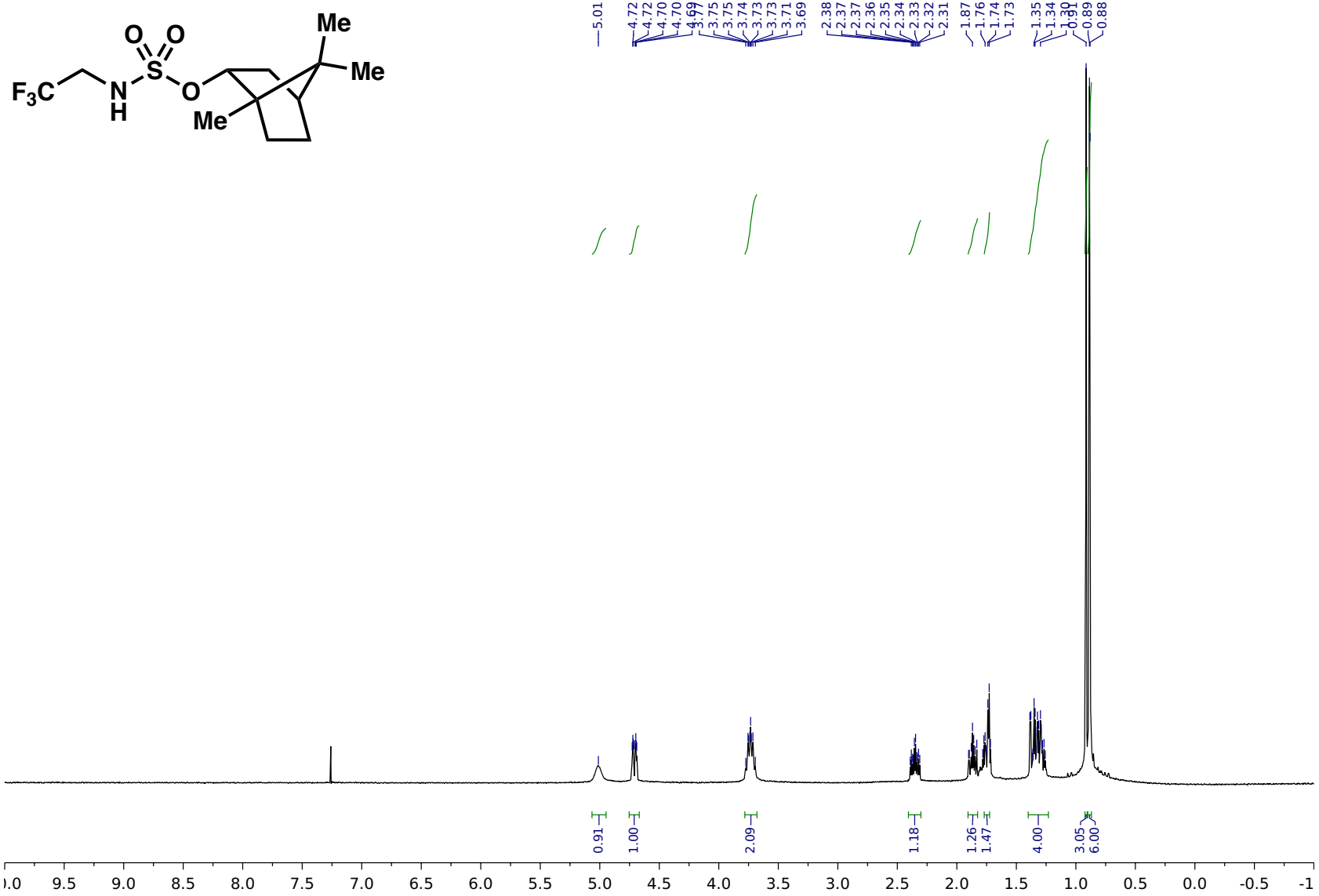
^{1}H NMR (400 MHz, $CDCl_3$) of (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (2,2,2-trifluoroethyl)sulfamate (**4p**)



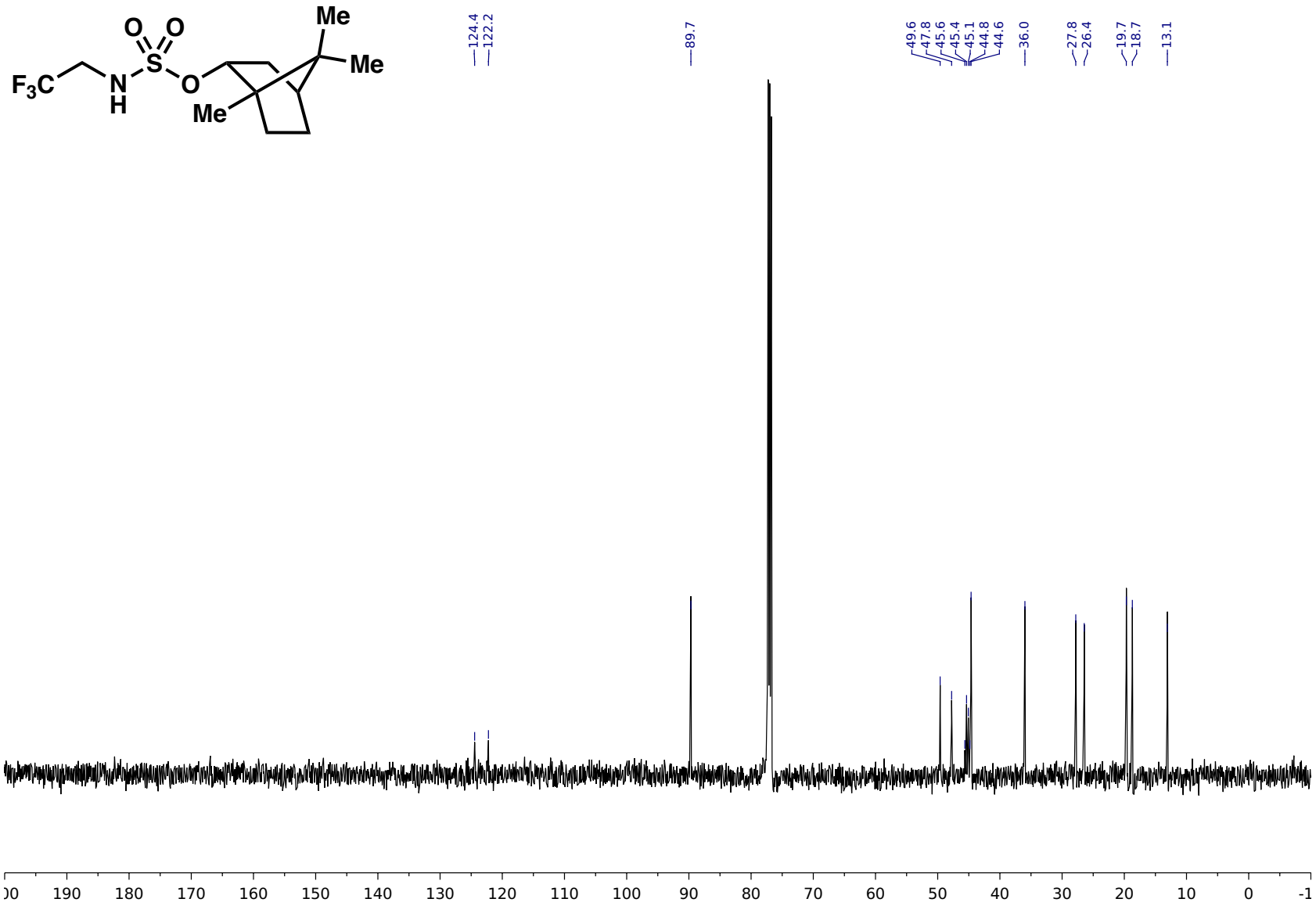
^{13}C NMR (126 MHz, $CDCl_3$) of (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (2,2,2-trifluoroethyl)sulfamate (**4p**)



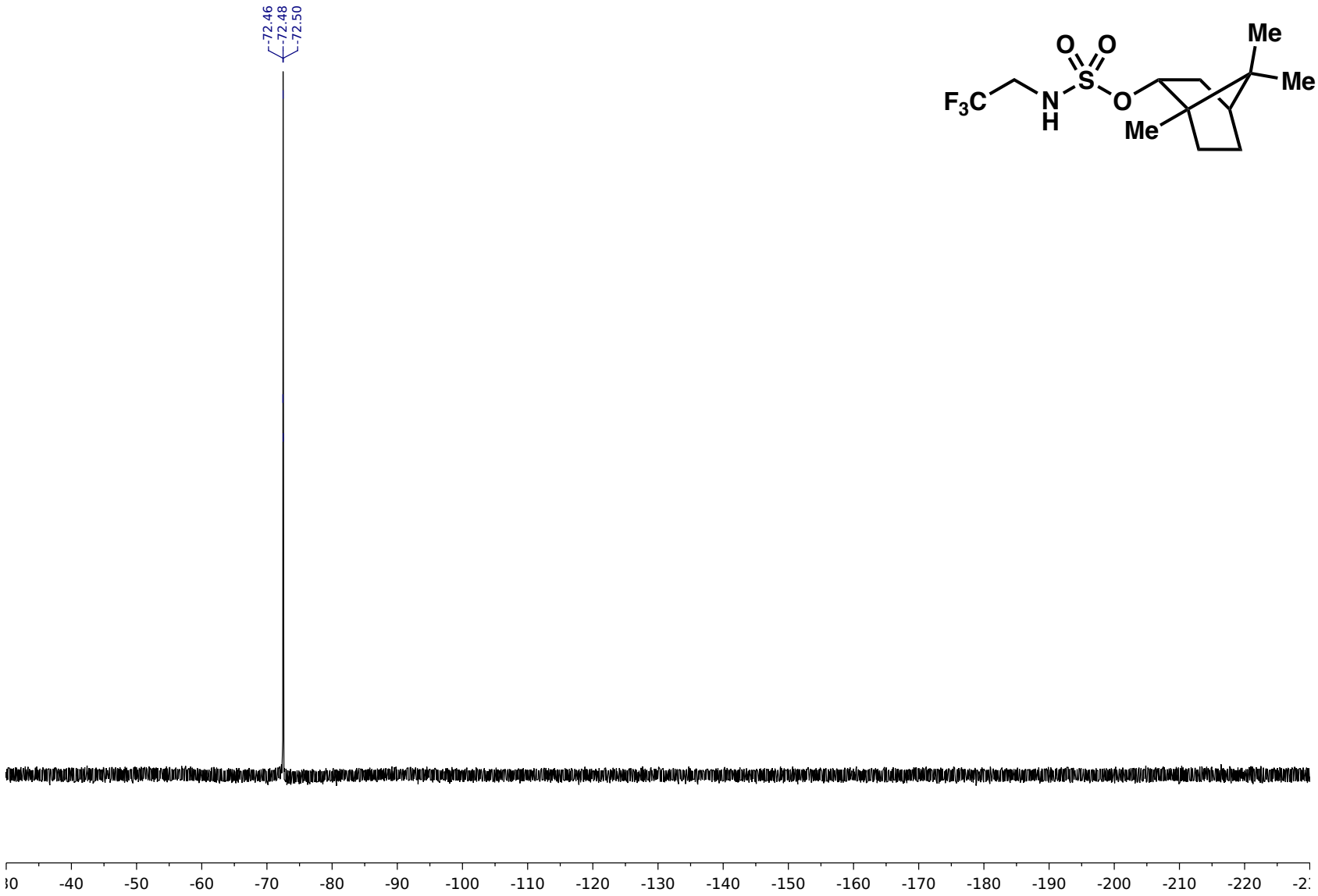
^{19}F NMR (376 MHz, $CDCl_3$) of (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (2,2,2-trifluoroethyl)sulfamate (**4p**)



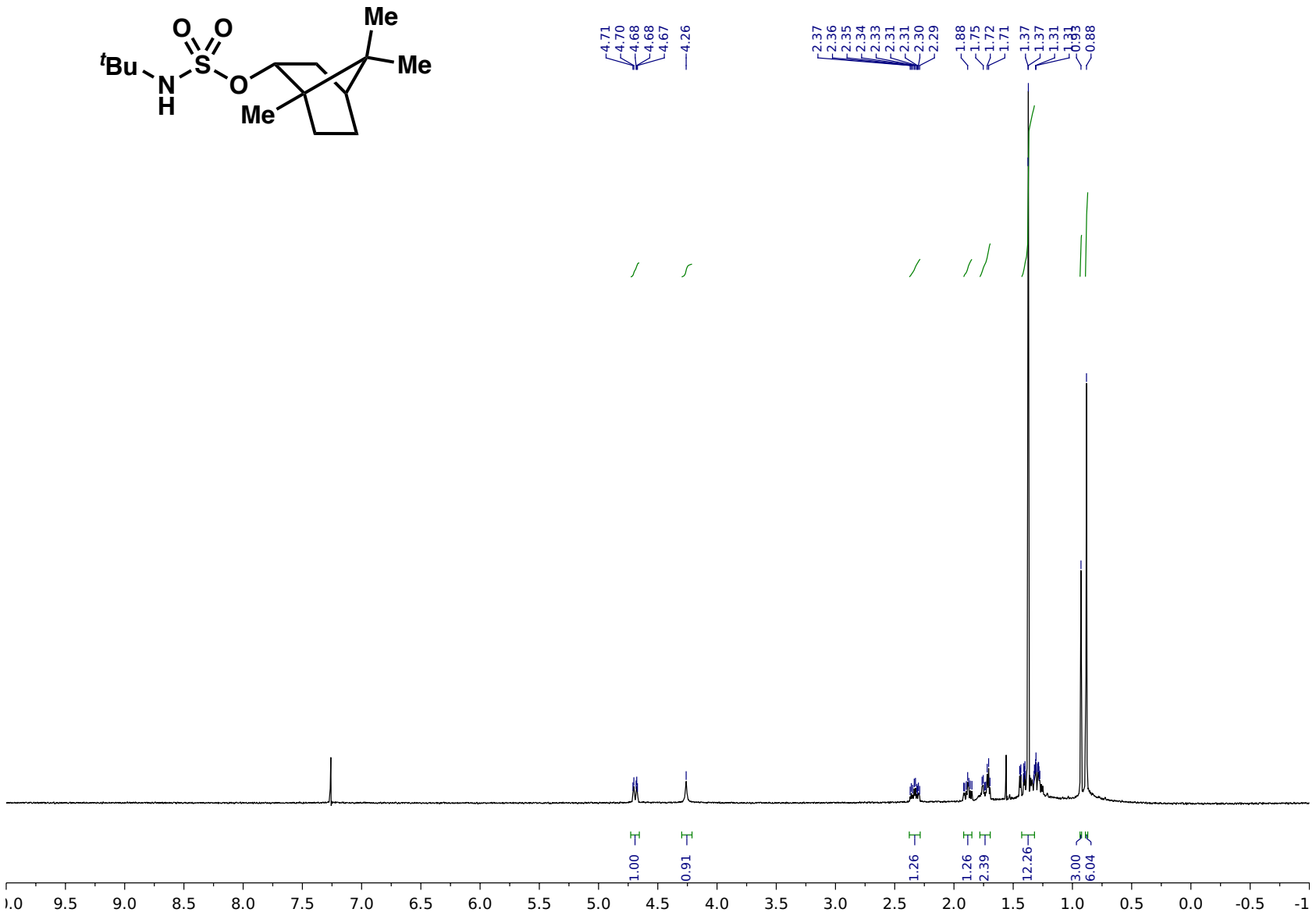
^{1}H NMR (400 MHz, $CDCl_3$) of (1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (2,2,2)-trifluoroethylsulfamate (**4q**)



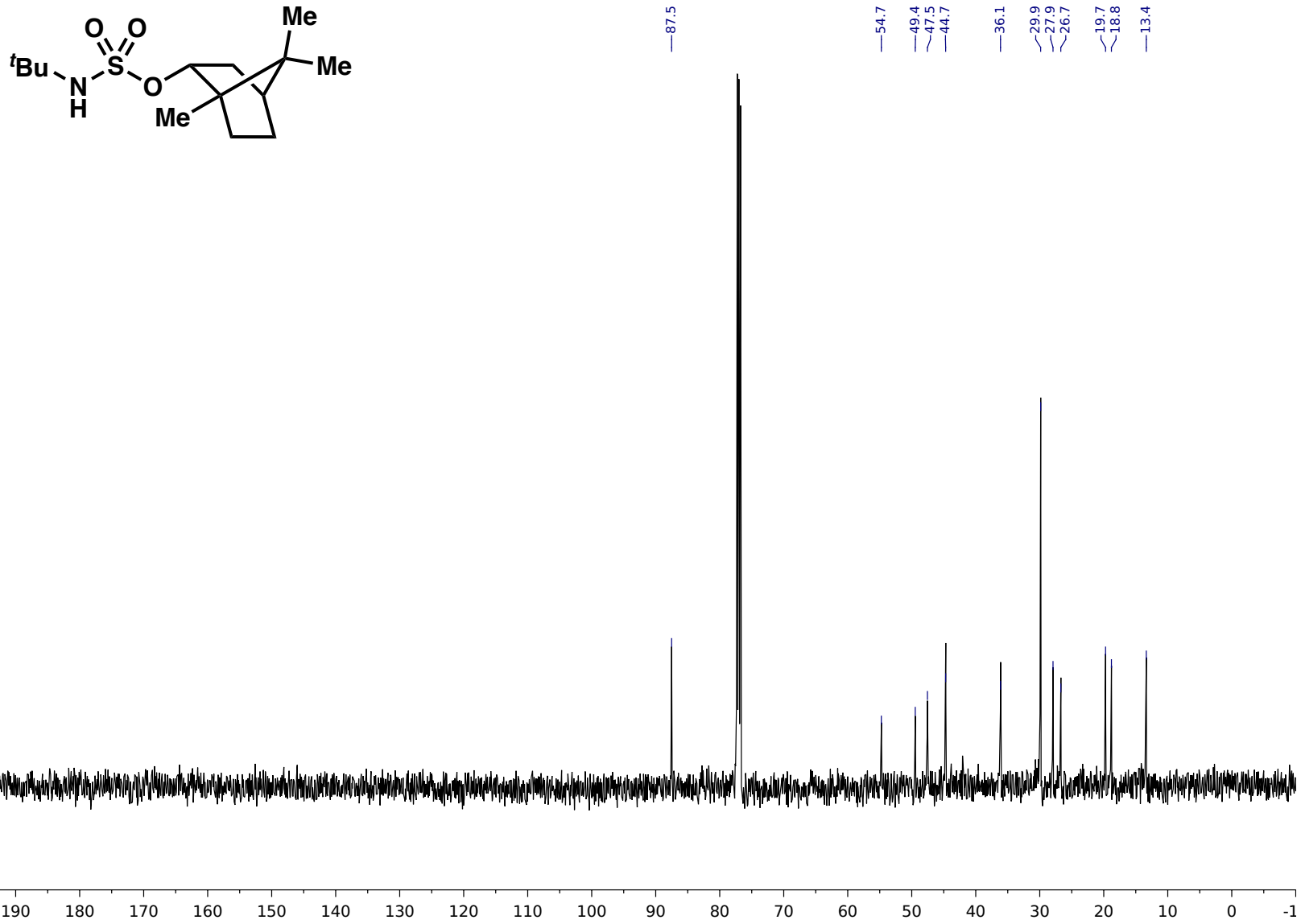
^{13}C NMR (126 MHz, $CDCl_3$) of (1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (2,2,2)-trifluoroethylsulfamate (**4q**)



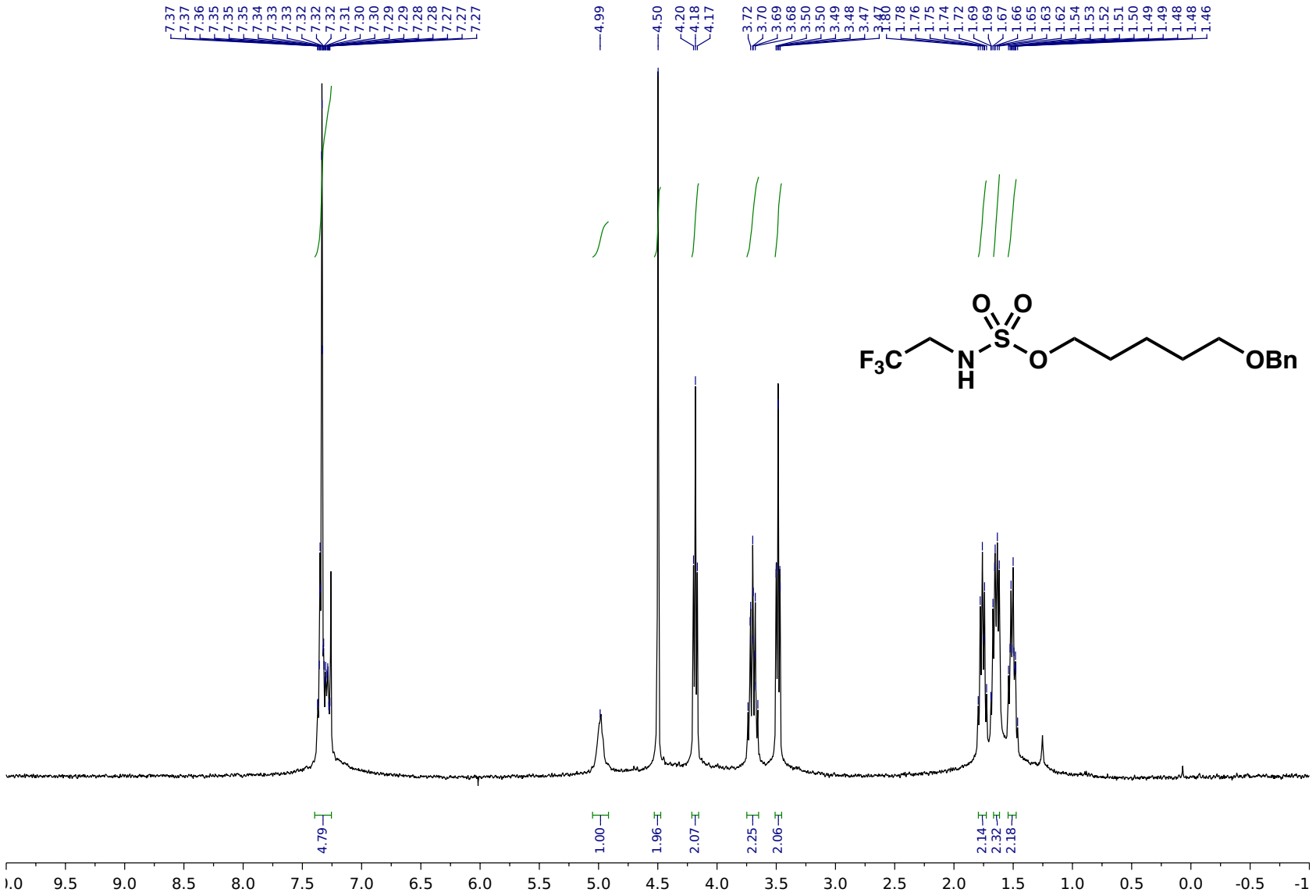
^{19}F NMR (376 MHz, $CDCl_3$) of (1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (2,2,2)-trifluoroethylsulfamate (**4q**)



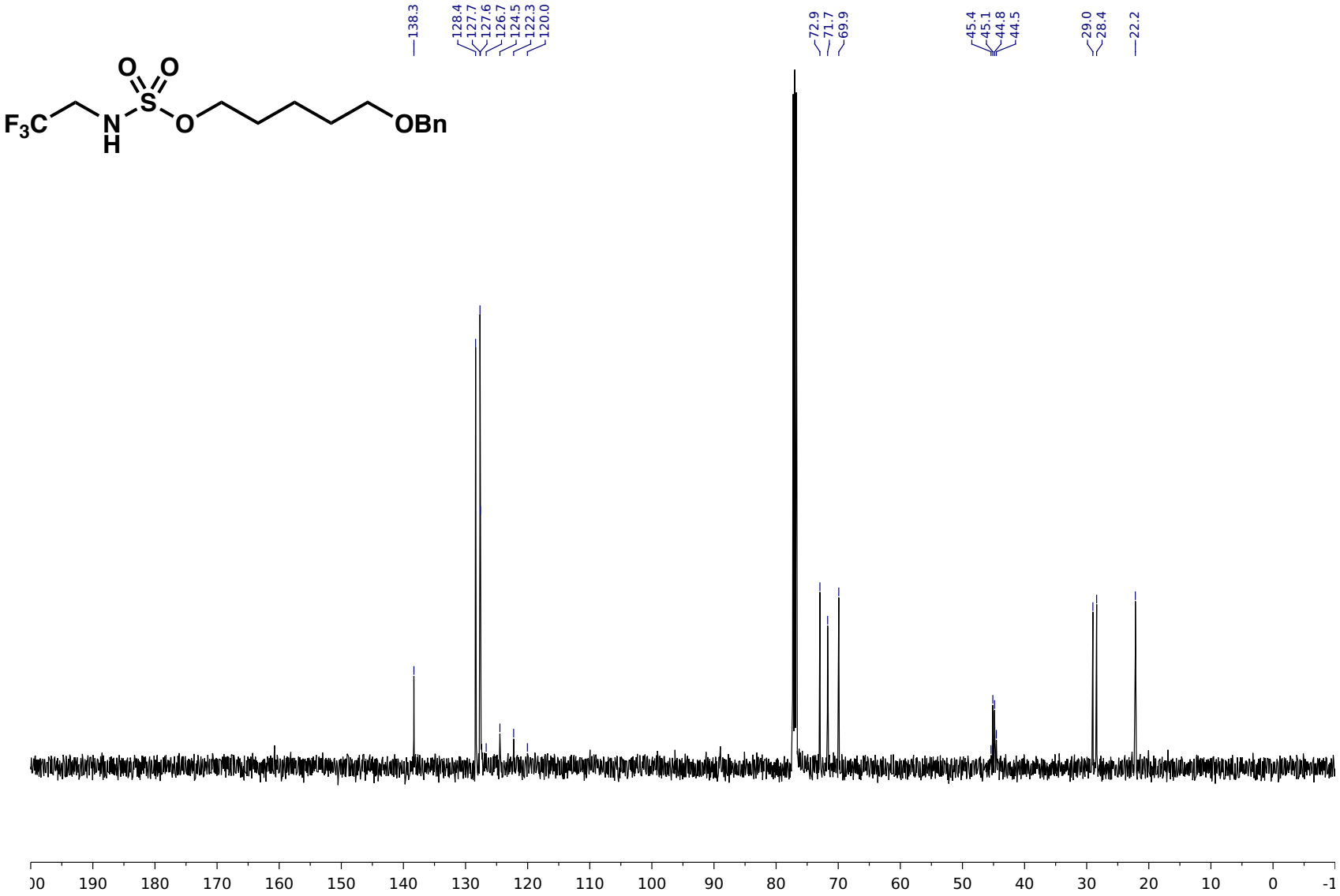
^{1}H NMR (400 MHz, $CDCl_3$) of (1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl *tert*-butylsulfamate (**S4b**)



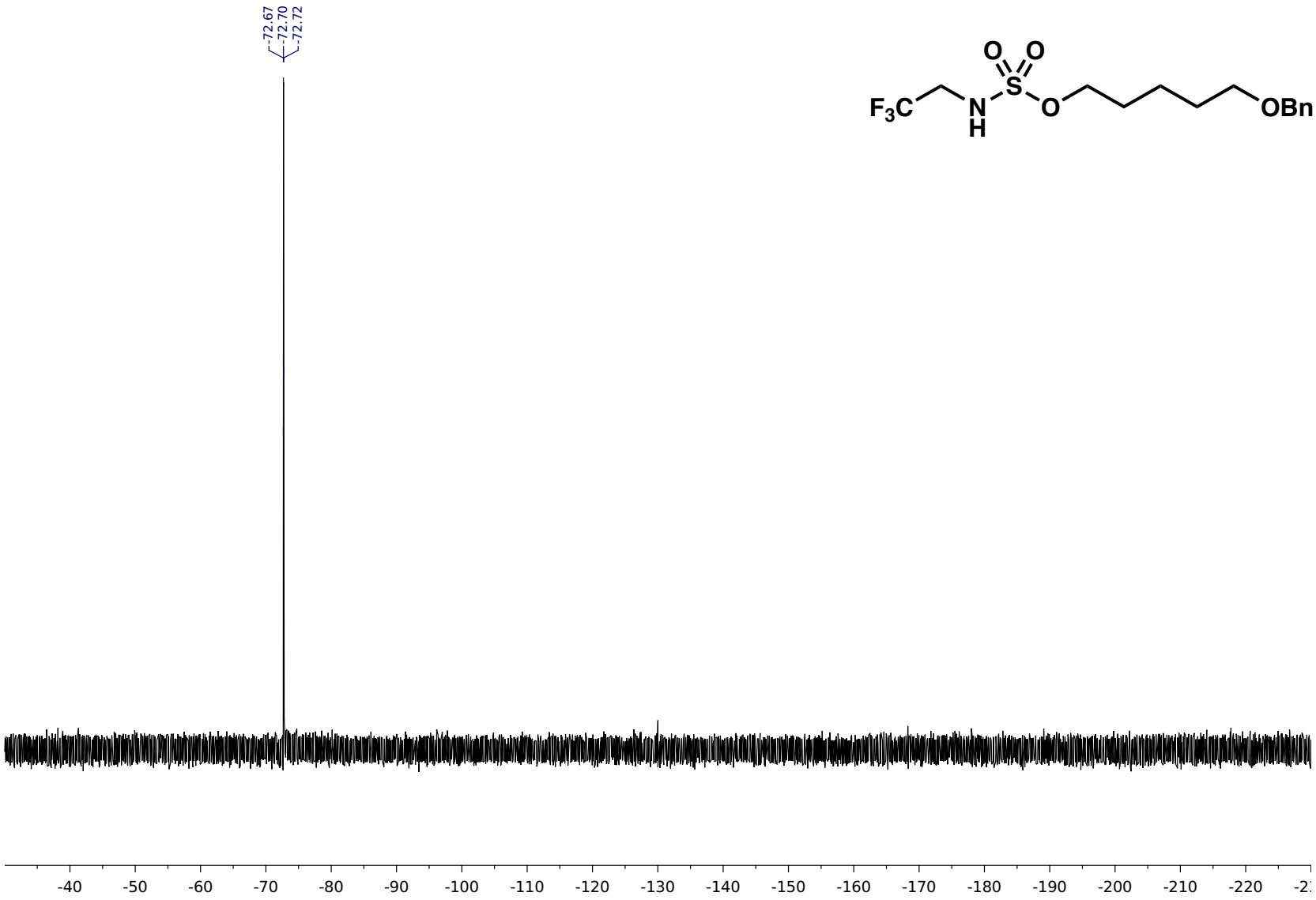
^{13}C NMR (126 MHz, $CDCl_3$) of (1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl *tert*-butylsulfamate (**S4b**)



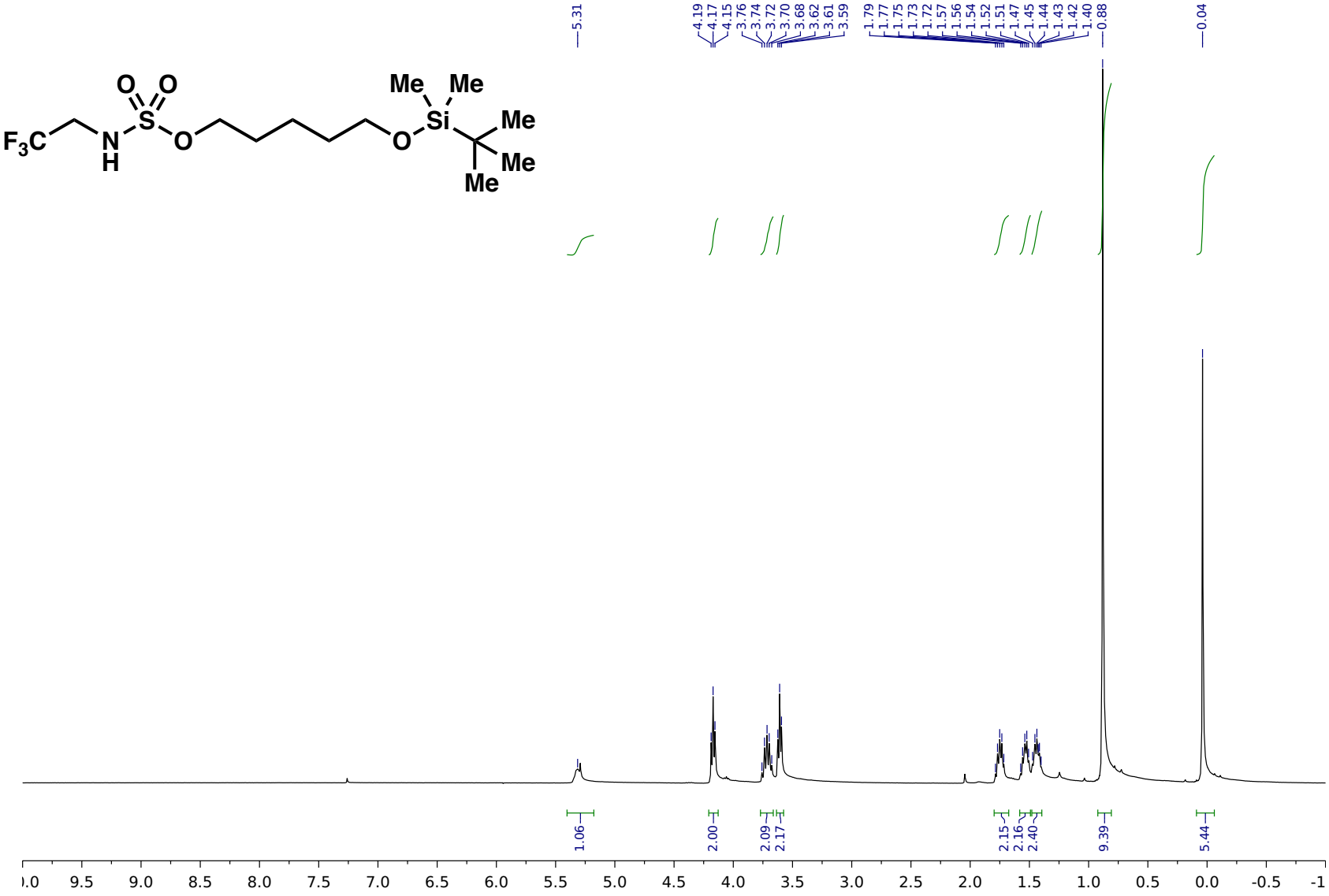
^{1}H NMR (400 MHz, $CDCl_3$) of 5-(benzyloxy)pentyl (2,2,2-trifluoroethyl)sulfamate (**4r**)



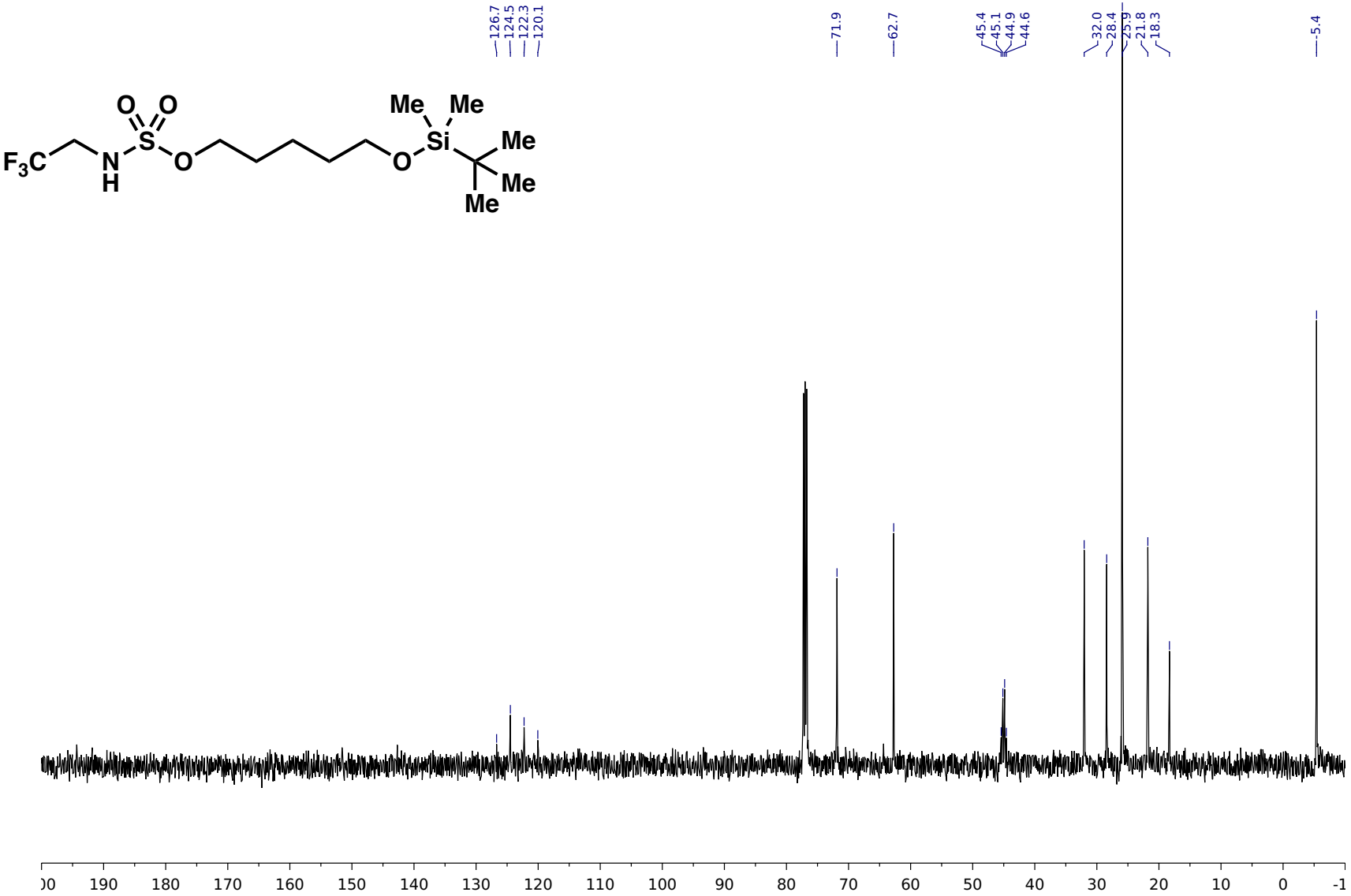
^{13}C NMR (126 MHz, $CDCl_3$) of 5-(benzyloxy)pentyl (2,2,2-trifluoroethyl)sulfamate (**4r**)



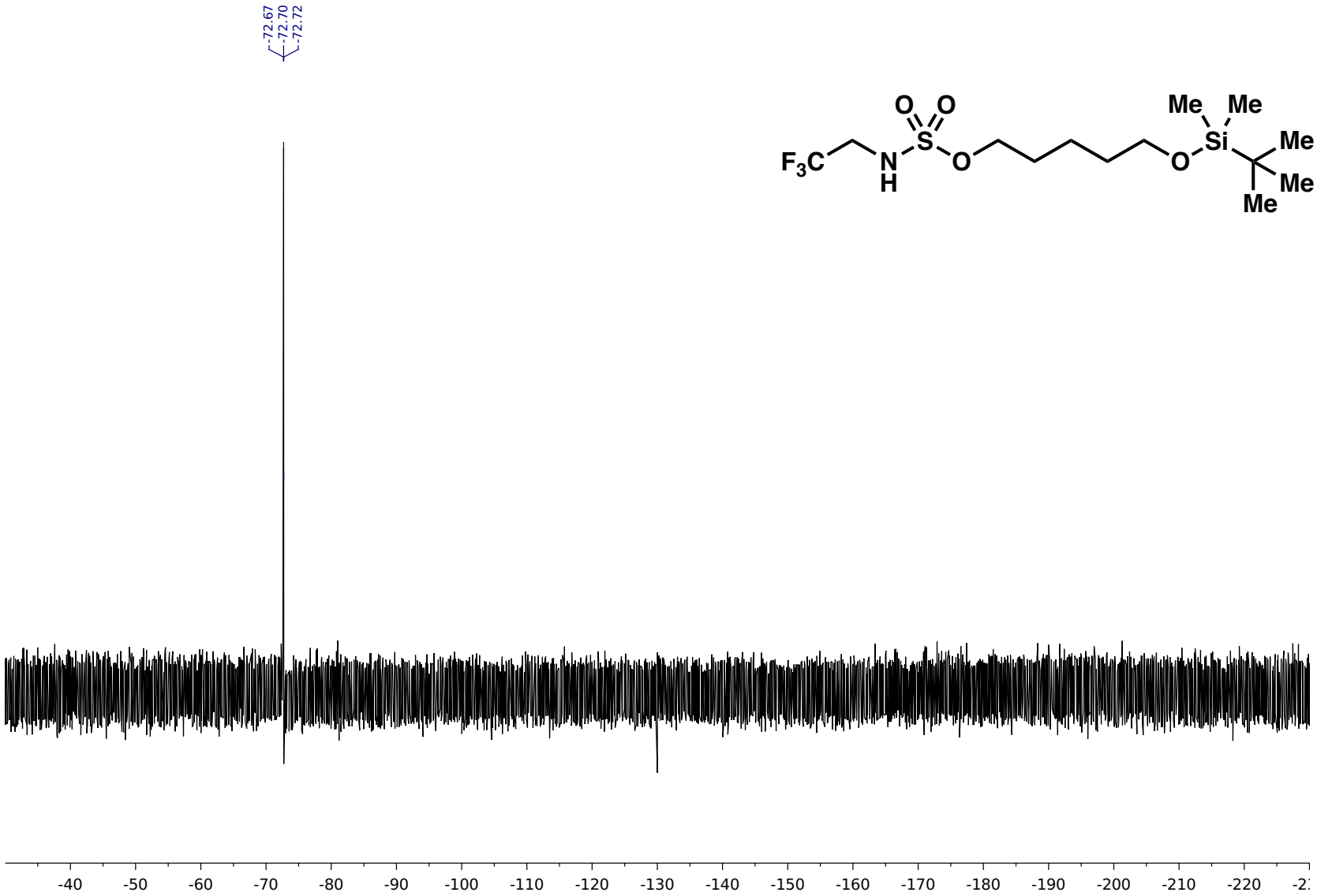
^{19}F NMR (376 MHz, $CDCl_3$) of 5-(benzyloxy)pentyl (2,2,2-trifluoroethyl)sulfamate (**4r**)



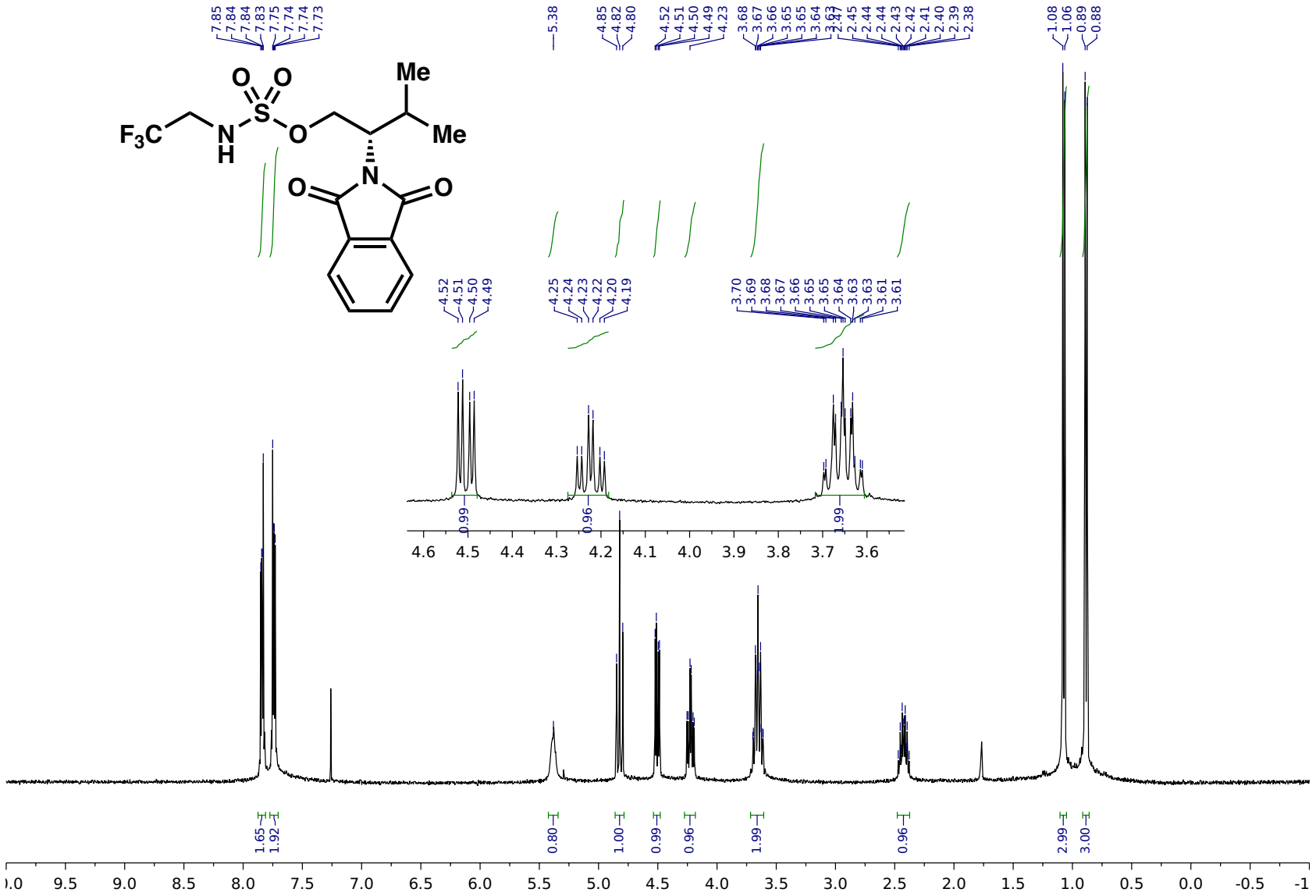
^{1}H NMR (400 MHz, $CDCl_3$) of 5-((*tert*-Butyldimethylsilyl)oxy)pentyl (2,2,2-trifluoroethyl)sulfamate (**4s**)



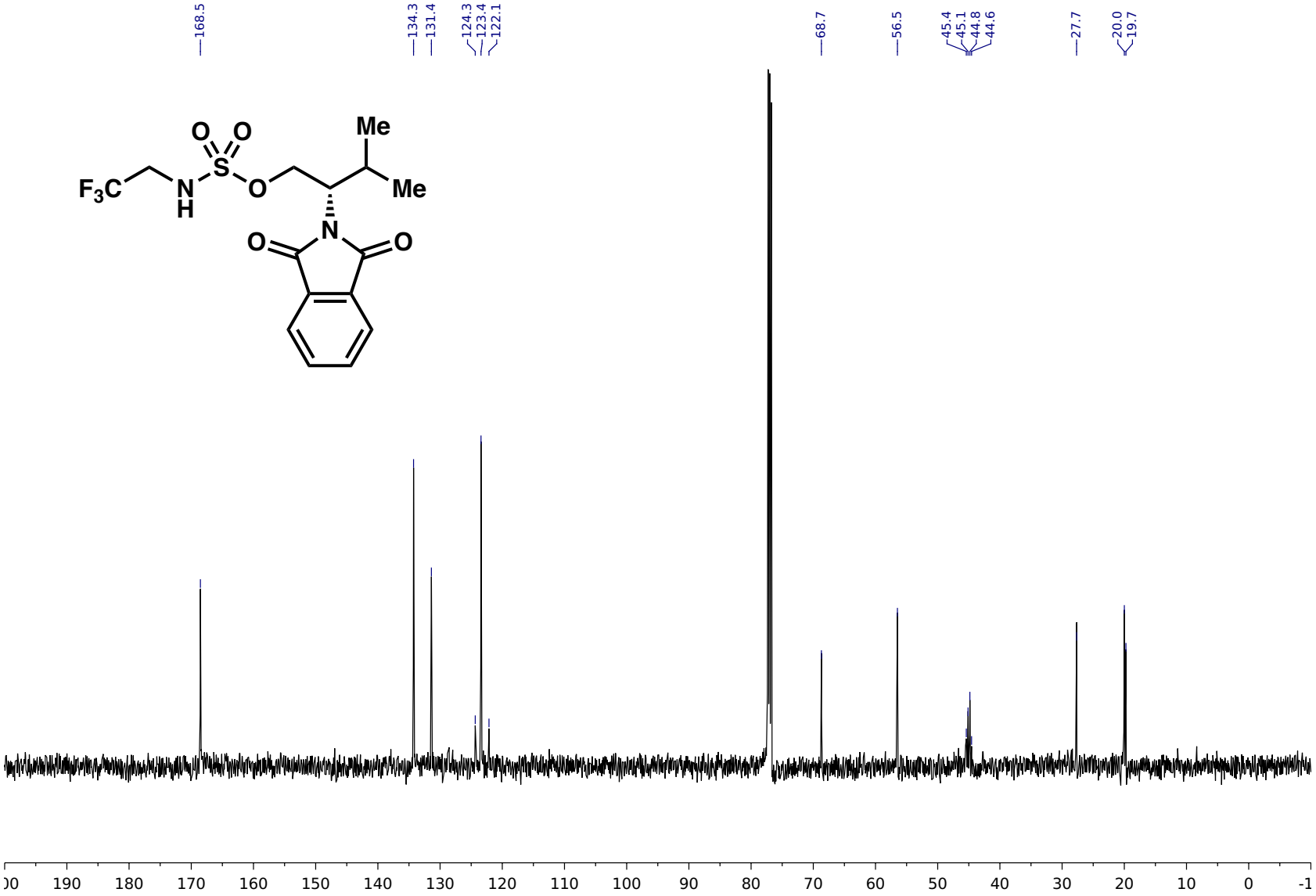
^{13}C NMR (126 MHz, $CDCl_3$) of 5-((*tert*-Butyldimethylsilyl)oxy)pentyl (2,2,2-trifluoroethyl)sulfamate (**4s**)



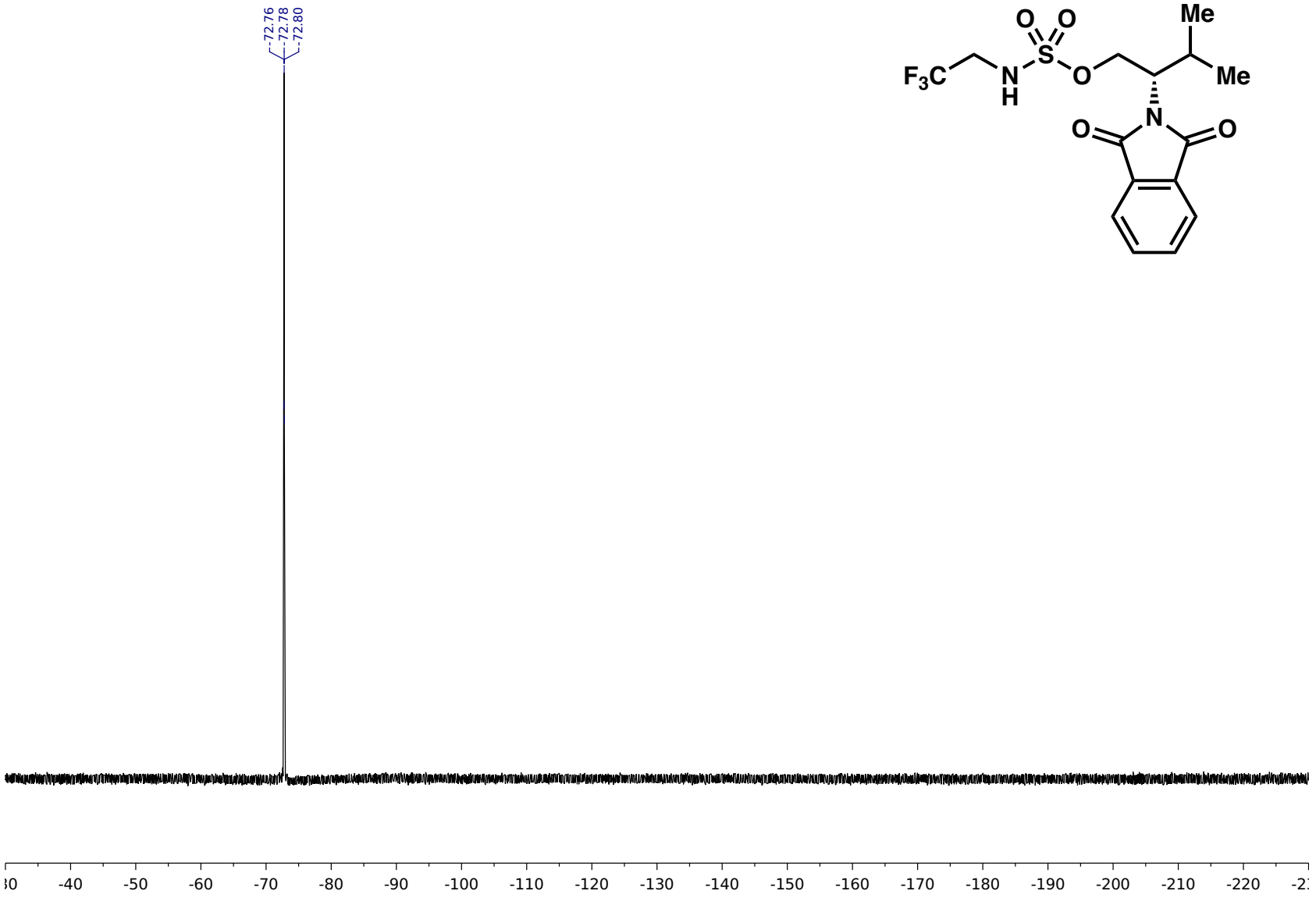
^{19}F NMR (376 MHz, $CDCl_3$) of 5-((*tert*-Butyldimethylsilyl)oxy)pentyl (2,2,2-trifluoroethyl)sulfamate (**4s**)



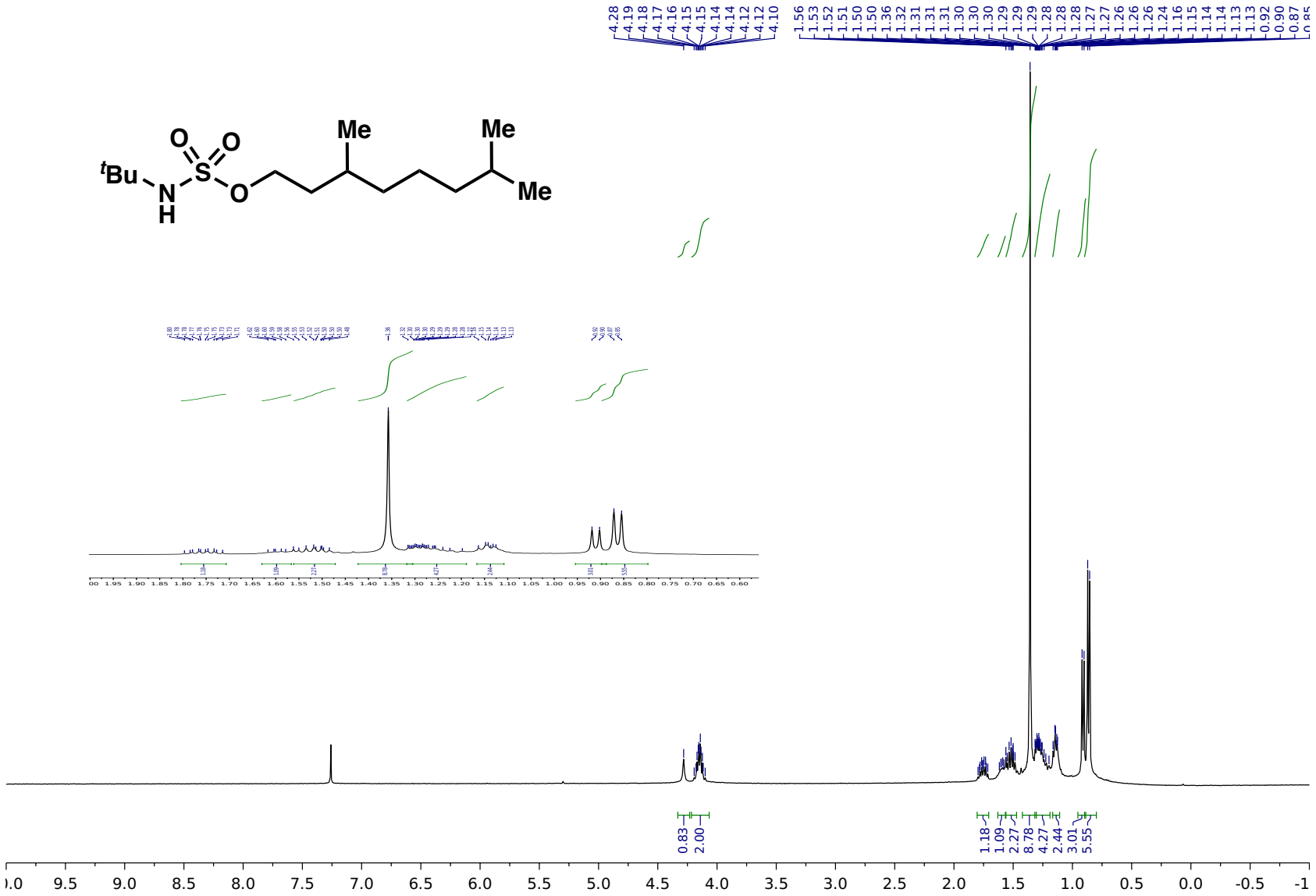
^{1}H NMR (400 MHz, $CDCl_3$) of (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-methylbutyl (2,2,2-trifluoroethyl)sulfamate (**4t**)



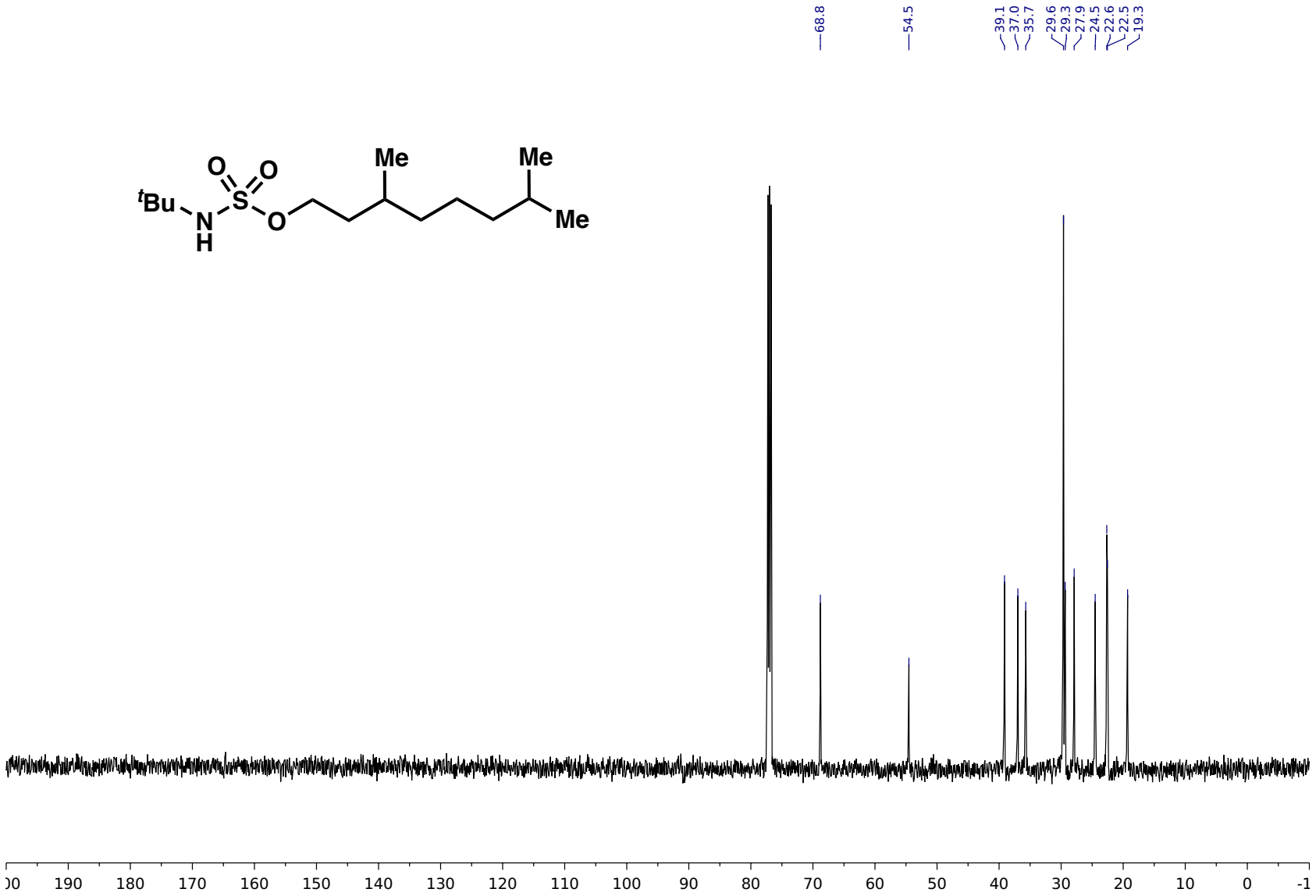
^{13}C NMR (126 MHz, $CDCl_3$) of (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-methylbutyl (2,2,2-trifluoroethyl)sulfamate (**4t**)



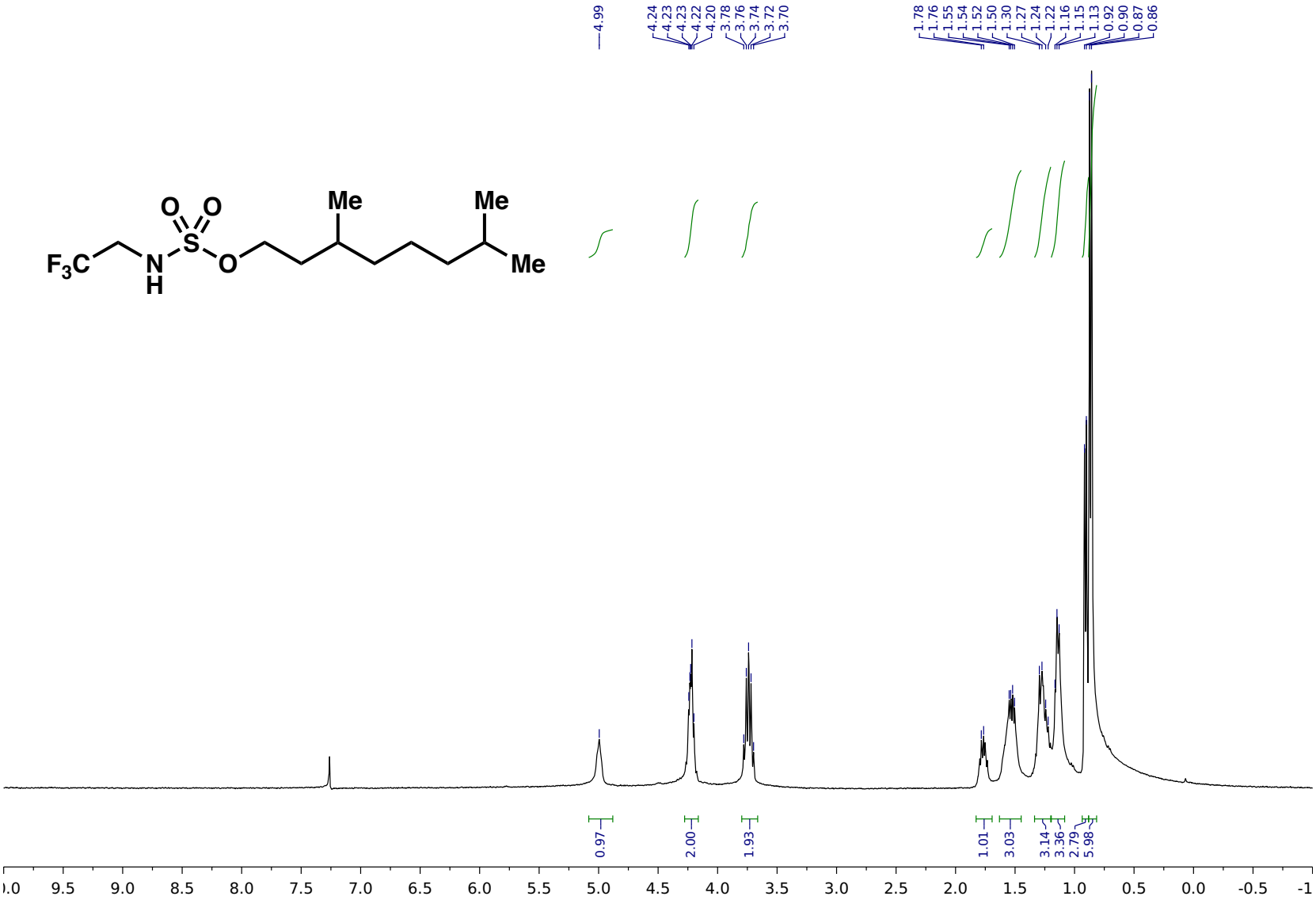
^{19}F NMR (376 MHz, $CDCl_3$) of (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-methylbutyl (2,2,2-trifluoroethyl)sulfamate (**4t**)



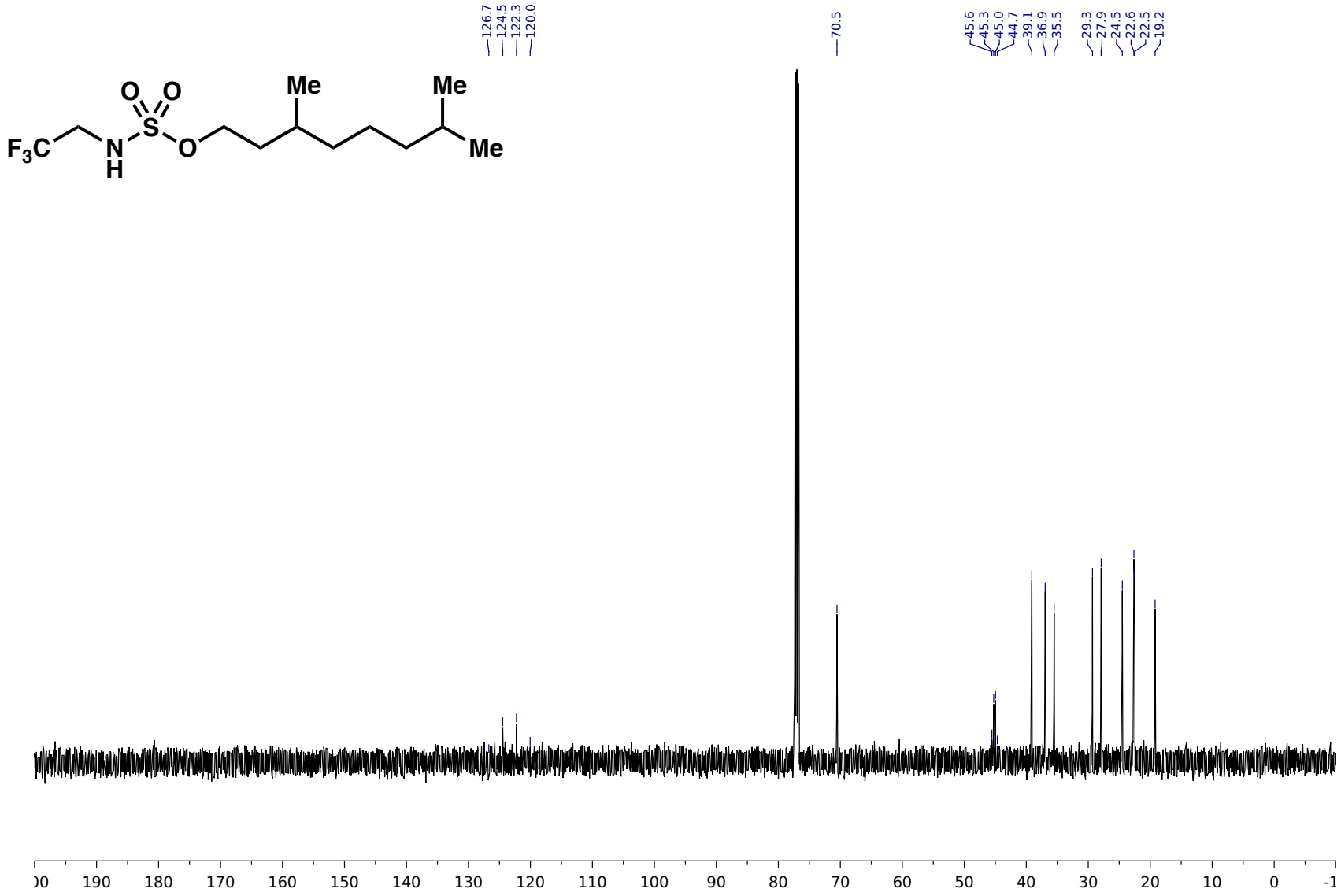
^{1}H NMR (400 MHz, $CDCl_3$) of 3,7-dimethyloctyl *tert*-butylsulfamate (**4u**)



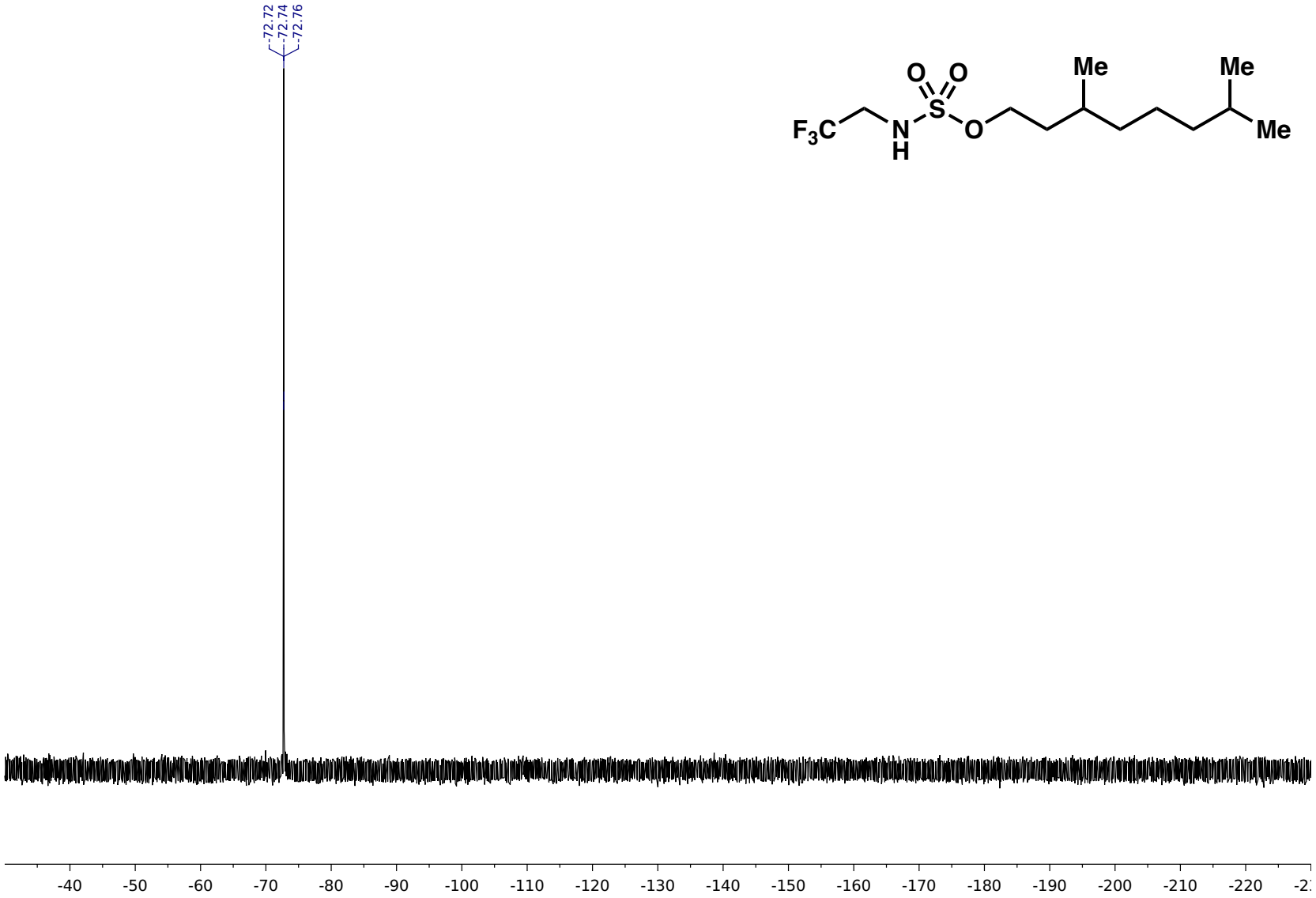
^{13}C NMR (126 MHz in $CDCl_3$) of 3,7-dimethyloctyl *tert*-butylsulfamate (**4u**)



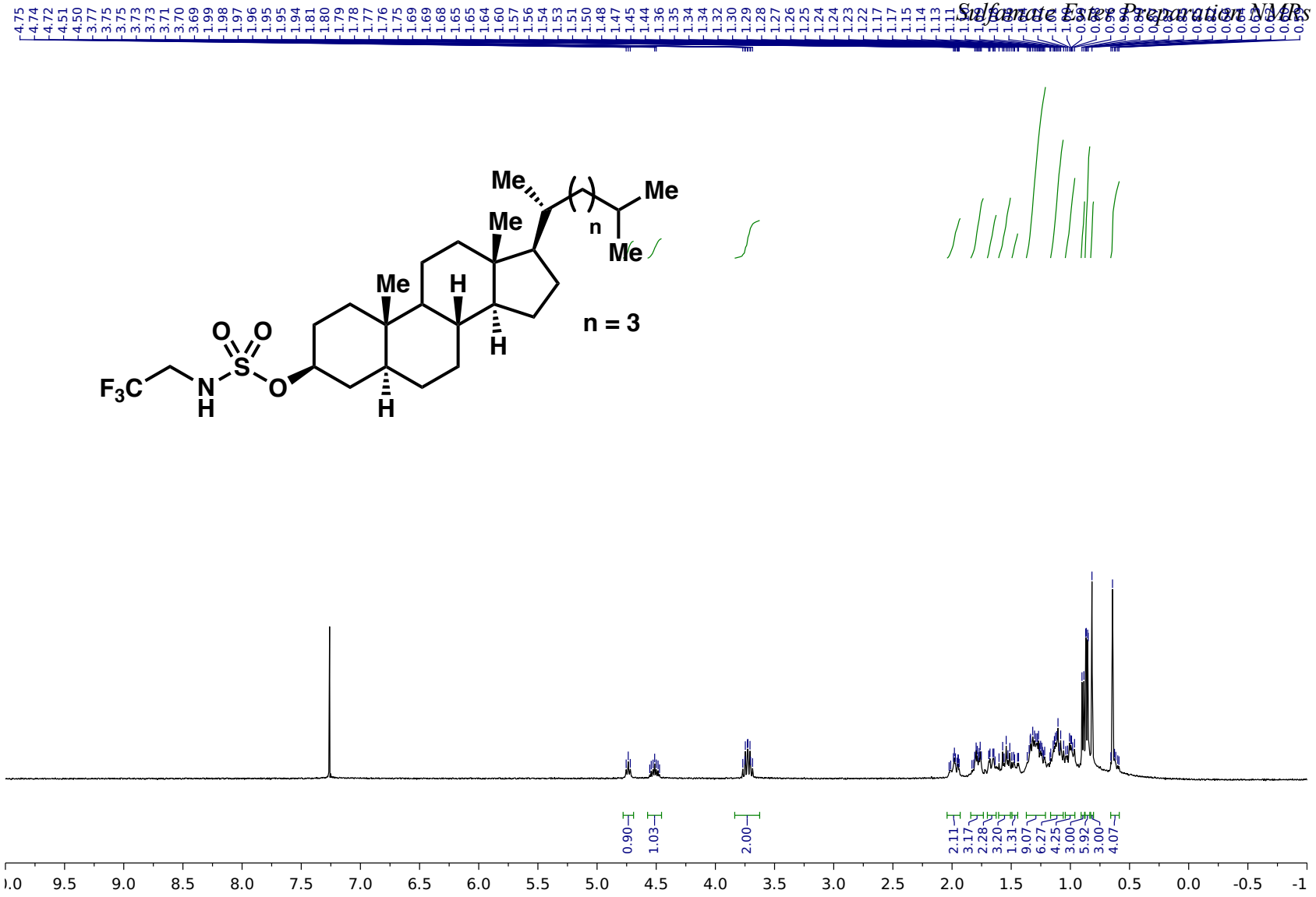
^{1}H NMR (400 MHz in $CDCl_3$) of 3,7-dimethyl (2,2,2-trifluoroethyl)sulfamate (**4v**)



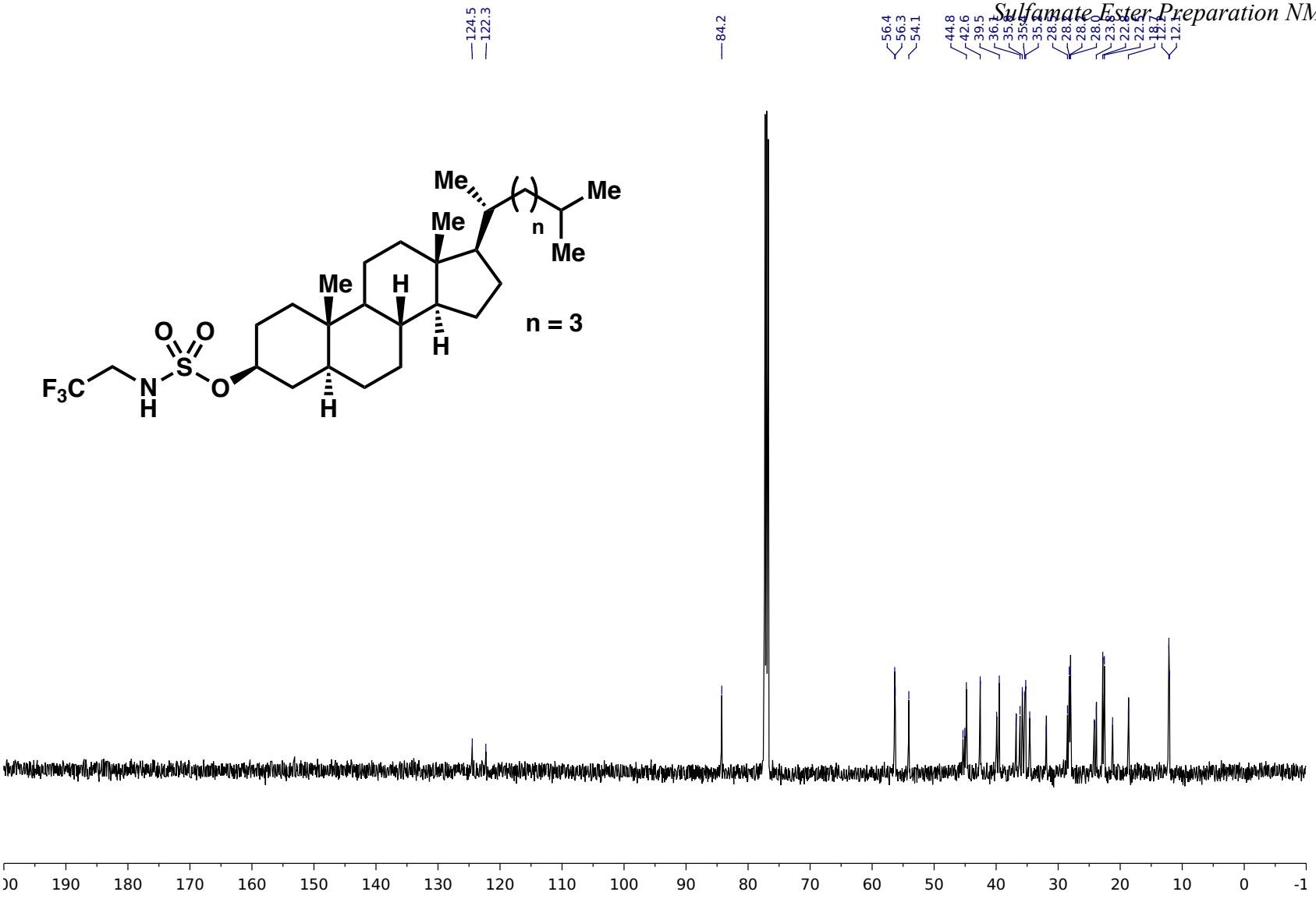
^{13}C NMR (126 MHz in $CDCl_3$) of 3,7-dimethyl (2,2,2-trifluoroethyl)sulfamate (**4v**)



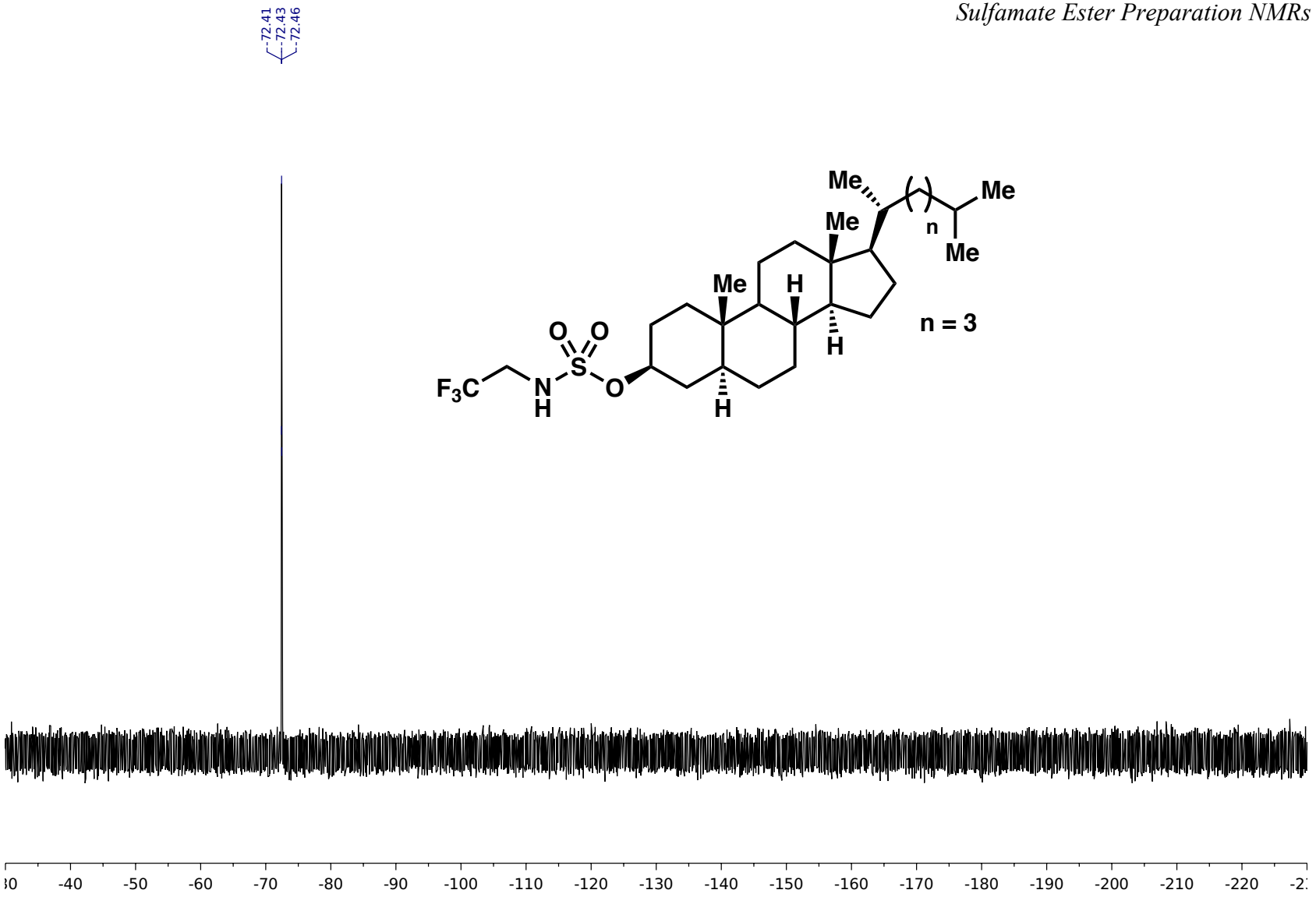
^{19}F NMR (376 MHz in $CDCl_3$) of 3,7-dimethyl (2,2,2-trifluoroethyl)sulfamate (**4v**)



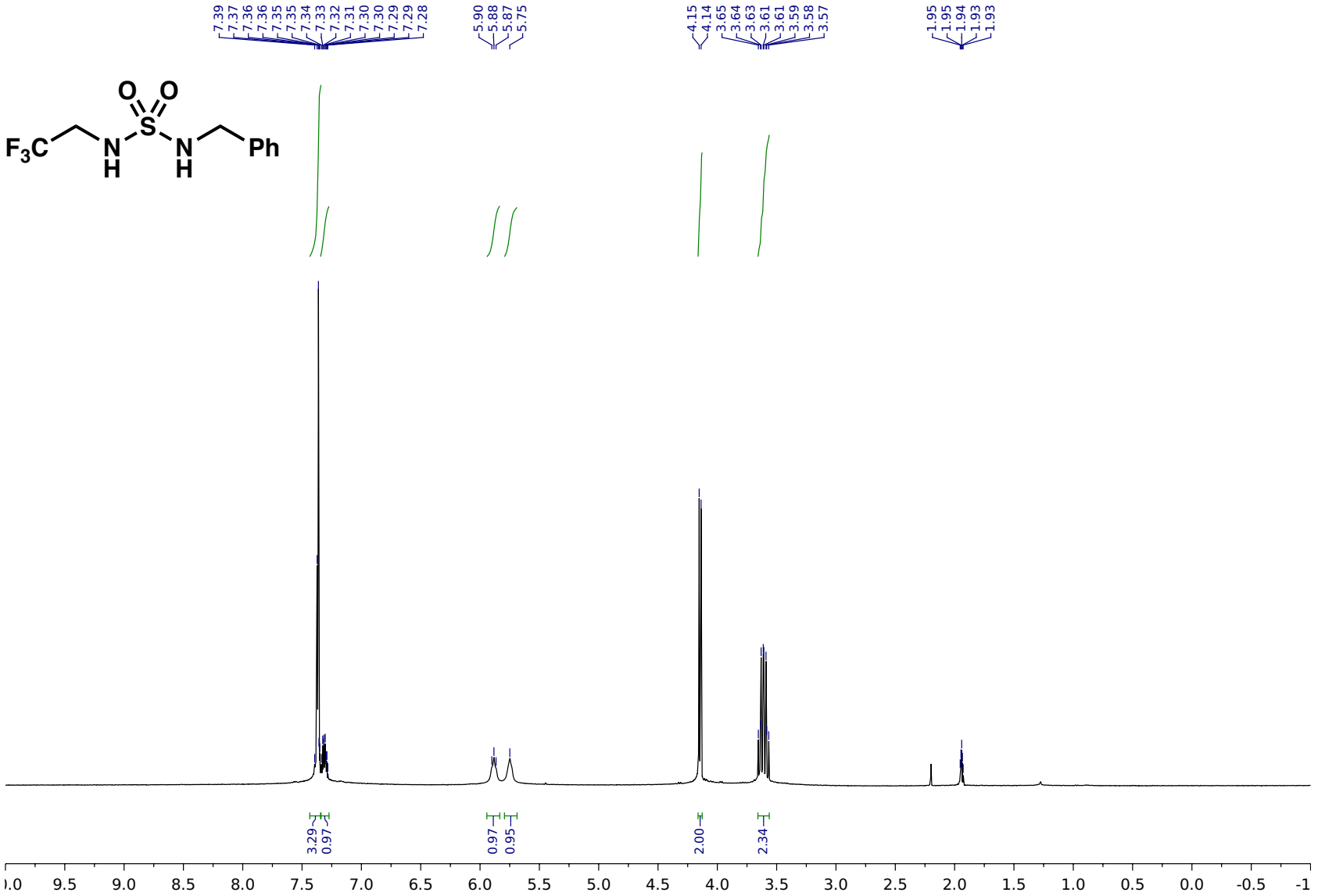
^{1}H NMR (400 MHz in $CDCl_3$) of (3*S*,5*S*,8*R*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (2,2,2-trifluoroethyl)sulfamate (**4w**)



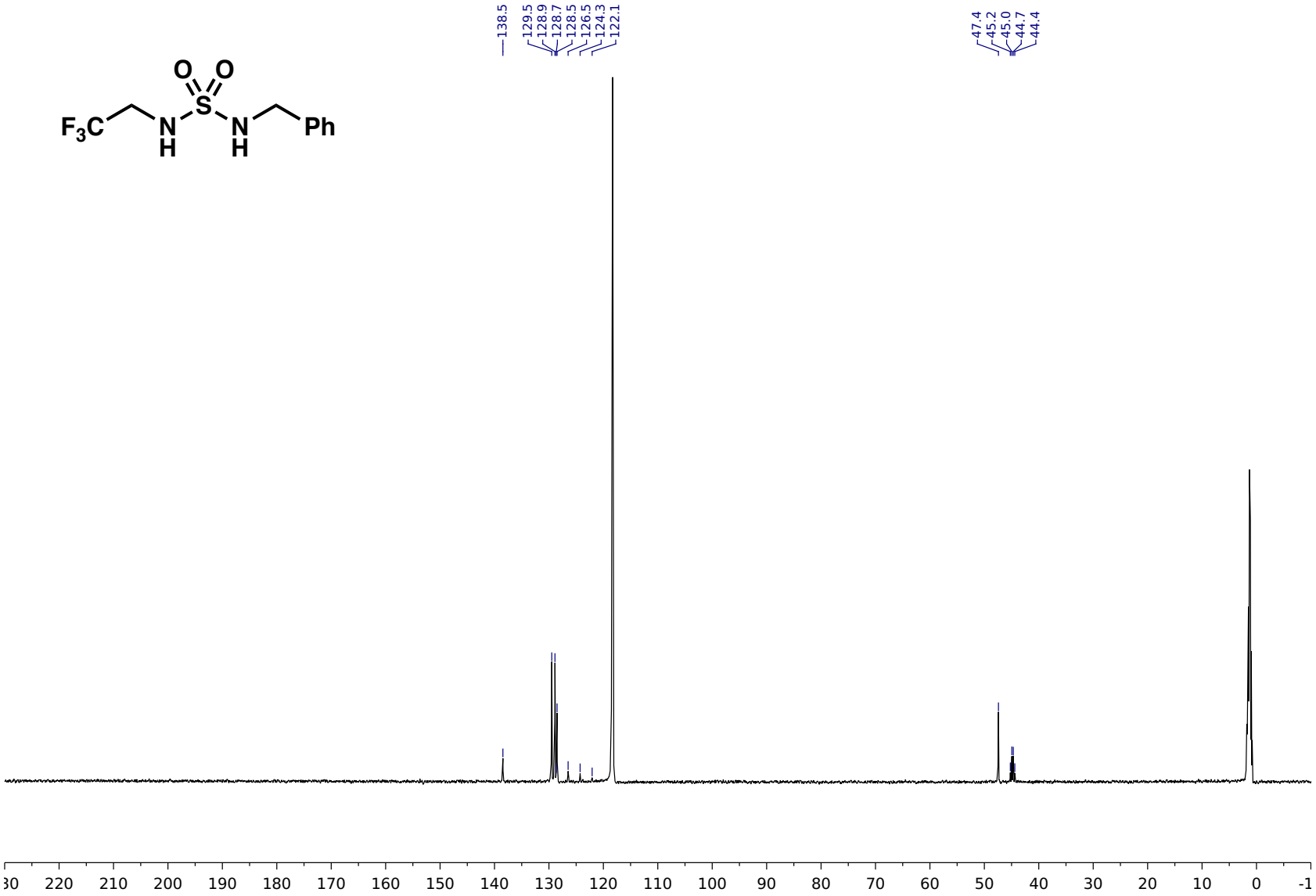
^{13}C NMR (126 MHz, $CDCl_3$) of (3*S*,5*S*,8*R*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (2,2,2-trifluoroethyl)sulfamate (**4w**)



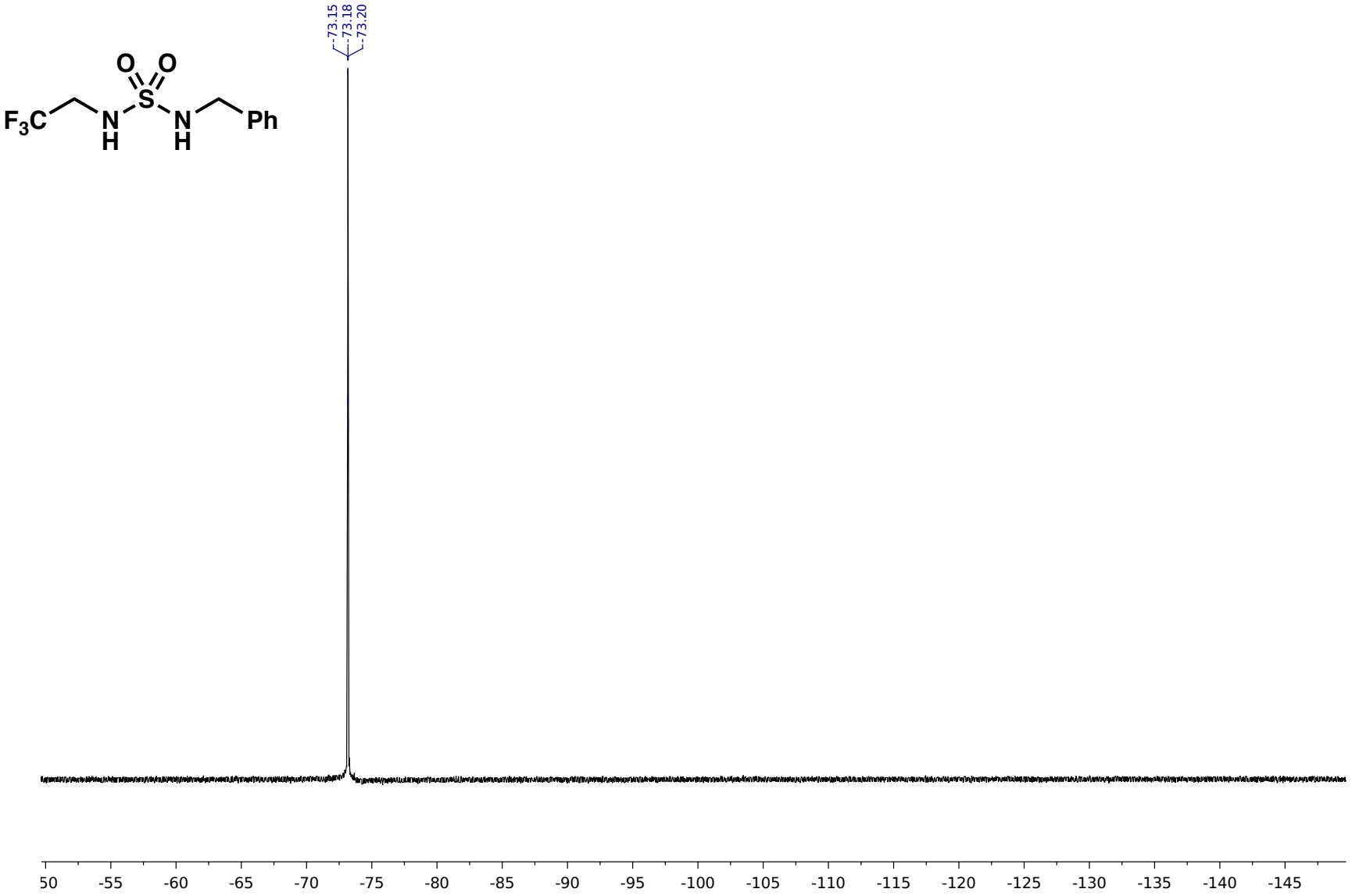
^{19}F NMR (376 MHz in $CDCl_3$) of (3*S*,5*S*,8*R*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (2,2,2-trifluoroethyl)sulfamate (**4w**)



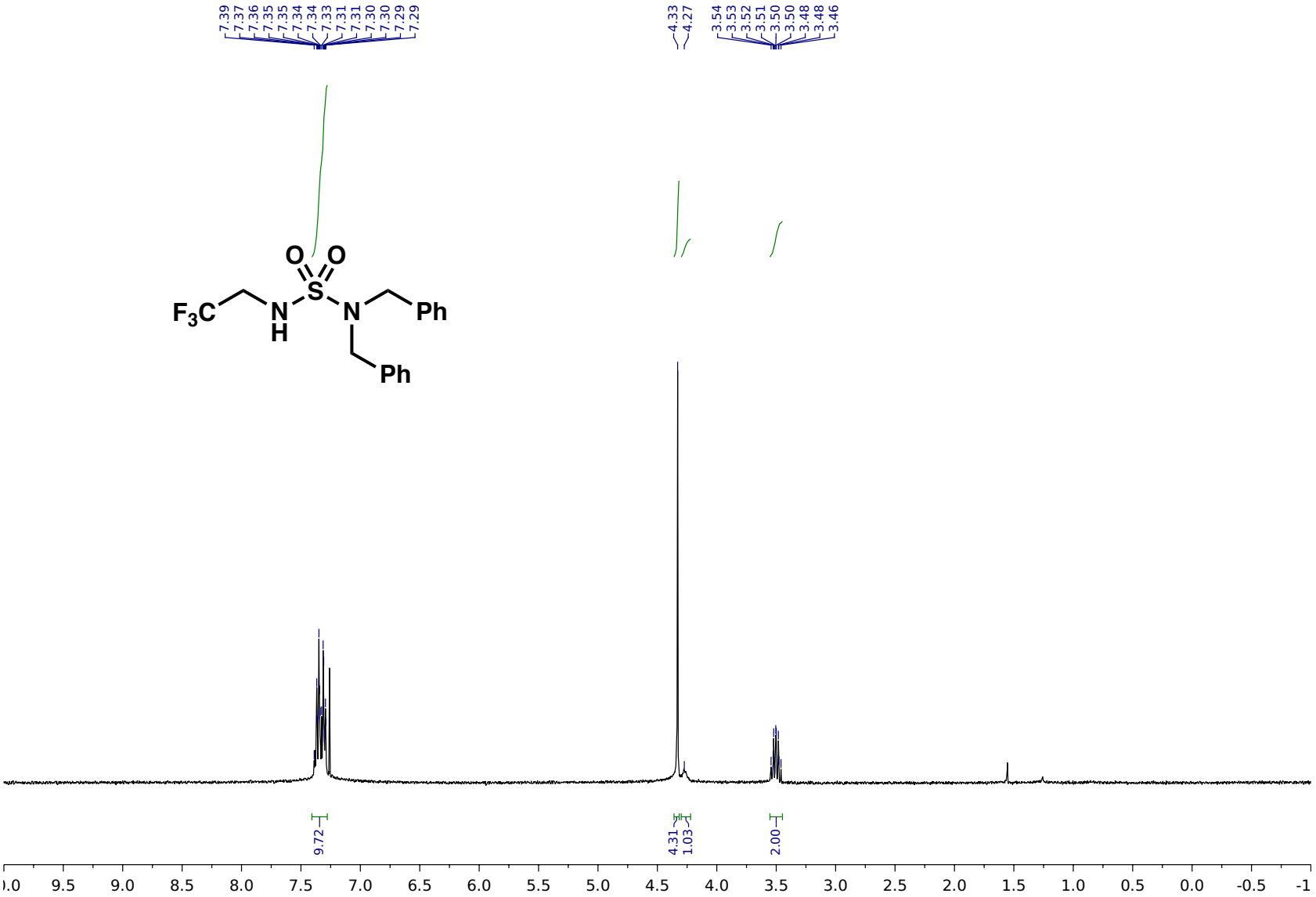
^{1}H NMR (400 MHz in CDCN) of *N*-(Benzyl)-*N*'-(2,2,2-trifluoroethyl)sulfamide (**6a**)



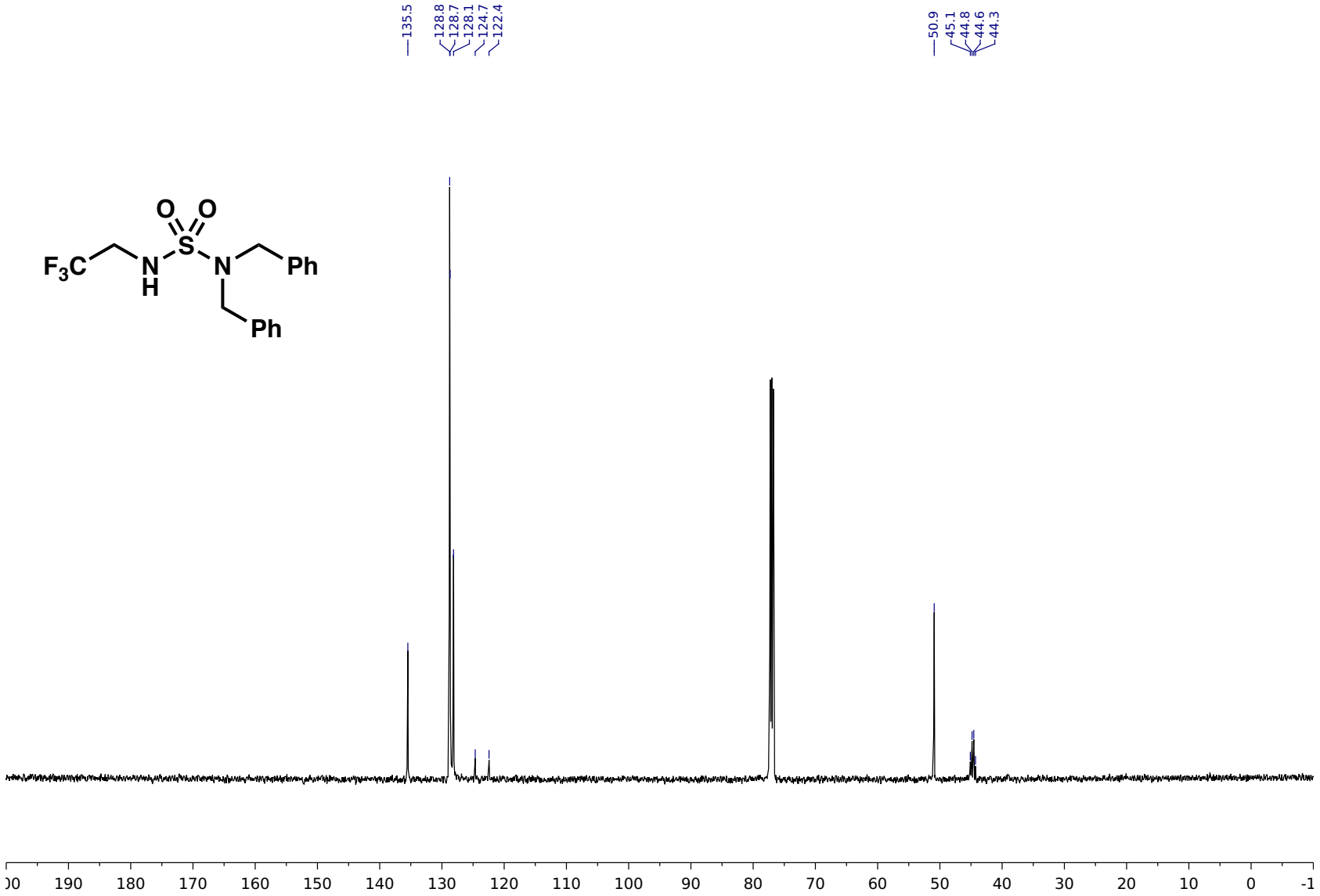
^{13}C NMR (126 MHz in CDCN) of *N*-(Benzyl)-*N*'-(2,2,2-trifluoroethyl)sulfamide (**6a**)



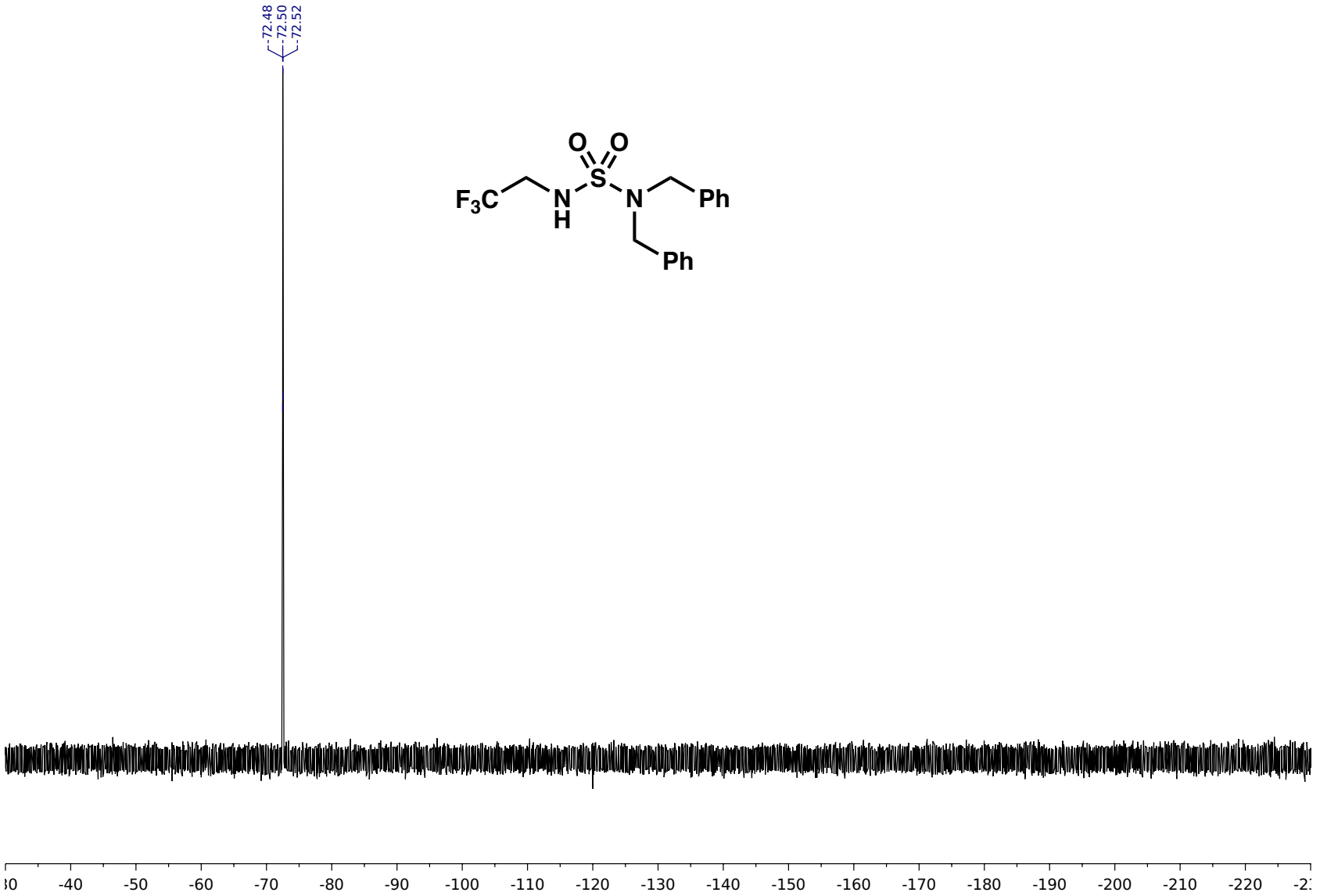
^{19}F NMR (376 MHz in CDCN) of *N*-(Benzyl)-*N*'-(2,2,2-trifluoroethyl)sulfamide (**6a**)



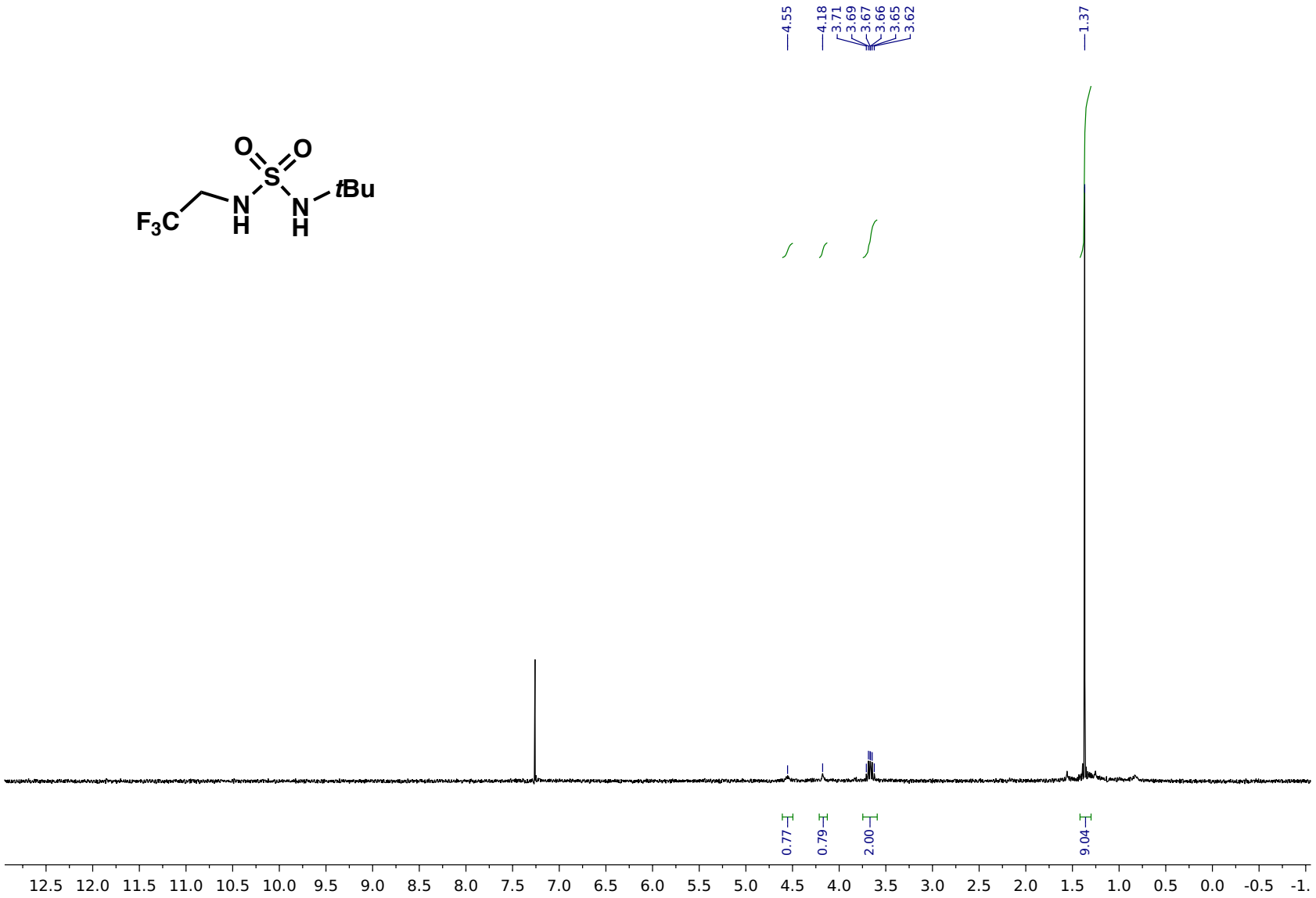
^{1}H NMR (400 MHz in $CDCl_3$) of *N,N*-Dibenzyl-*N*'-(2,2,2-trifluoroethyl)sulfamide (**6b**)



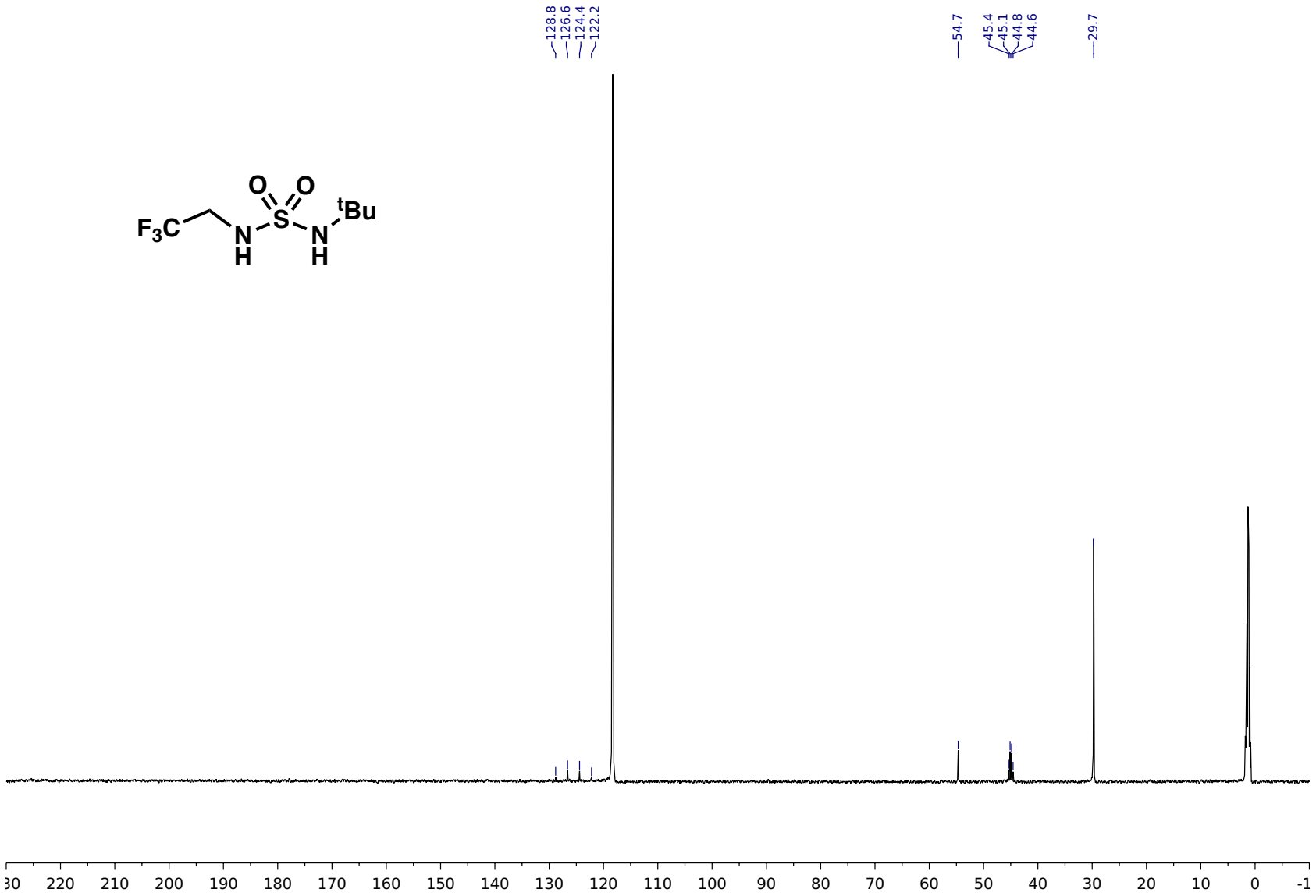
^{13}C NMR (126 MHz in $CDCl_3$) of *N,N*-Dibenzyl-*N*'-(2,2,2-trifluoroethyl)sulfamide (**6b**)



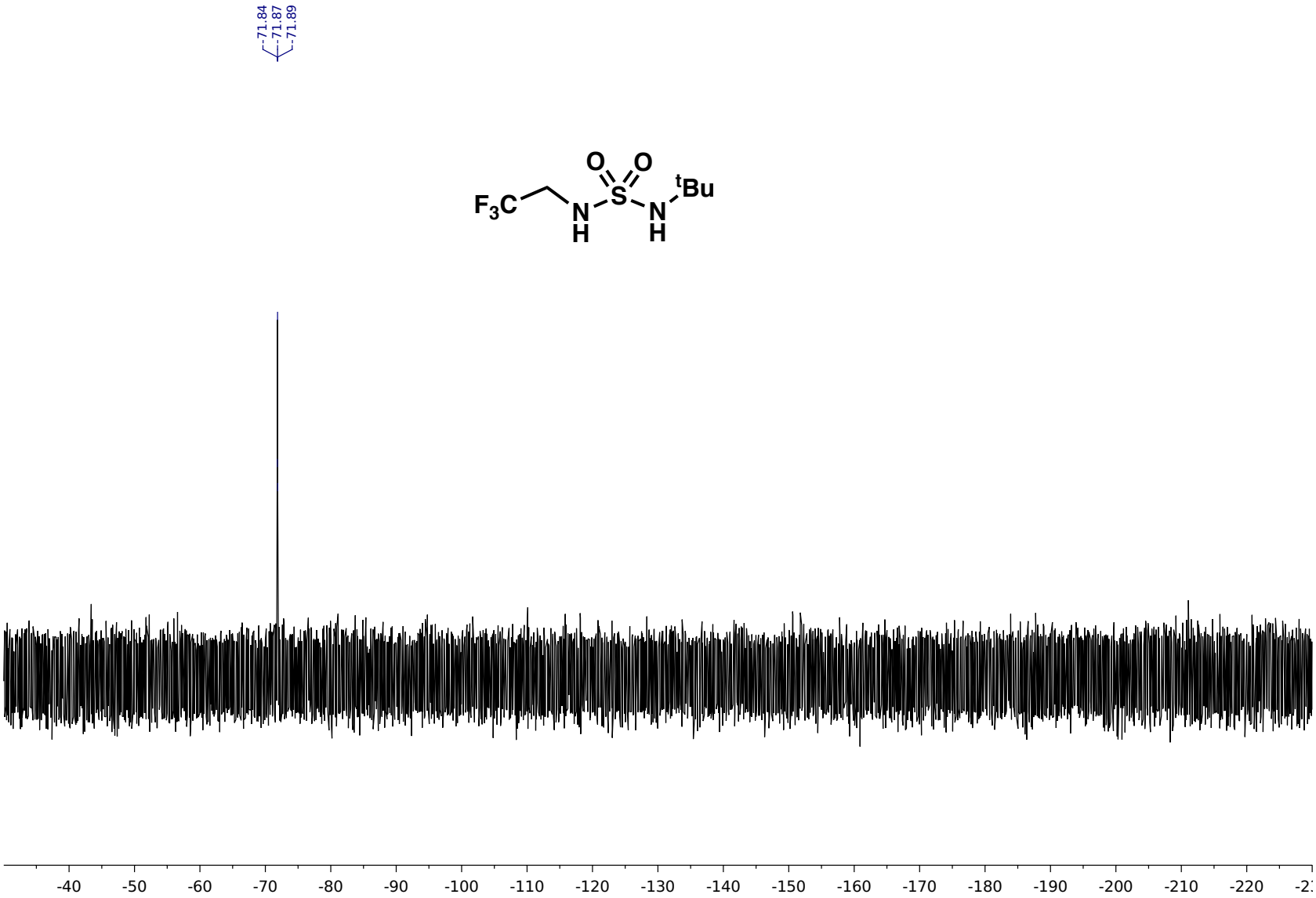
^{19}F NMR (376 MHz in $CDCl_3$) of *N,N*-Dibenzyl-*N*'-(2,2,2-trifluoroethyl)sulfamide (**6b**)



^{1}H NMR (400 MHz in $CDCl_3$) of *N*-(*t*-Butyl)-*N*'-(2,2,2-trifluoroethyl)-sulfamide (**6c**)



^{13}C NMR (126 MH2, in CDCN) of *N*-(*t*-Butyl)-*N*'-(2,2,2-trifluoroethyl)-sulfamide (**6c**)



NMR (376 MHz in $CDCl_3$) of *N*-(*t*-Butyl)-*N*'-(2,2,2-trifluoroethyl)-sulfamide (**6c**)

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