Electronic Supporting Information

Synthesis and [3,3]-Sigmatropic Rearrangements of (*E*)-5-(Pentafluoro-λ^6-sulfanyl)-pent-3-en-2-ol, its Homologues and Trifluoromethyl Analogues

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Optimization experiments of Johnson-Claisen rearrangements of (*E*)-1-(pentafluoro-λ⁶-sulfanyl)penta-1,4-dien-3-ol (2g)

Johnson-Claisen rearrangements were executed both with trimethyl- as well as with triethyl orthoacetate under the conditions shown in Table S1.

Table S1. Synthesis of ζ-SF_5-substituted γ,δ,ε,ζ-unsaturated esters **10g** by Johnson-Claisen rearrangement of **2g**.

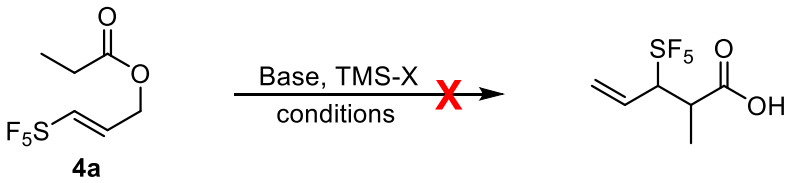
Entry	R	Solvent	Acid	Temperature, Time	Yield of **10** [%]
1	Me	Toluene	$C_2H_5CO_2H$	115 °C, 5 h	**10g1** (R=Me) 31
2	Me	$CH_3C(COMe)_3$	$C_2H_5CO_2H$	110 °C, 2 h	**10g1** (R=Me) 92*
3[a]	Et	$CH_3C(COEt)_3$	$C_2H_5CO_2H$	150 °C, 5 h	**10g2** (R=Et) 27**
4	Et	$CH_3C(COEt)_3$	*p*-TsOH	150 °C, 5 h	**10g2** (R=Et) 8**
5	Et	$CH_3C(COEt)_3$	$C_2H_5CO_2H$	120 °C, 0.5 h, μ = 150 W	**10c2** (R=Et) 26**

[a] trace amount of hydroquinone was added, *yield by ^{19}F NMR spectroscopy **yield by GC

The yield of product **10g1** (R = Me) could be increased when the orthoester was used as solvent and temperature was slightly reduced (entry 2). The rearrangement was also successful with triethyl orthoacetate preferably when propionic acid was used as catalyst (entries 3 and 4). The yield was not increased when lower temperature in combination with microwave irradiation was applied (entries 3 and 5).

Efforts for Ireland-Claisen rearrangements of (*E*)-1-(pentafluoro-λ⁶-sulfanyl)alk-1-en-3-yl-esters (4a-c)

Treatment of compound **4a** with 1.2 equiv of each Et_3N and TMSOTf in CH_2Cl_2 at different temperatures (r.t. to 50 °C) in a sealed tube for 24 hours resulted in complete decomposition of the **4a**. The same result was observed when this ester was treated with 1.2 equiv of LHMDS and 9.7 equiv of TMSCl in THF at 80 °C for 24 hours. When the latter components were reacted at r.t. for 6 h, in addition to the decomposition fragments some starting material was found in the black product mixture. In none of the experiments, were traces of the expected product detected in the crude product by ^{19}F NMR (Table S2).

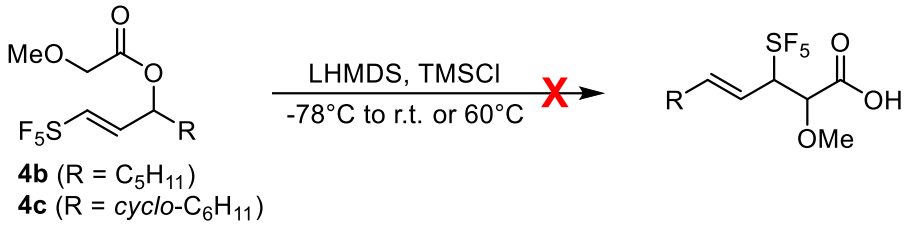


4a

Table S2. Efforts for Ireland-Claisen rearrangement of **4a**.

Entry	Base	equiv	Solvent	X (equiv)	Temp.	Time	Result
1	Et_3N	1.2	CH_2Cl_2	OTf (1.2)	50 °C	24 h	Decomp.
2	LHMDS	1.2	THF	Cl (9.7)	r.t.	6 h	Decomp.
3	LHMDS	1.2	THF	Cl (9.7)	80 °C	24 h	Decomp.

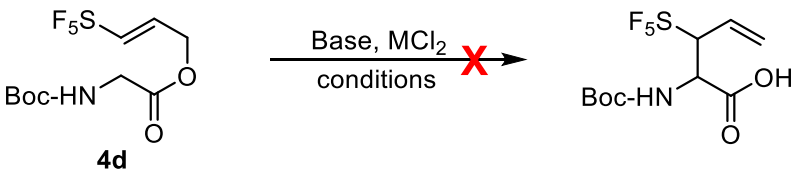
Then we treated the methoxy-substituted allylic acetates **4b** and **4c** with LHMDS/TMSCl in THF at room temperature or 60 °C, the conditions which were successfully used by Konno et al. [1] for the Ireland-Claisen rearrangement of corresponding CF_3 compounds. In none of the reactions were the expected products found in the crude product mixtures by ^{19}F NMR spectroscopy.



4b (R = C_5H_{11})
4c (R = *cyclo*-C_6H_{11})

Efforts for ester enolate-Claisen rearrangements of *N*-Boc-(*E*)-1-(pentafluoro-λ⁶-sulfanyl)alk-1-en-3-yl-glycinates (4d-f and 4i)

Analogously to the protocols used by Konno et al. [1] or Tranel et al. [2], we subsequently tried to rearrange the *N*-Boc-glycinate **4d** under the conditions shown in Table S3. To our regret, no traces of the target β-SF_5-γ,δ-unsaturated *N*-Boc-protected amino acid were found in the product mixtures by ^1H NMR spectroscopy. No new signals for vinylic hydrogens of the potential rearrangement product were found in the region between 5.2 and 6.4 ppm (Figure 1) (Table S3, entries 4, 5, 7 and 9). In cases where decomposition occurred (Table S3, entries 1-3, 6, 8), minor amount of the original 3-SF_5-prop-2-en-1-ol was identified by ^{19}F NMR spectroscopy. A similar observation was described by Tranel et al. in their corresponding experiments [2].



4d

Table S3: Efforts for ester enolate-Claisen rearrangement of the *N*-Boc-glycinate **4d**.

Entry	Base (equiv)	Solvent	MCl_2 (equiv)	Addition of $ZnCl_2$	Temperature	Time	Result
1[a]	LDA (3.0)	Et_2O	$ZnCl_2$ (1.2)	30 ml/h	-78 °C to r.t.	16 h	decomp.
2[a]	LDA (3.0)	THF	$ZnCl_2$ (1.2)	20 ml/h	-78 °C to r.t.	16 h	decomp.
3[a]	LDA (3.0)	THF	$ZnCl_2$ (1.2)	17 ml/h	-78 °C to r.t.	16 h	decomp.
4[b]	LHMDS (1.2)	THF	$ZnCl_2$ (5.5)	-	0 °C to r.t.	16h	s.m.[c]
5[b]	LHMDS (1.2)	THF	$ZnCl_2$ (5.5)	-	0 °C to reflux	3 h	s.m.[c]
6[b]	LHMDS (3.0)	Et_2O	$ZnCl_2$ (5.4)	-	-78 °C to r.t.	48 h	decomp.
7[b]	LHMDS (6.0)	THF	$ZnCl_2$ (6.0)	-	0 °C to reflux	4 h	s.m.[c]
8[b]	LHMDS (6.0)	THF	$ZnCl_2$ (6.0)	-	0 °C to reflux	10 h	decomp.
9[b]	LHMDS (6.0)	THF	$MgCl_2$ (6.0)	-	0 °C to reflux	10 h	s.m.[c]

[a] **Method A**: The ester and the solution of MCl_2 were added to the base, [b] **Method B**: The base was added to the solution of the ester and MCl_2, [c] Starting material recovered

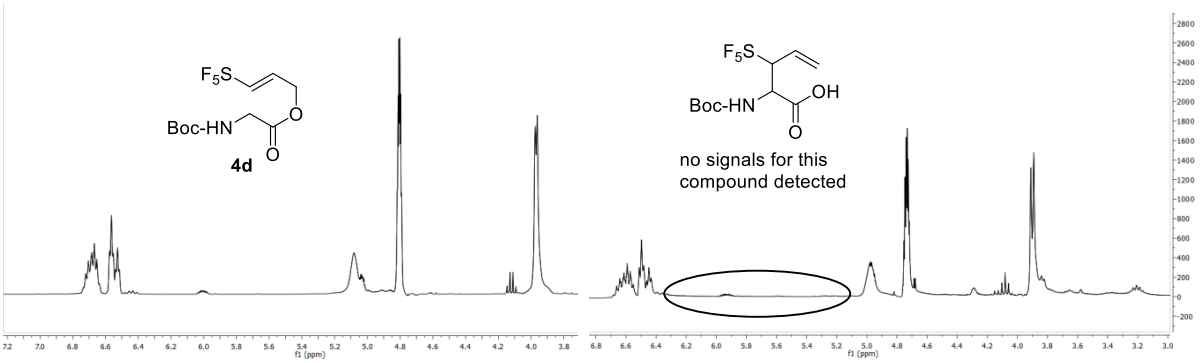


Fig. S1. ^1H NMR spectra of the starting Boc-glycinates **4d** (left) and the crude reaction mixture after workup (right).

Also our efforts to rearrange the *N*-Boc-protected glycinate **4e** were not successful. After workup of the reaction mixture, most of the starting material was recovered (Table S4).

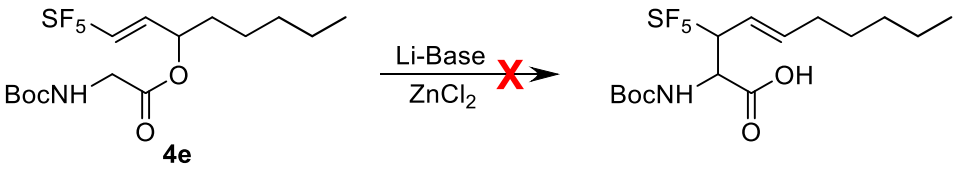


Table S4. Trials for ester enolate-Claisen rearrangement of allyl Boc-glycinate **4e**

Entry	Base (equiv)	Solvent	$ZnCl_2$ (equiv)	Temperature	Time	Result
1[b]	LHMDS (3.2)	THF	6.6	reflux	15 h	s.m.[c]
2[b]	LDA (2.5)	Et_2O	6.6	-78 °C to r.t.	18 h	s.m.[c]
3[b]	LHMDS (6.0)	THF	6.6	reflux	15 h	s.m.[c]
4[b]	LDA (2.6)	THF	2.6	reflux	15 h	s.m.[c]
5[a]	LDA (2.6)	THF	4.0	-78 °C to reflux	12 h	s.m.[c]
6[a]	LHMDS (4.0)	Toluene:THF, 1:6	3.0	0 °C to reflux	12 h	s.m.[c]
7[b]	LDA (3.0)	Toluene	6.0	-78 °C to reflux	12 h	s.m.[c]

[a] **Method A**: The ester and the solution of $ZnCl_2$ were added to the base, [b] **Method B**: The base was added to the solution of the ester and $ZnCl_2$, [c] Starting material recovered

In order to increase the C-H acidity of the α-methylene proton of the glycinates, the Boc group was replaced by the more electron withdrawing TFA protecting group. However, again no rearrangement product was identified after workup of the reaction mixture (Table S5).

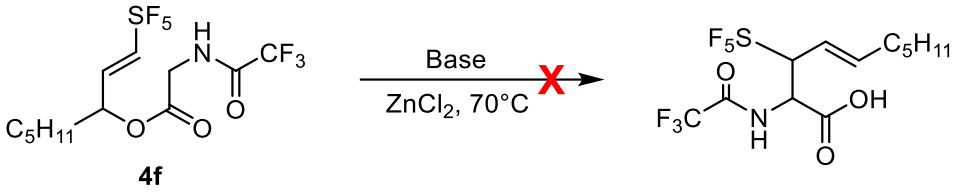


Tabelle S5. Efforts for ester enolate-Claisen rearrangement of **4f**.

Entry	Base	Equiv	$ZnCl_2$ (equiv)	Time [h]	Result
1[b]	LHMDS	6.0	6.0	2	SF_5-Elimination
2[b]	LDA	3.0	6.0	4	Partial hydrolysis
3[a]	LHMDS	6.0	6.0	6	Decomposition

[a] **Method A**: The ester and the solution of $ZnCl_2$ were added to the base, [b] **Method B**: The base was added to the solution of the ester and $ZnCl_2$.

In order to prove that the α-C-H position to the ester group is actually more C-H-acidic than the allylic position activated by the electron withdrawing effect of the SF_5-substituted double bond, we treated **4f** with different bases at very low temperature and added excess methyl iodide. Indeed, in all cases, the methylation occurred at the α-position to the ester group to form compounds **4f1**. The alternative product **4f2** was not found.

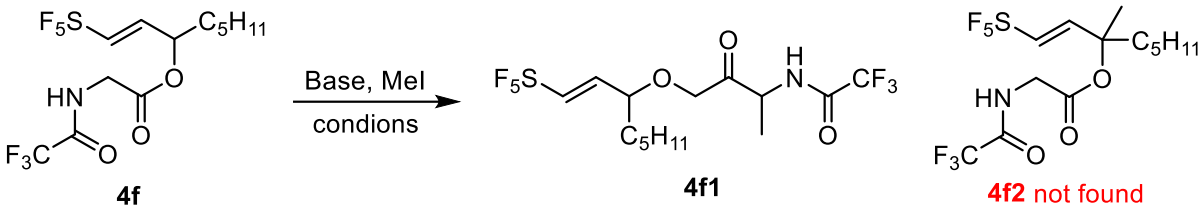


Table S6. Deprotonation of compound **4f** at low temperature and methylation with MeI.

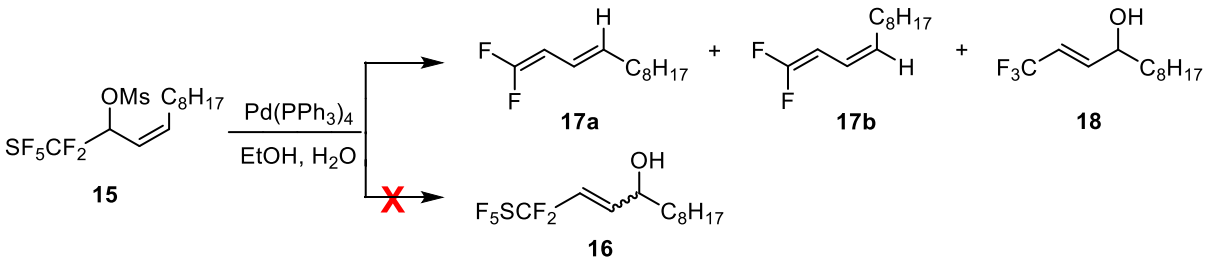
Entry	Base	Equiv	Solvent	Temperature [°C]	Produkt
1[b]	LDA	2.5	THF	-78	**4f1**
2[b]	LDA	2.5	Et_2O	-78	**4f1**
3[b]	LHMDS	2.5	THF	-78	**4f1**
4[b]	LHMDS	2.5	Et_2O	-78	**4f1**
5[b]	LHMDS	2.5	THF	-95	**4f1**
6[a]	LDA	2.5	THF	-78	**4f1**

[a] **Method A**: The ester and the solution of $ZnCl_2$ were added to the base, [b] **Method B**: The base was added to the solution of the ester and $ZnCl_2$.

This means that the first step of the desired [3,3]-sigmatropic rearrangements, namely the deprotonation of the α-C-H position and formation of the ester enolate can occur, but the formation of the transition state for the Claisen rearrangement is blocked by the sterically demanding SF_5 group.

Trials of Pd(0)-catalyzed allylic rearrangement of mesylate 15

The target rearrangement product **16** was not found in the product mixture of this reaction (see the main text). Instead, compounds **17a**, **17b**, and **18** were likely made as shown by NMR spectroscopy, but were not isolated in pure form. Figure S1 shows selected ^{19}F and ^{1}H NMR data of the products obtained after treatment of **15** with $Pd(PPh_3)_4$ and workup. The mechanism of formation is similar to that previously discussed for a related reaction [3].



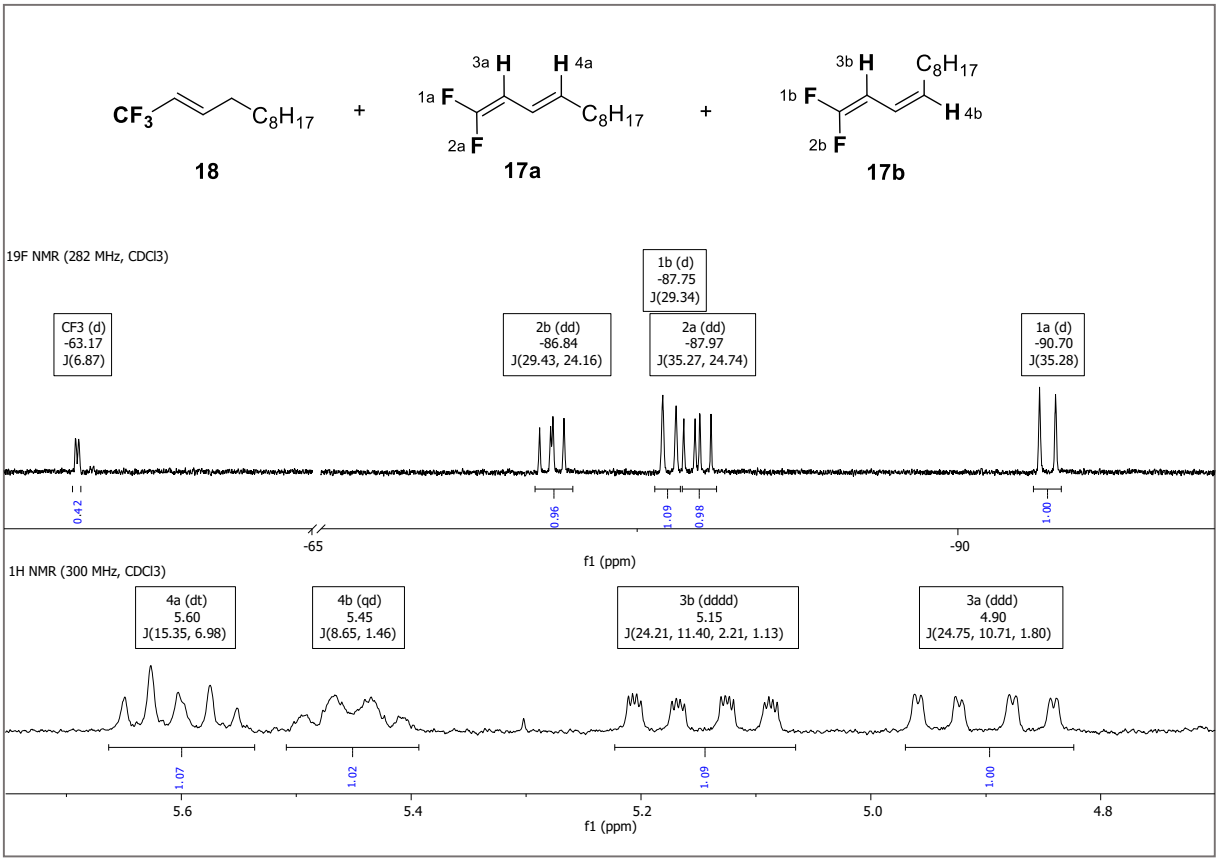


Figure S1. Selected ^{19}F and ^{1}H NMR data of the products obtained after treatment of **15** with $Pd(PPh_3)_4$.

References:

[1] T. Konno, H. Umetani and T. Kitazume, Highly Stereoselective Synthesis of Trifluoromethylated Compounds via Ester-Enolate [2,3]-Wittig and [3,3]-Ireland-Claisen Rearrangements, *J. Org. Chem.*, 1997, **62**, 137-150.

[2] F. Tranel, R. Fröhlich and G. Haufe, Synthesis of γ-fluoro-α-amino acids by Claisen rearrangement, *J. Fluorine Chem.*, 2005, **126**, 557–569.

[3] P. Dudziński, A. Matsnev, J. S. Thrasher and G. Haufe, Synthesis of SF_5CF_2-Containing Enones and Instability of This Group in Specific Chemical Environments and Reaction Conditions, *J. Org. Chem.*, 2016, **81**, 4454–4463.

X-Ray data

X-Ray diffraction: Data sets for compound **4d** (CCDC 1973261, HAF4760) were collected with a Bruker APEX CCD diffractometer. Programs used: data collection, COLLECT [1]; data reduction Denzo-SMN [2]; absorption correction, Denzo [3]; structure solution SHELXT-2015 [4]; structure refinement SHELXL-2015 [5] and graphics, *XP* [6]. *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections.

Exceptions and special features: The SF_5 unit was found disordered over two positions in the asymmetric unit. Several restraints (SIMU, SADI, SAME, ISOR) were used in order improve refinement stability. The hydrogen at N8 atom was refined freely.

X-ray crystal structure analysis of compound 4d, CCDC 1973261: A colorless plate-like specimen of $C_{10}H_{16}F_5NO_4S$, approximate dimensions 0.050 mm × 0.100 mm × 0.350 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an orthorhombic unit cell yielded a total of 2543 reflections to a maximum θ angle of 68.06° (0.83 Å resolution), of which 2543 were independent (average redundancy 1.000, completeness = 95.2%, R_{sig} = 3.06%) and 2274 (89.42%) were greater than 2σ(F^2). The final cell constants of a = 13.4208(12) Å, b = 26.557(2) Å, c = 8.6349(9) Å, volume = 3077.6(5) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4710 and 0.8840. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Aba*2, with Z = 8 for the formula unit, $C_{10}H_{16}F_5NO_4S$. The final anisotropic full-matrix least-squares refinement on F^2 with 243 variables converged at R1 = 5.74%, for the observed data and wR2 = 16.43% for all data. The goodness-of-fit was 1.047. The largest peak in the final difference electron density synthesis was 0.202 $e^-/Å^3$ and the largest hole was -0.280 $e^-/Å^3$ with an RMS deviation of 0.044 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.473 g/cm^3 and F(000), 1408 e^-.

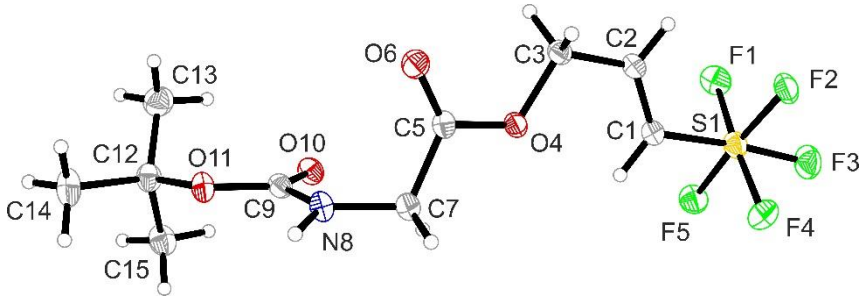
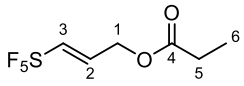


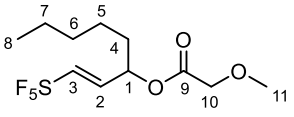
Figure S1: Crystal structure of compound **4d** (CCDC 1973261, HAF4760).
Thermal ellipsoids are set at 15% probability.

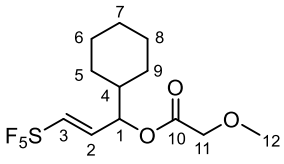
References X-Ray Part:

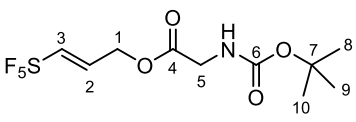
1. COLLECT, R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands.
2. Denzo-SMN, Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307-326.
3. Denzo, Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Cryst.*, 2003, **A59**, 228-234.
4. G. M. Sheldrick, SHELXT – Integrated space-group and crystal-structure determination, *Acta Cryst.*, 2015, **A71**, 3-8.
5. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst.*, 2015, **C71**, 3-8.
6. XP – Interactive molecular graphics, Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1998.

NMR data with signal assignments

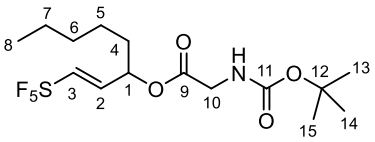
*(E)-3-(Pentafluoro-λ^6-sulfanyl)allyl propionate (**4a**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.73–6.50  (m, 2H, 3-/2-CH), 4.74 (m, 2H, 1-CH_2), 2.42 (q, $^3J_{H,H}$ = 7.6 Hz, 2H, 5-CH_2), 1.18 (t, $^3J_{H,H}$ = 7.6 Hz, 3H, 6-CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 173.5 (C-4), 141.6 (dqu, $^2J_{C,F}$ = 21.2 Hz, $^2J_{C,F}$ = 1.2 Hz, C-3), 132.7 (qu, $^3J_{C,F}$ = 7.1 Hz, C-2), 60.6 (C-1), 27.2 (C-5), 8.9 (C-6); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.42 (mqu, $^2J_{F,F}$ = 150.5 Hz 1F, SF), 62.80 (dm, $^2J_{F,F}$ = 150.5 Hz, 4F, SF_4).

*(E)-1-(Pentafluoro-λ^6-sulfanyl)oct-1-en-3-yl 2-methoxyacetate (**4b**)*. ^{1}H NMR (300 MHz,  $CDCl_3$): δ 6.51 (dqu, $^3J_{H,H}$ = 14.7 Hz, $^3J_{F,H}$ = 6.2 Hz, 1H, 3-CH), 6.36 (ddqu, $^3J_{H,H}$ = 14.7 Hz, $^3J_{H,H}$ = 5.8 Hz, $^4J_{F,H}$ = 1.5 Hz, 1H, 2-CH), 5.42 (dt, $^3J_{H,H}$ = 5.8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, 1-CH), 4.01 (s, 2H, 10-CH_2), 3.40 (s, 3H, 11-CH_3), 1.71–1.58 (m, 2 , 7-CH_2), 1.33–1.12 (m, 6H, 4-CH_2 to 6-CH_2), 0.82 (t, $^3J_{H,H}$ = 6.5 Hz, 3H, 8-CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.2 (C-9), 136.0 (dqu, $^3J_{C,F}$ = 21.1 Hz, C-3), 136.0 (dqu, $^4J_{C,F}$ = 6.9 Hz, C-2), 71.4 (C-1), 69.6 (C-10), 59.4 (C-11), 33.6 (C-4), 31.3 (C-5), 24.4 (C-6), 22.4 (C-7), 13.9 (C-8); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.48 (mqu, $^2J_{F,F}$ = 150.9 Hz, 1F, SF), 63.08 (dm, $^2J_{F,F}$ = 150.9 Hz, 4F, SF_4).

*(E)-1-cyclohexyl-3-(pentafluoro-λ^6-sulfanyl)allyl 2-methoxyacetate (**4c**)*. ^{1}H NMR (300 MHz,  $CDCl_3$): δ 6.56 (m, 1H, 3-CH), 6.42 (ddm, $^3J_{H,H}$ = 14.7, $^3J_{H,H}$ = 6.1, $^4J_{H,F}$ = 1.0 Hz, 1H, 2-CH), 5.35–5.27 (m, 1H, 1-CH), 4.09 (s, 2H, 11-CH_2), 3.47 (s, 3H, 12-CH_3), 1.85–0.95 (m, 13H, 4-CH/5-/6-/7-/8-/9-CH_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.2 (C-10), 142.1 (ddqu, $^2J_{C,F}$ = 20.7 Hz, $^2J_{C,F}$ = 1.0 Hz, C-3), 134.9 (dqu, $^3J_{C,F}$ = 7.0 Hz, C-2), 75.1 (C-1), 69.5 (C-11), 59.4 (C-12), 41.3 (C-4), 28.3 (C-5), 28.1 (C-9), 25.9 (C-6/-8), 25.6 (C-7); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.00 (mqu, $^2J_{F,F}$ = 150.9 Hz, 1F, SF), 62.59 (dm, $^2J_{F,F}$ = 150.9 Hz, 4F, SF_4).

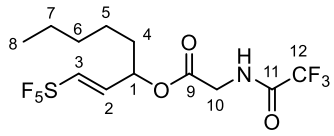
*(E)-3-(Pentafluoro-λ^6-sulfanyl)allyl (tert-butoxycarbonyl)glycinate (**4d**)*. ^{1}H NMR (300 MHz,  $CDCl_3$): δ 6.67 (m, 1H, 3-CH), 6.55 (dqu, $^3J_{H,H}$ = 14.7 Hz, $^4J_{H,F}$ = 4.5 Hz, 1H, 2-CH), 5.08 (s, 1H, 6-NH), 4.81 (m, 2H, 1-CH_2), 3.97 (bd, $^3J_{H,H}$ = 5.8 Hz, 2H, 5-CH_2), 1.46 (s, 9H, 8-/9-/10-CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.7 (C-4), 155.8 (C-6), 142.2 (dqu, $^2J_{C,F}$ = 21.2 Hz, C-3), 132.0 (dqu, $^3J_{C,F}$ = 7.2 Hz, C-2), 80.4 (C-5), 61.4 (C-1), 42.4 (C-7), 28.3 (C-8/-9/-10); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.19 (mqu, $^2J_{F,F}$ = 149.1 Hz, 1F, SF), 62.94 (dm, $^2J_{F,F}$ = 149.1 Hz, 4F, SF_4).

*(E)-1-(Pentafluoro-λ^6-sulfanyl)oct-1-en-3-yl (tert-butoxycarbonyl)glycinate (**4e**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.62 (m, 1H, 3-CH), 6.42 (dd, 1H, $^3J_{H,H}$ = 14.7 Hz, $^3J_{H,H}$ = 5.5 Hz, 1H, 2-CH), 5.44 (dd, $^3J_{H,H}$ = 5.5 Hz, 1H, 1-CH), 5.10 (s, 1H, N-H), 3.94 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, 10-



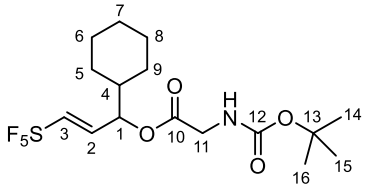
CH_2), 1.87–1.58 (m, 2H, 4-CH_2), 1.45 (s, 9H, /13-/14-/15-CH_3), 1.40–1.19 (m, 6H, 5-/6-/7-CH_2), 0.89 (t, $^3J_{H,H}$ = 6.6 Hz, 3H, 8-CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.4 (C-9), 155.7 (C-11), 141.6 (qu, $^2J_{C,F}$ = 21.1 Hz, C-3,), 135.9 (dqu, $^3J_{C,F}$ = 7.0 Hz, C-2), 80.2 (C-12), 71.9 (C-1), 42.4 (C-10), 33.6 (C-4), 31.2 (C-5), 28.2 (C-13/-14/-15), 24.3 (C-6), 22.3 (C-7), 13.8 (C-8); ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.67 (m, $^2J_{F,F}$ = 150.1, 1F, SF), 62.89 (dm, $^2J_{F,F}$ = 150.1, 4F, SF_4).

(E)-1-(Pentafluoro-λ^6-sulfanyl)oct-1-en-3-yl (2,2,2-trifluoroacetyl)glycinate (***4f***). ^1H NMR



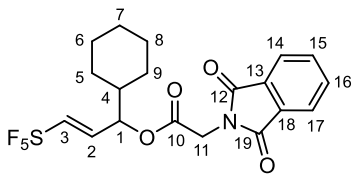
(300 MHz, $CDCl_3$): δ 7.03 (bs, 1H, NH), 6.67 – 6.54 (m, 1H, 3-CH), 6.42 (ddm, $^3J_{H,H}$ = 14.8 Hz, $^3J_{H,H}$ = 5.9 Hz, 1H, 2-CH), 5.45 (ddt, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 5.9 Hz, $^4J_{H,H}$ = 1.2 Hz, 1H, 1-CH), 4.17 (d, $^3J_{H,H}$ = 5.4 Hz, 2H, 10-CH_2), 1.80 – 1.64 (m, 2H, 4-CH_2), 1.40 – 1.24 (m, 6H, 4-CH_2 to 7-CH_2), 0.89 (t, 3H, 8-CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 167.4 (C-9), 157.5 (q, $^2J_{C,F}$ = 38.2 Hz, C-11), 142.2 (dqu, $^2J_{C,F}$ = 21.3 Hz, C-3), 135.4 (dqu, $^3J_{C,F}$ = 7.0 Hz, C-2), 115.6 (q, $^1J_{C,F}$ = 287.3 Hz, 12-CF_3), 73.2 (C-10), 41.3 (C-1), 33.6 (C-4), 31.3 (C-5), 24.3 (C-6), 22.4 (C-7), 13.9 (C-8); ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.63 (m, $^2J_{F,F}$ = 150.7, 1F, SF), 62.54 (dm, $^2J_{F,F}$ = 150.7 Hz, 4F, SF_4), -76.35 (s, 3 F, CF_3).

(E)-1-Cyclohexyl-3-(pentafluoro-λ^6-sulfanyl)allyl (tert-butoxycarbonyl)glycinate (***4g***). ^1H NMR



(300 MHz, $CDCl_3$): δ 6.57 (m, 1H, 3-CH), 6.40 (ddqu, $^3J_{H,H}$ = 14.7, $^4J_{H,H}$ = 5.9, $^4J_{H,F}$ = 0.9 Hz, 1H, 2-CH), 5.26 (m, 1H, 1-CH), 5.10 (s, 1H, N-H), 3.95 (dd, $^3J_{H,H}$ = 5.4, $^3J_{H,H}$ = 4.5 Hz, 2H, 11-CH_2), 1.80–1.60 (m, 5H, 4-CH, 9-/5-CH_2), 1.46 (s, 9H, 14-/15-/16-CH_3), 1.35–0.82 (m, 6H, 6-/7-/8-CH_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.5 (10-C), 155.7 (12-C), 142.2 (qu, $^2J_{C,F}$ = 20.4 Hz, 3-C), 134.9 (qu, $^3J_{C,F}$ = 6.8 Hz, C-2), 80.2 (C-13), 65.9 (C-1), 42.5 (C-11), 41.4 (C-4), 28.3 (5-/9-CH), 28.2 (C-14/-15/-16), 26.0 (6-/8-CH), 25.7 (7-CH); ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.82 (m, $^2J_{F,F}$ = 150.1, 1F, SF), 62.54 (dm, $^2J_{F,F}$ = 150.8, 4F, SF_4).

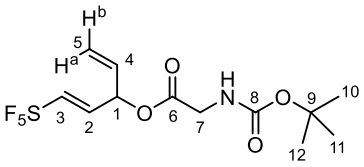
(E)-1-Cyclohexyl-3-(pentafluoro-λ^6-sulfanyl)allyl 2-(1,3-dioxoisoindolin-2-yl)acetate (***4h***).



^1H NMR (300 MHz, $CDCl_3$): δ 7.95–7.73 (m, 4H, 14- to 17-CH), 6.53 (ddqu, $^3J_{F,H}$ = 20.7 Hz, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 1.2 Hz, 1H, 3-CH), 6.40 (ddqu, $^3J_{H,H}$ = 14.7 Hz, $^3J_{H,H}$ = 5.6 Hz, $^4J_{F,H}$ = 0.9 Hz, 1H, 2-CH), 5.35–5.25 (m, 1H, 1-CH), 4.50 (s, 2H, 11-CH_2), 1.85–0.80 (m, 11H, 4-CH, 5 – 9-CH_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 167.4 (C-10). 166.3 (C-12/-19), 142.1 (qu, $^2J_{C,F}$ = 20.6 Hz, C-3), 134.4 (qu, $^3J_{C,F}$ = 7.0 Hz, C-2), 134.4 (C-13/-18), 131.9 (C-15/-16), 123.7 (C-14/-17), 76.3 (C-1), 41.4 (C-5), 38.9 (C-4), 28.4 (C-9), 27.9 (C-9), 26.0

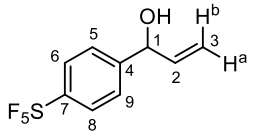
(C-7), 25.7 (C-6/-8); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.45 (m, $^2J_{F,F}$ = 150.0 Hz, 1F, SF), 63.17 (dm, $^2J_{F,F}$ = 150.0 Hz, $^3J_{F,H}$ =1.9 Hz, 4F, SF_4).

*(E)-1-(Pentafluoro-λ^6-sulfanyl)penta-1,4-dien-3-yl (tert-butoxycarbonyl)-glycinate (**4i**)*. ^{1}H NMR



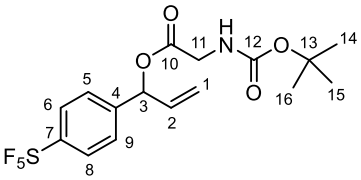
(300 MHz, $CDCl_3$): δ 6.67 (dqud, $^3J_{H,H}$ = 14.7 Hz, $^3J_{F,H}$ = 6.2 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H, 3-CH) 6.47 (dd, $^3J_{H,H}$ = 14.7 Hz, $^3J_{H,H}$ = 5.0 Hz, 1H, 2-CH), 5.95–5.86 (m, 2H, 5-CH_2) 5.80 (ddd, $^3J_{H,H}$ = 15.0, $^3J_{H,H}$ = 10.5, $^3J_{H,H}$ = 5.6 Hz, 1H, 4-CH), 5.08 (m, 1H, 1-CH), 3.97 (d, 2H, $^3J_{H,H}$ = 5.8 Hz, 7-CH_2), 1.45 (s, $^3J_{H,H}$ = 1.5 Hz, 9H, 10-/11-/12-CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.2 (C-6), 155.9 (C-8), 142.3 (qu, $^2J_{C,F}$ = 20.0 Hz, C-3), 134.8 (qu, $^3J_{C,F}$ = 7.2 Hz, C-2), 132.2 (C-4), 120.7 (C-5), 80.4 (C-9), 72.4 (C-7), 42.6 (C-1), 28.4 (C-10/-11/-12); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.06 (m, $^2J_{F,F}$ = 151.1 Hz, 1F, SF), 63.19 (dm, $^2J_{F,F}$ = 151.1 Hz, 4F, SF_4).

*1-[4-(Pentafluoro-λ^6-sulfanyl)phenyl]prop-2-en-1-ol (**8**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75



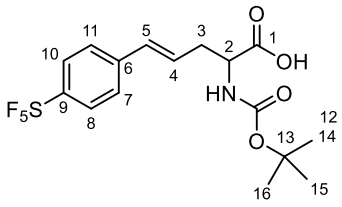
(dqu, $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,F}$ = 2.0 Hz 1H, 6-/8-CH), 7.46 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, 5-/9-CH), 5.97 (ddd, $^3J_{H,H}$ = 17.0 Hz, $^3J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 6.2 Hz, 1H, 2-CH), 5.37 (dd, $^3J_{H,H}$ = 17.0 Hz, $^2J_{H,H}$ = 1.2 Hz, 1H, 3-CH_b), 5.25 (dd, $^3J_{H,H}$ = 10.2 Hz, $^2J_{H,H}$ = 1.2 Hz, 1H, 3-CH_a), 5.23 (d, $^3J_{H,H}$ = 6.2 Hz, 1H, 1-CH), 2.34 (s, 1H, -OH); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 153.2 (dqu, $^3J_{C,F}$ = 1.2 Hz, $^3J_{C,F}$ = 17.2 Hz, C-7), 146.1 (C-4), 139.3 (C-2), 126.4 (C-5/-9), 126.1 (dqu, $^4J_{C,F}$ = 4.6 Hz, C-6/-8), 116.6 (C-3), 74.6 (C-1); ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.60 (mp, $^2J_{F,F}$ = 149.9 Hz, 1F, SF), 62.94 (d, $^2J_{F,F}$ = 149.9 Hz, 4F, SF_4).

*1-[4-(Pentafluoro-λ^6-sulfanyl)phenyl]allyl (tert-butoxycarbonyl)glycinate (**6**)*. ^{1}H NMR



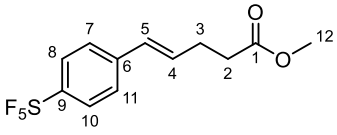
(300 MHz, $CDCl_3$): δ 7.75 (dd, $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,F}$ = 2.0 Hz, 2H, 6-/8-CH), 7.45 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, 5-/9-CH), 6.32 (d, $^3J_{H,H}$ = 6.1 Hz, 1H, 3-CH), 5.96 (ddd, $^3J_{H,H}$ = 16.8 Hz, $^3J_{H,H}$ = 10.4 Hz, $^3J_{H,H}$ = 6.1 Hz, 1H, 2-CH), 5.35 (m, 2H, 1-CH_2), 5.02 (bs, 1H, NH), 3.98 (m, 2H, 11-CH_2), 1.44 (s, 9H, 14 to 16-CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.4 (C-12), 155.7 (C-10), 153.6 (qu, $^2J_{C,F}$ = 17.6 Hz, C-7), 142.1 (C-4), 134.7 (C-5/-9), 127.3 (C-2), 126.4 (dqu, $^3J_{C,F}$ = 4.7 Hz, C-6/-8), 118.7 (C-1), 80.2 (C-13), 76.1 (C-3), 42.6 (C-11), 28.3 (C-14-16); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.24–82.94 (m, $^2J_{F,F}$ = 150.0, 1F, SF), 62.80 (d, $^2J_{F,F}$ = 150.0, 4F, SF_4).

*(E)-2-[(tert-Butoxycarbonyl)amino]-5-[4-(pentafluoro-λ^6-sulfanyl)phenyl]pent-4-enoic acid (**7**)*.



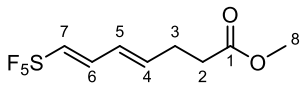
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (brs, 1H, COOH), 7.66 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, 8-/10-CH), 7.38 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, 7-/11-CH), 6.48 (d, $^3J_{H,H}$ = 15.8 Hz, 1H, 5-CH), 6.23 (td, $^3J_{H,H}$ = 15.7 Hz, $^3J_{H,H}$ = 7.5 Hz, 1H, 4-CH), 4.50 (q, $^3J_{H,H}$ = 6.4 Hz, 1H, 2-CH), 3.57 (s, 1H, NH), 2.90 – 2.60 (dm, 2H, 3-CH_2), 1.42 (s, 9H, 14-/15-/16-CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 175.9 (C-1) 155.4 (C-12), 152.6 (qu, $^2J_{C,F}$ = 17.0 Hz, C-9), 140.0 (C-6), 132.1 (C-5), 127.5 (C-7/-11), 126.2 (qu, C-8/-10), 126.1 (C-4), 80.5 (C-13), 52.9 (C-2), 36.0 (C-3), 28.2 (C-14/-15/-16); ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.37 (mqu, $^2J_{F,F}$ = 147.0 Hz, 1F, SF), 62.47 (dm, $^2J_{F,F}$ = 147.0 Hz, 4F, SF_4).

*Methyl (E)-5-[4-(pentafluoro-λ^6-sulfanyl)phenyl]pent-4-enoate (**9**)*. ^{1}H NMR (300 MHz, $CDCl_3$):



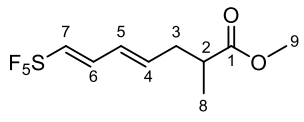
δ 7.69–7.63 (dqu, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,F}$ = 1.8 Hz, 2H, 8-/10-CH), 7.38 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, 7-/11-CH), 6.44 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 5-CH), 6.31 (dt, $^3J_{H,H}$ = 16.0 Hz, $^3J_{H,H}$ = 6.2 Hz, 1H, 4-CH), 3.69 (s, 3H, 12-CH_3), 2.54 (m, 4H, 3-/2-CH_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 173.1 (C-1), 152.3 (qu, $^2J_{C,F}$ = 17.1 Hz, C-9), 140.6 (C-6), 132.1 (C-11/-7), 129.2 (C-3), 126.1 (qu, $^3J_{C,F}$ = 10.5 Hz, C-10/-8), 126.0 (C-2), 51.6 (C-12), 33.3 (C-3), 28.1 (C-4); ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.58 (mqu, $^2J_{F,F}$ = 149.6 Hz, 1F, SF), 62.55 (dm, $^2J_{F,F}$ = 149.6 Hz, 4F, SF_4).

*Methyl (4E,6E)-7-(pentafluoro-λ^6-sulfanyl)hepta-4,6-dienoate (**10g**)*. ^{1}H NMR (300 MHz,



$CDCl_3$): δ 6.83 (dd, $^3J_{H,H}$ = 14.4, $^3J_{H,H}$ = 10.0 Hz, 1H, 6-CH), 6.49 (dqu, 1H, $^3J_{H,H}$ = 14.4, $^3J_{H,F}$ = 6.7 Hz, 1H, 7-CH), 6.20 – 5.95 (m, 2H, 4-/5-CH), 3.68 (s, 3H, 8-CH_3), 2.60 – 2.40 (m, 4H, 2-/3-CH_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 172.8 (1-C) 142.3 (qu, $^4J_{C,F}$ = 2.2 Hz, C-5) 140.2 (qu, $^2J_{C,F}$ = 20.1 Hz, C-7), 136.2 (qu, $^3J_{C,F}$ = 7.5 Hz, C-6), 125.7 (C-4), 51.7 (8-CH_3), 32.8 (C-2), 28.0 (C-3); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.64 – 83.47 (m, $^2J_{F,F}$ = 150.8 Hz, 1F, SF), 64.09 (dm, $^2J_{F,F}$ = 150.8, 4F, SF_4).

*Methyl (4E,6E)-2-methyl-7-(pentafluoro-λ^6-sulfanyl)hepta-4,6-dienoate (**10h**)*. ^{1}H NMR



(400 MHz, $CDCl_3$): δ 6.83 (dd, $^3J_{H,H}$ = 14.4, $^3J_{H,H}$ = 9.7 Hz, 1H, 5-CH). 6.48 (md $^3J_{H,H}$ = 14.1 Hz, 1H, 7-CH), 6.10 – 5.95 (m, 2H, 6-CH, 4-CH), 3.69 (s, 3H, 9-CH_3), 2.58 (dd, $^2J_{H,H}$ = 13.4, $^3J_{H,H}$ = 6.6 Hz, 1H, 3-CH_{2a}), 2.52 (dq, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 6.6 Hz, 1H, 2-CH), 2.31 (dt, $^2J_{H,H}$ = 13.4, $^3J_{H,H}$ = 6.6 Hz, 1H, 3-CH_{2a}), 1.18 (d, $^3J_{H,H}$ = 6.7 Hz, 3H, 8-CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 175.9 (C-1), 141.2 (C-5), 140.2 (qu, $^2J_{C,F}$ = 20.5 Hz, C-7), 136.1 (qu, $^3J_{C,F}$ = 7.5 Hz, C-6), 126.7 (C-4), 51.8 (C-2), 38.9 (C-3), 36.7 (C-9), 16.8 (C-8); ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.51 (qu, $^2J_{F,F}$ = 150.8 Hz, 1F, SF), 64.11 (dm, $^2J_{F,F}$ = 150.8, 4F, SF_4).

*Octyl 2,2-difluoro-2-(pentafluoro-λ^6-sulfanyl)acetate (**11**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.38 (t, $^3J_{H,H}$ = 6.7 Hz, 2H, H-3), 1.74 (dt, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 6.5 Hz, 2H, H-4), 1.45 – 1.24 (m, 10H, H-5 – H-9), 0.95 – 0.84 (m, 3H, H-10); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 69.2 (C-3), 31.7 (C-4), 29.05 (C-5), 28.96 (C-6), 28.0 (C-7), 25.4 (C-8), 22.6 (C-9), 14.1 (C-10). The signals for the CF_2 (C1) and CO (C2) carbon atoms were not observed, as an insufficient number of transients were recorded and these signals are expected to be highly coupled. ^{19}F NMR (282 MHz, $CDCl_3$): δ 65.99 (qum, $^2J_{F,F}$ = 148.0 Hz, 1F, SF), 40.95 (dtm, $^2J_{F,F}$ = 148.0, $^3J_{F,F}$ = 12.0 Hz, 4F, SF_4), -91.40 (qud, $^3J_{F,F}$ = 12.0, $^3J_{F,F}$ = 4.3 Hz, 2F, CF_2).

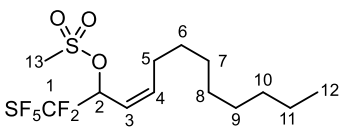
*1,1-Difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-3-yn-2-one (**12**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.51 (t, $^3J_{H,H}$ = 7.0 Hz, 2H, H-5), 1.65 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, H-6), 1.48 – 1.37 (m, 2H, H-7), 1.34 – 1.19 (m, 8H, H-8 – H-11), 0.89 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, H-12). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 119.1 (tm, C-1), 106.4 (C-4), 76.3 – 76.0 (m, C-3), 31.8 (C-5), 29.1 (C-6), 28.9 (C-7), 28.7 (C-8), 27.2 (C-9), 22.6 (C-10), 19.5 (C-11), 14.0 (C-12). The signal for the CO (C-2) carbon atom was not observed, as an insufficient number of transients were recorded and this signal is expected to be highly coupled, which would further reduce its intensity. ^{19}F NMR (282 MHz, $CDCl_3$): δ 65.95 (qum, $^2J_{F,F}$ = 147.1 Hz, 1F, SF_4), 43.88 (dtm, $^2J_{F,F}$ = 147.1, $^3J_{F,F}$ = 12.0 Hz, 4F, SF_4), -91.52 (qum, $^3J_{F,F}$ = 12.3, $^3J_{F,F}$ = 4.1 Hz, 2F, CF_2).

*1,1-Difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-3-yn-2-ol (**13**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.88 (t, $^3J_{H,F}$ = 9.1 Hz, 1H, H-2), 2.69 (bs, 1H, OH), 2.25 (td, $^3J_{H,H}$ = 7.0, $^5J_{H,H}$ = 2.1 Hz, 2H, H-5), 1.53 (qu, $^3J_{H,H}$ = 7.0 Hz, 2 H, H-6), 1.40 – 1.30 (m, 2H, H-7), 1.28 (m, 8H, H-8 – H-11), 0.89 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, H-12). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 127.2 (tm, $^1J_{C,F}$ = 304.4 Hz, C-1), 90.6 (C-3), 71.8 (C-4), 64.2 (t, $^2J_{C,F}$ = 25.6 Hz, C-2), 31.9 (C-5), 29.2 (C-6), 29.1 (C-7), 28.8 (C-8), 28.1 (C-9), 22.7 (C-10), 18.6 (C-11), 14.1 (C-12); ^{19}F NMR (282 MHz, $CDCl_3$): δ 68.73 (qum, $^2J_{F,F}$ = 145.6 Hz, 1F, SF), 41.80 (dtm, $^2J_{F,F}$ = 146.7, $^3J_{F,F}$ = 15.1 Hz, 4F, SF_4), AB spin system (J_{AB} = 188.3 Hz), -90.20 (bm, 1F, F-1) and -92.60 (bs, 1F, F-1');

*(Z)-1,1-Difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-3-en-2-ol (**14**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.89 (dt, $^3J_{H,H}$ = 10.6, $^3J_{H,H}$ = 7.6 Hz, 1H, H-3), 5.51 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, H-4), 4.98 (ddd, *J* = 14.8, *J* = 8.6, *J* = 6.1 Hz, 1H, H-2), 2.41 (bs, 1H, OH), 2.13 (q, $^3J_{H,H}$ = 7.3 Hz, 2H, H-5), 1.41 (qu, $^3J_{H,H}$ = 7.3 Hz, 1H, H-6), 1.28 (m, 10H, H-7 – H-11), 0.88 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, H-12); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 140.0 (C-3), 129.0 (t, $^1J_{C,F}$ = 304.0 Hz, C-1), 121.4 (C-4), 68.3 (t, $^2J_{C,F}$ = 23.4 Hz, C-2), 31.9 (C-5), 29.4 (C-6), 29.24 (C-7), 29.22 (C-8), 29.1 (C-9), 28.0 (C-10), 22.7 (C-11), 14.1 (C-12); ^{19}F NMR (282 MHz, $CDCl_3$): δ 69.53 (qu, $^2J_{F,F}$ = 145.5 Hz, 1F, SF), 40.41

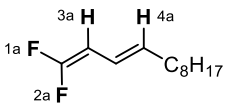
(dtm, $^2J_{F,F}$ = 145.5, $^3J_{F,F}$ = 15.6 Hz, 4F, SF_4), AB spin system (J_{AB} = 188.3 Hz), -89.06 (t, $^3J_{F,F}$ = 14.9 Hz, 1F, F-1) and -94.51 (bs, 1F, F-1‘).

*(Z)-1,1-Difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-3-en-2-yl methanesulfonate (**15**)*. ^{1}H NMR



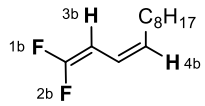
(300 MHz, $CDCl_3$): δ 6.09 (dt, $^3J_{H,H}$ = 11.0, $^3J_{H,H}$ = 7.6 Hz, 1H, H-4), 5.95 – 5.80 (m, 1H, H-3), 5.55 (t, $^3J_{H,H}$ = 10.3 Hz, 1H, H-2), 3.07 (s, 3H, H-13), 2.22 (qt, $^3J_{H,H}$ = 14.8, $^3J_{H,H}$ = 7.7 Hz, 2H, H-5), 1.47 – 1.38 (m, 2H, H-6), 1.36 – 1.20 (m, 10H, H-7 – H-11), 0.89 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, H-12); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 143.7 (C-3), 126.4 (m, C-1), 117.3 (C-4), 74.0 (ddm, $^2J_{C,F}$ = 28.5, $^2J_{C,F}$ = 22.3 Hz, C-2), 39.9 (C-13), 31.9 (C-5), 29.4 (C-6), 29.3 (C-7), 29.2 (C-8), 28.8 (C-9), 28.2 (C-10), 22.7 (C-11), 14.1 (C-12);^{19}F NMR (282 MHz, $CDCl_3$): δ 67.91 (qut, $^2J_{F,F}$ = 148.0, $^3J_{F,F}$ = 5.0 Hz, 1F, SF), 40.98 (dtm, $^2J_{F,F}$ = 146.6, $^3J_{F,F}$ = 15.2 Hz, 4F, SF_4), AB spin system (J_{AB} = 195.7 Hz): -88.24 (qud, $^3J_{F,F}$ = 14.2, $^3J_{F,H}$ = 7.9 Hz, 1F, F1*)* and -91.31 (qud, $^3J_{F,F}$ = 14.9 Hz, 1F, F1’).

*(E)-1,1-difluorododeca-1,3-diene (**17a**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.60 (dt, $^3J_{H,H}$ = 15.4,



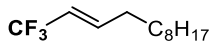
$^3J_{H,H}$ = 7.00 Hz, 1H, H-4a), 4.90 (ddd, $^3J_{H,F}$ = 24.8, $^3J_{H,H}$ = 10.7 Hz, *J* = 1.8 Hz, 1H, H-3a); ^{19}F NMR (282 MHz, $CDCl_3$): δ -87.97 (dd, $^2J_{F,F}$ = 35.3, $^3J_{F,H}$ = 24.7 Hz, 1F, F-2a), -90.70 (d, $^2J_{F,F}$ = 35.3 Hz, 1F, F-1a).

*(Z)-1,1-difluorododeca-1,3-diene (**17b**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.45 (qd, $^3J_{H,H}$ = 8.7,



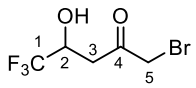
$^4J_{H,H}$ = 1.5 Hz, 1H, H-4b), 5.15 (dddd, $^3J_{H,F}$ = 24.2, *J* = 11.4 Hz, *J* = 2.2, *J* = 1.8 Hz, 1H, H-3b); ^{19}F NMR (282 MHz, $CDCl_3$): δ -86.84 (dd, $^2J_{F,F}$ = 29.4, $^3J_{F,H}$ = 24.2 Hz, 1F, F-2b), -87.75 (d, $^2J_{F,F}$ = 29.4, 1F, F-1b).

*(E)-1,1,1-Trifluorododec-2-ene (**18**)*. ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.17 (d, $^3J_{F,H}$ = 6.9 Hz,



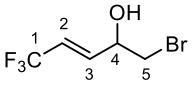
3F).

*1-Bromo-5,5,5-trifluoro-4-hydroxypentan-2-one (**24**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.55 (m,



1H, H-2), 4.16 (s, 2H, H-5), 3.44 (d, $^3J_{H,H}$ = 5.0 Hz, 1H, OH), AB spin system: 3.04 (dd, $^2J_{H,H}$ = 17.7, $^3J_{H,H}$ = 9.5 Hz, 1H, H-3) and 2.90 (dd, $^2J_{H,H}$ = 17.8, $^3J_{H,H}$ = 2.7 Hz, 1H, H-3’); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 200.2 (C-4), 124.4 (q, $^1J_{C,F}$ = 280.8 Hz, C-1), 66.4 (q, $^2J_{C,F}$ = 32.7 Hz, C-2), 48.4 (C-5), 39.7 (C-3); ^{19}F NMR (282 MHz, $CDCl_3$): δ -79.67 (d, $^3J_{F,H}$ = 6.7 Hz, 3F, CF_3).

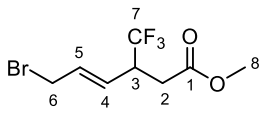
*(E)-1-Bromo-5,5,5-trifluoropent-3-en-2-ol (**20**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.32 (ddq, $^3J_{H,H}$ =



15.6, $^3J_{H,H}$ = 4.1, $^4J_{H,F}$ = 2.0 Hz, 1H, H-3), 6.00 (dqd, $^3J_{H,H}$ = 14.7, $^3J_{H,F}$ = 6.4, $^4J_{H,H}$ = 1.9 Hz, 1H, H-2), 4.46 (bs, 1H, H-4), AB spin system: 3.64 (dd, $^2J_{H,H}$ =11.3, $^4J_{H,H}$ = 3.9 Hz, 1H, H-5), 3.47 (dd, $^3J_{H,H}$ = 11.3, $^4J_{H,H}$ = 6.9 Hz, 1H, H-5’), 2.44 (d, $^3J_{H,H}$ = 4.9 Hz, 1H, OH); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.5 (q, $^3J_{C,F}$ = 6.3 Hz, C-3), 122.9 (q, $^1J_{C,F}$

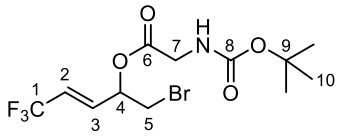
= 275.0 Hz, C-1), 120.8 (q, $^{2}J_{C,F}$ = 34.4 Hz, C-2), 69.8 (C-4), 48.4 (C-5); ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.46 (dt, $^{3}J_{F,H}$ = 6.2, $^{4}J_{F,H}$ = 2.1 Hz, 3F, CF_3).

*Methyl (E)-6-bromo-3-(trifluoromethyl)hex-4-enoate (**21**)*. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.93



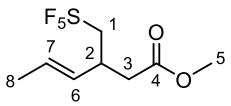
(dt, $^{3}J_{H,H}$ = 15.3, $^{3}J_{H,H}$ = 6.7 Hz, 1H, H-5), 5.66 (ddt, $^{3}J_{H,H}$ = 15.3, $^{3}J_{H,H}$ = 8.7, $^{4}J_{H,H}$ = 1.3 Hz, 1H, H-4), 4.03 (ddd, $^{3}J_{H,H}$ = 6.8, $J_{H,H}$ = 2.3, $^{4}J_{H,H}$ = 1.3 Hz, 2H, H-6), 3.71 (s, 3H, H-8), 3.40 (dqq, $^{3}J_{H,H}$ = 13.3, $^{3}J_{H,F}$ = 8.9, $J_{H,H}$ = 4.5 Hz, 1H, H-3), 2.76 (dd, $^{2}J_{H,H}$ = 16.0, $^{3}J_{H,H}$ = 4.4 Hz, 1H, H-2), 2.52 (dd, $^{2}J_{H,H}$ = 16.0, $^{3}J_{H,H}$ = 9.8 Hz, 1H, H-2'); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 170.3 (C-1), 132.9 (C-5), 128.6-128.1 (m, C-7), 126.0 (q, $^{3}J_{C,F}$ = 2.6 Hz, C-4), 52.1 (C-8), 43.6 (C-6), 43.3 (q, $^{2}J_{C,F}$ = 28.3 Hz, C-3), 33.3 (q, $^{3}J_{C,F}$ = 2.4 Hz, C-2); ^{19}F NMR (282 MHz, $CDCl_3$): δ -71.87 (d, $^{3}J_{F,H}$ = 8.7 Hz, 3F, CF_3).

*(E)-1,1,1-Trifluorododec-2-en-4-yl-(tert-butoxycarbonyl)glycinate (**27**)*. ^{1}H NMR (400 MHz,



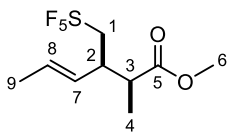
$CDCl_3$): δ 6.38 (ddq, $^{3}J_{H,H}$ = 15.8, $^{3}J_{H,H}$ = 4.3, $^{4}J_{H,F}$ = 2.0 Hz, 1H, H-3), 5.99 (dq, $^{3}J_{H,H}$ = 16.0, $^{3}J_{H,F}$ = 5.5 Hz, 1H, H-2), 5.68 – 5.61 (m, 1H, H-4), 4.00 (d, $^{3}J_{H,H}$ = 5.9 Hz, 2H, H-7), 5.03 (bs, 1H, NH), 3.67 (dd, $^{3}J_{H,H}$ = 5.5, $^{4}J_{H,H}$ = 2.7 Hz, 2H, H-5), 1.46 (s, 9H, H-10); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 169.2 (C-8), 155.7 (C-6), 133.7 (q, $^{3}J_{C,F}$ = 6.4 Hz, C-3), 122.4 (q, $^{1}J_{C,F}$ = 269.8 Hz, C-1), 122.3 (q, $^{2}J_{C,F}$ = 34.4 Hz, C-2), 80.4 (C-9), 71.5 (C-4), 44.0 (C-5), 42.4 (C-7), 28.3 (C-10); ^{19}F NMR (282 MHz, $CDCl_3$): δ -65.27 (dt, $^{3}J_{F,H}$ = 6.3, $^{4}J_{F,H}$ = 2.1 Hz, 3F, CF_3).

*Methyl (E)-3-[(pentafluoro-λ^{6}-sulfanyl)methyl]hex-4-enoate (**29a**)*. ^{1}H NMR (300 MHz, $CDCl_3$):



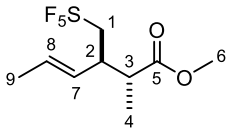
δ 5.62 (dqd, $^{3}J_{H,H}$ = 15.4, $^{3}J_{H,H}$ = 6.4, $^{4}J_{H,H}$ = 0.8 Hz, 1H, H-7), 5.33 (dd, $^{3}J_{H,H}$ = 15.3, $^{3}J_{H,H}$ = 8.4 Hz, 1H, H-6), 3.86 – 3.63 (m, 2H, H-1), 3.67 (s, 3H, H-5), 3.20 (sextet, $^{3}J_{H,H}$ = 6.9 Hz, 1H, H-2), 2.55 (AB, $^{2}J_{H,H}$ = 15.9, $^{3}J_{H,H}$ = 5.8 Hz, 1H, H-3'), 2.43 (dd, $^{2}J_{H,H}$ = 15.9, $^{3}J_{H,H}$ = 7.6 Hz, 1H, H-3), 1.66 (dd, $^{3}J_{H,H}$ = 6.4, $^{4}J_{H,H}$ = 1.5 Hz, 3H, H-8); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 171.5 (C-4), 129.6 (C-6), 128.6 (C-7), 75.5 (qu, $^{2}J_{C,F}$ = 11.2 Hz, C-1), 51.8 (C-5), 38.5 (m, C-3), 36.9 (qu, $^{3}J_{C,F}$ = 3.3 Hz, C-2), 17.9 (C-8); ^{19}F NMR (282 MHz, $CDCl_3$): δ 84.96 (nonet, $^{2}J_{F,F}$ = 147.6 Hz, 1F, SF), 66.41 (dtd, $^{2}J_{F,F}$ = 147.7, $^{3}J_{F,H}$ = 8.6, J = 2.1 Hz, 4F, SF_4).

*Methyl syn-(E)-2-methyl-3-[(pentafluoro-λ^{6}-sulfanyl)methyl]hex-4-enoates (syn-**29b**)*. ^{1}H NMR



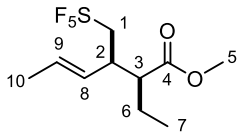
(600 MHz, $CDCl_3$): δ 5.60 (dq, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 6.5 Hz, 1H, H-8), 5.31 (ddd, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 9.2, $^{4}J_{H,H}$ = 1.9 Hz, 1H, H-7), 3.74 (m, 2H, H-1), 3.69 (s, 3H, H-6), 2.89 (tt, $^{3}J_{H,H}$ = 8.8 Hz, $^{3}J_{H2\text{-}H3}$ = 4.6 Hz, 1H, H-2), 2.65 (qd, $^{3}J_{H,H}$ = 7.1, $^{3}J_{H2\text{-}H3}$ = 4.6 Hz, 1H, H-3), 1.69 (dd, $^{3}J_{H,H}$ = 6.5, $^{4}J_{H,H}$ = 1.7 Hz, 3H, H-9), 1.15 (d, $^{3}J_{H,H}$ = 7.1 Hz, 3H, H-4); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 174.3 (C-5), 129.9 (C-8), 127.9 (C-7), 75.0 (quint, $^{2}J_{C,F}$ = 11.6 Hz, C-1), 51.7 (C-6), 43.3 (quint, $^{3}J_{C,F}$ = 3.3 Hz, C-2), 42.9 (C-3), 17.95 (C-9), 14.6 (C-4); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.33 (nonet, $^{2}J_{F,F}$ = 144.0 Hz, 1F, SF), 66.40 (dtd, $^{2}J_{F,F}$ = 144.0, $^{3}J_{F,H}$ = 8.5, J = 2.0 Hz, 4F, SF_4).

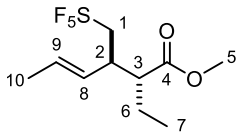
*Methyl anti-(E)-2-methyl-3-[(pentafluoro-λ^6-sulfanyl)methyl]hex-4-enoates (anti-**29b**)*. ^{1}H NMR



(600 MHz, $CDCl_3$): δ 5.61 (dq, $^3J_{H,H}$ = 15.2, $^3J_{H,H}$ = 6.5 Hz, 1H, H-8), 5.24 (ddd, $^3J_{H,H}$ = 15.2, $^3J_{H,H}$ = 9.5, $^4J_{H,H}$ = 1.8 Hz, 1H, H-7), 3.94 (dpd, $^2J_{H,H}$ = 16.8, $^3J_{H,F}$ = 8.5, $^3J_{H,H}$ = 4.2 Hz, 2H, H-1), 3.71 (s, 3H, H-6), 3.07 (dq, $^3J_{H2\text{-}H3}$ = 9.0 Hz, $^3J_{H,H}$ = 6.5 Hz, 1H, H-3), 2.53 (quint, $^3J_{H,H}$ = 7.1, 1H, H-2), 1.69 (dd, $^3J_{H,H}$ = 6.5, $^4J_{H,H}$ = 1.7 Hz, 3H, H-9), 1.14 (d, $^3J_{H,H}$ = 7.1 Hz, 3H, H-4); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 174.8 (C-5), 129.8 (C-8), 128.2 (C-7), 74.7 (quint, $^2J_{C,F}$ = 11.1 Hz, C-1), 51.9 (C-6), 43.1 (C-3), 42.6 (quint, $^3J_{C,F}$ = 3.1 Hz, C-2), 17.9 (C-9), 13.9 (C-4); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.08 (nonet, $^2J_{F,F}$ = 144.0 Hz, 1F, SF), 66.64 (dtd, $^2J_{F,F}$ = 144.0, $^3J_{F,H}$ = 8.5, J = 2.0 Hz, 4F, SF_4).

*Methyl (E)-2-ethyl-3-[(pentafluoro-λ^6-sulfanyl)methyl]hex-4-enoates (**29c**)*.

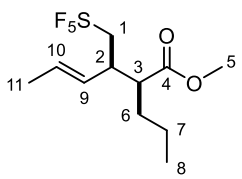




Major product. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.59 (dq, $^3J_{H,H}$ = 15.4, $^3J_{H,H}$ = 6.3 Hz, 1H, H-9), 5.33 (ddd, $^3J_{H,H}$ = 15.2, $^3J_{H,H}$ = 9.2, $^4J_{H,H}$ = 1.9 Hz, 1H, H-8), 3.73 – 3.63 (m, 2H, H-1), 3.68 (s, 3H, H-5), 2.92 (tt, $^3J_{H2\text{-}H8}$ = $^3J_{H2\text{-}H3}$ = 9.1, $^3J_{H,H}$ = 4.8 Hz, 1H, H-2), 2.41 (dt, $^3J_{H2\text{-}H3}$ = 9.3, $^3J_{H,H}$ = 5.4 Hz, 1H, H-3), 1.69 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 1.6 Hz, 3H, H-10), 1.59 (m, 2H, H-6), 0.91 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, H-7); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 173.9 (C-4), 129.7 (C-8), 128.1 (C-9), 75.2 (quint, $^2J_{C,F}$ = 11.1 Hz, C-1), 51.6 (C-5), 50.7 (C-3), 42.0 (quint, $^3J_{C,F}$ = 3.1 Hz. C-2), 22.8 (C-10), 17.9 (C-6), 12.0 (C-7); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.30 (quint, $^2J_{F,F}$ = 145.5 Hz, 1F, SF), 66.48 (dt, $^2J_{F,F}$ = 145.7, $^3J_{F,H}$ = 8.2 Hz, 4F, SF_4).

Minor product. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.59 (dq, $^3J_{H,H}$ = 15.4, $^3J_{H,H}$ = 6.3 Hz, 1H, H-9), 5.23 (ddd, $^3J_{H,H}$ = 15.2, $^3J_{H,H}$ = 9.3, $^4J_{H,H}$ = 1.8 Hz, 1H, H-8), 3.92 (dtt, $^2J_{H,H}$ = 21.6, $^3J_{H,H}$ = 8.4, $^3J_{H,H}$ = 4.6 Hz, 2H, H-1), 3.71 (s, 3H, H-5), 2.97 (qd, $^3J_{H,H}$ = $^3J_{H,H}$ = 8.4, $^3J_{H,H}$ = 4.0 Hz, 1H, H-2), 2.29 (dt, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 6.2 Hz, 1H, H-3), 1.70 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 1.6 Hz, 3H, H-10), 1.48 (dqd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 5.4 Hz, 2H, H-6), 0.89 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, H-7); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 174.5 (C-4), 129.4 (C-8), 129.1 (C-9), 74.8 (quint, $^2J_{C,F}$ = 11.3 Hz, C-1), 51.7 (C-5), 51.0 (C-3), 42.0 (quint, $^3J_{C,F}$ = 3.1 Hz. C-2), 23.2 (C-10), 17.9 (C-6), 11.7 (C-7); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.24 (quint, $^2J_{F,F}$ = 145.9 Hz, 1F, SF), 66.80 (dt, $^2J_{F,F}$ = 145.9, $^3J_{F,H}$ = 8.2 Hz, 4F, SF_4).

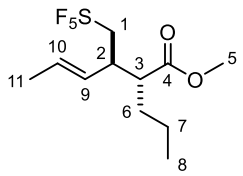
*Methyl syn-(E)-3-[(pentafluoro-λ^6-sulfanyl)methyl]-2-propylhex-4-enoates (syn-**29d**)*. ^{1}H NMR



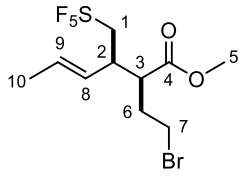
(600 MHz, $CDCl_3$): δ 5.58 (dq, $^3J_{H,H}$ = 15.2, $^3J_{H,H}$ = 6.5 Hz, 1H, H-10), 5.32 (dm, $^3J_{H,H}$ = 15.2 Hz, 1H, H-9), 3.74 – 3.62 (m, 2H, H-1), 3.67 (s, 3H, H-5), 2.90 (tt, $^3J_{H,H}$ = 9.1, $^3J_{H,H}$ = $^3J_{H,H}$ = 5.1 Hz, 1H, H-2), 2.50 (td, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 5.2 Hz, 1H, H-3), 1.69 (dt, $^3J_{H,H}$ = 6.9, $^4J_{H,H}$ = 1.7 Hz, 3H, H-11), 1.41 – 1.36 (m, 1H, H-6), 1.34 – 1.27 (m, 2H, H-6', H-7), 1.26 – 1.18 (m, 1H, H-7'), 0.91

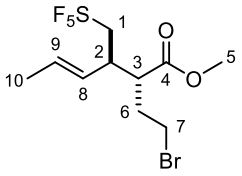
(t, $^{3}J_{H,H}$ = 7.3 Hz, 3H, H-8); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 174.0 (C-4), 129.7 (C-10), 128.2 (C-9), 75.2 (quint, $^{2}J_{C,F}$ = 11.1 Hz, C-1), 51.6 (C-5), 48.8 (C-3), 42.3 (quint, $^{3}J_{C,F}$ = 3.2 Hz, C-2), 31.8 (C-11), 20.7 (C-6), 17.95 (C-7), 13.9 (C-8); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.28 (quint, $^{2}J_{F,F}$ = 145.5 Hz, 1F, SF), 66.50 (dt, $^{2}J_{F,F}$ = 145.4, $^{3}J_{F,H}$ = 8.5 Hz, 4F, SF_4).

*Methyl anti-(E)-3-[(pentafluoro-λ⁶-sulfanyl)methyl]-2-propylhex-4-enoates (anti-**29d**)*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.58 (dq, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 6.5 Hz, 1H, H-10), 5.22 (ddd, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 9.2, $^{4}J_{H,H}$ = 1.8 Hz, 1H, H-9), 3.91 (dquintd, $^{2}J_{H,H}$ = 21.3, $^{3}J_{H,F}$ = 8.4, $^{3}J_{H1\text{-}H2}$ = 4.1 Hz, 2H, H-1), 3.69 (s, 3H, H-5), 2.96 (ddt, $^{3}J_{H,H}$ = 12.3, $^{3}J_{H,H}$ = 8.0, $^{3}J_{H1\text{-}H2}$ = 4.3 Hz, 1H, H-2), 2.38 (ddd, $^{3}J_{H,H}$ = 10.6, $^{3}J_{H,H}$ = 7.6, $^{3}J_{H,H}$ = 4.2 Hz, 1H, H-3), 1.70 (td, $^{3}J_{H,H}$ = 6.9, $^{4}J_{H,H}$ = 1.7 Hz, 3H, H-11), 1.68 – 1.62 (m, 2H, H-6), 1.60 – 1.54 (m, 1H, H-7), 1.49 – 1.44 (m, 1H, H-7'), 0.90 (t, $^{3}J_{H,H}$ = 7.3 Hz, 3H, H-8); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 174.7 (C-4), 129.4 (C-10), 129.1 (C-9), 74.8 (quint, $^{2}J_{C,F}$ = 11.0 Hz, C-1), 51.7 (C-5), 49.4 (C-3), 42.3 (quint, $^{3}J_{C,F}$ = 3.2 Hz, C-2), 32.0 (C-11), 20.6 (C-6), 17.94 (C-7), 13.9 (C-8); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.24 (quint, $^{2}J_{F,F}$ = 145.5 Hz, 1F, SF), 66.76 (dt, $^{2}J_{F,F}$ = 144.0, $^{3}J_{F,H}$ = 8.5 Hz, 4F, SF_4).



*Methyl (E)-2-(2-bromoethyl)-3-[(pentafluoro-λ⁶-sulfanyl)methy]hex-4-enoates (**29e**)*.



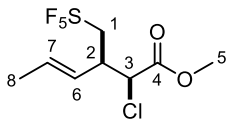


Major product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.62 (dq, $^{3}J_{H,H}$ = 15.1, $^{3}J_{H,H}$ = 6.0 Hz, 1H, H-9), 5.28 (dd, $^{3}J_{H,H}$ = 15.3, $^{3}J_{H,H}$ = 9.3 Hz, 1H, H-8), 3.71 (s, 3H, H-5), 3.71 – 3.64 (m, 2H, H-1), 3.45 (t, $^{3}J_{H,H}$ = 6.5 Hz, 1H, H-3), 3.34 (dtd, $^{3}J_{H,H}$ = 10.3, $^{3}J_{H,H}$ = 8.4, $^{3}J_{H,H}$ = 6.1 Hz, 1H, H-2), 2.91 (dt, $^{2}J_{H,H}$ = 8.9, $^{3}J_{H,H}$ = 4.6 Hz, 1H, H-7), 2.83 (dt, $^{2}J_{H,H}$ = 9.1, $^{3}J_{H,H}$ = 4.5 Hz, 1H, H-7'), 2.28 (ddt, $^{2}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 9.4, $^{3}J_{H,H}$ = 5.9 Hz, 1H, H-6), 1.90 (dddd, 1H, $^{2}J_{H,H}$ = 14.7, $^{3}J_{H,H}$ = 8.3, $^{3}J_{H,H}$ = 6.6, $^{3}J_{H,H}$ = 4.6 Hz, 1H, H-6'), 1.70 (ddd, $^{3}J_{H,H}$ = 6.4, $^{4}J_{H,H}$ = 4.5, $^{5}J_{H,H}$ = 1.6 Hz, 3H, H-10); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 172.8 (C-4), 130.5 (C-9), 127.1 (C-8), 74.9 (quint, $^{2}J_{C,F}$ = 11.6 Hz, C-1), 52.0 (C-5), 46.9 (C-3), 42.2 (quint, $^{3}J_{C,F}$ = 3.4 Hz, C-2), 32.8 (C-7), 30.8 (C-10), 18.0 (C-6); ^{19}F NMR (564 MHz, $CDCl_3$): δ 84.94 (quint, $^{2}J_{F,F}$ = 145.9 Hz, 1F, SF), 66.35 (dt, $^{2}J_{F,F}$ = 145.9, $^{3}J_{F,H}$ = 8.3 Hz, 4F, SF_4).

Minor product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.61 (dq, $^{3}J_{H,H}$ = 15.1, $^{3}J_{H,H}$ = 6.3 Hz, 1H, H-9), 5.21 (ddd, $^{3}J_{H,H}$ = 15.3, $^{3}J_{H,H}$ = 9.2 Hz, $^{4}J_{H,H}$ = 1.8 Hz, 1H, H-8), 3.94 (m, 2H, H-1), 3.72 (s, H, H-5), 3.47 (td, $^{3}J_{H,H}$ = 6.7, $J_{H,H}$ = 1.7 Hz, 1H, H-3), 3.28 (dtd, $^{3}J_{H,H}$ = 10.3, $^{3}J_{H,H}$ = 8.9, $^{3}J_{H,H}$ = 6.2 Hz, 1H, H-2), 3.08 (dt, $^{2}J_{H,H}$ = 9.0, $^{3}J_{H,H}$ = 6.8 Hz, 1H, H-7), 2.67 (ddd, $^{2}J_{H,H}$ = 10.5, $^{3}J_{H,H}$ = 7.1, $^{3}J_{H,H}$ = 3.5 Hz, 1H, H-7'), 2.20 (m, 1 H, H-6), 1.98 (dddd, $^{2}J_{H,H}$ = 14.5, $^{3}J_{H,H}$ = 8.9, $^{3}J_{H,H}$ = 7.0, $^{3}J_{H,H}$ = 3.5 Hz, 1H, H-6'), 1.70 (ddd, $^{3}J_{H,H}$ = 6.4, $^{4}J_{H,H}$ = 4.5, $^{5}J_{H,H}$ = 1.6 Hz, 3H, H-10);

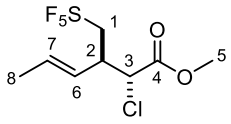
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 173.4 (C-4), 130.4 (C-9), 128.1 (C-8), 74.5 (quint, $^{2}J_{C,F}$ = 11.4 Hz, C-1), 52.1 (C-5), 47.7 (C-3), 41.9 (quint, $^{3}J_{C,F}$ = 3.6 Hz, C-2), 32.1 (C-7), 30.6 (C-10), 17.97 (C-6); ^{19}F NMR (564 MHz, $CDCl_3$): δ 84.74 (quint, $^{2}J_{F,F}$ = 146.4 Hz, 1F, *SF*), 66.83 (dt, $^{2}J_{F,F}$ = 146.4, $^{3}J_{F,H}$ = 8.3 Hz, 4F, *SF_4*).

*Methyl syn-(E)-2-chloro-3-[(pentafluoro-λ^6-sulfanyl)methyl]hex-4-enoates (syn-**29f**)*. ^{1}H NMR



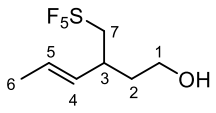
(600 MHz, $CDCl_3$): δ 5.71 (dq, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 6.5 Hz, 1H, H-7), 5.37 (m, 1H, H-6), 4.62 (d, $^{3}J_{H2\text{-}H3}$ = 3.5 Hz, 1H, H-3), 3.86 – 3.68 (m, 2H, H-1), 3.78 (s, 3H, H-5), 3.50 (tdd, $^{3}J_{H,H}$ = 9.2, $^{3}J_{H,H}$ = 6.3, $^{3}J_{H2\text{-}H3}$ = 3.3 Hz, 1H, H-2), 1.71 (ddd, $^{3}J_{H,H}$ = 8.4, $^{3}J_{H,H}$ = 6.5, $^{4}J_{H,H}$ = 1.7 Hz, 3H, H-8); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 167.9 (C-4), 132.2 (C-7), 124.9 (C-6), 73.0 (quint, $^{2}J_{C,F}$ = 12.2 Hz, C-1), 60.5 (quint, $^{4}J_{C,F}$ = 1.7 Hz, C-3), 53.2 (C-5), 43.8 (quint, $^{3}J_{C,F}$ = 3.5 Hz, C-2), 18.06 (C-8); ^{19}F NMR (564 MHz, $CDCl_3$): δ 84.69 (quint, $^{2}J_{F,F}$ = 146.0 Hz, 1F, SF), 66.92 (dt, $^{2}J_{F,F}$ = 146.0, $^{3}J_{F,H}$ = 8.4, 4F, SF_4).

*Methyl anti-(E)-2-chloro-3-[(pentafluoro-λ^6-sulfanyl)methyl]hex-4-enoates (anti-**29f**)*. ^{1}H NMR



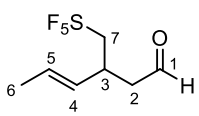
(600 MHz, $CDCl_3$): δ 5.73 (dq, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 6.5 Hz, 1H, H-7), 5.36 (m, 1H, H-6), 4.17 (d, $^{3}J_{H2\text{-}H3}$ = 7.3 Hz, 1H, H-3), 4.15 – 4.01 (m, 2H, H-1), 3.78 (s, 3H, H-5), 3.32 (qd, $^{3}J_{H,H}$ = $^{3}J_{H,H}$ = 9.4, $^{3}J_{H,H}$ = 2.7 Hz, 1H, H-2), 1.71 (ddd, $^{3}J_{H,H}$ = 8.4, $^{3}J_{H,H}$ = 6.5, $^{4}J_{H,H}$ = 1.7 Hz, 3H, H-8); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 168.2 (C-4), 132.3 (C-7), 126.4 (C-6), 72.9 (quint, $^{2}J_{C,F}$ = 12.8 Hz, C-1), 59.3 (C-3), 53.1 (C-5), 44.2 (quint, $^{3}J_{C,F}$ = 3.7 Hz, C-2), 18.04 (C-8); ^{19}F NMR (564 MHz, $CDCl_3$): δ 84.67 (quint, $^{2}J_{F,F}$ = 146.2 Hz, 1F, SF), 67.98 (dt, $^{2}J_{F,F}$ = 146.8, $^{3}J_{F,H}$ = 8.3 Hz, 4F, SF_4).

*(E)-3-[(Pentafluoro-λ^6-sulfanyl)methyl]hex-4-en-1-ol (**30**)*. H NMR (300 MHz, $CDCl_3$): δ 5.61



(dq, $^{3}J_{H,H}$ = 15.3, $^{3}J_{H,H}$ = 6.4 Hz, 1H, H-5), 5.22 (ddd, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 9.1, $^{4}J_{H,H}$ = 1.8 Hz, 1H, H-4), 3.74 – 3.59 (m, 4H, H-7 and H-1), 2.90 (ttd, $^{3}J_{H,H}$ = 10.2, $J_{H,H}$ = 6.6, $J_{H,H}$ = 4.1 Hz, 1H, OH), 1.81 (dddd, $^{3}J_{H,H}$ = 14.1, $^{3}J_{H,H}$ = 8.0, $^{3}J_{H,H}$ = 6.3, $J_{H,H}$ = 4.1, 1H, H-3), 1.70 (dd, $^{3}J_{H,H}$ = 6.5, $^{4}J_{H,H}$ = 1.7 Hz, 3H, H-6), 1.57 – 1.44 (m, 2H, H-2); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 130.9 (C-5), 128.5 (C-4), 77.2 (quint, $^{2}J_{C,F}$ = 10.2 Hz, C-7), 60.2 (C-1), 37.6 (quint, $^{3}J_{C,F}$ = 3.2 Hz, C-3), 36.7 (C-2), 17.9(C-6); ^{19}F NMR (282 MHz, $CDCl_3$): δ 85.53 (quint, $^{2}J_{F,F}$ = 145.8 Hz, 1F, SF), 66.42 (dtd, $^{2}J_{F,F}$ = 145.8, $^{3}J_{F,H}$ = 8.6, $^{4}J_{F,H}$ =2.0 Hz, 4F, SF_4).

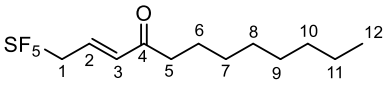
*(E)-3-[(Pentafluoro-λ^6-sulfanyl)methyl]hex-4-enal (**31**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.70 (t,



$^{3}J_{H,H}$ = 1.4, 1H, H-1), 5.70 – 5.58 (m, 1H, H-5), 5.34 (dd, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 8.2 Hz, 1H, H-4), 3.73 (quintd, $^{3}J_{H,F}$ = 8.5, $^{3}J_{H,H}$ = 6.5 Hz, 2H, H-7), 3.31 (m, 1H, H-3), 2.75 – 2.56 (AB, 2H, H-2), 1.68 (dd, $^{3}J_{H,H}$ = 6.4, $^{4}J_{H,H}$ = 1.6 Hz, 3H, H-6); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 199.8 (C-1), 129.7 (C-5), 129.0 (C-4), 75.6 (quint, $^{2}J_{C,F}$ = 11.3 Hz, C-7), 47.3 (quint, $^{3}J_{C,F}$ = 1.5 Hz, C-2), 35.0 (quint, $^{3}J_{C,F}$ = 3.0 Hz, C-3), 17.9 (C-6);

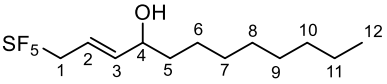
^{19}F NMR (282 MHz, $CDCl_3$): δ 84.85 (quint, $^2J_{F,F}$ = 145.6 Hz, 1F, SF), 66.38 (dtd, $^2J_{F,F}$ = 145.6, $^3J_{F,H}$ = 8.5, J = 2.1 Hz, 4F, SF_4).

*(E)-1-(Pentafluoro-λ^6-sulfanyl)dodec-2-en-4-one (**33b**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.83 (dt,



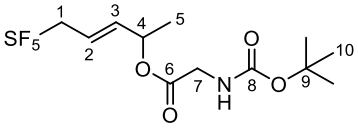
$^3J_{H,H}$ = 15.6, $^3J_{H,H}$ = 7.8 Hz, 1H, H-2), 6.31 (dt, $^3J_{H,H}$ = 15.8, $^4J_{H,H}$ = 1.3 Hz, 1H, H-3), 4.39 (sexted, $^3J_{H,H}$ = $^3J_{H,F}$ = 7.4, $^4J_{H,H}$ = 1.2 Hz, 2H, H-1), 2.59 (m, 2H, H-5), 1.62 (quint, $^3J_{H,H}$ = 7.2 Hz, 2H, H-6), 1.31 – 1.24 (m, 10H, H-7 – H-11), 0.88 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, H-12); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.4 (C-4), 136.0 (C-3), 132.2 (quint, $^3J_{C,F}$ = 4.3 Hz, C-2), 72.0 (quint, $^2J_{C,F}$ = 16.2 Hz, C-1), 41.0 (C-5), 31.9 (C-6), 29.4 (C-7), 29.2 (C-8), 29.2 (C-9), 23.9 (C-10), 22.7 (C-11), 14.2 (C-12); ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.06 (nonet, $^2J_{F,F}$ = 146.0 Hz, 1F, SF), 66.17 (dt, $^2J_{F,F}$ = 146.0, $^3J_{F,H}$ = 7.4 Hz, 4F, SF_4).

*(E)-1-(Pentafluoro-λ^6-sulfanyl)dodec-2-en-4-ol (**28b**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.90 – 5.80



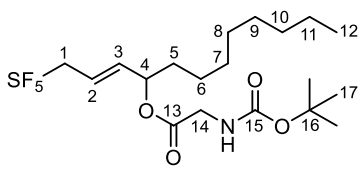
(m, 2H, H-2 and H-3), 4.28 (ddt, $^2J_{H,H}$ = 13.7, $^3J_{H,H}$ = 9.6, $J_{H,H}$ = 5.2 Hz, 2H, H-1), 4.17 (m, $^3J_{H,H}$ = 6.3 Hz, 1H, H-4), 2.11 (bs, 1H, OH), 1.53 (tt, $^3J_{H,H}$ = 9.7, $^3J_{H,H}$ = $^4J_{H,H}$ = 6.7 Hz, 2H, H-5), 1.31 – 1.24 (m, 12H, H-6 – H-11), 0.89 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, H-12); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.0 (C-3), 119.5 (quint, $^3J_{C,F}$ = 4.1 Hz, C-2), 73.5 (quint, $^2J_{C,F}$ = 14.4 Hz, C-1), 71.8 (C-4), 37.0 (C-5), 32.0 (C-6), 29.6 (C-7), 29.6 (C-8), 29.3 (C-9), 25.3 (C-10), 22.8 (C-11), 14.2 (C-12); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.60 (nonet, $^2J_{F,F}$ = 144.5 Hz, 1F, SF), 63.50 (dt, $^2J_{F,F}$ = 144.5, $^3J_{F,H}$ = 7.4 Hz, 4F, SF_4).

*(E)-5-(Pentafluoro-λ^6-sulfanyl)pent-3-en-2-yl (tert-butoxycarbonyl)glycinate (**34a**)*. ^{1}H NMR



(300 MHz, $CDCl_3$): δ 5.94 – 5.85 (m, 1H, H-2), 5.80 (dd, $^3J_{H,H}$ = 15.3, $^3J_{H,H}$ = 5.0 Hz, 1H, H-3), 5.41 (quint, $^3J_{H,H}$ = $^3J_{H,H}$ = 6.4 Hz, 1H, H-4), 5.08 (bt, $^3J_{H,H}$ = 5.8 Hz, 1H, NH), 4.23 (sextet, $^3J_{H,H}$ = $^3J_{H,F}$ = 7.1, 2H, H-1), 3.87 (d, $^3J_{H,H}$ = 5.3 Hz, 2H, H-7), 1.41 (s, 9H, 3 × H-10), 1.33 (d, $^3J_{H,H}$ = 6.6 Hz, 3H, H-5); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.5 (C-8), 155.7 (C-6), 138.4 (C-3), 121.2 (quint, $^3J_{C,F}$ = 4.1 Hz, C-2), 80.0 (C-4), 72.9 (quint, $^2J_{C,F}$ = 14.8 Hz, C-1), 70.5 (C-7), 42.5 (C-9), 28.2 (3 × C-10), 19.6 (C-5); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.22 (nonet, $^2J_{F,F}$ = 144.7 Hz, 1F, SF), 63.99 (dt, $^2J_{F,F}$ = 144.6, $^3J_{F,H}$ = 7.2 Hz, 4F, SF_4).

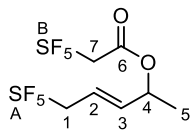
*(E)-1-(Pentafluoro-λ^6-sulfanyl)dodec-2-en-4-yl-(tert-butoxycarbonyl)glycinate (**34b**)*. ^{1}H NMR



(300 MHz, $CDCl_3$): δ 5.89 (dt, $^3J_{H,H}$ = 14.9, $^3J_{H,H}$ = 7.3 Hz, 1H, H-2), 5.76 (dd, $^3J_{H,H}$ = 15.5, $^3J_{H,H}$ = 6.3 Hz, 1H, H-3), 5.30 (q, $^3J_{H,H}$ = $^3J_{H,H}$ = 6.5 Hz, 1H, H-4), 5.01 (bs, 1H, NH), 4.24 (ddt, $^3J_{H,H}$ = 13.7, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 6.4 Hz, 2H, H-1), 3.89 (s, 2H, H-14), 1.63 (tdd, $^3J_{H,H}$ = 14.6, $^3J_{H,H}$ = 10.8, $^4J_{H,H}$ = 6.3 Hz, 2H, H-5), 1.44 (s, 9H, 3 × H-17), 1.31 – 1.24 (m, 12H, H-6 – H-11), 0.89 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, H-12); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.6 (C-15), 155.6 (C-13), 137.7 (C-3), 122.1 (quint, $^3J_{C,F}$ = 3.8 Hz, C-2), 80.0 (C-4), 74.4 (C-

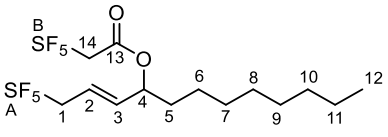
16), 72.9 (quint, $^{2}J_{C,F}$ = 14.9 Hz, C-1), 42.5 (C-5), 33.9 (C-6), 31.8 (C-7), 29.3 (C-8), 29.2 (C-9), 29.1 (C-10), 28.2 (3 × C-17), 24.7 (C-16), 22.6 (C-11), 14.1 (C-12); ^{19}F NMR (282 MHz, $CDCl_3$): δ 82.22 (nonet, $^{2}J_{F,F}$ = 144.5 Hz, 1F, SF), 64.03 (dt, $^{2}J_{F,F}$ = 144.5, $^{3}J_{F,H}$ = 7.0 Hz, 4F, SF_4).

*(E)-1-(Pentafluoro-λ^6-sulfanyl)pent-2-en-4-yl 2-(pentafluoro-λ^6-sulfanyl)acetate (**36a**)*. ^{1}H NMR



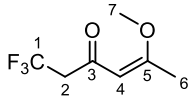
(300 MHz, $CDCl_3$): δ 5.96 (dt, $^{3}J_{H,H}$ = 14.9, $^{3}J_{H,H}$ = 5.8 Hz, 1H, H-2), 5.84 (dd, $^{3}J_{H,H}$ = 15.5, $^{3}J_{H,H}$ = 5.9 Hz, 1H, H-3), 5.47 (quint, $^{3}J_{H,H}$ = 6.4 Hz, 1H, H-4), 4.40 – 4.20 (m, 4H, H-1, H-7), 1.40 (d, $^{3}J_{H,H}$ = 6.5 Hz, 3H, H-5); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.2 (quint, $^{3}J_{C,F}$ = 4.5 Hz, C-6), 137.3 (broad, C-3), 122.3 (quint, $^{3}J_{C,F}$ = 4.1 Hz, C-2), 72.7 (quint, $^{2}J_{C,F}$ = 15.6 Hz, C-7), 72.2 (C-4), 70.8 (quint, $^{2}J_{C,F}$ = 16.9 Hz, C-1), 19.3 (C-5); ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.53 (nonet, $^{2}J_{F,F}$ = 148.4 Hz, 1F, SF^{B}), 78.88 (nonet, $^{2}J_{F,F}$ = 145.0 Hz, 1F, SF^{A}), 70.95 (dm, $^{2}J_{F,F}$ = 148.4, $^{3}J_{F,H}$ = 7.6 Hz, 4F, SF_4^{B}), 63.68 (dm, $^{2}J_{F,F}$ = 145.0, $^{3}J_{F,H}$ = 7.8 Hz, 4F, SF_4^{A}).

*(E)-1-(Pentafluoro-λ^6-sulfanyl)dodec-2-en-4-yl 2-(pentafluoro-λ^6-sulfanyl)acetate (**36b**)*. ^{1}H



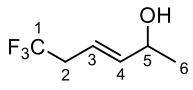
NMR (300 MHz, $CDCl_3$): δ 5.95 (dt, $^{3}J_{H,H}$ = 15.3, $^{3}J_{H,H}$ = 7.6 Hz, 1H, H-2), 5.78 (dd, $^{3}J_{H,H}$ = 15.5, $^{3}J_{H,H}$ = 6.8 Hz, 1H, H-3), 5.33 (q, $^{3}J_{H,H}$ = $^{3}J_{H,H}$ = 6.7 Hz, 1H, H-4), 4.30 (quint, $^{3}J_{H,H}$ = 7.7 Hz, 2H, H-14), 4.23 (sext, $^{3}J_{H,F}$ = $^{3}J_{H,H}$ = 7.0 Hz, 2H, H-1), 1.75 – 1.56 (m, 2H, H-5), 1.31 – 1.24 (m, 12H, H-6 – H-11), 0.89 (t, $^{3}J_{H,H}$ = 7.0 Hz, 3H, H-12); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.4 (quint, $^{3}J_{C,F}$ = 4.3 Hz, C-13), 136.7 (C-3), 123.2 (quint, $^{3}J_{C,F}$ = 4.1 Hz, C-2), 76.2 (C-4), 72.8 (quint, $^{2}J_{C,F}$ = 14.8 Hz, C-14), 71.0 (quint, $^{2}J_{C,F}$ = 16.8 Hz, C-1), 33.7 (C-5), 31.9 (C-6), 29.4 (C-7), 29.2 (C-8), 29.2 (C-9), 24.7 (C-10), 22.7 (C-11), 14.1 (C-12); ^{19}F NMR (282 MHz, $CDCl_3$): δ 81.55 (nonet, $^{2}J_{F,F}$ = 147.3 Hz, 1F, SF^{B}), 78.94 (nonet, $^{2}J_{F,F}$ = 144.6 Hz, 1F, SF^{A}), 71.03 (dm, $^{2}J_{F,F}$ = 147.3, $^{3}J_{F,H}$ = 7.5 Hz, 4F, SF_4^{B}), 63.69 (dt, $^{2}J_{F,F}$ = 144.6, $^{3}J_{F,H}$ = 7.7 Hz, 4F, SF_4^{A}).

*(Z)-1,1,1-Trifluoro-5-methoxyhex-4-en-3-one (**38**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.46 (s, 1H,



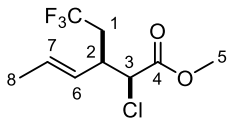
H-4), 3.68 (s, 3H, H-7), 3.18 (q, $^{3}J_{H,F}$ = 10.8 Hz, 3H, H-2), 2.31 (s, 3H, H-6); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 187.5 (C-3), 176.2 (C-5), 124.3 (q, $^{1}J_{C,F}$ = 276.7 Hz, C-1), 98.3 (C-4), 55.8 (C-7), 47.7 (q, $^{2}J_{C,F}$ = 27.4 Hz, C-2), 20.3 (C-6); ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.92 (t, $^{3}J_{F,H}$ = 10.8 Hz, 3F, CF_3).

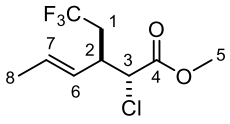
*(E)-6,6,6-Trifluorohex-3-en-2-ol (**42**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.78 (dd, $^{3}J_{H,H}$ = 15.8, $^{3}J_{H,H}$



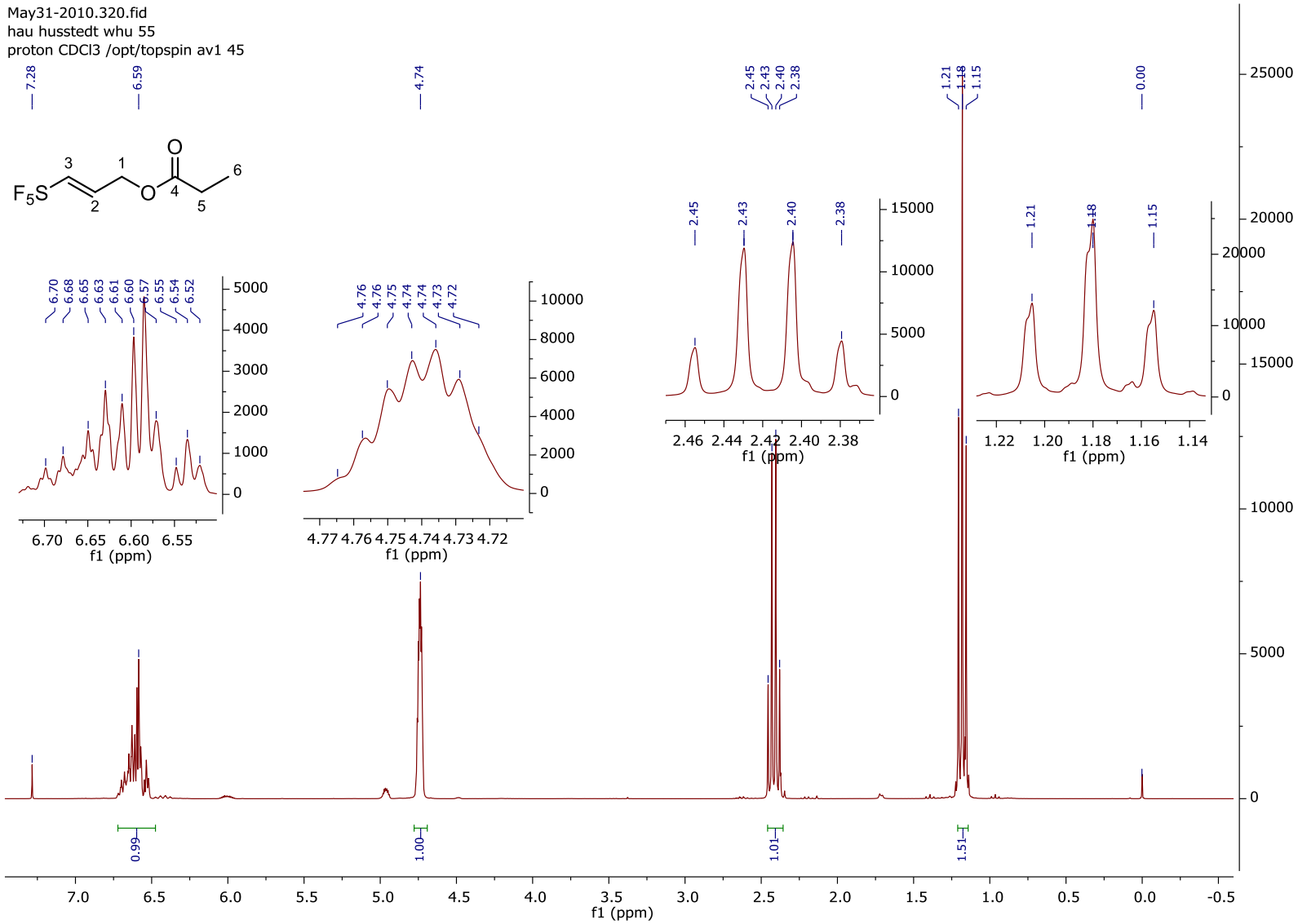
= 6.0 Hz, 1H, H-4), 5.65 – 5.55 (dtd, $^{3}J_{H,H}$ = 15.4, $^{3}J_{H,H}$ = 7.0, $^{3}J_{H,H}$ = 1.2 Hz, 1H, H-3), 4.32 (quint, $^{3}J_{H,H}$ = 6.3 Hz, 1H, H-5), 2.80 (qd, $^{3}J_{H,F}$ = 10.7, $^{3}J_{H,H}$ = 7.1 Hz, 3H, H-2), 1.85 (bs, 1H, OH), 1.27 (d, $^{3}J_{H,H}$ = 6.5 Hz, 3H, H-6); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.5 (C-4), 125.9 (q, $^{1}J_{C,F}$ = 276.4 Hz, C-1), 117.6 (q, $^{3}J_{C,F}$ = 3.7 Hz, C-3), 68.1 (C-5), 36.9 (q, $^{2}J_{C,F}$ = 29.8 Hz, C-2), 23.1 (C-6); ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.95 (t, $^{3}J_{F,H}$ = 10.8 Hz, 3F, CF_3).

*Methyl syn-(E)-2-chloro-3-(2,2,2-trifluoroethyl)hex-4-enoate and methyl anti-(E)-2-chloro-3-(2,2,2-trifluoroethyl)hex-4-enoate (**43**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ overlap 5.75-5.58 (m, 1H, 2× H-7), 5.42-5.23 (m, 1H, 2× H-6), 4.47 (d, 1H, $^{3}J_{H,H}$ = 3.9 Hz, H-3$_{syn}$), 4.17 (d, 1H, $^{3}J_{H,H}$ = 7.5 Hz, H-3$_{anti}$), 3.78 (s, 3H, H-5$_{syn}$), 3.77 (s, 3H, H5$_{anti}$), 3.12 (dq, $^{3}J_{H,H}$ = 12.5, $^{3}J_{H,H}$ = 4.4 Hz, 1H, H-2$_{syn}$), 3.00 (qd, $^{3}J_{H,H}$ = 10.1, $^{3}J_{H,H}$ = 3.0 Hz, 1H, H-2$_{anti}$), overlap 2.66-2.10 (m, 2H, 2× H-1), 1.68 (d, $^{3}J_{H,H}$ = 6.5, 3H, 2× H-8); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 168.6 (C-4$_{anti}$), 168.2 (C-4$_{syn}$), 131.3 (C-7$_{anti}$), 130.9 (C-7$_{syn}$), 129.4 (q, $^{1}J_{C,F}$ = 275 Hz, CF_3), 127.0 (C-6$_{anti}$), 126.2 (C-6$_{syn}$), 61.2 (C-3$_{anti}$), 60.3 (C-3$_{syn}$), 53.1 (C-5$_{syn}$), 53.0 (C-5$_{anti}$), 41.6 (q, $^{3}J_{C,F}$ = 2.5 Hz, C-2$_{anti}$), 41.1 (q, $^{3}J_{C,F}$ = 2.8 Hz, C-2$_{syn}$), 36.0 (d, $^{2}J_{C,F}$ = 27.8 Hz, C-1$_{syn}$), 35.3 (d, $^{2}J_{C,F}$= 27.0 Hz, C-1$_{anti}$), 18.1 (×2, C-8). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ -64.16 (s, 3F, CF_{3syn}) and -63.62 (s, 3F, CF_{3anti}).

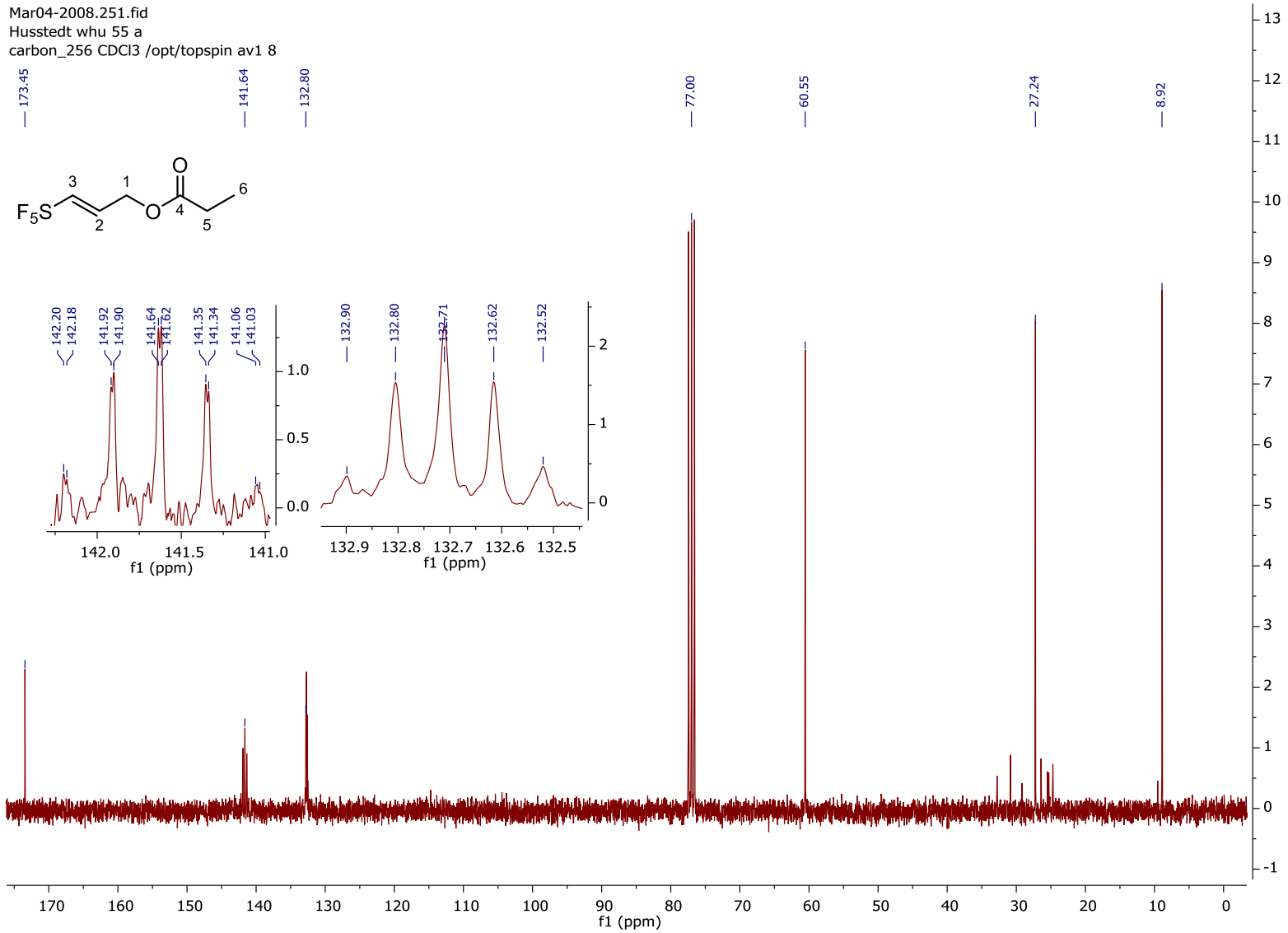




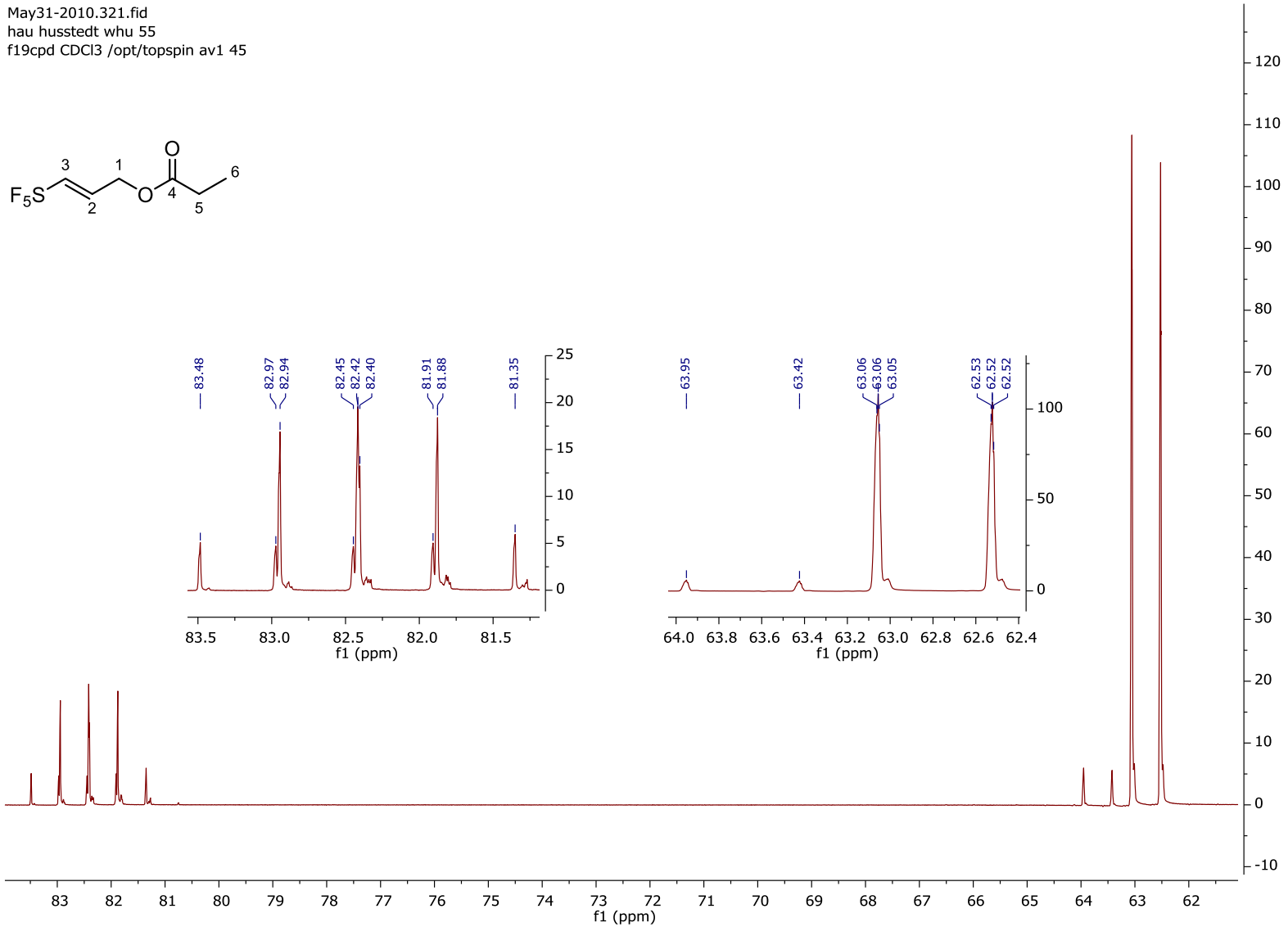
^{1}H NMR spectrum of compound **4a**



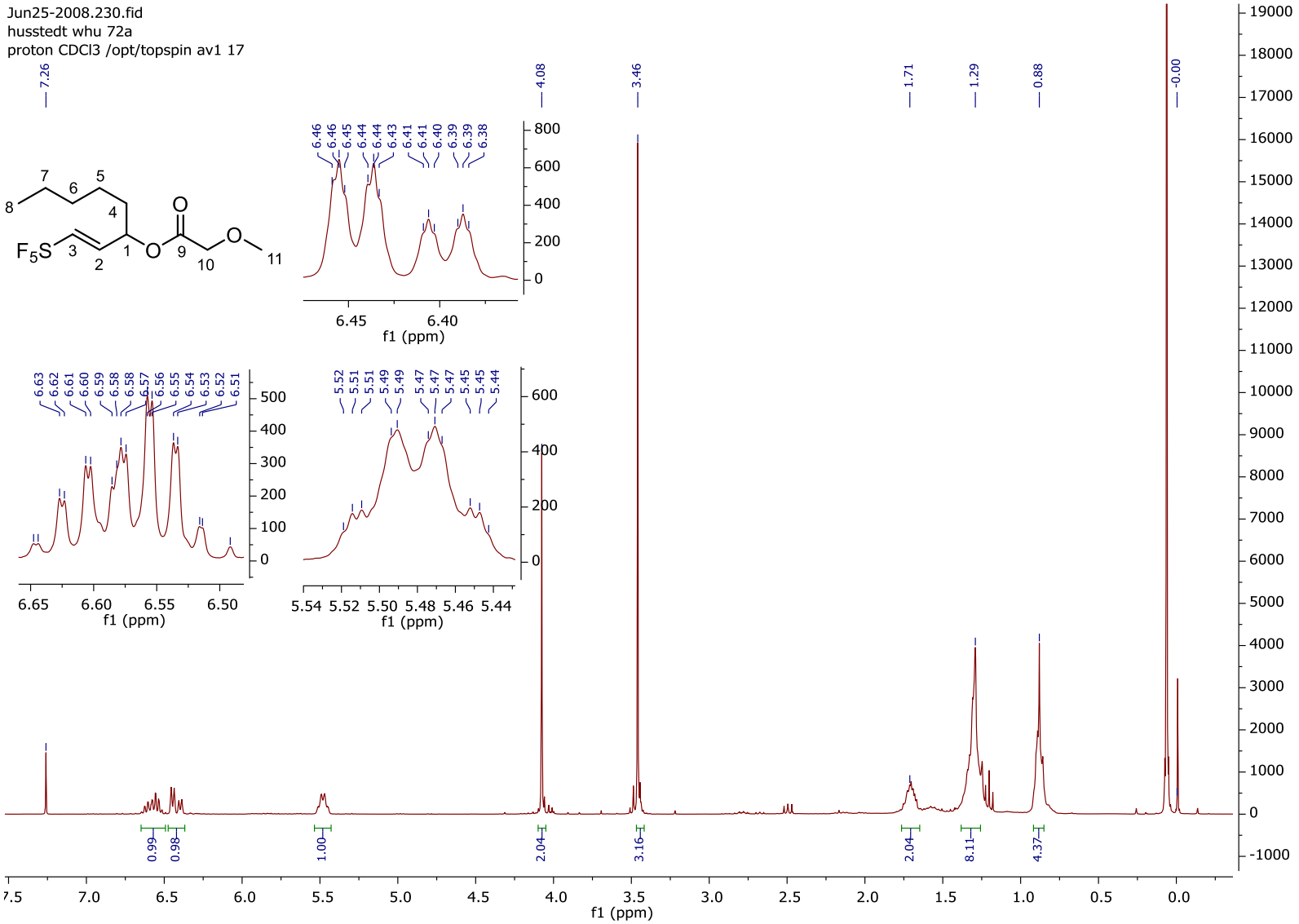
^{13}C NMR spectrum of compound **4a**



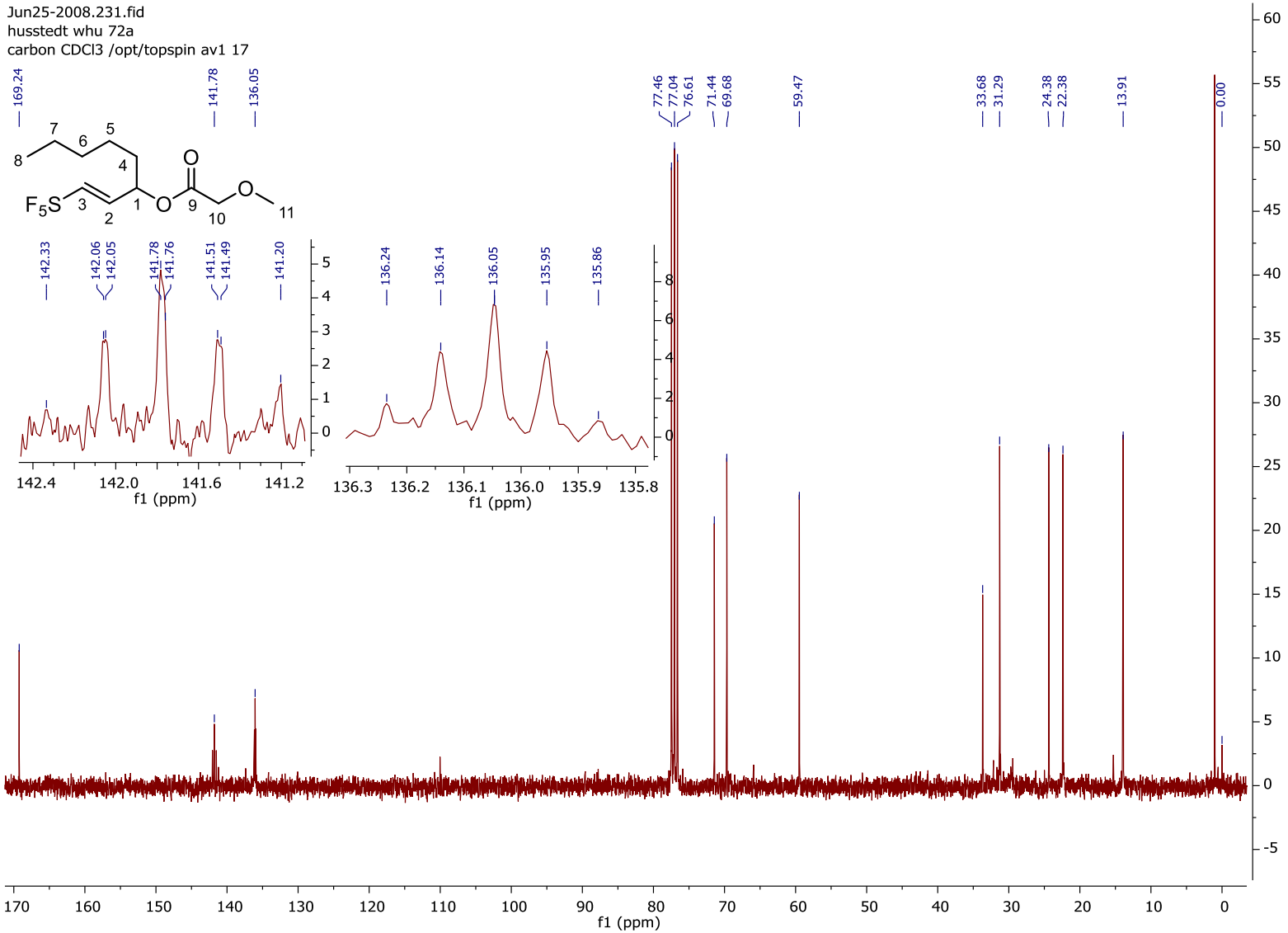
^{19}F NMR spectrum of compound **4a**



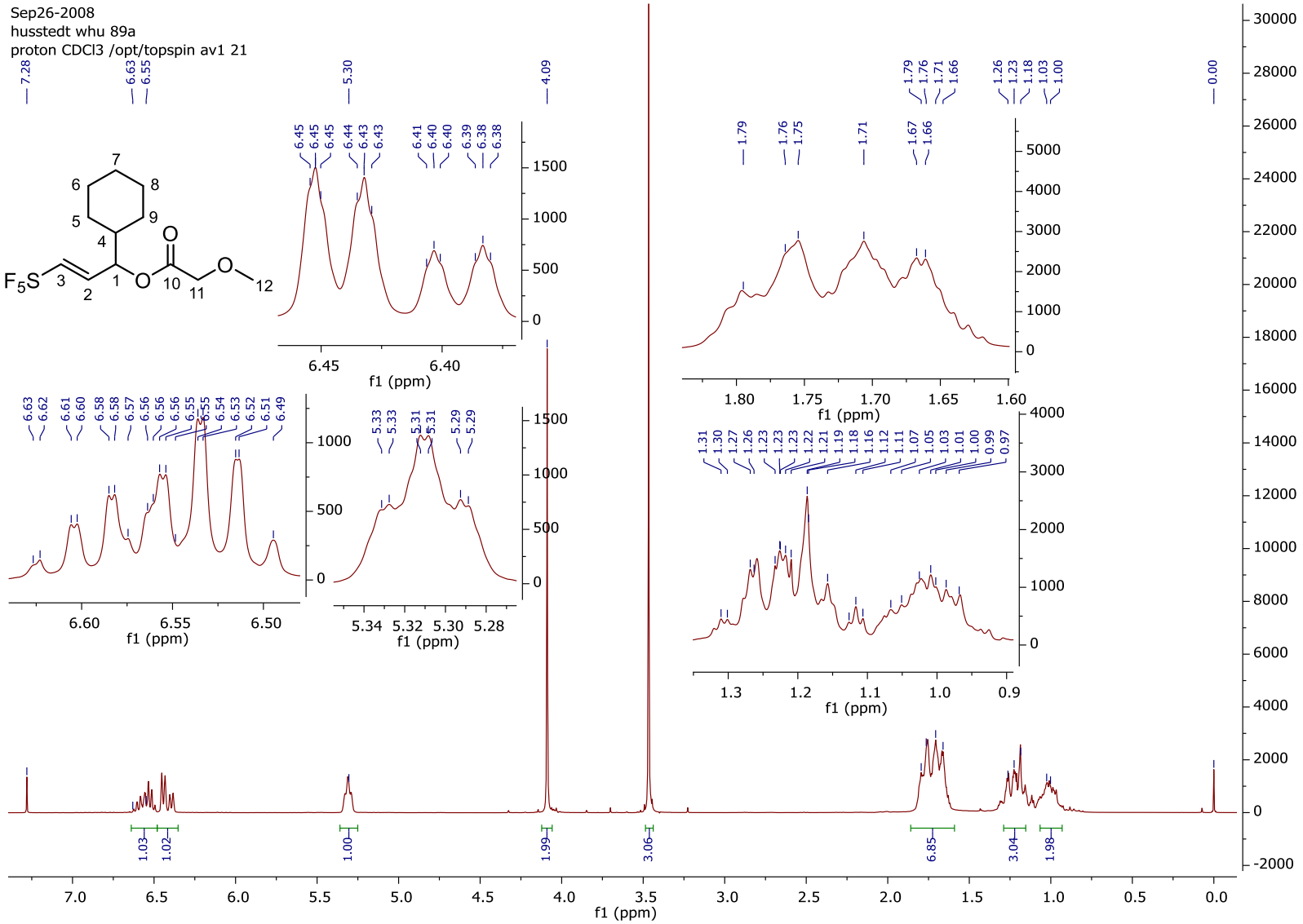
^{1}H NMR spectrum of compound **4b**



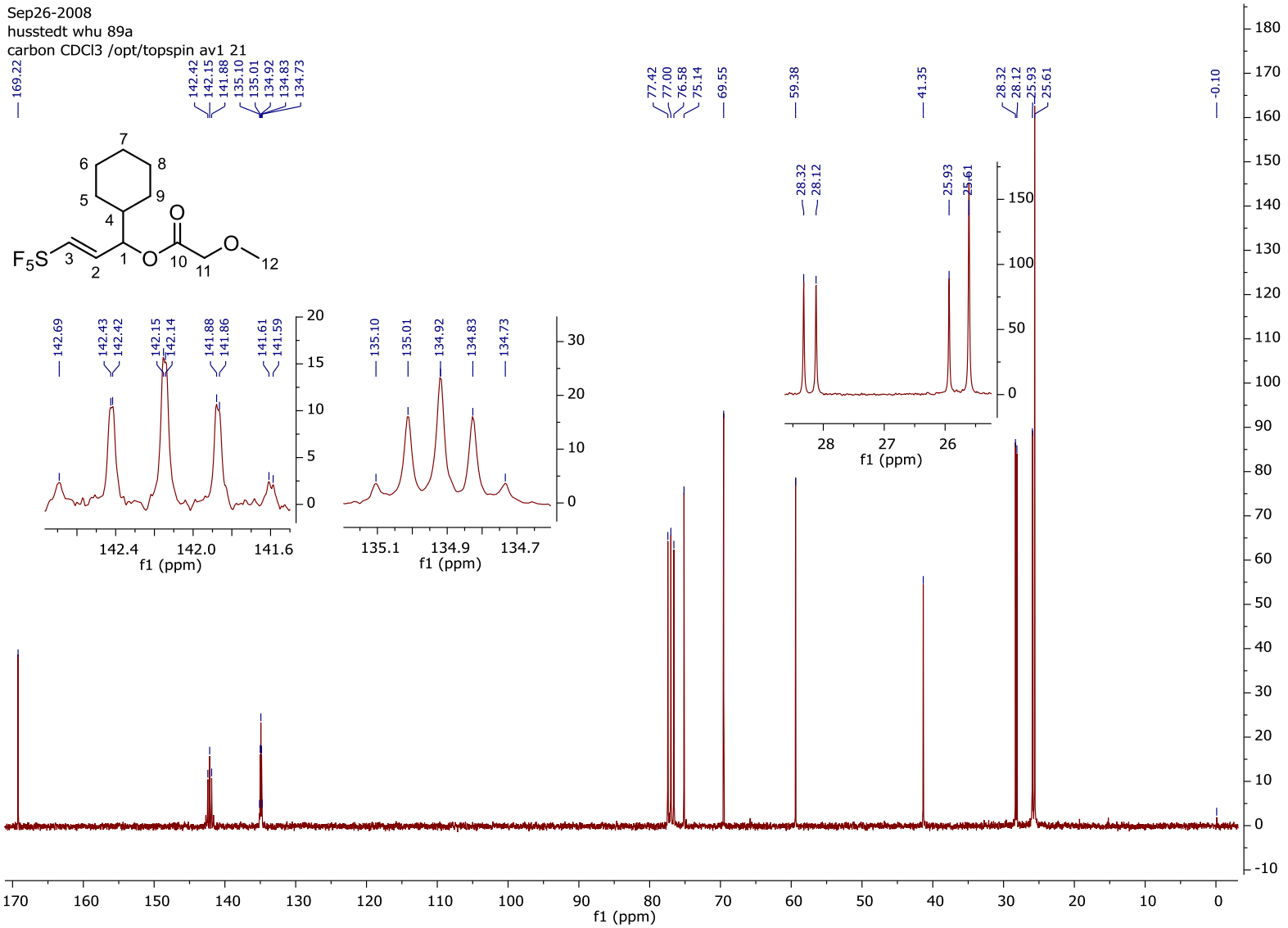
^{13}C NMR spectrum of compound **4b**



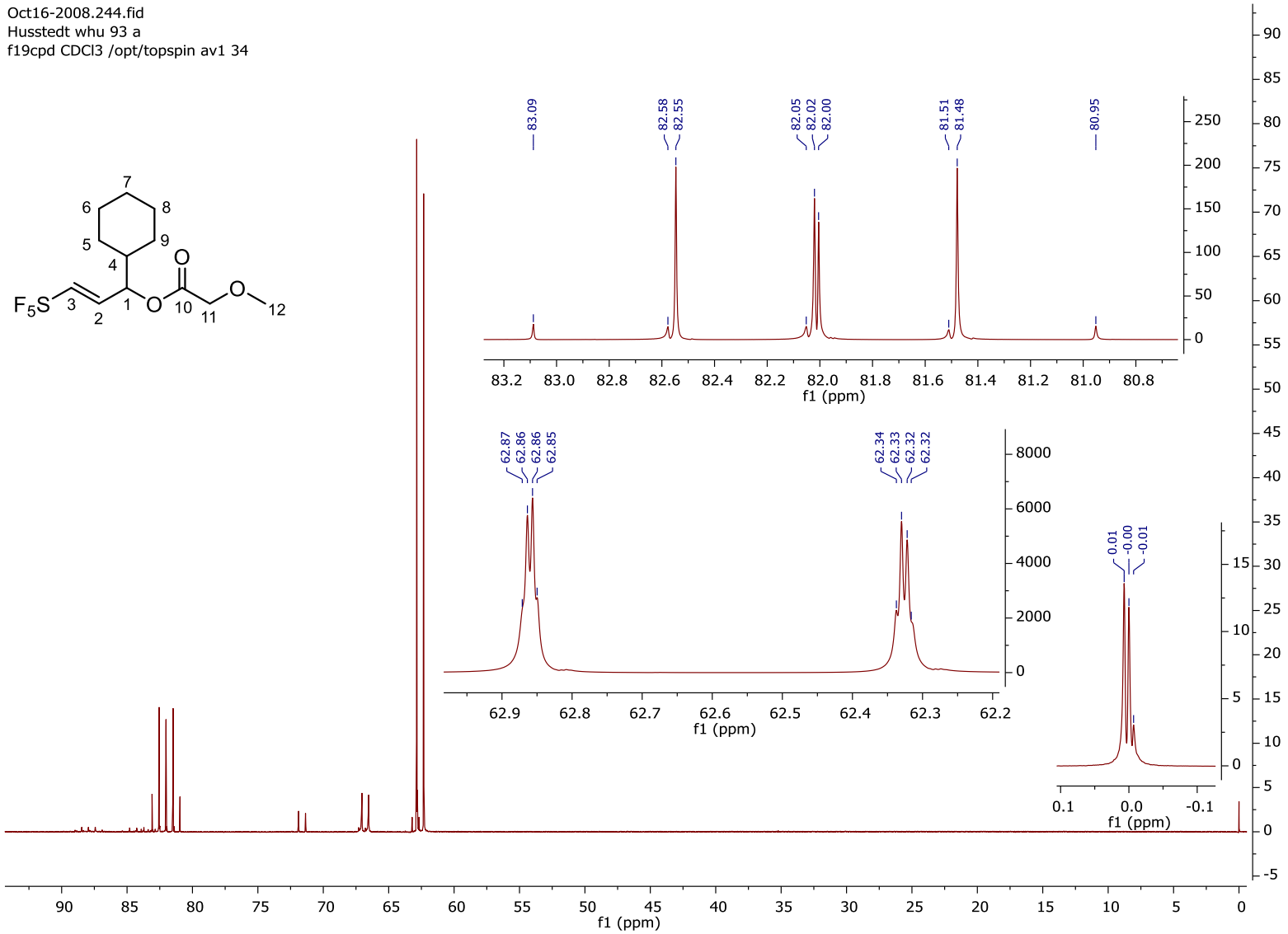
^{1}H NMR spectrum of compound **4c**



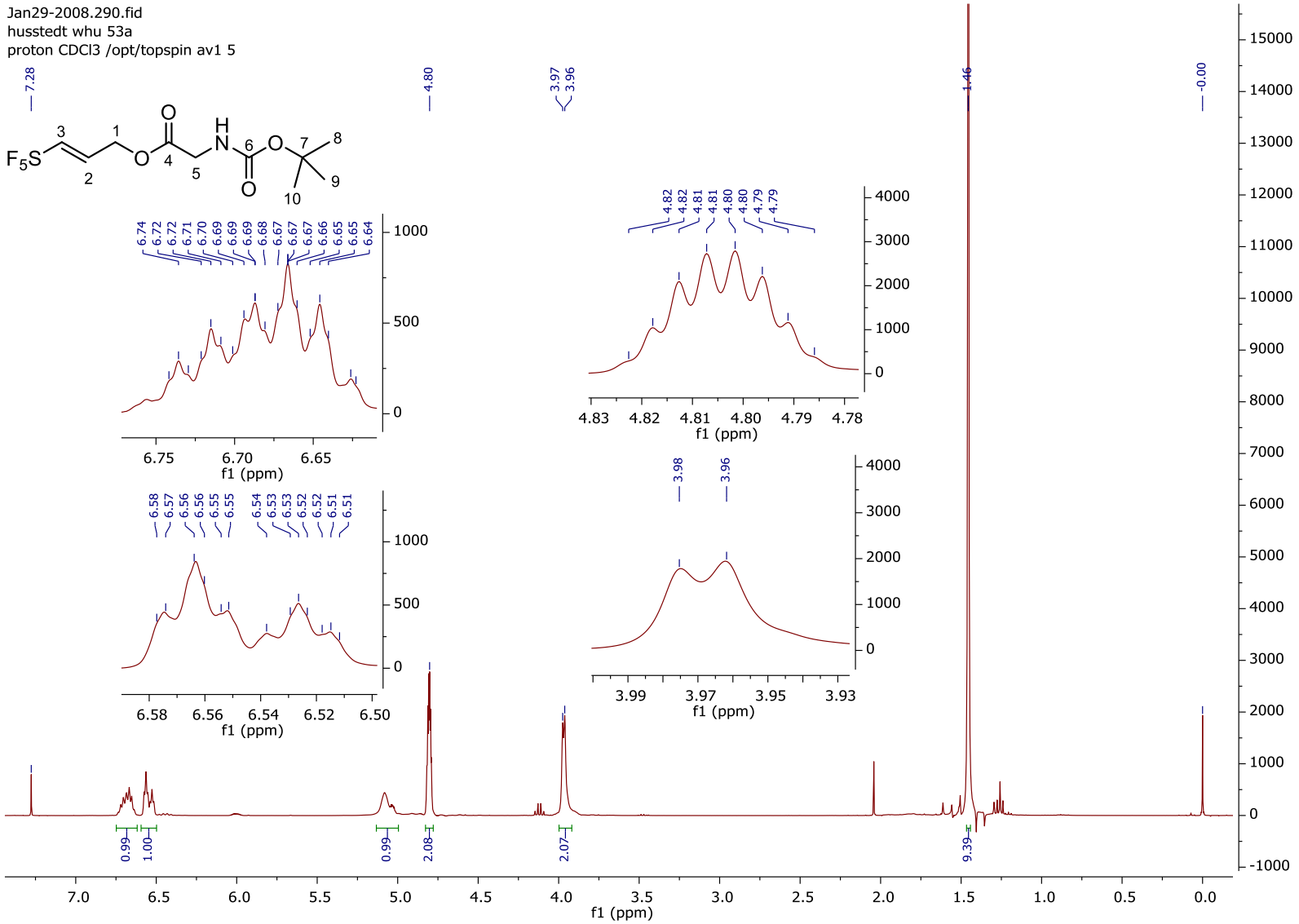
^{13}C NMR spectrum of compound **4c**



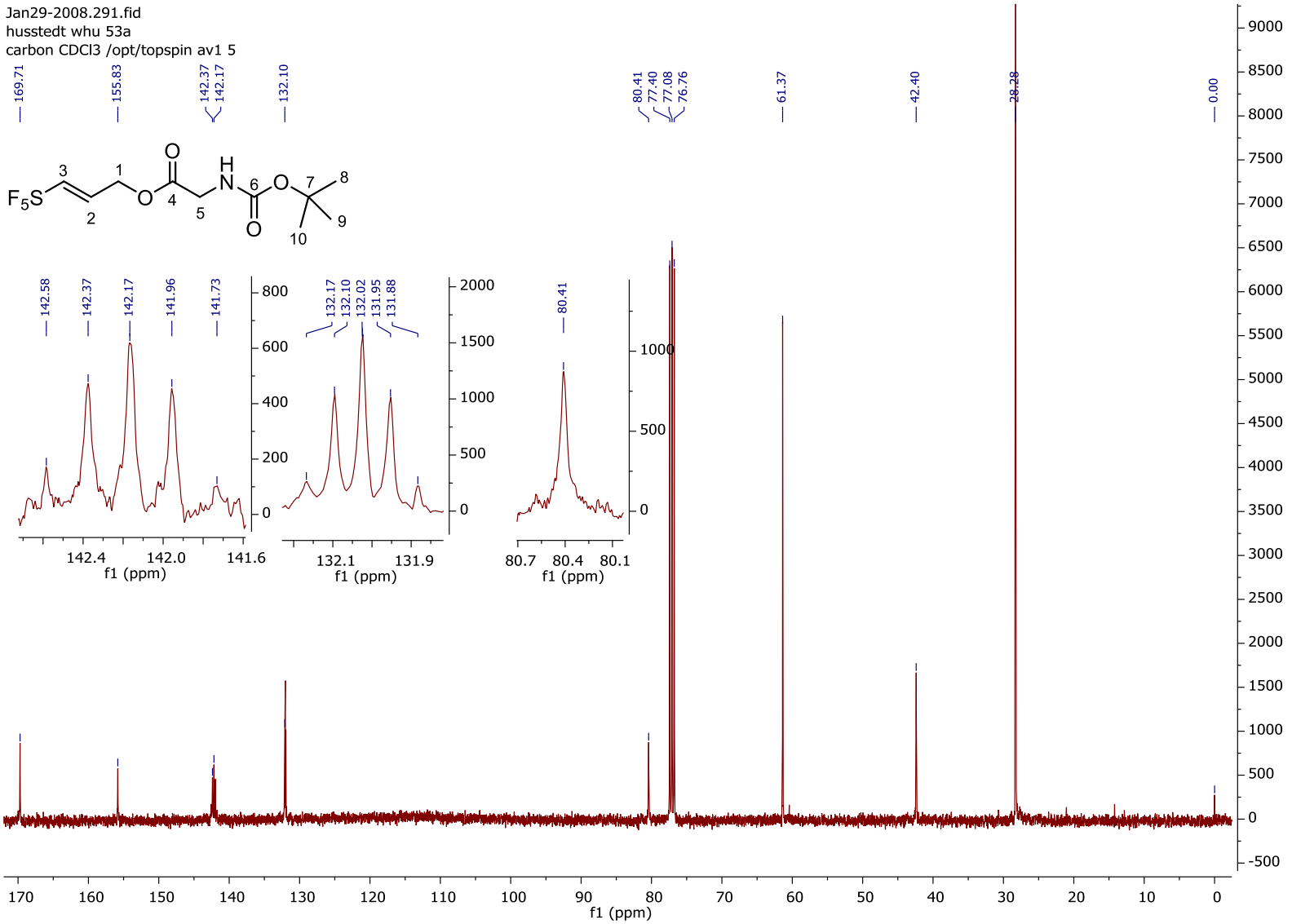
^{19}F NMR spectrum of compound **4c**



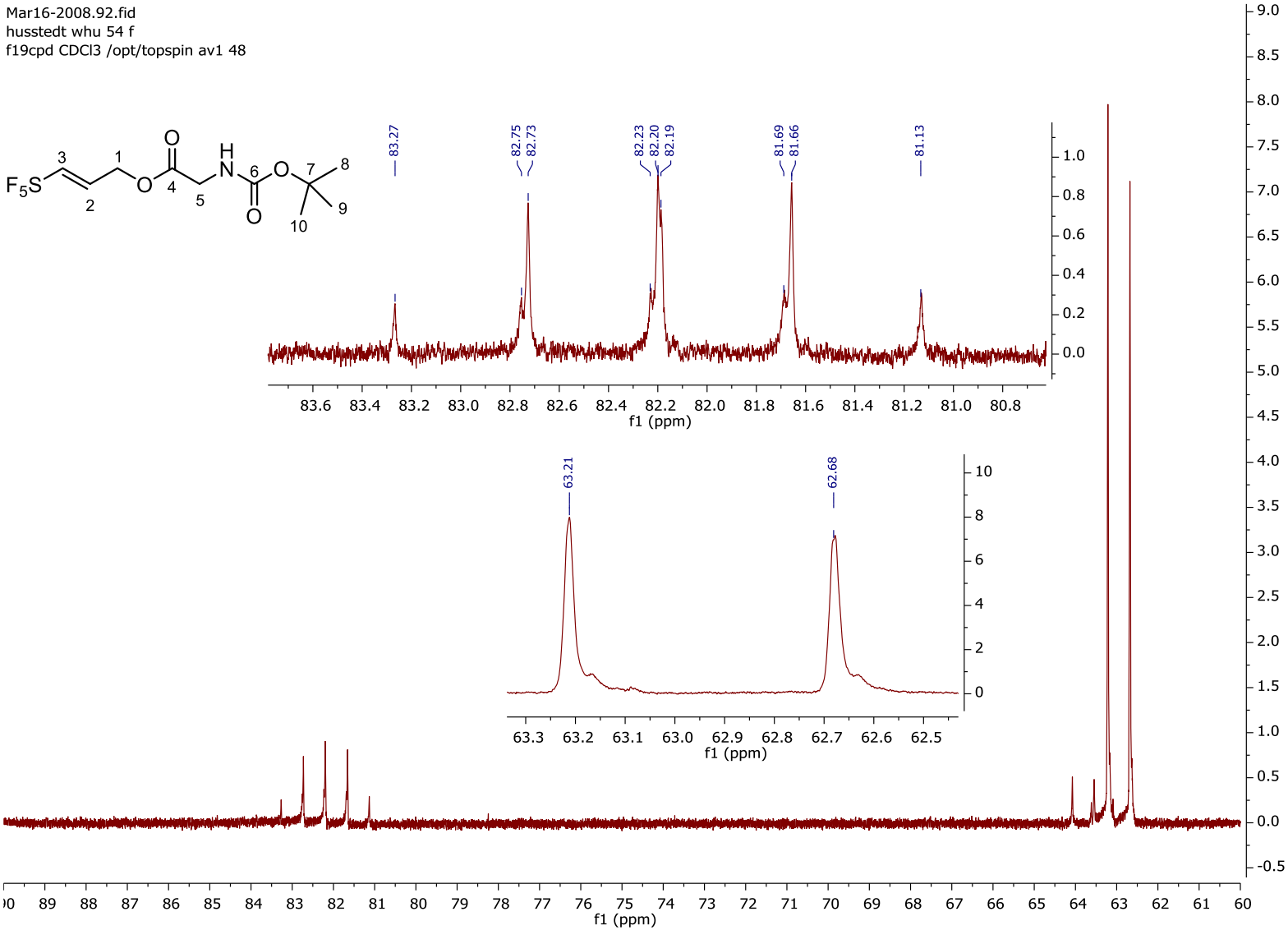
^{1}H NMR spectrum of compound **4d**



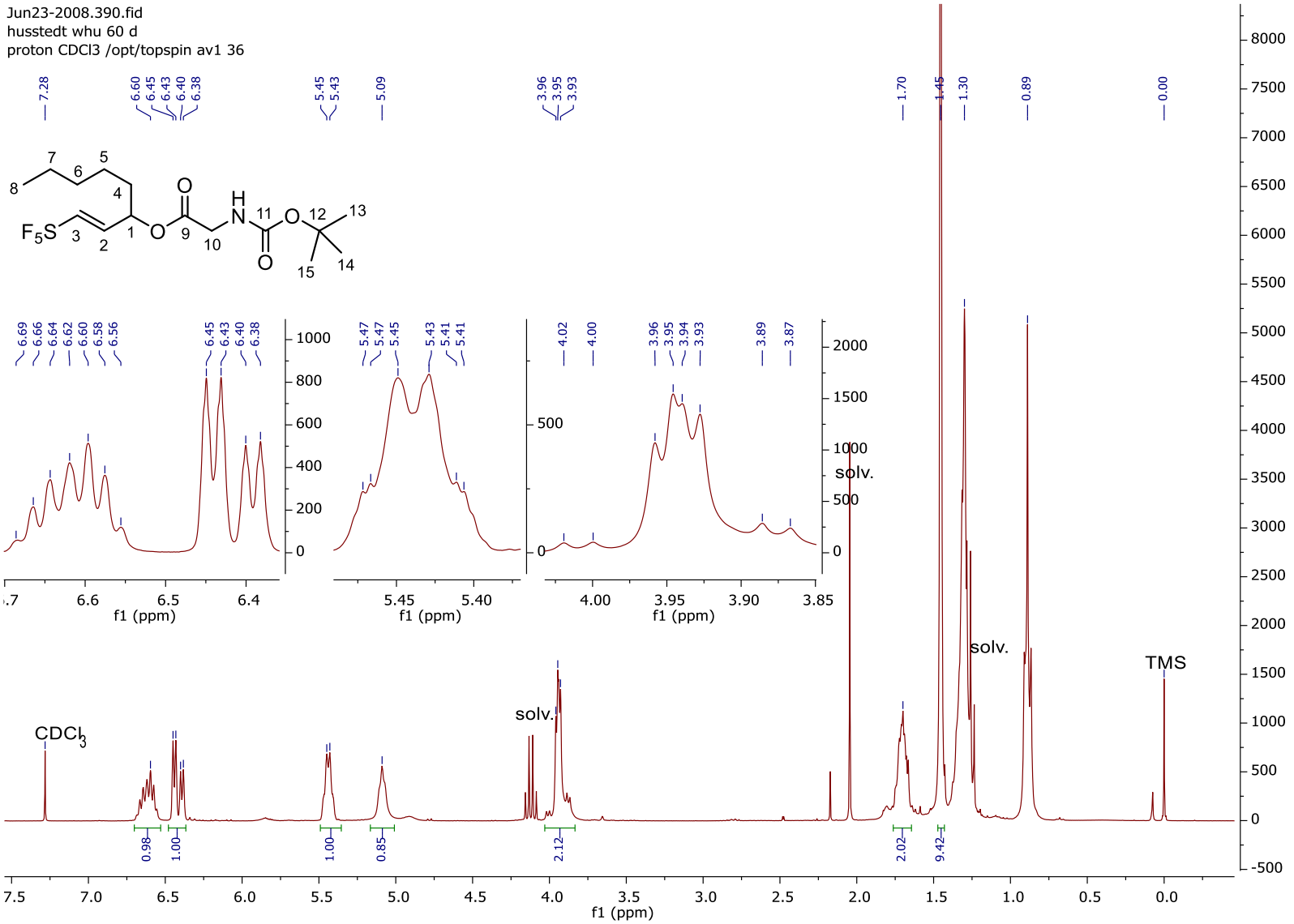
^{13}C NMR spectrum of compound **4d**



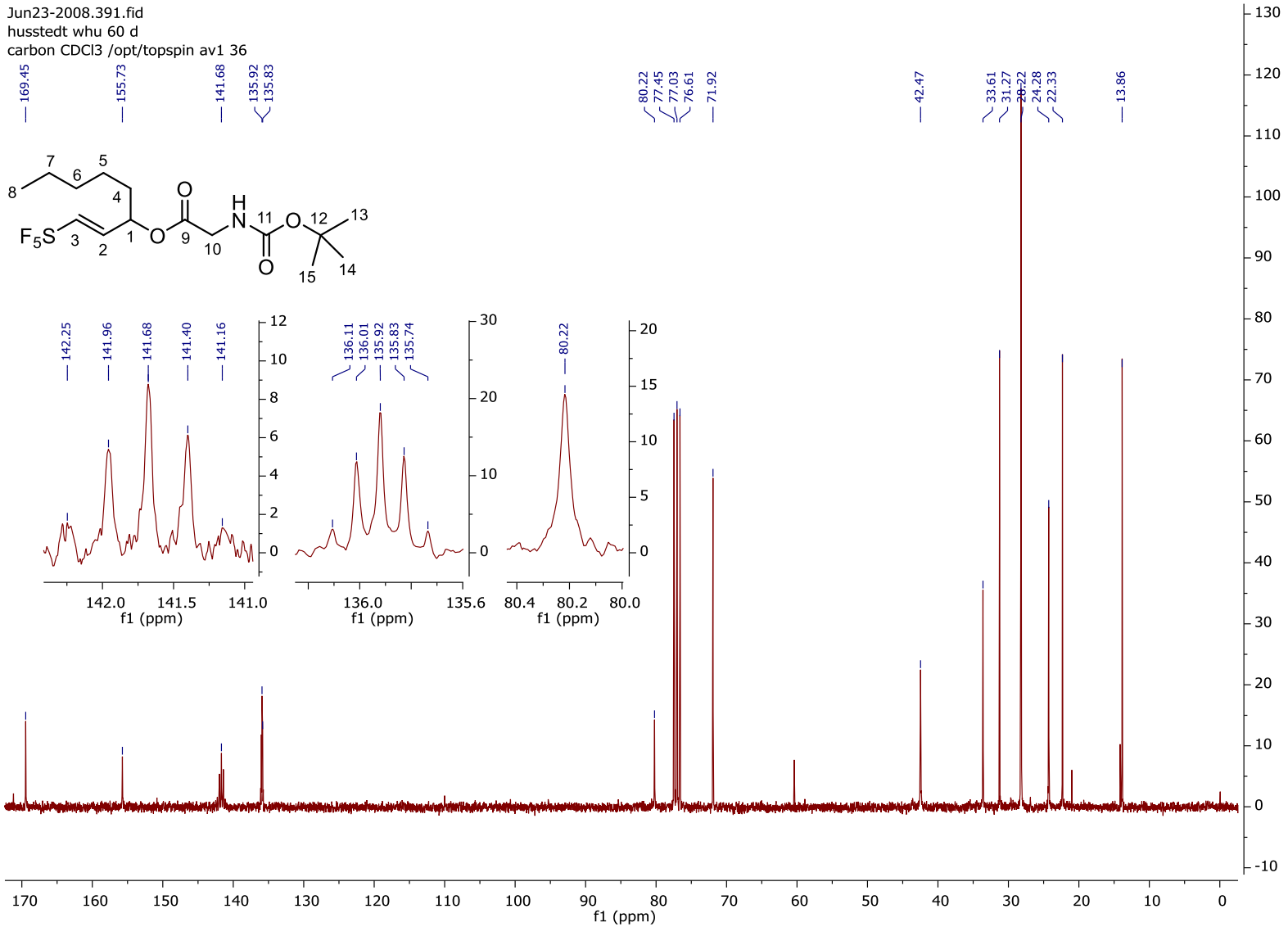
^{19}F NMR spectrum of compound **4d**



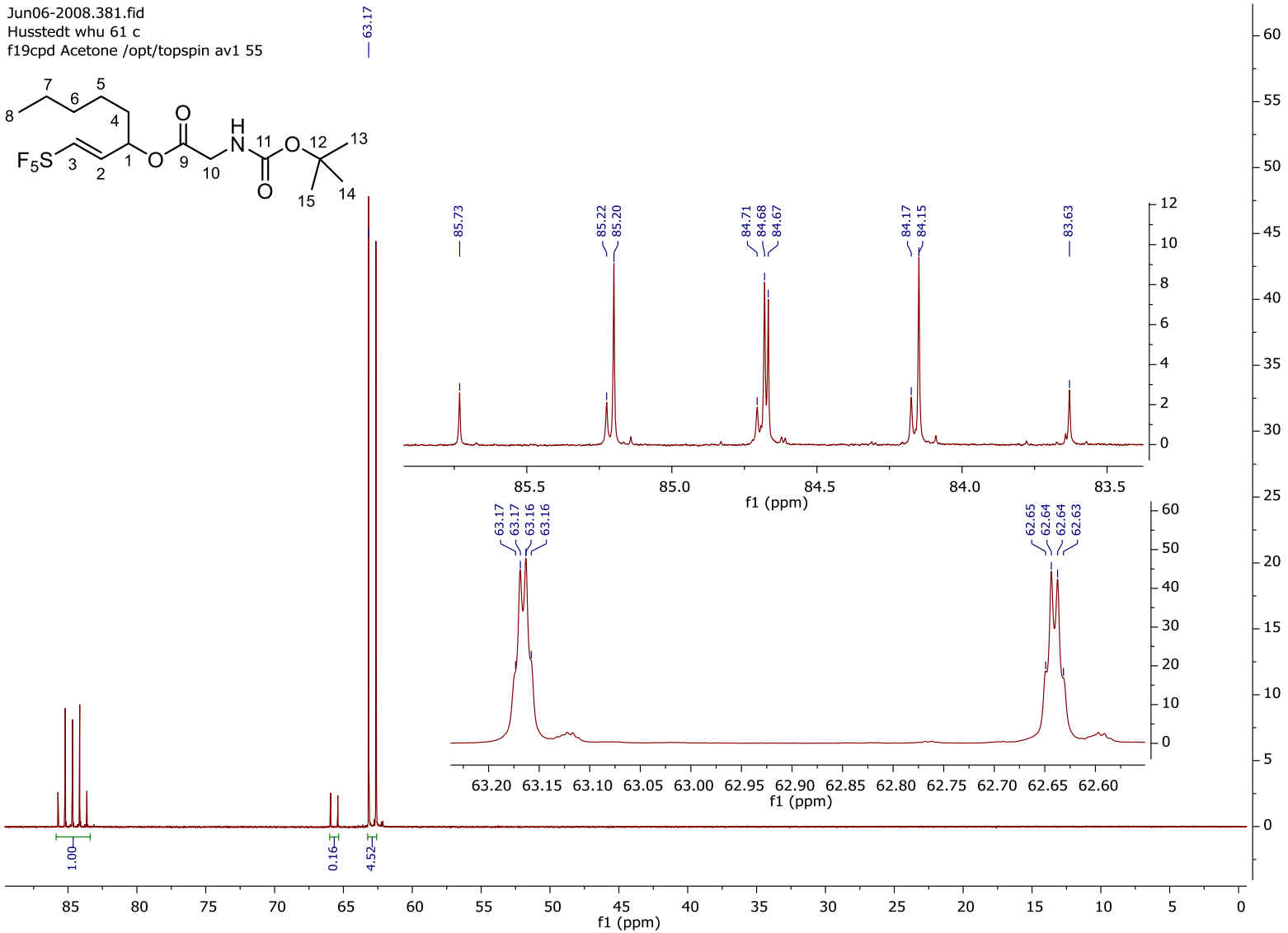
^{1}H NMR spectrum of compound **4e**



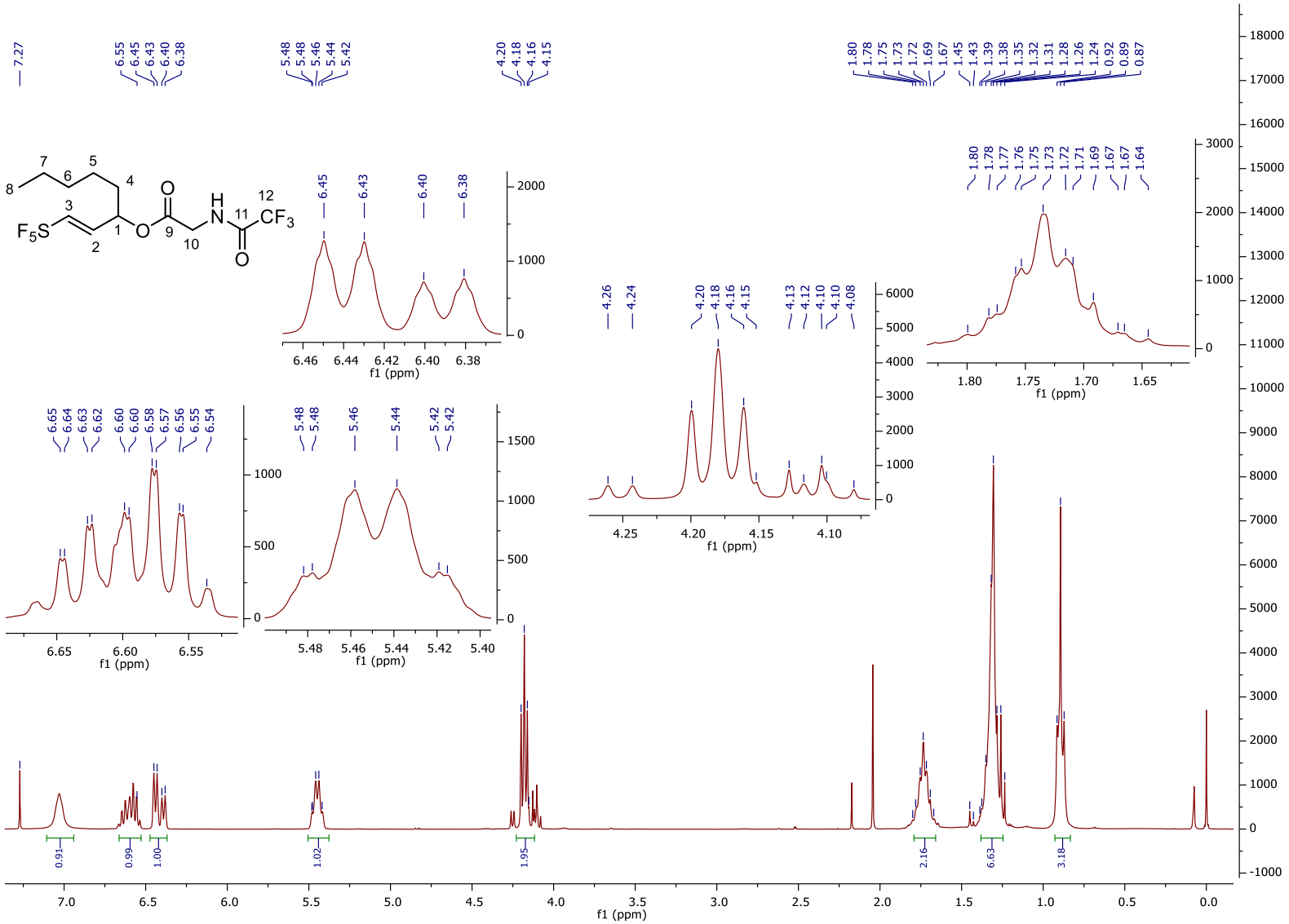
^{13}C NMR spectrum of compound **4e**



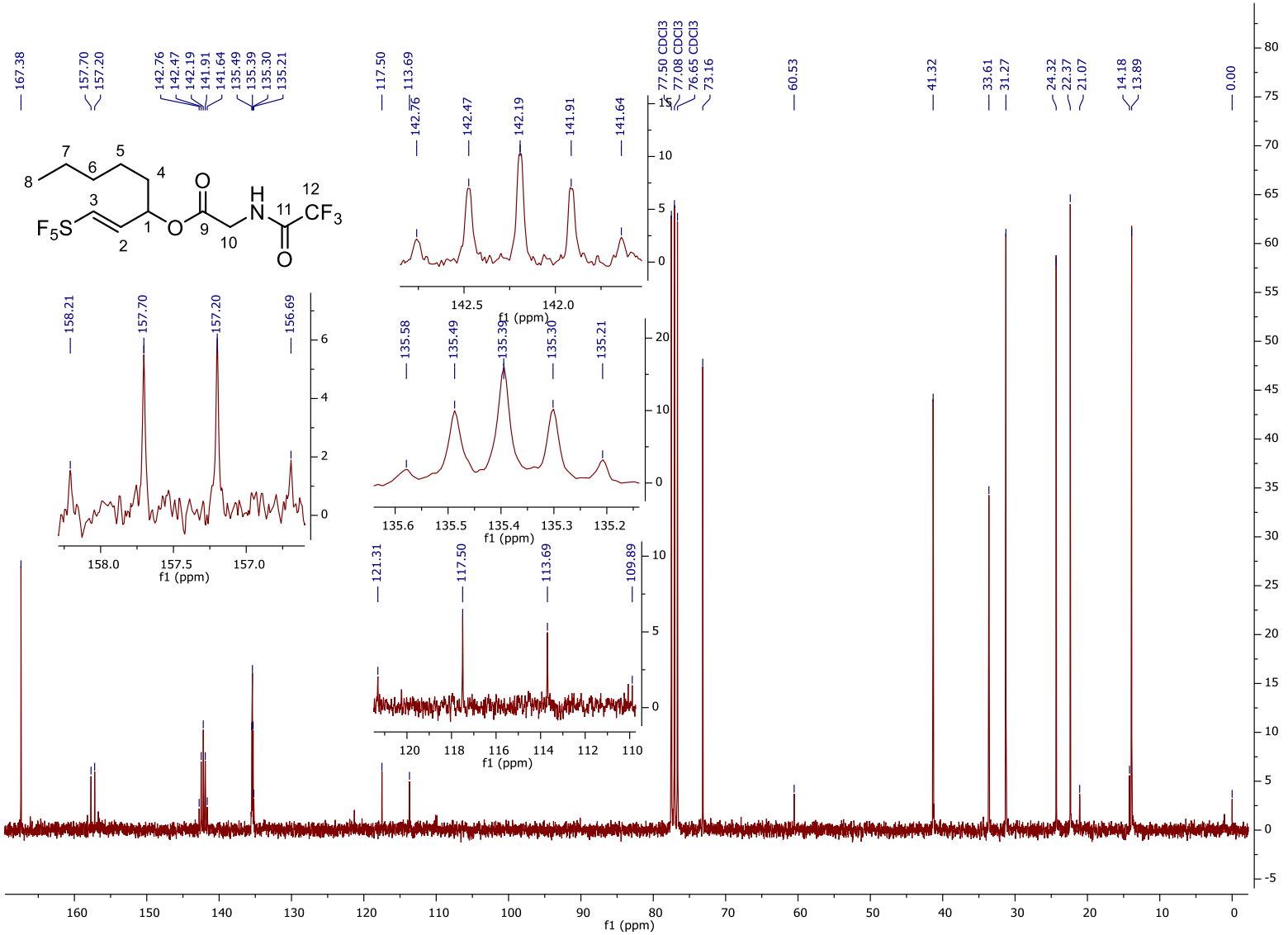
^{19}F NMR spectrum of compound **4e**



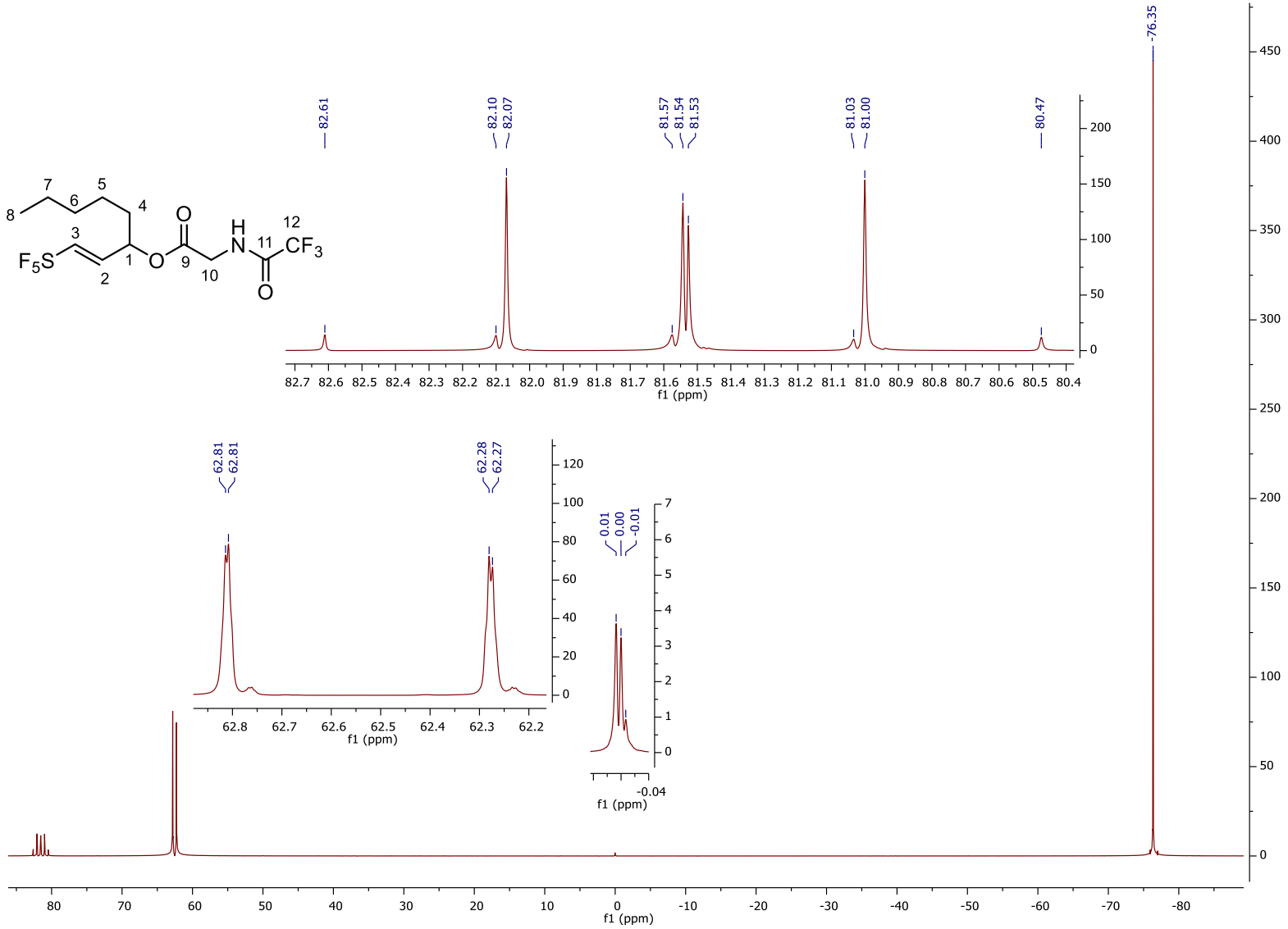
^{1}H NMR spectrum of compound **4f**



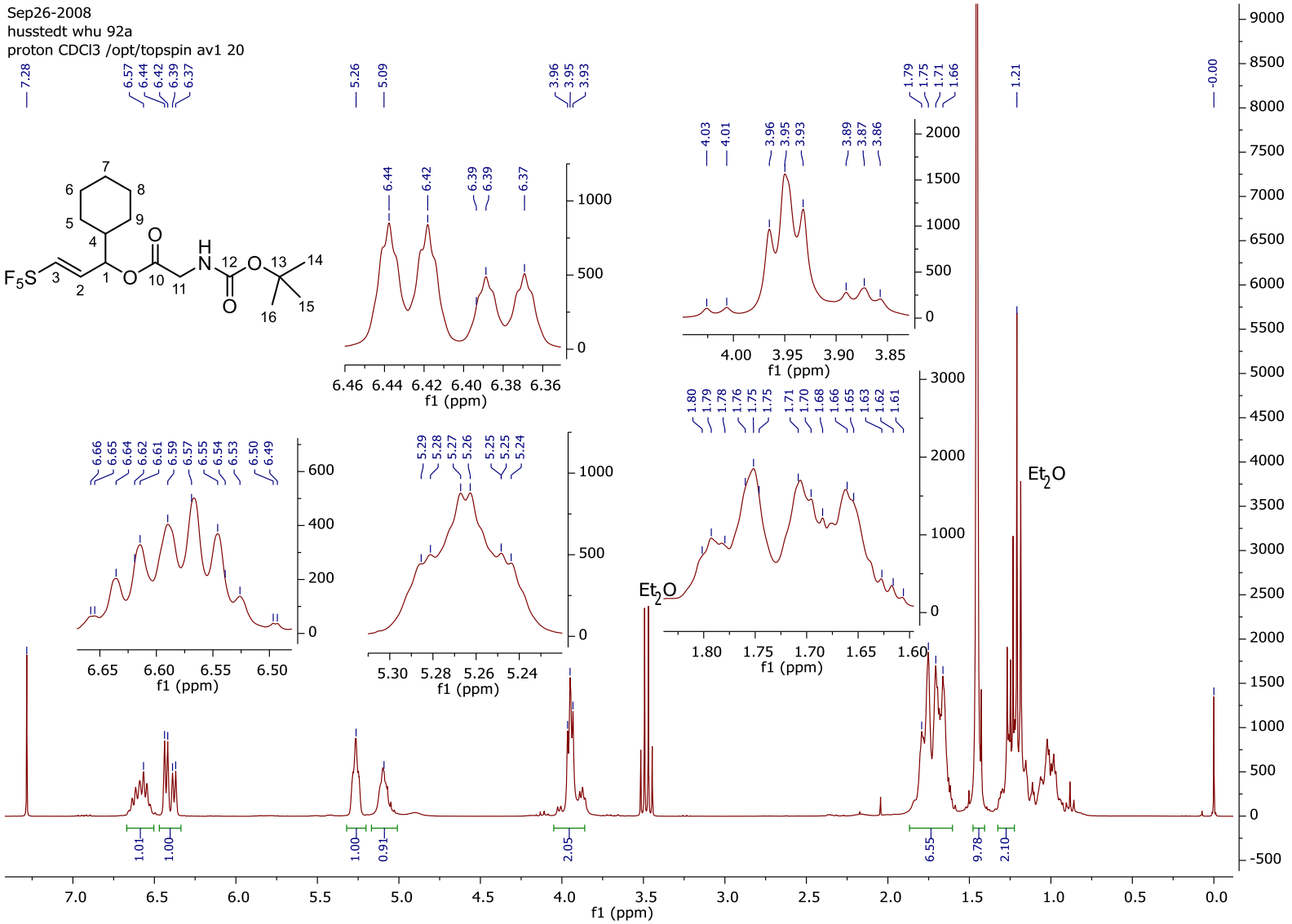
^{13}C NMR spectrum of compound **4f**



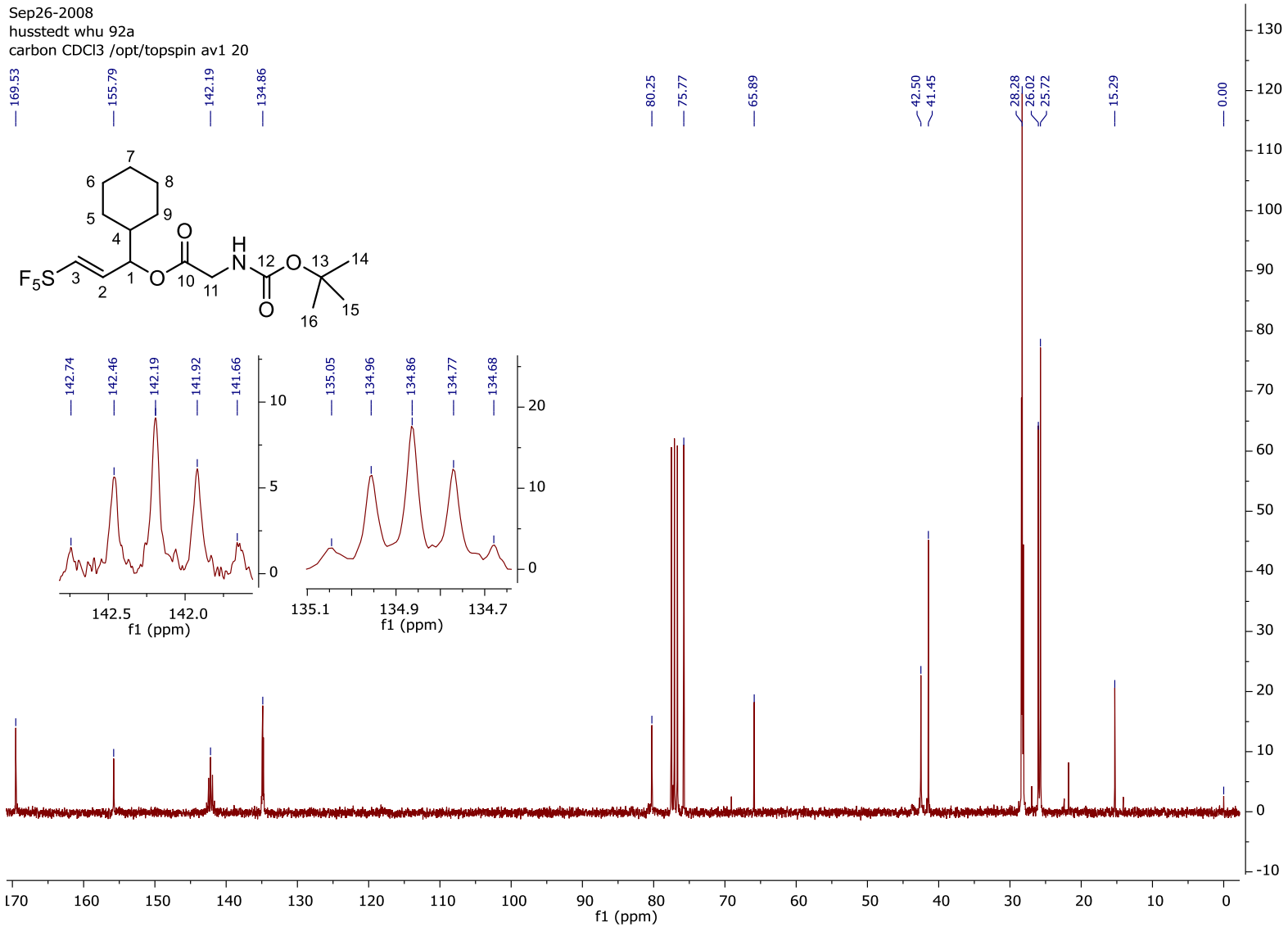
^{19}F NMR spectrum of compound **4f**



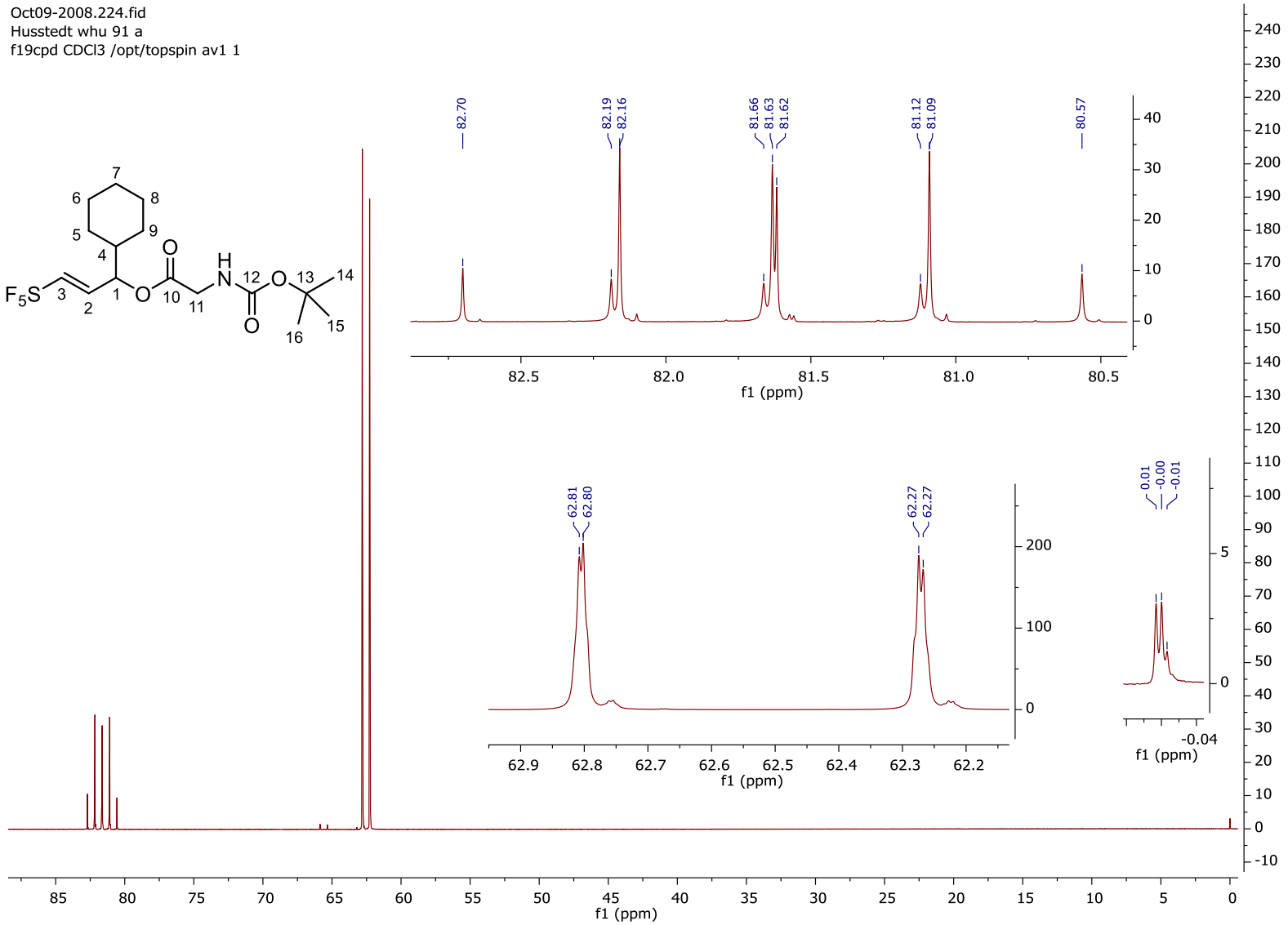
^{1}H NMR spectrum of compound **4g**



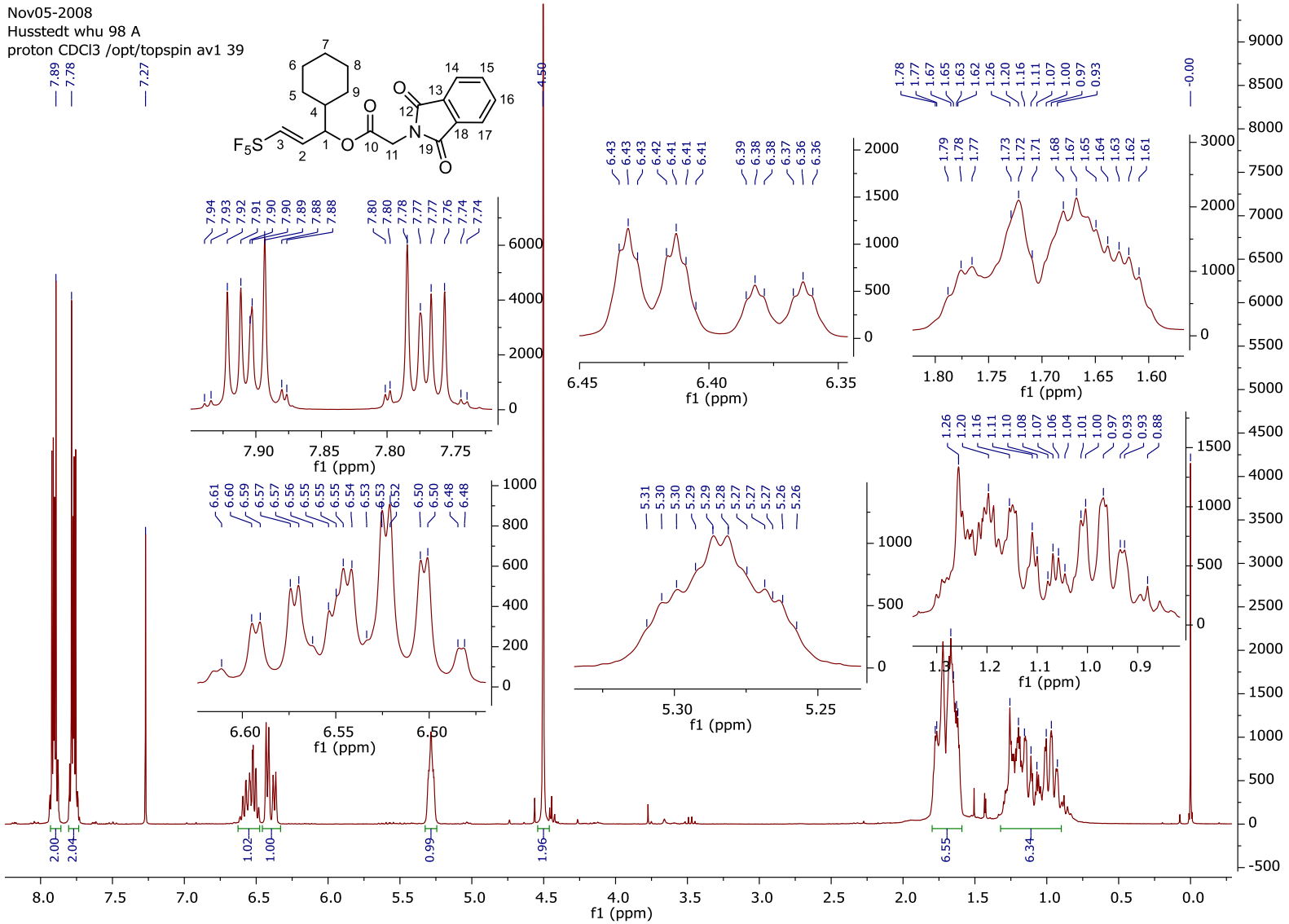
^{13}C NMR spectrum of compound **4g**



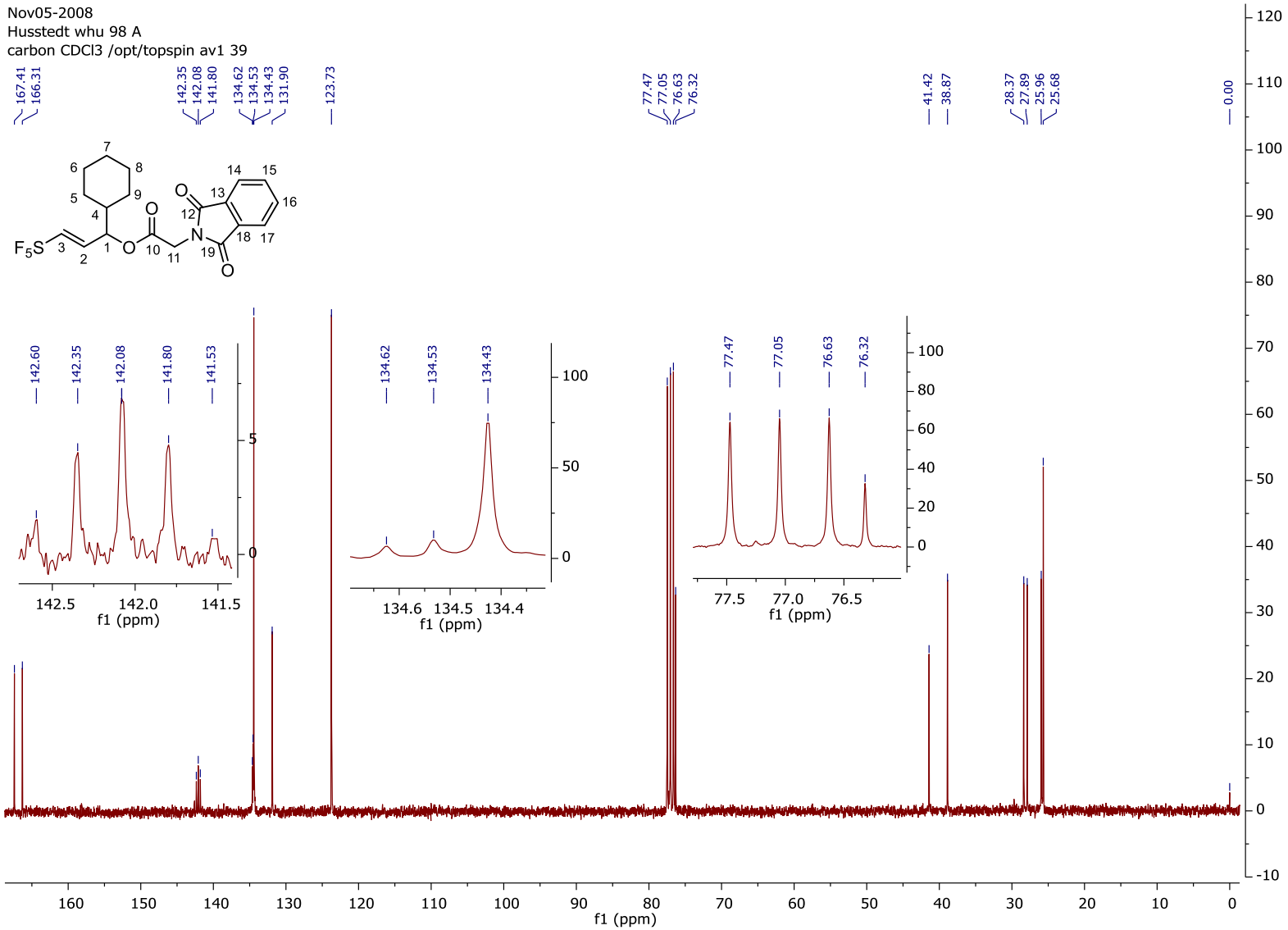
^{19}F NMR spectrum of compound **4g**



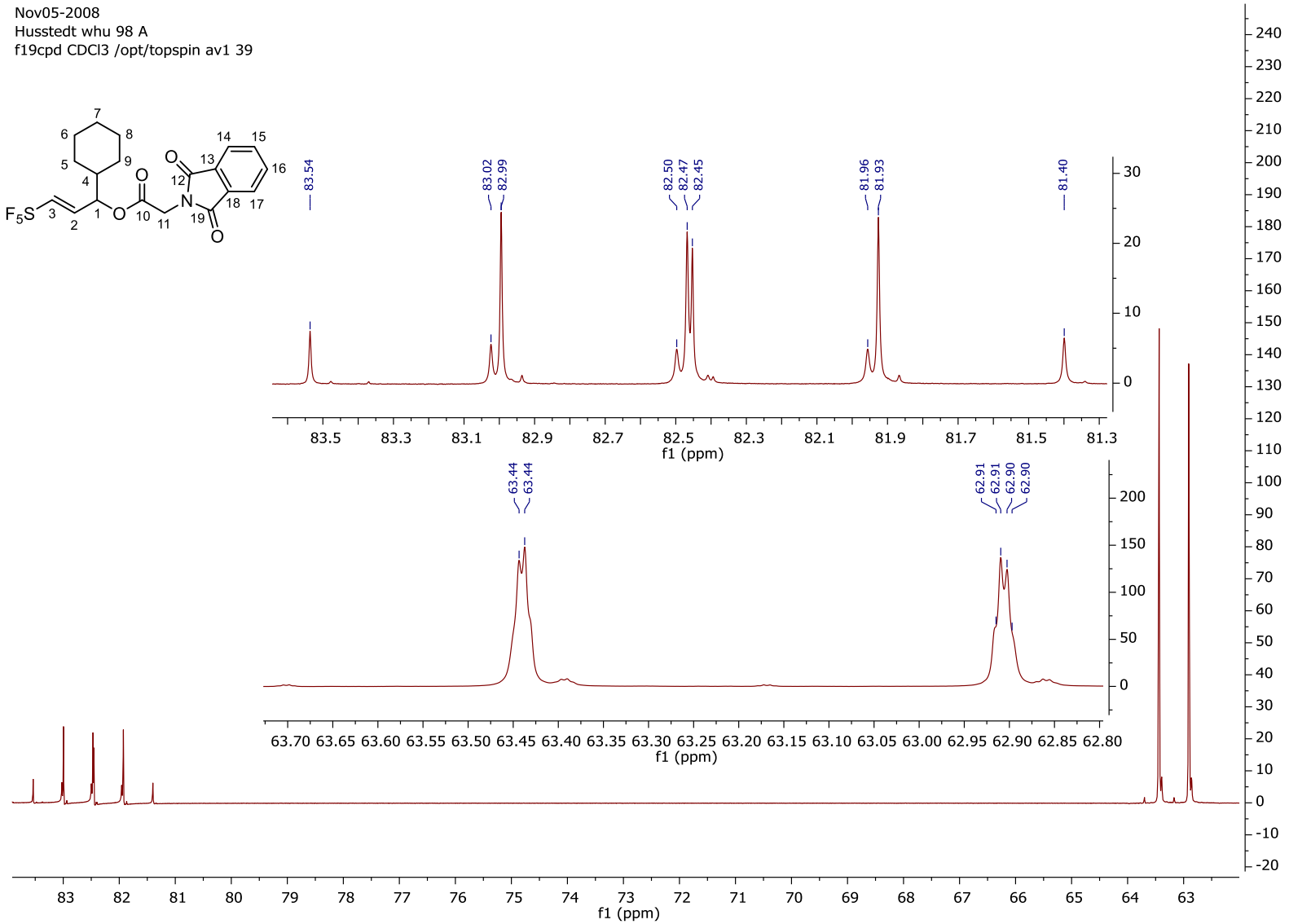
^{1}H NMR spectrum of compound **4h**



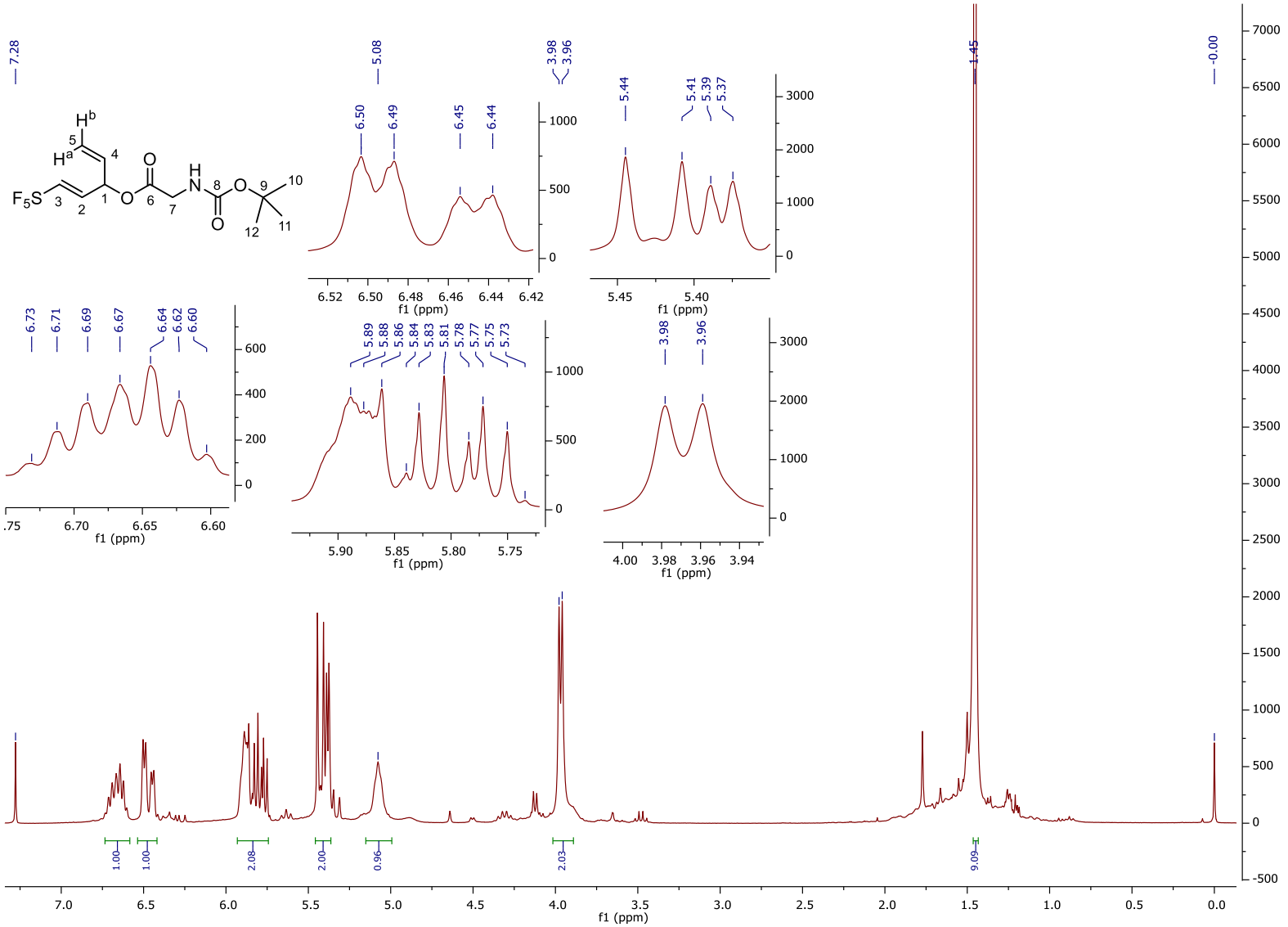
^{13}C NMR spectrum of compound **4h**



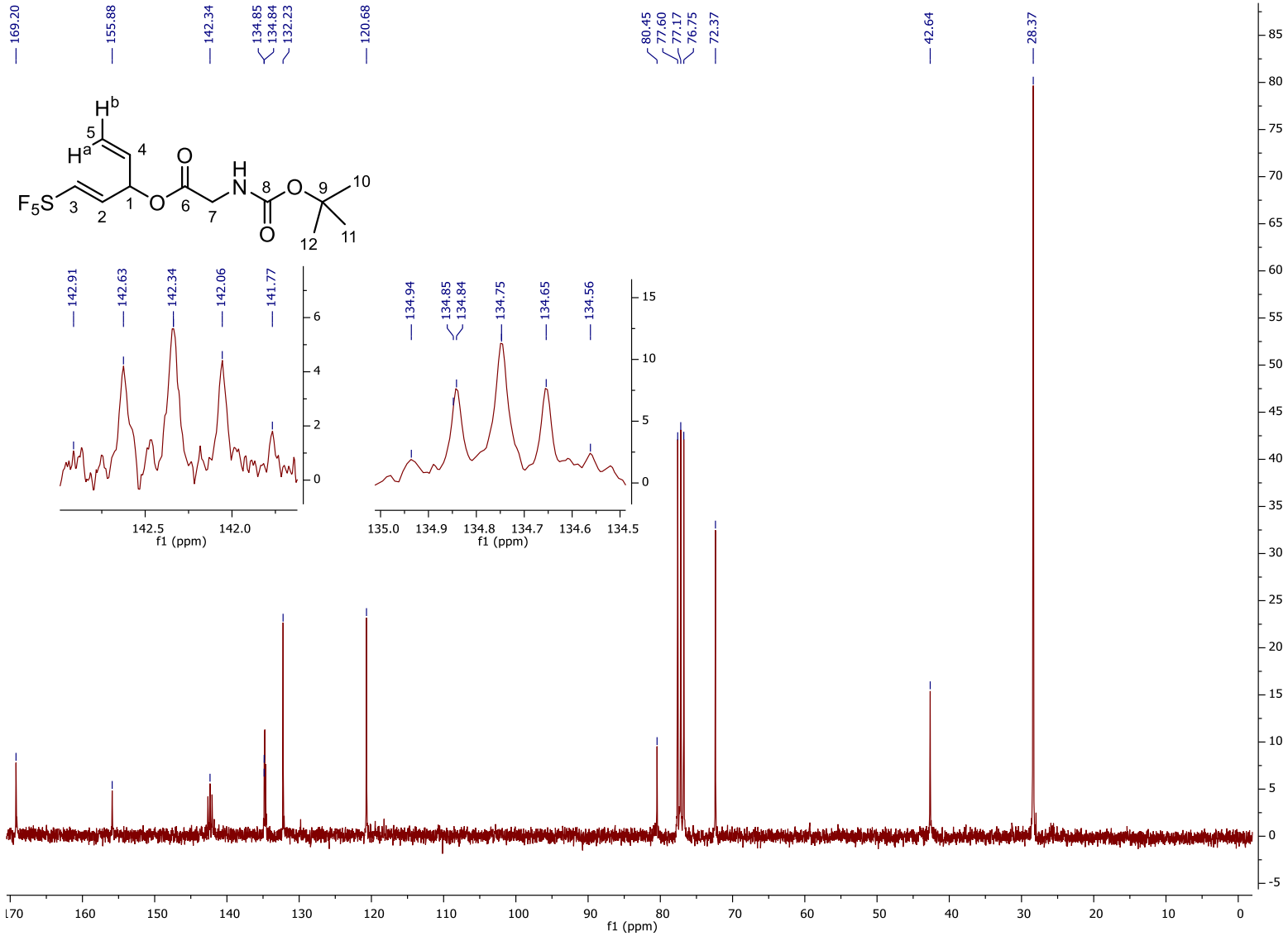
^{19}F NMR spectrum of compound **4h**



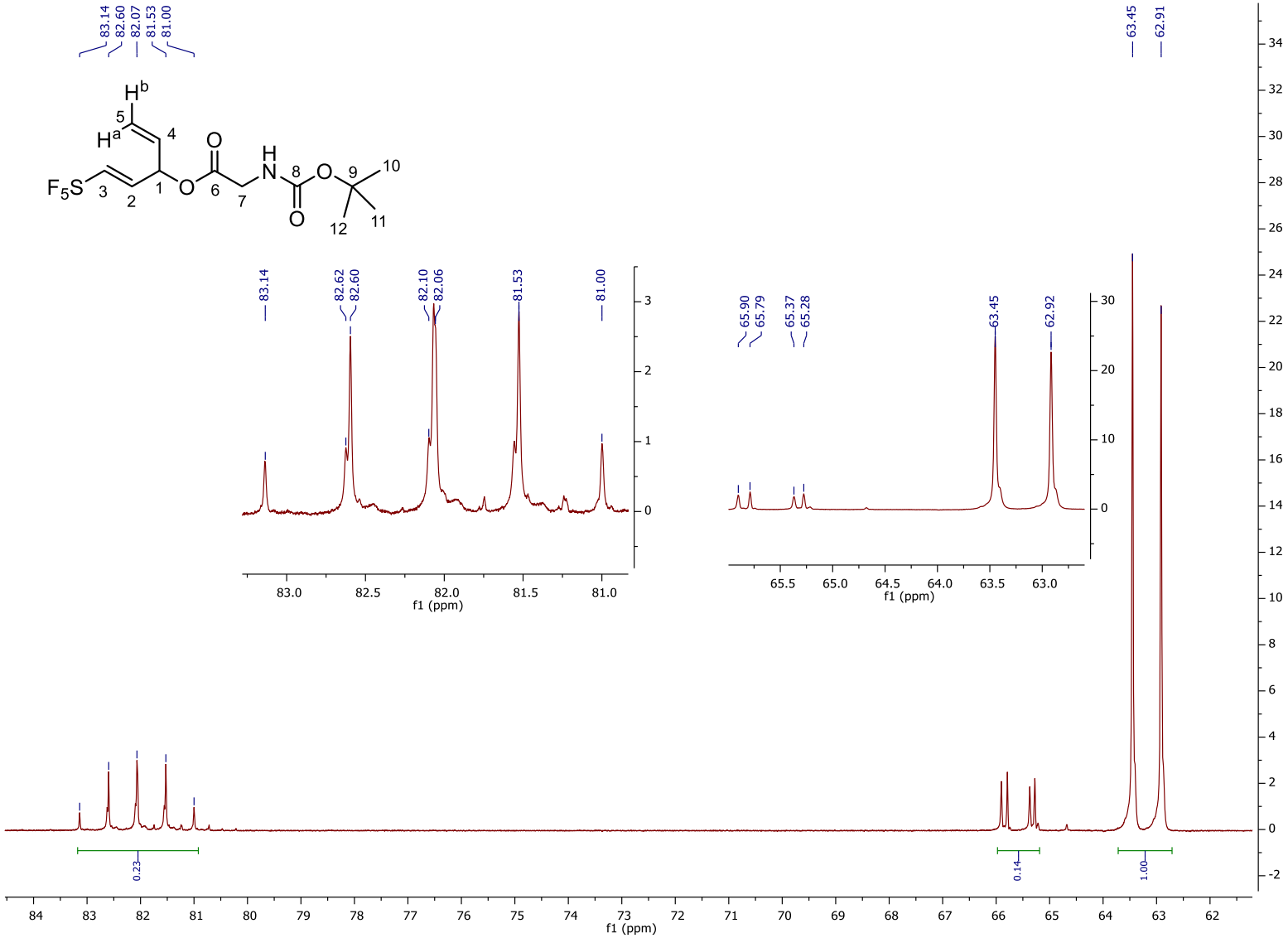
^{1}H NMR spectrum of compound **4i**



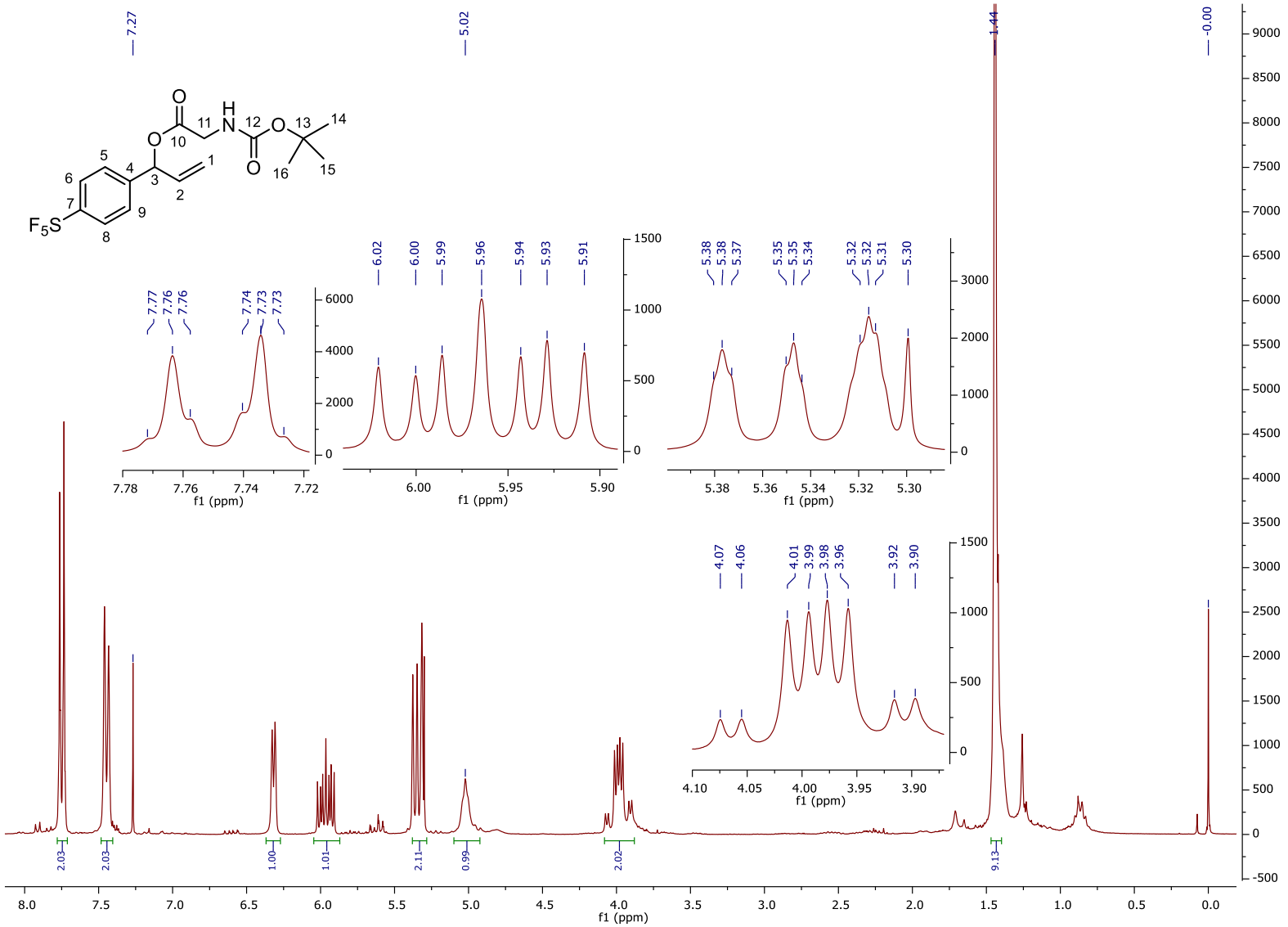
^{13}C NMR spectrum of compound **4i**



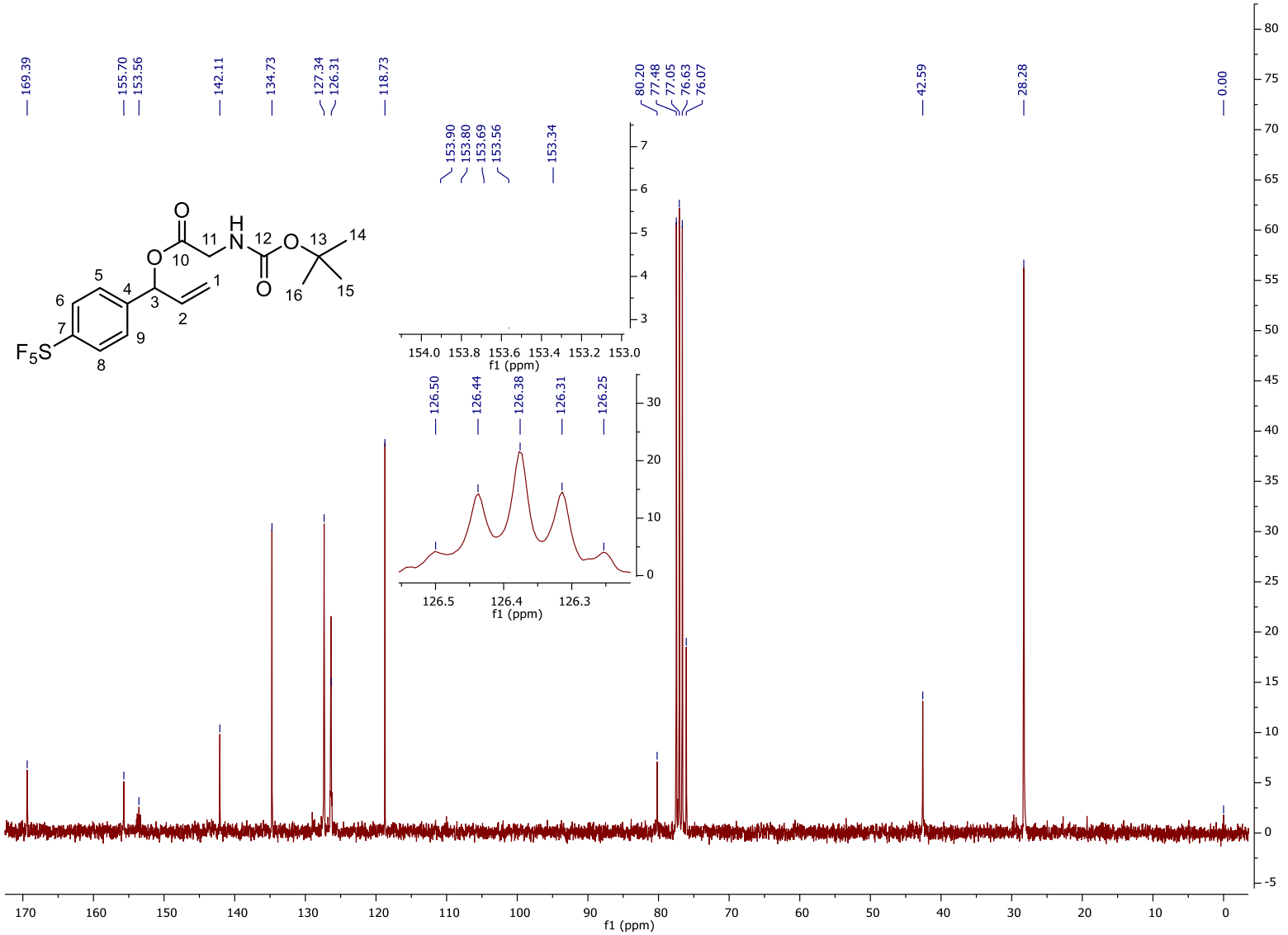
^{19}F NMR spectrum of compound **4i**



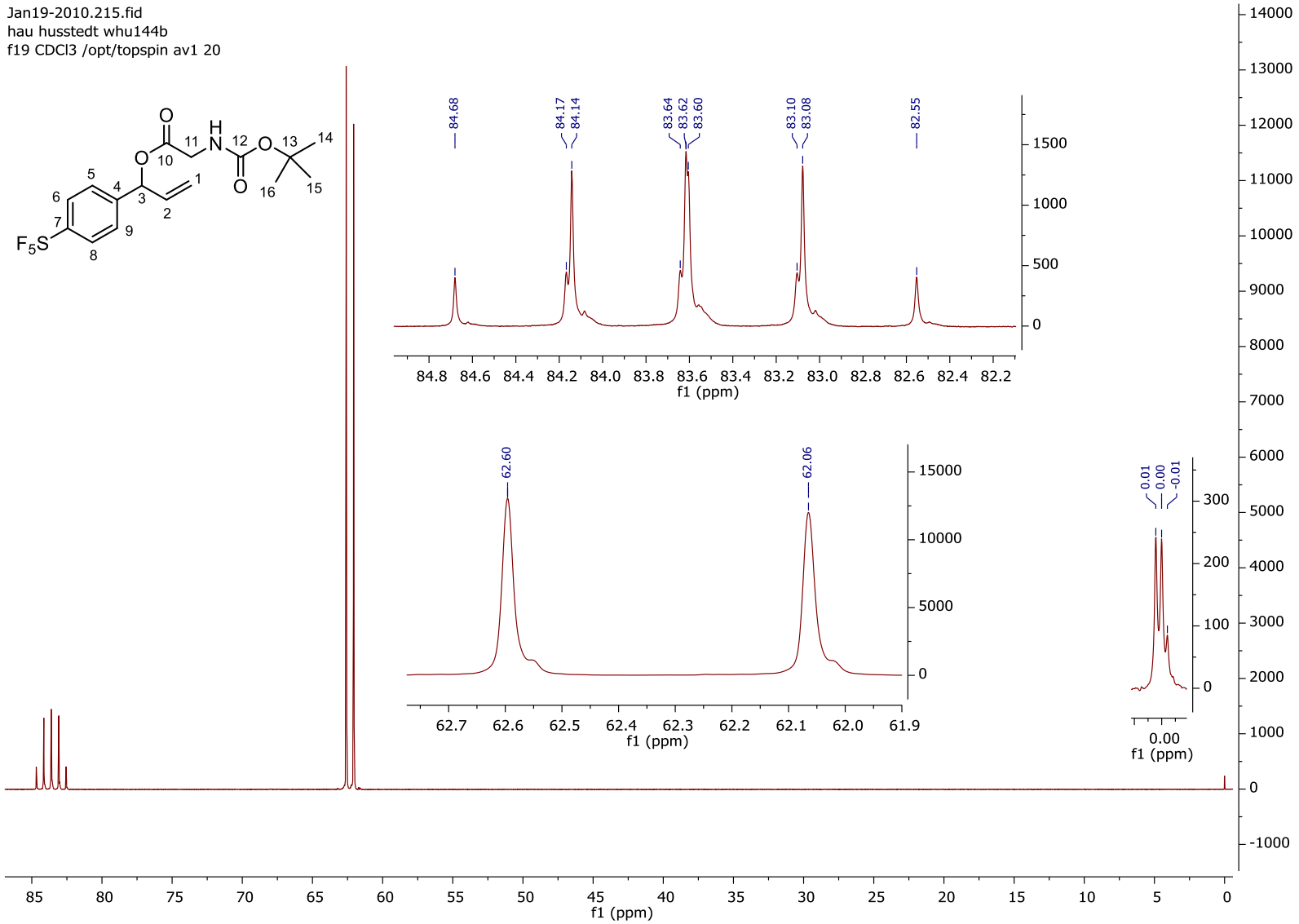
^{1}H NMR spectrum of compound **6**



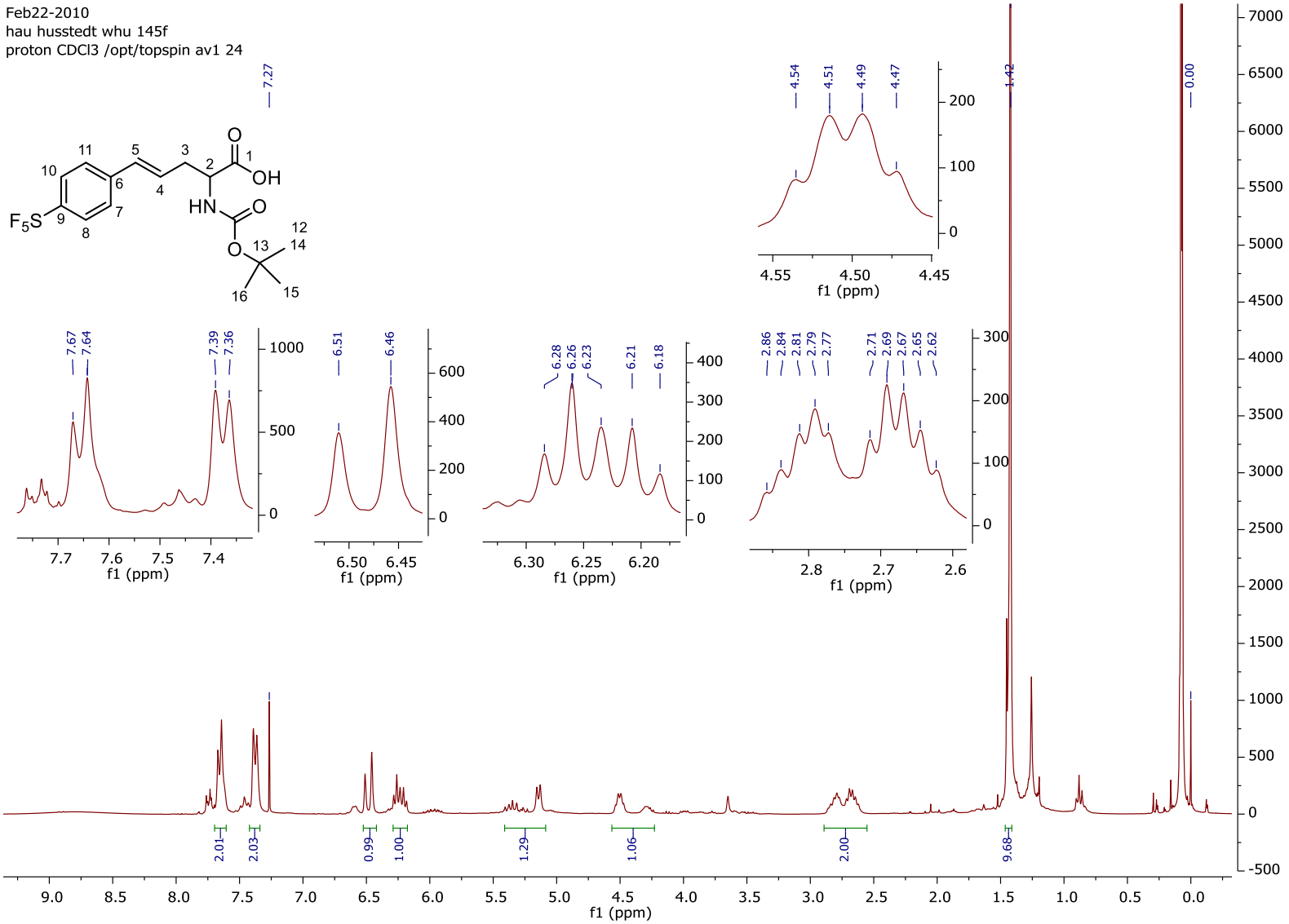
^{13}C NMR spectrum of compound **6**



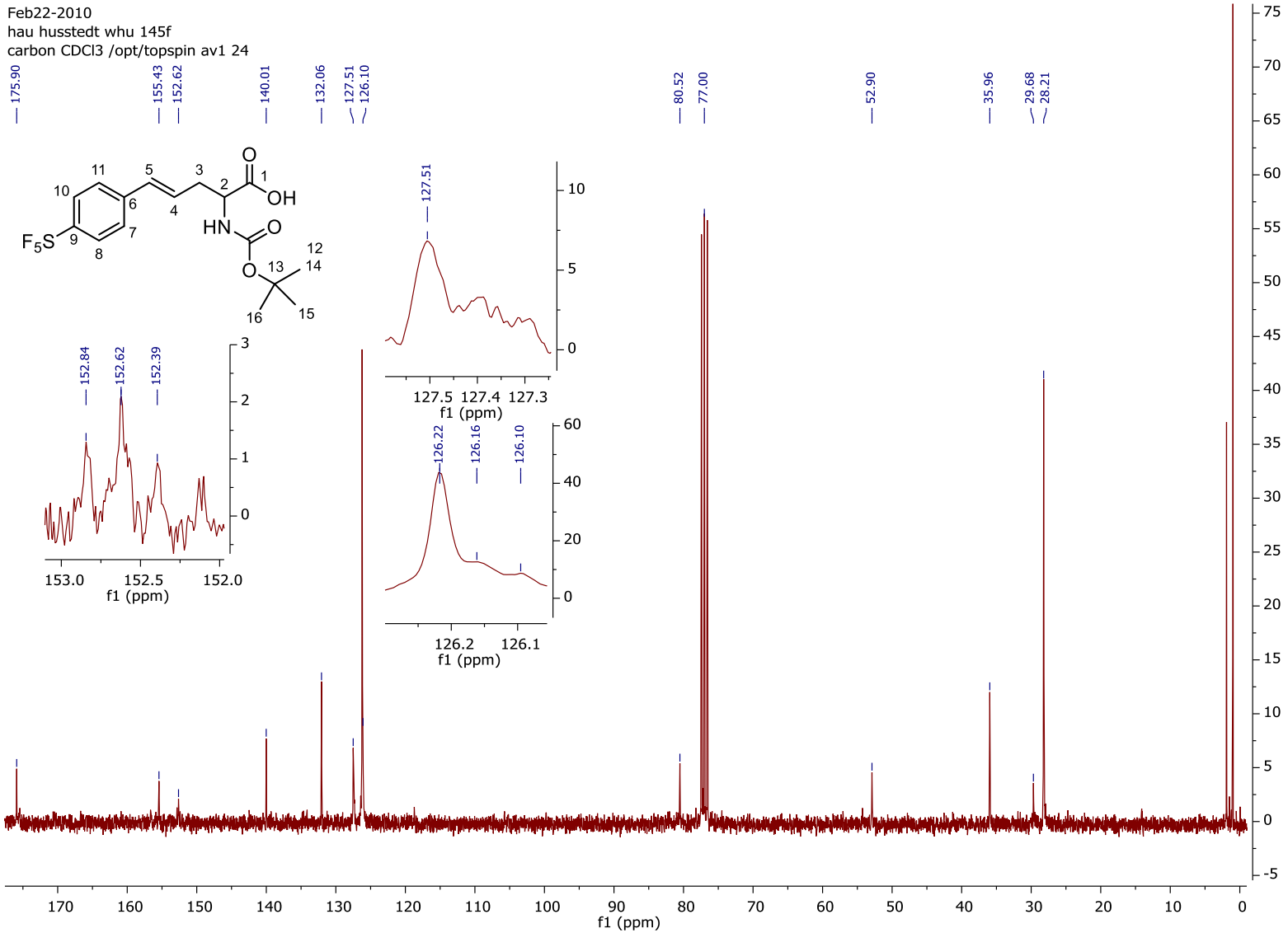
^{19}F NMR spectrum of compound **6**



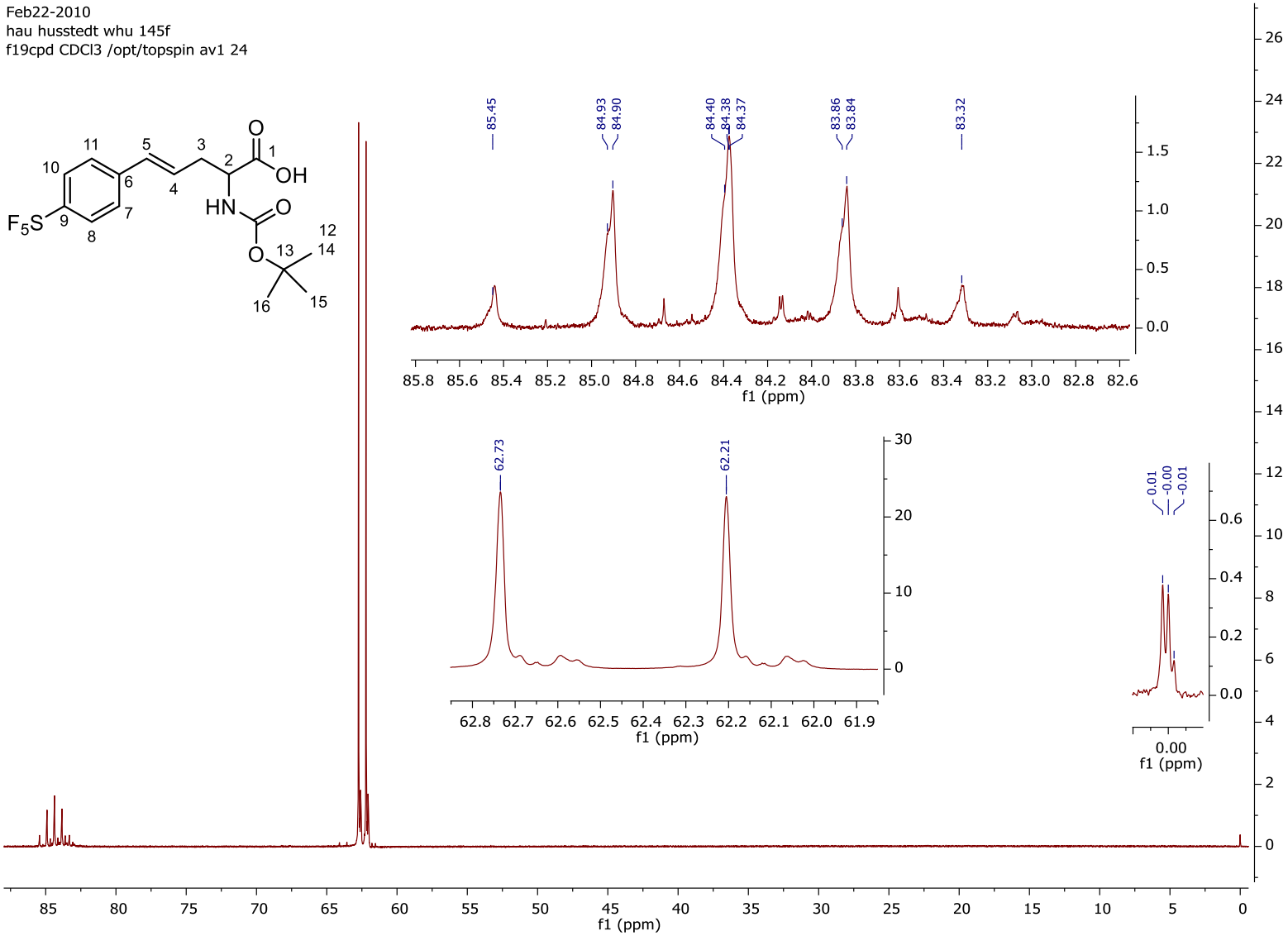
^{1}H NMR spectrum of compound **7**



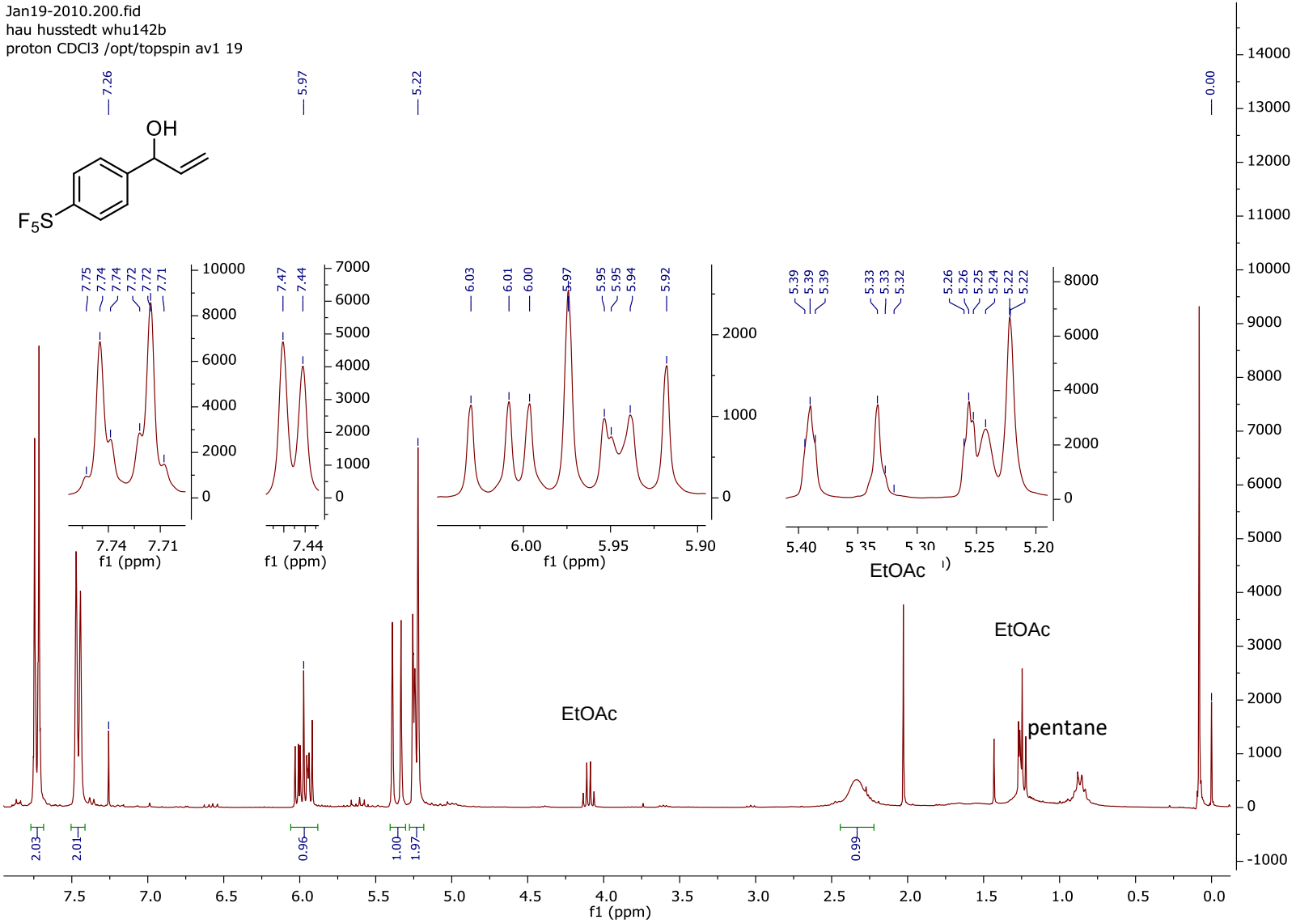
^{13}C NMR spectrum of compound **7**



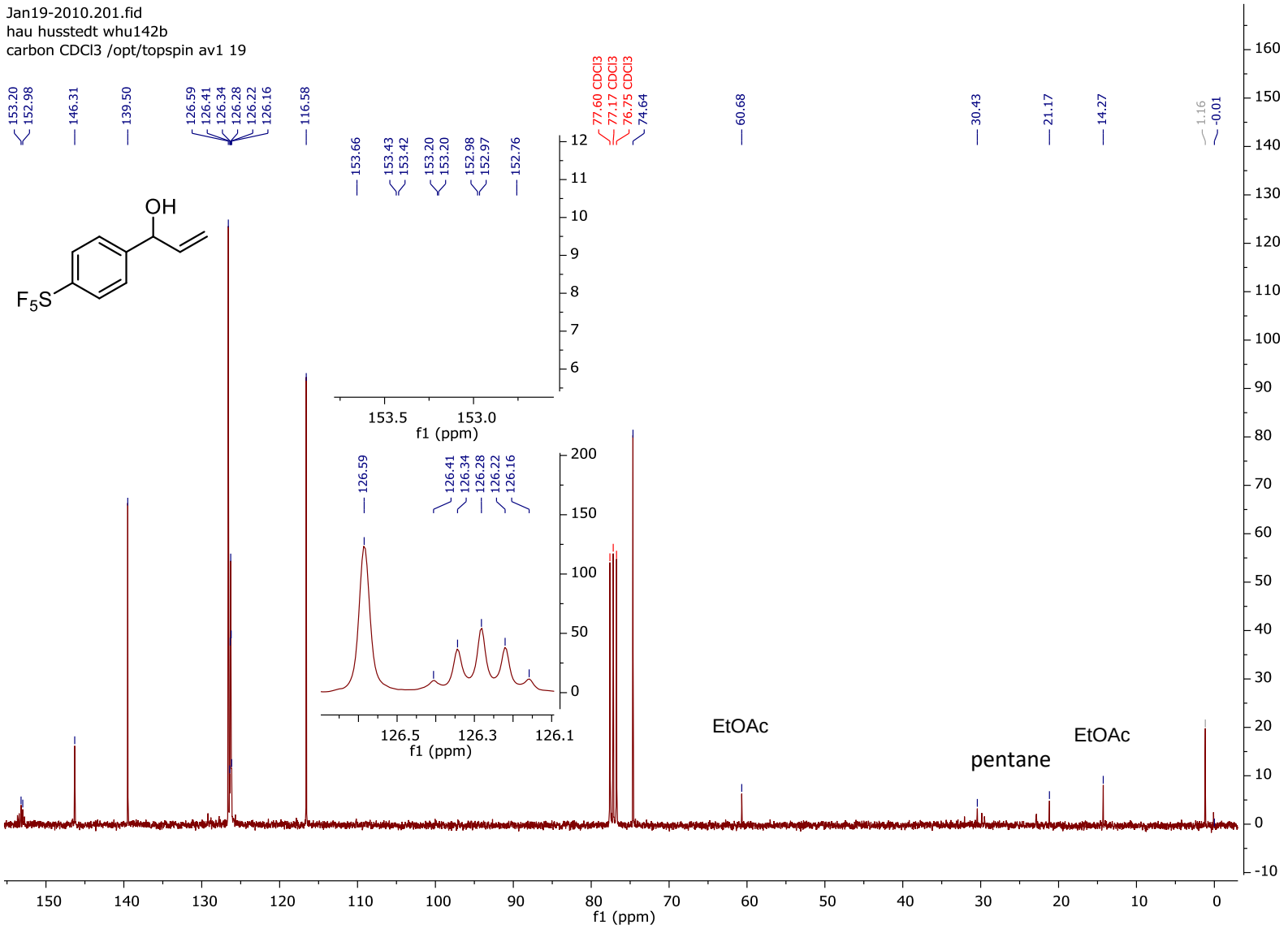
^{19}F NMR spectrum of compound **7**



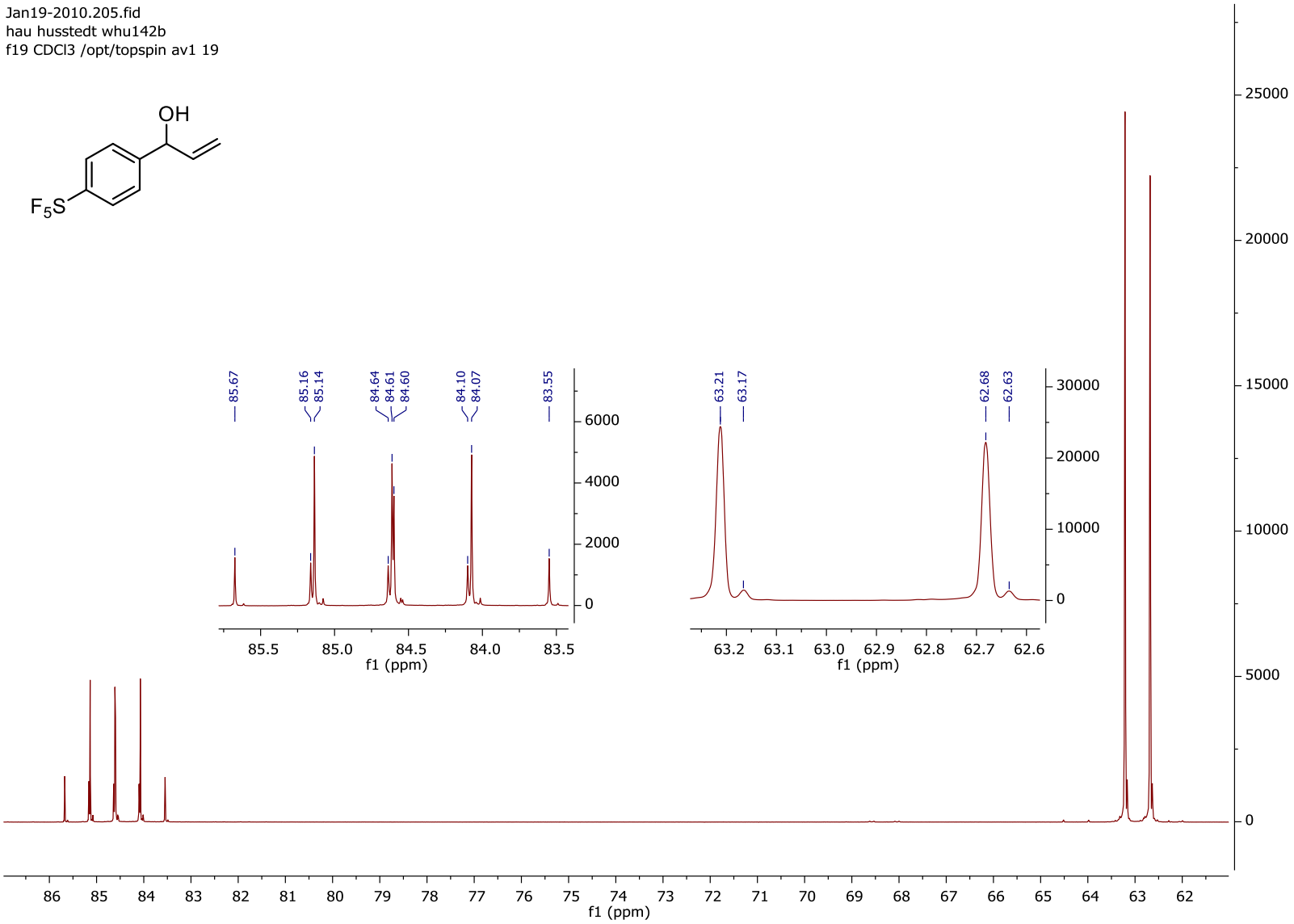
^{1}H NMR spectrum of compound **8**



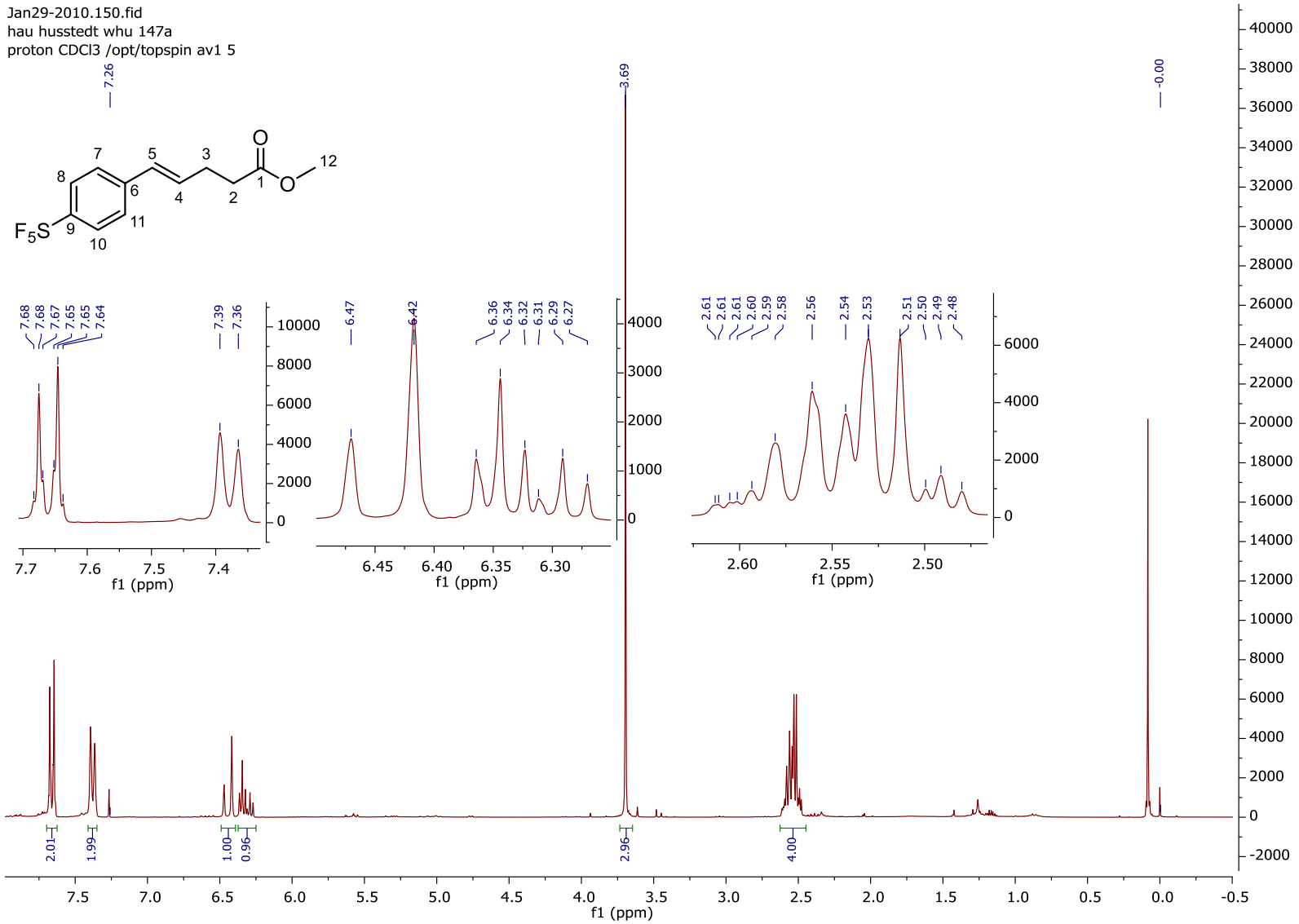
^{13}C NMR spectrum of compound **8**



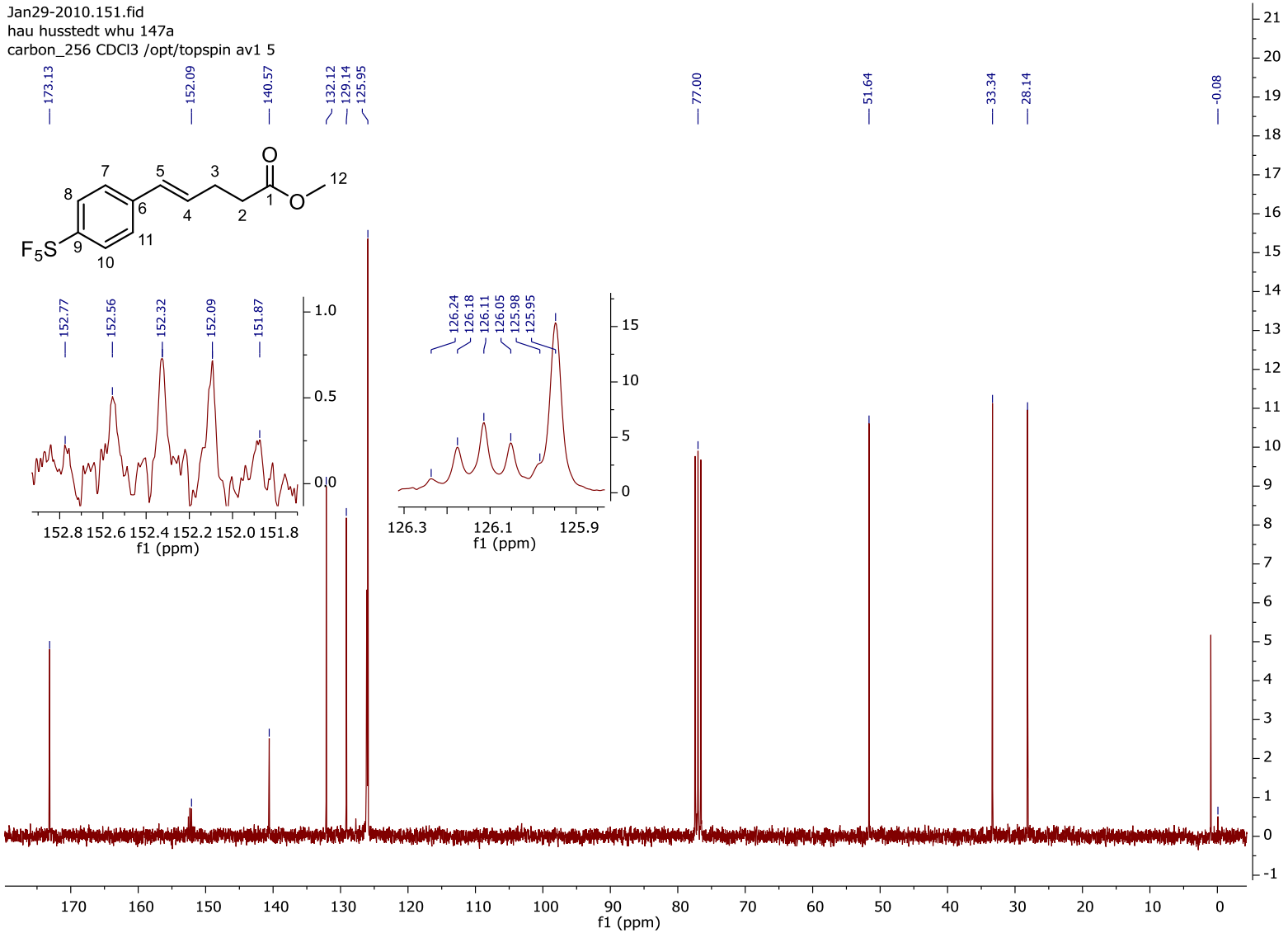
^{13}C NMR spectrum of compound **8**



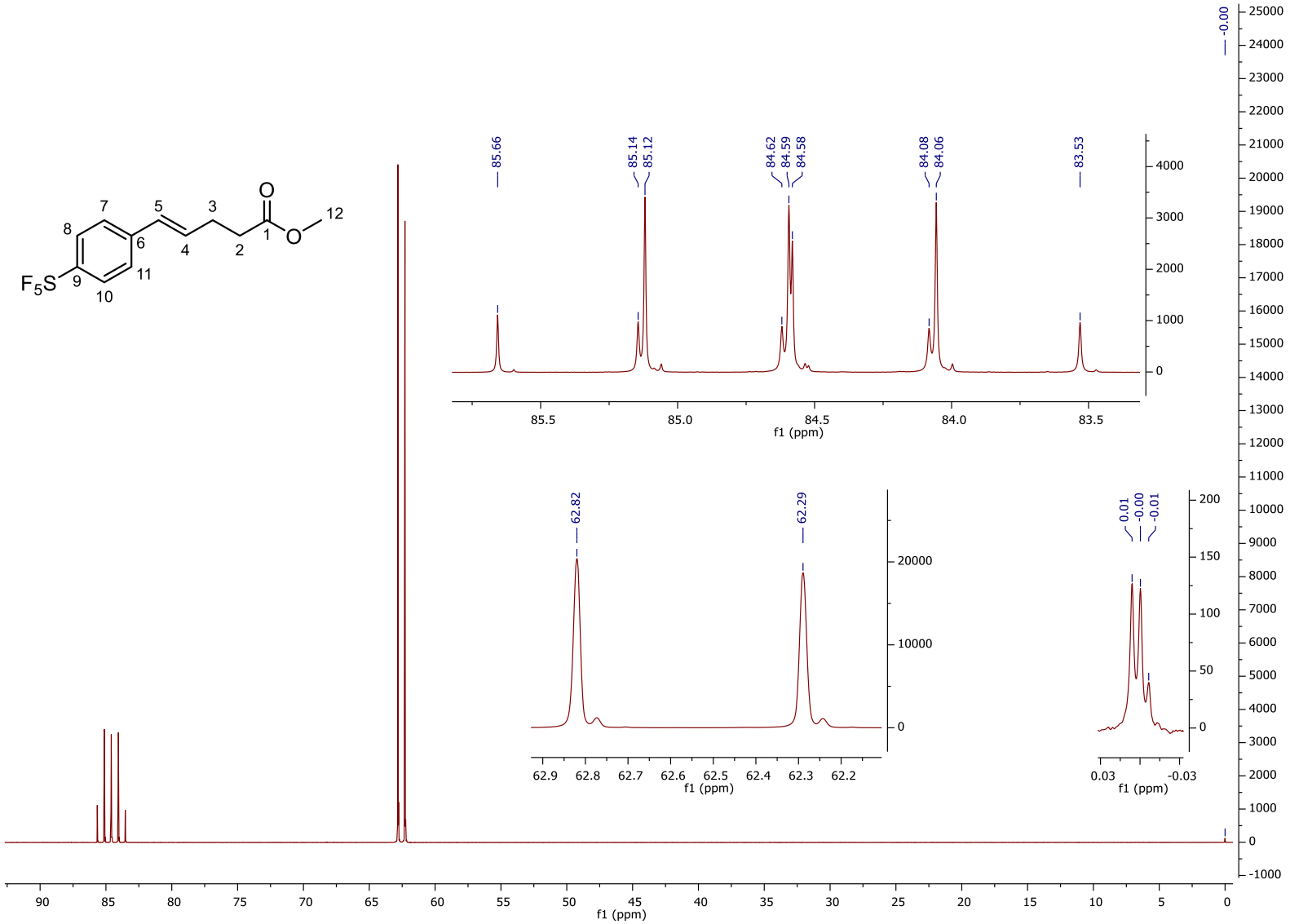
^{1}H NMR spectrum of compound **9**



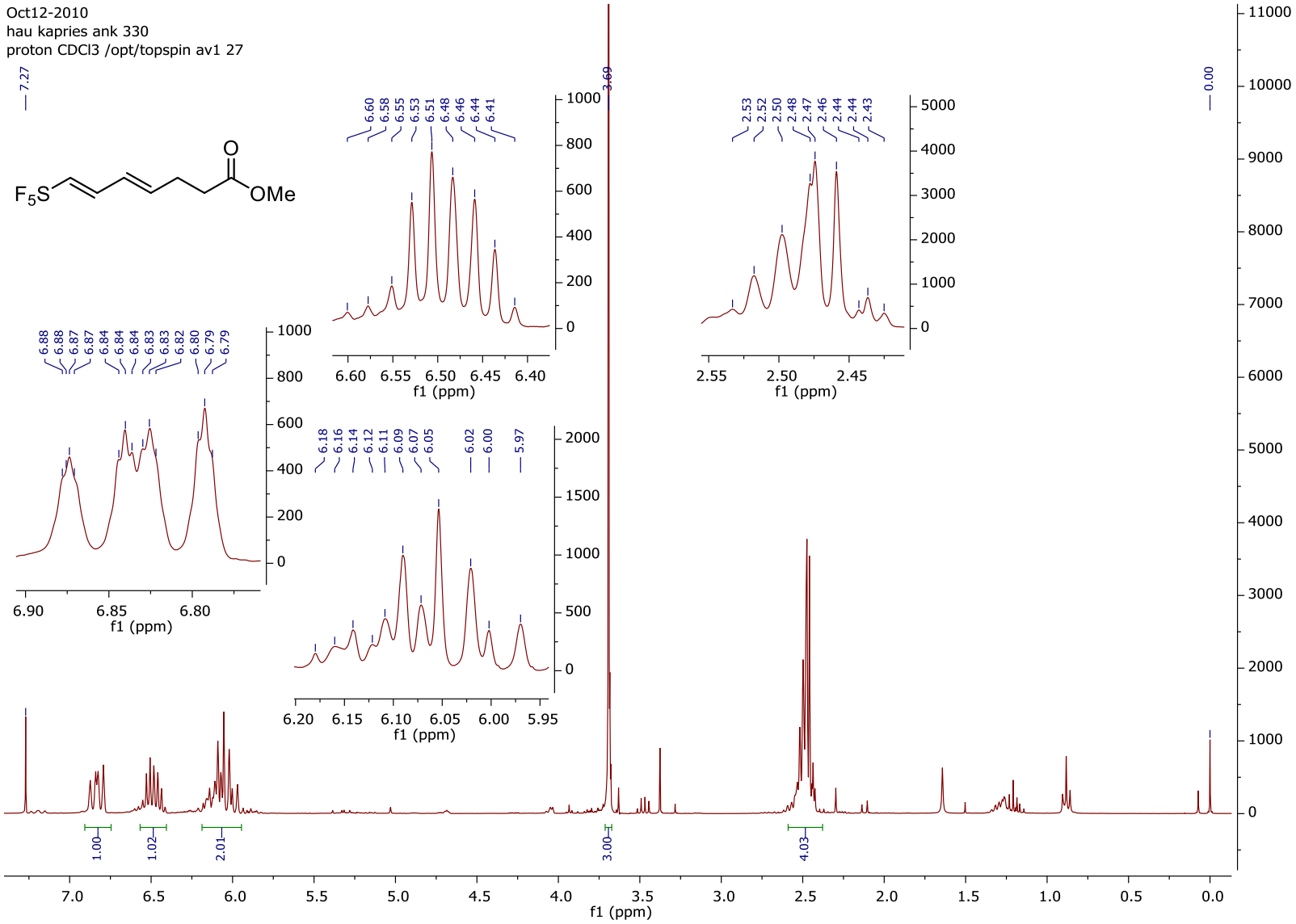
^{13}C NMR spectrum of compound **9**



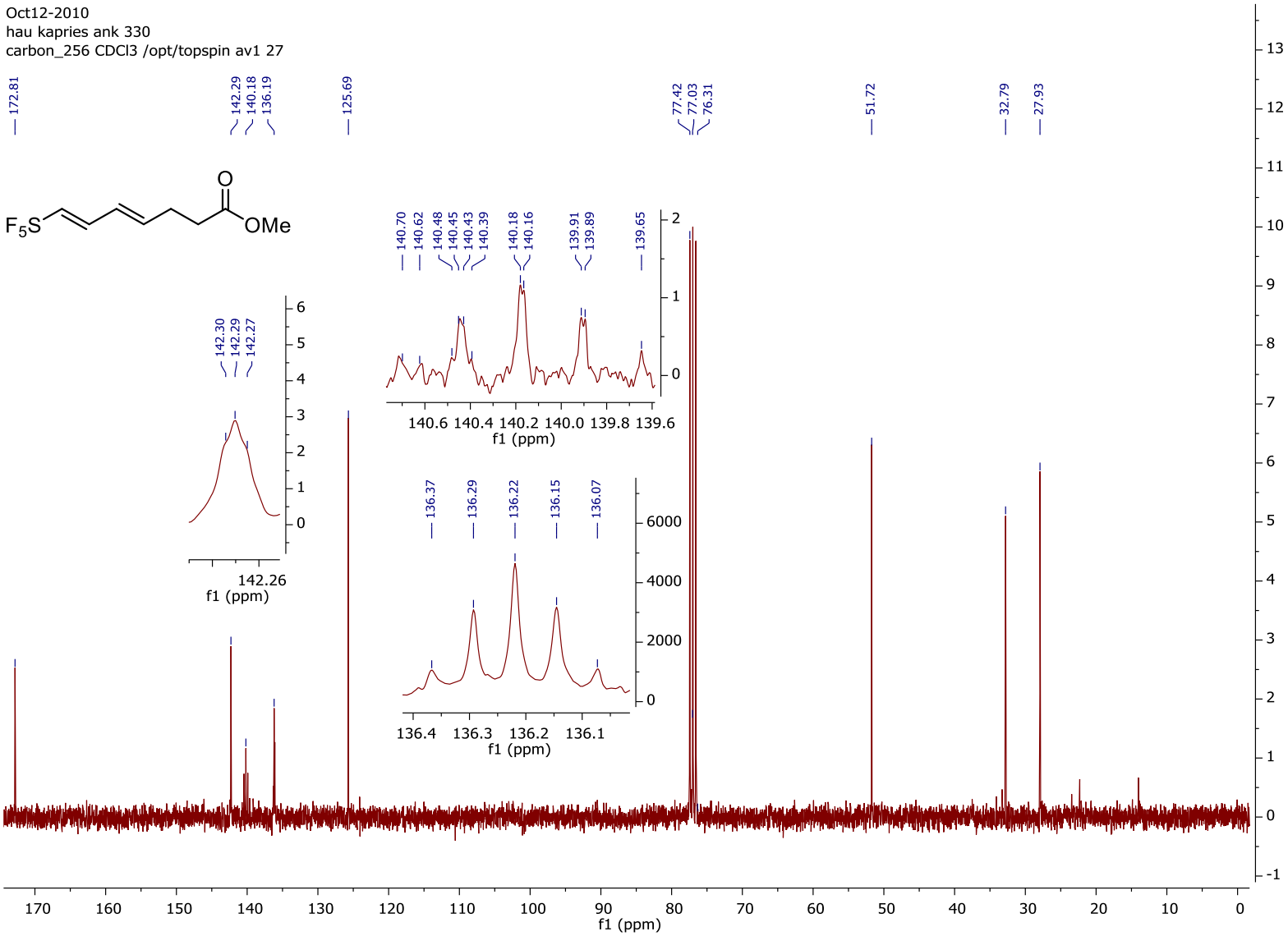
^{19}F NMR spectrum of compound **9**



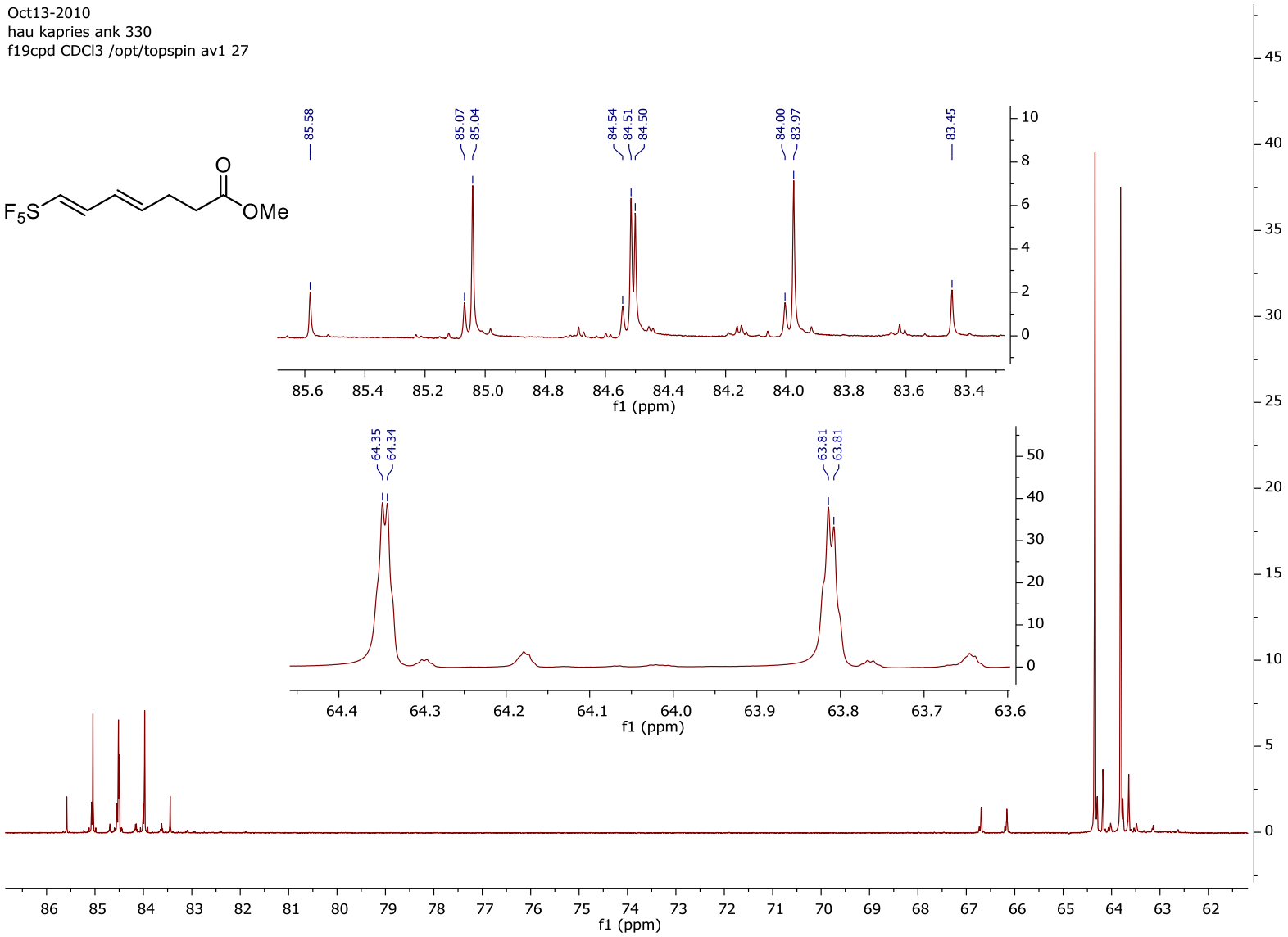
^{1}H NMR spectrum of compound **10g**



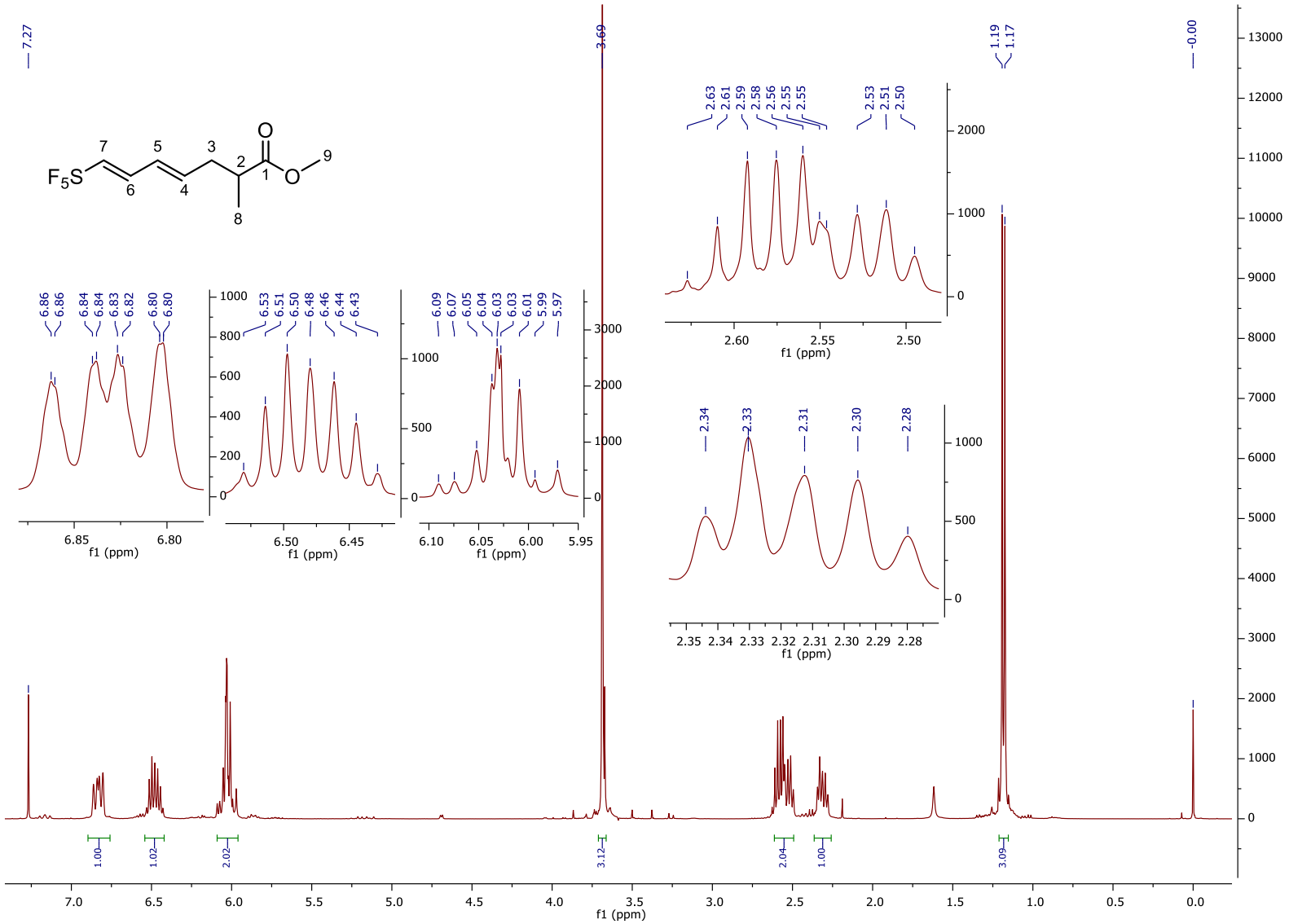
^{13}C NMR spectrum of compound **10g**



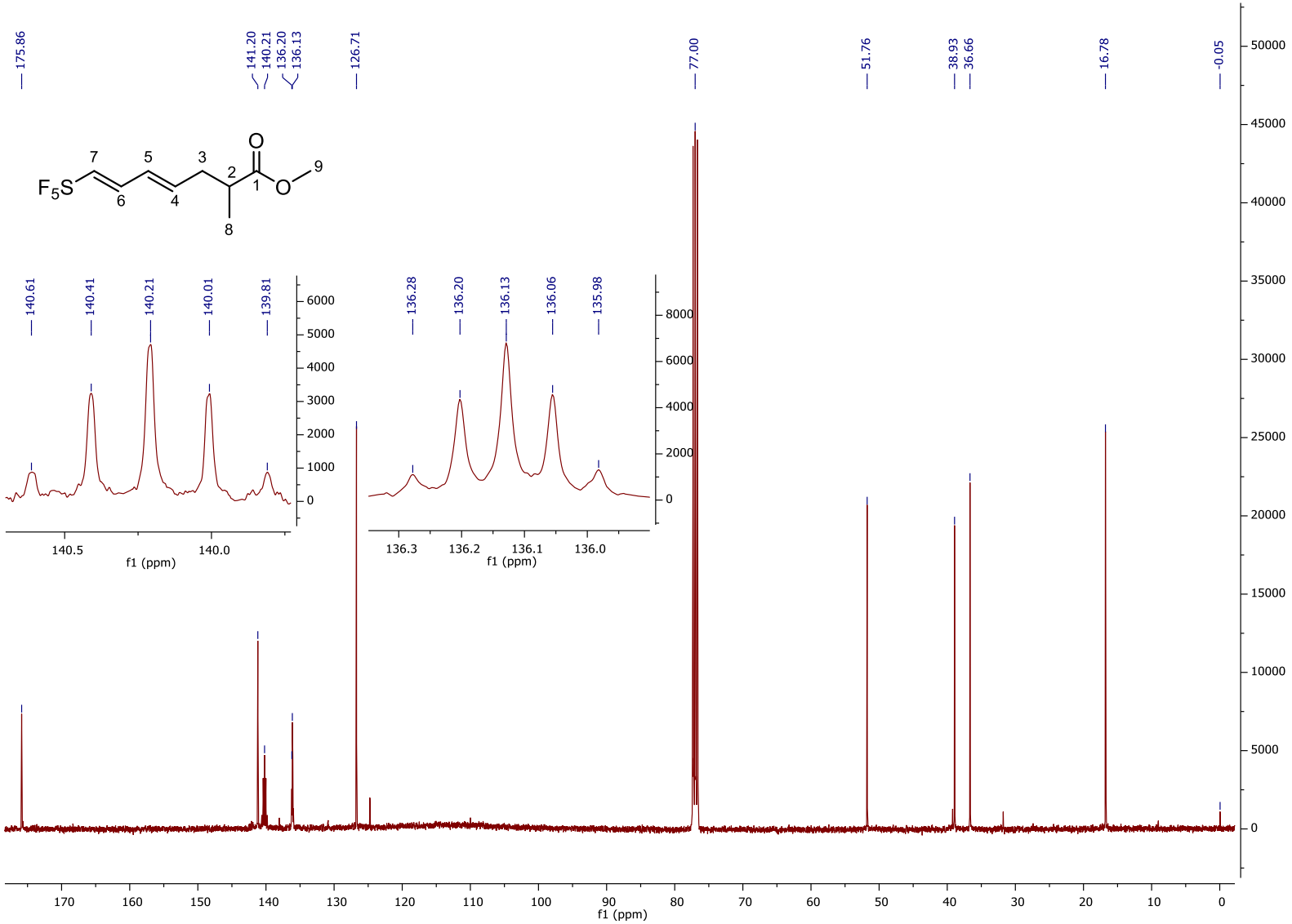
^{19}F NMR spectrum of compound **10g**



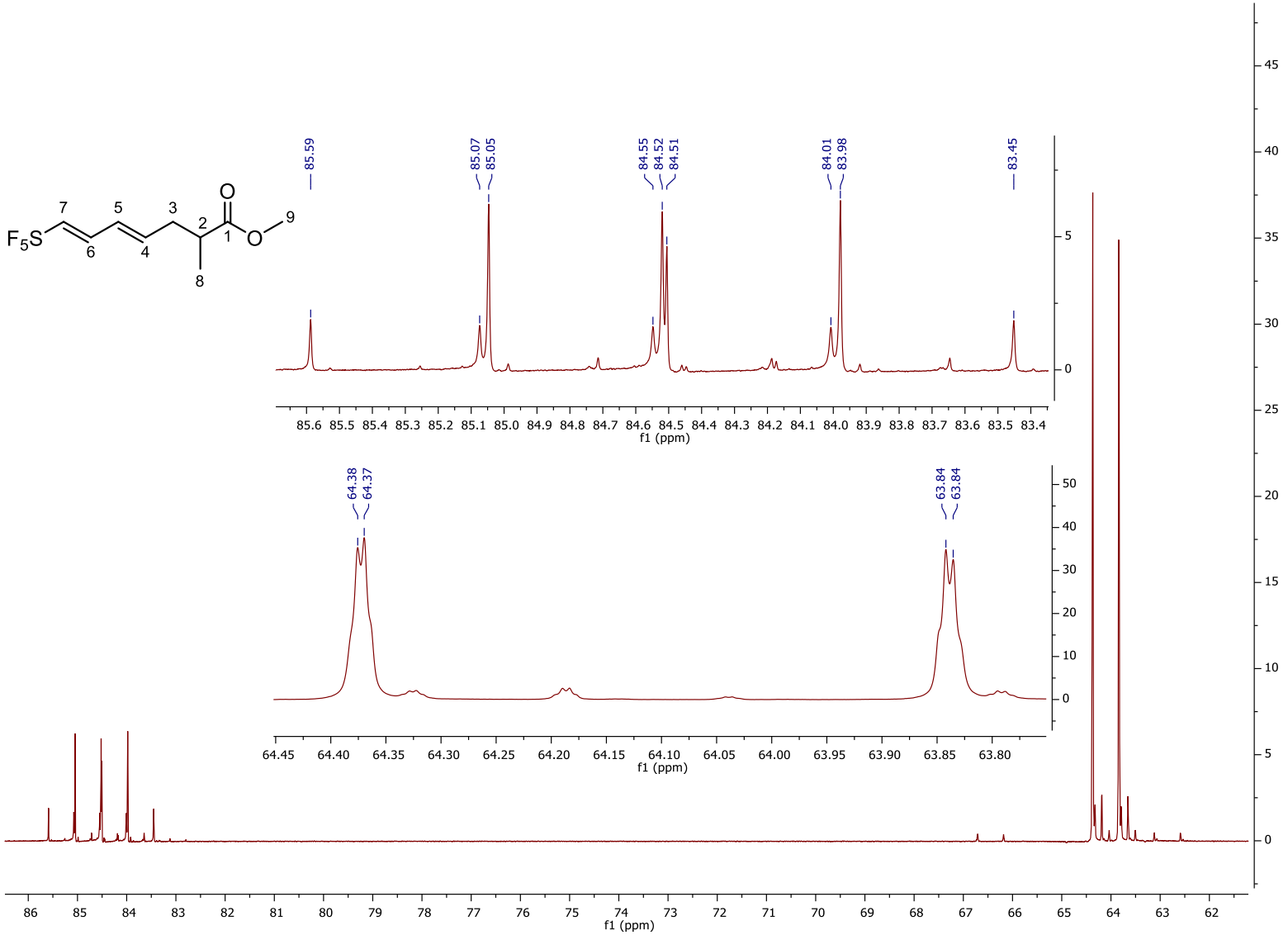
^{1}H NMR spectrum of compound **10h**



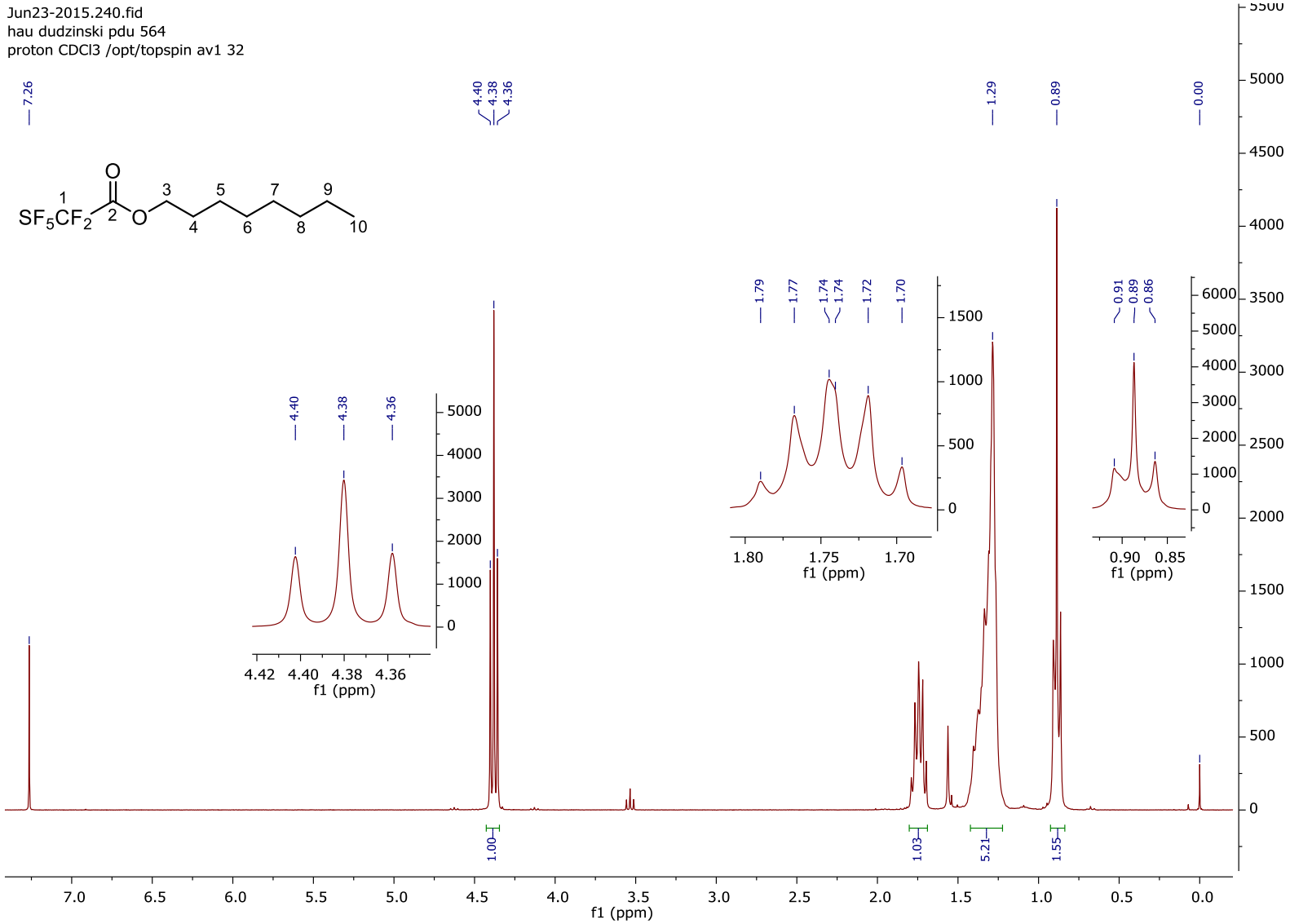
^{13}C NMR spectrum of compound **10h**



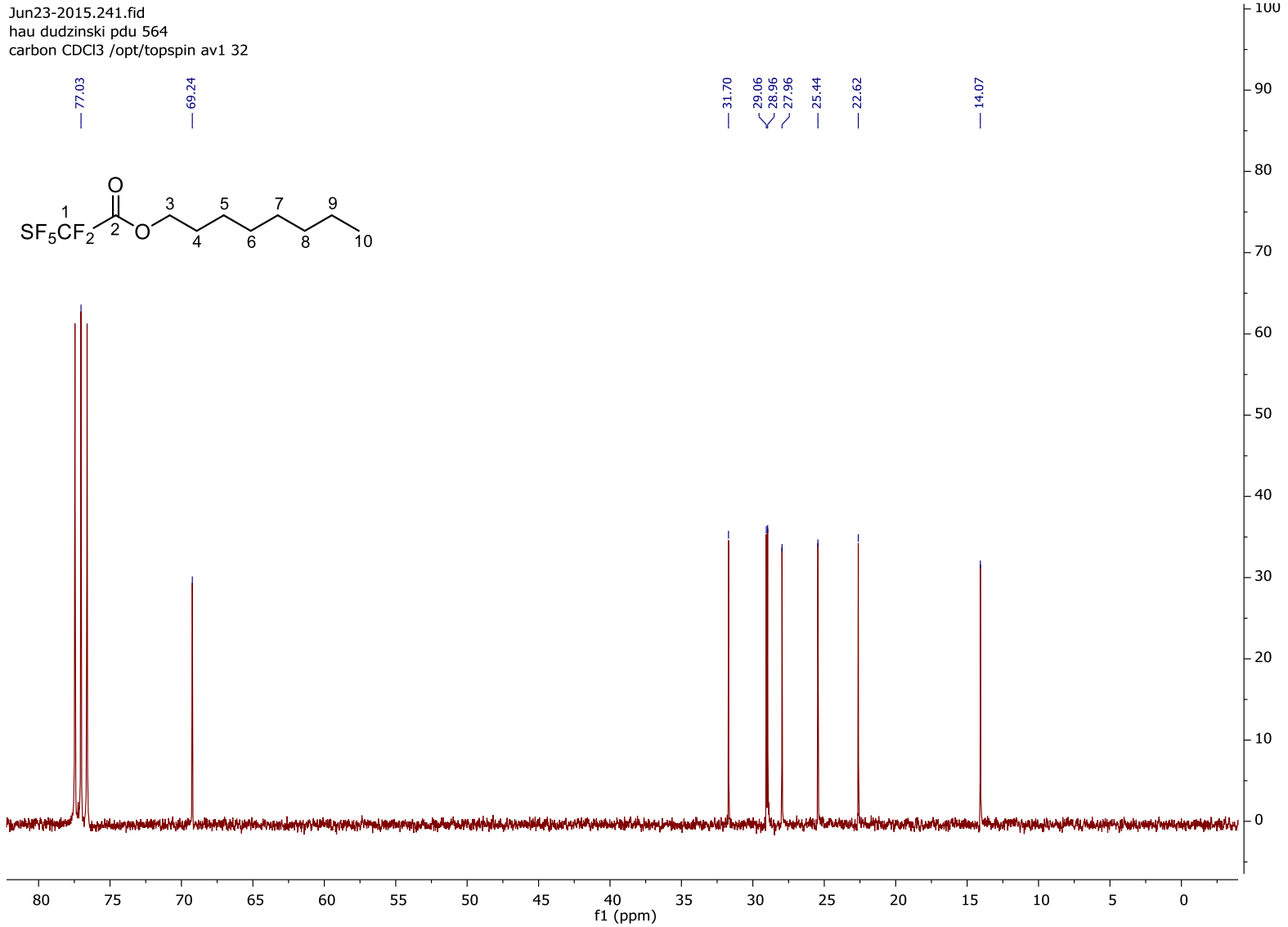
^{19}F NMR spectrum of compound **10h**



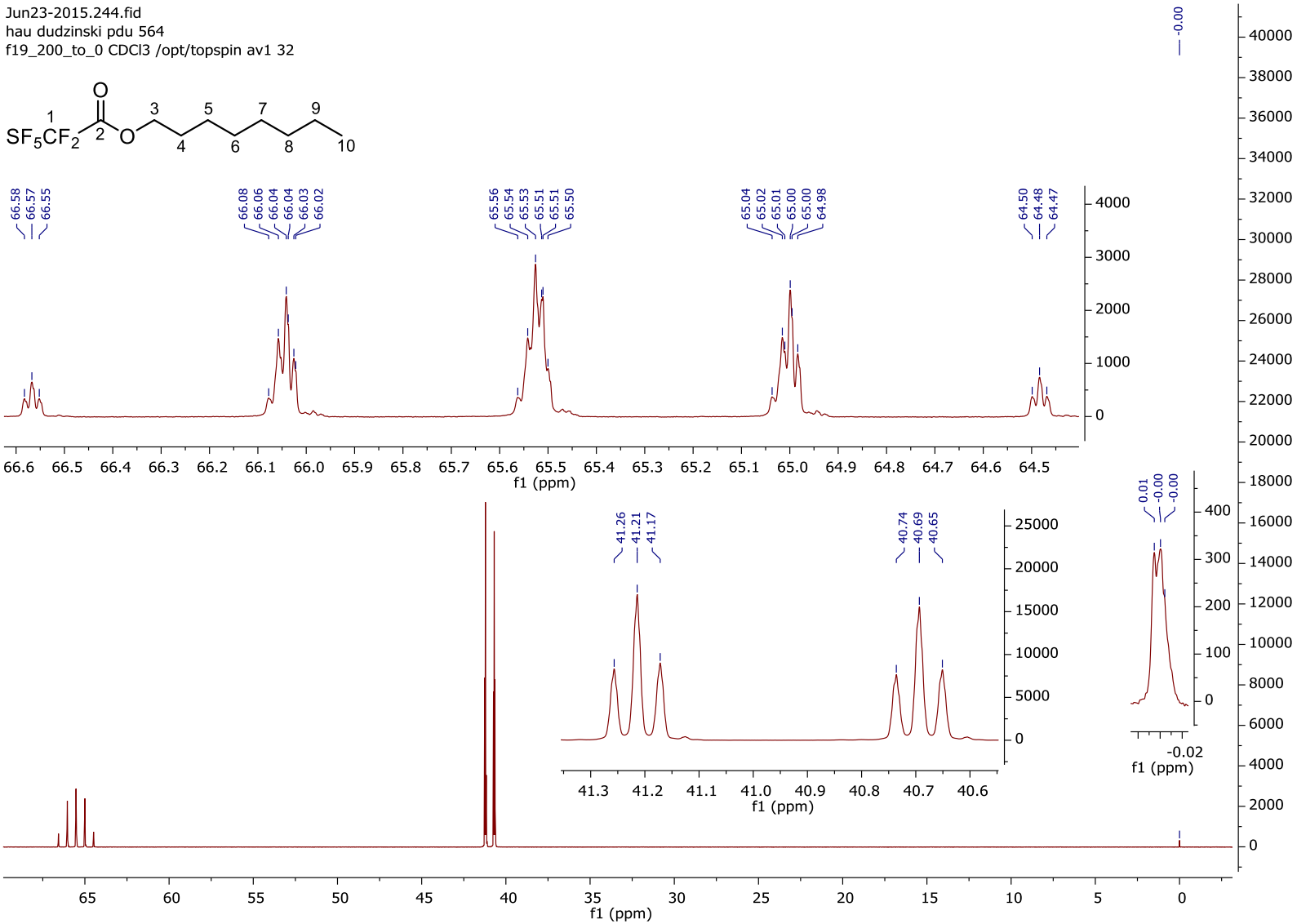
^{1}H NMR spectrum of compound **11**



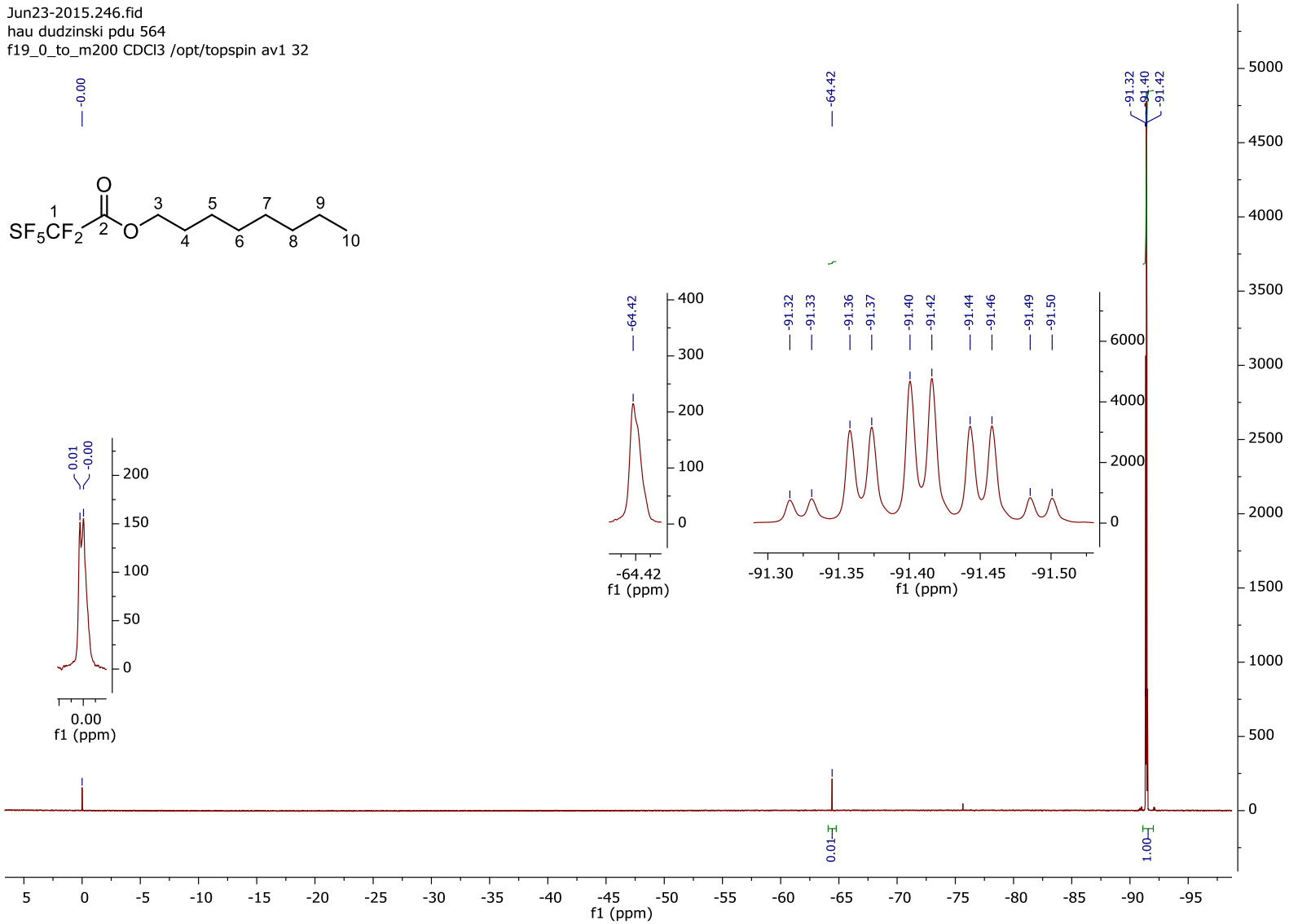
^{13}C NMR spectrum of compound **11**



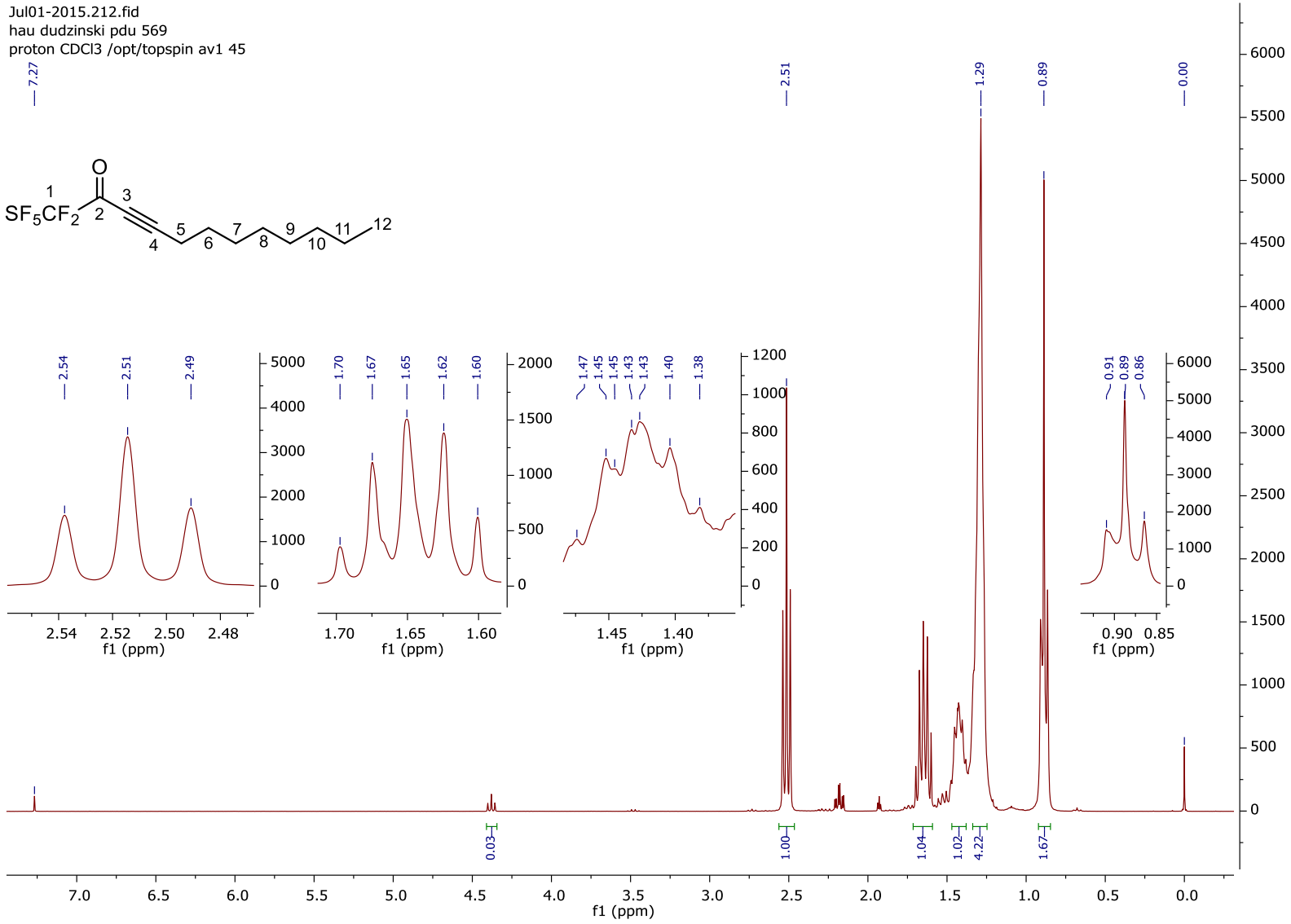
^{19}F NMR spectrum of compound **11** – positive part



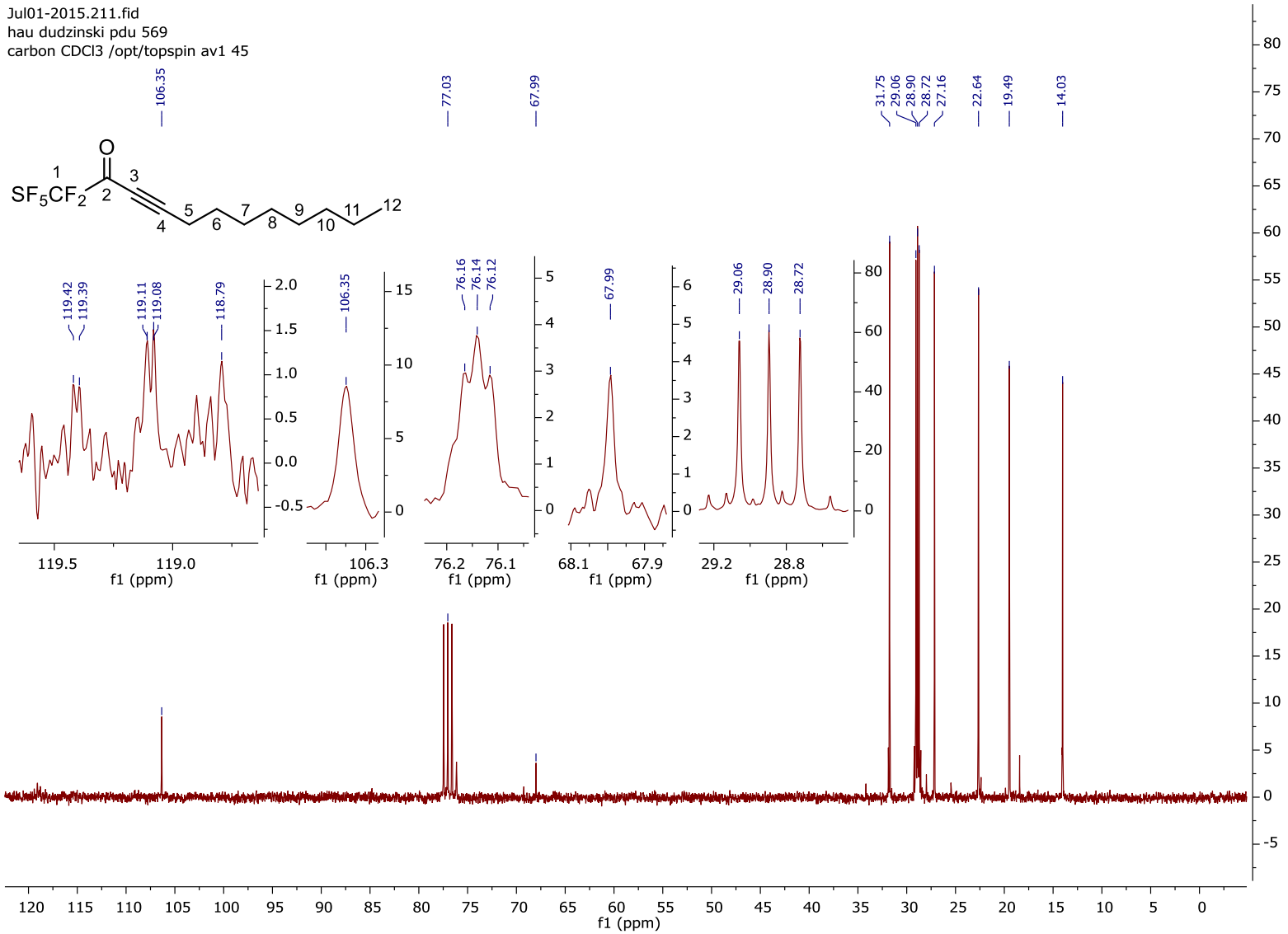
^{19}F NMR spectrum of compound **11** – negative part



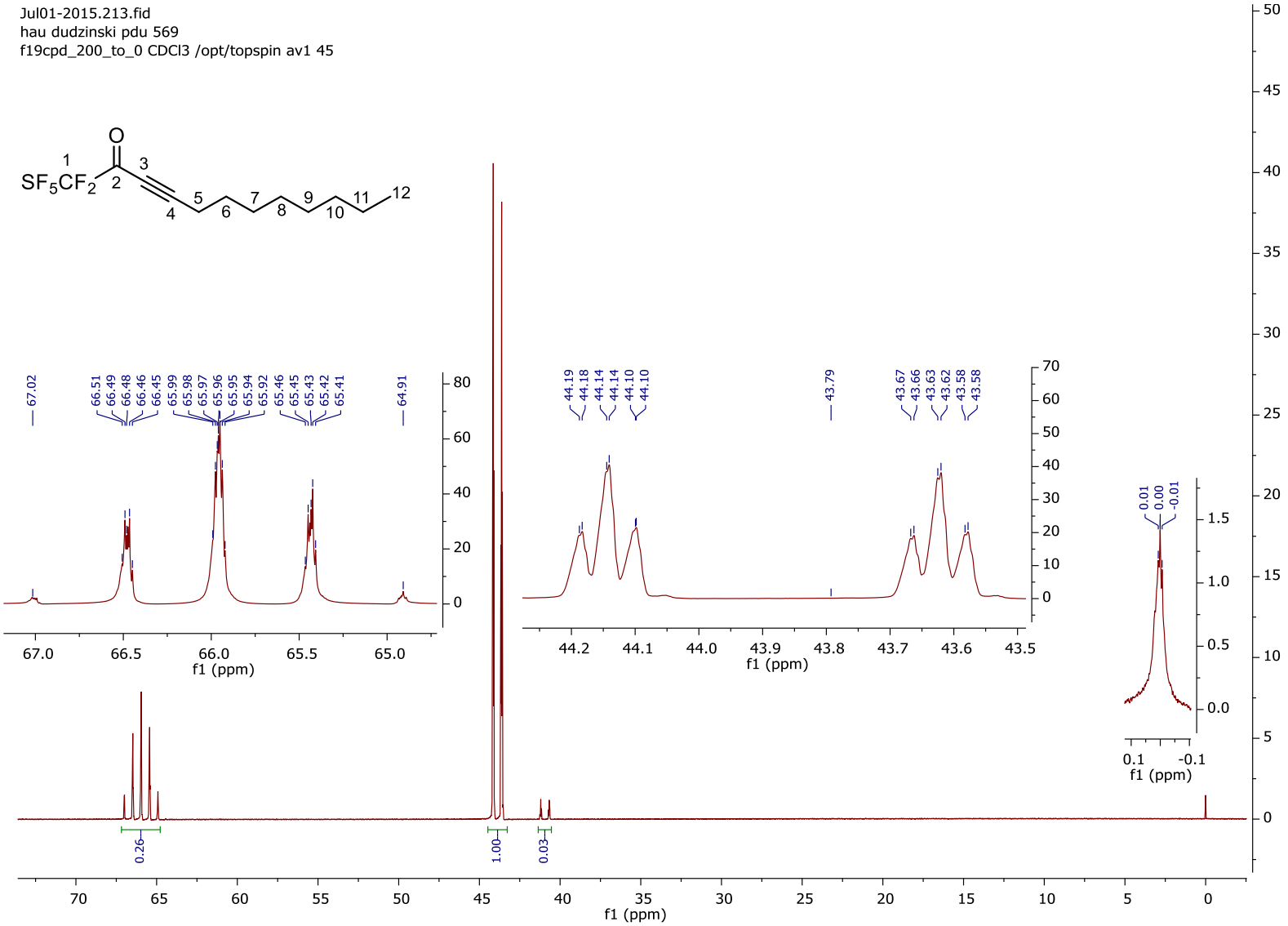
^{1}H NMR spectrum of 1,1-difluoro-1-(pentafluoro-λ^{6}-sulfaneyl)dodec-3-yn-2-one (**12**)



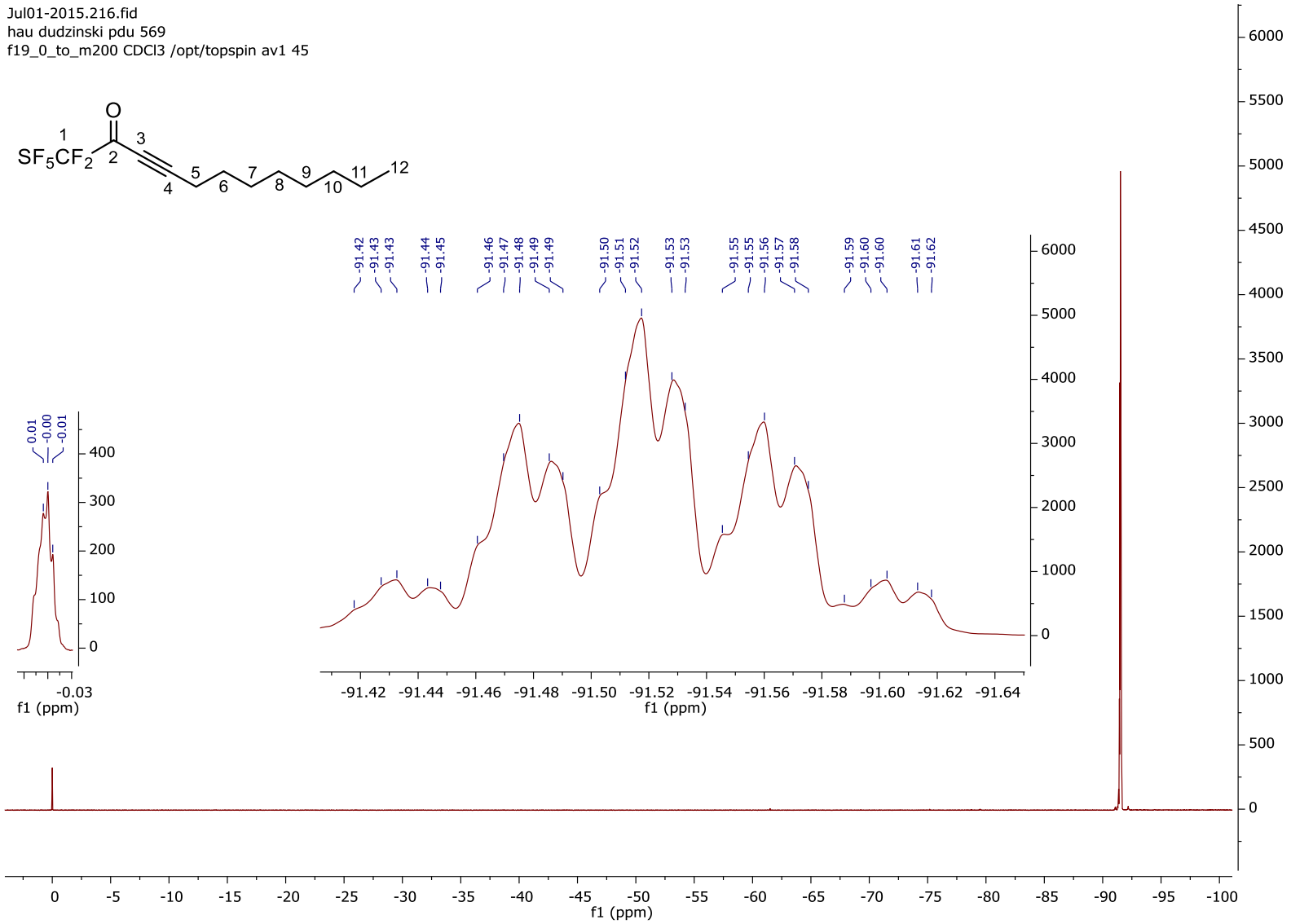
^{13}C NMR spectrum of 1,1-difluoro-1-(pentafluoro-λ^6-sulfaneyl)dodec-3-yn-2-one (**12**)



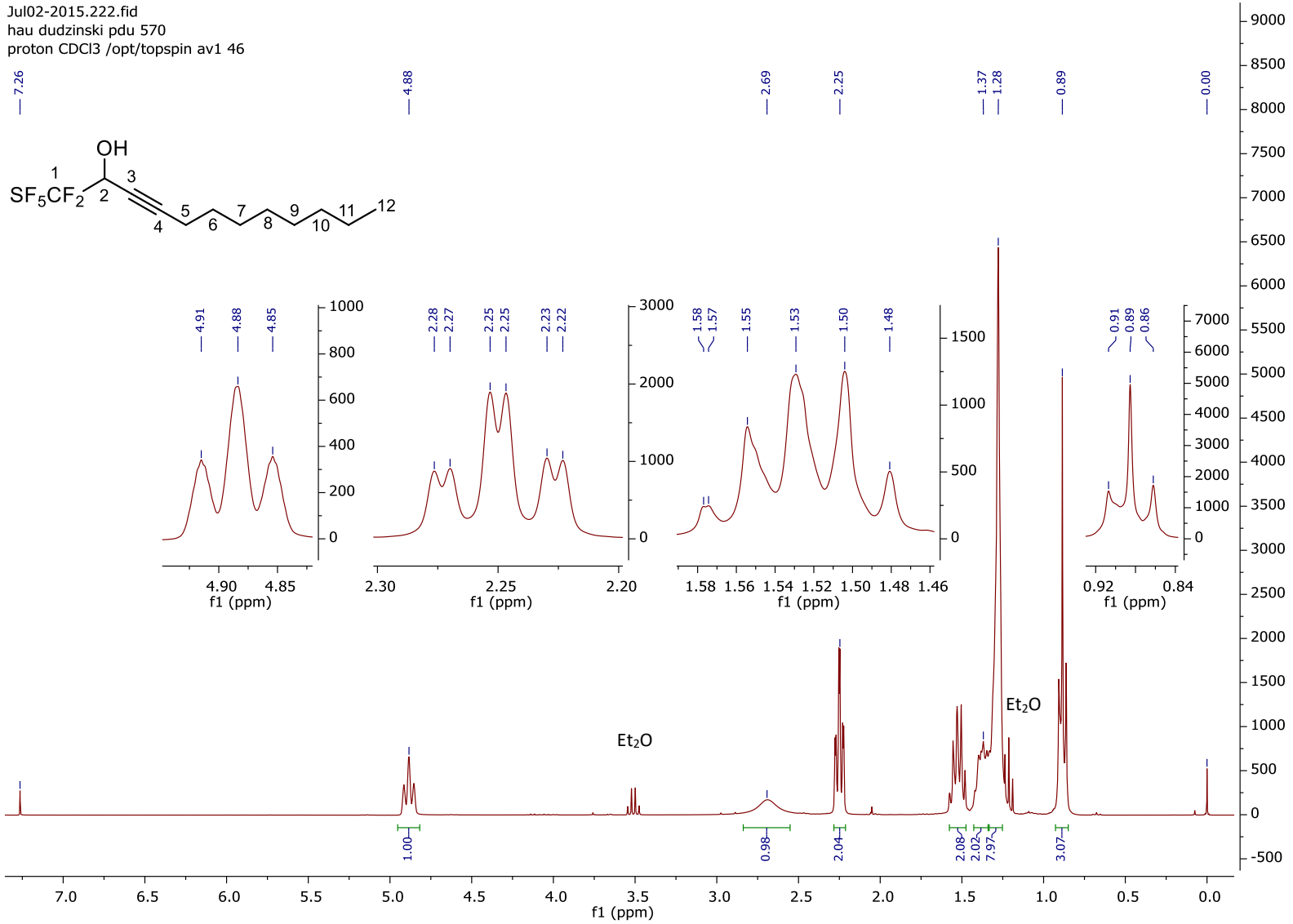
^{19}F NMR spectrum of 1,1-difluoro-1-(pentafluoro-λ^{6}-sulfaneyl)dodec-3-yn-2-one (**12**) – positive part



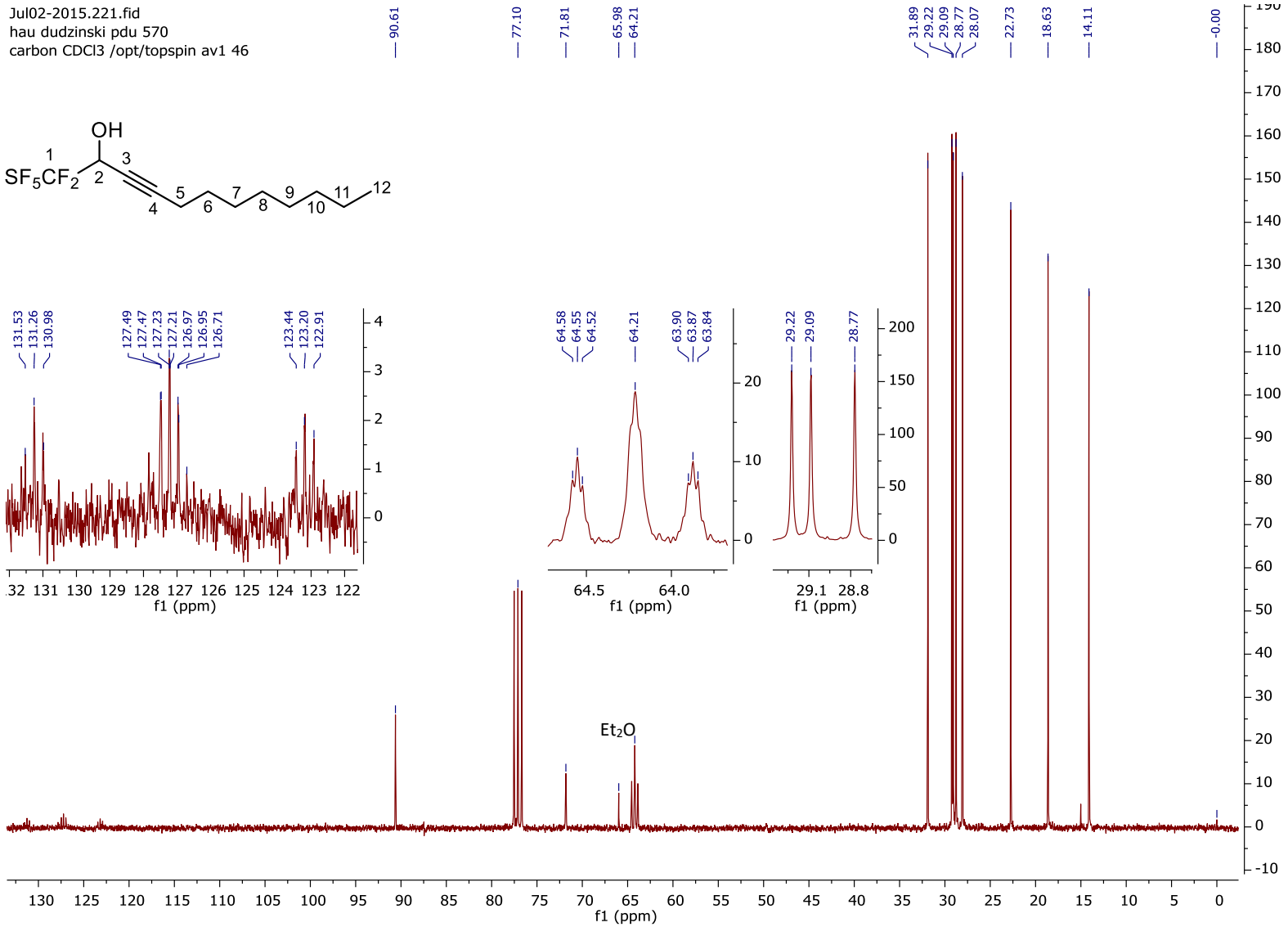
^{19}F NMR spectrum of 1,1-difluoro-1-(pentafluoro-λ^6-sulfaneyl)dodec-3-yn-2-one (**12**) – negative part



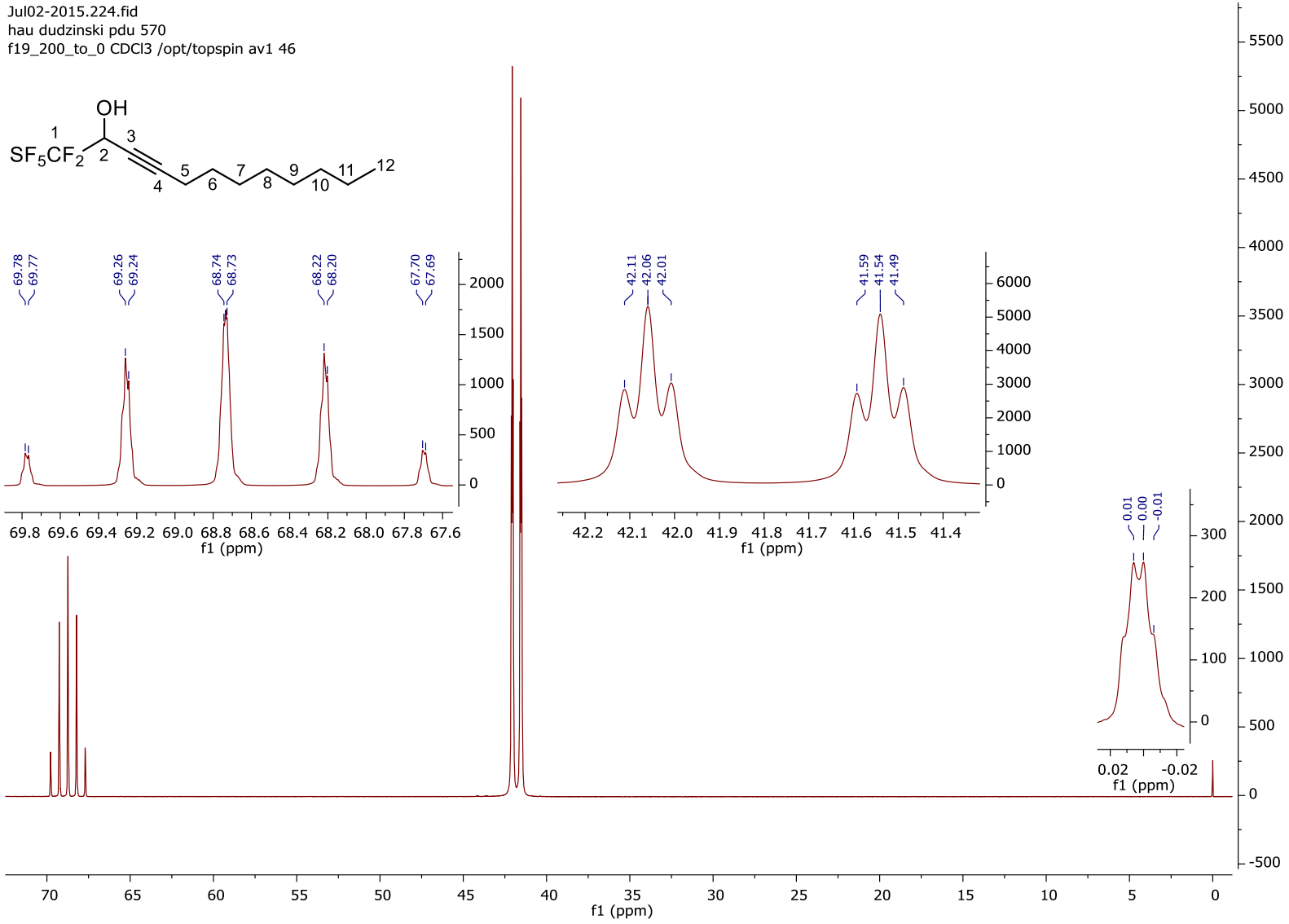
^{1}H NMR spectrum of 1,1-Difluoro-1-(pentafluoro-λ^{6}-sulfanyl)dodec-3-yn-2-ol (**13**)



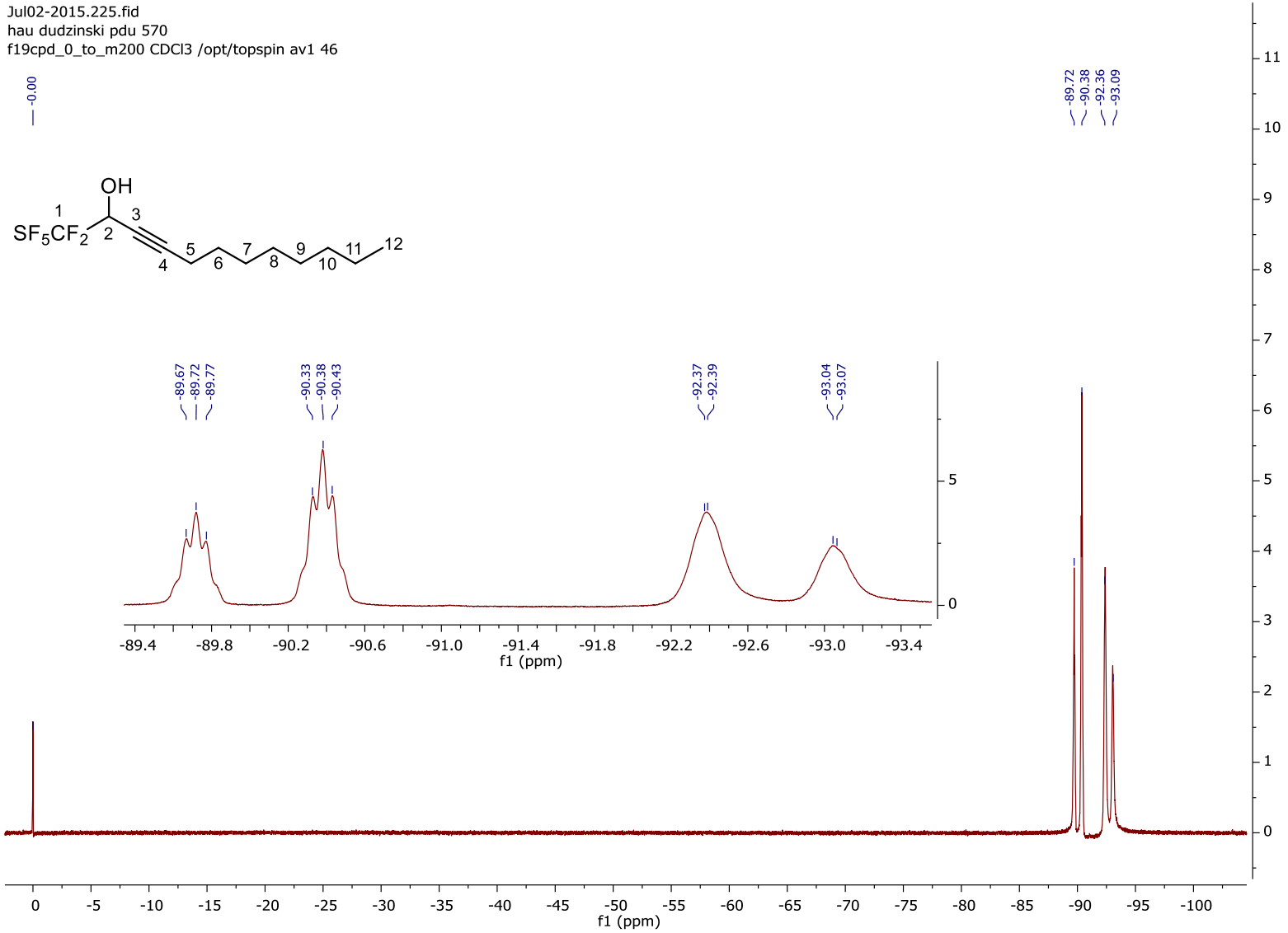
^{13}C NMR spectrum of 1,1-Difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-3-yn-2-ol (**13**)



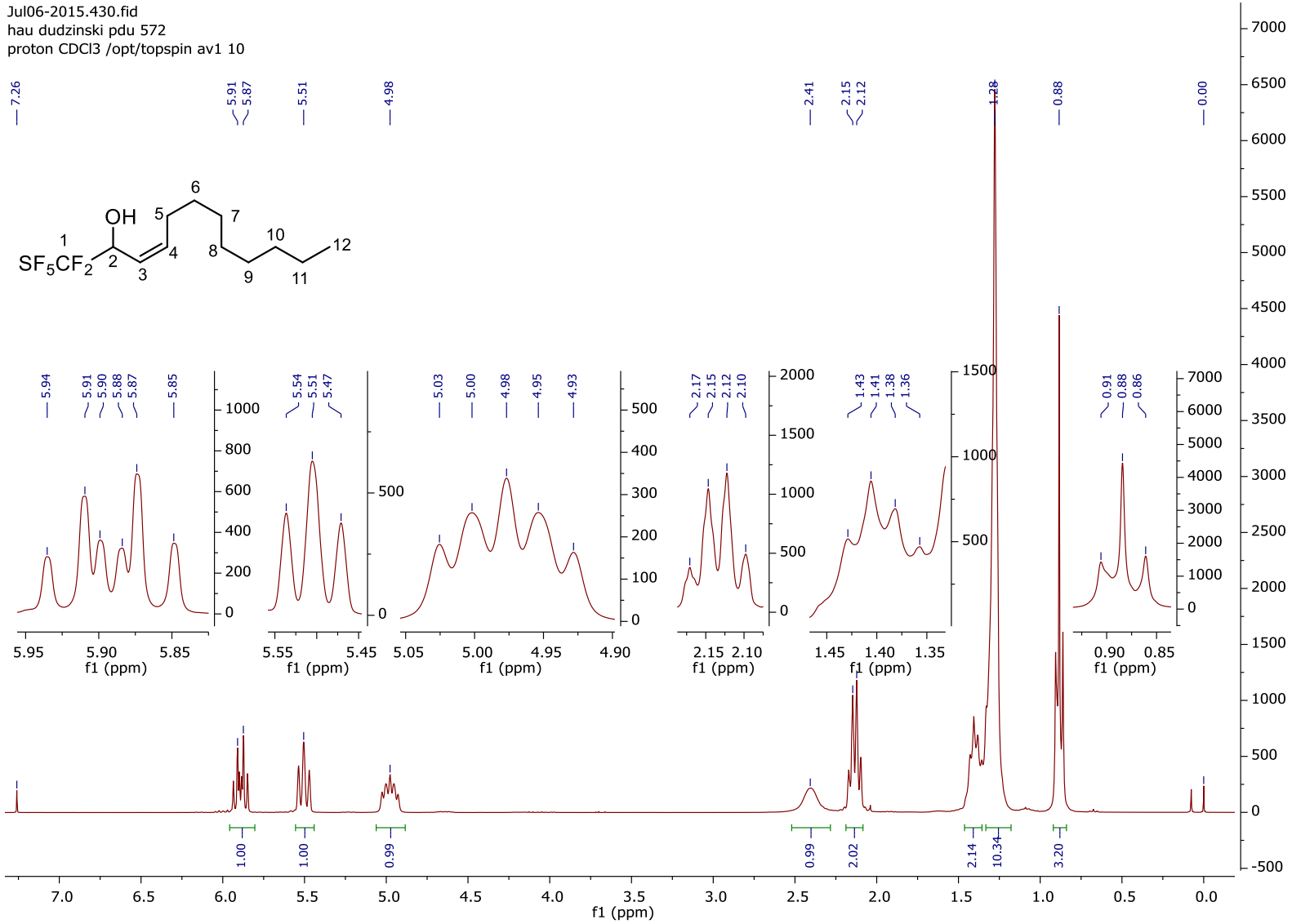
^{19}F NMR spectrum of 1,1-Difluoro-1-(pentafluoro-λ^{6}-sulfanyl)dodec-3-yn-2-ol (**13**) – positive part



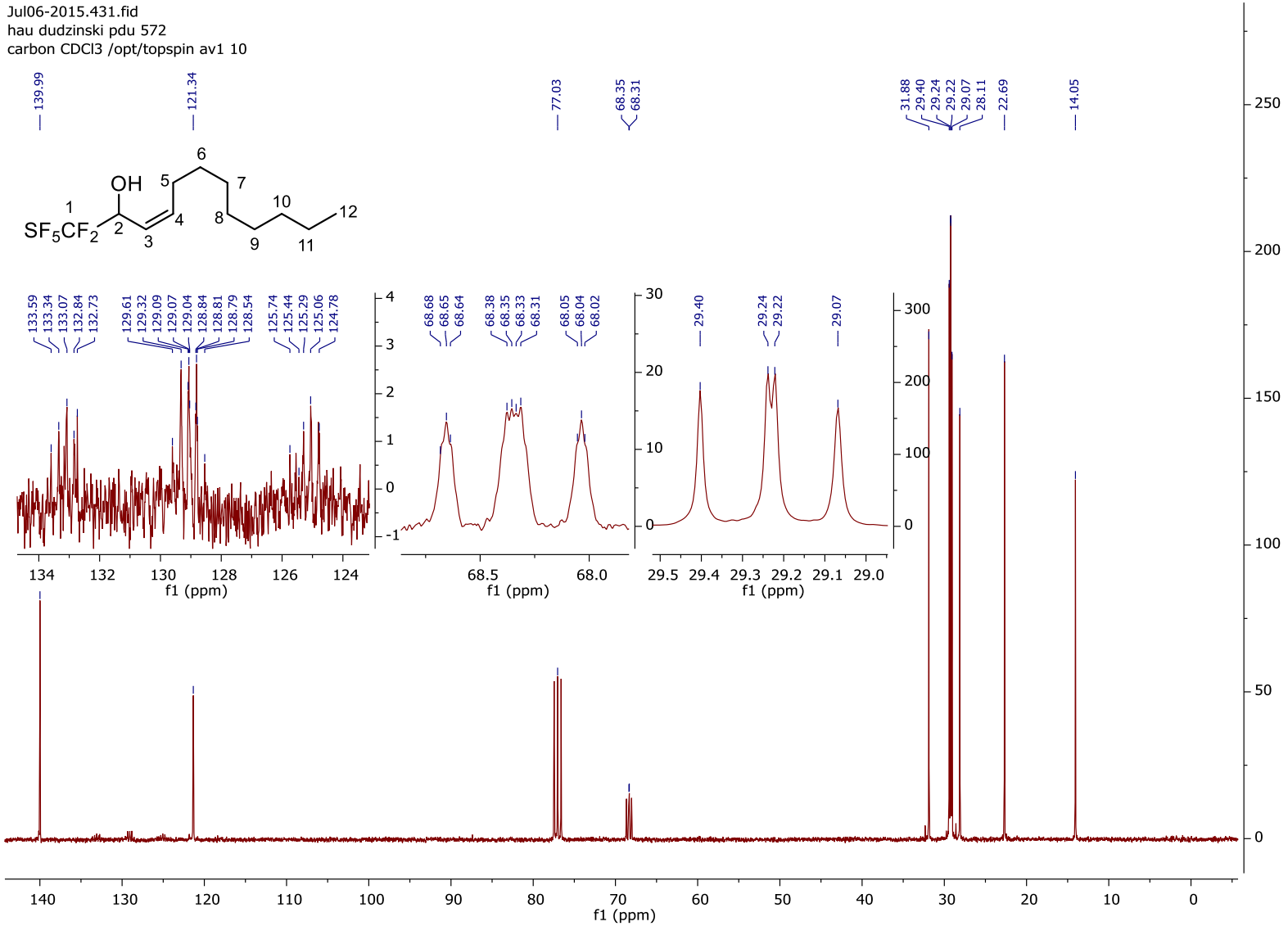
^{19}F NMR spectrum of 1,1-Difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-3-yn-2-ol (**13**) – negative part



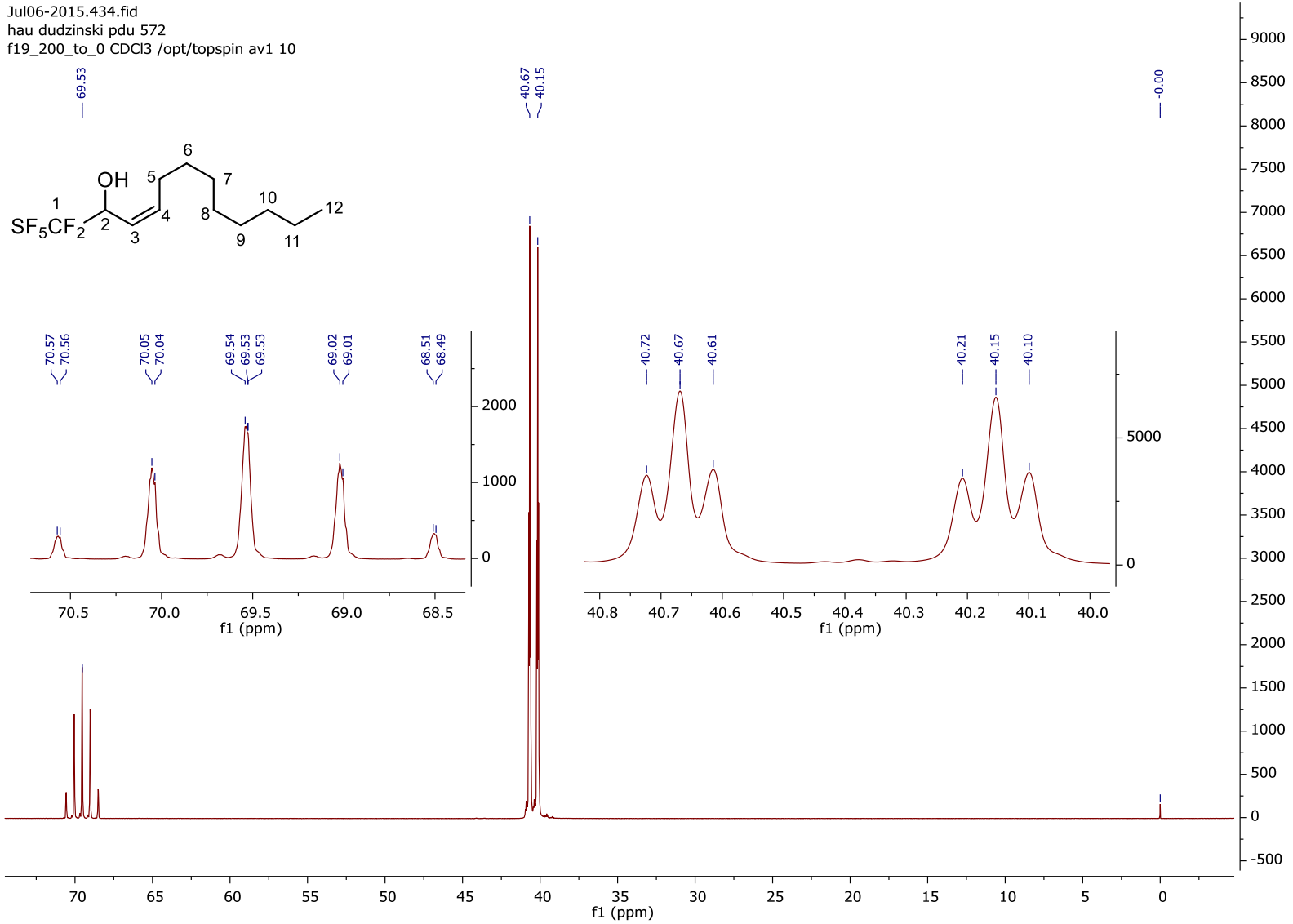
^{1}H NMR spectrum of (*Z*)-1,1-Difluoro-1-(pentafluoro-λ^{6}-sulfanyl)dodec-3-en-2-ol (**14**)



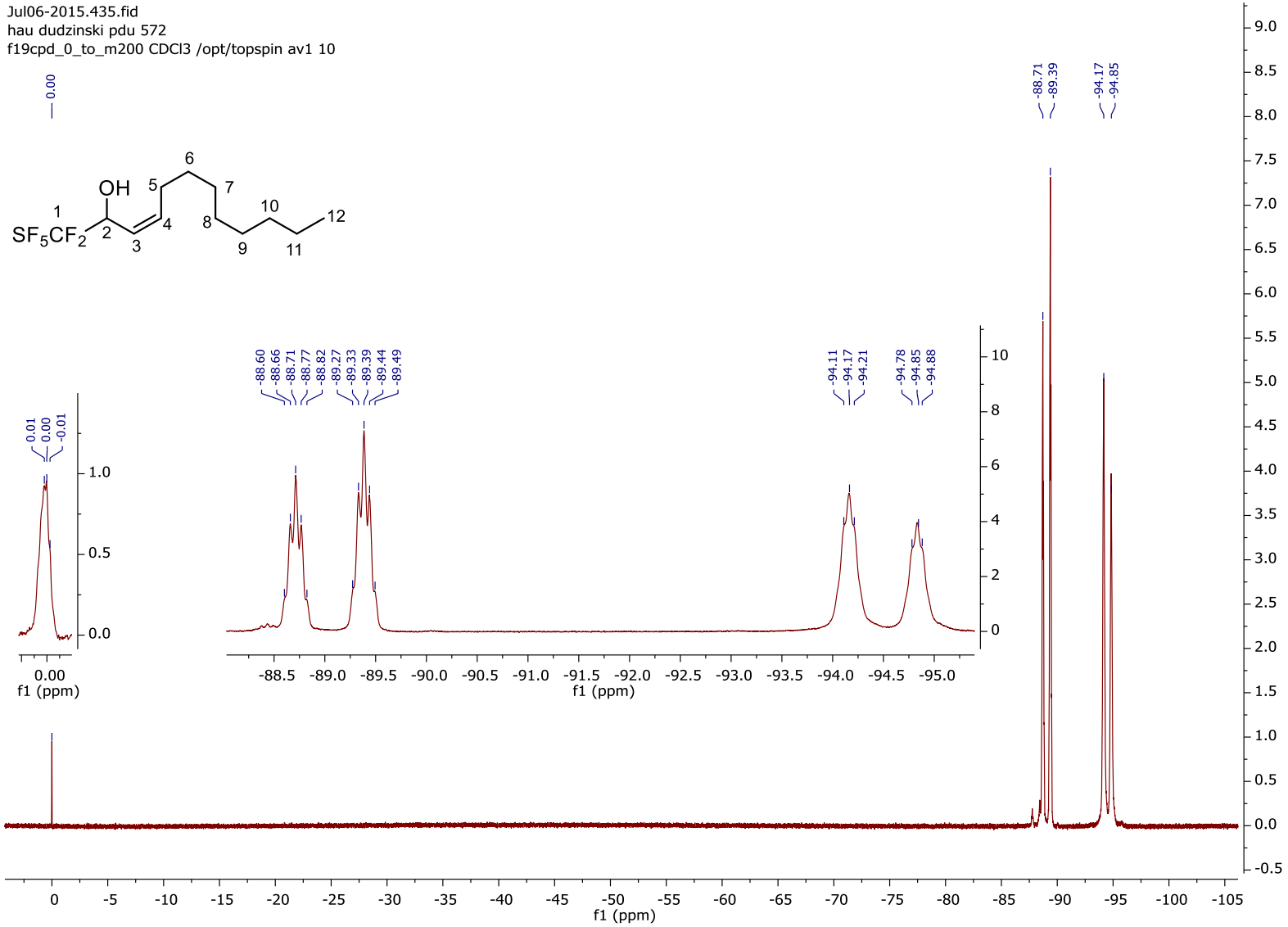
^{13}C NMR spectrum of (*Z*)-1,1-Difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-3-en-2-ol (**14**)



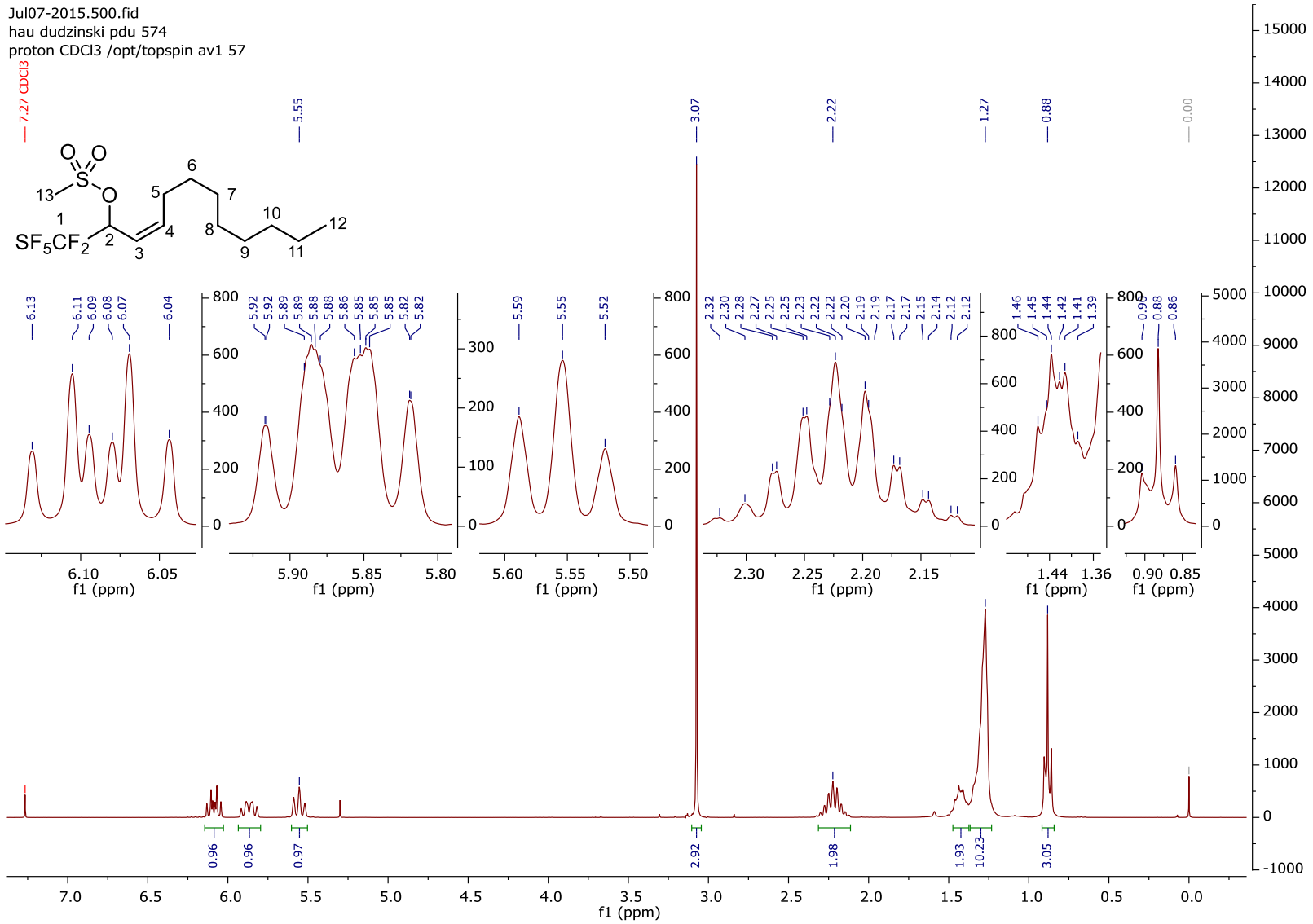
^{19}F NMR spectrum of (*Z*)-1,1-Difluoro-1-(pentafluoro-λ^{6}-sulfanyl)dodec-3-en-2-ol (**14**) – positive part



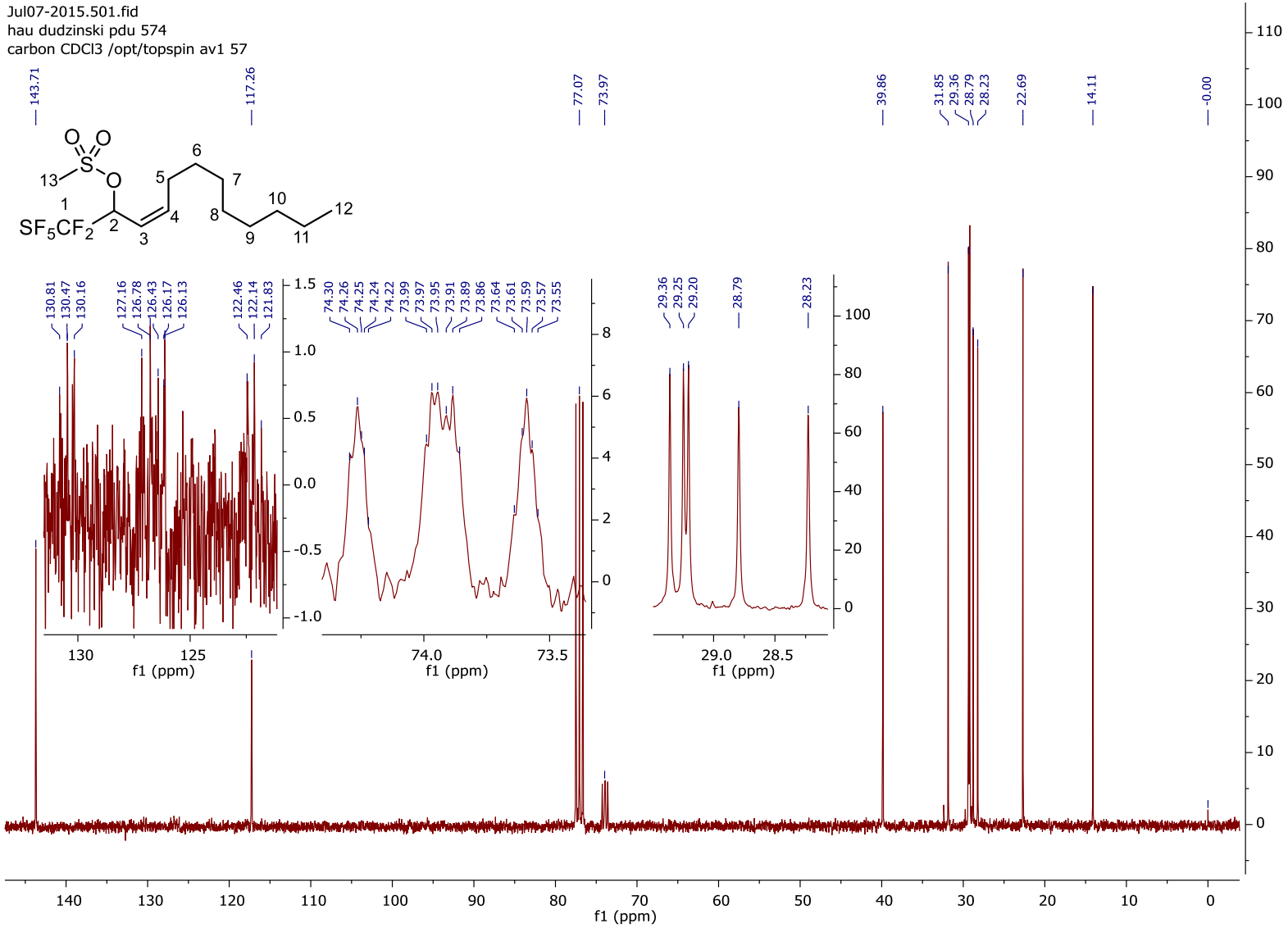
^{19}F NMR spectrum of (*Z*)-1,1-Difluoro-1-(pentafluoro-λ^6-sulfanyl)dodec-3-en-2-ol (**14**) – negative part



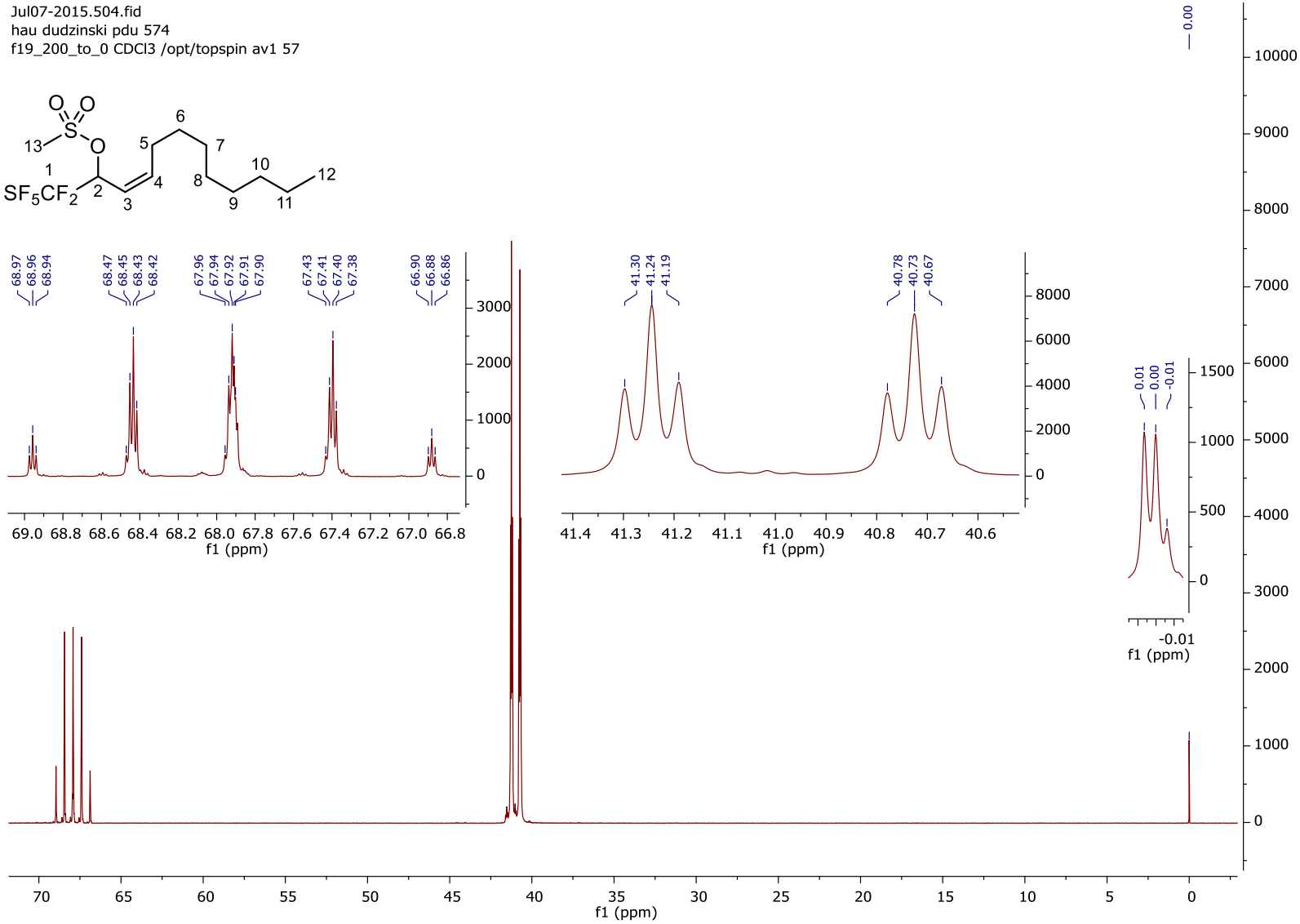
^{1}H NMR spectrum of (*Z*)-1,1-Difluoro-1-(pentafluoro-λ^{6}-sulfanyl)dodec-3-en-2-yl methanesulfonate (**15**)



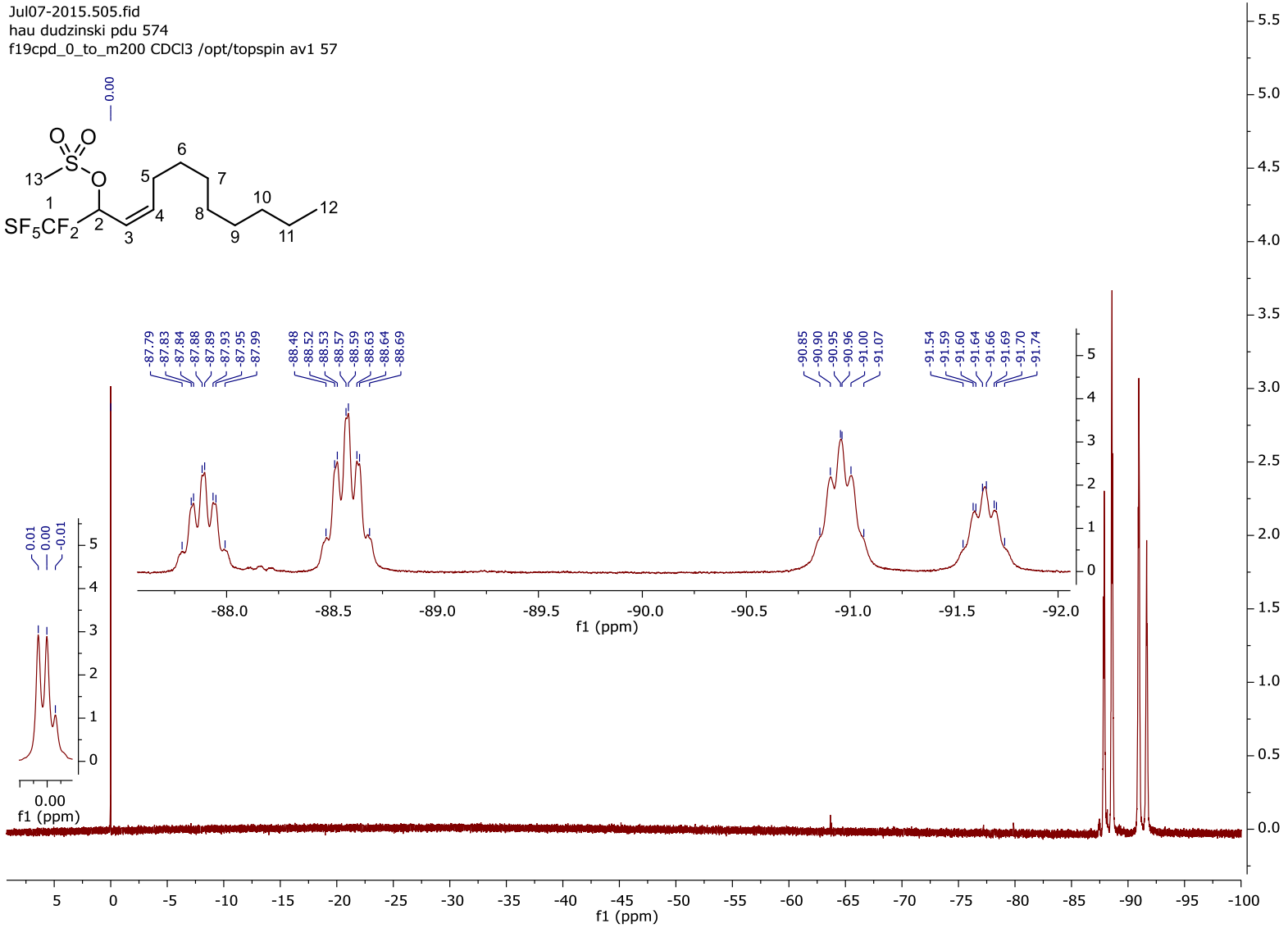
^{13}C NMR spectrum of (*Z*)-1,1-Difluoro-1-(pentafluoro-λ^{6}-sulfanyl)dodec-3-en-2-yl methanesulfonate (**15**)



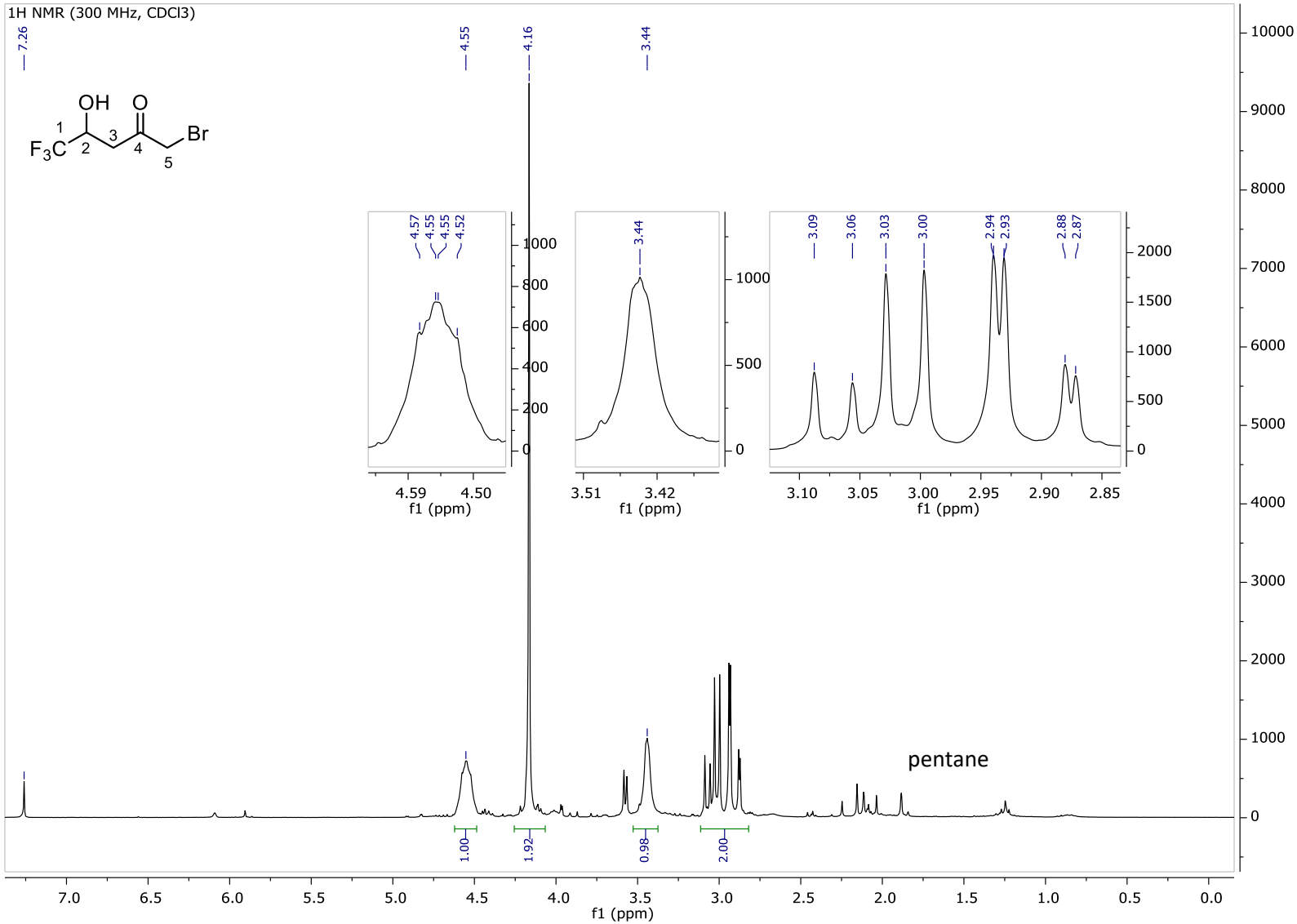
^{19}F NMR spectrum of (*Z*)-1,1-Difluoro-1-(pentafluoro-λ^{6}-sulfanyl)dodec-3-en-2-yl methanesulfonate (**15**) – positive part



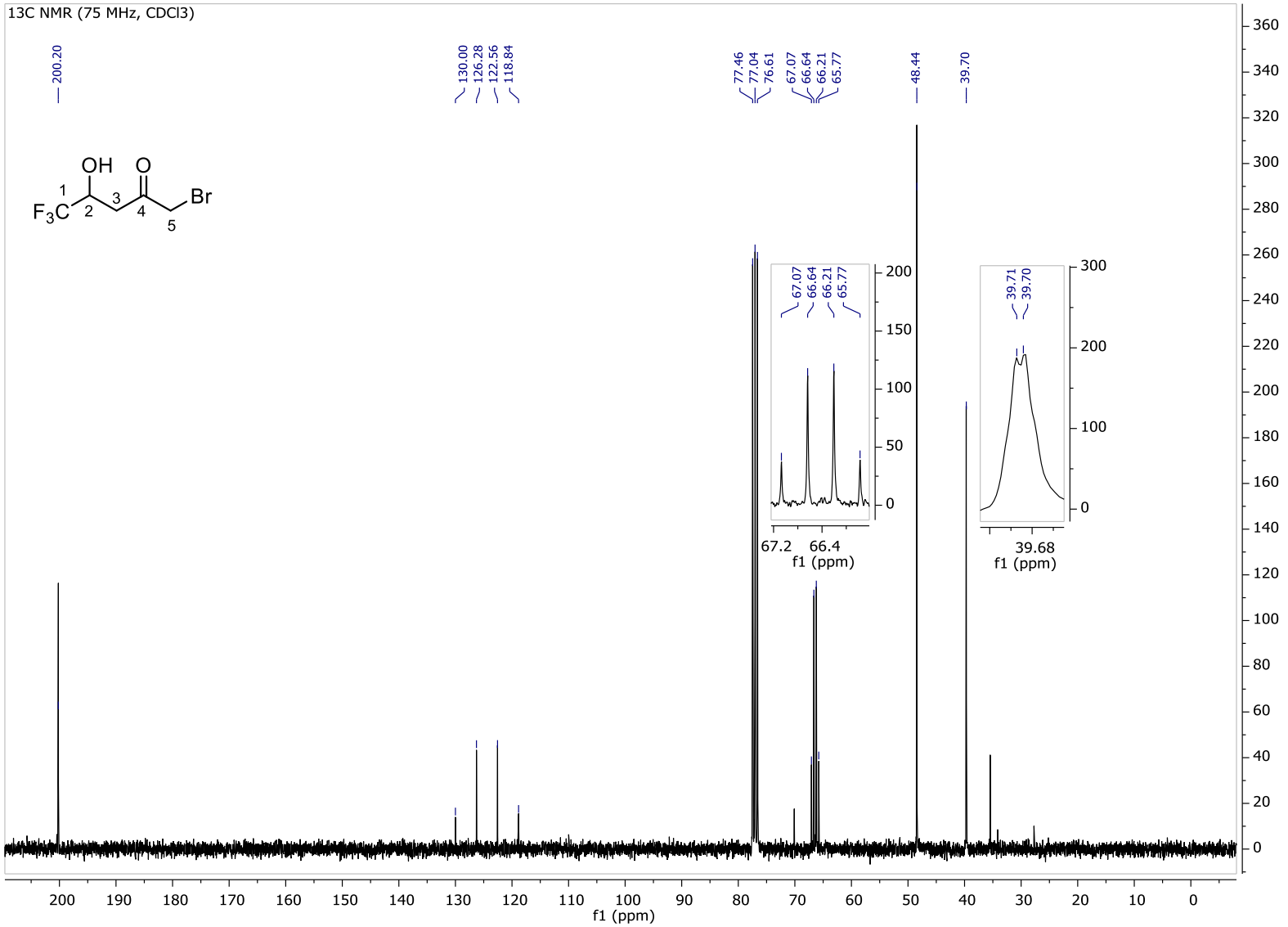
^{19}F NMR spectrum of (*Z*)-1,1-Difluoro-1-(pentafluoro-λ^{6}-sulfanyl)dodec-3-en-2-yl methanesulfonate (**15**) – negative part



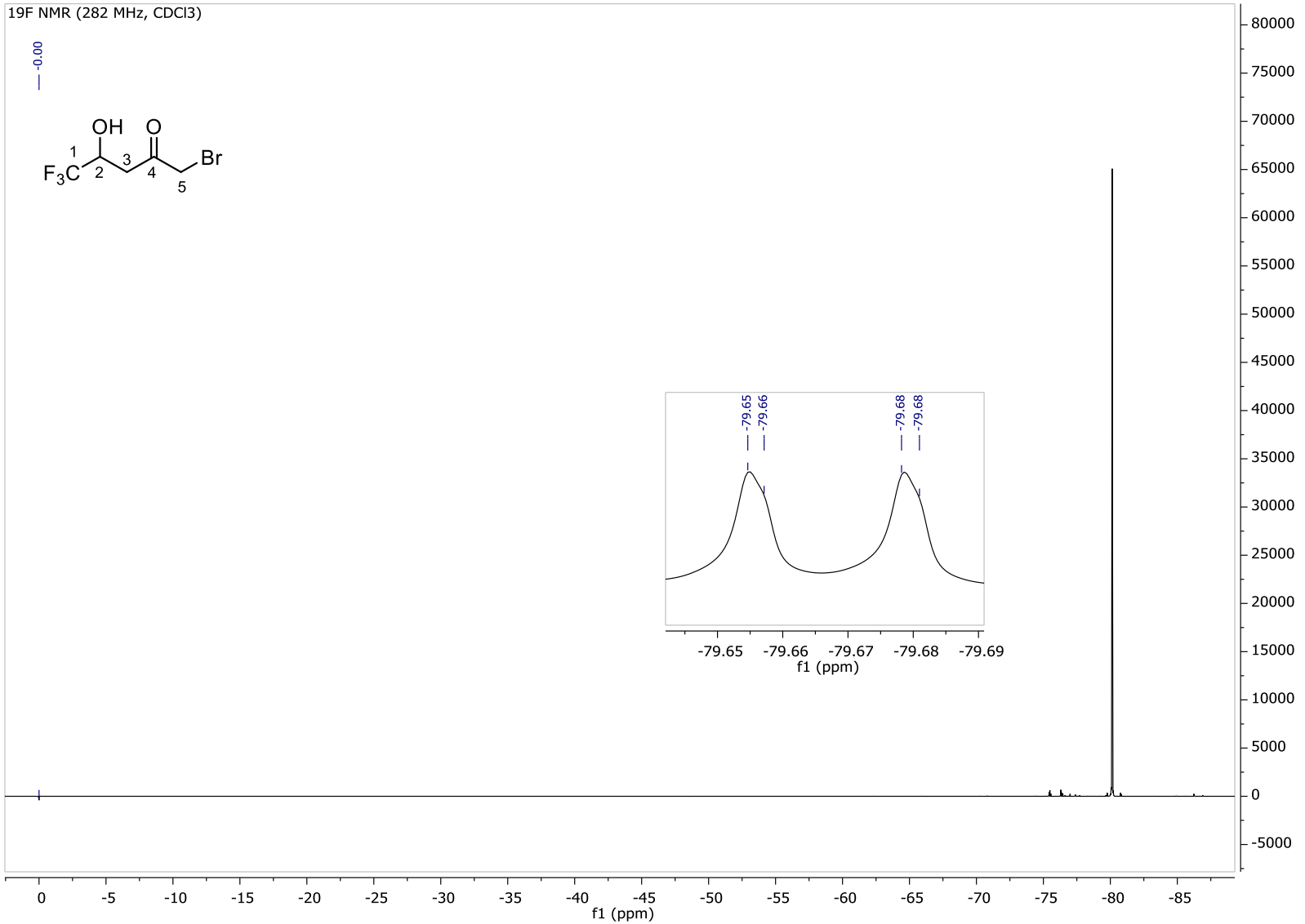
^{1}H NMR spectrum of 1-Bromo-5,5,5-trifluoro-4-hydroxypentan-2-one (**24**)



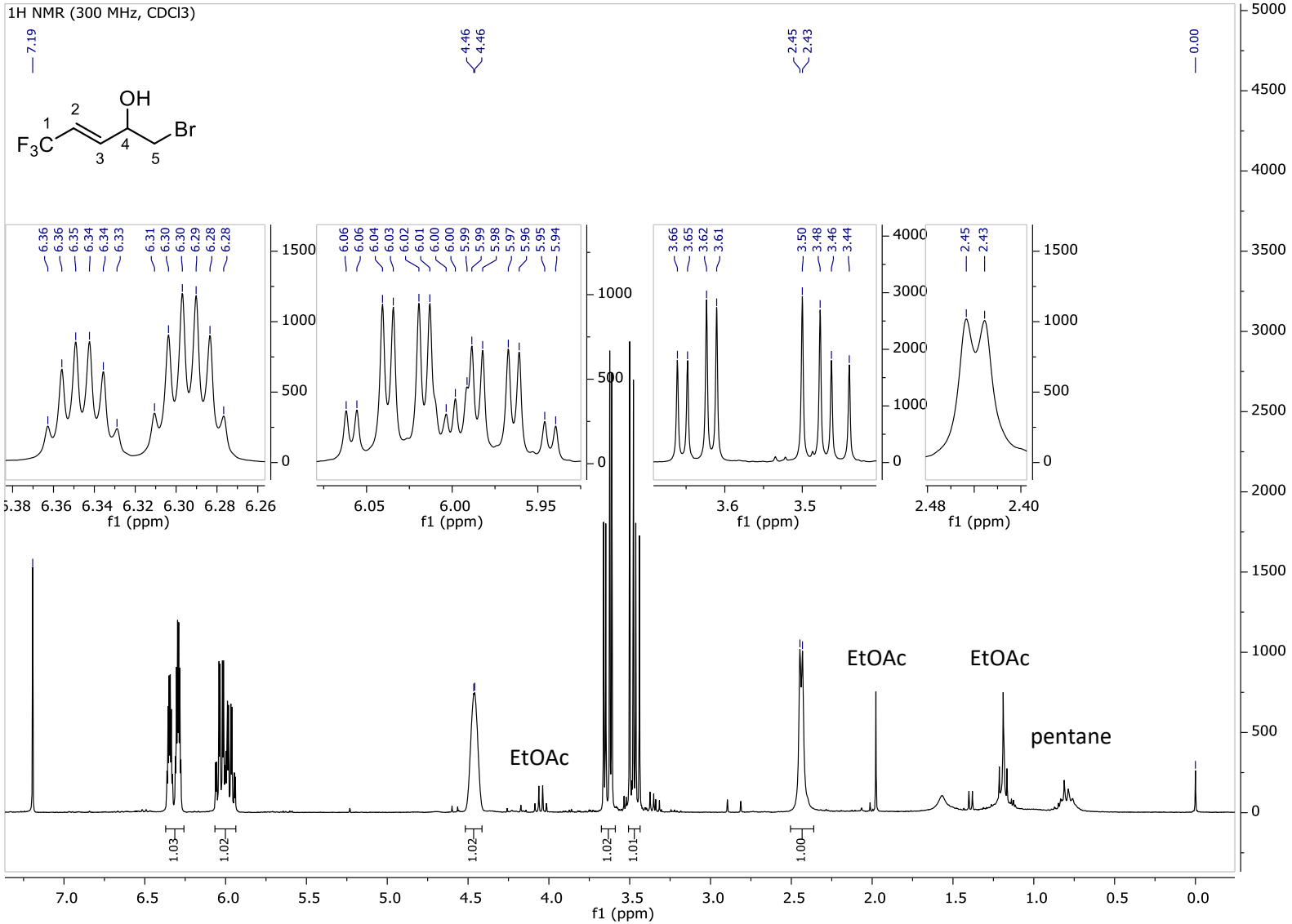
^{13}C NMR spectrum of 1-Bromo-5,5,5-trifluoro-4-hydroxypentan-2-one (**24**)



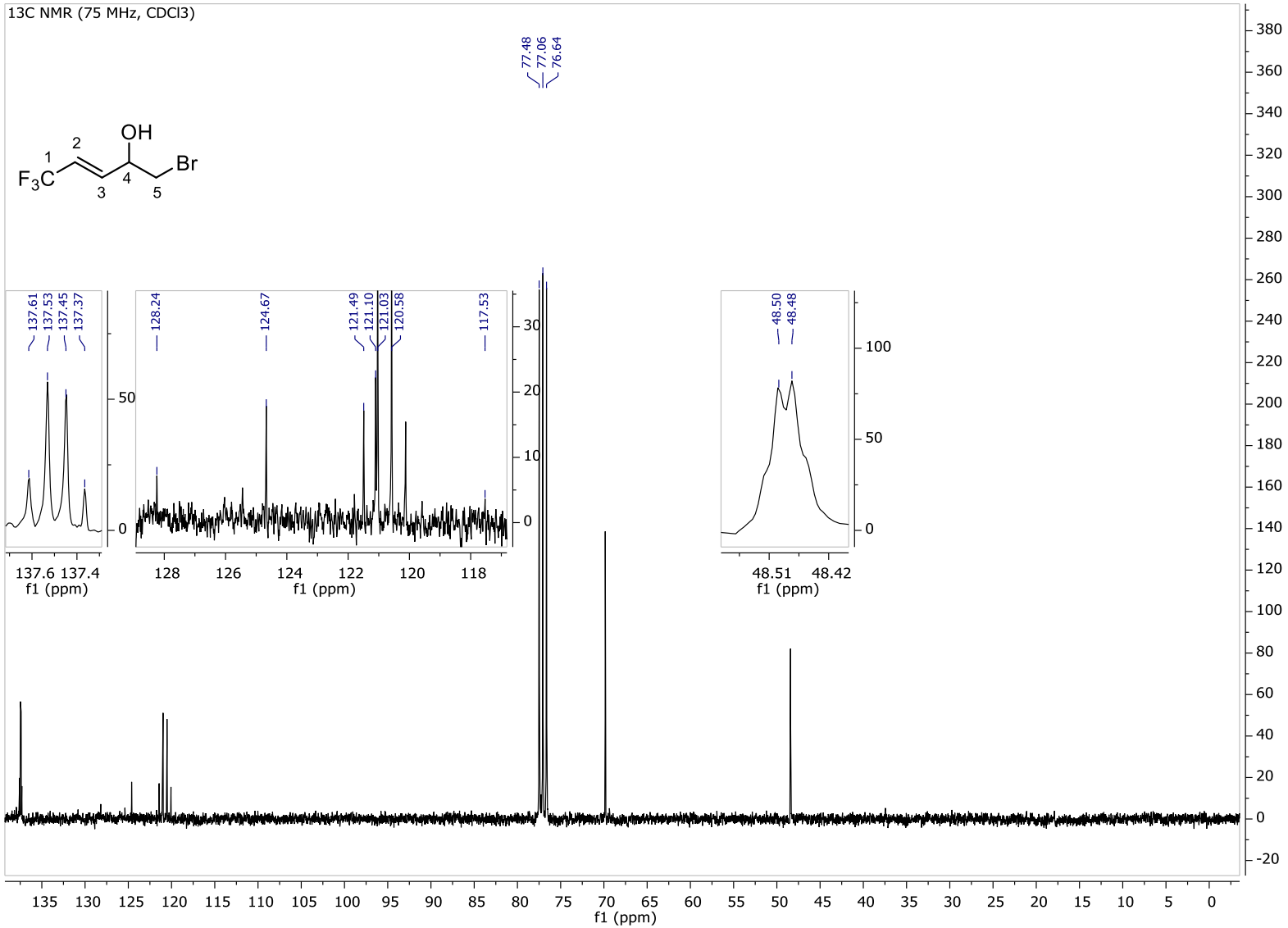
^{19}F NMR spectrum of 1-Bromo-5,5,5-trifluoro-4-hydroxypentan-2-one (**24**)



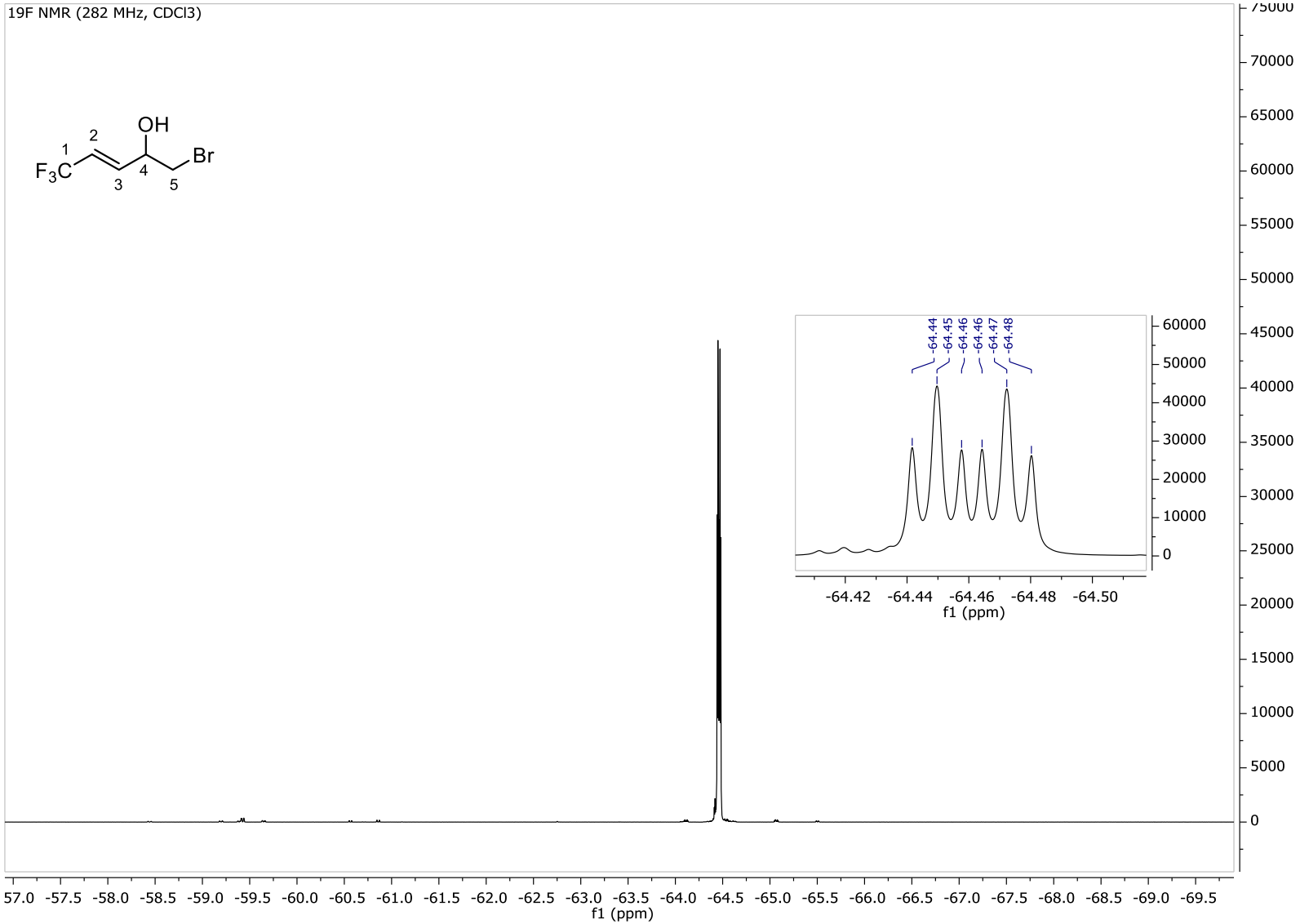
^{1}H NMR spectrum of (*E*)-1-Bromo-5,5,5-trifluoropent-3-en-2-ol (**20**)



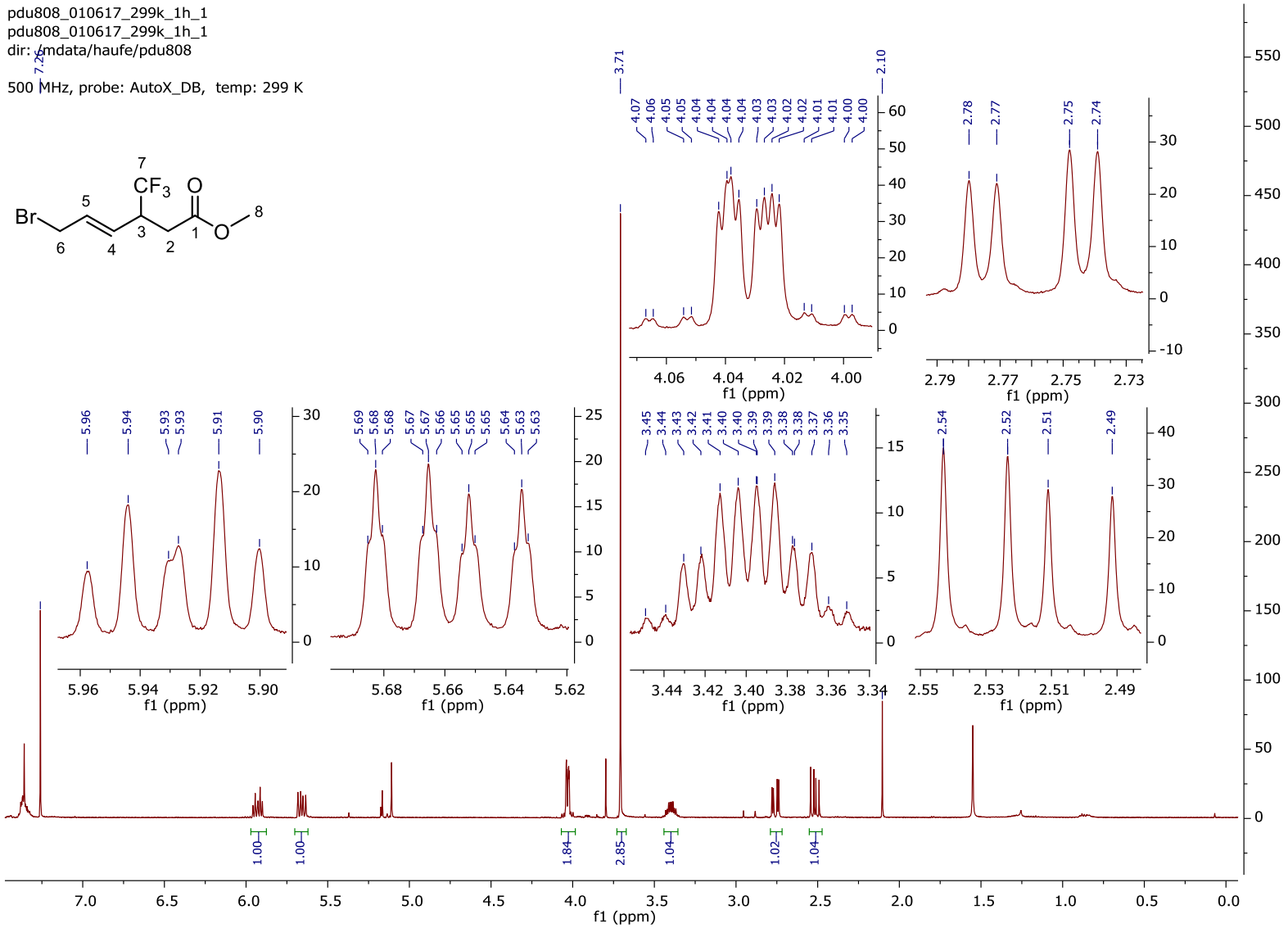
^{13}C NMR spectrum of (*E*)-1-Bromo-5,5,5-trifluoropent-3-en-2-ol (**20**)



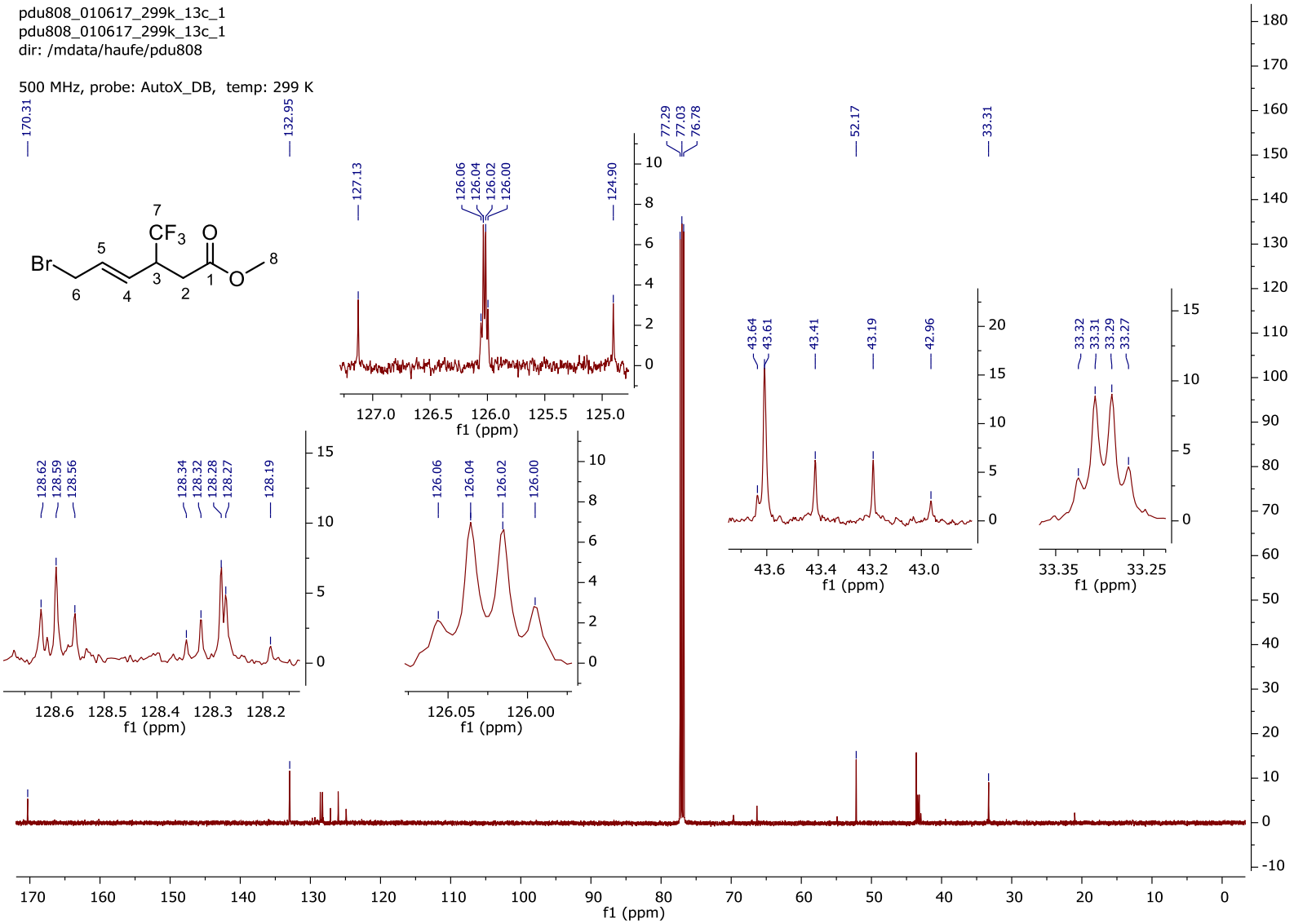
^{19}F NMR spectrum of (*E*)-1-Bromo-5,5,5-trifluoropent-3-en-2-ol (**20**)



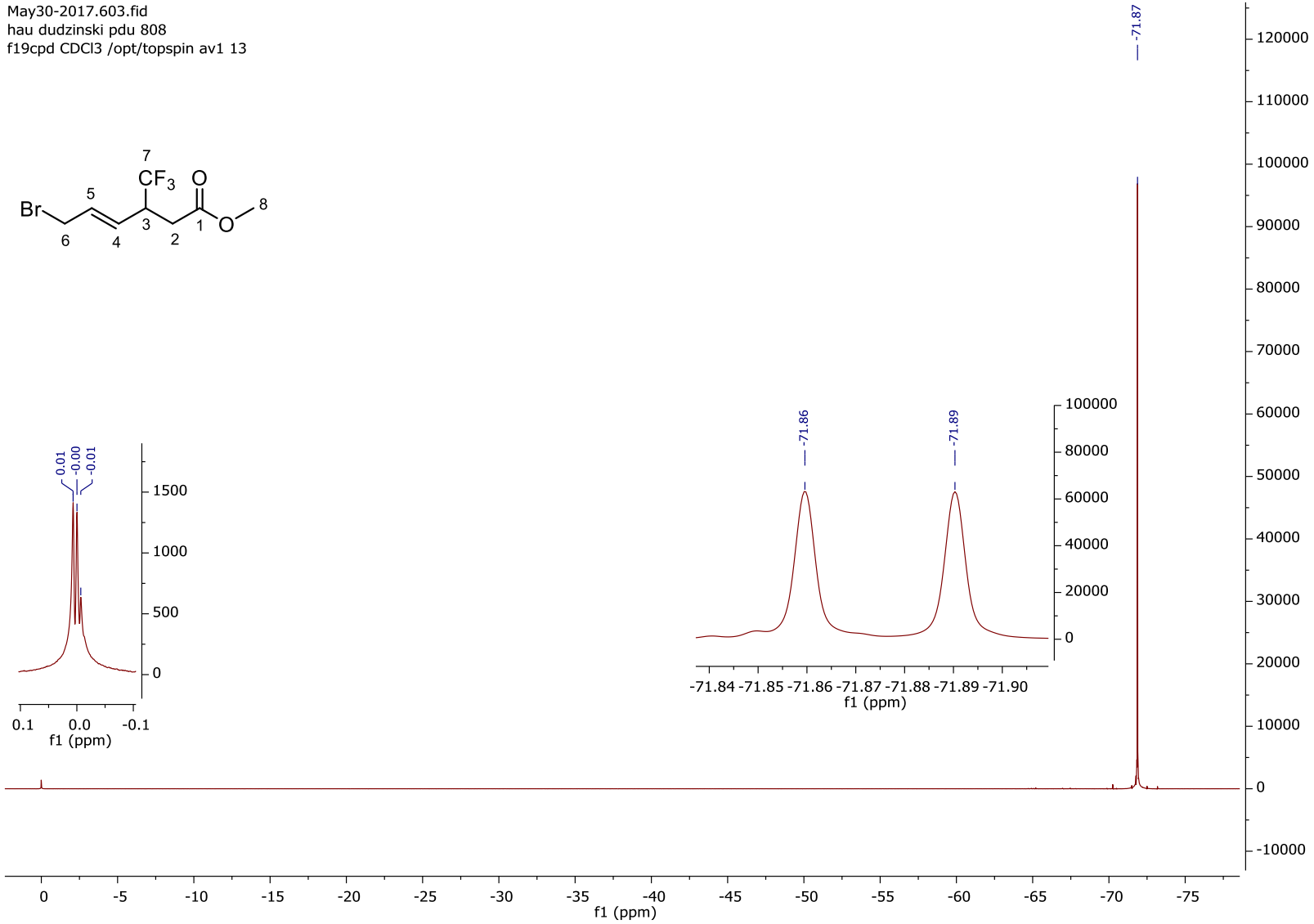
^{1}H NMR spectrum of compound **21**



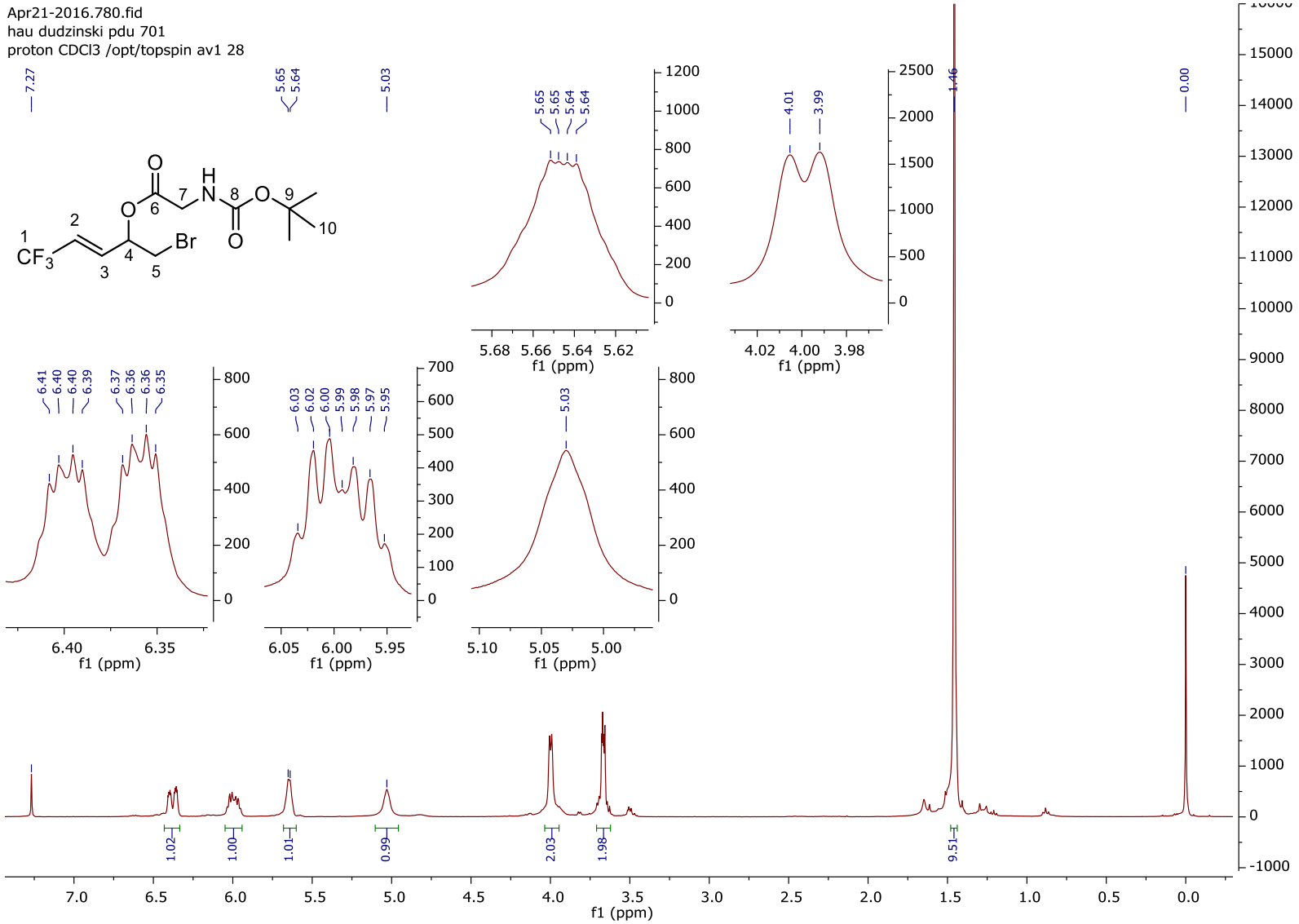
^{13}C NMR spectrum of compound **21**



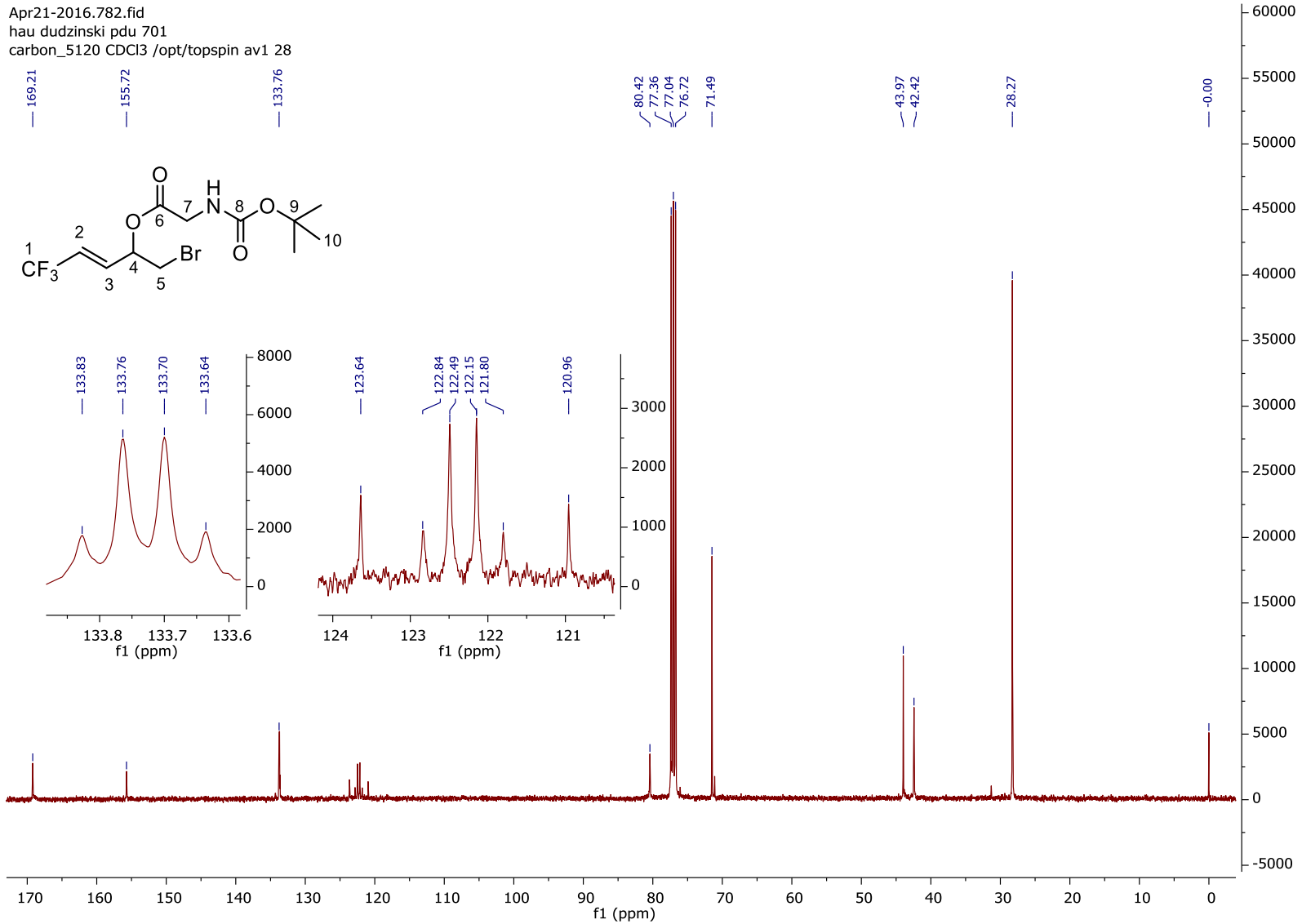
^{19}F NMR spectrum of compound **21**



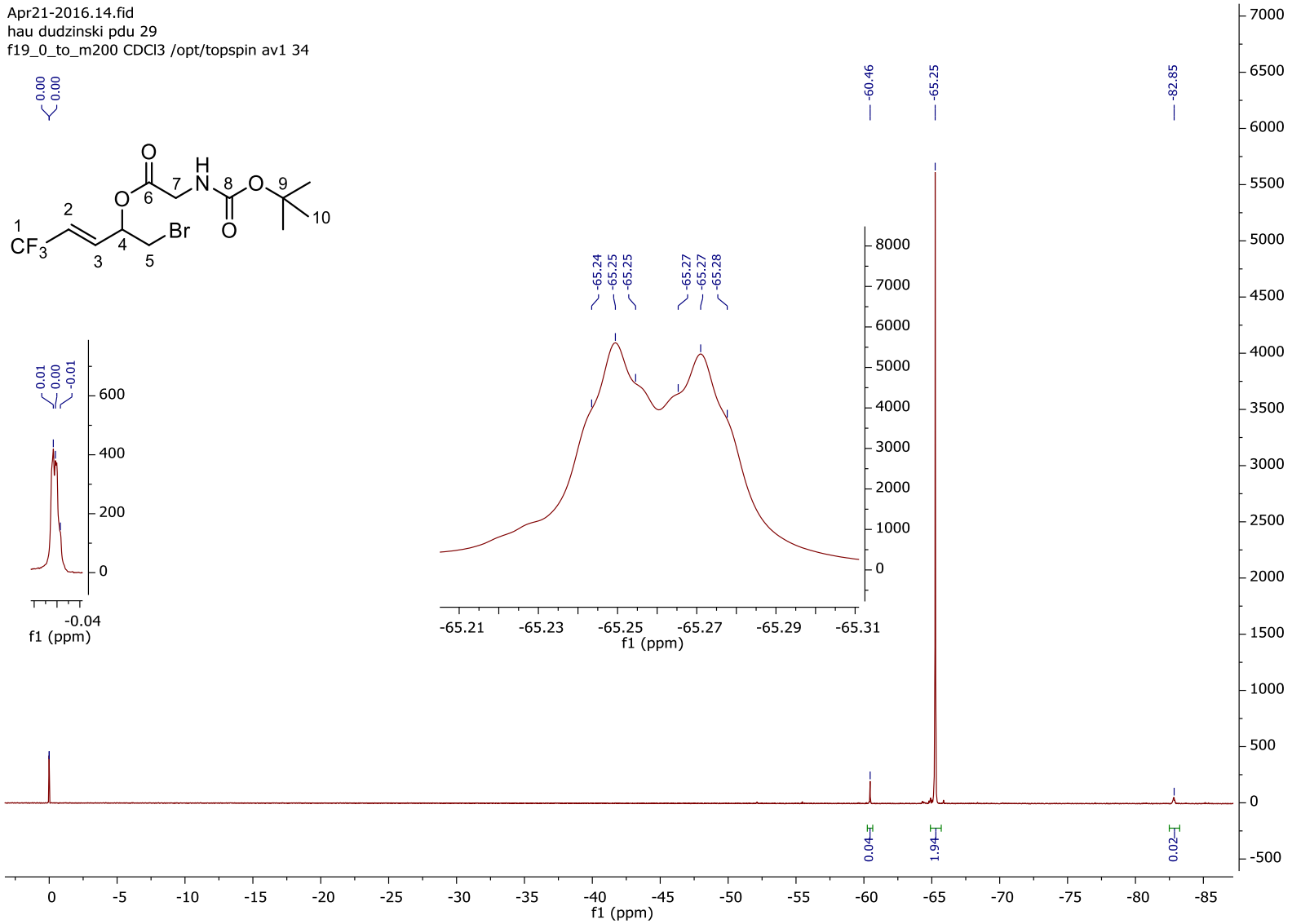
^{1}H NMR spectrum of compound **27**



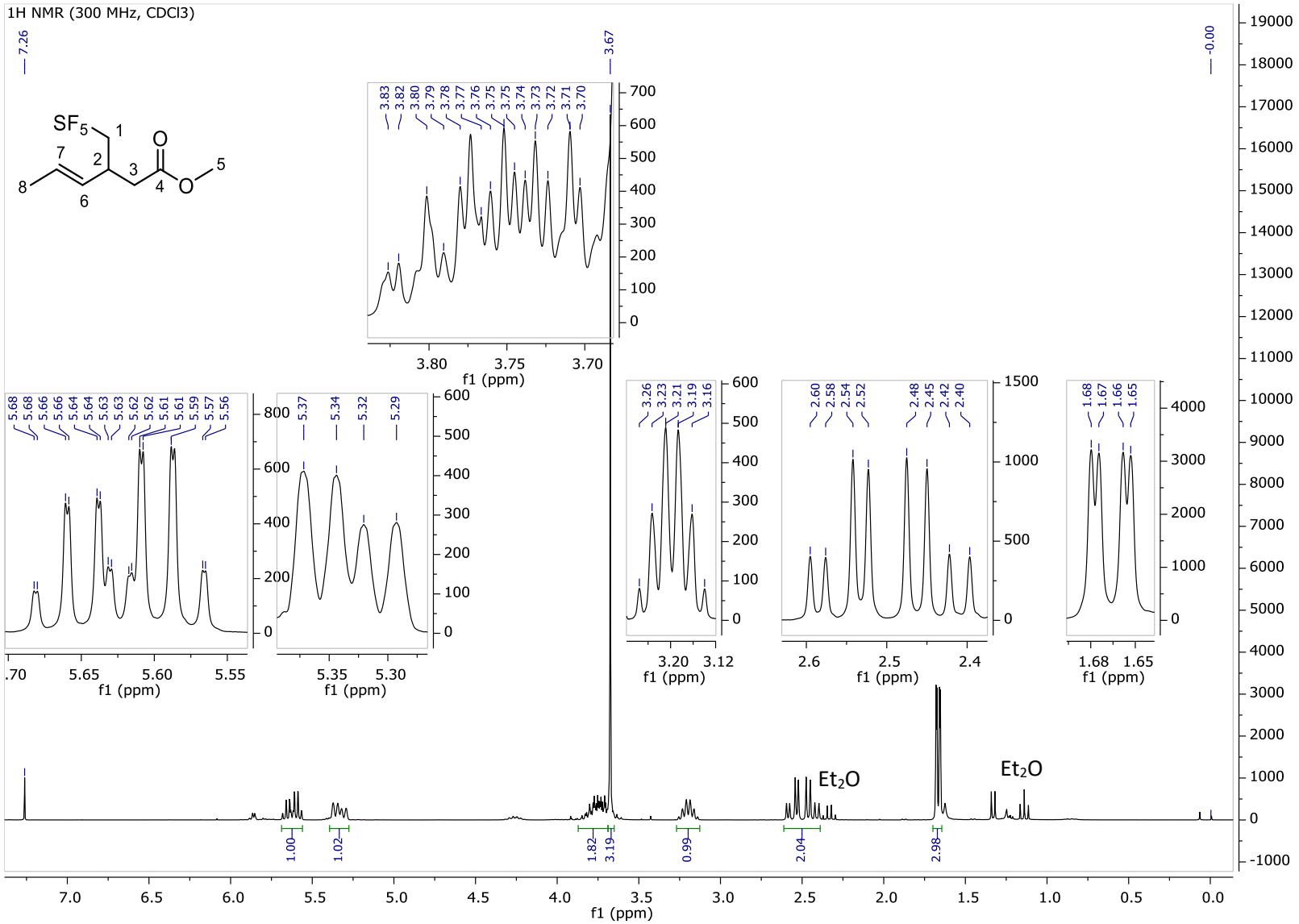
^{13}C NMR spectrum of compound **27**



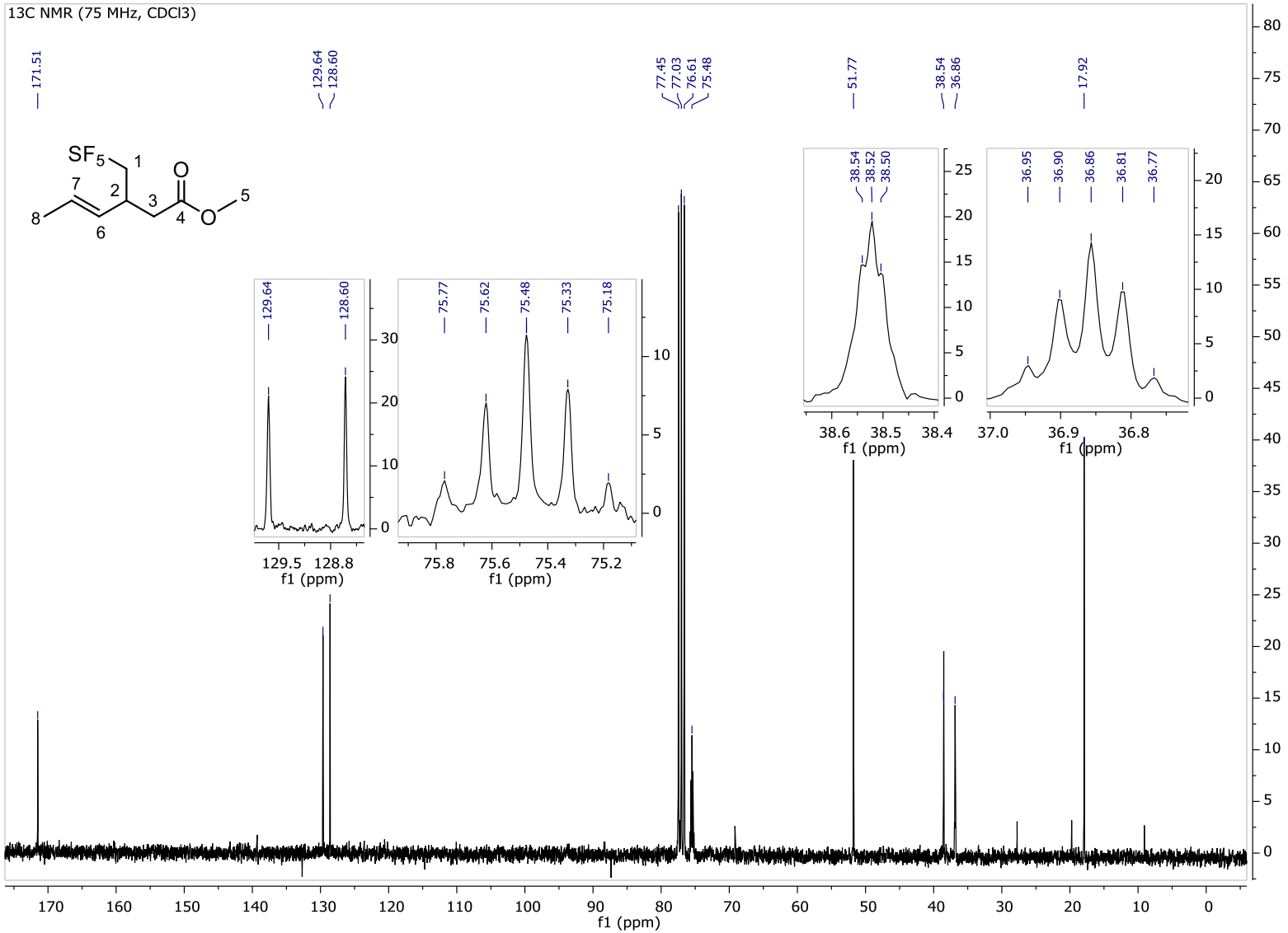
^{19}F NMR spectrum of compound **27**



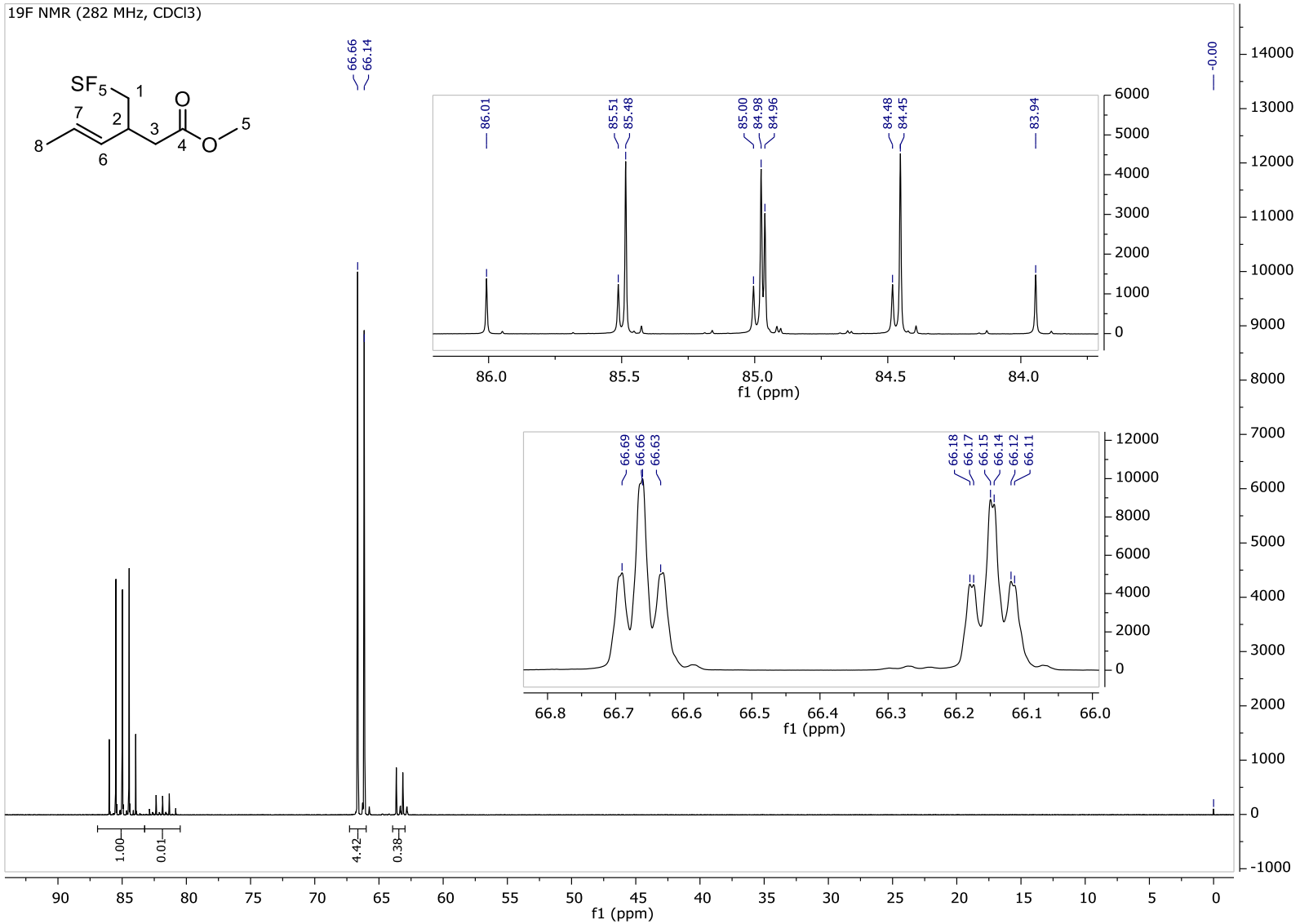
^{1}H NMR spectrum of compound **29a**



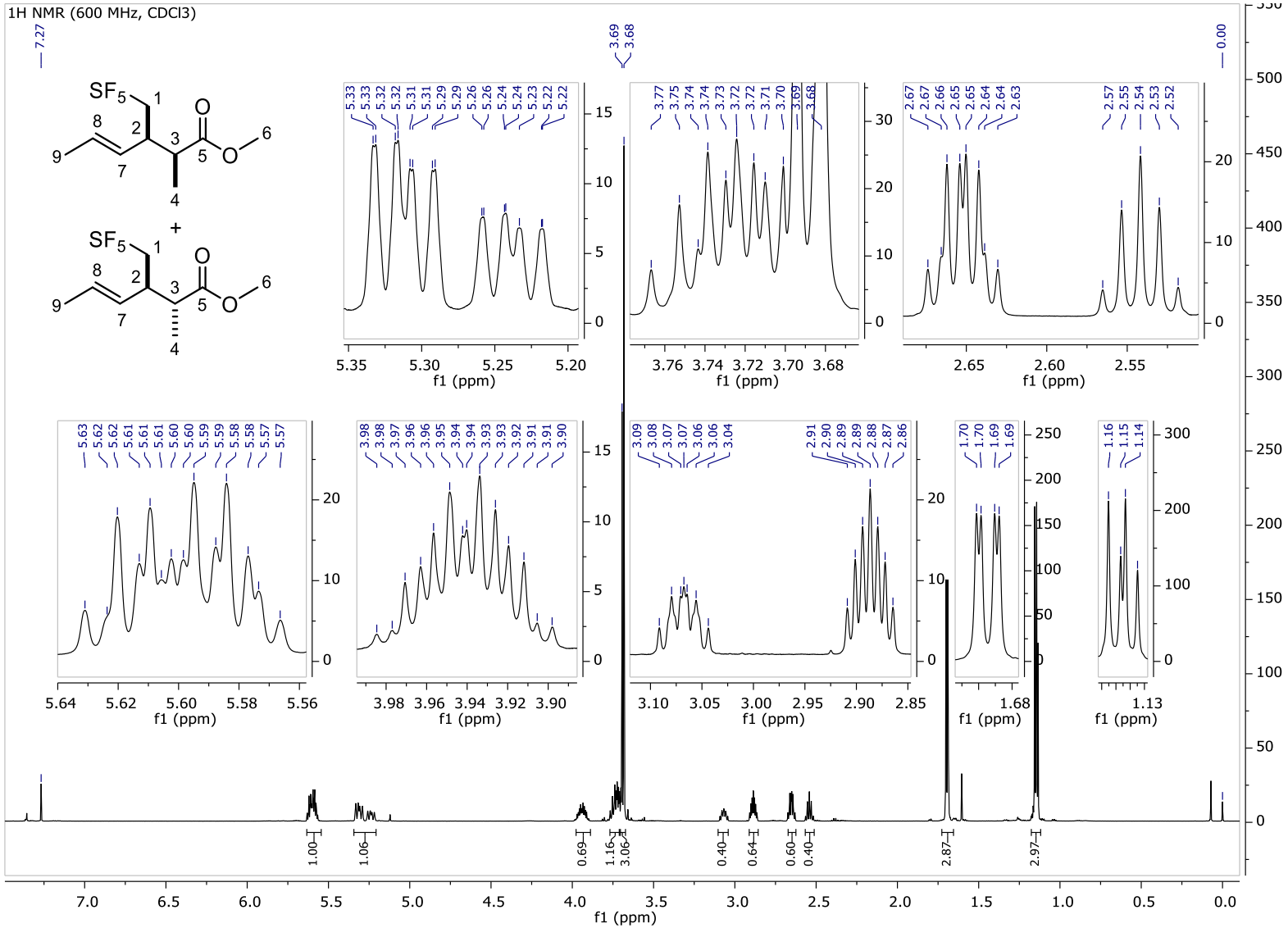
^{13}C NMR spectrum of compound **29a**



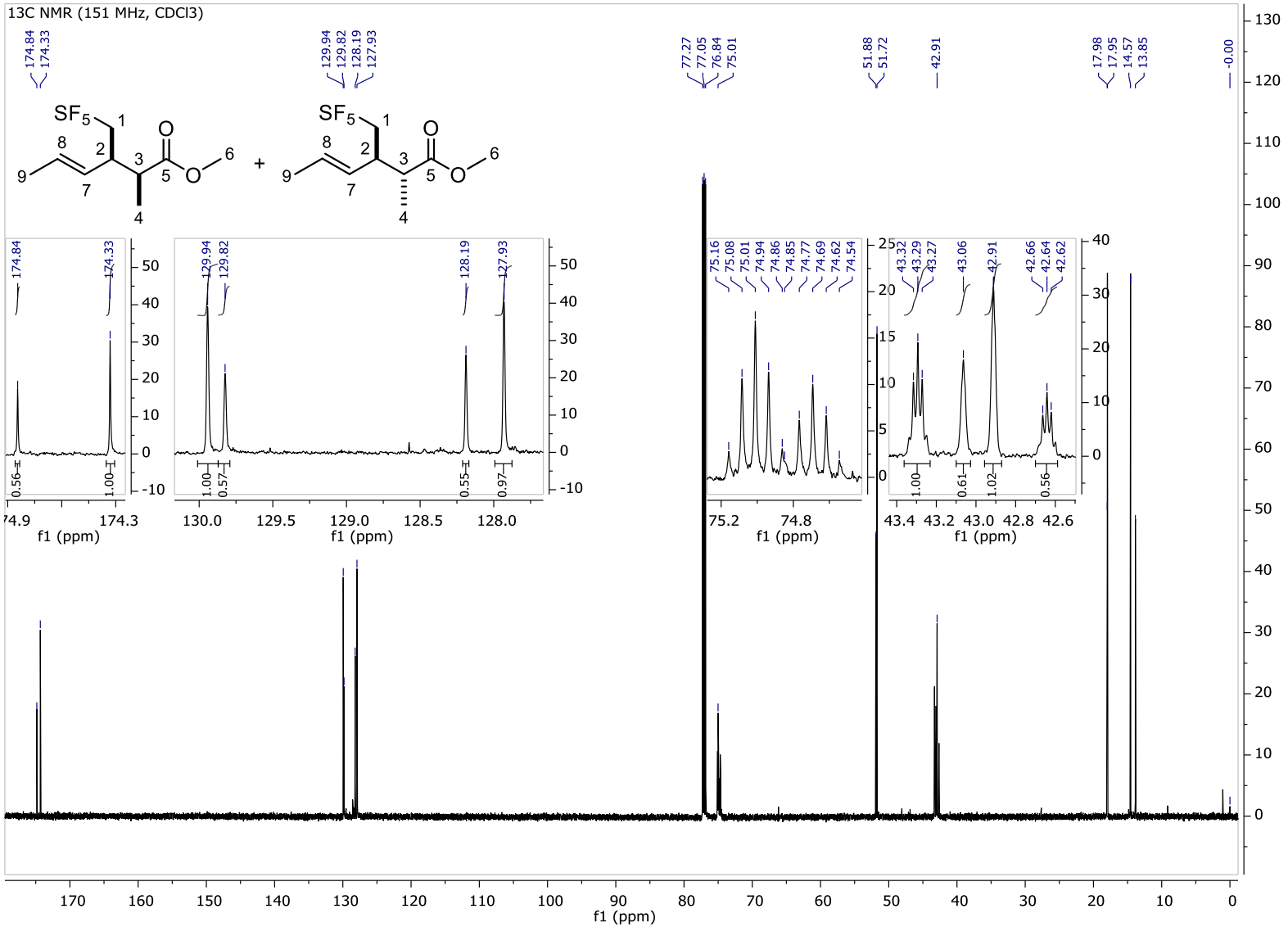
^{19}F NMR spectrum of compound **29a**



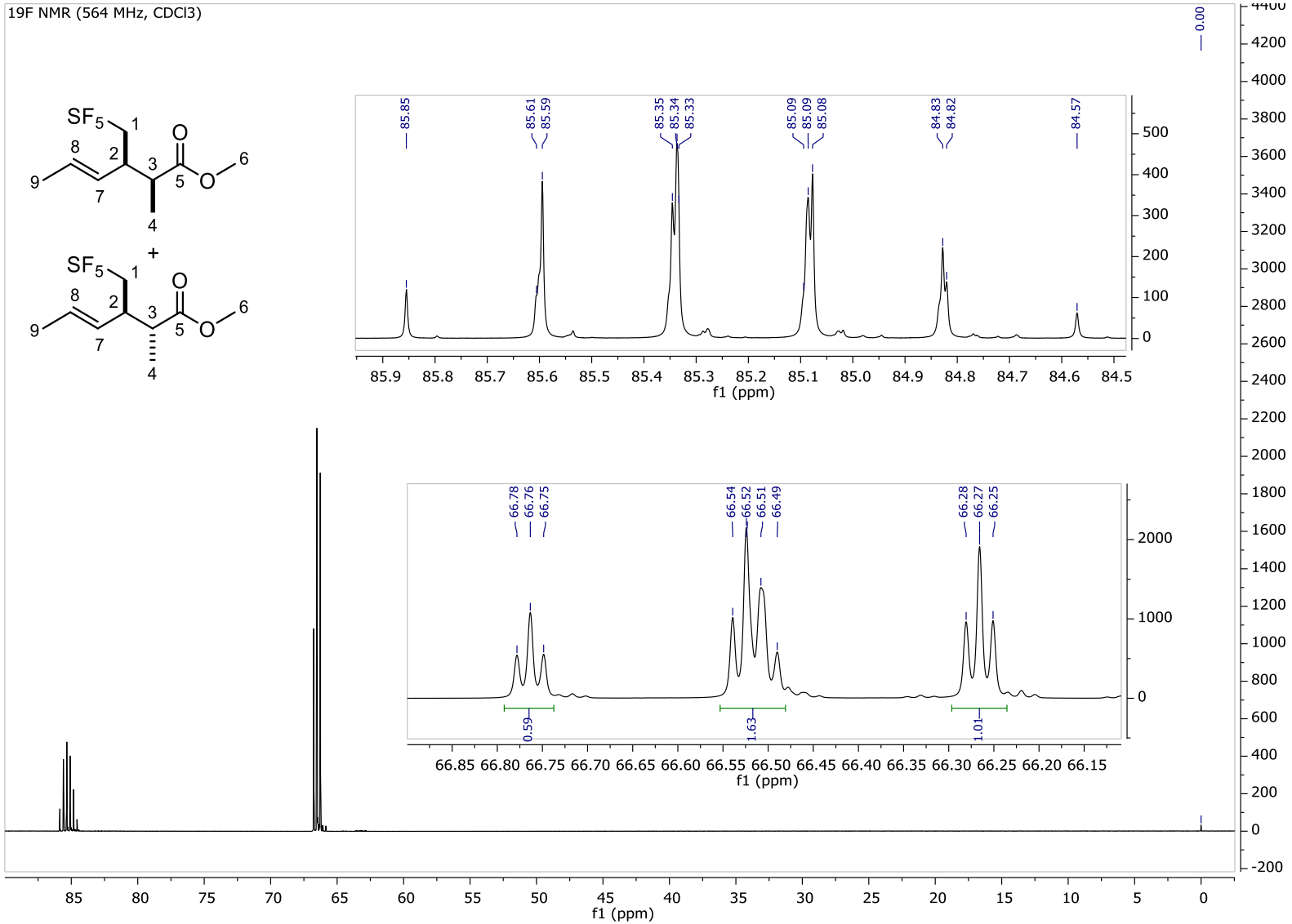
[1]H NMR spectrum of compound **29b**



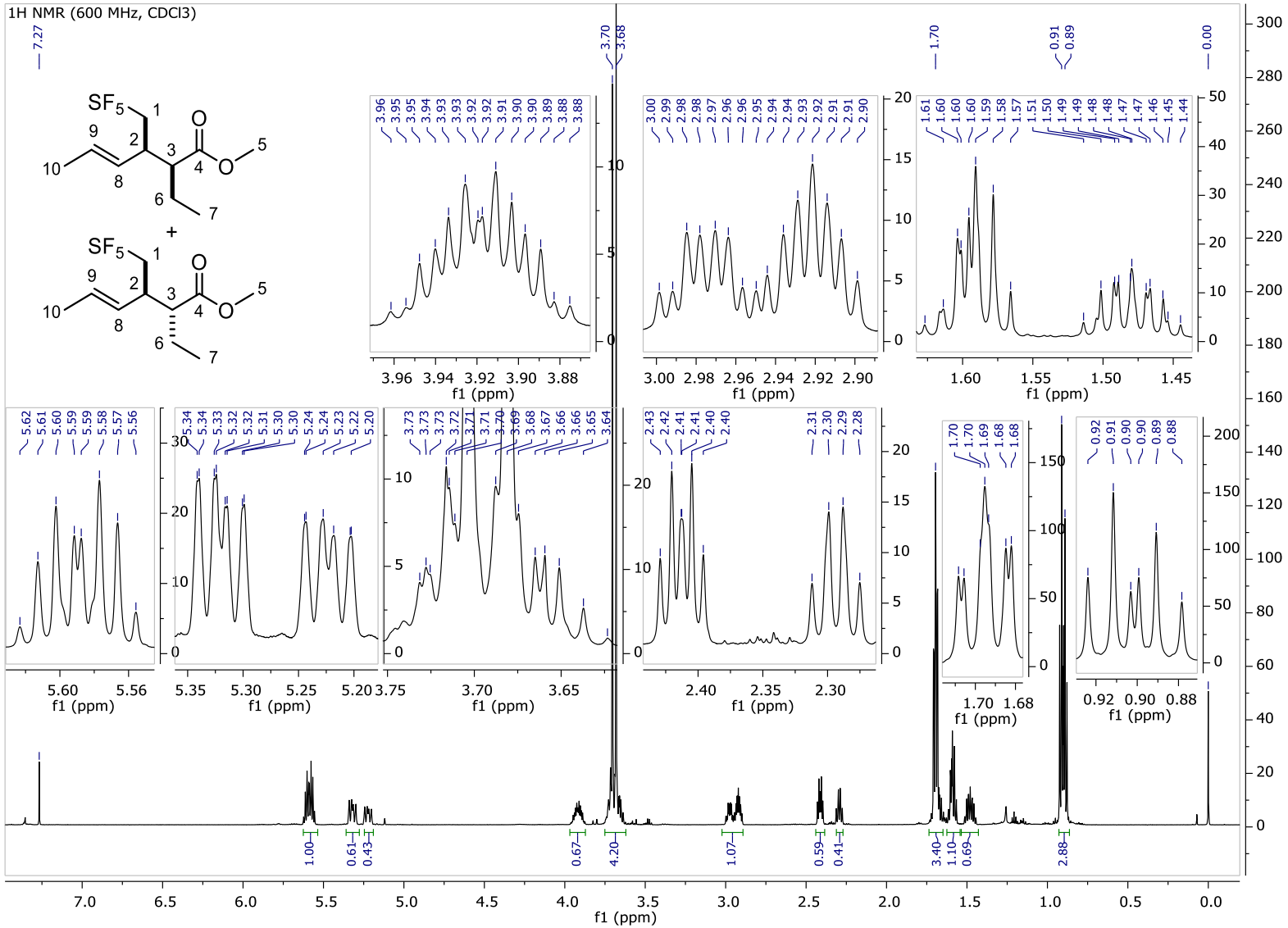
^{13}C NMR spectrum of compound **29b**



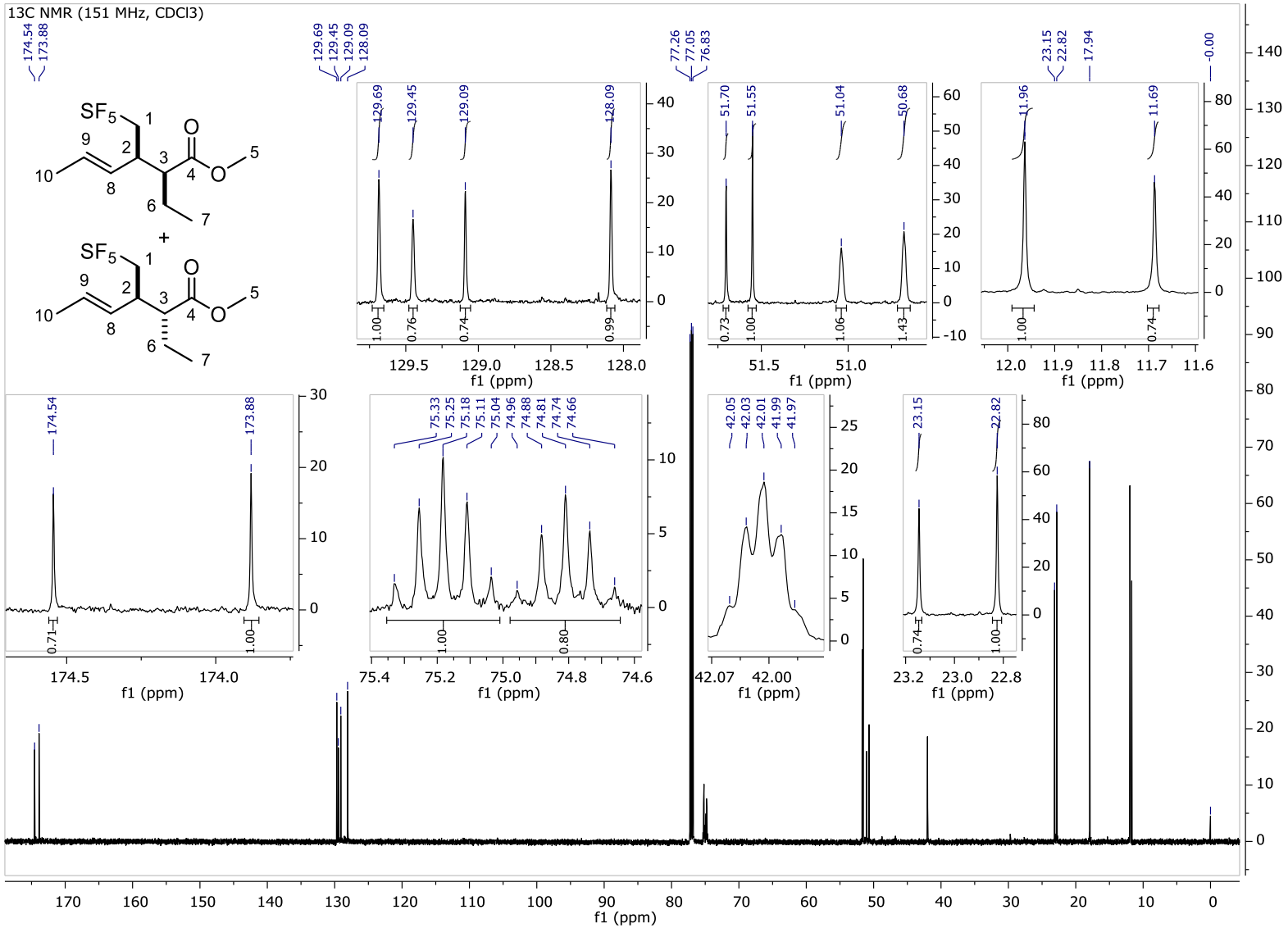
^{19}F NMR spectrum of compound **29b**



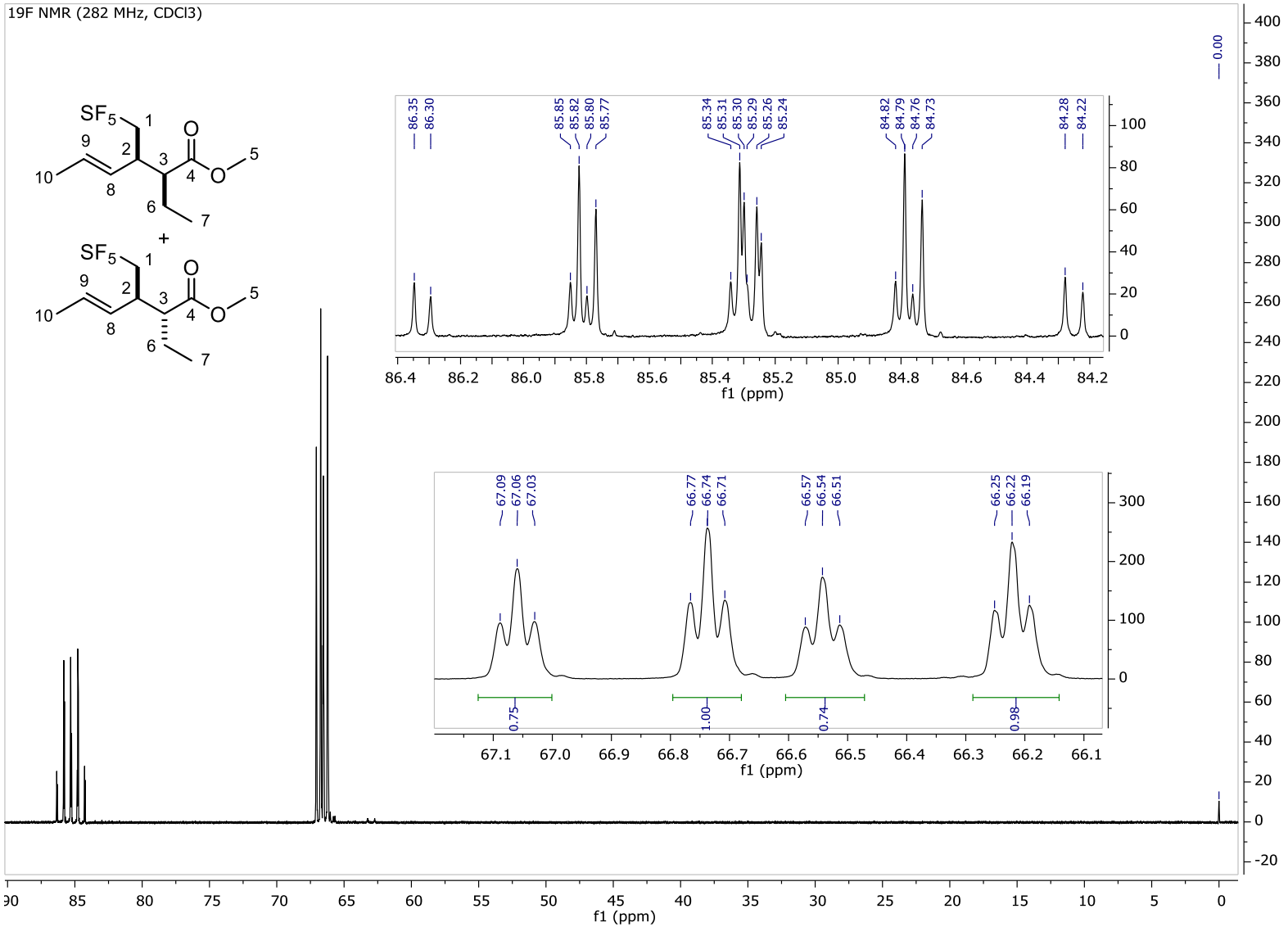
^{1}H NMR spectrum of compound **29c**



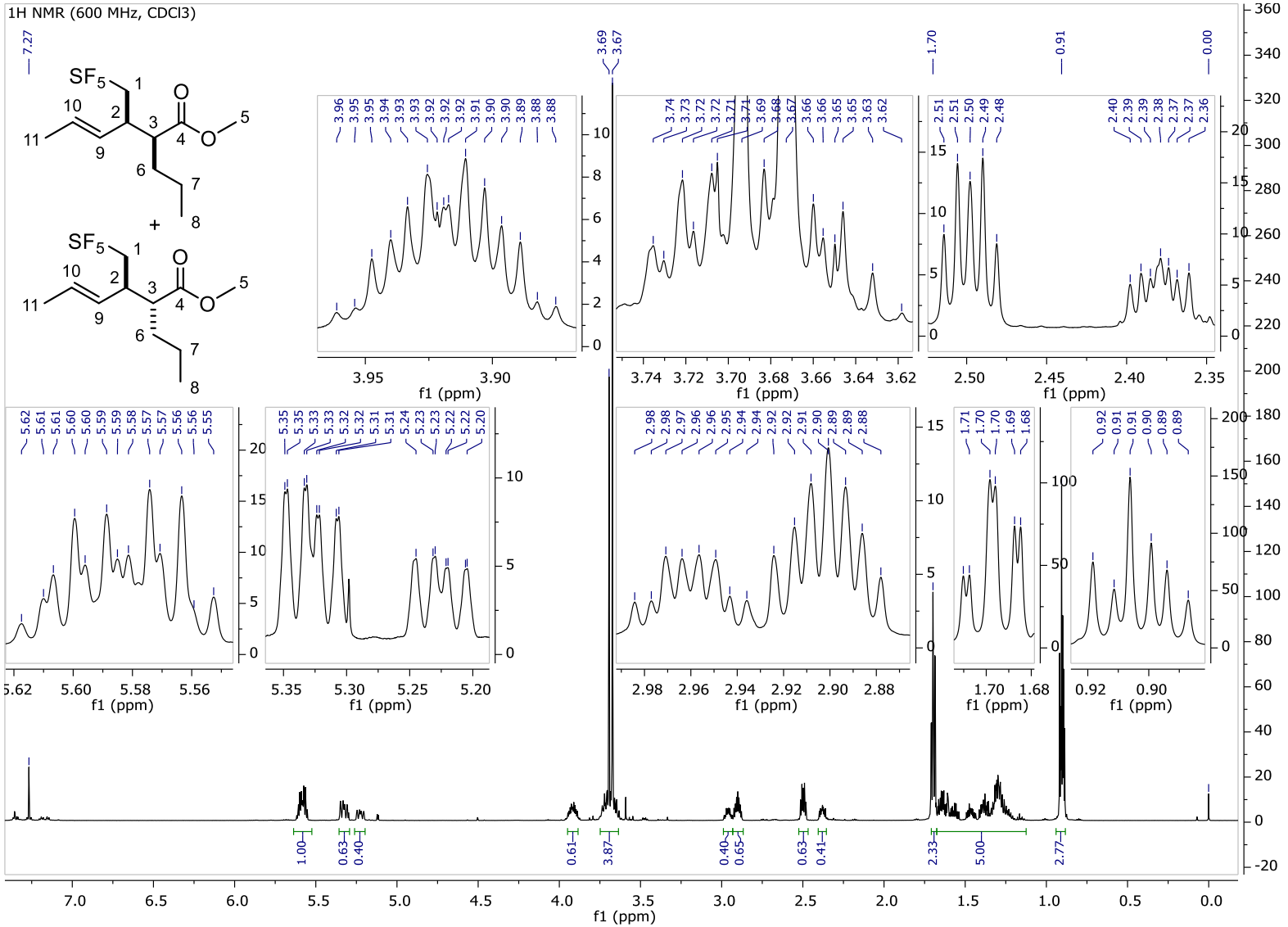
^{13}C NMR spectrum of compound **29c**



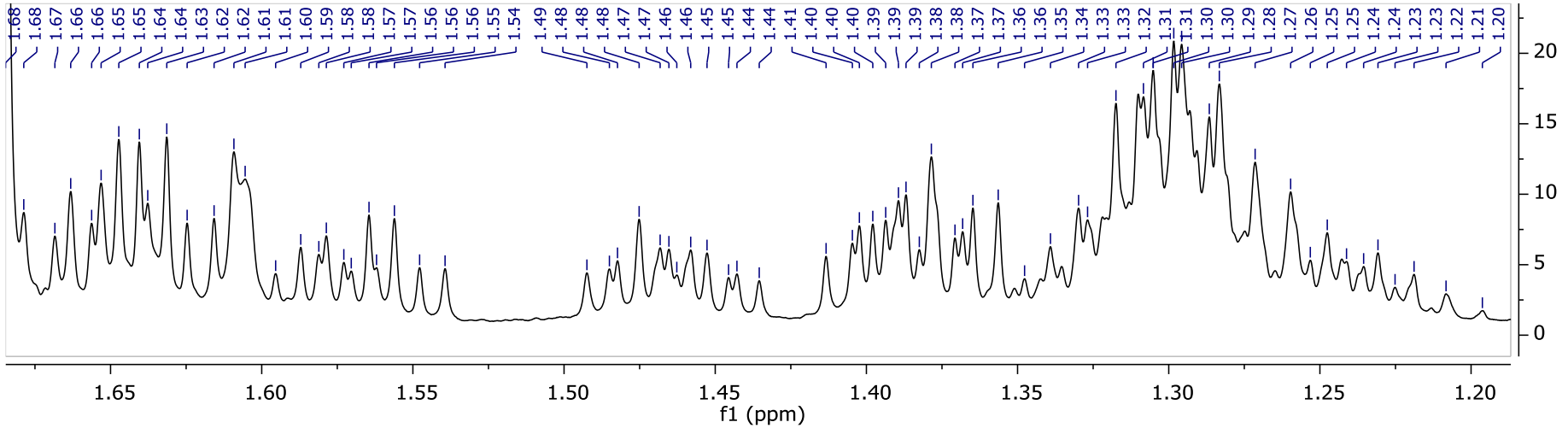
^{19}F NMR spectrum of compound **29c**



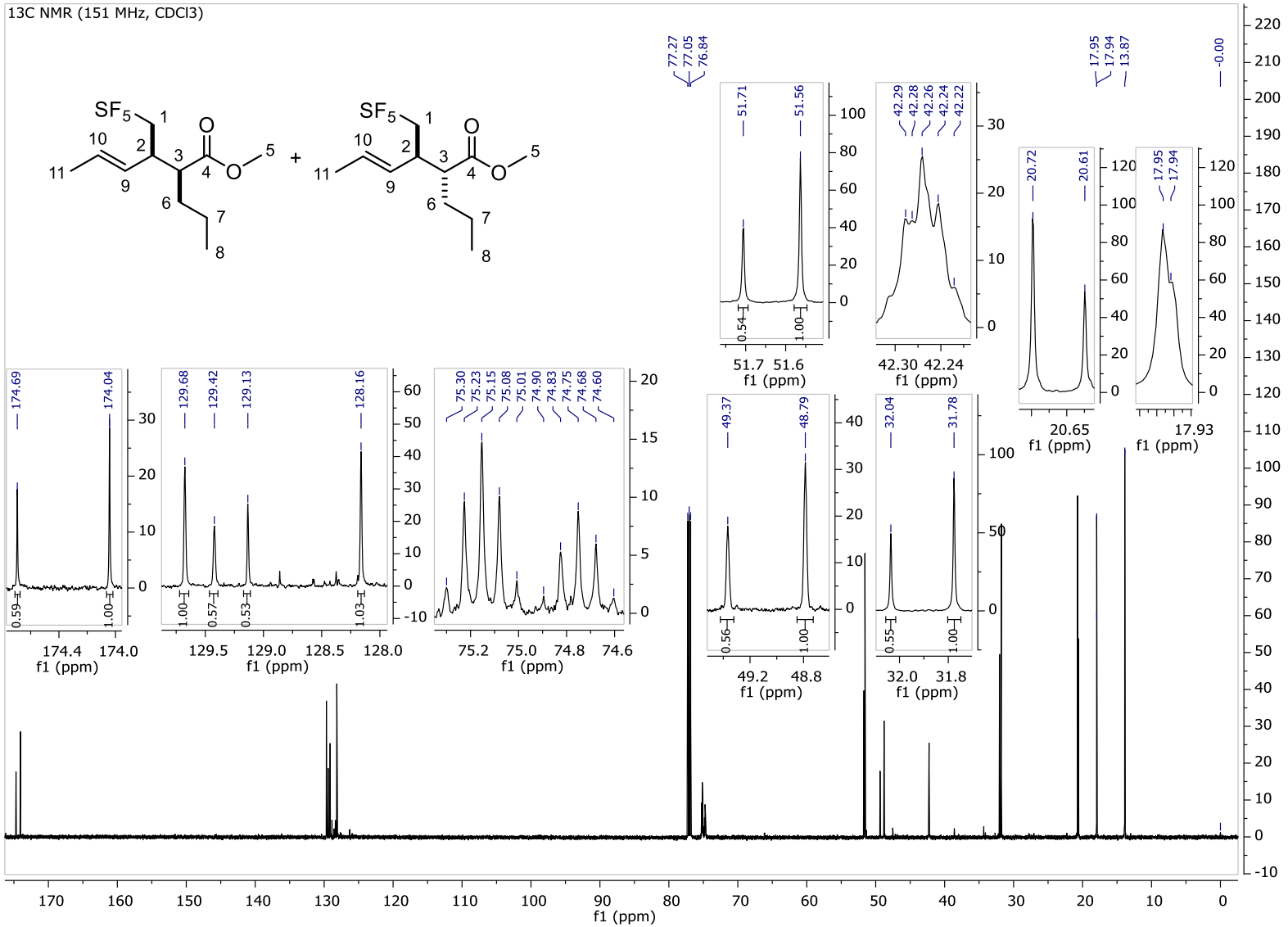
^{1}H NMR spectrum of compound **29d**



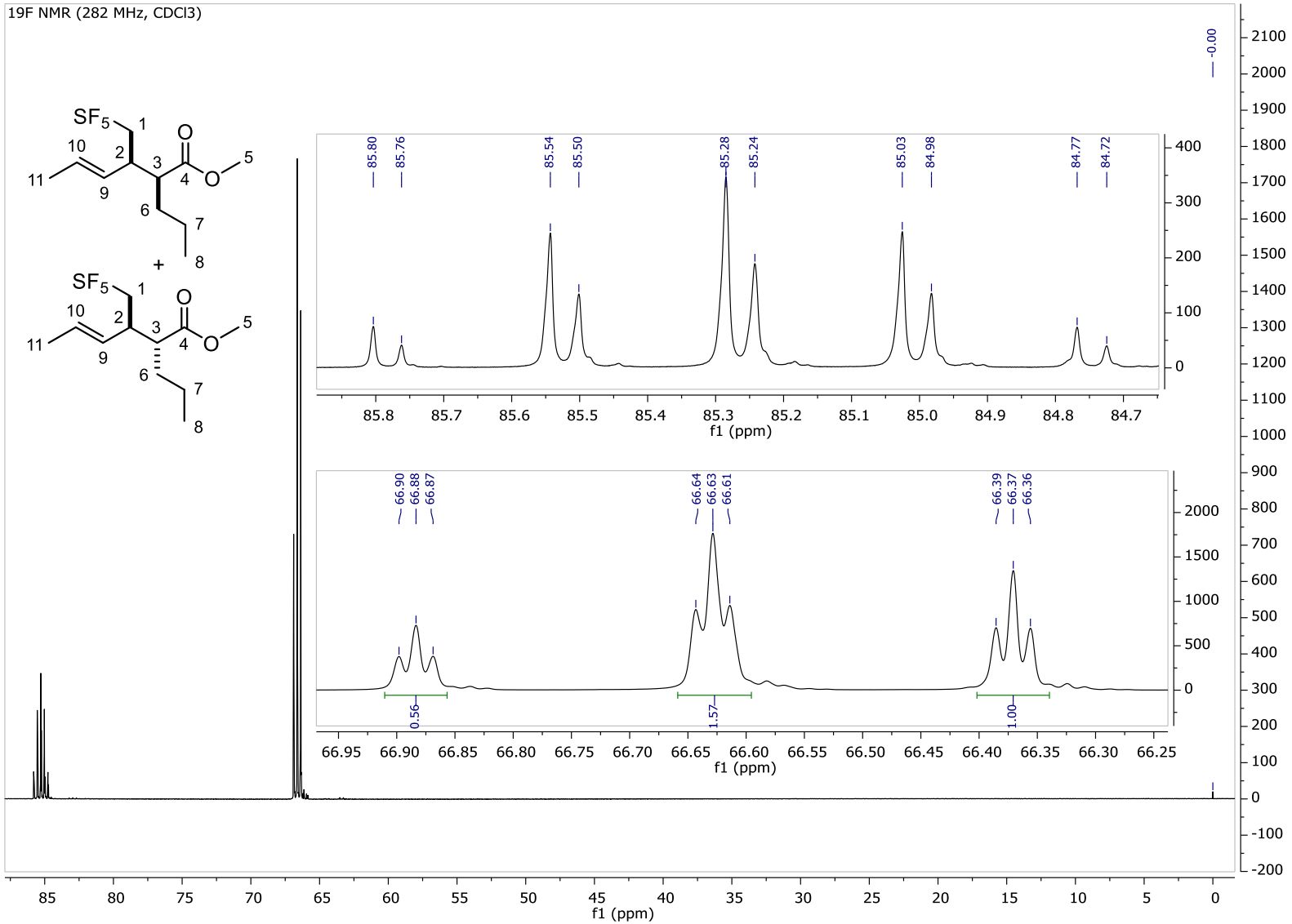
^{1}H NMR spectrum of compound **29d** (cutout 1.20 to 1.67 ppm)



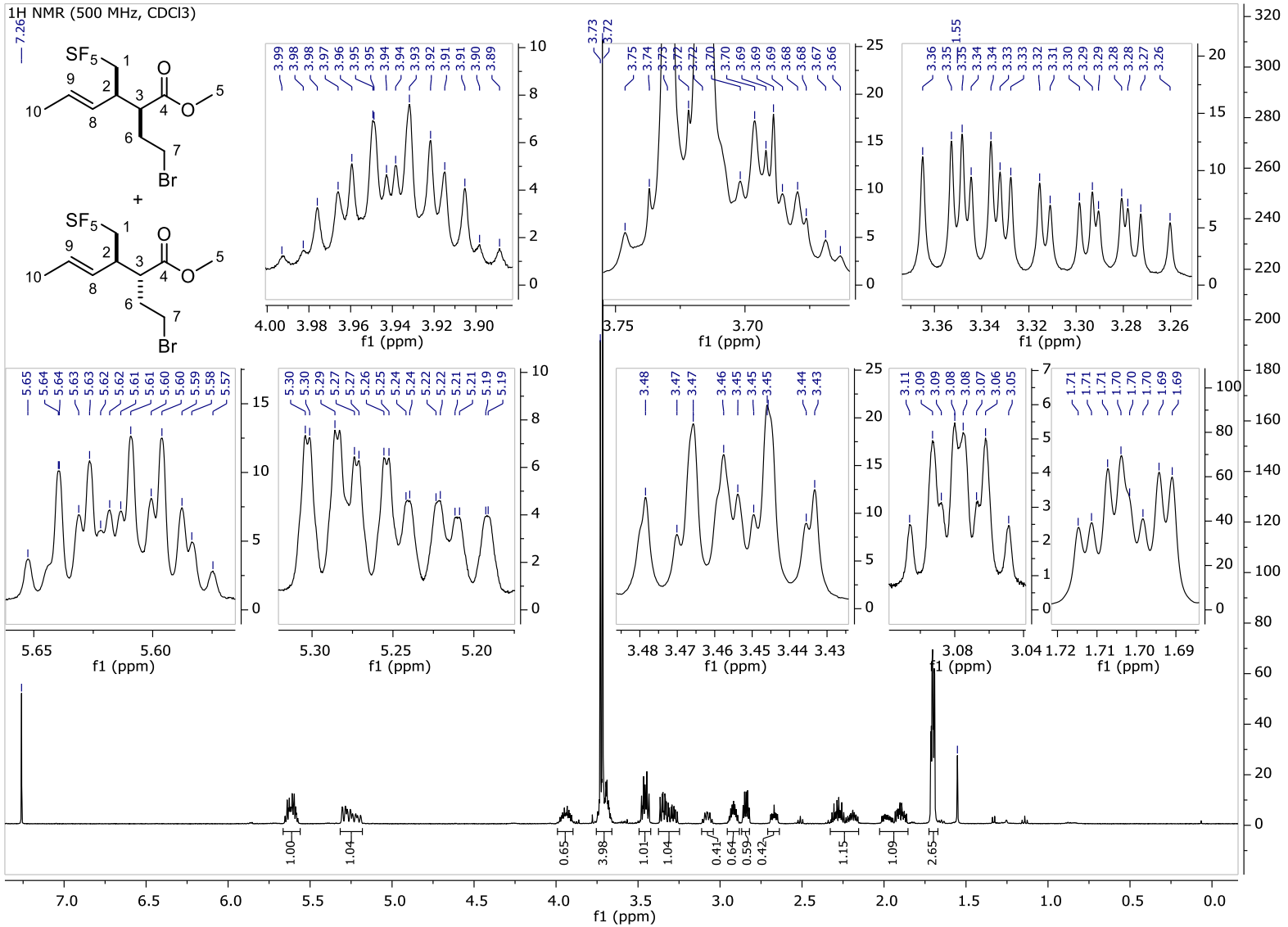
^{13}C NMR spectrum of compound **29d**



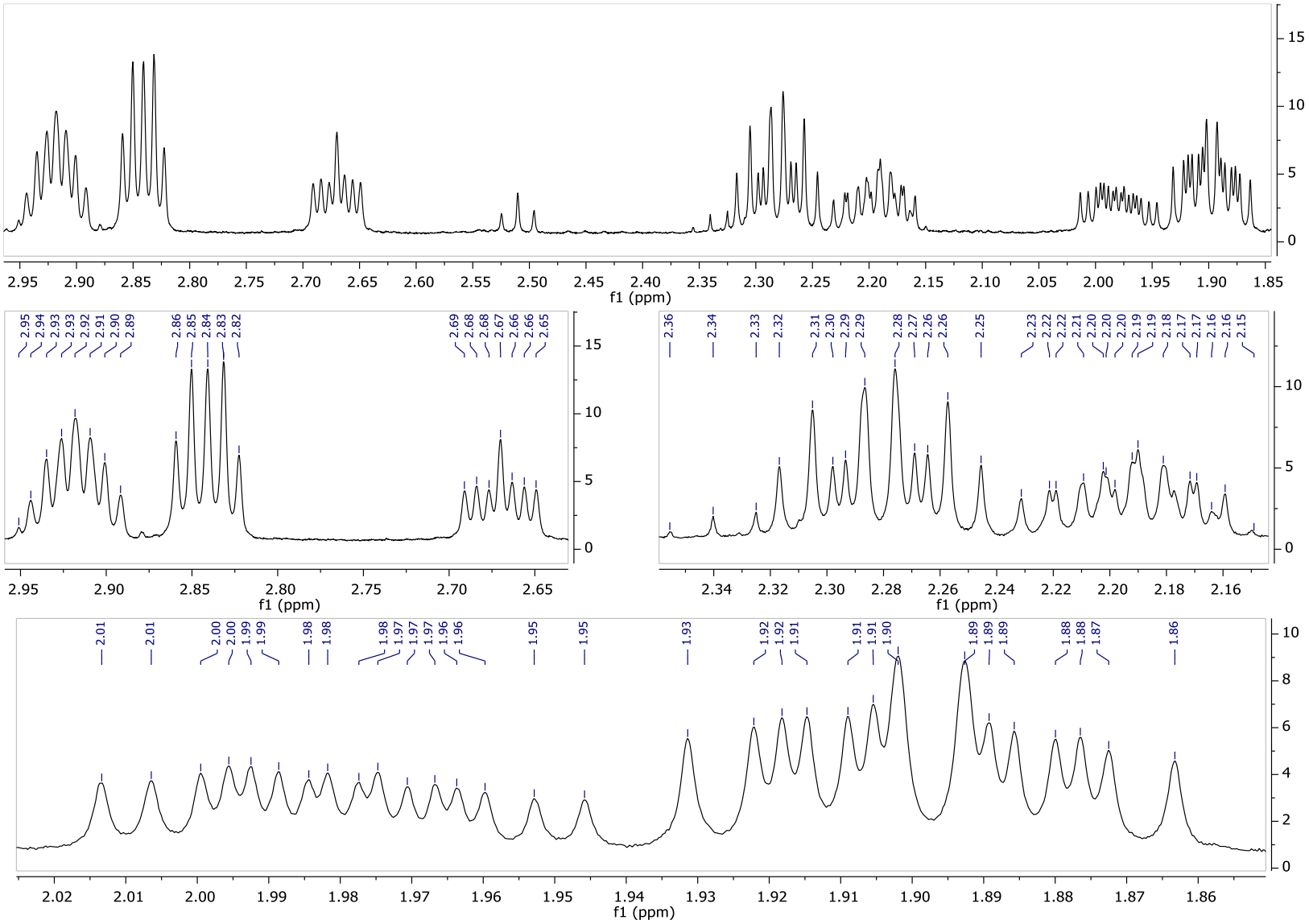
^{19}F NMR spectrum of compound **29d**



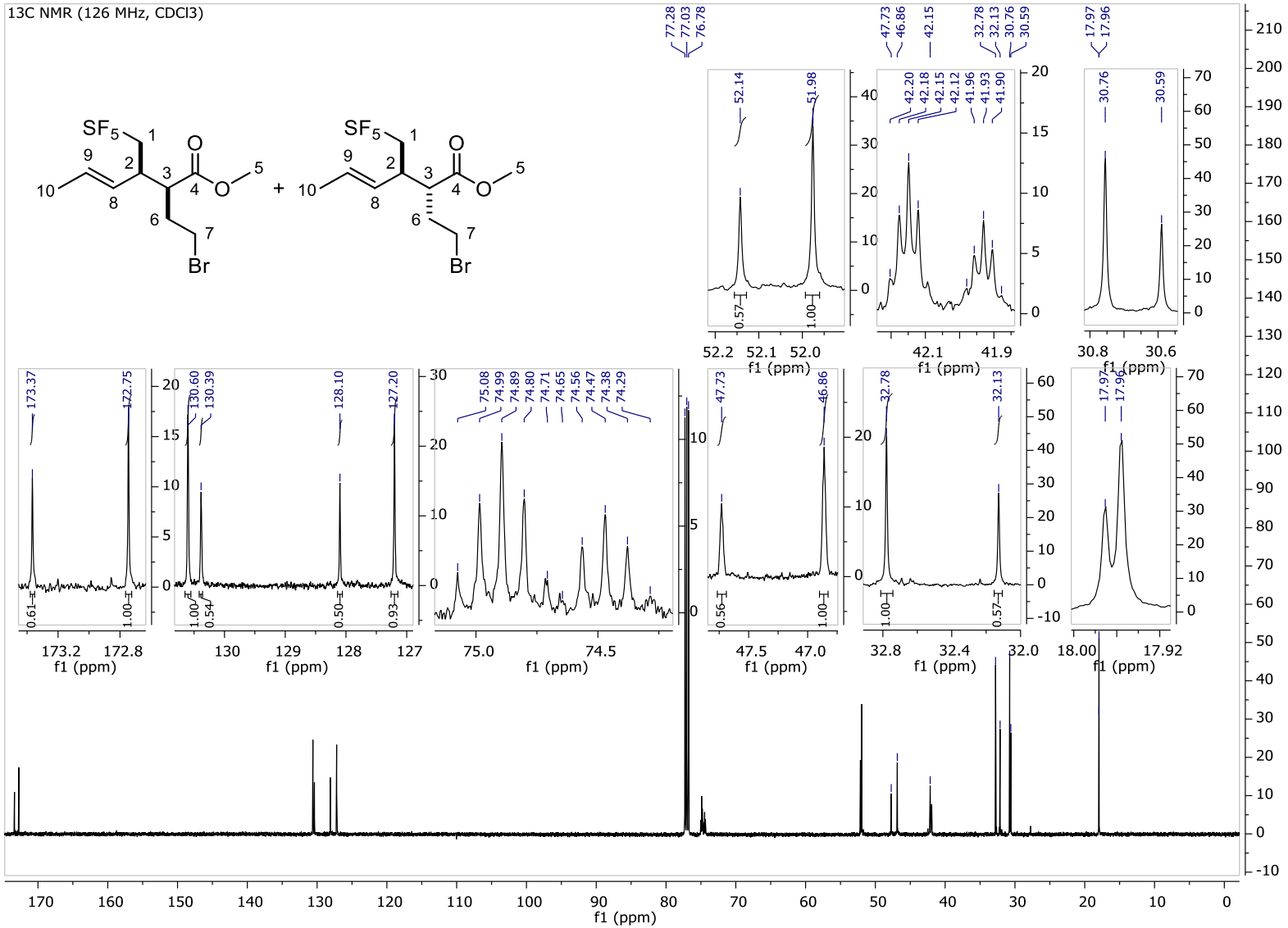
^{1}H NMR spectrum of compound **29e**



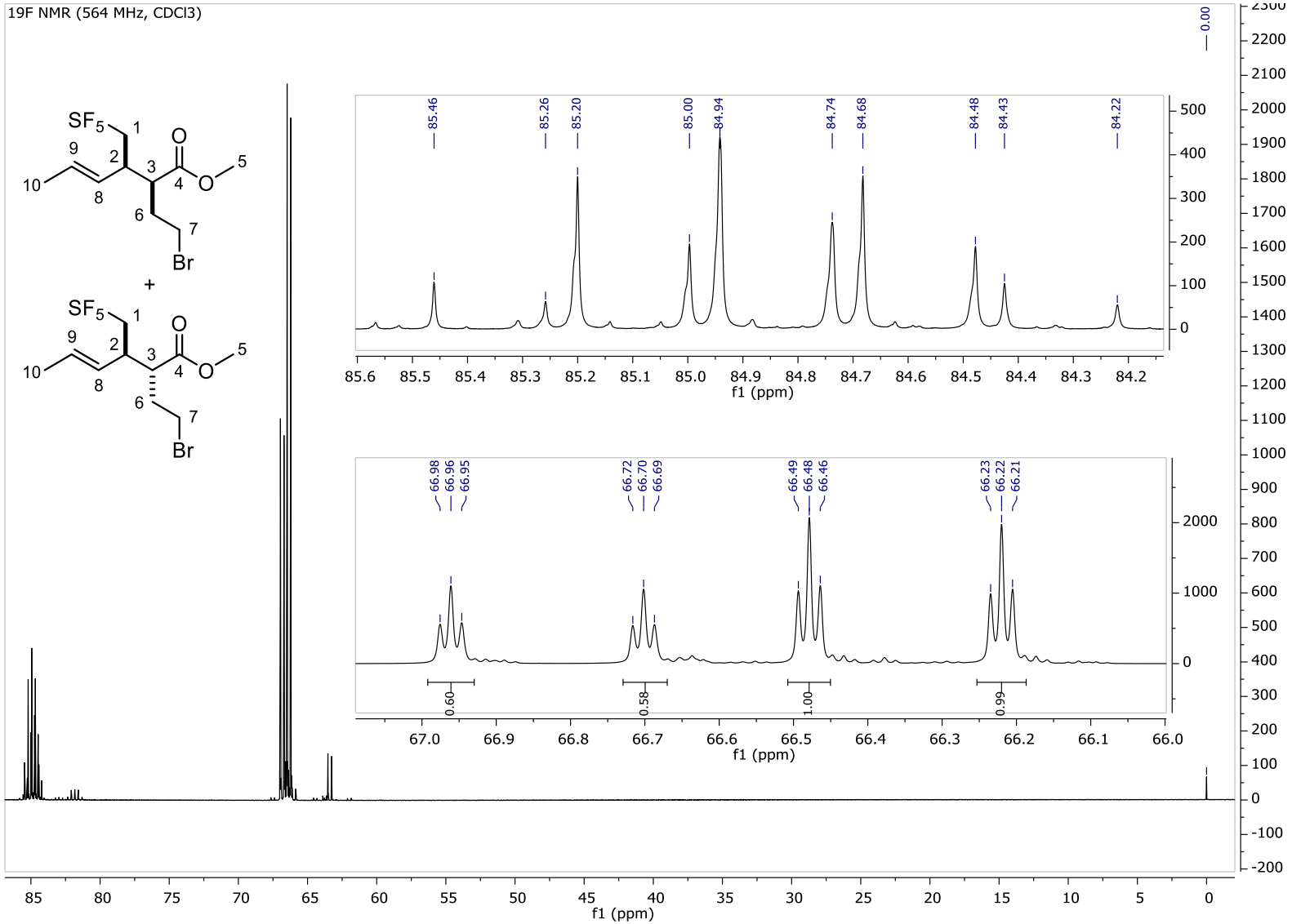
^{1}H NMR spectrum of compound **29e**, cutout (1.85-2.95 ppm)



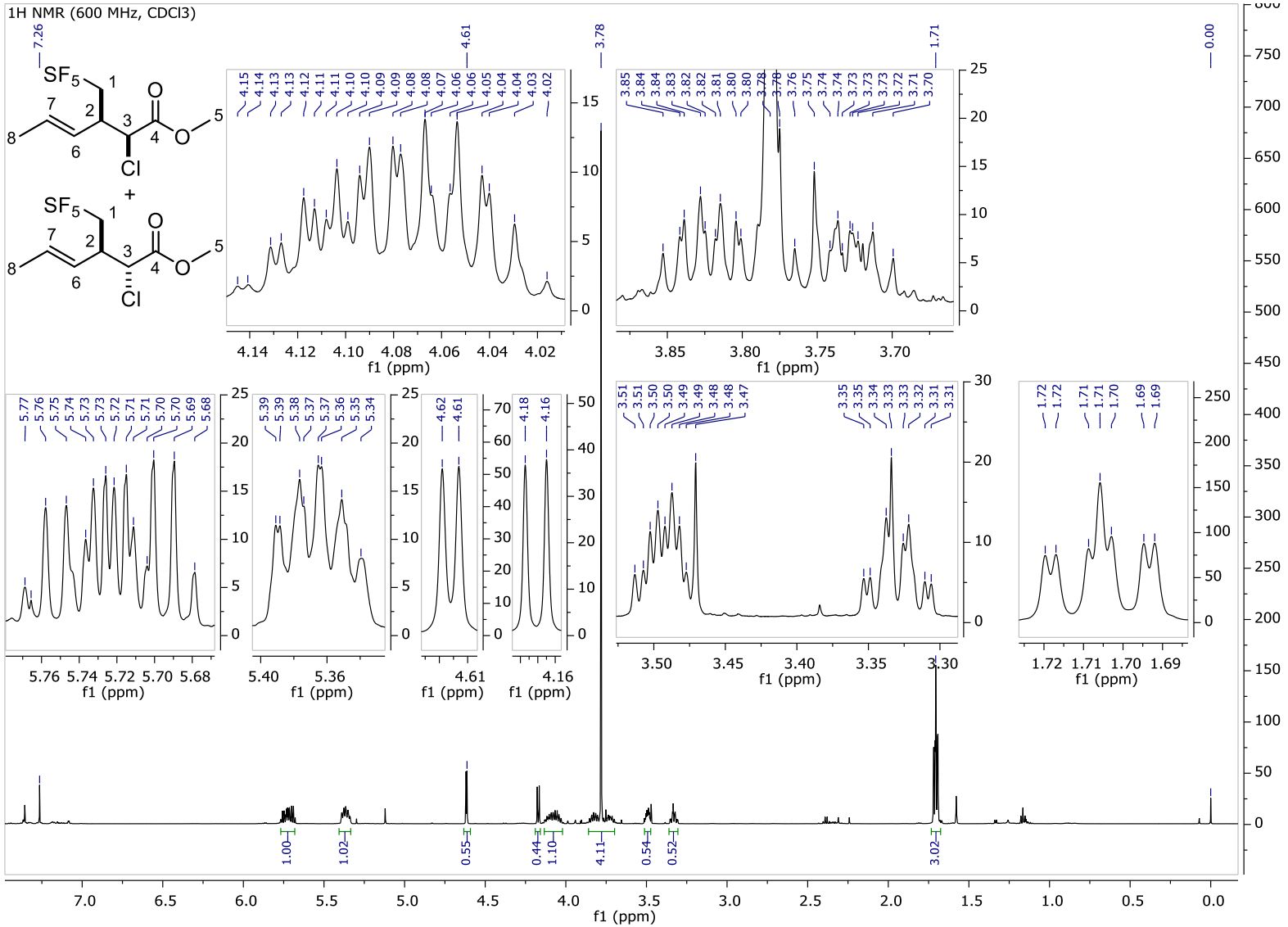
^{13}C NMR spectrum of compound **29e**



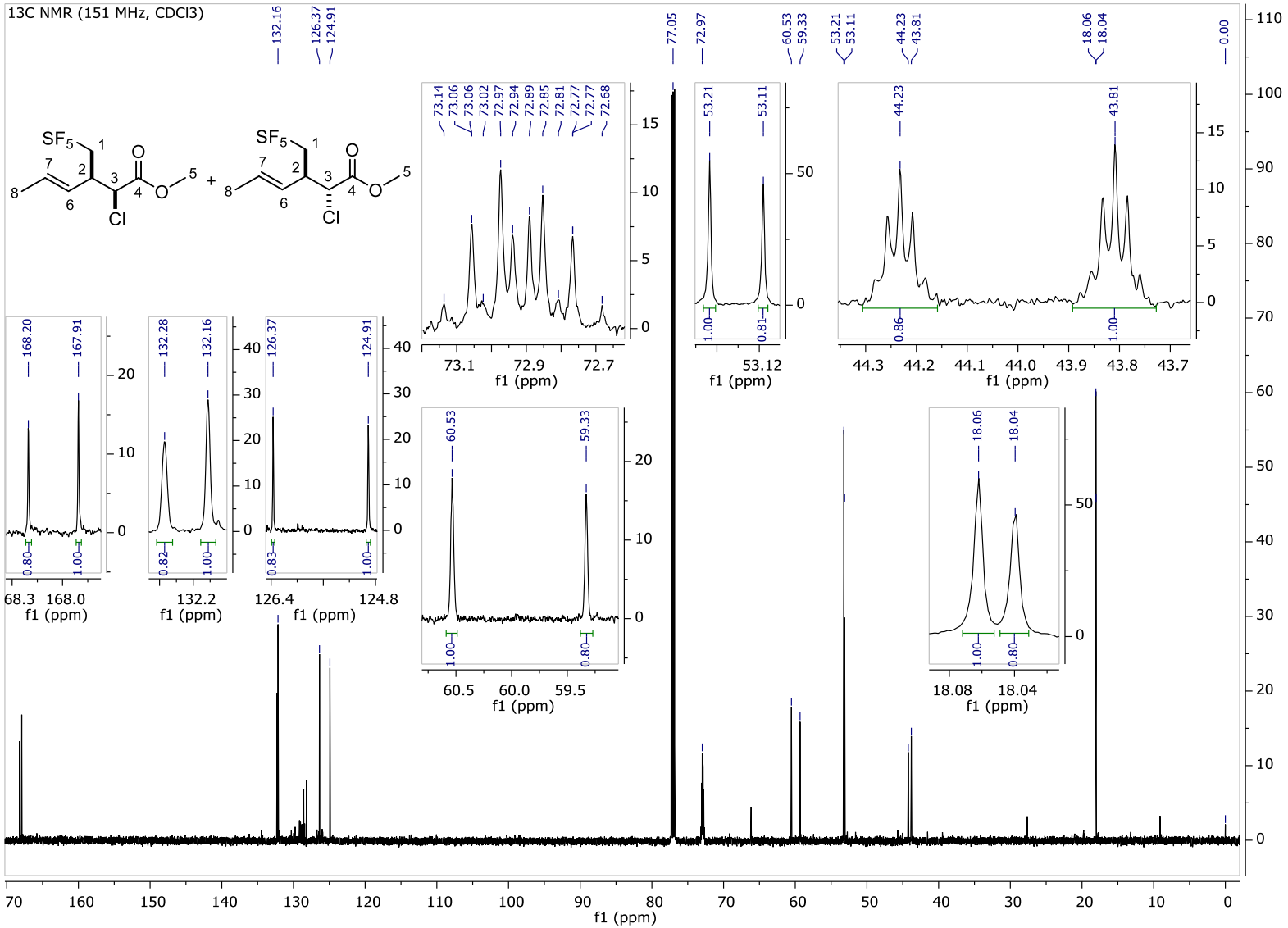
^{19}F NMR spectrum of compound **29e**



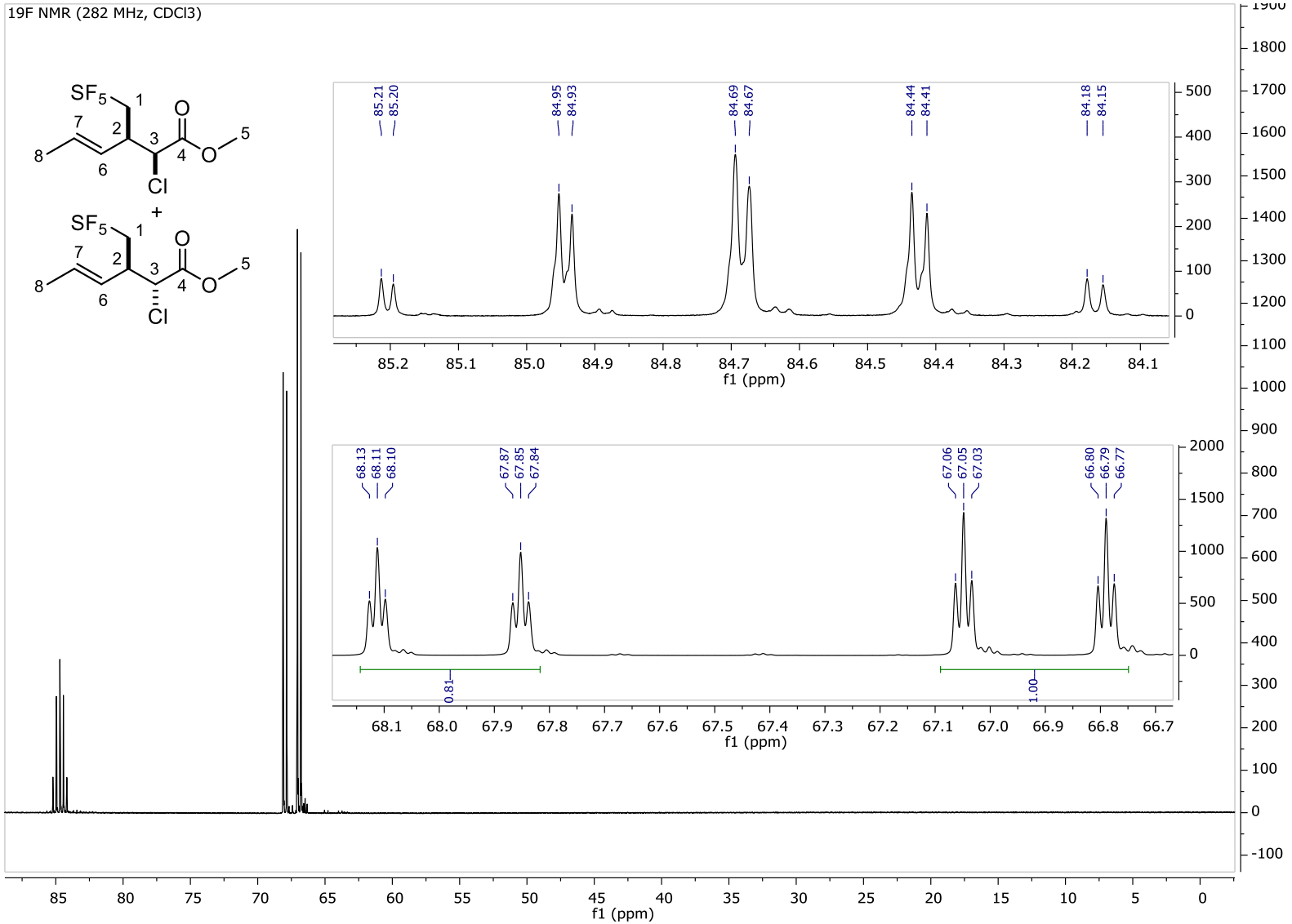
^{1}H NMR spectrum of compound **29f**



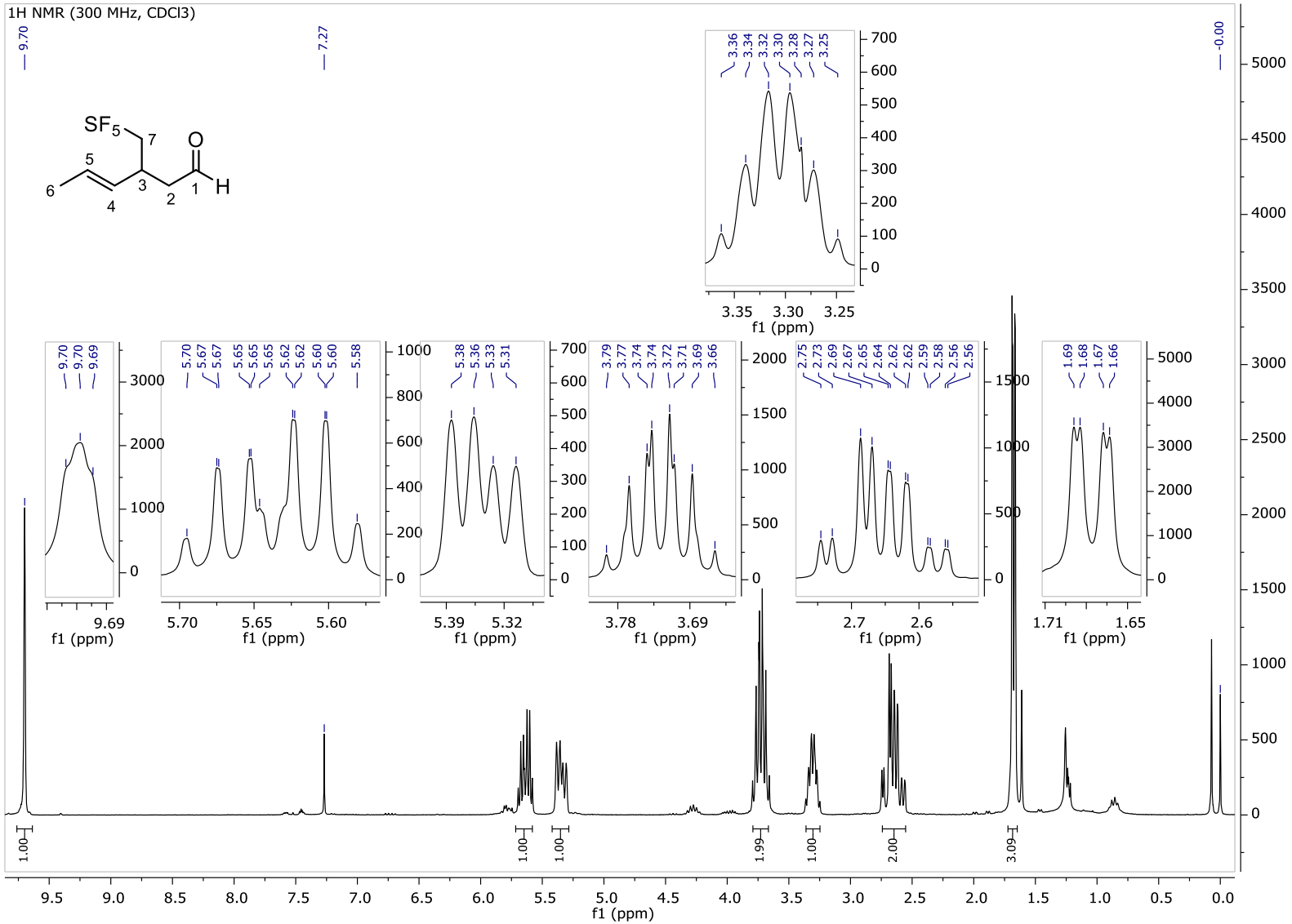
^{13}C NMR spectrum of compound **29f**



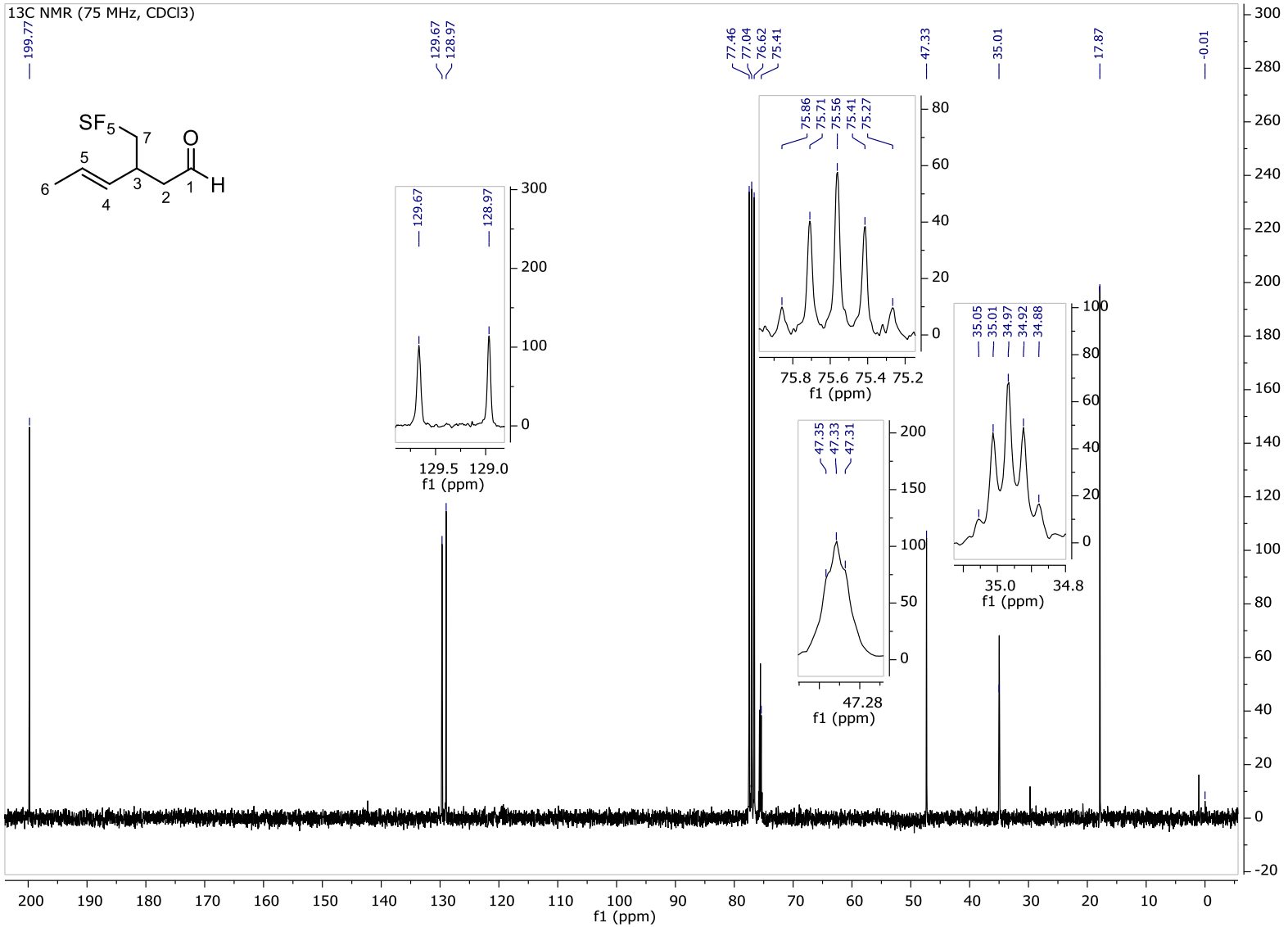
^{19}F NMR spectrum of compound **29f**



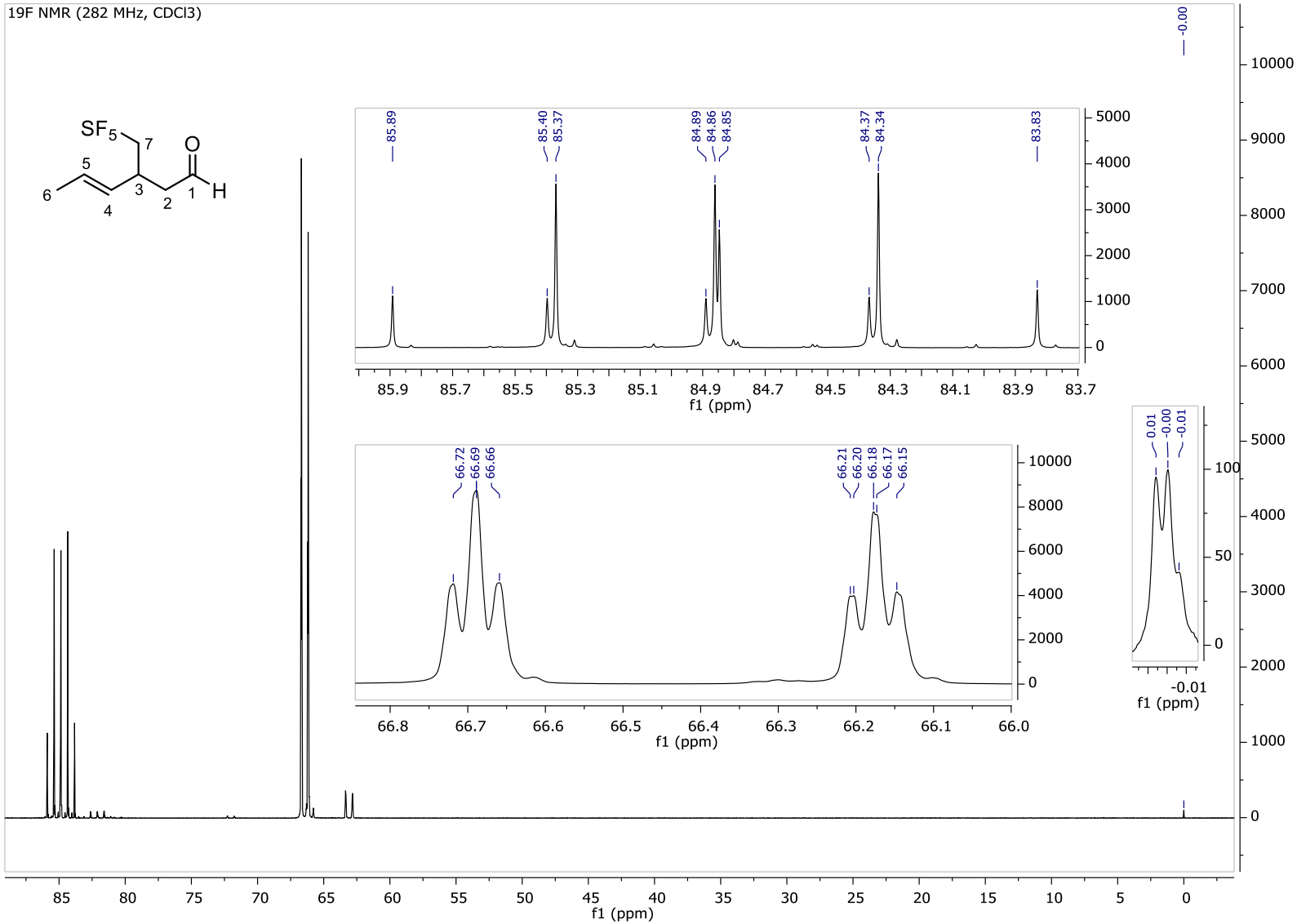
^{1}H NMR spectrum of compound **31**



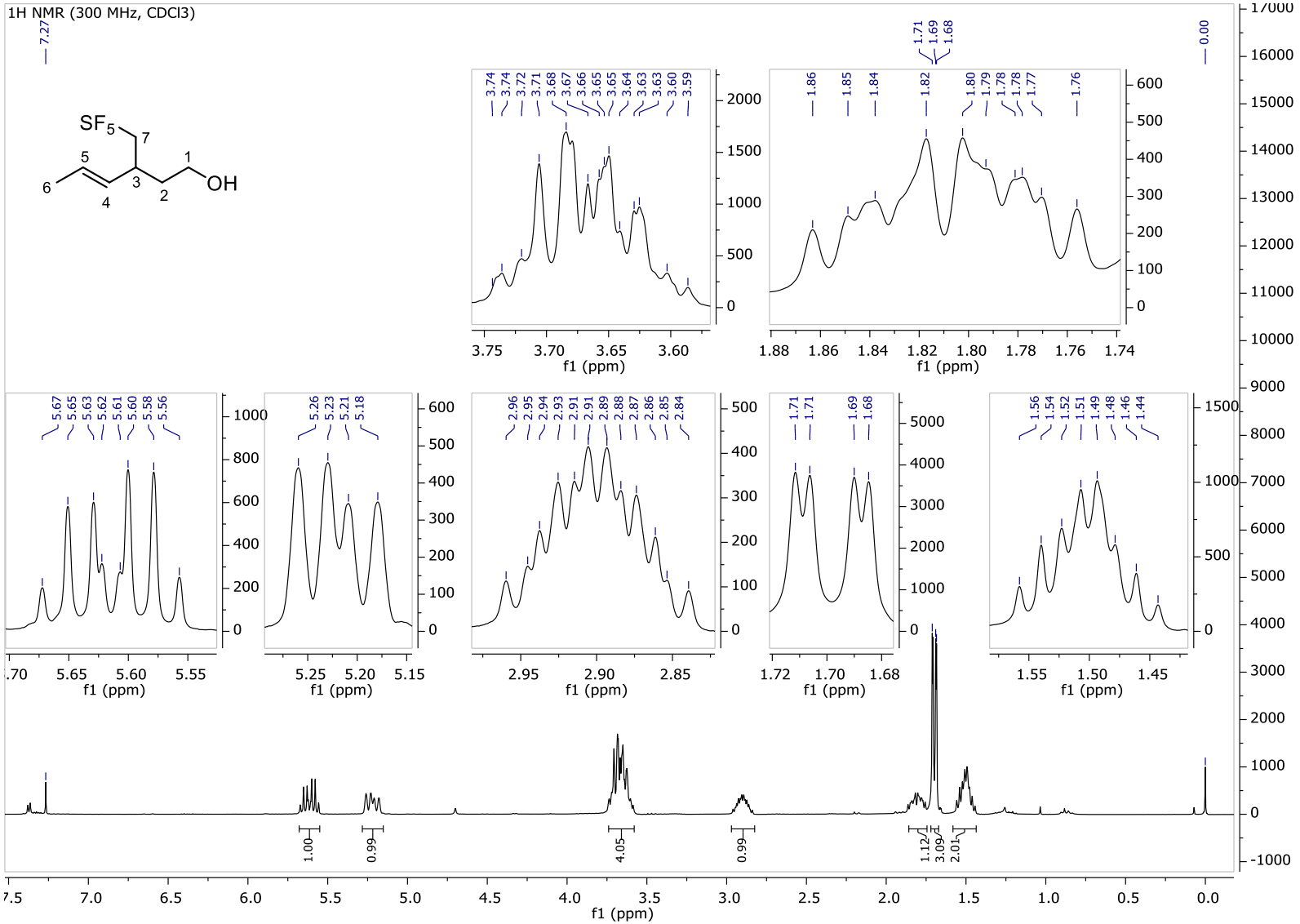
^{13}C NMR spectrum of compound **31**



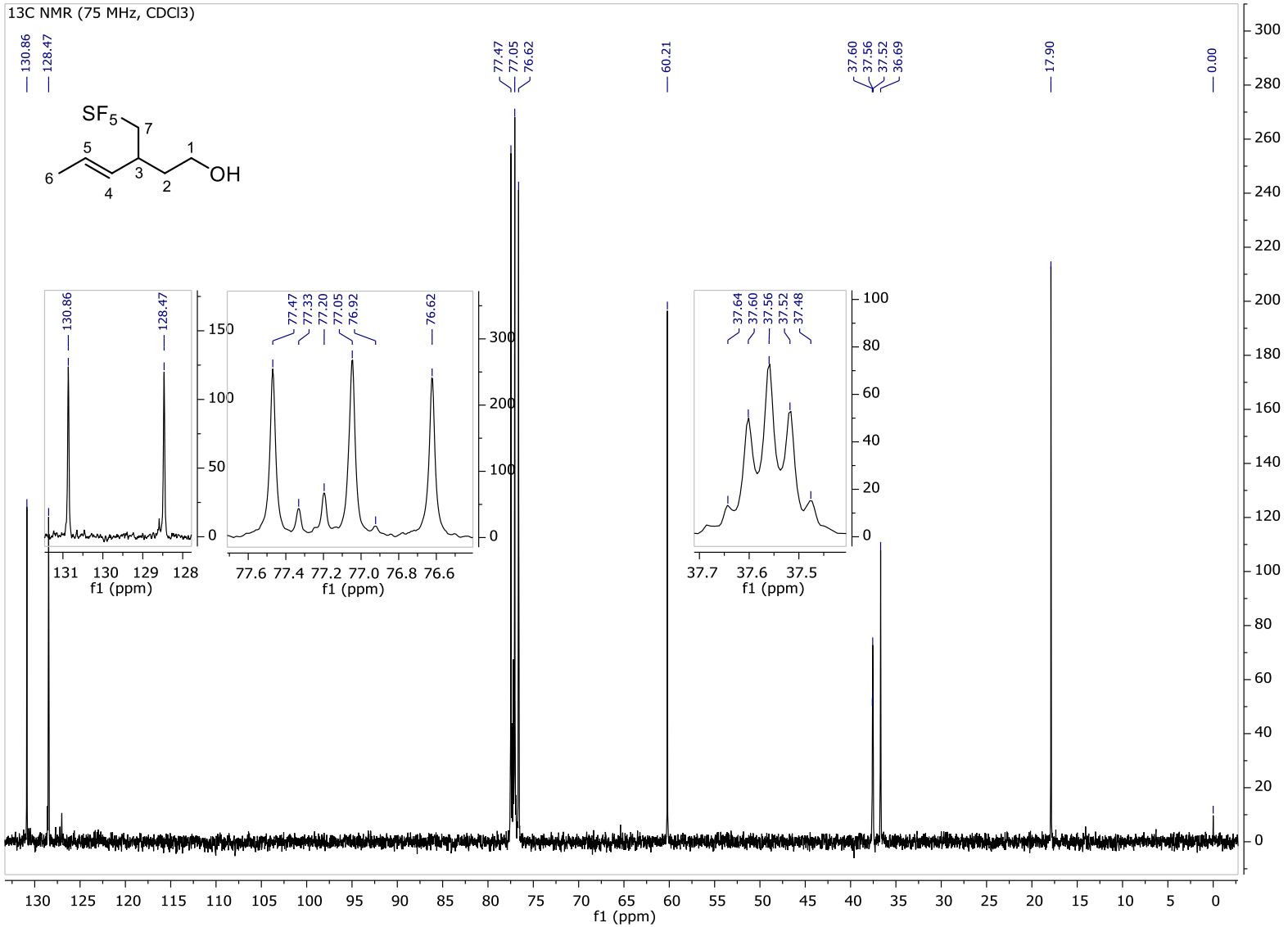
^{19}F NMR spectrum of compound **31**



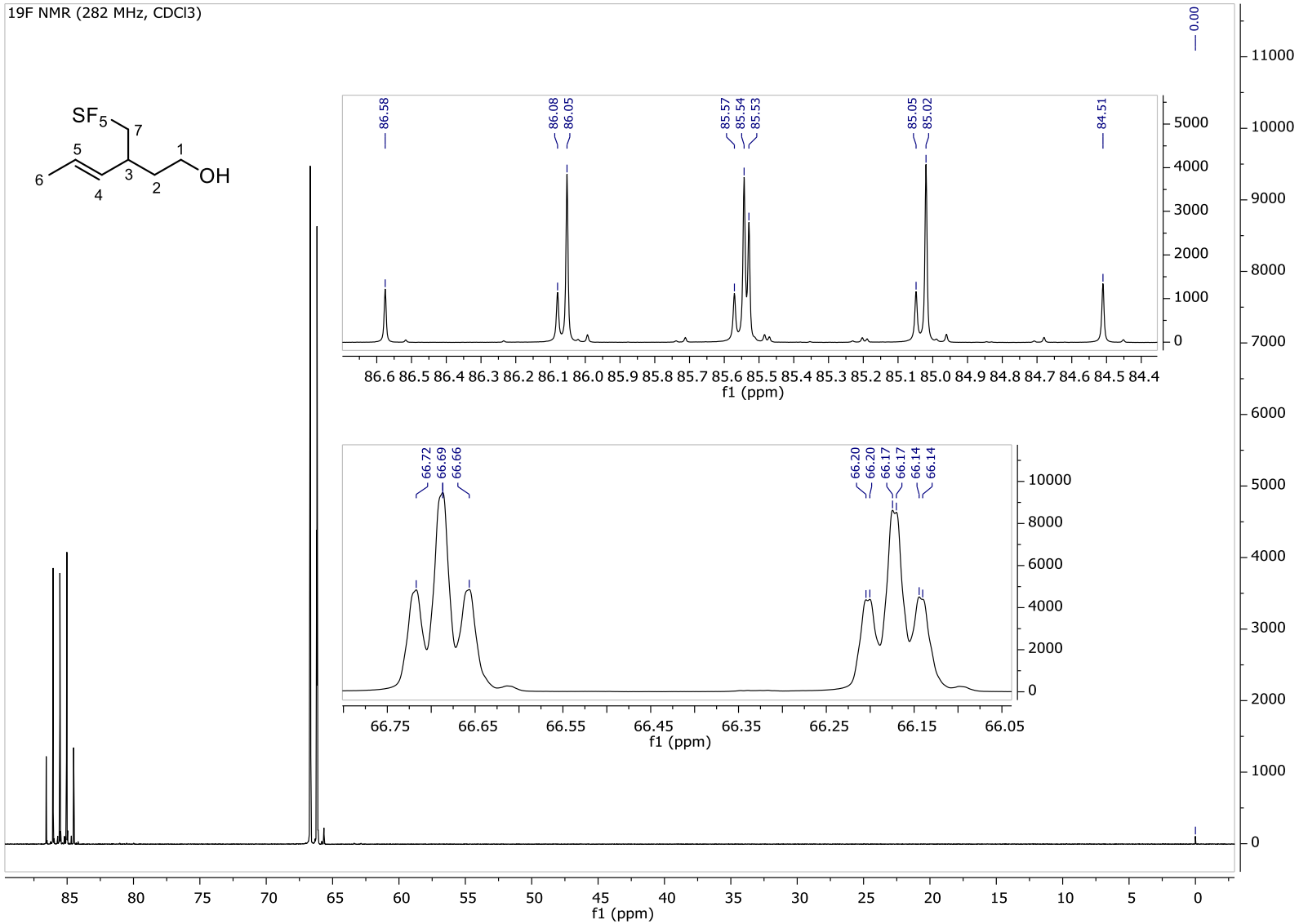
^{1}H NMR spectrum of compound **30**



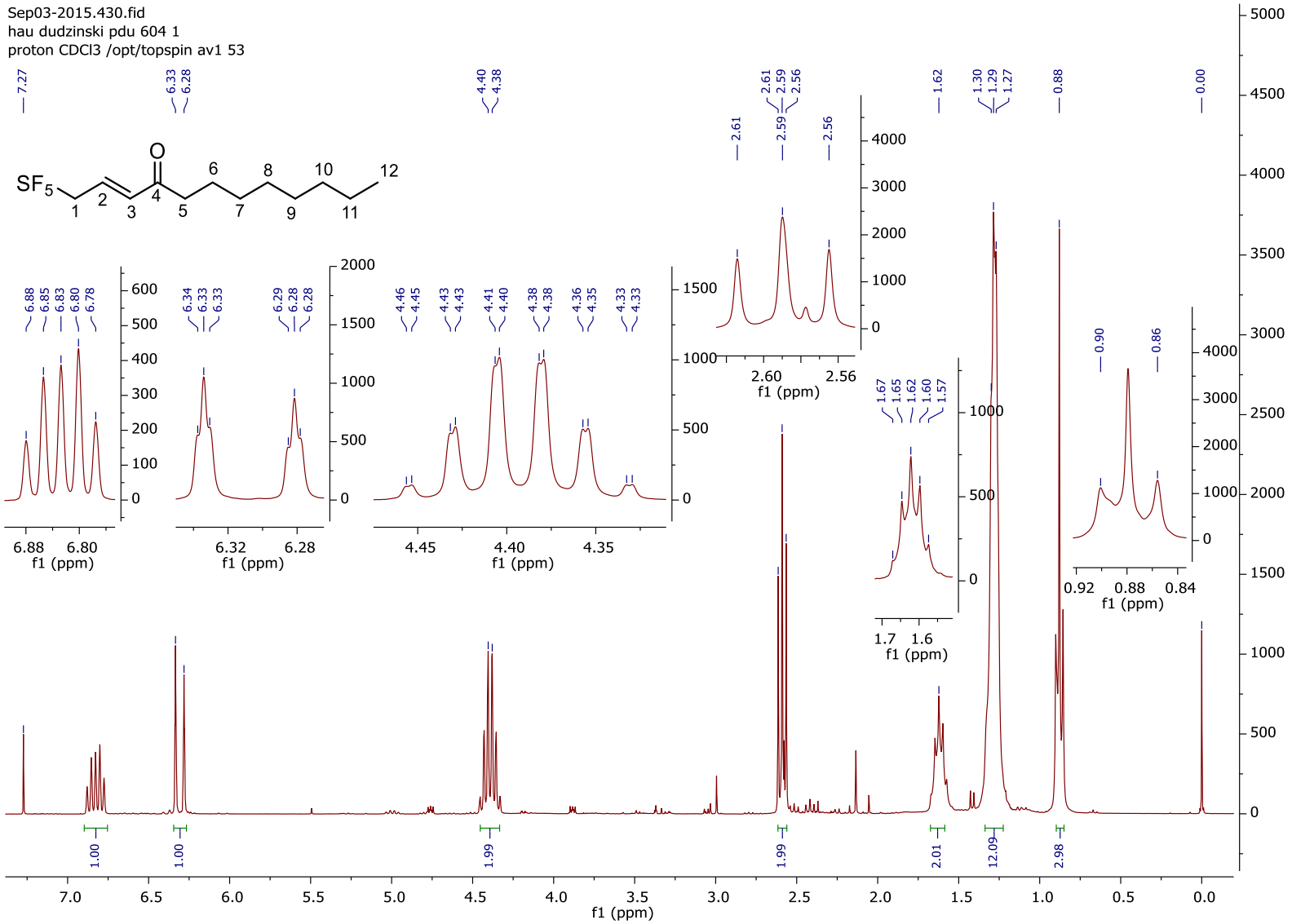
^{13}C NMR spectrum of compound **30**



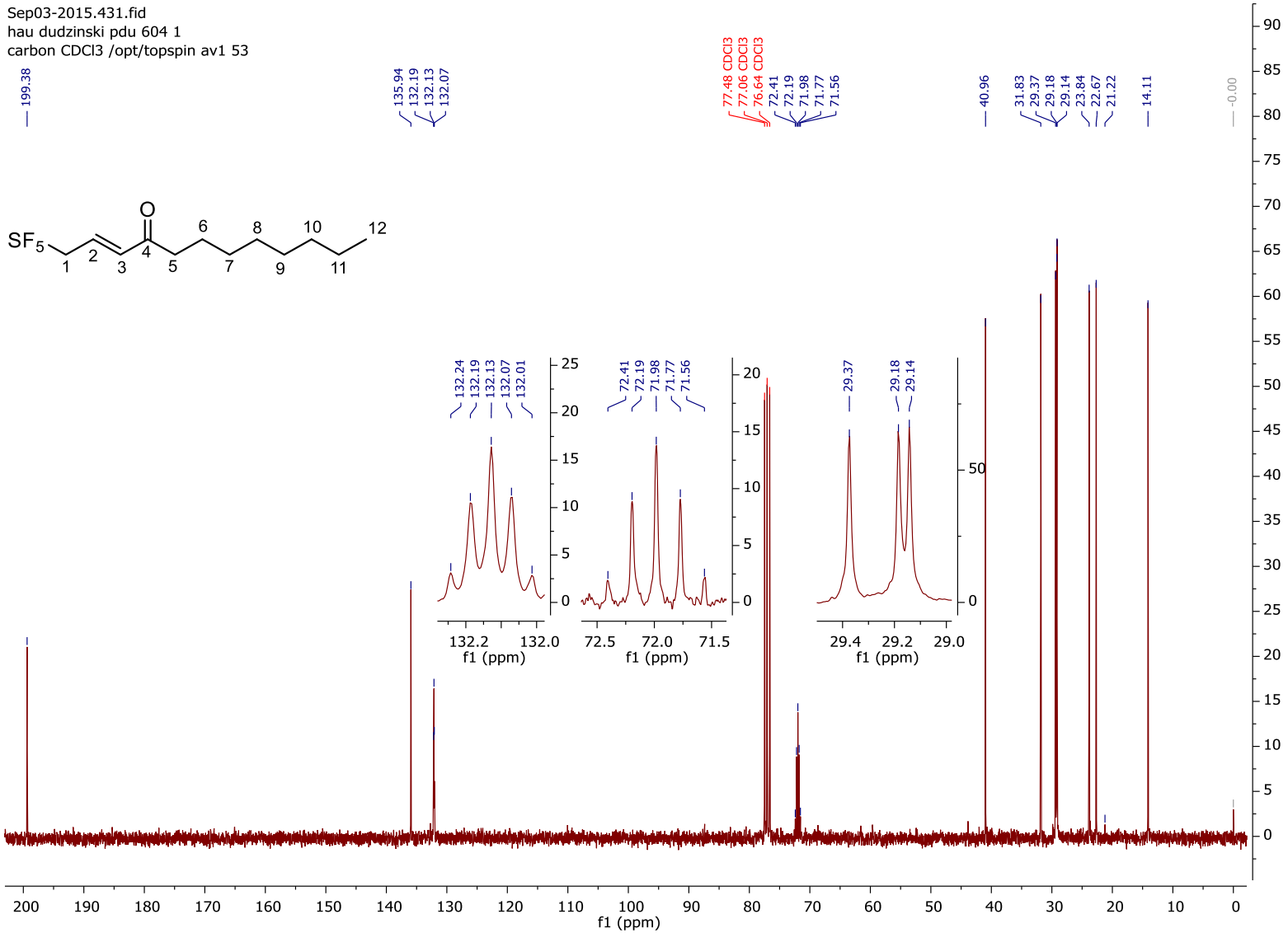
^{19}F NMR spectrum of compound **30**



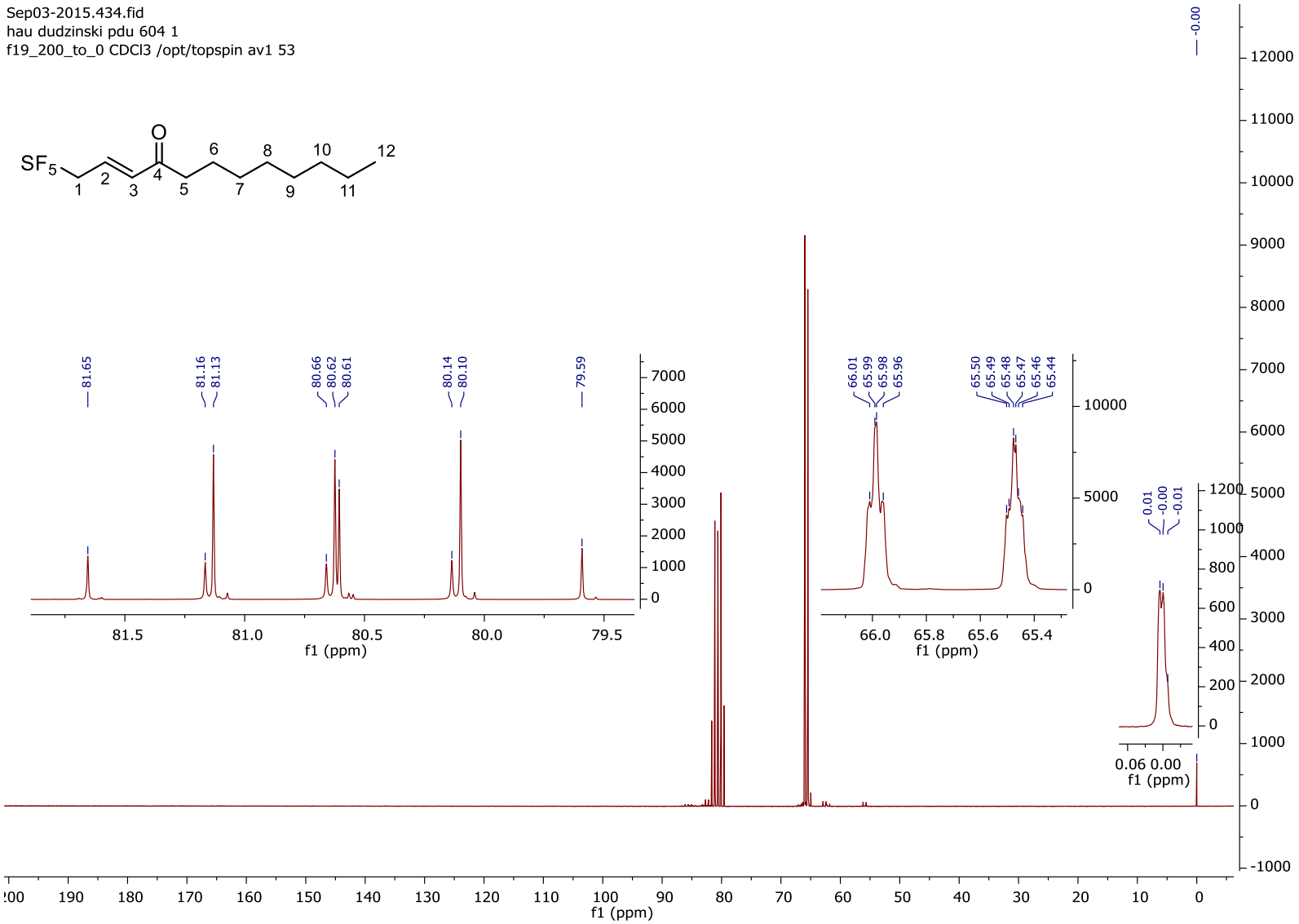
^{1}H NMR spectrum of compound **33b**



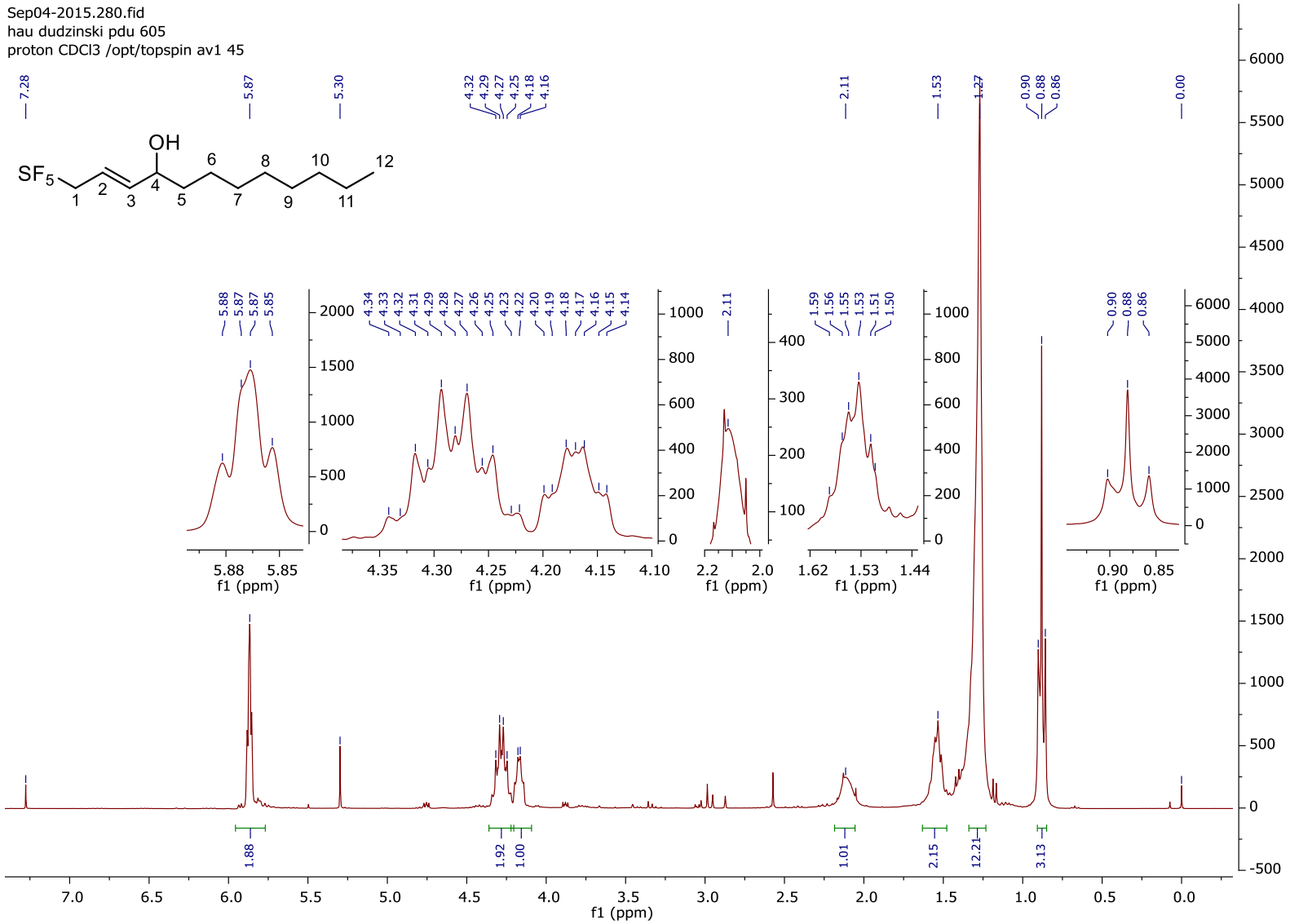
^{13}C NMR spectrum of compound **33b**



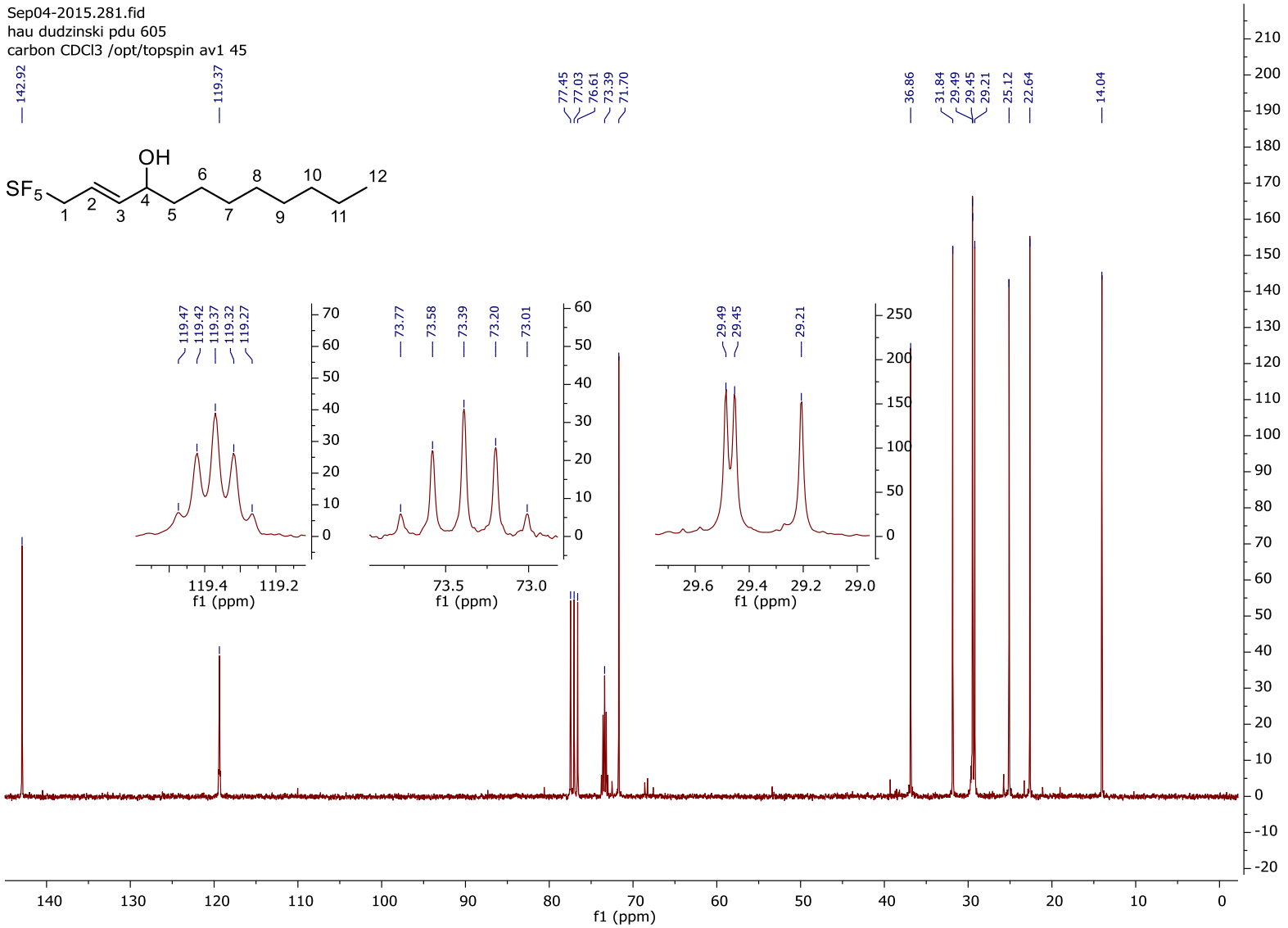
^{19}F NMR spectrum of compound **33b**



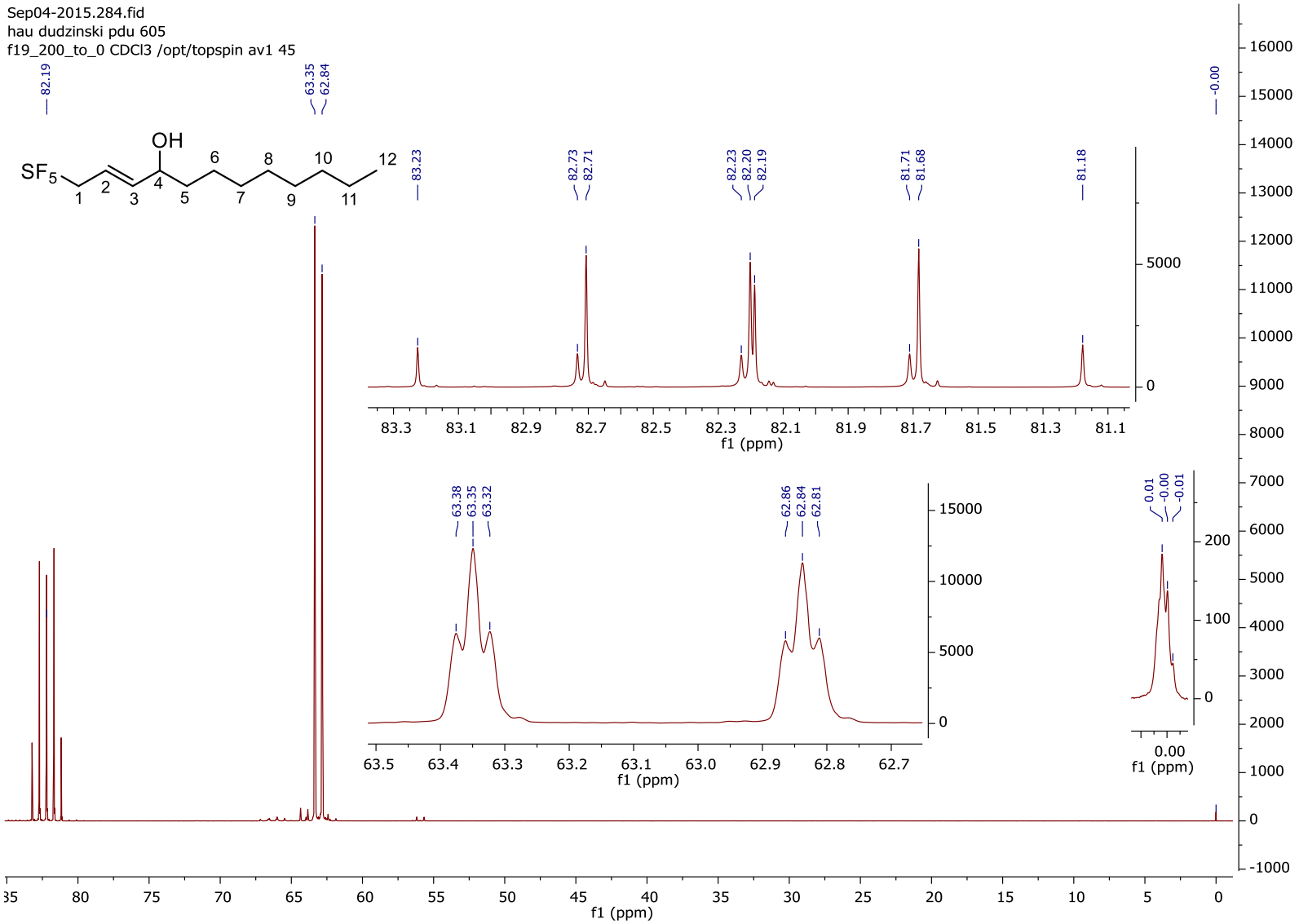
^{1}H NMR spectrum of compound **28b**



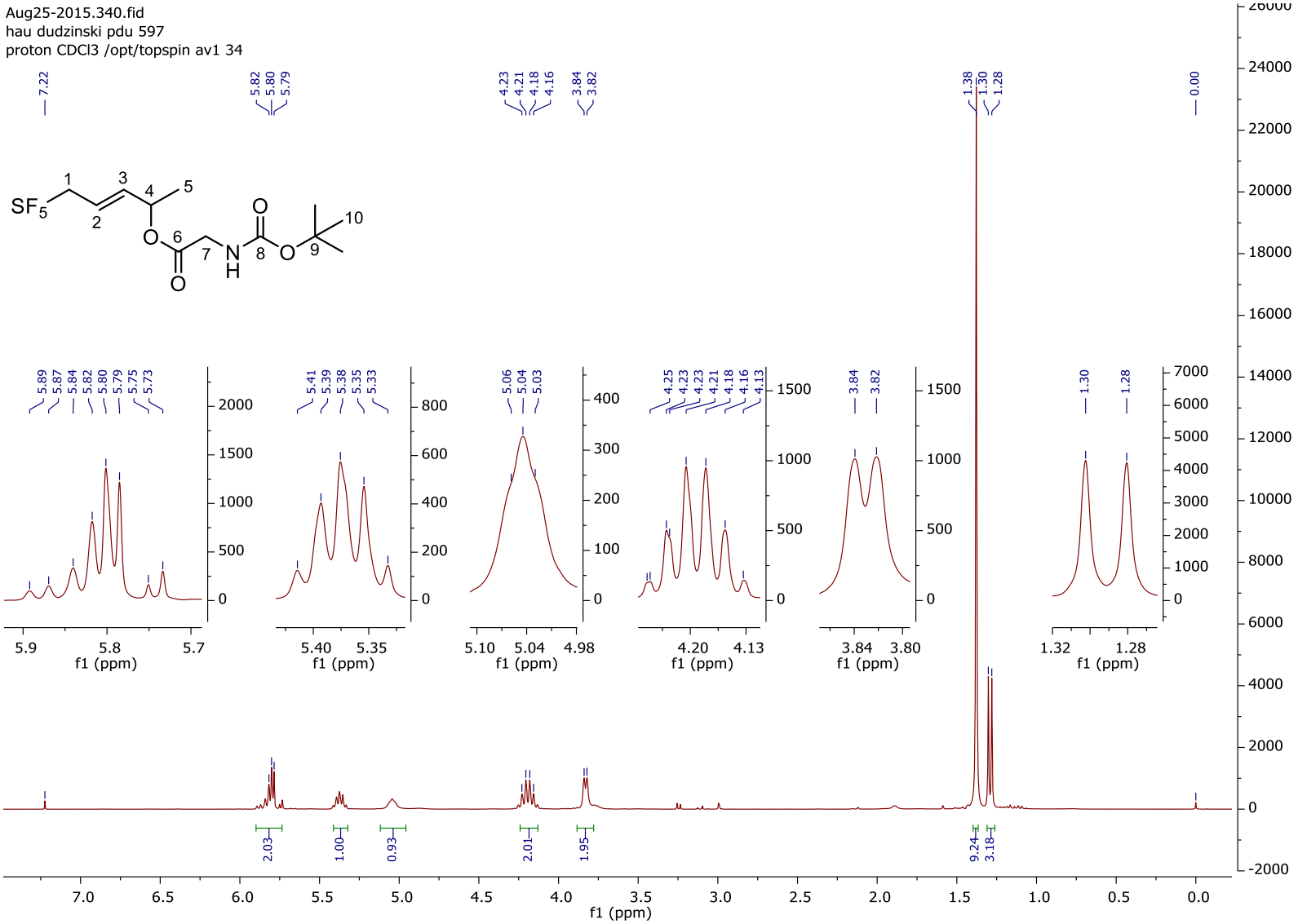
^{13}C NMR spectrum of compound **28b**



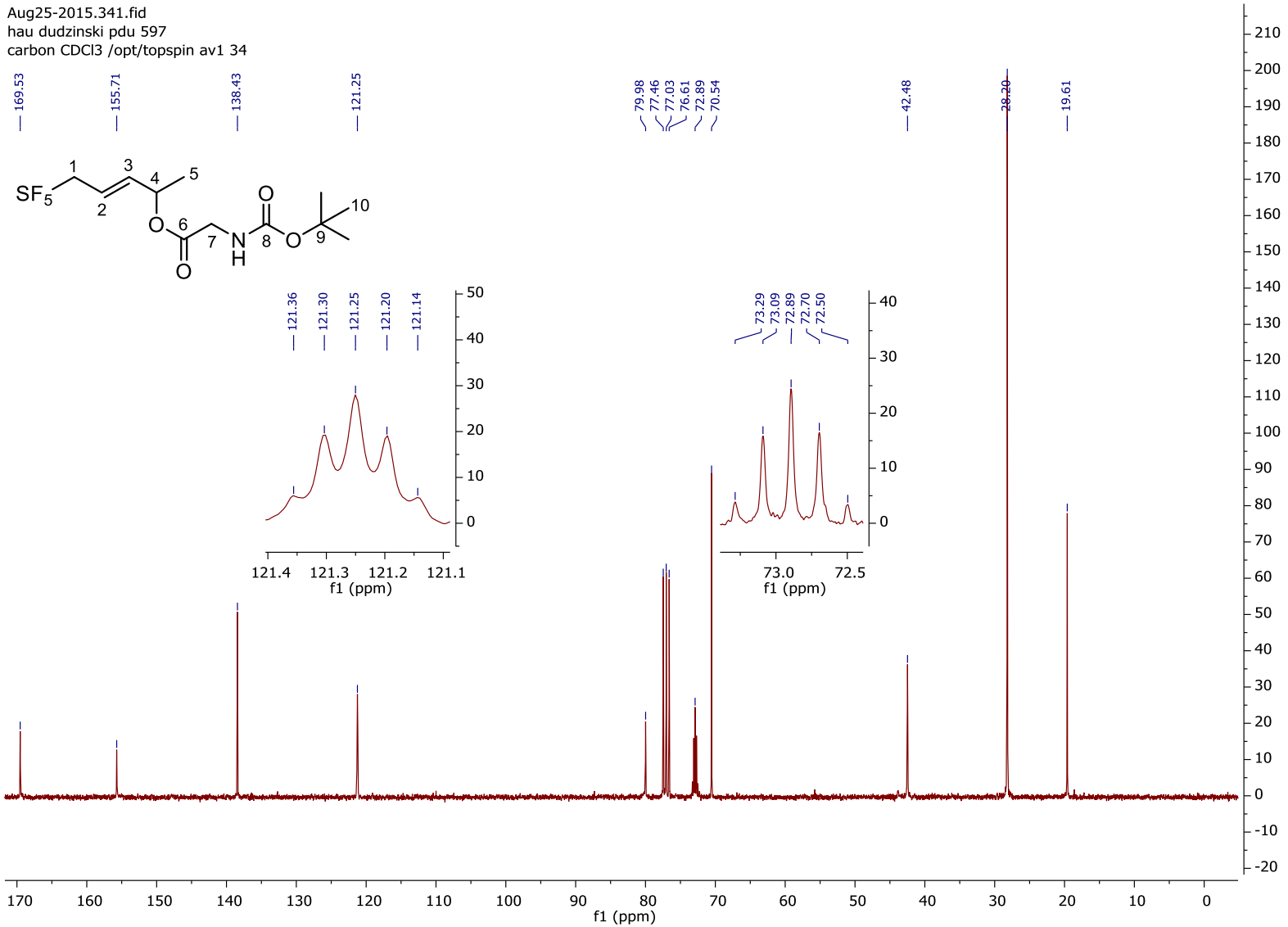
^{19}F NMR spectrum of compound **28b**



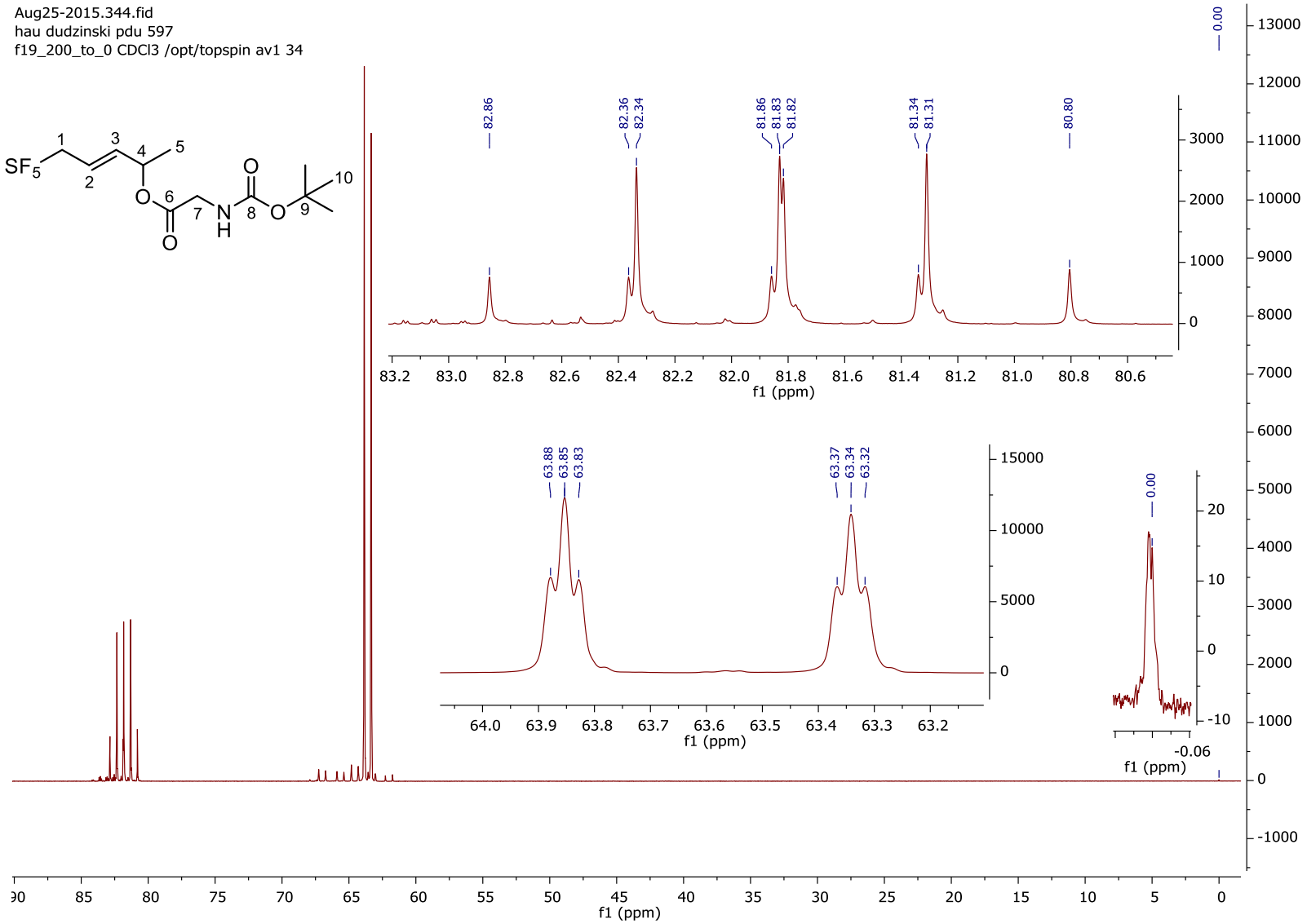
^{1}H NMR spectrum of compound **34a**



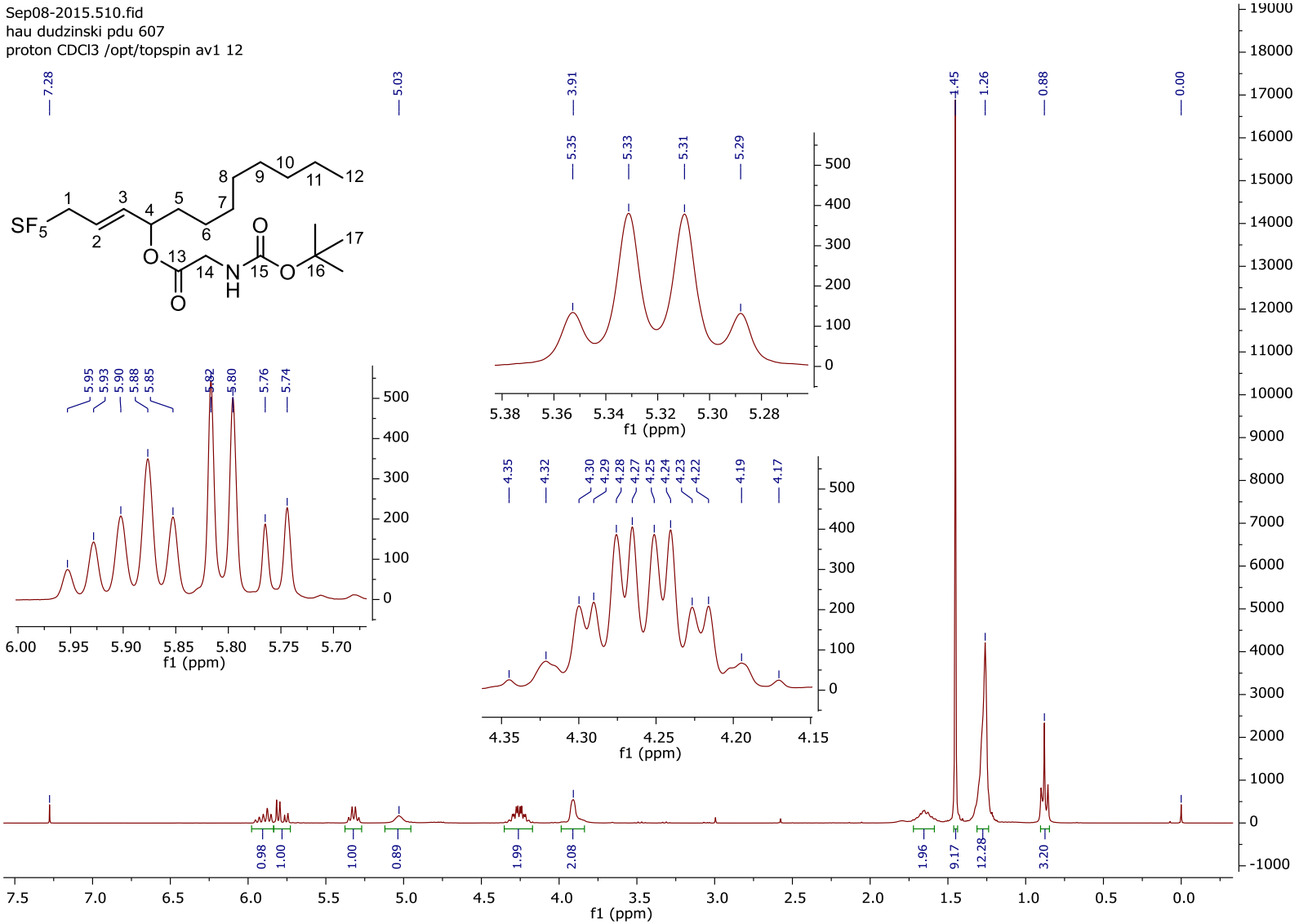
^{13}C NMR spectrum of compound **34a**



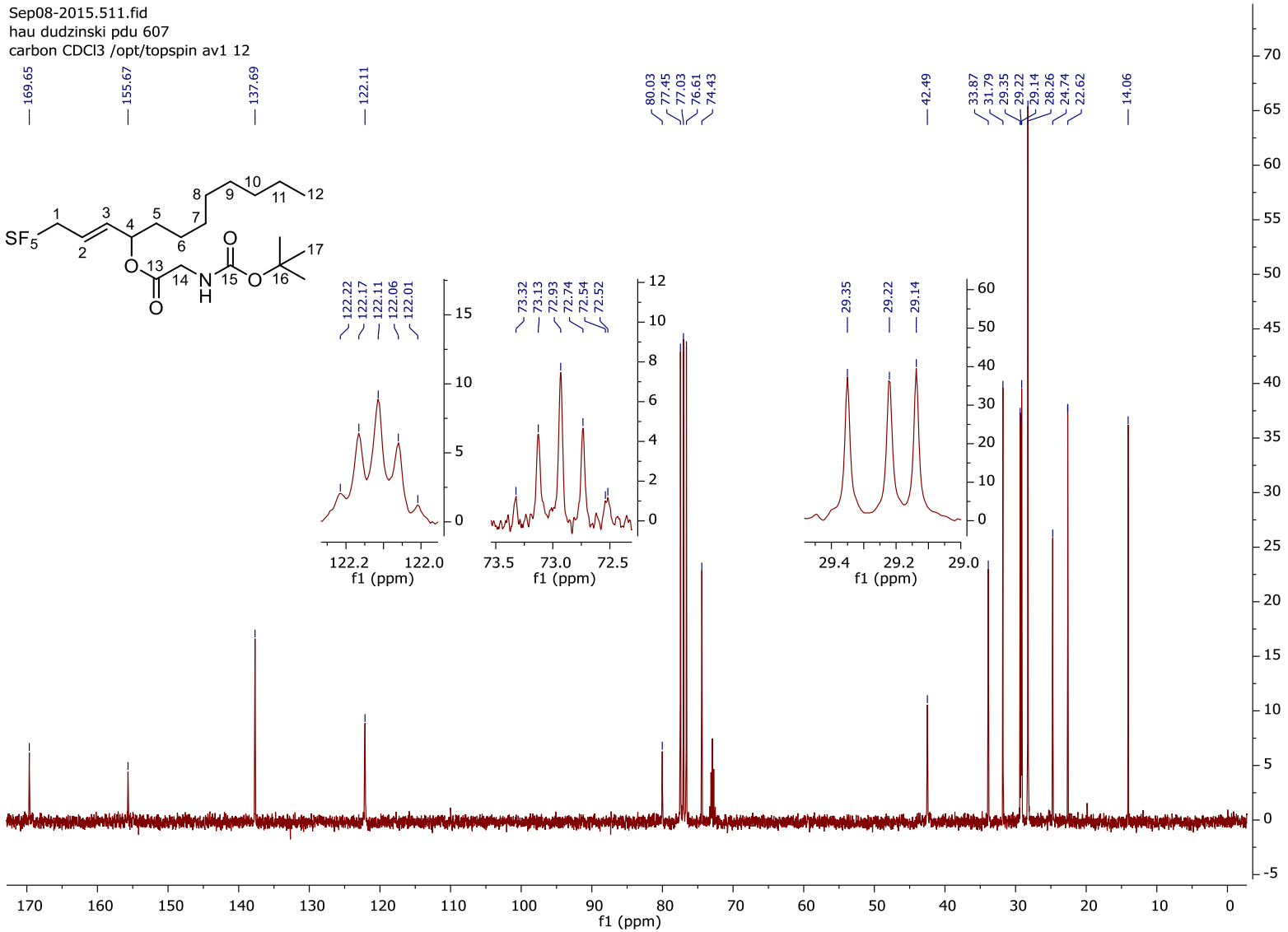
^{19}F NMR spectrum of compound **34a**



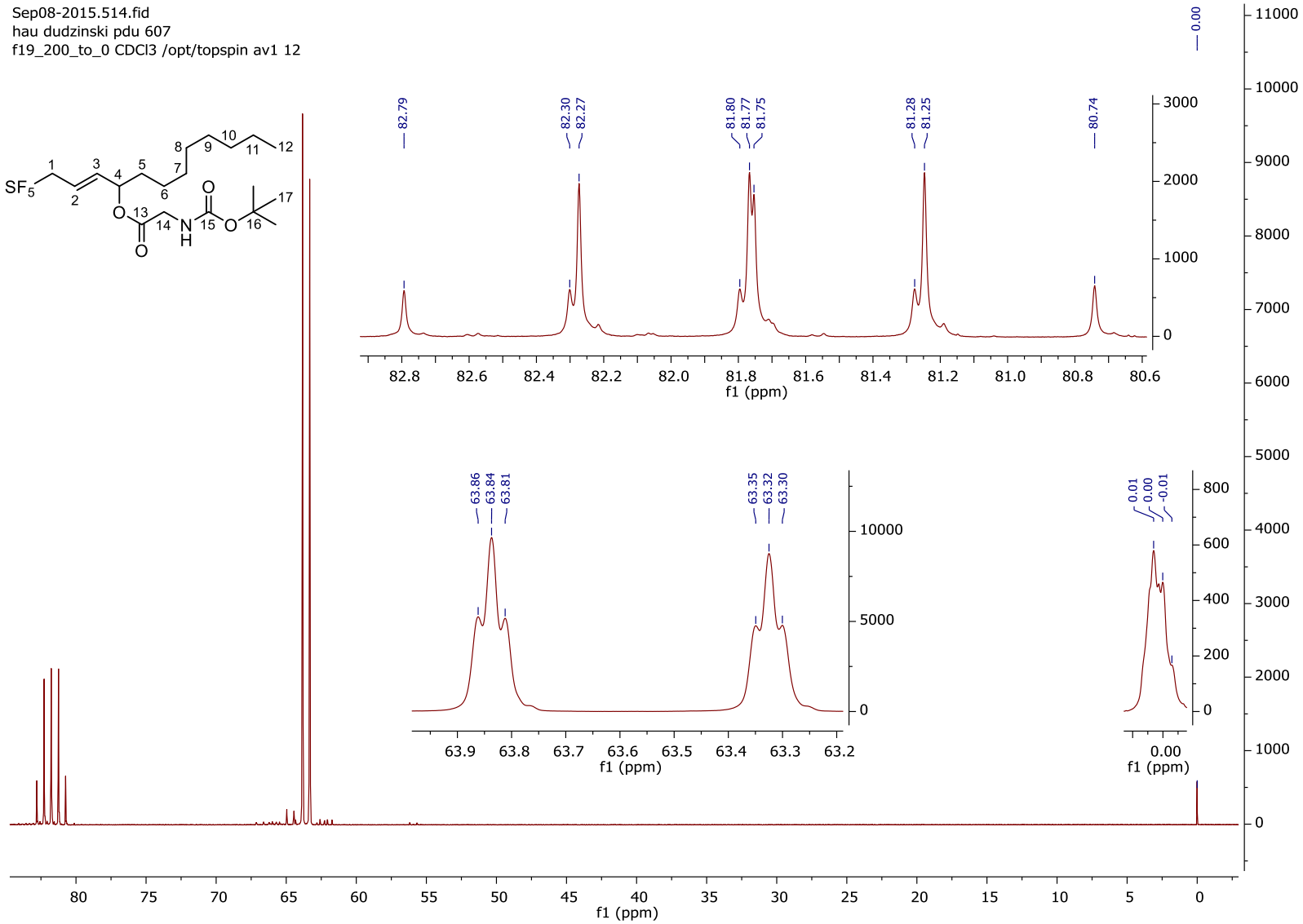
^{1}H NMR spectrum of compound **34b**



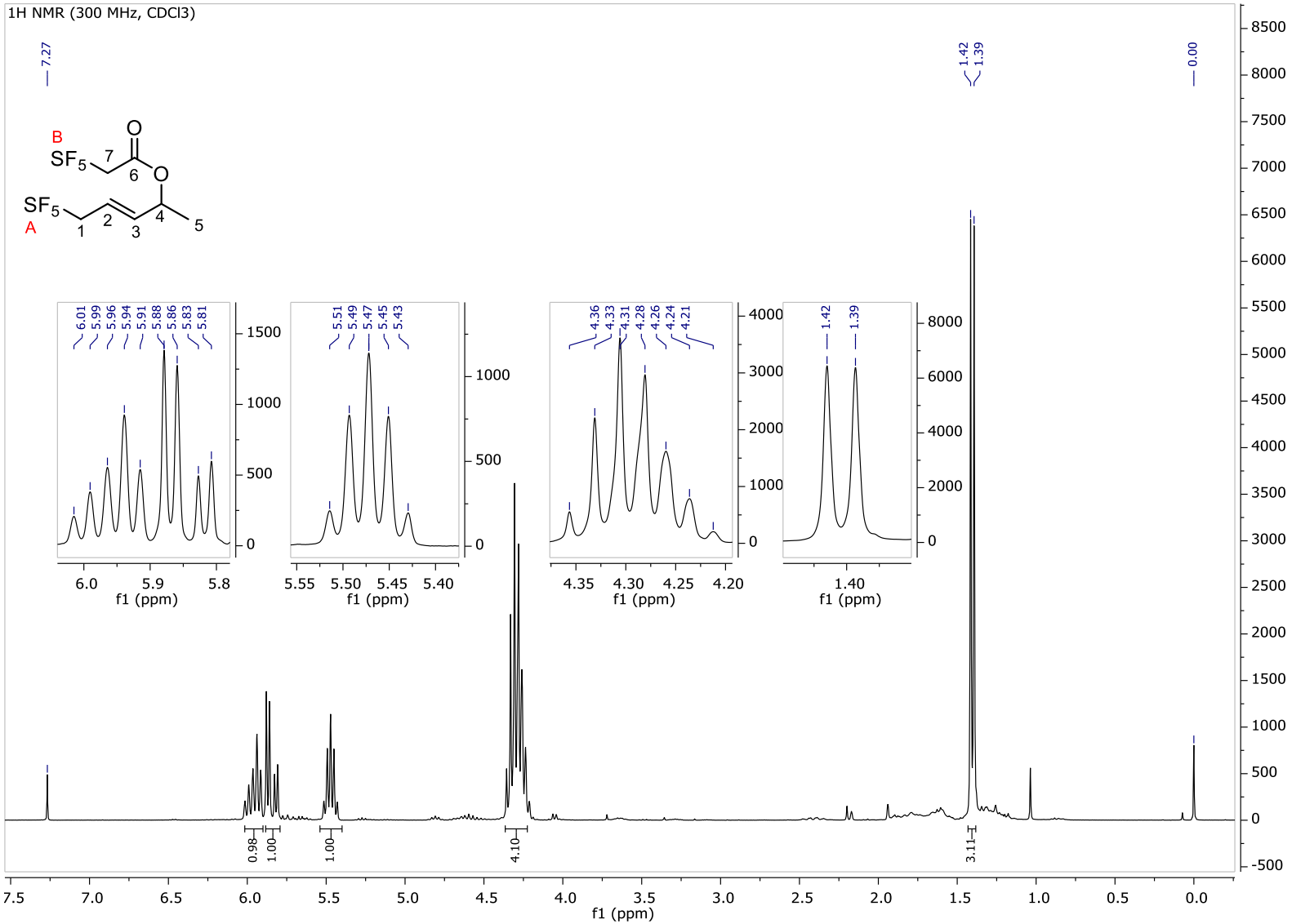
^{13}C NMR spectrum of compound **34b**



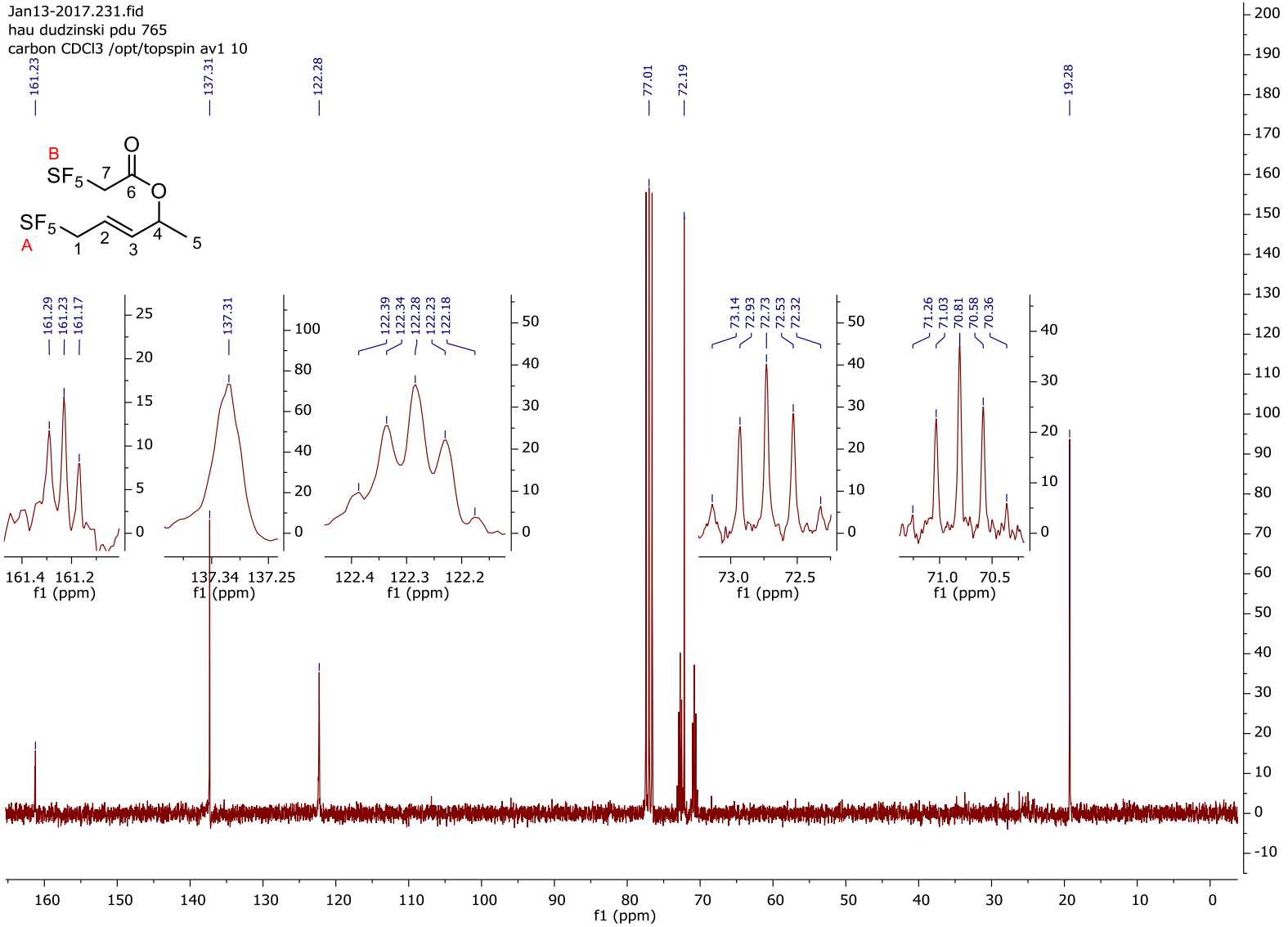
^{19}F NMR spectrum of compound **34b**



^{1}H NMR spectrum of compound **36a**



^{13}C NMR spectrum of compound **36a**



^{19}F NMR spectrum of compound **36a**

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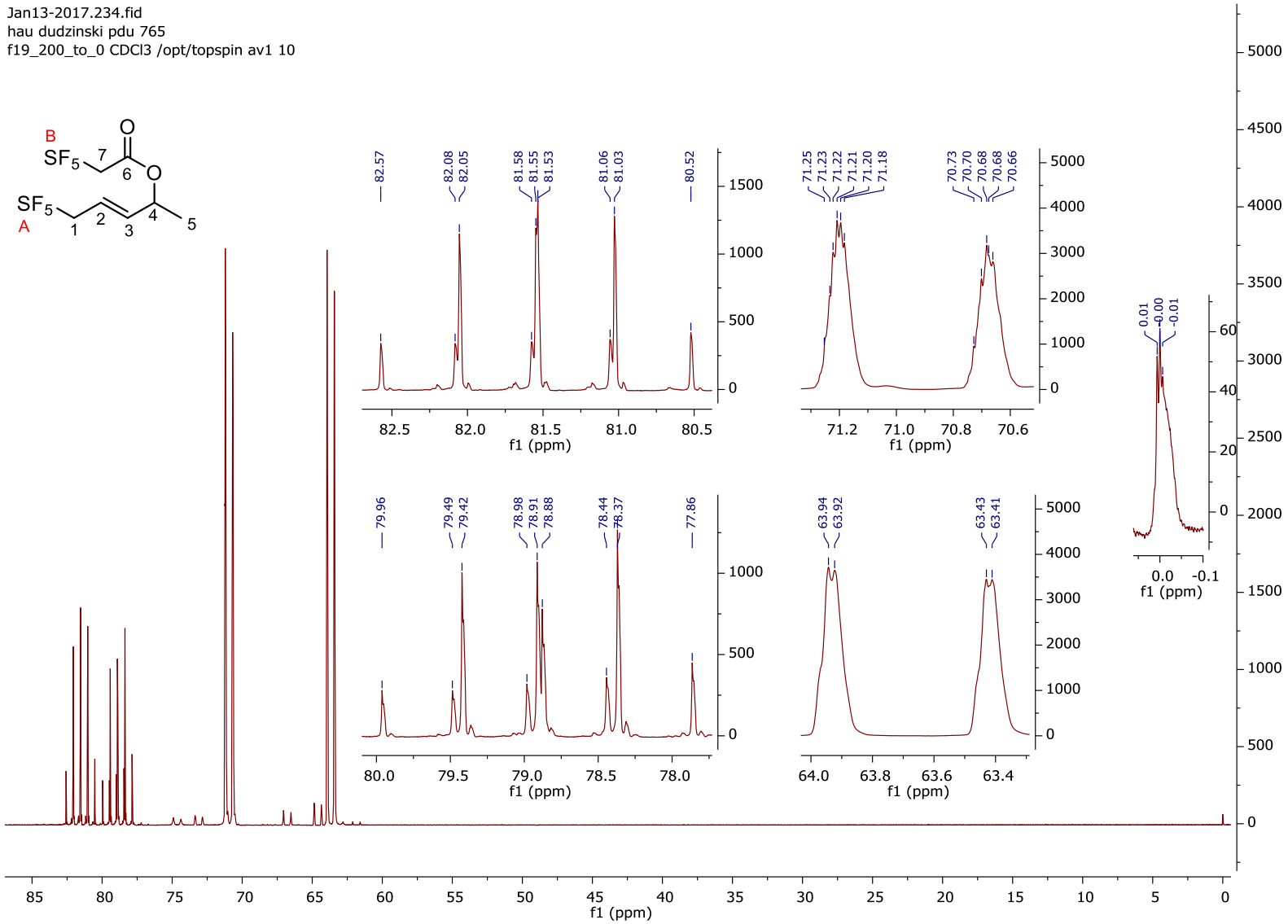
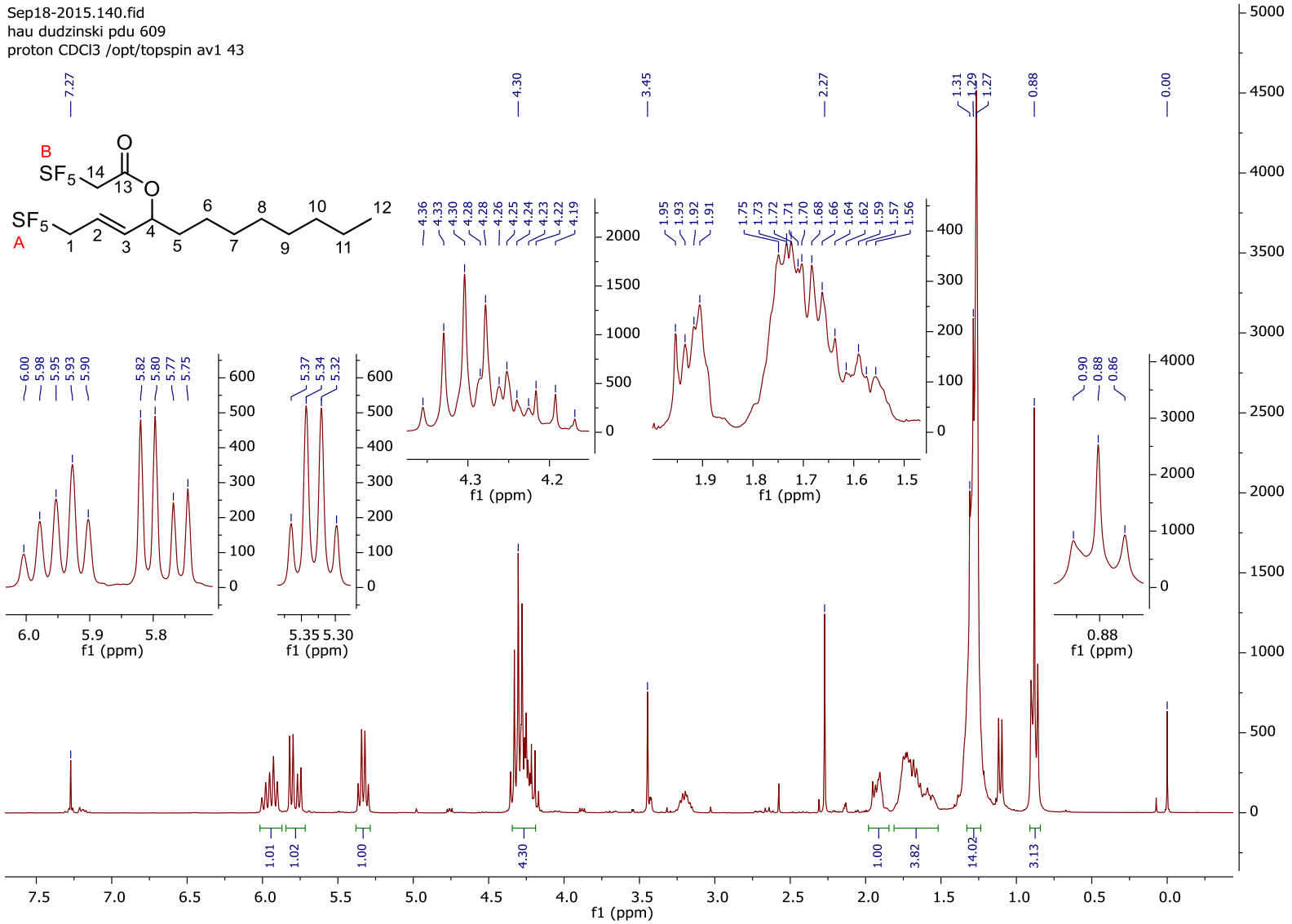
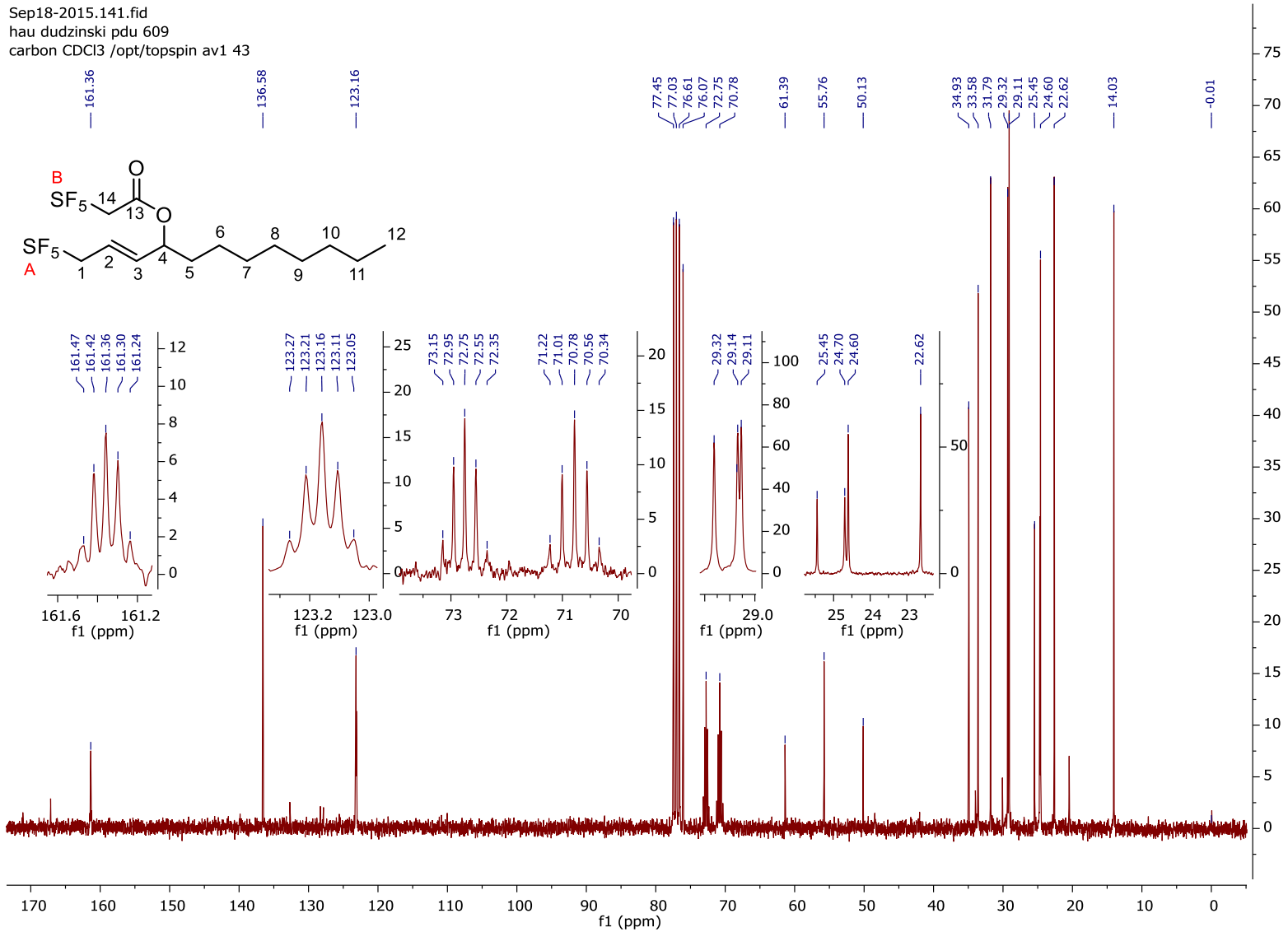


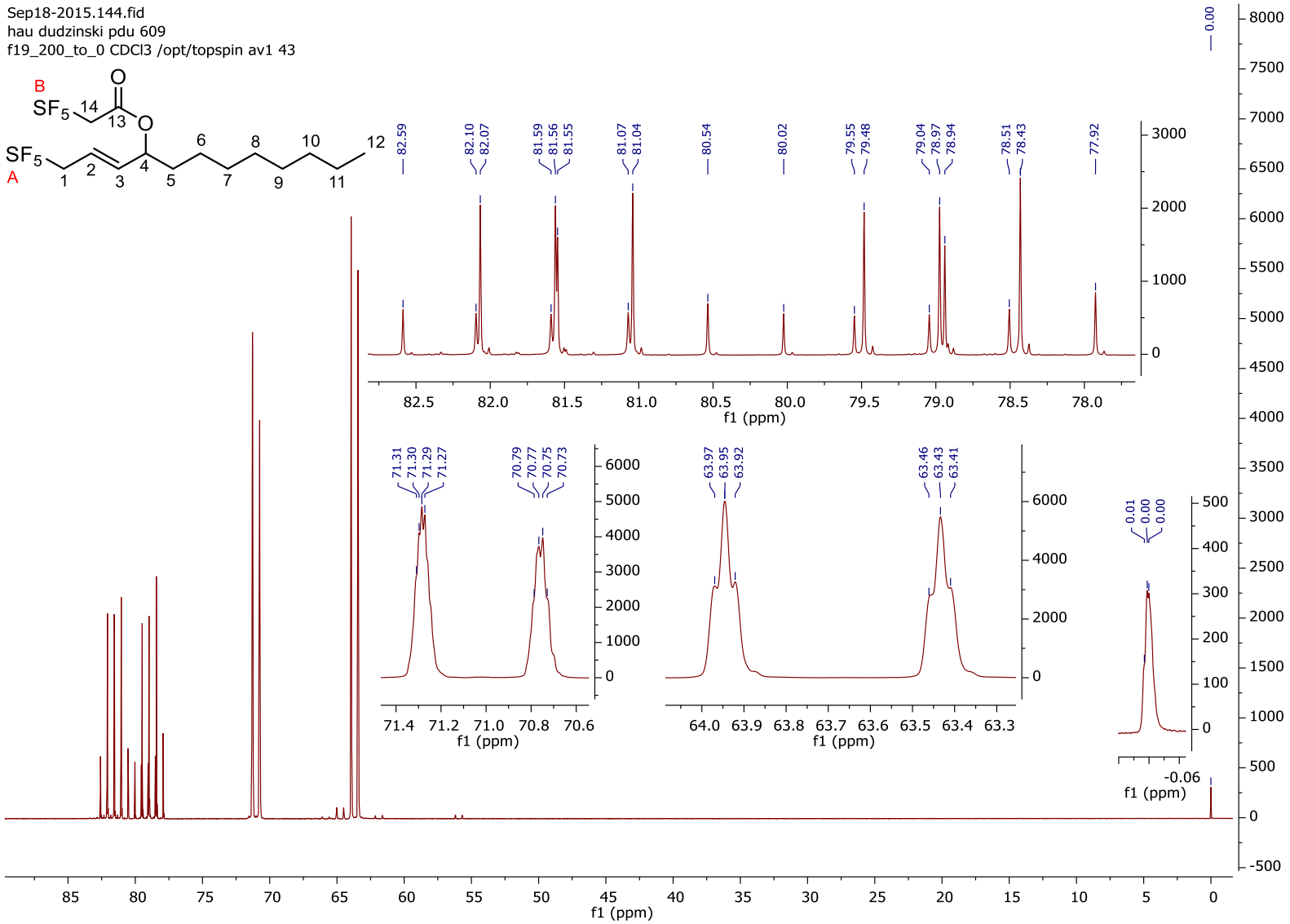
^{1}H NMR spectrum of compound **36b**



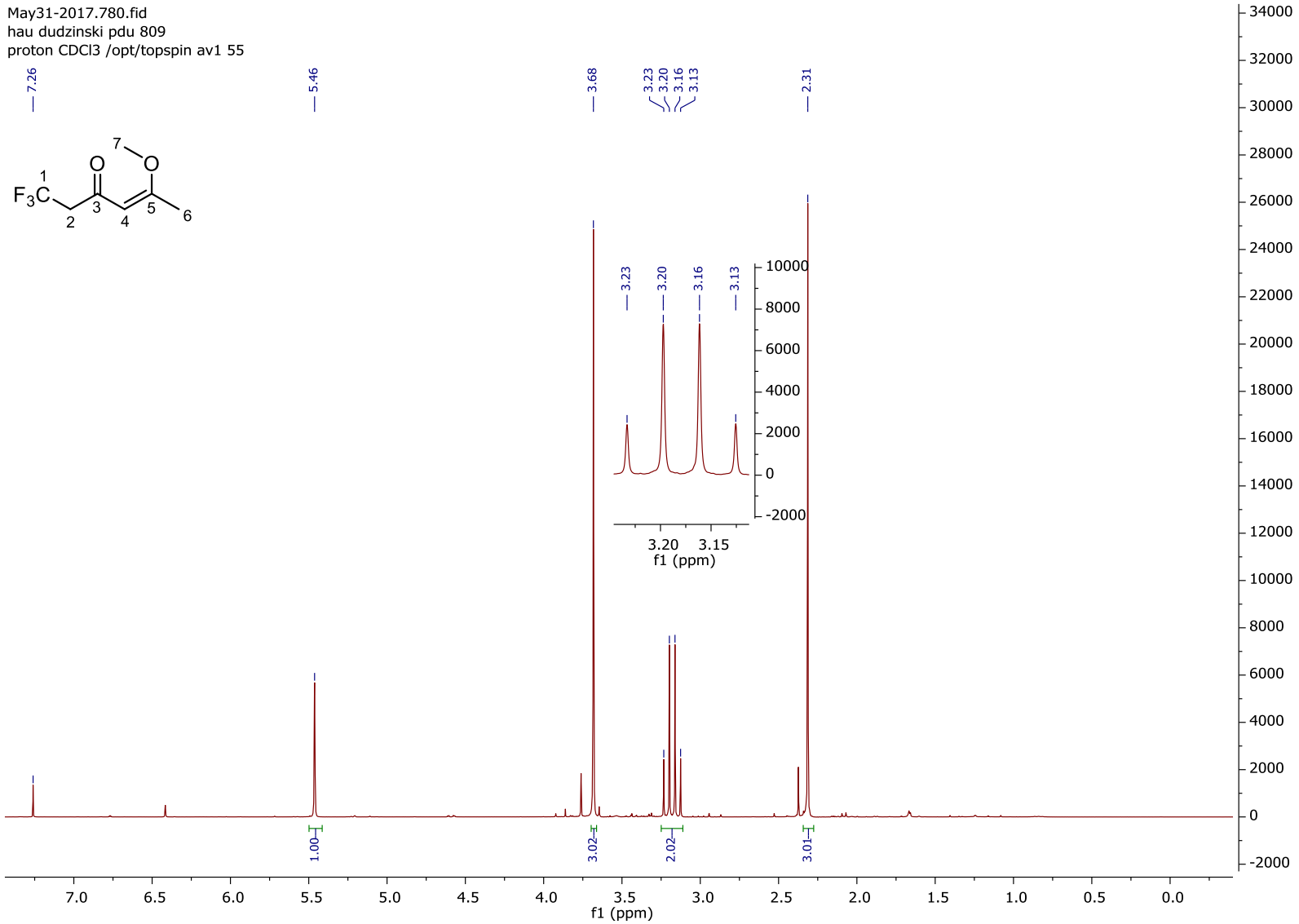
^{13}C NMR spectrum of compound **36b**



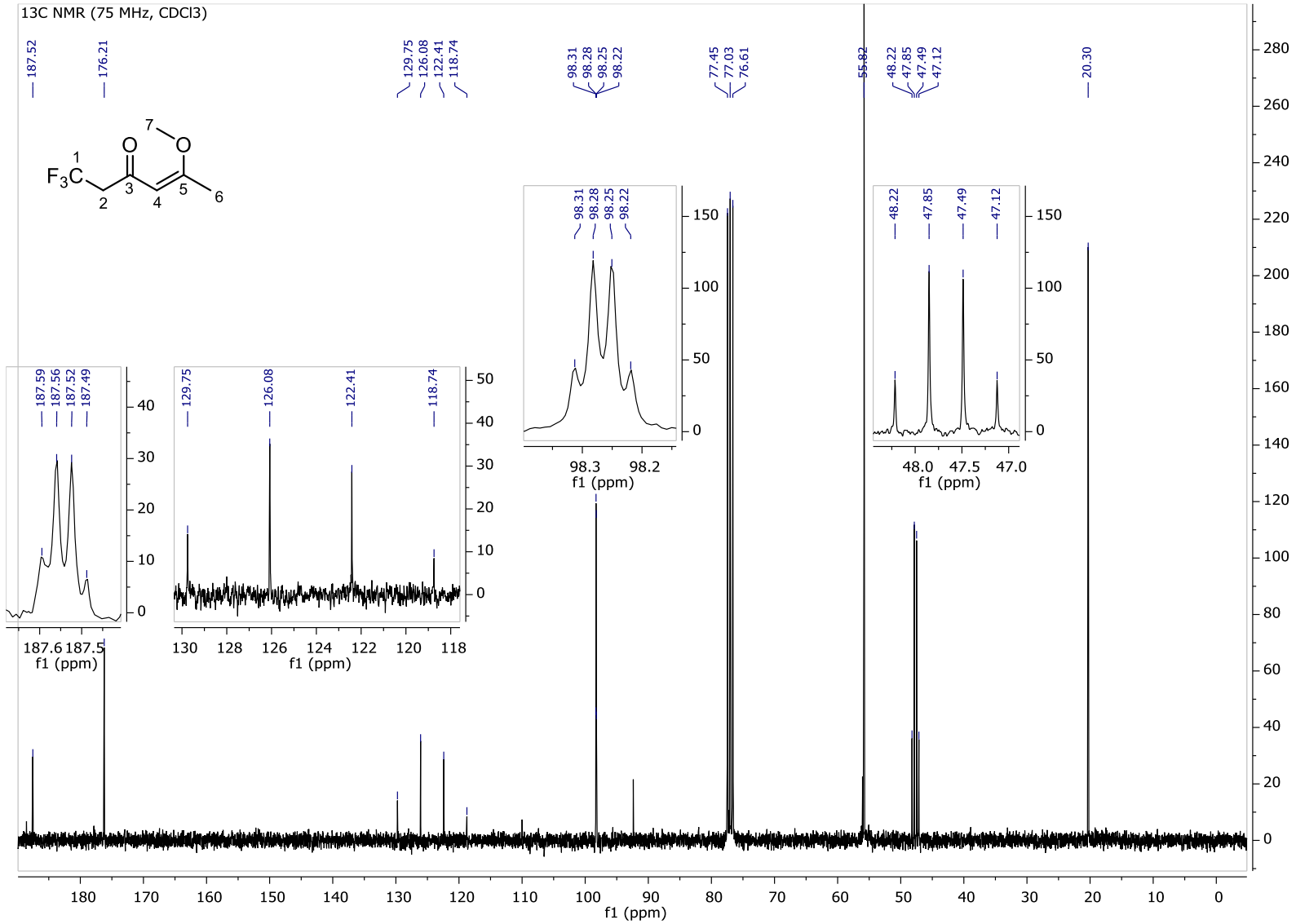
^{19}F NMR spectrum of compound **36b**



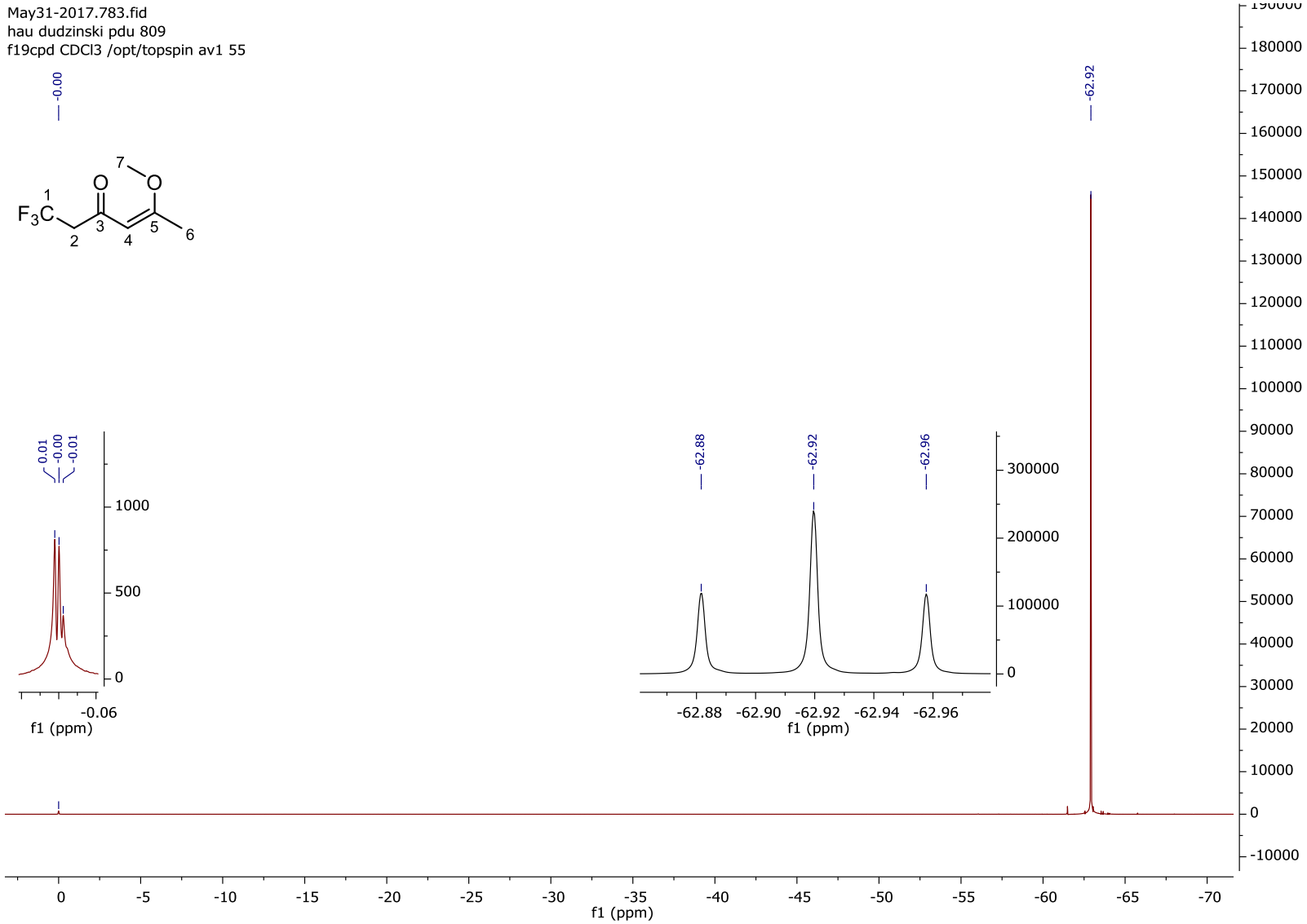
^{1}H NMR spectrum of compound **38**



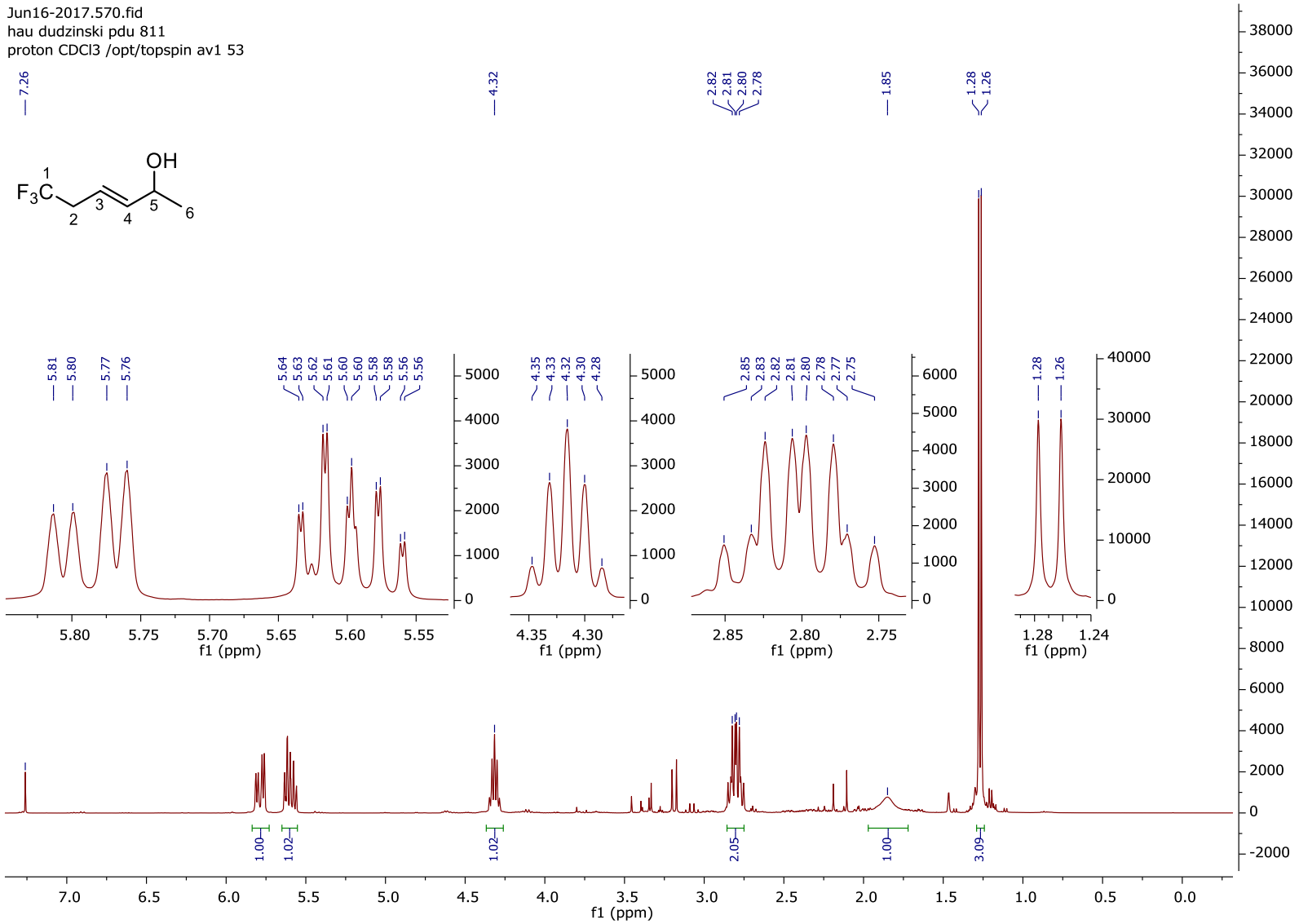
^{13}C NMR spectrum of compound **38**



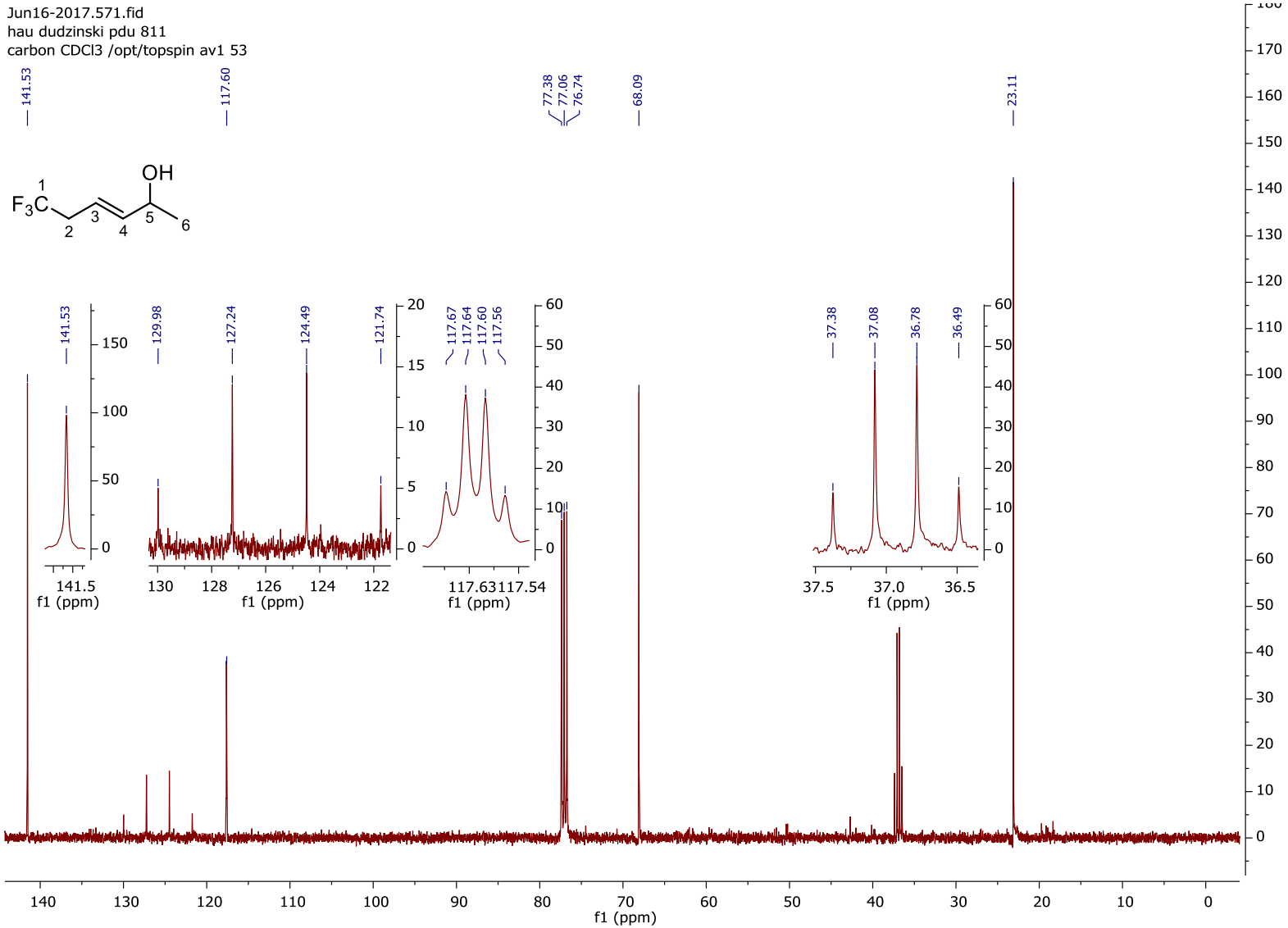
^{19}F NMR spectrum of compound **38**



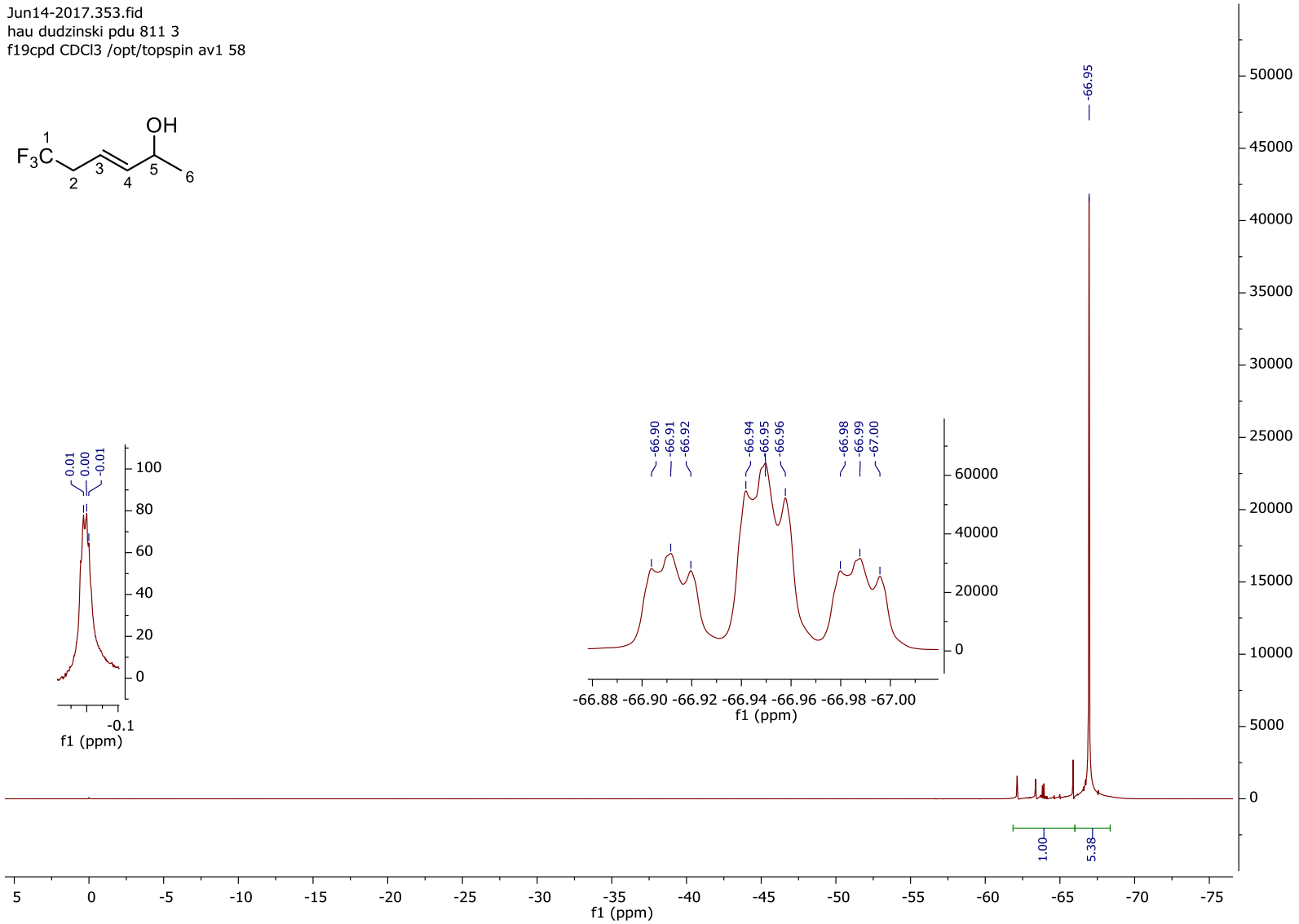
^{1}H NMR spectrum of (*E*)-6,6,6-trifluorohex-3-en-2-ol (**42**)



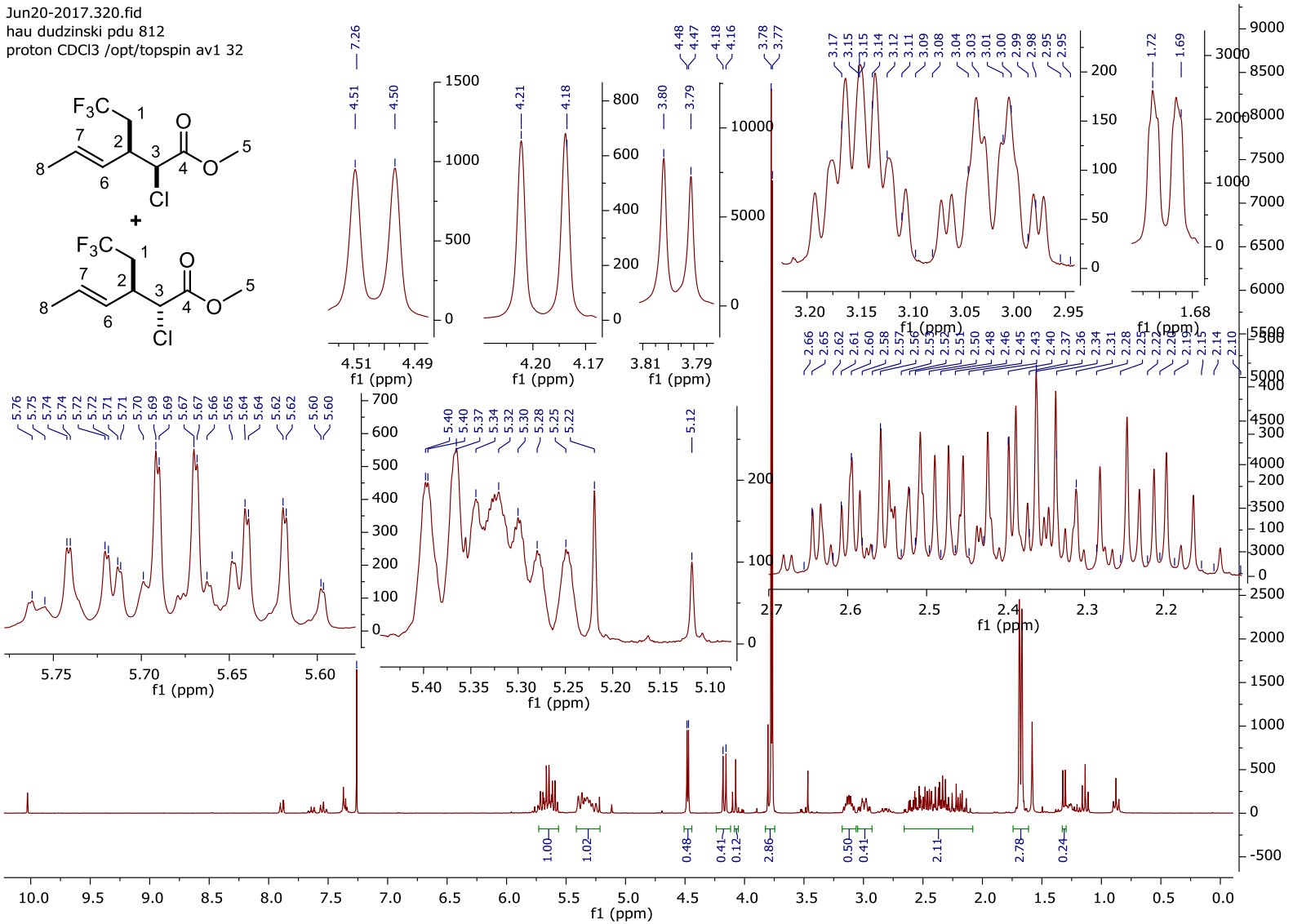
^{13}C NMR spectrum of (*E*)-6,6,6-trifluorohex-3-en-2-ol (**42**)



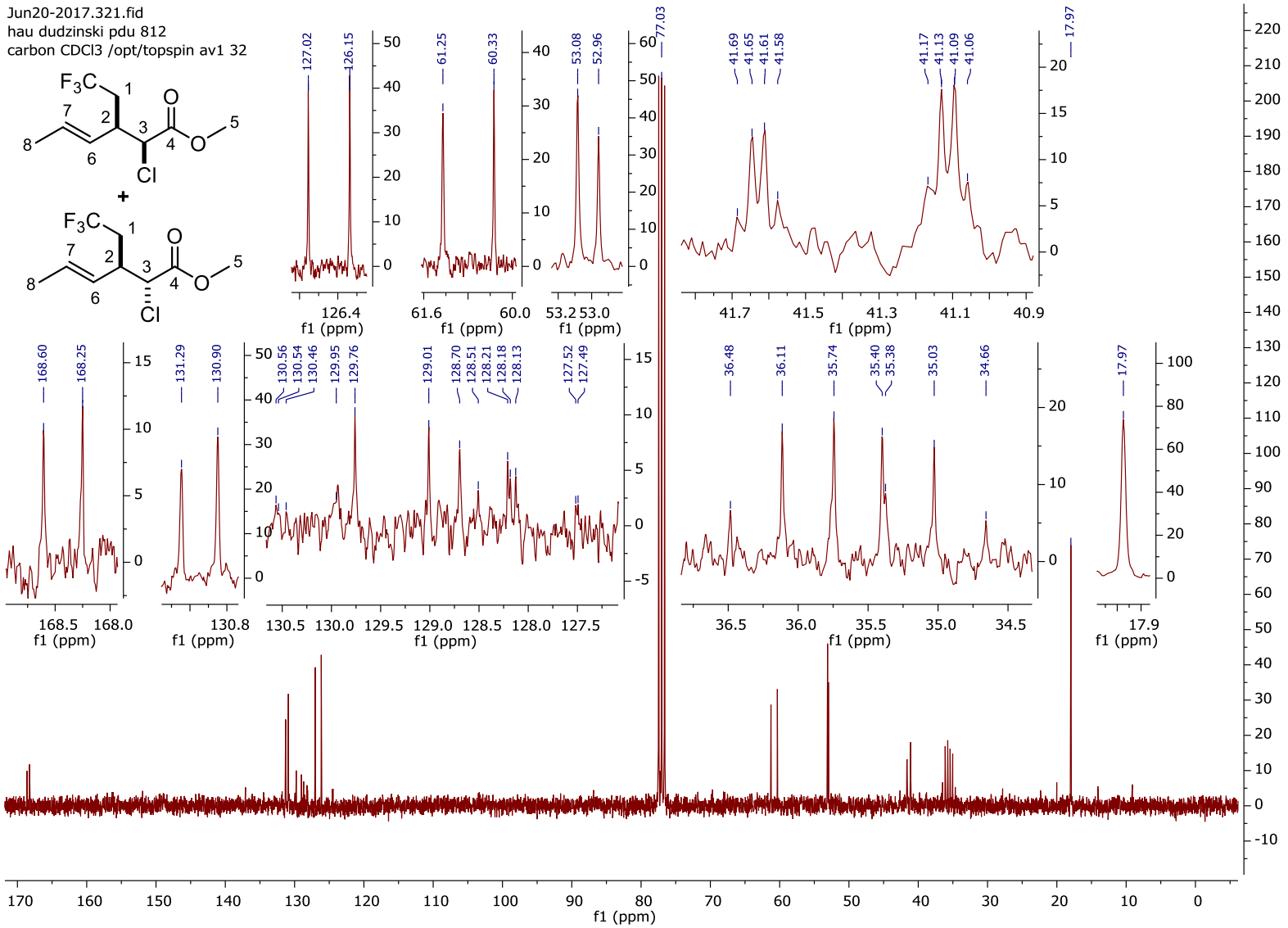
^{19}F NMR spectrum of (*E*)-6,6,6-trifluorohex-3-en-2-ol (**42**)



^{1}H NMR spectrum of methyl (*E*)-2-chloro-3-(2,2,2-trifluoroethyl)hex-4-enoate (**43**) (*syn*- and *anti*-; 45:55 ratio)



^{13}C NMR spectrum of methyl (*E*)-2-chloro-3-(2,2,2-trifluoroethyl)hex-4-enoate (**43**) (*syn*- and *anti*-; 45:55 ratio)



^{19}F NMR spectrum of methyl (*E*)-2-chloro-3-(2,2,2-trifluoroethyl)hex-4-enoate (**43**) (*syn*- and *anti*-; 45:55 ratio)