

## Supplementary Materials

### Fluorinated analogs of organosulfur compounds from garlic (*Allium sativum*). Synthesis, chemistry and anti-angiogenesis and antithrombotic studies

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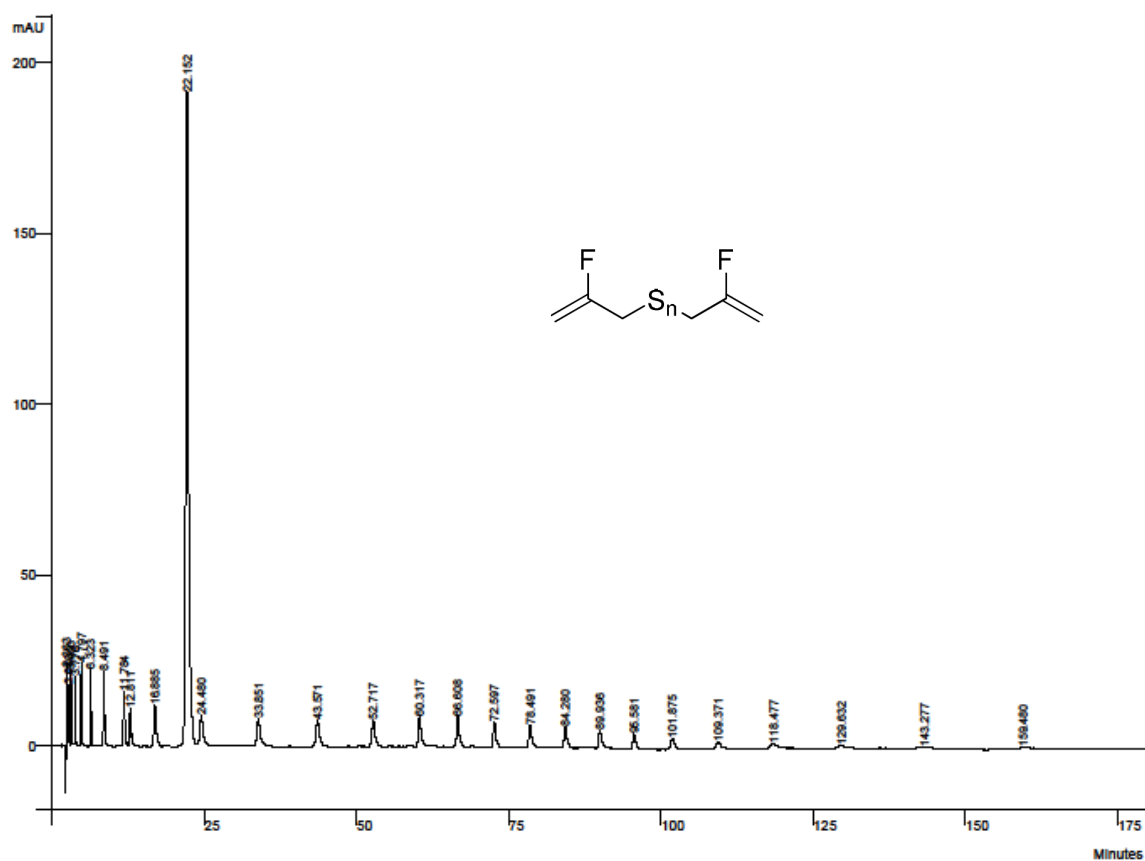
**Table S1.** Crystal data and structure refinement for **13**.

Compound	str949
Empirical formula	C <sub>6</sub> H <sub>10</sub> FNO <sub>2</sub> S
Formula weight	179.21
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub>
<i>a</i> (Å)	9.343(3)
<i>b</i> (Å)	5.2055(17)
<i>c</i> (Å)	16.632(6)
$\alpha$ (°)	90.00
$\beta$ (°)	92.240(5)
$\gamma$ (°)	90.00
<i>V</i> (Å <sup>3</sup> )	808.3(5)
<i>Z</i>	4
$\rho_{\text{calcd}}$ (g·cm <sup>-3</sup> )	1.473
$\mu$ (mm <sup>-1</sup> )	0.368
<i>F</i> (000)	376
Crystal size (mm)	0.12×0.08×0.02
$\vartheta$ range for data collection (°)	2.18-27.04
Reflections collected	6653
Independent reflections	3453
	[ <i>R</i> <sub>int</sub> = 0.0370]
Transmission factors (min/max)	0.9642/1
Data/restraints/params.	3453/1/199
Flack <i>x</i> parameter	-0.01(8)
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0497, 0.1012
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> (all data)	0.0701, 0.1111
Quality-of-fit <sup>c</sup>	0.982

<sup>a</sup> $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup> $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]$ .

<sup>c</sup>Quality-of-fit =  $[\sum [w(F_o^2 - F_c^2)^2] / (N_{\text{obs}} - N_{\text{params}})]^{1/2}$ , based on all data.

Ultra-performance liquid chromatography silver coordination ion spray mass spectrometry of bis(2-fluoroallyl) polysulfane mixture (21)



**Table S2. UPLC-(Ag<sup>+</sup>)-CIS-MS Analysis of Bis(2-fluoro-2-propenyl) Polysulfanes (21)**

Calcd smallest parent mass (exact): 352.853 Da		Found: 352.802 Da		S4
Mass of tallest peak: 355 Da [3.53 min]				
Formula: C <sub>6</sub> H <sub>8</sub> F <sub>2</sub> S <sub>4</sub> Ag				
m/z	%, calcd.	m/z measured	%, measured	
353	89.7	352.8	95.3	
355	100	354.79	100	
357	16.7	356.87	14.7	
Calcd smallest parent mass (exact): 384.825 Da		Found: 384.820 Da		S5
Mass of tallest peak: 387 Da [4.55 min]				
Formula: C <sub>6</sub> H <sub>8</sub> F <sub>2</sub> S <sub>5</sub> Ag				
m/z	%, calcd.	m/z measured	%, measured	
385	86.2	384.82	81.4	
387	100	386.8	100	
389	20.5	388.79	23.2	
391	1.9	390.83	2.3	
Calcd smallest parent mass (exact): 416.797 Da		Found: 416.777 Da		S6
Mass of tallest peak: 418 Da [5.64 min]				
Formula: C <sub>6</sub> H <sub>8</sub> F <sub>2</sub> S <sub>6</sub> Ag				
m/z	%, calcd.	m/z measured	%, measured	
416	82.9	416.78	79.8	
418	100	418.77	100	
420	24.1	420.69	25.2	
422	2.8	422.75	2.9	
424	0.2	424.64	0.35	
Calcd smallest parent mass (exact): 448.769 Da		Found: 448.712 Da		S7
Mass of tallest peak: 450 Da [6.50 min]				
Formula: C <sub>6</sub> H <sub>8</sub> F <sub>2</sub> S <sub>7</sub> Ag				
m/z	%, calcd.	m/z measured	%, measured	
448	79.8	448.71	73.8	
450	100	450.71	100	
452	27.7	452.65	29.0	
454	3.8	454.71	4.2	
Calcd smallest parent mass (exact): 480.741 Da		Found: 480.659		S8
Mass of tallest peak: 482 Da [7.56 min]				
Formula: C <sub>6</sub> H <sub>8</sub> F <sub>2</sub> S <sub>8</sub> Ag				
m/z	%, calcd.	m/z measured	%, measured	
480	77.0	480.66	73.6	
482	100	482.64	100	

484	31.2	484.58	34.9
486	4.9	486.66	5.1

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Calcd smallest parent mass (exact): 512.7131 Da    *Found: 512.607 Da*    **S9**

Mass of tallest peak: 514 Da [8.47 min]

Formula: **C<sub>6</sub>H<sub>8</sub>F<sub>2</sub>S<sub>9</sub>Ag**

<i>m/z</i>	%, calcd.	<i>m/z</i> measured	%, measured
512	74.4	512.6	73.4
514	100	514.6	100
516	34.6	516.5	38.4
518	6.2	518.5	7.4

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Calcd smallest parent mass (exact): 362.682 Da    *Found: 362.689 Da*    **sulfur**

Mass of tallest peak: 364 Da [8.99 min]

Formula: **S<sub>8</sub>Ag**

<i>m/z</i>	%, calcd.	<i>m/z</i> measured	%, measured
362	77.4	362.69	79.3
364	100	364.68	100
366	30.7	366.68	34.9
368	4.7	368.7	4.6

---

Calcd smallest parent mass (exact): 544.685 Da    *Found: 544,547 Da*    **S10**

Mass of tallest peak: 546. Da [9.24 min]

Formula: **C<sub>6</sub>H<sub>8</sub>F<sub>2</sub>S<sub>10</sub>Ag**

<i>m/z</i>	%, calcd.	<i>m/z</i> measured	%, measured
544	71.9	544.6	75.4
546	100	546.6	100
548	38.0	548.5	43.2
550	7.5	550.6	6.3

---

Calcd smallest parent mass (exact): 576.657 Da    *Found: 576.523 Da*    **S11**

Mass of tallest peak: 578. Da [9.99 min]

Formula: **C<sub>6</sub>H<sub>8</sub>F<sub>2</sub>S<sub>11</sub>Ag**

<i>m/z</i>	%, calcd.	<i>m/z</i> measured	%, measured
576	69.6	576.5	67.7
578	100	578.5	100
580	41.3	580.4	44.7
582	9.0	582.5	7.0

---

Calcd smallest parent mass (exact): 608.629 Da    *Found: 608.536 Da*    **S12**

Mass of tallest peak: 610. Da [10.78 min]

Formula: **C<sub>6</sub>H<sub>8</sub>F<sub>2</sub>S<sub>12</sub>Ag**

<i>m/z</i>	%, calcd.	<i>m/z</i> measured	%, measured
608	67.4	608.6	60.5
610	100	610.5	100

612 44.5 612.5 45.2

---

Calcd smallest parent mass (exact): 640.601 Da *Found: 640.365 Da* **S13**

Mass of tallest peak: 642 Da [11.63 min]

Formula: **C<sub>6</sub>H<sub>8</sub>F<sub>2</sub>S<sub>13</sub>Ag**

<i>m/z</i>	% calcd.	<i>m/z</i> measured	%, measured
640	65.330	640.4	62.0
642	100	642.4	100
644	47.7	644.4	48.8
646	12.3	646.3	9.3

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Calcd smallest parent mass (exact): 672.574 Da *Found: 672.385 Da* **S14**

Mass of tallest peak: 674 Da [12.75 min]

Formula: **C<sub>6</sub>H<sub>8</sub>F<sub>2</sub>S<sub>14</sub>Ag**

<i>m/z</i>	% calcd.	<i>m/z</i> measured	%, measured
672	63.4	672.4	67.8
674	100	674.4	100
676	50.8	676.3	47.0

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Calcd smallest parent mass (exact): 704.546 Da *Found: 704.310 Da* **S15**

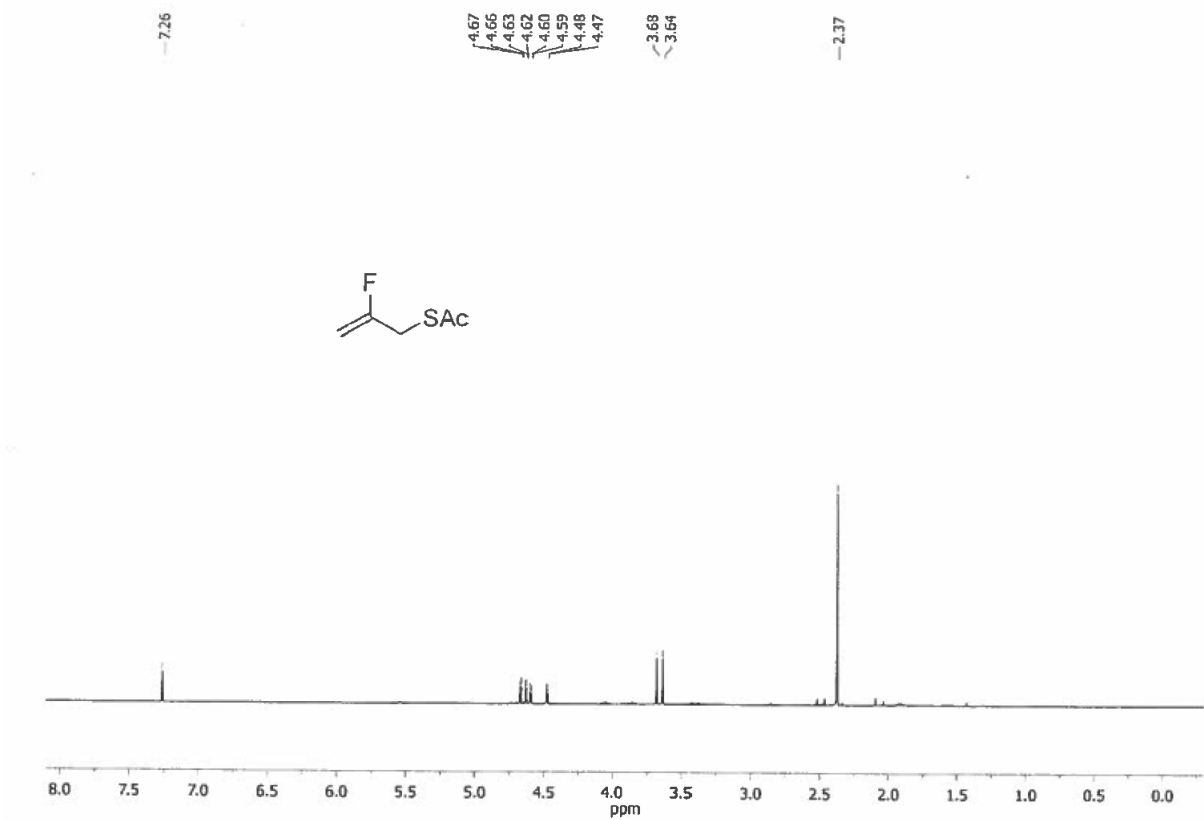
Mass of tallest peak: 706 Da [14.48 min]

Formula: **C<sub>6</sub>H<sub>8</sub>F<sub>2</sub>S<sub>15</sub>Ag**

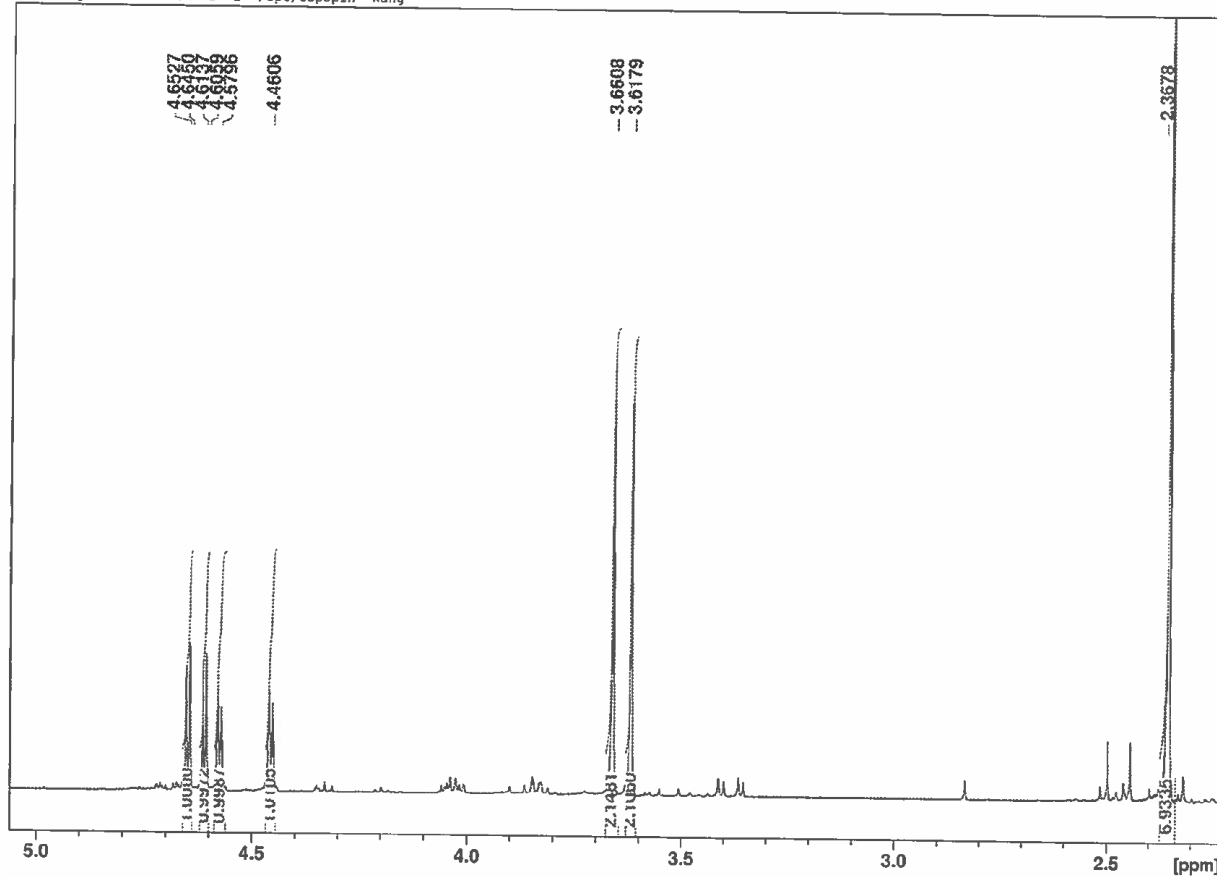
<i>m/z</i>	% calcd.	<i>m/z</i> measured	%, measured
704	61.6	704.3	51.2
706	100	706.3	100
708	53.9	708.3	60.2

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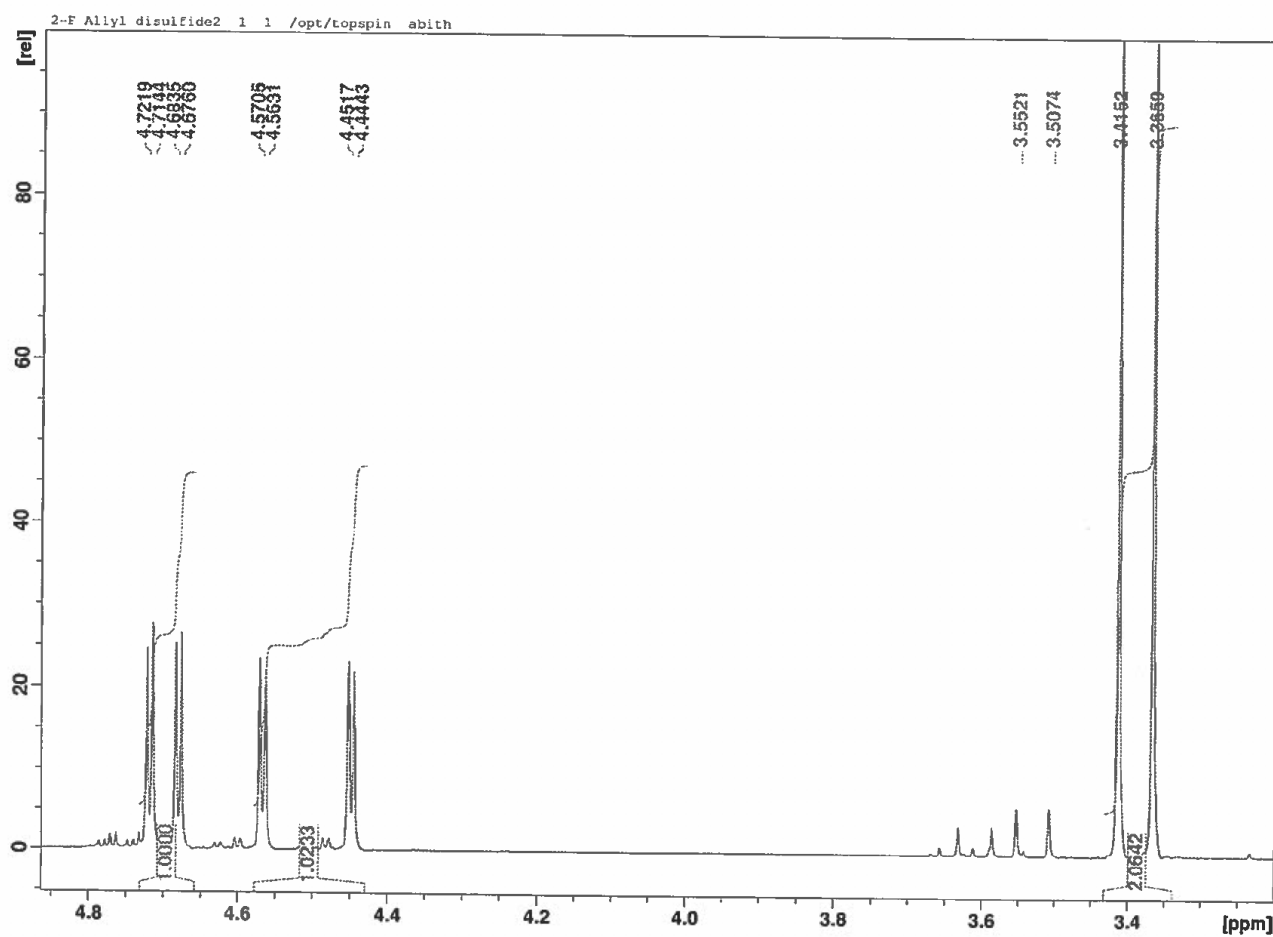
<sup>1</sup>H NMR spectra  
S-(2-Fluoroallyl) ethanethioate (11)



2-F Allyl SAc 12-7-07 1 1 /opt/topspin Wang

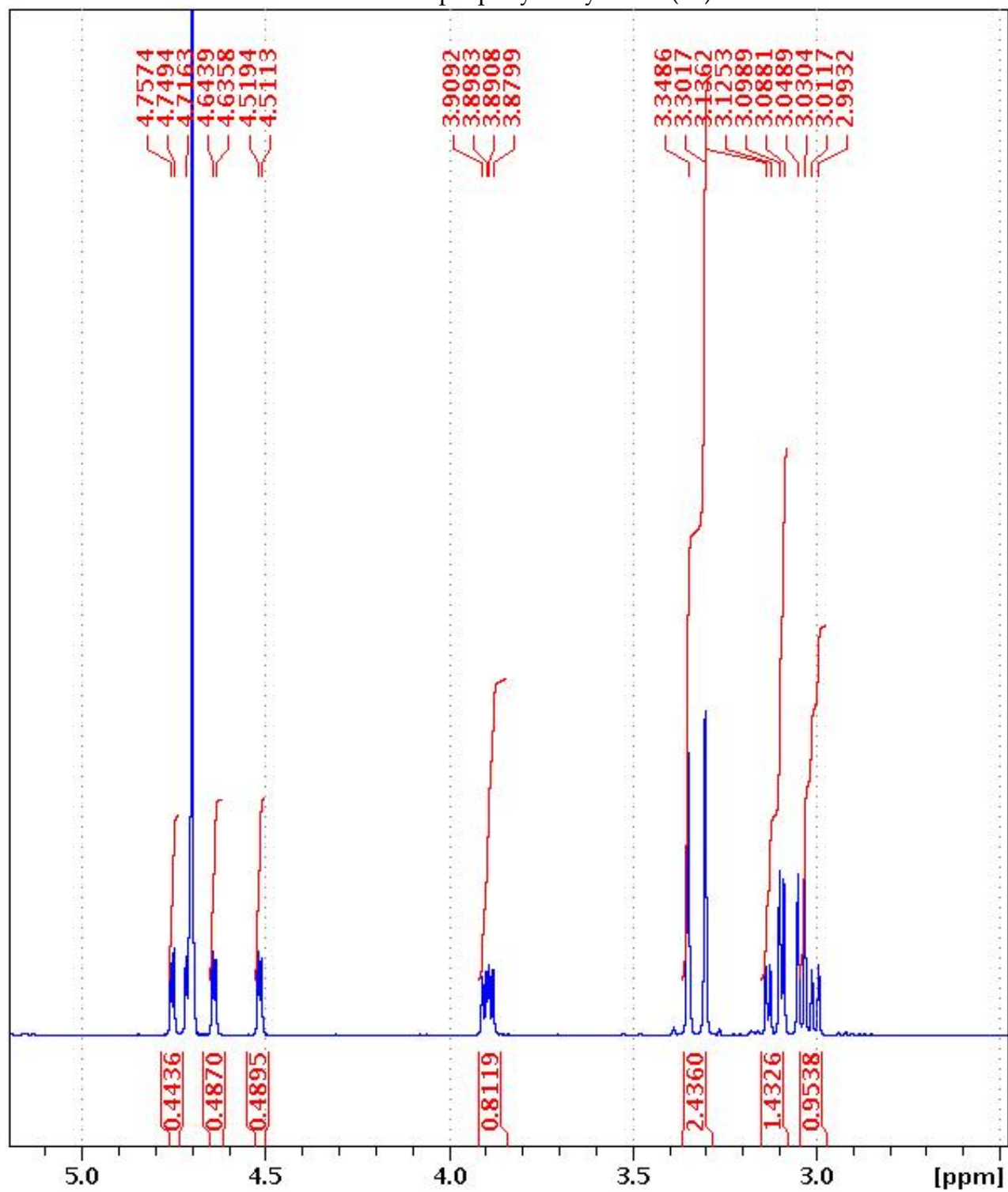


## 1,2-Bis(2-fluoroallyl)disulfane (12)



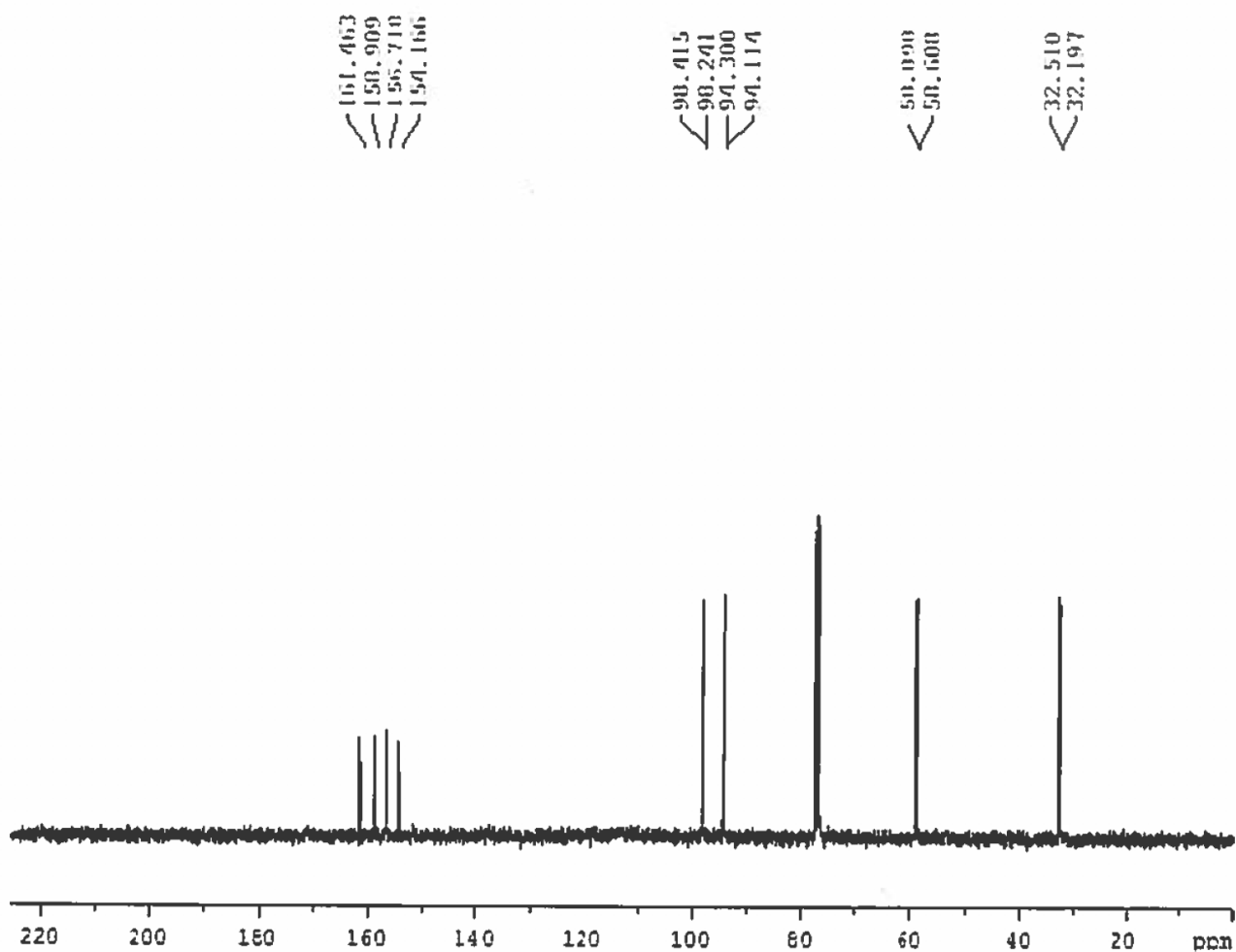


## S-2 -Fluoro-2-propenyl-L-cysteine (13)

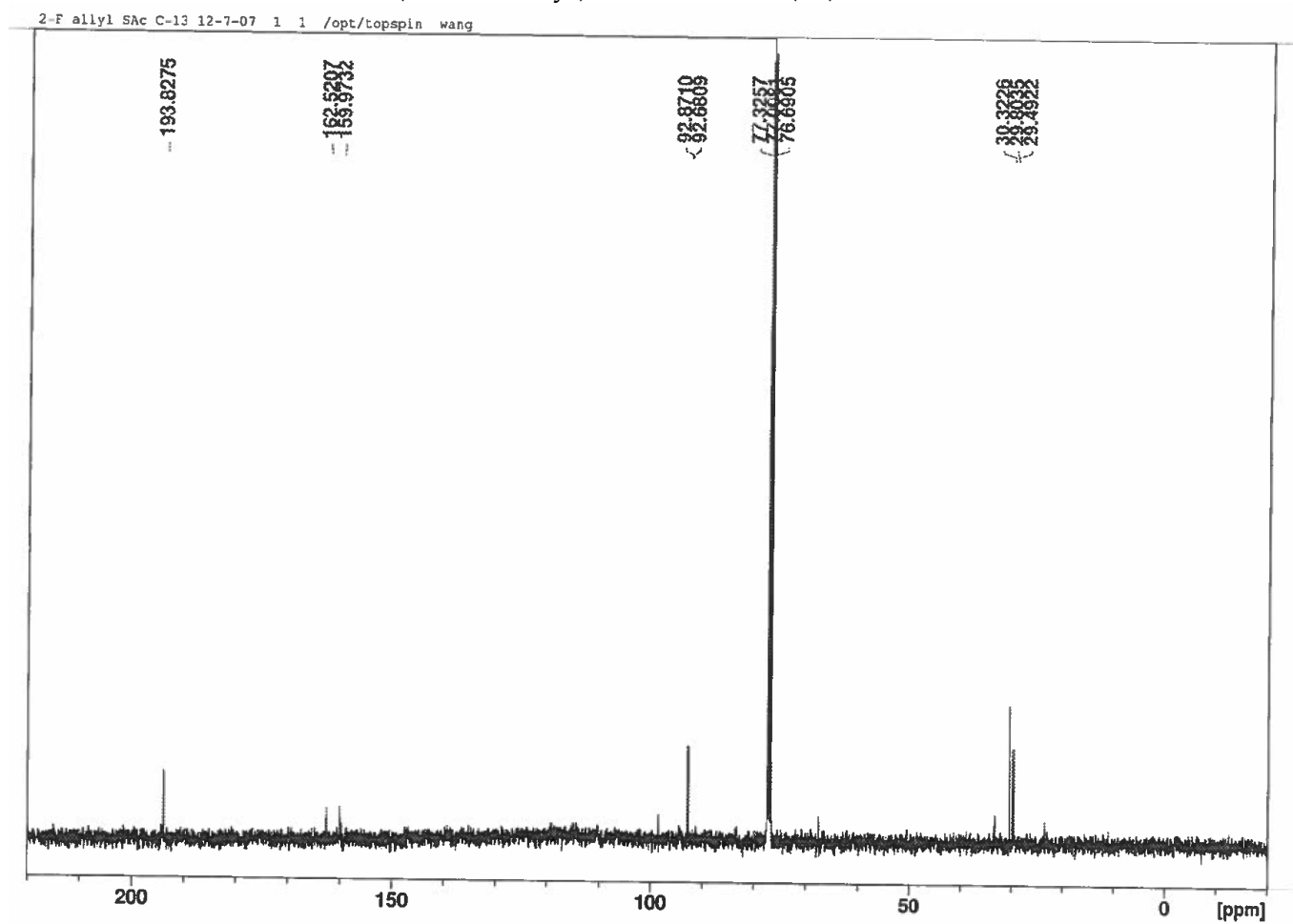


$^{13}\text{C}$  NMR Spectra

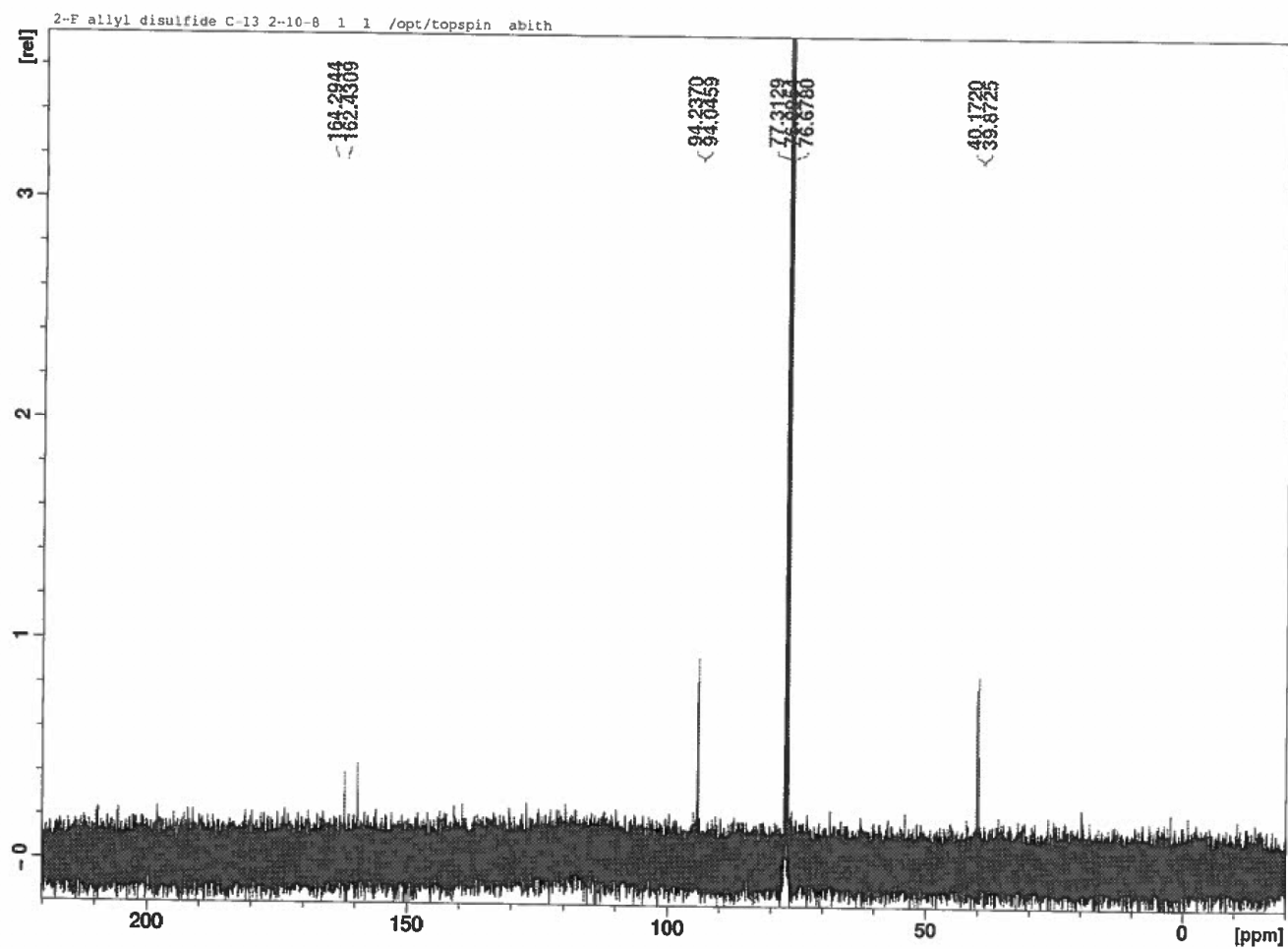
Difluoroallicin (9; S-(2-Fluoroallyl) 2-fluoroprop-2-ene-1-sulfinothioate)



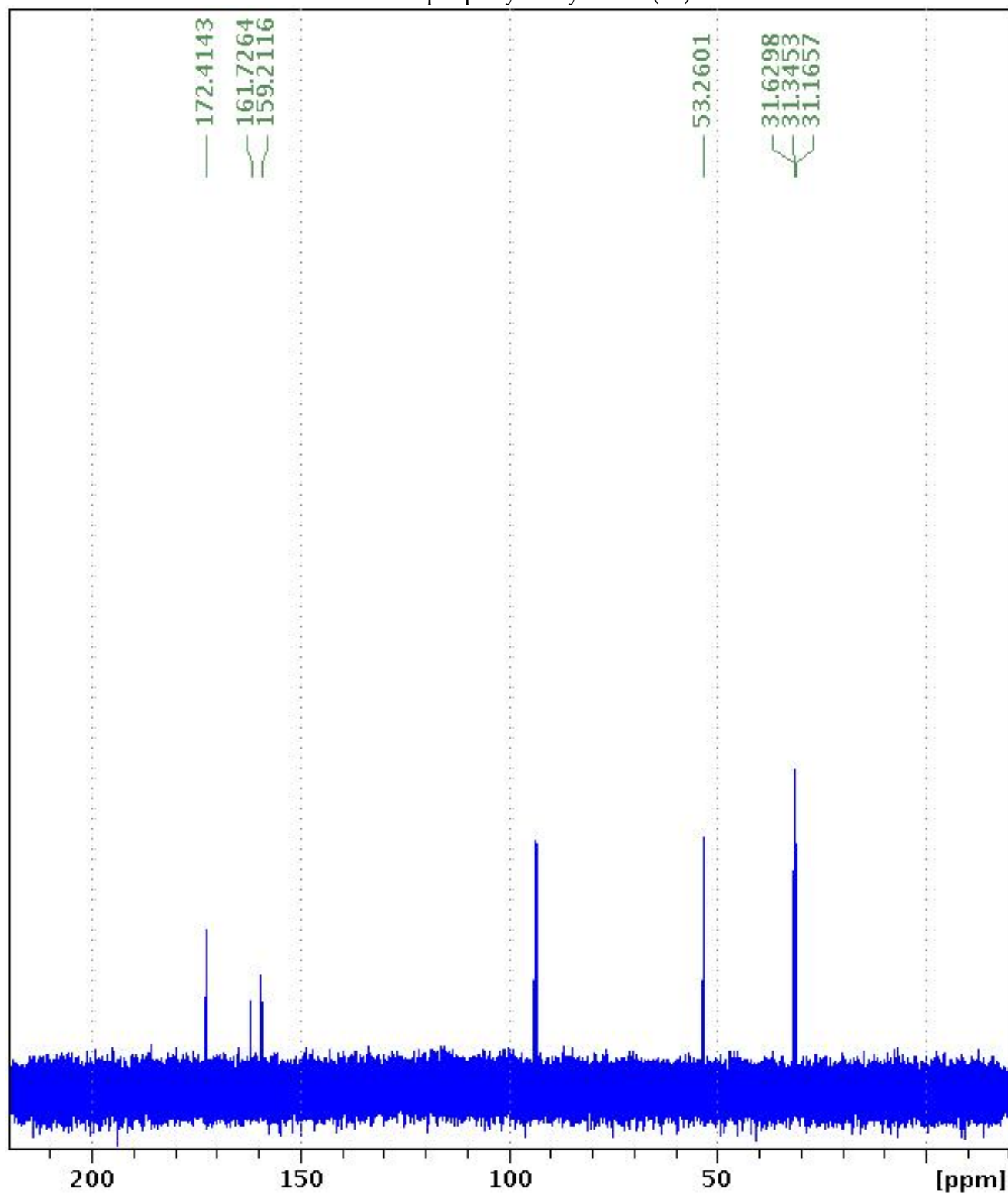
## S-(2-Fluoroallyl) ethanethioate (11)



## 1,2-Bis(2-fluoroallyl)disulfane (12)

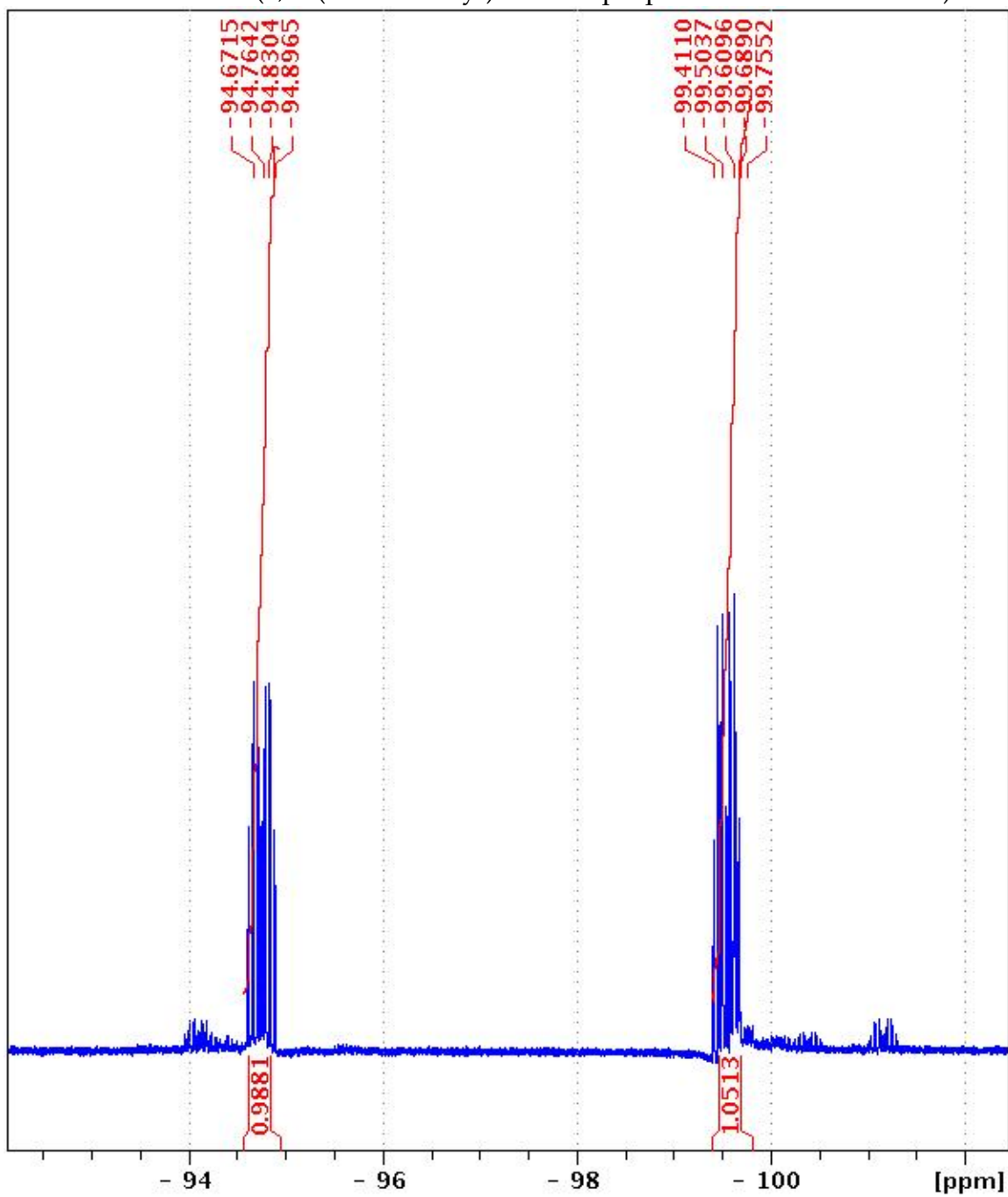


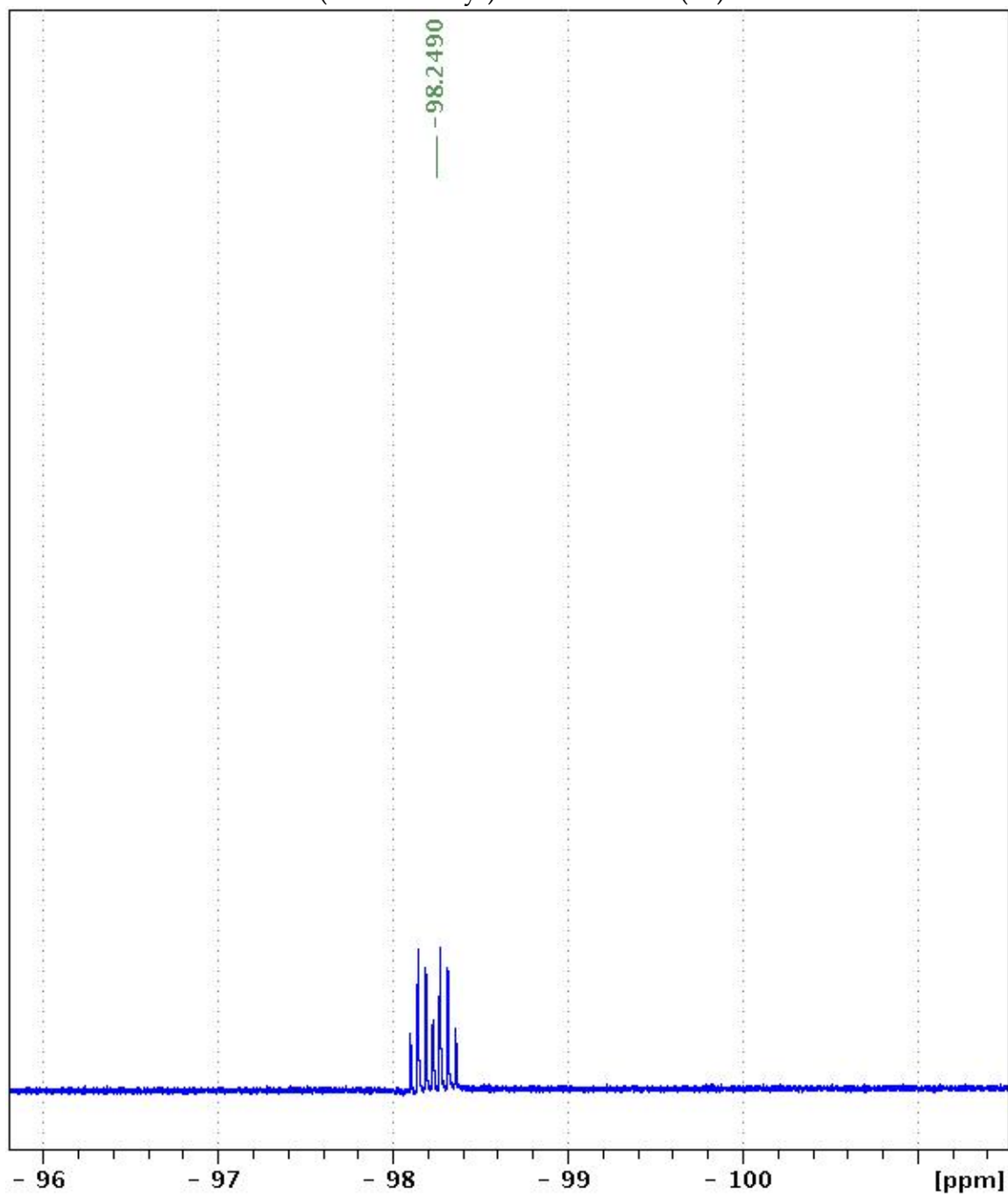
## S-2 -Fluoro-2-propenyl-L-cysteine (13)



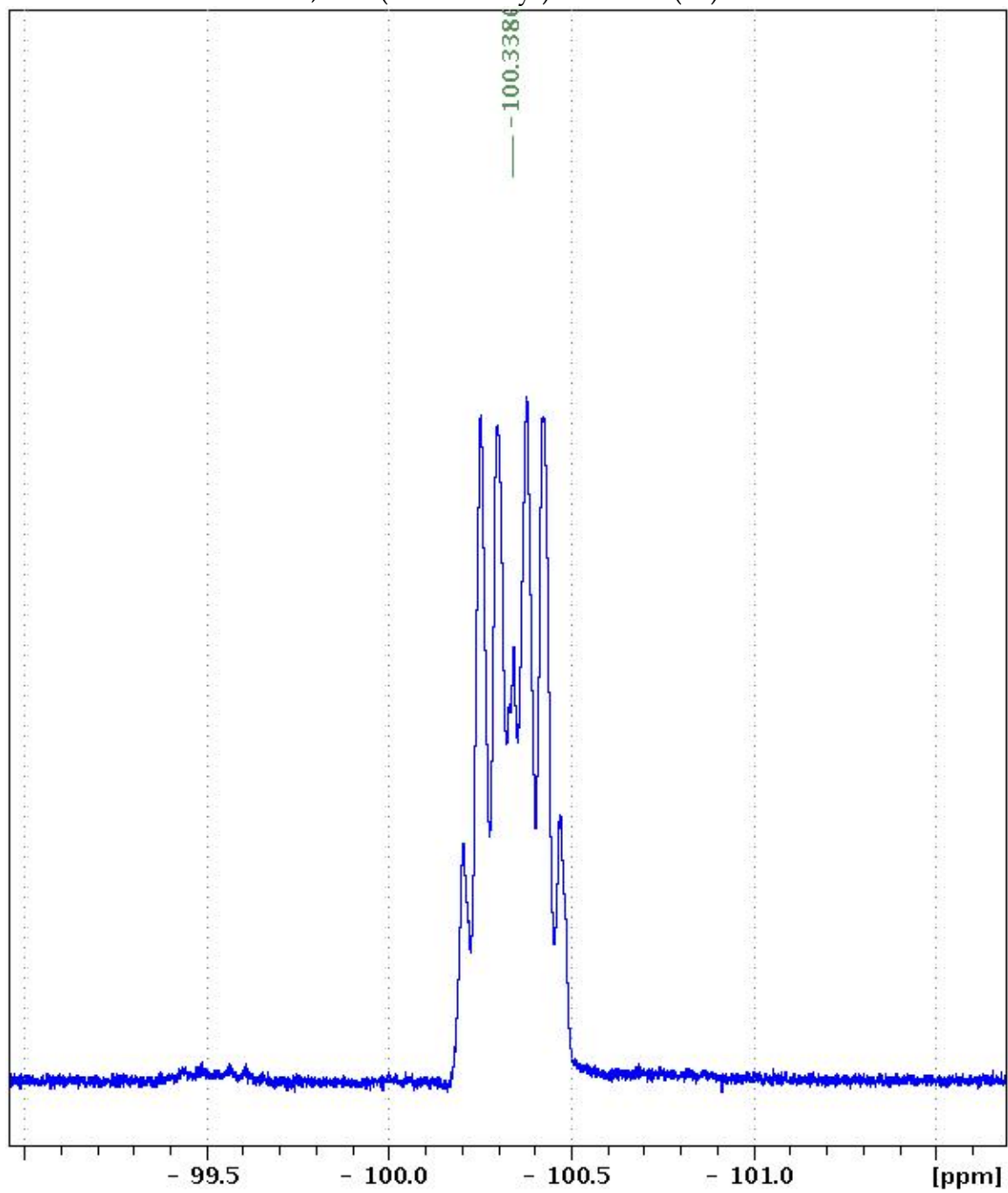
**$^{19}\text{F}$  NMR Spectra**

Difluoroallicin (9; S-(2-Fluoroallyl) 2-fluoroprop-2-ene-1-sulfinothioate)

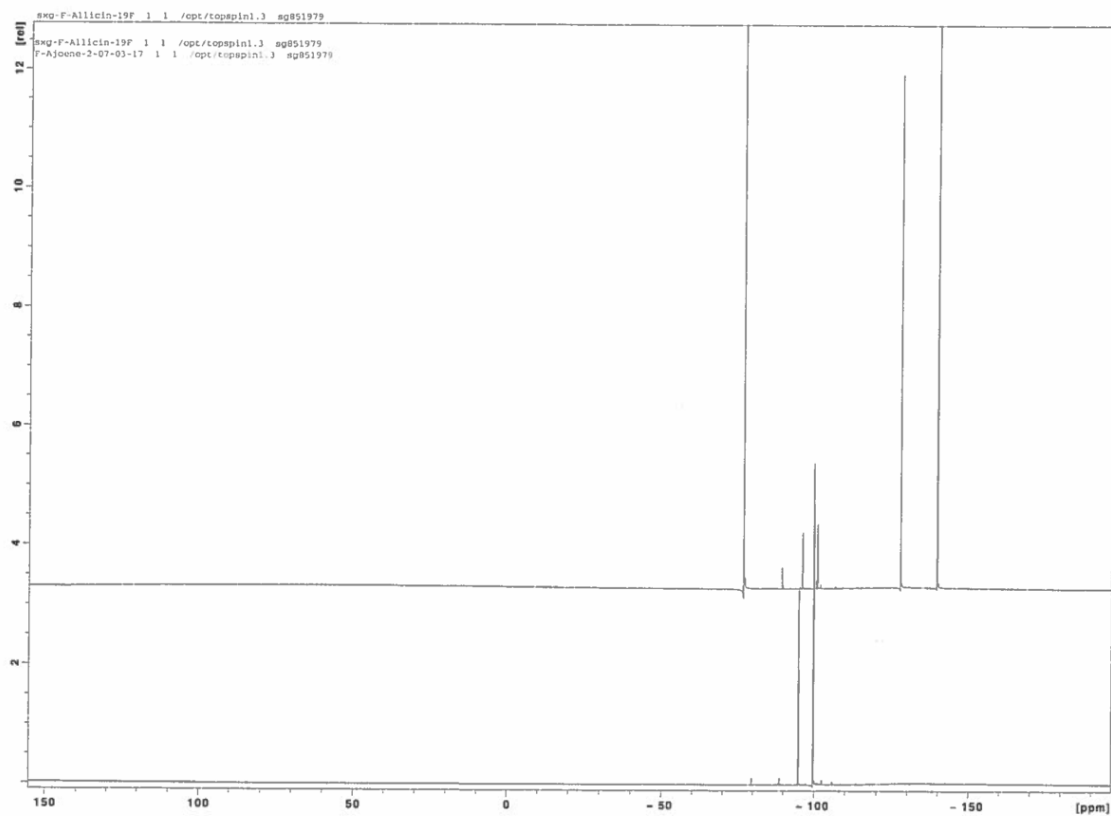


S-(2-Fluoroallyl) ethanethioate (**11**)

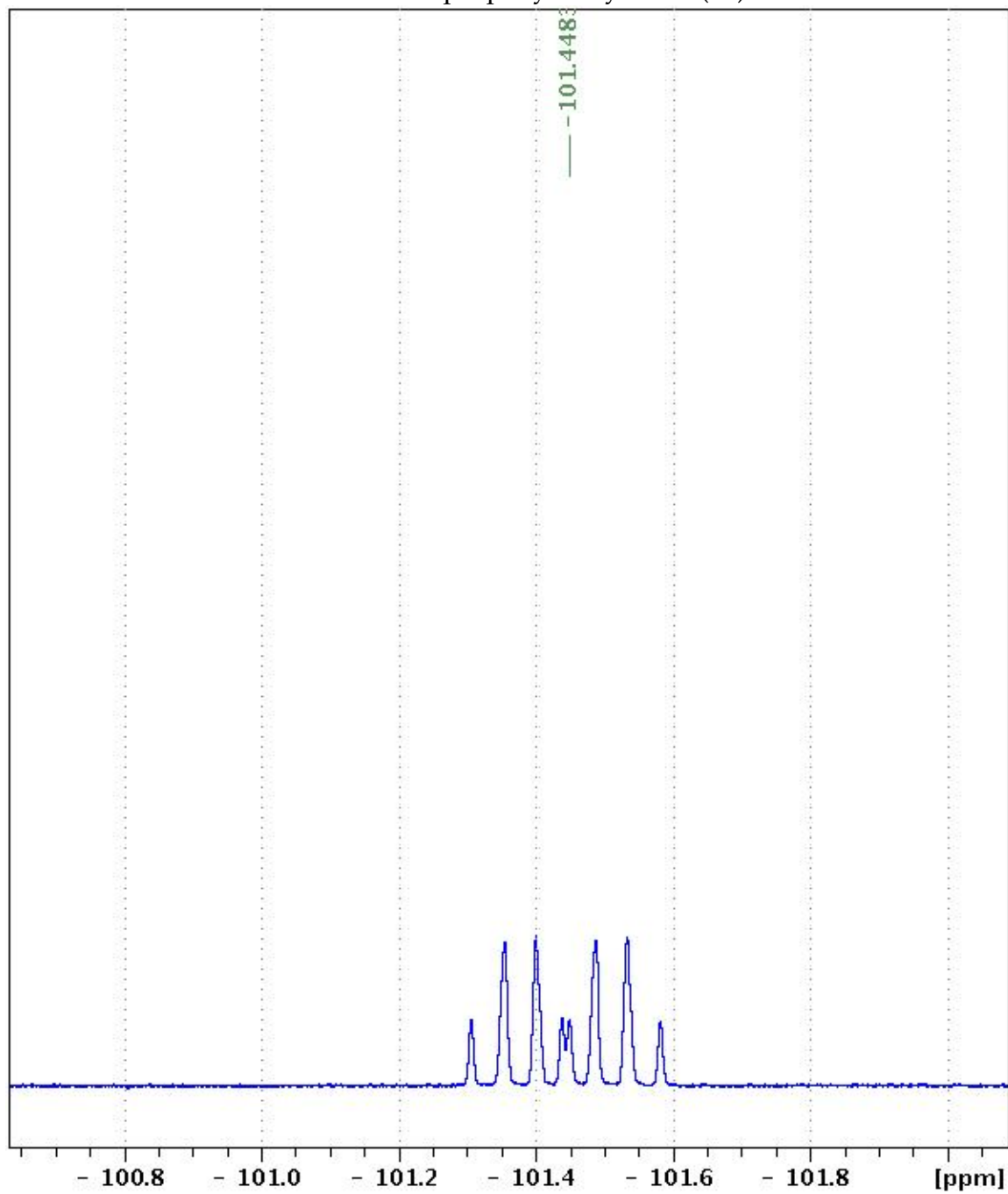
## 1,2-Bis(2-fluoroallyl)disulfane (12)



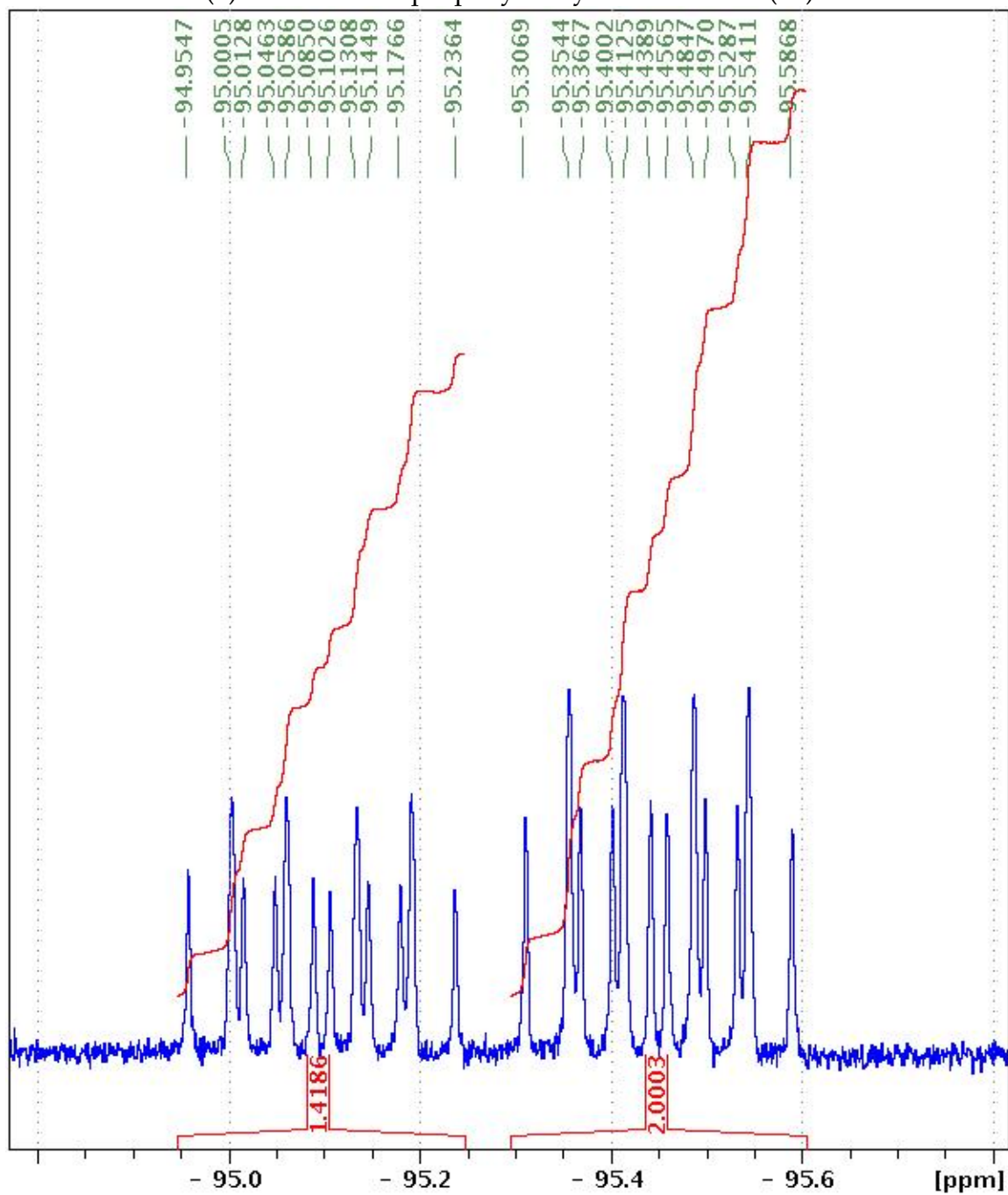


Mixture of difluoroallicin, **9**, and trifluoroajoene, **16**

## S-2 -Fluoro-2-propenyl-L-cysteine (13)

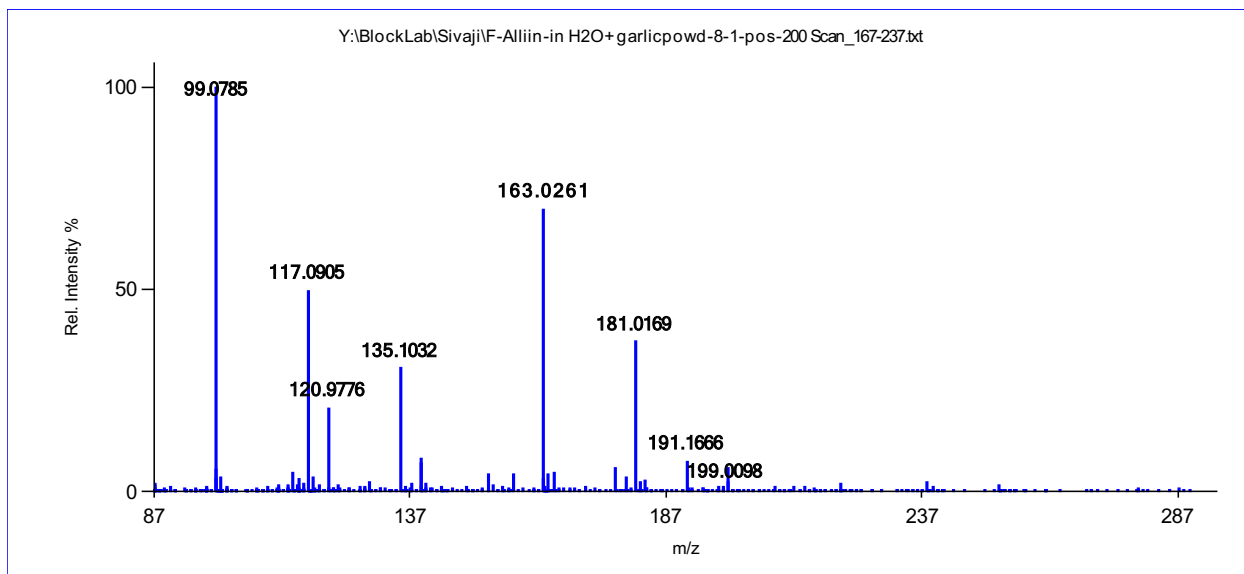


(+)-S-2-Fluoro-2-propenyl-L-cysteine S-oxide (22)



## DART Mass Spectra

DART MS of fluoroalliin with powdered garlic showing alliin, monofluoroallicin and difluoroallicin  
 $[C_6H_9O_1F_2S_2 (M+H) - \text{difluoroallicin Calc. } m/z \text{ } 199.0063 \text{ Found } 199.0098; C_6H_{10}O_1F_1S_2 (M+H) - \text{monofluoroallicin? Calc. } m/z \text{ } 181.0157 \text{ Found } 181.0169]$



## Mixture of difluoroallicin and trifluoroajoene

