

## Supporting Information

### Fluorinated enamines of nucleobases as precursors of nucleoside analogues. Synthesis, spectroscopic and structural studies

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**Table S-1** Crystal data and structure refinement for **(Z)-9b** at 293K and 100K

Empirical formula	<b>C<sub>14</sub>H<sub>9</sub>F<sub>4</sub>N<sub>3</sub>O<sub>2</sub></b>	
Formula weight	327.24	
Temperature	293(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Monoclinic, <i>Pn</i>
Unit cell dimensions	a = 15.3478(10) Å	a = 15.050(2) Å
	b = 6.2126(5) Å	b = 12.1206(19) Å
	c = 15.3478(10) Å	c = 15.425(2) Å
	β = 105.82 °	β = 105.596(12)°
Volume	1407.99(17) Å <sup>3</sup>	2710.1(7) Å <sup>3</sup>
Z, Calculated density	4, 1.544 g/cm <sup>3</sup>	8, 1.604 g/cm <sup>3</sup>
Absorption coefficient	0.141 mm <sup>-1</sup>	0.147 mm <sup>-1</sup>
F(000)	664	1328
Crystal size	0.5 x 0.3 x 0.1 mm	0.5 x 0.3 x 0.1 mm
Theta range for data collection	2.76 to 29.61°	2.74° to 29.28°
Limiting indices	-19 ≤ h ≤ 20, -8 ≤ k ≤ 8, -20 ≤ l ≤ 20	-20 ≤ h ≤ 15, -15 ≤ k ≤ 16, -21 ≤ l ≤ 18
Reflections collected / unique	13124 / 3655 [R(int) = 0.1225]	17292 / 8467 [R(int) = 0.0404]
Completeness to θ = 29.61°	92.2%	91.2 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3655 / 0 / 285	8467 / 8 / 874
Goodness-of-fit on F <sup>2</sup>	1.132	1.140
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0603, wR <sub>2</sub> = 0.1239	R <sub>1</sub> = 0.0822, wR <sub>2</sub> = 0.2454
R indices (all data)	R <sub>1</sub> = 0.1133, wR <sub>2</sub> = 0.1884	R <sub>1</sub> = 0.0969, wR <sub>2</sub> = 0.2706
Absolute structure parameter	-	-0.3(10)
Largest diff. peak and hole	0.390 and -0.378 e.Å <sup>-3</sup>	1.750 and -0.683 e.Å <sup>-3</sup>

**Table S-2.** Intramolecular contacts for **(Z)-9b** [Å and °].

<b>D-H...A</b>	<b>d(H...A)</b>	<b>d(D...A)</b>	<b>&lt;(DHA)</b>
C5A-H5A...O10A	2.17	2.77(1)	121
C5B-H5B...O10B	2.18	2.76(1)	119

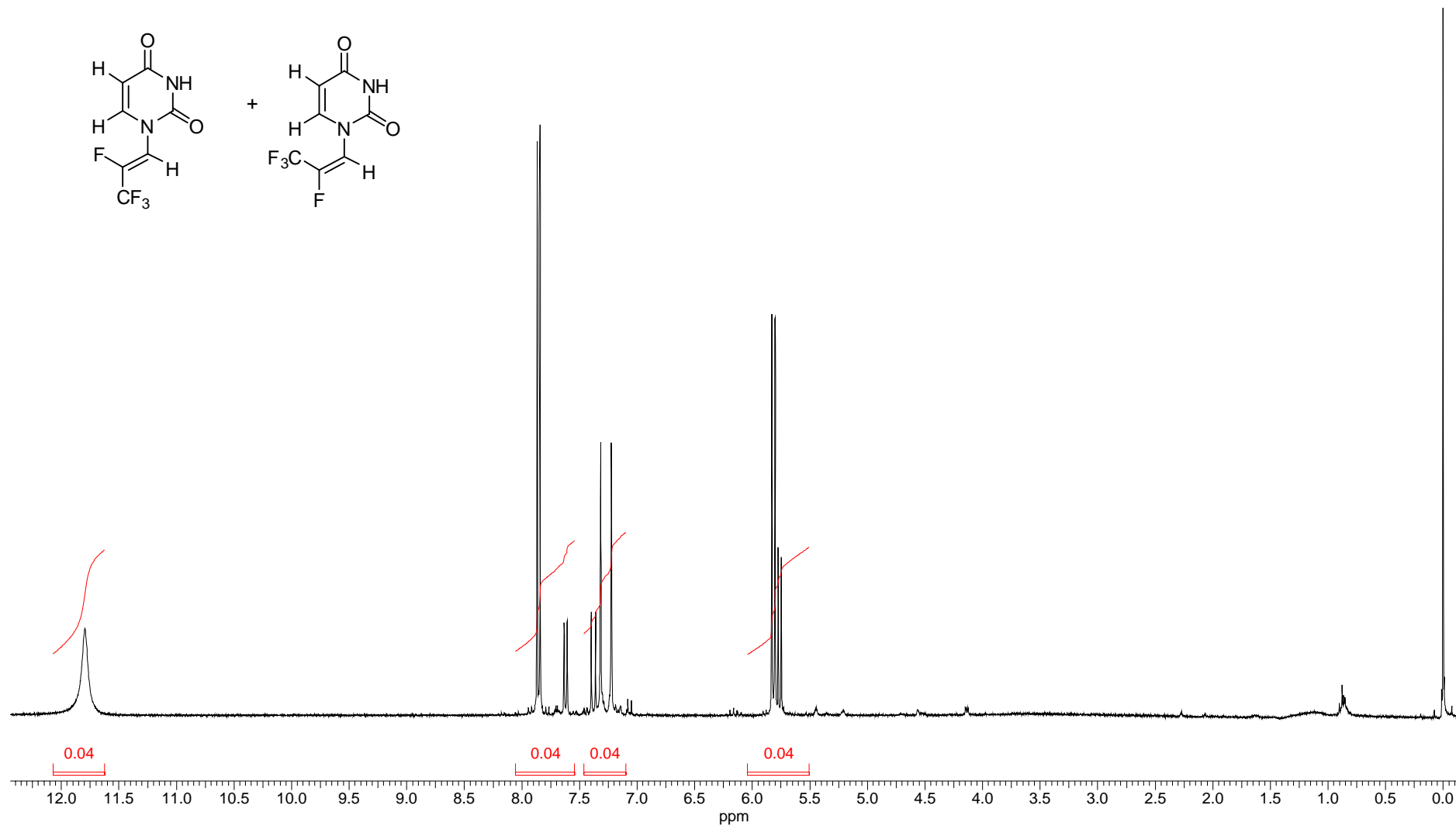
C5D-H5D...O10D	2.20	2.79(1)	120
C8B-H8B...O2B	2.28	2.79(1)	114
C5C-H5C...O10C	2.28	2.83(1)	117
C16D-H16D...O10D	2.41	2.75(1)	102
C16A-H16A...O10A	2.41	2.73(1)	100
C16B-H16B...O10B	2.42	2.73(1)	100
C8DD-H8DD...O2D	2.45	2.91(1)	111
C16C-H16C...O10C	2.49	2.79(1)	100
C8CC-H8CC...O2C	2.49	3.02(2)	116

**Table S-3** Shortest intermolecular contacts for **(Z)-9b** [ $\text{\AA}$  and  $^\circ$ ] at 100 K. The hydrogen bonds with  $d(\text{D}\cdots\text{A})$  shorter than the sum of van der Waals radii have been highlighted in bold.

D-H...A	d(H...A)	d(D...A)	<(DHA)	symmetry code
<b>N4B-H4B...O2C</b>	<b>2.08</b>	<b>2.91(1)</b>	<b>163</b>	<b>-0.5+x,-y,0.5+z</b>
<b>N4C-H4C...O2A</b>	<b>2.15</b>	<b>2.94(1)</b>	<b>154</b>	<b>0.5+x,1-y,-0.5+z</b>
<b>N4D-H4D...O2B</b>	<b>2.21</b>	<b>3.05(1)</b>	<b>163</b>	<b>0.5+x,-y,-0.5+z</b>
<b>C6B-H6B...O10D</b>	<b>2.25</b>	<b>3.16(2)</b>	<b>165</b>	<b>x,y,1+z</b>
<b>C6A-H6A...O10C</b>	<b>2.30</b>	<b>3.09(1)</b>	<b>143</b>	<b>x,y,1+z</b>
<b>C6D-H6D...O10B</b>	<b>2.31</b>	<b>3.22(1)</b>	<b>163</b>	<b>x,y,-1+z</b>
<b>C6C-H6C...O10A</b>	<b>2.38</b>	<b>3.15(1)</b>	<b>141</b>	<b>x,y,-1+z</b>
C12B-H12B...O2C	2.39	3.30(1)	167	-0.5+x,-y,0.5+z
C12C-H12C...O2A	2.41	3.33(1)	170	0.5+x,1-y,-0.5+z
<b>C13B-H13B...F1D</b>	<b>2.41</b>	<b>3.04(1)</b>	<b>124</b>	<b>-0.5+x,-1-y,0.5+z</b>
C12A-H12A...O2D	2.45	3.35(1)	162	-0.5+x,-y,0.5+z
C12A-H12A...O2D	2.45	3.35(1)	162	-0.5+x,-y,0.5+z
C8B-H8B...F1A	2.49	3.38(1)	159	x,-1+y,z
<b>C15A-H15A...F4D</b>	<b>2.49</b>	<b>2.95(1)</b>	<b>110</b>	<b>x,y,1+z</b>
C12D-H12D...O2B	2.50	3.41(1)	166	0.5+x,-y,-0.5+z
<b>C15B-H15B...F4C</b>	<b>2.55</b>	<b>3.16(1)</b>	<b>123</b>	<b>x,-1+y,1+z</b>
C16A-H16A...F4CC	2.55	3.33(2)	142	x,y,1+z
C8C-H8C...O2D	2.56	3.36(1)	144	x, y, z
C15C-H15C...F3D	2.56	3.35(1)	143	x,1+y,-1+z
C15A-H15A...F2B	2.57	3.27(1)	132	x,y,1+z
C15D-H15D...F1C	2.58	3.35(1)	141	x,y,-1+z
<b>C12B-H12BA...F1D</b>	<b>2.59</b>	<b>3.12(1)</b>	<b>117</b>	<b>-0.5+x,-1-y,0.5+z</b>
C8A-H8A...O2B	2.62	3.38(1)	139	x,1+y,z
C15B-H15B...F2A	2.64	3.49(1)	152	x,-1+y,1+z
C8C-H8C...N3D	2.97	3.87(1)	164	x, y, z
C8A-H8A...N3B	2.98	3.89(1)	168	x,1+y,z

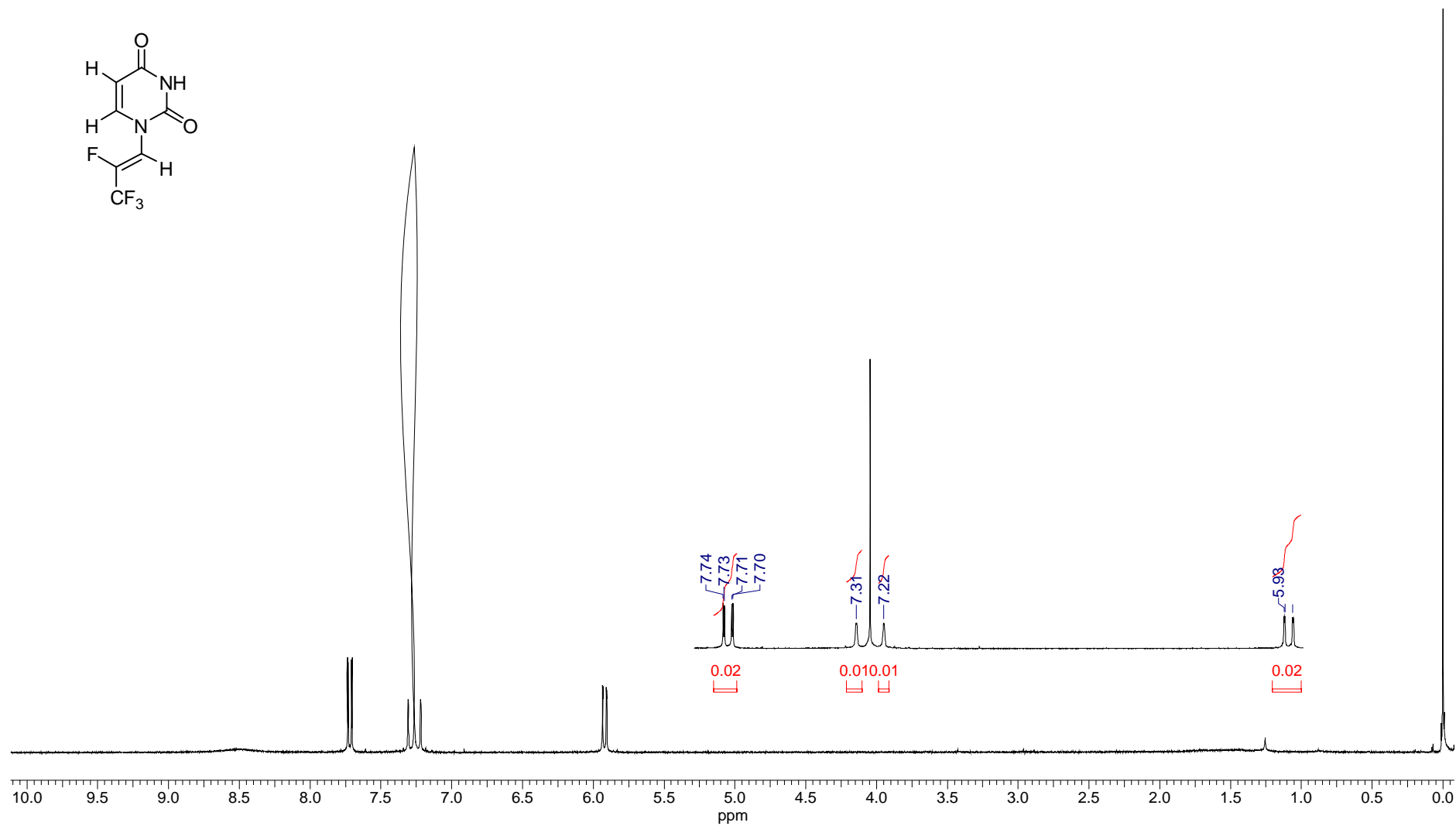
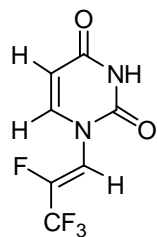
**Compounds (Z)-2c and (E)-2c**

<sup>1</sup>H NMR, 300 MHz, DMSO-d<sub>6</sub>



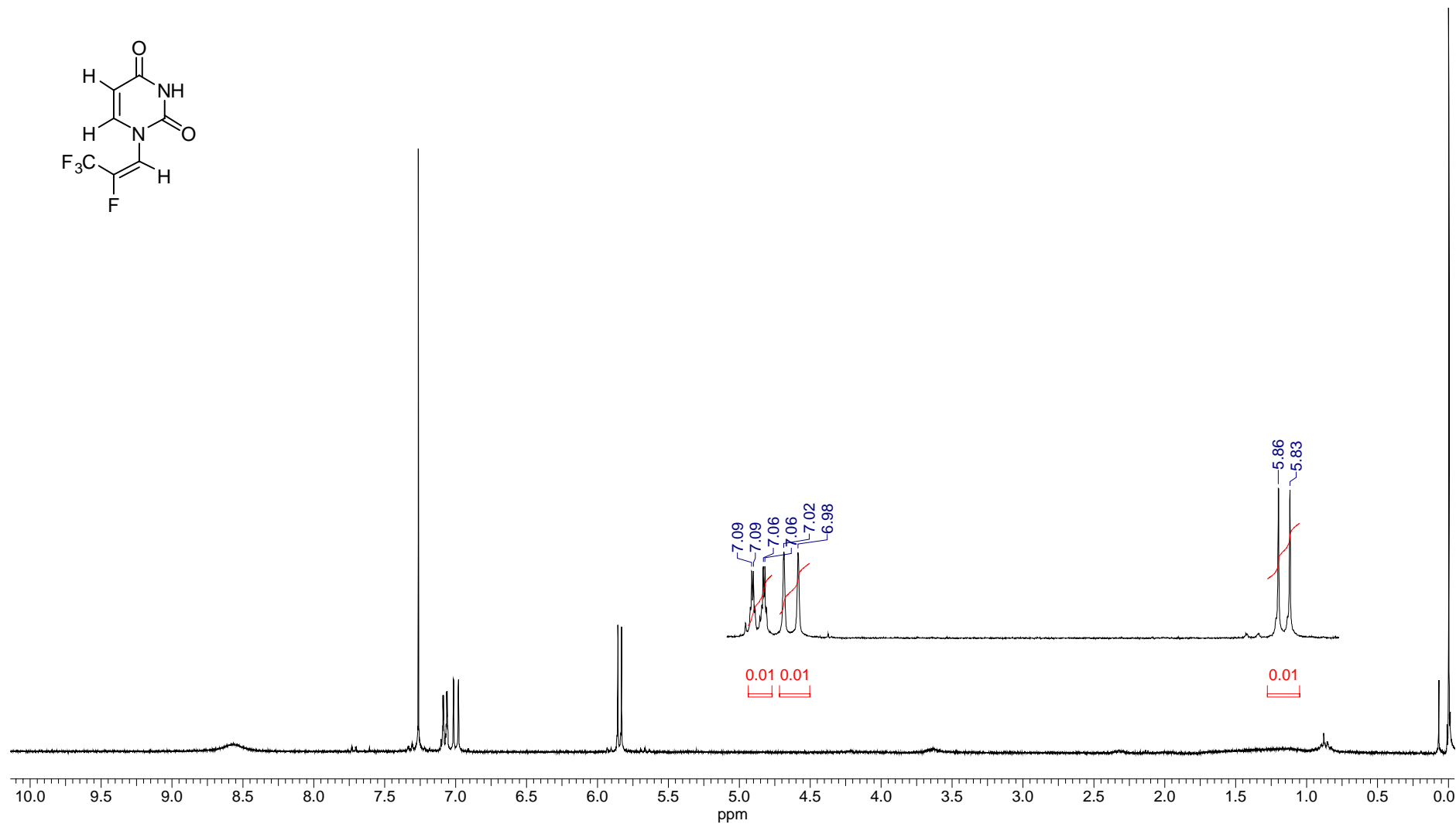
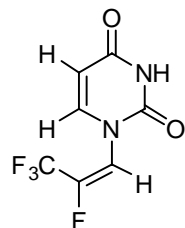
**Compound (Z)-2c**

$^1\text{H}$  NMR, 300 MHz,  $\text{CDCl}_3$



**Compound (E)-2c**

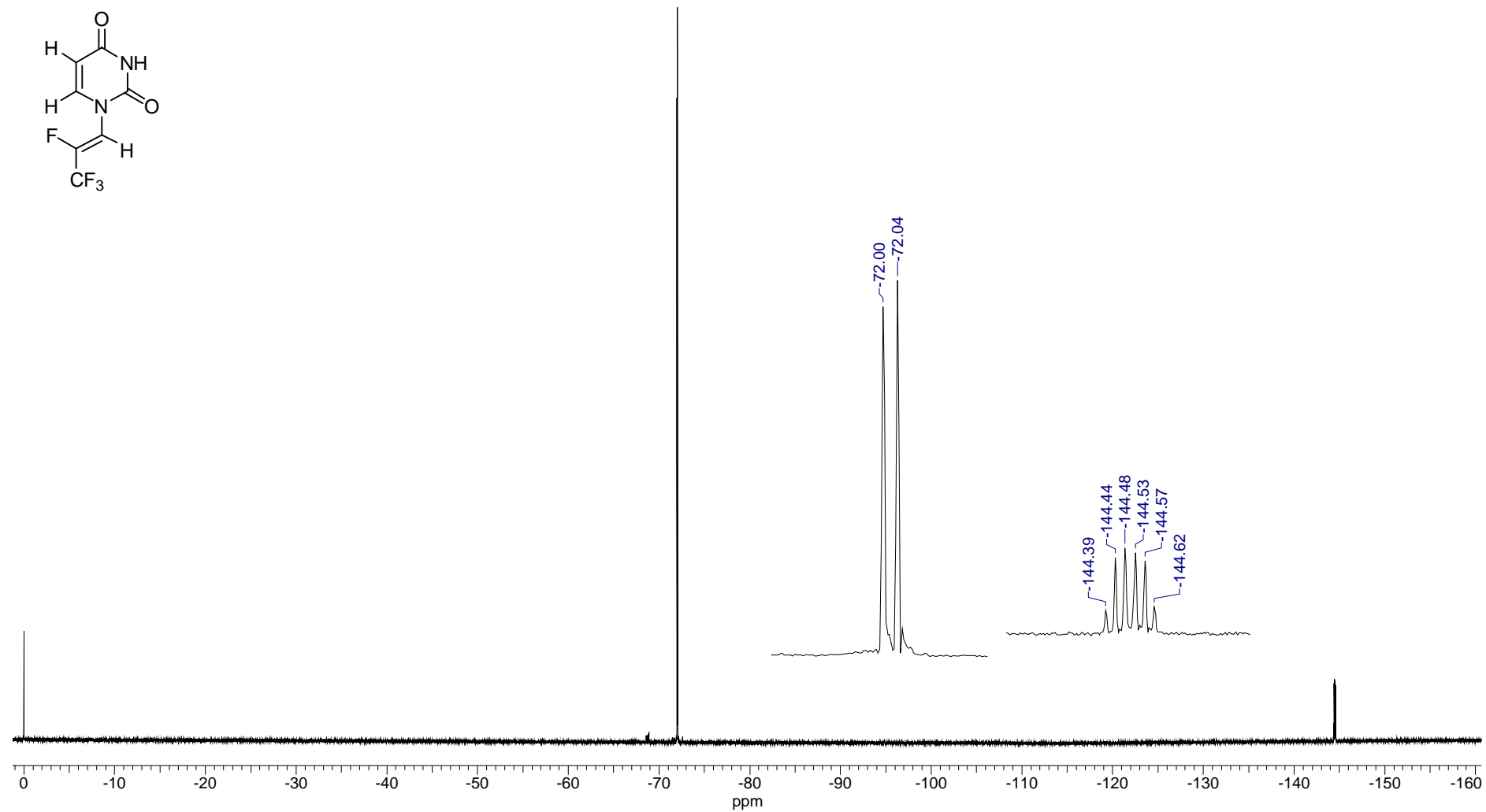
<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



**Compound (Z)-2c**

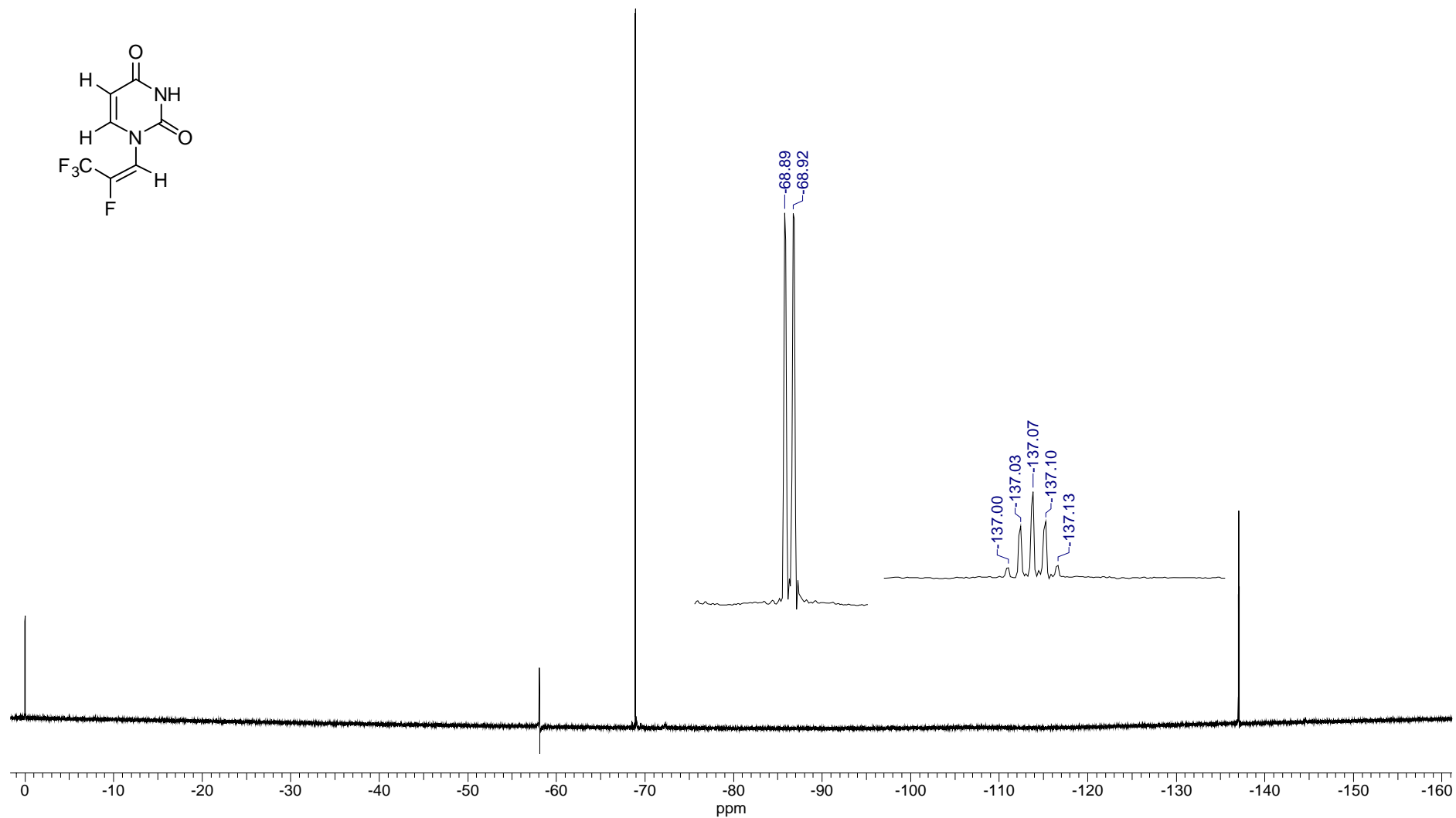
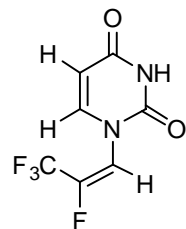


$^{19}\text{F}$  NMR, 282 MHz,  $\text{CDCl}_3$



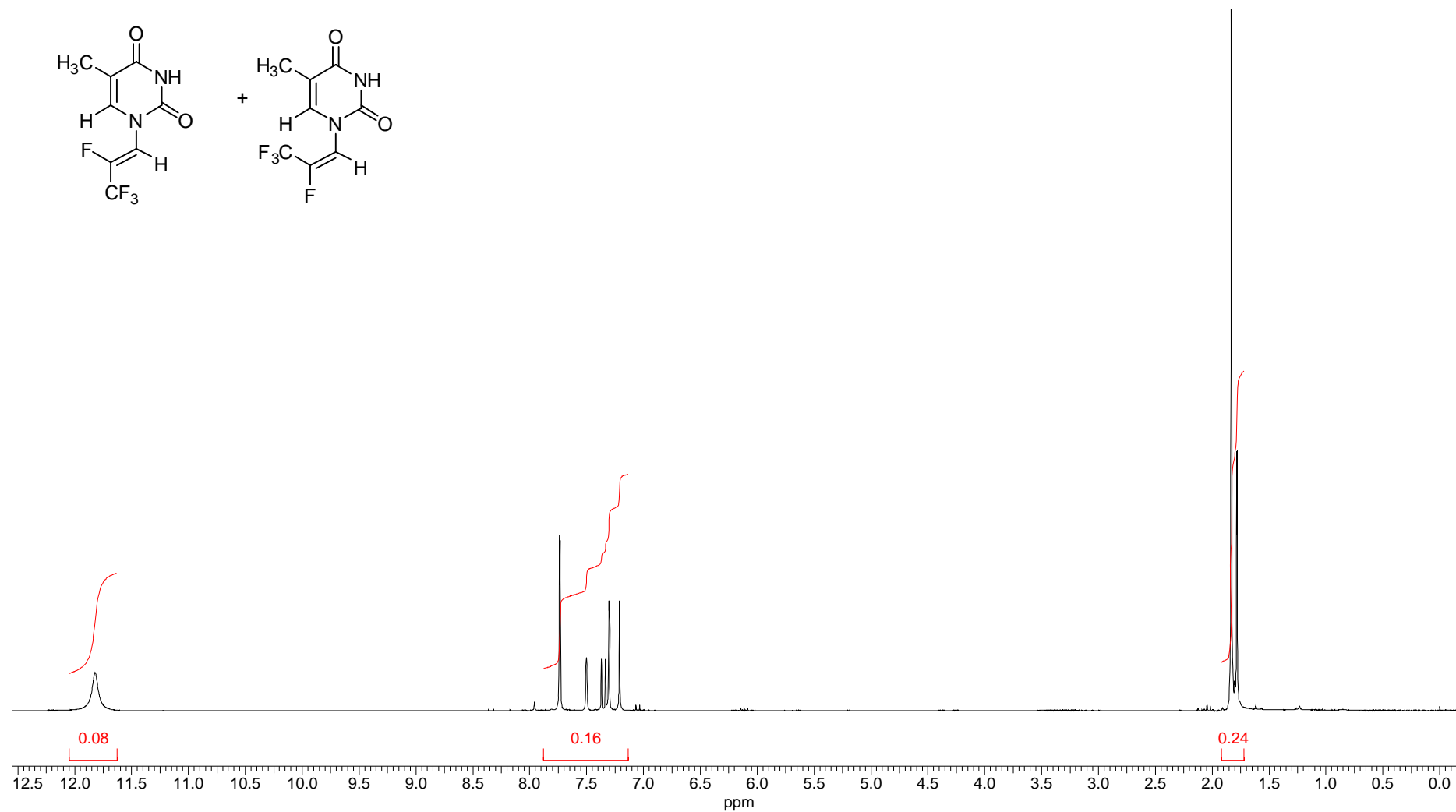
**Compound (E)-2c**

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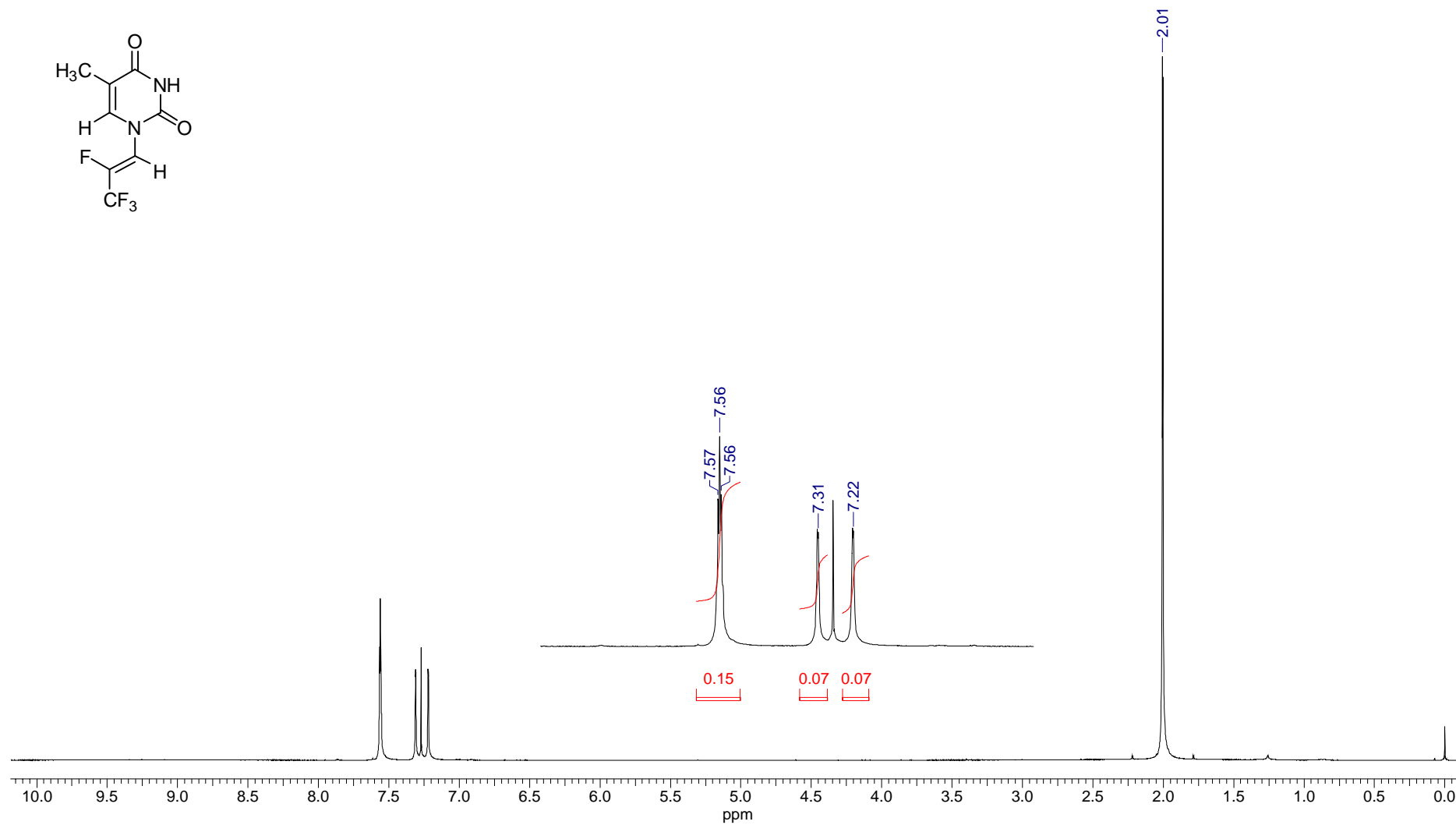
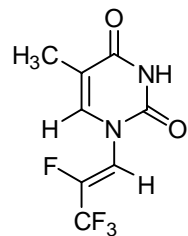
**Compounds (Z)-3c and (E)-3c**

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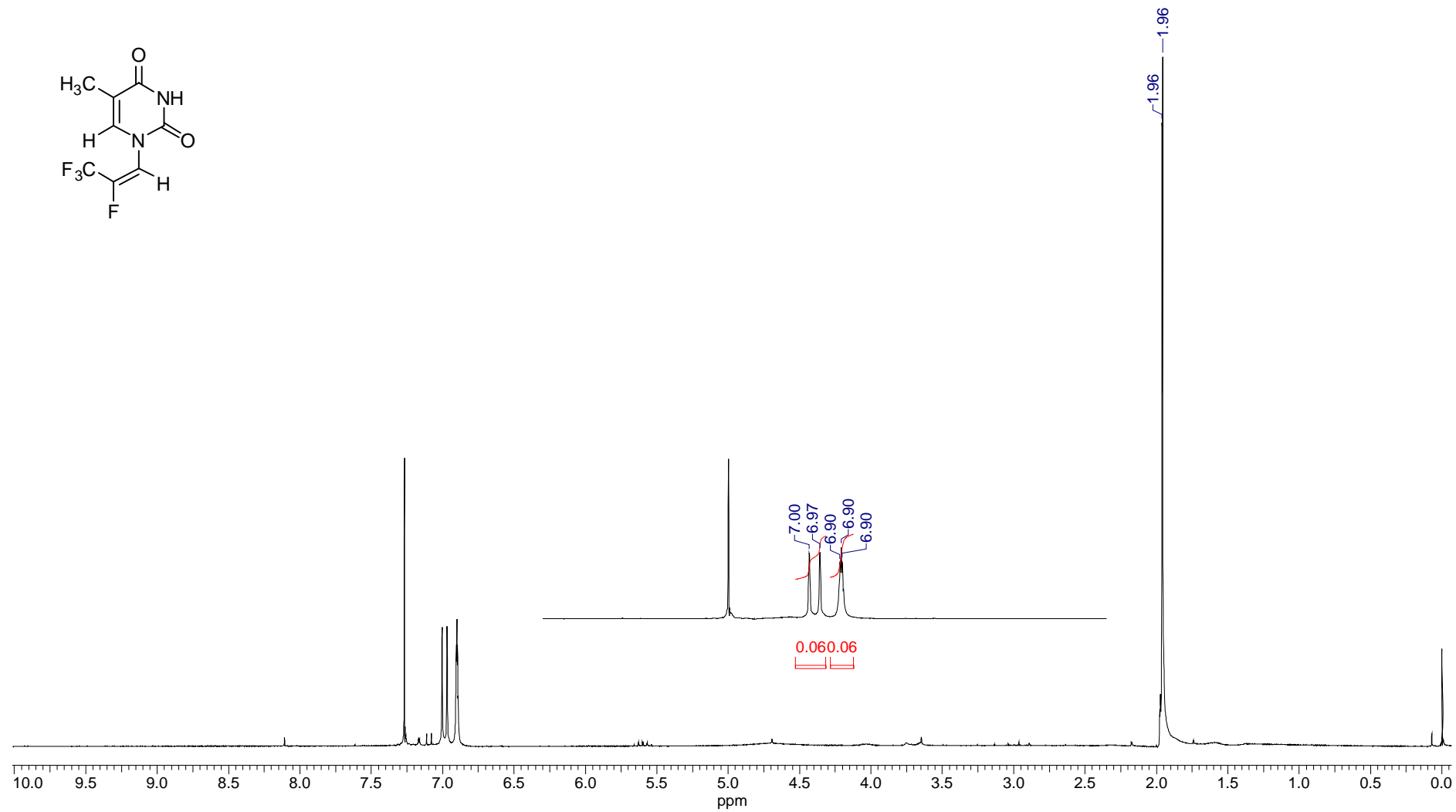
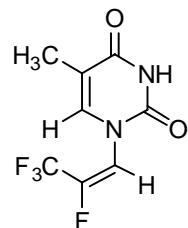
**Compound (Z)-3c**

<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



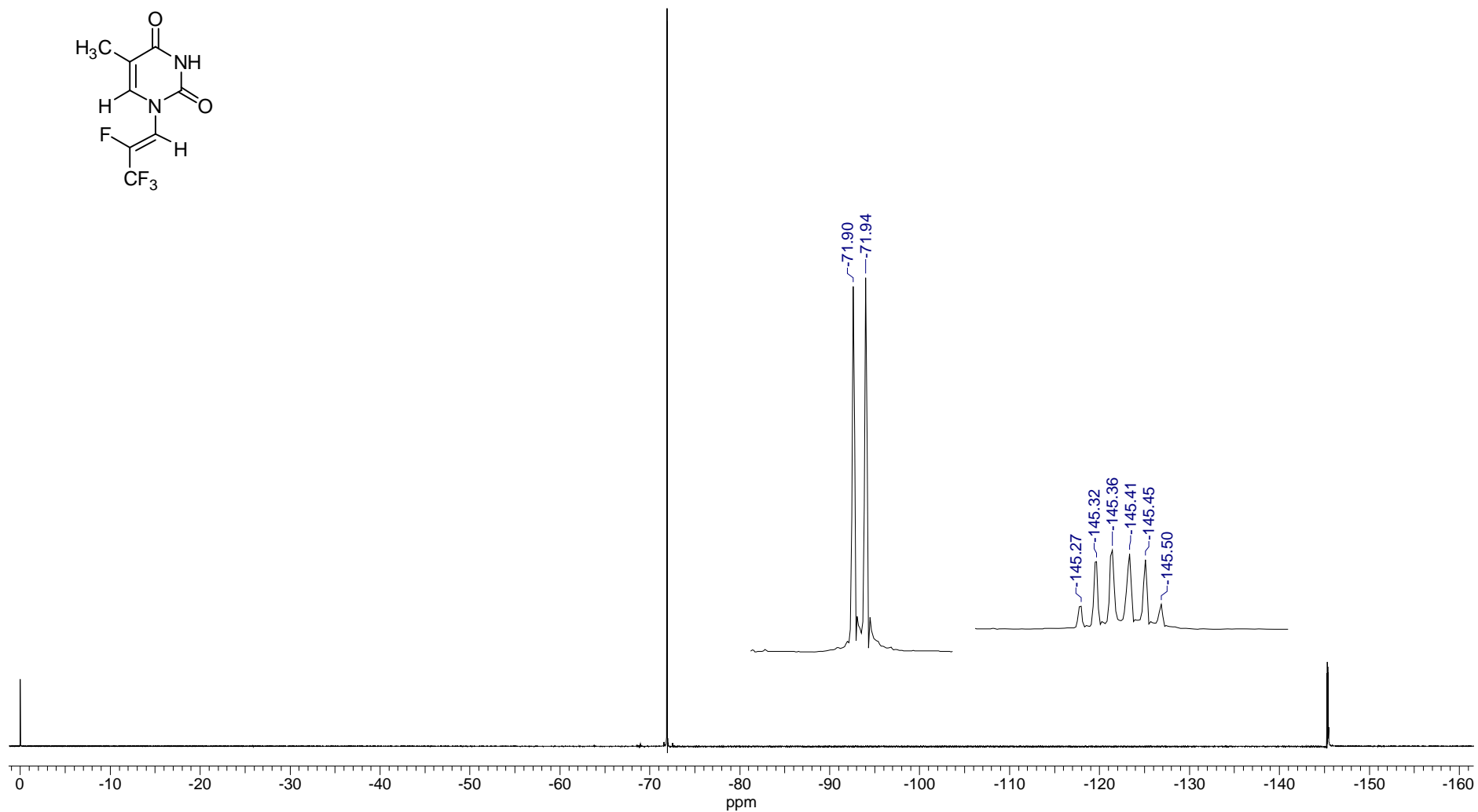
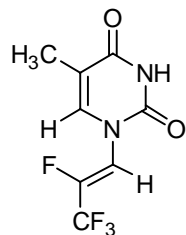
**Compound (E)-3c**

$^1\text{H}$  NMR, 300 MHz,  $\text{CDCl}_3$



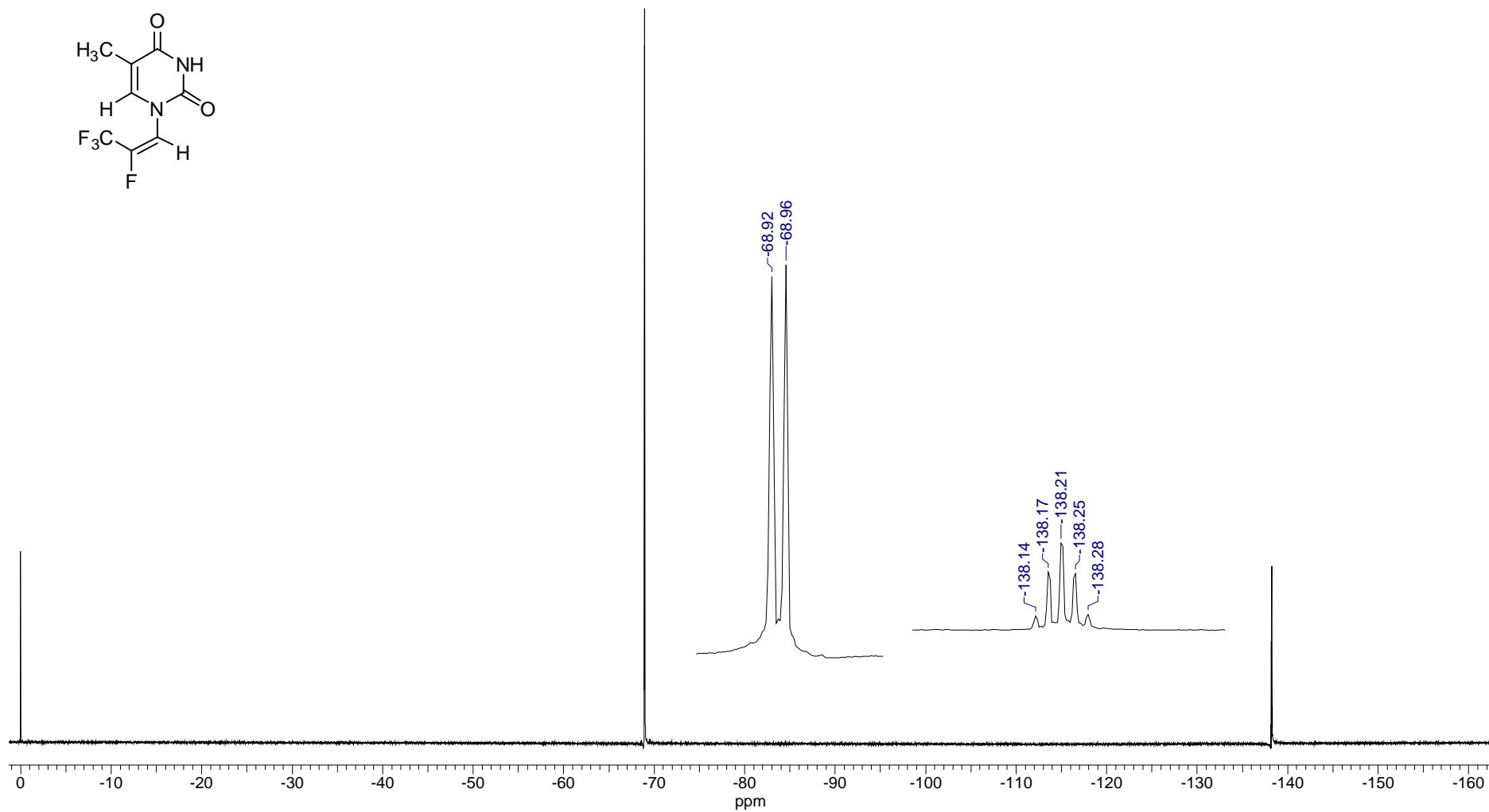
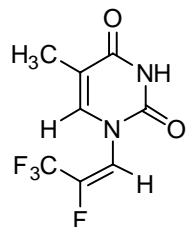
**Compound (Z)-3c**

$^{19}\text{F}$  NMR, 282 MHz,  $\text{CDCl}_3$



**Compound (E)-3c**

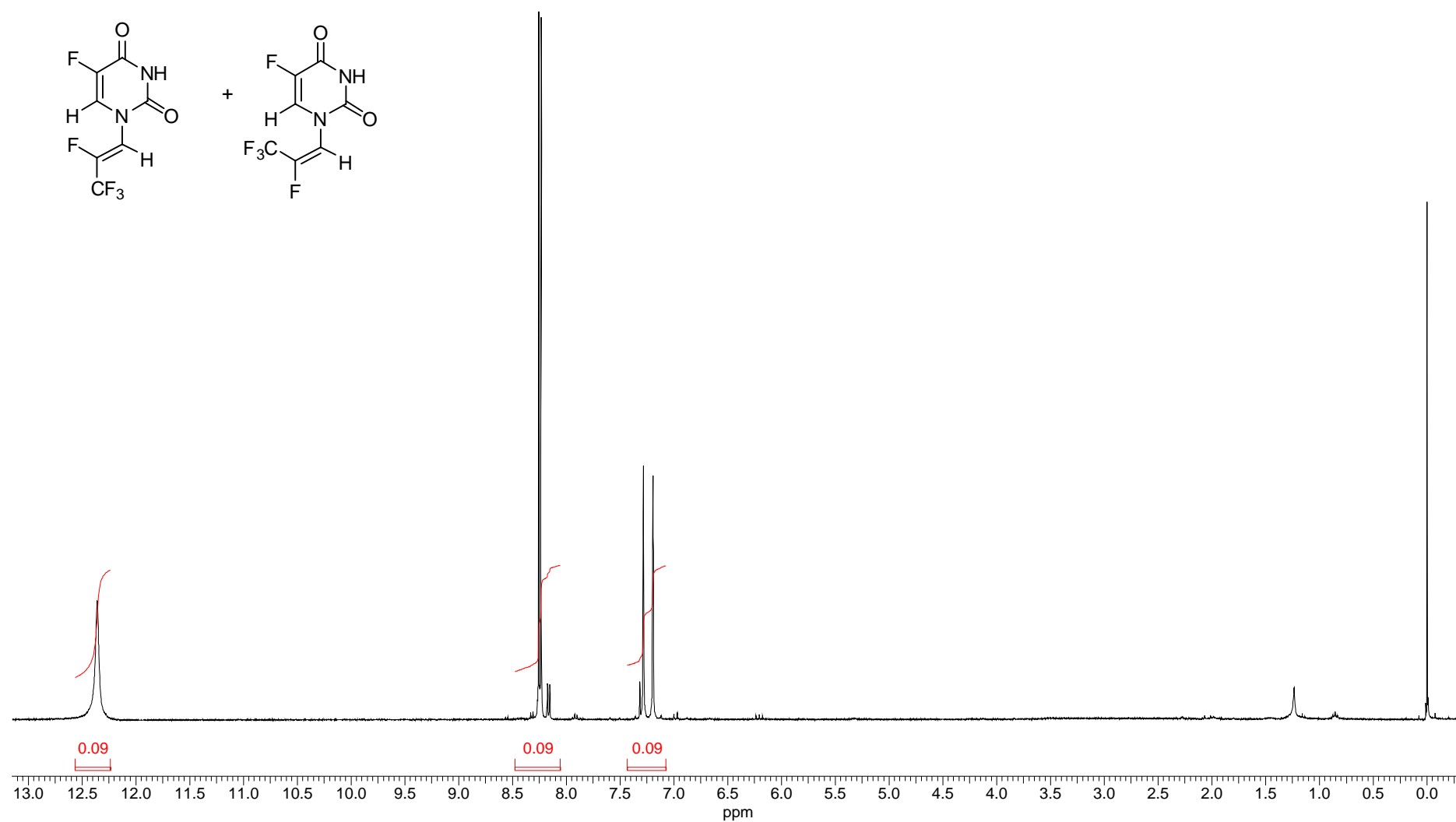
$^{19}\text{F}$  NMR, 282 MHz,  $\text{CDCl}_3$



**Compounds (Z)-4c and (E)-4c**

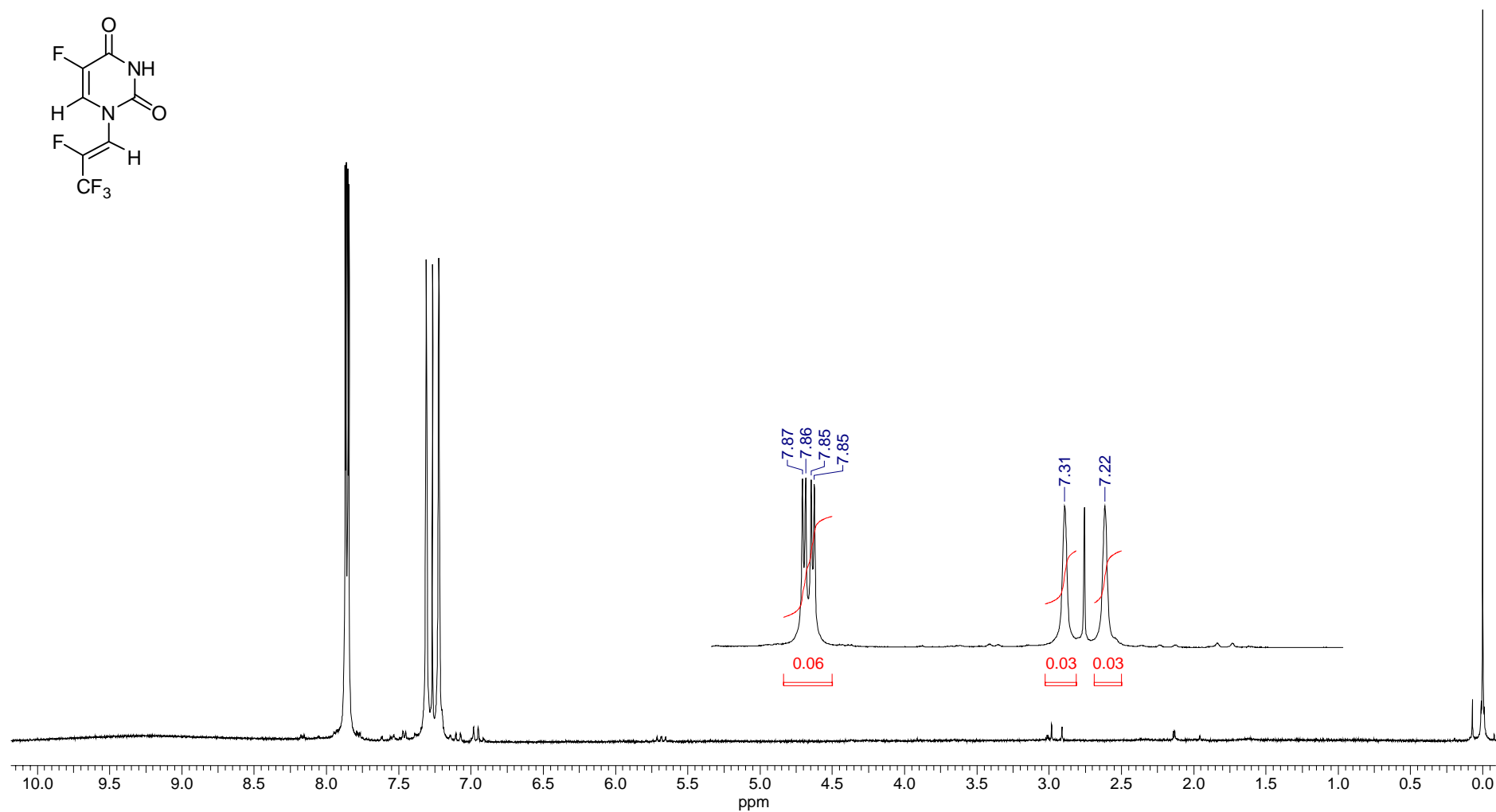
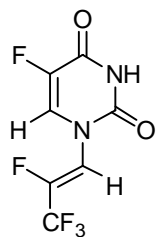


$^1\text{H}$  NMR, 300 MHz,  $\text{DMSO-d}_6$



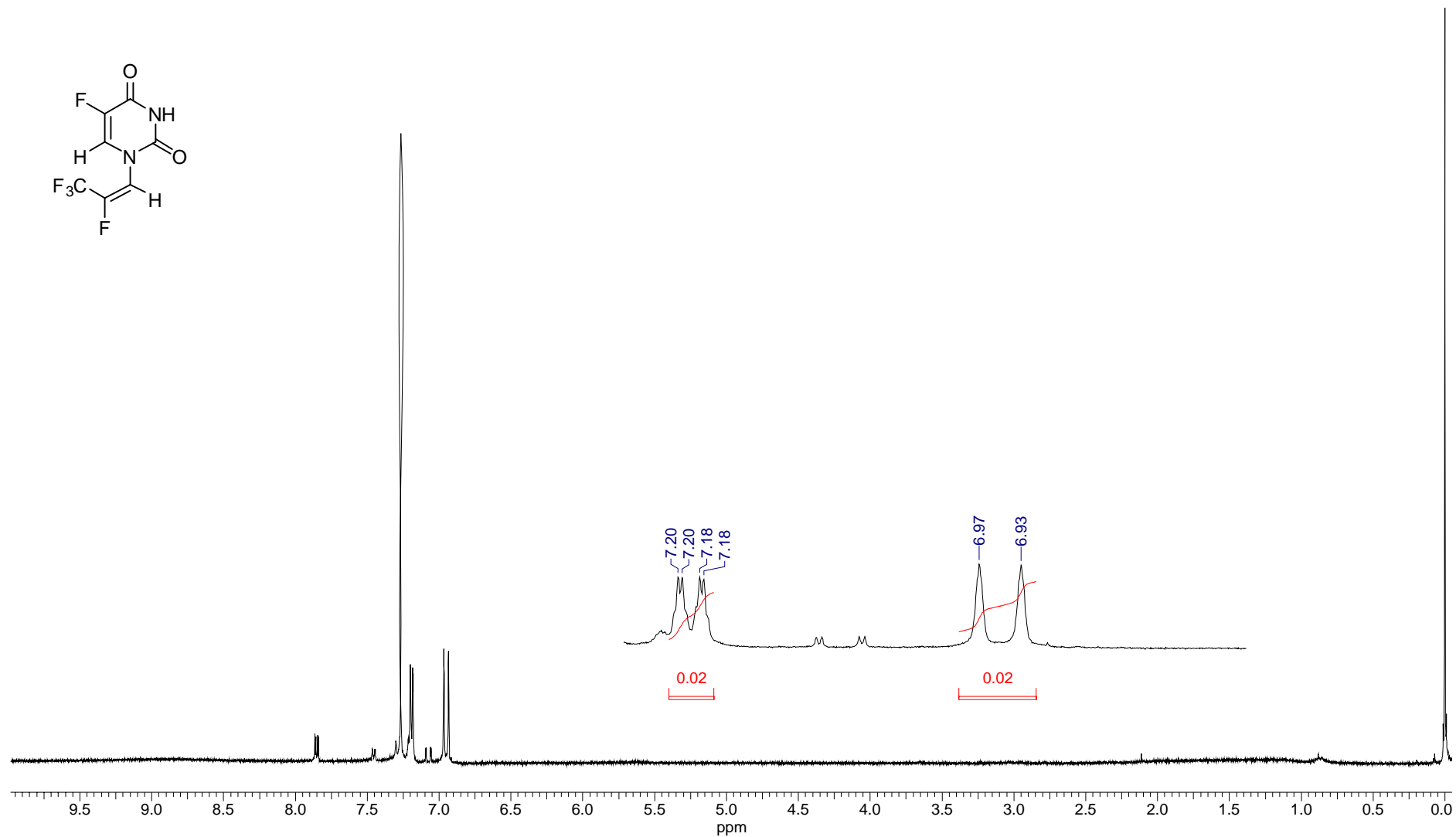
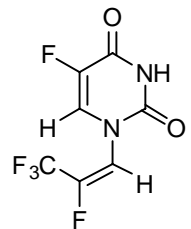
### Compound (Z)-4c

$^1\text{H}$  NMR, 300 MHz,  $\text{CDCl}_3$



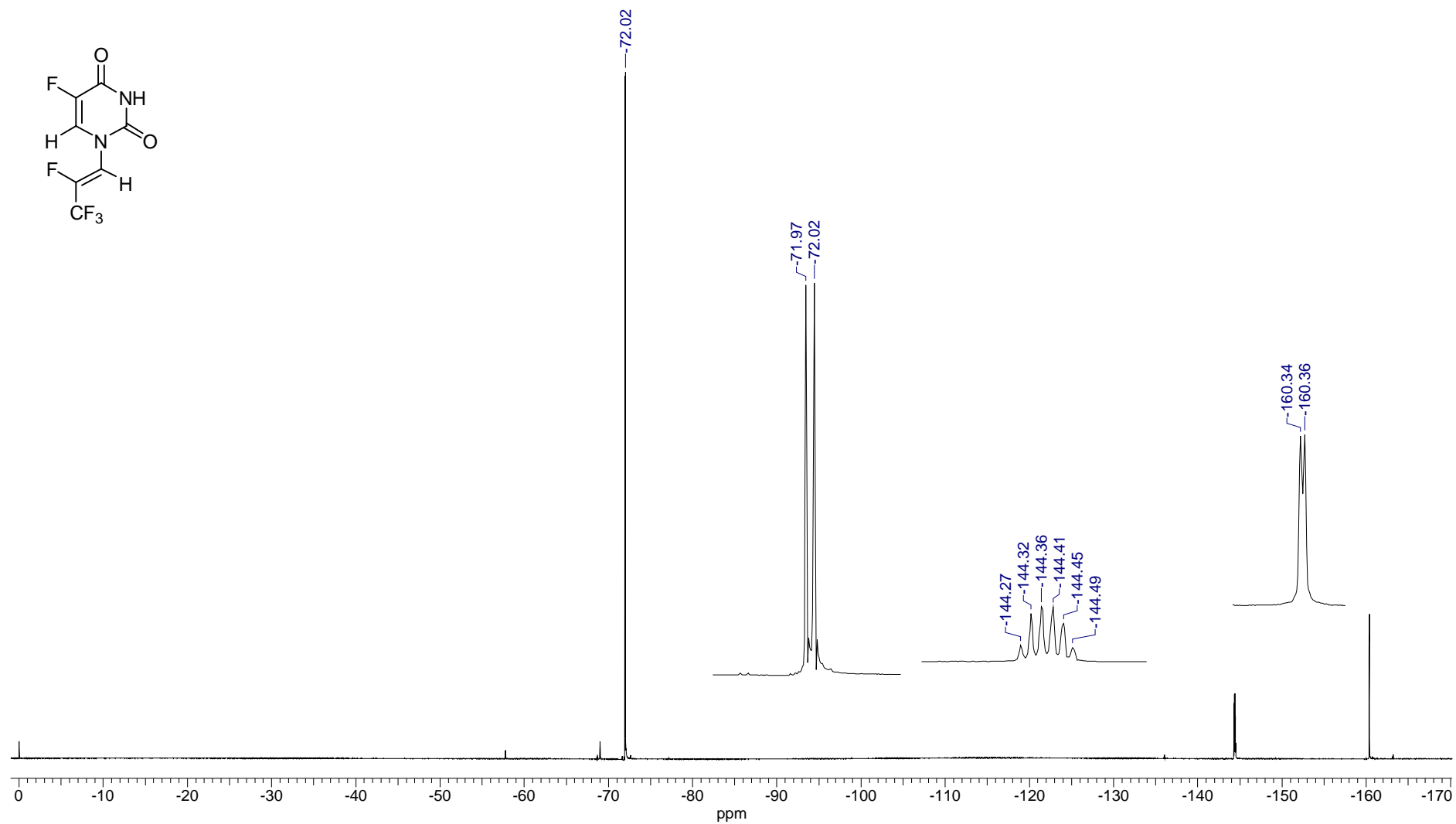
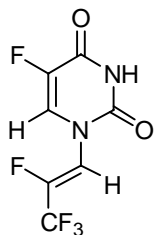
**Compound (E)-4c**

$^1\text{H}$  NMR, 300 MHz,  $\text{CDCl}_3$



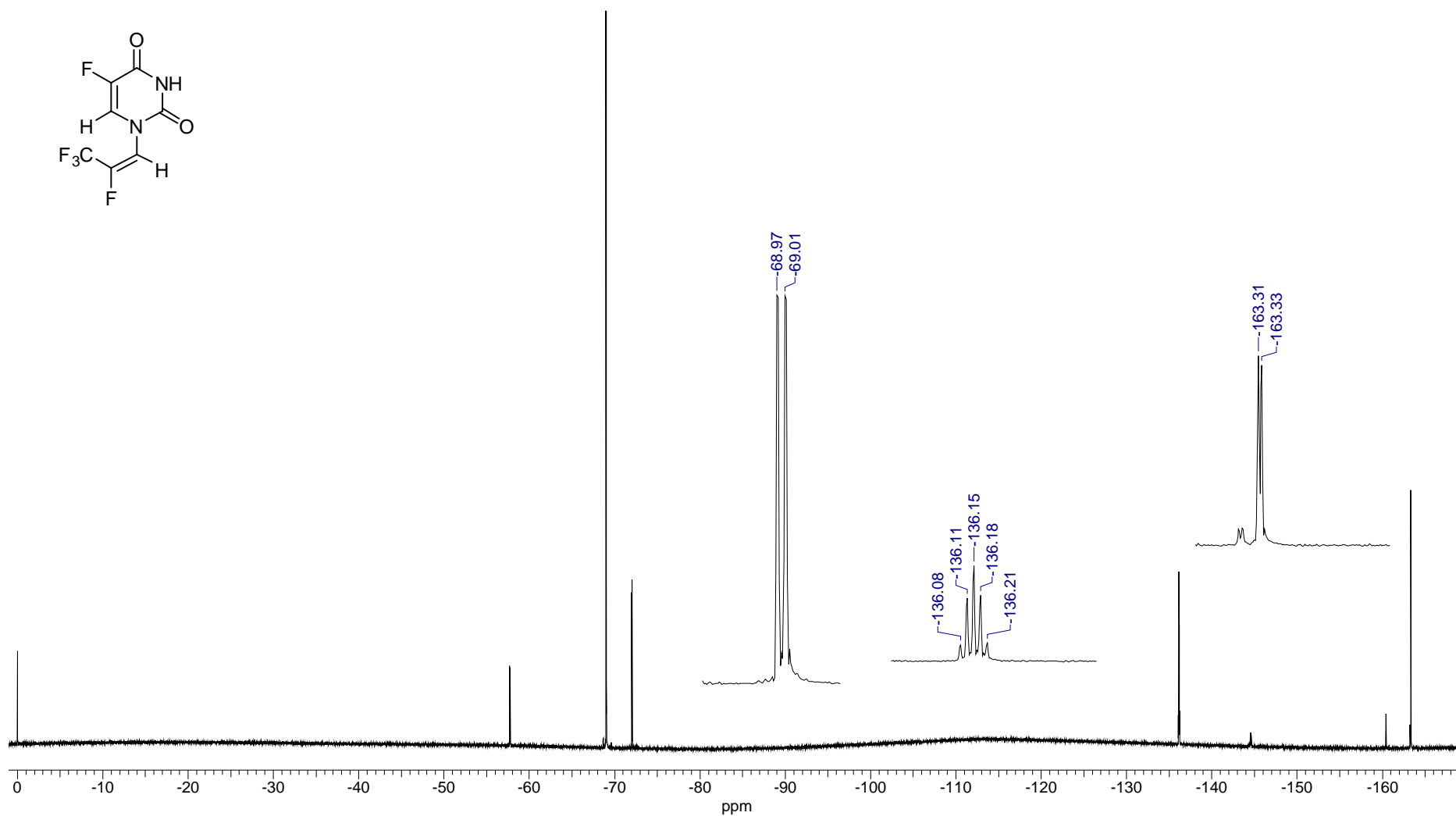
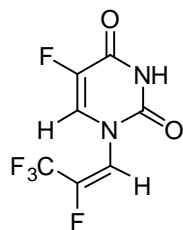
**Compound (Z)-4c**

$^{19}\text{F}$  NMR, 282 MHz,  $\text{CDCl}_3$



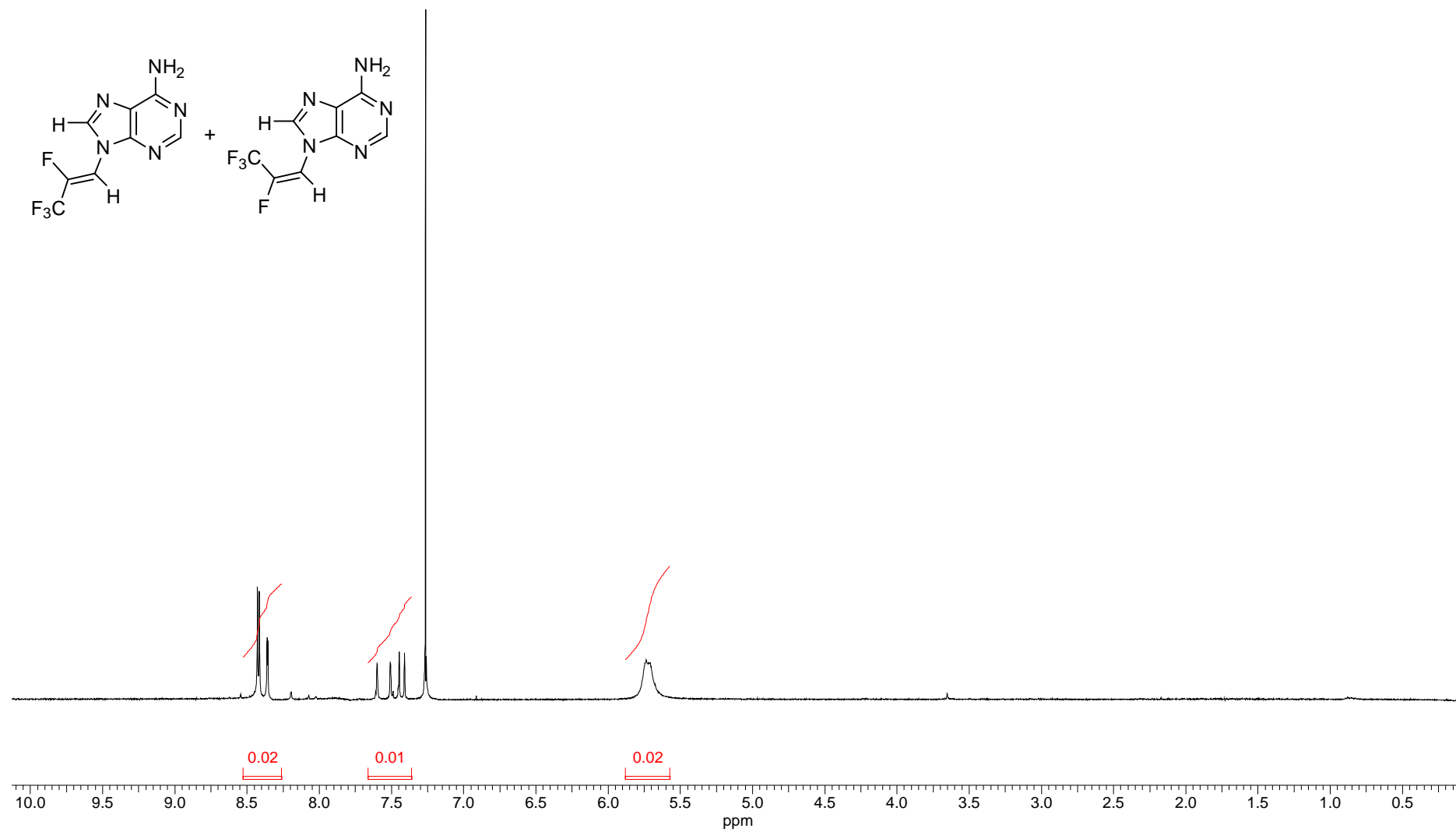
**Compound (E)-4c**

$^{19}\text{F}$  NMR, 282 MHz,  $\text{CDCl}_3$



Compounds (Z)-6c and (E)-6c

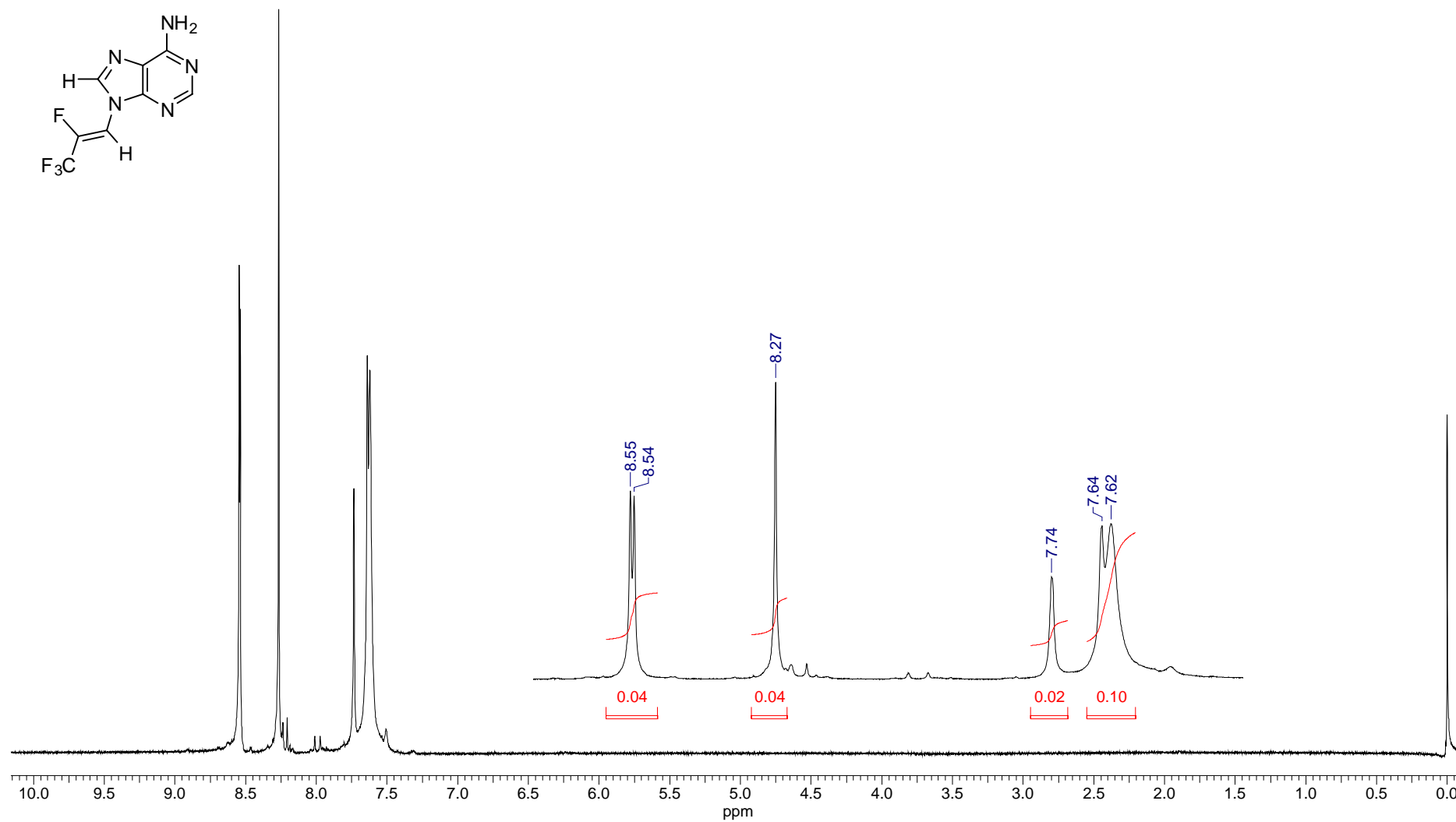
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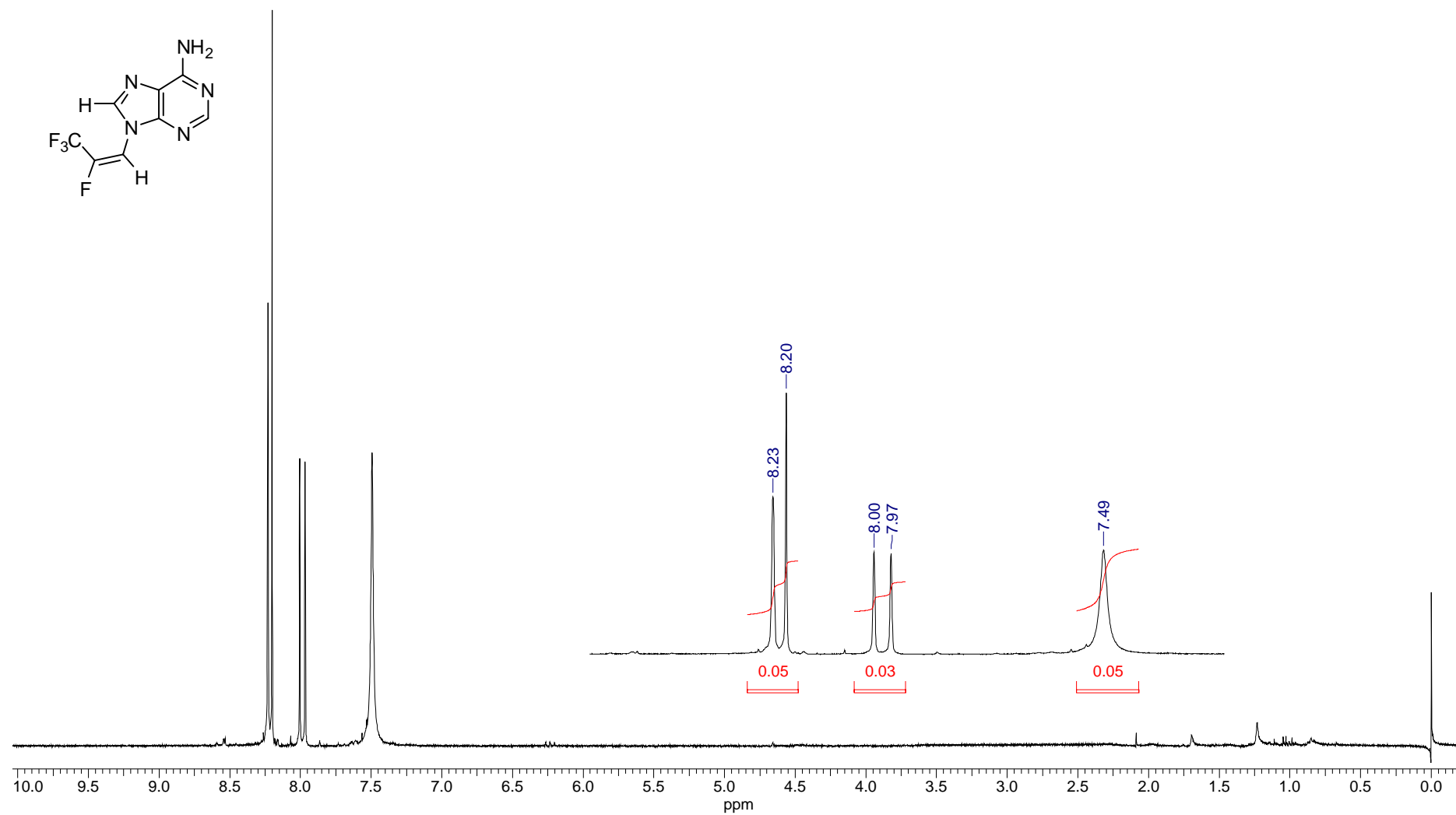
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<sup>1</sup>H NMR, 300 MHz, DMSO-d<sub>6</sub>



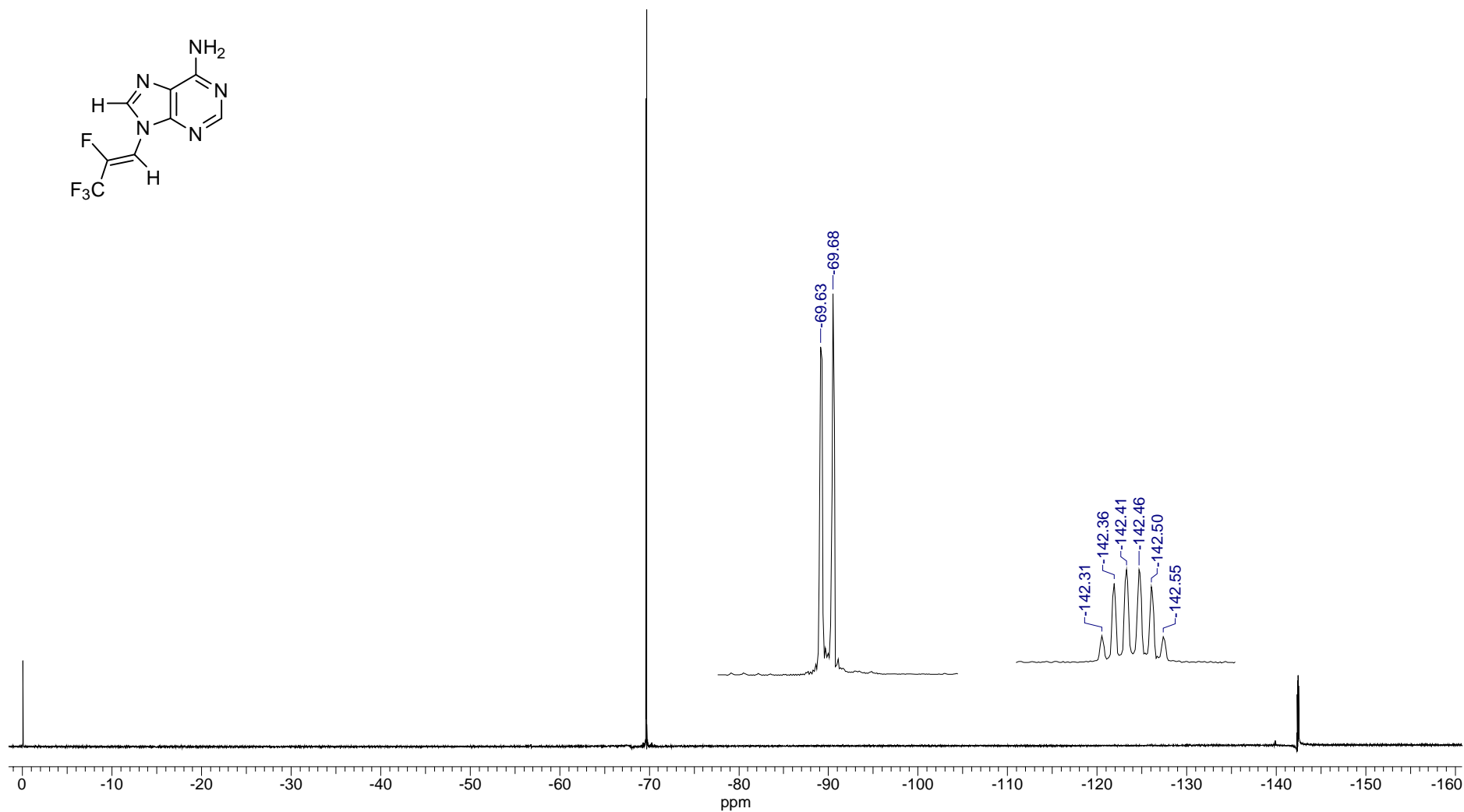
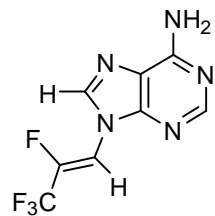
**Compound (E)-6c**

$^1\text{H}$  NMR, 300 MHz, DMSO- $d_6$



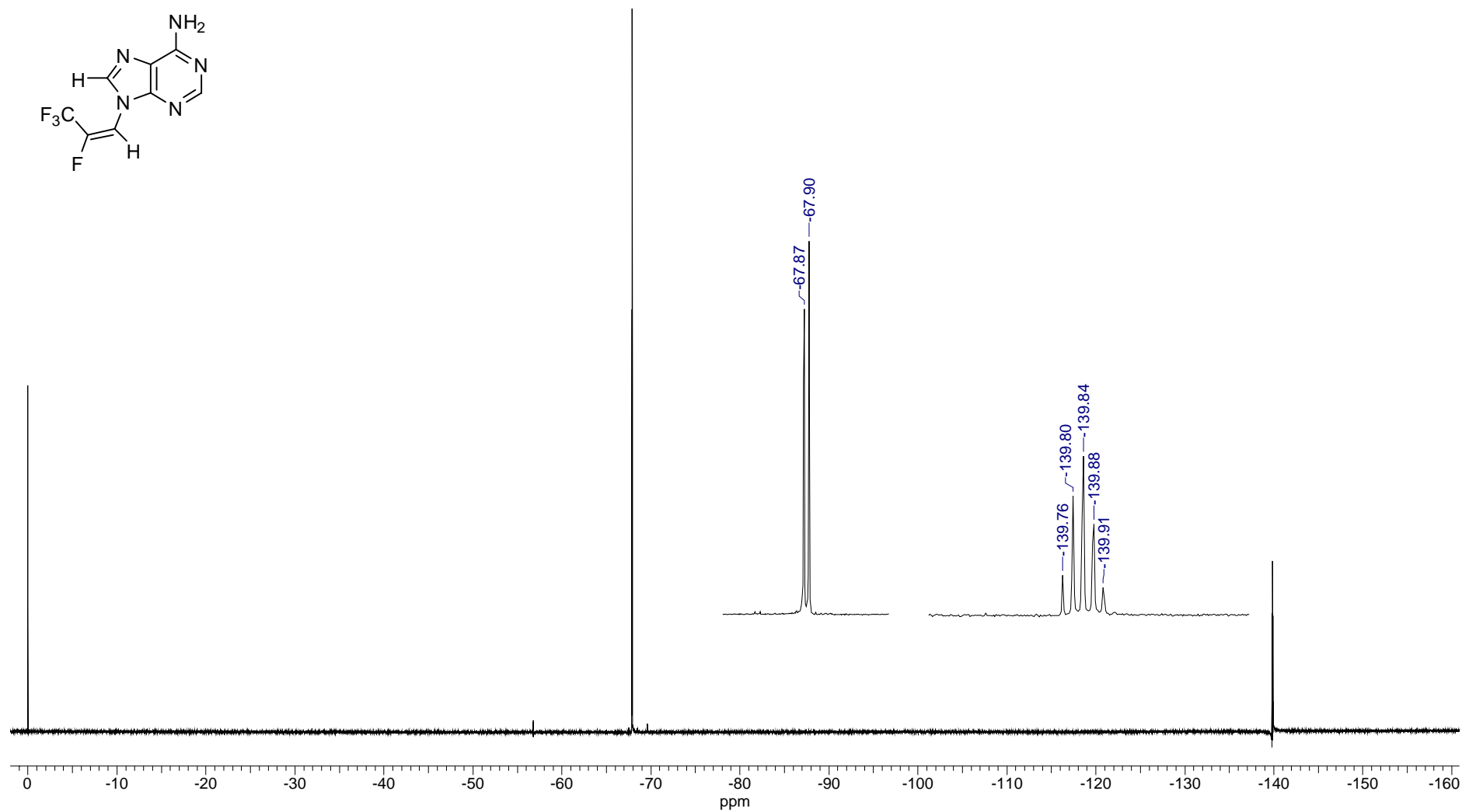
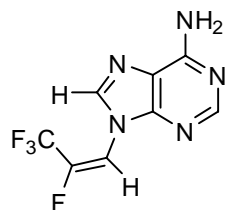
**Compound (Z)-6c**

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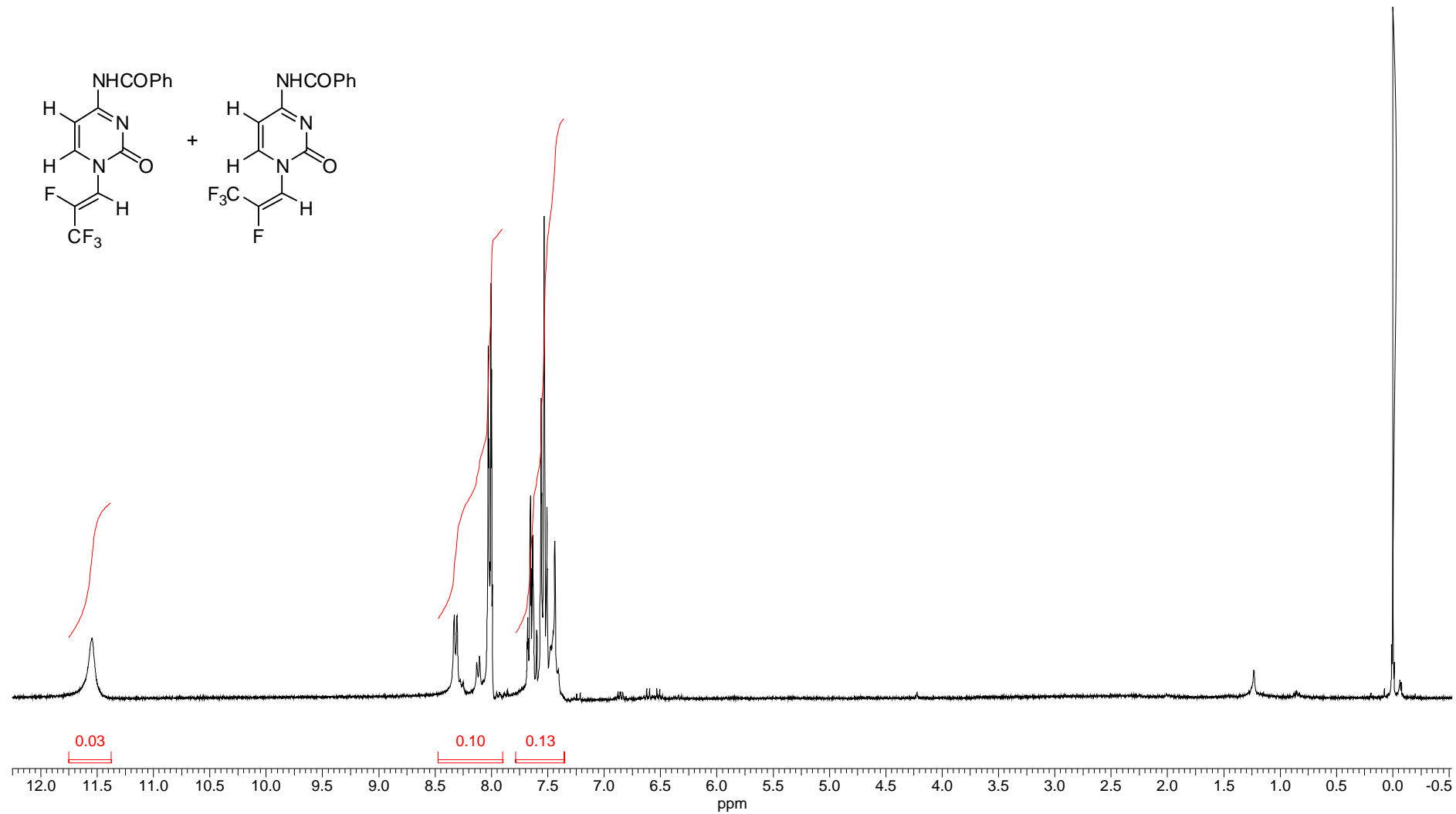
**Compound (E)-6c**

$^{19}\text{F}$  NMR, 282 MHz, DMSO- $d_6$



### Compounds (Z)-9c and (E)-9c

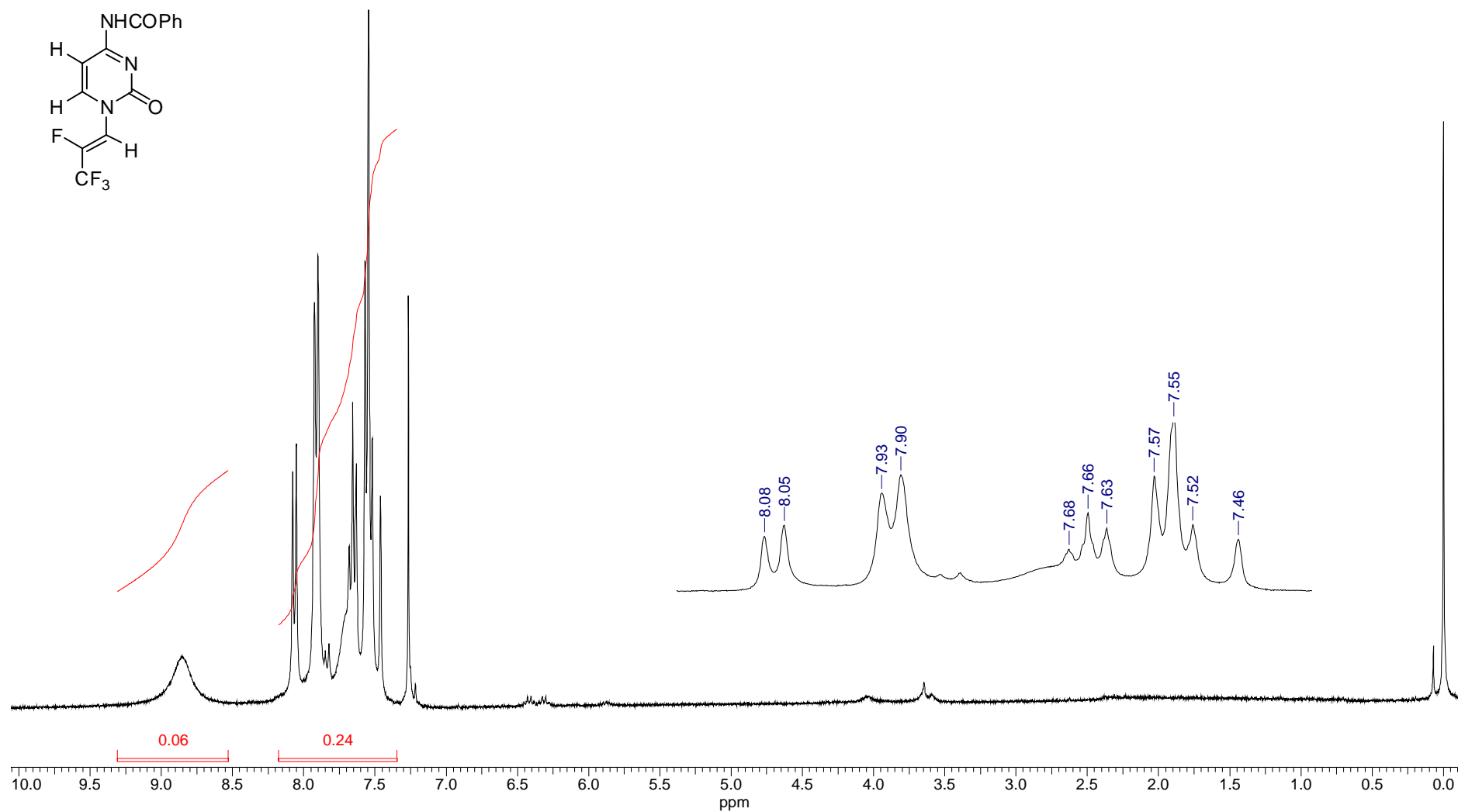
$^1\text{H}$  NMR, 300 MHz, DMSO- $d_6$



**Compound (Z)-9c**

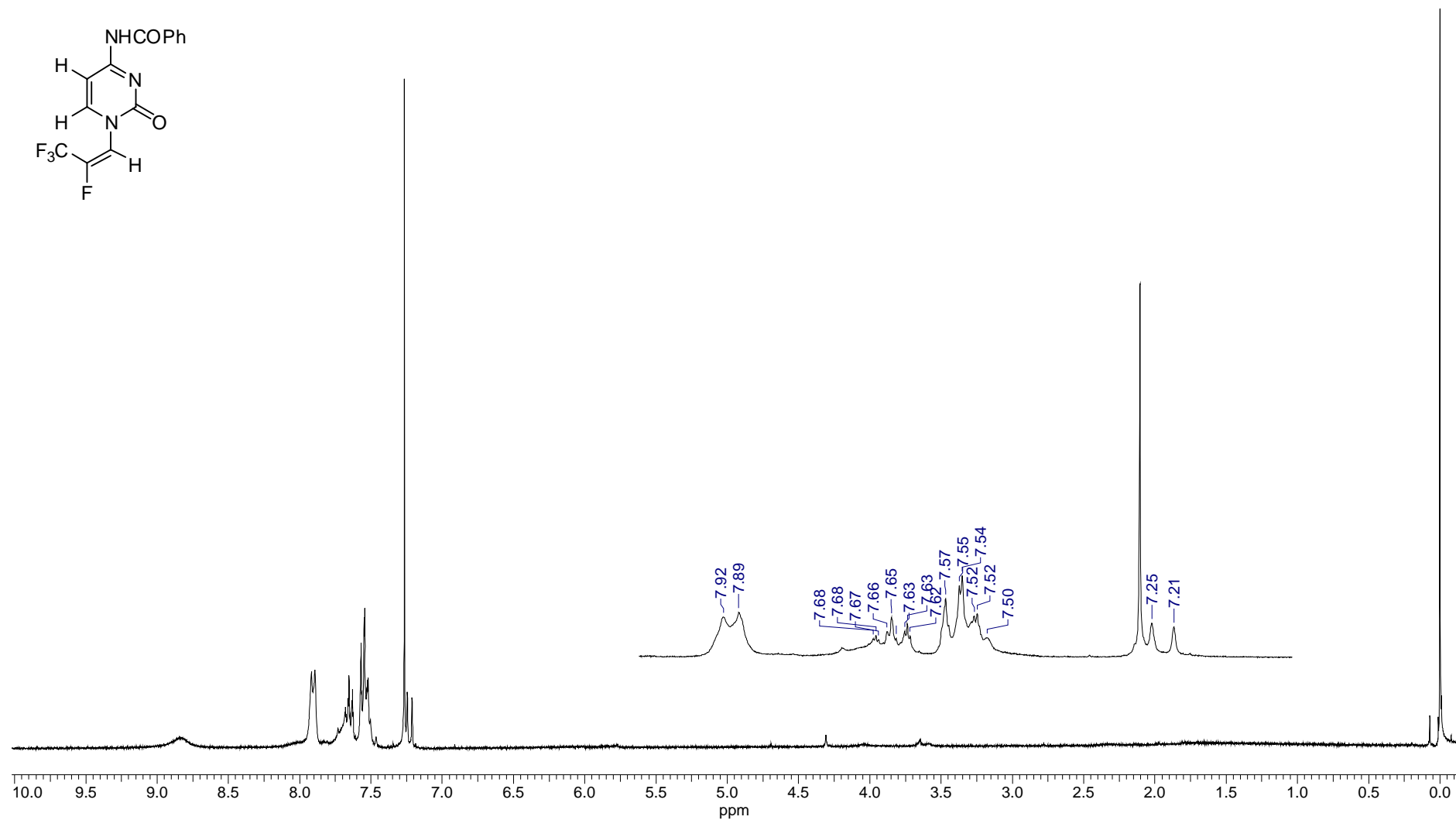
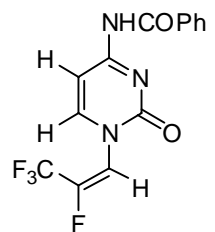
<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>





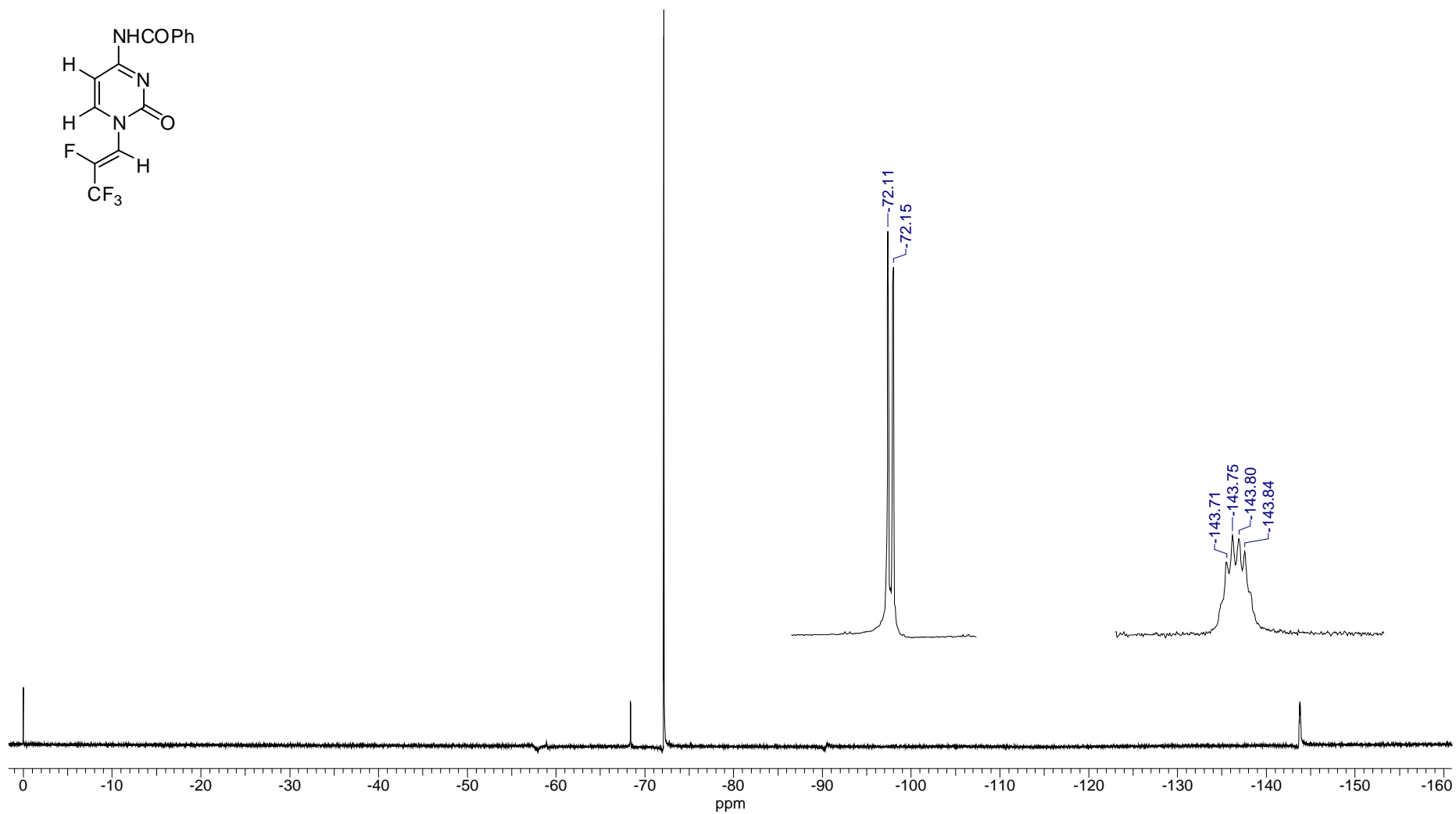
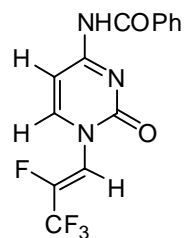
**Compound (E)-9c**

$^1\text{H}$  NMR, 300 MHz,  $\text{CDCl}_3$



**Compound (Z)-9c**

$^{19}\text{F}$  NMR, 282 MHz,  $\text{CDCl}_3$



**Compound (E)-9c** as a mixture with the isomer **Z**

$^{19}\text{F}$  NMR, 282 MHz,  $\text{CDCl}_3$

