

# Effective isomerization of 3', 5'-*O*-(tetraisopropylidisiloxane-1,3-diyl)nucleosides in the presence of trimethylsilyl trifluoromethanesulfonate

Irina V. Kulikova, Daria A. Muradova and Sergey N. Mikhailov\*

*Engelhardt Institute of Molecular Biology, Russian Academy of Sciences, Vavilov str. 32, Moscow, 119991 Russia;*

*E-mail: [smikh@eimb.ru](mailto:smikh@eimb.ru)*

**Table 1.** <sup>1</sup>H NMR (300 MHz) chemical shifts (ppm) and coupling constants (Hz) of 3',5'-*O*-TIPDS-nucleosides (**1a-f**) and 2',3'-*O*-TIPDS-nucleosides (**2a-f**) in DMSO-d<sub>6</sub> at 27°C.

**Table 2.** <sup>13</sup>C NMR (75 MHz) chemical shifts (ppm) of 3',5'-*O*-TIPDS-nucleosides (**1a-f**) and 2',3'-*O*-TIPDS-nucleosides (**2a-f**) in DMSO-d<sub>6</sub> at 27°C.

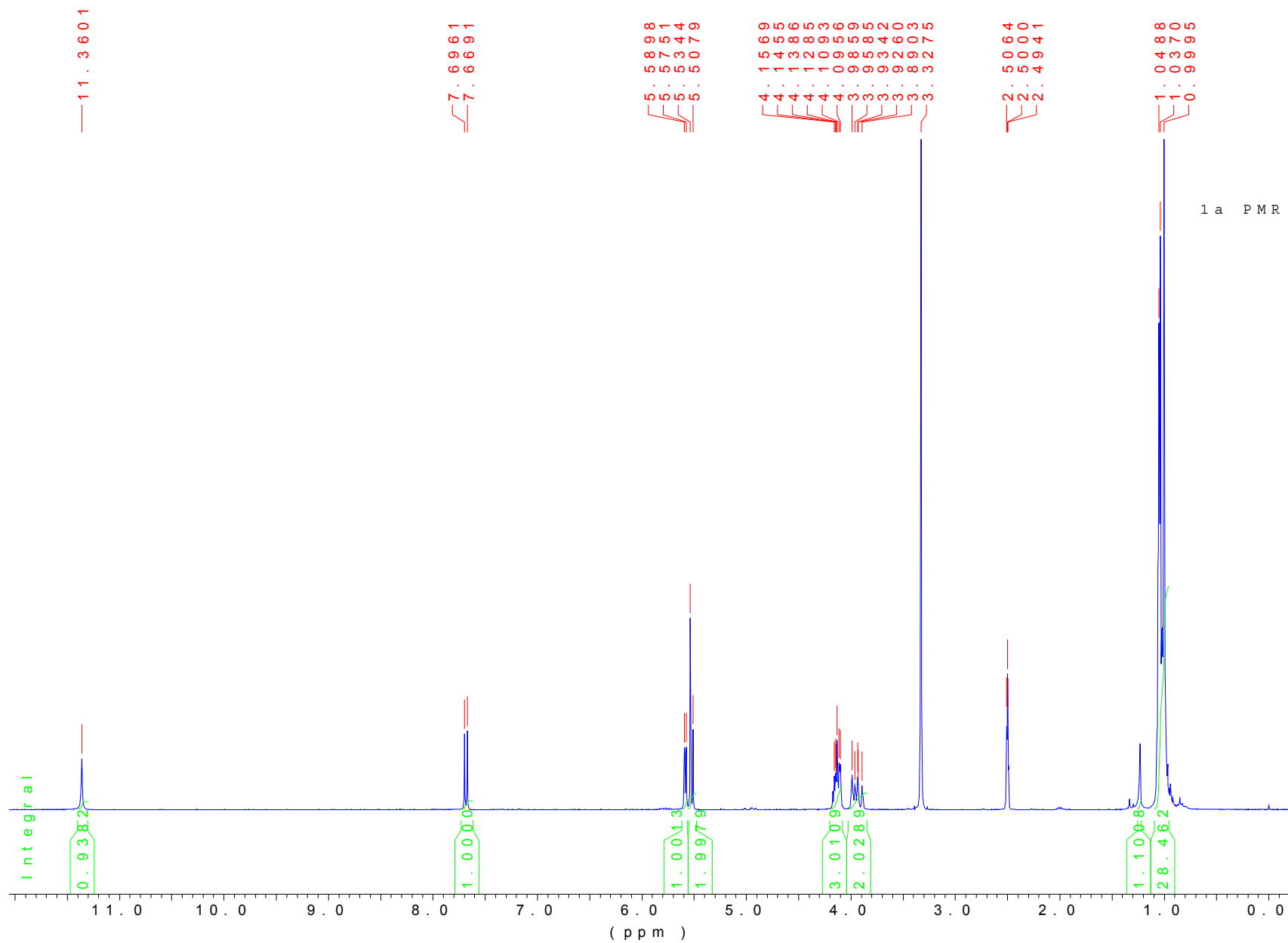
<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **1a-f** and **2a-f** in DMSO-d<sub>6</sub> at 300 K.

**Table 1.** <sup>1</sup>H NMR (300 MHz) chemical shifts (ppm) and coupling constants (Hz) of 3',5'-*O*-TIPDS-nucleosides (**1a-f**) and 2',3'-*O*-TIPDS-nucleosides (**2a-f**) in DMSO-d<sub>6</sub> at 27°C.

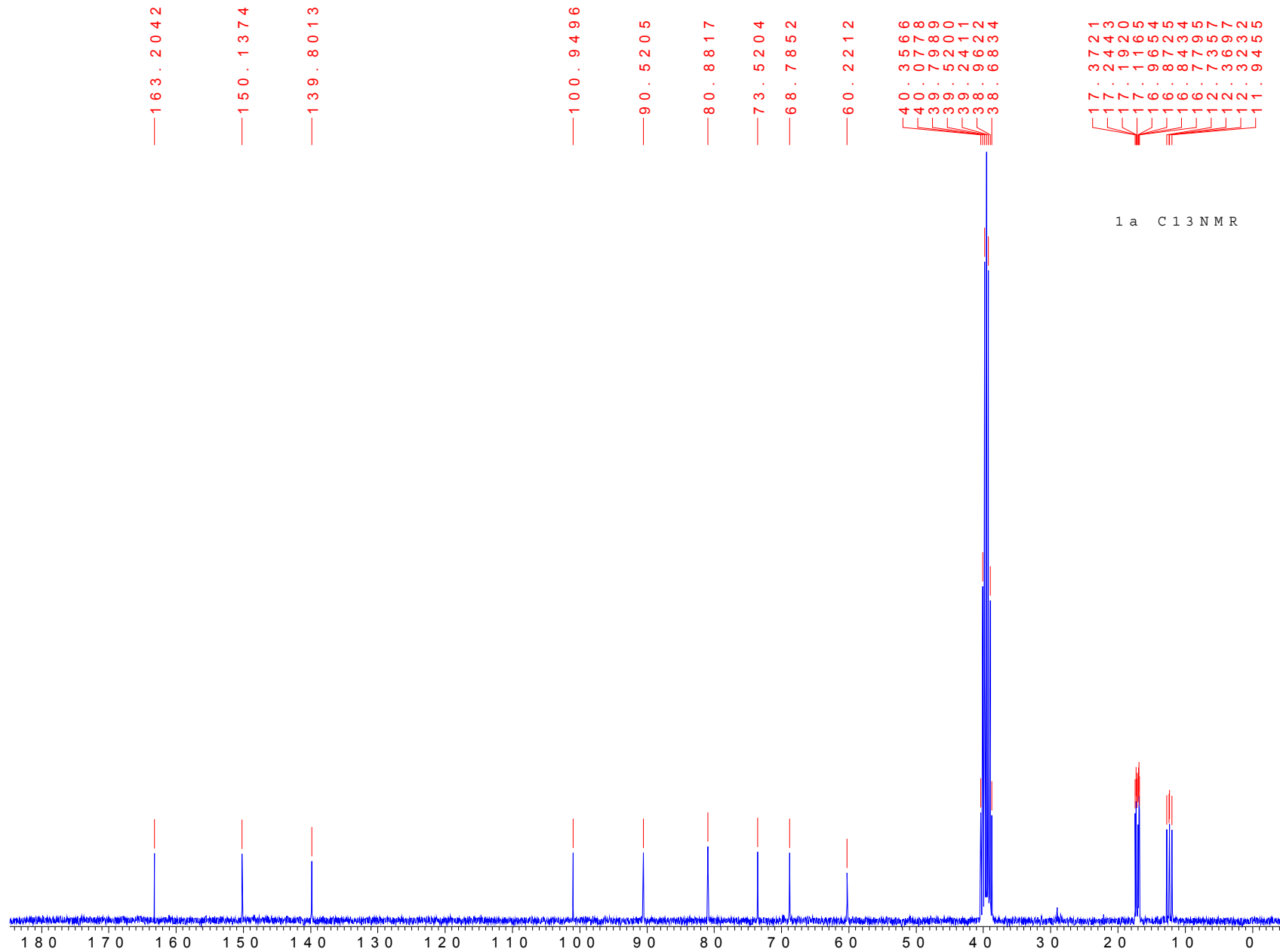
Chemical shifts, ppm (coupling constants, Hz)	Urd		Ado <sup>Bz</sup>		Ctd <sup>Bz</sup>		Guo <sup>iBu</sup>		Ado		Ctd	
	<b>1a</b>	<b>2a</b>	<b>1b</b>	<b>2b</b>	<b>1c</b>	<b>2c</b>	<b>1d</b>	<b>2d</b>	<b>1e</b>	<b>2e</b>	<b>1f</b>	<b>2f</b>
H-1' (J <sub>1',2'</sub> )	5.54 d (0.6)	5.79 d (4.1)	5.99 d (1.0)	6.13 d (5.7)	5.64 d (<1)	5.86 d (2.6)	5.79 d (1.1)	5.83 d (6.5)	5.87 d (<1)	5.96 d (5.9)	5.55 d (<1)	5.79 d (3.7)
H-2' (J <sub>2,3</sub> )	4.13 m (4.7)	4.52 dd (4.4)	4.63 ddd (5.2)	5.25 dd (4.9)	4.11 m (ND)	4.56 dd (4.3)	4.31 ddd (4.9)	4.95 dd (4.9)	4.52 ddd (5.1)	5.07 dd (4.4)	3.93 t (4.4)	4.41 dd (4.4)
H-3' (J <sub>3',4'</sub> )	4.16 dd (8.3)	4.37 dd (5.0)	4.81 dd (8.2)	4.68 dd (4.0)	4.11 m (ND)	4.38 dd (7.1)	4.35 dd (7.9)	4.58 dd (3.1)	4.80 dd (8.3)	4.63 dd (4.4)	4.08 dd (9.0)	4.34 dd (5.9)
H-4' (J <sub>4',5'a</sub> )	3.98 ddd (2.2)	3.94 ddd (3.3)	4.03 m (ND)	4.09 ddd (4.8)	4.11 m (<1)	4.01 ddd (2.9)	4.04 ddd (3.0)	4.01 ddd (5.2)	3.99 ddd (3.1)	4.06 ddd (4.0)	4.00 ddd (1.0)	3.91 ddd (3.1)
H-5'a (J <sub>5'a,5'b</sub> )	4.13 m (-13.0)	3.71 ddd (-12.2)	4.03 m (-12.5)	3.73 ddd (-12.0)	4.24 dd (-13.2)	3.84 ddd (-12.4)	4.12 dd (-12.9)	3.63 ddd (-11.9)	4.06 dd (-12.3)	3.70 ddd (-11.8)	4.15 dd (-12.8)	3.71 ddd (-12.1)
H-5'b (J <sub>4',5'b</sub> )	3.91 dd (2.5)	3.58 ddd (3.0)	3.93 dd (2.5)	3.62 ddd (4.0)	3.95 dd (<1)	3.64 ddd (3.0)	3.95 dd (2.6)	3.56 ddd (4.6)	3.93 dd (2.1)	3.58 ddd (4.4)	3.91 dd (2.5)	3.57 ddd (3.4)
<b>2'-OH (J<sub>2',2'-OH</sub>) 5'-OH (J<sub>5'a,5'OH</sub>, J<sub>5'b,5'OH</sub>)</b>	<b>5.58 d (4.4)</b>	<b>5.25 t (5.0, 5.0)</b>	<b>5.67 d (4.6)</b>	<b>5.15 t (5.2, 5.2)</b>	<b>5.80 d (3.9)</b>	<b>5.32 dd (4.8, 5.0)</b>	<b>5.69 d (4.8)</b>	<b>5.16 t (5.5, 5.5)</b>	<b>5.62 d (4.6)</b>	<b>5.33 dd (5.3, 5.9)</b>	<b>5.57 d (4.4)</b>	<b>5.15 t (5.3, 5.3)</b>
H-6 (J <sub>6,5</sub> ) / H-8	7.68 (8.0)	7.95 (8.1)	8.65 s	8.78 s	8.21 (7.5)	8.51 (7.4)	8.05 s	8.32 s	8.21 s	8.38 s	7.70 (7.5)	7.88 (7.5)
H-5 / H-2	5.52 d	5.64 d	8.52 s	8.76 s	7.37 d	7.34 d	--	--	8.08 s	8.13 s	5.68 d	5.71 d
NH	11.36 brs	11.33 s	11.22 brs	11.23 s	11.27 brs	11.22 brs	12.12 brs, 11.61 brs		7.33 brs	7.23 brs	7.15 brs, 7.07 brs	
Bz / iBu (1H)	--	--	8.02 d (2H, J 7.2), 7.63 t (1H), 7.57 t (2H)				2.78 sept (1H, J 6.9), 1.12 d (6H)		--	--	--	--
iPr	1.15-0.95 m (28H)											

**Table 2.**  $^{13}\text{C}$  NMR (75 MHz) chemical shifts (ppm) of 3',5'-*O*-TIPDS-nucleosides (**1a-f**) and 2',3'-*O*-TIPDS-nucleosides (**2a-f**) in DMSO- $d_6$  at 27°C.

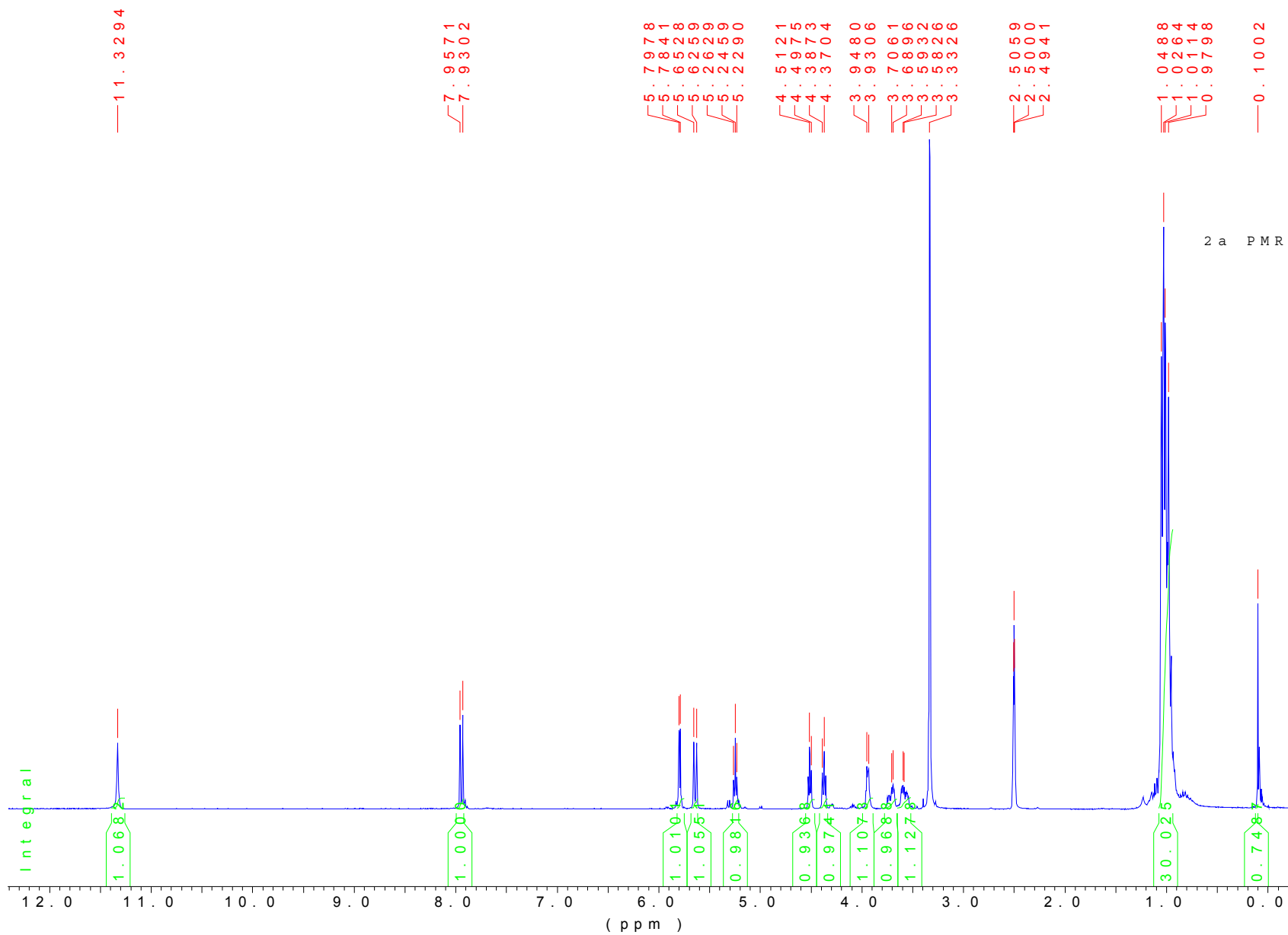
Chemical shifts, ppm	Urd		Ado <sup>Bz</sup>		Ctd <sup>Bz</sup>		Guo <sup>iBu</sup>		Ado		Ctd	
	<b>1a</b>	<b>2a</b>	<b>1b</b>	<b>2b</b>	<b>1c</b>	<b>2c</b>	<b>1d</b>	<b>2d</b>	<b>1e</b>	<b>2e</b>	<b>1f</b>	<b>2f</b>
C-2	150.60	150.95	151.90	152.62	154.62	154.83	148.75	149.54	139.20	139.71	155.76	155.06
C-4	163.66	163.62	150.99	150.96	163.64	163.55	148.48	148.79	148.62	149.16	166.71	165.57
C-5	101.41	102.10	126.44	126.29	96.06	96.55	120.85	120.68	119.25	119.25	93.84	93.92
C-6	140.26	140.57	151.90	152.23	144.18	145.32	155.29	155.25	156.09	156.14	140.77	141.04
C-8	--	--	143.55	143.39	--	--	136.68	137.78	152.48	152.56	--	--
C-1'	90.98	88.94	90.01	88.04	91.77	90.91	88.63	86.56	89.33	87.79	91.28	89.54
C-2'	73.98	76.18	73.86	76.07	74.27	76.75	74.47	75.90	73.64	75.45	74.57	75.96
C-3'	69.25	71.87	70.35	72.82	68.52	71.24	69.97	72.68	69.81	72.59	68.94	71.45
C-4'	81.34	85.00	81.43	86.26	81.38	84.66	81.68	86.32	80.75	85.84	81.01	83.96
C-5'	60.68	60.22	61.21	61.16	60.26	59.58	61.07	61.24	60.80	61.08	60.44	59.87



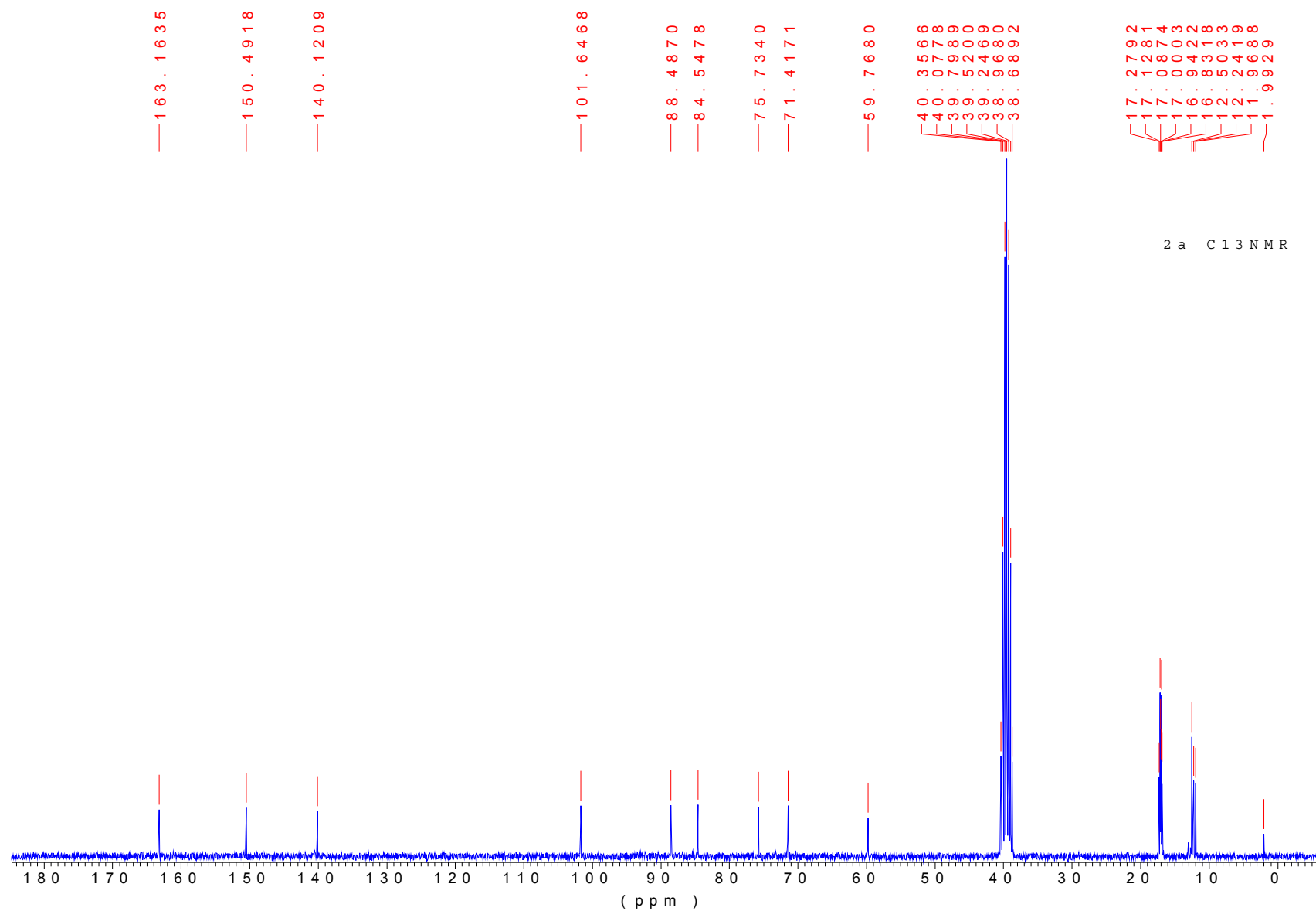
$^1\text{H}$  NMR spectrum (300 MHz) of 3',5'-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)uridine (**1a**) in DMSO- $d_6$  at 300 K.



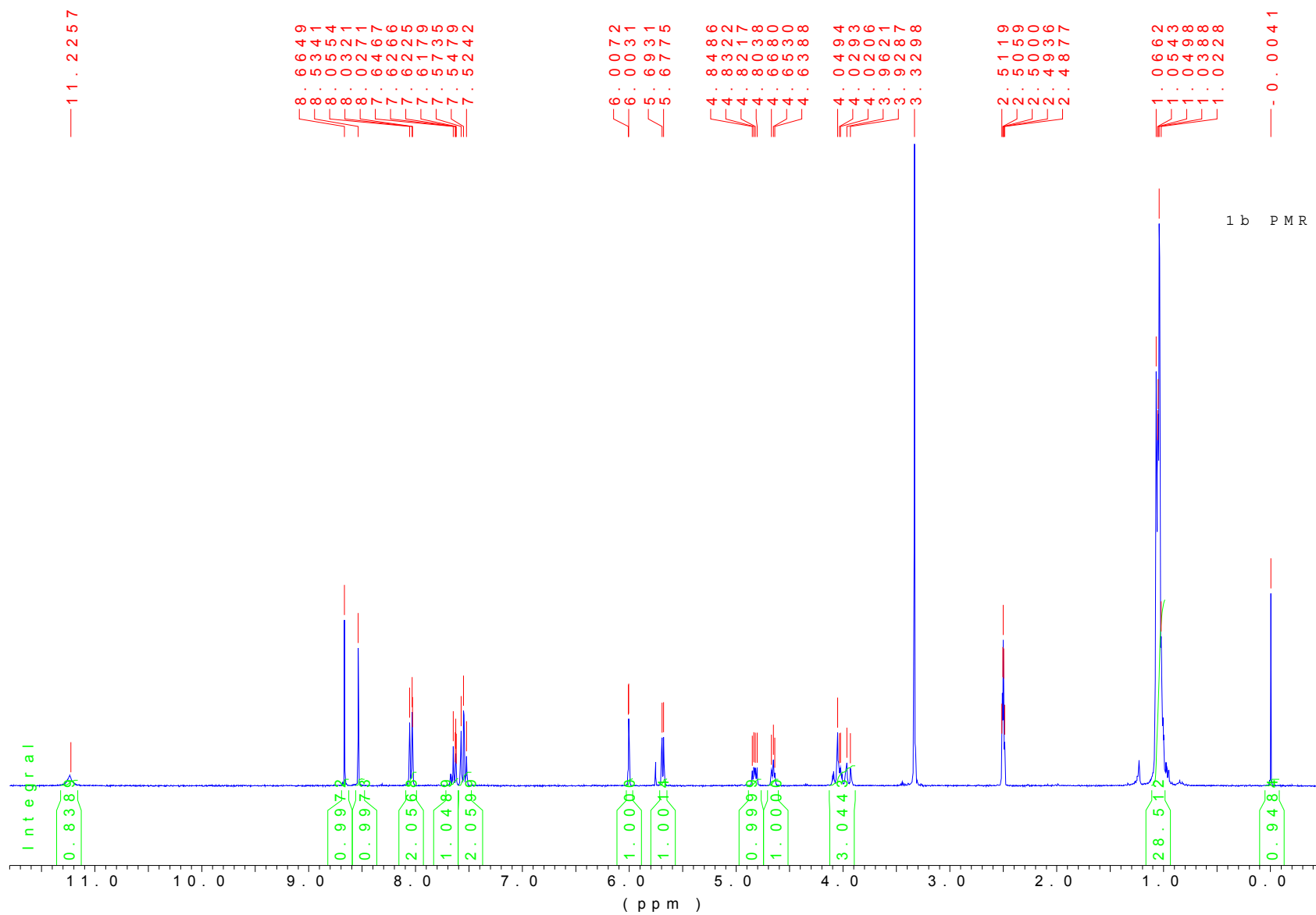
$^{13}\text{C}$  NMR spectrum (75 MHz) of 3',5'-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)uridine (**1a**) in DMSO- $d_6$  at 300 K.



$^1\text{H}$  NMR spectrum (300 MHz) of 2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)uridine (**2a**) in DMSO- $d_6$  at 300 K.

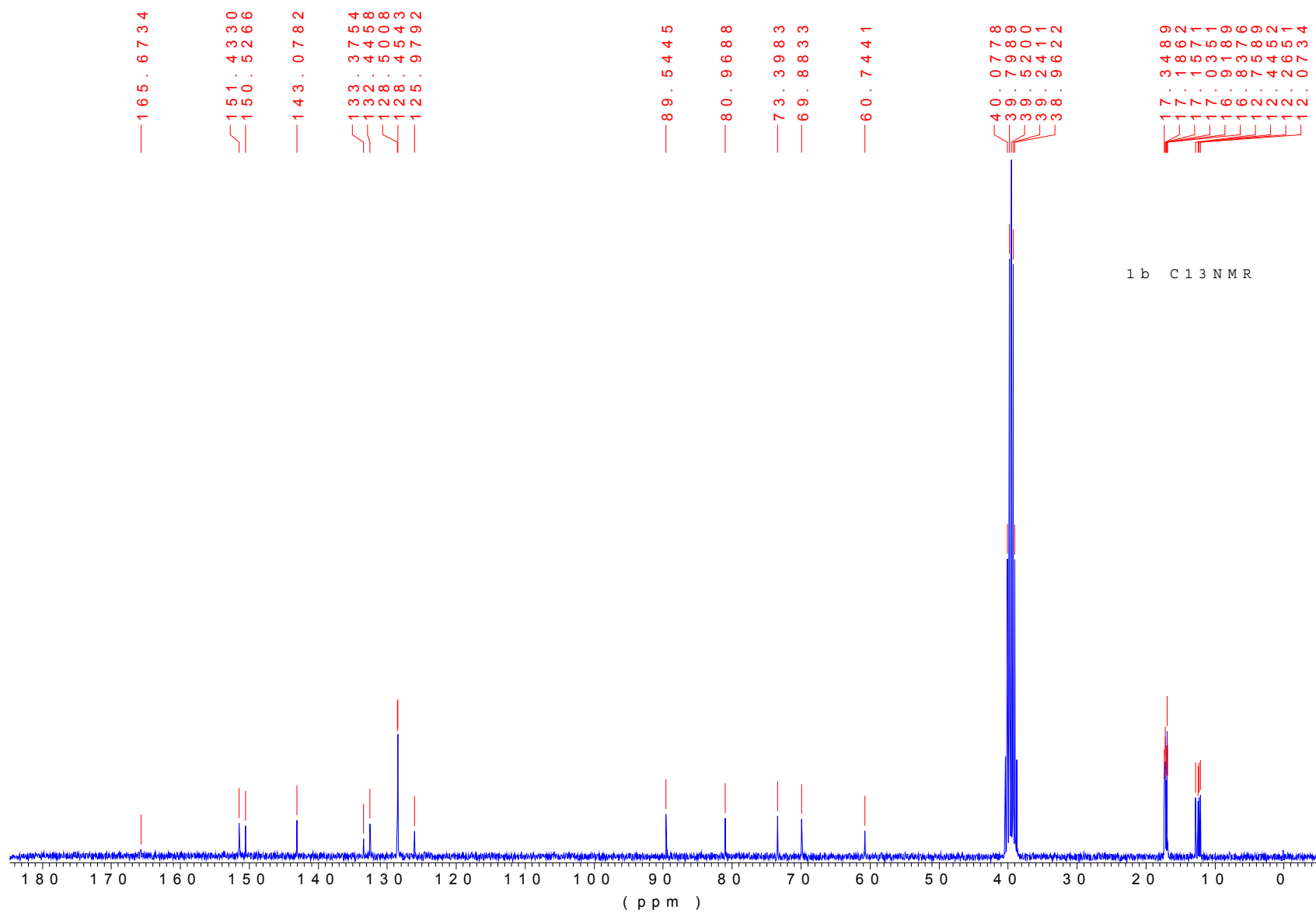


$^{13}\text{C}$  NMR spectrum (75 MHz) of 2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)uridine (**2a**) in DMSO- $d_6$  at 300 K.

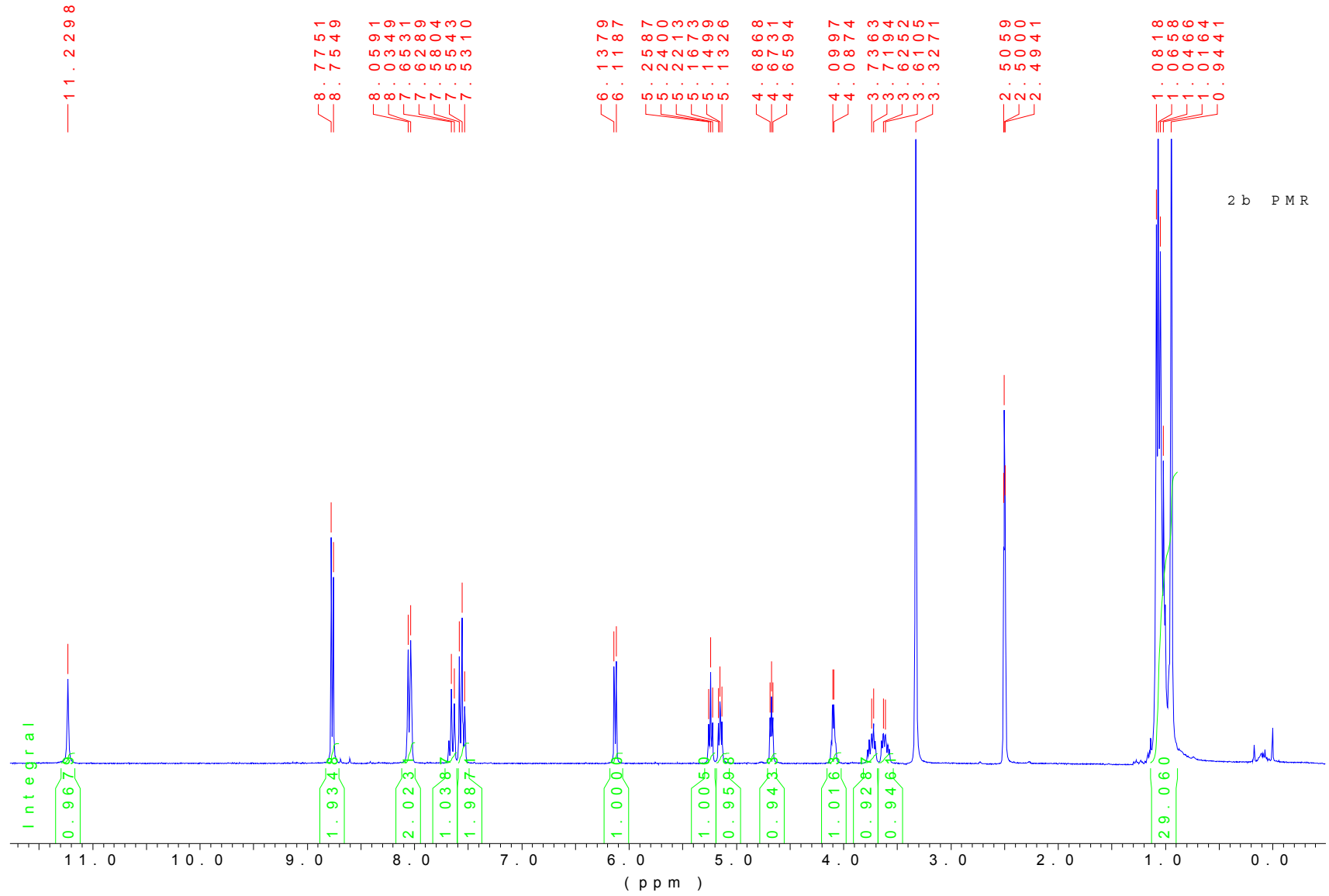


$^1\text{H}$  NMR spectrum (300 MHz) of  $\text{N}^6$ -Benzoyl-3',5'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)adenosine (**1b**) in DMSO- $d_6$  at 300 K.

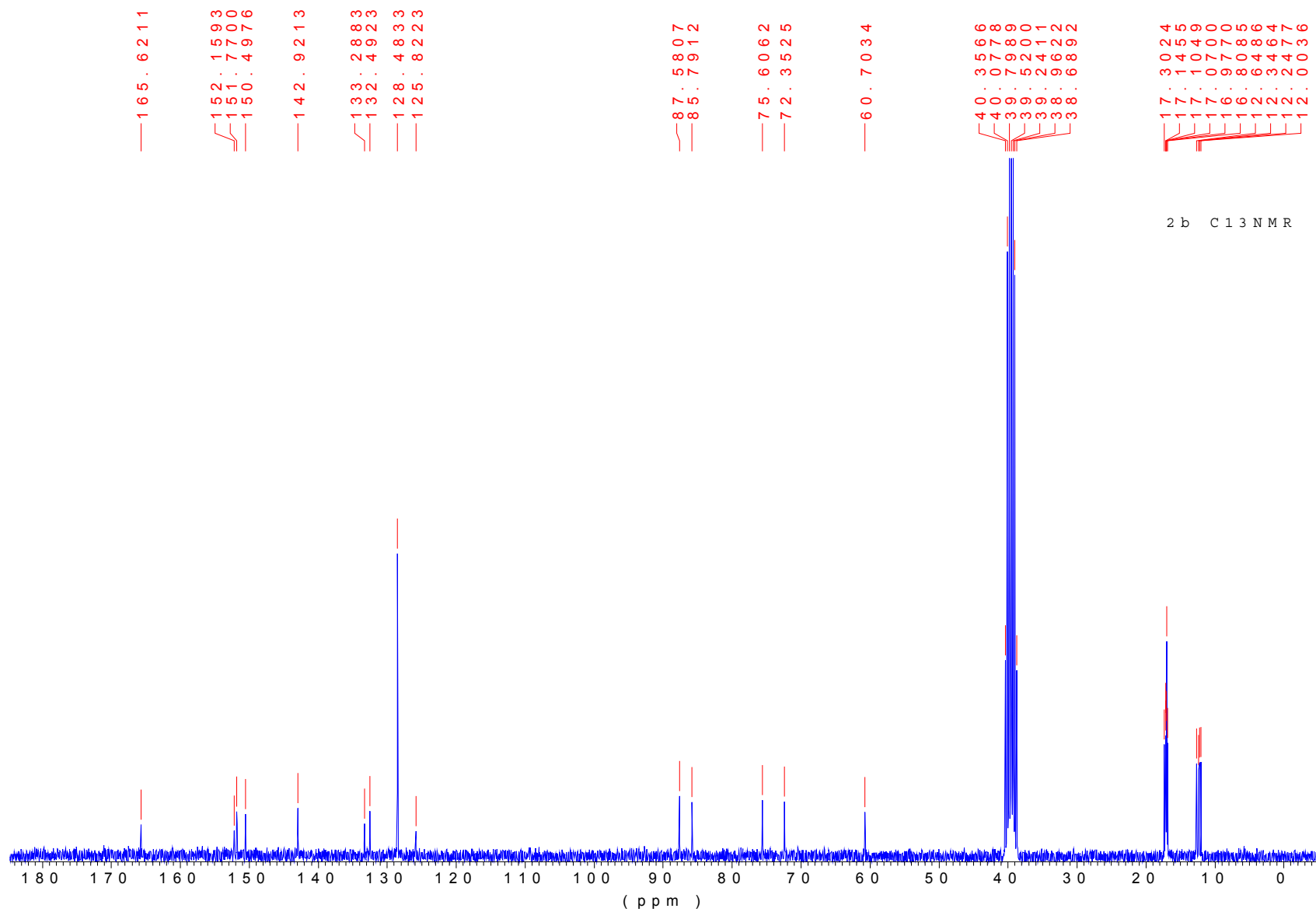




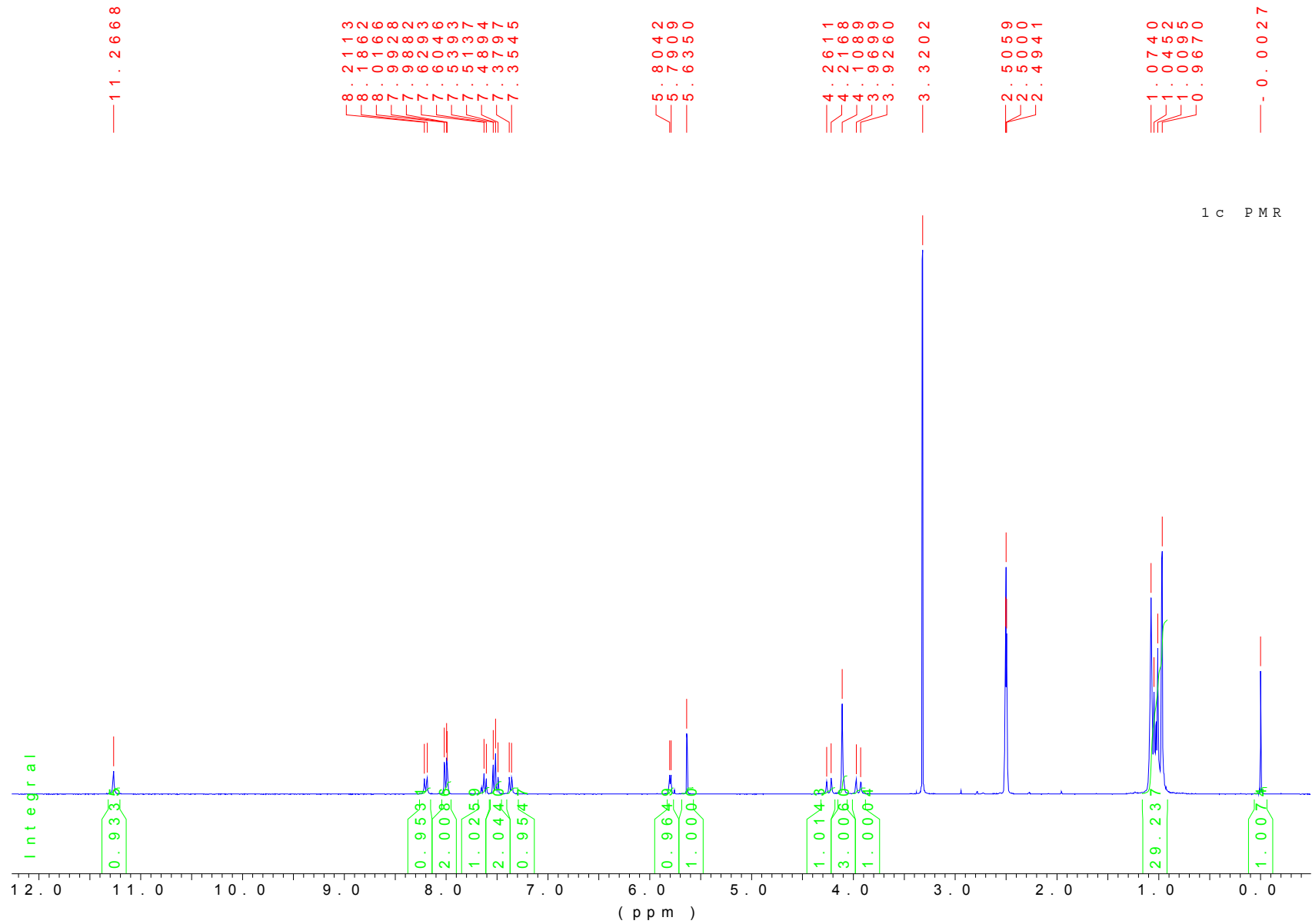
$^{13}\text{C}$  NMR spectrum (75 MHz) of  $\text{N}^6$ -Benzoyl-3',5'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)adenosine (**1b**) in DMSO- $d_6$  at 300 K.



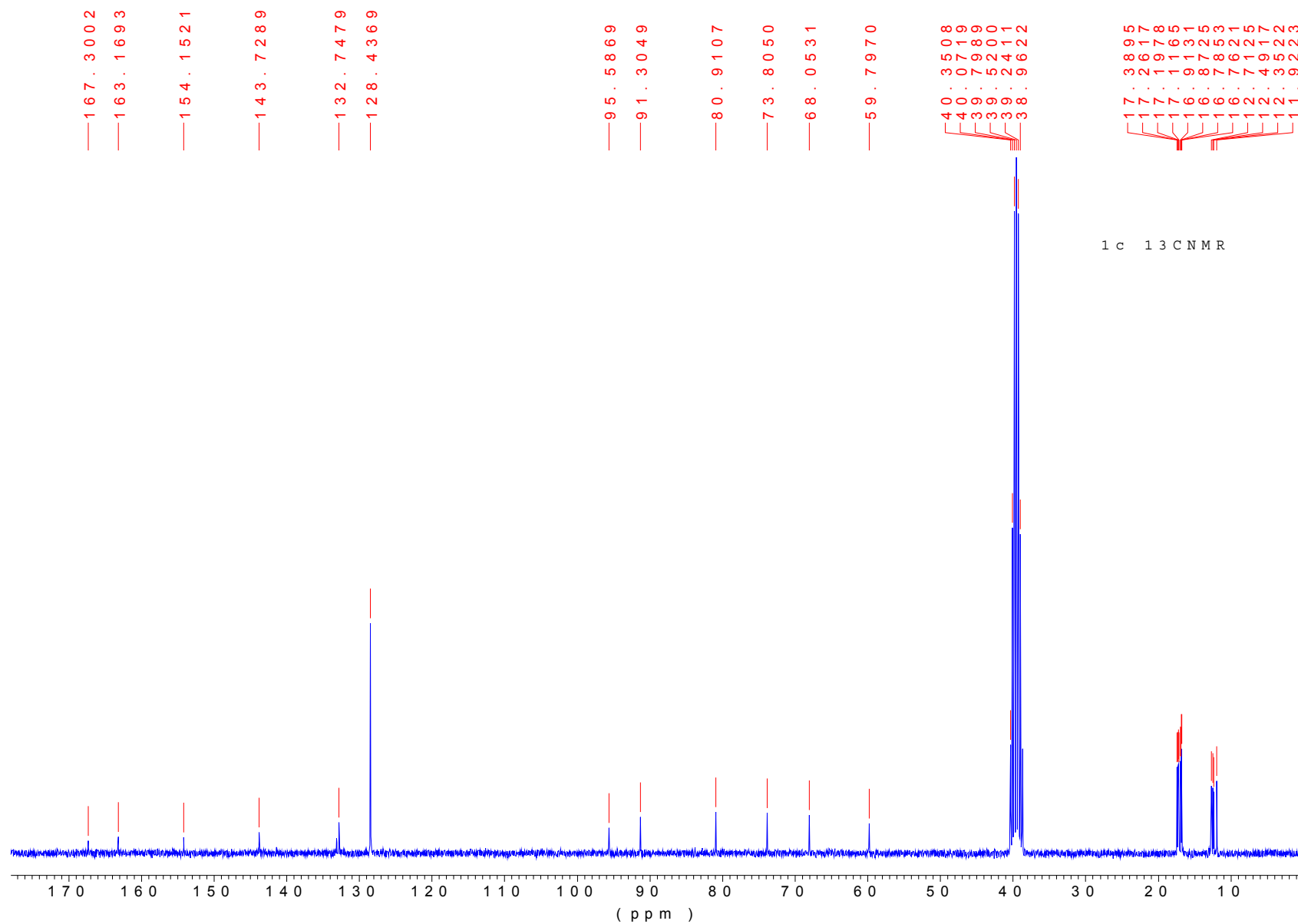
$^1\text{H}$  NMR spectrum (300 MHz) of  $N^6$ -Benzoyl-2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)adenosine (**2b**) in DMSO- $d_6$  at 300 K.



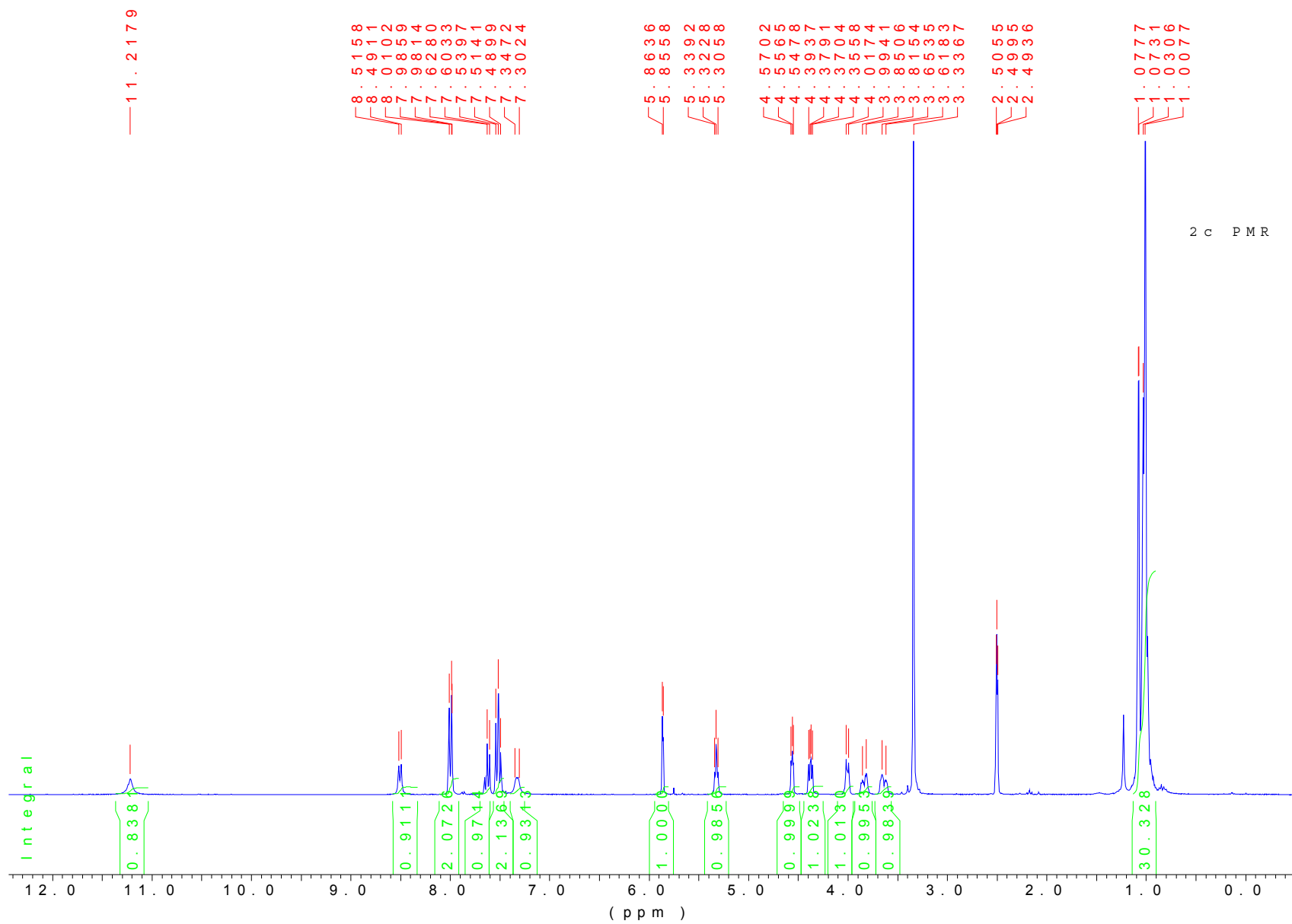
$^{13}\text{C}$  NMR spectrum (75 MHz) of  $\text{N}^6$ -Benzoyl-2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)adenosine (**2b**) in DMSO- $d_6$  at 300 K.



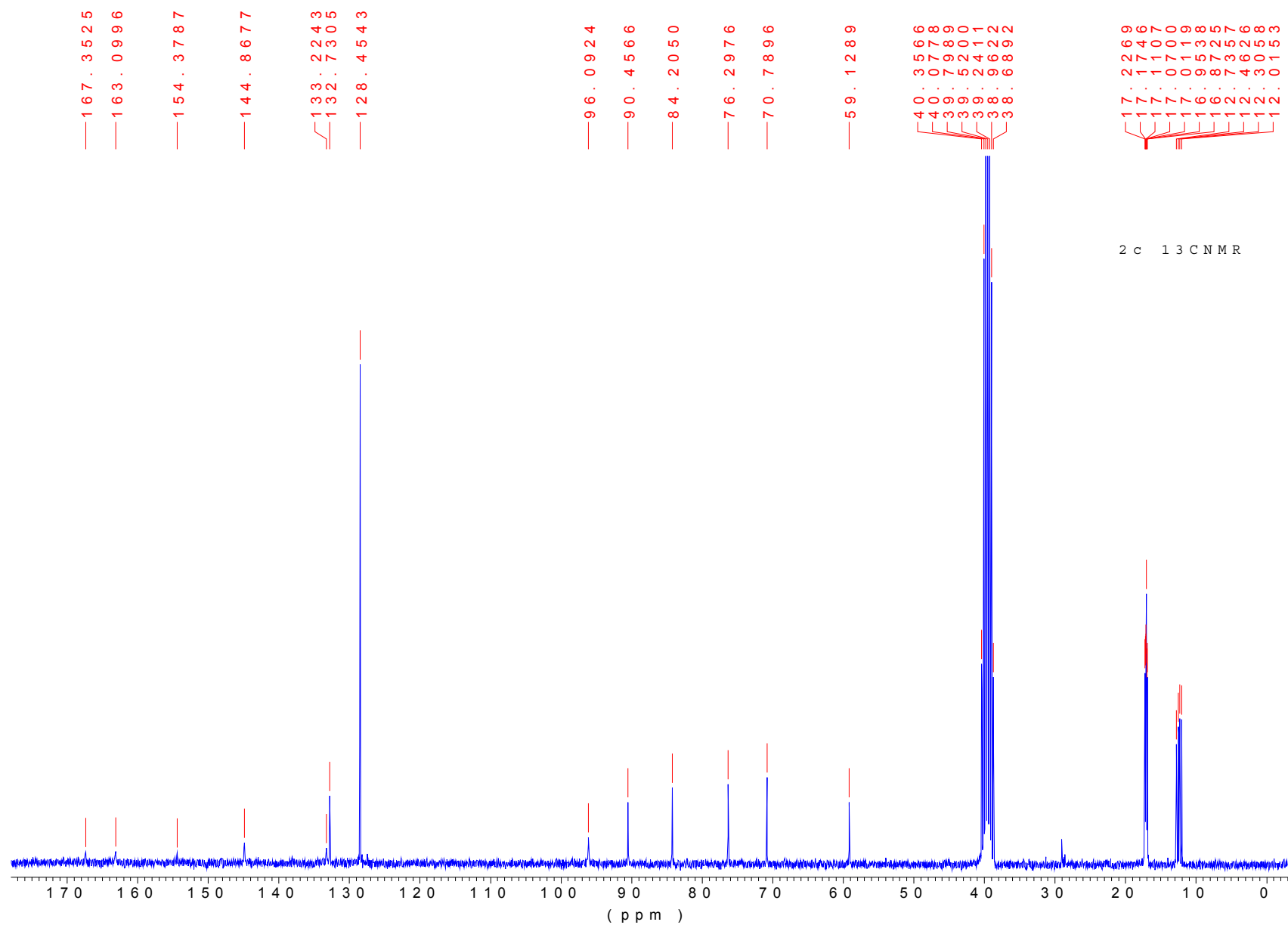
<sup>1</sup>H NMR spectrum (300 MHz) of N<sup>4</sup>-Benzoyl-3',5'-O-(1,1,3,3-tetraisopropylidisiloxane-1,3-diyl)cytidine (**1c**) in DMSO-d<sub>6</sub> at 300 K.



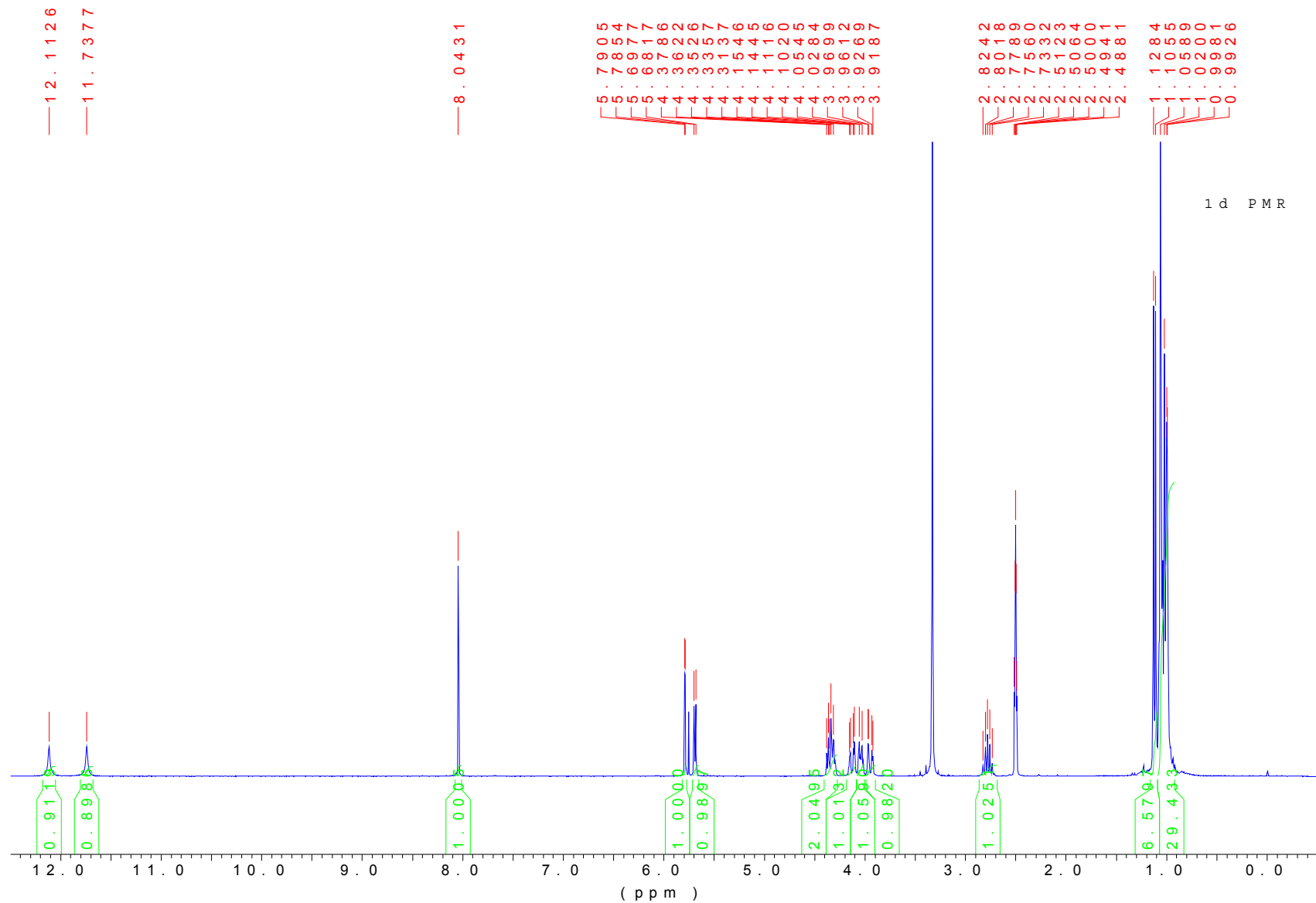
<sup>13</sup>C NMR spectrum (75 MHz) of N<sup>4</sup>-Benzoyl-3',5'-O-(1,1,3,3-tetraisopropylidisiloxane-1,3-diyl)cytidine (**1c**) in DMSO-d<sub>6</sub> at 300 K.



$^1\text{H}$  NMR spectrum (300 MHz) of  $\text{N}^4$ -Benzoyl-2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)cytidine (**2c**) in DMSO- $d_6$  at 300 K.

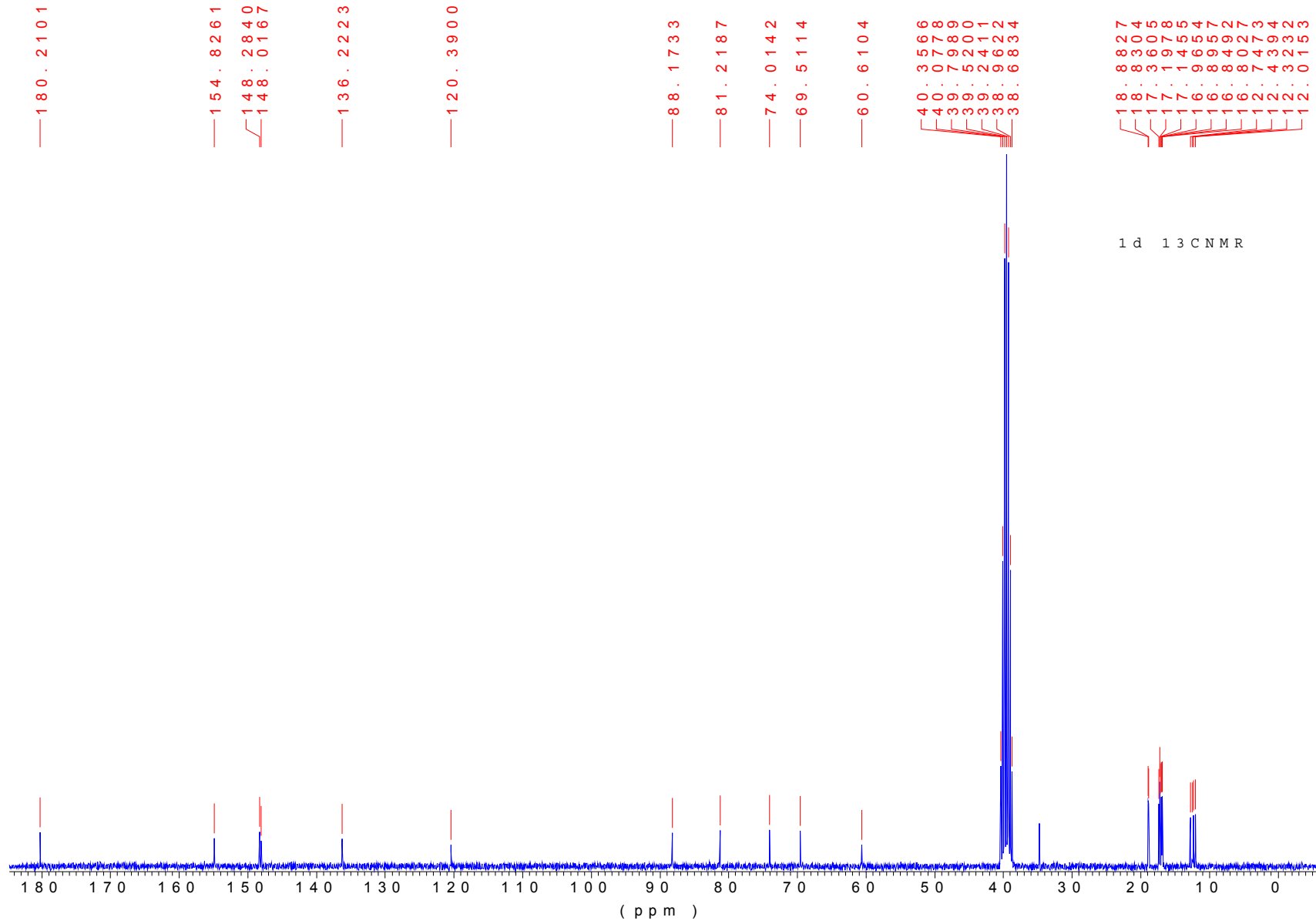


$^{13}\text{C}$  NMR spectrum (75 MHz) of  $\text{N}^4$ -Benzoyl-2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)cytidine (**2c**) in  $\text{DMSO-d}_6$  at 300 K.

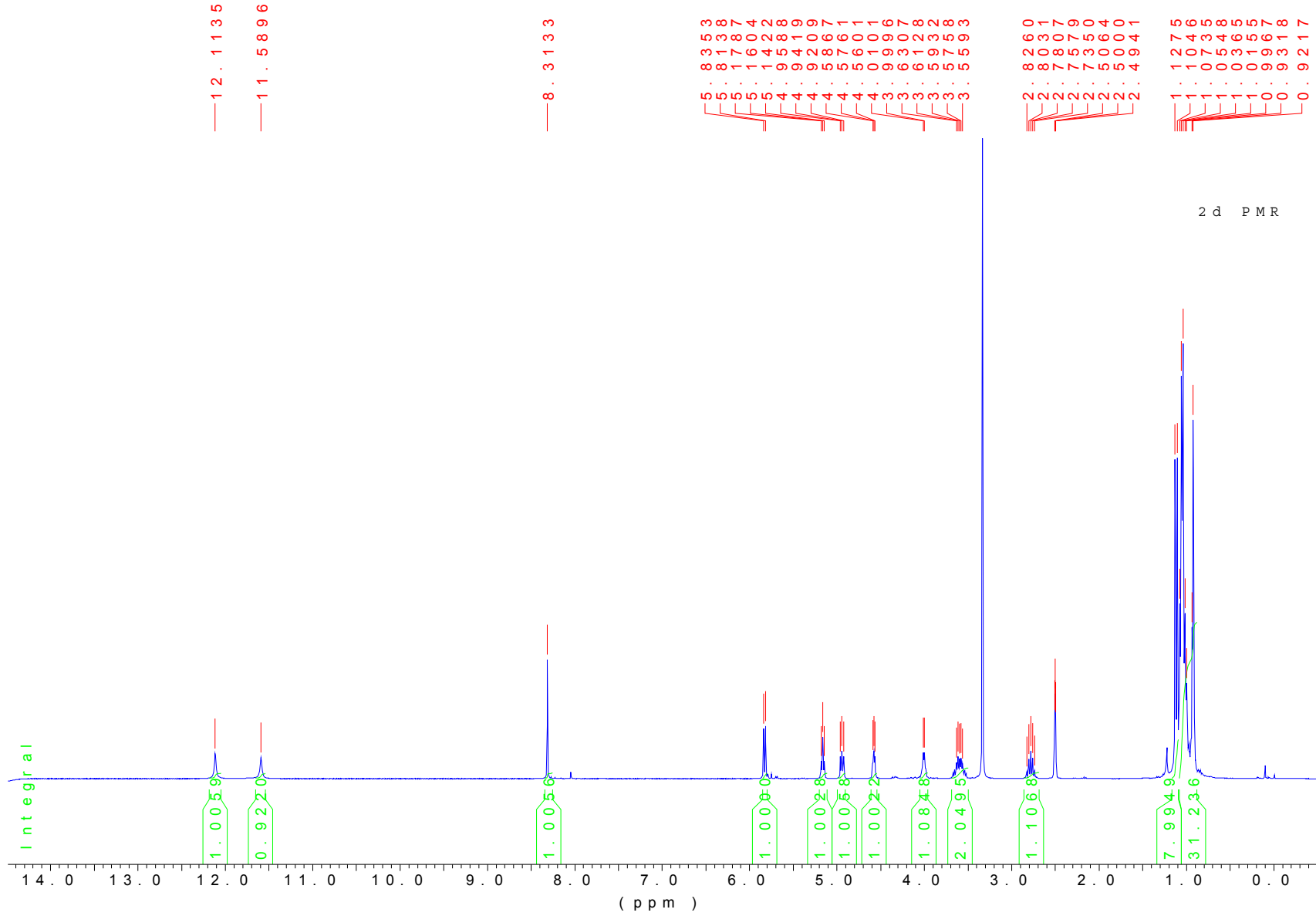


$^1\text{H}$  NMR spectrum (300 MHz) of  $\text{N}^2$ -Isobutyryl-3',5'-O-(1,1,3,3-tetraisopropylidisiloxane-1,3-diyl)guanosine (**1d**) in  $\text{DMSO-d}_6$  at 300 K.

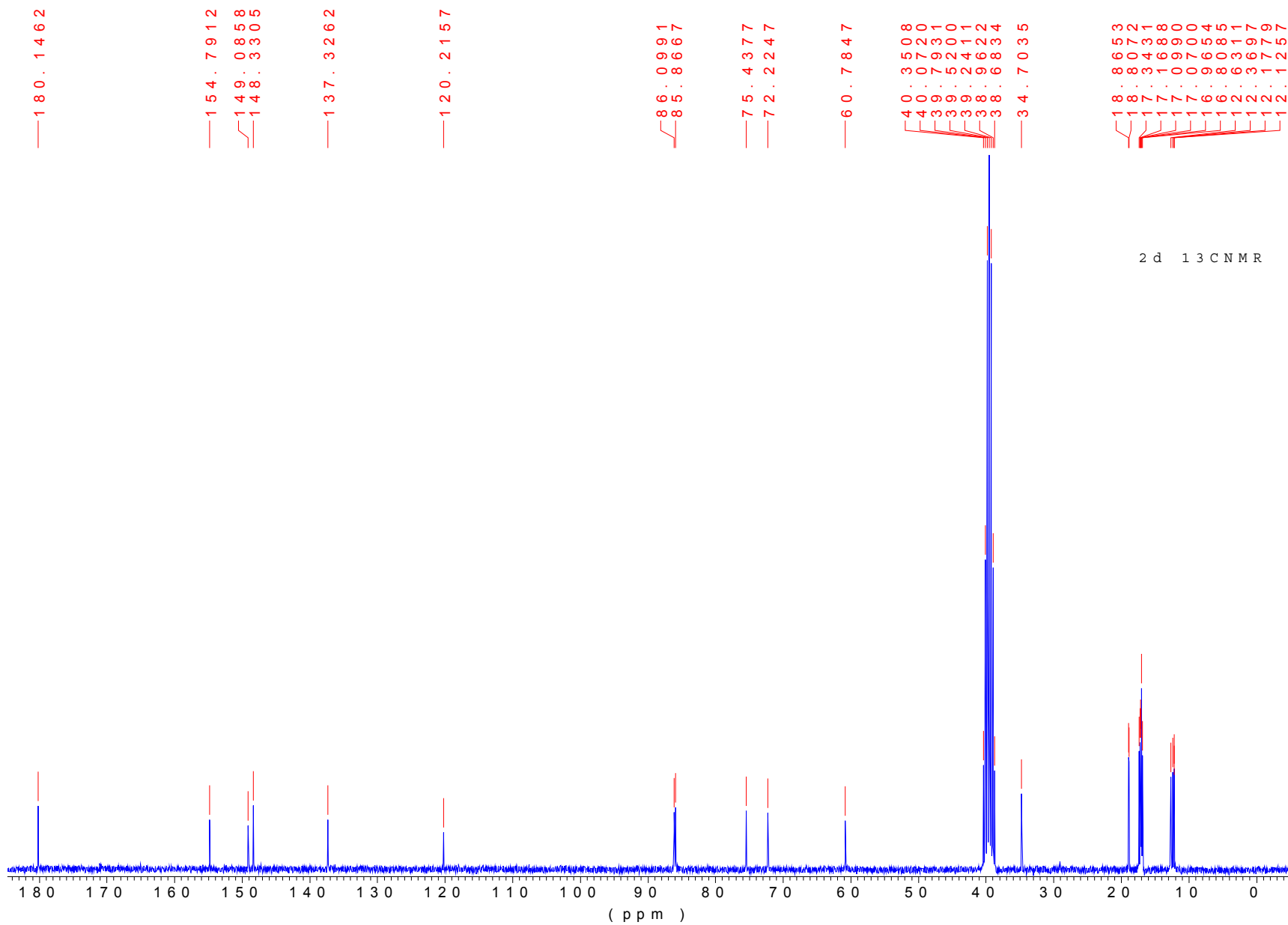




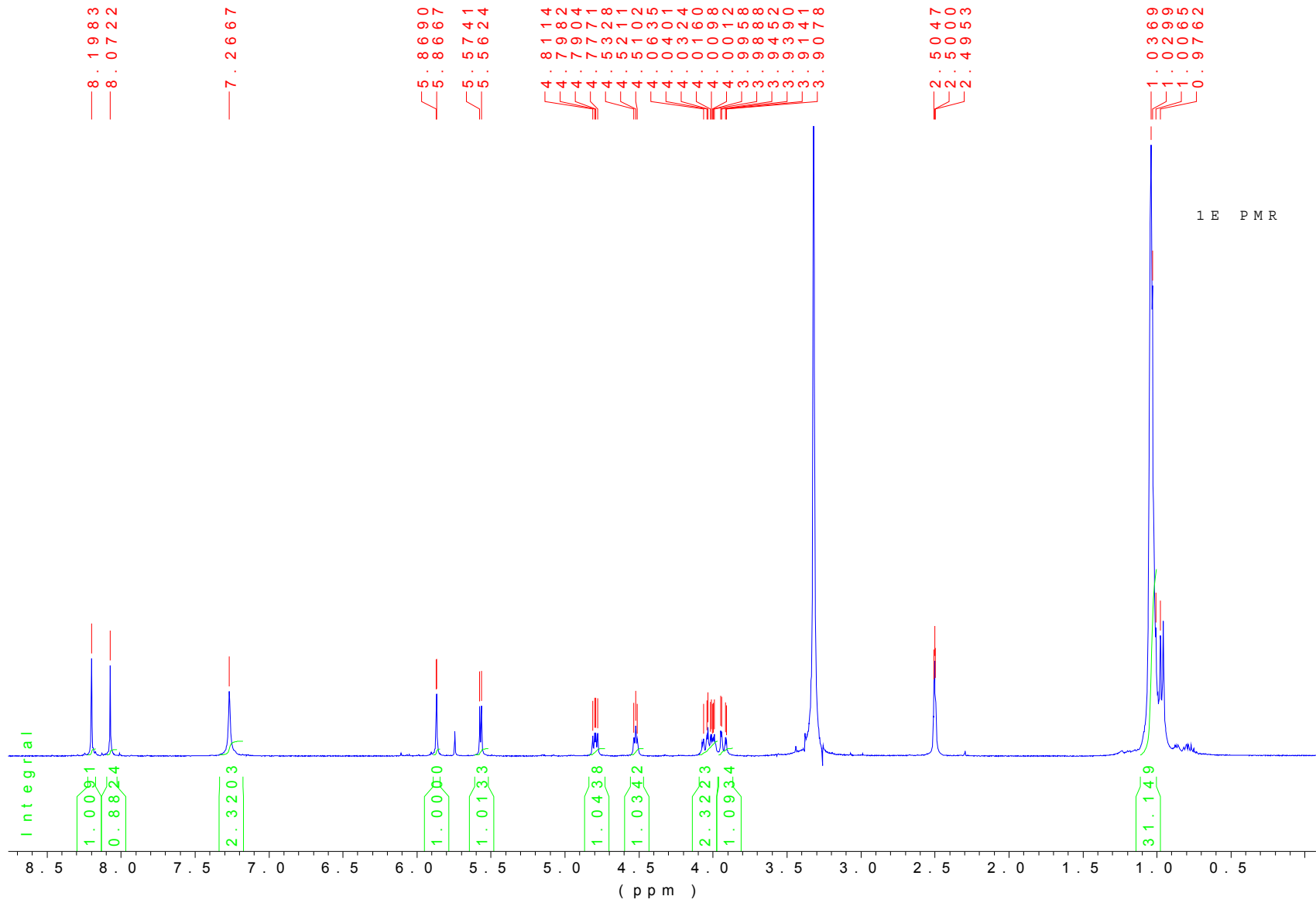
$^{13}\text{C}$  NMR spectrum (75 MHz) of  $\text{N}^2$ -Isobutyryl-3',5'-O-(1,1,3,3-tetraisopropylidisiloxane-1,3-diyl)guanosine (**1d**) in  $\text{DMSO-d}_6$  at 300 K.



$^1\text{H}$  NMR spectrum (300 MHz) of  $N^2$ -Isobutyryl-2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)guanosine (**2d**) in DMSO- $d_6$  at 300 K.

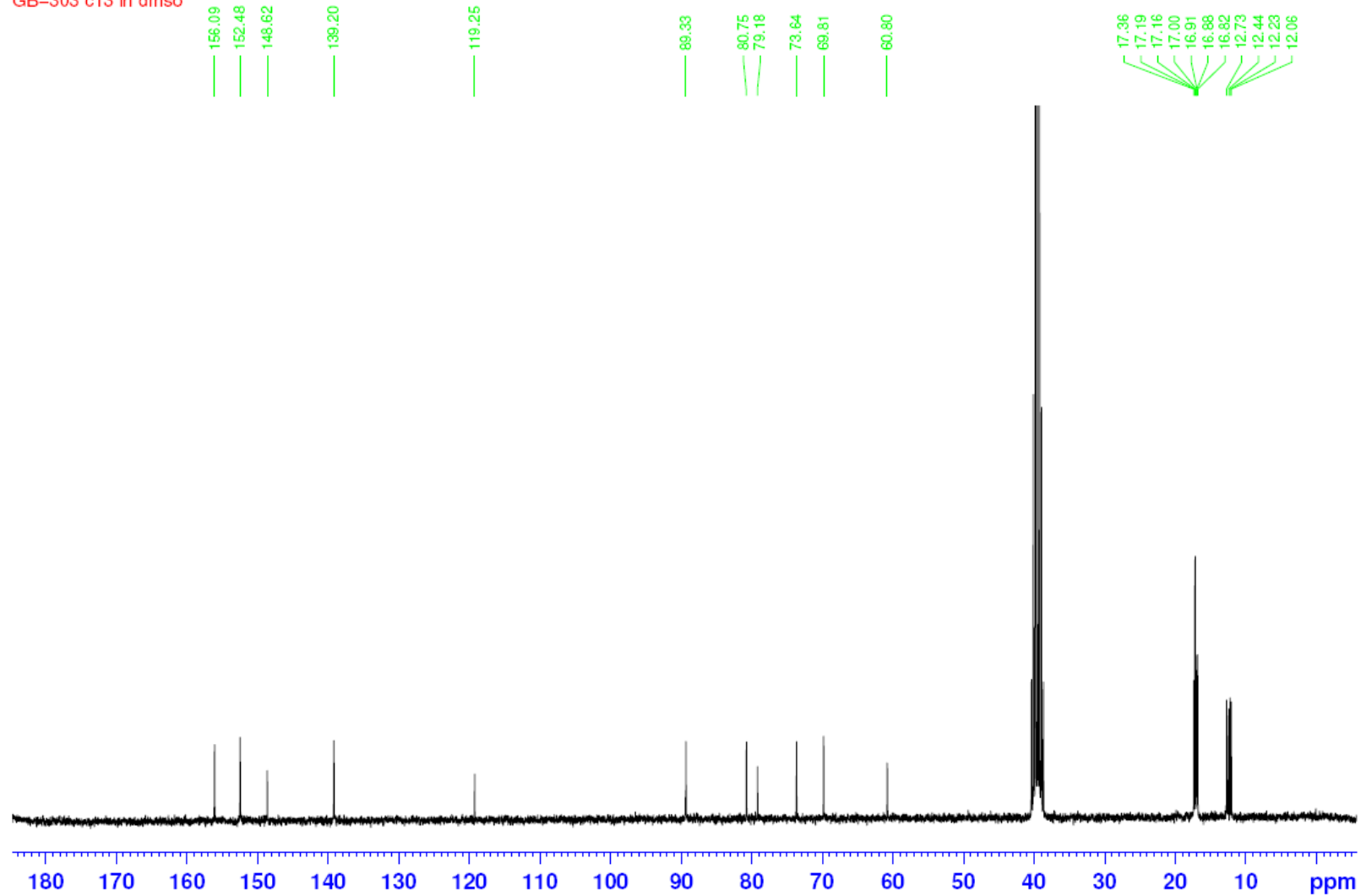


<sup>13</sup>C NMR spectrum (75 MHz) of N<sup>2</sup>-Isobutyryl-2',3'-O-(1,1,3,3-Tetraisopropyldisiloxane-1,3-diyl)guanosine (**2d**) in DMSO-d<sub>6</sub> at 300 K.

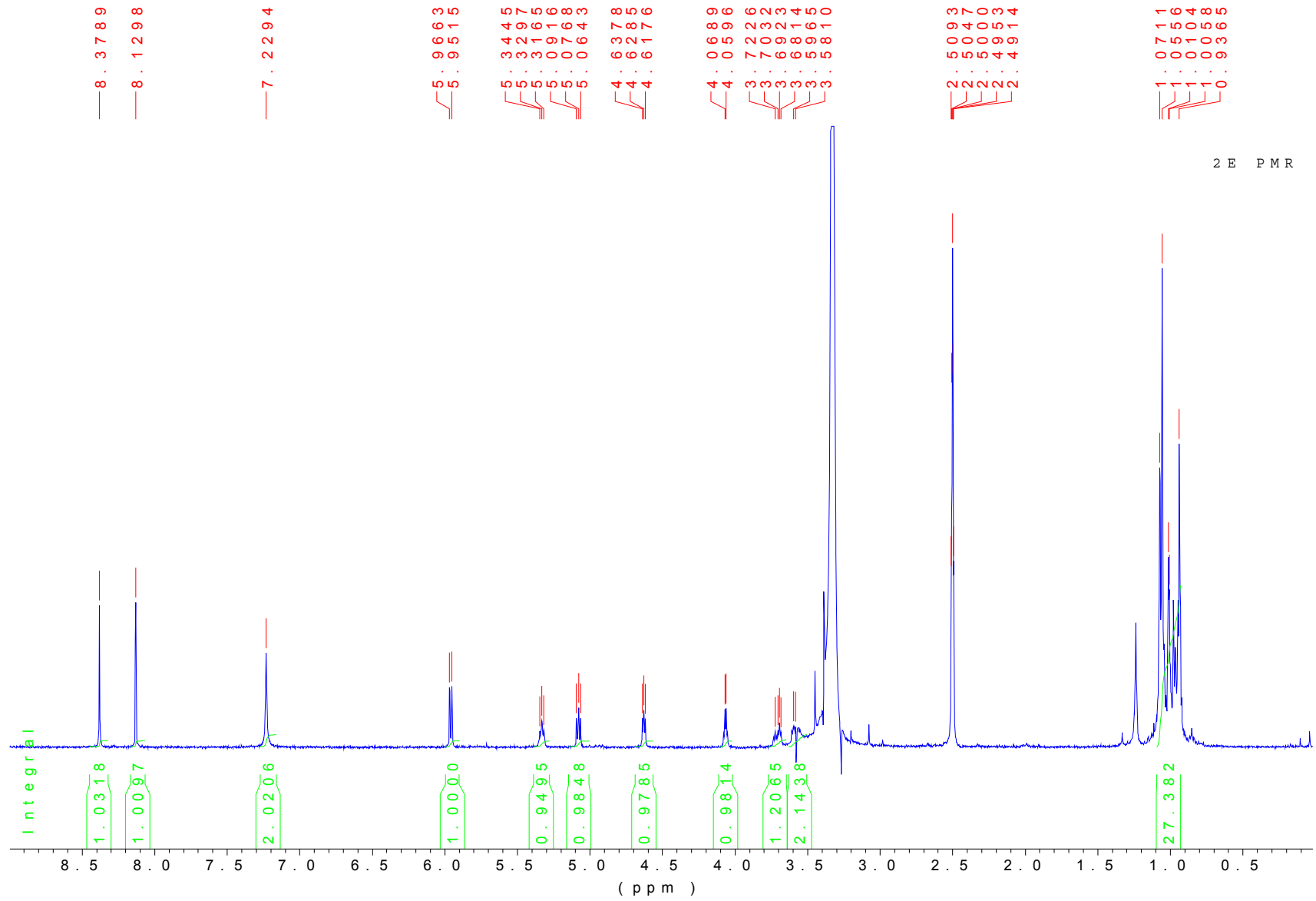


$^1\text{H}$  NMR spectrum (400 MHz) of 3',5'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)adenosine (**1e**) in DMSO- $d_6$  at 300 K.

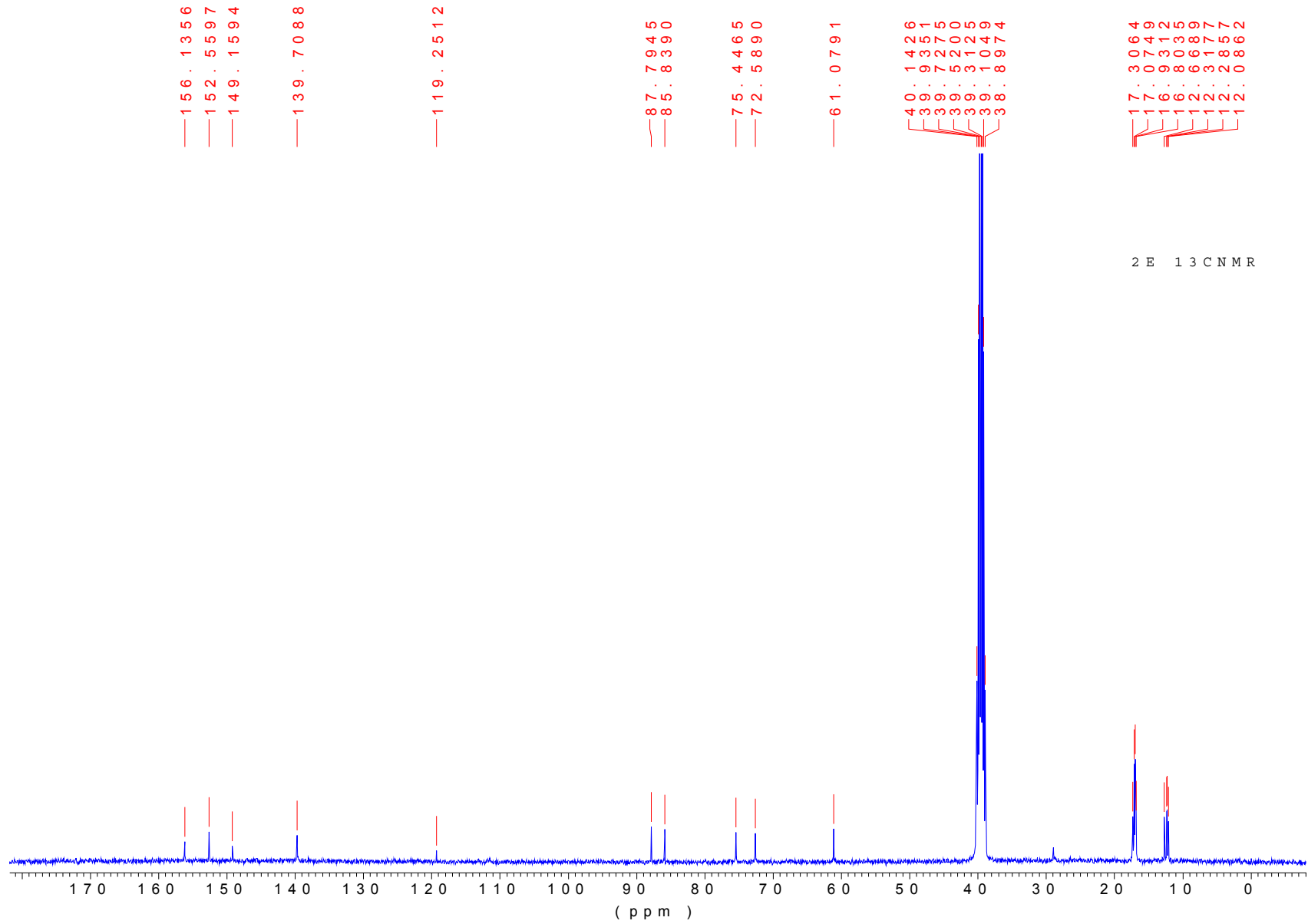
3,5-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)adenosine  
GB-303 c13 in dmsd



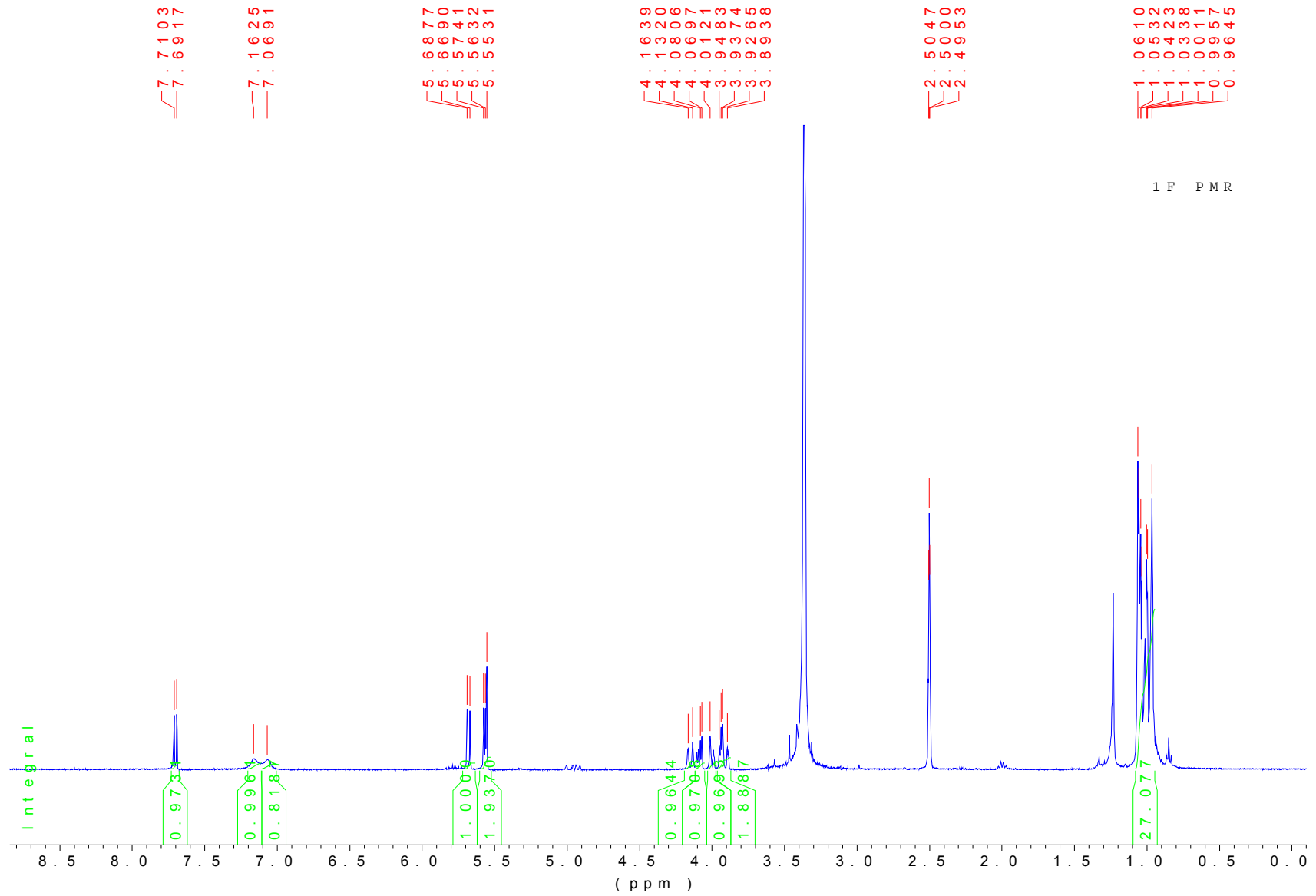
$^{13}\text{C}$  NMR spectrum (100 MHz) of 3',5'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)adenosine (**1e**) in DMSO- $d_6$  at 300 K.



$^1\text{H}$  NMR spectrum (400 MHz) of 2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)adenosine (**2e**) in DMSO- $d_6$  at 300 K.

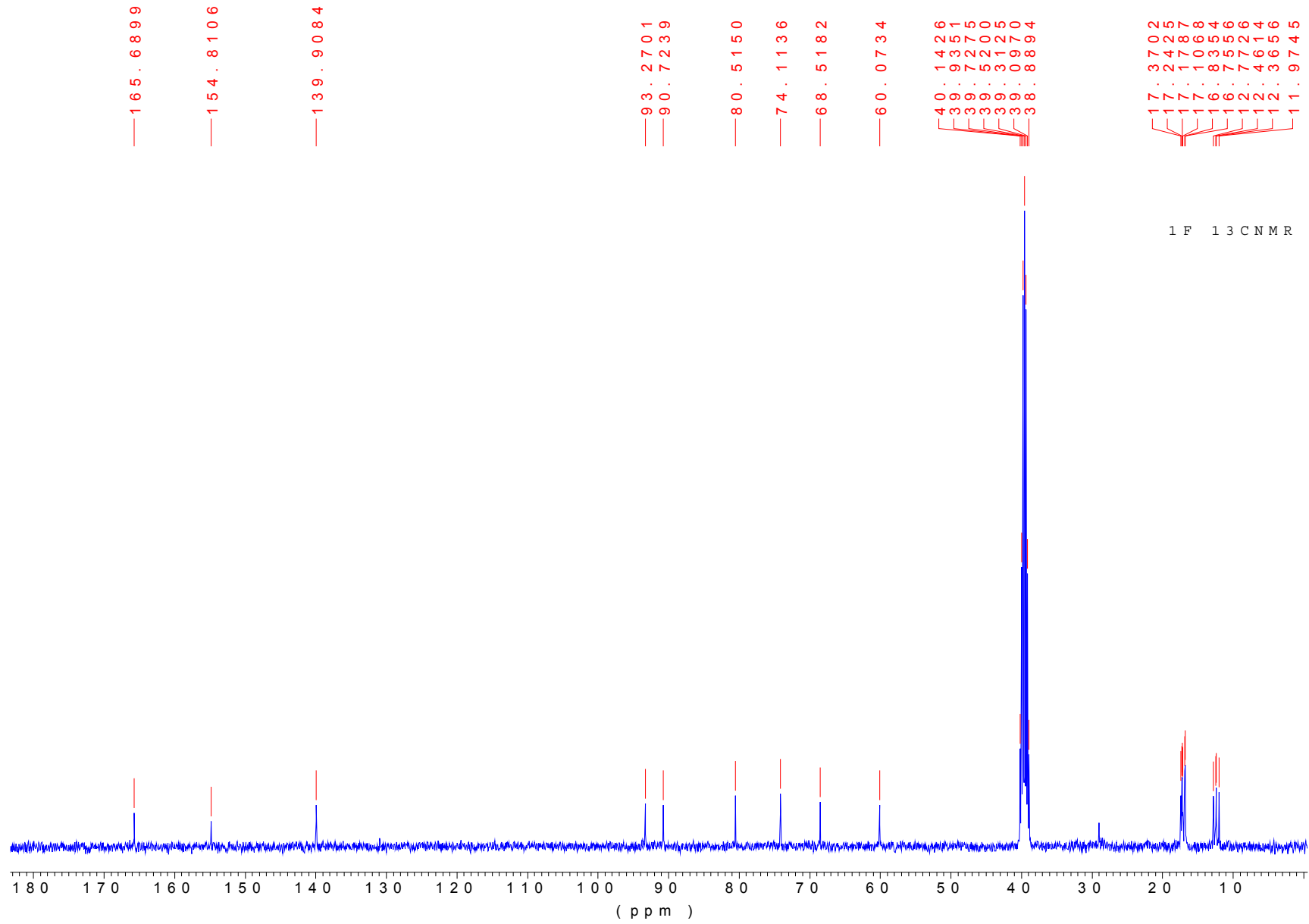


$^{13}\text{C}$  NMR spectrum (100 MHz) of 2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)adenosine (**2e**) in DMSO- $d_6$  at 300 K.

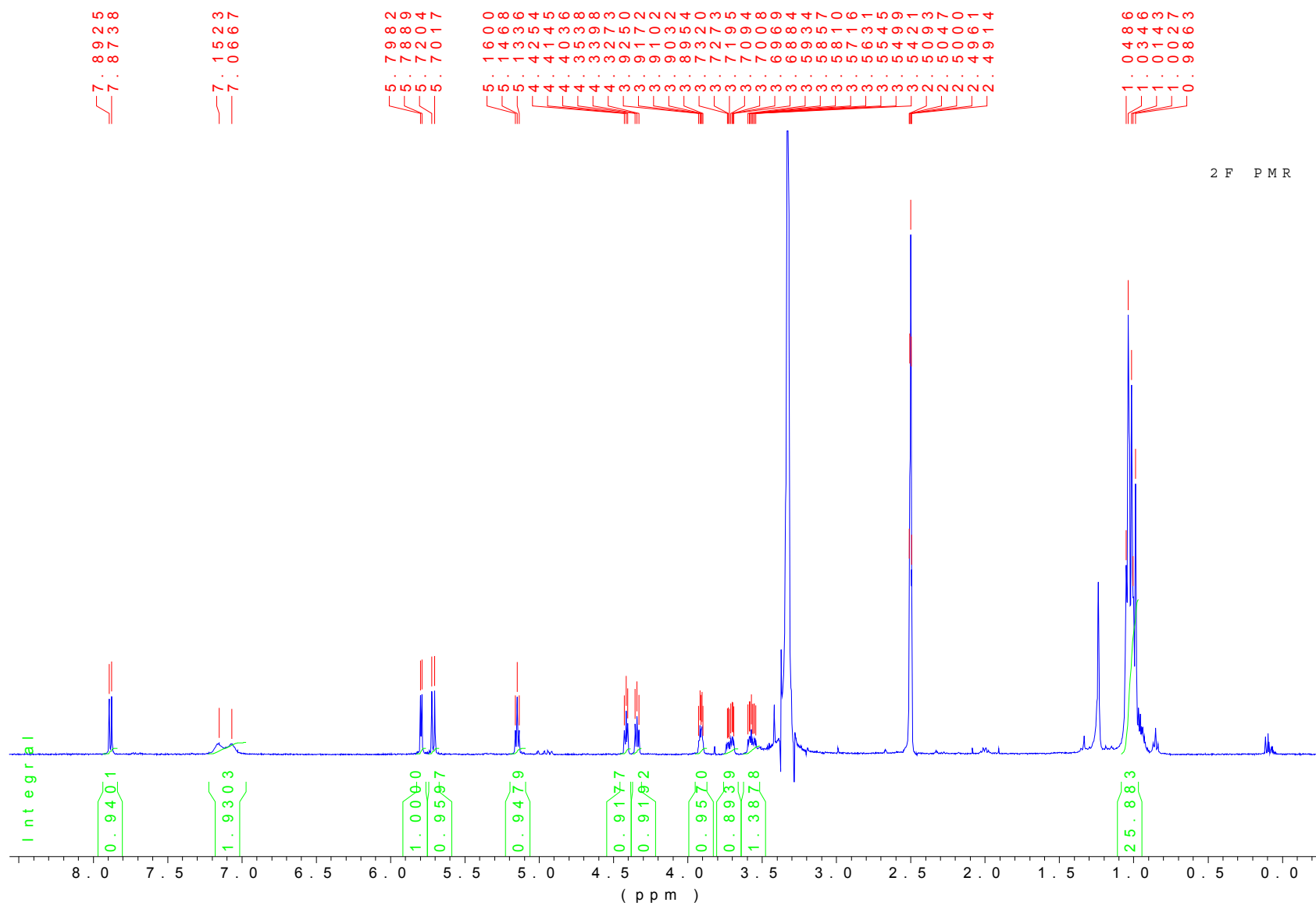


$^1\text{H}$  NMR spectrum (400 MHz) of 3',5'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)cytidine (**1f**) in DMSO- $d_6$  at 300 K.

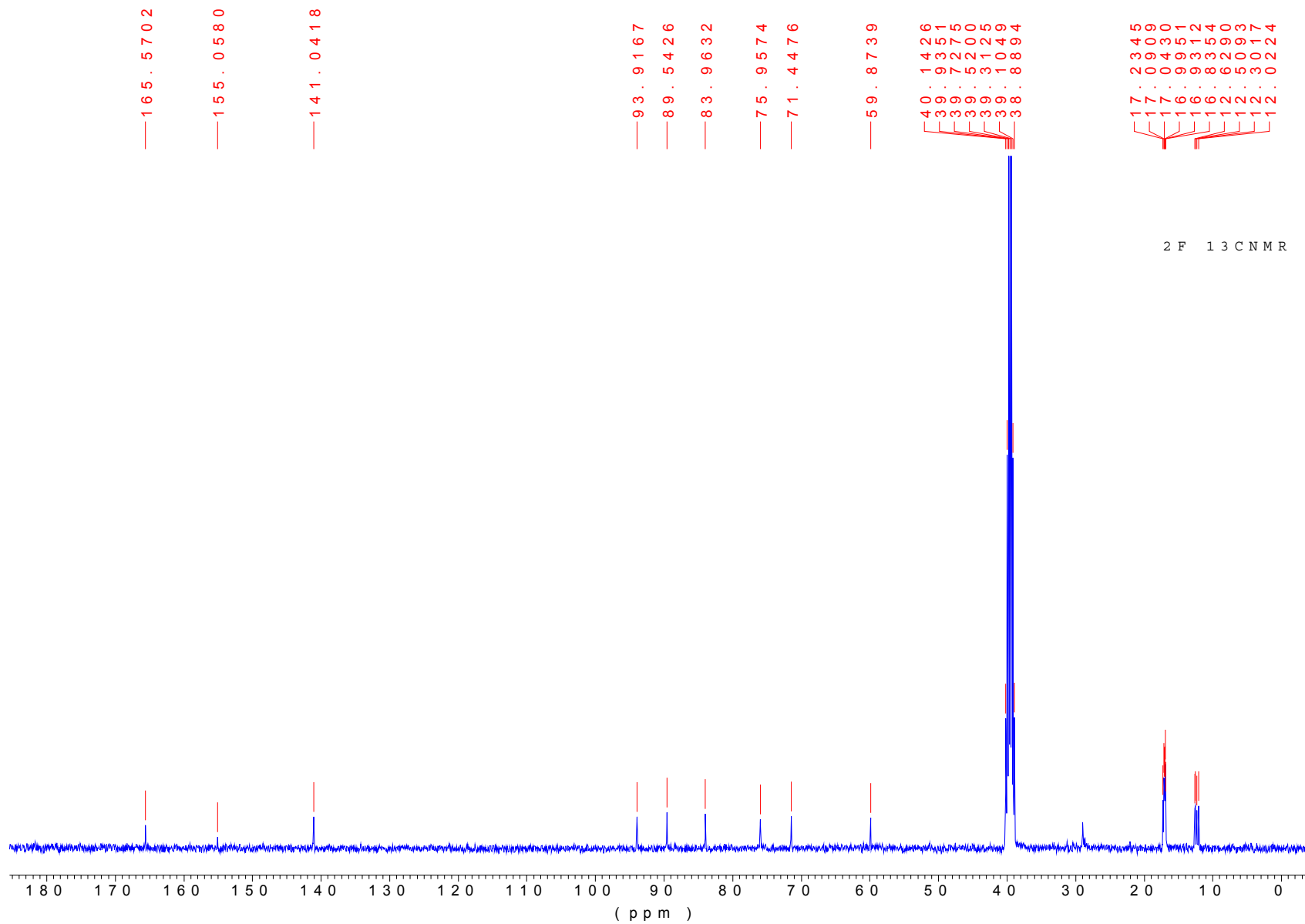




$^{13}\text{C}$  NMR spectrum (100 MHz) of 3',5'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)cytidine (**1f**) in DMSO- $d_6$  at 300 K.



$^1\text{H}$  NMR spectrum (400 MHz) of 2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)cytidine (**2f**) in DMSO- $d_6$  at 300 K.



<sup>13</sup>C NMR spectrum (100 MHz) of 2',3'-O-(1,1,3,3-Tetraisopropylidisiloxane-1,3-diyl)cytidine (**2f**) in DMSO-d<sub>6</sub> at 300 K.