Supporting Information

Salvadenosine, a 5'-Deoxy-5'-methylthio Nucleoside from the Bahamian Tunicate, *Didemnum* sp.

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Page	*Title*	*Content*
S1	Table S1	^{1}H and ^{13}C NMR data for salvadenosine formate salt (DMSO-d_6)
S2	Table S2	^{1}H and ^{13}C NMR data for **5** and **2** (DMSO-d_6)
S3	Table S3	^{1}H and ^{13}C NMR Data (CD_3OD) of Natural and Synthetic **1** (formate salts)
S4	Figure S1	HPLC co-injection experiment (UV-vis)
S5	Figure S2	^{1}H NMR spectrum of **1**• HCO_2H (600 MHz, CD_3OD)
S6	Figure S3	^{1}H NMR spectrum of **1**• HCO_2H (500 MHz, DMSO-d_6)
S7	Figure S4	^{13}C NMR spectrum of **1**• HCO_2H (125 MHz, CD_3OD)
S8	Figure S5	^{13}C NMR spectrum of **1**• HCO_2H (125 MHz, DMSO-d_6)
S9	Figure S6	COSY spectrum of **1**• HCO_2H (600 MHz, CD_3OD)
S10	Figure S7	gHSQC spectrum of **1**• HCO_2H (600 MHz, CD_3OD)
S11	Figure S8	gHMBC (J_{CH} = 8 Hz) spectrum **1**• HCO_2H (600 MHz, CD_3OD)
S12	Figure S9	^{1}H NMR spectrum of **5**, free base (500 MHz, DMSO-d_6)
S13	Figure S10	^{13}C NMR spectrum of **5**, free base (125 MHz, DMSO-d_6)
S14	Figure S11	^{1}H NMR of synthetic salvadenosine **1**• HCO_2H (500 MHz, CD_3OD)
S15	Figure S12	^{13}C NMR of synthetic salvadenosine **1**• HCO_2H (125 MHz, CD_3OD)
S16	Figure S13	COSY spectrum of synthetic salvadenosine **1**• HCO_2H (500 MHz, CD_3OD)
S17	Figure S14	gHSQC spectrum of synthetic salvadenosine **1**• HCO_2H (500 MHz, CD_3OD)
S18	Figure S15	gHMBC spectrum of synthetic salvadenosine **1**• HCO_2H (500 MHz, CD_3OD)
S19	Figure S16	^{1}H NMR of synthetic salvadenosine, free base (**1**) (500 MHz, CD_3OD)
S20	Figure S17	^{13}C NMR of synthetic salvadenosine, free base (**1**) (500 MHz, CD_3OD)
S21	Figure S18	COSY spectrum of synthetic salvadenosine, free base (**1**) (500 MHz, CD_3OD)
S22	Figure S19	Multiplicity edited gHSQC spectrum of synthetic salvadenosine, free base (**1**) (500 MHz, CD_3OD)
S23	Figure S20	gHMBC spectrum of synthetic salvadenosine, free base (**1**) (500 MHz, CD_3OD)
S24	Figure S21	^{1}H NMR spectrum of **7** (500 MHz, CD_3OD)
S25	Figure S22	^{13}C NMR spectrum of **7** (125 MHz, CD_3OD)
S26	Figure S23	COSY spectrum of **7** (500 MHz, CD_3OD)
S27	Figure S24	gHSQC spectrum of **7** (500 MHz, CD_3OD)
S28	Figure S25	gHMBC spectrum of **7** (500 MHz, CD_3OD, $^{n}J_{CH}$ = 8 Hz)
S29	Figure S26	^{1}H NMR spectrum of **6** (500 MHz, DMSO-d_6)
S30	Figure S27	^{1}H NMR spectrum of **11** (500 MHz, CD_3OD)

Table S1. ^{1}H and ^{13}C NMR data for **1**[a] (DMSO-d_6)

Atom	**1** δ ^{13}C[a]	**1** δ ^{1}H (mult, *J*, integ.)[b]
1		
2	150.8	8.00 (s, 1H)
3		
4	146.7	
5	103.6	
6	147.2	
7		
8	151.7	
1'	85.8	5.65 (d, *J* = 5.3 Hz, 1H)
2'	69.9	4.96 (ddd, *J* = 5.4, 5.4, 5.4 Hz, 1H)
2'-OH		5.35 (d, *J* = 4.7 Hz)
3'	72.9	4.19 (ddd, *J* = 4.9, 4.9, 4.9 Hz, 1H)
3'-OH		5.22 (d, *J* = 3.9 Hz)
4'	83.0	3.88 (ddd, 4.9, 5.3, 7.6, 1H)
5'a	36.1	2.80 (dd, *J* = 5.3, –13.5 Hz, 1H)
5'b		2.69 (dd, *J* = 7.6, –13.5 Hz, 1H)
6'	15.5	2.03 (s, 3H)
NH		6.80 (s)
NH_2		10.90 (bs)

a Formate salt. 125 MHz. *b* 600 MHz.

Table S2. ^{13}C NMR data for **5** and **2** (DMSO-d_6)

Atom	5 δ ^{1}H[a]	5 δ ^{13}C[b]	**2** δ ^{1}H[c]	**2** δ ^{13}C[c]	Δδ ^{1}H (**5** – **2**)[d]	Δδ ^{13}C (**5** – **2**)[e]
1						
2		153.7		153.5		0.2
3						
4		151.4		153.0		– 1.6
5		116.7		118.0		– 1.3
6		156.7		157.2		– 0.5
7						
8	7.92	135.7	7.90	135.0	0.02	0.7
1'	5.68	86.4	5.60	87.0	0.08	– 0.6
2'	4.56	72.5	4.50	74.0	0.06	– 1.5
3'	3.96	72.6	3.95	71.5	0.01	1.1
4'	4.03	83.6	4.05	84.0	– 0.02	– 0.4
5'a	2.82	36.1	2.80	35.0	0.02	1.1
5'b	2.74		2.70		0.04	
6'	2.06	15.6	2.05	16.0	0.01	– 0.4

a 600MHz *b* 125 MHz *c* Ref.[7] *d* RMS Δ = 0.04 *e* RMS Δ = 0.97

Table S3. Comparison ^{1}H and ^{13}C NMR Data (CD_3OD) of Natural and Synthetic **1** (formate salts)

Atom	*nat*-**1** δ ^{13}C[a]	*syn*-**1** δ ^{13}C[a]	*nat*-**1** δ ^{1}H[b]	*syn*-**1** δ ^{1}H[c]	Δδ ^{13}H (*nat*-**1** – *syn*-**1**)[d]	Δδ ^{13}C (*nat*-**1** – *syn*-**1**)[e]
1						
2	152.3	152.3	8.08	8.08	0.00	0.0
3						
4	148.7	148.8				– 0.1
5	105.2	105.2				0.0
6	148.7	148.7				0.0
7						
8	154.0	154.0				0.0
1'	87.9	87.9	5.87	5.89	– 0.02	0.0
2'	72.0	72.0	5.12	5.13	– 0.01	0.0
3'	74.5	74.5	4.42	4.42	0.00	0.0
4'	85.1	85.1	4.07	4.07	0.00	0.0
5'a	37.4	37.5	2.88	2.89	– 0.01	– 0.1
5'b			2.81	2.81	0.00	
6'	16.1	16.2	2.10	2.10	0.00	– 0.1

a 125 MHz *b* 600 MHz *c* 500 MHz *d* RMS Δ = 0.009 *e* RMS Δ = 0.05

Figure S1. Co-injection of **1**, synthetic **1**, and combined. UV 270 nm absorbance, 0-18min

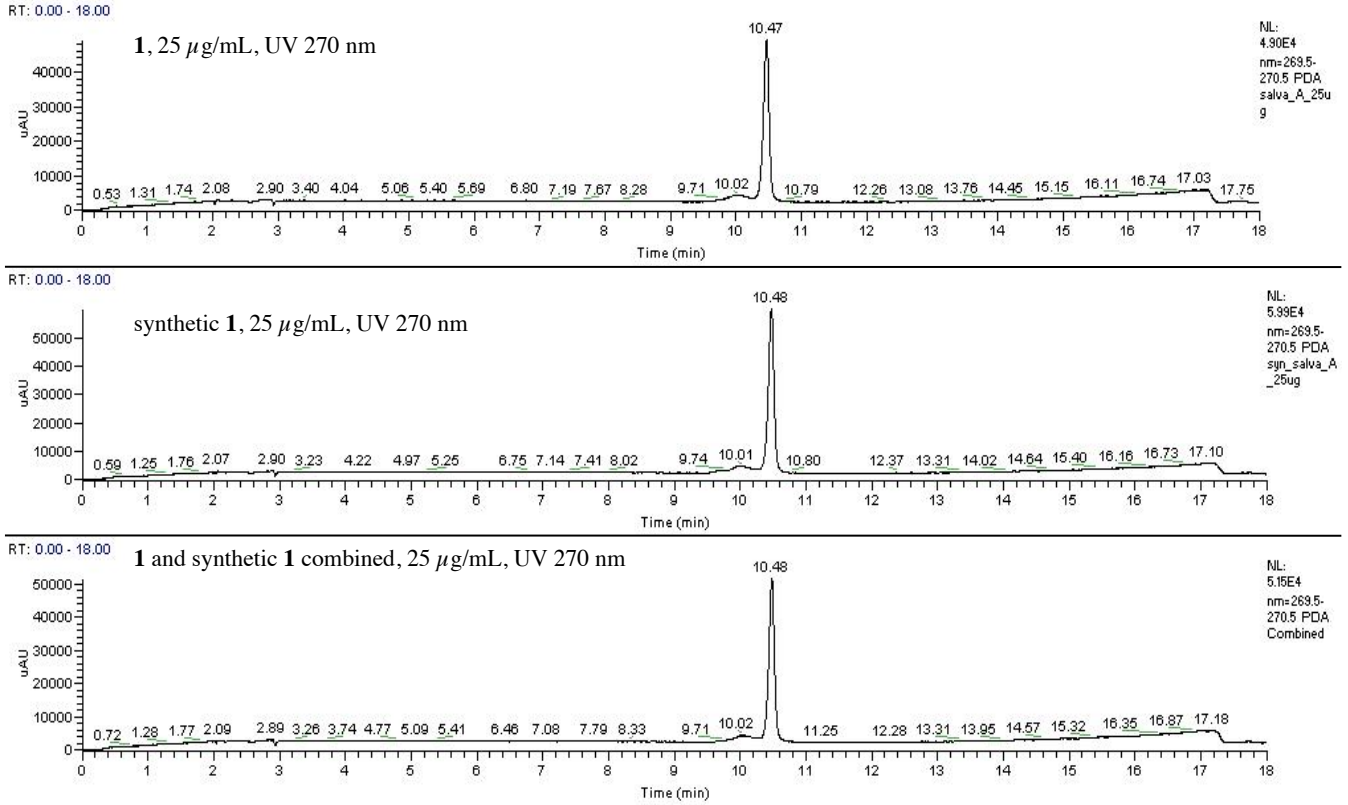

Figure S2. ^{1}H NMR of salvadenosine, formate salt (**1**) in CD_3OD at 600 MHz

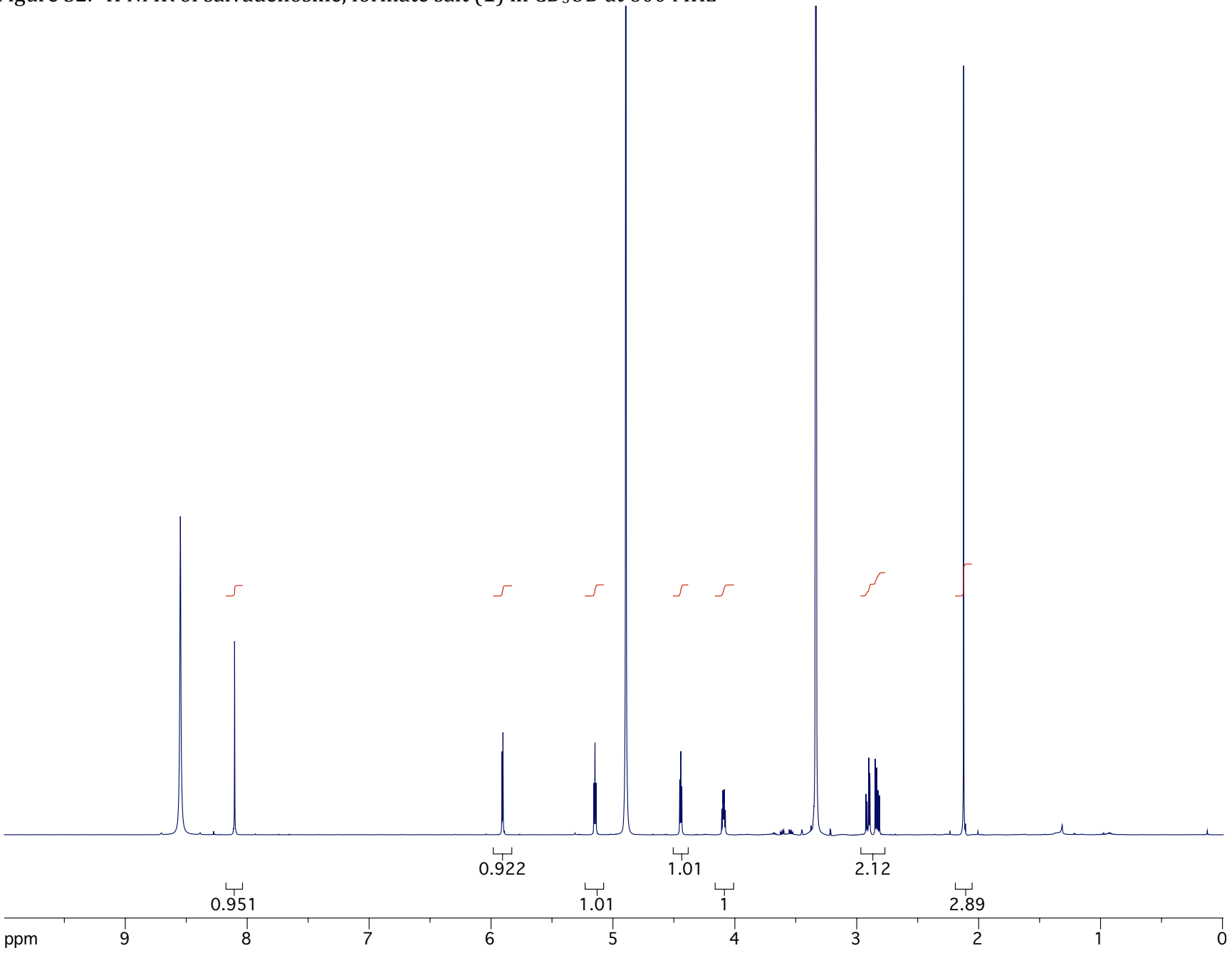

Figure S3. ^{1}H NMR spectrum of salvadenosine, formate salt (**1**) (500 MHz, DMSO-d_6).

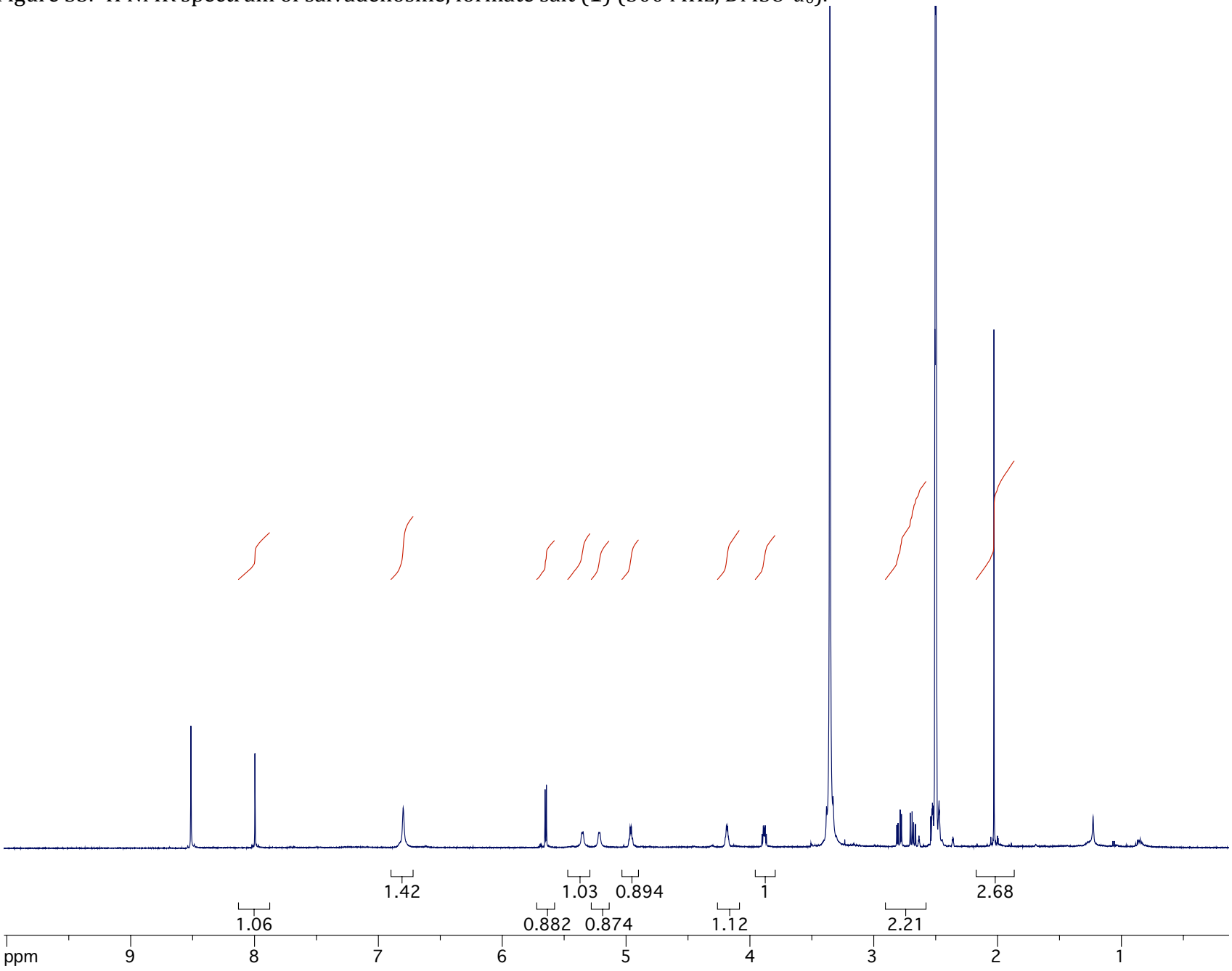

Figure S4. ^{13}C NMR of salvadenosine, formate salt (**1**) in CD_3OD at 125 MHz

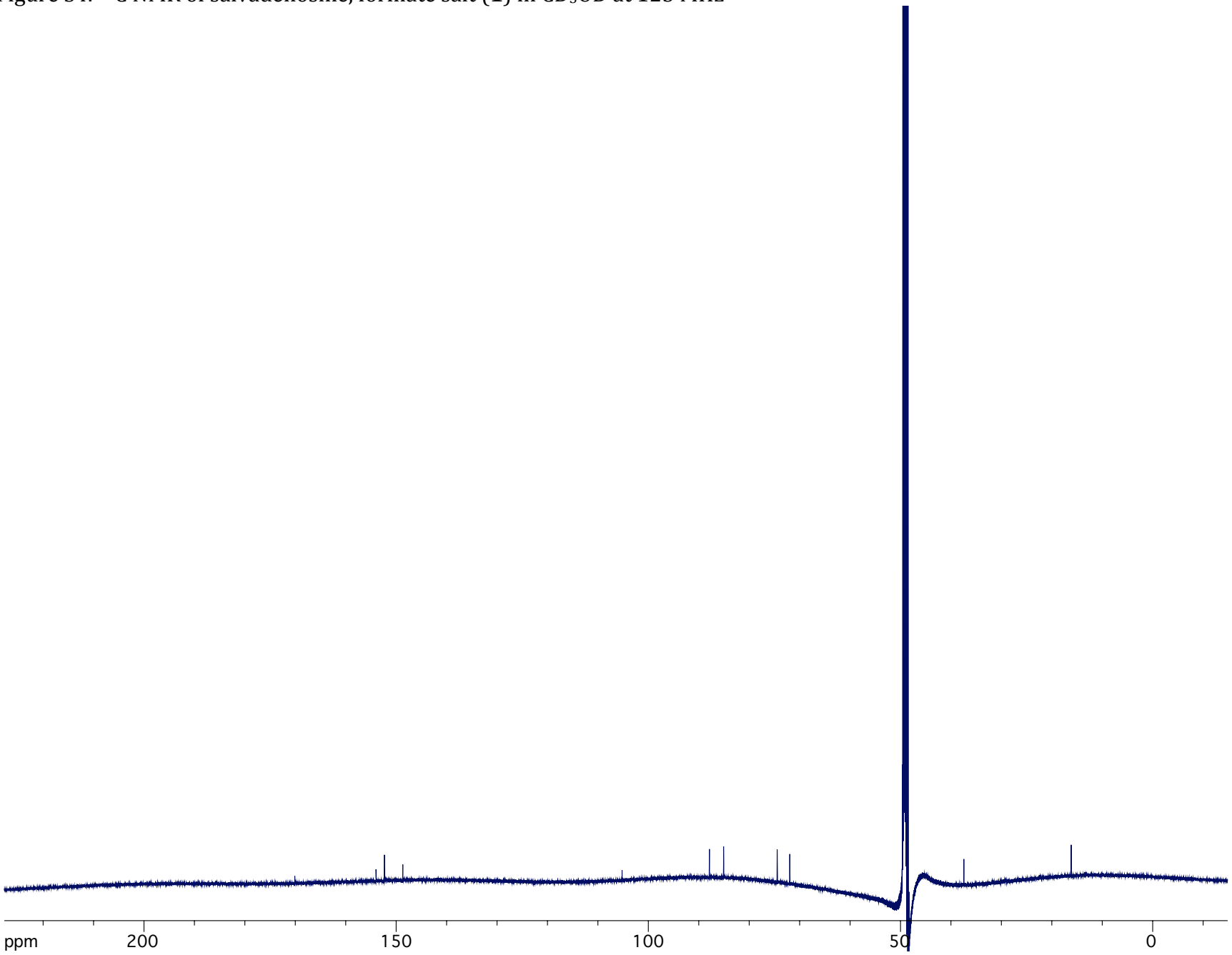

Figure S5. ^{13}C NMR spectrum of salvadenosine, formate salt (**1**) in DMSO-d_6 at 125 MHz

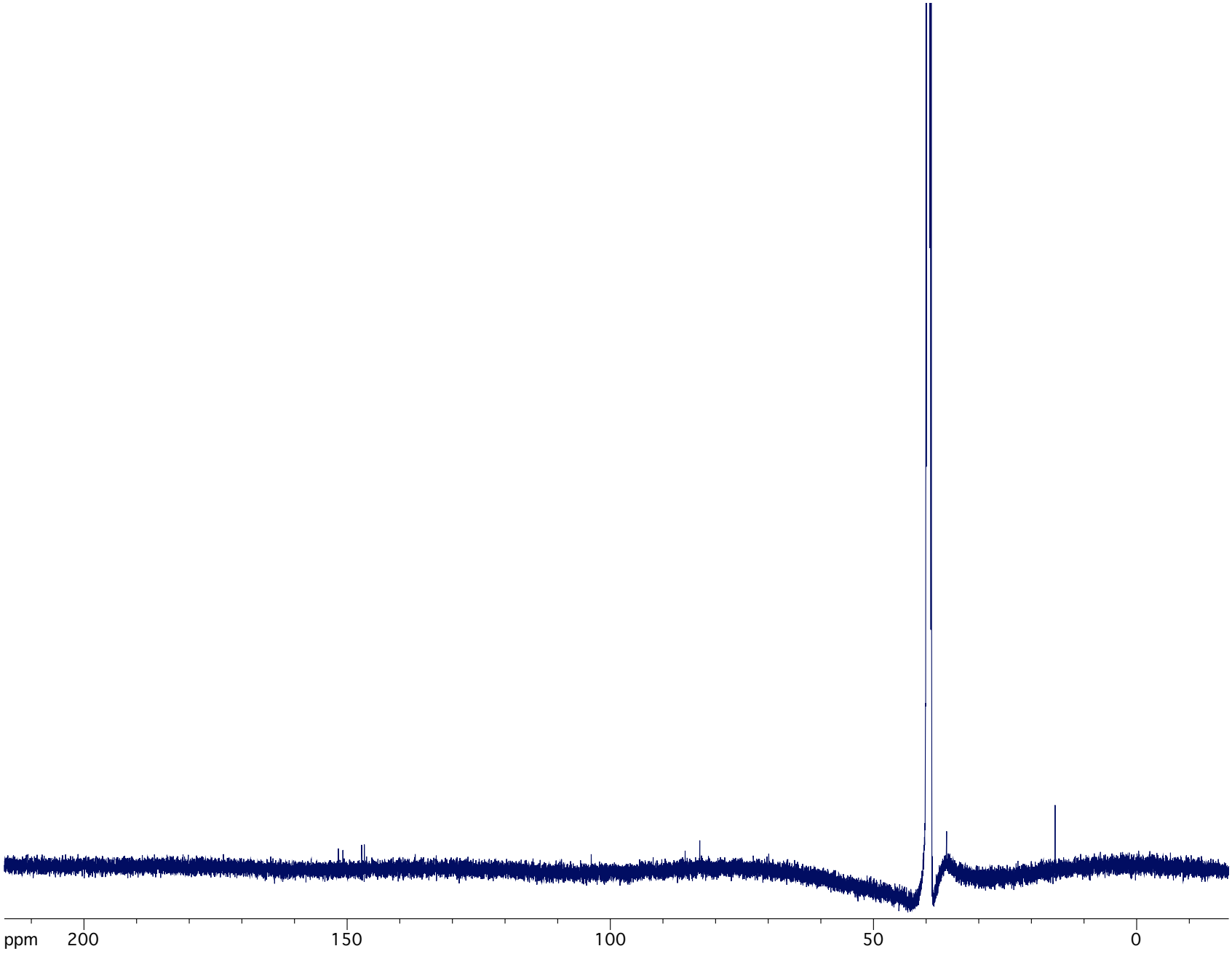

Figure S6. COSY spectrum of salvadenosine, formate salt (**1**) in CD_3OD at 600 MHz

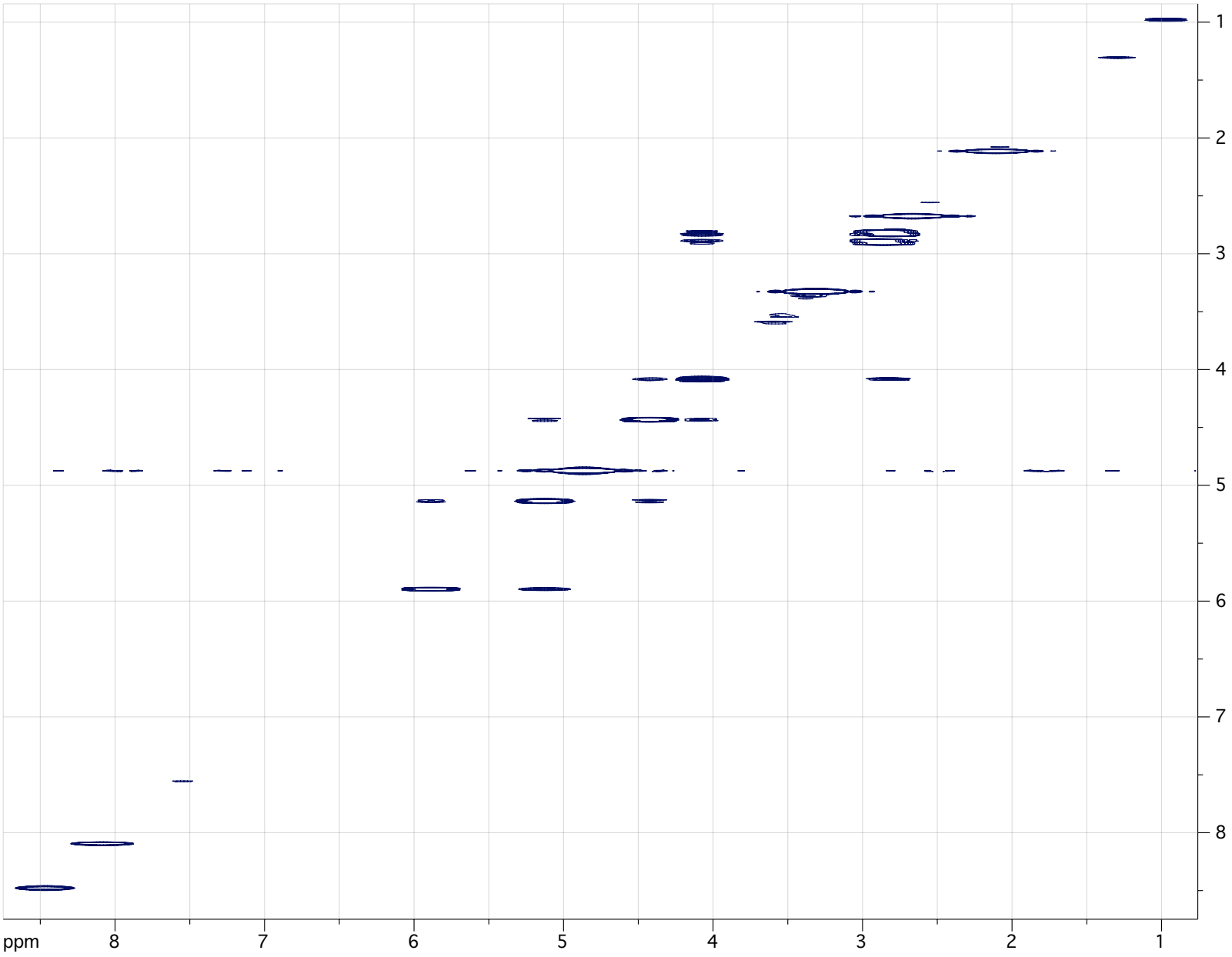

Figure S7. Multiplicity edited gHSQC spectrum of salvadenosine (**1**), formate salt in CD_3OD at 600 MHz

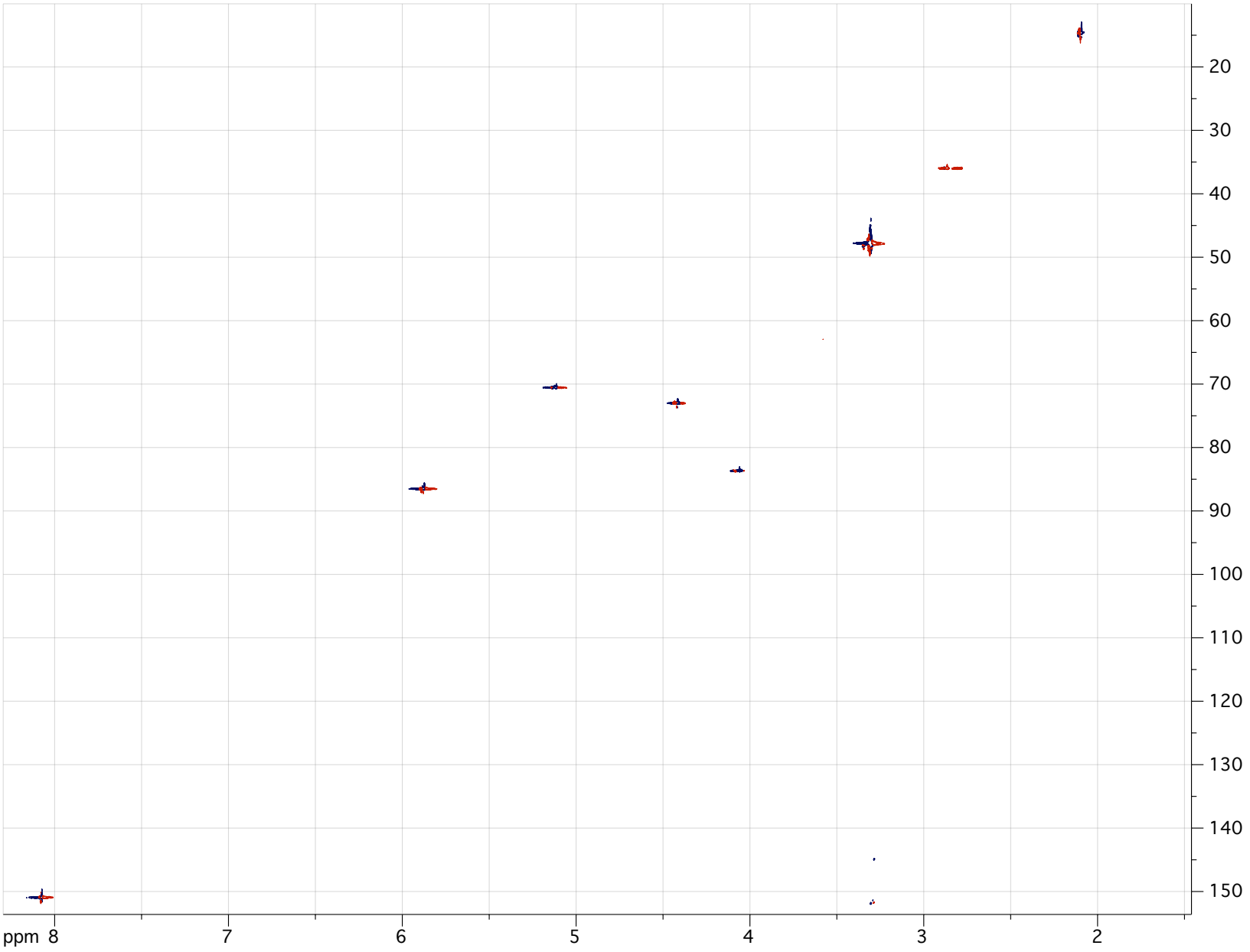

Figure S8. gHMBC ($^{n}J_{CH}$ = 8 Hz) spectrum of salvadenosine, formate salt (**1**) in CD_3OD at 600 MHz

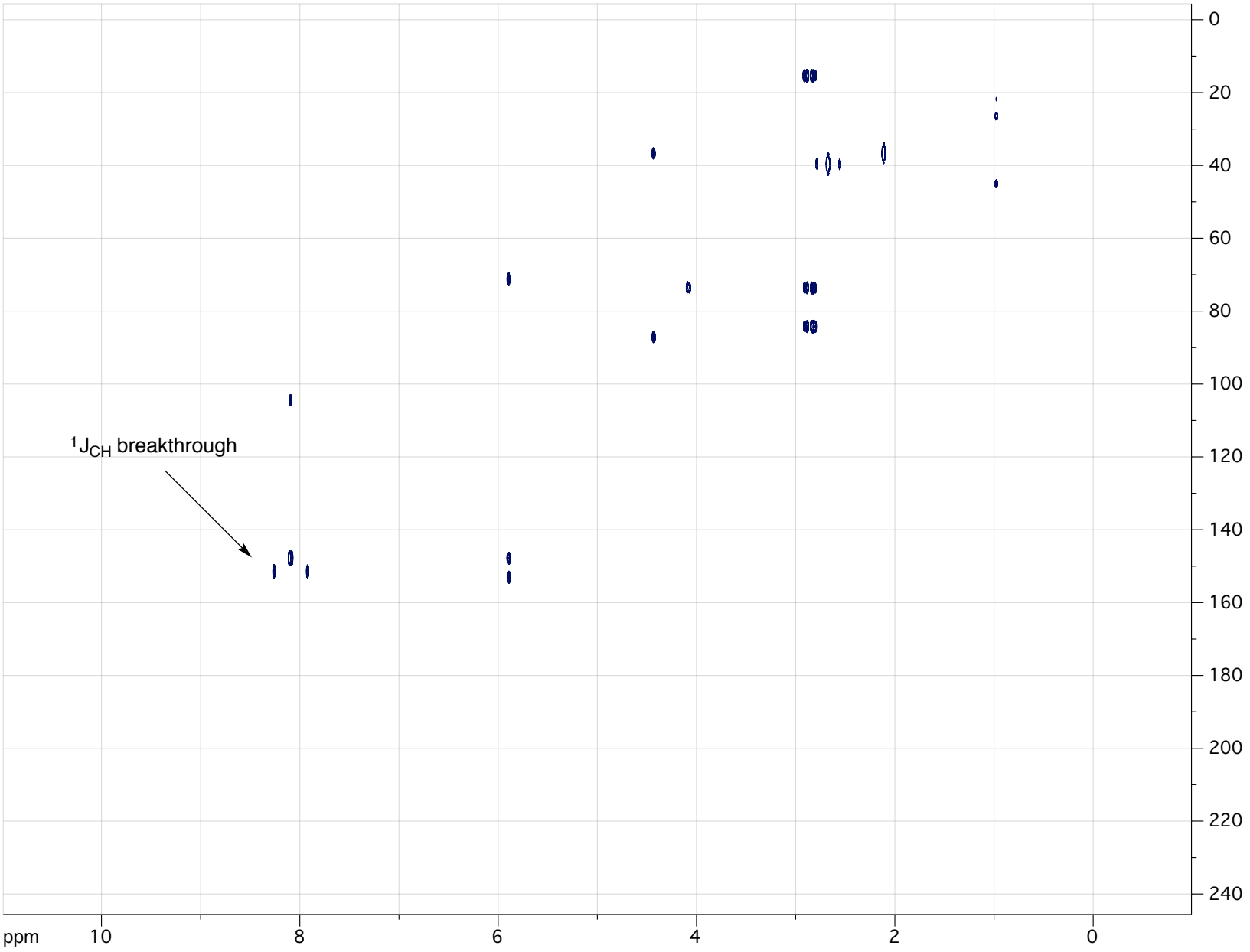

Figure S9. ^{1}H NMR spectrum of 5'-deoxy-5'-methylthioguanosine (**5**), free base in DMSO-d_6 at 500 MHz

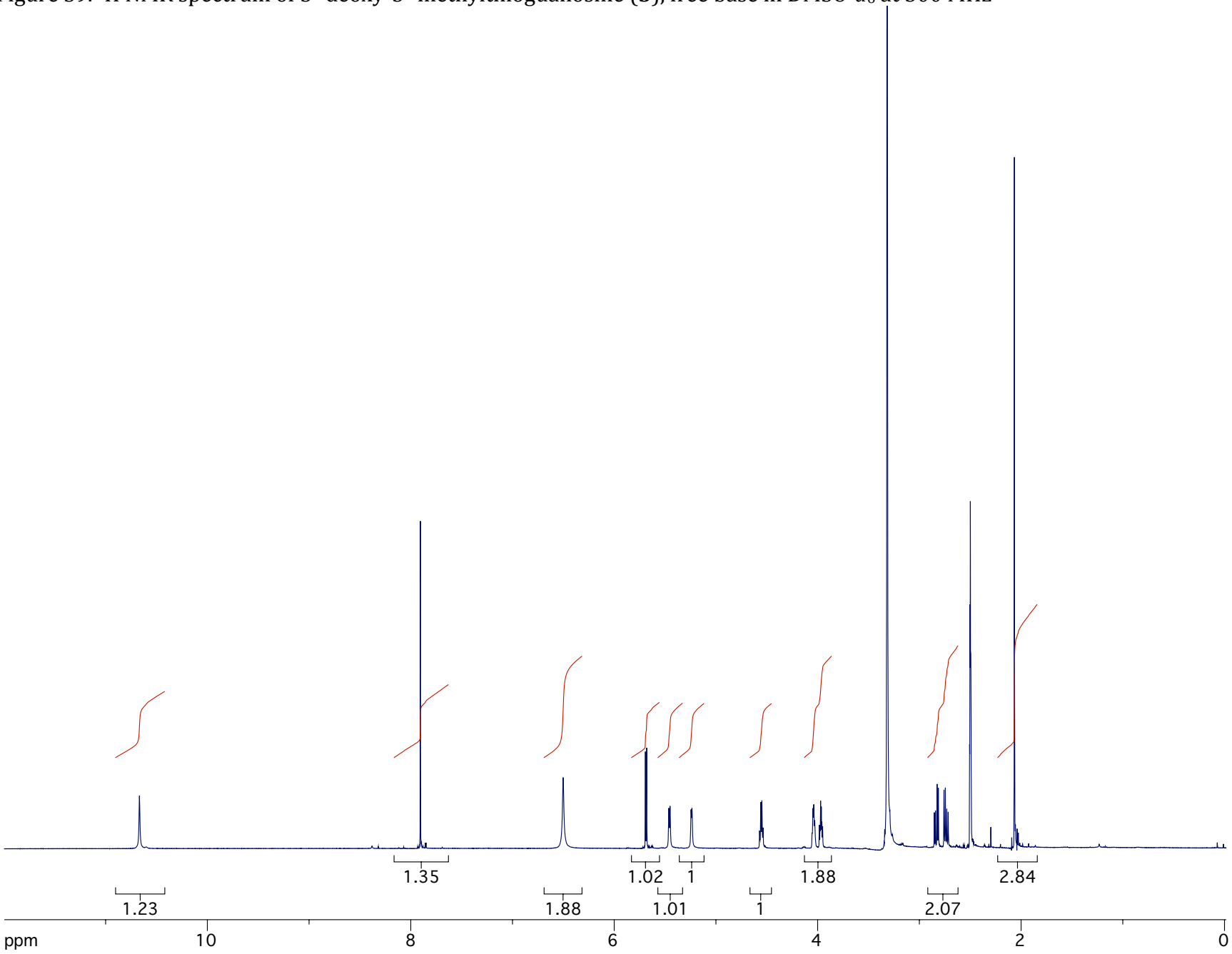

Figure S10. ^{13}C NMR spectrum of 5'-deoxy-5'-methylthioguanosine (**5**), free base in DMSO-d_6 at 125 MHz

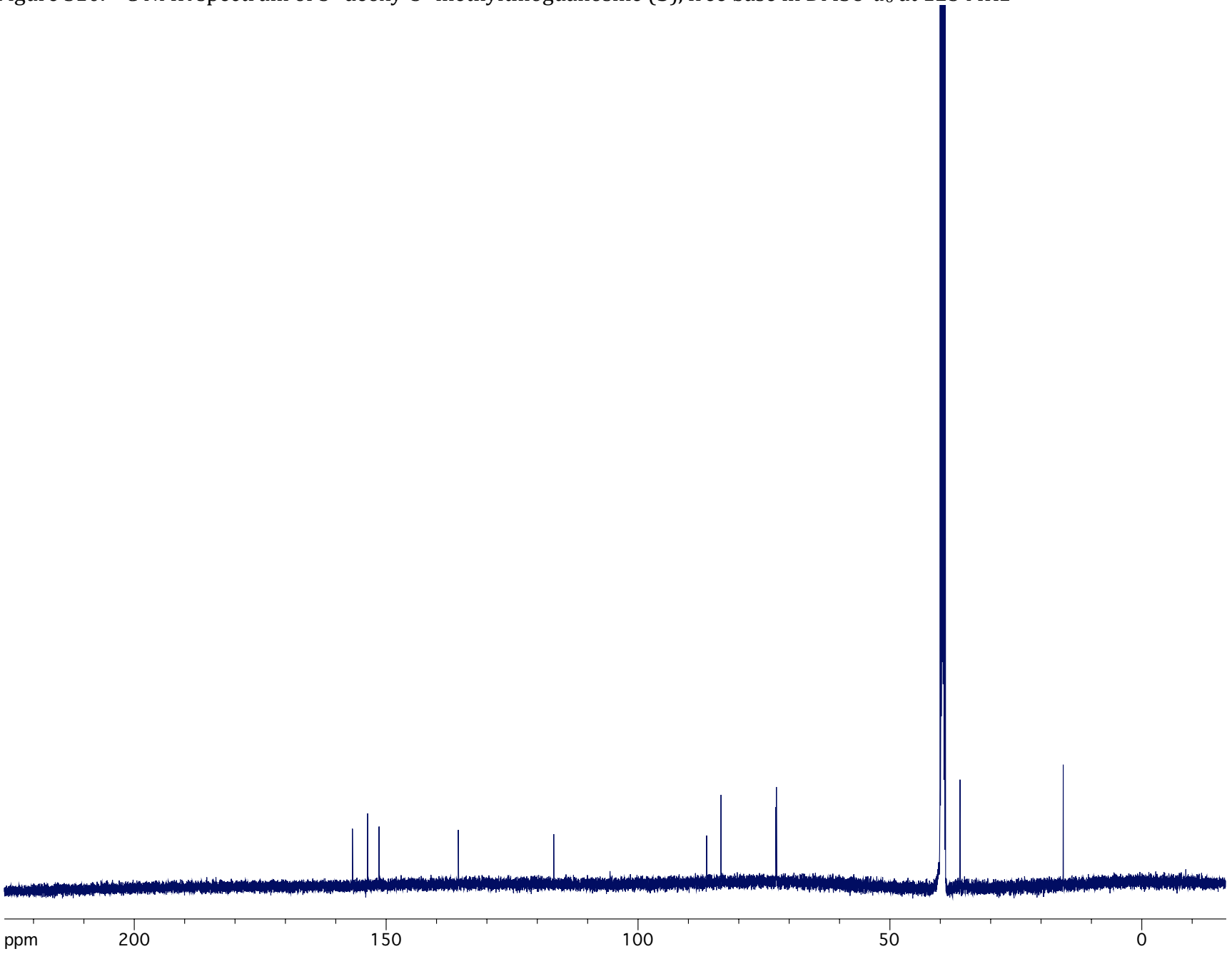

Figure S11. ^{1}H NMR of synthetic salvadenosine (**1**), formate salt in CD_3OD at 500 MHz

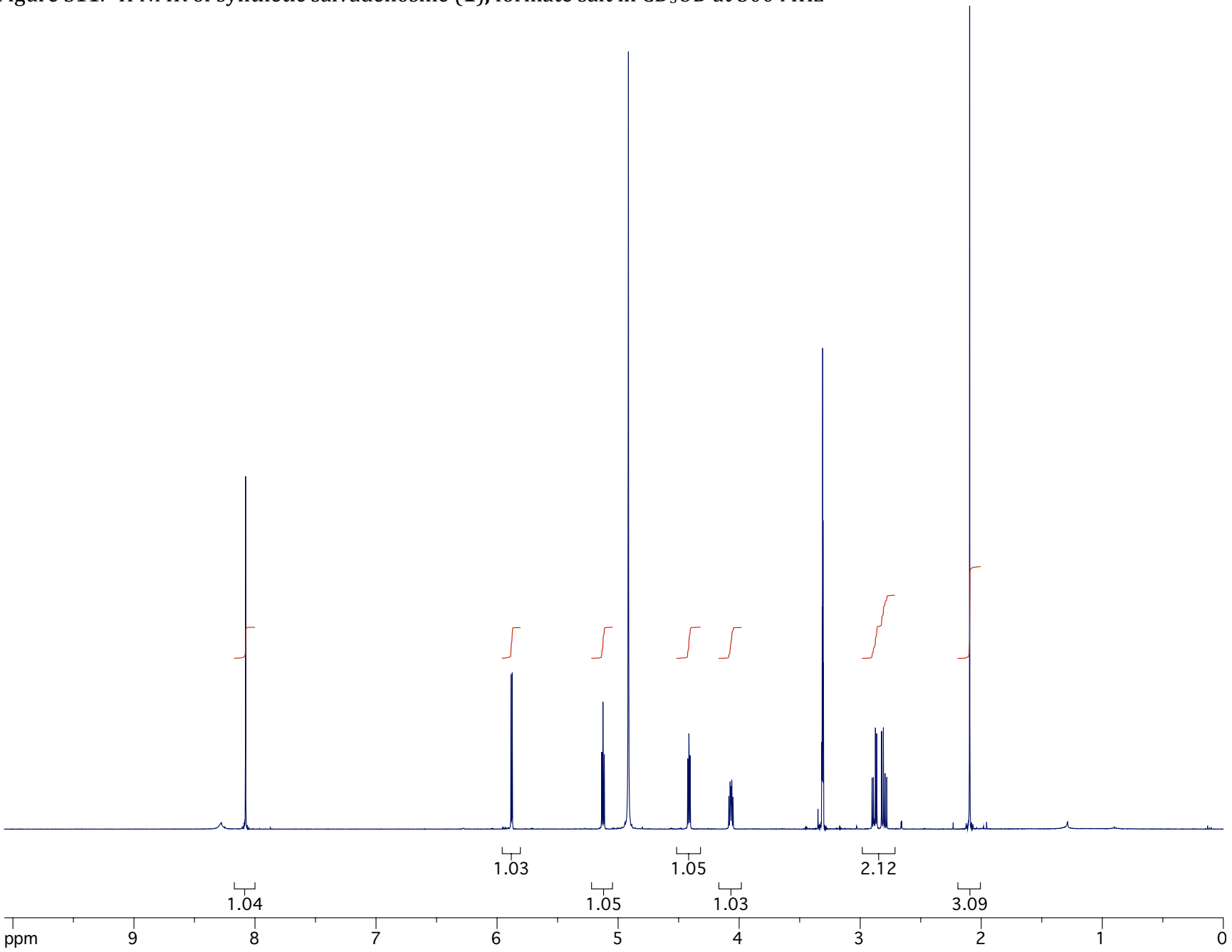

Figure S12. ^{13}C NMR of synthetic salvadenosine (**1**), formate salt in CD_3OD at 125 MHz

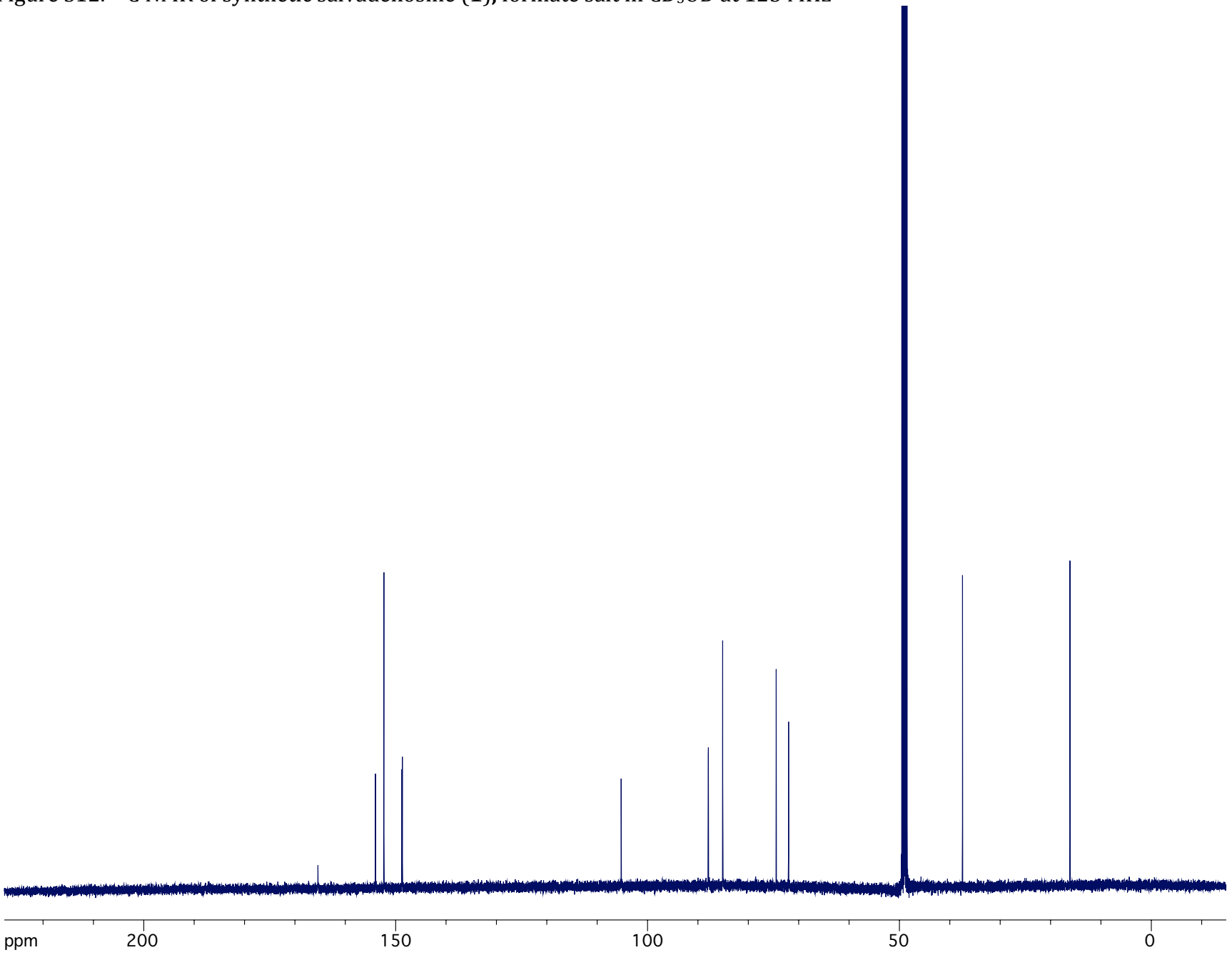

Figure S13. COSY spectrum of synthetic salvadenosine (**1**), formate salt in CD_3OD at 500 MHz

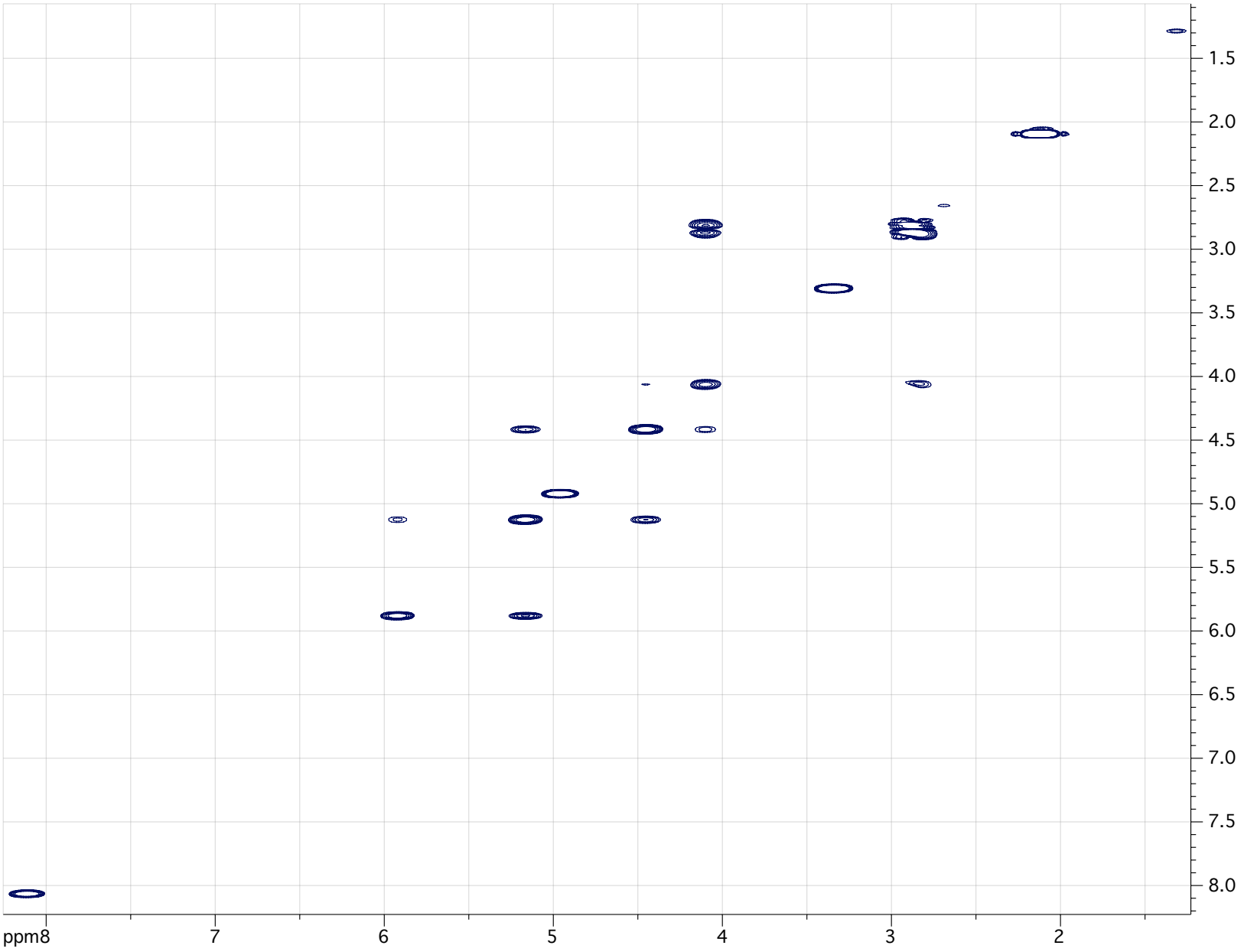

Figure S14. gHSQC spectrum of synthetic salvadenosine (**1**), formate salt in CD_3OD at 500 MHz

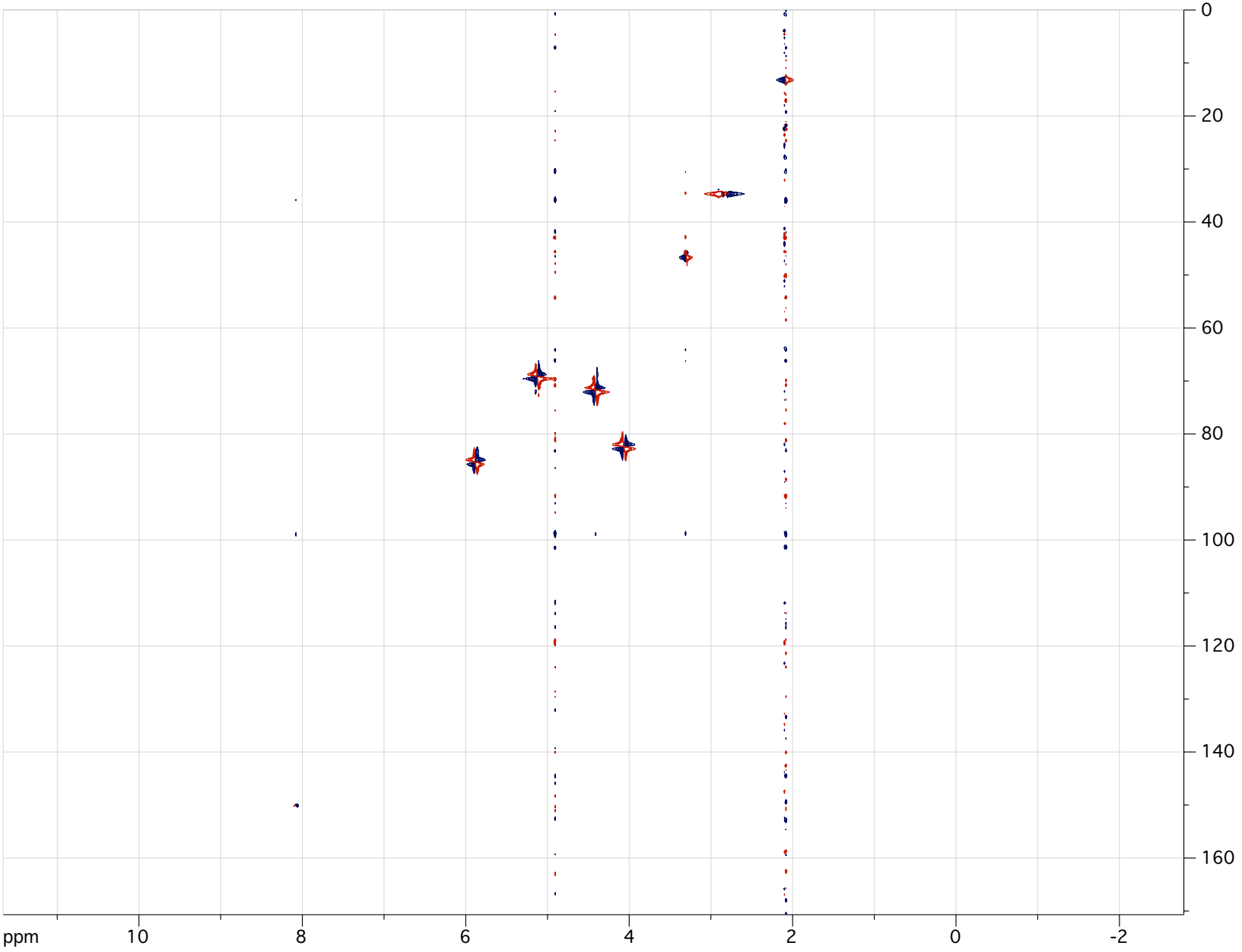

Figure S15. gHMBC spectrum of synthetic salvadenosine (**1**), formate salt in CD_3OD at 500 MHz

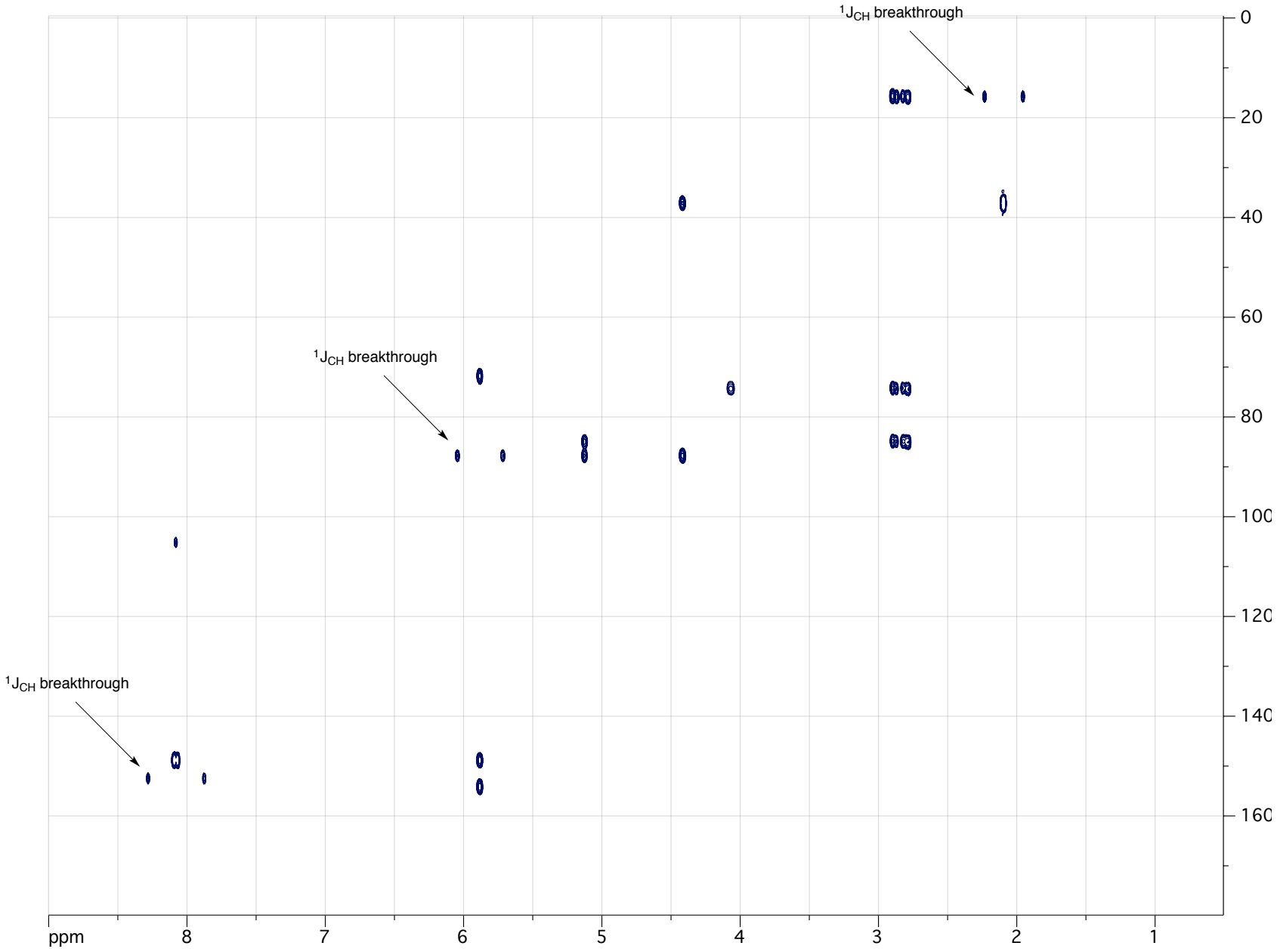

Figure S16. ^{1}H NMR of synthetic salvadenosine, free base (**1**) in CD_3OD at 500 MHz

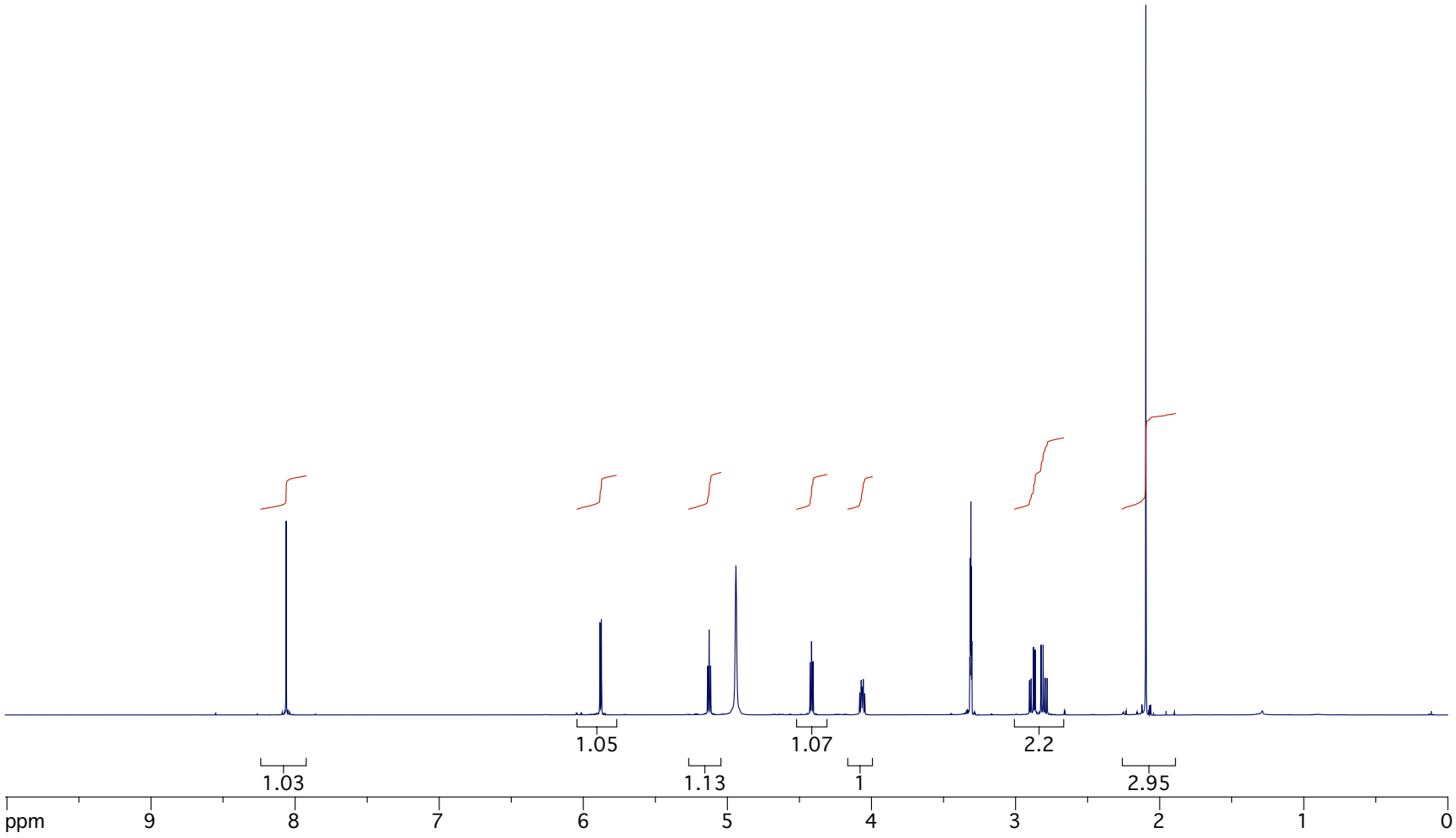

Figure S17. ^{13}C NMR of synthetic salvadenosine, free base (**1**) in CD_3OD at 125 MHz

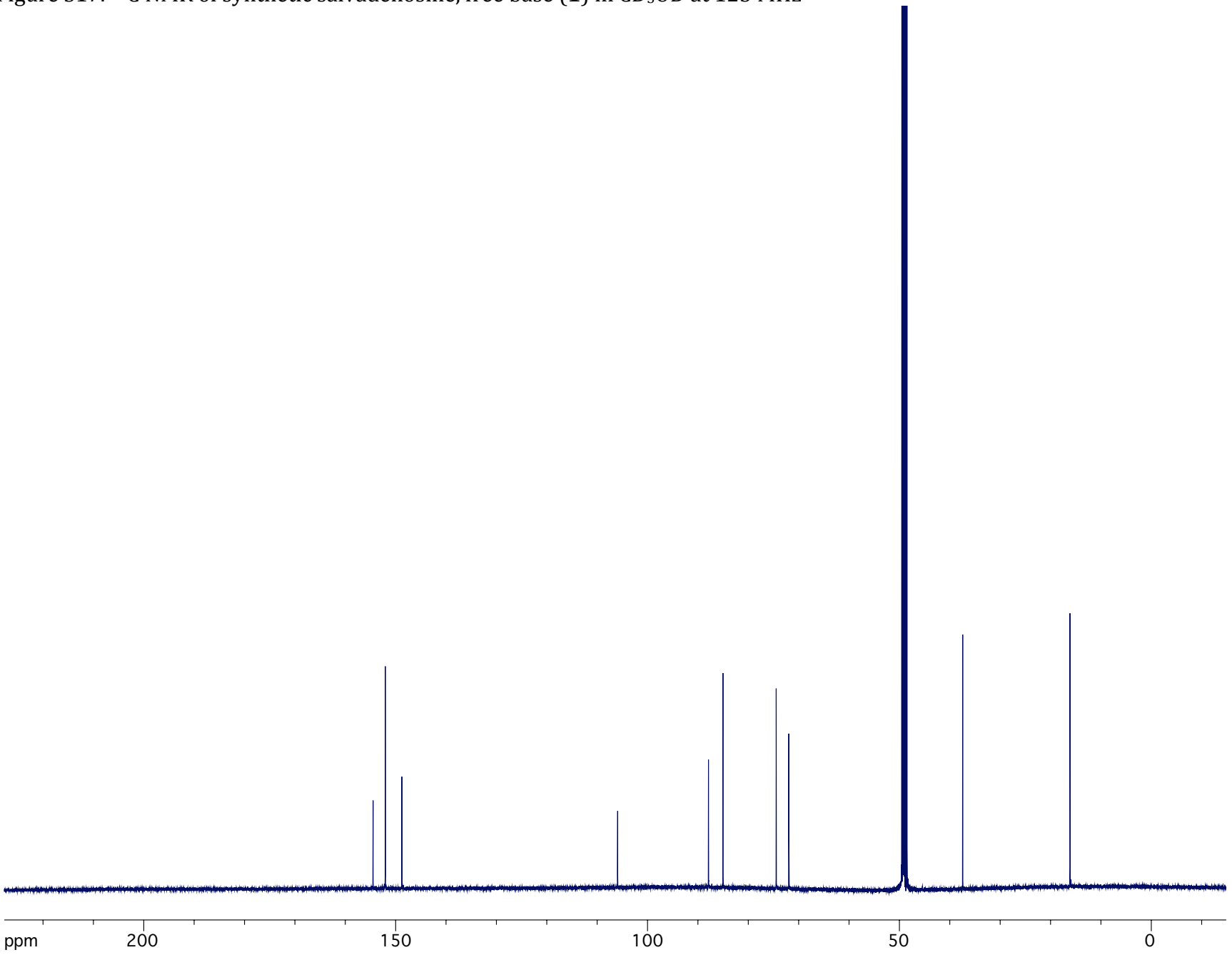

Figure S18. COSY spectrum of synthetic salvadenosine, free base (**1**) in CD_3OD at 500 MHz

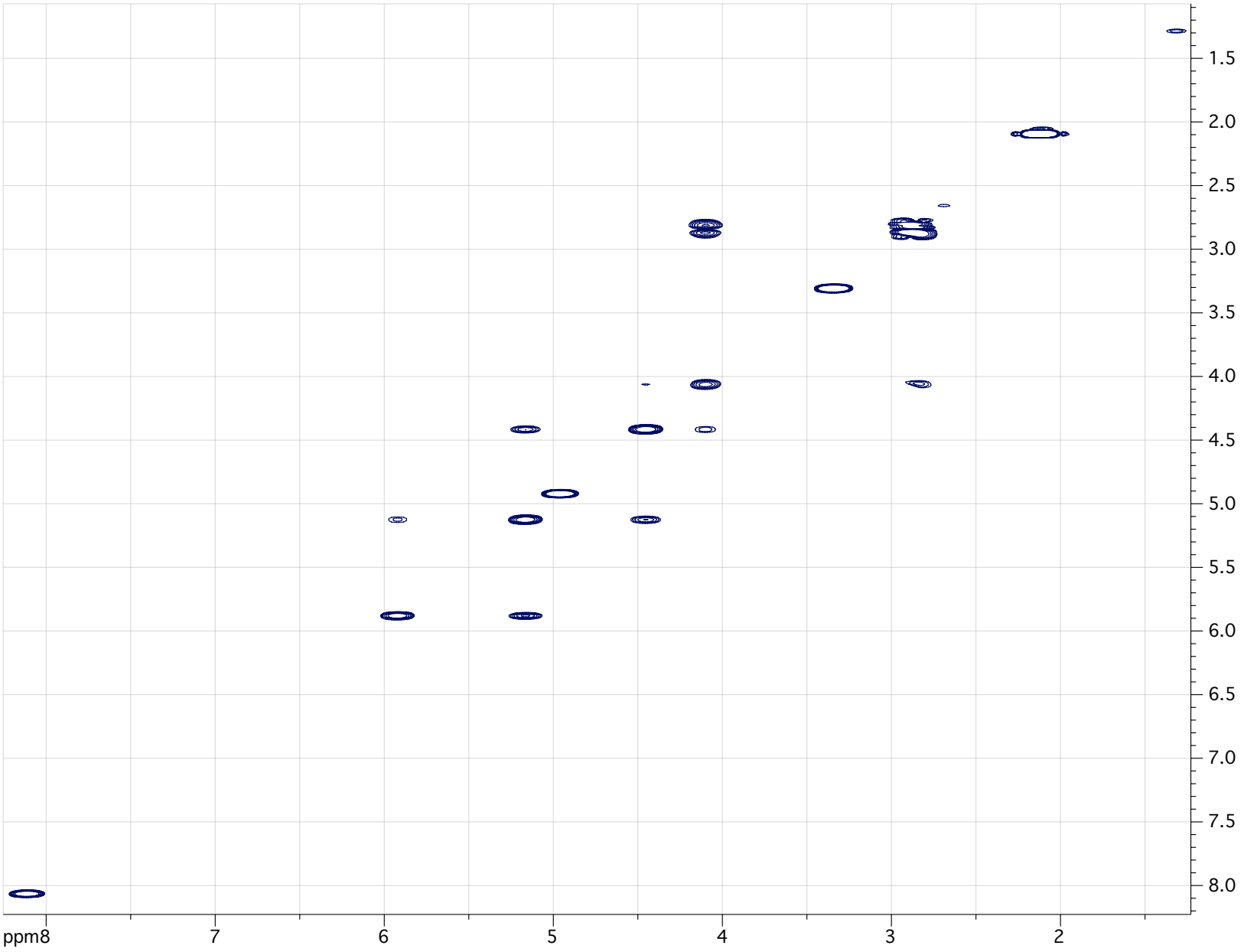

Figure S19. Multiplicity edited gHSQC spectrum of synthetic salvadenosine, free base (**1**) in CD_3OD at 500 MHz

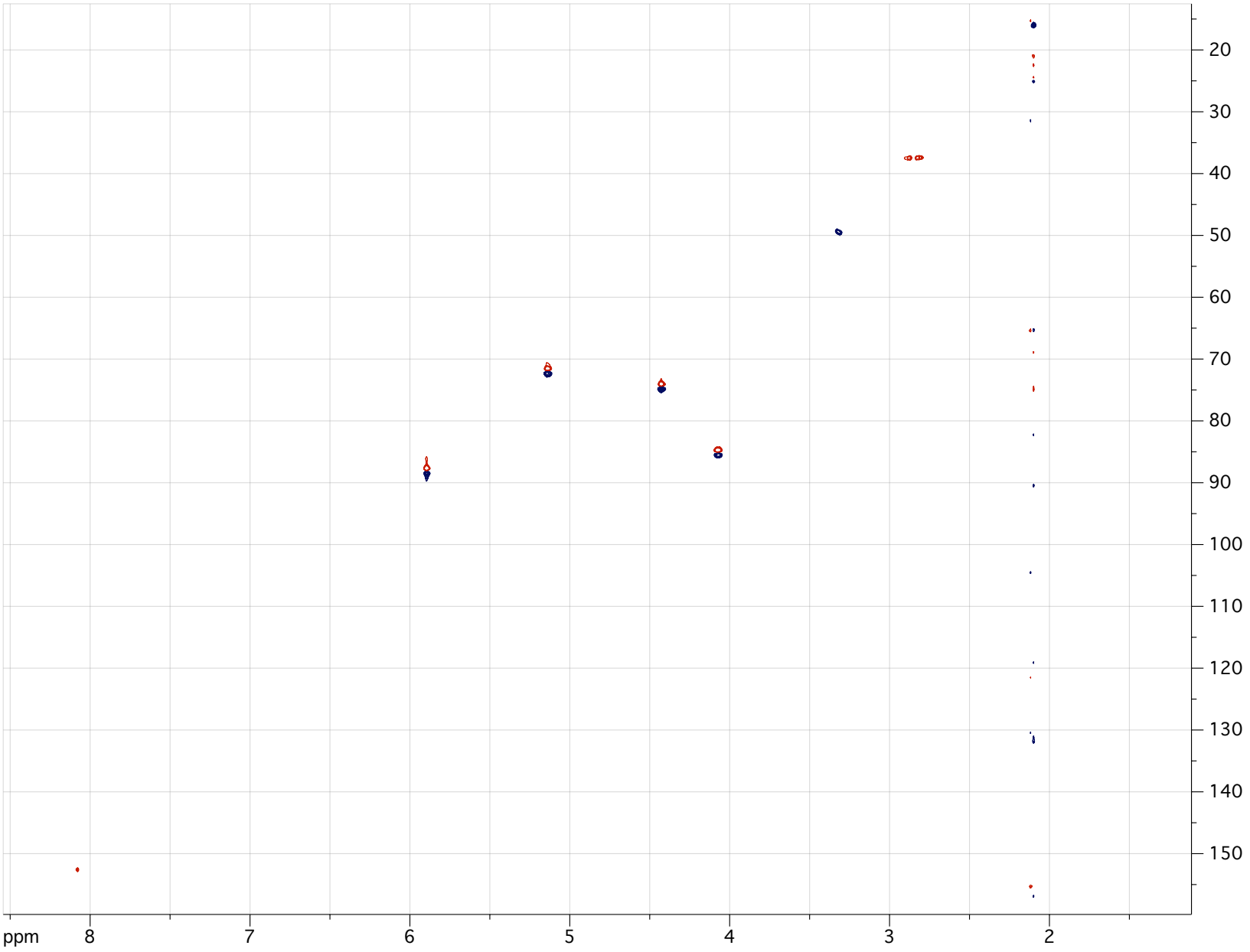

Figure S20. gHMBC spectrum of synthetic salvadenosine, free base (**1**) in CD_3OD at 500 MHz

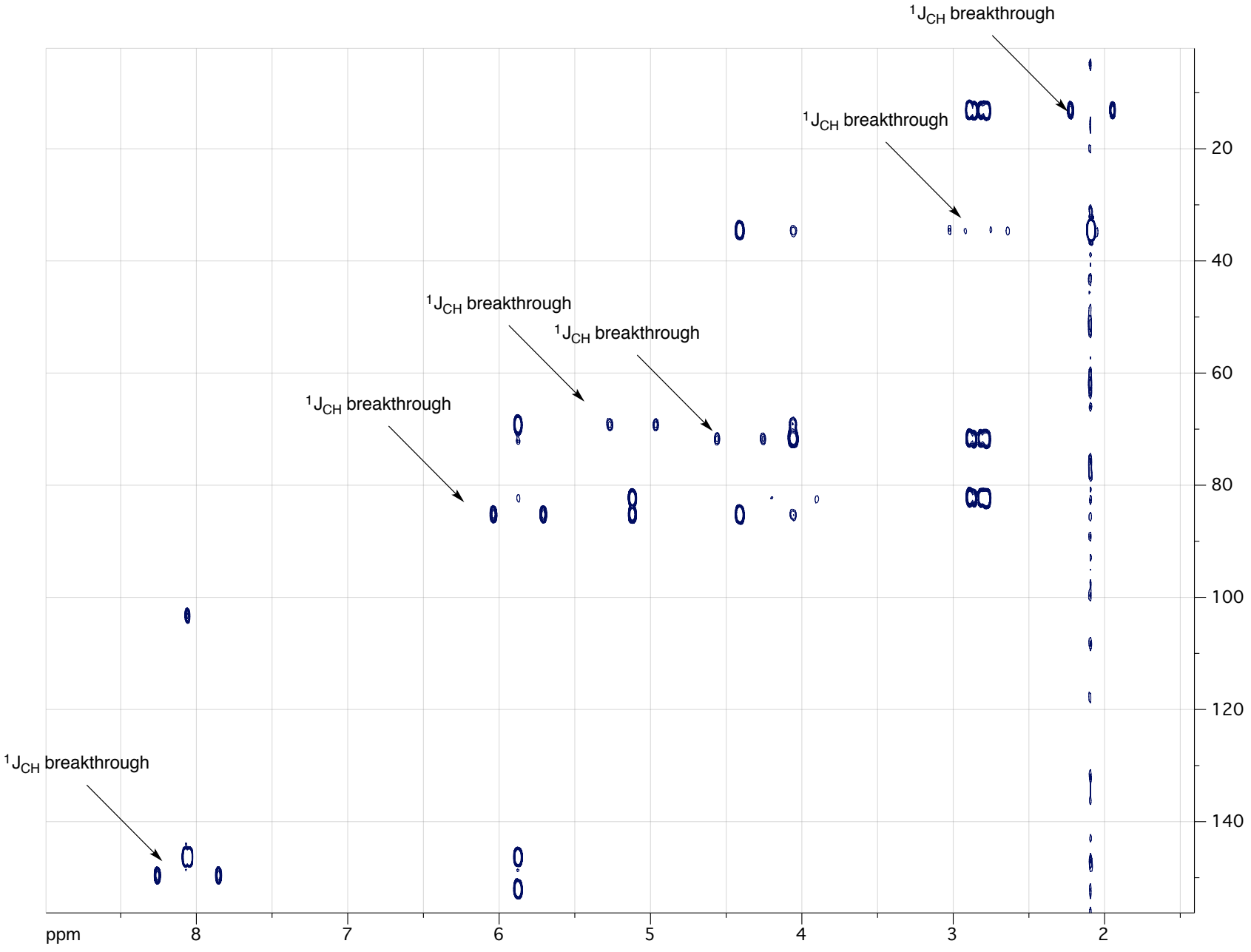

Figure S21 ^{1}H NMR spectrum of **7** in CD_3OD at 500 MHz

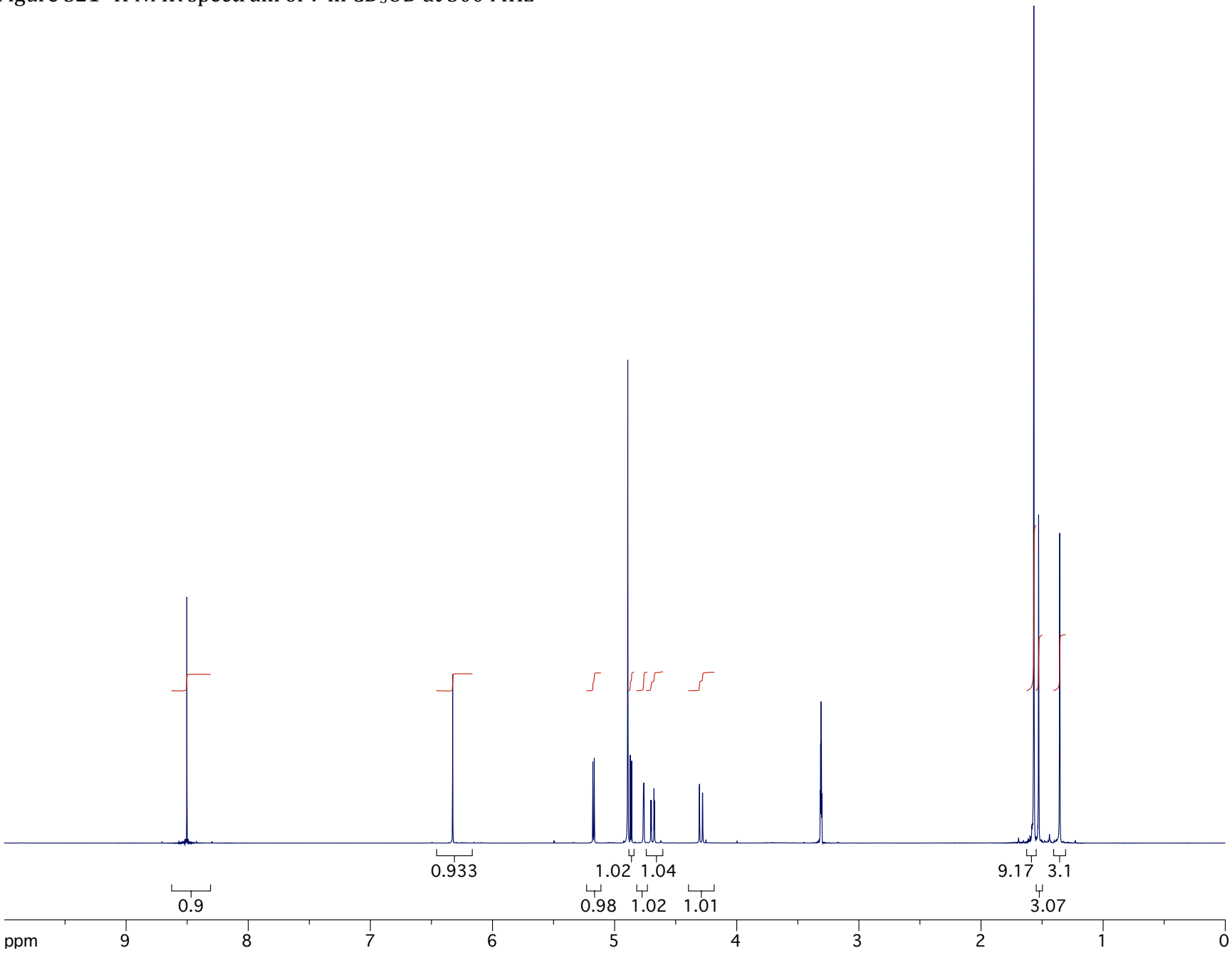

Figure S22. ^{13}C NMR spectrum of **7** in CD_3OD at 125 MHz

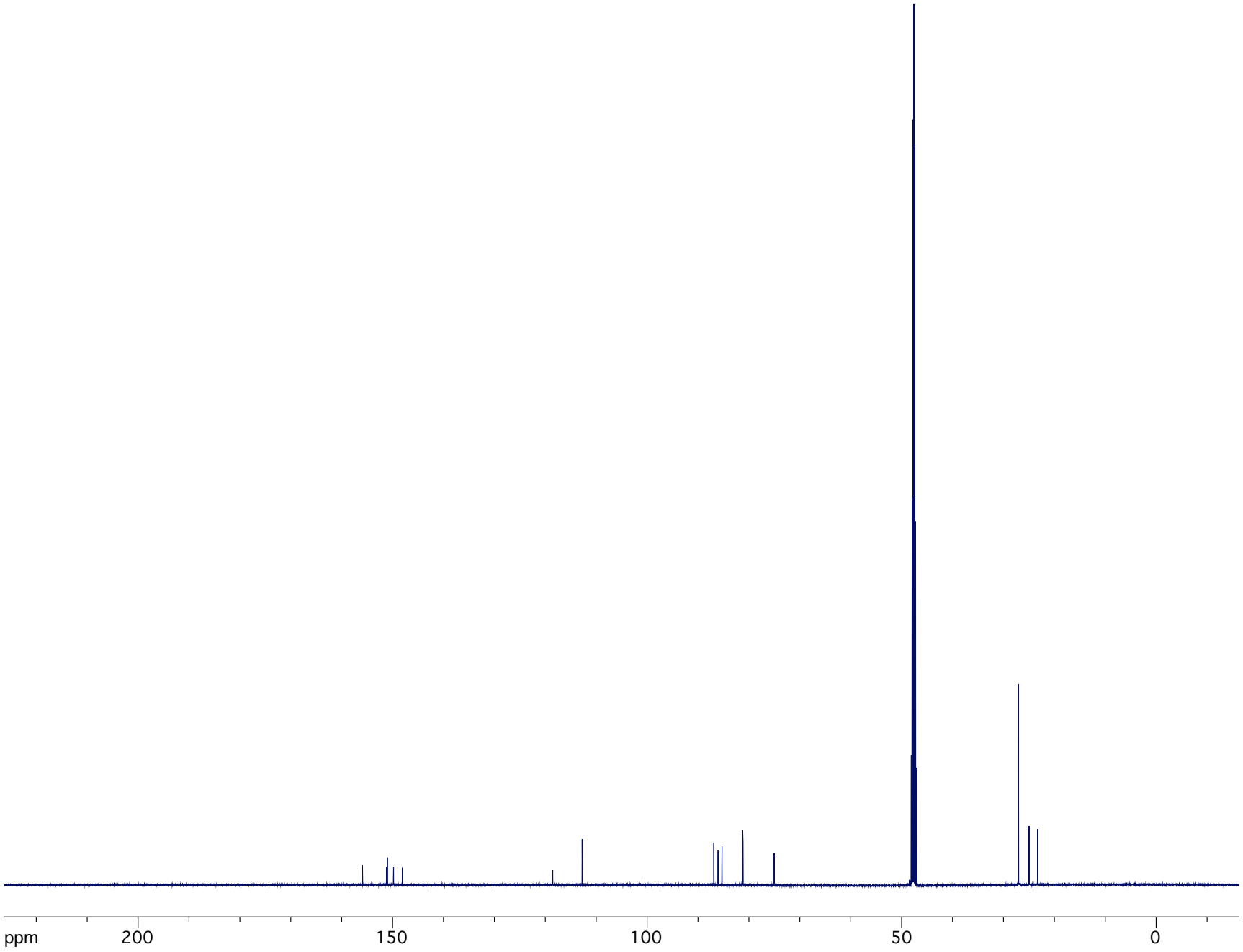

Figure S23. COSY spectrum of **7** in CD_3OD at 500 MHz

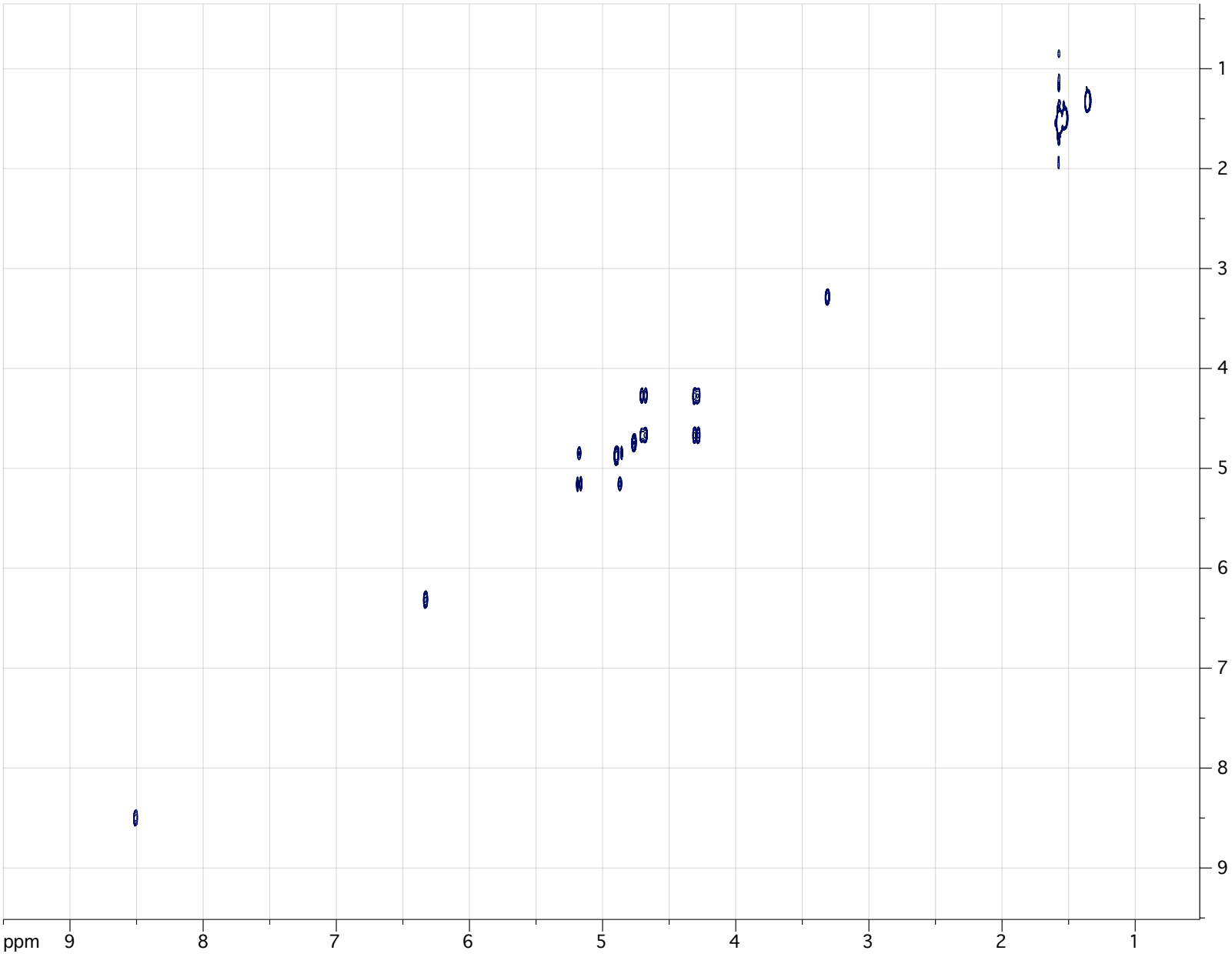

Figure S24. gHSQC spectrum of **7** in CD_3OD at 500 MHz

Figure S25. gHMBC spectrum of **7** in CD_3OD at 500 MHz, $^{n}J_{CH}$ = 8 Hz

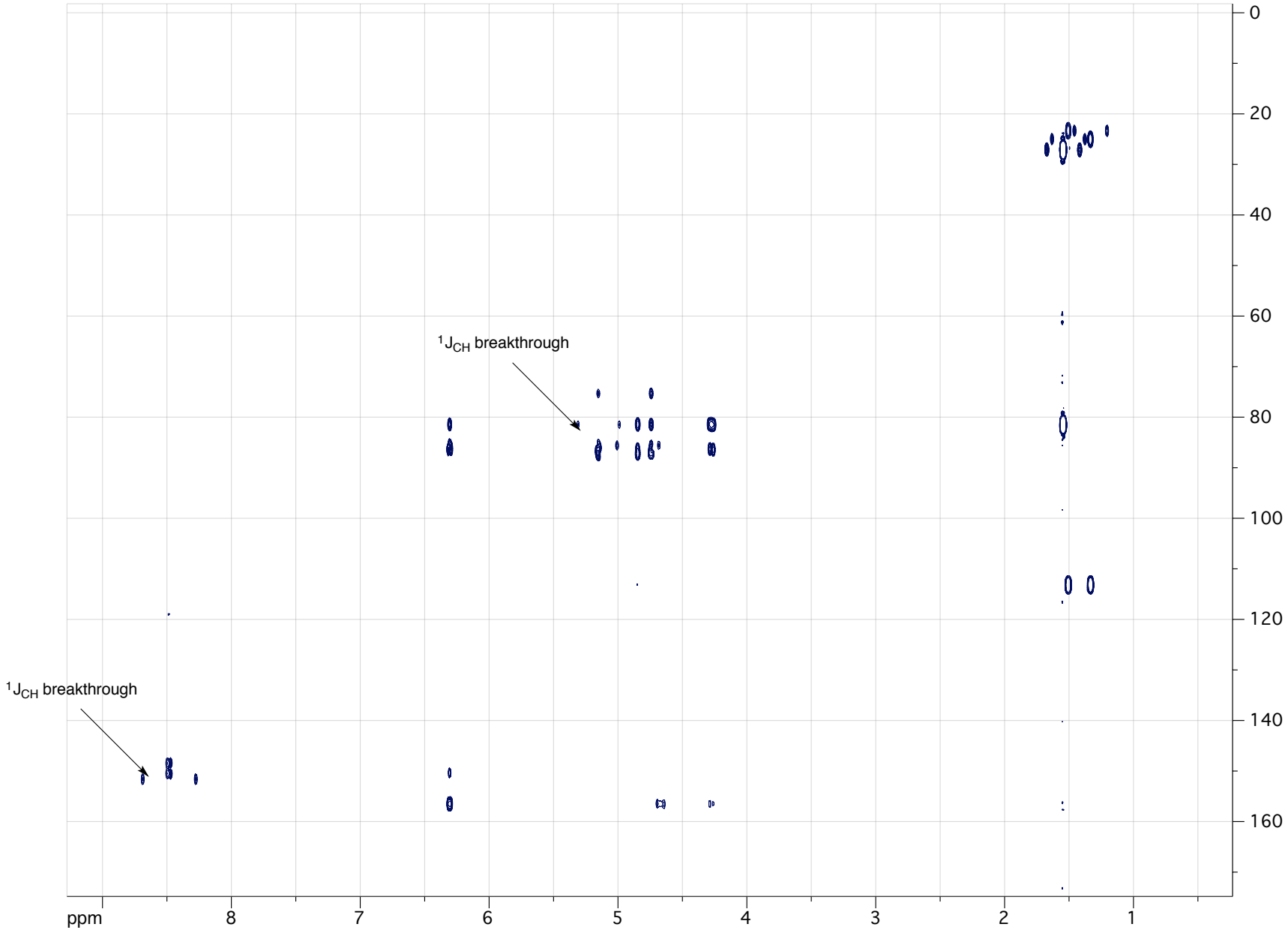

Figure S26. ^{1}H NMR spectrum of **6** (500 MHz, DMSO-d_6)

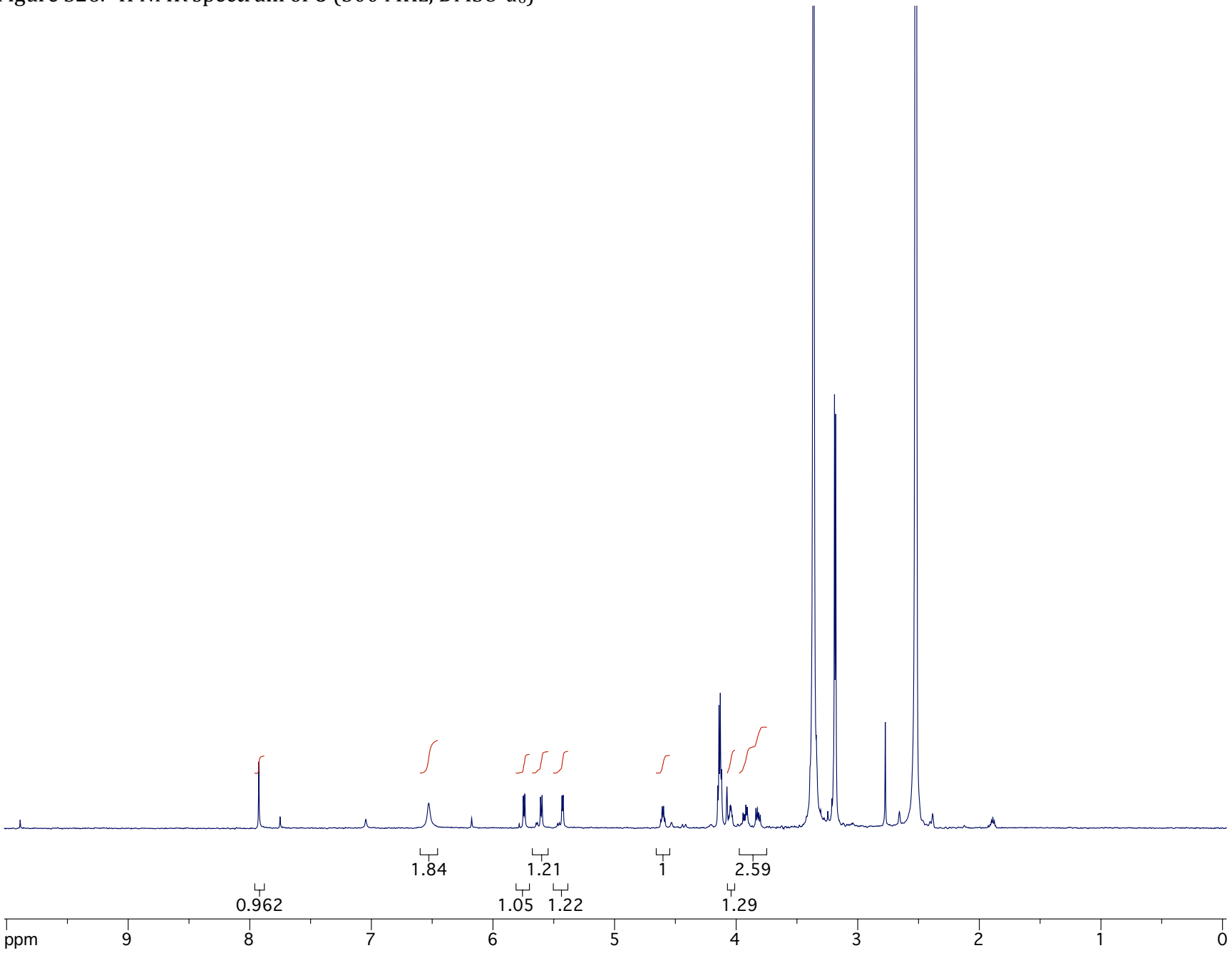

Figure S27. ^{1}H NMR spectrum of **11** (500 MHz, CD_3OD)