Supplementary Material

Temperature dependent analysis of Octenidine (*N,N´*-(decane-1,10-diyldipyridin-1-yl-4-ylidene)dioctan-1-amine) dihydrochloride by NMR and NIR spectroscopy

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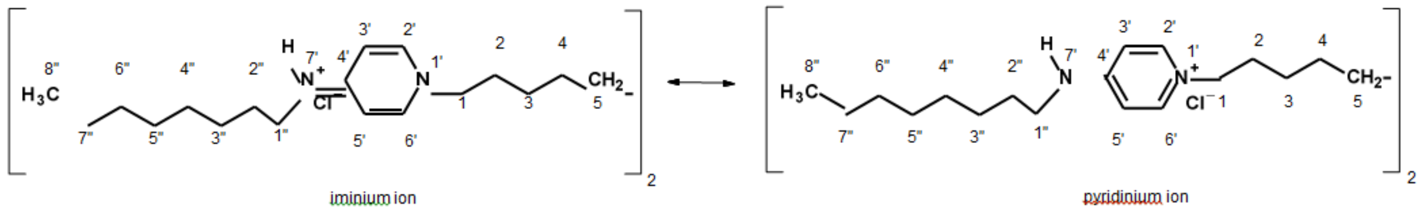
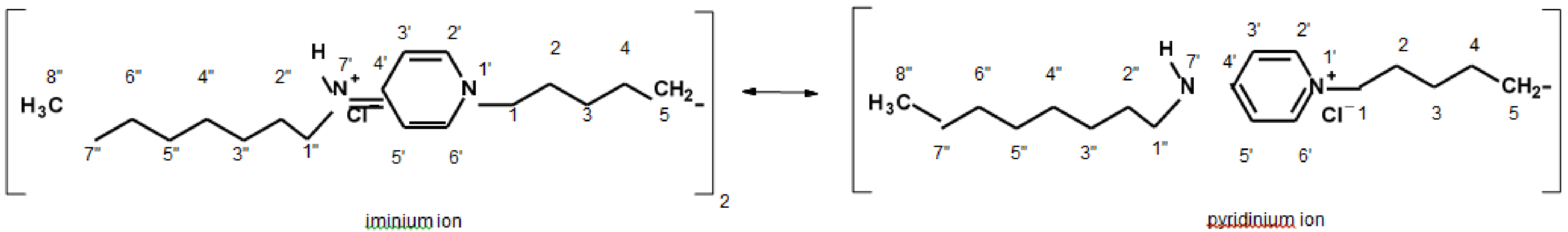
Table of Contents

Table S1. Comparison of observed ^{13}C NMR shifts and predicted values for the two mesomeric forms, all values are given in ppm

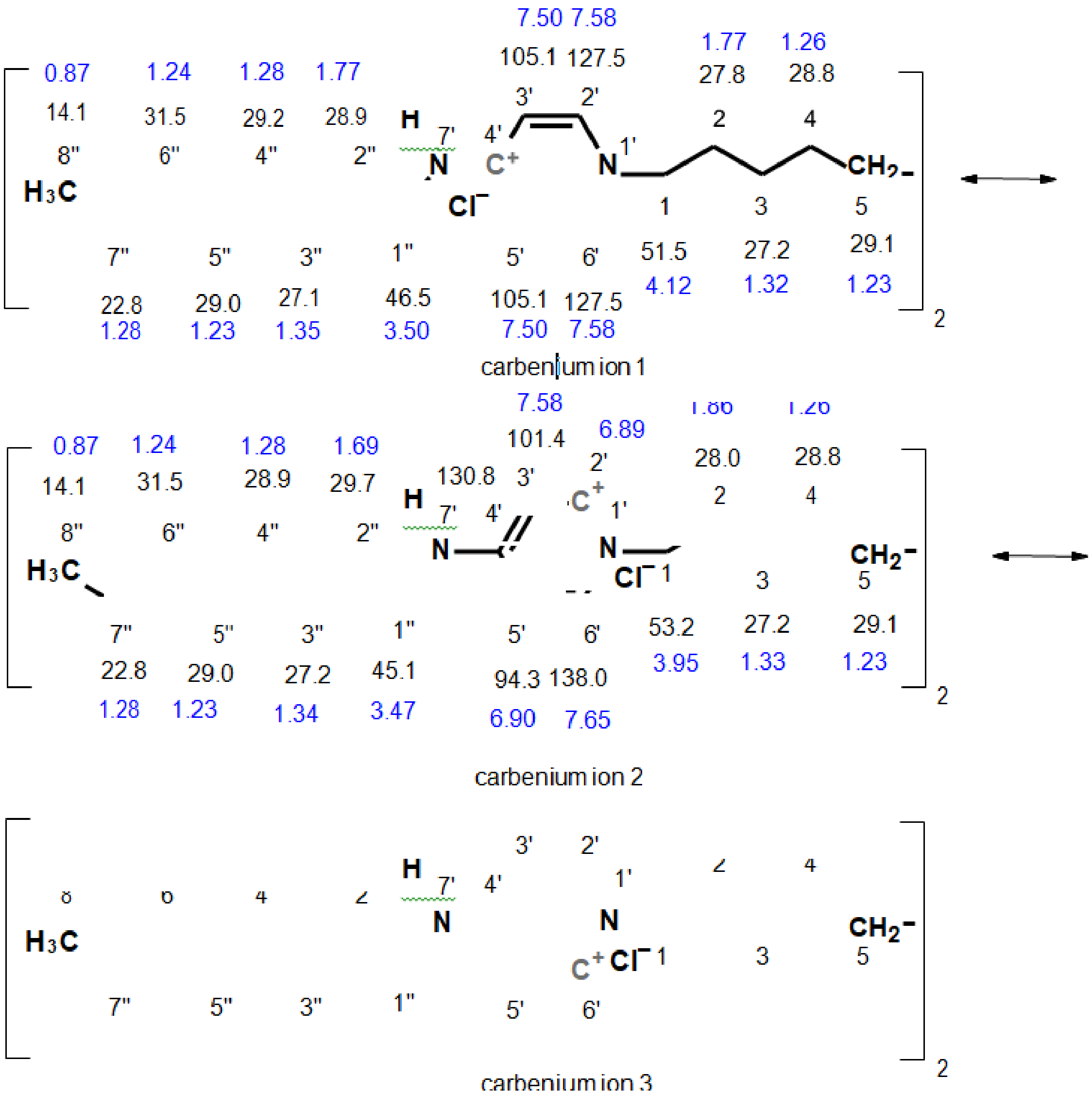


	^{13}C shifts observed	^{13}C shifts predicted	^{13}C shifts predicted	Differences D*d* observed - predicted		selected differences D*d* observed - predicted	
position		iminium ion	pyridinium ion	iminium ion	pyridinium ion	iminium ion	pyridinium ion
1	56.69	51.5	60.9	5.19	-4.21	5.19	-4.21
2	30.22	27.8	29.0	2.42	1.22	2.42	1.22
3	25.37	27.2	27.1	-1.83	-1.73		
4	28.37	28.8	28.6	-0.43	-0.23		
5	28.67	29.1	28.5	-0.43	0.17		
2'	141.19	137.2	143.8	3.99	-2.61	3.99	-2.61
3'	110.26	111.8	111.1	-1.54	-0.84	-1.54	-0.84
4'	156.62	151.2	154.5	5.42	2.12	5.42	2.12
5'	105.1	111.4	111.1	-6.3	-6	-6.30	-6.00
6'	143.57	137.2	143.8	6.37	-0.23	6.37	-0.23
1''	42.18	50.1	43.8	-7.92	-1.62	-7.92	-1.62
2''	27.90	29.6	29.7	-1.7	-1.8	-1.70	-1.80
3''	26.28	26.3	27.2	-0.02	-0.92		
4''	28.62	29.0	28.9	-0.38	-0.28		
5''	28.61	29.0	29.0	-0.39	-0.39		
6''	31.21	31.5	31.5	-0.29	-0.29		
7''	21.98	22.8	22.8	-0.82	-0.82		
8''	13.93	14.1	14.1	-0.17	-0.17		
	standard deviation			3.69	1.86	5.27	2.54

Table S2. Comparison of observed ^{1}H NMR shifts and predicted values for the two mesomeric forms, all values are given in ppm



	^{1}H shifts observed	^{1}H shifts predicted	^{1}H shifts predicted	Differences D*d* observed - predicted		selected differences D*d* observed - predicted	
position		iminium ion	pyridinium ion	iminium ion	pyridinium ion	iminium ion	pyridinium ion
1	4.11	3.93	4.34	0.18	-0.23	0.18	-0.23
2	1.74	1.69	1.78	0.05	-0.04	0.05	-0.04
3	1.20	1.34	1.35	-0.14	-0.15		
4	1.25	1.26	1.26	-0.01	-0.01		
5	1.22	1.23	1.23	-0.01	-0.01		
2'	8.16	7.95	8.55	0.21	-0.39	0.21	-0.39
3'	7.05	6.68	7.21	0.37	-0.16	0.37	-0.16
5'	6.90	6.61	7.21	0.29	-0.31	0.29	-0.31
6'	8.35	7.95	8.55	0.40	-0.20	0.40	-0.20
1''	3.24	3.69	3.47	-0.45	-0.23	-0.45	-0.23
2''	1.56	1.90	1.68	-0.34	-0.12	-0.34	-0.12
3''	1.31	1.34	1.34	-0.03	-0.03		
4''	1.27	1.27	1.28	0	-0.01		
5''	1.27	1.23	1.23	0.04	0.04		
6''	1.24	1.24	1.24	0	0		
7''	1.24	1.28	1.28	-0.04	-0.04		
8''	0.86	0.87	0.87	-0.01	-0.01		
	standard deviation			0.22	0.13	0.32	0.11



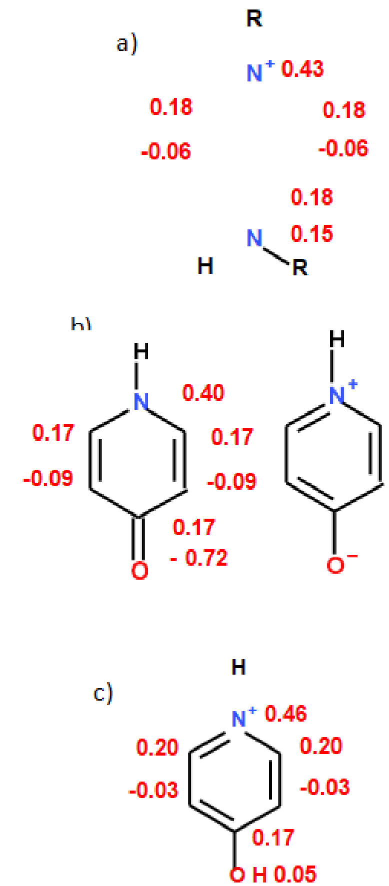


Figure S1. Further mesomeric forms with predicted ^{1}H and ^{13}C NMR shifts, ^{13}C shifts of positively charged carbons are not predicted by any of the prediction tools employed.

Figure S2a-c. HMO charge densities.

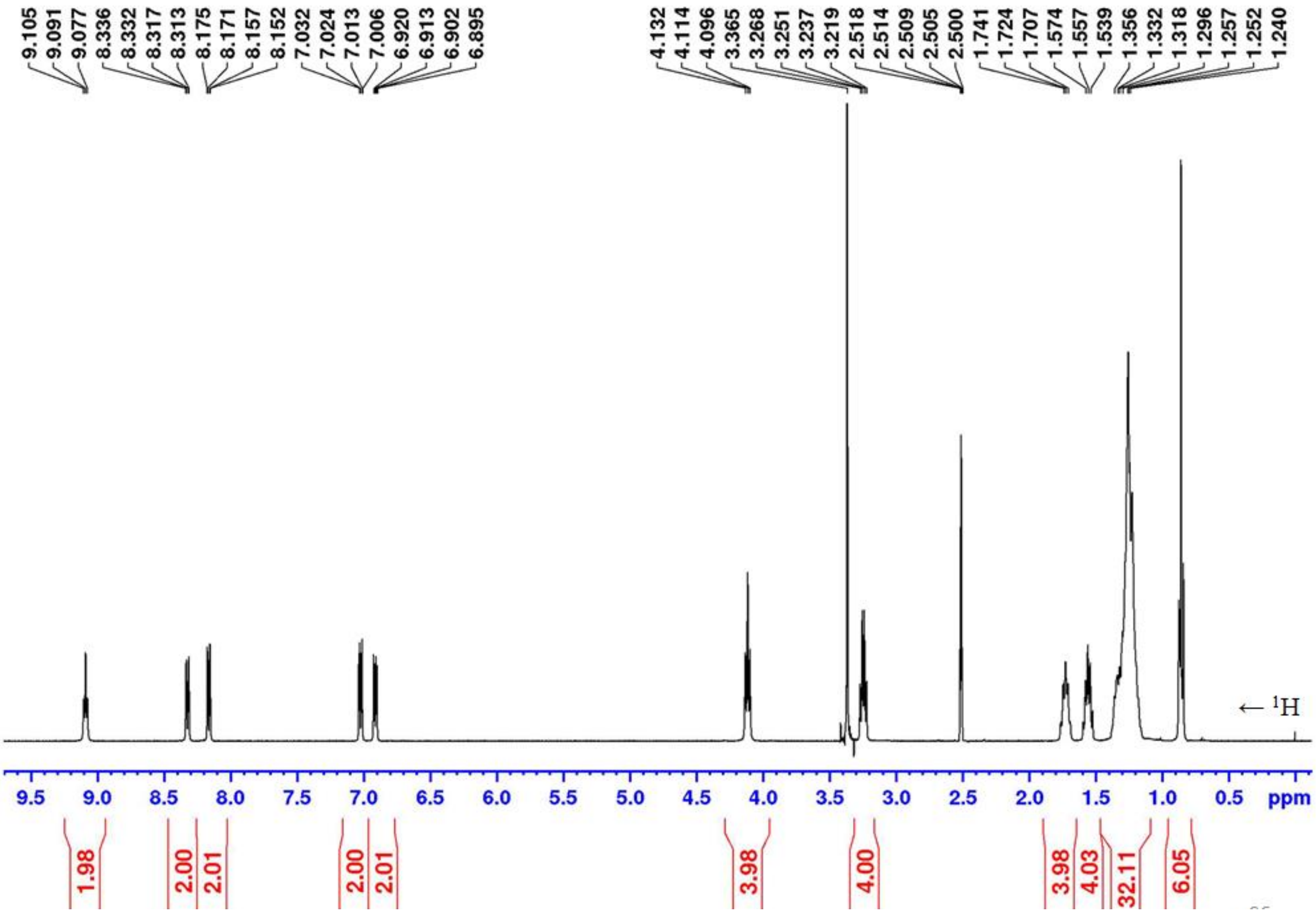


Figure S3. ^{1}H NMR spectrum, 400 MHz, 298 K, DMSO-d_6.

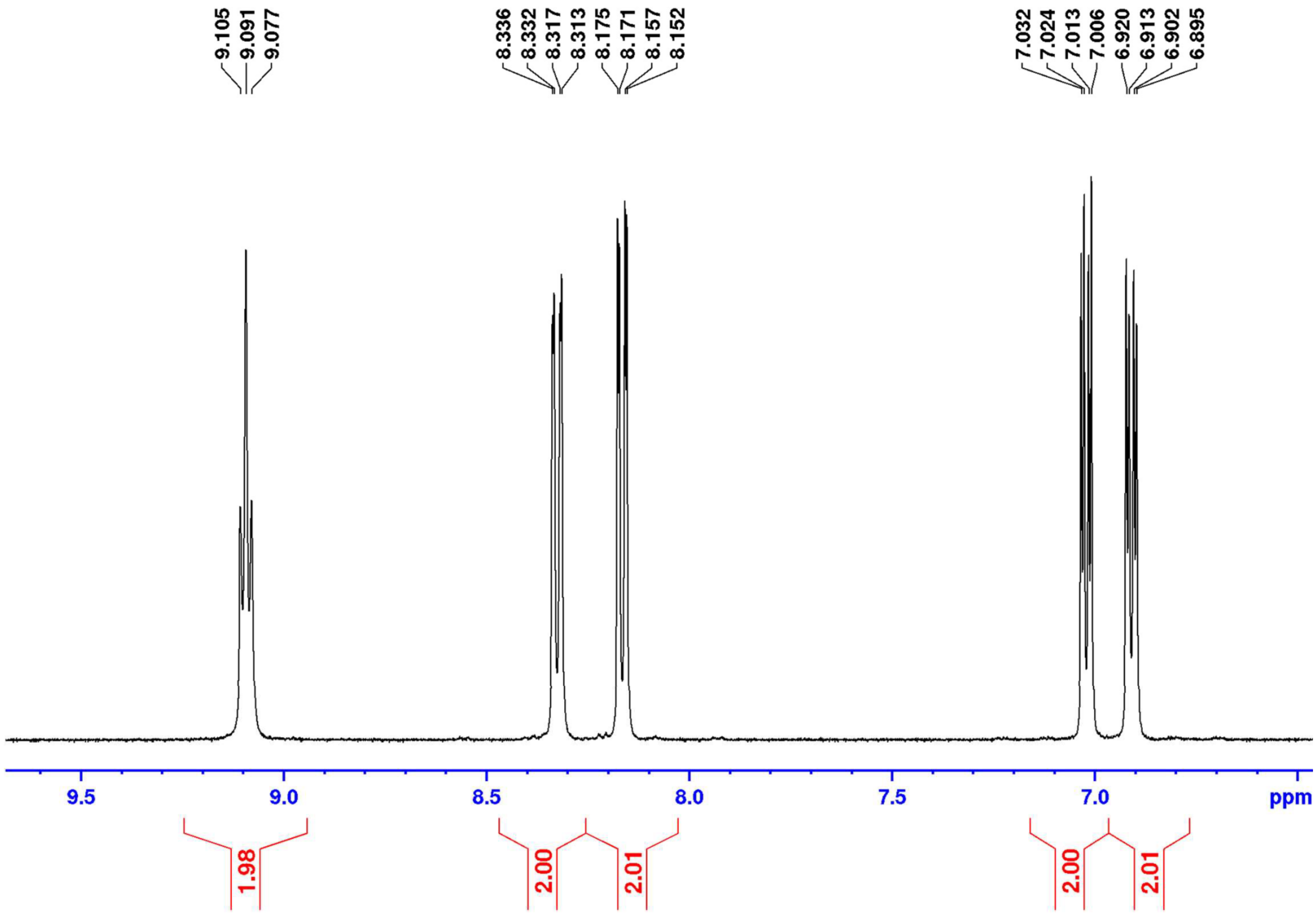


Figure S4. ^{1}H NMR spectrum, 400 MHz, 298 K, DMSO- d_6, expansion.

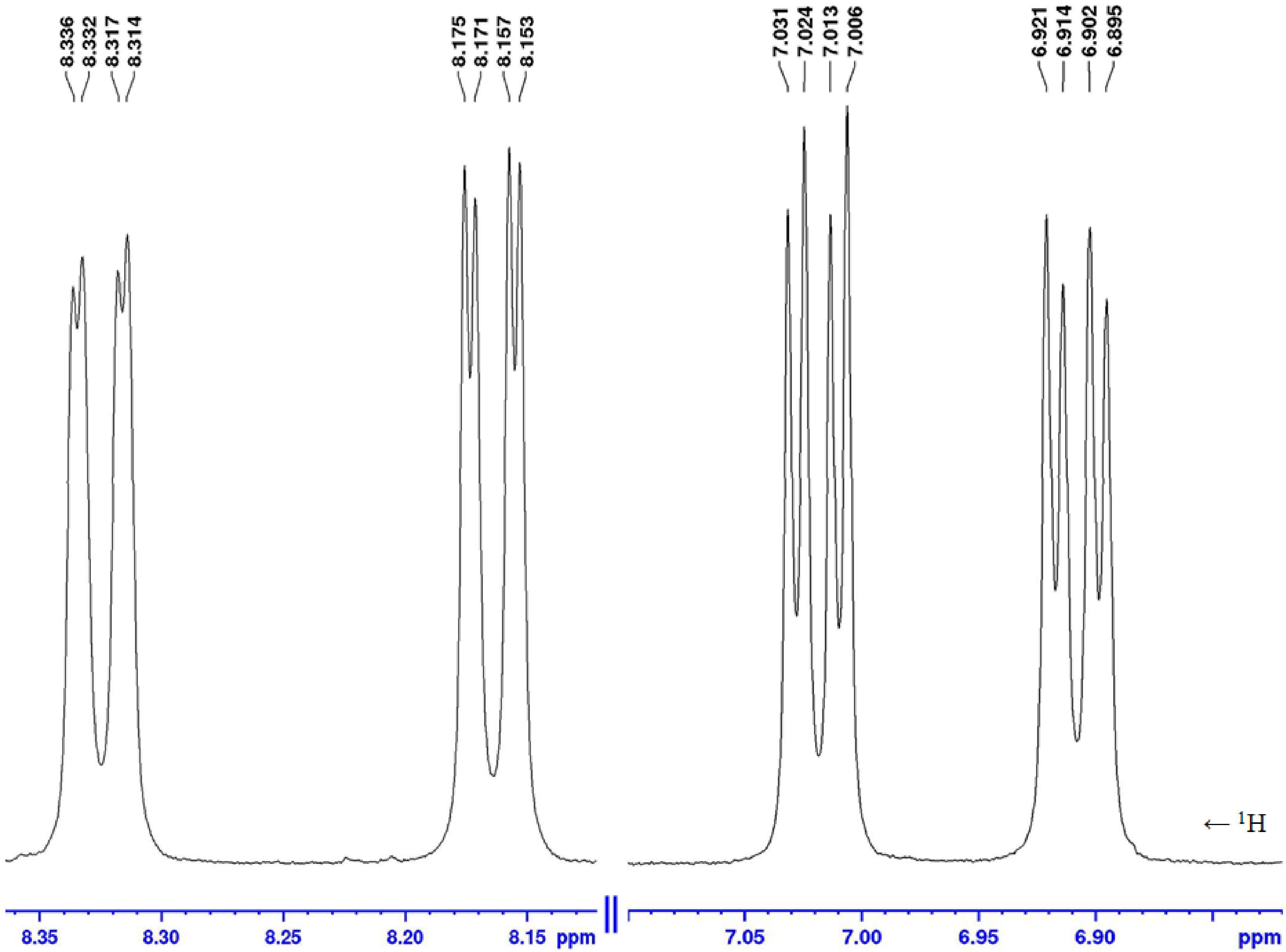


Figure S5. ^{1}H NMR spectrum, 400 MHz, 298 K, DMSO- d_6, expansion.

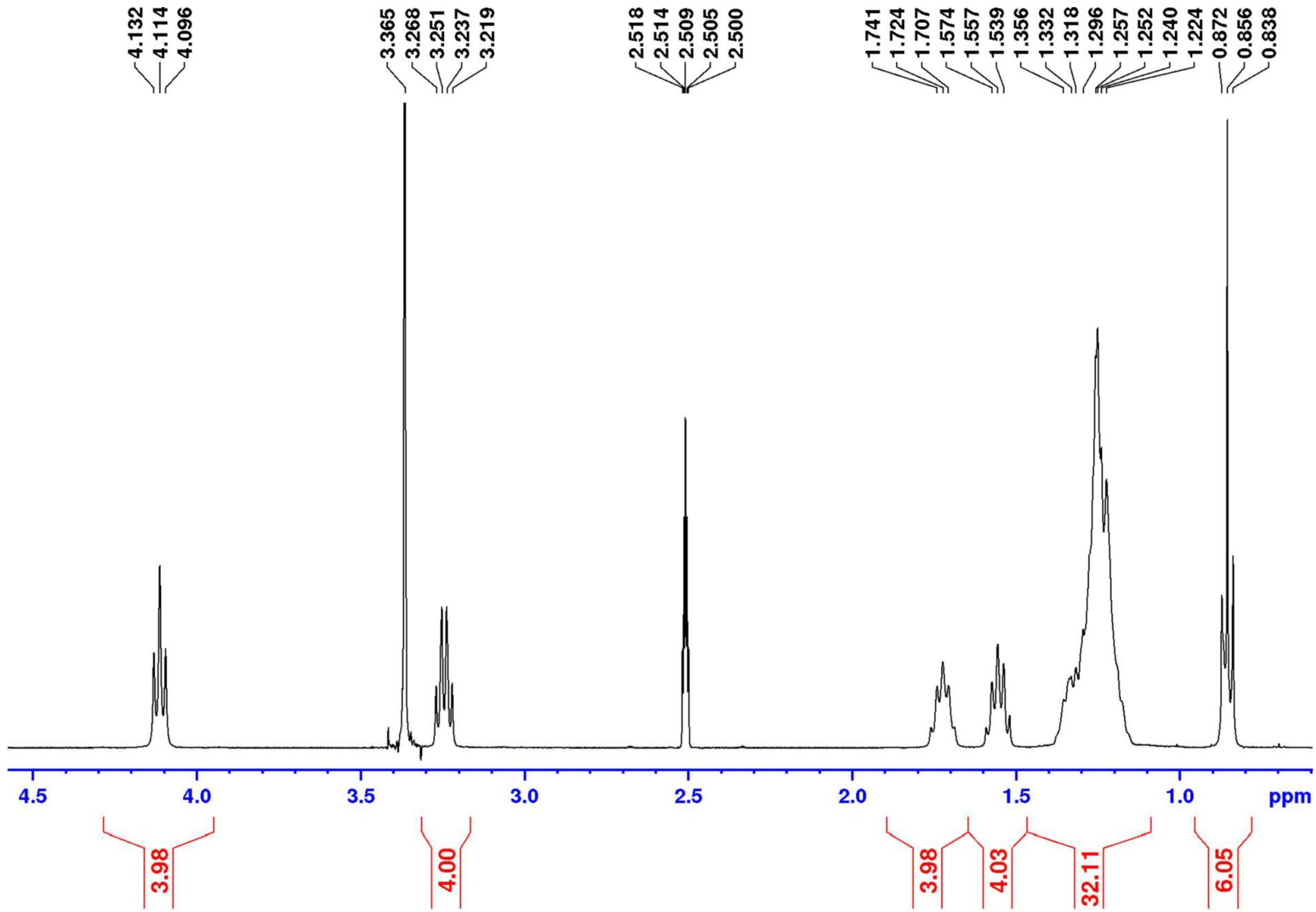


Figure S6. ^{1}H NMR spectrum, 400 MHz, 298 K, DMSO- d_6, expansion.

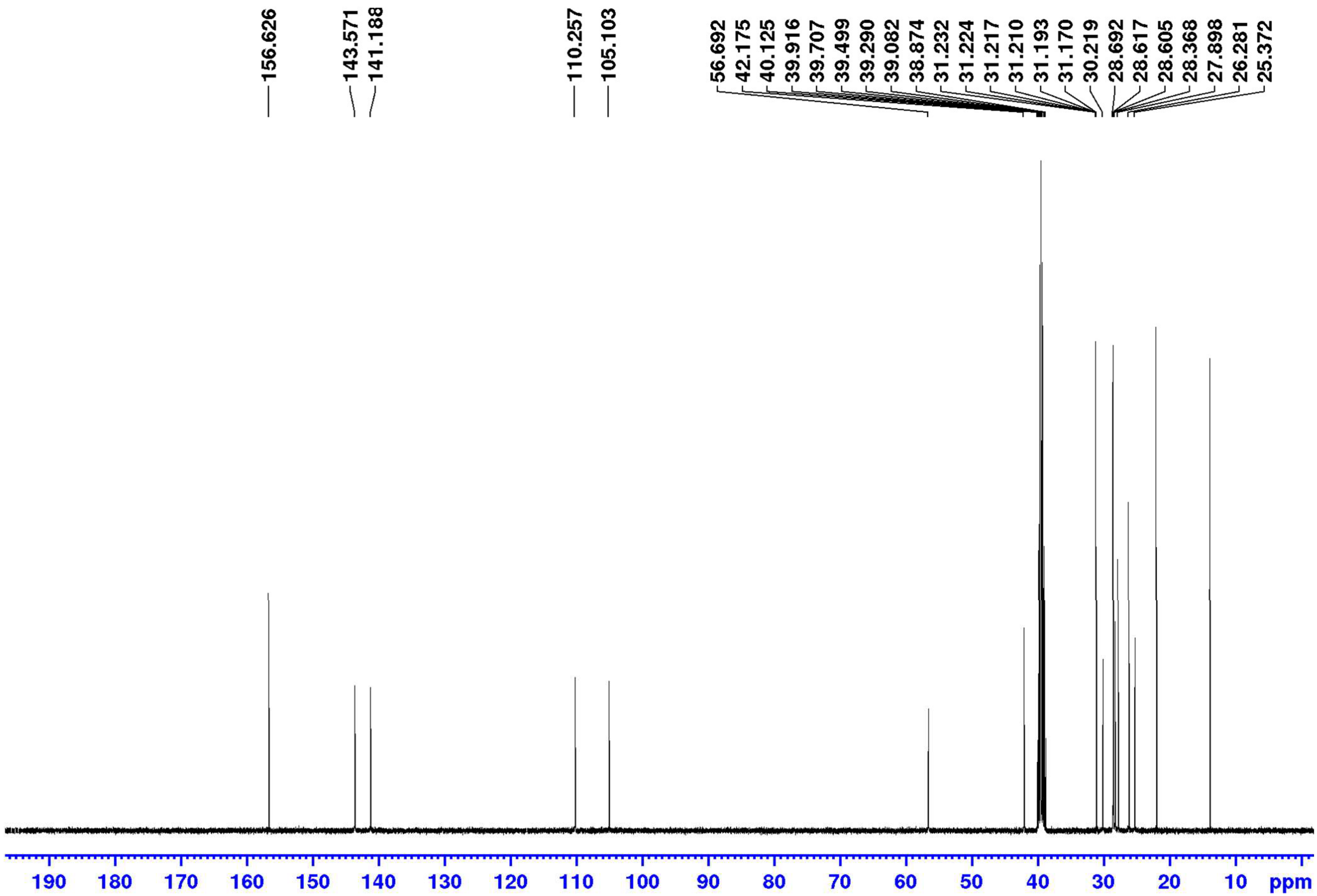


Figure S7. ^{13}C NMR spectrum, 100 MHz, 298 K, DMSO- d_6.

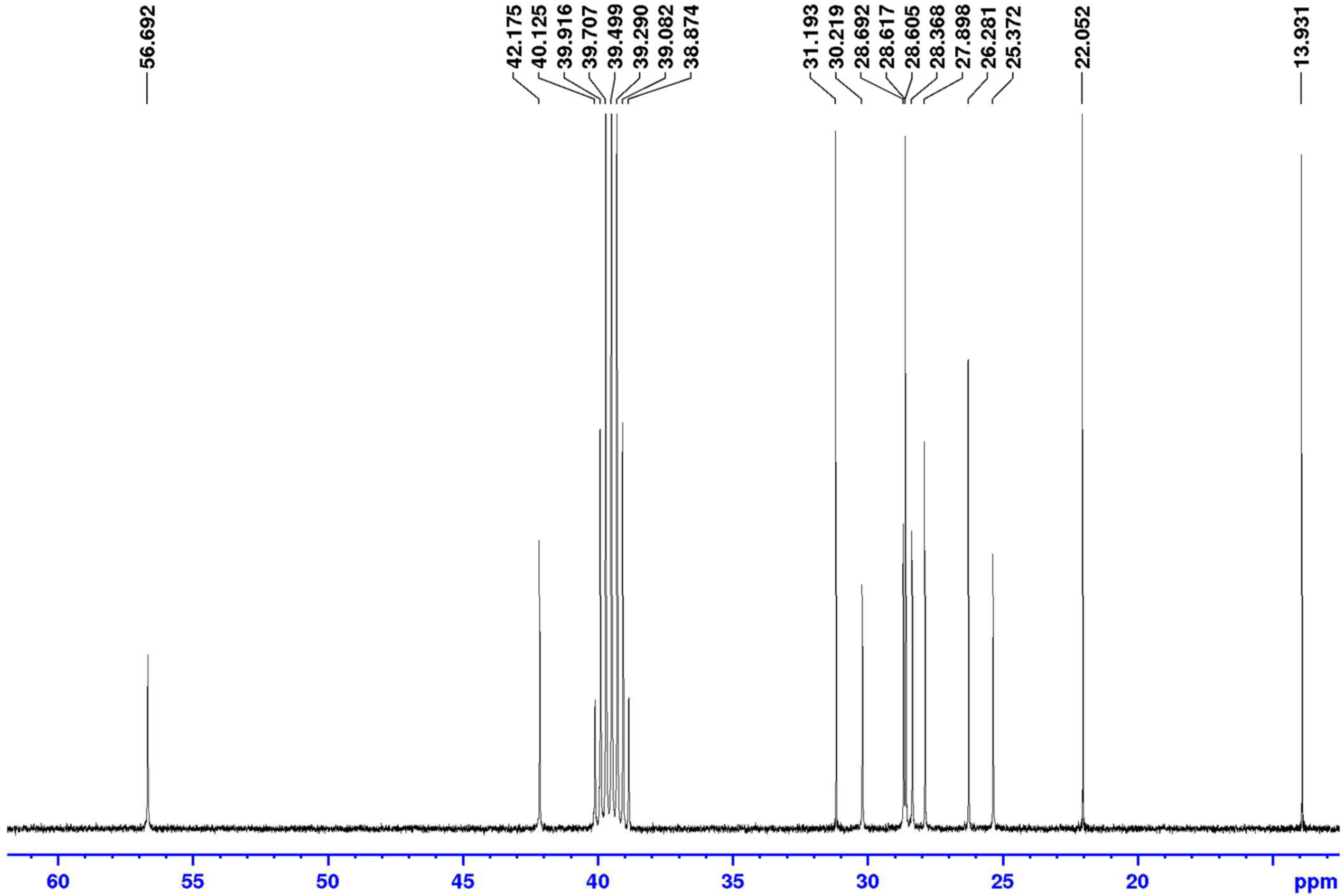


Figure S8. ^{13}C NMR spectrum, 100 MHz, 298 K, DMSO- d_6, expansion.

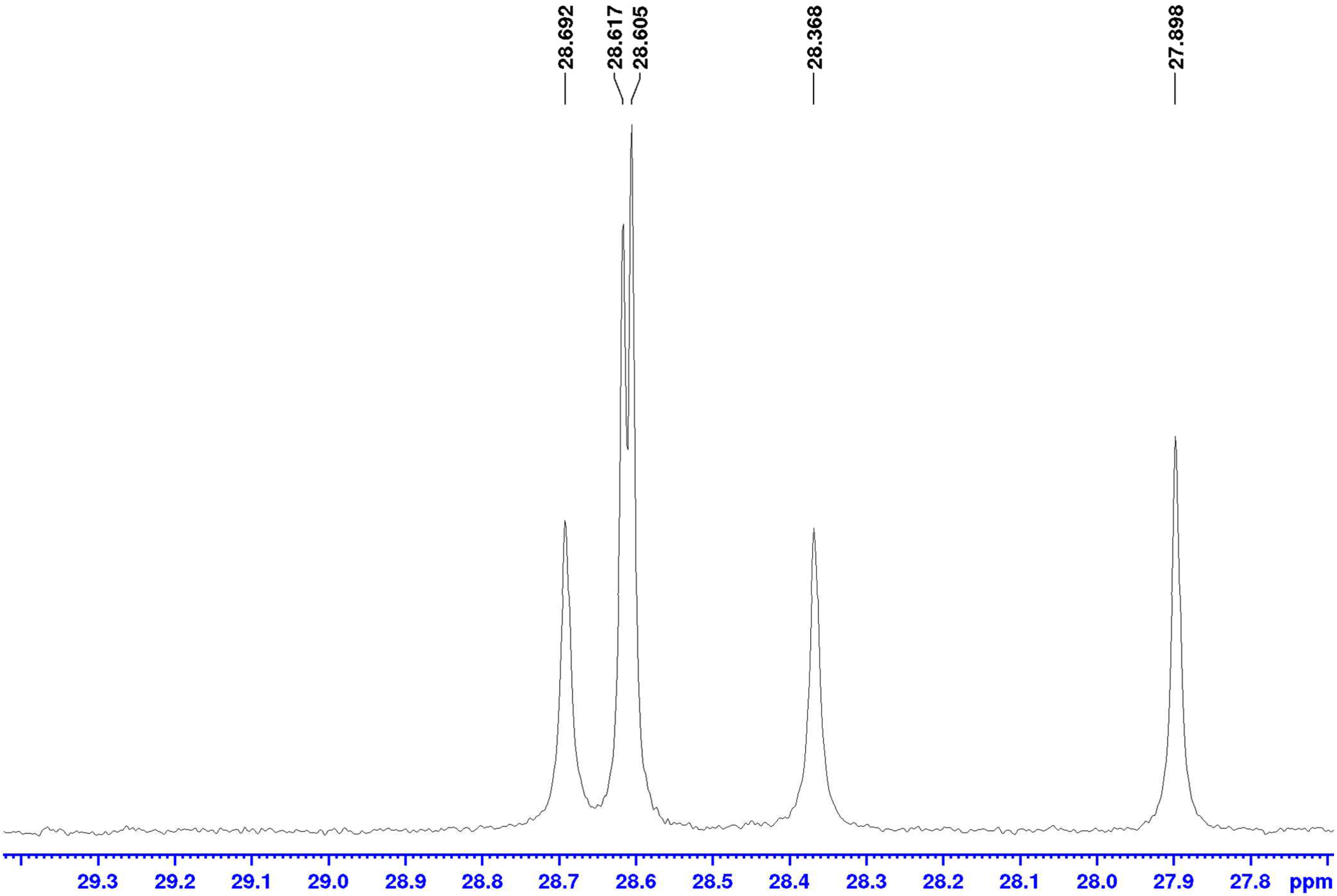


Figure S9. ^{13}C NMR spectrum, 100 MHz, 298 K, DMSO- d_6, expansion.

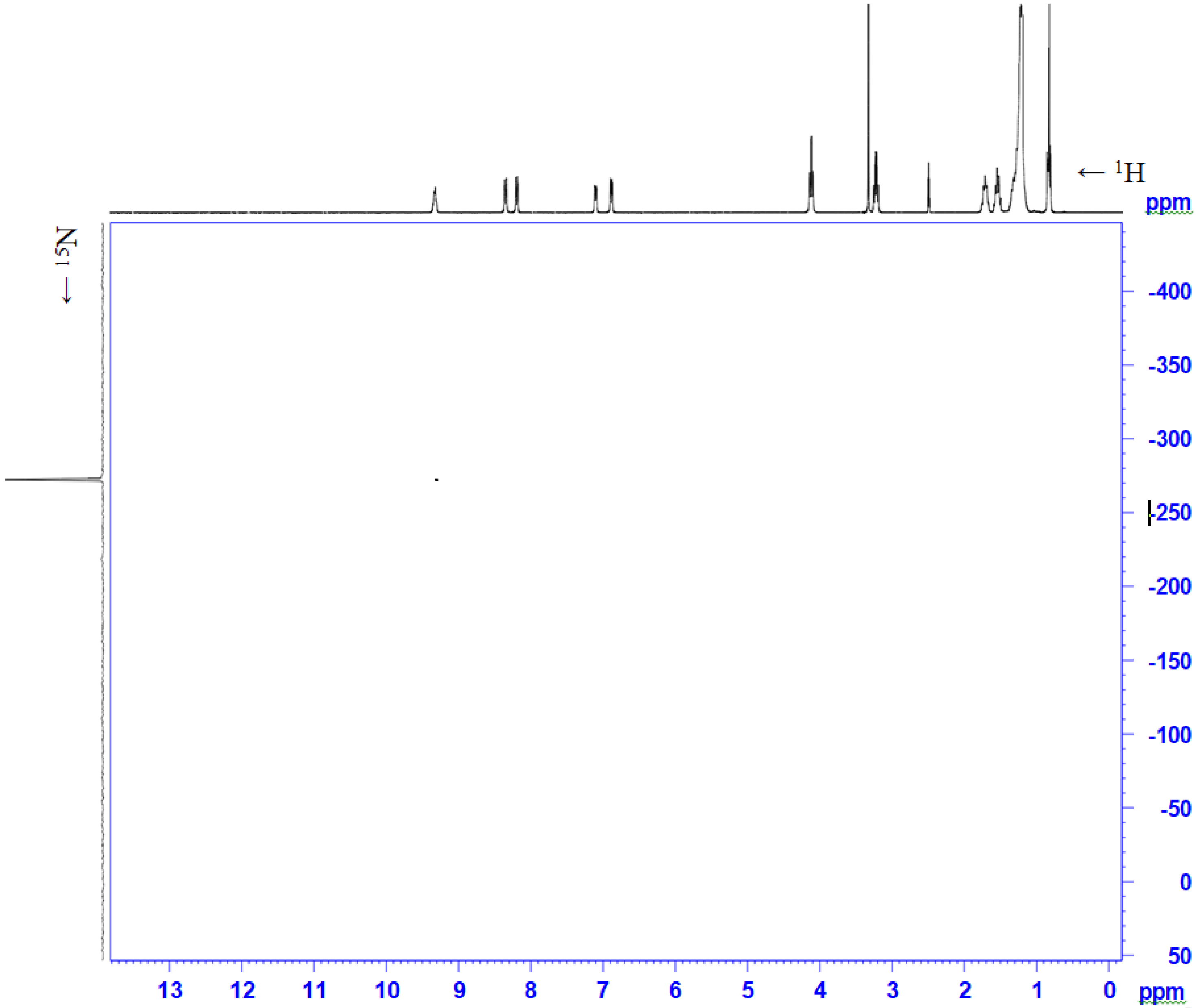


Figure S10. ^{1}H,^{15}N HSQC spectrum, 300 MHz, 310 K, DMSO- d_6, referenced to external nitromethane.

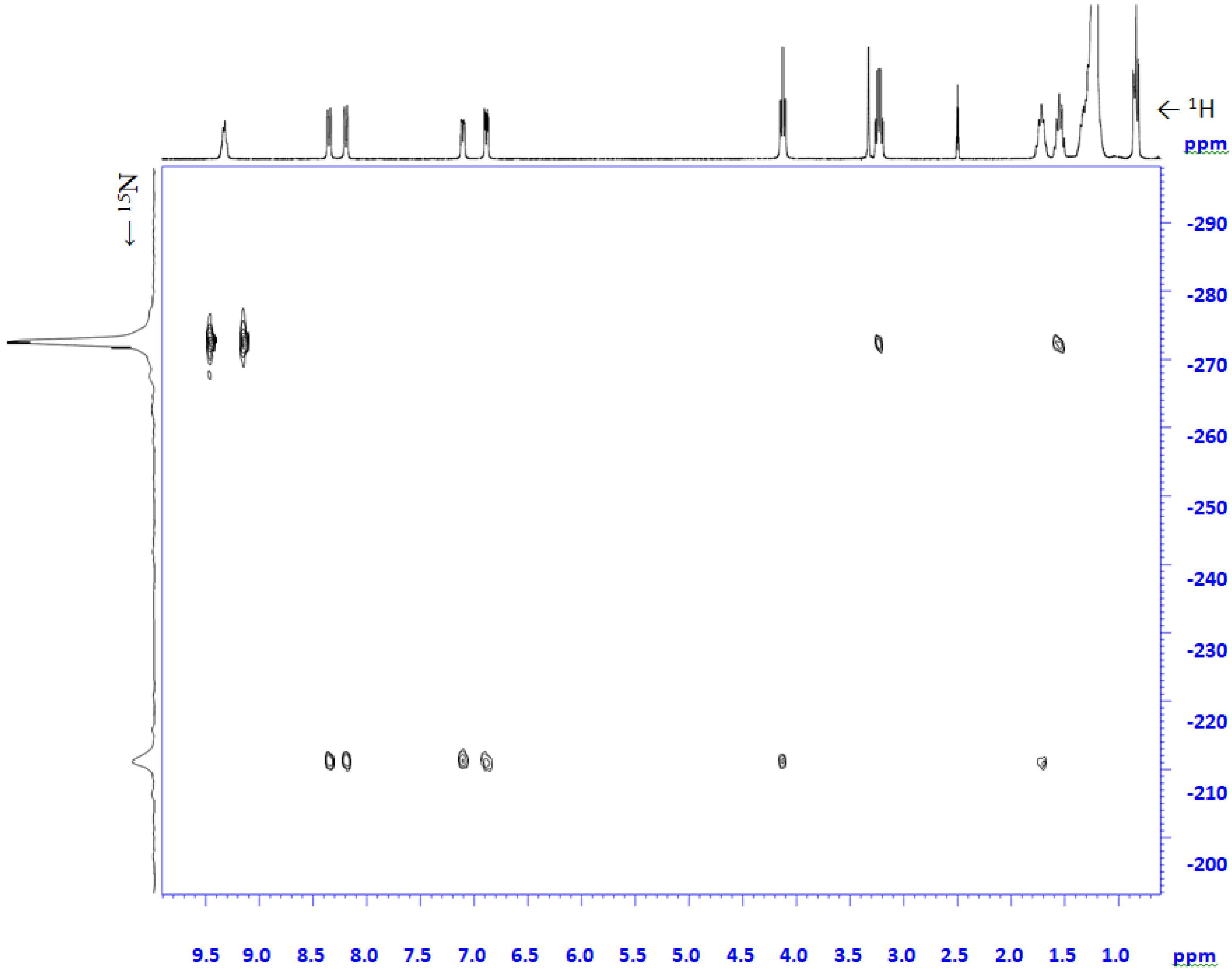


Figure S11: $^{1}H,^{15}N$ HMBC spectrum, 300 MHz, 310 K, DMSO-d_6, referenced to external nitromethane in DMSO-d_6

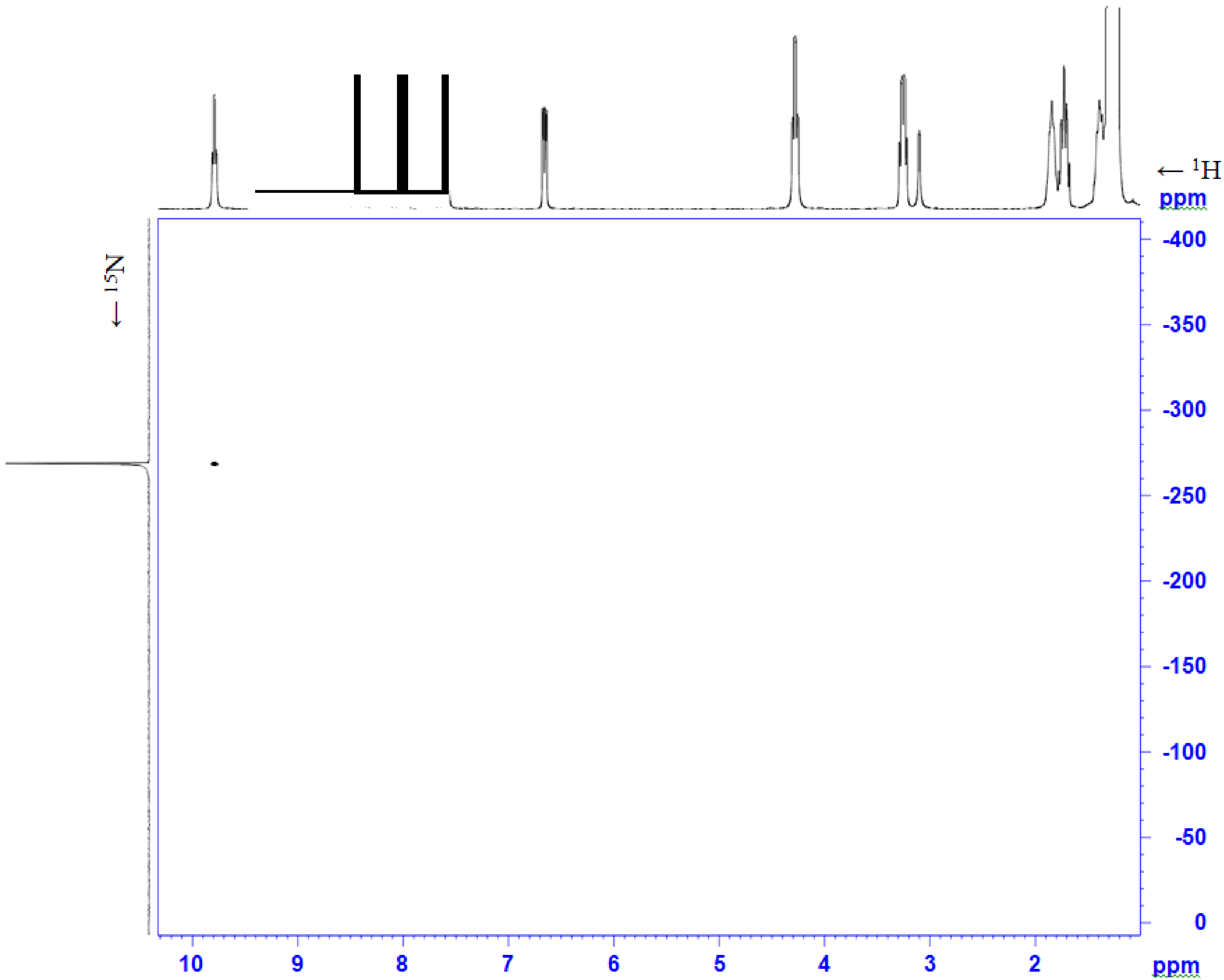


Figure S12. $^{1}H,^{15}N$ HSQC spectrum, 300 MHz, 298 K, $CDCl_3$, referenced to external nitromethane in $CDCl_3$.

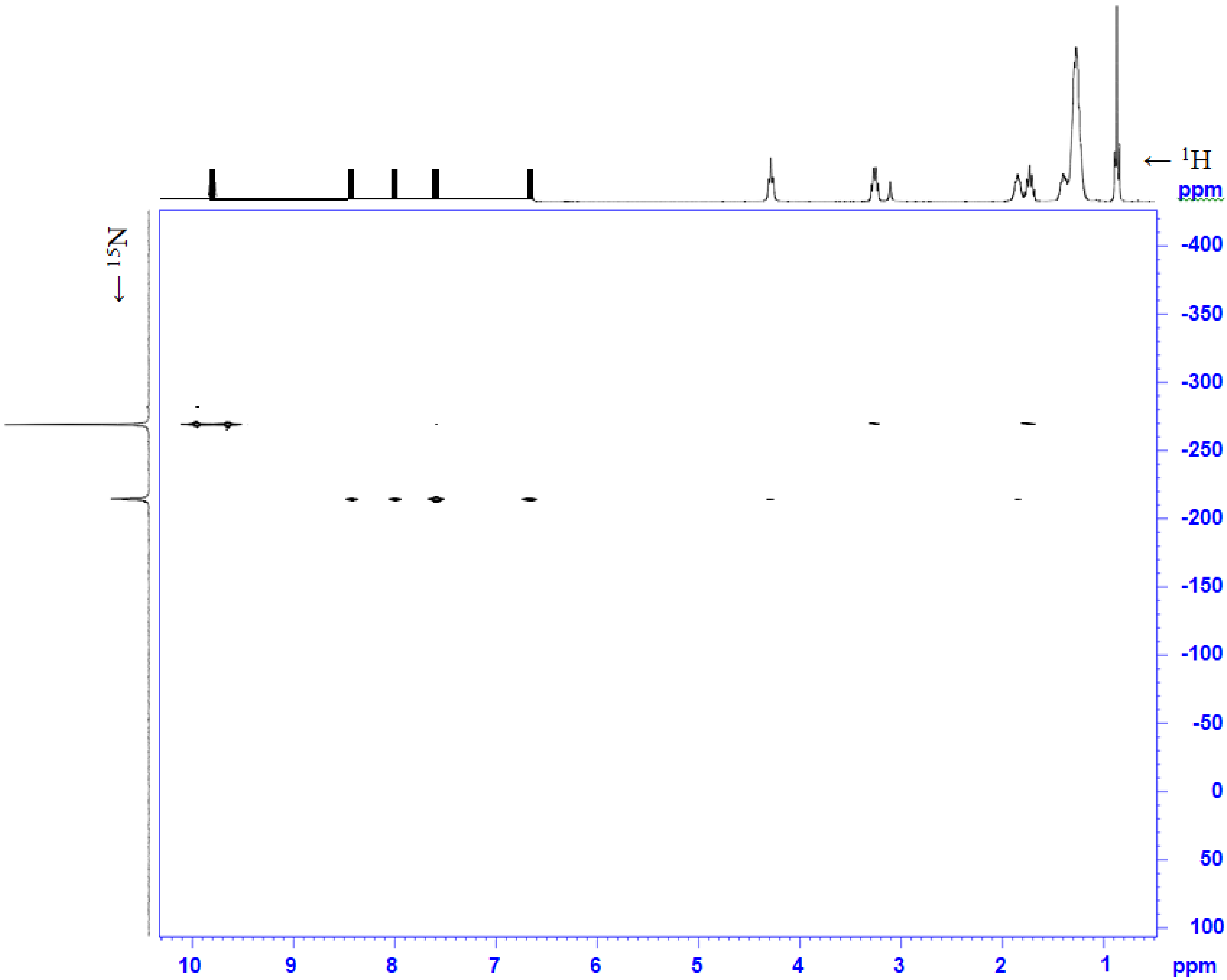


Figure S13. $^{1}H,^{15}N$ HMBC spectrum, 300 MHz, 298 K., $CDCl_3$, referenced to external nitromethane in $CDCl_3$.

Table S3. Calibration/Referencing of ^{15}N NMR spectra

from liquid ammonia to external nitromethane	–380.2 ppm
from nitromethane in DMSO-d_6 to external nitromethane	+2.0 ppm
so from external nitromethane in DMSO-d_6 to the ammonia scale is added	+382.2 ppm
15N chemical shift of N,N-dimethylformaide is in DMSO-d6 relative to internal nitromethane is set identical to external nitromethane (own measurement)	276.6 ppm
15N chemical shift of N,N-dimethylformaide is in DMSO-d6 relative to ammonia	105.6 ppm
or the calibration of the ^{15}N NMR shifts in $CDCl_3$ external nitromethane in $CDCl_3$ was used. For the referencing to the ammonia scale the same value as above was added	382.2 ppm

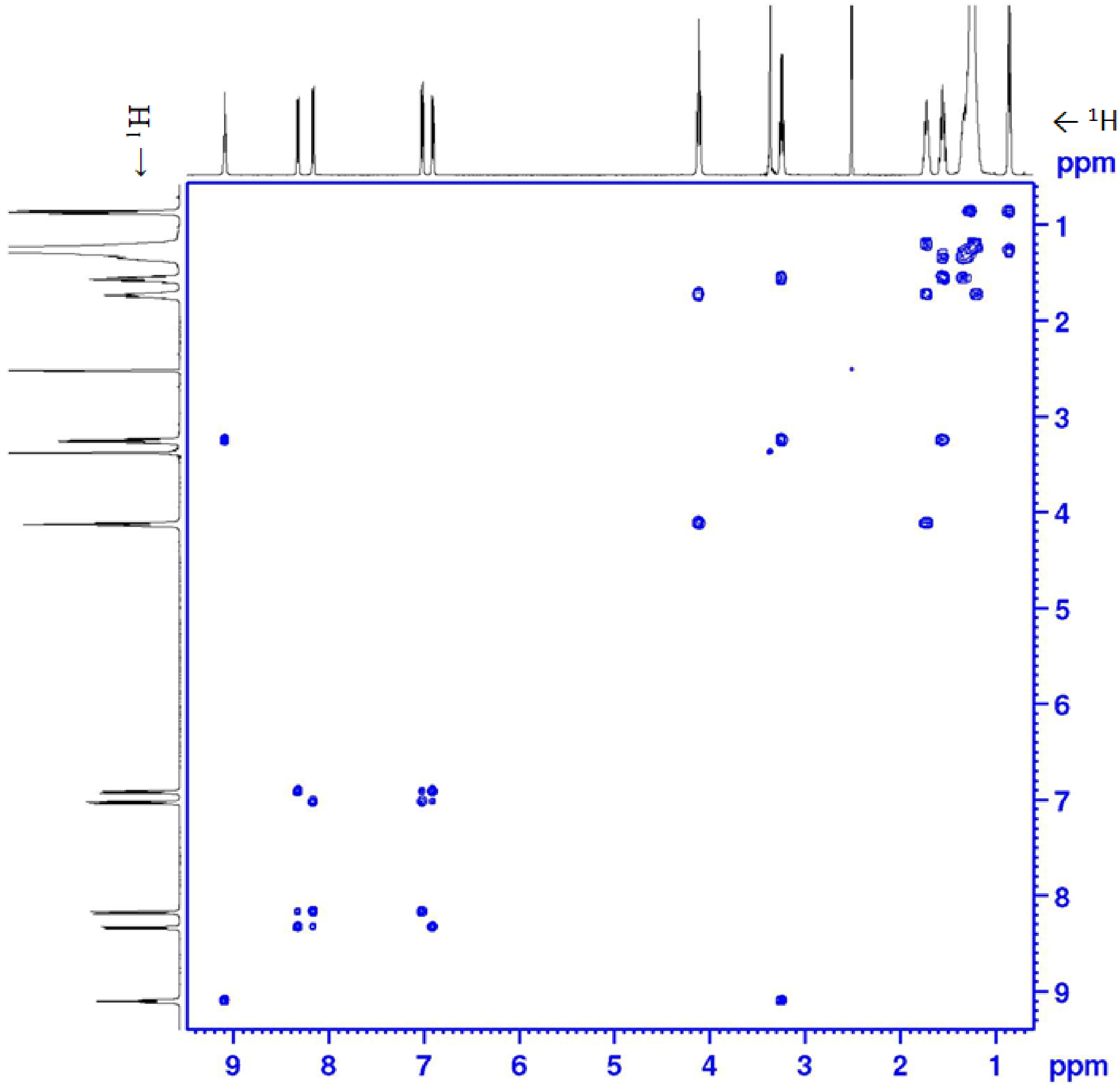


Figure S14. ^{1}H,^{1}H COSY spectrum, 400 MHz, 298 K, DMSO-d_6.

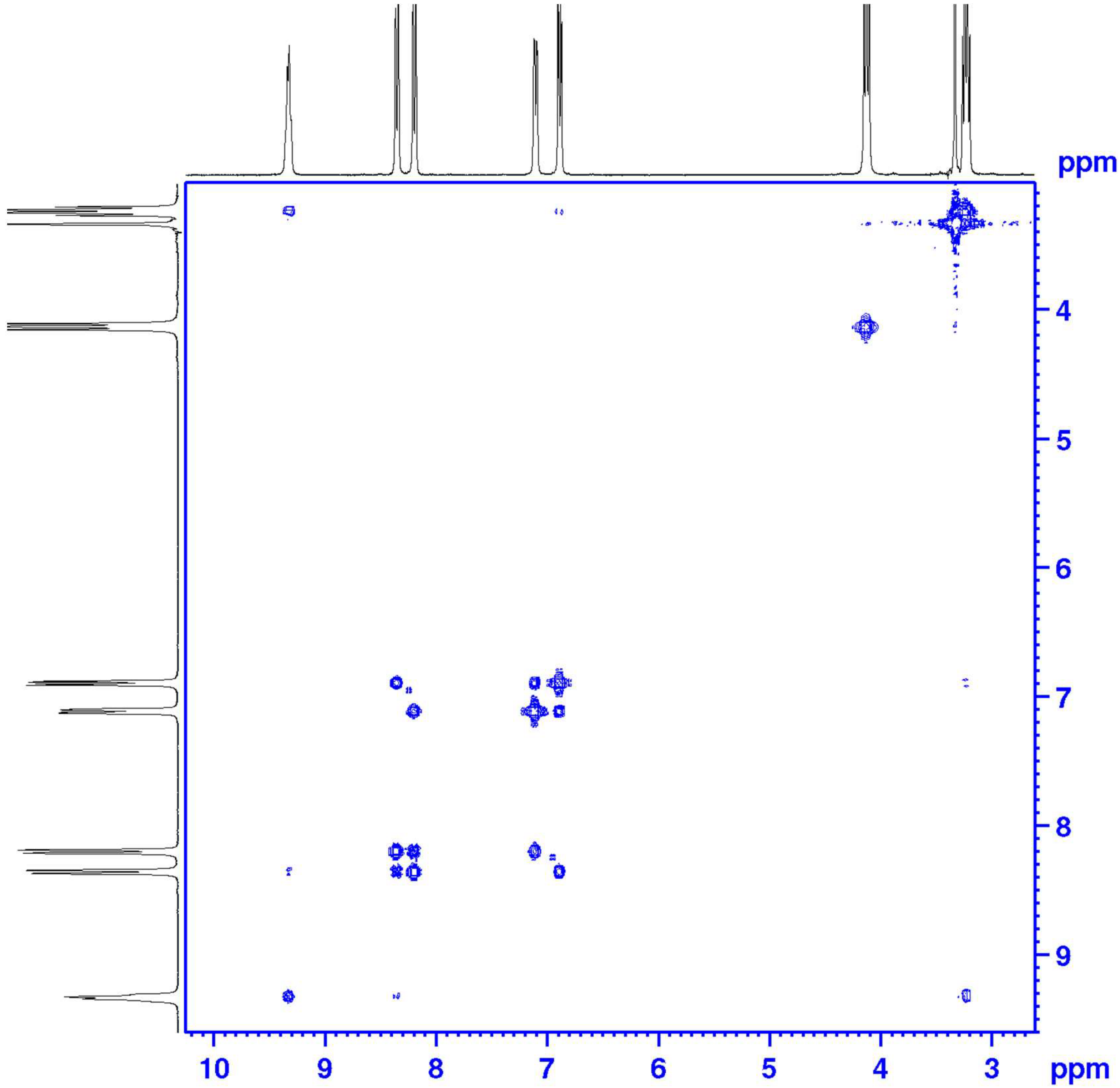


Figure S15. Expansion of the $^1H,^1H$ long-range COSY spectrum, 300 MHz, 298 K, DMSO-d_6, d0 = 0.25 s.

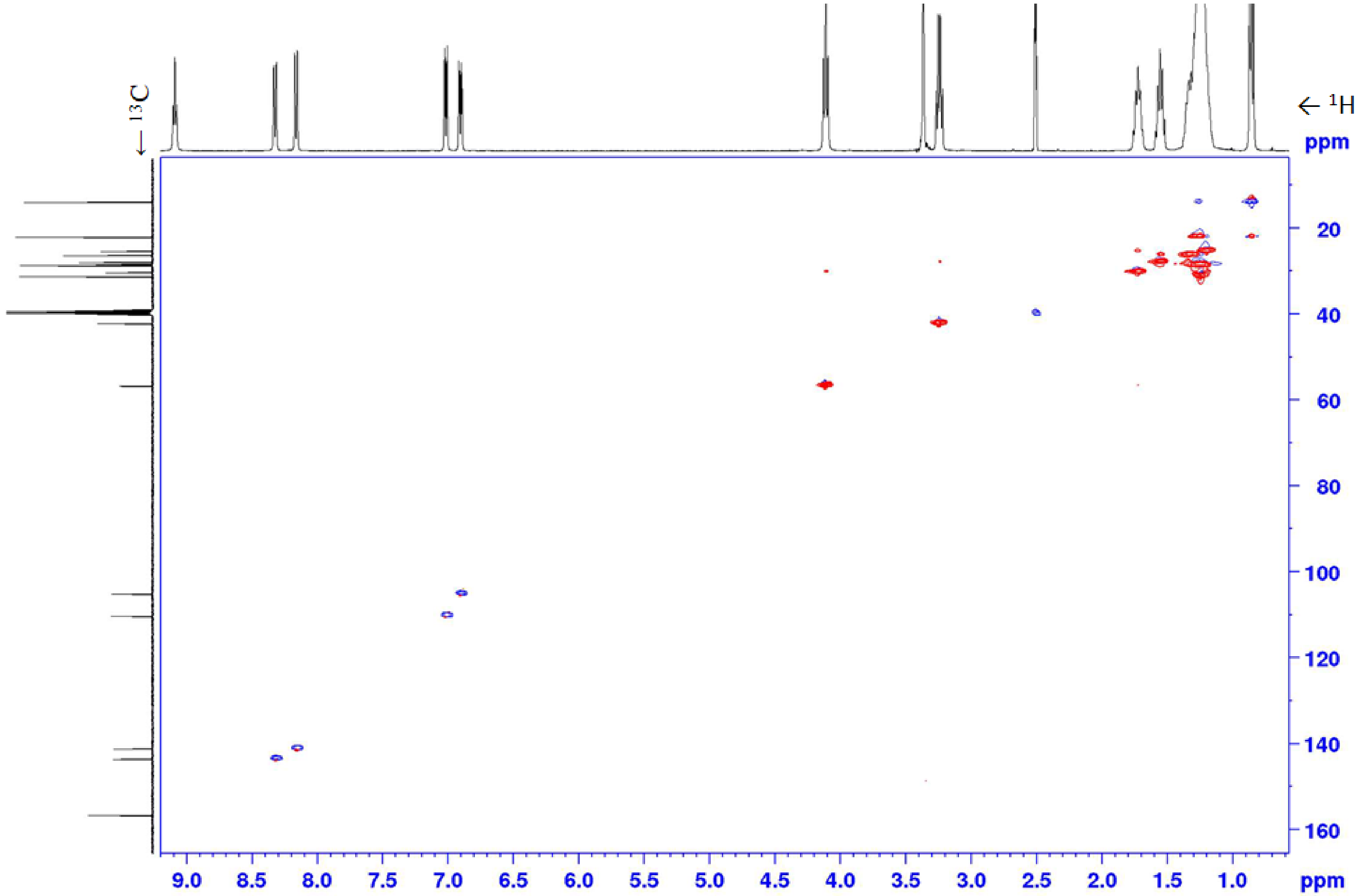


Figure S16. ^{1}H,^{13}C HSQC spectrum, 400 MHz, 298 K, DMSO-d_6**.**

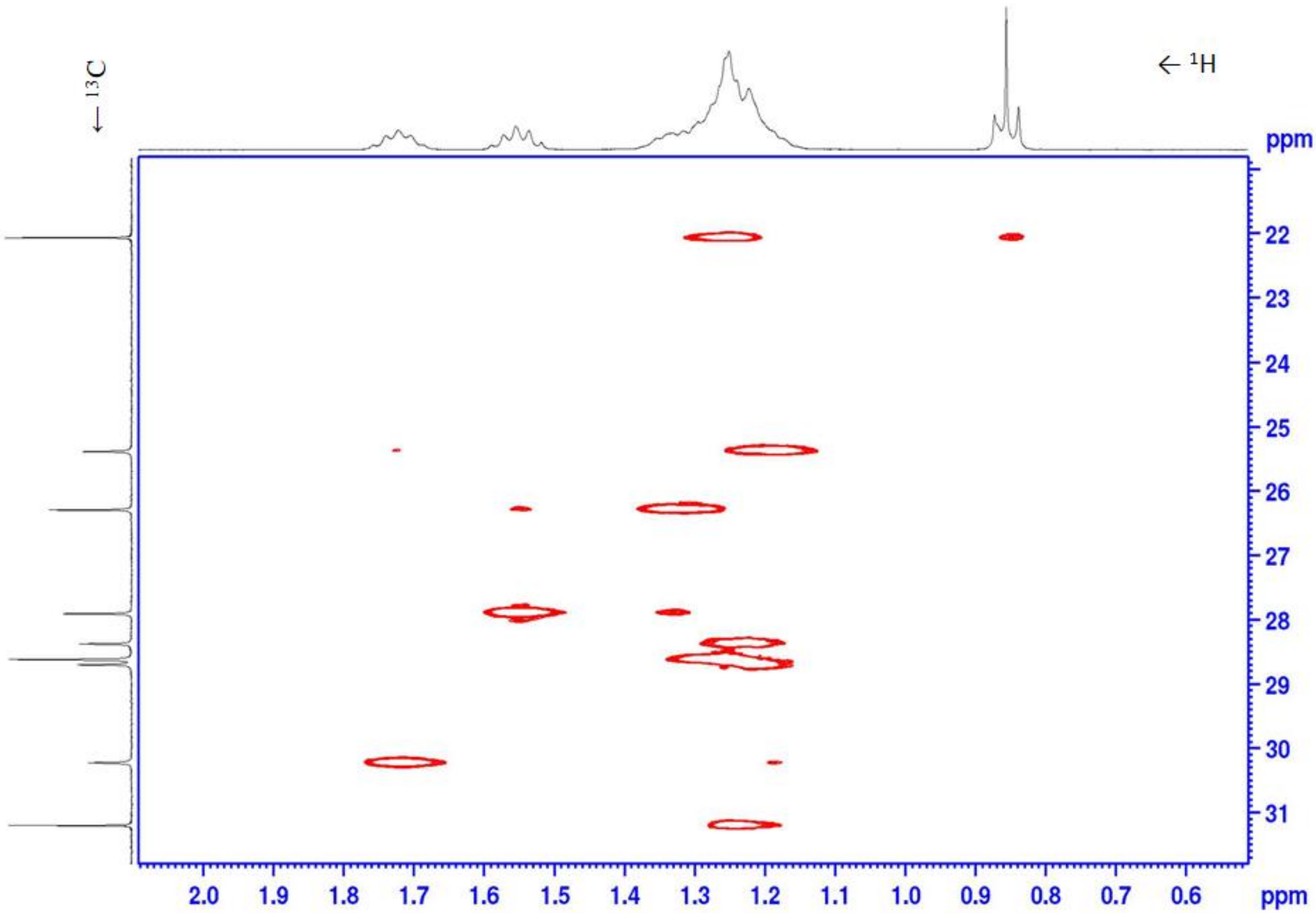


Figure S17. ^{1}H,^{13}C HSQC band selective HSQC spectrum for the ^{13}C shift range from 20 to 32 ppm, 298 K, 400 MHz, with breakthrough of some diagnostic ^{2}J(C.H) couplings.

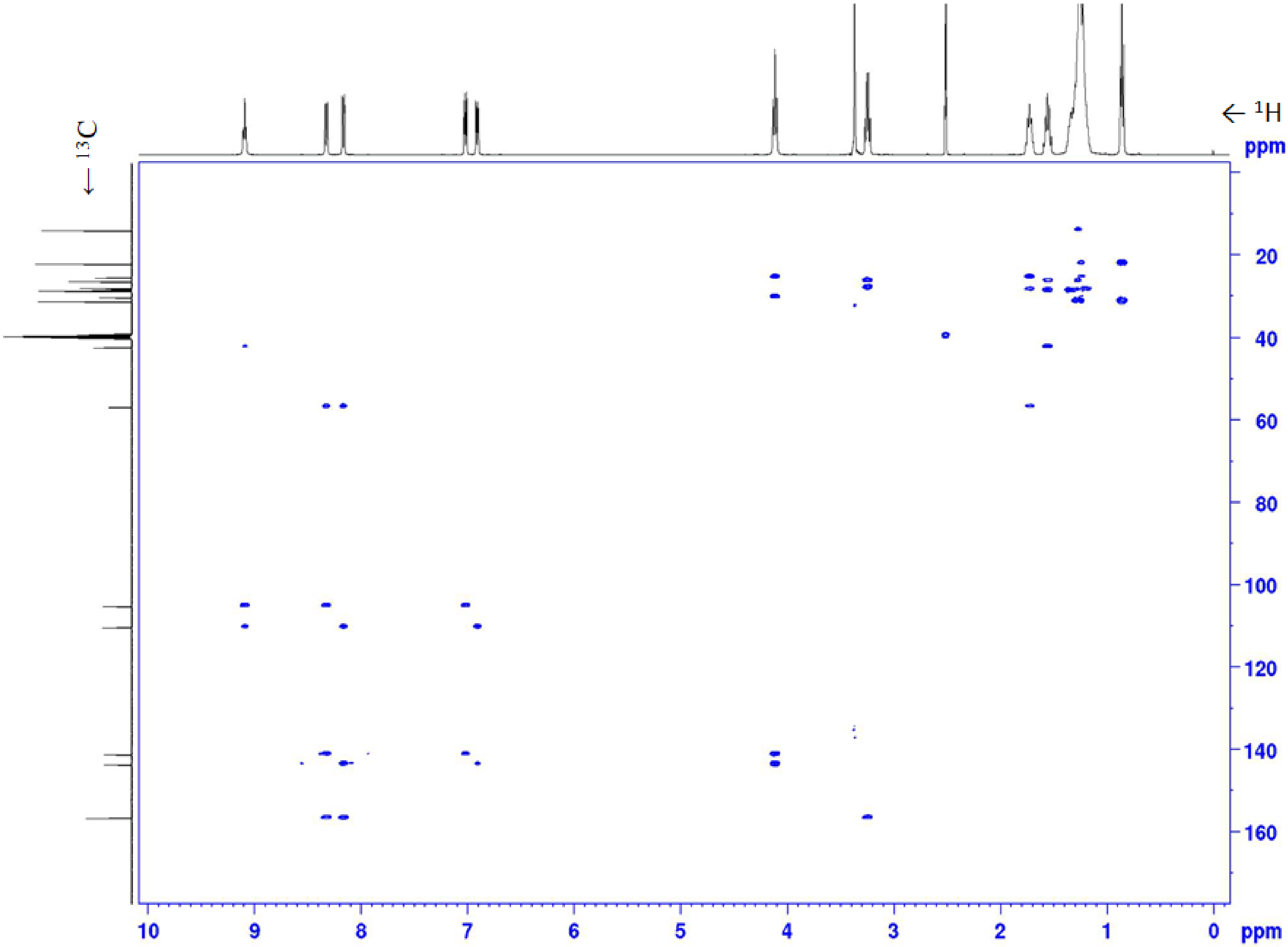


Figure S18. ^{1}H,^{13}C HMBC spectrum, 400 MHz, 298 K, DMSO-d_6.

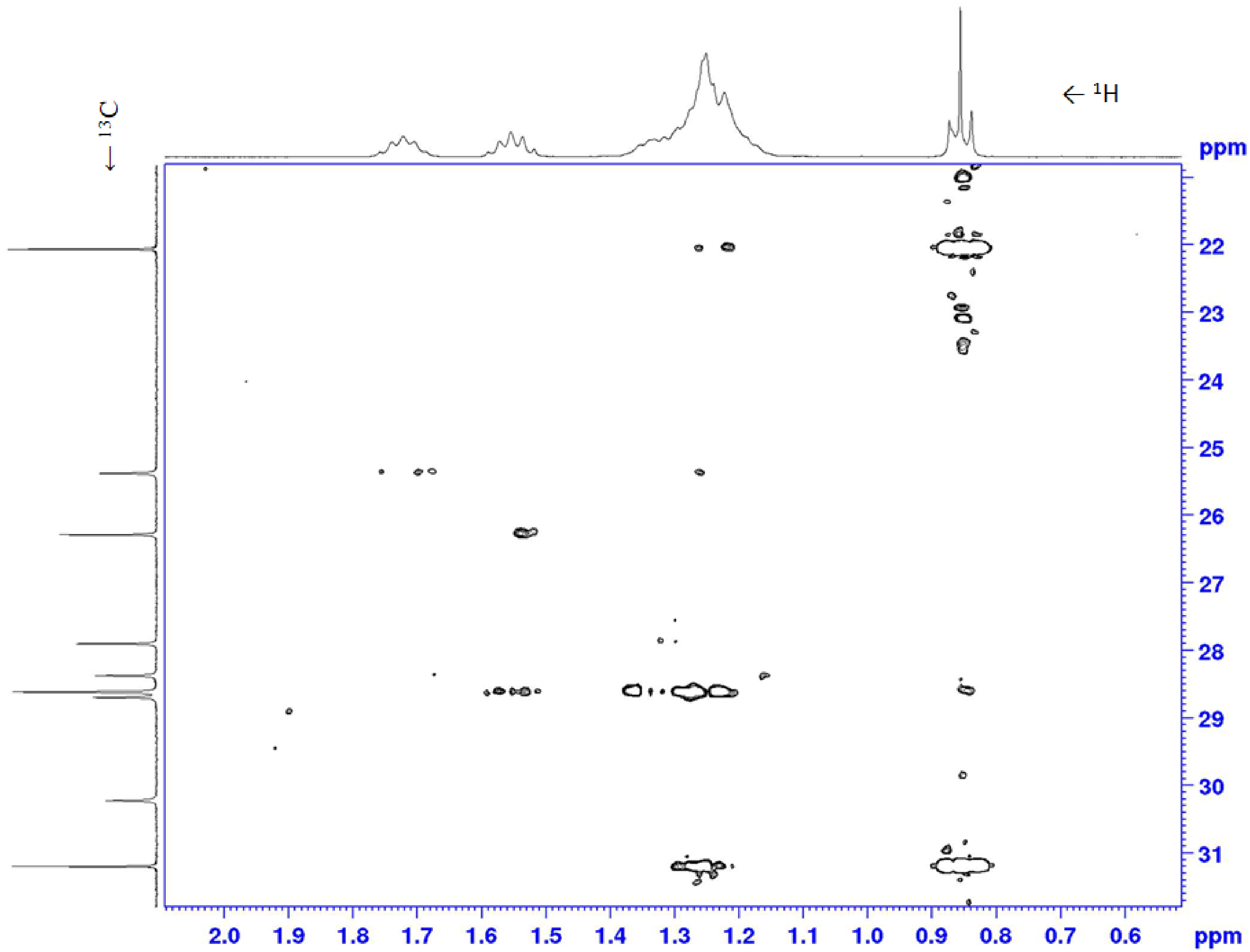


Figure S19. ^{1}H,^{13}C HMBC band selective spectrum for the ^{13}C shift range from 20 to 32 ppm, 298 K, 400 MHz, DMSO-d_6.

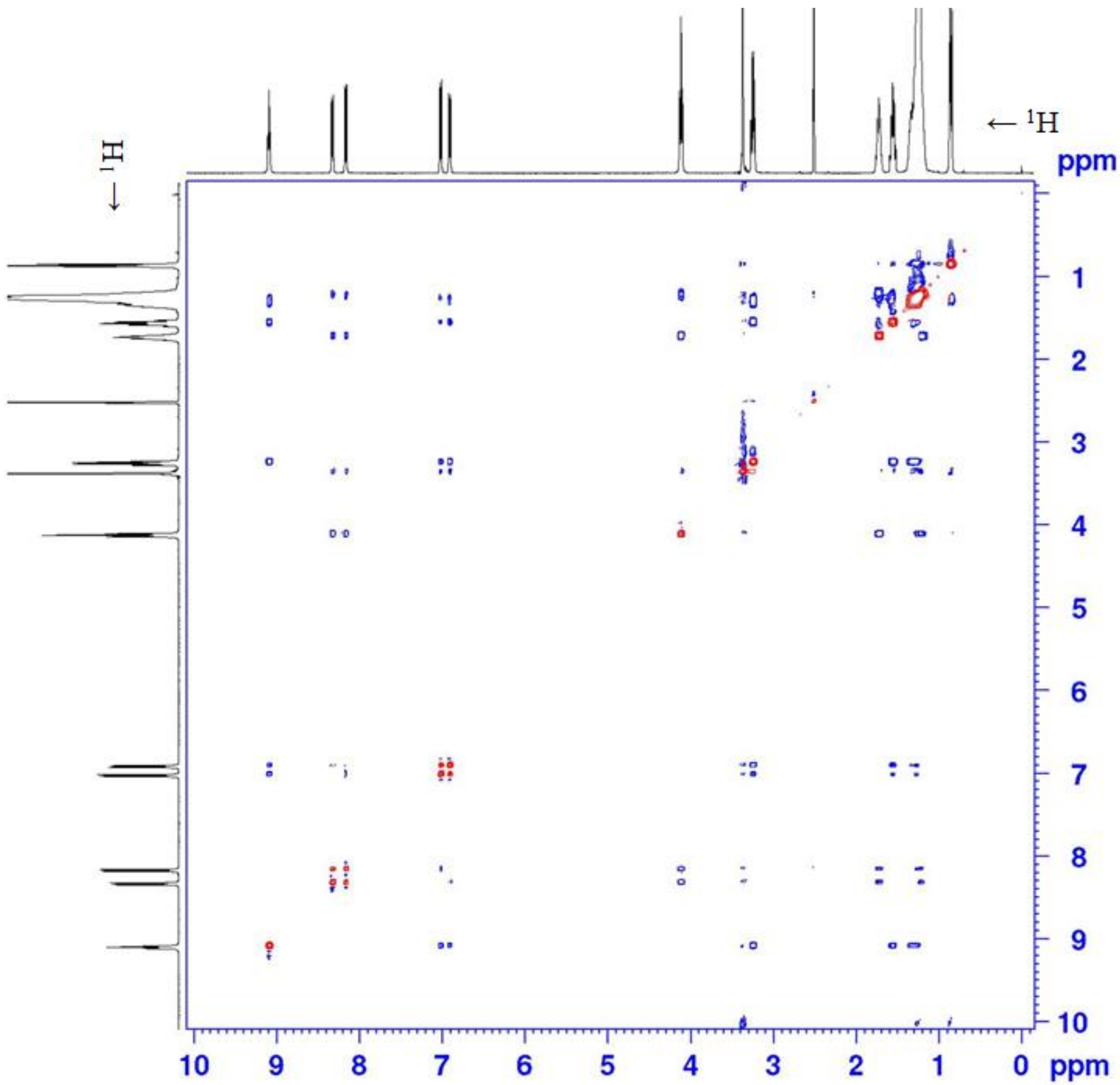


Figure S20. ^{1}H,^{1}H NOESY spectrum, 400 MHz, 298 K, DMSO-d_6, d8 = 0.7 s.

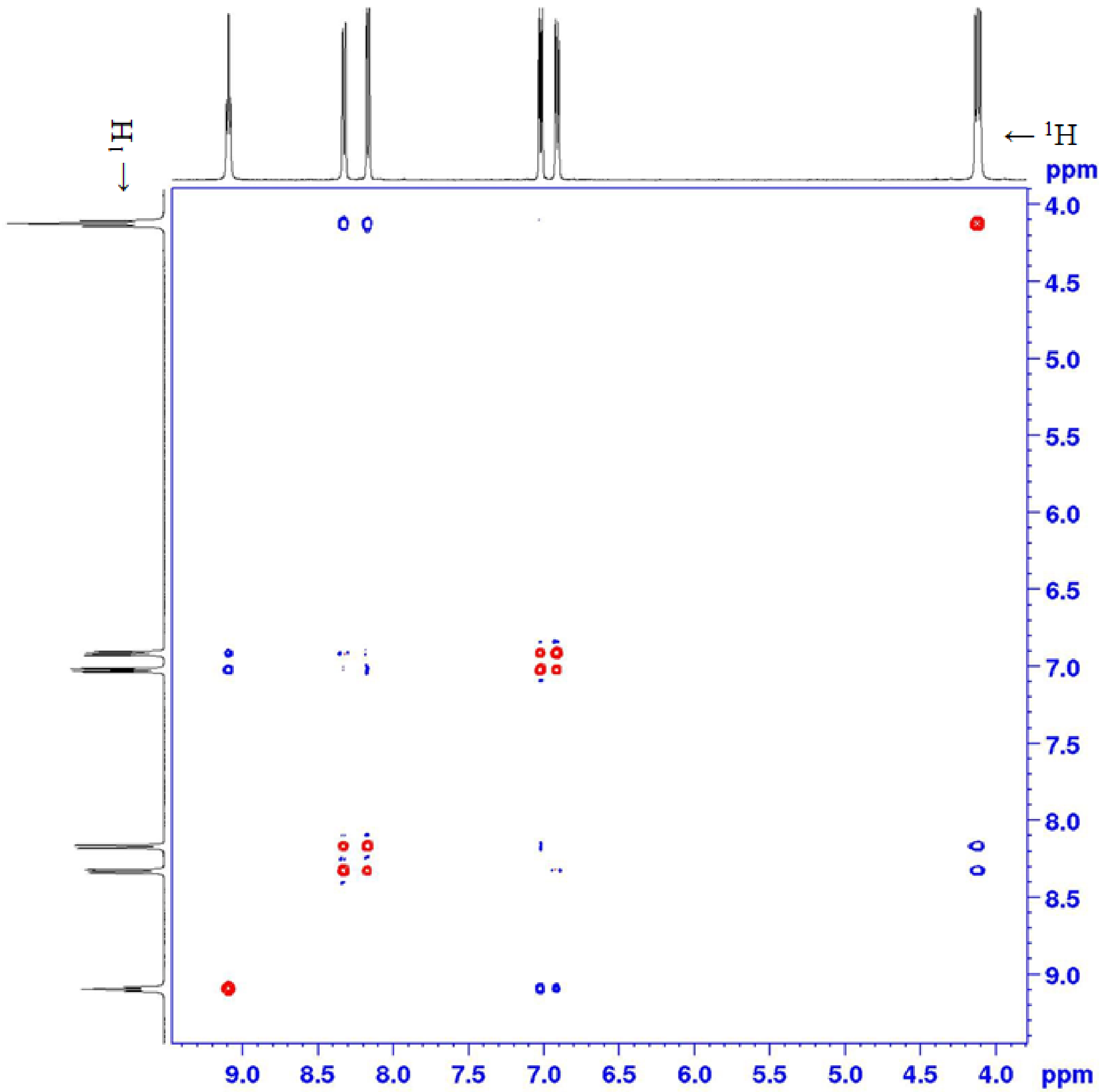
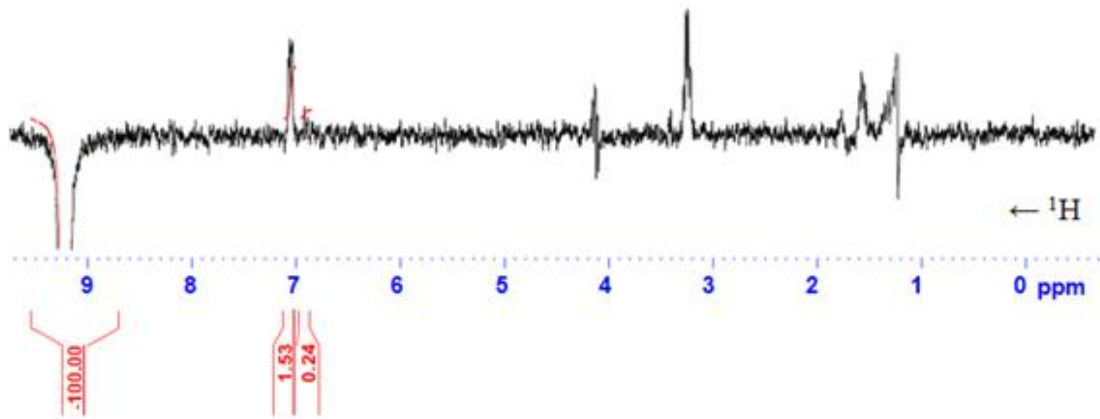


Figure S21. ^1H,^1H NOESY spectrum, 400 MHz, 298 K, DMSO-d_6, expansion, d8 = 0.7 s.

Selective excitation of NH and NOE investigation

a) delay 0.3 s



b) delay 0.5 s

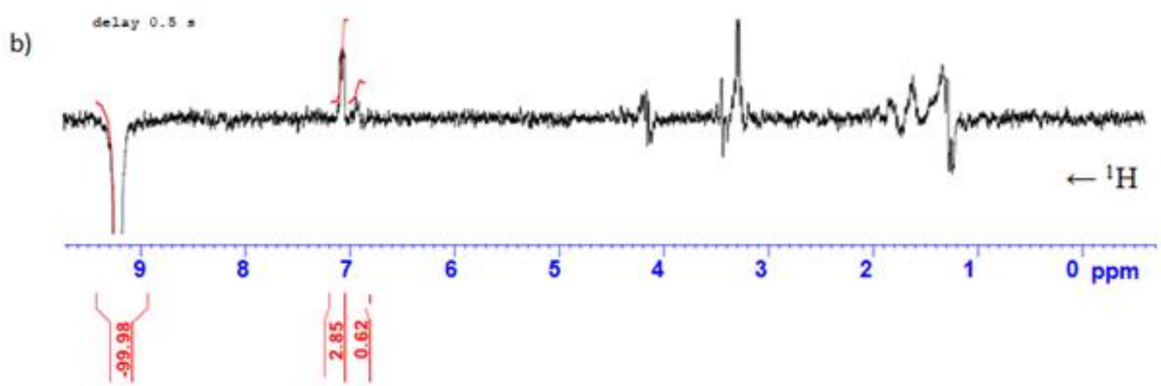


Figure S22a) and b): 1D NOESY spectra with selective excitation of the NH proton with a) d8 = 0.3 s and b) d8 = 0.5 s, 300 MHz, 298 K, DMSO-d_6.

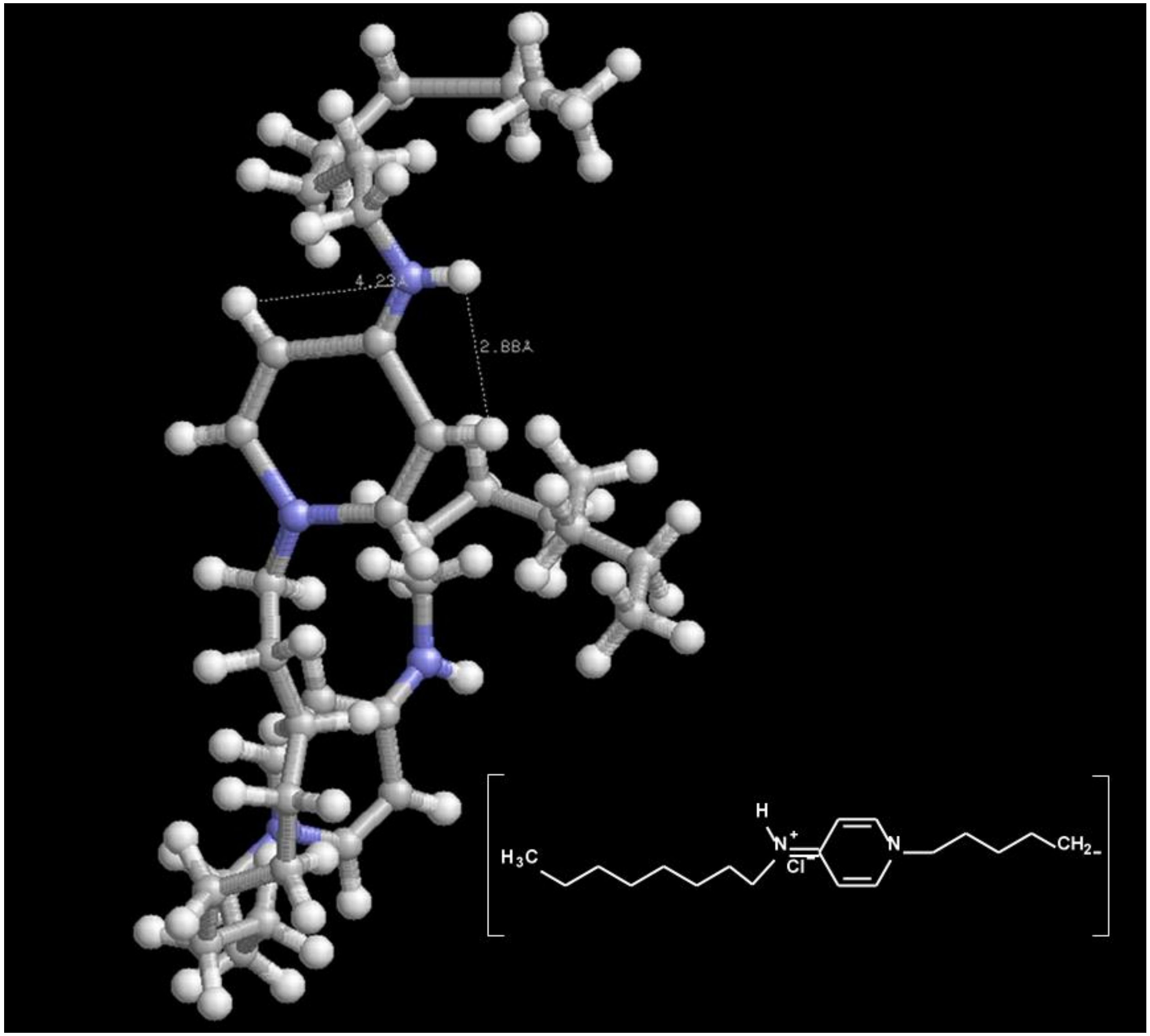


Figure S23

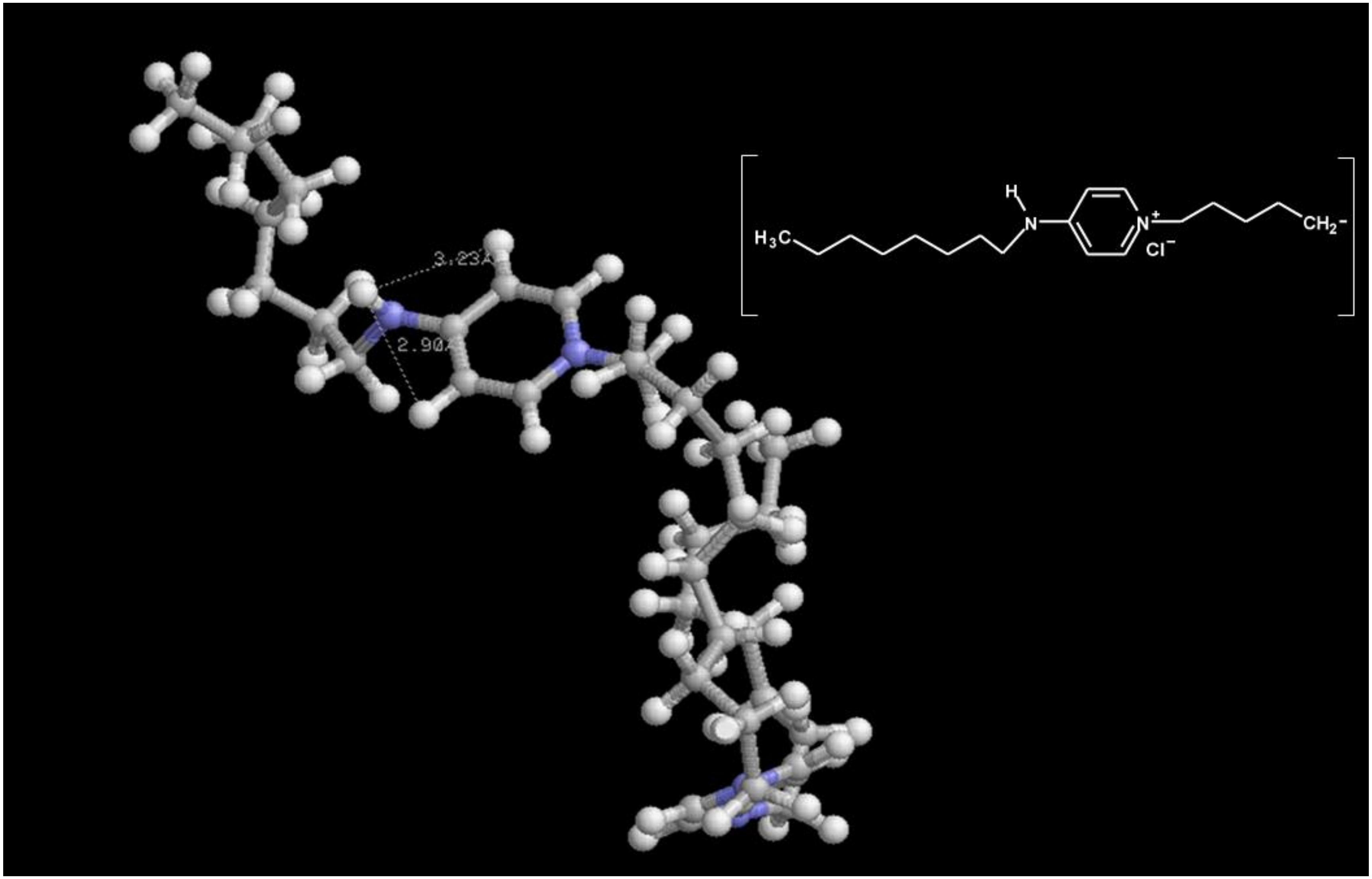


Figure S24

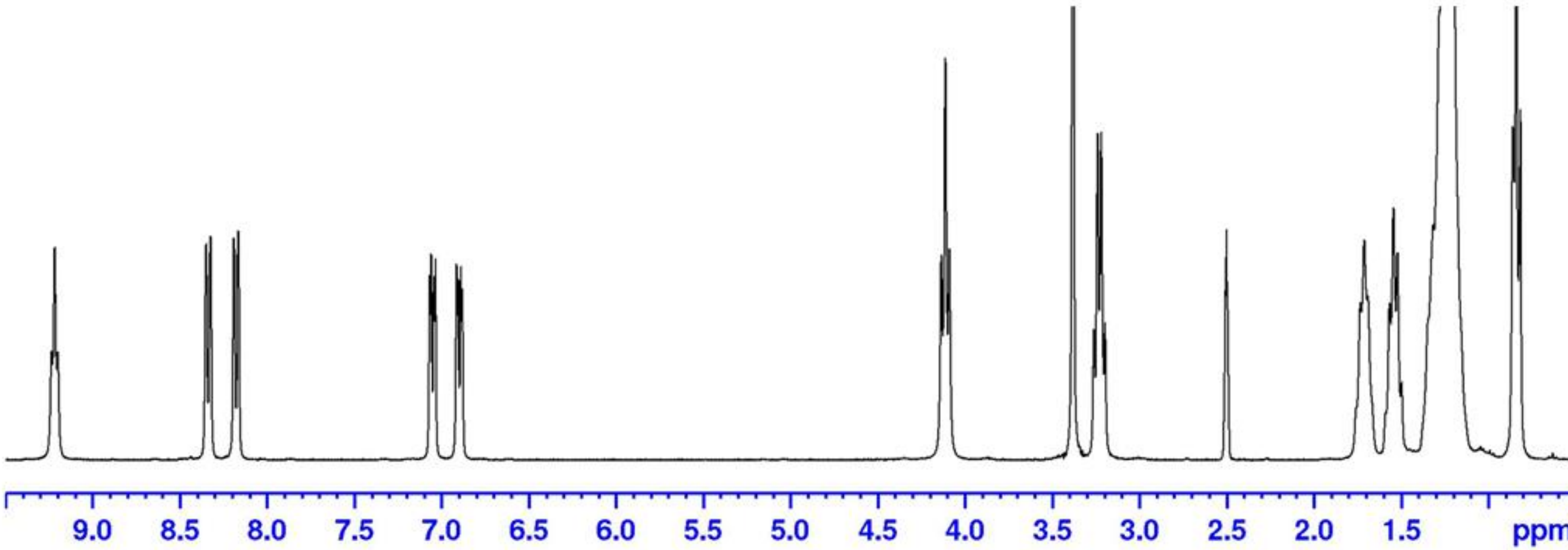


Figure S25. ^{1}H NMR spectrum, 300 MHz, 295 K, DMSO-d_6.

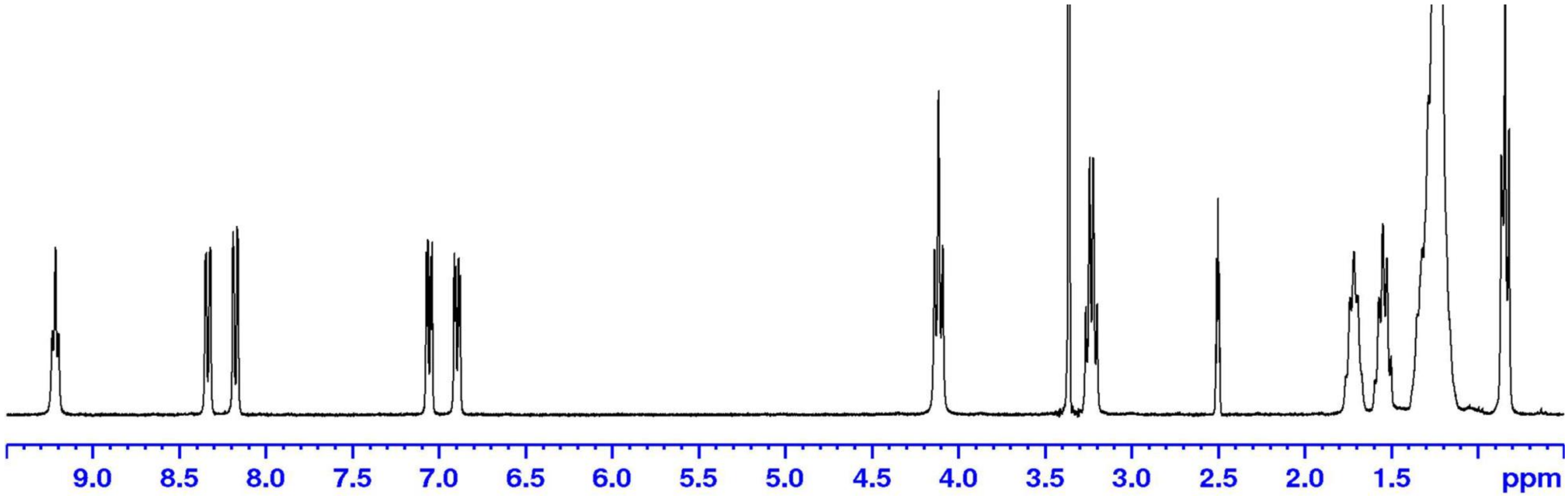


Figure S26. ^{1}H NMR spectrum, 300 MHz, 300 K, DMSO-d_6.

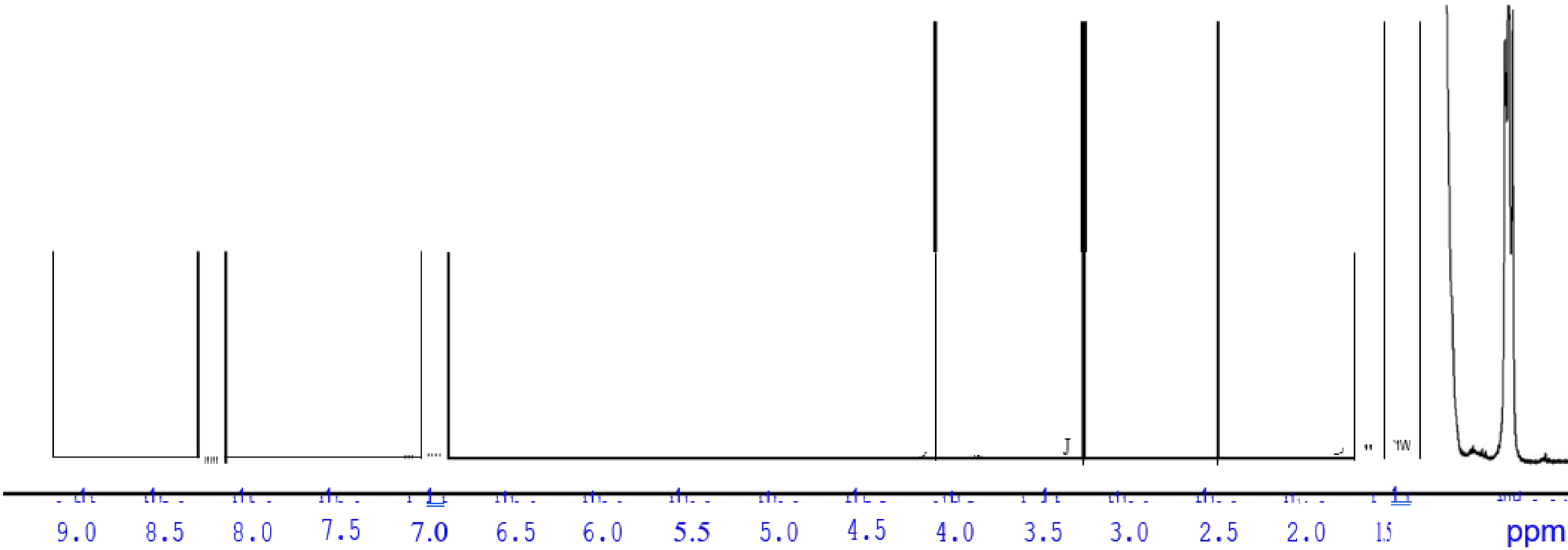


Figure S27. ^{1}H NMR SJlectrum, 300 MHz, 310 K, DMSO-d_6

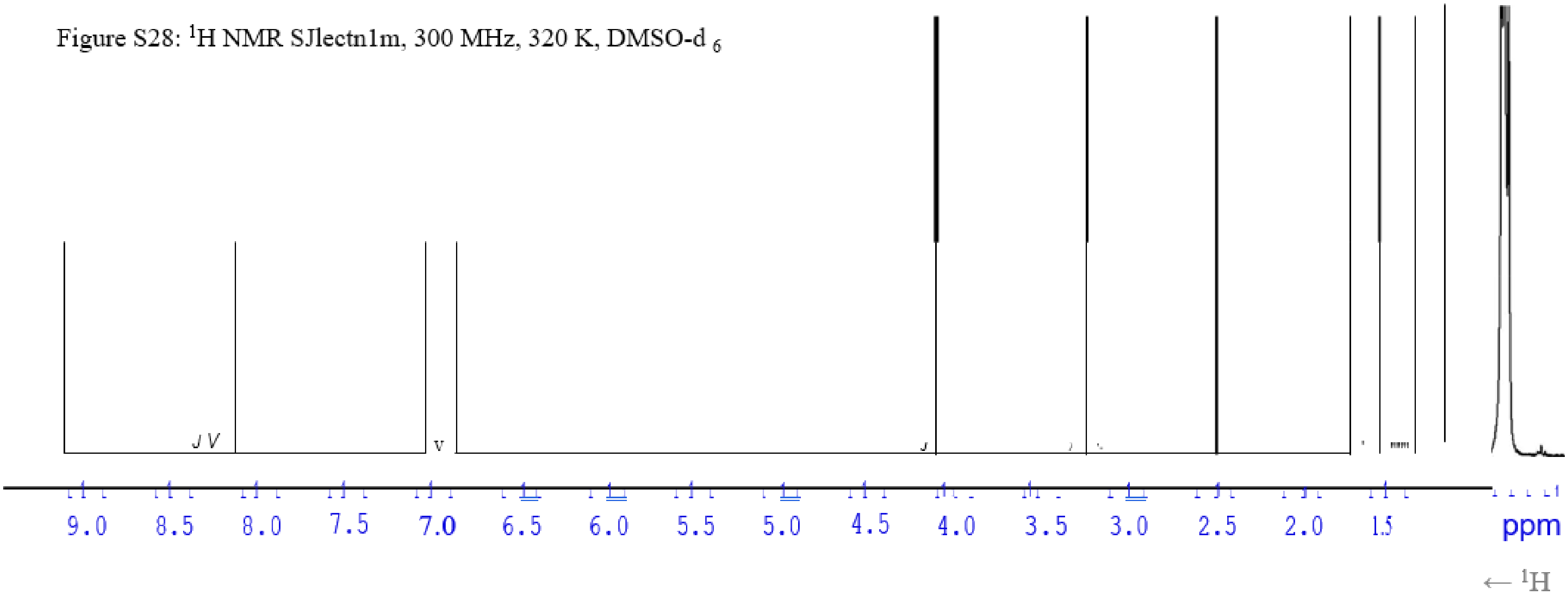


Figure S28. ^{1}H NMR SJlectn1m, 300 MHz, 320 K, DMSO-d_6.

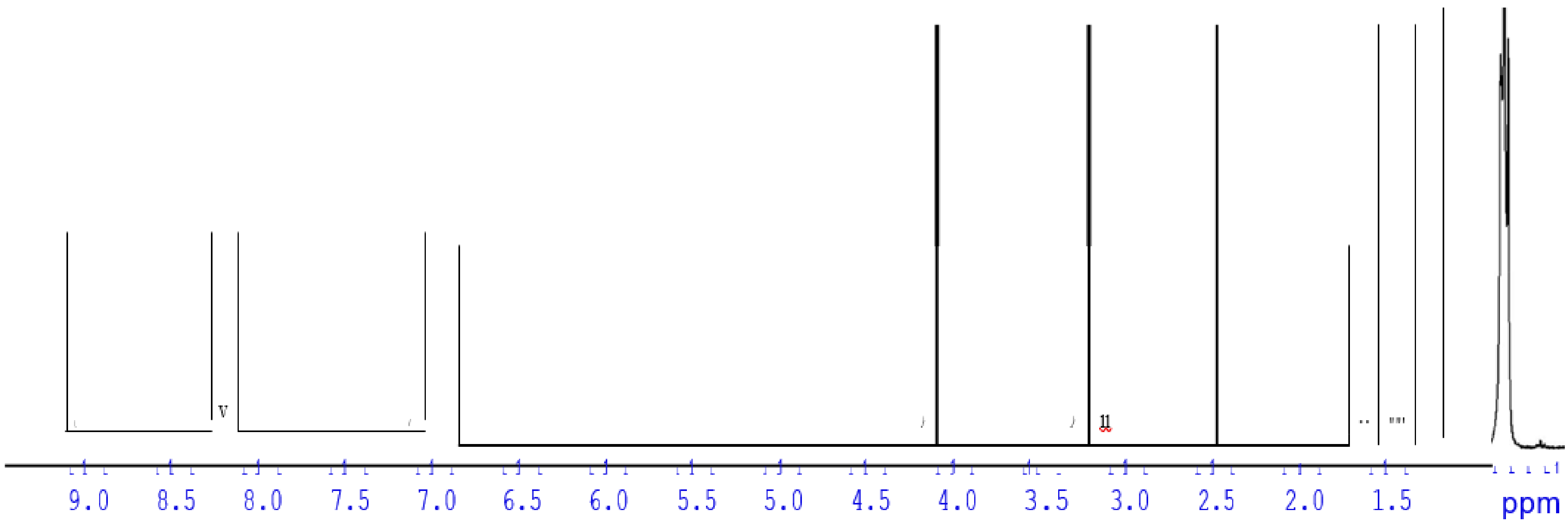


Figure S29: ^{1}H NMR SJlectrum, 300 MHz, 330 K, DMSO-d_6.

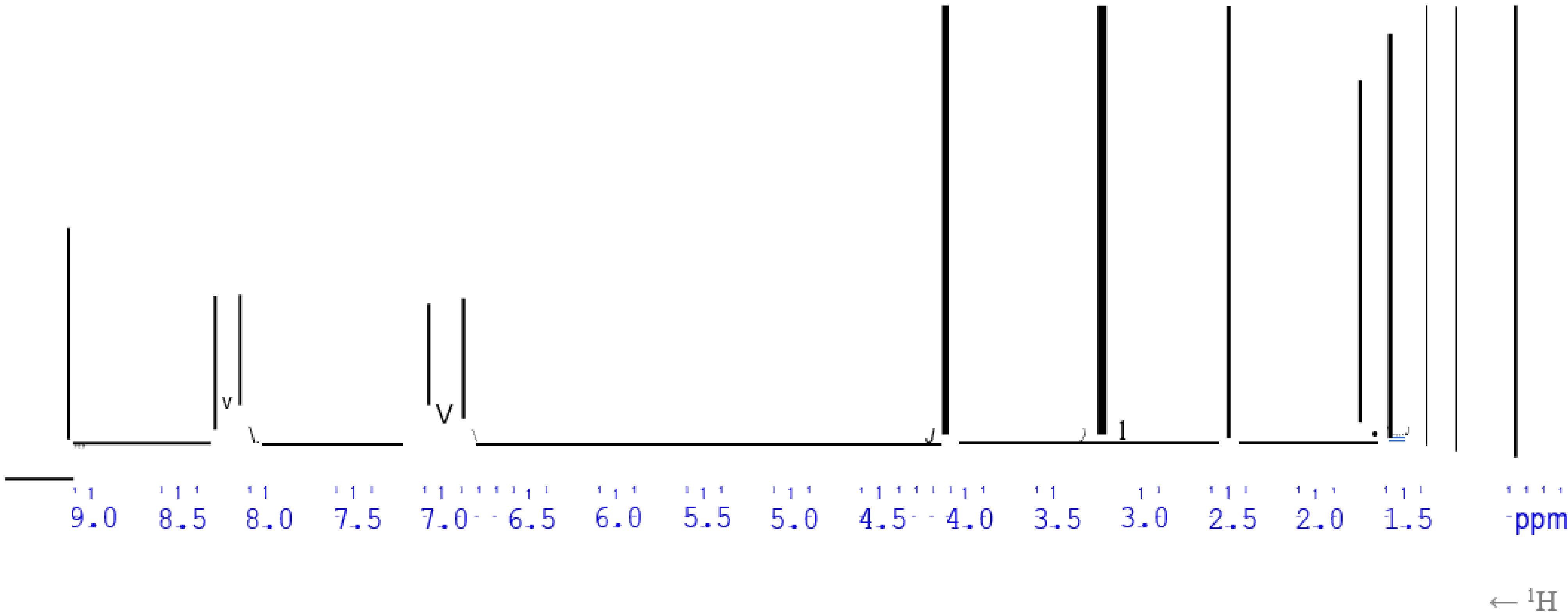


Figure S30. ¹H NMR SJlectn1m, 300 MHz, 340 K, DMSO-d_6.

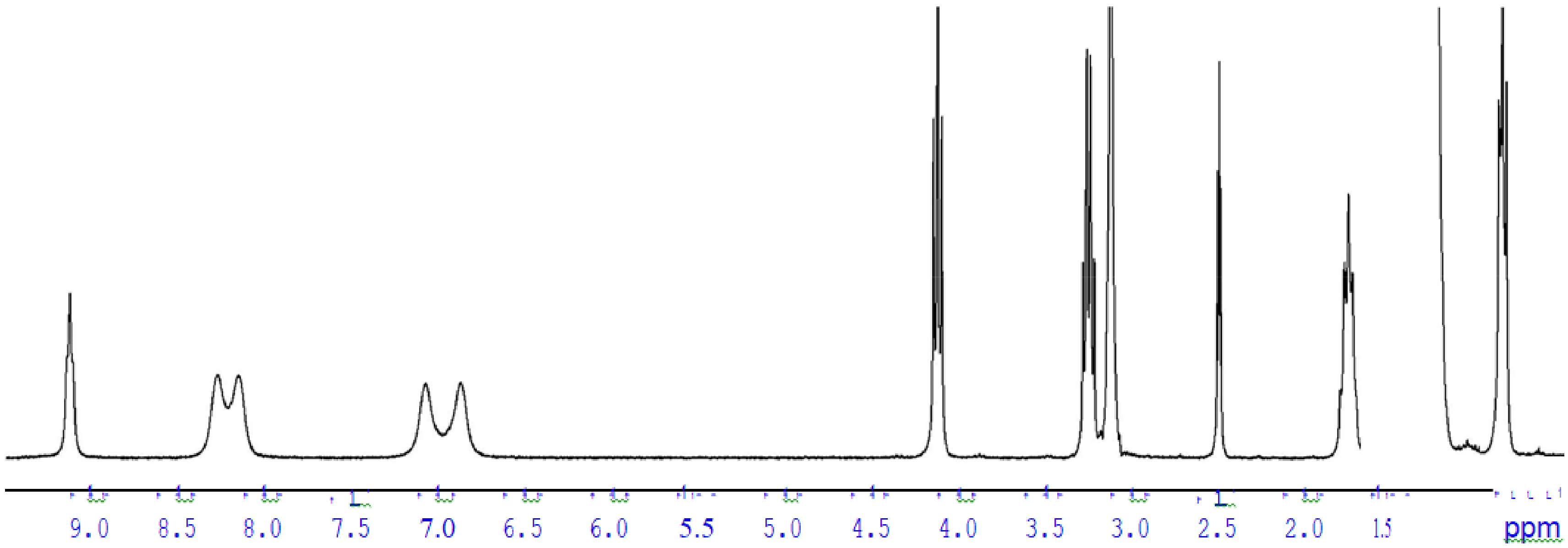


Figure S31. ^{1}H NMR SJlectrum, 300 MHz, 350 K, DMSO-d_6.

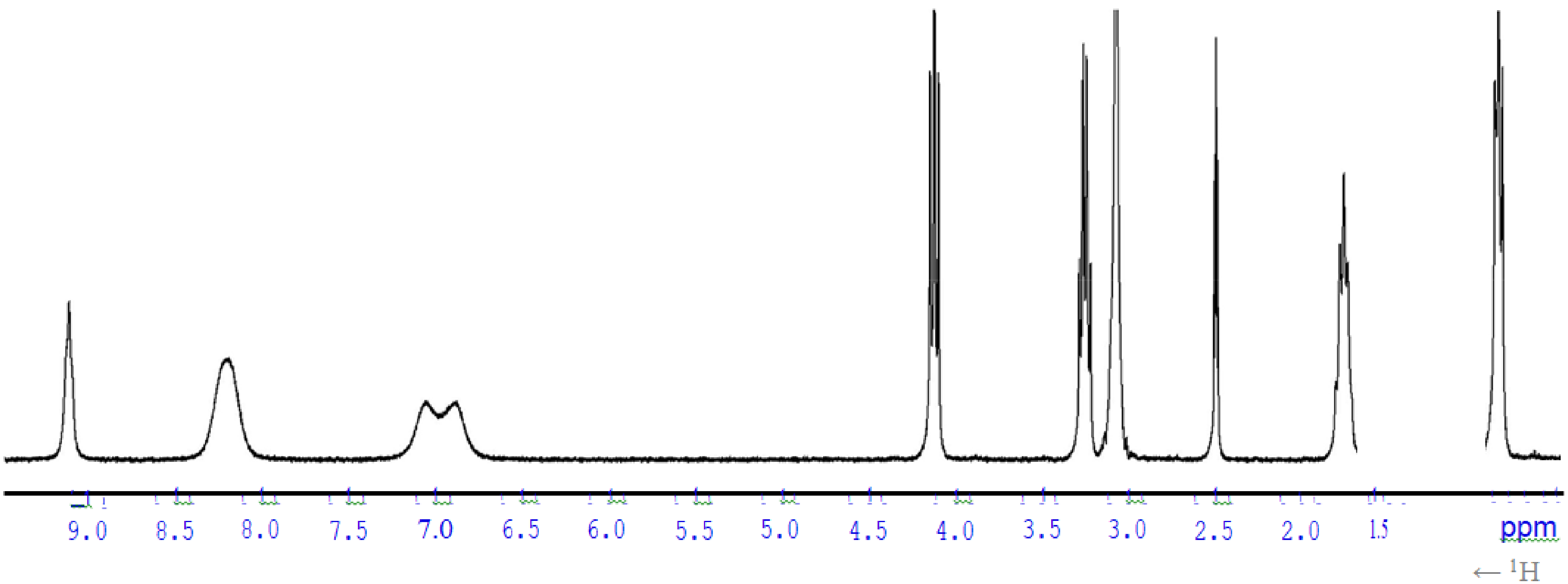


Figure S32: ^{1}H NMR SJlectrum, 300 MHz, 360 K, DMSO-d_6.

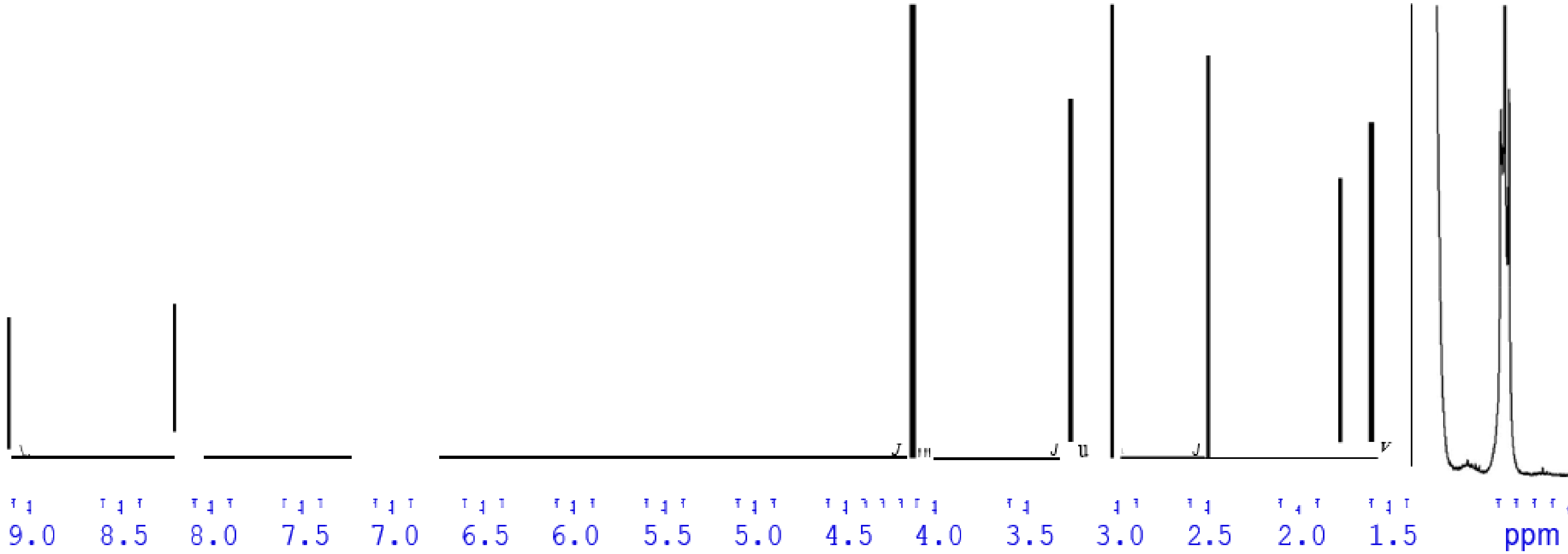


Figure S33: ^{1}H NMR SJlectrum, 300 MHz, 370 K, DMSO-d_{6}.

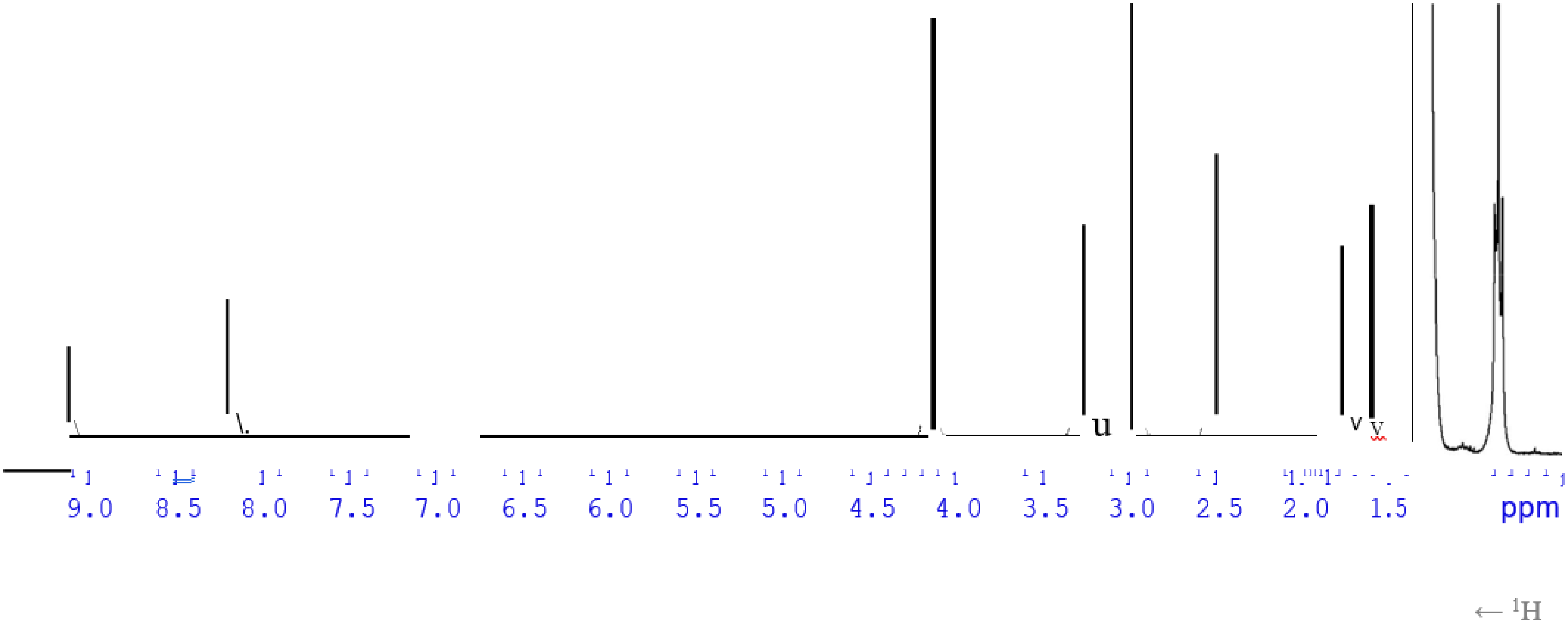


Figure S34. ^{1}H NMR SJlectn1m, 300 MHz, 380 K, DMSO-d$_6$.

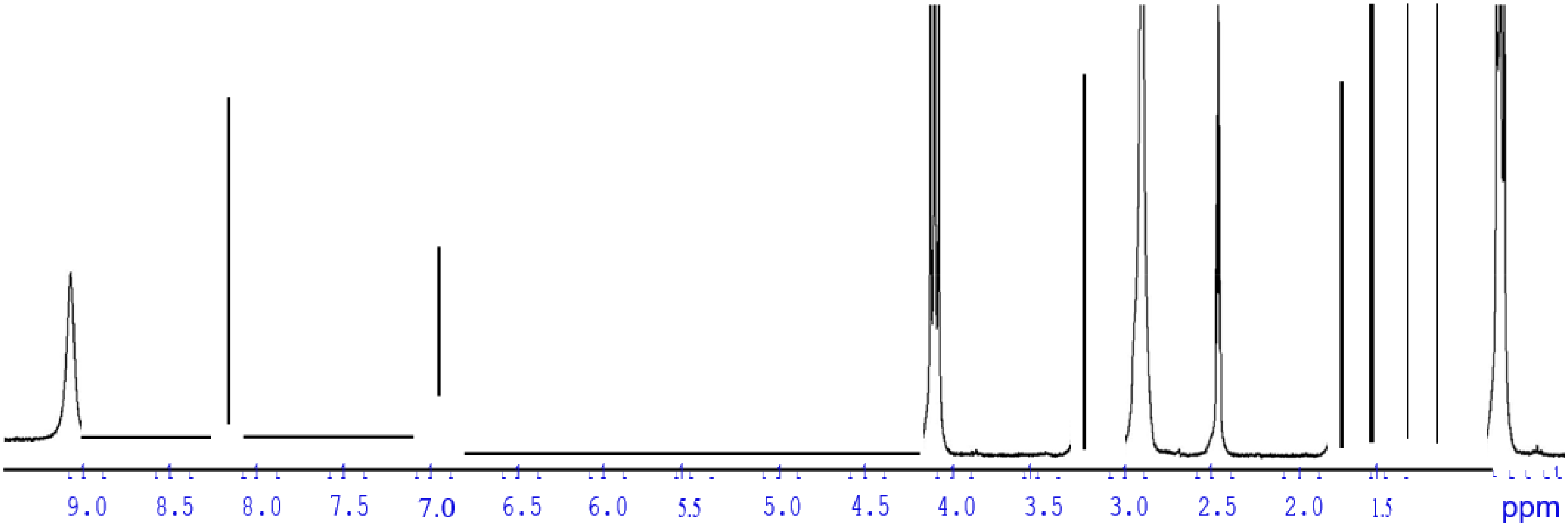


Figure S35: ^{1}H NMR SJ)ect111m, 300 MHz, 390 K, DMSO-d_6.

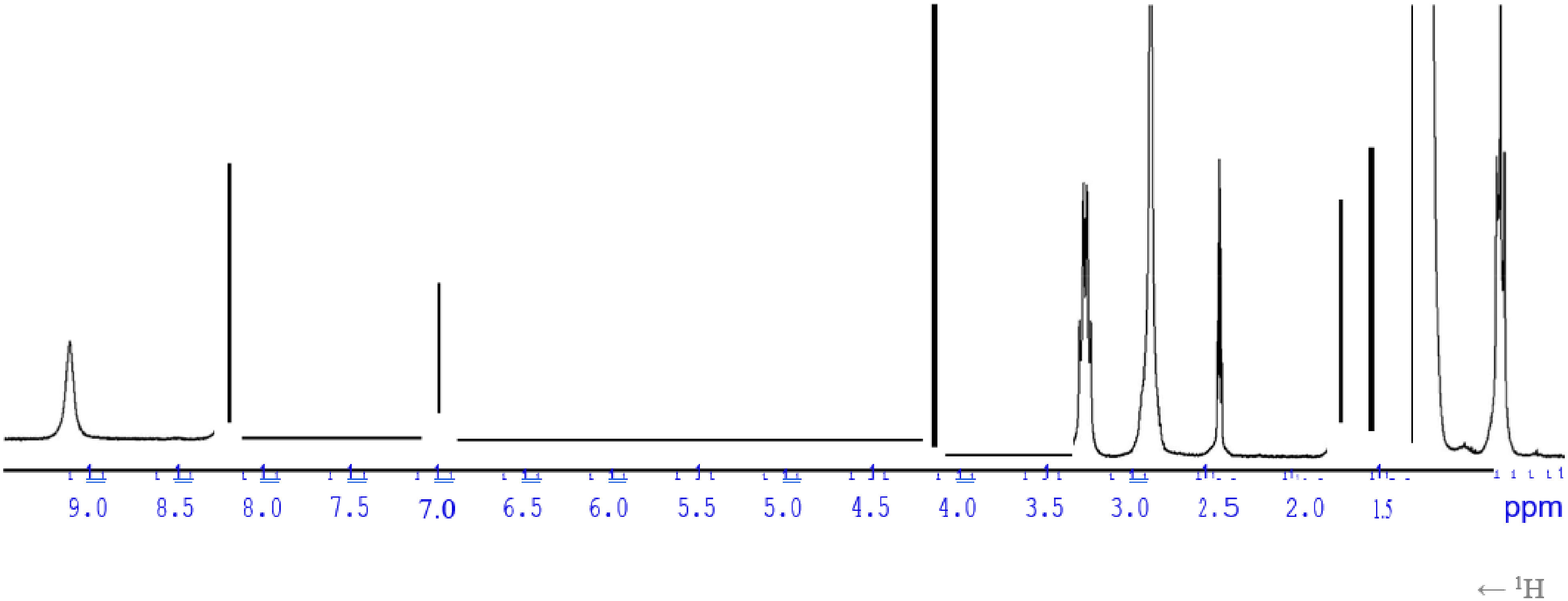


Figure S36: ^{1}H NMR SJlectn1m, 300 MHz, 400 K, DMSO-d_6.

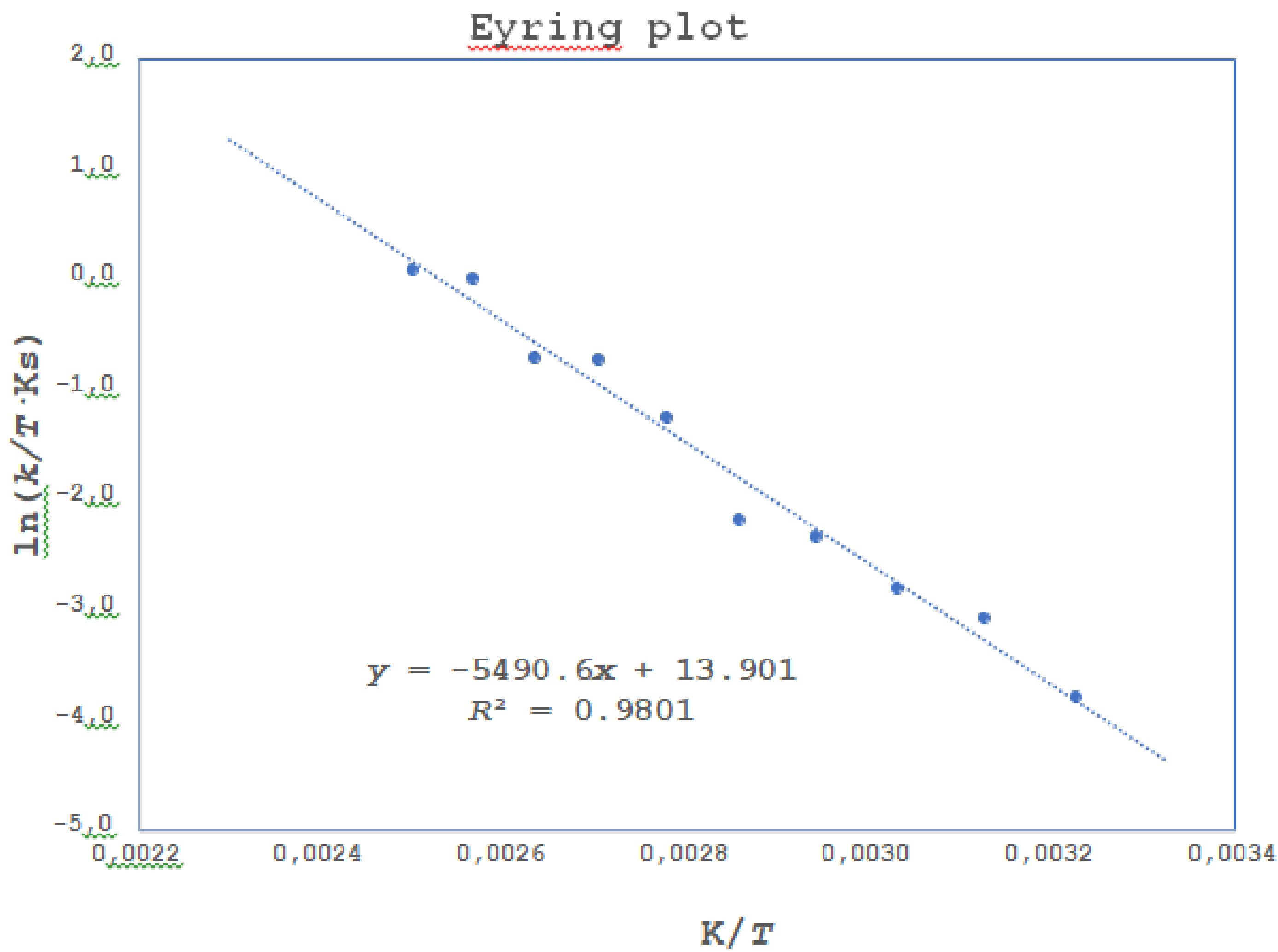


Figure S37. Eyring plot and Table S4 data used for curve fitting (300 MHz data, *n* = 10, *T* from 310 to 400 K).

Table 4

Table S5. Results of curve fitting (400 MHz data)

T/K	k*s
310	7
320	15
330	20
340	33
350	40
360	105
370	180
380	190
390	400
400	440

DH‡ = 45.7 kJ/mol
DS ‡ = -82 J/(mol K)
E_A = 48.6 kJ/mol

Results for an independent experiment at 400 MHz with $n = 8$, T from 308 to 353 K with 5 K intervals (data and plot not shown), deliver the equation $y = -6079.1 + 15.35$ with $R^2 = 0.987$ and the thermodynamic parameters on the right

D*H*‡ = 50.6 kJ/mol
D*S* ‡ = -70 J/(mol K)
E_A = 53.4 kJ/mol

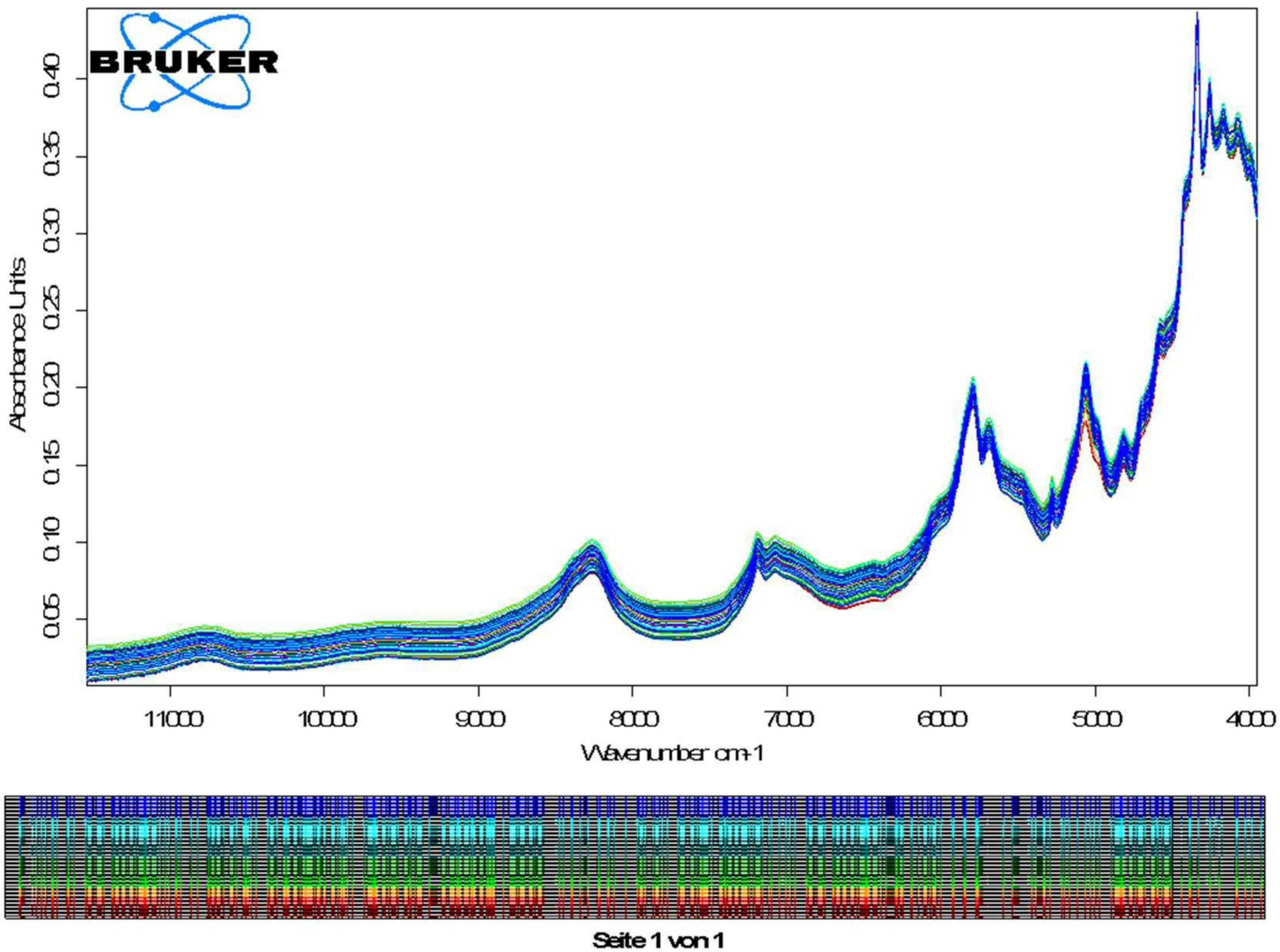


Figure S38. Original NIR spectra of solid-state Octenidine dihydrochloride at different temperatures (25 °C to 60 °C).

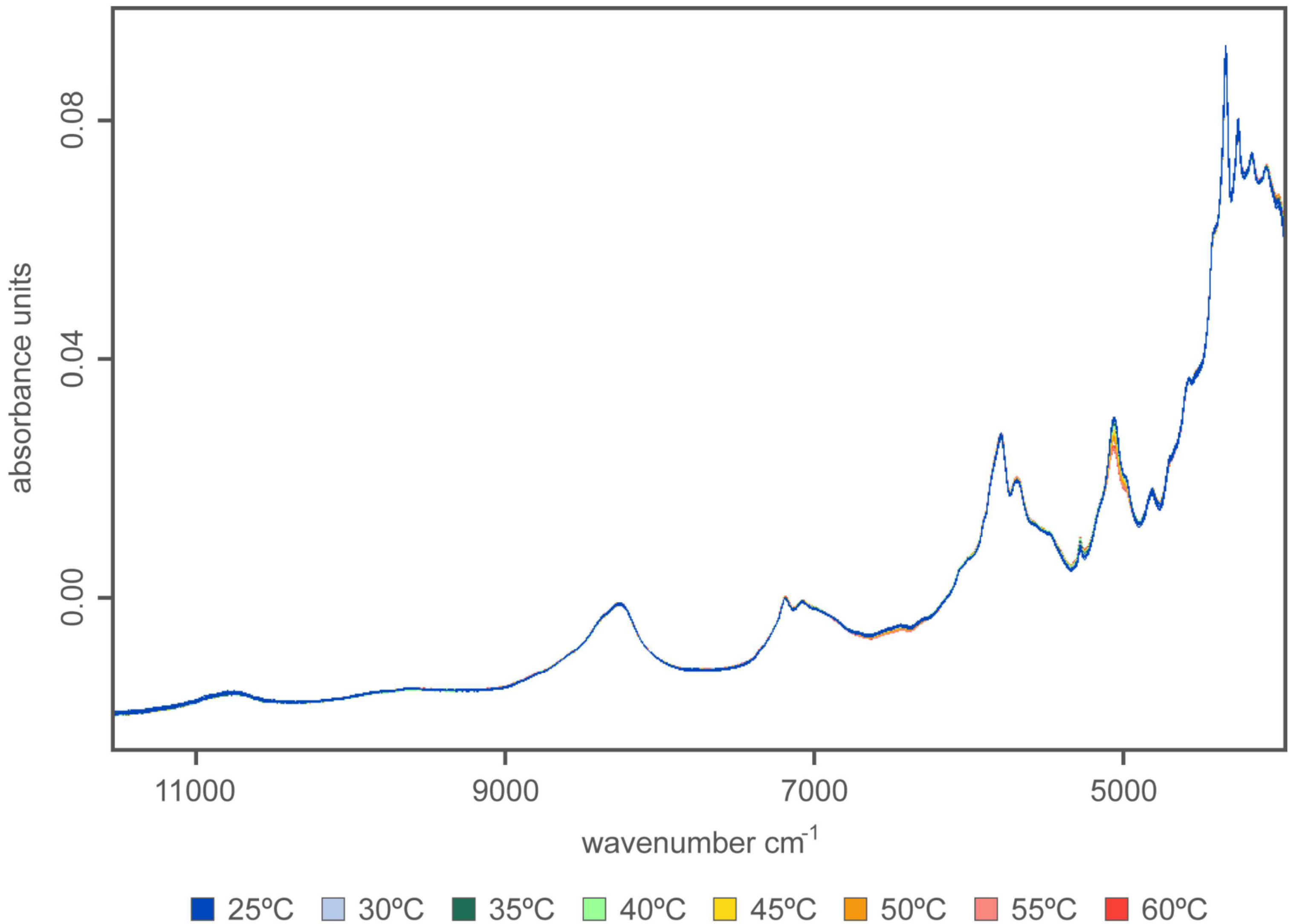


Figure S39: SNV-corrected NIR spectra of solid-state Octenidine dihydrochloride at different temperatures (25 °C to 60 °C).

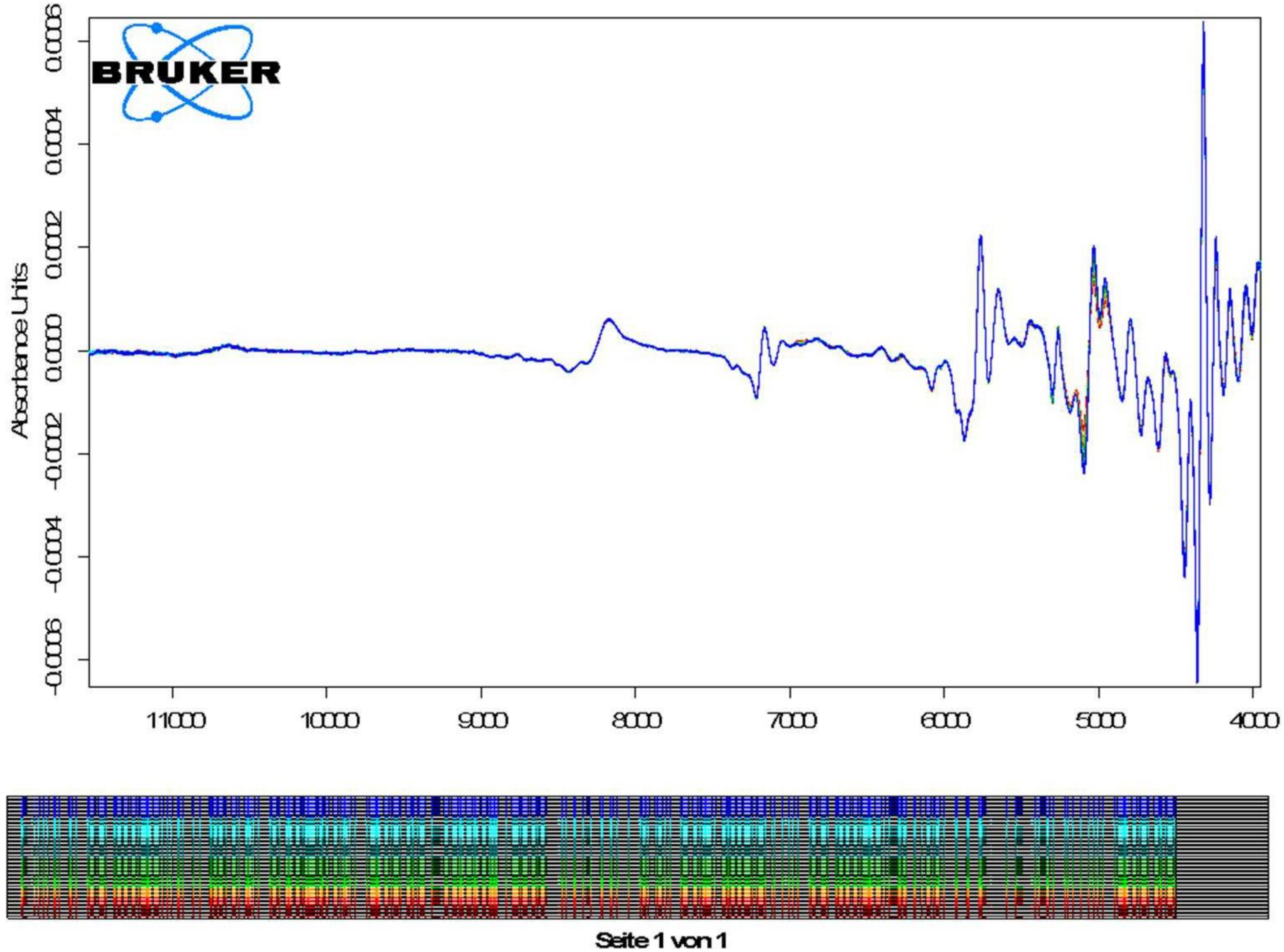
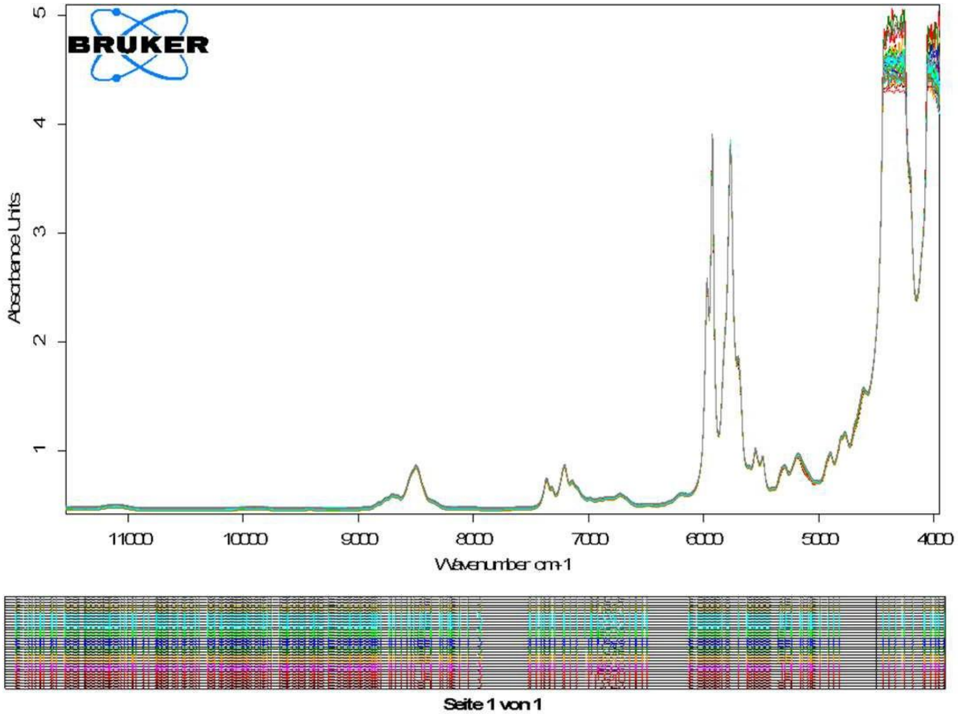
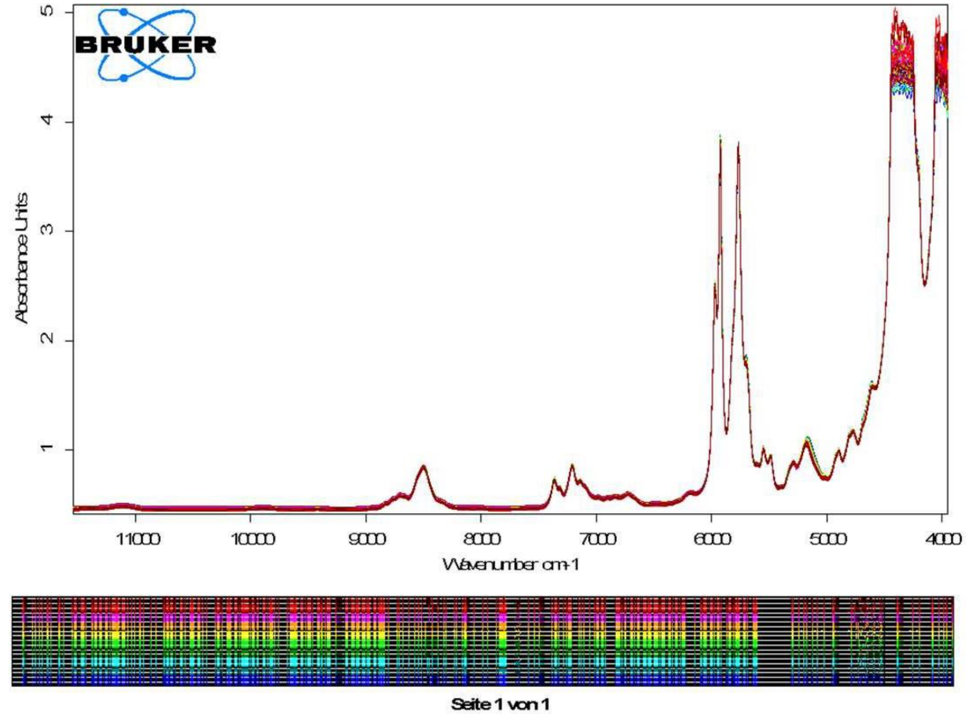


Figure S40. SNV- and 1. Derivative-corrected NIR spectra of solid-state Octenidine dihydrochloride at different temperatures (25 °C to 60 °C).

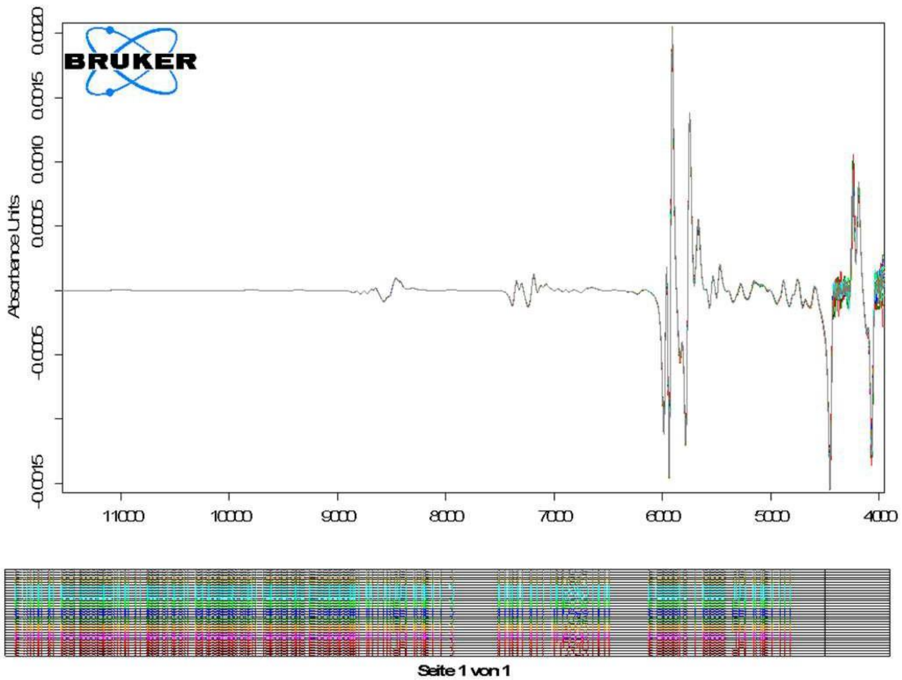


only DMSO solution

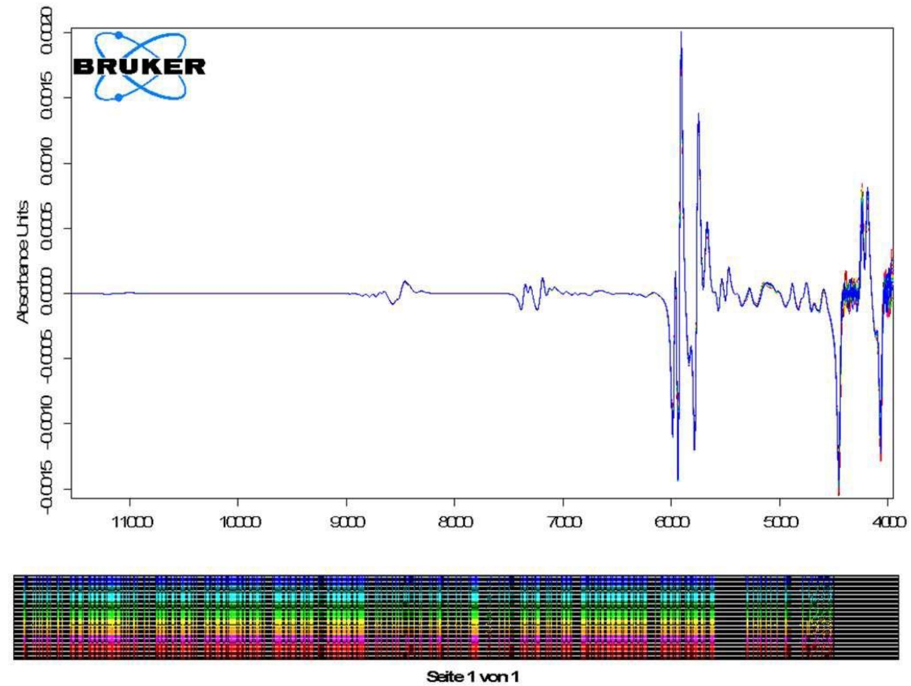


Octenidine-DMSO solution

Figure S41. Original NIR spectra of Octenidine dihydrochloride in DMSO and pure DMSO at different temperatures (25 °C to 60 °C).

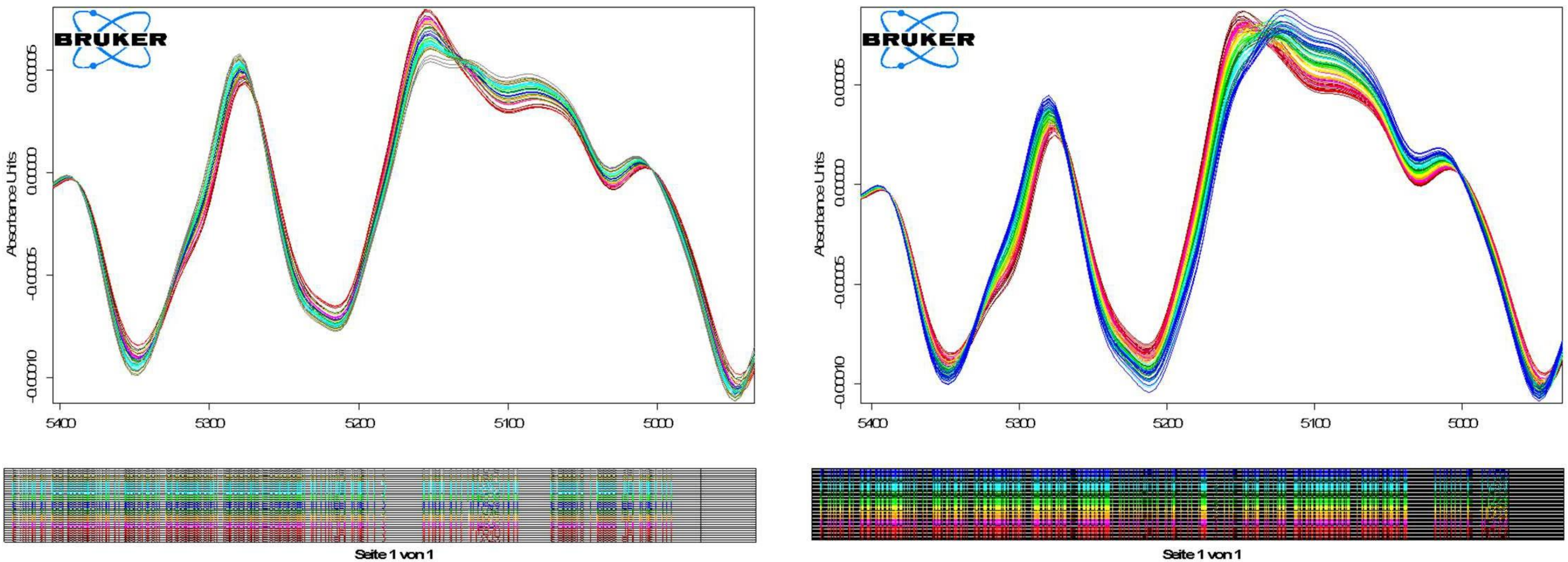


only DMSO solution



Octenidine-DMSO solution

Figure S42. SNV- and 1. Derivative-corrected NIR spectra of Octenidine dihydrochloride in DMSO and pure DMSO at different temperatures (25 °C to 60 °C).



only DMSO solution Octenidine-DMSO solution

Figure S43. SNV- and 1. Derivative-corrected NIR spectra of Octenidine dihydrochloride in DMSO and pure DMSO at different temperatures (25 °C to 60 °C).

