Supporting Information

Bacterial Production of the Tunicate-derived Antitumor Cyclic Depsipeptide Didemnin B

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Table S1. ^{1}H and ^{13}C NMR Data for Didemnin B (Ref. 1c) and **1** in C_5D_5N

		Didemnin B[a]		1[b]	
	position	δ_C	δ_H	δ_C	δ_H
isoSta[1]	NH		7.56		7.58
	C4H	55.8	4.70	55.8	4.71
	C5H	34.3	2.56	34.3	2.59
	$C6H_2$	28.3	1.72	28.3	1.74
			1.46		1.47
	$C7H_3$	12.4	1.10	12.4	1.12
	CH_3-C5	14.6	1.17	14.6	1.19
	C3H	67.0	4.79	67.0	4.82
	$C2H_a$	41.1	4.34	41.0	4.36
	$C2H_b$		3.06		3.06
	CO	172.6		172.6	
Hip[2]	C4H	80.6	5.65	80.6	5.67
	C5H	30.4	2.48	30.3	2.50
	$C6H_3$	19.0	0.83	19.0	0.83
	CH_3-C5	16.9	0.88	16.8	0.90
	C3	205.6		205.5	
	C2H	49.5	4.72	49.5	4.75
	CH_3-C2	16.0	1.75	15.9	1.76
	CO	169.9		169.9	
Leu[3]	NH		8.47		8.49
	$C_\alpha H$	49.9	5.19	49.9	5.19
	$C_\beta H_a$	42.1	1.85	42.0	1.83
	$C_\beta H_b$		1.55		1.57
	$C_\gamma H$	24.2	1.79	24.7	1.80
	$C_\delta H_3$	23.7	0.88	23.8	0.89
	$C_\delta' H_3$	21.1	0.98	21.1	1.00
	CO	171.1		171.1	
Pro[4]	$C_\alpha H$	57.6	4.75	57.6	4.75
	$C_\beta H_a$	28.7	1.82	28.7	1.84
	$C_\beta H_b$		1.65		1.69
	$C_\gamma H_a$	26.0	1.71	26.0	1.72
	$C_\gamma H_b$		1.53		1.52
	$C_\delta H_a$	47.6	3.55	47.5	3.56
	$C_\delta H_b$		3.37		3.34
	CO	170.9		170.9	
N, *O*-diMeTyr[5]	NCH_3	38.6	2.64	38.5	2.63
	$C_\alpha H$	65.8	4.20	65.8	4.23
	$C_\beta H_a$	34.6	3.60	34.6	3.61
	$C_\beta H_b$		3.52		3.51
	C_γ	130.6		130.6	
	$C_\delta H$	131.0	7.25	131.0	7.27
	$C_\varepsilon H$	114.4	7.00	114.4	7.01
	C_ζ	159.1		159.0	
	OCH_3	55.2	3.72	55.2	3.73
	CO	169.3		169.3	
Thr[6]	NH		8.25		8.29
	$C_\alpha H$	58.8	5.07	58.7	5.08
	$C_\beta H$	71.0	5.81	71.0	5.83
	CH_3C_β	17.1	1.80	17.0	1.82
	CO	169.7		169.6	
D-MeLeu[7]	NCH_3	31.3	3.24	31.3	3.24
	$C_\alpha H$	55.0	5.80	55.0	5.80
	$C_\beta H_a$	36.6	2.06	36.6	2.05
	$C_\beta H_b$		1.72		1.74
	$C_\gamma H$	24.9	1.56	25.2	1.54
	$C_\delta H_3$	23.6	0.86	23.5	0.89
	$C_\delta' H_3$	21.4	0.97	21.4	1.00
	CO	172.6		172.5	
Pro[8]	$C_\alpha H$	56.7	4.72	56.7	4.75
	$C_\beta H_a$	27.7	2.02	27.7	2.06
	$C_\beta H_b$		1.91		1.90
	$C_\gamma H_a$	24.8	2.06	24.9	2.04
	$C_\gamma H_b$		1.84		1.78
	$C_\delta H_a$	47.0	3.89	47.0	3.91
	$C_\delta H_b$		3.67		3.66
	CO	173.7		173.7	
Lac[9]	C2H	66.9	4.53	66.9	4.53
	CH_3-C2	20.3	1.49	20.3	1.51
	CO	173.6		173.6	

[a] 400 MHz for ^{1}H NMR and 100.53 MHz for ^{13}C NMR. [b] 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR.

Table S2. ^{1}H and ^{13}C NMR Data for **1** and **2** in $CDCl_3$

		1		**2**	
	position	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)
isoSta^{1} or norSta^{1}	NH		7.20, d (9.7)		7.31, d (10.2)
	C4H	55.4	4.10, m	57.5	4.00, m
	C5H	34.0	1.85, m	27.9	1.98, m
	$C6H_2$ or $C6H_3$	27.1	1.43, m	17.9	0.93 d (6.8)
			1.20, m		
	$C7H_3$	11.6	0.92, t (7.2)		
	CH_3-C5	14.7	0.91, d (6.8)	20.3	0.97, d (6.8)
	C3H	67.9	4.06, m	68.5	4.07, m
	$C2H_a$	38.8	3.27, brd (16.9)	38.6	3.11, brd (16.9)
	$C2H_b$		2.64, dd (16.9, 10.3)		2.69, dd (16.9, 10.3)
	CO	172.4		172.4	
Hip^{2}	C4H	81.4	5.19, d (3.4)	81.7	5.16, d (3.4)
	C5H	31.3	2.36, m	31.3	2.36, m
	$C6H_3$	18.6	0.91, d (6.8)	18.5	0.90, d (6.8)
	CH_3-C5	16.9	0.88, d (6.8)	17.0	0.89, d (6.8)
	C3	205.0		204.8	
	C2H	49.5	4.25, q (6.9)	49.5	4.24, q (6.9)
	CH_3-C2	15.2	1.33, d (6.9)	15.2	1.33, d (6.9)
	CO	169.6		169.6	
Leu^{3}	NH		7.81, d (9.2)		7.78, d (9.3)
	$C_\alpha H$	49.5	4.81, ddd (12, 9.5, 2.0)	49.8	4.81, m
	$C_\beta H_a$	41.3	1.61, m	41.2	1.61, m
	$C_\beta H_b$		1.22, m		1.22, m
	$C_\gamma H$	24.8	1.52, m	24.8	1.54, m
	$C_\delta H_3$	23.7	0.94, d (6.8)	23.7	0.94, d (6.8)
	C_δ'H_3	20.9	0.91, d (6.8)	21.0	0.91, d (6.8)
	CO	171.2		171.3	
Pro^{4}	$C_\alpha H$	57.2	4.64, dd (8.0, 5.2)	57.2	4.63, dd (7.8, 5.4)
	$C_\beta H_a$	27.9	2.14, m	28.0	2.15, m
	$C_\beta H_b$		1.77, m		1.79, m
	$C_\gamma H_a$	25.0	2.14, m	25.1	2.15, m
	$C_\gamma H_b$		2.04, m		2.04, m
	$C_\delta H_a$	46.9	3.70, m	47.0	3.71, m
	$C_\delta H_b$		3.61, m		3.61, m
	CO	170.6		170.6	
N, *O*-diMeTyr^{5}	NCH_3	38.7	2.56, s	38.7	2.58, s
	$C_\alpha H$	66.4	3.58, dd (10.9, 4.0)	66.6	3.58, dd (10.9, 4.0)
	$C_\beta H_a$	33.9	3.38, dd (14.3, 4.0)	33.9	3.38, dd (14.3, 4.0)
	$C_\beta H_b$		3.18, m		3.18, m
	C_γ	130.0		130.3	
	$C_\delta H$	130.3	7.07, d (8.6)	130.3	7.07, d (8.6)
	$C_\varepsilon H$	114.1	6.85, d (8.6)	114.1	6.85, d (8.6)
	C_ζ	158.6		158.6	
	OCH_3	55.2	3.80, s	55.3	3.80, s
	CO	168.4		168.4	
Thr^{6}	NH		7.67, d (5.2)		7.68, d (5.3)
	$C_\alpha H$	57.6	4.55, dd (5.2, 2.3)	57.7	4.58, dd (5.4, 2.4)
	$C_\beta H$	70.4	5.41, qd (6.3, 2.3)	70.5	5.38, m
	CH_3C_β	16.3	1.39, d (6.3)	16.3	1.41, d (6.3)
	CO	169.4		166.5	
D-MeLeu^{7}	NCH_3	31.3	3.15, s	31.2	3.14, s
	$C_\alpha H$	54.8	5.38, dd (11.5, 4.0)	54.9	5.38, m
	$C_\beta H_a$	36.1	1.84, m	36.2	1.84, m
	$C_\beta H_b$		1.71, m		1.69, m
	$C_\gamma H$	24.8	1.43, m	24.9	1.43, m
	$C_\delta H_3$	23.4	0.90, d (6.8)	23.4	0.89, d (6.8)
	C_δ'H_3	21.3	0.87, d (6.8)	21.4	0.87, d (6.8)
	CO	171.7		172.0	
Pro^{8}	$C_\alpha H$	56.7	4.74, t (7.6)	56.7	4.75, t (7.6)
	$C_\beta H_a$	28.4	2.22, m	28.4	2.22, m
	$C_\beta H_b$		1.98, m		1.98, m
	$C_\gamma H_a$	26.0	2.23, m	26.0	2.22, m
	$C_\gamma H_b$		1.97, m		1.97, m
	$C_\delta H_a$	47.0	3.68, m	47.1	3.68, m
	$C_\delta H_b$		3.57, m		3.57, m
	CO	172.8		172.9	
Lac^{9}	C2H	66.0	4.39, m	66.0	4.39, m
	CH_3-C2	20.2	1.39, d (6.5)	20.2	1.39, d (6.5)
	CO	173.9		173.9	

500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR.

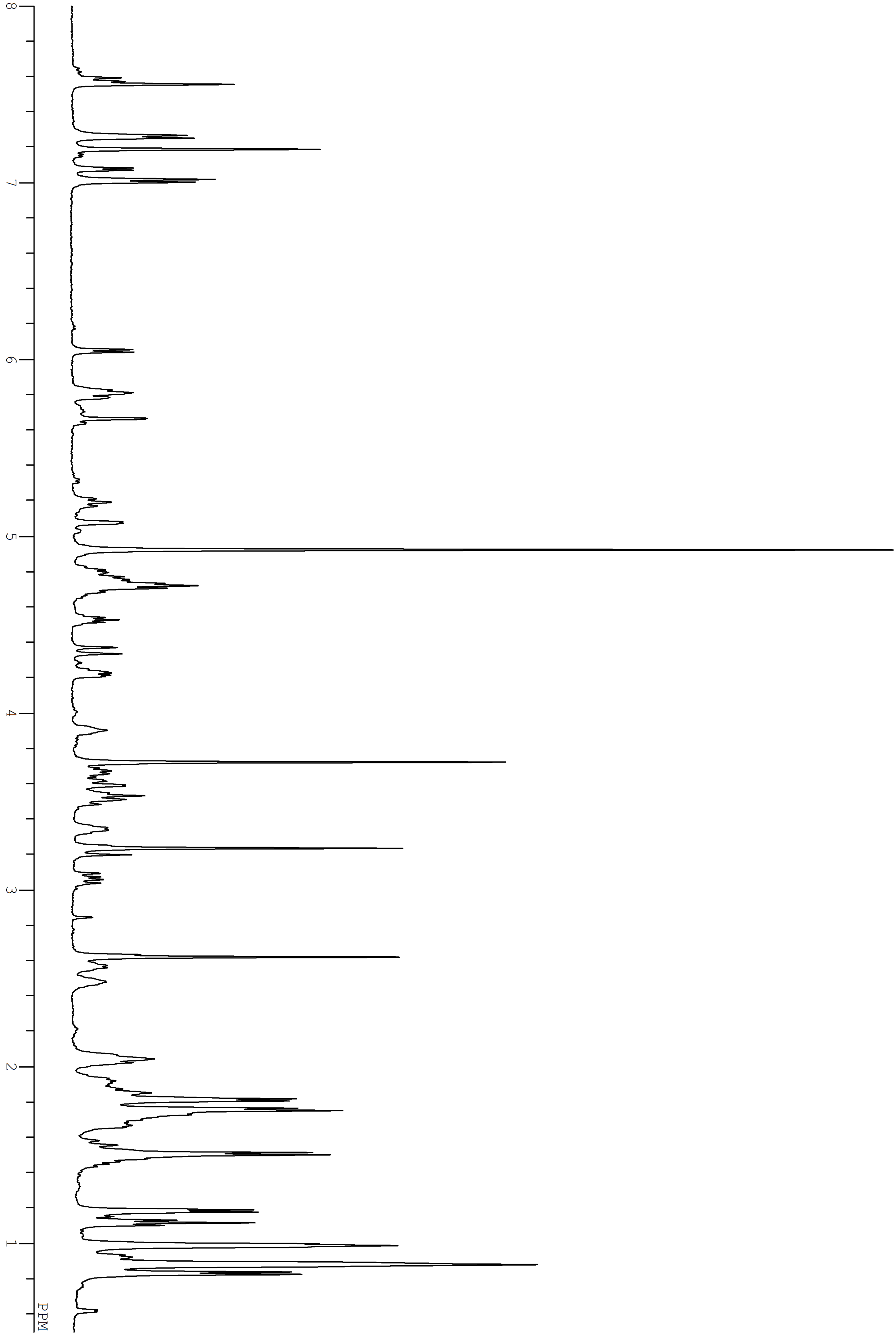

Figure S1. ^{1}H NMR spectrum of **1** in C_5D_5N (500 MHz)

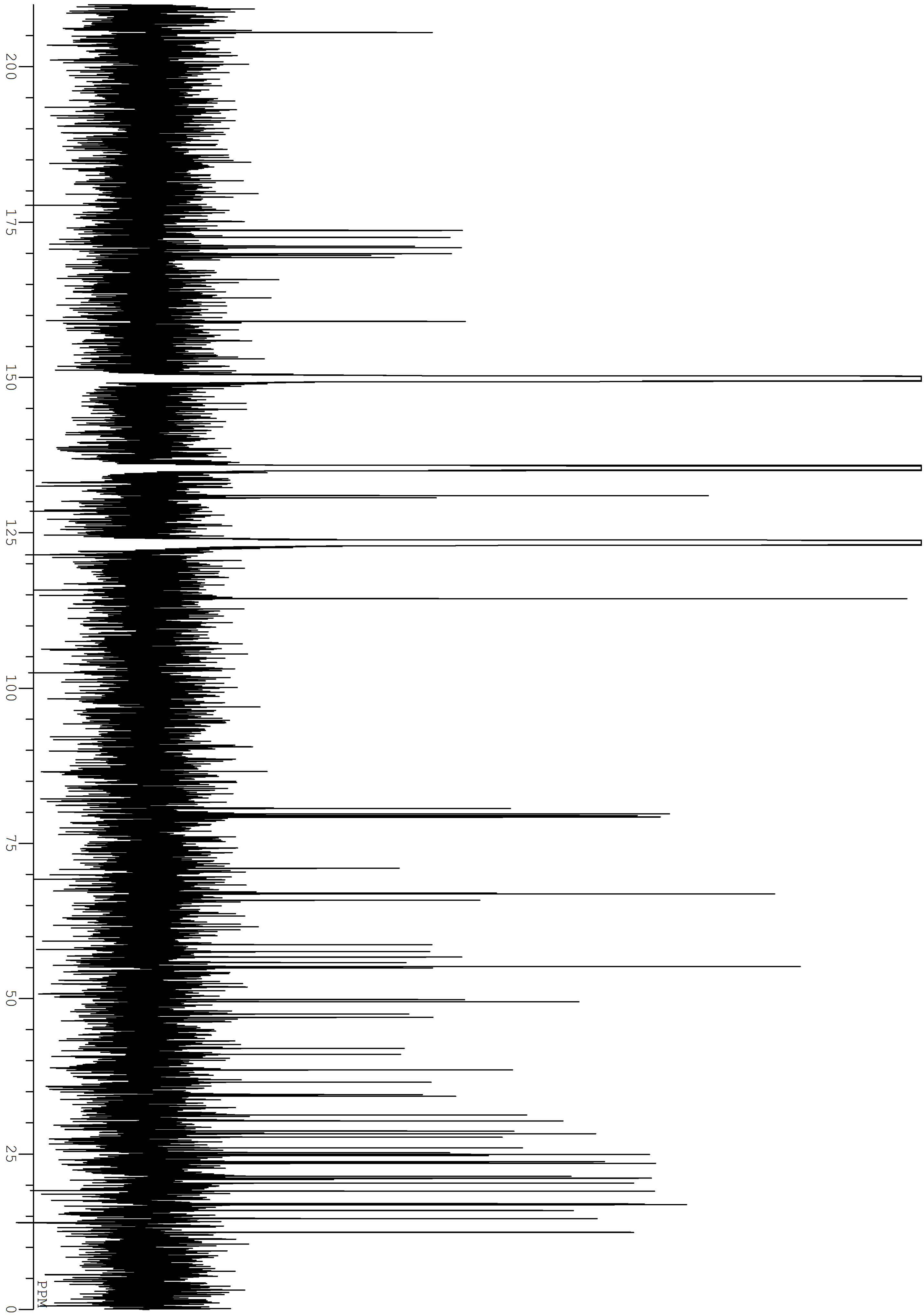

Figure S2. ^{13}C NMR spectrum of **1** in C_5D_5N (125 MHz)

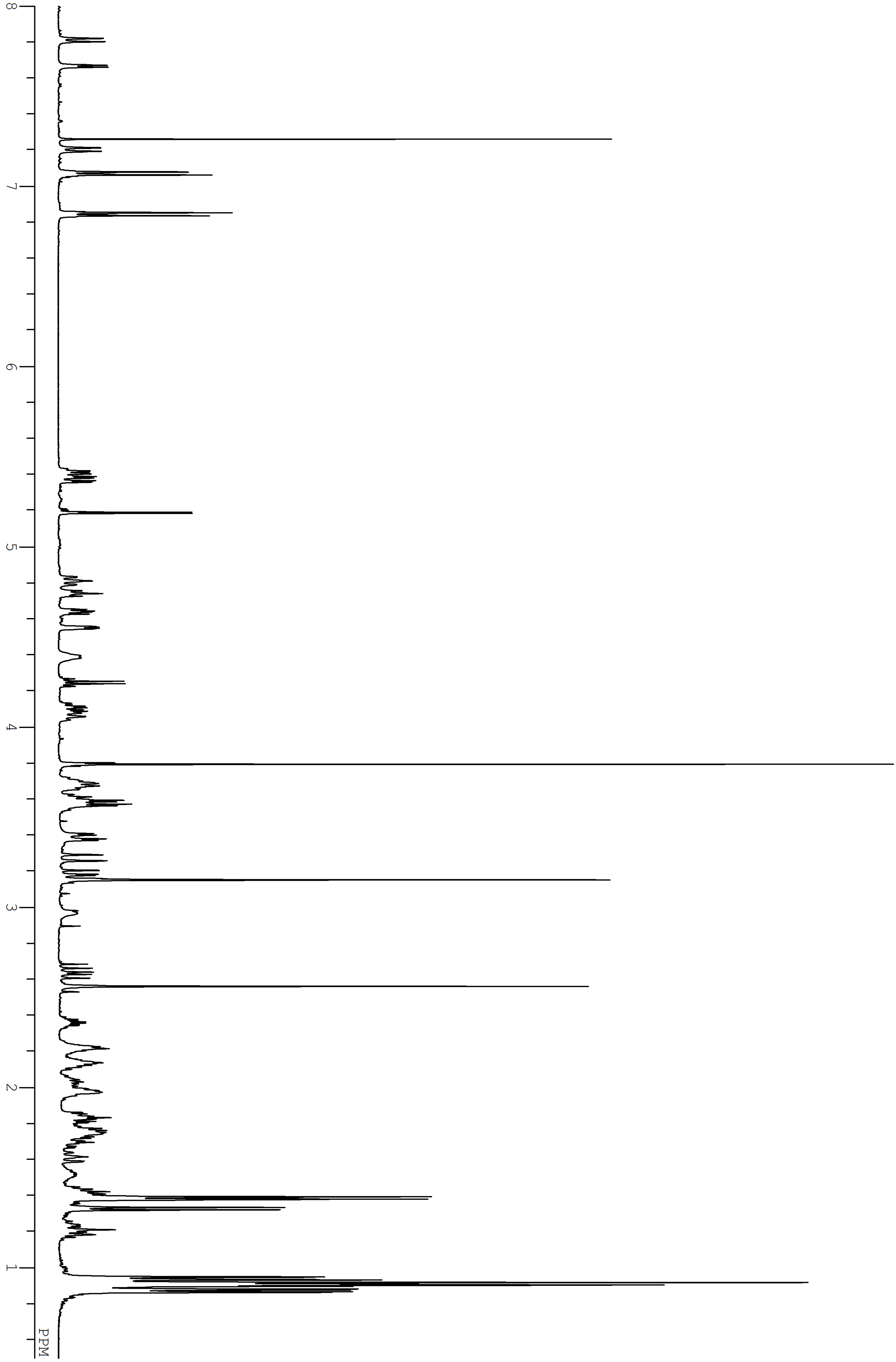

Figure S3. ^{1}H NMR spectrum of **1** in $CDCl_3$ (500 MHz)

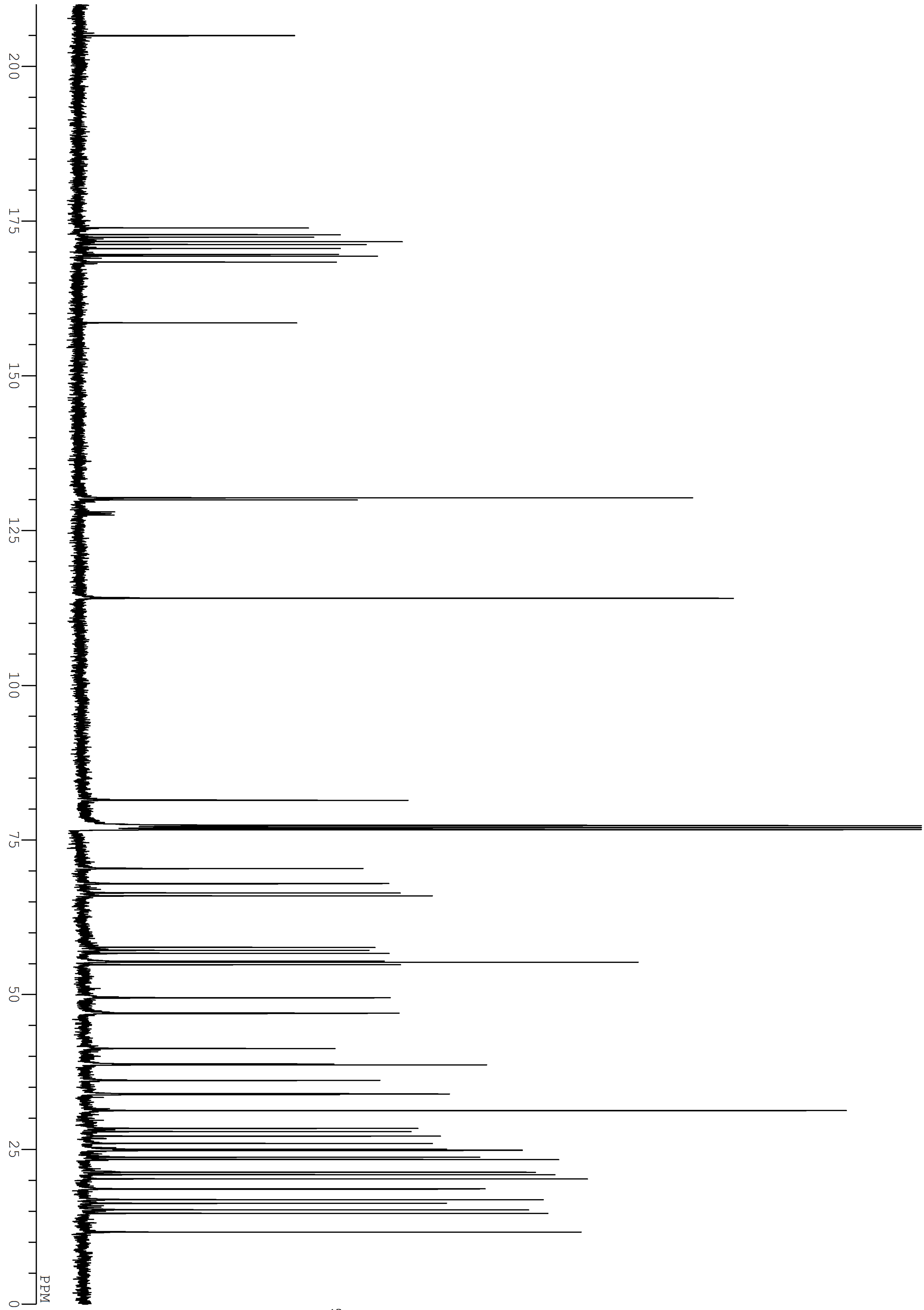

Figure S4. ^{13}C NMR spectrum of **1** in $CDCl_3$ (125 MHz)

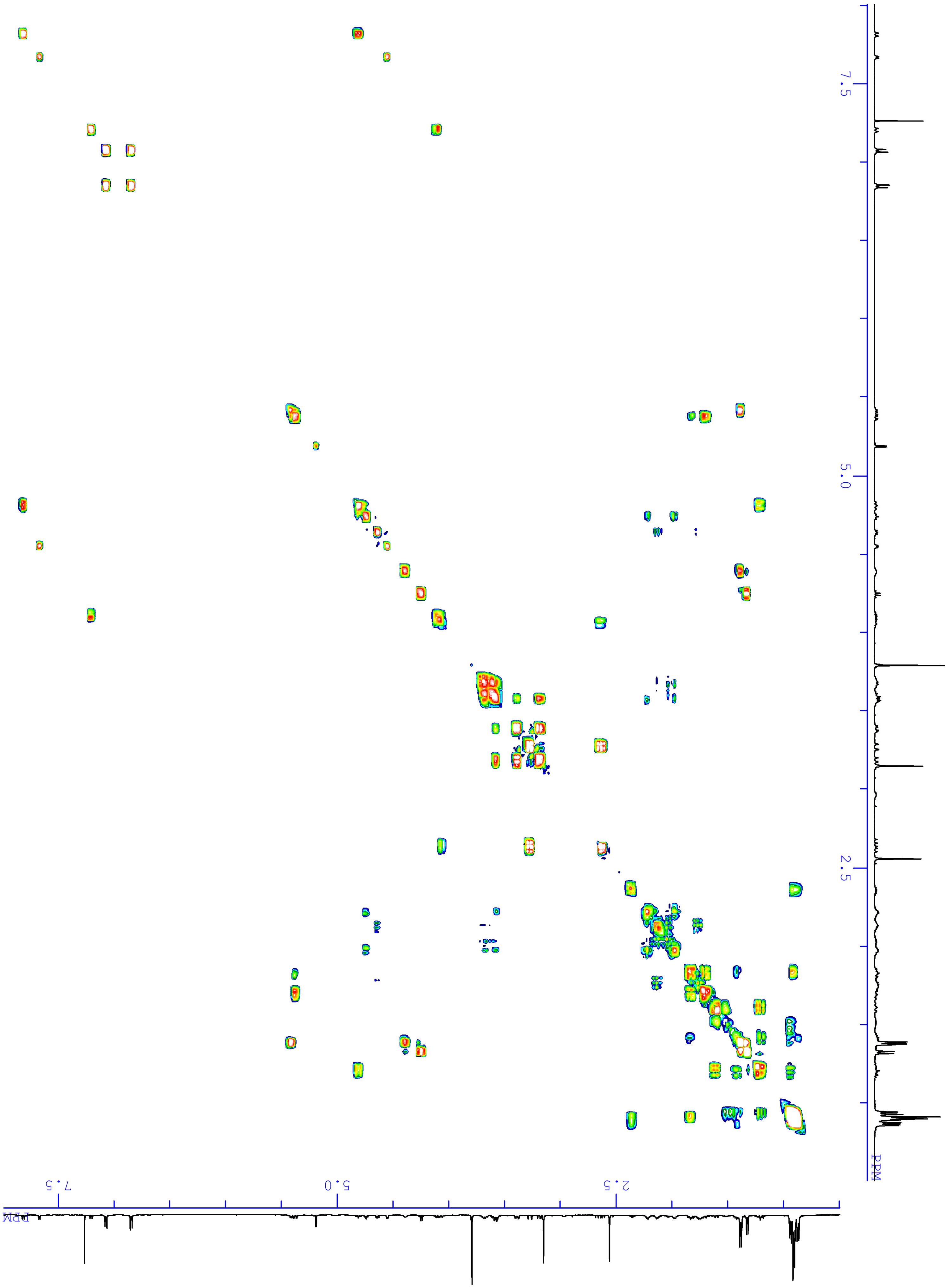

Figure S5. COSY spectrum of **1** in $CDCl_3$ (500 MHz)

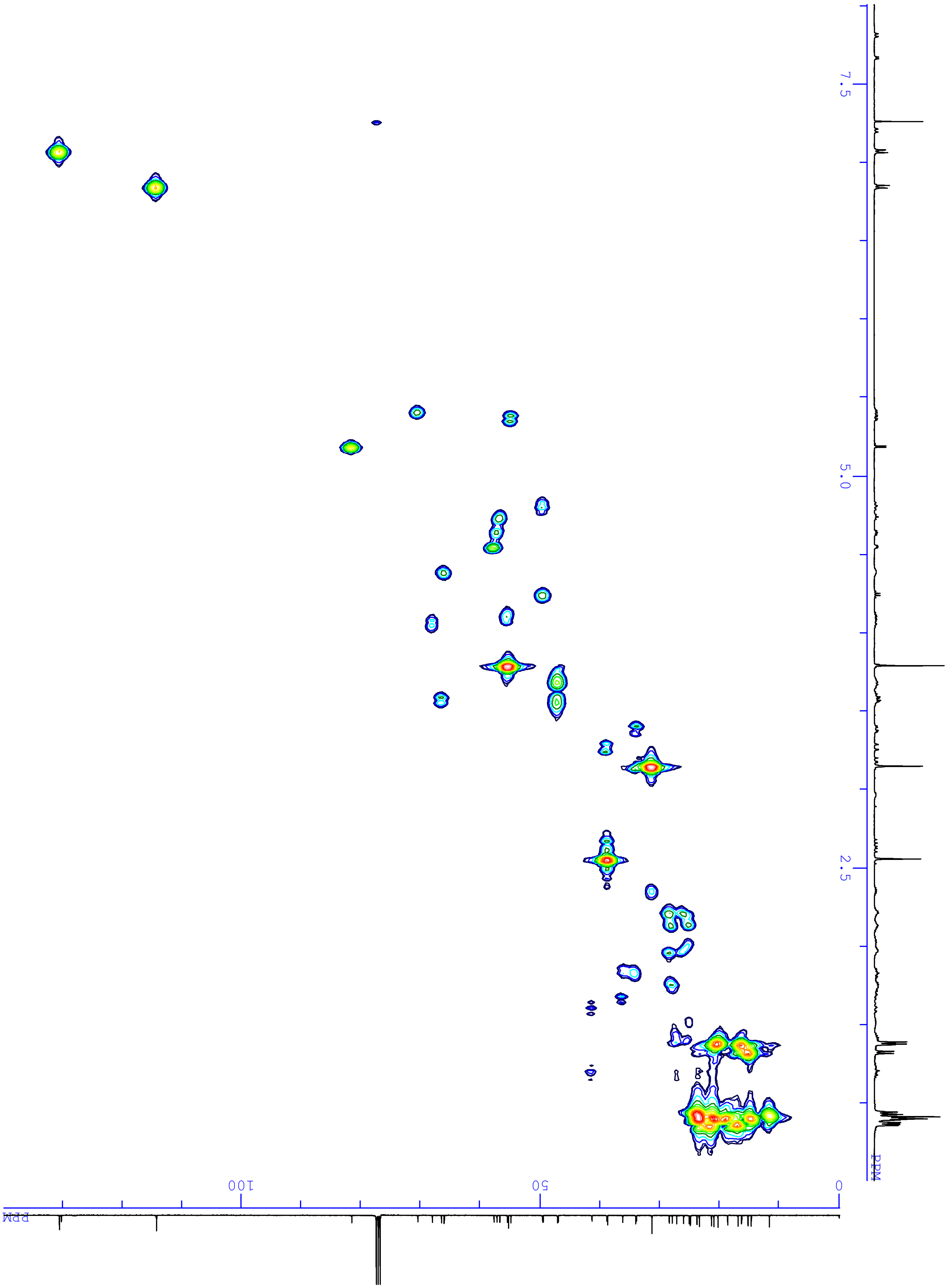

Figure S6. HMQC spectrum of **1** in $CDCl_3$ (500 MHz)

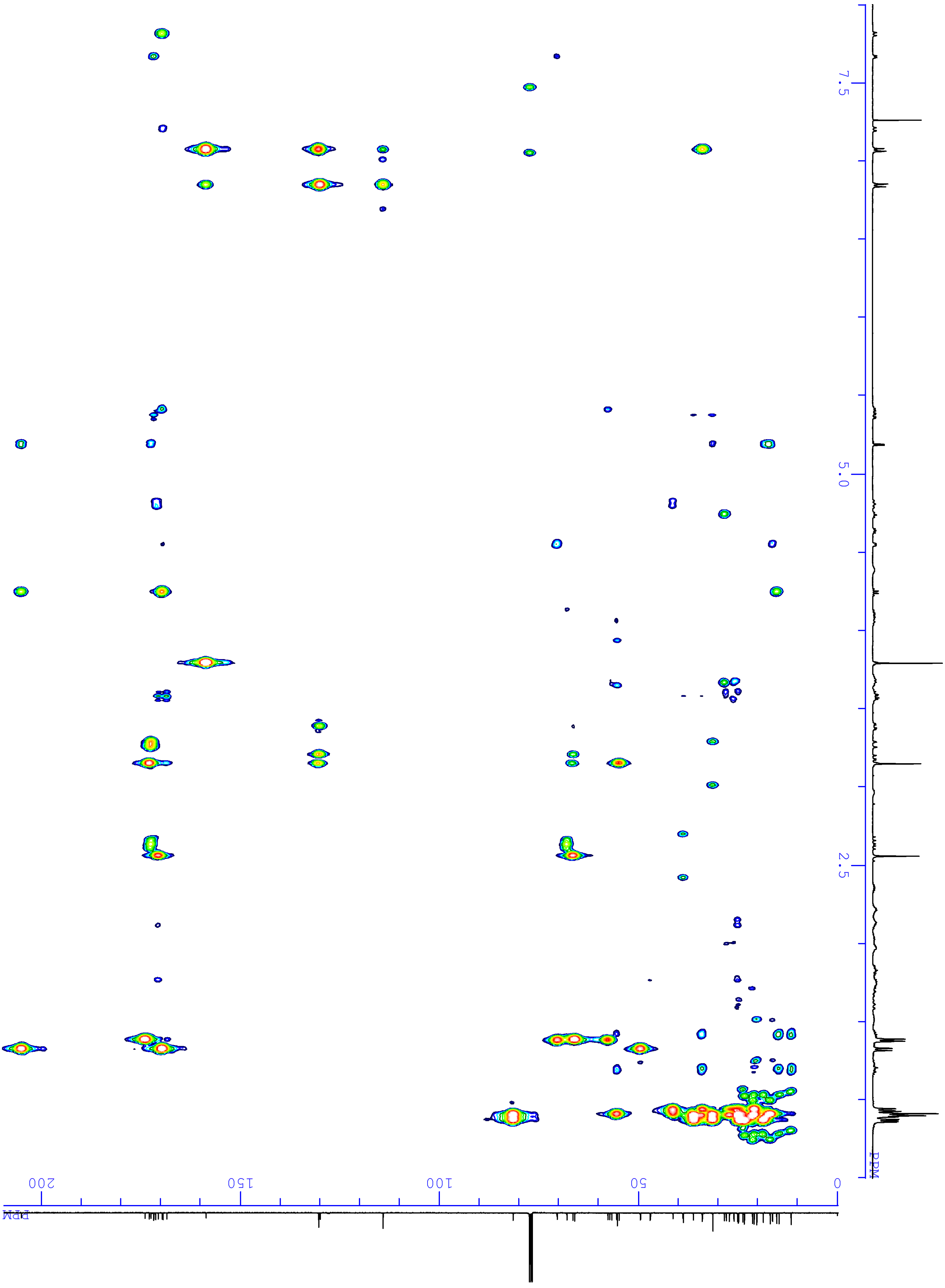

Figure S7. HMBC spectrum of **1** in $CDCl_3$ (500 MHz)

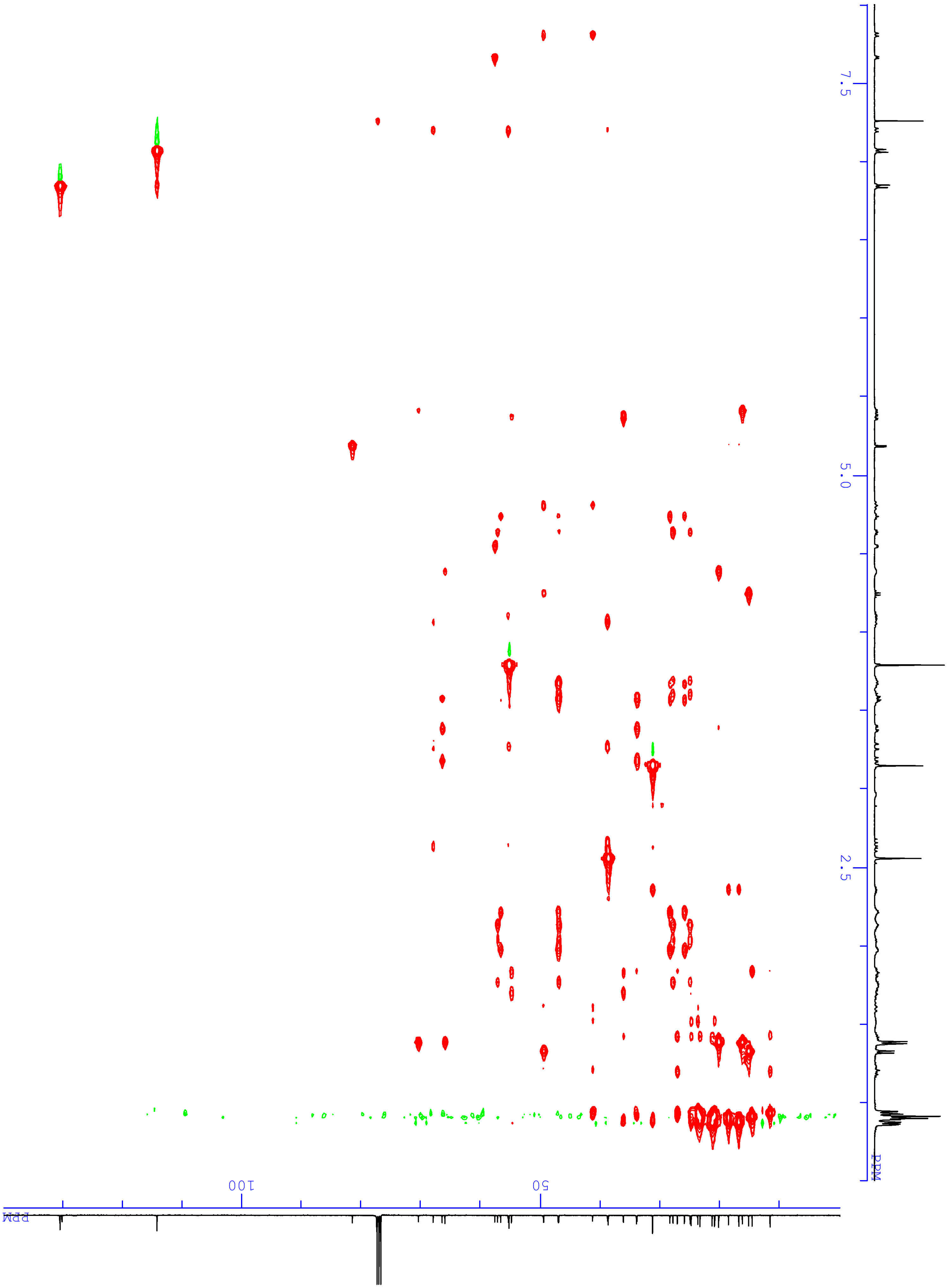

Figure S8. HSQC-TOCSY spectrum of **1** in $CDCl_3$ (500 MHz)

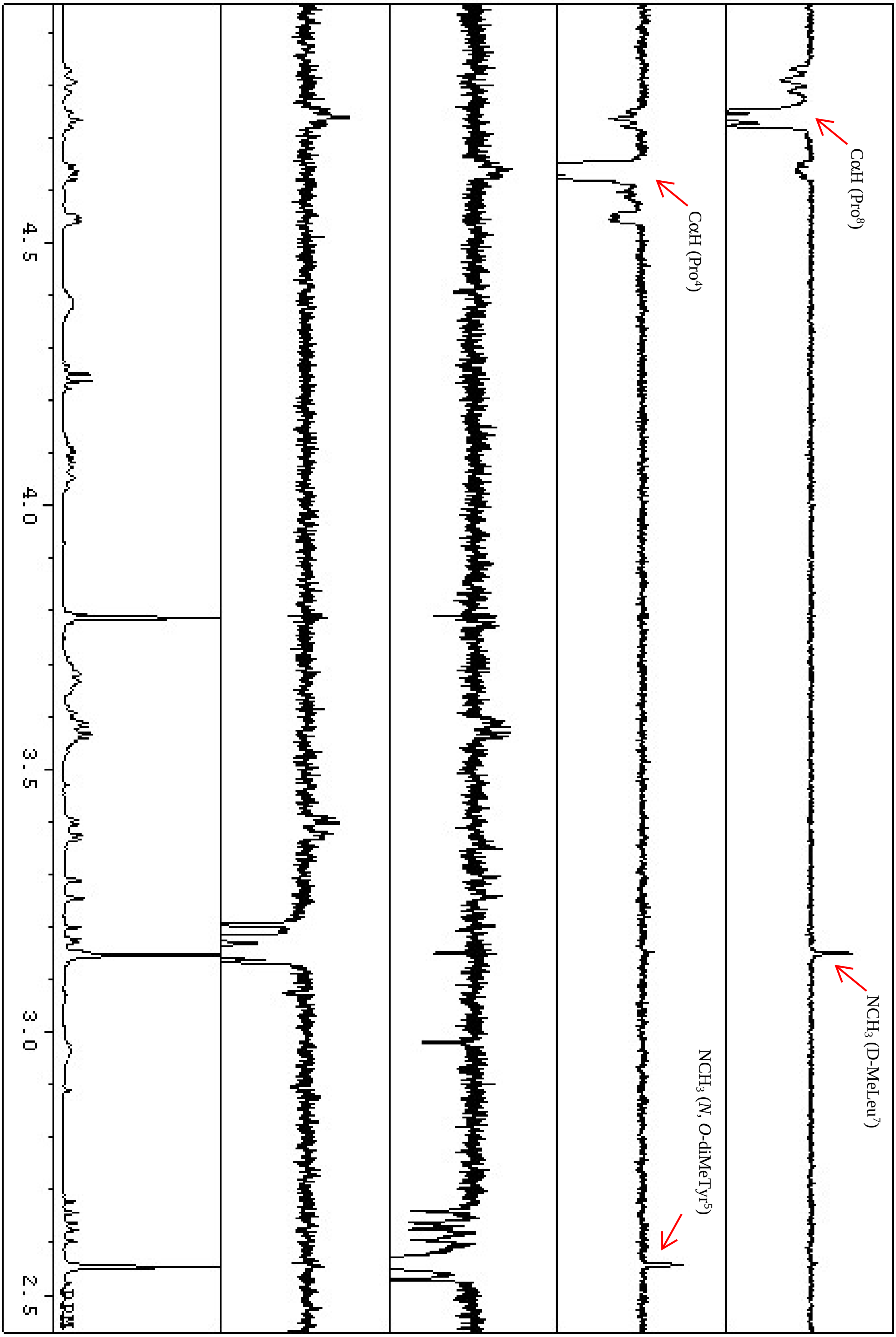

Figure S9. NOE correlations between *N*-methyls and α carbon of prolines of **1** in $CDCl_3$ (500 MHz)

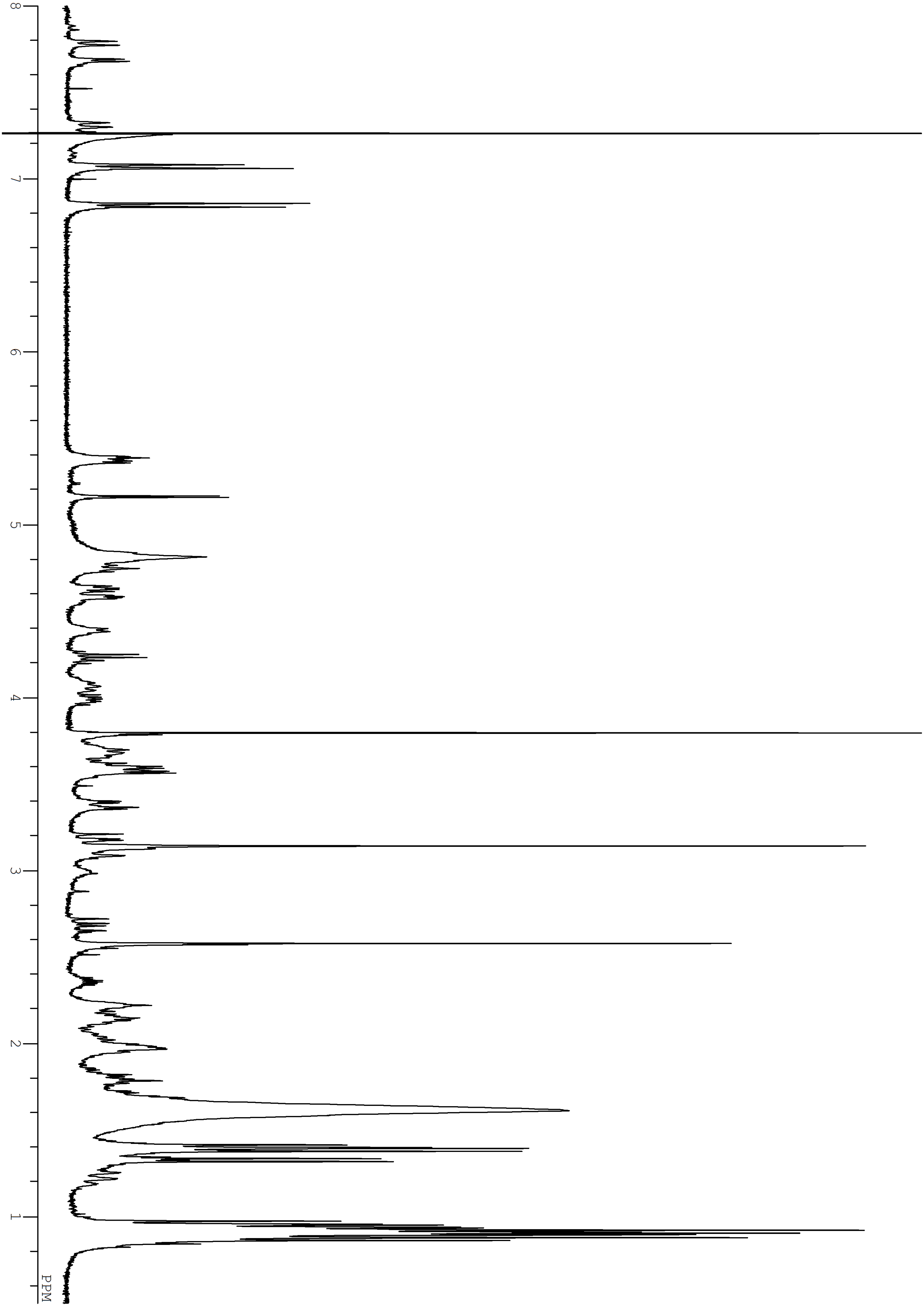

Figure S10. ^{1}H NMR spectrum of **2** in $CDCl_3$ (500 MHz)

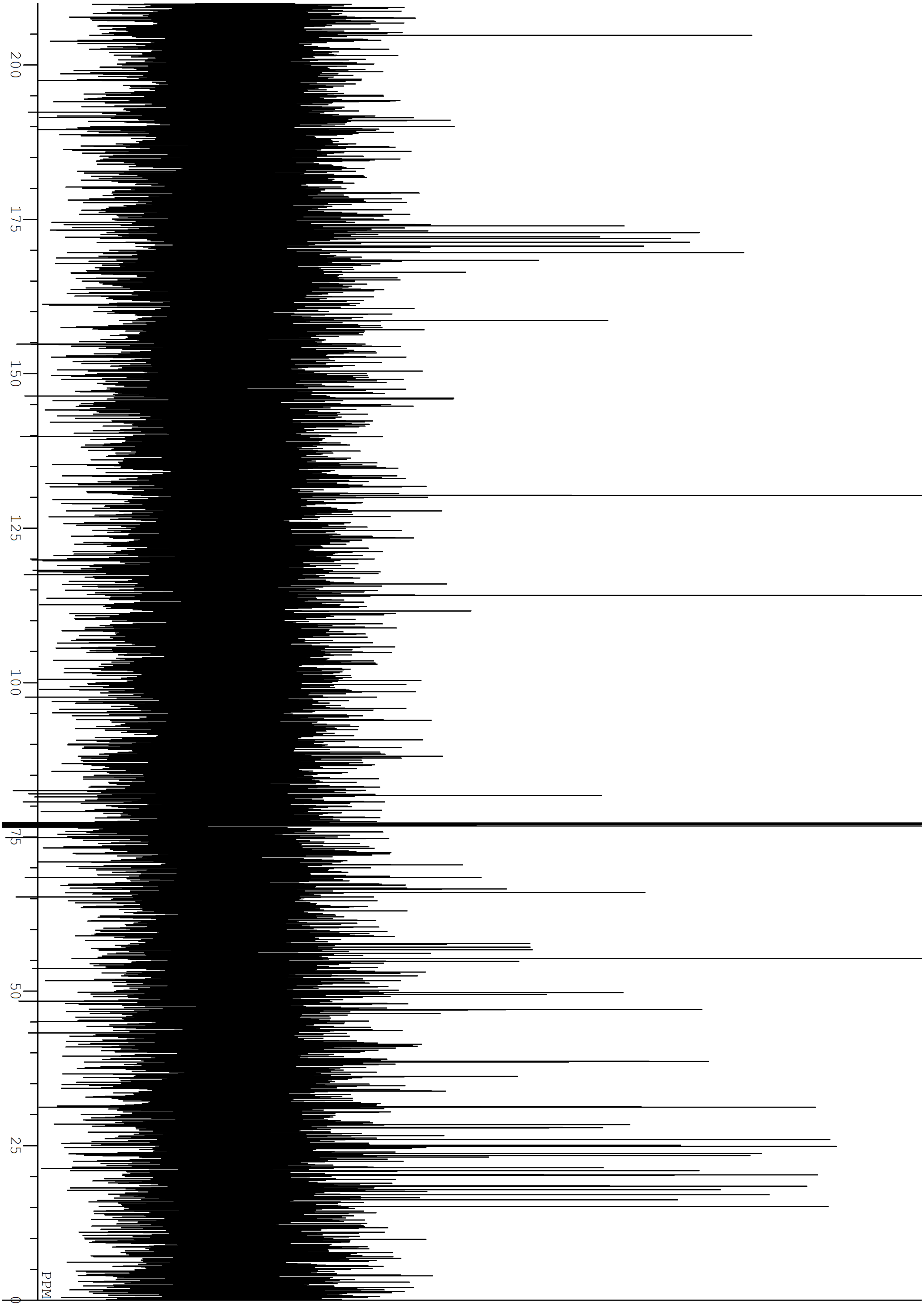

Figure S11. ^{13}C NMR spectrum of **2** in $CDCl_3$ (125 MHz)