Supporting Information for

A New Diketopiperazine, Cyclo-(4-*S*-Hydroxy-*R*-Proline-*R*-Isoleucine), from an Australian Specimen of the Sponge *Stelletta* Sp.

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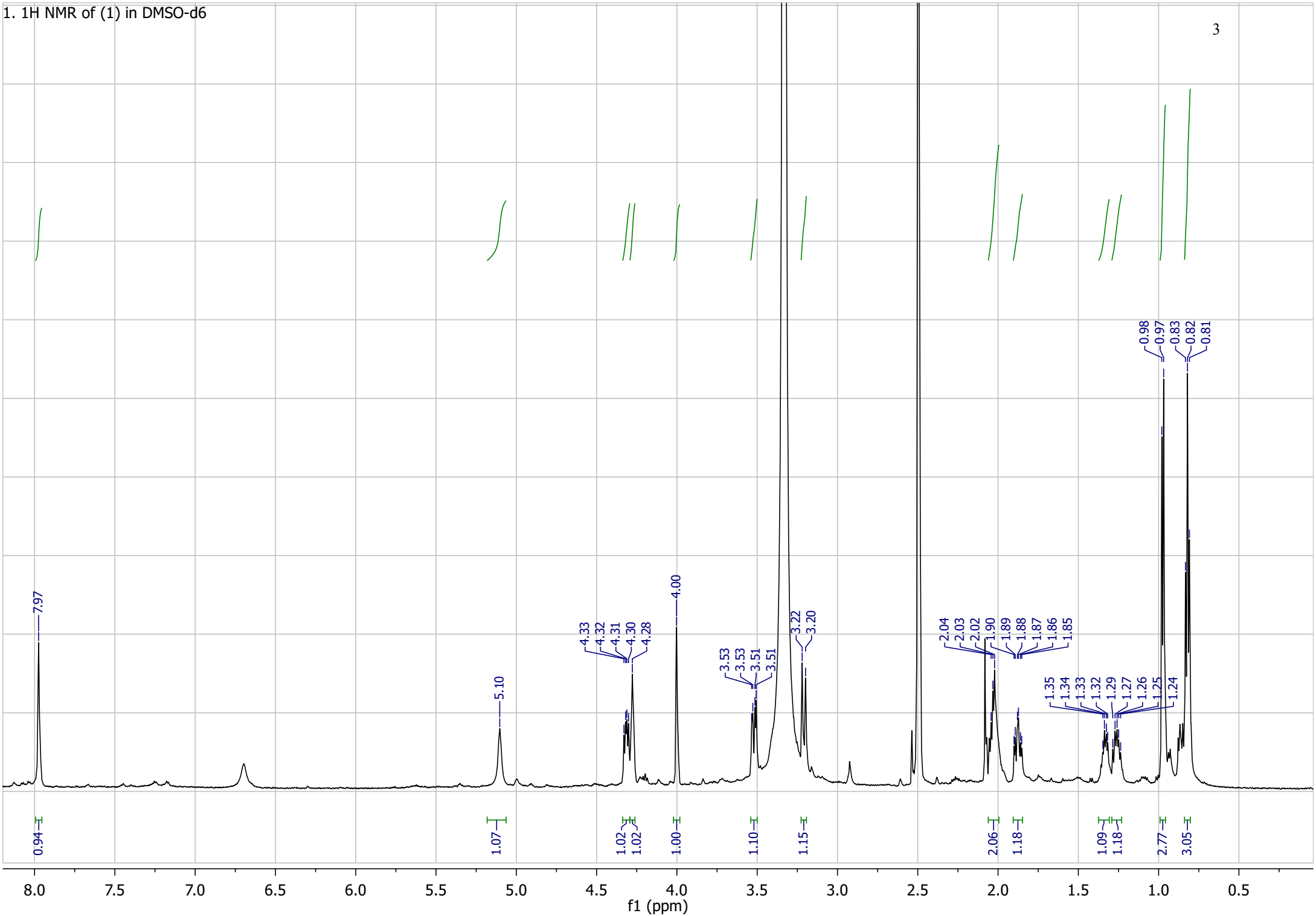
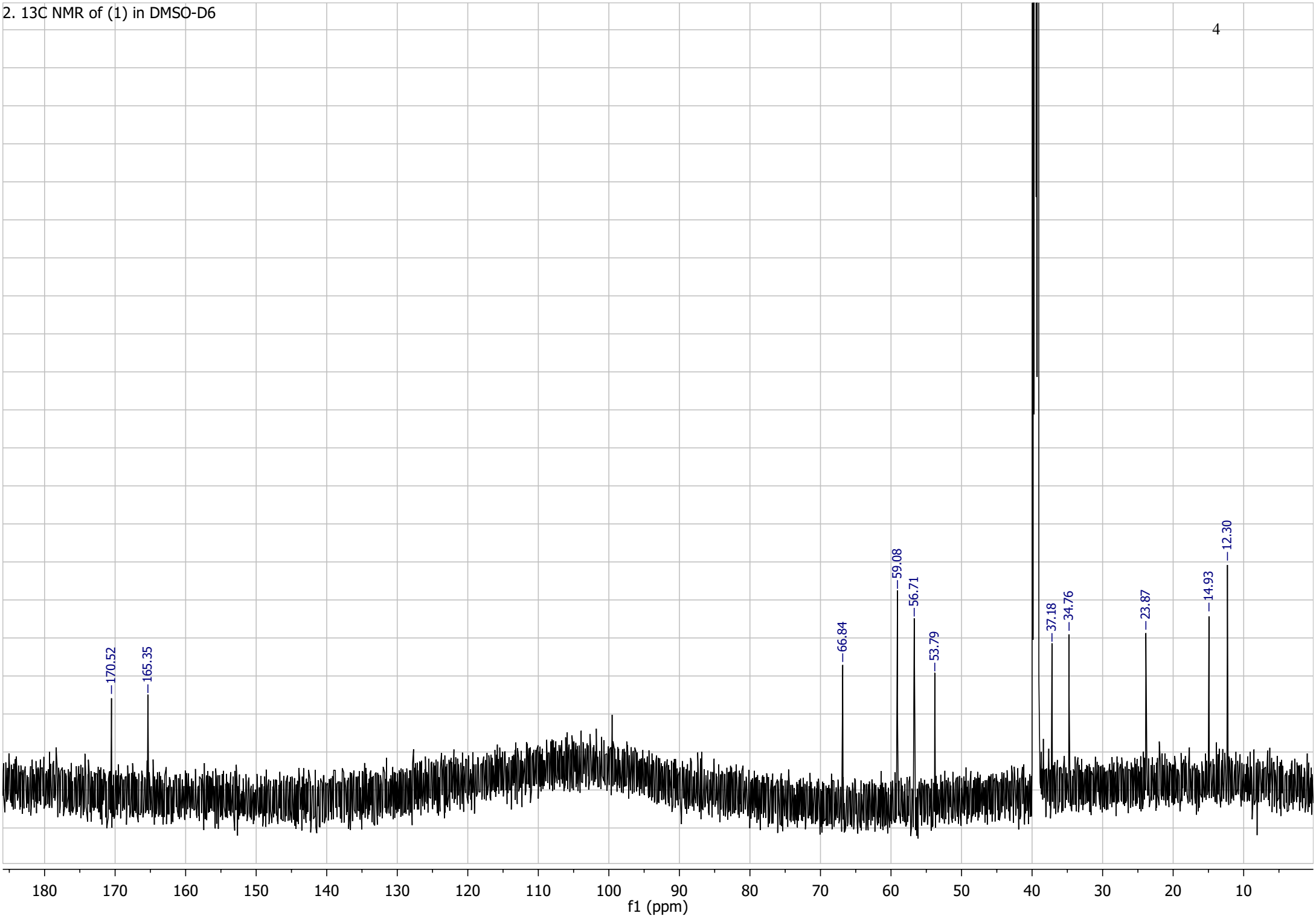
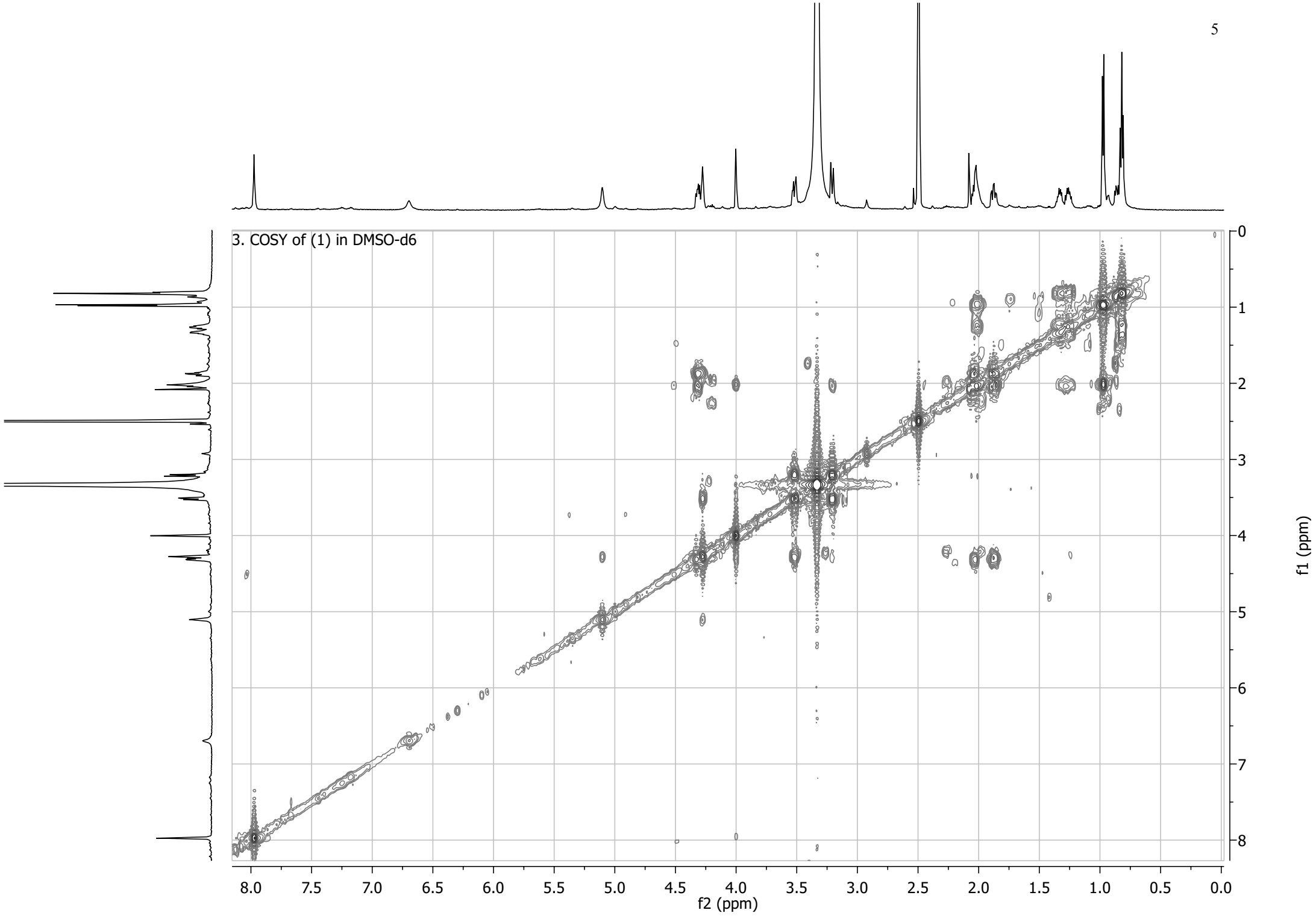
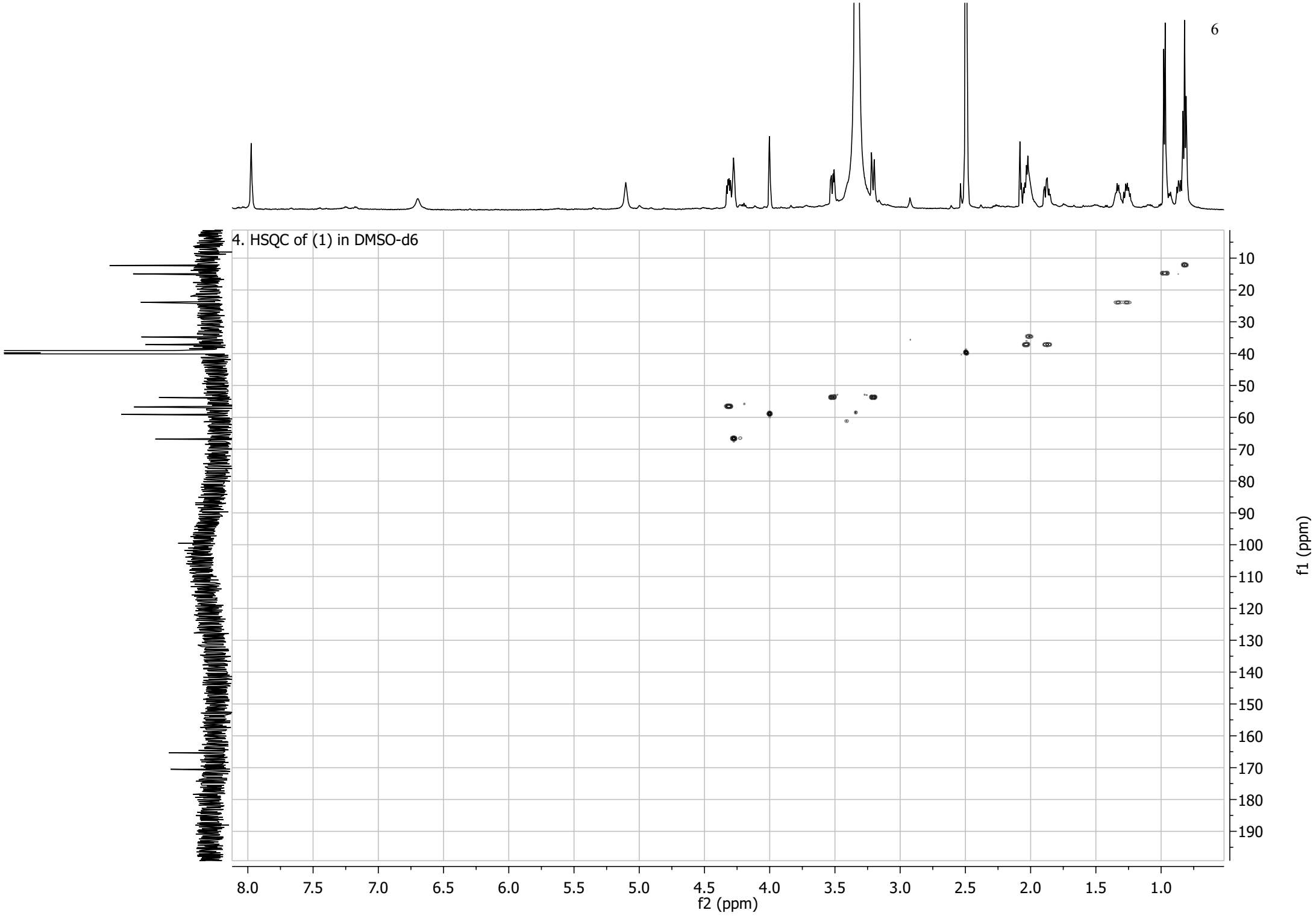
1. 1H NMR of (1) in DMSO-d6




2. 13C NMR of (1) in DMSO-D6
4
170.52
165.35
66.84
59.08
56.71
53.79
37.18
34.76
23.87
14.93
12.30
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


3. COSY of (1) in DMSO-d6
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)


4. HSQC of (1) in DMSO-d6
f2 (ppm)
f1 (ppm)

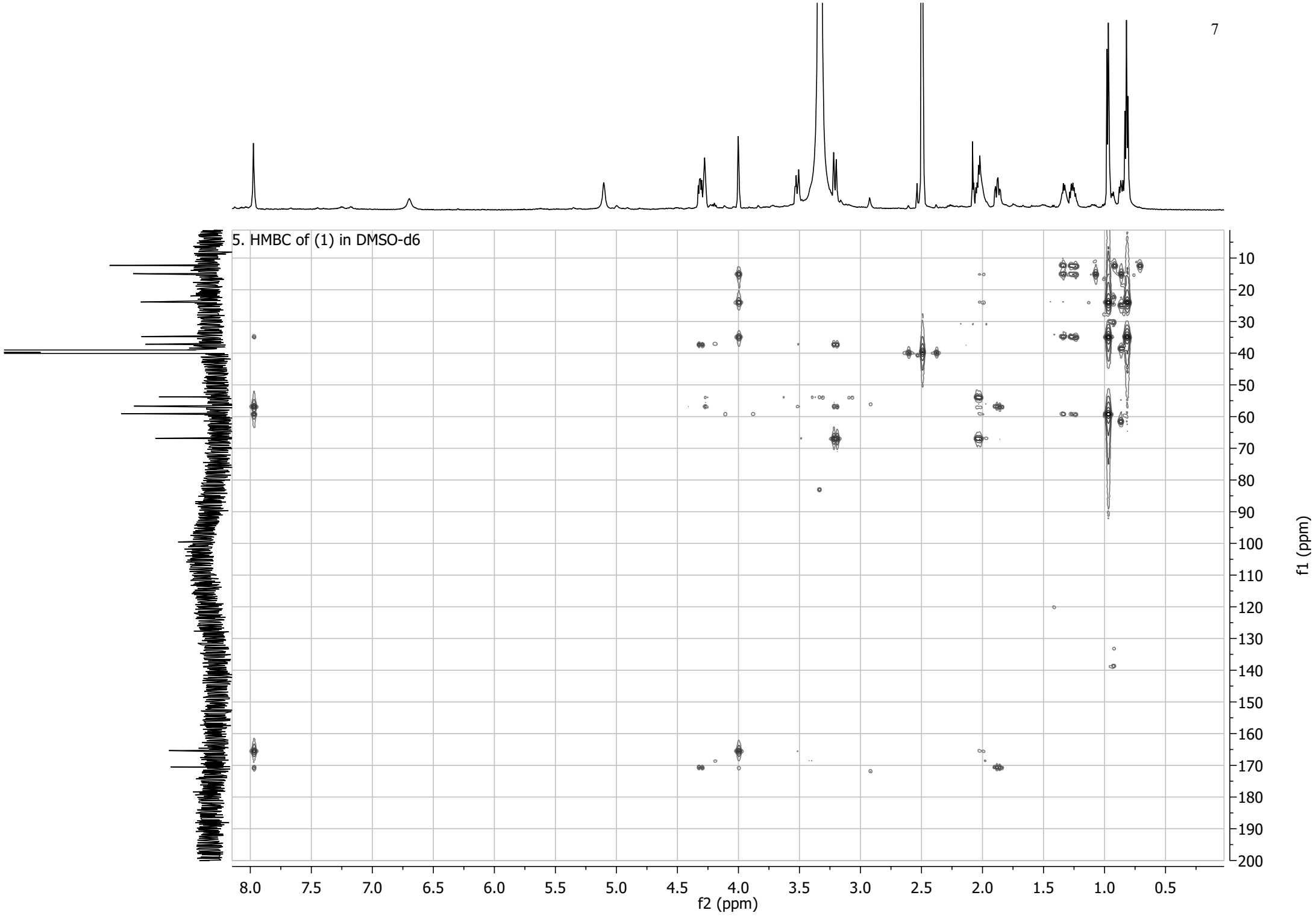

5. HMBC of (1) in DMSO-d6
f2 (ppm)
f1 (ppm)

Figure S6. Molecular model of (**1**) with SRR configuration

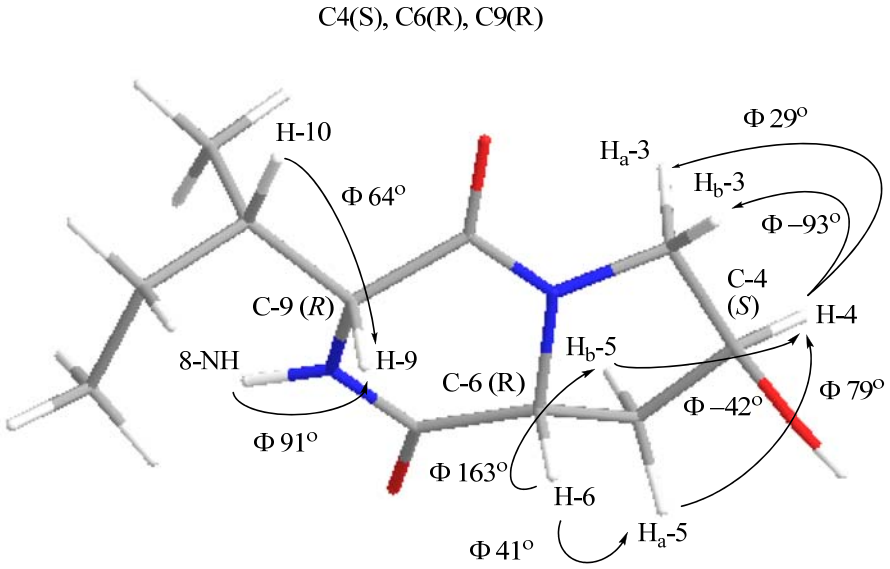


Figure S7. Molecular model of (**1**) with RRR configuration

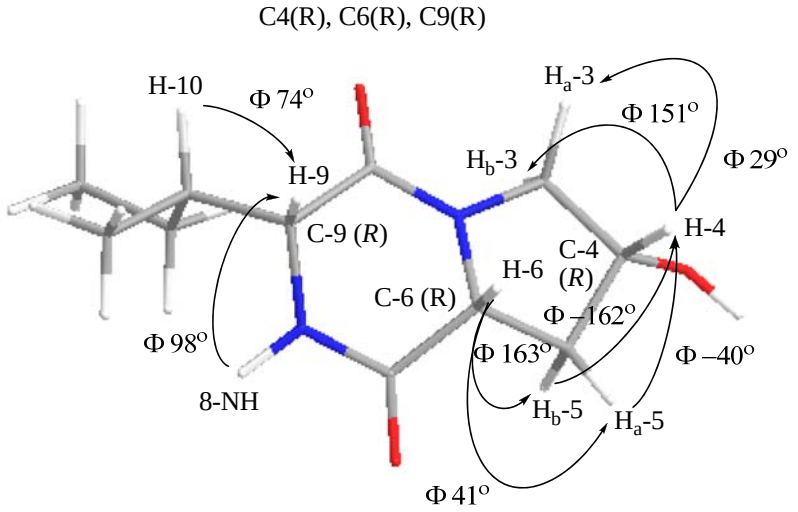


Figure S8. Molecular model of (**1**) with RSS configuration

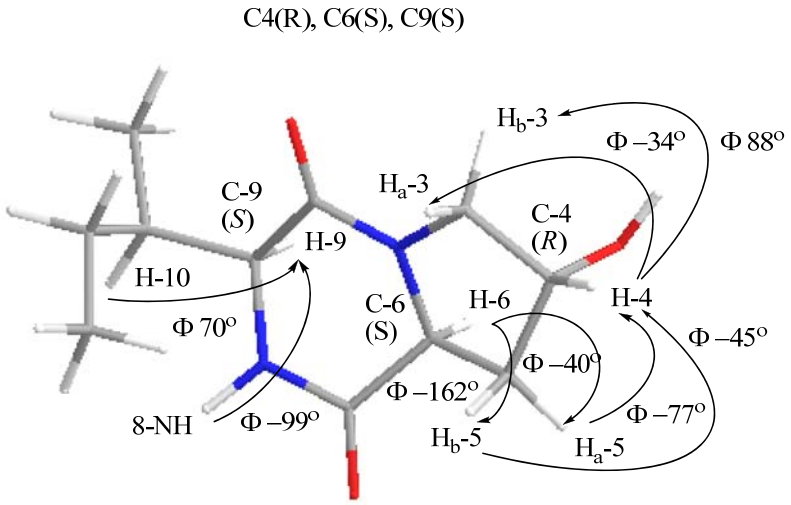


Figure S9. Molecular model of (**1**) with SSS configuration

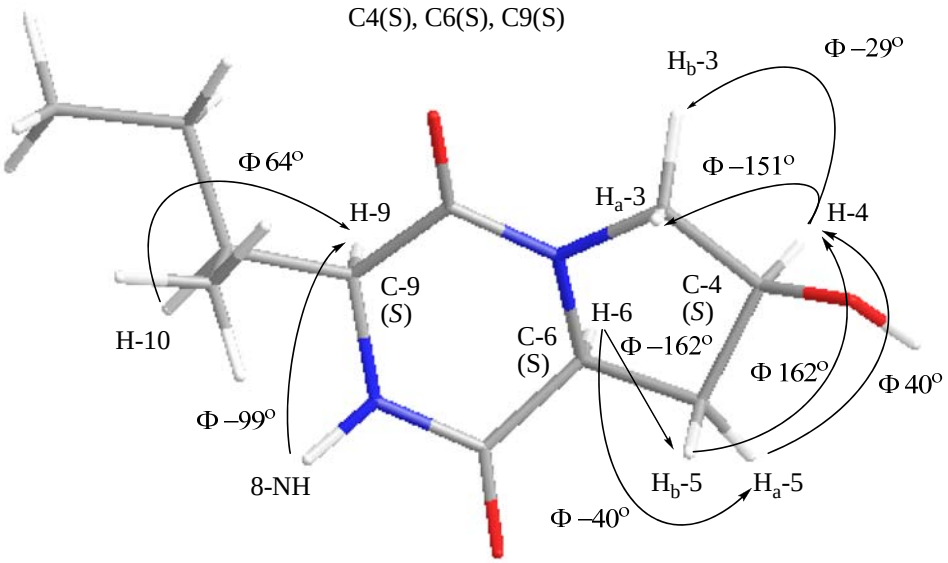


Figure S10. Molecular model of (**1**) with SSR configuration

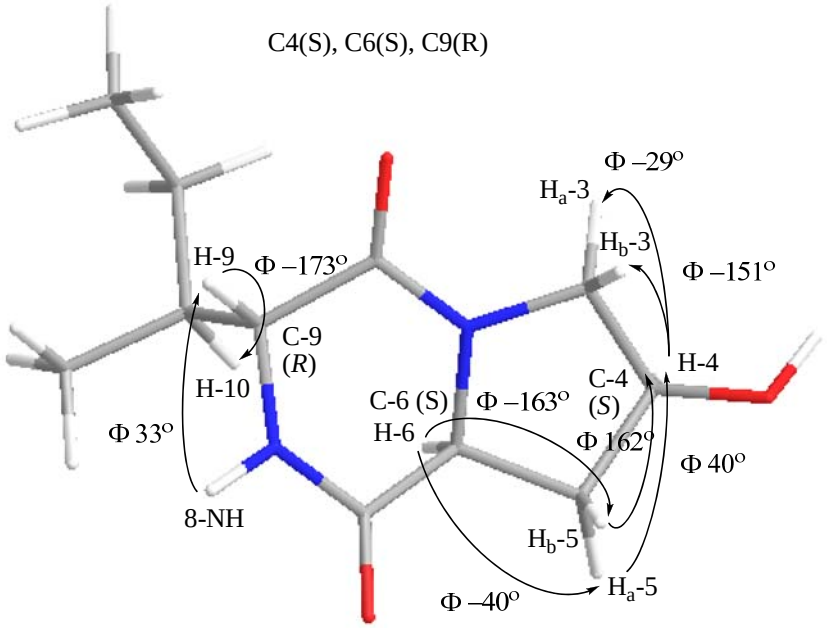


Figure S11. Molecular model of (**1**) with RSR configuration

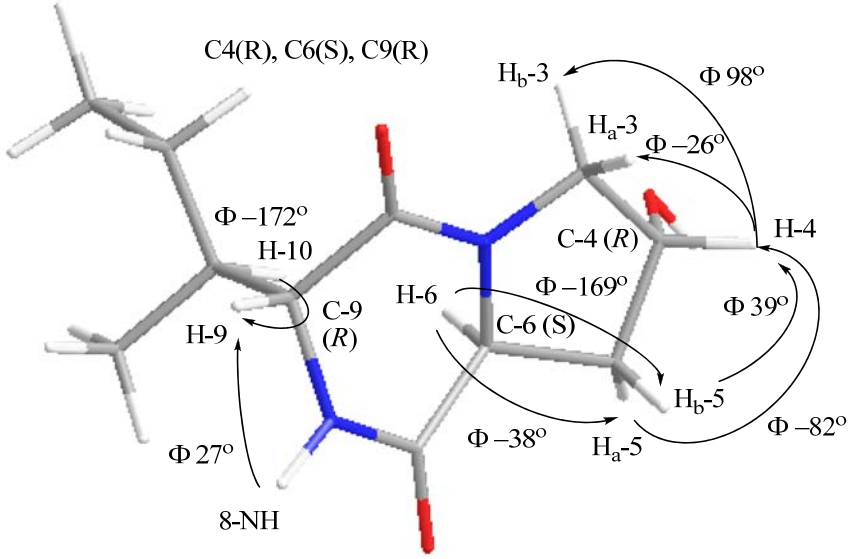


Figure S12. Molecular model of (**1**) with SRS configuration

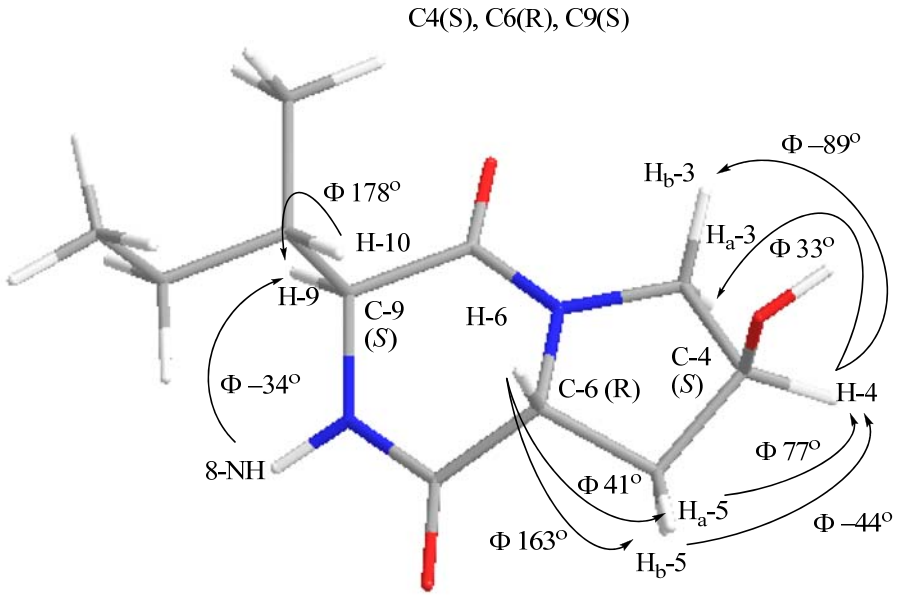


Figure S13. Molecular model of (**1**) with RRS configuration

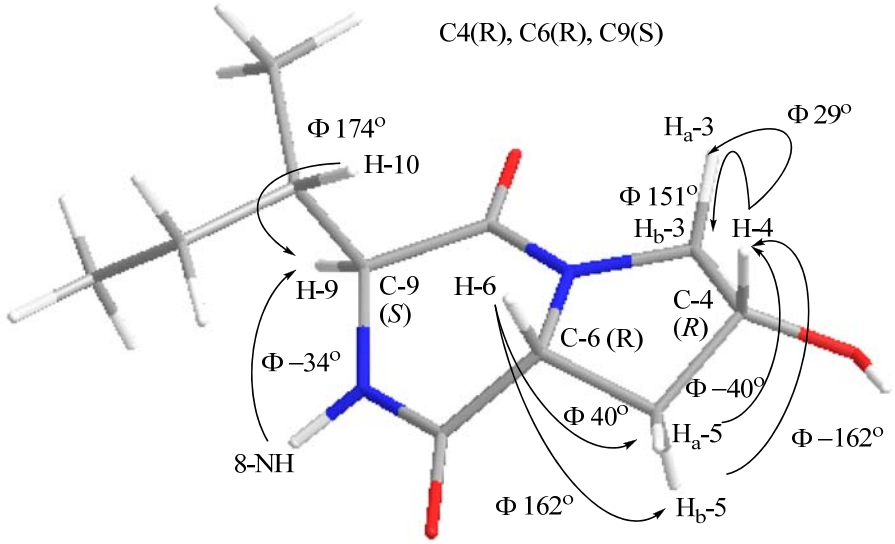


Table S1. Comparison of calculated dihedral angles from the eight possible stereoisomers of **1** with observed ^{1}H-^{1}H couplings from the ^{1}H NMR of **1**.

C-4,C-6,C-9 configuration	^{1}H-^{1}H Correlation	Calculated dihedral angle Φ	Calculated *J* (Hz) [a]	Relevant observed ^{1}H-^{1}H couplings	C-4,C-6,C-9 configuration	^{1}H-^{1}H Correlation	Calculated dihedral angle Φ	Calculated *J* (Hz) [a]	Relevant observed ^{1}H-^{1}H couplings
RRR	H-9 – 8NH	98	0.74 [b]	8NH (br s), H-9 (br s)	RSR	H-9 – 8NH	27	6.88 [b]	NA
	H-9 – H-10	74	1.16	H-9 (br s)		H-9 – H-10	-172	10.16	NA
	H-6 – H5b	163	11.26	H-6 – H5b (11.0 Hz)		H-6 – H5b	-169	11.65	H-6 – H5b (11.0 Hz)
	H-6 – H5a	41	5.63	H-6 – H5a (6.1 Hz)		H-6 – H5a	-38	6.09	H-6 – H5a (6.1 Hz)
	H-4 – H5a	-162	10.00	NA		H-4 – H5a	-82	1.50	No observed coupling
	H-4 – H5b	-40	7.14	NA		H-4 – H5b	39	4.83	H-4 (4.6, 4.6 Hz), H-5b (4.6 Hz)
	H-4 – H3a	151	8.37	NA		H-4 – H3a	-26	6.09	H-4 (4.6, 4.6 Hz), H-3a (4.6 Hz)
	H-4 – H3b	29	8.54	NA		H-4 – H3b	98	1.57	No observed coupling
SRR	H-9 – 8NH	91	0.42 [b]	8NH (br s), H-9 (br s)	SSR	H-9 – 8NH	33	6.09 [b]	NA
	H-9 – H-10	64	1.93	H-9 (br s)		H-9 – H-10	-173	10.22	NA
	H-6 – H5b	163	11.26	H-6 – H5b (11.0 Hz)		H-6 – H5b	-163	11.26	H-6 – H5b (11.0 Hz)
	H-6 – H5a	41	5.63	H-6 – H5a (6.1 Hz)		H-6 – H5a	-40	5.78	H-6 – H5a (6.1 Hz)
	H-4 – H5a	79	1.70	No observed coupling		H-4 – H5a	40	7.14	NA
	H-4 – H5b	-42	4.36	H-4 (4.6, 4.6 Hz), H-5b (4.6 Hz)		H-4 – H5b	162	10.00	NA
	H-4 – H3a	29	5.65	H-4 (4.6, 4.6 Hz), H-3a (4.6 Hz)		H-4 – H3a	-29	8.54	NA
	H-4 – H3b	-93	1.43	No observed coupling		H-4 – H3b	-152	8.51	NA
RSS	H-9 – 8NH	-99	0.80 [b]	8NH (br s), H-9 (br s)	SRS	H-9 – 8NH	-34	5.95 [b]	NA
	H-9 – H-10	70	1.86	H-9 (br s)		H-9 – H-10	178	10.40	NA
	H-6 – H5b	-162	11.18	H-6 – H5b (11.0 Hz)		H-6 – H5b	163	11.26	H-6 – H5b (11.0 Hz)
	H-6 – H5a	-40	5.78	H-6 – H5a (6.1 Hz)		H-6 – H5a	41	5.63	H-6 – H5a (6.1 Hz)
	H-4 – H5a	-77	1.86	No observed coupling		H-4 – H5a	77	1.86	No observed coupling
	H-4 – H5b	-45	3.90	H-4 (4.6, 4.6 Hz), H-5b (4.6 Hz)		H-4 – H5b	-44	4.05	H-4 (4.6, 4.6 Hz), H-5b (4.6 Hz)
	H-4 – H3a	-34	4.90	H-4 (4.6, 4.6 Hz), H-3a (4.6 Hz)		H-4 – H3a	33	5.05	H-4 (4.6, 4.6 Hz), H-3a (4.6 Hz)
	H-4 – H3b	88	1.43	No observed coupling		H-4 – H3b	-89	1.42	No observed coupling
SSS	H-9 – 8NH	-99	0.80 [b]	8NH (br s), H-9 (br s)	RRS	H-9 – 8NH	-34	5.95 [b]	NA
	H-9 – H-10	64	2.47	H-9 (br s)		H-9 – H-10	174	10.26	NA
	H-6 – H5b	-162	11.18	H-6 – H5b (11.0 Hz)		H-6 – H5b	162	11.18	H-6 – H5b (11.0 Hz)
	H-6 – H5a	-40	5.78	H-6 – H5a (6.1 Hz)		H-6 – H5a	40	5.78	H-6 – H5a (6.1 Hz)
	H-4 – H5a	40	4.94	NA		H-4 – H5a	-40	7.14	NA
	H-4 – H5b	162	11.31	NA		H-4 – H5b	-162	10.00	NA
	H-4 – H3a	-151	8.37	NA		H-4 – H3a	29	8.54	NA
	H-4 – H3b	-29	8.54	NA		H-4 – H3b	151	8.37	NA

[a] Predicted couplings calculated using the Karplus equation for ^{3}J H,H according to C.A.G. Haasnoot, F.A.A.M. DeLeeuw and C. Altona; *Tetrahedron* 36 (1980) 2783-2792.

[b] Predicted couplings calculated using the Karplus equation for ^{3}J HNCH according to V.F. Bystrov *Prog. NMR Spectrosc.* 10 (1976) 41-81.