Supplementary information

Tricholides A and B and unnarmicin D: new hybrid PKS-NRPS macrocycles isolated from an environmental collection of *Trichodesmium thiebautii*

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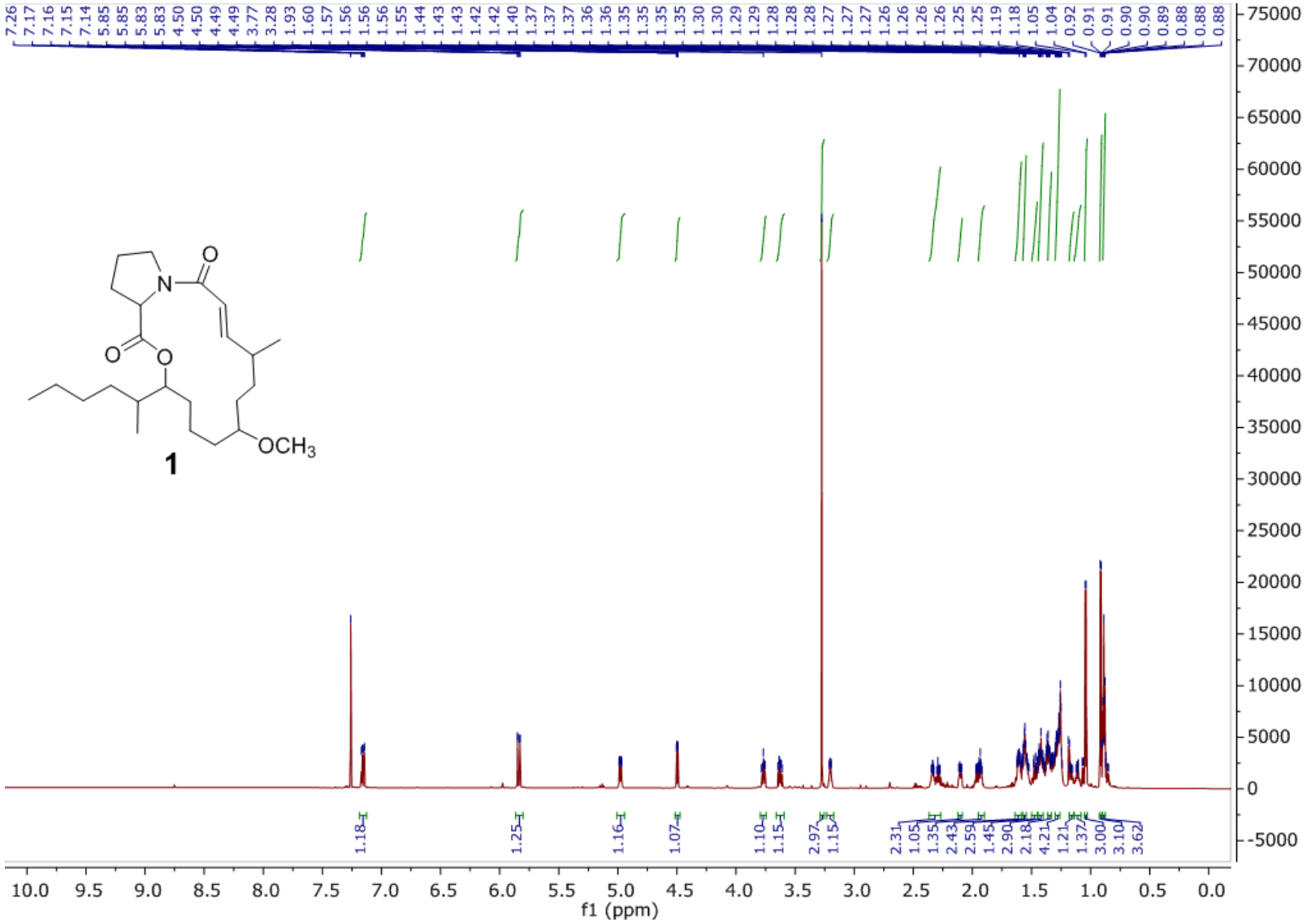
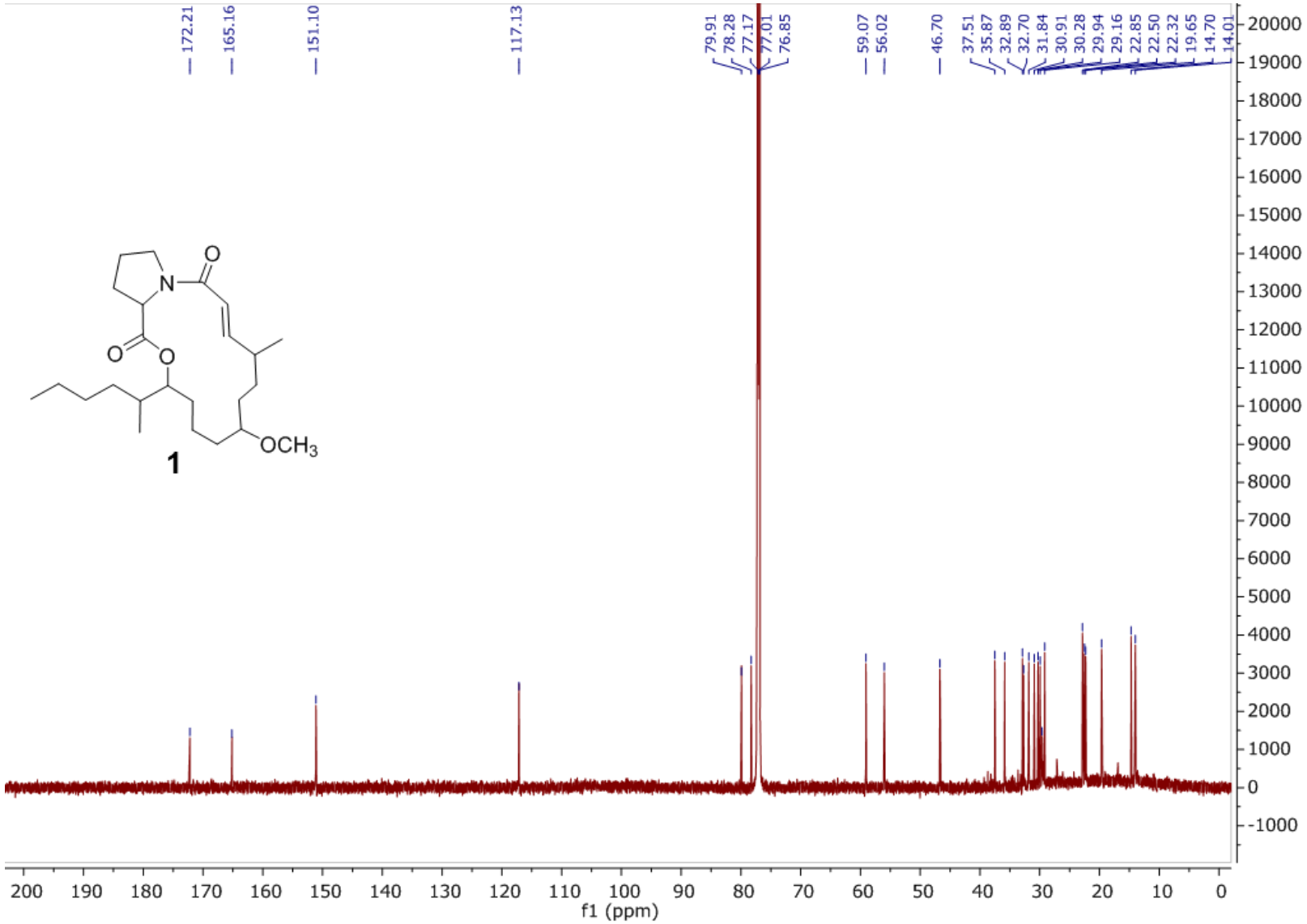
Table S1. NMR data for tricholide B (**2**) (800MHz, $CDCl_3$)

Position	δ_C	δ_H (*J* in Hz)	HMBC	COSY
1	171.7, qC			
2	60.7, CH	4.69, dd (8.5, 3.4)	1, 3, 4, 5	2a, 2b
3a	31.7, CH_2	2.38, m	1, 2, 4, 5	2, 3a, 4b
3b		2.18, m	1, 2, 4, 5	2, 3a, 4a
4a	22.7, CH_2	1.93, m	2, 3, 5	4b, 5b
4b		1.79, m	2, 3, 5	3a, 4a, 5a, 5b
5a	46.6, CH_2	3.76, m	2, 3, 4, 6	4a, 4b, 5b,
5b		3.54, m	2, 3, 4, 6	4a, 4b, 5a
6	173.0, qC			
7	133.0, qC			
8	136.1, CH	5.24, d (9.5)	6, 9, 24, 25	9
9	32.6, CH	2.43, m	7, 8, 10, 11, 24	8, 10b, 24
10a	33.2, CH_2	1.72, m	8, 9, 11, 24	10b, 11a
10b		1.10, m	8, 9, 11, 24	9, 10a
11a	30.8, CH_2	1.53, m	10, 12	10a, 11b
11b		1.27, ovlp[a]	10, 12	11a
12	80.3, CH	3.09, m	10, 13, 14, 23	11a, 11b, 13a, 13b
13a	30.9, CH_2	1.69, m	11, 12, 14	11a, 12, 13b
13b		1.30, ovlp	11, 12, 14	12, 13a
14a	19.9, CH_2	1.37, m	13, 15, 16	14b
14b		1.20, m	13, 15, 16	13a, 14a
15	30.2, CH_2	1.52, m	13, 14, 16	16
16	78.7, CH	4.81, m	1, 14, 17, 18, 22	15, 17
17	36.6, CH	1.63, m	16, 18, 19, 22	22
18a	32.2, CH_2	1.32, ovlp	16, 17, 19, 20, 22	17, 18b
18b		1.04, m	16, 17, 19, 20, 22	17, 18a
19a	29.2, CH_2	1.30, ovlp	17, 20	19b
19b		1.22, m	17, 20	19a
20a	22.9, CH_2	1.29, ovlp	18, 19, 21	14
20b		1.25, ovlp	18, 19, 21	14
21	14.0, CH_3	0.88, t (6.4)	19, 20	20b
22	15.0, CH_3	0.86, d (6.8)	16, 17, 18	17
23	56.3, CH_3	3.30, s	12	
24	21.3, CH_3	0.99, d (6.6)	8, 9, 10	9
25	14.8, CH_3	1.84, s	6, 7, 8	8

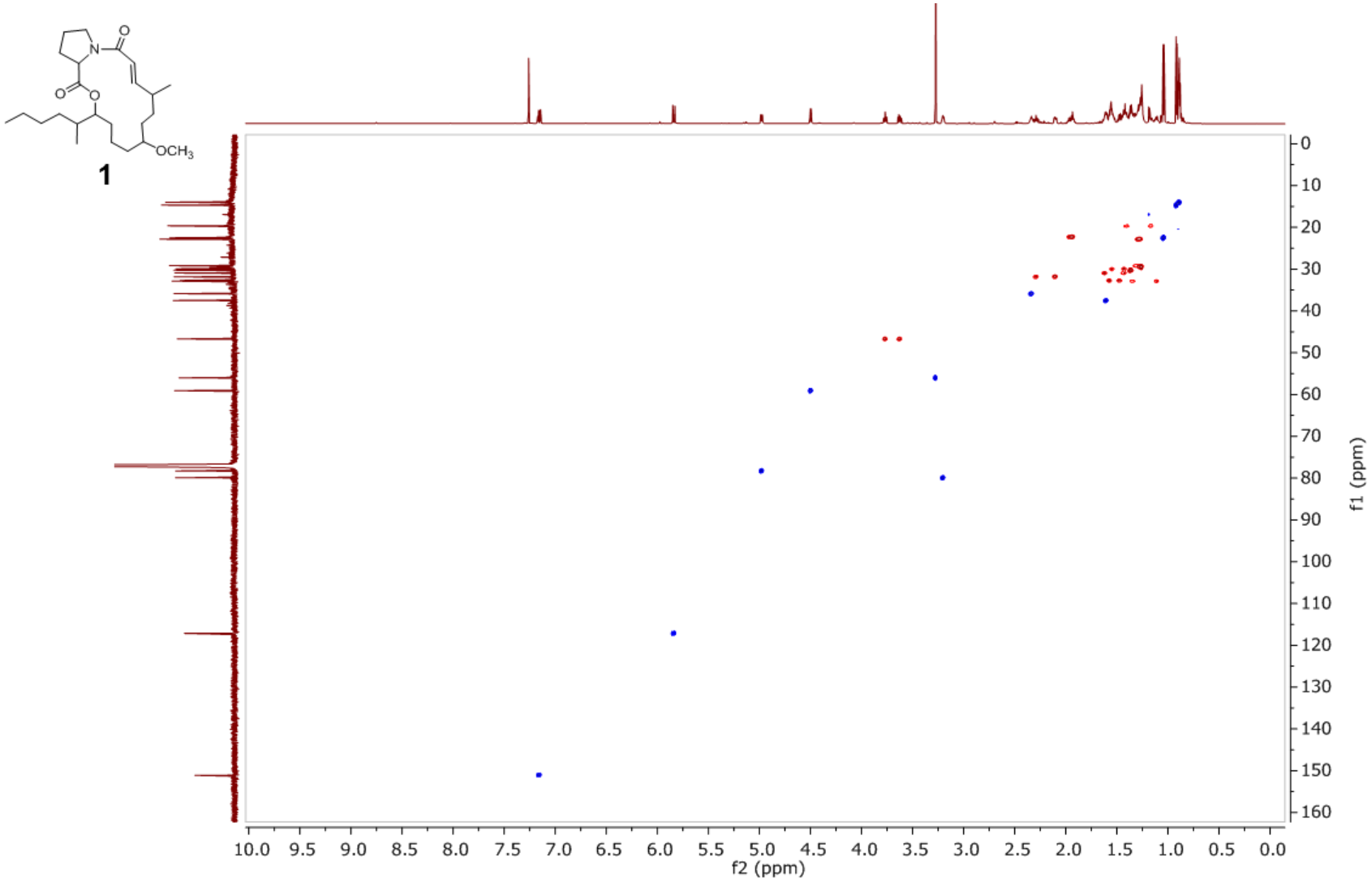
[a]overlapping signals



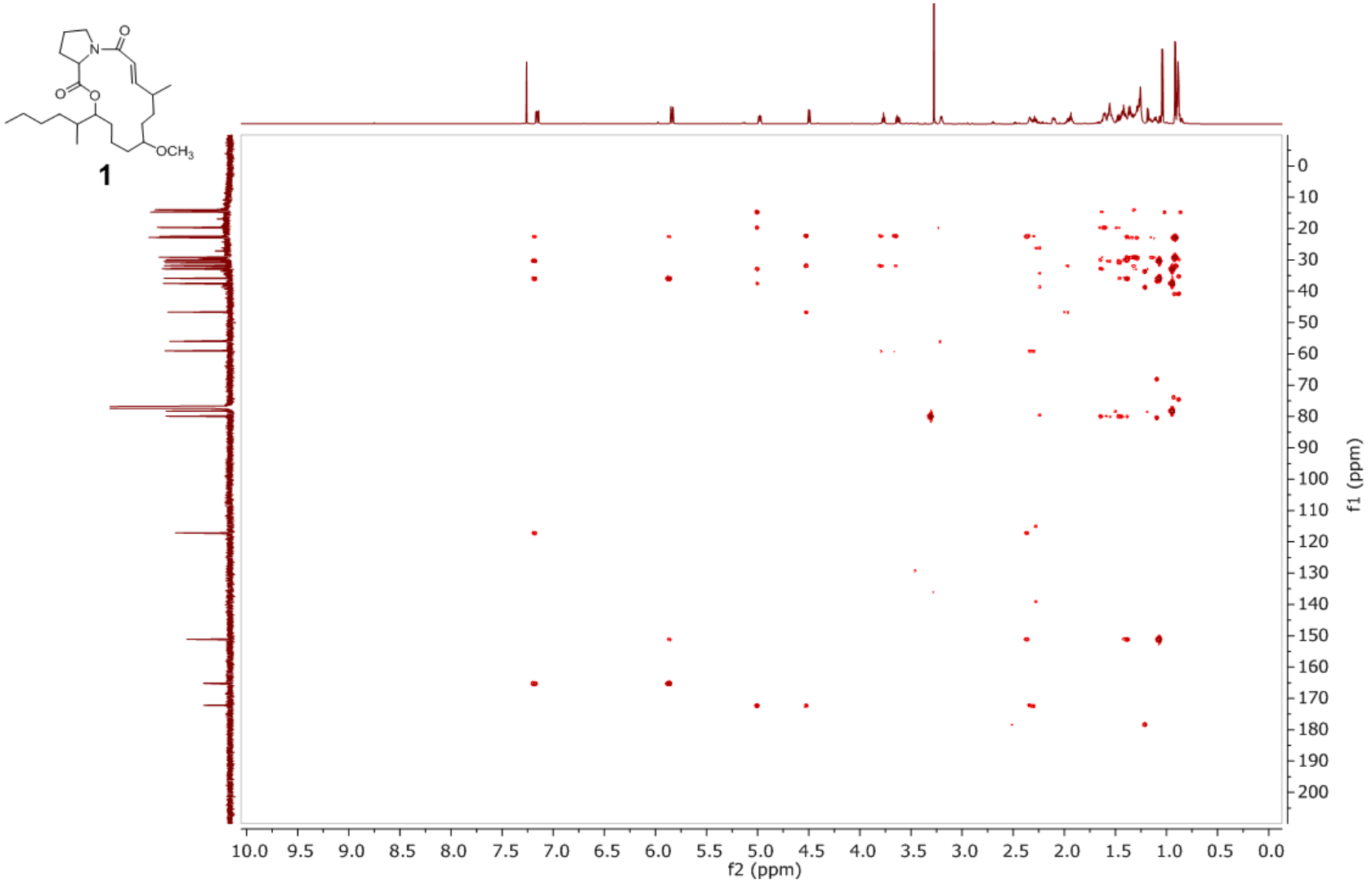
S1. ^{1}H NMR spectrum of tricholide A (**1**) (800 MHz, $CDCl_3$).



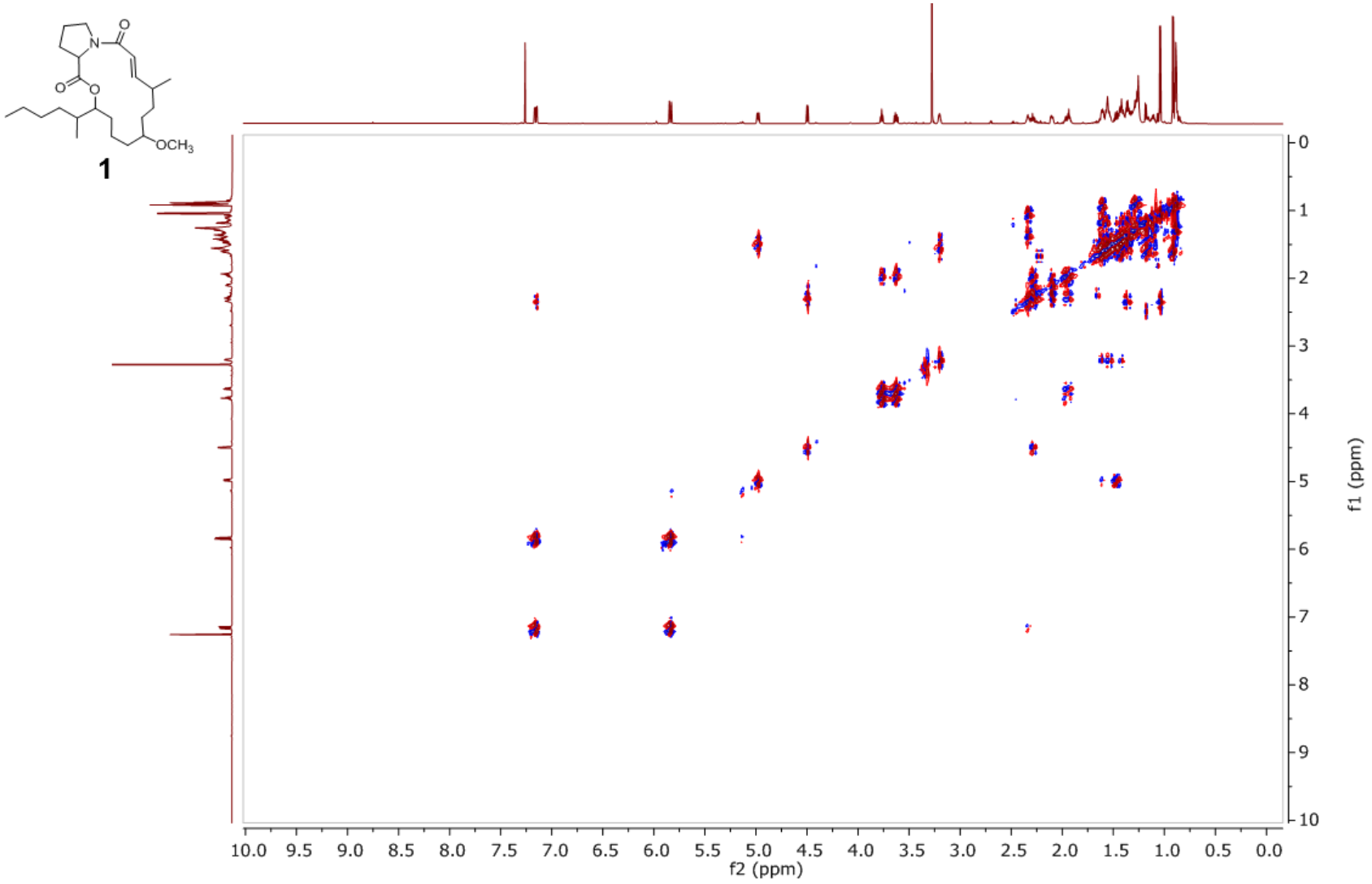
S2. ^{13}C NMR spectrum of **1** (200 MHz, $CDCl_3$).



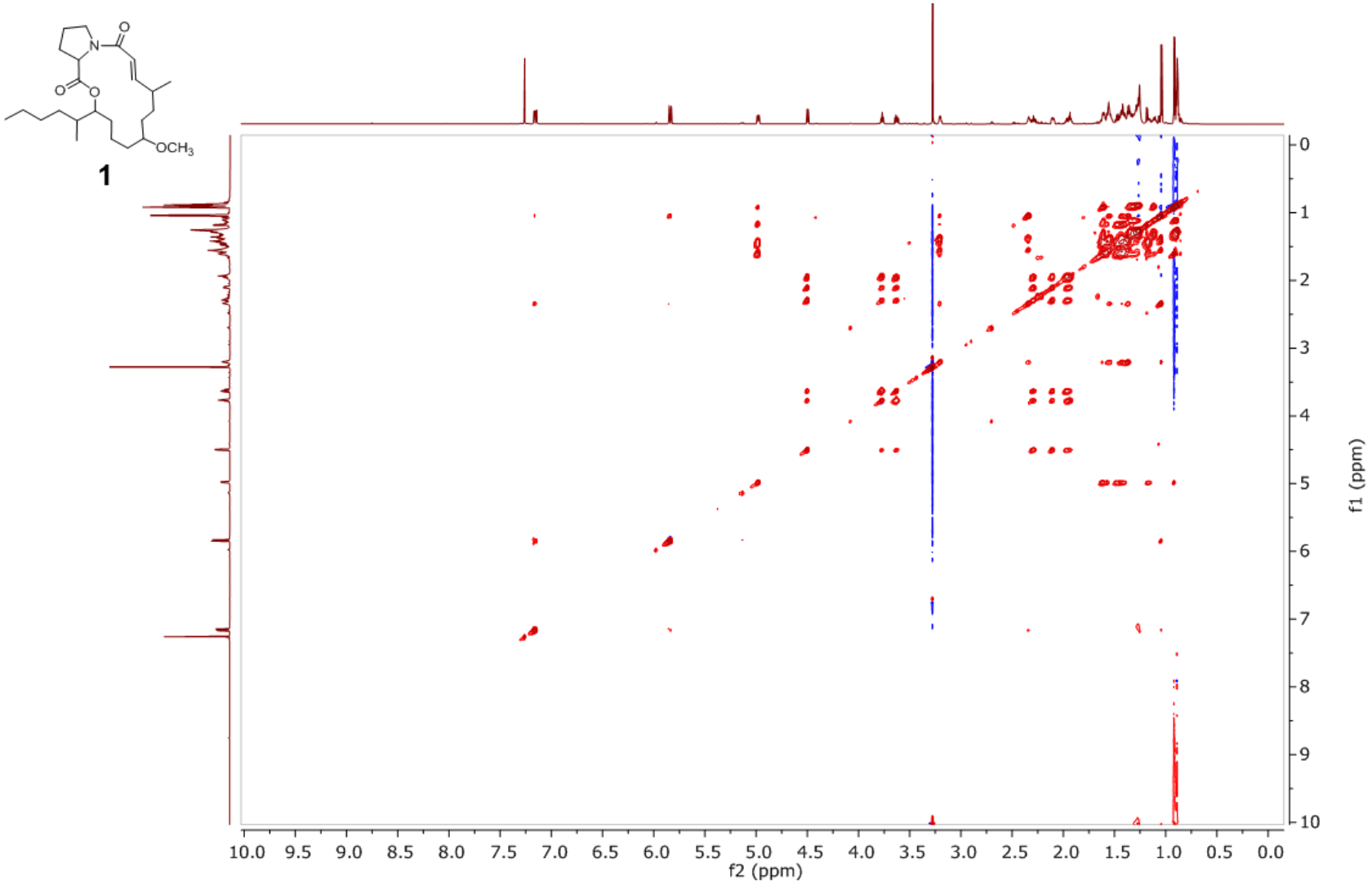
S3. HSQC spectrum of **1**.



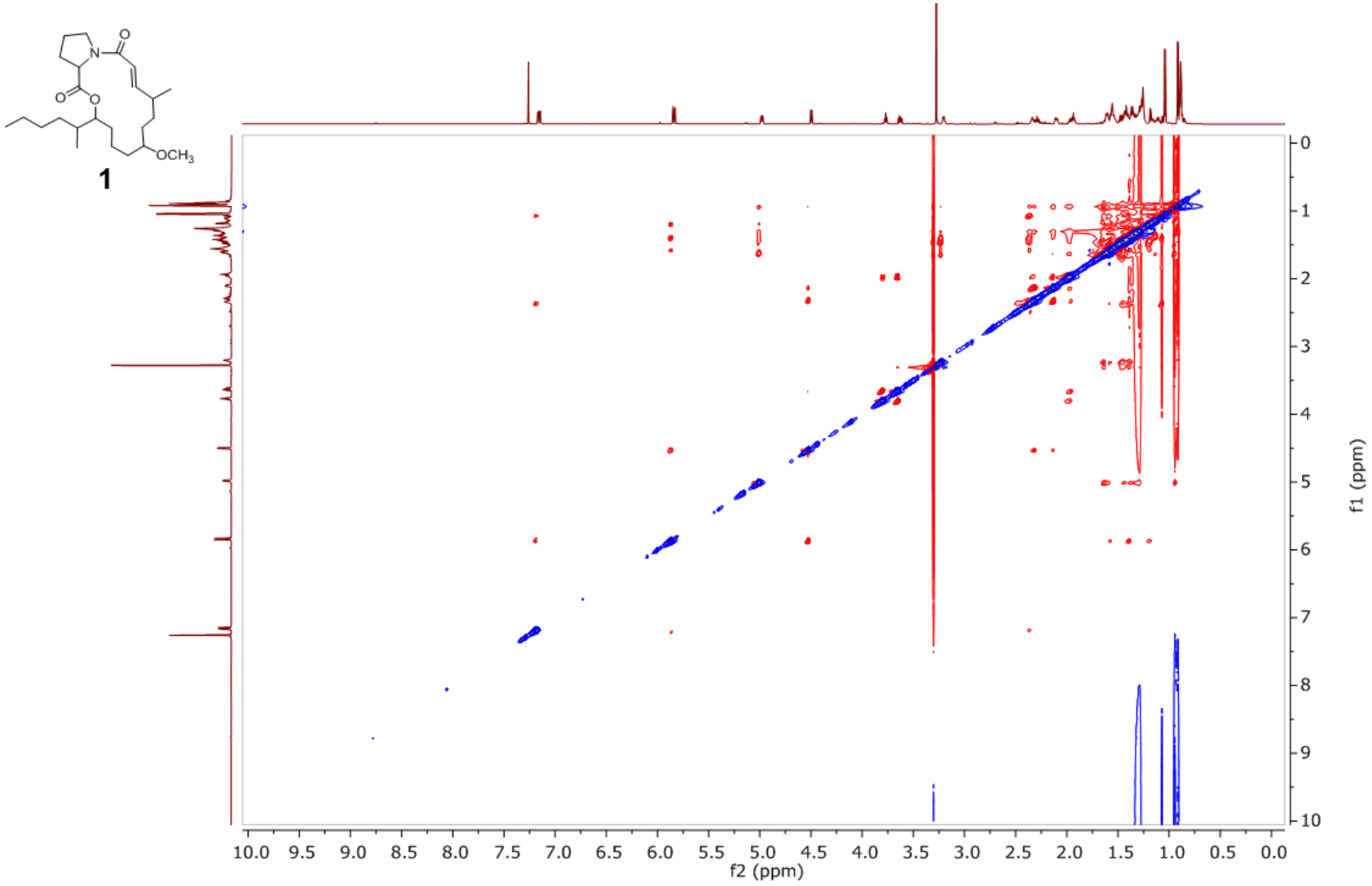
S4. HMBC spectrum of **1**.



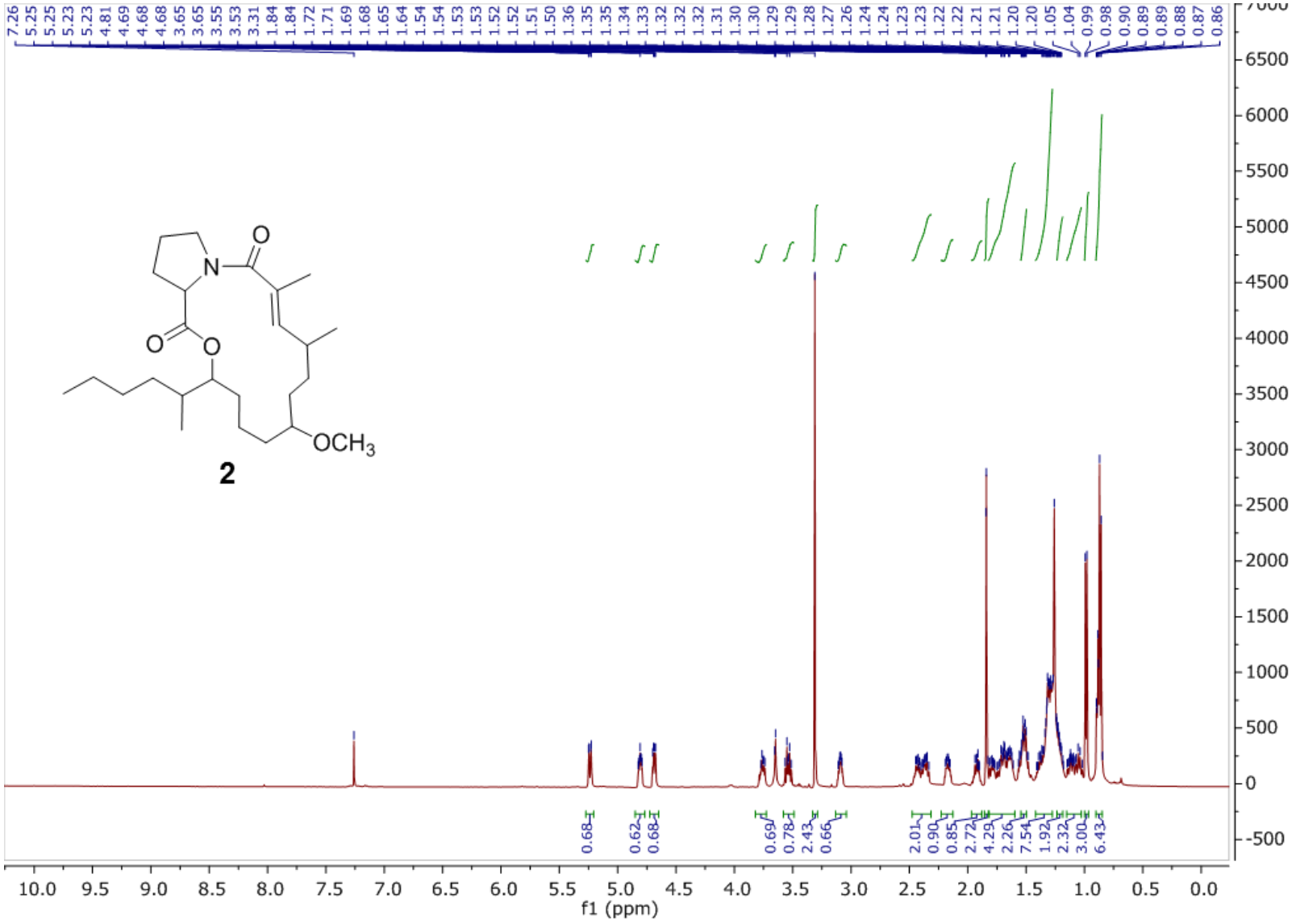
S5. COSY spectrum of **1**.



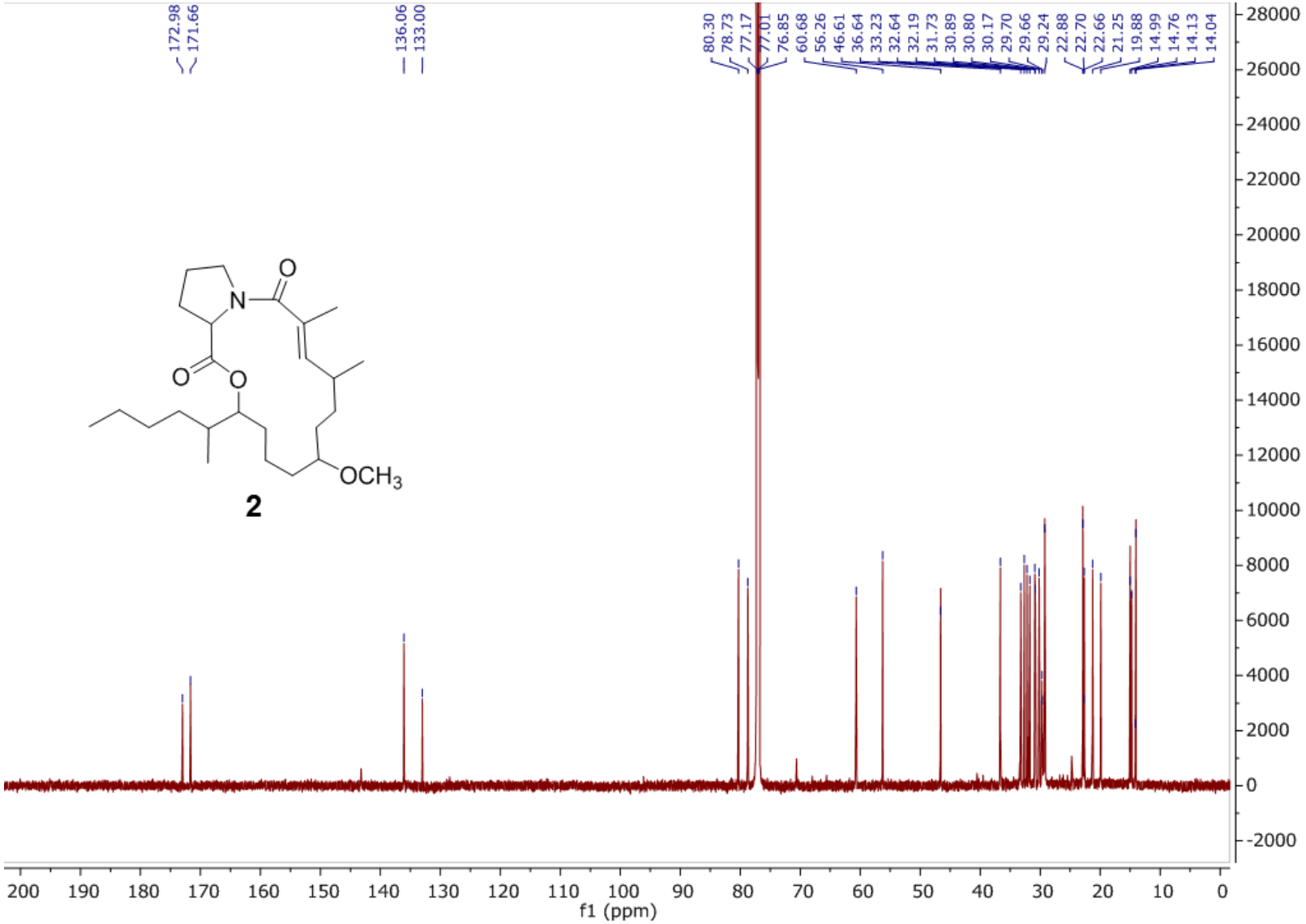
S6. TOCSY spectrum of **1**.



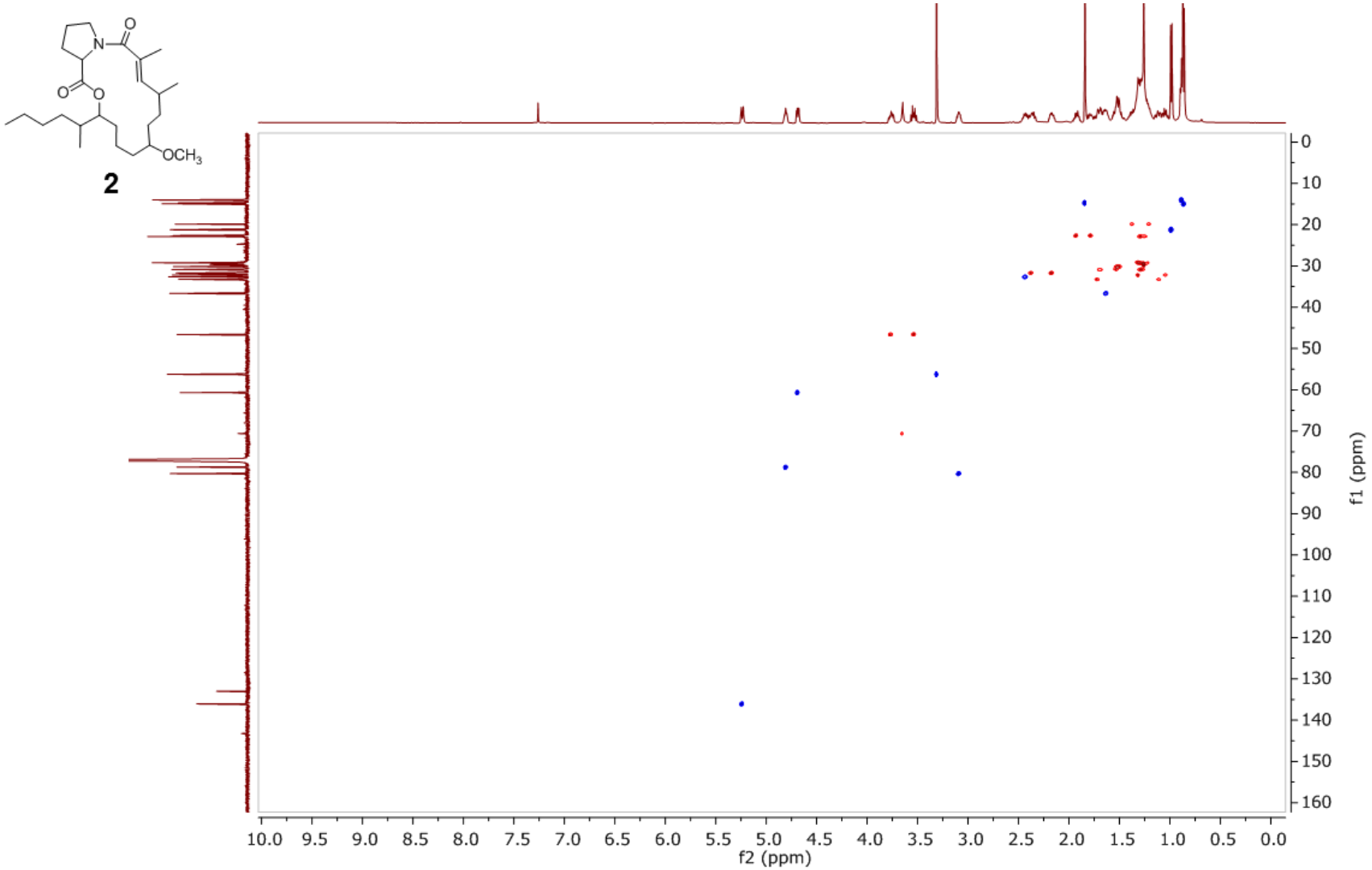
S7. NOESY spectrum of **1**.



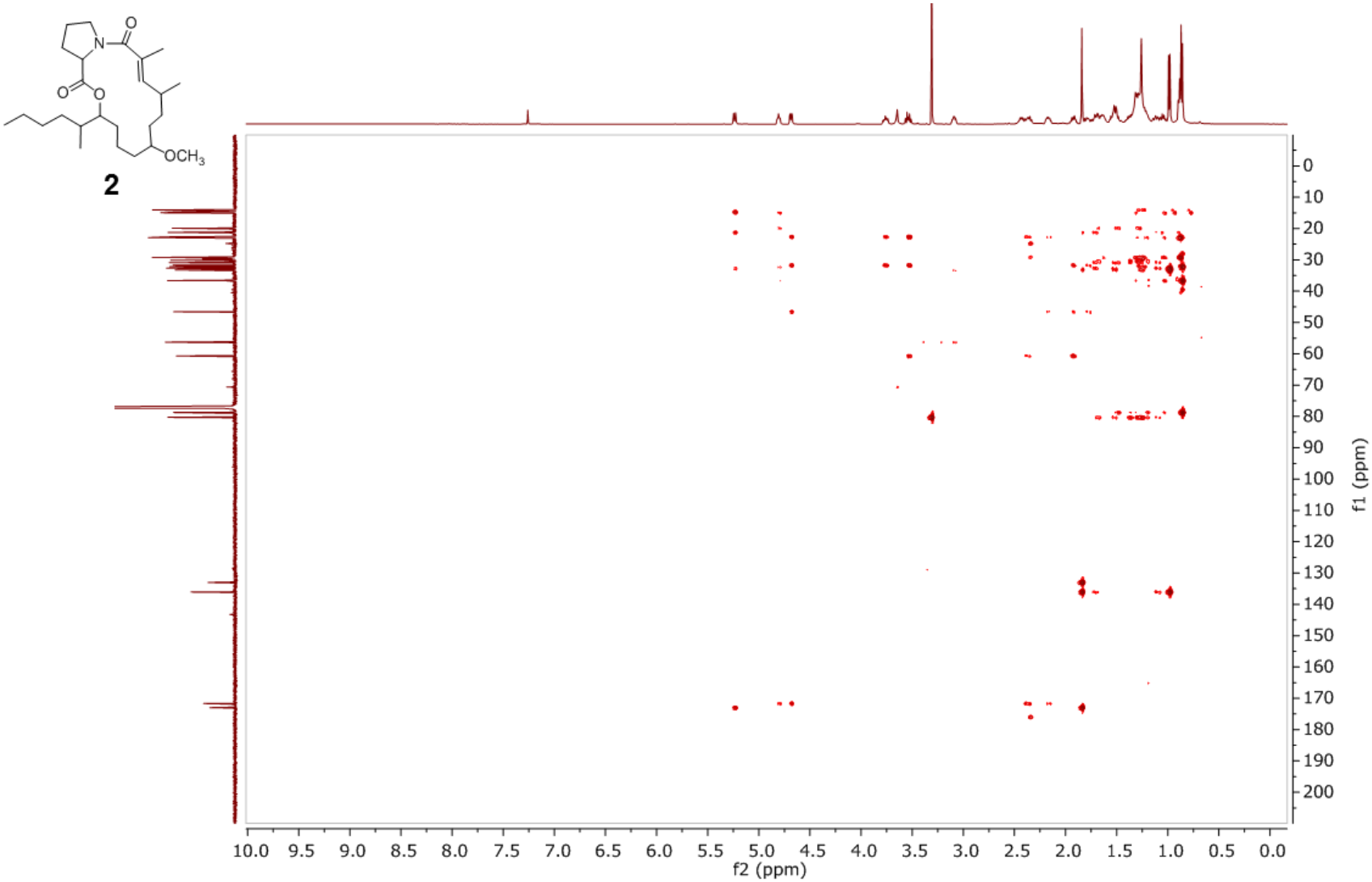
S8. ^{1}H NMR spectrum of tricholide B (**2**) (800 MHz, $CDCl_3$).



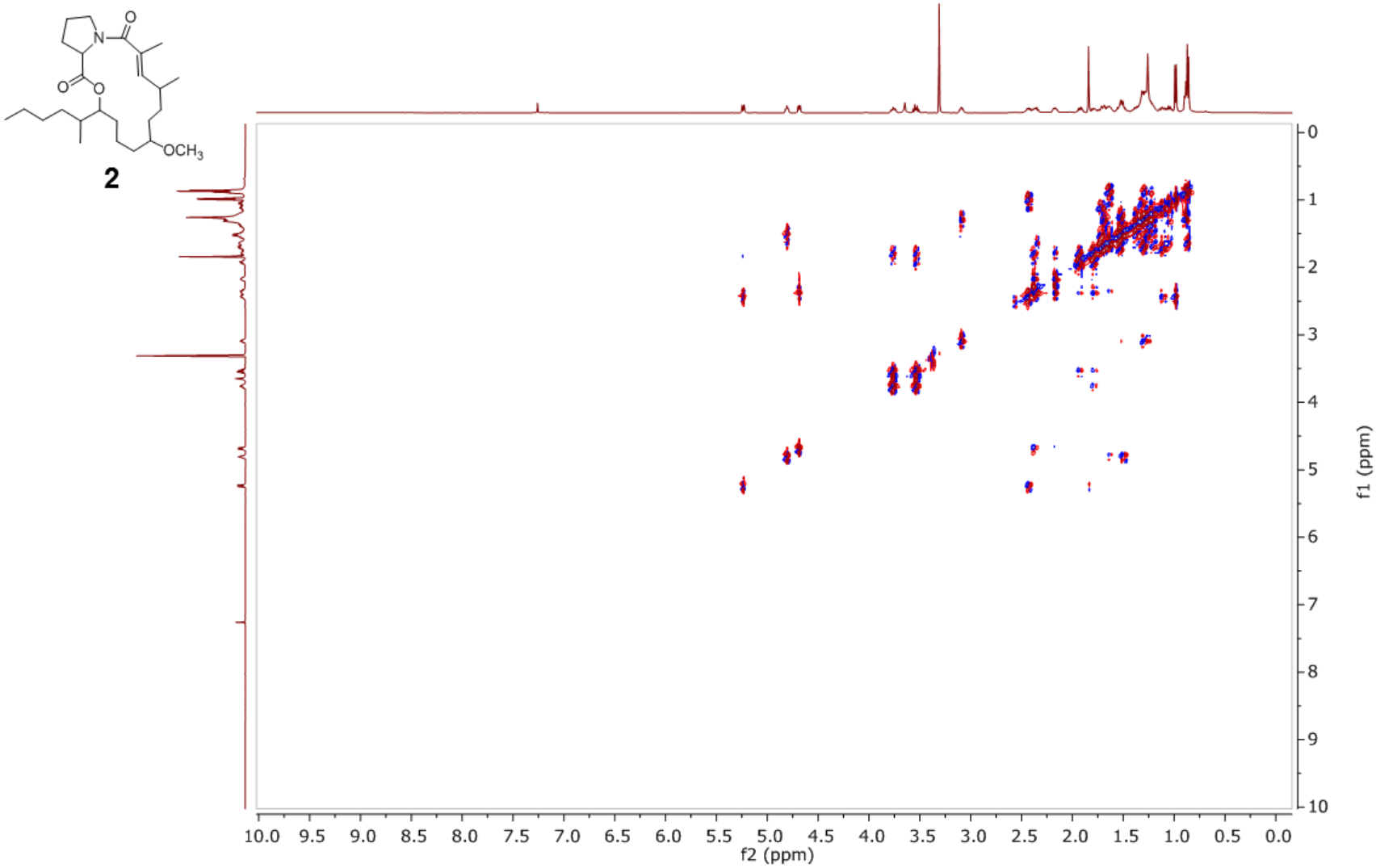
S9. ^{13}C NMR spectrum of **2** (200 MHz, $CDCl_3$).



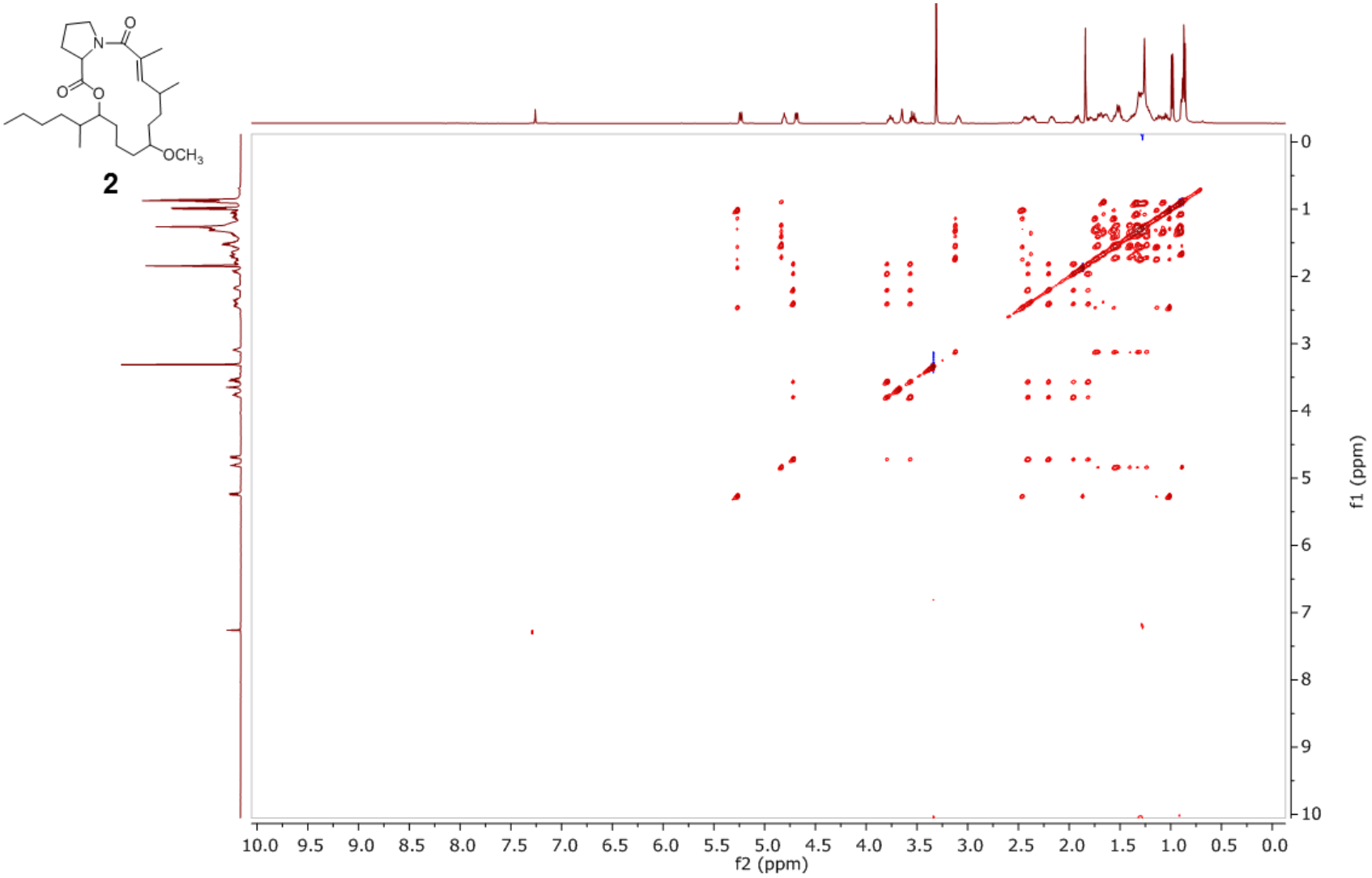
S10. HSQC spectrum of **2**.



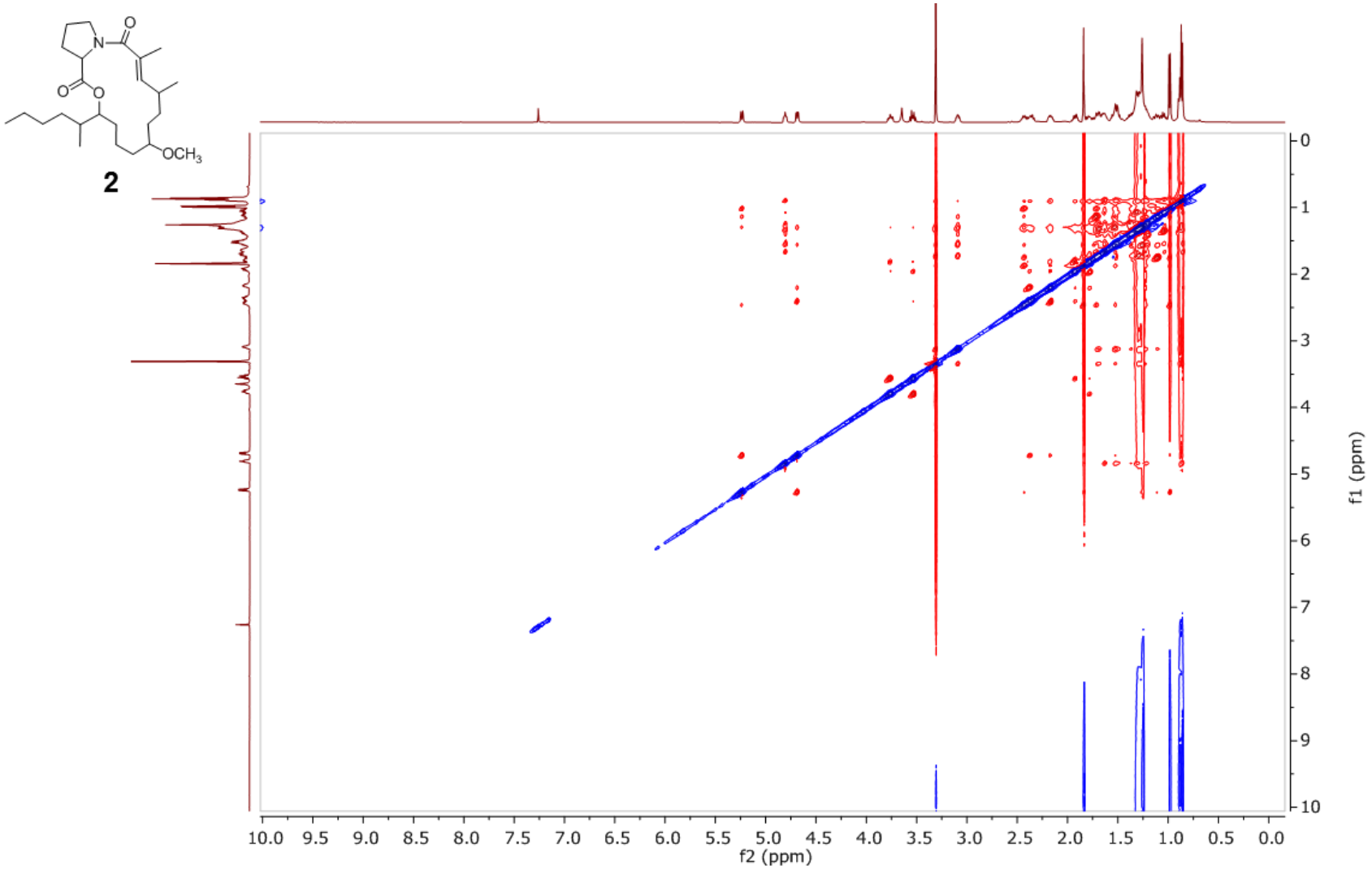
S11. HMBC spectrum of **2**.



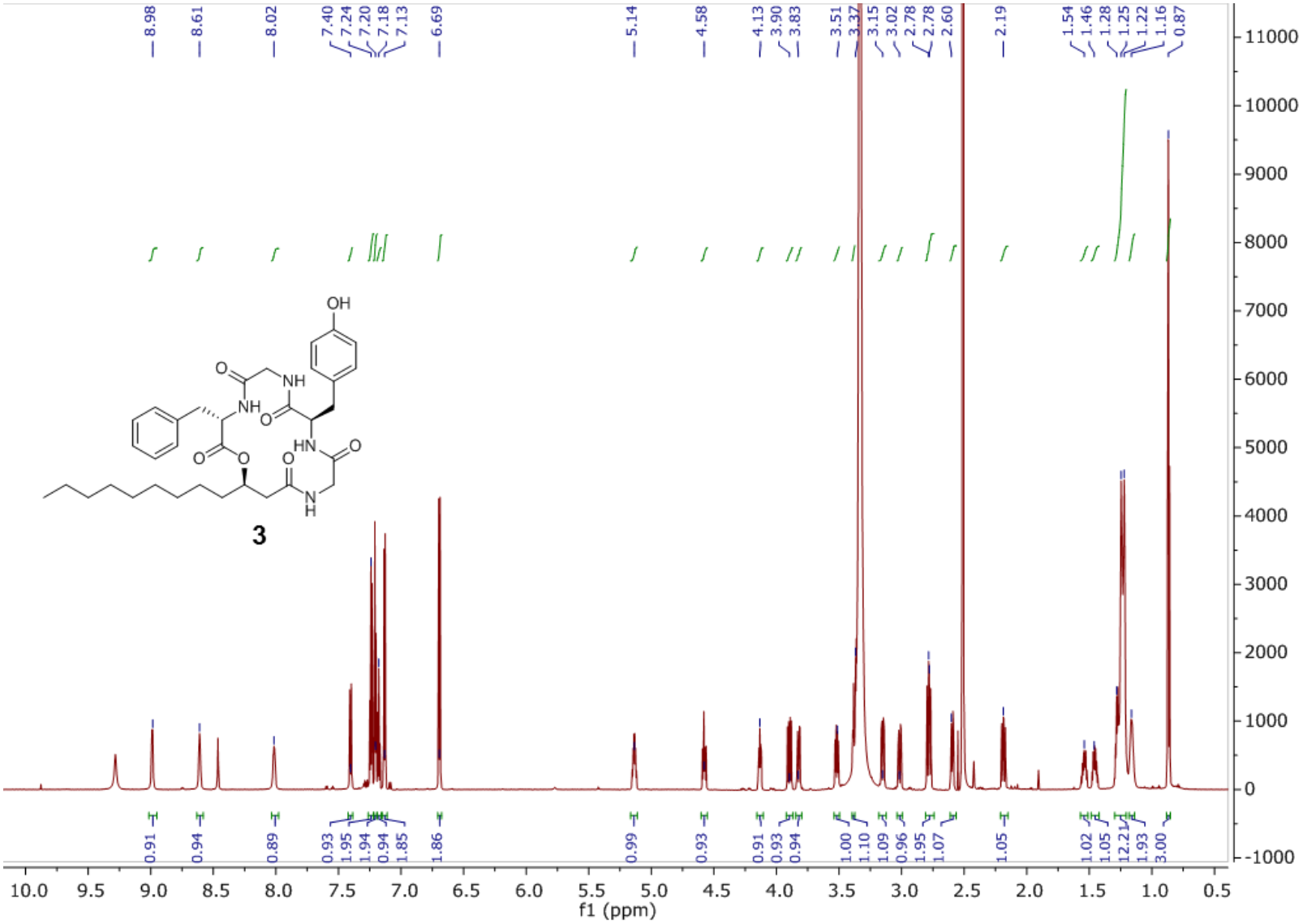
S12. COSY spectrum of **2**.



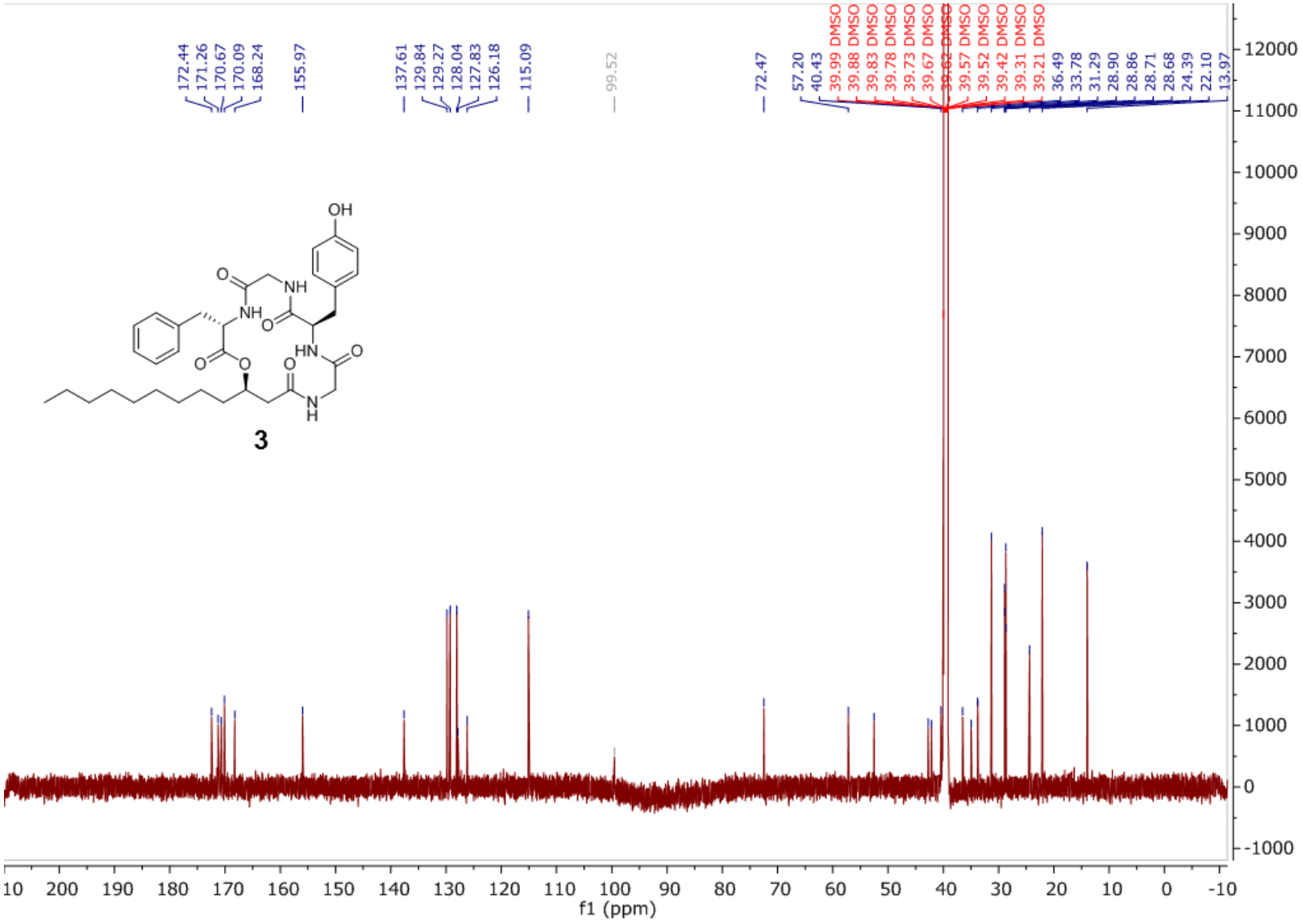
S13. TOCSY spectrum of **2**.



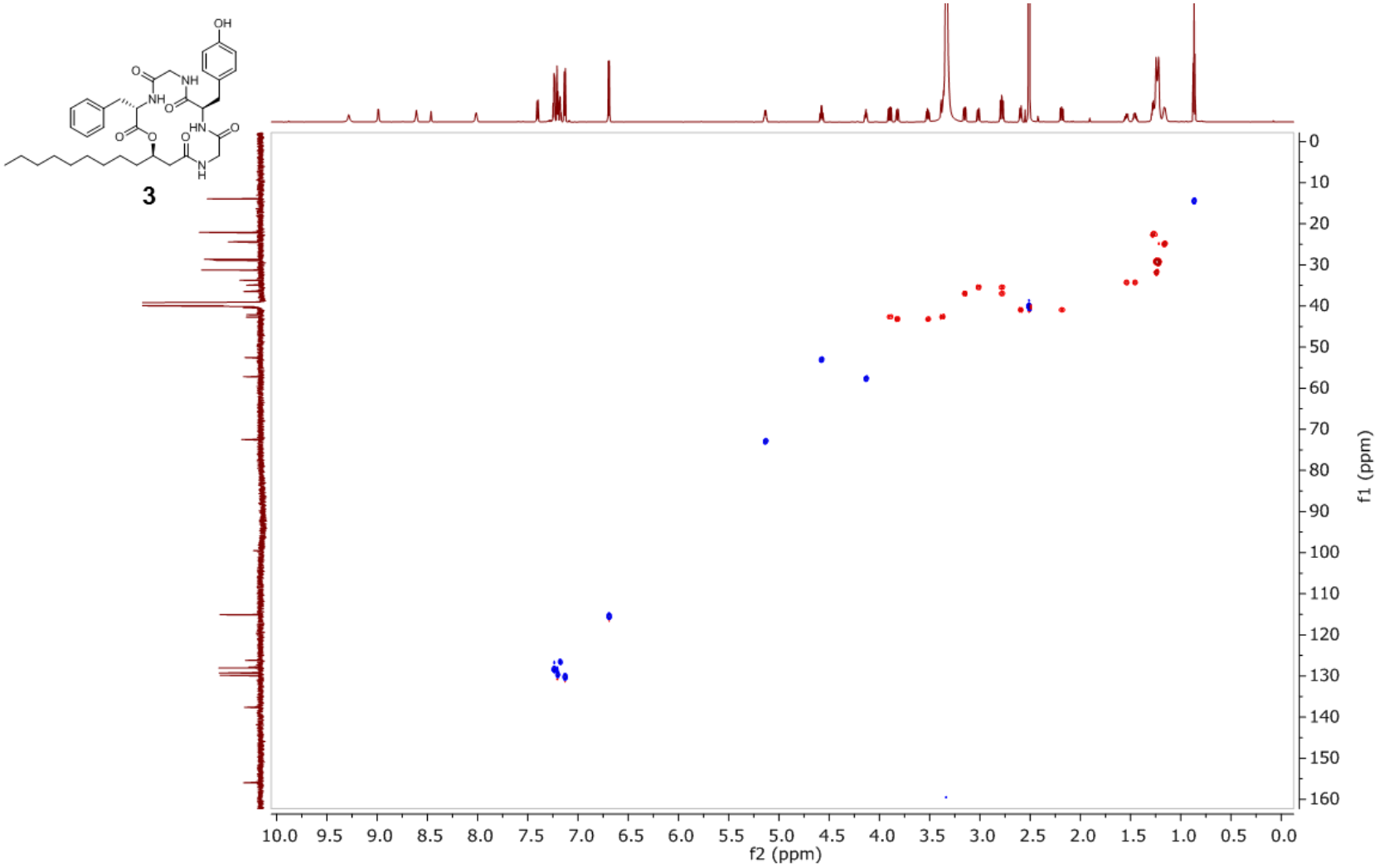
S14. NOESY spectrum of **2**.



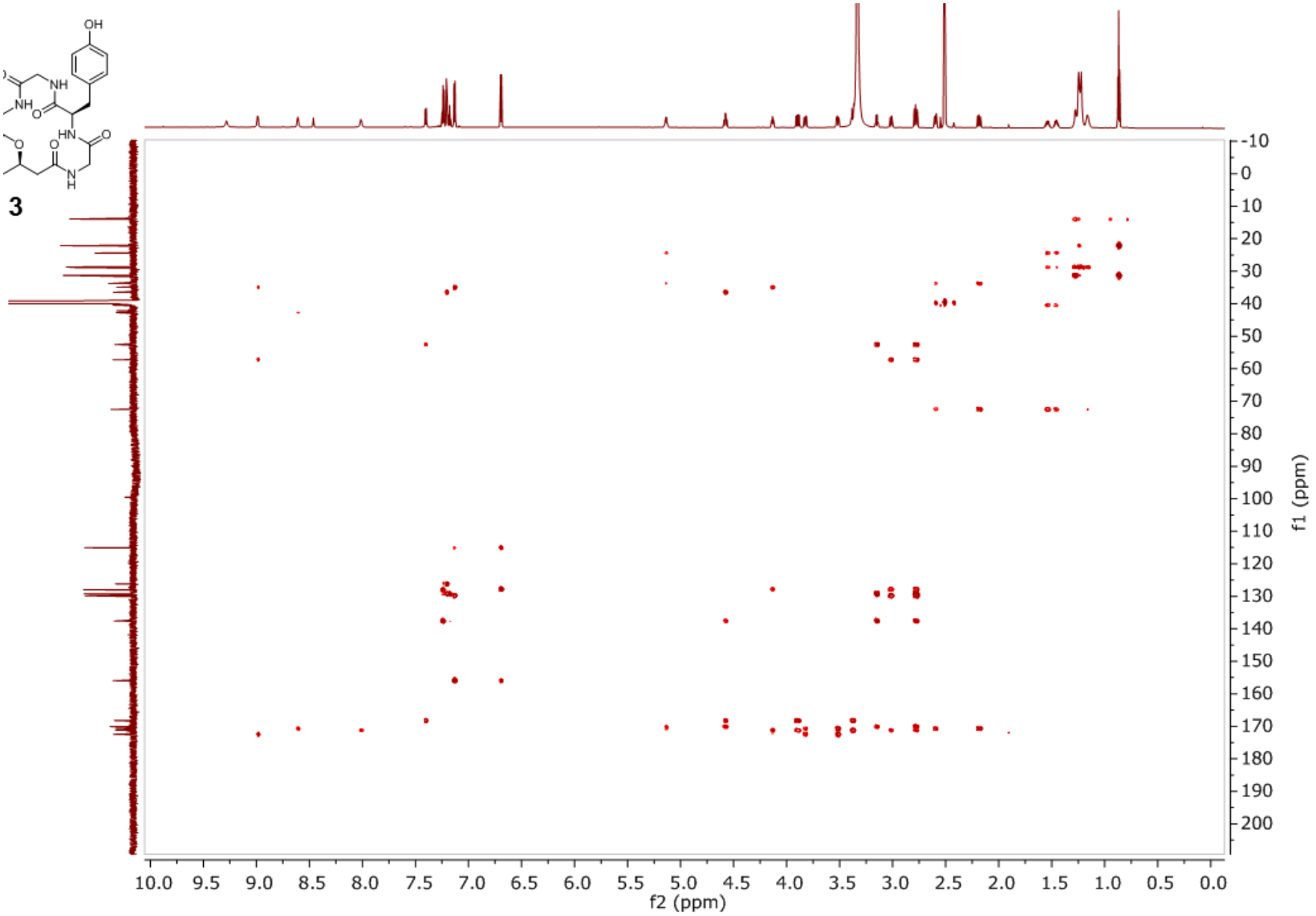
S15. ^{1}H NMR spectrum of unnarmicin D (**3**) (800 MHz, DMSO).



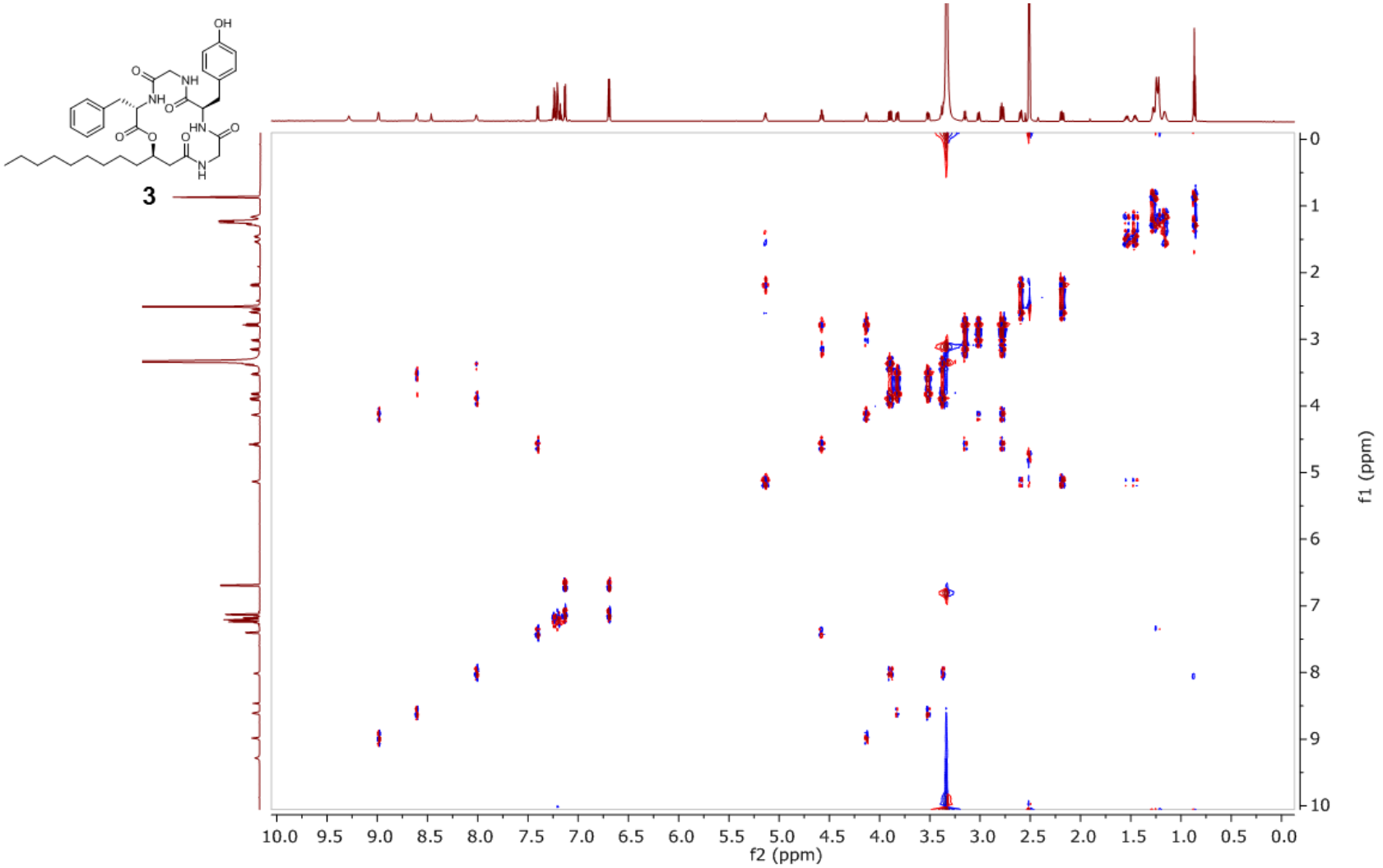
S16. ^{13}C NMR spectrum of **3** (200 MHz, DMSO).



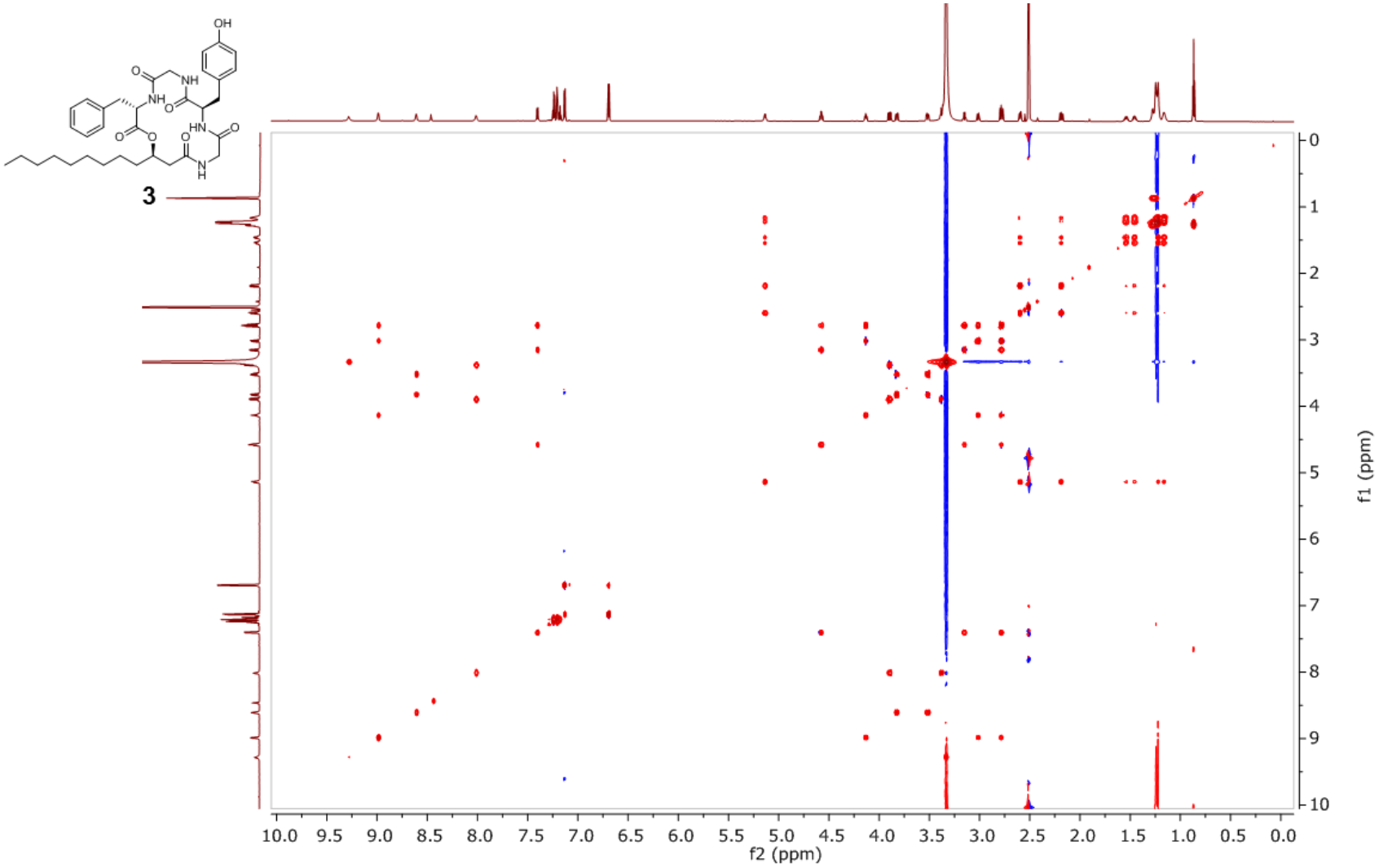
S17. HSQC spectrum of **3**.



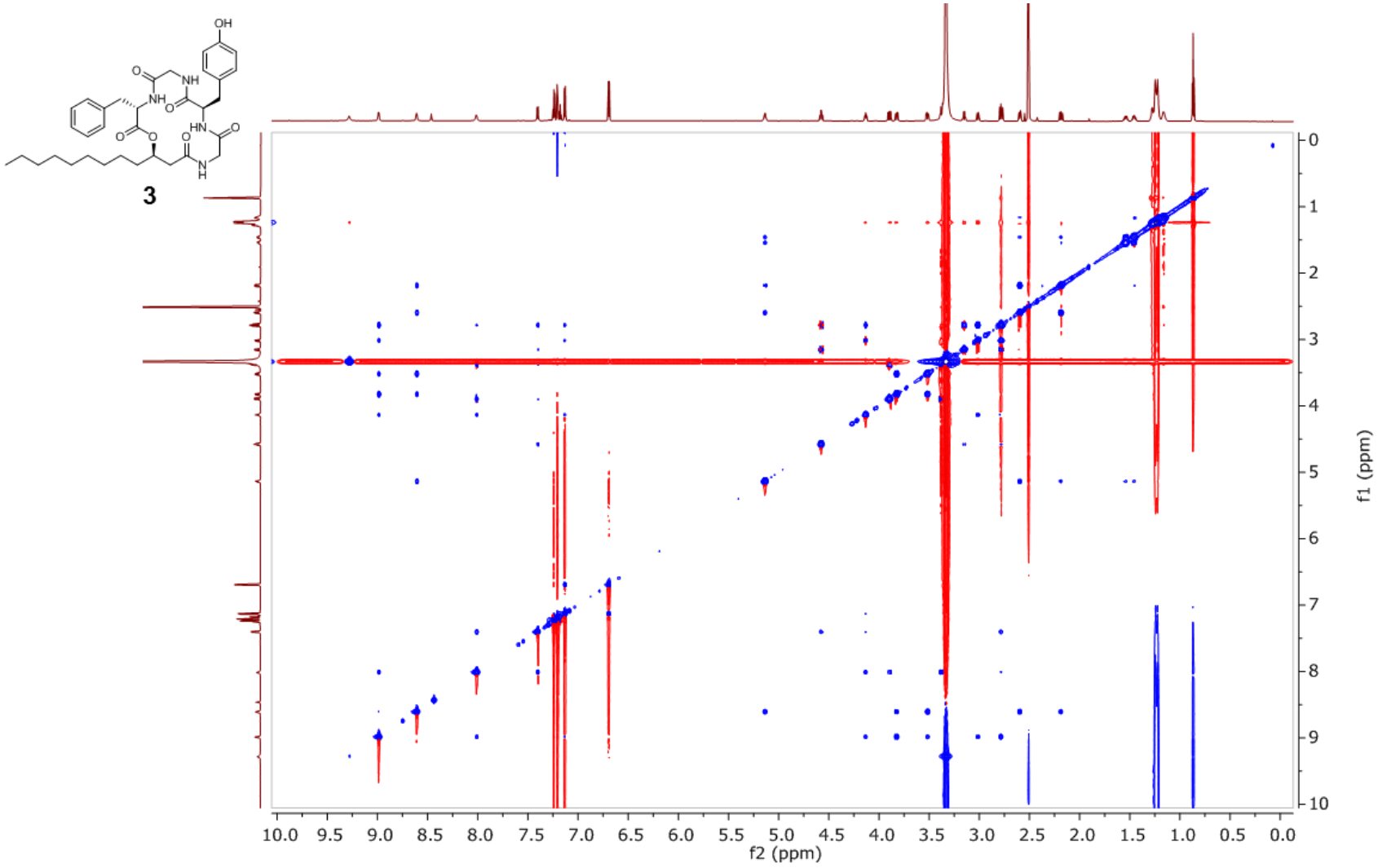
S18. HMBC spectrum of **3**.



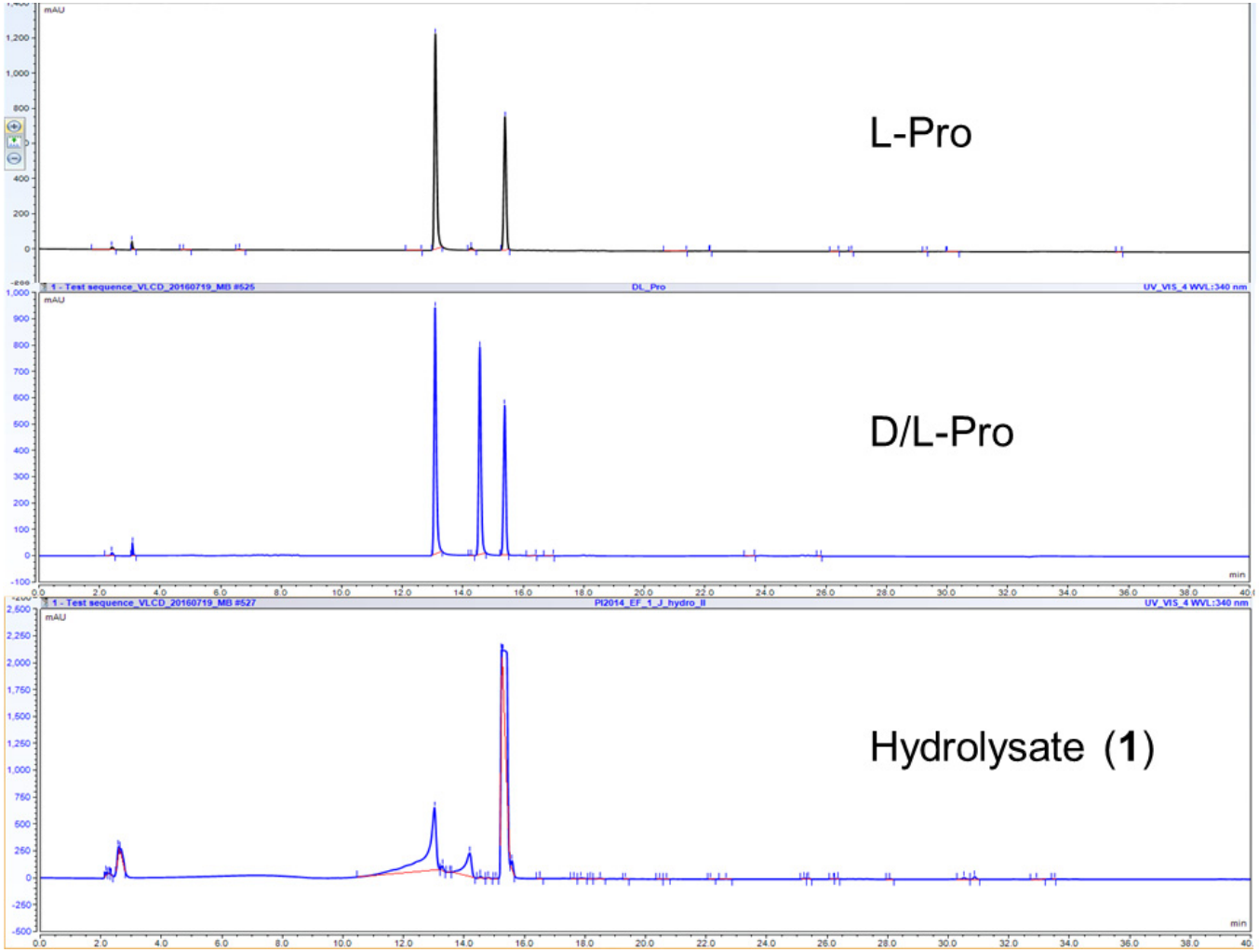
S19. COSY spectrum of **3**.



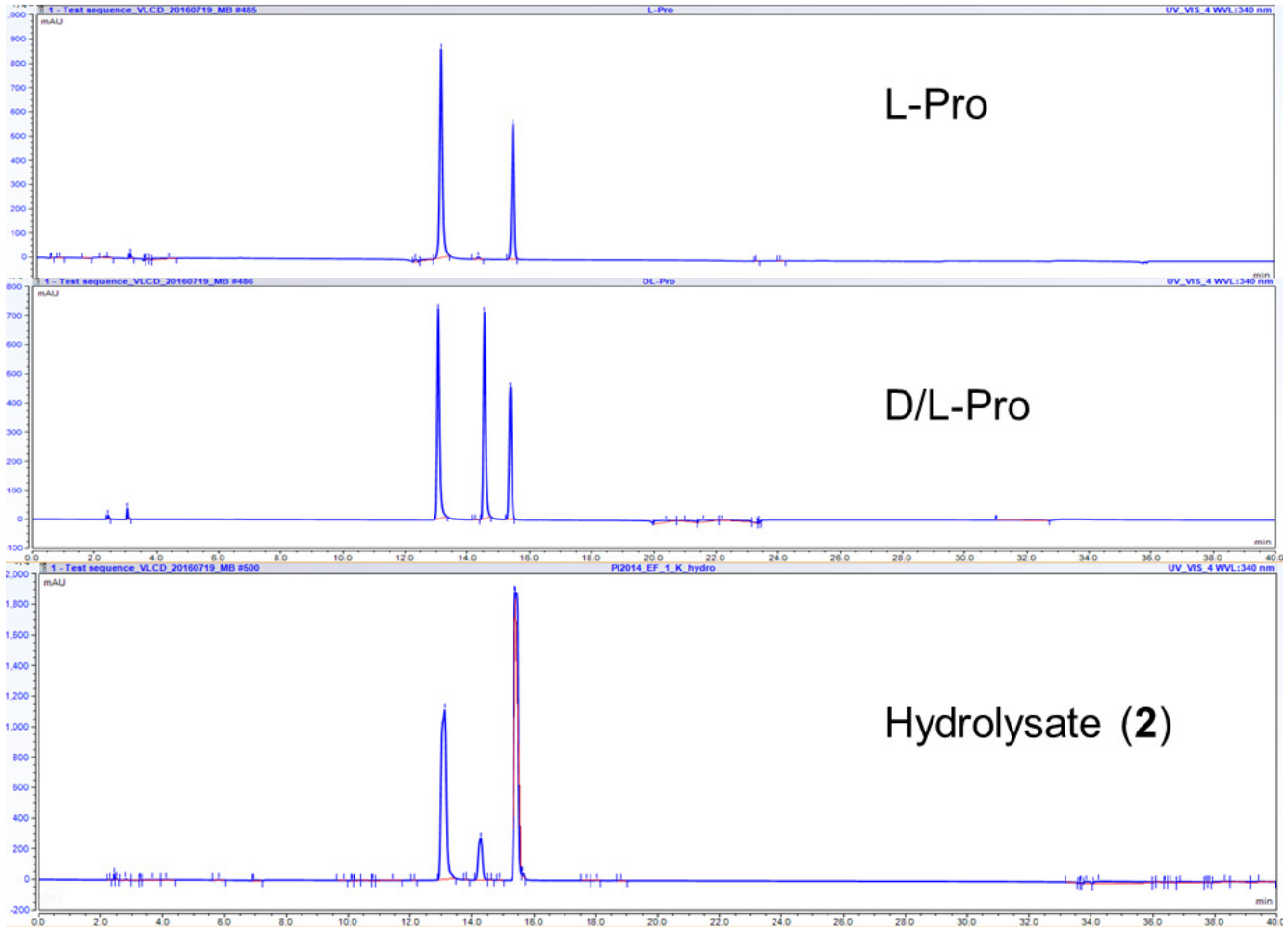
S20. TOCSY spectrum of **3**.



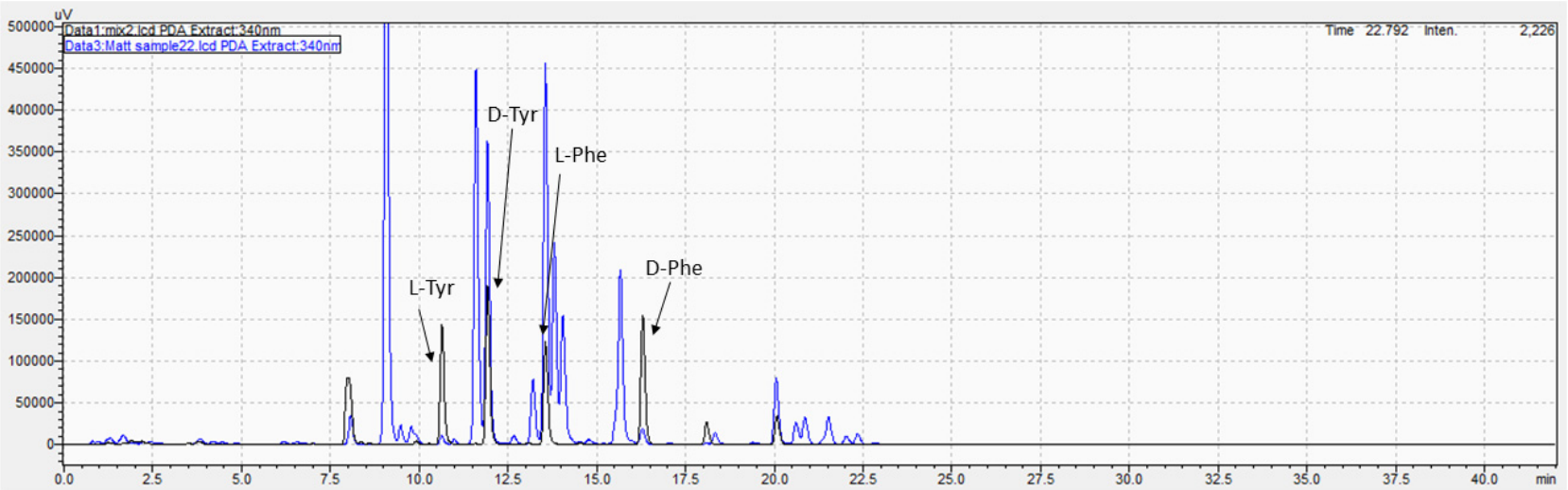
S21. NOESY spectrum of **3**.



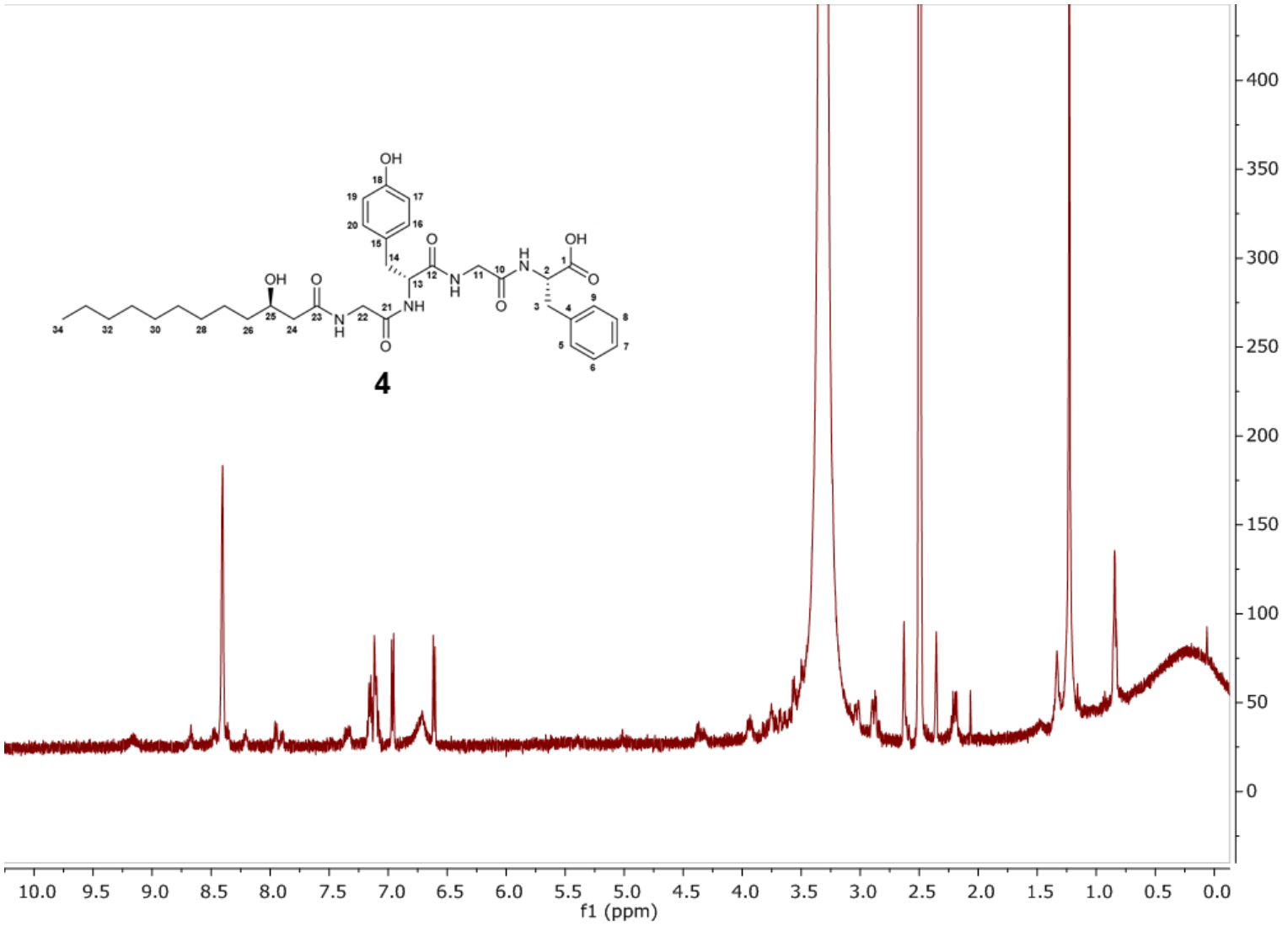
S22. Chromatographic comparison of the L-FDVA reacted acid hydrolyzate of **1** compared to authentic amino acid standards reacted with L-FDVA.



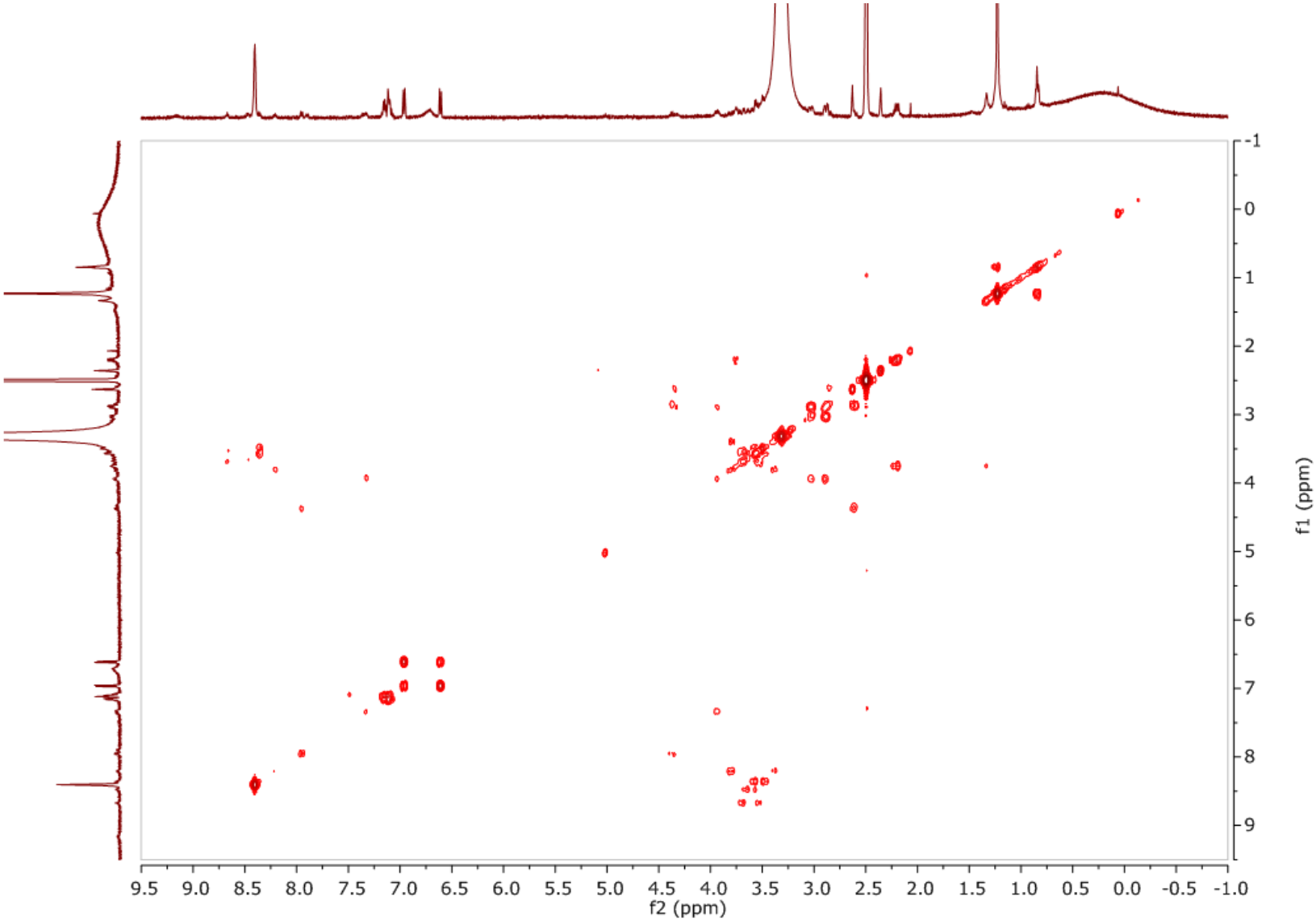
S23. Chromatographic comparison of the L-FDVA reacted acid hydrolyzate of **2** compared to authentic amino acid standards reacted with L-FDVA.



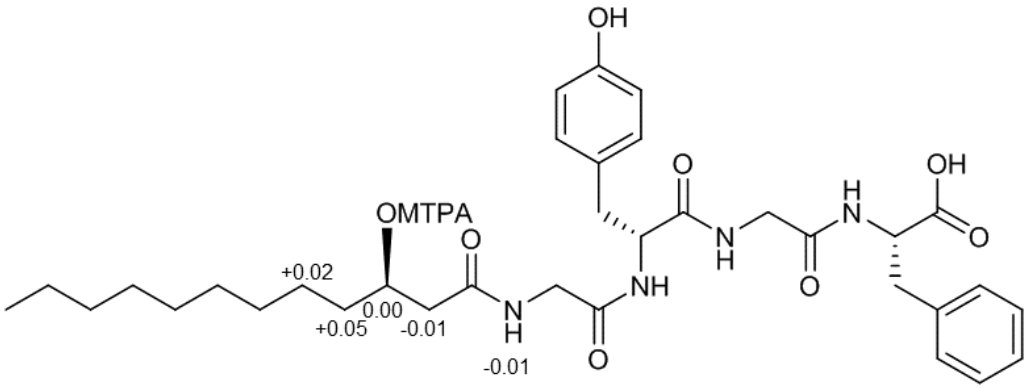
S24. Chromatographic comparison of the L-FDVA reacted acid hydrolyzate of **3** (blue UV trace) compared to authentic amino acid standards reacted with L-FDVA (black UV trace).



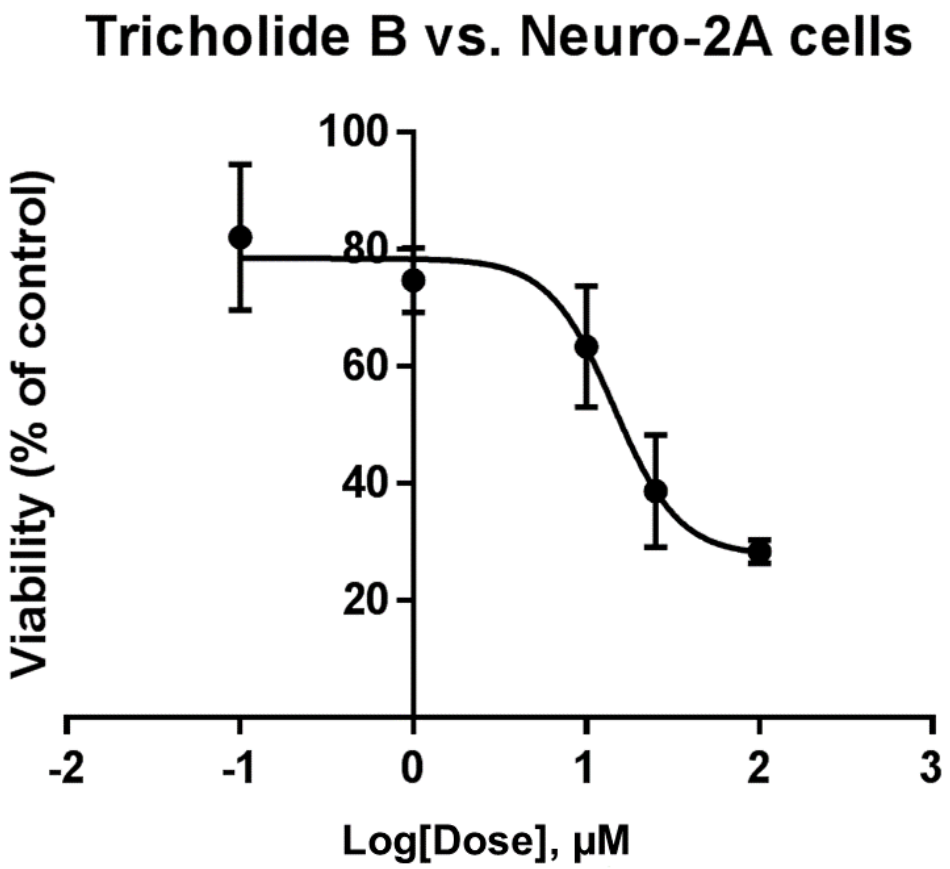
S25. ^{1}H NMR spectrum of unnarmicin D linear derivative (**4**) (500 MHz, DMSO).



S26. COSY spectrum of unnarmicin D linear derivative (**4**).



S27. $\Delta(\delta_H S\text{-}\delta_H R)$ values of *S*-MTPA and *R*-MTPA esters of **4**.



S28. Cytotoxicity of **2** against Neuro-2A mouse neuroblastoma cells. The dosing regime was carried out in triplicate.