SUPPORTING INFORMATION

Dechdigliotoxins A–C, three novel disulfide-~~B~~bridged gliotoxin dimers from deep-sea sediment derived fungus *Dichotomomyces cejpii*

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Figure S1. ^{1}H NMR spectrum of **1** in DMSO.

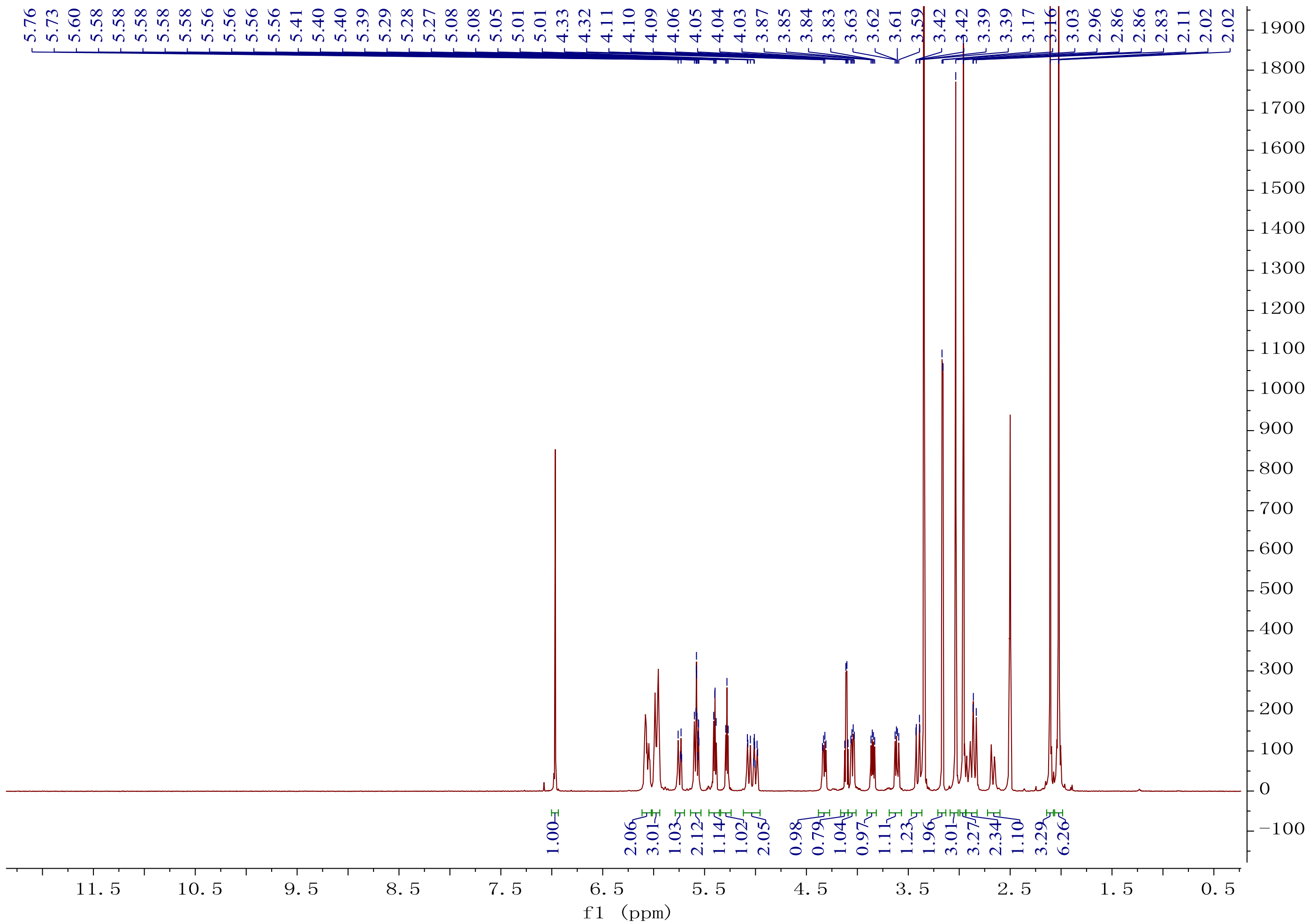


Figure S2. ^{13}C NMR spectrum of **1** in DMSO.

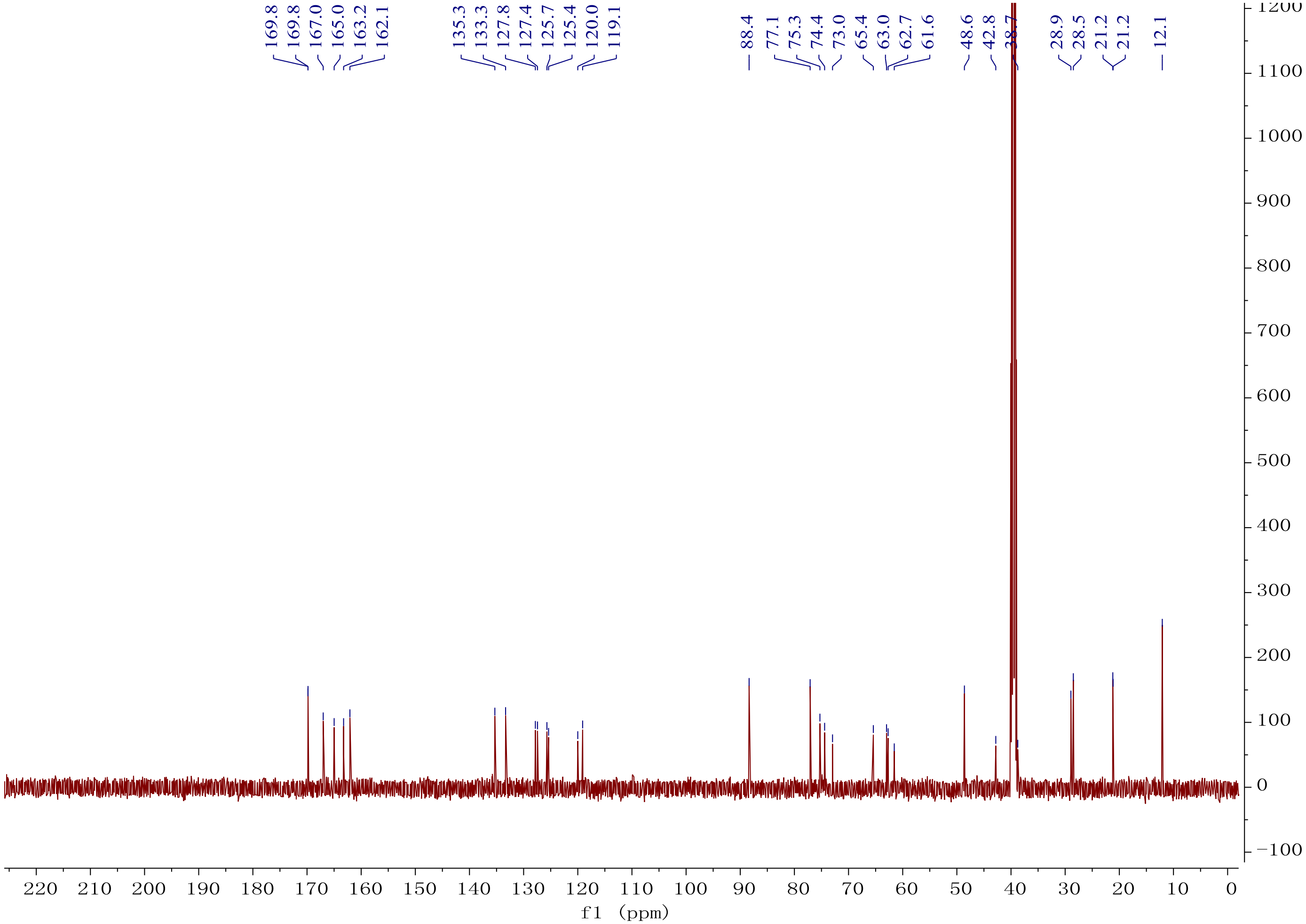


Figure S3. ^{1}H, ^{1}H-COSY spectrum of **1** in DMSO.

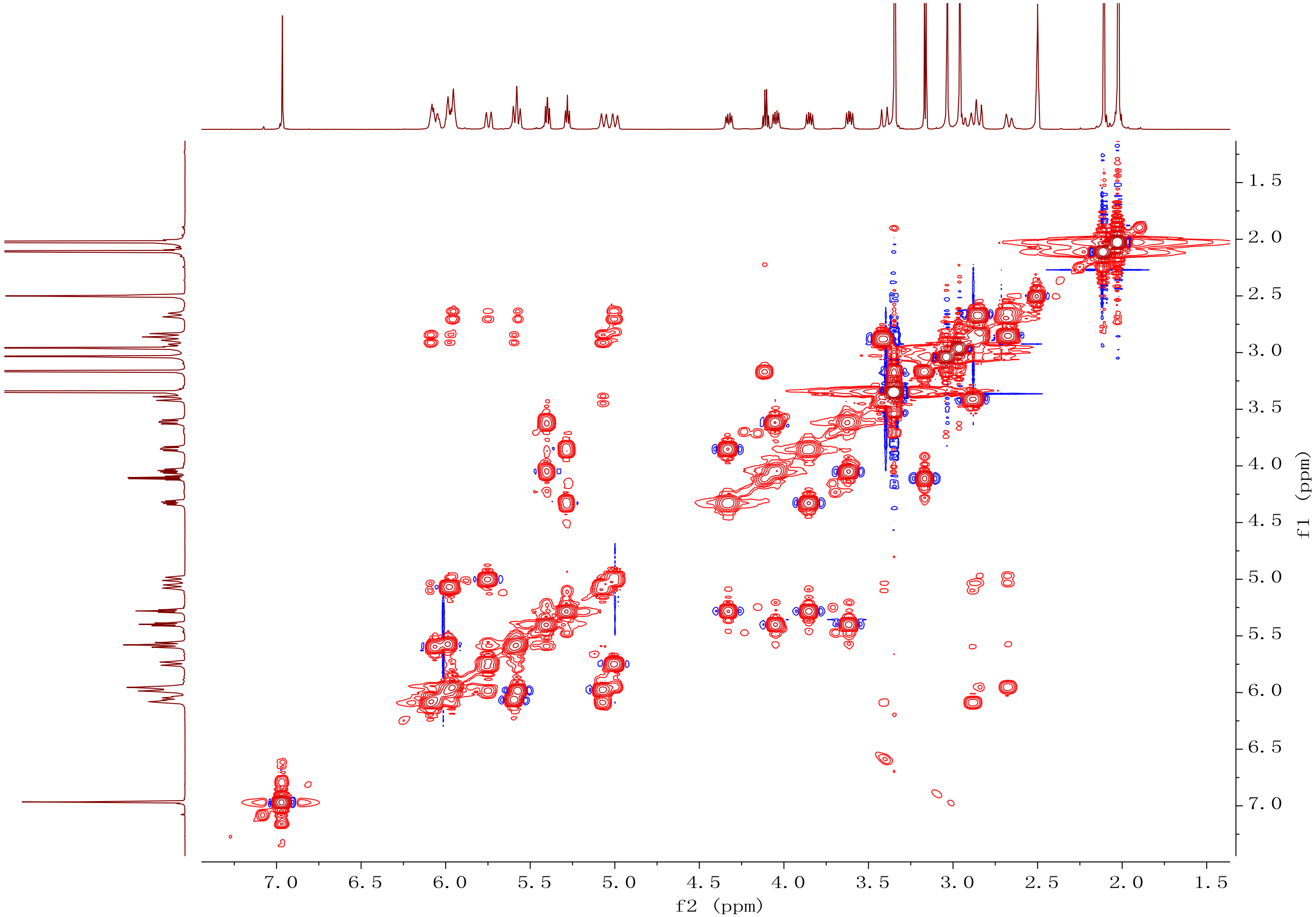


Figure S4. HSQC spectrum of **1** in DMSO.

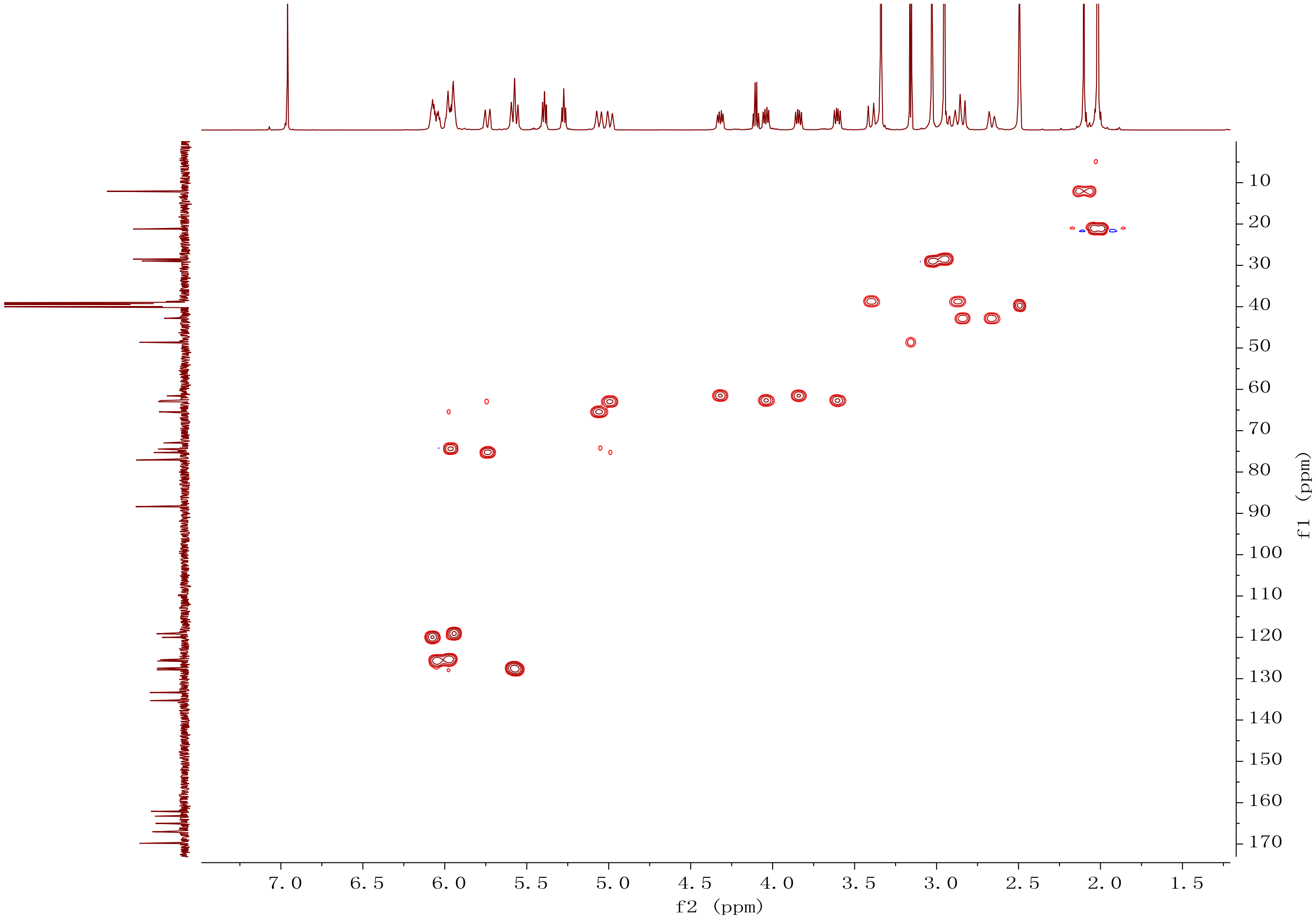


Figure S5. ^1H-^1H COSY **1** in DMSO.

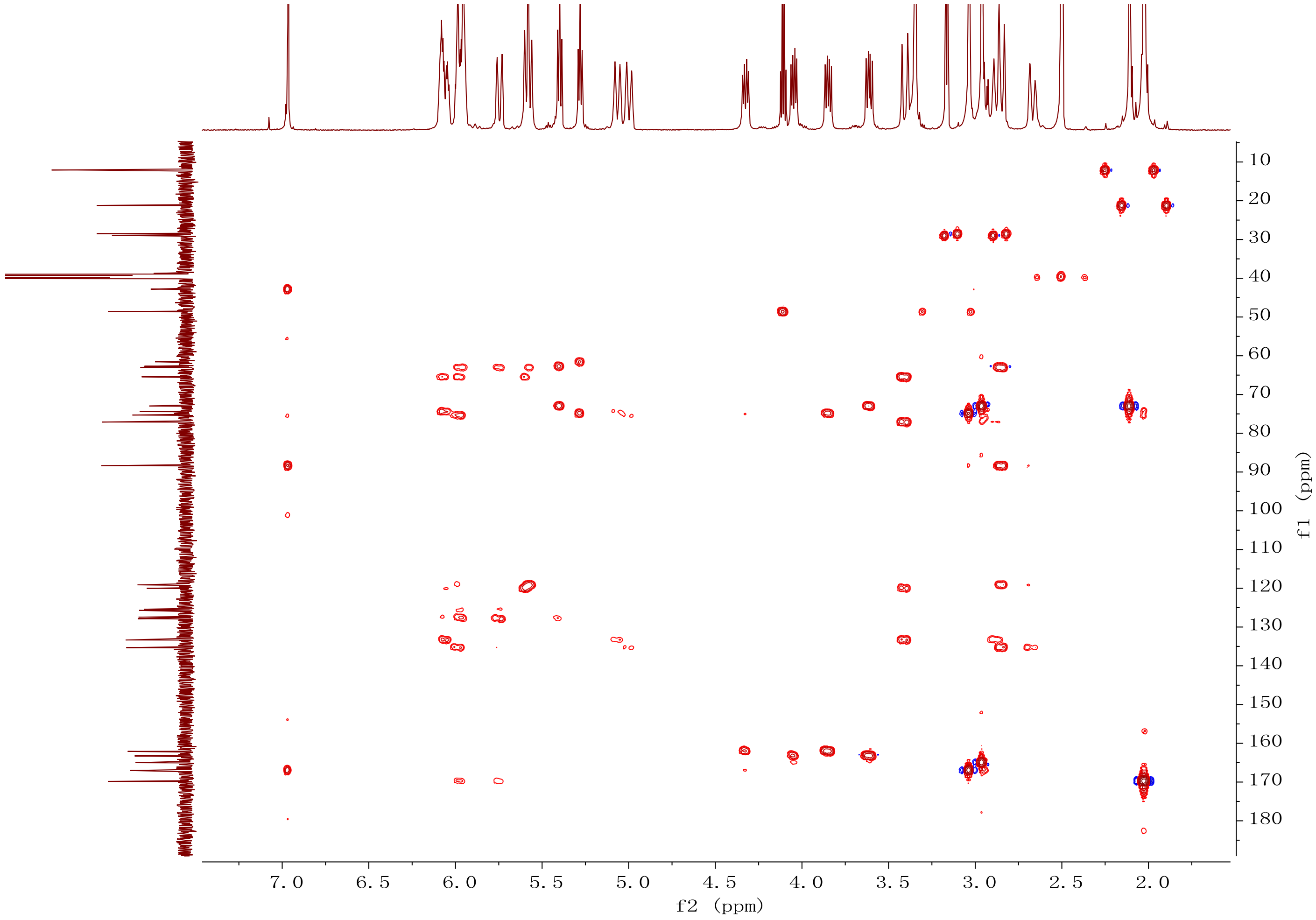


Figure S6. NOESY spectrum of **1** in DMSO.

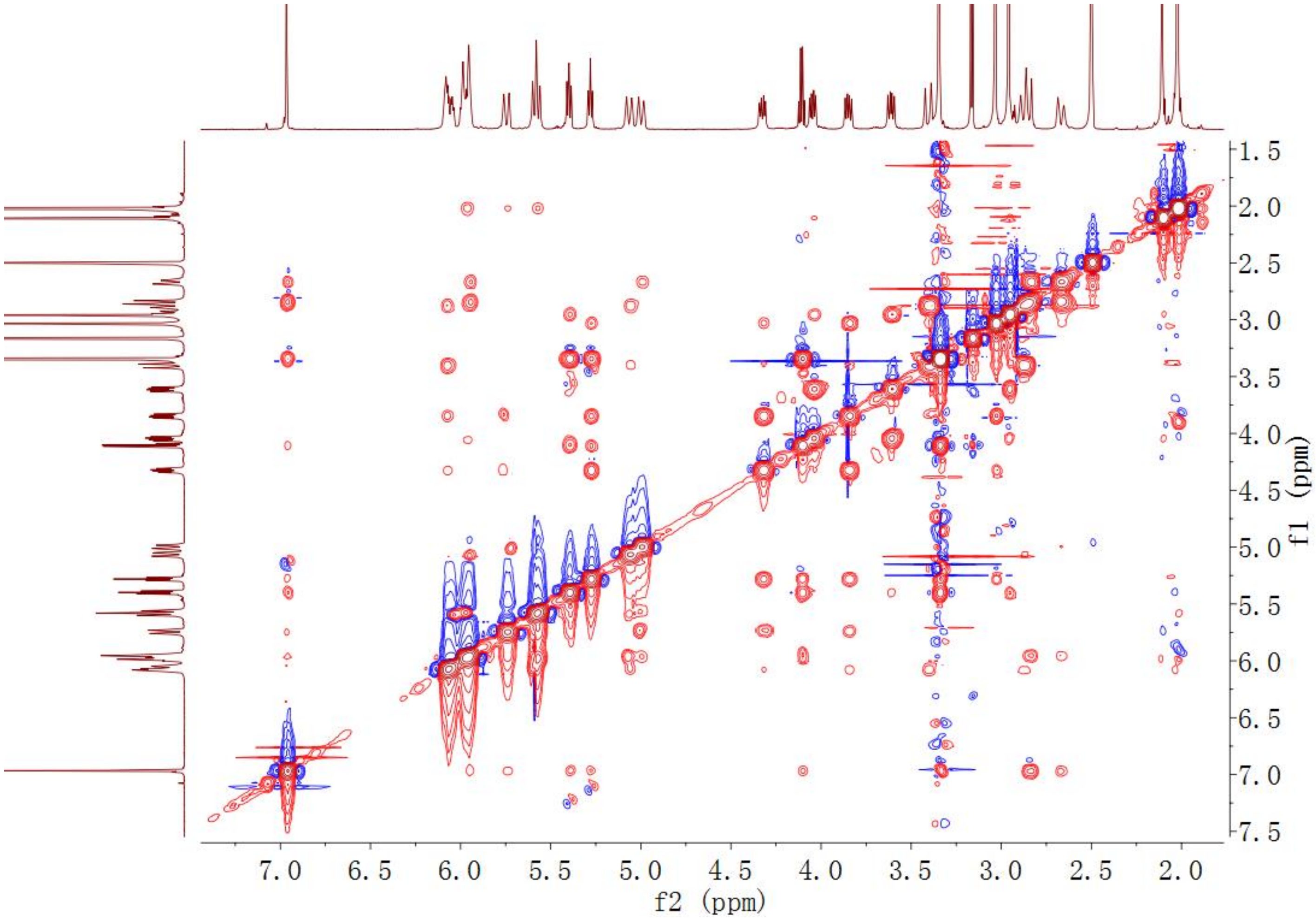


Figure S7. ^{1}H-NMR spectrum of **2** in MeOD.

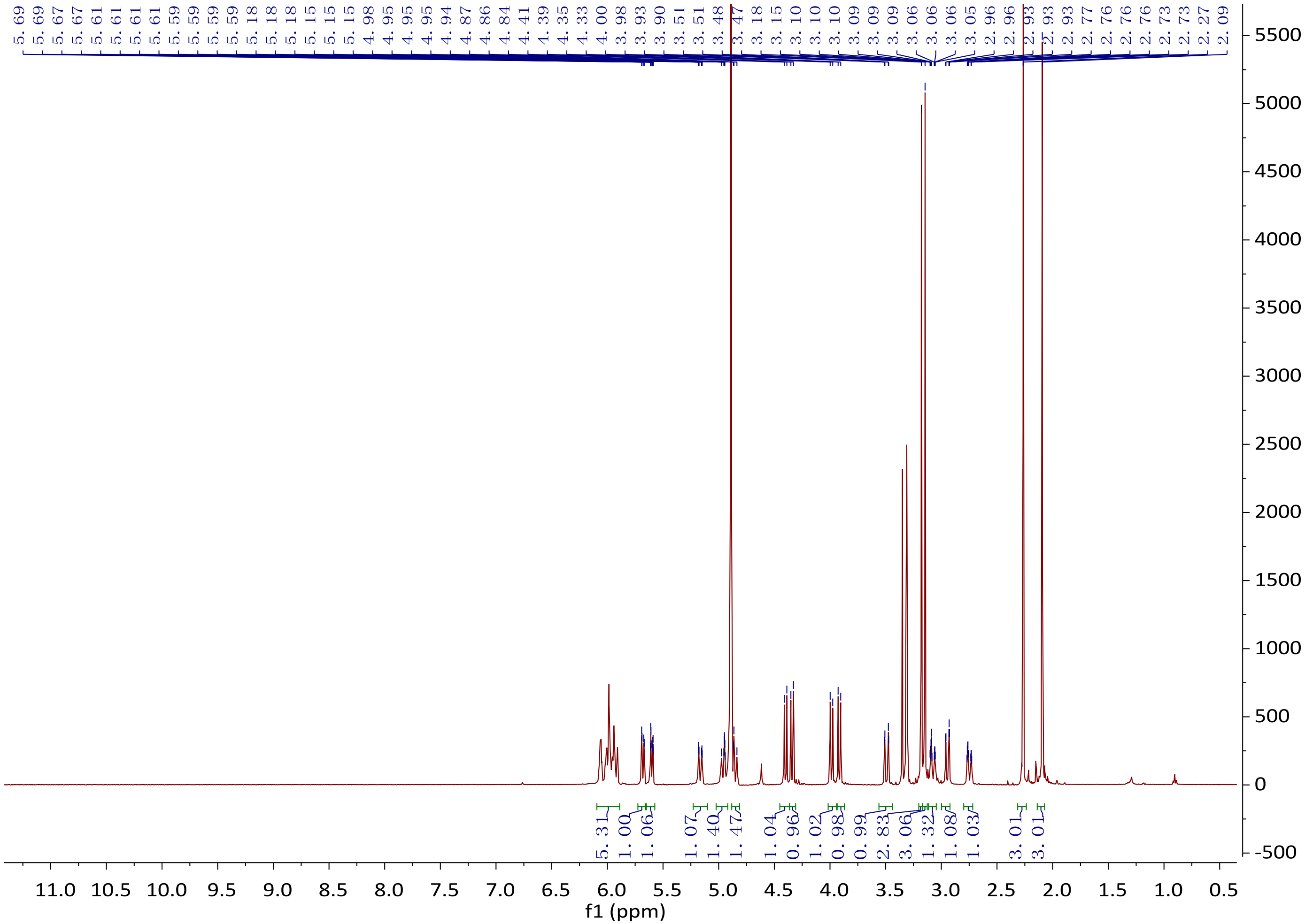


Figure S8. ^{13}C-NMR spectrum of **2** in MeOD.

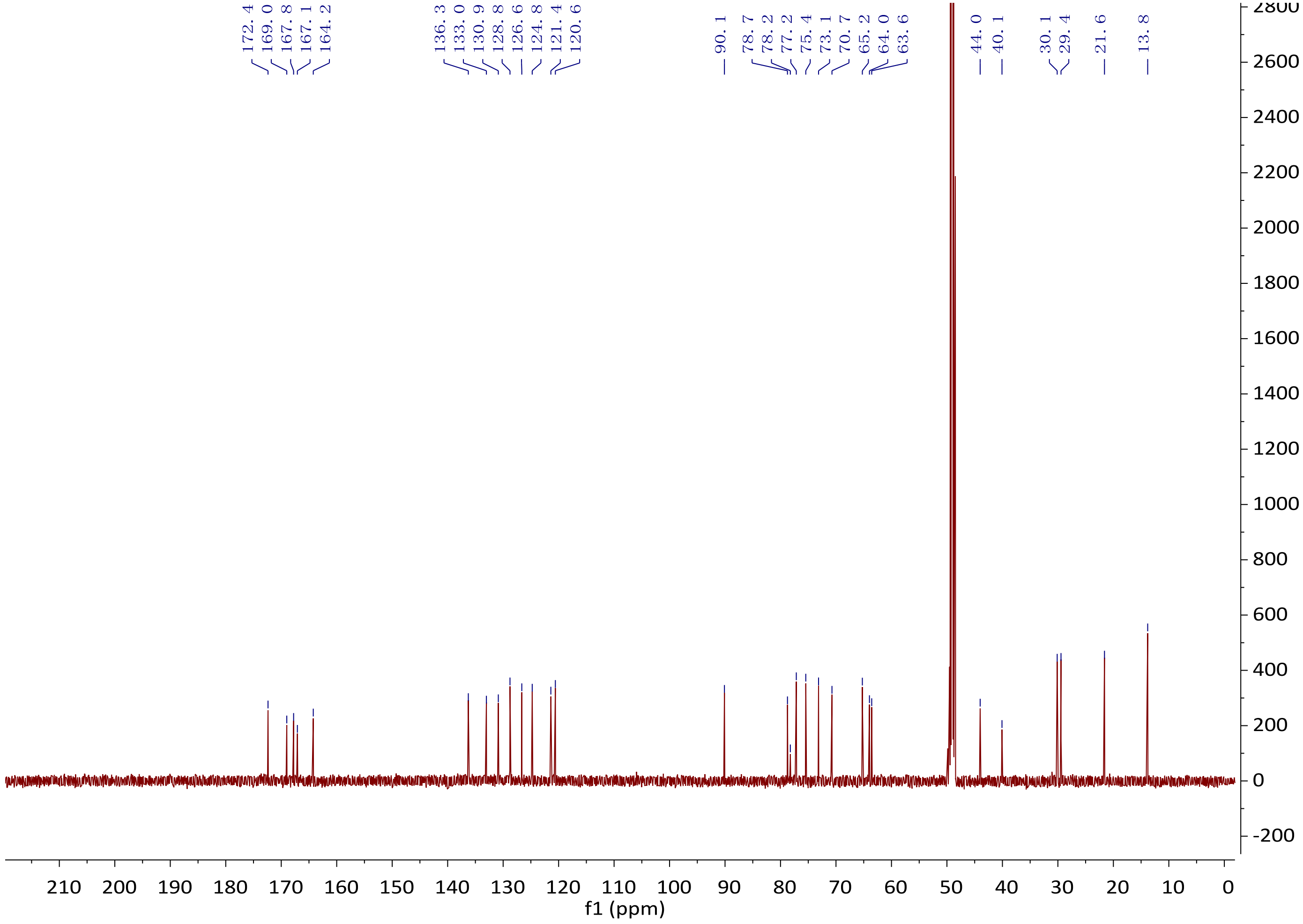


Figure S9. ^{1}H-^{1}H COSY spectrum of **2** in MeOD.

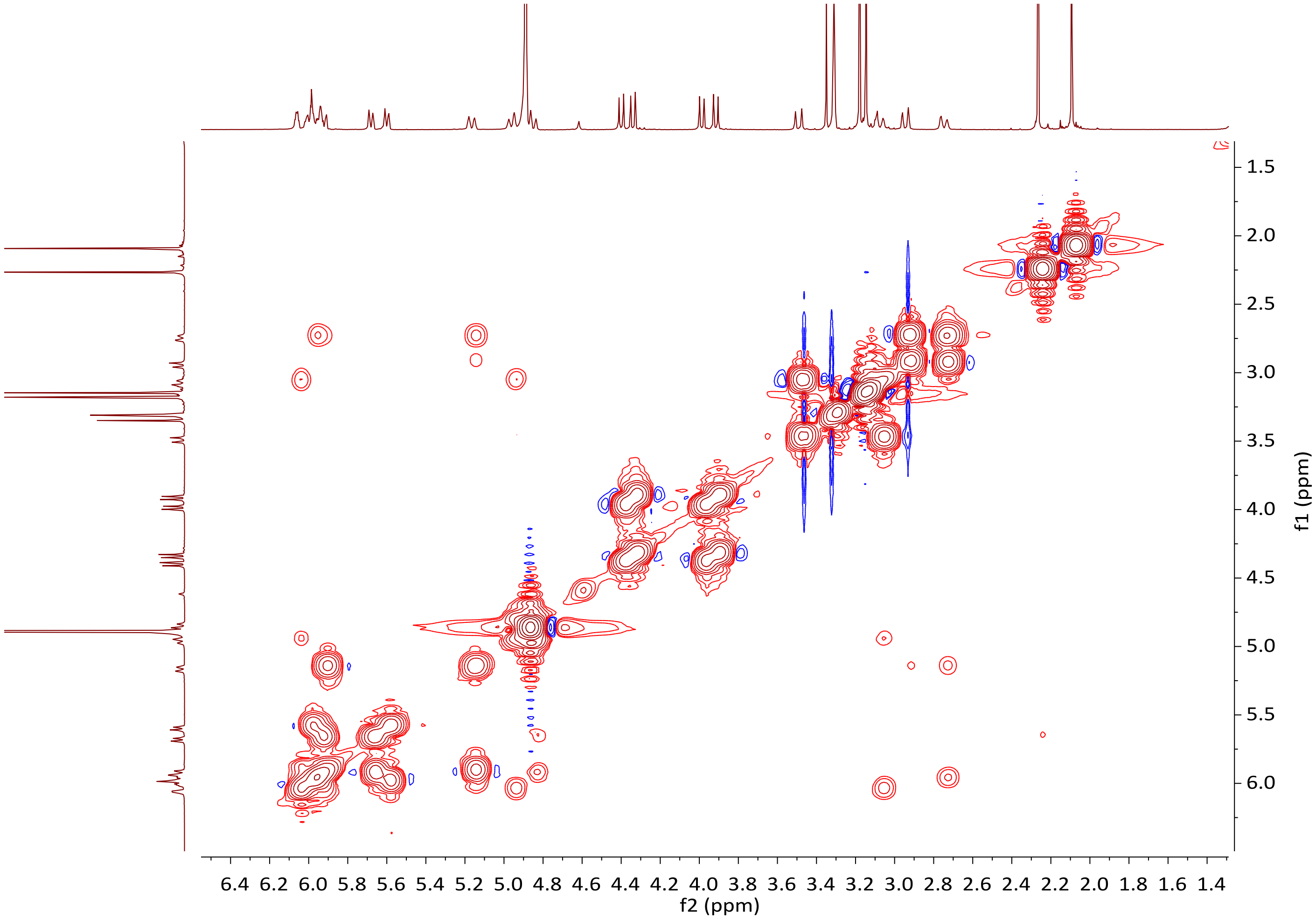


Figure S10. HSQC spectrum of **2** in MeOD.

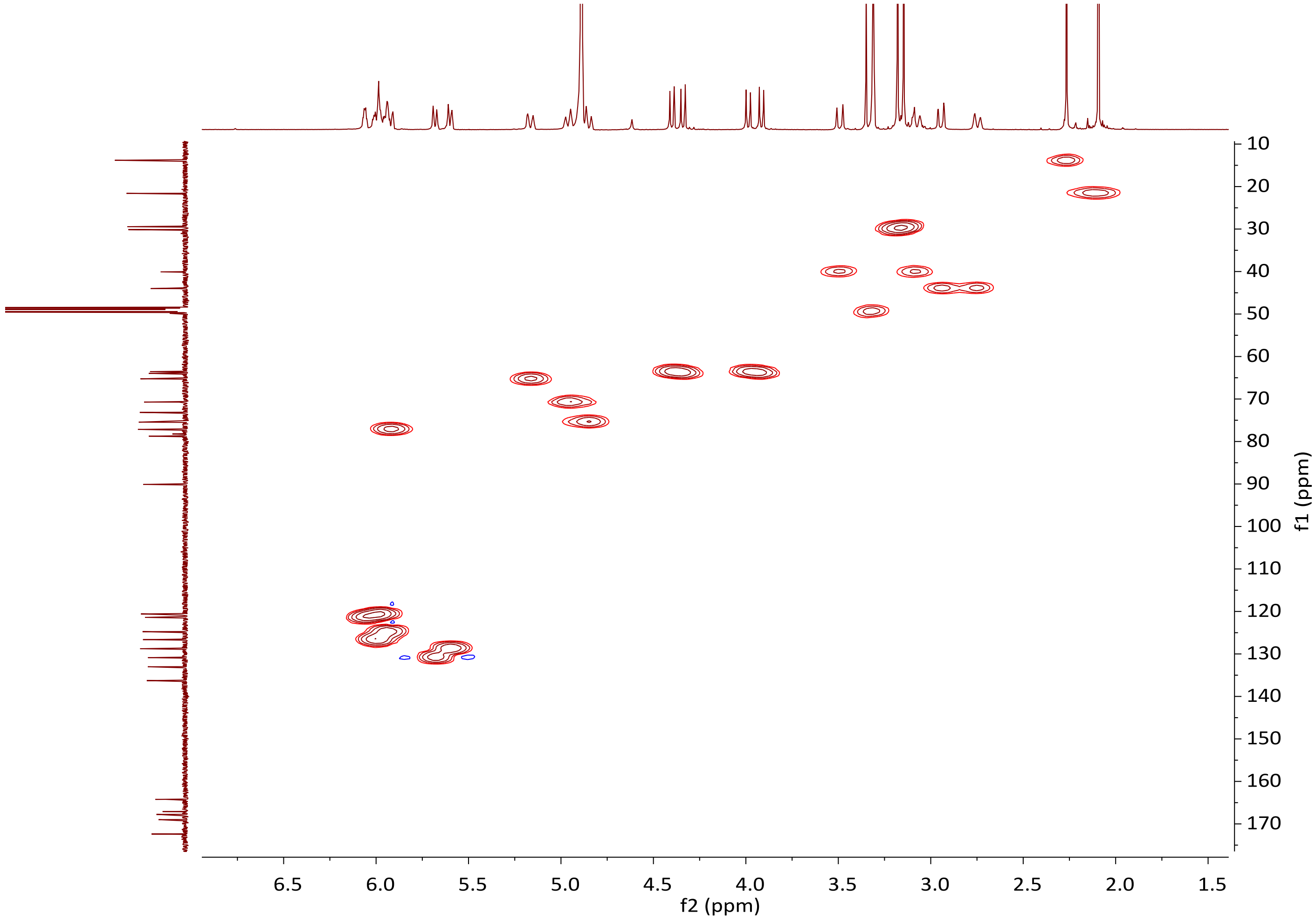


Figure S11. HMBC spectrum of **2** in MeOD.

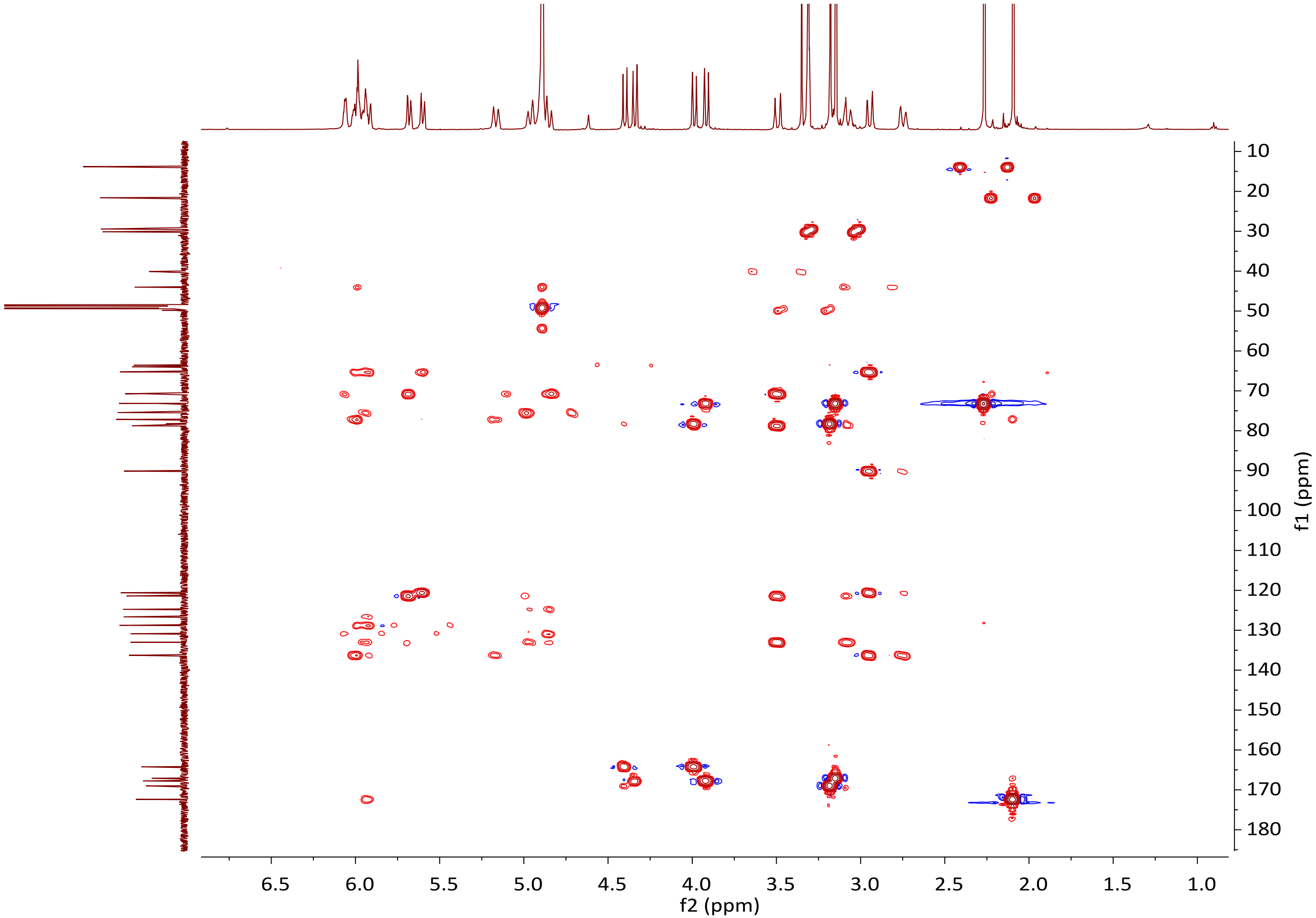


Figure S12. ^{1}H NMR spectrum of **2** in DMSO.

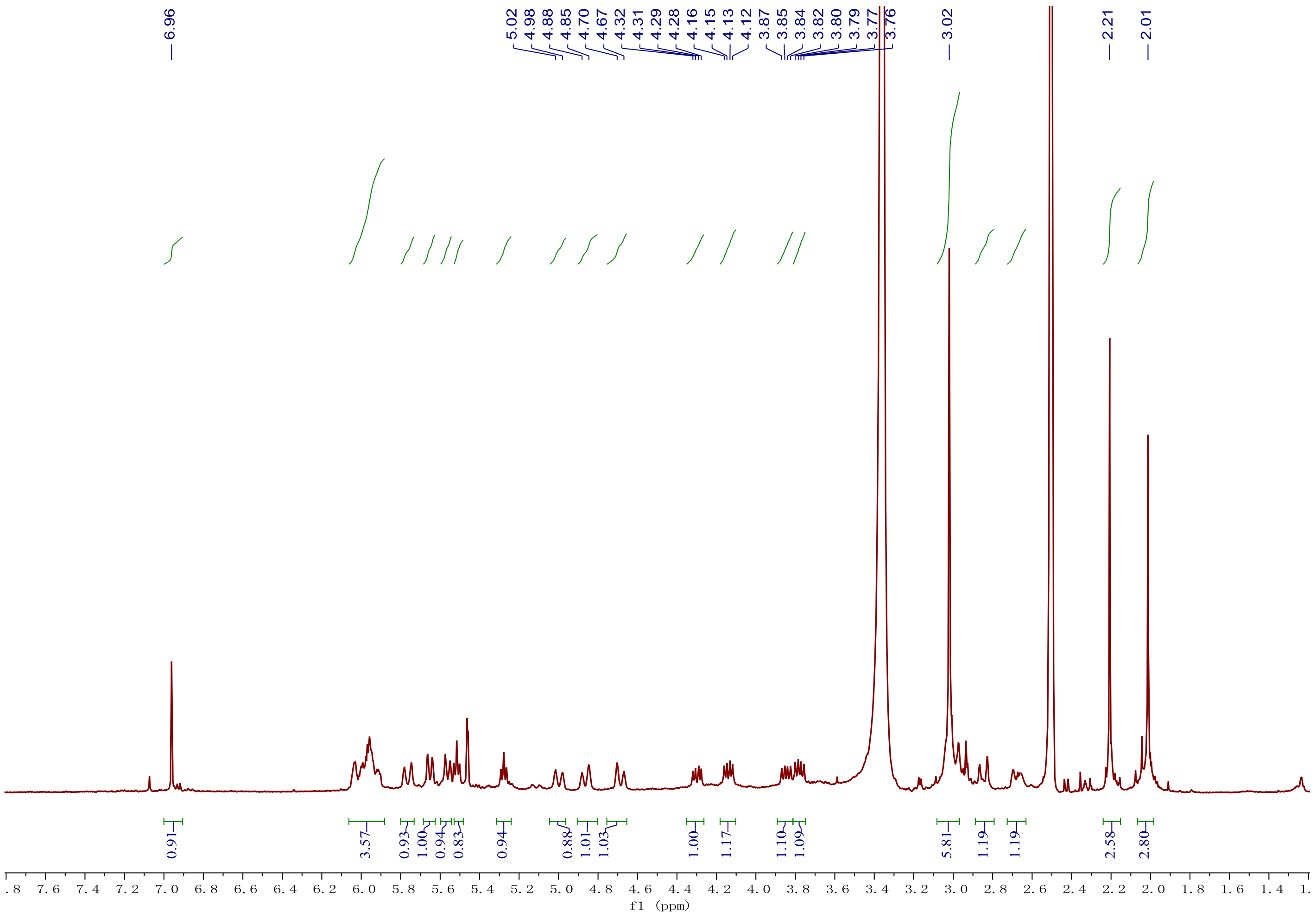


Figure S13. NOESY spectrum of **2** in DMSO.

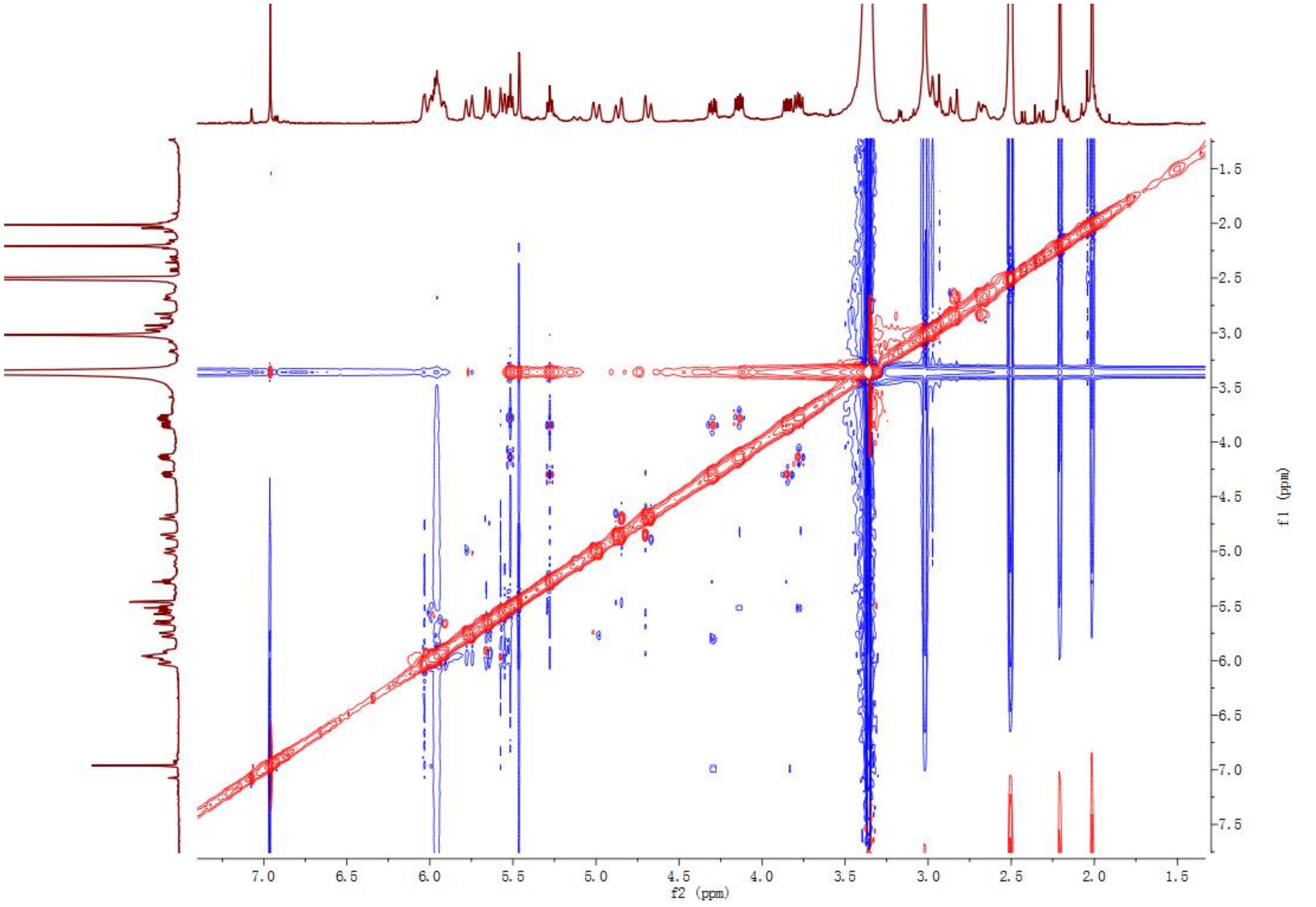


Figure S14. ^{1}H NMR spectrum of **3** in MeOD.

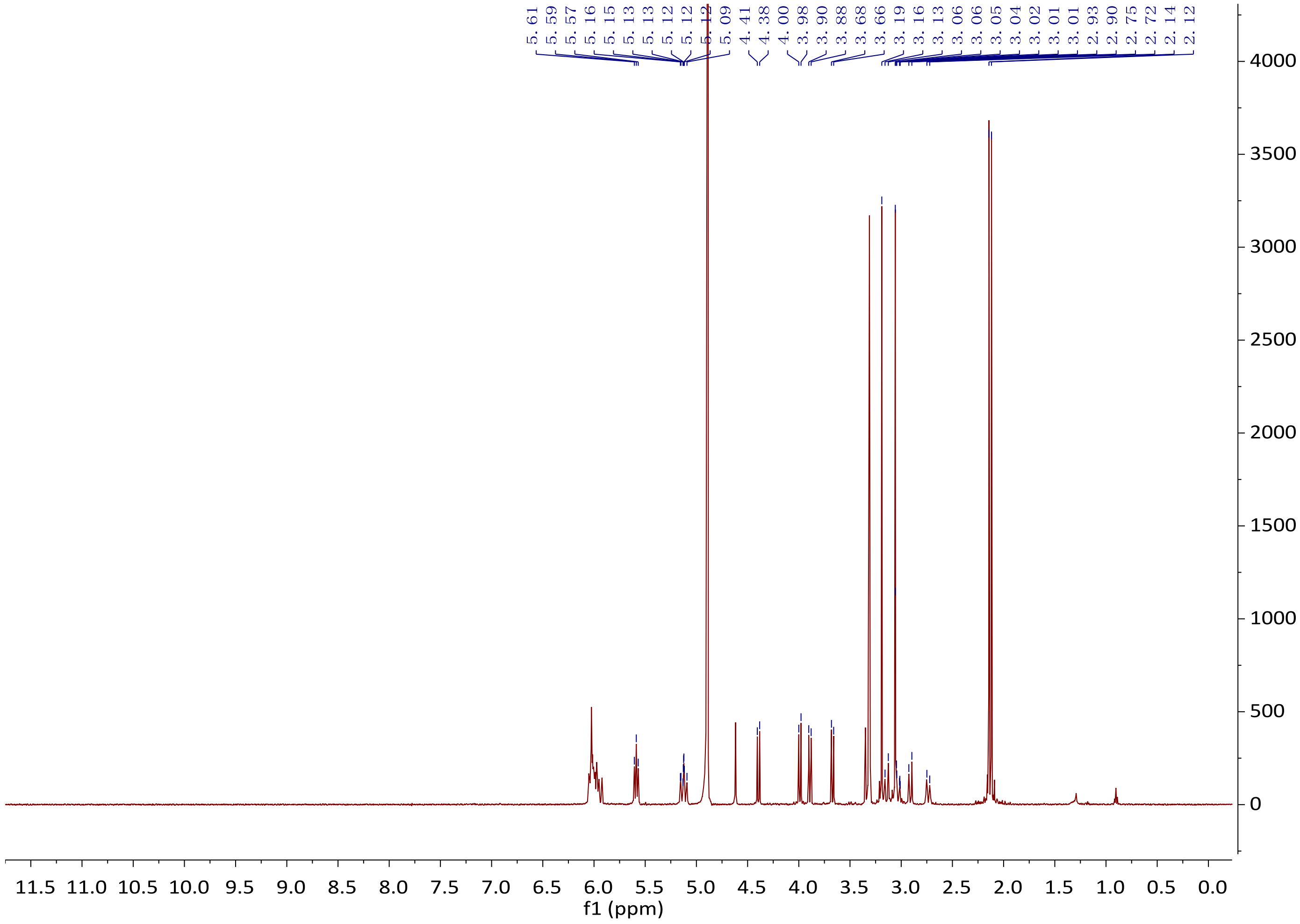


Figure S15. ^{13}C NMR spectrum of **3** in MeOD.

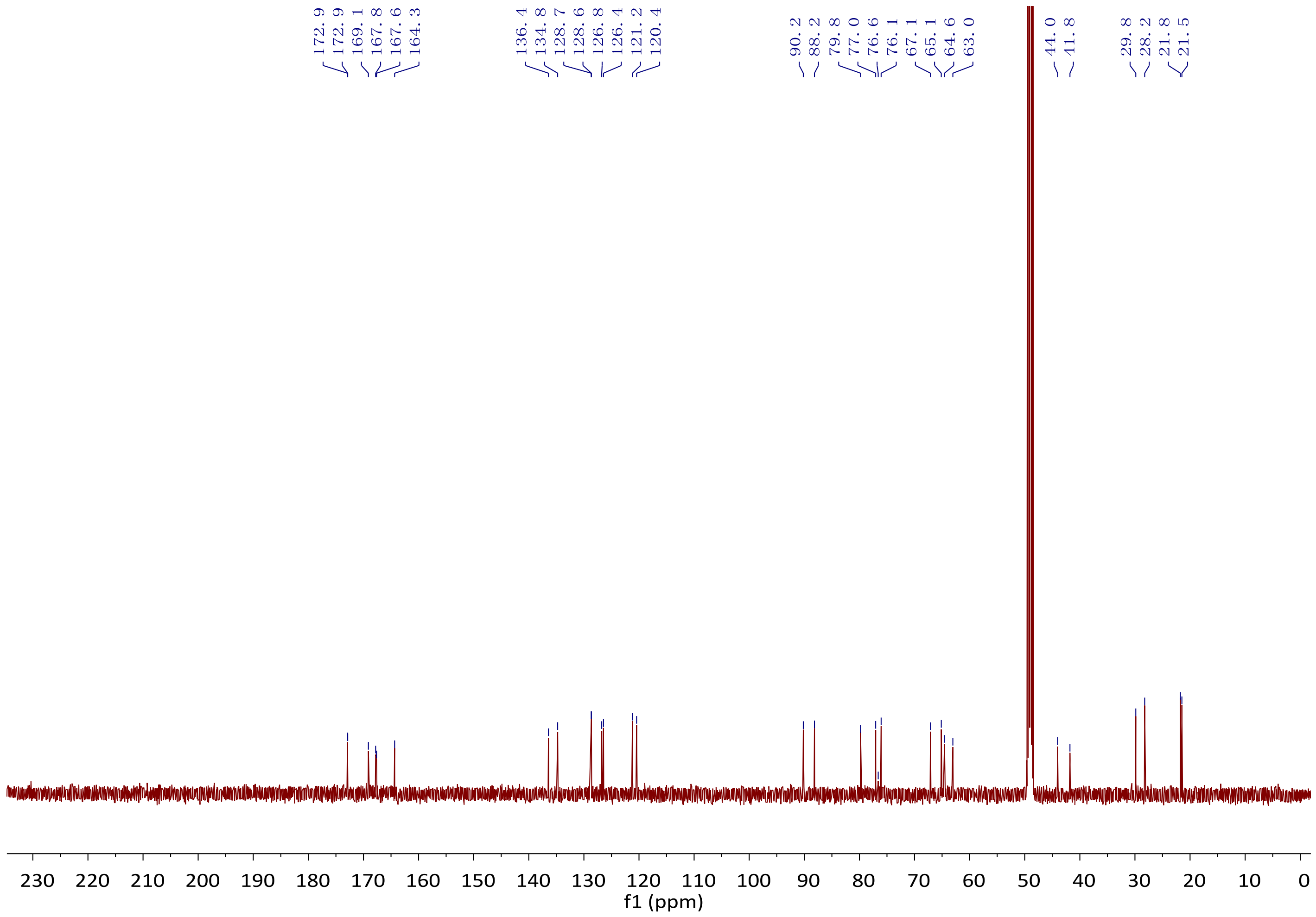


Figure S16. ^{1}H-^{1}H COSY spectrum of **3** in MeOD.

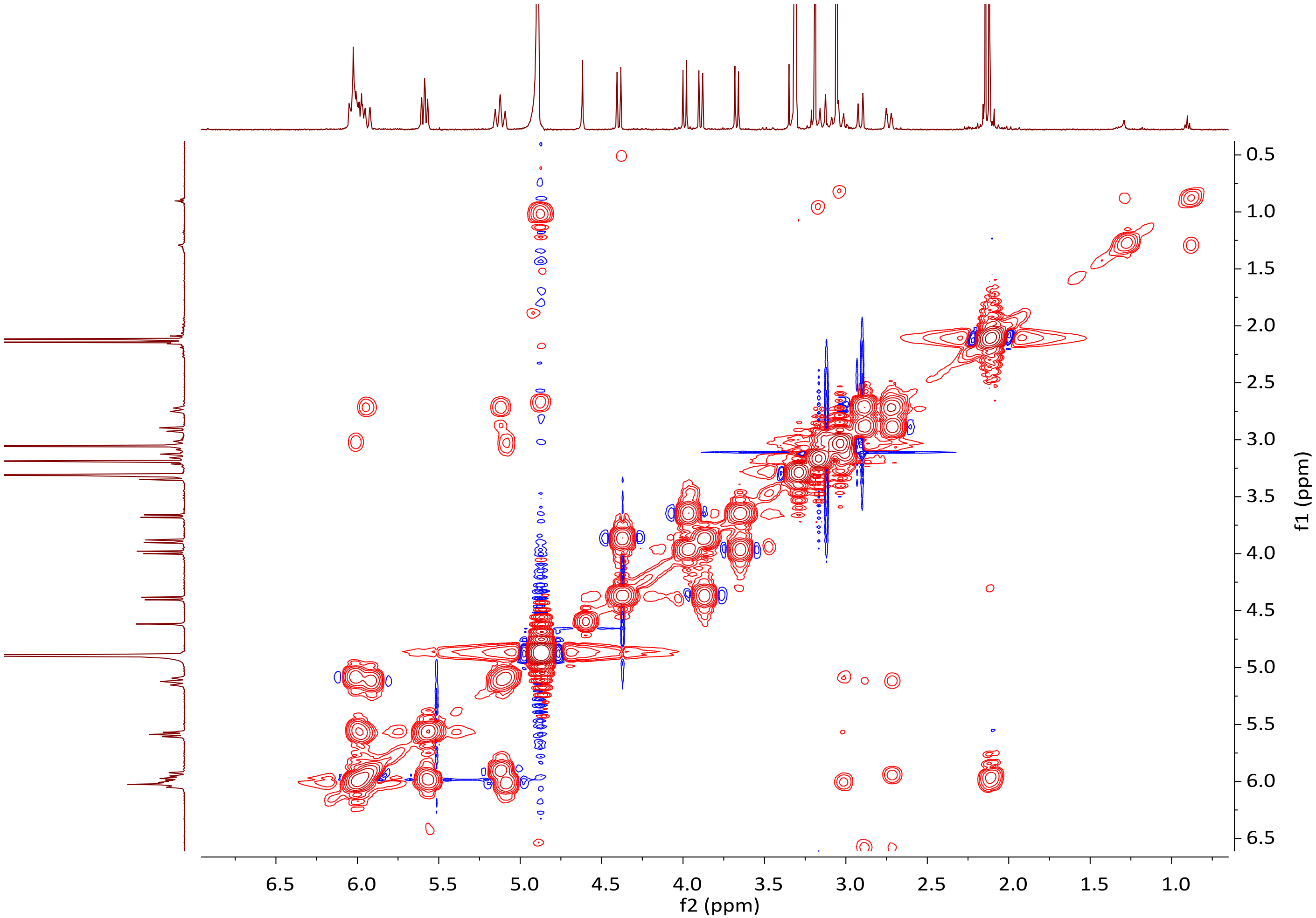


Figure S17. HSQC spectrum of **3** in MeOD.

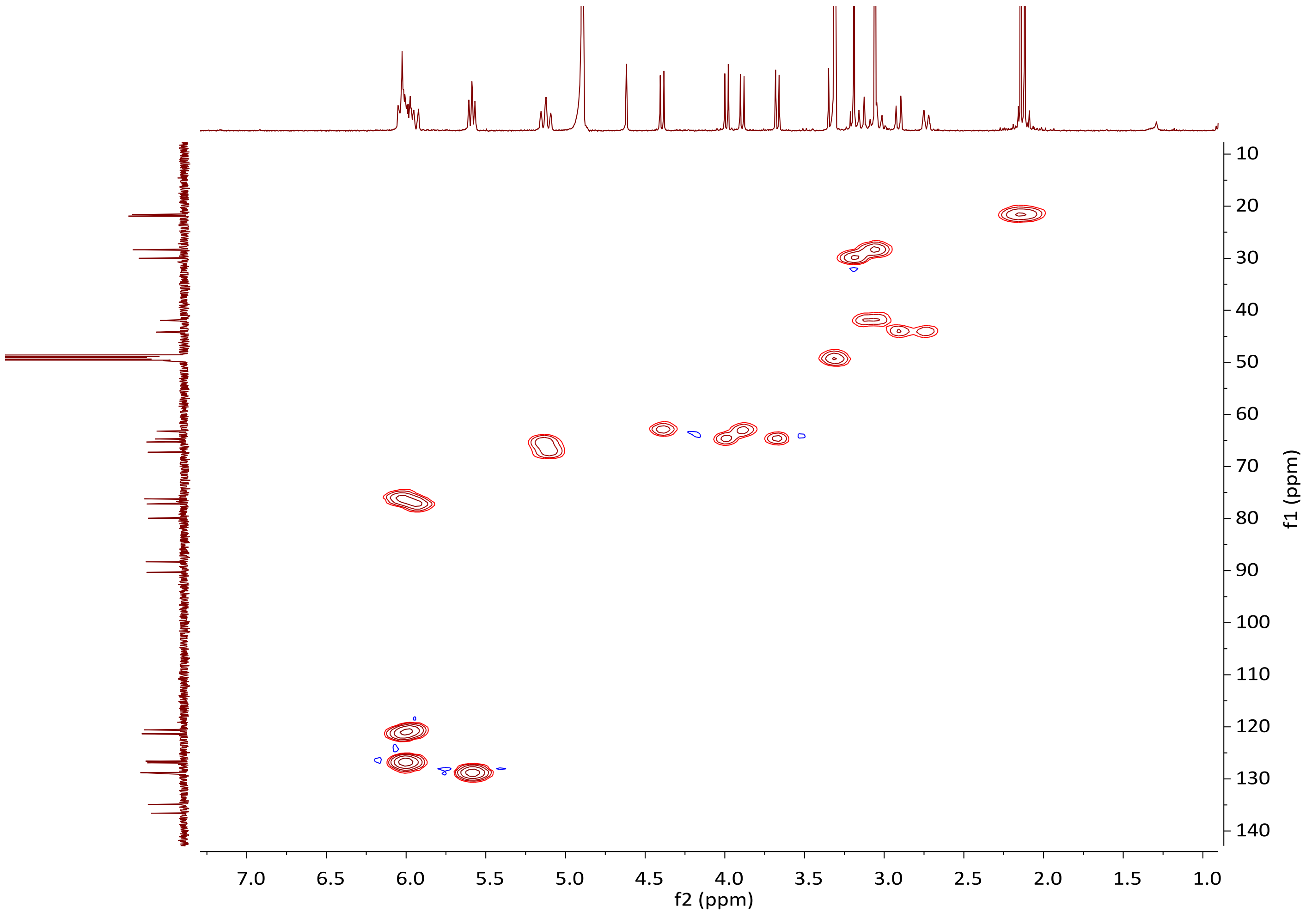


Figure S18. HMBC spectrum of **3** in MeOD.

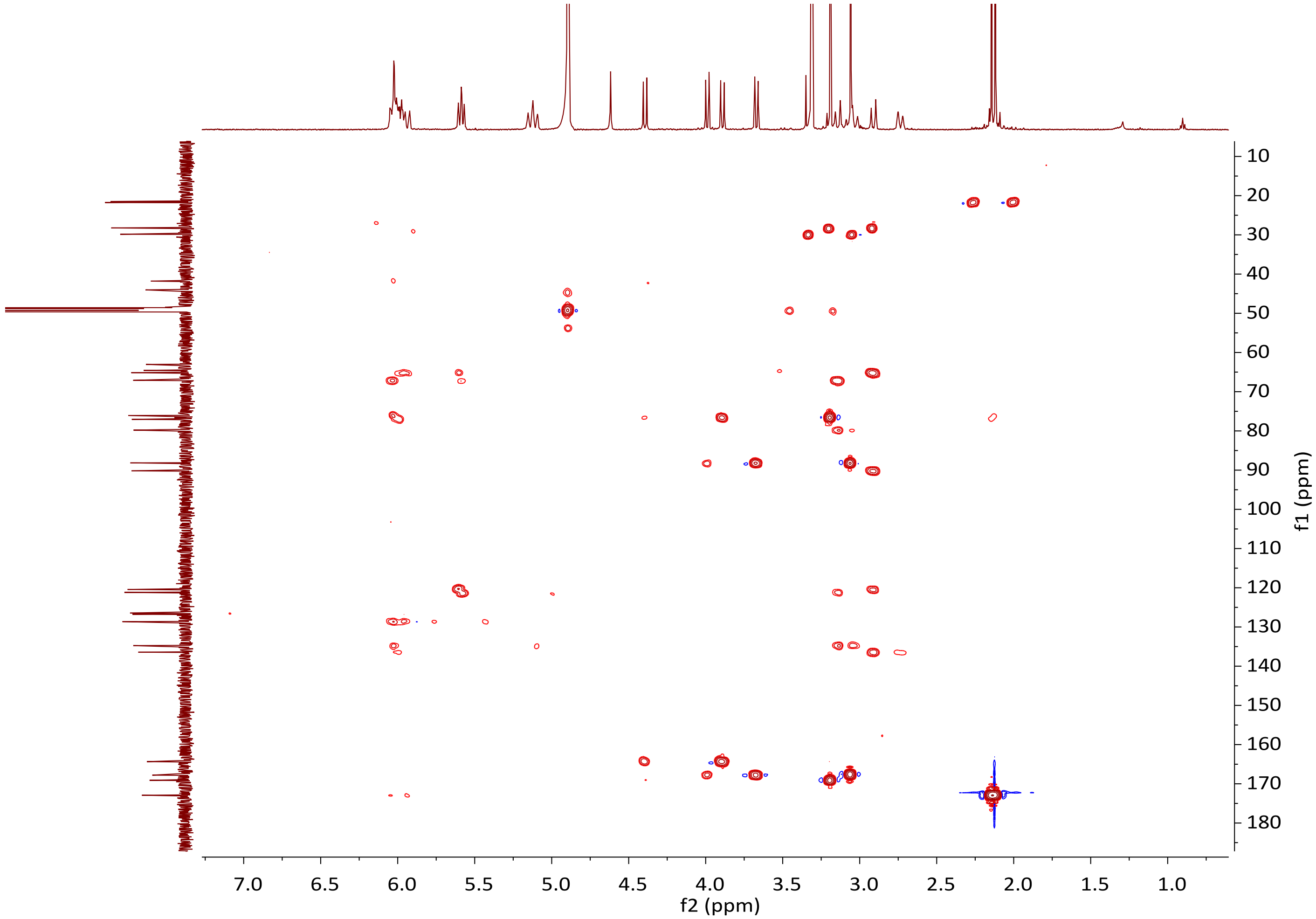


Figure S19. ^{1}H NMR spectrum of **3** in DMSO.

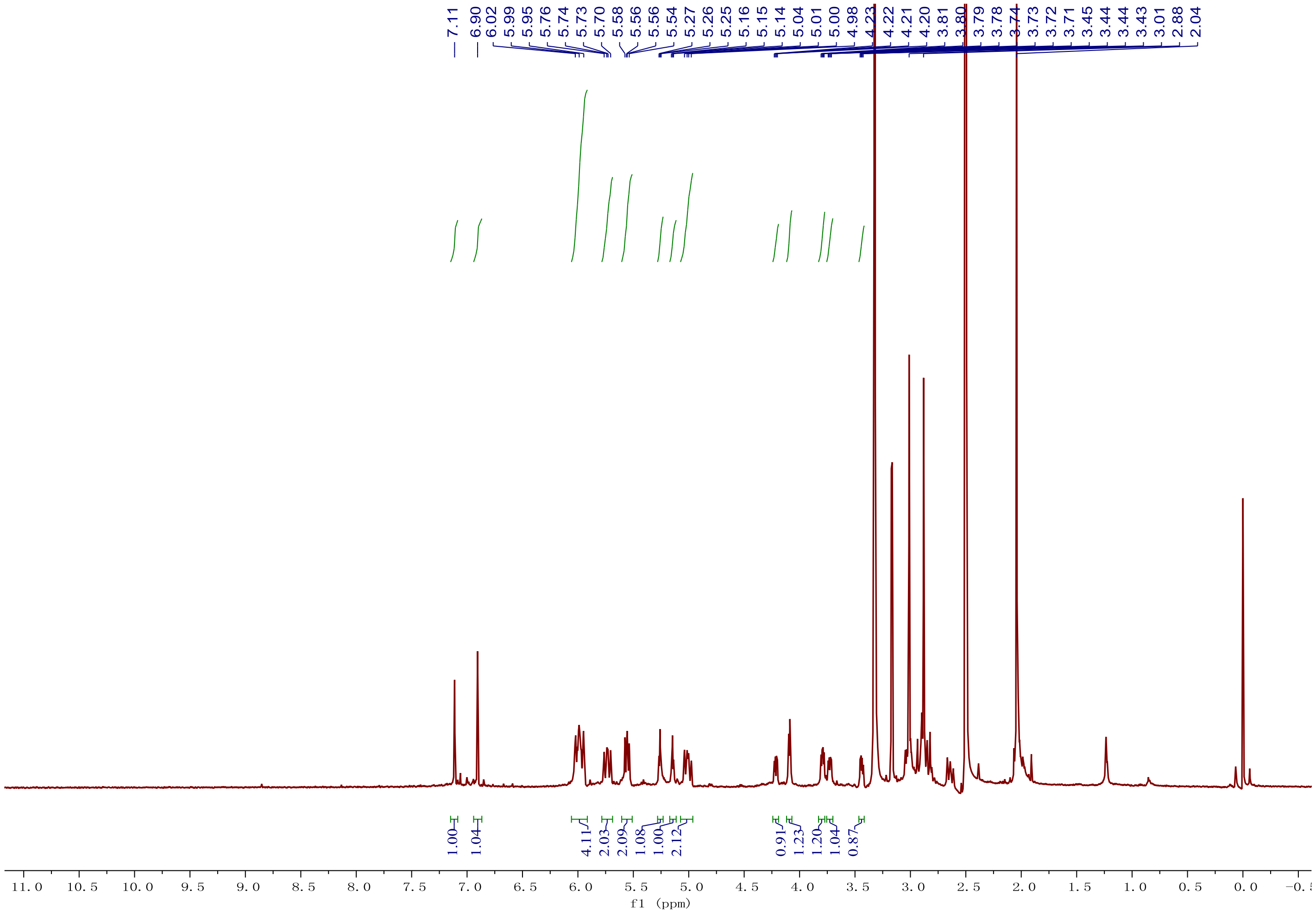


Figure S20. ^{13}C NMR spectrum of **3** in DMSO.

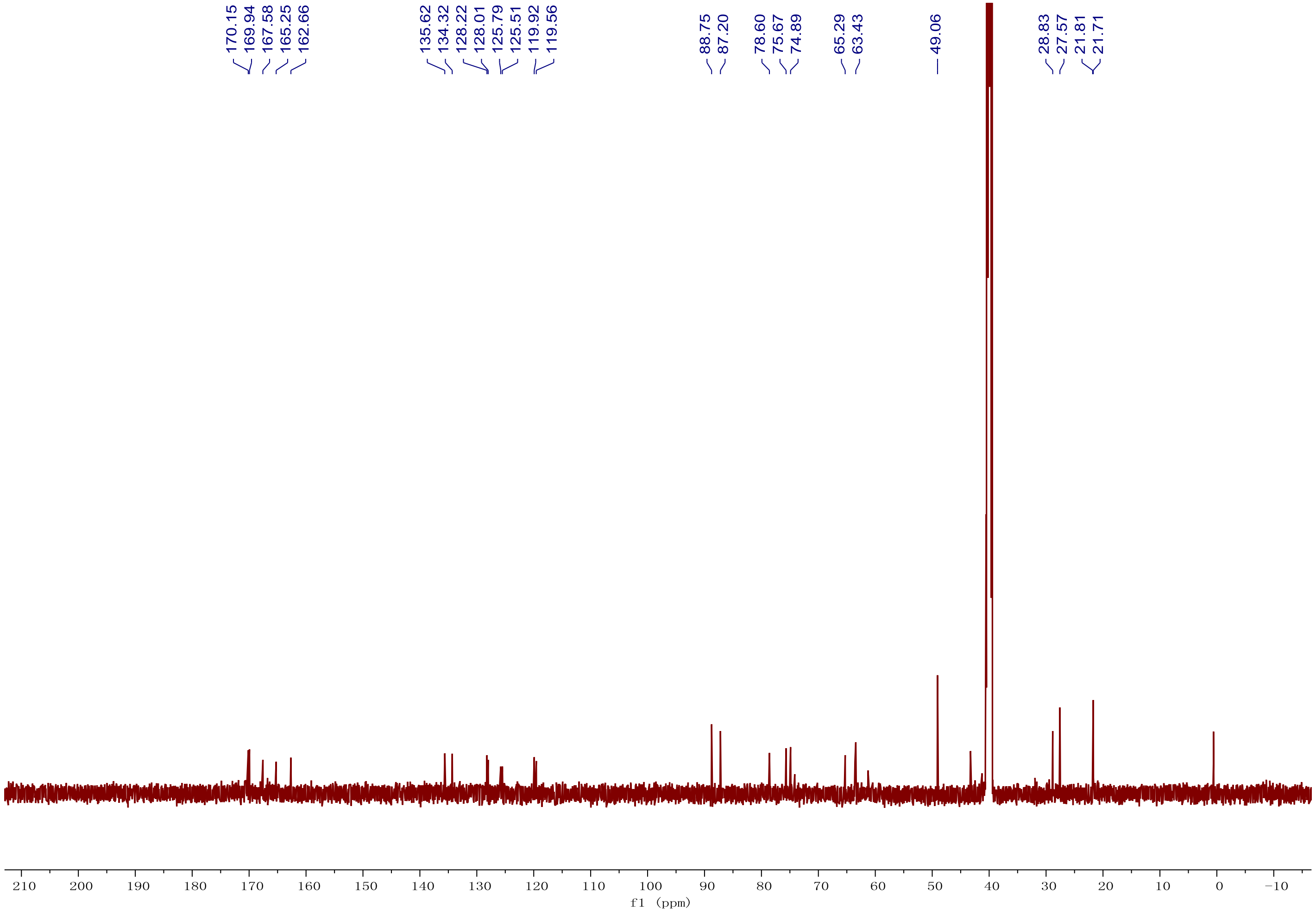


Figure S21. ^1H, ^1H-COSY spectrum of **3** in DMSO.

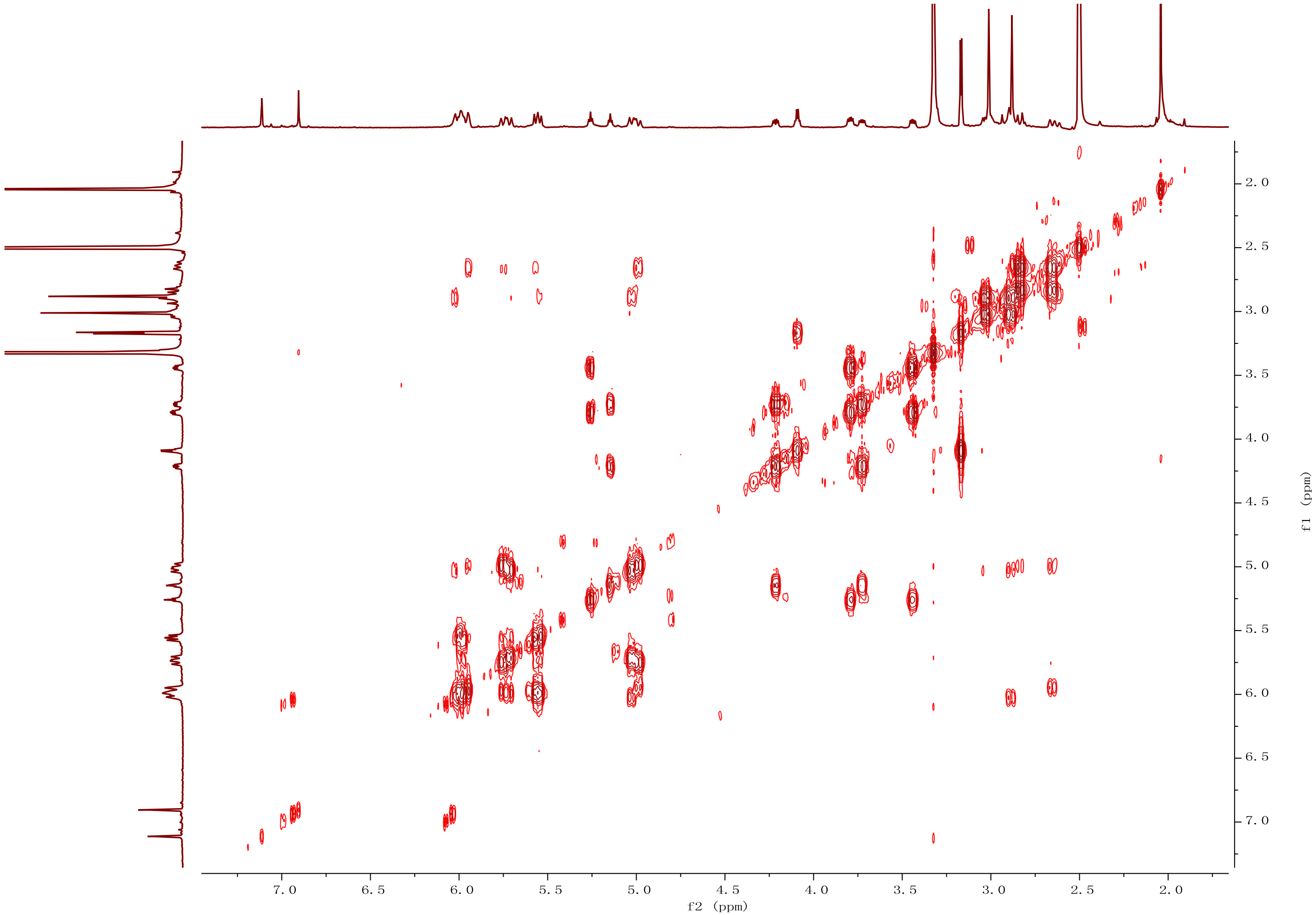


Figure S22. HSQC spectrum of **3** in DMSO.

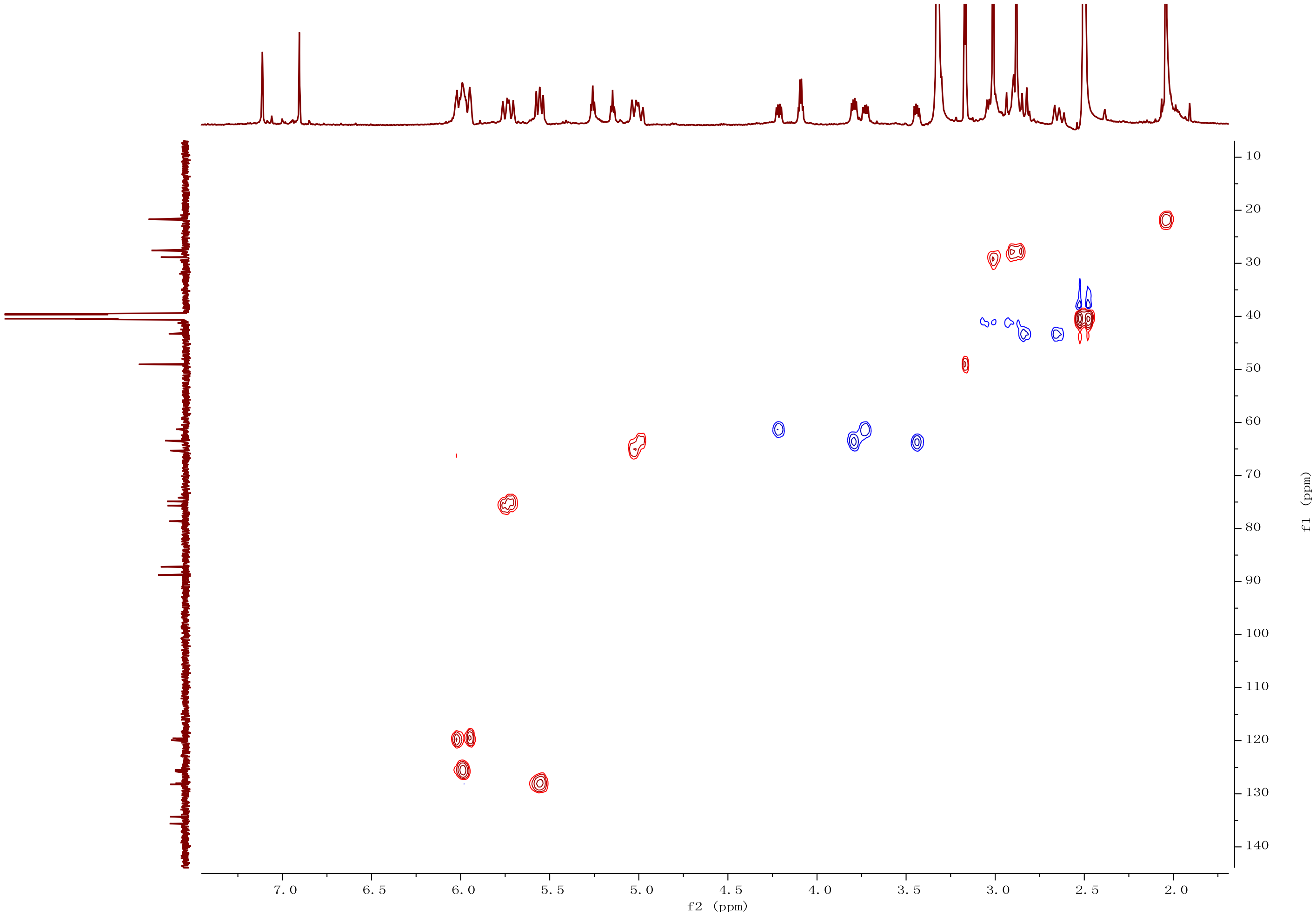


Figure S23. HMBC spectrum of **3** in DMSO.

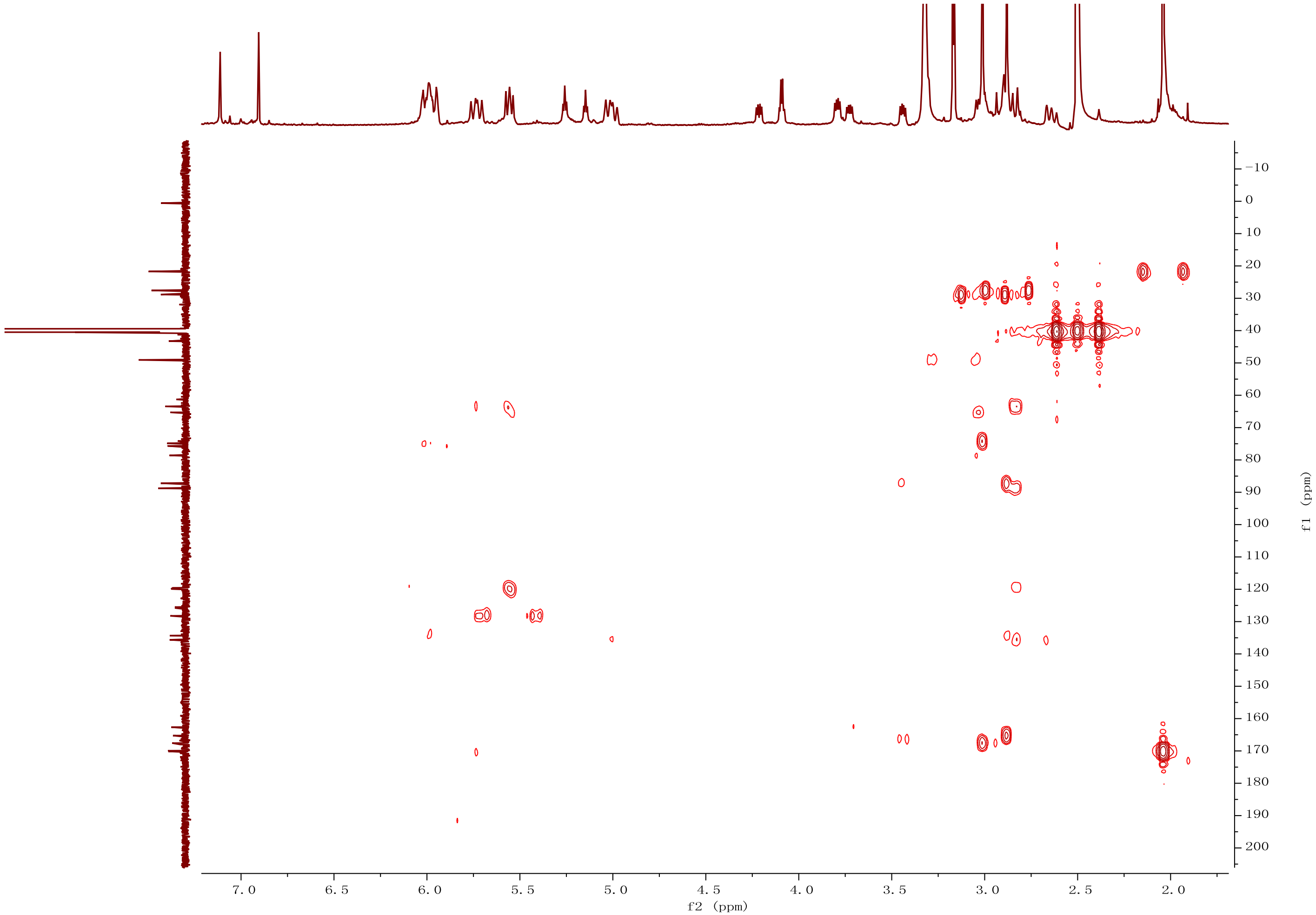


Figure S24. NOESY spectrum of **3** in DMSO.

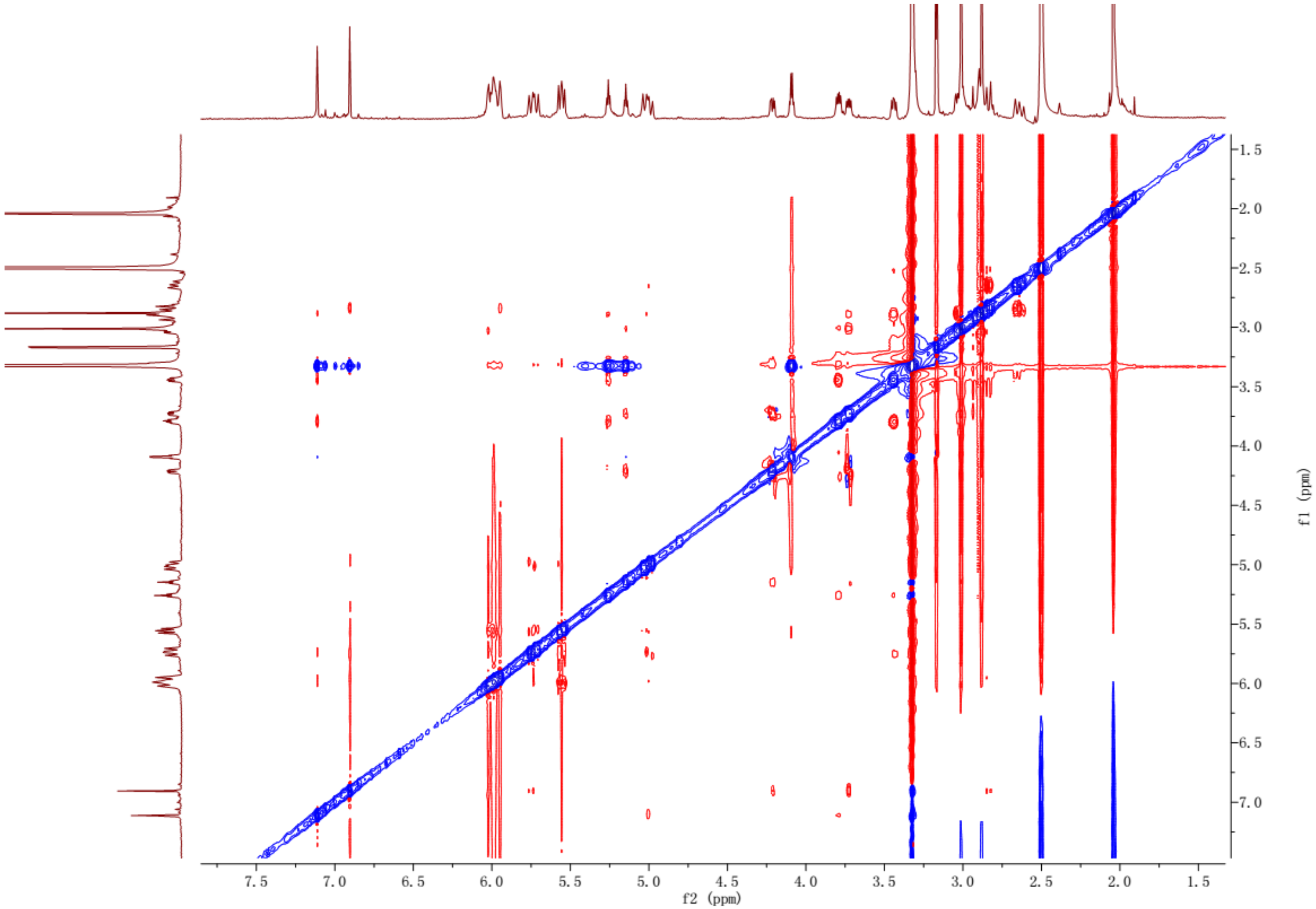
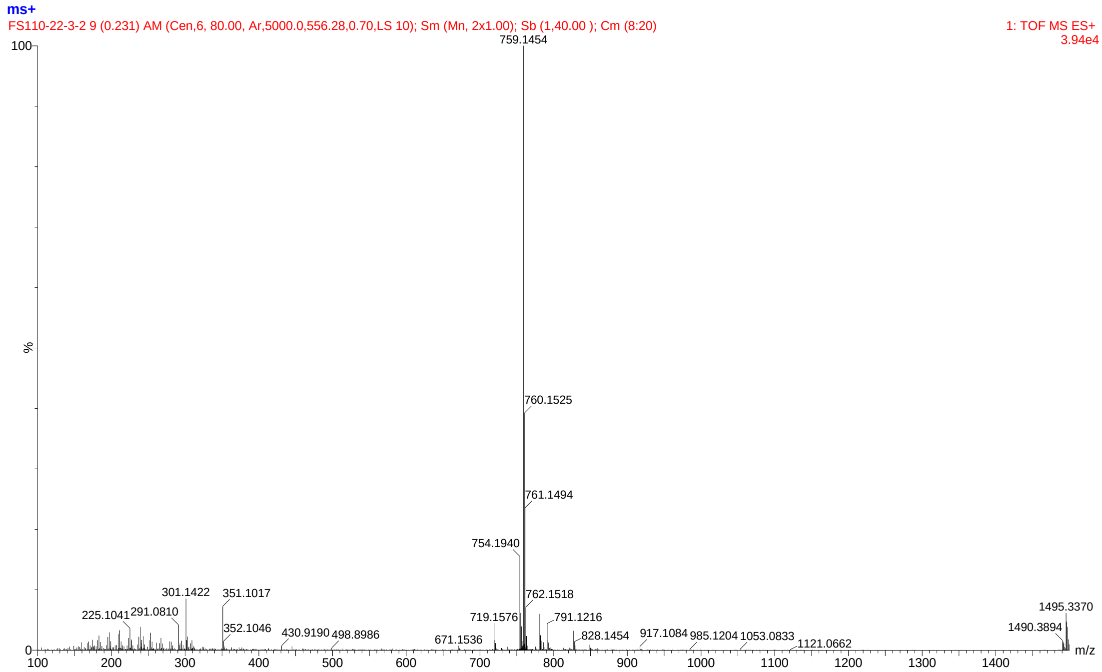


Figure S25. HRESIMS spectrum of **1**.



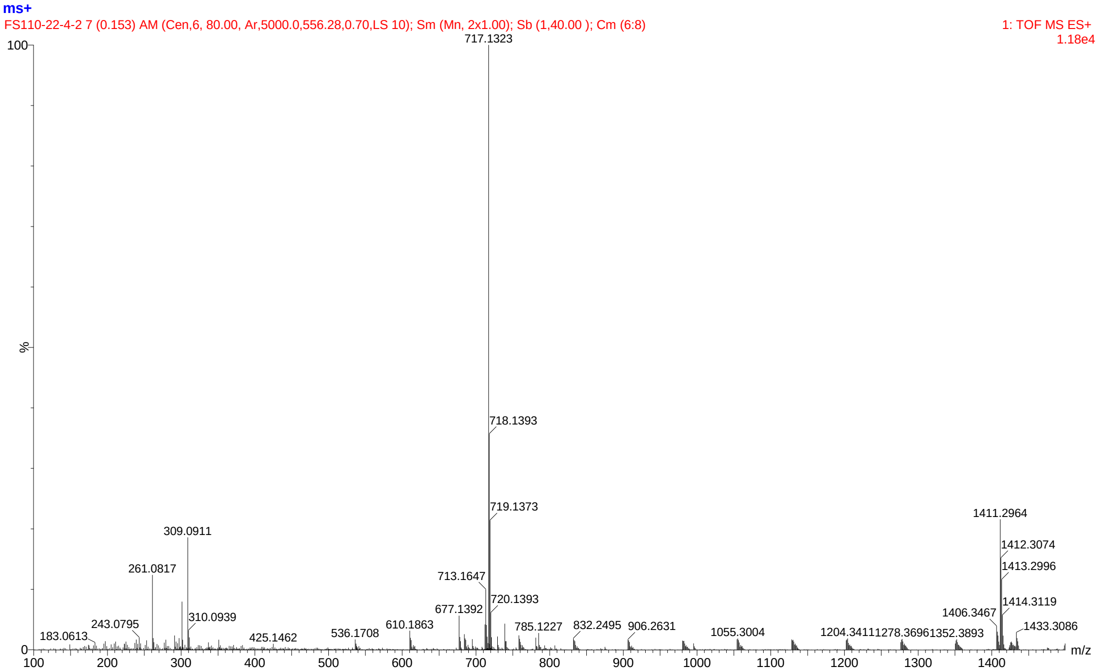
SPECTRUM - simulation :

m/z	Theo. Mass	Composition
759.1454	759.1440	$C_{31}H_{36}O_{11}N_4S_3Na$

Limits:

1) Charge: -1
2) Nitrogen-role: Do not use
3) Mass tolerance: 5 ppm
4) Element in use: $^{12}C(0\text{~}30)$, $^{1}H(0\text{~}60)$, $^{16}O(0\text{~}10)$

Figure S26. HRESI MS spectrum of **2**.

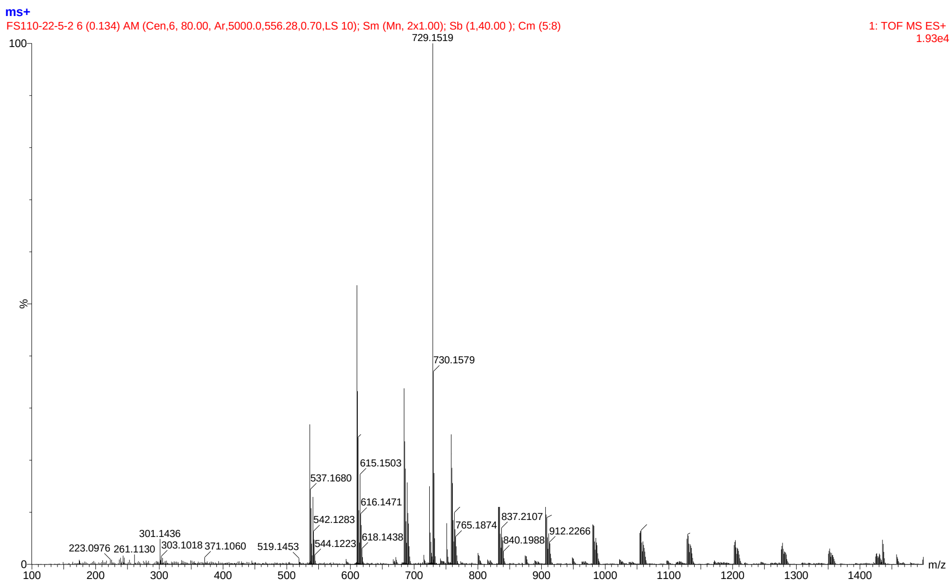


SPECTRUM - simulation :		
m/z	Theo. Mass	Composition
717.1323	717.1335	$C_{29}H_{24}O_{10}N_4S_3Na$

Limits:

1) Charge: +1
2) Nitrogen-role: Do not use
3) Mass tolerance: 5 ppm
4) Element in use: $^{12}C(0\sim30)$, $^{1}H(0\sim60)$, $^{16}O(0\sim10)$, $^{35}Cl(0\sim1)$

Figure S27. HRESI TOF MS spectrum of **7**.



SPECTRUM - simulation :		
m/z	Theo. Mass	Composition
729.1519	729.1512	$C_{30}H_{34}O_{12}N_4S_2Na$

Elemental Composition Report

1. Monoisotopic Mass
2. Elements Used: C: 0-40 H: 0-100 O: 0-20
3. Tolerance = 5.0 PPM

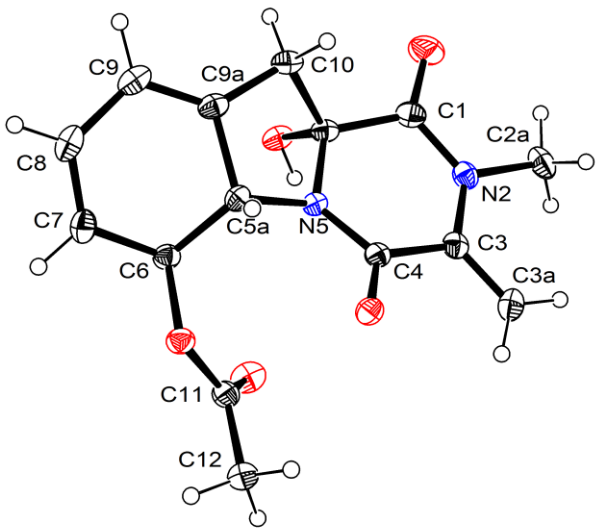


Figure S28. The crystal structure of **5**.

Table S1. ^{1}H and ^{13}C NMR data of **1−3**.

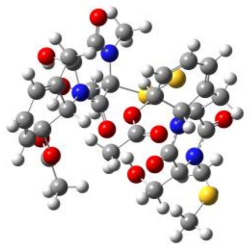
position	δ_H (J in Hz)	δ_C, *mult.*	δ_H (J in Hz)	δ_C, *mult.*	δ_H (J in Hz)	δ_C, *mult.*
		a		b		b
1		167.0, C		169.0, C		169.1, C
2						
3		74.4, C		78.2, C		76.6, C
4		162.1, C		164.2, C		164.3, C
5						
5a	5.00, d 14.2	63.0, CH	5.17, brd, 14.4	65.2, CH	5.13, m	65.1, CH
6	5.75, d (14.2)	75.3, CH	5.93, m	77.2, CH	5.93, m	77.1, CH
7	5.99, m	127.8, CH	5.60, m	128.8, CH	5.98, m	126.6, CH
8	5.58, t (10.3)	125.4, CH	5.99, m	126.6, CH	5.60, brd, 9.5	128.7, CH
9	5.95, m	119.1, CH	5.98, m	120.6, CH	5.96, m	120.4, CH
9a		135.5, C		136.3, C		136.4, C
10	2.85, d (16.6)	42.8, CH_2	2.94, d, 14.8	44.0, CH_2	2.91, d 14.7	44.0, CH_2
	2.67, d (16.6)		2.75, brd 14.8		2.74, m	
10a		88.4, C		90.1, C		90.2, C
11		169.8, C		172.4, C		172.9, C
12	2.0, s	21.2, CH_3	2.09, s	21.6, CH_3	2.14, s	21.8, CH_3
13	3.03, s	28.9, CH_3	3.18, s	30.1, CH_3	3.19, s	29.9, CH_3
14	4.33, dd 11.7 5.3	61.7, CH_2	4.40, d 11.6	64.0, C H_2	4.39, d 11.6	63.0, CH_2
	3.85, dd 11.7 6.3		3.99, d 11.6		3.89, d 11.6	
1′		165.0, C		167.1, C		167.6, C
2′						
3′		73.0, C		73.1, C		88.2, C
4′		163.2, C		167.8, C		167.8, C
5′						
5a′	5.06, d 14.3	65.4, CH	4.96, brd 13.6	70.7, CH	5.13, m	67.1, CH
6′	6.0, m	74.4, CH	4.86, brd 13.6	75.4, CH	6.04, m	76.1, CH
7′		127.4, CH	5.68, m	130.9, CH	5.98, m	126.4, CH
8′		125.7, CH	5.94, m	124.8, CH	5.58, brd, 9.5	128.7, CH
9′		120.0, CH	6.06, m	121.4, CH	6.02, m	121.2, CH
9a′		133.3, C		133.0, C		134.8, C
10′	3.41, d 16.4	38.8, CH_2	3.49, d 16.2	40.1, CH_2	3.14, d 16.1	41.8, CH_2
	2.86, d 16.4		3.08, d 16.2		3.03, m	
10a′		77.1, C		78.7, C		79.8, C
11′		169.8, C	-	-		172.9, C
12′	2.0, s	21.2, CH_3	-	-	2.12, s	21.5, CH_3
13′	2.96, s	28.5, CH_3	3.15, s	29.4, CH_3	3.06, s	28.2, CH_3
14′	4.05, dd 11.4 5.3	62.7, CH_2	4.34, d 11.7	63.6, CH_2	3.99, d 10.9	64.6, CH_2
	3.61, dd 11.3 6.6		3.92, d 11.7		3.67, d 10.9	

10a-OH	6.97, s		-	-	-	-
14-OH	5.28, t 5.8		-	-	-	-
S-CH_3	2.11, s	12.1, CH_3	2.27, s	13.8, CH_3	-	-
14′-OH	5.4, dd 6.6, 5.4		-	-	-	-

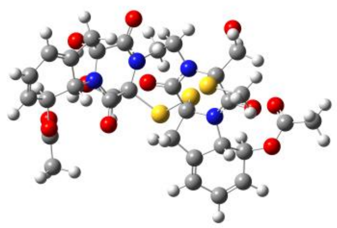
[a]Measured in dimethyl sulphoxide-d_6; [b]Measured in methanol-d_4.

Table S2. Energy analysis for the Conformers of **1a**.

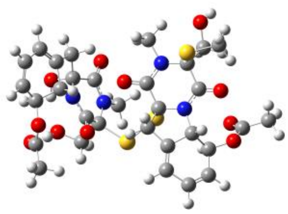
compounds	Conformation	G (Hartree)	G (Kcal/mol)	ΔG (Kcal/mol)	Boltzmann Dist (%)
1a	**1a-1**	-3444.16452700	-2161223.229	0.644276052	22.23%
	1a-2	-3444.16555385	-2161223.873	0	66.00%
	1a-3	-3444.16392671	-2161222.852	1.021035069	11.77%



1a-1



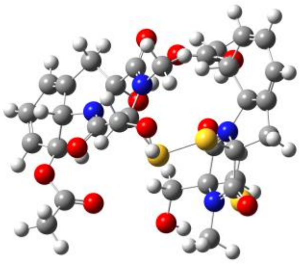
1a-2



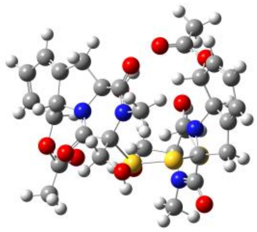
1a-3

Table S3. Energy analysis for the Conformers of **1b**.

compounds	Conformation	G (Hartree)	G (Kcal/mol)	ΔG (Kcal/mol)	Boltzmann Dist (%)
1a	**1a-1**	-3444.15263300	-2161223.229	0.644276052	22.23%
	1a-2	-3444.14852934	-2161223.873	0	66.00%



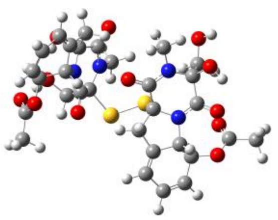
1b-1



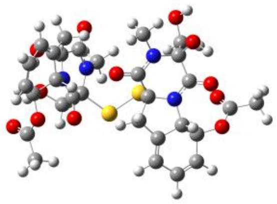
1b-2

Table S4. Energy analysis for the Conformers of **3a**.

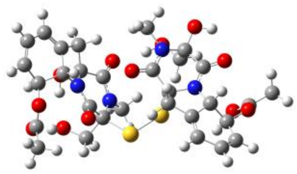
compounds	Conformation	G (Hartree)	G (Kcal/mol)	ΔG (Kcal/mol)	Boltzmann Dist (%)
3a	**3a-1**	-3081.90018400	-1933901.303	0	62.89%
	3a-2	-3081.89466060	-1933897.837	3.465729892	0.18%
	3a-3	-3081.89968119	-1933900.987	0.315295107	36.39%



3a-1



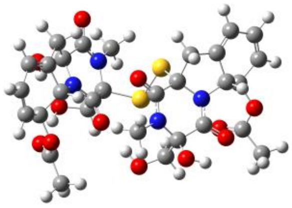
3a-2



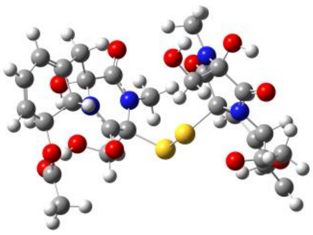
3a-3

Table S5. Energy analysis for the Conformers of **3b**.

compounds	Conformation	G (Hartree)	G (Kcal/mol)	ΔG (Kcal/mol)	Boltzmann Dist (%)
3a	**3b-1**	-3081.89794900	-1933899.901	0.098950932	45.83%
	3b-2	-3081.89810710	-1933900.000	0	54.16%



3b-1



3b-2