Supporting Information

C-Methylated Flavonoid Glycosides from *Pentarhizidium orientale* Rhizomes and Their Inhibitory Effects on the H1N1 Influenza Virus

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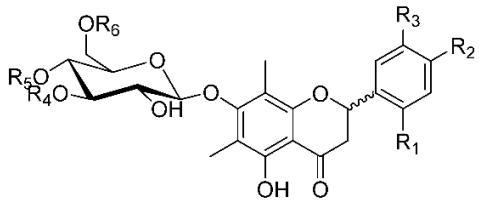
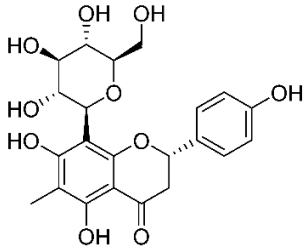
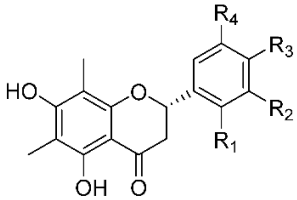
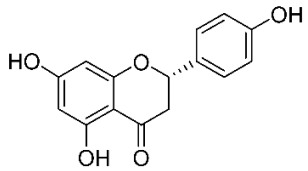




17 matteuorienin

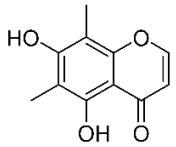
	R_1	R_2	R_3	R_4	R_5	R_6		
14	H	OCH_3	H	H	H	(*S*)-HMG	2*S*	matteuorienate A
15	H	H	H	H	H	(*S*)-HMG	2*S*	matteuorienate B
16	H	H	H	H	H	(*S*)-HMG	Δ^2	matteuorienate C
18	H	H	H	H	H	H	2*S*	demethoxymatteucinol 7-*O*-glucoside
19	H	OCH_3	H	H	H	H	2*S*	matteucinol 7-*O*-glucoside
20	OH	H	OCH_3	H	H	(*S*)-HMG	2*S*	myrciacitrin II





27 naringenin

	R_1	R_2	R_3	R_4	
21	H	H	H	H	demethoxymateucinol
22	H	H	OCH_3	H	matteucinol
23	OH	H	H	H	matteucin
24	H	H	OH	H	farrerol
25	OH	H	OCH_3	H	methoxymatteucin
26	H	OH	H	OCH_3	3′-hydroxy 5′-methoxy 6, 8-dimethyl huazhongilexone



28 leptorumol

Table S1. ^{1}H and ^{13}C NMR of matteuorienates A−C in DMSO-d_6 **(14−16)**

position	matteuorienate A (**14**)[a]		matteuorienate B (**15**)[b]		matteuorienate C (**16**)[c]	
	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
2	77.9, CH	5.55 dd (12.3, 2.7)	78.0, CH	5.60 dd (12.6, 2.9)	163.7, C	
3	42.3, CH_2	2.84 dd (17.4, 3.0) 3.22 m	42.4, CH_2	2.87 dd (17.0, 3.1) 3.24 m	105.2, CH	7.09 s
4	198.4, C		198.2, C		182.9, C	
5	157.8, C		157.9, C		156.0, C	
6	111.1, C		111.3, C		114.6, C	
7	161.1, C		161.2, C		158.9, C	
8	110.1, C		110.2, C		110.3, C	
9	157.2, C		157.1, C		152.2, C	
10	104.8, C		104.9, C		107.1, C	
1'	130.8, C		138.9, C		130.9, C	
2'	128.0, CH	7.46 d (8.7)	128.6, CH	7.51 d (7.5)	126.5, CH	8.11 dd (8.0, 1.5)
3'	113.9, CH	6.99 d (8.7)	126.3, CH	7.41 t (7.6)	129.3, CH	7.63 m
4'	159.3, C		128.4, CH	7.35 t (7.3)	132.2, CH	7.63 m
5'	113.9, CH	6.99 d (8.7)	126.3, CH	7.41 t (7.6)	129.3, CH	7.63 m
6'	128.0, CH	7.46 d (8.7)	128.6, CH	7.51 d (7.5)	126.5, CH	8.11 dd (8.0, 1.5)
1"	104.0, CH	4.62 d (7.5)	104.0, CH	4.59 d (7.7)	104.4, CH	4.70 d (7.7)
2"	73.9, CH	3.29 m	73.9, CH	3.29 m	73.9, CH	3.37 m
3"	76.0, CH	3.22 m	76.0, CH	3.22 m	76.0, CH	3.28 m
4"	70.0, CH	3.18m	69.8, CH	3.16 m	69.8, CH	3.21 m
5"	73.5, CH	3.29 m	73.6, CH	3.29 m	73.7, CH	3.33 m

6''	63.0, CH_2	4.03 dd (12.0, 5.7) 4.21 dd (11.7, 1.5)	63.0, CH_2	4.01 dd (11.8, 6.1) 4.18 dd (11.7, 1.8)	63.0, CH_2	4.04 dd (11.8, 6.1) 4.19 dd (11.7, 1.7)
1'''	170.2, C		170.3, C		170.3, C	
2'''	45.6, CH_2	2.59 d (14.1)	45.5, CH_2	2.57 d (14.1) 2.44 d (14.1)	45.7, CH_2	2.50 overlap 2.38 d (14.0)
3'''	68.9, C		69.4, C		68.8, C	
4'''	45.4, CH_2	2.43 s	45.4, CH_2	2.41 d (1.91)	45.5, CH_2	2.32 d (14.9) 2.25 d (14.9)
5'''	172.5, C		172.4, C		173.1, C	
6'''	27.2, CH_3	1.18 s	27.2, CH_3	1.15 s	27.4, CH_3	1.07 s
CH_3-6	8.6, CH_3	2.05 s	8.6, CH_3	2.02 s	9.0, CH_3	2.17 s
CH_3-8	9.2, CH_3	2.02 s	9.1, CH_3	2.01 s	9.2, CH_3	2.40 s
OCH_3-4'	55.2, CH_3	3.77 s				

Recorded at [a]300/125 MHz, [b]600/150 MHz, [c]500/125 MHz

Table S2. ^{1}H and ^{13}C NMR of known flavonoid glycosides in DMSO-d_6 **(17−20)**

position	**17**[a]		**18**[b]		**19**[b]		**20**[c]	
	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
2	77.9, CH	5.42 dd (12.6, 3.0)	78.0, CH	5.65 dd (12.6, 3.0)	77.8, CH	5.56 dd (12.5, 2.9)	73.9, CH	5.69 dd (13.0, 3.1)
3	42.9, CH_2	2.76 dd (17.6, 3.7) 2.99 (17.1, 12.7)	42.3, CH_2	2.92 dd (17.1, 3.3) 3.12 m	42.2, CH_2	2.85 dd (17.0, 2.9) 3.09 m	41.3, CH_2	2.82 dd (17.1, 3.0) 3.14 m
4	197.0, C		198.2, C		198.5, C		198.6, C	
5	159.9, C		157.8, C		157.8, C		157.9, C	
6	104.2, C		111.3, C		111.2, C		111.2, C	
7	162.7, C		161.4, C		161.4, C		161.4, C	
8	103.8, C		110.2, C		110.1, C		110.1, C	
9	158.3, C		157.0, C		157.2, C		157.5, C	
10	101.2, C		104.8, C		104.8, C		104.7, C	
1'	129.1, C		128.6, C		130.8, C		125.7, C	
2'	127.9, CH	7.34 d (8.5)	128.6, CH	7.54, d (8.0)	128.0, CH	7.46 d (8.8)	148.0, C	
3'	115.0, CH	6.78 d (8.6)	126.3, CH	7.36−7.47 m	113.9, CH	6.99 d (8.6)	116.2, CH	6.82 d (8.8)
4'	157.2, C		128.4, CH	7.36−7.47 m	159.3, C		114.2, CH	6.79 d (8.8, 3.0)
5'	115.0, CH	6.78 d (8.6)	126.3, CH	7.36−7.47 m	113.9, CH	6.99 d (8.6)	152.1, C	
6'	127.9, CH	7.34 d (8.5)	128.6, CH	7.54, d (8.0)	128.0, CH	7.46 d (8.8)	112.2, CH	7.04 d (3.2)

1"	72.9, CH	4.62 d (9.7)	104.2, CH	4.59, d (7.2)	104.2, CH	4.58 d (7.5)	104.3, CH	4.60 d (7.9)
2"	71.8, CH	3.52 m	76.3, CH	3.00−3.38 m	76.3, CH	3.01−3.39 m	74.1, CH	3.14−3.30 m
3"	77.9, CH	3.17−3.27 m	77.0, CH	3.00−3.38 m	77.0, CH	3.01−3.39 m	77.1, CH	3.14−3.30 m
4"	69.3, CH	3.17−3.27 m	69.8, CH	3.00−3.38 m	69.8, CH	3.01−3.39 m	69.8, CH	3.14−3.30 m
5"	80.9, CH	3.17−3.27 m	74.0, CH	3.00−3.38 m	74.0, CH	3.01−3.39 m	76.3, CH	3.14−3.30 m
6"	60.0, CH_2	3.56 m 3.60 m	61.0, CH_2	3.40 m 3.62 dd (11.7, 1.8)	61.0, CH_2	3.41 m 3.60 m	61.0, CH_2	3.42 dd (11.8, 5.7) 3.60 m
CH_3-6	7.2, CH_3	1.94 s	8.7, CH_3	2.09 s	8.7, CH_3	2.08 s	8.8, CH_3	2.10 s
CH_3-8			9.3, CH_3	2.09 s	9.2, CH_3	2.06 s	9.3, CH_3	2.09 s
OCH_3-4'					55.2, CH_3	3.77 s		
OCH_3-5'							55.4, CH_3	3.69 s

Recorded at [a]500/125 MHz [b]300/125 MHz, [c]600/150 MHz

Figure S2. ^{1}H NMR spectrum (500 MHz) of compound **1** in DMSO-d_6

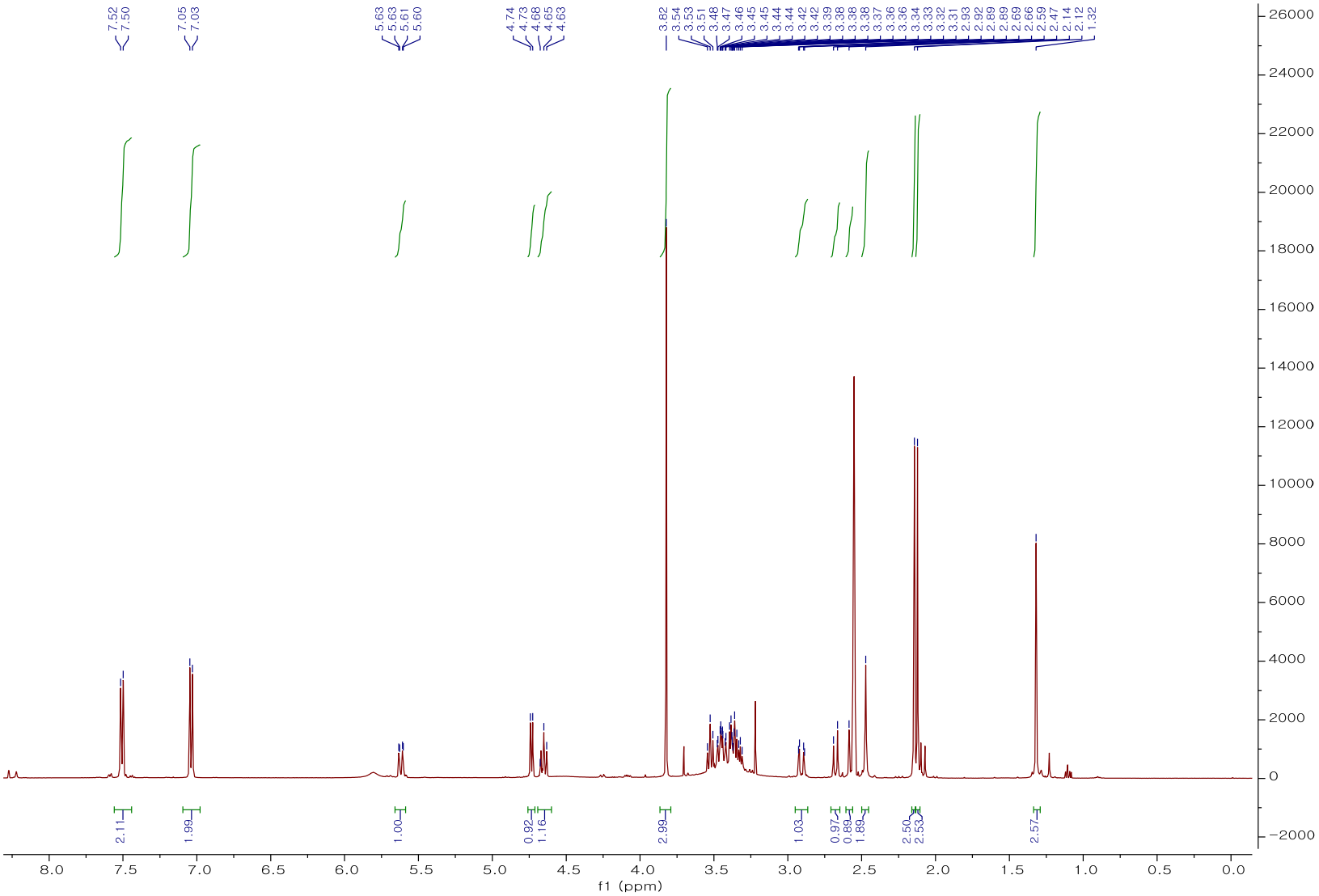


Figure S3. ^{13}C NMR spectrum (125 MHz) of compound **1** in DMSO-d_6

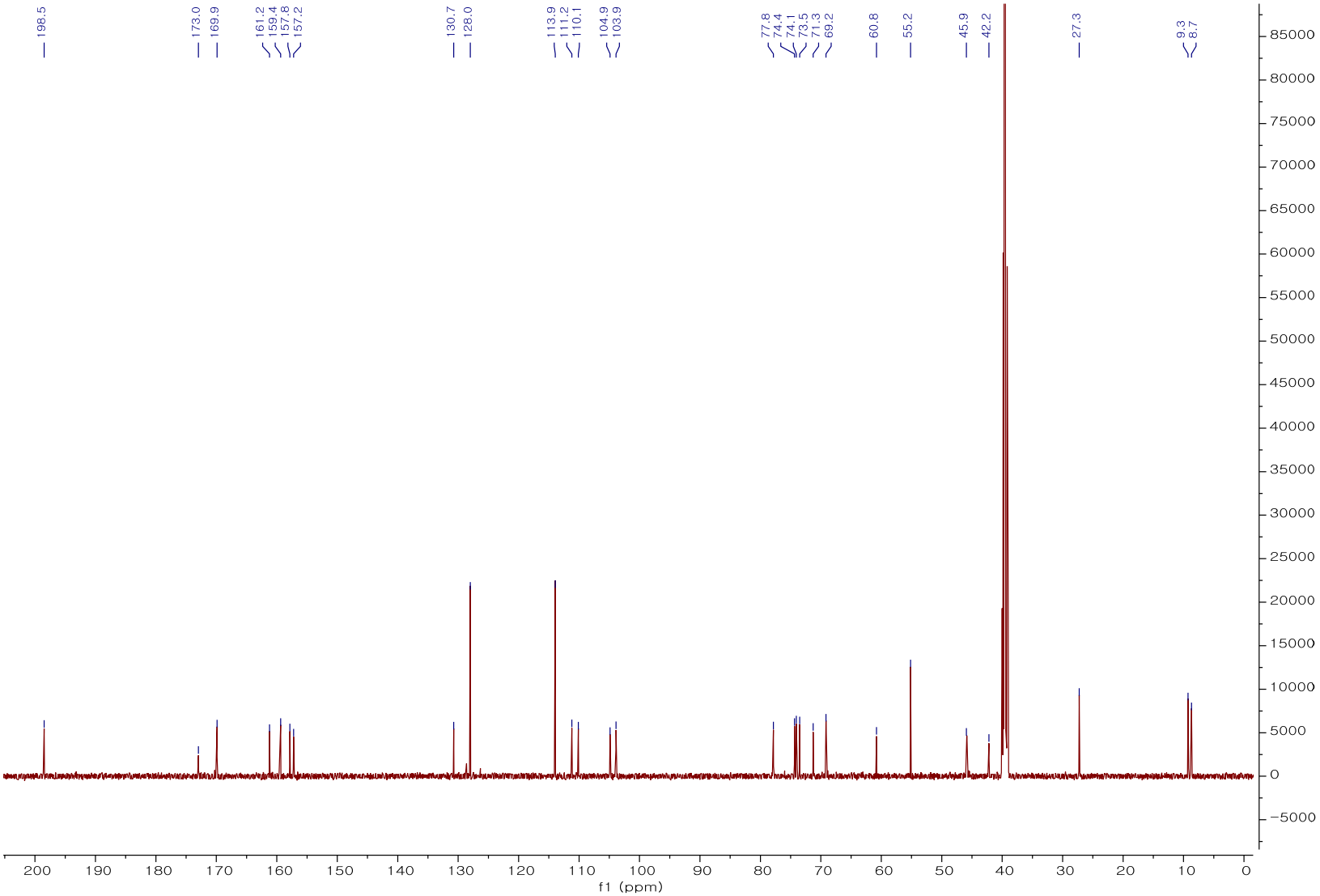


Figure S4. HSQC spectrum of compound **1**

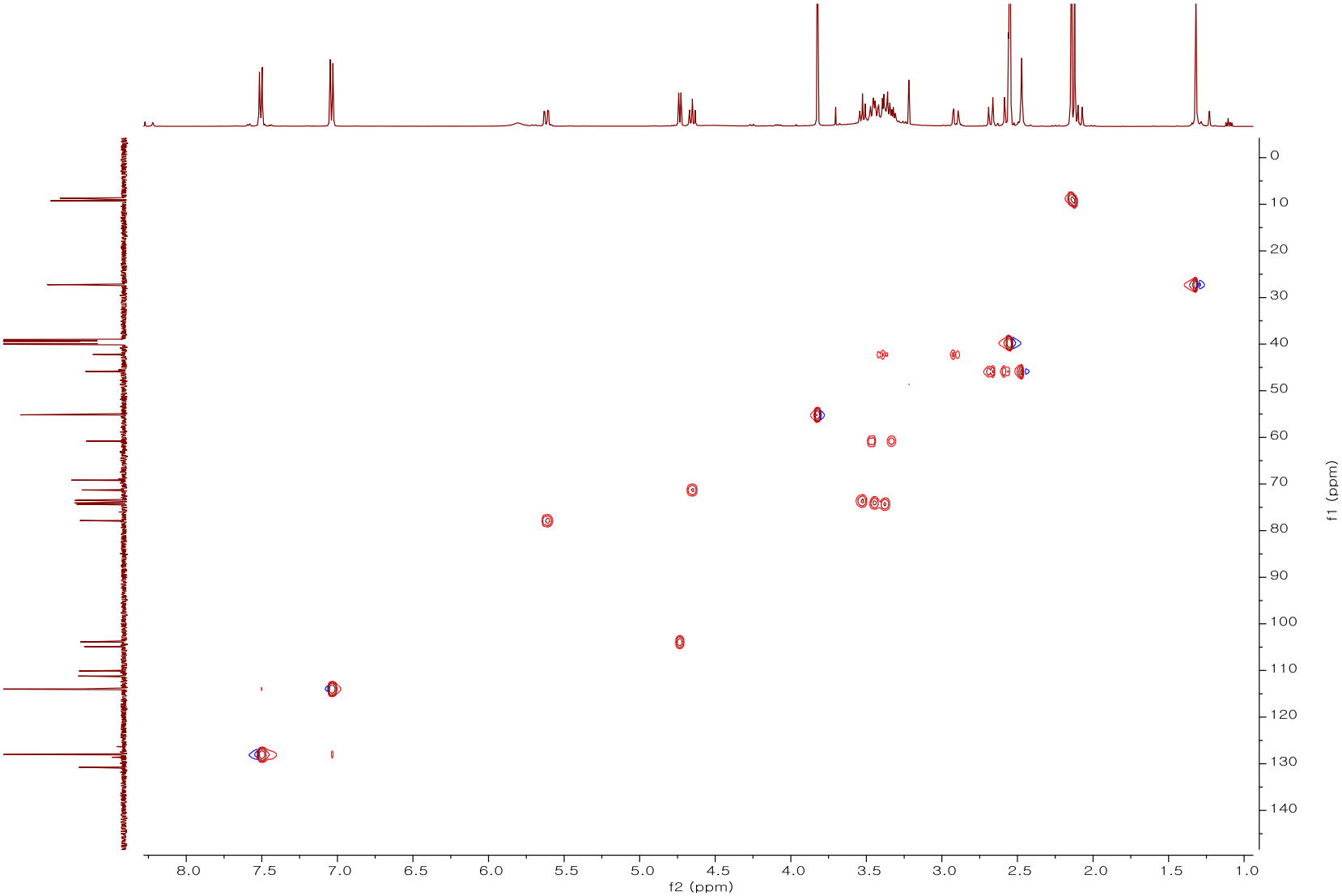


Figure S5. COSY spectrum of compound **1**

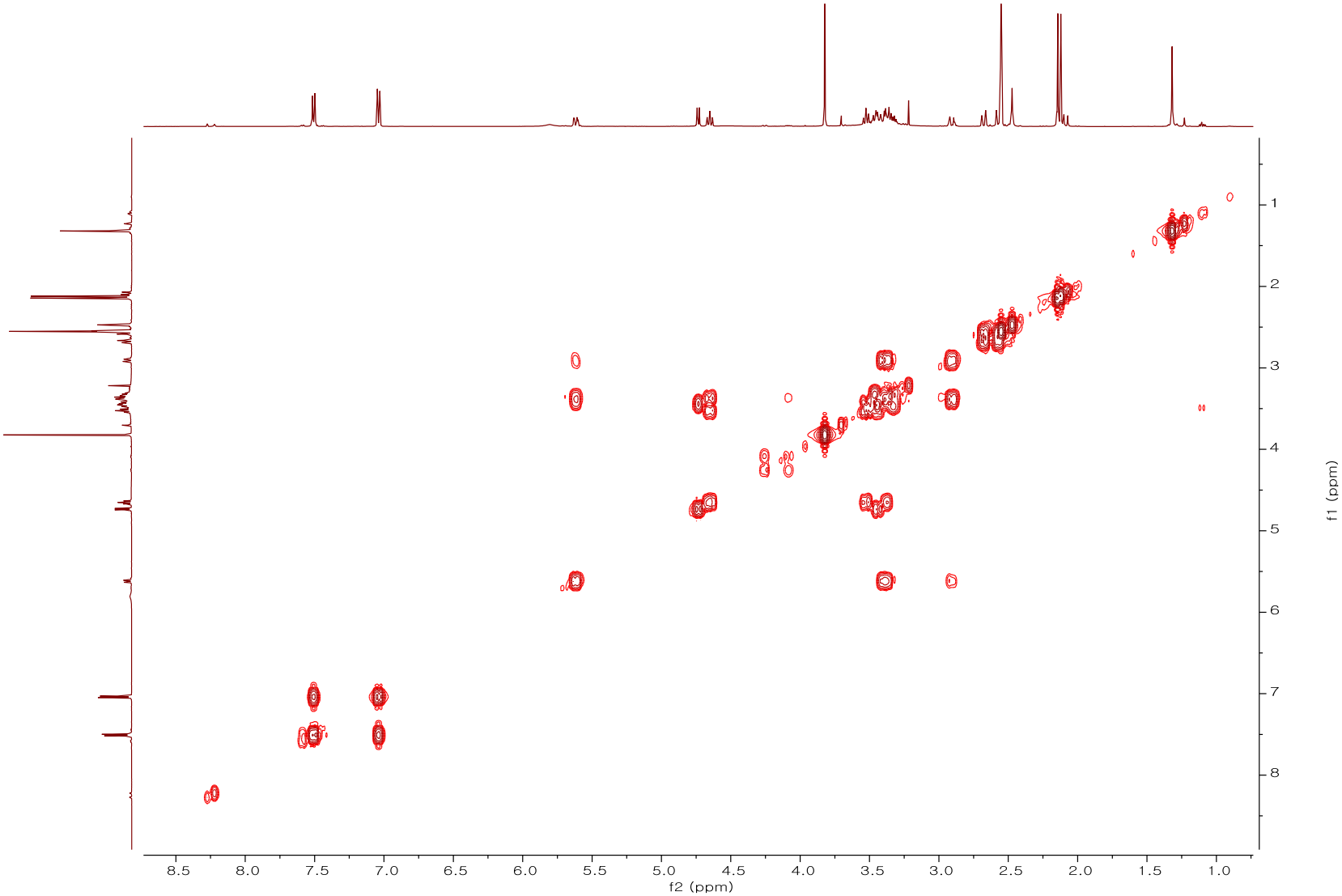


Figure S6. HMBC spectrum of compound **1**

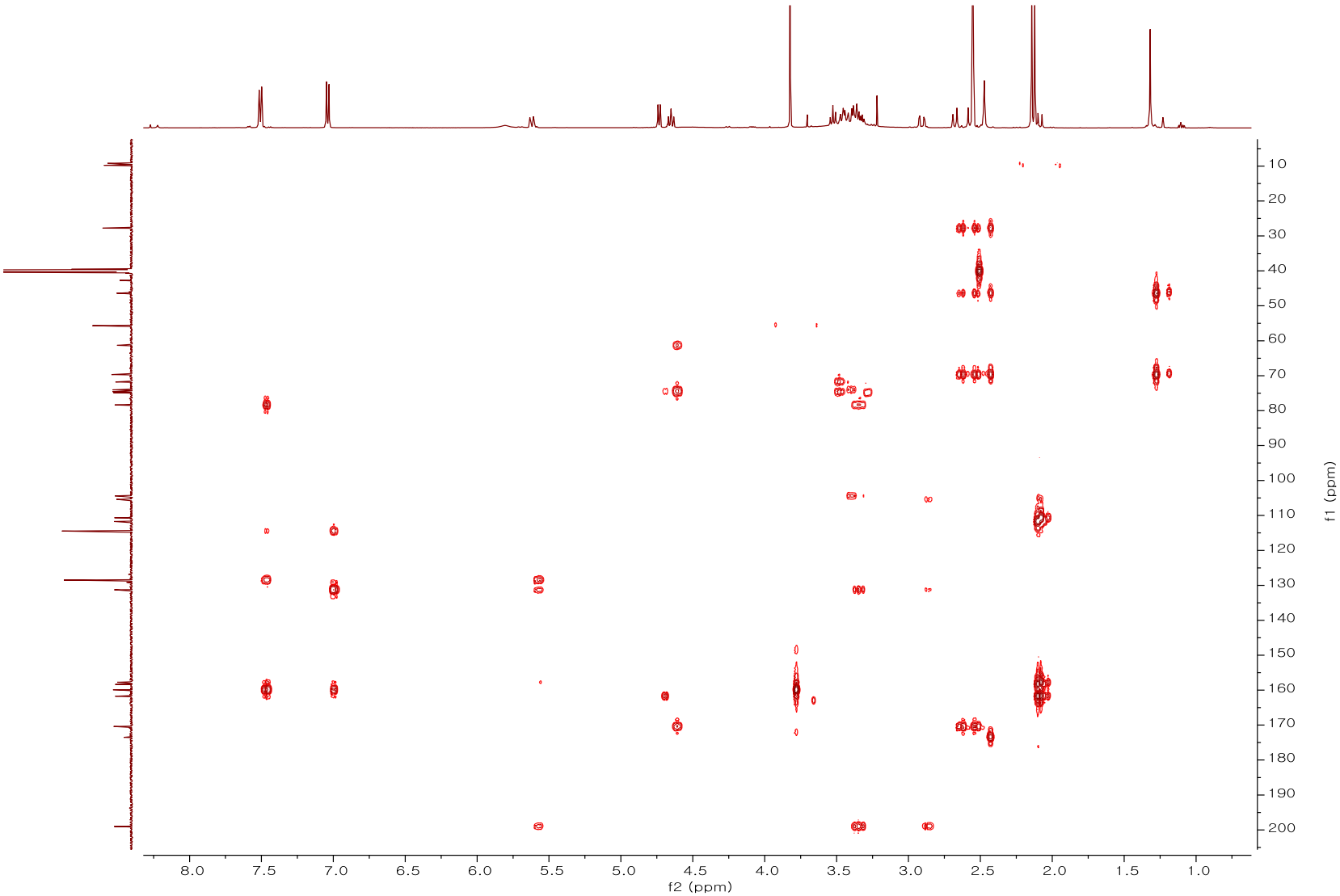


Figure S7. ^{1}H NMR spectrum (500 MHz) of compound **2** in DMSO-d_6

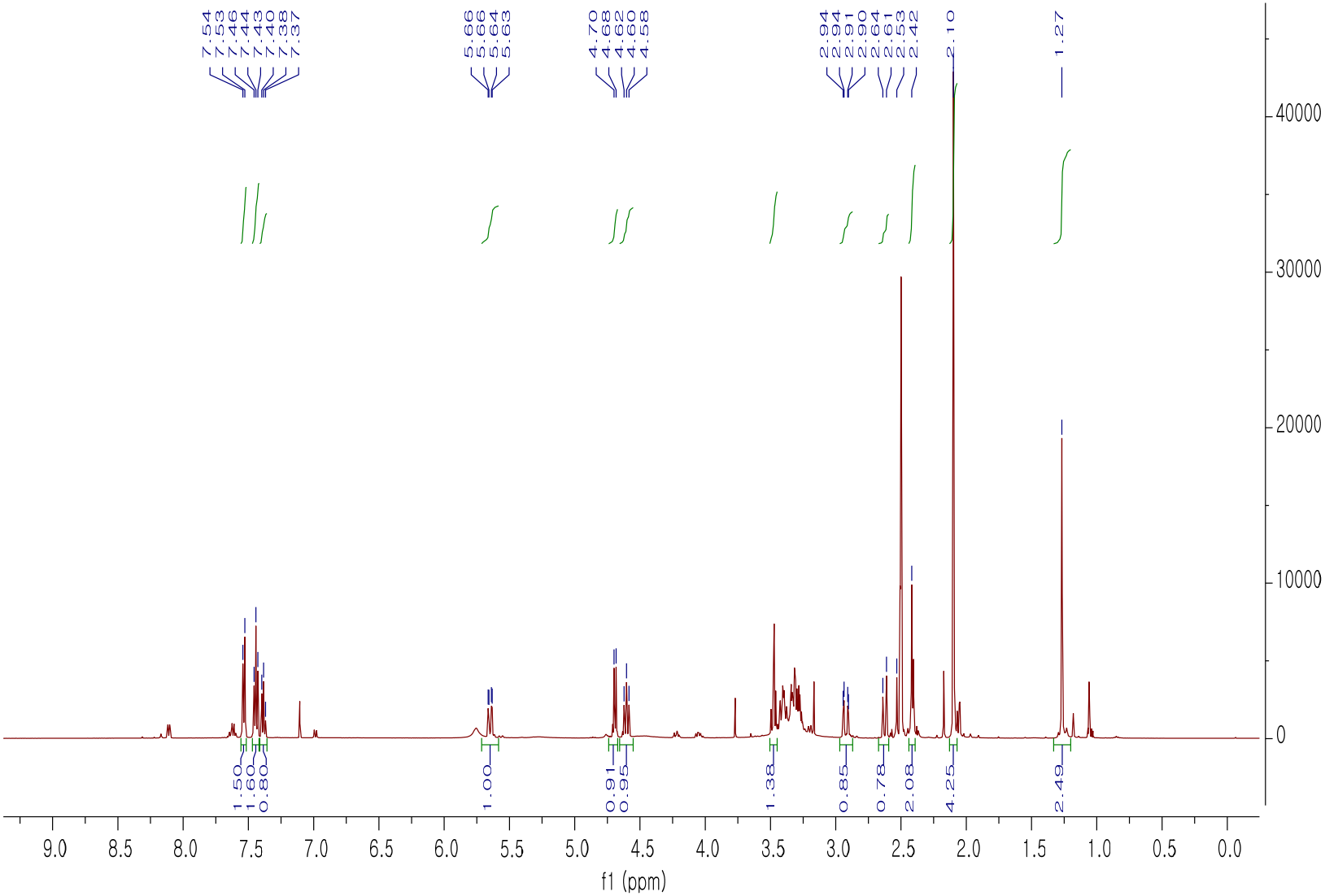


Figure S8. ^{13}C NMR spectrum (125 MHz) of compound **2** in DMSO-d_6

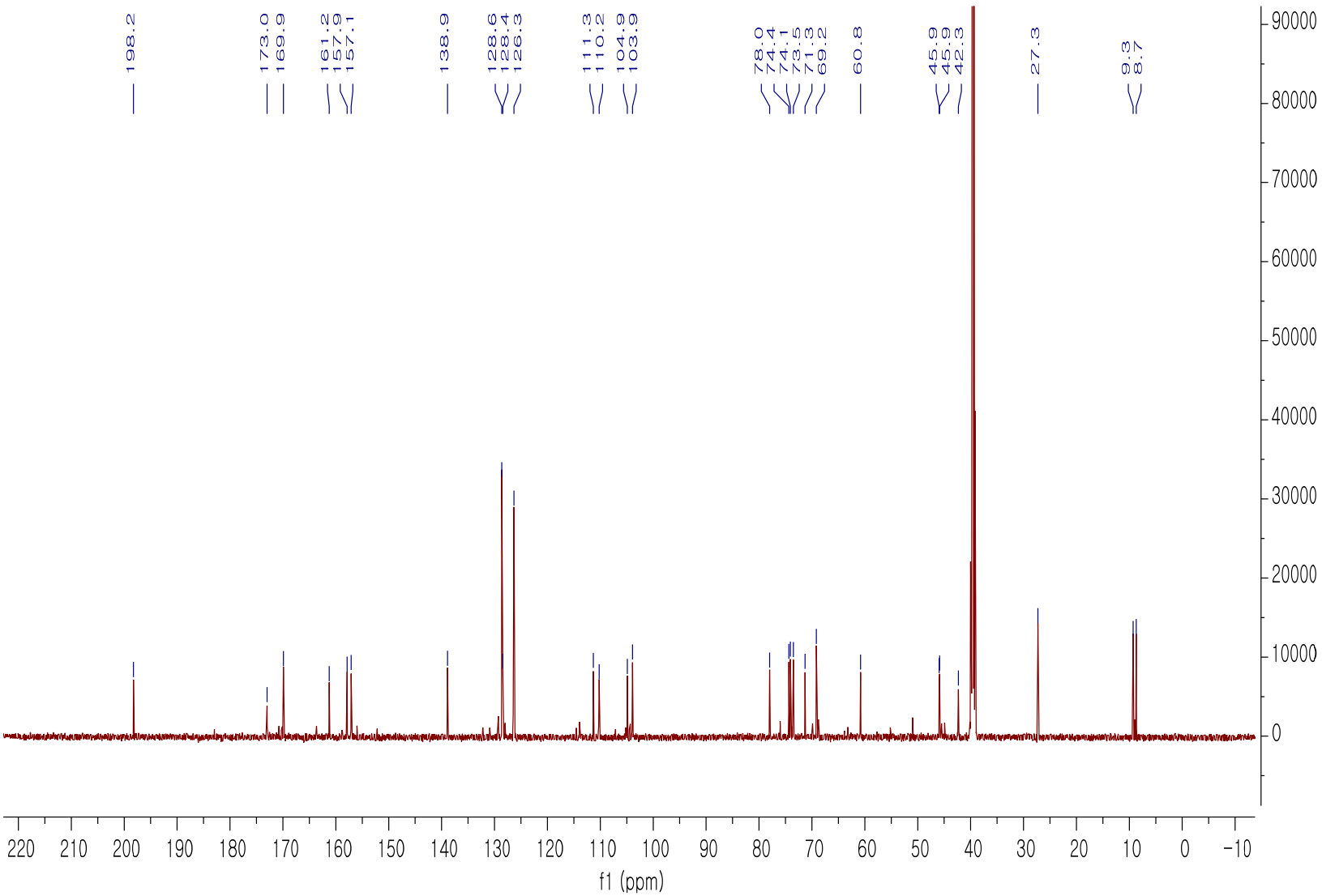
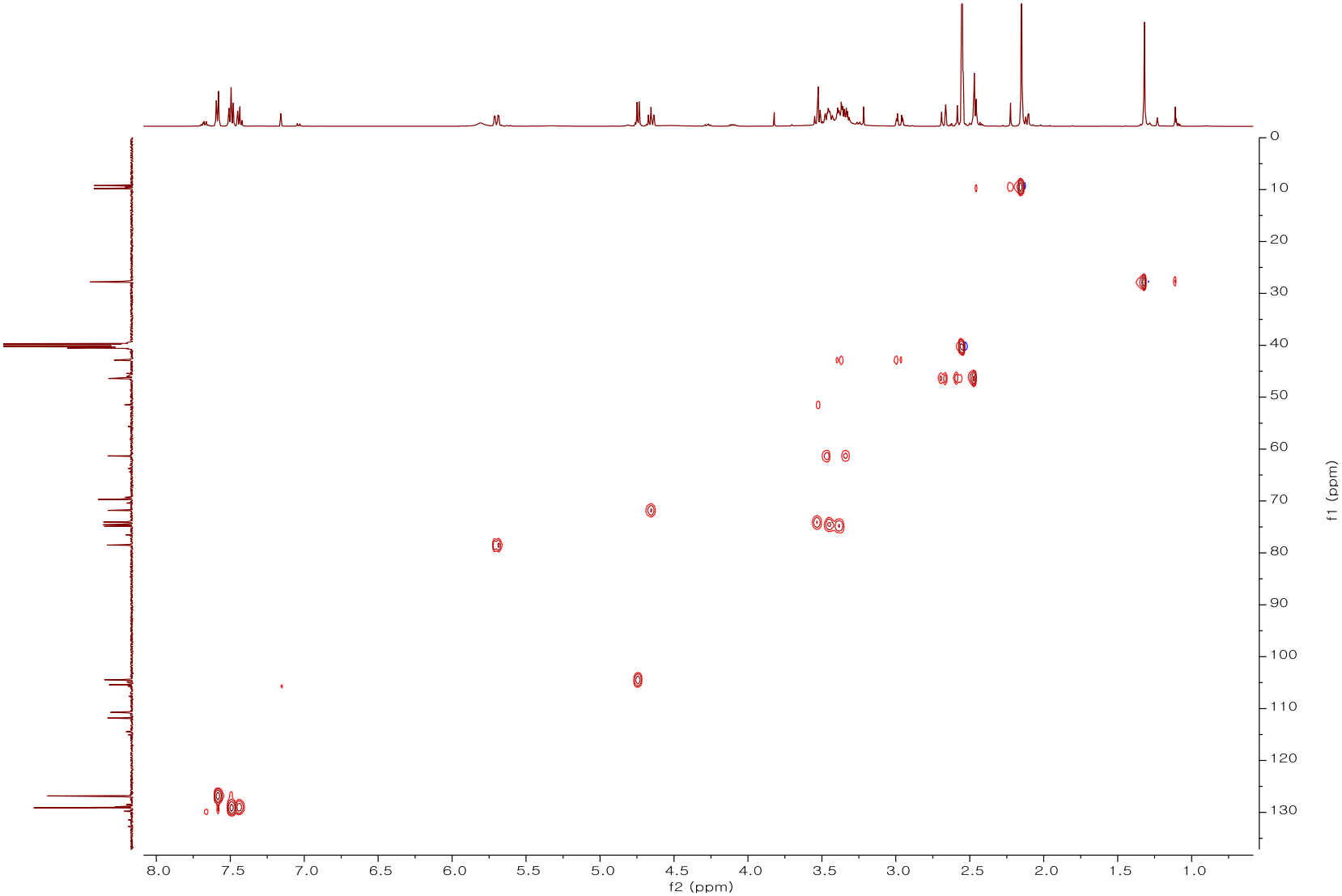


Figure S9. HSQC spectrum of compound **2**



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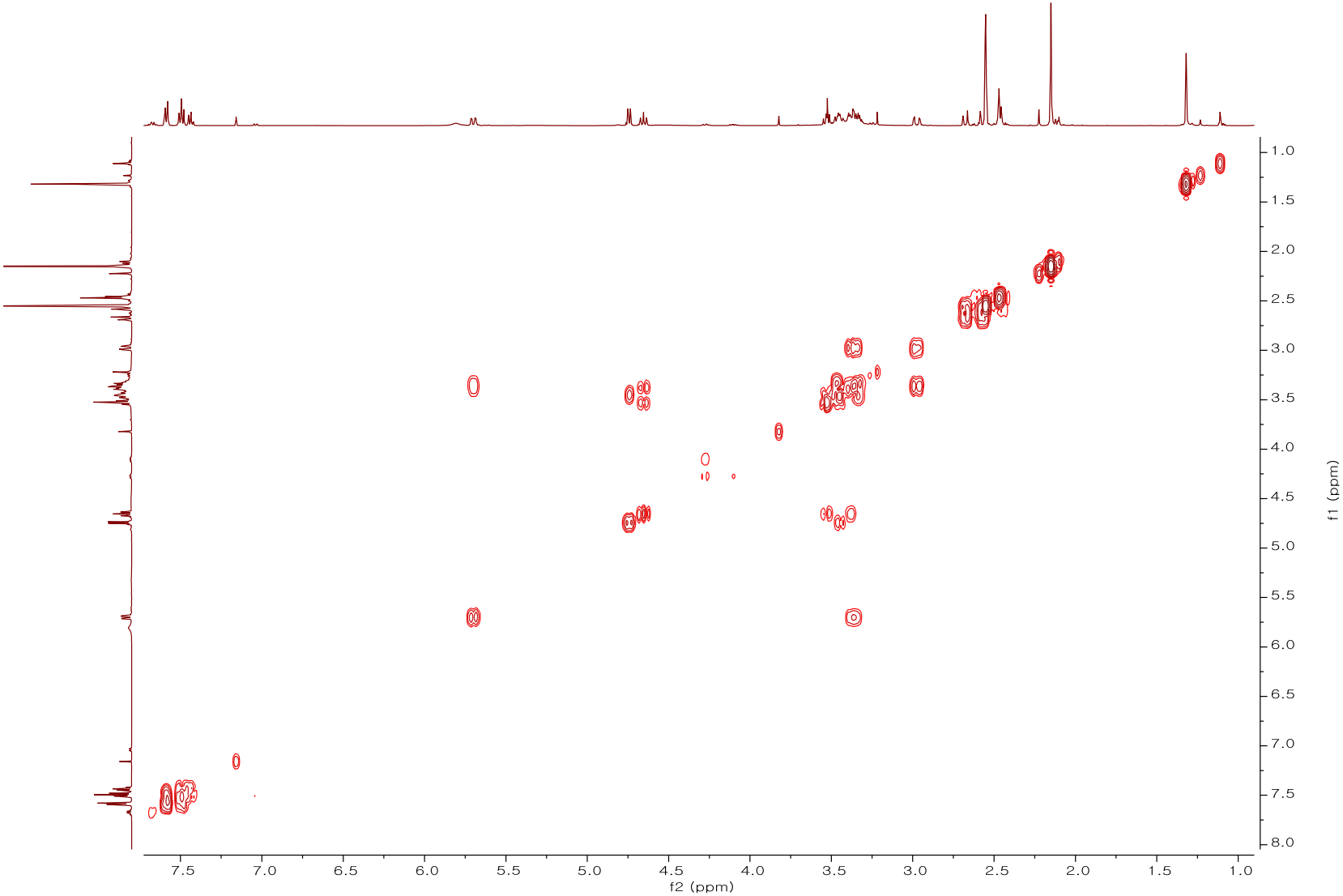


Figure S11. HMBC spectrum of compound **2**

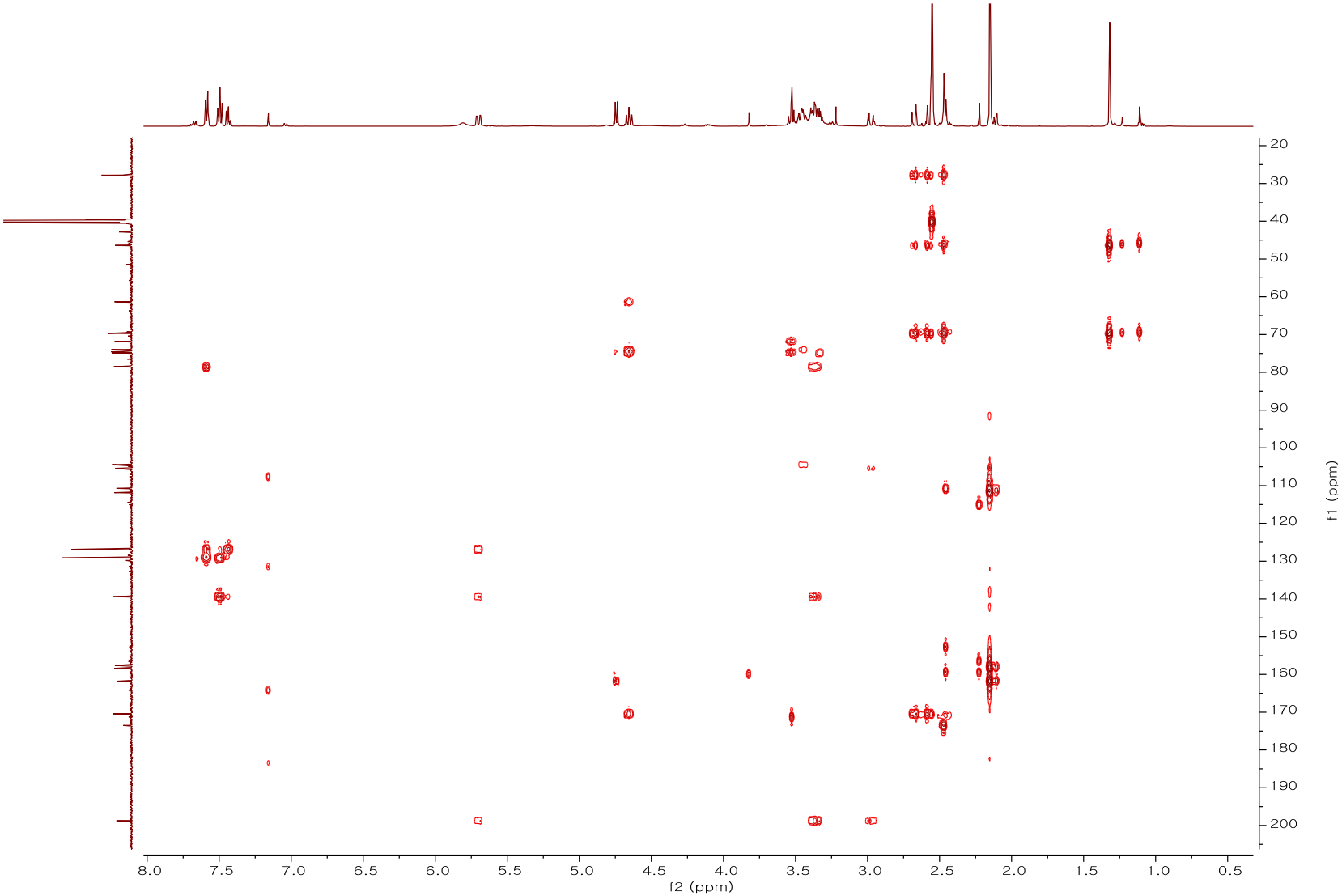


Figure S12. ^{1}H NMR spectrum (500 MHz) of compound **3** in DMSO-d_6

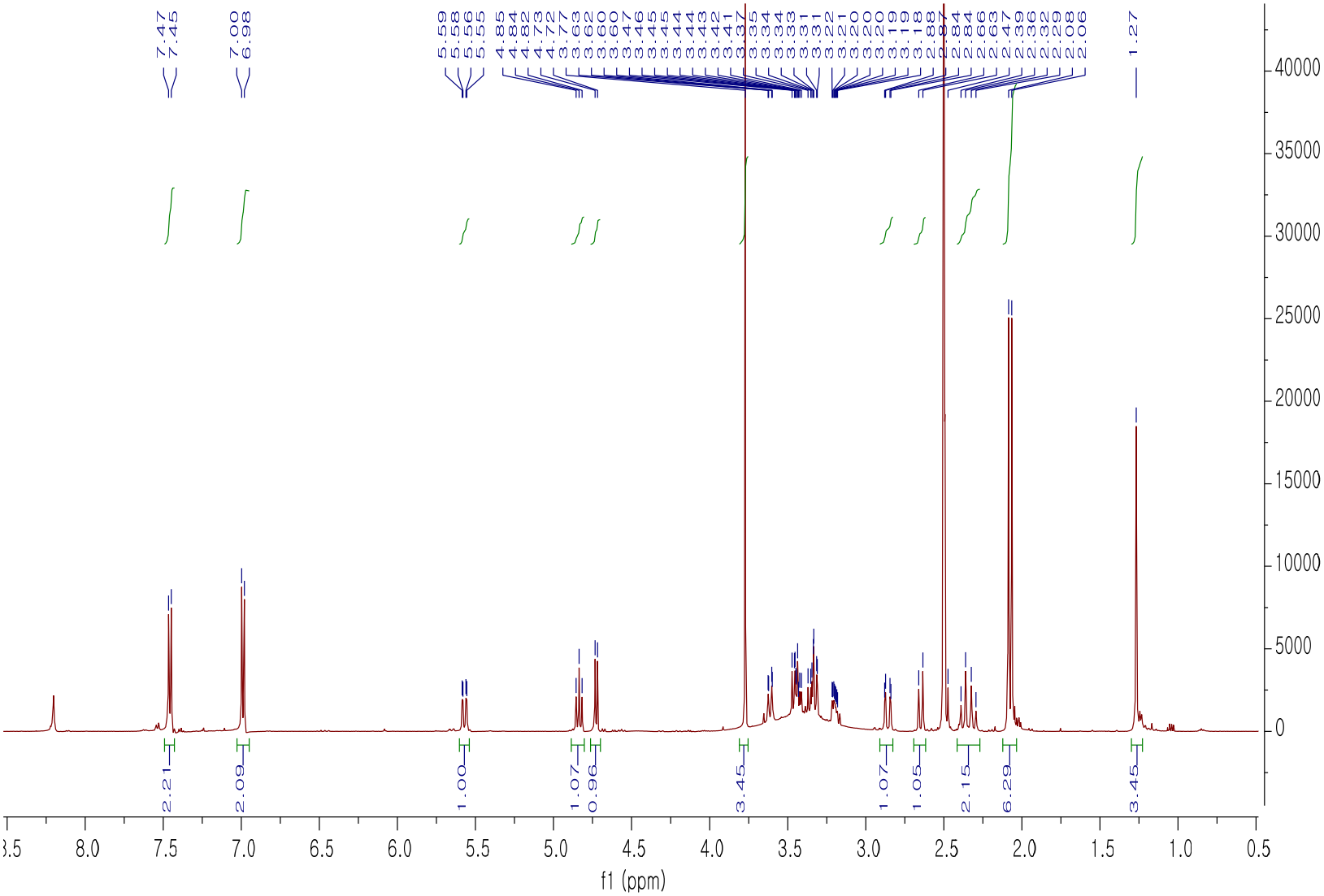


Figure S13. ^{13}C NMR spectrum (125 MHz) of compound **3** in DMSO-d_6

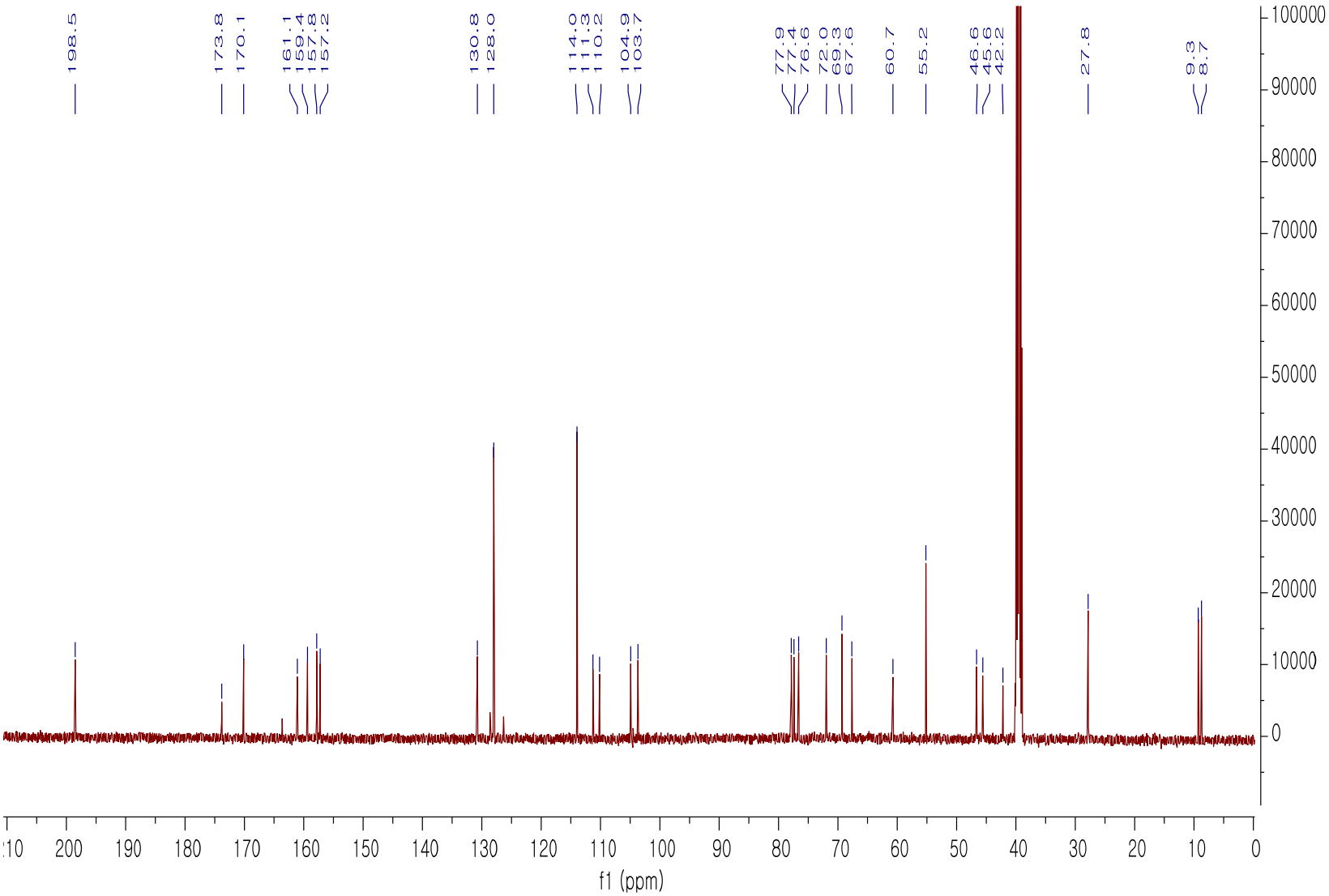


Figure S14. HSQC spectrum of compound **3**

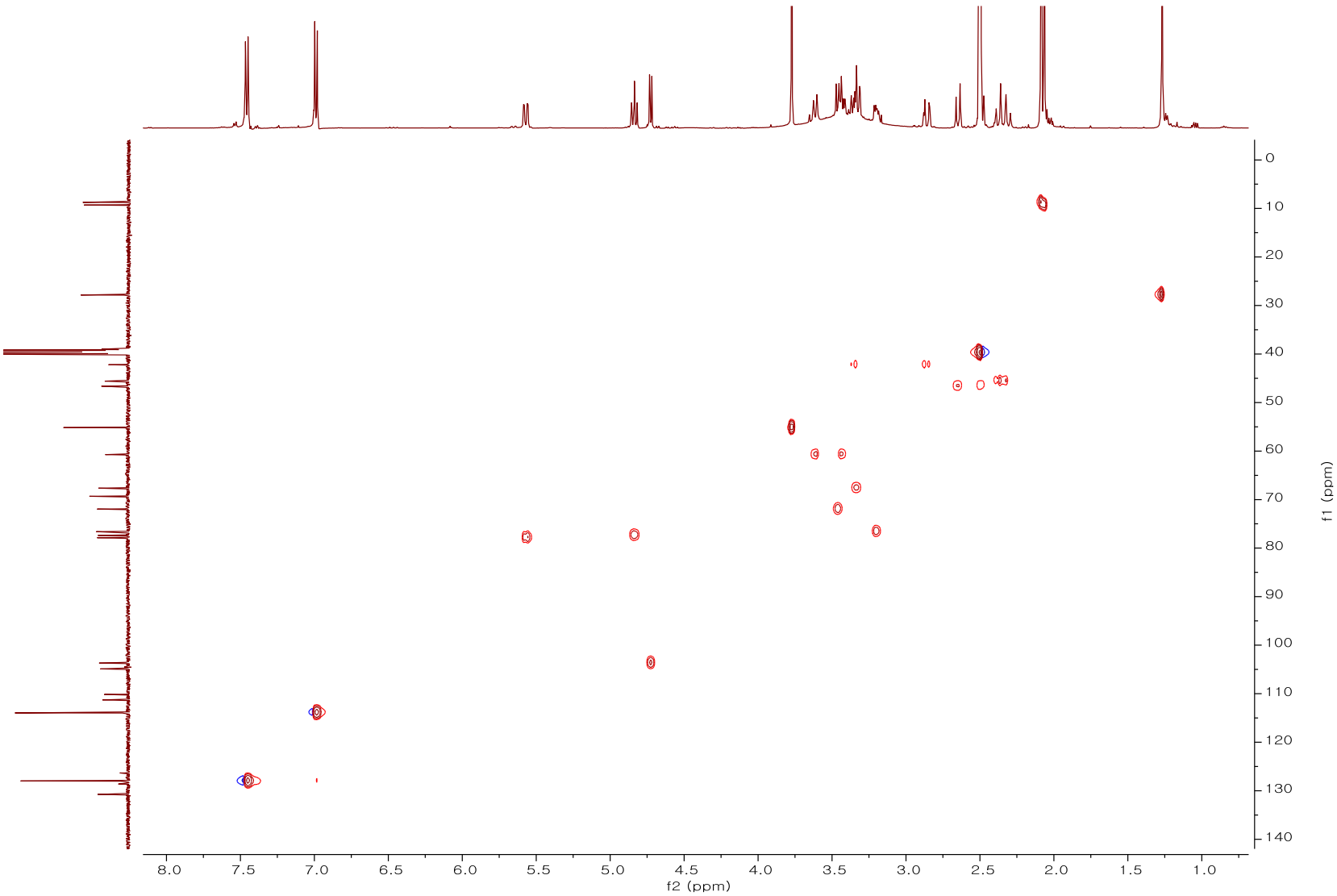


Figure S15. COSY spectrum of compound **3**

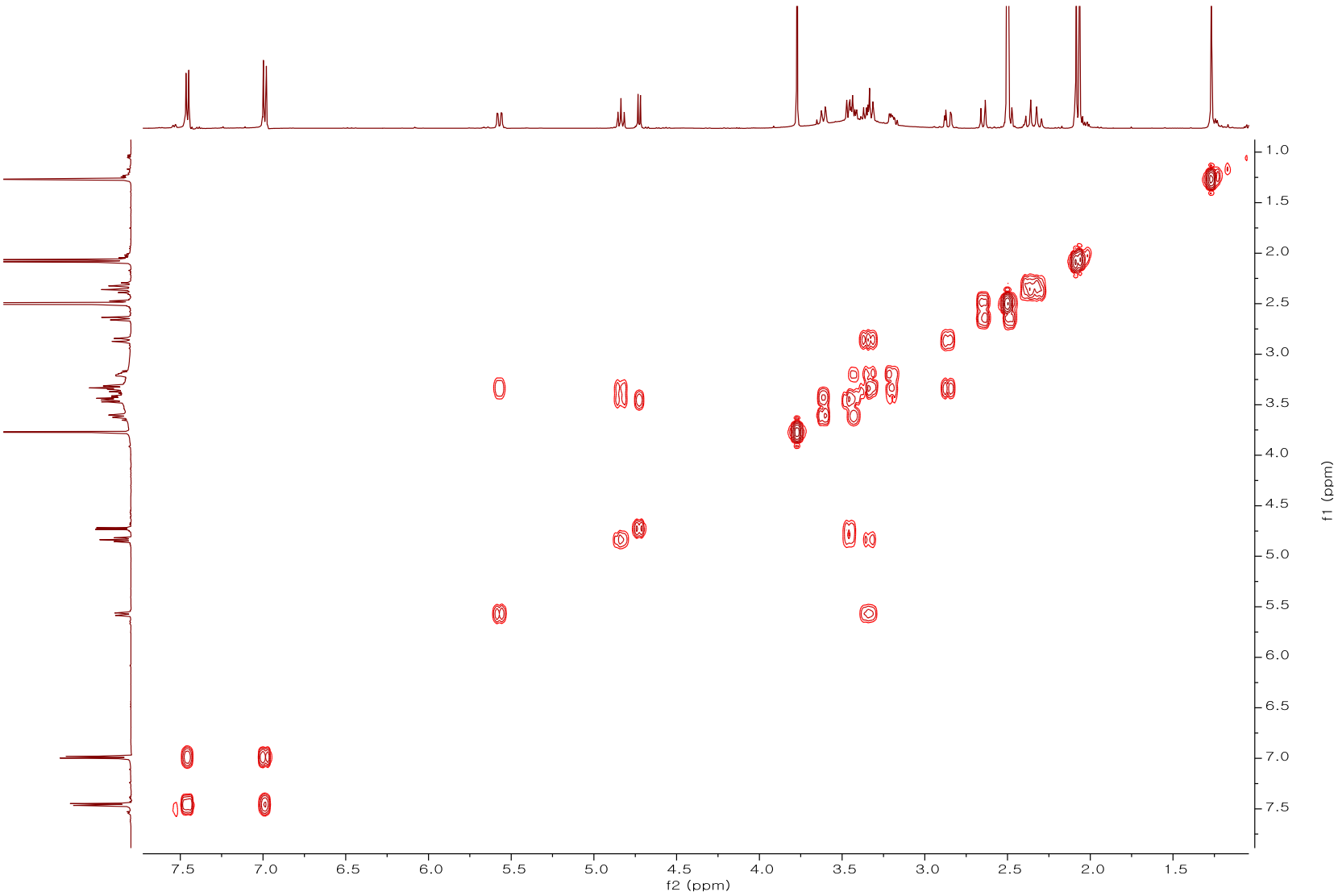


Figure S16. HMBC spectrum of compound **3**

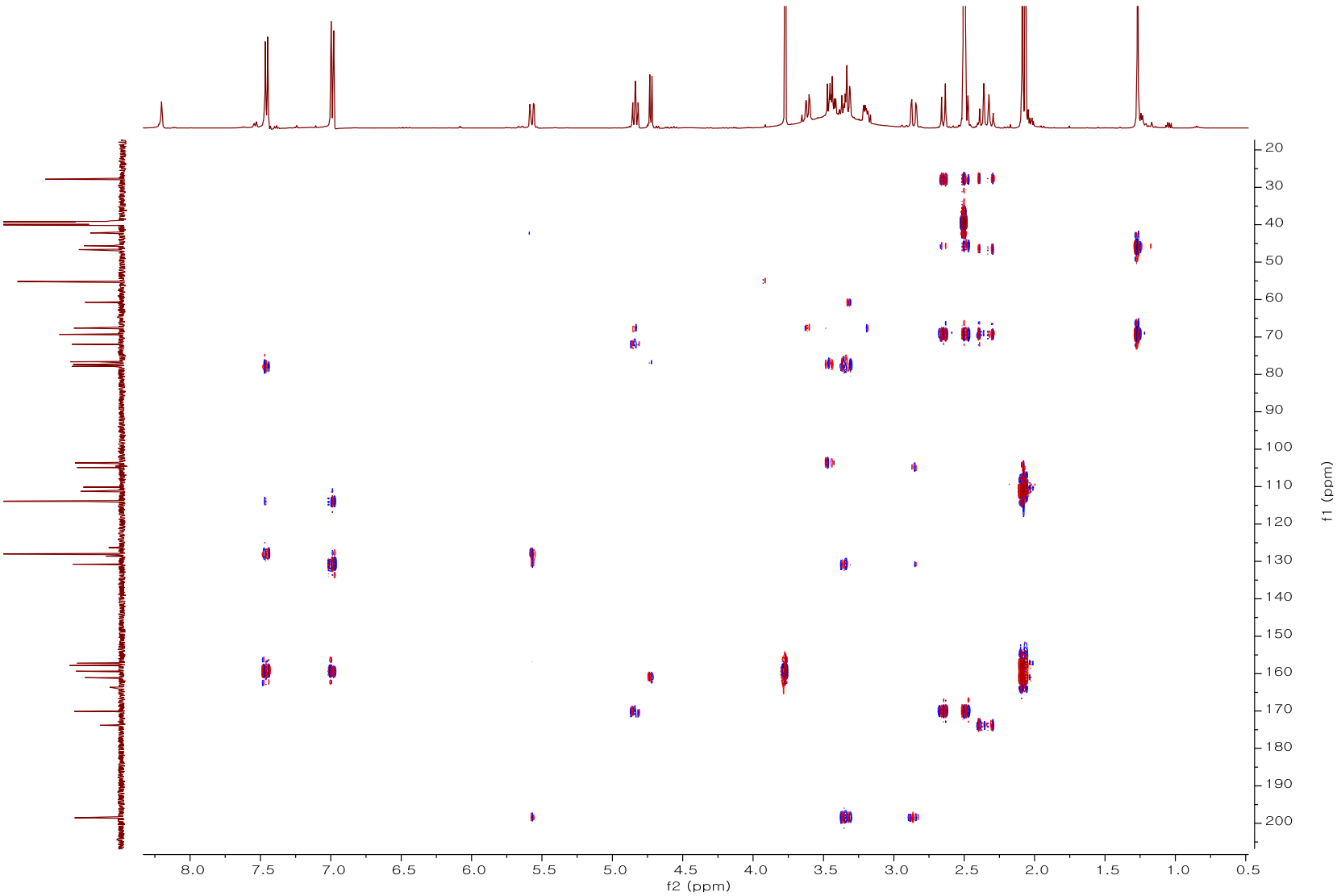


Figure S17. ^{1}H NMR spectrum (500 MHz) of compound **4** in DMSO-d_6

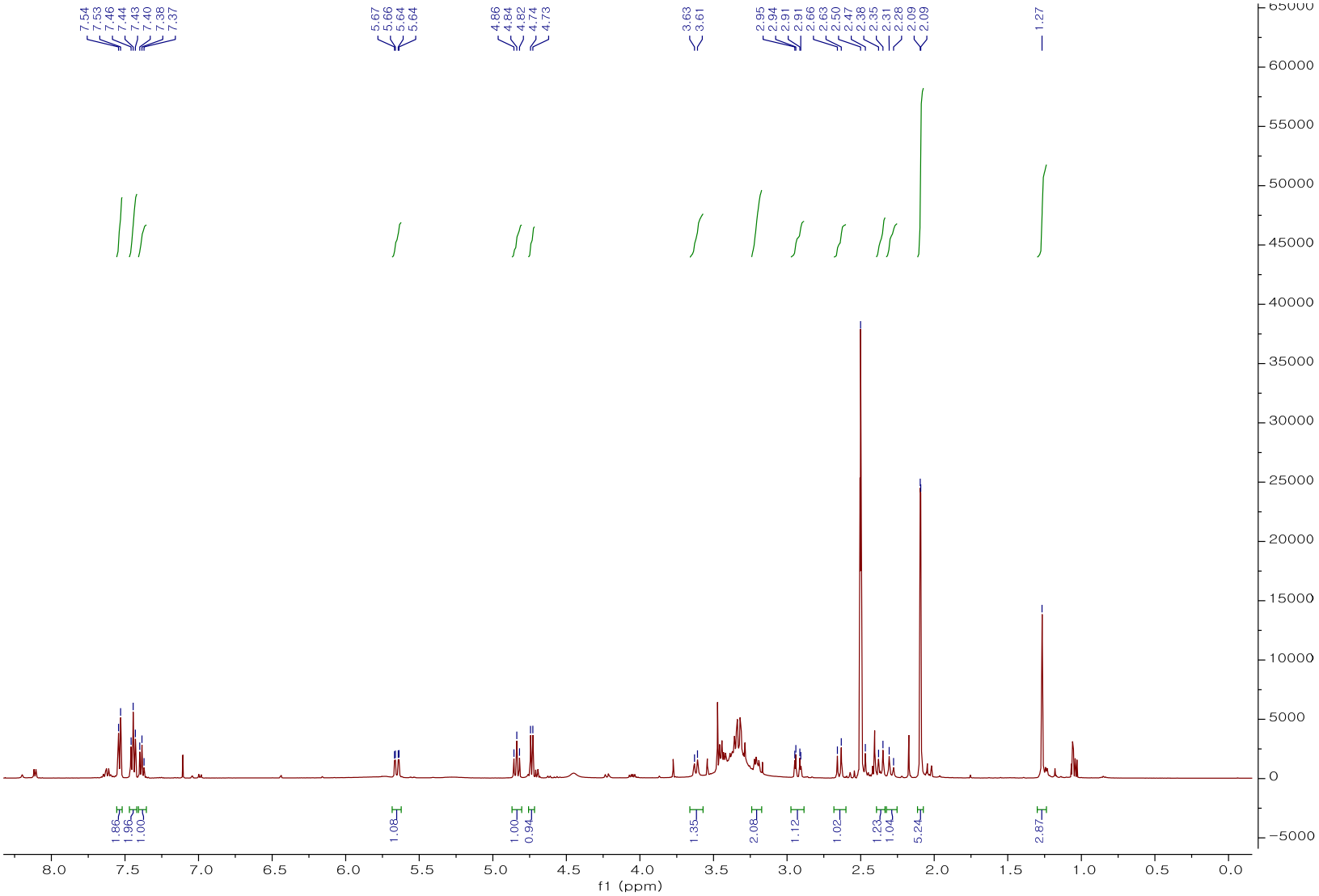


Figure S18. ^{13}C NMR spectrum (125 MHz) of compound **4** in DMSO-d_6

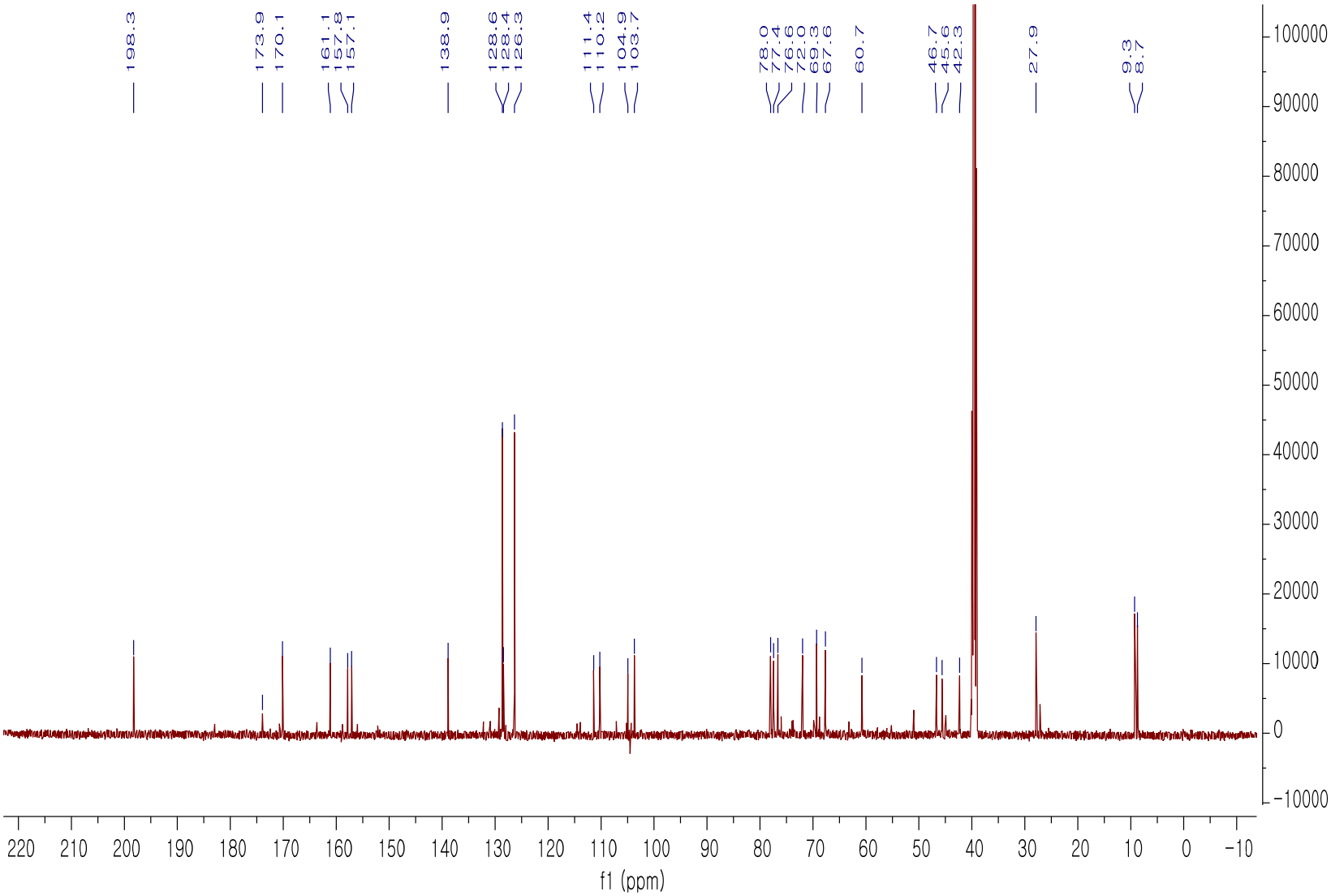


Figure S19. HSQC spectrum of compound **4**

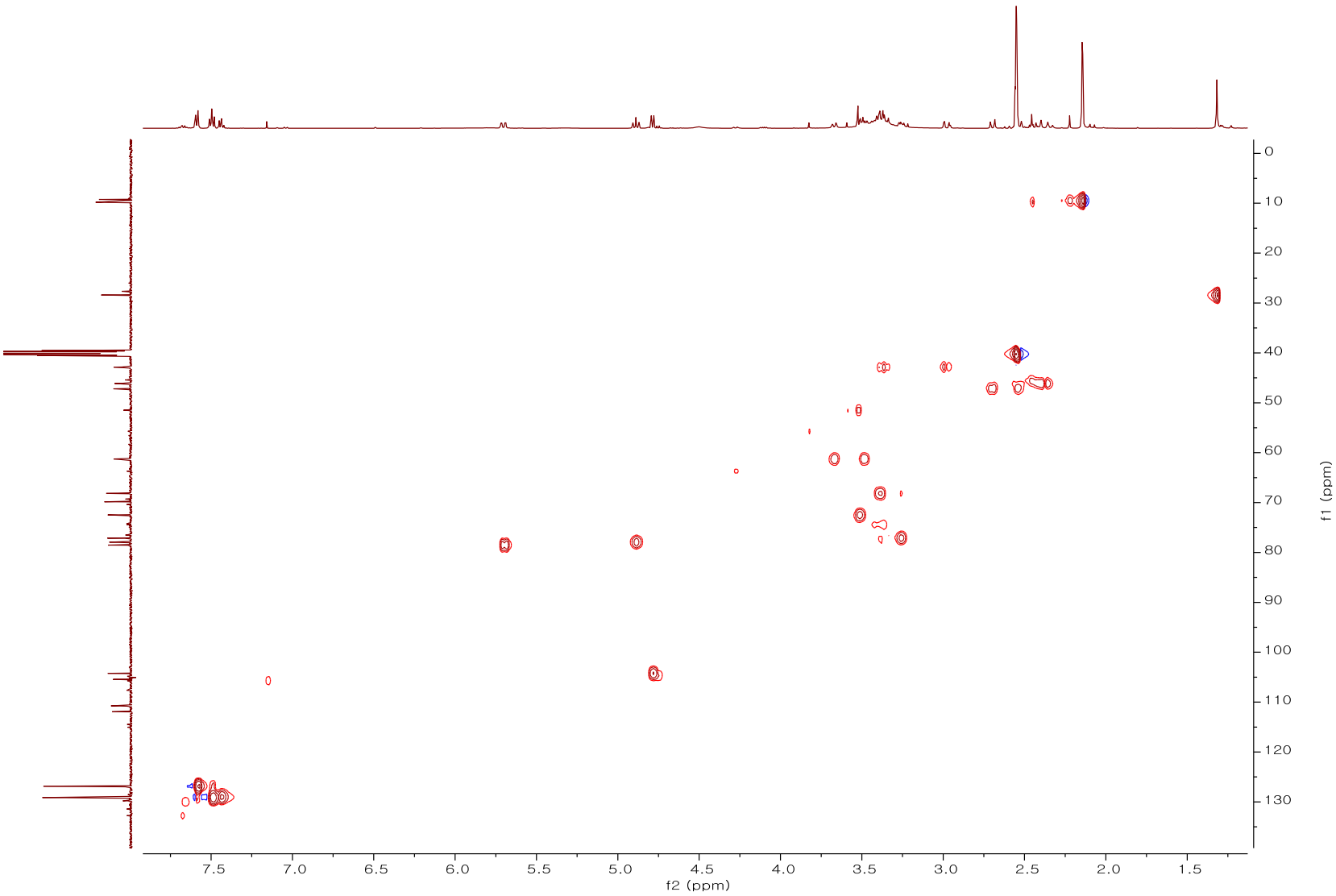


Figure S20. COSY spectrum of compound **4**

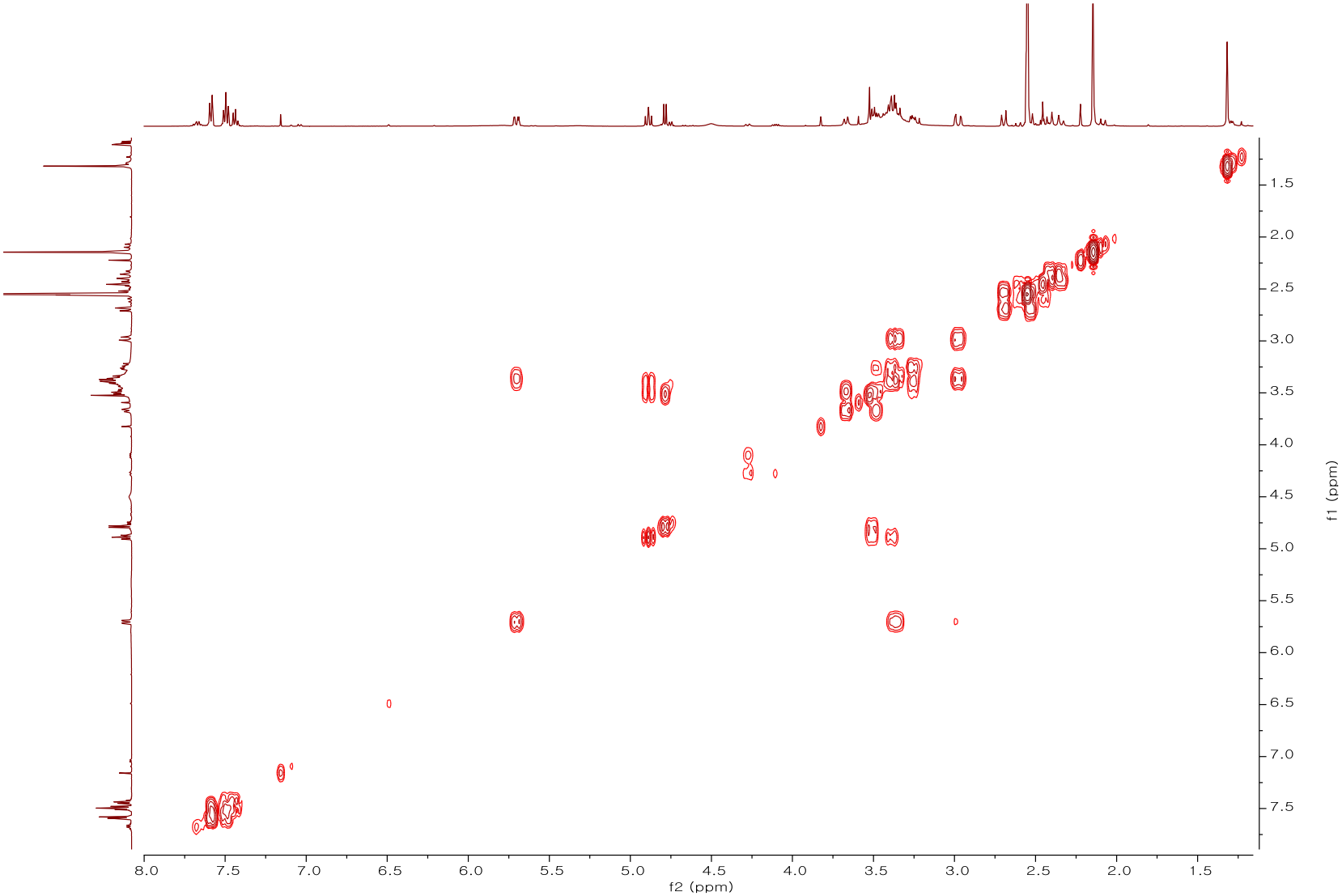


Figure S21. HMBC spectrum of compound **4**

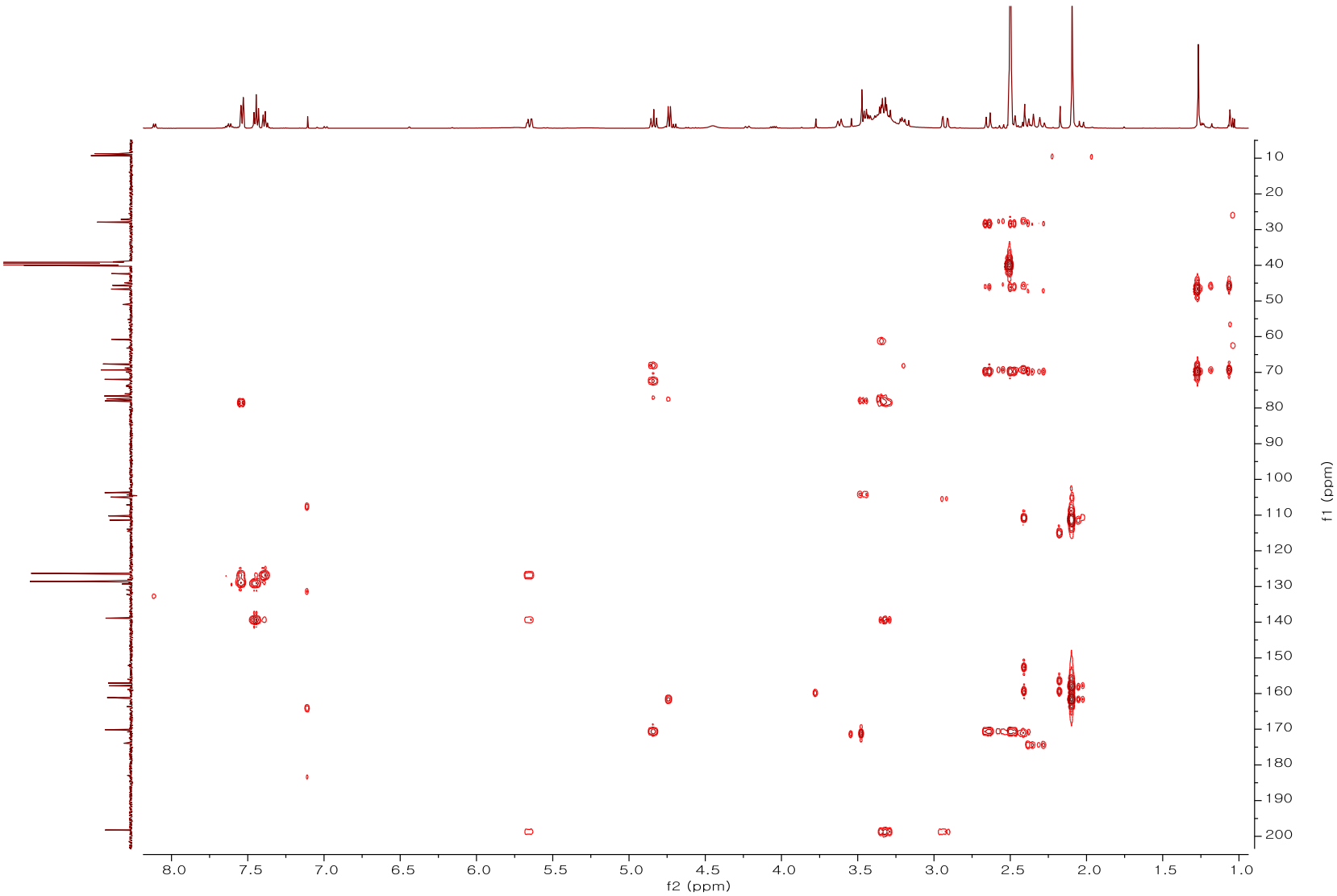


Figure S22. ^{1}H NMR spectrum (600 MHz) of compound **5** in DMSO-d_6

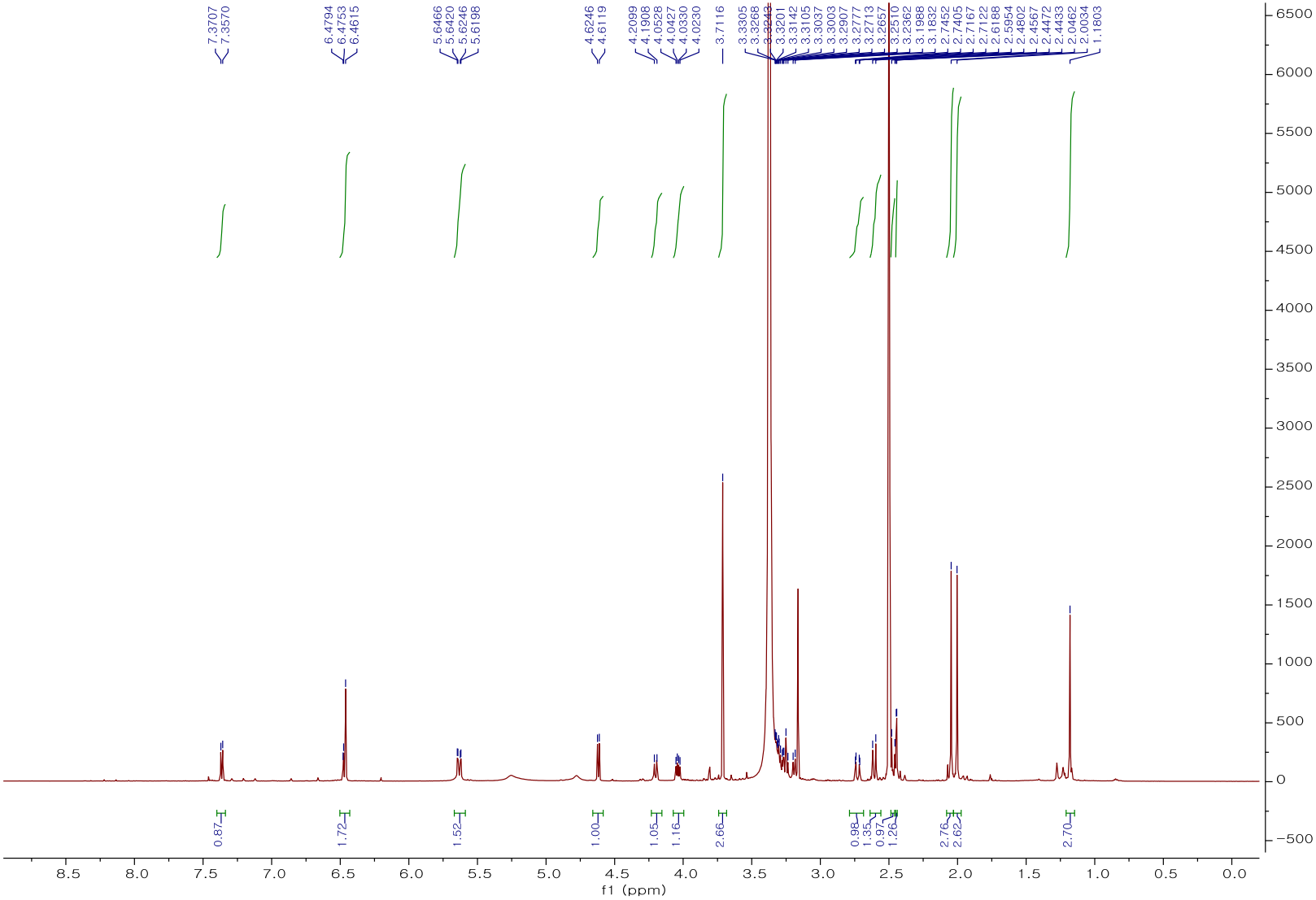


Figure S23. ^{13}C NMR spectrum (150 MHz) of compound **5** in DMSO-d_6

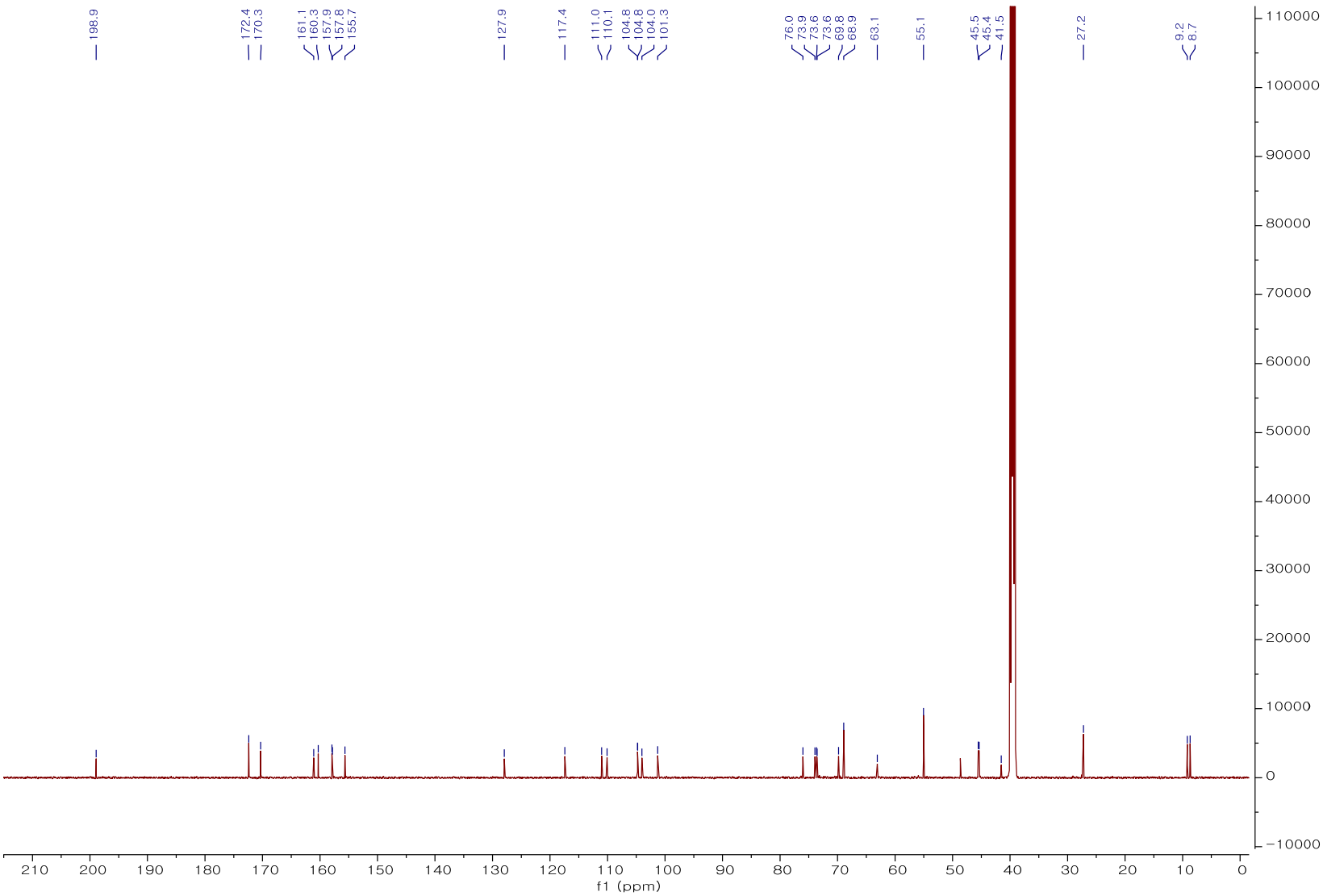


Figure S24. Edited-HSQC spectrum of compound **5**

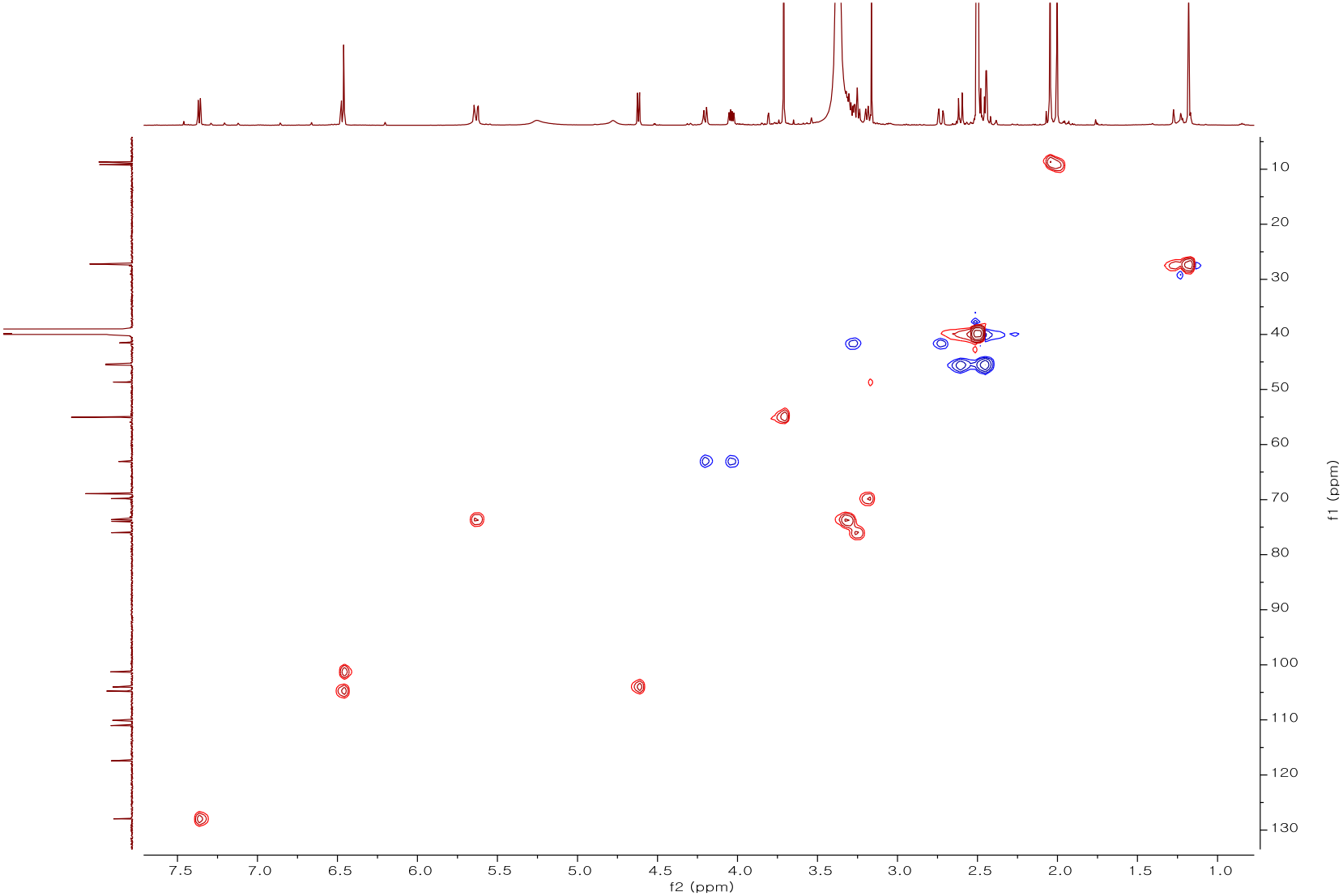


Figure S25. COSY spectrum of compound **5**

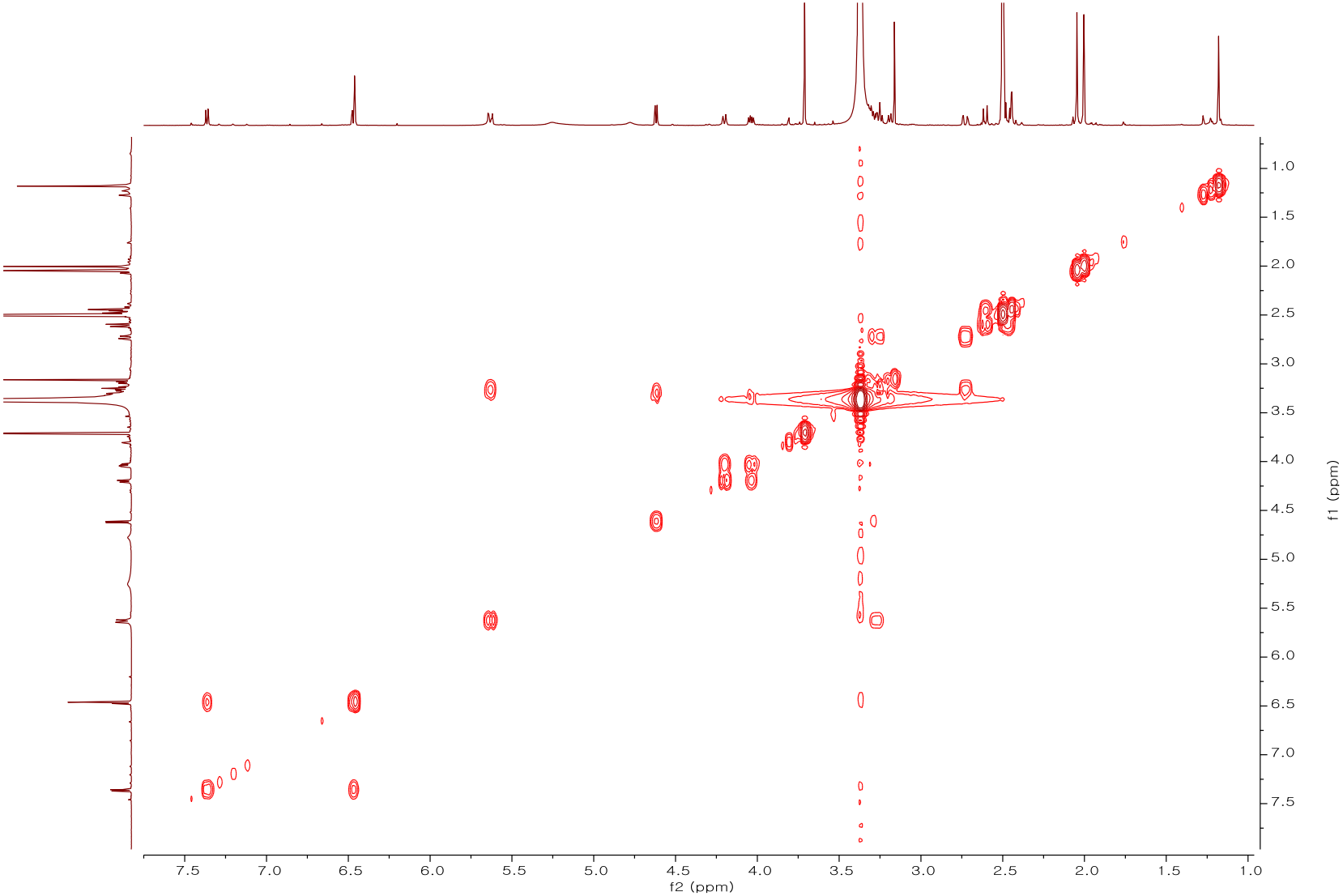


Figure S26. HMBC spectrum of compound **5**

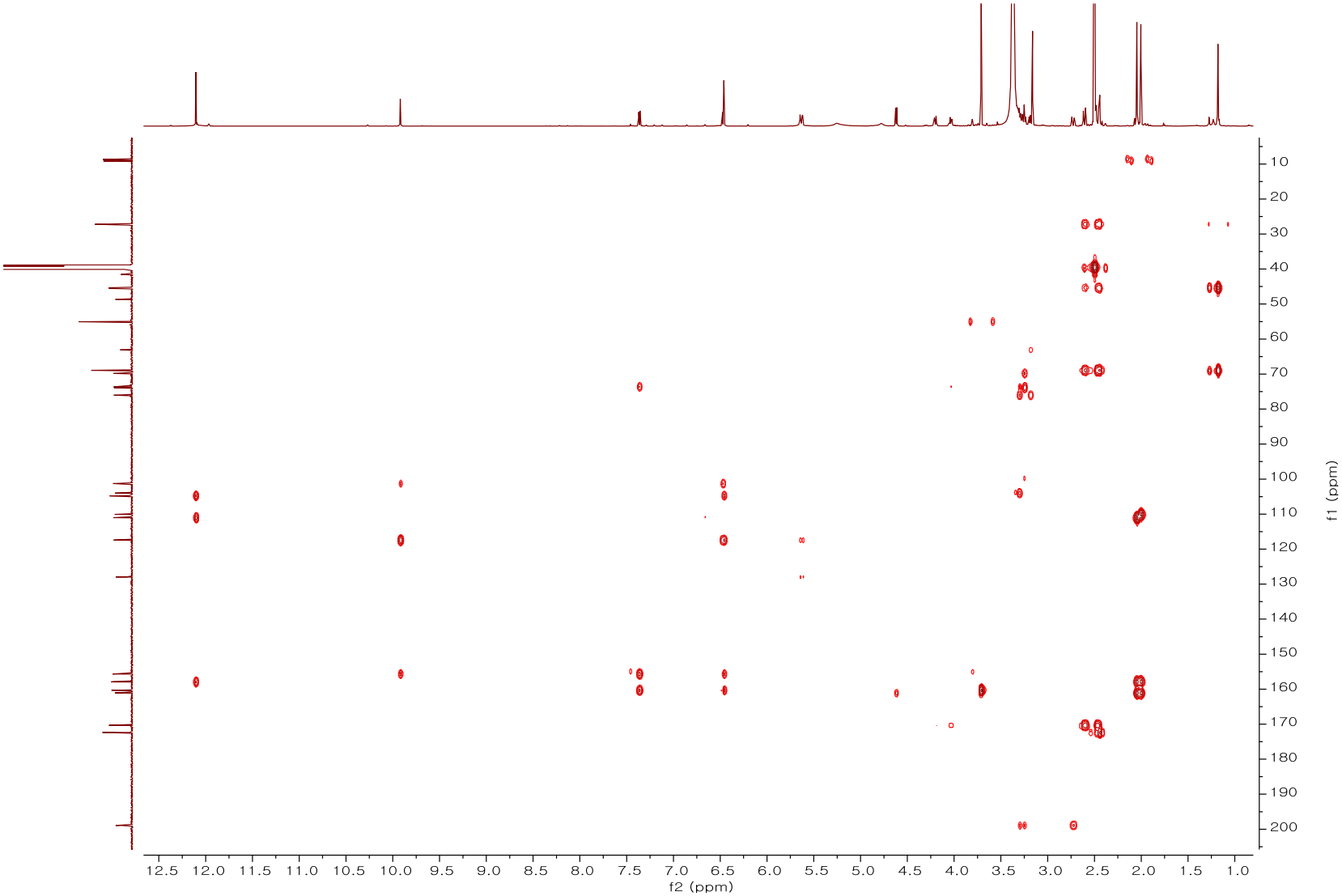


Figure S27. ^{1}H NMR spectrum (600 MHz) of compound **6** in DMSO-d_6

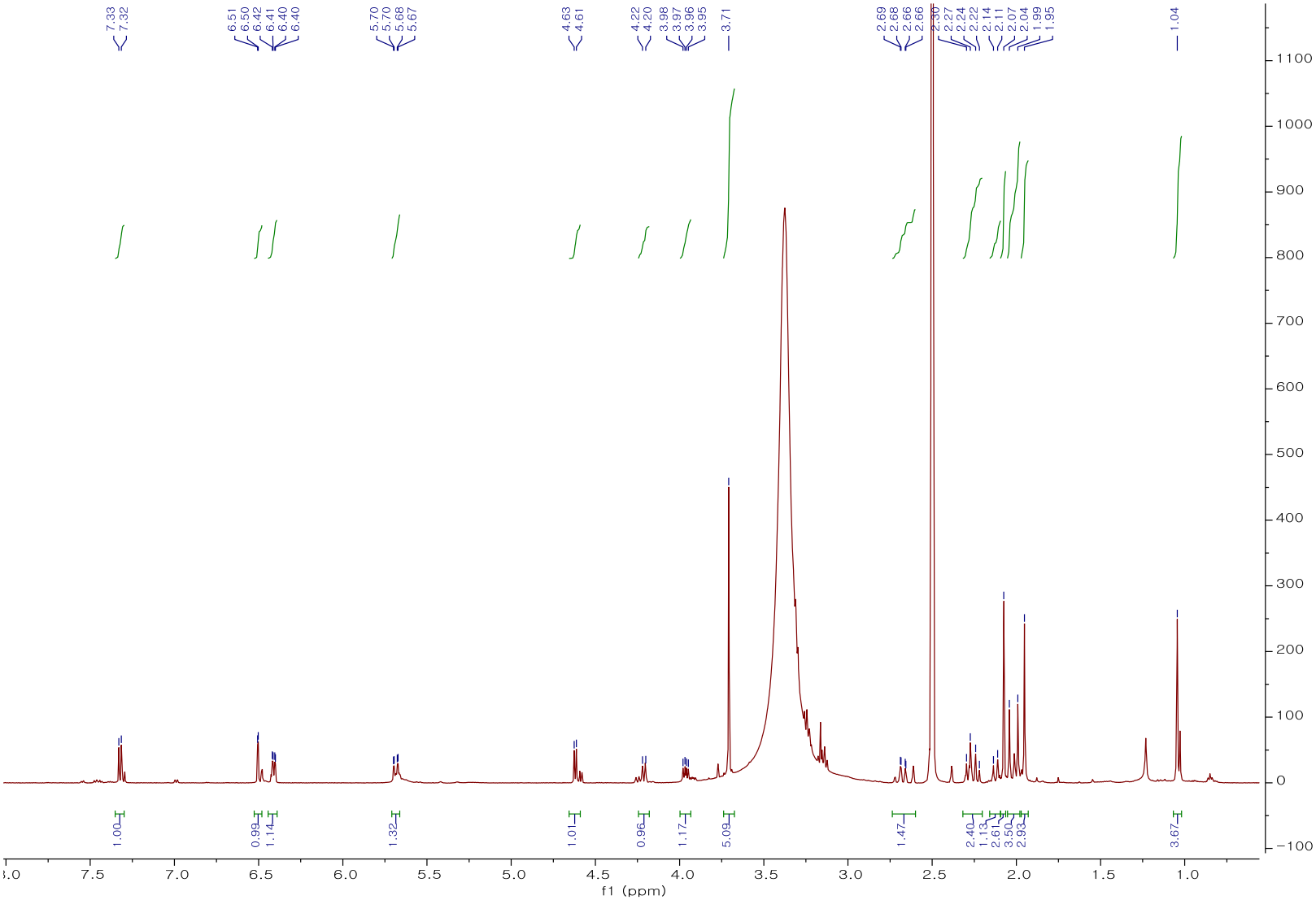


Figure S28. ^{13}C NMR spectrum (150 MHz) of compound **6** in DMSO-d_6

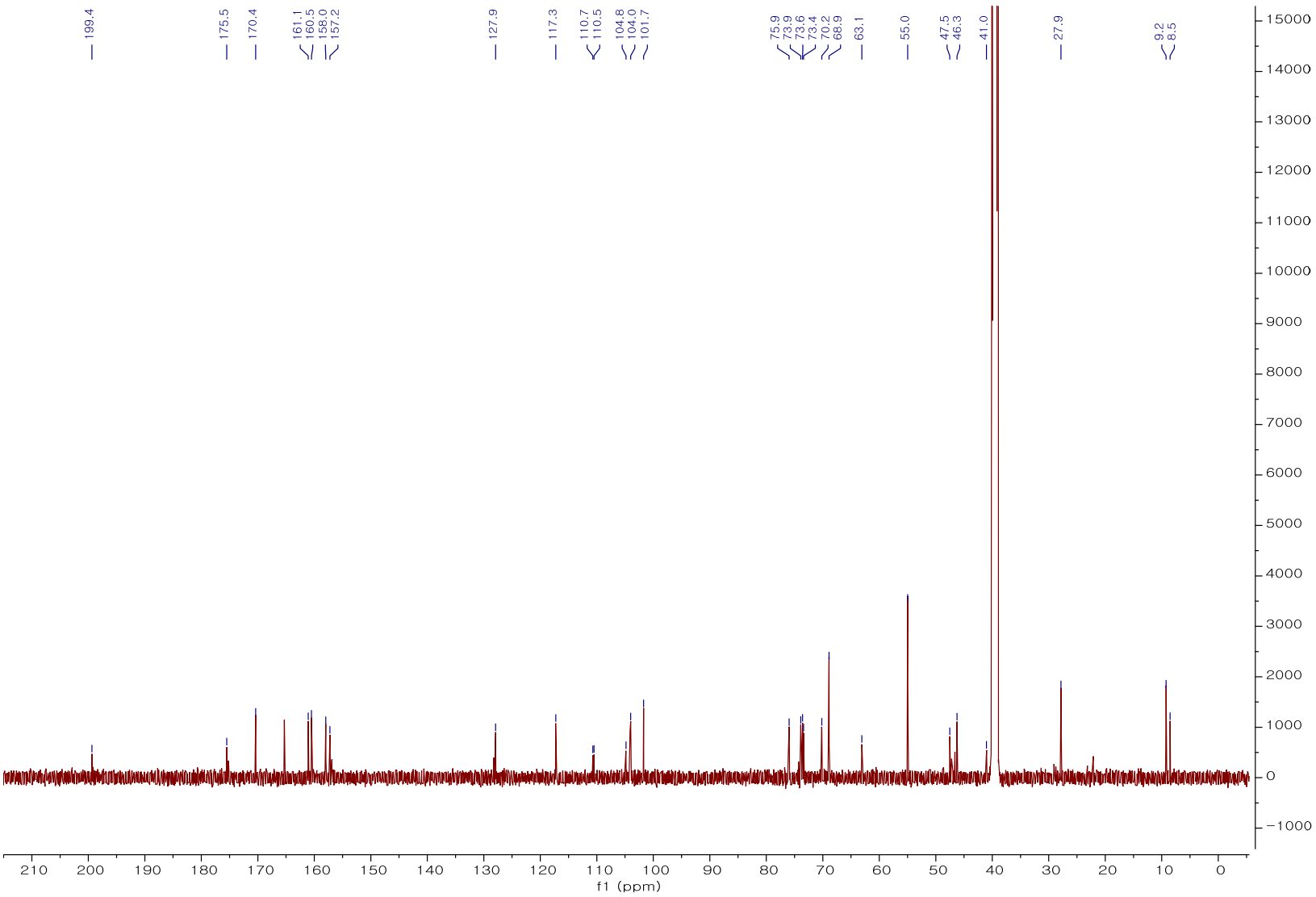


Figure S29. Edited-HSQC spectrum of compound **6**

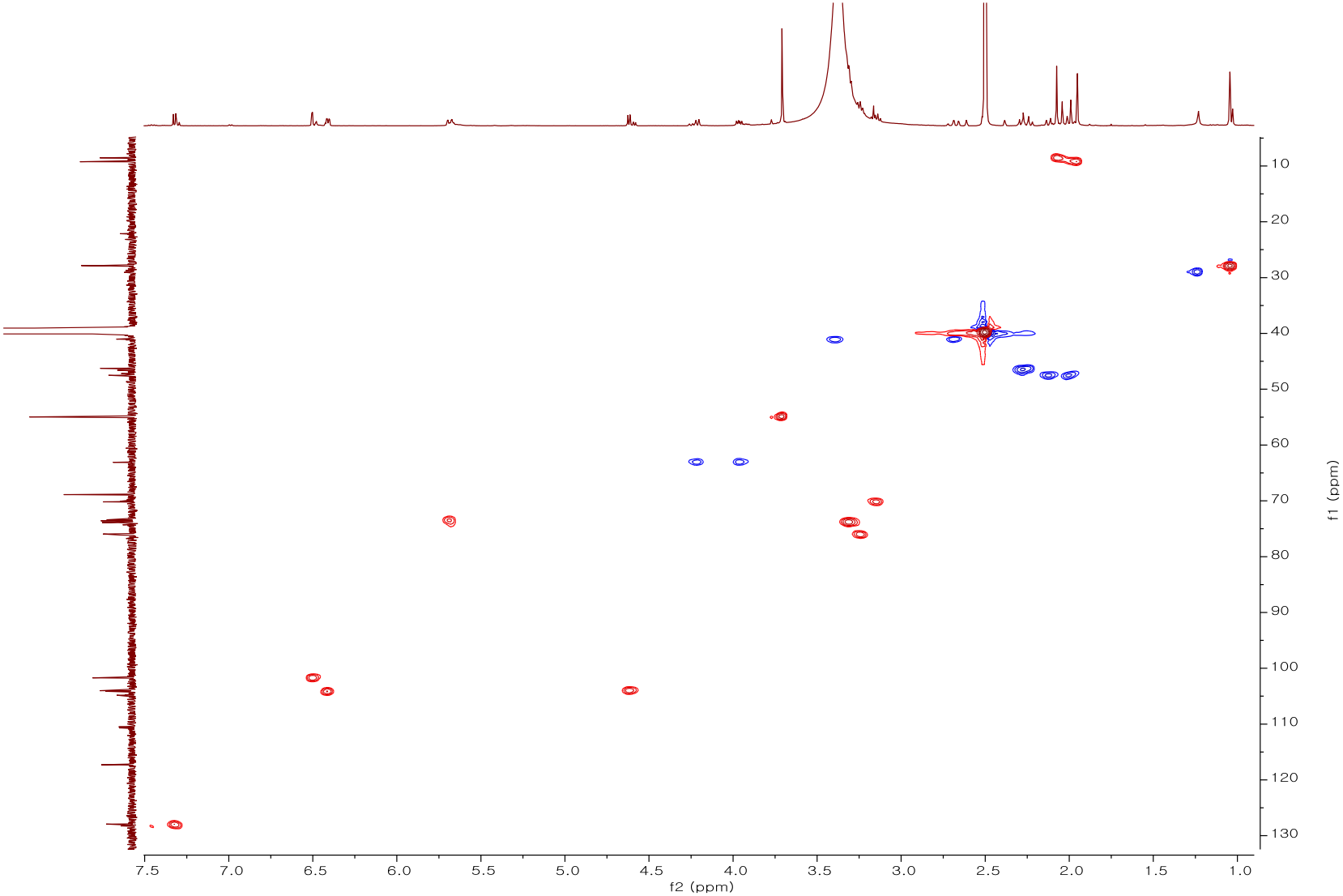


Figure S30. COSY spectrum of compound **6**

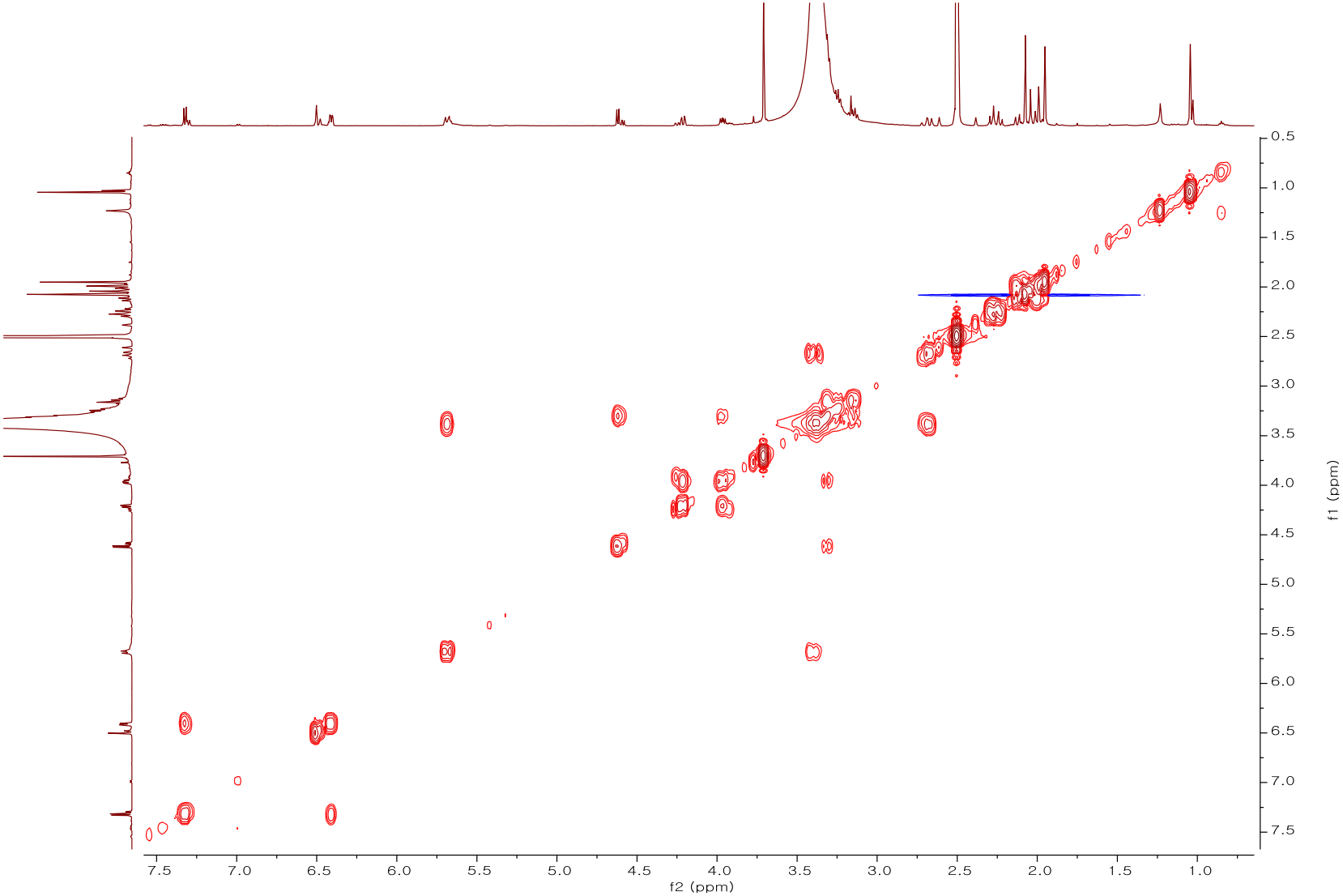


Figure S31. HMBC spectrum of compound **6**

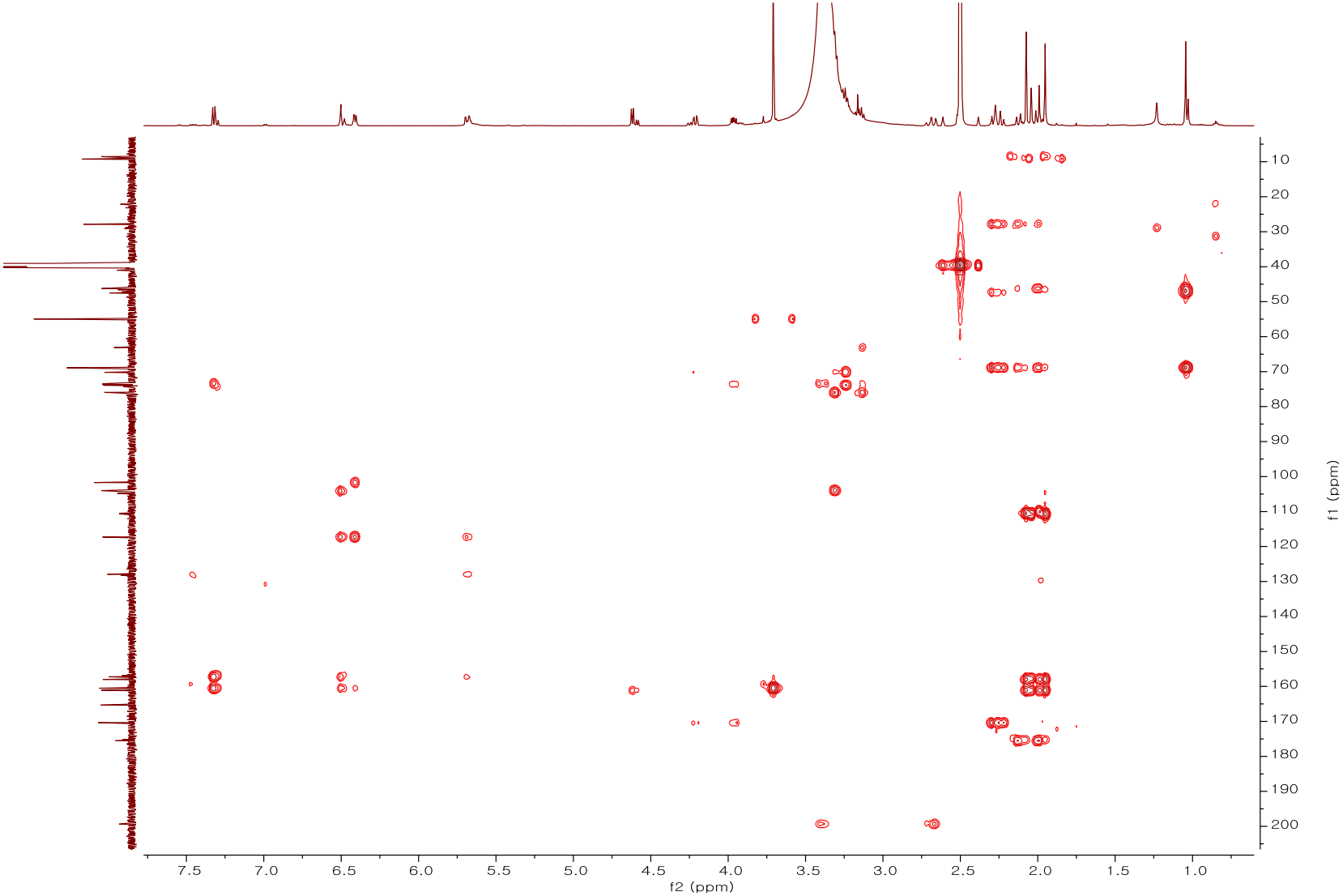


Figure S32. ^{1}H NMR spectrum (600 MHz) of compound **7** in DMSO-d_6

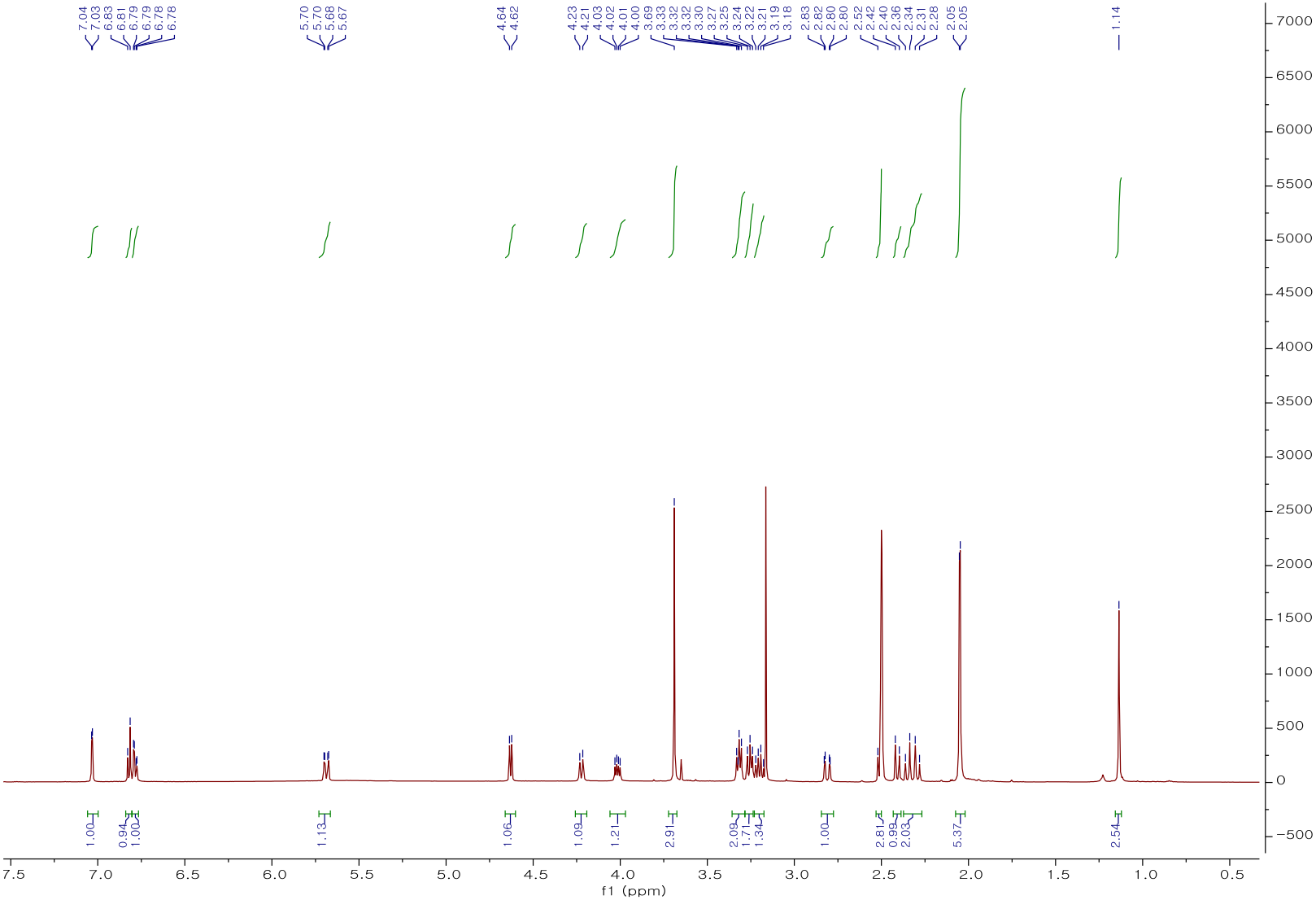


Figure S33. ^{13}C NMR spectrum (600 MHz) of compound **7** in DMSO-d_6

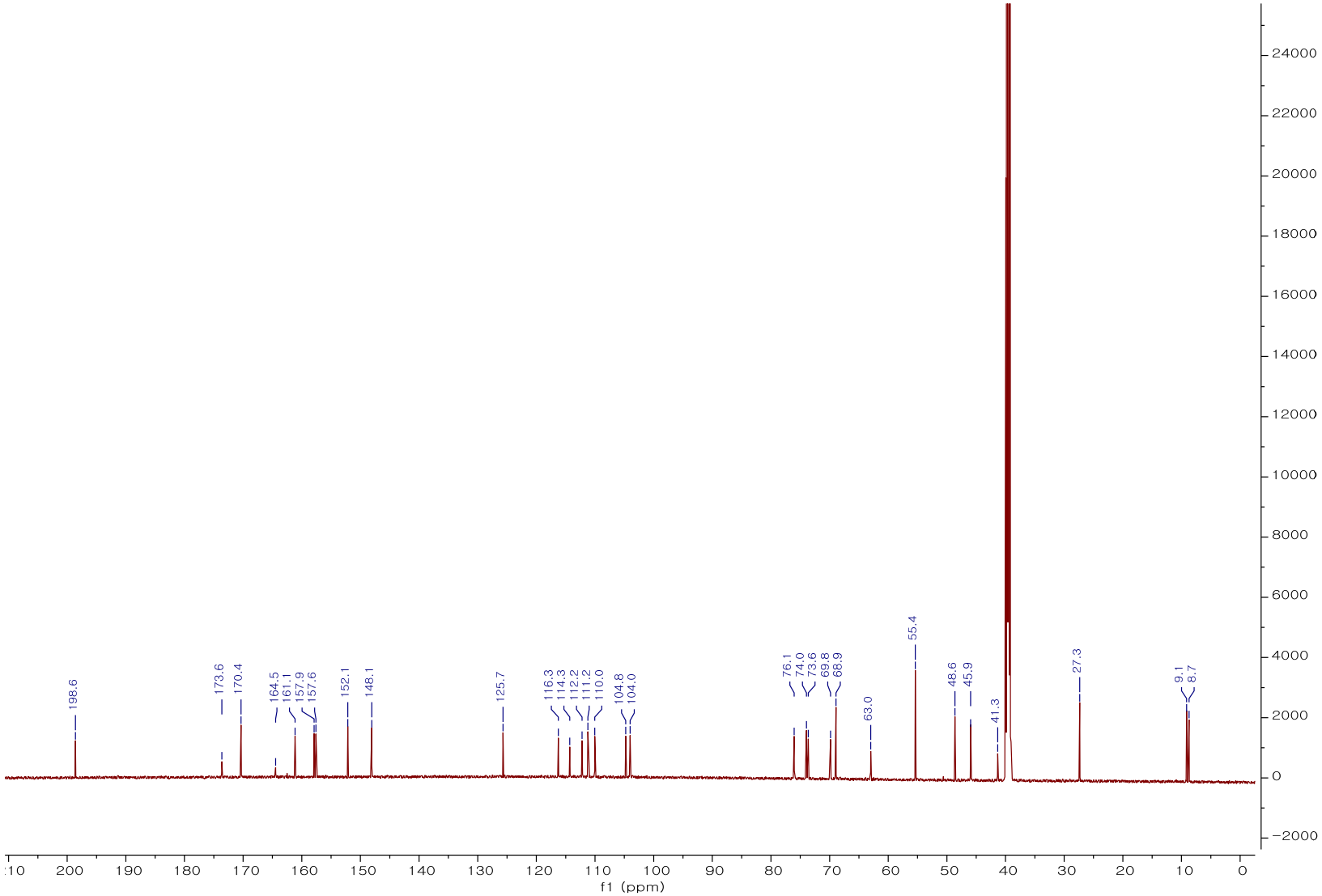


Figure S34. Edited-HSQC spectrum of compound **7**

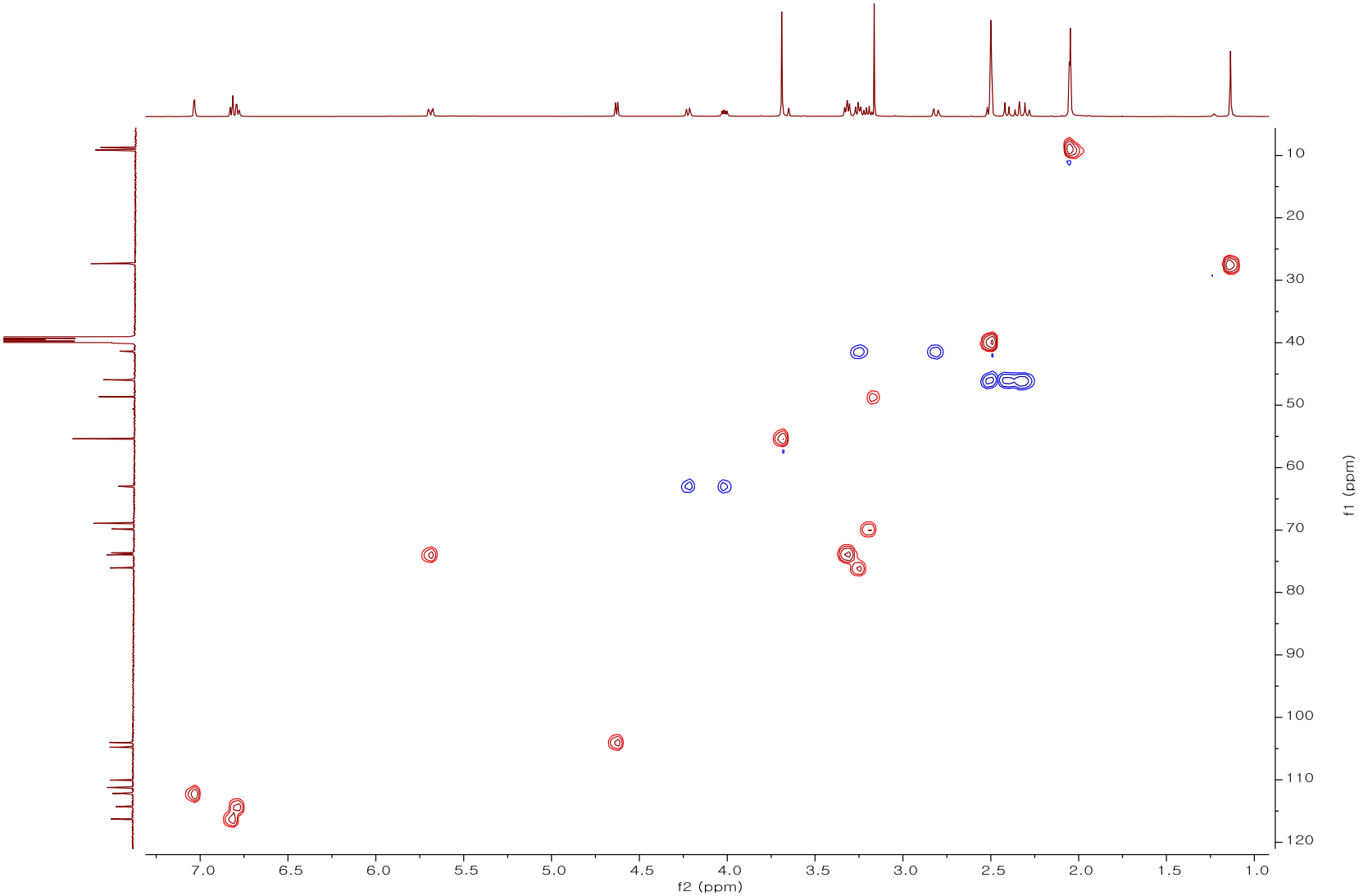


Figure S35. COSY spectrum of compound **7**

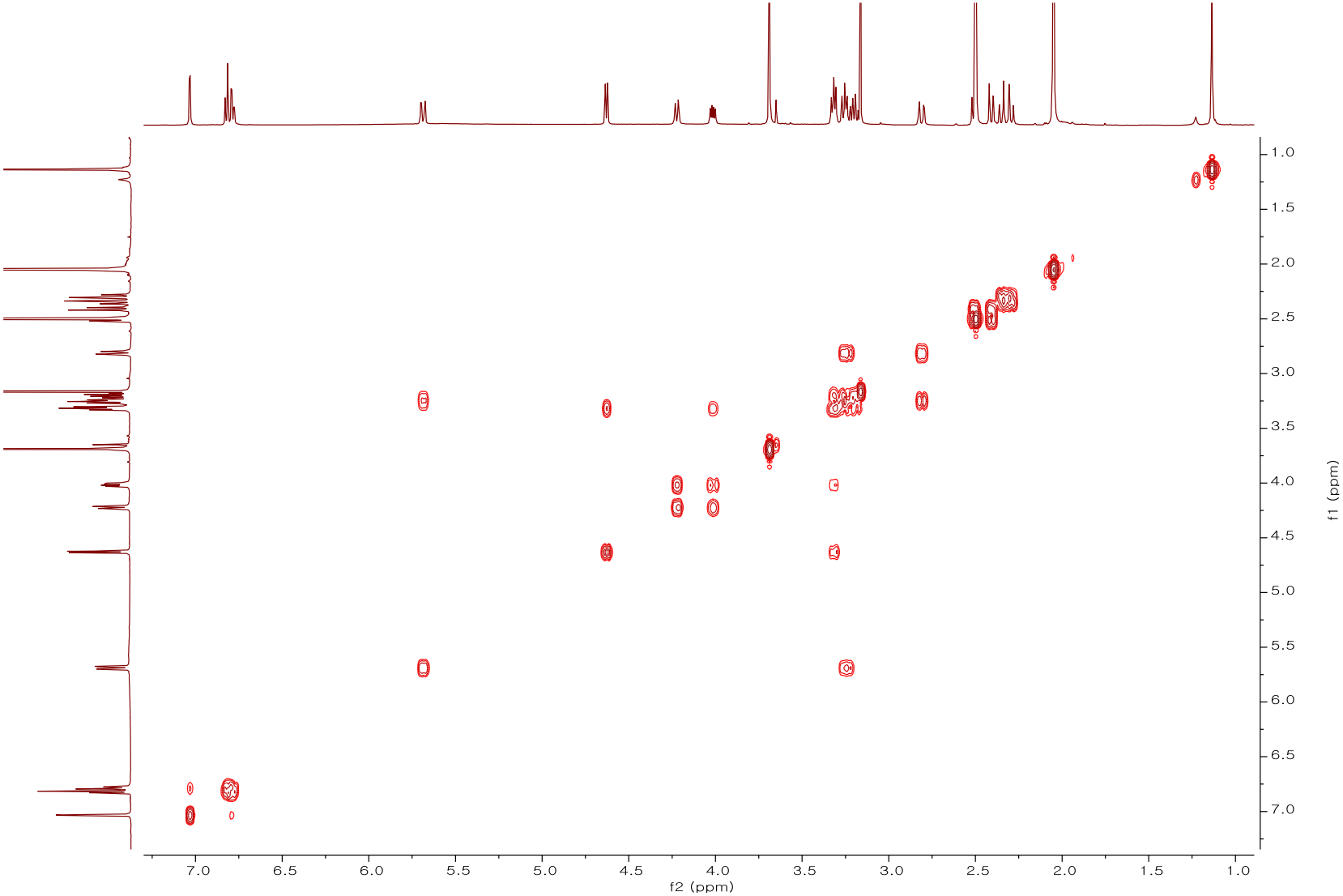


Figure S36. HMBC spectrum of compound **7**

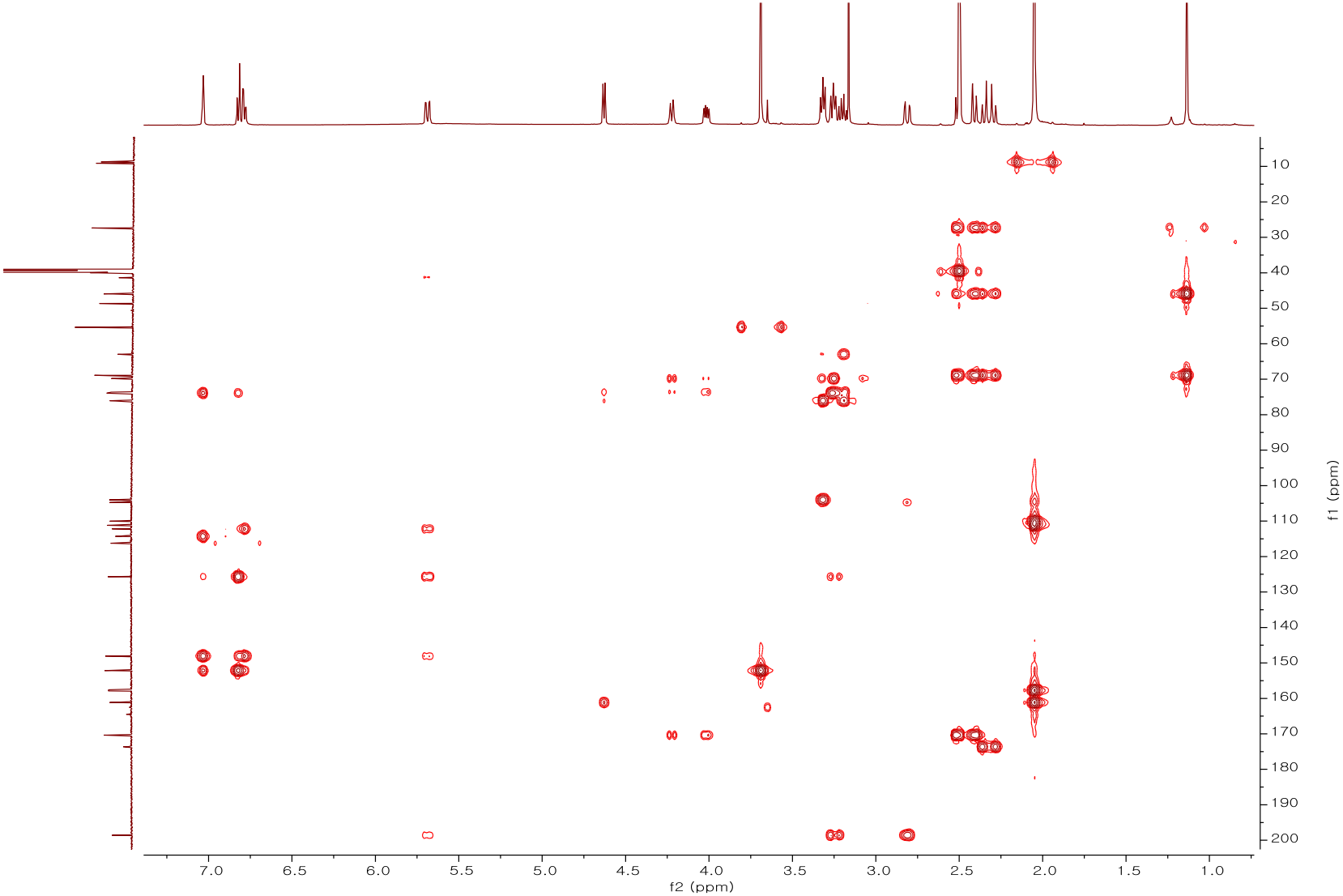


Figure S37. ^{1}H NMR spectrum (600 MHz) of compound **8** in DMSO-d_6

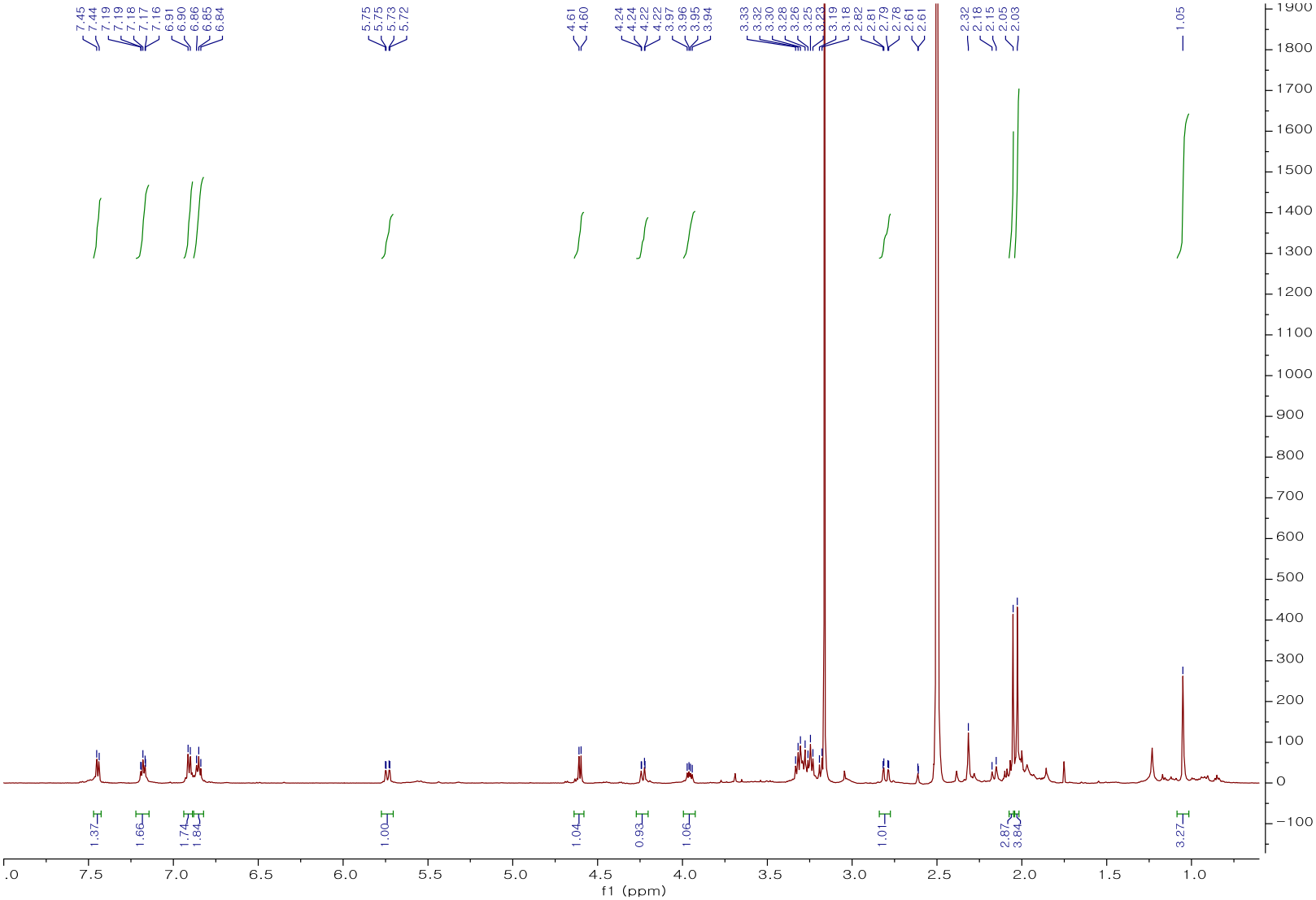


Figure S38. ^{13}C NMR spectrum (150 MHz) of compound **8** in DMSO-d_6

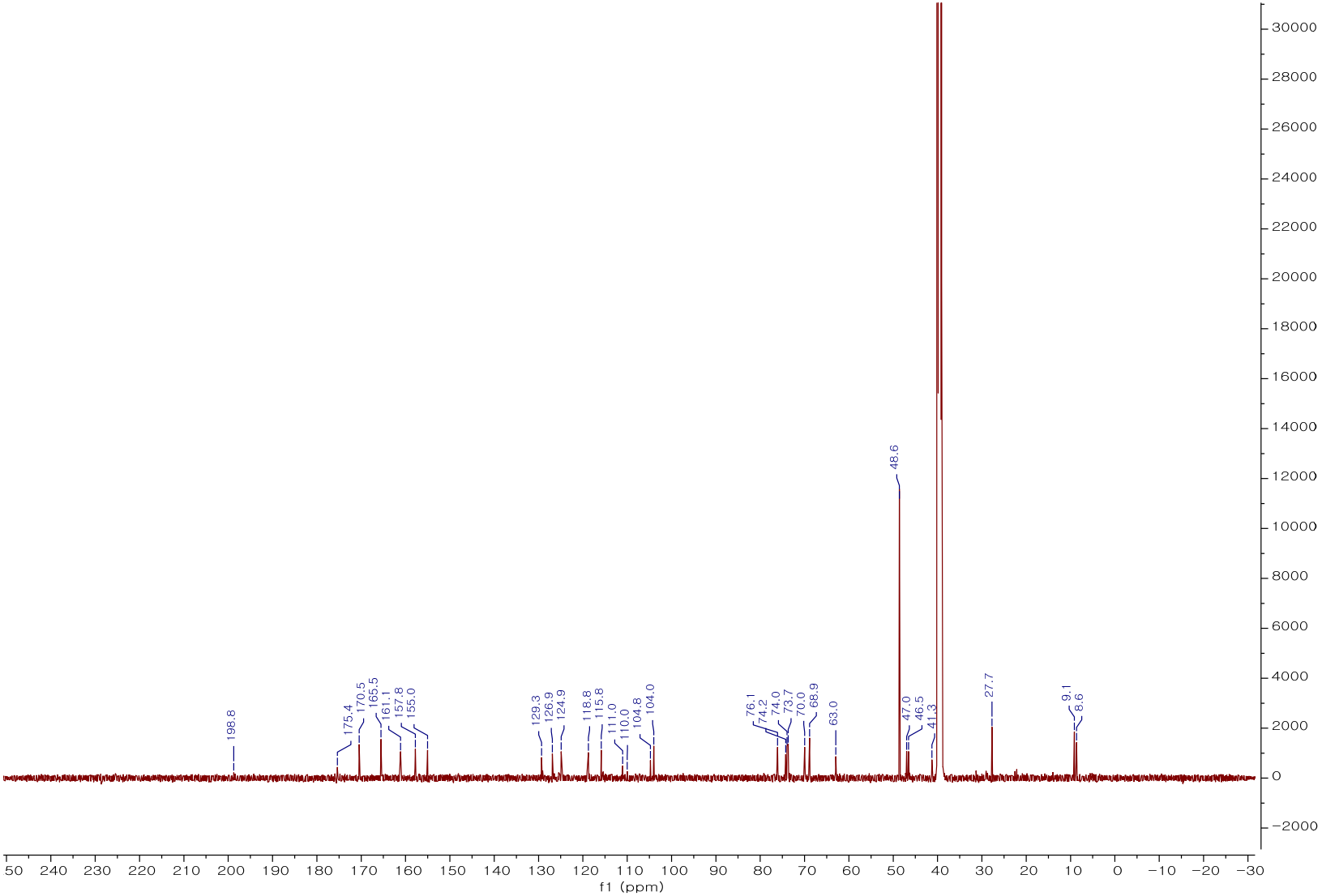


Figure S39. Edited-HSQC spectrum of compound **8**

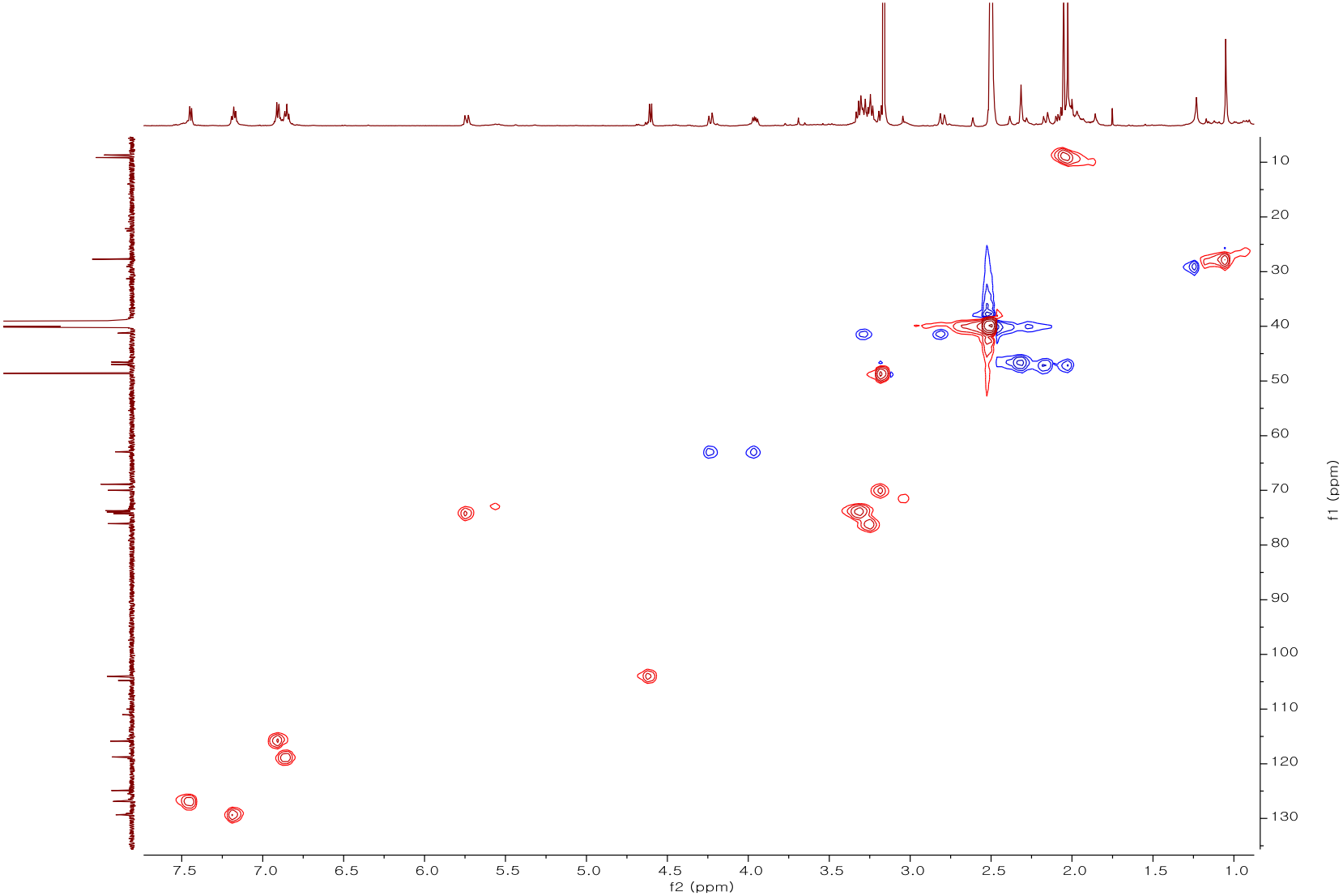


Figure S40. COSY spectrum of compound **8**

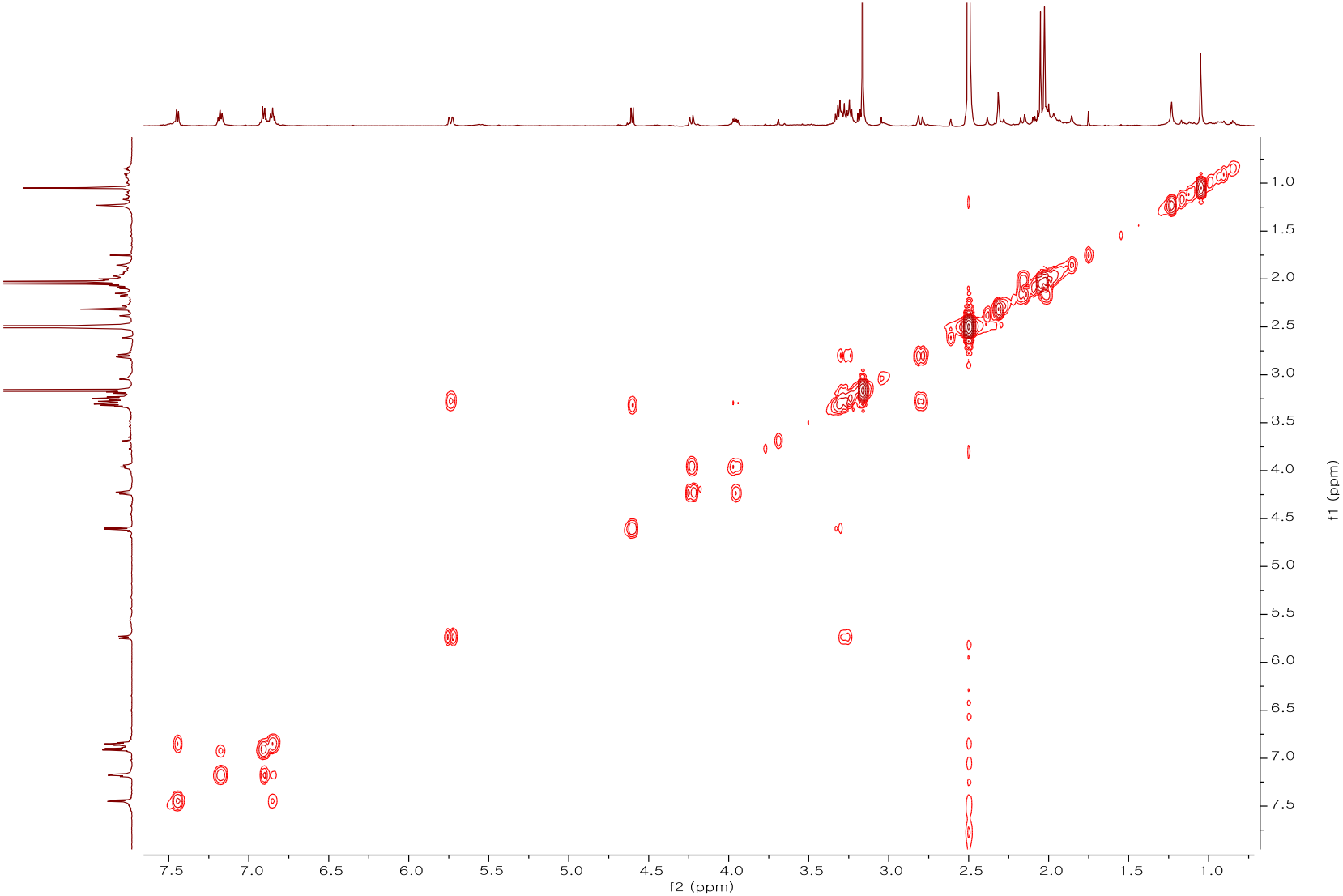


Figure S41. HMBC spectrum of compound **8**

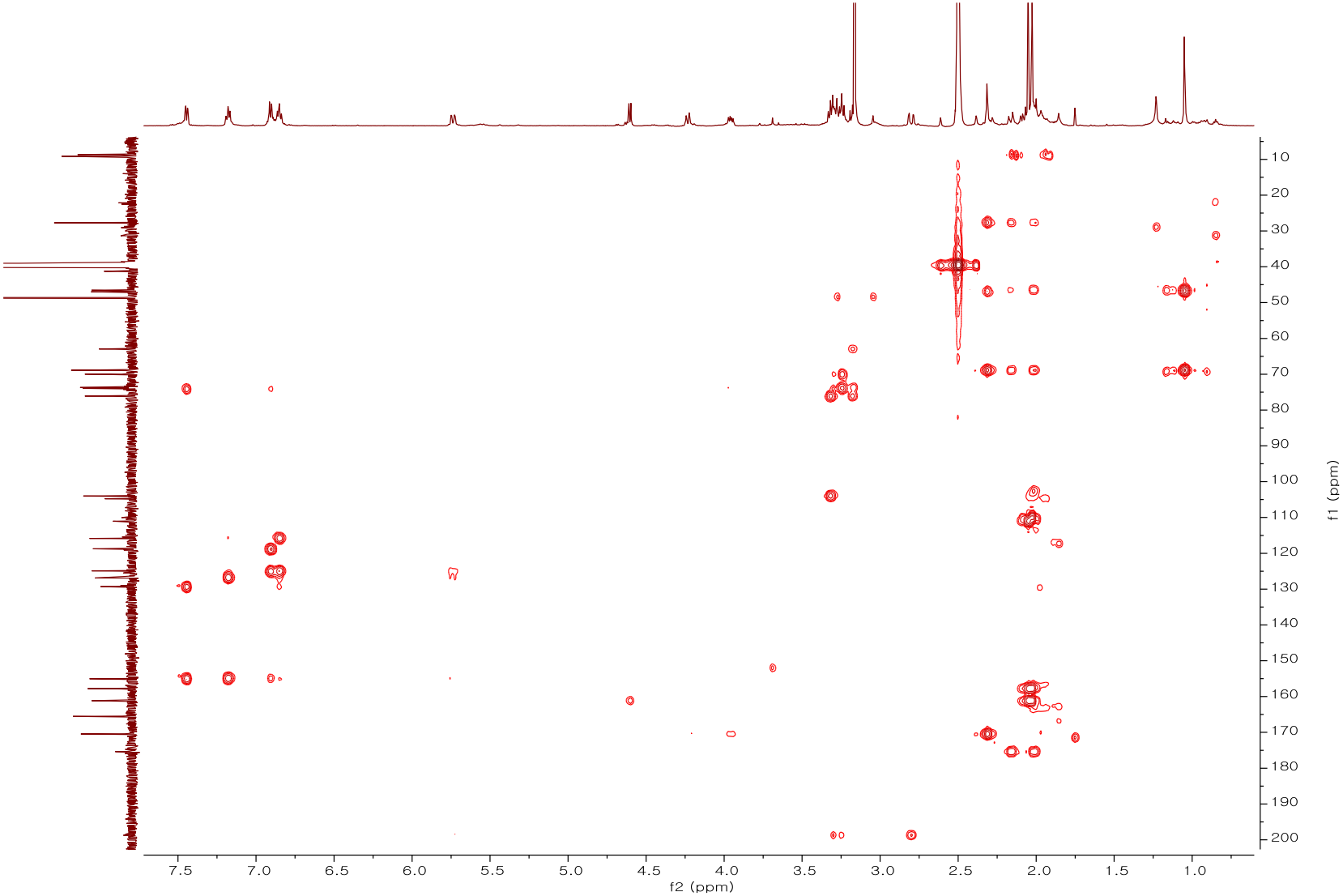


Figure S42. ^{1}H NMR spectrum (850 MHz) of compound **9** in DMSO-d_6

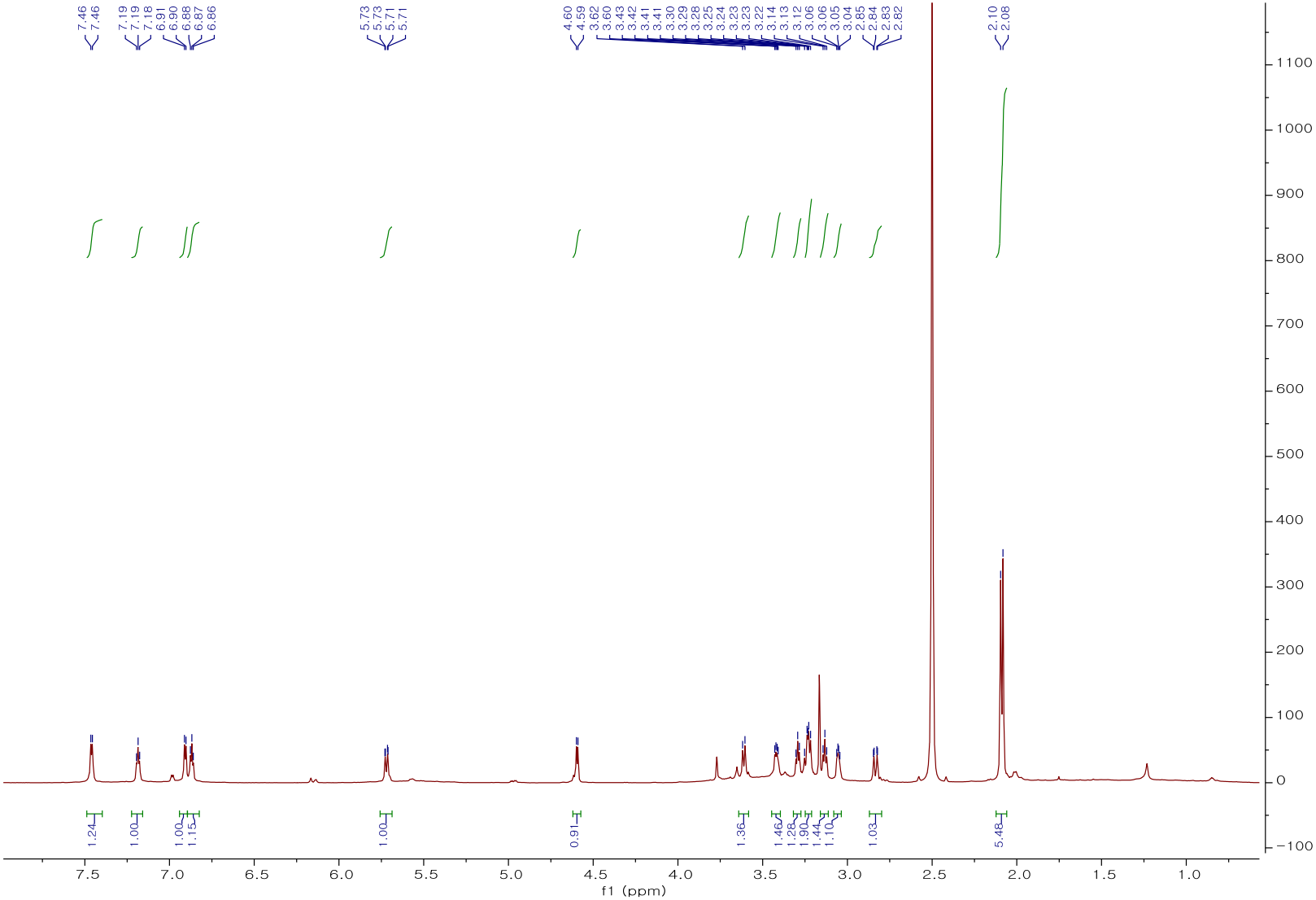


Figure S43. ^{13}C NMR spectrum (213 MHz) of compound **9** in DMSO-d_6

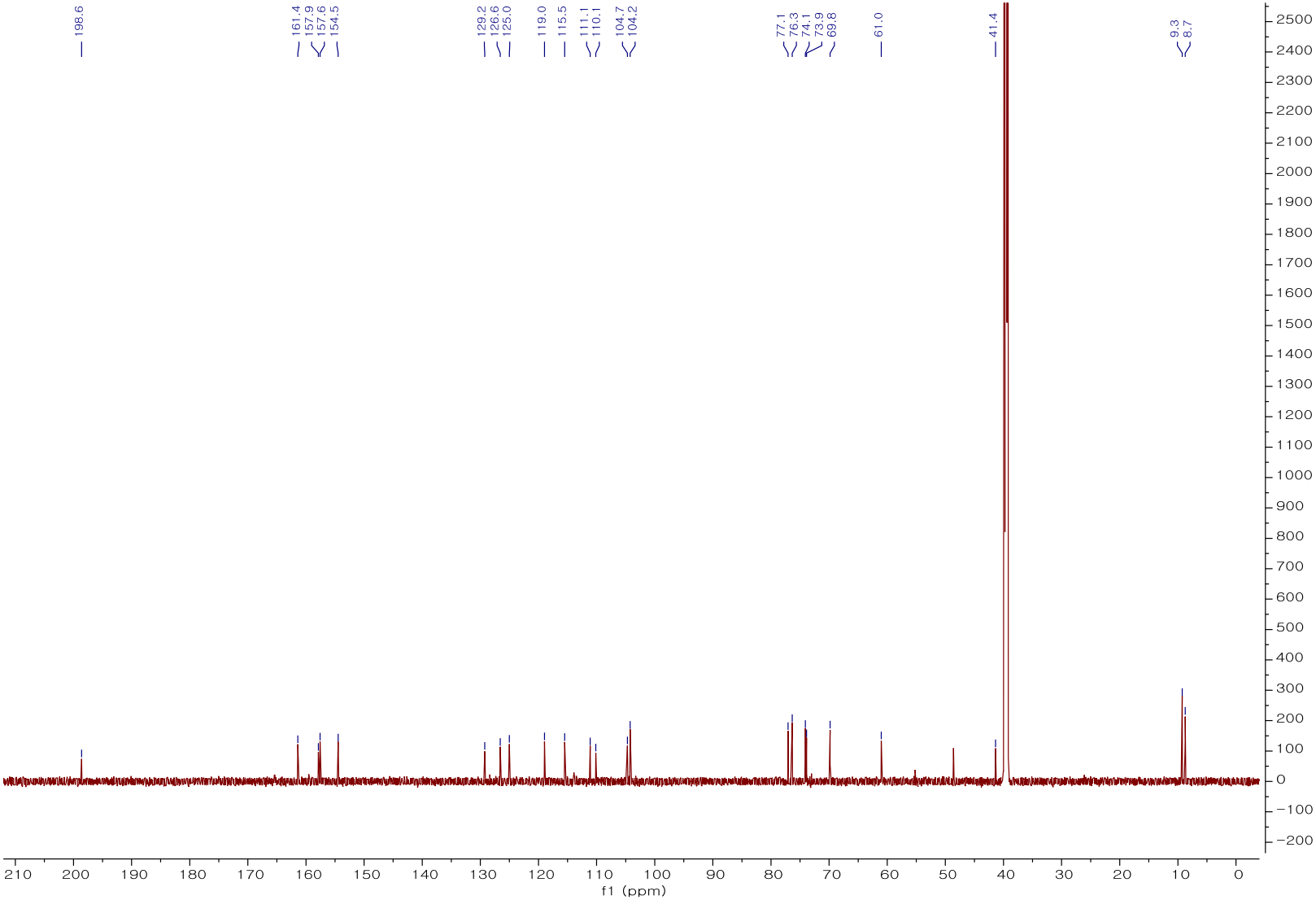


Figure S44. Edited-HSQC spectrum of compound **9**

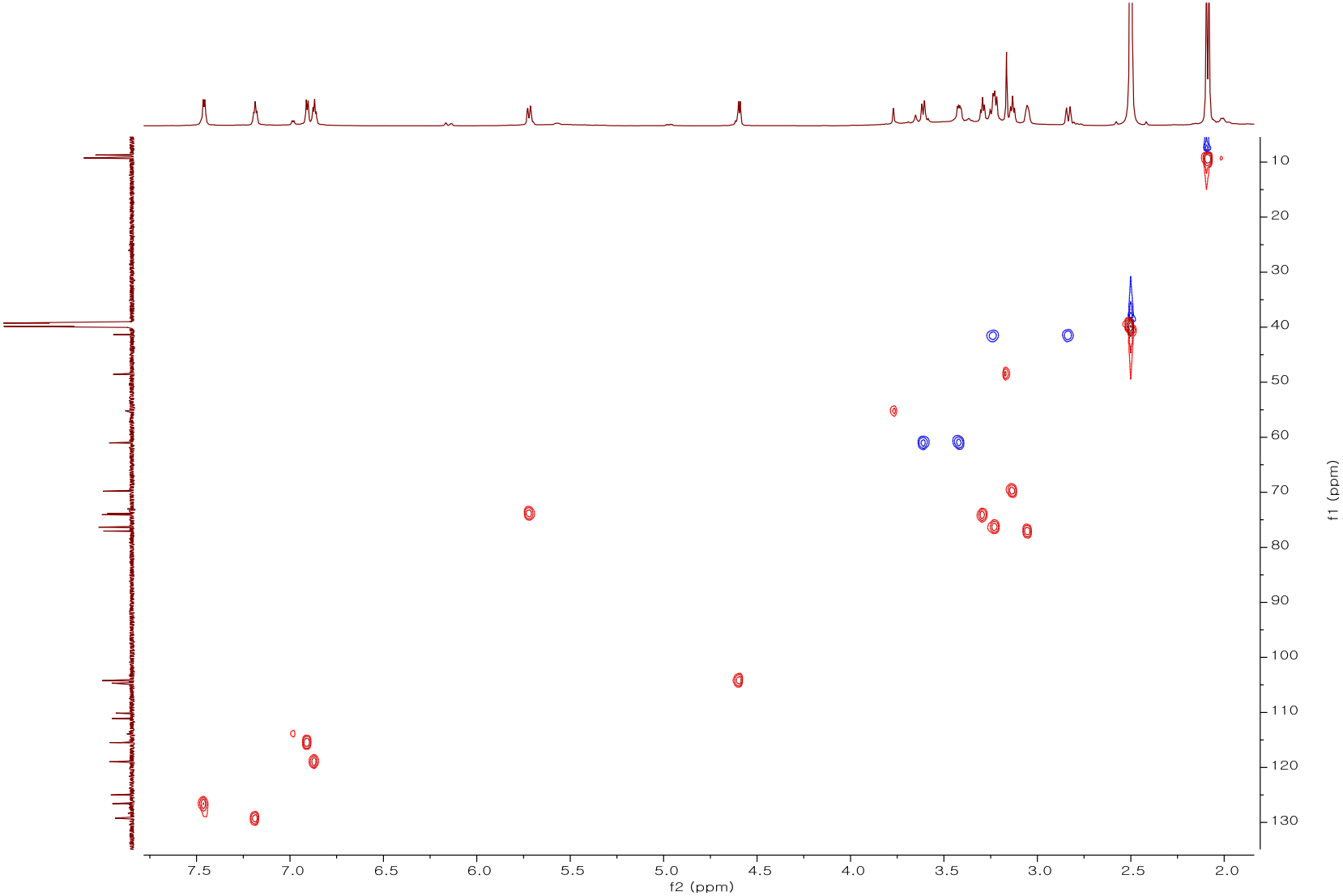


Figure S45. COSY spectrum of compound **9**

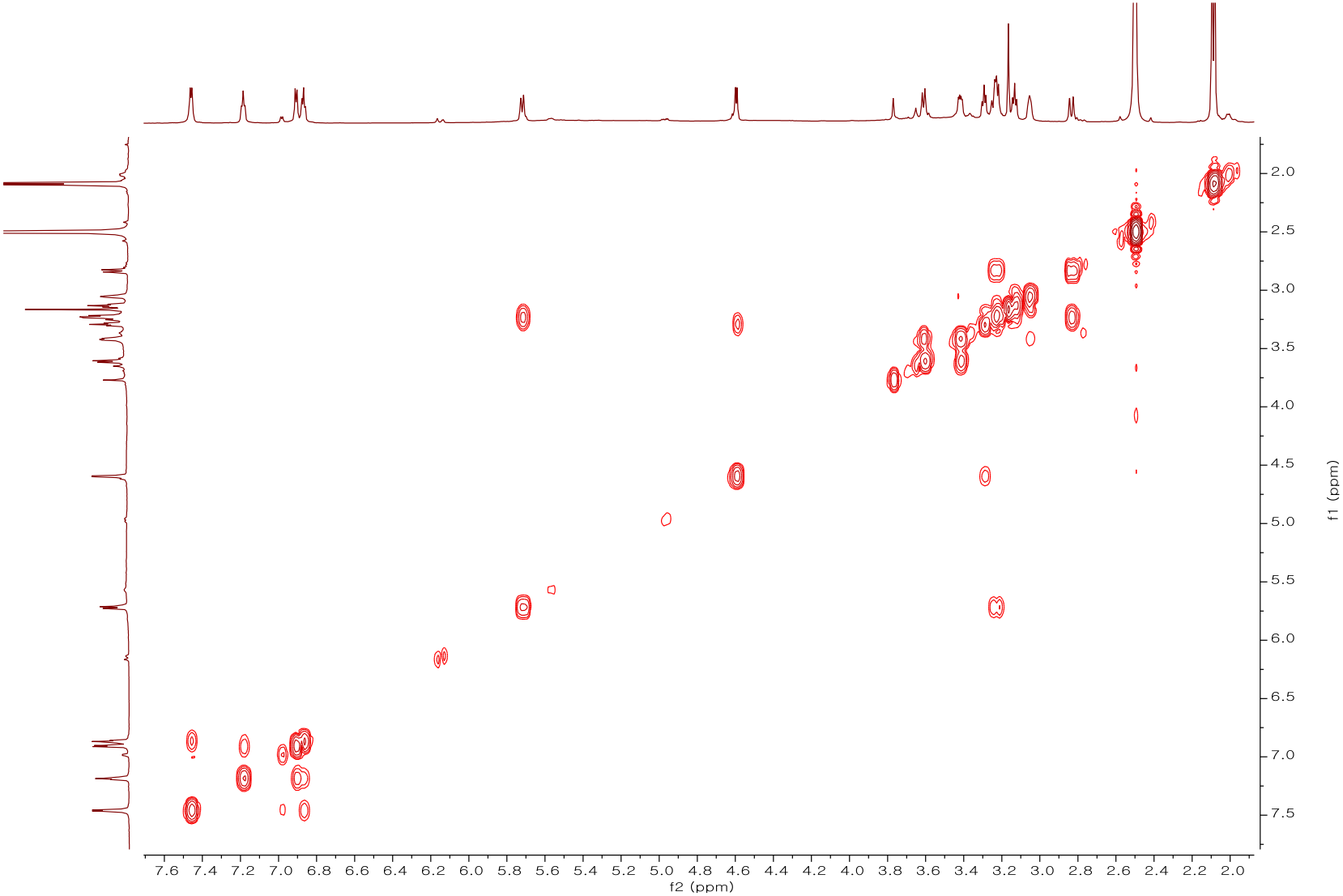


Figure S46. HMBC spectrum of compound **9**

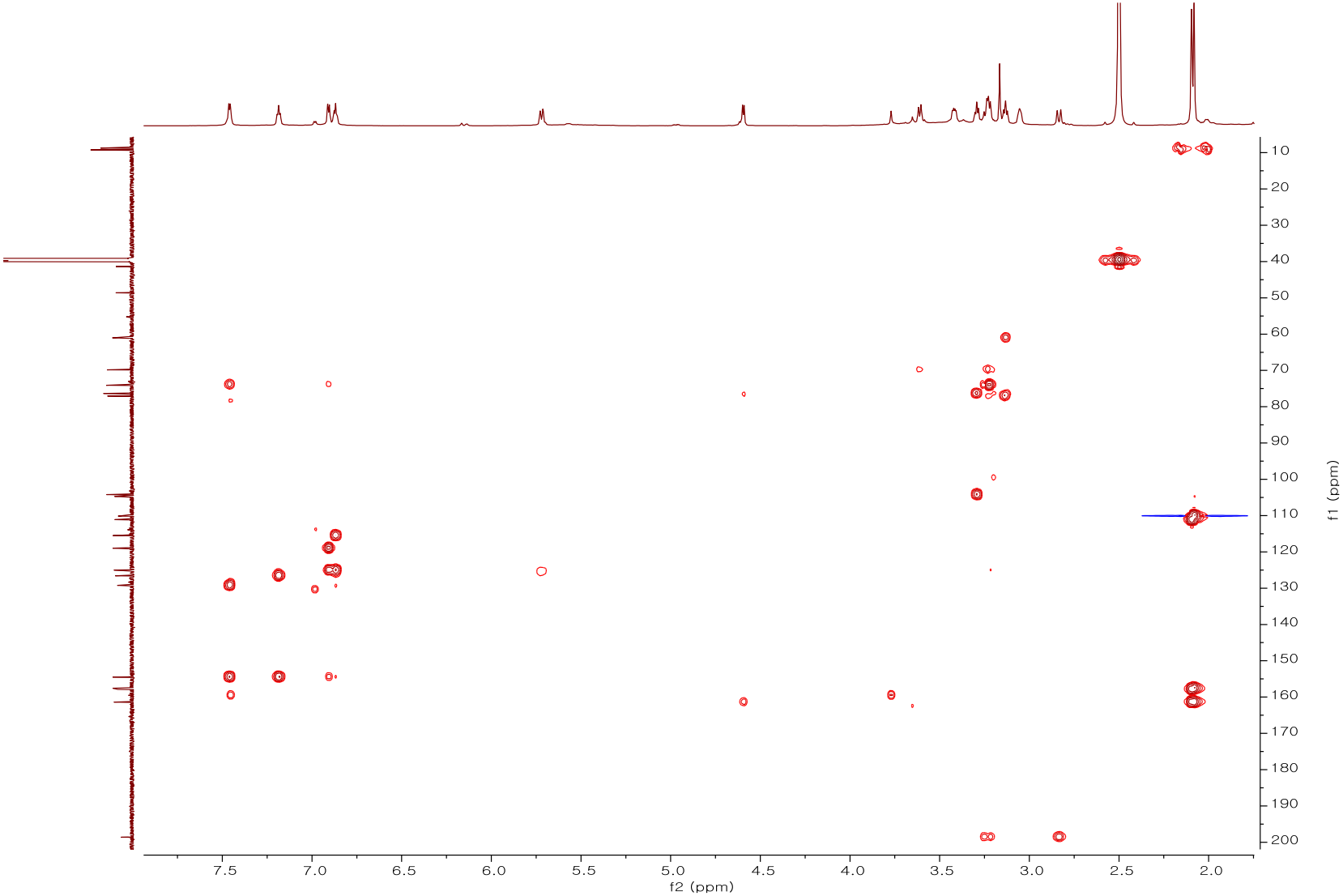


Figure S47. ^{1}H NMR spectrum (500 MHz) of compound **10** in DMSO-d_6

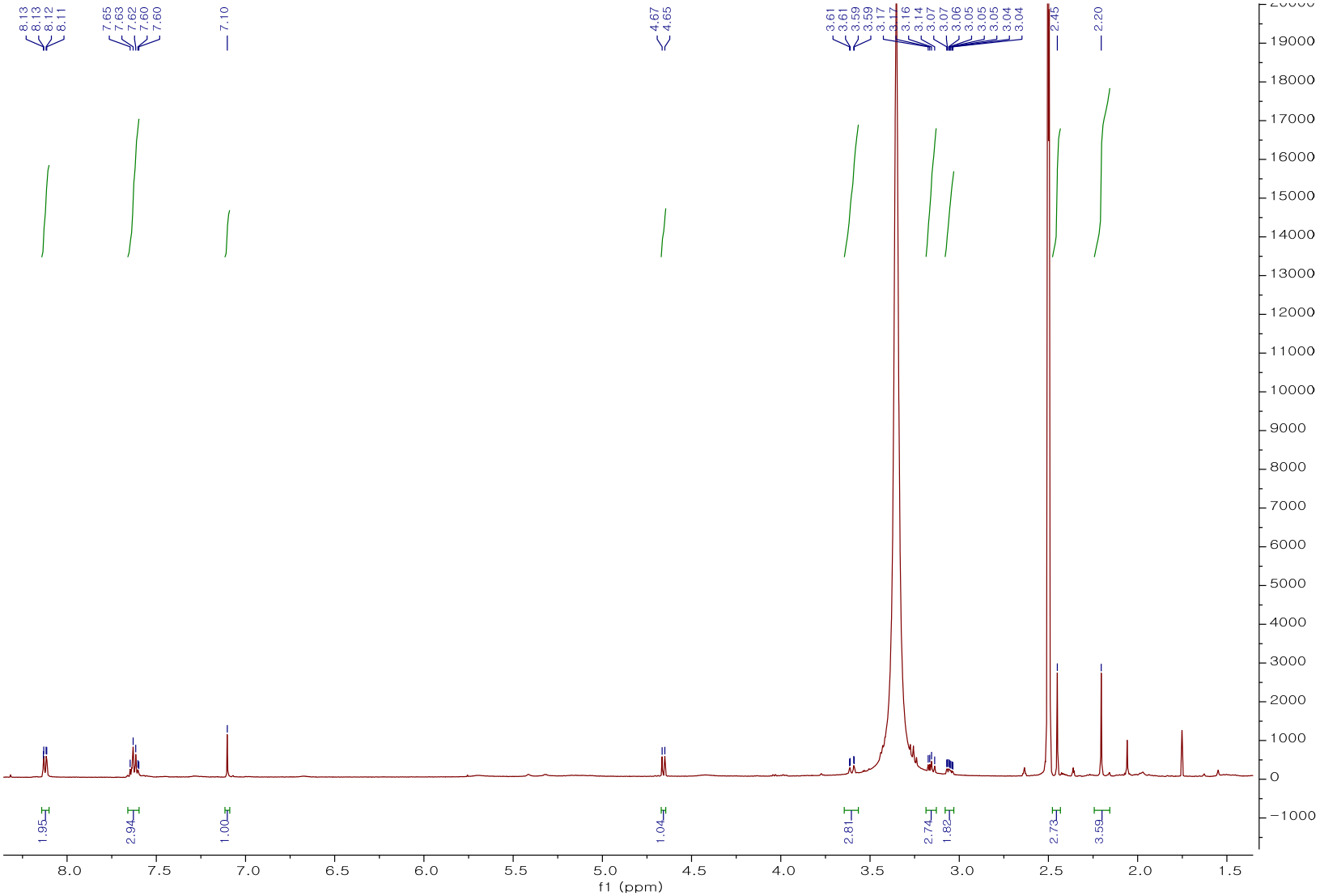


Figure S48. ^{13}C NMR spectrum (125 MHz) of compound **10** in DMSO-d_6

Figure S49. HSQC spectrum of compound **10**

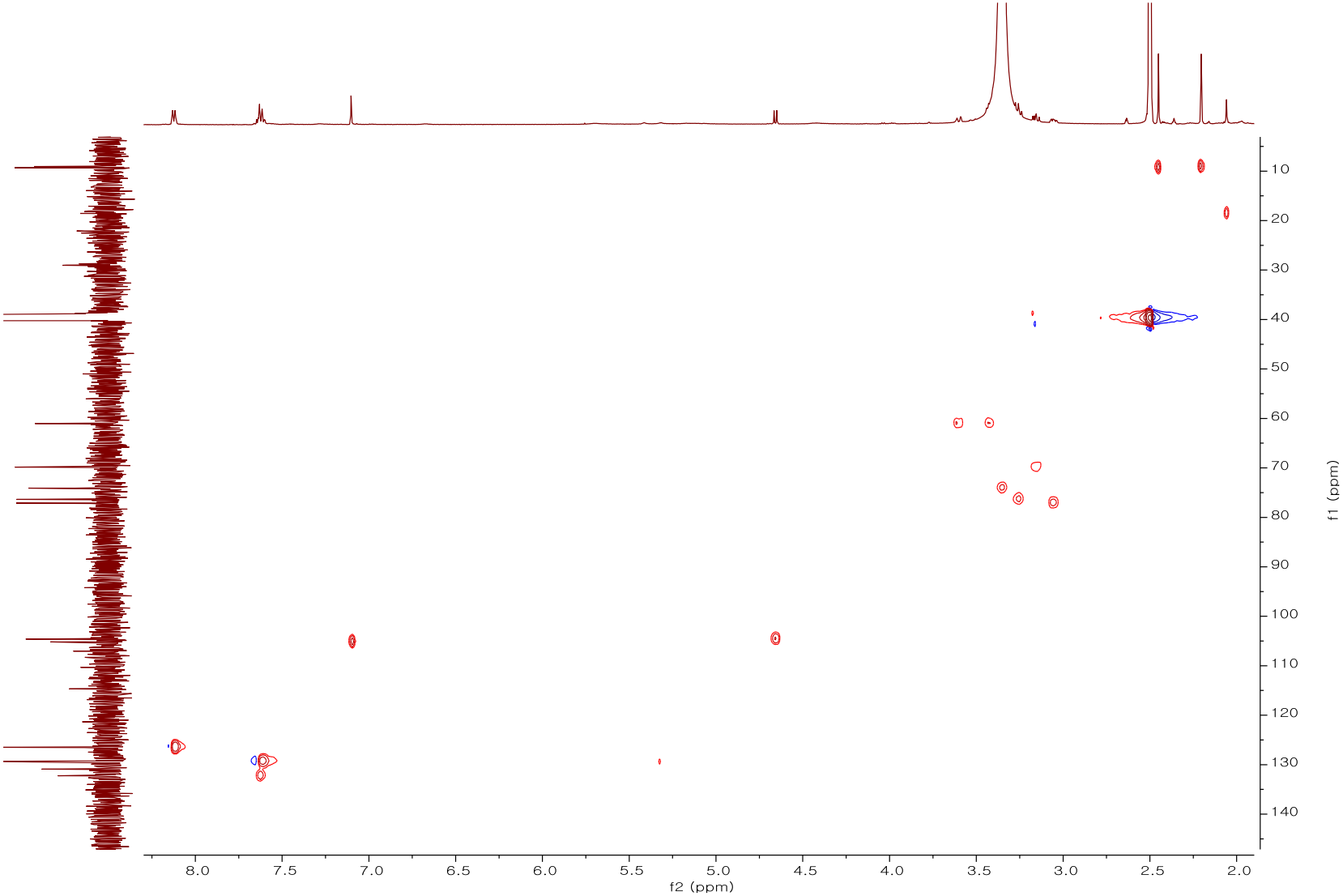


Figure S50. COSY spectrum of compound **10**

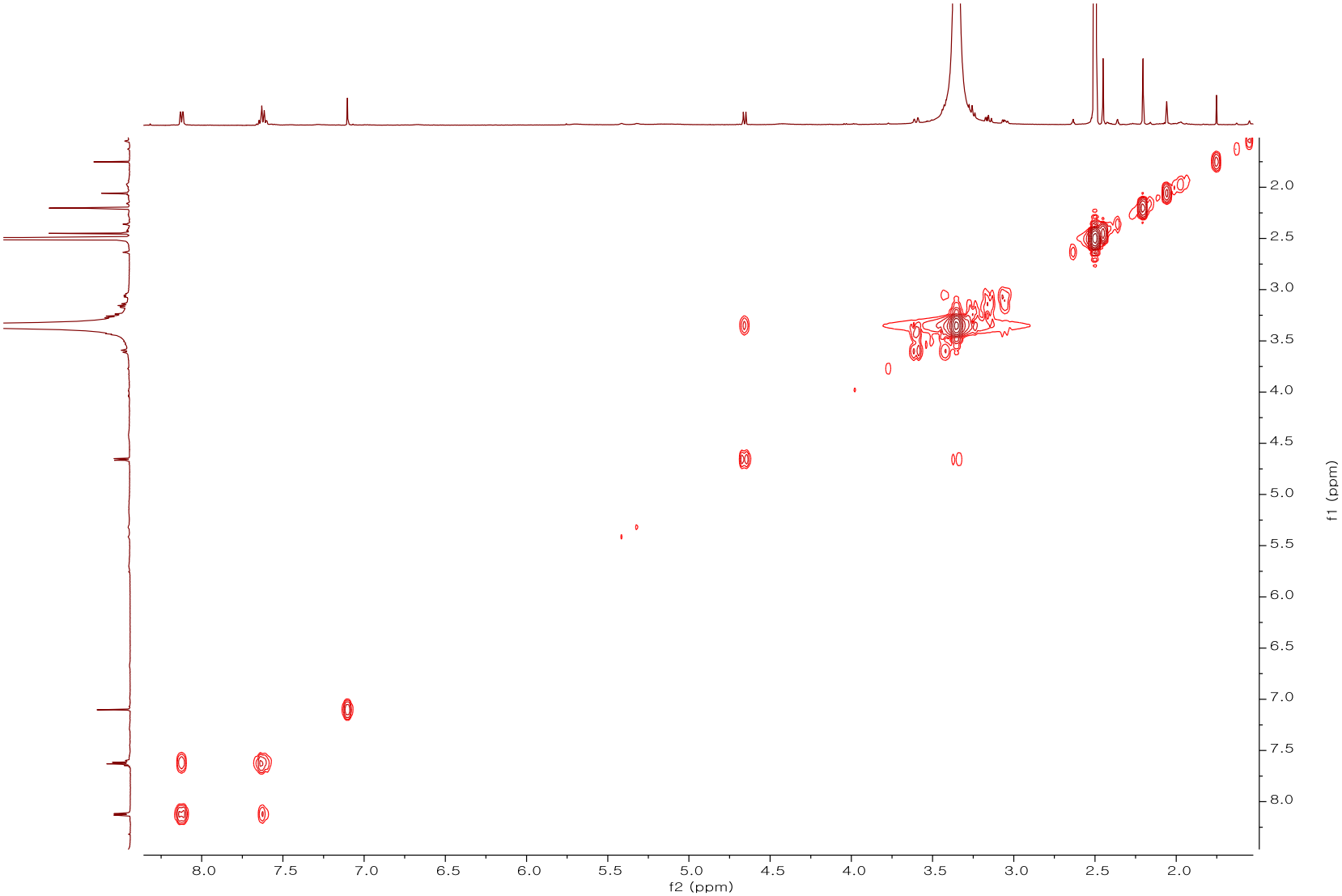


Figure S51. HMBC spectrum of compound **10**

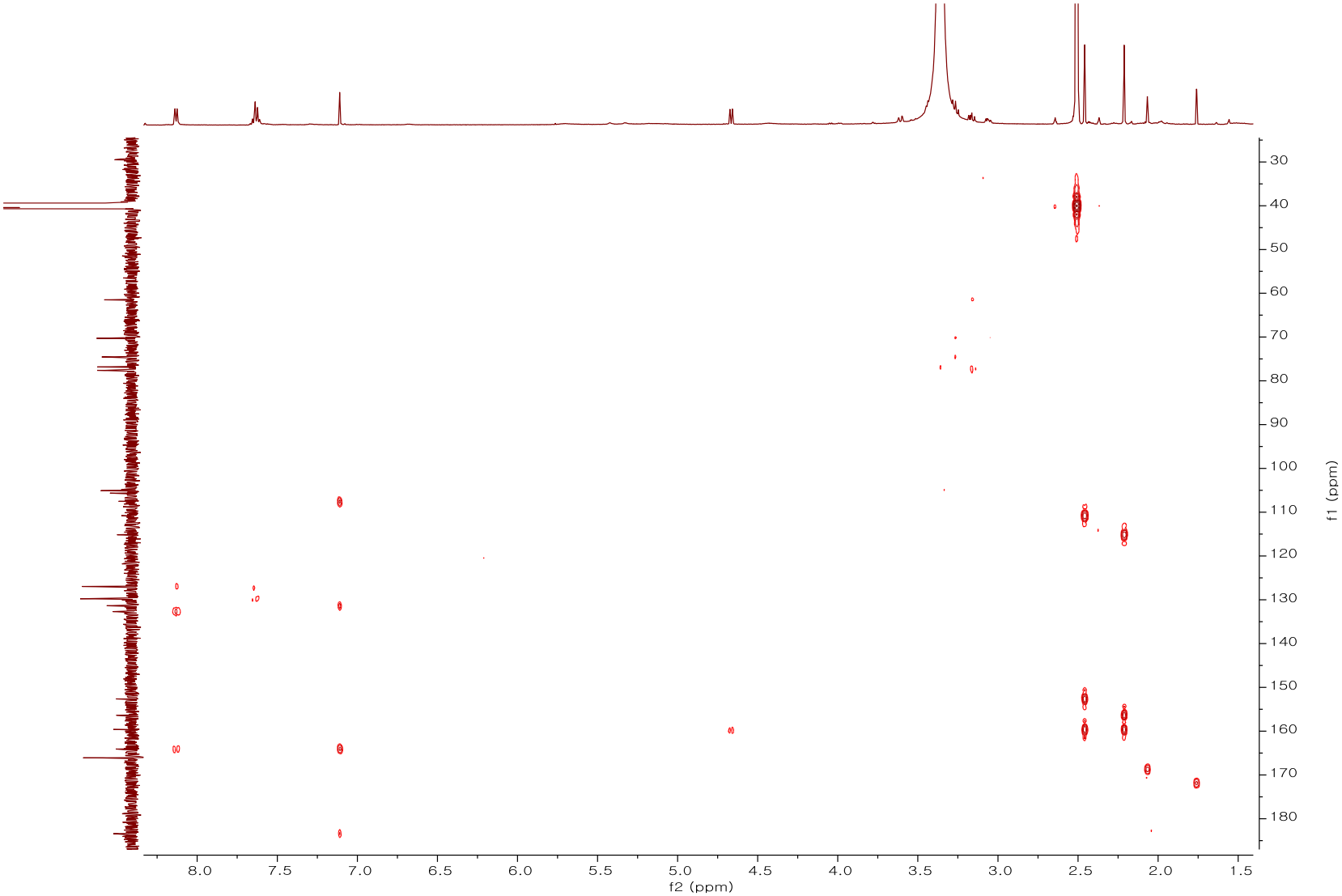


Figure S52. ^{1}H NMR spectrum (600 MHz) of compound **11** in DMSO-d_6

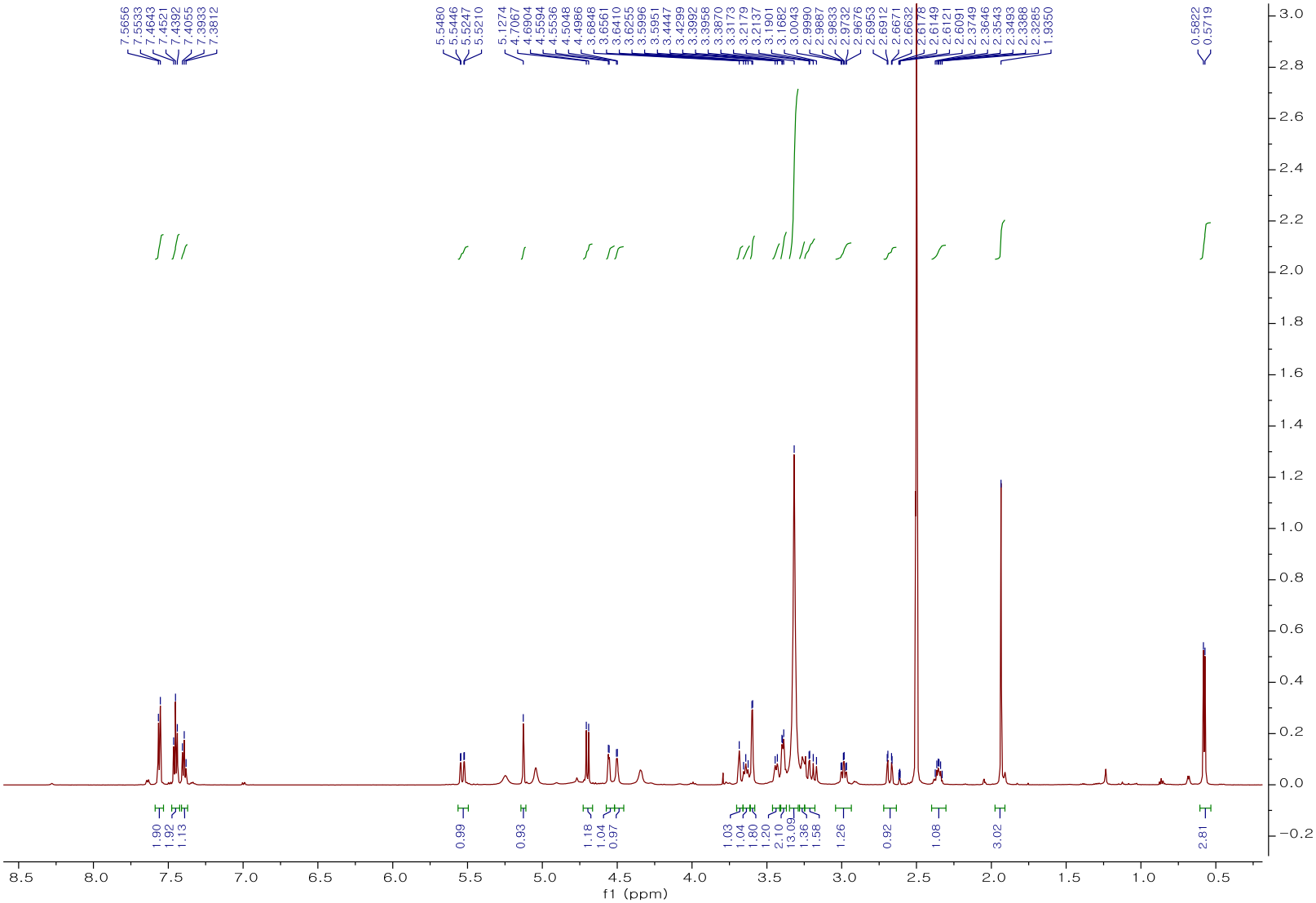


Figure S53. ^{13}C NMR spectrum (150 MHz) of compound **11** in DMSO-d_6

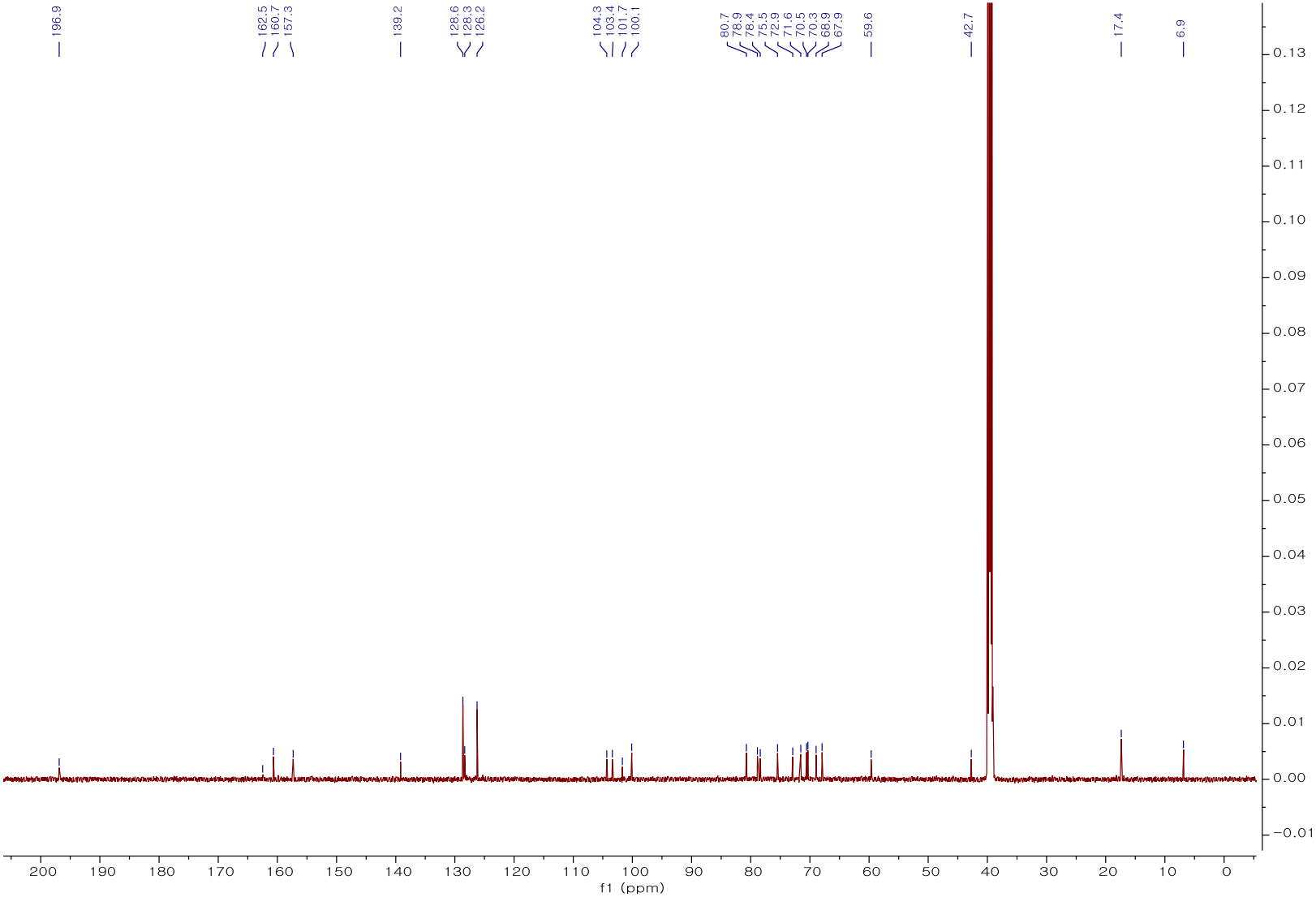


Figure S54. HSQC spectrum of compound **11**

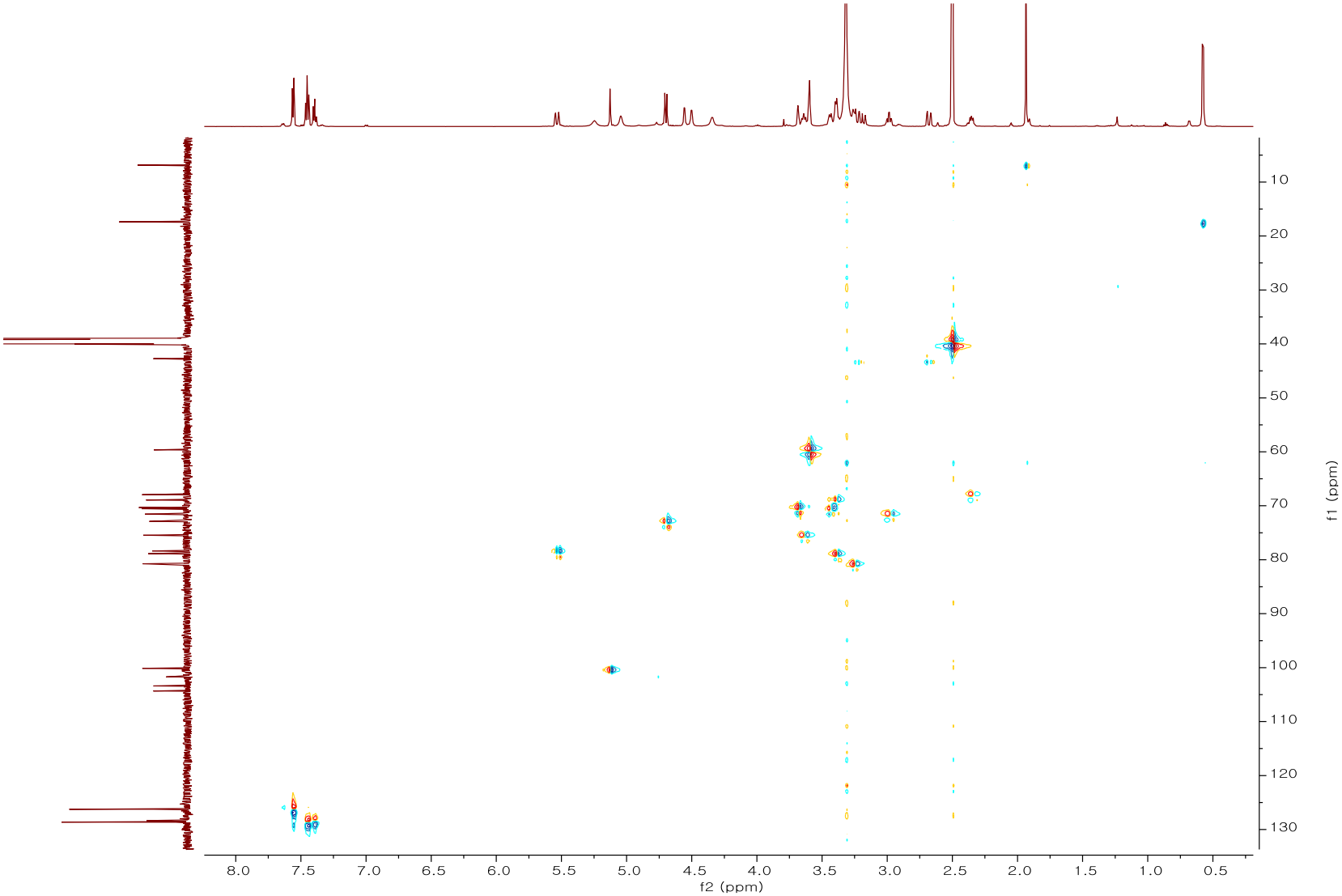


Figure S55. COSY spectrum of compound **11**

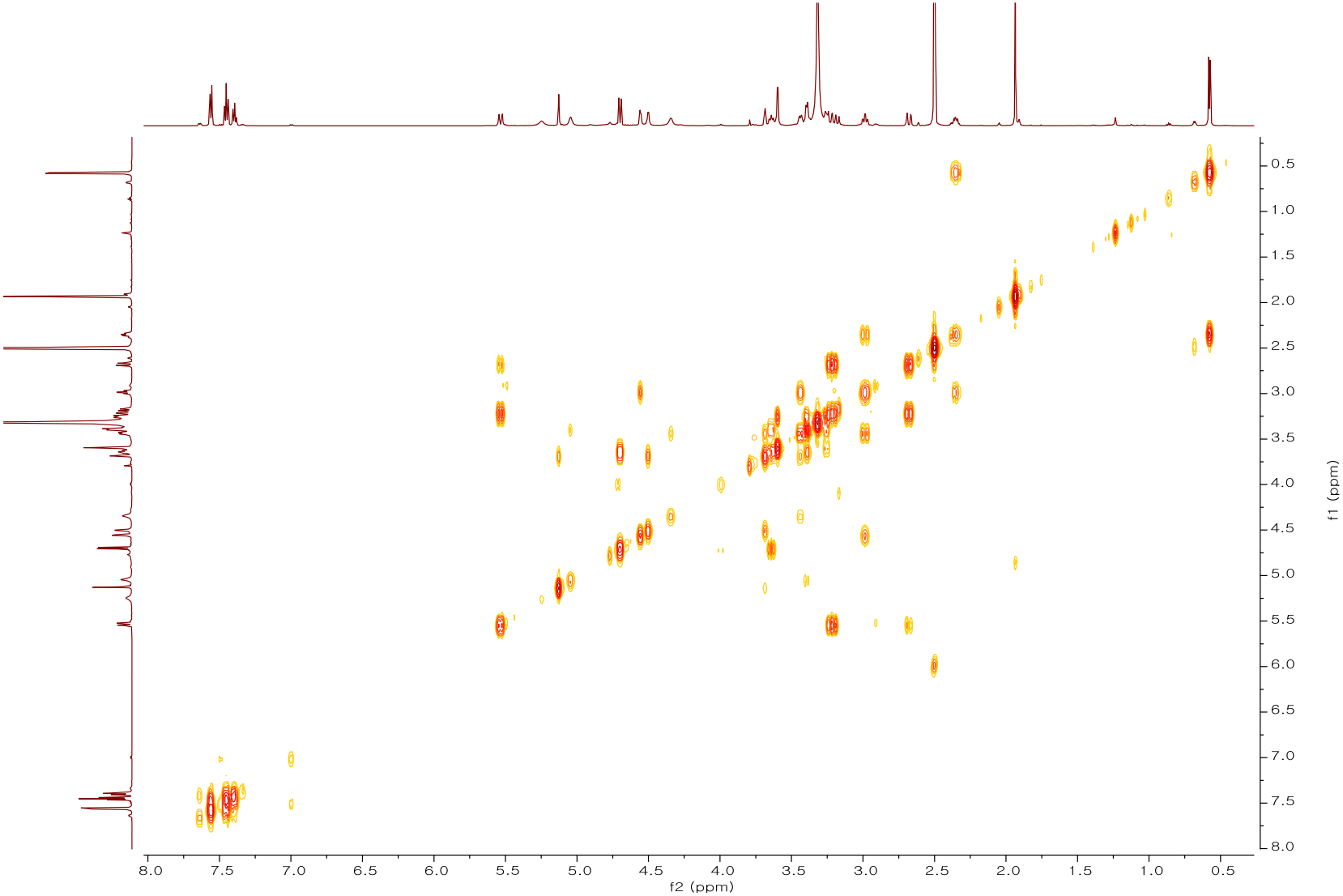


Figure S56. HMBC spectrum of compound **11**

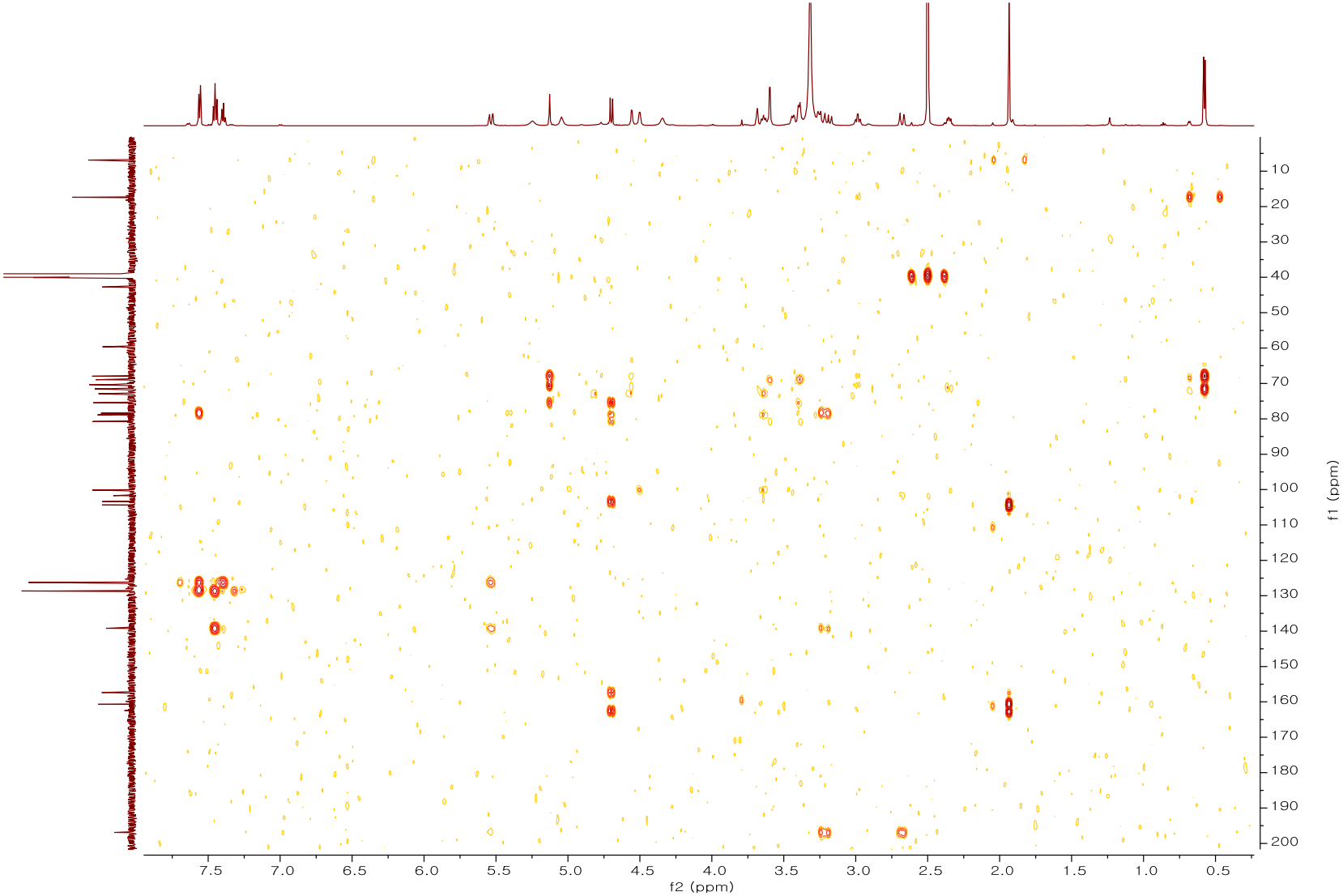


Figure S57. ^{1}H NMR spectrum (600 MHz) of compound **12** in DMSO-d_6

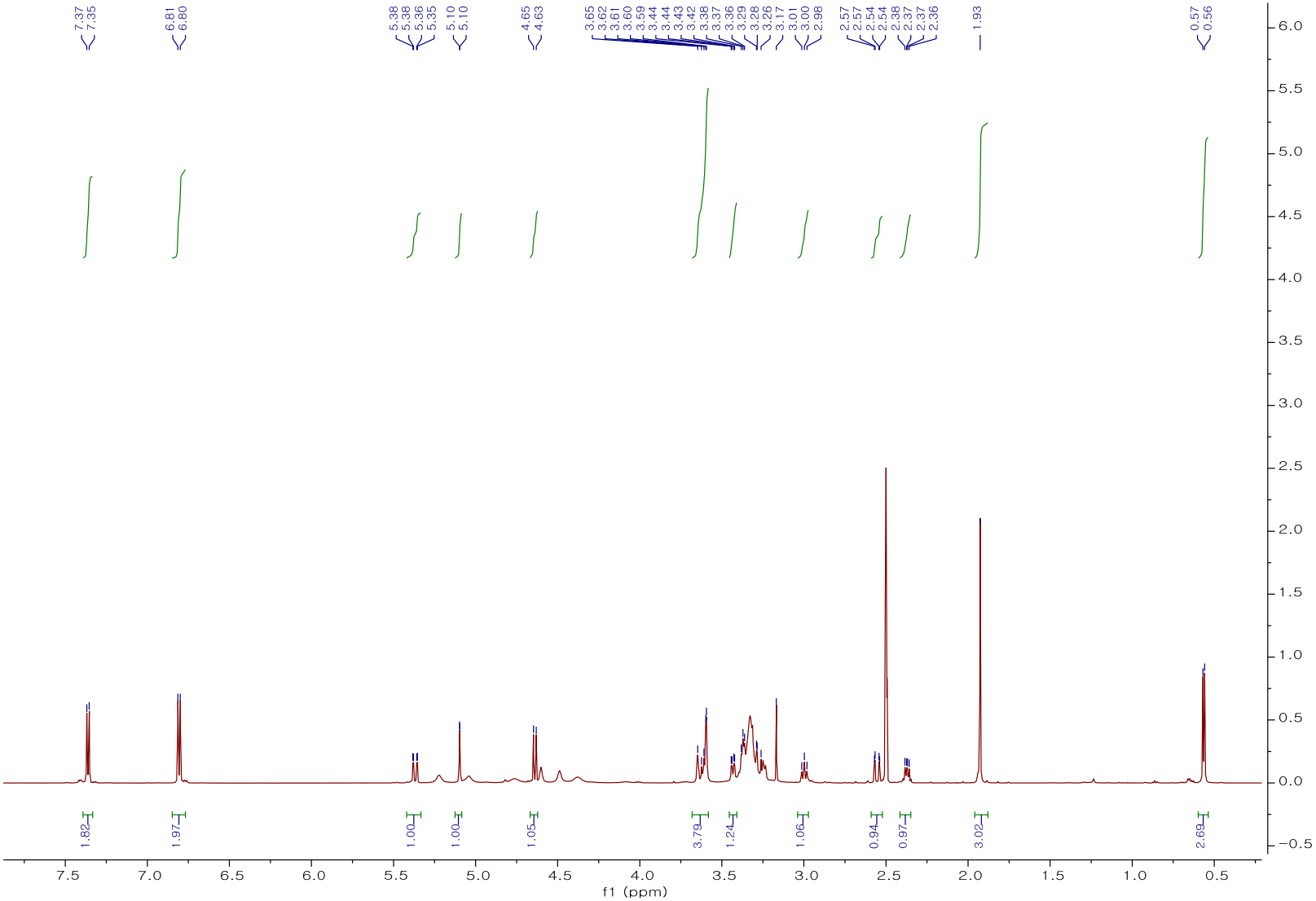


Figure S58. ^{13}C NMR spectrum (150 MHz) of compound **12** in DMSO-d_6

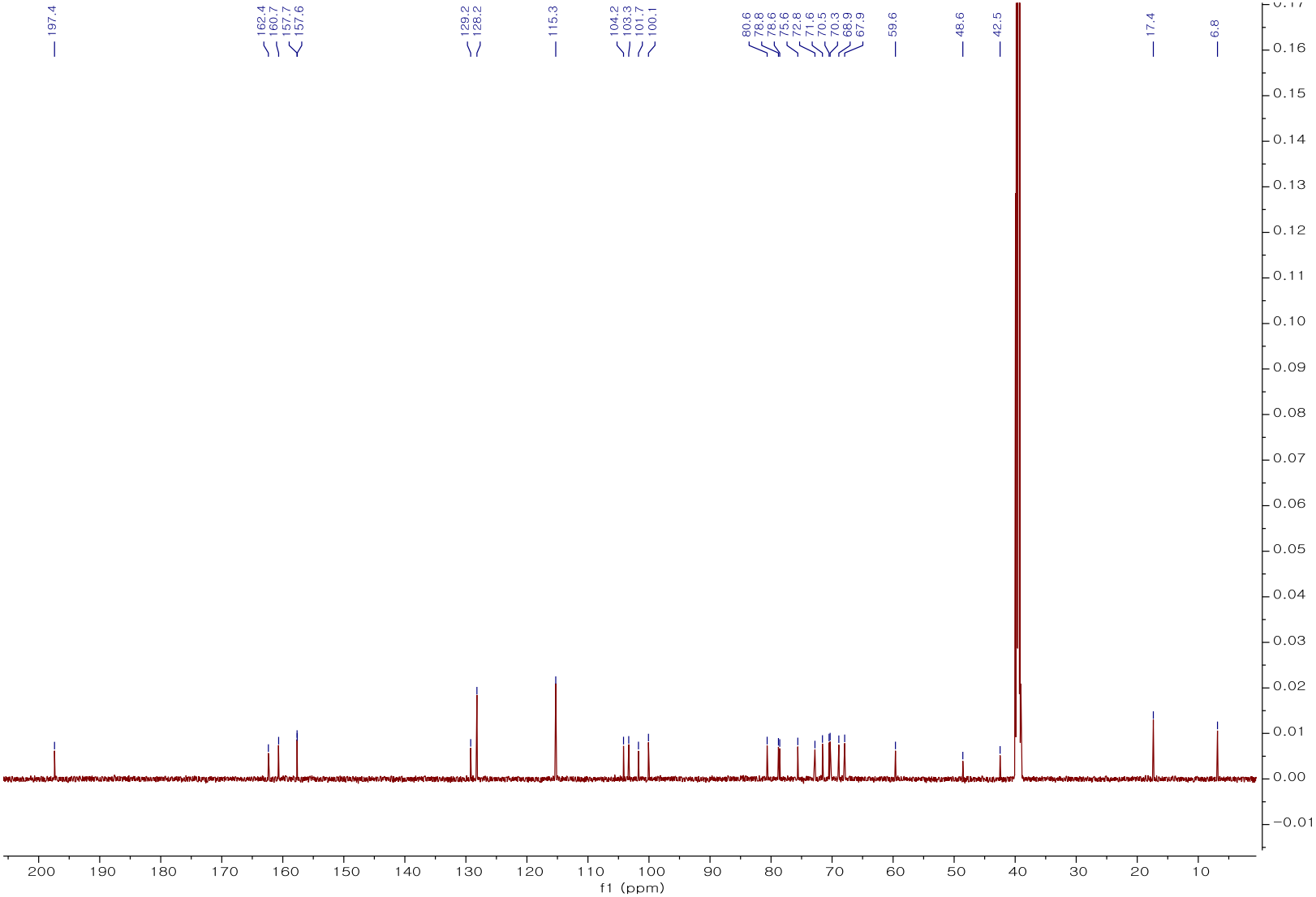


Figure S59. HSQC spectrum of compound **12**

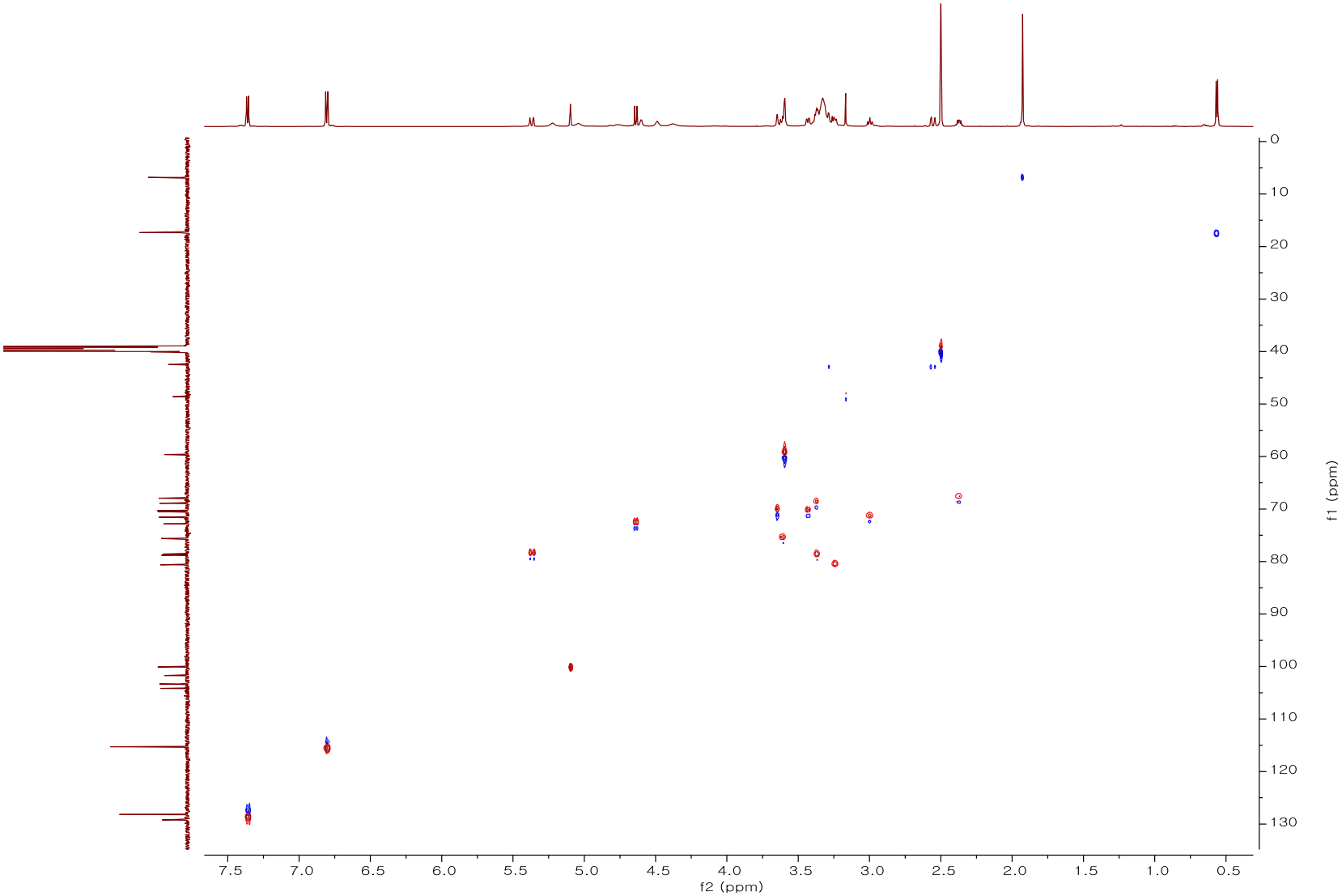


Figure S60. COSY spectrum of compound **12**

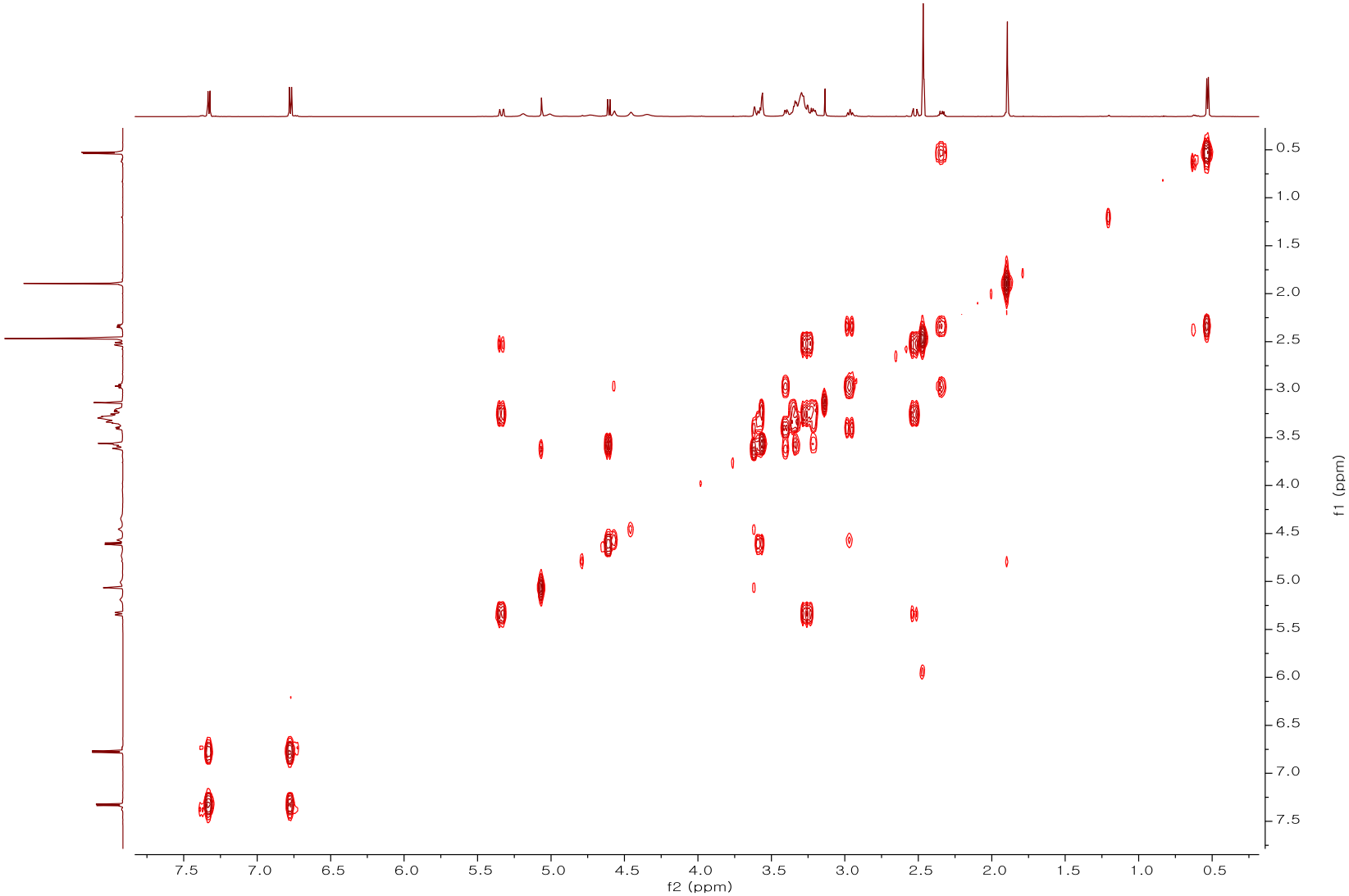


Figure S61. HMBC spectrum of compound **12**

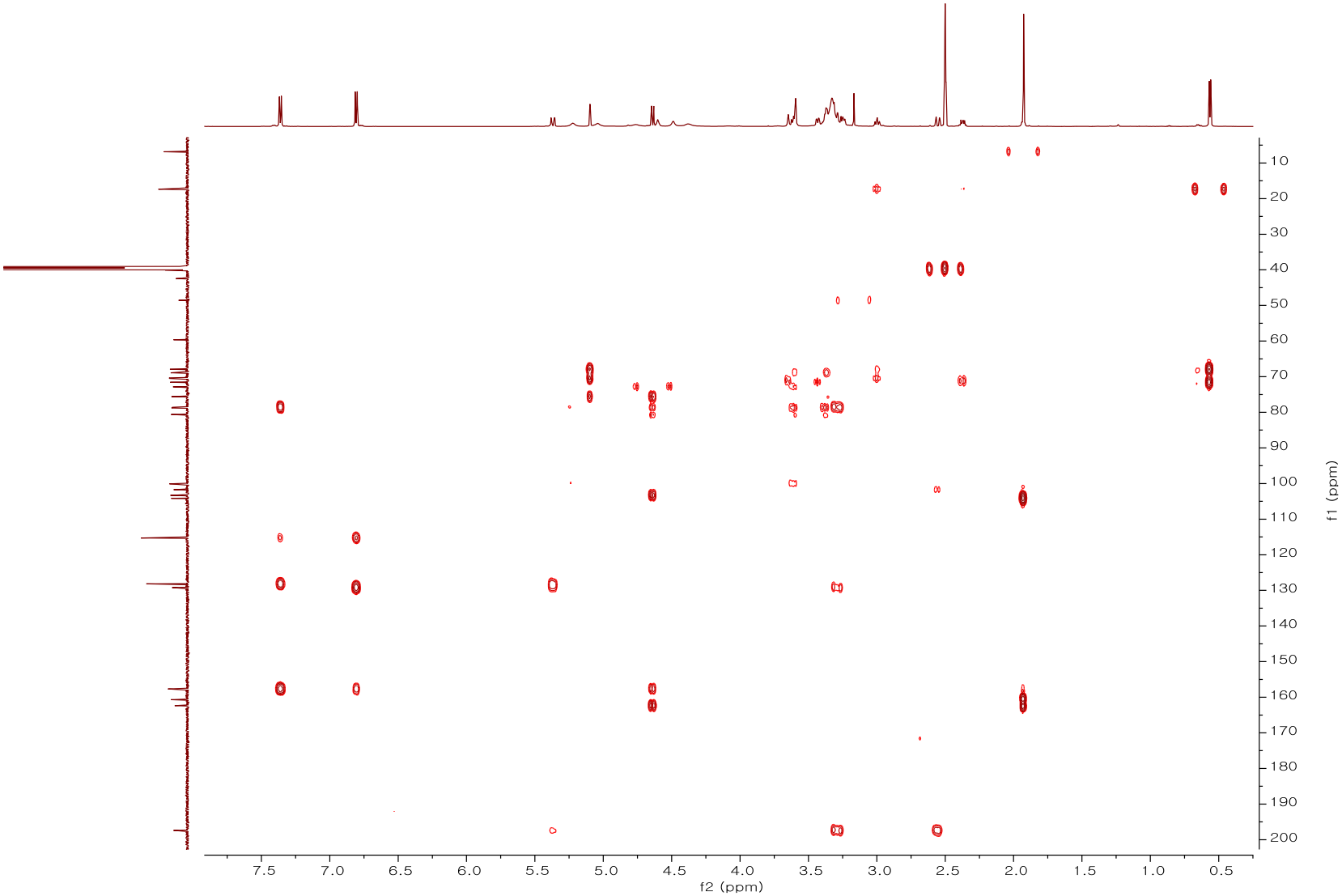


Figure S62. ^{1}H NMR spectrum (600 MHz) of compound **13** in DMSO-d_6

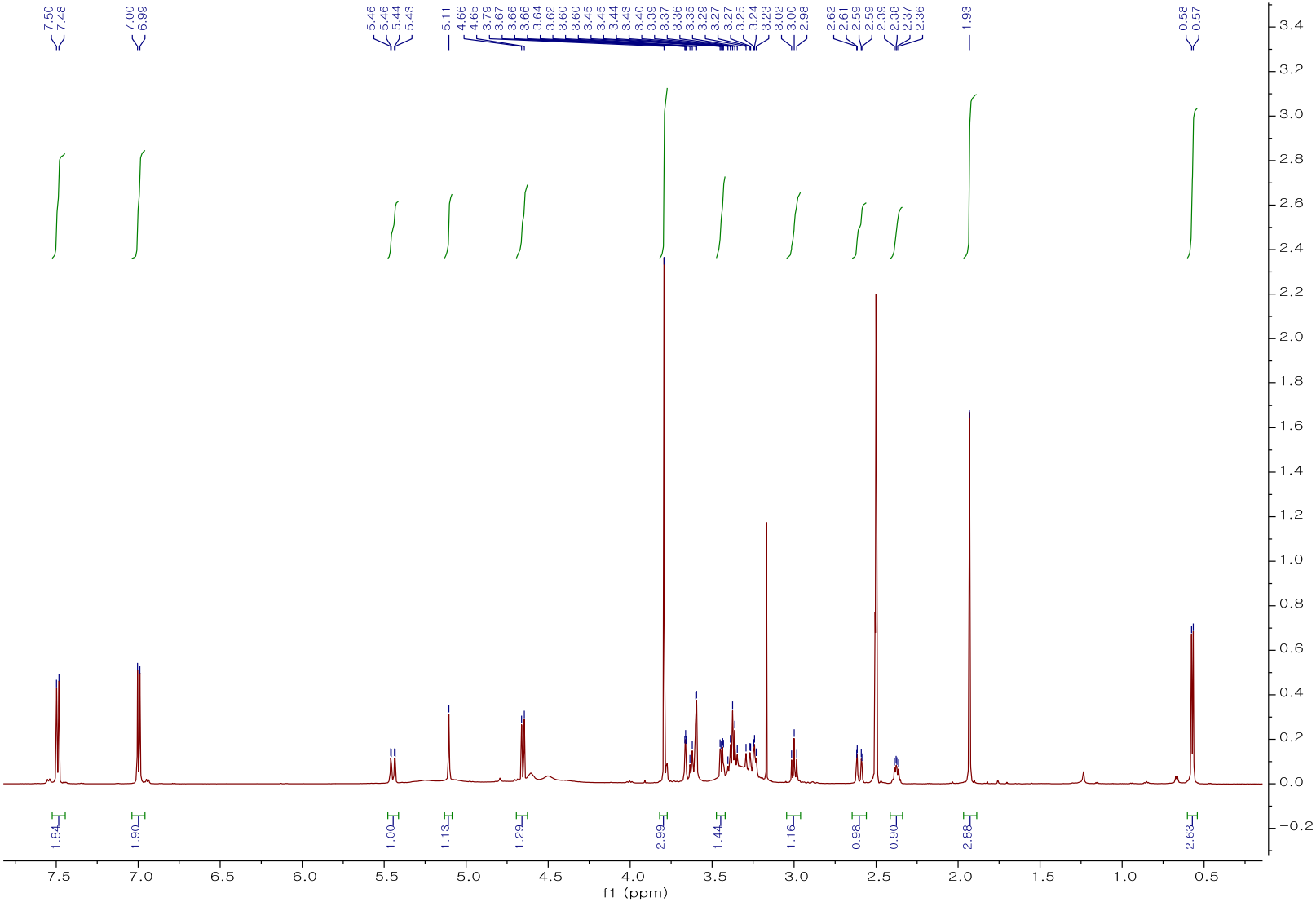


Figure S63. ^{13}C NMR spectrum (150 MHz) of compound **13** in DMSO-d_6

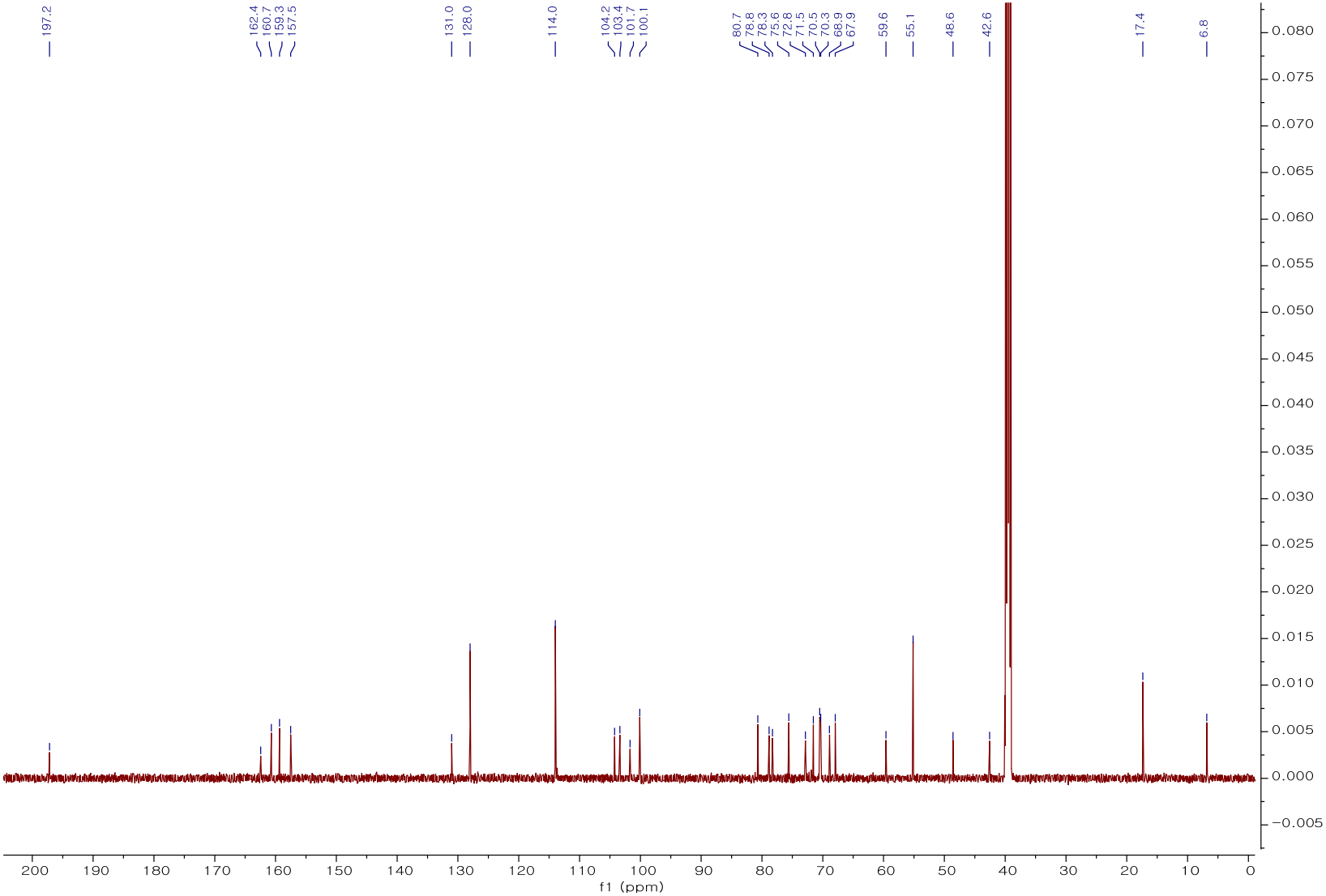


Figure S64. HSQC spectrum of compound **13**

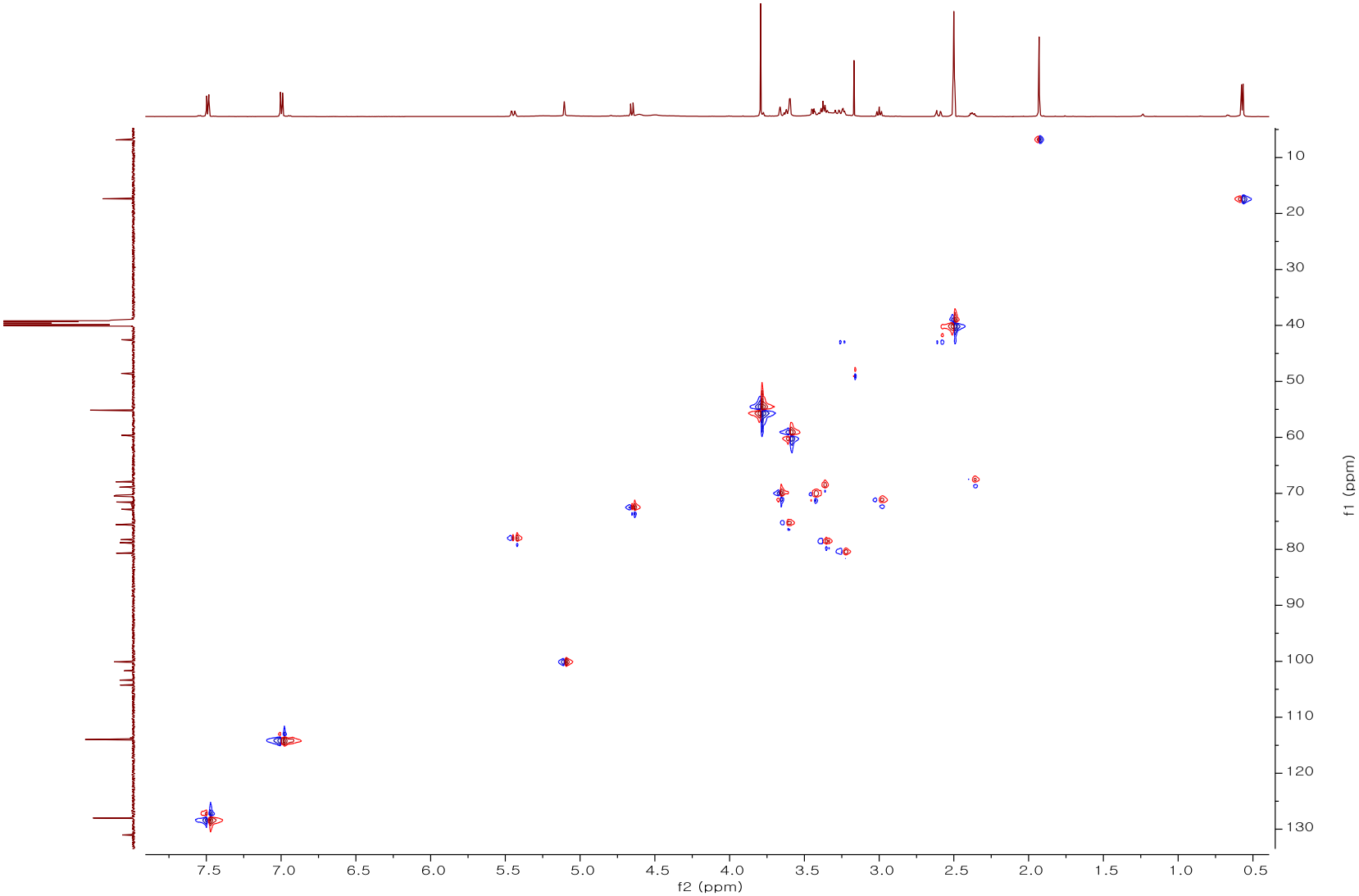


Figure S65. COSY spectrum of compound **13**

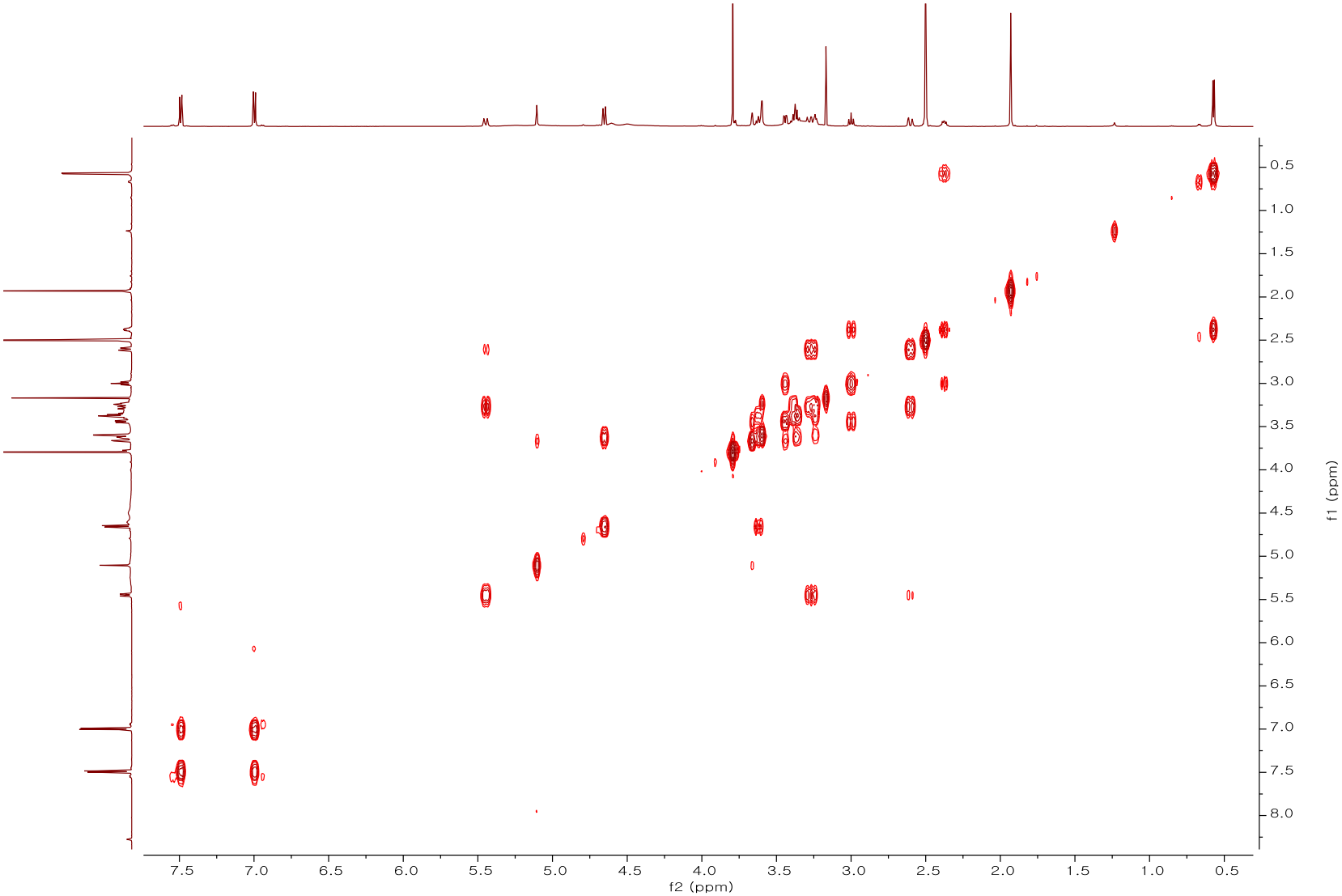


Figure S66. HMBC spectrum of compound **13**

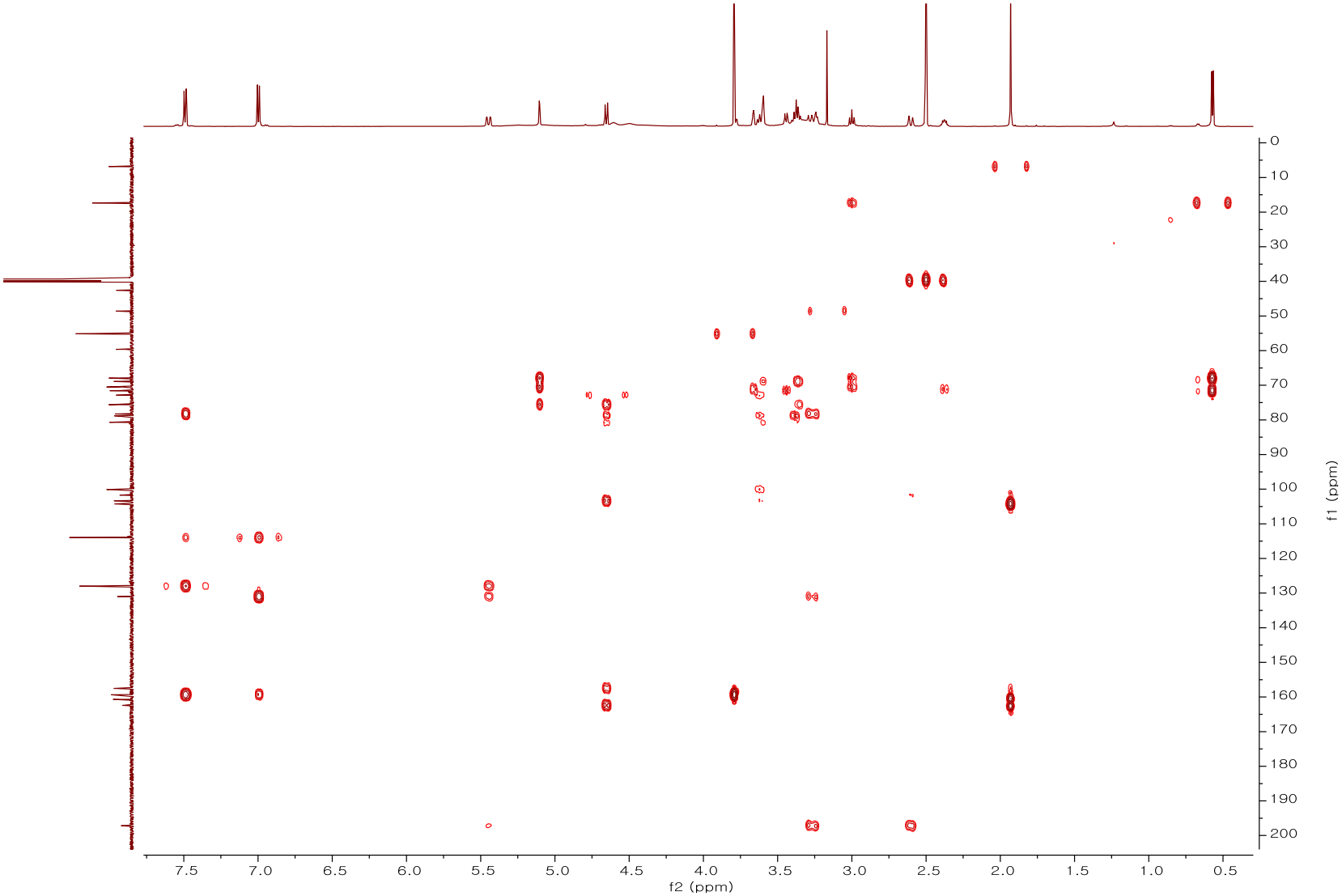
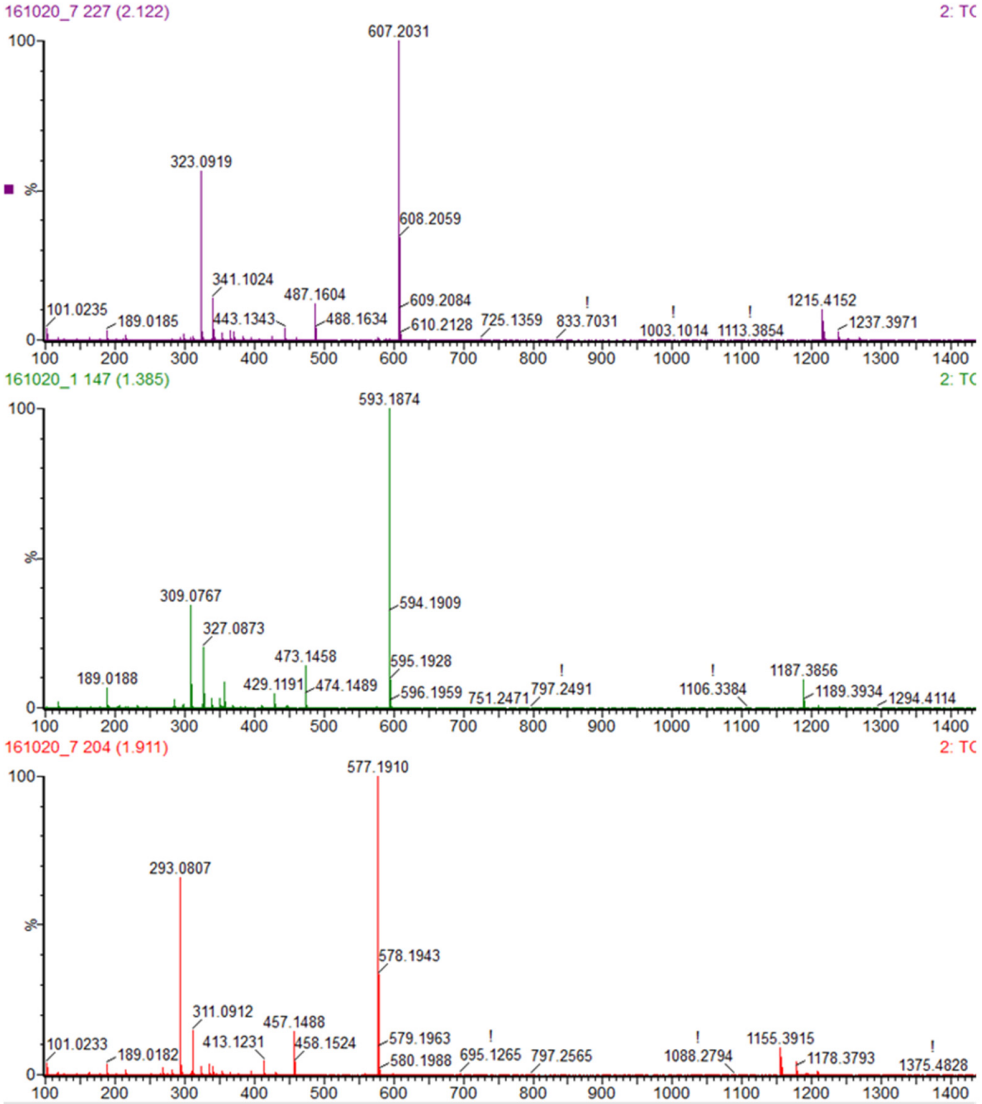


Figure S67. Pseudo MS/MS data of compounds **11−13**



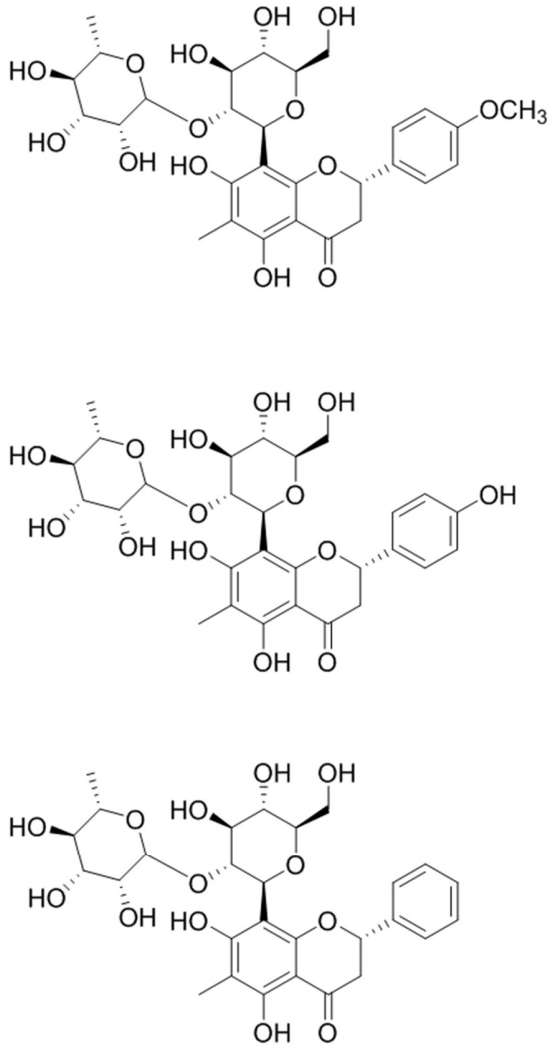
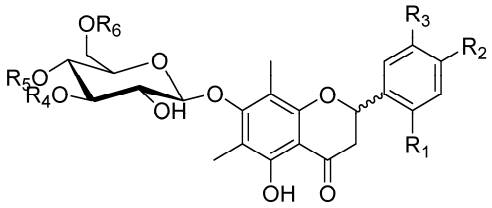
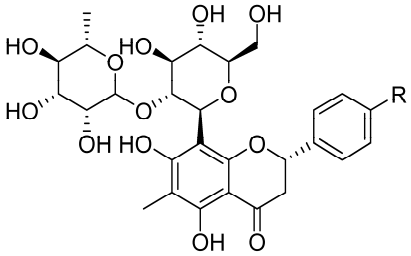


Figure S68. Chemical structures of compounds **9**−**13**





	R_1	R_2	R_3	R_4	R_5	R_6		
9	OH	H	H	H	H	H	2*R*	matteucin 7-O-glucoside
10	H	H	H	H	H	H	Δ^2	matteuorien 7-O-glucoside

	R	
11	H	matteuorienin B
12	OH	matteuorienin C
13	OCH_3	matteuorienin D

Table S3. ^{1}H and ^{13}C NMR data of compounds **9−13**

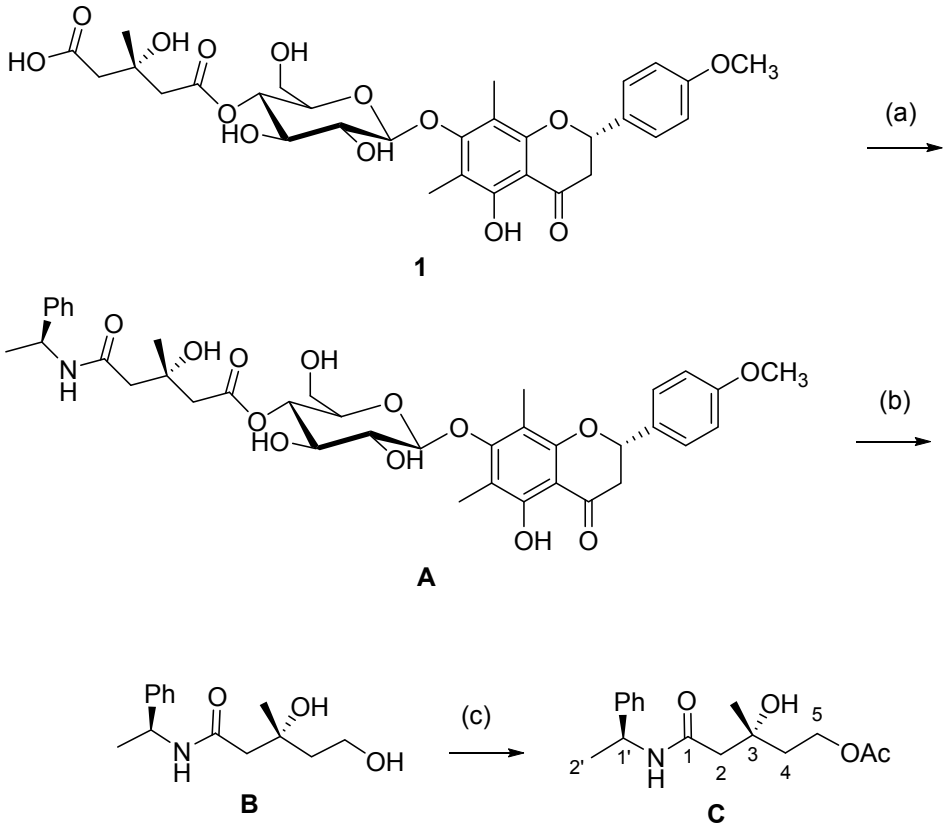
	Matteucin 7-*O*-*β*-D-glucoside (**9**)[a]		Matteuorien 7-*O*-*β*-D-glucoside (**10**)[b]		Matteuorienin B (**11**)[c]		Matteuorienin C (**12**)[c]		Matteuorienin D (**13**)[c]	
position	δ_C, type	δ_H, (*J* in Hz)	δ_C, type	δ_H, (*J* in Hz)	δ_C, type	δ_H, (*J* in Hz)	δ_C, type	δ_H, (*J* in Hz)	δ_C, type	δ_H, (*J* in Hz)
2	73.9, CH	5.72 dd (13.0, 2.9)	163.6, C		78.4, CH	5.53 dd (14.1, 2.1)	78.6, CH	5.37 dd (14.2, 2.3)	78.3, CH	5.45, dd (14.1, 2.2)
3	41.4, CH_2	2.83 dd (17.1, 3.0) 3.23 m	105.2, CH	7.10 s	42.7, CH_2	2.68 dd (2.4, 16.9) 3.22 dd (14.3, 16.8)	42.5, CH_2	2.56 dd (2.4, 16.9) 3.25 m	42.6, CH_2	2.60, dd (16.7, 2.3) 3.27, m
4	198.6, C		182.9, C		196.9, C		197.4, C		197.2, C	
5	157.9, C		155.9, C		160.7, C		160.7, C		160.7, C	
6	111.1, C		114.7, C		104.3, C		104.2, C		104.2, C	
7	161.4, C		159.2, C		162.5, C		162.4, C		162.4, C	
8	110.1, C		110.3, C		103.4, C		103.3, C		103.4, C	
9	157.6, C		152.2, C		157.3, C		157.7, C		157.5, C	
10	104.2, C		107.0, C		101.7, C		101.7, C		101.7, C	
1'	125.0, C		130.9, C		139.2, C		129.2, C		131.0, C	
2'	154.5, C		126.5, CH	8.12 dd (1.6, 8.1)	128.6, CH	7.56 d (7.4)	128.2, CH	7.36 d (8.6)	128.0, CH	7.49 d (8.7)
3'	115.5, CH	6.91 d (8.1)	129.3, CH	7.62 m	126.2, CH	7.45 dd (7.5, 7.5)	115.3, CH	6.81 d (8.6)	114.0, CH	7.00 d (8.7)
4'	129.2, CH	6.87 t (7.4)	132.2, CH	7.62 m	128.3, CH	7.39 t (7.3)	157.7, C		159.3, C	

5'	119.0, CH	7.19 t (7.8)	129.3, CH	7.62 m	126.2, CH	7.45 dd (7.5, 7.5)	115.3, CH	6.81 d (8.6)	114.0, CH	7.00 d (8.7)
6'	126.6, CH	7.46 d (7.7)	126.5, CH	8.12 dd (1.6, 8.1)	128.6, CH	7.56 d (7.4)	128.2, CH	7.36 d (8.6)	128.0, CH	7.49 d (8.7)
1"	104.7, CH	4.59 d (7.7)	104.6, CH	4.66 d (7.7)	72.9, CH	4.70 d (9.8)	72.8, CH	4.64 d (9.8)	72.8, CH	4.65 d (9.8)
2"	76.3, CH	3.23 m	76.4, CH	3.26 m	75.5, CH	3.64 m	75.6, CH	3.61 m	75.6, CH	3.63 m
3"	77.1, CH	3.05 m	77.1, CH	3.06 m	78.9, CH	3.39 m	78.8, CH	3.38 m	78.8, CH	3.38 m
4"	69.8, CH	3.13 t (9.2)	69.8, CH	3.16 m	68.9, CH	3.39 m	68.9, CH	3.38 m	68.9, CH	3.38 m
5"	74.1, CH	3.29 t (8.5)	74.1, CH	3.35[d]	80.7, CH	3.26 m	80.6, CH	3.25 m	80.7, CH	3.24, m
6"	61.0, CH_2	3.61 d (11.6) 3.42 dd (11.7, 5.7)	61.0, CH_2	3.60 m 3.43[d]	59.6, CH_2	3.60 d (2.7)	59.6, CH_2	3.60, d (2.6)	59.6, CH_2	3.60, d (2.9)
1'''					100.1, CH	5.13 br s	100.1, CH	5.10 d (1.1)	100.1, CH	5.11, br s
2'''					70.3, CH	3.68 br s	70.3, CH	3.64 br s	70.3, CH	3.66 br s
3'''					70.5, CH	3.44 d (8.8)	70.5, CH	3.43 dd (9.3, 3.0)	70.5, CH	3.44, dd (9.3, 3.2)
4'''					71.6, CH	2.99 td (9.4, 3.2)	71.6, CH	3.00 t (9.5)	71.5, CH	3.00 t (9.4)
5'''					67.9, CH	2.35 dd (9.3, 6.2)	67.9, CH	2.37 m	67.9, CH	2.38, dd (9.2, 6.2)
6'''					17.4, CH_3	0.58 d (6.2)	17.4, CH_3	0.56 d (6.2)	17.4, CH_3	0.57 d (6.2)
CH_3-6	8.7, CH_3	2.10 s	9.1, CH_3	2.45 s	6.9, CH_3	1.94 s	6.9, CH_3	1.93 s	6.8, CH_3	1.93, s

CH_3-8	9.3, CH_3	2.08 s	9.3, CH_3	2.20 s		
OCH_3-4'					55.1, CH_3	3.79, s

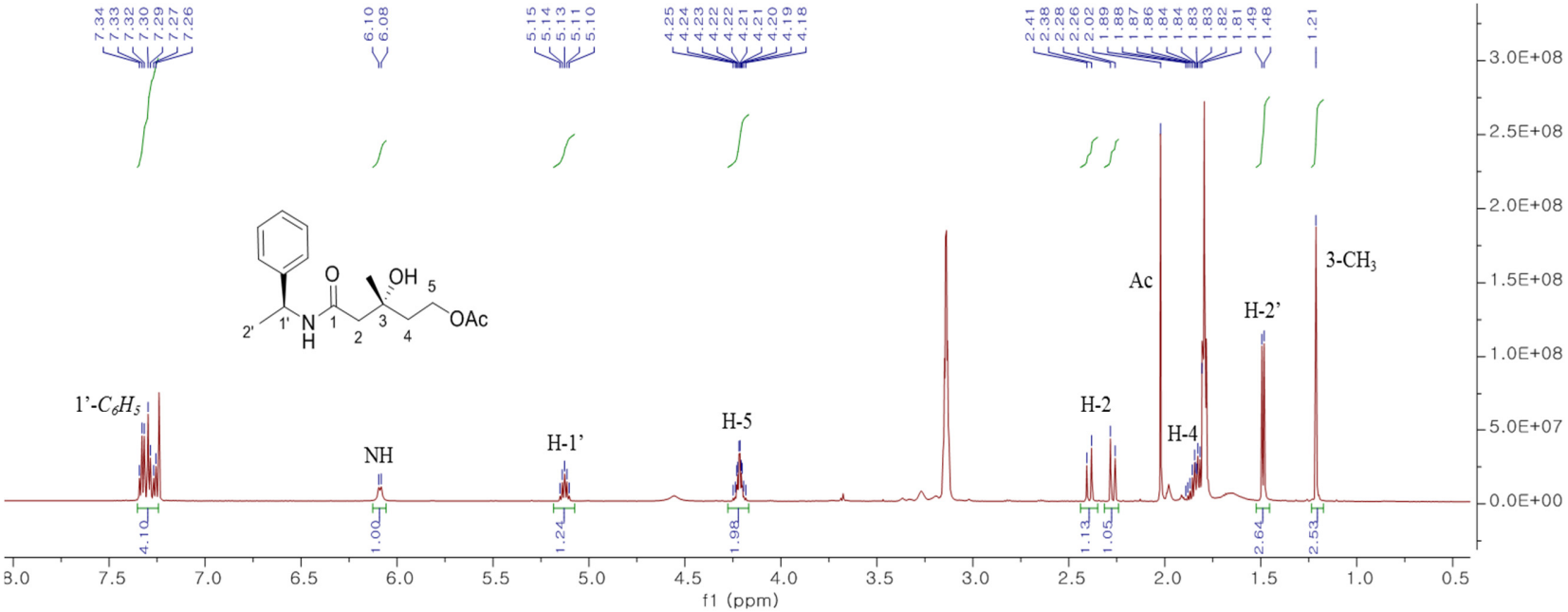
Recorded at [a]850/213 MHz, [b]500/125 MHz, [c]600/150 MHz, [d]Obscured by solvent

Scheme S1. Determination of the Absolute Configuration of HMG moiety in compound **1**



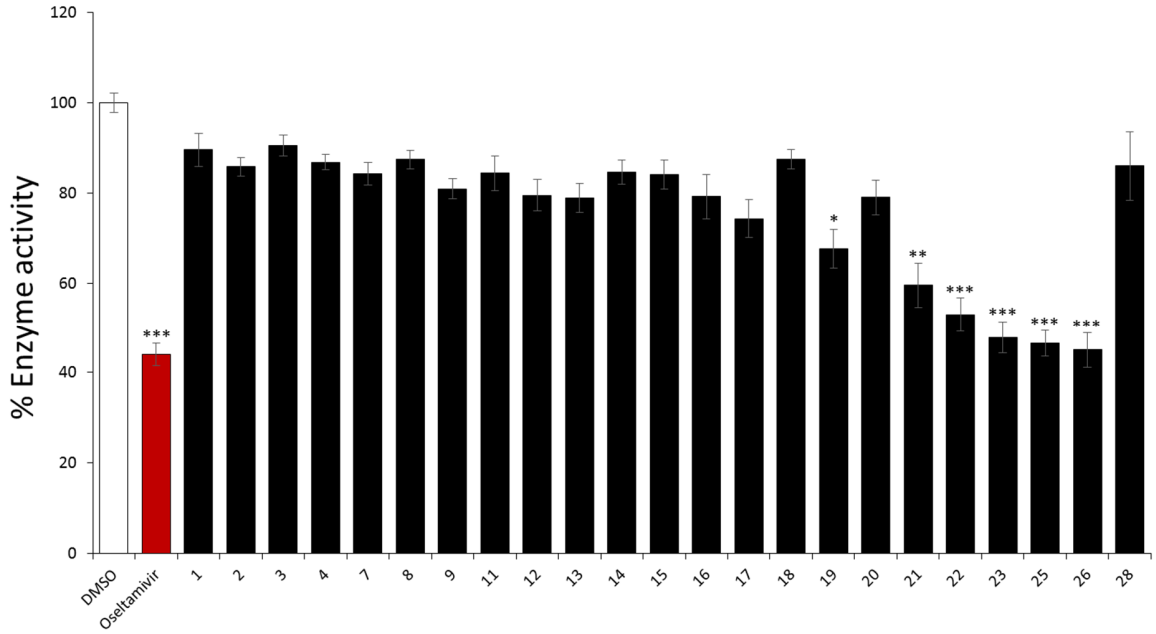
(a) (S)-1-phenylethylamine, PyBOP, HOBt, Et_3N, DMF
(b) $LiBH_4$, THF
(c) Ac_2O, pyridine

Figure S69. ^{1}H NMR data ($CDCl_3$, 600 MHz) of compound **1C** (representive)



^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.30 (5H, m, 1′-$C_6\underline{H_5}$), 6.09 (1H, d, J = 7.4 Hz, N$\underline{H}$), 5.13 (1H, p, J = 7.1, 7.1, 7.1, 7.1 Hz, H-1′), 4.22 (1H, td, J = 6.9, 3.0 Hz, H-5), 2.39, 2.27 (1H, d, J = 14.8 Hz, H-2), 2.02 (3H, s, 5-OCO$\underline{CH_3}$), 1.85 (2H, m, H-4), 1.49 (3H, d, J = 6.9 Hz, H-2′), and 1.21 (3H, s, 3-CH_3)

Figure S70. The Screening data of isolated compounds from *P. orientale* on the H1N1 neuraminidase enzyme



Effects of several compounds (25 μM) from *P. orientale* on the H1N1 neuraminidase enzyme using oseltamivir (100 nM) as a positive control. After 2 h of enzymatic reaction, the fluorescence intensity was measured and the data was expressed as the mean ± SD of three independent experiments (* $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$ using ANOVA statistics).