Supporting Information

Sumalactones A−D, Four New Curvularin-type Macrolides from a Marine Deep Sea Fungus *Penicillium Sumatrense*

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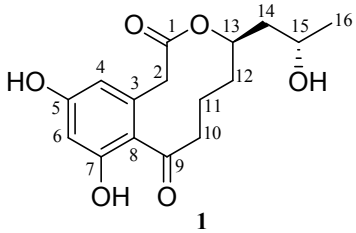
CONTENT

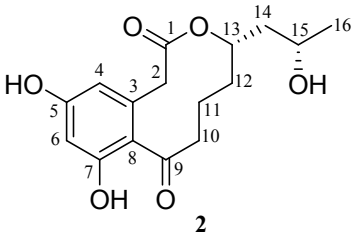
S1. The NMR data assignments of 1−4



1

Table S1 ^{13}C NMR (125 MHz) and ^{1}H NMR (500 MHz) data of **1** in CD_3OD

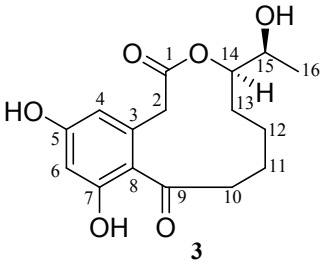
No.	δ_C, mult.	δ_H (J in Hz)	^{1}H-^{1}H COSY	HMBC
1	171.8, qC			
2	41.3, CH_2	3.44, d (18.3), a	H-2b	C-1, 3, 4, 8
		3.96, d (18.4), b	H-2a	C-1, 3, 4, 5, 7, 8
3	136.3, qC			
4	110.6, CH	6.12, d (1.8)	H-6	C-2, 5, 6, 8
5	161.0, qC			
6	102.4, CH	6.24, d (2.0)	H-4	C-4, 5, 7, 8, 9
7	158.8, qC			
8	122.6, qC			
9	211.6, qC			
10	46.7, CH_2	2.70, m, a	H-10b, 11	C-9, 11,12
		3.06, m, b	H-10a, 11	C-9, 11, 12
11	23.4, CH_2	1.87, m	H-10a, 10b, 12a, 12b	C-9, 10, 12, 13
12	35.4, CH_2	1.47, overlapped, a	H-11, 12b, 13	C-10
		1.95, m, b	H-11, 12a, 13	C-10
13	76.3, CH	4.91, m	H-12a, 12b, 14a, 14b	C-1, 12
14	45.3, CH_2	1.47, overlapped, a	H-13, 14b, 15	C-12, 13, 15, 16
		1.70, ddd (6.6, 7.5, 14.1), b	H-13, 14a, 15	C-12, 13, 15, 16
15	65.5, CH	3.69, m	H-14a, 14b, 16	C-13, 14
16	23.9, CH_3	1.12, d (6.2)	H-15	C-14, 15



2

Table S2 ^{13}C NMR (125 MHz) and ^{1}H NMR (500 MHz) data of **2** in CD_3OD

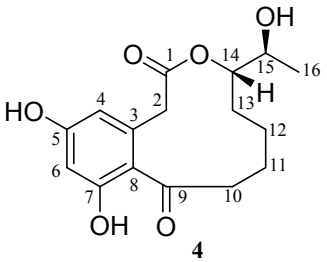
No.	δ_C, mult.	δ_H (J in Hz)	^{1}H-^{1}H COSY	HMBC
1	172.7, qC			
2	41.3, CH_2	3.49, d (18.5), a	H-2b	C-1, 3, 4, 8
		3.98, d (18.4), b	H-2a	C-1, 3, 4, 5, 7, 8
3	136.2, qC			
4	110.6, CH	6.13, d (1.6)	H-6	C-2, 5, 6, 8
5	161.0, qC			
6	102.4, CH	6.24, d (2.0)	H-4	C-4, 5, 7, 8, 9
7	158.9, qC			
8	122.6, qC			
9	211.5, qC			
10	46.6, CH_2	2.70, ddd (2.1, 7.7, 15.9), a	H-10b, 11	C-9, 11,12
		3.06, ddd (2.2, 10.5, 15.4), b	H-10a, 11	C-9, 11, 12
11	23.4, CH_2	1.87, overlapped	H-10a, 10b, 12a, 12b	C-9, 10, 12, 13
12	36.3, CH_2	1.47, overlapped, a	H-11, 12b, 13	C-11
		1.87, overlapped, b	H-11, 12a, 13	C-11
13	76.3, CH	4.90, m	H-12a, 12b, 14a, 14b	C-1, 15
14	45.9, CH_2	1.47, overlapped, a	H-13, 14b, 15	C-12, 13, 15, 16
		1.56, ddd (3.8, 7.9, 14.2), b	H-13, 14a, 15	C-12, 13, 15, 16
15	65.1, CH	3.65, m	H-14a, 14b, 16	
16	23.6, CH_3	1.09, d (6.2)	H-15	C-14, 15



3

Table S3^{13}C NMR (125 MHz) and ^{1}H NMR (500 MHz) data of **3**in CD_3OD

No.	$\delta_{C,}$ mult.	δ_H (J in Hz)	^{1}H-^{1}H COSY	HMBC
1	172.4, qC			
2	41.1, CH_2	3.46, d (17.2), a	H-2b	C-1, 3, 4, 8
		4.14, d (17.1), b	H-2a	C-1, 3, 4, 7, 8
3	136.3, qC			
4	111.5, CH	6.16, d (2.2)	H-6	C-2, 5, 6, 8, 9
5	160.9, qC			
6	102.6, CH	6.25, d (2.2)	H-4	C-4, 5, 7, 8, 9
7	158.8, qC			
8	122.0, qC			
9	209.8, qC			
10	41.7, CH_2	2.87, ddd (3.4, 6.1, 17.5), a	H-10b, 11a, 11b	C-9, 11,12
		3.17, ddd (3.1, 11.6, 17.4), b	H-10a, 11a, 11b	C-9, 11, 12
11	23.9, CH_2	1.47, overlapped, a	H-10a, 10b, 11b, 12a, 12b	C-9, 10, 12, 13
		1.89, m, b	H-10a, 10b, 11a, 12a, 12b	C-9, 10, 12, 13
12	22.0, CH_2	1.23, m, a	H-11a, 11b, 12b, 13a, 13b	C-10 ,11, 13, 14
		1.66, m, b	H-11a, 11b, 12a, 13a, 13b	C-10, 11, 13, 14
13	26.1, CH_2	1.47, overlapped,a	H-12a, 12b, 13b, 14a, 14b	C-12, 14, 15
		1.75, m, b	H-12a, 12b, 13a, 14a, 14b	C-12, 15
14	79.8, CH	4.75, ddd (3.3, 5.1, 10.5)	H-13a, 13b, 15	C-1, 12, 13, 15, 16
15	69.4, CH	3.63, dq (5.3, 6.3)	H-14, 16	C-13, 14, 16
16	18.7, CH_3	0.98, d (6.4)	H-15	C-14, 15



4

Table S4 ^{13}C NMR (125 MHz) and ^{1}H NMR (500 MHz) data of **4** in CD_3OD

No.	δ_C, mult.	δ_H (J in Hz)	^{1}H-^{1}H COSY	HMBC
1	172.5, qC			
2	41.1, CH_2	3.50, d (17.1), a	H-2b	C-1, 3, 4, 8
		4.11, d (17.1), b	H-2a	C-1, 3, 4, 8
3	136.3, qC			
4	111.7, CH	6.17, d (2.2)	H-6	C-2, 5, 6, 8
5	160.9, qC			
6	102.6, CH	6.24, d (2.2)	H-4	C-4, 5, 7, 8
7	158.7, qC			
8	122.0, qC			
9	209.9, qC			
10	41.8, CH_2	2.86, ddd (3.3, 6.0, 17.3), a	H-10b, 11a, 11b	C-9, 11
		3.19, ddd (3.2, 11.6, 17.3), b	H-10a, 11a, 11b	C-9, 11
11	23.9, CH_2	1.47, overlapped, a	H-10a, 10b, 11b, 12a, 12b	C-9, 12
		1.89, m, b	H-10a, 10b, 11a, 12a, 12b	C-9, 12
12	22.1, CH_2	1.23, m, a	H-11a, 11b, 12b, 13a, 13b	C-11, 13, 14
		1.67, overlapped, b	H-11a, 11b, 12a, 13a, 13b	C-11, 13, 14
13	26.3, CH_2	1.47, overlapped, a	H-12a, 12b, 13b, 14	C-11, 12
		1.67, overlapped, b	H-12a, 12b, 13a, 14	C-11, 12
14	79.9, CH	4.78, ddd (2.7, 6.0, 10.2)	H-13a, 13b, 15	C-1, 12, 13, 15, 16
15	69.2, CH	3.62, p (6.4)	H-14, 16	C-13, 14, 16
16	18.9, CH_3	1.02, d (6.5)	H-15	C-14, 15

S2. Preparation of (*S*)- and (*R*)- MTPA esters of 1 and 3

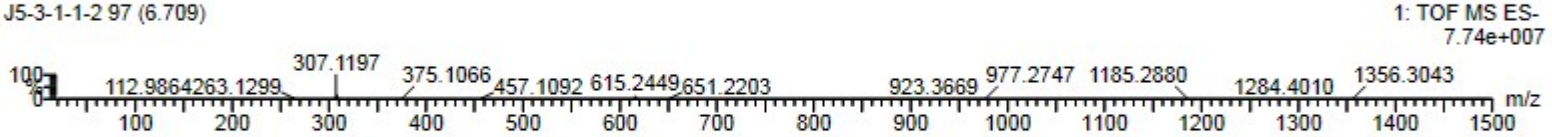
A solution of **1/3**(1.0 mg) in pyridine-d_5 (0.5 mL) was treated with (*S*)-MTPA chloride (15μL) under an atmosphere of nitrogen in an NMR tube. The mixture was stirred at room temperature for 4 h to obtain the (*R*)-MTPA ester (**1b**/**3b**). The same procedure was used to prepare the (*S*)-MTPA ester (**1a**/**3a**) with (*R*)-MTPA chloride.

The key $\Delta\delta$ values ($\Delta\delta_{H\text{-}11}$: +0.12, +0.18; $\Delta\delta_{H\text{-}12}$: +0.07, +0.12; $\Delta\delta_{H\text{-}13}$: +0.15; $\Delta\delta_{H\text{-}14}$: +0.07, +0.07; $\Delta\delta_{H\text{-}16}$: -0.07) of the (*S*)- and (*R*)-MTPA esters of **1** (**1a** and **1b**) indicated the *S* configuration for C-15 in **1**.

The key $\Delta\delta$ values ($\Delta\delta_{H\text{-}11}$: +0.16, +0.21; $\Delta\delta_{H\text{-}12}$: +0.08, +0.08; $\Delta\delta_{H\text{-}13}$: +0.01, +0.09; $\Delta\delta_{H\text{-}14}$: +0.02; $\Delta\delta_{H\text{-}16}$: -0.10) of the (*S*)- and (*R*)-MTPA esters of **3**(**3a** and **3b**) indicated the *S* configuration for C-15 in **3**.

Figure S1. HRESIMS spectrum of **1**

Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-30 O: 0-10
09-Mar-2017
J5-3-1-1-2 97 (6.709)



Minimum:				-1.5				
Maximum:		2.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
307.1197	307.1182	1.5	4.9	7.5	837.5	n/a	n/a	C16 H19 O6

Figure S2. ^{1}H NMR spectrum of **1** in CD_3OD (500 MHz)

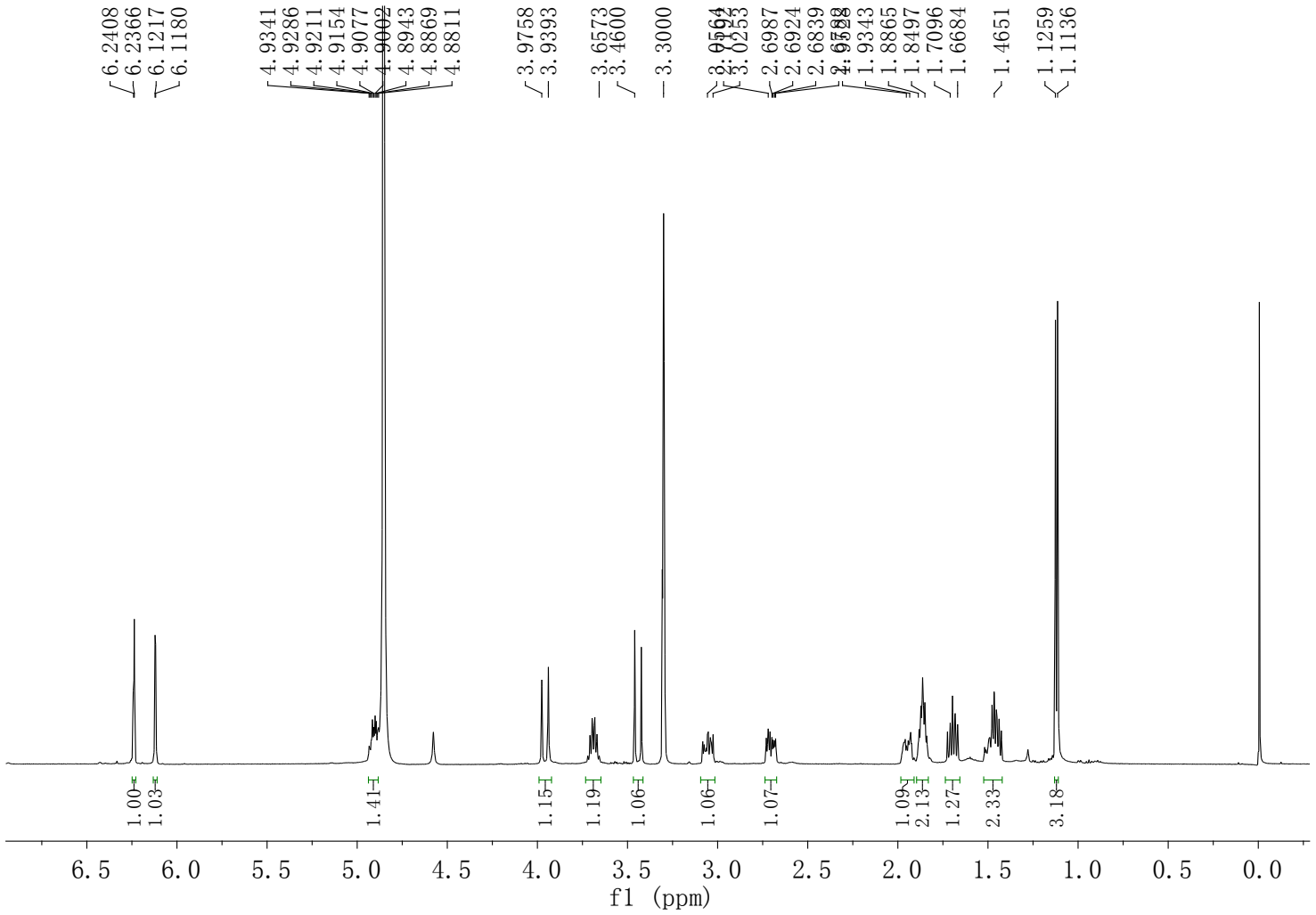


Figure S3. ^{13}C NMR spectrum of **1** in CD3OD (125 MHz)

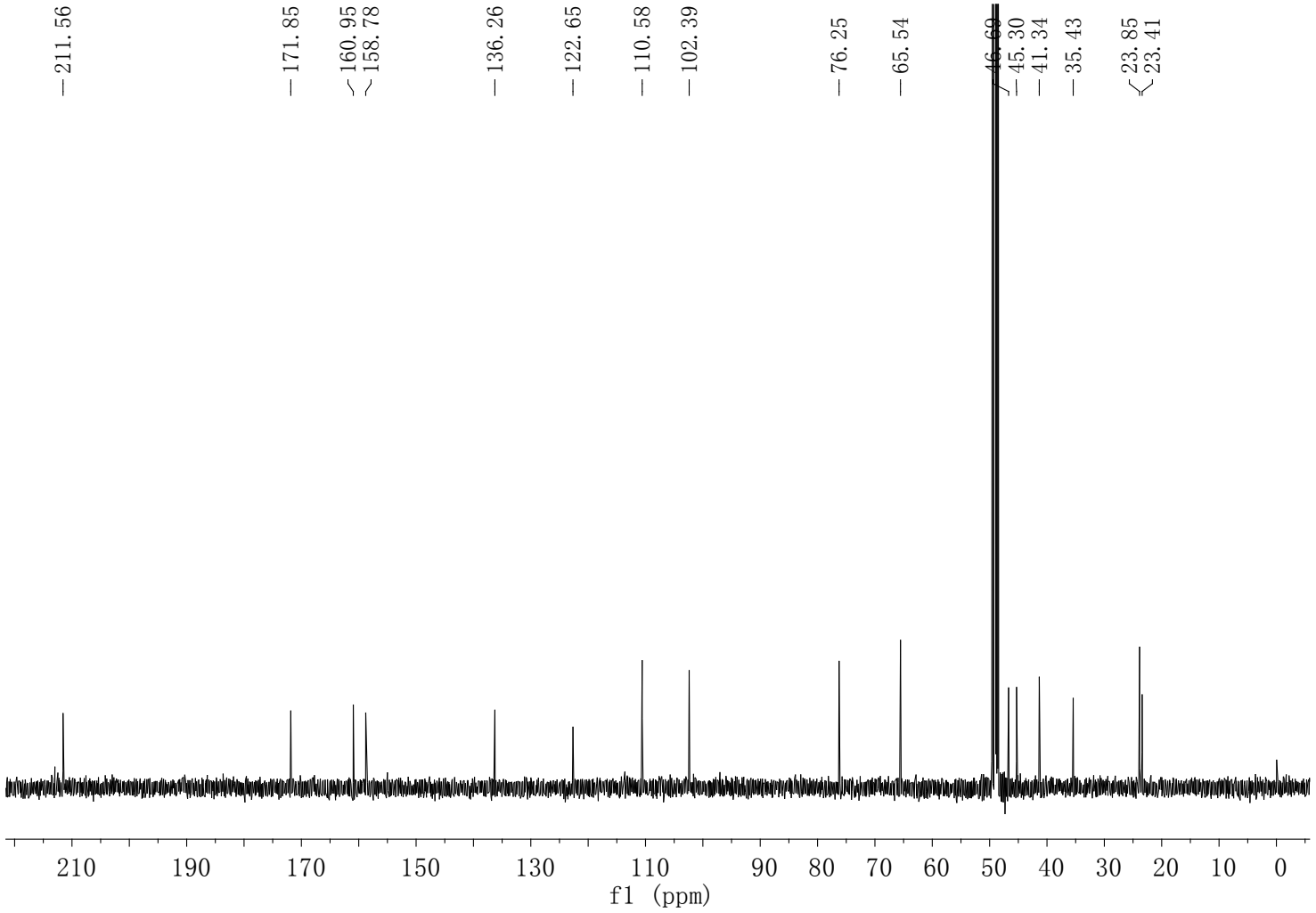


Figure S4. ^{1}H-^{1}H COSY spectrum of **1** in CD_3OD

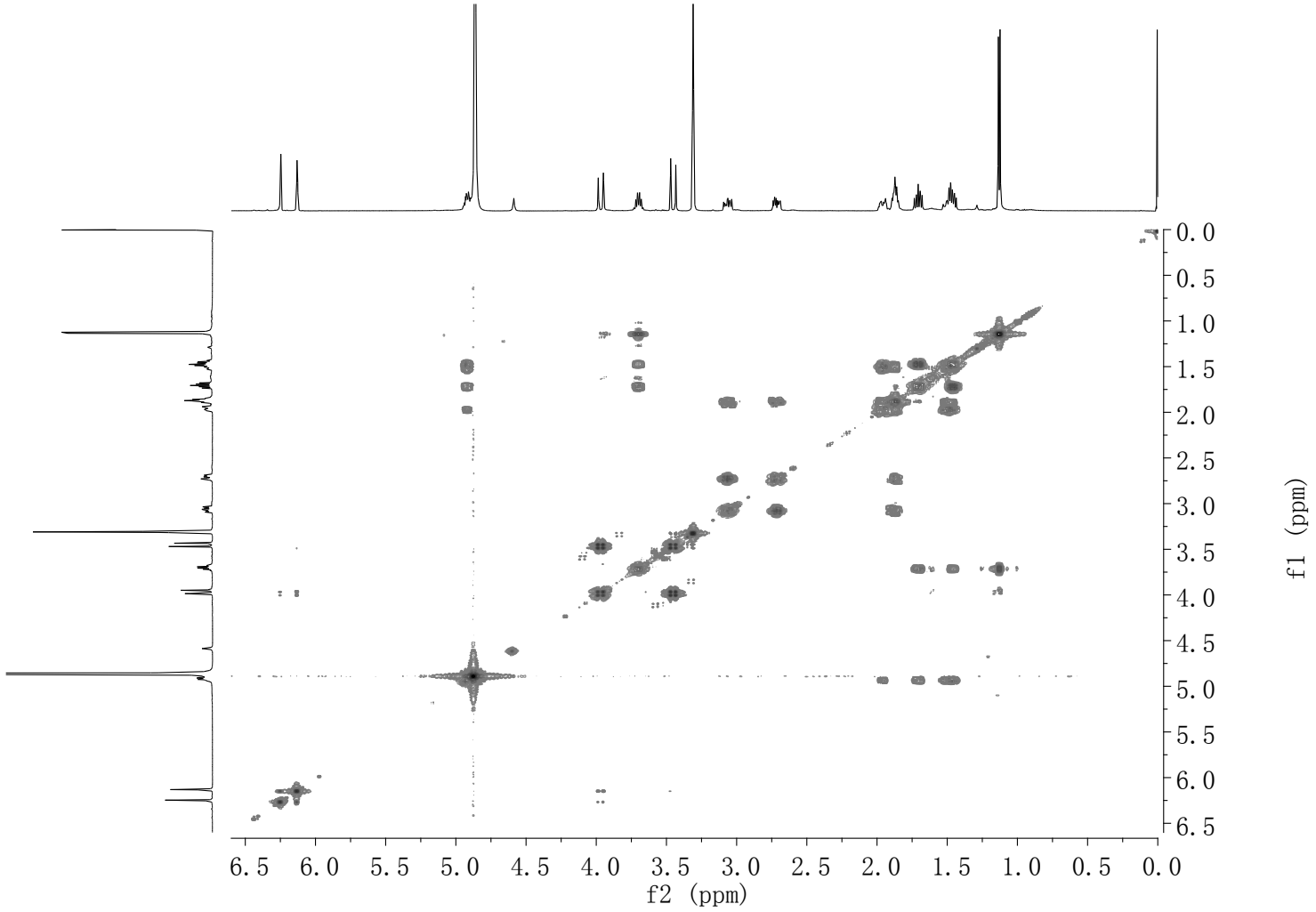


Figure S5. HSQC spectrum of **1** in CD_3OD

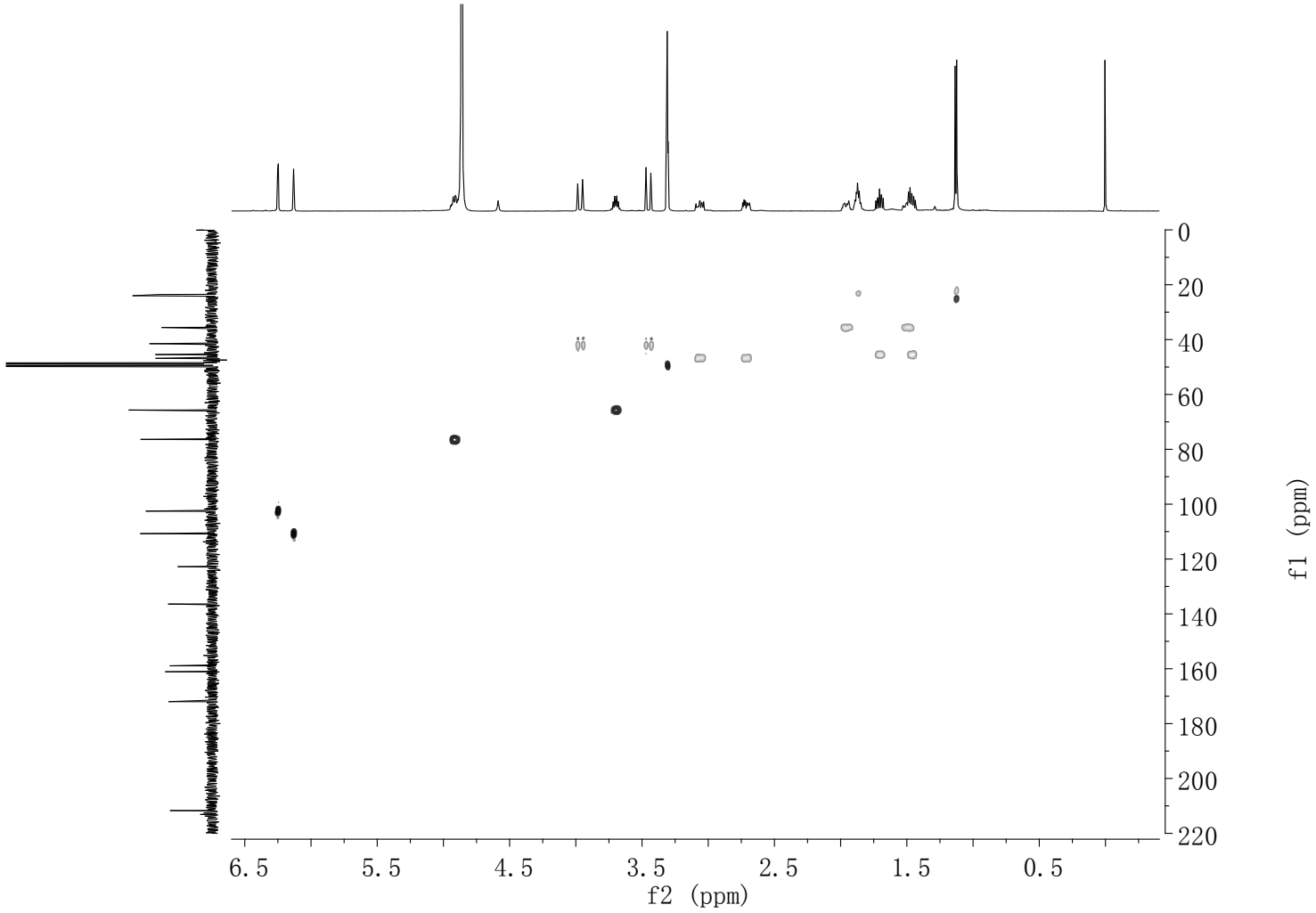


Figure S6. HMBC spectrum of **1** in CD_3OD

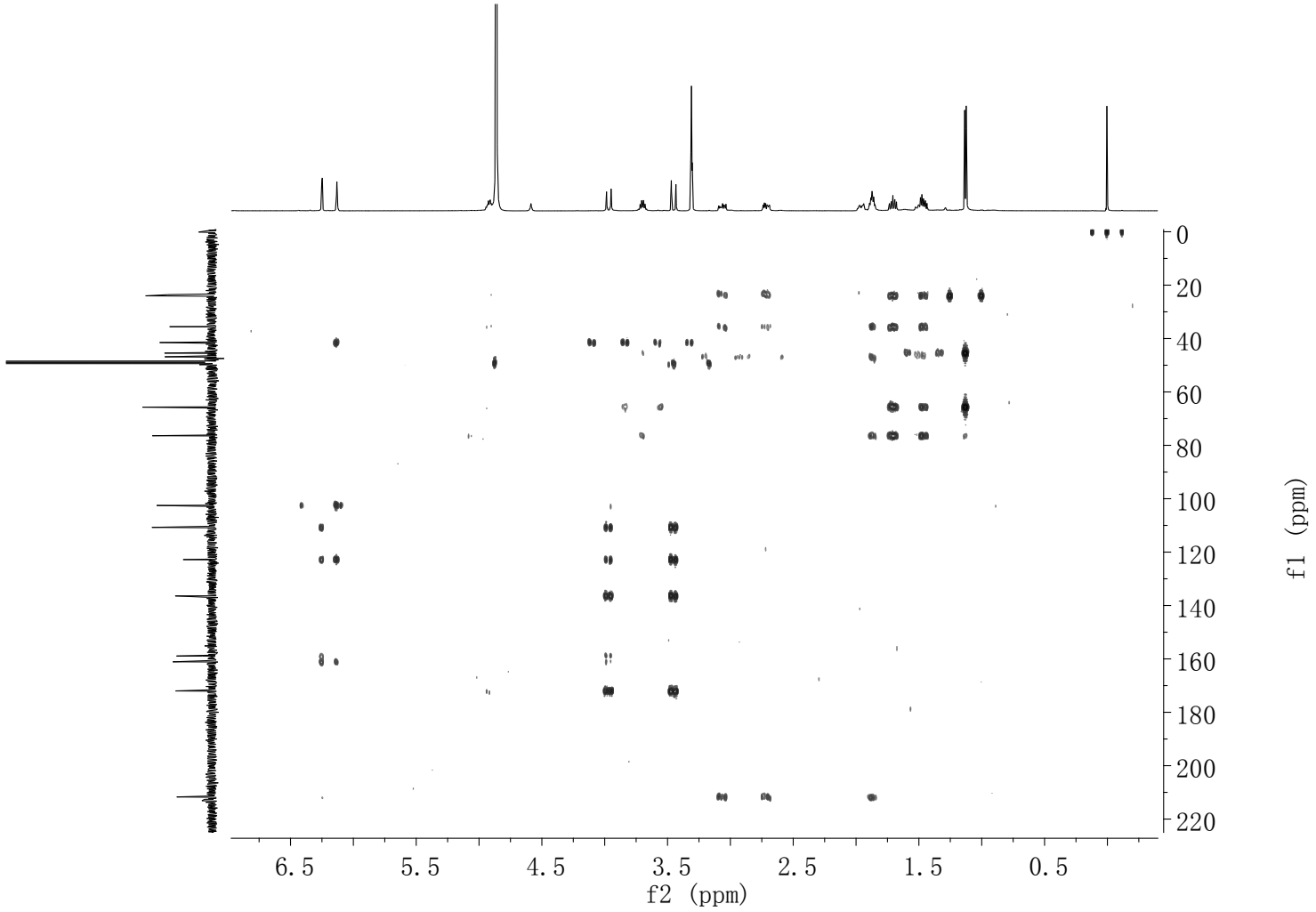
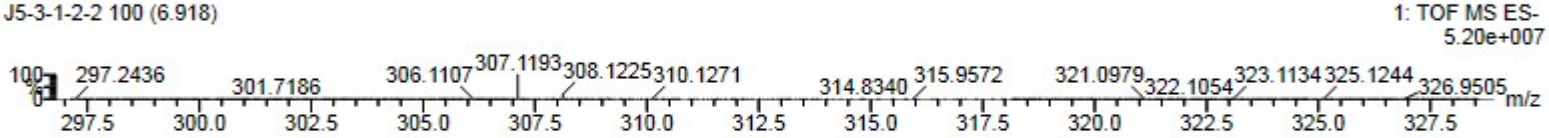


Figure S7. HRESIMS spectrum of **2**

Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-30 O: 0-10
09-Mar-2017
J5-3-1-2-2 100 (6.918)



Minimum:				-1.5				
Maximum:		2.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
307.1193	307.1182	1.1	3.6	7.5	759.2	n/a	n/a	C16 H19 O6

Figure S8. ^{1}H NMR spectrum of **2** in CD_3OD (500 MHz)

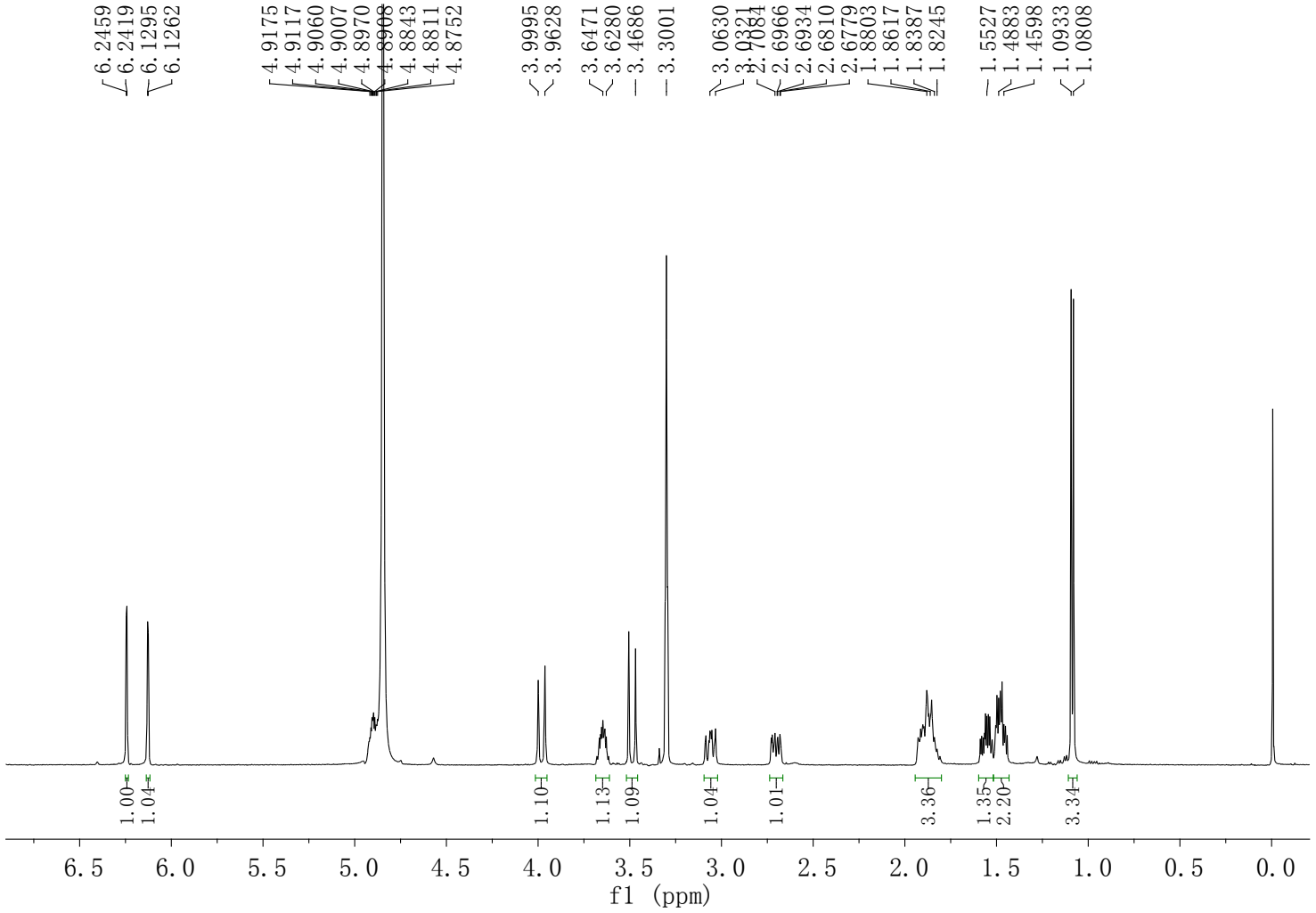


Figure S9. ^{13}C NMR spectrum of **2** in CD_3OD (125 MHz)

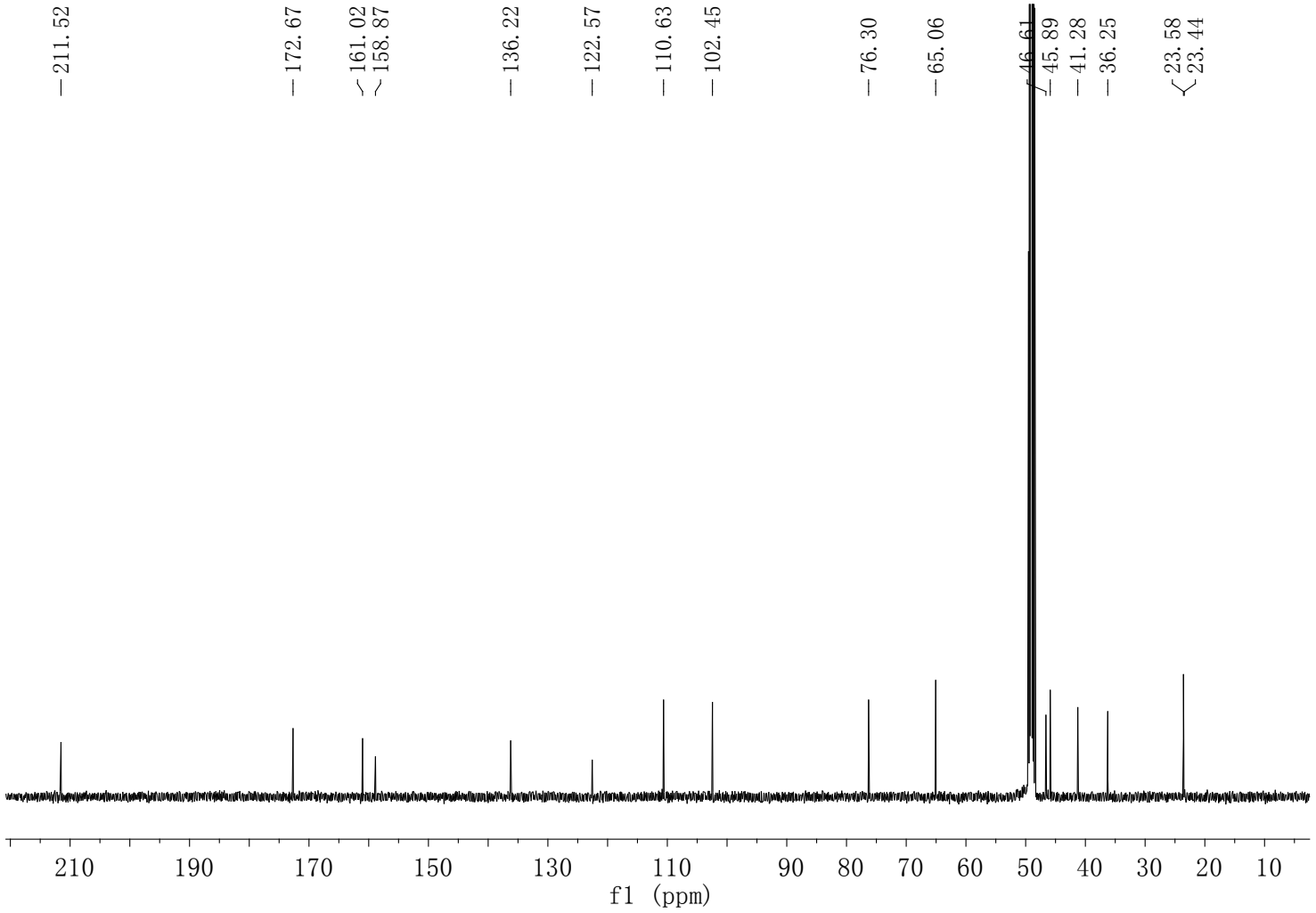


Figure S10. ^{1}H-^{1}H COSY spectrum of **2** in CD_3OD

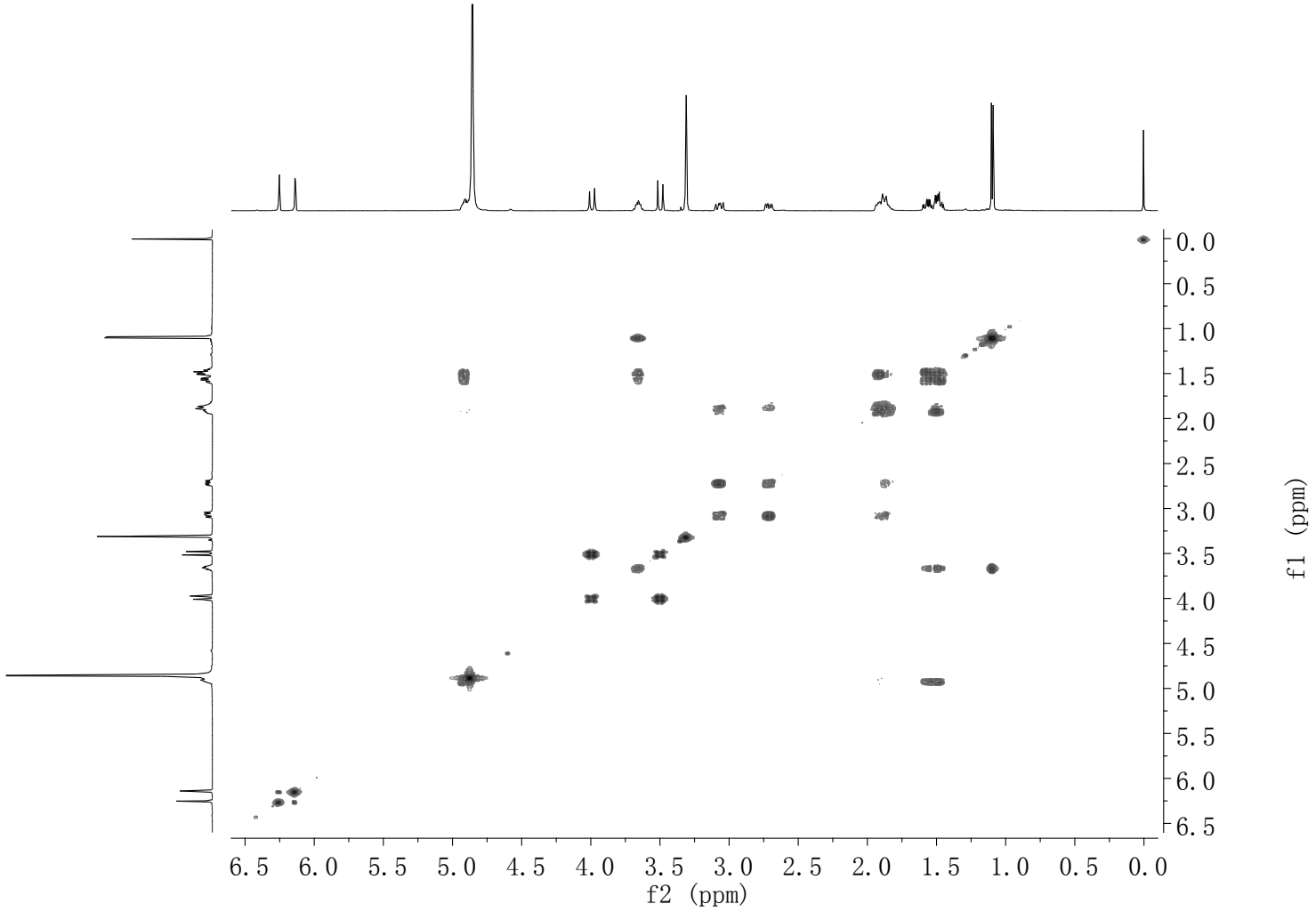


Figure S11. HSQC spectrum of **2** in CD_3OD

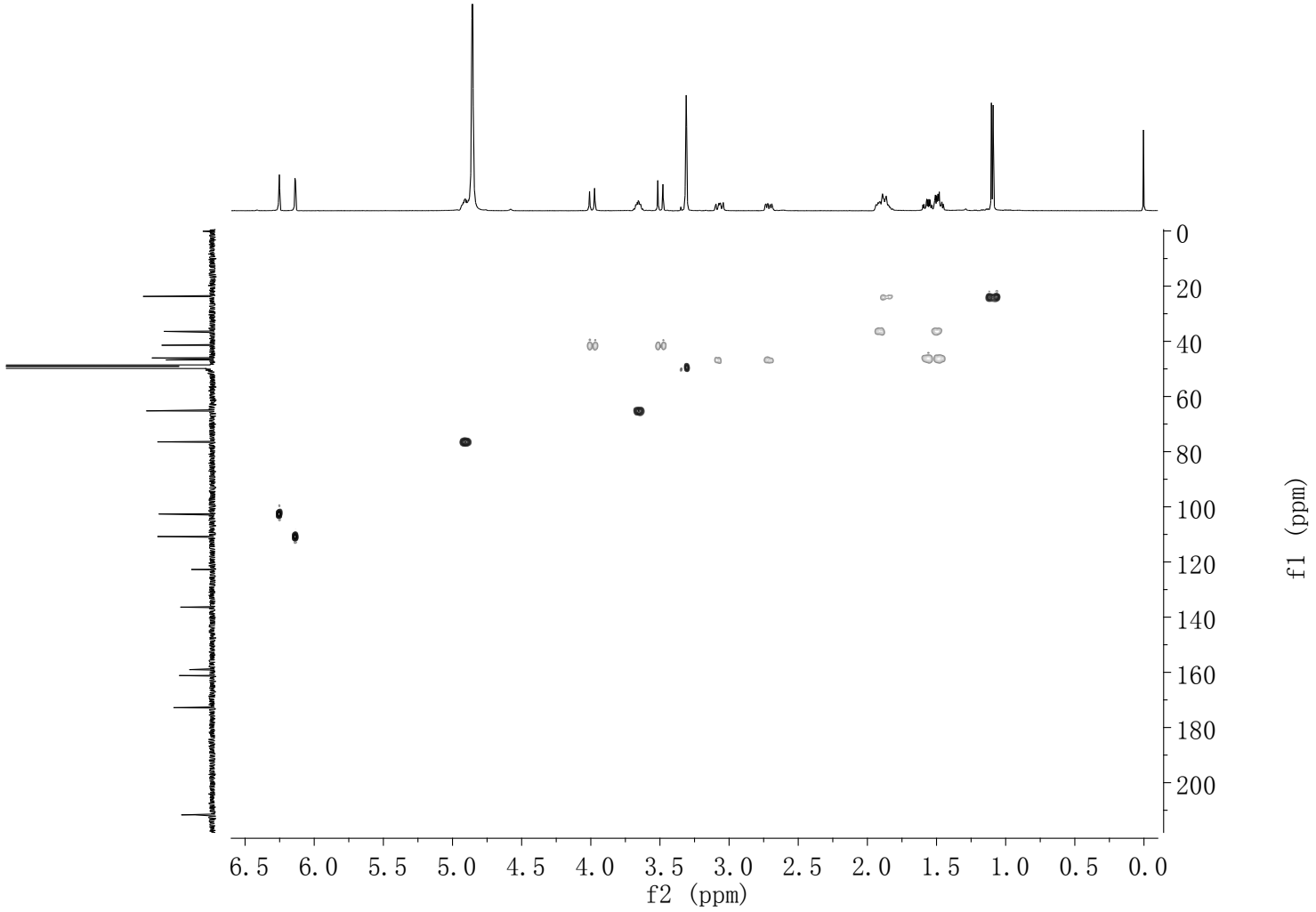


Figure S12. HMBC spectrum of **2** in CD_3OD

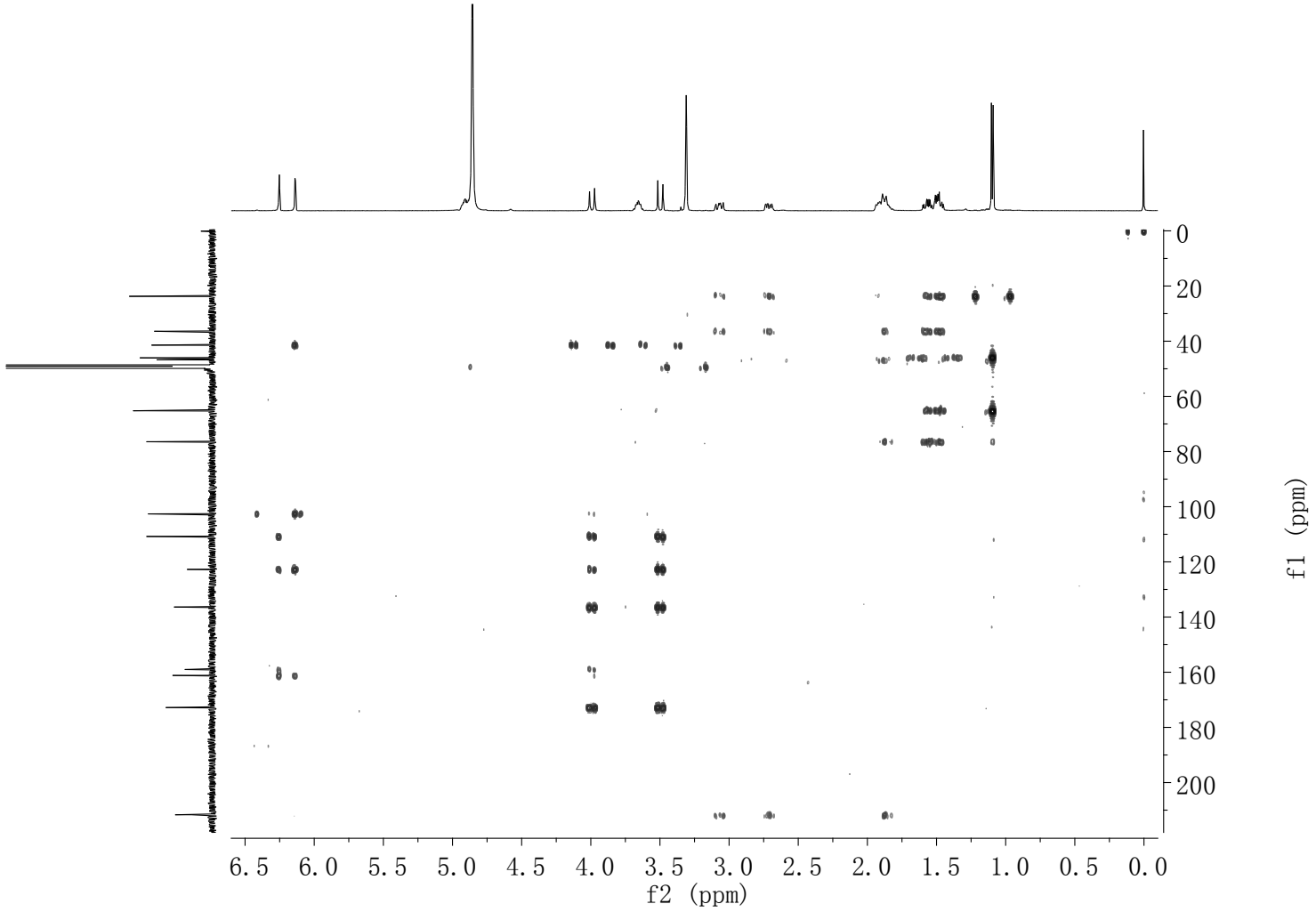


Figure S13. HRESIMS spectrum of **3**

Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
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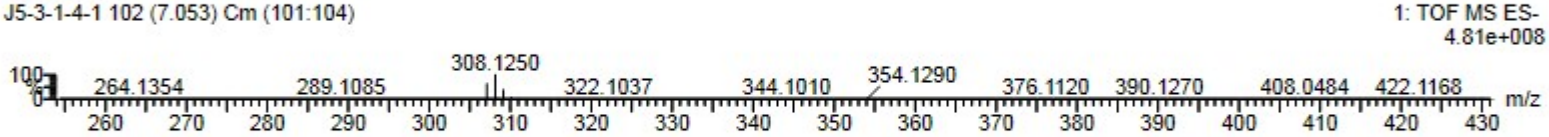
09-Mar-2017
J5-3-1-4-1 102 (7.053) Cm (101:104)



Minimum:				-1.5				
Maximum:		2.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
307.1191	307.1182	0.9	2.9	7.5	1345.6	n/a	n/a	C16 H19 O6

Figure S14. ^{1}H NMR spectrum of **3** in CD_3OD (500 MHz)

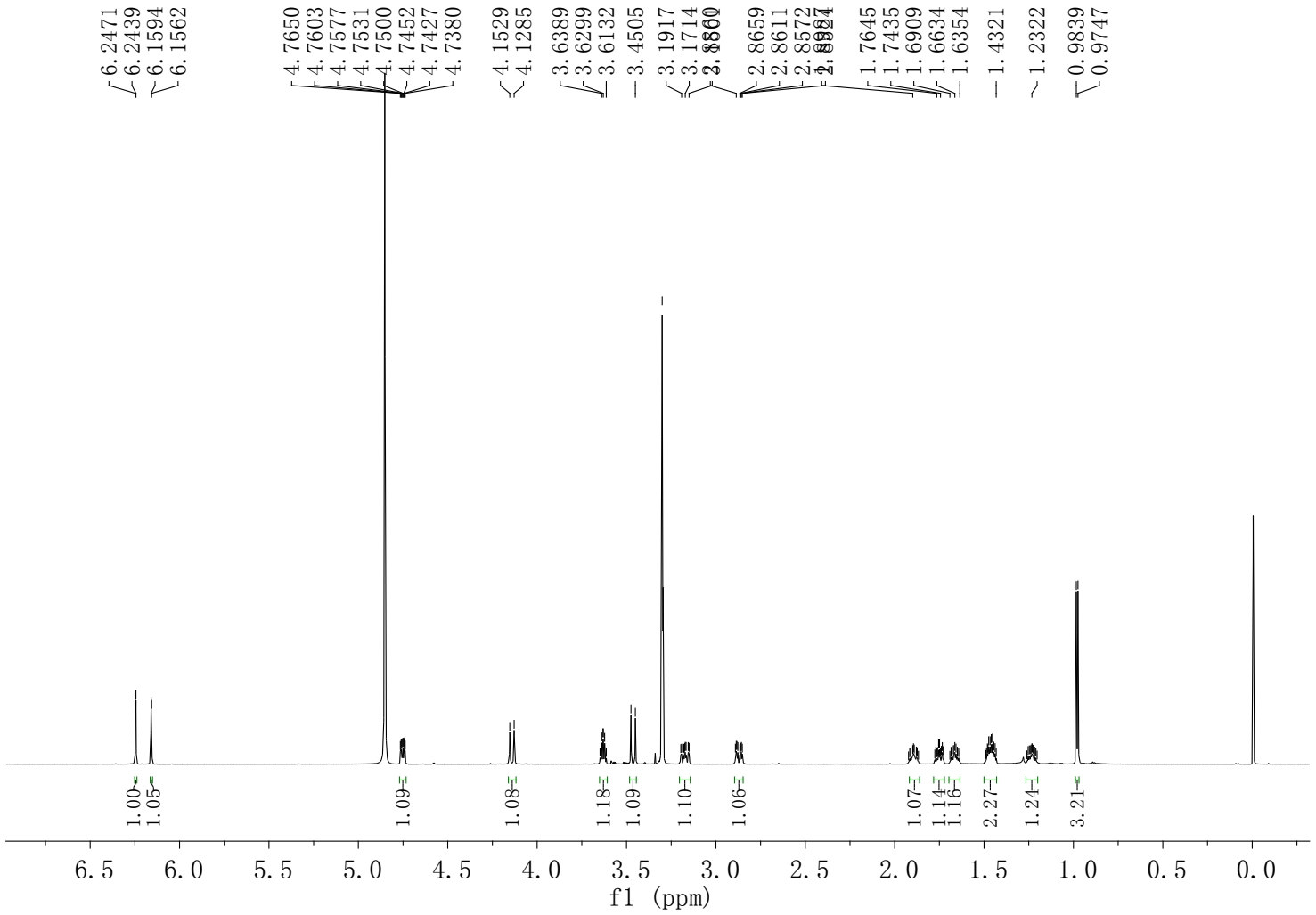


Figure S15. ^{13}C NMR spectrum of **3** in CD_3OD (125 MHz)

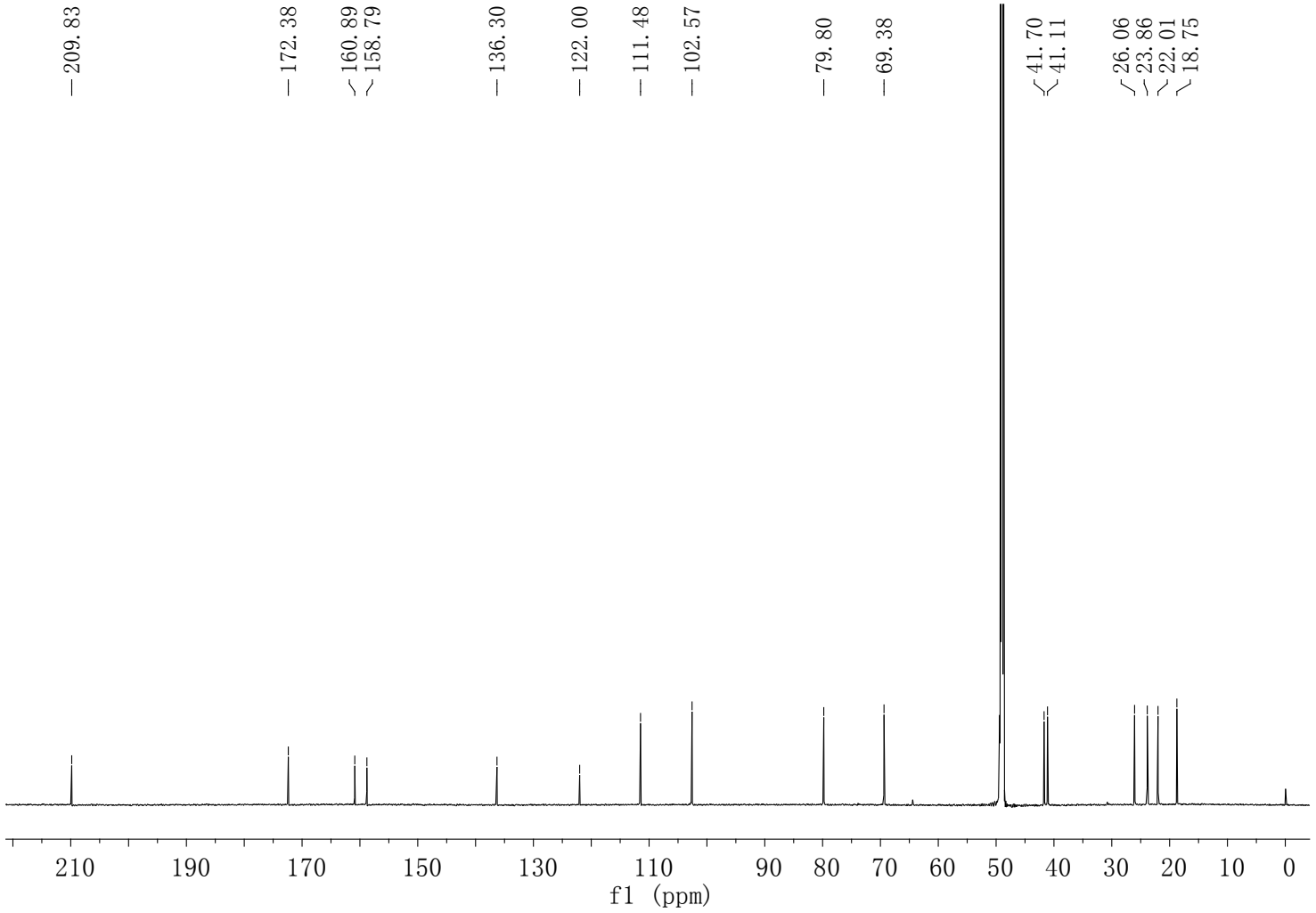


Figure S16. ^{1}H-^{1}H COSY spectrum of **3** in CD_3OD

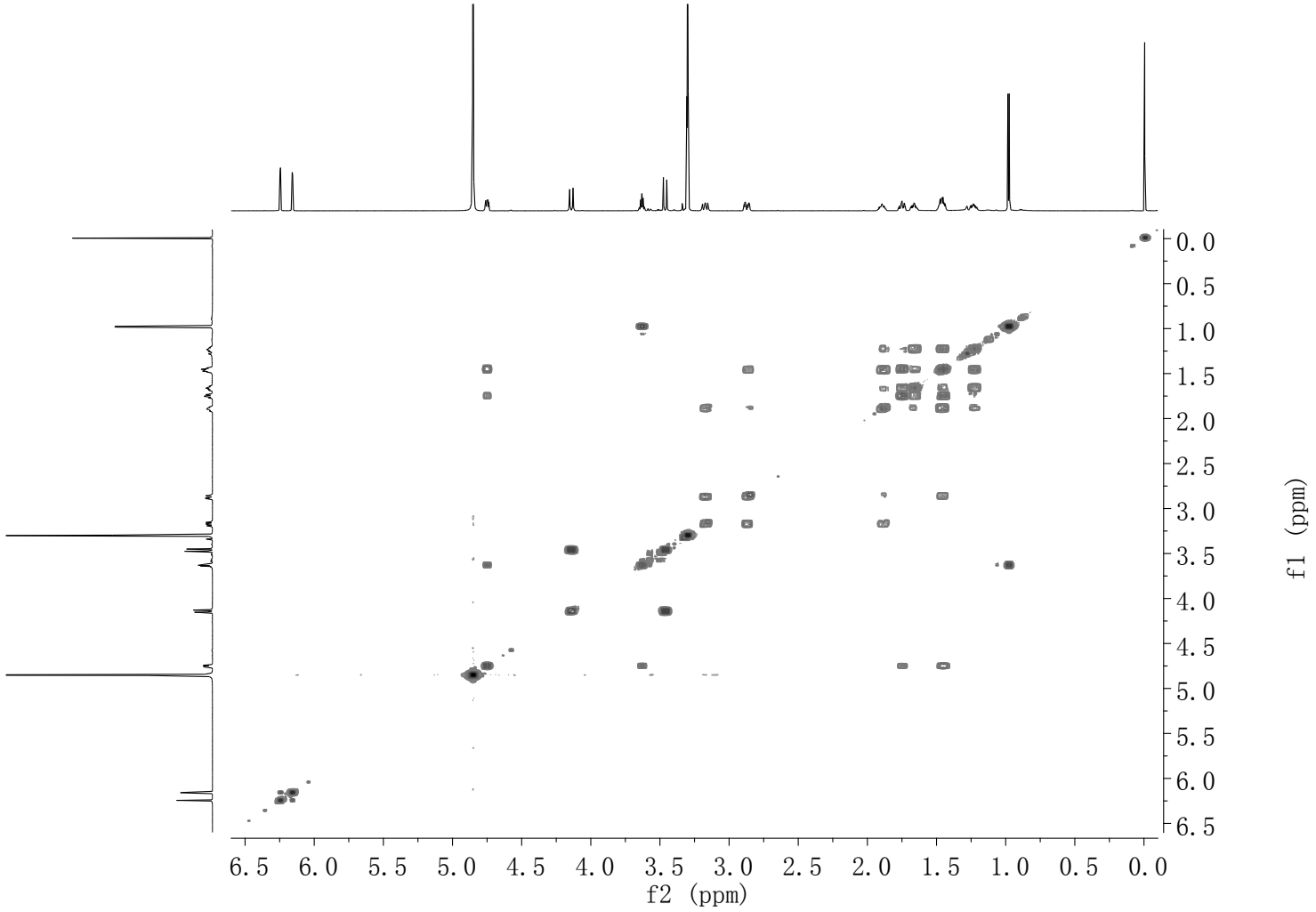


Figure S17. HSQC spectrum of **3** in CD_3OD

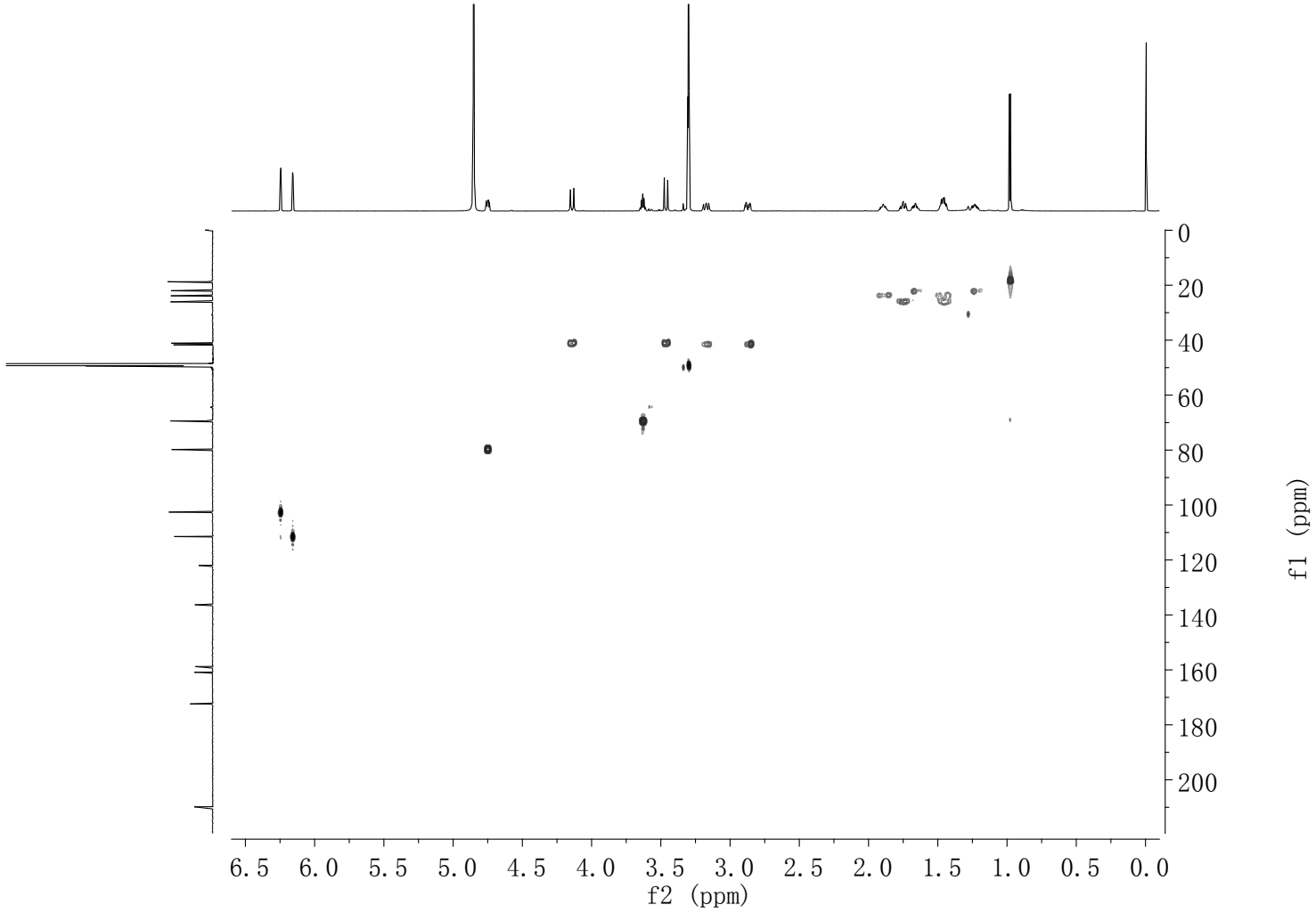


Figure S18. HMBC spectrum of **3** in CD_3OD

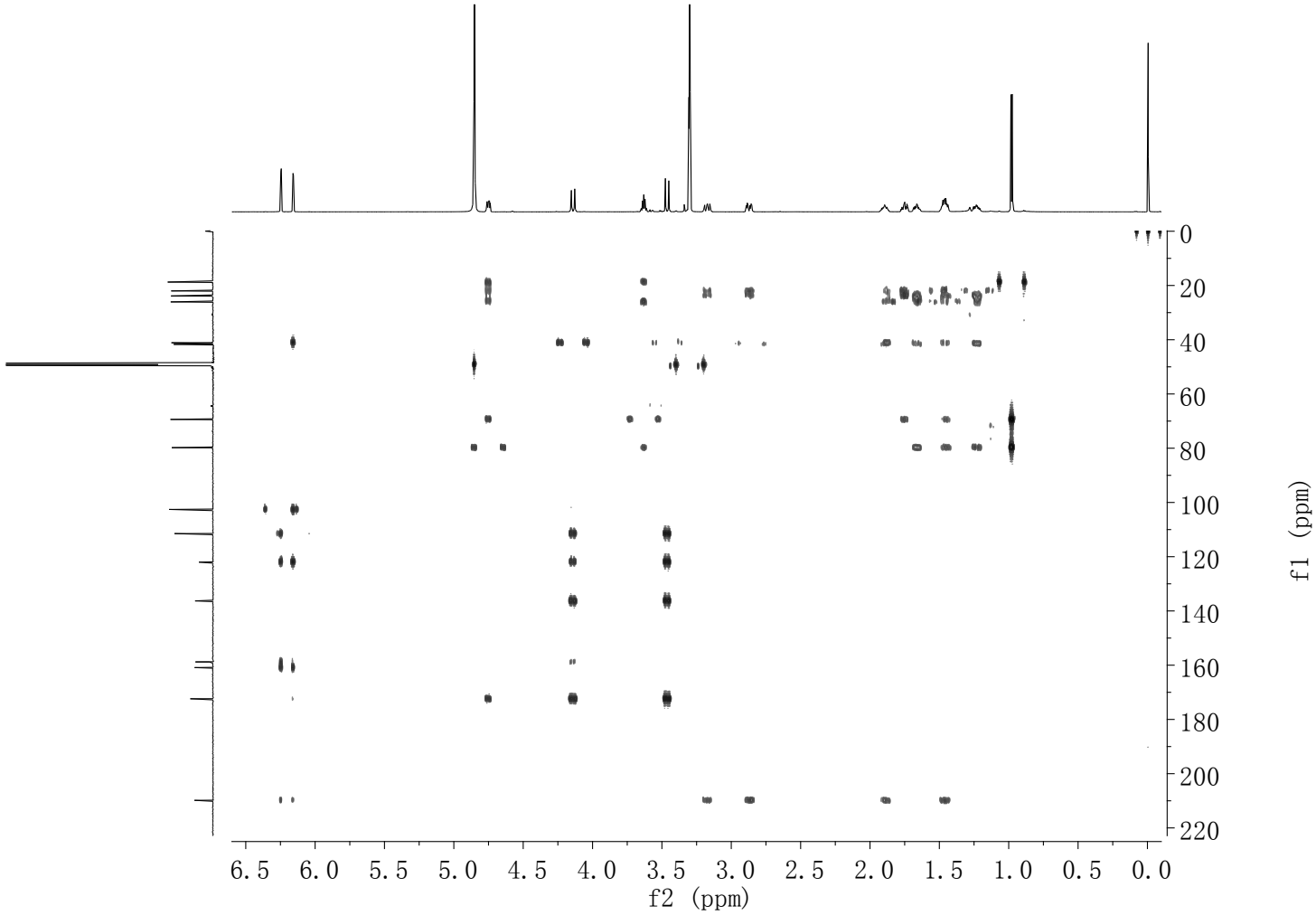
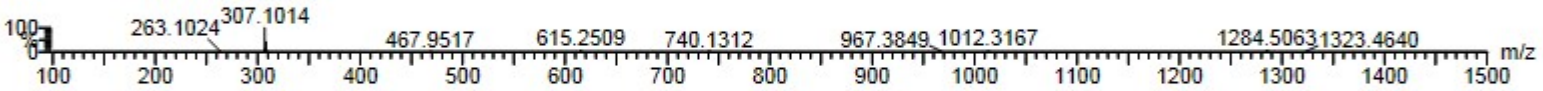


Figure S19. HRESIMS spectrum of **4**

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 14-18 H: 0-50 O: 4-8
08-Nov-2016
1108-J5-3-1-5-1 80 (3.102) Cm (79:81)

1: TOF MS ES-
6.46e+007



Minimum:				-1.5				
Maximum:		20.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
307.1014	307.1182	-16.8	-54.7	7.5	1092.4	0.592	55.31	C16 H19 O6
	307.0818	19.6	63.8	8.5	1092.6	0.805	44.69	C15 H15 O7

Figure S20. ^{1}H NMR spectrum of **4** in CD_3OD (500 MHz)

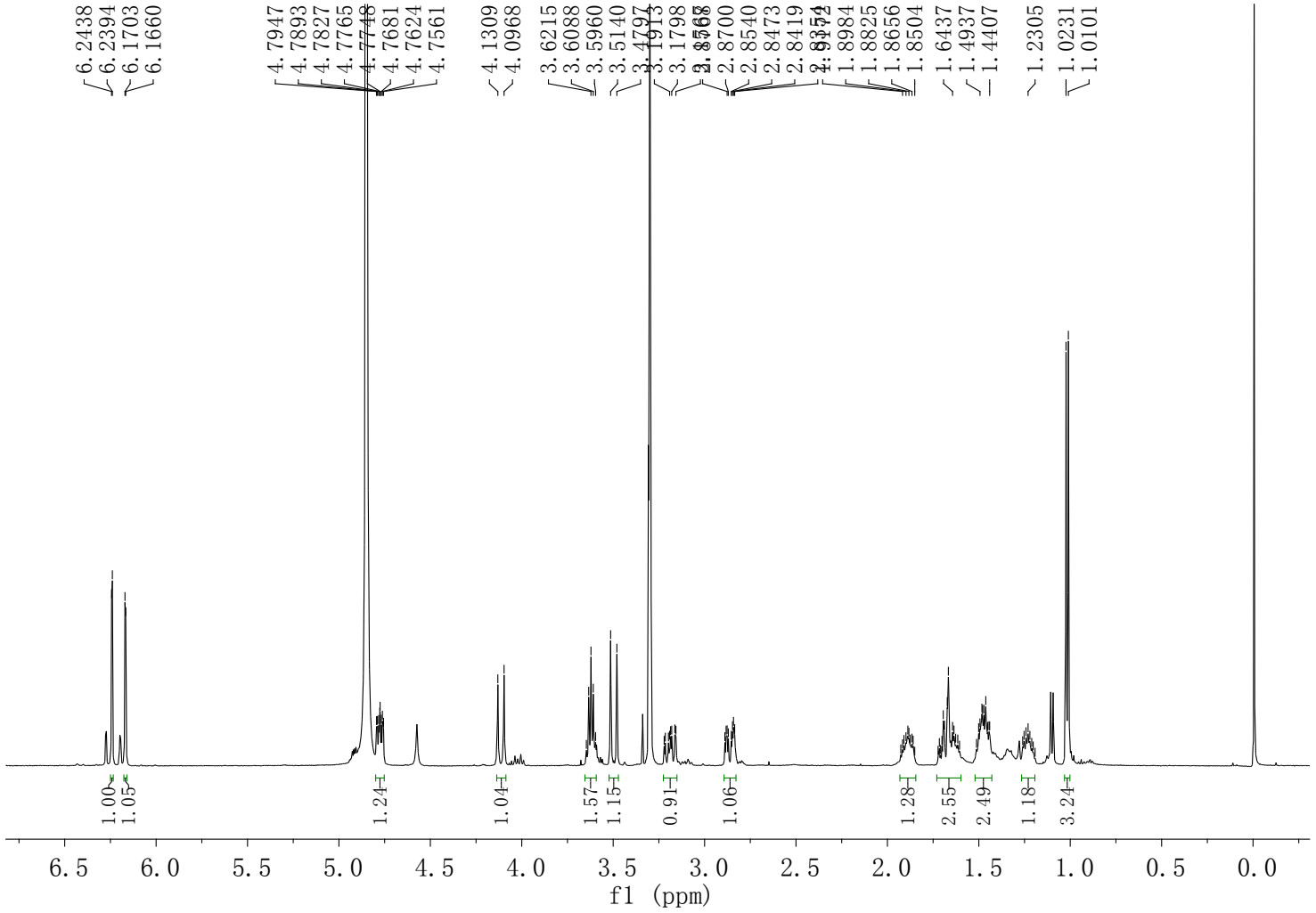


Figure S21. ^{13}C NMR spectrum of **4** in CD_3OD (125 MHz)

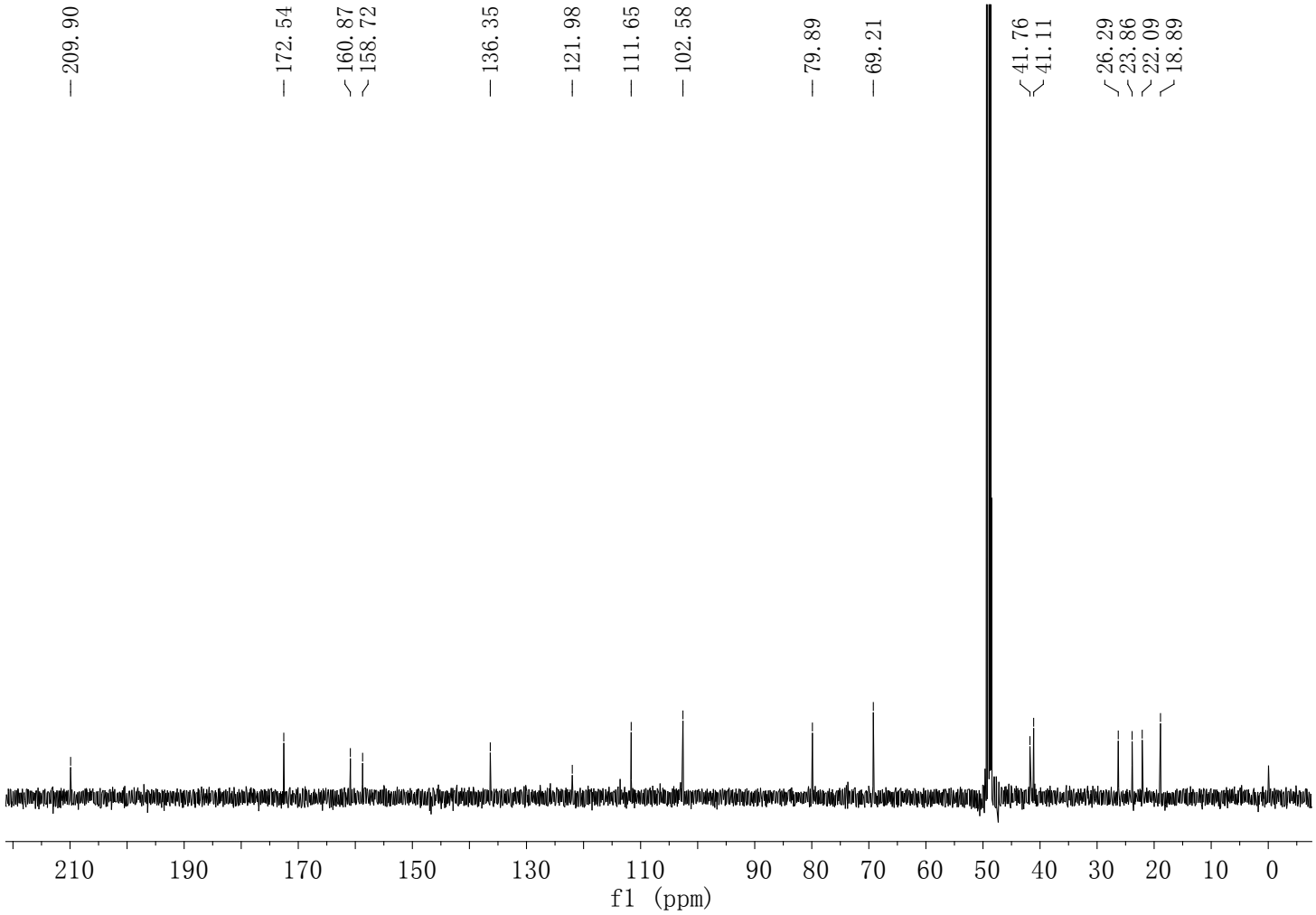


Figure S22. ^{1}H-^{1}H COSY spectrum of **4** in CD_3OD

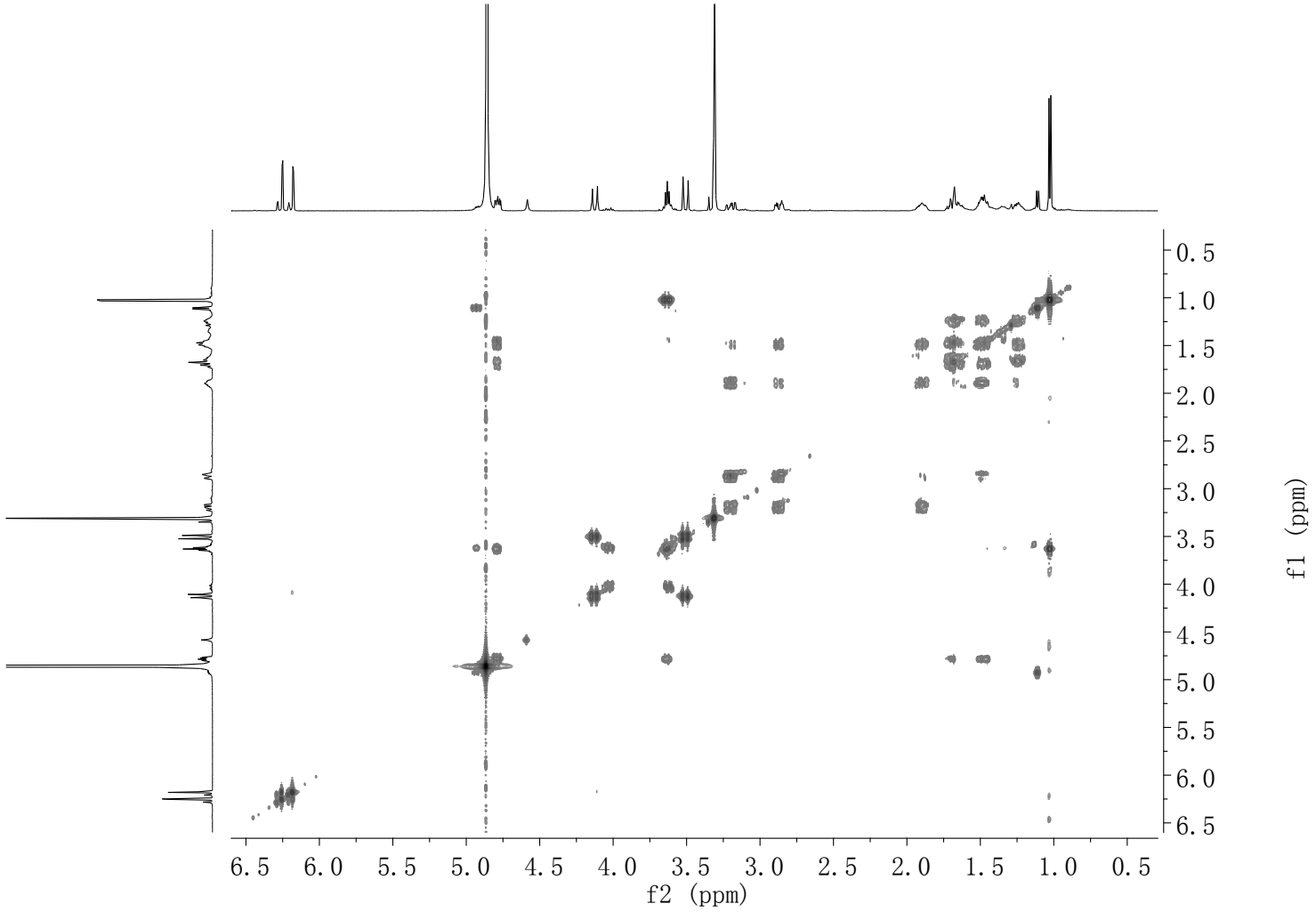


Figure S23. HSQC spectrum of **4** in CD_3OD

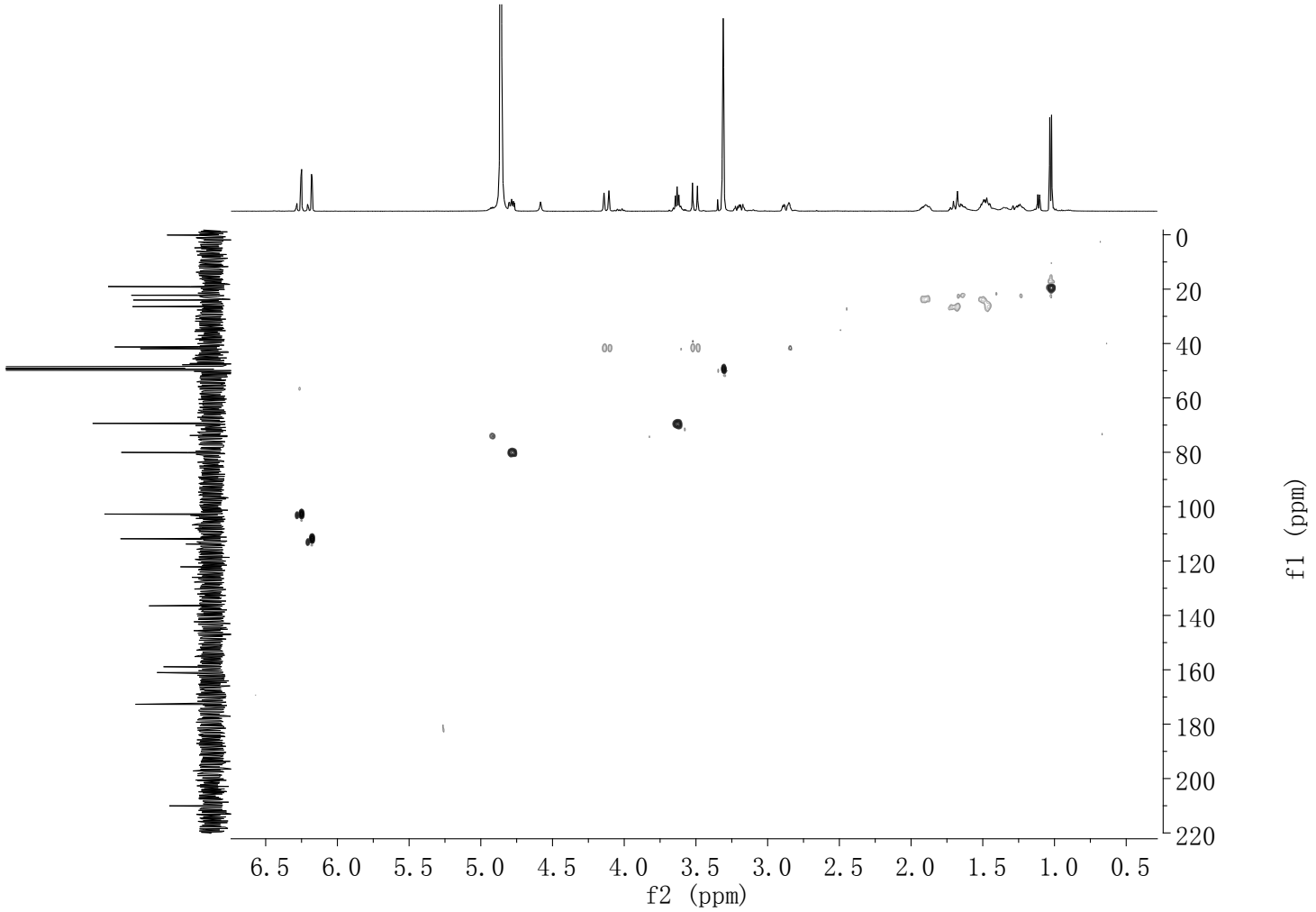


Figure S24. HMBC spectrum of **4** in CD_3OD