Supporting Information for

Sphenostylisins A-K: Bioactive Modified Isoflavonoid Constituents of the Root Bark of *Sphenostylis marginata* ssp. *erecta*

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Contents:

Table S1. 1D and 2D NMR Spectroscopic Data of Compounds 1–3[a].

no.	1				2				3			
	δ_H[b]	δ_C[c]	COSY	HMBC[d]	δ_H[b]	δ_C[c]	COSY	HMBC[d]	δ_H[b]	δ_C[c]	COSY	HMBC[d]
2α		159.9				160.1			3.77, t (9.7)	69.2	2β, 3	3, 4, 8a, 1′
2β									4.09, br d, (9.7)		2α, 3	3, 4, 8a, 1′
3		120.4				121.4			3.25, m	31.4	2α,β, 4α,β	2, 1′, 2′, 6′
4α	7.73, s	142.2		2, 4a, 5, 8a, 1′	7.56, s	141.8		2, 4a, 5, 8a, 1′	2.87, dd (15.1, 11.7)	29.7	4β, 3	2, 3, 4a, 5, 8a,
4β									2.64, dd (15.1, 3.5)		4α, 3	2, 3, 4a, 5, 8a,
4a		111.1				111.0				111.6		
5	7.46, s	126.6		4, 7, 8a, 9	7.37, s	126.4		4, 7, 8a, 9	6.81, s	127.7		4, 7, 8a, 9
6		131.6				131.5				126.1		
7		159.3				159.3				154.5		
OH-7	10.53, s			6-8					9.07, s			6-8
8	6.77, s	102.4		4a, 6, 7, 8a	6.68, s	102.2		4a, 6, 7, 8a	6.24, s	103.4		4a, 6, 7, 8a
8a		153.1				153.0				152.6		
9		39.9				39.8				39.5		
10	6.26, dd (17.5, 10.7)	147.1	11a,b	6, 9, 12, 13	6.21, dd (17.5, 10.7)	147.1	11a,b	6, 9, 12, 13	6.24, dd (17.5, 10.7)	148.0	11a,b	6, 9, 12, 13
11a	4.97, br d (10.7)	110.6	10	6, 9, 10, 12, 13	4.93, br d (10.7)	110.5	10	9, 10	4.92, br d (17.5)	109.6	10	6, 9, 10, 12,
11b	4.95, br d (17.5)		10	6, 9, 10, 12, 13	4.91, br d (17.5)		10	9, 10	4.90, br d (10.7)		10	6, 9, 10, 12,
12	1.48, s	26.9		6, 9-11, 13	1.43, s	26.9		6, 9, 10, 13	1.40, s	26.9		6, 9-11, 13
13	1.48, s	26.9		6, 9-12	1.43, s	26.9		6, 9, 10, 12	1.40, s	26.9		6, 9-12
1′		114.6				113.7				118.6		
2′		157.8				153.9				157.8		
OH-2′	9.85, s			1′-3′					9.89, s			1′-3′
3′	6.35, s	102.8		1′, 2′, 4′, 5′	6.41, s	103.9		1′, 2′, 4′, 5′	6.32, s	102.6		1′, 2′, 4′, 5′
4′		155.9				155.5				154.7		
OH-4′	10.04, s			3′-5′					9.75, s			3′-5′
5′		108.4				116.8				108.3		
6′	7.52, s	131.7		3, 2′, 4′, 2″	6.67, s	131.4		3, 2′, 4′, 8″	7.23, s	128.1		3, 2′, 4′, 2″
2″		152.2				149.3				153.0		
3″		114.0				114.7				113.7		
3″a		120.1				121.9				120.1		
4″	7.33, d (8.4)	120.6	5″	3″, 6″, 7″, 7″a	7.19, d (8.4)	119.8	5″	3″, 6″, 7″a	7.38, d (8.4)	120.4	5″	3″, 6″, 7″, 7″a
5″	6.78, dd (8.4, 1.6)	112.7	4″, 7″	3″a, 4″, 6″, 7″	6.60, dd (8.4, 1.8)	111.0	4″, 7″	3″a, 4″, 6″, 7″	6.77, dd (8.4, 1.6)	112.6	4″, 7″	3″a, 4″, 6″, 7″
6″		155.8				154.8				155.7		
OH-6″	9.67, s			5″-7″					9.65, s			5″-7″
7″	6.98, d (1.6)	97.4	5″	3″a, 5″, 6″, 7″a	6.80, d (1.8)	97.3	5″	3″a, 5″, 6″, 7″a	6.97, d (1.6)	97.4	5″	3″a, 5″, 6″,
7″a		154.2				154.7				154.2		
8″		194.7			3.71, s	22.6		4′-6′, 2″, 3″, 3″a		194.6		
9″		112.9				108.1				112.8		
10″		162.5				154.6				162.4		
OH-10″	12.66, s			9″-11″					12.64, s			9″-11″
11″	6.34, s	103.2		8″-10″, 12″, 13″	6.44, s	102.4		9″, 10″, 12″, 13″	6.29, s	103.1		8″-10″, 12″,
12″		163.2				157.2				163.0		
OH-12″	10.54, s			11″-13″					10.47, s			11″-13″
13″		125.8				124.7				125.6		
14″	7.32, s	131.4		8″, 10″, 12″, 15″	7.01, s	129.5		2″, 10″, 12″, 15″	7.21, s	131.1		8″, 10″, 12″,
15″		39.2				39.4				39.0		
16″	5.84, dd (17.5, 10.7)	147.2	17″a,b	13″, 15″, 18″, 19″	6.10, dd (17.5, 10.7)	147.9	17″a,b	13″, 15″, 18″, 19″	5.78, dd (17.5, 10.7)	147.2	17″a,b	13″, 15″, 18″,
17″a	4.74, br d (10.7)	110.2	16″	15″, 18″, 19″	4.78, br d (17.5)	109.6	16″	15″, 16″	4.73, br d (10.7)	110.0	16″	15″, 16″, 18″,
17″b	4.67, br d (17.5)		16″	15″, 16″, 18″, 19″	4.75, br d (10.7)		16″	15″, 16″	4.61, br d (17.5)		16″	15″, 16″, 18″,
18″	1.09, s	26.6		13″, 15″-17″, 19″	1.27, s	26.7		13″, 15″, 16″, 19″	1.04, s	26.7		13″, 15″-17″,
19″	1.09, s	26.6		13″, 15″-18″	1.27, s	26.7		13″, 15″, 16″, 18″	1.04, s	26.7		13″, 15″-18″

[a] NMR data obtained in DMSO-d_6. Assignments are based on ^{1}H–^{1}H COSY, HSQC, and HMBC spectroscopic data.
[b] Measured at 800 MHz for ^{1}H NMR; δ in ppm, mult. (J in Hz).
[c] Measured at 150 MHz for ^{13}C NMR; δ in ppm.
[d] HMBC correlations are presented from proton to indicated carbons.

Table S2. 1D and 2D NMR Spectroscopic Data of Compounds 4–7[a].

no	**4**				**5**				**6**				**7**			
	δ_H[b]	δ_C[c]	COSY	HMBC[d]	δ_H[b]	δ_C[c]	COSY	HMBC[d]	δ_H[b]	δ_C[c]	COSY	HMBC[d]	δ_H[b]	δ_C[c]	COSY	HMBC[d]
2		160.3				163.7				164.0				160.3		
3		121.0				122.9				122.9				120.9		
4	7.80, s	142.1		2, 5, 8a, 1'	7.87, s	144.2		2, 5, 8a, 1'	7.79, s	144.1		2, 5, 8a, 1'	7.80, s	142.2		2, 5, 8a, 1'
4a		111.2				115.3				113.7				111.3		
5	7.45, s	126.4		4, 7, 8a, 9	7.38, s	122.6		4, 7, 8a, 9	7.33, s	132.7		4, 7, 8a, 12	7.45, s	128.3		4, 7, 8a, 9
6		131.6				137.2				124.4				129.1		
7		159.1				162.8				161.4				159.2		
8	6.74, s	102.3		4a, 6, 7, 8a	6.76, s	98.4		4a, 6, 7, 8a	6.75, s	103.4		4a, 6, 7, 8a	6.72, s	102.3		4a, 6, 7, 8a
8a		153.0				156.0				155.2				153.0		
9		39.9				43.7				75.3				46.1		
10	6.23, dd (17.5, 10.7)	147.1	11a,b	6, 9, 12, 13	4.45, dd (6.3, 5.3)	95.6	11a,b	6, 7, 9, 11-13	6.01, dd (17.3, 10.8)	146.0	11a,b	9, 12, 13	6.26, dd (17.6, 10.8)	144.1	11a,b	6, 9, 12, 13
11a	4.95, dd (10.7, 1.2)	110.5	10	9, 10	3.86, br d (5.3)	61.9	10	9, 10	5.20, dd (17.3, 1.2)	112.2	10	9, 10	5.02, dd (10.8, 1.1)	112.5	10	9
11b	4.93, dd (17.5, 1.2)		10	9, 10	3.85, br d (6.3)		10	9, 10	5.00, dd (10.8, 1.2)		10	9	4.92, dd (17.6, 1.1)		10	9, 10
12a	1.45, s	26.9		6, 9, 10, 13	1.44, s	28.2		6, 9, 10, 13	2.92, d (13.9)	43.6	12b	5-7, 9, 10	3.79, d (10.3)	67.1	12b	6, 9, 10, 13
12b									2.87, d (13.9)		12a	5-7, 9, 13	3.72, d (10.3)		12a	6, 9, 10, 13
13	1.45, s	26.9		6, 9, 10, 12	1.25, s	23.2		6, 9, 10, 12	1.26, s	27.0		9, 10, 12	1.41, s	21.8		6, 9, 10, 12
1′		113.8				115.4				115.6				113.7		
2′		156.0				157.4				157.4				156.0		
3′	6.35, d (2.2)	102.6	5'	1′, 2′, 4′, 5′	6.38, d (2.3)	104.0	5'	1′, 2′, 4′, 5′	6.38, d (2.3)	104.0	5'	1′, 2′, 4′, 5′	6.35, d (2.2)	102.6	5'	1′, 2′, 4′, 5′
4′		158.3				160.0				160.0				158.3		
5′	6.26, dd (8.3, 2.2)	106.2	3', 6'	1′, 3′, 4′, 6′	6.35, dd (8.2, 2.3)	107.9	3', 6'	1′, 3′, 4′, 6′	6.35, dd (8.2, 2.3)	107.9	3', 6'	1′, 3′, 4′	6.25, dd (8.3, 2.2)	106.2	3', 6'	1′, 3′, 4′
6′	7.03, d (8.3)	131.5	5'	3, 2′, 4′	7.12, d (8.2)	132.7	5'	3, 2′, 4′	7.11, d (8.2)	132.7	5'	3, 2′, 4′	7.02, d (8.3)	131.5	5	3, 2′, 4′

[a] NMR data obtained in DMSO-d_6 for **4** and **7**, and in CD_3OD for **5** and **6**. Assignments are based on ^1H–^1H COSY, HSQC, and HMBC spectroscopic data.

[b] Measured at 400 MHz for ^1H NMR; δ in ppm, mult. (J in Hz).

[c] Measured at 100 MHz for ^{13}C NMR; δ in ppm.

[d] HMBC correlations are presented from proton to indicated carbons.

Table S3. 1D and 2D NMR Spectroscopic Data of Compound 8[a].

no	**8**			
	δ_H[b]	δ_C[c]	COSY	HMBC[d]
2	8.10, s	156.3		3, 4, 8a, 1′
3		124.1		
4		179.2		
4a		117.0		
5	8.13, s	127.4		4, 7, 8a, 9
6		133.3		
7		164.1		
8	6.86, s	104.0		4, 4a, 6, 7, 8a
8a		158.5		
9		48.0		
10	6.33, dd (17.4, 10.6)	144.6	11a,b	6, 9, 12, 13
11a	5.14, br d (10.6)	113.8	10	9
11b	5.04, br d (17.4)		10	9, 10
12a	4.03, d (10.7)	69.3	12b	6, 9, 10, 13
12b	3.89, d (10.7)		12a	6, 9, 10, 13
13	1.53, s	22.4		6, 9, 10, 12
1′		112.3		
2′		158.0		
3′	6.40, d (2.2)	104.7	5'	1′, 2′, 4′, 5′
4′		160.2		
5′	6.38, dd (8.2, 2.2)	108.3	3', 6'	1′, 3′, 4′
6′	7.05, d (8.2)	132.9	5'	3, 2′, 4′

[a] NMR data obtained in CD_3OD. Assignments are based on ^1H–^1H COSY, HSQC, and HMBC spectroscopic data.
[b] Measured at 400 MHz for ^1H NMR; δ in ppm, mult. (J in Hz).
[c] Measured at 100 MHz for ^{13}C NMR; δ in ppm.
[d] HMBC correlations are presented from proton to indicated carbons

Table S4. 1D and 2D NMR Spectroscopic Data of Compounds 9–11[a].

no	**9**				**10**				**11**			
	δ_H[b]	δ_C[c]	COSY	HMBC[d]	δ_H[b]	δ_C[c]	COSY	HMBC[d]	δ_H[b]	δ_C[c]	COSY	HMBC[d]
1		112.3				112.2				112.2		
2		164.4				164.5				164.5		
3	6.24, d (2.3)	102.4	5	1, 2, 4, 5	6.23, d (2.3)	102.4	5	1, 2, 4, 5	6.19, d (2.3)	102.4	5	1, 2, 4, 5
4		164.7				164.6				164.8		
5	6.38, dd (8.8, 2.3)	108.0	3, 6	1, 3, 4	6.34, dd (8.9, 2.3)	108.0	3, 6	1, 3, 4	6.32, dd (8.9, 2.3)	108.1	3, 6	1, 3, 4
6	7.94, d (8.8)	133.1	5	2, 4, 7	7.89, d (8.9)	133.2	5	2, 4, 7	7.91, d (8.9)	133.2	5	2, 4, 7
7		202.9				203.2				203.1		
8a	4.11, d (16.3)	38.7	8b	7, 1′, 2′, 6′	4.01, d (15.7)	38.4	8b	7, 1′, 2′, 6′	3.99, br s	38.5		7, 1′, 2′, 6′
8b	4.03, d (16.3)		8a	7, 1′, 2′, 6′	3.96, d (15.7)		8a	7, 1′, 2′, 6′				
1′		113.4				111.9				111.3		
2′		154.8				153.9				153.9		
3′	6.23, s	96.8		1′, 2′, 4′, 5′	6.30, s	102.7		1′, 2′, 4′, 5′	6.29, s	103.5		1′, 2′, 4′, 5′
4′		157.5				155.2				155.2		
5′		127.6				114.9				121.6		
6′	6.83, s	124.2		8, 2′, 4′, 7′	6.73, s	134.2		8, 2′, 4′, 7′	6.83, s	130.5		8, 2′, 4′, 7′
7′		42.1			2.57, s	42.1		4′-6′, 8′, 9′, 11′		45.6		
8′	4.16, dd (6.7, 5.2)	92.8	9′	9′-11′		73.5			6.20, dd (17.6, 10.6)	145.0	9′a,b	5′, 7′, 10′, 11′
9′a	3.65, m	60.0	8′	7′	5.89, dd (17.3, 10.7)	146.0	10′a,b	8′	4.96, br d (10.6)	111.7	8′	7′, 8′
9′b									4.89, br d (17.6)		8′	7′, 8′
10′a	1.27, s	27.2		5′, 7′, 8′, 11′	5.08, dd (17.3, 1.9)	110.7	9′, 10′b	8′, 9′	3.67, d (10.5)	67.6	10′b	5′, 7′, 8′, 11′
10′b					4.87, dd (10.7, 1.9)		9′, 10′a	8′	3.65, d (10.5)		10′a	5′, 7′, 8′, 11′
11′	1.02, s	23.2		5′, 7′, 8′, 10′	1.07, s	26.4		7′-9′	1.29, s	21.4		5′, 7′, 8′, 10′

[a] NMR data obtained in DMSO-d_6 for **9**-**11**. Assignments are based on ^{1}H–^{1}H COSY, HSQC, and HMBC spectroscopic data.

[b] Measured at 400 MHz for ^{1}H NMR; δ in ppm, mult. (J in Hz).

[c] Measured at 100 MHz for ^{13}C NMR; δ in ppm.

[d] HMBC correlations are presented from proton to indicated carbons.

Scheme S1. A Plausible Biogenetic Pathway of the New Compounds 1–11.

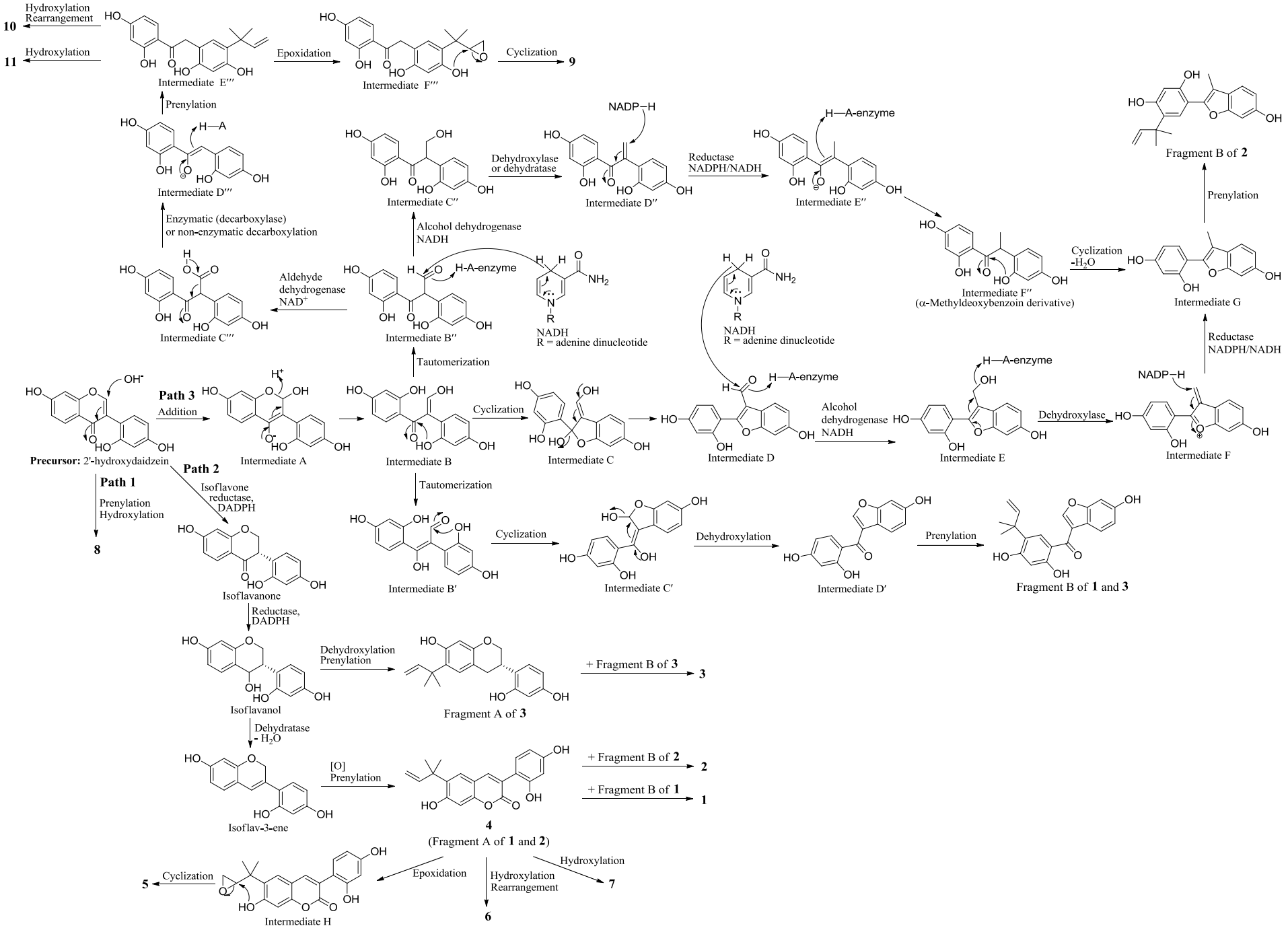


Figure S1a. ^{1}H NMR spectrum of compound **1**.

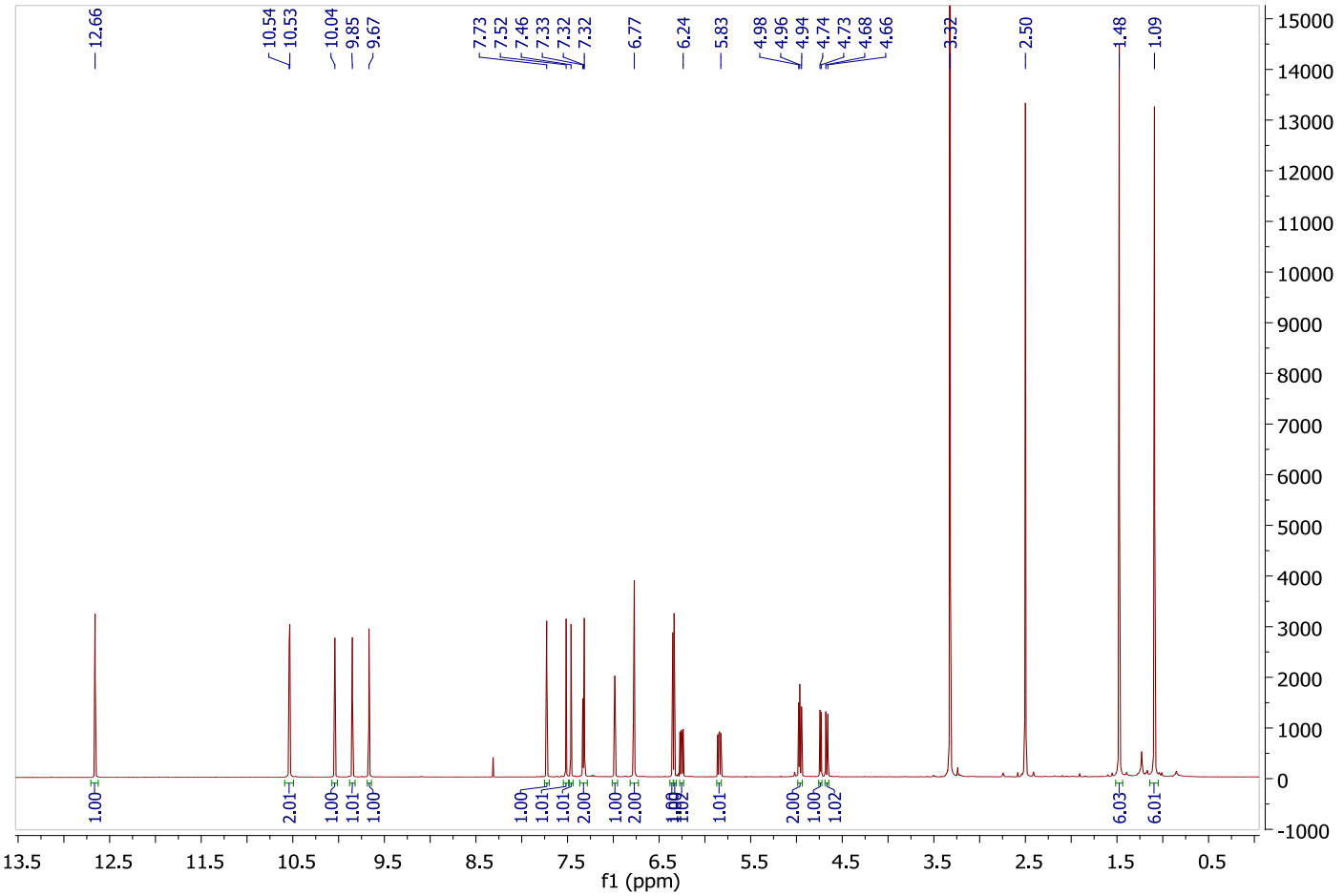


Figure S1b. ^{13}C NMR spectrum of compound **1**.

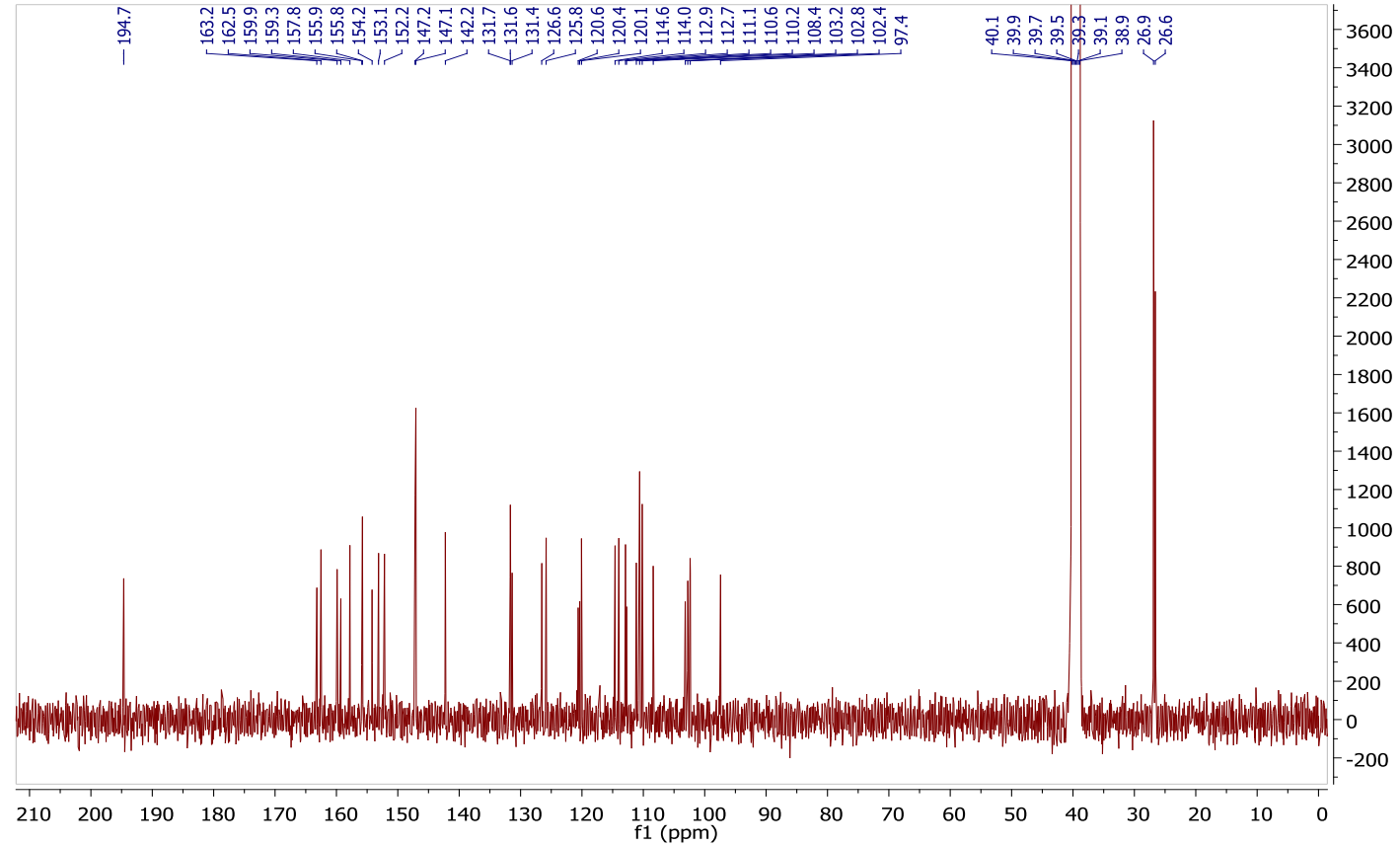


Figure S1c. ^{13}C DEPT 135 NMR spectrum of compound **1**.

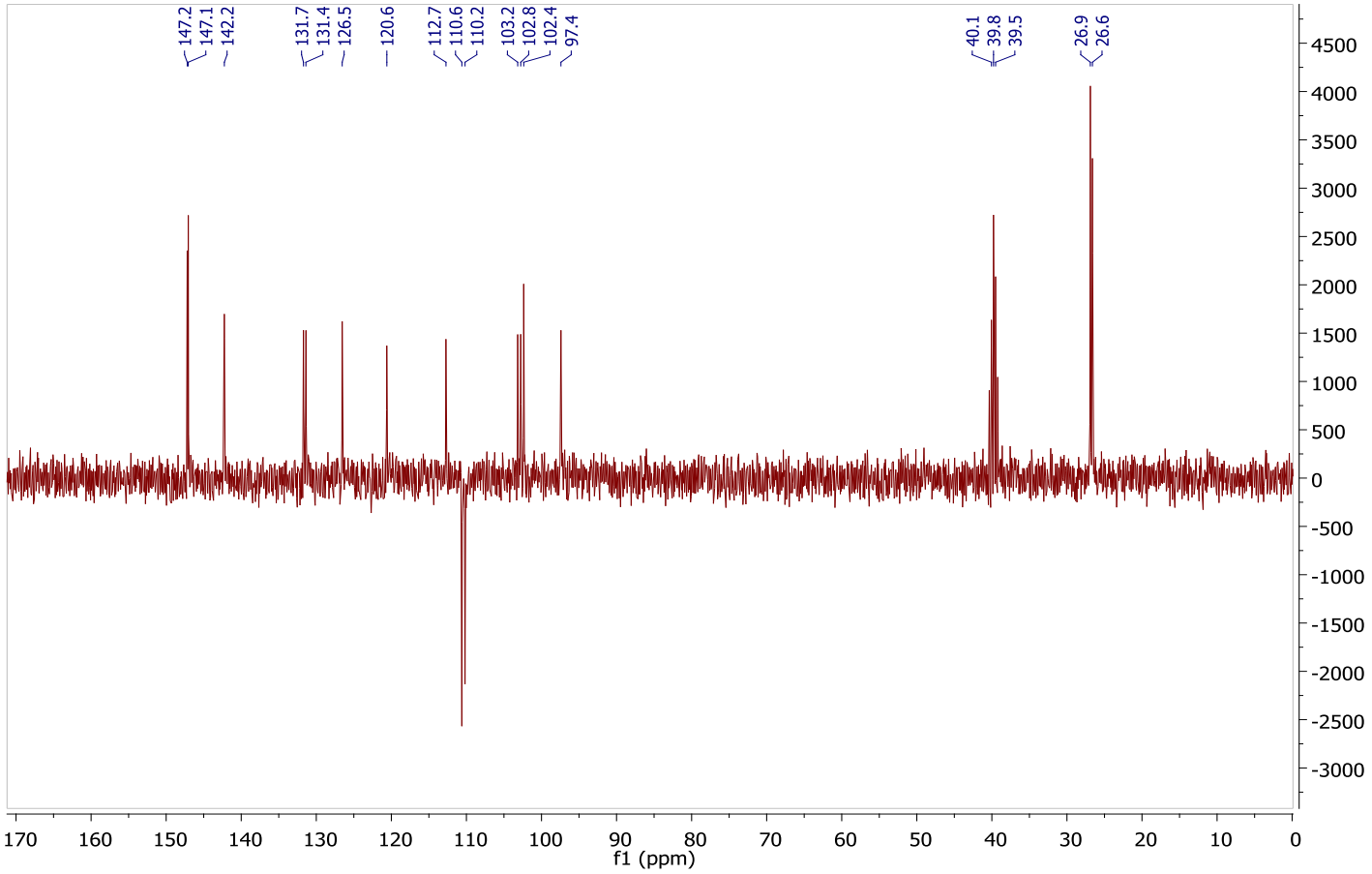


Figure S1d. HSQC spectrum of compound **1**.

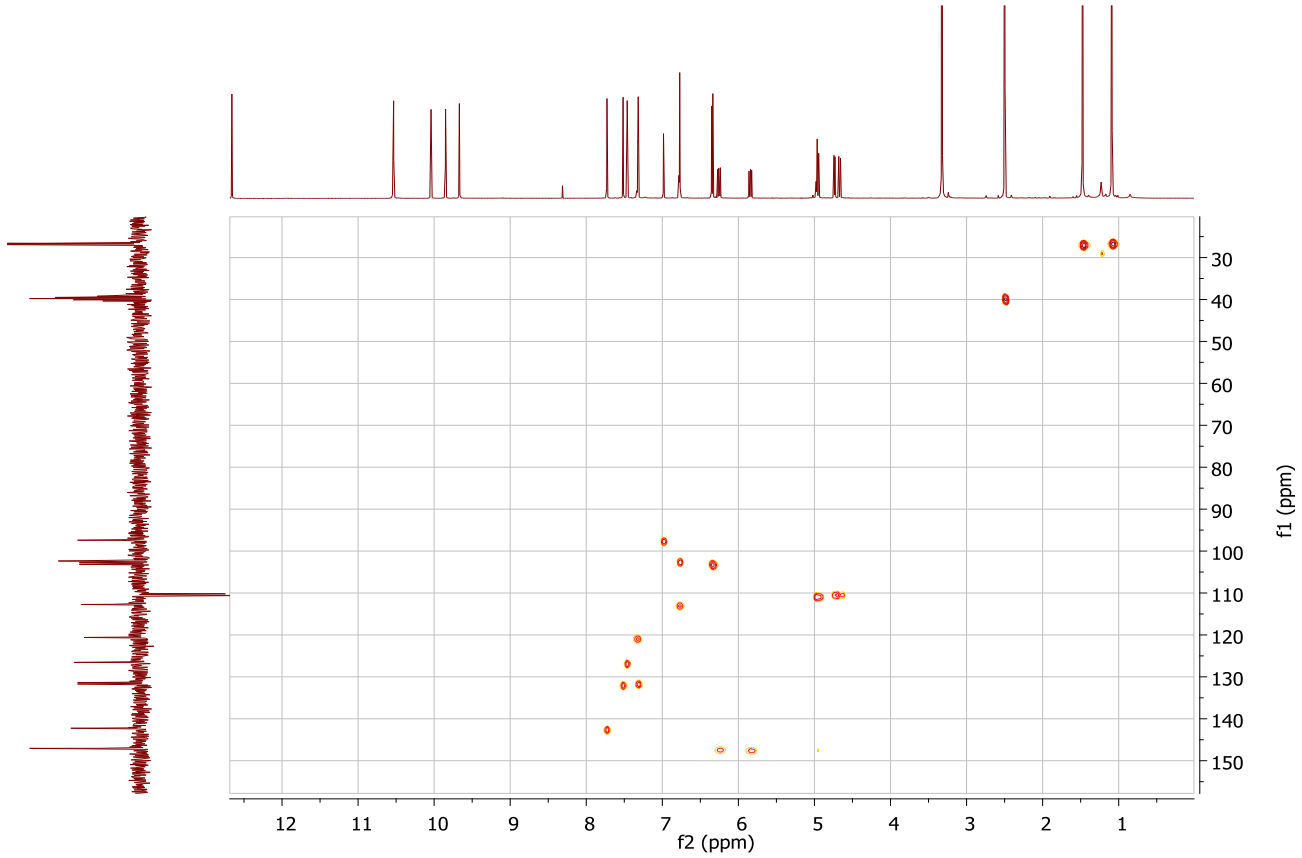


Figure S1e. HMBC spectrum of compound **1**.

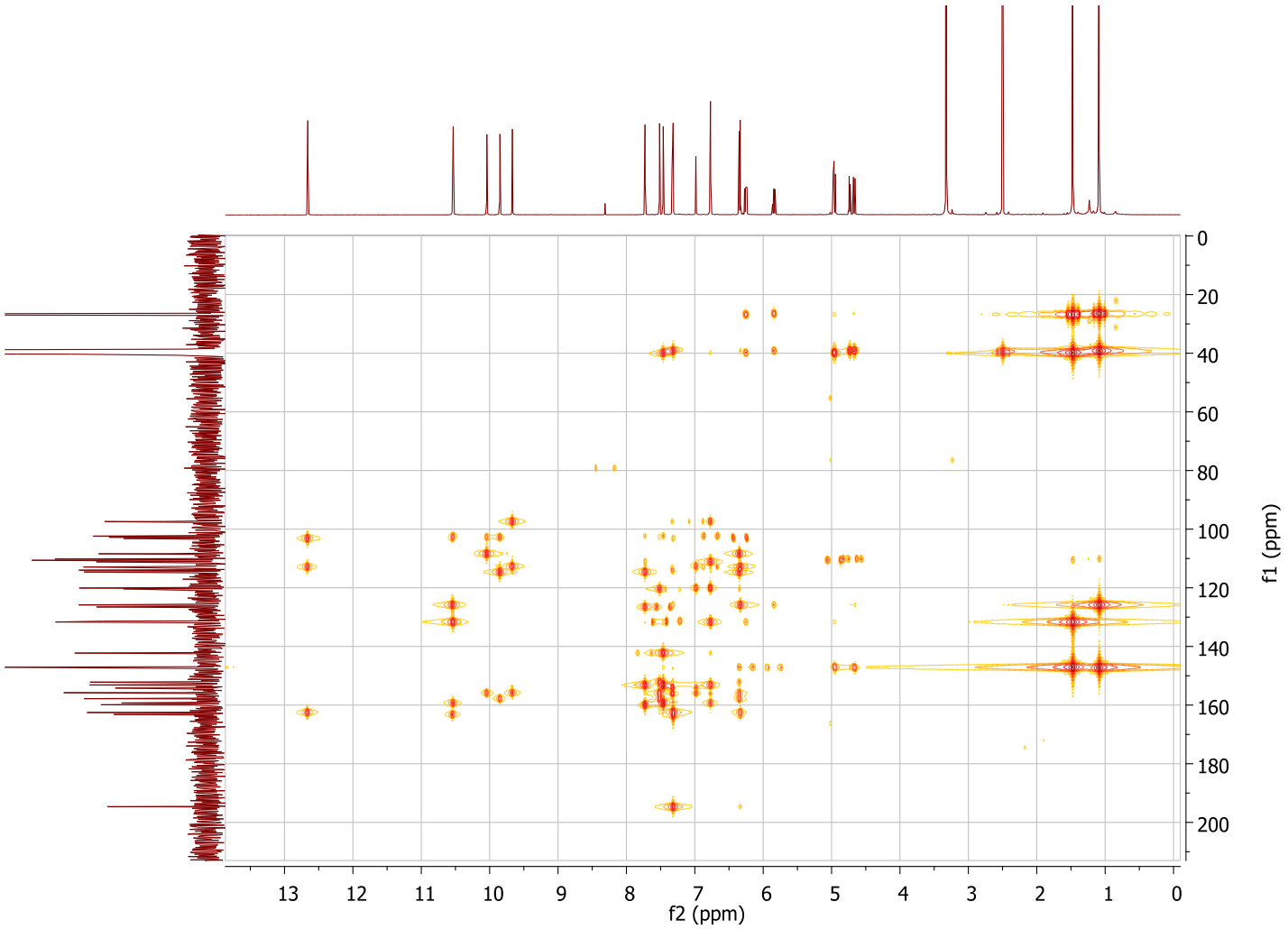


Figure S1f. Expanded HMBC spectrum of compound **1** showing the correlation of H-6′ (δ 7.52) to C-2″ (δ 152.2).

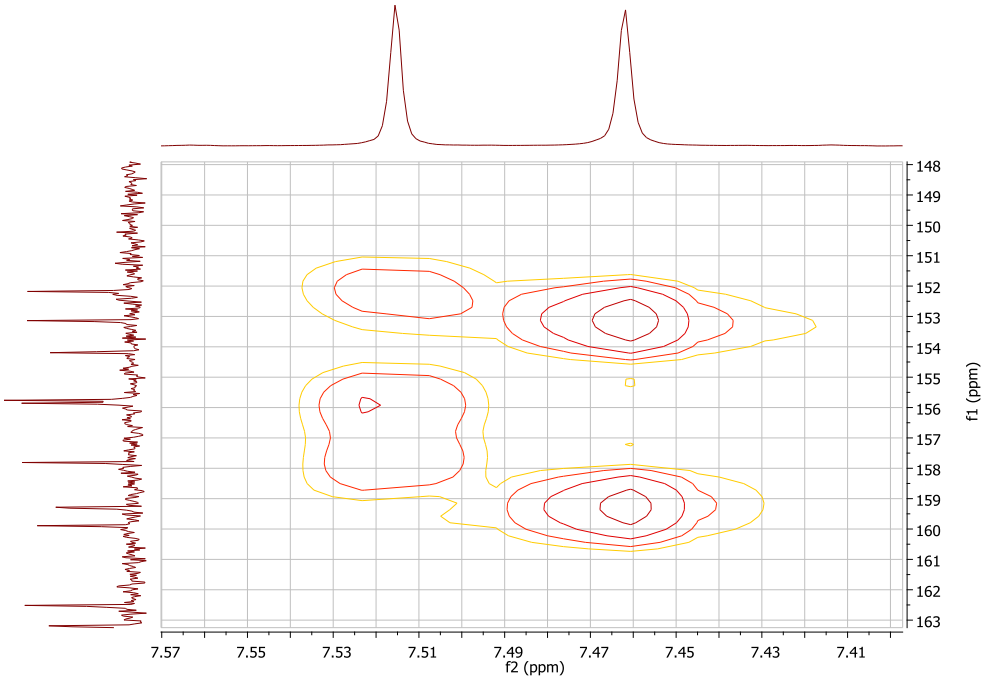


Figure S1g. ^{1}H-^{1}H COSY spectrum of compound **1**.

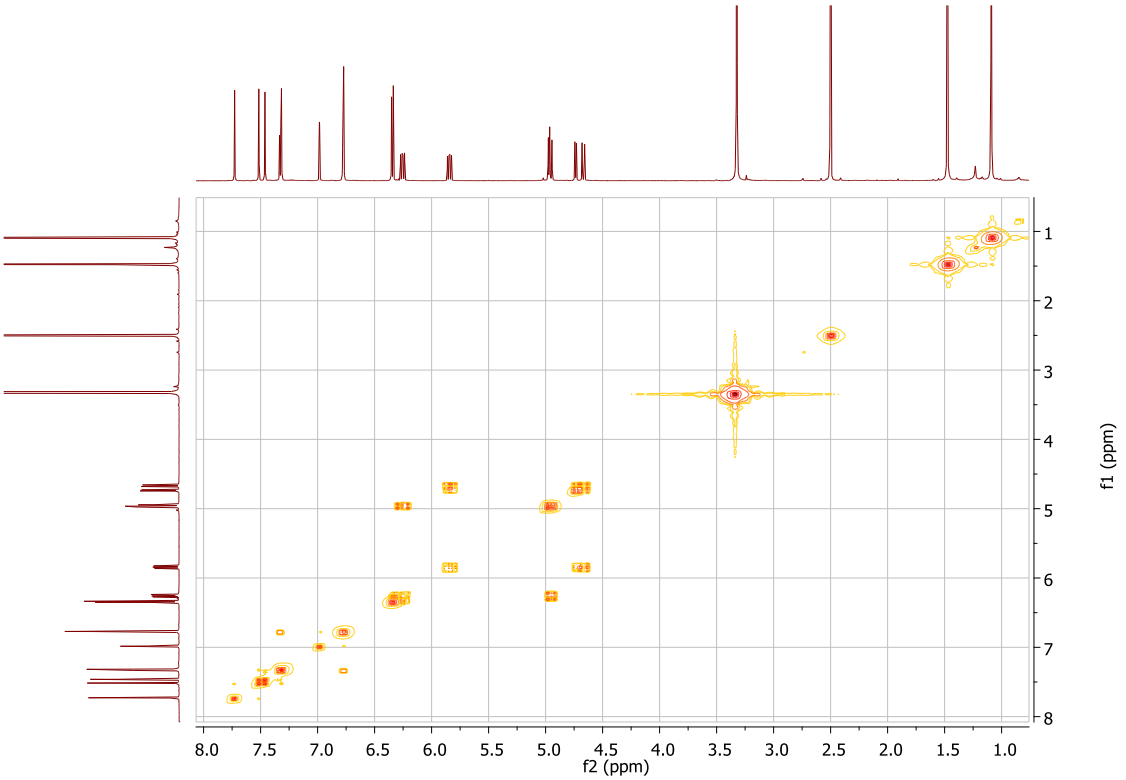


Figure S2a. ^{1}H NMR spectrum of compound **2**.

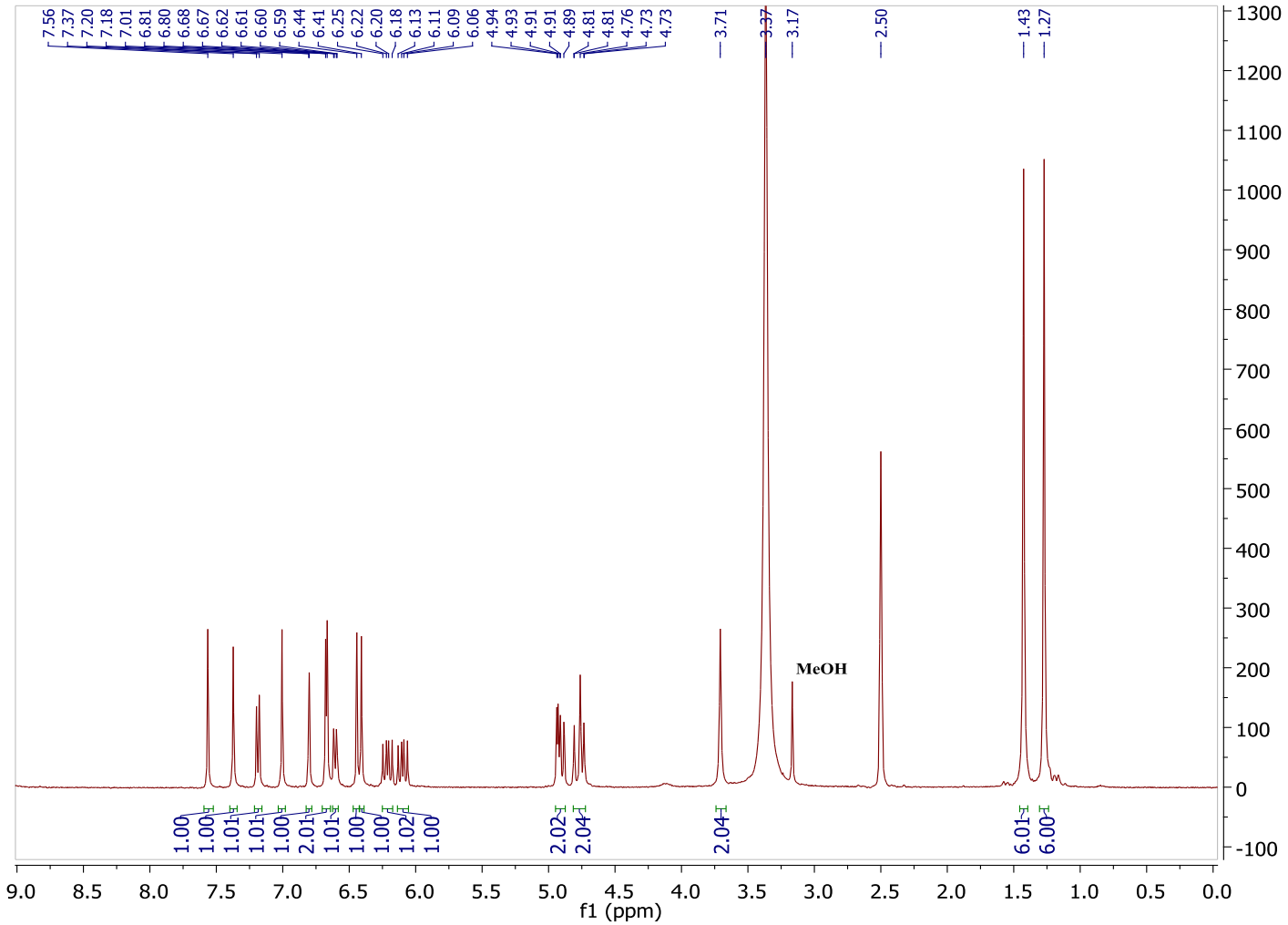


Figure S2b. ^{13}C NMR spectrum of compound **2**.

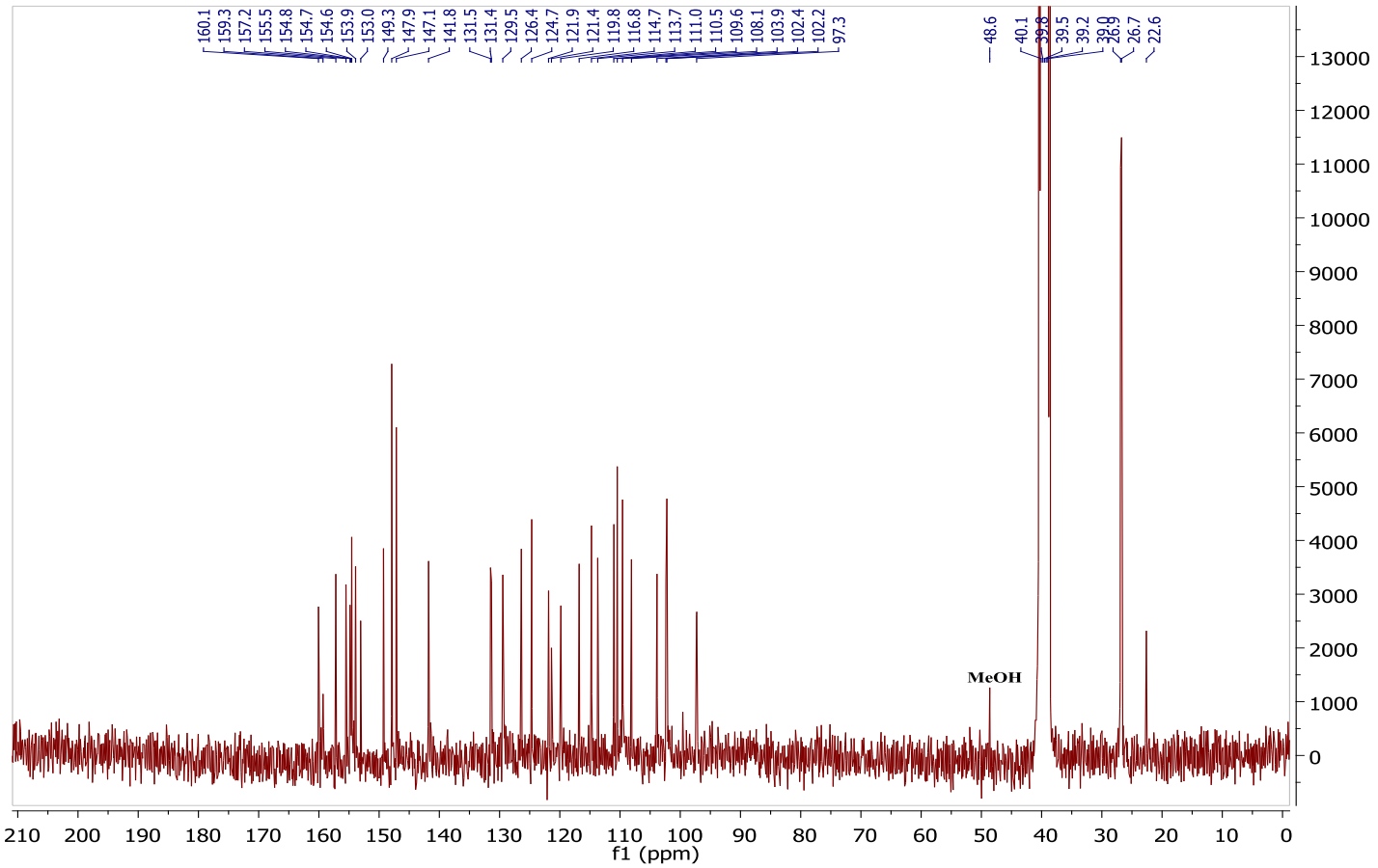


Figure S2c. ^{13}C DEPT 135 NMR spectrum of compound **2**.

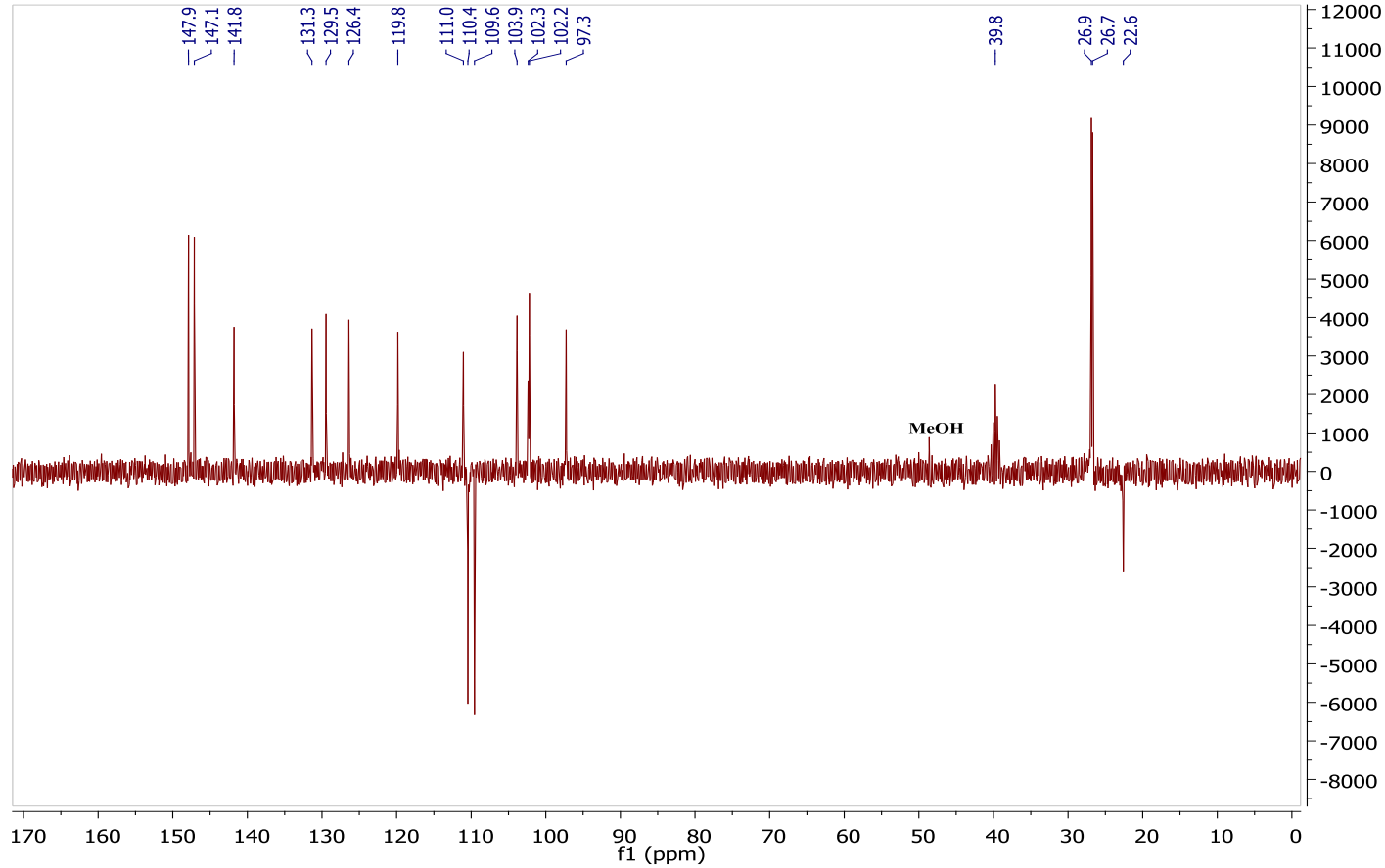


Figure S2d. HSQC spectrum of compound **2**.

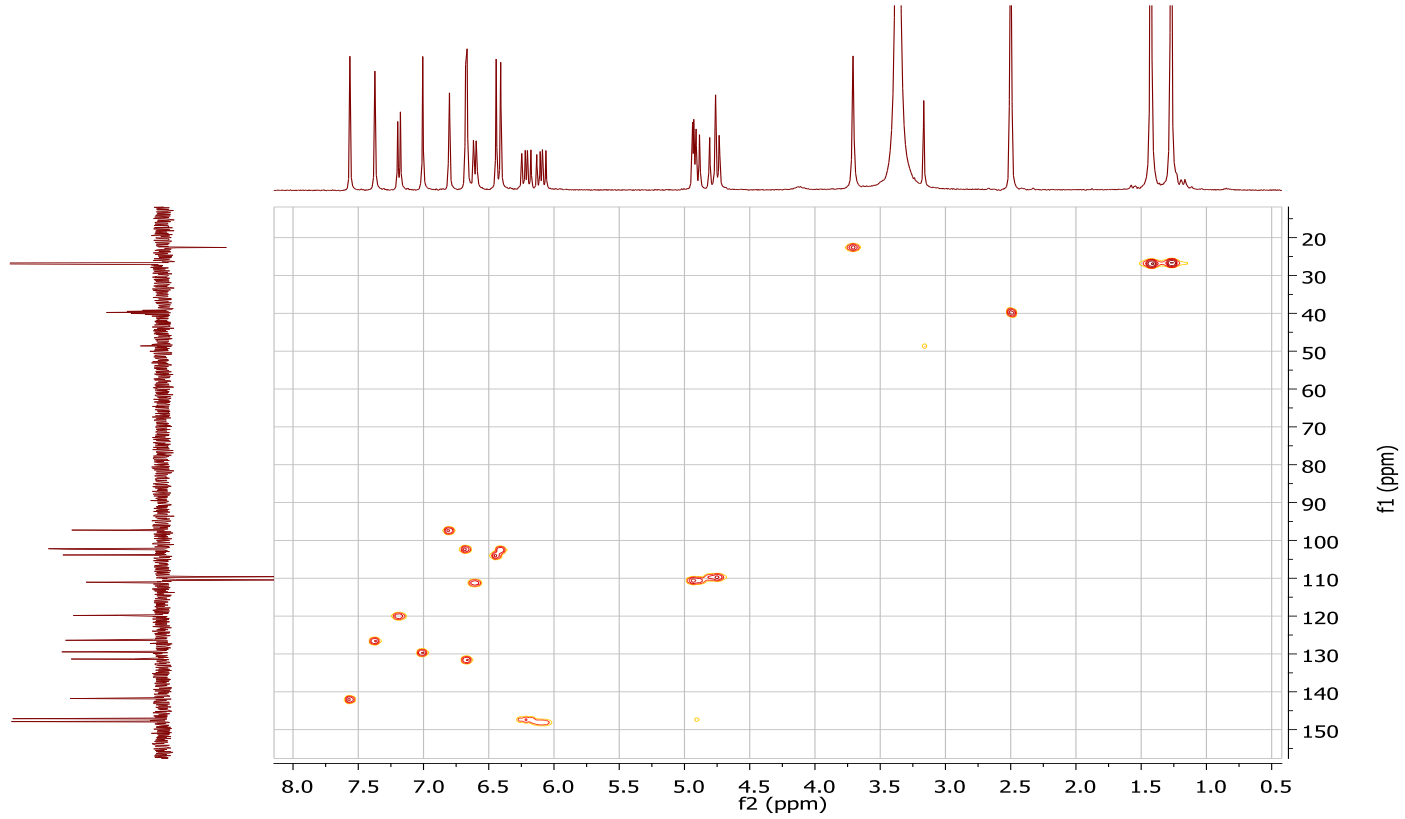


Figure S2e. HMBC spectrum of compound **2**.

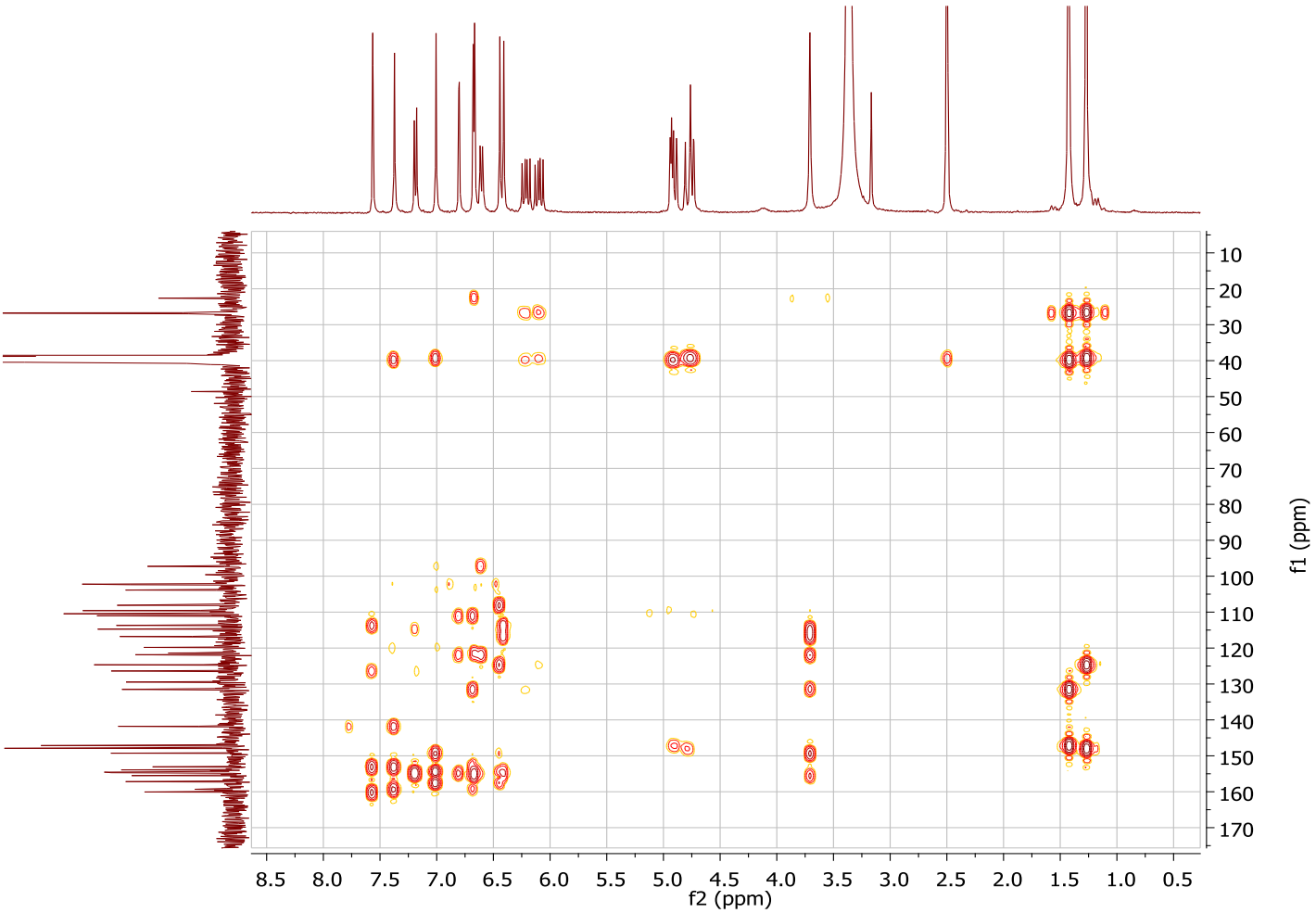


Figure S2f. Expanded HMBC spectrum of compound **2** showing the correlation of H-14″ (δ 7.01) to C-2″ (δ 149.3).

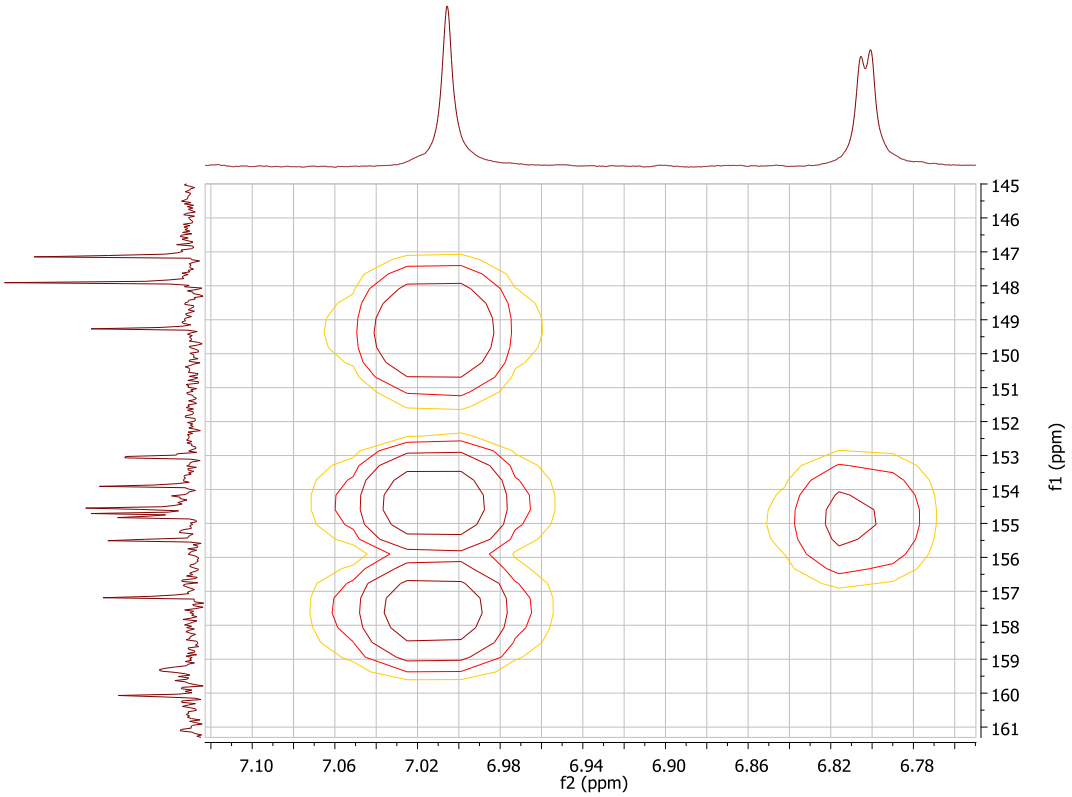


Figure S2g. Expanded HMBC spectrum of compound **2** showing the correlation of H-8″ (δ 3.71) to C-4′ (δ 155.5), C-5′ (δ 116.8), C-6′ (δ 131.4), C-2″ (δ 149.3), C-3″ (δ 114.7), and C-3″a (δ 121.9).

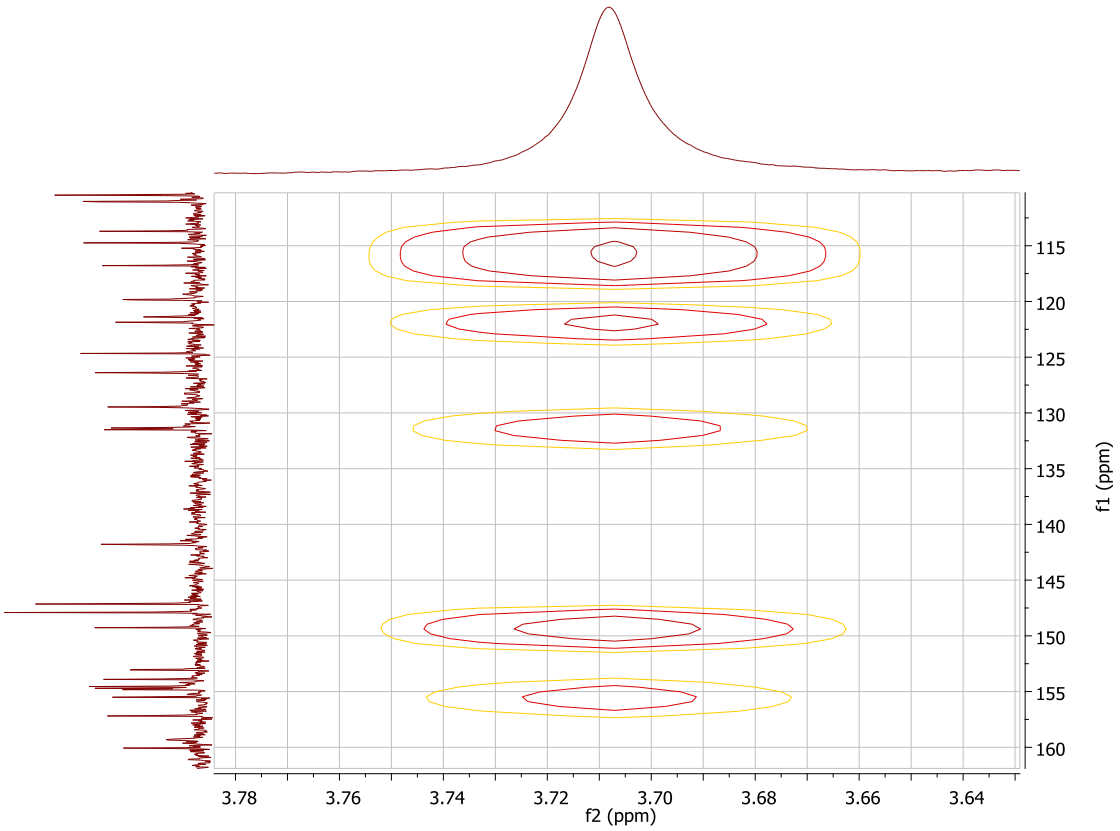


Figure S2h. ^{1}H-^{1}H COSY spectrum of compound **2**.

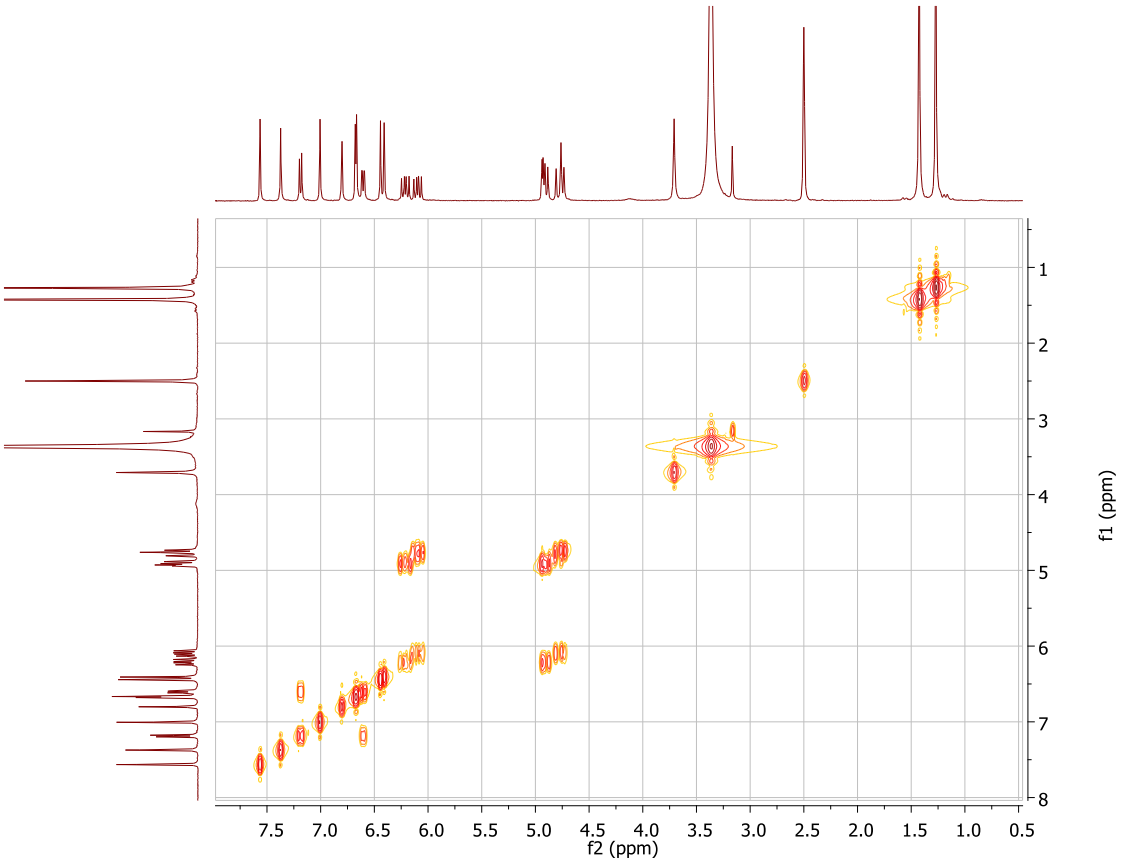


Figure S3a. ^{1}H NMR spectrum of compound **3**.

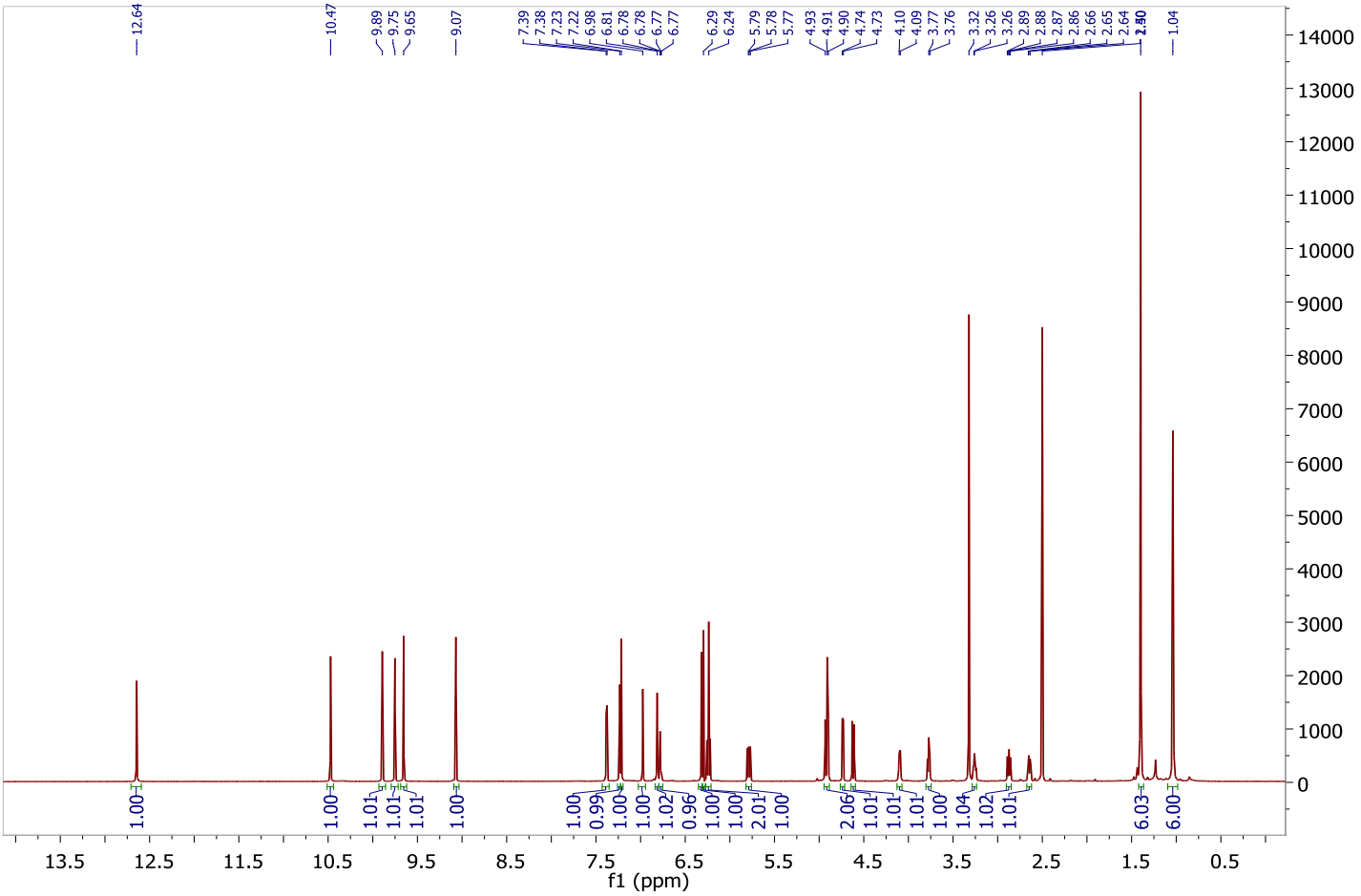


Figure S3b. Expanded ^{1}H NMR spectrum of the dihydropyran ring of compound **3**, showing the coupling constants to determine the orientation of H-3 as axial and the 3-phenyl group as equatorial.

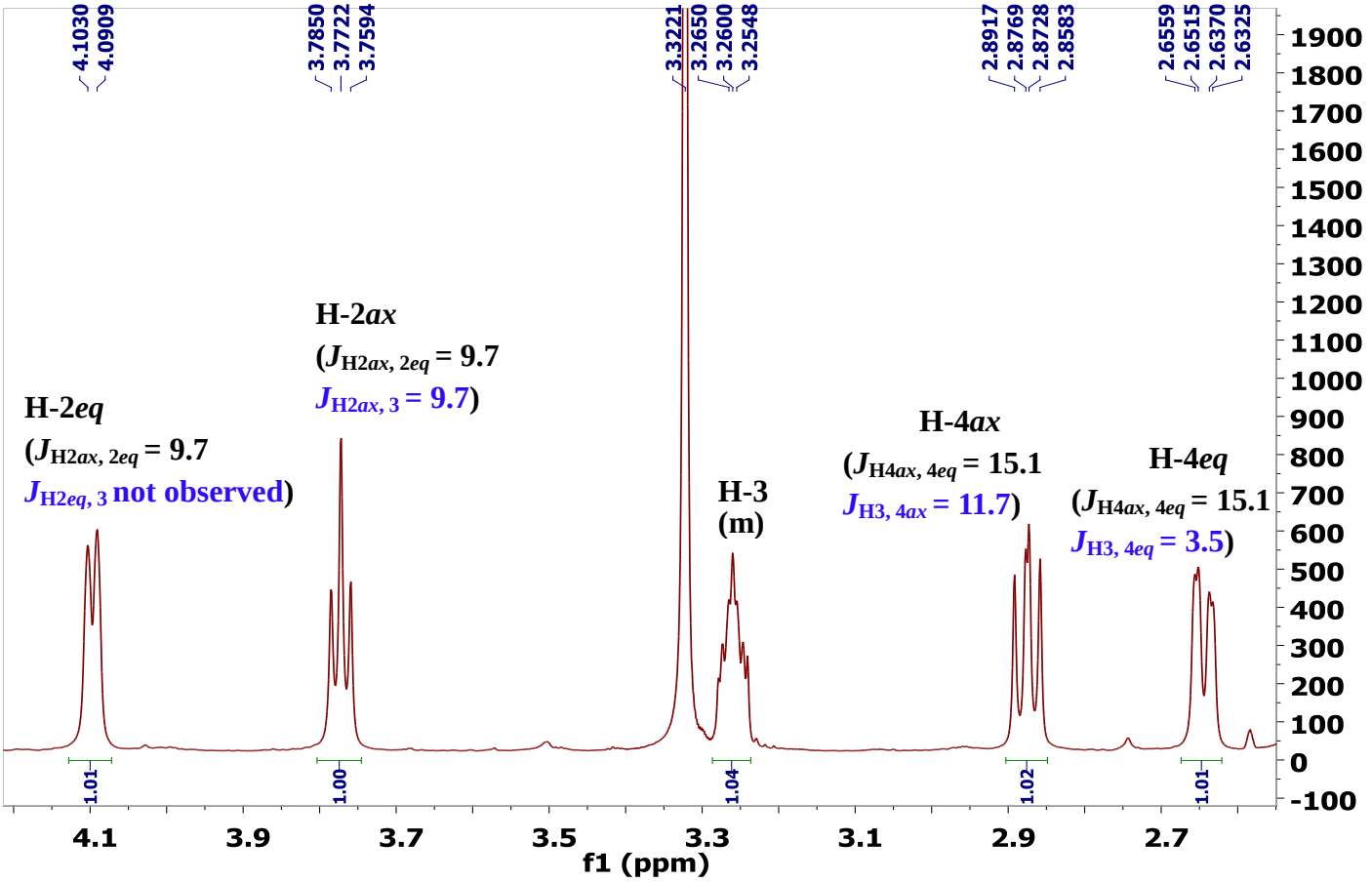


Figure S3c. ^{13}C NMR spectrum of compound **3**.

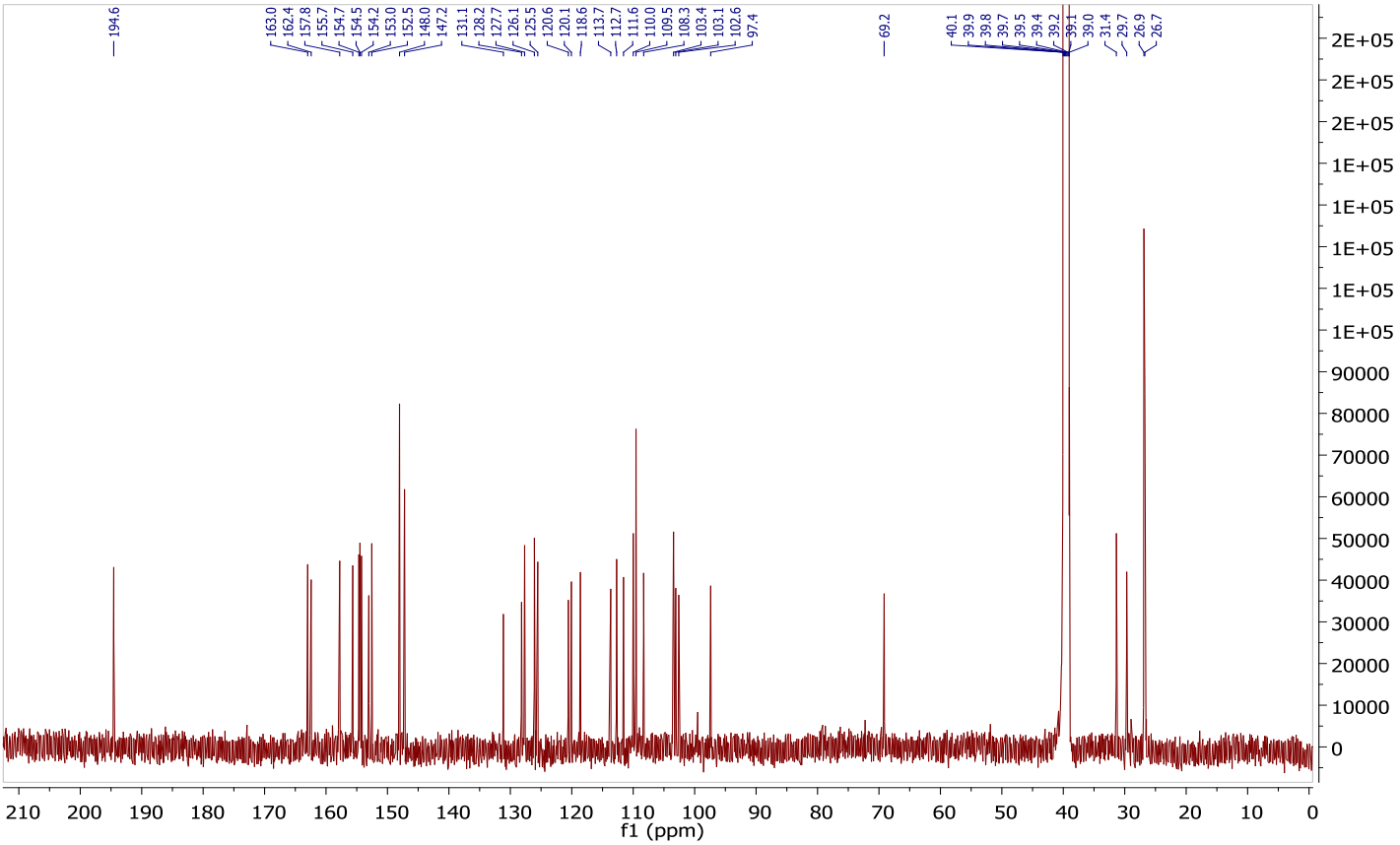


Figure S3d. ^{13}C DEPT 135 NMR spectrum of compound **3**.

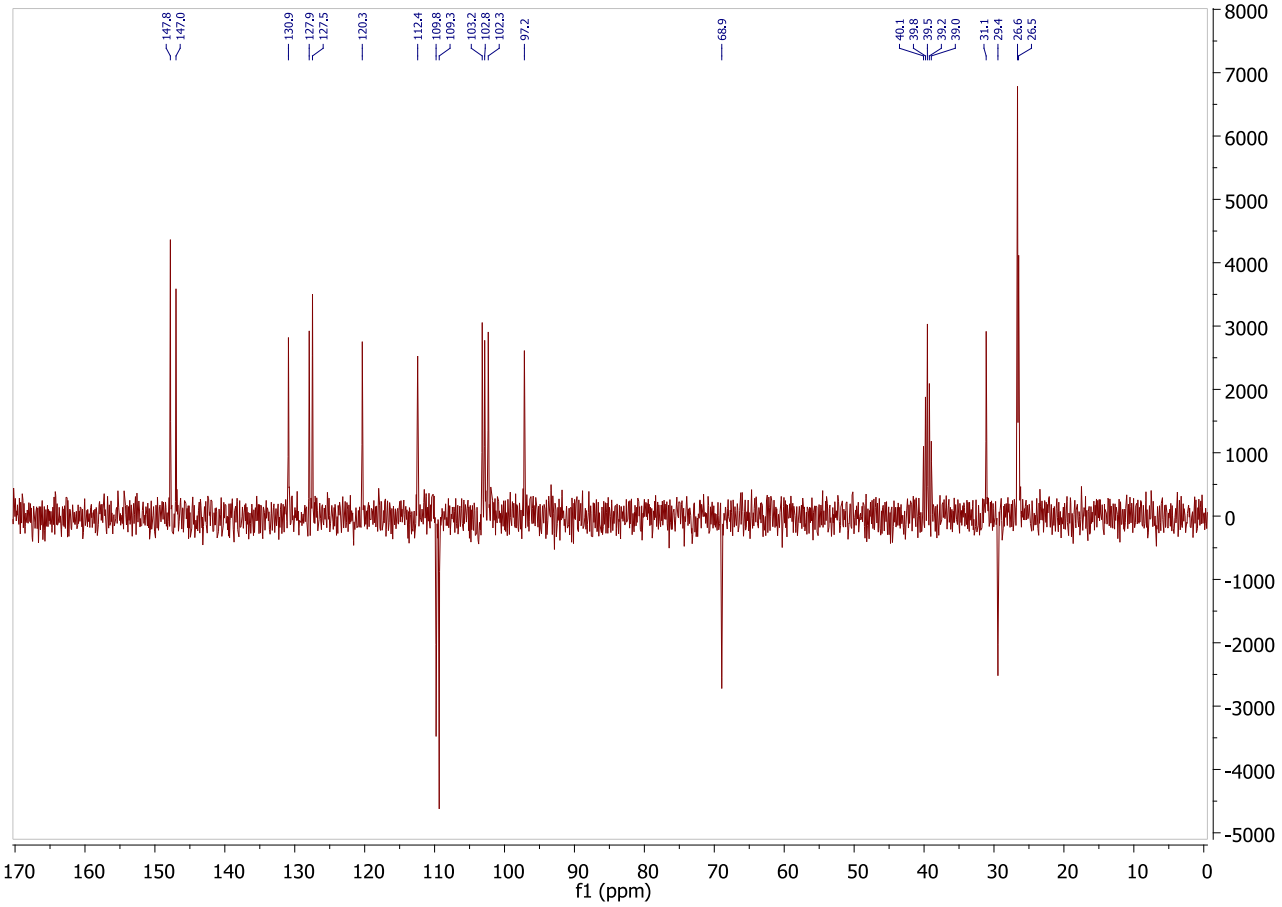


Figure S3e. HSQC spectrum of compound **3**.

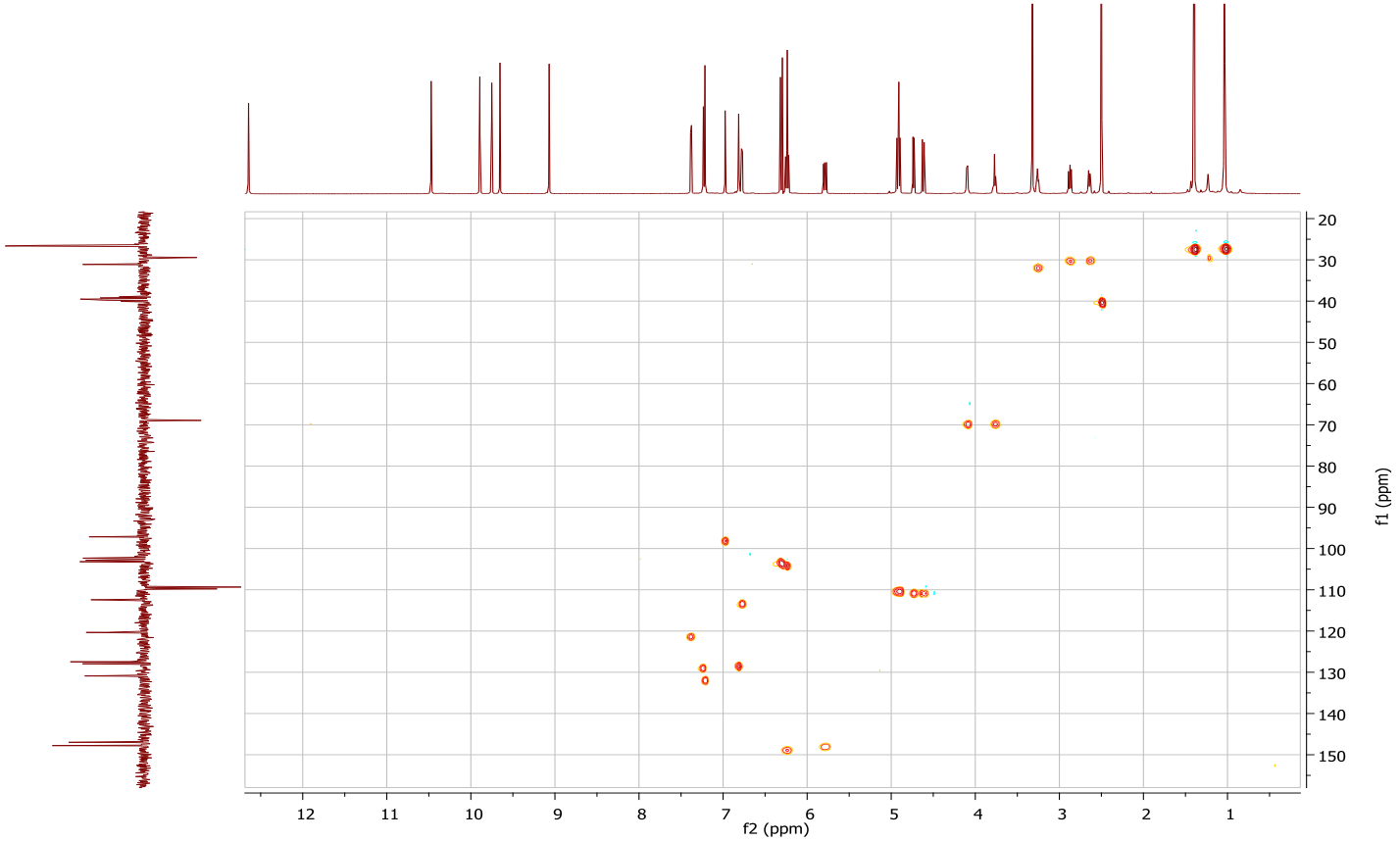


Figure S3f. HMBC spectrum of compound **3**.

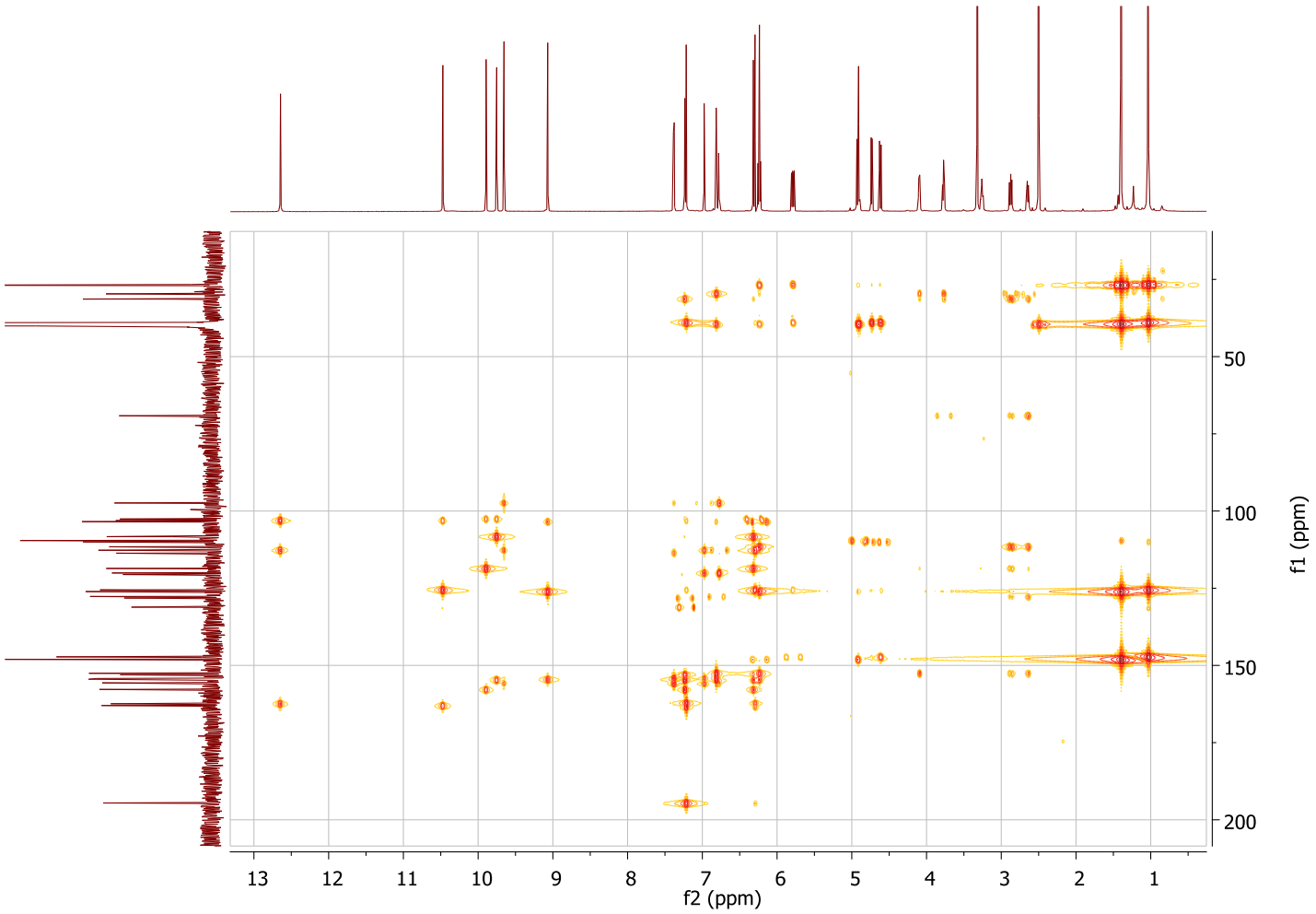


Figure S3g. Expanded HMBC spectrum of compound **3** showing the correlation of H-6′ (δ 7.23) to C-2″ (δ 153.0).

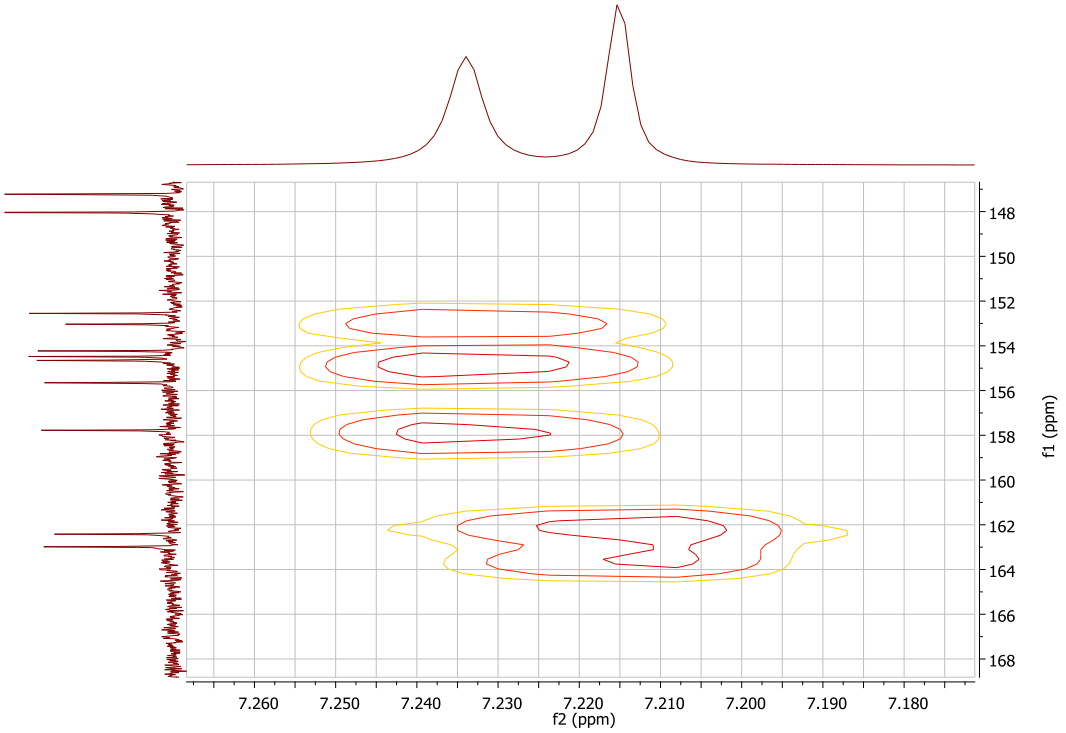


Figure S3h. ^{1}H-^{1}H COSY spectrum of compound **3**.

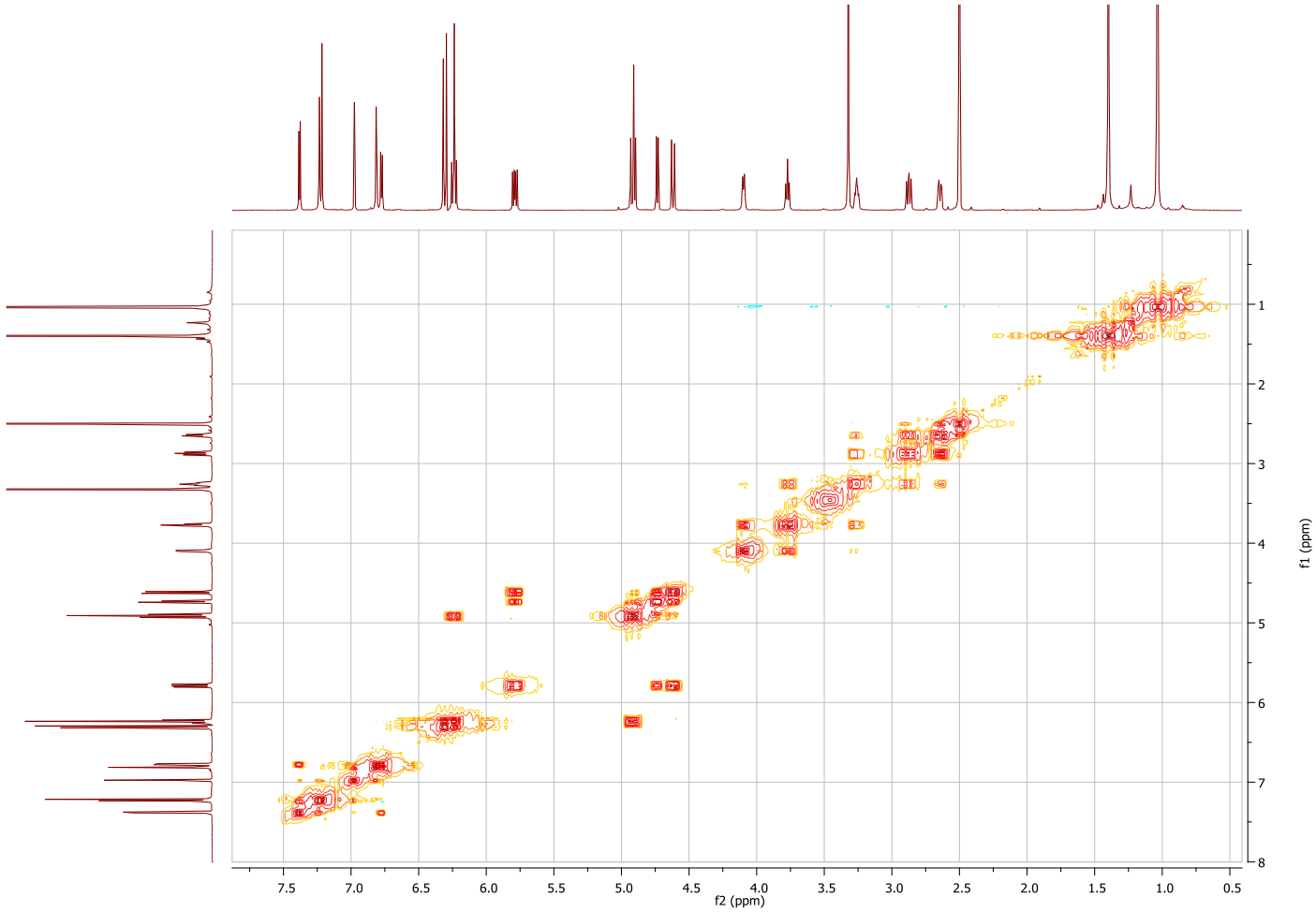


Figure S3i. NOESY spectrum of compound **3**.

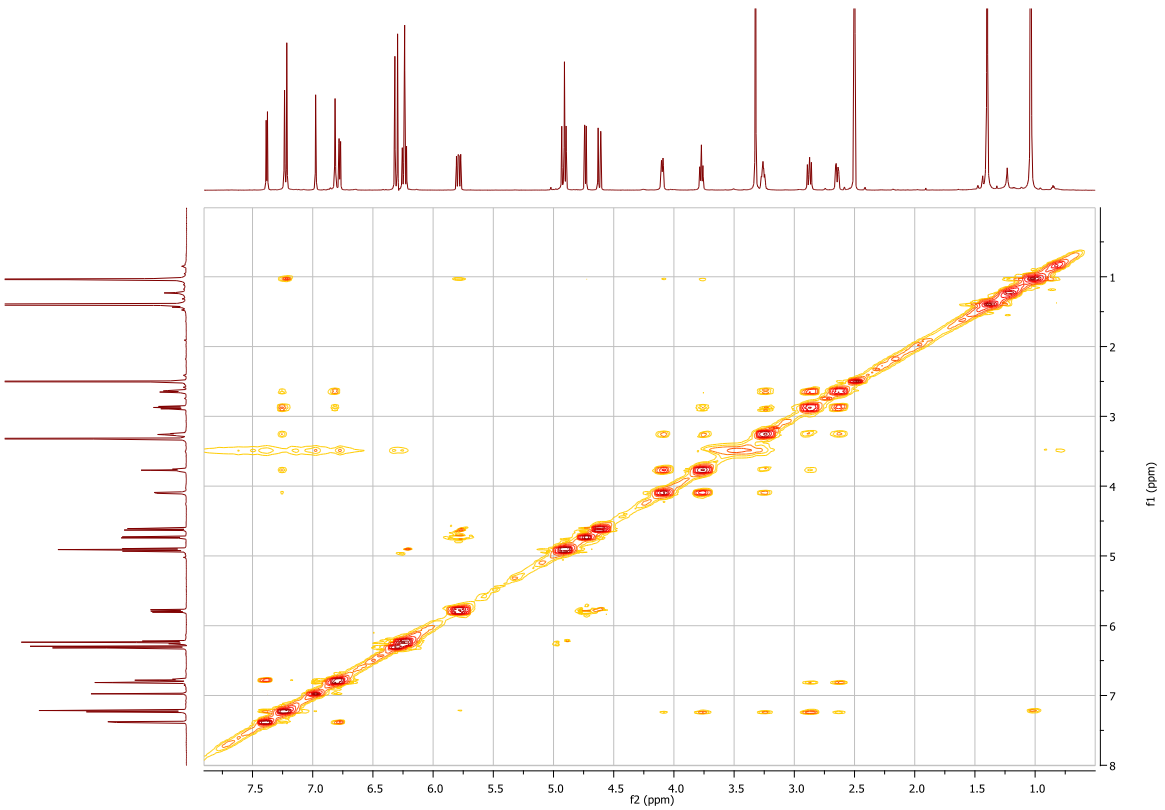


Figure S4a. ^{1}H NMR spectrum of compound **4**.

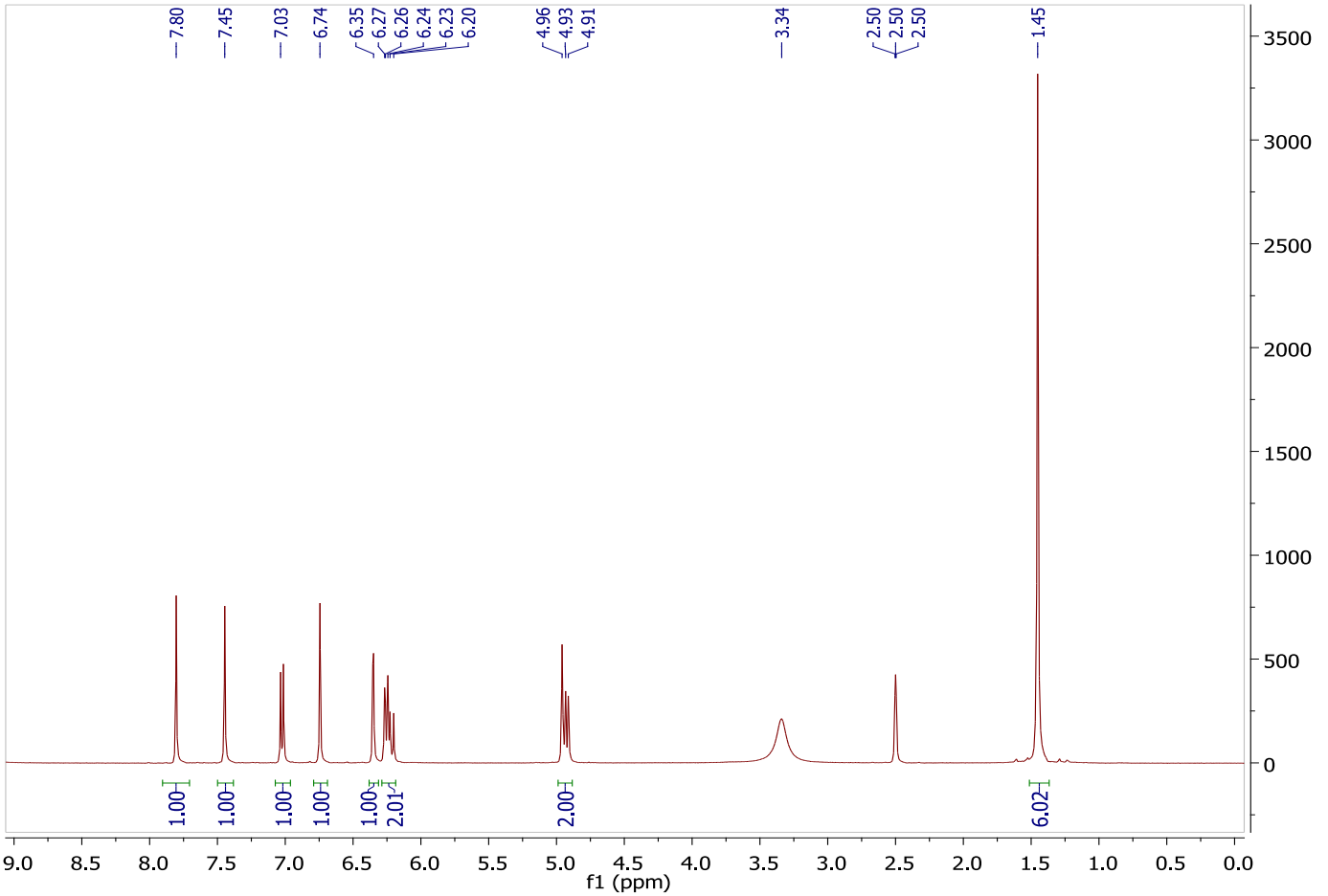


Figure S4b. ^{13}C NMR spectrum of compound **4**.

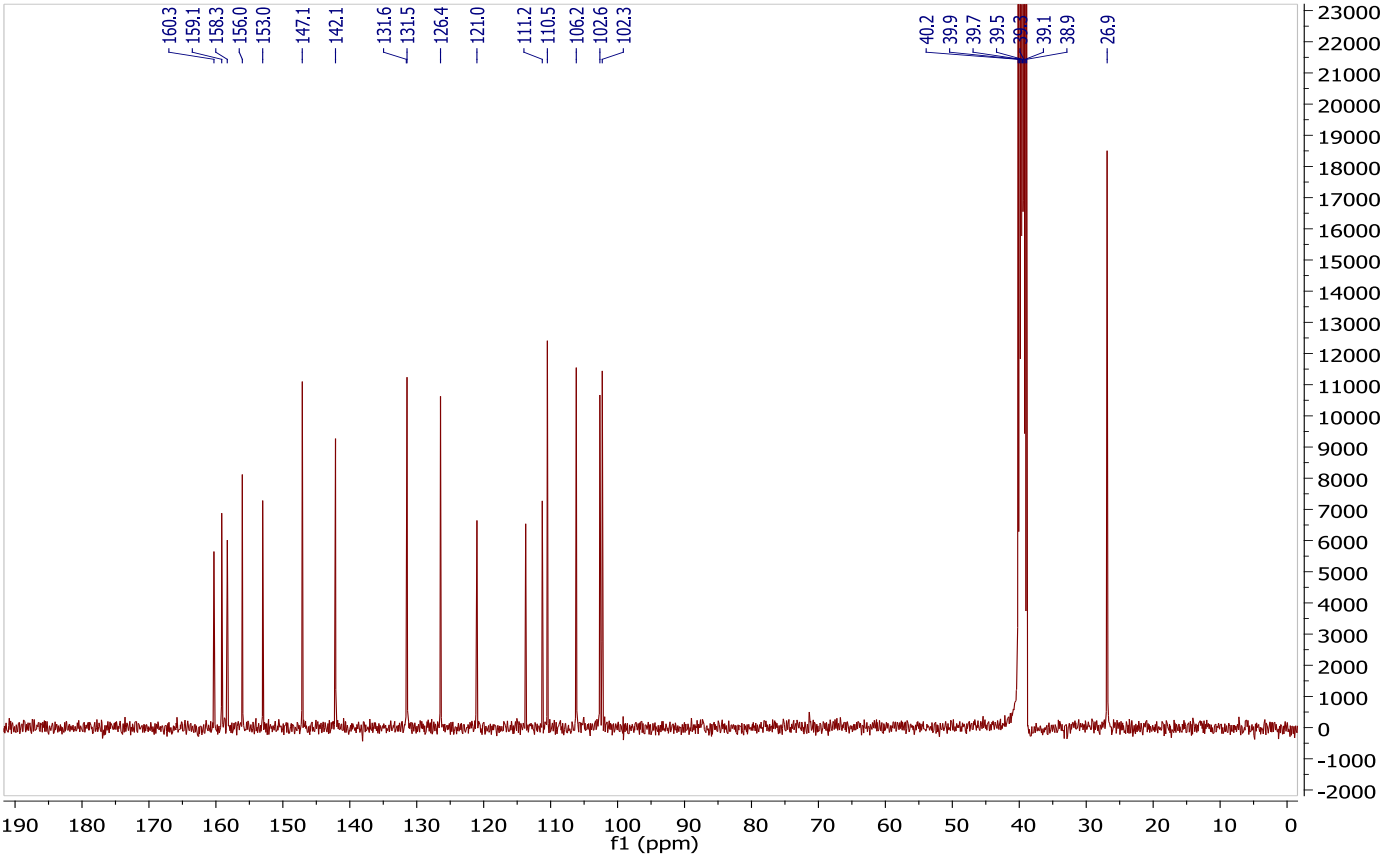


Figure S4c. ^{13}C DEPT 135 NMR spectrum of compound **4.**

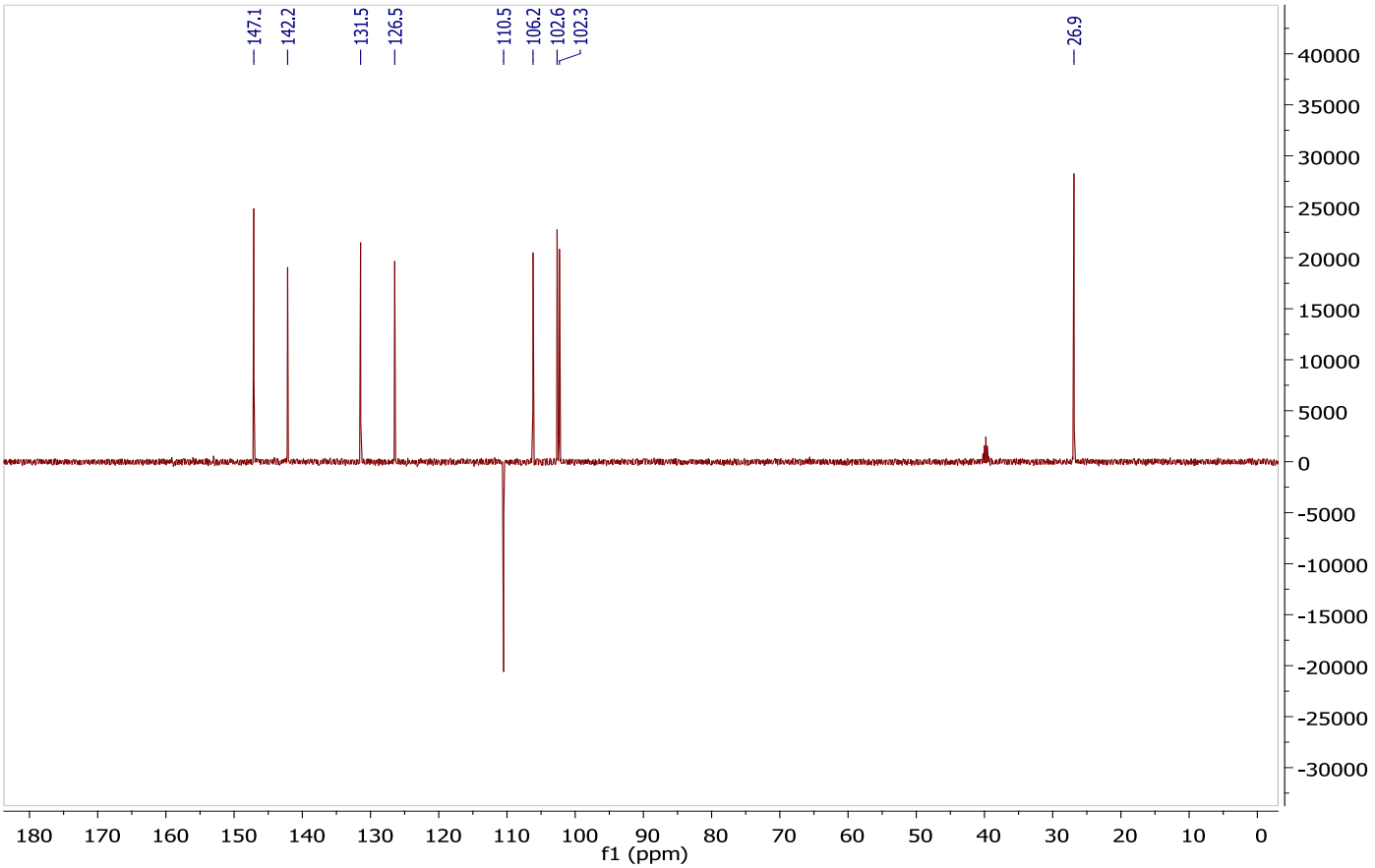


Figure S4d. HSQC spectrum of compound **4**.

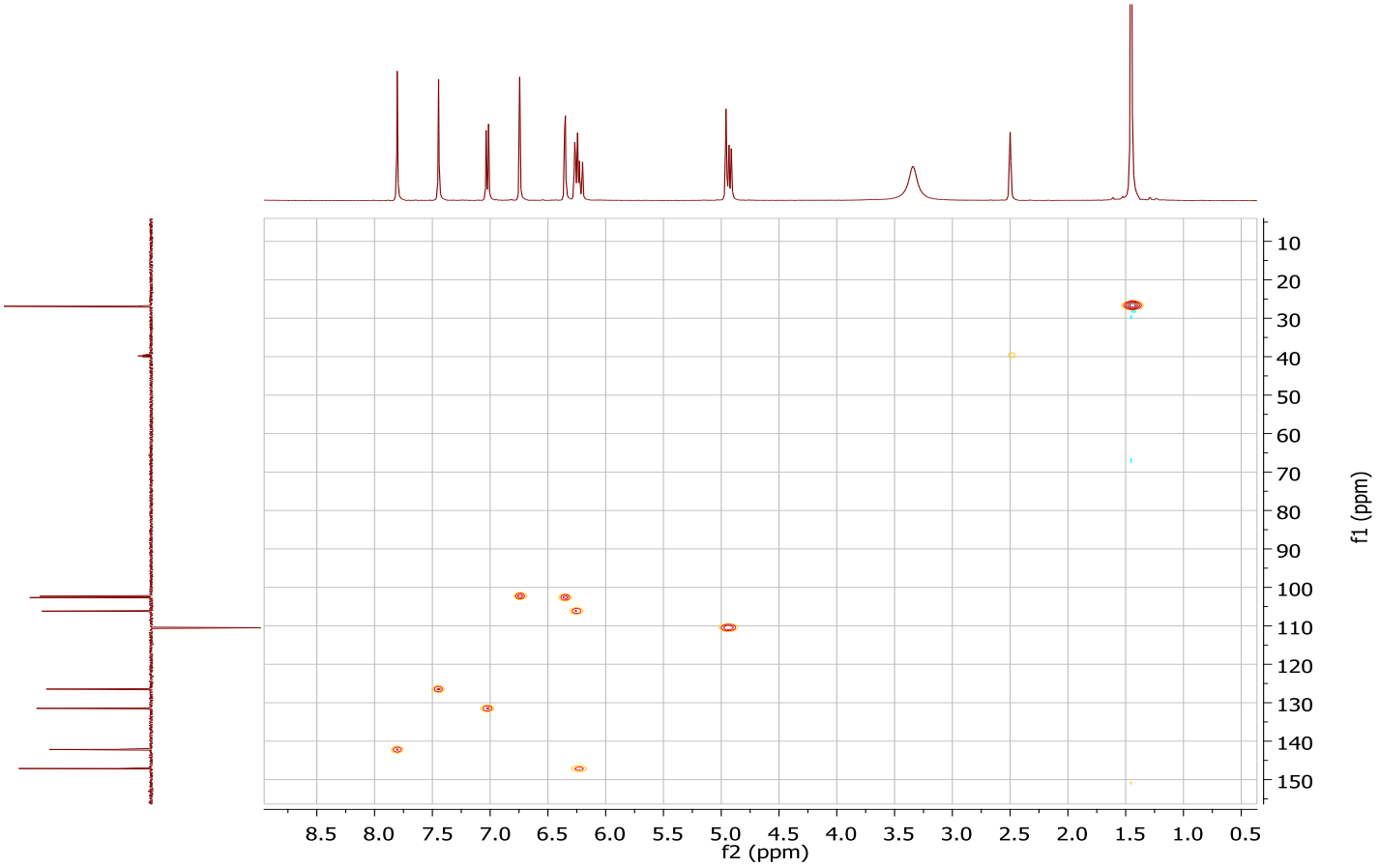


Figure S4e. HMBC spectrum of compound **4**.

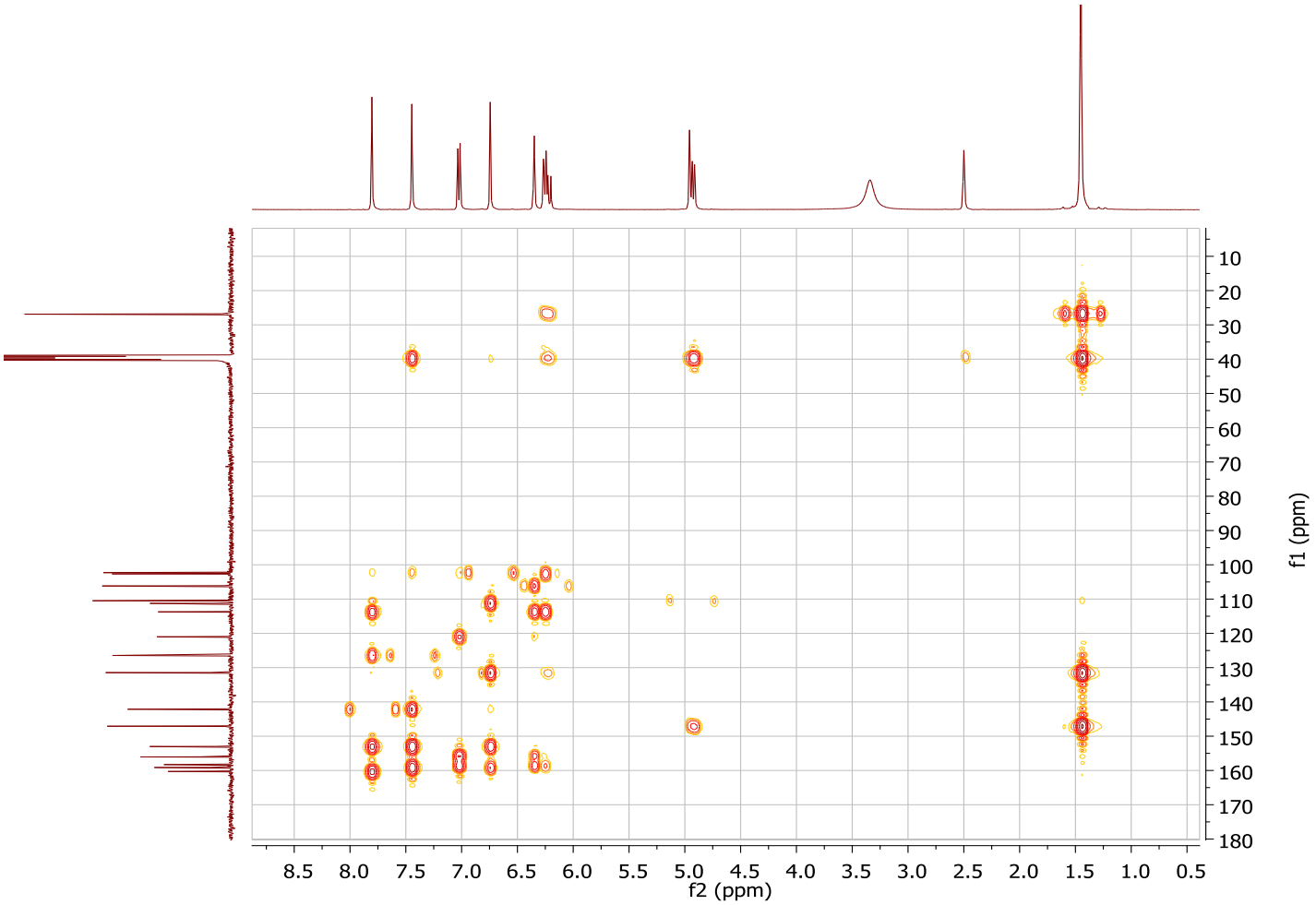


Figure S4f. ^{1}H-^{1}H COSY spectrum of compound **4**.

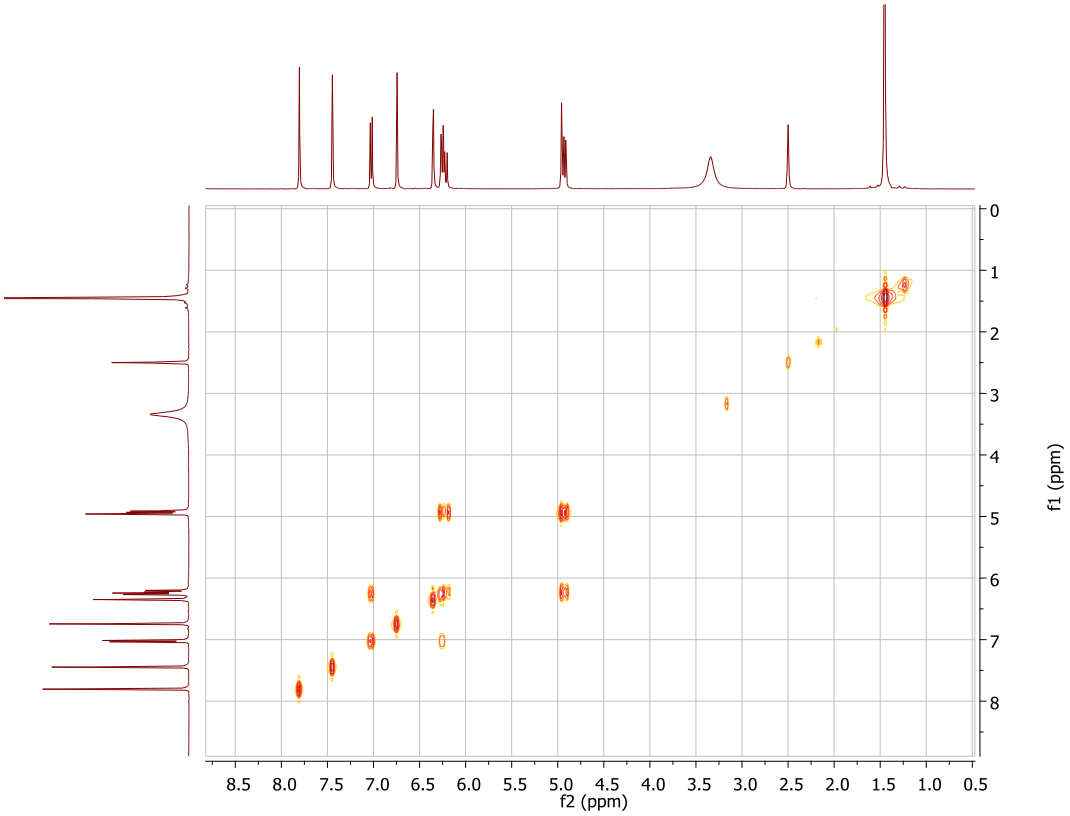


Figure S5a. ^{1}H NMR spectrum of compound **5**.

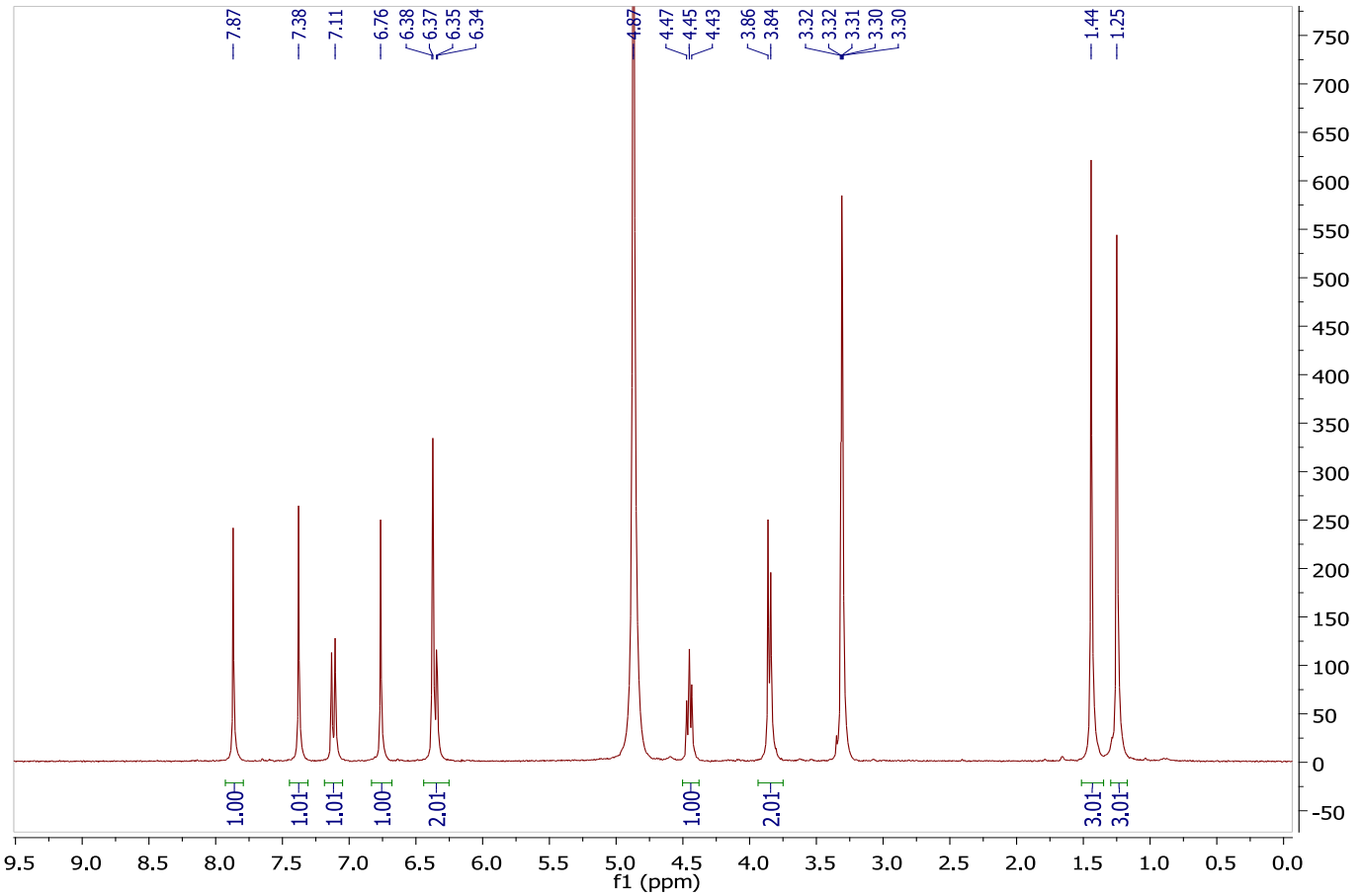


Figure S5b. ^{13}C NMR spectrum of compound **5**.

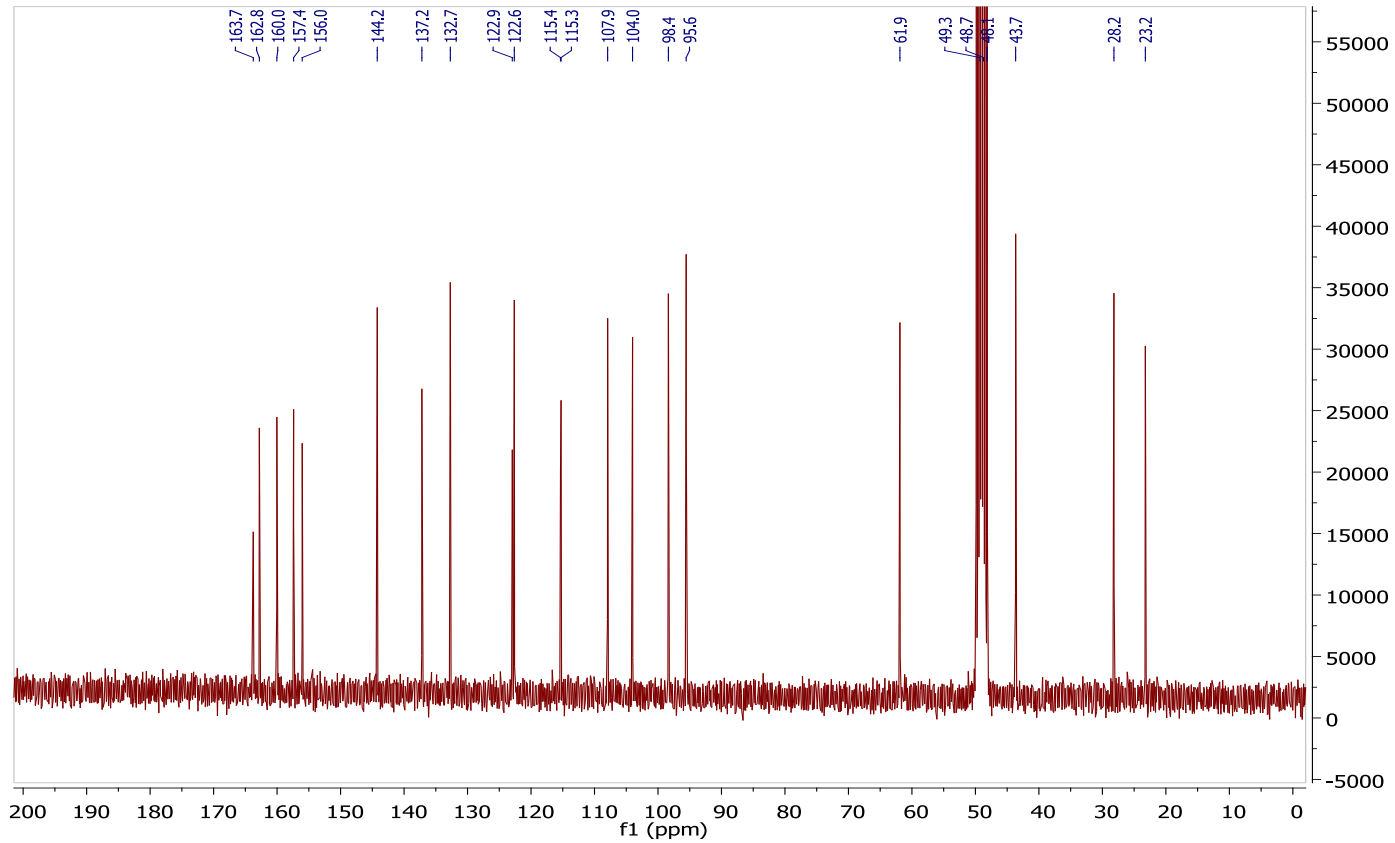


Figure S5c. ^{13}C DEPT 135 NMR spectrum of compound **5**.

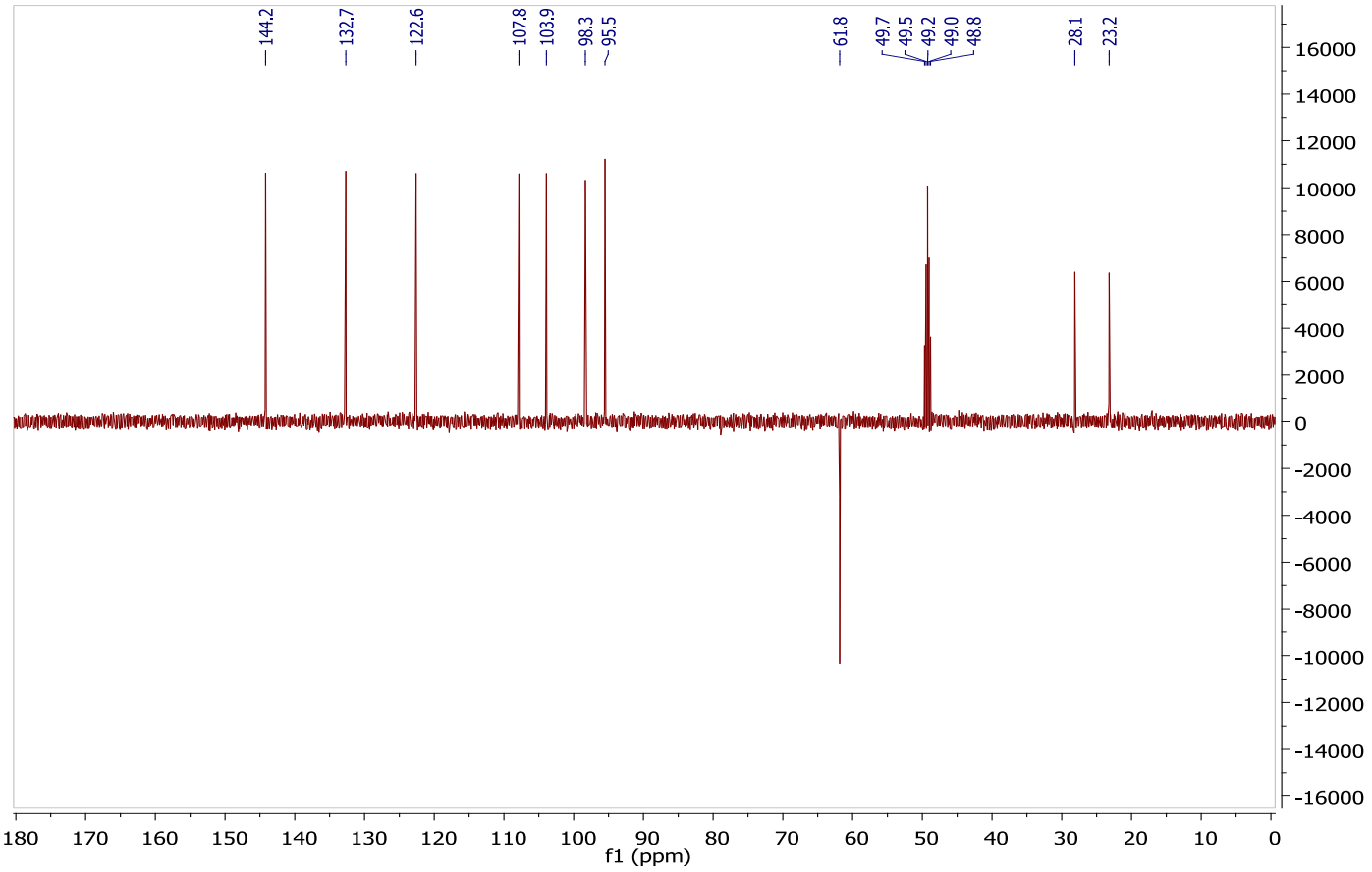


Figure S5d. HSQC spectrum of compound **5**.

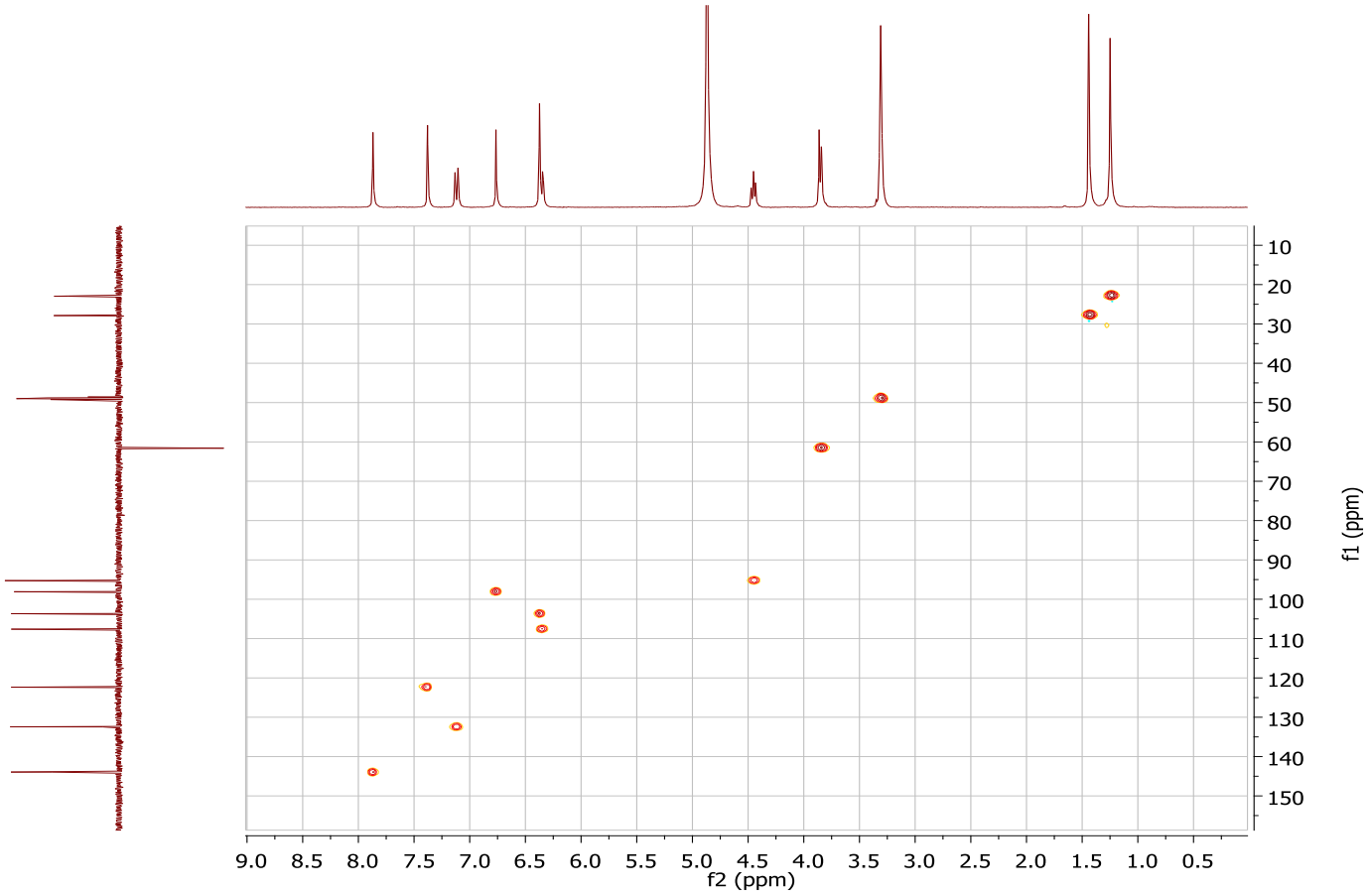


Figure S5e. HMBC spectrum of compound **5**.

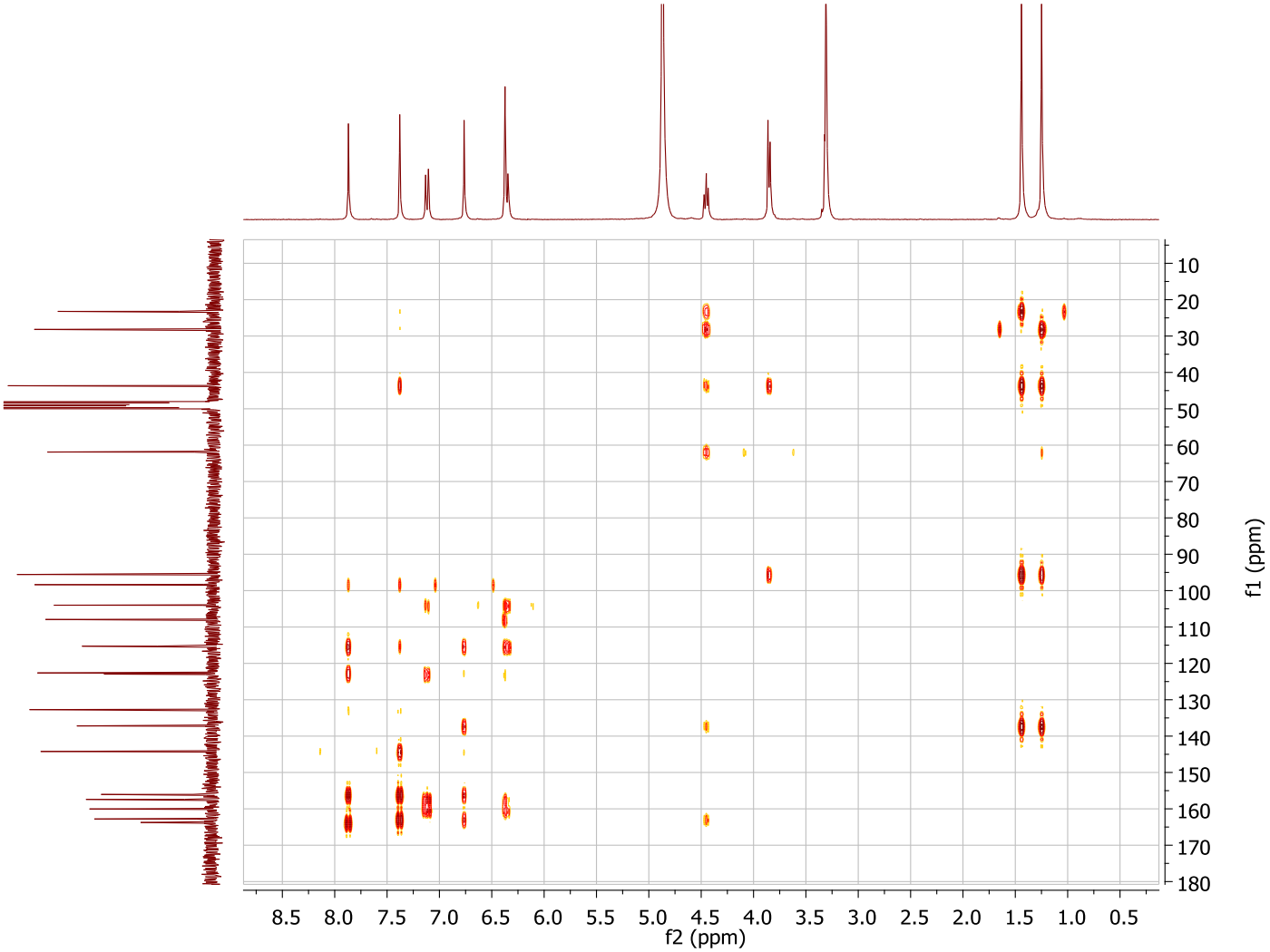


Figure S5f. ^{1}H-^{1}H COSY spectrum of compound **5**.

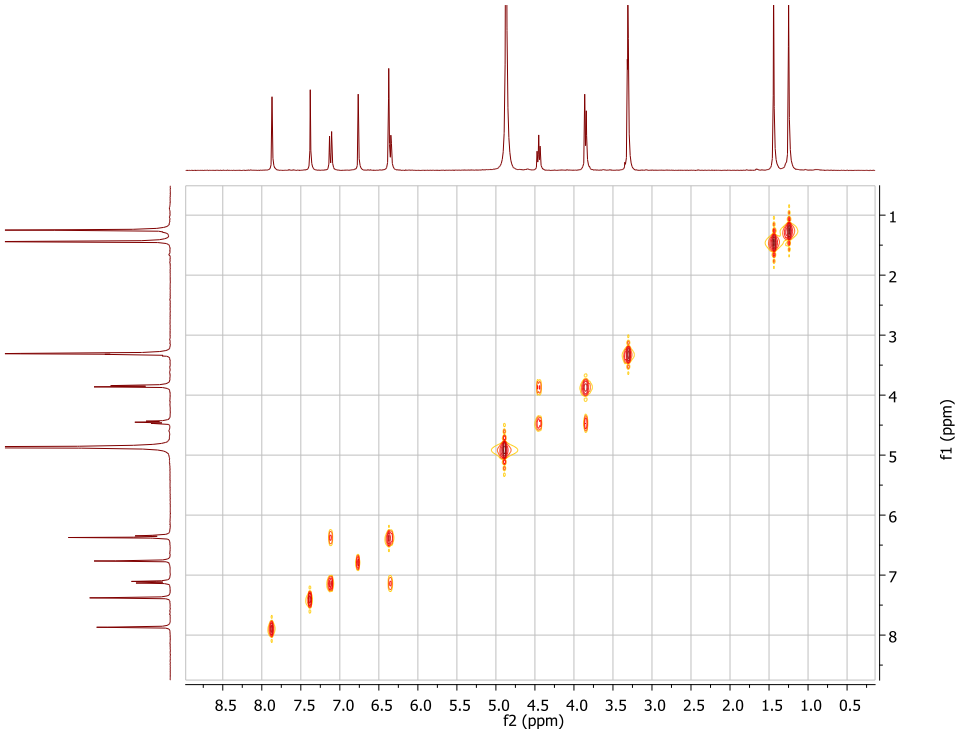


Figure S6a. ^{1}H NMR spectrum of compound **6**.

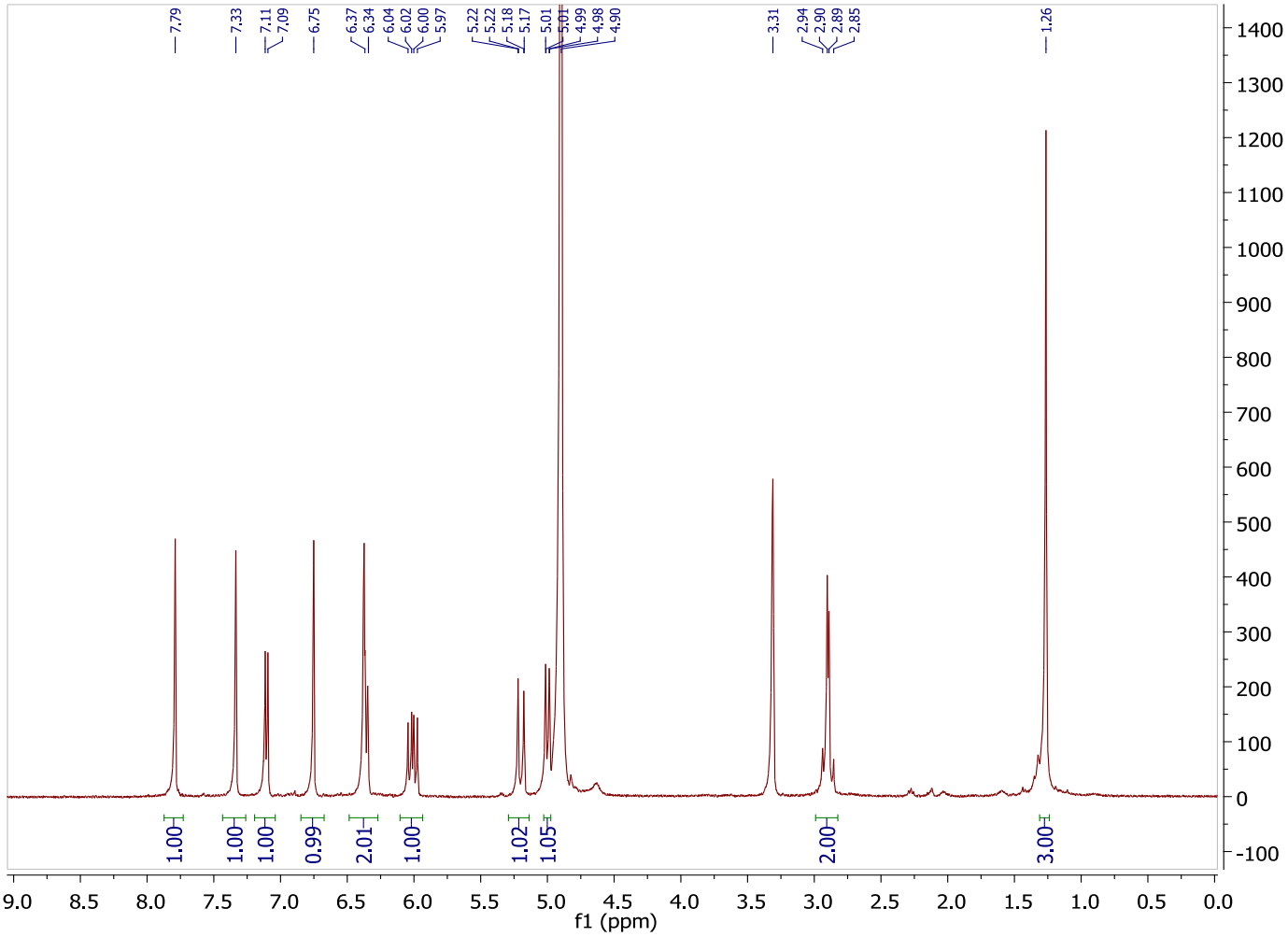


Figure S6b. ^{13}C NMR spectrum of compound **6**.

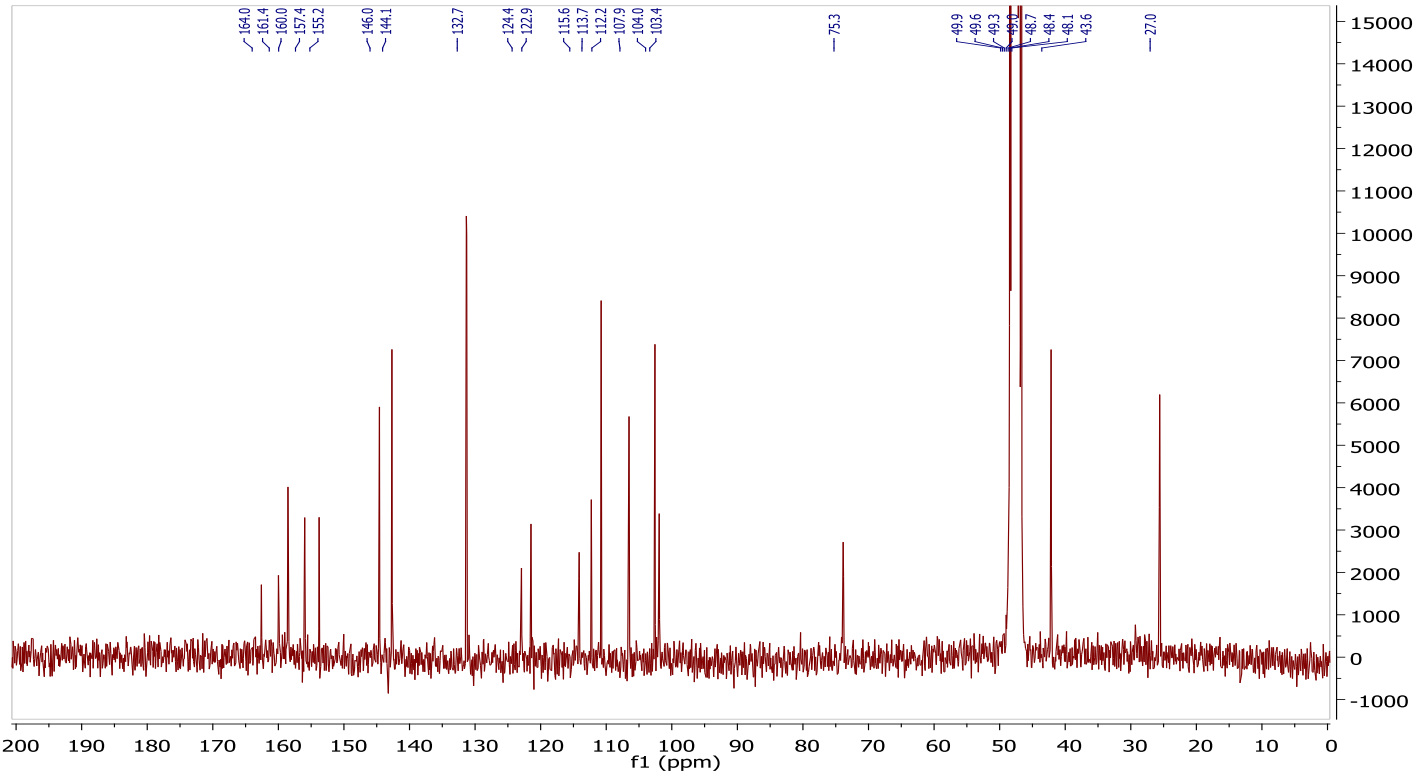


Figure S6c. ^{13}C DEPT 135 NMR spectrum of compound **6**.

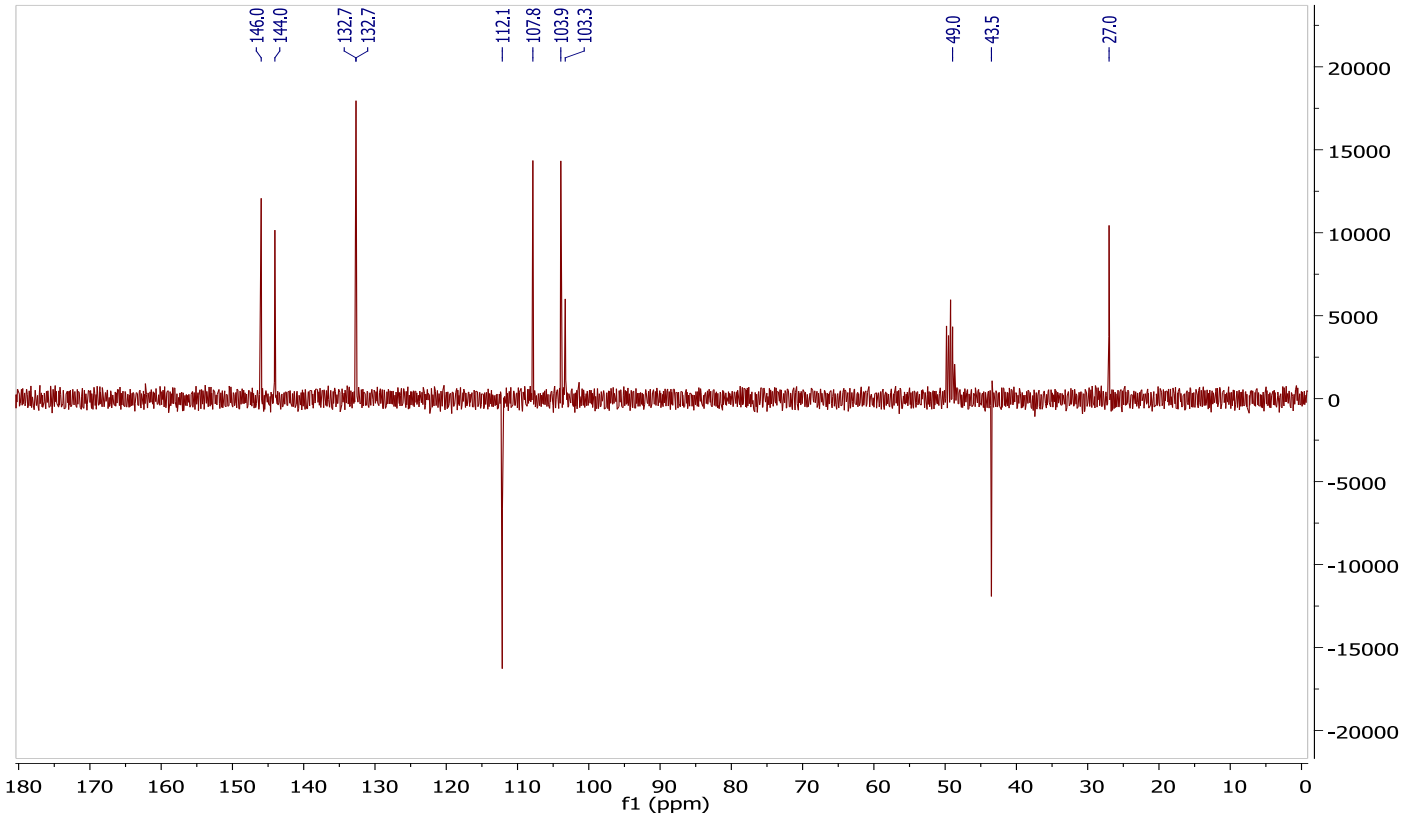


Figure S6d. HSQC spectrum of compound **6**.

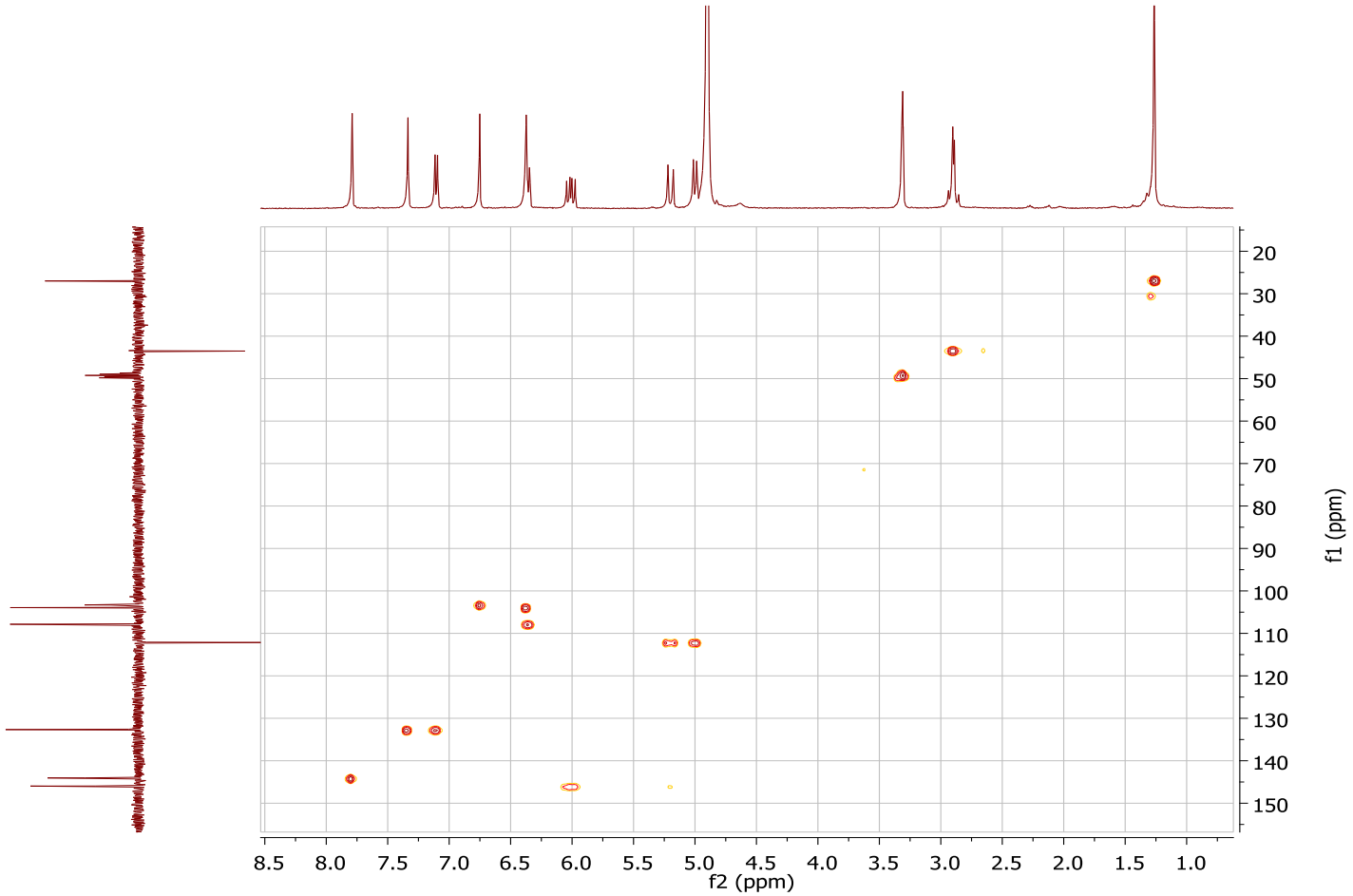


Figure S6e. HMBC spectrum of compound **6**.

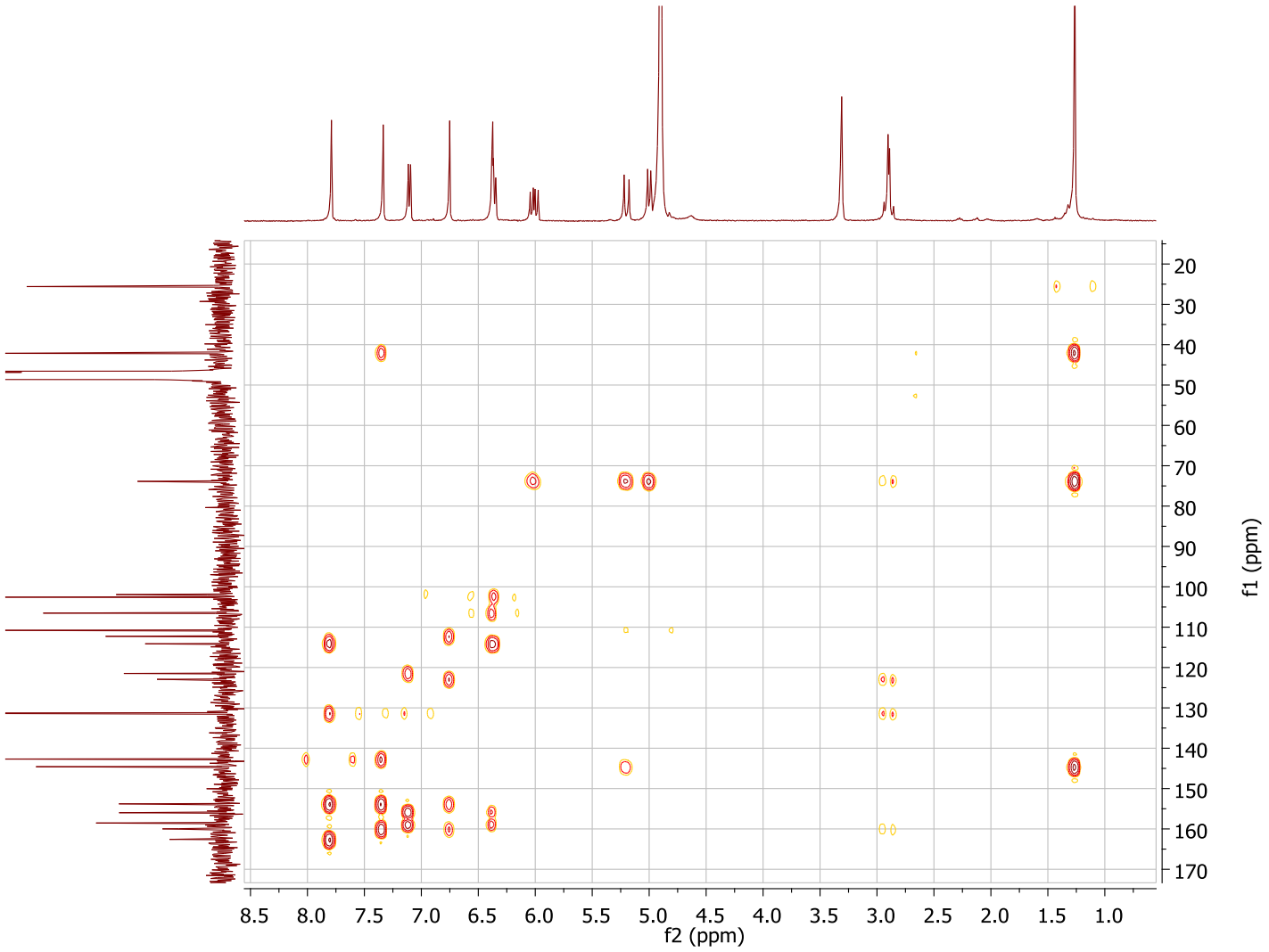


Figure S6f. ^{1}H-^{1}H COSY spectrum of compound **6**.

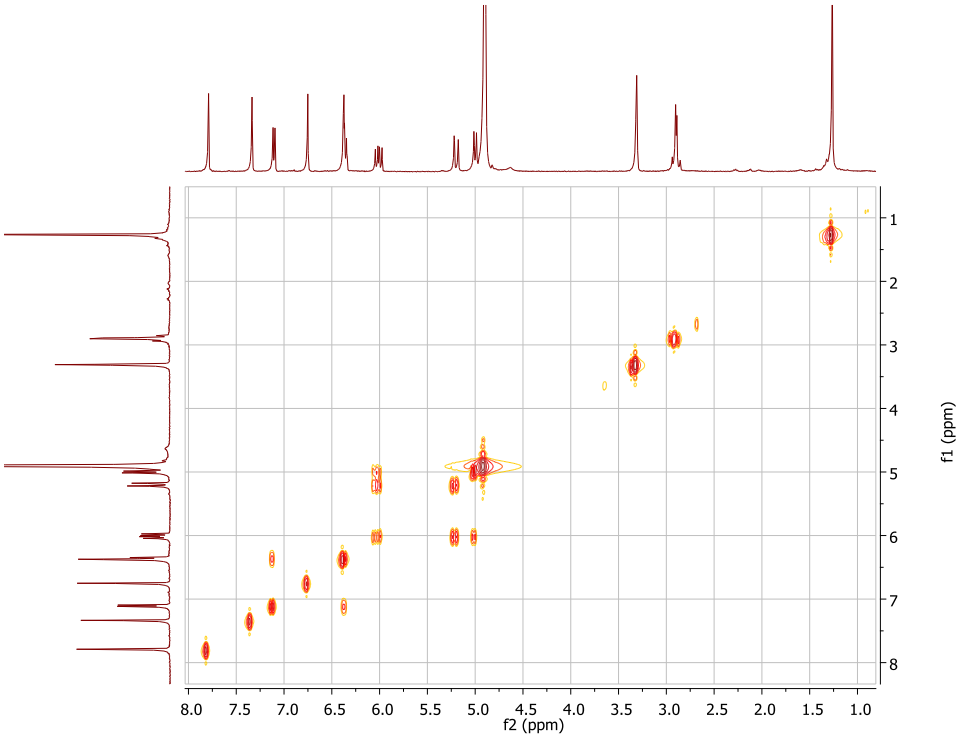


Figure S7a. ^{1}H NMR spectrum of compound **7**.

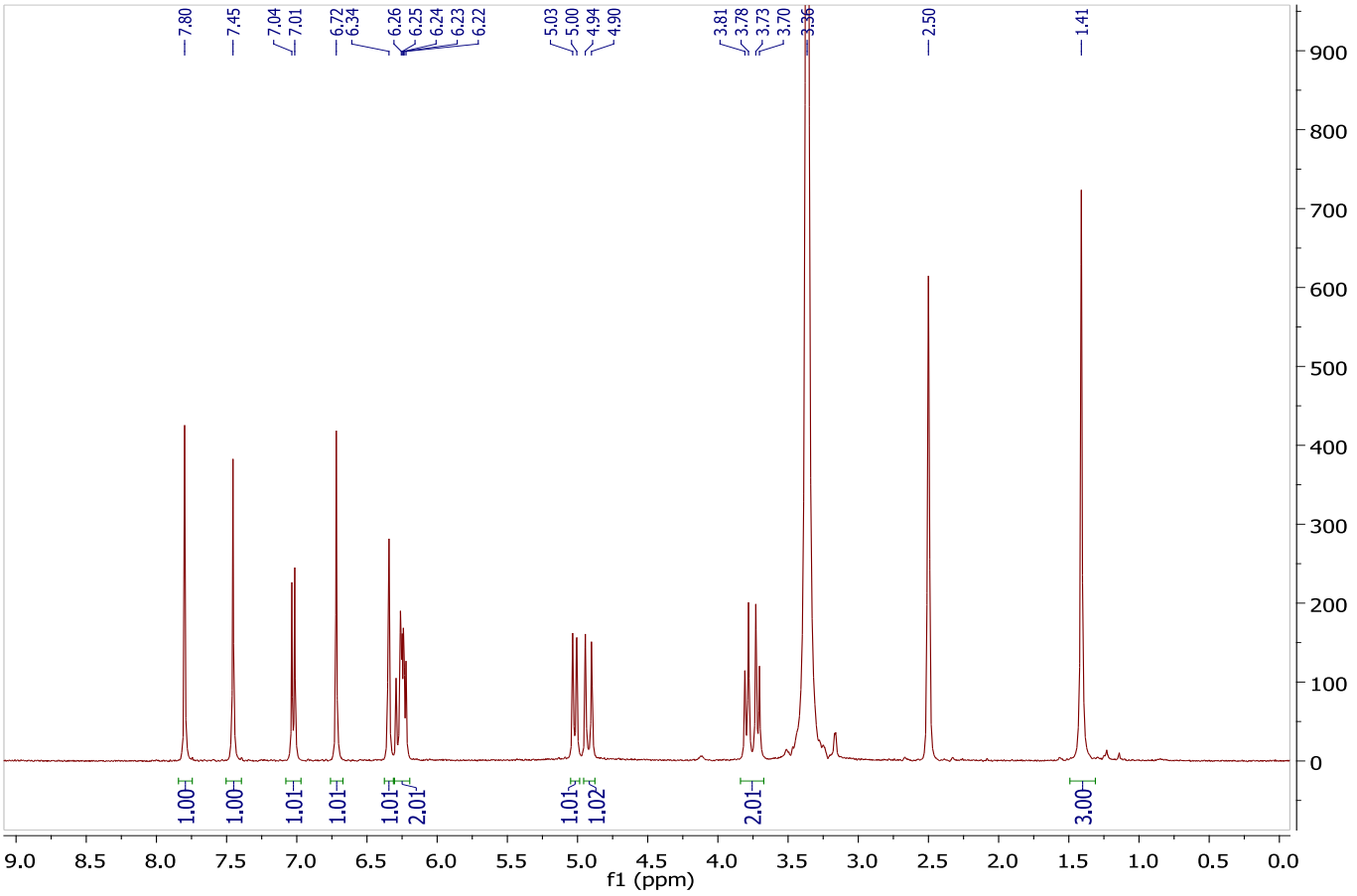


Figure S7b. ^{13}C NMR spectrum of compound **7**.

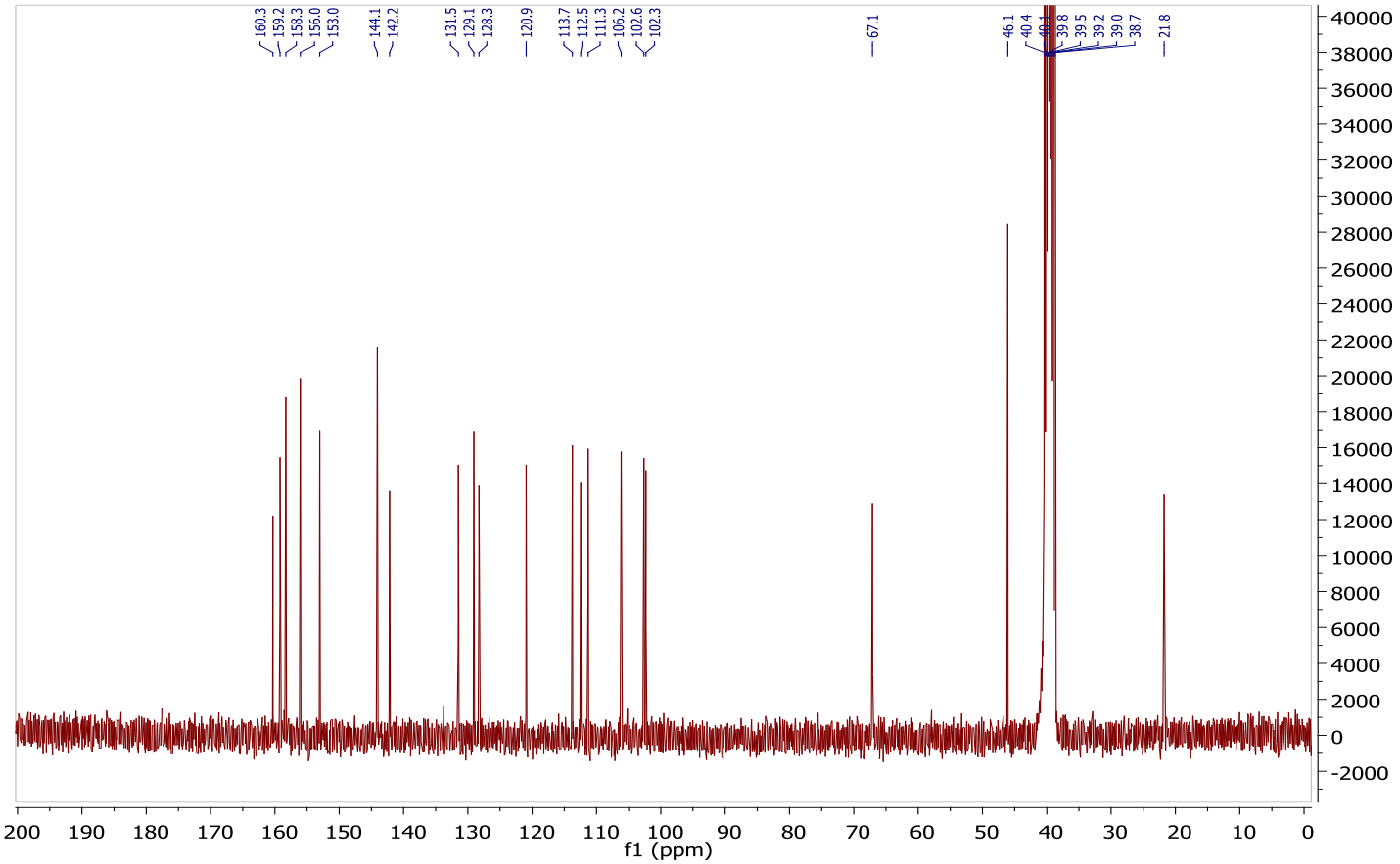


Figure S7c. ^{13}C DEPT 135 NMR spectrum of compound **7**.

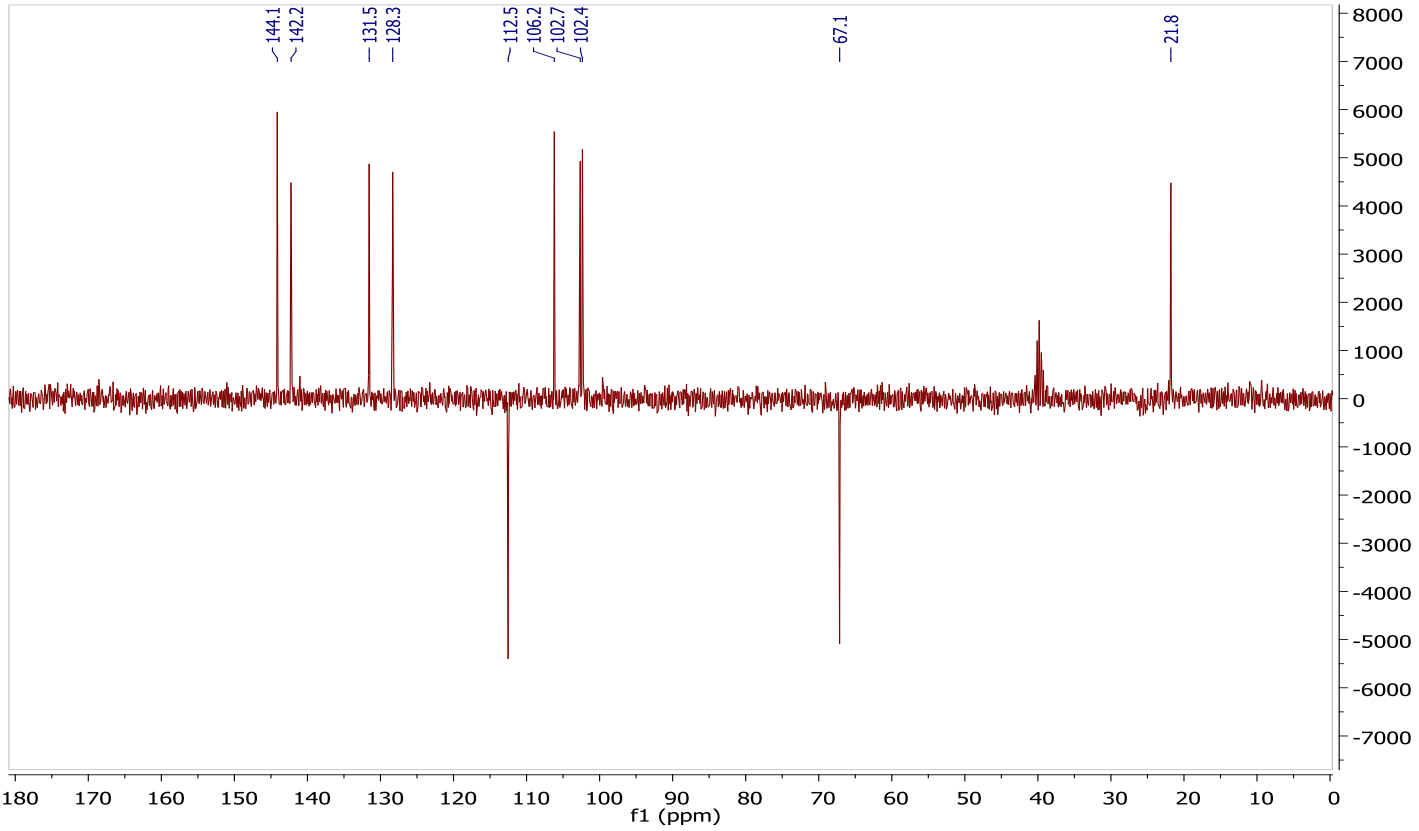


Figure S7d. HSQC spectrum of compound **7**.

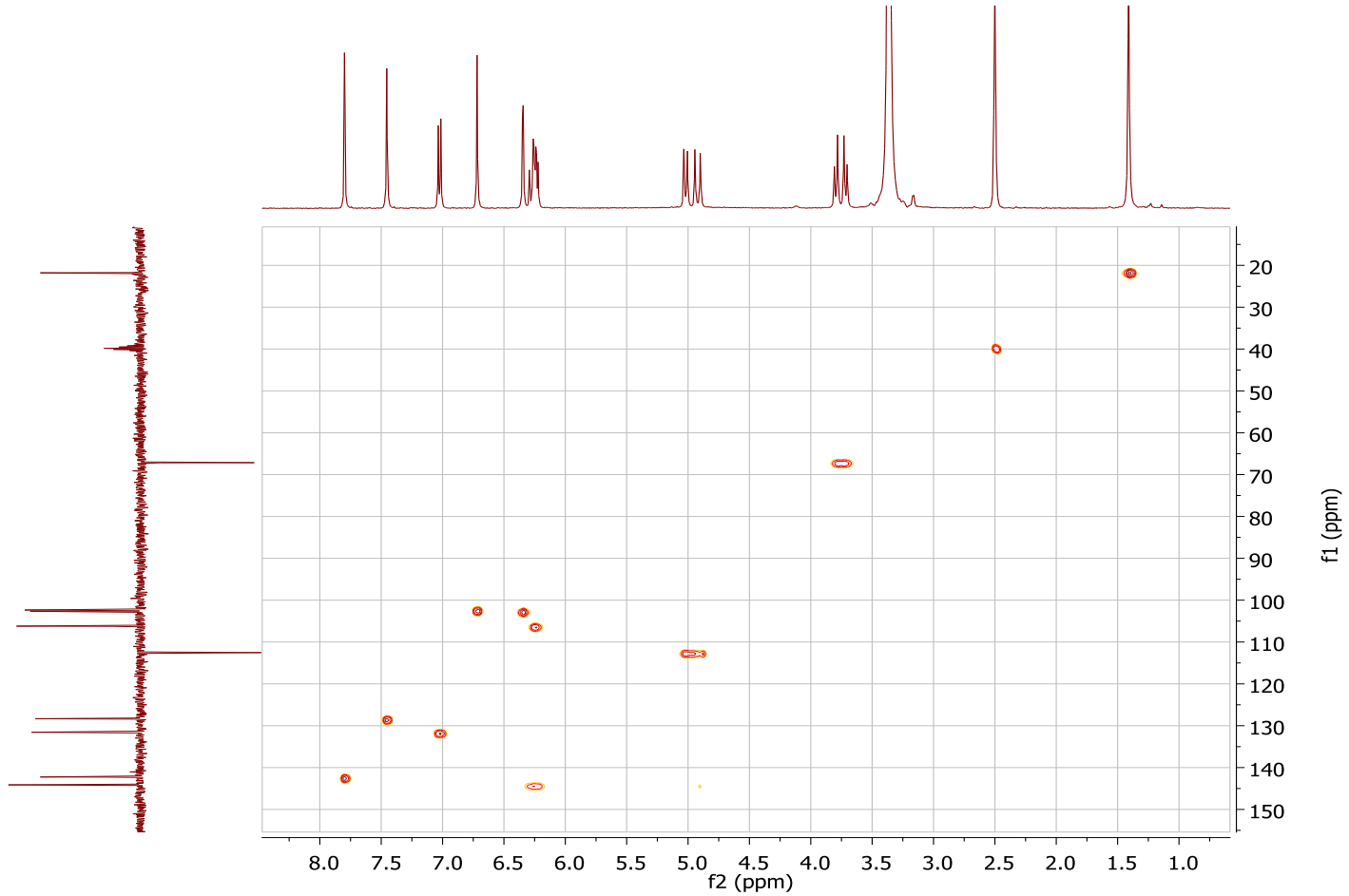


Figure S7e. HMBC spectrum of compound **7**.

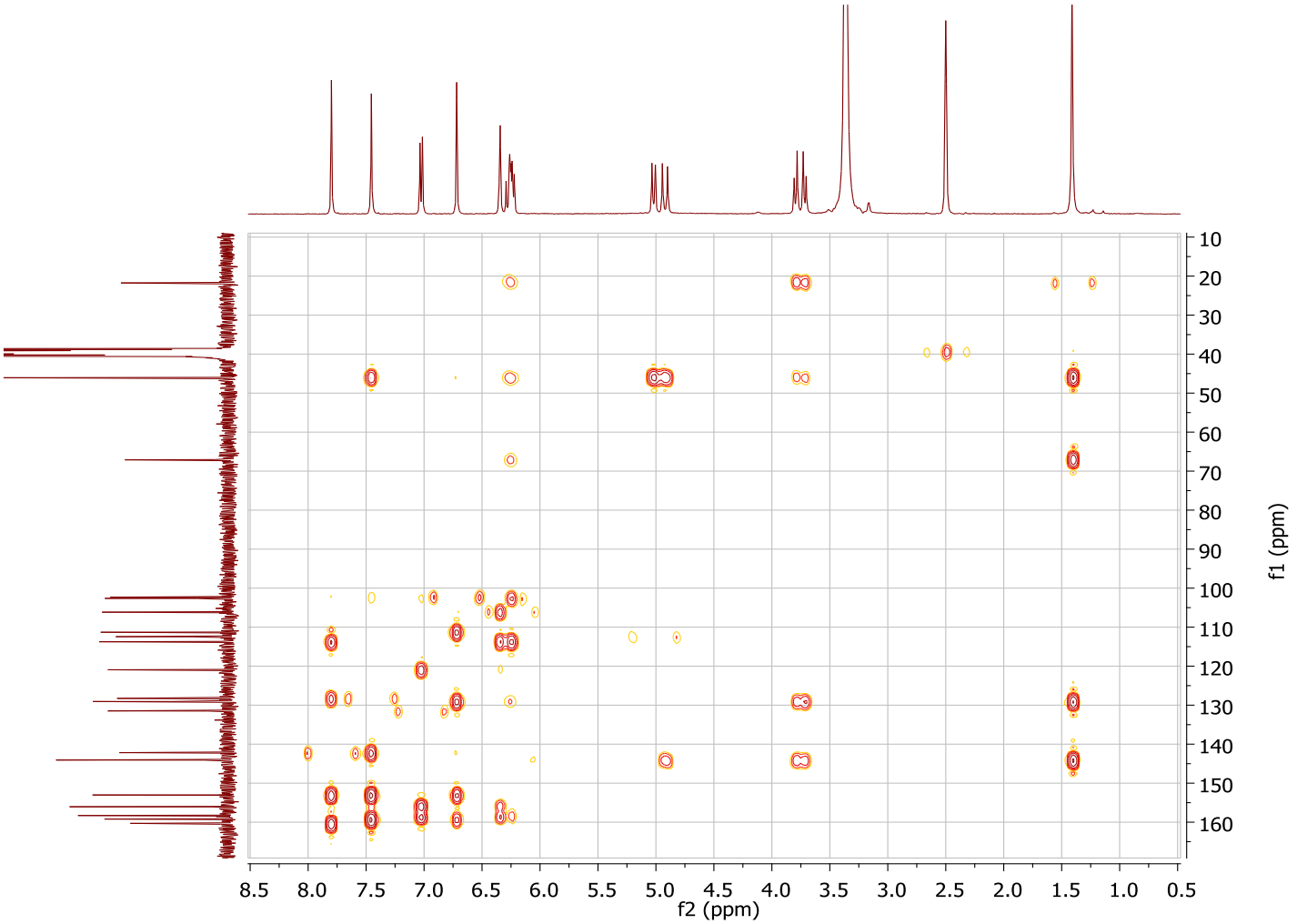


Figure S7f. ^{1}H-^{1}H COSY spectrum of compound **7**.

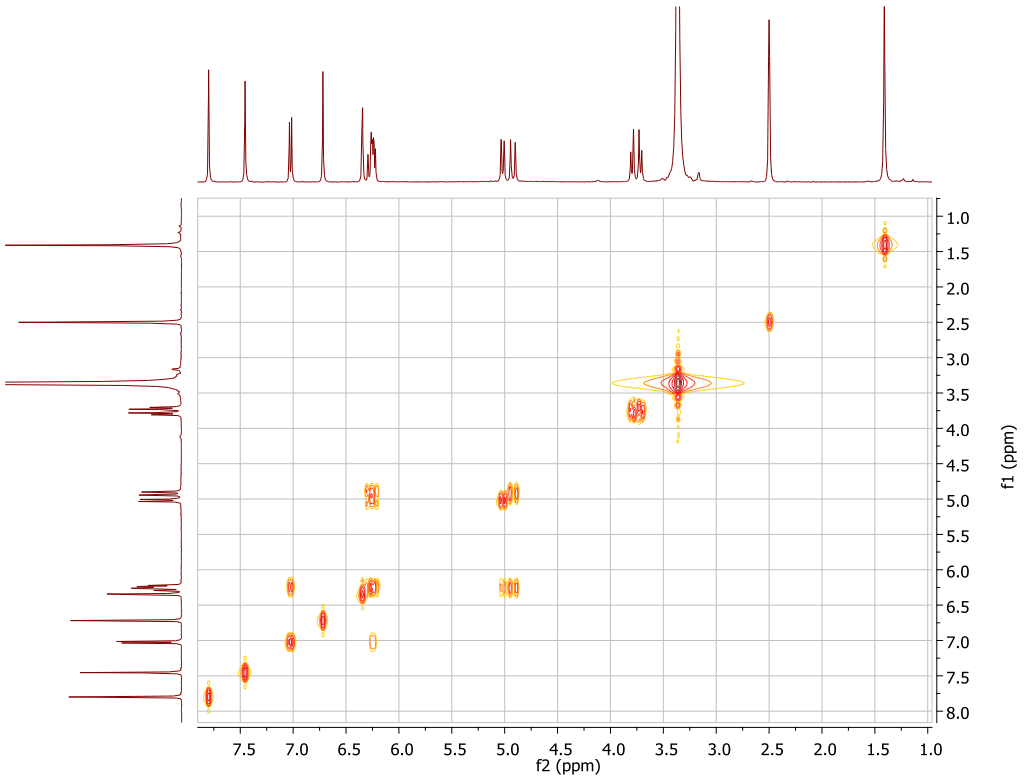


Figure S8a. ^{1}H NMR spectrum of compound **8**.

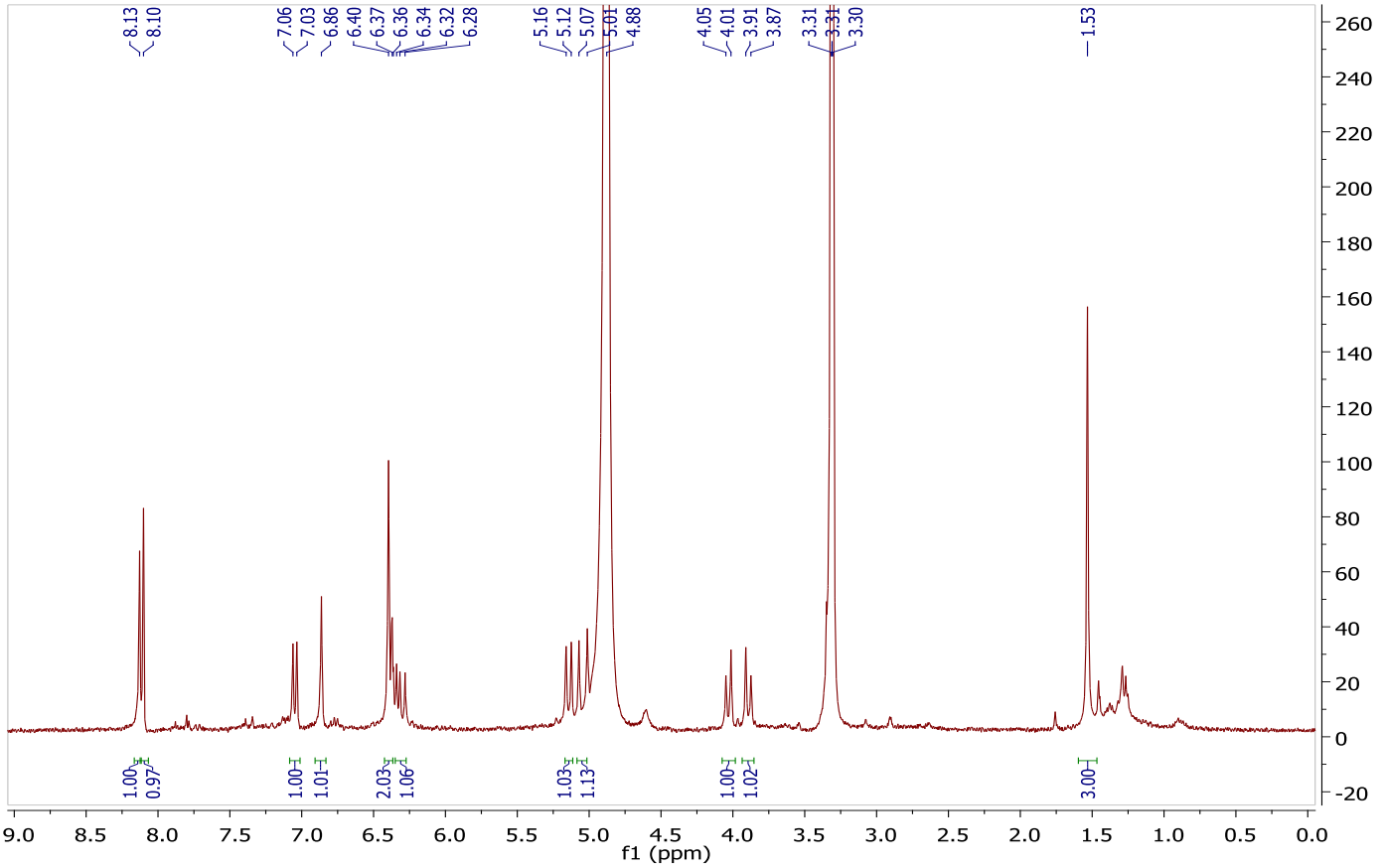


Figure S8b. ^{13}C NMR spectrum of compound **8**.

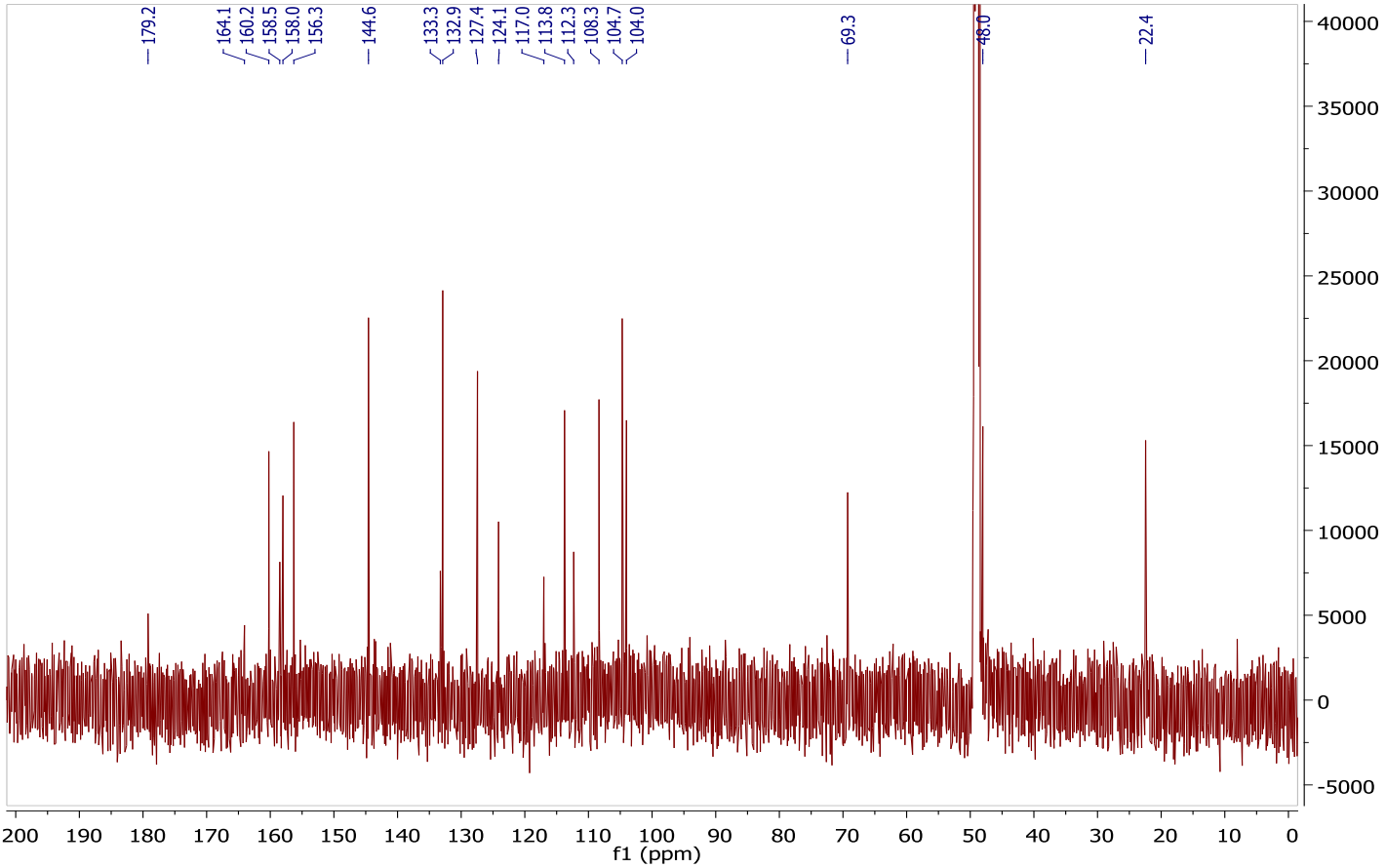


Figure S8c. ^{13}C DEPT 135 NMR spectrum of compound **8**.

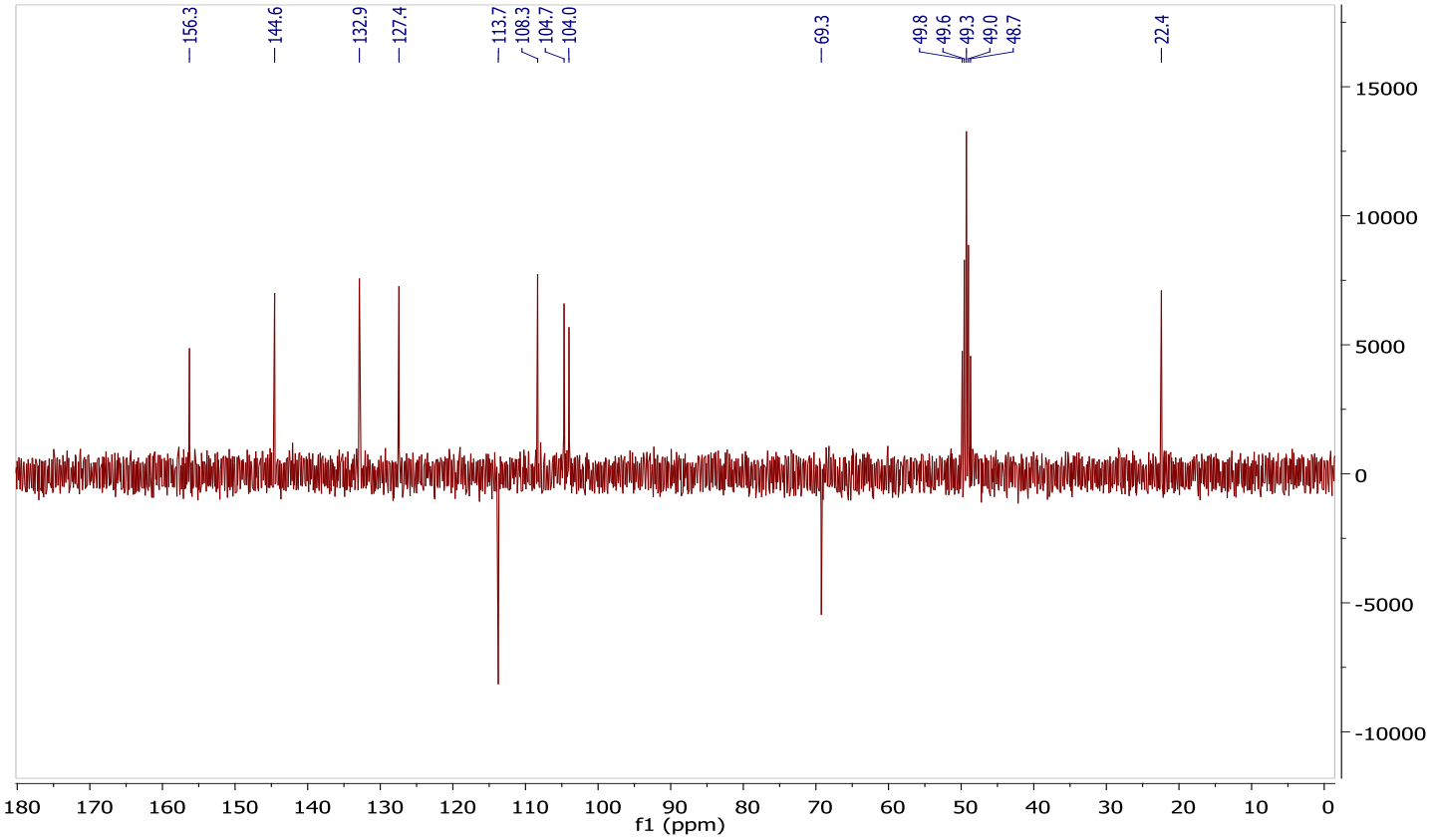


Figure S8d. HSQC spectrum of compound **8**.

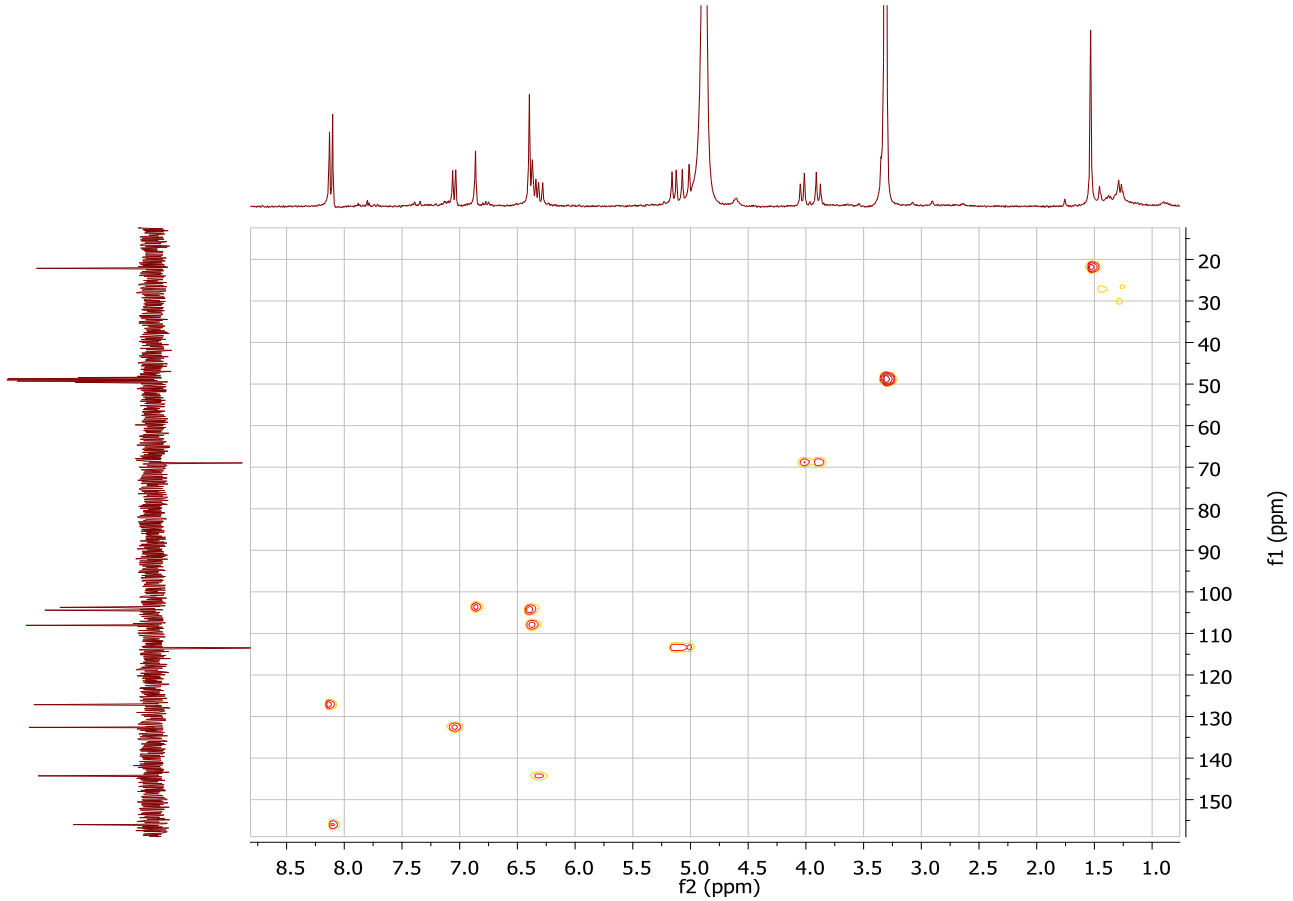


Figure S8e. HMBC spectrum of compound **8**.

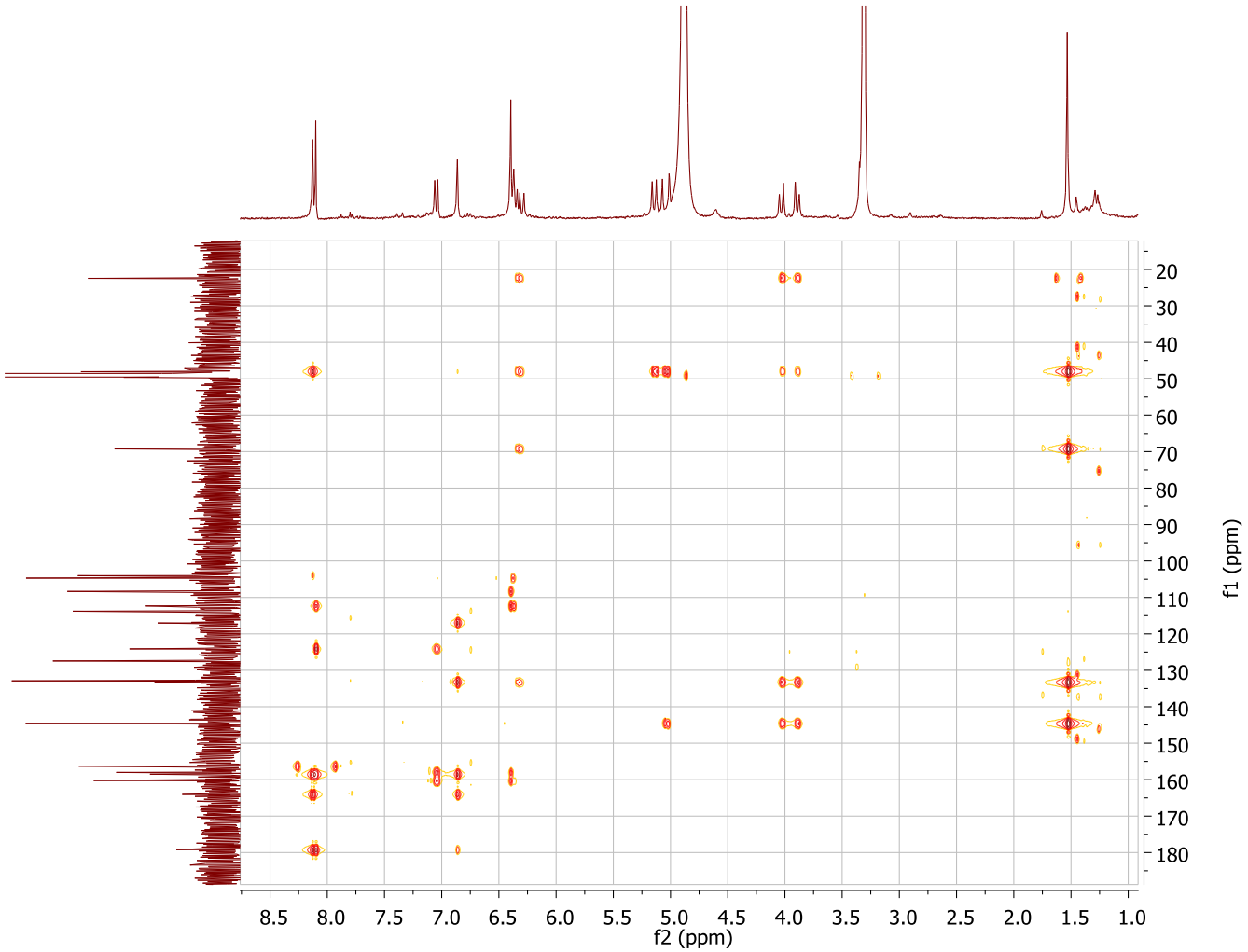


Figure S8f. ^{1}H-^{1}H COSY spectrum of compound **8**.

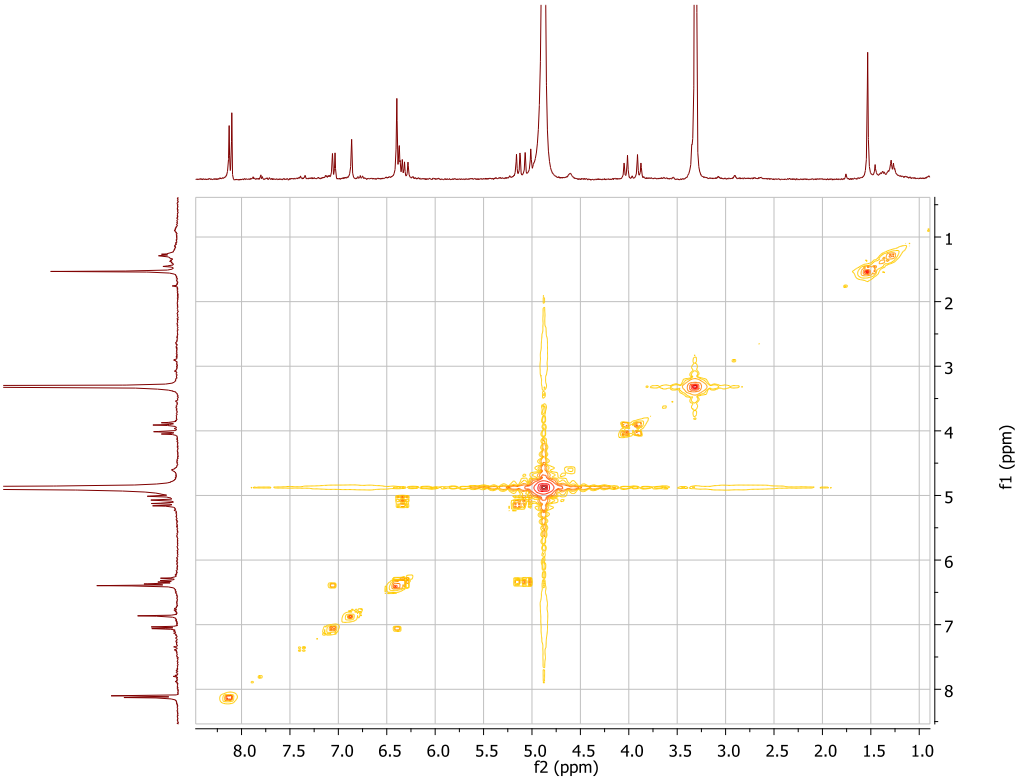


Figure S9a. ^{1}H NMR spectrum of compound **9**.

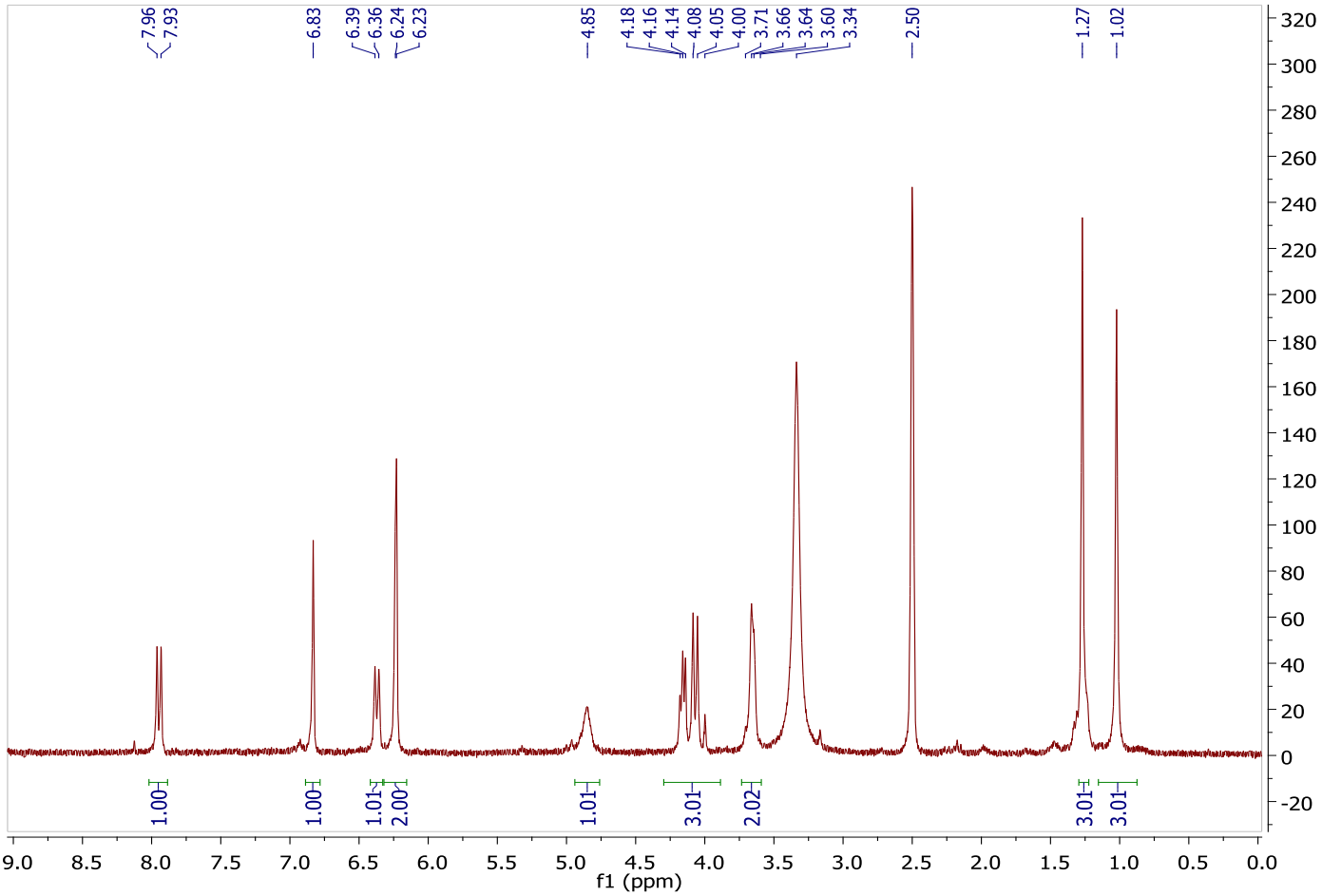


Figure S9b. ^{13}C NMR spectrum of compound **9**.

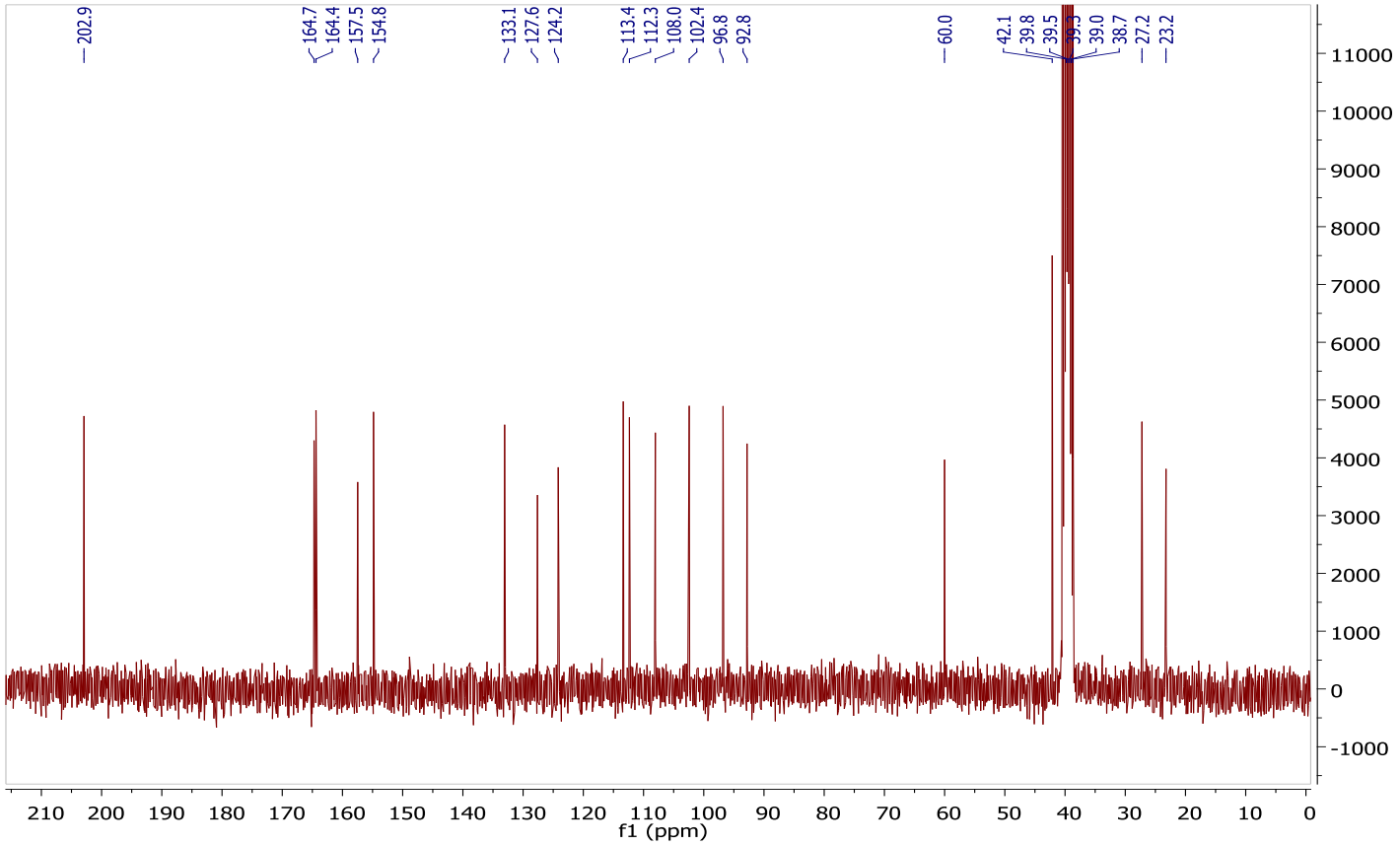


Figure S9c. ^{13}C DEPT 135 NMR spectrum of compound **9**.

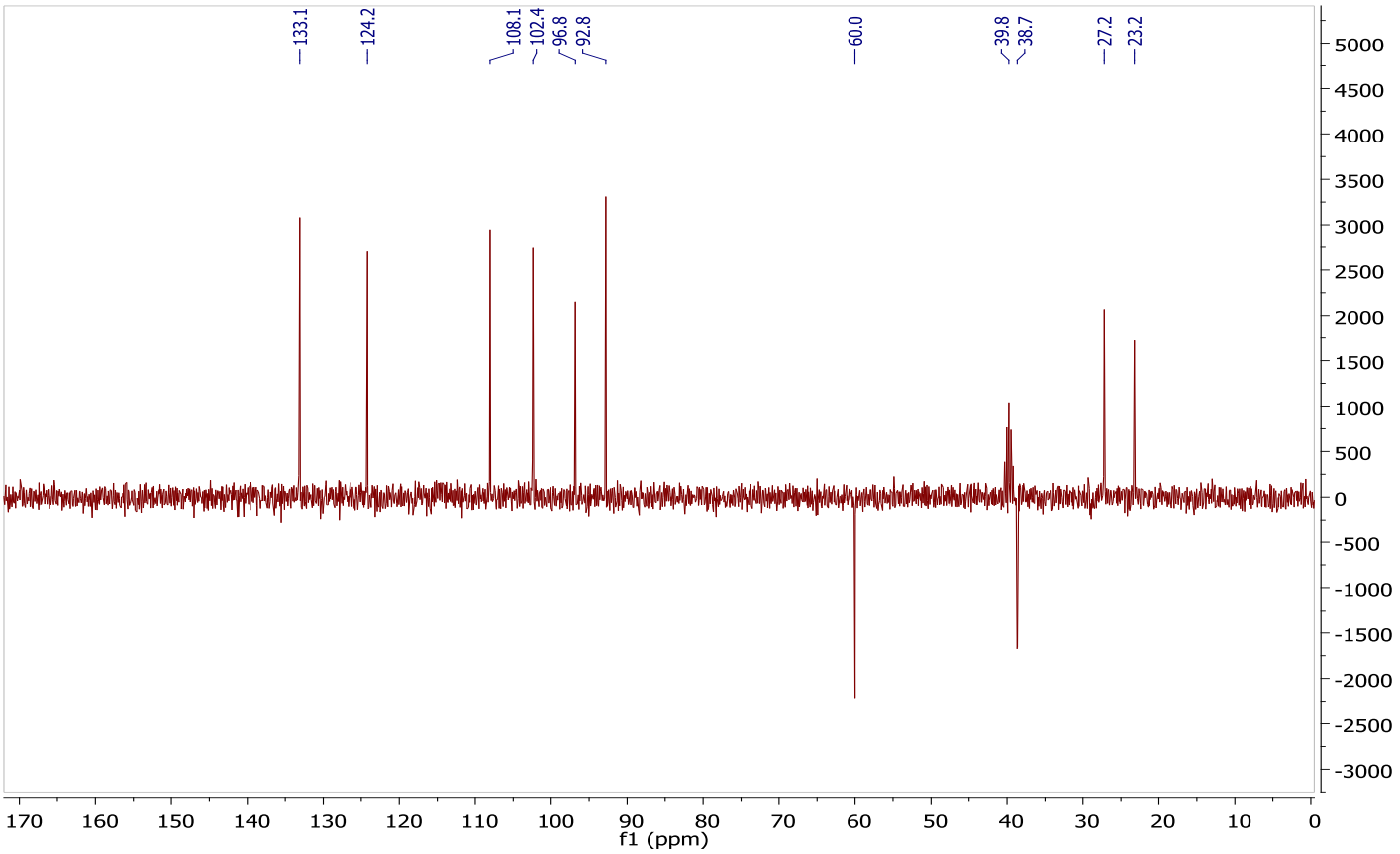


Figure S9d. HSQC spectrum of compound **9**.

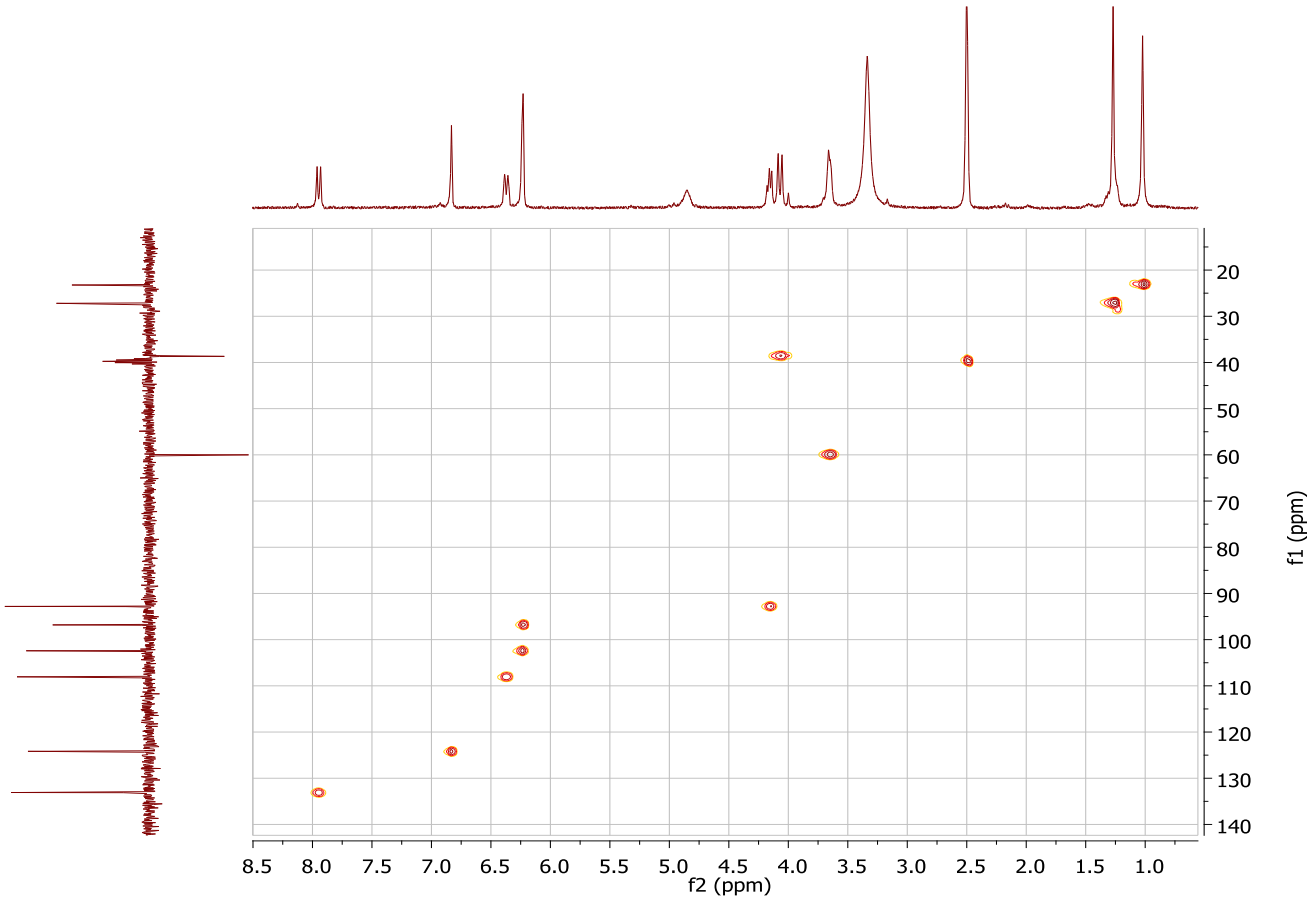


Figure S9e. HMBC spectrum of compound **9**.

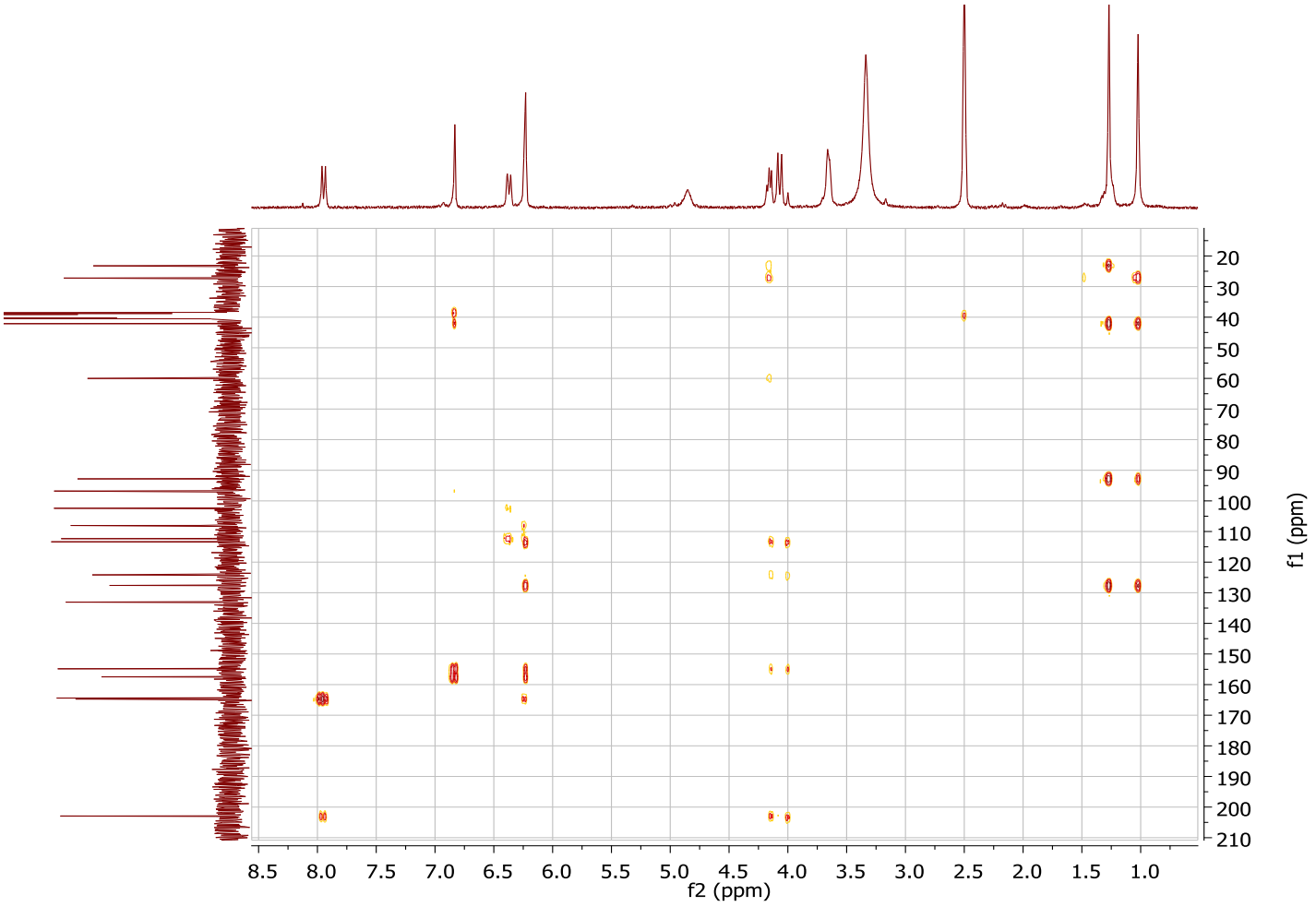


Figure S9f. ^{1}H-^{1}H COSY spectrum of compound **9**.

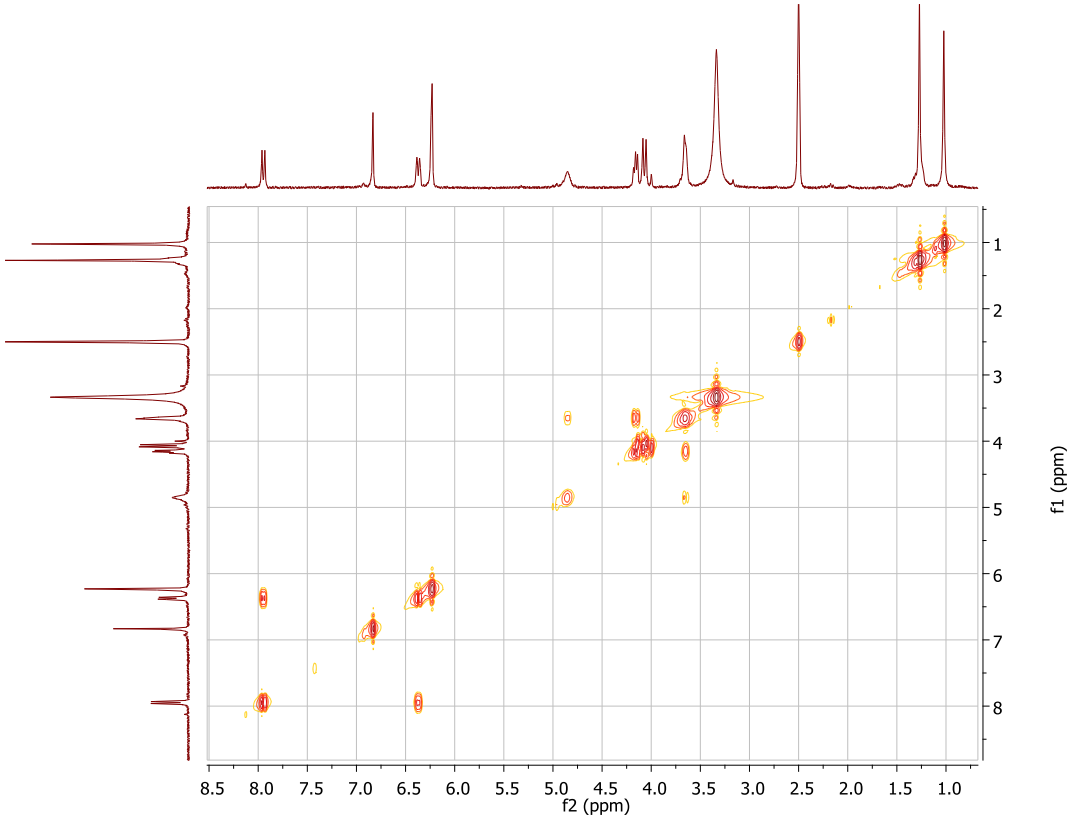


Figure S10a. ^{1}H NMR spectrum of compound **10**.

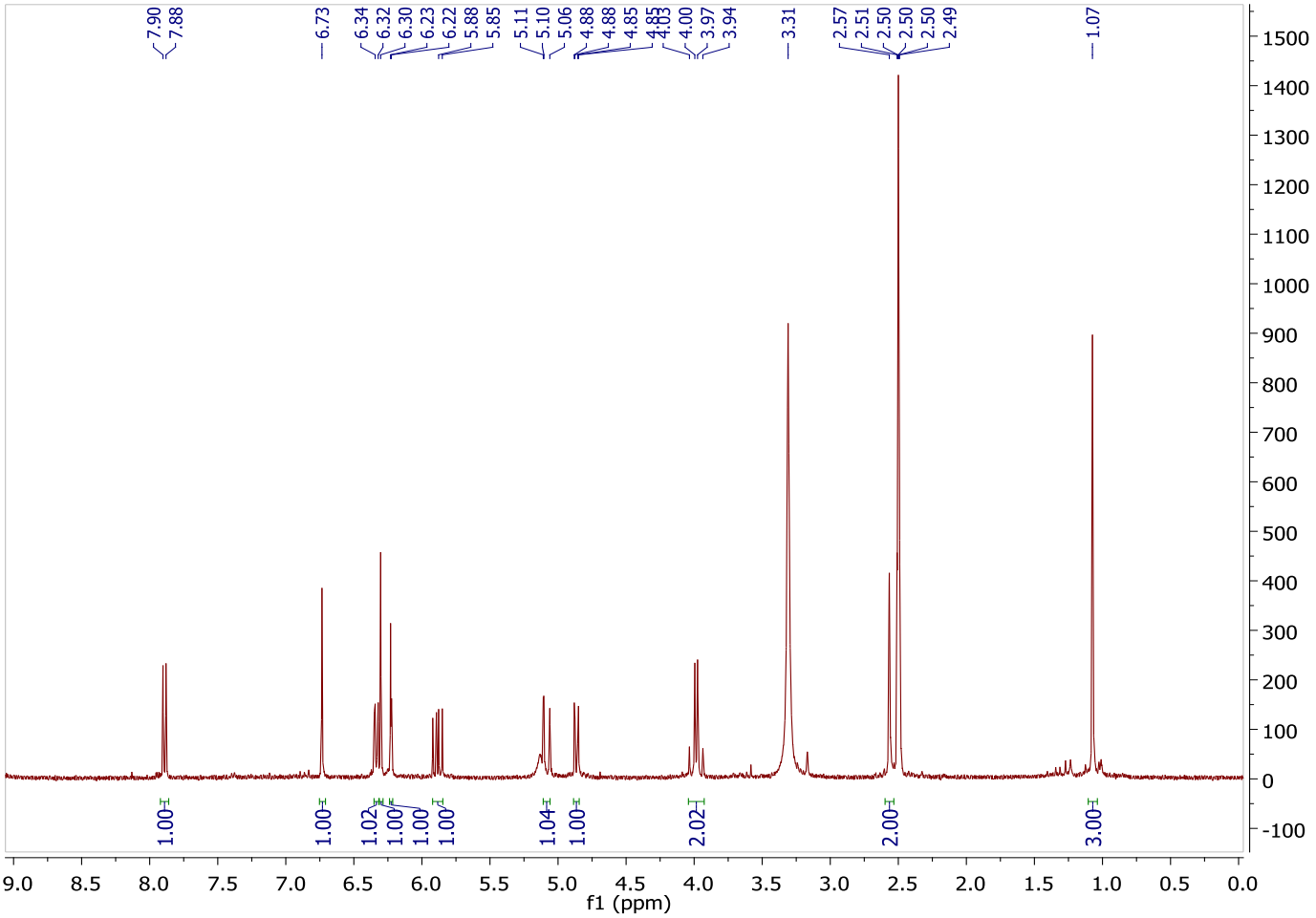


Figure S10b. ^{13}C NMR spectrum of compound **10**.

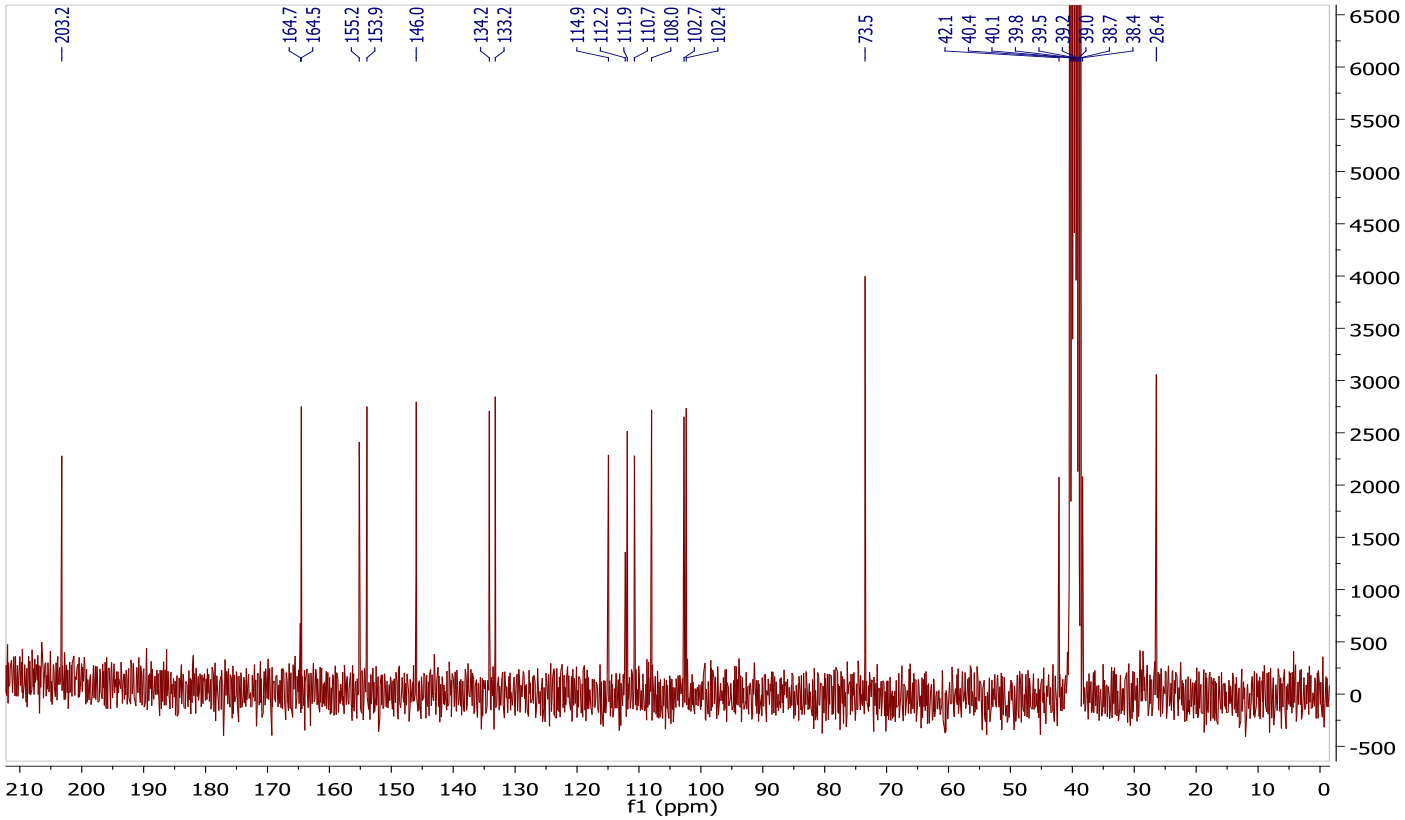


Figure S10c. ^{13}C DEPT 135 NMR spectrum of compound **10**.

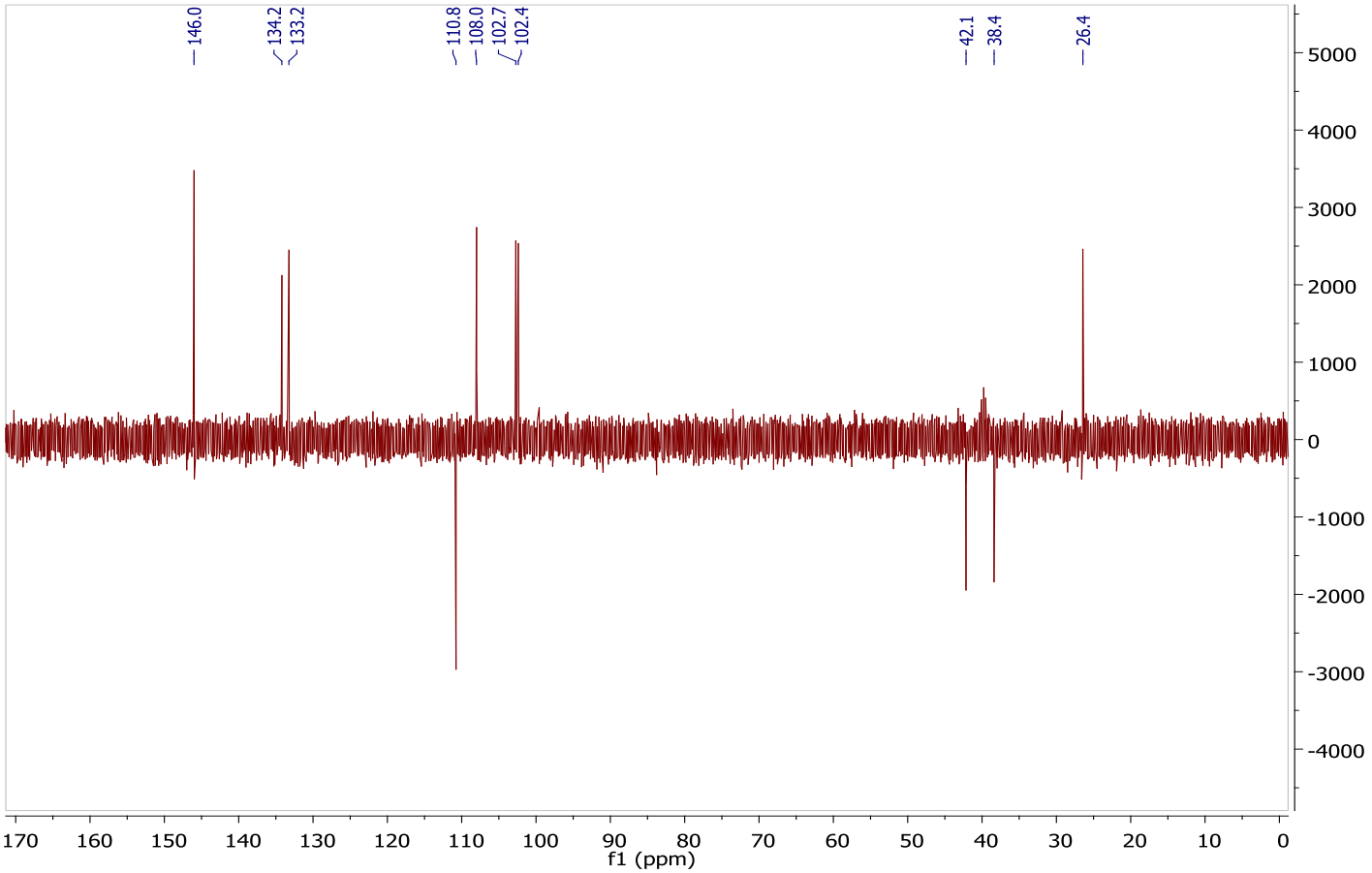


Figure S10d. HSQC spectrum of compound **10**.

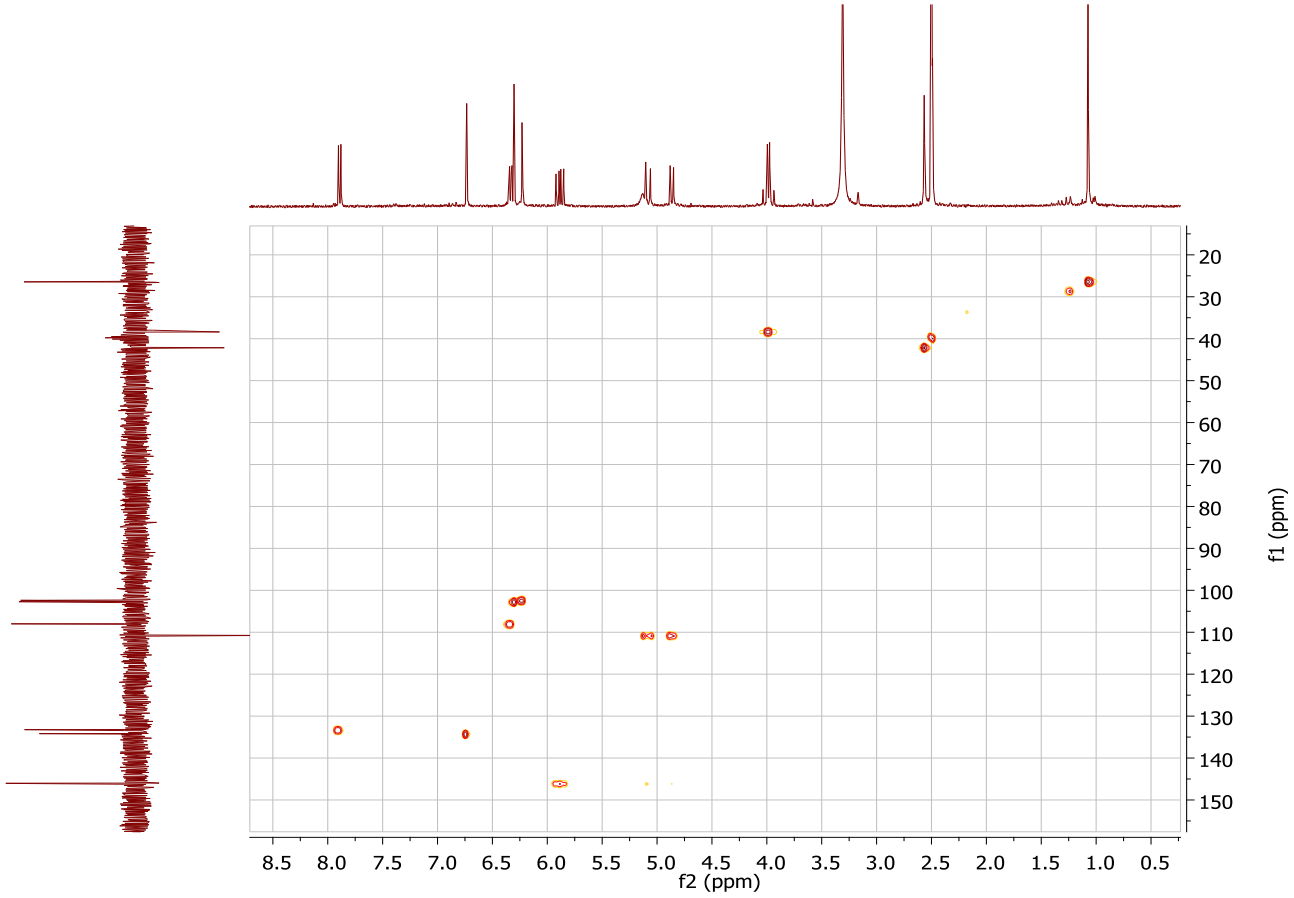


Figure S10e. HMBC spectrum of compound **10**.

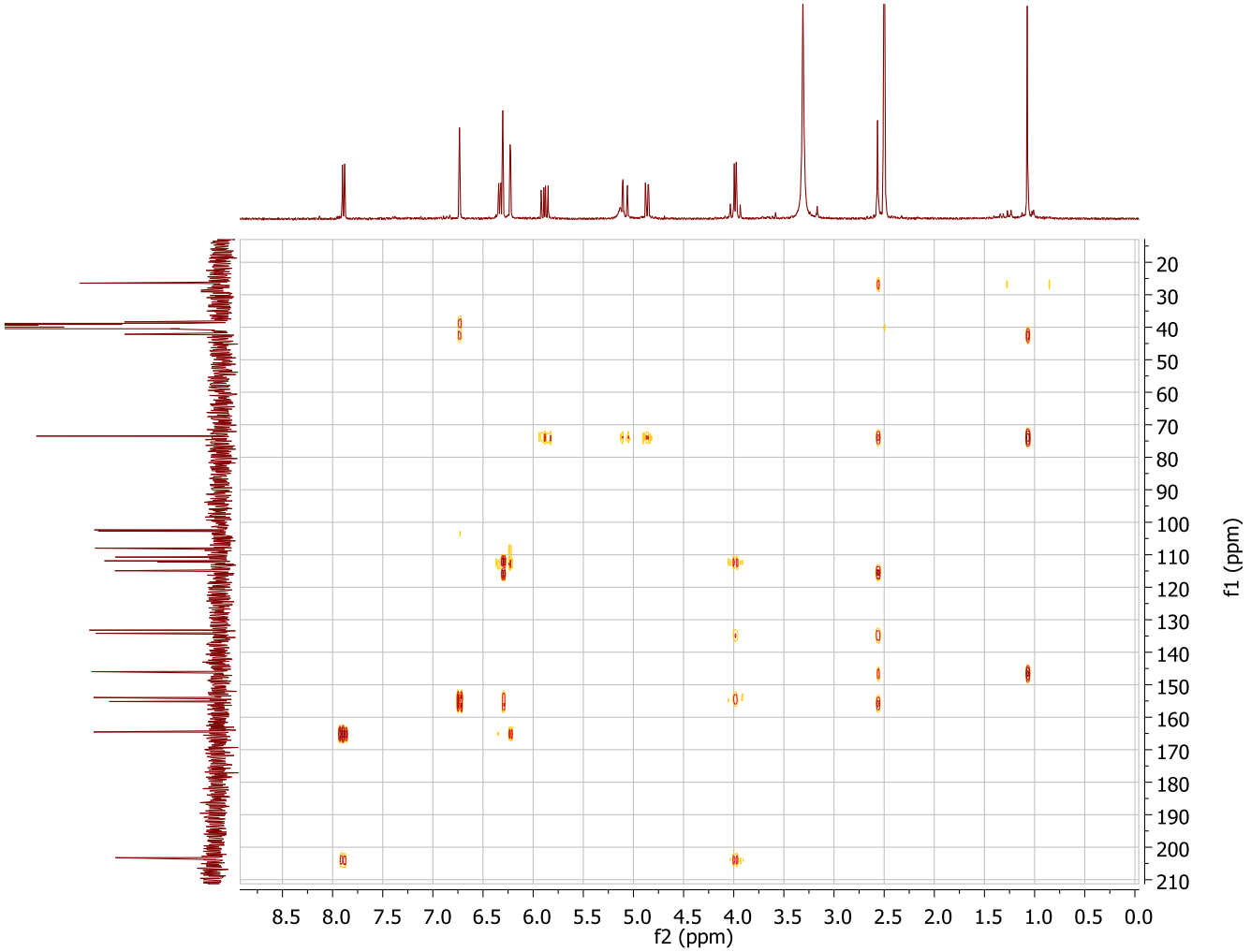


Figure S10f. ^{1}H-^{1}H COSY spectrum of compound **10**.

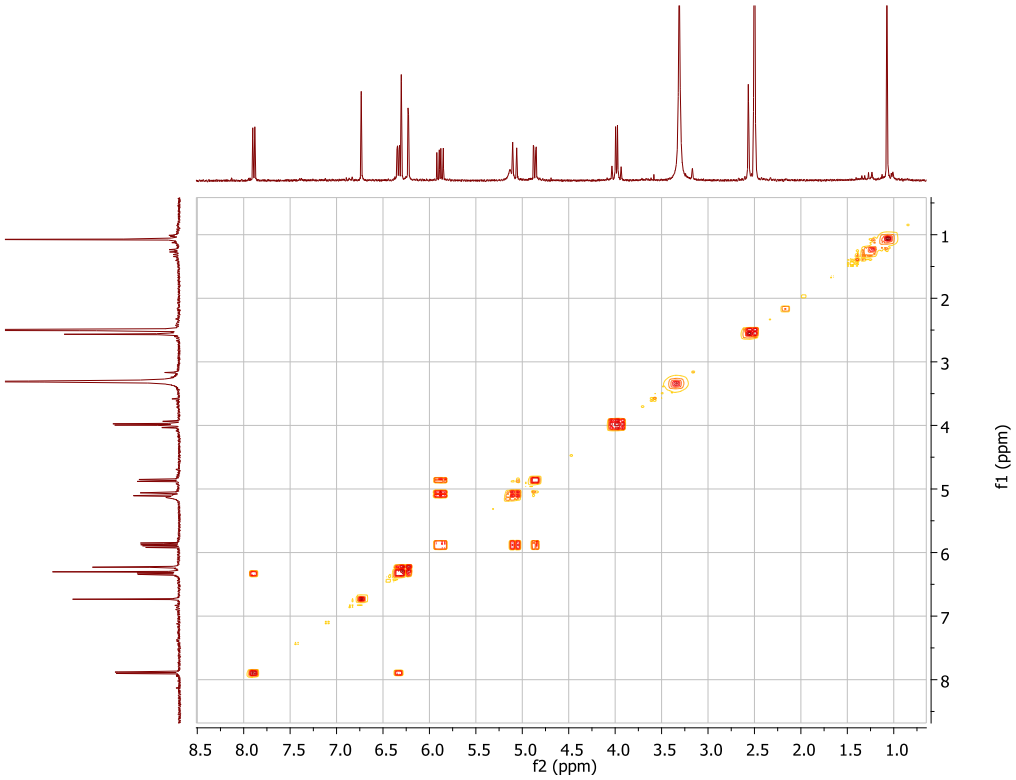


Figure S11a. ^{1}H NMR spectrum of compound **11**.

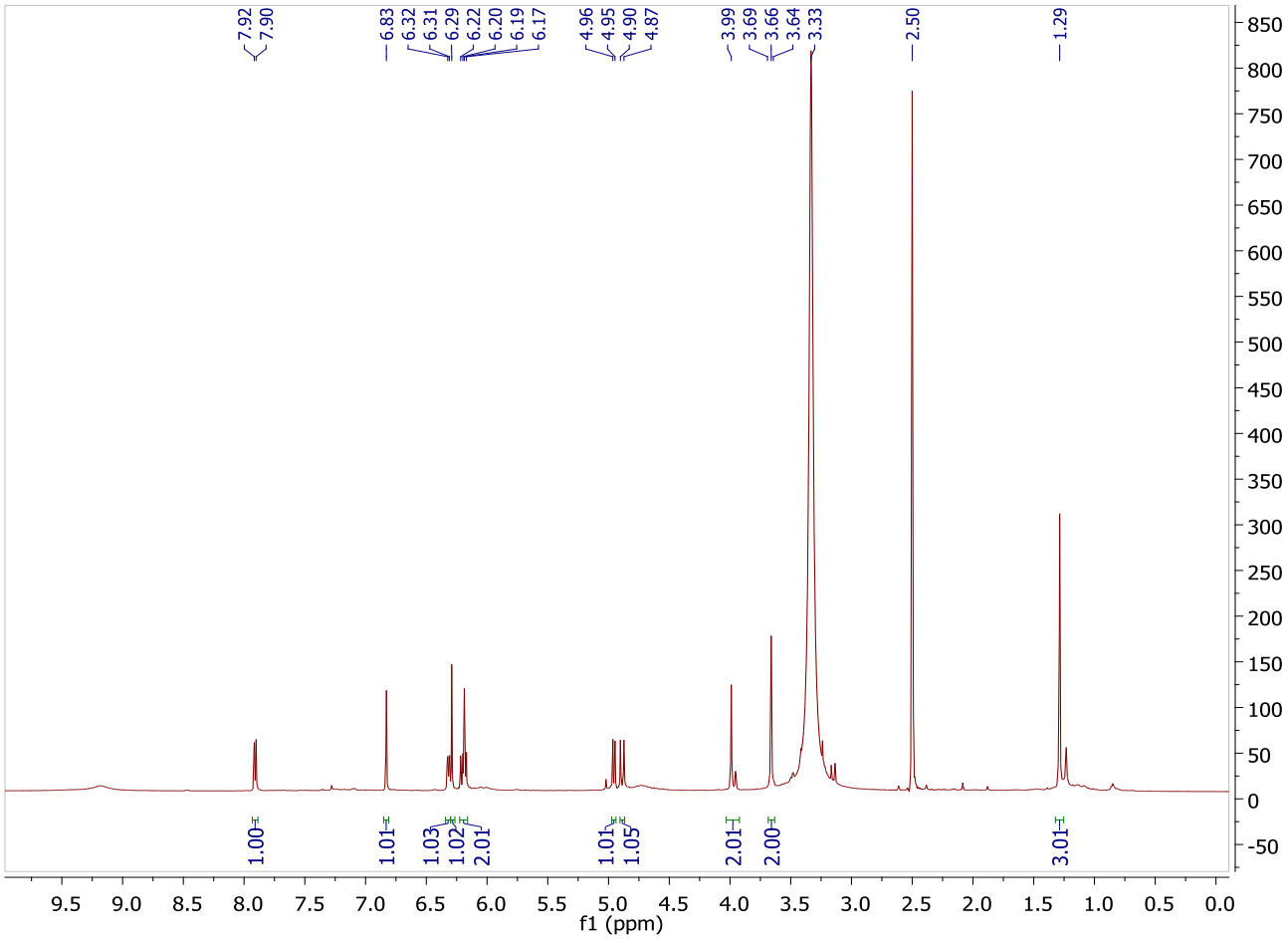


Figure S11b. ^{13}C NMR spectrum of compound **11**.

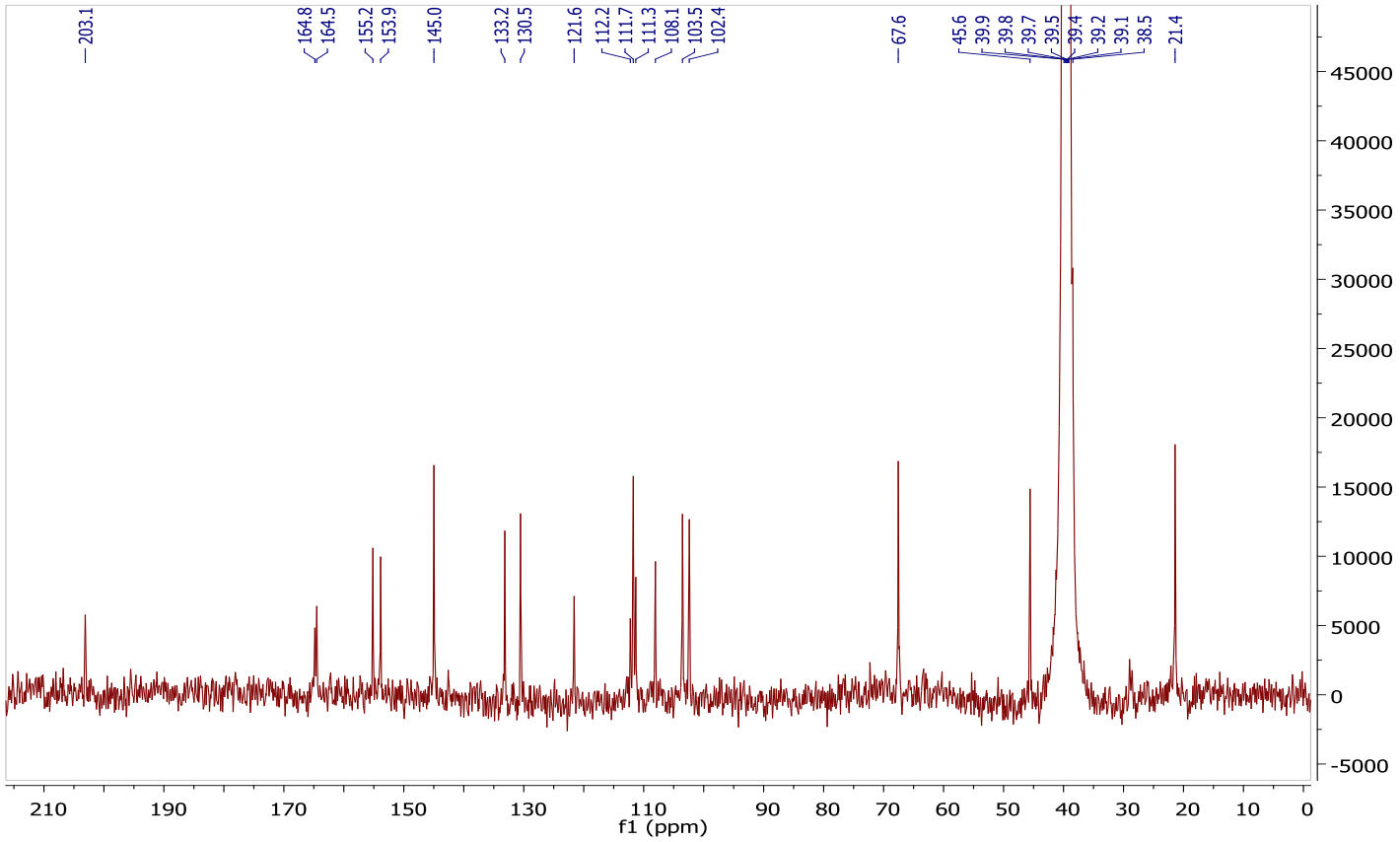


Figure S11c. ^{13}C DEPT 135 NMR spectrum of compound **11**.

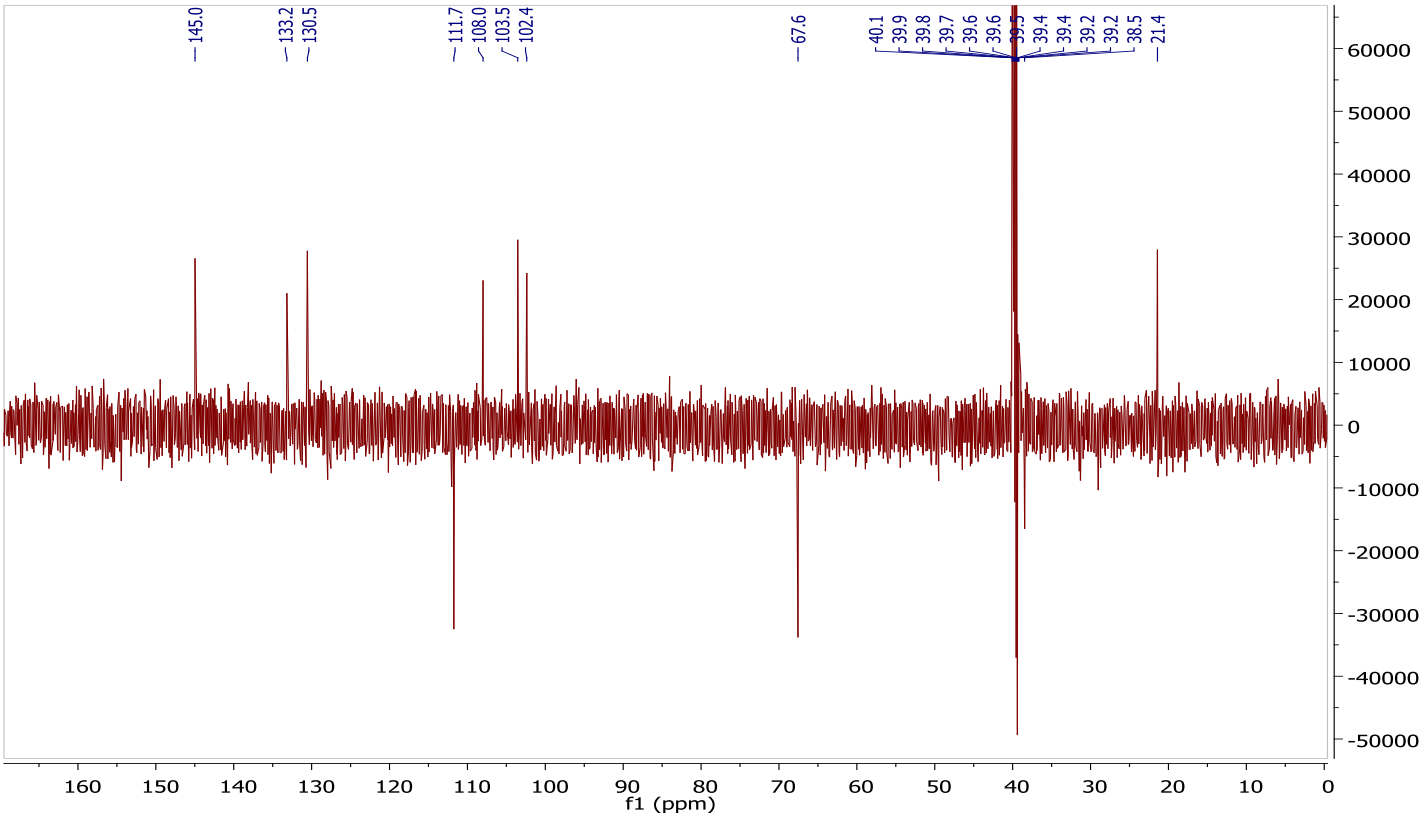


Figure S11d. HSQC spectrum of compound **11**.

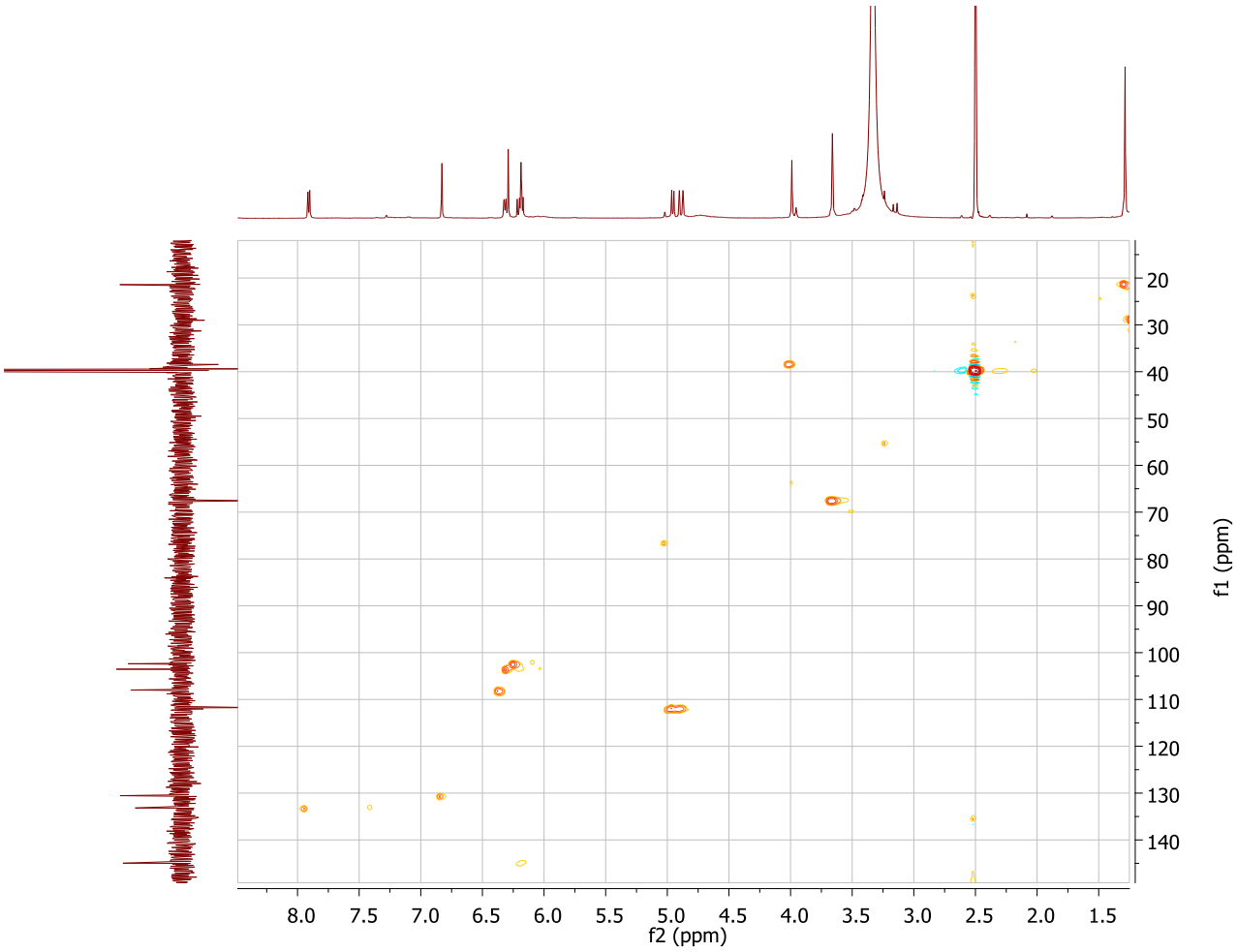


Figure S11e. HMBC spectrum of compound **11**.

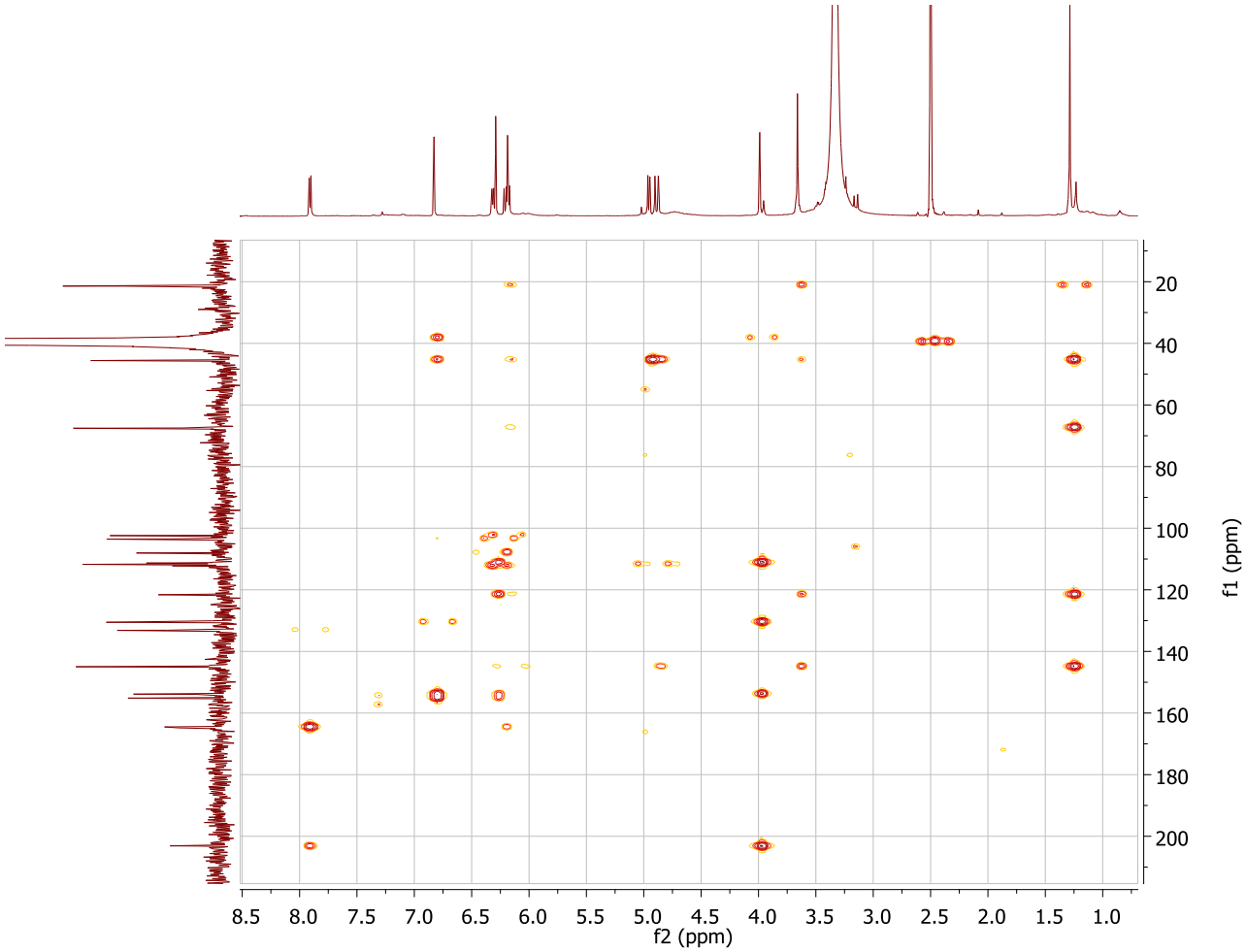


Figure S11f. ^{1}H-^{1}H COSY spectrum of compound **11**.

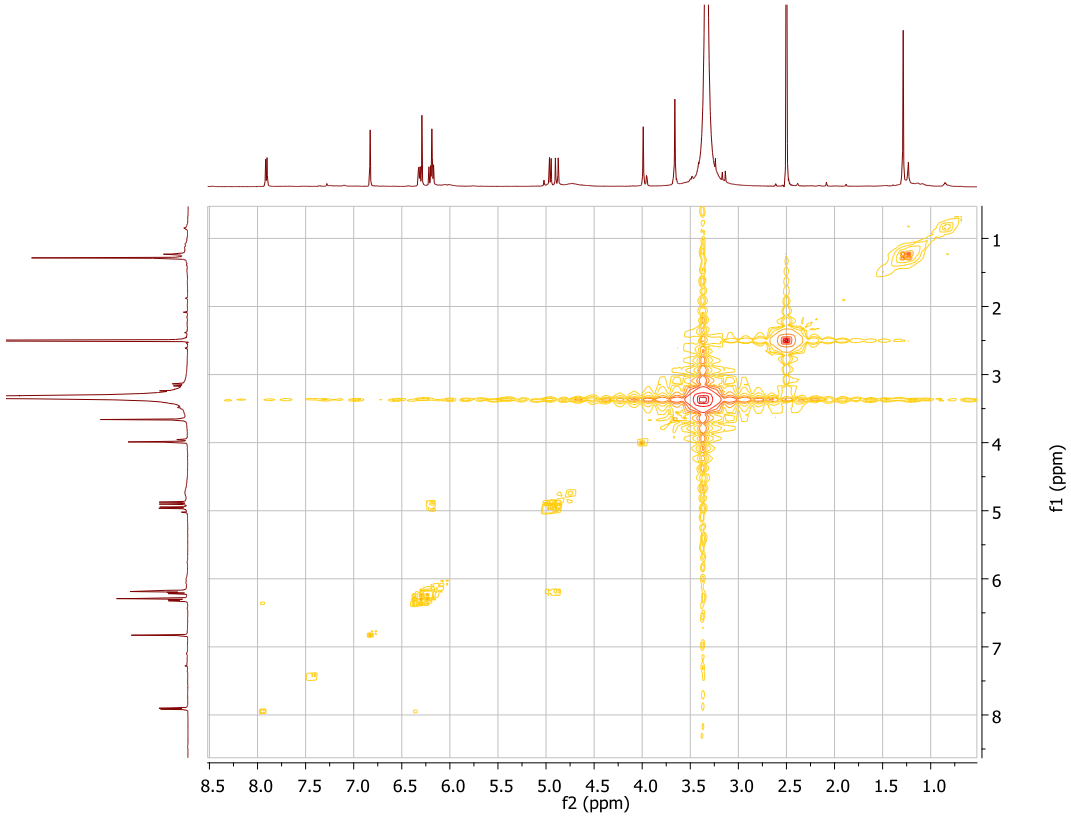


Figure S12a. ^{1}H NMR spectrum of unpurified product mixture of the reaction in scheme 1, showing the presence of extra singlets at δ_H 7.02 and 7.20 (H-3) in the product and the disappearance of H-8 signal (δ_H 4.07) of the starting material, which indicated that the expected 2-arylbenzofuran skeleton was generated.

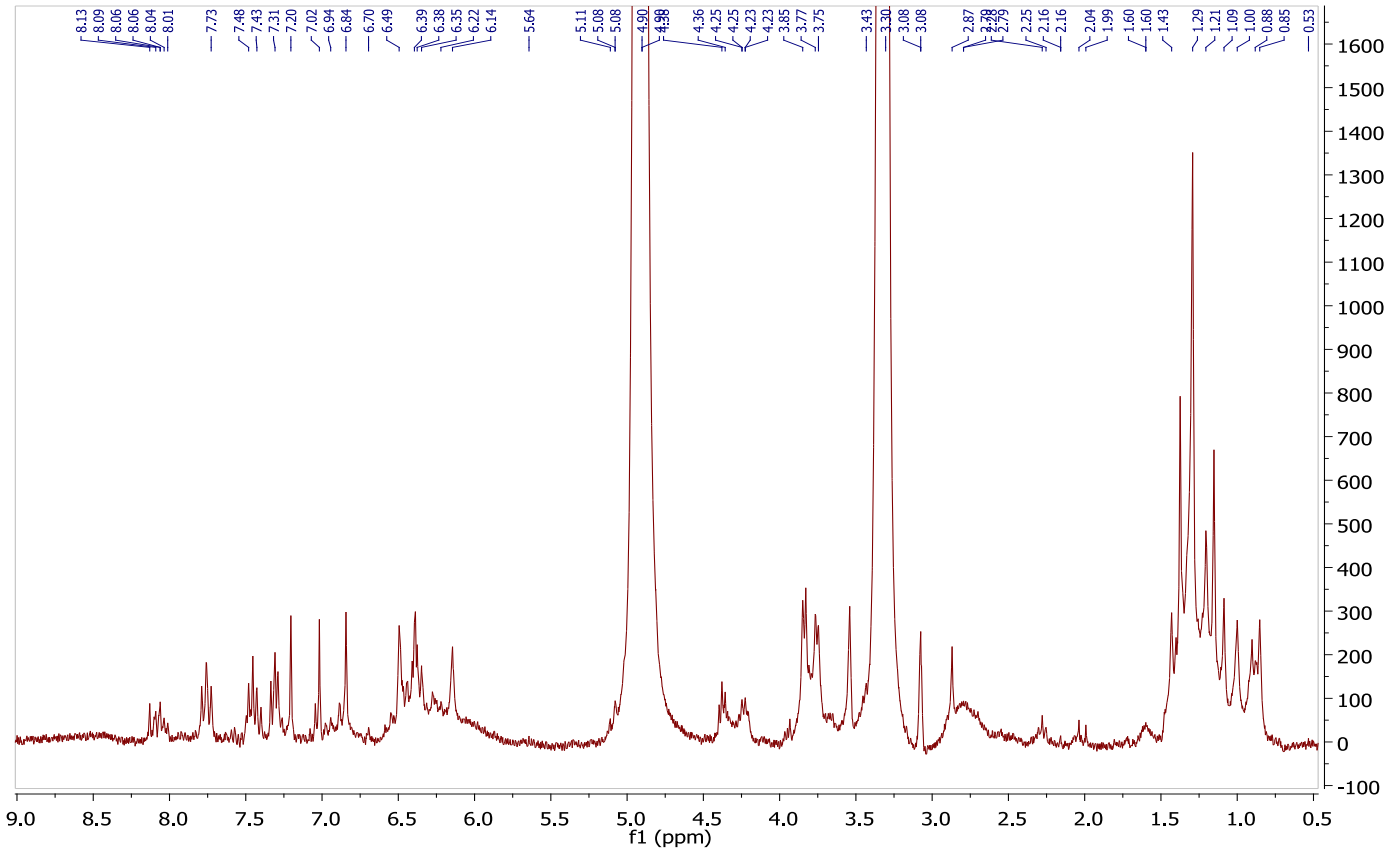
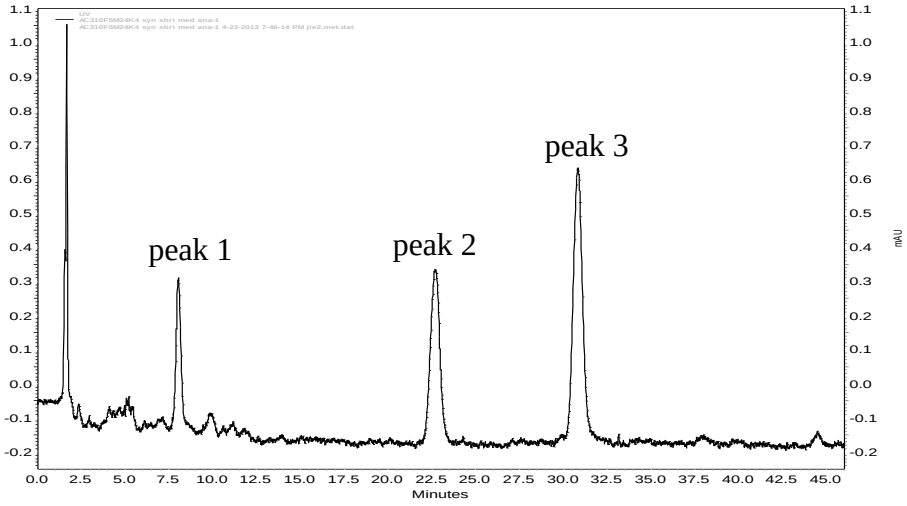
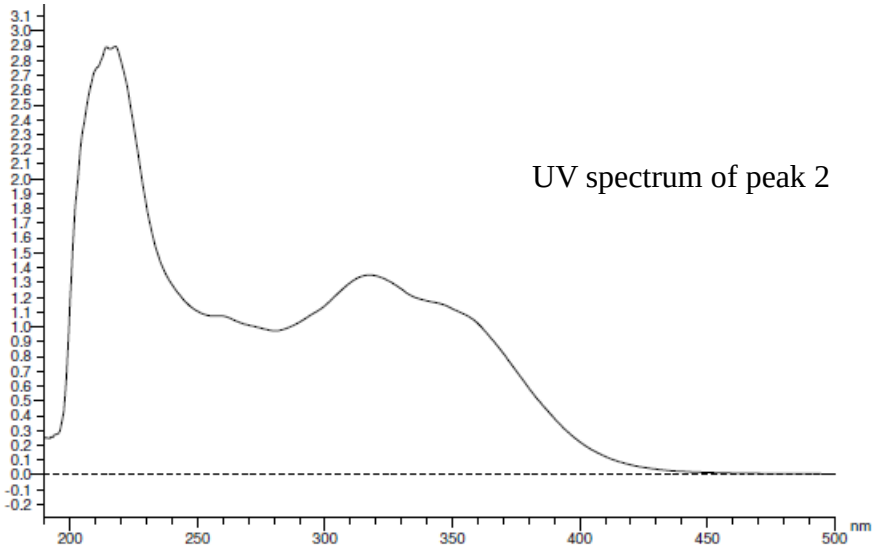


Figure S12b. HPLC separation chromatogram of the reaction solution of Scheme 2, along with the UV spectra of peaks 2 and 3 which are characteristic of a 2-arylbenzofuran skeleton.





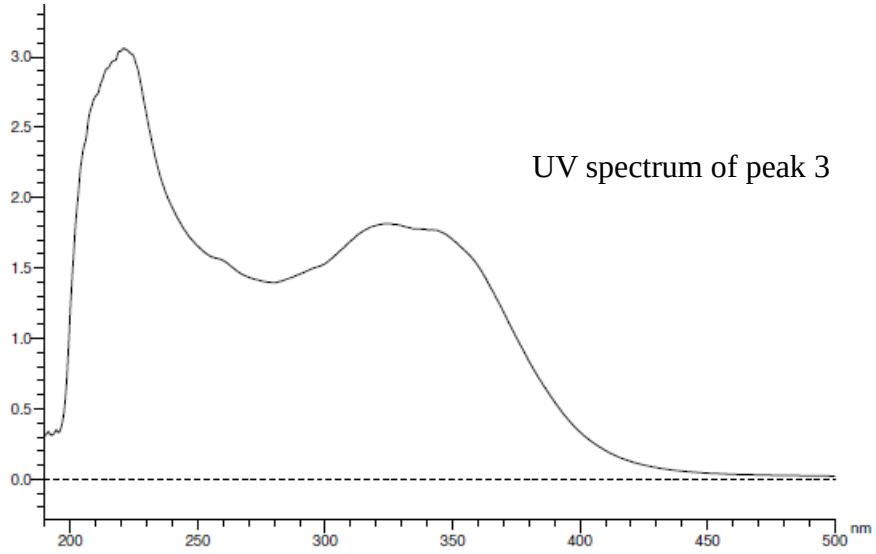


Figure S13a. HRESIMS of compound **1**.

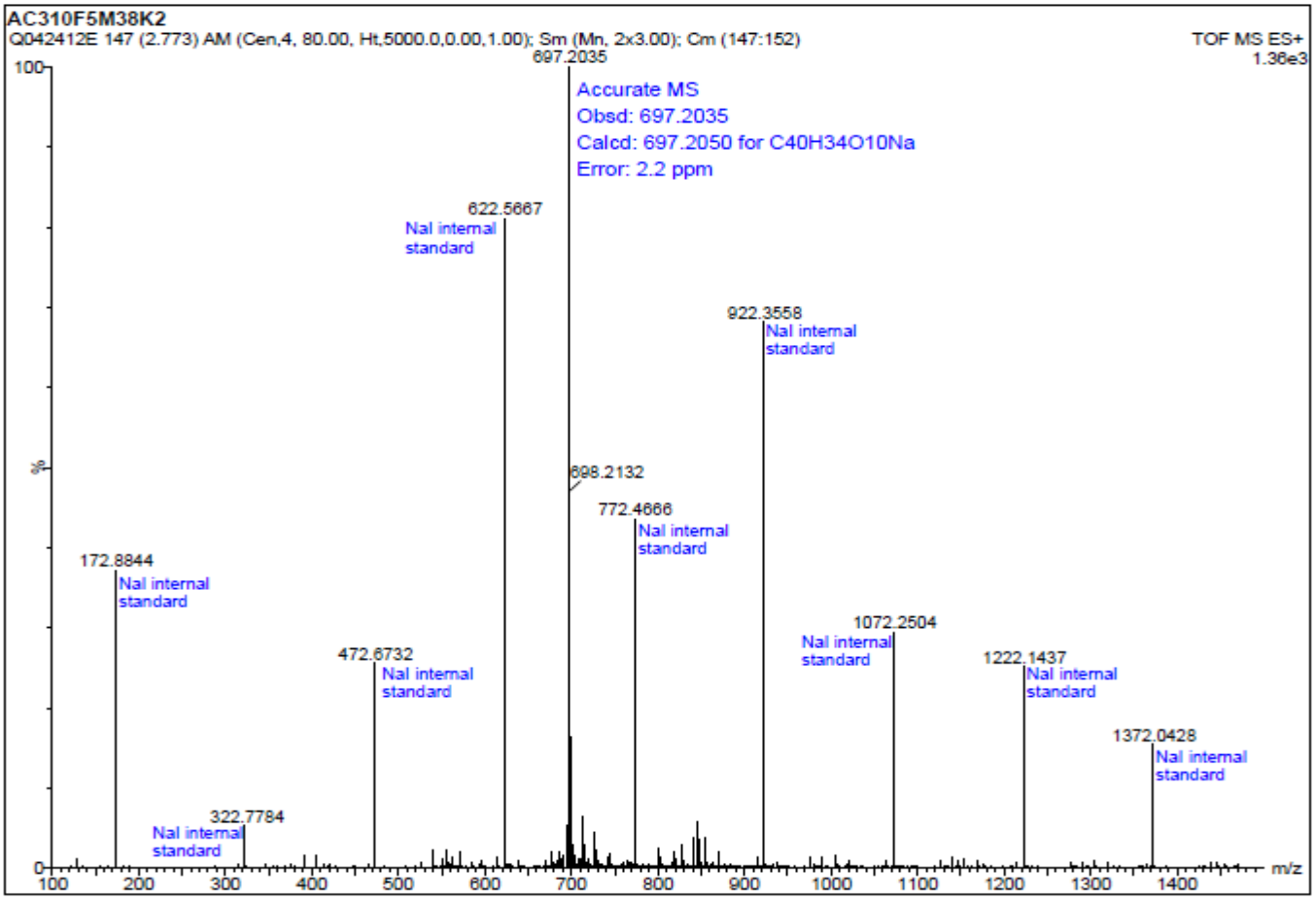


Figure S13b. HRESIMS of compound **2**.

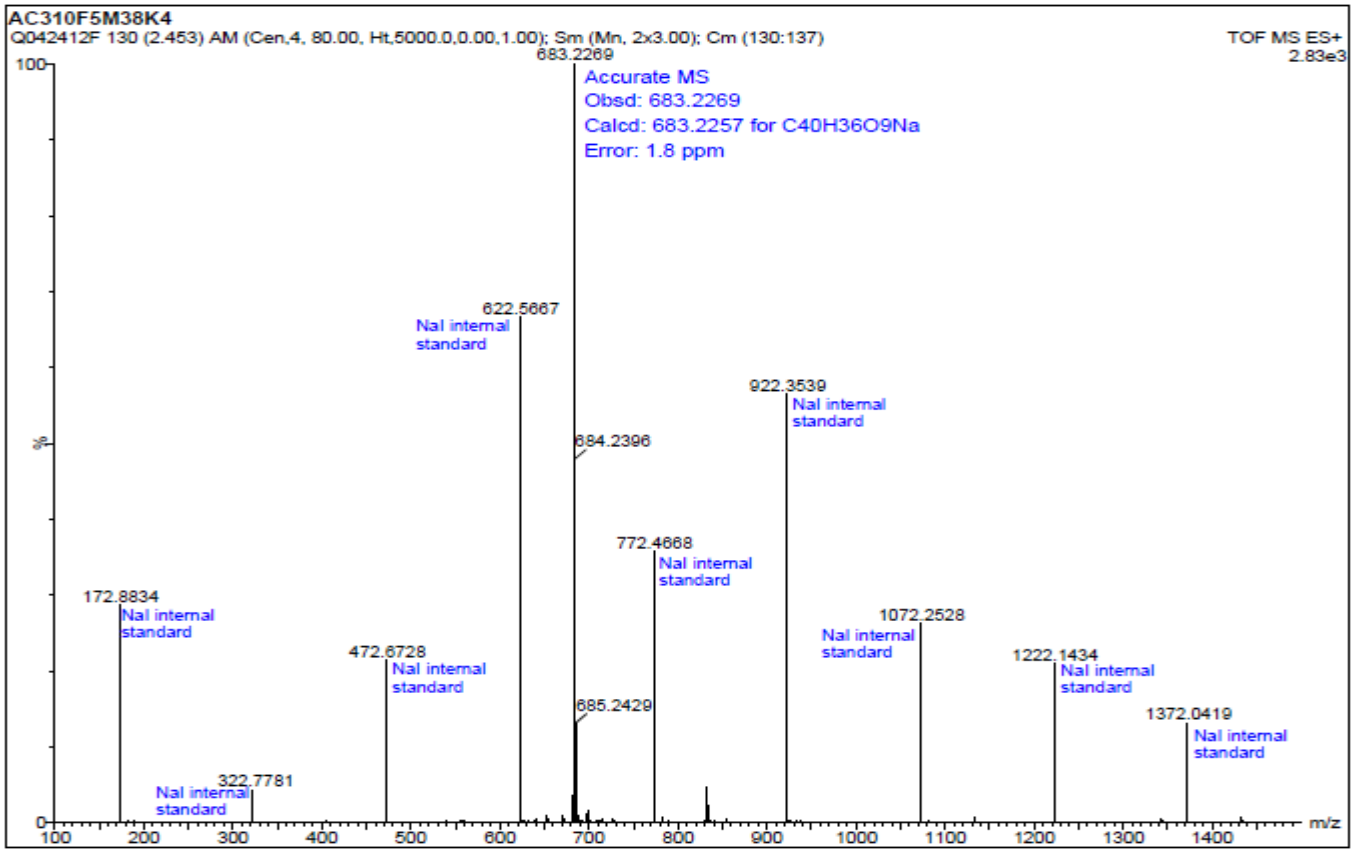


Figure S13c. HRESIMS of compound **3**.

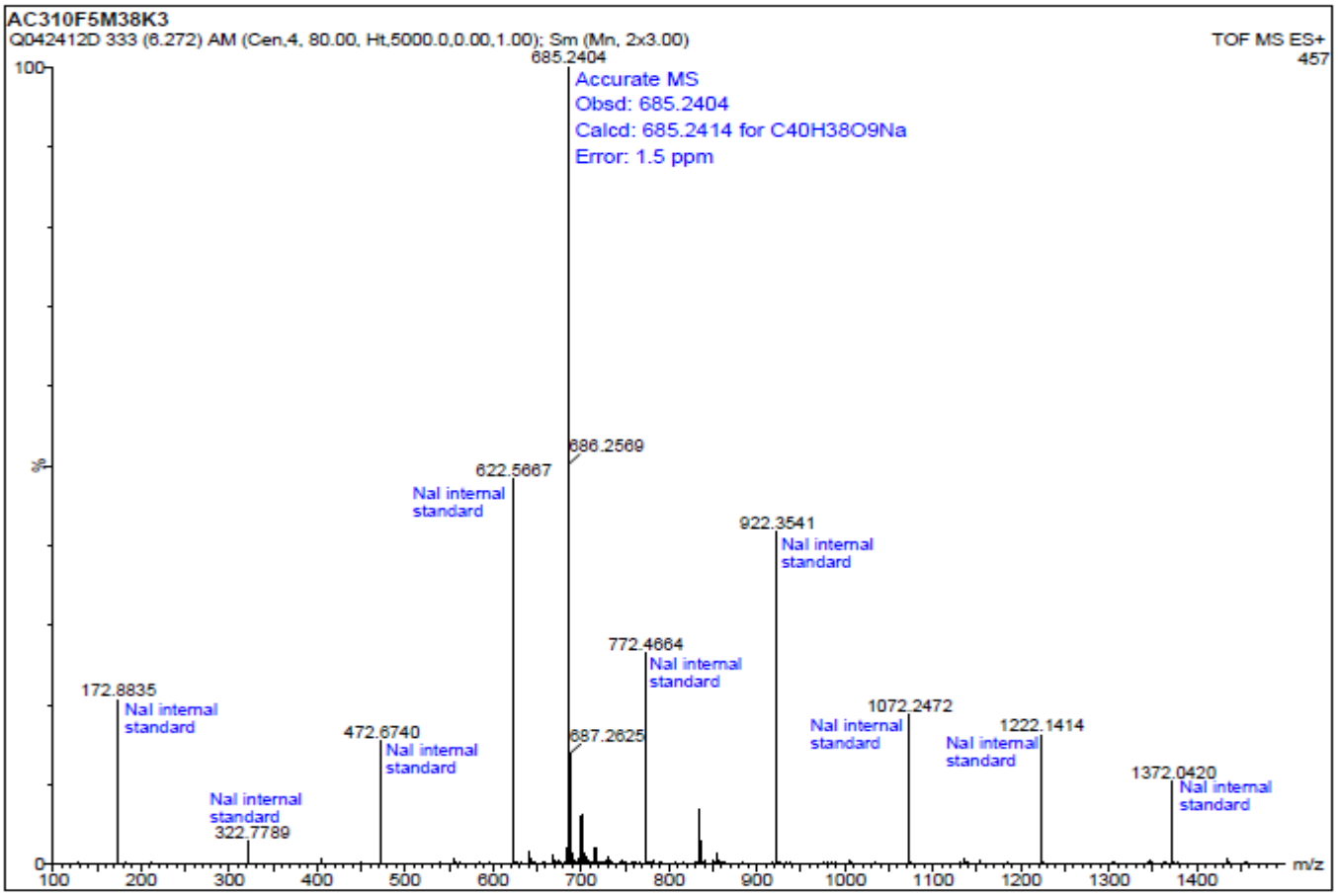


Figure S13d. HRESIMS of compound **4**.

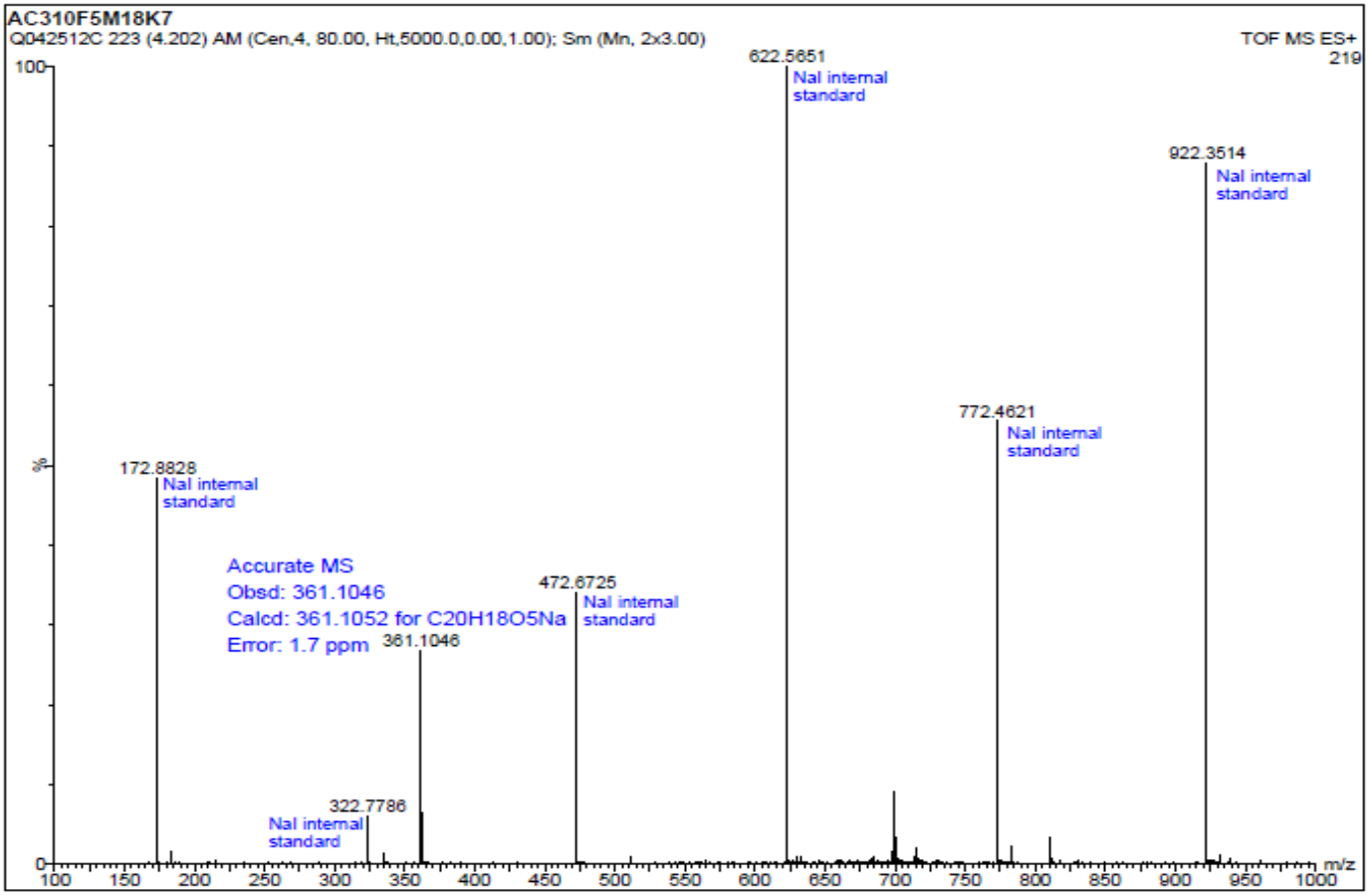


Figure S13e. HRESIMS of compound **5**.

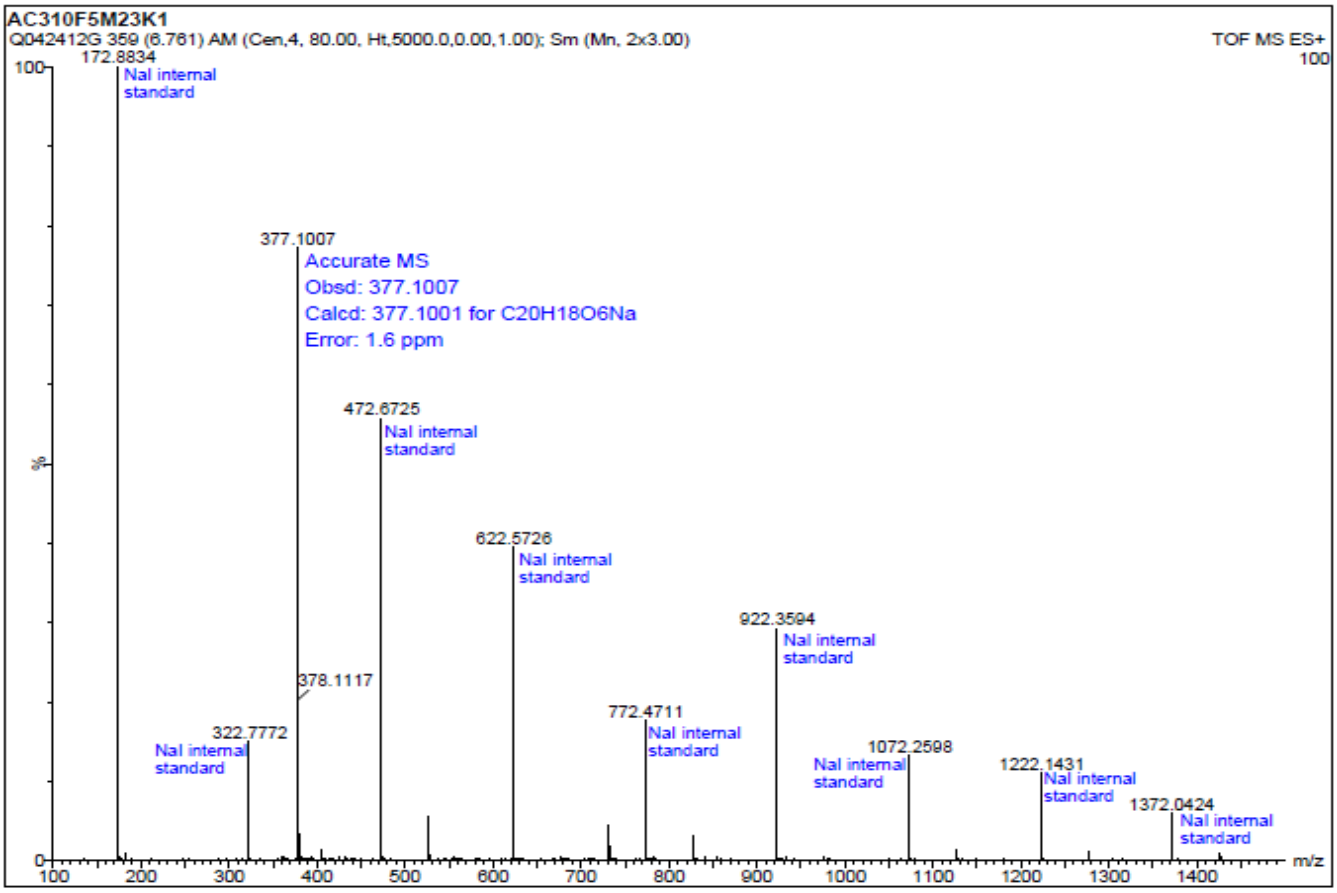


Figure S13f. HRESIMS of compound **6**.

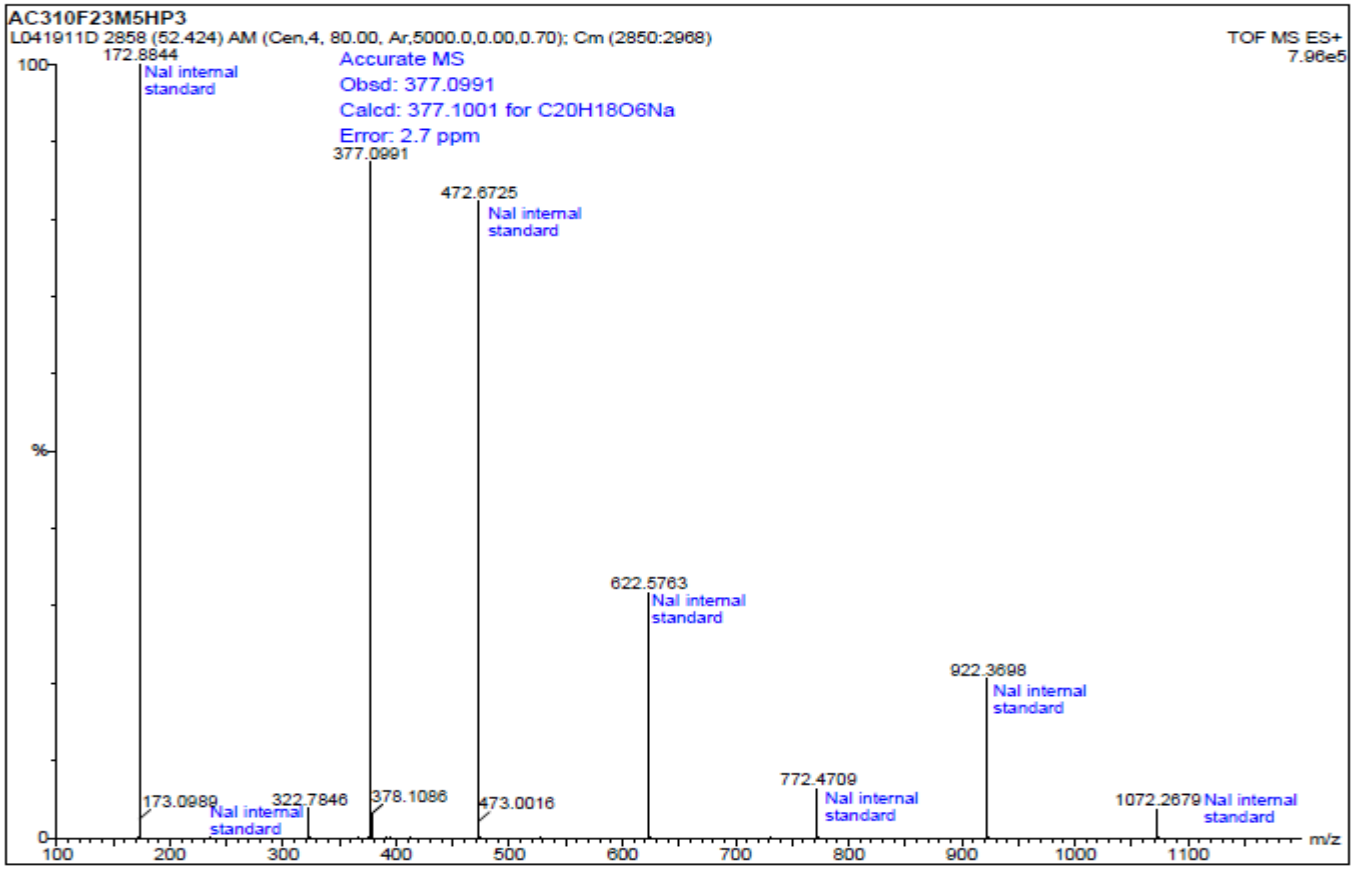


Figure S13g. HRESIMS of compound **7**.

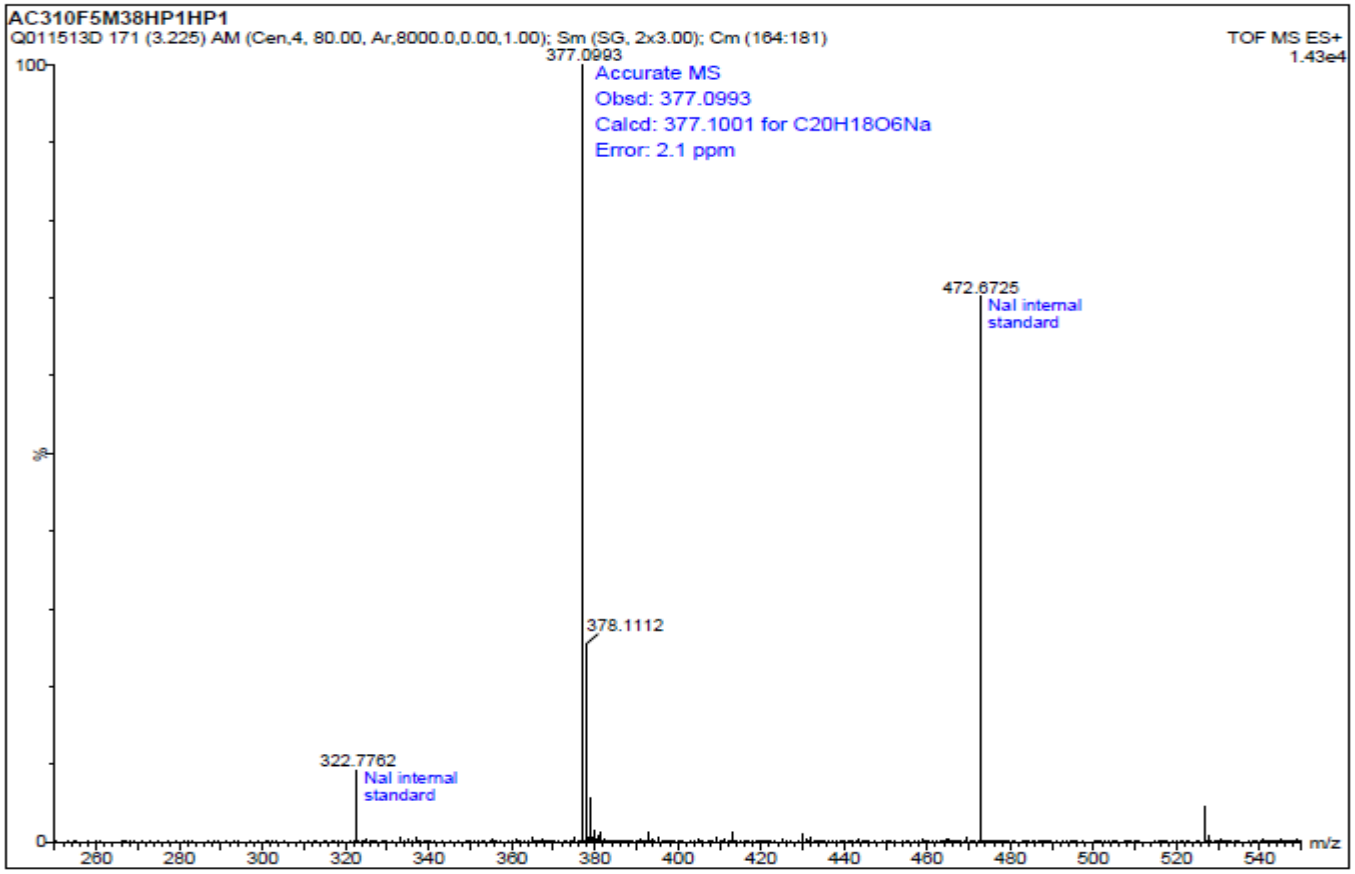


Figure S13h. HRESIMS of compound **8**.

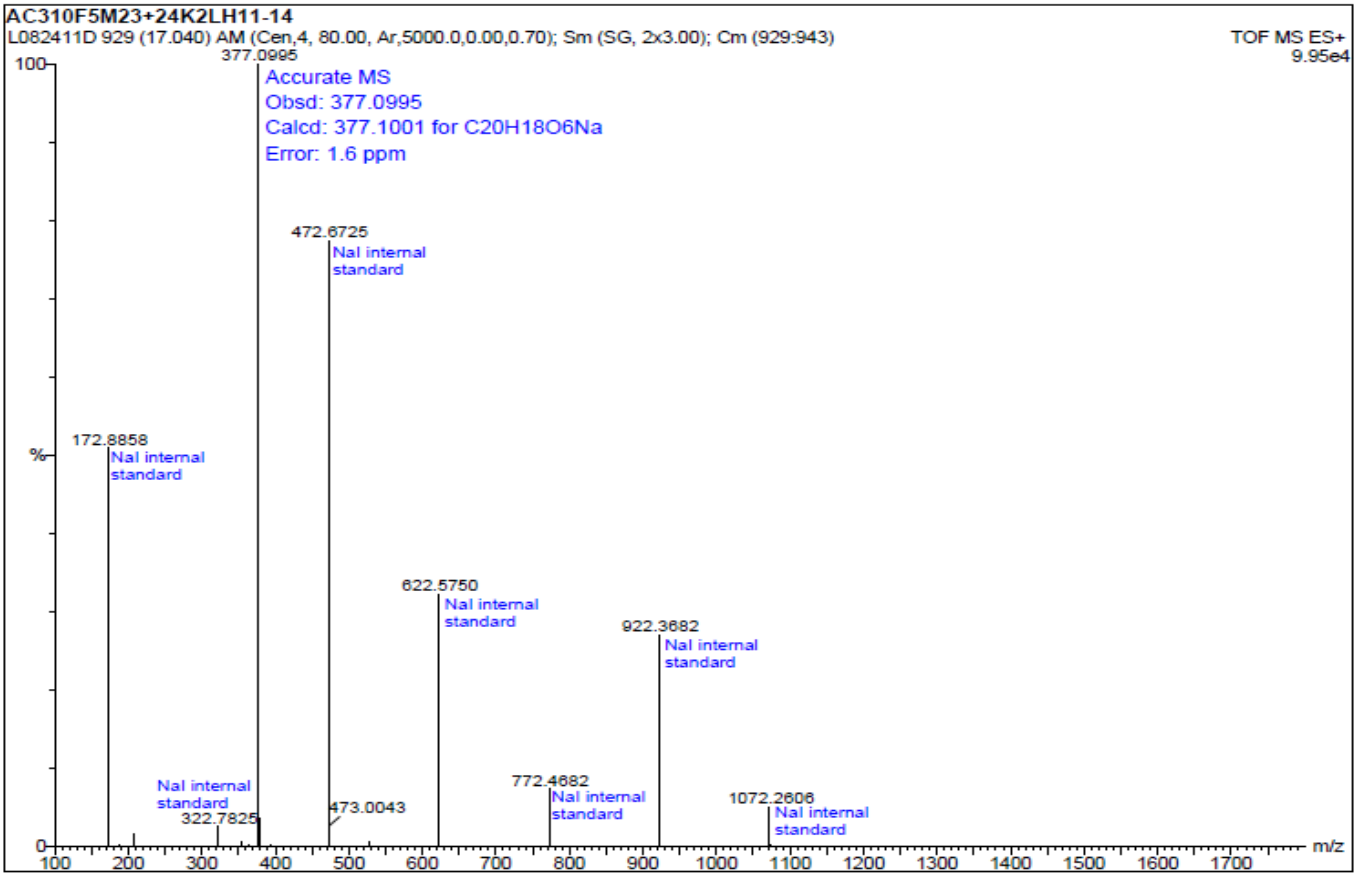


Figure S13i. HRESIMS of compound **9**.

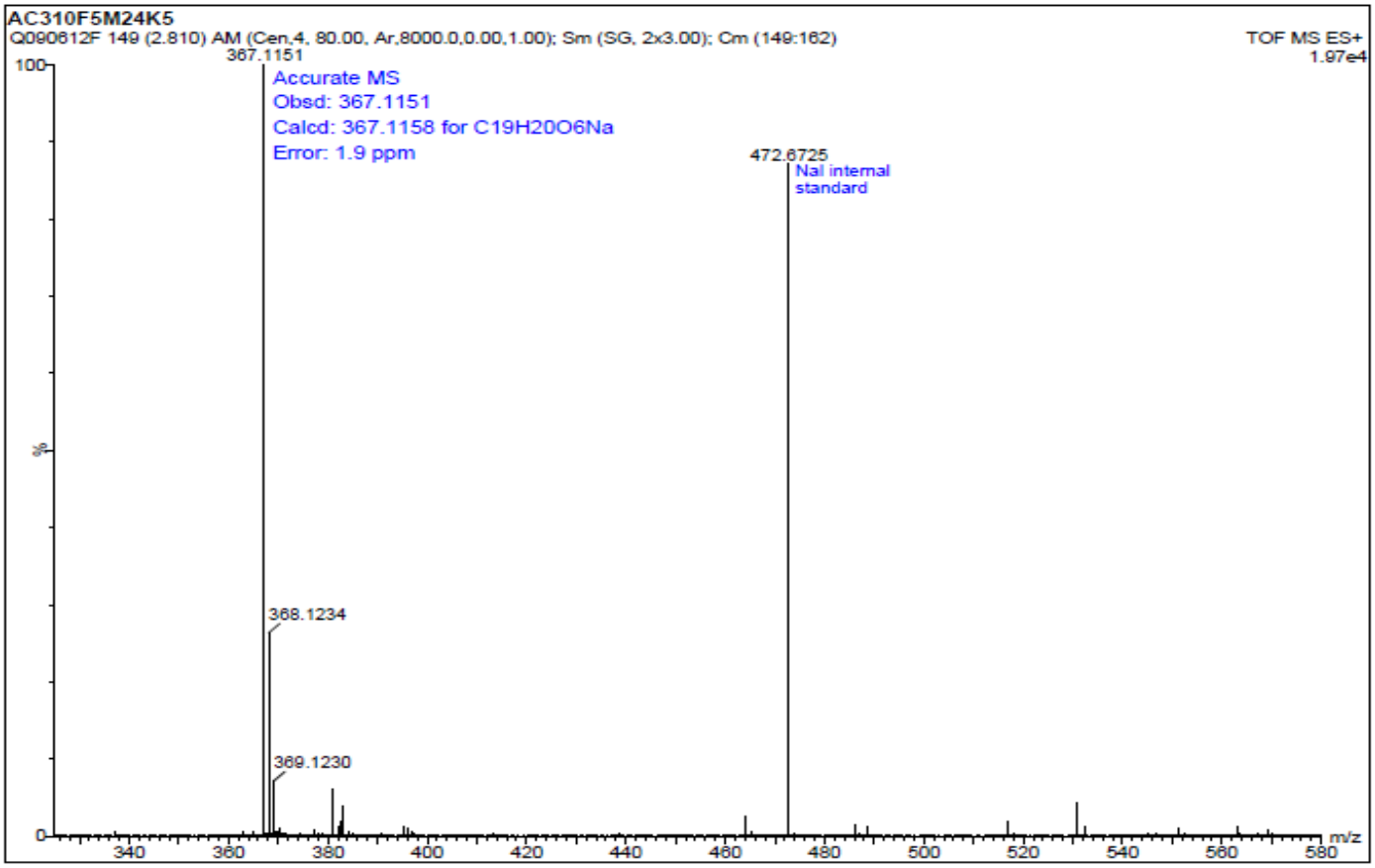


Figure S13j. HRESIMS of compound **10**.

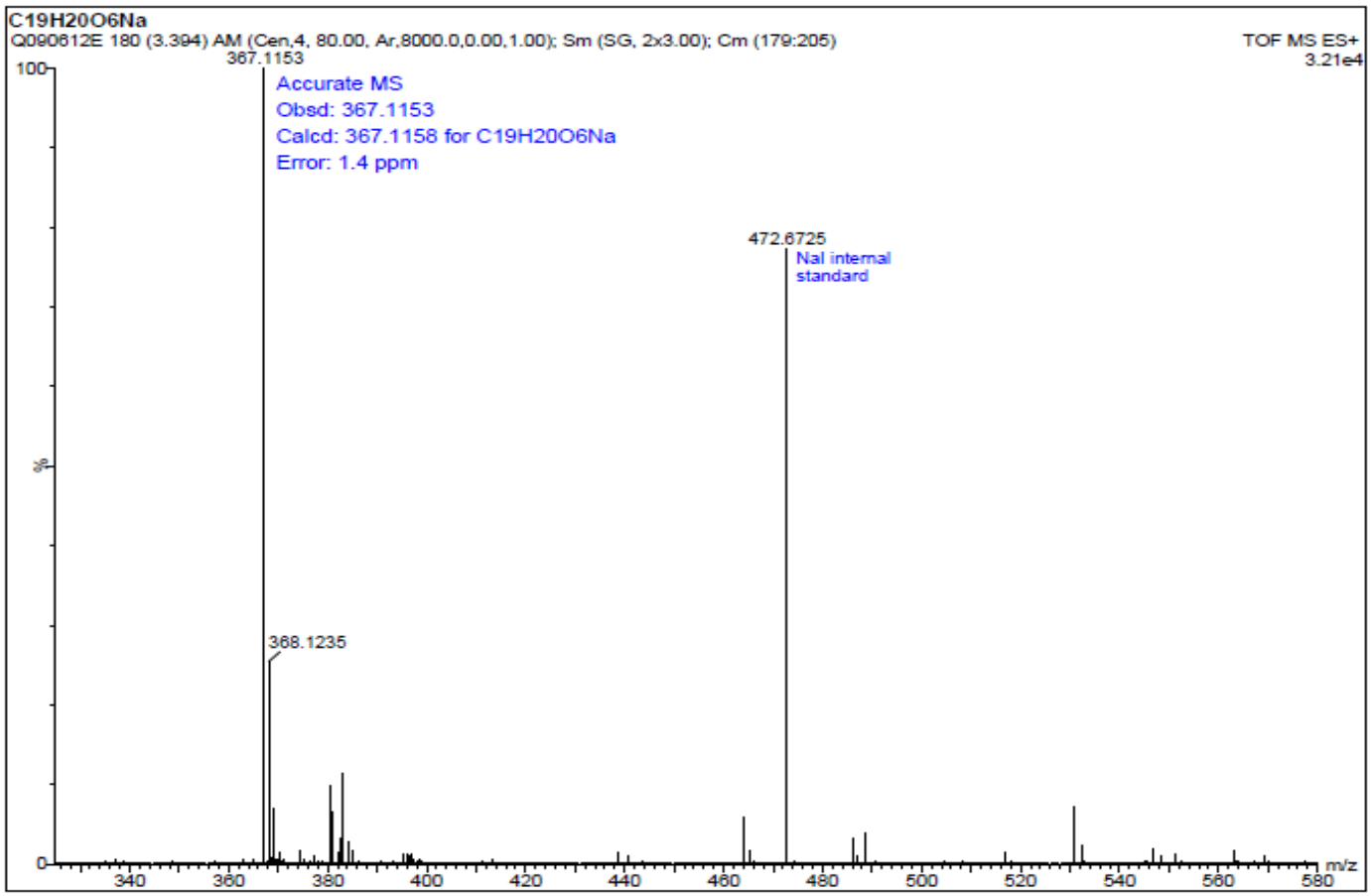


Figure S13k. HRESIMS of compound **11**.

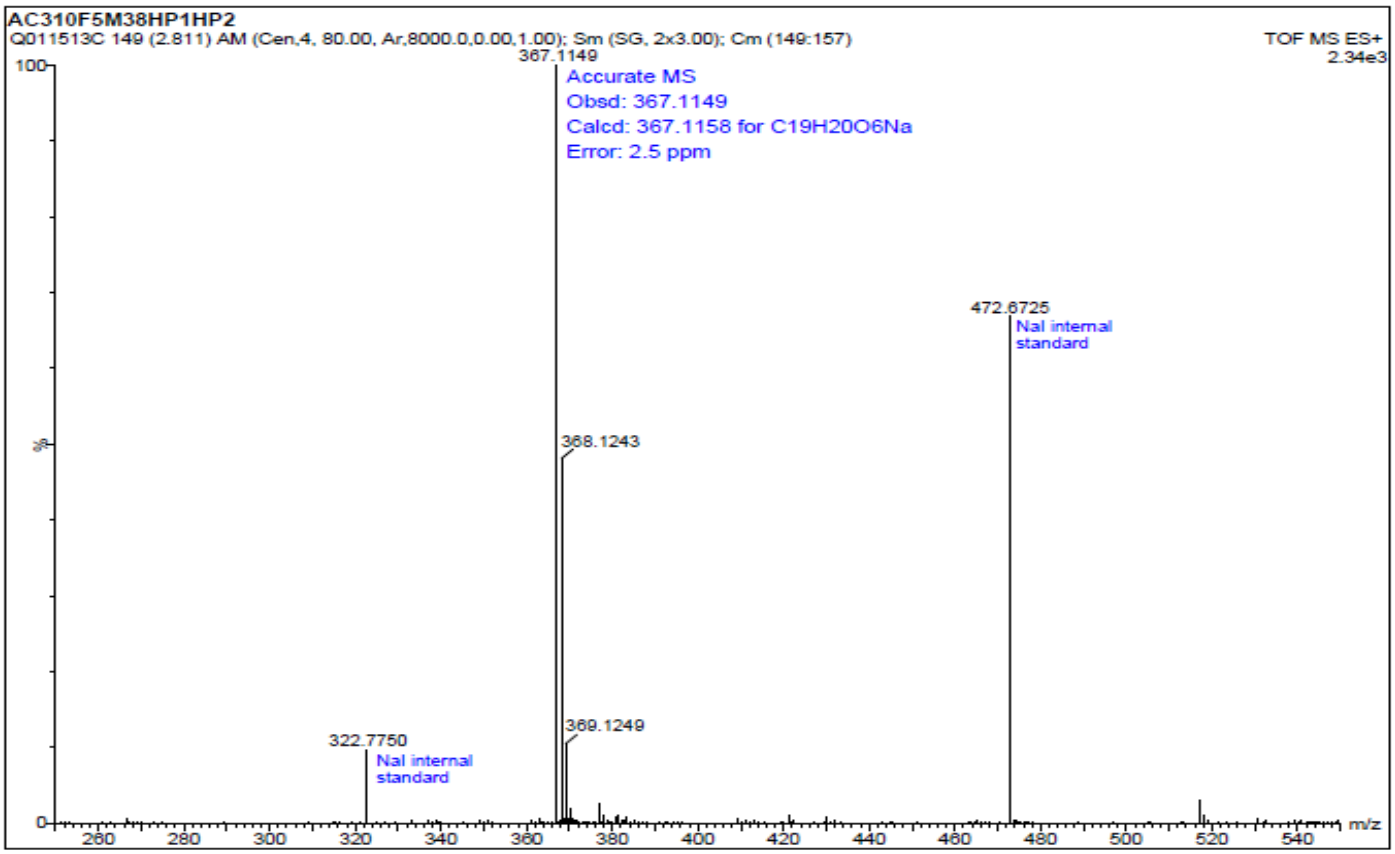


Figure S13l. ESIMS/MS of compound **1**.

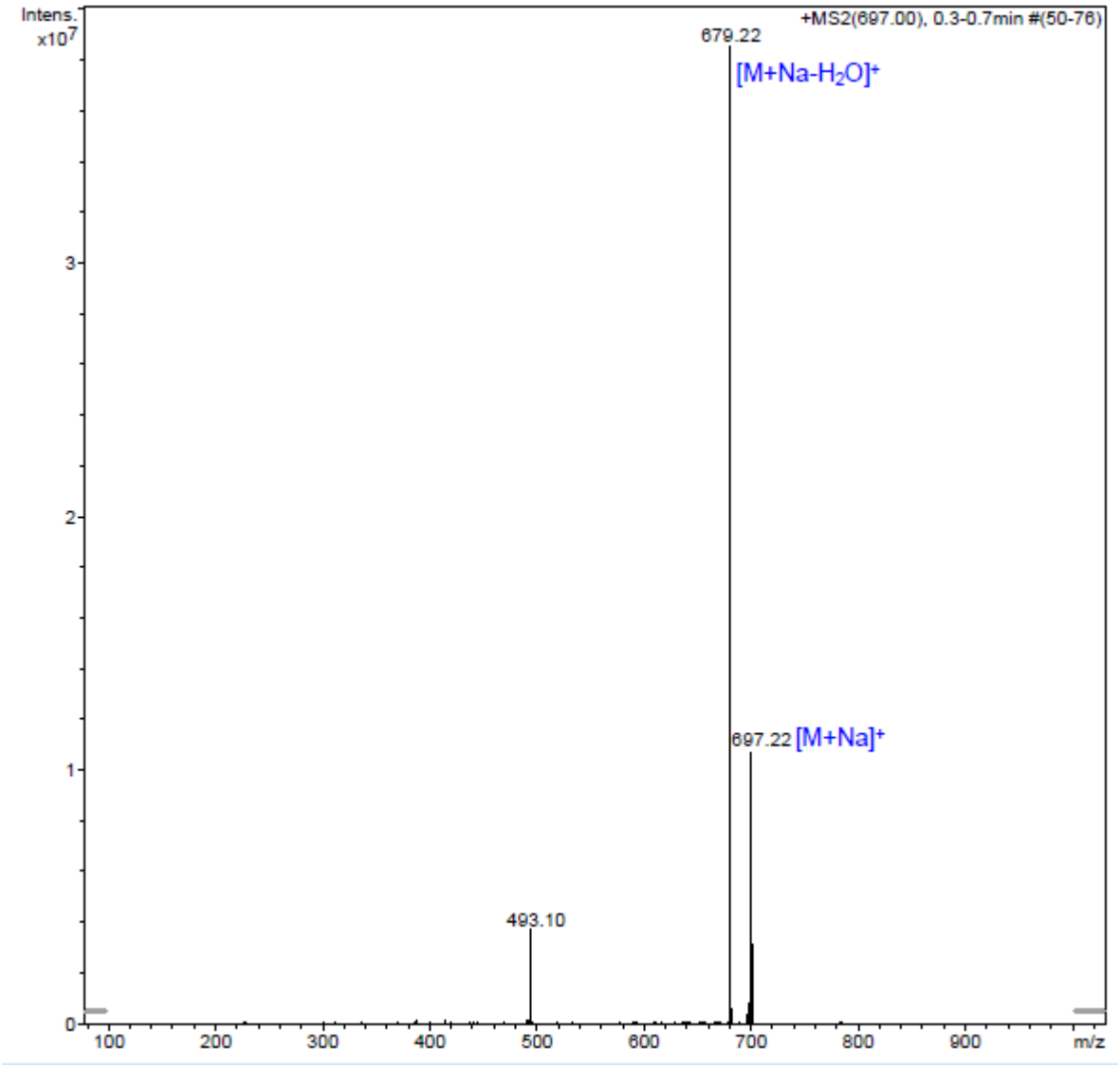


Figure S13m. ESIMS/MS of compound **2**.

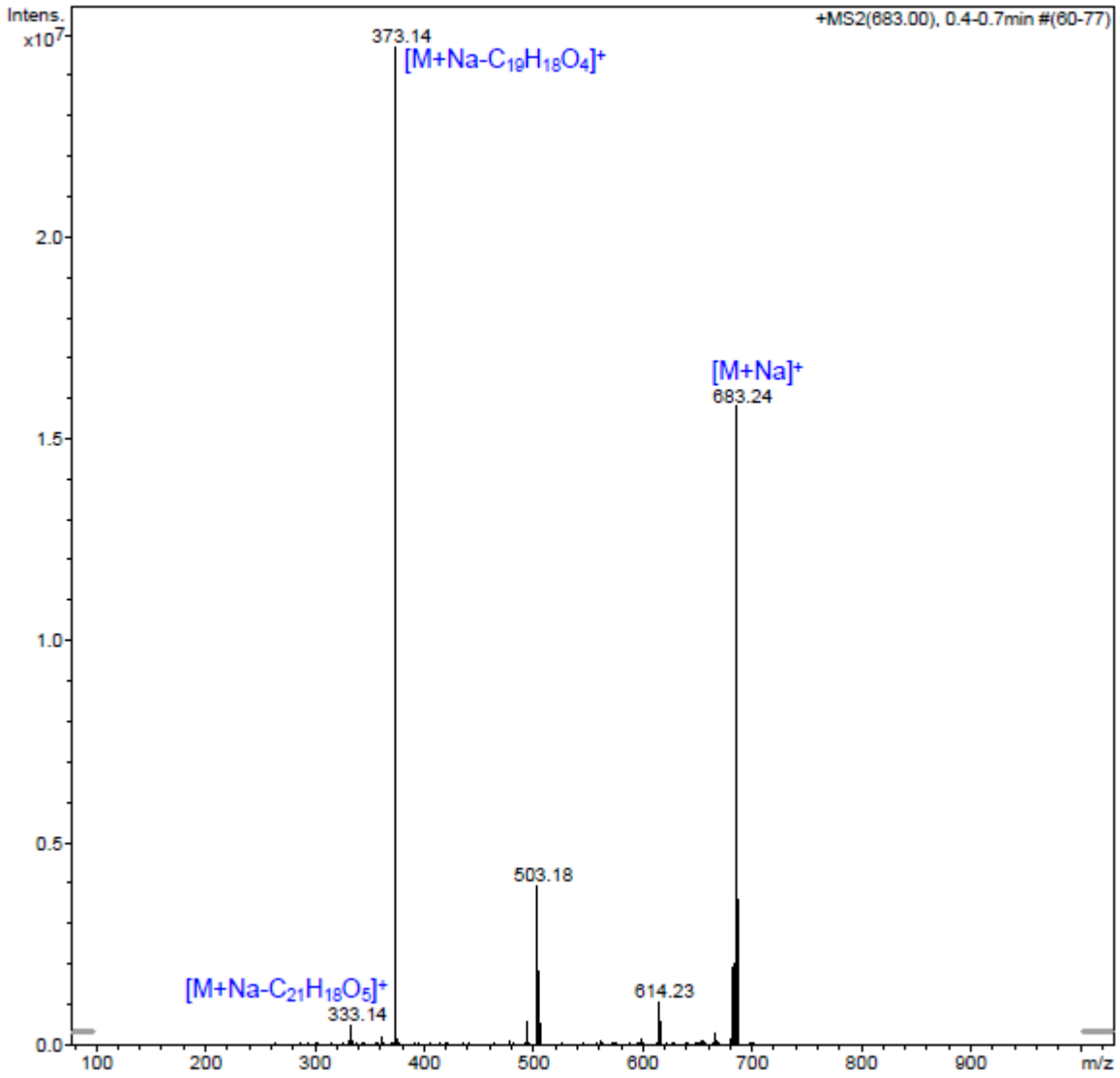


Figure S13n. ESIMS/MS of compound **3**.

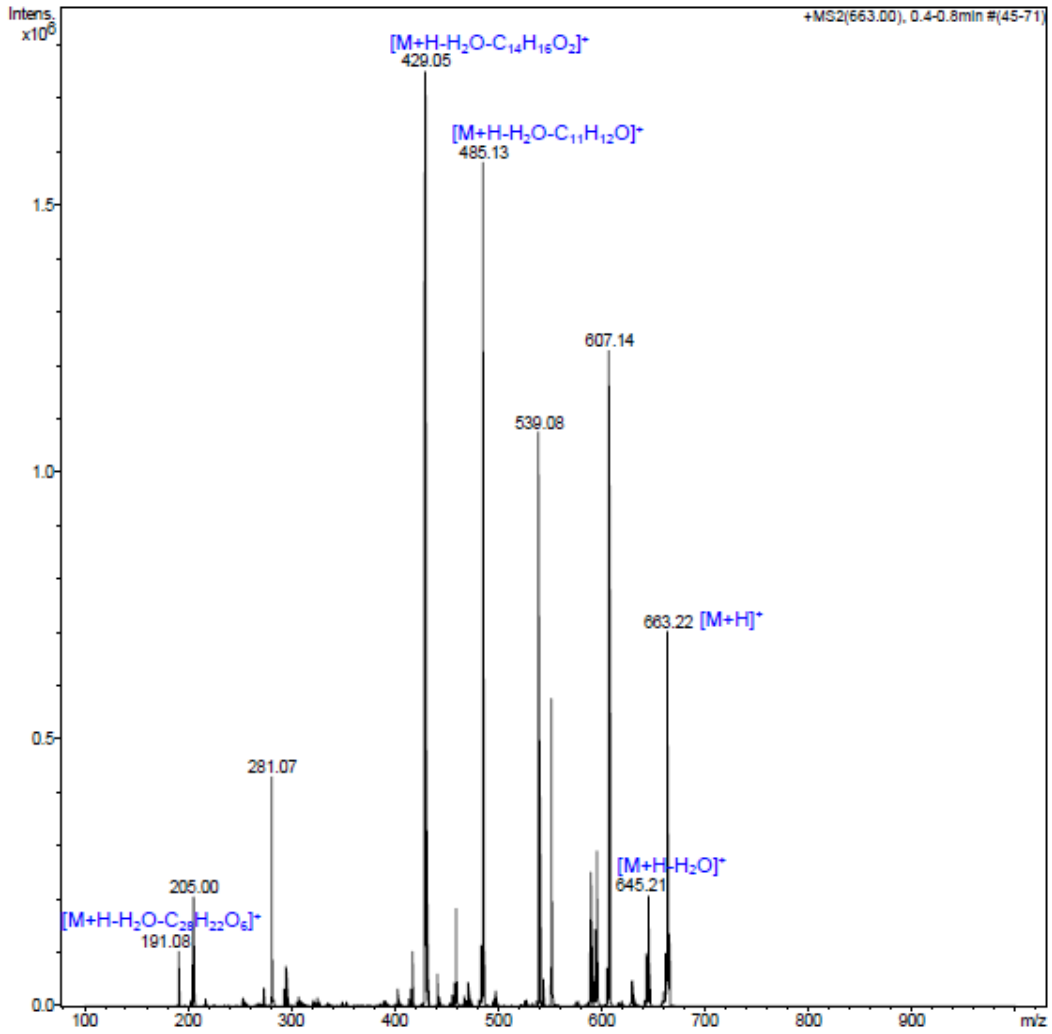


Figure S14. Proposed ESIMS/MS fragmentation pathway of compound **3**.

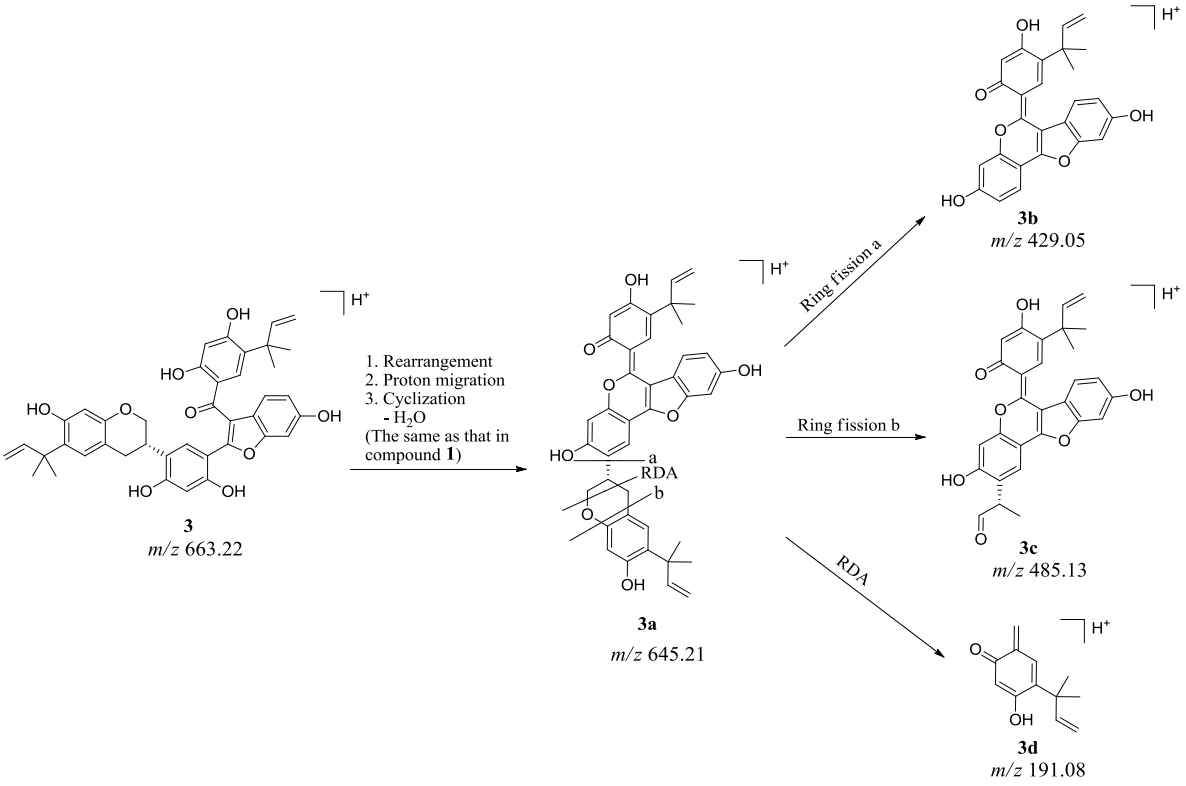
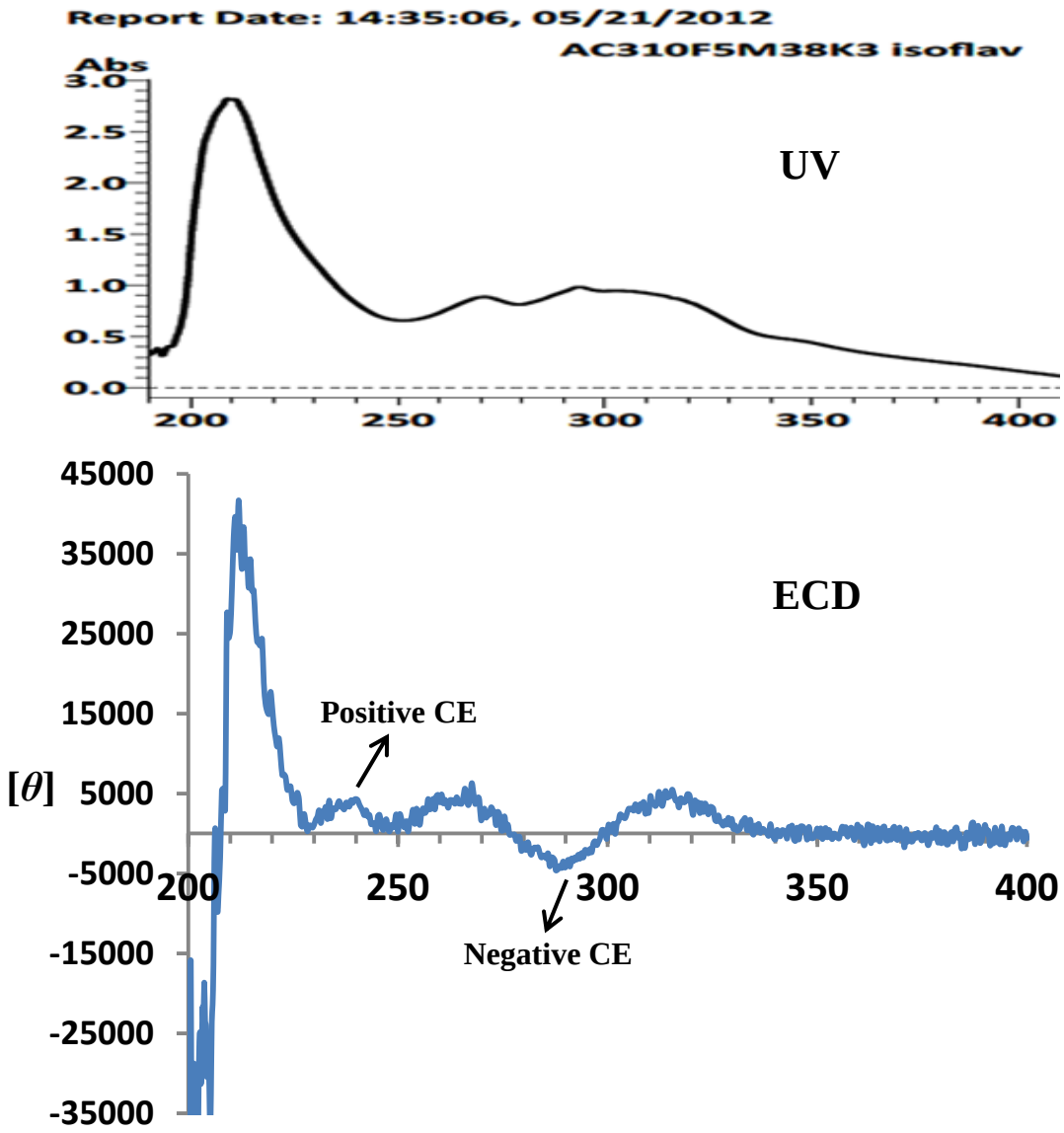


Figure S15. UV and ECD spectra of compound **3**.



Evaluation of Hydroxyl Radical-scavenging Activity. A 160 μL aliquot of freshly prepared mixed solution (80 μL of 1.25 mM H_2O_2 and 80 μL of 0.2 mM $FeSO_4$ in 50 mM phosphate buffer at pH 7.4) was added into each well containing 10 μL of test sample in 25% DMSO solution, and then incubated at 37 ℃ for 5 min. Then, 80 μL of esterase (1.0 unit/mL)-treated 2′,7′-dichlorodihydrofluorescin diacetate (H_2DCF-DA, 2 μM) in 50 mM phosphate buffer (pH 7.4) were rapidly added and mixed well. The final assay volume was 250 μL. Changes in hydroxyl radicals were measured using a FL 800 fluorescence spectrophotometer (Bio-Tek) at an excitation wavelength of 485 nm and an emission wavelength of 528 nm after 30 min. Quercetin was used as a positive

control. Data were processed using nonlinear regression analysis (TableCurve2DV4; AISN Software Inc., Mapleton, OR).

Evaluation of Quinone Reductase-inducing Activity. Briefly, the murine hepa1c1c7 cells (ATCC CRL-2026) were seeded onto 96-well plates at a density of 1.5×10^4 cells/mL in 190 μL of cell culture medium/well. After incubation for 24 h, the cells were then dosed with 10 μL of each test compound in 10% DMSO, or the positive control (L-sulforaphane), or the negative control (10% DMSO), and were incubated for 48 h. Two plates were used for each test sample in order to determine both cytotoxicity, using crystal violet staining of protein content, and QR-inducing activity, by measuring the NADPH-dependent reduction of 3-(4,5-dimethylthiazo-2-yl)-2,5-diphenyltetrazolium bromide (MTT) mediated by menadiol. Both the cytotoxicity and QR-inducing activity were measured at 595 nm with an ELISA plate reader. QR-inducing activity was presented as CD, the concentration required to double the specific activity of QR. Cytotoxicity was expressed as IC_{50}, the concentration inhibiting cell growth by 50%. CI (Chemoprevention Index, IC_{50}/CD) value was also determined. Data were processed using nonlinear regression analysis (TableCurve2DV4; AISN Software Inc., Mapleton, OR).

Evaluation of NF-κB Inhibition Activity. In brief, a nuclear extract was prepared from HeLa cells purchased from the American Type Culture Collection. An EZ-Detect™ Transcription Factor Assay System ELISA kit (Pierce Biotechnology, Rockford, IL) was used to assess the specific binding ability of activated NF-κB to the biotinylated-consensus sequence under the presence of tested compounds. The activity of the p65 subunit of NF-κB was measured by detecting the chemiluminescent signal in a Fluostar Optima plate reader (BMG Labtech Inc., Durham, NC). The IC_{50} values were calculated using nonlinear regression analysis (Table curve2Dv4; AISN Software, Inc., Mapleton, OR). Rocaglamide was used as a positive control with an IC_{50} value of 0.08 μM in this assay.

Evaluation of Cytotoxicity. Human colon cancer cells (HT-29) were obtained from American Type

Collection (ATCC catalog no. HTB-38). Cells were incubated in a humidified incubator with an atmosphere of 95% air and 5% CO_2 at 37 ℃. The harvested cells were seeded in 96-well (9500 cells/190 μL) plates, and treated with the test compounds (10 μL/well in triplicate) at various concentrations. For the control groups, 10 μL of 10% DMSO were also added to each well. After incubation for three days at 37 ℃ in 5% CO_2, the cells were fixed to the plates by addition of 100 μL cold 20% trichloroacetic acid (TCA) and incubated at 4 ℃ for 30 min. The plates were washed three times with tap water and dried overnight. The fixed cells were dyed with sulforhodamine B (SRB, an anionic protein stain) solution at 0.4% (w/v) in 1% acetic acid, and incubated at room temperature for 30 min. The plates were washed three times with 1% acetic acid and allowed to air dry. The bound SRB stain was then solubilized with 10 mM unbuffered Tris base (pH 10, 200 μL/well), and the absorbance was read at 515 nm using a Bio-Tek μQuant microplate reader. The IC_{50} values were calculated using nonlinear regression analysis (Table curve2Dv4; AISN Software, Inc., Mapleton, OR).