

Supplementary Materials for

Halogenated Diterpenes with *in vitro* Anti-Tumor Activity from the Red Alga *Sphaerococcus coronopifolius*

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Table S1. ^1H (400 MHz) and ^{13}C (50 MHz) NMR chemical shifts (CDCl_3), NOESY and HMBC correlations of iodocoronol (**1**).

No.	^1H (δ)	m (J)	NOESY	^{13}C (δ)	Type	HMBC ($^{13}\text{C} \rightarrow ^1\text{H}$)
1	2.88	br. s	2, 13, 14, 15	49.4	CH	2, 17a
2	1.34	m	1, 14, 20	35.6	CH_2	3, 14
3	1.17	m	14, 17b	48.8	CH	1, 17a, 17b, 19, 20
4	-			51.9	C	1, 2, 3, 5 α , 13, 17b
5	α 1.73	m	16	22.8	CH_2	3
	β 1.31	ddd 14.2, 4.0, 3.8				
6	α 1.86	ddd 12.9, 4.0, 2.2		37.8	CH_2	12, 16
	β 1.38	ddd 12.9, 12.9, 3.8	8, 12, 17a			
7	-			41.5	C	16
8	4.09	dd 12.6, 4.0	6 β , 9 β , 10 β , 12	68.5	CH	16
9	α 2.48	dddd 13.4, 13.4, 12.6, 4.6	16	31.0	CH_2	10b
	β 2.08	dddd 13.4, 4.6, 4.0, 3.0	8, 10 β			
10	α 1.59	ddd 14.5, 4.6, 3.0		43.6	CH_2	15
	β 1.68	ddd 14.5, 13.4, 4.6	8, 9 β , 12			
11	-			73.6	C	15
12	1.97	d 12.1	6 β , 8, 10 β , 15, 17a	47.6	CH	15, 16
13	1.81	br. d 12.1	1, 15, 16, 19	44.8	CH	2, 5, 12, 14, 17b
14	3.98	dd 8.6, 5.6	1, 2, 3, 17b	25.9	CH	1, 2, 13, 17a
15	1.56	s	1, 12, 13	32.9	CH_3	
16	1.16	s	5 α , 9 α , 13	16.6	CH_3	12
17	a 2.60	dd 14.2, 5.6	6 β , 12	50.2	CH_2	3, 5 α , 13
	b 1.75	dd 14.2, 8.6	3, 14			
18	1.72	m		28.3	CH	2, 3, 19, 20
19	0.85	d 6.7	13	23.4	CH_3	3, 20
20	0.84	d 6.7	2	18.7	CH_3	3, 19

Table S2. ^1H (400 MHz) and ^{13}C (50 MHz) NMR chemical shifts (CDCl_3), NOESY and HMBC correlations of bromocoronol (**2**).

No.	^1H (δ)	m (J)	NOESY	^{13}C (δ)	Type	HMBC ($^{13}\text{C} \rightarrow ^1\text{H}$)
1	2.90	br d 4.1	2α , 2β , 13, 14, 15	49.3	CH	2α , 13
2	α 1.48	m	1, 13	34.0	CH_2	3, 14, 18
	β 1.34	m	1, 14			
3	1.14	m	14, 17b	48.9	CH	2β , 5α , 17a, 17b, 19, 20
4	–			51.3	C	1, 3, 6α , 13, 17a
5	α 1.76	m	16	22.9	CH_2	6α
	β 1.36	m	17a			
6	α 1.88	ddd 13.2, 4.7, 2.3	16	37.7	CH_2	5β , 16
	β 1.40	ddd 13.2, 13.2, 3.2	8, 12, 17a			
7	–			41.4	C	6α , 12, 16
8	4.07	dd 12.6, 4.1	6β , 9β , 10β , 12	68.6	CH	9α , 10α , 10β , 12, 16
9	α 2.47	dddd 13.4, 13.4, 12.6, 4.7	16	30.9	CH_2	10α , 10β
	β 2.06	dddd 13.4, 4.7, 4.1, 2.9	8, 10β			
10	α 1.58	ddd 14.3, 4.7, 2.9		43.7	CH_2	15
	β 1.66	ddd 14.3, 13.4, 4.7	8, 9β , 12			
11	–			73.5	C	15
12	1.93	d 12.0	6β , 8, 10β , 15, 17a	47.9	CH	15, 16
13	1.74	m	1, 2α , 16	44.5	CH	2β , 3, 5α , 14, 17b
14	4.03	dd 8.5, 5.0	1, 2β , 3, 17b	52.5	CH	1, 2α , 2β , 17a, 17b
15	1.49	s	1, 12	33.2	CH_3	
16	1.16	s	5α , 6α , 9α , 13	16.3	CH_3	12
17	a 2.52	dd 14.3, 5.0	5β , 6β , 12	48.6	CH_2	1
	b 1.75	dd 14.3, 8.5	3, 14			
18	1.71	m		28.3	CH	3, 19, 20
19	0.86	d 6.4		23.4	CH_3	3, 20
20	0.85	d 6.4		18.8	CH_3	3, 18, 19

Table S3. ^1H (600 MHz) and ^{13}C (75 MHz) NMR chemical shifts (CDCl_3), NOESY and HMBC correlations of bromotetrasphaereniol (**3**).

No.	^1H (δ)	m (J)	NOESY	^{13}C (δ)	Type	HMBC ($^{13}\text{C} \rightarrow ^1\text{H}$)
1	2.13	br. s	2α , 14α , 14β , $17a$, $17b$	34.7	CH	2α , 14α , $17a$, $17b$
2	α 1.89	br. d 14.4	1, 14α , 20	41.0	CH_2	14α , $17a$, $17b$
	β 2.20	br. d 14.4	$17b$, 20			
3	–			139.0	C	1, 5α , 13, $17b$, 19, 20
4	–			52.8	C	1, 5α , 5β , 6α , 14α , $17a$, $17b$
5	α 2.60	ddd 13.9, 13.8, 4.1	6α , 16, 19	24.4	CH_2	6β
	β 1.60	dm 13.9	6α , 6β , $17b$			
6	α 1.92	ddd 13.2, 4.2, 3.0	5α , 5β , 16	38.7	CH_2	5α , 8, 16
	β 1.17	m	5β , 8, 12, $17a$			
7	–			41.0	C	5β , 8, 12, 16
8	3.97	dd 12.6, 4.2	6β , 9β , 10β , 12	68.5	CH	9α , 10α , 10β , 12, 16
9	α 2.48	dddd 13.8, 13.8, 12.6, 4.8	16	30.9	CH_2	8, 10β
	β 2.04	dddd 13.8, 4.2, 4.2, 3.0	8			
10	α 1.58	m	15	43.3	CH_2	9α , 15
	β 1.54	m	8, 12, 15			
11	–			72.9	C	10β , 15
12	1.07	d 11.0	6β , 8, 10β , 14β , 15, $17a$	56.4	CH	6α , 10α , 13, 14α , 15, 16
13	1.77	ddd 11.0, 8.4, 4.8	15, 16	39.0	CH	1, 5β , 12, $17b$
14	α 1.66	ddd 12.0, 8.4, 2.4	1, 2α , 15	43.1	CH_2	2α , 2β , 12, 13, $17b$
	β 1.55	m	1, 12, 15, $17a$			
15	1.14	s	10α , 10β , 12, 13, 14α , 14β	32.7	CH_3	
16	1.18	s	5α , 6α , 9α , 13, 19	16.9	CH_3	8, 12
17	a 1.83	br. d 9.6	1, 6β , 12, 14β	43.9	CH_2	2α , 5α , 14α
	b 1.01	br. d 9.6	1, 2β , 5β			
18	–			119.9	C	19, 20
19	1.84	br. s	5α , 16, 20	20.3	CH_3	20
20	1.57	br. s	2α , 2β , 19	23.9	CH_3	19

Table S4. ^1H (400 MHz) and ^{13}C (50 MHz) NMR chemical shifts (CDCl_3), NOESY and HMBC correlations of 1-methoxy-ioniol I (**4**).

No.	^1H (δ)	m (J)	NOESY	^{13}C (δ)	Type	HMBC
1	3.58	ddd 7.5, 7.5, 1.4	2 β , 14, 17b	81.9	CH	2 α , 2 β , 3, 14, 17a, 21
2	α 1.60	m		25.1	CH ₂	14
	β 2.10	m	1			
3	1.61	m	17b	48.3	CH	17a, 19, 20
4	–			43.5	C	2, 6 α , 14, 17a
5	α 1.62	ddd 13.2, 13.2, 4.4	16	24.0	CH ₂	17a
	β 0.92	m	6 β			
6	α 1.90	ddd 13.2, 4.4, 2.9	16	37.0	CH ₂	12, 16
	β 1.34	ddd 13.2, 13.2, 4.0	5 β , 8, 17a			
7	–			39.3	C	5 α , 12, 16
8	4.04	dd 12.8, 4.0	6 β , 9 β , 10 β , 12	68.7	CH	12, 16
9	α 2.49	dddd 13.4, 13.4, 12.8, 4.4	16	30.6	CH ₂	
	β 2.05	m	8			
10	α 1.67	ddd 13.4, 4.4, 2.9		42.5	CH ₂	15
	β 1.54	m	8			
11	–			72.6	C	15
12	1.49	d 9.9	8, 14, 15, 17a	52.0	CH	6 β , 10 α , 15, 16
13	2.02	m	16	31.8	CH	1, 12, 17b
14	2.27	dd 7.3, 1.4	1, 12, 15	40.9	CH	2 β , 12, 17a
15	1.10	s	12, 14	30.3	CH ₃	
16	1.05	s	5 α , 6 α , 9 α , 13	16.0	CH ₃	12
17	a 2.44	dd 9.5, 7.3	6 β , 12	34.2	CH ₂	13
	b 0.61	dd 9.5, 5.4	1, 3			
18	2.04	m		27.6	CH	19, 20
19	0.91	d 6.9		15.8	CH ₃	20
20	0.89	d 6.9		22.6	CH ₃	19
21	3.30	s		55.9	OCH ₃	1

Table S5. ^1H (400 MHz) and ^{13}C (50 MHz) NMR chemical shifts (CDCl_3), NOESY and HMBC correlations of corotrienone (**5**).

No.	^1H (δ)	m (J)	NOESY	^{13}C (δ)	Type	HMBC ($^{13}\text{C} \rightarrow ^1\text{H}$)
1	α 2.28	m	13	28.1	CH_2	2, 13, 14
	β 1.82	m	14			
2	a 1.85	m	19	32.2	CH_2	18
	b 1.72	m	13			
3	1.76	m	17a	55.8	CH	1 α , 17a, 17b, 19, 20
4	-		-	153.3	C	3, 5b, 6
5	a 2.09	dt 16.6, 4.6	13, 16, 18	25.0	CH_2	6, 17a, 17b
	b 1.84	m				
6	1.73	m		39.3	CH_2	5b, 8, 12, 16
7	-		-	41.4	C	9, 12, 16
8	6.81	d 10.2	16	164.8	CH	16
9	5.92	d 10.2		124.6	CH	
10	-		-	200.6	C	8, 15
11	-		-	73.5	C	9, 15
12	2.13	d 10.0	14, 15, 17b	58.5	CH	6, 8, 14, 15, 16
13	5.60	ddd 15.8, 10.0, 1.1	1 α , 2b, 5a, 16	124.2	CH	12, 14
14	5.72	dt 15.8, 6.7	1 β , 12, 15, 17a	136.1	CH	1 α , 12
15	1.20	s	12, 14	25.2	CH_3	
16	1.27	s	5a, 8, 13	20.4	CH_3	12
17	a 4.87	br s	3, 14, 20	112.3	CH_2	3, 5a
	b 4.76	br s	12			
18	1.42	br. hept 6.6	5a	29.9	CH	3, 19, 20
19	0.85	d 6.6	2a	20.7	CH_3	20
20	0.76	d 6.6	17a	21.5	CH_3	19

Table S6. ¹H (400 MHz) and ¹³C (50 MHz) NMR chemical shifts (CDCl₃), NOESY and HMBC correlations of iso-bromocorodienol (**6**).

No.	¹ H (δ)	m (J)	NOESY	¹³ C (δ)	Type	HMBC (¹³ C→ ¹ H)
1	a 2.23	m	14	29.7	CH ₂	2α, 13
	b 1.75	dddd 12.6, 12.6, 10.5, 5.6	13			
2	α 1.25	m	17, 18	24.8	CH ₂	1a, 1b
	β 1.63	dddd 12.6, 12.0, 6.2, 5.0	3, 14			
3	2.01	ddd 12.0, 10.2, 4.3	2β, 6β, 14, 19, 20	44.4	CH	1b, 17, 18, 19, 20
4	—	—	—	133.3	C	2β, 6α, 6β, 17
5	5.27	dd 12.0, 6.2	6α, 16, 17	125.7	CH	3, 6α, 6β, 17
6	α 2.23	dd 14.0, 6.2	5, 16	40.1	CH ₂	12, 16
	β 1.93	dd 14.0, 12.0	3, 8, 12, 20			
7	—	—	—	44.7	C	6α, 6β, 12, 16
8	4.00	dd 12.6, 4.1	6β, 9β, 10β, 12	68.0	CH	9α, 12, 16
9	α 2.53	dddd 13.8, 13.8, 12.6, 4.4	10α, 16	31.1	CH ₂	10β
	β 2.11	dddd 13.8, 4.7, 4.1, 2.6	8, 10α, 10β			
10	α 1.69	ddd 14.3, 4.4, 2.6	9α, 9β, 15	40.8	CH ₂	9α, 15
	β 1.46	ddd 14.3, 13.8, 4.7	8, 9β, 15			
11	—	—	—	71.7	C	15
12	1.79	d 9.6	6β, 8, 14, 15	62.3	CH	6β, 10α, 14, 15, 16
13	5.27	dd 14.9, 9.6	1b, 16	128.1	CH	1b, 12
14	5.18	ddd 14.9, 10.5, 2.2	1a, 2β, 3, 12	133.0	CH	2β, 12, 13
15	1.06	s	10α, 10β, 12	30.9	CH ₃	
16	1.28	s	5, 6α, 9α, 13	15.2	CH ₃	12
17	1.52	br. s	2α, 5	19.1	CH ₃	
18	1.43	d hept 10.2, 6.7	2α, 19, 20	30.4	CH	19, 20
19	0.90	d 6.7	3, 18	21.1	CH ₃	20
20	0.67	d 6.7	3, 6β, 18	21.3	CH ₃	19

Table S7. ^1H (400 MHz) and ^{13}C (50 MHz) NMR chemical shifts (CDCl_3), NOESY and HMBC correlations of debromosphaerol (7).

No.	^1H (δ)	m (J)	NOESY	^{13}C (δ)	Type	HMBC ($^{13}\text{C} \rightarrow ^1\text{H}$)
1	5.55	dm 10.2	2α , 2β	127.0	CH	2β
2	α 1.93	m	1, 17, 19, 20	23.3	CH_2	3, 14, 18
	β 2.02	m	1, 3, 19			
3	1.57	ddd 10.5, 7.3, 3.2	2β , 5β , 13, 18, 19	52.0	CH	17, 19, 20
4	-			38.2	C	3, 6α , 12, 14, 17
5	α 1.49	m	17, 18	31.6	CH_2	6β , 17
	β 1.29	ddd 14.3, 14.0, 2.9	3, 8, 13, 18			
6	α 1.49	m	12, 16, 17	34.8	CH_2	16
	β 1.84	ddd 14.0, 3.5, 2.9	8, 16			
7	-			39.5	C	5α , 6β , 12, 16
8	4.55	dd 12.9, 4.7	5β , 6β , 9β , 10β , 13	60.6	CH	6β , 10α , 10β , 12, 16
9	α 2.53	dddd 13.1, 13.1, 12.9, 4.4	16	30.9	CH_2	10β
	β 2.08	dddd 13.1, 4.7, 4.4, 3.8	8, 10β			
10	α 1.45	ddd 14.0, 4.4, 3.8		38.5	CH_2	15
	β 1.71	ddd 14.0, 13.1, 4.4	8, 9β , 13			
11	-			75.7	C	12, 15
12	1.74	dd 12.3, 1.8	6α , 14, 15, 16, 17	53.6	CH	14, 15, 16
13	1.93	dm 12.3	3, 5β , 8, 10β , 15	45.4	CH	1, 3, 5α , 12, 14, 17
14	5.80	dm 10.2	12, 15	131.9	CH	2α , 12
15	1.33	s	12, 13, 14	35.4	CH_3	
16	1.34	s	6α , 6β , 9α , 12	28.1	CH_3	8
17	0.77	s	2α , 5α , 6α , 12	17.7	CH_3	3, 5β
18	2.13	d hept 7.0, 3.2	3, 5α , 5β , 19, 20	26.5	CH	3, 19, 20
19	0.86	d 7.0	2α , 2β , 3, 18	23.4	CH_3	3, 20
20	0.78	d 7.0	2α , 18	16.6	CH_3	3, 19

Table S8. ^1H (400 MHz) and ^{13}C (50 MHz) NMR chemical shifts (CDCl_3), NOESY and HMBC correlations of 8-methoxy-dihydro-sphaerococcenol (**8**).

No.	^1H (δ)	m (J)	NOESY	^{13}C (δ)	Type	HMBC ($^{13}\text{C} \rightarrow ^1\text{H}$)
1	5.69	dm 10.5	2 α , 2 β	127.7	CH	2 α , 2 β , 3, 13
2	α 1.98	m	1, 20	22.7	CH ₂	1, 3, 14, 18
	β 2.10	m	1, 3, 17b			
3	1.74	m	2 β	42.0	CH	5 α , 5 β , 13, 17a, 17b, 18, 19, 20
4	-			40.1	C	2 α , 3, 5 α , 5 β , 6 α , 14, 17a, 17b, 18
5	α 1.73	ddd 14.0, 14.0, 4.0	13, 16, 18	24.7	CH ₂	6 β , 17a, 17b
	β 1.50	ddd 14.0, 4.7, 2.9	6 α , 6 β			
6	α 0.97	ddd 14.0, 4.0, 2.9	5 β , 8, 16	29.1	CH ₂	5 α , 8, 16
	β 2.13	ddd 14.0, 14.0, 4.7	5 β , 12, 17a, 21			
7	-			39.8	C	5 α , 5 β , 6 α , 8, 9 β , 12, 16
8	3.09	br d 6.9	6 α , 9 α , 16, 21	83.8	CH	9 β , 12, 16, 21
9	α 2.81	dd 18.4, 6.9	8, 16	38.9	CH ₂	8
	β 2.67	d 18.4	15, 21			
10	-			216.9	C	8, 9 α , 9 β , 15, 11OH
11	-			76.3	C	9 α , 12, 15, 11OH
12	2.46	d 12.9	6 β , 14, 15, 17a	42.9	CH	8, 14, 15, 16, 11OH
13	2.71	dm 12.9	5 α , 16, 19	35.4	CH	1, 3, 5 α , 5 β , 12, 14
14	5.95	br d 10.5	12, 15, 11OH	129.0	CH	2 α , 12, 13
15	1.29	s	9 β , 12, 14, 11OH	31.2	CH ₃	12
16	0.76	s	5 α , 6 α , 8, 9 α , 13, 11OH	17.2	CH ₃	8, 6 β , 12
17	a 3.93	d 10.5	6 β , 12	40.6	CH ₂	3, 5 α , 5 β
	b 3.70	dd 10.5, 1.8	2 β			
18	1.94	dhept 6.7, 2.0	5 α	25.8	CH	19, 20
19	0.87	d 6.7	13	19.3	CH ₃	3, 18, 20
20	0.93	d 6.7	2 α	25.8	CH ₃	3, 18, 19
21	3.36	s	6 β , 8, 9 β	57.5	CH ₃	8
11OH	3.48	s	14, 15, 16	-	OH	

Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3) of iodocoronol (**1**).

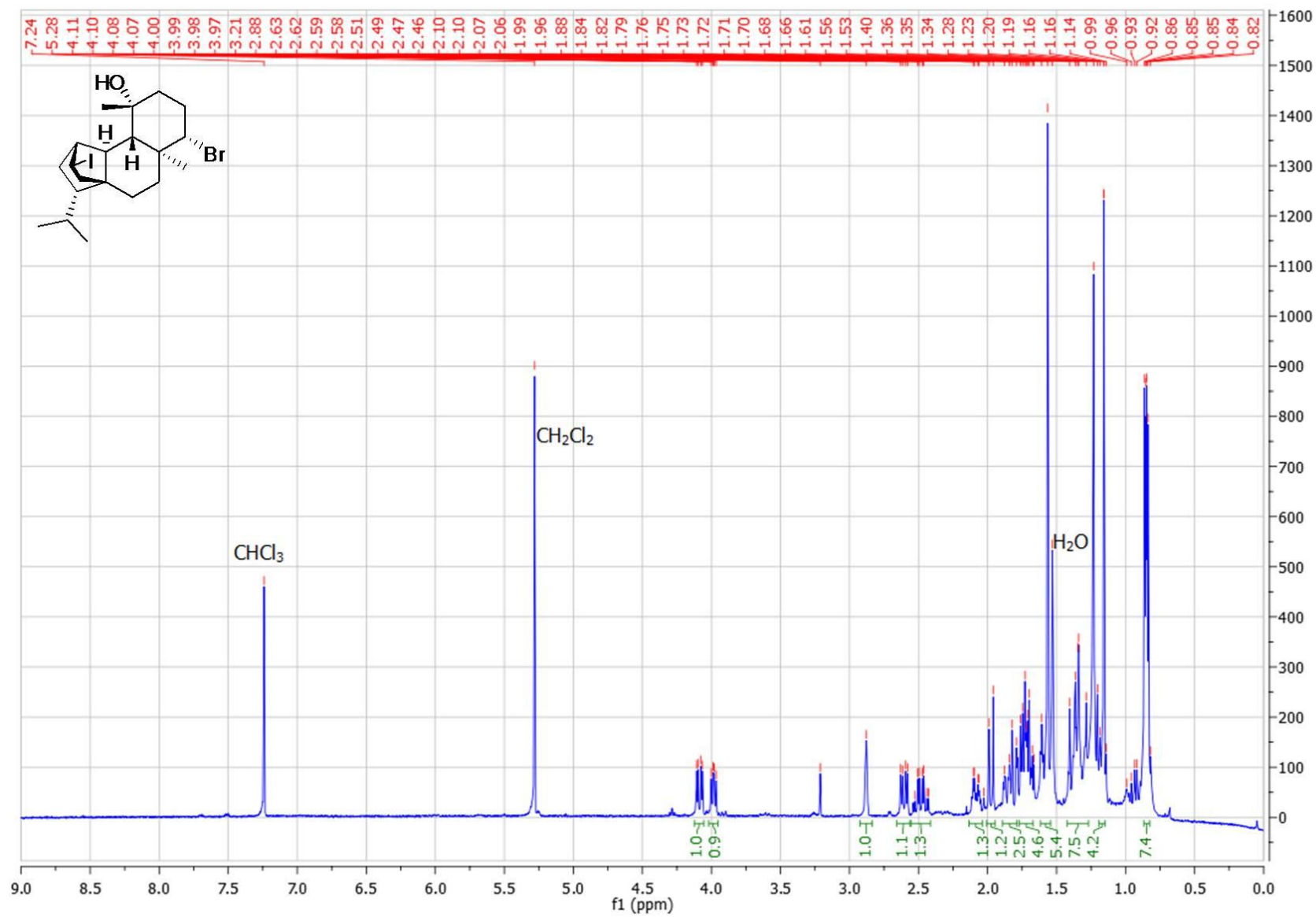


Figure S2. ^{13}C NMR spectrum (50 MHz, CDCl_3) of iodocoronol (1).

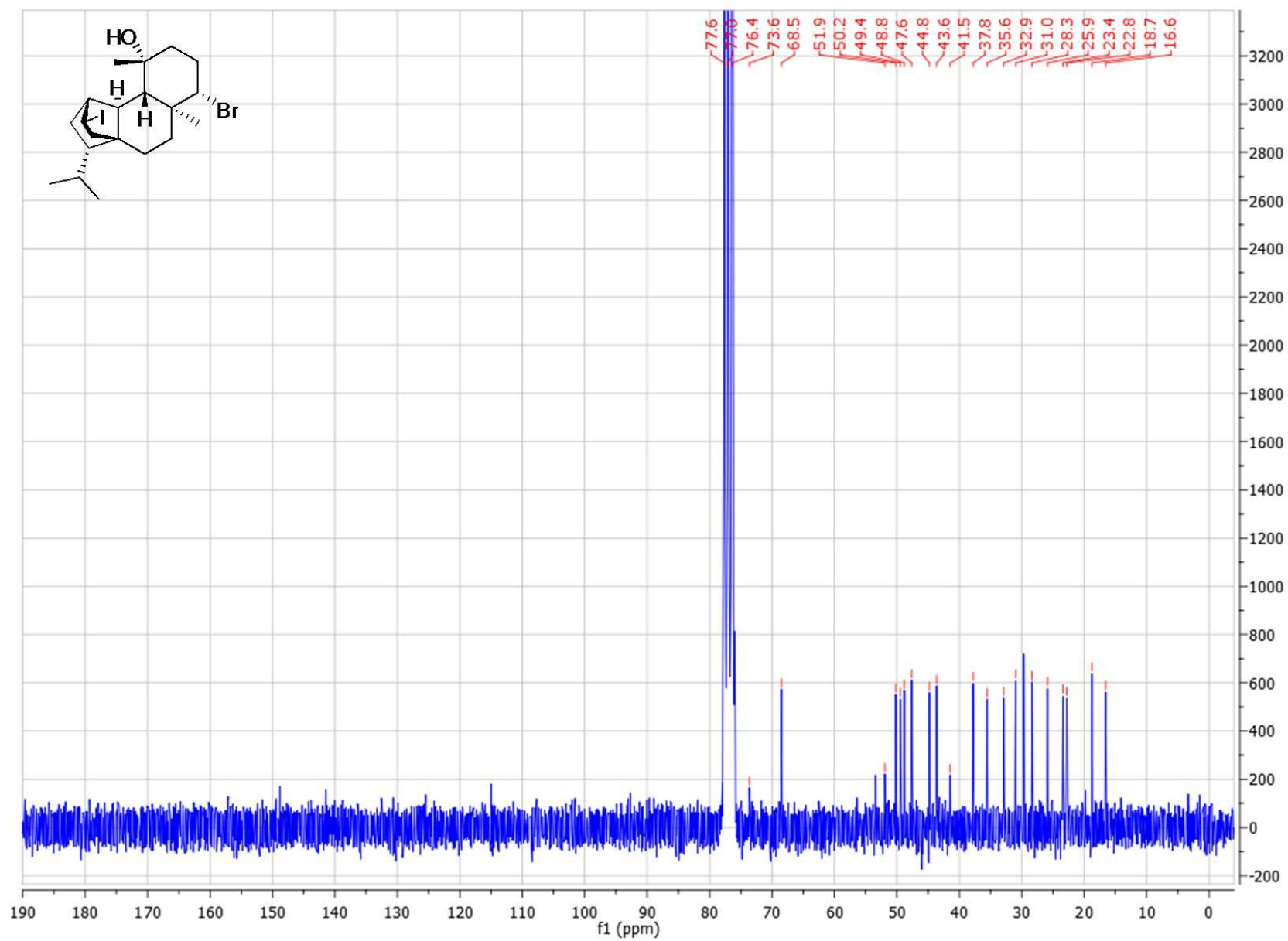


Figure S3. COSY spectrum (400 MHz, CDCl₃) of iodocoronol (1).

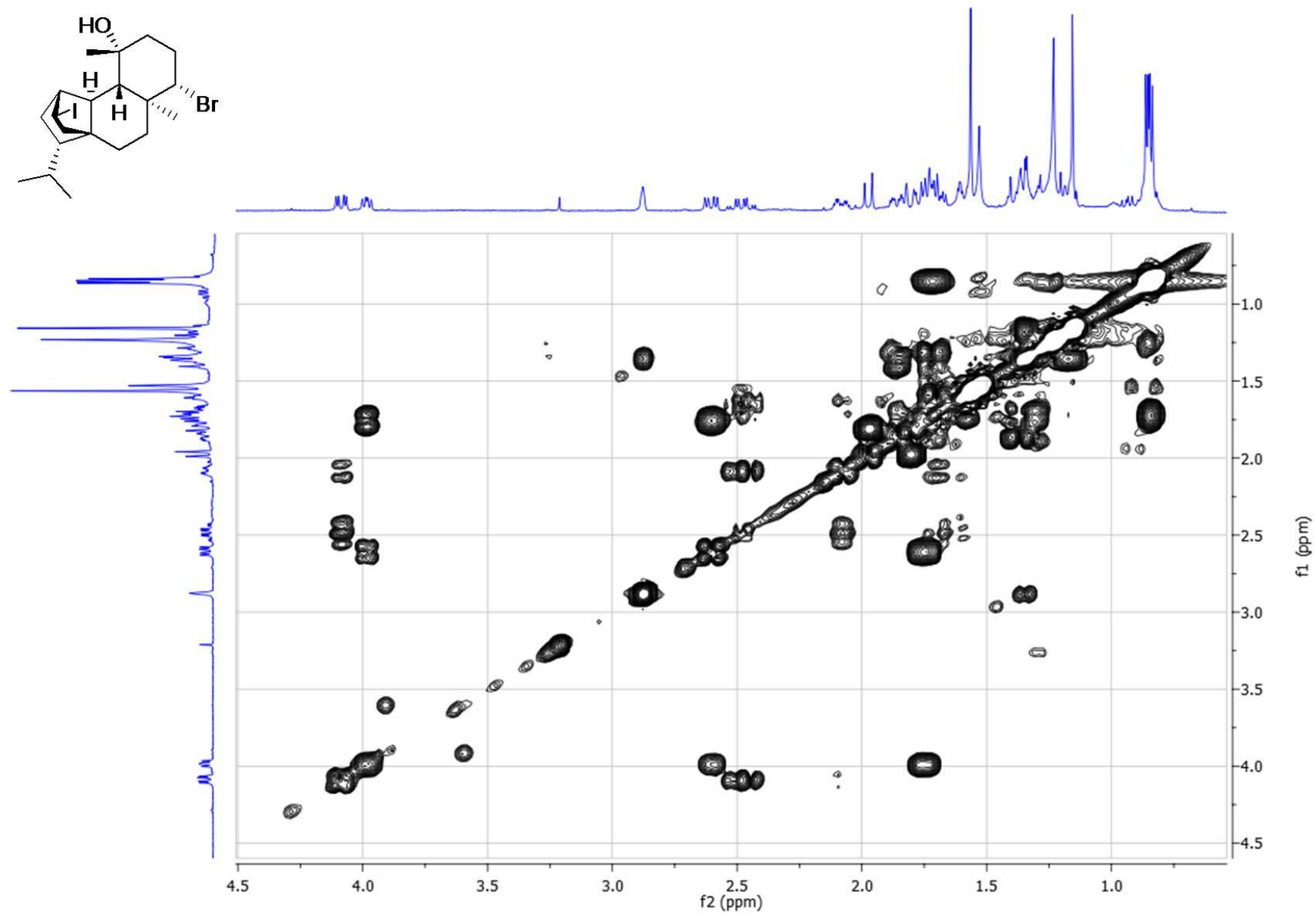


Figure S4. HSQC-DEPT spectrum (400 MHz, CDCl₃) of iodocoronol (1).

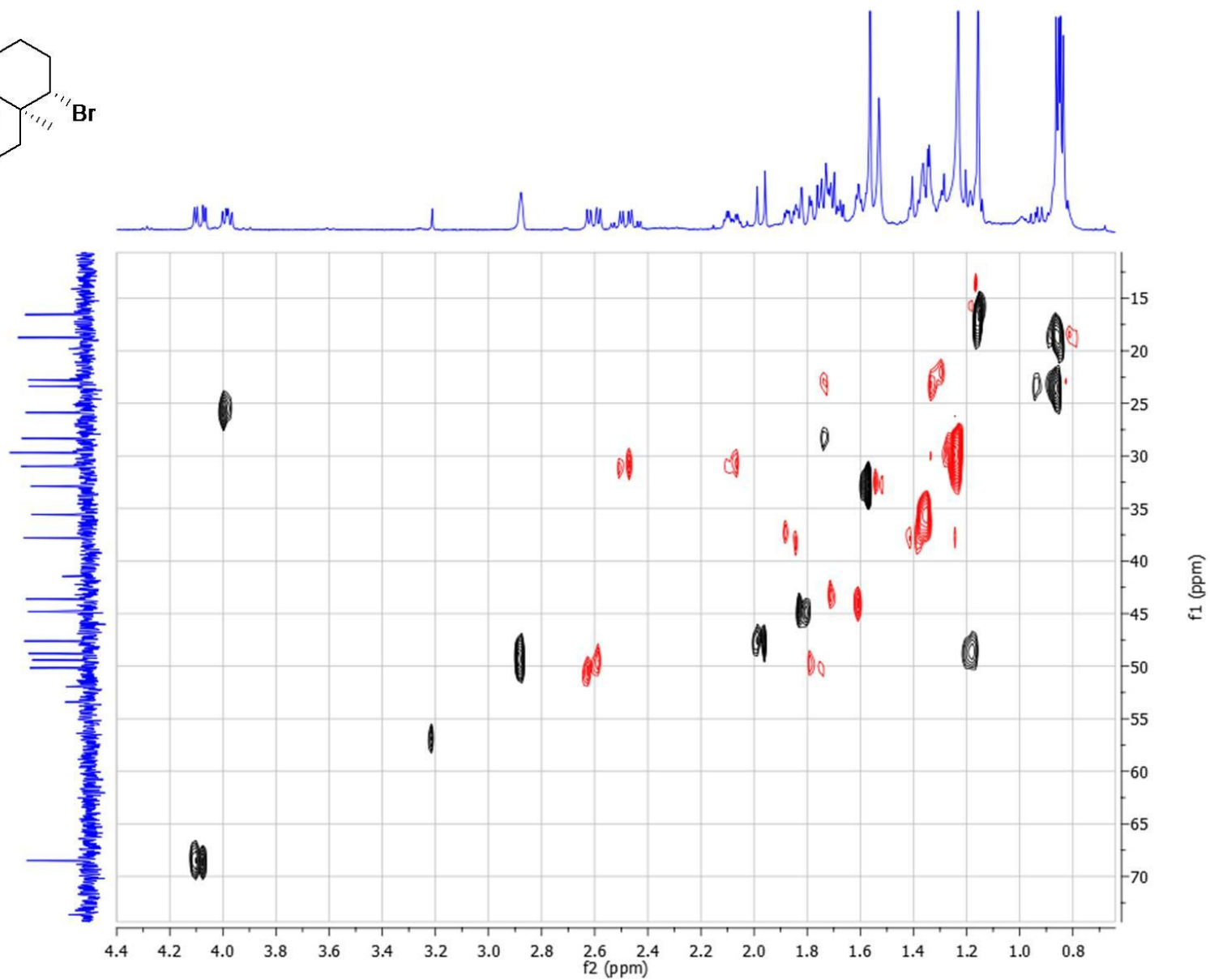
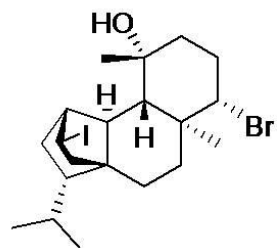


Figure S5. HMBC spectrum (400 MHz, CDCl₃) of iodocoronol (1).

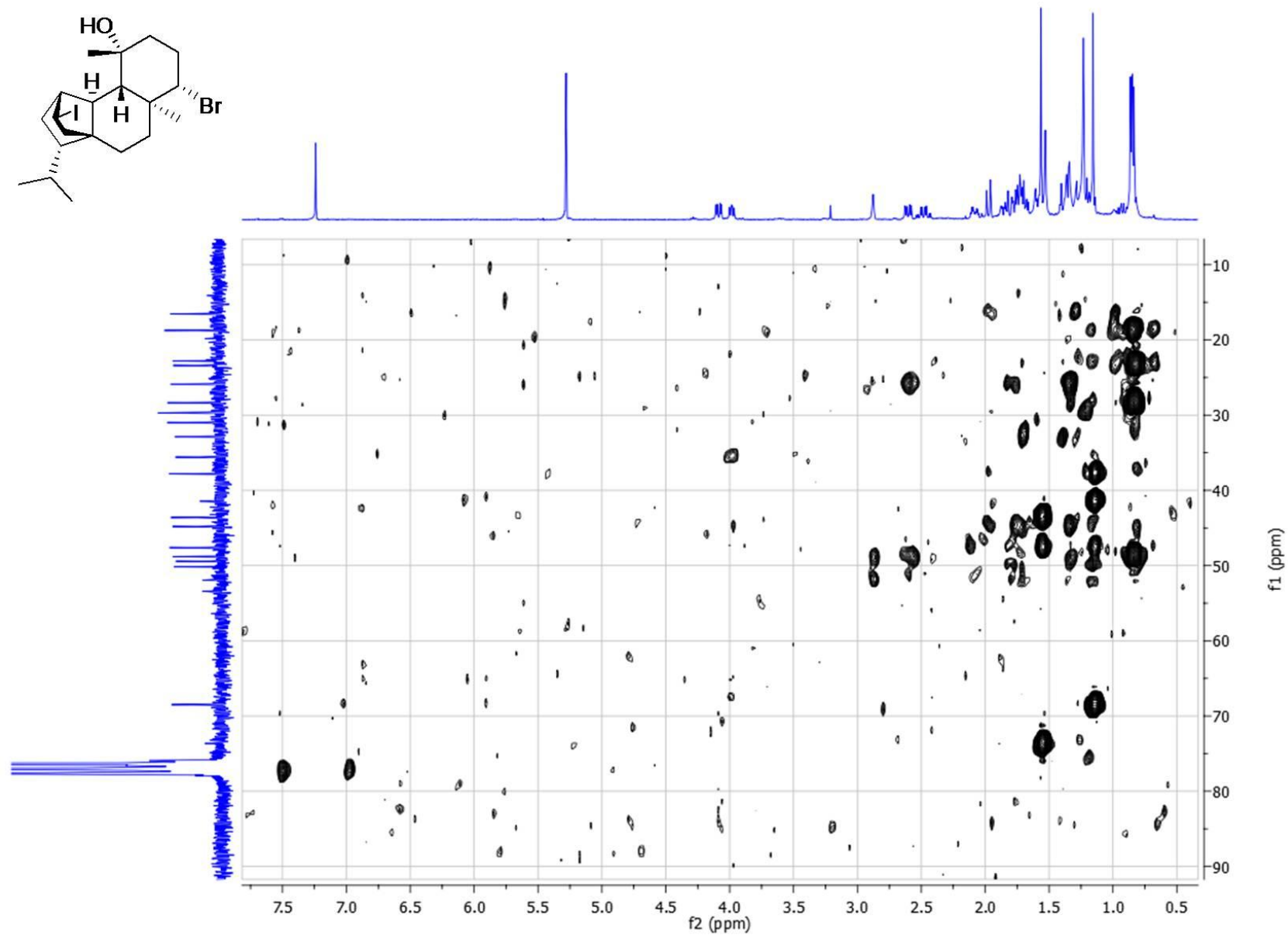


Figure S6. NOESY spectrum (400 MHz, CDCl_3) of iodocoronol (**1**).

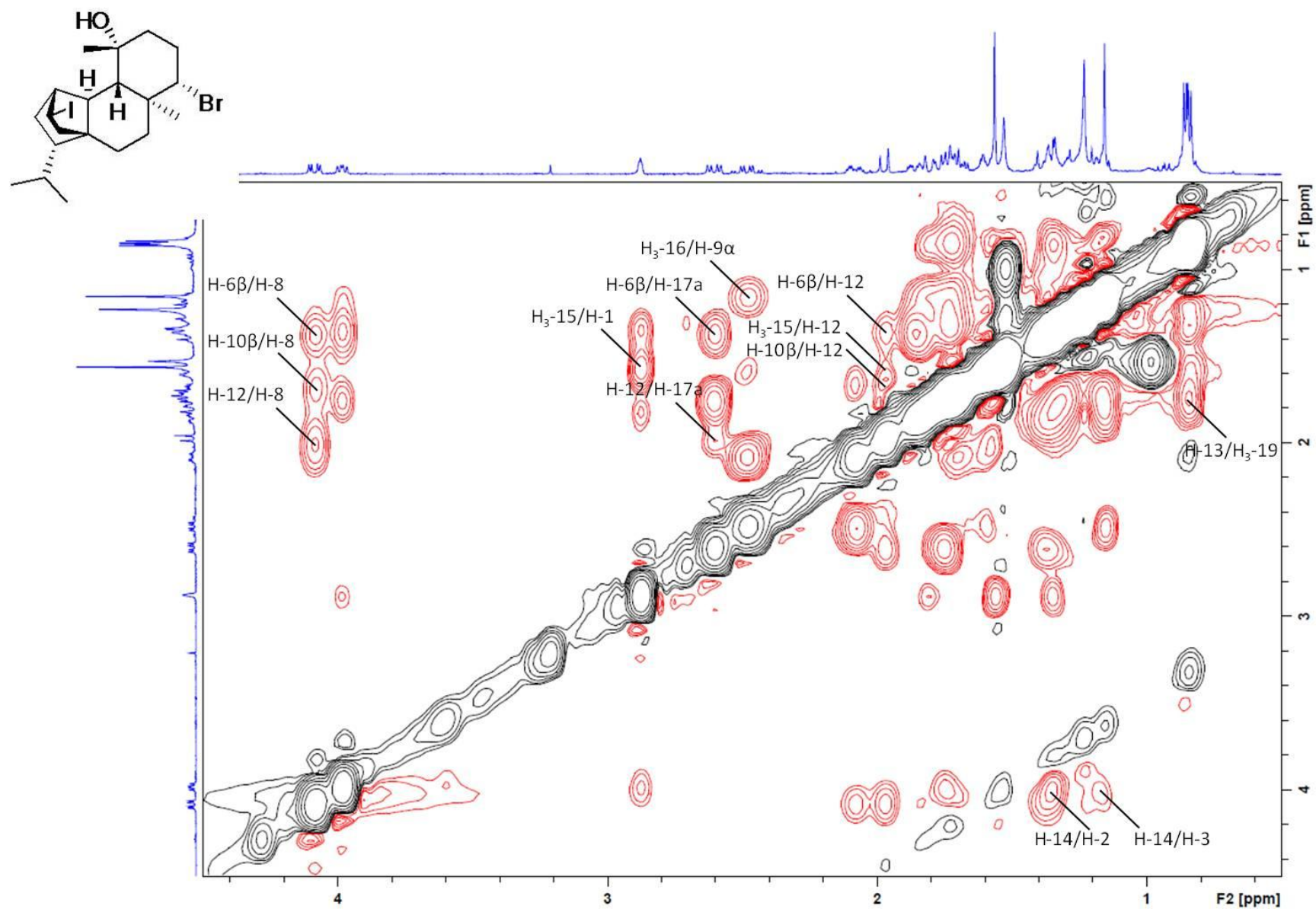


Figure S7. HRMS (ESI-) measurement of iodocoronol (**1**).

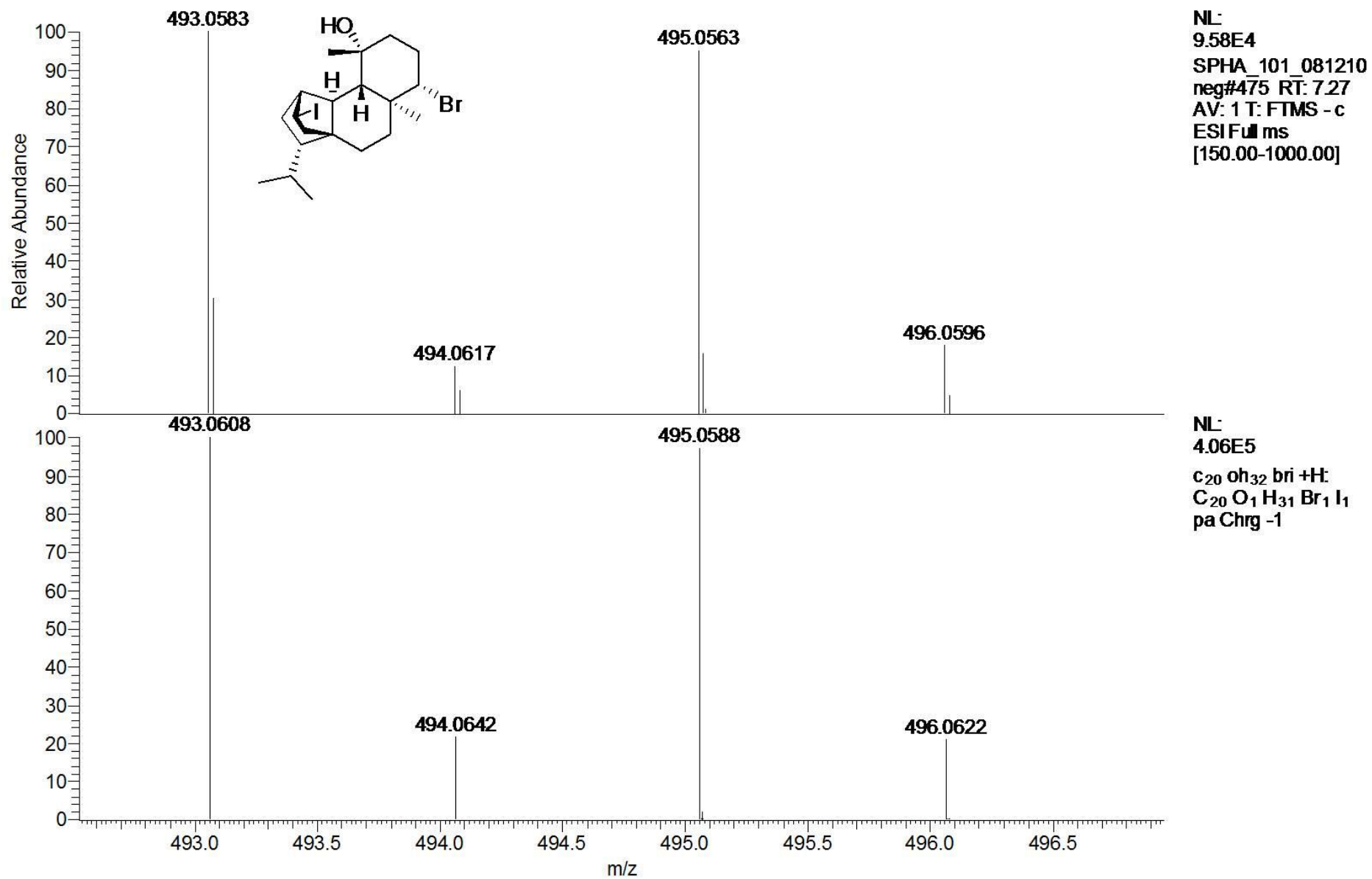


Figure S8. IR spectrum of iodocoronol (**1**).

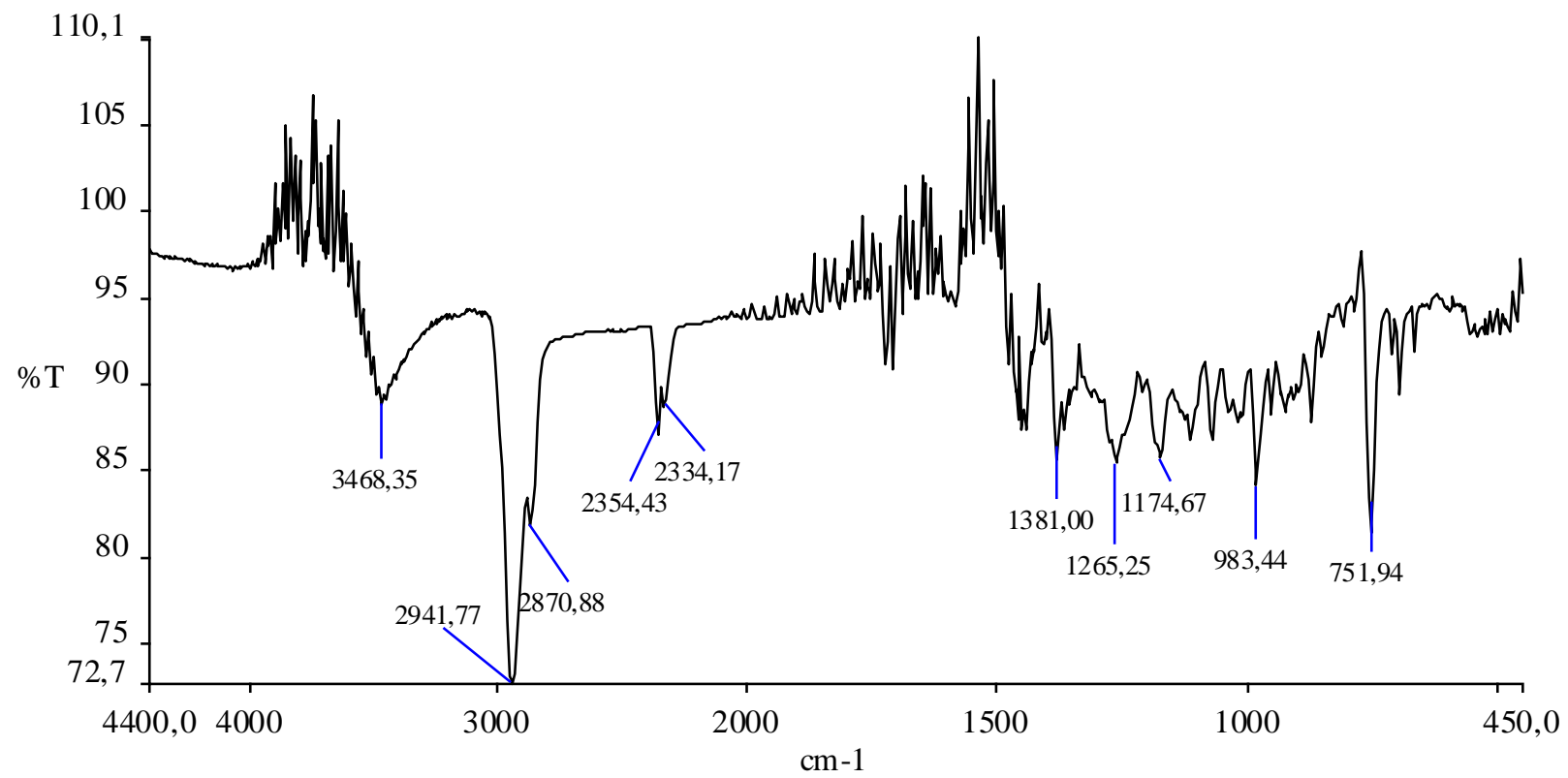


Figure S9. ^1H NMR spectrum (400 MHz, CDCl_3) of bromocoronol (2).

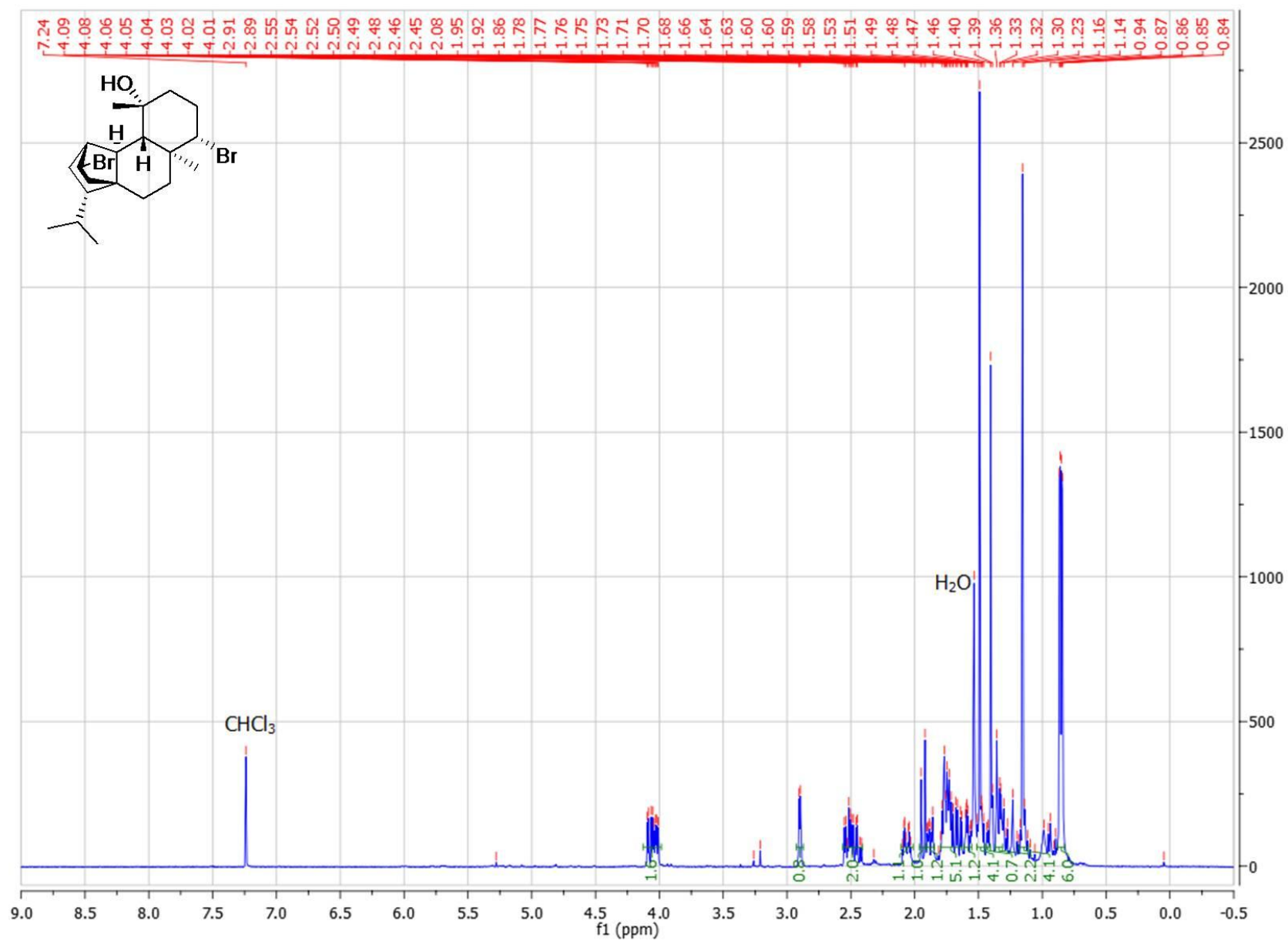


Figure S10. ^{13}C NMR spectrum (50 MHz, CDCl_3) of bromocoronol (**2**).

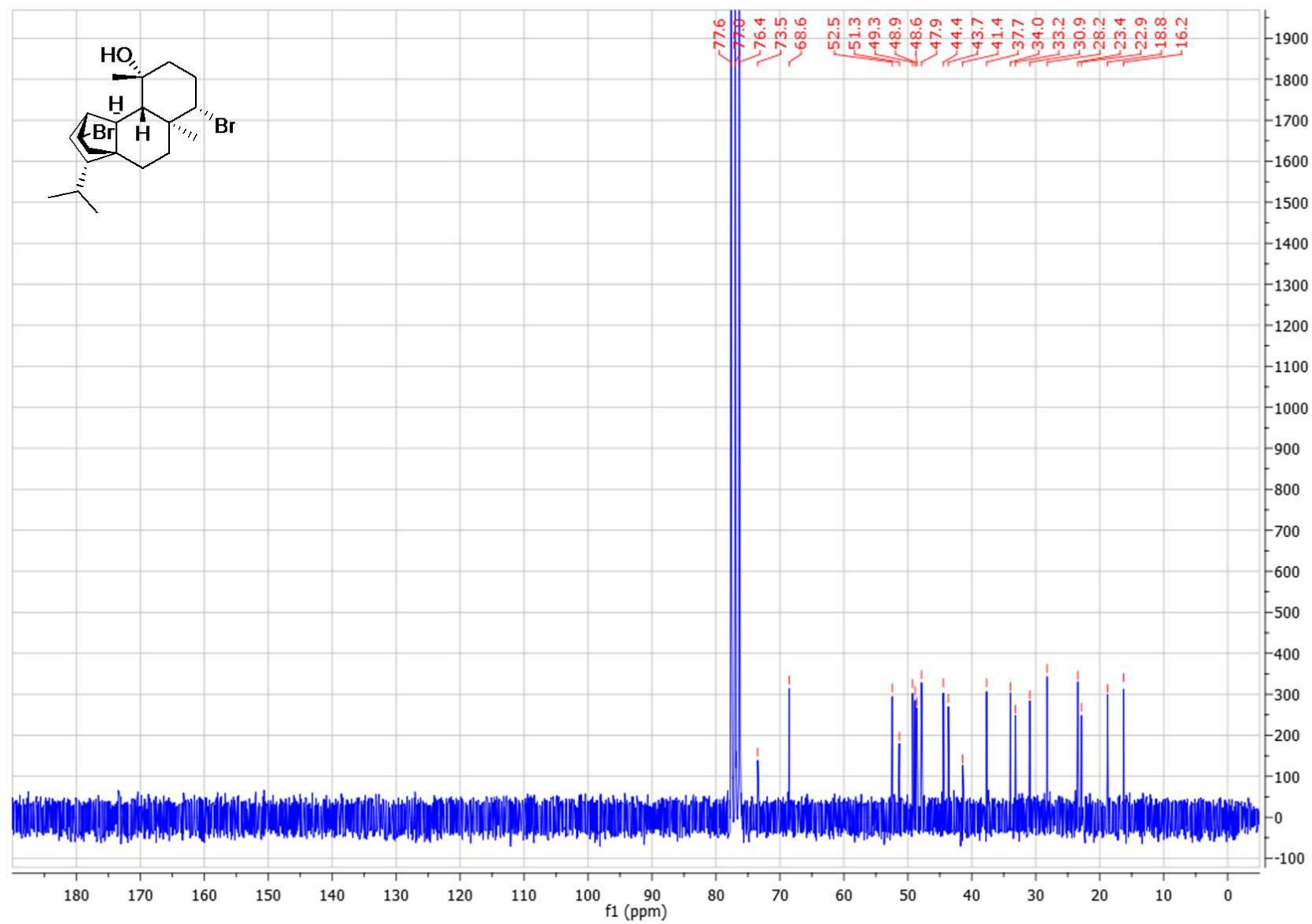


Figure S11. DEPT-135 spectrum (50 MHz, CDCl₃) of bromocoronol (2).

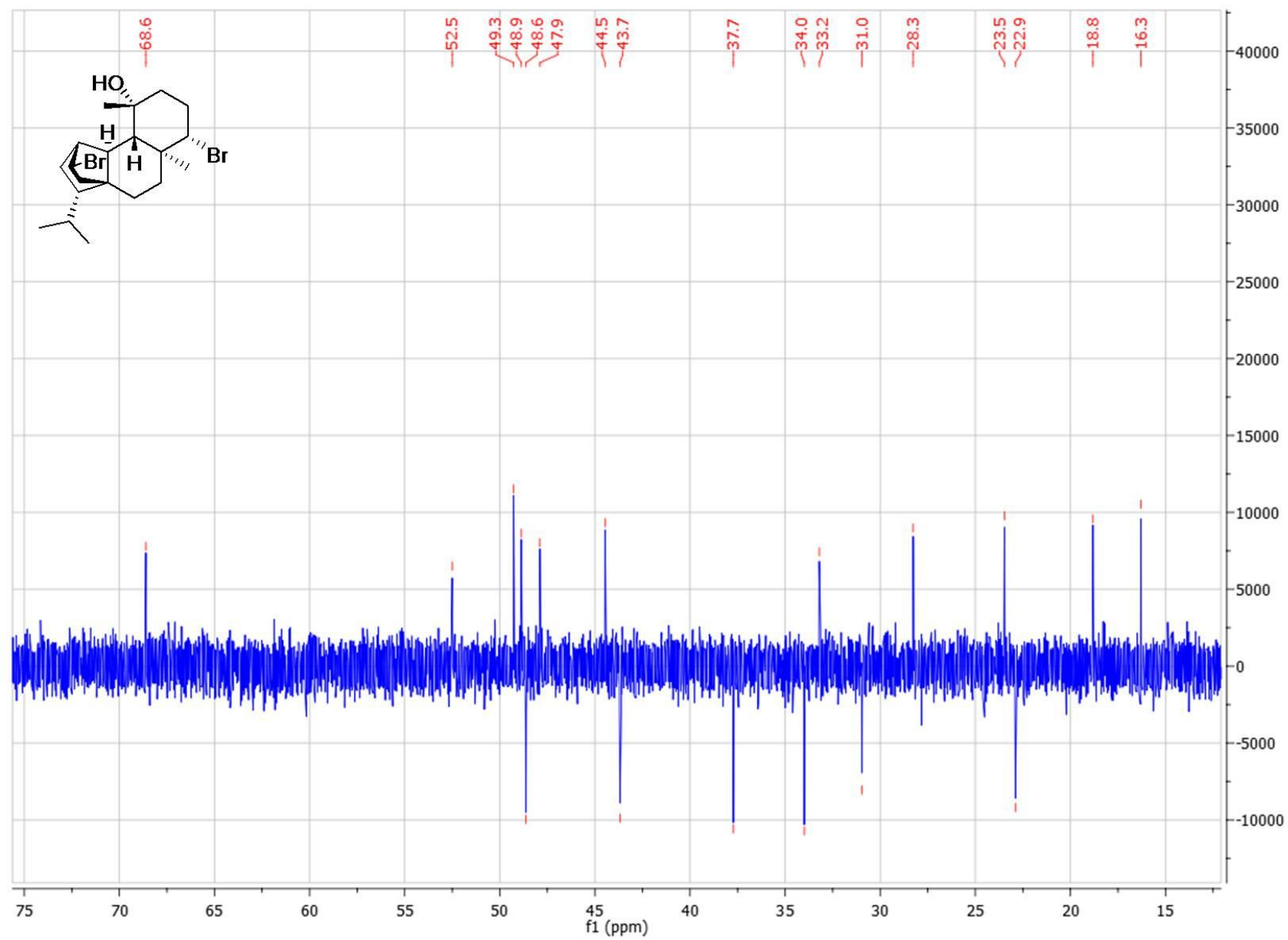


Figure S12. COSY spectrum (400 MHz, CDCl₃) of bromocoronol (2).

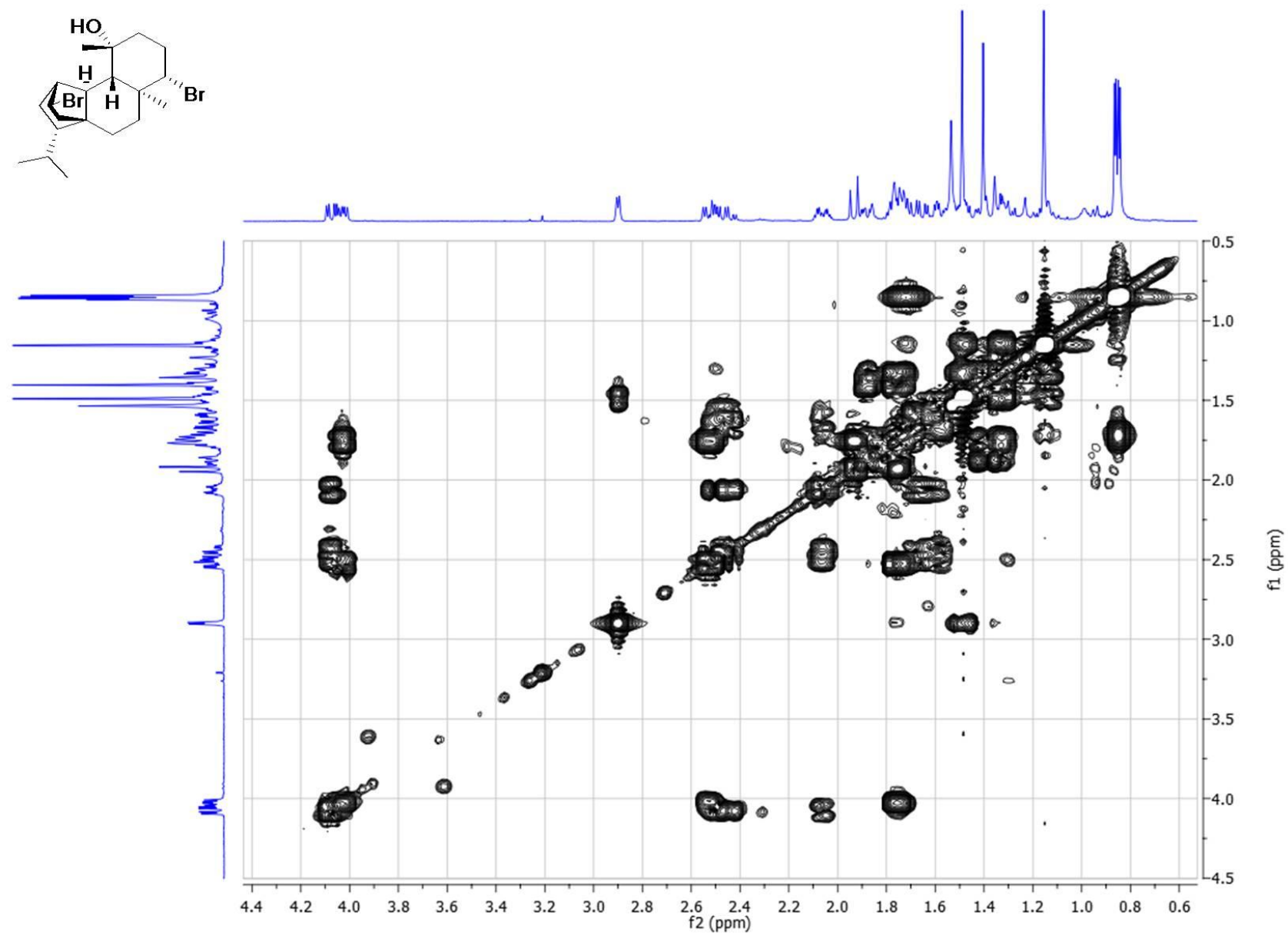
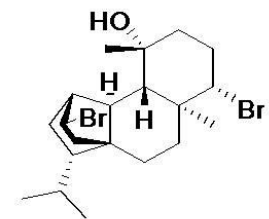


Figure S13. HSQC spectrum (400 MHz, CDCl₃) of bromocoronol (2).

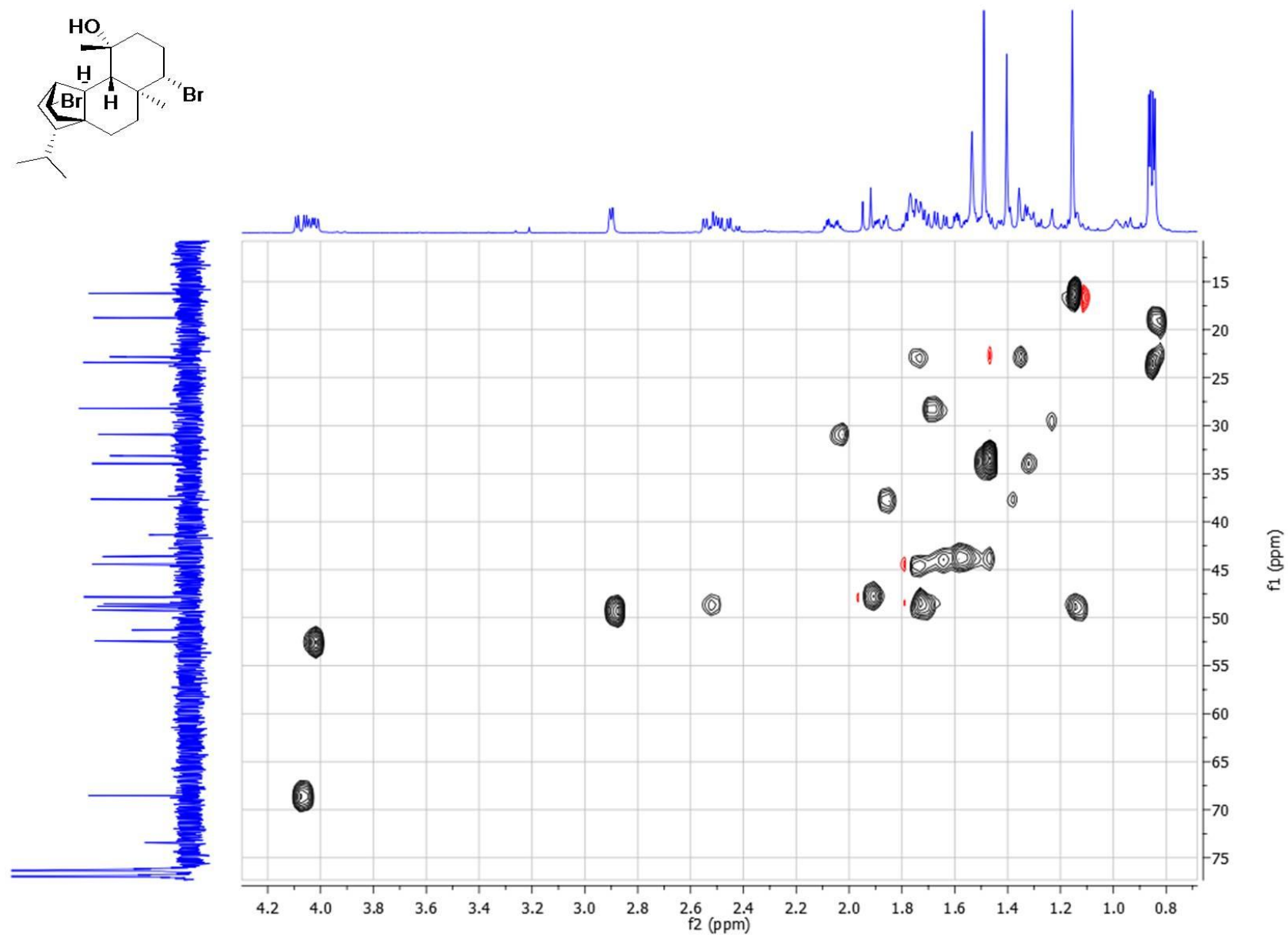
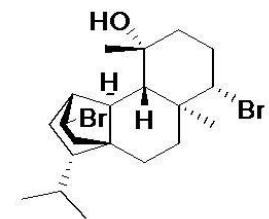


Figure S14. HSQC-TOCSY spectrum (400 MHz, CDCl_3) of bromocoronol (**2**).

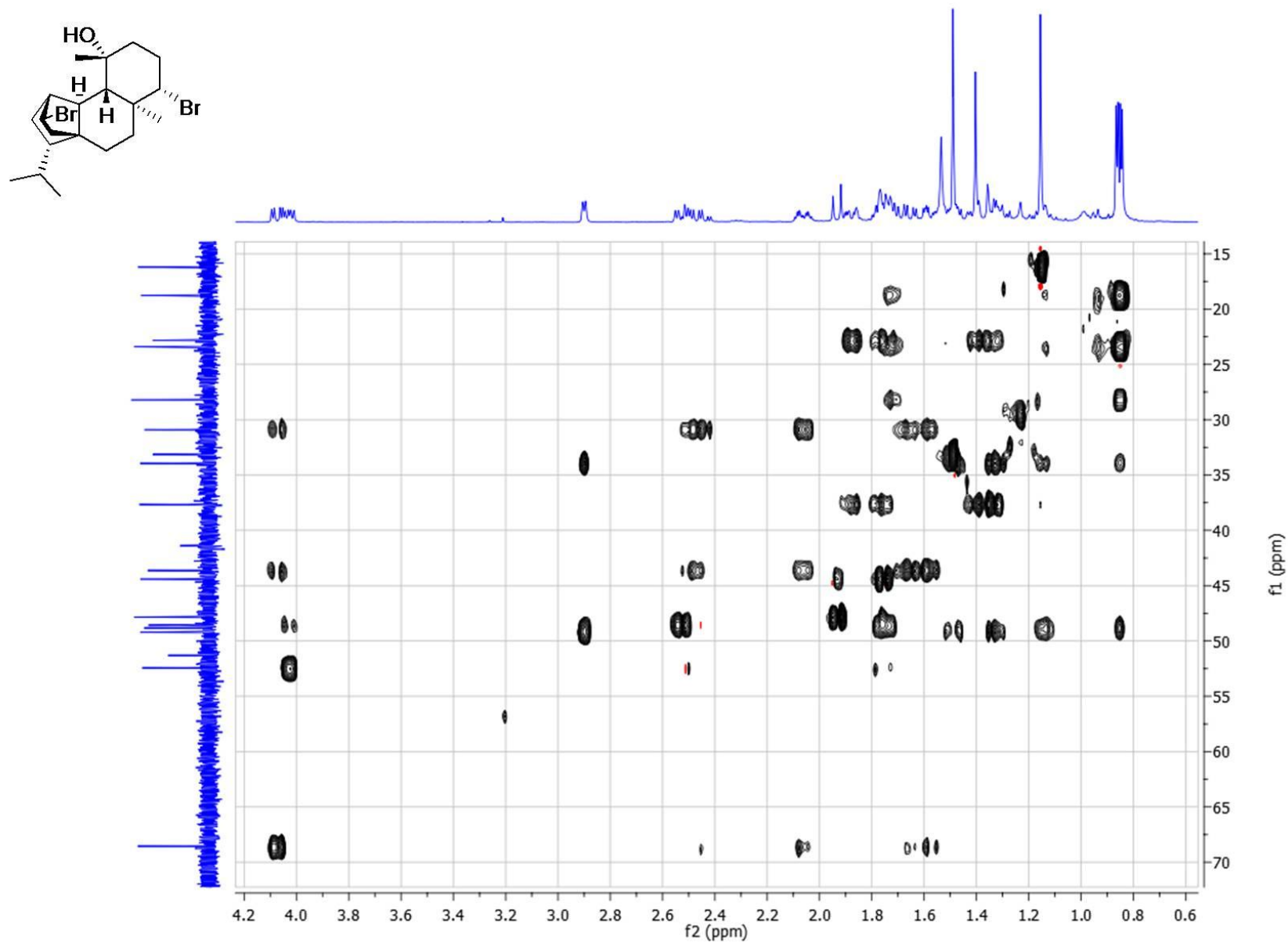


Figure S15. HMBC spectrum (400 MHz, CDCl₃) of bromocoronol (2).

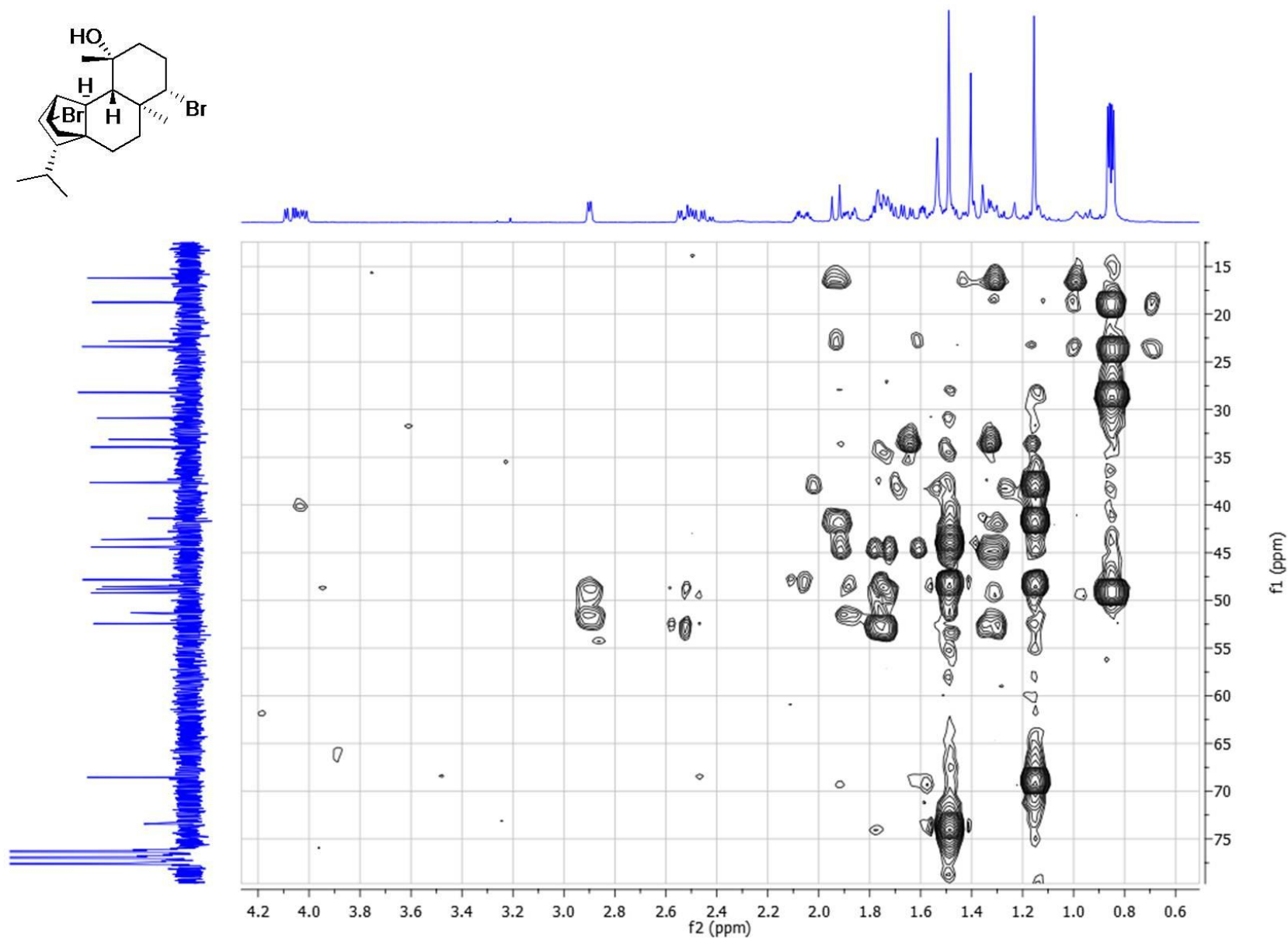


Figure S16. NOESY spectrum (400 MHz, CDCl_3) of bromocoronol (**2**).

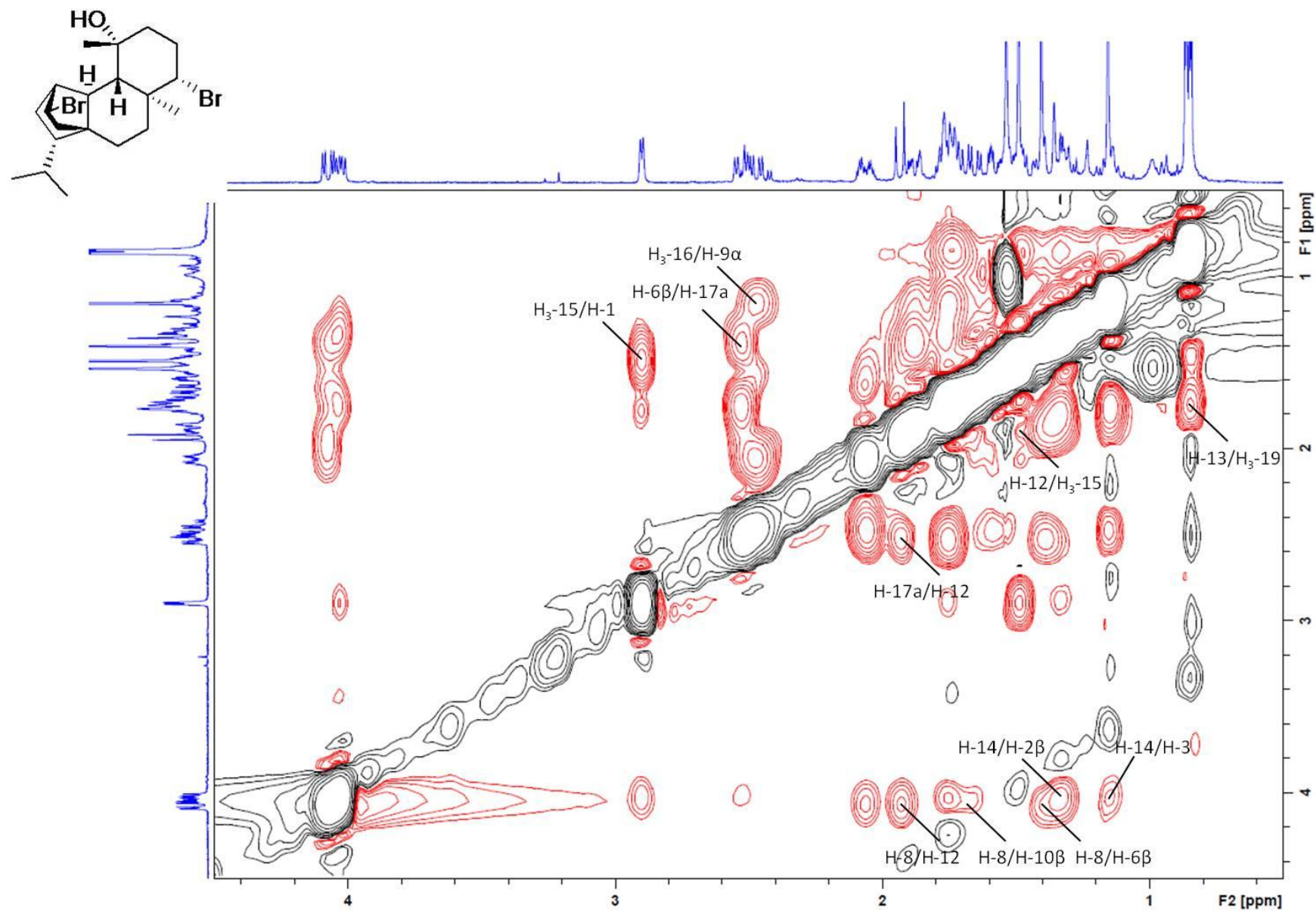


Figure S17. HRMS (ESI+) measurement of bromocoronol (**2**).

SPHA_106_091210poz1 #208-226 RT: 2.98-3.23 AV: 19 NL: 1.37E6
T: FTMS + c ESI sid=30.00 Full ms [250.00-1000.00]

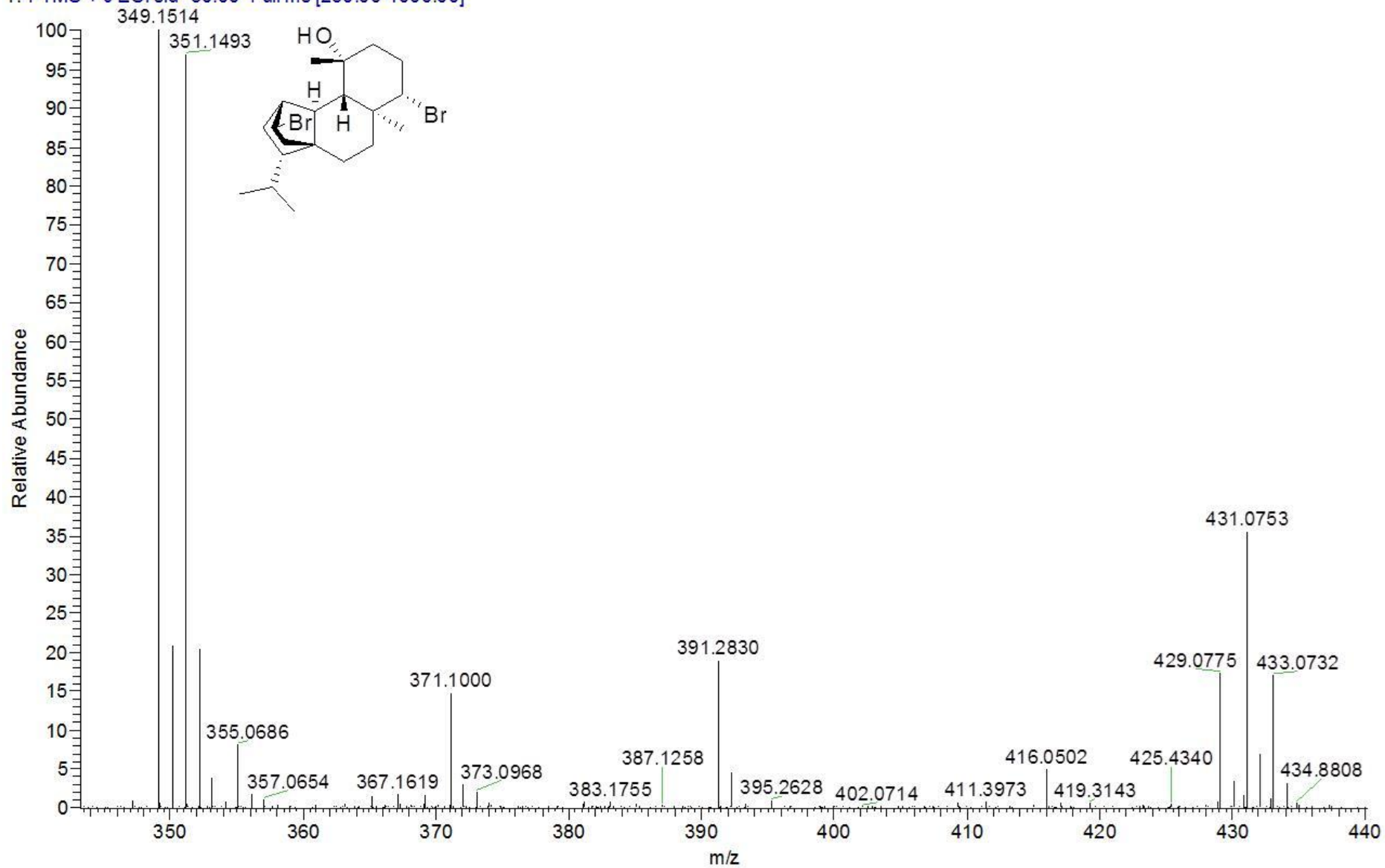


Figure S18. IR spectrum of bromocoronol (**2**).

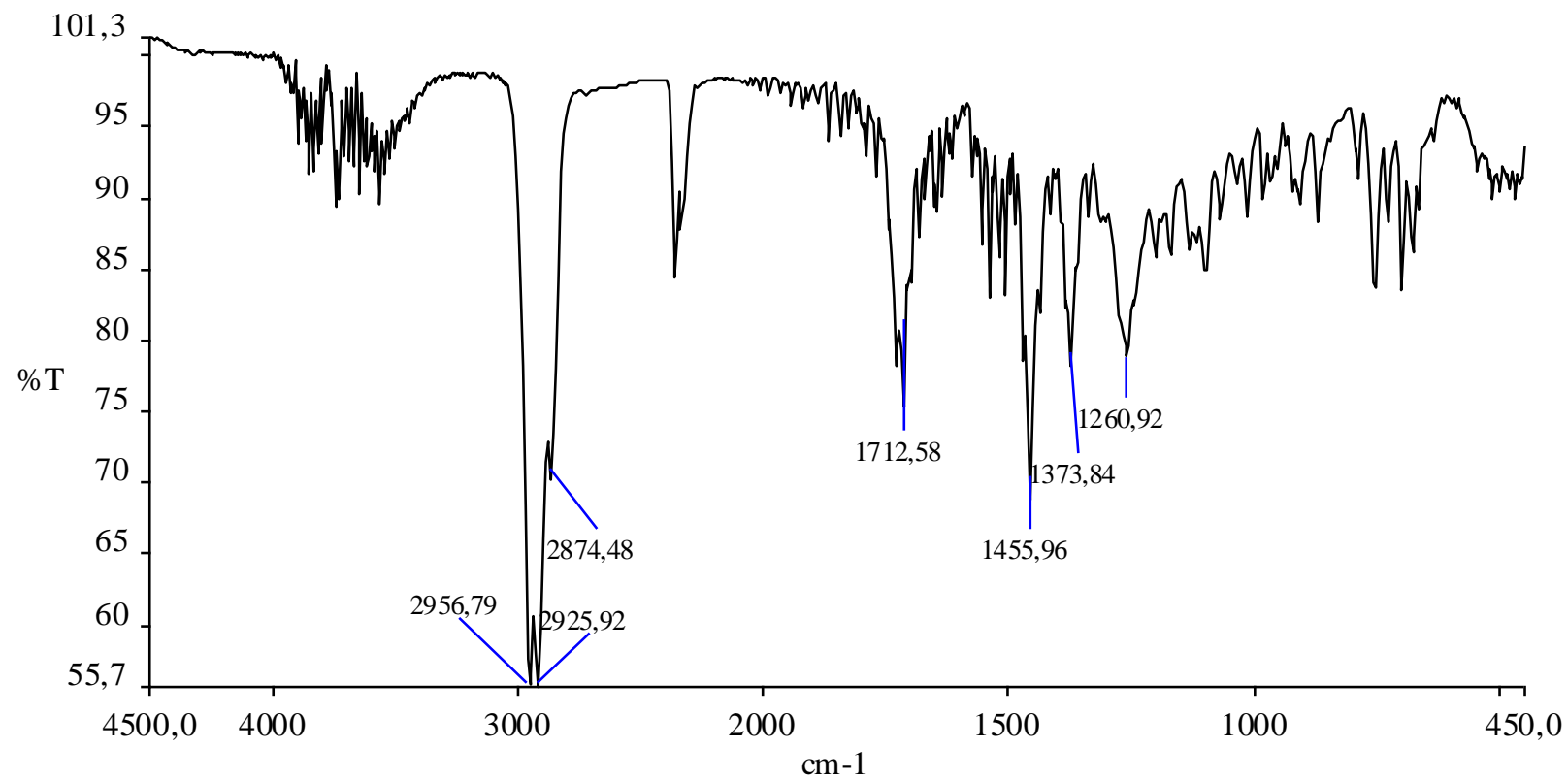


Figure S19. ^1H NMR spectrum (600 MHz, CDCl_3) of bromotetrasphaereniol (**3**).

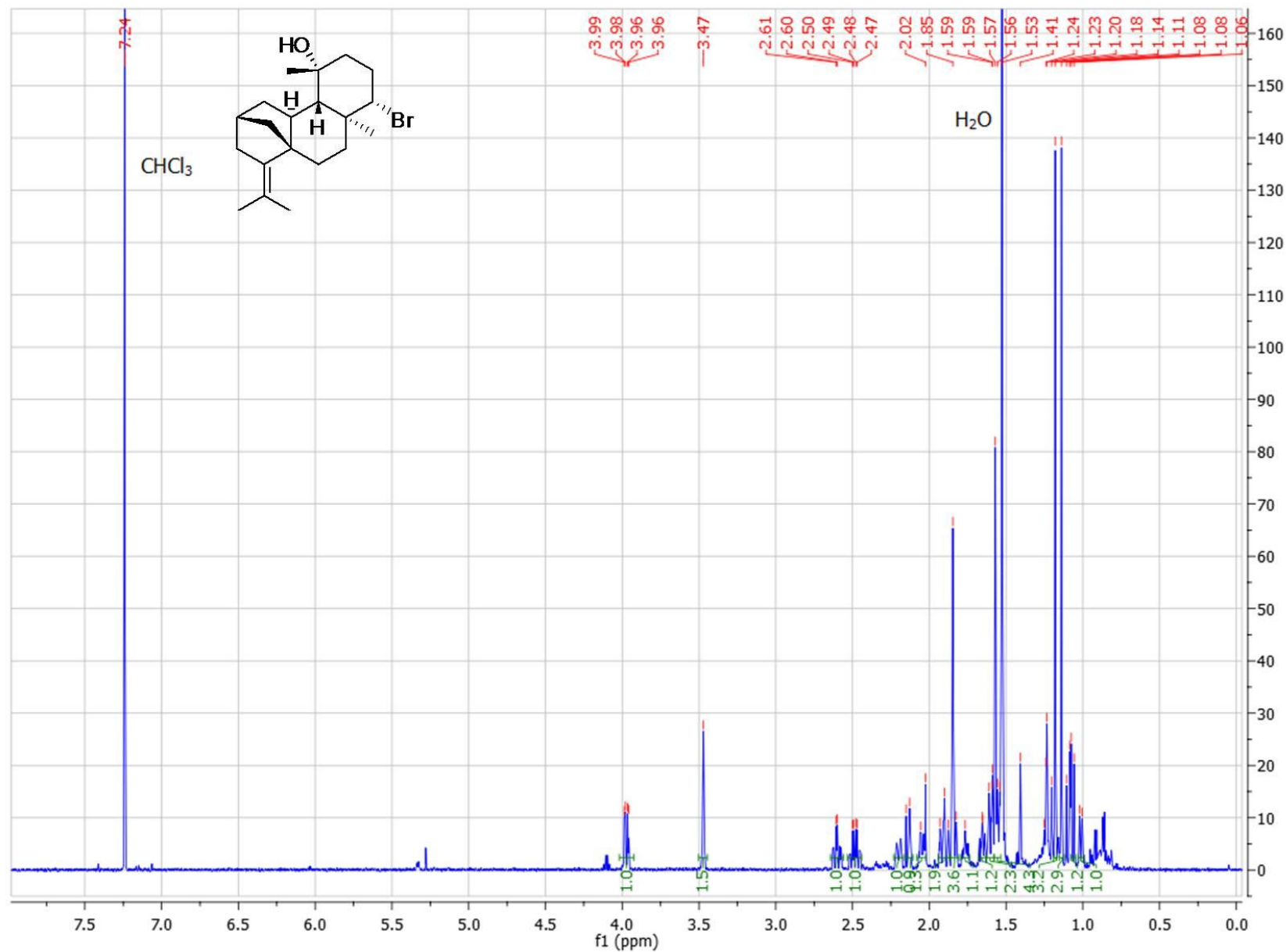


Figure S20. ^{13}C NMR spectrum (75 MHz, CDCl_3) of bromotetrasphaereniol (**3**).

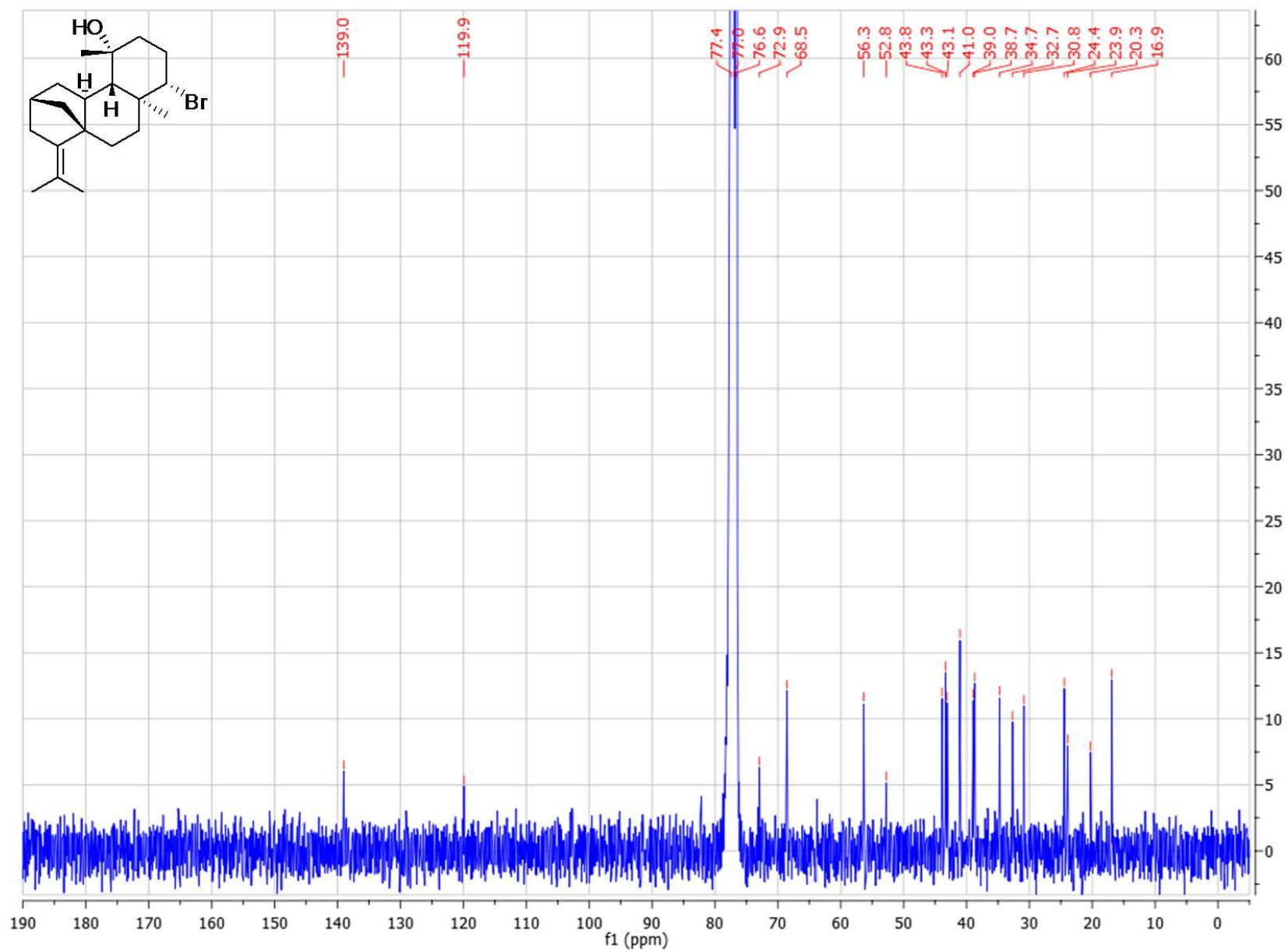


Figure S21. COSY spectrum (600 MHz, CDCl₃) of bromotetrasphaereniol (3).

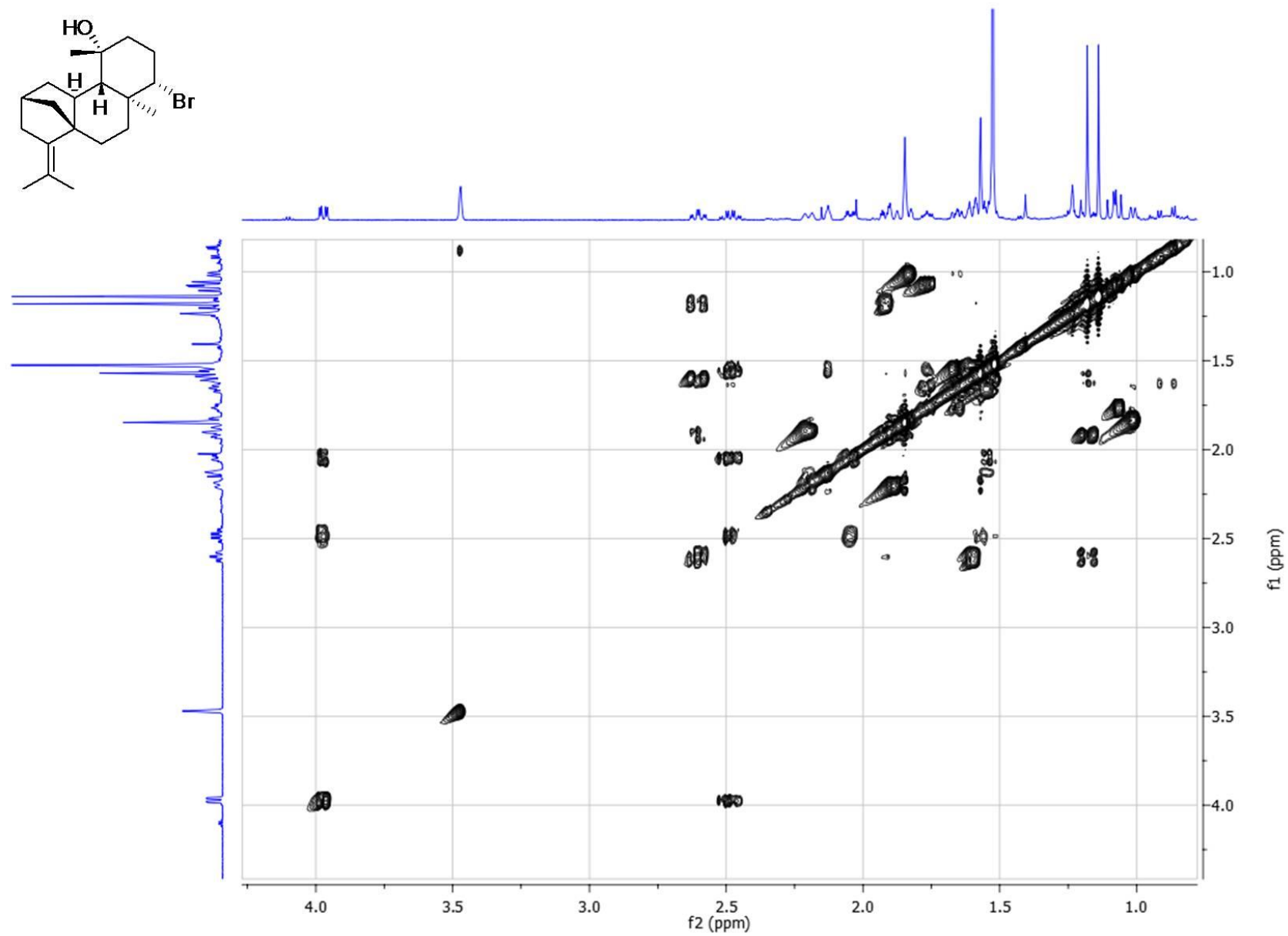


Figure S22. HSQC-DEPT spectrum (400 MHz, CDCl₃) of bromotetrasphaereniol (**3**).

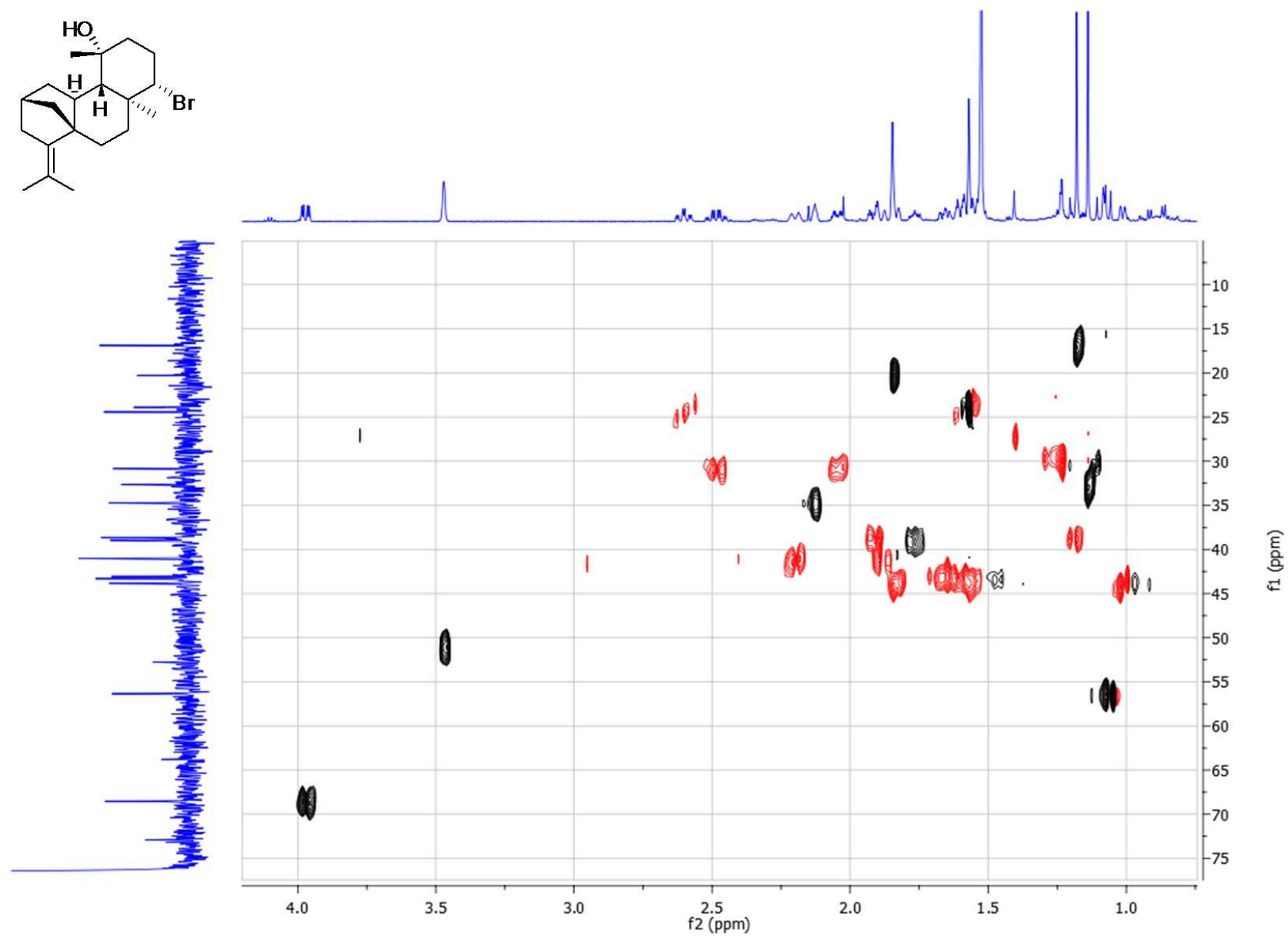
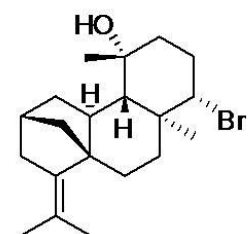


Figure S23. HMBC spectrum (600 MHz, CDCl₃) of bromotetrasphaereniol (**3**).

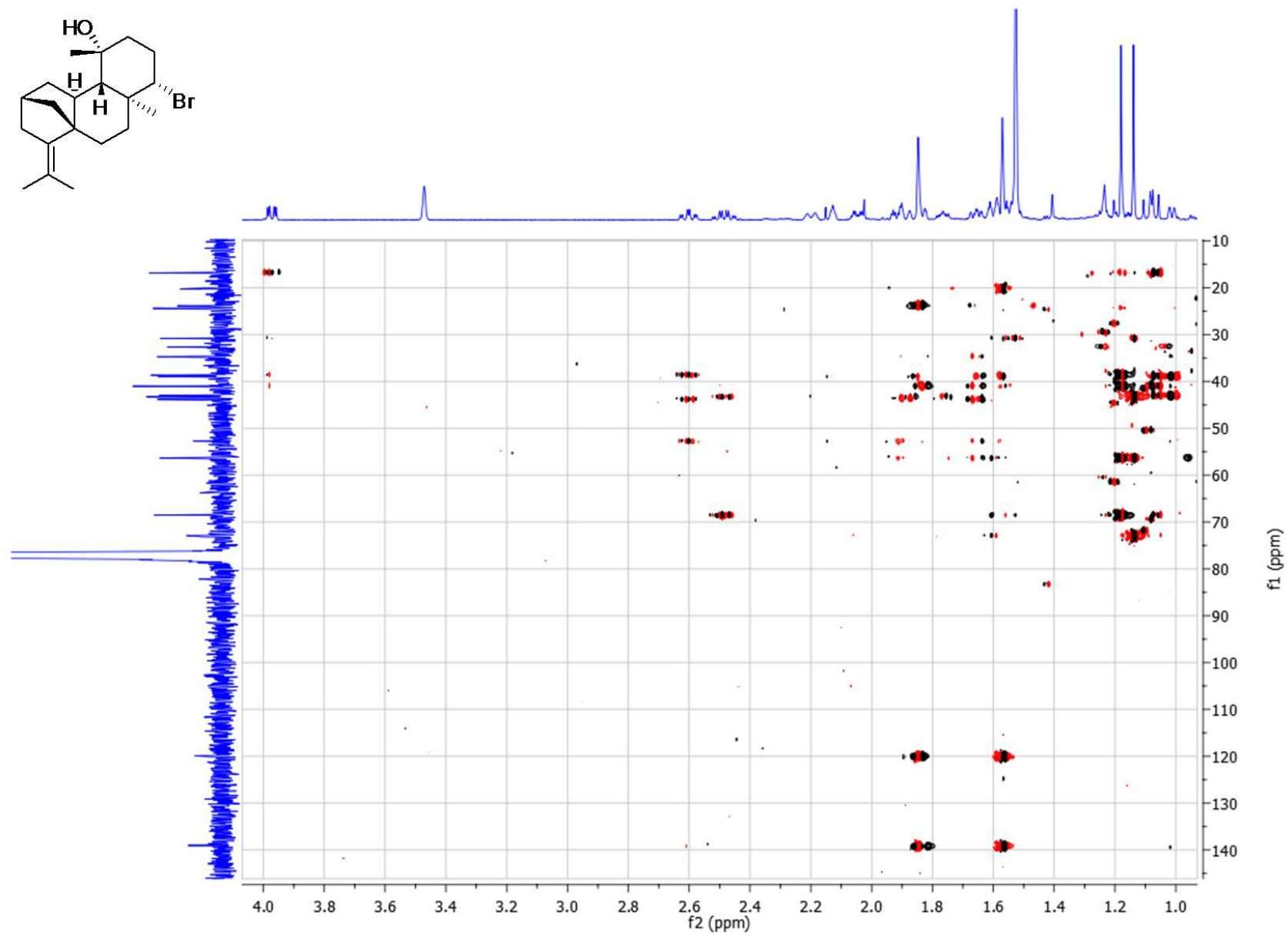


Figure S24. NOESY spectrum (600 MHz, CDCl_3) of bromotetrasphaereniol (**3**).

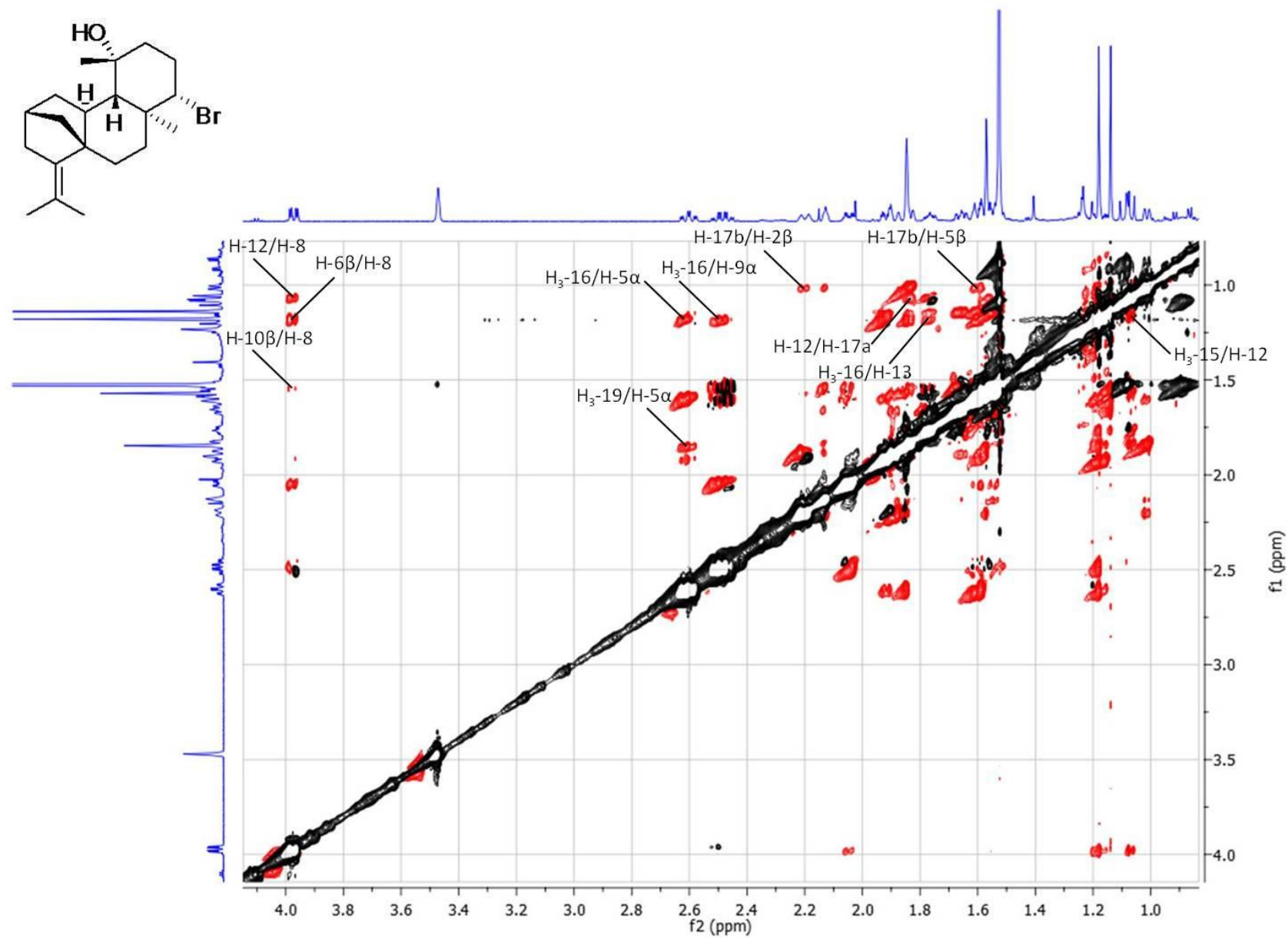
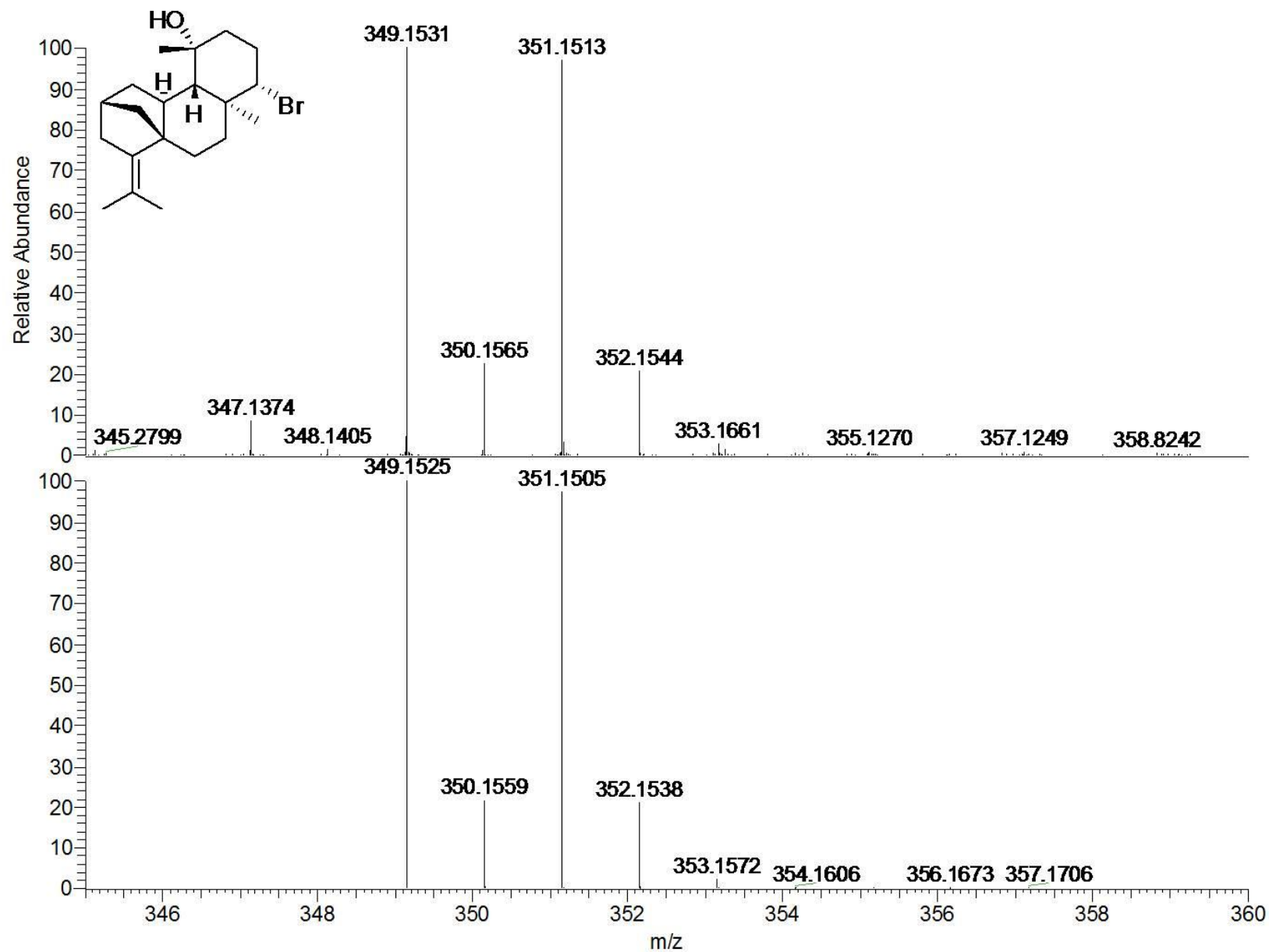


Figure S25. HRMS (ESI+) measurement of bromotetrasphaereniol (**3**).



NL:
1.86E6
Spha108#215 RT: 1.61
AV: 1 SB: 248 1.85 ,
0.00-1.85 T: FTMS + c
ESI Full ms
[250.00-500.00]

NL:
4.07E5
C₂₀H₂₉Br + H⁺
C₂₀H₃₀Br₁
pa Chrg 1

Figure S26. IR spectrum of bromotetrasphaereniol (**3**).

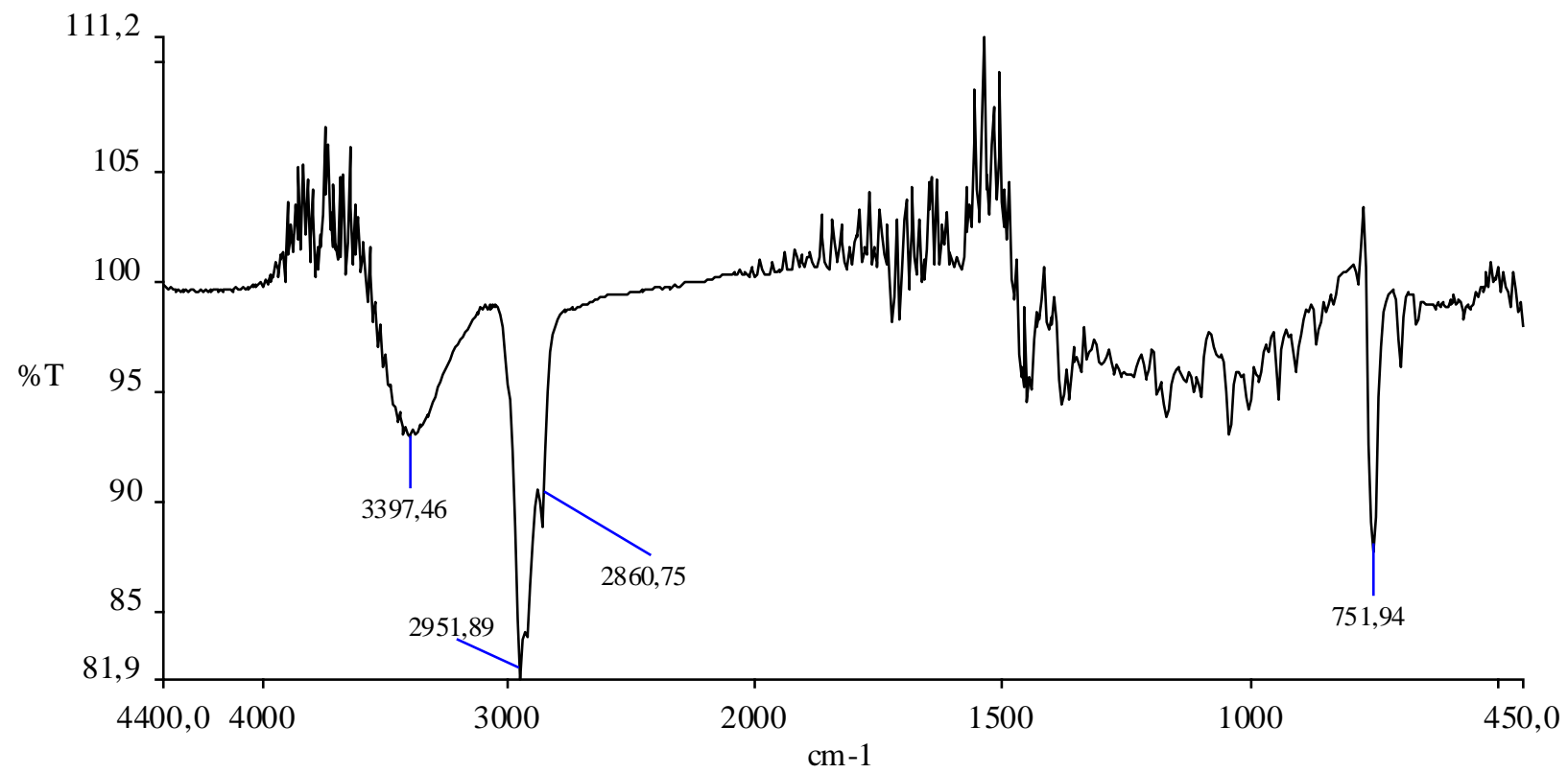


Figure S27. ^1H NMR spectrum (400 MHz, CDCl_3) of 1-methoxy-ioniol I (4).

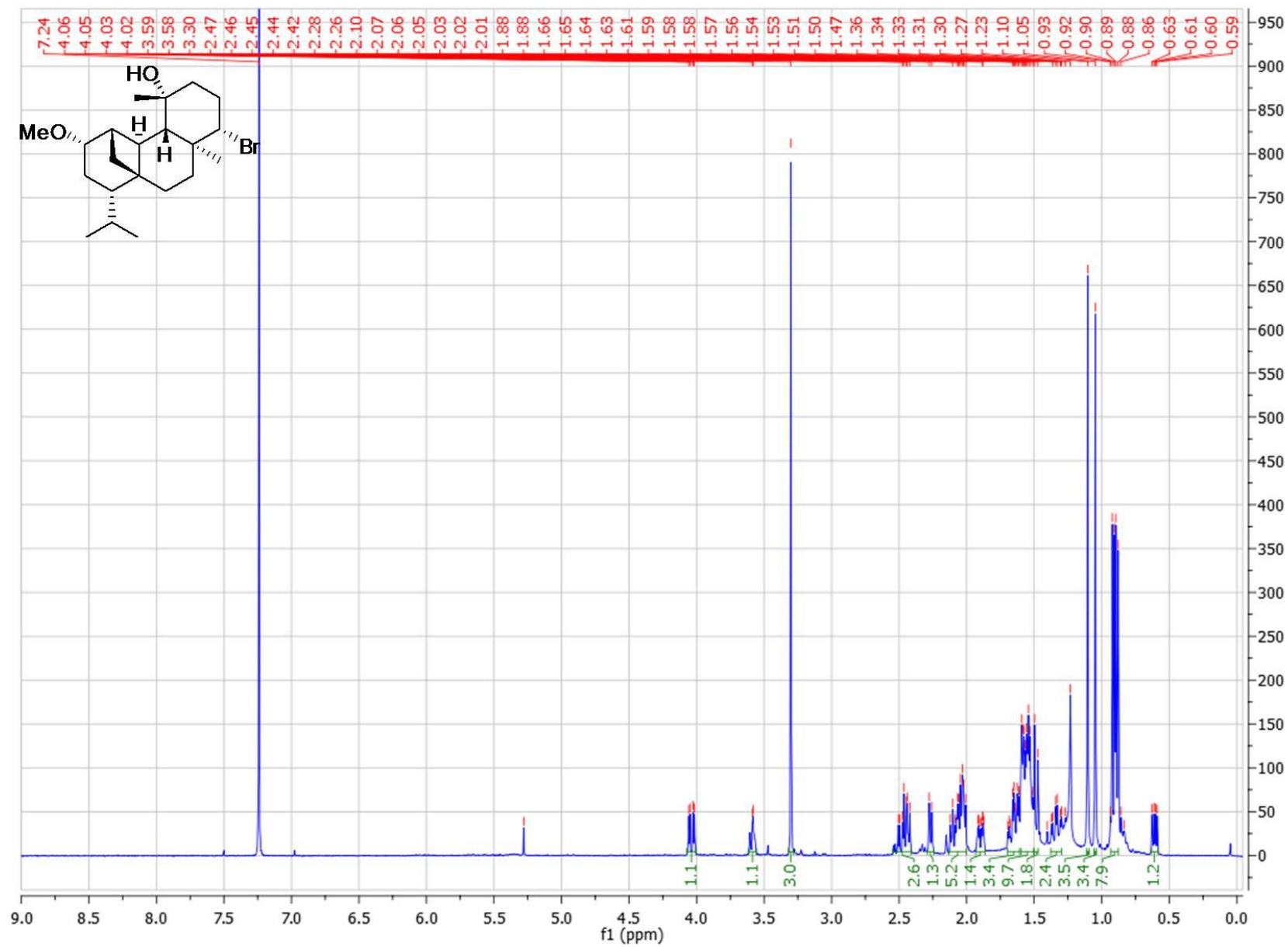


Figure S28. ^{13}C NMR spectrum (50 MHz, CDCl_3) of 1-methoxy-ioniol I (4).

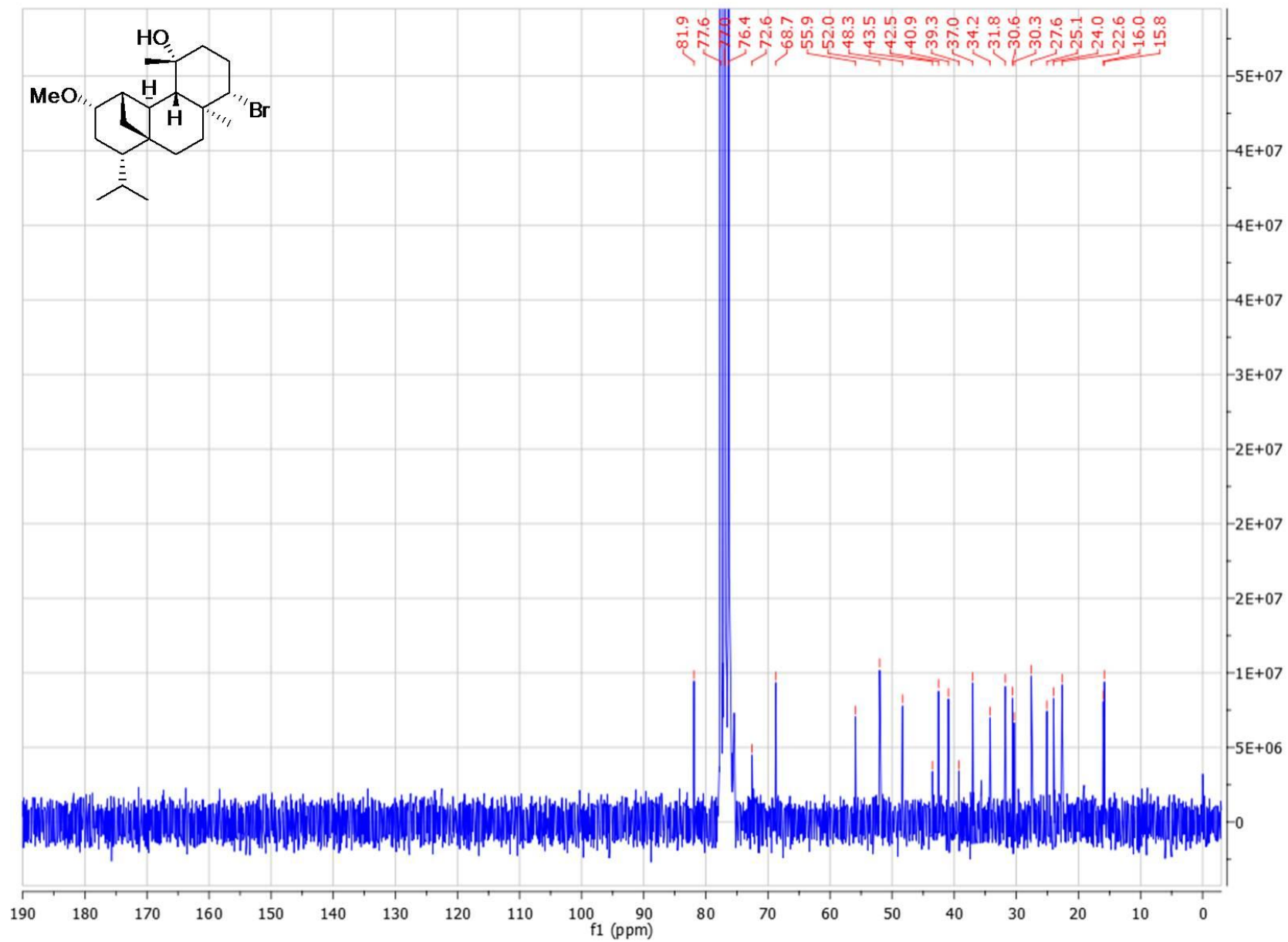


Figure S29. COSY spectrum (400 MHz, CDCl₃) of 1-methoxy-ioniol I (4).

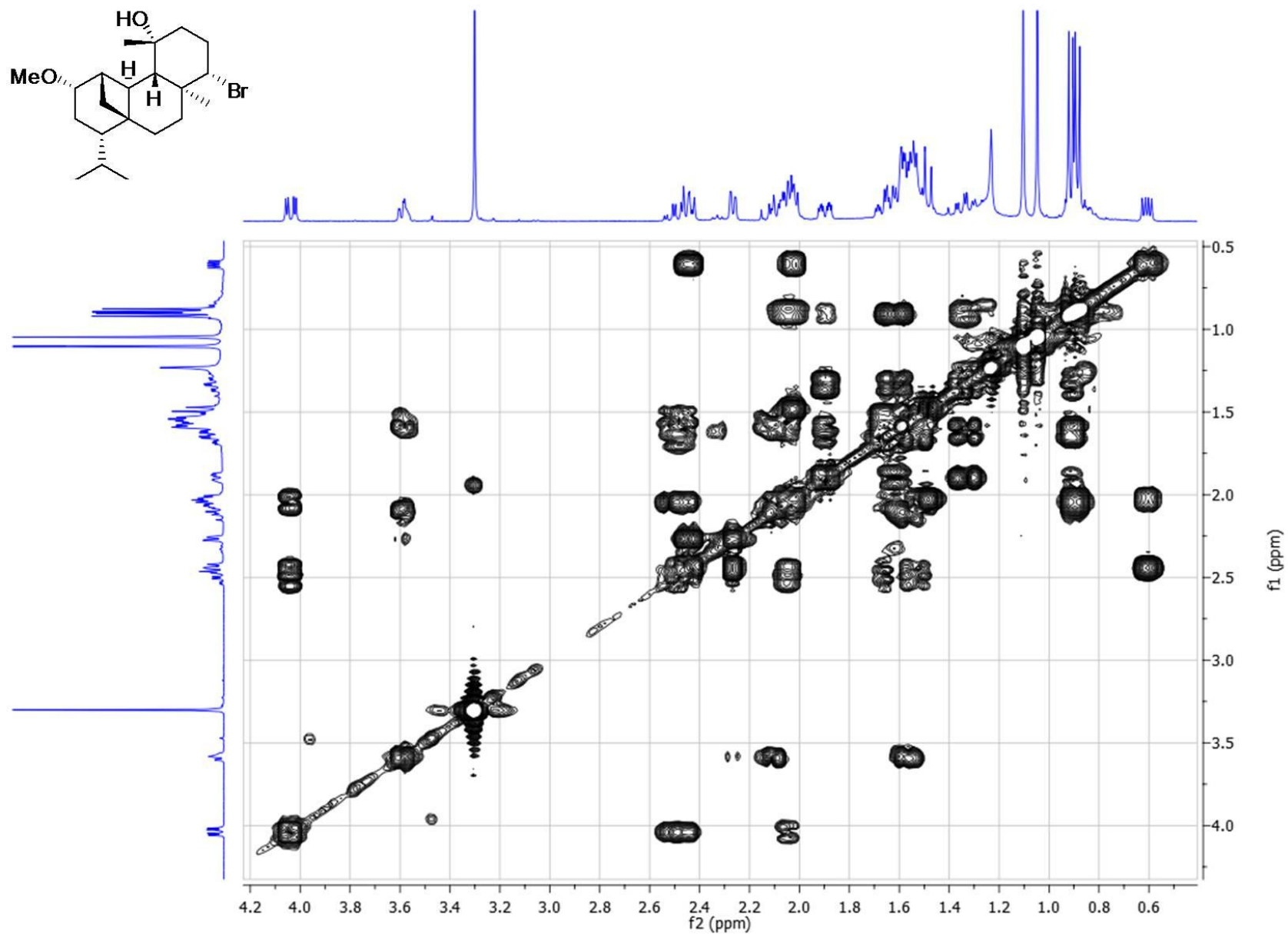


Figure S30. HSQC spectrum (400 MHz, CDCl₃) of 1-methoxy-ioniol I (4).

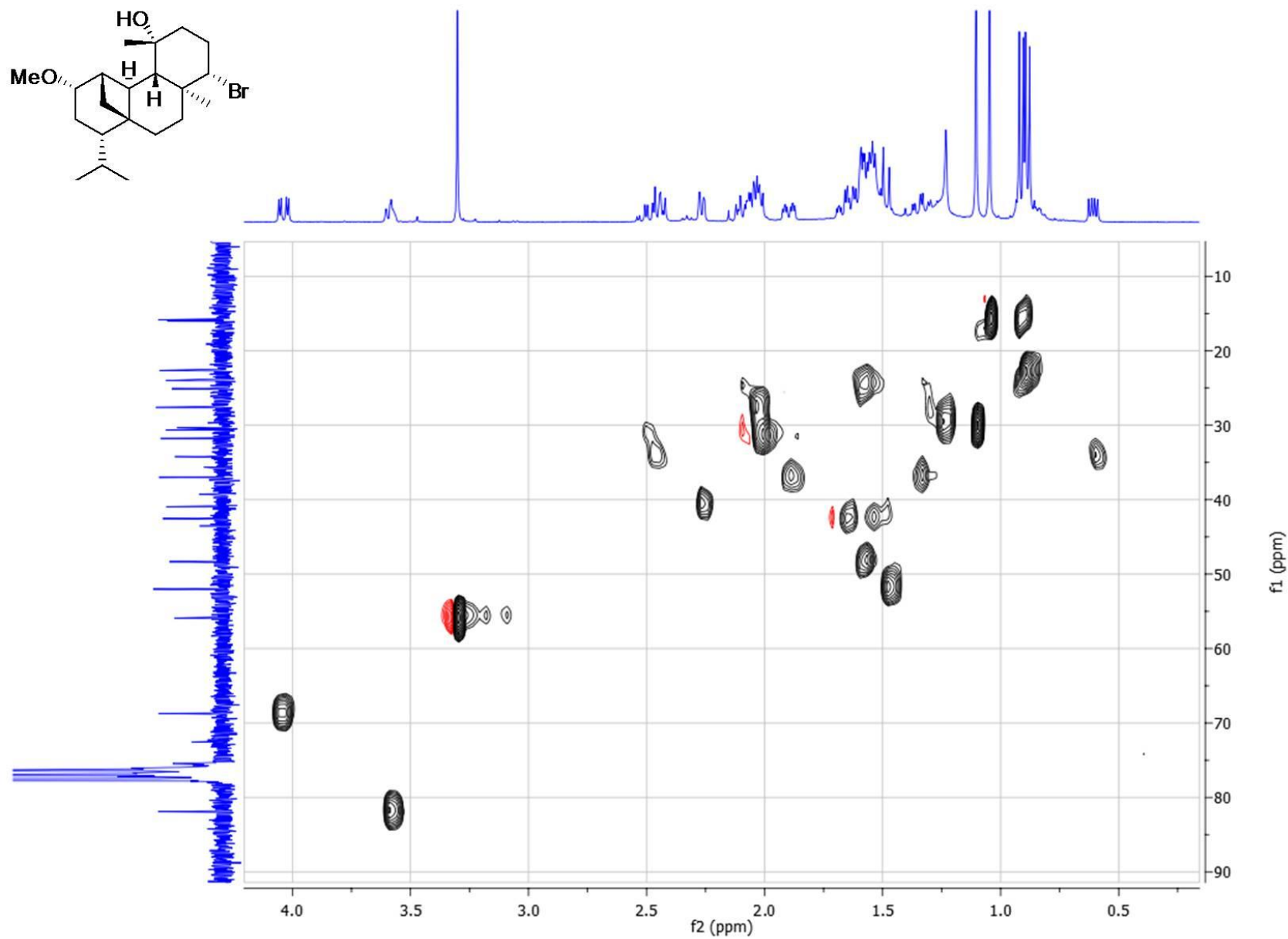
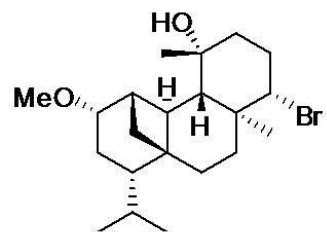


Figure S31. HMBC spectrum (400 MHz, CDCl₃) of 1-methoxy-ioniol I (4).

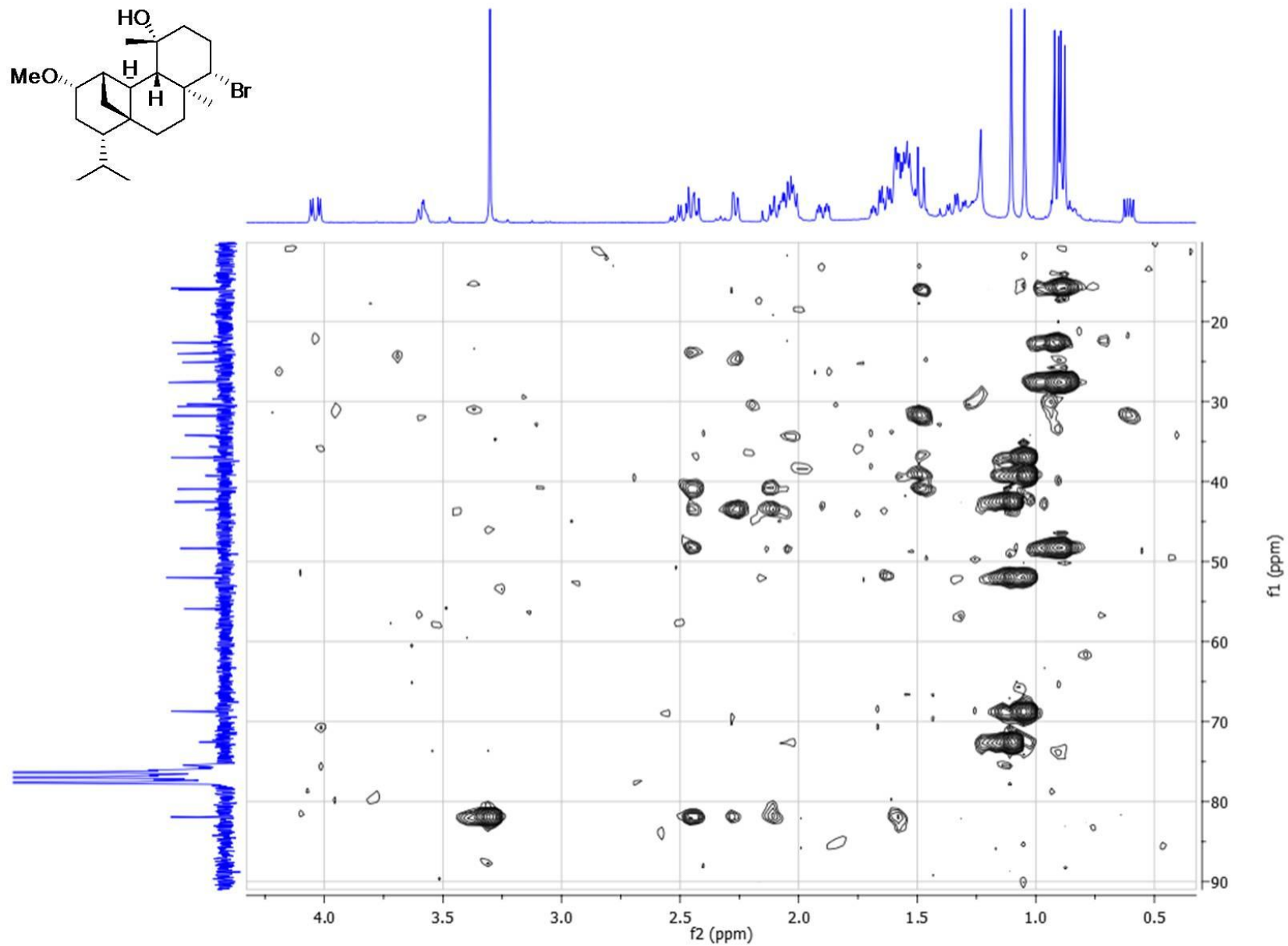


Figure S32. NOESY spectrum (400 MHz, CDCl_3) of 1-methoxy-ioniol I (4).

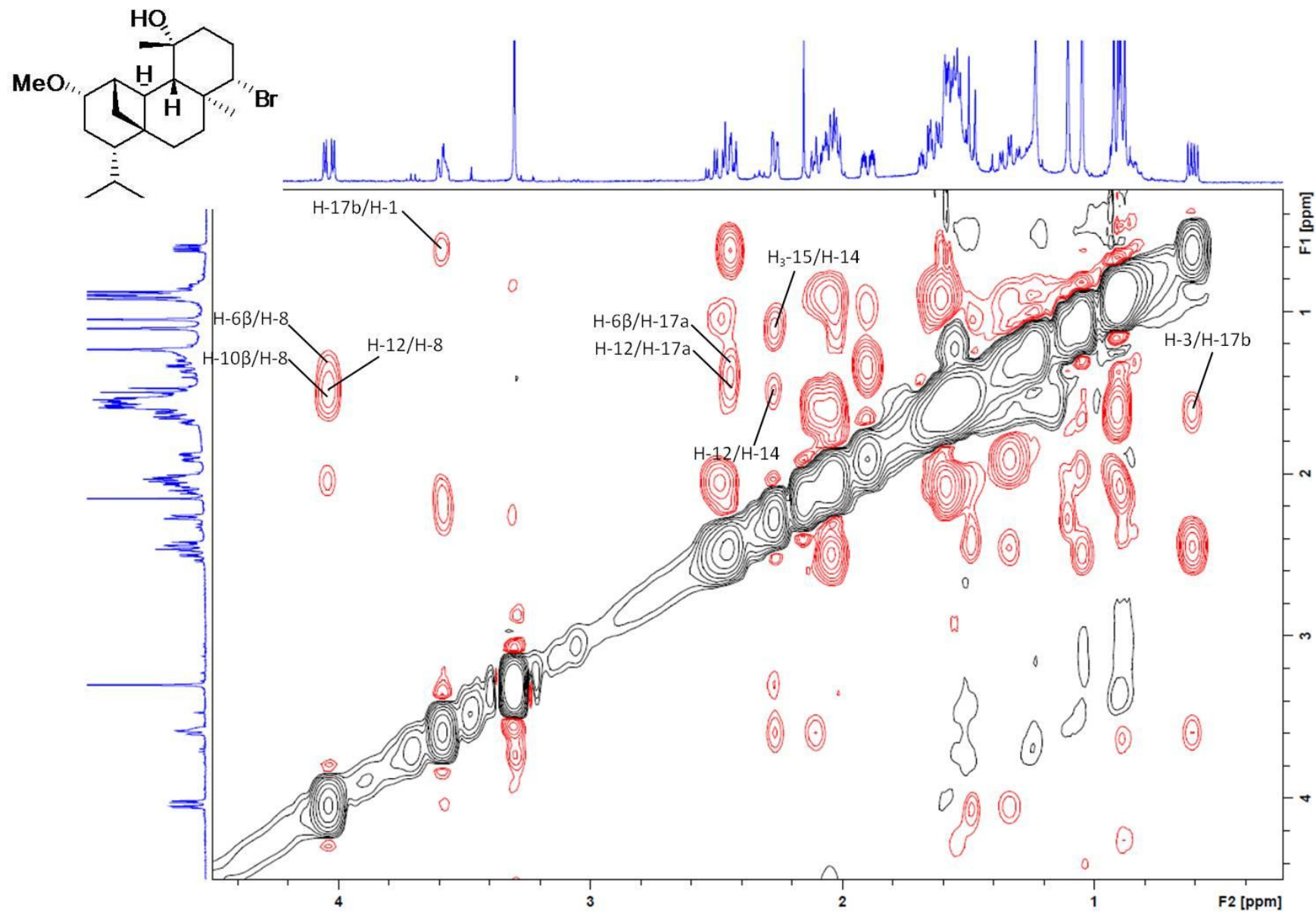


Figure S33. HRMS (ESI+) measurement of 1-methoxy-ioniol I (4).

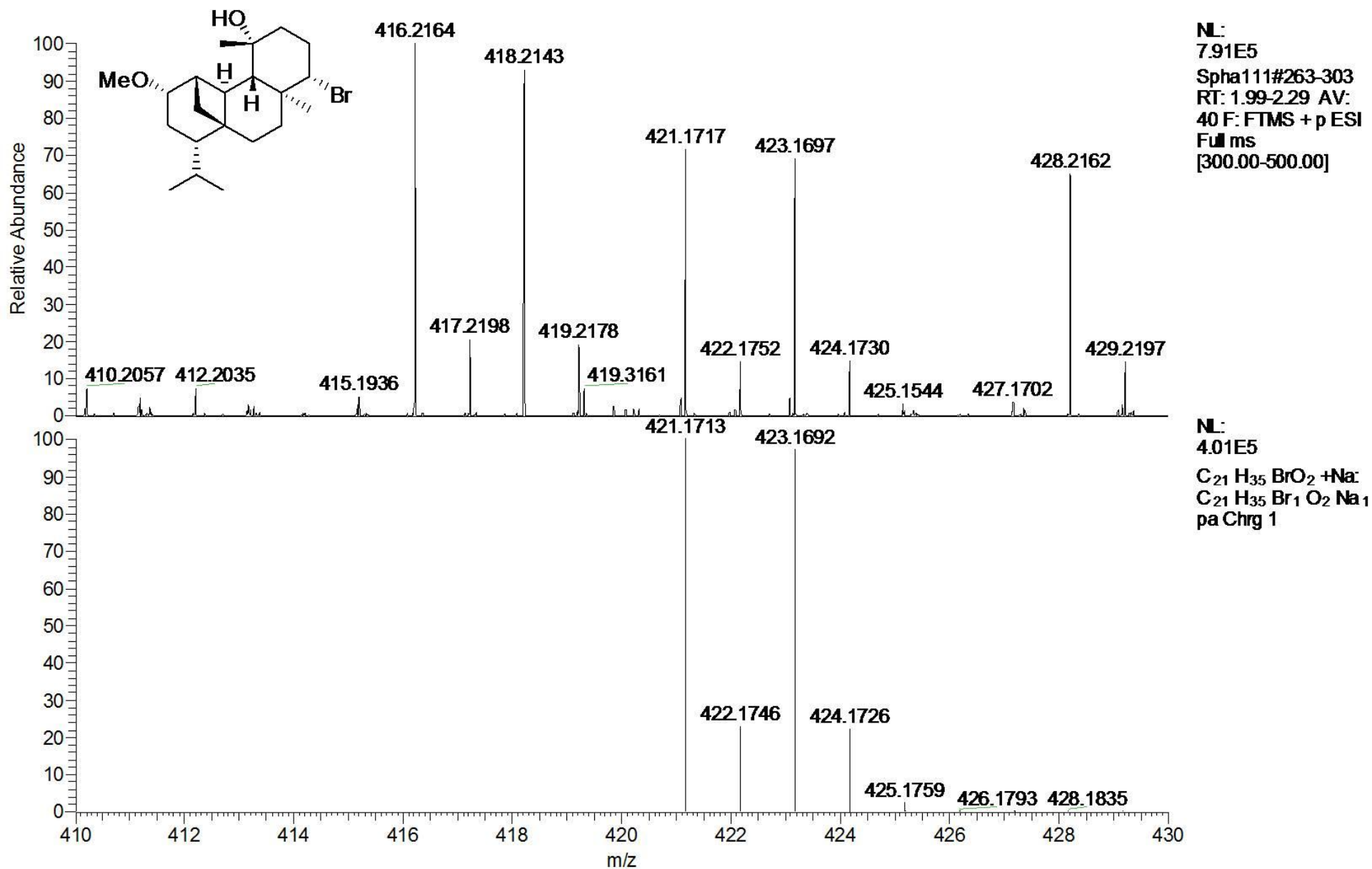


Figure S34. IR spectrum of 1-methoxy-ioniol I (**4**).

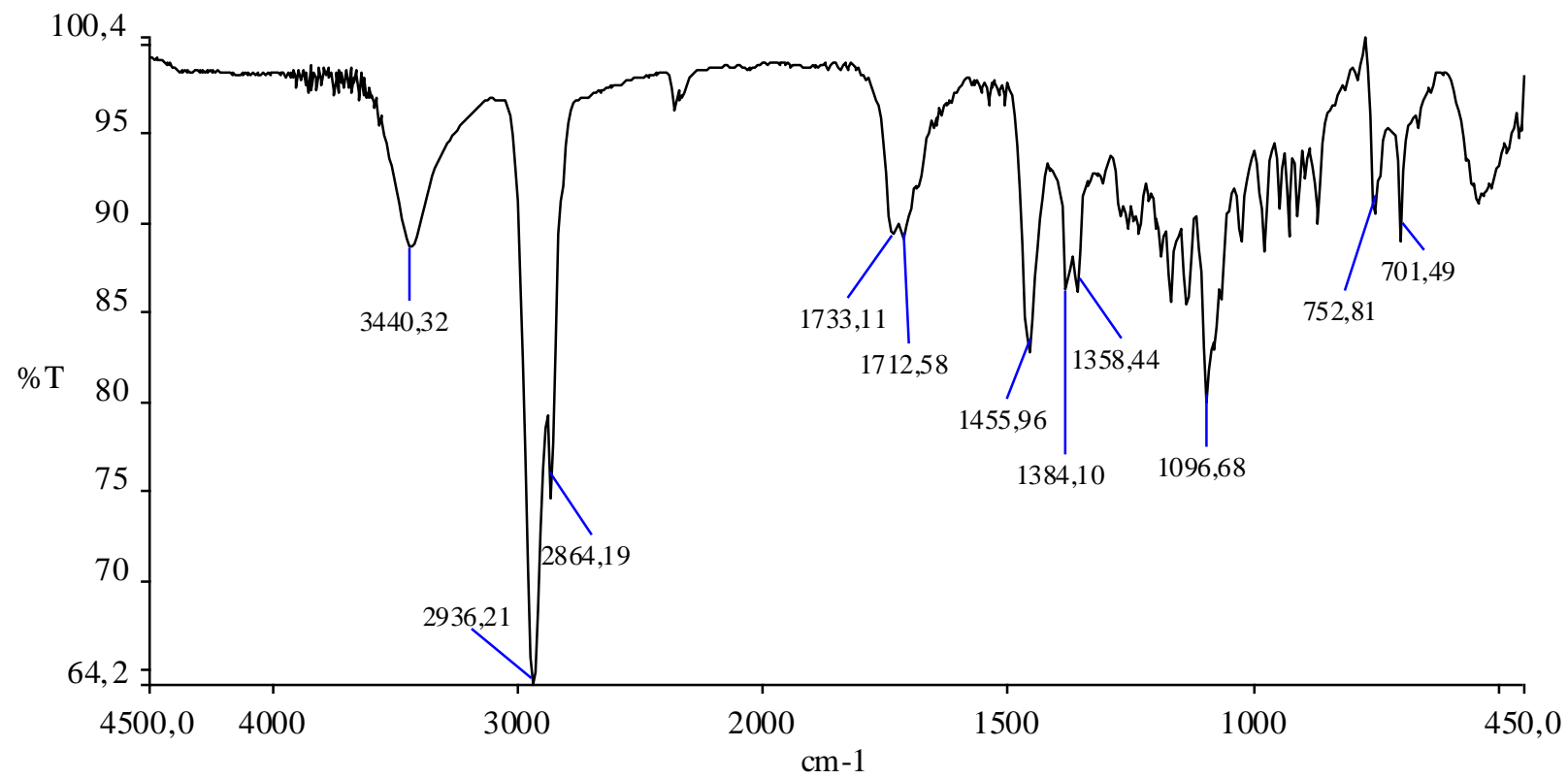


Figure S35. ^1H NMR spectrum (400 MHz, CDCl_3) of corotrienone (5).

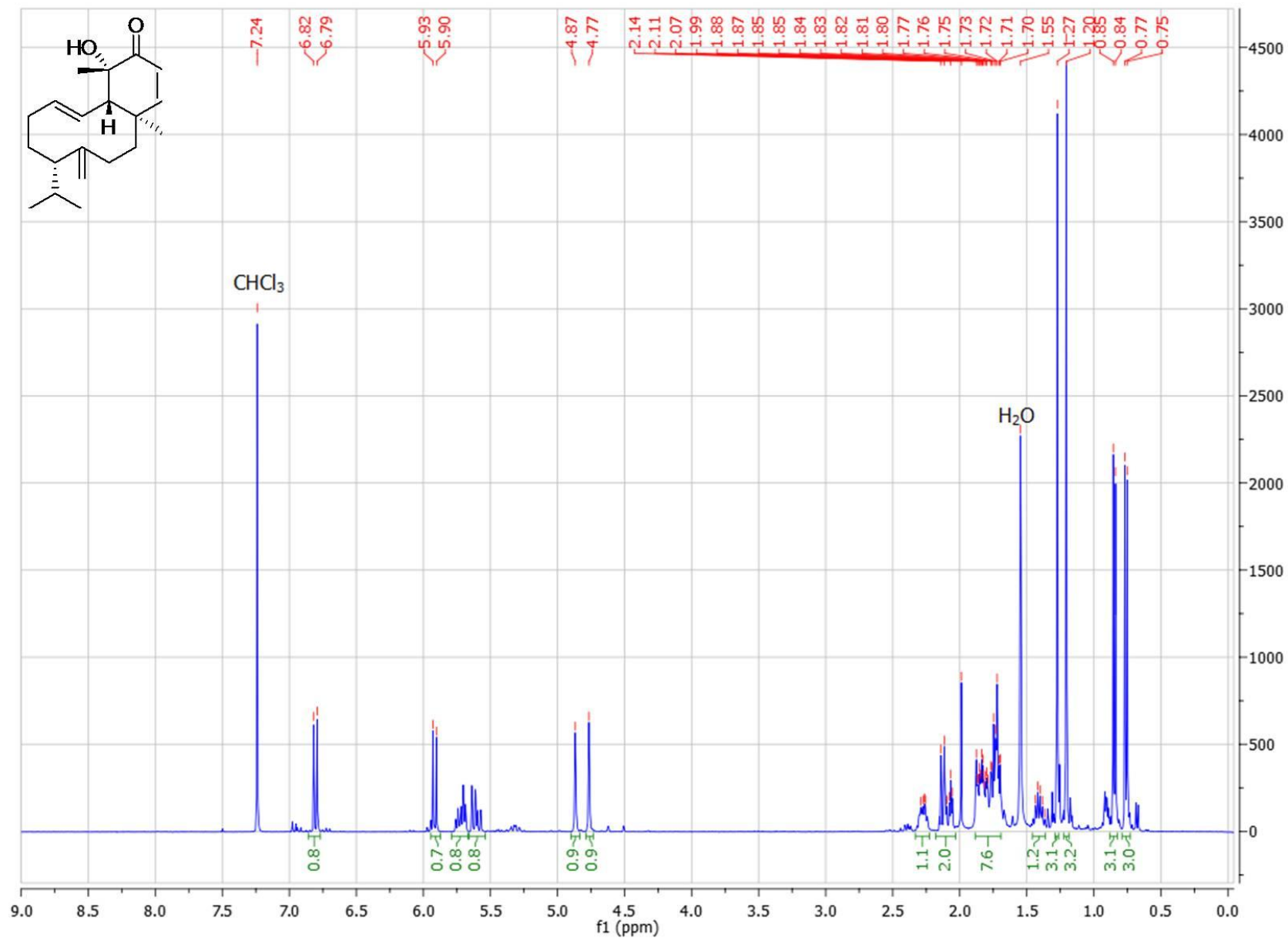


Figure S36. ^{13}C NMR spectrum (50 MHz, CDCl_3) of corotrienone (5).

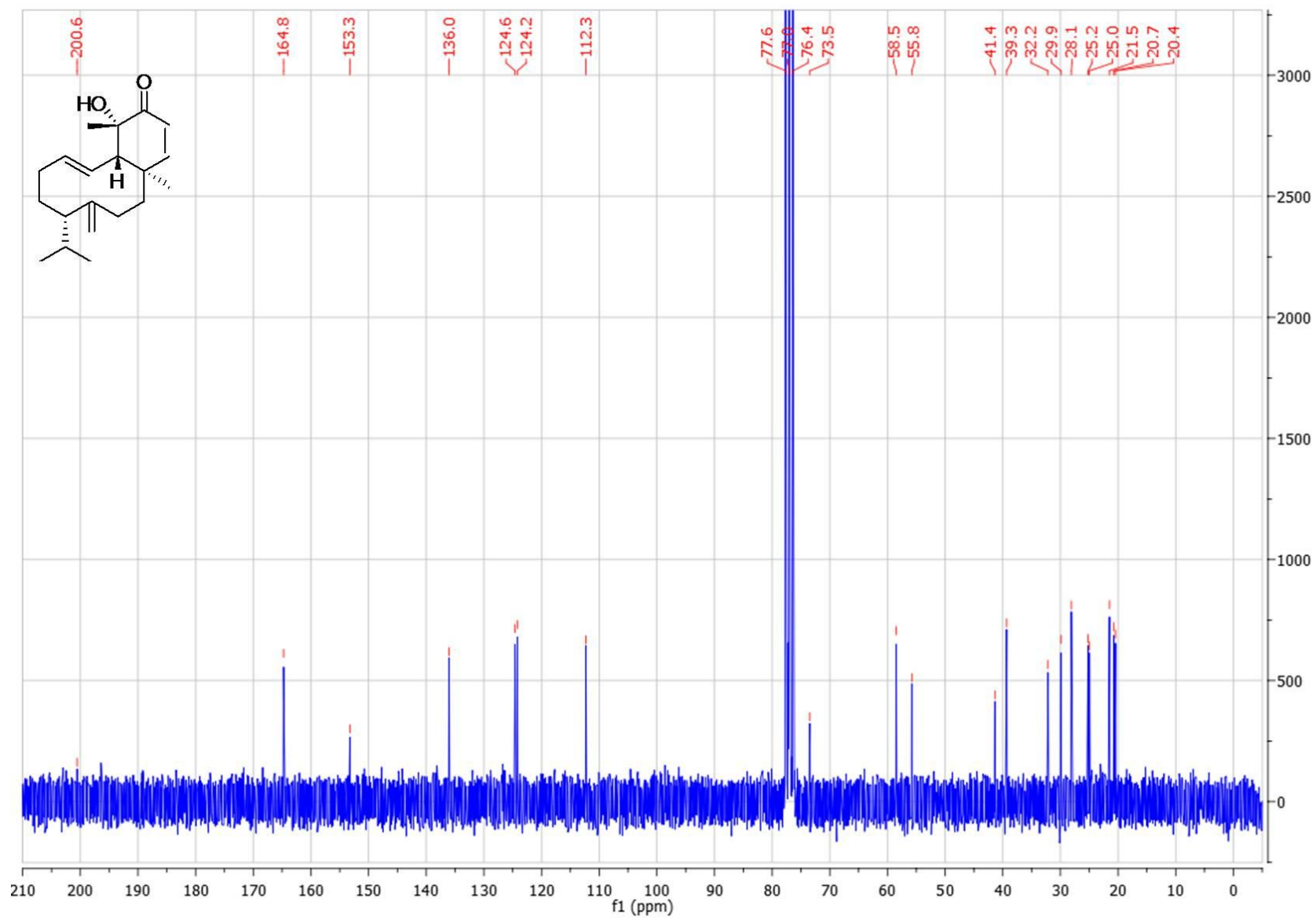


Figure S37. COSY spectrum (400 MHz, CDCl₃) of corotrienone (5).

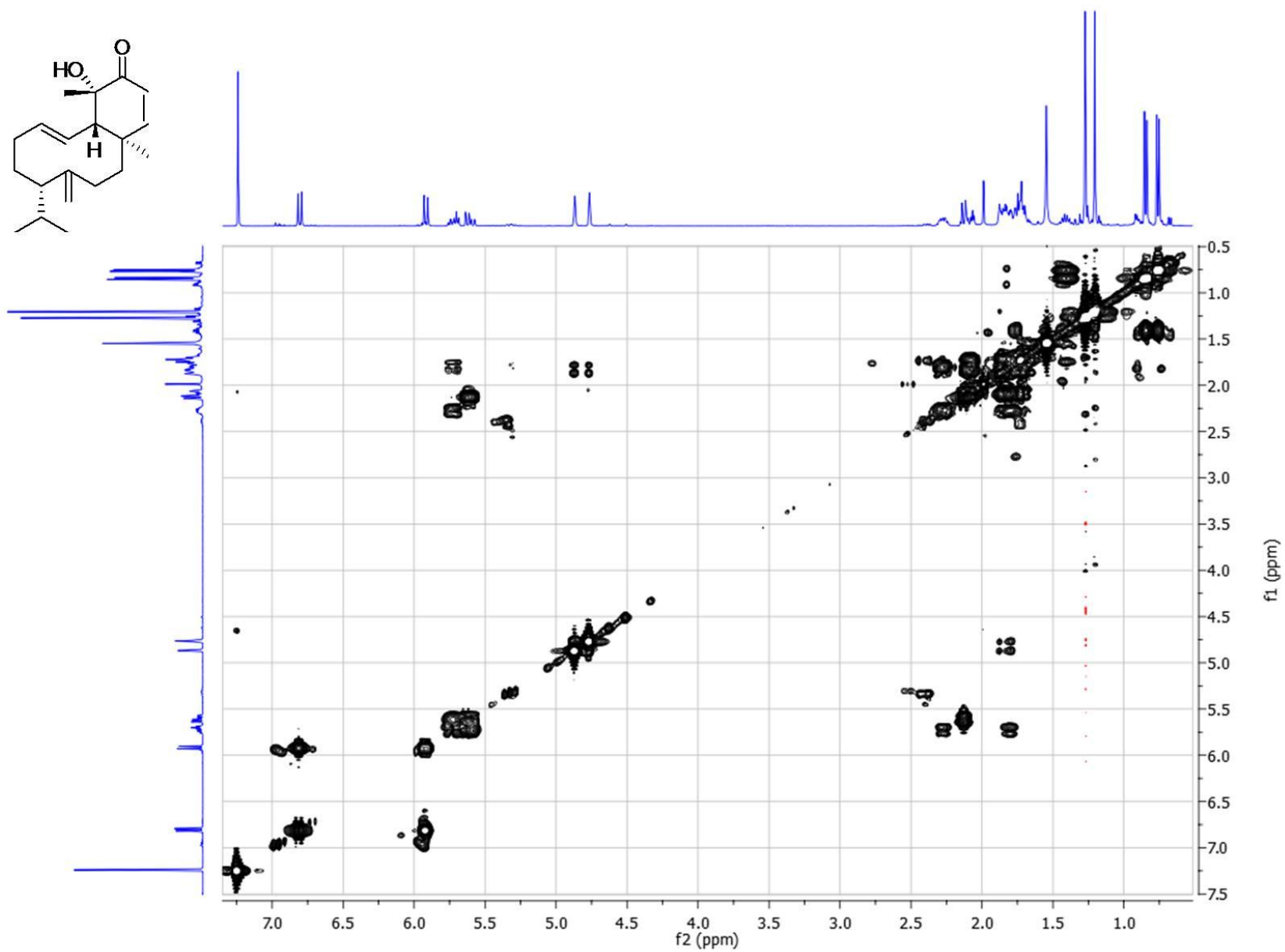


Figure S38. HSQC-DEPT spectrum (400 MHz, CDCl₃) of corotrienone (5).

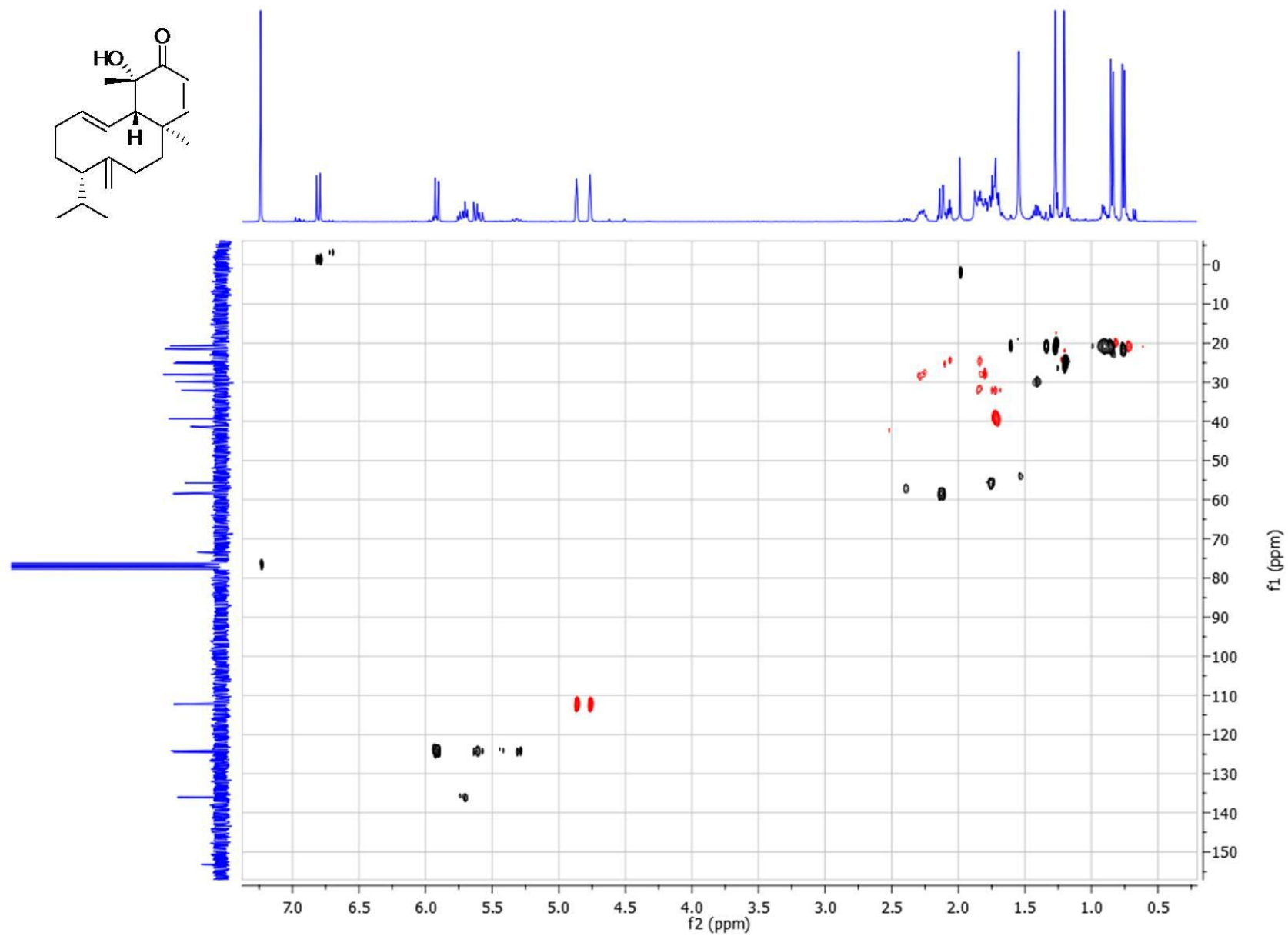


Figure S39. HMBC spectrum (400 MHz, CDCl₃) of corotrienone (5).

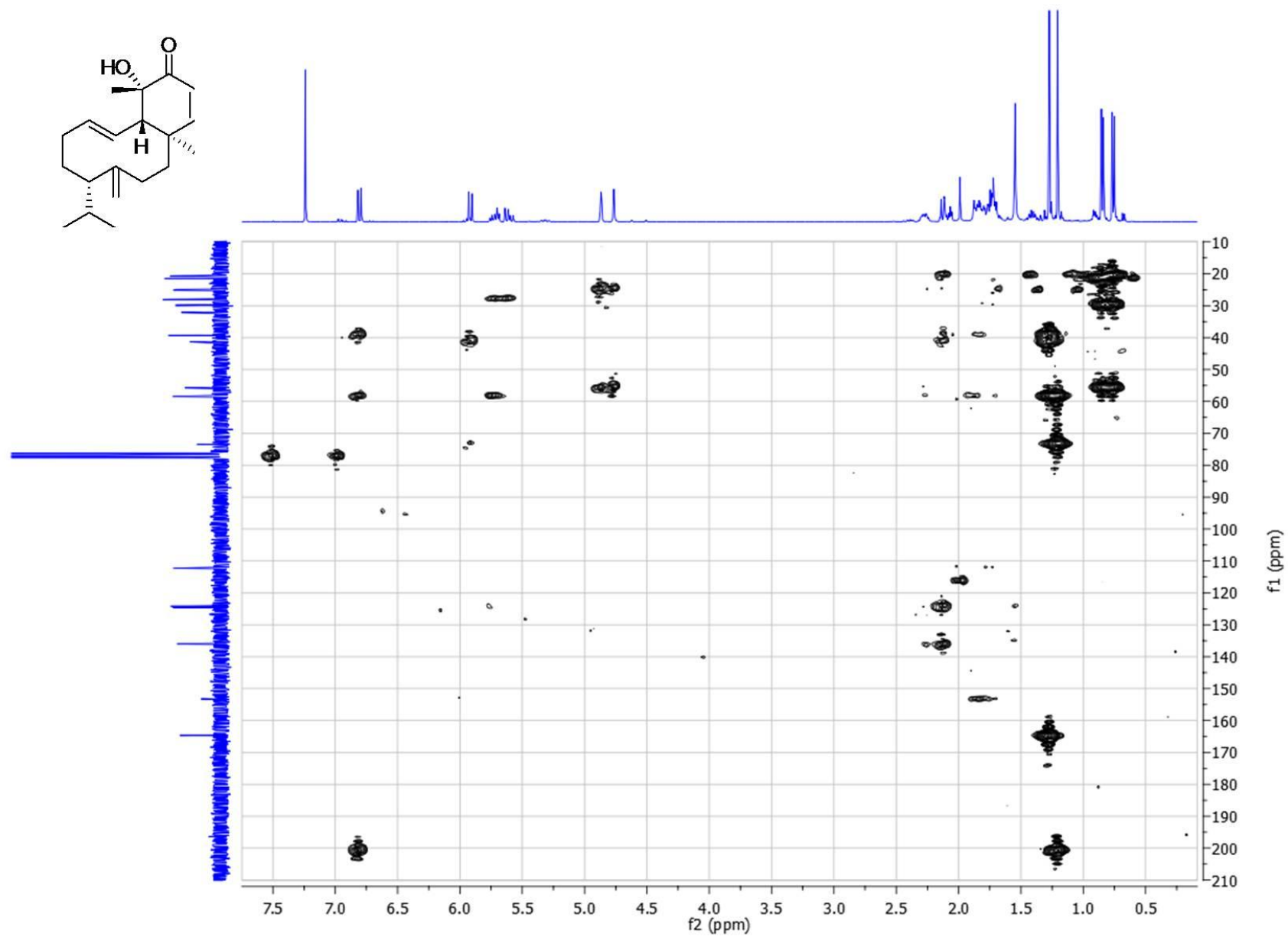


Figure S40. NOESY spectrum (400 MHz, CDCl_3) of corotrienone (**5**).

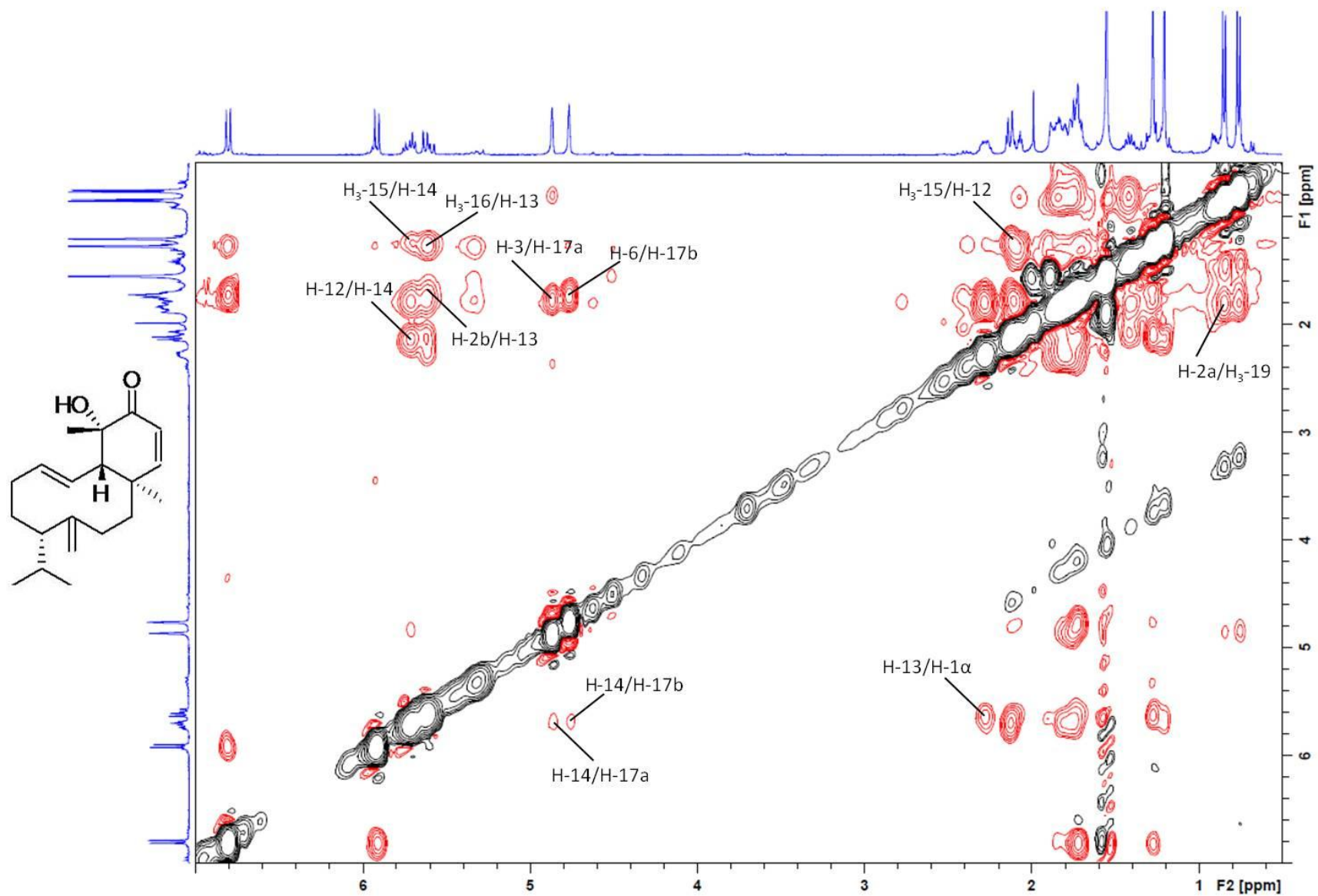
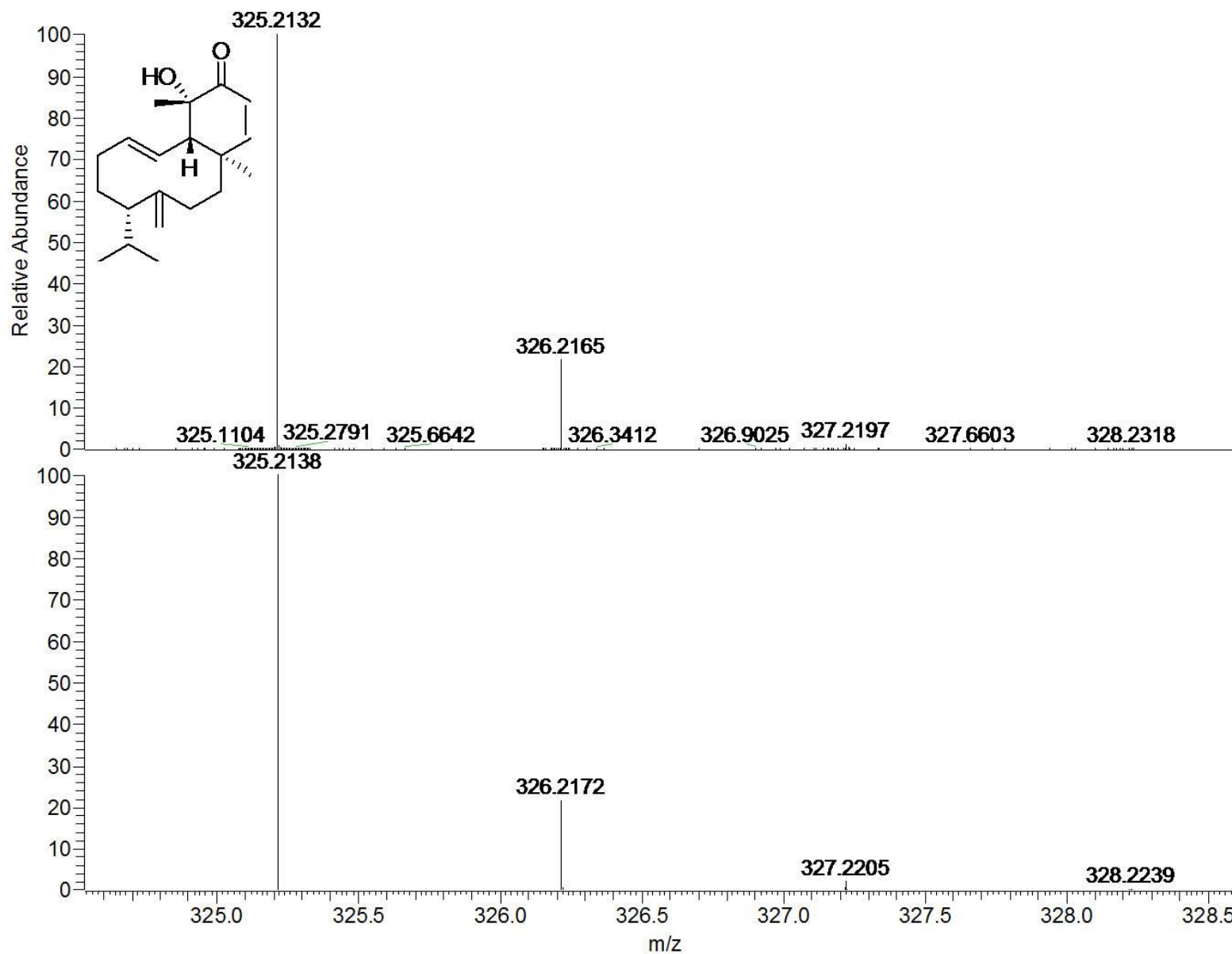


Figure S41. HRMS (ESI+) measurement of corotrienone (5).



NL:
3.50E7
SPHA_010_081210#4
39.477 RT: 6.30-6.82
AV: 39 T: FTMS + c
ESI Full ms
[170.00-1000.00]

NL:
8.00E5
C₂₀H₃₀O₂+Na:
C₂₀H₃₀O₂Na₁
pa Chrg 1

Figure S42. IR spectrum of corotrienone (**5**).

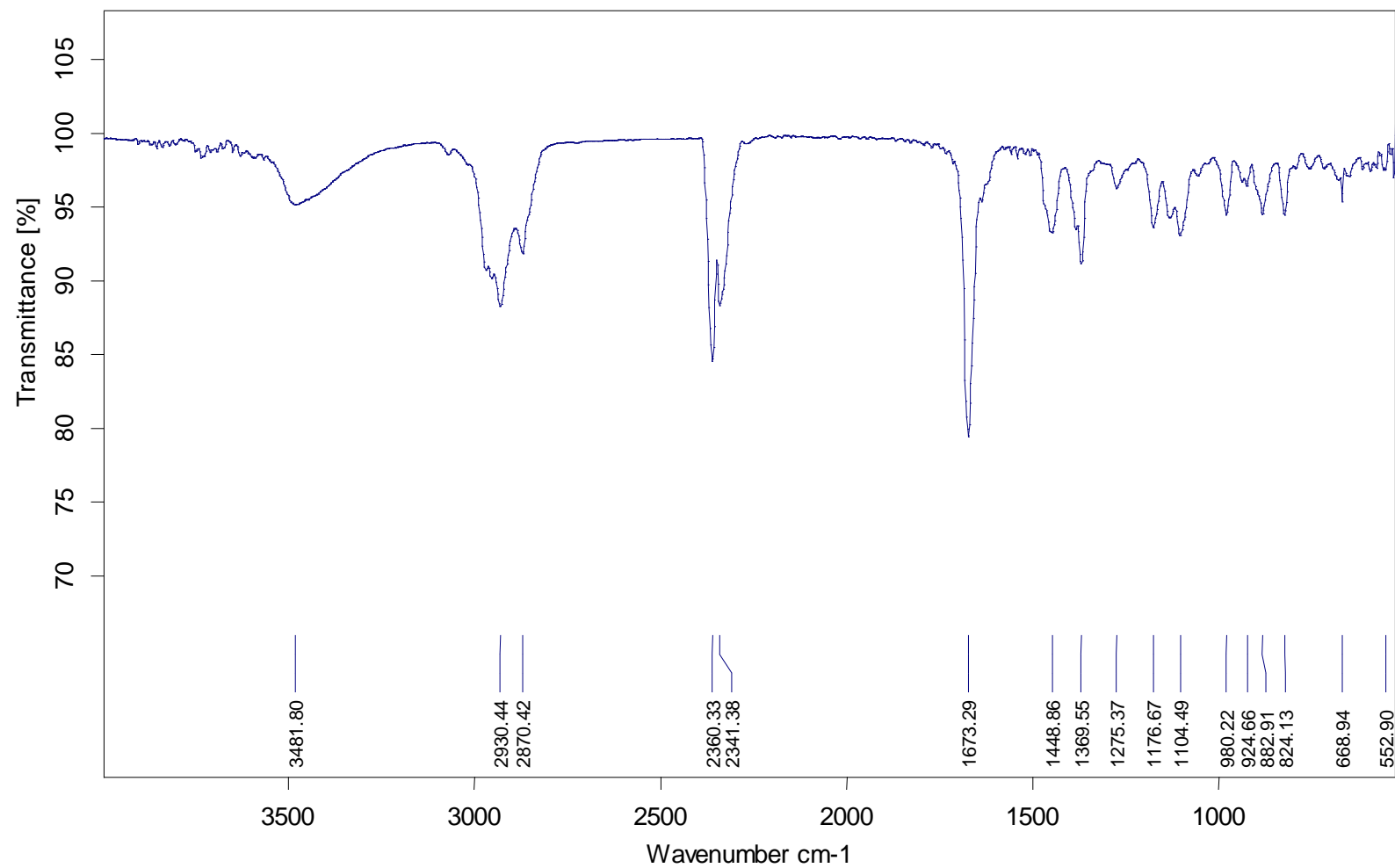


Figure S42. ^1H NMR spectrum (400 MHz, CDCl_3) of iso-bromocorodienol (**6**).

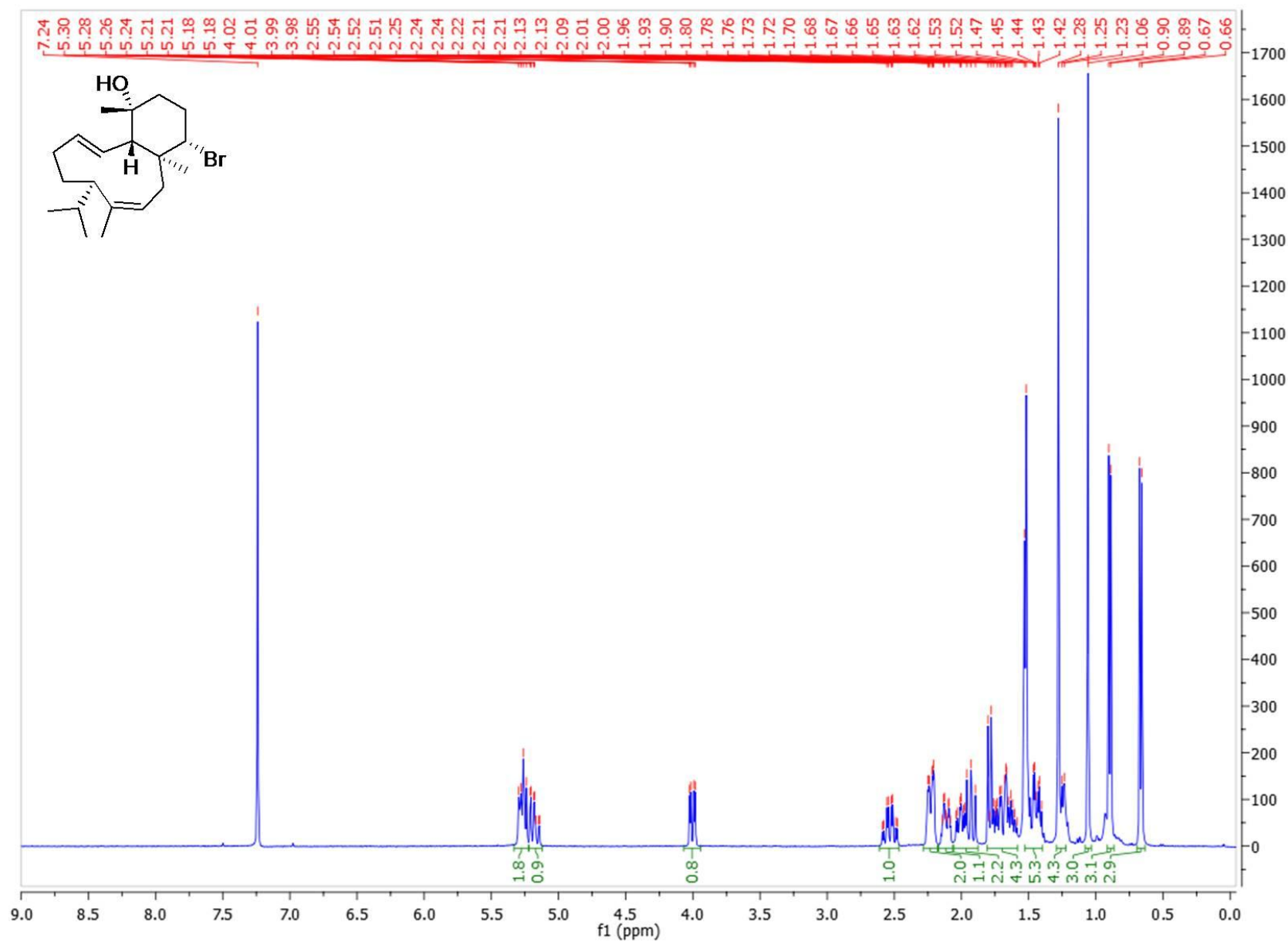


Figure S43. ^{13}C NMR spectrum (50 MHz, CDCl_3) of iso-bromocorodienol (**6**).

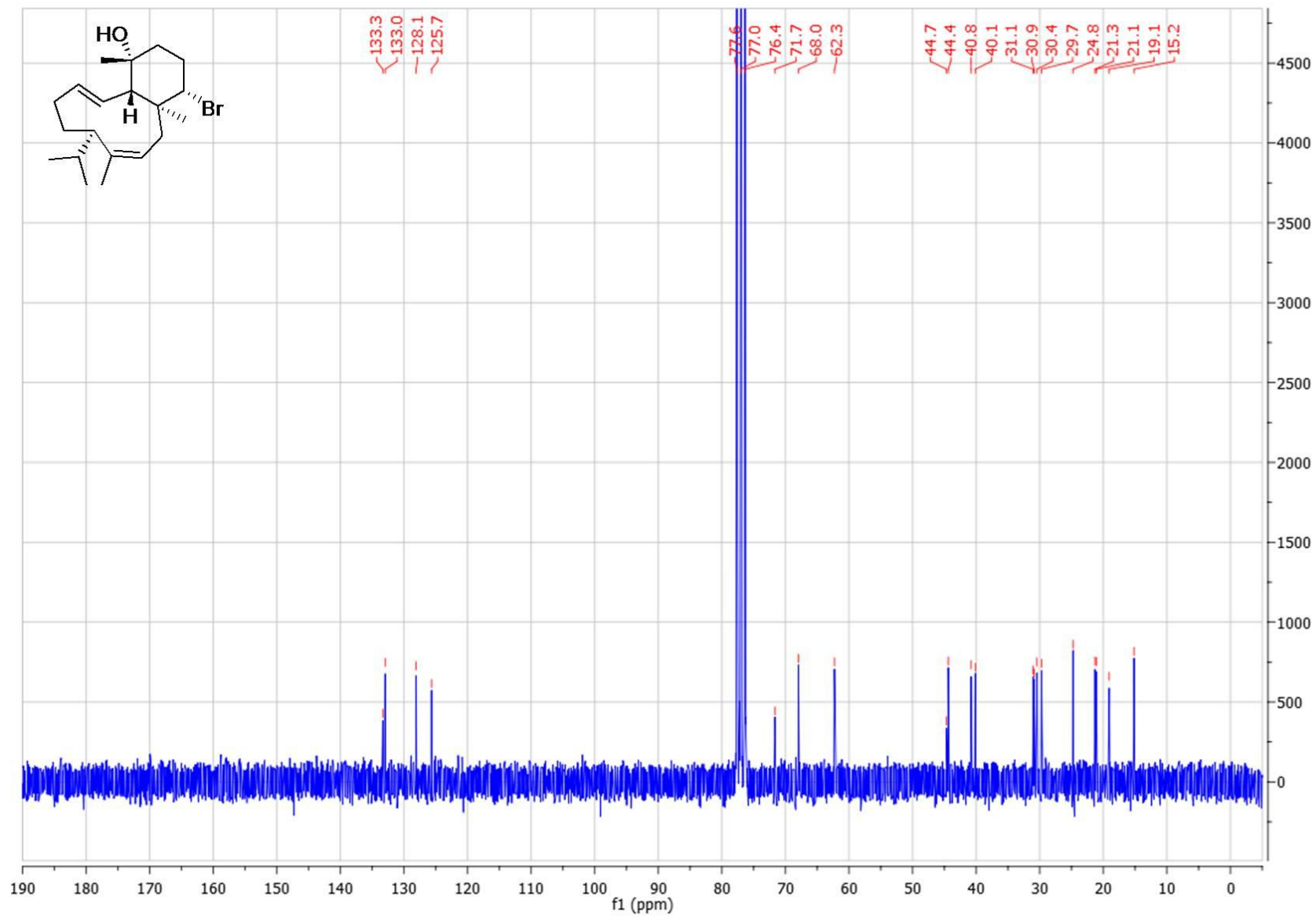


Figure S44. COSY spectrum (400 MHz, CDCl₃) of iso-bromocorodienol (**6**).

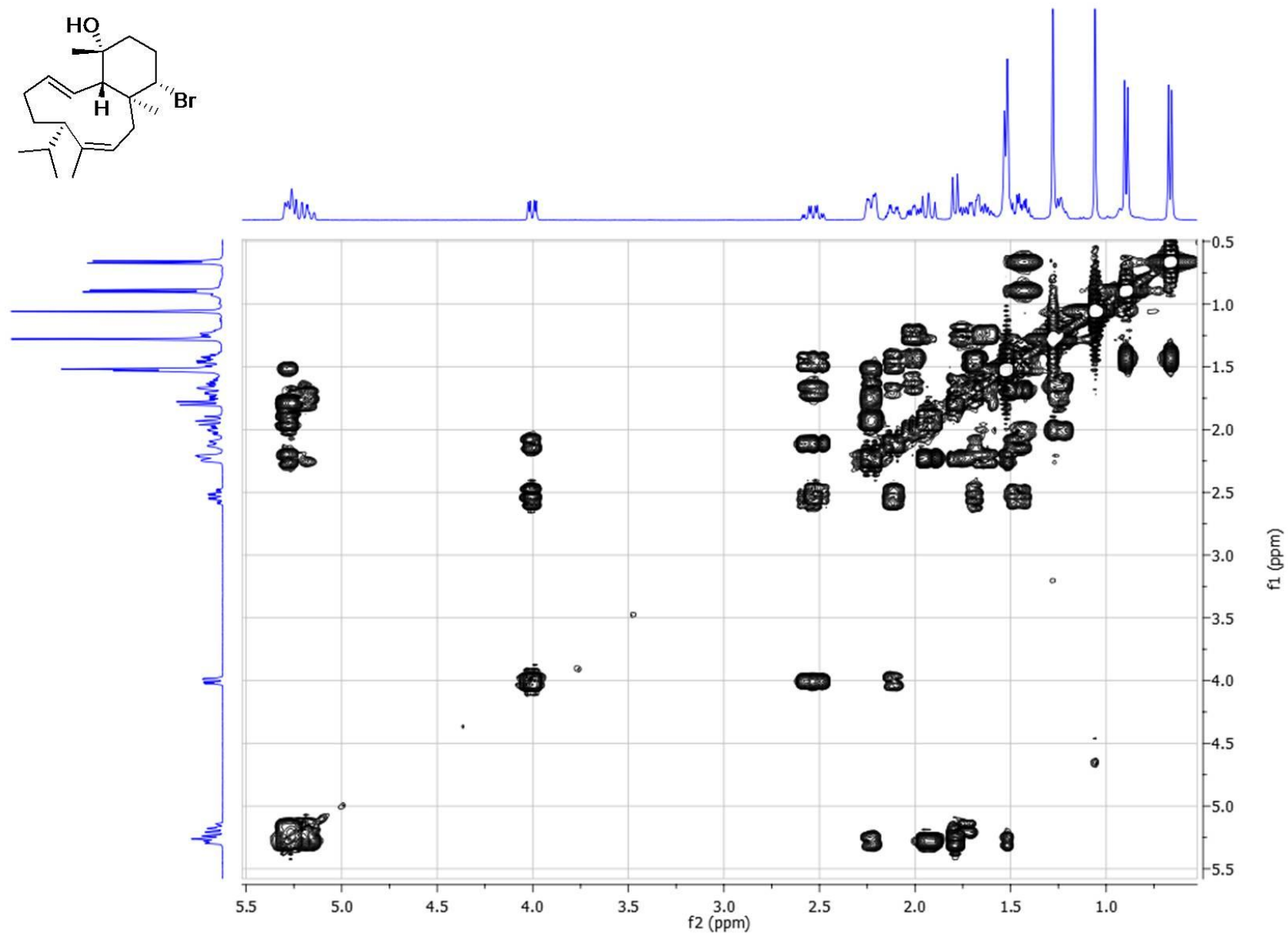


Figure S45. HSQC-DEPT spectrum (400 MHz, CDCl₃) of iso-bromocorodienol (**6**).

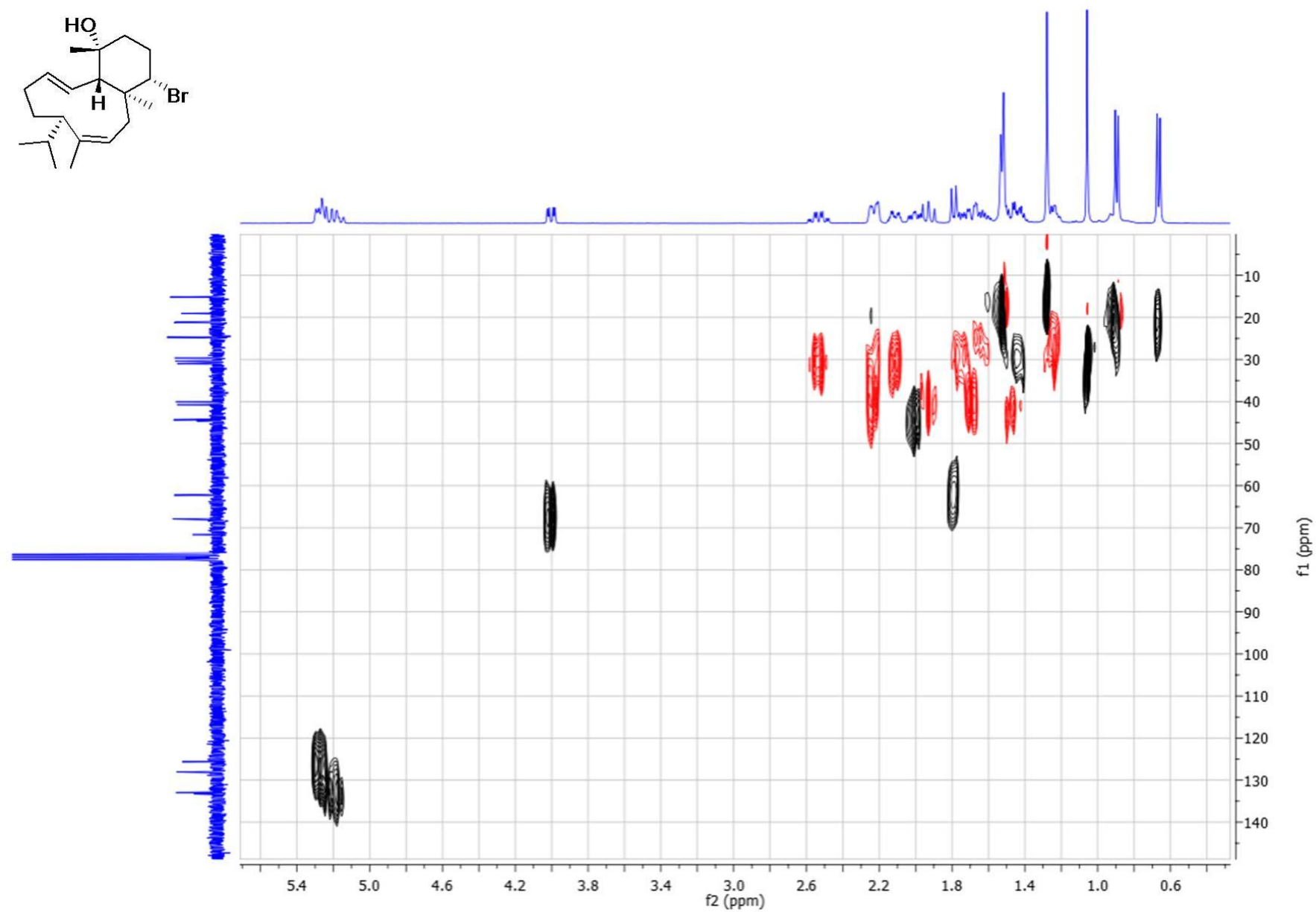
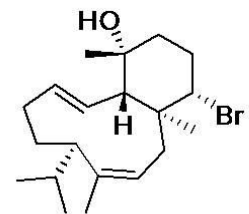


Figure S46. HMBC spectrum (400 MHz, CDCl₃) of iso-bromocorodienol (**6**).

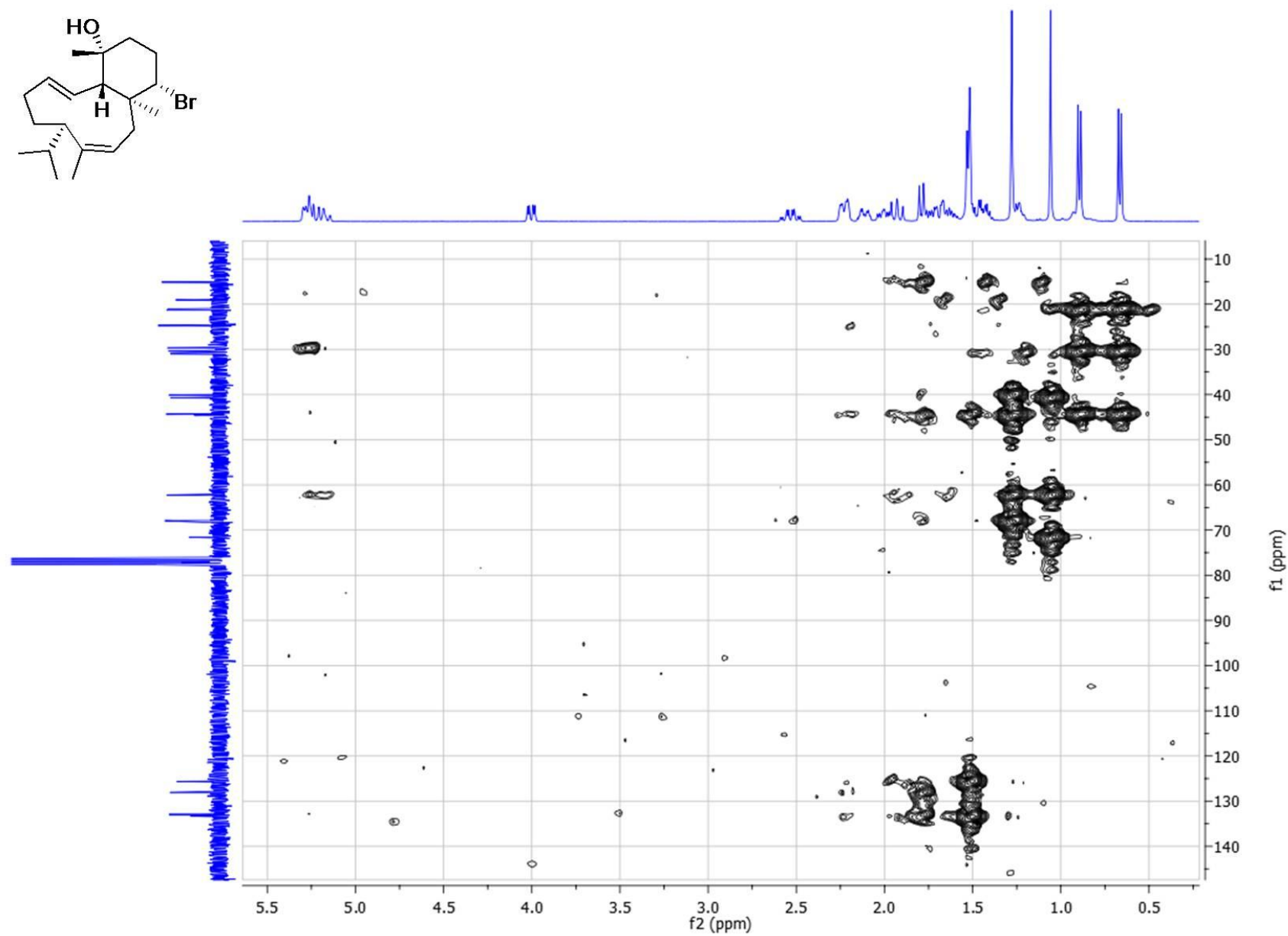
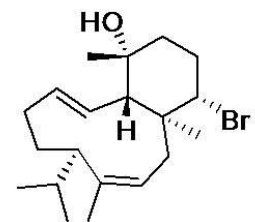


Figure S47. NOESY spectrum (400 MHz, CDCl₃) of iso-bromocorodienol (6).

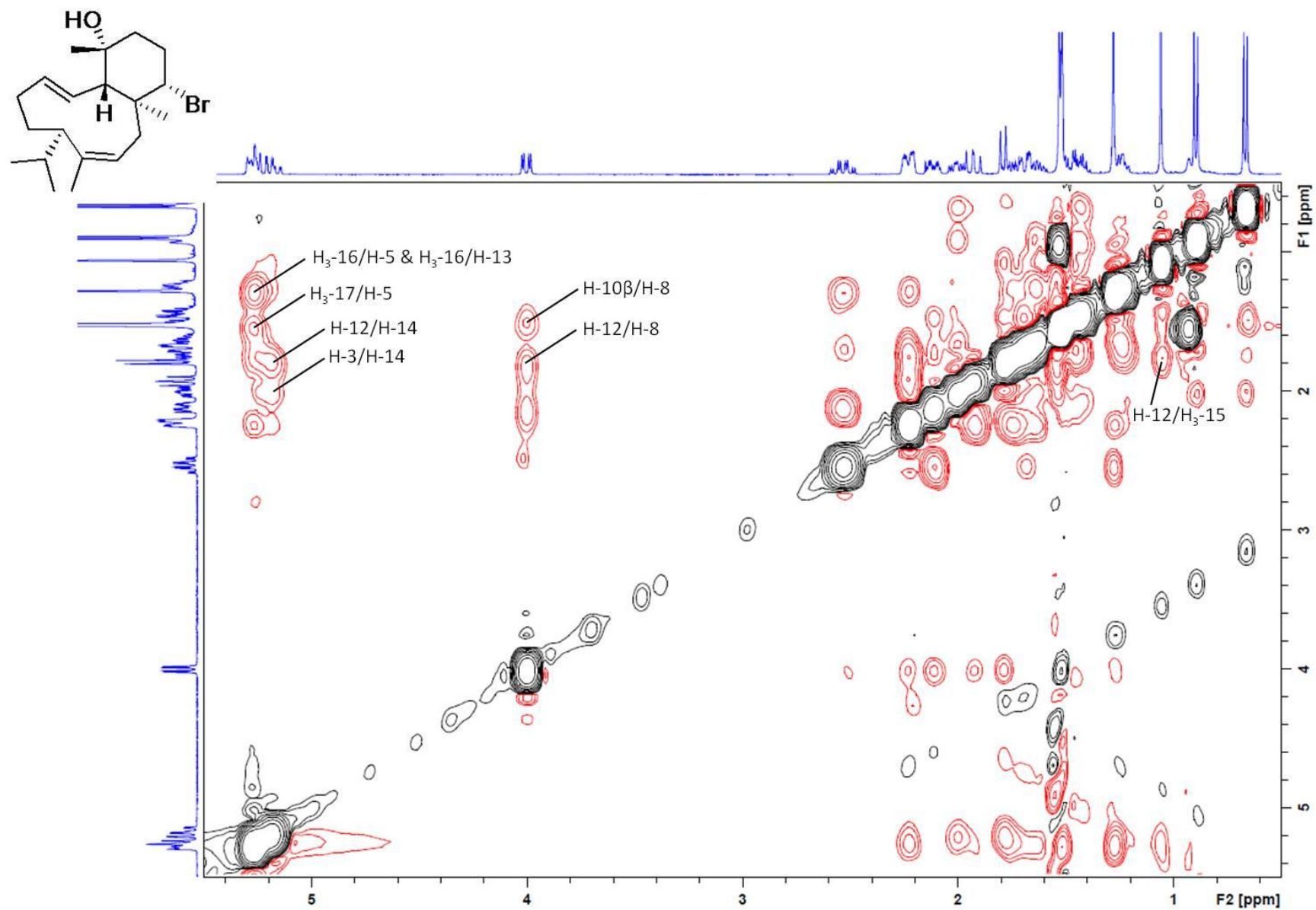


Figure S48. 1D NOE spectrum (400 MHz, CDCl₃), excitation of H-6 β of iso-bromocorodienol (**6**).

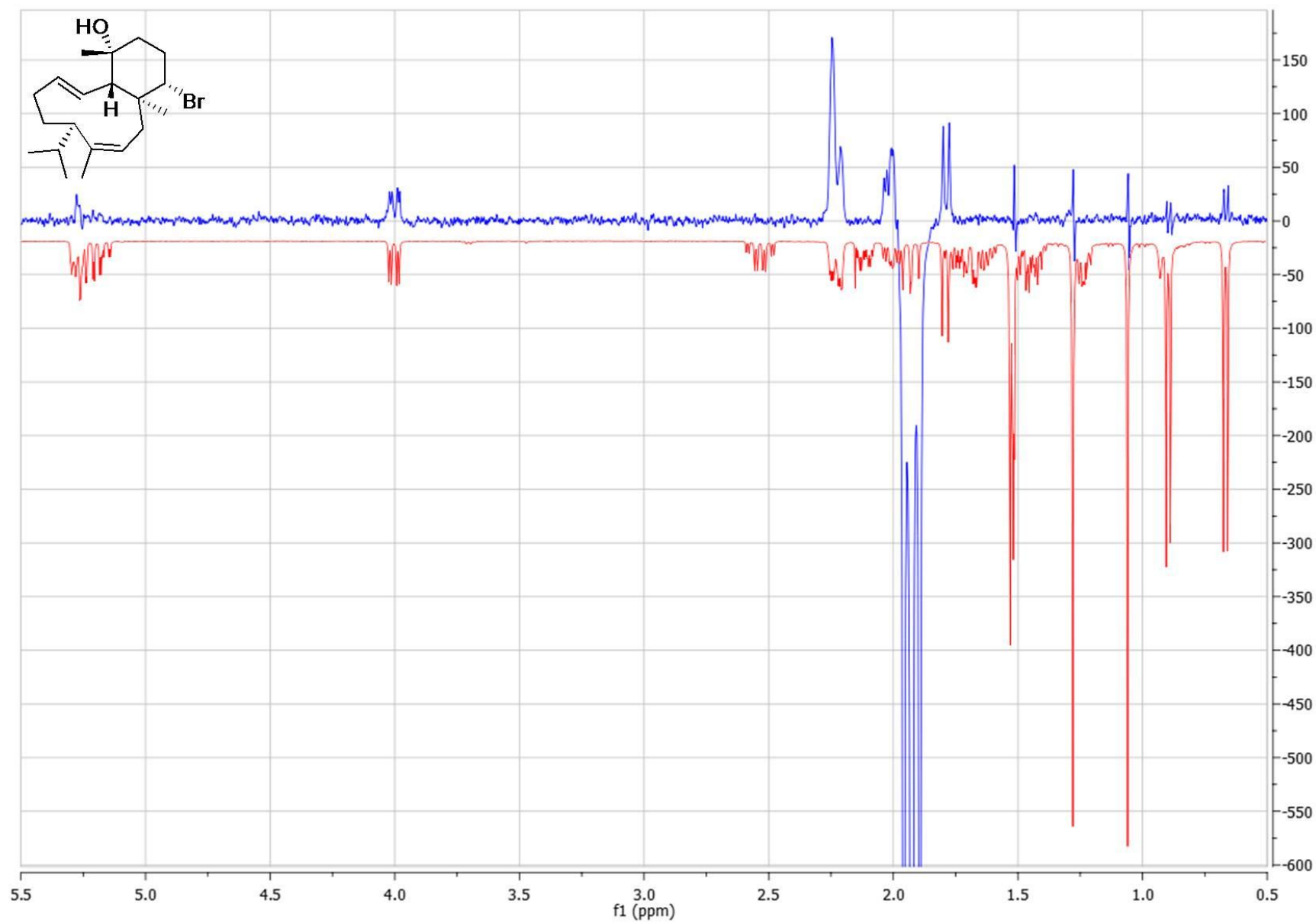


Figure S49. HRMS (ESI+) measurement of iso-bromocorodienol (**6**).

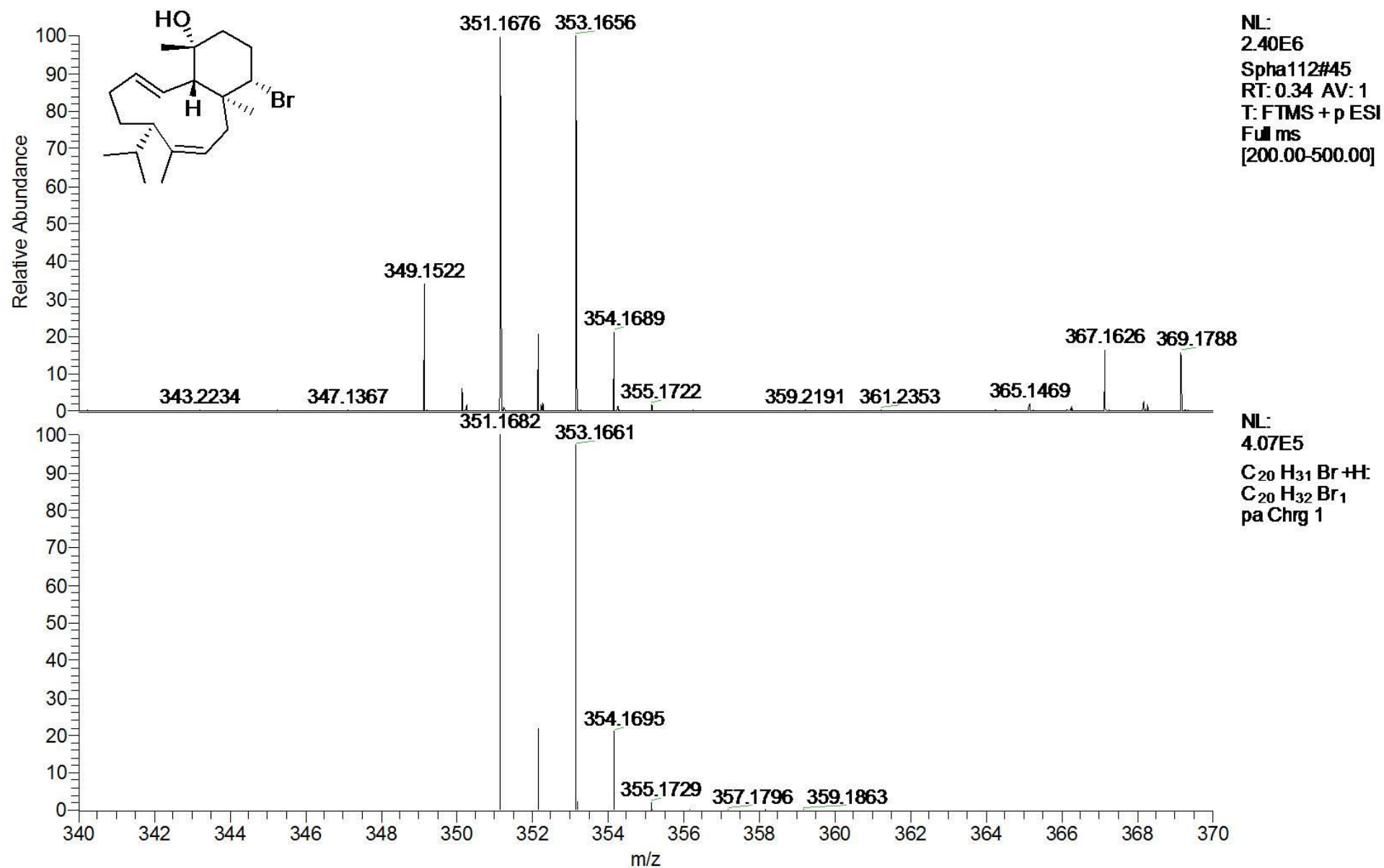


Figure S50. IR spectrum of iso-bromocorodienol (**6**).

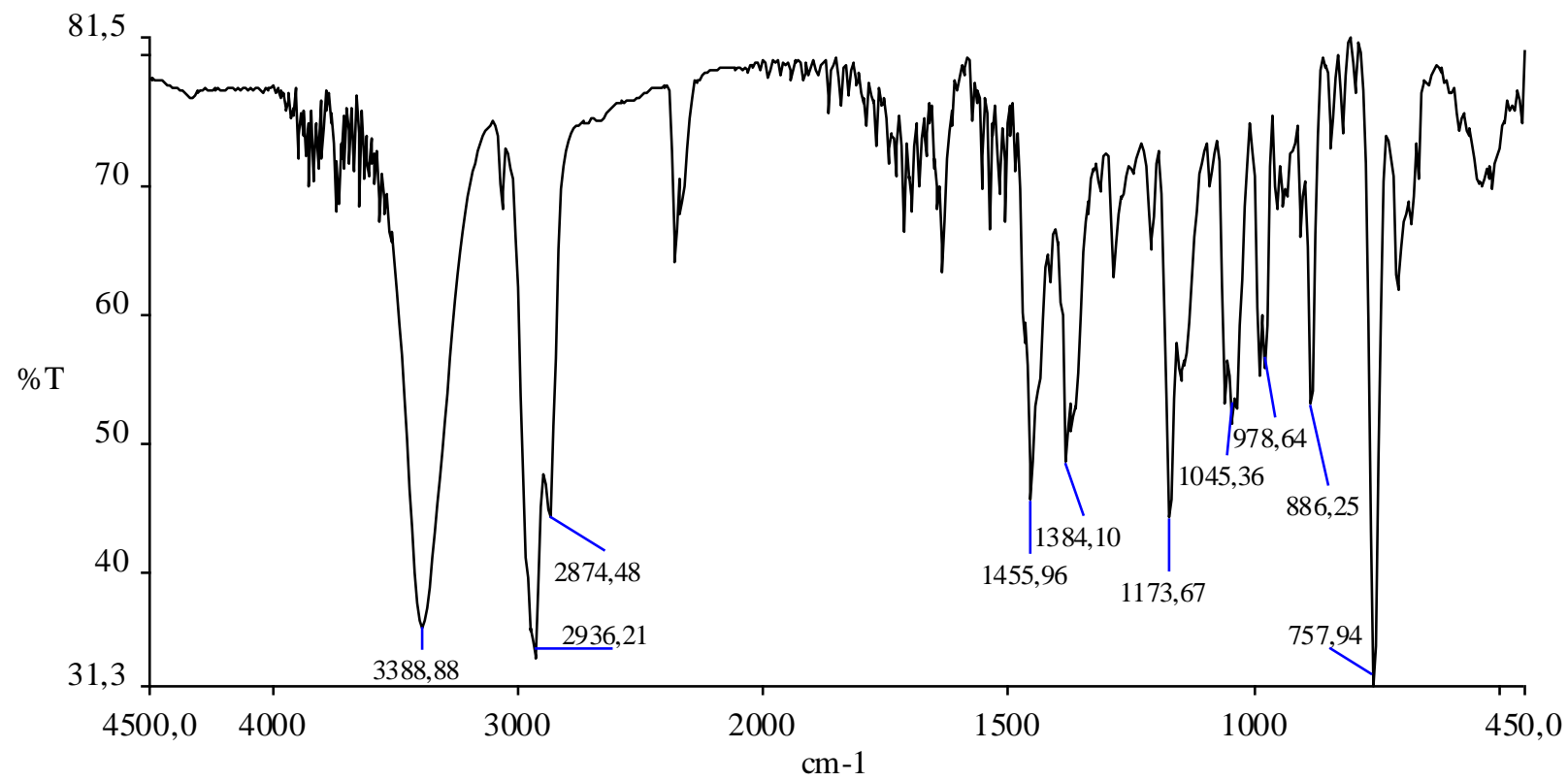


Figure S51. ^1H NMR spectrum (400 MHz, CDCl_3) of debromosphaerol (**7**).

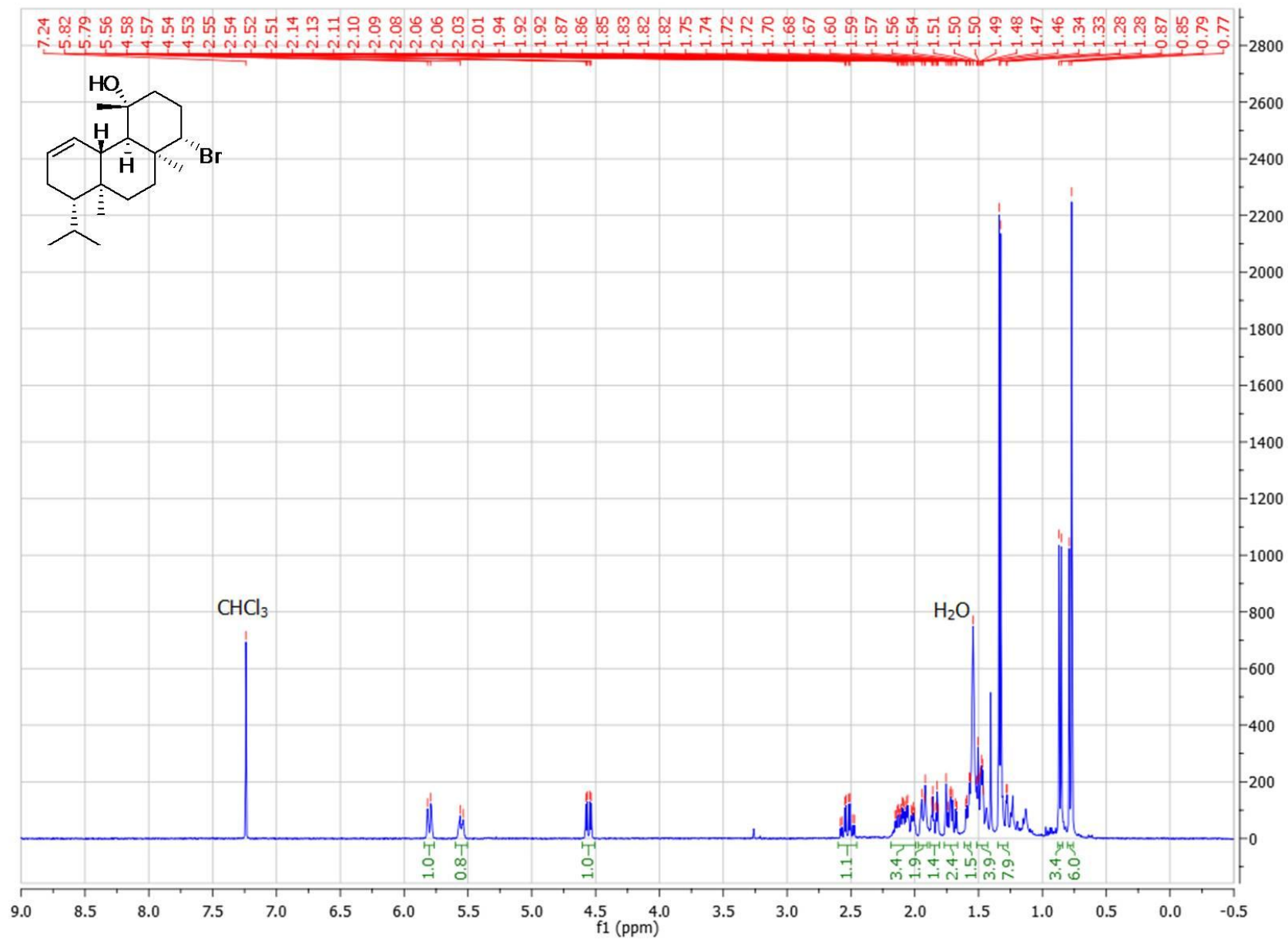


Figure S52. ^{13}C NMR spectrum (50 MHz, CDCl_3) of debromosphaerol (7).

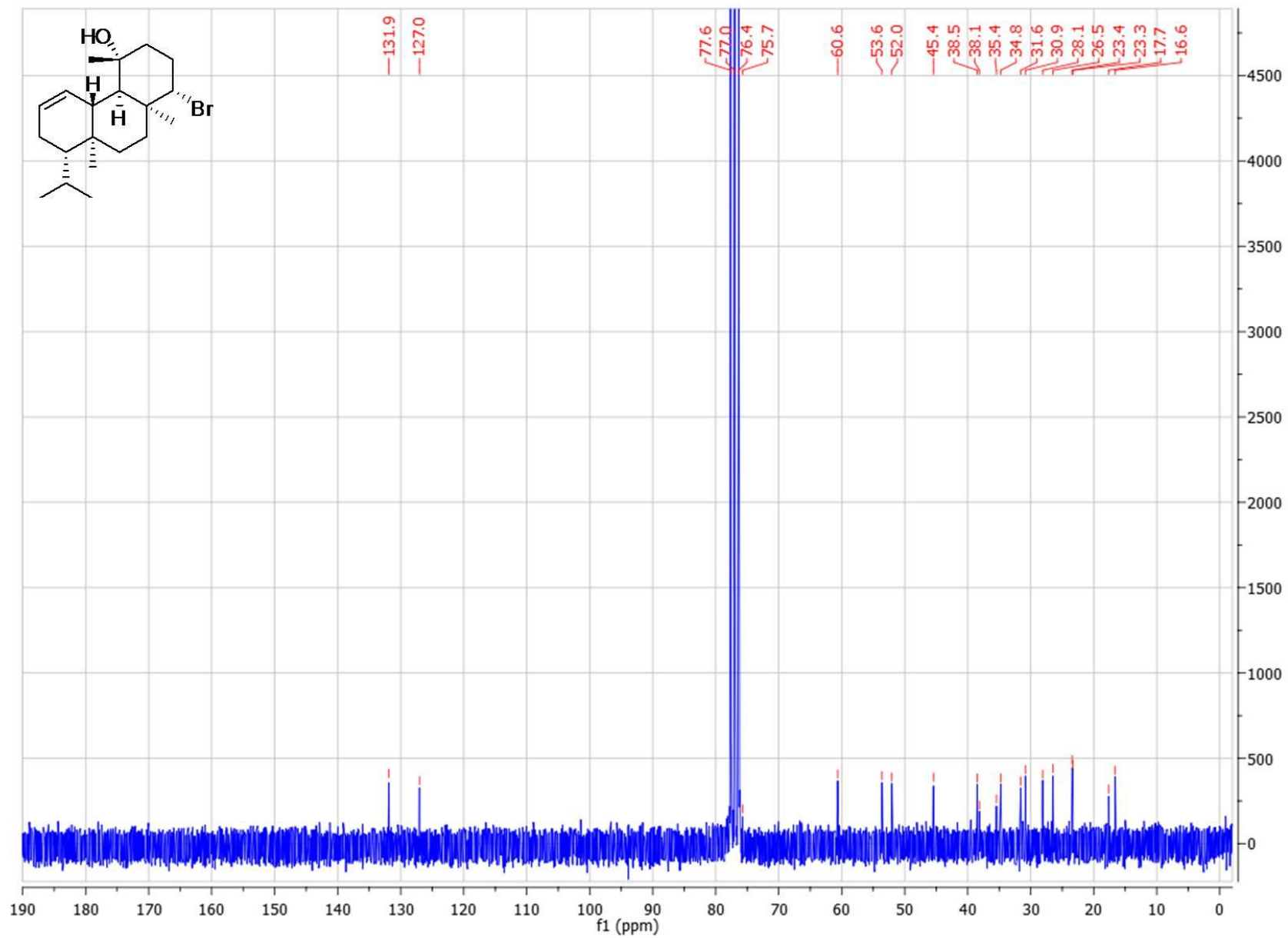


Figure S53. DEPT-135 spectrum (50 MHz, CDCl₃) of debromosphaerol (7).

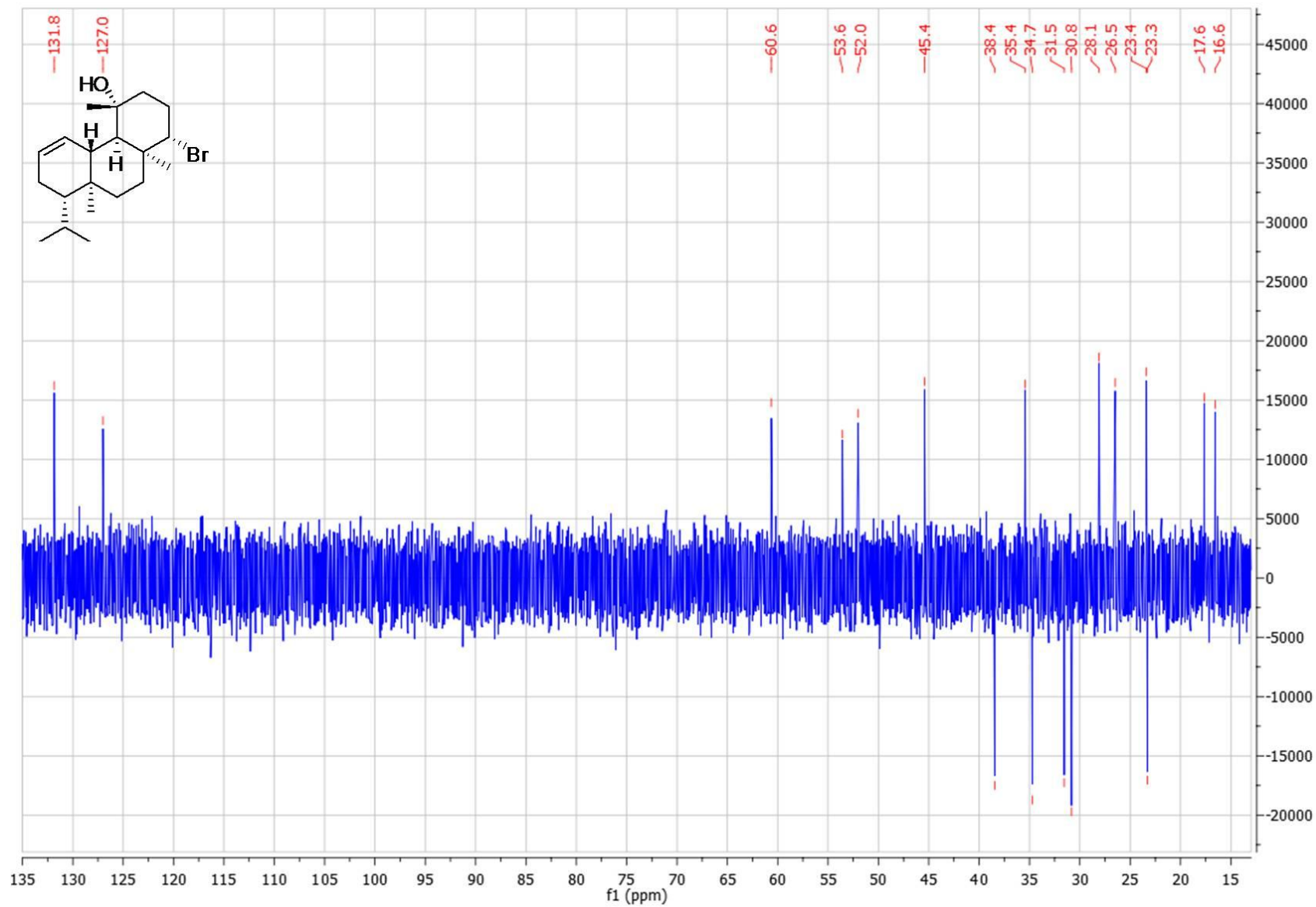


Figure S54. COSY spectrum (400 MHz, CDCl₃) of debromosphaerol (7).

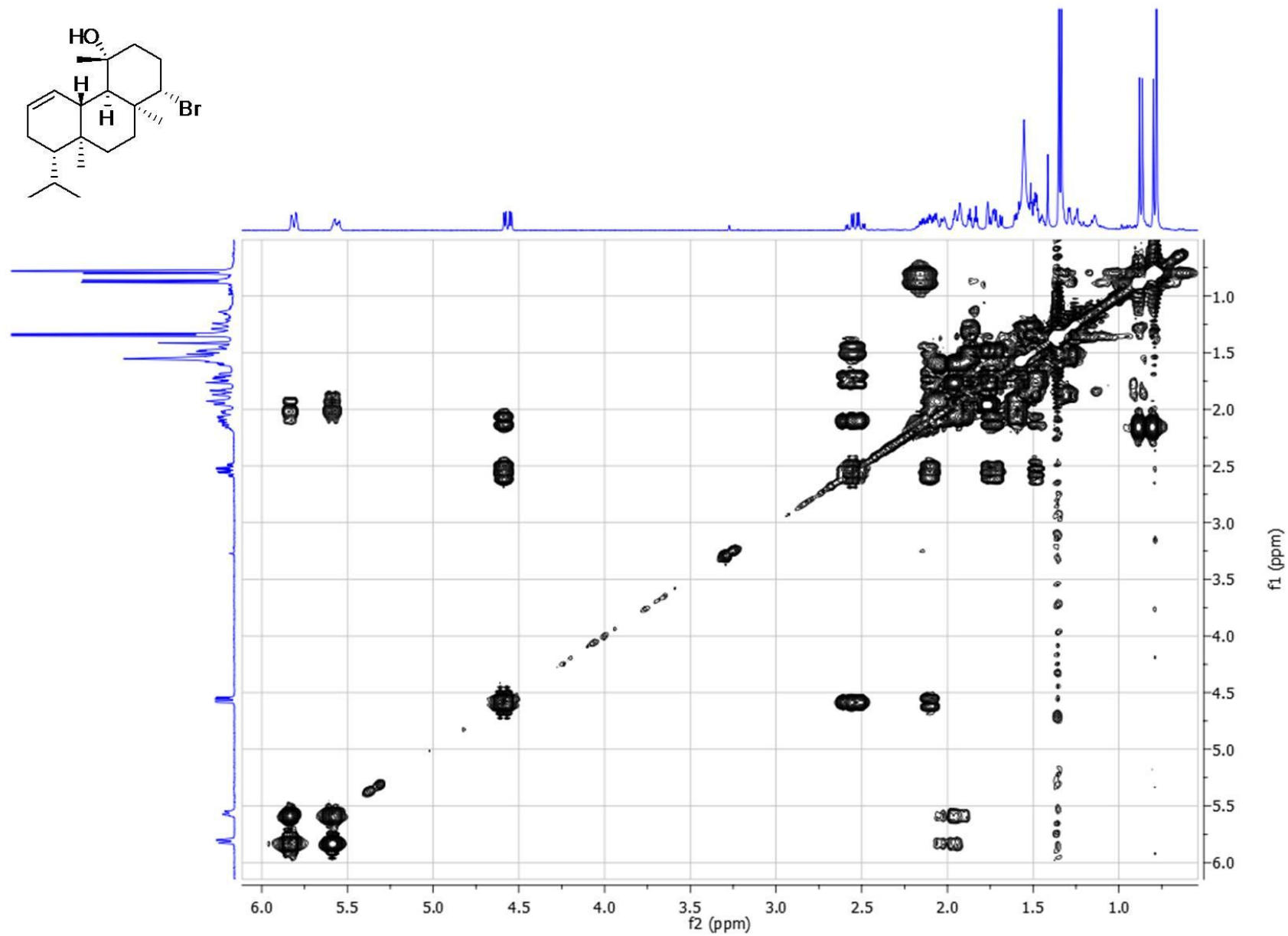


Figure S55. HSQC-DEPT spectrum (400 MHz, CDCl₃) of debromosphaerol (7).

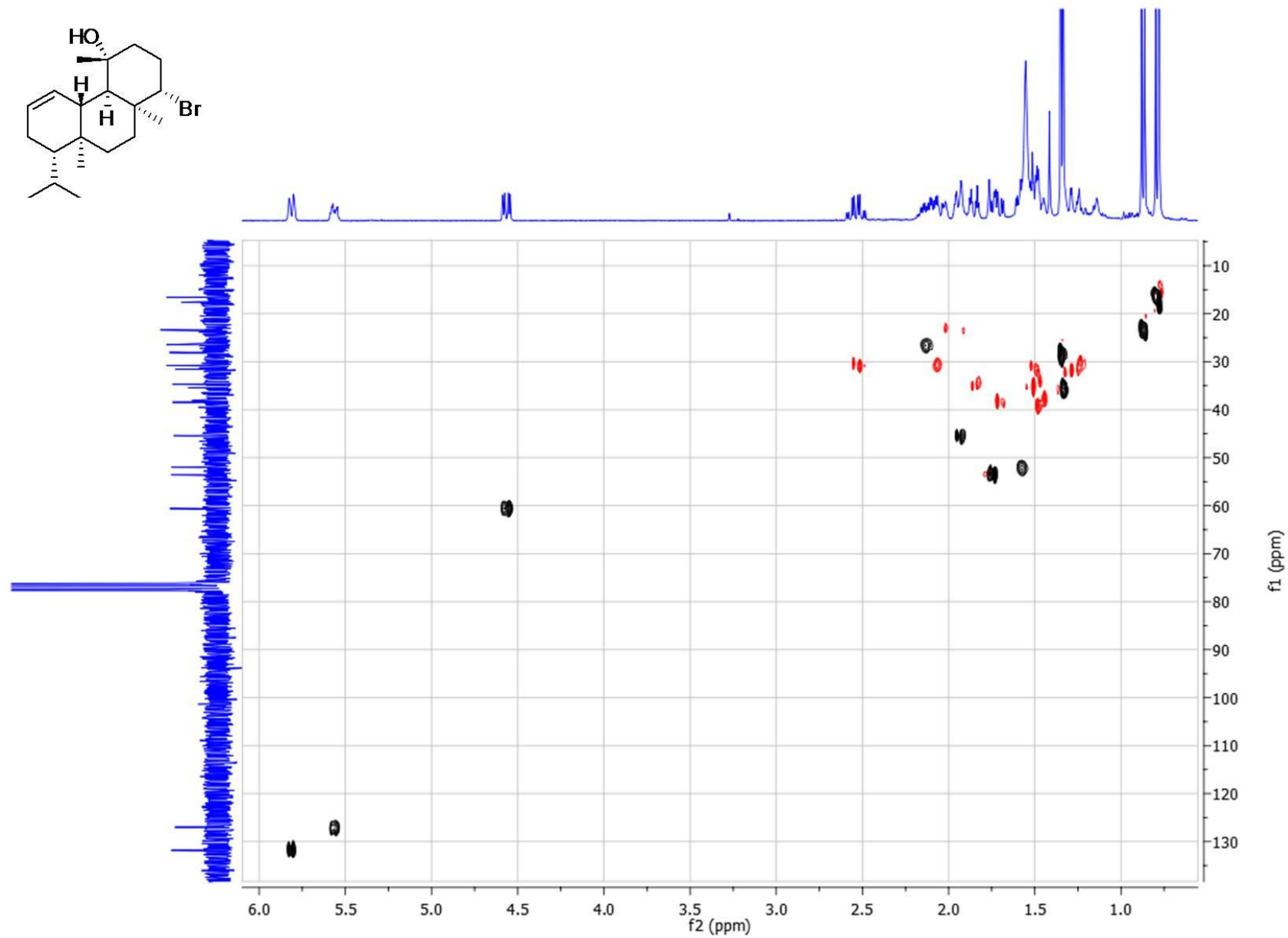


Figure S56. HMBC spectrum (400 MHz, CDCl₃) of debromosphaerol (7).

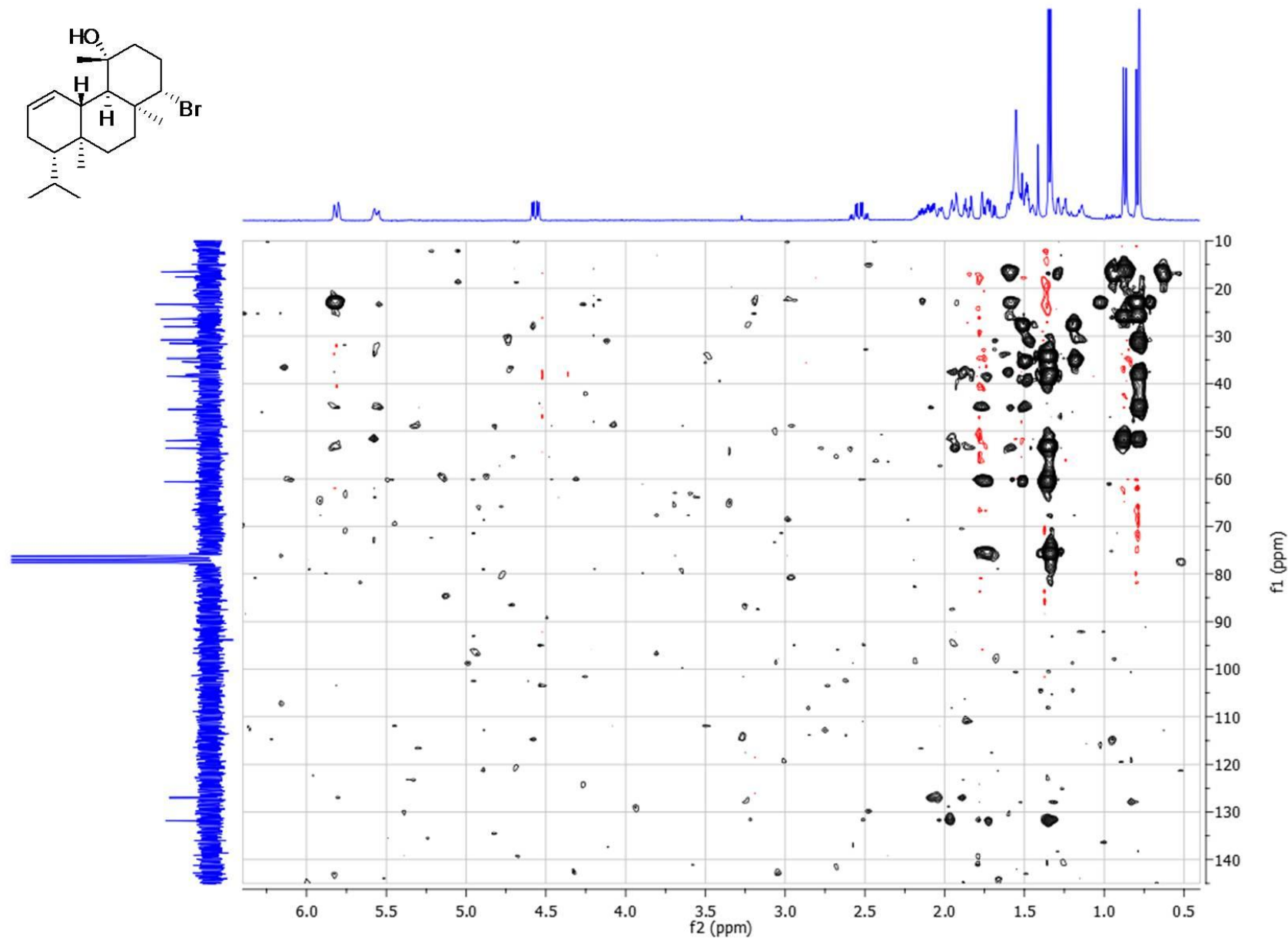


Figure S57. NOESY spectrum (400 MHz, CDCl_3) of debromosphaerol (7).

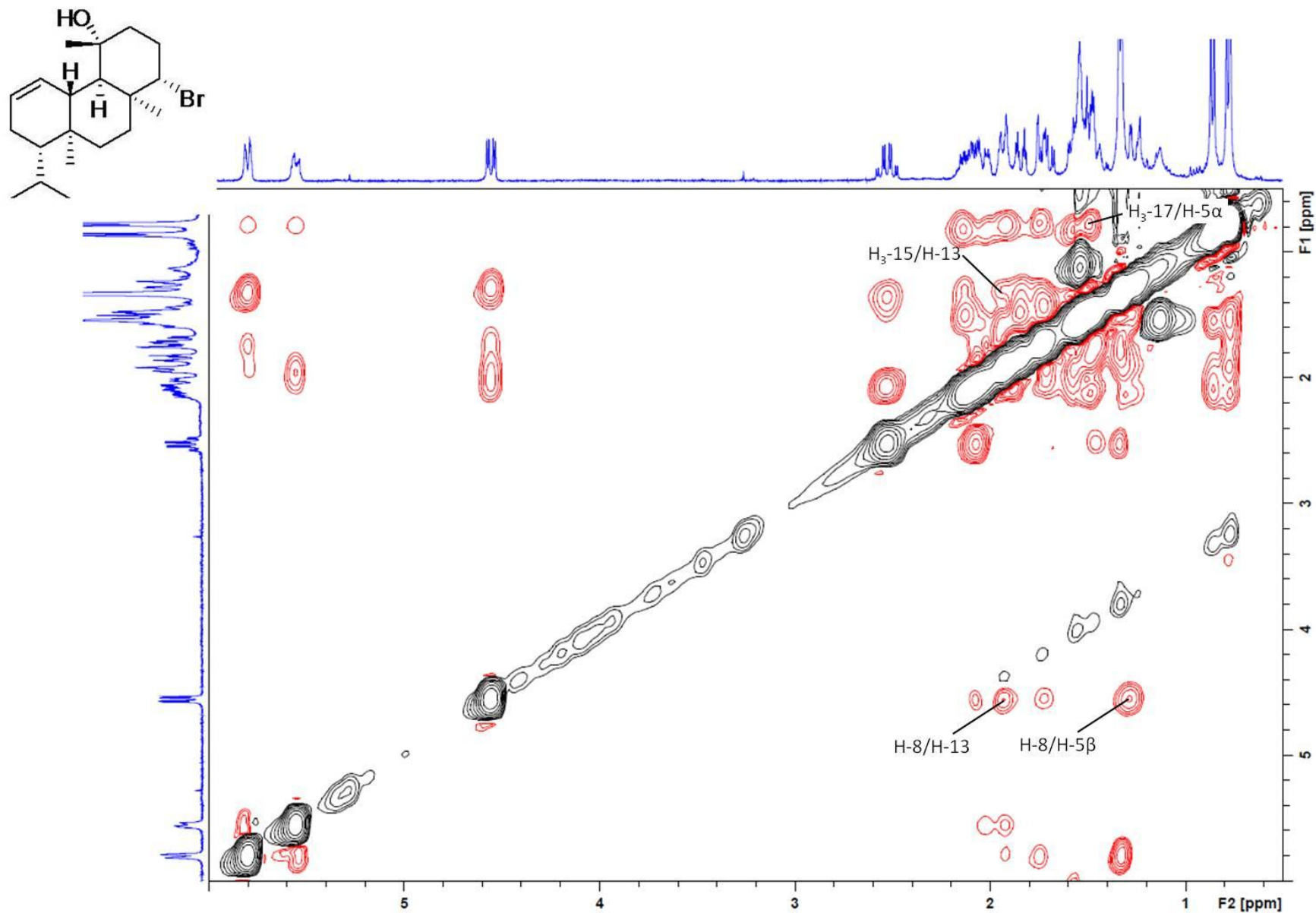


Figure S58. 1D NOE spectrum (400 MHz, CDCl₃), excitation of H-3 of debromosphaerol (**7**).

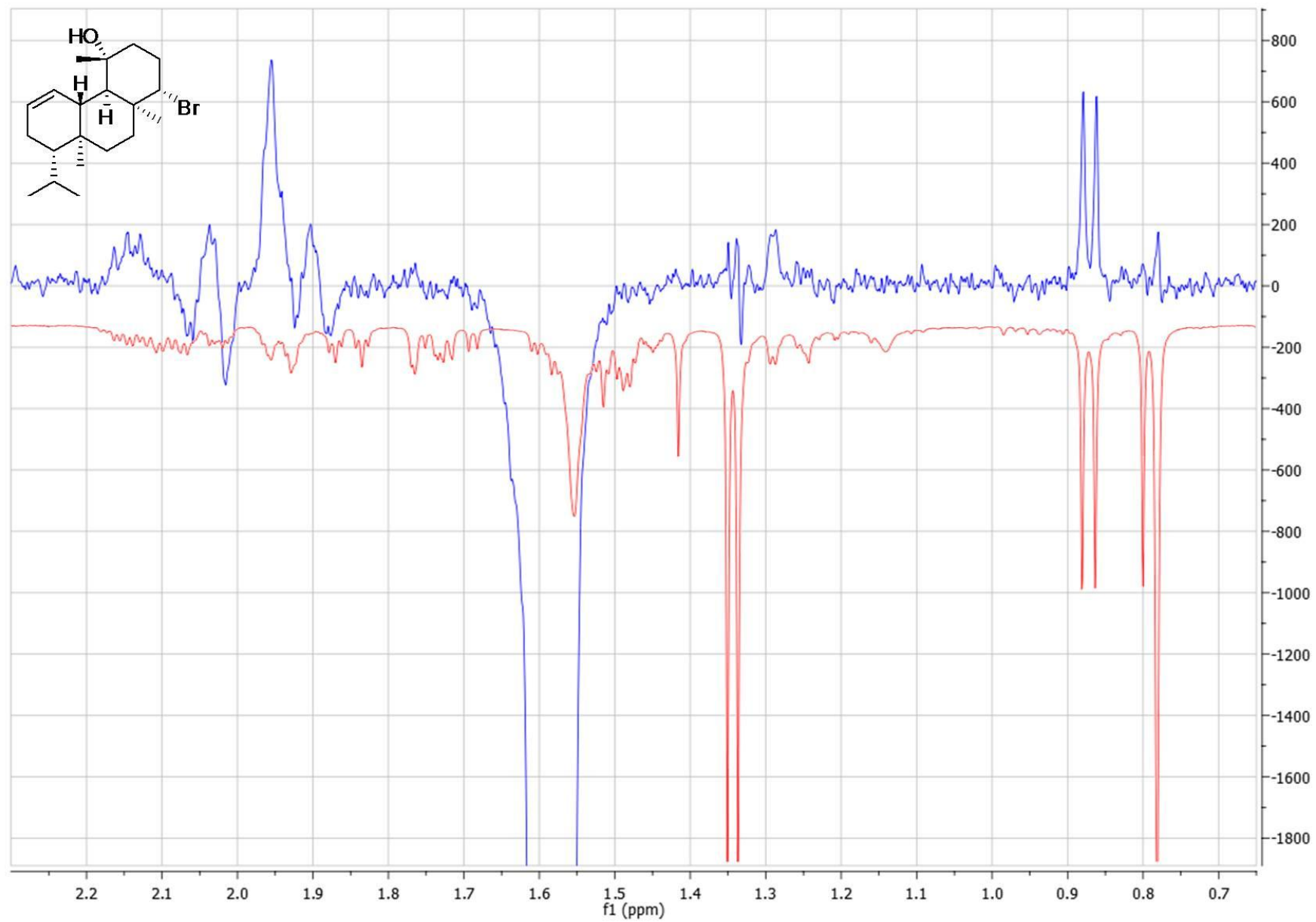


Figure S59. 1D NOE spectrum (400 MHz, CDCl₃), excitation of H-12 of debromosphaerol (**7**).

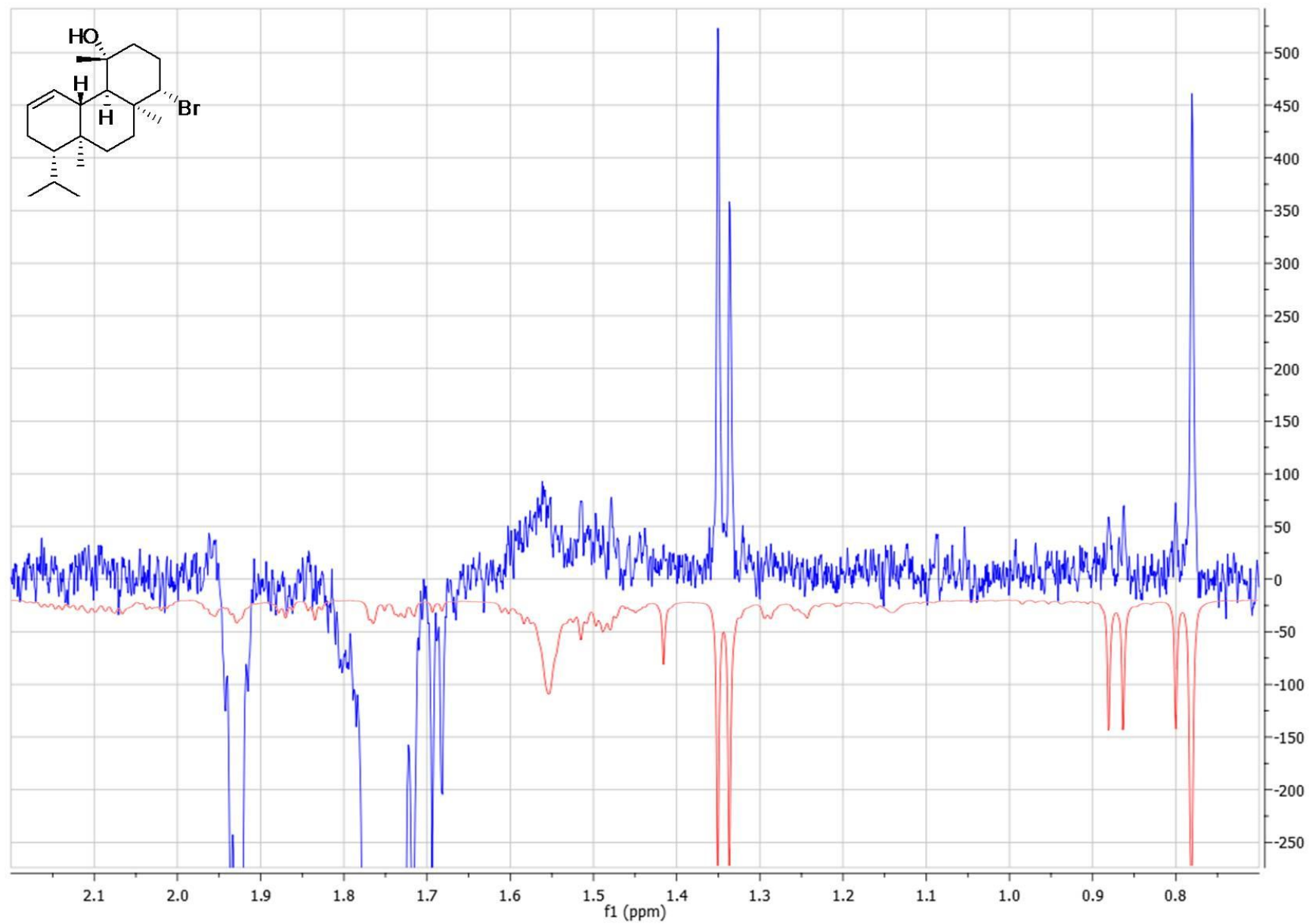


Figure S60. 1D NOE spectrum (400 MHz, CDCl₃), excitation of H-13 and H-2 α of debromosphaerol (**7**).

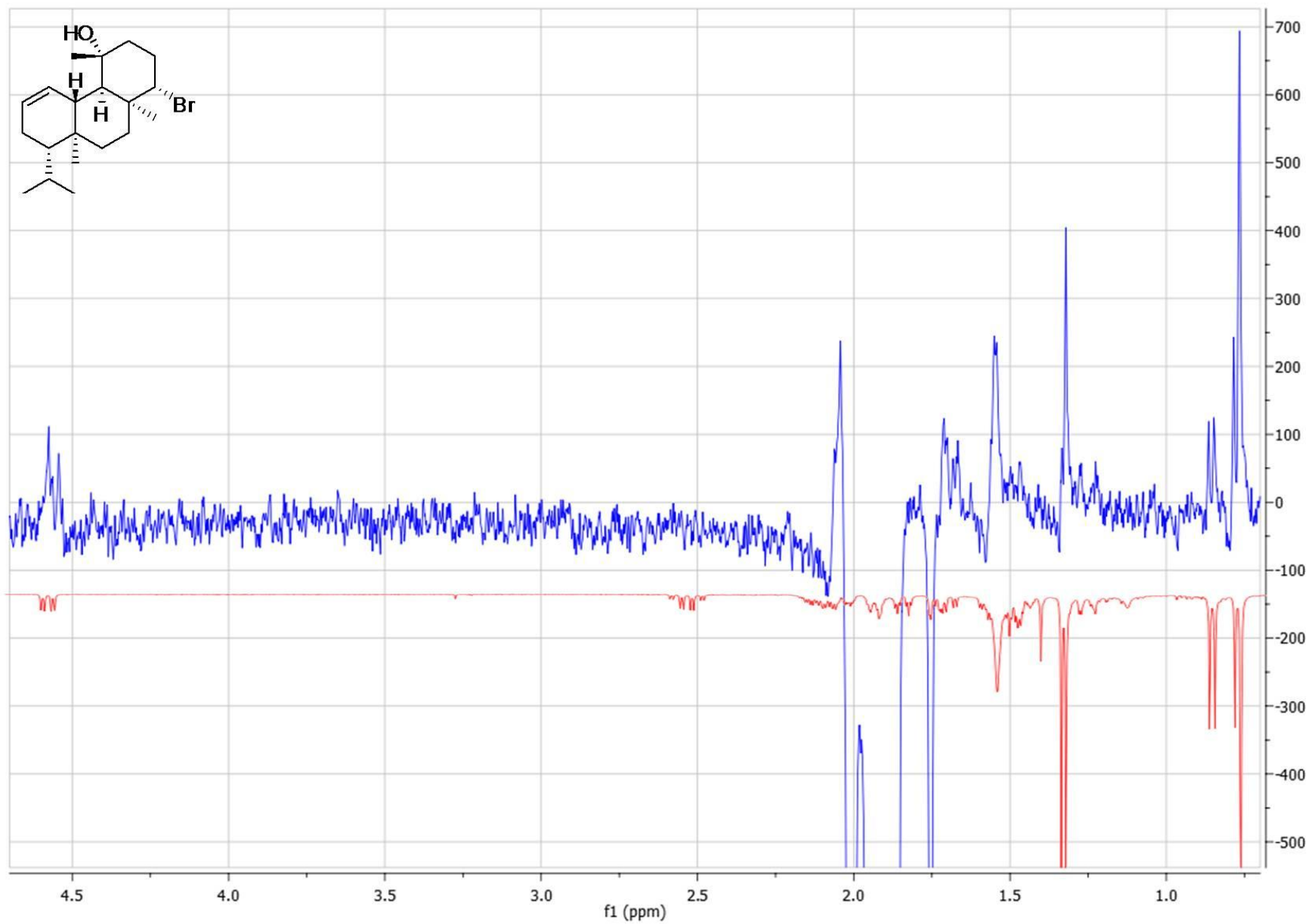
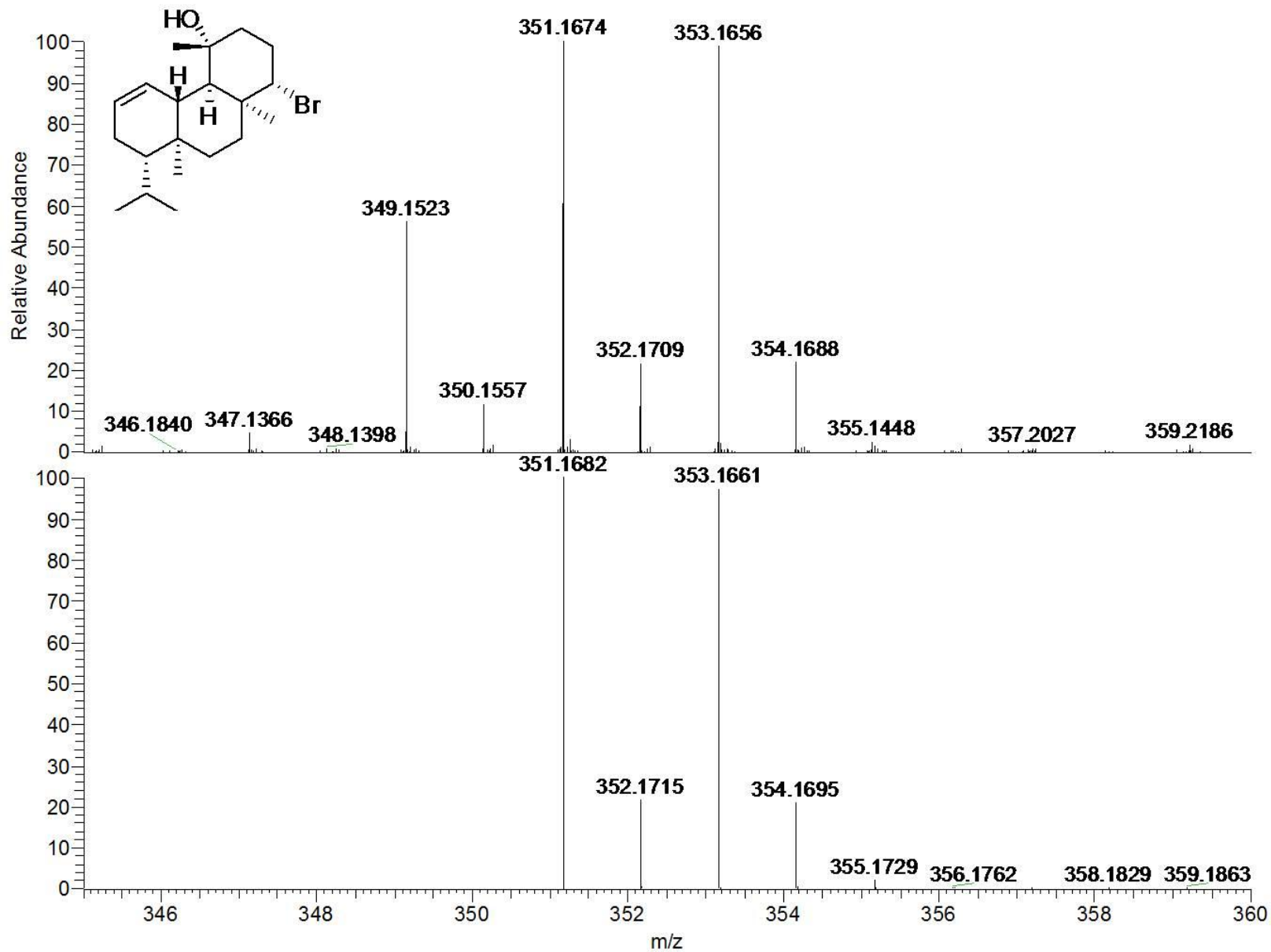


Figure S61. HRMS (ESI+) measurement of debromosphaerol (7).



NL:
9.36E5
Spha107#290 RT: 2.18
AV: 1 SB: 373 2.72 ,
0.00-2.72 T: FTMS + c
ESI Full ms
[220.00-500.00]

NL:
4.07E5
C₂₀ H₃₁ Br + H:
C₂₀ H₃₂ Br₁
pa Chrg 1

Figure S62. IR spectrum of debromosphaerol (7).

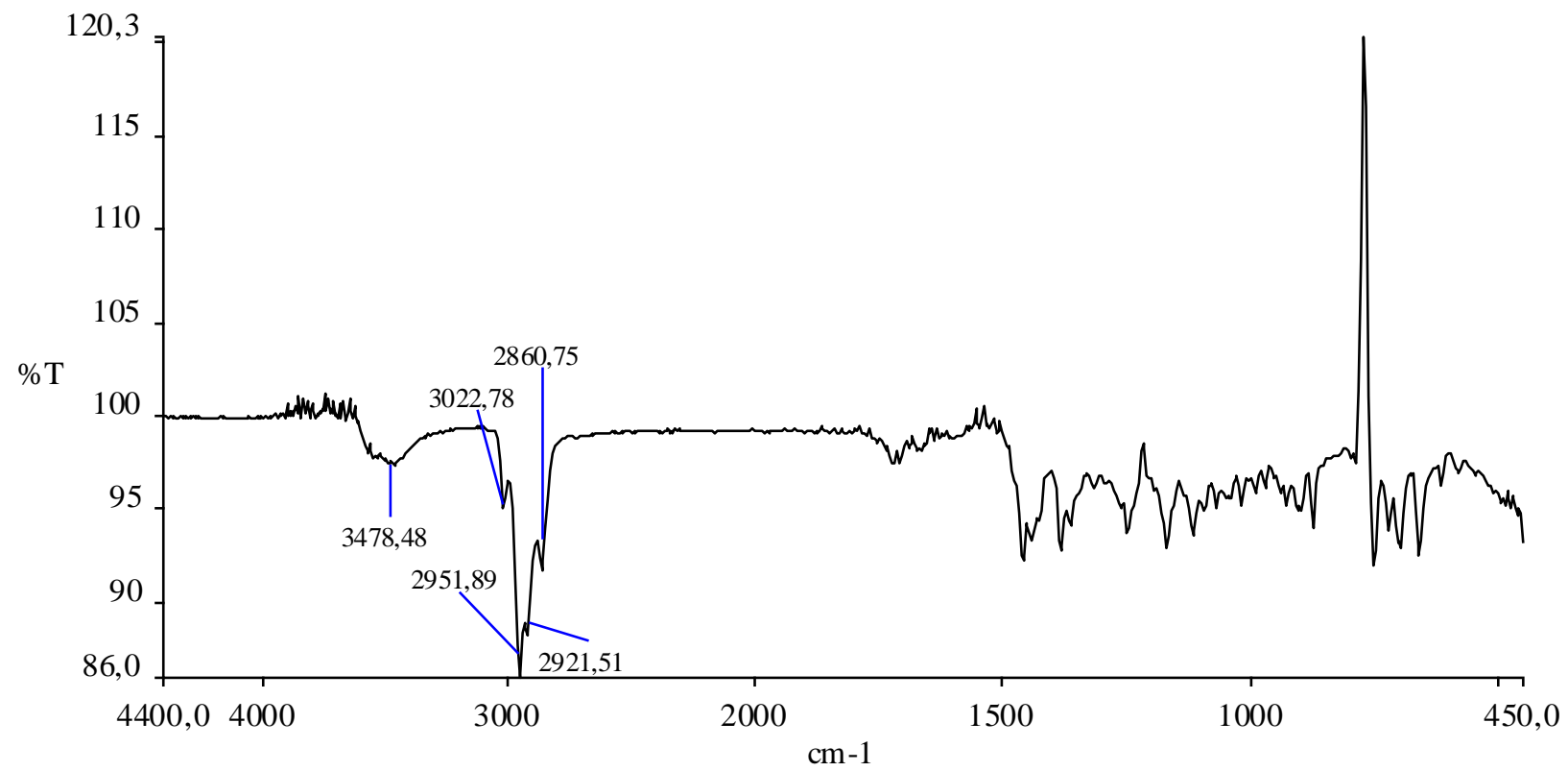


Figure S63. ^1H NMR spectrum (400 MHz, CDCl_3) of 8-methoxy-dihydro-sphaerococcenol (**8**).

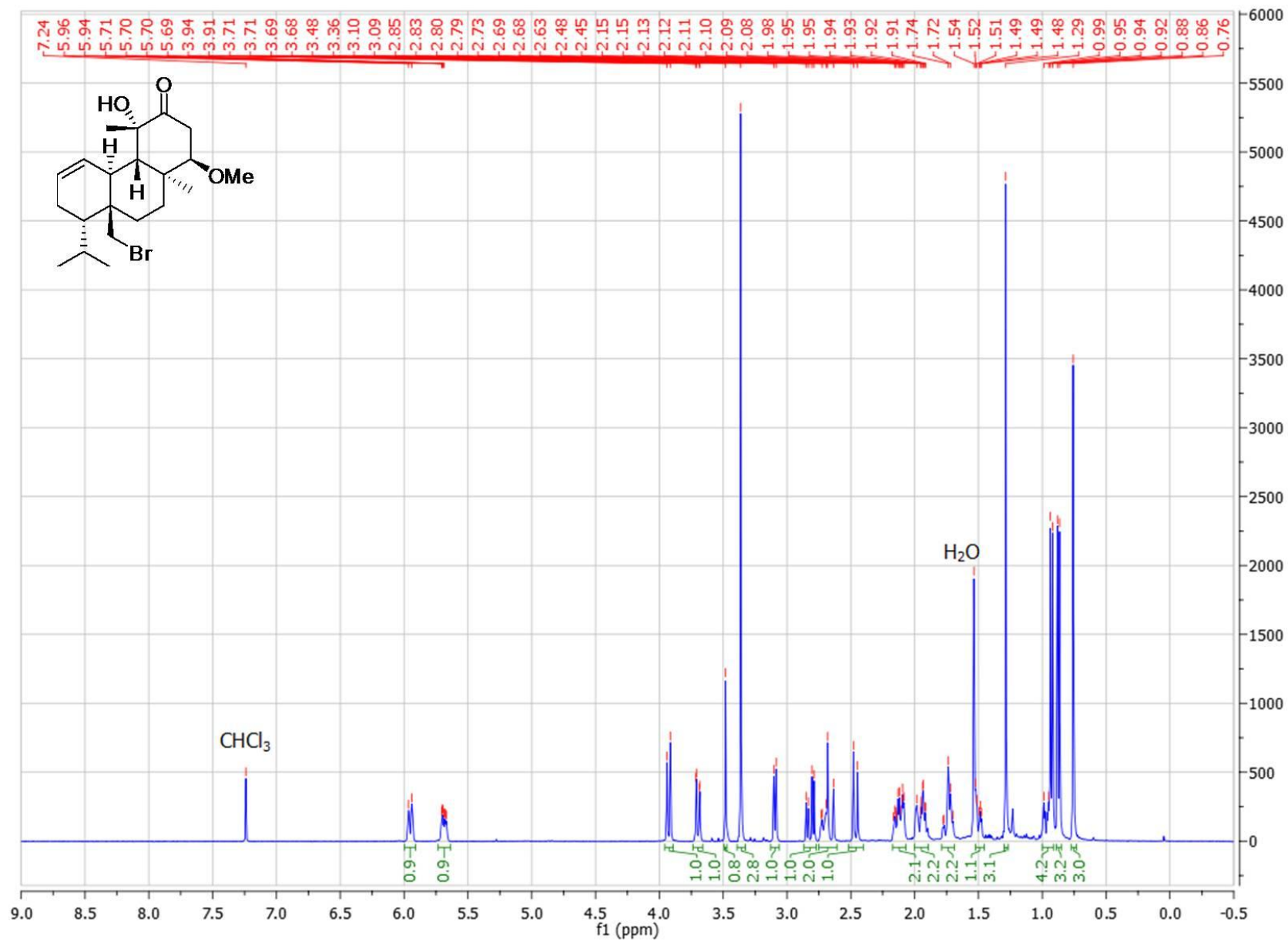


Figure S64. ^{13}C NMR spectrum (50 MHz, CDCl_3) of 8-methoxy-dihydro-sphaerococcol (8).

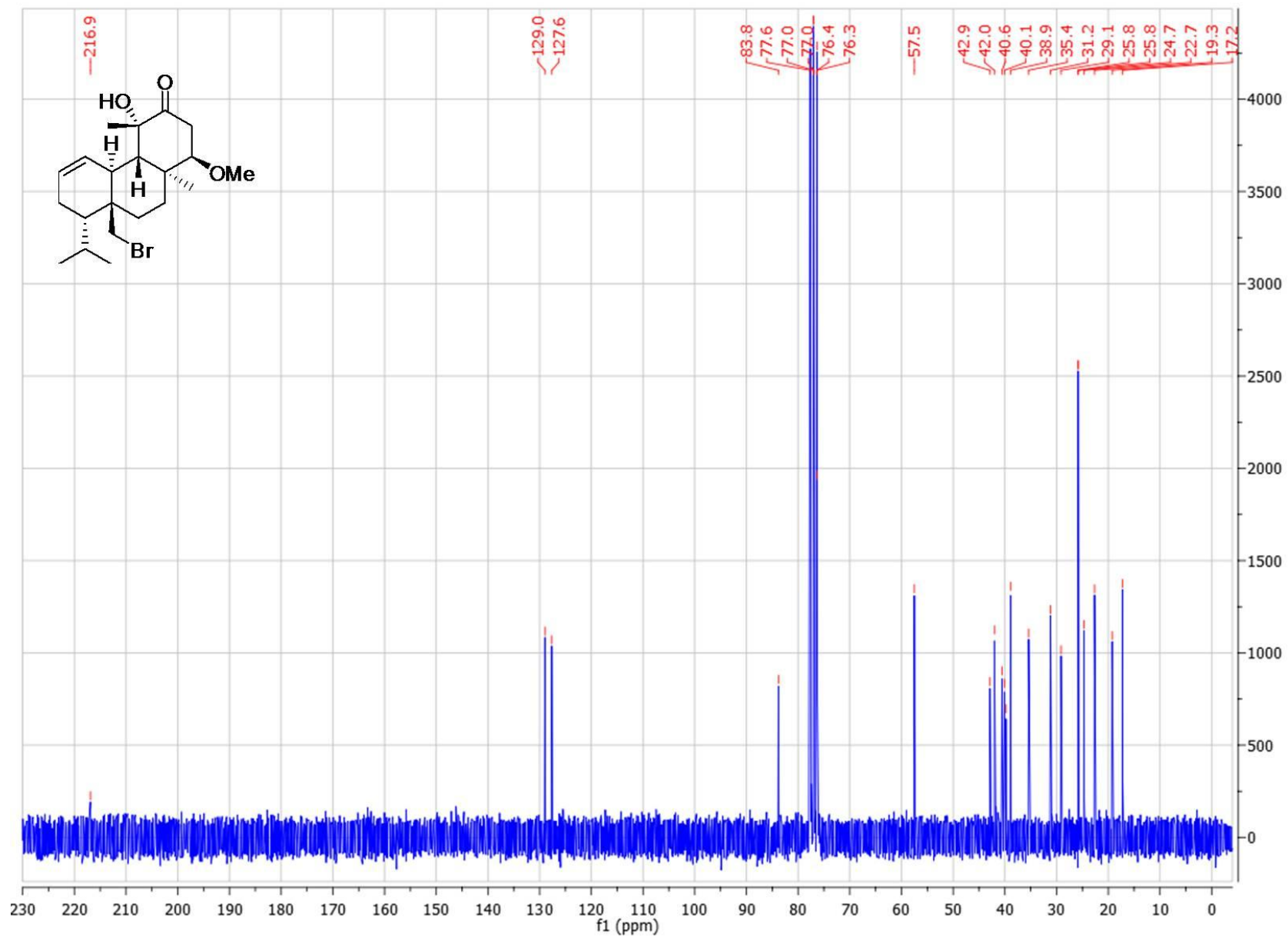


Figure S65. DEPT-135 spectrum (50 MHz, CDCl₃) of 8-methoxy-dihydro-sphaerococcenol (**8**).

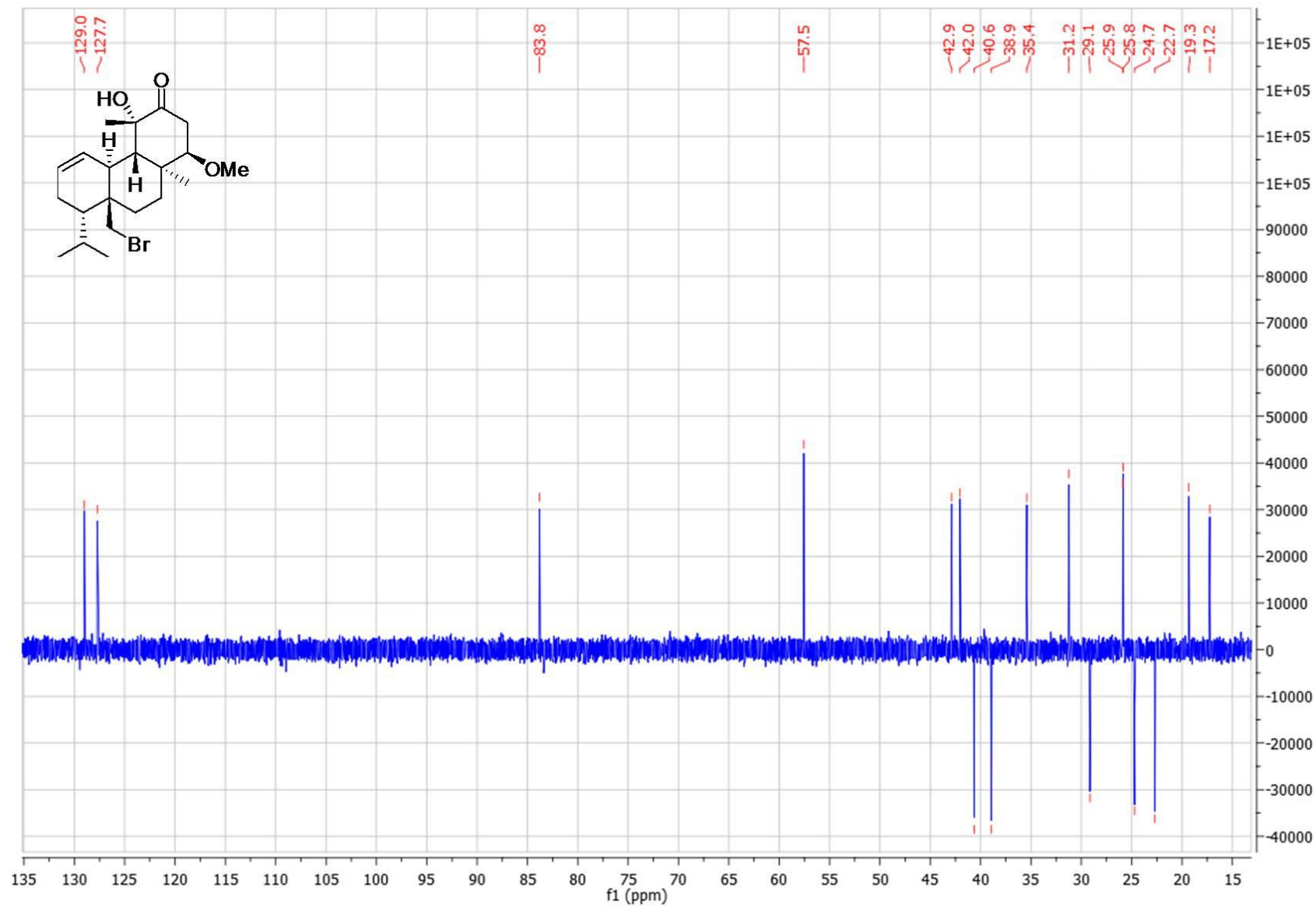


Figure S66. COSY spectrum (400 MHz, CDCl₃) of 8-methoxy-dihydro-sphaerococcenol (**8**).

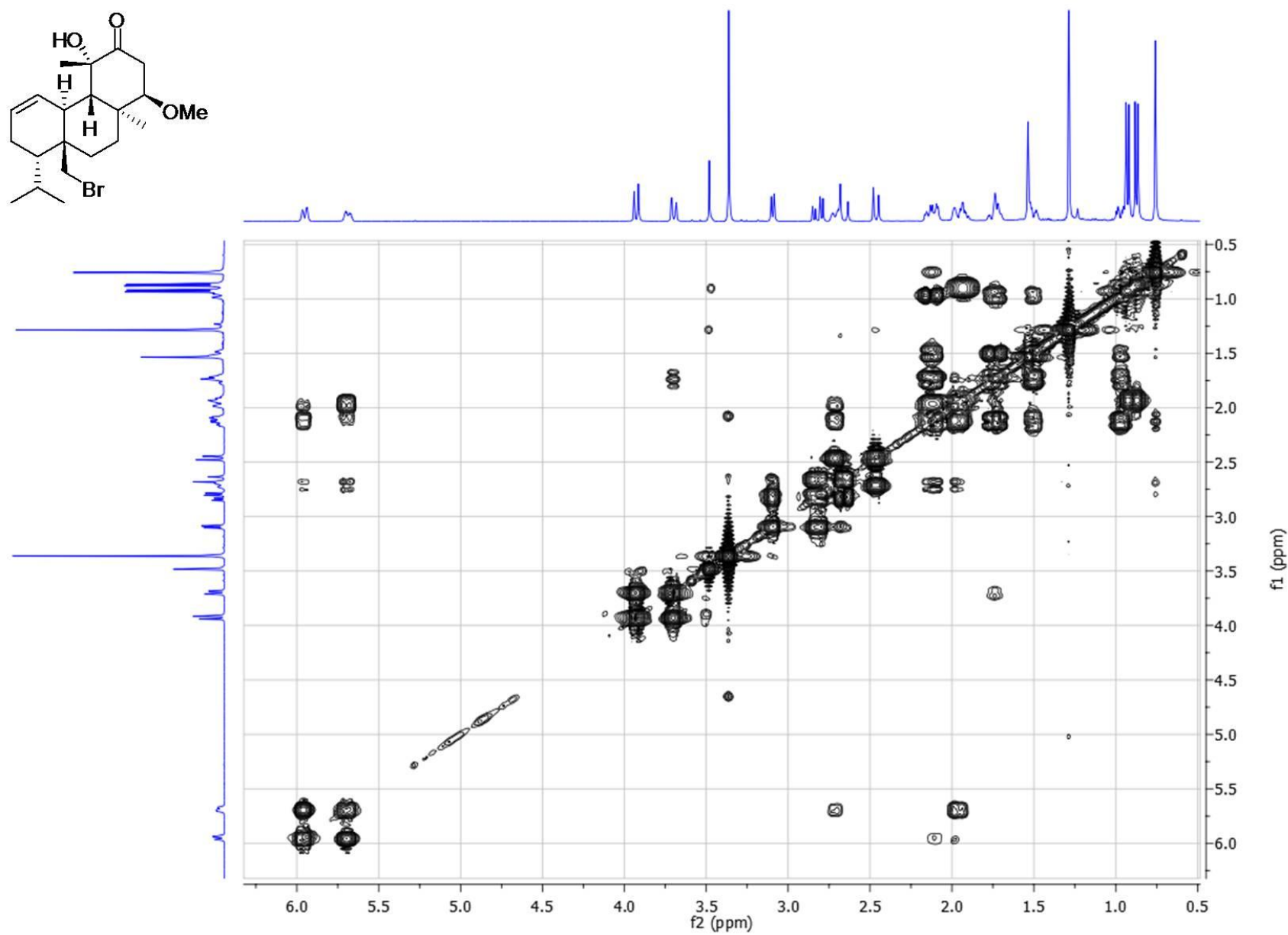
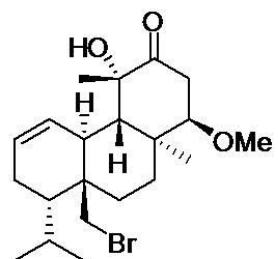


Figure S67. HSQC spectrum (400 MHz, CDCl₃) of 8-methoxy-dihydro-sphaerococcenol (**8**).

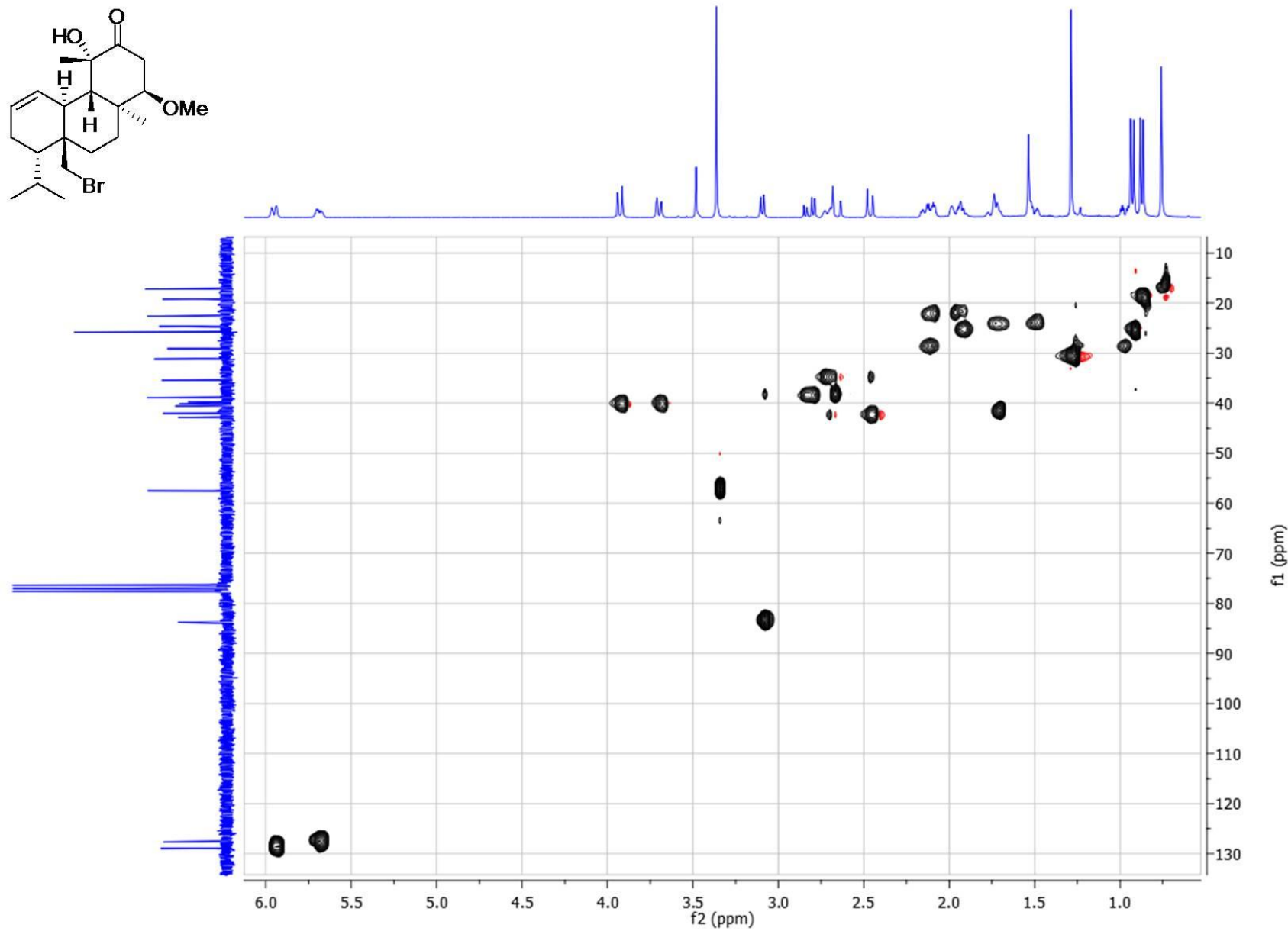


Figure S68. HMBC spectrum (400 MHz, CDCl₃) of 8-methoxy-dihydro-sphaerococcenol (**8**).

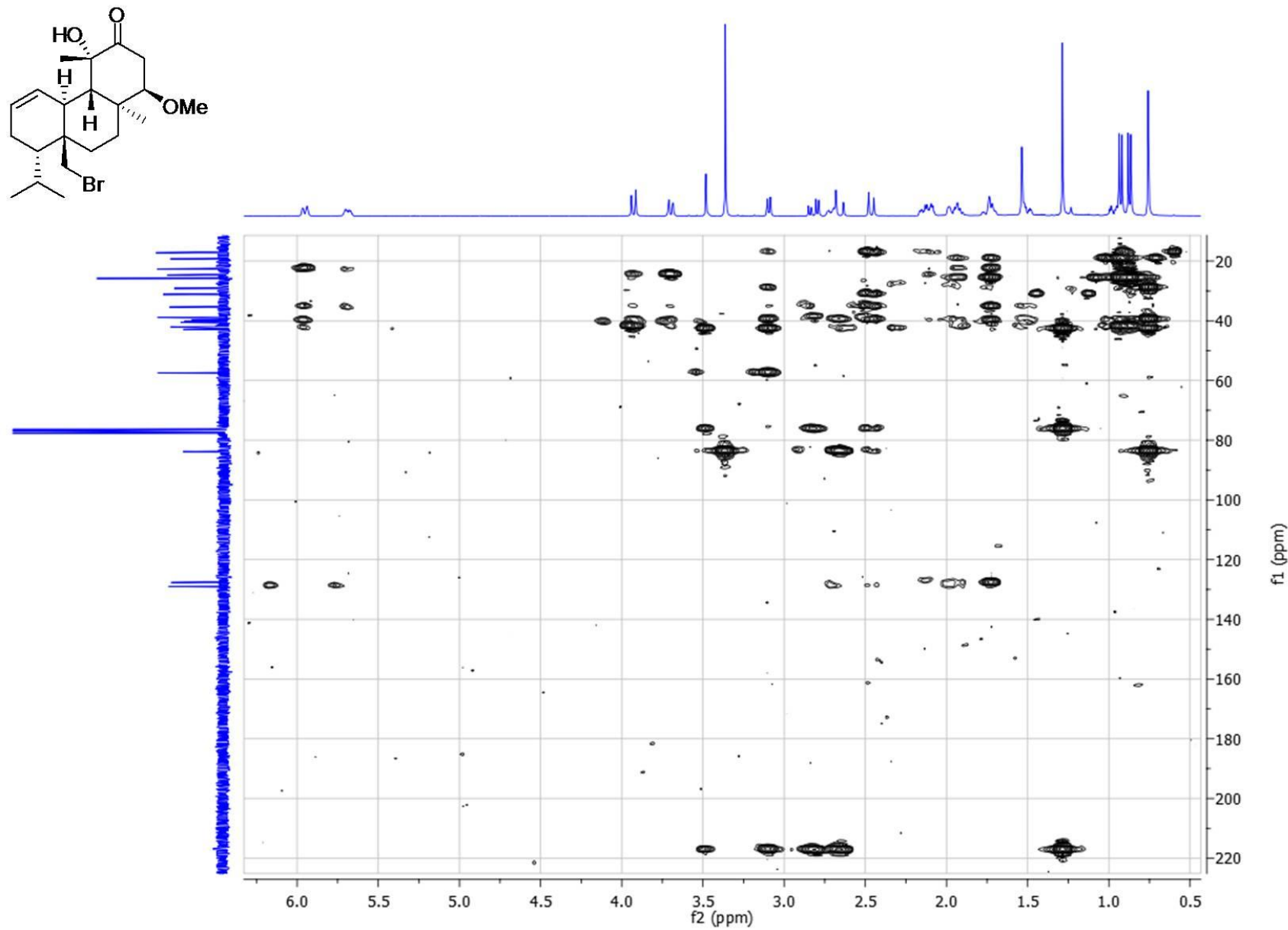


Figure S69. NOESY spectrum (400 MHz, CDCl_3) of 8-methoxy-dihydro-sphaerococcenol (**8**).

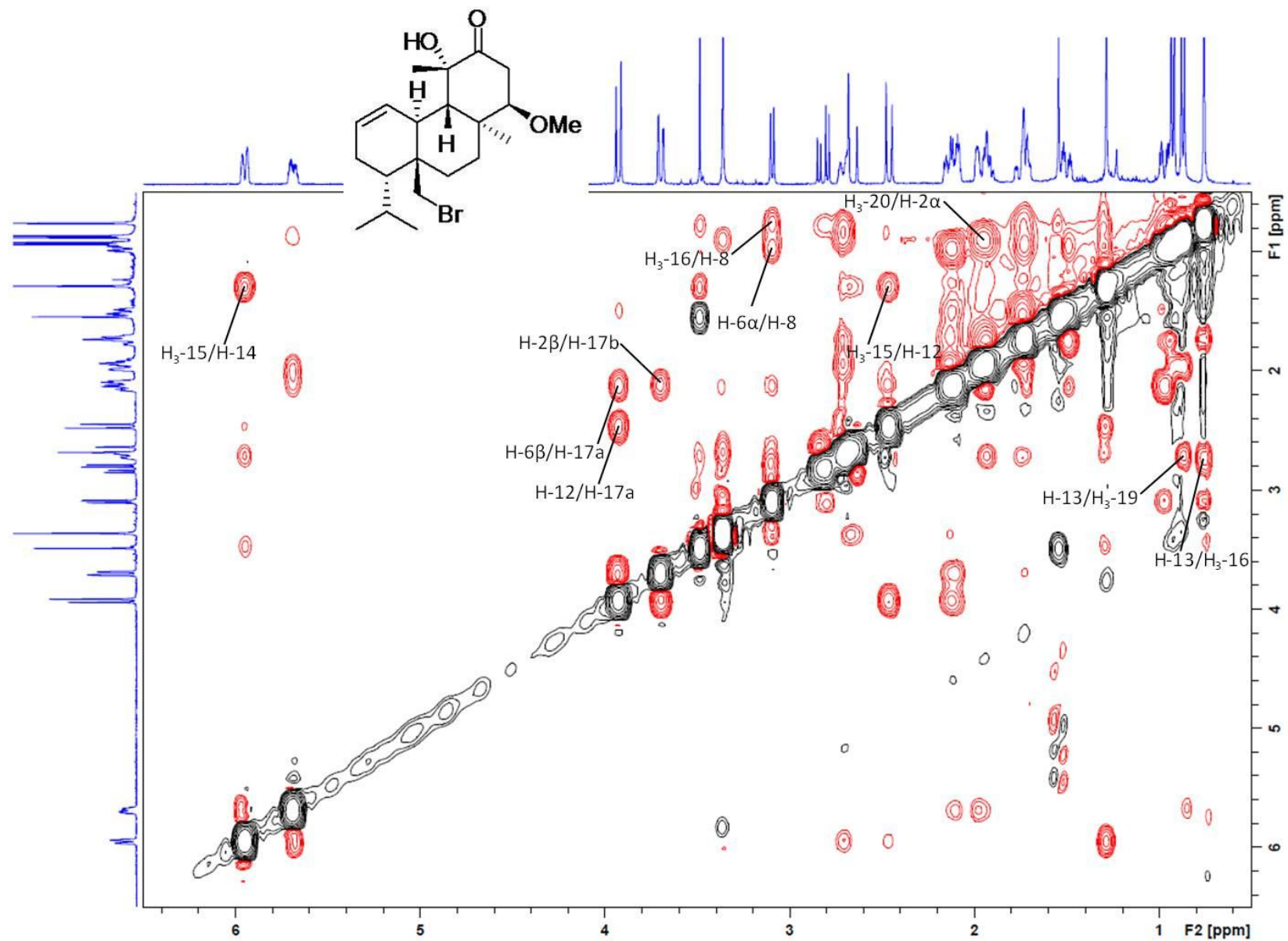


Figure S70. Chair conformation of 8-methoxy-dihydro-sphaerococcenol (**8**), energy: 59.57 Kcal/mole.

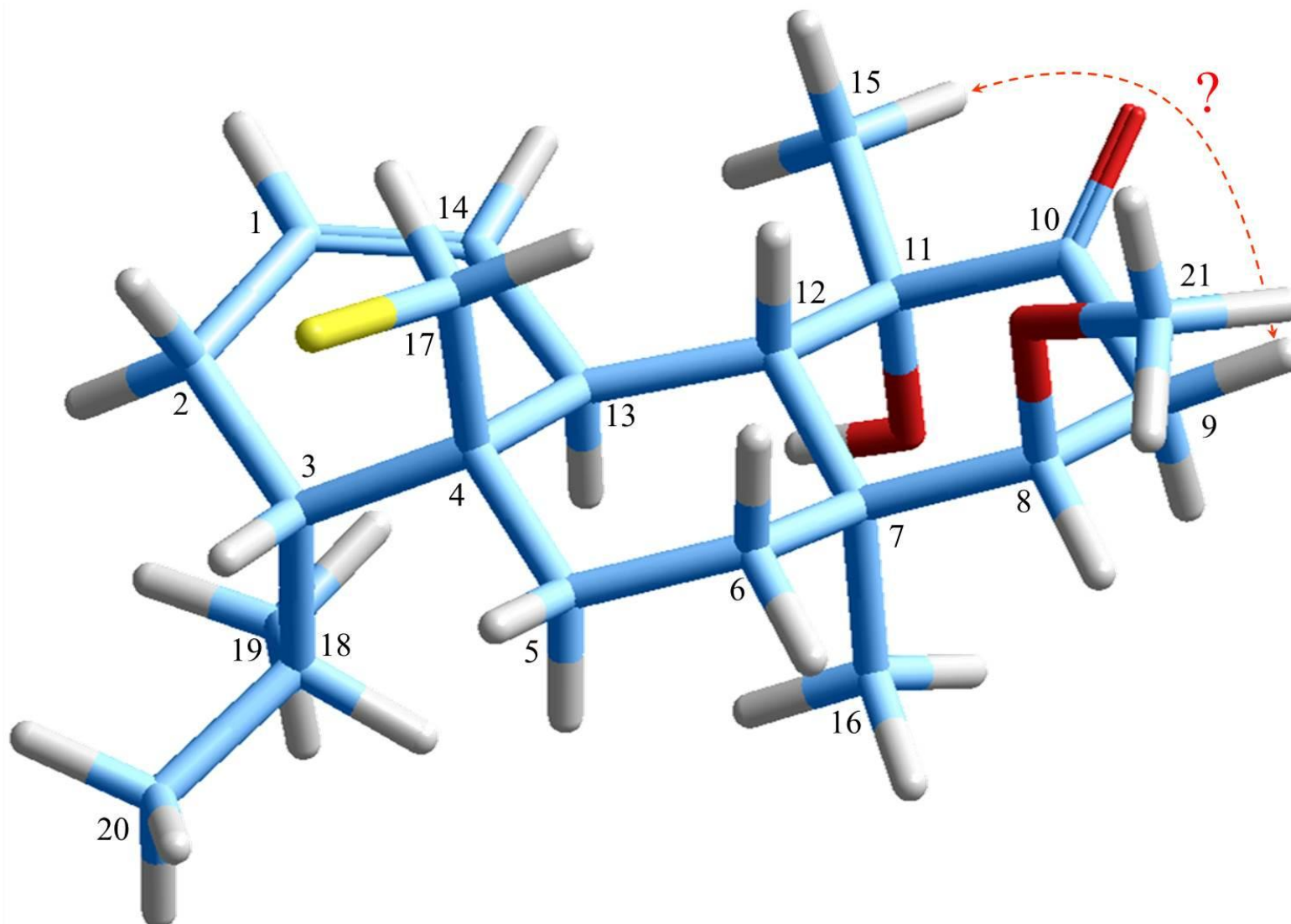
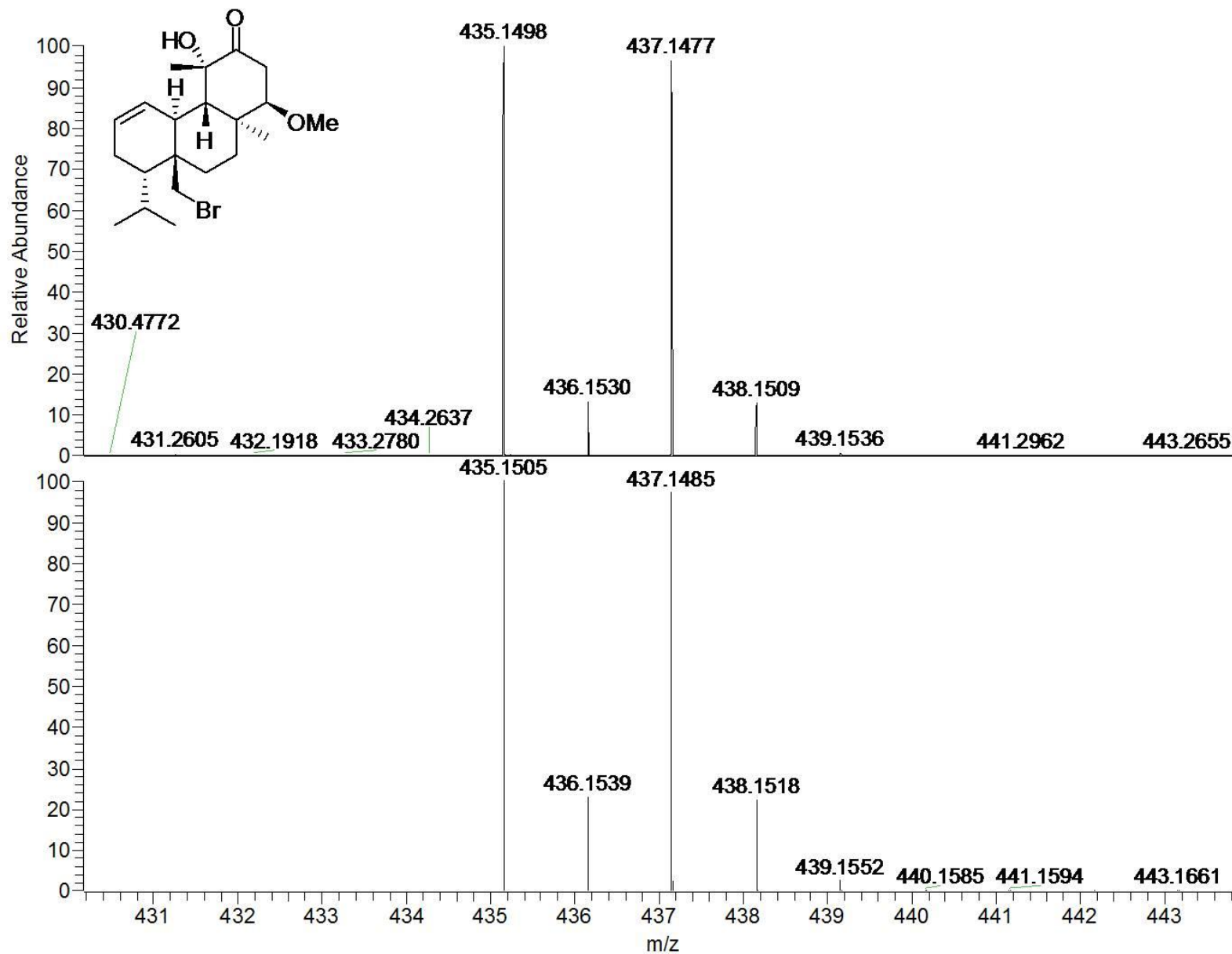


Figure S71. HRMS (ESI+) measurement of 8-methoxy-dihydro-sphaerococcenol (8).



NL:
5.65E6
spha104_081210#2-
58 RT: 0.03-0.80
AV: 57 T: FTMS + p
ESIFull ms
[100.00-1000.00]

NL:
4.00E5
C₂₁H₃₃O₃Br+Na:
C₂₁H₃₃O₃Br₁Na₁
pa Chrg 1

Figure S72. IR spectrum of 8-methoxy-dihydro-sphaerococcenol (**8**).

