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Electronic Supplementary Information

(*Chemical Communications*)

Triangeliphthalides A-D: Bioactive Phthalide Trimers with New Skeletons from *Angelica sinensis* and Their Production Mechanism

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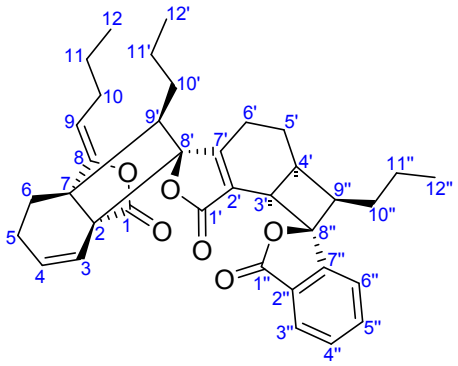


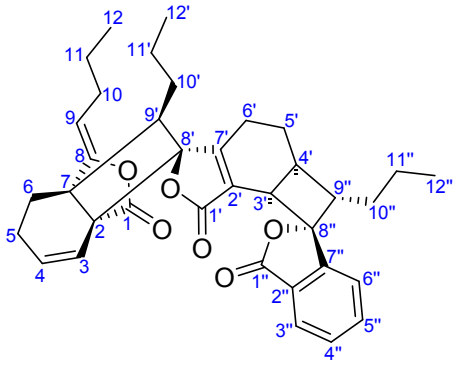
1

Table S1. NMR data of **1** in $CDCl_3$ (600 MHz for ^1H; 150 MHz for ^{13}C)

No.	δ_C, mult.	δ_H (*J* in Hz)*	$^1H,^1H$-COSY	HMBC	NOESY
1	173.3, qC				
2	54.4, qC				
3	118.5, CH	5.42, dd (9.8, 2.5)	4, 5a	1, 2, 5, 7, 8′	
4	134.3, CH	6.07, ddd (9.8, 6.1, 1.6)	3, 5a, 5b	2, 5, 6	
5	20.7, CH_2	1.90, Ha	3, 4, 5b, 6a, 6b	3, 4, 6, 7	
		2.10, Hb	4, 5a, 6a, 6b	3, 4, 6, 7	
6	20.7, CH_2	1.84, Ha	5a, 5b, 6b	2, 4, 5, 7, 8,	9
		2.10, Hb	5a, 5b, 6a	4, 5, 7, 8, 9′	10′a, 10′b
7	45.6, qC				
8	152.8, qC				
9	103.7, CH	4.68, t (7.5)	10	7, 8, 11	6a
10	27.0, CH_2	2.17	9, 11	8, 9, 11, 12	12
11	22.7, CH_2	1.43	10, 12	9, 10, 12	
12	13.6, CH_3	0.92, t (7.4)	11	10, 11	10
1′	170.1, qC				
2′	124.3, qC				
3′	38.6, CH	3.57, br d (7.8)	4′, 6′	1′, 2′, 4′, 5′, 7′, 7″, 8″	6″, 9″
4′	32.2, CH	2.75	3′, 5′a, 5′b, 9″	2′, 3′, 5′, 6′, 8″, 9″	
5′	21.8, CH_2	1.98, Ha	4′, 5′b, 6′	3′, 4′, 7′, 9″	10″a, 10″b
		2.08, Hb	4′, 5′a, 6′	3′, 4′, 7′, 9″	10″b
6′	22.4, CH_2	2.43	3′, 5′a, 5′b	2′, 4′, 5′, 7′, 8′	9′
7′	164.7, qC				
8′	90.5, qC				
9′	49.7, CH	2.92, dd (8.5, 6.9)	10′a, 10′b	6, 7, 8, 7′, 10′, 11′	6′
10′	25.8, CH_2	1.46, Ha	9′, 10′b, 11′a, 11′b	7, 8′, 9′, 11′, 12′	6b, 12′
		1.58, Hb	9′, 10′a, 11′a, 11′b	7, 8′, 9′, 11′, 12′	6b, 12′
11′	20.4, CH_2	1.19, Ha	10′a, 10′b, 11′b, 12′	9′, 10′, 12′	
		1.26, Hb	10′a, 10′b, 11′a, 12′	9′, 10′, 12′	
12′	14.2, CH_3	0.96, t (7.3)	11′a, 11′b	10′, 11′	10′a, 10′b

1″	169.3, qC				
2″	124.9, qC				
3″	125.5, CH	7.79, br d (7.6)	4″, 5″	1″, 5″, 7″	
4″	129.3, CH	7.51, br t (7.6)	3″, 5″, 6″	1″, 2″, 3″, 5″, 6″	
5″	134.3, CH	7.72, br t (7.5)	3″, 4″, 6″	3″, 4″, 7″, 8″	
6″	121.0, CH	7.62, br d (7.7)	4″, 5″	2″, 4″, 8″	3′, 9″
7″	150.6, qC				
8″	90.8, qC				
9″	47.2,CH	3.11, q (7.8)	4′, 10″a, 10″b	4′, 5′, 7″, 8″, 10″, 11″	3′, 6″, 11″
10″	26.2, CH_2	1.38, Ha	9″, 10″b, 11″	4′, 8″, 9″, 11″, 12″	5′a, 12″
		1.46, Hb	9″, 10″a, 11″	4′, 8″, 9″, 11″, 12″	5′a, 5′b, 12″
11″	20.5, CH_2	0.96	10″a, 10″b, 12″	9″, 10″, 12″	9″
12″	14.0, CH_3	0.74, t (7.3)	11″	10″, 11″	10″a, 10″b

* Indiscernible signals from overlap or complex multiplicity are reported without designating multiplicity.



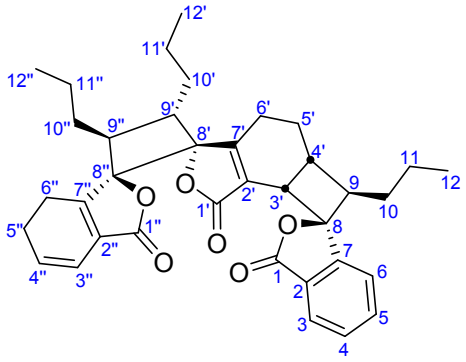
2

Table S2. NMR data of **2** in $CDCl_3$ (600 MHz for ^1H; 150 MHz for ^{13}C)

No.	δ_C, mult.	δ_H (J in Hz)*	$^1H,^1H$-COSY	HMBC	NOESY
1	173.1, qC				
2	55.1, qC				
3	118.5, CH	5.45, dd (9.8, 2.5)	4, 5a	1, 2, 5, 7, 8′	
4	134.3, CH	6.11, ddd (9.8, 6.3, 1.8)	3, 5a, 5b	2, 6	
5	20.6, CH_2	1.94, Ha	3, 4, 5b, 6a, 6b	3, 4, 6, 7	
		2.12, Hb	4, 5a, 6a, 6b	3, 4, 6, 7	
6	20.9, CH_2	1.90, Ha	5a, 5b, 6b	2, 4, 5, 7, 8,	9
		2.11, Hb	5a, 5b, 6a	4, 5, 7, 8, 9′	10′b
7	45.7, qC				
8	153.1, qC				
9	104.2, CH	4.72, t (7.5)	10	7, 8, 11	6a
10	27.1, CH_2	2.20	9, 11	8, 9, 11, 12	12
11	22.7, CH_2	1.45	10, 12	9, 10, 12	
12	13.6, CH_3	0.93, t (7.4)	11	10, 11	10
1′	170.2, qC				
2′	125.2, qC				
3′	39.4, CH	3.57, br d (8.3)	4′, 6′a, 6′b	1′, 2′, 4′, 5′, 7′, 8″, 9″	
4′	33.8, CH	3.00	3′, 5′a, 5′b, 9″	2′, 3′, 5′, 6′, 8″, 9″, 10″	10″a, 10″b
5′	21.8, CH_2	1.80, Ha	4′, 5′b, 6′a, 6′b	3′, 4′, 7′, 9″	
		1.96, Hb	4′, 5′a, 6′a, 6′b	3′, 4′, 7′, 9″	9″
6′	20.2, CH_2	2.34, Ha	3′, 5′a, 5′b, 6′b	2′, 4′, 5′, 7′, 8′	6″
		2.71, Hb	3′, 5′a, 5′b, 6′a	2′, 4′, 5′, 7′, 8′	9′
7′	162.2, qC				
8′	89.3, qC				
9′	49.7, CH	3.00	10′a, 10′b	6, 7, 8, 7′, 10′, 11′	6′b
10′	26.5, CH_2	1.44, Ha	9′, 10′b, 11′a, 11′b	7, 8′, 9′, 11′, 12′	6″
		1.82, Hb	9′, 10′a, 11′a, 11′b	7, 8′, 9′, 11′, 12′	6b
11′	20.9, CH_2	1.34, Ha	10′a, 10′b, 11′b, 12′	9′, 10′, 12′	
		1.42, Hb	10′a, 10′b, 11′a, 12′	9′, 10′, 12′	
12′	14.4, CH_3	1.04, t (7.2)	11′a, 11′b	10′, 11′	
1″	169.4, qC				
2″	126.0, qC				

3″	126.1, CH	7.86, br d (7.3)	4″, 5″	1″, 5″, 7″	
4″	129.6, CH	7.48, td (7.3, 1.1)	3″, 5″, 6″	1″, 2″, 3″, 5″, 6″	
5″	133.4, CH	7.45, td (7.3, 1.4)	3″, 4″, 6″	3″, 4″, 7″, 8″	
6″	120.6, CH	6.87, br d (7.3)	4″, 5″	2″, 4″, 8″	6′a, 10′a, 9″
7″	148.3, qC				
8″	89.5, qC				
9″	45.7, CH	2.44	4′, 10″a, 10″b	4′, 5′, 7″, 8″, 10″, 11″	5′b, 6″
10″	30.7, CH_2	1.53, Ha	9″, 10″b, 11″a, 11″b	4′, 8″, 9″, 11″, 12″	4′, 12″
		1.59, Hb	9″, 10″a, 11″a, 11″b	4′, 8″, 9″, 11″, 12″	4′, 12″
11″	20.4, CH_2	0.94, Ha	10″a, 10″b, 11″b, 12″	9″, 10″, 12″	
		1.05, Hb	10″a, 10″b, 11″a, 12″	9″, 10″, 12″	
12″	14.0, CH_3	0.75, t (7.3)	11″a, 11″b	10″, 11″	10″a, 10″b

* Indiscernible signals from overlap or complex multiplicity are reported without designating multiplicity.



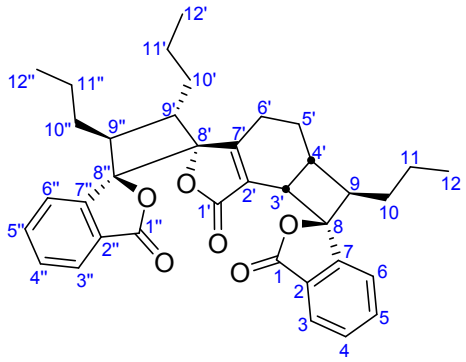
3

Table S3. NMR data of **3** in $CDCl_3$ (600 MHz for ^1H; 150 MHz for ^{13}C)

No.	δ_C, mult.	δ_H (J in Hz)*	$^1H,^1H$-COSY	HMBC	NOESY
1	169.4, qC				
2	126.0, qC				
3	126.0, CH	7.86, br d (7.2)	4, 5	1, 5, 7	
4	129.6, CH	7.48	3, 5, 6	2, 5, 6	
5	133.4, CH	7.46	3, 4, 6	3, 6, 7	
6	120.7, CH	6.90 br d (7.2)	4, 5	2, 4, 7, 8	9, 6′a, 10′a, 11′a
7	148.2, qC				
8	89.6, qC				
9	45.5, CH	2.46	10, 4′	7, 10, 11, 4′, 5′	6, 5′a, 5′b, 6′b
10	30.7, CH_2	1.56	9, 11a, 11b	8, 11, 12, 4′	12, 4′
11	20.4, CH_2	0.95, Ha	10, 11b, 12	9, 10, 12	
		1.03, Hb	10, 11a, 12	9, 10, 12	
12	14.0, CH_3	0.75, t (7.4)	11a, 11b	10, 11	10
1′	169.9, qC				
2′	125.9, qC				
3′	39.3, CH	3.47, br d (8.0)	4′, 6′a, 6′b	8, 9, 1′, 2′, 4′, 5′, 7′	
4′	34.0, CH	2.96	3′, 5′a, 5′b, 9	9, 10, 2′, 3′, 6′	10
5′	21.7, CH_2	1.62, Ha	4′, 5′b, 6′a, 6′b	9, 3′, 4′, 6′, 7′	9
		1.96, Hb	4′, 5′a, 6′a, 6′b	9, 3′, 4′, 6′, 7′	9
6′	20.7, CH_2	2.47, Ha	3′, 5′a, 5′b, 6′b	2′, 4′, 5′, 7′, 8′	6
		3.16, Hb	3′, 5′a, 5′b, 6′a	2′, 4′, 5′, 7′, 8′	9, 9′
7′	162.8, qC				
8′	93.5, qC				
9′	45.0, CH	2.88 dt (10.5, 7.3)	9″, 10′a, 10′b	7′, 8′, 10′, 11′, 9″, 10″	6′b, 10″a
10′	30.8, CH_2	1.63, Ha	9′, 10′b, 11′a, 11′b	8′, 9′, 11′, 12′, 9″	6, 12′
		1.69, Hb	9′, 10′a, 11′a, 11′b	8′, 9′, 11′, 12′, 9″	12′
11′	21.1, CH_2	1.38, Ha	10′a, 10′b, 11′b, 12′	9′, 10′, 12′	6
		1.45, Hb	10′a, 10′b, 11′a, 12′	9′, 10′, 12′	
12′	14.4, CH_3	1.06, t (7.3)	11′a, 11′b	10′, 11′	10′a, 10′b
1″	169.1, qC				
2″	125.9, qC				
3″	116.5, CH	6.11, br d (9.6)	4″, 5″	1″, 2″, 4″, 5″, 7″	

4″	130.6, CH	5.95, dt (9.5, 4.2)	3″, 5″	1″, 2″, 3″, 5″, 6″	
5″	22.5, CH_2	2.34	3″, 4″, 6″a, 6″b	3″, 4″, 6″, 7″	
6″	21.7, CH_2	2.55, Ha	5″, 6″b	2″, 4″, 5″, 7″, 8″	9″
		2.69, Hb	5″, 6″a	2″, 4″, 5″, 7″, 8″, 9″	
7″	158.4, qC				
8″	93.6, qC				
9″	45.5, CH	2.78, ddd (10.6, 9.5, 5.7)	9′, 10″a, 10″b	8′, 9′, 10′, 7″, 8″, 10″, 11″	6″a
10″	31.2, CH_2	1.57, Ha	9″, 10″b, 11″	9′, 8″, 9″, 11″, 12″	9′, 12″
		1.74, Hb	9″, 10″a, 11″	9′, 8″, 9″, 11″, 12″	12″
11″	20.6, CH_2	1.14	10″a, 10″b, 12″	9″, 10″, 12″	
12″	14.1, CH_3	0.88, t (7.3)	11″	10″, 11″	10″a, 10″b

* Indiscernible signals from overlap or complex multiplicity are reported without designating multiplicity.



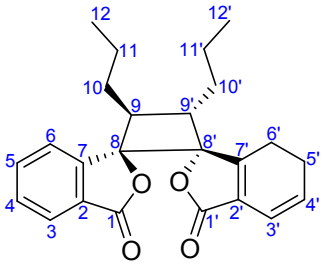
4

Table S4. NMR data of **4** in $CDCl_3$ (600 MHz for ^1H; 150 MHz for ^{13}C)

No.	δ_C, mult.	δ_H (J in Hz)*	$^1H,^1H$-COSY	HMBC	NOESY
1	169.4, qC				
2	126.0, qC				
3	126.0, CH	7.85	4, 5	1, 2, 5, 7	
4	129.6, CH	7.49	3, 5, 6	2, 3, 5, 6	
5	133.4, CH	7.49	3, 4, 6	3, 4, 6, 7	
6	120.7, CH	6.94	4, 5	2, 4, 7, 8	9, 6′a, 10′a, 11′a
7	148.2, qC				
8	89.6, qC				
9	45.6, CH	2.44 dd (9.0, 7.7)	10, 4′	7, 10, 11, 4′, 5′	6, 5′b
10	30.6, CH_2	1.52	9, 11a, 11b	8, 11, 12, 4′	12, 4′
11	20.4, CH_2	0.94, Ha	10, 11b, 12	9, 10, 12	
		1.02, Hb	10, 11a, 12	9, 10, 12	
12	14.0, CH_3	0.74, t (7.2)	11a, 11b	10, 11	10
1′	169.9, qC				
2′	126.1, qC				
3′	39.3, CH	3.29, br d (8.2)	4′, 6′a, 6′b	8, 9, 1′, 2′, 4′, 5′, 7′	
4′	33.9, CH	2.88	3′, 5′a, 5′b, 9	9, 10, 2′, 3′, 6′	10
5′	21.7, CH_2	1.55, Ha	4′, 5′b, 6′a, 6′b	9, 3′, 4′, 6′, 7′	
		1.96, Hb	4′, 5′a, 6′a, 6′b	9, 3′, 4′, 6′, 7′	9
6′	20.7, CH_2	2.51, Ha	3′, 5′a, 5′b, 6′b	2′, 4′, 5′, 7′, 8′	6, 9′
		3.22, Hb	3′, 5′a, 5′b, 6′a	2′, 4′, 5′, 7′, 8′	9′
7′	162.3, qC				
8′	92.4, qC				
9′	45.5, CH	3.03, dt (10.9, 7.2)	9″, 10′a, 10′b	7′, 8′, 10′, 11′, 8″, 9″, 10″	6′a, 6′b, 10″a 10″b
10′	30.7, CH_2	1.72, Ha	9′, 10′b, 11′a, 11′b	8′, 9′, 11′, 12′, 9″	6, 12′
		1.78, Hb	9′, 10′a, 11′a, 11′b	8′, 9′, 11′, 12′, 9″	12′
11′	21.3, CH_2	1.43, Ha	10′a, 10′b, 11′b, 12′	9′, 10′, 12′	6
		1.53, Hb	10′a, 10′b, 11′a, 12′	9′, 10′, 12′	
12′	14.5, CH_3	1.09, t (7.3)	11′a, 11′b	10′, 11′	10′a, 10′b
1″	168.7, qC				
2″	125.3, qC				
3″	125.5, CH	7.80, br d (7.7)	4″, 5″	1″, 2″, 4″, 5″, 7″	

4″	130.2, CH	7.51, br t (7.4)	3″, 5″, 6″	1″, 2″, 3″, 5″, 6″	
5″	134.8, CH	7.65, br t (7.4)	3″, 4″, 6″	3″, 4″, 6″, 7″	
6″	124.9, CH	7.73, br d (7.7)	4″, 5″	2″, 4″, 5″, 7″, 8″	9″
7″	145.6, qC				
8″	93.0, qC				
9″	49.0, CH	2.94, ddd (10.8, 9.5, 5.4)	9′, 10″a, 10″b	8′, 9′, 10′, 7″, 8″, 10″, 11″	6″
10″	31.1, CH_2	1.58, Ha	9″, 10″b, 11″a, 11″b	9′, 8″, 9″, 11″, 12″	9′, 12″
		1.73, Hb	9″, 10″a, 11″a, 11″b	9′, 8″, 9″, 11″, 12″	9′, 12″
11″	20.6, CH_2	0.87, Ha	10″a, 10″b, 11″b, 12″	9″, 10″, 12″	
		0.93, Hb	10″a, 10″b, 11″a, 12″	9″, 10″, 12″	
12″	14.0, CH_3	0.73, t (7.3)	11″a, 11″b	10″, 11″	10″a, 10″b

* Indiscernible signals from overlap or complex multiplicity are reported without designating multiplicity.

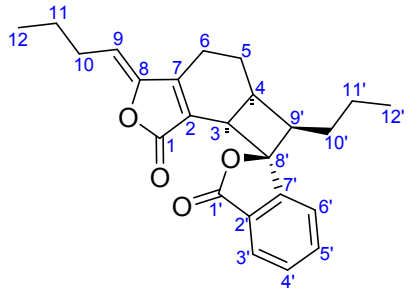


5

Table S5. NMR data of **5** in $CDCl_3$ (400 MHz for ^1H; 100 MHz for ^{13}C)

No.	δ_C, mult.	δ_H (J in Hz)*	$^1H,^1H$-COSY	HMBC	NOESY
1	168.9, qC				
2	125.6, qC				
3	125.4, CH	7.80	4, 5	1, 2, 4, 5, 7	
4	130.0, CH	7.52, td (7.6, 0.9)	3, 5, 6	2, 3, 5, 6	
5	134.5, CH	7.69, td (7.6, 0.9)	3, 4, 6	3, 4, 6, 7	
6	124.8, CH	7.82	4, 5	2, 4, 5, 7, 8	9, 10′a, 10′b
7	145.6, qC				
8	92.7, qC				
9	48.7, CH	2.91	9′, 10a, 10b	10, 11, 9′, 10′	6
10	30.6, CH_2	1.56	9, 10b, 11	8, 9, 11, 12, 9′	12
		1.61	9, 10a, 11	8, 9, 11, 12, 9′	6′a, 6′b, 12
11	20.5, CH_2	0.93	10a, 10b, 12	9, 10, 12	
12	13.9, CH_3	0.72, t (7.3)	11	10, 11	10a, 10b
1′	169.7, qC				
2′	126.1, qC				
3′	116.5, CH	6.02, dt (9.6, 1.9)	4′, 5′	1′, 2′, 4′, 5′, 7′	
4′	130.2, CH	5.89, dt (9.6, 4.2)	3′, 5′	2′, 5′, 6′	
5′	22.5, CH_2	2.35	3′, 4′, 6′a, 6′b	3′, 4′, 6′, 7′	
6′	21.7, CH_2	2.65, dt (18.7, 9.2)	5′, 6′b	2′, 4′, 5′, 7′, 8′	10b, 9′
		2.77, dt (18.7, 10.6)	5′, 6′a	2′, 4′, 5′, 7′, 8′	10b
7′	158.0, qC				
8′	92.3, qC				
9′	45.8, CH	2.90	9, 10′a, 10′b	9, 10, 10′, 11′	6′a
10′	30.8, CH_2	1.57	9′, 10′b, 11′	9, 8′, 9′, 11′, 12′	6, 12′
		1.73	9′, 10′a, 11′	9, 9′, 11′, 12′	6, 12′
11′	20.7, CH_2	1.18	10′a, 10′b, 12′	9′, 10′, 12′	
12′	14.1, CH_3	0.89, t (7.3)	11′	10′, 11′	10′a, 10′b

* Indiscernible signals from overlap or complex multiplicity are reported without designating multiplicity.



6

Table S6. NMR data of **6** in $CDCl_3$ (400 MHz for ^1H; 100 MHz for ^{13}C)

No.	δ_C, mult.	δ_H (J in Hz)*	$^1H,^1H$-COSY	HMBC	NOESY
1	168.4, qC				
2	122.4, qC				
3	38.5, CH	3.65, br d (7.9)	4, 6a	1, 2, 4, 5, 7, 7′, 8′	6′, 9′
4	32.1, CH	2.74	3, 5a, 5b, 9′	3, 6, 8′, 9′	
5	21.0, CH_2	2.08, Ha	4, 5b, 6a, 6b	3, 4, 6, 7	10′b
		2.17, Hb	4, 5a, 6a, 6b	6, 7	10′a, 10′b
6	19.7, CH_2	2.19, Ha	3, 5a, 5b, 6b	5, 7, 8	
		2.61, Hb	5a, 5b, 6a	2, 4, 5, 7, 8	9
7	154.6, qC				
8	149.1, qC				
9	112.2, CH	5.23, t (7.9)	10	7, 8, 11	6b
10	28.0, CH_2	2.31	9, 11	8, 9, 11, 12	12
11	22.3, CH_2	1.48	10, 12	9, 10, 12	
12	13.9, CH_3	0.94, t (7.4)	11	10, 11	10
1′	169.8, qC				
2′	124.9, qC				
3′	125.5, CH	7.81, br d (7.6)	4′, 5′	1′, 5′, 7′	
4′	129.4, CH	7.52, br t (7.5)	3′, 5′, 6′	2′, 6′	
5′	134.5, CH	7.73, br t (7.4)	3′, 4′, 6′	3′, 4′, 7′	
6′	121.0, CH	7.63, br d (7.6)	4′, 5′	2′, 4′, 8′	3, 9′
7′	150.7, qC				
8′	90.9, qC				
9′	47.4, CH	3.13, q (7.8)	4, 10′a, 10′b	4, 5, 7′, 8′, 10′, 11′	3, 6′
10′	26.2, CH_2	1.43, Ha	9′, 10′b, 11′a, 11′b	8′, 9′, 11′, 12′	5b, 12′
		1.48, Hb	9′, 10′a, 11′a, 11′b	8′, 9′, 11′, 12′	5a, 5b, 12′
11′	20.6, CH_2	0.93, Ha	10′a, 10′b, 11′b,	9′, 10′, 12′	
		1.02, Hb	12′	9′, 10′, 12′	
			10′a, 10′a, 11′a, 12′		
12′	14.0, CH_3	0.75, t (7.3)	11′a, 11′b	10′, 11′	10′a, 10′b

*Indiscernible signals from overlap or complex multiplicity are reported without designating multiplicity.

2. Structure elucidations of 2−6

Triangeliphthalide B (**2**) was isolated as a yellow oil. The molecular formula of **2** was established as $C_{36}H_{40}O_6$ (17 degrees of unsaturation) from its HR-ESI-MS (*m/z* 569.2900 $[M + H]^+$, calcd. for $[C_{36}H_{41}O_6]^+$: 569.2903). The NMR data of **2** are very similar to those of **1**. Detailed analyses of the 1D and 2D NMR data established the same planar structure as that of **1**. The assignments of all proton and carbon resonances are provided in **Table S2**. The geometry of the double bond of Δ^8 in **2** was assigned as *Z* configuration by the NOESY correlation between H-9 and Ha-6. In the 4,5-dihydro-1*H*,3*H*-3a,7a-ethanoisobenzofuran system, the relative configurations of C-2 and C-7 should be fixed as 2*R**, 7*R**. Furthermore, the NOESY correlations between Hb-6 and Hb-10′, and between Hb-6′ and H-9′ indicated that the relative configurations of C-2, C-7, C-8′, and C-9′ should be fixed as 2*R**, 7*R**, 8′*S**, and 9′*R**, respectively. The NOESY correlations between H-4′ and Ha-10″/Hb-10″, between Hb-5′ and H-9″, and between Ha-6′/H-9″ and H-6″ indicated that the relative configurations of C-3′, C-4′, C-8″ and C-9″ should be fixed as 3′*R**, 4′*S**, 8″*S**, and 9″*S**, respectively. The NOESY correlation between Ha-10′ and H-6″ establish the whole relative configuration of **2** as 2*R**, 7*R**, 8′*S**, 9′*R**,3′*R**, 4′*S**, 8″*S**, 9″*S**. By the same structure elucidation procedures as compound **2**, the planar structures of triangeliphthalides C–D (**3**–**4**) were established (**Figure 1**), and the relative configurations of **3**–**4** were determined as 8*R**, 9*R**, 3′*S**, 4′*R**, 8′*R**, 9′*S**, 8″*R**, 9″*S** and 8*R**, 9*R**, 3′*S**, 4′*R**, 8′*R**, 9′*S**, 8″*R**, 9″*S**, respectively. The assignments of all proton and carbon resonances are provided in **Table S3** and **Table S4**.

Diangeliphthalide A (**5**) was isolated as a yellow oil. The molecular formula of **5** was established as $C_{24}H_{26}O_4$ (11 degrees of unsaturation) from its HR-ESI-MS (*m/z* 379.1904 $[M + H]^+$, calcd. for $[C_{24}H_{27}O_4]^+$: 379.1909). Detailed analyses of the 1D and 2D NMR data (**Table S5**) established the planar structure of **5**, and the relative configuration of **5** was determined as 8*R**, 9*S**, 8′*R**, 9′*S**. Another related known phthalide dimer (compound **6**) was identified as gelispirolide by comparison of the NMR data with literature values (**Table S6**).[1] Detailed analyses of the 1D and 2D NMR data of **6** confirmed the above deduction.

3. Structural characterizations of 1−6

Triangeliphthalide A (**1**): colorless crystals (MeOH); mp 172–174 °C; [α]27 D 0.2 (*c* 0.5, $CHCl_3$); ESI-MS (positive) *m/z* 569 $[M + H]^+$; HRESIMS (positive) *m/z* 569.2910 $[M + H]^+$ (calcd. for $[C_{36}H_{41}O_6]^+$, 569.2903); ^1H and ^{13}C NMR see **Table S1**.

(+) (2*R*, 7*R*, 8′*S*, 9′*R*, 3′*R*, 4′*S*, 8″*R*, 9″*R*) **Triangeliphthalide A** (**1a**); [α]27 D +125.2 (*c* 0.5, $CHCl_3$); CD (1.5×10^{-4} M, $CHCl_3$) λ_{max} (Δε): 238 (+12.60) nm.

(−) (2*S*, 7*S*, 8′*R*, 9′*S*, 3′*S*, 4′*R*, 8″*S*, 9″*S*) **Triangeliphthalide A** (**1b**); [α]27 D −115.8 (*c* 0.5, $CHCl_3$); CD (1.5×10^{-4} M, $CHCl_3$) λ_{max} (Δε): 238 (−14.20) nm.

Triangeliphthalide B (**2**): yellow oil; [α]27 D 0.2 (*c* 0.5, $CHCl_3$); ESI-MS (positive) *m/z* 591 $[M + Na]^+$; HRESIMS (positive) *m/z* 569.2900 $[M + H]^+$ (calcd. for $[C_{36}H_{41}O_6]^+$, 569.2903); ^1H and ^{13}C NMR see **Table S2**.

(+) (2*R*, 7*R*, 8'*S*, 9'*R*, 3'*R*, 4'*S*, 8"*S*, 9"*S*) **Triangeliphthalide B** (**2a**); [α]27 D +158.2 (*c* 0.5, $CHCl_3$); CD (1.5×10^{-4} M, $CHCl_3$) λ_{max} (Δε): 246 (+24.00) nm.

(−) (2*S*, 7*S*, 8'*R*, 9'*S*, 3'*S*, 4'*R*, 8"*R*, 9"*R*) **Triangeliphthalide B** (**2b**); [α]27 D −164.0 (*c* 0.5, $CHCl_3$); CD (1.5×10^{-4} M, $CHCl_3$) λ_{max} (Δε): 246 (−23.46) nm.

Triangeliphthalide C (**3**): yellow oil; [α]27 D 0.3 (*c* 0.5, $CHCl_3$); ESI-MS (positive) *m/z* 591 $[M + Na]^+$; HRESIMS (positive) *m/z* 591.2725 $[M + Na]^+$ (calcd. for $[C_{36}H_{40}O_6Na]^+$, 591.2723); ^1H and ^{13}C NMR see **Table S3**.

(−) (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*) **Triangeliphthalide C** (**3a**); [α]27 D −56.5 (*c* 0.5, $CHCl_3$); CD (1.5×10^{-4} M, $CHCl_3$) λ_{max} (Δε): 234 (−4.62), 258 (+2.65), 307 (−0.31) nm.

(+) (8*S*, 9*S*, 3'*R*, 4'*S*, 8'*S*, 9'*R*, 8"*S*, 9"*R*) **Triangeliphthalide C** (**3b**); [α]27 D +58.8 (*c* 0.5, $CHCl_3$); CD (1.5×10^{-4} M, $CHCl_3$) λ_{max} (Δε): 234 (+3.72), 258 (−2.60), 307 (+0.53) nm.

Triangeliphthalide D (**4**): yellow oil; [α]27 D 0.3 (*c* 0.5, $CHCl_3$); ESI-MS (positive) *m/z* 589 $[M + Na]^+$; HRESIMS (positive) *m/z* 589.2564 $[M + Na]^+$ (calcd. for $[C_{36}H_{40}O_6Na]^+$, 589.2566); ^1H and ^{13}C NMR see **Table S4**.

(+) (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*) **Triangeliphthalide D** (**4a**); [α]27 D +69.8 (*c* 0.5, $CHCl_3$); CD (1.5×10^{-4} M, $CHCl_3$) λ_{max} (Δε): 247 (+4.07), 279 (+5.65), 286 (+5.60) nm.

(−) (8*S*, 9*S*, 3'*R*, 4'*S*, 8'*S*, 9'*R*, 8"*S*, 9"*R*) **Triangeliphthalide D** (**4b**); [α]27 D −72.5 (*c* 0.5, $CHCl_3$); CD (1.5×10^{-4} M,

$CHCl_3$) λ_{max} ($\Delta\varepsilon$): 247 (–4.21), 279 (–4.89), 286 (–4.94) nm.

Diangeliphthalide A (**5**): yellow oil; [α]25 D 0 (*c* 0.5, $CHCl_3$); ESI-MS (positive) *m/z* 401 $[M + Na]^+$; HR-ESI-MS (positive) *m/z*379.1904 $[M+H]^+$ (calcd. for $[C_{24}H_{27}O_4]^+$, 379.1909); ^1H and ^{13}C NMR see **Table S5**.

(−) (8*R*, 9*S*, 8′*R*, 9′*S*) **Diangeliphthalide A** (**5a**); [α]27 D–43.8 (*c* 0.3, $CHCl_3$); CD (5.2×10^{-4} M, $CHCl_3$) λ_{max} ($\Delta\varepsilon$): 243 (+5.55), 285 (+2.06) nm, 304 (−0.41) nm.

(+) (8*S*, 9*R*, 8′*S*, 9′*R*) **Diangeliphthalide A** (**5b**); [α]27 D+42.0 (*c* 0.3, $CHCl_3$); CD (5.2×10^{-4} M, $CHCl_3$) λ_{max} ($\Delta\varepsilon$): 243 (–6.07), 286(–2.24) nm, 304 (+0.49) nm.

Gelispirolide (**6**): yellow oil; [α]25 D 0 (*c* 0.5, $CHCl_3$); ESI-MS (positive) *m/z* 401 $[M + Na]^+$; HR-ESI-MS (positive) *m/z*401.1743 $[M+Na]^+$ (calcd. for $[C_{24}H_{26}O_4Na]^+$, 401.1729); ^1H and ^{13}C NMR see **Table S6**. The NMR data of **6** was consistent with those of literature values[1].

(−) (3*S*, 4*R*, 8′*S*, 9′*S*) **Gelispirolide** (**6a**); [α]27 D–59.2 (*c* 1.0, $CHCl_3$); CD (1.5×10^{-4} M, $CHCl_3$) λ_{max} ($\Delta\varepsilon$): 275 (−4.50) nm.

(+) (3*R*, 4*S*, 8′*R*, 9′*R*) **Gelispirolide** (**6b**); [α]27 D+61.9 (*c* 1.0, $CHCl_3$); CD (1.5×10^{-4} M, $CHCl_3$) λ_{max} ($\Delta\varepsilon$): 275 (+4.33) nm.

4. General experimental procedures

Methanol (MeOH) was purchased from Yuwang Industrial Co. Ltd (Yucheng, China). Acetonitrile (MeCN) was obtained from Oceanpak Alexative Chemical Co. Ltd (Gothenburg, Sweden). Ethanol (EtOH), Ethyl acetate (EtOAc), Cyclohexane, Petroleum ether, and chloroform ($CHCl_3$) were analytical grade from Fine Chemical Co. Ltd (Tianjin, China).

Melting points were measured on a BÜCHI B-545 melting point measurement (BÜCHI Labortechnik AG, Flawil, Switzerland) without correction. UV data were recorded by using a JASCO V-550 UV/vis spectrometer (Jasco International Co. Ltd, Tokyo, Japan). IR data were recorded on a JASCO FT/IR-480 plus spectrometer (Jasco International Co. Ltd, Tokyo, Japan). Optical rotations were measured on a JASCO P1020 digital polarimeter (Jasco International Co. Ltd, Tokyo, Japan). ECD spectra were recorded in $CHCl_3$ by using a JASCO J-810 spectrophotometer (Jasco International Co. Ltd, Tokyo, Japan) at room temperature. ESIMS spectra were obtained on Finnigan LCQ Advantage MAX mass spectrometer (Finnigan MAT GmbH, Bremen, Germany). HRESIMS spectra were obtained on Waters Synapt G2 TOF mass spectrometer (Waters Corporation, Milford, USA). 1D and 2D NMR spectra were acquired with Bruker AV 400, and Bruker AV 600 spectrometers (Bruker BioSpin Group, Faellanden, Switzerland) by using the solvent signals ($CDCl_3$: δ_H 7.26/δ_C 77.0) as internal standards. Column chromatography (CC) was carried out on silica gel (200–300 mesh) (Qingdao Haiyang Chemical Group Corporation, Qingdao, China), and HP-20 (Mitsubishi Chemical Co. Ltd. Japan). TLC was performed on precoated silica gel plate (SGF254, 0.2 mm, Yantai Chemical Industry Research Institute, China). Analytical HPLC was performed on a Dionex HPLC system equipped with an Ultimate 3000 pump, an Ultimate 3000 diode array detector, an Ultimate 3000 column compartment, an Ultimate 3000 autosampler (Dionex, USA), and an Alltech (Grace) 2000ES evaporative light scattering detector (Alltech USA) by using a Phenomenex Gemini C_{18} column (4.6 × 250 mm, 5 μm), a Phenomenex Biphenyl column (4.6 × 250 mm, 5 μm), a Phenomenex Cellulose-2 column (4.6 × 250 mm, 3 μm), and a Phenomenex Amylose-2 column (4.6 × 250 mm, 5 μm). Semi-preparative HPLC was carried out on Shimadzu LC-6AD system equipped with UV detectors, using a Phenomenex Biphenyl column (10.0 × 250 mm, 5 μm). Preparative HPLC was carried out on Shimadzu LC-6AD system equipped with UV detectors, using a Phenomenex Gemini C_{18} column (21.2 × 250 mm, 5 μm). Medium pressure liquid chromatography (MPLC) was performed on ODS column (4.0 × 30 cm, 50 μm) and equipped with a dual pump gradient system, a UV preparative detector, and a Dr Flash II fraction collector system (Shanghai Lisui E-Tech Co., Ltd.).

5. Plant material

The dried root of *Angelica sinensis* was collected from GAP base (CFDA, No. 5, 5.23, 2014.) of *Angelica sinensis* from Zhanyi County of Yunnan province in China by Zhanyi Yikang Chinese Herbal Medicine Co. Ltd. in November 2014. The plant materials were identified by associate Professor Ying Zhang in the College of Pharmacy, Jinan University, Guangzhou, China.

6. Extraction and isolation

The dried root of *Angelica sinensis* (45.0 kg) was refluxed four times with 125 L of 95% EtOH–H_2O for 2 h each time. After filtration, the EtOH was removed under reduced pressure to yield a concentrated solution (10 L). The solution was passed through a HP-20 macroporous resin column (20 × 125 cm) and successively eluted with 0, 40, and 95% EtOH–H_2O, yielding three fractions (F1–F3, 3.8, 0.4, and 1.6 kg, respectively). A portion (800.0 g) of F3 was subjected to open silica-gel CC, which was eluted with Cyclohexane–EtOAc–MeOH (39:1:0, 0:100:0, and 0:0:100) to yield three fractions (F3.1–F3.3, 271.9, 383.3, and 117.7 g, respectively). F3.2 was subjected to silica-gel CC, which was eluted with Petroleum ether–EtOAc–MeOH (98:2:0, 95:5:0, 91:9:0, 80:20:0, 70:30:0, 60:40:0, 50:50:0, 0:100:0, and 0:0:100) to yield nine fractions (F3.2.1–F3.2.9, 1.2, 30.3, 60.3, 80.5, 40.3, 30.3, 33.3, 41.3, and 31.3 g, respectively). A portion (70.5 g) of F3.2.4 was subjected to MPLC, which was eluted successively with MeOH–H_2O (60:40, 70:30, 80:20, 90:10, and 100:0) to yield five fractions (F3.2.4.1–F3.2.4.5, 13.9, 36.3, 5.7, 3.6, and 5.4 g respectively). F3.2.4.2 was subjected to MPLC, which was eluted with MeOH–H_2O (70:30) for 500 min to yield six fractions (F3.2.4.2.1–F3.2.4.2.6, 4.3, 5.1, 8.1, 8.2, 4.3, and 5.3 g respectively). F3.2.4.2.3 was separated using preparative HPLC eluted with MeOH–H_2O (60:40, v/v) at a flow rate of 8 mL/min to yield two fractions (F3.2.4.2.3.1–F3.2.4.2.3.2, 3.8, and 4.1 g respectively). F3.2.4.2.2 was isolated using semi-preparative HPLC eluted with MeOH–H_2O (70:30, v/v) at a flow rate of 3 mL/min to yield **5** (t_R: 40.5 min, 10.0 mg) and **6** (t_R: 46.3 min, 5.0 mg). F3.2.4.3 was subjected to MPLC, which was eluted with MeOH–H_2O (80:20) for 500 min to yield three fractions (F3.2.4.3.1–F3.2.4.3.3, 0.3, 2.1, and 3.1 g, respectively). F3.2.4.3.2 was subjected to open silica-gel CC, which was eluted successively with $CHCl_3$–MeOH (119:1, 99:1, 98:2, 95:5, 1:1, and 0:100) to yield six fractions (F3.2.4.3.2.1–F3.2.4.3.2.6, 660.5, 400.2, 300.4, 100.2, 87.0, and 356.5 mg, respectively). F3.2.4.3.2.1 was isolated by using semi-preparative HPLC eluted with MeCN–H_2O (75:25, v/v) at a flow rate of 3 mL/min to yield **3** (t_R: 75.2 min, 12.5 mg) and **4** (t_R: 85.2 min, 8.6 mg). F3.2.4.3.2.2 was isolated by using semi-preparative HPLC eluted with MeCN–H_2O (80:20, v/v) at a flow rate of 3 mL/min to yield **1** (t_R: 80.4 min, 10.5 mg) and **2** (t_R: 85.6 min, 5.6 mg).

7. Chiral separations of 1–6

The chiral HPLC separations of compounds **1–6** were separated successfully to give **1a** (t_R: 11.2 min [α]27 D= +125.2 (*c* 0.5, $CHCl_3$)) / **1b** (t_R: 13.7 min [α]27 D = –115.8 (*c* 0.5, $CHCl_3$)) by using a Phenomenex Cellulose-2 column (3 μm, 250 × 4.6 mm) at the rate of 1 mL/min, and **2a** (t_R: 7.5 min [α]27 D= +158.2 (*c* 0.5, $CHCl_3$)) / **2b** (t_R: 9.8 min [α]27 D = –164.0 (*c* 0.5, $CHCl_3$)), **3a** (t_R: 5.2 min [α]27 D= –56.5 (*c* 0.5, $CHCl_3$)) / **3b** (t_R: 7.2 min [α]27 D = +58.8 (*c* 0.5, $CHCl_3$)), **4a** (t_R: 5.2 min [α]27 D= +69.8 (*c* 0.5, $CHCl_3$)) / **4b** (t_R: 6.5 min [α]27 D = –72.5 (*c* 0.5, $CHCl_3$)), **5a** (t_R: 12.4 min [α]27 D= –43.8 (*c* 0.3, $CHCl_3$)) / **5b** (t_R: 14.0 min [α]27 D = +42.0 (*c* 0.3, $CHCl_3$), and **6a** (t_R: 8.1 min [α]27 D= –59.2 (*c* 1.0, $CHCl_3$)) / **6b** (t_R: 9.9 min [α]27 D = +61.9 (*c* 1.0, $CHCl_3$)) by using a Phenomenex Amylose-2 column (5 μm, 250 × 4.6 mm) at the rate of 1 mL/min, respectively.

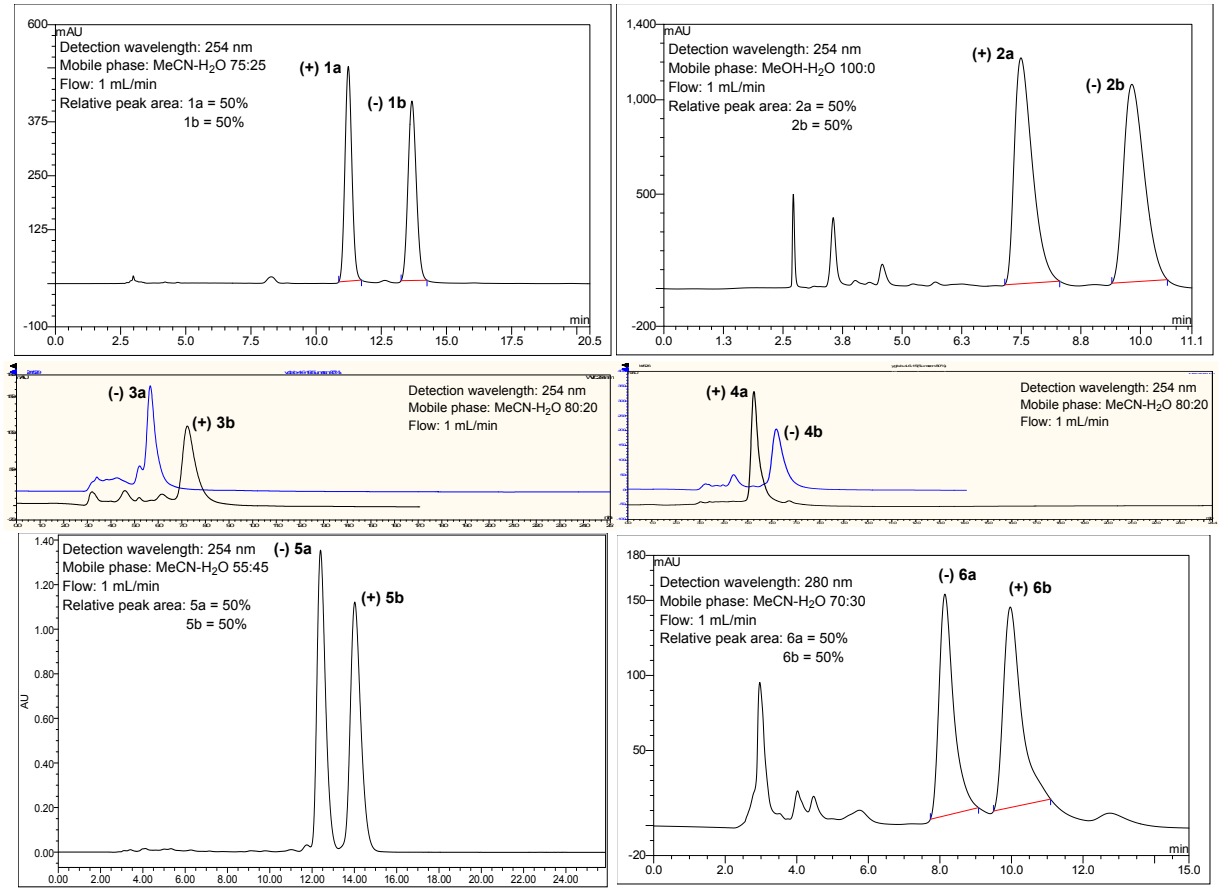


Figure S1. The chiral HPLC chromatograms of **1–6**

8. X-ray crystallographic analysis of 1

Upon crystallization from MeOH using the vapor diffusion method, colorless needle-like crystals of **1** were obtained. Data were collected by using a Sapphire CCD with graphite monochromated Cu Kα radiation, λ = 1.54184 Å at 173.00(10) K. Crystal data:$C_{36}H_{40}O_6$, M = 568.68, space group monoclinic, *Cc*; unit cell dimensions were determined to be a = 13.1653(12) Å, b = 27.523(2) Å, c = 8.5035(7)Å, α = 90.00 °, β = 102.221(9) °, γ = 90.00 °, V = 3011.5(5) Å^3, Z = 4, Dx = 1.254 g/cm^3, F (000) = 1216.0, μ(Cu Kα) = 0.676 mm^{-1}.23463 reflections were collected to θ_{max} = 63.14°, in which 4147 independent unique reflections (R_{int} = 0.0895, R_{sigma} = 0.0402) were used in all calculations. The structure was solved by direct methods using the SHELXS program, and refined by the SHELXL program and full-matrix least-squares calculations.[2] In the structure refinements, hydrogen atoms were placed on the geometrically ideal positions by the "ride on" method. The final refinement gave R_1 = 0.0502 (I > 2σ(I)), $_wR_2$ = 0.1208 (all data), S = 1.067. Crystallographic data for triangeliphthalide A (**1**) have been deposited in the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1883156. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033, or e-mail: deposit@ccdc.cam.ac.uk).

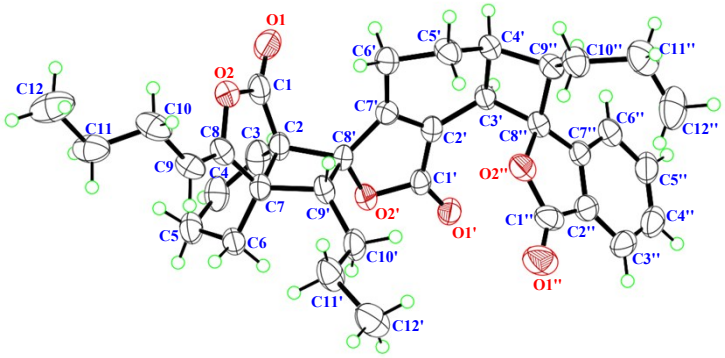


Figure S2. X-ray crystallographic analysis of **1**

9. Conformational analysis and quantum chemical ^{13}C NMR calculation of 1

The molecules of (2*R**, 7*R**, 8'*S**, 9'*R**, 3'*R**, 4'*S**, 8"*R**, 9"*R**)–**1**–**A** and (2*R**, 7*R**, 8'*S**, 9'*R**, 3'*S**, 4'*R**, 8"*S**, 9"*S**)–**1**–**B** were converted into SMILES codes before their initial 3D structures were generated with CORINA version 3.4. Conformer databases were generated in CONFLEX version 7.0 by using the MMFF94s force-field, with an energy window for acceptable conformers (ewindow) of 2 kcal/mol above the ground state, a maximum number of conformations per molecule (maxconfs) of 100, and an RMSD cutoff (rmsd) of 0.5Å. Then each acceptable conformer was optimized with HF/6-31G(d) method in Gaussian09.[3] Further optimization at the B3LYP/6-31G(d) level determined the dihedral angles. From this, (22 for A and 19 for B) stable conformers were determined. The optimized conformers (22 for A and 19 for B) were used for ^{13}C NMR calculations, which were performed with Gaussian09 (B3LYP/6-31+G(d, p)). The solvent effects were taken into account by the polarizable-conductor calculation model (PCM, chloroform as the solvent). The comparison was judged by DP4+ probability.[4]

Table S7. The Boltzmann distribution for two possible structures (**1**–**A** and **1**–**B**) of triangeliphthalide A (**1**)

1–A				**1–B**			
conformers	contribution %	conformers	contribution %	conformers	contribution %	conformers	contribution %
1	12.15	12	2.09	1	18.38	12	2.72
2	12.13	13	1.82	2	17.31	13	2.61
3	10.98	14	1.78	3	12.27	14	1.73
4	7.44	15	1.72	4	10.29	15	1.58
5	7.43	16	1.68	5	6.17	16	1.48
6	6.83	17	1.51	6	4.26	17	1.43
7	6.57	18	1.50	7	4.03	18	1.36
8	6.17	19	1.46	8	3.67	19	1.06
9	4.52	20	1.36	9	3.49		
10	4.35	21	1.32	10	3.39		
11	4.02	22	1.17	11	2.77		

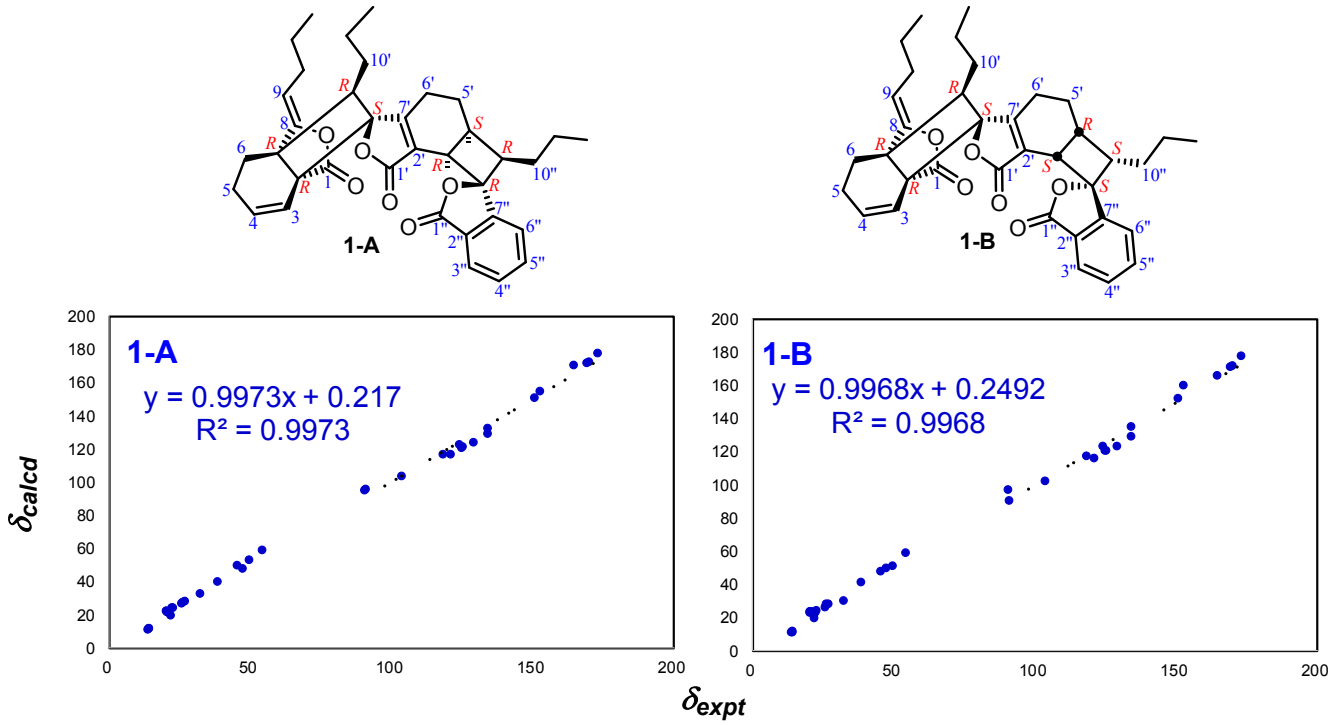


Figure S3. Linear correlation plots of calculated vs experimental ^{13}C NMR chemical shift values for **1**–**A**/**1**–**B** of triangeliphthalide A (**1**).

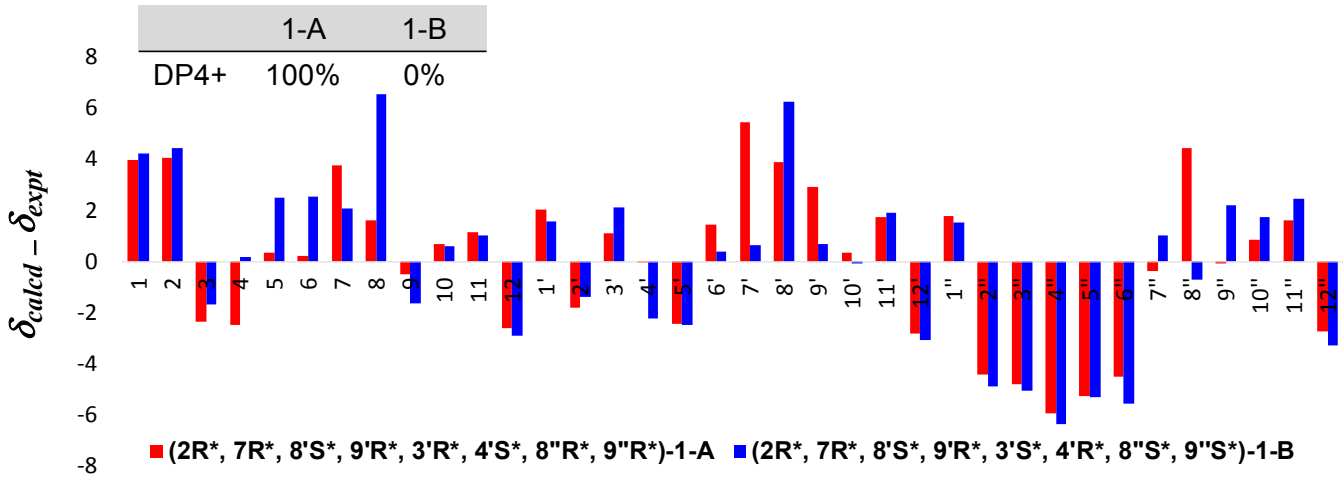


Figure S4. Relative errors between the calculated ^{13}C NMR chemical shifts of **1-A**/**1-B** and the recorded ^{13}C NMR data of **1**, and the DP4+ Probability analysis.

10. Quantum chemical ECD calculations of 1′–6′

10.1. Quantum chemical ECD calculation of 1′

The molecules of (2*R*, 7*R*, 8'*S*, 9'*R*, 3'*R*, 4'*S*, 8"*R*, 9"*R*)–**1′** and (2*S*, 7*S*, 8'*R*, 9'*S*, 3'*S*, 4'*R*, 8"*S*, 9"*S*)–**1′** were converted into SMILES codes before their initial 3D structures were generated with CORINA version 3.4. Conformer databases were generated in CONFLEX version 7.0 by using the MMFF94s force-field, with an energy window for acceptable conformers (ewindow) of 5 kcal/mol above the ground state, a maximum number of conformations per molecule (maxconfs) of 100, and an RMSD cutoff (rmsd) of 0.5Å. Then each acceptable conformer was optimized with HF/6-31G(d) method in Gaussian09.[3] Further optimization at the APFD/6-31G(d) level determined the dihedral angles. From this, eight stable conformers were determined. The optimized conformers were used for the ECD calculations, which were performed with Gaussian09 (APFD/6-311++G(2d,p)). The solvent effects were taken into account by the polarizable-conductor calculation model (IEFPCM, chloroform as the solvent). Comparisons of the experimental and calculated spectra were performed with the software SpecDis.[5, 6] This was also used to apply a UV shift to the ECD spectra, Gaussian broadening of the excitations, and Boltzmann weighting of the spectra.

Table S8. Stable conformers of (2*R*, 7*R*, 8'*S*, 9'*R*, 3'*R*, 4'*S*, 8"*R*, 9"*R*)-**1′** at the APFD/6-31G(d) level in $CHCl_3$

conformers	contribution %	conformers	contribution %
1	53.70	5	3.26
2	19.66	6	3.02
3	12.05	7	2.54
4	4.73	8	1.04

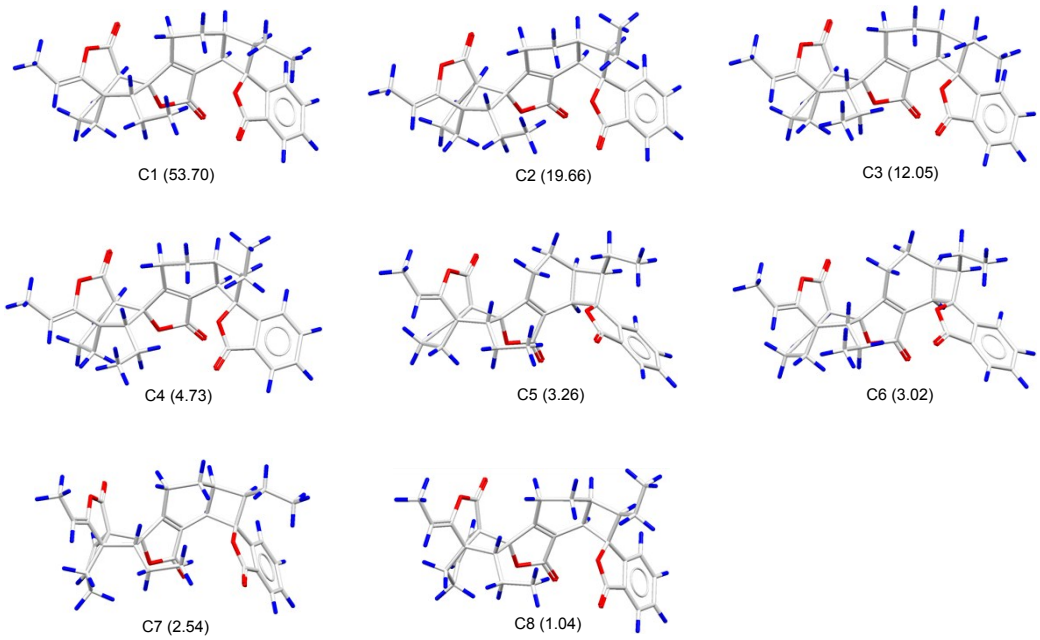
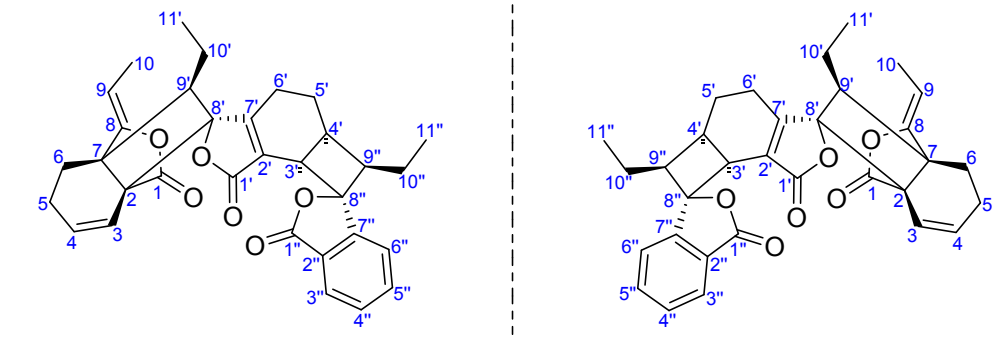


Figure S5. Stable conformers of (2*R*, 7*R*, 8'*S*, 9'*R*, 3'*R*, 4'*S*, 8"*R*, 9"*R*)-**1′** (the relative populations are in parentheses)



(2R, 7R, 8'S, 9'R, 3'R, 4'S, 8"R, 9"R)-1'

(2S, 7S, 8'R, 9'S, 3'S, 4'R, 8"S, 9"S)-1'

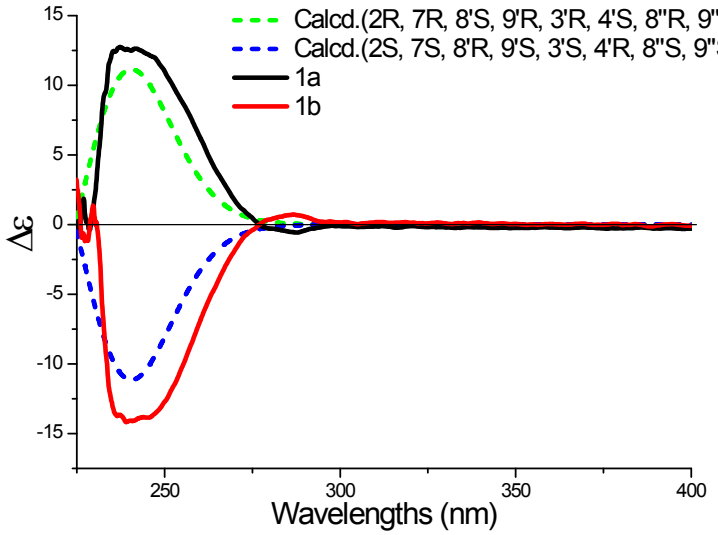


Figure S6. Experimental ECD spectra of **1a** and **1b**, and calculated ECD spectra of (2*R*, 7*R*, 8'*S*, 9'*R*, 3'*R*, 4'*S*, 8"*R*, 9"*R*)-**1′** and (2*S*, 7*S*, 8'*R*, 9'*S*, 3'*S*, 4'*R*, 8"*S*, 9"*S*)–**1′** (UV correction = – 20 nm, band width σ = 0.3 eV)

10.2. Quantum chemical ECD calculation of 2′

The molecules of (2*R*, 7*R*, 8'*S*, 9'*R*, 3'*R*, 4'*S*, 8"*S*, 9"*S*)–**2′** and (2*S*, 7*S*, 8'*R*, 9'*S*, 3'*S*, 4'*R*, 8"*R*, 9"*R*)–**2′** were converted into SMILES codes before their initial 3D structures were generated with CORINA version 3.4. Conformer databases were generated in CONFLEX version 7.0 by using the MMFF94s force-field, with an energy window for acceptable conformers (ewindow) of 5 kcal/mol above the ground state, a maximum number of conformations per molecule (maxconfs) of 100, and an RMSD cutoff (rmsd) of 0.5Å. Then each acceptable conformer was optimized with HF/6-31G(d) method in Gaussian09.[3] Further optimization at the wb97XD/6-31G(d) level determined the dihedral angles. From this, five stable conformers were determined. The optimized conformers were used for the ECD calculations, which were performed with Gaussian09 (wb97XD/TZVP). The solvent effects were taken into account by the polarizable-conductor calculation model (IEFPCM, chloroform as the solvent). Comparisons of the experimental and calculated spectra were performed with the software SpecDis.[5, 6] It was also used to apply a UV shift to the ECD spectra, Gaussian broadening of the excitations, and Boltzmann weighting of the spectra.

Table S9. Stable conformers of (2*R*, 7*R*, 8'*S*, 9'*R*, 3'*R*, 4'*S*, 8"*S*, 9"*S*)-**2′** at the wb97XD/6-31G(d) level in $CHCl_3$

conformers	contribution %	conformers	contribution %
1	38.45	4	13.38
2	28.12	5	1.72
3	18.33		

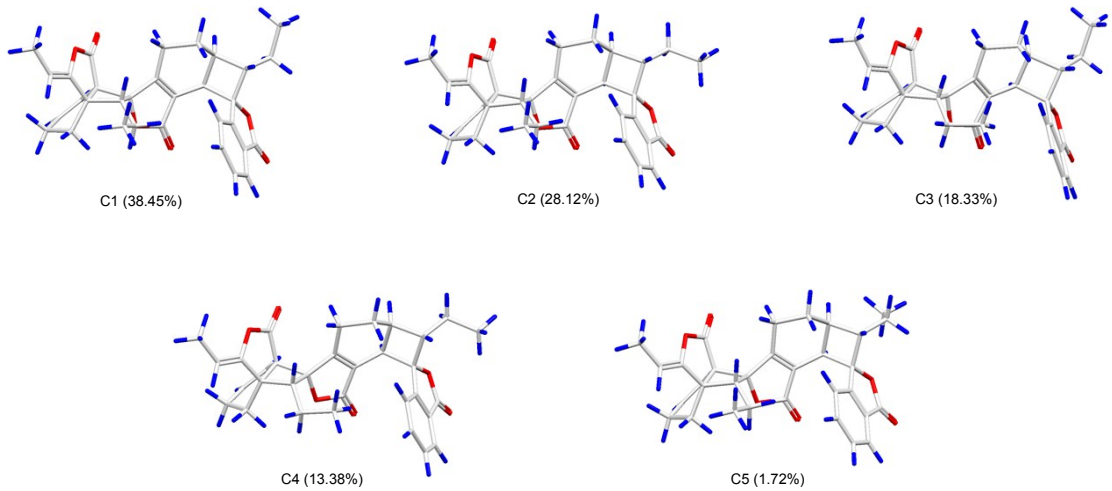
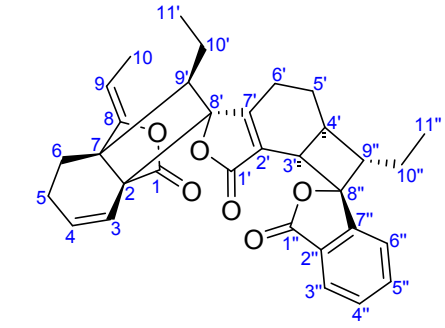
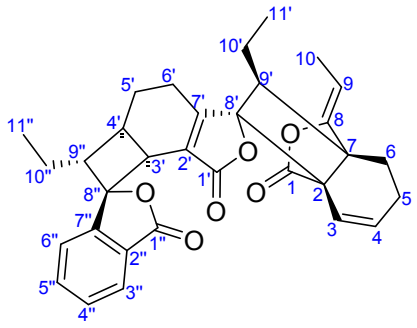


Figure S7. Stable conformers of (2*R*, 7*R*, 8'*S*, 9'*R*, 3'*R*, 4'*S*, 8"*S*, 9"*S*)-**2′** (the relative populations are in parentheses)



(2R, 7R, 8'S, 9'R, 3'R, 4'S, 8"S, 9"S)-2'



(2S, 7S, 8'R, 9'S, 3'S, 4'R, 8"R, 9"R)-2'

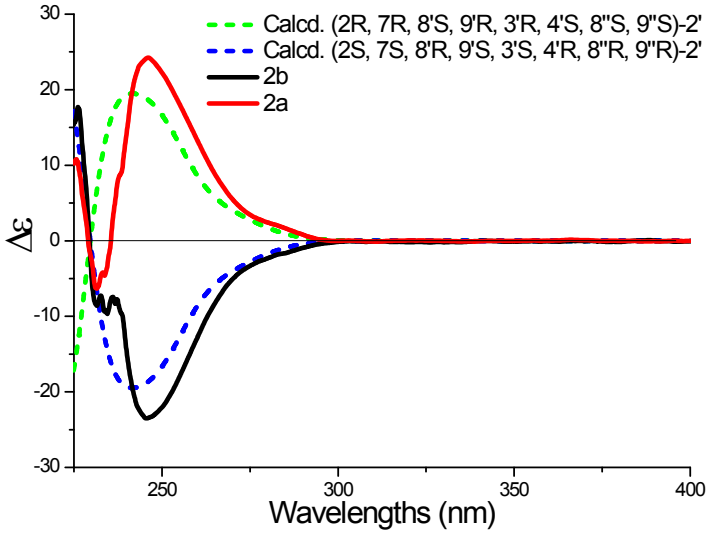


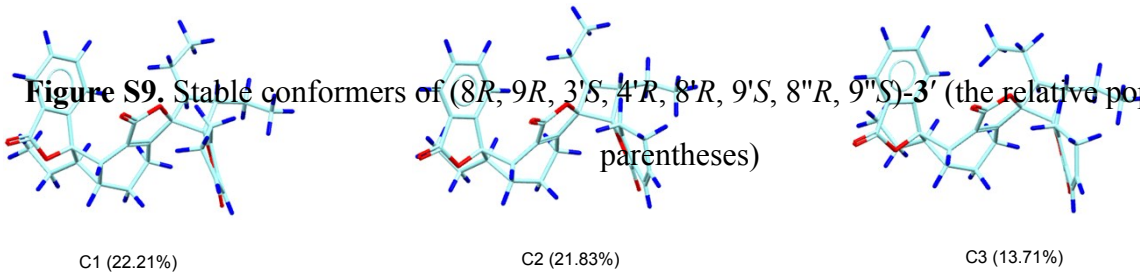
Figure S8. Experimental ECD spectra of **2a** and **2b**, and calculated ECD spectra of (2*R*, 7*R*, 8'*S*, 9'*R*, 3'*R*, 4'*S*, 8"*S*, 9"*S*)-**2′** and (2*S*, 7*S*, 8'*R*, 9'*S*, 3'*S*, 4'*R*, 8"*R*, 9"*R*)–**2′** (UV correction = +25 nm, band width σ = 0.3 eV)

10.3. Quantum chemical ECD calculation of 3′

The molecules of (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*)–**3′** and (8*S*, 9*S*, 3'*R*, 4'*S*, 8'*S*, 9'*R*, 8"*S*, 9"*R*)–**3′** were converted into SMILES codes before their initial 3D structures were generated with CORINA version 3.4. Conformer databases were generated in CONFLEX version 7.0 by using the MMFF94s force-field, with an energy window for acceptable conformers (ewindow) of 5 kcal/mol above the ground state, a maximum number of conformations per molecule (maxconfs) of 100, and an RMSD cutoff (rmsd) of 0.5Å. Then each acceptable conformer was optimized with HF/6-31G(d) method in Gaussian09.[3] Further optimization at the APFD/6-31G(d) level determined the dihedral angles. From this, twelve stable conformers were determined. The optimized conformers were used for the ECD calculations, which were performed with Gaussian09 (APFD/6-311++G(2d,p)). The solvent effects were taken into account by the polarizable-conductor calculation model (IEFPCM, chloroform as the solvent). Comparisons of the experimental and calculated spectra were performed with the software SpecDis.[5, 6] It was also used to apply a UV shift to the ECD spectra, Gaussian broadening of the excitations, and Boltzmann weighting of the spectra.

Table S10. Stable conformers of (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*)-**3′** at the APFD/6-31G(d) in the solvated model in $CHCl_3$

conformers	contribution %	conformers	contribution %
1	22.21	7	3.52
2	21.83	8	3.35
3	13.71	9	3.09
4	11.67	10	3.05
5	7.01	11	2.38
6	6.09	12	2.09



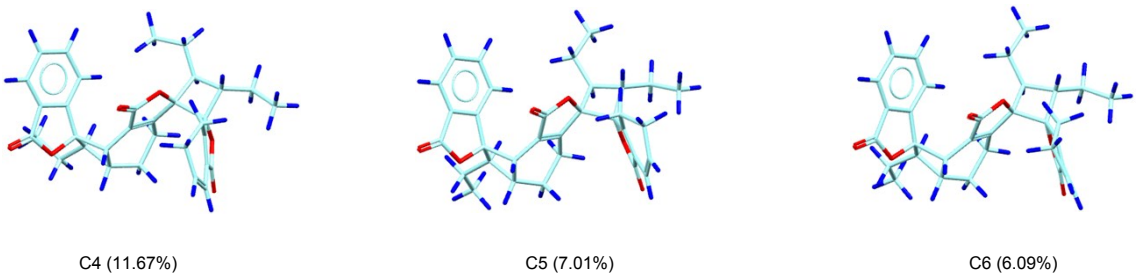
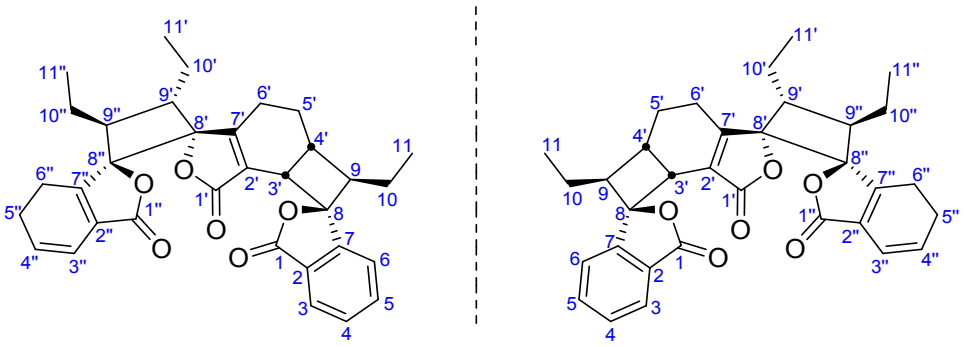


Figure S9. Stable conformers of (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*)-**3′** (the relative populations are in parentheses)



(8R, 9R, 3'S, 4'R, 8'R, 9'S, 8"R, 9"S)-3'

(8S, 9S, 3'R, 4'S, 8'S, 9'R, 8"S, 9"R)-3'

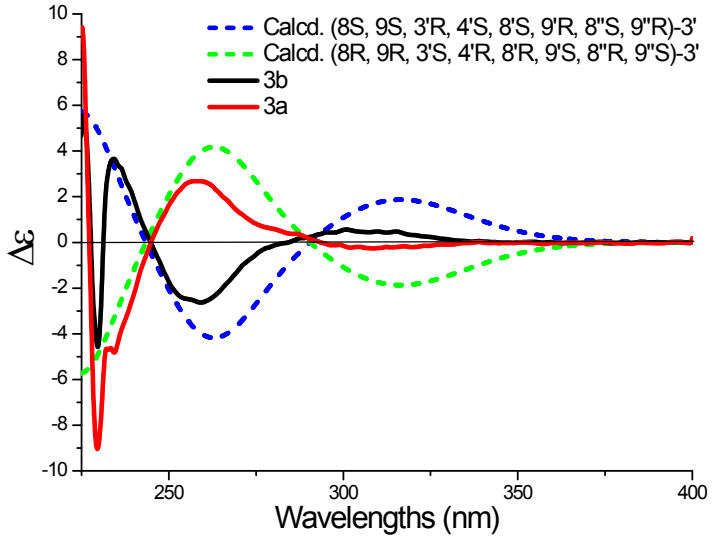


Figure S10. Experimental ECD spectra of **3a** and **3b**, and calculated ECD spectra of (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*) –**3′** and (8*S*, 9*S*, 3'*R*, 4'*S*, 8'*S*, 9'*R*, 8"*S*, 9"*R*)–**3′** (UV correction = –10 nm, band width σ = 0.3 eV)

10.4. Quantum chemical ECD calculation of 4′

The molecules of (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*)–**4′** and (8*S*, 9*S*, 3'*R*, 4'*S*, 8'*S*, 9'*R*, 8"*S*, 9"*R*)–**4′** were converted into SMILES codes before their initial 3D structures were generated with CORINA version 3.4. Conformer databases were generated in CONFLEX version 7.0 by using the MMFF94s force-field, with an energy window for acceptable conformers (ewindow) of 5 kcal/mol above the ground state, a maximum number of conformations per molecule (maxconfs) of 100, and an RMSD cutoff (rmsd) of 0.5Å. Then each acceptable conformer was optimized with HF/6-31G(d) method in Gaussian09.[3] Further optimization at the wb97XD/6-31G(d) level determined the dihedral angles. From this, nine stable conformers were determined. The optimized conformers were used for the ECD calculations, which were performed with Gaussian09 (wb97XD/TZVP). The solvent effects were taken into account by the polarizable-conductor calculation model (IEFPCM, chloroform as the solvent). Comparisons of the experimental and calculated spectra were performed with the software SpecDis.[5, 6] It was also used to apply a UV shift to the ECD spectra, Gaussian broadening of the excitations, and Boltzmann weighting of the spectra.

Table S11. Stable conformers of (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*)-**4′** at the wb97XD/6-31G(d) in solvated model in $CHCl_3$

conformers	contribution %	conformers	contribution %
1	44.94	6	3.26
2	17.51	7	2.22
3	16.42	8	1.62
4	7.92	9	1.31
5	4.81		

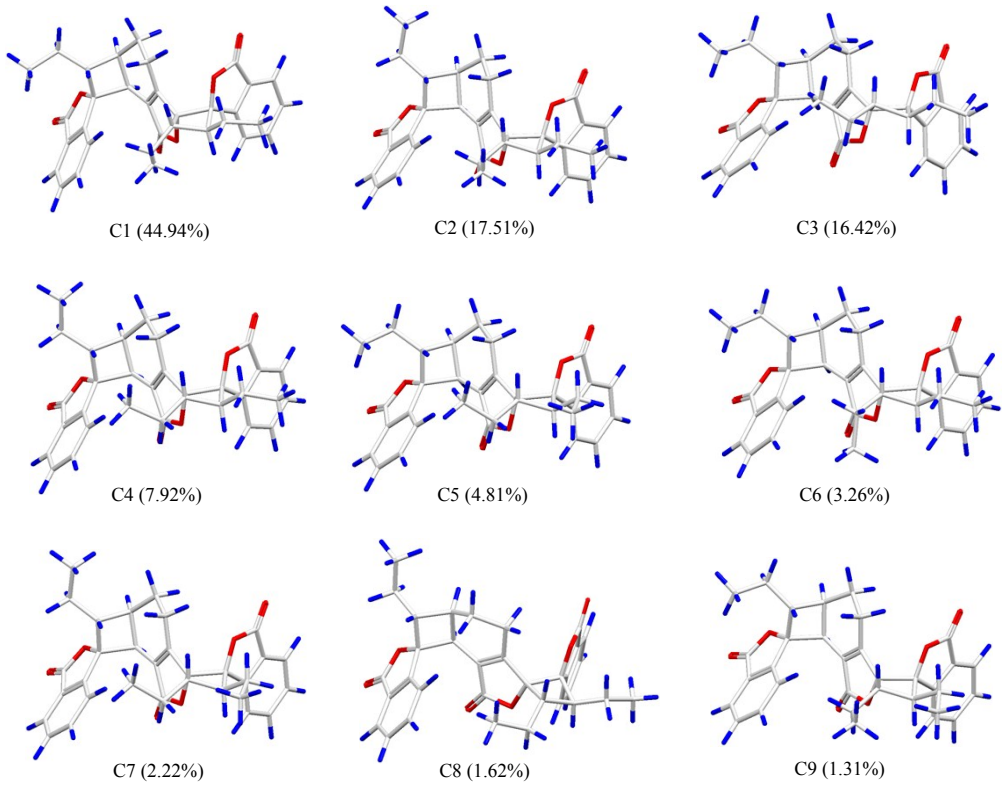
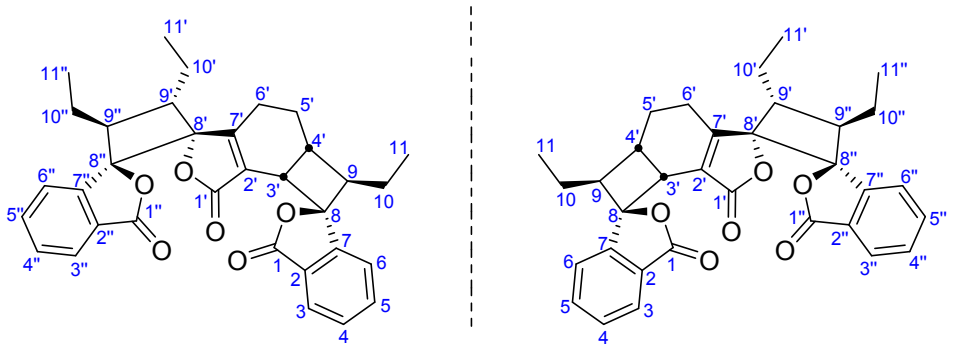


Figure S11. Stable conformers of (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*)-**4′** (the relative populations are in parentheses)



(8R, 9R, 3'S, 4'R, 8'R, 9'S, 8"R, 9"S)-4' (8S, 9S, 3'R, 4'S, 8'S, 9'R, 8"S, 9"R)-4'

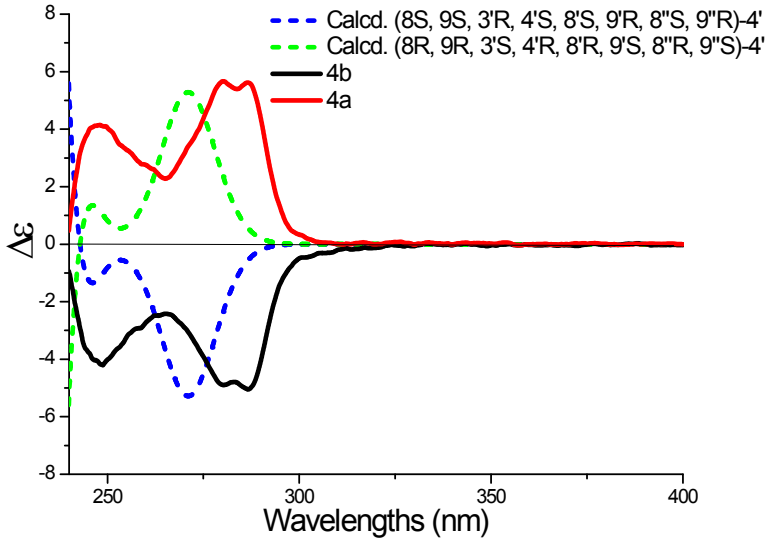


Figure S12. Experimental ECD spectra of **4a** and **4b**, and calculated ECD spectra of (8*R*, 9*R*, 3'*S*, 4'*R*, 8'*R*, 9'*S*, 8"*R*, 9"*S*)-**4′** and (8*S*, 9*S*, 3'*R*, 4'*S*, 8'*S*, 9'*R*, 8"*S*, 9"*R*)–**4′** (UV correction = +25 nm, band width σ = 0.3 eV)

10.5. Quantum chemical ECD calculation of 5′

The molecules of (8*R*, 9*S*, 8′*R*, 9′*S*)–**5′** and (8*S*, 9*R*, 8′*S*, 9′*R*)–**5′** were converted into SMILES codes before their initial 3D structures were generated with CORINA version 3.4. Conformer databases were generated in CONFLEX version 7.0 by using the MMFF94s force-field, with an energy window for acceptable conformers (ewindow) of 5 kcal/mol above the ground state, a maximum number of conformations per molecule (maxconfs) of 100, and an RMSD cutoff (rmsd) of 0.5Å. Then each acceptable conformer was optimized with HF/6-31G(d) method in Gaussian09.[3] Further optimization at the B3LYP/6-31G(d) level determined the dihedral angles. From this, eight stable conformers were determined. The optimized conformers were used for the ECD calculations, which were performed with Gaussian09 (B3LYP/TZVP). The solvent effects were taken into account by the polarizable-conductor calculation model (IEFPCM, chloroform as the solvent). Comparisons of the experimental and calculated spectra were performed with the software SpecDis.[5, 6] It was also used to apply a UV shift to the ECD spectra, Gaussian broadening of the excitations, and Boltzmann weighting of the spectra.

Table S12. Stable conformers of (8*R*, 9*S*, 8′*R*, 9′*S*)-**5′** at the B3LYP/6-31G(d) in solvated model in $CHCl_3$

conformers	contribution %	conformers	contribution %
1	22.49	5	13.36
2	19.74	6	13.27
3	14.59	7	1.57
4	13.51	8	1.49

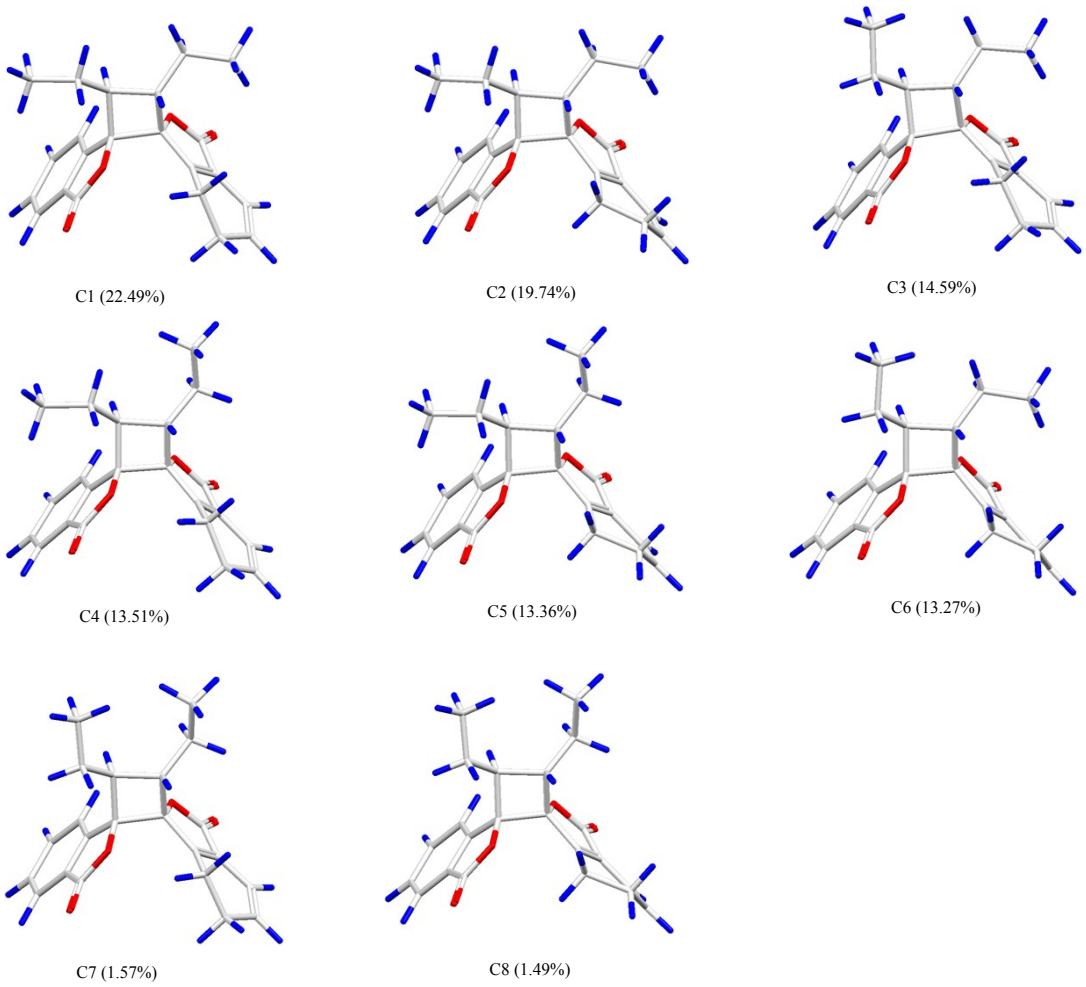


Figure S13. Stable conformers of (8*R*, 9*S*, 8′*R*, 9′*S*)-**5**′ (the relative populations are in parentheses)

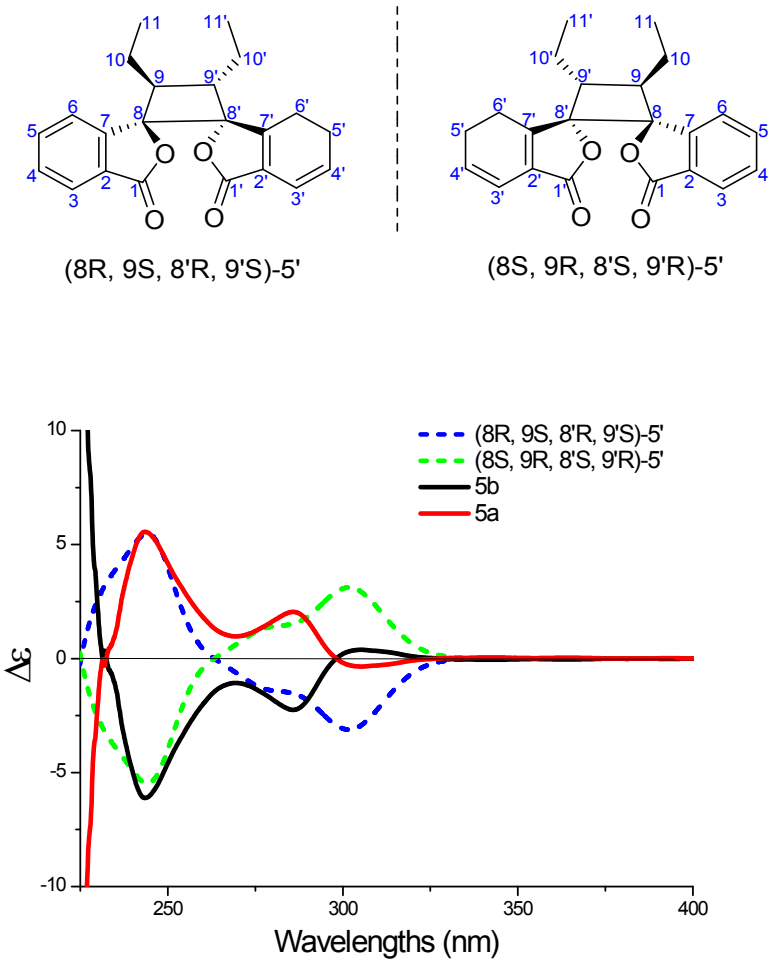


Figure S14. Experimental ECD spectra of **5a** and **5b**, and calculated ECD spectra of (8*R*, 9*S*, 8′*R*, 9′*S*)-**5′** and (8*S*, 9*R*, 8′*S*, 9′*R*)–**5′** (UV correction = –20 nm, band width σ = 0.16 eV)

10.6. Quantum chemical ECD calculation of 6′

The molecules of (3*S*, 4*R*, 8′*S*, 9′*S*)–**6′** and (3*R*, 4*S*, 8′*R*, 9′*R*)–**6′** were converted into SMILES codes before their initial 3D structures were generated with CORINA version 3.4. Conformer databases were generated in CONFLEX version 7.0 by using the MMFF94s force-field, with an energy window for acceptable conformers (ewindow) of 5 kcal/mol above the ground state, a maximum number of conformations per molecule (maxconfs) of 100, and an RMSD cutoff (rmsd) of 0.5Å. Then each acceptable conformer was optimized with APFD/6-31G(d) method in Gaussian09.[3] Further optimization at the APFD/6-31G(d) level determined the dihedral angles. From this, four stable conformers were determined. The optimized conformers were used for the ECD calculations, which were performed with Gaussian09 (APFD/6-311++G(2d, p)). The solvent effects were taken into account by the polarizable-conductor calculation model (IEFPCM, chloroform as the solvent). Comparisons of the experimental and calculated spectra were performed with the software SpecDis.[5, 6] It was also used to apply a UV shift to the ECD spectra, Gaussian broadening of the excitations, and Boltzmann weighting of the spectra.

Table S13. Stable conformers of (3*S*, 4*R*, 8′*S*, 9′*S*)-**6′** at the APFD/6-31G(d) in solvated model in $CHCl_3$

conformers	contribution %
1	65.58
2	22.26
3	9.99
4	2.16

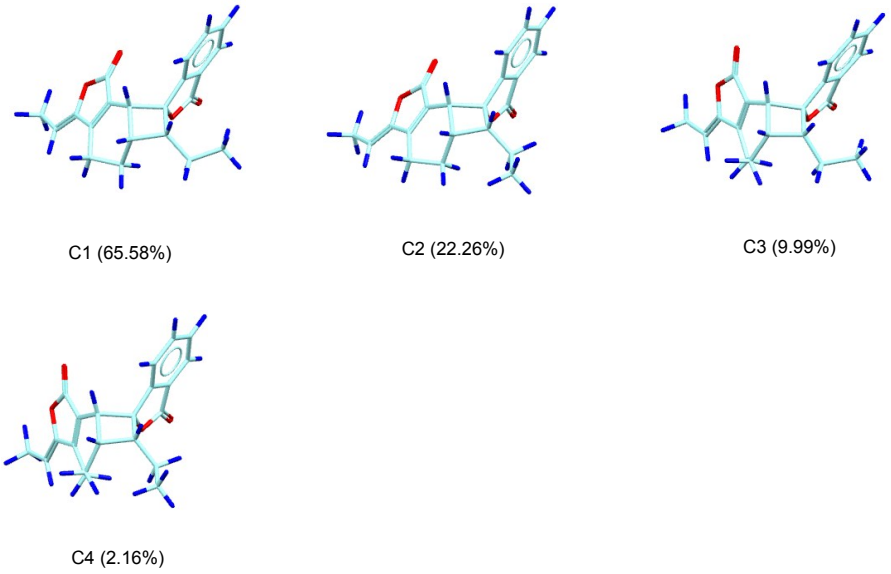


Figure S15. Stable conformers of (3*S*, 4*R*, 8′*S*, 9′*S*)-**6′** (the relative populations are in parentheses)

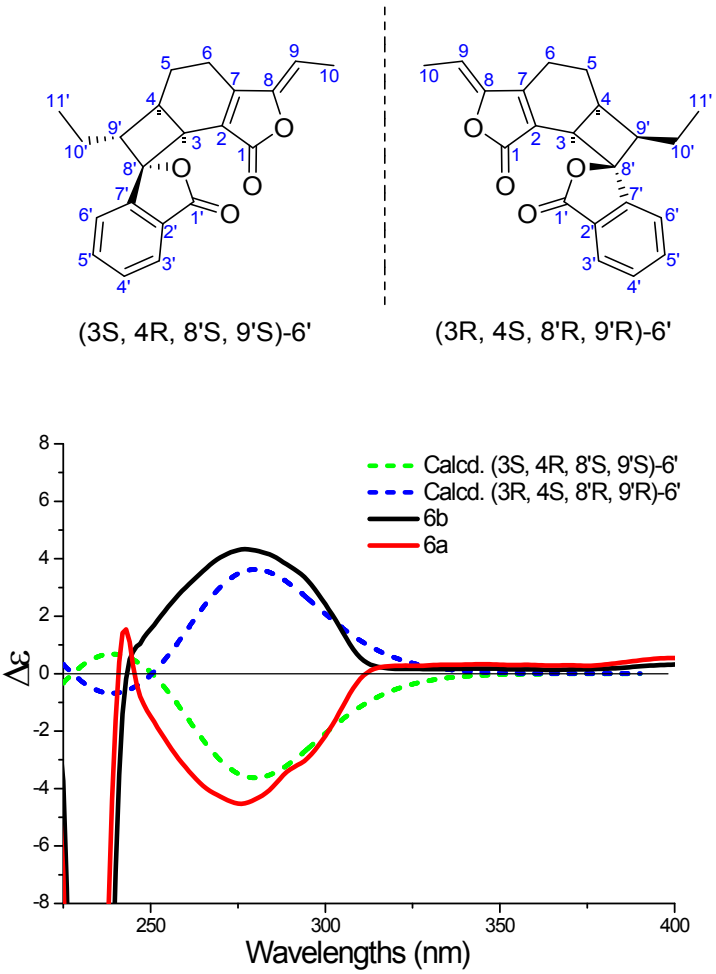


Figure S16. Experimental ECD spectra of **6a** and **6b**, and calculated ECD spectra of (3*S*, 4*R*, 8′*S*, 9′*S*)-**6′** and (3*R*, 4*S*, 8′*R*, 9′*R*)–**6′** (UV correction = -10 nm, band width σ = 0.4 eV)

11. Anti-inflammatory assay of 1−5

11.1. Cell culture and treatment

RAW264.7 murine macrophage cell line was obtained from American Type Culture Collection (ATCC, Manassas, VA, USA). Cells were cultured in DMEM medium (Gibco, Life technologies, USA) that supplemented with 10% heat-inactivated FBS (Excell biotech Co. Ltd, Shanghai, China), 2 mM L-glutamine (Gibco), 100 U/ml penicillin, and 100 μg/ml streptomycin (Gibco) at 37 °C with 5% CO_2. The cells were cultured for 2–3 days to reach the logarithmic phase and then used for experiments. The cells were treated with compounds **3**–**4** and positive control (Hydrocortisone (Sigma, USA)) at different concentrations (2.5, 5, 10, 20, 40 μM) and then stimulated with LPS (Sigma, USA) for the incubated time. The stock solutions of compounds **3**–**4** were prepared in DMSO, and the final concentration of DMSO was less than 0.1%.

11.2. Cell viability assay

The cytotoxic effect of compounds **1**–**5** on RAW264.7 cells were evaluated by MTT assay. RAW264.7 cells were dispensed in 96-well plate at a density of 1×10^5 cells per well. After being incubated at 37 °C for 24 h, cells were treated with the tested agents for the indicated periods of time. Then, 20 μL aliquot of 0.5% MTT (Sigma, USA) solution was added to each well, following by 4 h incubation. The culture medium was removed, and the formazan precipitates were dissolved with 150 μL of DMSO. The optical densities (OD) at 570 nm were measured with an ELISA reader (Thermo Fisher Scientific, Franklin, MA, USA). Compounds **1**–**2** and **5** showed the cytotoxic effect on RAW264.7 cells. Compounds **3**–**4** showed no cytotoxic effect on RAW264.7 cells at different concentrations (2.5, 5, 10, 20, 40 μM)

11.3. Determination of production of pro-inflammation cytokines

The amounts of TNF-α and IL-6 in the culture media were determined by using ELISA kits (invitrogen, Thermo Fisher Scientific, Franklin, MA, USA). RAW264.7 cells were cultured in 24-well plates, pretreated for 2 h with different concentrations (2.5, 5, 10, 20, 40 μM) of compounds **3**–**4** and positive control (Hydrocortisone), and then stimulated with LPS (100 ng/mL) for 24 h. The culture supernatants were collected immediately after treatment, spun at 12,000× g for 3 min to remove the particulate matter. The levels of TNF-α and IL-6 in each sample were measured according to the manufacturer's instructions.

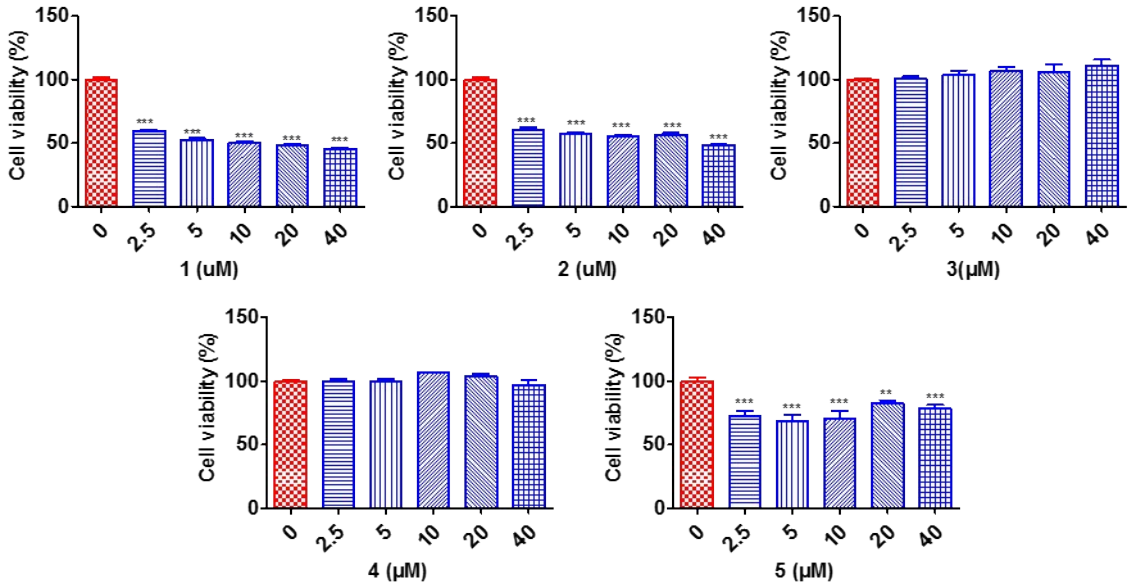
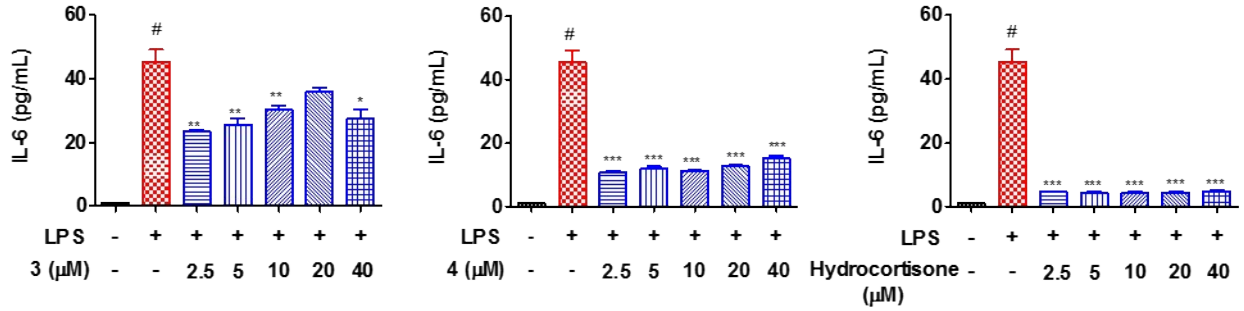


Figure S17. The cytotoxic effect of compounds **1**–**5** on RAW264.7 cells were evaluated by MTT assay. The data represent the mean ± SD of five experiments. $^{**}p < 0.01$, $^{***}p < 0.001$ compared with the blank group.

(a)



(b)

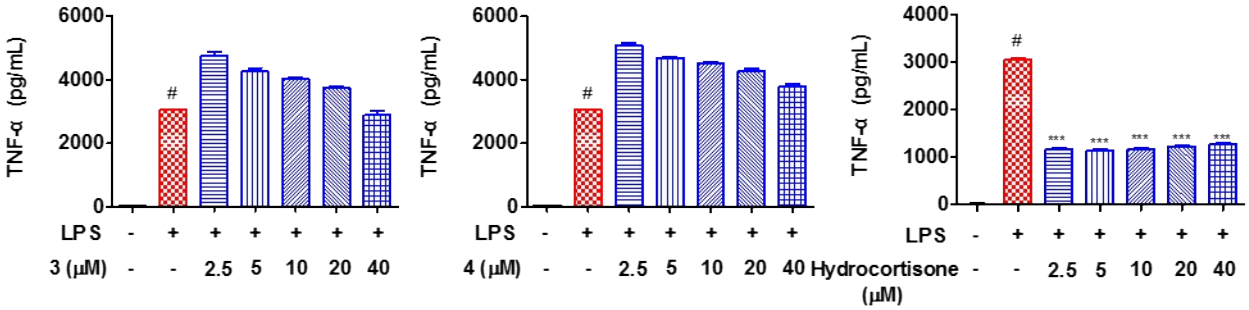


Figure S18. Effects of compounds **3**–**4** and positive control (hydrocortisone) on the inhibition of IL-6 (a) and TNF-α (b). The data represent the mean ± SD of three experiments. $^{*}p < 0.1$, $^{**}p < 0.01$, $^{***}p < 0.001$ compared with the LPS group; $^{\#}p < 0.001$ compared with the control group

12. Antiplatelet aggregation assay of 1−5

The antiplatelet aggregation activities of compounds **1−5** were measured by turbidimetric method.[7] Blood samples collected from male SD rats (weighing (250 ± 20) g, obtained from the Experimental Animal Center of Guangdong Province (Guangzhou, China)) were anticoagulated with 3.8% sodium citrate in the proportion of 9 to 1. The citrated blood samples were immediately centrifuged at 1000 rpm for 10 min to obtain platelet-rich plasma (PRP), and the remaining blood was further centrifuged at 3000 rpm for 10 min to give platelet-poor plasma (PPP). The PRP (250 μL) along with tested compounds **1−5** (100 μM, 100 μL, diluted with saline) were incubated for 5min at 37°C before the addition of the inducer AA (arachidonic acid) (1.5 mM) (Sigma, USA). The maximal aggregation in 5 min was recorded by the LBY–NJ2 platelet aggregation instrument (Beijing Precil instrument Co. Ltd., China). The same experiment was done for the positive control drugs aspirin (Aladdin, China), and the blank solvent DMSO (0.5%). The platelet aggregation inhibition (%) was calculated according to the formula: Inhibition (%) = (1–maximal aggregation in the presence of compounds/maximal aggregation in the presence of solvent) ×100.

Table S14. Antiplatelet aggregation activities of compounds **1−5**

compounds	inhibit rate (100 μM)
1	36.4 ± 4.2
2	30.6 ± 5.6
3	25.6 ± 5.6
4	24.6 ± 4.1
5	31.0 ± 2.6
aspirin	95.4 ± 0.2

13. Antimicrobial assay of 1−5

The antimicrobial activities of compounds were measured in sterile 96-well plates by using broth microdilution method [8, 9]. Seed culture of two bacteria (*S. aureus* 209P, *E. coli* ATCC0111) and two fungi (*C. albicans* FIM709, *A. niger* R330) were prepared by incubating the organism for 12 h at 32 °C (fungi) or 37 °C (bacteria). Beef extract agar medium for bacterium and sabouraud's dextrose agar medium for fungus were used, respectively. The above seed cultures were diluted to a concentration of 1.8×10^{10} CFU/mL and then added to each well of 96-well plate (100 μL/well). These microbes were treated with the continuous 2-fold dilution of compounds (from 128 to 0.5 μg/mL). The 96-well plates were placed in an incubator at 32 °C (fungi) for 24 hours or 37 °C (bacteria) for 12 hours, respectively. The MICs were defined as the lowest concentration at which no microbial growth could be observed. Amphotericin B was used as the positive control for antifungal, and tobramycin for antibacterial assays.

Table S15. Antimicrobial activities of compounds **1−5**

compounds	anti-*S. aureus* assay MIC (μg/mL)	anti-*E. coli* assay MIC (μg/mL)	anti-*C. albicans* assay MIC (μg/mL)	anti-*A.niger* assay MIC (μg/mL)
1	> 128	> 128	> 128	> 128
2	> 128	> 128	> 128	> 128
3	> 128	> 128	> 128	> 128
4	> 128	> 128	> 128	> 128
5	> 128	> 128	> 128	> 128
tobramycin	< 0.5	< 0.5	-	-
amphotericin B	-	-	< 0.5	< 0.5

14. The related operation of LC-HR-ESI(+)MS analysis

The fresh plant material (50 g) was extracted using cooling extraction twice with 95% ethanol/water (500 mL) for 24 hours each time in the dark place. After evaporation under reduced pressure, the extract was obtained. The extract and compounds **6** and **1** were analyzed directly by LC-HR-ESI(+)MS (**Figure S19–S22**).

Chromatography was performed using a Dionex Ultimate 3000 UPLC system (Thermo Fisher Scientific). The separation was performed on a Phenomenex Biphenyl column (4.6 mm × 250 mm, 5 μm, Phenomenex Inc.). Analysis was conducted on the gradient elution component using (A) methanol and (B) water as the mobile phase at 1.0 mL/min. Gradient of 0−50 min, 65−100% A, 50−60 min, 100−100% A, 60−65 min, 100−65% A, 65−75 min, 65−65% A. The injection volume of the sample solution was 10 μL. Mass spectrometry was carried out on a Q-exactive hybrid-quadrupole-orbitrap mass spectrometer (Thermo Fisher Scientific) equipped with an ESI interface and controlled by Xcalibur 4.0 software（Thermo Fisher Scientific). Mass spectra were acquired in positive ion mode with a mass range of 100−1500.

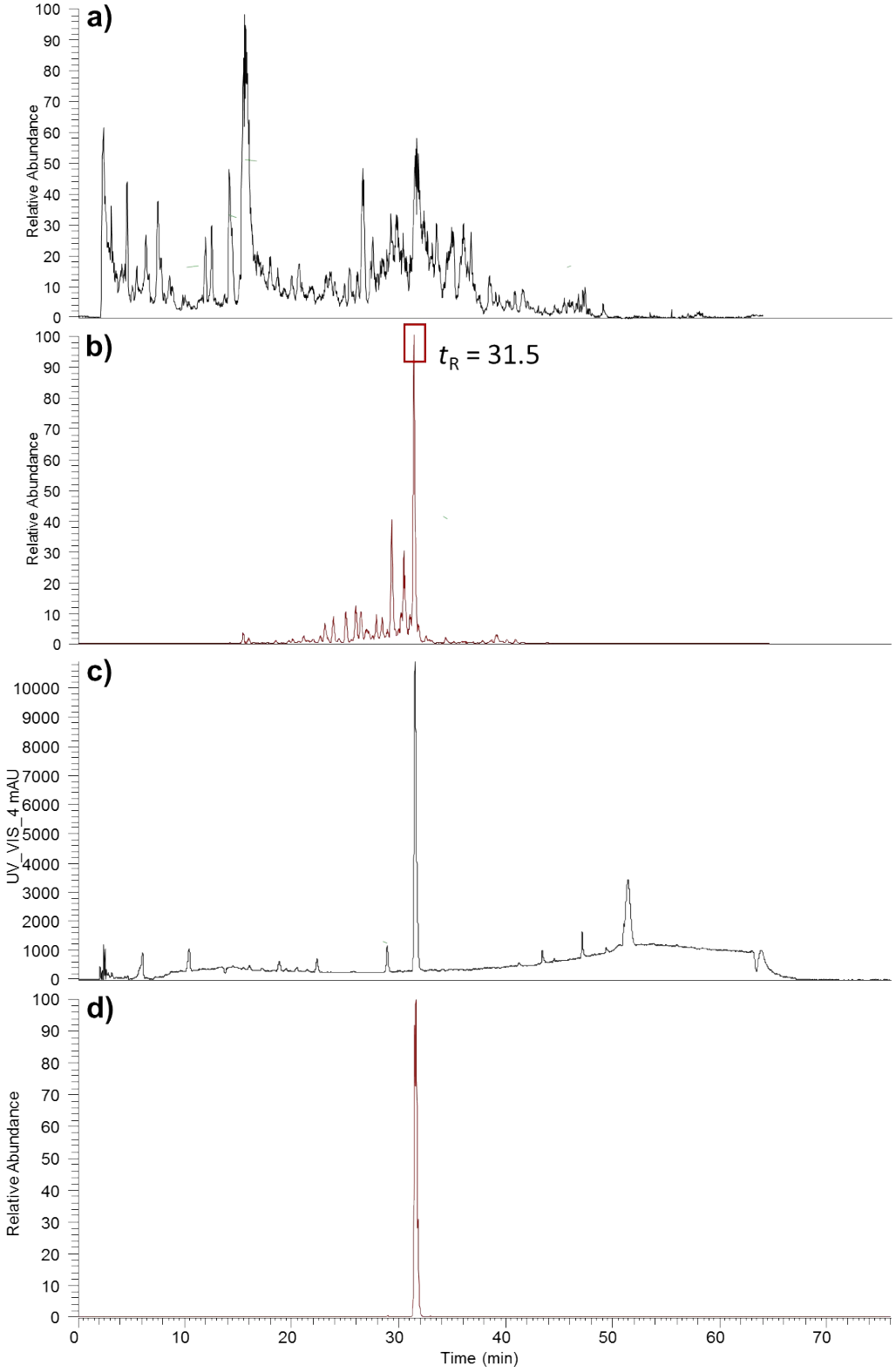


Figure S19. a) the (+)-TIC (Total Ion Chromatogram) of the extract; b) the extracted ion chromatogram of *m/z* 379.1898 of the extract; c) the LC-UV spectrum of compound **6** at 254 nm; d) the extracted ion chromatogram of *m/z* 379.1898 of compound **6**

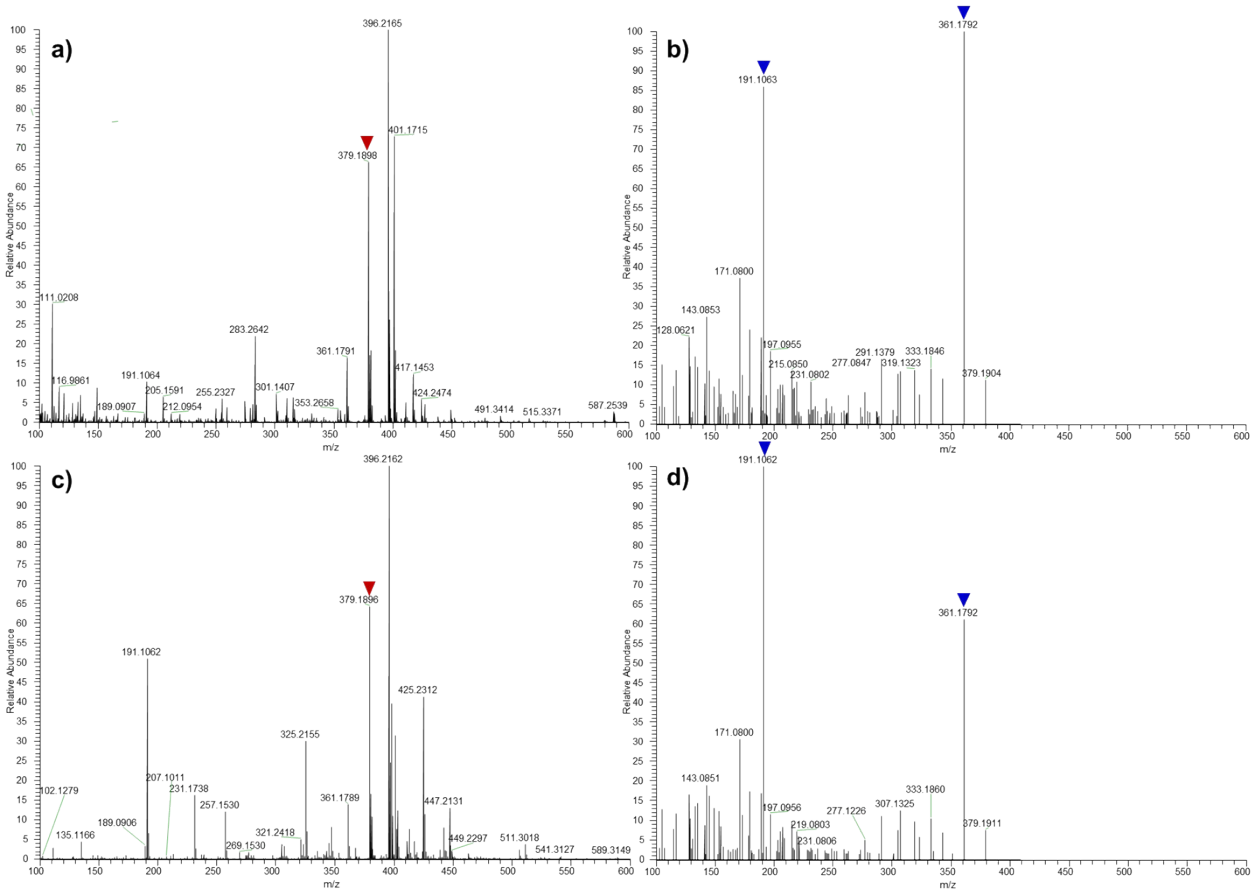


Figure S20. a) the MS spectrum of the compound **6** ($[M+H]^+$ = 379.1898, $C_{24}H_{27}O_4$); b) the MS^2 spectrum of *m/z* 379.1898; c) the MS spectrum of the peak at t_R = 31.5 min ($[M+H]^+$ = 379.1896, $C_{24}H_{27}O_4$) in the extract; d) the MS^2 spectrum of *m/z* 379.1896

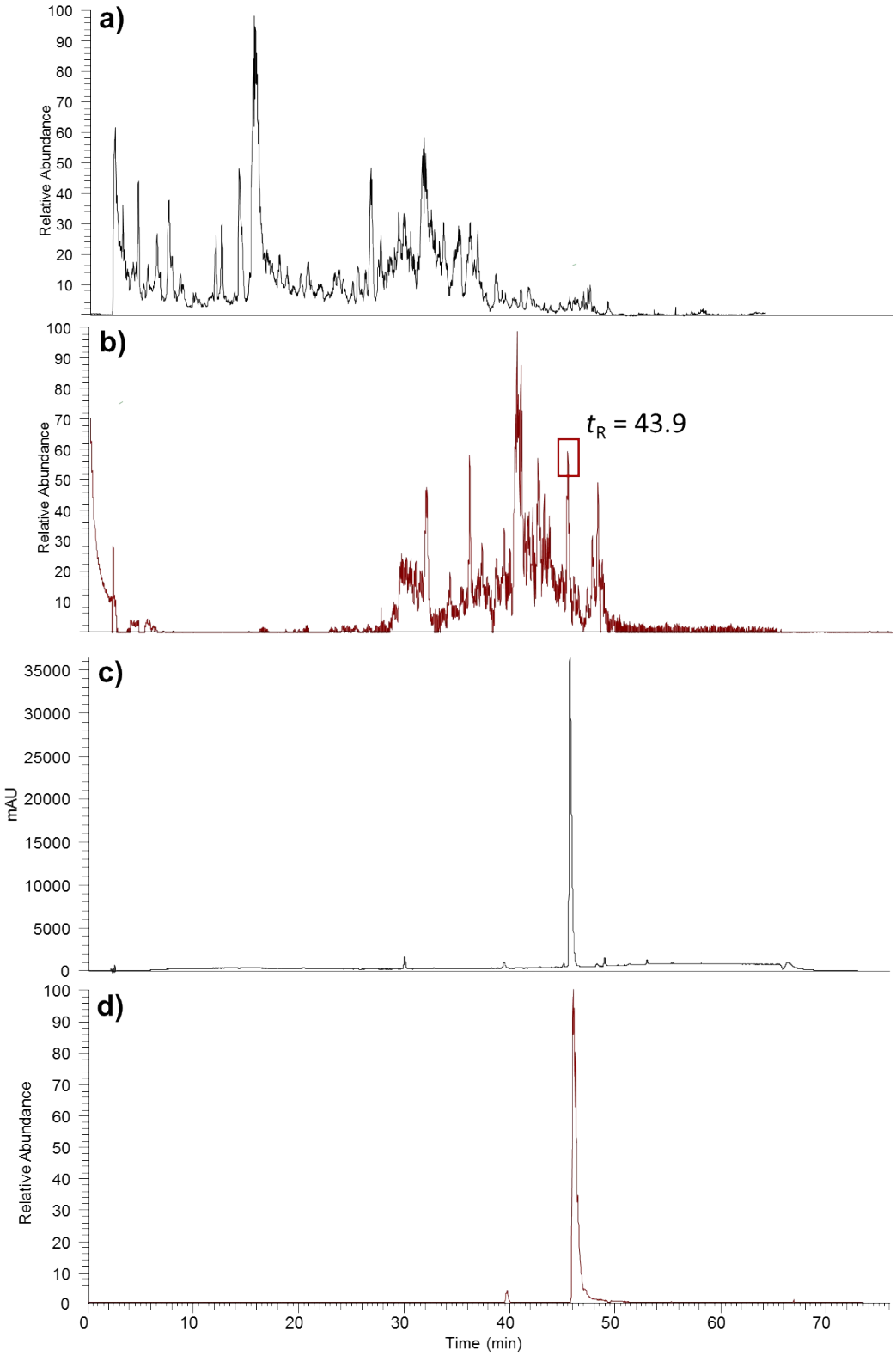


Figure S21. a) the (+)-TIC (Total Ion Chromatogram) of the extract; b) the extracted ion chromatogram of *m/z* 569.2886 of the extract; c) the LC-UV spectrum of compound **1** at 254 nm; d) the extracted ion chromatogram of *m/z* 569.2886 of compound **1**

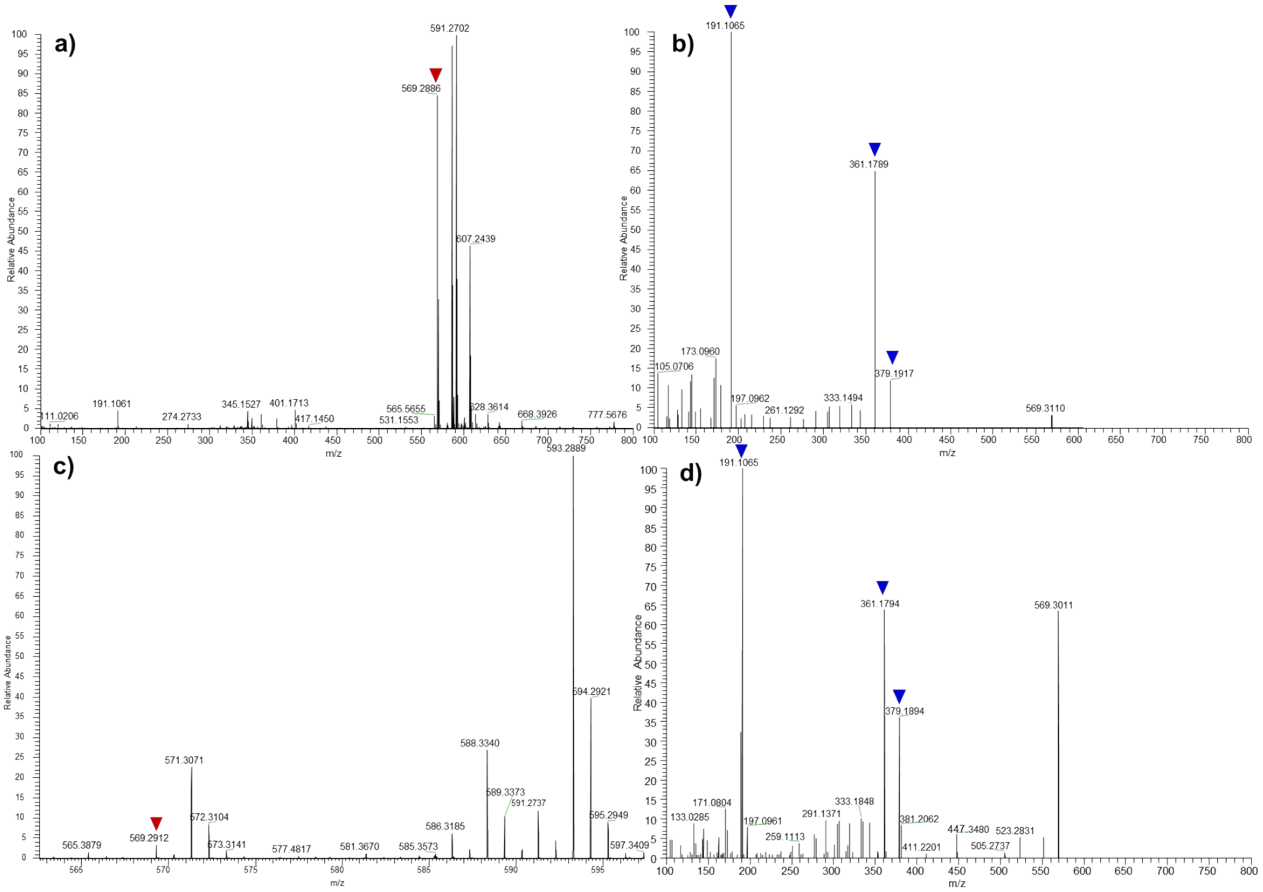


Figure S22. a) the MS spectrum of the compound **1** ($[M+H]^+$ = 569.2886, $C_{36}H_{41}O_6$); b) the MS^2 spectrum of *m/z* 569.2886; c) the MS spectrum of the peak at t_R = 43.9 min ($[M+H]^+$ = 569.2912, $C_{36}H_{41}O_6$) in the extract; d) the MS^2 spectrum of *m/z* 569.2912

15. Computational Details

The molecular geometries of the complexes were optimized using density functional theory (DFT) calculations at the B3LYP-D3 level.[10] Frequency calculations were also performed at the same level of theory to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency), and the free energies at 298.15 K. An IRC[11] analysis was performed to confirm that all the stationary points were smoothly connected to each other. The 6-31G*[12] basis set was used for the C H and O atoms. Free energy calculations were conducted using the polarizable continuum model (PCM)[13] to optimize all the species in ethanol. All calculations were performed using the Gaussian 09 package.[3]

15.1. TDDFT Results of Z-ligustilide, Z-butylidenephthalide, 6 and 1

In order to determine the excitation energies of **Z-ligustilide**, **Z-butylidenephthalide**, **6** and **1**, the TDDFT calculation was carried out. In **table S16**, the results show that **Z-ligustilide** possesses the lowest excited energy (3.5703 eV), the longest excitation wavelength ($\lambda_{excitation}$ = 347.26 nm), and corresponding to HOMO / LUMO transition (orbital 51 to 52), which indicate that **Z-ligustilide** is the most likely species to be excited.

Table S16. Calculation of excited energy, corresponding wavelength, and excited contribution.

species	excited energy	wavelength	contribution (S_0 to S_1)
Z-ligustilide	3.5703 eV	347.26 nm	94.6% from orbital 51 to 52
Z-butylidenephthalide	4.1714 eV	297.23 nm	82.3% from orbital 50 to 51
6	4.2035 eV	294.95 nm	58.2% from orbital 101 to 102
1	4.3961 eV	282.03 nm	73.4% from orbital 152 to 153

15.2. Other possible reaction pathways

Based on the TDDFT calculation results, the triplet **Z-ligustilide (T)** was considered as the "reference point" (0 kcal/mol) in the following discussion.

As **Figure S23** shown, the photo-induce [2+2] cycloaddition reaction can provide **6** and **1** via **TS-6-2 (T)** and **TS-1-2 (T)**. Due to the steric effect, the energy barriers of which are 24.7 kcal/mol and 21.4 kcal/mol, are higher than **TS-6 (T)** and **TS-1 (T)**. Therefore, these pathways are ruled out.

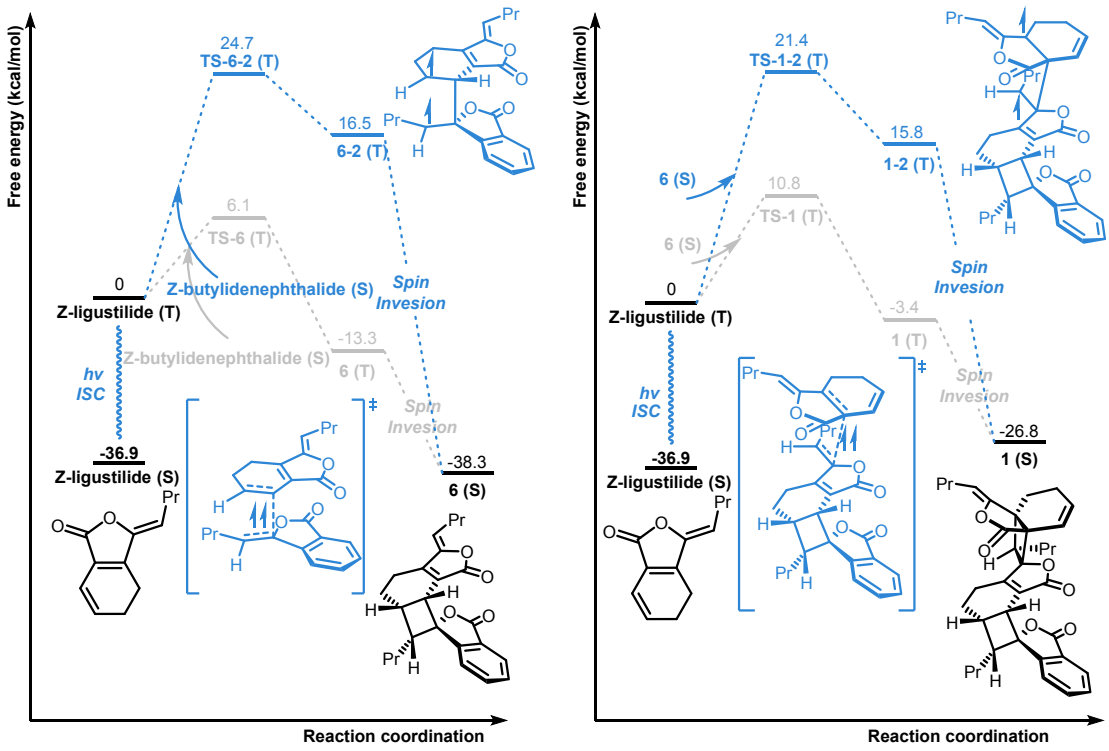


Figure S23. Calculated energy profiles for photo-induce [2+2] cycloaddition reaction of **6** and **1** via **TS-6-2 (T)** and **TS-1-2 (T).** Free energies are given in kcal/mol.

Table S17. Calculated imaginary frequencies of all transition states species

species	frequencies
TS-6 (T)	-369.19
TS-6-2 (T)	-433.87
TS-1 (T)	-362.17
TS-1-2 (T)	-427.69

Table S18. Calculated energy values of all transition states species

species	E_0	E	H_{298}	G_{298}
Z-ligustilide (S)	-615.933997	-615.920994	-615.920049	-615.974539
Z-ligustilide (T)	-615.873959	-615.86063	-615.859686	-615.915744
Z-butylidenephthalide (S)	-614.773547	-614.761334	-614.76039	-614.813117
Z-butylidenephthalide (T)	-614.694229	-614.681441	-614.680497	-614.736024
6 (S)	-1230.733206	-1230.708182	-1230.707238	-1230.789875
6 (T)	-1230.690947	-1230.665049	-1230.664105	-1230.750132
1 (S)	-1846.67568	-1846.637601	-1846.636657	-1846.748294
1 (T)	-1846.63731	-1846.59873	-1846.597785	-1846.711097
TS-6 (T)	-1230.660497	-1230.634411	-1230.633467	-1230.719119
TS-6-2 (T)	-1230.63048	-1230.604087	-1230.603143	-1230.689487
TS-1 (T)	-1846.613986	-1846.575043	-1846.574099	-1846.688355
TS-1-2 (T)	-1846.595564	-1846.556328	-1846.555384	-1846.671517
1-2 (T)	-1846.60242	-1846.562824	-1846.56188	-1846.680401
6-2 (T)	-1230.643053	-1230.616412	-1230.615468	-1230.702559

E_0= Sum of electronic and zero-point Energies

E= Sum of electronic and thermal Energies

H_{298}= Sum of electronic and thermal Enthalpies

G_{298}= Sum of electronic and thermal Free Energies

15.3. Cartesian coordinates

Z-ligustilide (S)

C	-2.92594500	-1.93190200	-0.40140900
C	-1.77154300	0.61648100	0.00969500
C	-0.98519800	-0.47810200	0.19956100
C	-1.57815700	-1.84453000	0.35279100
C	-0.90966700	1.79517500	-0.00508200
O	0.39831000	1.36027400	0.17509200
C	0.38570700	-0.03499800	0.31116000
O	-1.16137100	2.97849000	-0.13817500
C	1.51539800	-0.73284300	0.50830800
C	2.89699200	-0.16647300	0.58924300
C	3.79866300	-0.66651600	-0.55945600
C	5.23031300	-0.13942400	-0.43860500
C	-3.77069700	-0.67785300	-0.29128800
C	-3.21582600	0.53776400	-0.12617800
H	-2.73388100	-2.11422400	-1.47142100
H	-3.48677500	-2.80183200	-0.04328900
H	-0.89251100	-2.62494000	0.00763800
H	-1.73673900	-2.01939000	1.42824100
H	1.40521700	-1.81243000	0.58853400
H	3.34878200	-0.47286400	1.54470400
H	2.86355300	0.92859000	0.58395300
H	3.36290100	-0.35216600	-1.51693900
H	3.80469100	-1.76507200	-0.56265900
H	5.85522500	-0.49830800	-1.26538400
H	5.69385400	-0.46815600	0.50037500
H	5.25049000	0.95780500	-0.45459900
H	-4.84580900	-0.77822500	-0.42176300
H	-3.80475300	1.45043000	-0.10517500

Z-ligustilide (T)

C	3.16248900	-1.64347200	0.48143600
C	1.64349600	0.73134100	-0.04739600
C	0.99760700	-0.56834300	-0.18849000
C	1.81651700	-1.81304200	-0.27185900
C	0.60764300	1.73934100	-0.13643300
O	-0.59948800	1.06779200	-0.29900200
C	-0.35359400	-0.32406100	-0.34577200
O	0.64186100	2.96110700	-0.07485900
C	-1.44401100	-1.17477000	-0.54615800
C	-2.85480000	-0.69310500	-0.66606900
C	-3.52351700	-0.42755500	0.70614700
C	-4.96489200	0.06534900	0.56071700
C	3.77059600	-0.27500300	0.38195600
C	3.00508900	0.87268500	0.17585900
H	3.00168600	-1.85059000	1.55313400
H	3.88063200	-2.39850000	0.14118400
H	1.27354500	-2.68399100	0.11156800
H	2.03951100	-2.02593800	-1.32876700
H	-1.23235500	-2.24016600	-0.54134400
H	-3.45112900	-1.43470900	-1.21256900
H	-2.88470900	0.23949400	-1.24645300
H	-2.92601200	0.31543000	1.25029900
H	-3.50018400	-1.34947600	1.30232500
H	-5.42134900	0.25150100	1.54068800
H	-5.58512600	-0.67342600	0.03676700
H	-5.00602100	1.00107700	-0.01169500
H	4.83827400	-0.17798200	0.56032100
H	3.45852900	1.85989500	0.21180200

Z-butylidenephthalide (S)

C	-2.99665000	-1.93453300	0.09839200
C	-3.79244800	-0.78412400	0.25912300
C	-3.21775600	0.48564700	0.23501000
C	-1.83792800	0.56183800	0.04717700
C	-1.04011800	-0.57825700	-0.11247400
C	-1.61592400	-1.85089800	-0.08885100
C	-0.96356700	1.73601500	-0.02304200
O	0.32709100	1.27970100	-0.22106900
C	0.33649200	-0.12475300	-0.28125700
O	-1.20403000	2.92349000	0.06142600
C	1.47437400	-0.80431600	-0.46453300
C	2.84245600	-0.21037800	-0.59858400
C	3.77424800	-0.62534600	0.55885300
C	5.18769200	-0.06284800	0.39149700
H	-3.47041900	-2.91211700	0.12071400
H	-4.86355500	-0.89173300	0.40296400
H	-3.81358700	1.38529400	0.35685100
H	-1.01339600	-2.74569700	-0.21144000
H	1.38887400	-1.88895000	-0.49070900
H	2.78164700	0.88240400	-0.64924600
H	3.28714800	-0.55323800	-1.54477200
H	3.81361200	-1.72179800	0.61648400
H	3.34233600	-0.27716700	1.50649200

H	5.64818600	-0.42205500	-0.53783900
H	5.83482800	-0.36276100	1.22469000
H	5.17459400	1.03401000	0.35510000

Z-butylidenephthalide (T)

C	-2.82587500	-1.94390500	-0.24194000
C	-3.59328200	-0.80474700	-0.58649900
C	-3.04958000	0.47622300	-0.50555700
C	-1.72842000	0.59372000	-0.07406000
C	-0.95162800	-0.54257700	0.27478000
C	-1.51104400	-1.83603900	0.18861400
C	-0.89449100	1.76761200	0.10757000
O	0.35333900	1.30366300	0.56102700
C	0.32318900	-0.08113000	0.66452500
O	-1.08676500	2.95994100	-0.05500900
C	1.52519900	-0.77458600	1.08884100
C	2.63480900	-1.06890900	0.12537800
C	3.57729200	0.14473100	-0.08508900
C	4.69846000	-0.16630100	-1.07906800
H	-3.28241000	-2.92697200	-0.31866300
H	-4.61888300	-0.93601600	-0.91862500
H	-3.62888000	1.35661400	-0.76862500
H	-0.92698200	-2.71272600	0.45169700
H	1.70352800	-0.89560900	2.15718200
H	2.21578500	-1.35823500	-0.84829400
H	3.22620400	-1.91606100	0.49730900
H	4.00312300	0.43838400	0.88325900
H	2.98482700	0.99739500	-0.44037600
H	5.31589000	-1.00434300	-0.73101800
H	5.35598700	0.70102500	-1.21518900
H	4.29146000	-0.43684100	-2.06175200

6 (S)

C	0.44027800	-2.51130200	-1.54566200
C	0.91656600	0.25402500	-1.02975200
C	1.70653600	-0.67960500	-0.44424300
C	1.29145200	-2.10684700	-0.31752900
C	1.60006900	1.53920900	-0.96506000
O	2.82565700	1.33195700	-0.34194100
C	2.92514500	-0.02467100	-0.00734900
O	1.27329700	2.64815700	-1.34746600
C	4.00599000	-0.51886600	0.61381300
C	5.22343400	0.25606200	1.00755200
C	6.49228800	-0.24816900	0.28900200
C	7.74526600	0.51010100	0.73291700
C	-4.20916000	2.64263400	-0.94621300
C	-4.18234000	3.13933300	0.36858700
C	-3.34296400	2.56843400	1.32560500
C	-2.54427300	1.49926700	0.92186300
C	-2.56641100	1.00281000	-0.38002600
C	-3.40161500	1.56969800	-1.33869200
C	-1.58523600	0.69818400	1.69535800
O	-1.06035500	-0.24920200	0.86224200
C	-1.58961100	-0.12364400	-0.48504000
O	-1.25333400	0.77323100	2.86286000
C	-1.99880400	-1.50222500	-1.07840000
C	-2.33800400	-2.63249400	-0.11534300
C	-3.63167100	-2.37863400	0.67074400
C	-3.97831200	-3.52855900	1.61933200
C	-0.69000300	-1.53671800	-1.93220800
C	-0.43396400	-0.03258100	-1.55923700
H	1.12021100	-2.58827400	-2.40274000
H	0.02389000	-3.51193100	-1.38398300
H	2.15828000	-2.76923800	-0.22311800
H	0.70659300	-2.21242900	0.60510400
H	3.99545700	-1.58579400	0.82677800
H	5.37281000	0.15110500	2.09275900
H	5.08068500	1.32285500	0.80303800
H	6.35455100	-0.14164000	-0.79514200
H	6.61688000	-1.32180500	0.48566500
H	8.63644500	0.14257500	0.20986000
H	7.91643200	0.39361500	1.81082700
H	7.65249800	1.58355500	0.52401600
H	-4.87216600	3.10350200	-1.67346800
H	-4.82231800	3.97457000	0.63793500
H	-3.30775700	2.93541100	2.34715900
H	-3.42837900	1.19460200	-2.35768200
H	-2.85370300	-1.33169400	-1.74387300
H	-1.51076800	-2.79166900	0.58635900
H	-2.43876800	-3.56085400	-0.69513700
H	-4.45836300	-2.21785400	-0.03588700
H	-3.53225100	-1.44775400	1.24430600
H	-4.11102300	-4.46921400	1.06895600
H	-4.90648000	-3.32854000	2.16874500
H	-3.18072500	-3.68530800	2.35721300
H	-0.90077900	-1.67222300	-2.99654000
H	-0.72130000	0.66865300	-2.34681100

6 (T)

C	1.46842300	-2.34587300	1.57424400
C	-0.22846900	-0.13805200	1.95217500
C	-0.68045700	-1.15646100	1.09635400
C	0.15716300	-2.34481000	0.75079300
C	-1.30332700	0.86989600	2.03535500
O	-2.32043500	0.46015900	1.20167100
C	-1.95590500	-0.76528800	0.59762300
O	-1.37393700	1.91266700	2.65354900
C	-2.75586300	-1.32529900	-0.34018700
C	-4.05271900	-0.76568100	-0.83220100
C	-5.25419300	-1.67574700	-0.50096200
C	-6.56882700	-1.12191300	-1.05528300
C	0.25286000	3.67611200	0.12359700
C	-0.74743500	3.52273100	-0.86708300
C	-0.80859300	2.37173700	-1.64883900
C	0.14691100	1.38079500	-1.41977800
C	1.14363800	1.51677700	-0.41682300
C	1.20052500	2.69144600	0.36389600
C	0.30055200	0.06797900	-2.01426400
O	1.39246700	-0.53404500	-1.35853800
C	1.86604000	0.30400800	-0.37687600
O	-0.29890800	-0.53544800	-2.88680900
C	2.82114000	-0.24148900	0.62859100
C	3.89906300	-1.14037100	-0.00837200
C	4.80898500	-0.38794900	-0.98770200
C	5.88369600	-1.29221800	-1.59626700
C	2.09336600	-0.95488200	1.85639100
C	1.06268400	-0.01556900	2.41771800
H	1.25553600	-2.78556100	2.55634900
H	2.20150400	-3.00019400	1.09404200
H	-0.39741800	-3.27185600	0.94900100
H	0.36707500	-2.34640300	-0.32388000
H	-2.41253000	-2.26680400	-0.76304400
H	-3.99409200	-0.65007400	-1.92532400
H	-4.22042600	0.23272600	-0.41323000
H	-5.32527100	-1.78867600	0.58905800
H	-5.07059200	-2.67923500	-0.90865000
H	-7.41226900	-1.77714800	-0.80571800
H	-6.52836700	-1.02803800	-2.14819100
H	-6.78315500	-0.12748300	-0.64311900
H	0.26870200	4.58604400	0.71698800
H	-1.47699200	4.31395500	-1.01186800
H	-1.57732600	2.23749200	-2.40426700
H	1.95189300	2.81113400	1.13779100
H	3.31659100	0.63406400	1.06818500
H	3.42039800	-1.97733900	-0.53047200
H	4.50440800	-1.57455800	0.79791600
H	5.28468200	0.45508900	-0.46701300
H	4.19859500	0.04771700	-1.79057700
H	6.52823700	-1.72064100	-0.81771100
H	6.52411600	-0.73724300	-2.29266900
H	5.43144600	-2.12562100	-2.14935500
H	2.89719900	-1.10092800	2.58806000
H	1.35902400	0.83364000	3.02611100

1 (S)

C	-4.43693100	-2.62044600	-0.95022300
C	-3.76907000	-2.35838400	-2.27999400
C	-2.83576400	-1.41681200	-2.46206400
C	-2.44273700	-0.50290300	-1.34183700
C	-3.01851900	-0.79734100	0.07087100
C	-3.52958500	-2.22845100	0.22941000
C	-2.93177800	0.90676000	-1.63349800
O	-3.83890000	1.28995500	-0.69409300
C	-4.04384400	0.28412300	0.27701800
O	-2.63579400	1.62874200	-2.55919900
C	-5.01324300	0.41406600	1.17948300
C	-5.99266300	1.54898300	1.27700800
C	-7.44304000	1.08733100	1.03751900
C	-8.45138000	2.22842500	1.19117700
C	1.18124400	2.45799300	-1.97086100
C	1.18303300	-0.36114500	-1.55655200
C	0.12788000	0.36199300	-1.14034600
C	0.21095500	1.83878100	-0.93959200
C	0.84393000	-1.78083800	-1.47117200
O	-0.44761300	-1.88409100	-1.01801500
C	-0.98031100	-0.56524500	-0.76516700
O	1.51157100	-2.76900800	-1.71527900
C	-1.59419000	-0.45550900	0.66201000
C	-0.95904600	-1.26606400	1.77921300
C	-1.63138500	-1.03731700	3.13870800
C	-0.92605500	-1.80065200	4.26285300
C	6.55364300	-1.72152500	-0.48571500
C	6.35389500	-2.30214200	0.77877300
C	5.23769100	-1.96587300	1.54512900
C	4.34516900	-1.04054100	1.00567200
C	4.53756400	-0.46158000	-0.24776000

C	5.64853800	-0.79606600	-1.01666200
C	3.10418600	-0.49406100	1.57036800
O	2.58955700	0.39605000	0.67271000
C	3.39653700	0.45993900	-0.53612300
O	2.55213700	-0.72108000	2.63144900
C	3.62612500	1.92388700	-1.00910000
C	3.52382600	3.03913800	0.02346800
C	4.64873900	2.99164100	1.06671000
C	4.54332900	4.12096600	2.09436800
C	2.54070200	1.74928300	-2.12107400
C	2.52085400	0.20939300	-1.82824200
H	-4.70438400	-3.68094200	-0.87432900
H	-5.38315800	-2.06136400	-0.89652800
H	-4.06742800	-2.97938000	-3.12312000
H	-2.36152400	-1.25044600	-3.42653100
H	-4.05639100	-2.34711900	1.18181200
H	-2.67305200	-2.90939200	0.24642600
H	-5.11647100	-0.39680500	1.89767400
H	-5.92761800	1.99596400	2.28031700
H	-5.73601900	2.33833600	0.56114100
H	-7.51709800	0.65470300	0.03047100
H	-7.68614800	0.27948900	1.74184700
H	-8.41254400	2.65580900	2.20155900
H	-8.24398300	3.03806300	0.47950400
H	-9.47651000	1.88111500	1.01349400
H	0.67791900	2.42662600	-2.94493900
H	1.33936800	3.51557000	-1.73172900
H	-0.76593000	2.32392200	-1.00597400
H	0.57471300	2.00748200	0.08321900
H	-1.58086000	0.60568700	0.93856100
H	0.09807800	-0.97427500	1.84329100
H	-0.97054800	-2.33360300	1.53307900
H	-2.68542800	-1.34221600	3.08343000
H	-1.63218300	0.03809400	3.36563100
H	-1.40358300	-1.61914700	5.23353000
H	0.12549800	-1.49546400	4.34061900
H	-0.94436500	-2.88244300	4.07715900
H	7.43103200	-1.99911300	-1.06363700
H	7.07677000	-3.01801400	1.15912200
H	5.06366000	-2.40187400	2.52448400
H	5.81018800	-0.35604800	-1.99650200
H	4.61555200	1.96379600	-1.48036900
H	2.55473400	2.99392900	0.53361900
H	3.55423200	4.00240600	-0.50486100
H	5.62019600	3.04387900	0.55484600
H	4.62457600	2.02310300	1.58347500
H	4.59038300	5.10416600	1.60816000
H	5.35678800	4.07148600	2.82861700
H	3.59408800	4.06669100	2.64306900
H	2.93428000	1.98157200	-3.11429500
H	3.08572500	-0.38762500	-2.54859800

1 (T)

C	-3.08261300	-2.92370200	-1.61829600
C	-2.38994900	-2.18049600	-2.72301200
C	-2.27088500	-0.80605600	-2.72611500
C	-2.74487800	-0.06762400	-1.64146500
C	-3.28840300	-0.69304300	-0.38099100
C	-3.97615100	-2.02412800	-0.73914000
C	-2.89649600	1.36726000	-1.55520600
O	-3.71609300	1.63903100	-0.47113000
C	-4.21752400	0.42864000	0.05598400
O	-2.44873900	2.27106900	-2.24258300
C	-5.35069800	0.41883200	0.75321100
C	-6.22103200	1.61037000	1.03812800
C	-7.62208400	1.46546900	0.41410900
C	-8.52993200	2.65549100	0.73372700
C	0.88159200	2.21303800	-1.19183000
C	1.23649400	-0.61006200	-0.90807500
C	0.21056100	0.03099200	-0.22066400
C	0.24401600	1.50605600	0.02832100
C	0.90513600	-2.00526600	-1.00470800
O	-0.34378200	-2.16544400	-0.35755800
C	-0.75340100	-0.93412300	0.08021100
O	1.46271700	-2.97236100	-1.50416700
C	-2.09542800	-0.80816000	0.71331400
C	-2.27435800	-1.89828500	1.79546600
C	-3.44188900	-1.69282800	2.76641700
C	-3.39122900	-2.69090200	3.92737900
C	6.84146500	-1.39878000	-1.00312100
C	6.99624300	-1.95418800	0.27894800
C	6.05098800	-1.71161200	1.27585600
C	4.96297500	-0.90505500	0.94485400
C	4.80422700	-0.35113500	-0.32414500
C	5.74420900	-0.59174900	-1.32253000
C	3.83252900	-0.46680300	1.77492700
O	3.03272500	0.33177800	1.00740800
C	3.54123200	0.44783300	-0.34858500

O	3.56651700	-0.70465000	2.93751400
C	3.52150900	1.91883700	-0.85258700
C	3.57078400	3.03710600	0.18145700
C	4.91454400	3.10820900	0.91971000
C	4.96512800	4.24924200	1.93862800
C	2.22473500	1.63284100	-1.67682500
C	2.42807500	0.09470500	-1.41631300
H	-2.31952900	-3.42532800	-1.00725300
H	-3.69159400	-3.72884200	-2.04933700
H	-1.97941100	-2.75703500	-3.54801900
H	-1.83309700	-0.28419500	-3.57376300
H	-4.88408300	-1.77492100	-1.30027500
H	-4.29300500	-2.56724600	0.15414400
H	-5.69508700	-0.54518700	1.11682100
H	-6.33128800	1.72647300	2.12685700
H	-5.74682600	2.52621200	0.66775700
H	-7.51746900	1.35692300	-0.67401900
H	-8.08510200	0.53687400	0.77633200
H	-8.67115100	2.76522500	1.81683600
H	-8.09925100	3.59267800	0.35799100
H	-9.52009400	2.53547600	0.27727600
H	0.16463200	2.14383000	-2.01805600
H	1.00500400	3.27928700	-0.97065600
H	-0.75839800	1.90526200	0.21117400
H	0.83688300	1.69926800	0.93044500
H	-2.07869800	0.16573900	1.21346400
H	-1.34320900	-1.91374400	2.37814900
H	-2.34894400	-2.88427500	1.32302900
H	-4.39595500	-1.80282100	2.24183600
H	-3.41816500	-0.66640800	3.15682600
H	-4.23657400	-2.54758600	4.61137600
H	-2.46652500	-2.57758800	4.50763600
H	-3.42914300	-3.72505300	3.56093000
H	7.59184900	-1.60129500	-1.76251000
H	7.86104000	-2.57590300	0.49189100
H	6.15210500	-2.12859700	2.27359000
H	5.63324400	-0.16873000	-2.31674700
H	4.36315600	2.03685100	-1.54589300
H	2.76161300	2.91377400	0.91086300
H	3.38540800	3.99057500	-0.33295700
H	5.72482500	3.22844100	0.18652700
H	5.10089300	2.15400100	1.42978400
H	4.81182900	5.22154200	1.45231900
H	5.93224300	4.28243900	2.45527400
H	4.18334600	4.13219400	2.70039500
H	2.34402200	1.89419400	-2.73194700
H	2.88680300	-0.43344300	-2.25618600

TS-6 (T)

C	1.52088500	-1.89591400	2.12418400
C	-0.23596900	0.32717800	1.89378200
C	-0.62524300	-0.90188400	1.26951000
C	0.28717000	-2.08335700	1.20356300
C	-1.34160400	1.26662300	1.73167500
O	-2.32725200	0.61751400	1.00858500
C	-1.89432000	-0.69485000	0.70356100
O	-1.48879800	2.41886800	2.10205400
C	-2.67505500	-1.49977200	-0.08508000
C	-3.98333100	-1.11543700	-0.69823300
C	-5.15352000	-2.00105500	-0.22079900
C	-6.47301600	-1.63810100	-0.90606900
C	0.19677400	3.75062500	-0.42333200
C	-0.92816600	3.38092500	-1.19597300
C	-1.03415200	2.10288900	-1.73666600
C	0.00994700	1.20867600	-1.48946400
C	1.12548700	1.56400400	-0.70244600
C	1.22980000	2.85590100	-0.16478400
C	0.17218100	-0.17846800	-1.89316600
O	1.39533100	-0.61035100	-1.37072500
C	1.96224400	0.39863500	-0.59965100
O	-0.52330500	-0.93538200	-2.54668500
C	3.03642300	0.12210900	0.21248700
C	3.91218600	-1.08614700	0.01972400
C	4.97208300	-0.85014100	-1.07737500
C	5.89545700	-2.05813400	-1.25283600
C	1.99484900	-0.47301100	2.28555400
C	1.02591600	0.56748300	2.38706000
H	1.26252400	-2.24610700	3.13745600
H	2.33914700	-2.53965200	1.78872300
H	-0.24351200	-3.00331800	1.48015100
H	0.62160100	-2.22784100	0.16953400
H	-2.29012100	-2.49788500	-0.27961000
H	-3.90180900	-1.20967700	-1.79283700
H	-4.20890100	-0.06382300	-0.48779800
H	-5.25642100	-1.89963700	0.86792300
H	-4.91054000	-3.05484500	-0.41508800
H	-7.29317200	-2.27501000	-0.55273800
H	-6.39882000	-1.75928300	-1.99456300

H	-6.74863000	-0.59468900	-0.70545100
H	0.24837800	4.75621200	-0.01573100
H	-1.71918700	4.10600000	-1.36287600
H	-1.89525800	1.80166400	-2.32559200
H	2.08462800	3.14409100	0.43900200
H	3.47704300	0.98607300	0.70238600
H	3.30325500	-1.95485600	-0.25426200
H	4.41821600	-1.32648100	0.96219600
H	5.56478100	0.03924900	-0.82420800
H	4.45986200	-0.62827500	-2.02283900
H	6.43578800	-2.28113400	-0.32381100
H	6.63933600	-1.87720600	-2.03825900
H	5.32534900	-2.95393500	-1.53055600
H	2.95912600	-0.32906900	2.76364800
H	1.29737100	1.55158000	2.75800300

TS-6-2 (T)

C	0.54757900	2.84336300	-1.68027700
C	-0.43057100	0.17692100	-1.39887600
C	-1.08007200	1.18771500	-0.73873600
C	-0.47436900	2.53962200	-0.55260700
C	-1.28491400	-1.00996000	-1.36191200
O	-2.42919500	-0.67567500	-0.65112500
C	-2.32760800	0.66349300	-0.24307300
O	-1.14656300	-2.12213000	-1.83452700
C	-3.28040000	1.23763800	0.51176500
C	-4.53722700	0.58106400	0.98609600
C	-5.79935800	1.22544100	0.37366000
C	-7.08634100	0.59332800	0.90860200
C	1.39561300	-3.98813200	-0.38851700
C	0.44818500	-4.02901900	0.65483700
C	0.11597700	-2.87239300	1.35613100
C	0.75172800	-1.68711700	0.98362900
C	1.68328600	-1.63753600	-0.06599800
C	2.02002000	-2.79985100	-0.76613600
C	0.60201900	-0.33583300	1.51930700
O	1.45656700	0.48170100	0.80011600
C	2.06731000	-0.23588900	-0.25165700
O	-0.08928100	0.11246000	2.41575200
C	3.36319900	0.24243500	-0.63539600
C	3.98717700	1.47113100	-0.05898900
C	4.75139600	1.18486600	1.25867600
C	5.38252100	2.44982100	1.84486800
C	1.34006800	1.65978800	-2.15373200
C	0.91433400	0.30475800	-1.90012900
H	-0.00285900	3.25285800	-2.54587200
H	1.21984800	3.64919400	-1.35817000
H	-1.24481400	3.31721700	-0.51505600
H	0.03383600	2.54990200	0.42001200
H	-3.12219800	2.28133200	0.77499500
H	-4.59374700	0.67674400	2.08076800
H	-4.52040500	-0.48984500	0.75571400
H	-5.75683600	1.12259100	-0.71870100
H	-5.79575700	2.30286600	0.58787400
H	-7.97216700	1.05741300	0.45819100
H	-7.16155000	0.71185200	1.99719100
H	-7.12083400	-0.48098900	0.68682400
H	1.63926500	-4.90658600	-0.91583900
H	-0.02383800	-4.97308300	0.91050900
H	-0.61032400	-2.88195500	2.16359400
H	2.73637600	-2.77911800	-1.58179700
H	3.91175700	-0.37198000	-1.34316000
H	3.21911900	2.22731700	0.14755200
H	4.68481400	1.90699200	-0.78575700
H	5.52722000	0.43104700	1.06944400
H	4.05259500	0.74410900	1.98140600
H	6.09777500	2.89741000	1.14267700
H	5.91946000	2.23059000	2.77592300
H	4.61779800	3.20488700	2.06846900
H	2.22992500	1.83227100	-2.75017800
H	1.28602600	-0.47781200	-2.55754200

TS-1 (T)

C	-2.85386700	-2.91917800	-1.73458100
C	-2.01009800	-2.13796900	-2.69927700
C	-1.92492400	-0.75874100	-2.67870100
C	-2.64473800	-0.05086500	-1.71407500
C	-3.50554500	-0.69170900	-0.73174700
C	-3.94666600	-2.09892500	-1.00706100
C	-2.78661200	1.38283700	-1.56152700
O	-3.73843400	1.60458100	-0.57649500
C	-4.30940000	0.37284000	-0.18890800
O	-2.24965500	2.32169100	-2.12900700
C	-5.45818500	0.35965600	0.52298300
C	-6.22488900	1.56603500	0.96917700
C	-7.61823100	1.65428800	0.31206600
C	-8.42140400	2.85668800	0.81334000
C	0.85174400	2.33544500	-1.04303900

C	1.17931500	-0.50053200	-0.86044400
C	0.18031600	0.11016700	-0.13816400
C	0.19887300	1.57934300	0.13888600
C	0.94193400	-1.92366800	-0.85463100
O	-0.22707900	-2.13828000	-0.10744000
C	-0.70201700	-0.90929500	0.32237900
O	1.54821700	-2.86947000	-1.33623800
C	-1.87780900	-0.86654600	1.05448800
C	-2.34066400	-2.06341000	1.84943800
C	-3.58476600	-1.82048000	2.70852000
C	-3.92575700	-3.03269200	3.57788700
C	6.74770000	-1.38416300	-1.14460800
C	6.90941700	-2.01898500	0.09924200
C	5.98810400	-1.81210100	1.12628600
C	4.91659500	-0.95950000	0.86414200
C	4.75039400	-0.32766900	-0.36713400
C	5.66687000	-0.53205500	-1.39525600
C	3.81172200	-0.54293100	1.73898300
O	3.02132900	0.32003000	1.03518300
C	3.50395000	0.49480300	-0.32423800
O	3.56004600	-0.84200200	2.89085700
C	3.49477600	1.98915200	-0.75244800
C	3.56660700	3.05141200	0.33724300
C	4.91751400	3.07100300	1.06587400
C	4.98851900	4.15602700	2.14308100
C	2.18150600	1.76060700	-1.56867500
C	2.36117200	0.21339700	-1.38392800
H	-2.17171500	-3.37011100	-0.99998700
H	-3.31992400	-3.76371700	-2.25742300
H	-1.42071900	-2.69938800	-3.41943200
H	-1.31209900	-0.22203900	-3.39747300
H	-4.83505500	-2.03861900	-1.65443500
H	-4.26961500	-2.61516300	-0.09783400
H	-5.87052800	-0.61742400	0.76033300
H	-6.35906900	1.52281900	2.06116400
H	-5.65953500	2.47961100	0.75381600
H	-7.49430400	1.71453400	-0.77750100
H	-8.17136000	0.72634100	0.51293900
H	-8.58051100	2.80157700	1.89806700
H	-7.89764000	3.79763000	0.60105900
H	-9.40585500	2.90546700	0.33216300
H	0.13520800	2.32231500	-1.86958500
H	0.99234700	3.38623500	-0.76478700
H	-0.80713400	1.96876000	0.32475700
H	0.77730300	1.74051100	1.05816500
H	-2.15485200	0.11804600	1.41949800
H	-1.50637300	-2.35403800	2.50885600
H	-2.49745100	-2.92951100	1.19597800
H	-4.43532500	-1.58094800	2.06452600
H	-3.41887500	-0.93937400	3.34374700
H	-4.81826600	-2.84606500	4.18718100
H	-3.10012100	-3.27896700	4.25812400
H	-4.12193900	-3.91846800	2.95959300
H	7.47944500	-1.56001800	-1.92849700
H	7.76053700	-2.67470800	0.25847100
H	6.09518900	-2.29095600	2.09522400
H	5.54968800	-0.04792200	-2.36050100
H	4.32818100	2.13494000	-1.45047900
H	2.76202800	2.89787400	1.06625700
H	3.38627900	4.03233600	-0.12476900
H	5.72224700	3.22288100	0.33238900
H	5.09983900	2.08946000	1.52304100
H	4.84004000	5.15406700	1.71039800
H	5.96077500	4.15299400	2.65108800
H	4.21297200	4.00613600	2.90548500
H	2.29125200	2.07227300	-2.61121400
H	2.79080100	-0.28548700	-2.25673000

TS-1-2 (T)

C	-2.68668900	-3.18747700	-1.85117500
C	-1.72646000	-2.30030400	-2.60012600
C	-1.57149100	-0.97665100	-2.39401200
C	-2.28907700	-0.32108300	-1.30648300
C	-3.39920300	-1.06961400	-0.70797700
C	-3.35173300	-2.55316000	-0.59735900
C	-2.81626200	1.06027800	-1.45459600
O	-3.99793100	1.14432700	-0.76054200
C	-4.38815000	-0.15674200	-0.33967400
O	-2.35768500	2.02439000	-2.03569100
C	-5.58451700	-0.31615200	0.31481200
C	-6.55749700	0.77287300	0.63830900
C	-7.92510600	0.57132400	-0.04883400
C	-8.93178500	1.65932100	0.33215200
C	1.34708800	1.95783500	-2.04756200
C	1.09040200	-0.55390000	-0.71014000
C	0.23084900	0.45118500	-0.42297100
C	0.54965100	1.87737000	-0.72357500
C	0.53496200	-1.80202700	-0.20444100

O	-0.68328600	-1.50402200	0.38998800
C	-0.97186200	-0.13459300	0.19444000
O	0.96594100	-2.94057400	-0.20676200
C	-1.64006400	0.51232400	1.28917800
C	-2.34305900	-0.19811600	2.39736000
C	-3.43438700	0.66667000	3.04941700
C	-4.25883100	-0.10907200	4.07720900
C	6.38898800	-2.44109400	-0.09503800
C	6.41785400	-2.51280100	1.30851800
C	5.54872100	-1.73708900	2.07616900
C	4.66436700	-0.90143400	1.39551500
C	4.63091200	-0.82587600	0.00435300
C	5.49556500	-1.59894200	-0.76584400
C	3.65534900	0.02688900	1.92412000
O	3.04888200	0.63668800	0.86296000
C	3.56854200	0.14424800	-0.40214600
O	3.34384800	0.28644500	3.07071200
C	3.86174700	1.30235000	-1.39914600
C	4.13005200	2.69072600	-0.83232300
C	5.45330200	2.77526800	-0.05931700
C	5.71486000	4.17441300	0.50355800
C	2.53870100	0.98856900	-2.17112600
C	2.40664000	-0.34487300	-1.35220500
H	-2.17391800	-4.11520300	-1.56636900
H	-3.46584100	-3.49248700	-2.56636300
H	-1.16844100	-2.77721200	-3.40422900
H	-0.90151900	-0.38305500	-3.00861100
H	-4.35364700	-2.96837100	-0.44812600
H	-2.75950900	-2.82555700	0.28613000
H	-5.83750800	-1.33289000	0.60602300
H	-6.71948500	0.79868400	1.72772700
H	-6.14648700	1.74889600	0.35677300
H	-7.77880600	0.56062100	-1.13719300
H	-8.32246200	-0.41623600	0.22316500
H	-9.11459500	1.66694600	1.41452200
H	-8.56383400	2.65409800	0.04963900
H	-9.89465100	1.50339500	-0.16951700
H	0.64326800	1.73749700	-2.85934900
H	1.69195200	2.98650400	-2.20160400
H	-0.35169200	2.49001800	-0.78448800
H	1.15153000	2.26551700	0.10842500
H	-1.66087400	1.59850500	1.25553200
H	-1.61282400	-0.50114000	3.16924200
H	-2.77662200	-1.13654900	2.02804100
H	-4.09570900	1.05666900	2.26614700
H	-2.96365900	1.53871500	3.52391800
H	-5.01532300	0.53195800	4.54589800
H	-3.62220000	-0.51509100	4.87408000
H	-4.77967000	-0.95227300	3.60518200
H	7.07666300	-3.05431800	-0.67117700
H	7.12452300	-3.17833700	1.79577200
H	5.55491400	-1.77573200	3.16154800
H	5.48017200	-1.55270200	-1.85094400
H	4.71542600	0.99683100	-2.01602200
H	3.30595200	2.99534900	-0.17690100
H	4.14716600	3.40704800	-1.66577800
H	6.27923300	2.48041800	-0.72218500
H	5.44332700	2.04664600	0.76194200
H	5.75363500	4.92293300	-0.29867300
H	6.66685000	4.21637700	1.04695800
H	4.91983500	4.47376800	1.19884400
H	2.71935900	0.80877800	-3.23445800
H	2.73305200	-1.23089900	-1.90307400

1-2 (T)

C	-3.37191300	-2.37288500	2.71224200
C	-2.49515400	-3.13335600	1.74899800
C	-2.02319200	-2.65807500	0.59021500
C	-2.27862600	-1.23747300	0.15270200
C	-3.33746100	-0.58250200	0.99712800
C	-3.39964700	-0.84088400	2.46272700
C	-2.90063600	-1.13074000	-1.24410200
O	-3.99569400	-0.32603100	-1.19201200
C	-4.30213100	-0.02041800	0.16236900
O	-2.54381400	-1.63561400	-2.28466100
C	-5.42502900	0.72450700	0.42174900
C	-6.39265500	1.22785400	-0.60271100
C	-7.76615000	0.52633800	-0.51304400
C	-8.76821000	1.08286400	-1.52714900
C	1.68577100	-2.56571300	-1.86363100
C	1.19188000	-1.25413700	0.61260700
C	0.30707300	-1.09213500	-0.38725200
C	0.63916300	-1.43012500	-1.80362800
C	0.64229000	-0.68210800	1.83741400
O	-0.60129900	-0.18531100	1.55698600
C	-0.91751600	-0.37815800	0.15118000
O	1.12298000	-0.59100200	2.95291200
C	-1.07989600	0.95014600	-0.52100600

C	-1.41223400	2.21549600	0.19329100
C	-2.41347200	3.08930600	-0.58582200
C	-2.76768100	4.37478900	0.16427900
C	6.17600200	0.50374500	2.49782100
C	5.82048900	1.85800300	2.62121800
C	4.76895300	2.38648200	1.87166200
C	4.10074000	1.52215600	1.00585500
C	4.44855200	0.17751300	0.87952500
C	5.49352400	-0.35508900	1.62906500
C	2.98235000	1.78819900	0.08977500
O	2.71208100	0.63436900	-0.58539100
C	3.51928700	-0.47109900	-0.09464600
O	2.35055500	2.80857500	-0.11355200
C	4.01284300	-1.38253000	-1.25073400
C	4.13930200	-0.77285400	-2.64135600
C	5.23886100	0.29480800	-2.72380500
C	5.36913200	0.89736900	-4.12481200
C	2.89539000	-2.42698600	-0.92187200
C	2.60006300	-1.65971200	0.40929300
H	-3.05277000	-2.57472300	3.74262800
H	-4.39244800	-2.77548000	2.62831900
H	-2.27193700	-4.16527100	2.01770000
H	-1.42295600	-3.27725300	-0.07191700
H	-4.29946500	-0.40410200	2.90606500
H	-2.53218100	-0.39061000	2.95703800
H	-5.63277600	0.93197600	1.46832300
H	-6.54542700	2.30751500	-0.45357700
H	-5.98532400	1.09967000	-1.61182100
H	-7.62599000	-0.55053700	-0.67641000
H	-8.16339300	0.63965200	0.50494400
H	-8.94123500	2.15451800	-1.36434000
H	-8.40210600	0.95680800	-2.55422200
H	-9.73561300	0.57152100	-1.45109600
H	1.17063400	-3.49861500	-1.60254500
H	2.03372600	-2.67879900	-2.89658400
H	-0.25464900	-1.71222700	-2.36326800
H	1.03277700	-0.51850100	-2.27324200
H	-0.94680300	0.96412600	-1.59936900
H	-0.48747100	2.79909100	0.35520200
H	-1.80621600	1.99390300	1.19204000
H	-3.32473700	2.50754400	-0.77503800
H	-1.98796400	3.33398600	-1.56881300
H	-3.47131300	4.98978300	-0.41005400
H	-1.87282900	4.98010700	0.35853300
H	-3.23367000	4.14863300	1.13221500
H	6.99945500	0.11571800	3.09129100
H	6.37145700	2.49567400	3.30643800
H	4.47807500	3.42985700	1.95112100
H	5.77370300	-1.40108000	1.54396600
H	4.98377500	-1.79418200	-0.94966400
H	3.18365500	-0.33218000	-2.94872800
H	4.35509200	-1.58004700	-3.35538700
H	6.19795800	-0.14748400	-2.41877800
H	5.02345300	1.09285300	-2.00068300
H	5.61312700	0.12588100	-4.86683200
H	6.15838900	1.65828800	-4.16157700
H	4.43081500	1.37371300	-4.43743500
H	3.30780800	-3.42503900	-0.75074200
H	3.03652200	-2.12016100	1.29877000

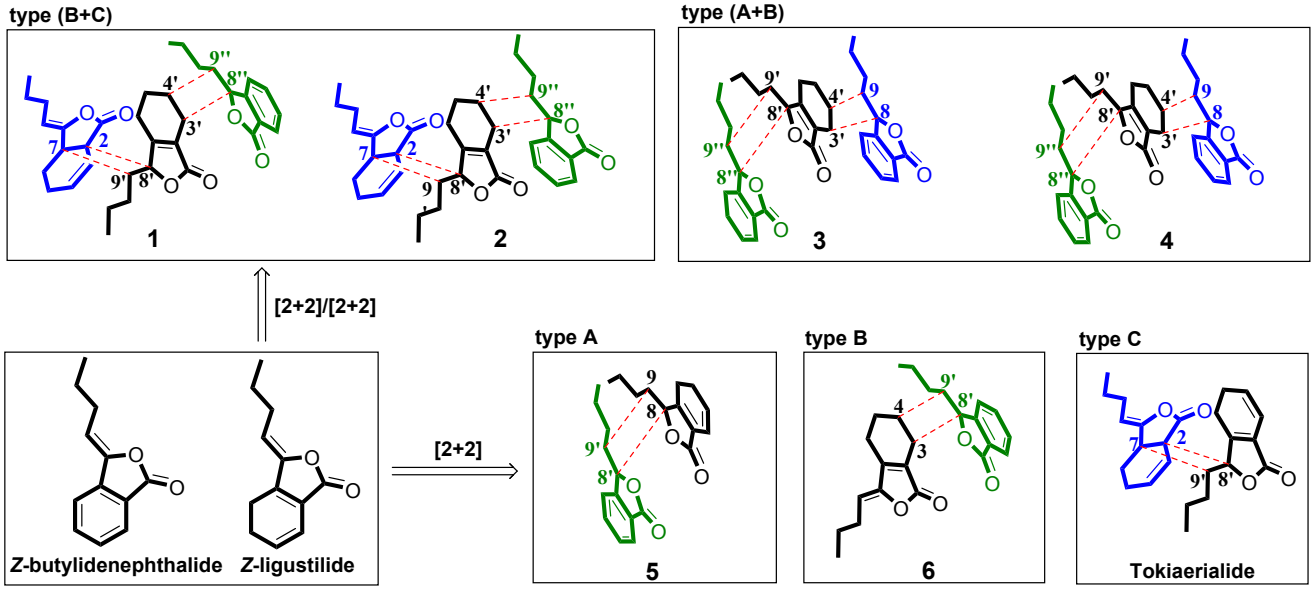
6-2 (T)

C	0.44796800	-3.36325800	-0.67675600
C	0.70641400	-0.55249600	-1.02563100
C	1.52099700	-1.19466500	-0.15143100
C	1.20456700	-2.54503400	0.40084700
C	1.35221900	0.69752100	-1.41508000
O	2.54859200	0.78784000	-0.71380100
C	2.68962600	-0.36347200	0.06855200
O	1.03038800	1.56595100	-2.20440800
C	3.76490700	-0.55834300	0.84562700
C	4.93139900	0.36973900	0.97108800
C	6.22773800	-0.24903200	0.40600700
C	7.43051400	0.68231200	0.57338400
C	-1.85858900	3.32895900	-1.02968400
C	-1.48778100	3.66708700	0.28354100
C	-1.25230200	2.67215700	1.23204400
C	-1.39634000	1.34698500	0.82116400
C	-1.75515300	1.00796000	-0.48152300
C	-1.99766900	1.99646600	-1.43024200
C	-1.24446200	0.10696800	1.59468000
O	-1.54035900	-0.94307600	0.77501300
C	-1.80090800	-0.50423900	-0.59625700
O	-0.92616400	-0.06527700	2.75629400
C	-3.13153100	-1.00978100	-1.05302600
C	-4.22183500	-1.39815600	-0.11184500
C	-4.92120500	-0.19181900	0.56752700
C	-6.06003500	-0.63288200	1.48941000
C	-0.61390100	-2.58807400	-1.39599700

C	-0.61548500	-1.08693600	-1.48141400
H	1.19484000	-3.73161600	-1.40364000
H	0.01488200	-4.26196600	-0.21897600
H	2.11190700	-3.06907700	0.71686900
H	0.57071900	-2.42245300	1.28795200
H	3.79416900	-1.48904600	1.40804900
H	5.08886600	0.59978600	2.03510500
H	4.72273200	1.31704800	0.46182300
H	6.07758800	-0.47949500	-0.65695900
H	6.42261700	-1.20532600	0.91024800
H	8.34124100	0.22971300	0.16275100
H	7.61384200	0.90489200	1.63242300
H	7.26672200	1.63586300	0.05532100
H	-2.03884000	4.12204400	-1.75026000
H	-1.38862400	4.71302000	0.55899200
H	-0.97149900	2.90976800	2.25389900
H	-2.27745300	1.74634000	-2.44874800
H	-3.35293000	-0.83630500	-2.10319900
H	-3.82187600	-2.04834900	0.67793800
H	-4.97712900	-1.97824400	-0.65812400
H	-5.30317700	0.48517100	-0.20810200
H	-4.17756000	0.37632400	1.13972700
H	-6.83076900	-1.18159800	0.93272800
H	-6.54127100	0.22945800	1.96707000
H	-5.68981900	-1.29306900	2.28447500
H	-1.43174200	-3.12264500	-1.86967200
H	-0.83200800	-0.74152700	-2.50239600

16. The plausible formation modes of compounds 1−6.

The plausible modes of formation of **1**−**6** are proposed as shown in **Scheme S1**. Three biosynthetically related phthalide dimers with three types of linkages (type A, 8–8′ / 9–9′, diangeliphthalide A (**5**); type B, 3–8′ / 4–9′, gelispirolide (**6**); type C, 2–8′ / 7–9′, tokiaerialide[14]) derive from two molecules of monomer phthalides (*Z*-ligustilide or *Z*-butylidenephthalide) through [2+2] cycloaddition. Whereas four novel phthalide trimers with two new types of linkages (type B+C, 2−8′/7−9′, 3′−8″/4′−9″, triangeliphthalides A−B (**1**−**2**); type A+B, 3′−8/4′−9, 8′−8″/9′−9″, triangeliphthalides C−D (**3**−**4**)) originate from three molecules of monomer phthalides (*Z*-ligustilide or *Z*-butylidenephthalide) through [2+2]/[2+2] cycloaddition.



Scheme S1. The plausible formation modes of compounds **1**−**6**.

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17. The 1D and 2D NMR spectra of 1−6

The 1D and 2D NMR spectra of 1

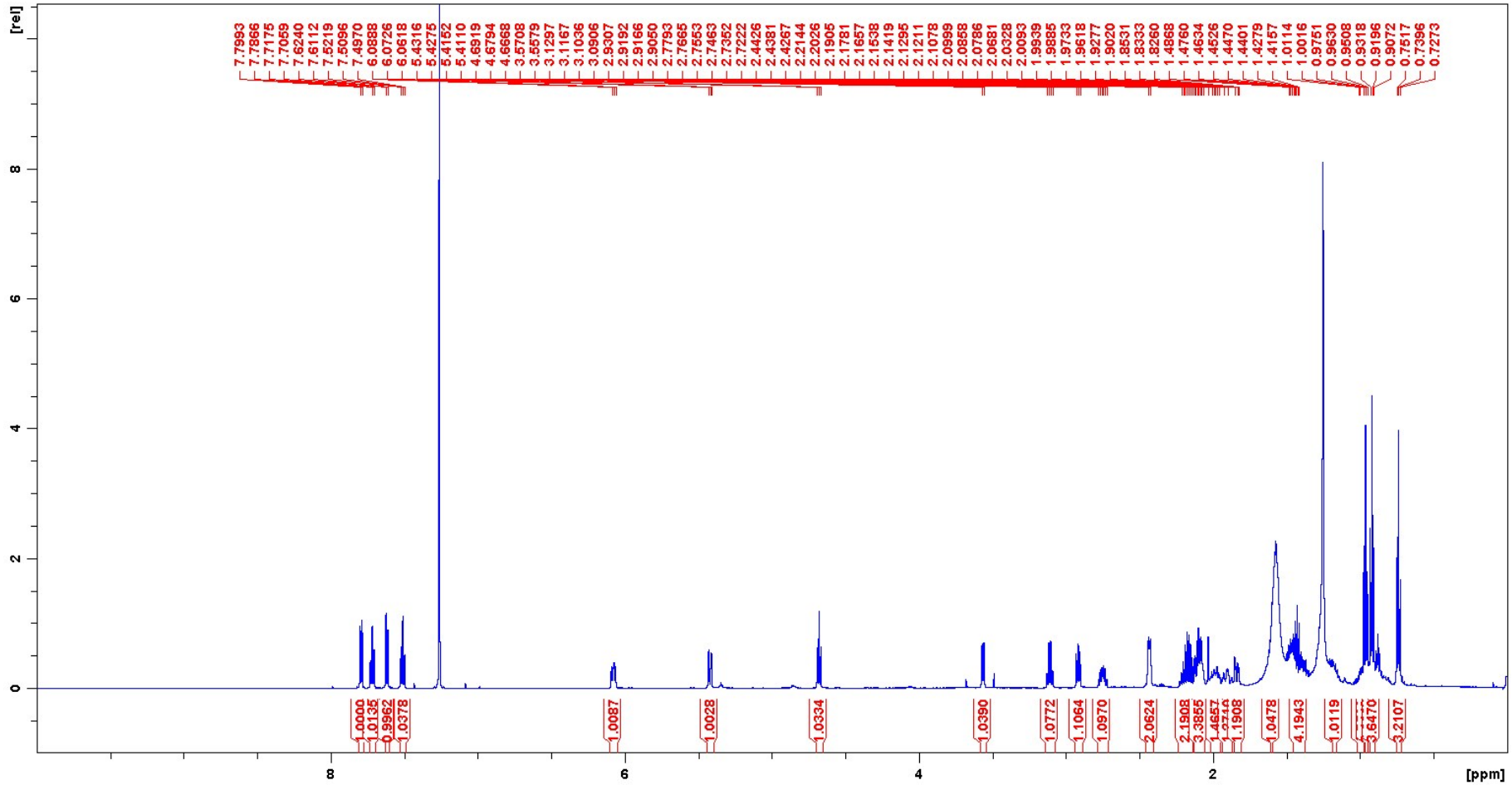

Figure S24. ^{1}H spectrum of triangeliphthalide A (600 MHz, in $CDCl_3$)

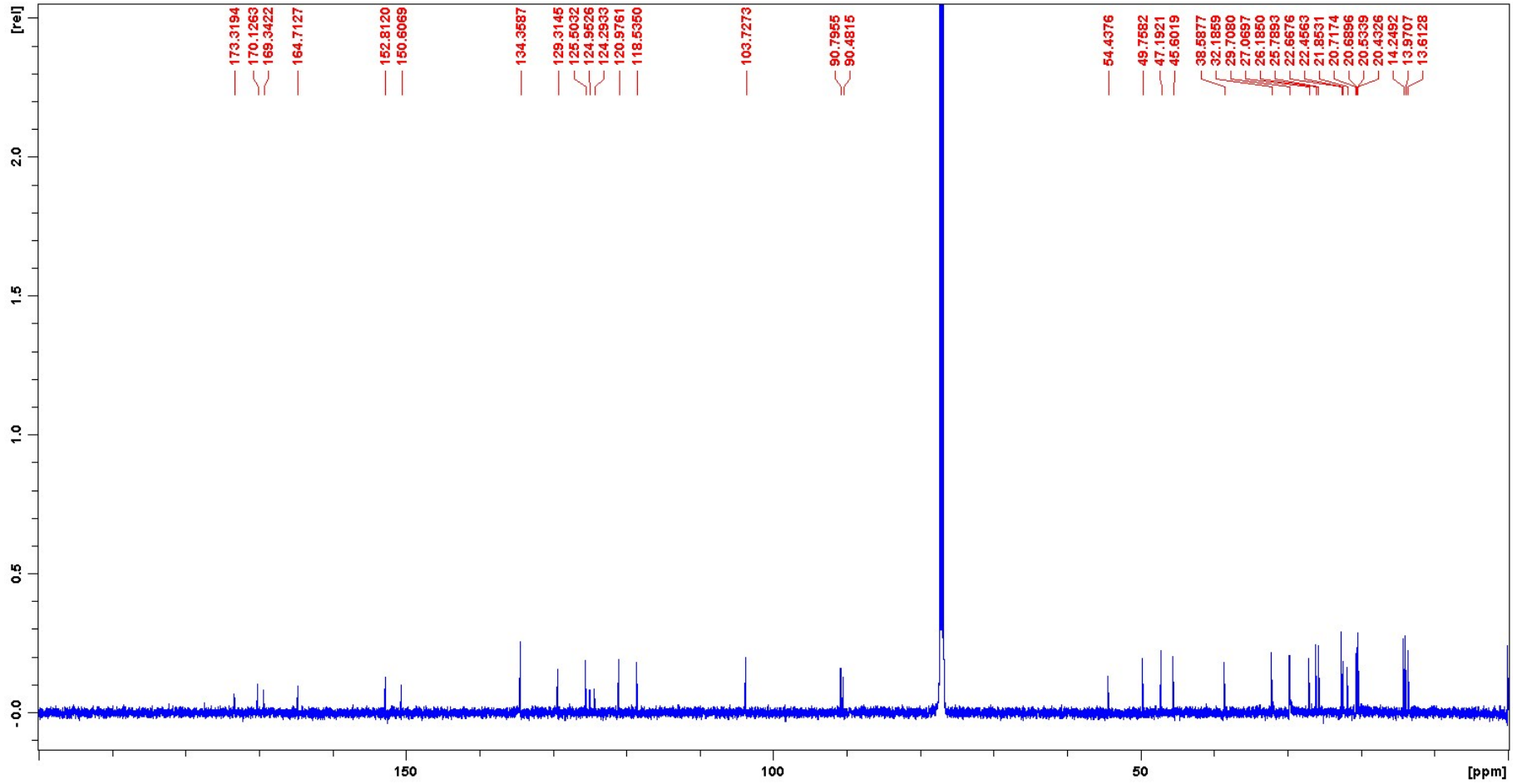

Figure S25. ^{13}C spectrum of triangeliphthalide A (150 MHz, in $CDCl_3$)

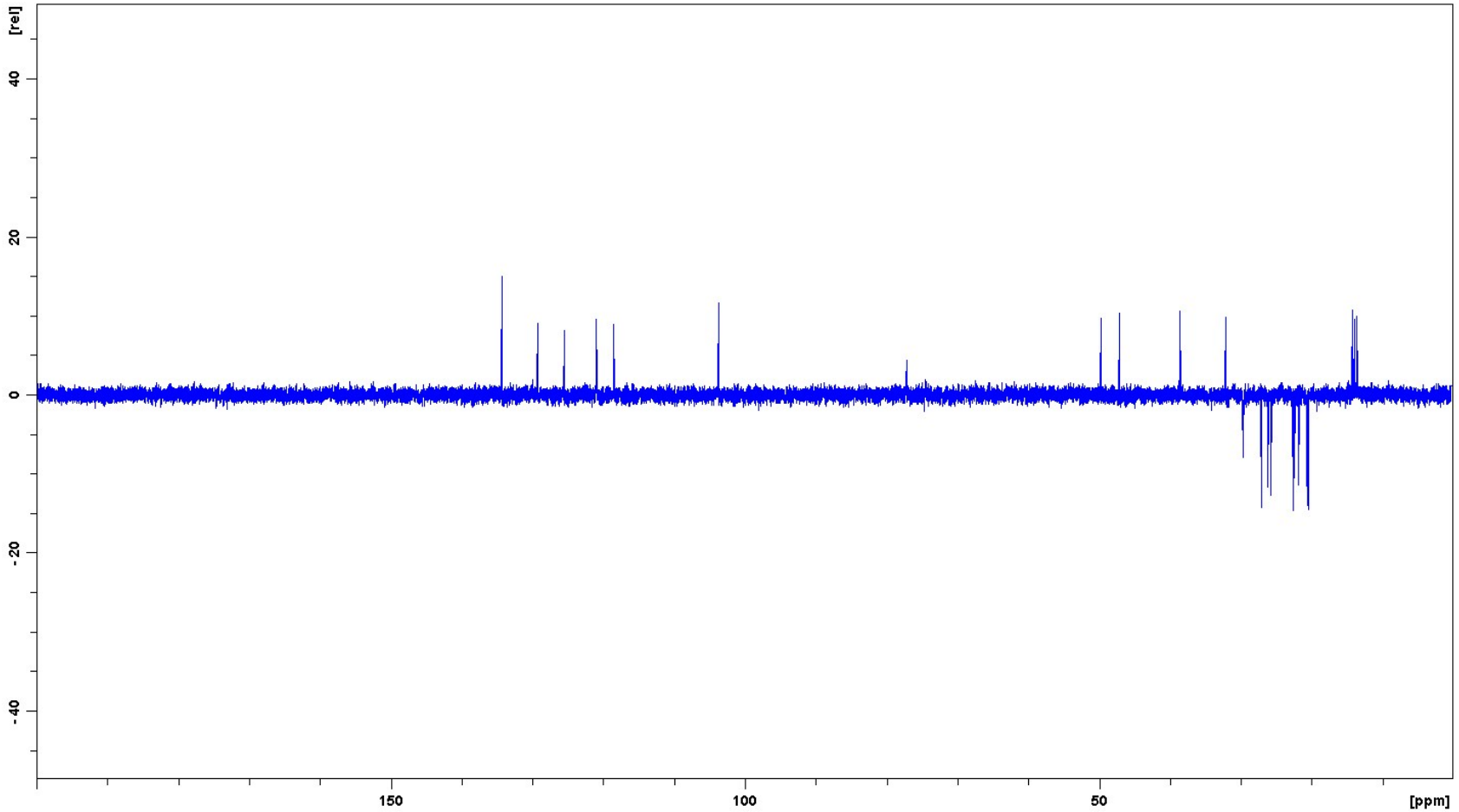

Figure S26. DEPT135 spectrum of triangeliphthalide A (150 MHz, in $CDCl_3$)

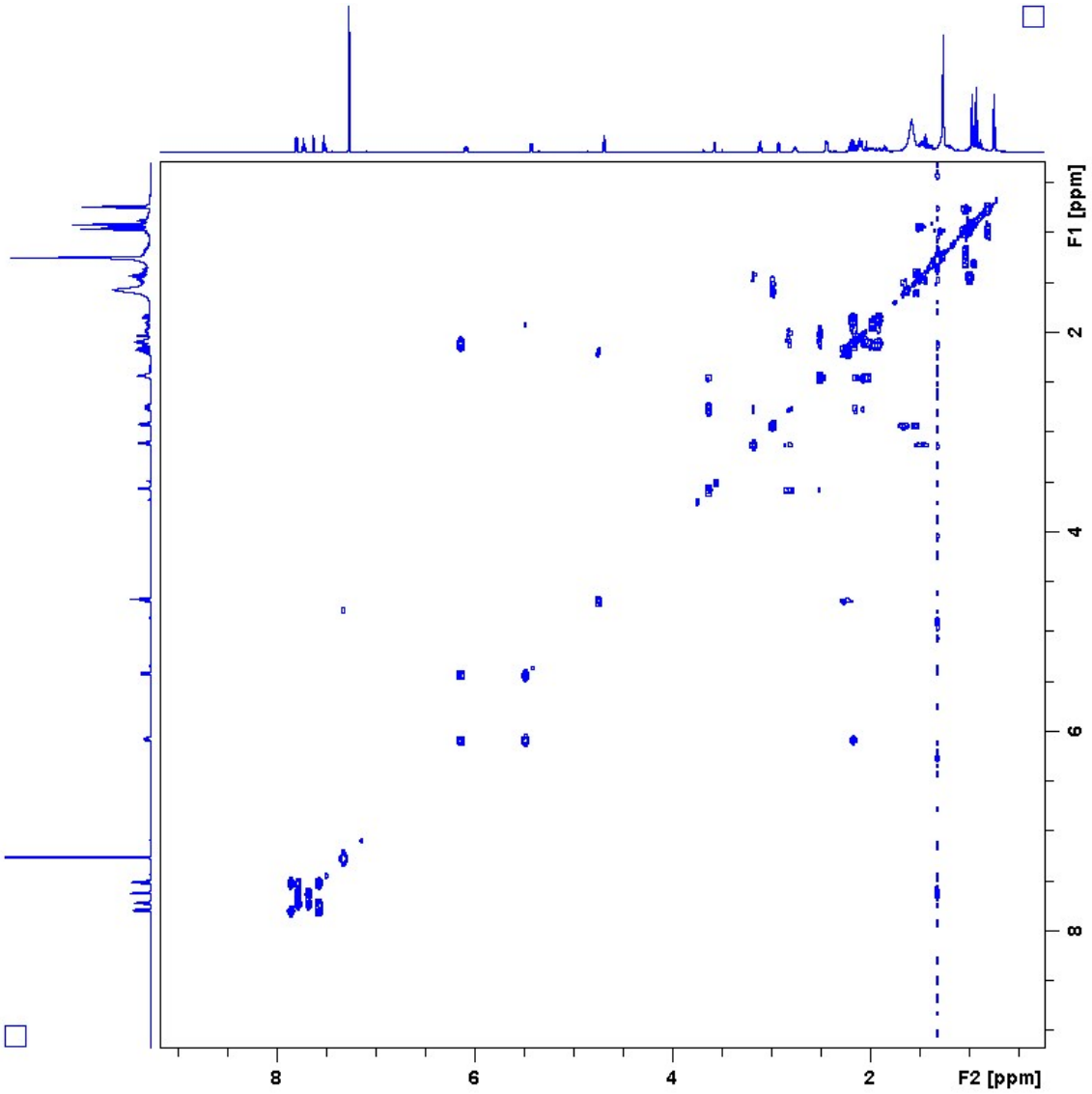

Figure S27. ^{1}H, ^{1}H-COSY spectrum of triangeliphthalide A ($CDCl_3$)

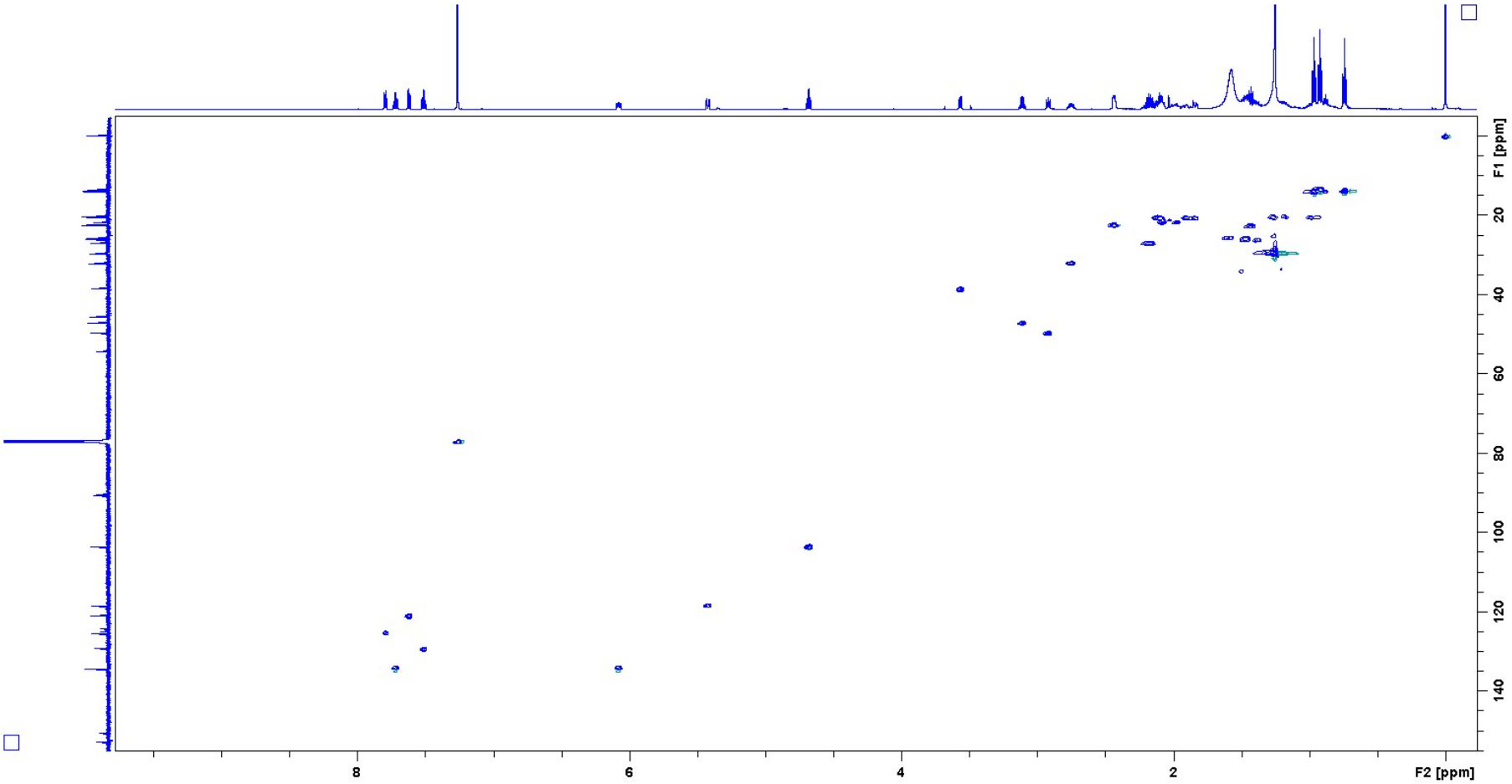

Figure S28. HSQC spectrum of triangeliphthalide A ($CDCl_3$)

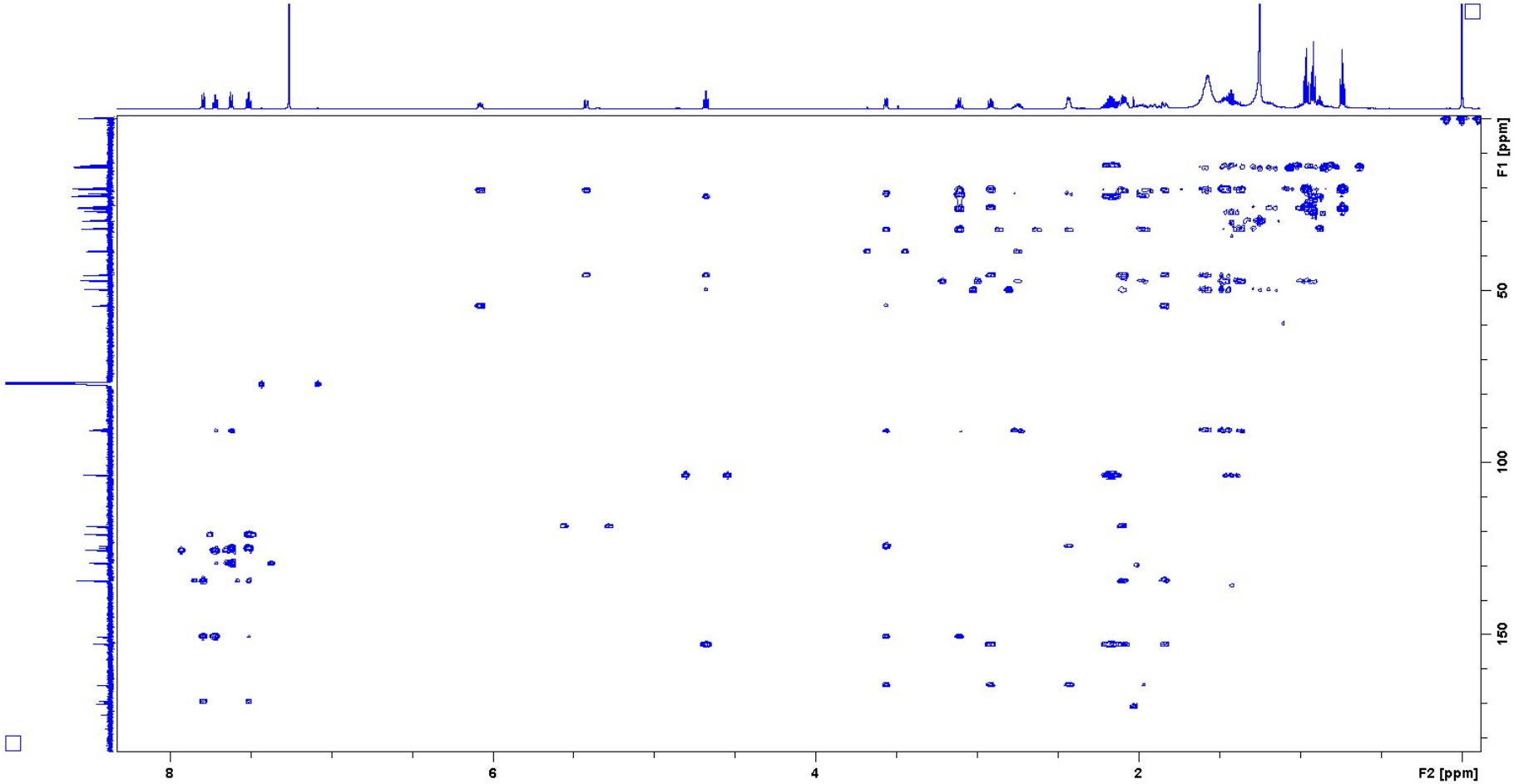

Figure S29. HMBC spectrum of triangeliphthalide A ($CDCl_3$)

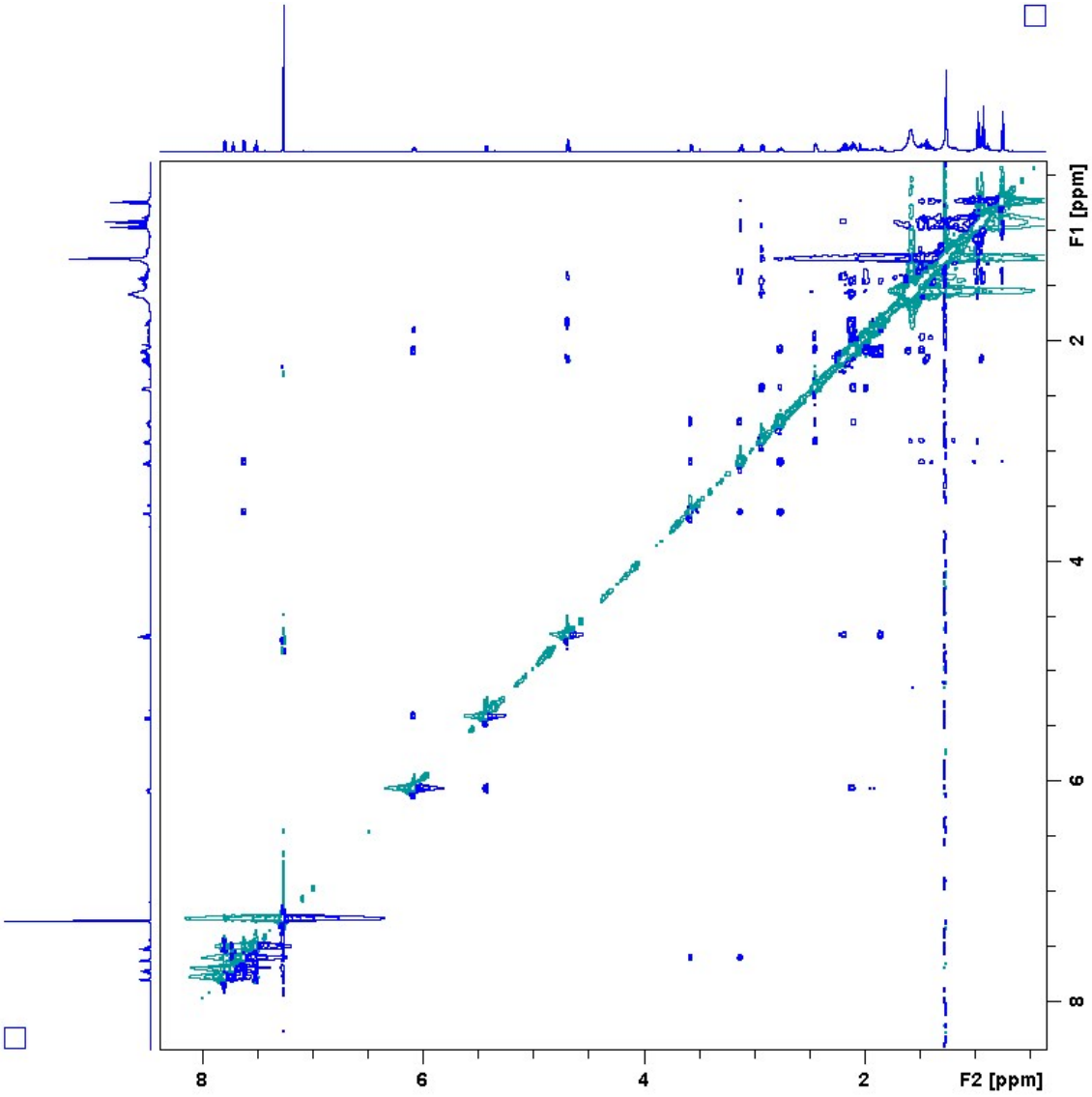

Figure S30. NOESY spectrum of triangeliphthalide A ($CDCl_3$)

The 1D and 2D NMR spectra of 2

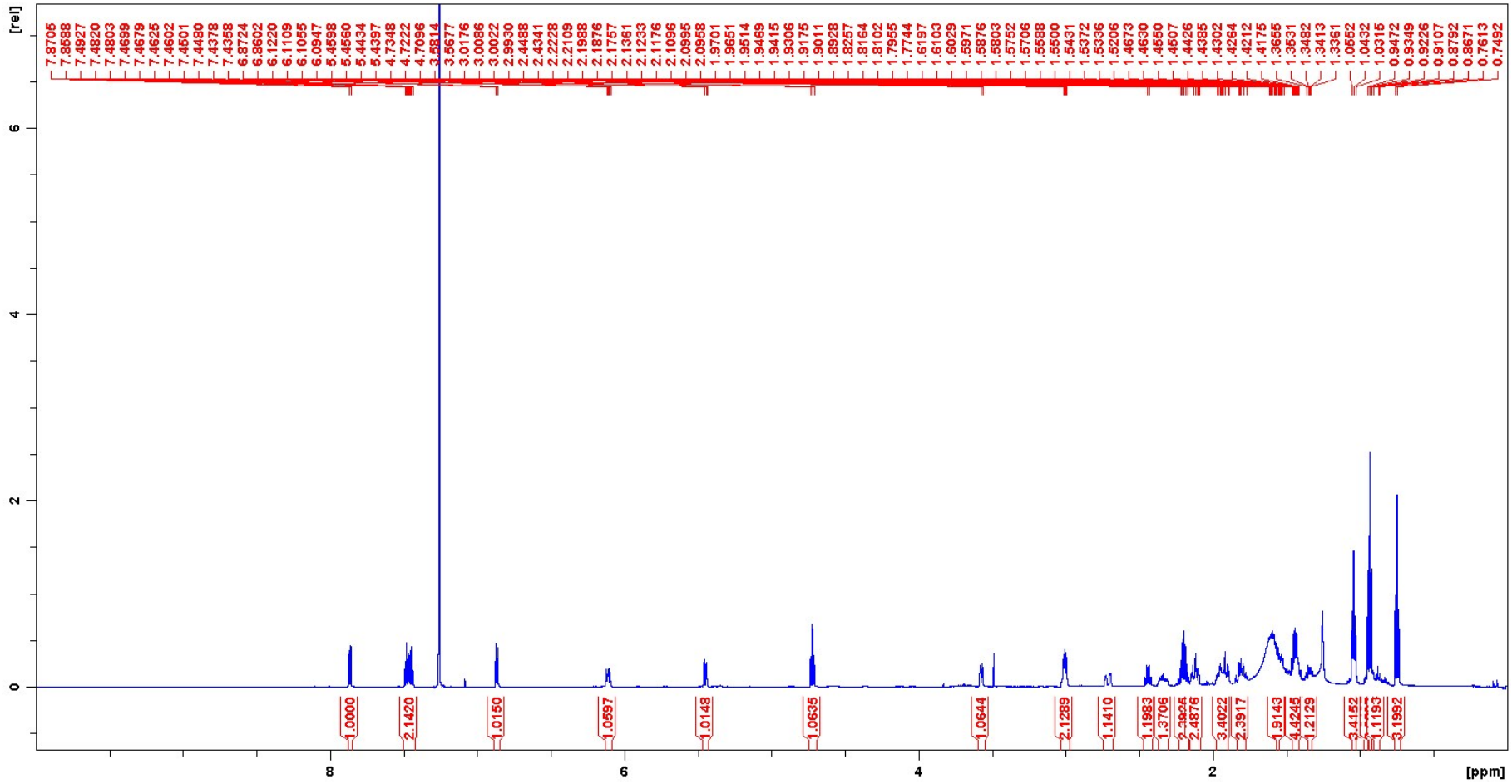

Figure S31. ^{1}H spectrum of triangeliphthalide B (600 MHz, in $CDCl_3$)

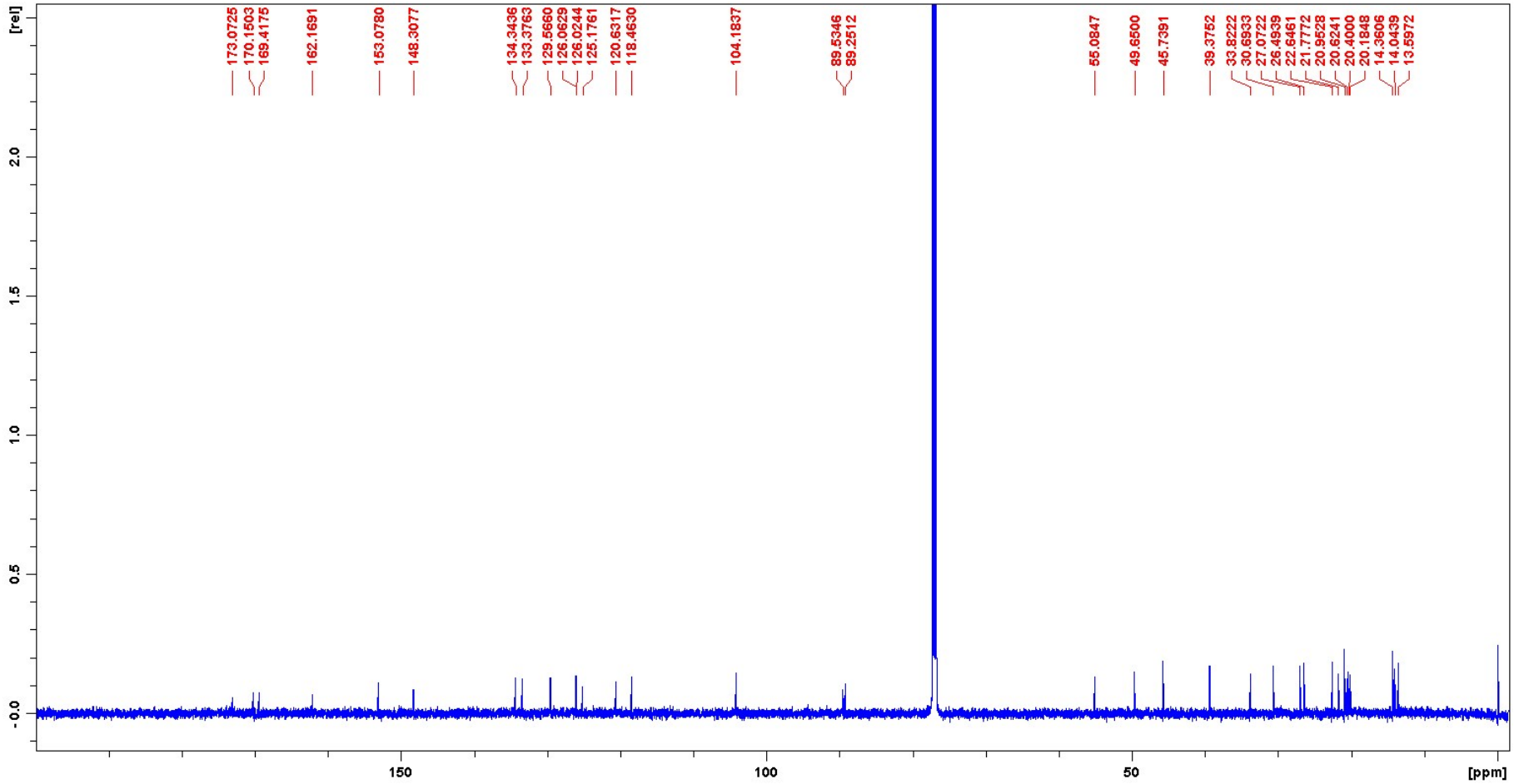

Figure S32. ^{13}C spectrum of triangeliphthalide B (150 MHz, in $CDCl_3$)

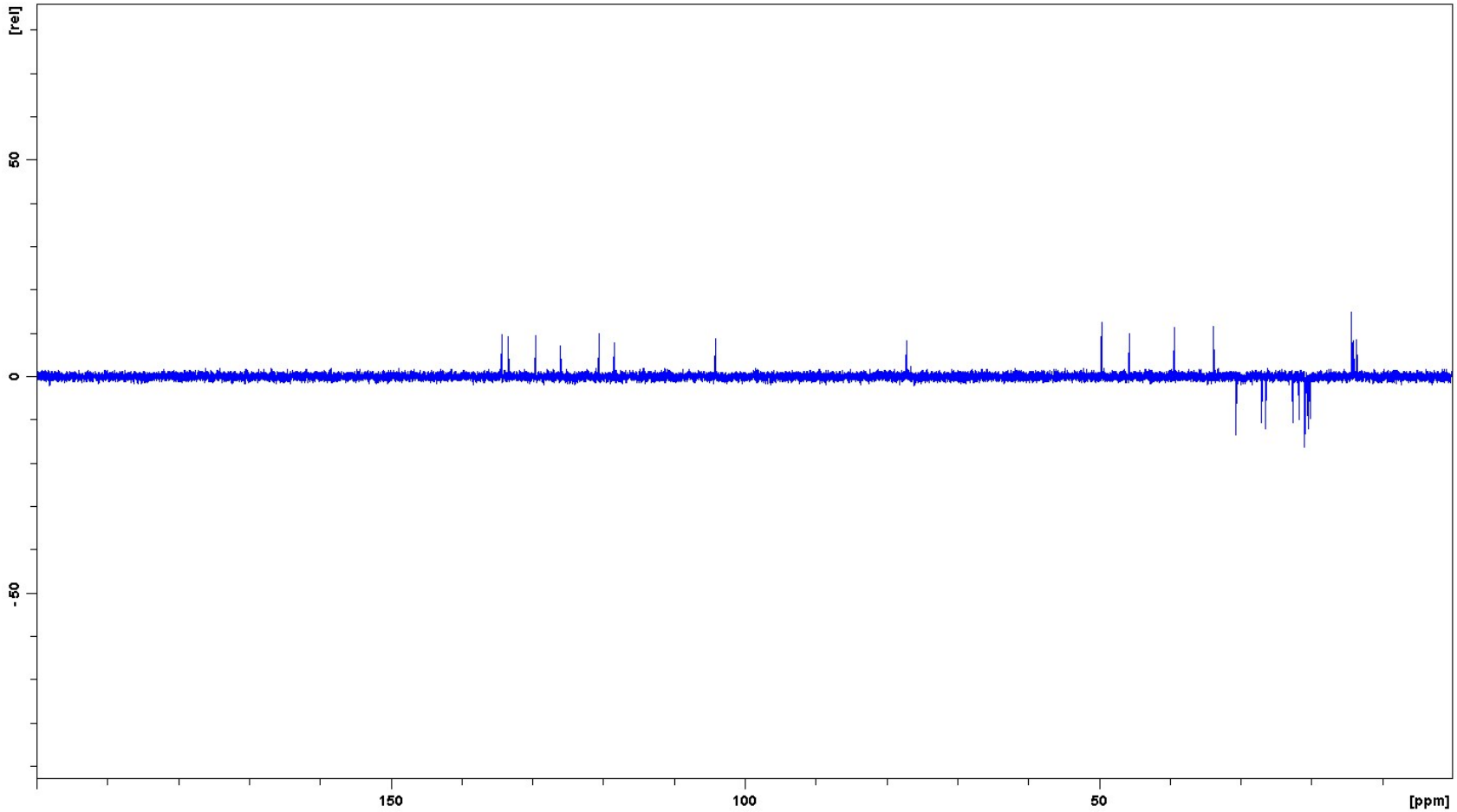

Figure S33. DEPT135 spectrum of triangeliphthalide B (150 MHz, in $CDCl_3$)

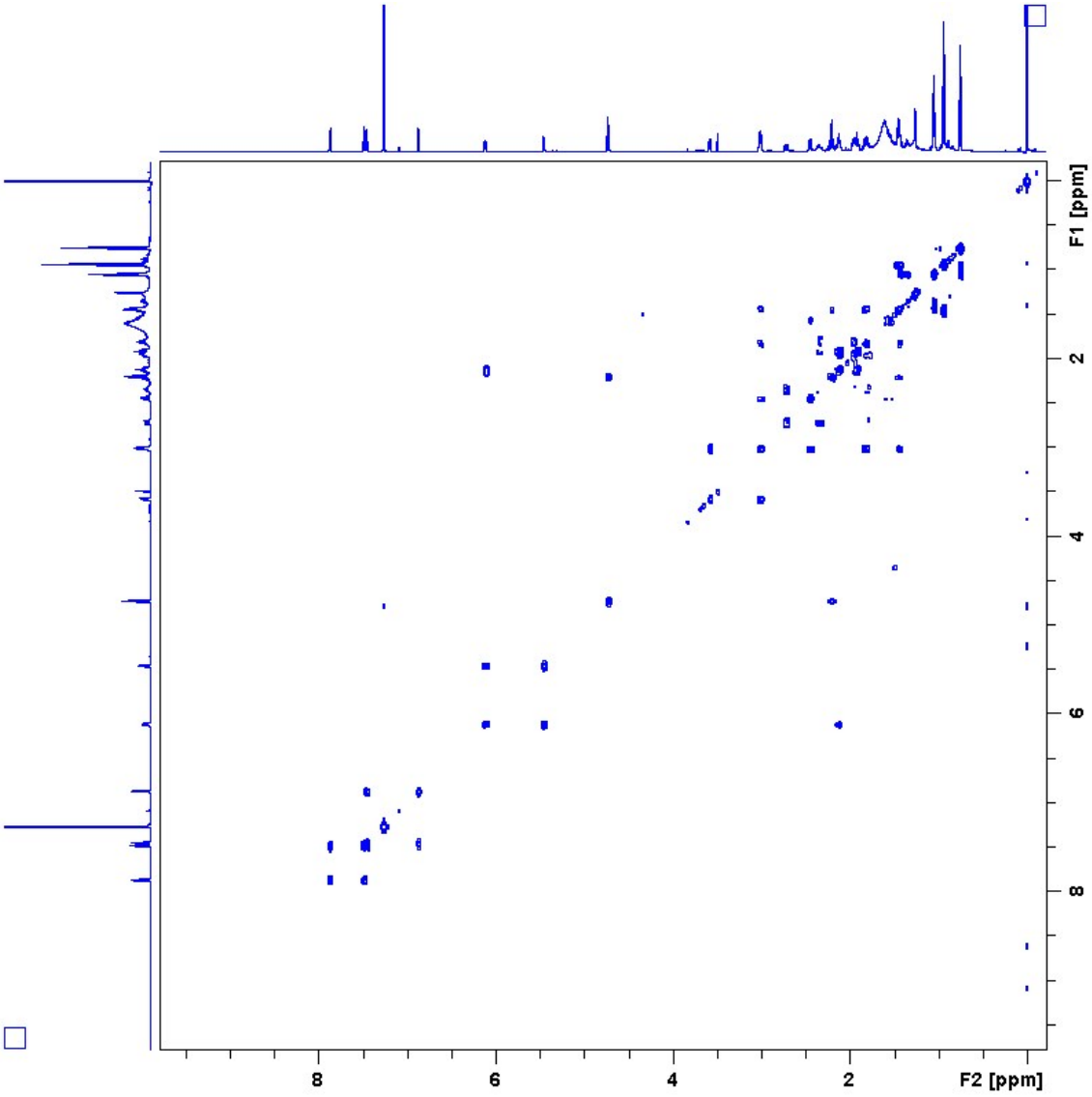

Figure S34. ^{1}H, ^{1}H-COSY spectrum of triangeliphthalide B ($CDCl_3$)

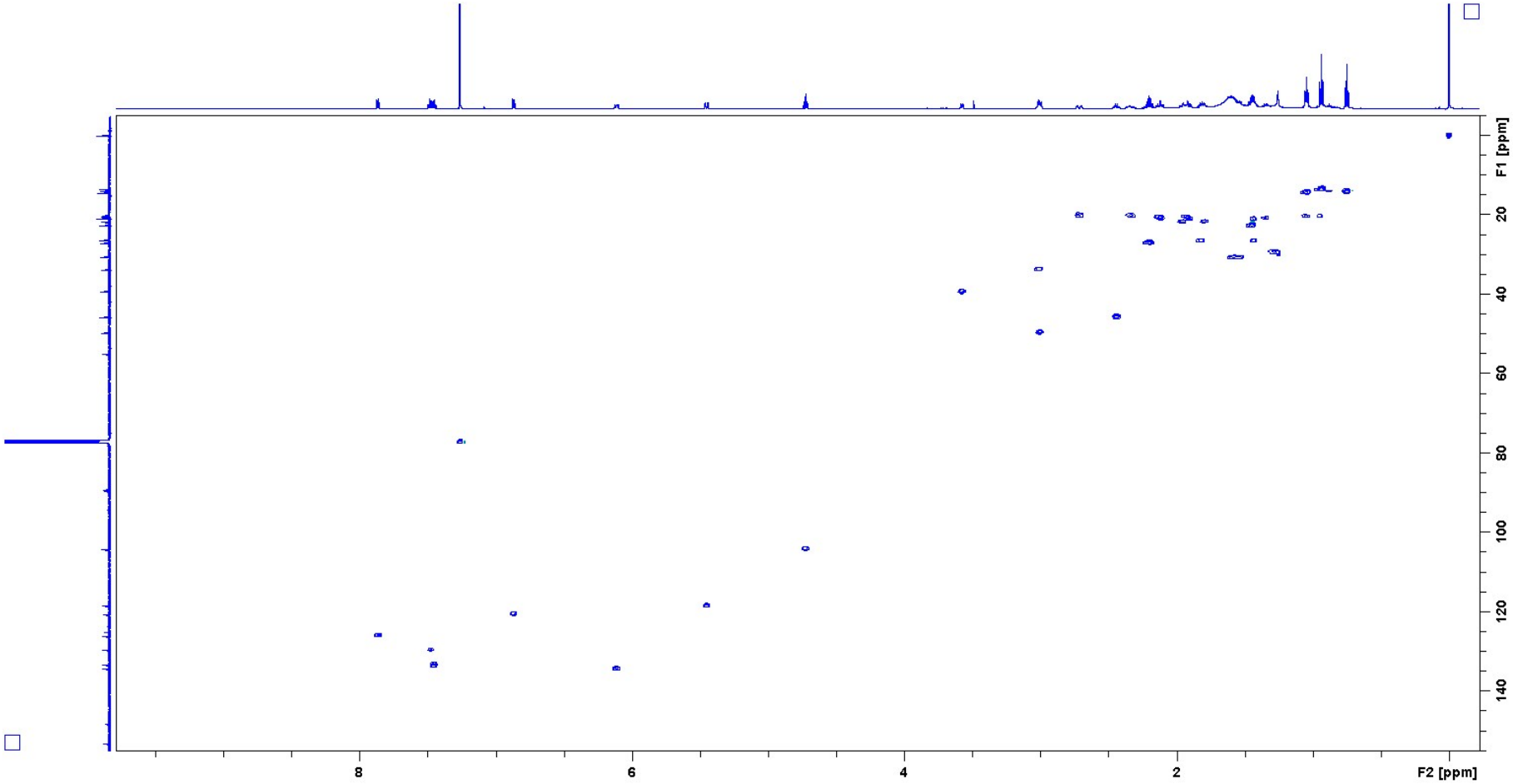

Figure S35. HSQC spectrum of triangeliphthalide B ($CDCl_3$)

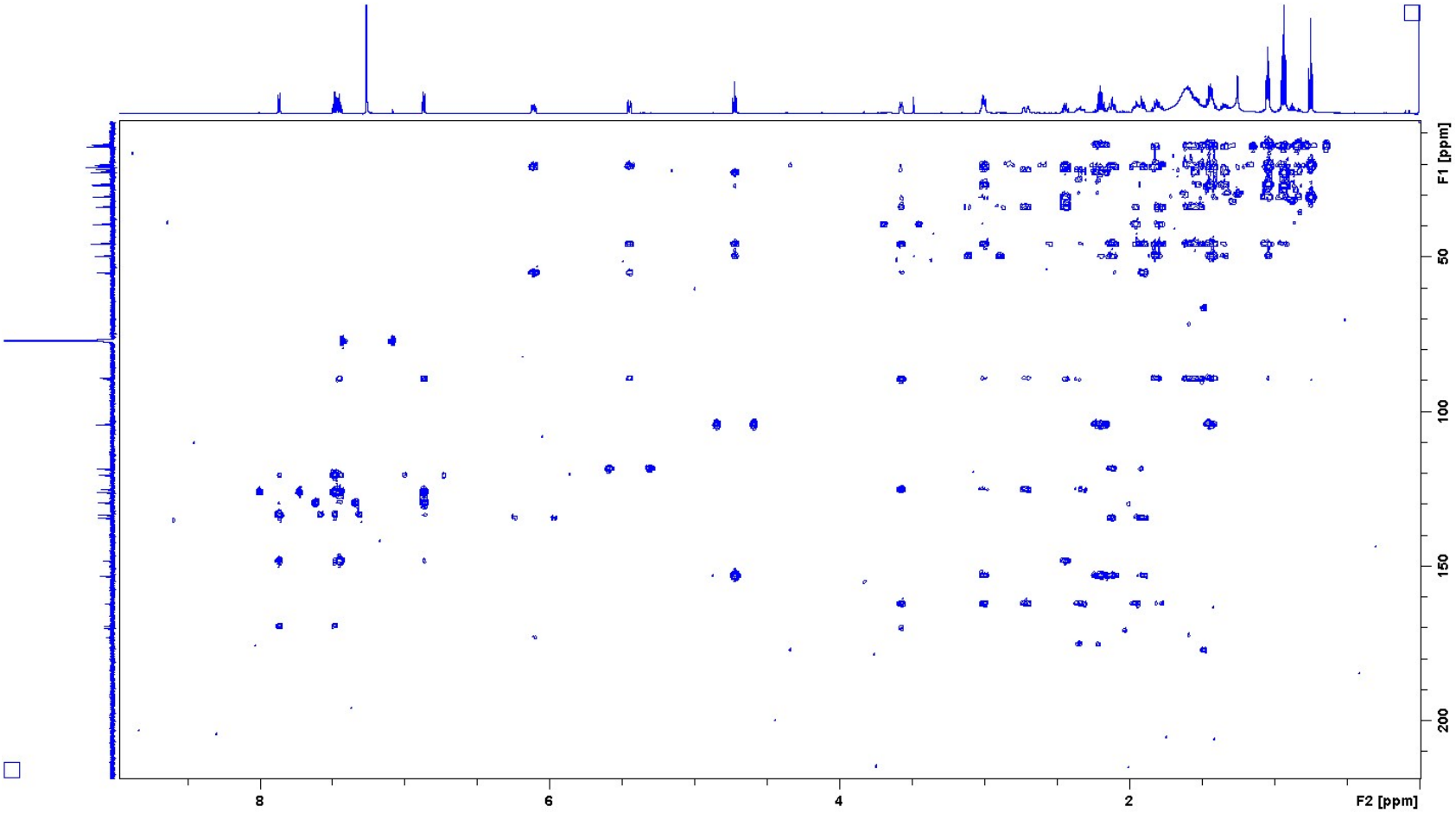

Figure S36. HMBC spectrum of triangeliphthalide B ($CDCl_3$)

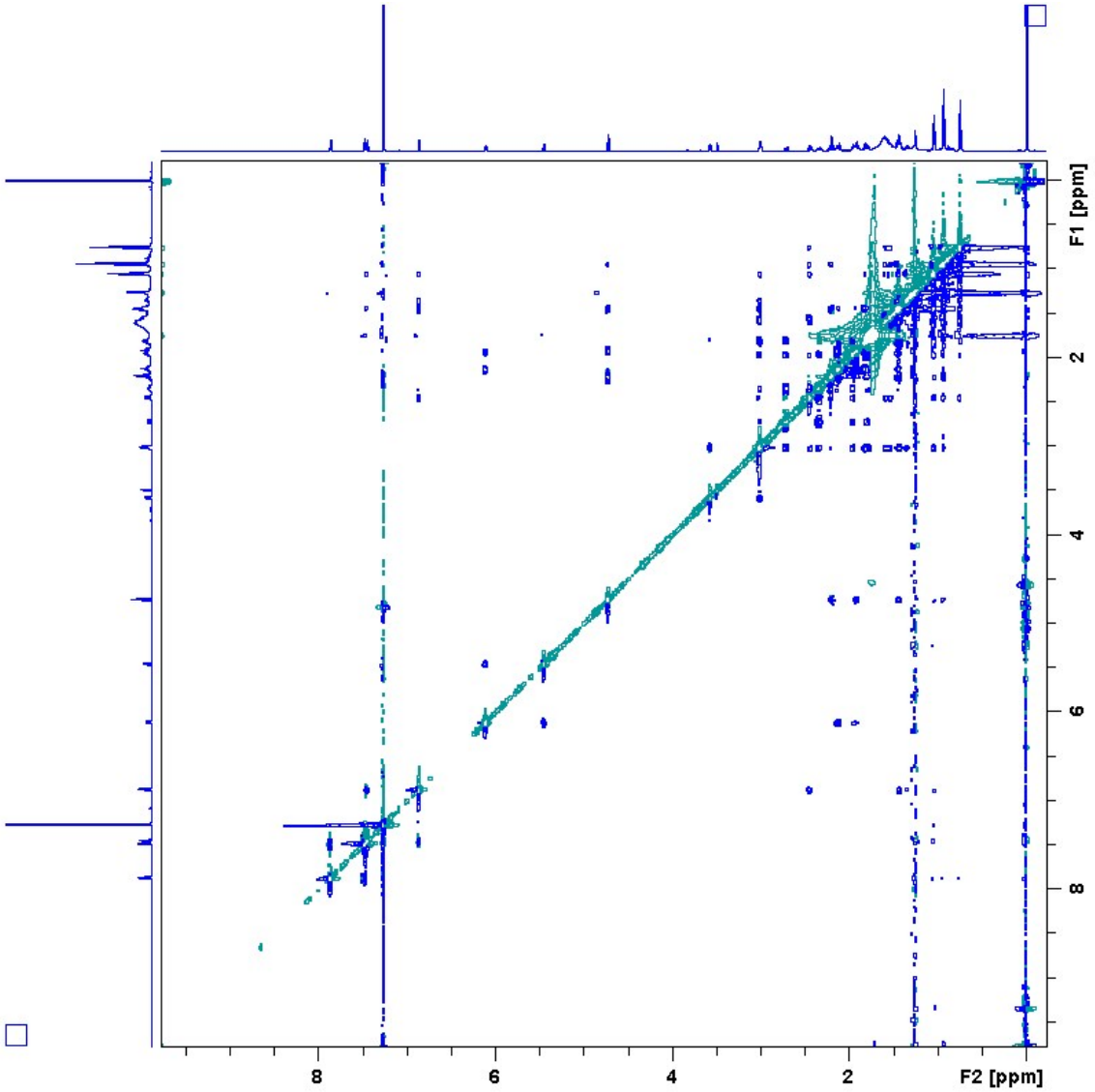

Figure S37. NOESY spectrum of triangeliphthalide B ($CDCl_3$)

The 1D and 2D NMR spectra of 3

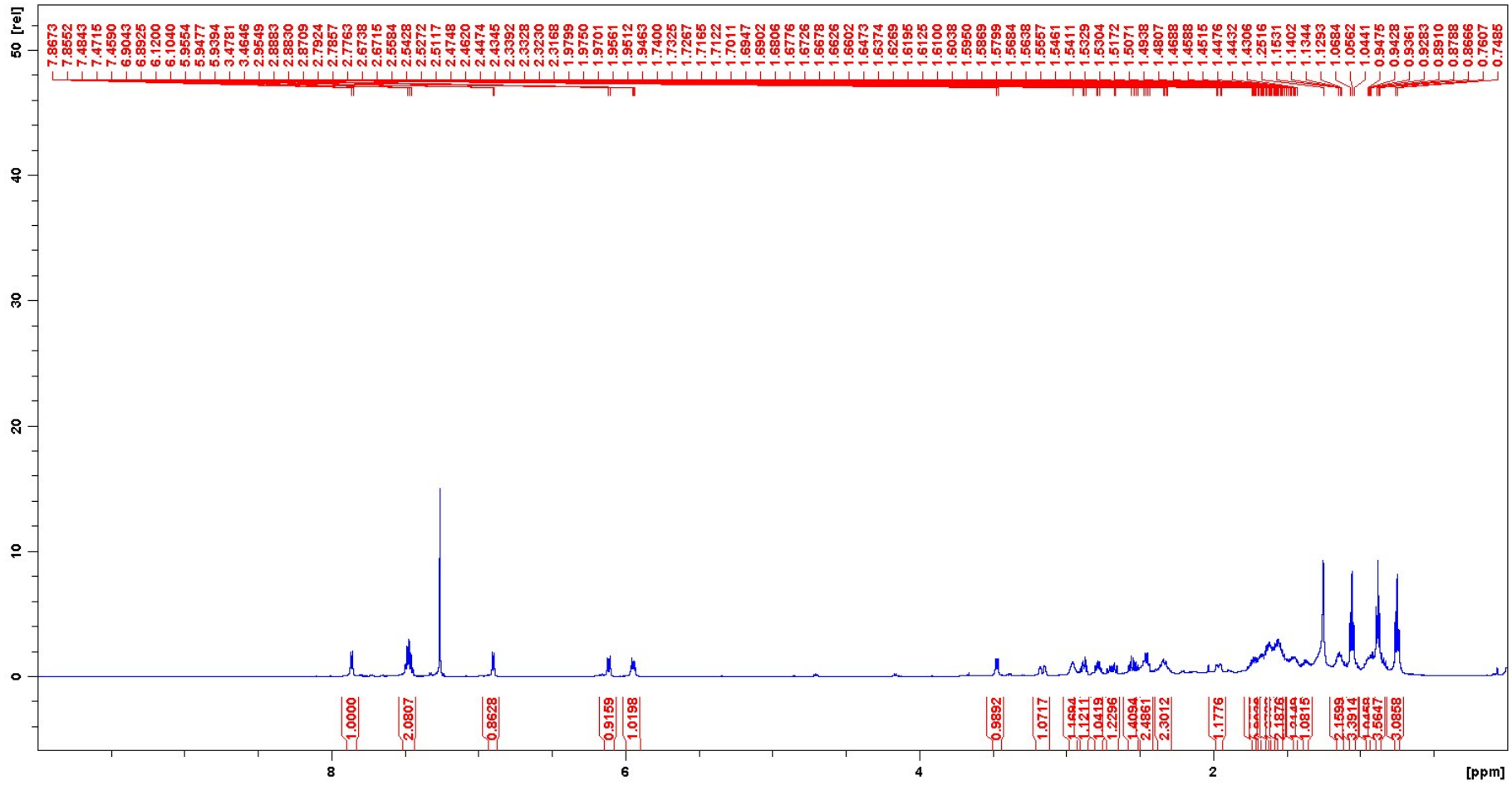

Figure S38. ^{1}H spectrum of triangeliphthalide C (600 MHz, in $CDCl_3$)

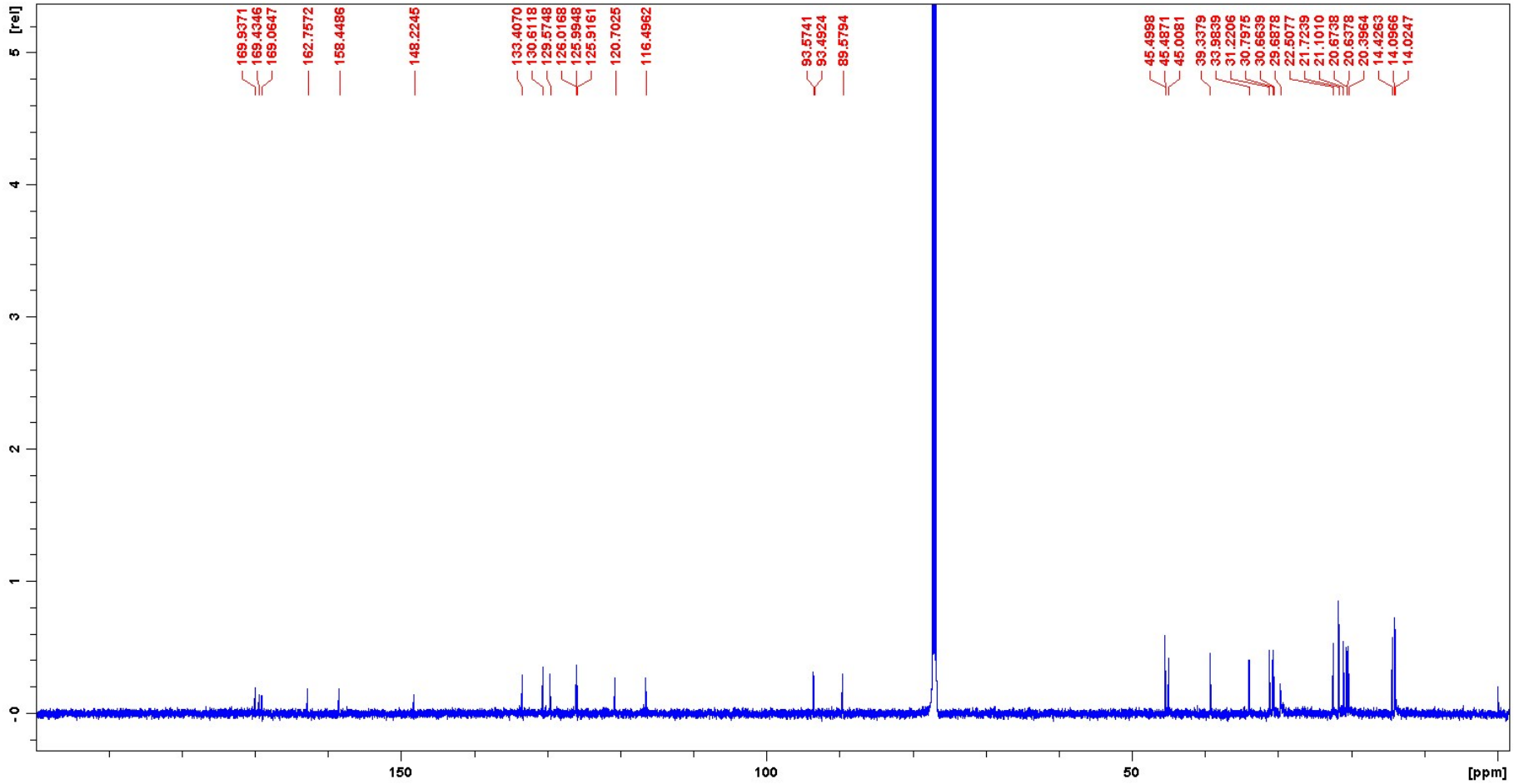

Figure S39. ^{13}C spectrum of triangeliphthalide C (150 MHz, in $CDCl_3$)

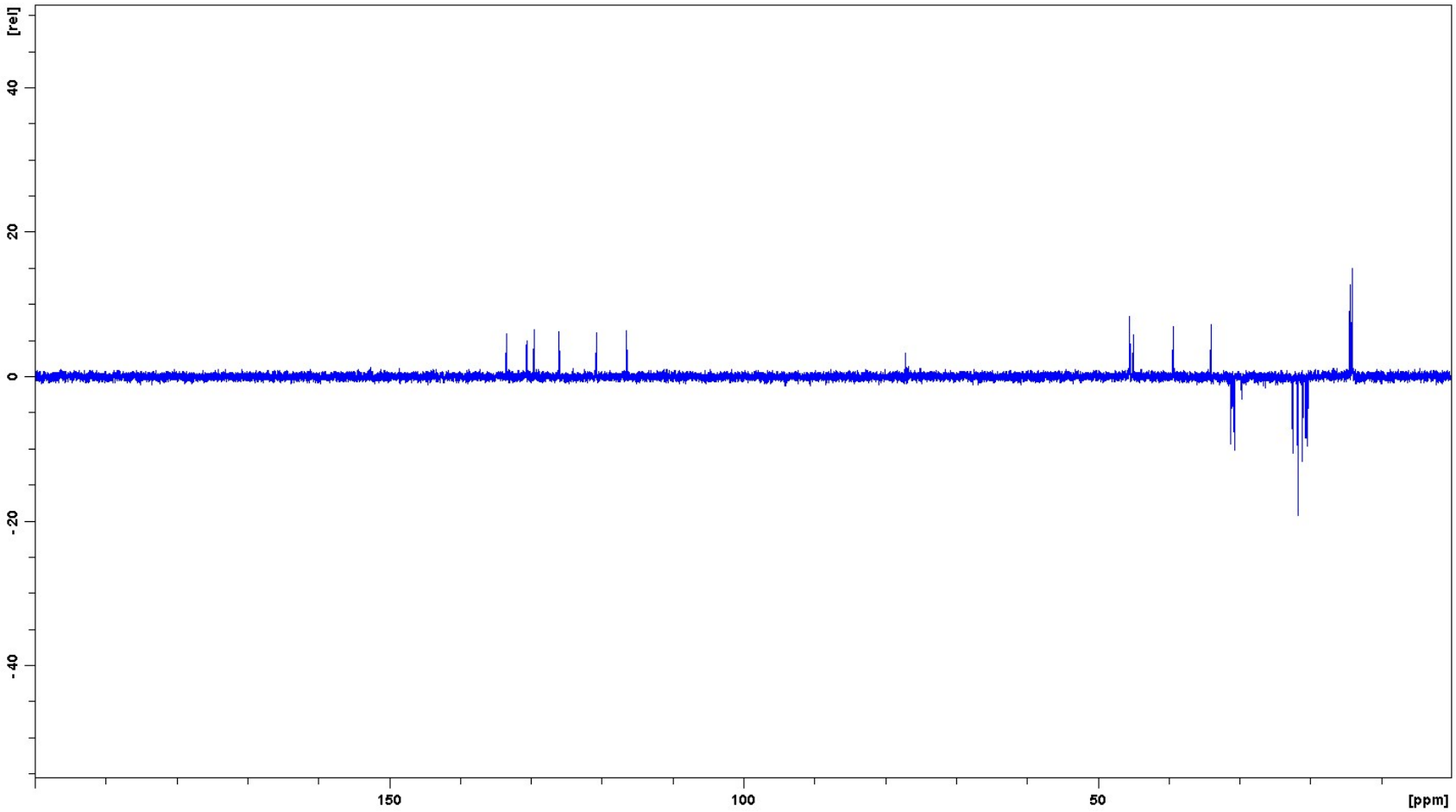

Figure S40. DEPT135 spectrum of triangeliphthalide C (150 MHz, in $CDCl_3$)

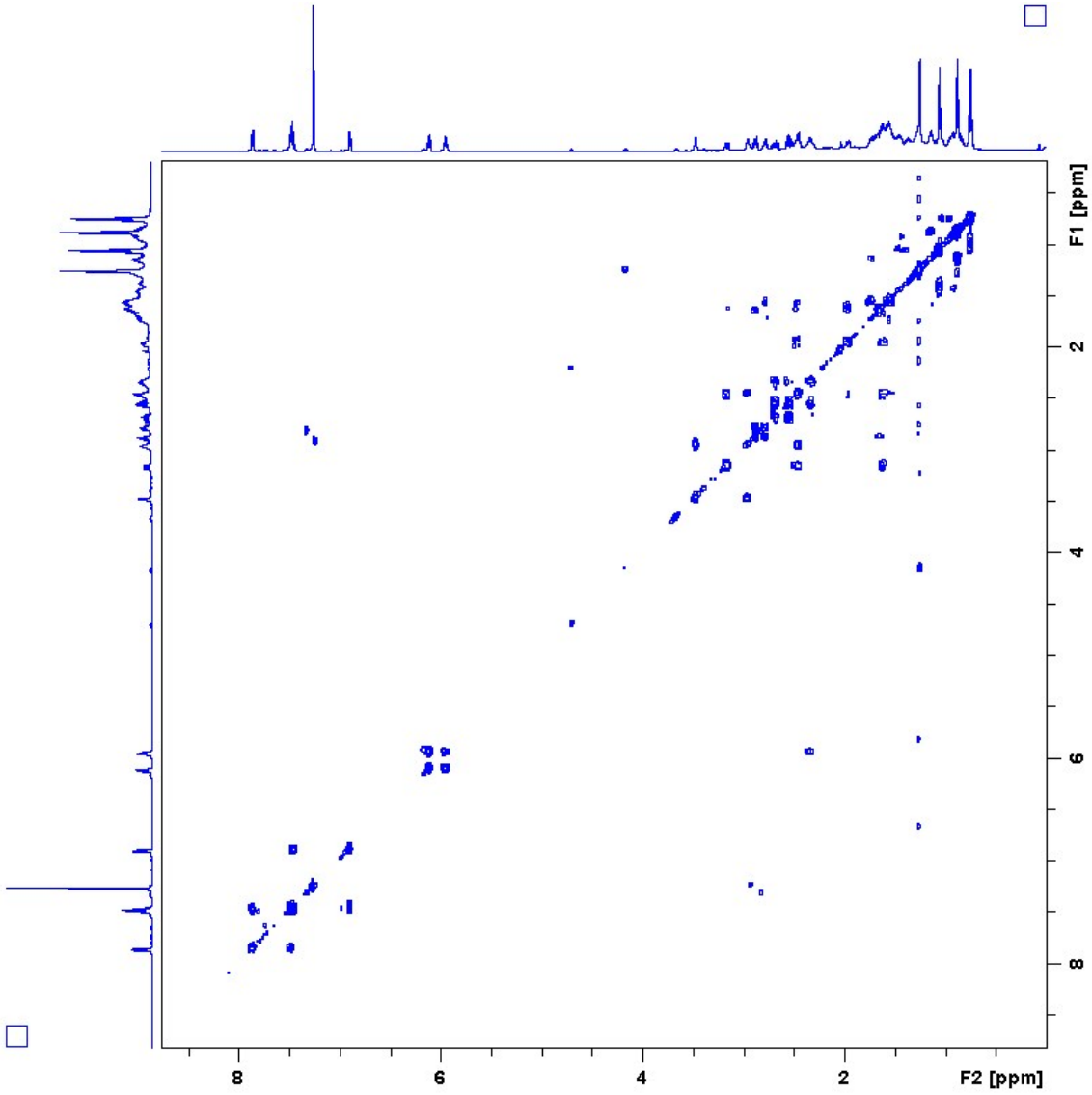

Figure S41. ^{1}H, ^{1}H-COSY spectrum of triangeliphthalide C ($CDCl_3$)

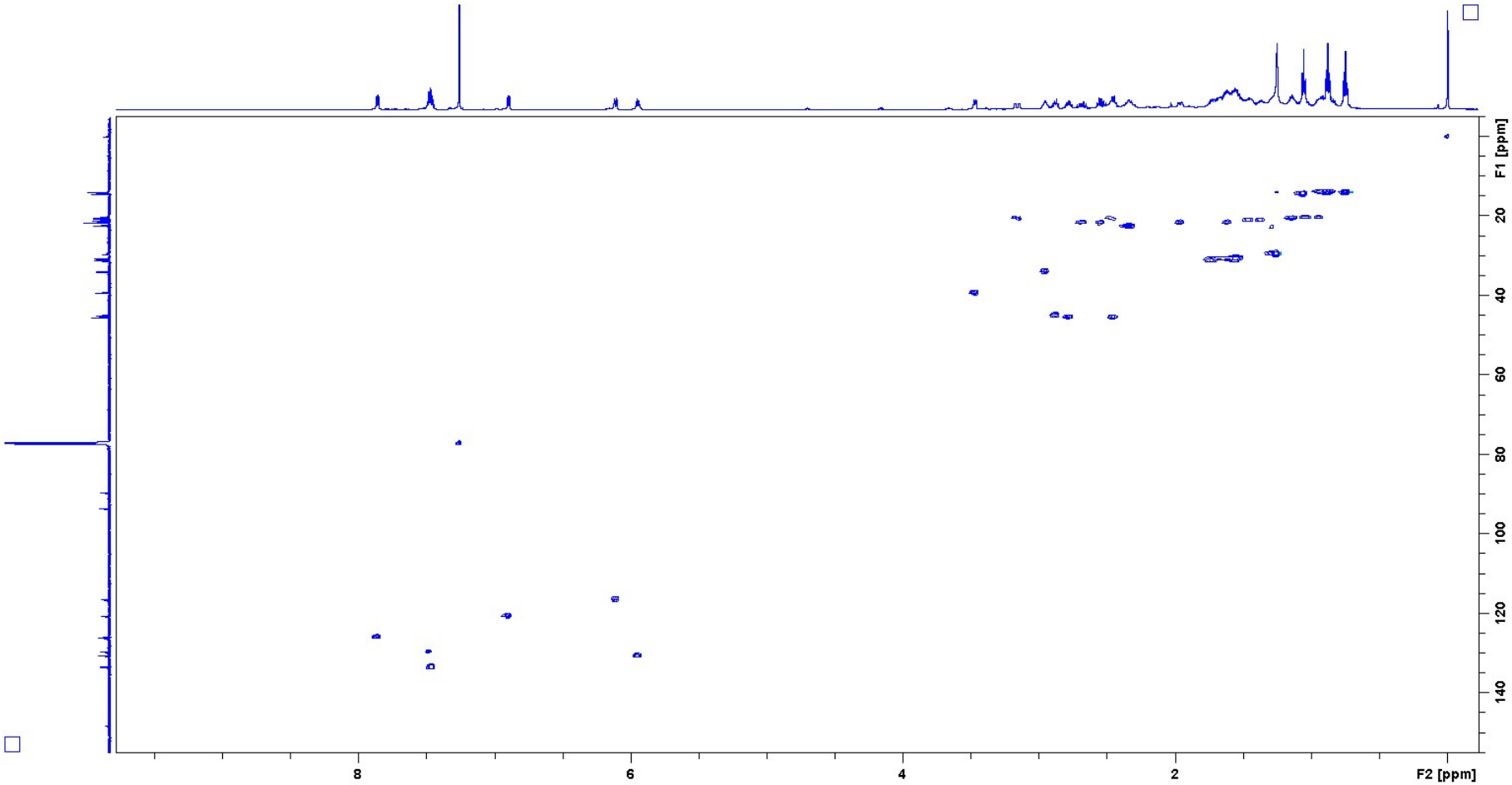

Figure S42. HSQC spectrum of triangeliphthalide C ($CDCl_3$)

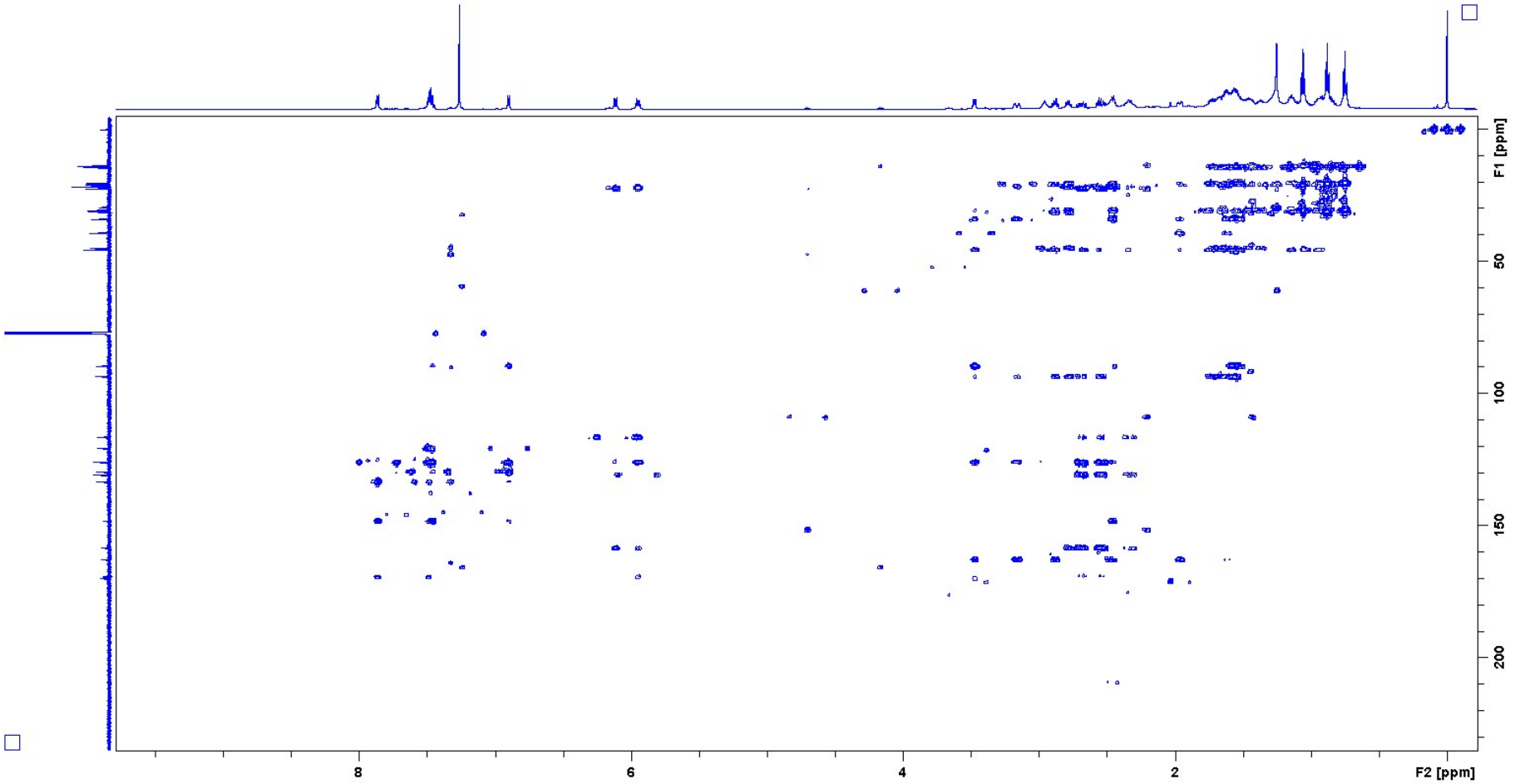

Figure S43. HMBC spectrum of triangeliphthalide C ($CDCl_3$)

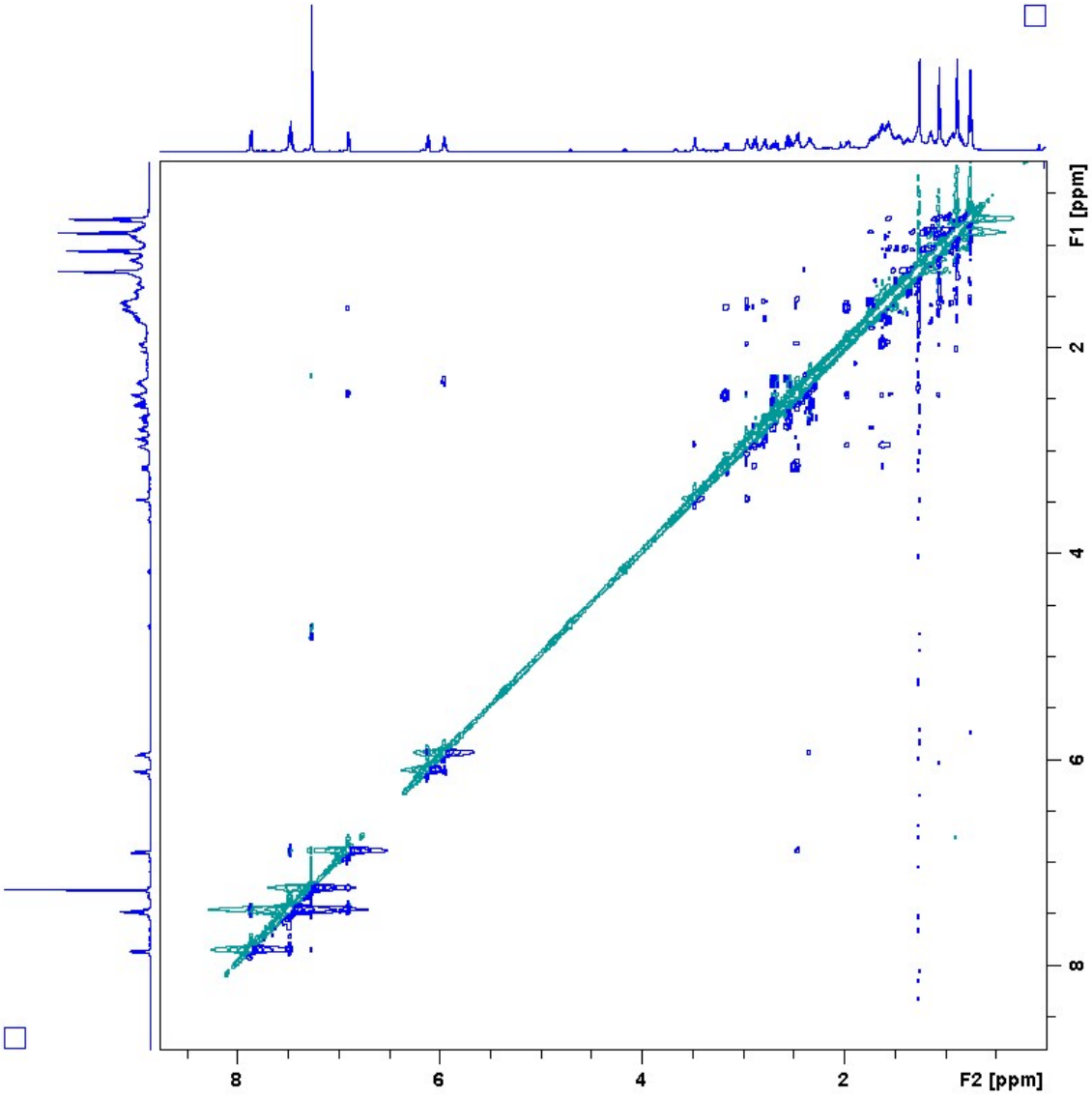

Figure S44. NOESY spectrum of triangeliphthalide C ($CDCl_3$)

The 1D and 2D NMR spectra of 4

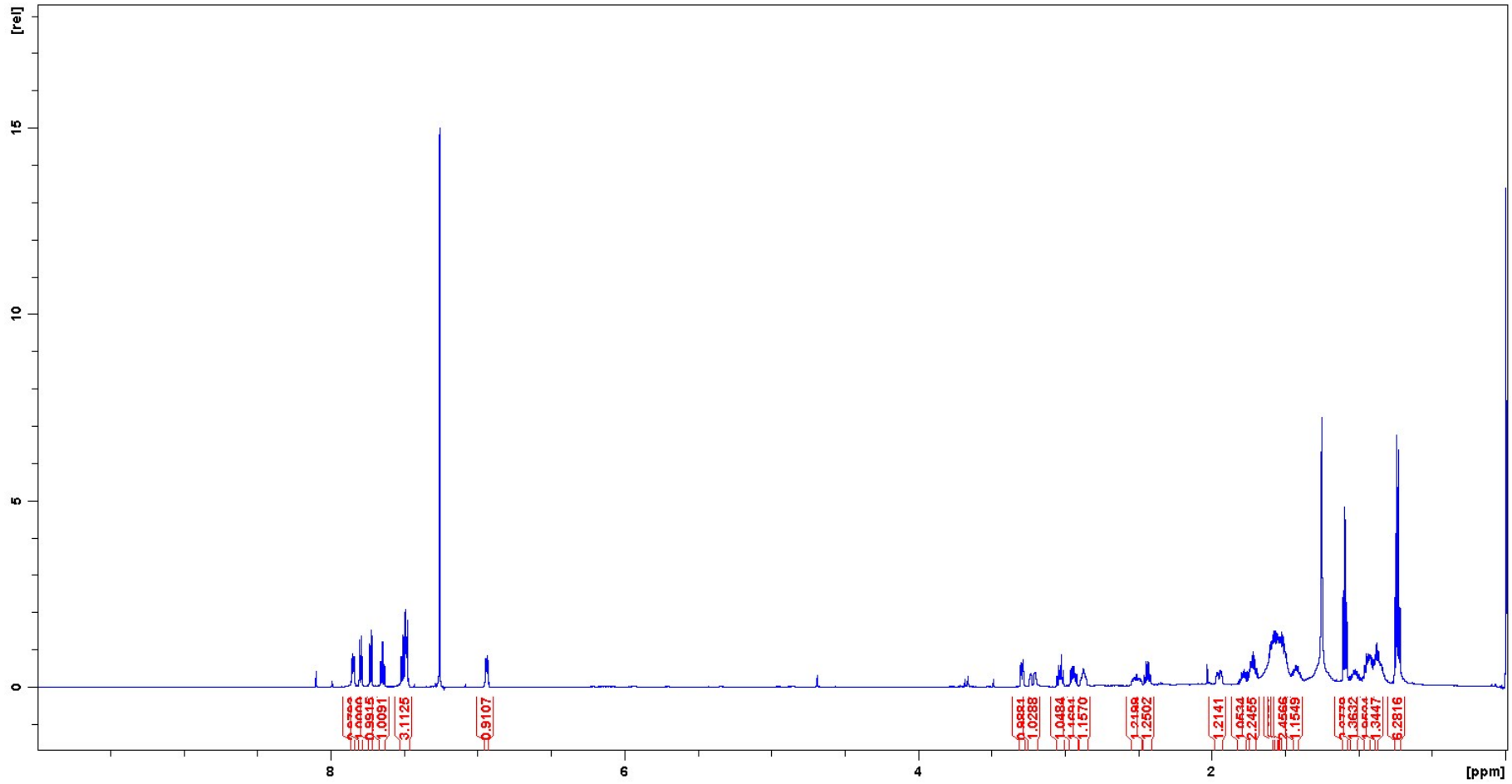

Figure S45. ^{1}H spectrum of triangeliphthalide D (600 MHz, in $CDCl_3$)

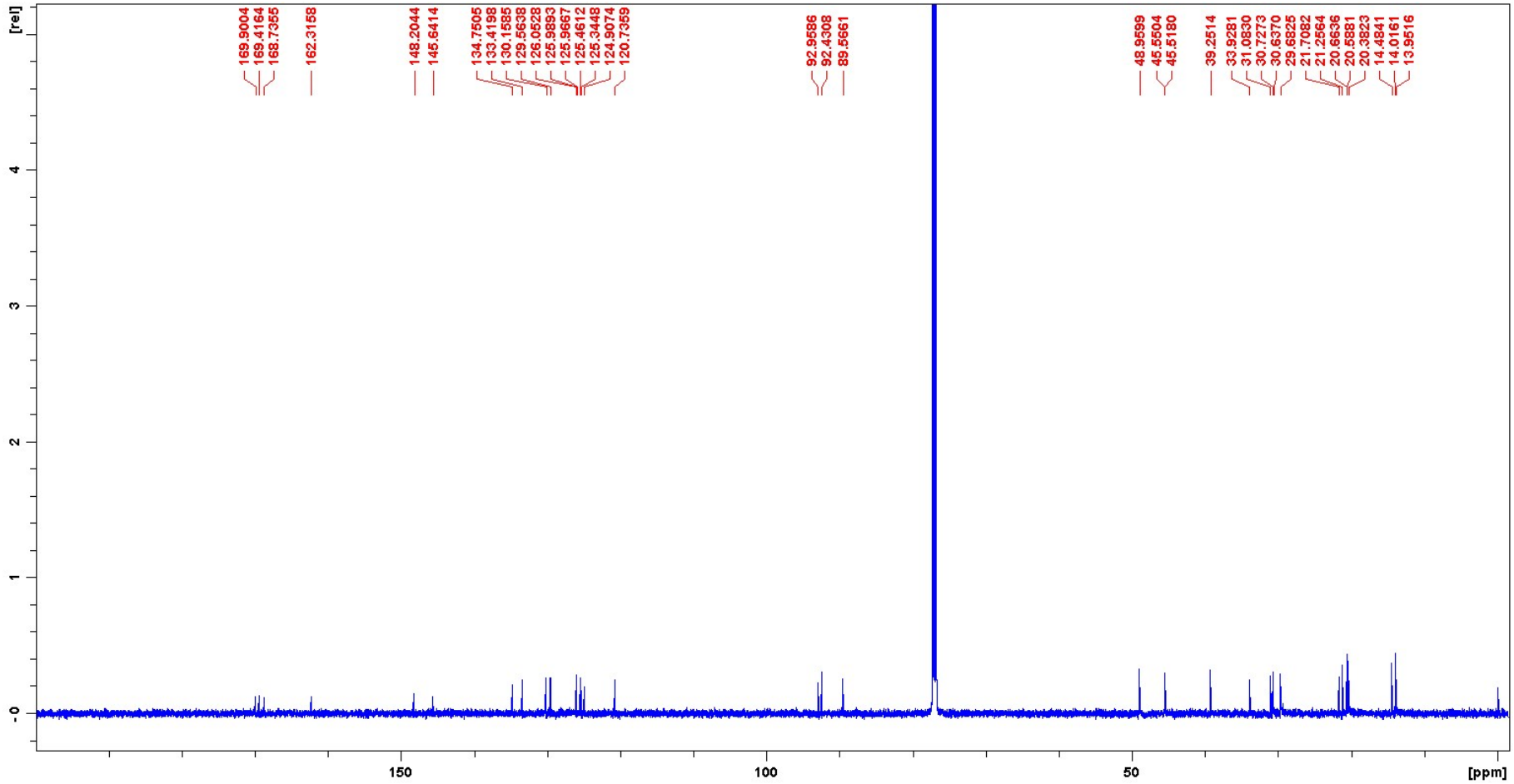

Figure S46. ^{13}C spectrum of triangeliphthalide D (150 MHz, in $CDCl_3$)

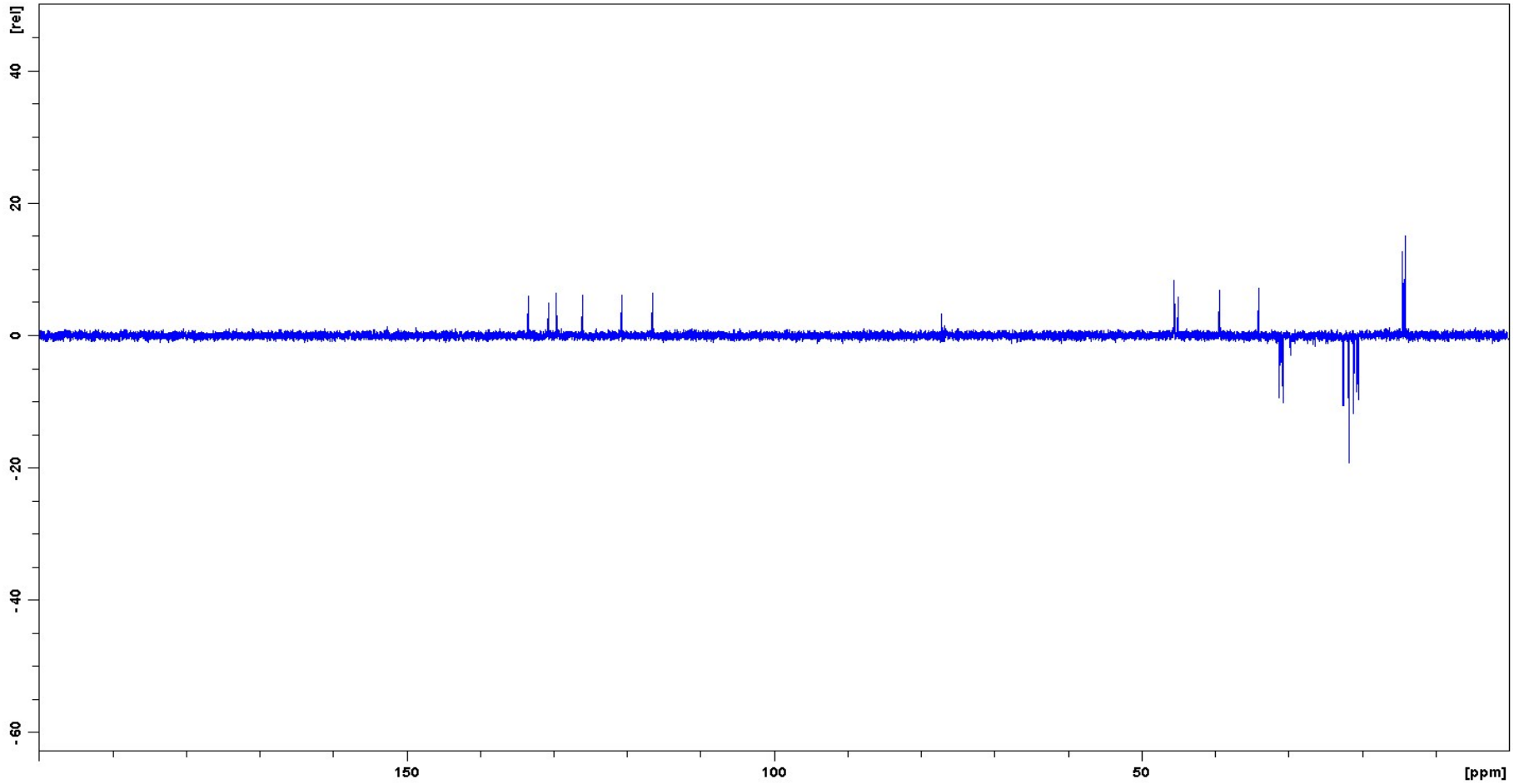

Figure S47. DEPT135 spectrum of triangeliphthalide D (150 MHz, in $CDCl_3$)

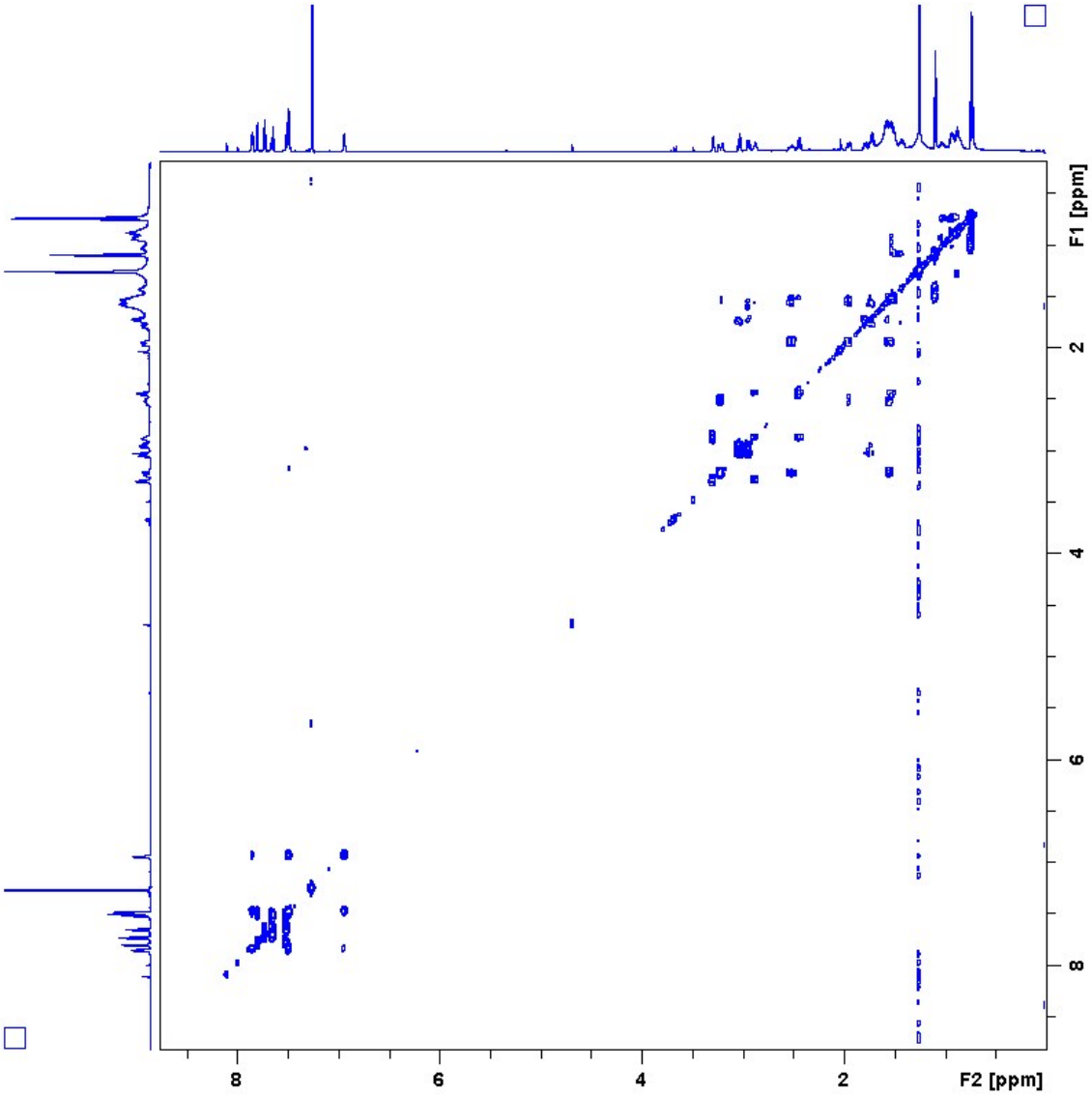

Figure S48. ^{1}H, ^{1}H-COSY spectrum of triangeliphthalide D ($CDCl_3$)

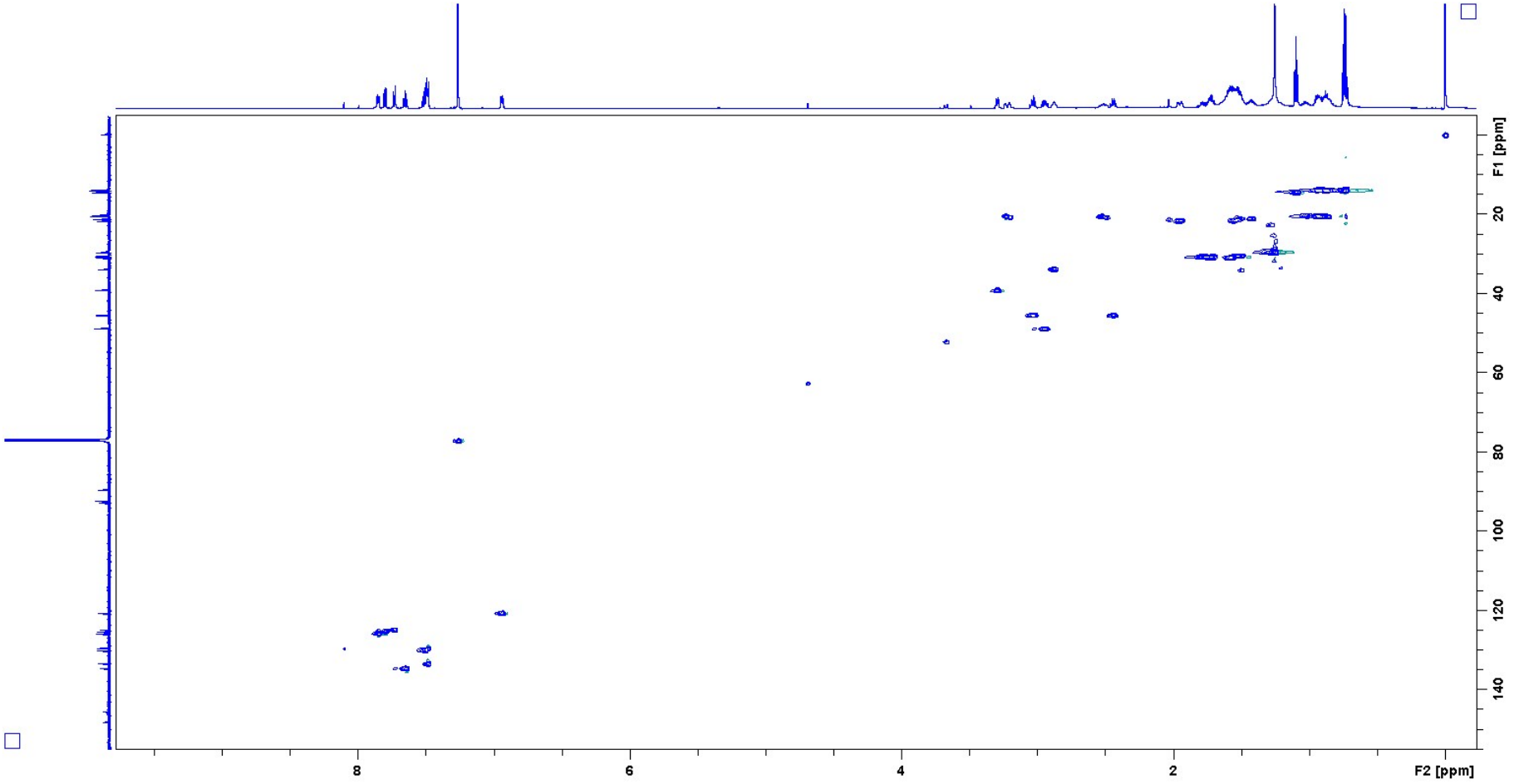

Figure S49. HSQC spectrum of triangeliphthalide D ($CDCl_3$)

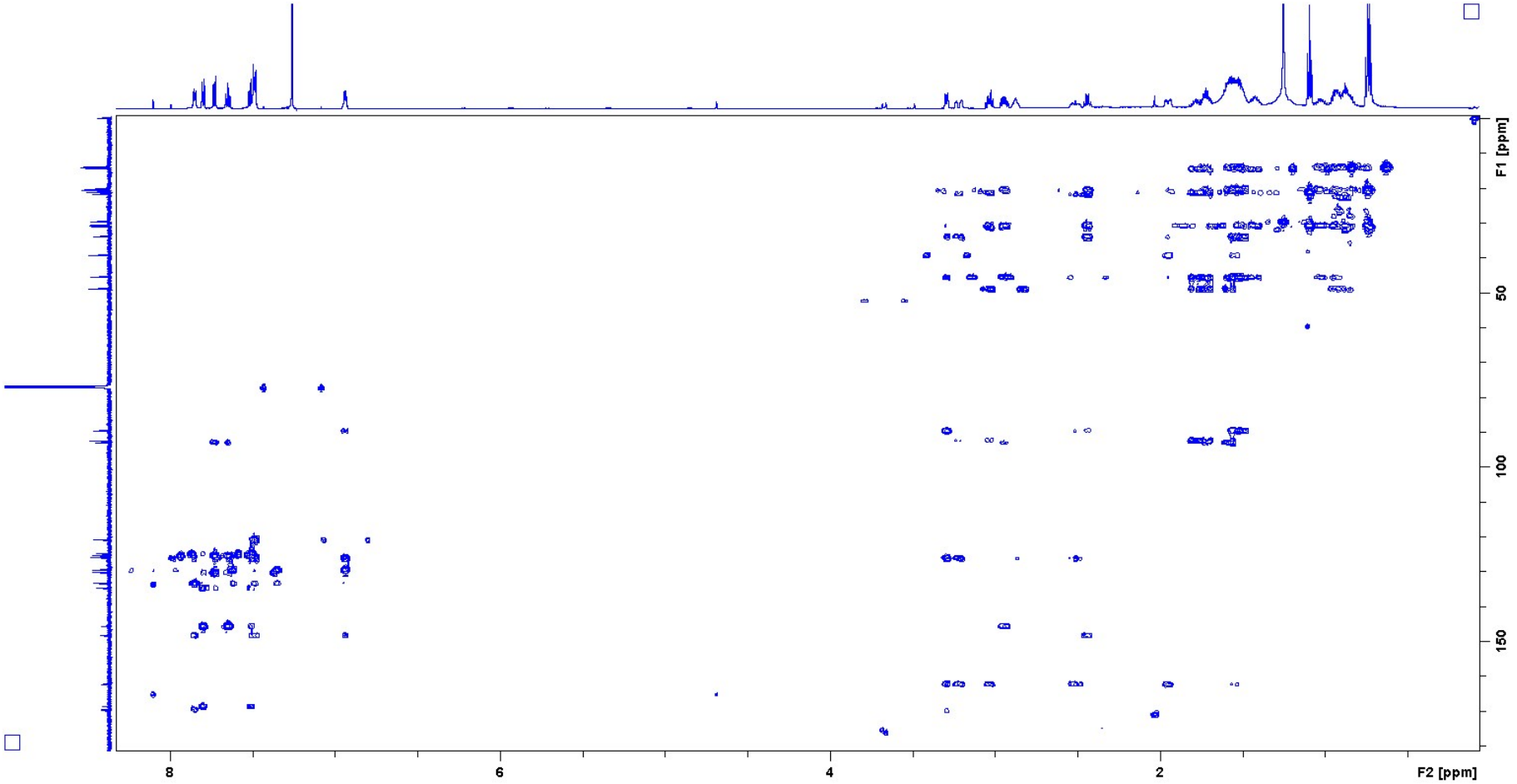

Figure S50. HMBC spectrum of triangeliphthalide D ($CDCl_3$)

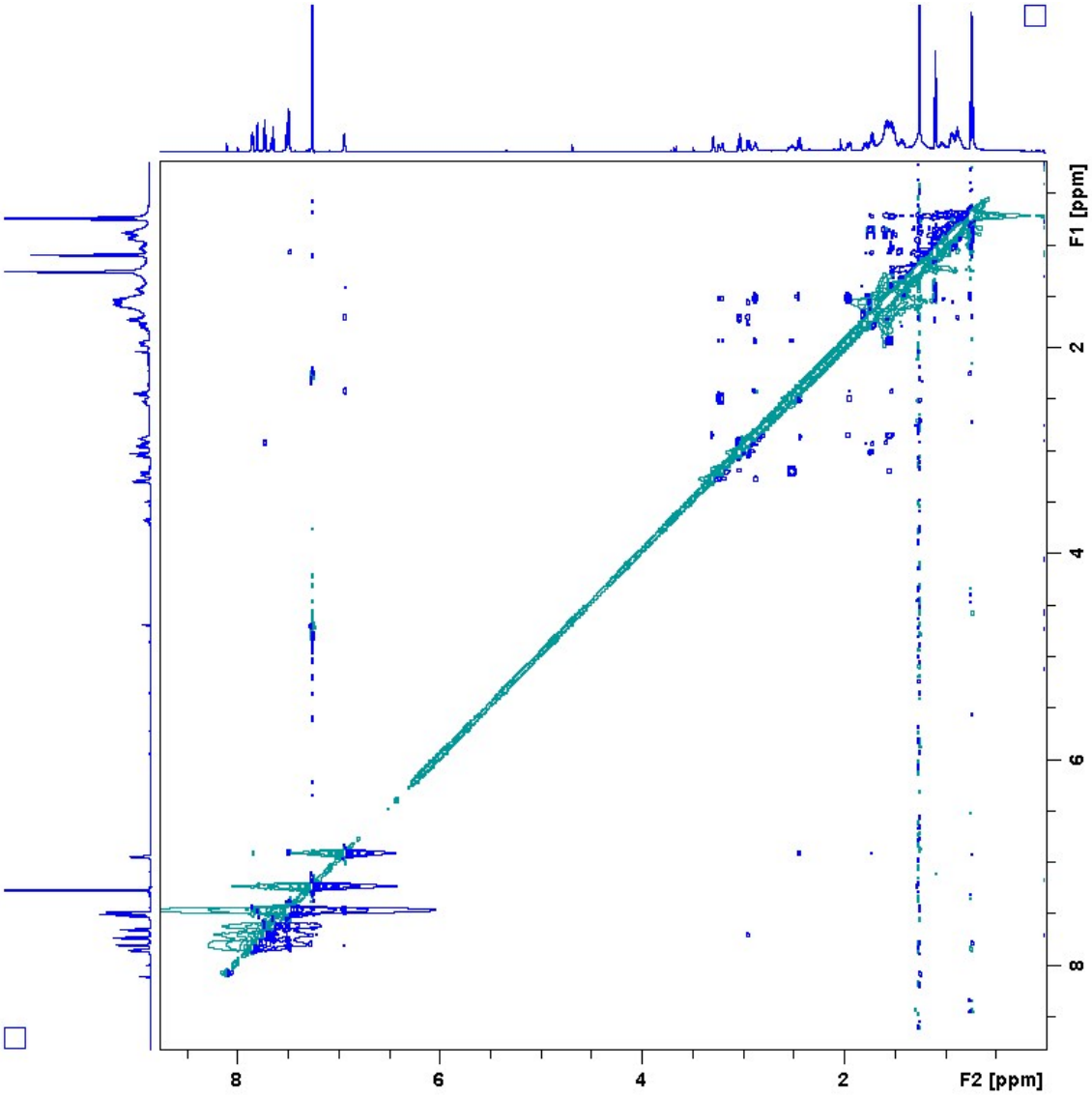

Figure S51. NOESY spectrum of triangeliphthalide D ($CDCl_3$)

The 1D and 2D NMR spectra of 5

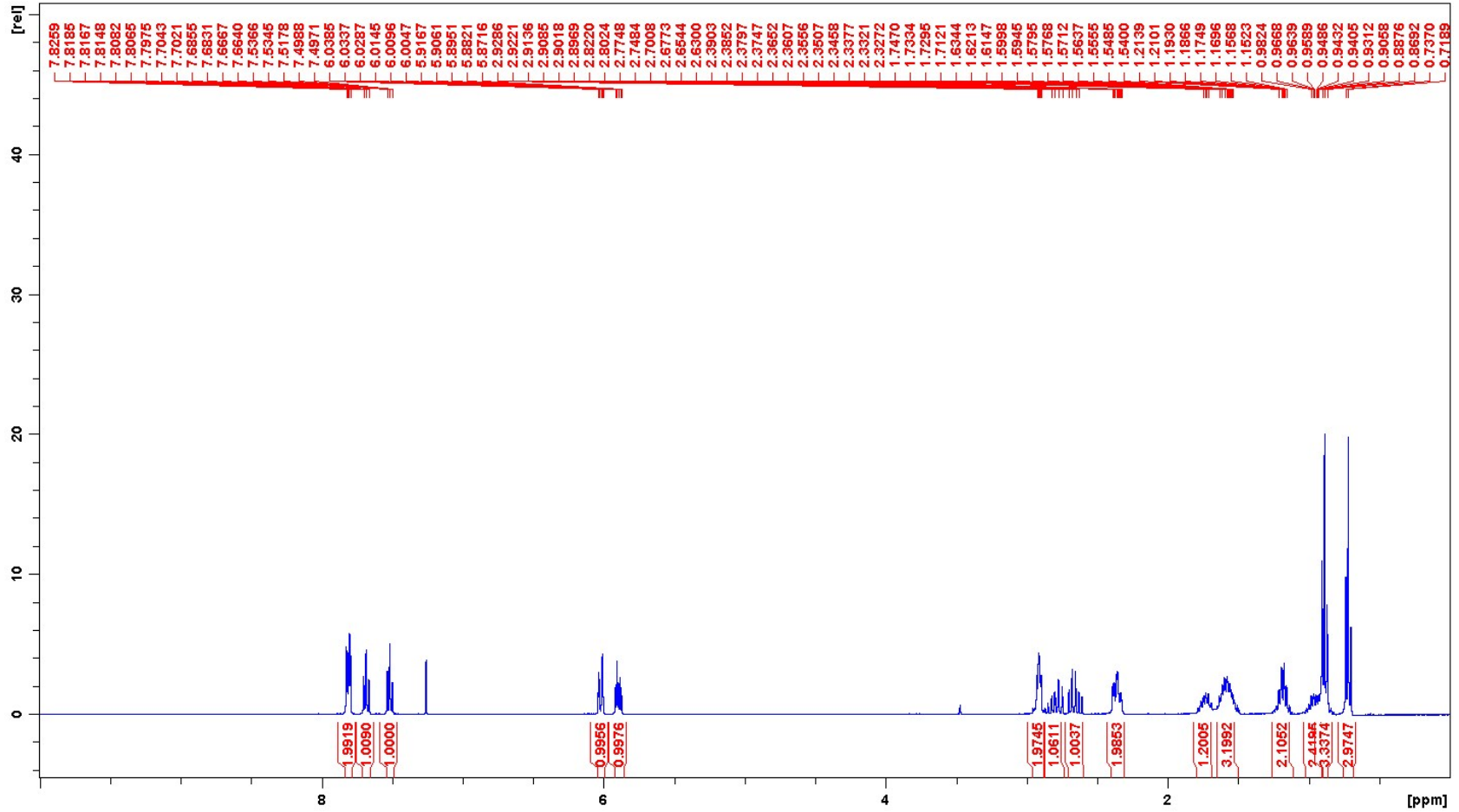

Figure S52. ^{1}H spectrum of diangeliphthalide A (400 MHz, in $CDCl_3$)

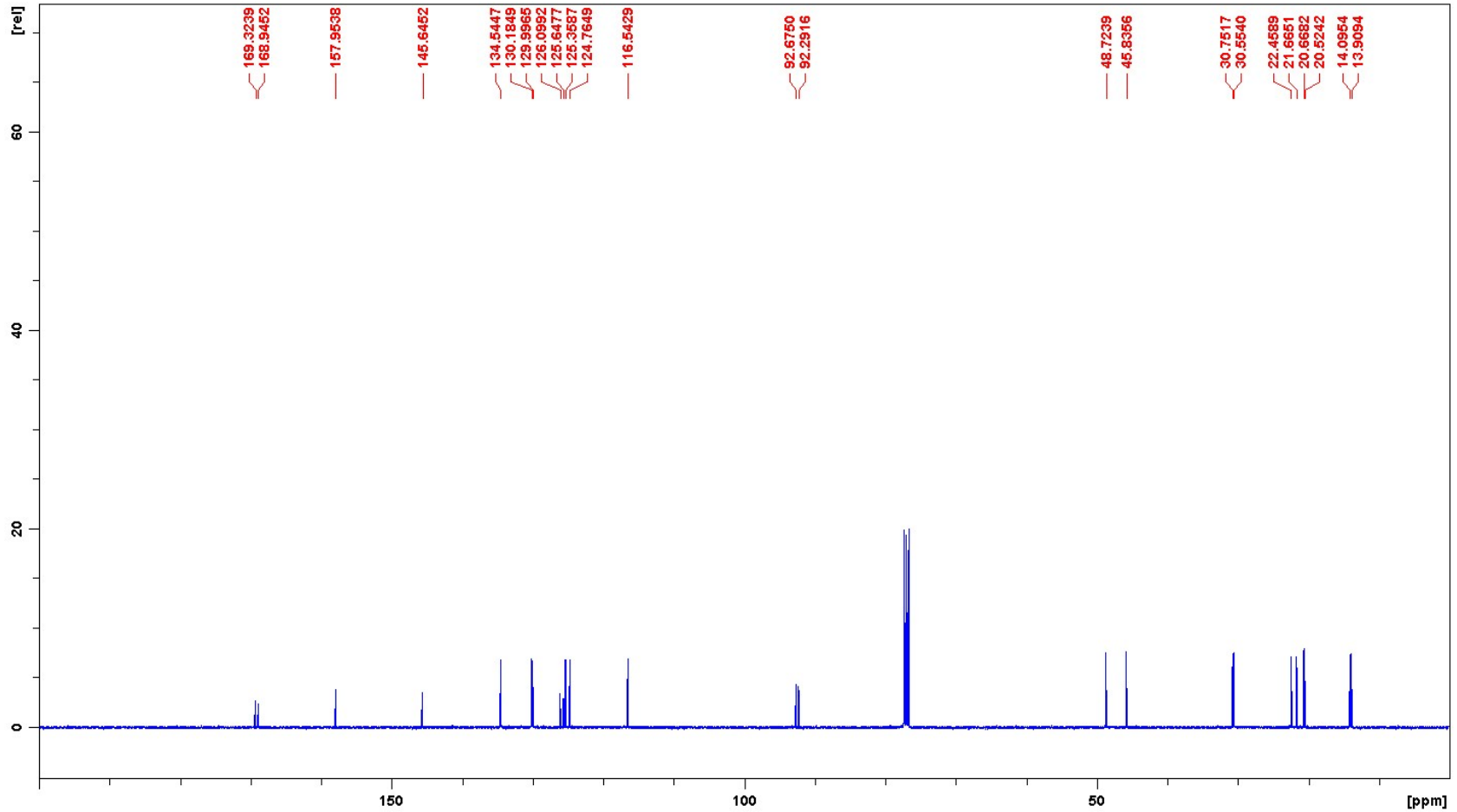

Figure S53. ^{13}C spectrum of diangeliphthalide A (100 MHz, in $CDCl_3$)

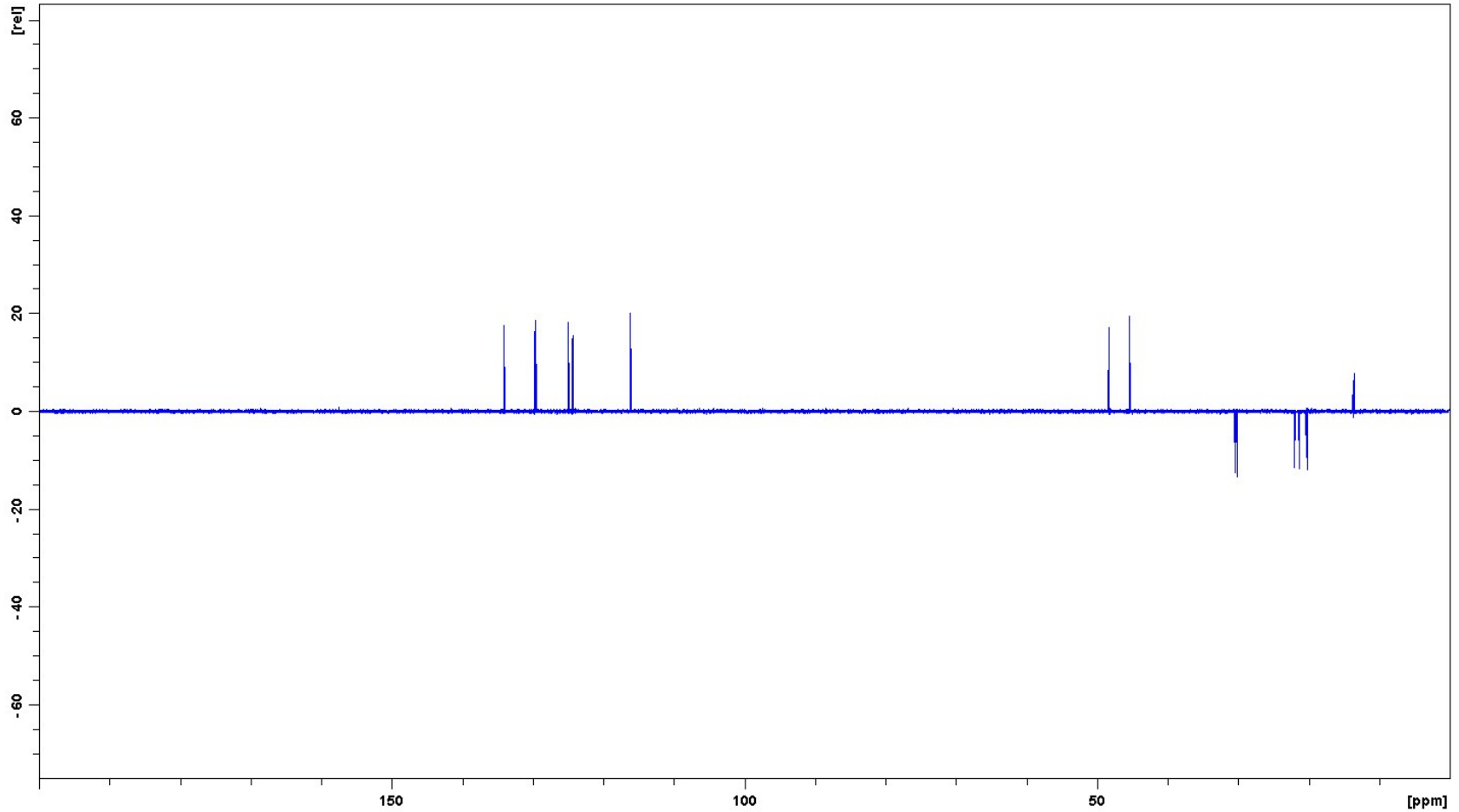

Figure S54. DEPT135 spectrum of diangeliphthalide A (100 MHz, in $CDCl_3$)

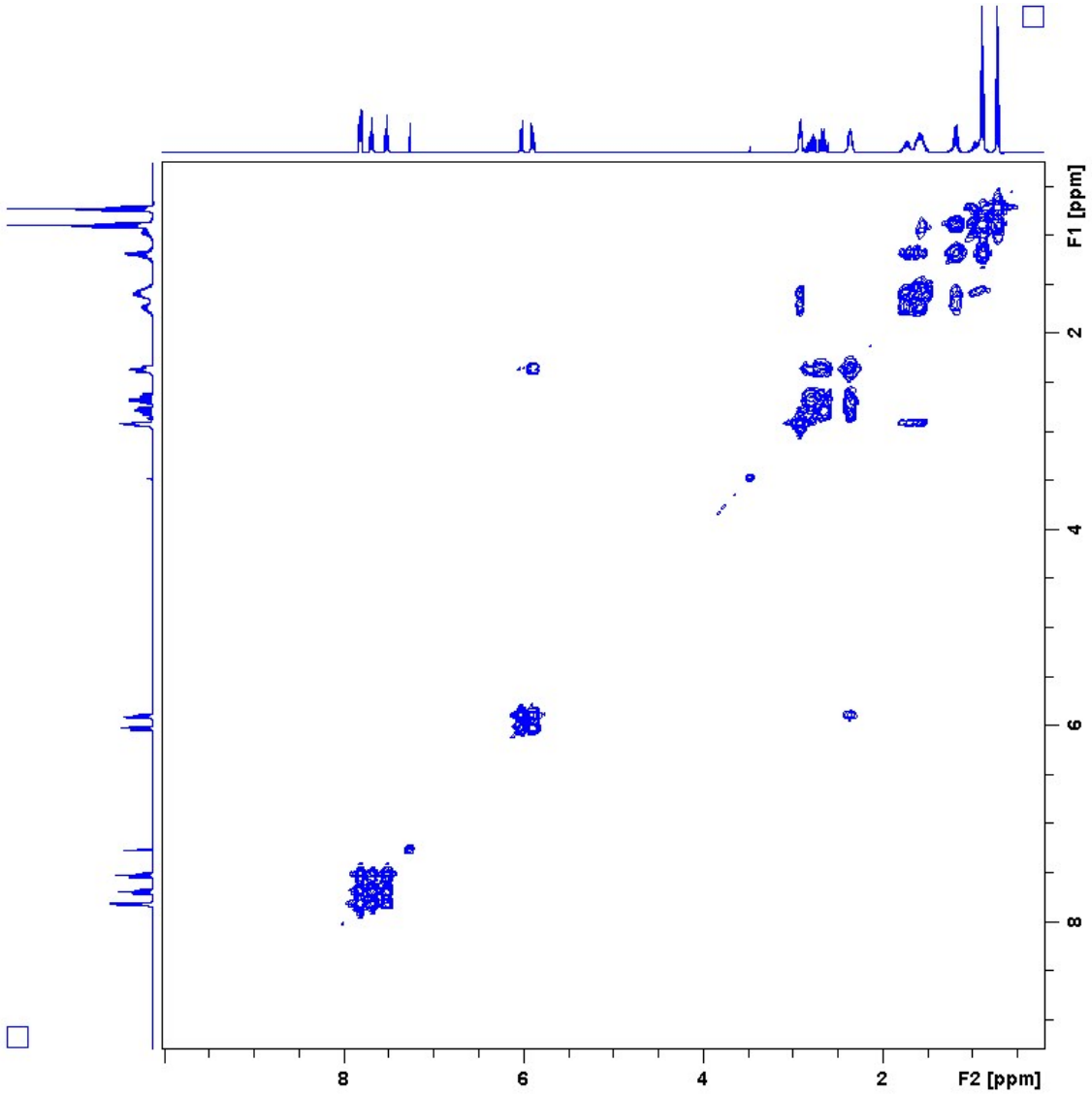

Figure S55. ^{1}H, ^{1}H-COSY spectrum of diangeliphthalide A ($CDCl_3$)

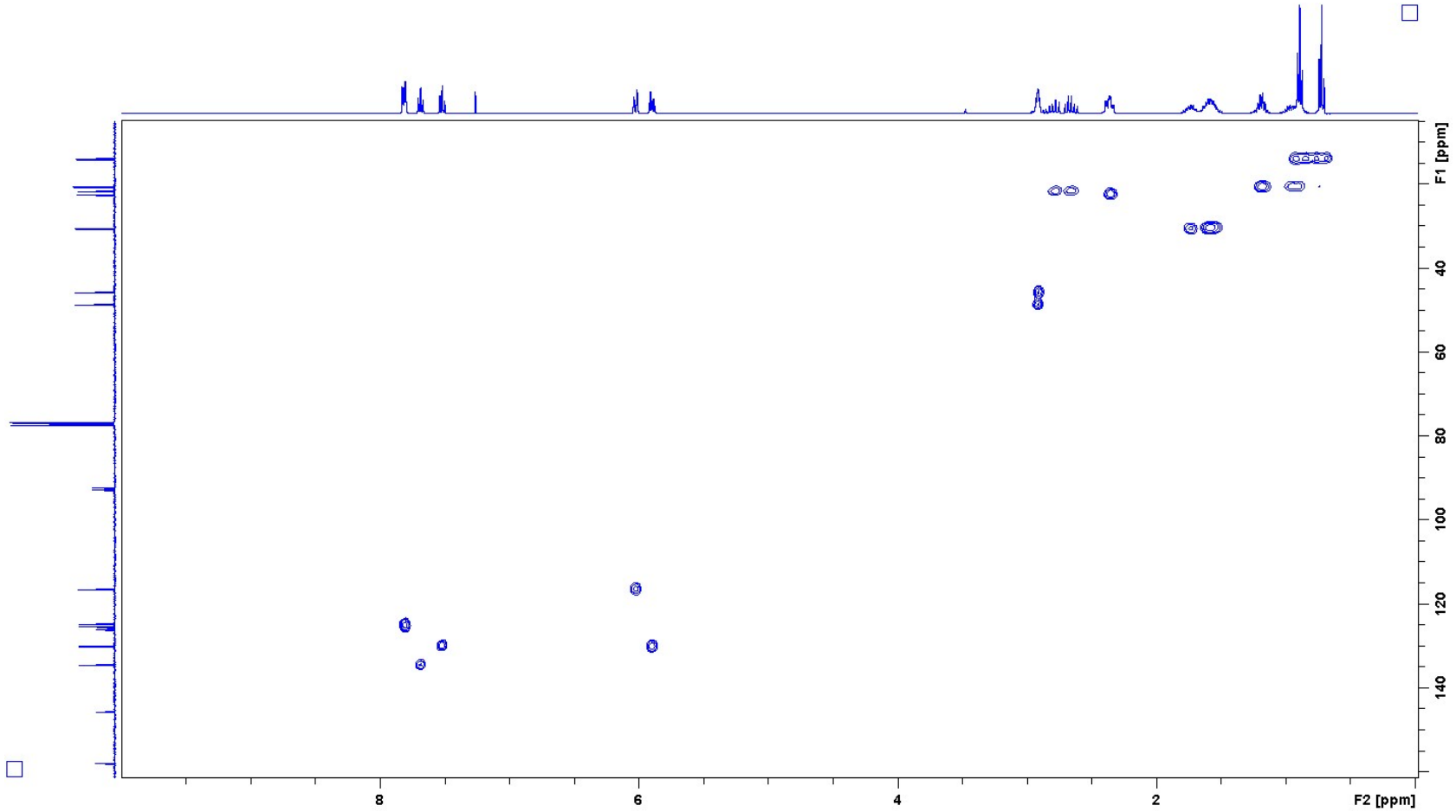

Figure S56. HSQC spectrum of diangeliphthalide A ($CDCl_3$)

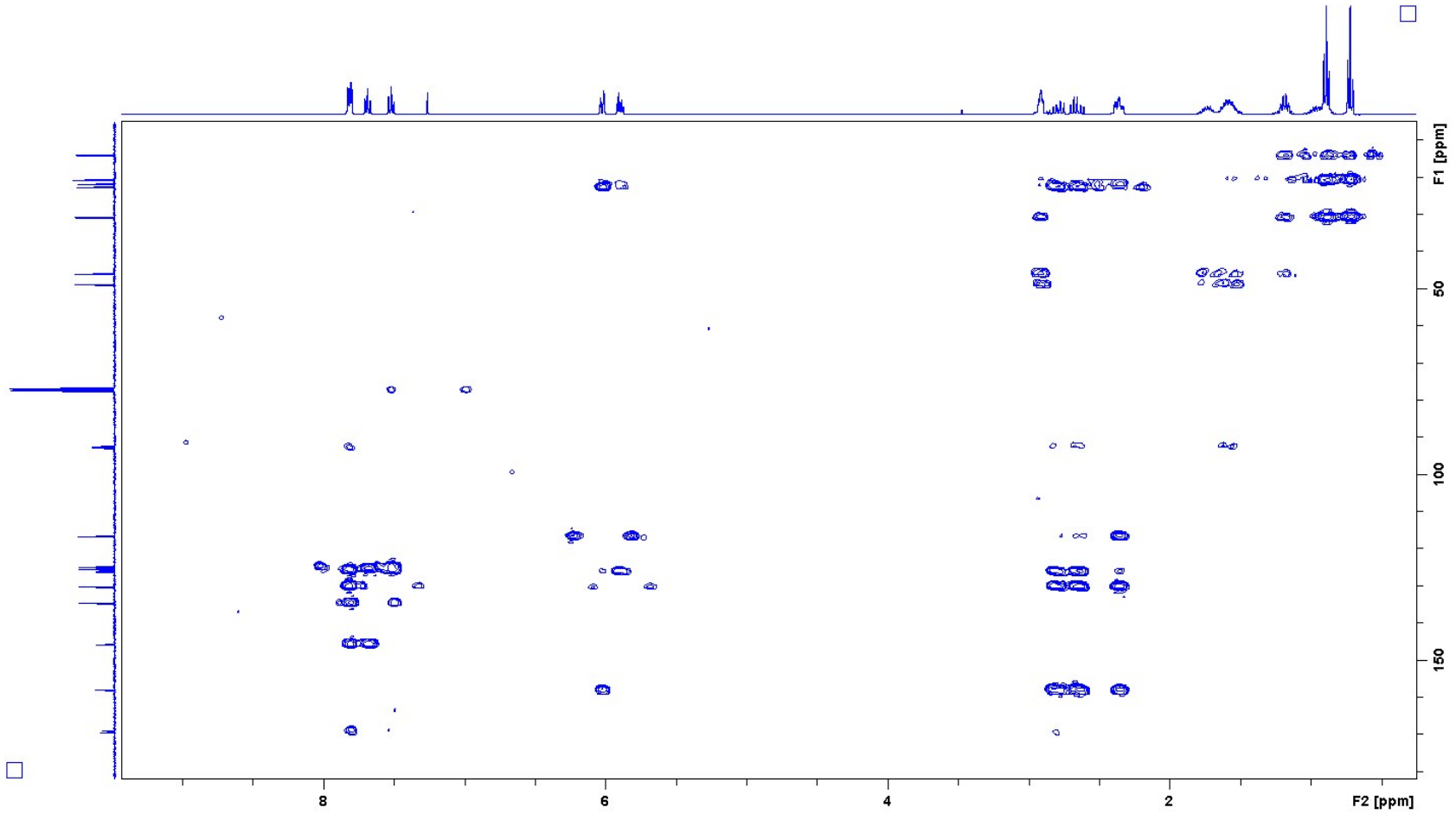

Figure S57. HMBC spectrum of diangeliphthalide A ($CDCl_3$)

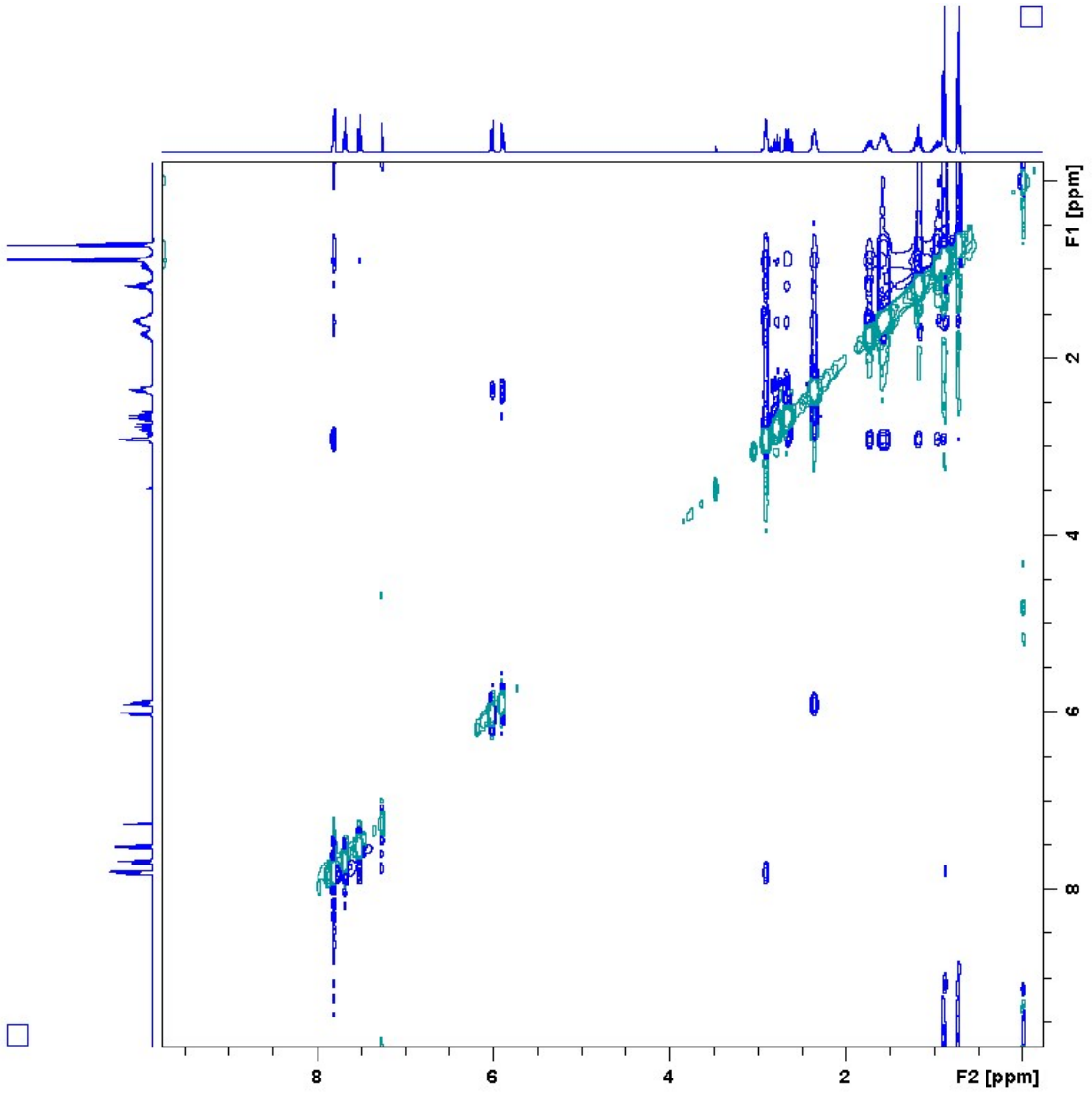

Figure S58. NOESY spectrum of diangeliphthalide A ($CDCl_3$)

The 1D NMR spectra of 6

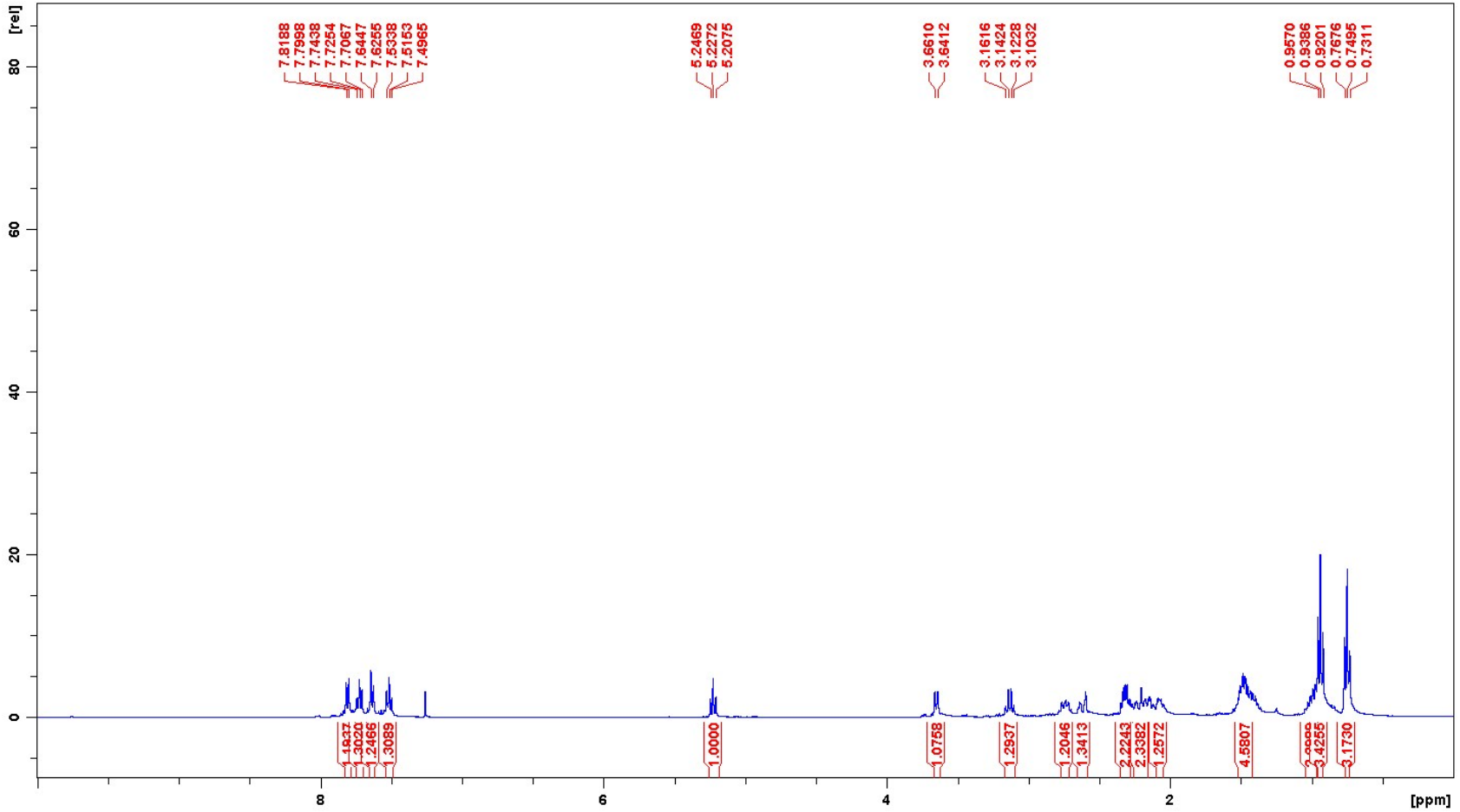

Figure S59. ^{1}H spectrum of gelispirolide (400 MHz, in $CDCl_3$)

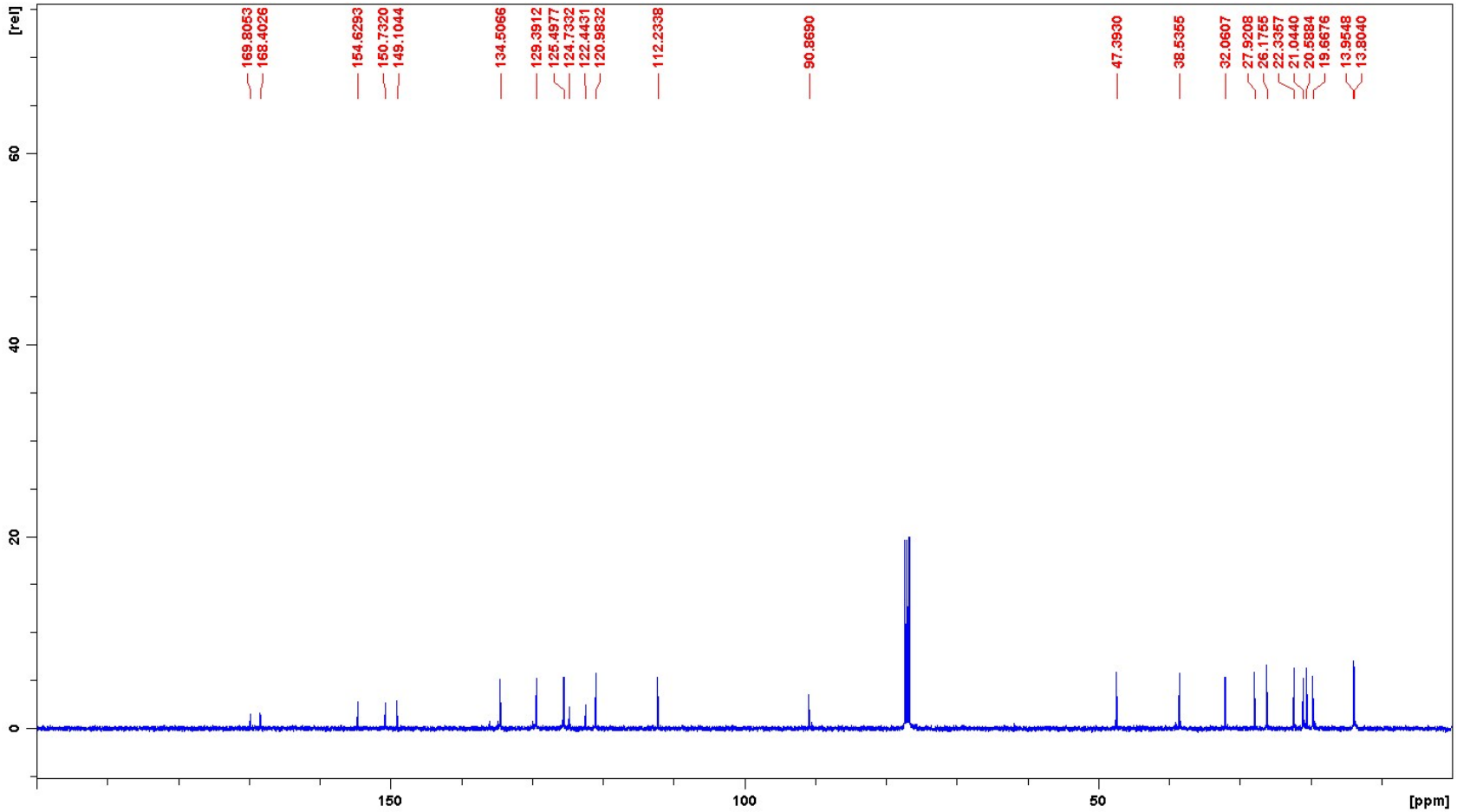

Figure S60. ^{13}C spectrum of gelispirolide (100 MHz, in $CDCl_3$)

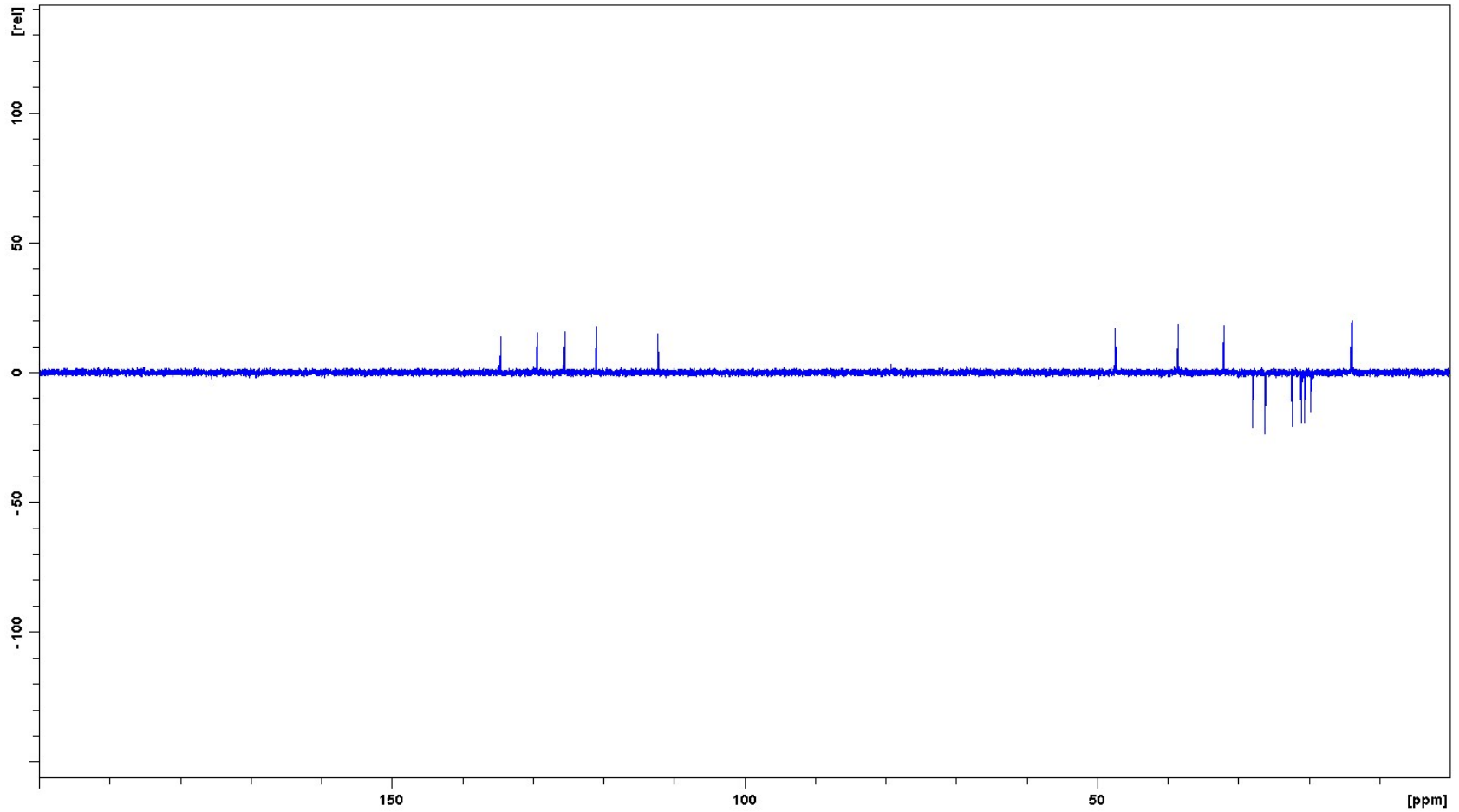

Figure S61. DEPT135 spectrum of gelispirolide (100 MHz, in $CDCl_3$)

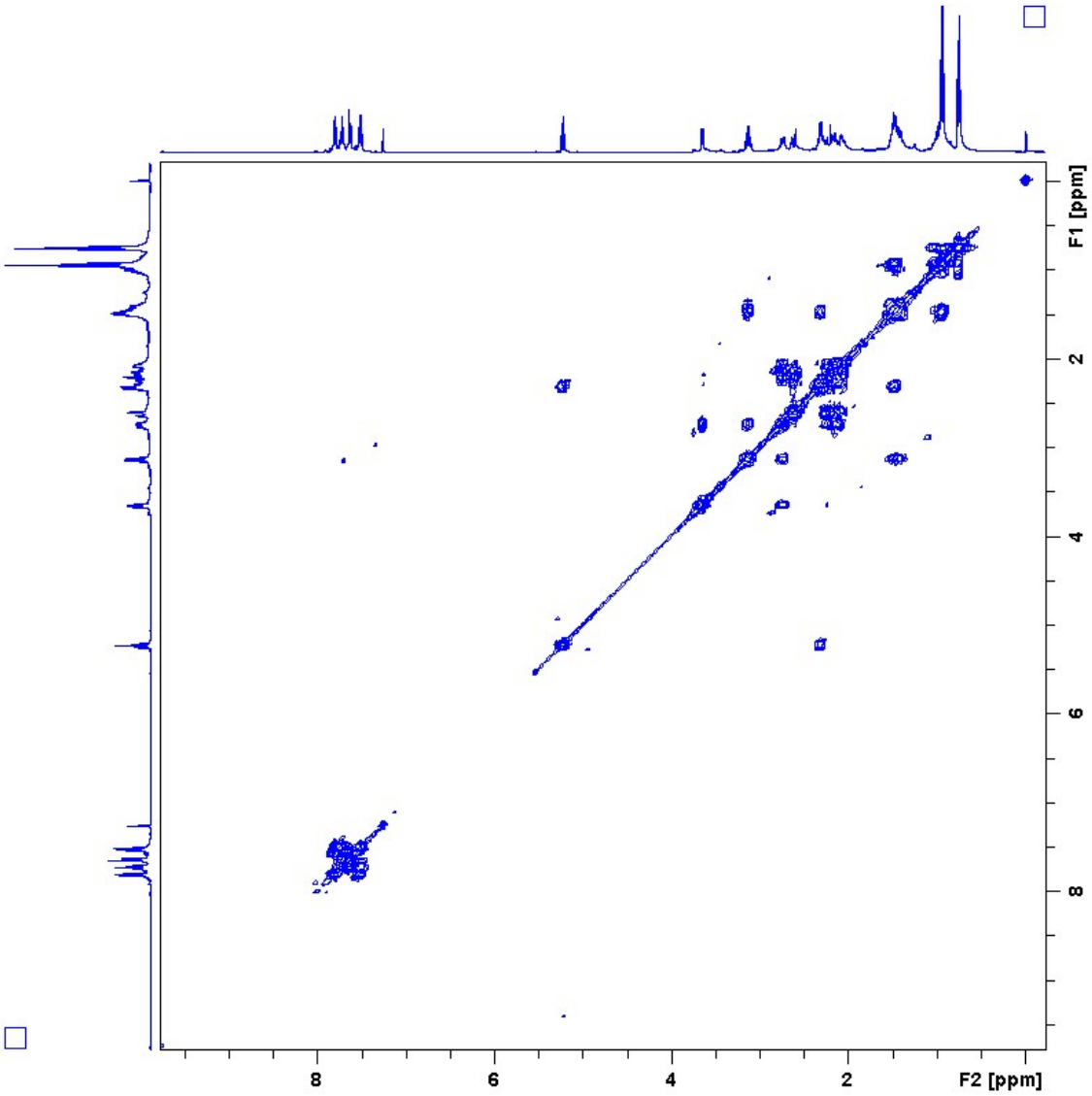

Figure S62. ^{1}H, ^{1}H-COSY spectrum of gelispirolide ($CDCl_3$)

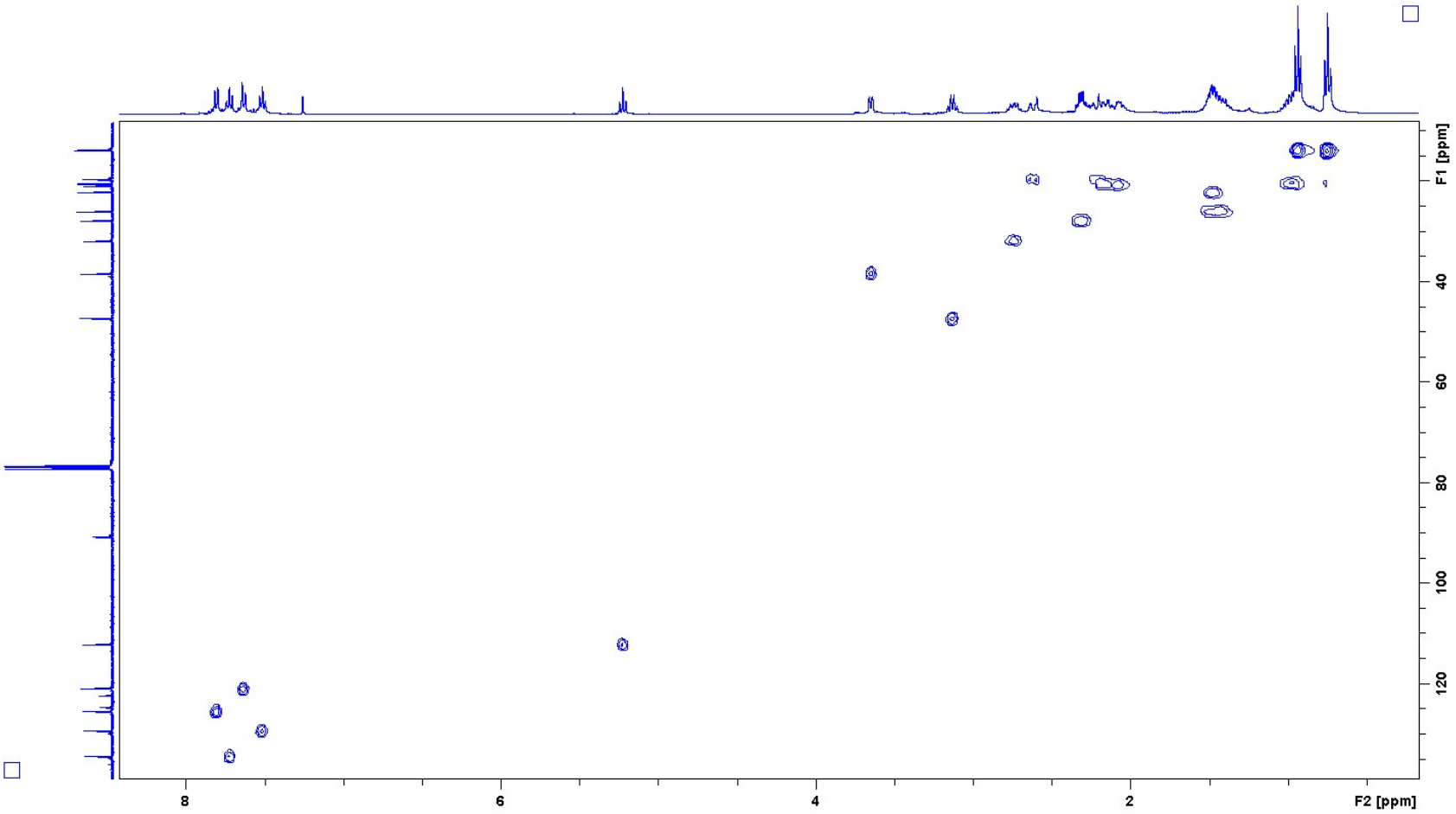

Figure S63. HSQC spectrum of gelispirolide ($CDCl_3$)

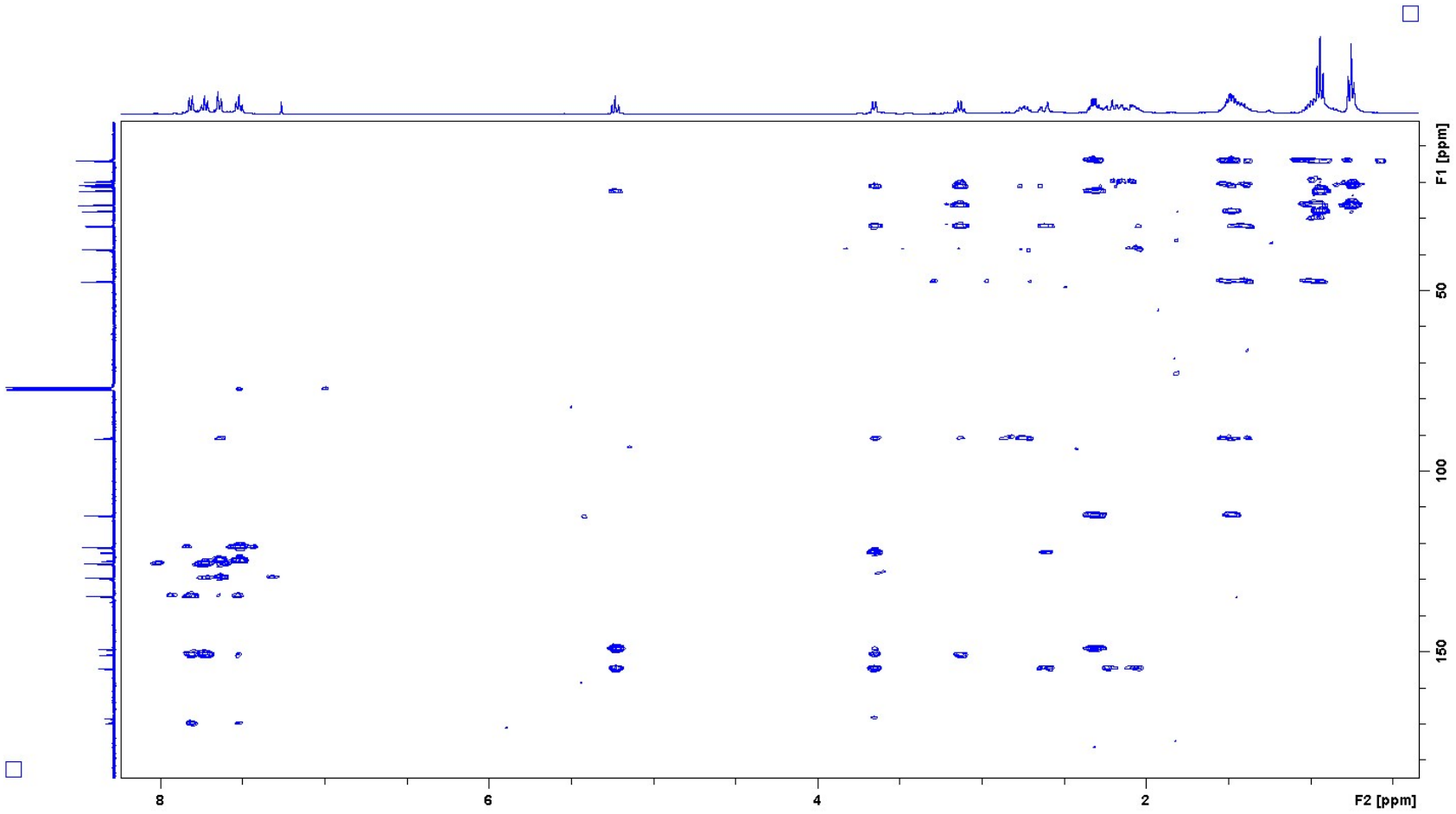

Figure S64. HMBC spectrum of gelispirolide ($CDCl_3$)

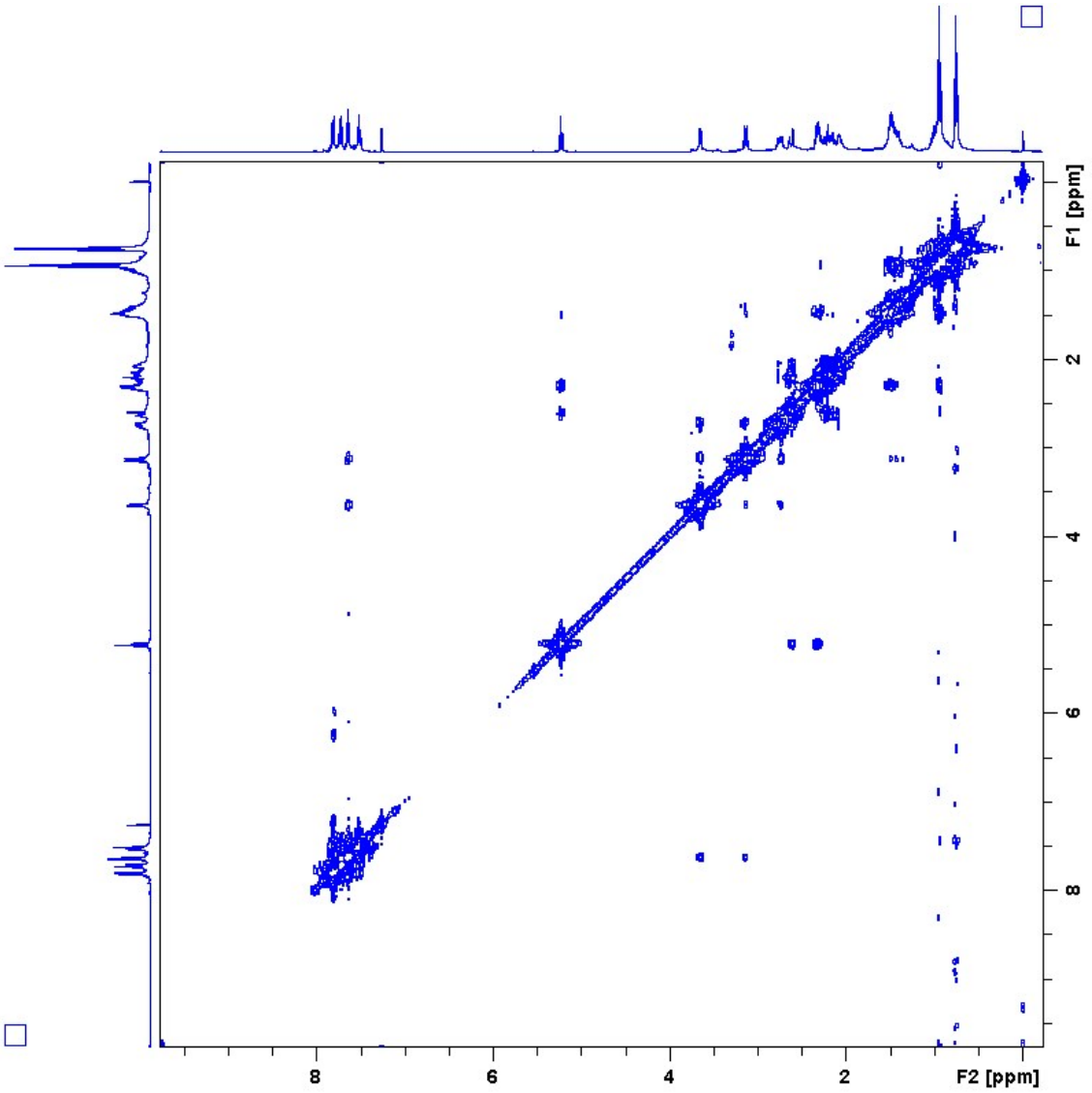

Figure S65. NOESY spectrum of gelispirolide ($CDCl_3$)