Mandelalides A-D, cytotoxic macrolides from a new *Lissoclinum* species of South African tunicate.

Justyna Sikorska,[†] Andrew M. Hau,[†] Clemens Anklin,[‡] Shirley Parker-Nance,[§] Michael T. Davies-Coleman,[||] Jane E. Ishmael,[†] Kerry L. McPhail*[,†]

Department of Pharmaceutical Sciences, College of Pharmacy, 203 Pharmacy Building, Oregon State University, Corvallis, Oregon 97331, United States, Bruker BioSpin, 15 Fortune Drive, Billerica, Massachusetts 01821, United States, Department of Zoology, Nelson Mandela Metropolitan University, Port Elizabeth 6001, South Africa, Department of Chemistry, Rhodes University, PO Box 94, Grahamstown 6140, South Africa

* Corresponding author. Tel: +1 541 737 5808. Fax: +1 541 737 3999. E-mail: kerry.mcphail@oregonstate.edu

† Oregon State University.

‡ Bruker BioSpin.

§ Department of Zoology, University.

|| Rhodes University.

Table of Contents

Table S1. NMR data for mandelalide A (**1**) in pyridine-d_5, 700 MHz

No.	δ_C (mult)	δ_H (*J* in Hz)	COSY	HMBC	ROESY
1	167.0	-			
2	124.1	6.19 (dd, 15.4, 1.3)	3, 4a	1, 4	3[a], 4b[a]
3	146.9	7.18 (ddd, 15.0, 10.5, 4.5)	2, 4a, 4b	1	2[a], 4a, 4b[a]
4a	39.4	2.22 (m)	3	2, 3, 5	5[a], 6ax
4b	39.4	2.28 (m)	3, 5	2, 3, 5	5[a], 6ax, 6eq
5	74.2	3.24 (dd, 10.9, 10.9)	4b, 6ax		4a[a], 4b[a], 6ax[a], 6eq, 9
6ax	38.3	1.20 (m)	5, 6eq, 7	4, 5, 7	4a, 4b, 5[a], 6eq, 8eq[a]
6eq	38.3	2.04 (m)	6ax, 7	7, 8	4a, 4b[a],5, 6ax, 8ax[a], 1′
7	73.3	4.02 (m)	6ax, 8ax	1′	5, 6eq, 8eq, 8ax[a], 9, 1′, 5′, 6′
8ax	40.6	1.34 (m)	7, 8eq, 9	6, 7, 10	6eq[a], 7[a], 9[a], 8eq,
8eq	40.6	1.99 (dd, 12.2, 3.9)	7, 8ax	6, 7	7, 8ax, 9, 10a, 1′, 5′
9	72.7	3.27 (dd, 10.8, 10.8)	8ax, 10b		5, 8ax[a], 8eq, 10a, 10b[a], 11, 25
10a	43.7	1.18 (m)	9, 10b, 11	8	8ax, 8eq, 9, 10b[a], 11[b], 12, 25
10b	43.7	1.60 (ddd, 14.2, 11.7, 3.6)	9, 10a, 11	9, 25	8ax, 9[a], 10a, 11
11	34.6	2.72 (m)	10a, 12, 25		9, 10a[c], 10b, 12[a], 13, 25[a]
12	141.9	5.43 (dd, 14.8, 9.8)	11, 13	10, 11, 14, 25	13[a], 14
13	124.8	6.52 (dd, 14.7, 10.8)	12, 14	11, 14, 15	11, 12[a], 14[a], 16b, 21
14	131.7	6.11 (dd, 10.6, 10.6)	13, 15	12, 13, 16	12, 13[a], 15
15	128.2	5.36 (ddd, 11.1, 11.1, 5.6)	14, 16a, 16b	13, 16	14, 17, 16a[a],16b[a]
16a	31.9	1.85 (m)	15, 16b	14, 16	15[a], 16b[a], 17, 26
16b	31.9	2.36 (ddd, 13.5, 11.0, 11.0)	15, 16a, 17	14, 15, 17	13, 15[a], 16a[a], 21
17	81.5	4.01 (m)	18	15, 19, 20	15, 18, 19b, 26
18	37.9	2.33 (m)	17, 19a, 26	16, 19, 26	17, 19a[a], 19b[a], 20, 26[a]
19a	37.0	1.36 (m)	18, 19b, 20	18, 21, 20, 26	18[a], 19b, 21, 22b, 26
19b	37.0	1.87 (m)	18, 19a, 20	17, 18	19a, 20, 22a, 22b
20	85.0	3.91 (m)	19a, 19b	21	18, 19b, 22a[a], 22b
21	73.5	3.94 (ddd, 8.3, 8.3, 1.6)	22a	20	13, 16b, 19a, 22a[a], 22b[a], 23
22a	35.9	2.02 (ddd, 13.8, 11.1, 1.5)	21, 22b, 23	20, 21	19b, 21[a], 23[a], 24a, 24b
22b	35.9	2.21 (m)	21, 22a, 23	23	19a, 19b, 21, 22a[a], 23[a], 24a, 24b
23	72.6	5.98 (ddd, 10.0, 4.5, 4.5)	22b, 24a, 24b	1, 22	21, 22a[a], 22b[a], 24a[a], 24b[a]
24a	64.7	4.13 (dd, 11.4, 4.2)	23, 24b	22	22a, 22b, 23
24b	64.7	4.22 (m)	23, 24a	22	22a, 22b, 23, 24a[a]
25	18.9	0.91 (d, 6.5)	11	10, 11, 12	9, 10a, 11[a]
26	14.7	0.94 (d, 6.8)	18	17, 18	17, 18[a], 19a, 19b
1′	96.4	5.46 (d, 0.9)	2′	2′, 3′, 5′	6eq, 7, 2′, 7′
2′	83.1	3.91 (m)	1′, 3′	4′, 7′	1′, 3′[a], 7′
3′	72.9	4.51 (dd, 8.9, 3.3)	2′, 4′	4′	2′[a], 4′[a]
4′	74.7	4.20 (dd, 9.2, 9.2)	3′	3′, 5′, 6′	6′, 3′[a]
5′	70.7	4.23 (m)	6′	3′, 4′	6′[a], 7′, 6eq or 8eq
6′	19.1	1.72 (d, 5.9)	5′	4′, 5′	7, 4′, 5′
7′	59.8	3.65 (s)		2′	1′, 2′, 3′

^{13}C chemical shifts were measured from HMBC spectrum. HMBC correlations are presented from proton to indicated carbon. a - COSY artifacts observed in ROESY spectrum.

Table S2. NMR data for mandelalide B (**2**) in $CDCl_3$, 700 MHz

No.	δ_C (mult)	δ_H (*J* in Hz)	COSY	HMBC	ROESY
1	175.6 (s)	-			
2	79.3 (s)	-			
3	69.5 (d)	5.48 (dd, 6.0, 1.7)	4a, 4b	2, 4, 5, 1″	4a[a], 4b, 5, 9, 11, 23, 24b
4a	36.3 (t)	1.59 (m)	3, 4b	3	3[a], 4b[a], 5, 6eq
4b		2.14 (ddd, 15.0, 11.7, 1.5)	3, 4a, 5	2, 5	3, 4a[a], 5[a], 6ax, 28
5	72.7 (d)	3.30 (dddd, 11.4, 11.4, 1.5, 1.5)	4b, 6ax	3, 4, 7, 9	3, 4a, 4b[a], 7, 8eq, 9
6ax	37.4 (t)	1.10 (ddd, 11.7, 11.7, 11.7)	5, 6eq, 7	4, 5, 8	4b, 5[a], 6eq[a], 7[a]
6eq		1.89 (m)	6ax, 7	7, 8	4a, 5, 6ax[a], 7, 1′
7	73.3 (d)	3.75 (m)	6ax, 6eq, 8ax, 8eq	8, 1′	5, 6ax[a], 6eq, 8ax[a], 8eq, 9, 1′
8ax	39.6 (t)	1.23 (m)	7, 8eq, 9	6, 7, 9, 10	6eq[a], 7[a], 9[a], 10b
8eq		1.81 (dddd, 12.4, 4.8, 1.8, 1.8)	7, 8ax	6, 7	7, 8ax, 9, 10a, 5′
9	72.4 (d)	3.39 (dddd, 11.0, 11.0, 2.2, 2.2)	6ax, 10b		3, 5, 7, 8ax[a], 8eq, 10a, 10b[a], 11, 25
10a	42.2 (t)	1.18 (ddd, 14.1, 12.3, 2.8)	9, 10b, 11	11	8eq, 9, 10b[a], 11[a], 12
10b		1.57 (m)	9, 10a, 11	8, 9, 11, 25	8ax, 9[a], 10a[a], 11
11	33.9 (d)	2.50 (m)	10a, 10b, 12, 25	13	9, 10a[a], 10b, 12[a], 13, 23, 25[a]
12	142.1 (d)	5.50 (dd, 15.1, 9.8)	11, 13	10, 11, 14, 25	10a, 11[a], 13[a], 14, 25
13	123.3 (d)	6.40 (dd, 14.7, 11.3)	12, 14	11, 14, 15	11, 12[a], 14[a], 16b, 21
14	131.0 (d)	6.10 (dd, 11.1, 11.1)	13, 15	12, 13, 16	12, 13[a], 15[a]
15	127.1 (d)	5.28 (ddd, 11.1, 11.1, 5.2)	14, 16a, 16b	13, 16, 17	14[a], 16a, 16b[a], 17
16a	30.7 (t)	1.90 (m)	15, 16b	14, 15, 17	15, 16b, 17, 26
16b		2.31 (ddd, 13.6, 11.6, 11.5,)	15, 16a, 17	14, 15,17, 18	13, 15[a], 16a, 17[a], 19a, 21, 26
17	81.5 (d)	3.95 (ddd, 11.6, 7.46, 1.6)	16a, 16b, 18	15, 19, 20	15, 16a, 16b[a], 18, 20[b], 26
18	38.3 (d)	2.52 (m)	17, 19a, 19b, 26	16, 17, 19, 26	17, 19a[a], 19b, 20, 26[a]
19a	35.6 (t)	1.33 (ddd, 12.2, 12.2, 8.2)	18, 19b, 20	18, 20, 21, 26	16b, 18[a], 19b, 20 or 21, 22a, 26
19b		2.05 (ddd, 12.8, 6.9, 6.9)	18, 19a, 20	17, 18, 21	18, 19a, 20, 22a, 26
20	82.1 (t)	3.77 (m)	19a, 19b	21	18, 19a, 19b, 22a, 22b
21	74.5 (d)	3.76 (m)	22b	20, 23	13, 16b, 23, 27
22a	37.9 (t)	1.51 (m)	22b, 23	23	19a, 19b, 20 or 21, 22b[a], 23[a], 24a
22b		1.64 (m)	21, 22a	21	20[a] or 21 [a], 22a[a], 23, 24a
23	74.9 (d)	4.84 (dddd, 10.4, 10.4, 4.9, 1.0)	22a, 24a, 24b	21, 22	3, 11, 21, 22a[a], 22b, 24a[a], 24b, 25
24a	39.7 (t)	1.93 (dd, 12.7, 10.7)	23, 24b	2, 3, 22, 23	22a, 22b, 23[a], 24b
24b		2.39 (dd, 12.8, 4.9)	23, 24a	1, 2, 3	3, 23, 24a
25	18.5 (q)	1.07 (d, 6.6)	11	10, 11, 12	9, 10a, 11, 12, 23
26	14.2 (q)	1.03 (d, 6.9)	18	17, 18, 19	16a, 16b, 17, 18[a], 19a, 19b
	OH-21	2.70 (br s)	21, 22a	22	21
	OH-2	2.87 (s)		1, 2, 3, 24	4b
1′	94.8 (d)	5.04 (s)	2′	7, 2′, 3′, 5′	6eq, 7 or 3′, 2′, 5′, 7′
2′	80.9 (d)	3.33 (ddd, 3.0, 1.5. 1.3)	1′, 3′	3\`, 4\`, 7′	1′, 3′, 7′
3′	66.6 (d)	3.74 (m)	2′, 4′, 8′	1′	2′, 5′, 8′
4′	73.3 (d)	3.49 (ddt, 11.8, 3.3, 1.2, 1.2)	3′, 9′	3′	5′, 6′, 9′
5′	67.4 (d)	3.85(br q, 6.6)	6′	1′, 4′, 6′	7 or 3′, 8eq, 4′, 7′
6′	16.6 (q)	1.23 (d, 6.5)	5′	4′, 5′	4′, 5′, 9′
7′	59.6 (q)	3.45 (s)		2′	1′, 2′
	OH-3′	2.86 (d, 11.6)	3′	3′	2′, 3′, 4′
	OH-4′	2.74 (d, 11.6)	4′	3′, 4′	3′, 4′[a], 6′
1″	173.6 (s)	-			
2″	36.3 (t)	2.35 (t, 7.5)	3″	1″, 3″, 4″	3″[a], 4″
3″	18.8 (t)	1.67 (tq, 7.4, 7.4)	2″, 4″	1″, 2″, 4″	2″[a], 4″[a]
4″	14.0 (q)	0.95 (t, 7.4)	2″, 3″	2″, 3″	2″, 3″[a]

Table S3. NMR data for mandelalide B (**2**) in pyridine-d_5, 700 MHz

No.	δ_C (mult)	δ_H (J in Hz)	COSY	HMBC	ROESY
1	176.4 (s)	-			
2	80.0 (s)	-			
3	70.2 (d)	6.17 (d, 6.8)	4a	5, 1″	4a[a], 4b, 5, 11, 23, 24b
4a	37.2 (t)	2.12 (ddd, 15.5, 6.7, 1.6)	3, 4b	3	3[a], 4b, 5, 6eq
4b		2.96 (dd, 15, 11.6)	4a, 5		3, 4a[a], 6ax
5	73.2 (d)	3.60 (ddt, 11.2, 11.2, 1.6)	4b, 6ax		3, 4a, 6eq, 7
6ax	37.9 (t)	1.22 (m)	5, 6eq, 7	5 and/or 7	4b, 6eq
6eq		2.00 (dd, 13.1, 4.5)	6ax, 7		4a, 5, 6ax, 7, 1′
7	73.4 (d)	3.97 (m)	6ax, 8ax		5, 6eq, 9, 1′
8ax	40.1 (t)	1.39 (ddd, 11.4, 11.3, 11.3)	7, 8eq, 9	7, 9	8eq, 10b
8eq		2.03 (dd, 13.4, 4.5)	7, 8ax		7, 8ax, 9, 5′
9	72.3 (d)	3.54 (dddd, 11.5, 11.2, 1.9, 1.9)	8ax, 10b		7, 8eq, 10a, 25
10a	42.5 (t)	1.28 (m)	10b, 11		8eq, 9, 10b, 11[a]
10b		1.81 (ddd, 14.0, 11.3, 3.8)	9, 10a		8ax, 10a, 11
11	34.5 (d)	3.10 (m)	10a, 12, 25		3, 10b, 13, 23, 25
12	141.8 (d)	5.54 (dd, 14.7, 9.9)	11, 13		10a, 14, 25
13	123.9 (d)	6.75 (dd, 14.9, 11.3)	12, 14		14[a], 16b, 21
14	131.2 (d)	6.14 (dd, 10.8, 10.8)	13, 15		12, 13[a], 15
15	127.5 (d)	5.34 (ddd, 11.1, 11.1, 5.2)	14, 16a, 16b		14, 16a, 17
16a	30.8 (t)	1.75 (m)	15, 16b		16b, 17, 26
16b		2.29 (ddd, 11.7, 11.7, 11.7)	15, 16a, 17		13, 15[a], 16a[a], 17[a], 19a, 21, 26
17	81.3 (d)	3.97 (m)	18	20	15, 16a[a], 16b[a], 18
18	38.4 (d)	2.33 (m)	19a, 26		17, 19a[a], 19b[b], 26[a]
19a	35.6 (t)	1.29 (m)	18, 19b, 21		18[a], 19b, 21
19b		1.88 (ddd, 12.9, 7.0, 7.0)	19a	17	18[b], 19a
20	82.9 (d)	3.95 (m)	19a, 19b, 21		19b , 21[a], 22a
21	74.9 (d)	4.14 (dd, 9.4, 9.4)	20, 22b		11, 13, 16b, 19a, 22a, 22b[a], 23
22a	38.9 (t)	1.65 (m)	22b, 23		20, 21, 22b[a], 23[a], 24a[b]
22b		1.77 (m)	21, 22a		20, 21[a], 22a[a],24a
23	74.7 (d)	5.38 (dddd, 11.0, 10.8, 5.0, 0.9)	22a, 24a, 24b		3, 11, 21, 22a[a], 22b[a], 24b
24a	40.8 (t)	2.39 (dd, 11.5, 12.5)	23	2, 3, 23	22b, 24b
24b		2.83 (dd, 12.8, 4.8)	23, 24a	1, 2, 3	3, 22b, 23, 24a
25	18.8 (q)	1.46 (d, 6.6)	11	10, 11, 12	9, 11[a],12, 23
26	13.8 (q)	0.86 (d, 6.8)	18	17, 18, 19	16a, 18[a], 19a[a]
1′	95.9 (d)	5.37 (d, 1.2)		7, 2′, 3′, 5′	6eq, 7, 2′, 7′
2′	82.0 (d)	3.68 (ddd, 2.9, 1.1, 1.1)	3′		1′, 3′, 7′
3′	67.4 (d)	4.25 (dd, 3.2, 2.8)	2′, 4′		2′, 4′, 5′
4′	74.0 (d)	3.92 (br s)			3′, 5′, 6′
5′	68.1 (d)	4.10 (q, 6.6)	6′	4′	8eq , 3′, 4′, 6′
6′	17.2 (q)	1.51 (d, 6.7)	5′	4′, 5′	8eq, 4′, 5′
7′	59.5 (q)	3.46 (s)		2′	2′, 3′
1″	174.0 (s)	-			
2″	36.3 (t)	2.47 (m)	3″	1″, 3″, 4″	3″[a], 4″[a]
3″	19.0 (t)	1.67 (m)	2″, 4″	1″, 2″, 4″	2″[a], 1″[a]
4″	14.3 (q)	0.87 (t, 7.3)	3″	2″, 3″	2″[a], 3″[a]

HMBC correlations are presented from proton to indicated carbon. a - COSY artifacts observed in ROESY spectrum. b- TOCSY artifacts observed in ROESY spectrum.

Table S4. NMR data for mandelalide C (**3**) in $CDCl_3$, 700 MHz

No.	δ_C (mult)	δ_H (*J* in Hz)	COSY	HMBC	TOCSY	ROESY
1	174.7 (s)	-				
2	82.0 (s)	-				
3	68.3 (d)	5.51 (dd, 6.6, 0.88)	4a, 4b	1, 2, 4, 5	4a, 4b, 5, 6ax, 6eq	4a[a], 4b, 5, 9, 23, 24
4a	36.4 (t)	1.65 (m)	3, 4b	3	3, 4b, 5, 6ax, 6eq, 7	3[a], 4b[a], 5, 6ax
4b		2.14 (ddd, 15.6, 11.7, 1.0)	3, 4a, 5	2, 5, 6	3, 4a, 5, 6ax, 6eq, 7	3, 4a[a], 5[a], 6ax, 6eq
5	72.3 (d)	3.25 (dddd, 11.4, 11.4, 1.8, 1.8)	4a, 4b, 6ax, 6eq	4, 7, 9	3, 4a, 4b, 6ax, 6eq, 7, 9	3, 4a, 4b[a], 6ax[a], 6eq, 7, 9
6ax	41.2 (t)	1.11 (ddd, 12.5, 11.4, 11.4)	5, 6eq, 7	4, 5, 7	4a, 4b, 5, 6eq, 7, 8eq	4a, 4b, 5[c], 7, 8eq[b]
6eq		1.86 (m)	6ax, 7	7, 8	4a, 4b, 5, 6ax, 7	4a, 4b, 5, 7, 8ax[b]
7	68.3 (d)	3.76 (dddd, 10.9, 10.9, 4.6, 4.1)	6ax, 6eq, 8ax, 8eq	8, 9	4a, 4b, 5, 6ax, 8ax, 8eq, 9, 10b	5, 6ax, 6eq, 8ax, 8eq, 9
8ax	41.8 (t)	1.13 (ddd, 12.5, 11.2, 11.2)	7, 8eq, 9	6, 7, 9, 10	7, 8eq, 9, 10b, 11	6eq[b], 7, 9[a], 10b
8eq		1.83 (m)	7, 8ax	6, 7	8ax, 9, 10a, 10b	6ax[b], 9
9	72.3 (d)	3.37 (dddd, 10.9, 10.9, 2.1, 2.1)	8ax, 8eq, 10a,10b	5, 7, 10	7, 8ax, 8eq, 10a, 10b, 11, 25	3, 5, 7, 8eq, 10a[a], 10b[a], 11, 25
10a	42.1 (t)	1.19 (ddd, 14.2, 12.1, 2.8)	9, 10b, 11	11, 12, 25	7, 8eq, 9, 10b, 11, 12, 13, 14, 25	9, 10b[a], 11[a], 12
10b		1.57 (m)	9, 10a, 11	8, 9, 11, 12, 25	8ax, 9, 10a, 11, 12, 13, 25	9[a], 10a[a], 11, 12
11	34.0 (t)	2.49 (m)	10a, 10b, 12, 25	10, 12, 13, 25	9, 10a, 10b, 12, 13,14, 25	9, 10a[a], 10b, 12[a], 13, 14, 21, 23, 25[a]
12	142.2 (d)	5.50 (dd, 14.6, 9.6)	11, 13	10, 11, 14, 25	10a, 10b, 11, 13, 14, 15, 16a, 16b, 17, 25	10a, 11[a], 13[a], 14[a], 25
13	123.2 (d)	6.39 (dd, 14.6, 11.4)	12, 14	11, 14, 15	10a, 10b, 11, 12, 14, 15, 16a, 16b, 17, 25	11, 12[a], 14[a], 15[a], 16b, 21
14	131.1 (d)	6.10 (dd, 11.0, 11.0)	13, 15, 16a	12, 13, 16, 17	10a, 11, 12, 13, 15, 16a, 16b, 17, 25	11, 12[a], 13[b], 15[a], 16a, 16b, 21
15	127.1 (d)	5.28 (ddd, 11.0, 11.0, 5.4)	14, 16a, 16b	13, 16, 17	12, 13, 14, 16a, 16b, 17, 18	13[a], 14[a], 16a, 16b[a], 17
16a	30.7 (t)	1.90 (ddd, 13.6, 5.2, 1.1)	15, 16b	14, 15, 17	12, 13, 14, 15, 16b, 17, 18, 19a, 26	14, 15, 16b, 17[a], 26
16b		2.30 (ddd, 13.8, 11.9, 11.9)	15, 16a, 17	14, 15, 17, 18	12, 13, 14, 15, 16a, 17, 18, 26	13, 15[a],16a, 17[a], 19a, 21, 26
17	81.6 (d)	3.95 (ddd, 11.5, 7.5, 1.1)	16b, 18	15, 19, 20	14, 15, 16a, 16b, 18, 19a, 19b, 20, 21	15, 16a[a], 16b[a], 18, 26
18	38.3 (d)	2.53 (m)	17, 19a, 19b, 26	16, 17, 19, 26	15, 16a, 16b, 17, 19a, 19b, 20, 21, 26	17, 19a[a], 19b, 20, 26[a]
19a	35.7 (t)	1.33 (ddd, 12.2, 12.2, 9.1)	18, 19b, 20	18, 20, 21, 26	16b, 17, 18, 19b, 20, 21, 22a, 22b, 26	16b, 18, 19b, 20[a], 21, 22b, 26
19b		2.10 (ddd, 12.5, 7.0, 6.8)	18, 19a, 20	17, 18, 21	16b, 17, 18, 19a, 20, 21, 22a, 26	18, 19a, 20, 22b, 26
20	82.4 (d)	3.82 (ddd, 9.2, 9.2, 7.0)	19a, 19b, 21	17, 21, 22	17, 18, 19a, 19b, 21, 22a, 22b, 23, 26	18, 19a[a], 19b, 22a, 22b
21	74.4 (d)	3.73 (ddd, 10.8, 9.5, 1.2)	20, 22a	19, 20, 22, 23	17, 18, 19a, 19b, 20, 22a, 22b, 23, 26	11, 13, 14, 16b, 19a, 22a[a], 23, 27
22a	32.1 (t)	1.59 (m)	21, 22b	20, 21	19a, 19b, 20, 21, 22b, 23	20, 21[a], 22b[a], 23, 24
22b		1.82 (ddd, 14.4, 11.0, 1.0)	22a, 23	20, 23	19a, 20, 21, 22a, 23, 24	19a, 19b, 20, 22a[a], 23[a]
23	78.9 (d)	5.01 (ddd, 11.2, 2.0, 2.0)	22b, 24	21, 22, 24	20, 21, 22a, 22b, 24	3, 11, 21, 22a[a], 22b[a], 24[a], 25
24	72.2 (d)	3.98 (d, 2.8)	23	1, 2, 3, 23	22a, 22b, 23	3, 23[a]
25	18.4 (q)	1.06 (d, 6.2)	11	10, 11, 12	9, 10a, 10b, 11, 12, 13, 14,	
26	14.2 (q)	1.03 (d, 6.9)	18	17, 18, 19	16a, 16b, 17, 18, 19a, 19b, 20, 21	
27	OH	2.80 (br s)	21, 22b		22a	21
1′	173.4 (s)	-				
2′	36.3 (t)	2.34 (td, 7.5, 1.2)	3′	1′, 3′, 4′	3′, 4′	3′, 4′
3′	18.7 (t)	1.65 (m)	2′, 3′	1′, 2′, 4′	2′, 4′	2′, 4′
4′	13.9 (q)	0.94 (t, 7.5)	3′	2′, 3′	2′, 3′	

HMBC correlations are presented from proton to indicated carbon. a - COSY artifacts observed in ROESY spectrum. b - TOCSY artifacts observed in ROESY spectrum.

Table S5. NMR data for mandelalide D (**4**) in $CDCl_3$, 700 MHz

No.	δ_C (mult)	δ_H (*J* in Hz)	COSY	HMBC	TOCSY	ROESY
1	172.9 (s)	-				
2	81.3 (s)	-				
3	68.6 (d)	5.56 (dd,6.6, 0.7)	4a, 4b	2, 4, 5, 24, 1′	4a, 4b, 5, 6ax, 6eq	4a[a], 4b, 5, 9, 11, 24, 25
4a	36.2 (t)	1.68 (m)	3, 4b	3	3, 4b, 5, 6ax, 6eq	3[a], 4b[a], 5, 6ax
4b		2.18 (ddd, 15.4, 11.5, 0.9)	3, 4a, 5	2, 5, 6	3, 4a, 5, 6ax, 6eq, 7	3, 4a[a], 5[a], 6ax, 6eq
5	72.2 (d)	3.21 (dddd, 11.2, 11.2, 1.3, 1.3)	4a, 4b, 6ax, 6eq	4, 7, 9	3, 4a, 4b, 6ax, 6eq, 7	3, 4a, 4b[a], 6ax[a], 6eq, 7, 9
6ax	41.2 (t)	1.12 (ddd, 11.3, 11.3, 11.3)	5, 6eq, 7	4, 5, 7, 8	4a, 4b, 5, 7	6eq[b], 4b, 7[a], 5[a]
6eq		1.85 (dddd, 12.2, 4.6, 1.5, 1.5)	5, 6ax, 7	7, 8	4a, 4b, 5, 6ax, 7	4a, 4b, 5, 6ax[b], 7
7	68.4 (d)	3.75 (m)	6ax, 6eq, 8ax, 8eq		4b, 5, 6ax, 6eq, 8ax, 8eq, 9, 10b	5, 6ax[a], 6eq, 8ax[a], 8eq, 9
8ax	41.8 (t)	1.12 (ddd, 11.3, 11.3, 11.3)	7, 8eq, 9	6, 7	7, 8eq, 9, 10a, 10b	7[a], 8eq[b], 9[a], 10b
8eq		1.83 (dddd, 12.2, 4.6, 1.5, 1.5)	7, 8ax, 9	6, 7	9, 10a, 10b	8ax[b], 9, 10b
9	72.2 (d)	3.36 (dddd, 11.0, 11.0, 2.2, 2.2)	8ax, 8eq, 10a, 10b	7, 10	7, 8ax, 8eq, 10a, 10b, 11, 25	5, 7, 8eq, 10a[a], 10b[a], 11, 25
10a	42.1 (t)	1.19 (ddd, 13.9, 11.5, 2.8)	9, 10b, 11	11, 12	8eq, 9, 10b, 11, 25	9, 10b[a], 11[a]
10b		1.57 (ddd, 14.0, 11.5, 4.0)	9, 10a, 11	8, 9, 11, 25	7, 8eq, 9, 10a, 11, 25	8eq, 9[a], 10a[a], 11
11	34.2 (d)	2.48 (m)	10a, 10b, 12, 25	10, 12, 13	8ax, 9, 10a, 10b, 12, 13, 25	3, 9, 10a[a], 10b, 12[a], 13, 14, 21, 23, 25[a]
12	142.3 (d)	5.50 (dd, 14.8, 9.7)	11, 13	10, 11, 14, 25	10a, 10b, 11, 13, 14, 15,16a, 16b, 25	10a, 10b, 11[a], 13[a], 14[a], 15[a], 25
13	123.1 (d)	6.38 (dd, 15.0, 11.3)	12, 14	11, 14, 15	10a, 10b, 11, 12, 14, 15, 16a, 16b, 25	11, 12[a], 14[b], 15[a], 16b, 21, 28
14	131.1 (d)	6.10 (dd, 11.0, 11.0)	13, 15, 16a	12,13, 16, 17	10a, 11, 12, 13, 15, 16a, 16b, 17, 25	11, 12[a], 13[a], 15[a], 16a, 16b, 21
15	127.1 (d)	5.28 (ddd, 11.3, 11.3, 5.4)	14, 16a, 16b	13, 16, 17	12, 13, 14, 16a, 16b, 17, 18	12[a], 13[a], 14[a], 16a, 16b[a], 17
16a	30.6 (t)	1.90 (ddd, 13.6, 5.3, 1.0)	15, 16b, 17	14, 15, 17	12, 13, 14 ,15, 16b, 17	14, 15, 16b, 17[a], 26
16b		2.29 (ddd, 13.1, 11.3, 11.3)	15, 16a, 17	14, 15, 17, 18	12, 13, 14, 15, 16a, 17	13, 15[a], 16a, 17[a], 19a, 21, 26
17	81.6 (d)	3.94 (ddd, 12.0, 7.5, 1.1)	16a, 16b, 18	15, 19, 20	14, 15, 16a, 16b, 18, 19a, 19b, 26	15, 16a[a], 16b[a], 18, 26
18	38.3 (d)	2.54 (dddq, 12.3, 7.5, 7.02, 6.8)	17, 19a,19b, 26	16, 17, 19, 26	16a, 17, 19a, 19b, 20, 21, 26	17, 19a[c], 19b, 20, 26
19a	35.7 (t)	1.34 (ddd, 12.3, 12.3, 9.2)	18, 19b, 20	18, 20, 21, 26	18, 19b, 20, 21, 26	16b, 18[a], 19b, 21, 26
19b		2.08 (ddd, 12.2, 7.02, 7.02)	18, 19a, 20	17, 18, 21	17, 18, 19a, 20, 21, 22a, 26	18, 19a, 20, 22a, 22b, 26
20	82.2 (d)	3.79 (ddd, 9.3, 9.3, 7.0)	19a, 19b, 21	17, 21, 22	17, 18, 19a, 19b, 21, 22a, 22b, 23, 26	16b, 19a[a], 19b, 18, 22a, 22b, 28
21	74.3 (d)	3.73 (ddd, 10.0, 10.0, 1.6)	20, 22a, 28	19, 20, 22, 23	18, 19a, 19b, 20, 22a, 22b, 23, 26	11, 13, 14, 16b, 19a, 19b, 22a[a], 22b[a], 23, 28
22a	32.5 (t)	1.47 (ddd, 14.2, 10.5, 1.0)	21, 22b, 23	20, 21,	19b, 20, 21, 23, 28	20, 21[a], 22b[b], 23
22b		1.65 (m)	22a, 23, 28	23	21, 22a, 23, 28	19a, 20, 21[a], 22a, 23[a]
23	76.7 (d)	5.13 (ddd, 10.8, 3.3, 0.8)	22a, 22b	22, 24	20, 21, 22a, 22b, 24	3, 11, 21, 22b[a], 23[a], 25, 28
24	74.0 (d)	5.17 (d, 3.3)		1, 2, 3, 23, 1``	21, 22a, 22b, 23	3, 22a, 3``
25	18.3 (q)	1.07 (d, 6.6)	11	10, 11, 12	9, 10a, 10b, 11	9, 11[a], 12[a], 23, 28
26	14.3 (q)	1.04 (d, 6.8)	18	17, 18, 19	17, 18, 19a, 19b, 20	16a, 16b, 18[a], 19a, 19b
27	OH	2.71 (br s)		1, 2, 3		4b, 22b
28	OH	2.78 (br s)	21, 22b	21, 22	20, 21, 22a, 22b, 23	11, 13, 20, 21, 22b, 23, 25
1′	173.6 (s)	-				

2′a	36.3 (t)	2.40 (dt, 15.5, 7.3)	3′	1′, 3′, 4′	3′, 4′	3′[a], 4′
2′b		2.43 (dt, 15.5, 7.3)	3′	1′, 3′, 4′	3′, 4′	3′[a], 4′
3′	18.6 (t)	1.70 (m)	2′, 4′	1′, 2′, 4′	2′, 4′	2′, 4′
4′	13.9 (q)	0.96 (t, 7.4)	3′	2′, 3′	2′, 3′	2′[a], 3′[a]
1″	173.1 (s)	-				
2″a	36.0 (t)	2.31 (dt, 12.8, 7.5)	3″	1″, 3″, 4″	3″, 4″	3″[a], 4″[a]
2″b		2.33 (dt, 12.8, 7.5)	3″	1″, 3″, 4″	3″, 4″	3″[a], 4″[a]
3″	18.6 (t)	1.63 (m)	2″, 4″	1″, 2″, 4″	2″, 4″	2″[a], 4″[a]
4″	13.8 (q)	0.93 (t, 7.3)	3″	2″, 3″	2″, 3″	2″[a], 3″[a]

HMBC correlations are presented from proton to indicated carbon. a - COSY artifacts observed in ROESY spectrum. b- TOCSY artifacts observed in ROESY spectrum

Table S6. NMR data for deacylmandelalide D (**4b**) in CD_3OD, 700 MHz

No.	δ_C (mult)	δ_H (*J* in Hz)	COSY	HMBC
1	176.3 (s)	-		
2	82.4 (s)	-		
3	66.6 (d)	4.06 (d, 7.5)	4a	2, 4, 5
4a	37.4 (t)	1.56 (ddd, 15.1, 7.7, 1.6)	3, 4b	3
4b		2.02 (dd, 15.2, 11.1)	4a, 5	5
5	72.3 (d)	3.39 (m)	4b, 6ax	
6ax	40.3 (t)	1.11 (m)	5, 6eq, 7	5, 7
6eq		1.88 (dddd, 12.1, 4.7, 1.6, 1.6)	6ax, 7	
7	67.1 (d)	3.76 (m)	6ax, 8ax	
8ax	40.7 (t)	1.08 (m)	7, 8eq, 9	7, 9
8eq		1.83 (m)	7, 8ax	6, 7
9	71.1 (d)	3.39 (m)	8ax, 10b	
10a	41.2 (t)	1.23 (m)	10b, 11	
10b		1.49 (ddd, 13.8, 11.4, 4.1)	9, 10a	25
11	33.5 (d)	2.49 (m)	10a, 12, 25	
12	140.7 (d)	5.51 (dd, 14.6, 9.9)	11, 13	11, 14, 25
13	122.8 (d)	6.42 (dd, 14.6, 11.2)	12, 14	11, 14, 15
14	130.0 (d)	6.10 (dd, 10.9, 10.9)	13, 15	12, 16
15	126.3 (d)	5.30 (ddd, 16.0, 10.9, 5.1)	14, 16a, 16b	
16a	31.2 (t)	1.94 (ddd, 13.5, 5.2, 1.8)	15, 16b	14, 15
16b		2.38 (ddd, 13.1, 11.4, 11.4)	15, 16a, 17	17
17	81.0 (d)	3.98 (ddd, 11.6, 7.3, 1.4)	16b, 18	19, 20
18	37.6 (d)	2.52 (m)	19a, 26	16, 17, 19
19a	34.7 (t)	1.37 (m)	18, 19b, 20	18, 20, 21, 26
19b		2.14 (m)	18, 19a, 20	17, 18
20	82.2 (d)	3.84 (ddd, 9.6, 9.6, 6.8)	19a, 19b, 21	17
21	73.9 (d)	3.75 (dd, 9.1, 9.1)	20, 22a	20, 22, 23
22a	32.0 (t)	1.52 (ddd, 13.7, 9.7, 1.0)	21, 22b	21
22b		1.81 (m)	22a, 23	23
23	78.3 (d)	4.81 (dd, 10.8, 2.6)	22b	21
24	71.7 (d)	4.32 (d, 3.0)		1, 2, 3, 23
25	17.0 (q)	1.01 (d, 6.6)	11	10, 11, 12
26	12.3 (q)	1.08 (d, 7.0)	18	17, 18, 19

Table S7. Cartesian coordinates for Mandelalide B (**2**) optimized at the B3LYP/6-31G** level

DFT SCF Energy = -2422.75682693076 Hartree

Nuclear Repulsion Energy = 7278.259669929 Hartree

Coordinates (Angstroms)

Atom	x	y	z
O1	4.2603010000	-2.5090310000	-3.8919780000
C2	5.4921000000	-3.1553510000	-4.1534280000
C3	5.9065350000	-2.7349890000	-5.5779810000
C4	4.8551250000	-1.7010620000	-5.9991840000
C5	4.1450410000	-1.3468650000	-4.6949830000
H6	5.2947070000	-4.2284800000	-4.1608210000
H7	5.8085390000	-3.6011740000	-6.2348340000
H8	5.2902300000	-0.8253530000	-6.4822310000
H9	4.1394480000	-2.1750030000	-6.6725190000
H10	3.0795270000	-1.1591190000	-4.8335140000
C11	7.3403140000	-2.2094170000	-5.7314900000
H12	7.5005060000	-1.3038990000	-5.1492220000
H13	8.0502310000	-2.9738660000	-5.4156310000
H14	7.5243900000	-1.9812690000	-6.7817320000
C15	6.5050990000	-2.8948950000	-3.0208610000
H16	7.3787770000	-3.5248630000	-3.1887430000
H17	6.8300270000	-1.8615410000	-3.0335270000
C18	5.8832950000	-2.5202570000	-0.5464110000
C19	5.9130350000	-3.2835370000	-1.6576280000
H20	5.4303700000	-2.9548830000	0.3334630000
H21	5.4764260000	-4.2691690000	-1.5818570000
C22	6.4730790000	-0.4650450000	0.7335350000
C23	6.4319710000	-1.1481650000	-0.4231570000
H24	6.8451190000	-0.6573700000	-1.2895900000
H25	6.0823110000	-0.9111860000	1.6368840000
C26	7.0800620000	0.9386180000	0.7922910000
H27	6.7519190000	1.4543050000	-0.1069880000
H28	5.5242710000	1.7447210000	2.0819300000
H29	7.0301540000	1.3358870000	2.9169450000
C30	8.6095510000	0.7820480000	0.7501120000
H31	9.0979750000	1.7340400000	0.5504420000
H32	8.9691720000	0.3821350000	1.6986550000
H33	8.8967310000	0.0981630000	-0.0491100000
C34	6.6123620000	1.7685370000	2.0070910000
C35	7.4401720000	5.4674680000	2.8473030000
C36	6.7842770000	4.1015830000	3.1002400000
C37	7.0741340000	3.2316520000	1.8783250000
O38	6.4258870000	3.8455050000	0.7784810000
C39	7.0854880000	5.0321030000	0.3691780000
C40	6.9679780000	6.0579050000	1.5080370000
H41	8.5215120000	5.3290830000	2.8007760000
H42	5.7071750000	4.2144470000	3.2327280000
H43	7.2145560000	3.6484910000	3.9942100000
H44	8.1556050000	3.2269890000	1.7580440000

H45	8.1233000000	4.7598270000	0.1692470000
H46	5.9218790000	6.3492870000	1.6133850000
H47	7.5562070000	6.9425530000	1.2624870000
C48	6.4946120000	5.5845800000	-0.9487620000
H49	7.2490970000	6.2741550000	-1.3334460000
H50	5.6048290000	6.1743630000	-0.7109100000
C51	4.7769060000	-0.1405550000	-3.9879420000
H52	5.8601000000	-0.1758480000	-4.0737160000
C53	6.3248090000	4.4551510000	-2.0184740000
O54	4.4469060000	-0.2338080000	-2.6163950000
H55	4.6587970000	-1.1208970000	-2.3167860000
C56	4.2338850000	1.2098280000	-4.4706190000
H57	4.0717790000	1.3447660000	-5.5404660000
H58	3.2294530000	1.2751190000	-4.0488200000
C59	5.0671640000	2.3537740000	-3.8750120000
C60	4.1823820000	3.4498660000	-3.3105310000
C61	5.2571140000	4.5627870000	-3.1696080000
O62	5.9209090000	3.0409170000	-4.8002070000
H63	3.6110310000	3.0182540000	-2.4779140000
C64	5.9514030000	4.3529280000	-4.5205460000
O65	6.4402800000	5.2010360000	-5.2155390000
O66	4.6581330000	5.8410440000	-3.1410170000
H67	5.3285370000	6.4930330000	-3.3589480000
H68	6.1079330000	3.5556350000	-1.4716360000
H69	3.4680180000	3.7558000000	-4.0779540000
C70	7.4360010000	8.3850700000	5.2251610000
C71	7.1381300000	7.7040160000	6.5673270000
C72	8.3960890000	7.0364100000	7.1362580000
C73	8.9842170000	6.0866910000	6.0841200000
O74	9.2313590000	6.7736990000	4.8485060000
C75	8.0598930000	7.3602560000	4.2644350000
H76	6.4951730000	8.7472960000	4.8067130000
H77	6.3817310000	6.9340950000	6.4096430000
H78	8.1241140000	6.4616800000	8.0225830000
O79	9.3626460000	8.0133770000	7.5208230000
O80	6.6076980000	8.6469410000	7.4980090000
H81	6.4519400000	8.1975450000	8.3317580000
O82	8.3382360000	9.4820590000	5.4201970000
H83	5.5615460000	1.9995990000	-2.9736000000
O84	7.6591310000	4.3860360000	-2.5848680000
C85	8.3214460000	3.2199760000	-2.5601160000
O86	7.9175960000	2.1732920000	-2.1367200000
C87	9.7047210000	3.4206050000	-3.1746820000
H88	10.0856900000	4.4042200000	-2.8954360000
H89	10.3839430000	2.6669820000	-2.7742500000
C90	9.6824510000	3.3113520000	-4.7038510000
H91	8.9778650000	4.0346010000	-5.1150290000
H92	10.6785320000	3.5436370000	-5.0825420000
C93	9.3019420000	1.9035050000	-5.1727640000
H94	10.0024750000	1.1750710000	-4.7635760000
H95	8.2921380000	1.6509450000	-4.8508280000
H96	9.3436350000	1.8637370000	-6.2615100000
H97	8.2731860000	5.2773300000	5.9132300000

C98	10.2889390000	5.4516270000	6.5743490000
H99	10.6356100000	4.7247570000	5.8391600000
H100	11.0584960000	6.2125210000	6.7069530000
H101	10.1179850000	4.9422050000	7.5230790000
O102	7.1015820000	6.3535880000	3.9200930000
H103	8.3658960000	7.8650270000	3.3486940000
C104	8.1777980000	10.5392580000	4.4695040000
H105	8.9290170000	11.3038250000	4.6670190000
H106	8.3099400000	10.1713220000	3.4523840000
H107	7.1881580000	10.9861830000	4.5696440000
H108	9.5710420000	8.5477320000	6.7503060000

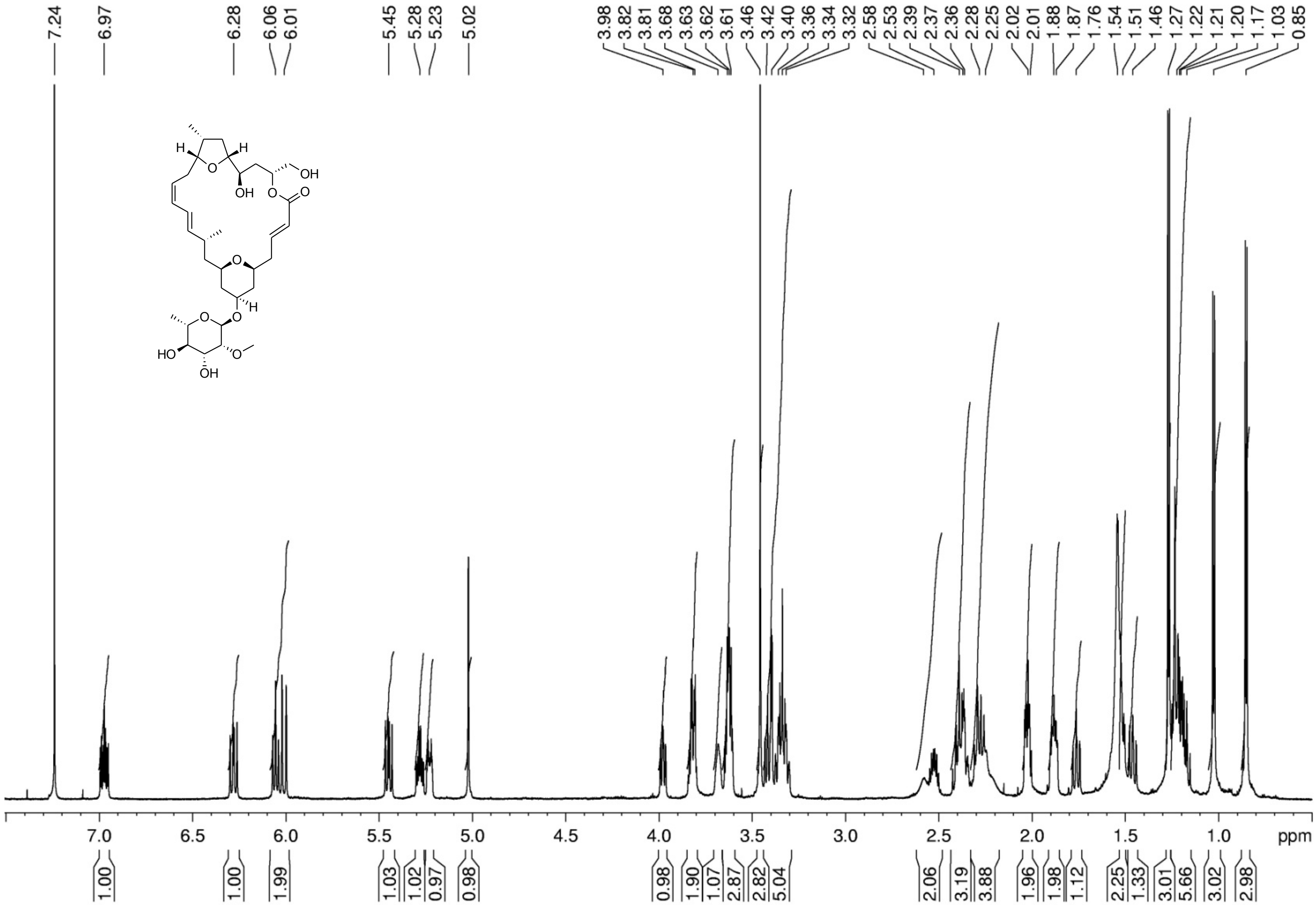


Figure S1. ^{1}H NMR spectrum for mandelalide A (**1**; 700 MHz, $CDCl_3$)

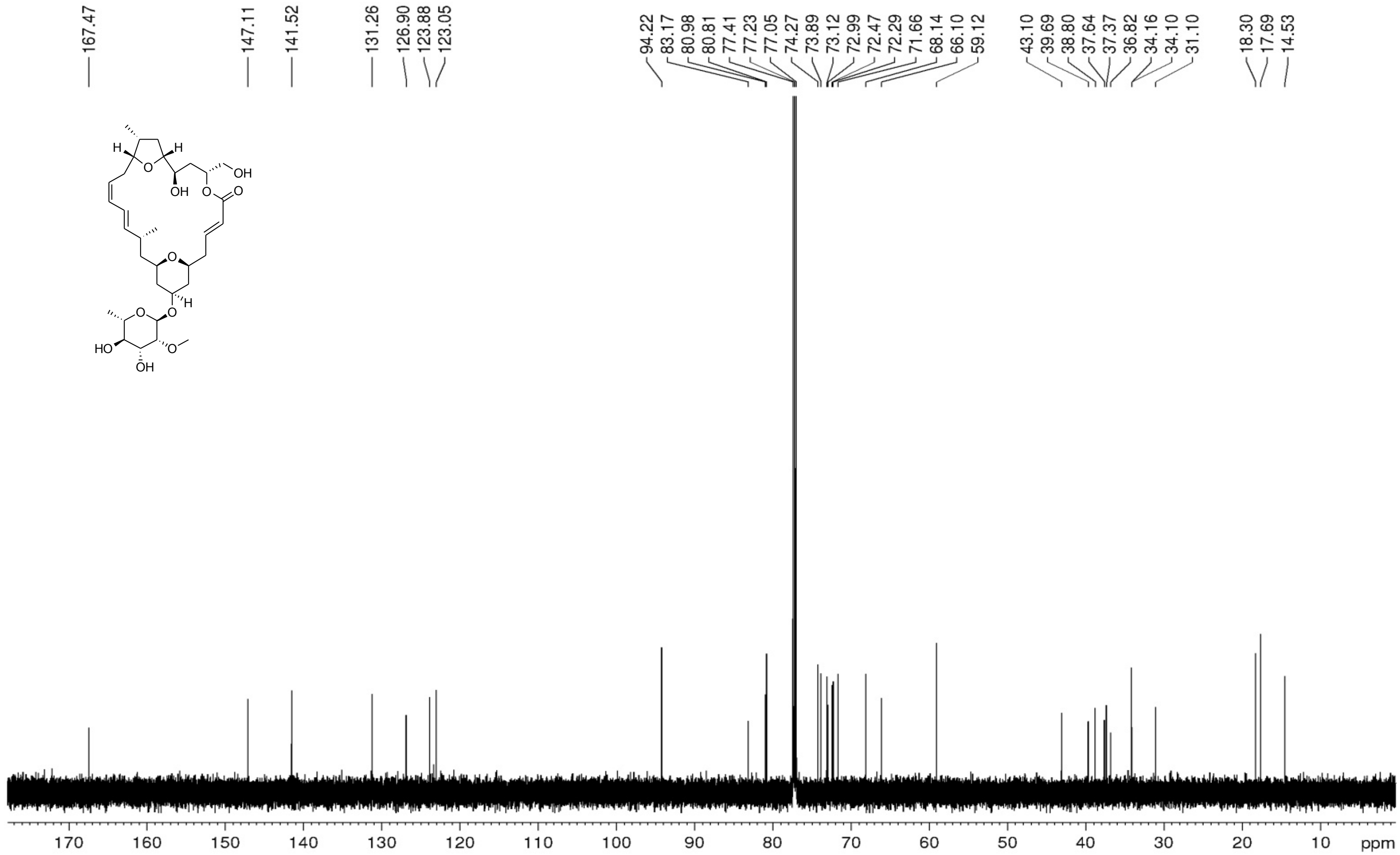


Figure S2. ^{13}C NMR spectrum for mandelalide A (**1**; 175 MHz, $CDCl_3$)

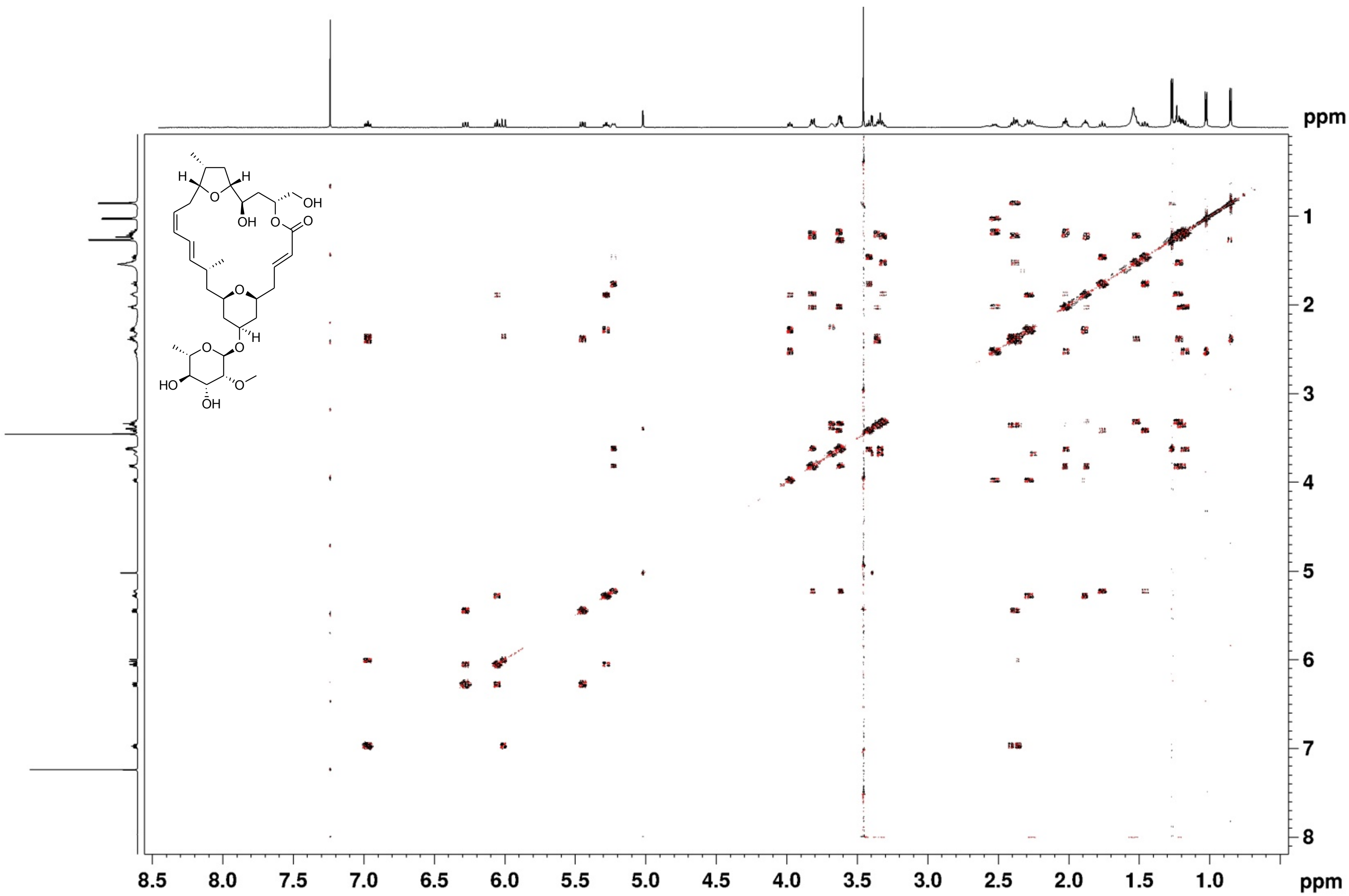


Figure S3. COSY spectrum for mandelalide A (**1**; 700 MHz, $CDCl_3$)

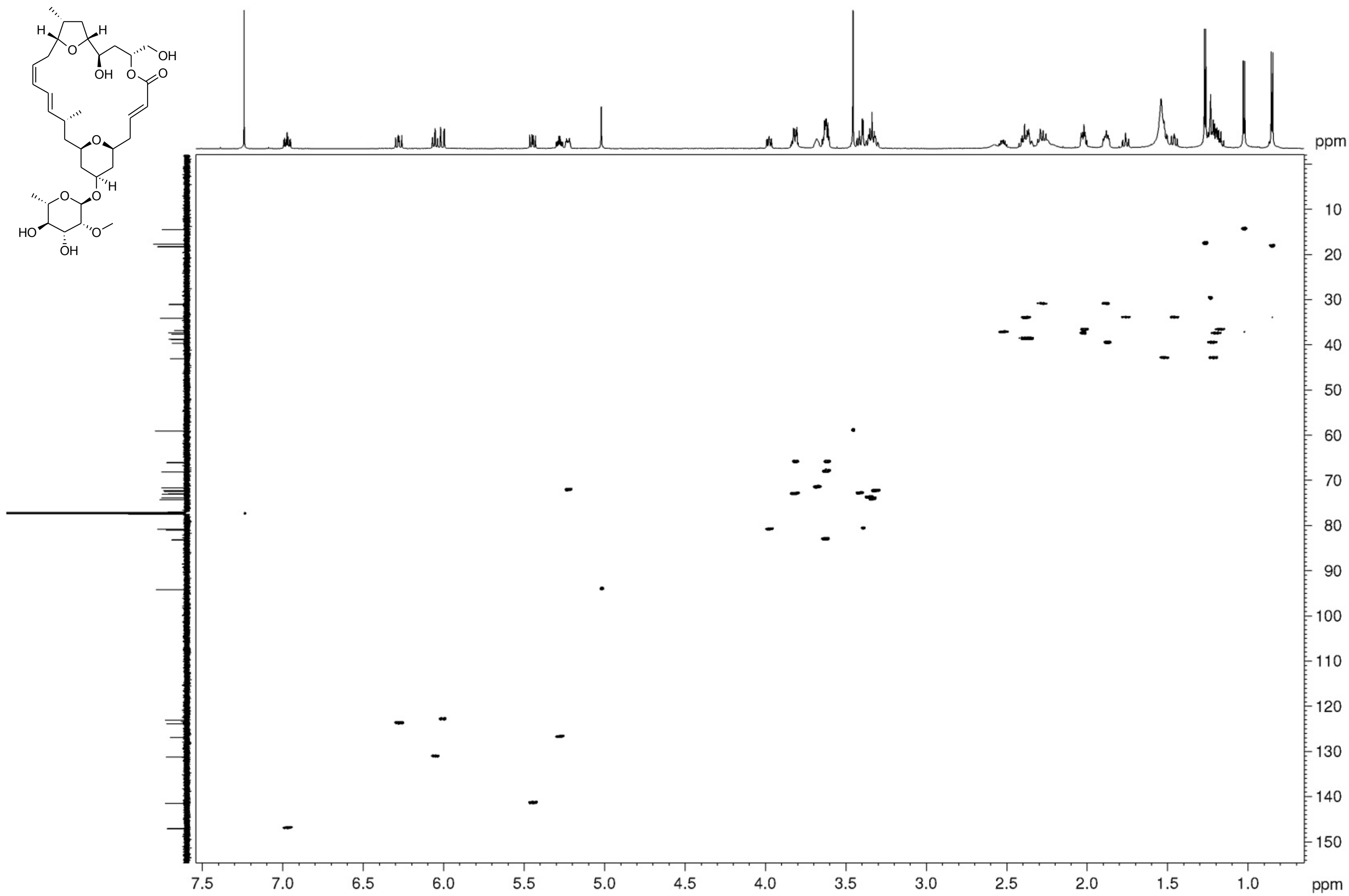


Figure S4. HSQC spectrum for mandelalide A (**1**; 700 MHz, $CDCl_3$)

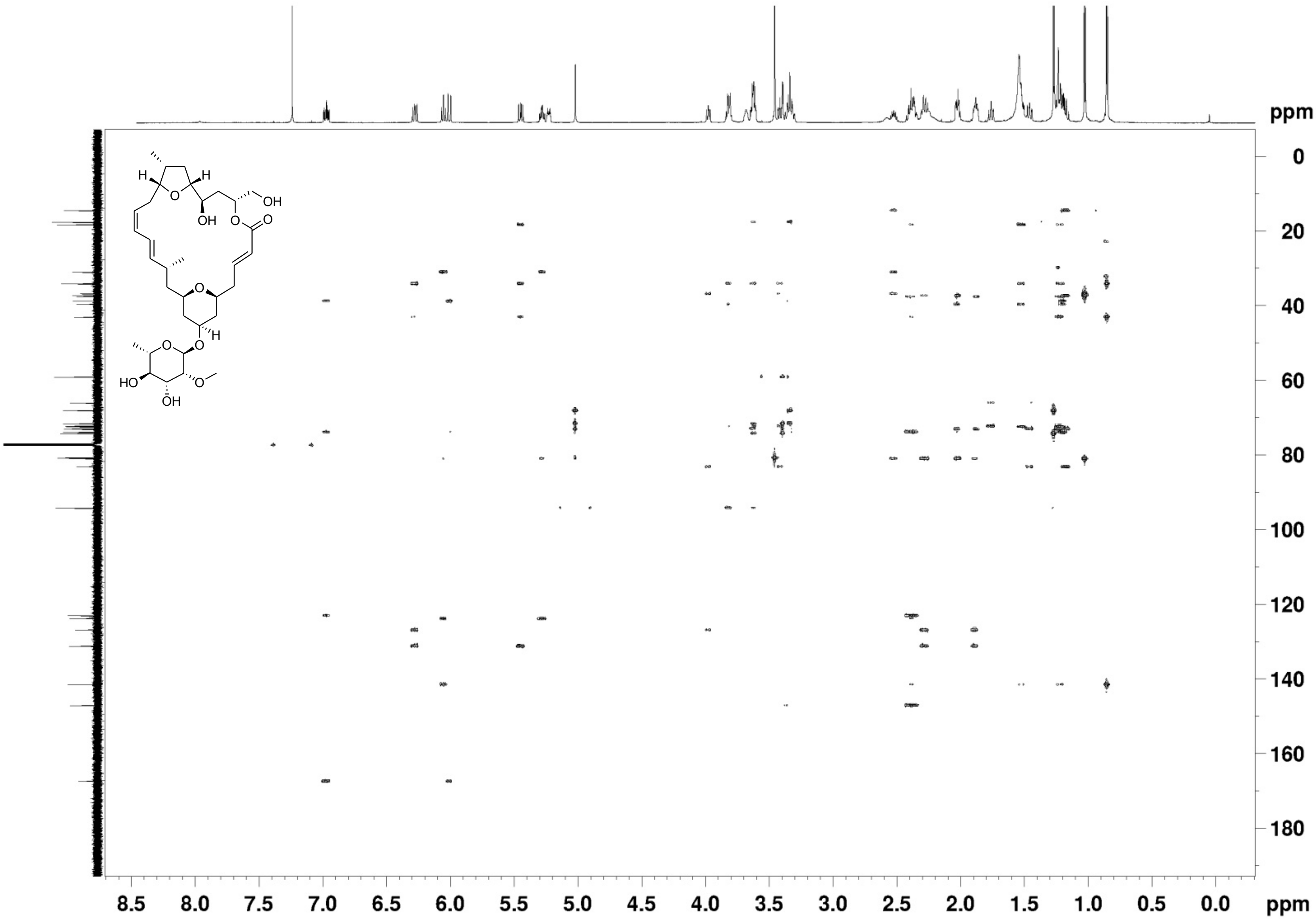


Figure S5. HMBC spectrum for mandelalide A (**1**; 700 MHz, $CDCl_3$)

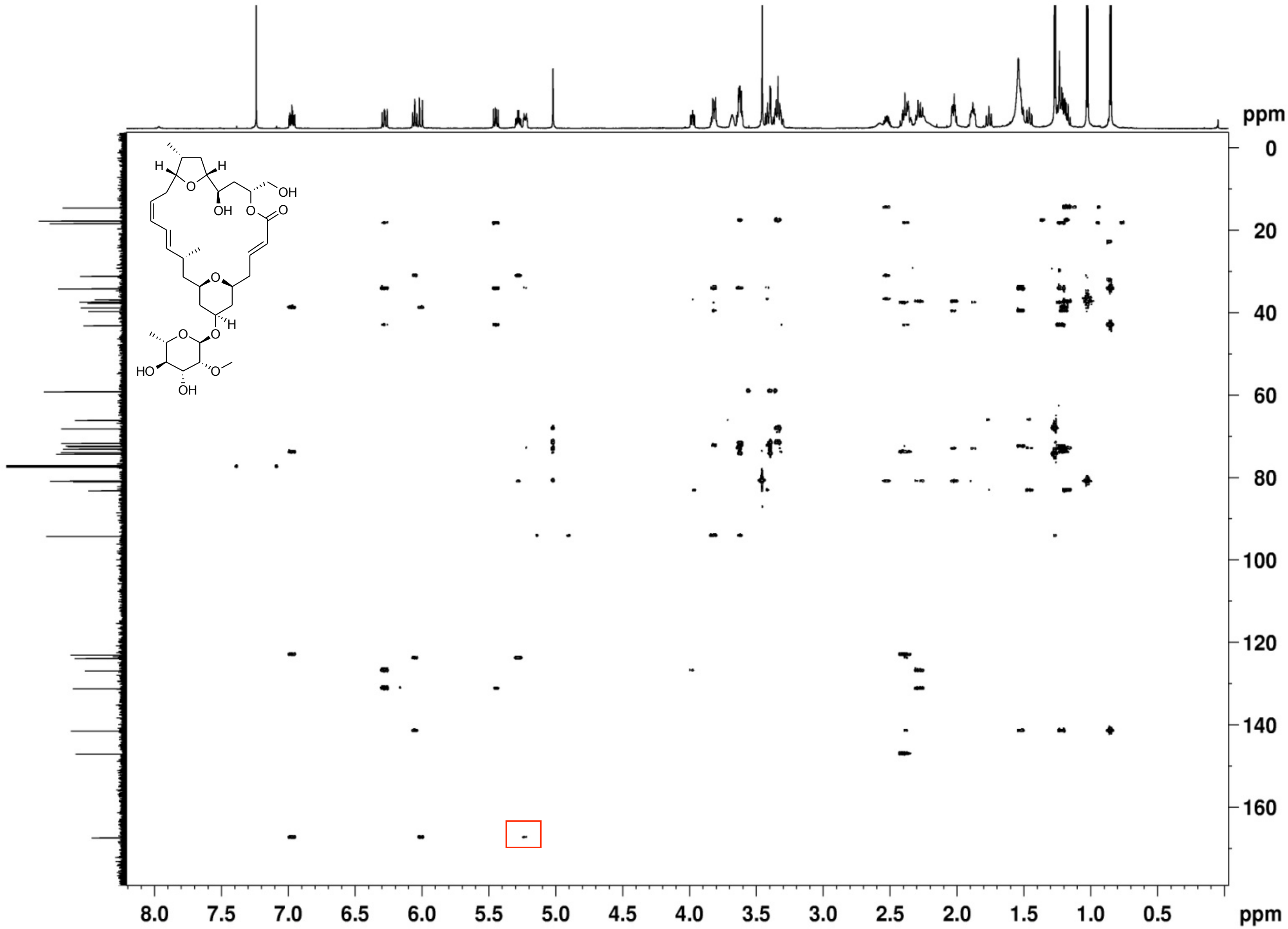


Figure S6. HMBC spectrum for mandelalide A (**1**), long range *J* = 4 Hz (700 MHz, $CDCl_3$)

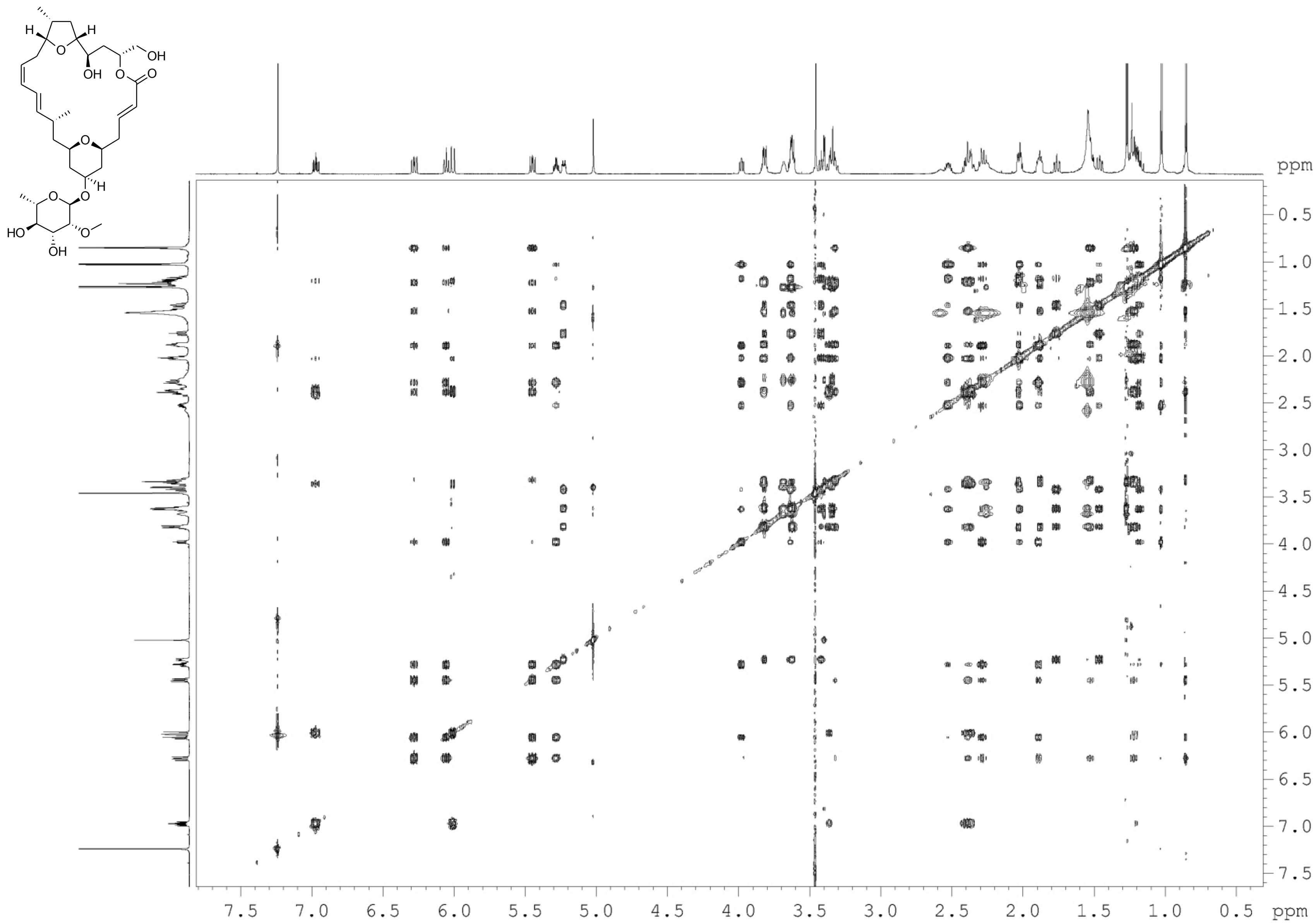
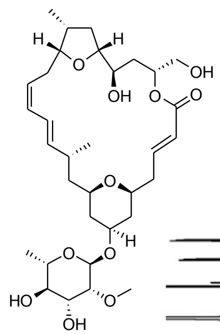


Figure S7. TOCSY spectrum for mandelalide A (**1**), TOCSY mixing time = 60 ms (700 MHz, $CDCl_3$)



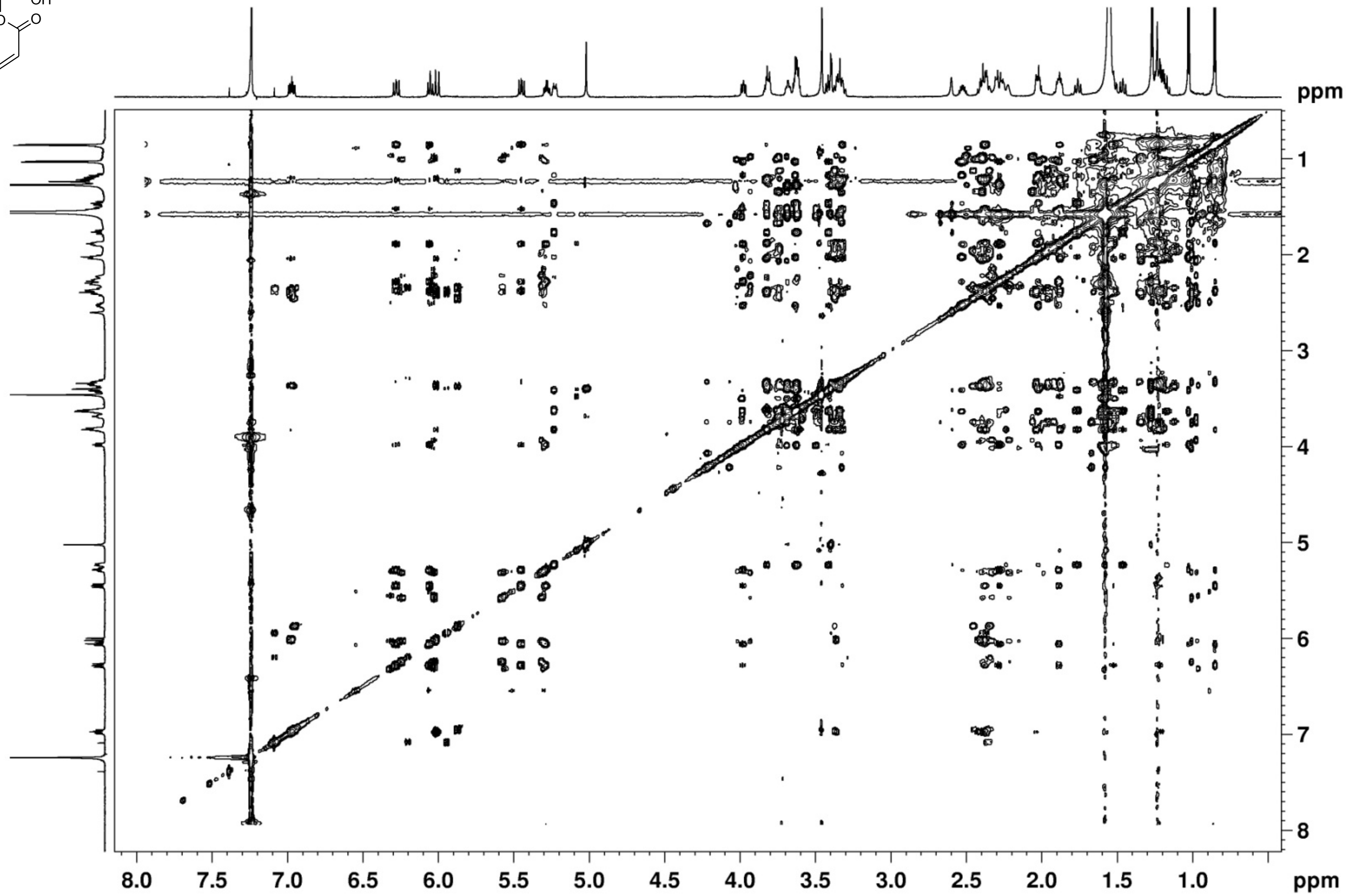
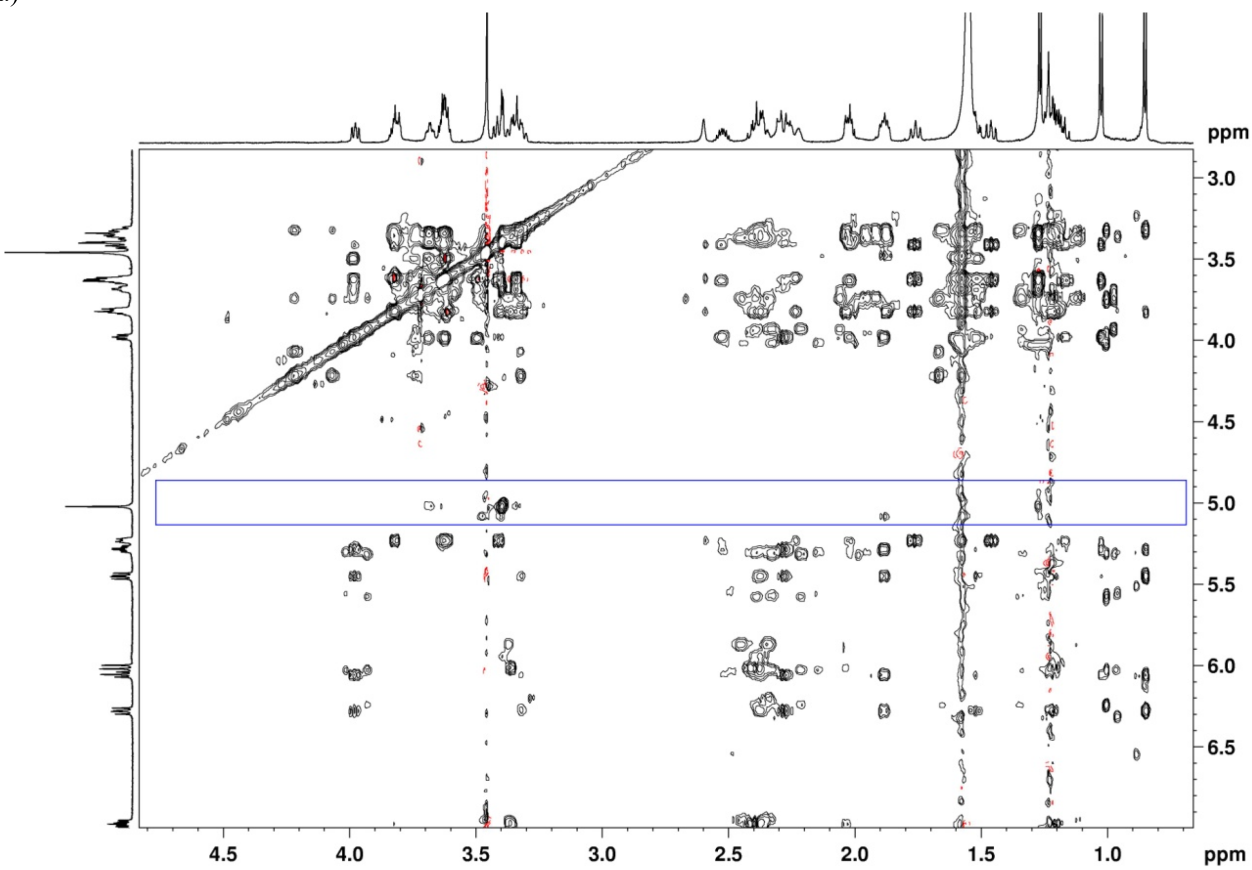


Figure S8. TOCSY spectrum for mandelalide A (**1**), TOCSY mixing time = 100 ms (700 MHz, $CDCl_3$)

a)



b)

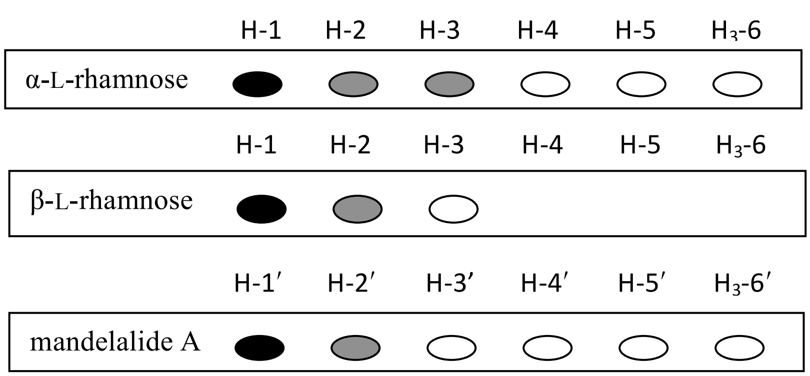


Figure S9. a) Partial TOCSY spectrum for mandelalide A (**1**) showing the α-2-*O*-methylrhamnose region, TOCSY mixing time = 100 ms (700 MHz, $CDCl_3$), b) The magnetization transfer pattern of TOCSY signals for the mandelalide A monosaccharide and α- and β-L-rhamnose. The grey ovals indicate intensity or signal greater than 1.5 % of intensity measured for the anomeric ^{1}H signal, while white ovals indicate intensity of at least 0.5 % but no more than 1.5% intensity measured for the anomeric ^{1}H signal.

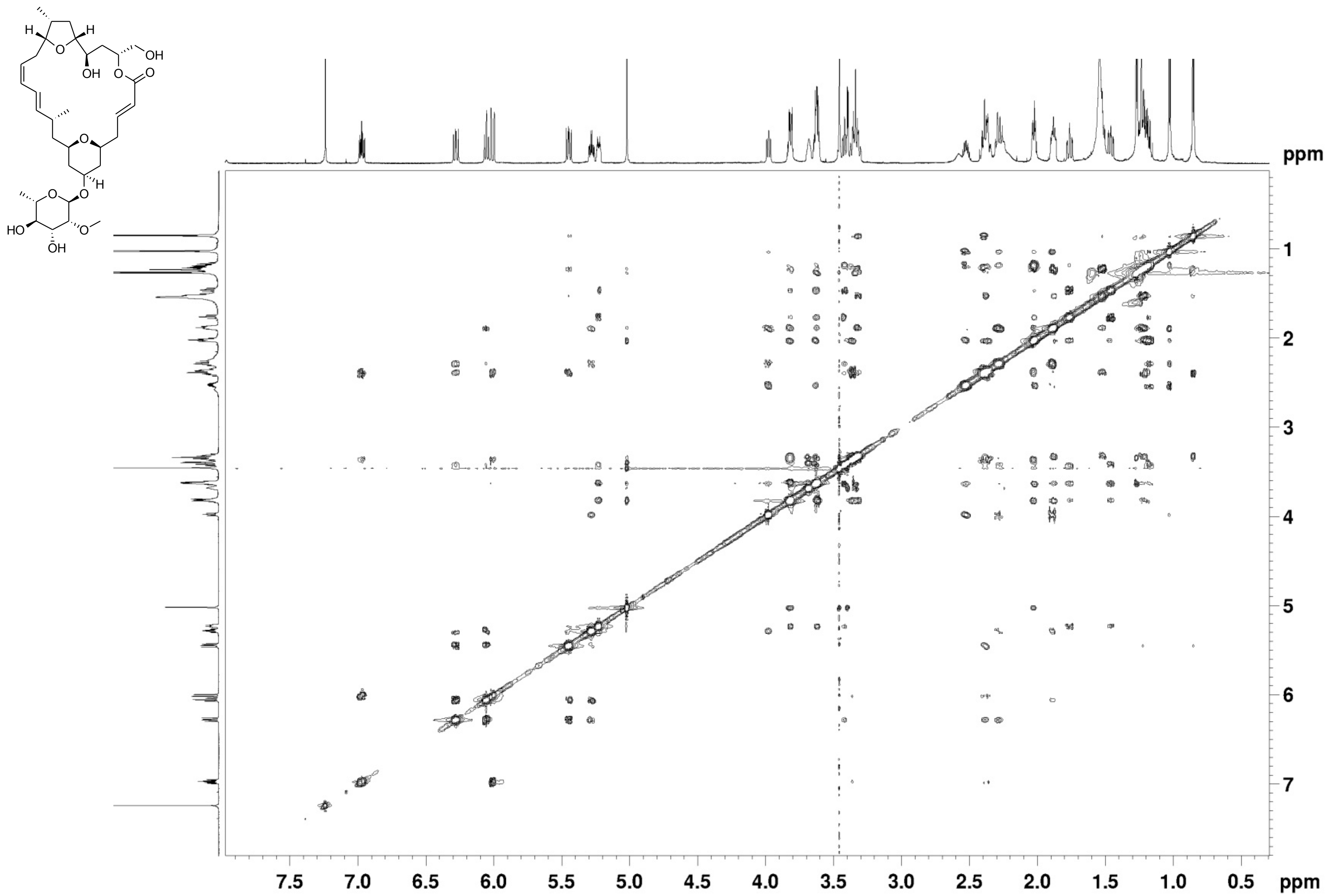


Figure S10. ROESY spectrum for mandelalide A (**1**; 700 MHz, $CDCl_3$)

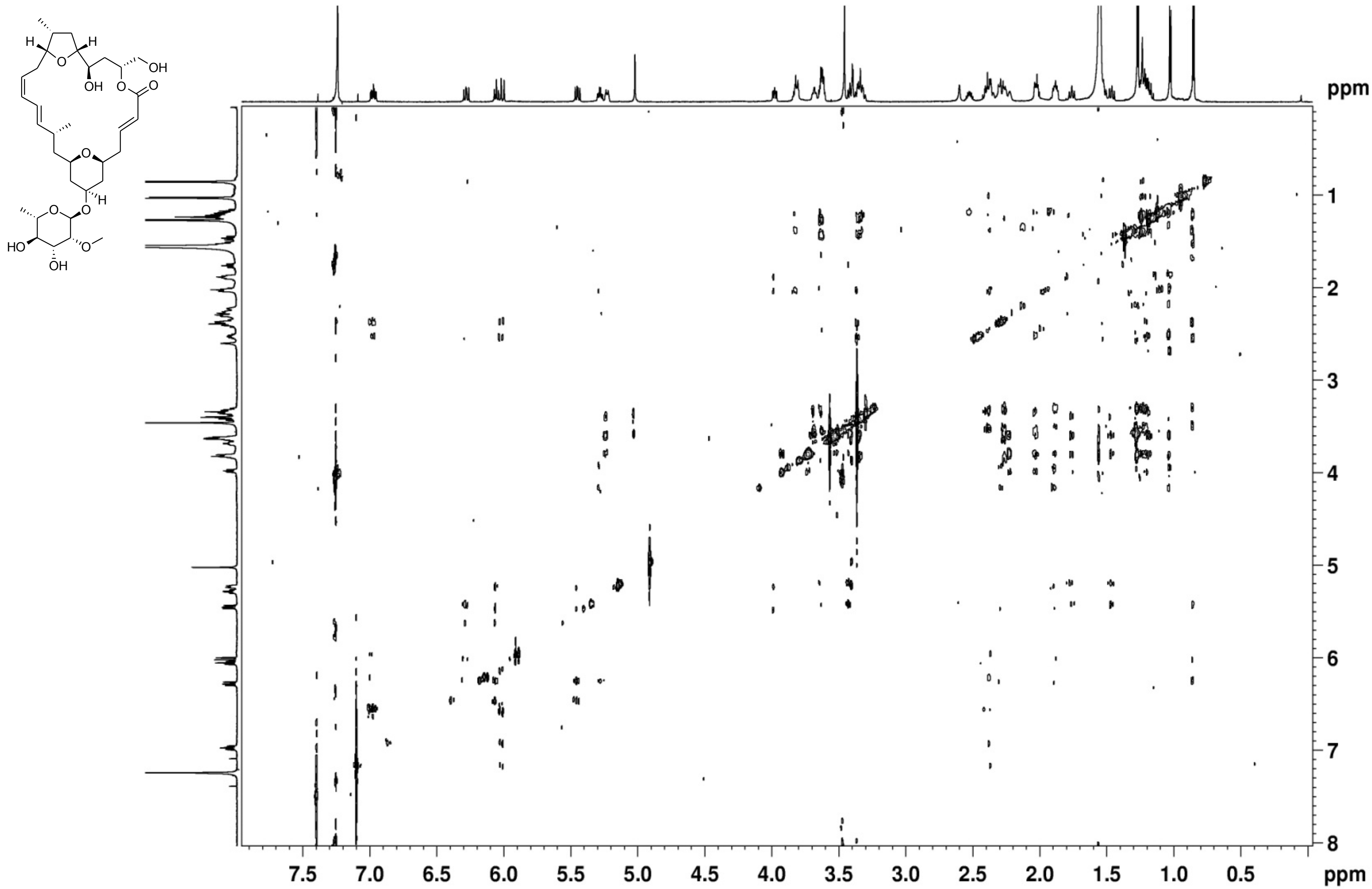


Figure S11. HETLOC spectrum for mandelalide A (**1**; 700 MHz, $CDCl_3$)

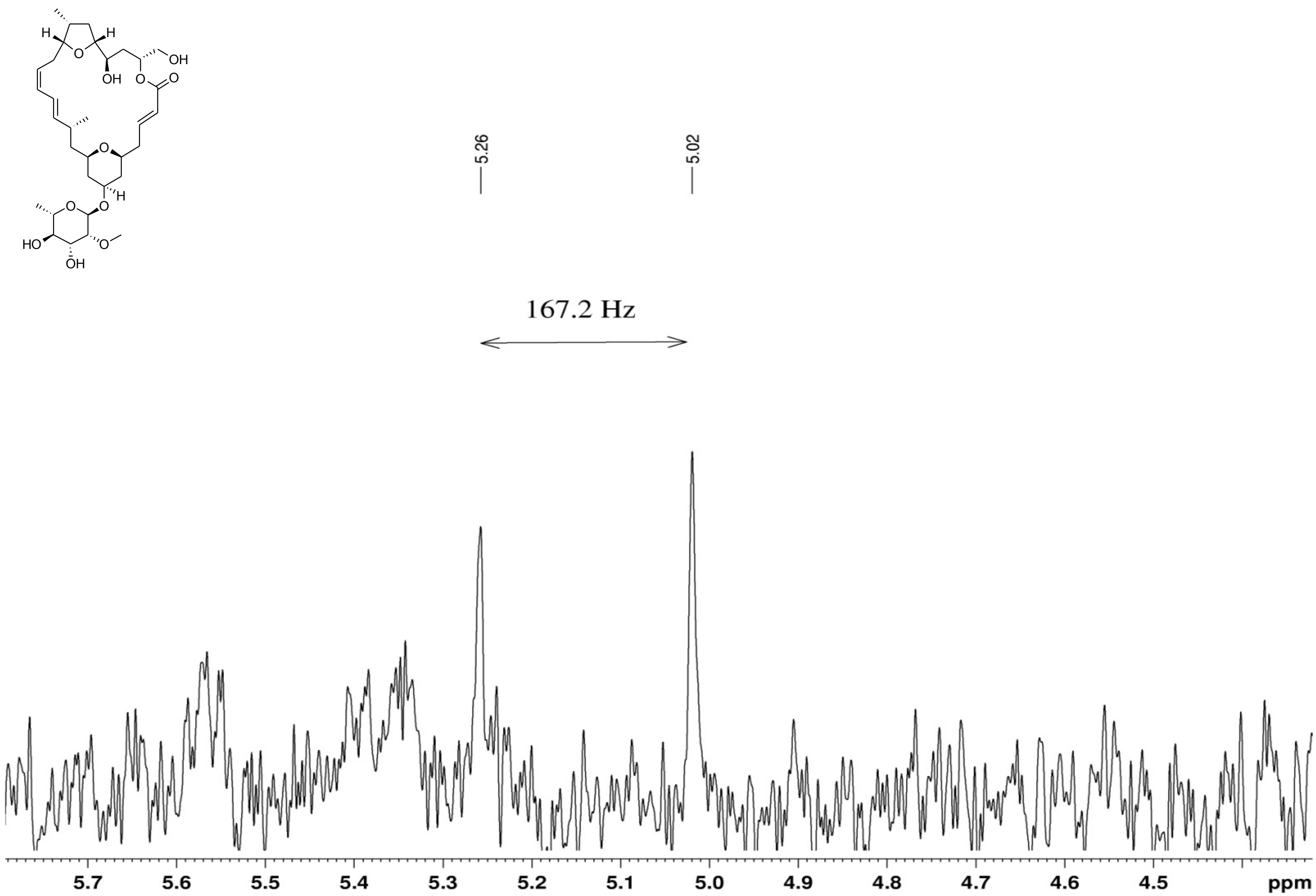


Figure S12. *F2* slice of HETLOC spectrum for mandelalide A (**1**) anomeric C-1′ (700 MHz, $CDCl_3$)

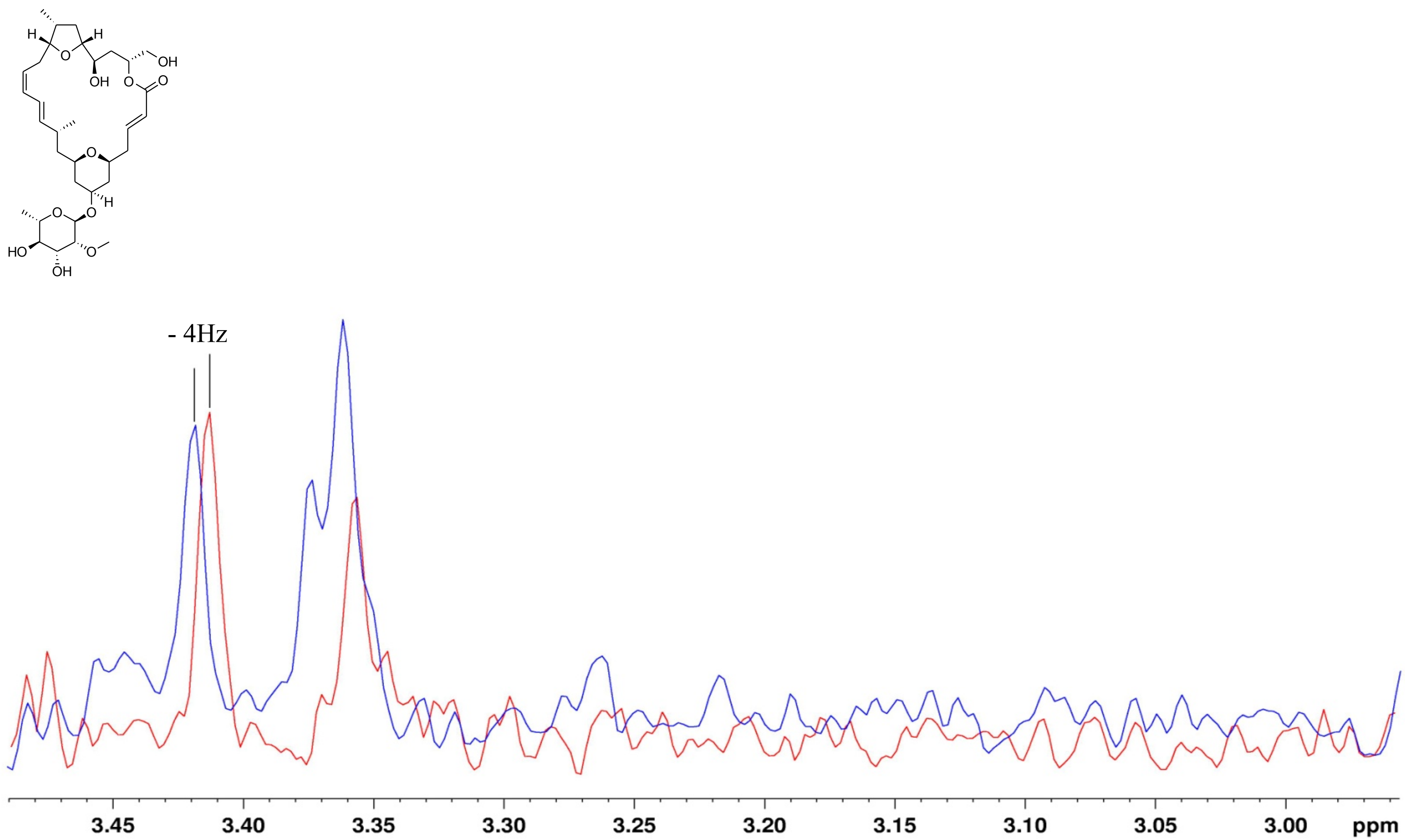
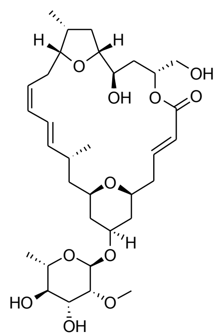


Figure S13. *F2* slice of HETLOC spectrum for C-20 of mandelalide A (**1**, 700 MHz, $CDCl_3$)



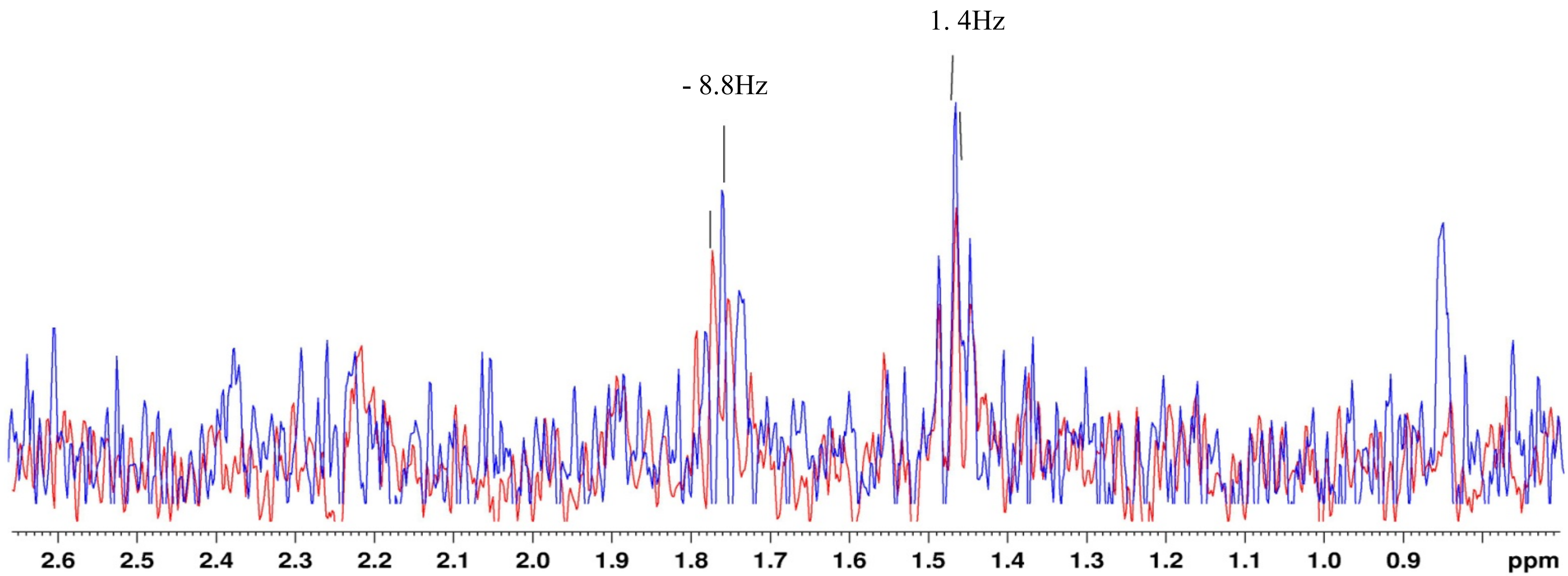


Figure S14. *F2* slice of HETLOC spectrum for mandelalide A (**1**) for C-23 (700 MHz, $CDCl_3$)

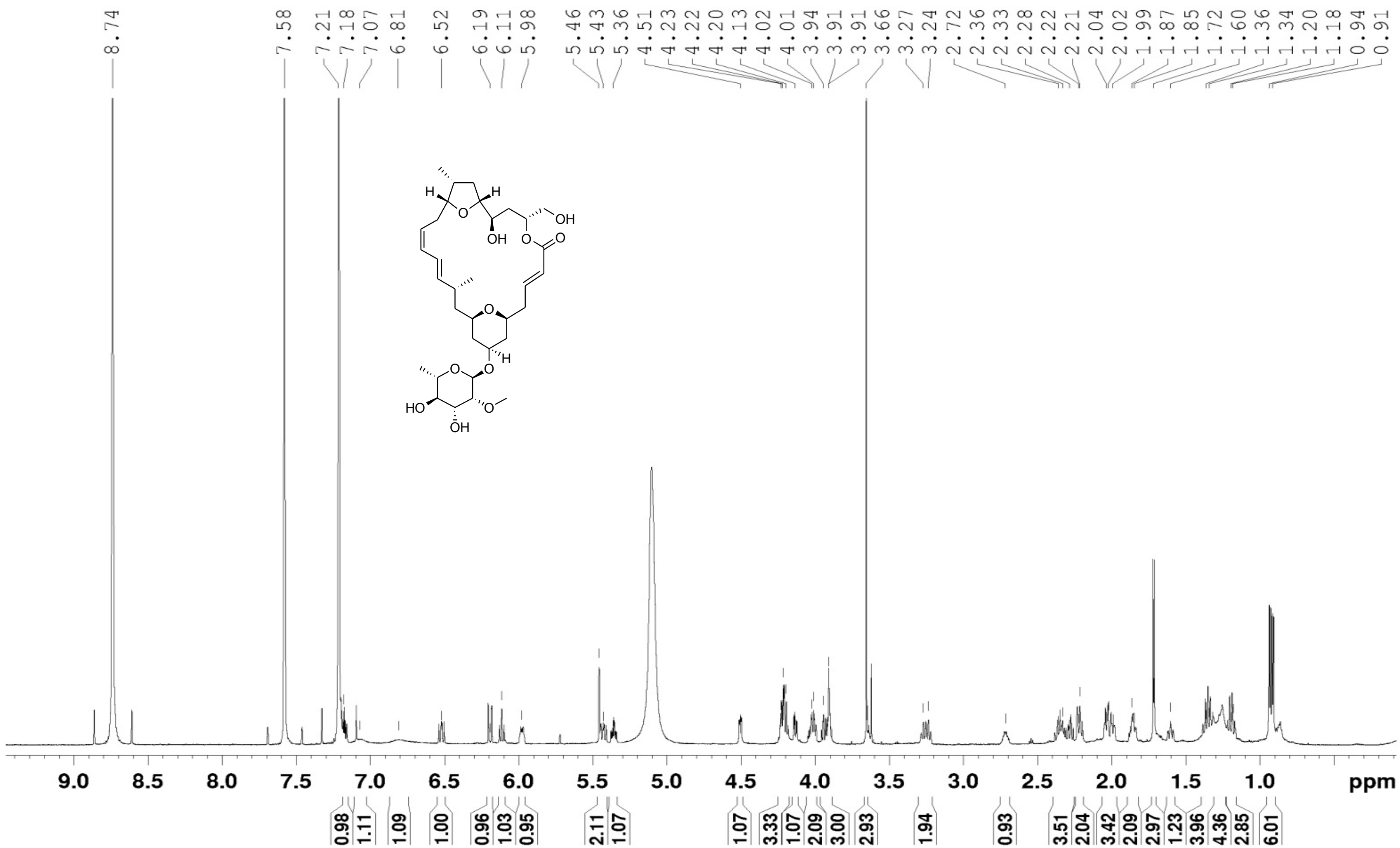
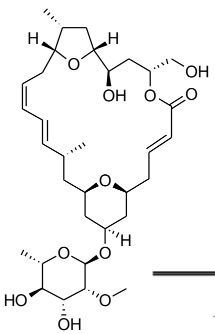


Figure S15. ^{1}H NMR spectrum for mandelalide A (**1**; 700 MHz, py-d_5)



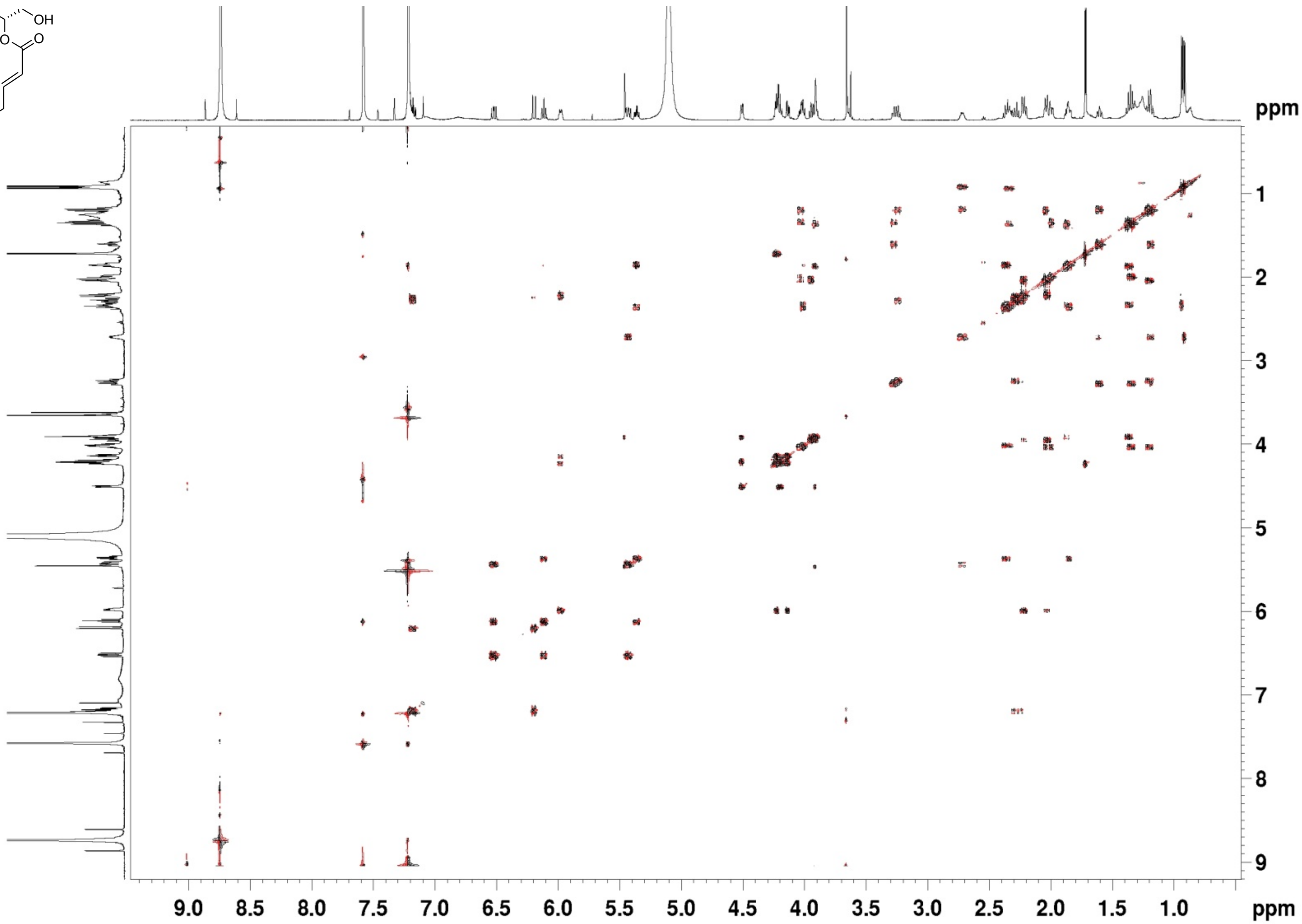


Figure S16. COSY NMR spectrum for mandelalide A (**1**; 700 MHz, py-d_5)

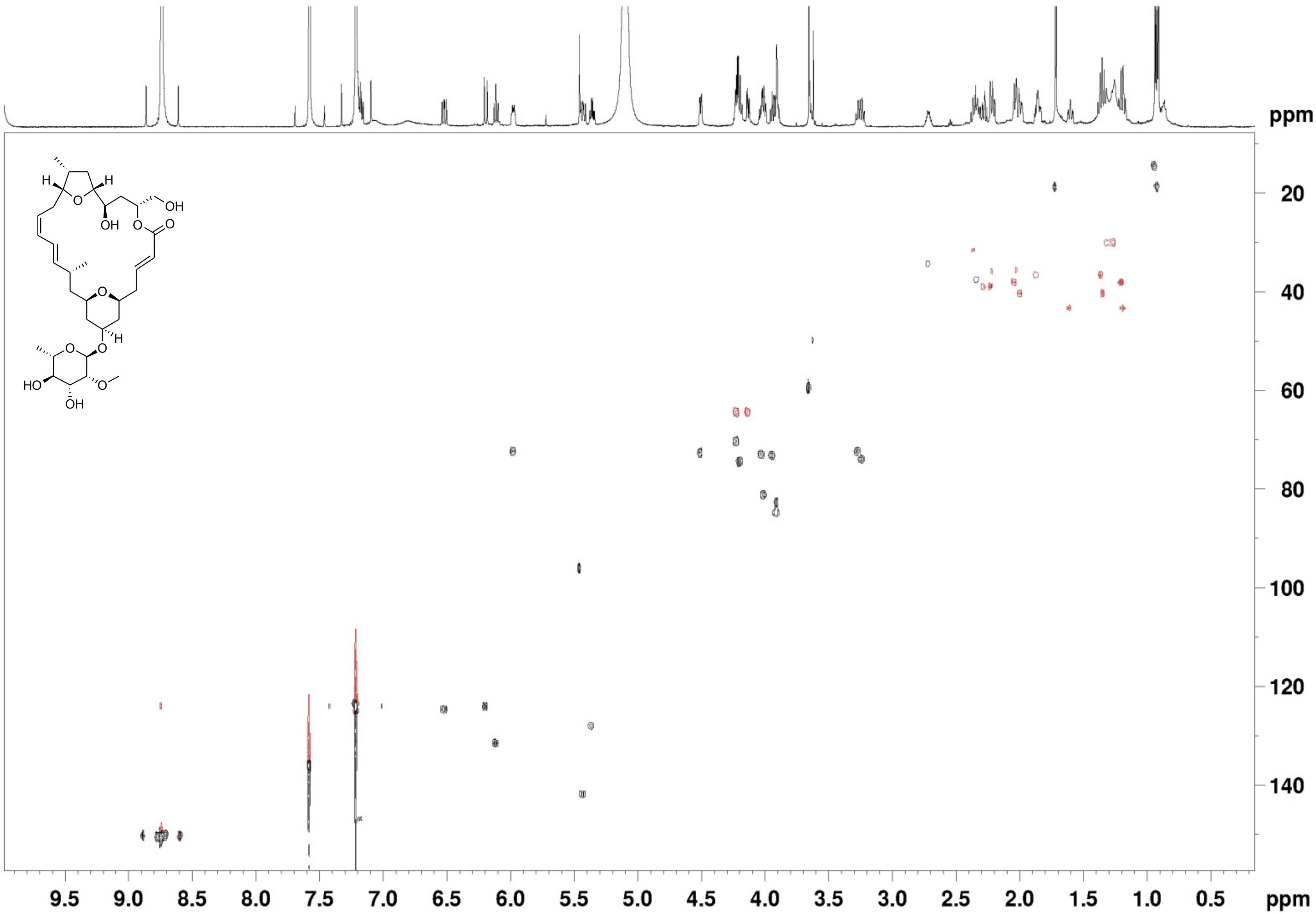


Figure S17. HSQC NMR spectrum for mandelalide A (**1**; 700 MHz, py-d_5)

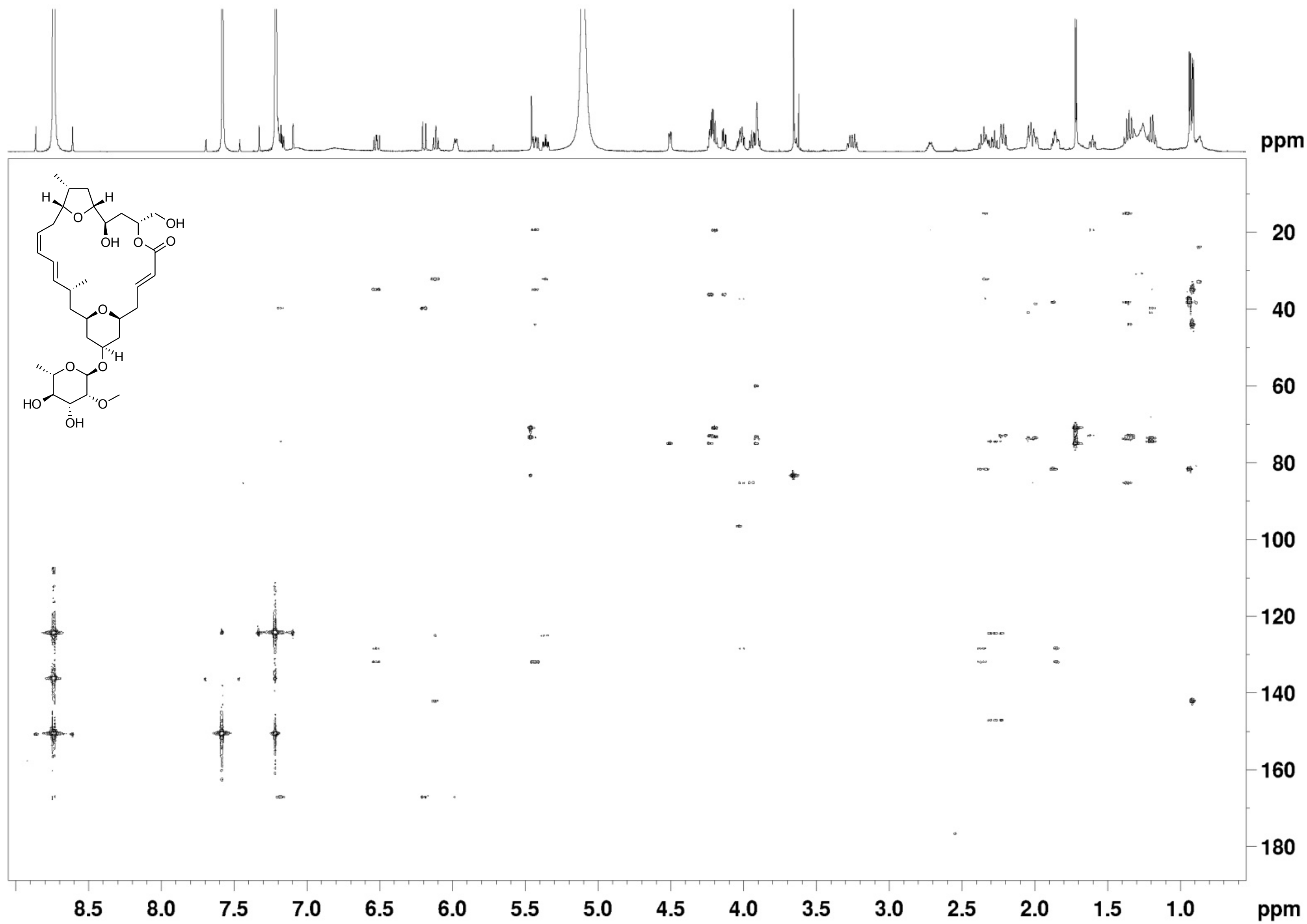


Figure S18. HMBC NMR spectrum for mandelalide A (**1**; 700 MHz, py-d_5)

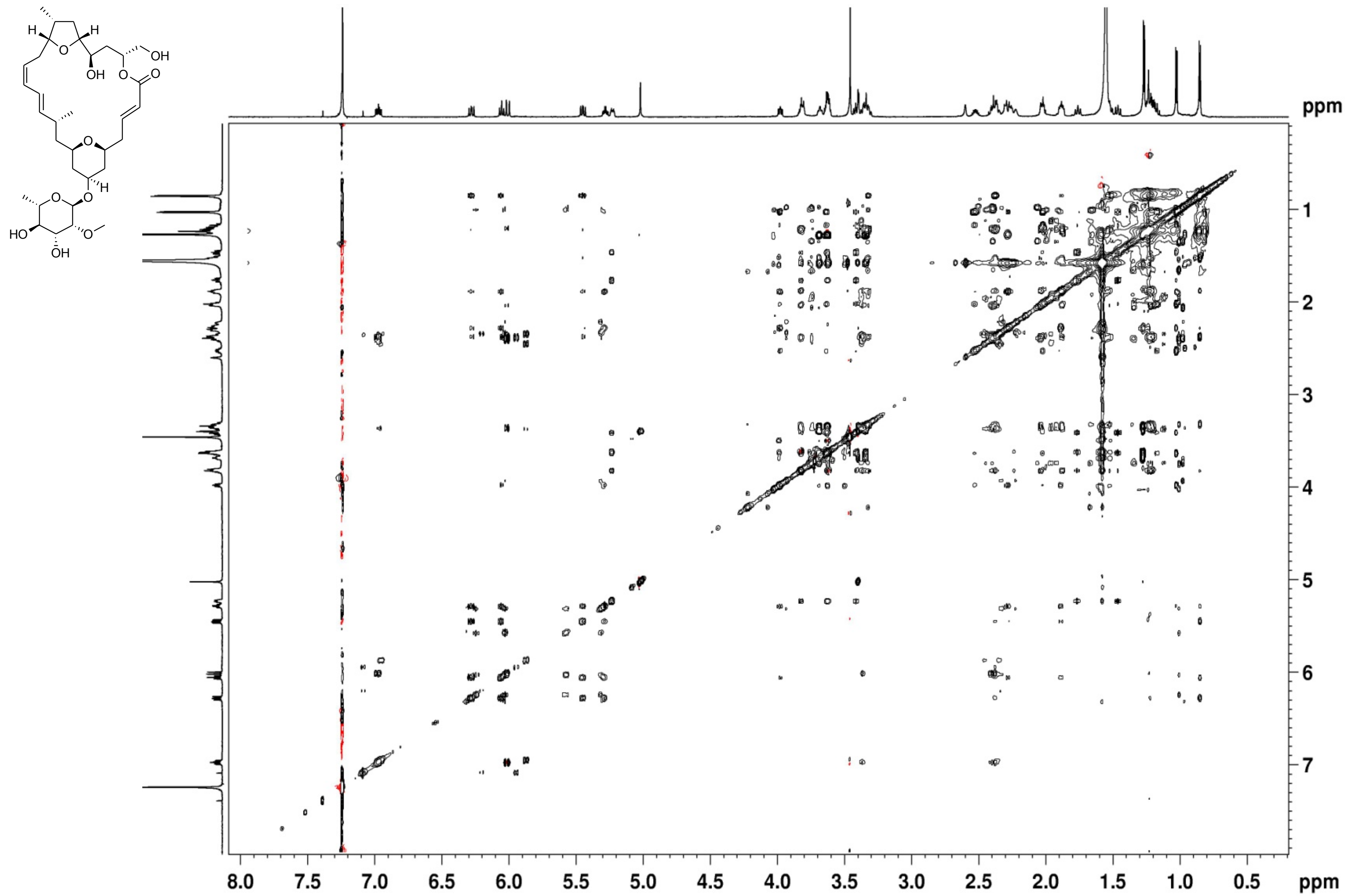
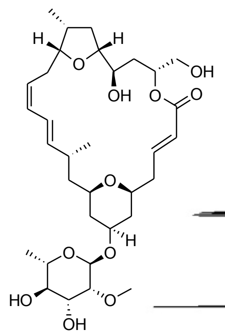


Figure S19. TOCSY NMR spectrum for mandelalide A (**1**), TOCSY mixing time = 100 ms (700 MHz, py-d_5)



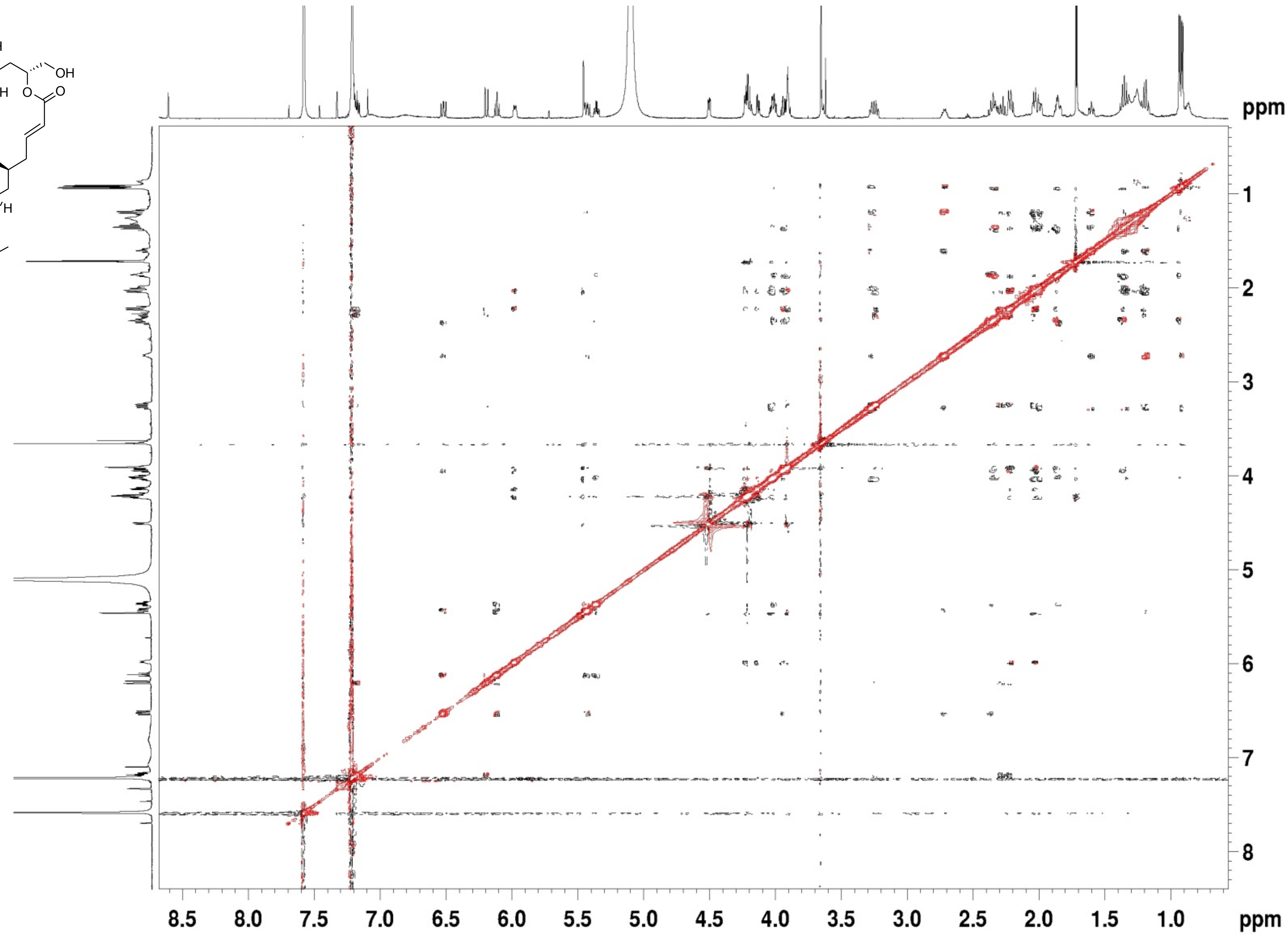


Figure S20. ROESY NMR spectrum for mandelalide A (**1**; 700 MHz, py-d_5)

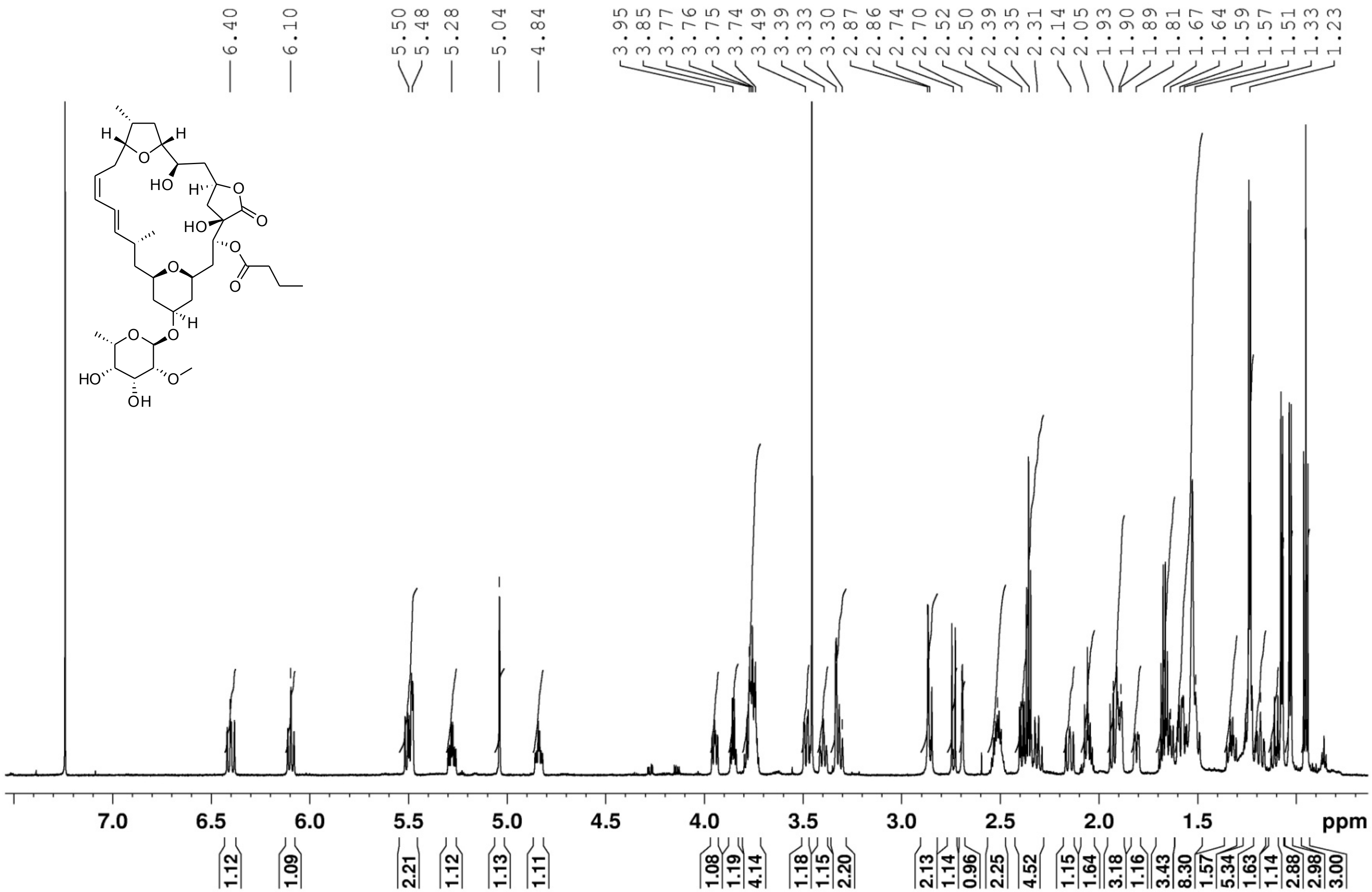


Figure S21. [1]H NMR spectrum for mandelalide B, (**2**; 700 MHz, CDCl$_3$)

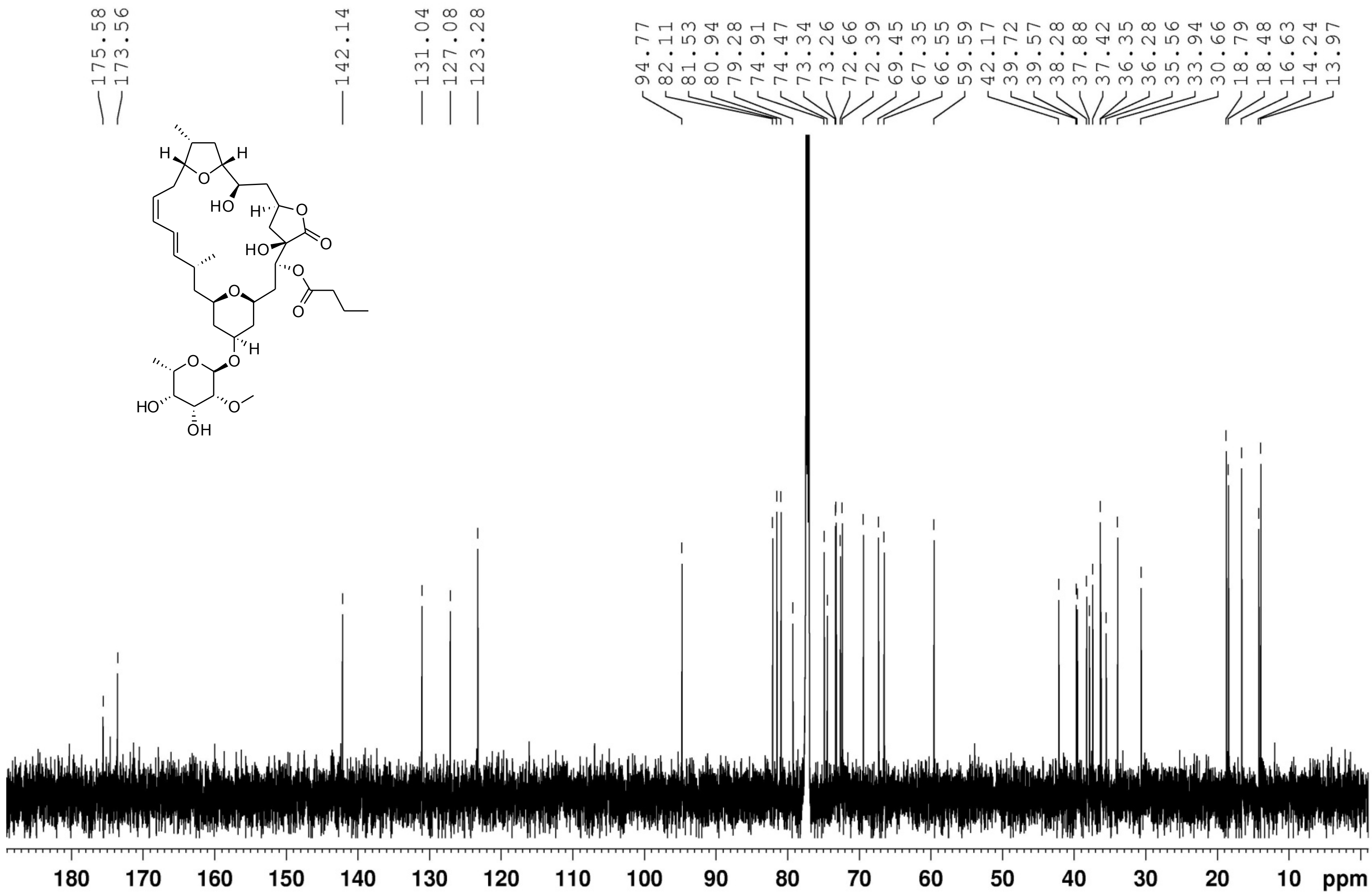


Figure S22. ^{13}C NMR spectrum for mandelalide B, (**2**; 175 MHz, $CDCl_3$

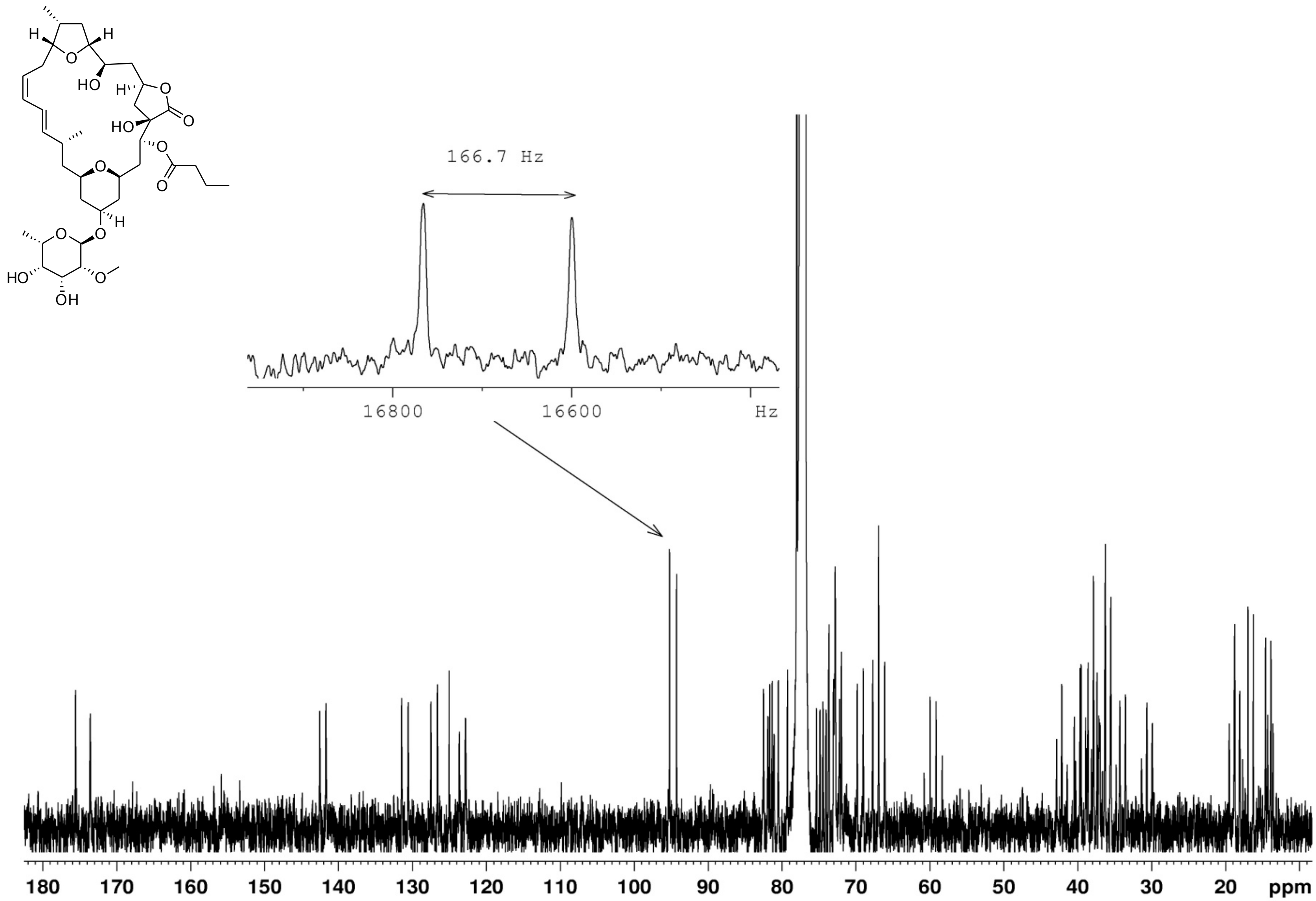
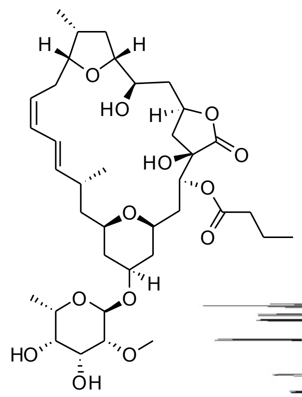


Figure S23. ^{13}C gated decoupled NMR spectrum for mandelalide B (**2**; 175 MHz, $CDCl_3$)



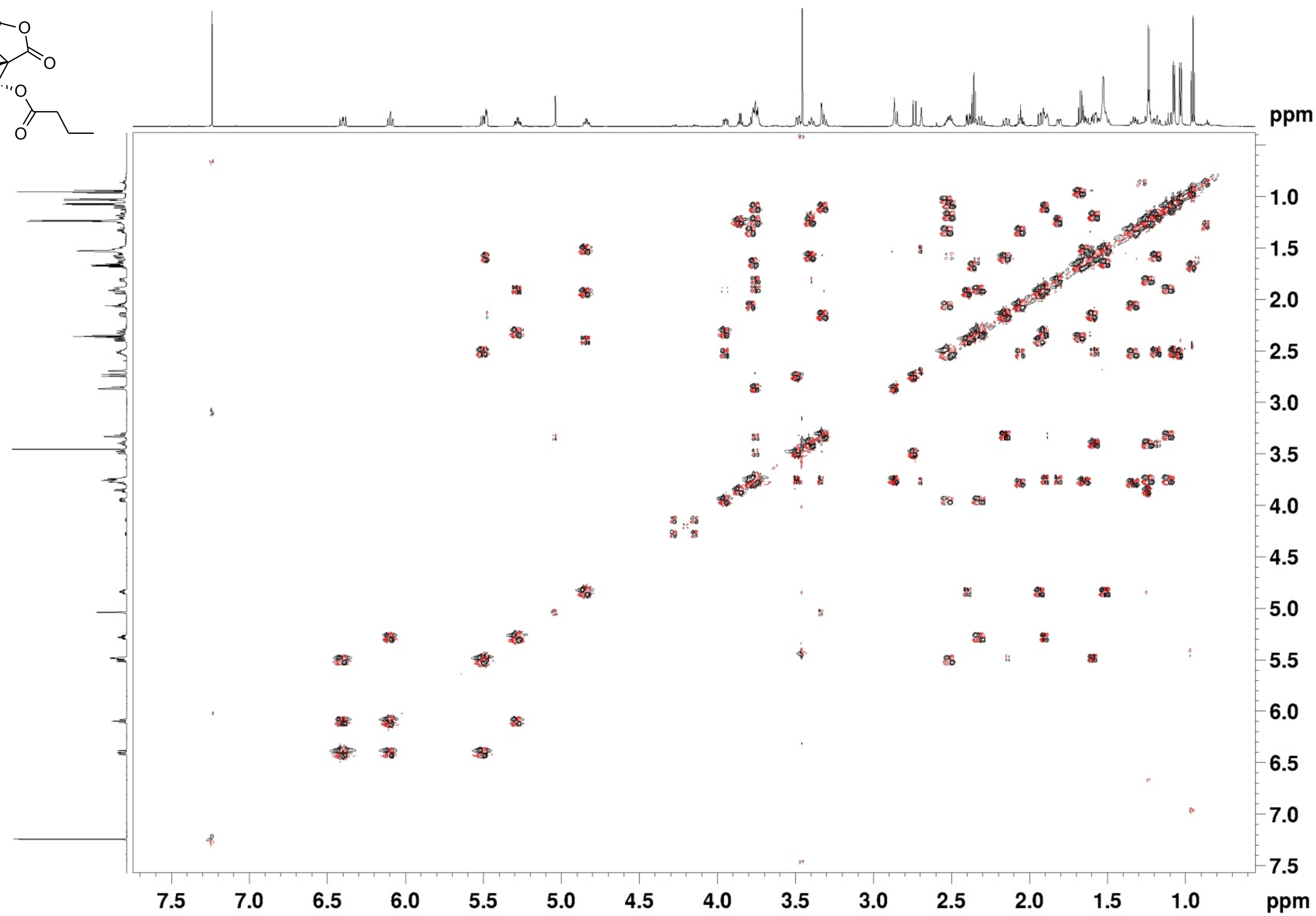


Figure S24. COSY NMR spectrum for mandelalide B, (**2**; 700 MHz, $CDCl_3$)

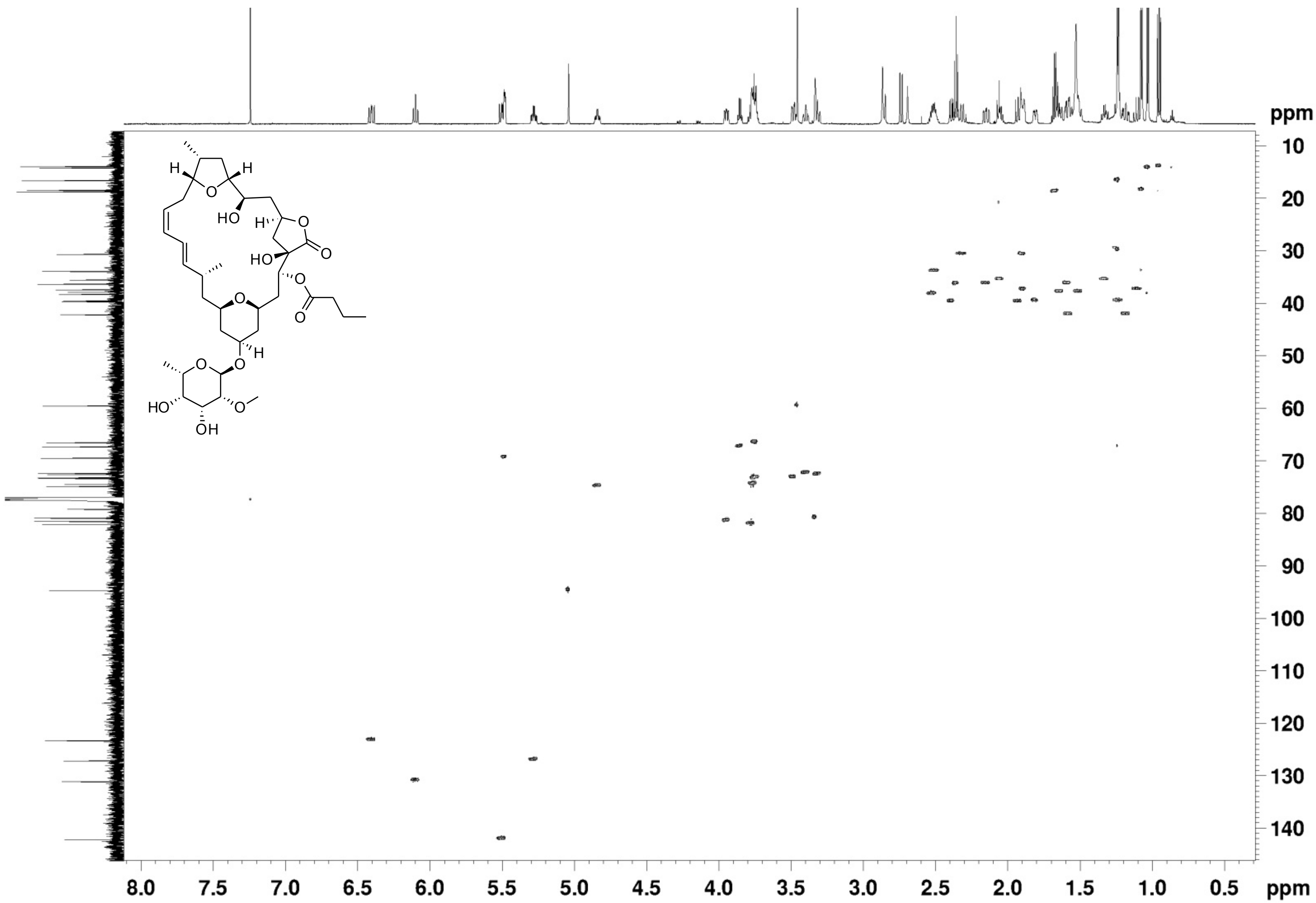


Figure S25. HSQC NMR spectrum for mandelalide B, (**2**; 700 MHz, $CDCl_3$)

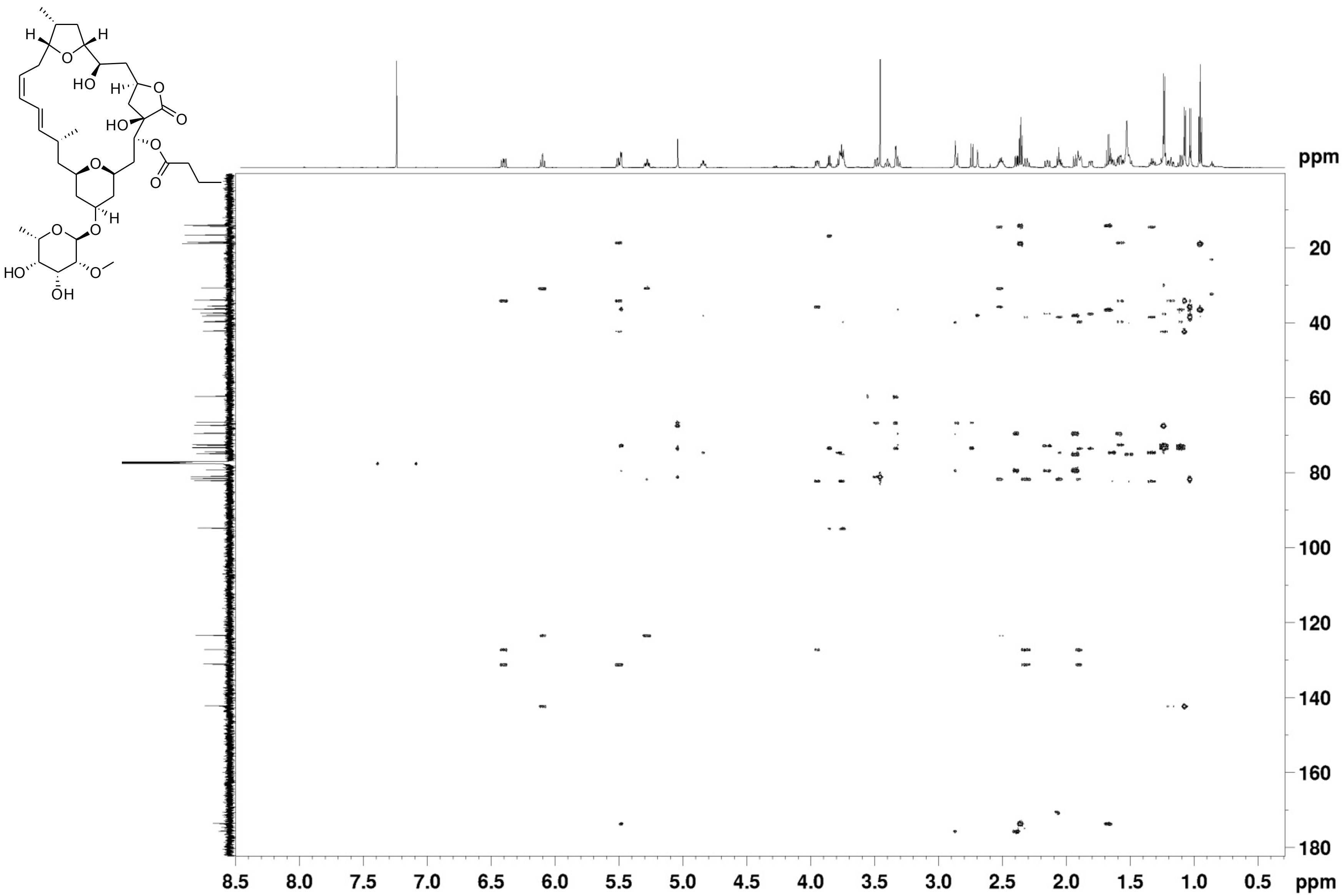
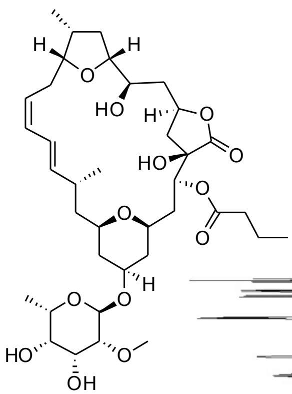


Figure S26. HMBC NMR spectrum for mandelalide B, (**2**; 700 MHz, $CDCl_3$)



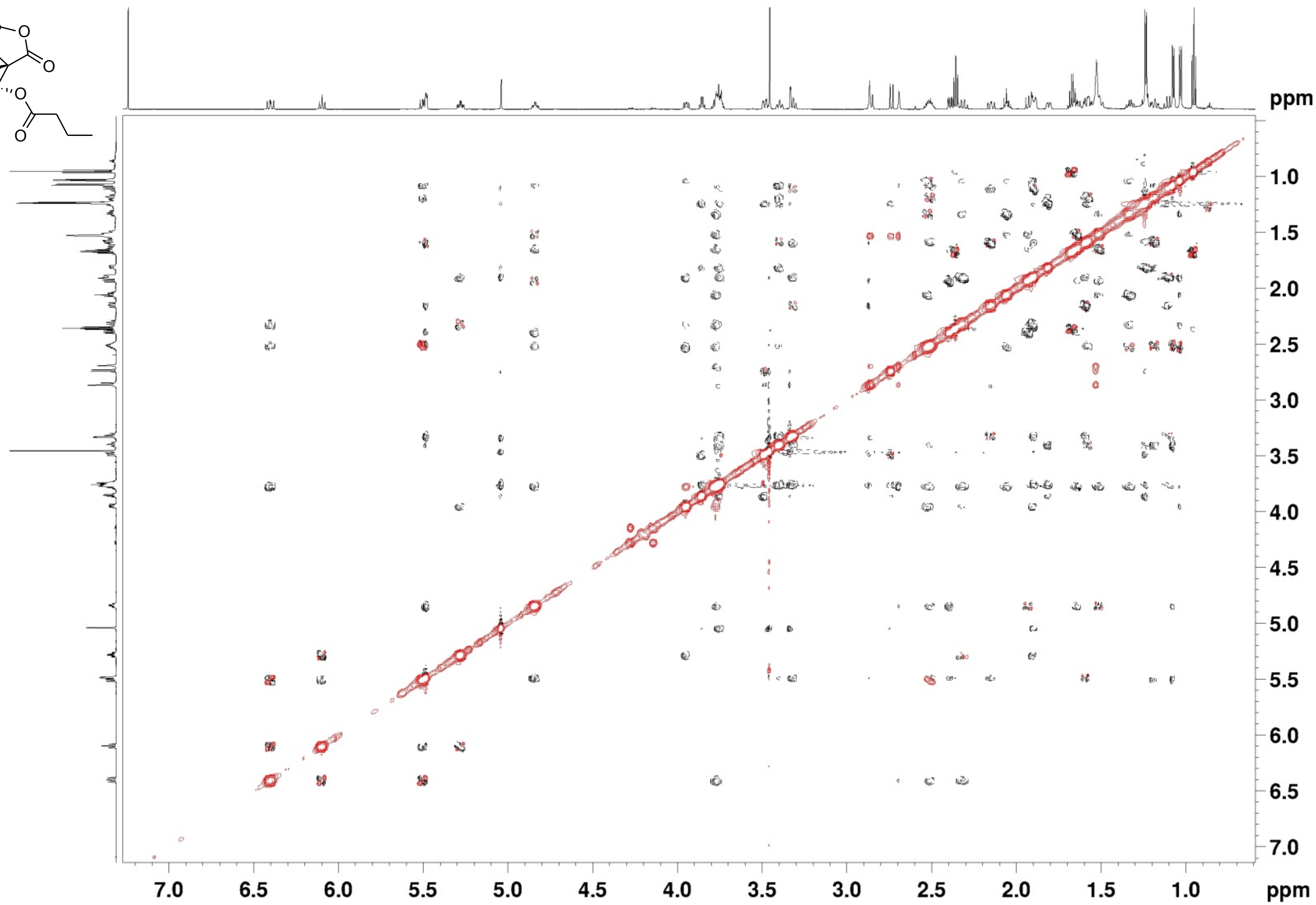
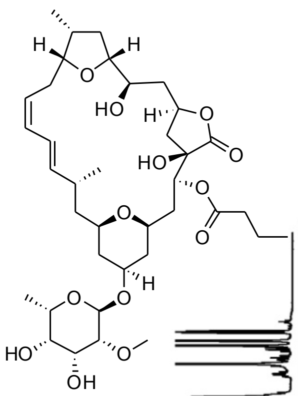


Figure S27. ROESY NMR spectrum for mandelalide B, (**2**; 700 MHz, $CDCl_3$)



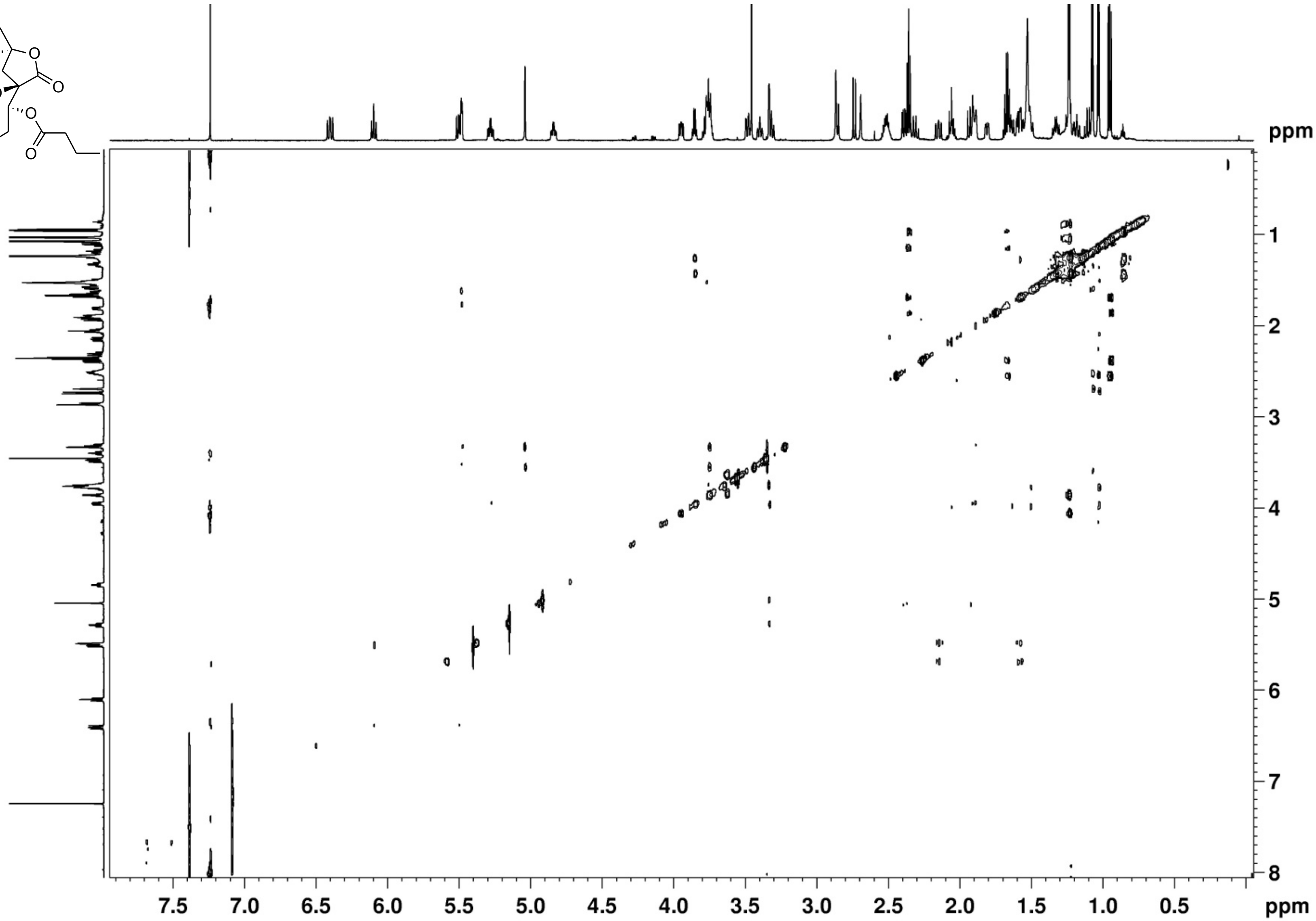


Figure S28. HETLOC NMR spectrum for mandelalide B, (**2**; 700 MHz, $CDCl_3$)

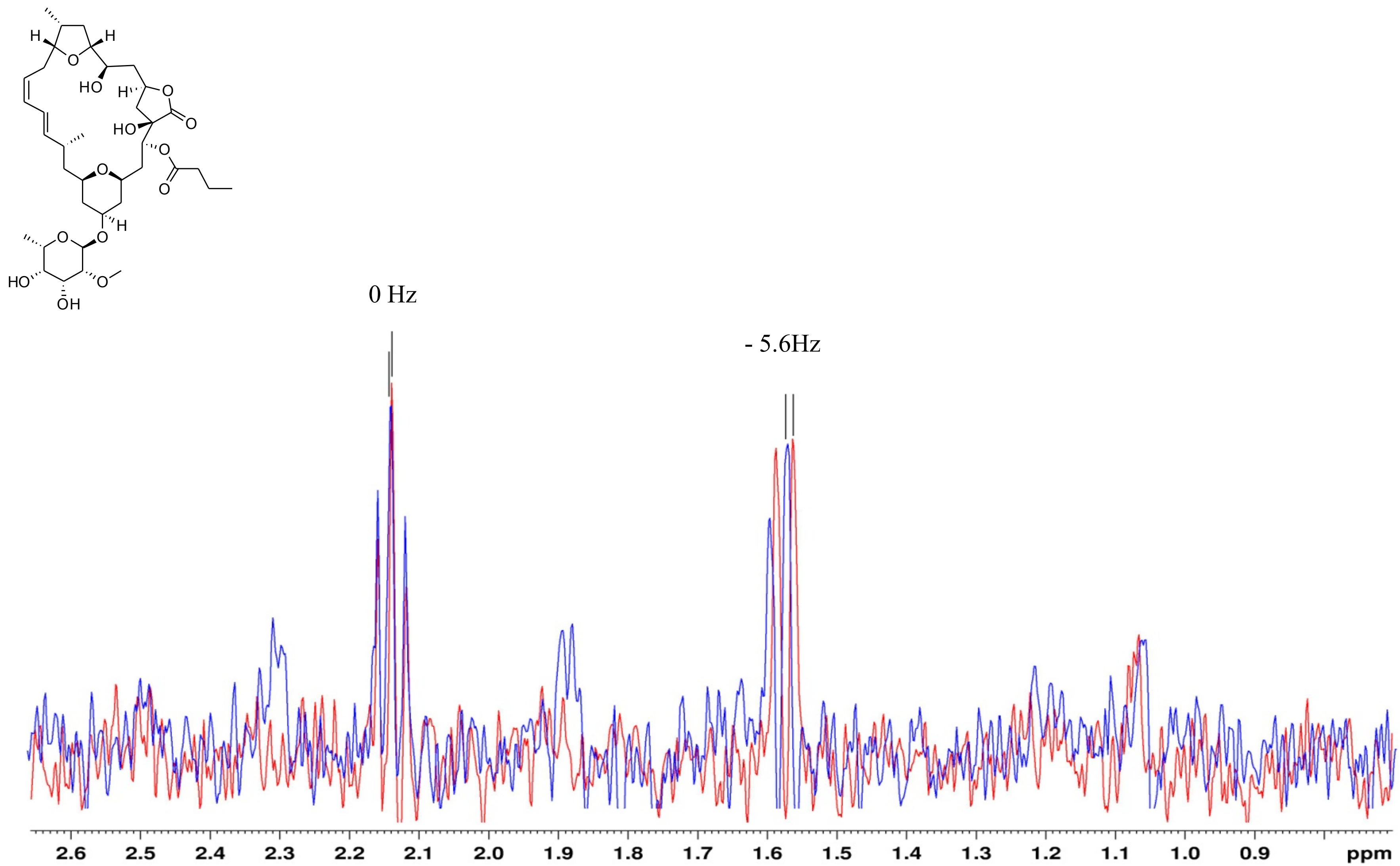


Figure S29. *F2* slice of HETLOC spectrum for C-3 of mandelalide B (**2**; 700 MHz, $CDCl_3$)

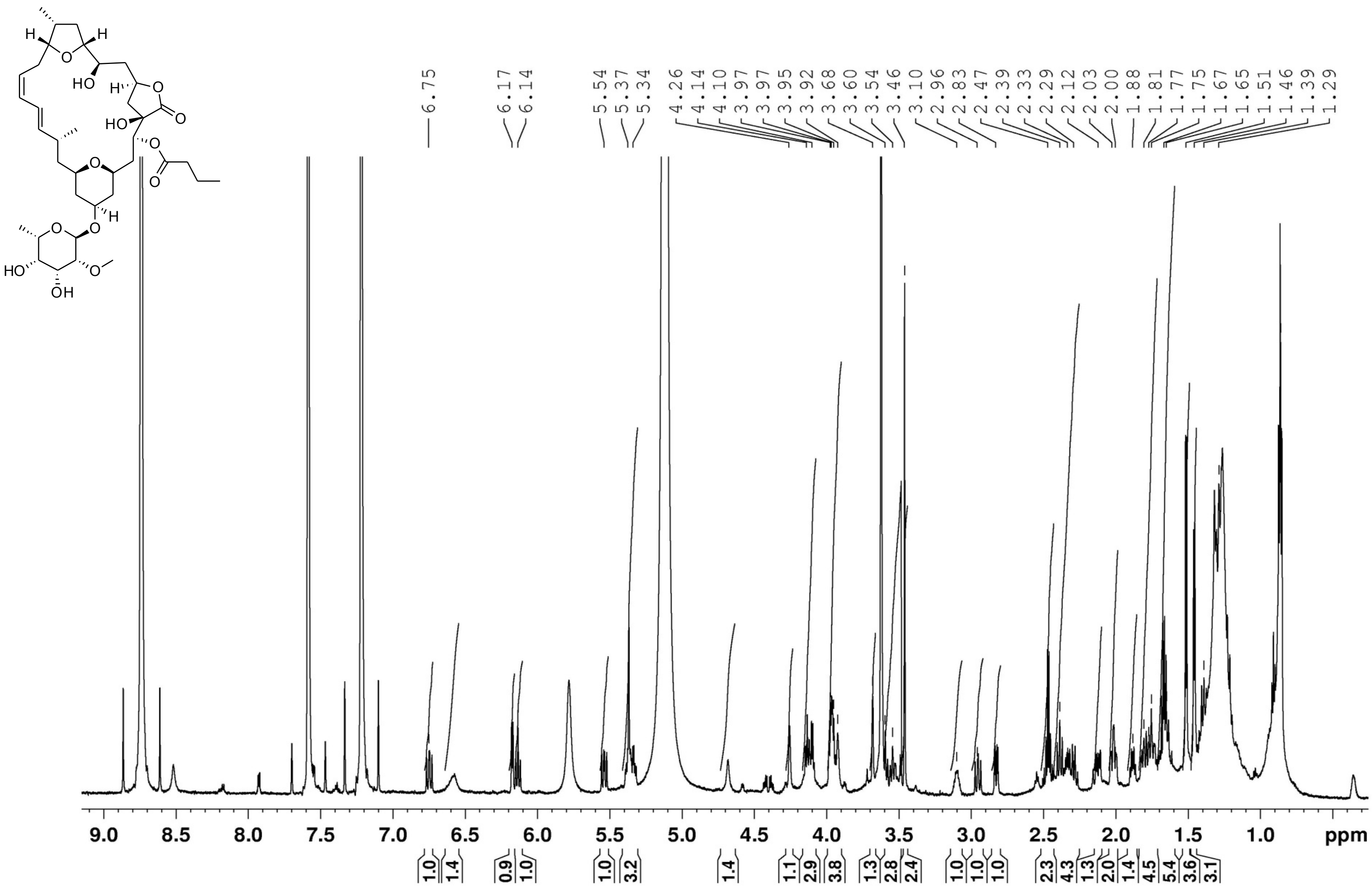


Figure S30. [1]H NMR spectrum for mandelalide B, (**2**; 700 MHz, py-d_5)

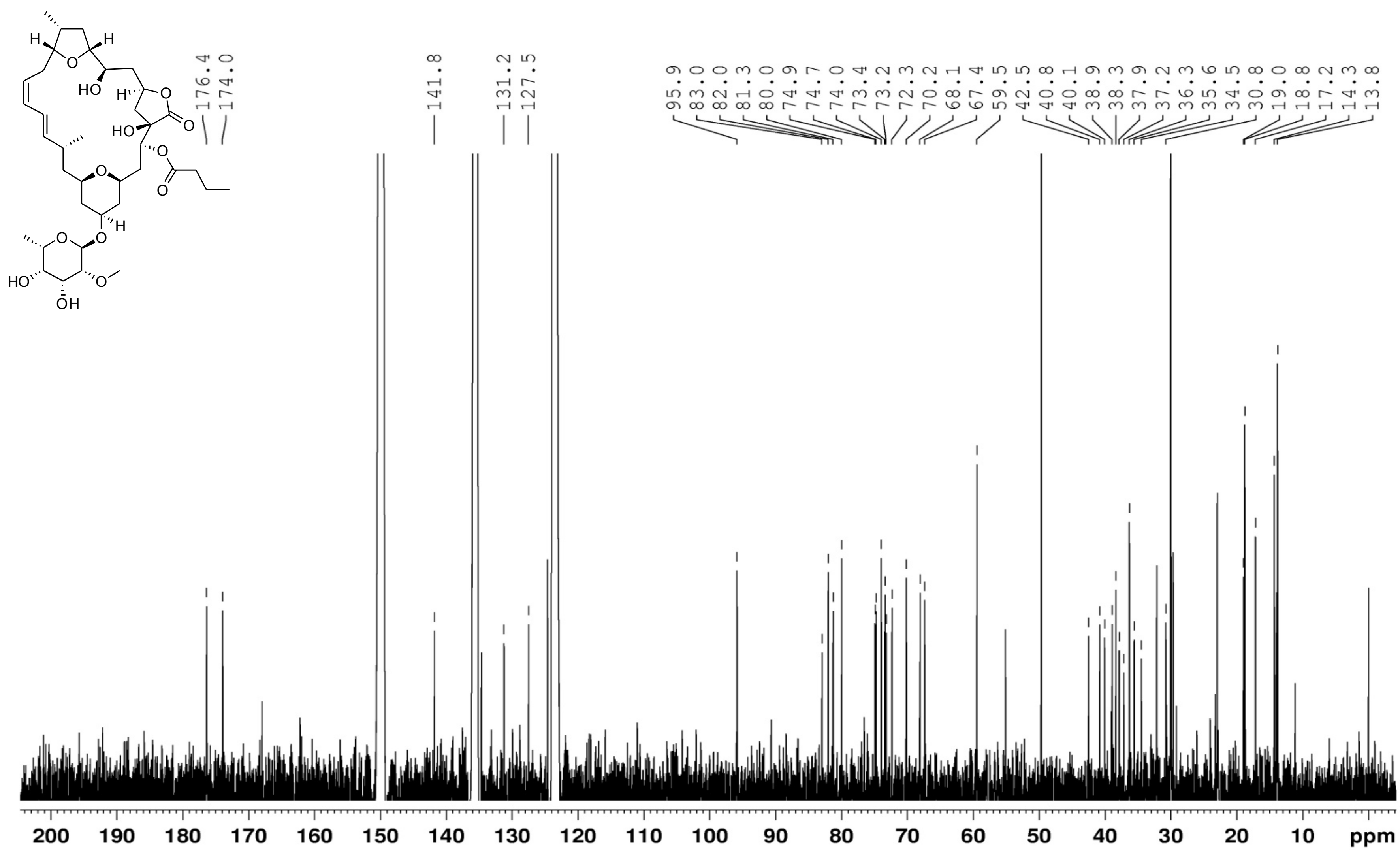


Figure S31. ^{13}C NMR spectrum for mandelalide B (**2**; 175 MHz, py-d_5)

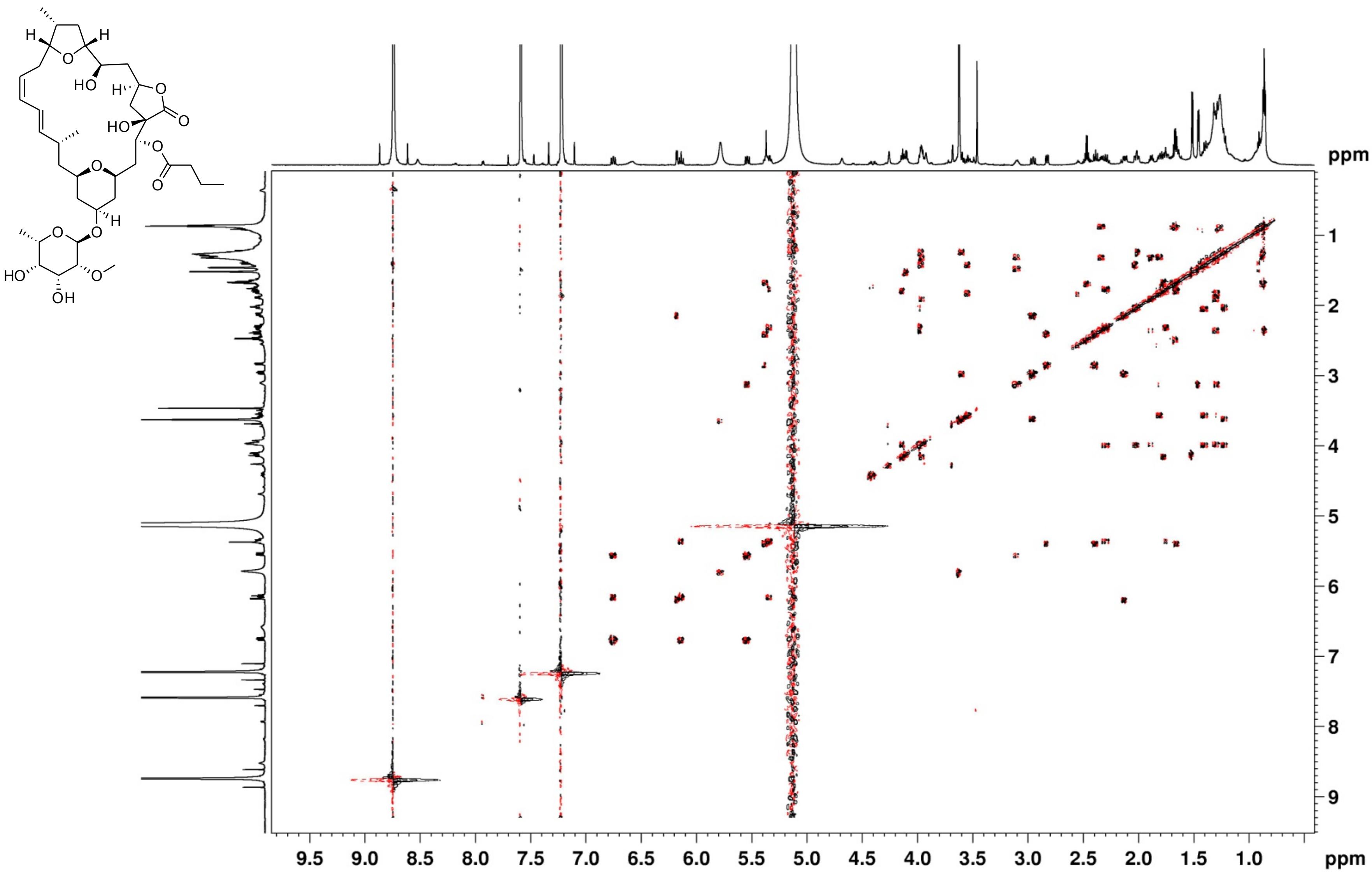


Figure S32. COSY NMR spectrum for mandelalide B (**2**; 700 MHz, py-d_5)

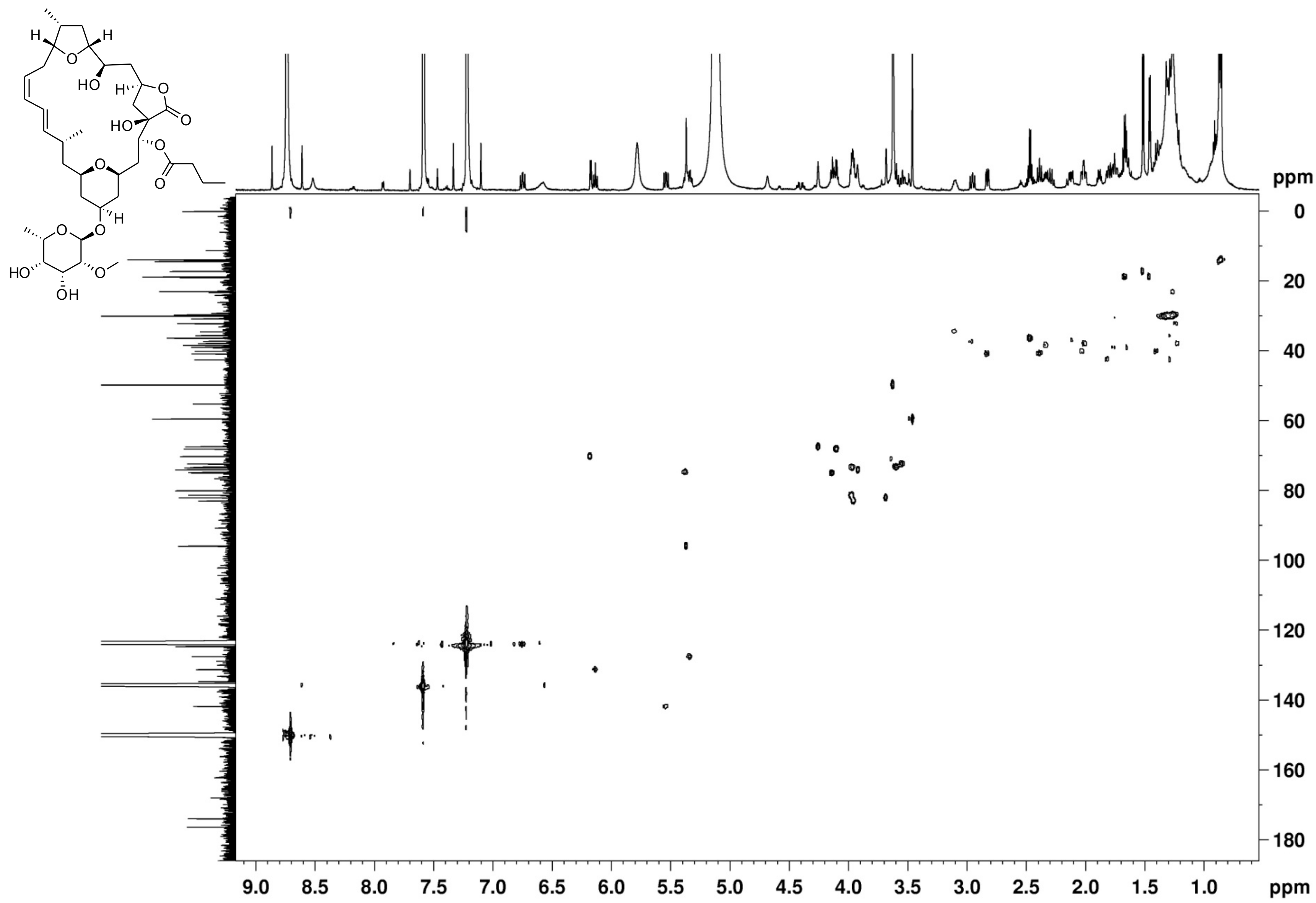


Figure S33. HSQC NMR spectrum for mandelalide B, (**2**; 700 MHz, py-d_5)

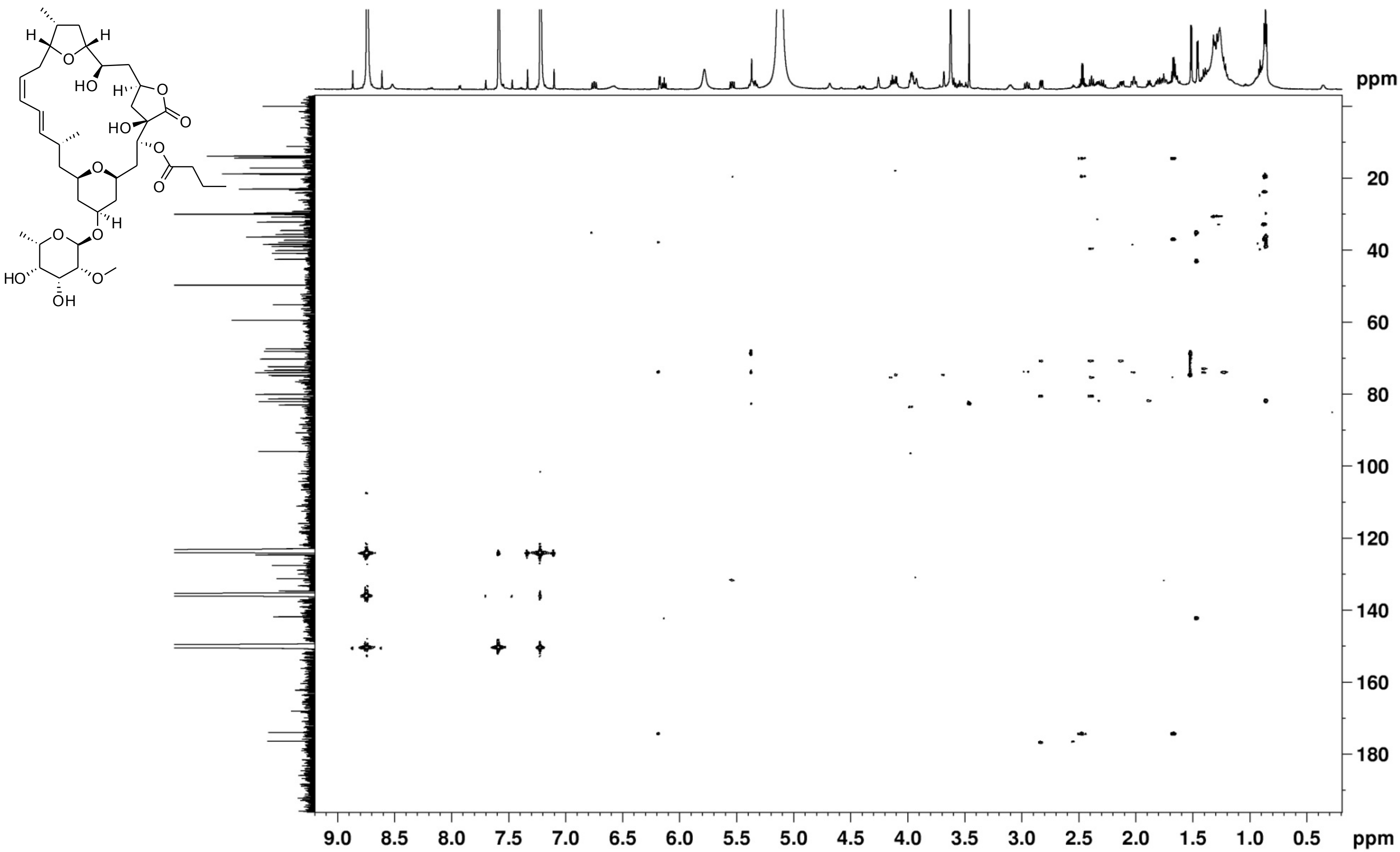
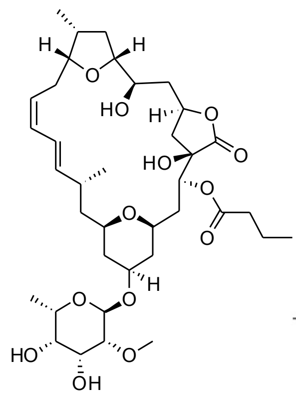


Figure S34. HMBC NMR spectrum for mandelalide B (**2**; 700 MHz, py-d_5)



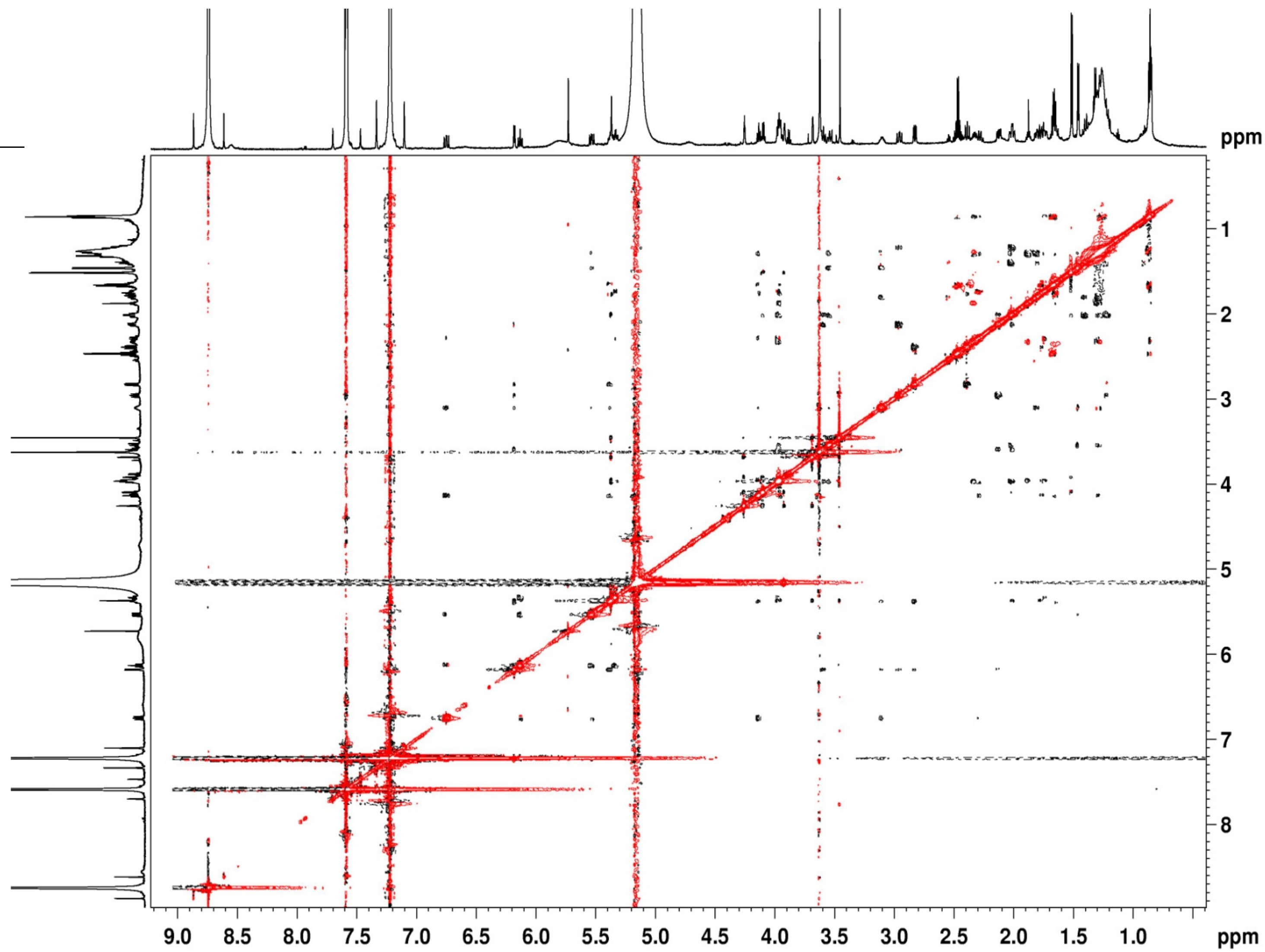


Figure S35. ROESY NMR spectrum for mandelalide B (**2**), spinlock mixing time 400 ms, (700 MHz, py-d_5)

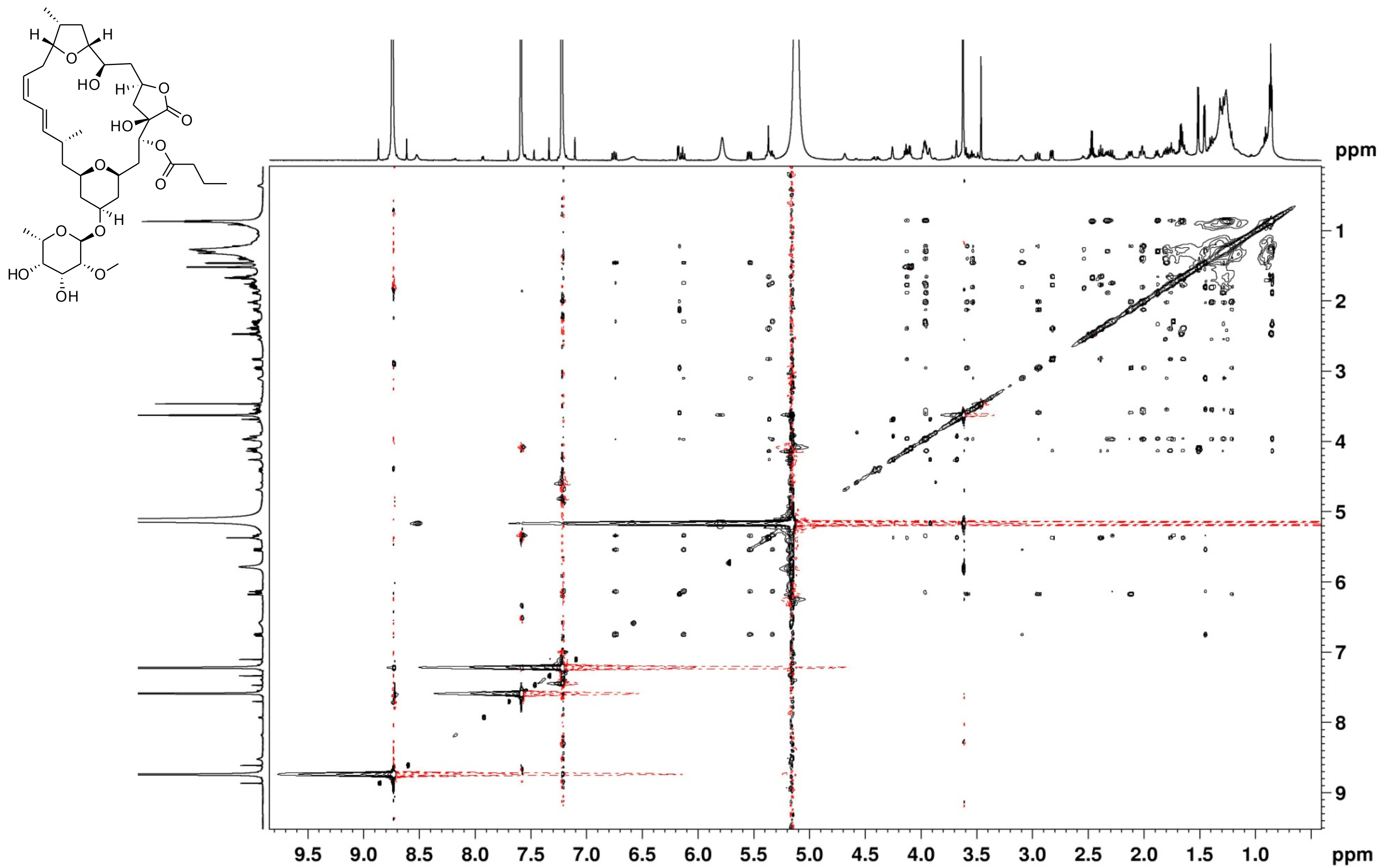


Figure S36. TOCSY NMR spectrum for mandelalide B, (**2**; 700 MHz, py-d_5)

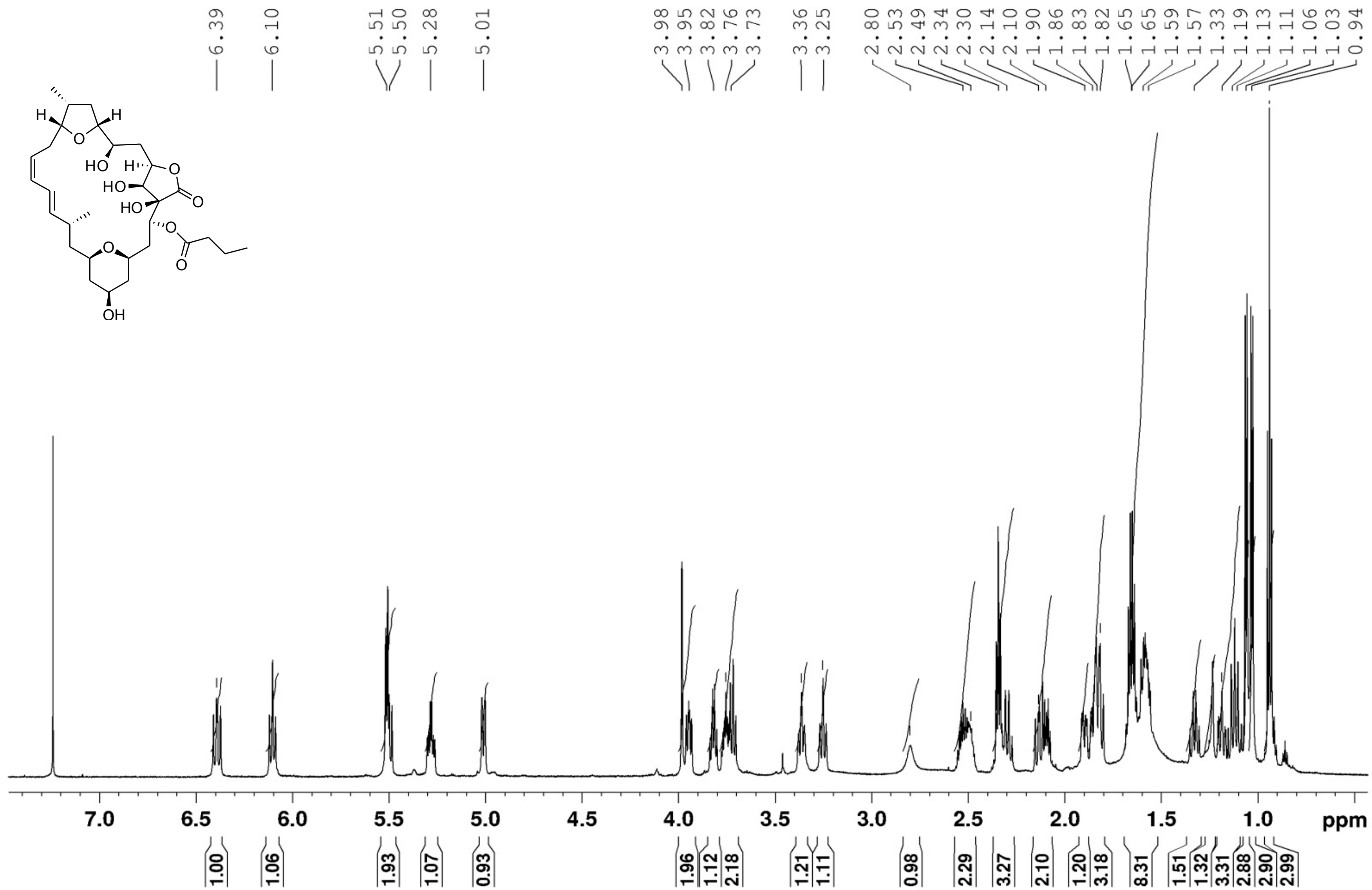


Figure S37. [1]H NMR spectrum for mandelalide C (**3**; 700 MHz, $CDCl_3$)

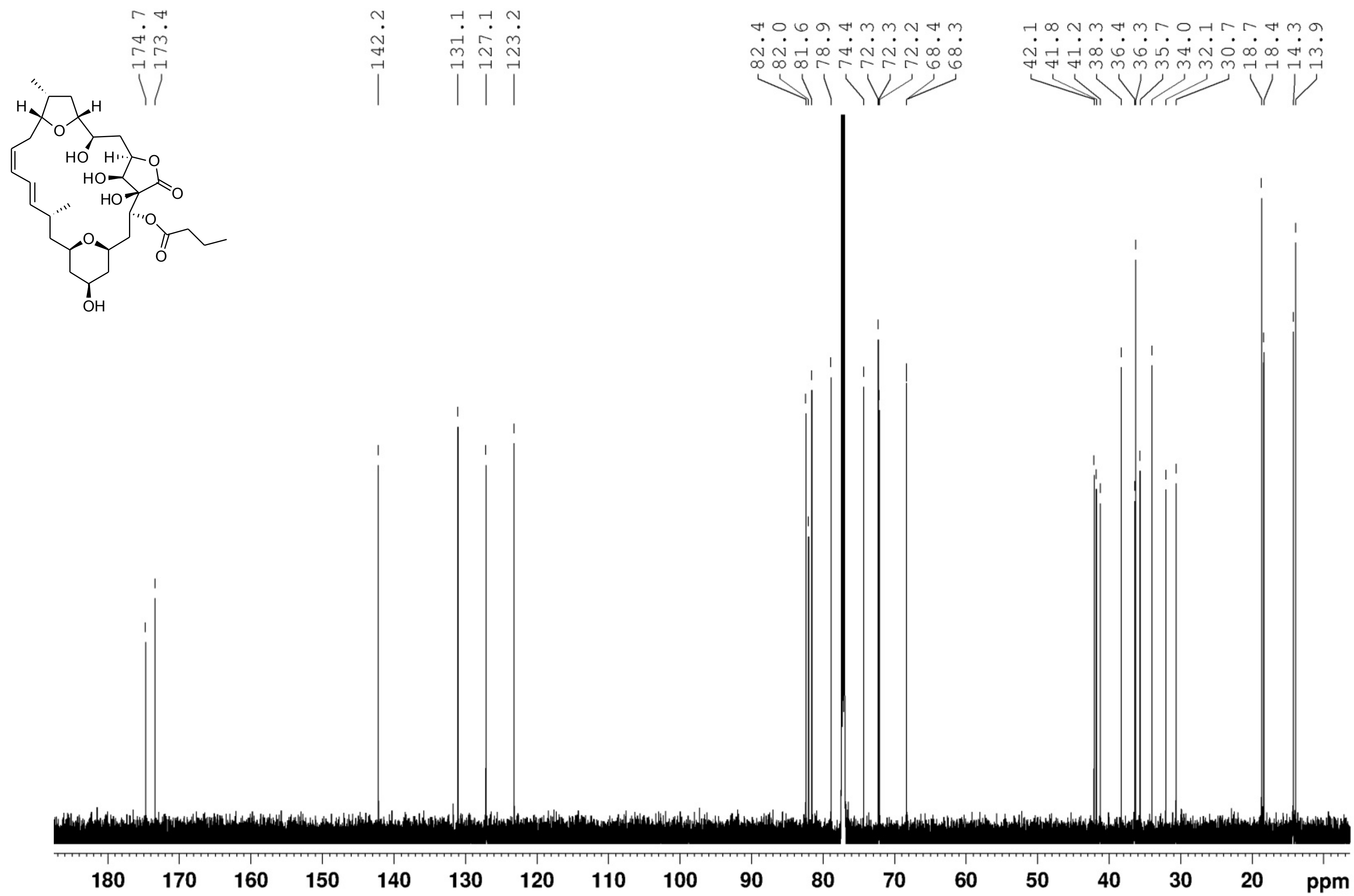


Figure S38. ^{13}C NMR spectrum for mandelalide C (**3**; 175 MHz, $CDCl_3$)

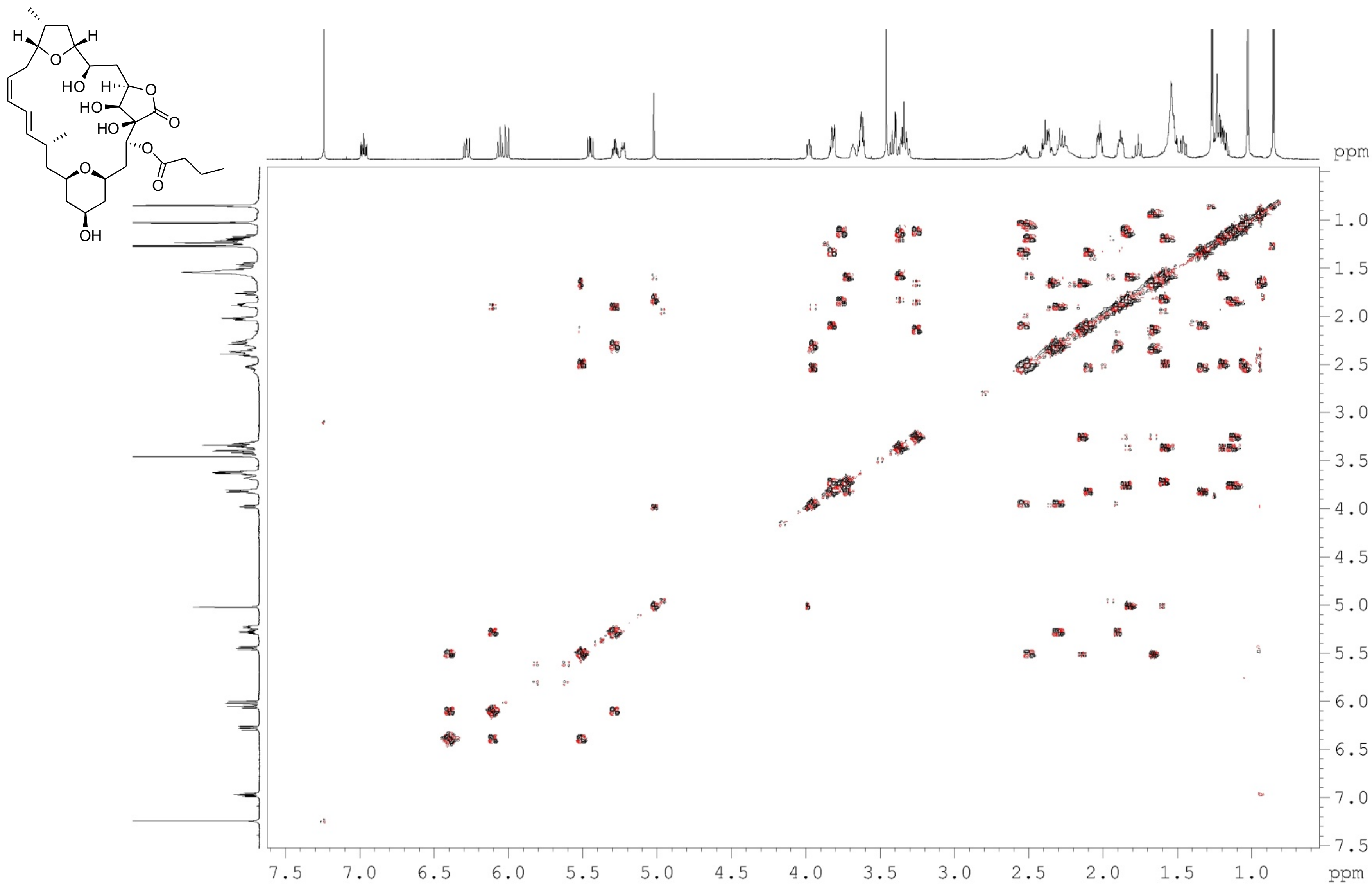


Figure S39. COSY NMR spectrum for mandelalide C (**3**; 700 MHz, $CDCl_3$)

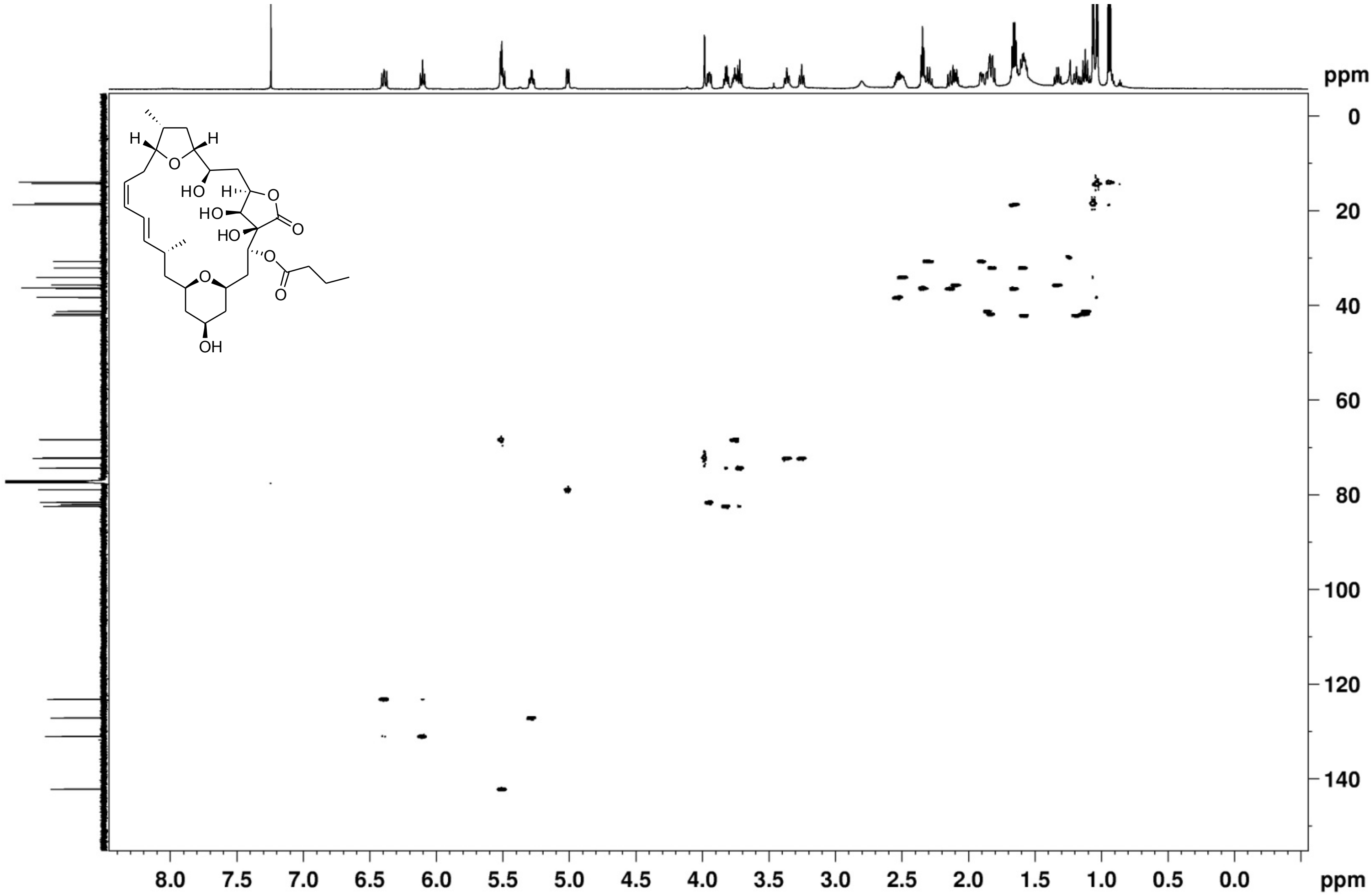


Figure S40. HSQC NMR spectrum for mandelalide C (**3**; 700 MHz, $CDCl_3$)

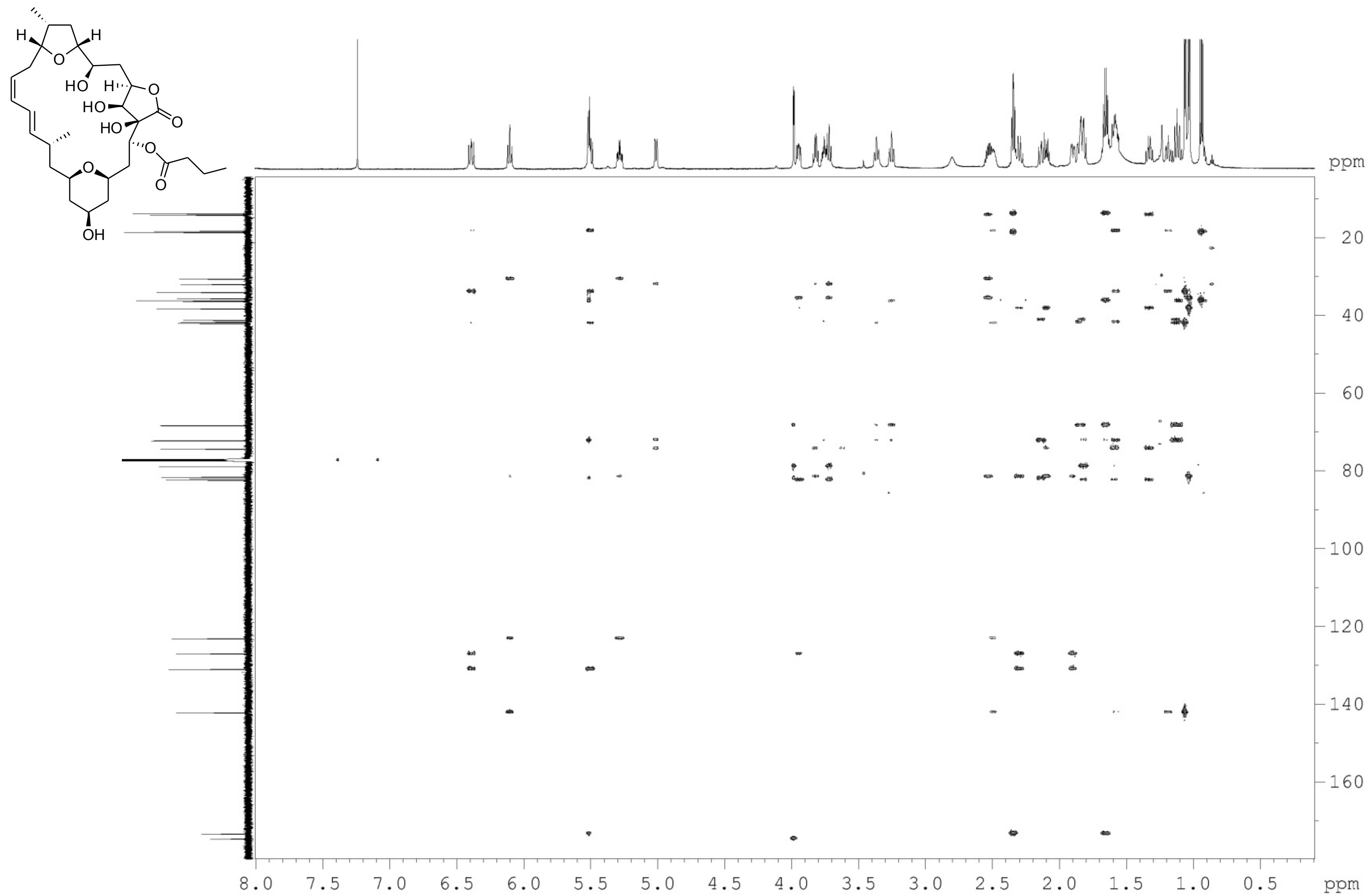


Figure S41. HMBC NMR spectrum for mandelalide C (**3**; 700 MHz, $CDCl_3$)

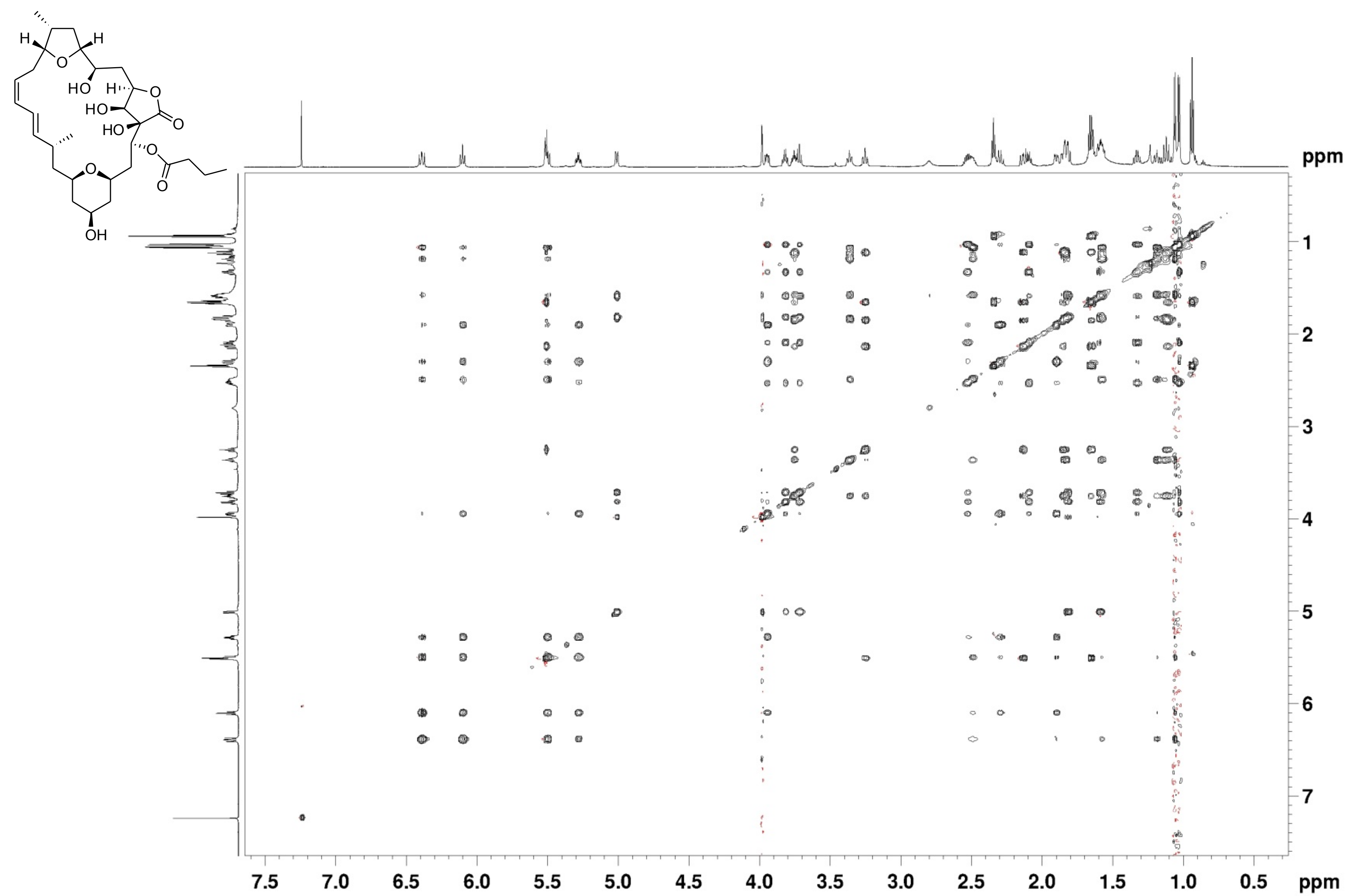


Figure S42. TOCSY NMR spectrum for mandelalide C (**3**; 700 MHz, $CDCl_3$)

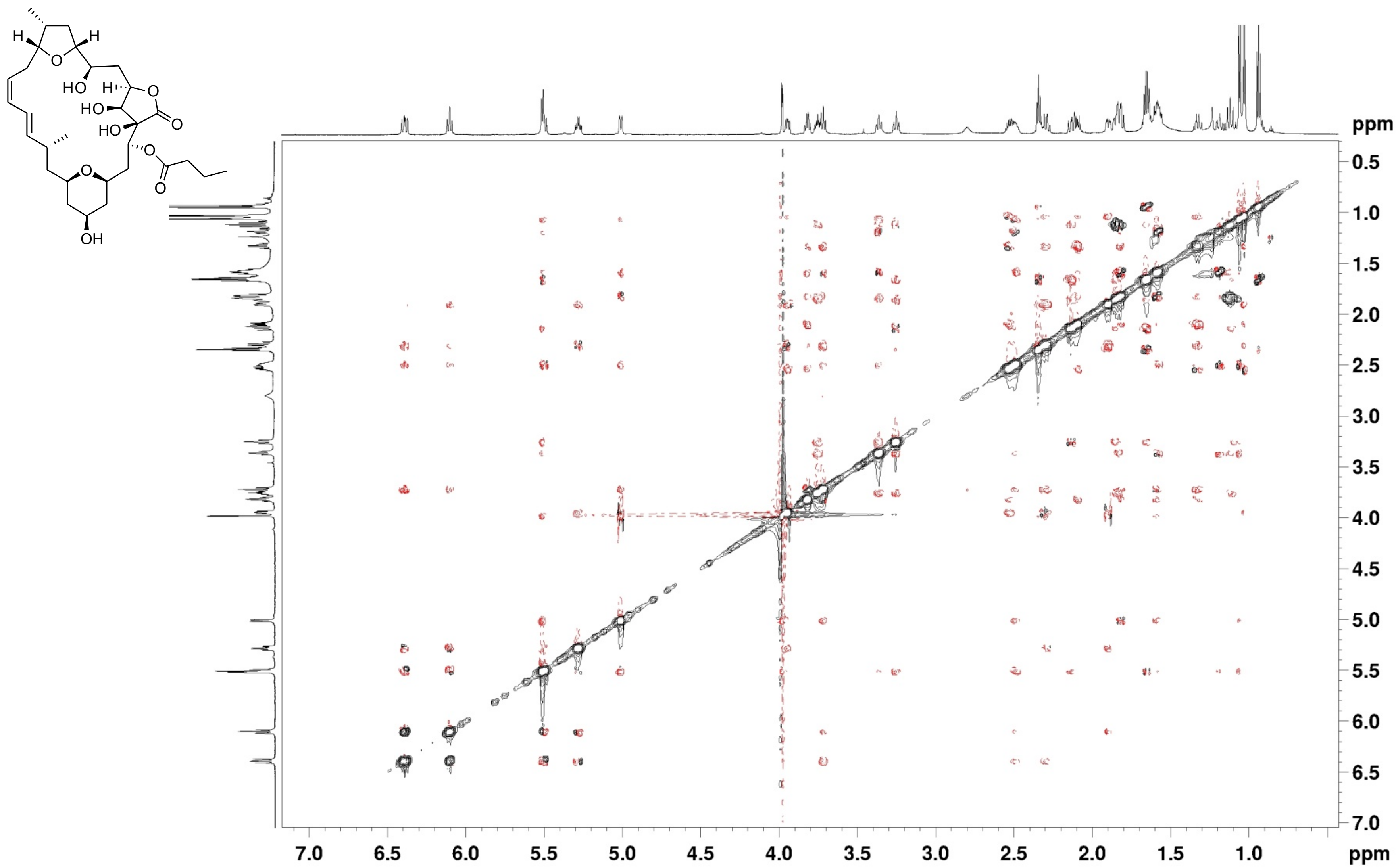


Figure S43. ROESY NMR spectrum for mandelalide C (**3**; 700 MHz, $CDCl_3$)

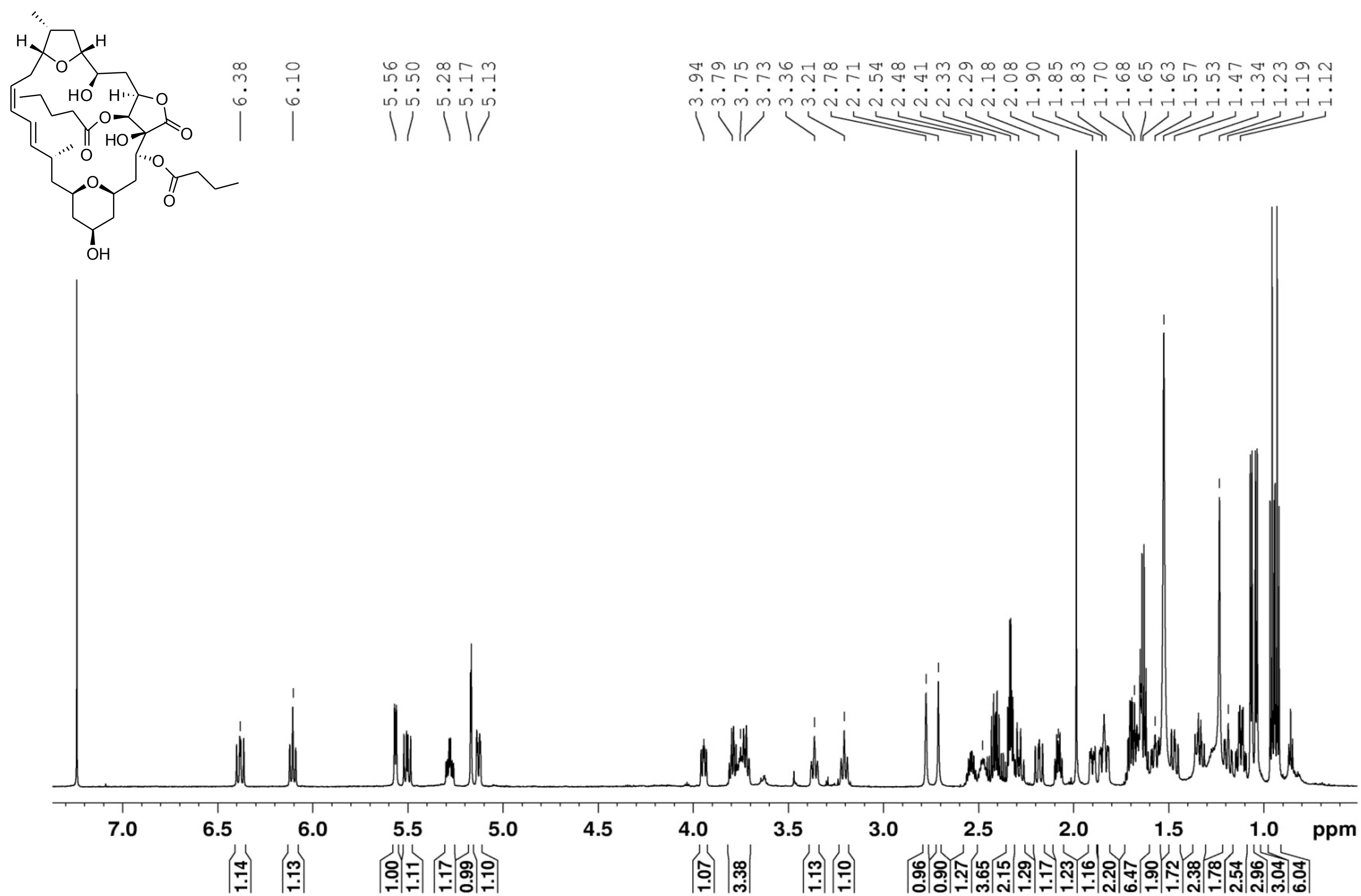


Figure S44. ^{1}H NMR spectrum for mandelalide D (**4**; 700 MHz, $CDCl_3$)

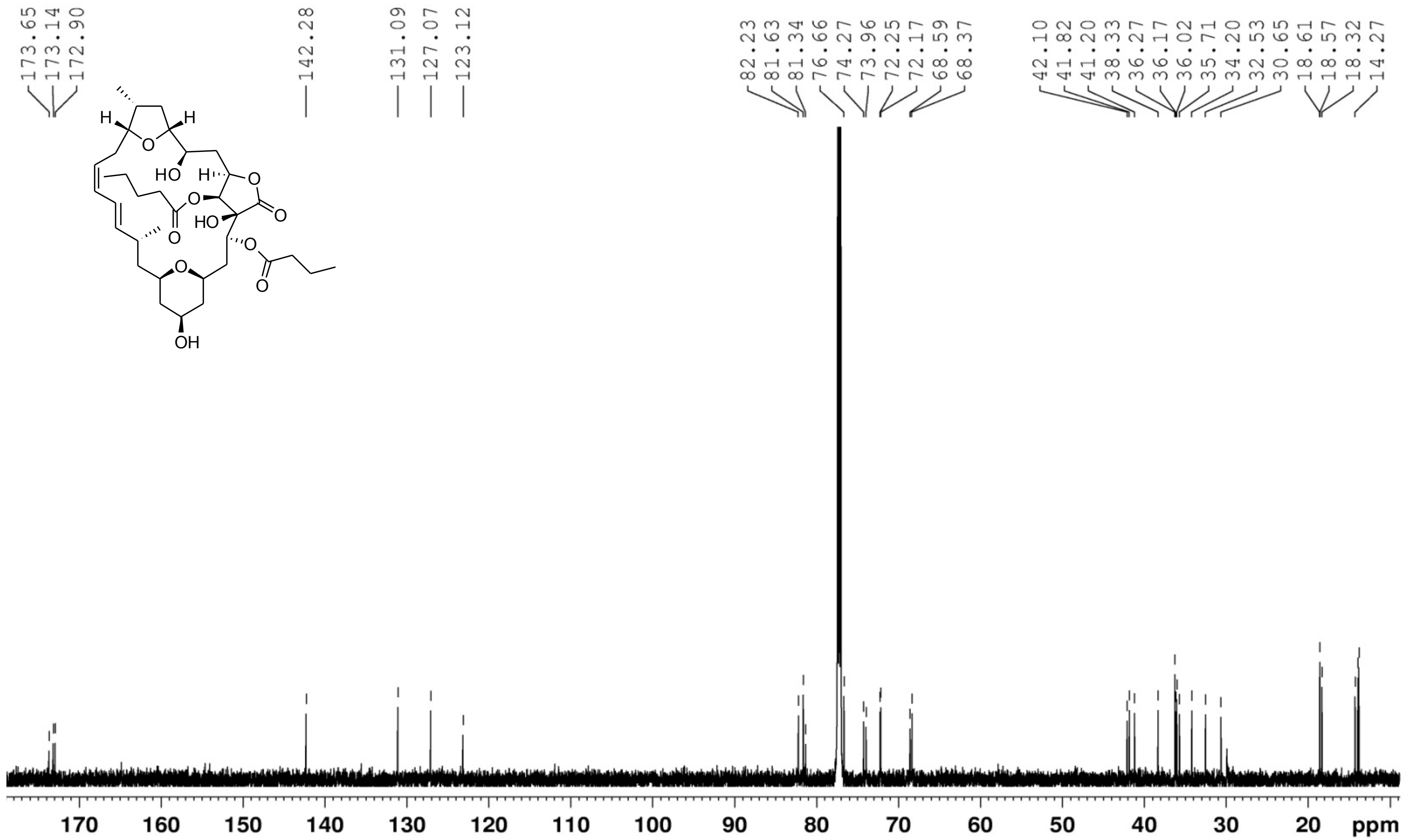


Figure S45. ^{13}C NMR spectrum for mandelalide D (**4**; 175 MHz, $CDCl_3$)

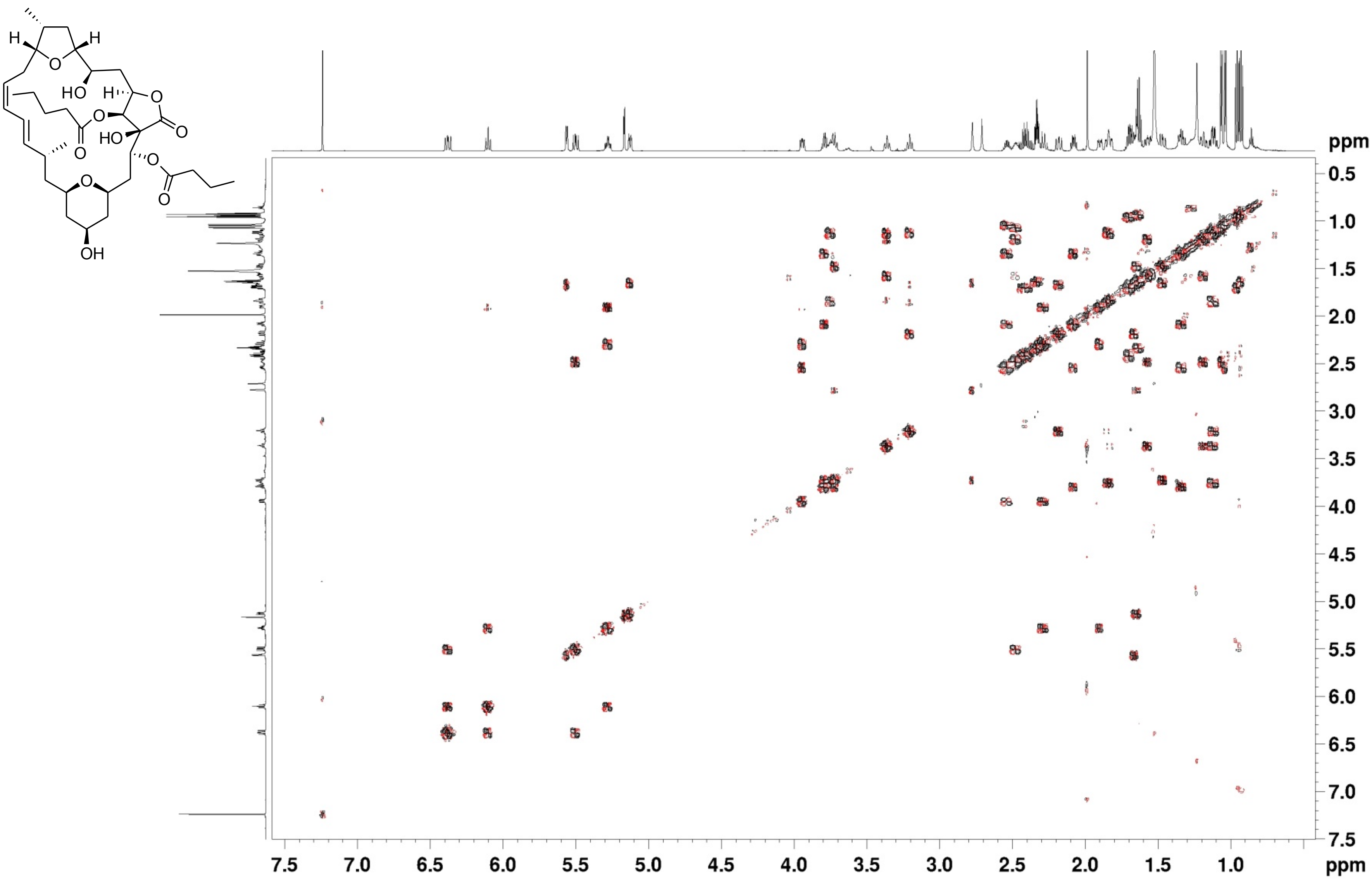


Figure S46. COSY NMR spectrum for mandelalide D (**4**; 700 MHz, $CDCl_3$)

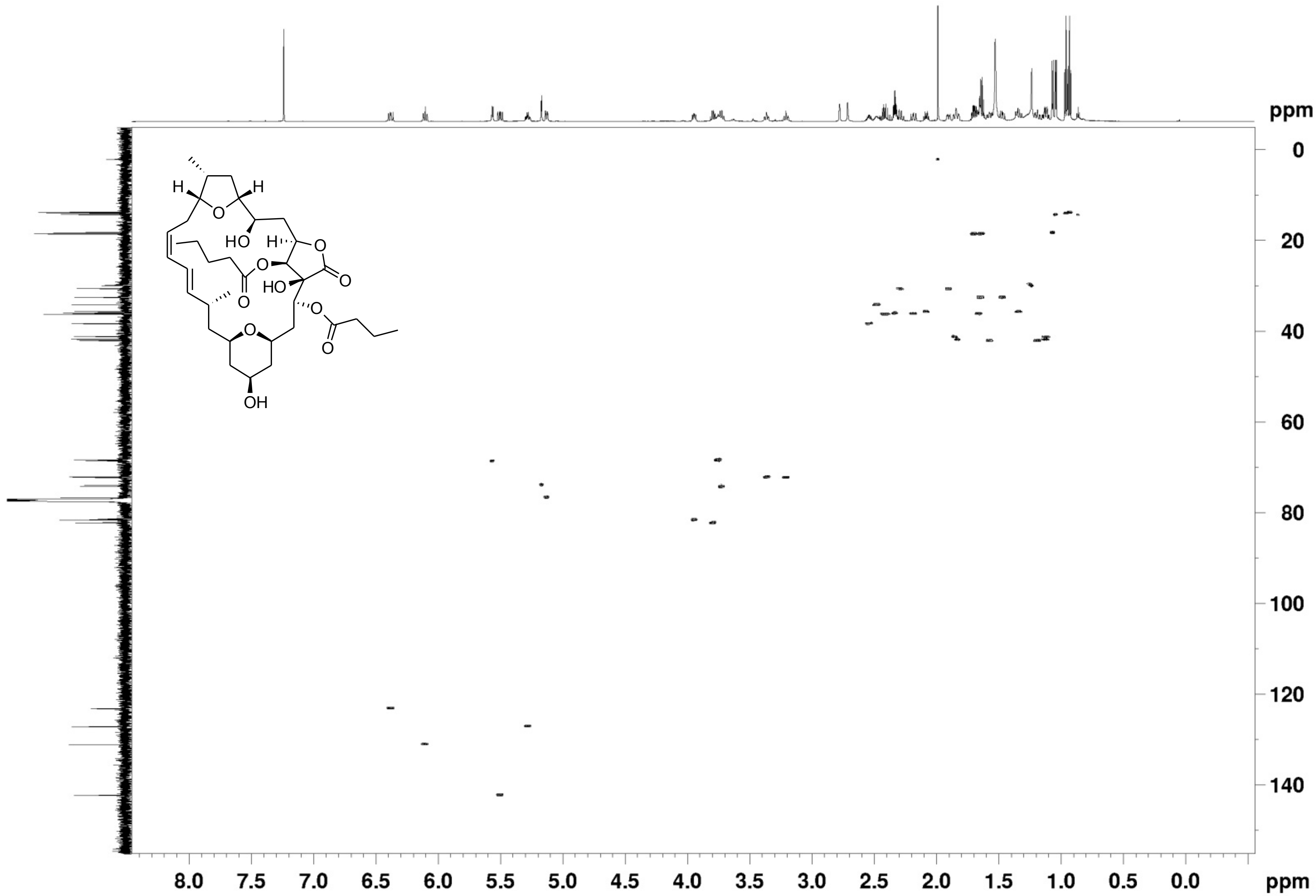


Figure S47. HSQC NMR spectrum for mandelalide D (**4**; 700 MHz, $CDCl_3$)

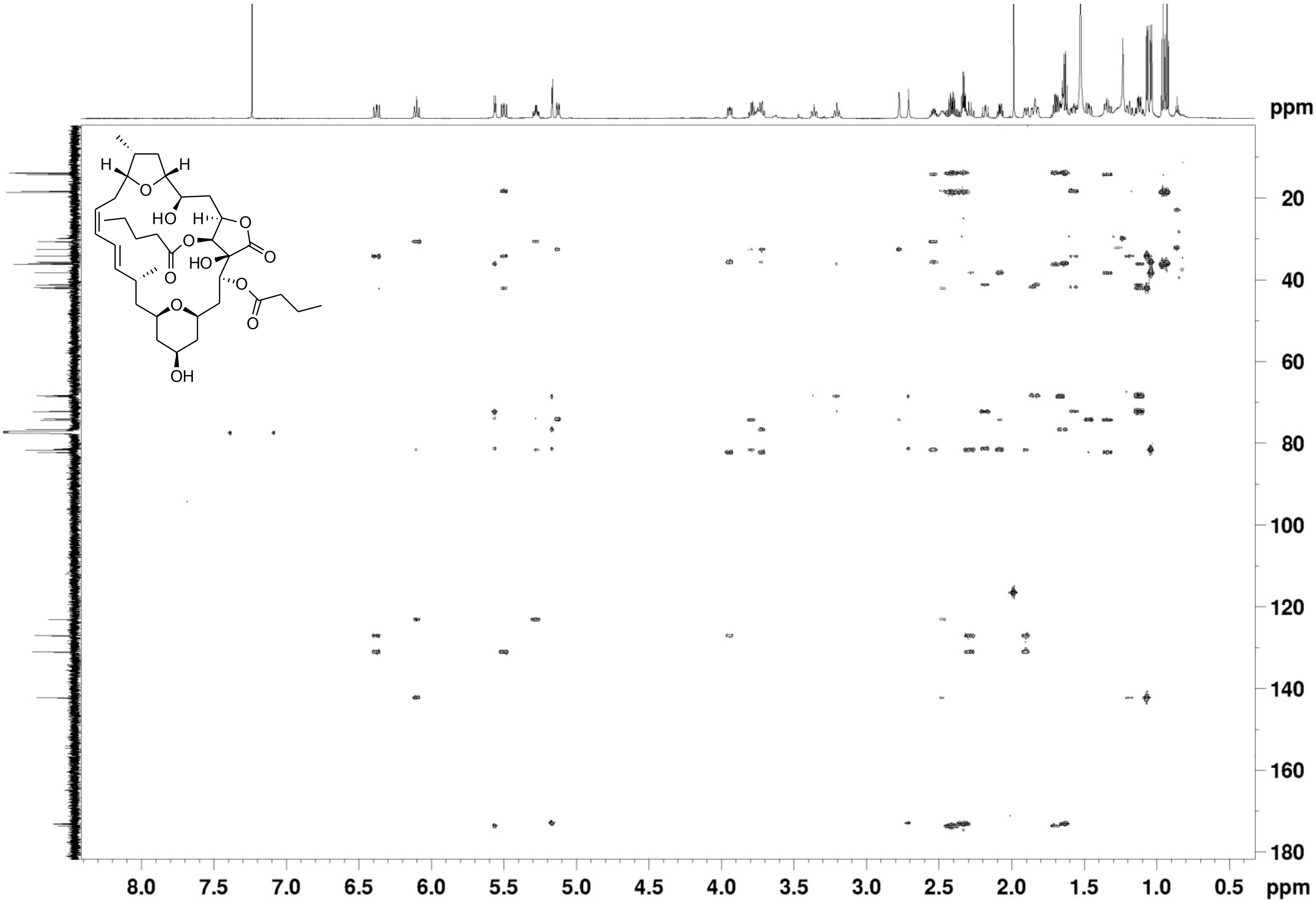
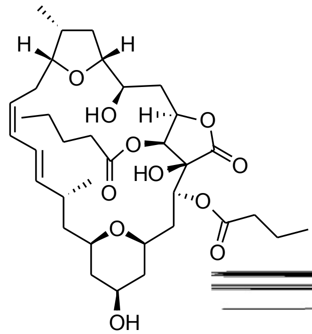


Figure S48. HMBC NMR spectrum for mandelalide D (**4**; 700 MHz, $CDCl_3$)



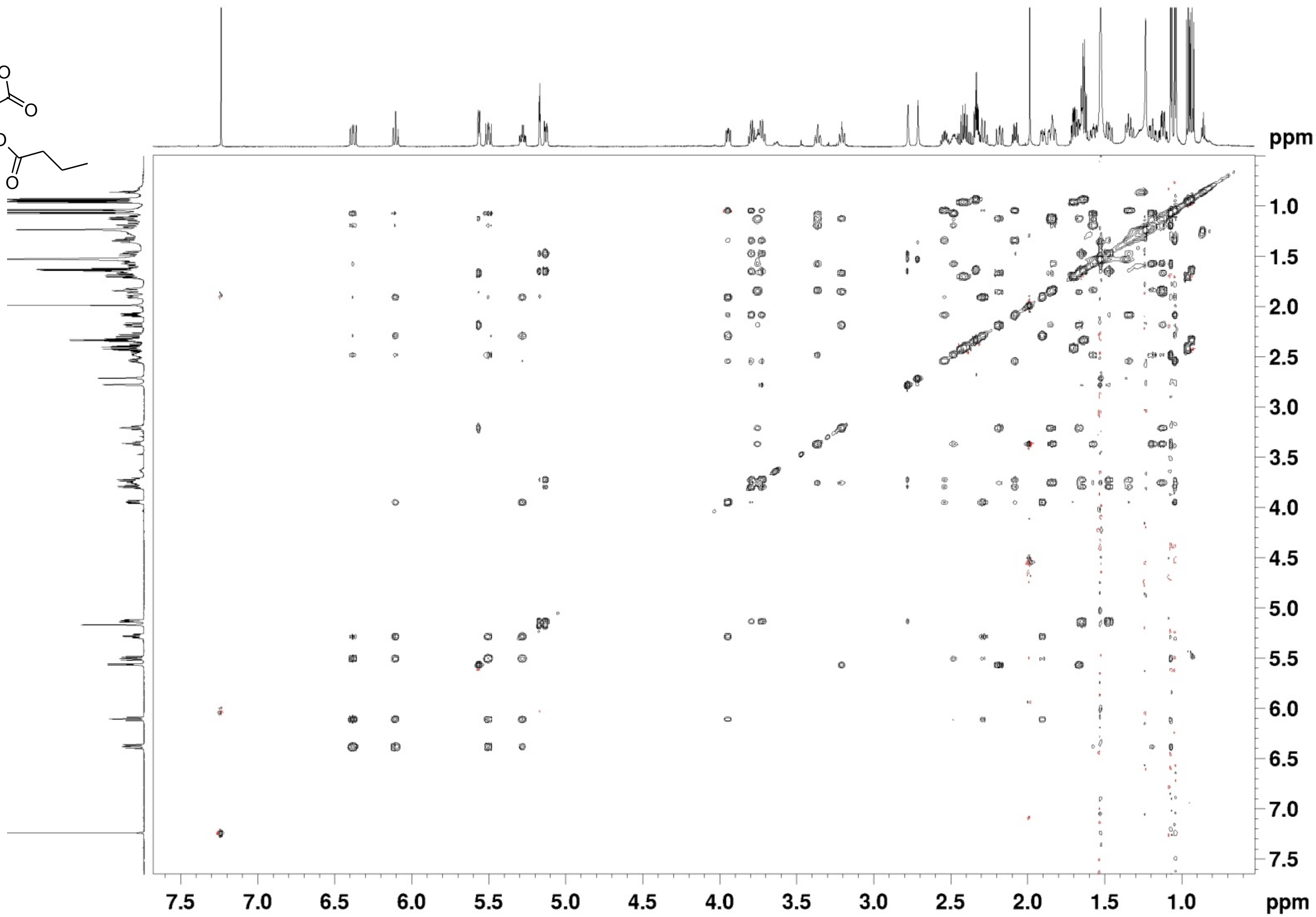


Figure S49. TOCSY NMR spectrum for mandelalide D (**4**; 700 MHz, $CDCl_3$)

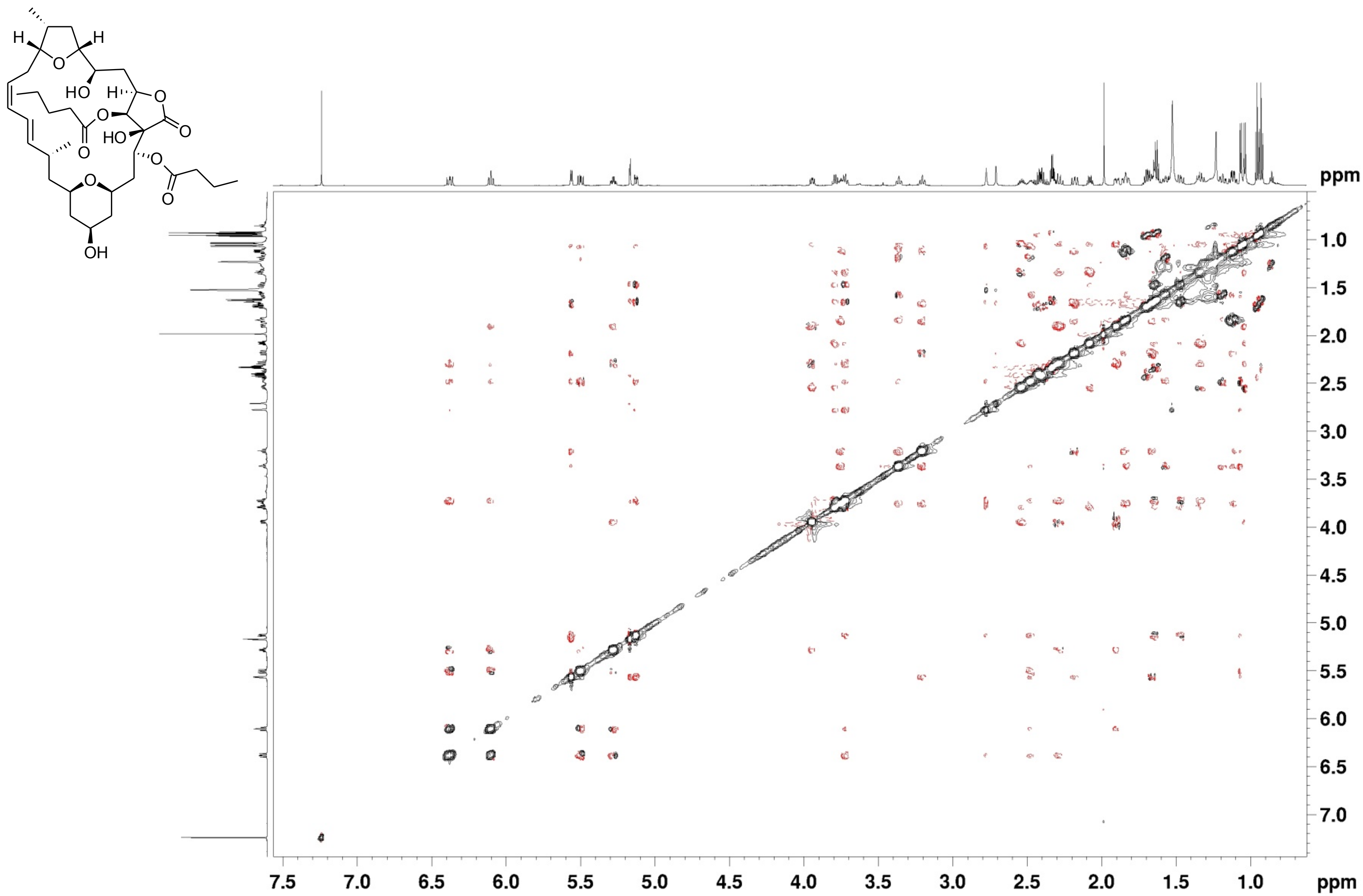


Figure S50. ROESY NMR spectrum for mandelalide D (**4**; 700 MHz, $CDCl_3$)

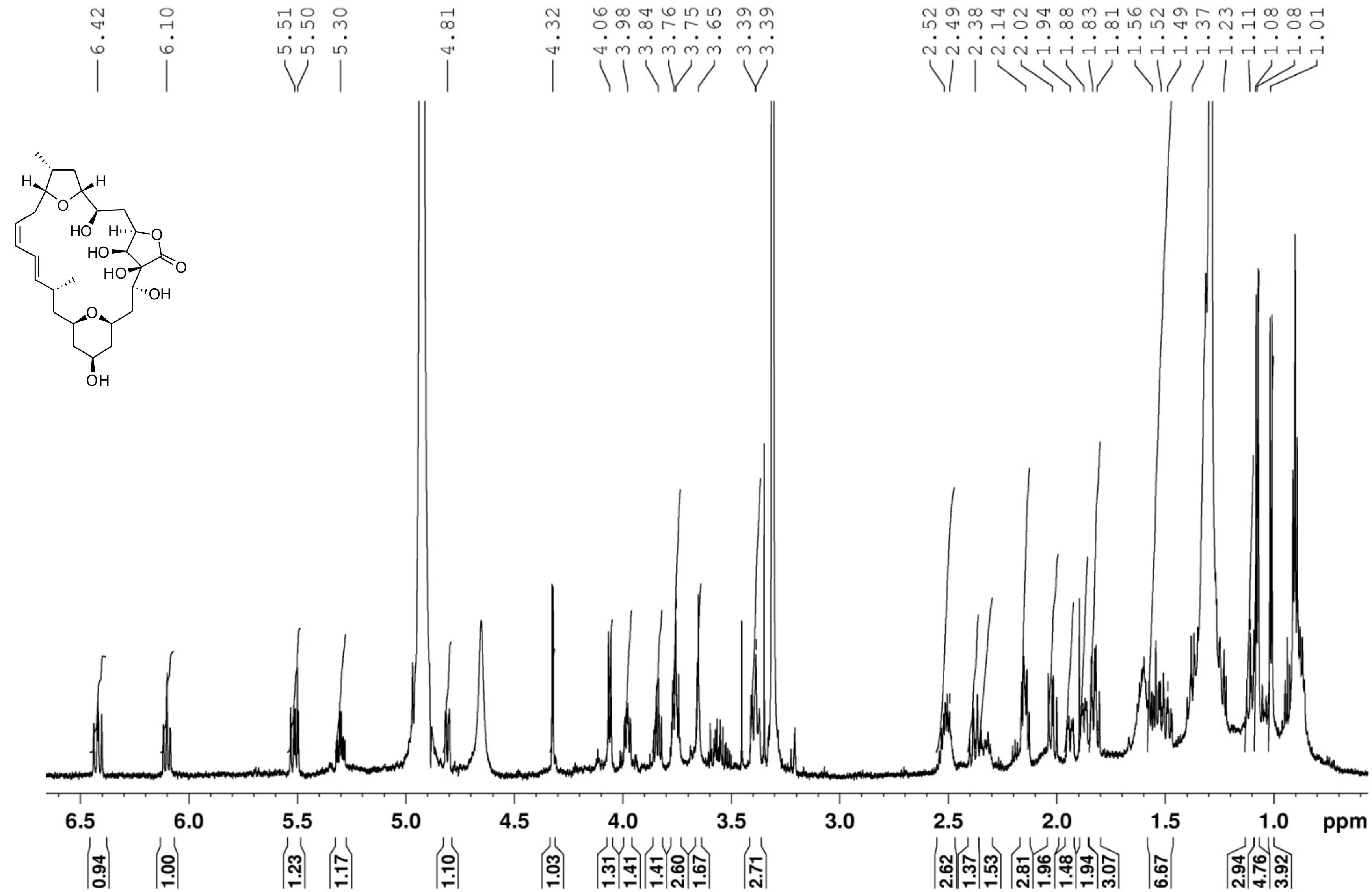


Figure S51. ^{1}H NMR spectrum for deacylmandelalide D (**4b**; 700 MHz, MeOD)

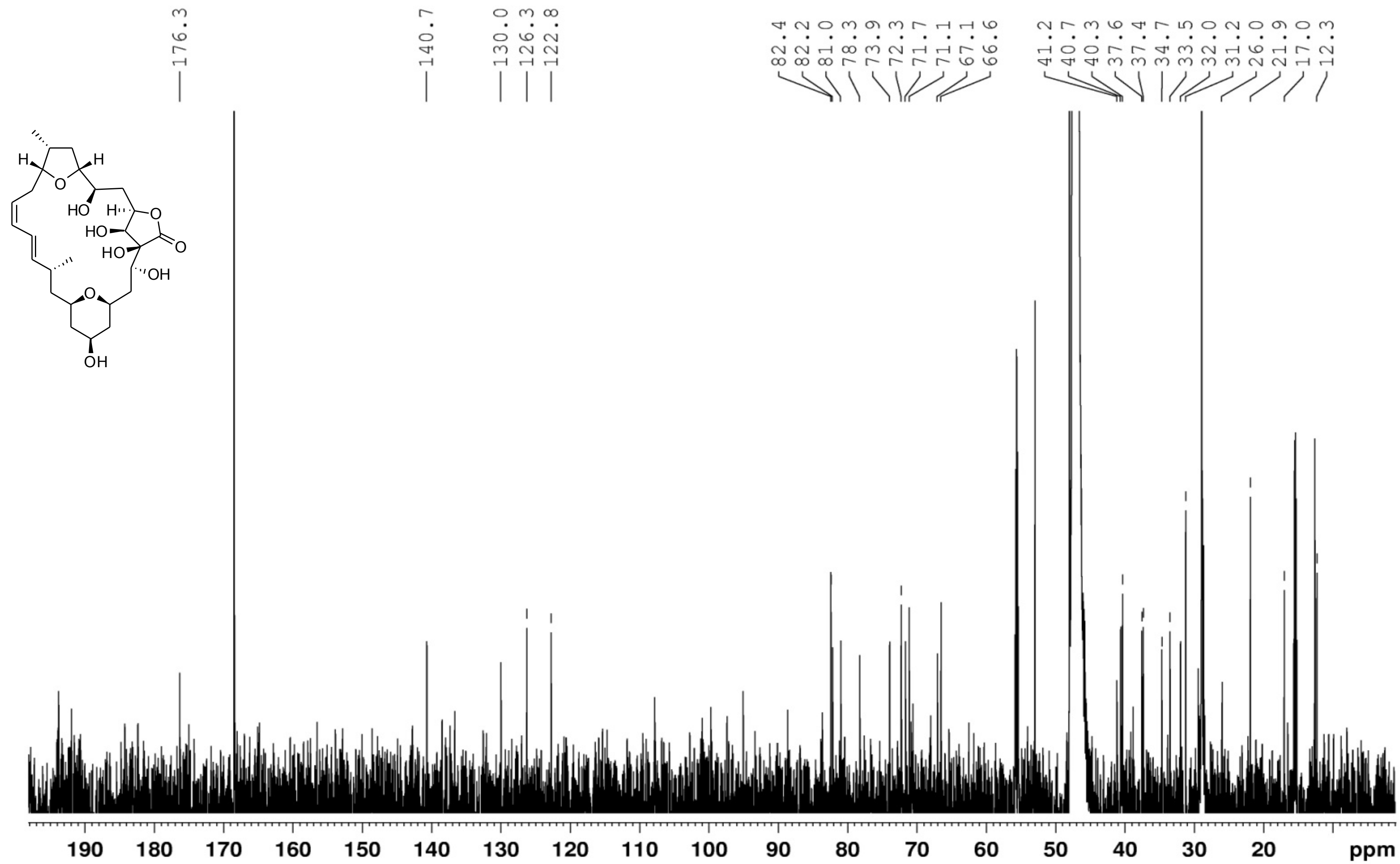
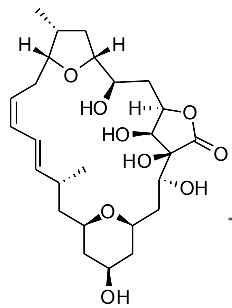


Figure S52. ^{13}C NMR spectrum for deacylmandelalide D (**4b**; 175 MHz, MeOD)



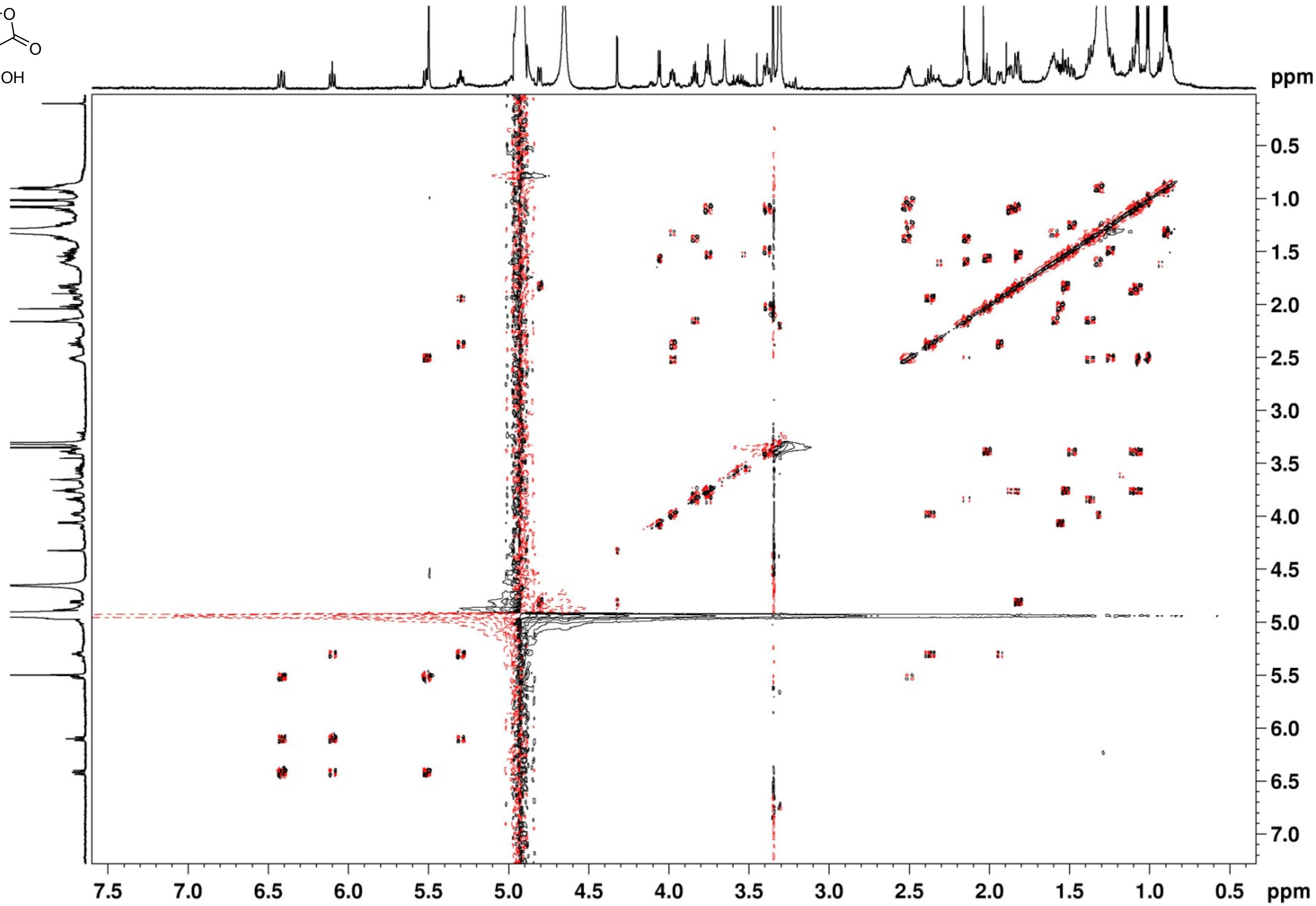
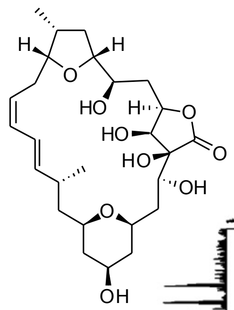


Figure S53. COSY NMR spectrum for deacylmandelalide D (**4b**; 700 MHz, MeOD)



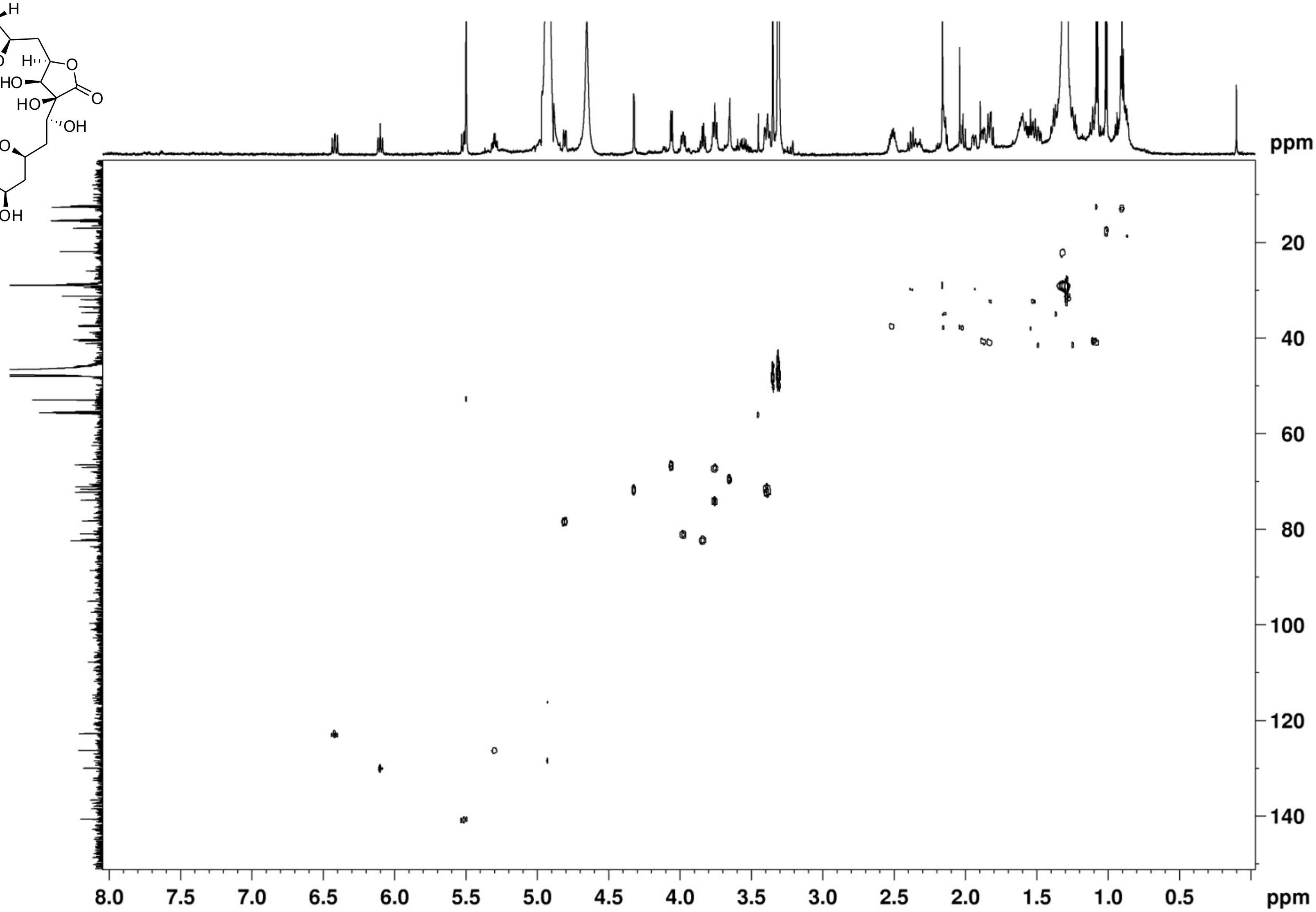
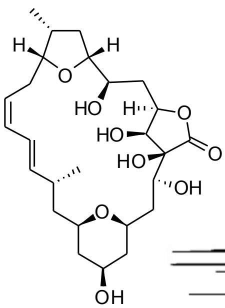


Figure S54. HSQC NMR spectrum for deacylmandelalide D (**4b**; 700 MHz, MeOD)



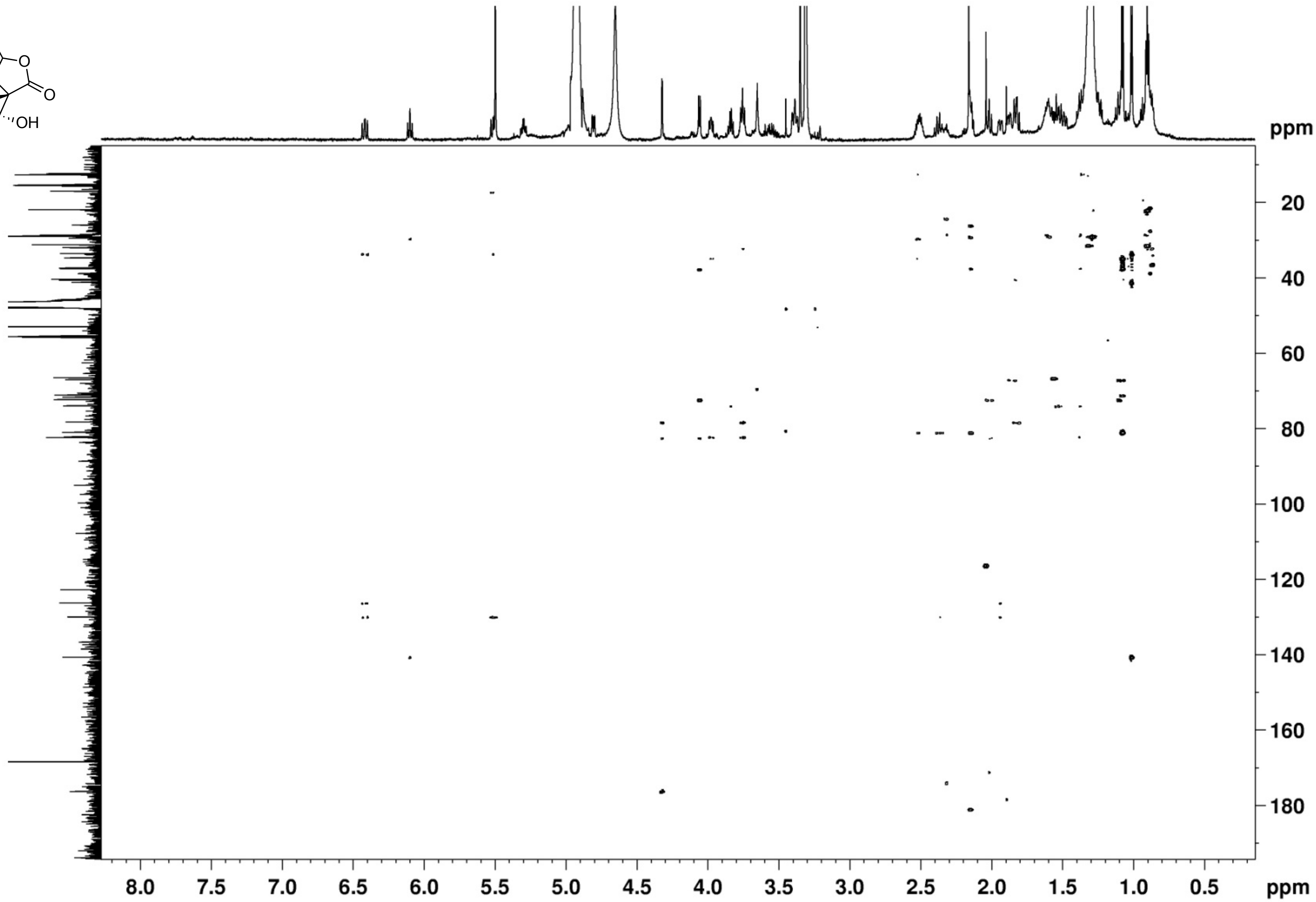


Figure S55. HMBC NMR spectrum for deacylmandelalide D (**4b**; 700 MHz, MeOH)

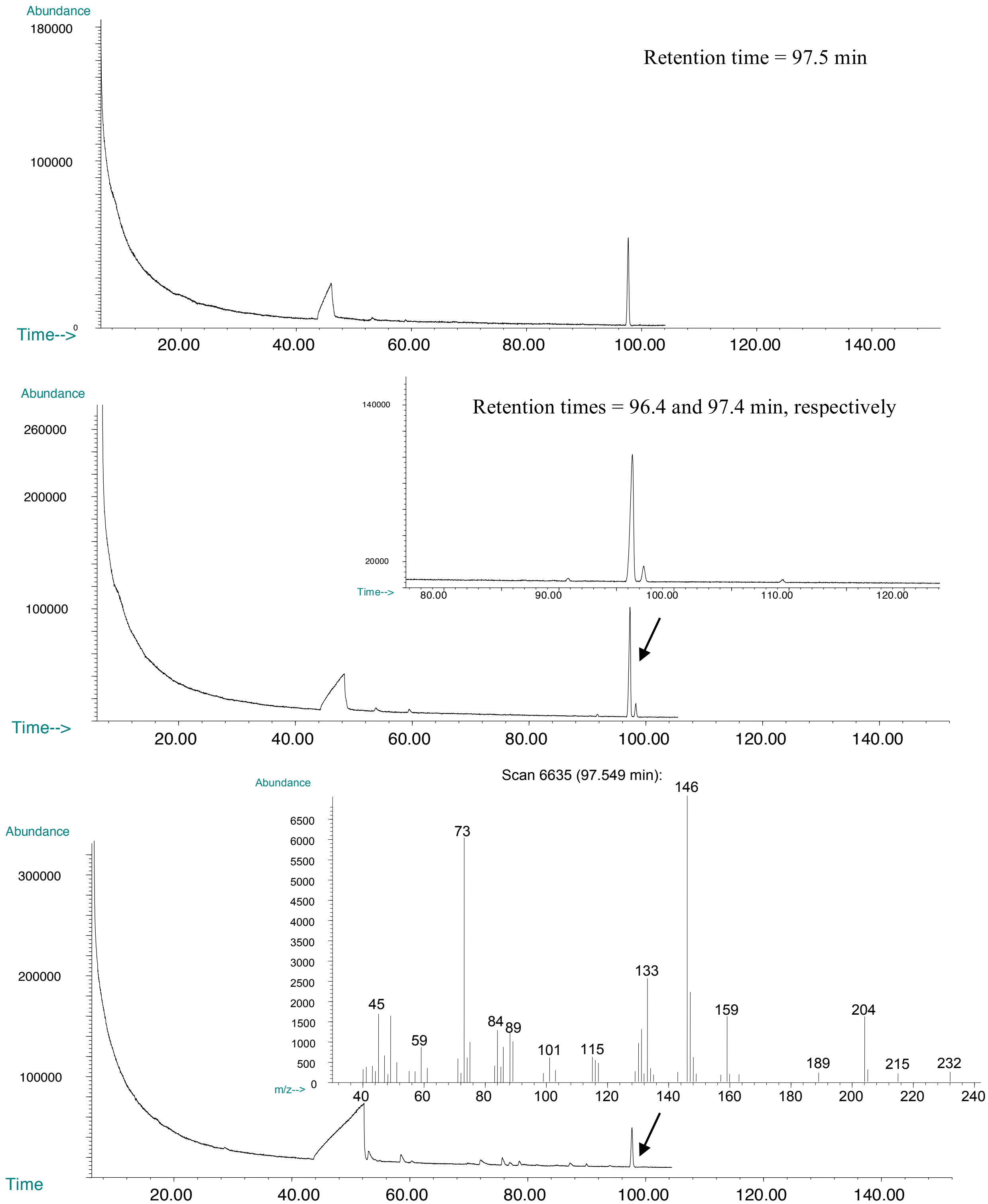
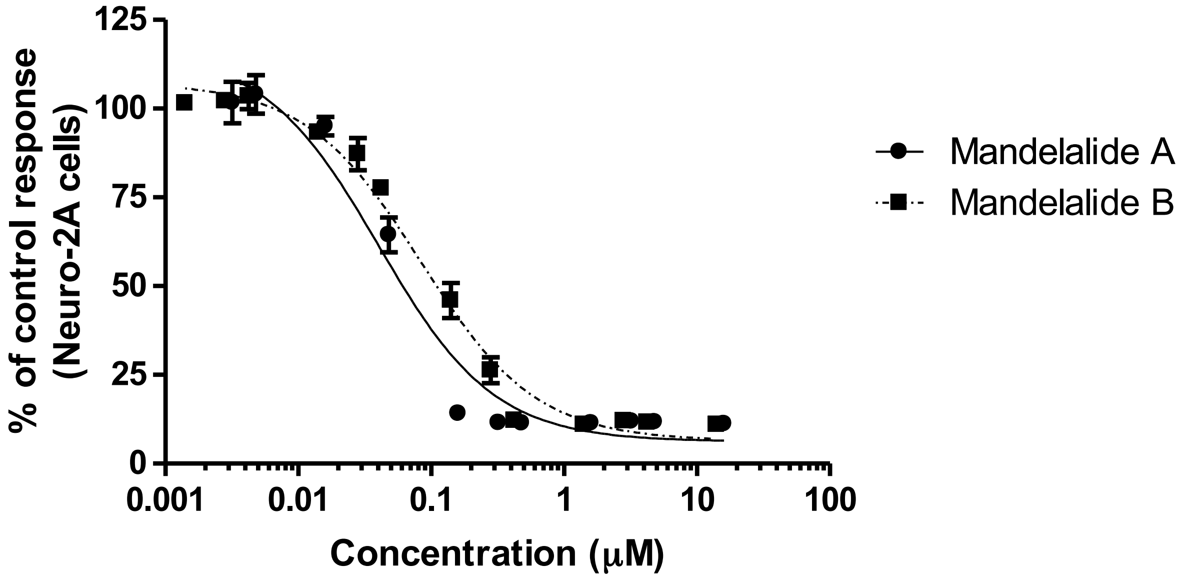


Figure S56. GCMS chromatograms for 1,2-di-*O*-methyl-3,4-di-*O*-TMS-α-L-rhamnose co-injected with the permethylated/silylated hydrolysate of mandelalide A (upper), 1,2-di-*O*-methyl-3,4-di-*O*-TMS-α-D-rhamnose co-injected with the permethylated/silylated hydrolysate of mandelalide A (middle chromatogram, left and right peaks, respectively), and the permethylated and silylated hydrolysate of mandelalide A with EI mass spectrum (bottom).



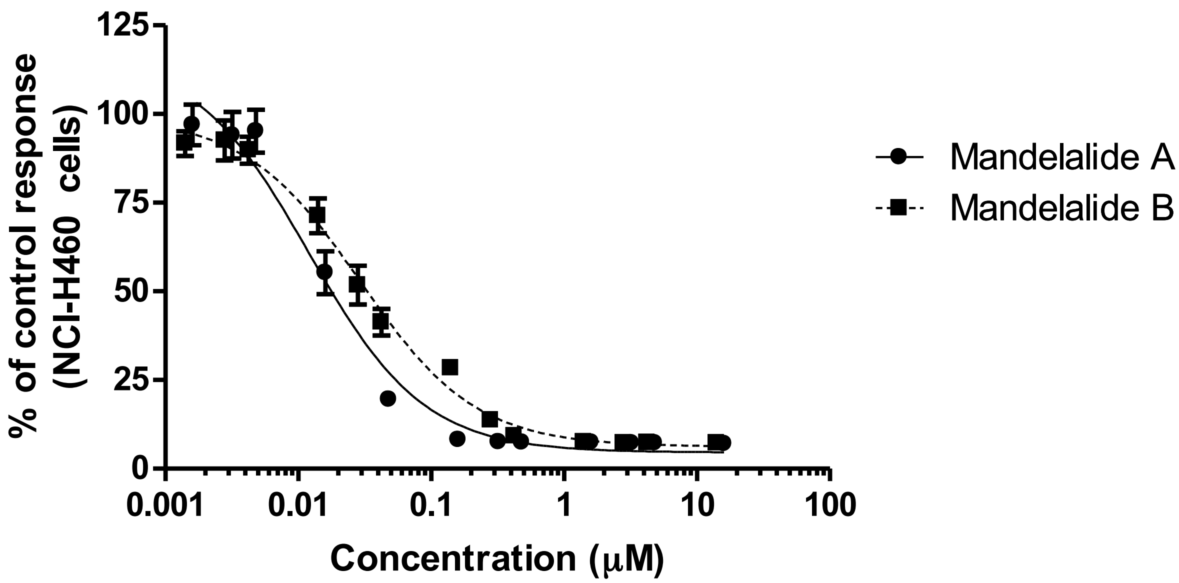


Figure S57. The dose response curves for mandelalides A and B in mouse Neuro2A neuroblastoma and human NCI-H460 cell lines, following 48 h incubation. Cell viability was assessed by MTT assay and is expressed relative to the response of solvent vehicle-treated cells.