Supporting Information

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Secondary metabolites of the tree fern *Metaxya rostrata* C. Presl

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S1:

Table 1. ^{1}H NMR and ^{13}C NMR data for compound **1** (in MeOH, δ in ppm, *J* in Hz).

Position	Multiplicity	^{1}H (ppm)	$J_{H,H}$ (Hz)	^{13}C (ppm)
1 (glucose)	CH	4.27	d (7.8)	104.7
2 (glucose)	CH	3.19	dd (7.8 / 9.2)	75.0
3 (glucose)	CH	3.36	dd (9.2 / 8.9)	77.9
4 (glucose)	CH	3.28	dd (8.9 / 9.8)	71.6
5 (glucose)	CH	3.27	ddd (9.8 / 1.8 / 5.6)	78.0
6 (glucose)	CH_2	3.87	dd (1.8 / 11.9)	62.7
		3.67	dd (5.6 / 11.9)	
1’	CH_2	4.12	dd (5.5 / 10.4)	69.8
		3.72	dd (3.6 / 10.4)	
2’	CH	3.99	ddd (3.6 / 5.5 / 7.9)	54.6
3’	CH	4.15	dd (7.9 / 7.4)	72.8
4’	CH	5.49	ddt (15.4 / 7.4 / 1.4)	131.4
5’	CH	5.74	dtd (15.4 / 6.5 / 0.8)	134.4
6‘	CH_2	2.08	m	33.7
7‘	CH_2	2.13	m	27.9
8‘	CH	5.38	m	129.9[a]
9’	CH	5.38	m	131.4[a]
10’	CH_2	2.04	m	28.3
ω’-2	CH_2	1.29	m	33.1[d]
ω’-1	CH_2	1.33	m	23.8[c]
ω’	CH_3	0.90[b]	t (7.0)	14.5[b]
1’’	C	-	-	177.2
2’’	CH	4.12	dd (10.3 / 5.5)	73.1
3’’	CH_2	1.72	m	35.9
		1.56	m	
4’’	CH_2	1.42	m	26.2
ω’’-2	CH_2	1.29	m	33.1[d]
ω’’-1	CH_2	1.33	m	23.8[c]
ω’’	CH_3	0.91[b]	t (7.0)	14.5[b]
Further CH_2 groups in ^{13}C (ppm): 30.89, 30.82, 30.80, 30.77, 30.74, 30.72, 30.53, 30.49, 30.46				

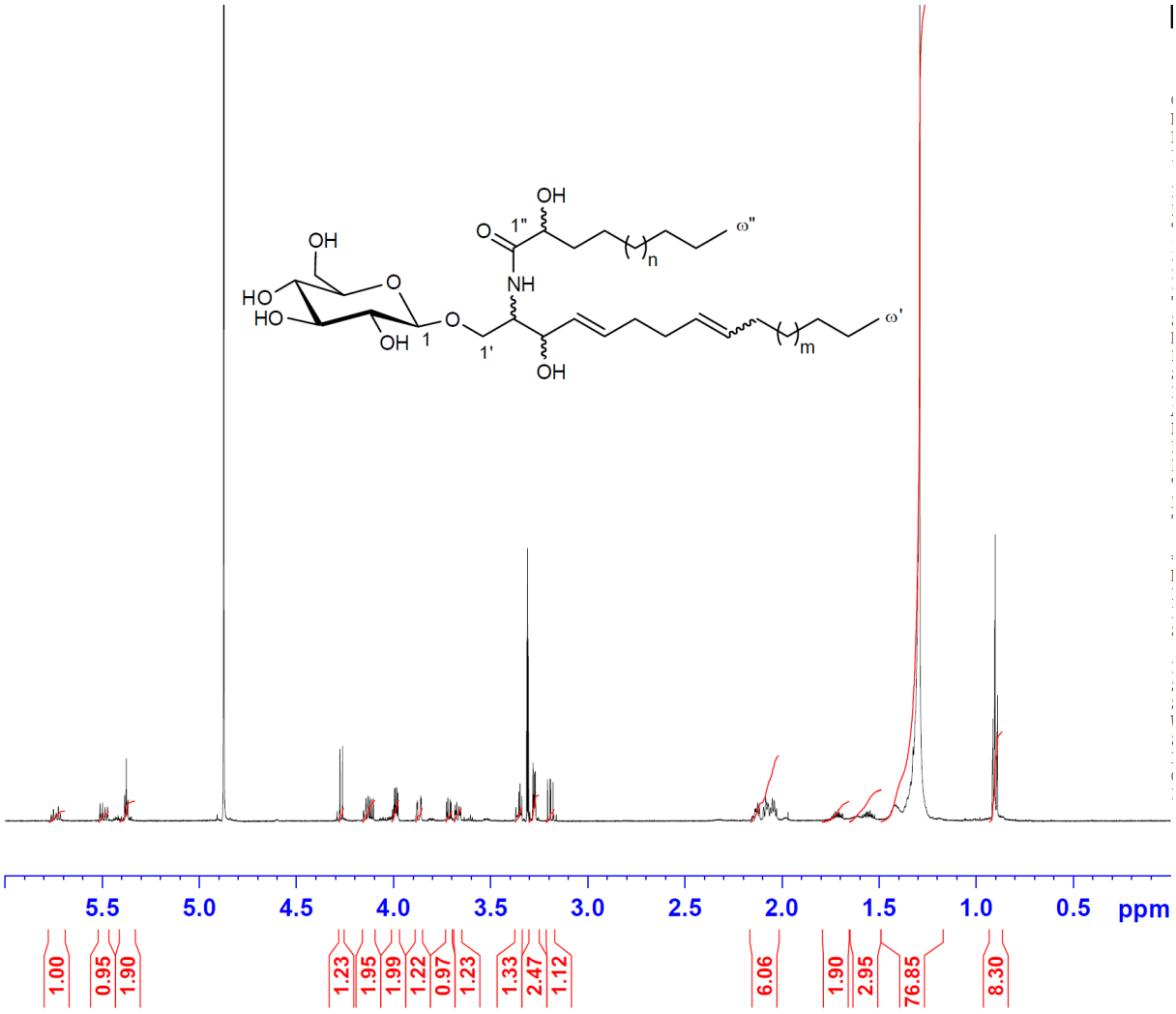
[a, b, c, and d] Interchangeable

*(4E)-1-O-(β-glucopyranosyl)-N-(2’-hydroxytetracosanoyl)-4,8-sphingadienine (d18:2/h24:0-Glc Cer) (**1**)*

^{1}H and ^{13}C NMR (Table 1); +ESI-MS *m/z* 832.8 $[M+Li]^+$, 848.7 $[M+Na]^+$; ESI-MS^2 (832.8 →) *m/z* 832.7 (15), 814.7 (35), 670.7 (100), 652.7 (34), 622.7 (13), 466.3 (73), 304.2 (13); ESI-MS^3 (832.8 → 670.7 →) *m/z* 670.6 (10), 652.6 (100), 634.6 (17), 622.6 (60), 345.3 (14), 304.2 (40), 296.1 (12), 286.2 (17), 271.1 (18), 256.1 (14); ESI-MS^3 (832.8 → 466.3 →) *m/z* 466.3 (14), 449.2 (91), 448.2 (46), 304.2 (100), 303.2 (15), 287.1 (32), 286.2 (13), 257.1 (12), 256.1 (11), 187.0 (61), 186.0 (13), 169.0 (51); HR-ESI-MS *m/z* 832.6844 $[M+Li]^+$ (calcd for $C_{48}H_{91}NO_9Li^+$, 832.6848, Δ = -0.5 ppm); CD (MeOH) $\Delta\varepsilon_{200}$ −3. 9579.

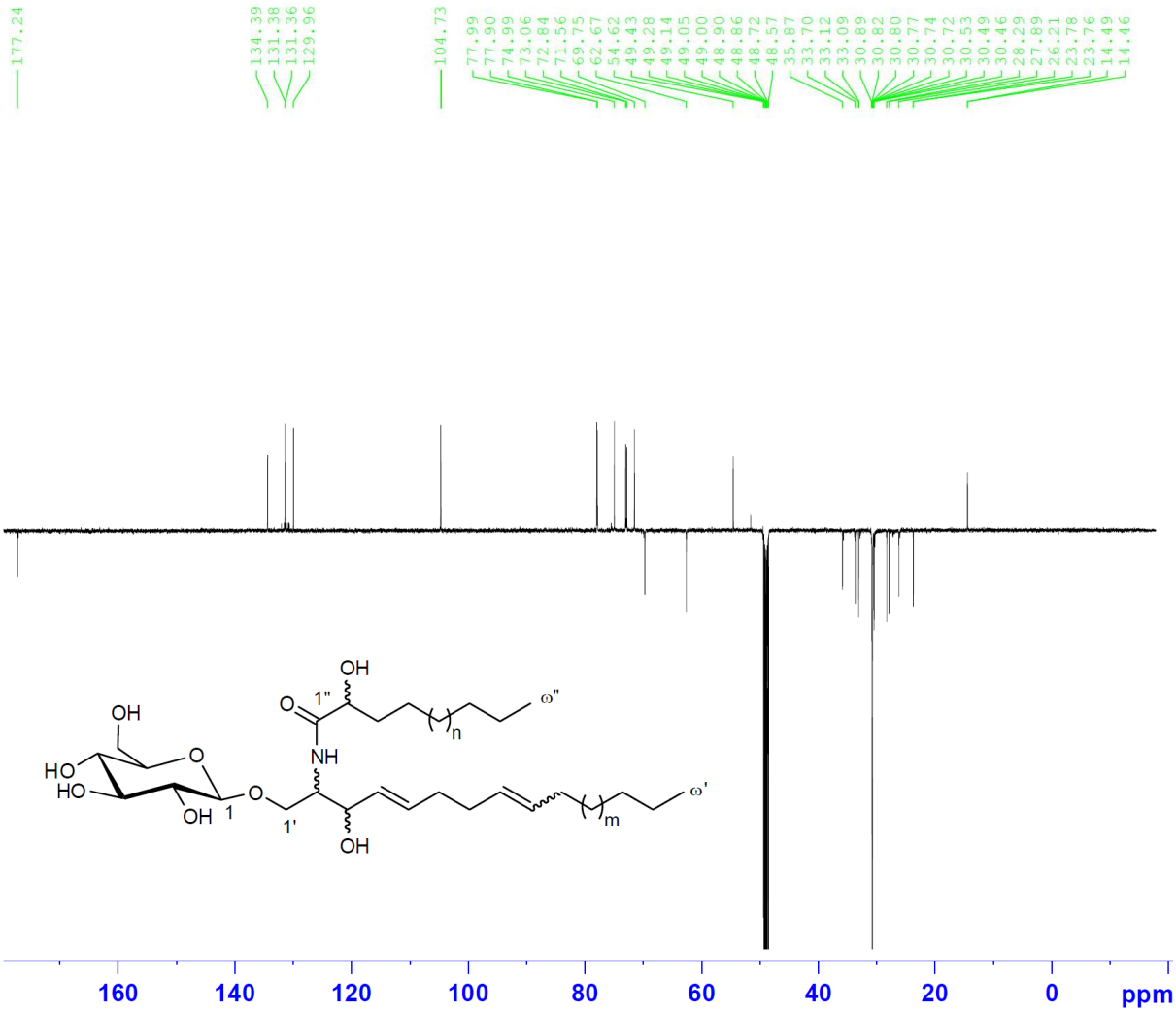
S2:

^{1}H NMR (MeOH-d4, 600 MHz) of Compound **1** (m=5, n=17)



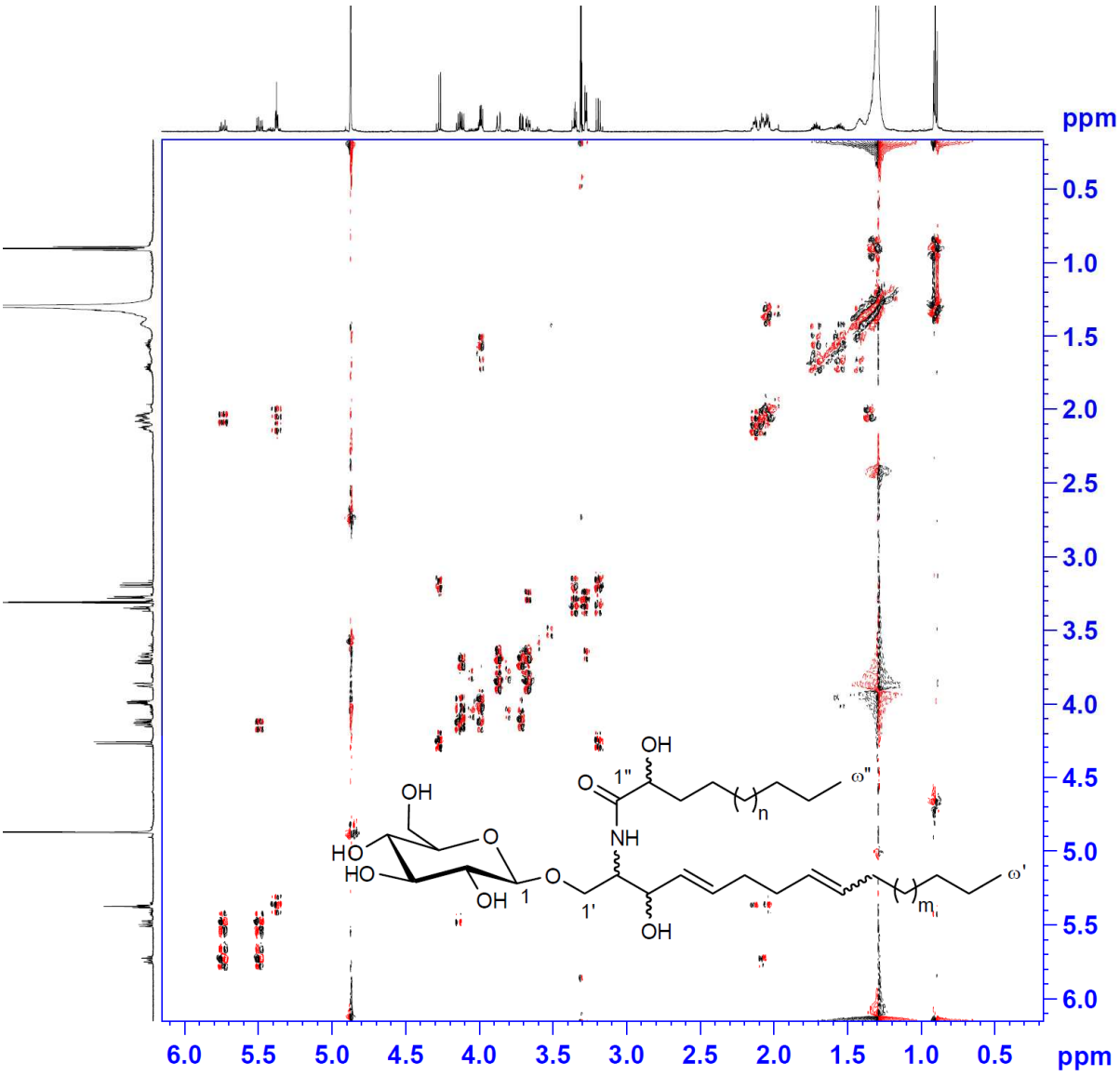
S3:

^{13}C NMR (MeOH-d4, 150 MHz) of Compound **1** (m=5, n=17)



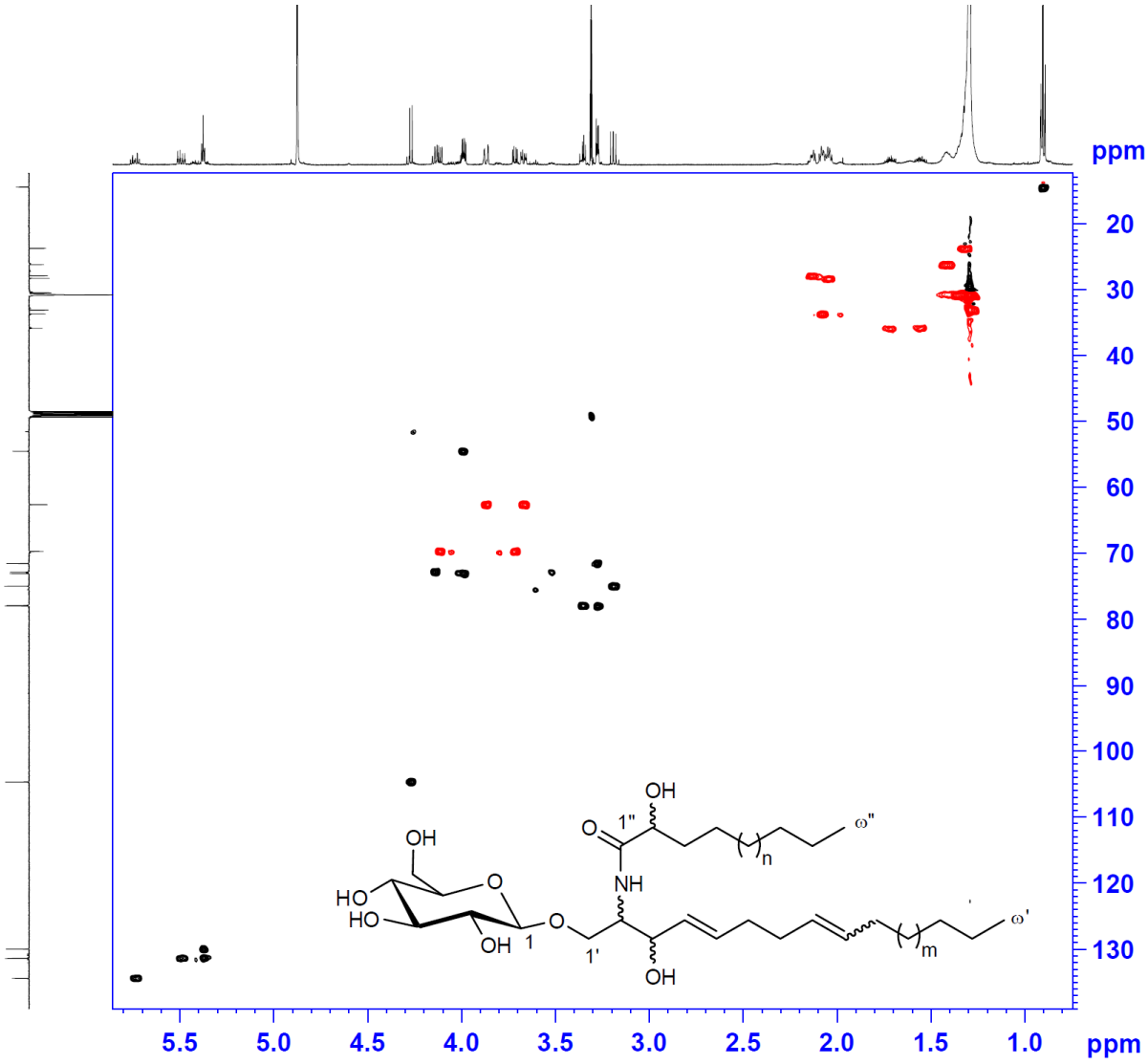
S4:

^{1}H 1H COSY (MeOH-d4, 600 MHz) of Compound **1** (m=5, n=17)



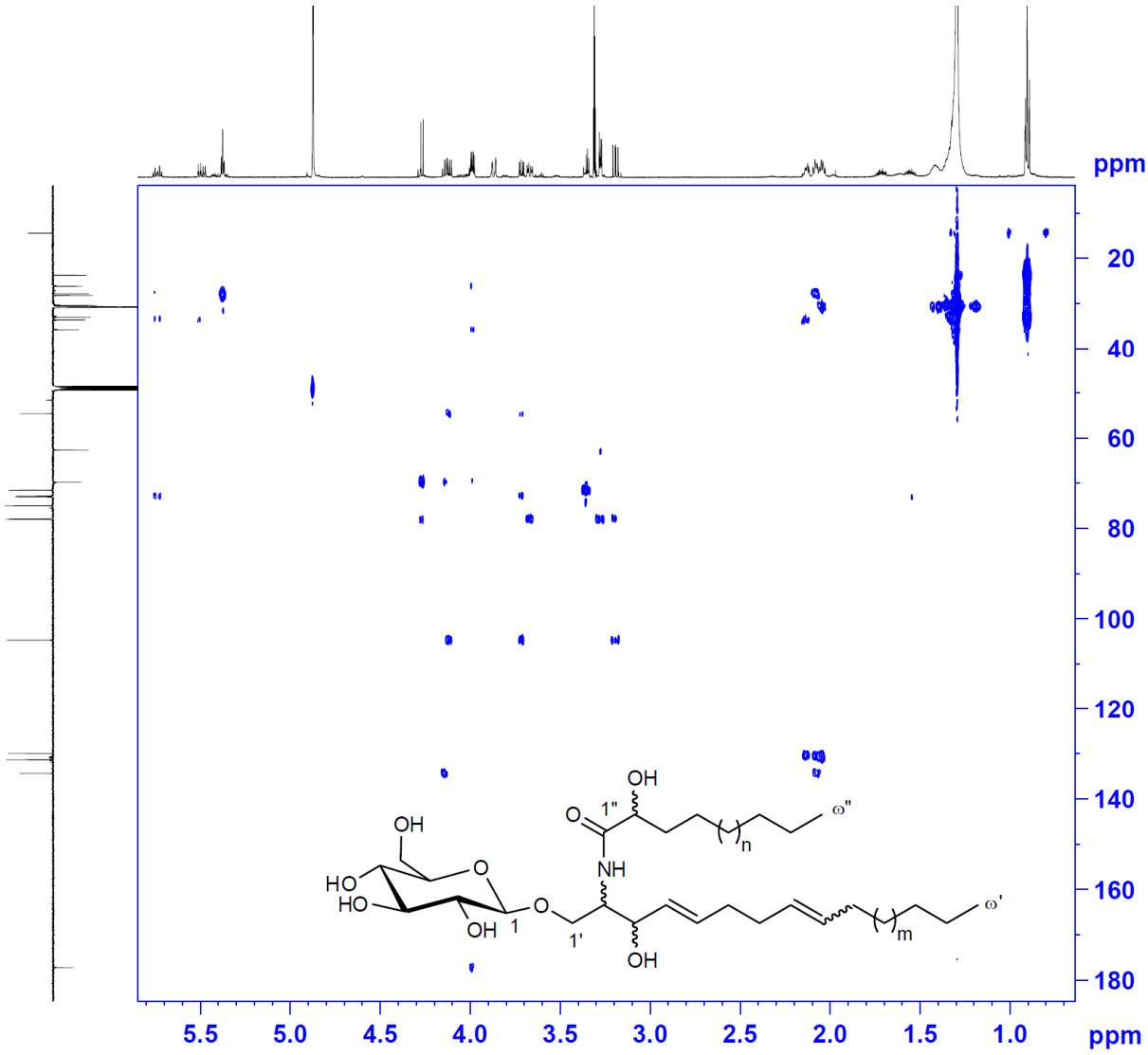
S5:

HSQC (MeOH-d4, 600 MHz) of Compound **1** (m=5, n=17)



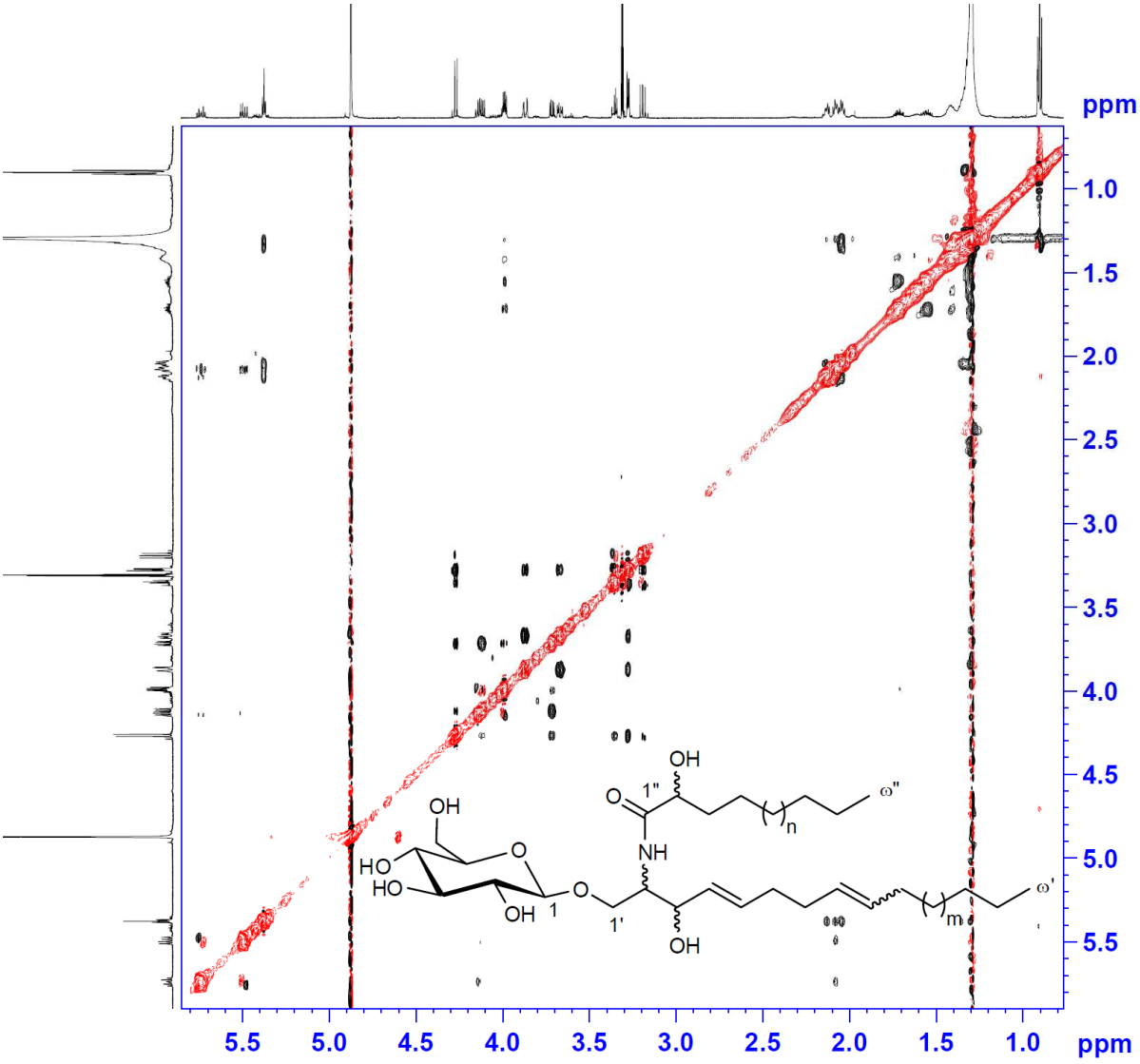
S6:

HMBC (MeOH-d4, 600 MHz) of Compound **1** (m=5, n=17)



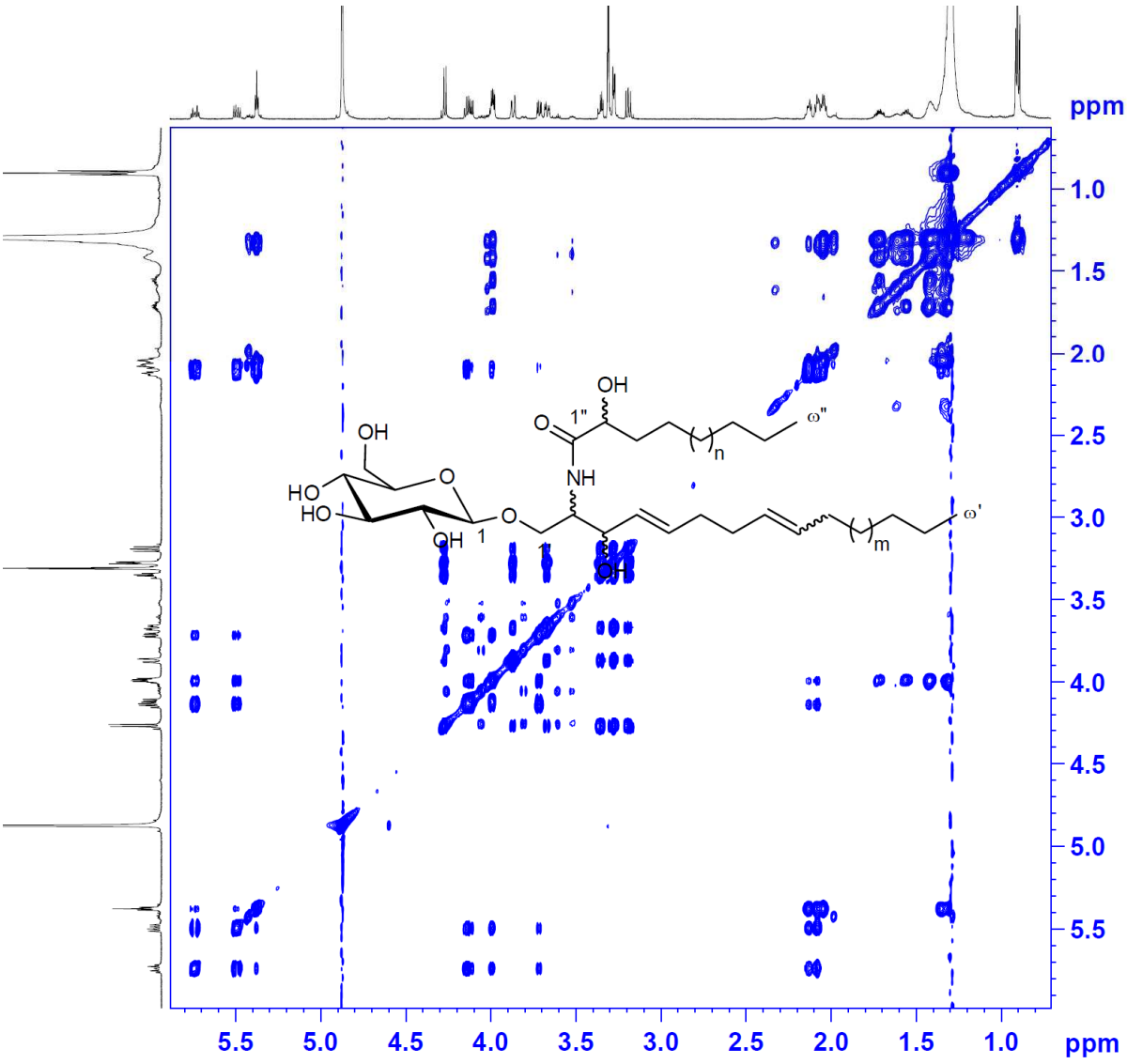
S7:

NOESY (MeOH-d4, 600 MHz) of Compound **1** (m=5, n=17)



S8:

TOCSY (MeOH-d4, 600 MHz) of Compound **1** (m=5, n=17)



S9:

Table 2. ^{1}H NMR and ^{13}C NMR data for compound **2** (in MeOH, δ in ppm, *J* in Hz).

Position	Multiplicity	^{1}H (ppm)	$J_{H,H}$ (Hz)	^{13}C (ppm)
1	C	---		165.0
2	CH	6.12	s	93.9
3	C	---		166.9
4	C	---		114.1
4a	C	---		154.4
4b	C	---		144.5[a]
5	C	---		134.7
6	C	---		143.2[a]
7	C			142.9[a]
8	CH	7.10	s	100.2
8a	C	---		113.5
9	C	---		181.7
9a	C	---		104.1
11	C	---		45.0
12	CH_3	1.61	s	26.0
13	CH_3	1.33	s	21.4
14	CH	4.53	q (6.6)	92.2
15	CH_3	1.40	d (6.6)	14.6

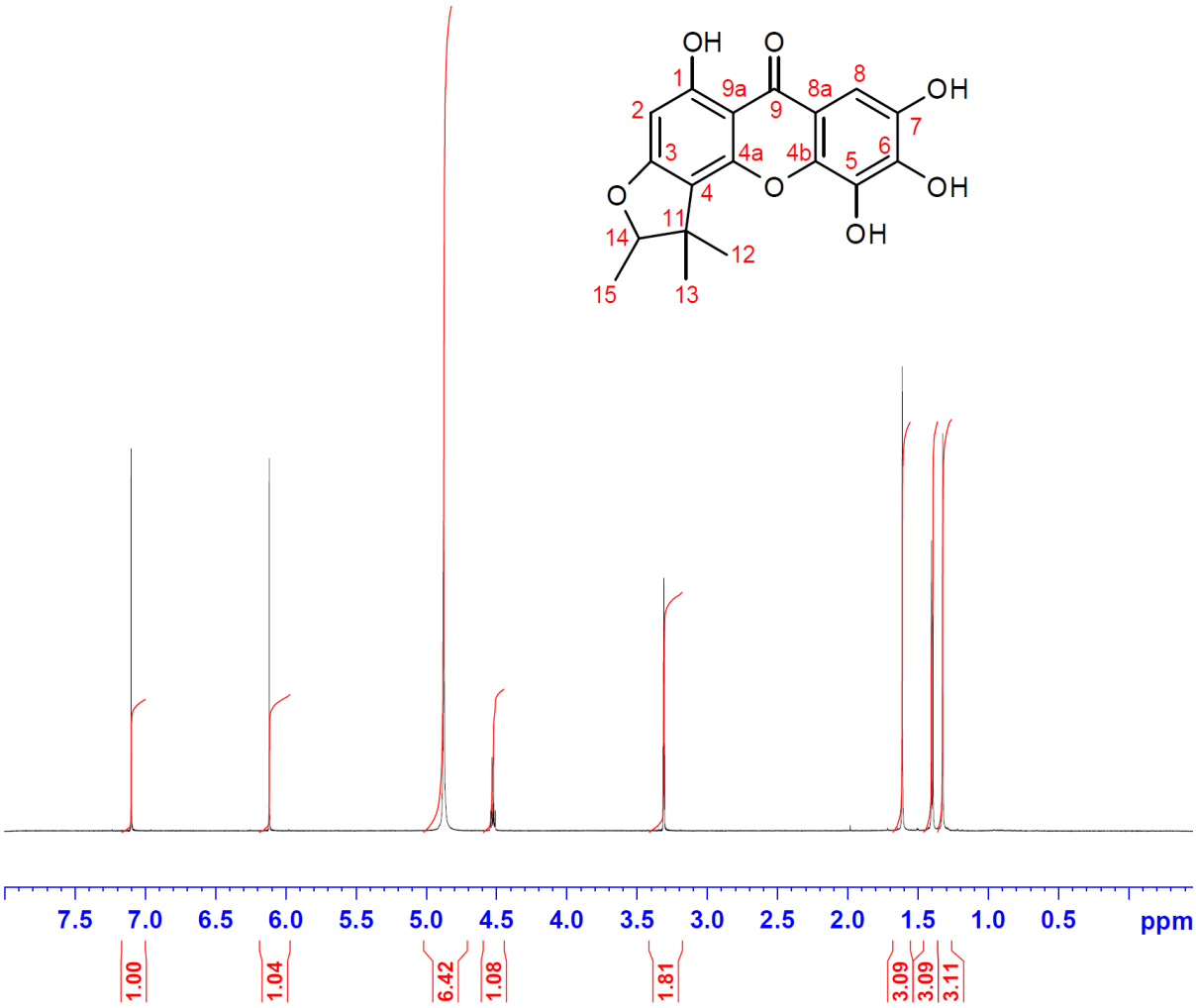
[a] Interchangeable.

*2-deprenyl-7-hydroxy-rheediaxanthone B (**2**)*

^{1}H and ^{13}C NMR (Table 2); +ESI-MS *m/z* 344.7 $[M+H]^+$; ESI-MS^2 (344.7 →) *m/z* 302.7 (27), 288.7 (100); ESI-MS^3 (344.7 → 288.7 →) *m/z* 260.6 (100), 178.7 (35); -ESI-MS *m/z* 342.7 $[M-H]^-$; ESI-MS^2 (342.7 →) *m/z* 312.7 (100); HR-ESI-MS *m/z* 345.1005 $[M+H]^+$ (calcd for $C_{18}H_{17}O_7^+$, 345.0969, Δ = +10.5 ppm); CD (MeOH) $\Delta\varepsilon_{299}$ +1.7318, $\Delta\varepsilon_{252}$ −1.3418.

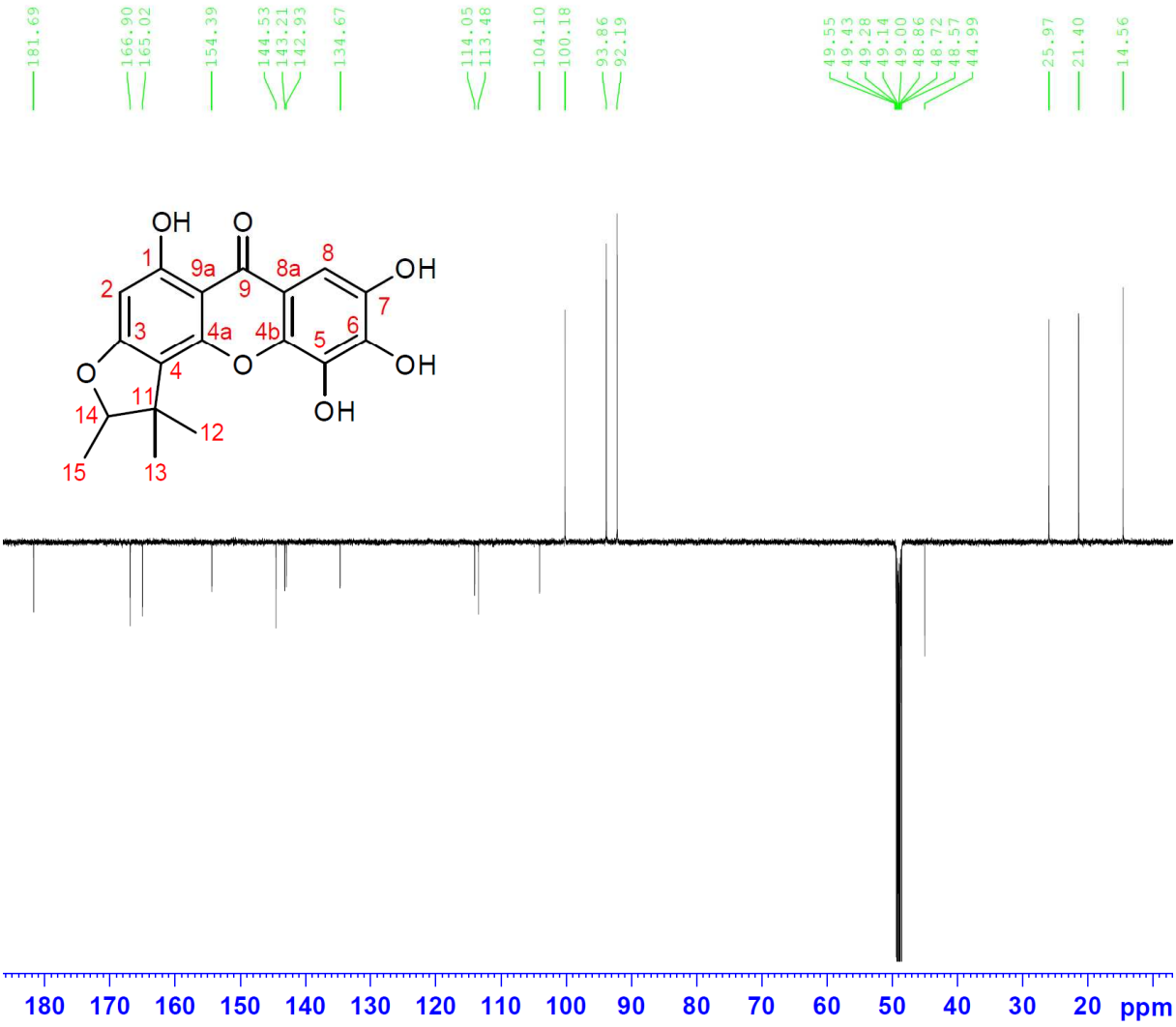
S10:

^{1}H NMR (MeOH-d4, 600 MHz) of Compound **2**



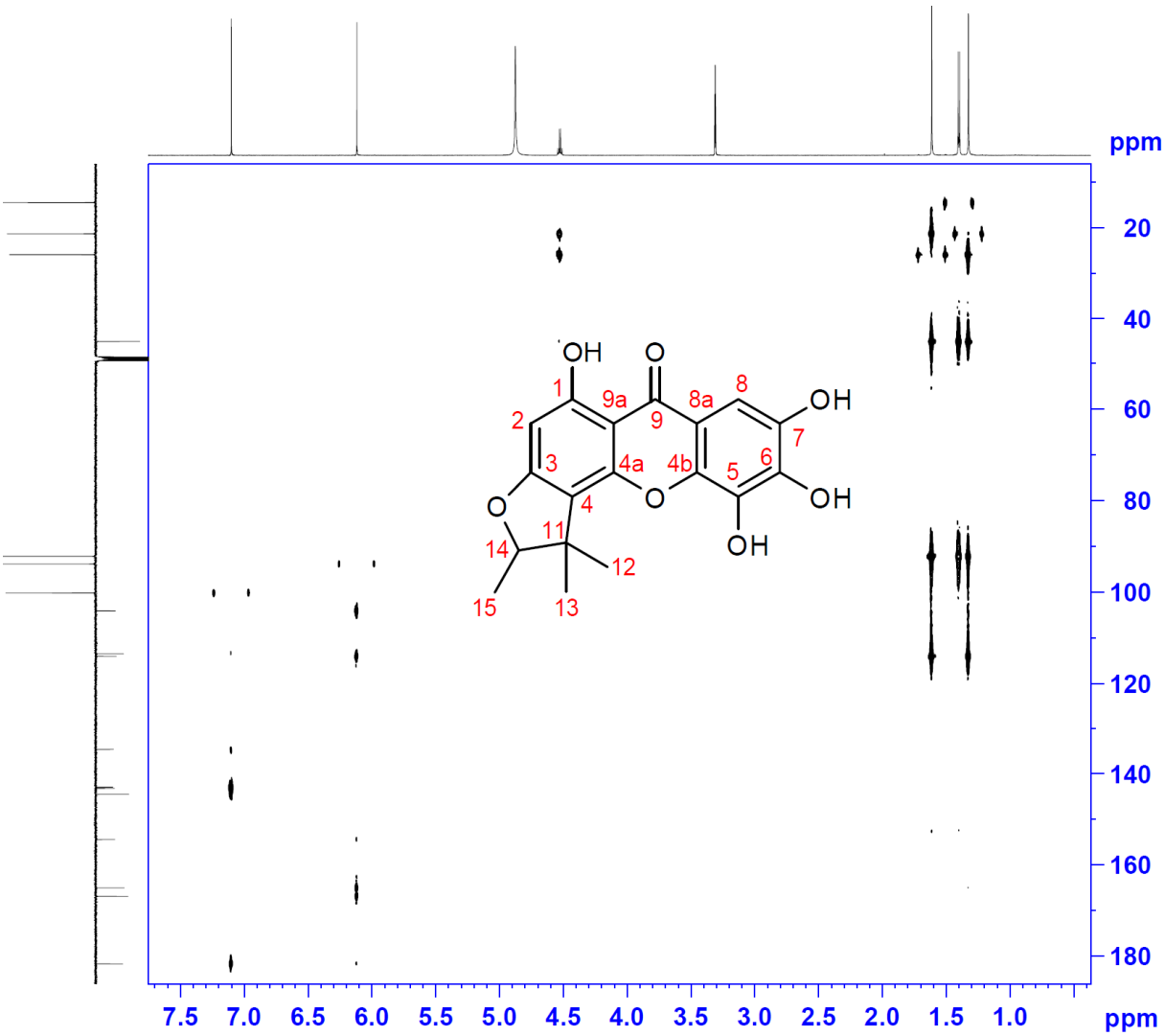
S11:

^{13}C NMR (MeOH-d4, 150 MHz) of Compound **2**



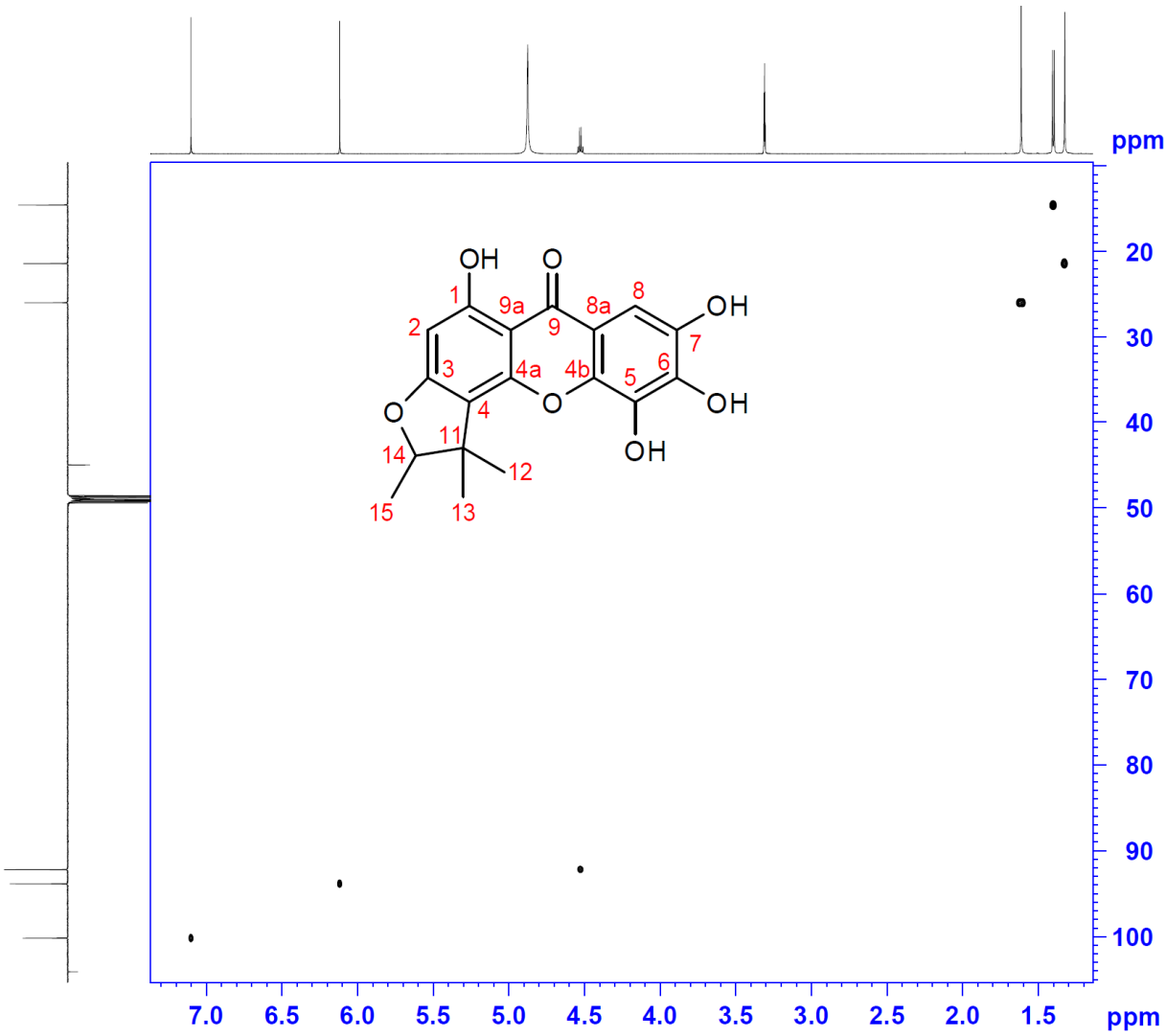
S12:

HMBC (MeOH-d4, 600 MHz) of Compound **2**



S13:

HSQC (MeOH-d4, 600 MHz) of Compound **2**



S14:

Table 3. ^{1}H NMR and ^{13}C NMR data for compound **3** (in MeOH, δ in ppm, *J* in Hz).

Position	Multiplicity	^{1}H (ppm)	$J_{H,H}$ (Hz)	^{13}C (ppm)
1	CH_2	3.54	t (6.7)	62.9
2	CH_2	1.55	tt (7.8 / 6.7)	33.5
3	CH_2	1.39	tt (7.5 / 7.8)	26.6
4	CH_2	1.51	tt (7.5 / 7.5)	29.8
5	CH_2	2.24	ttdd (7.5 / 1.8 / 6.8 / 1.0)	32.5
6	CH	6.12	tdt (2.7 / 1.1 / 6.8)	124.1
7	C	-	-	123.8
8a	CH_2	1.34	dddt (10.1 / 6.2 / 2.7 / 1.8)	11.9
8b		1.25	dddt (10.1 / 2.7 / 2.7 / 1.8)	
9	CH	4.18	dddt (6.2 / 2.7 / 1.1 / 1.0)	52.7
1’	CH	4.45	d (7.9)	103.7
2’	CH	3.34	dd (7.9 / 9.2)	74.1
3’	CH	3.55	dd (9.2 / 8.9)	87.9
4’	CH	3.42	dd (8.9 / 9.8)	70.0
5’	CH	3.35	ddd (9.8 / 2.2 / 5.6)	77.8[a]
6’	CH_2	3.89	dd (2.2 / 11.9)	62.7
		3.71	dd (5.6 / 11.9)	
1’’	CH	4.55	d (7.9)	105.2
2’’	CH	3.26	dd (7.9 / 9.2)	75.5
3’’	CH	3.37	dd (9.2 / 8.9)	77.7[a]
4’’	CH	3.27	dd (8.9 / 9.8)	71.5
5’’	CH	3.32	ddd (9.8 / 2.3 / 6.4)	78.2
6’’	CH_2	3.88	dd (2.3 / 11.9)	62.6
		3.63	dd (6.4 / 11.9)	

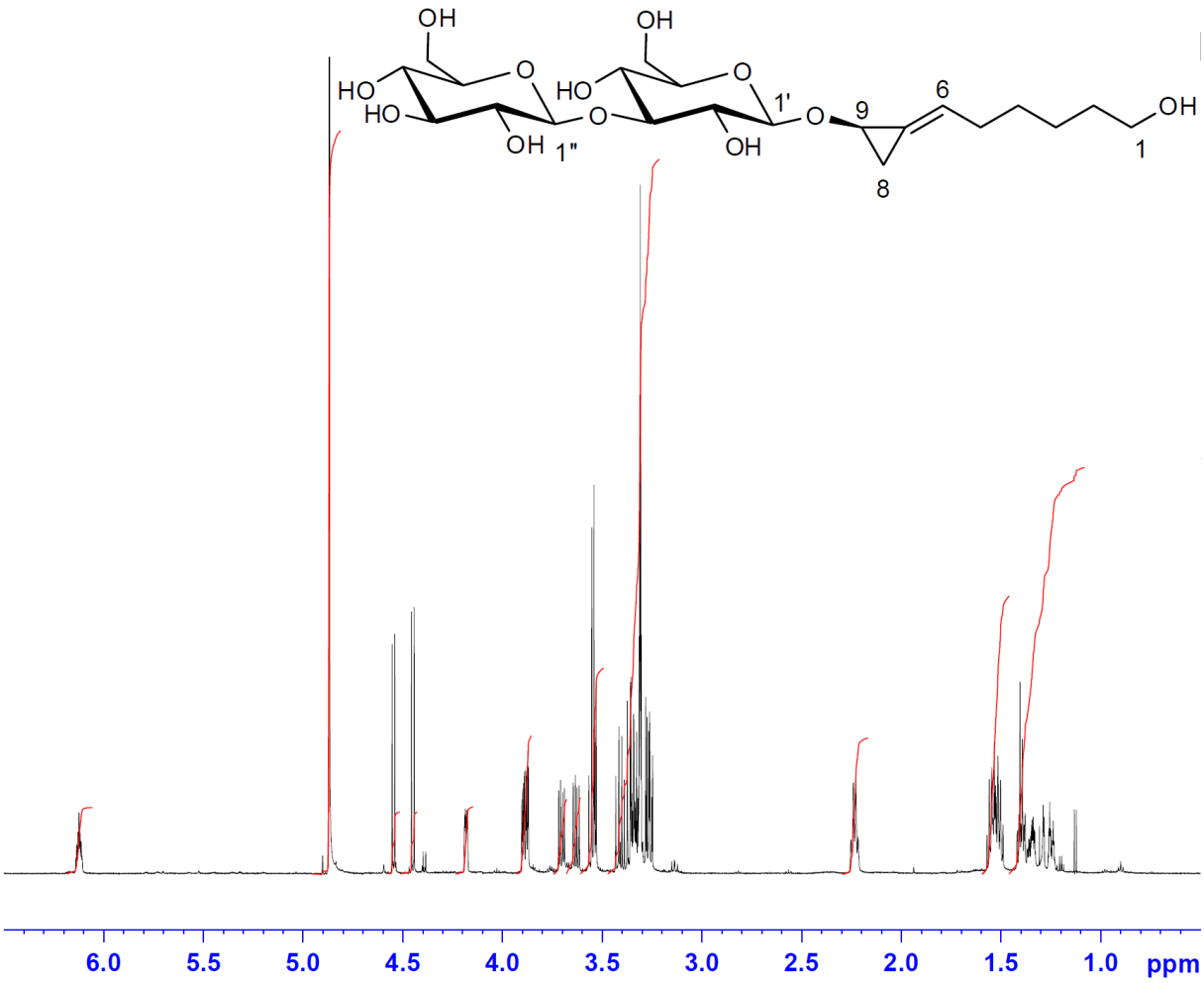
[a] Interchangeable.

*(2E)-2-(hydroxy-hexyliden)cyclopropyl-1→3-diglucoside (**3**)*

^{1}H and ^{13}C NMR (Table 3); +ESI-MS *m/z* 503.0 $[M+Na]^+$; ESI-MS^2 (503.0 →) *m/z* 346.7 (100); ESI-MS^3 (503.0 → 346.7 →) *m/z* 328.6 (36), 184.7 (100); -ESI-MS *m/z* 479.0 $[M-H]^-$; ESI-MS^2 (479.0 →) *m/z* 322.6 (10), 316.7 (21), 178.6 (49), 160.7 (100), 142.6 (25); ESI-MS^3 (479.0 → 160.7 →) *m/z* 142.7 (29), 112.8 (100), 100.9 (14); HR-ESI-MS *m/z* 503.2177 $[M+Na]^+$ (calcd for $C_{21}H_{36}O_{12}Na^+$, 503.2099, Δ = +15.6 ppm); CD (MeOH) $\Delta\varepsilon_{215}$ −2.4582.

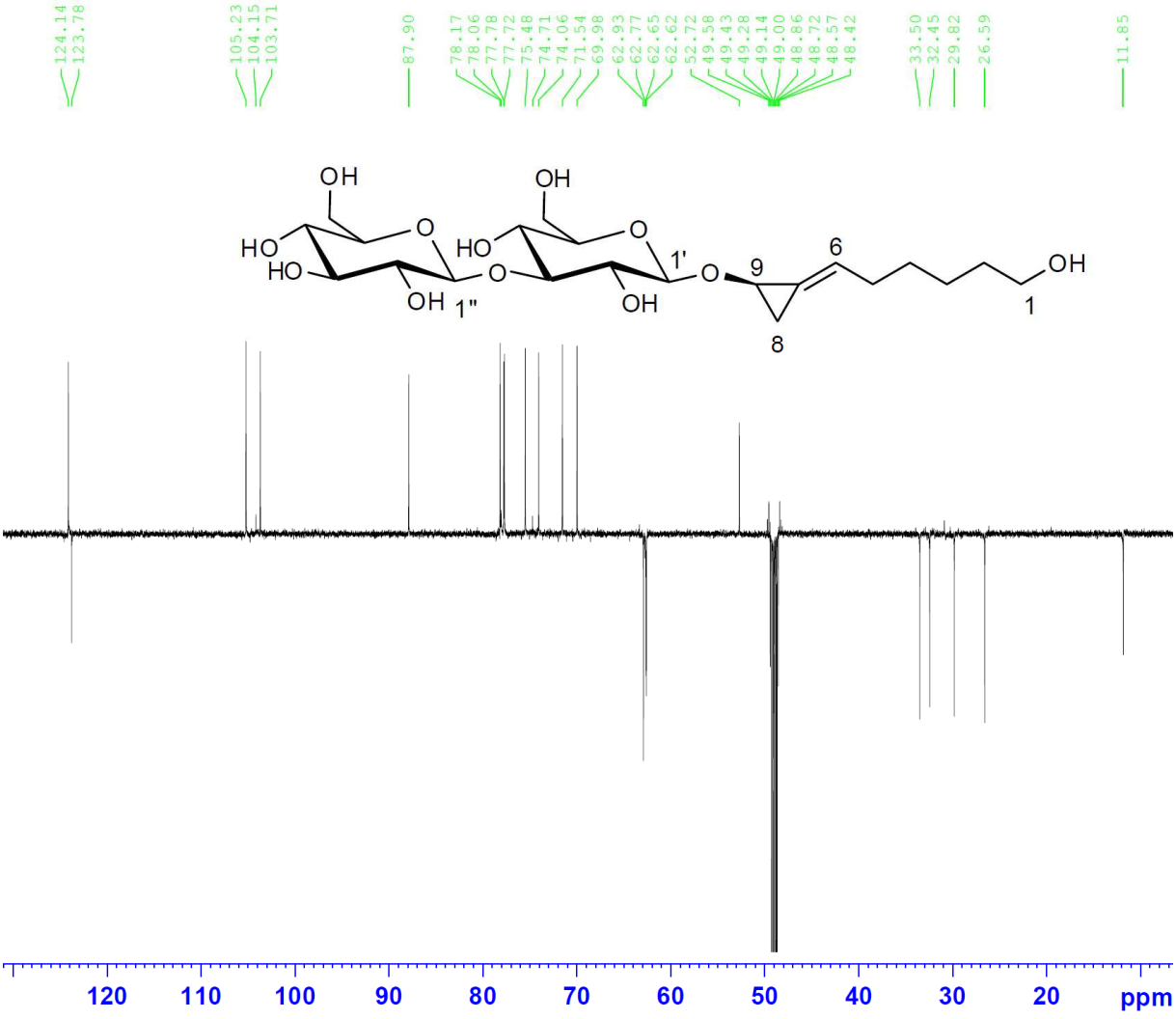
S15:

^{1}H NMR (MeOH-d4, 600 MHz) of Compound **3**



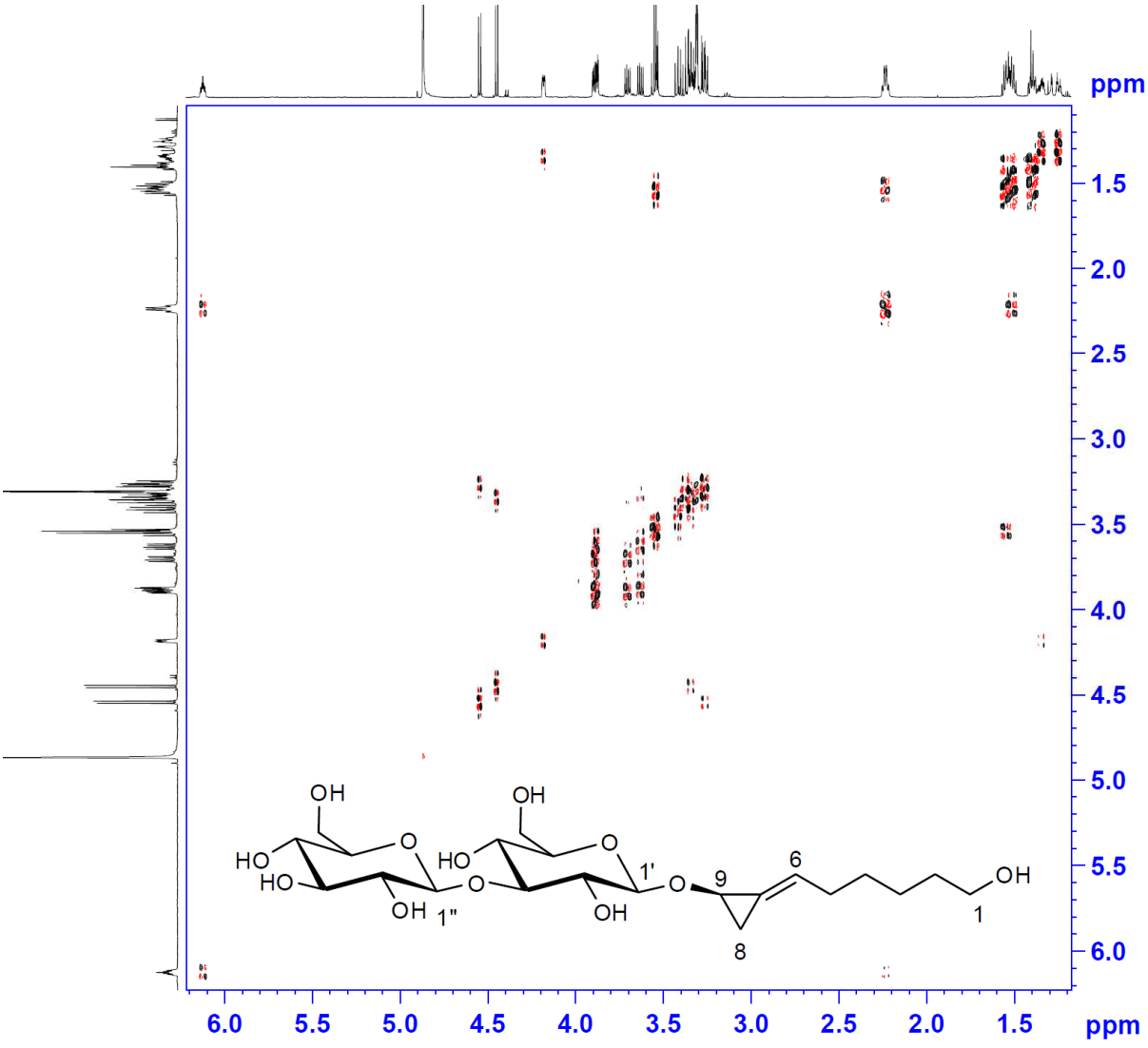
S16:

^{13}C NMR (MeOH-d4, 150 MHz) of Compound **3**



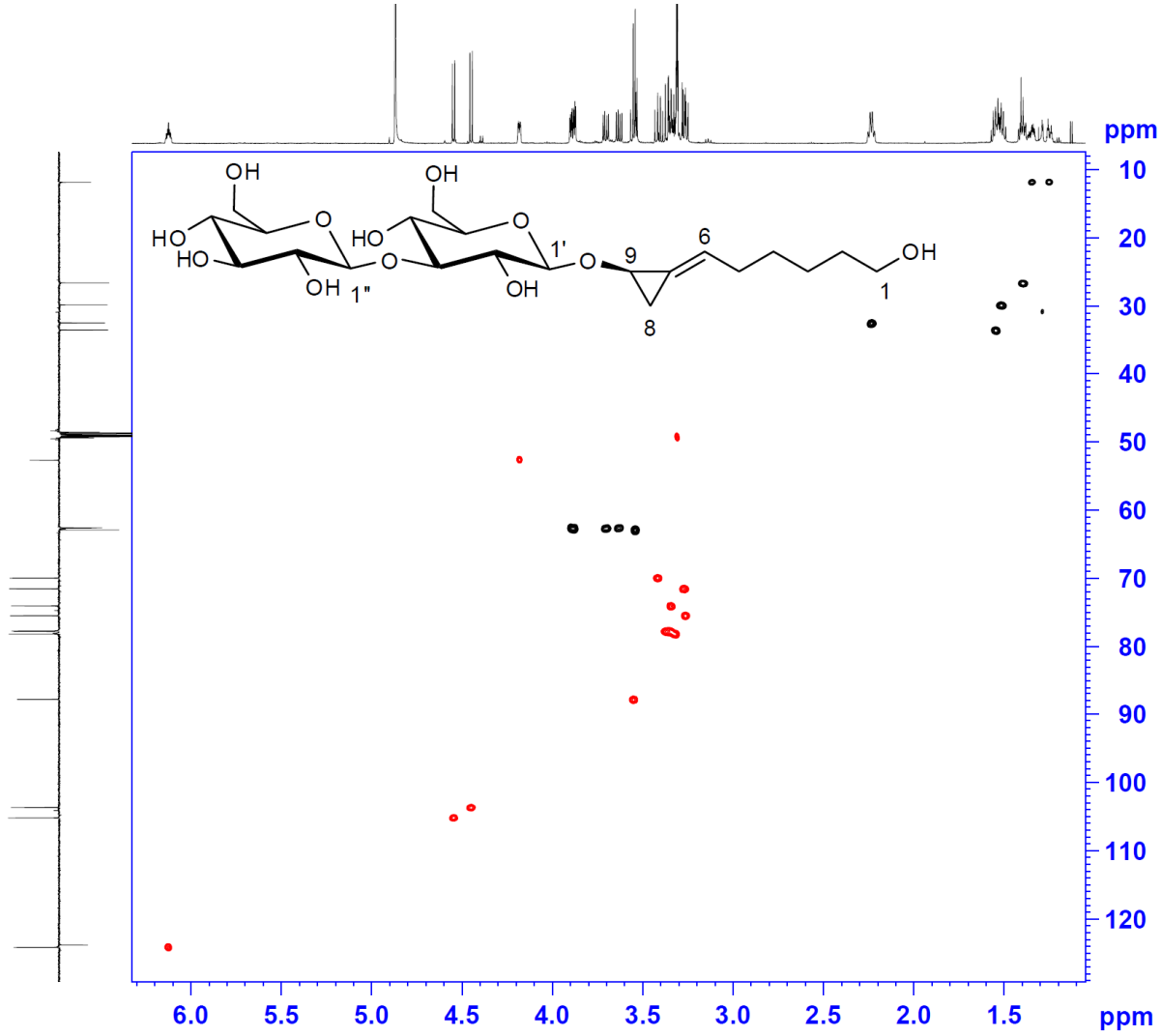
S17:

^{1}H 1H COSY (MeOH-d4, 600 MHz) of Compound **3**



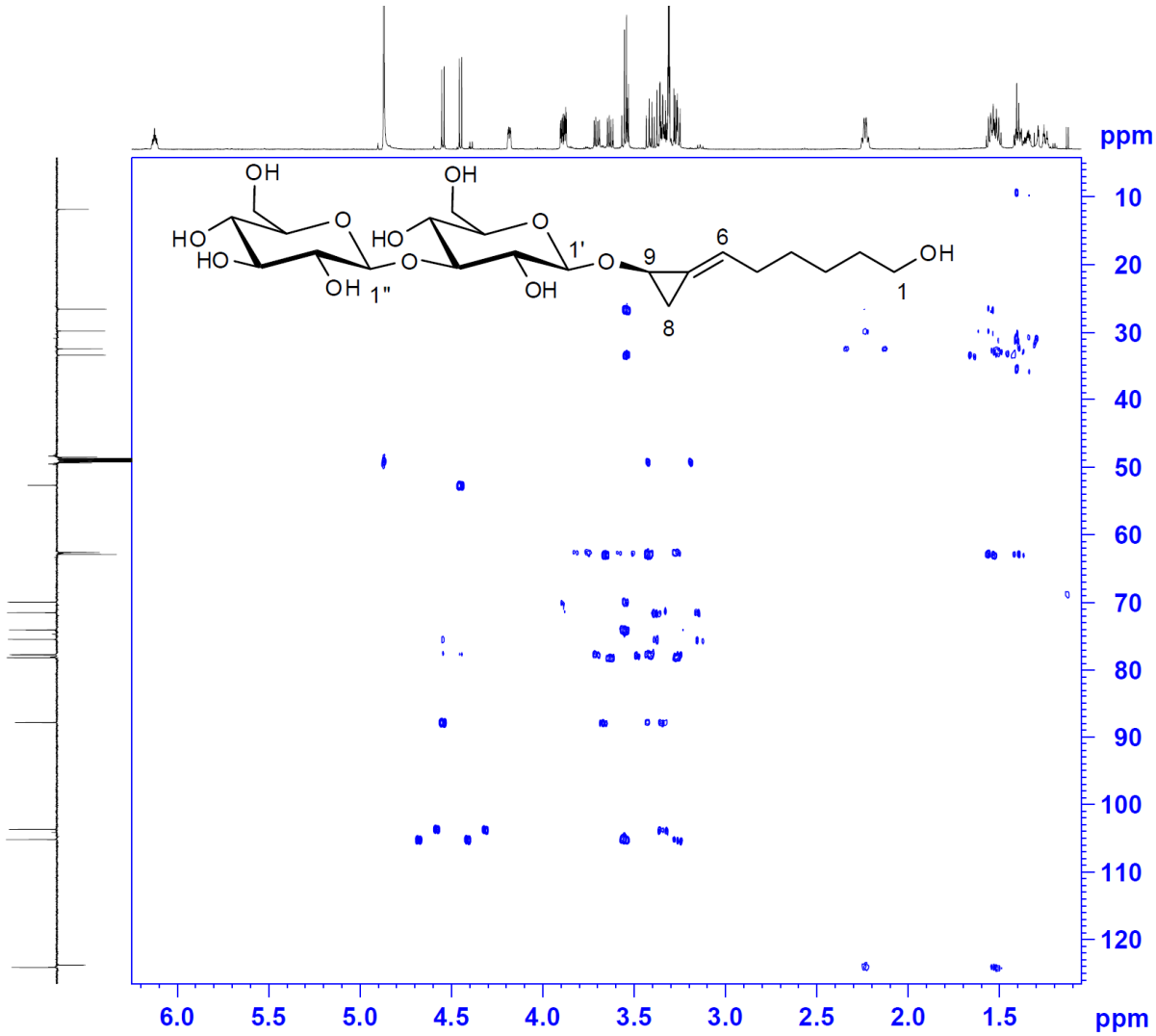
S18:

HSQC (MeOH-d4, 600 MHz) of Compound **3**



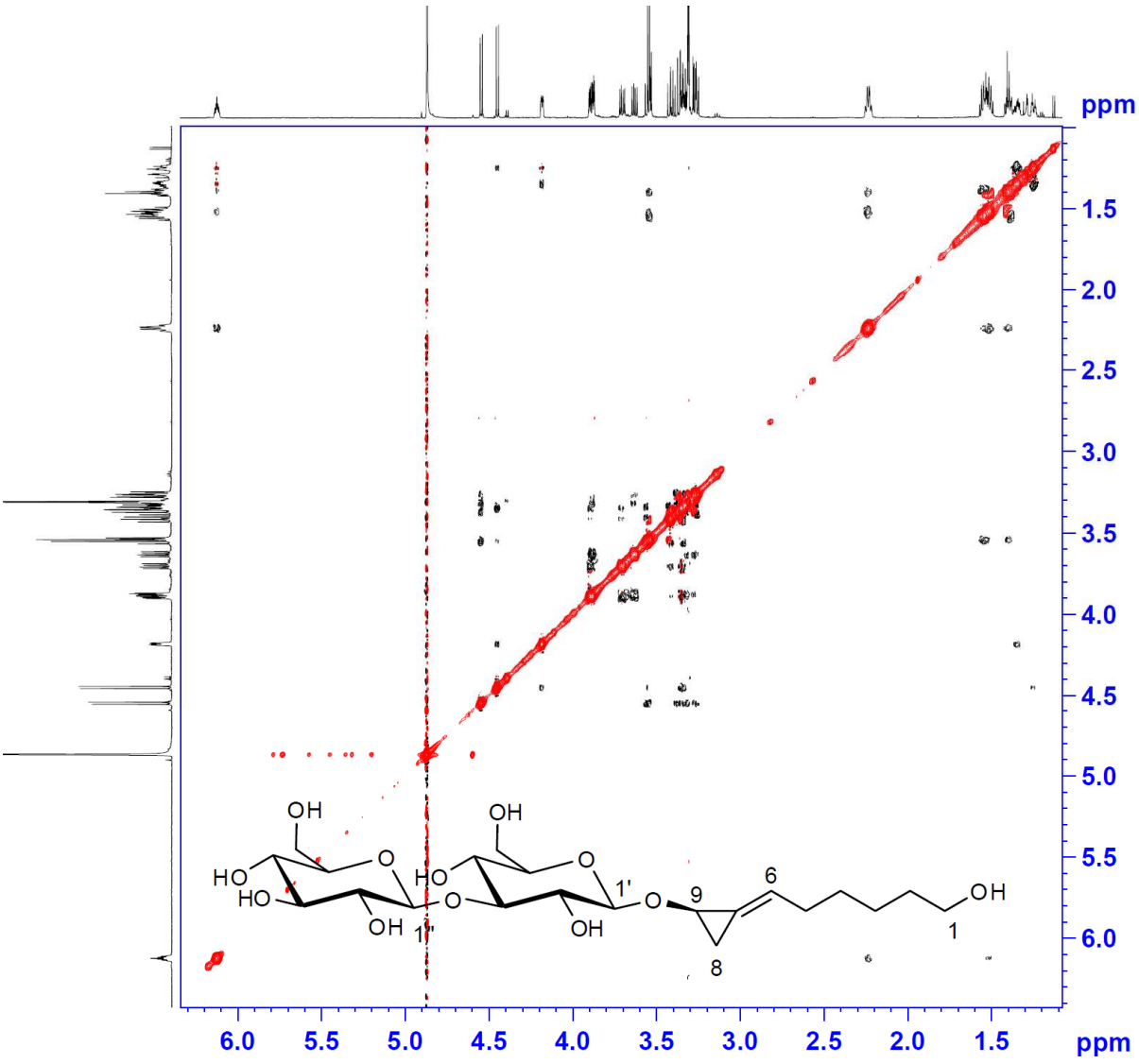
S19:

HMBC (MeOH-d4, 600 MHz) of Compound **3**



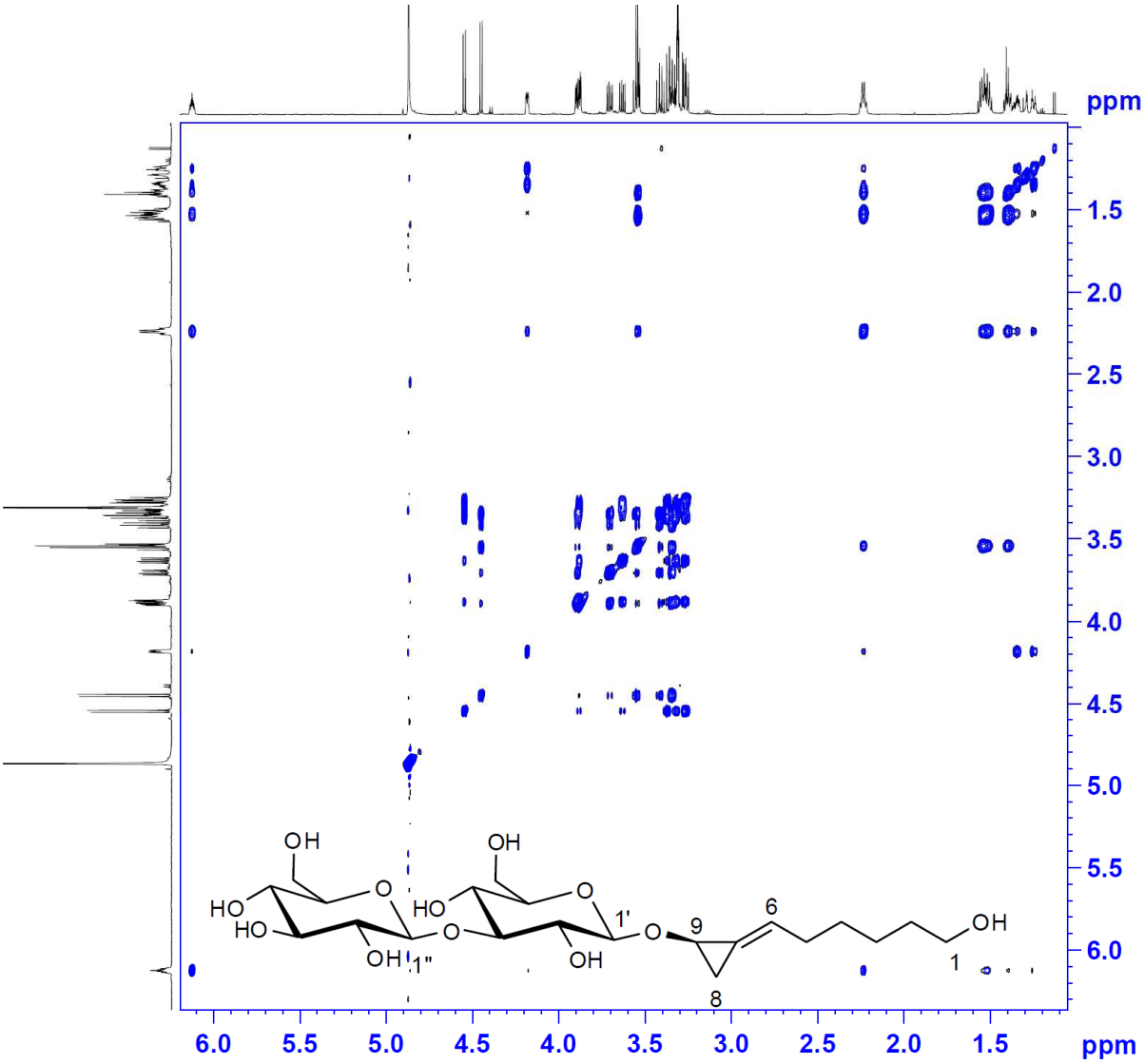
S20:

NOESY (MeOH-d4, 600 MHz) of Compound **3**



S21:

TOCSY (MeOH-d4, 600 MHz) of Compound **3**



S22:

Table 4. ^{1}H NMR and ^{13}C NMR data for compound **4** (in MeOH, δ in ppm, *J* in Hz).

Position	Multiplicity	^{1}H (ppm)	$J_{H,H}$ (Hz)	^{13}C (ppm)
1	C	-	-	175.9
2	CH_2	2.34	t (7.4)	34.6
3	CH_2	1.64	m	25.6
4	CH_2	1.51	m	29.4
5	CH_2	2.23	ttdd (7.5 / 1.8 / 6.8 / 1.0)	32.1
6	CH	6.11	tdt (2.7 / 1.1 / 6.8)	123.7
7	C	-	-	124.2
8a	CH_2	1.34	dddt (10.1 / 6.2 / 2.7 / 1.8)	11.9
8b		1.25	dddt (10.1 / 2.7 / 2.7 / 1.8)	
9	CH	4.18	dddt (6.2 / 2.7 / 1.1 / 1.0)	52.7
1’	CH	4.39	d (7.9)	104.2
2’	CH	3.14	dd (7.9 / 9.2)	74.7
3’	CH	3.35	dd (9.2 / 8.9)	78.1[a]
4’	CH	3.29	dd (8.9 / 9.8)	71.6
5’	CH	3.30	dd (9.8 / 2.0 / 5.5)	78.1[a]
6’	CH_2	3.88	dd (2.3 / 11.9)	62.8
		3.68	dd (5.5 / 11.9)	
	CH_3	3.65	s	52.0

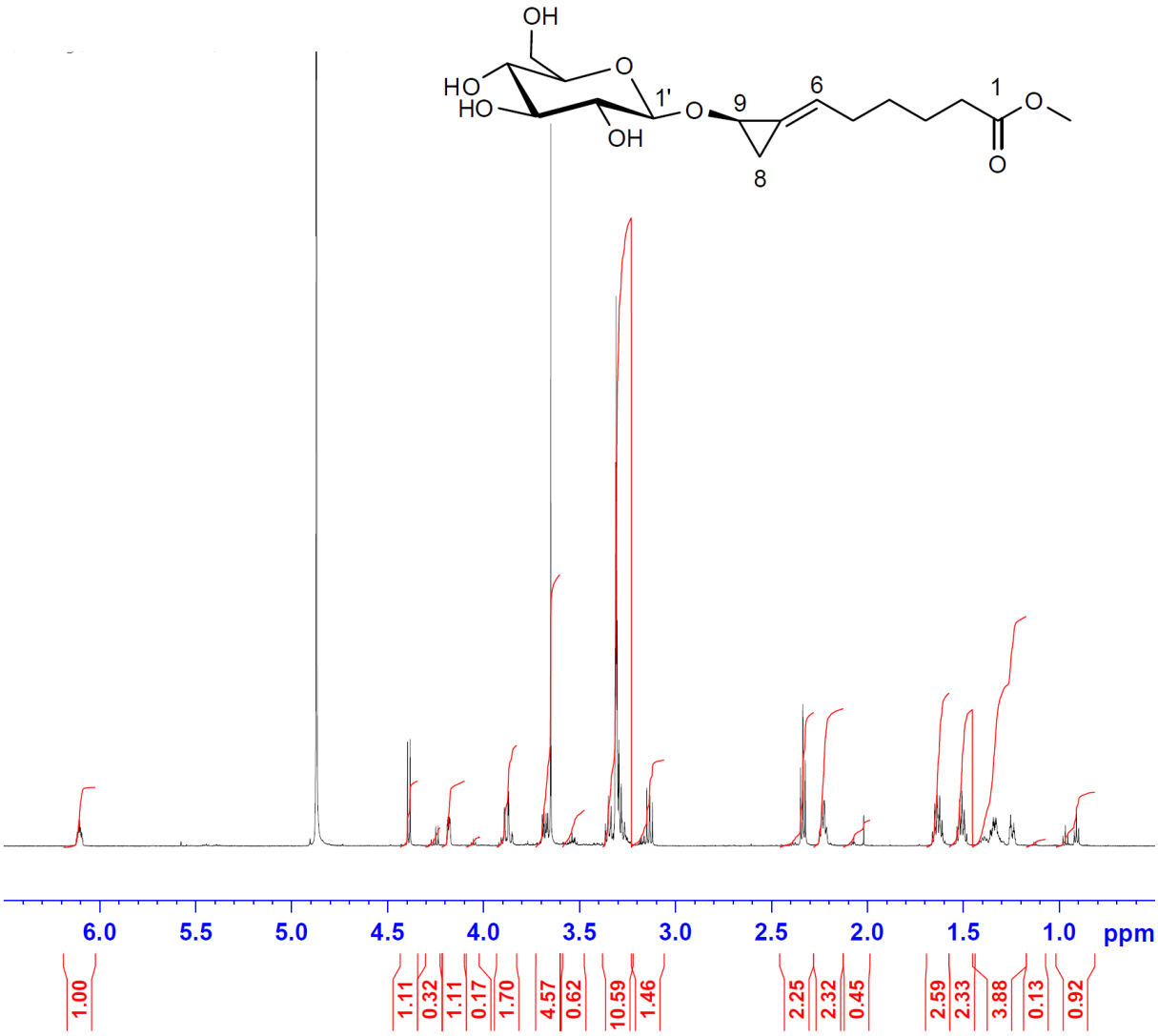
[a] Interchangeable.

*(6E)-6[2-(ß-glucopyranosyloxy)cyclopropyliden]-hexanoic acid methylester (**4**)*

^{1}H and ^{13}C NMR (Table 4); +ESI-MS *m/z* 363.8 $[M+NH_4]^+$, 368.8 $[M+Na]^+$; ESI-MS^2 (368.8 →) *m/z* 206.7 (100); ESI-MS^2 (363.8 →) *m/z* 346.5 (56), 184.7 (100), 152.8 (62), 134.8 (49), 107.0 (23); ESI-MS^3 (363.8 → 184.7 →) *m/z* 152.8 (100), 134.8 (55), 107.0 (18); -ESI-MS *m/z* 390.8 $[M+HCOO]^-$; ESI-MS^2 (390.8 →) *m/z* 312.7 (100); ESI-MS^3 (390.8 → 312.7 →) *m/z* 168.7 (100), 160.6 (13), 150.7 (11), 124.9 (29), 112.9 (10); HR-ESI-MS *m/z* 347.1706 $[M+H]^+$ (calcd for $C_{16}H_{27}O_8^+$, 347.1700, Δ = +1.6 ppm); CD (MeOH) $\Delta\varepsilon_{215}$ −2.3833.

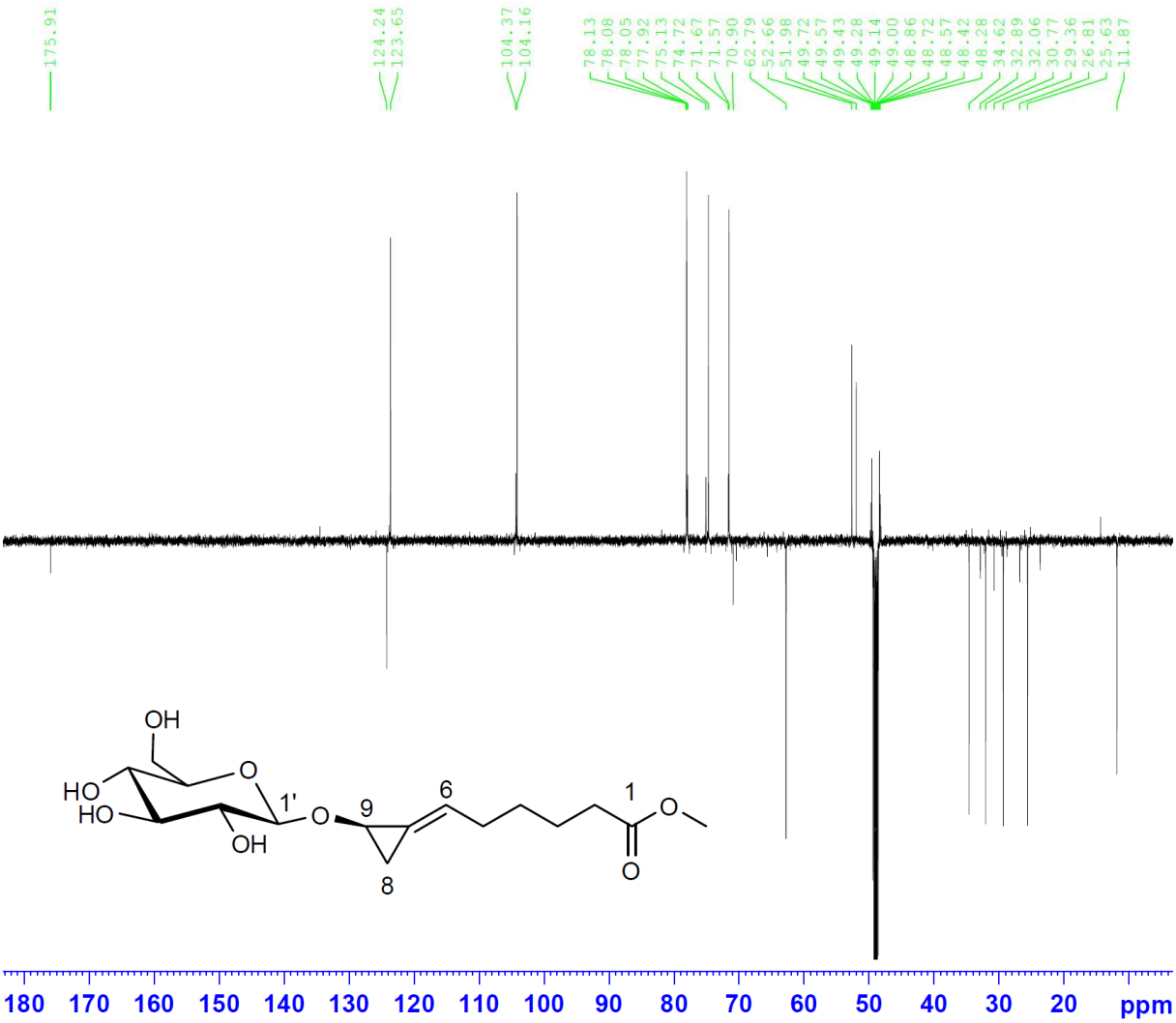
S23:

^{1}H NMR (MeOH-d4, 600 MHz) of Compound **4**



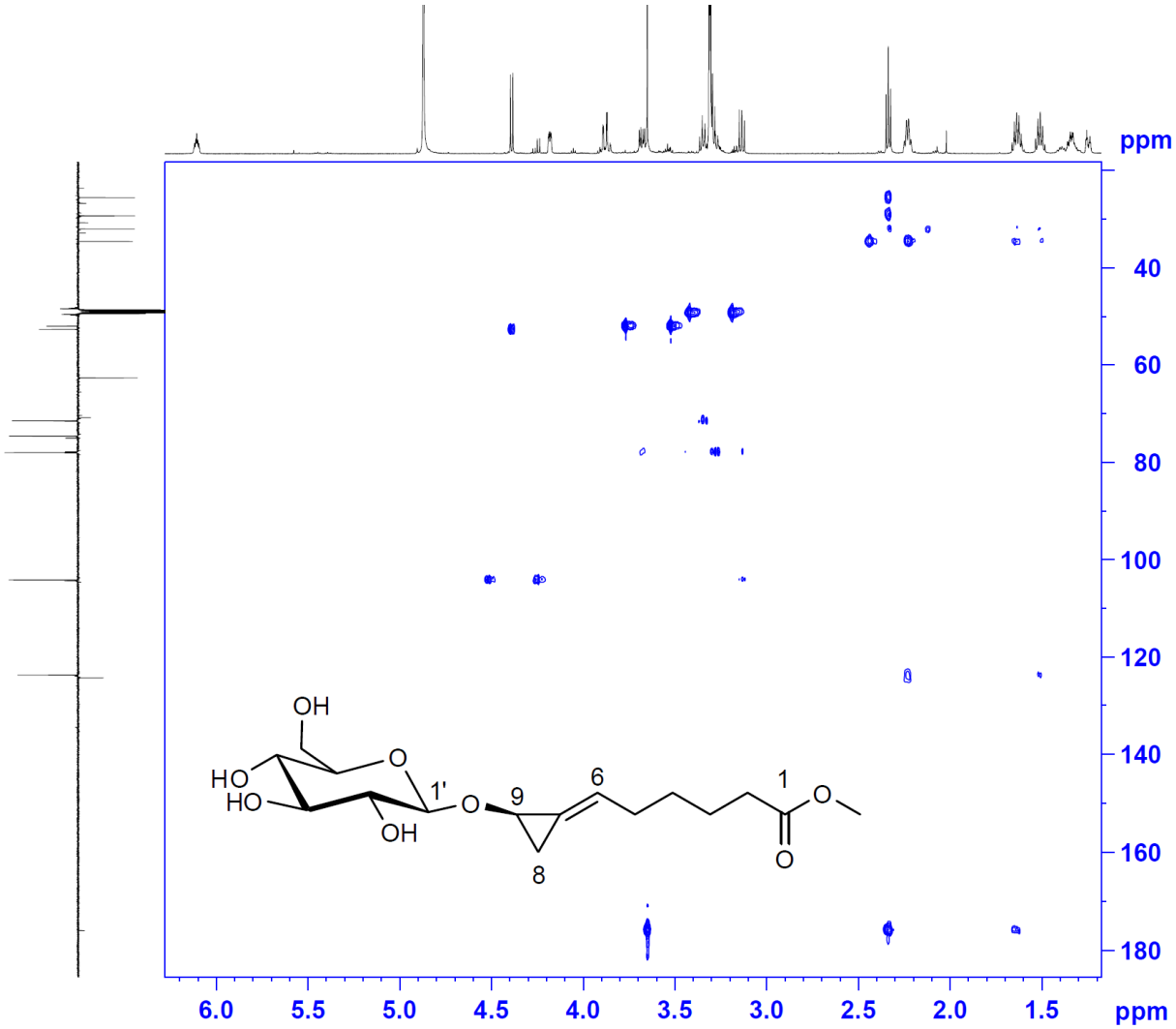
S24:

^{13}C NMR (MeOH-d4, 150 MHz) of Compound **4**



S25:

HMBC (MeOH-d4, 600 MHz) of Compound **4**



S26:

HSQC (MeOH-d4, 600 MHz) of Compound **4**