

**SUPPORTING INFORMATION:**

**Lignans, Amides, and Saponins from *Haplophyllum tuberculatum* and their Antiprotozoal Activity**

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**Table S 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectroscopic Data for Compound **1** and **2** (DMSO-*d*<sub>6</sub>; 500.13 MHz for  $^1\text{H}$  and 125.77 for  $^{13}\text{C}$  NMR;  $\delta$  in ppm)

Position	<b>1</b>		<b>2</b>	
	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)
2	81.9, CH	4.98, d (6.4)	86.5, CH	4.34, d (5.8)
3	40.7, CH	2.62, m	43.8, CH	2.20, m
4	40.7, CH	2.62, m	43.8, CH	2.20, m
5	81.9, CH	4.98, d (6.4)	86.5, CH	4.34, d (5.8)
1', 1''	131.4, C		133.1, C	
2', 2''	110.7, CH	6.94, s	110.8, CH	6.95, s
3', 3''	147.2, C		147.5, C	
4', 4''	145.3, C		146.1, C	
5', 5''	115.1, CH	6.79 <sup>b</sup>	115.3, CH	6.78 <sup>b</sup>
6', 6''	118.7, CH	6.79 <sup>b</sup>	118.8, CH	6.81 <sup>b</sup>
3-Me	11.5, CH <sub>3</sub>	0.51, d (6.4)	12.6, CH <sub>3</sub>	0.94, d (6.1)
4-Me	11.5, CH <sub>3</sub>	0.51, d (6.4)	12.6, CH <sub>3</sub>	0.94, d (6.1)
3'-OMe, 3''-OMe	55.6, CH <sub>3</sub>	3.76, s	55.6, CH <sub>3</sub>	3.75, s

<sup>a</sup>  $^{13}\text{C}$  NMR data extracted from HSQC and HMBC spectra, <sup>b</sup> Overlapping signals.

**Table S2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectroscopic Data for Compounds **5-8** (DMSO-*d*<sub>6</sub>; 500.13 MHz for  $^1\text{H}$  and 125.77 for  $^{13}\text{C}$  NMR;  $\delta$  in ppm)

Position	<b>5</b>		<b>6</b>		<b>7</b>		<b>8</b>	
	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)
1	132.2, C		126.8, C		<sup>c</sup>		<sup>c</sup>	
2	112.7, CH	6.76, d (1.5)	111.3, CH	7.14, br s	112.0, CH	7.01, d (1.5)	111.0, CH	7.11, br s
3	147.4, C		148.1, C		<sup>c</sup>		<sup>c</sup>	
4	144.8, C		148.6, C		<sup>c</sup>		<sup>c</sup>	
5	115.2, CH	6.70 <sup>b</sup>	116.1, CH	6.87, d (8.2)	114.8, CH	6.76, d (8.2)	115.9, CH	6.82, d (8.2)
6	120.3, CH	6.59, dd (7.8, 1.4)	121.9, CH	7.03 <sup>b</sup>	124.5, CH	7.14, dd (8.2, 1.5)	121.5, CH	6.98, br d (8.2)
7	30.8, CH <sub>2</sub>	2.72, t (7.6)	139.6, CH	7.46, d (15.6)	<sup>c</sup>		138.8, CH	7.32, d (15.9)
8	37.4, CH <sub>2</sub>	2.34, t (7.8)	119.3, CH	6.56, d (15.6)	<sup>c</sup>		119.3, CH	6.46, d (15.9)
9	171.6, C		166.2, C		16.9, CH <sub>3</sub>	2.03, s	<sup>c</sup>	
10							38.3, CH <sub>2</sub>	3.20 <sup>b</sup>
11							26.9, CH <sub>2</sub>	1.50, m
1'	132.2, C		129.8, C		<sup>c</sup>		<sup>c</sup>	
2'	129.3, CH	6.95, d (8.4)	129.7, CH	7.05 <sup>b</sup>	112.0, CH	7.01, d (1.5)	111.0, CH	7.11, br s
3'	115.2, CH	6.70 <sup>b</sup>	115.5, CH	6.76, d (8.2)	<sup>c</sup>		<sup>c</sup>	
4'	155.7, C		155.9, C		<sup>c</sup>		<sup>c</sup>	
5'	115.2, CH	6.70 <sup>b</sup>	115.5, CH	6.76, d (8.2)	114.8, CH	6.76, d (8.2)	115.9, CH	6.82, d (8.2)
6'	129.3, CH	6.95, d (8.4)	129.7, CH	7.05 <sup>b</sup>	124.5, CH	7.14, dd (8.2, 1.5)	121.5, CH	6.98, br d (8.2)
7'	34.4, CH <sub>2</sub>	2.58, t (7.3)	34.7, CH <sub>2</sub>	2.73, t (7.0)	<sup>c</sup>		138.8, CH	7.32, d (15.9)
8'	40.5, CH <sub>2</sub>	3.22, dt (5.2, 6.7)	40.9, CH <sub>2</sub>	3.45, dt (5.5, 5.5)	<sup>c</sup>		119.3, CH	6.46, d (15.9)
9'					16.9, CH <sub>3</sub>	2.03, s	<sup>c</sup>	
10'							38.3, CH <sub>2</sub>	3.20 <sup>b</sup>
11'							26.9, CH <sub>2</sub>	1.50, m
3-OMe	55.7, CH <sub>3</sub>	3.75, s	55.9, CH <sub>3</sub>	3.81, s				
3'-OMe					55.5, CH <sub>3</sub>	3.70, s	55.5, CH <sub>3</sub>	3.81, s
NH		7.77, t (5.2)		7.97, t (5.5)				7.93, t (4.9)

<sup>a</sup> $^{13}\text{C}$  NMR data extracted from HSQC and HMBC spectra, <sup>b</sup> Overlapping signals, <sup>c</sup> Signal not visible due to low amount of compound.

**Table S3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectroscopic Data for Compounds **9-10** (DMSO-*d*<sub>6</sub>; 500.13 MHz for  $^1\text{H}$  and 125.77 for  $^{13}\text{C}$  NMR;  $\delta$  in ppm)

Position	<b>9</b>		<b>10</b>	
	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)
1	126.3, C		132.3, C	
2	111.1, CH	7.11 <sup>b</sup>	113.1, CH	6.68 <sup>b</sup>
3	147.8, C		147.2, C	
4	147.6, C		144.2, C	
5	115.7, CH	6.82, d (7.9)	115.0, CH	6.70 <sup>b</sup>
6	121.7, CH	6.97, dd (7.9, 1.5)	121.0, CH	6.57, dt (7.8, 2.5)
7	139.1, CH	7.31, d (15.6)	32.0, CH <sub>2</sub>	2.56, dd (13.7, 5.5) 2.32 <sup>b</sup>
8	119.0, CH	6.52, d (15.9)	45.7, CH	1.67, m
9	165.5, C		61.0, CH <sub>2</sub>	3.34, dd (12.5, 7.0)
1'	130.5, C		132.3, C	
2'	127.7, CH	7.11 <sup>b</sup>	113.1, CH	6.68 <sup>b</sup>
3'	115.1, CH	6.77, d (8.2)	147.2, C	
4'	157.2, C		144.2, C	
5'	115.1, CH	6.77, d (8.2)	115.0, CH	6.70 <sup>b</sup>
6'	127.7, CH	7.11 <sup>b</sup>	121.0, CH	6.57, dt (7.8, 2.5, 2.5)
7'	79.5, CH	4.28, dd (7.5, 5.0)	39.1, CH <sub>2</sub>	2.64, dd (13.7, 6.4) 2.32 <sup>b</sup>
8'	45.3, CH <sub>2</sub>	3.34, d	33.6, CH	2.04, m
9'			15.1, CH <sub>3</sub>	0.82, d (6.7)
1''	63.3, CH <sub>2</sub>	3.31, q (7.0)		
2''	15.1, CH <sub>3</sub>	1.10, t (6.9)		
3-OMe	55.7, CH <sub>3</sub>	3.81, s	55.4, CH <sub>3</sub>	3.73, s
3'-OMe			55.4, CH <sub>3</sub>	3.73, s
NH		7.86, t (5.5)		

<sup>a</sup>  $^{13}\text{C}$  NMR data extracted from HSQC and HMBC spectra, <sup>b</sup> Overlapping signals.

**Table S4.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectroscopic Data for Compounds **11-13** (DMSO-*d*<sub>6</sub>; 600.18 Hz for  $^1\text{H}$  and 150.92 for  $^{13}\text{C}$  NMR;  $\delta$  in ppm)

Position	11		12		13	
	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)	$\delta_{\text{C}}^a$	$\delta_{\text{H}}$ (mult <i>J</i> in Hz)
1	37.2, CH <sub>2</sub>	1.78 <sup>b</sup> 0.96 <sup>b</sup>	37.2, CH <sub>2</sub>	1.78 <sup>b</sup> 0.96 <sup>b</sup>	37.1, CH <sub>2</sub>	1.76 <sup>b</sup> 0.96 <sup>b</sup>
2	29.4, CH <sub>2</sub>	1.77 <sup>b</sup> 1.44 <sup>b</sup>	29.4, CH <sub>2</sub>	1.77 <sup>b</sup> 1.44 <sup>b</sup>	29.4, CH <sub>2</sub>	1.78 <sup>b</sup> 1.43 <sup>b</sup>
3	76.9, CH	3.46 <sup>b</sup>	76.9, CH	3.46 <sup>b</sup>	76.9, CH	3.46 <sup>b</sup>
4	38.1, CH <sub>2</sub>	2.39, br d (11.4) 2.15, dd (11.4, 11.4)	38.1, CH <sub>2</sub>	2.39, br d (11.4) 2.15, dd (11.4, 11.4)	38.0, CH <sub>2</sub>	2.38 <sup>c</sup> 2.15 <sup>c</sup>
5	140.7, C		140.7, C		140.6, C	
6	121.8, CH	5.33, m	121.8, CH	5.33, m	121.5, CH	5.30 <sup>c</sup>
7	31.9, CH <sub>2</sub>	1.91 <sup>b</sup> 1.49 <sup>b</sup>	31.9, CH <sub>2</sub>	1.91 <sup>b</sup> 1.49 <sup>b</sup>	31.8, CH <sub>2</sub>	1.92 <sup>b</sup> 1.47 <sup>b</sup>
8	31.4, CH	1.54 <sup>b</sup>	31.4, CH	1.54 <sup>b</sup>	31.3, CH	1.53 <sup>b</sup>
9	50.0, CH	0.88 <sup>b</sup>	50.0, CH	0.88 <sup>b</sup>	50.0, CH	0.87 <sup>b</sup>
10	36.8, C		36.8, C		36.8, C	
11	20.8, CH <sub>2</sub>	1.47 <sup>b</sup> 1.38 <sup>b</sup>	20.8, CH <sub>2</sub>	1.47 <sup>b</sup> 1.38 <sup>b</sup>	20.7, CH <sub>2</sub>	1.46 <sup>b</sup> 1.37 <sup>b</sup>
12	39.5, CH <sub>2</sub>	1.67 <sup>b</sup> 1.12 <sup>b</sup>	39.5, CH <sub>2</sub>	1.67 <sup>b</sup> 1.12 <sup>b</sup>	39.5, CH <sub>2</sub>	1.67 <sup>b</sup> 1.11 <sup>b</sup>
13	40.2, C		40.2, C		39.8, C	
14	56.2, CH	1.07 <sup>b</sup>	56.2, CH	1.07 <sup>b</sup>	56.2, CH	1.05 <sup>b</sup>
15	31.8, CH <sub>2</sub>	1.88 <sup>b</sup> 1.17 <sup>b</sup>	31.8, CH <sub>2</sub>	1.88 <sup>b</sup> 1.17 <sup>b</sup>	31.4, CH <sub>2</sub>	1.86 <sup>b</sup> 1.17 <sup>b</sup>
16	80.7, CH	4.27 <sup>b</sup>	80.7, CH	4.27 <sup>b</sup>	80.5, CH	4.26 <sup>b</sup>
17	62.0, CH	1.65 <sup>b</sup>	62.0, CH	1.65 <sup>b</sup>	61.8, CH	1.64 <sup>b</sup>
18	16.4, CH <sub>3</sub>	0.72, s	16.4, CH <sub>3</sub>	0.72, s	16.3, CH <sub>3</sub>	0.71 <sup>b</sup>
19	19.4, CH <sub>3</sub>	0.94, s	19.4, CH <sub>3</sub>	0.94, s	19.2, CH <sub>3</sub>	0.93, s
20	42.0, CH	1.75 <sup>b</sup>	42.0, CH	1.75 <sup>b</sup>	41.4, CH	1.78 <sup>b</sup>
21	14.9, CH <sub>3</sub>	0.92, d (5.6)	14.9, CH <sub>3</sub>	0.92, d (5.6)	14.6, CH <sub>3</sub>	0.88 <sup>c</sup>
22	109.4, C		109.4, C		108.5, C	
23	25.9, CH <sub>2</sub>	1.80 <sup>b</sup> 1.26 <sup>b</sup>	25.9, CH <sub>2</sub>	1.80 <sup>b</sup> 1.26 <sup>b</sup>	30.9, CH <sub>2</sub>	1.60 <sup>b</sup> 1.45 <sup>b</sup>
24	25.8, CH <sub>2</sub>	1.87 <sup>b</sup> 1.33 <sup>b</sup>	25.8, CH <sub>2</sub>	1.87 <sup>b</sup> 1.33 <sup>b</sup>	28.5, CH <sub>2</sub>	1.54 <sup>b</sup> 1.29 <sup>b</sup>
25	26.8, CH	1.63 <sup>b</sup>	26.8, CH	1.63 <sup>b</sup>	30.1, CH	1.50 <sup>b</sup>
26	64.7, CH <sub>2</sub>	3.78, br d (10.0) 3.21 <sup>b</sup>	64.7, CH <sub>2</sub>	3.78, br d (10.0) 3.21 <sup>b</sup>	65.9, CH <sub>2</sub>	3.38 <sup>b</sup> 3.17 <sup>b</sup>
27	16.3, CH <sub>3</sub>	0.99, d (6.0)	16.3, CH <sub>3</sub>	0.99, d (6.0)	17.4, CH <sub>3</sub>	0.71 <sup>b</sup>
1- Glc1	98.4, CH	4.43, d (7.5)	98.4, CH	4.43, d (7.5)	98.4, CH	4.41 <sup>b</sup>
2- Glc1	76.4, CH	3.22 <sup>b</sup>	76.4, CH	3.22 <sup>b</sup>	76.0, CH	3.23 <sup>b</sup>
3- Glc1	76.4, CH	3.50 <sup>b</sup>	76.4, CH	3.50 <sup>b</sup>	76.3, CH	3.51 <sup>b</sup>
4- Glc1	81.1, CH	3.32 <sup>b</sup>	81.1, CH	3.32 <sup>b</sup>	81.0, CH	3.34 <sup>b</sup>
5- Glc1	74.9, CH	3.28 <sup>b</sup>	74.9, CH	3.28 <sup>b</sup>	74.7, CH	3.27 <sup>b</sup>
6- Glc1	60.5, CH <sub>2</sub>	3.69 <sup>b</sup> 3.58 <sup>b</sup>	60.5, CH <sub>2</sub>	3.69 <sup>b</sup> 3.58 <sup>b</sup>	60.5, CH <sub>2</sub>	3.70 <sup>b</sup> 3.59 <sup>b</sup>

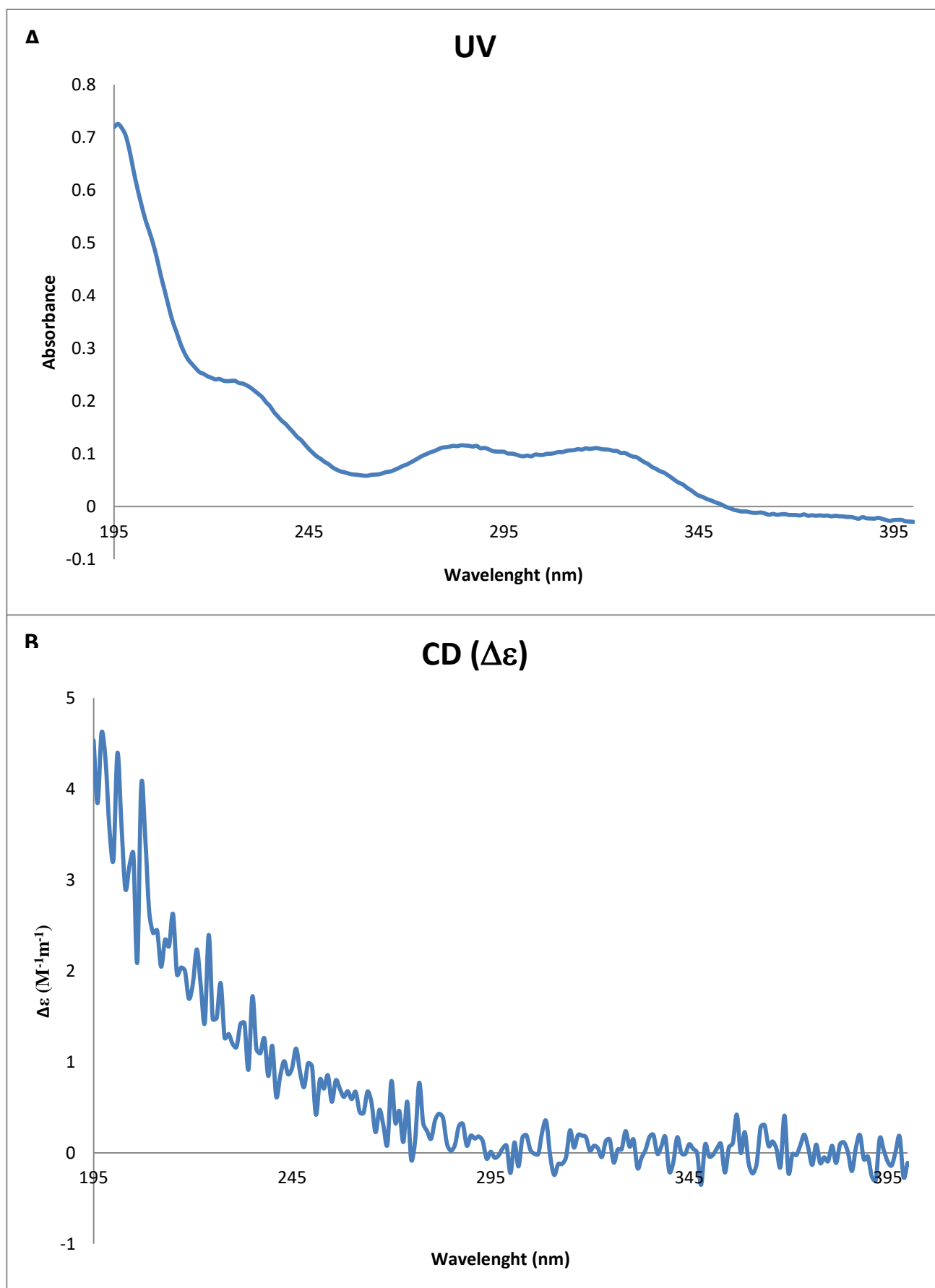
<sup>a</sup>  $^{13}\text{C}$  NMR data extracted from HSQC and HMBC spectra, <sup>b</sup> Overlapping signals, <sup>c</sup> broad signal due to concentrated sample.

(continued next page)

**Table S4.** (continued)

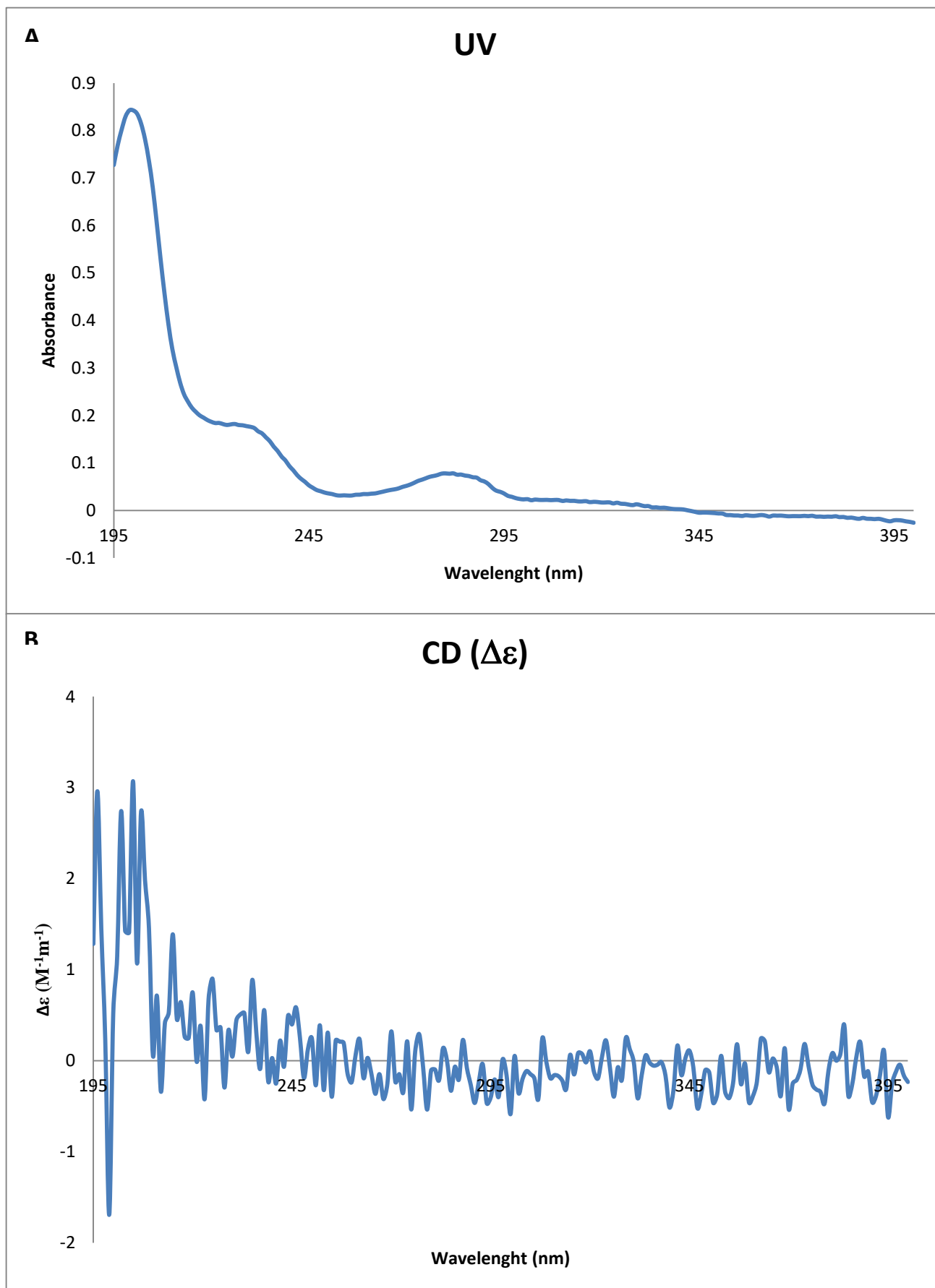
Position	11		12		13	
	$\delta_c^a$	$\delta_H$ (mult $J$ in Hz)	$\delta_c^a$	$\delta_H$ (mult $J$ in Hz)	$\delta_c^a$	$\delta_H$ (mult $J$ in Hz)
1- Rha1	100.4, CH	5.04, br s	100.4, CH	5.04, br s		
2- Rha1	70.8, CH	3.63 <sup>b</sup>	70.8, CH	3.63 <sup>b</sup>	70.7, CH	3.64 <sup>b</sup>
3- Rha1	71.0, CH	3.40 <sup>b</sup>	71.0, CH	3.40 <sup>b</sup>	70.9, CH	3.40 <sup>b</sup>
4- Rha1	72.3, CH	3.18 <sup>b</sup>	72.3, CH	3.18 <sup>b</sup>	72.2, CH	3.19 <sup>b</sup>
5- Rha1	68.3, CH	3.97, m	68.3, CH	3.97, m	68.2, CH	3.97 <sup>c</sup>
6- Rha1	18.2, CH <sub>3</sub>	1.07 <sup>b</sup>	18.2, CH <sub>3</sub>	1.07 <sup>b</sup>	18.0, CH <sub>3</sub>	1.08 <sup>b</sup>
1- Glc2	103.0, CH	4.34, d (7.5)	103.2, CH	4.28 <sup>b</sup>	102.9, CH	4.34 <sup>b</sup>
2- Glc2	73.1, CH	3.18 <sup>b</sup>	74.4, CH	3.09 <sup>b</sup>	72.9, CH	3.20 <sup>b</sup>
3- Glc2	86.4, CH	3.40 <sup>b</sup>	81.3, CH	3.38 <sup>b</sup>	86.2, CH	3.41 <sup>b</sup>
4- Glc2	68.4, CH	3.16 <sup>b</sup>	68.7, CH	3.11 <sup>b</sup>	68.3, CH	3.16 <sup>b</sup>
5- Glc2	76.9, CH	3.24 <sup>b</sup>	77.0, CH	3.24 <sup>b</sup>	76.4, CH	3.26 <sup>b</sup>
6- Glc2	61.1, CH <sub>2</sub>	3.66 <sup>b</sup> 3.42 <sup>b</sup>	61.1, CH <sub>2</sub>	3.66 <sup>b</sup> 3.42 <sup>b</sup>	60.9, CH <sub>2</sub>	3.68 <sup>b</sup> 3.41 <sup>b</sup>
1- Xyl	105.0, CH	4.38, d (7.1)	-	-	104.7, CH	4.38 <sup>b</sup>
2- Xyl	74.1, CH	3.05 <sup>b</sup>	-	-	73.9, CH	3.06 <sup>b</sup>
3- Xyl	76.6, CH	3.13 <sup>b</sup>	-	-	76.1, CH	3.14 <sup>b</sup>
4- Xyl	69.8, CH	3.29 <sup>b</sup>	-	-	69.6, CH	3.30 <sup>b</sup>
5- Xyl	66.2, CH <sub>2</sub>	3.72 <sup>b</sup> 3.06 <sup>b</sup>	-	-	66.0, CH <sub>2</sub>	3.73 <sup>b</sup> 3.08 <sup>b</sup>
1- Rha2	-	-	101.0, CH	5.01, br s		
2- Rha2	-	-	70.9, CH	3.69 <sup>b</sup>		
3- Rha2	-	-	70.9, CH	3.47 <sup>b</sup>		
4- Rha2	-	-	72.4, CH	3.17 <sup>b</sup>		
5- Rha2	-	-	68.5, CH	3.87, m		
6- Rha2	-	-	18.2, CH <sub>3</sub>	1.07 <sup>b</sup>		

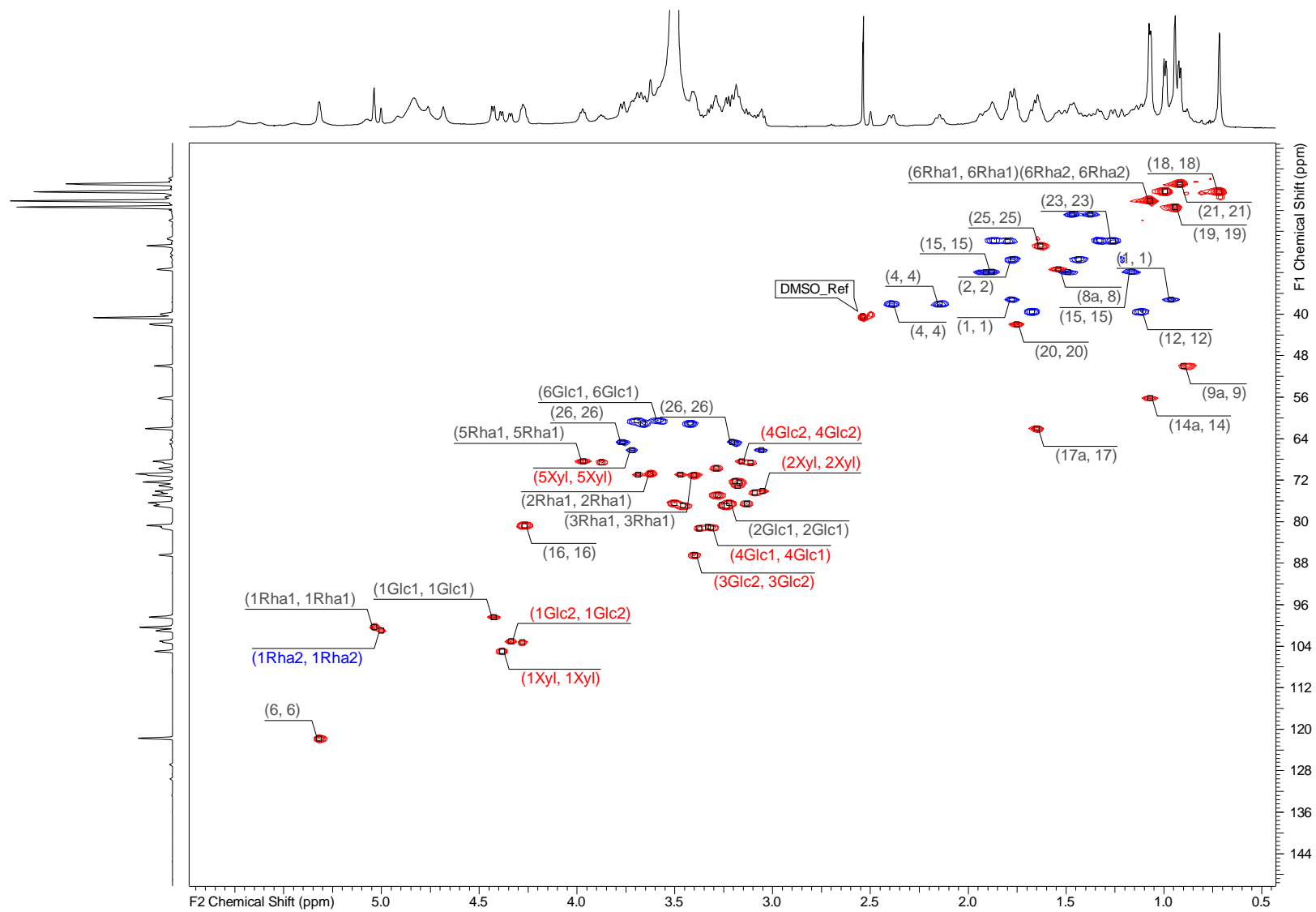
<sup>a</sup> <sup>13</sup>C NMR data extracted from HSQC and HMBC spectra, <sup>b</sup> Overlapping signals, <sup>c</sup> broad signal due to concentrated sample.



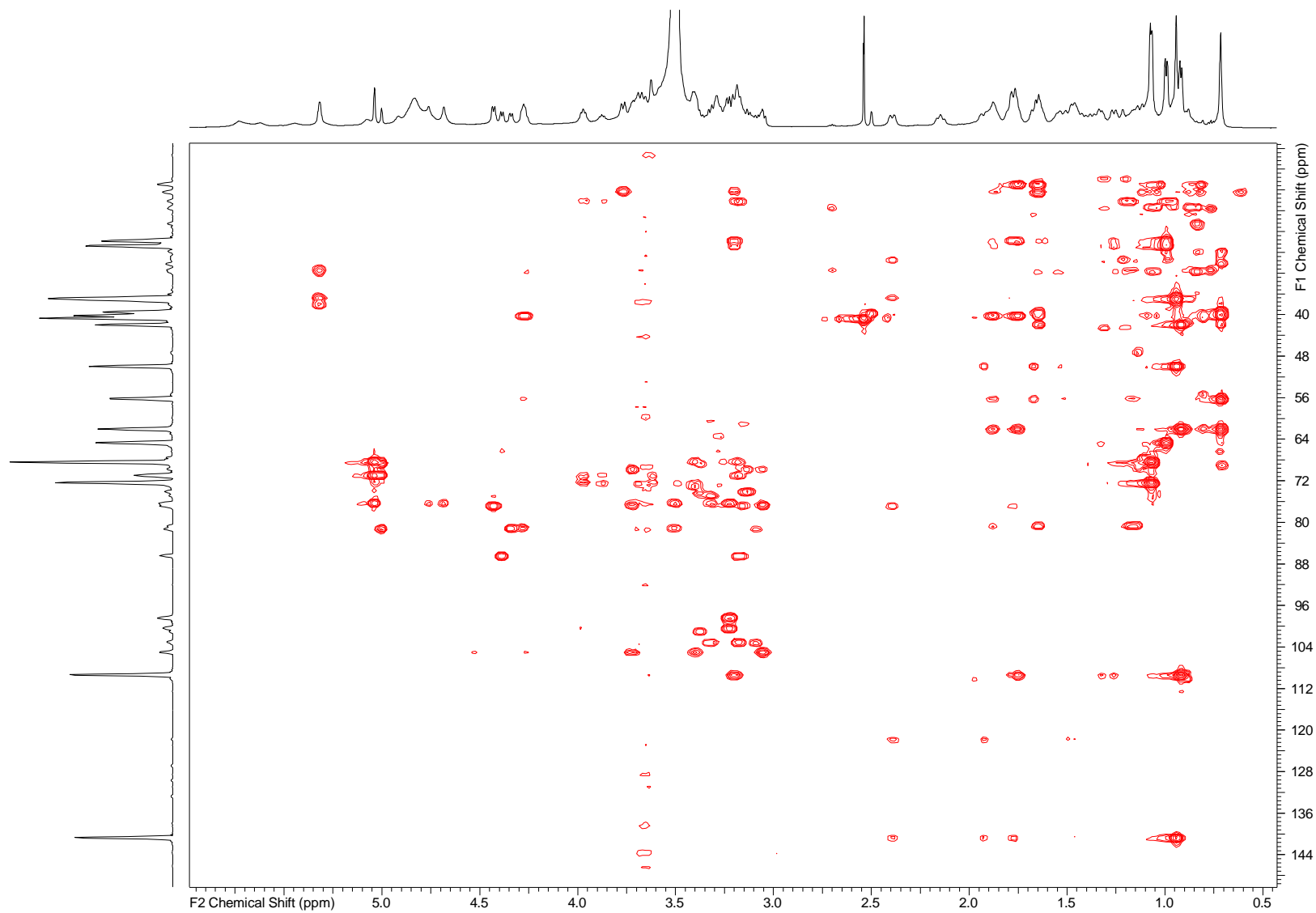
**Figure S2.** UV (A) and ECD (B) spectra for compound **9** in MeOH (0.07 mg/mL).



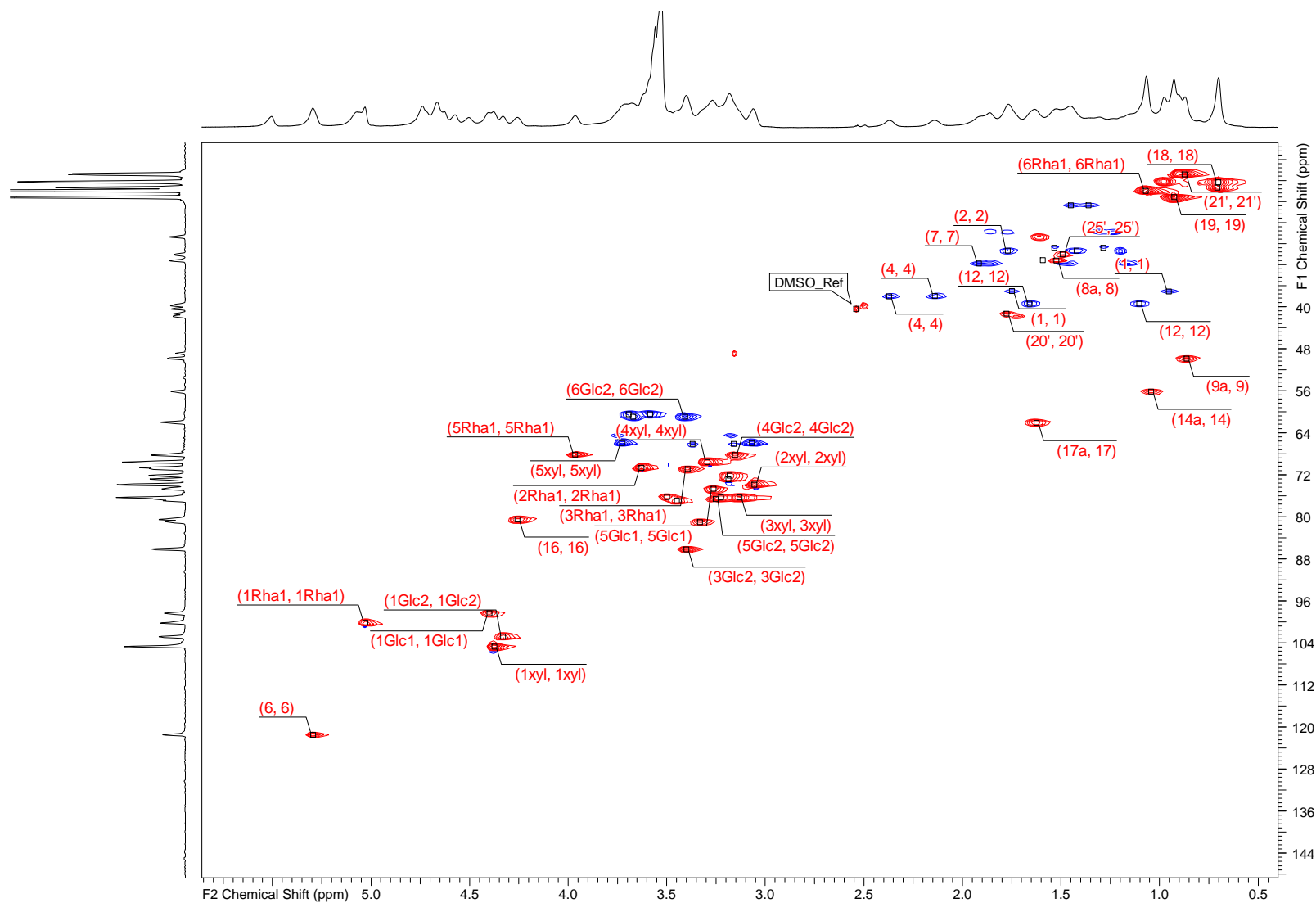




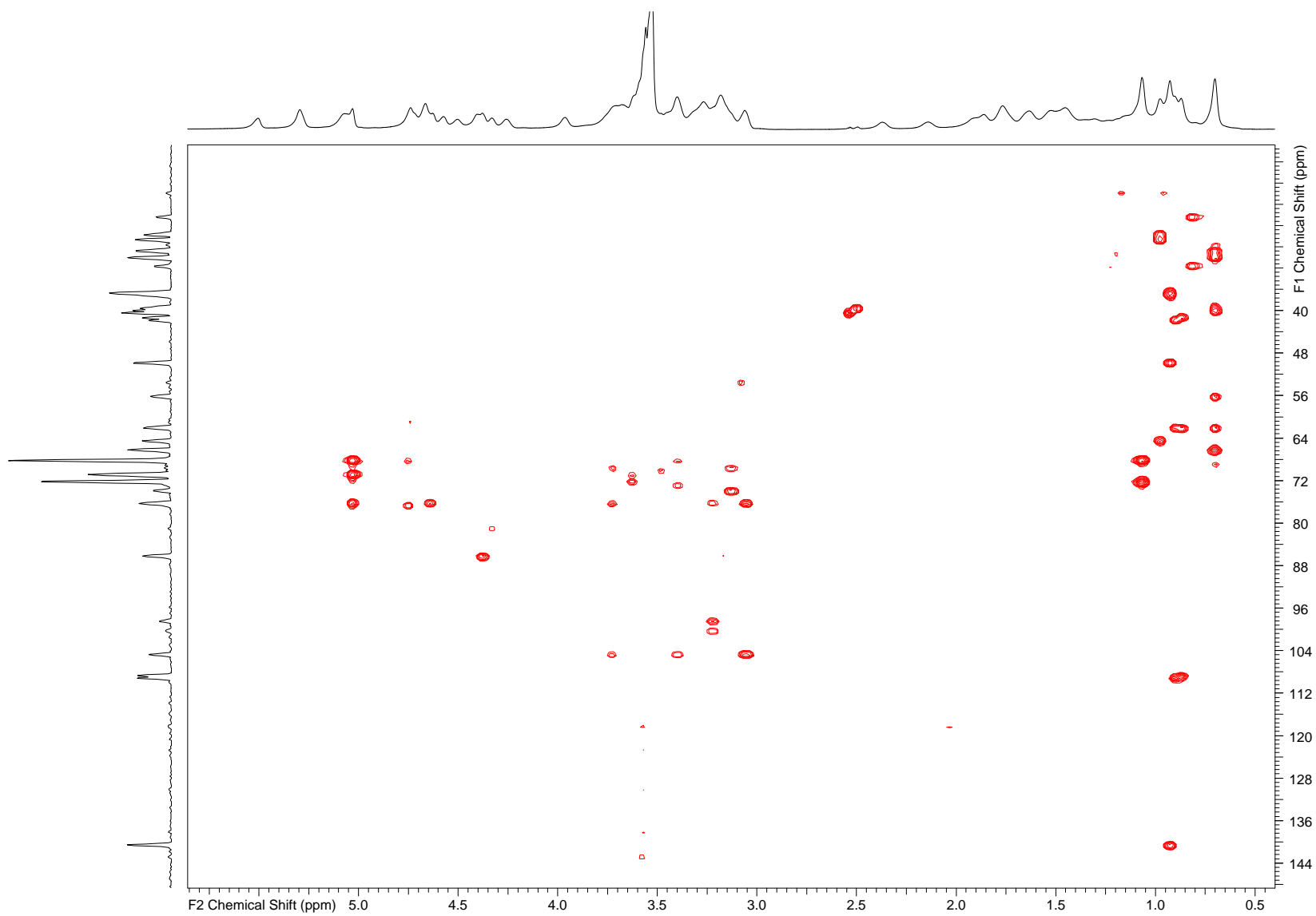
**Figure S3.** HSQC-DEPT spectrum of the mixture of compounds **11** (in red and black) and **12** (in blue and black) (500 MHz, DMSO)



**Figure S4.** HMBC spectrum of the mixture of compounds **11** and **12** (500 MHz, DMSO)



**Figure S5.** HSQC-DEPT spectrum of the mixture of compounds **11** and **13** (labelled in red, a prime was added for signals differing from **11**) (500 MHz, DMSO)



**Figure S6.** HMBC spectrum of the mixture of compounds **11** and **13** (500 MHz, DMSO)