

*Supplementary Materials*

# Friends or Foes? Cytotoxicity, HPTLC and NMR Analyses of Some Important Naturally Occurring Hydroxyanthraquinones

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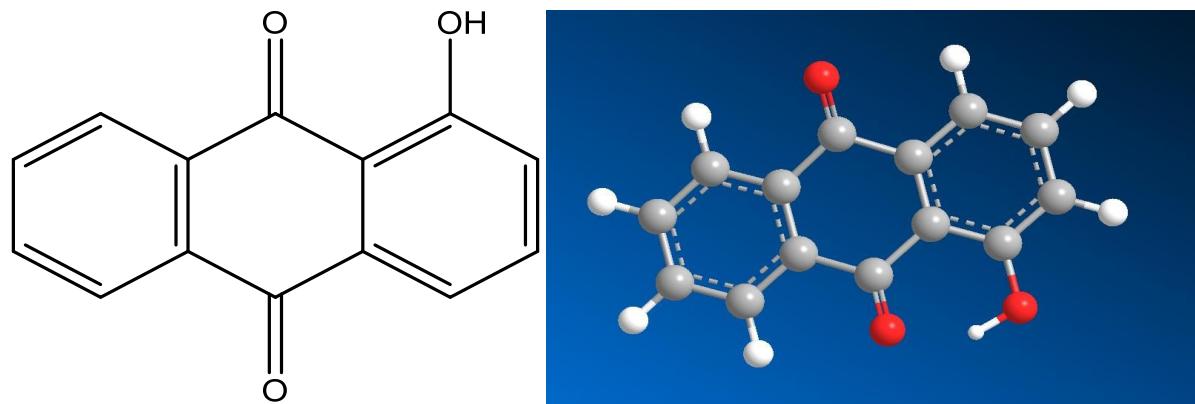
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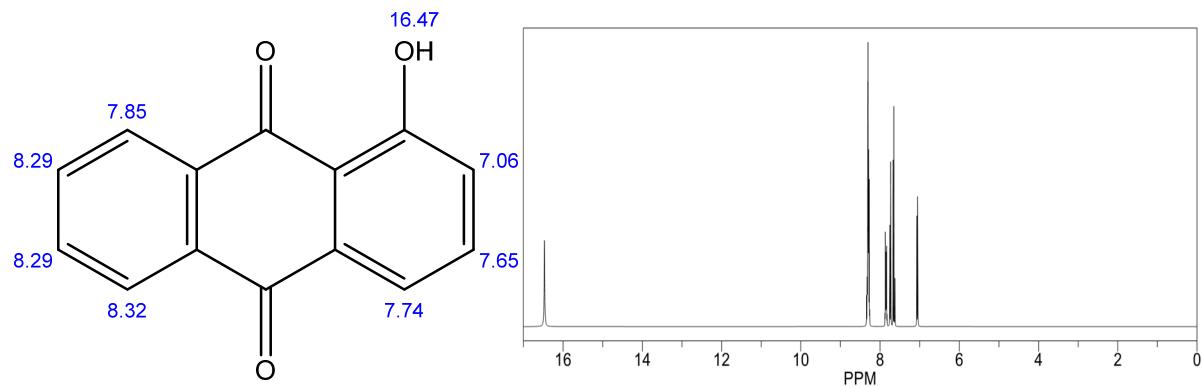
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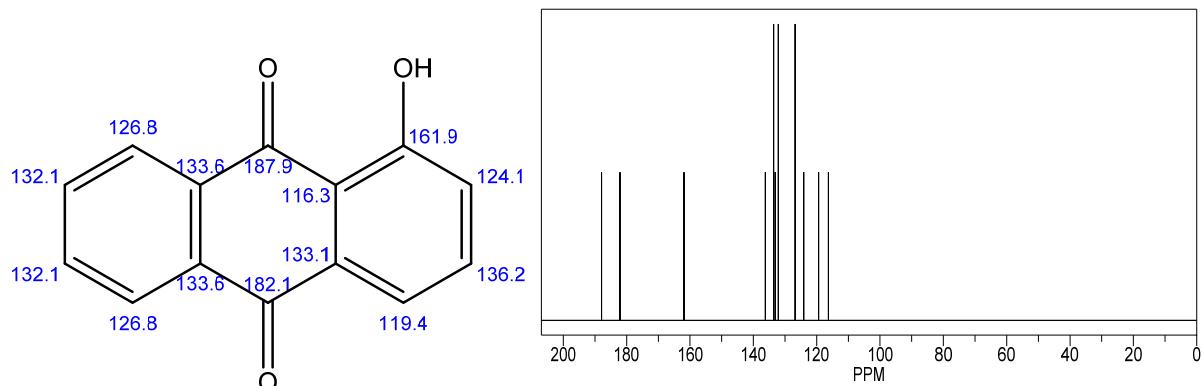
## 1. NMR Prediction



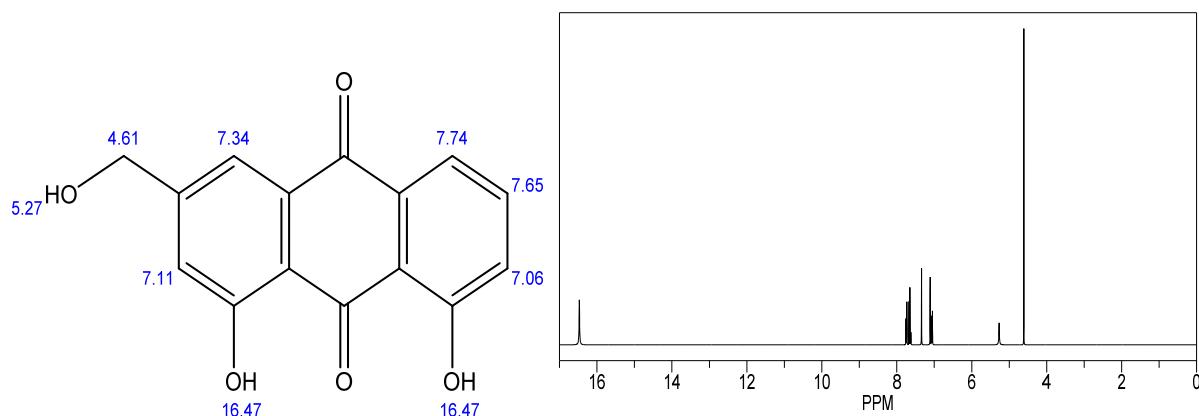
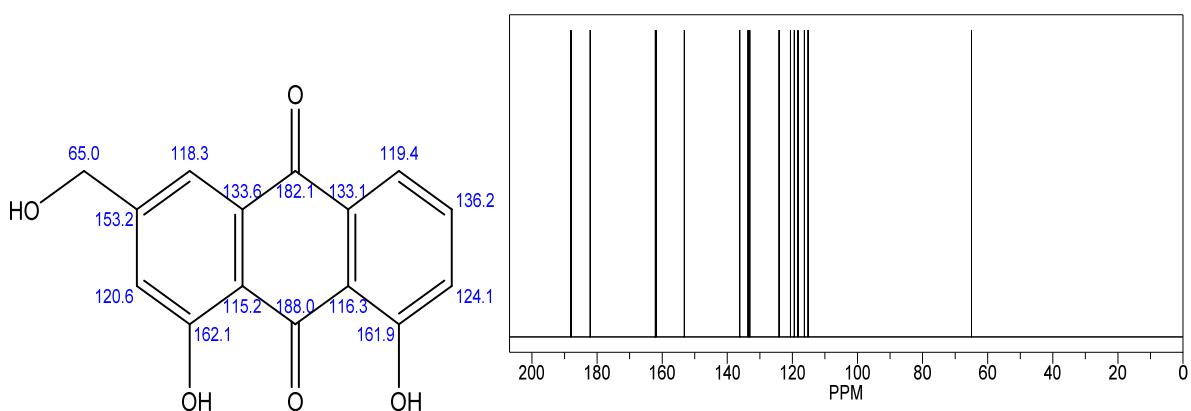
**Figure S1-1** 2D and 3D chemical structure of Hydroxyanthraquinones (Source: ChemDraw Professional).



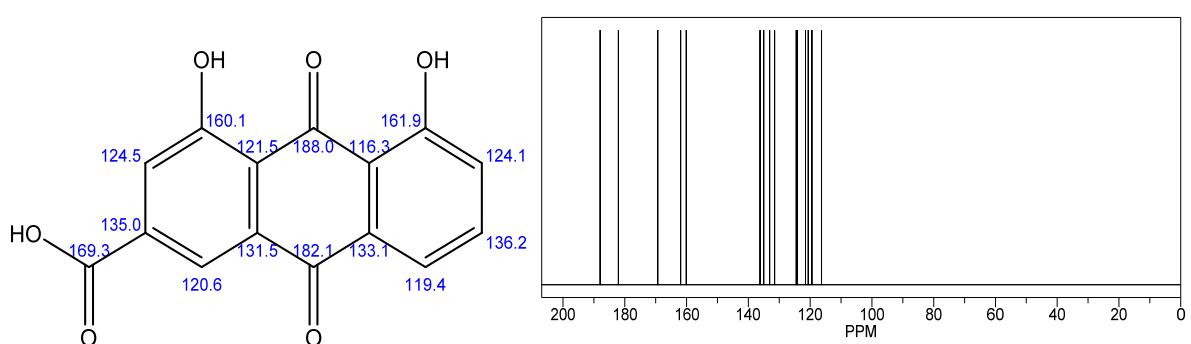
**Figure S0-1** Chem NMR <sup>1</sup>H Estimation of Hydroxyanthraquinones (Source: ChemDraw Professional)



**Figure S0-2** Chem NMR <sup>13</sup>C Estimation of Hydroxyanthraquinones (Source: ChemDraw Professional)

**Aloe-emodin****Figure S0-3 Chem NMR  $^1\text{H}$  Estimation of Aloe-emodin (Source: ChemDraw Professional)****Figure S0-4 Chem NMR  $^{13}\text{C}$  Estimation of Aloe-emodin (Source: ChemDraw Professional)**

As per literature “ $^1\text{H}$  NMR (DMSO-d6):  $\delta$  = 4.62 (2H, d,  $J = 6$  Hz), 5.60 (1H, t,  $J = 6$  Hz), 7.29 (1H, s), 7.38 (1H, br d,  $J = 8.4$  Hz), 7.72-7.69 (2H, m), 7.80 (1H, t,  $J = 8.4$  Hz), 11.9 (2H, br s);  $^{13}\text{C}$  NMR (DMSO-d6):  $\delta$  = 62.7, 115.2, 116.7, 117.8, 120.0, 121.4, 125.1, 133.9, 134.1, 138.0, 154.4, 162.0, 162.3, 182.2, 192.4.” (Sanchez et al., 2011)

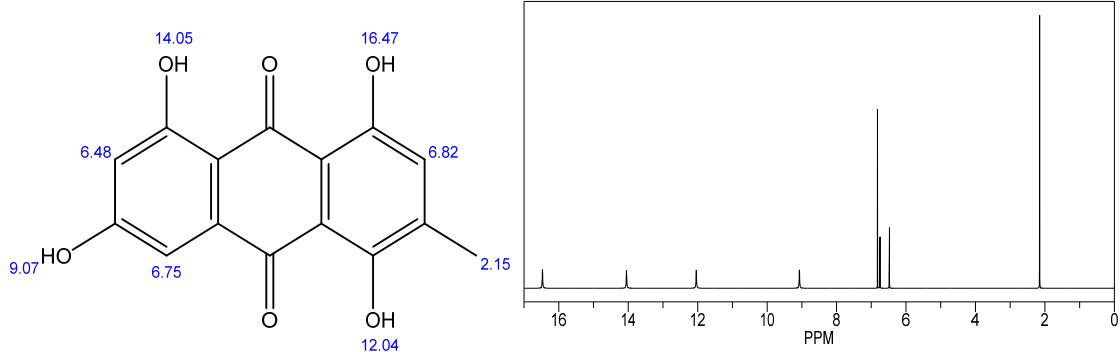
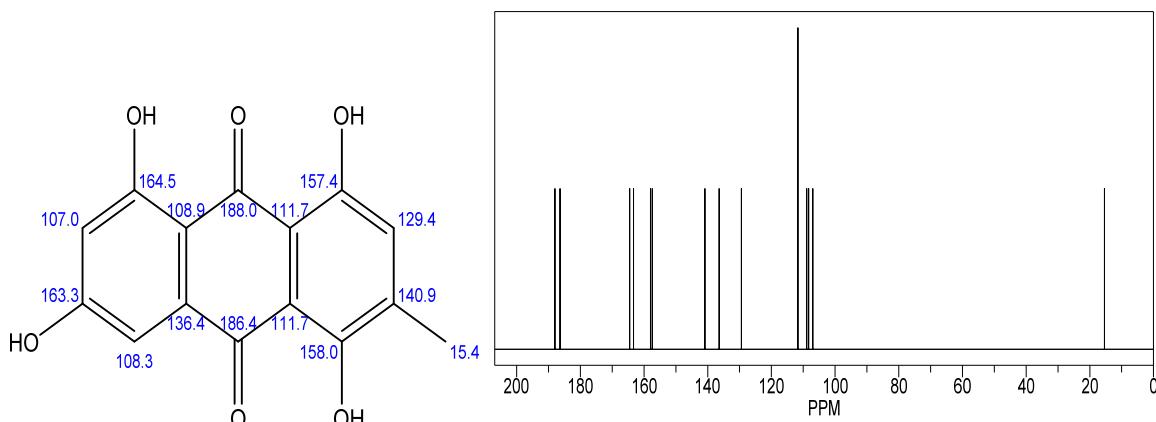
**Rhein****Figure S0-5 Chem NMR  $^{13}\text{C}$  Estimation of Rhein (Source: ChemDraw Professional)**

**Table 1.** <sup>1</sup>H NMR chemical shifts and coupling constants for anthraquinones 1–5

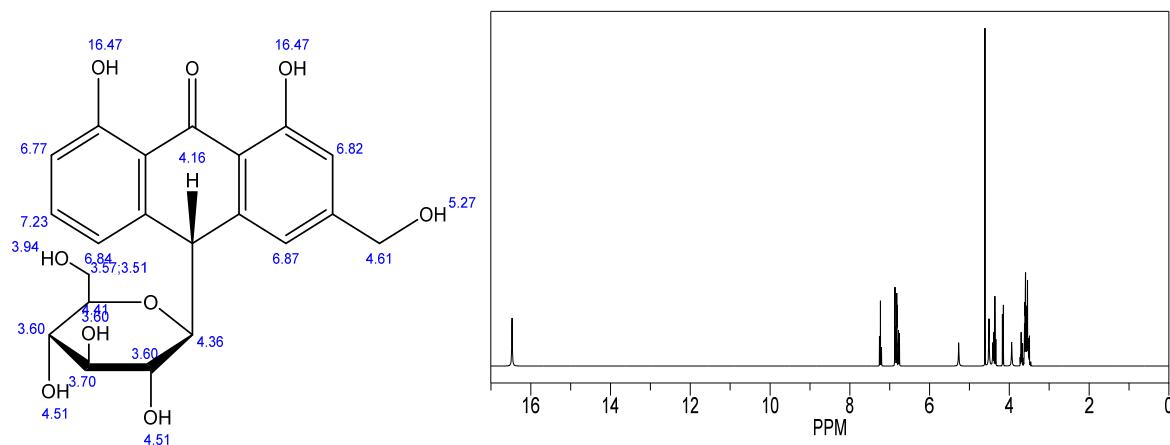
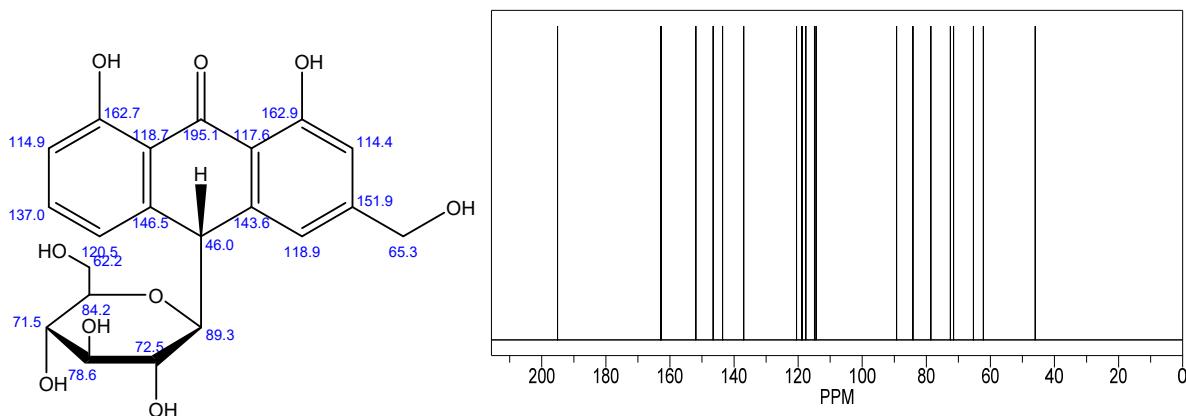
Proton	Chrysophanol (1)	Physcion (2)	Emodin (3)	Aloe-emodin (4)	Rhein (5)	Carbon
H-2	7.22	6.68	6.59	7.29	7.77	C-1
H-4	7.55	7.36	7.12	7.69	8.14	C-2
H-5	7.71	7.62	7.49	7.72	7.75	C-3
H-6	7.80	—	—	7.80	7.84	C-4
H-7	7.38	7.07	7.16	7.38	7.41	C-5
OH-1	11.87	12.30	12.08	11.91	—	C-6
OH-8	11.97	12.11	12.01	11.97	—	C-7
OH-3	—	—	11.37	5.62	—	C-8
CH <sub>3</sub>	2.44	2.44	2.41	—	—	C-9
OCH <sub>3</sub>	—	3.93	—	—	—	C-10
CH <sub>2</sub>	—	—	—	4.63	—	C-11
H-2(m)	0.82, 1.15	2.57	2.46, 0.35	1.66	1.47	C-12
H-4(m)	0.49, 1.15	2.57	2.28, 0.35	1.66	1.47	C-13
H-5(m)	1.31	0.55, 0.92	0.35, 0.53	1.16	1.10	C-14
H-5(α)	7.55	—	—	7.63	7.54	CH <sub>3</sub>
H-6(α)	7.55, 8.37	—	—	7.63, 8.29	7.54, 8.22	21.71
H-7(m)	1.31	0.74, 0.92	0.35, 0.70	1.16	1.10	OCH <sub>3</sub>
H-7(α)	8.37	—	—	8.29	8.22	CH <sub>2</sub>
CH <sub>3</sub> (m)	0.82, 0.49	0.55, 0.74	0.53, 0.70	—	—	COOH

**Table 2.** <sup>13</sup>C NMR chemical shifts for anthraquinones 1–5\*

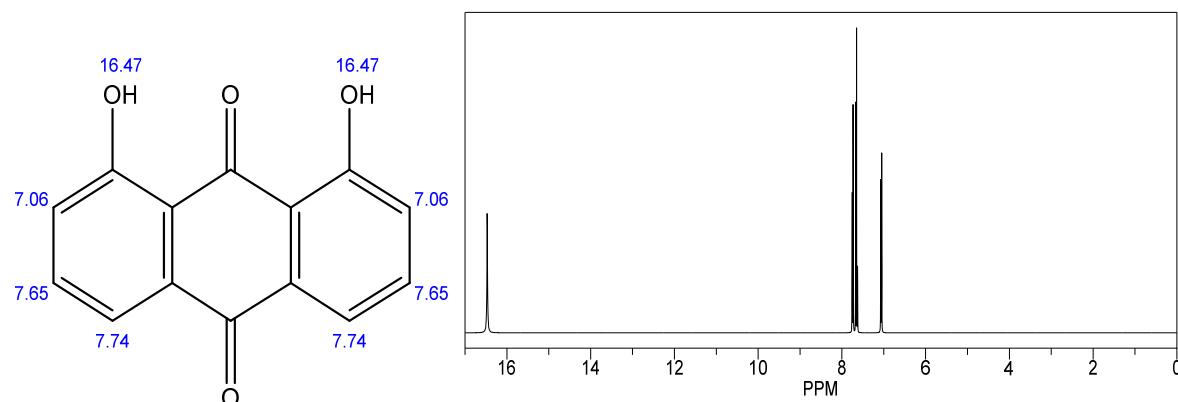
Chrysophanol (1)	Physcion (2)	Emodin (3)	Aloe-emodin (4)	Rhein (5)	Chrysophanol (1)	Physcion (2)	Emodin (3)	Aloe-emodin (4)	Rhein (5)
161.67	165.20	164.54	161.72	161.51	161.67	165.20	164.54	161.72	161.51
124.16	106.78	108.02	120.78	124.21	124.16	106.78	108.02	120.78	124.21
149.26	166.56	165.64	153.80	138.20	149.26	166.56	165.64	153.80	138.20
120.64	108.22	108.84	117.18	119.05	120.64	108.22	108.84	117.18	119.05
119.41	121.29	120.58	119.43	119.48	119.41	121.29	120.58	119.43	119.48
137.41	148.44	148.35	137.42	137.63	137.41	148.44	148.35	137.42	137.63
124.49	124.51	124.23	124.49	124.64	124.49	124.51	124.23	124.49	124.64
161.41	162.51	161.51	161.43	161.27	161.41	162.51	161.51	161.43	161.27
191.72	190.82	189.83	191.74	191.49	191.72	190.82	189.83	191.74	191.49
181.57	182.05	181.48	181.59	181.25	181.57	182.05	181.48	181.59	181.25
133.40	133.23	132.91	133.54	133.41	133.40	133.23	132.91	133.54	133.41
115.94	113.69	113.46	116.01	116.33	115.94	113.69	113.46	116.01	116.33
113.85	110.27	109.06	114.57	118.48	113.85	110.27	109.06	114.57	118.48
133.10	135.27	135.21	133.22	133.61	133.10	135.27	135.21	133.22	133.61
21.71	22.15	21.60	—	—	21.71	22.15	21.60	—	—
—	56.07	—	—	—	—	56.07	—	—	—
—	—	—	62.15	—	—	—	—	62.15	—
—	—	—	—	165.52	—	—	—	—	165.52

Figure S0-6 <sup>1</sup>H and <sup>13</sup>C NMR Chemical Shift of Rhein (Source: Danielsen, Aksnes and Francis, 1992)**Catenarin**Figure S0-7 Chem NMR <sup>1</sup>H Estimation of Catenarin (Source: ChemDraw Professional)Figure S0-8 Chem NMR <sup>13</sup>C Estimation of Catenarin (Source: ChemDraw Professional)

As per literature “<sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum was as follows: 6'-CH<sub>3</sub>: δH 2.35 (d, 3H, J6',7 = 0.8 Hz); 2-H: δH 6.66 (d, 1H, J2,4 = 2.4 Hz); 7-H: δH 7.13 (m, 1H, J7,6' = 0.8 Hz, J7,8 = 0.5 Hz); 4H: δH 7.32 (d, 1H, J4,2 = 2.4 Hz); OH: δH 12.35, 12.42, 13.34.” (Kalidhar, 1989).

**Barbaloin****Figure S0-9 Chem NMR  $^1\text{H}$  Estimation of Barbaloin (Source: ChemDraw Professional)****Figure S0-10 Chem NMR  $^{13}\text{C}$  Estimation of Barbaloin (Source: ChemDraw Professional)**

As per literature “ $^1\text{H}$  NMR (400 MHz, MeOH-d4) δ 7.49 (1H, t,  $J$  7.8 Hz, H6), 7.07 (1H, H5), 7.05 (1H, s, H4), 6.88 (1H, s, 8, H2), 6.82 (1H, d,  $J$  8.2 Hz, H7), 4.66 (1H, s, H15b), 4.65 (1H, s, H15a), 4.61 (1H, d,  $J$  40.9 Hz, H10), 3.56 (1H, dd,  $J$  11.4, 1.6 Hz, H-6b'), 3.41 (1H, dd,  $J$  9.7, 2.4 Hz, H-6a'), 3.37 (1H, m, H-1'), 3.25 (1H, t,  $J$  48.7 Hz, H-3'), 3.01 (1H, t,  $J$  48.7 Hz, H-2'), 2.91 (1H, br s, H-5'), 2.90 (1H, br s, H-4')” (Kim et al., 2017).

**Chrysazin****Figure S0-11 Chem NMR  $^1\text{H}$  Estimation of Chrysazin (Source: ChemDraw Professional)**

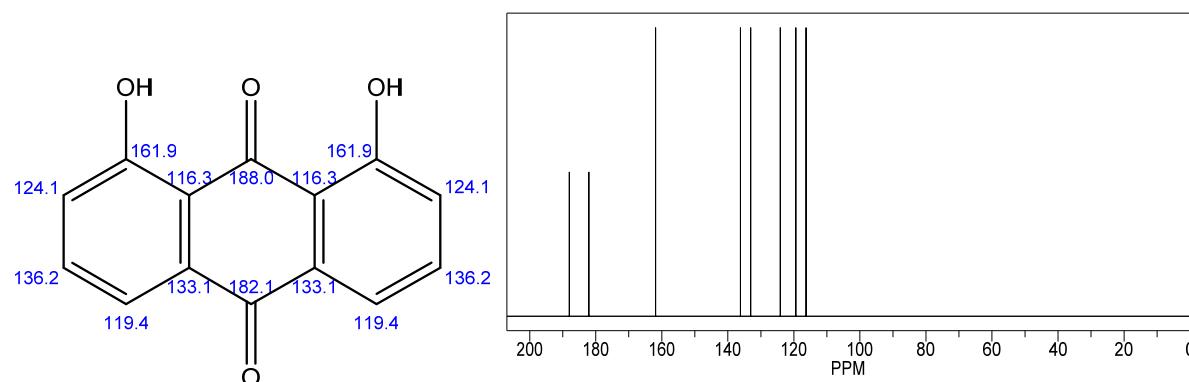


Figure S0-12 Chem NMR  $^{13}\text{C}$  Estimation of Chrysazin (Source: ChemDraw Professional)

As per literature “<sup>1</sup>H NMR (500 MHz, d6-DMSO) δ 11.90 (s, 2H, 2 × OH), 7.80 (dd, J = 8.0, 7.5 Hz, 2H, H3, H6), 7.70 (dd, J = 7.5, 1.0 Hz, 2H, H4, H5), 7.37 (dd, J = 8.5, 1.0 Hz, 2H, H2, H7). <sup>1</sup>H NMR (500 MHz, d5-pyridine) δ 12.20 (s, 2H, 2 × OH), 7.87 (dd, J = 7.5, 1.0 Hz, 1H, H4, H5), 7.62 (dd, J = 8.5, 7.5 Hz, 1H, H3, H6), 7.35 (dd, J = 8.3, 0.8 Hz, 1H, H2, H7); <sup>13</sup>C NMR (125 MHz, d5-pyridine) δ 193.4 (C9), 182.0 (C10), 163.0 (C1, C8), 138.0 (C3, C6), 134.4 (C4a, C10a), 125.1 (C2, C7), 120.2 (C4, C5), 116.7 (C8a, C9a)” (Pullella et al., 2017).

Rugulosin

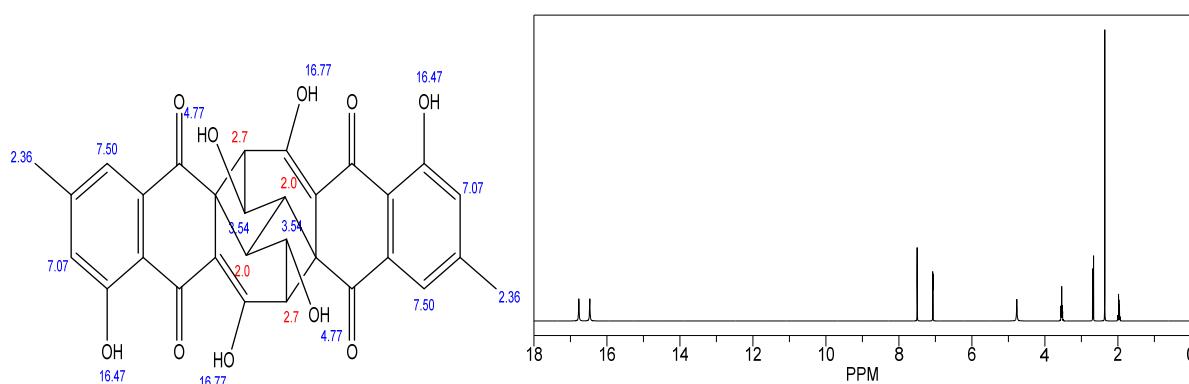
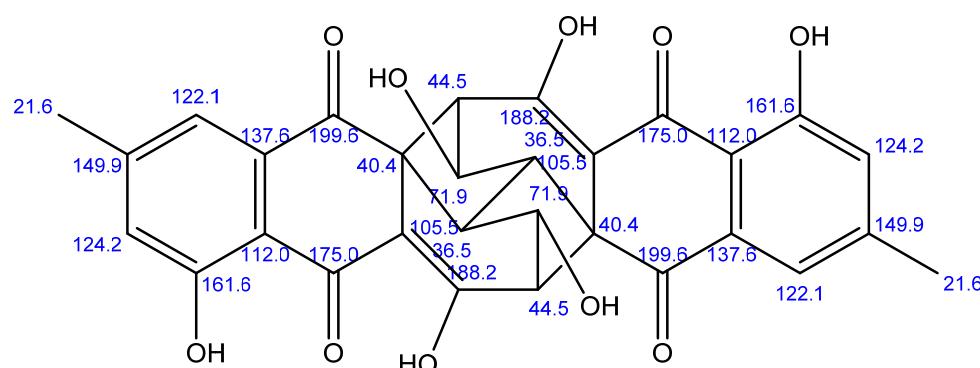
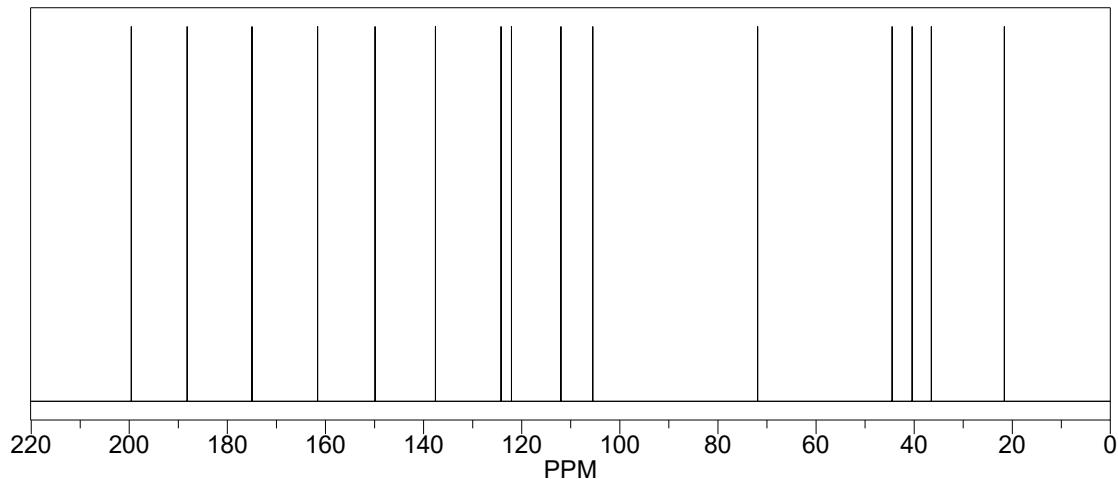


Figure S0-13 Chem NMR  $^1\text{H}$  Estimation of Rugulosin (Source: ChemDraw Professional)

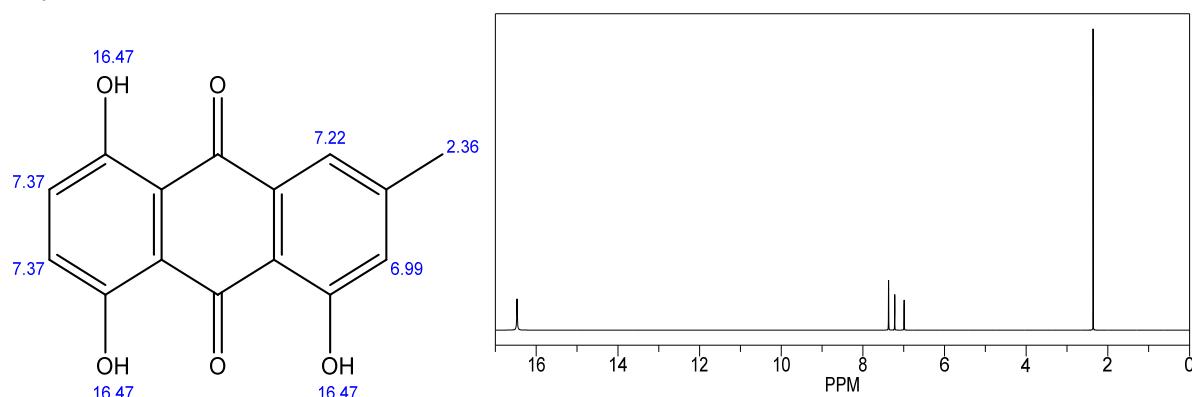




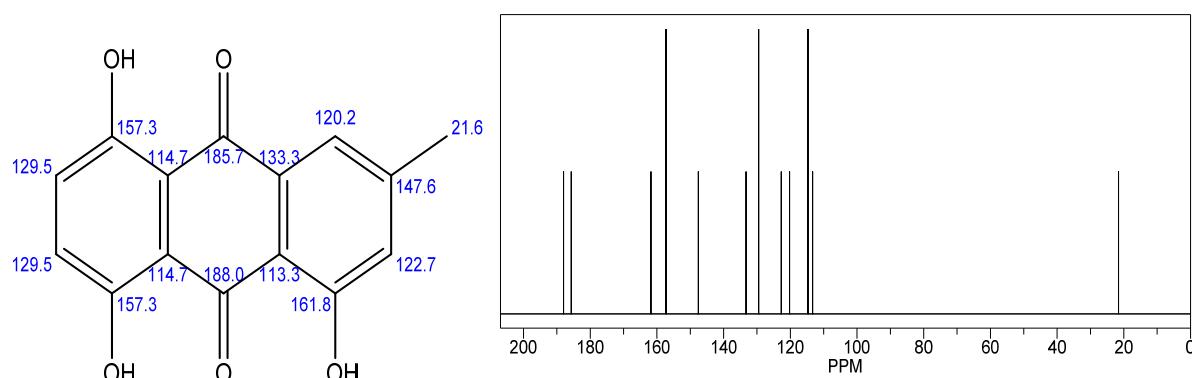
**Figure S0-14 Chem NMR <sup>13</sup>C Estimation of Rugulosin (Source: ChemDraw Professional)**

As per literature “<sup>1</sup>H NMR (DMSO-d<sub>6</sub>) 14.7 (s, OH-1/OH-1’), 11.4 (s, OH-9/OH-9’), 7.44 (d, 1.2, H-6/H-6’), 7.18 (d, 1.2, H-8/H-8’), 4.38 (dd, 6.0, 2.3, H-3/H-3’), 3.36 (brs, H-4/H-4’), 2.77 (d, 6.0, H-2/H-2’), 2.41 (s, H-15/H-15’); <sup>13</sup>C NMR 194.6, 186.7, 181.7, 160.8, 148.3, 132.7, 124.7, 121.2, 114.8, 106.8, 69.2, 59.0, 56.3, 48.4, 22.2” (Yamazaki et al., 2010).

### *Helminthosporin*



**Figure S0-15 Chem NMR <sup>1</sup>H Estimation of Helminthosporin (Source: ChemDraw Professional)**

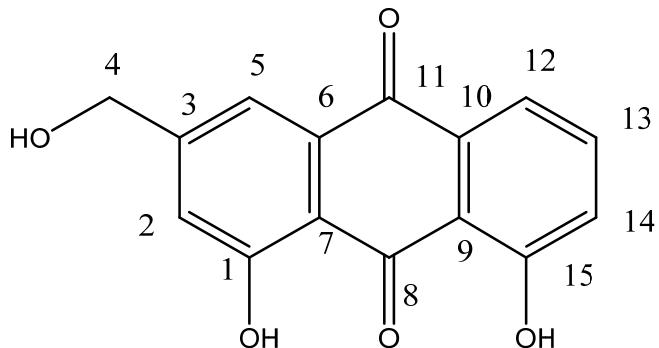


**Figure S0-16 Chem NMR <sup>13</sup>C Estimation of Helminthosporin (Source: ChemDraw Professional)**

As per literature “<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub> Me,Si) δ 2-49 (H-3’, 3H, t, I,<sub>1,2</sub> = 0.8 Hz, I<sub>1,3</sub> = 0.7 Hz) 7-13 (H-2, 1H, m, J<sub>1,2</sub> = 0.8 Hz, J<sub>1,3</sub> = 1.7 Hz) 7.30 (H-6, H-7, 2H, s) 771 (H-4, 1H, m, I<sub>1,2</sub> = 1.7 Hz, I<sub>1,3</sub> = 0.7 Hz) 12.16, 12.34 (20H, 2H, 2s) 13.03 (OH1, 1H, s)” (Engström et al., 1993).

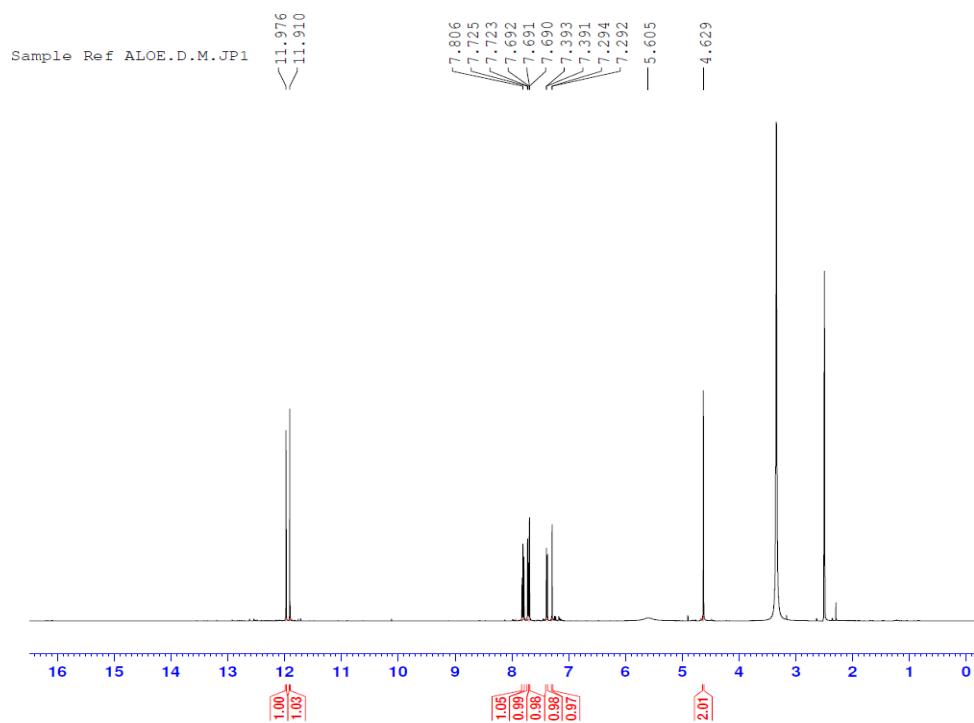
## 2. Experimental NMR

### *Aloe-emodin*

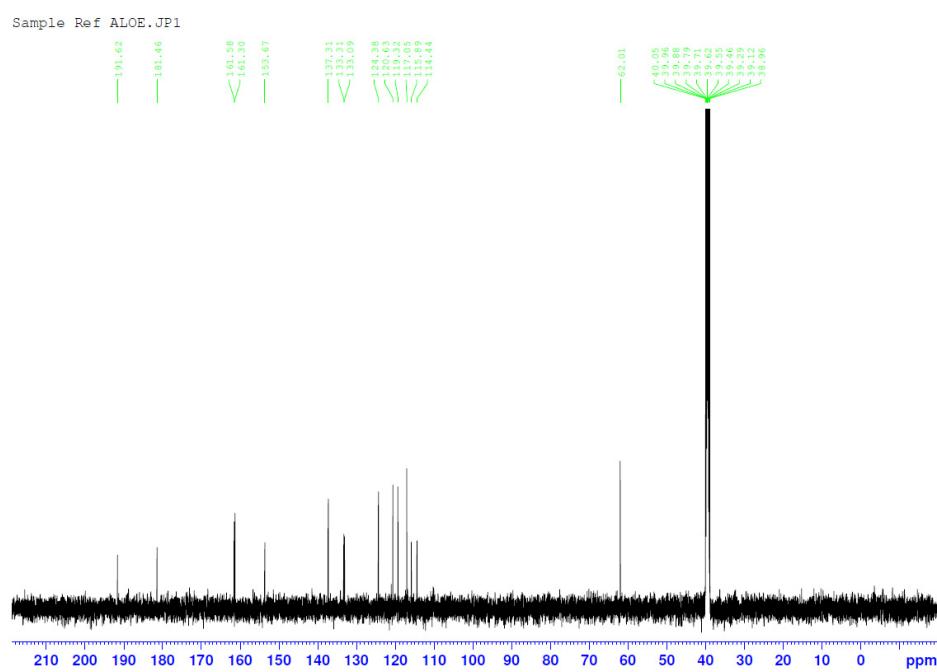


Position	(500MHz) (DMSO- <i>d</i> 6)	Peak shape	C13	ChemDraw prediction (300 MHz) (DMSO)	C13	Literature review (500MHz) (DMSO- <i>d</i> 6) (Sanchez et al., 2011)	C13
1	--	--	161.62	--	162.1	--	162.3
2	7.29	S	120.64	7.11	120.6	7.29	121.4
3	--	--	153.9	--	153.2	--	154.4
4	4.62	S	62.12	4.61	65.0	4.62	62.7
5	7.69	S	117.01	7.34	118.3	7.69	117.8
6	--	--	133.09	--	133.6	--	133.9
7	--	--	114.48	--	115.2	--	115.2
8	--	--	191.62	--	188.0	--	192.4
9	--	--	115.91	--	116.3	--	116.7
10	--	--	133.31	--	133.1	--	134.1
11	--	--	181.46	--	182.1	--	182.2
12	7.71	D	119.34	7.74	119.4	7.72	120.0
13	7.80	T	137.74	7.65	136.2	7.80	138.0
14	7.38	D	124.38	7.06	124.1	7.38	125.1
15	--	--	161.33	--	161.9	--	162.0

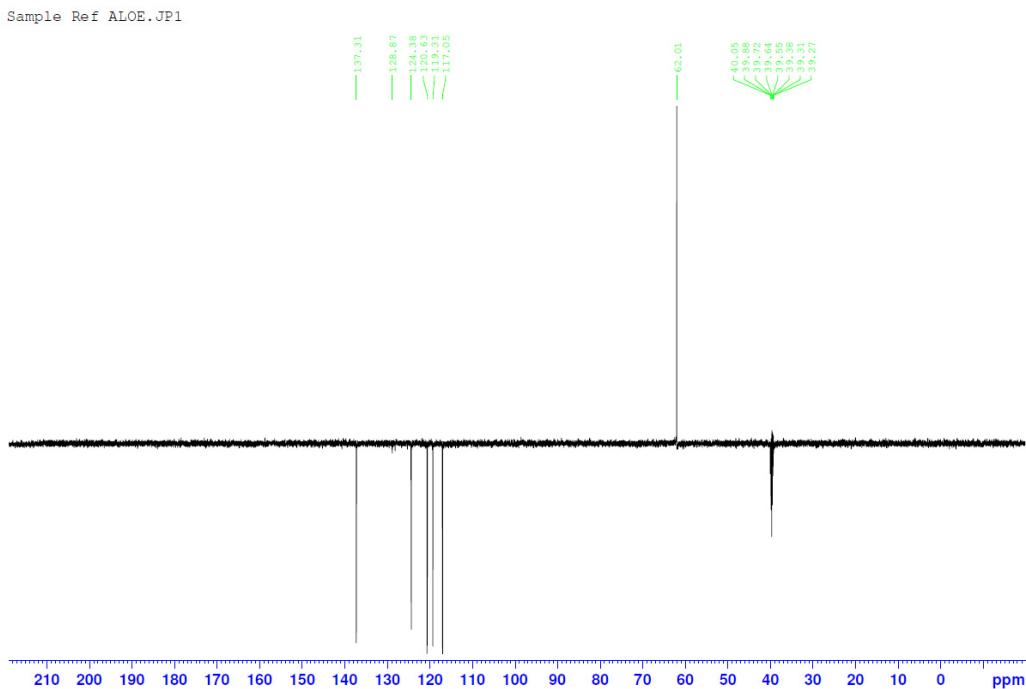
Table S0-1 <sup>1</sup>H and <sup>13</sup>C NMR Chemical Shift of Aloe-emodin



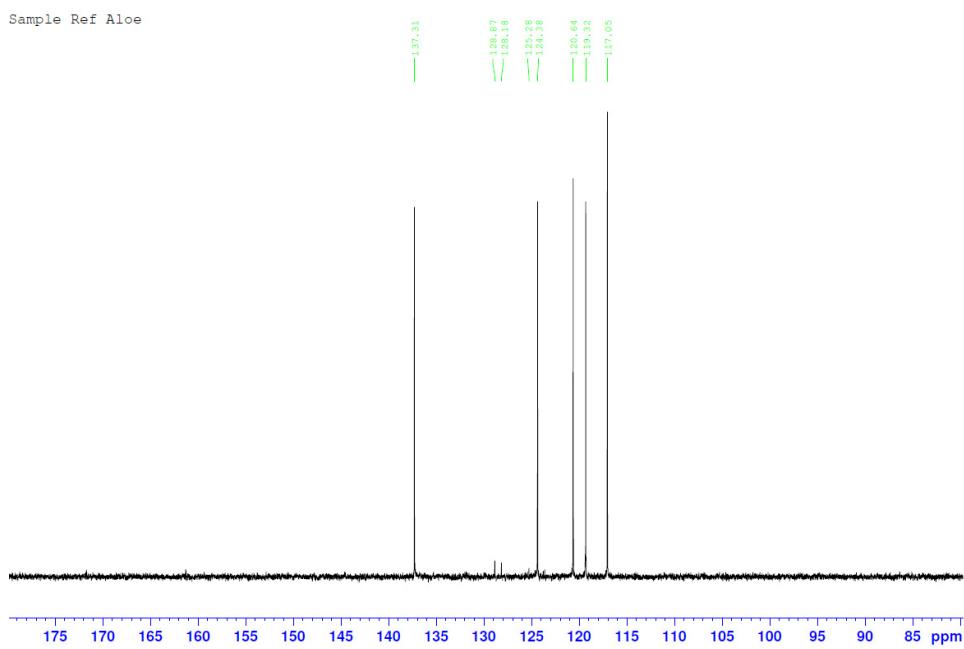
**Figure S0-1 <sup>1</sup>H NMR Chemical Shift of Aloe-emodin**



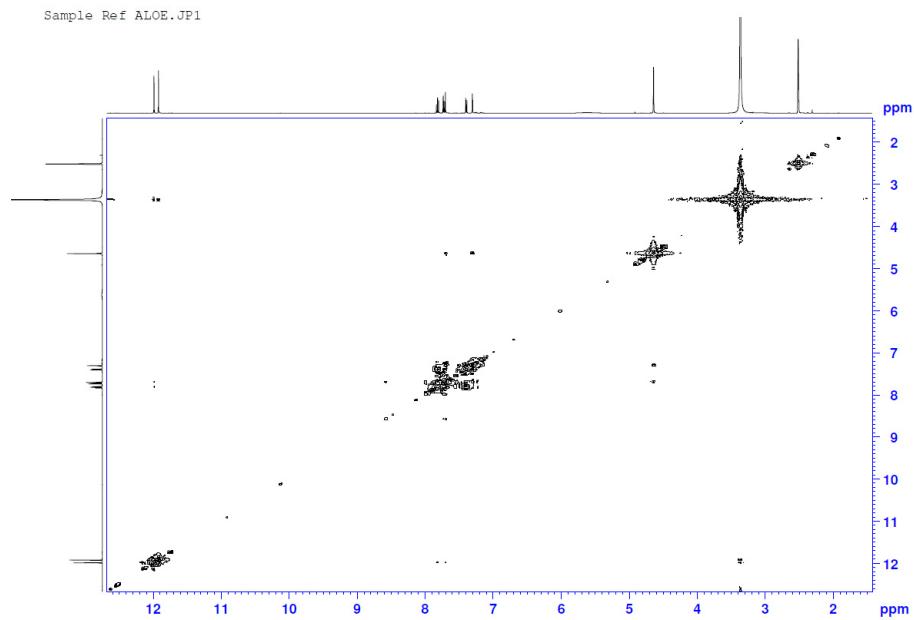
**Figure S0-2 <sup>13</sup>C NMR Chemical Shift of Aloe-emodin**



**Figure S0-3 Dept 135 of Aloe-emodin**

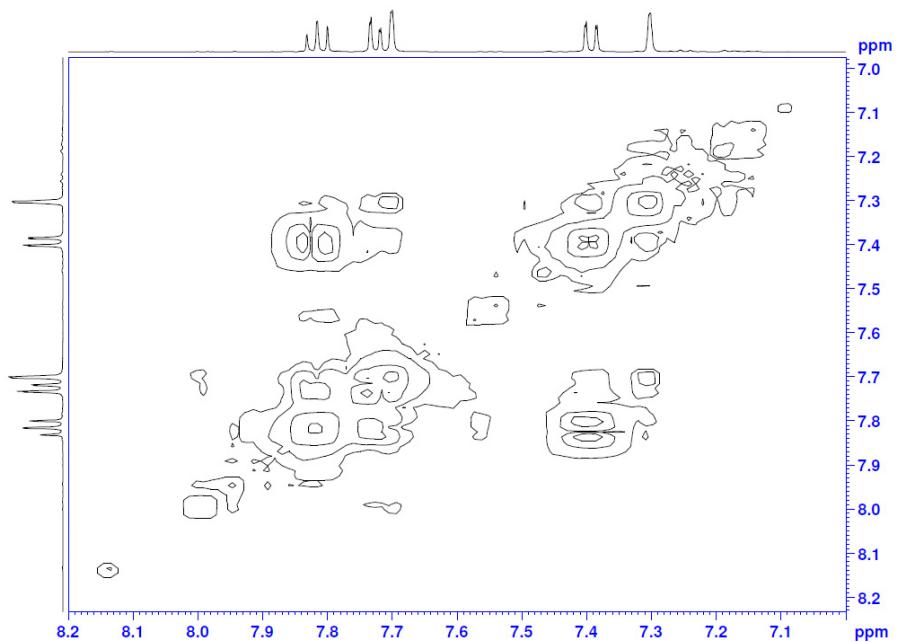


**Figure S0-4 Dept 90 of Aloe-emodin**

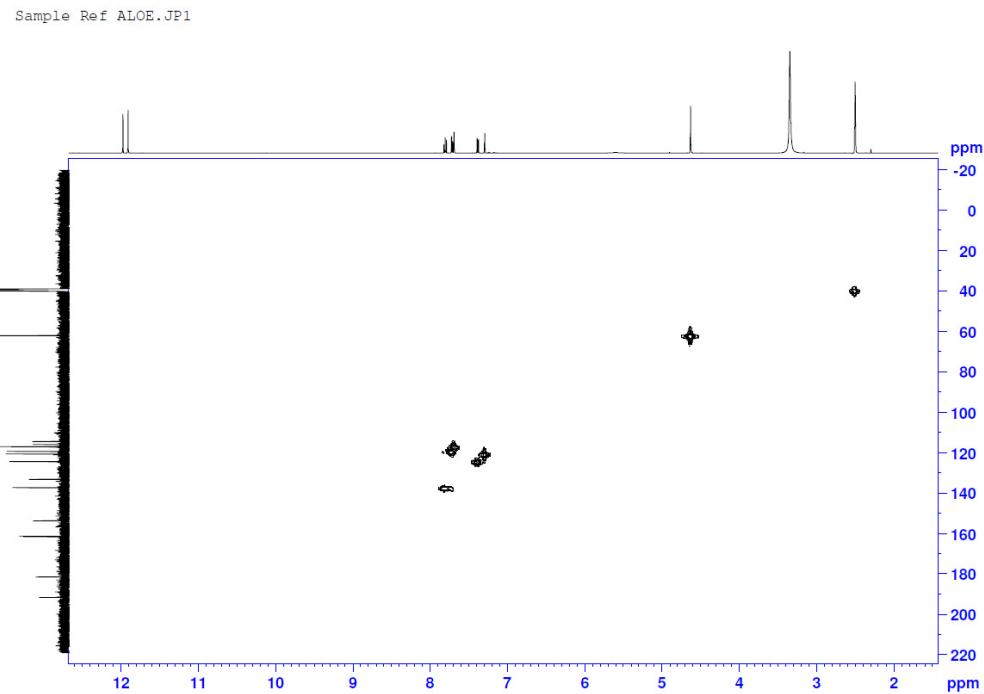


**Figure S0-5 Cosy of Aloe-emodin**

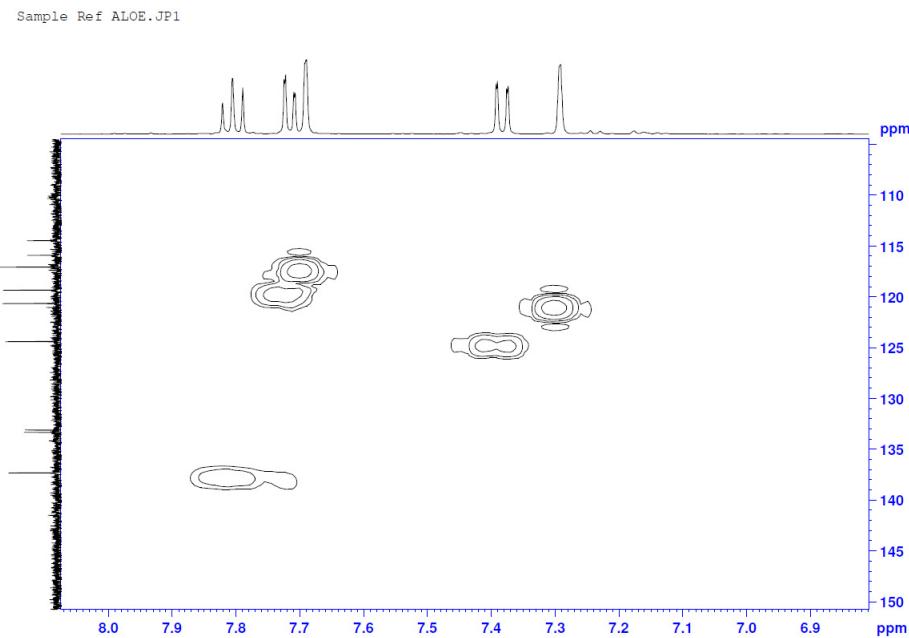
Sample Ref ALOE.JP1



**Figure S0-6 Expand cosy of Aloe-emodin**



**Figure S0-7** HMQC of Aloe-emodin



**Figure S0-8** Expand HMQC of Aloe-emodin

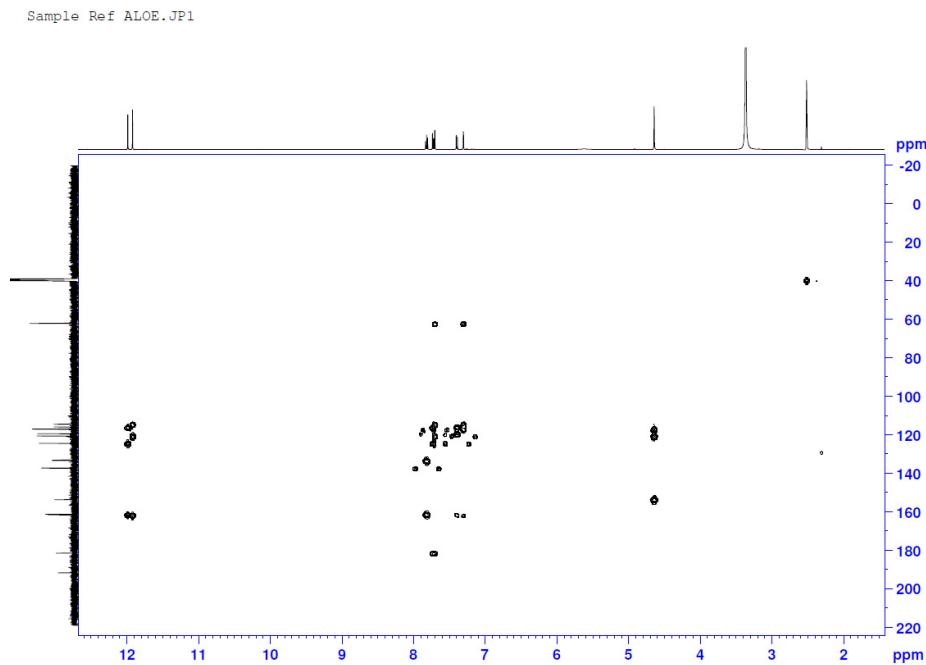
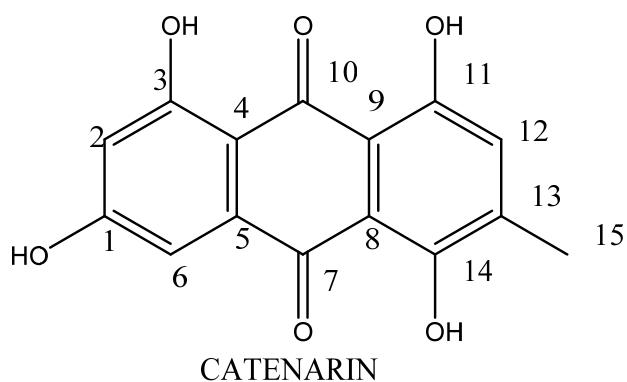


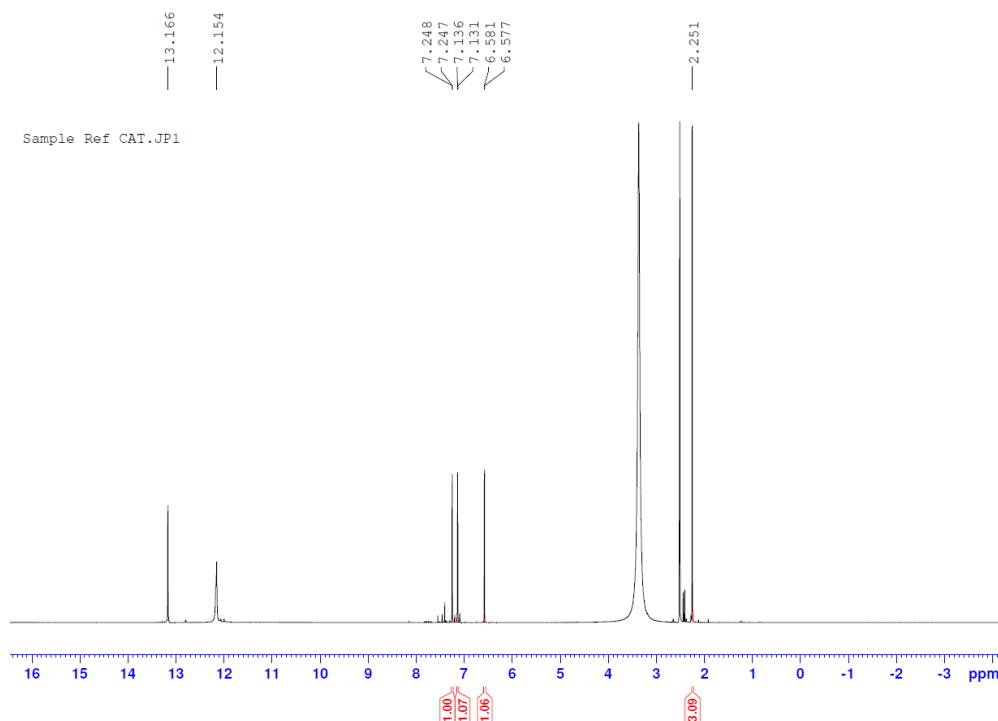
Figure S0-9 HMBC of Aloe-emodin

*Catenarin*

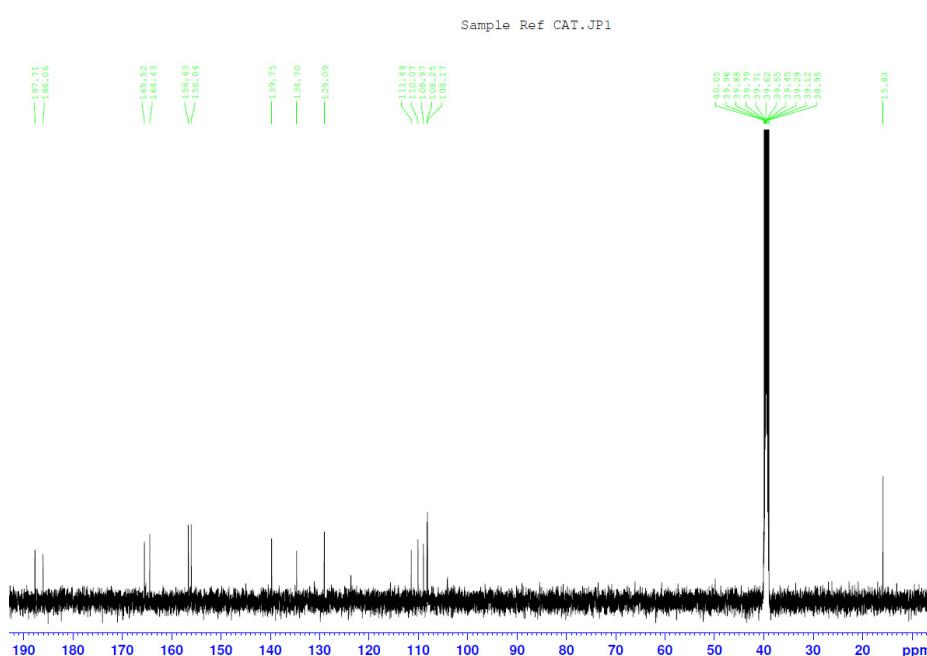
Position	(500MHz) (DMSO- <i>d</i> 6)	Peak shape	C13	ChemDraw Prediction (300MHz) (DMSO)	C13	Literature review PPM(400MHz) (DMSO- <i>d</i> 6) (Kalidhar, 1989)	C13
1	--	--	164.43	--	163.3		NO Data
2	6.58	DS	108.19	6.48	107.0	6.66	
3	--	--	165.51	--	164.5		
4	--	--	108.97	--	108.9		
5	--	--	134.70	--	136.4		
6	7.13	DS	108.30	6.75	108.3	7.13	
7	--	--	186.0	--	186.4		
8	--	--	110.07	--	111.7		
9	--	--	111.43	--	111.7		
10	--	--	187.71	--	188.0		
11	--	--	156.04	--	157.4		
12	7.24	S	129.09	6.82	129.4	7.32	

13	--	--	139.75	--	140.9
14	--	--	156.74	--	158.0
15	2.25	S	15.87	2.15	15.4      2.35

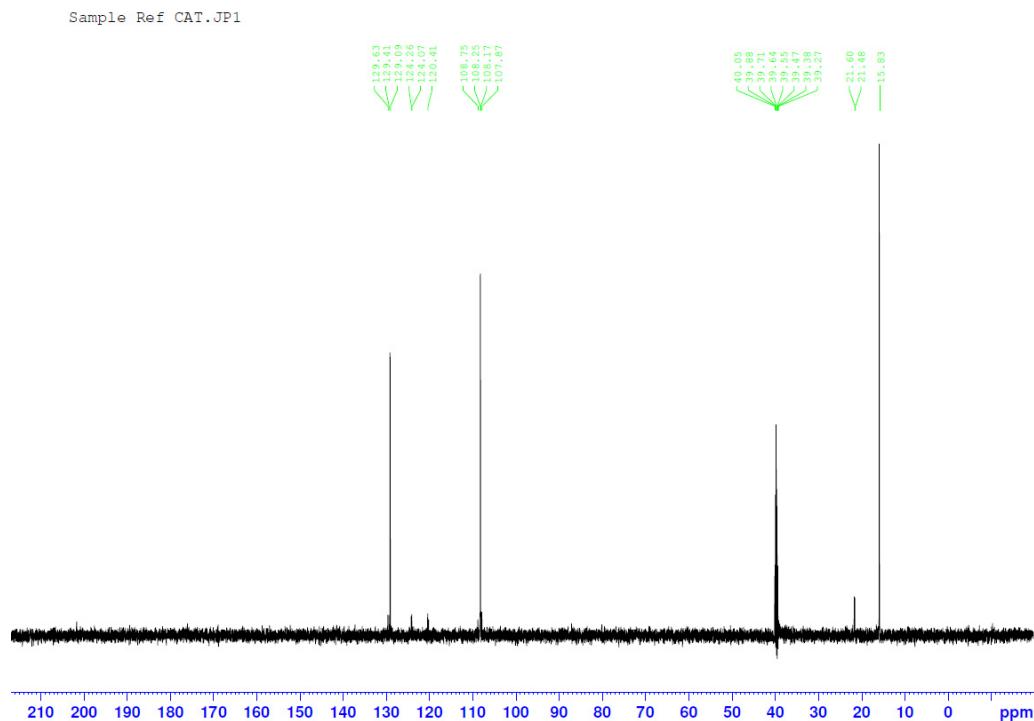
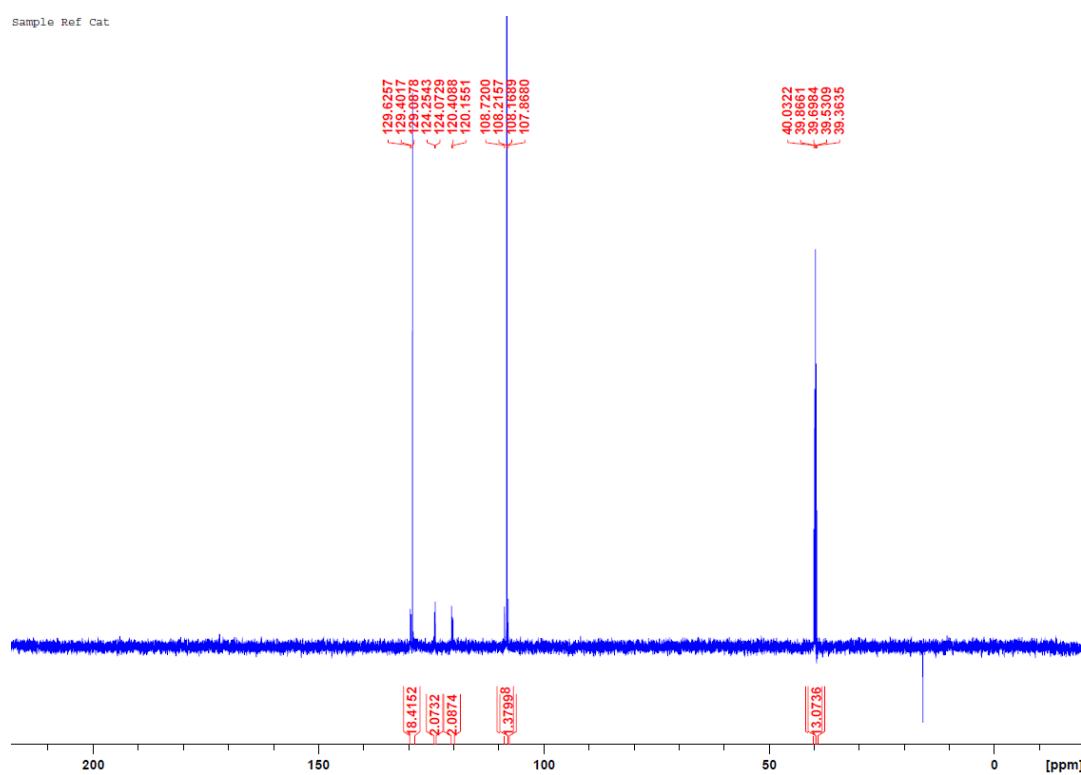
**Table S0-2**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Chemical Shift of catenarin



**Figure S0-10**  $^1\text{H}$  NMR Chemical Shift of catenarin



**Figure S0-11**  $^{13}\text{C}$  NMR Chemical Shift of catenarin

**Figure S0-12 Dept 135 of catenarin****Figure S0-13 Dept 90 of catenarin**

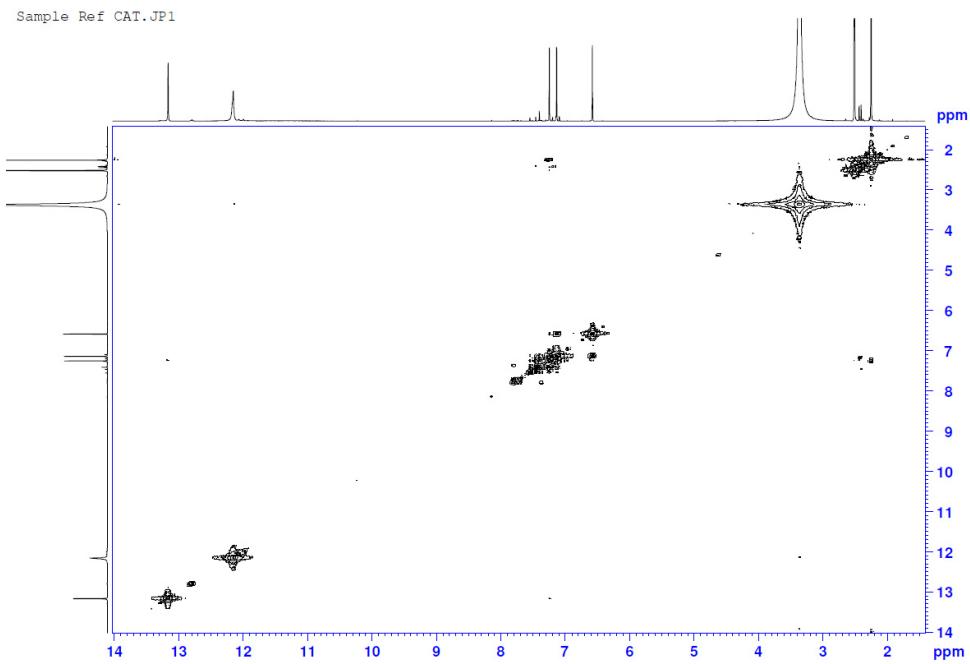


Figure S0-14 Cosy of catenarin

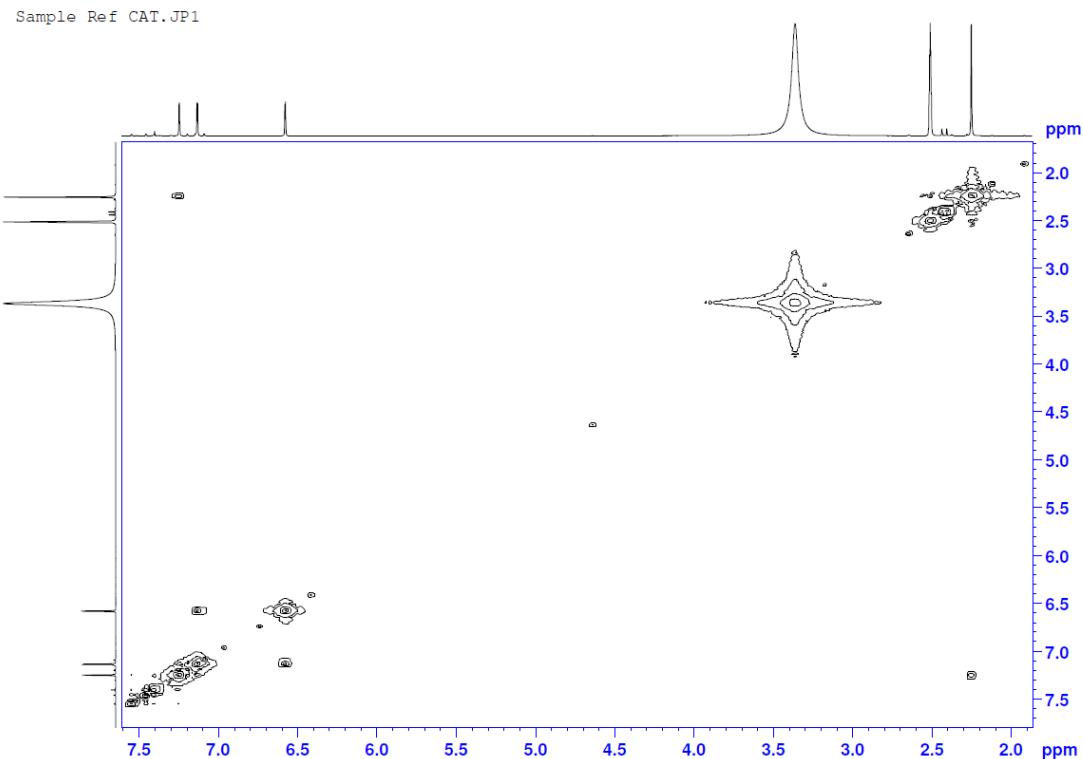
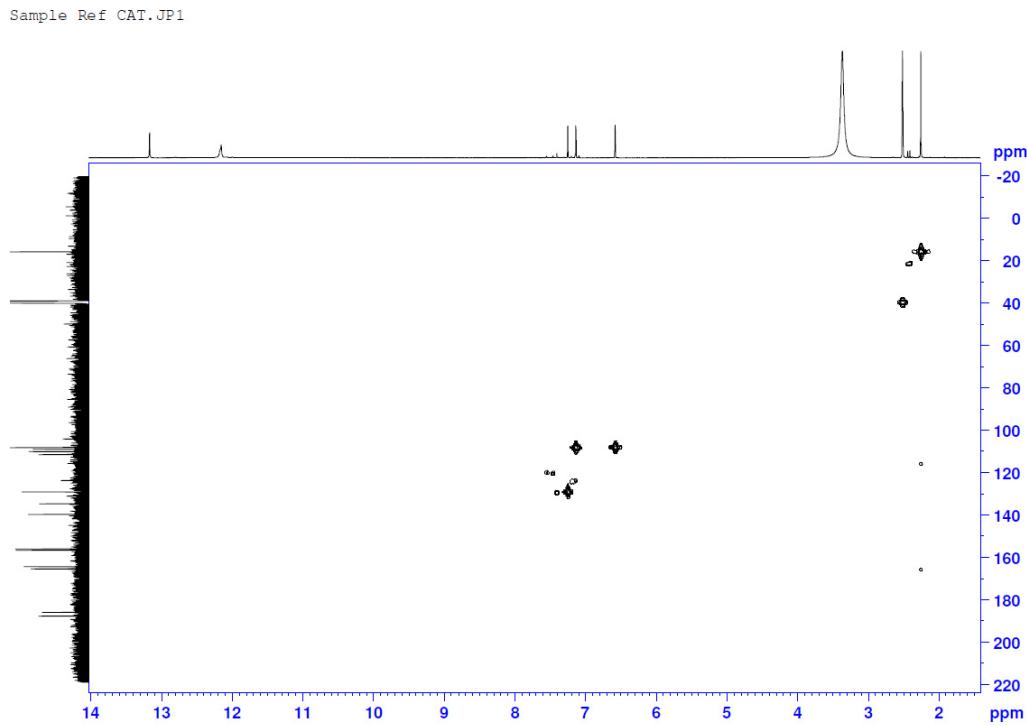
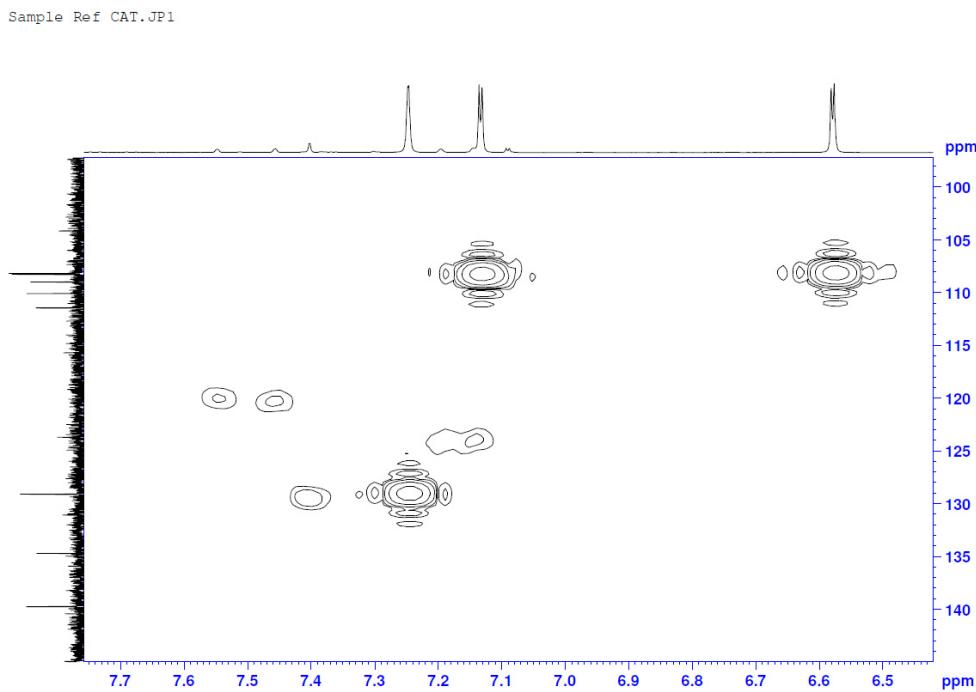


Figure S0-15 Expand cosy of catenarin



**Figure S0-16** HMQC of catenarin



**Figure S0-17** Expand HMQC of catenarin

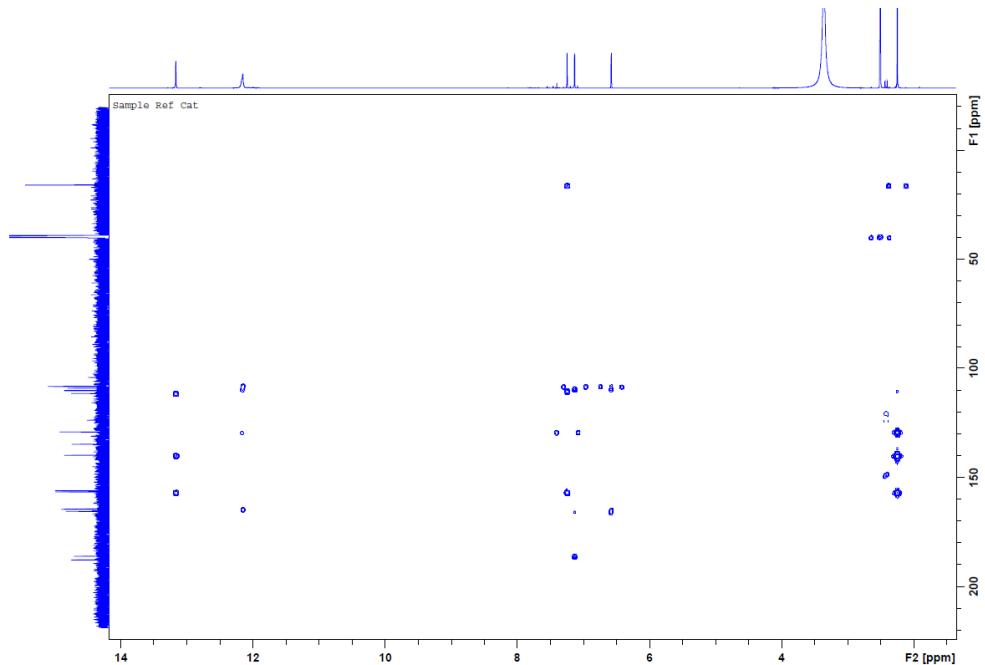
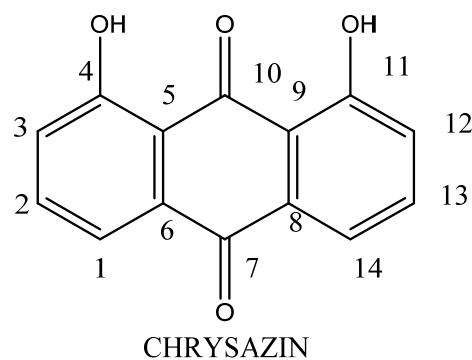
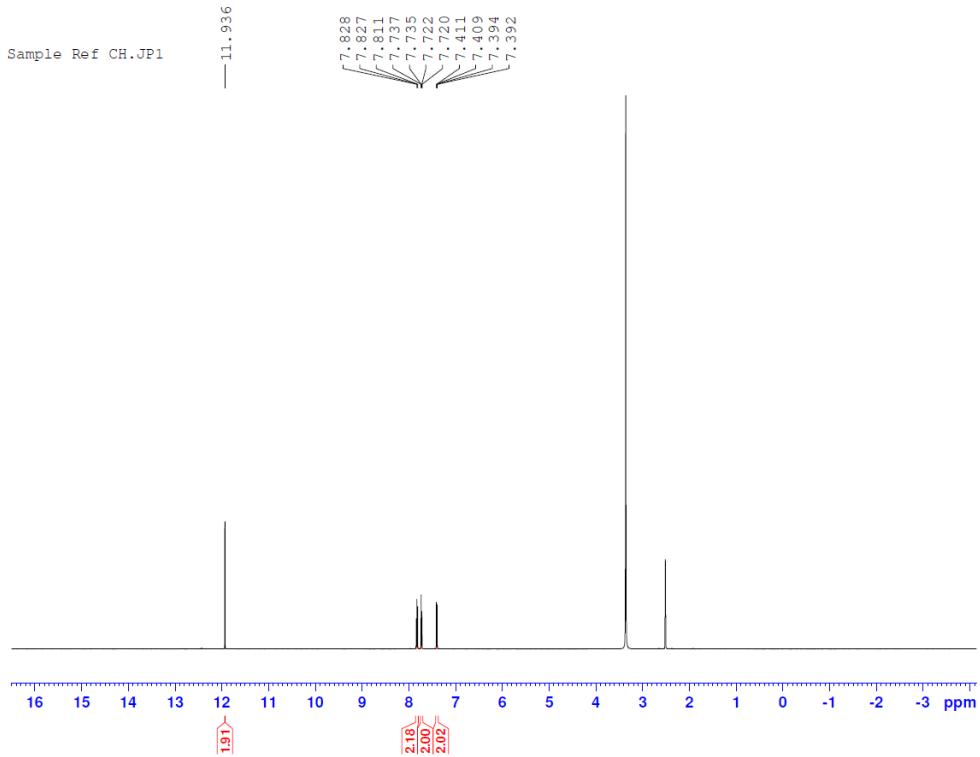


Figure S0-18 HMBC of catenarin

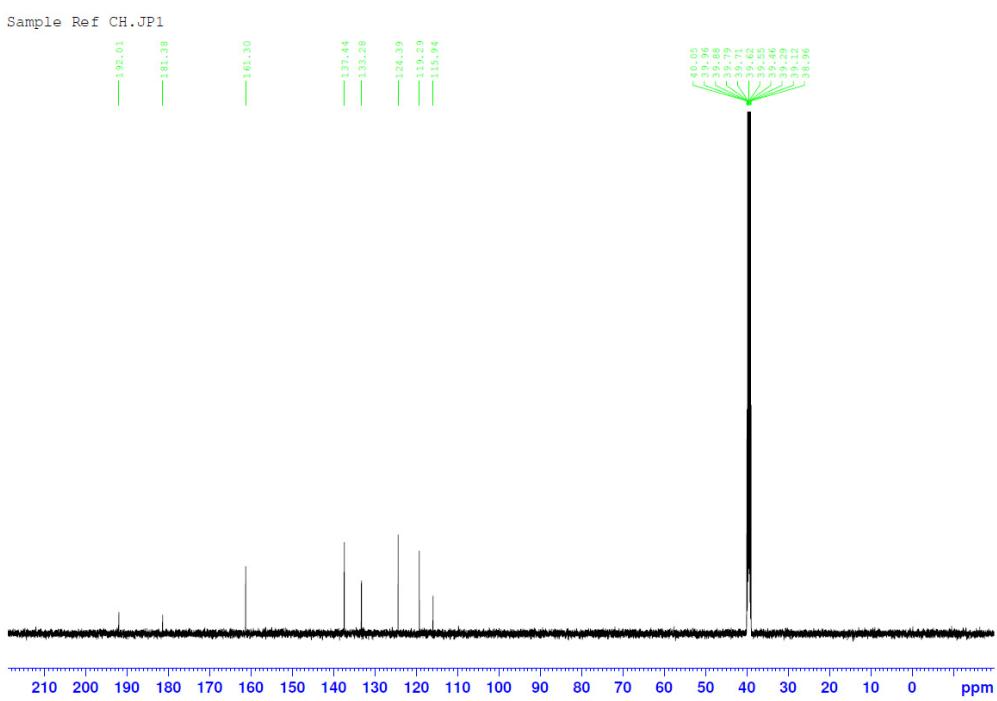
*Chrysazin*

Position	(500MHz) (DMSO- <i>d</i> 6)	Peak shape	C13	ChemDraw prediction (300MHz) (DMSO)	C13	Literature review (500MHz) (DMSO- <i>d</i> 6) (Pullella et al., 2017)	C13
1	7.71	DD	119.29	7.74	119.4	7.70	120.2
2	7.81	DD	137.44	7.65	136.2	7.80	138.0
3	7.39	DD	124.39	7.06	124.1	7.37	125.1
4	--	--	161.30	--	161.9	--	163.0
5	--	--	115.94	--	116.3	--	116.7
6	--	--	133.28	--	133.1	--	134.4
7	--	--	181.38	--	182.1	--	182.0
8	--	--	133.28	--	133.1	--	134.4
9	--	--	115.94	--	116.3	--	116.7
10	--	--	192.01	--	188.0	--	193.4
11	--	--	161.30	--	161.9	--	163.0
12	7.39	DD	124.39	7.06	124.1	7.37	125.1
13	7.81	DD	137.44	7.65	136.2	7.80	138.0
14	7.71	DD	119.29	7.74	119.4	7.70	120.2

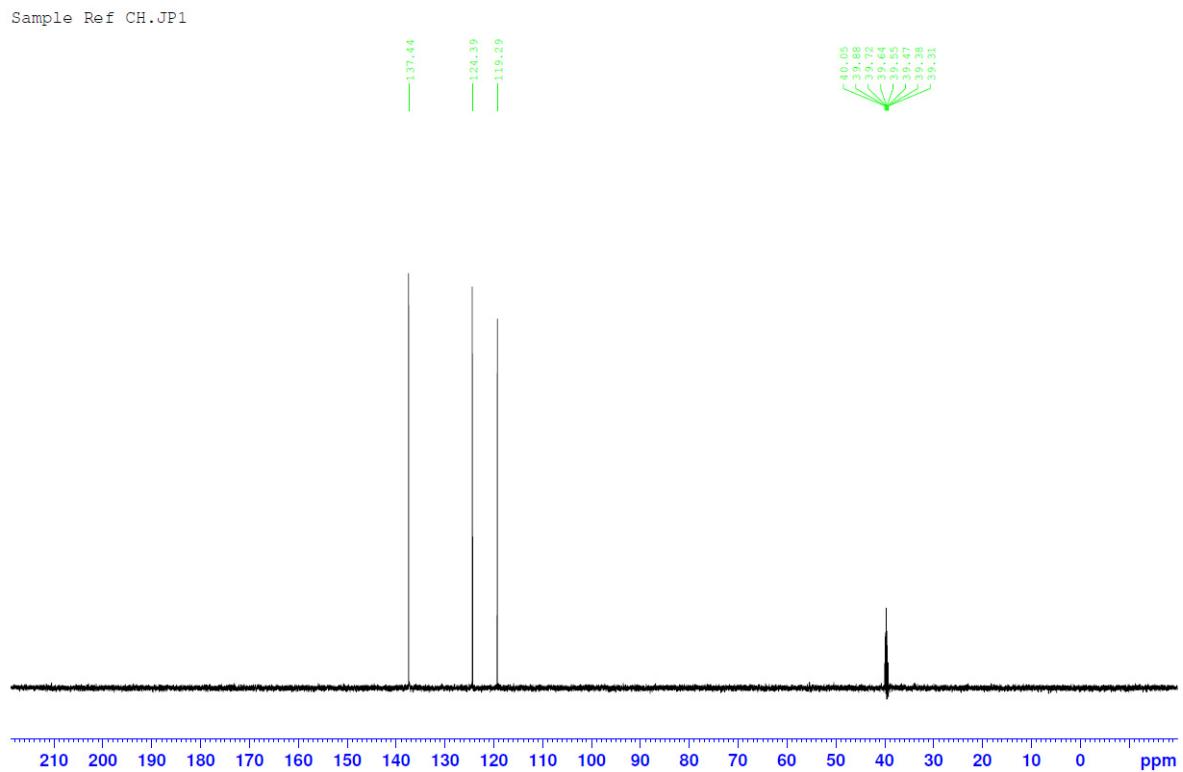
Table S0-3 1H and 13C NMR Chemical Shift of chrysazin



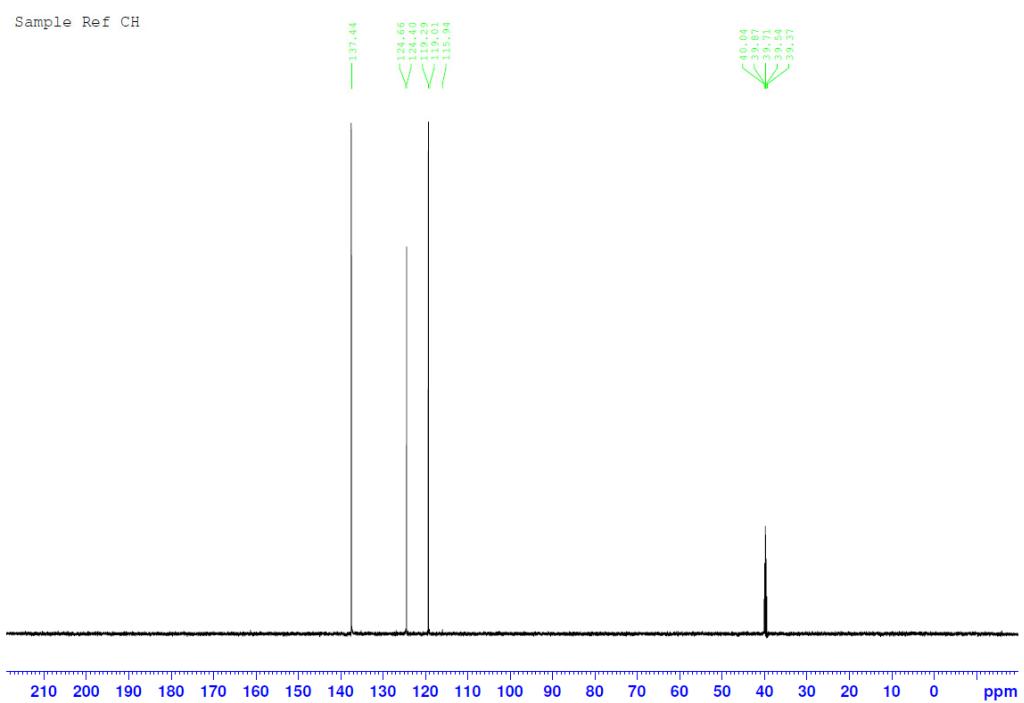
**Figure S0-19 <sup>1</sup>H NMR Chemical Shift of chrysazin**



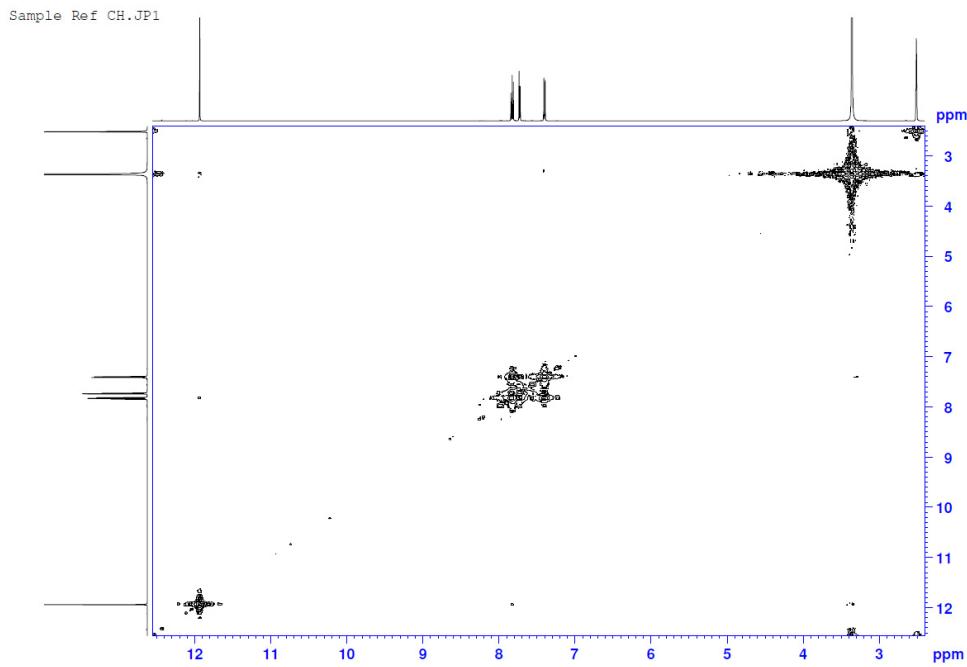
**Figure S0-20 <sup>13</sup>C NMR Chemical Shift of chrysazin**



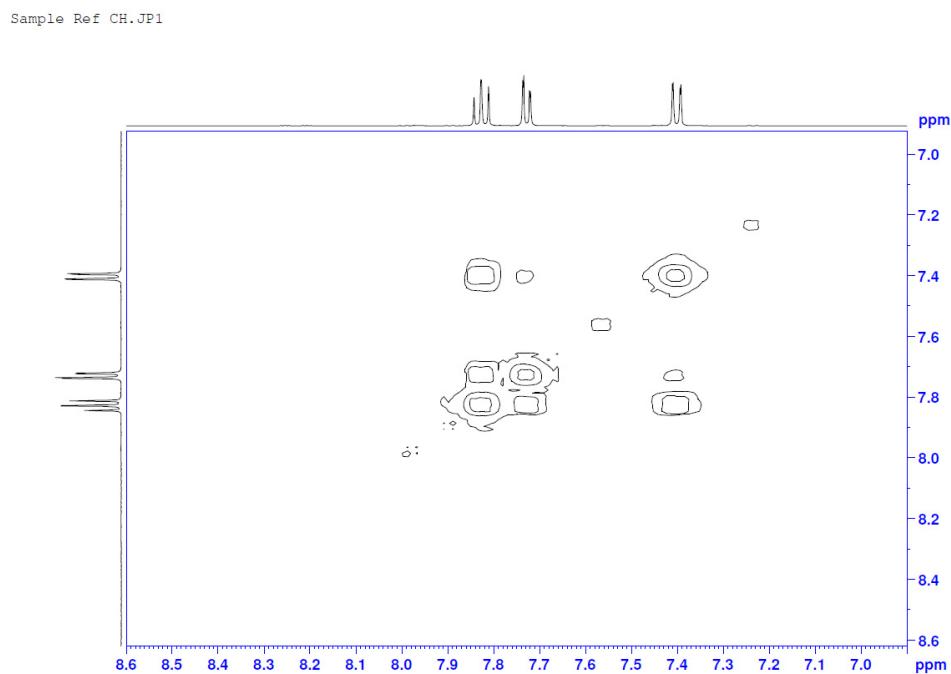
**Figure S0-21 Dept 135 of chrysazin**



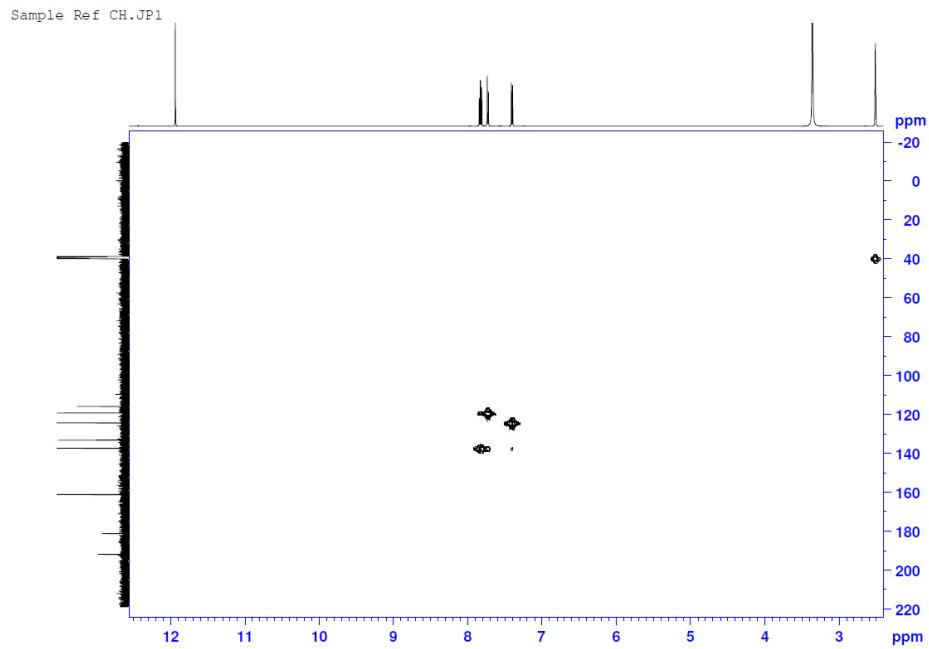
**Figure S0-22 Dept 90 of chrysazin**



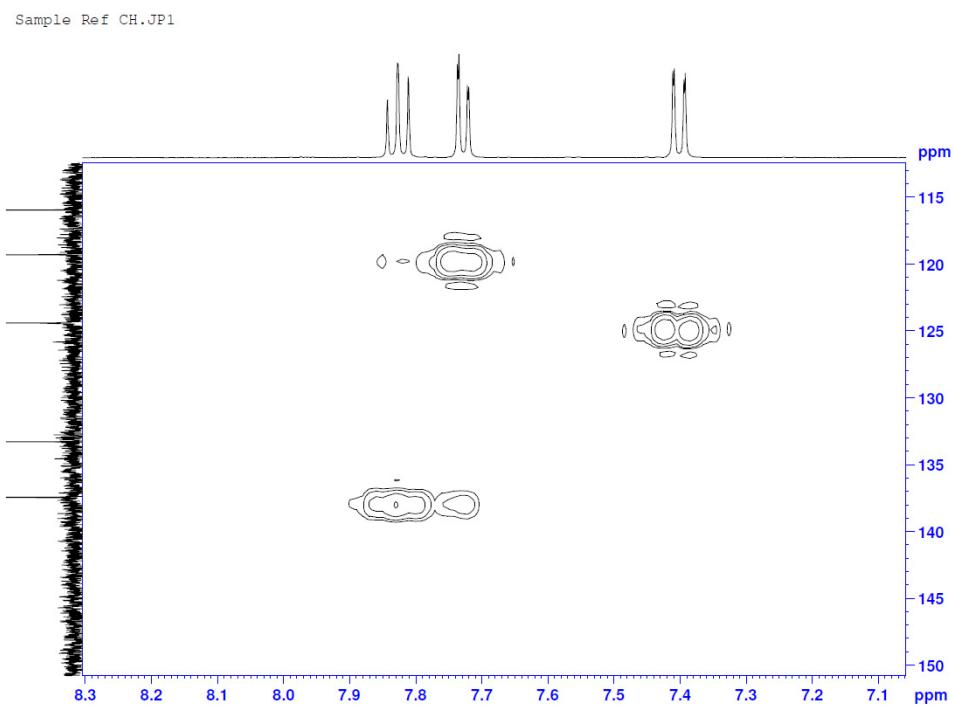
**Figure S0-23 Cosy of chrysazin**



**Figure S0-24 Expand cosy of chrysazin**



**Figure S0-25** HMQC of chrysazin



**Figure S0-26** Expand HMQC of chrysazin

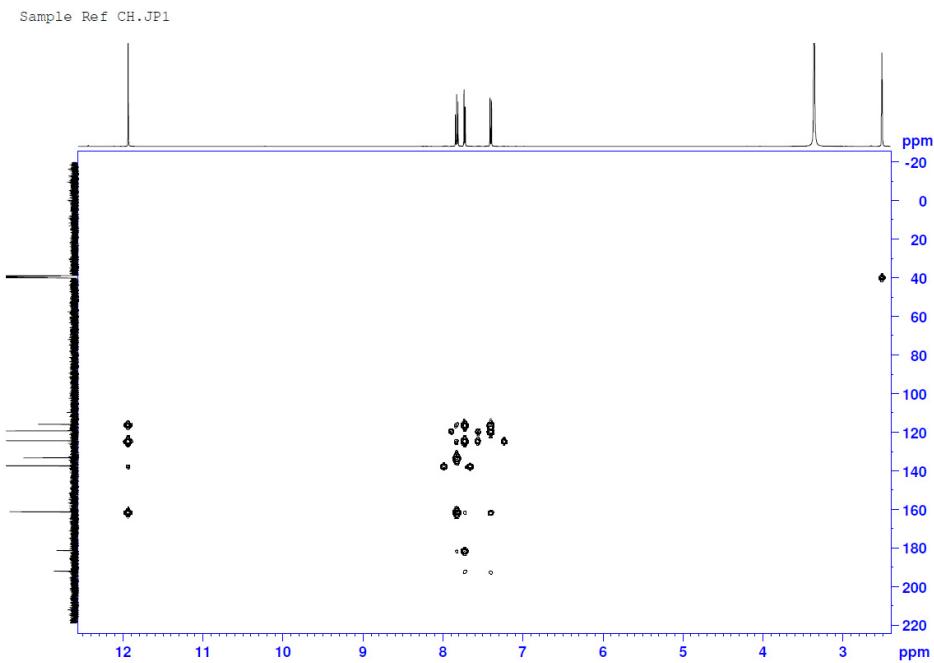
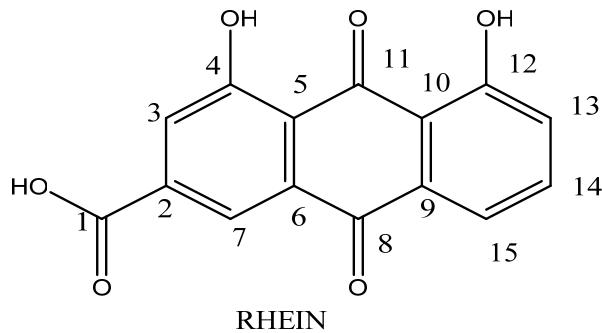
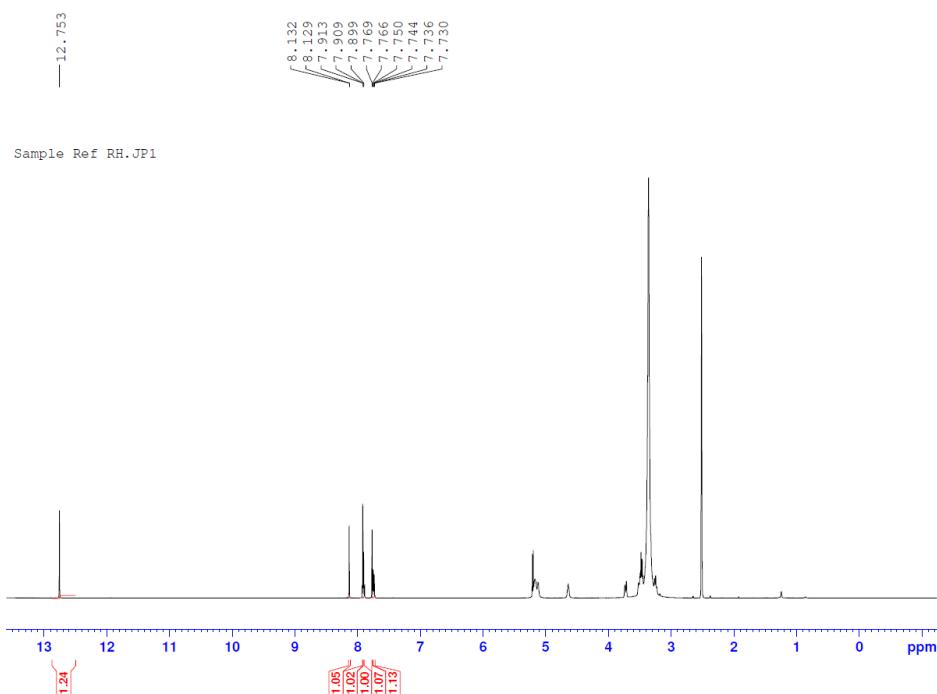


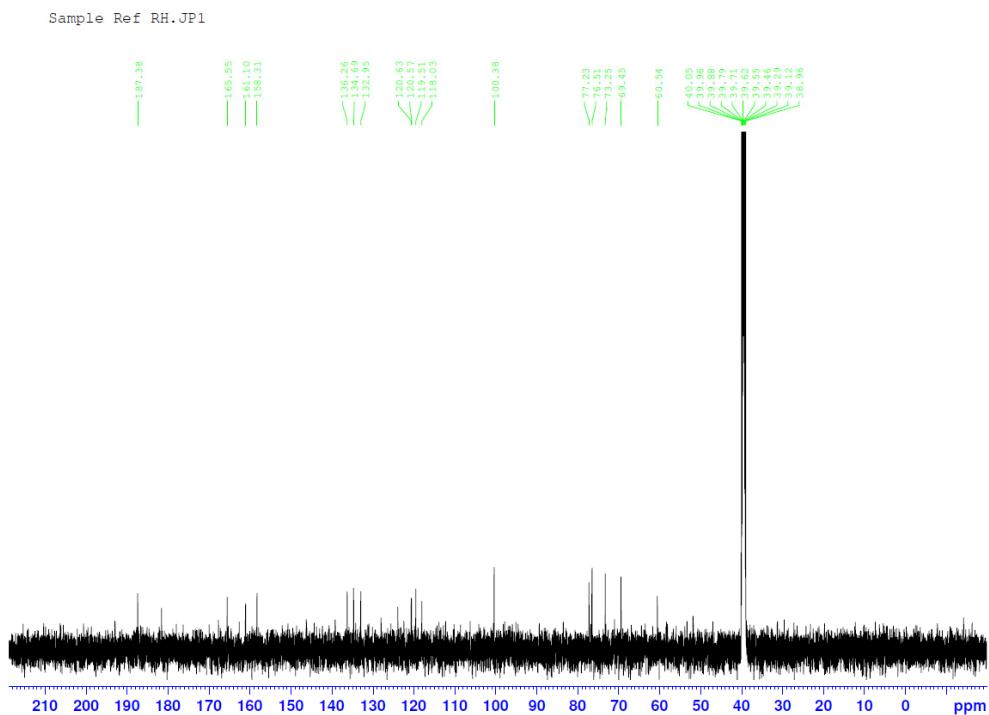
Figure S0-27 HMBC of chrysazin

*Rhein*

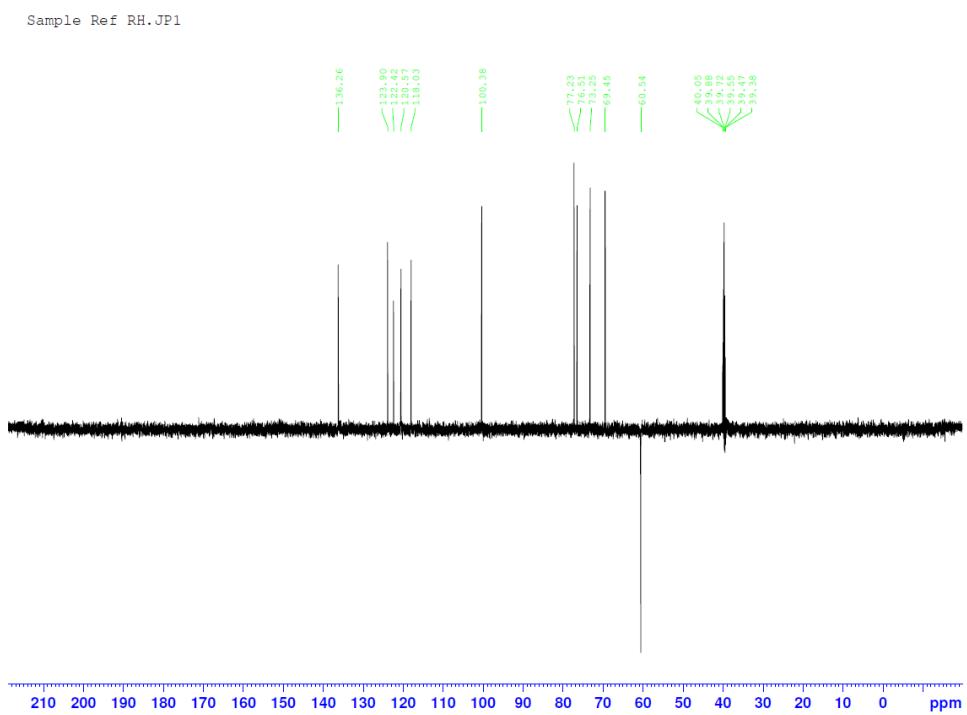
Position	(500MHz) (DMSO- <i>d</i> 6)	Peak shape	C13	ChemDraw pre- diction (300MHz)	C13 (DMSO)	Literature review (500MHz) (DMSO- <i>d</i> 6) Daniels, Ak- snes and Francis, 1992	C13
1	--	--	165.55	--	169.3	--	165.52
2	--	--	128.01	--	135.0	--	138.20
3	7.76	DS	123.93	7.81	124.5	7.77	124.21
4	--	--	161.10	--	160.1	--	161.51
5	--	--	119.6	--	121.5	--	118.48
6	--	--	132.95	--	131.5	--	133.61
7	8.13	DS	118.03	7.56	120.6	8.14	119.05
8	--	--	181.7	--	182.1	--	181.25
9	--	--	134.8	--	133.1	--	133.41

10	--	--	120.63	--	116.3	--	116.33
11	--	--	187.38	--	188.0	--	191.49
12	--	--	158.31	--	161.9	--	161.27
13	7.74	DD	122.42	7.06	124.1	7.41	124.64
14	7.91	--	136.26	7.65	136.2	7.84	137.63
15	7.90	--	120.57	7.74	119.4	7.75	119.48

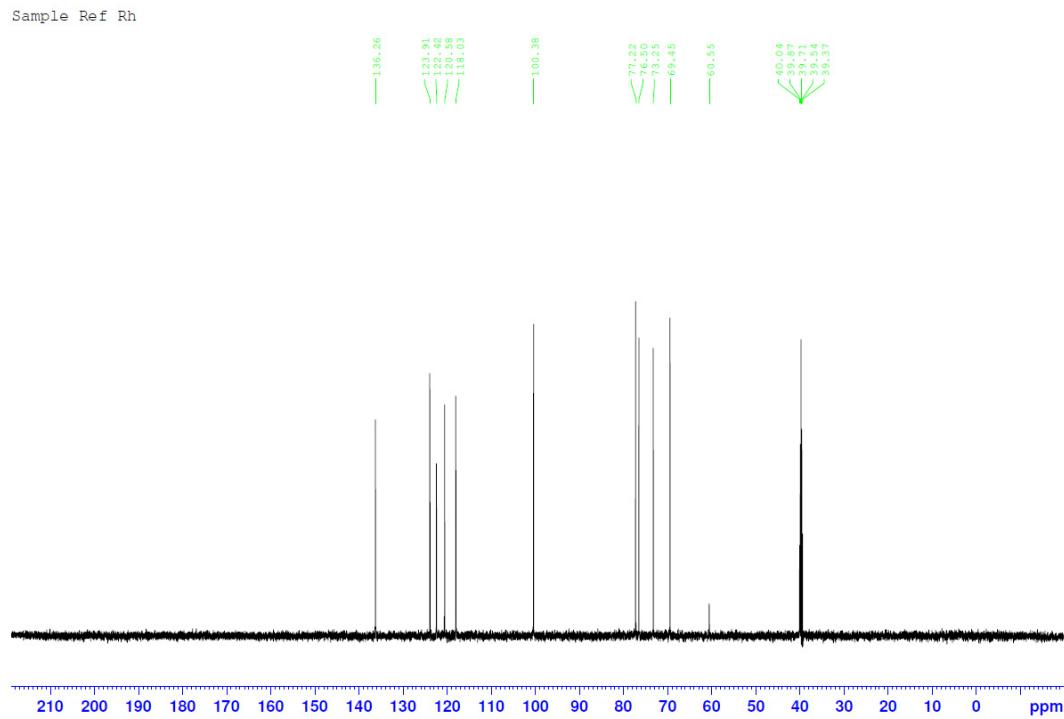
**Table S0-4 1H and 13C NMR Chemical Shift of rhein****Figure S0-28 1H NMR Chemical Shift of rhein**



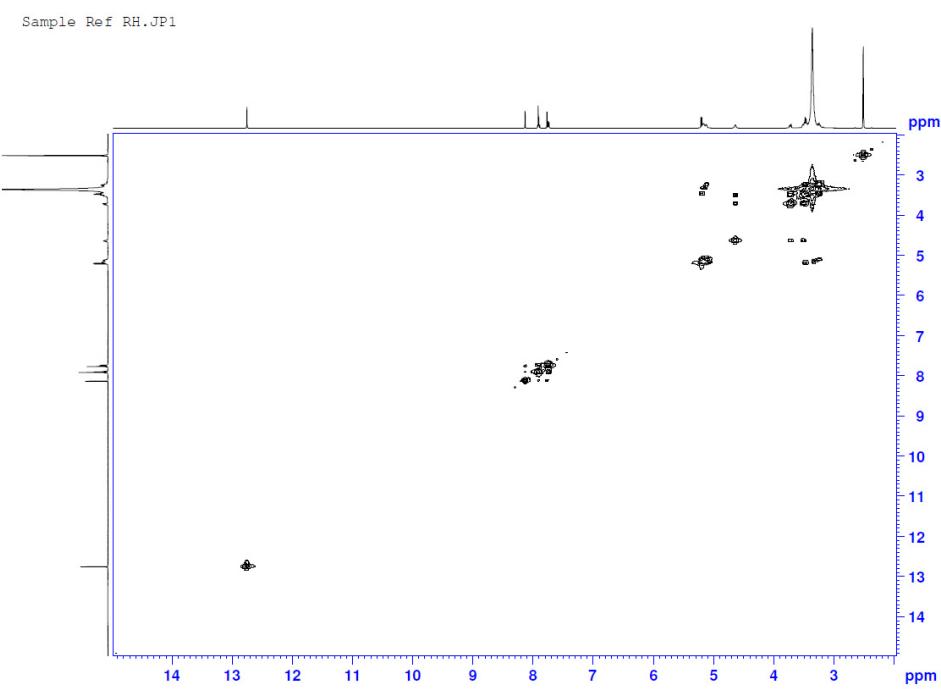
**Figure S0-29  $^{13}\text{C}$  NMR Chemical Shift of rhein**



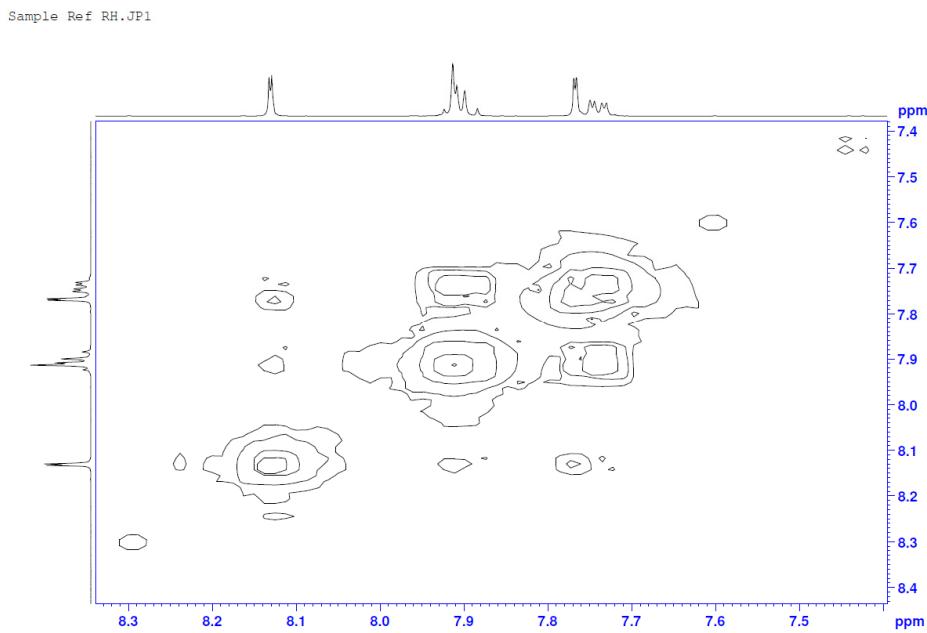
**Figure S0-30 Dept 135 of rhein**



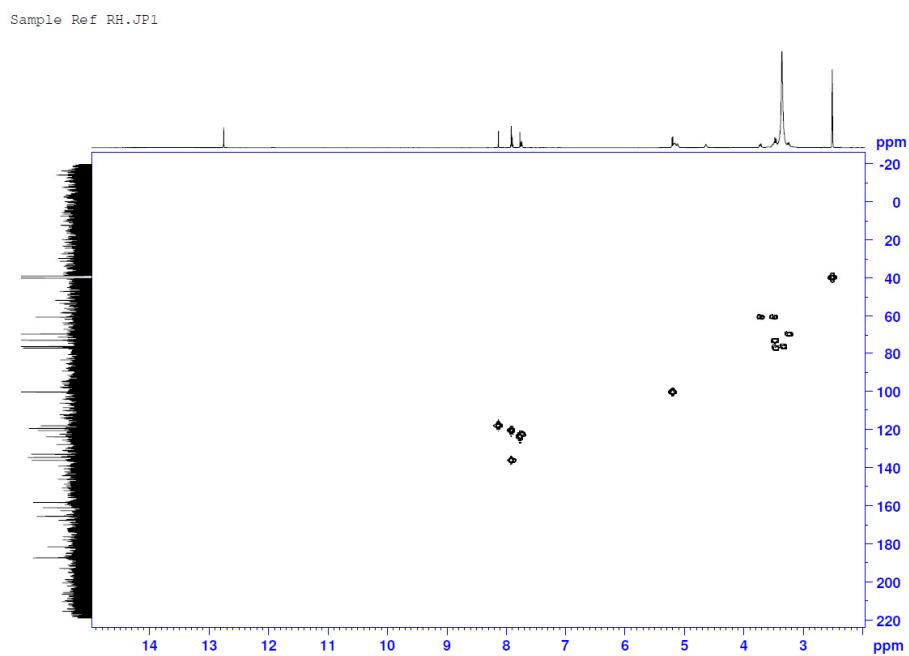
**Figure S0-31 Dept 90 of rhein**



**Figure S0-32 Cosy of rhein**

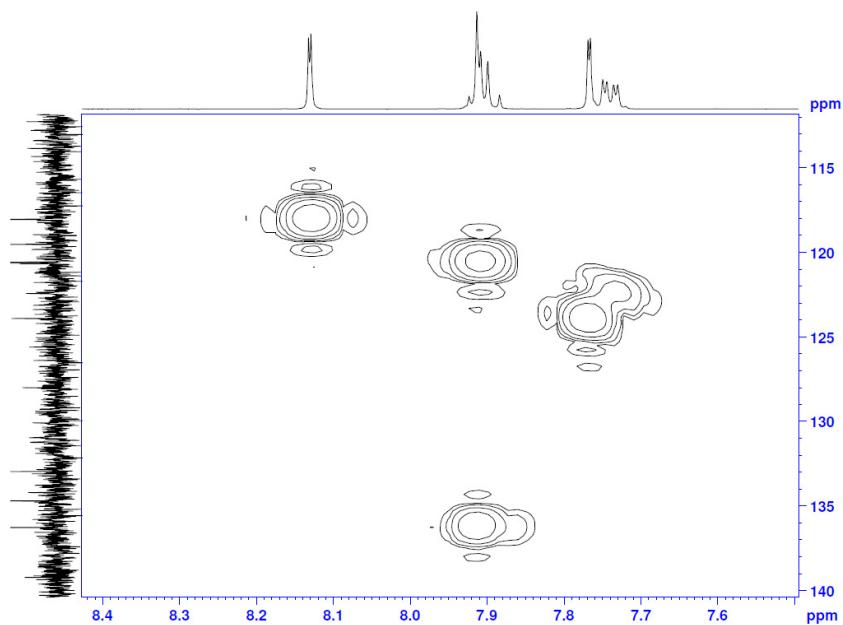


**Figure S0-33 Expand cosy of rhein**

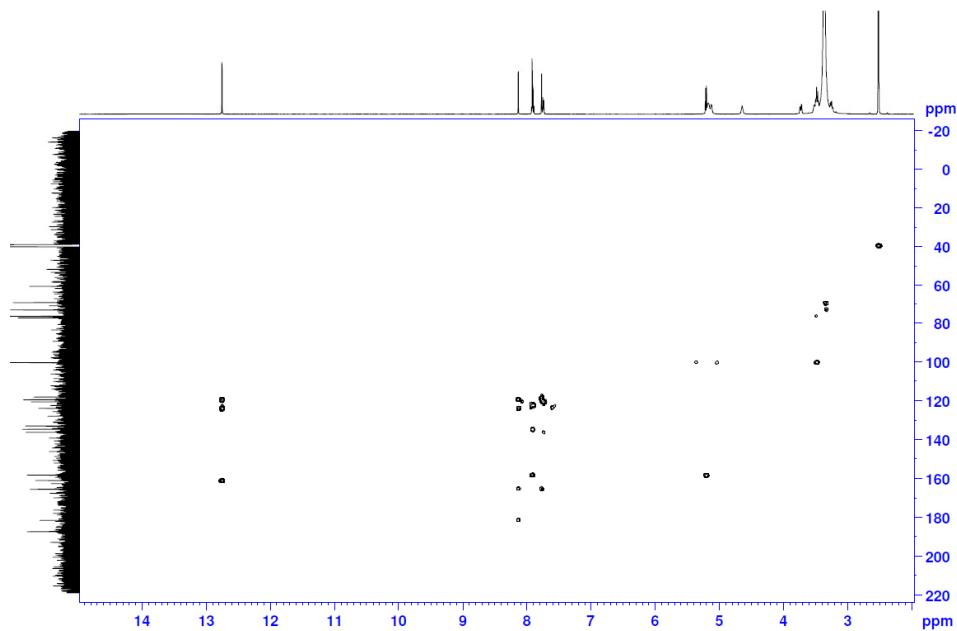


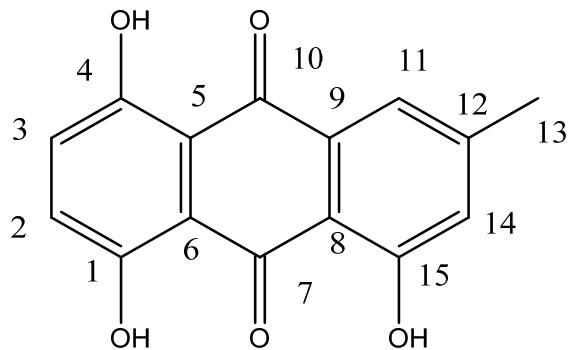
**Figure S0-34 HMQC of rhein**

Sample Ref RH.JP1

**Figure S0-35 Expand HMQC of rhein**

Sample Ref RH.JP1

**Figure S0-36 HMBC of rhein**

*Helminthosporin*

HELMINTHOSPORIN

Position	(500MHz) (DMSO- <i>d</i> 6)	Peak shape	C13	ChemDraw prediction (300MHz) (DMSO)	C13	Literature review (500MHz) (DMSO- <i>d</i> 6) (Eng- ström et al., 1993)	C13
1	--	--	157.06	--	157.3	--	158.2
2	7.44	S	129.43	7.37	129.5	7.44	129.5
3	7.44	S	129.69	7.37	129.5	7.44	129.6
4	--	--	156.39	--	157.3	--	157.6
5	--	--	112.71	--	114.7	--	112.8
6	--	--	112.55	--	114.7	--	112.5
7	--	--	189.94	--	188.0	--	190.6
8	--	--	113.84	--	113.3	--	114.0
9	--	--	132.88	-	133.3	--	133.2
10	--	--	186.36	--	185.5	--	186.6
11	7.64	S	120.29	7.22	120.2	7.65	120.8
12	--	--	149.14	--	147.6	--	149.1
13	2.46	S	21.63	2.36	21.6	2.45	22.3
14	7.26	S	124.3	6.66	122.7	7.26	124.6
15	--	--	161.68	--	161.8	--	162.8

Table S0-5 1H and 13C NMR Chemical Shift of helminthosporin

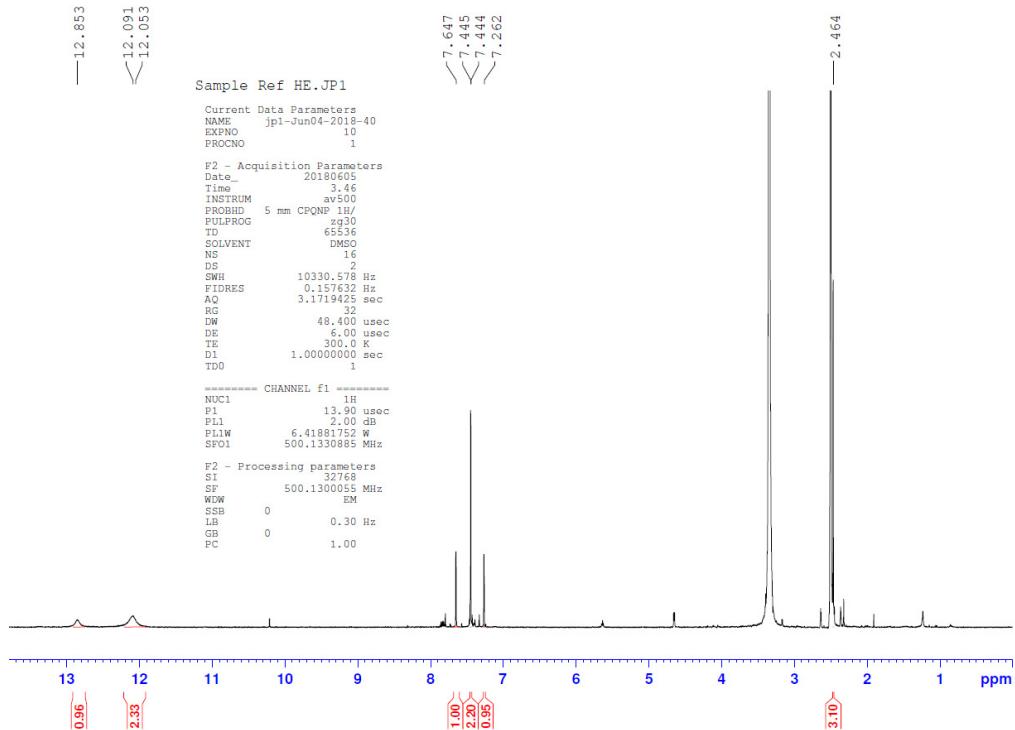


Figure S0-37 1H NMR Chemical Shift of helminthosporin

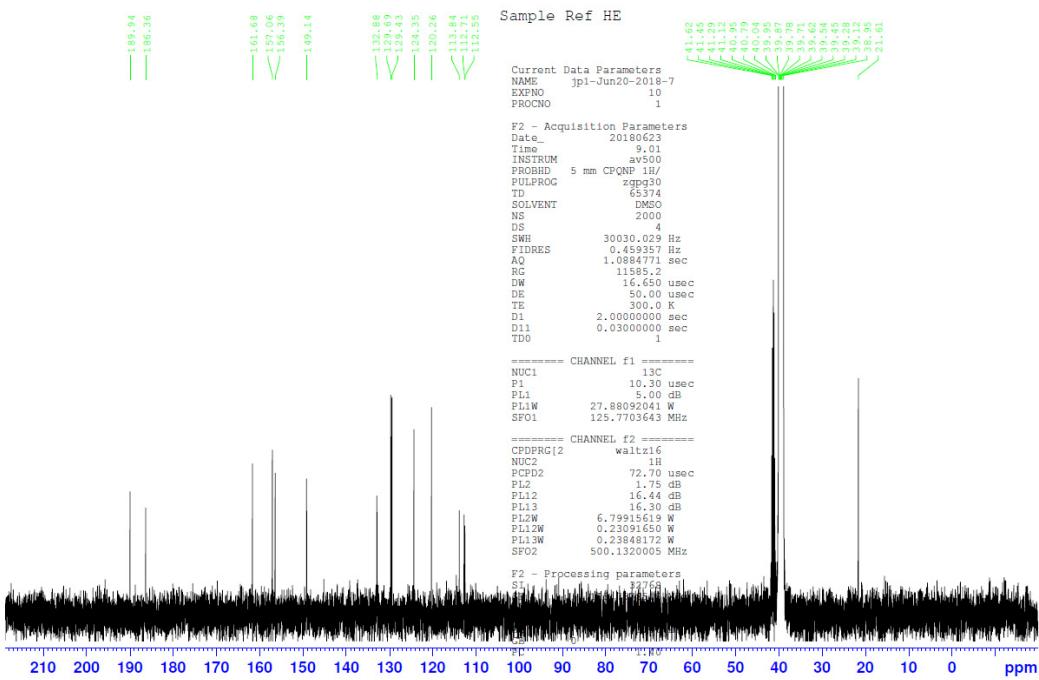


Figure S0-38 13C NMR Chemical Shift of helminthosporin

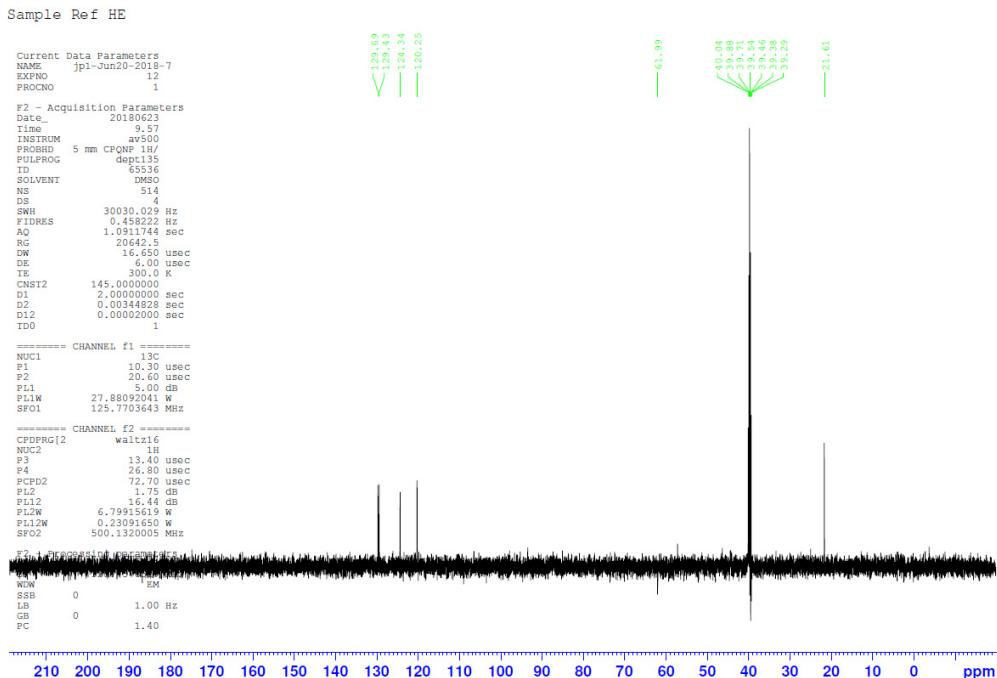


Figure S0-39 Dept 135 of helminthosporin

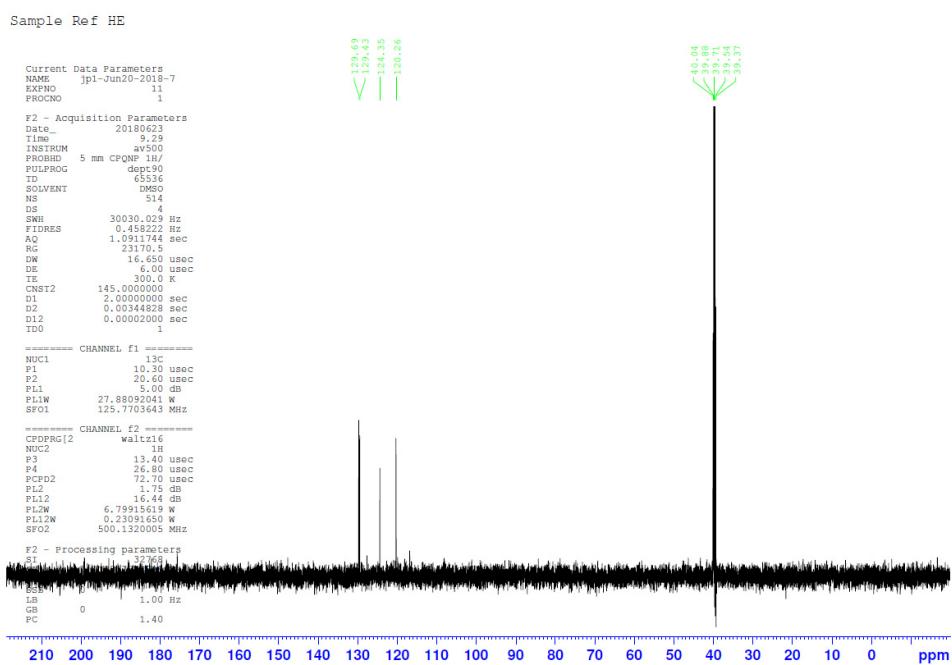
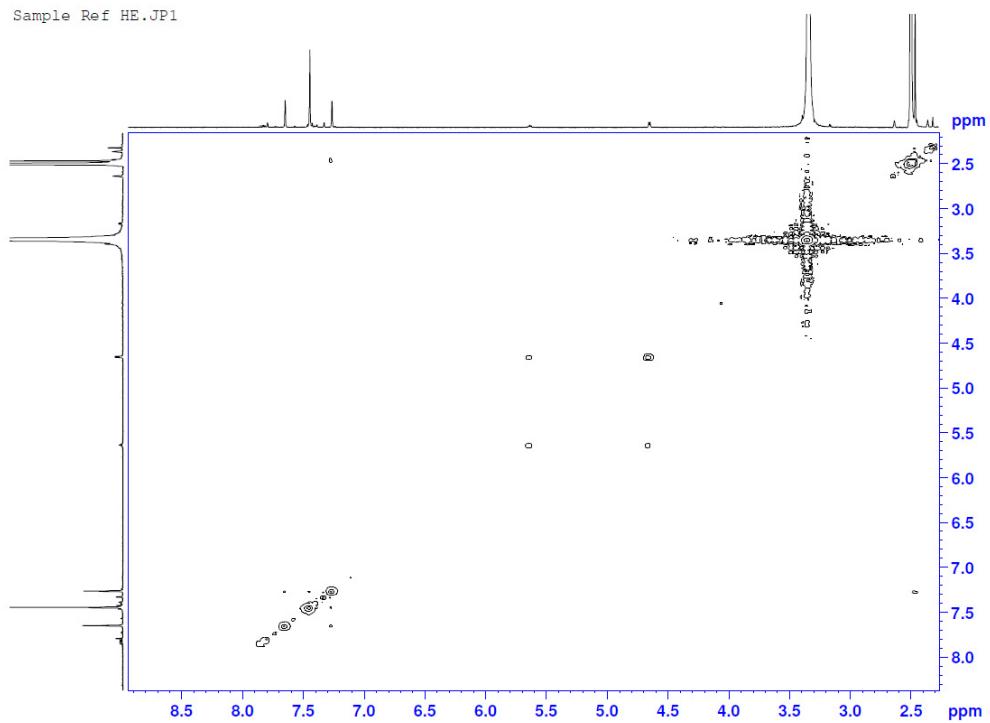
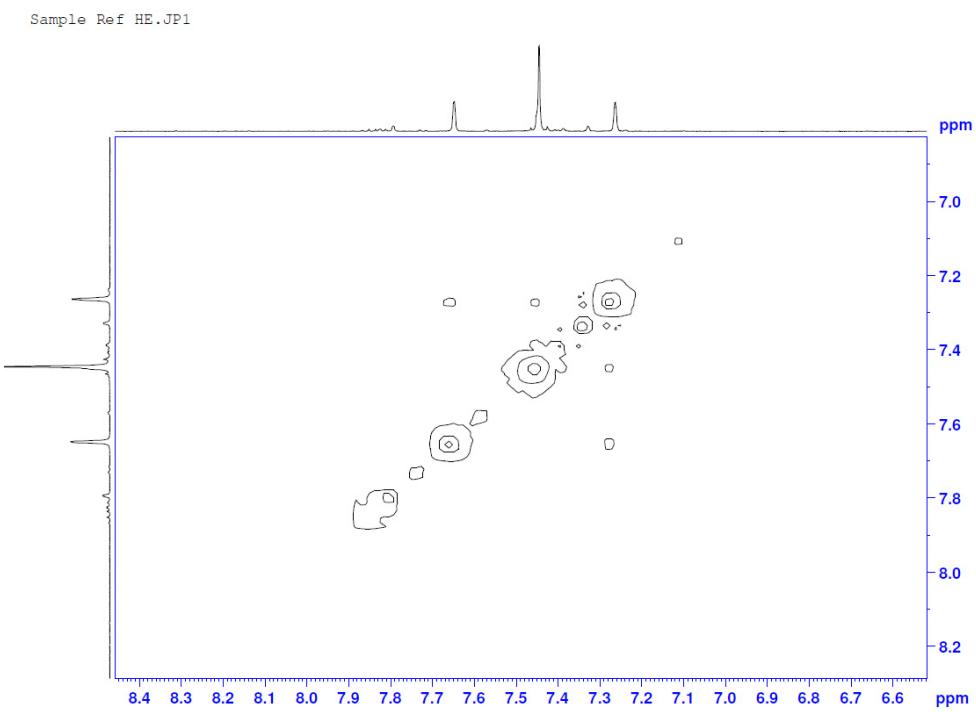


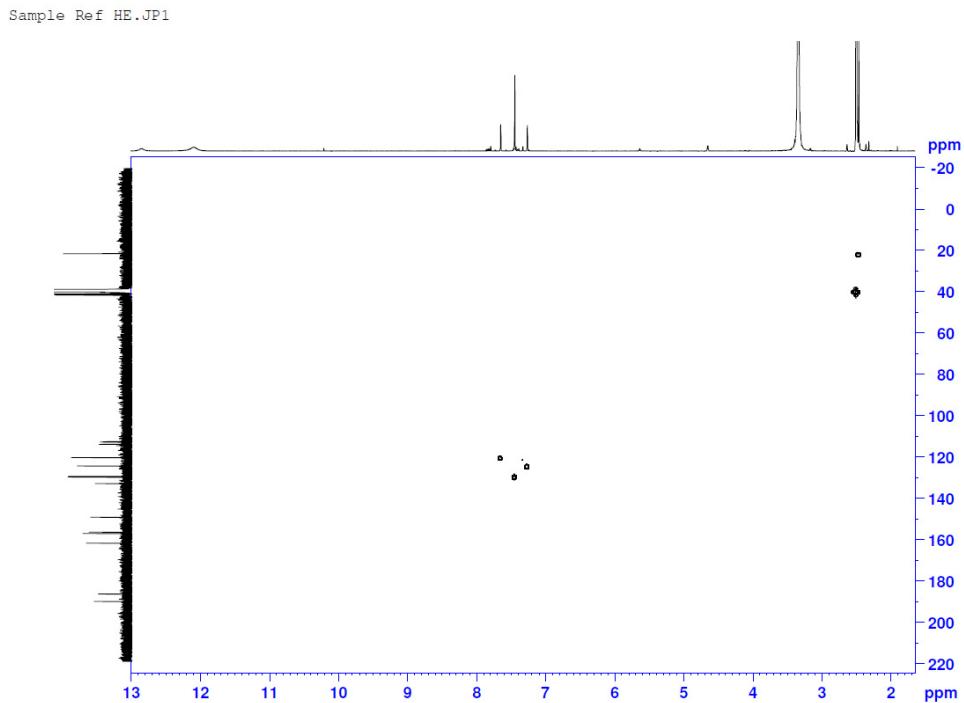
Figure S0-40 Dept 90 of helminthosporin



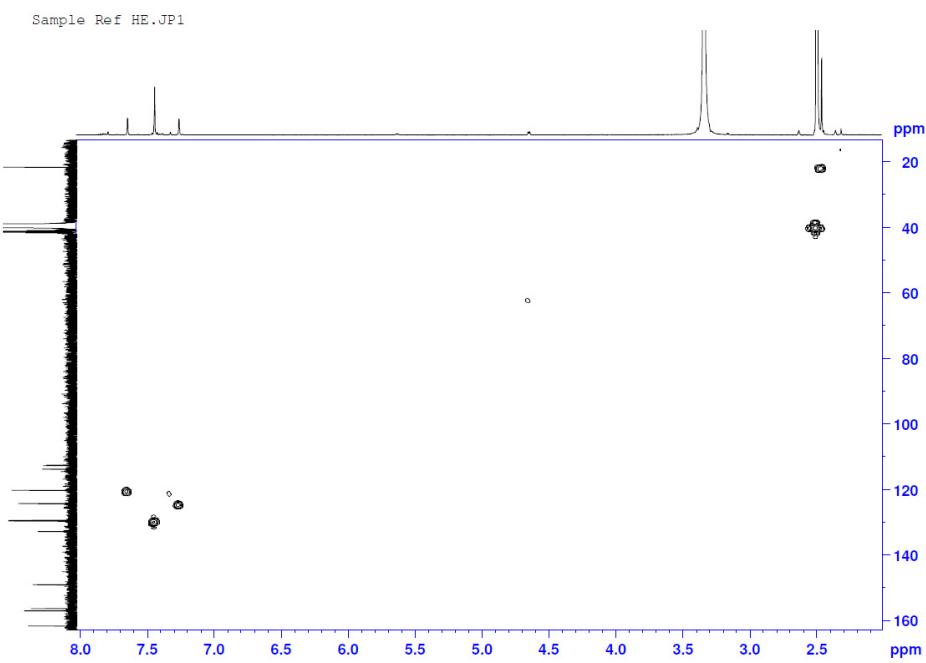
**Figure S0-41 Cosy of helminthosporin**



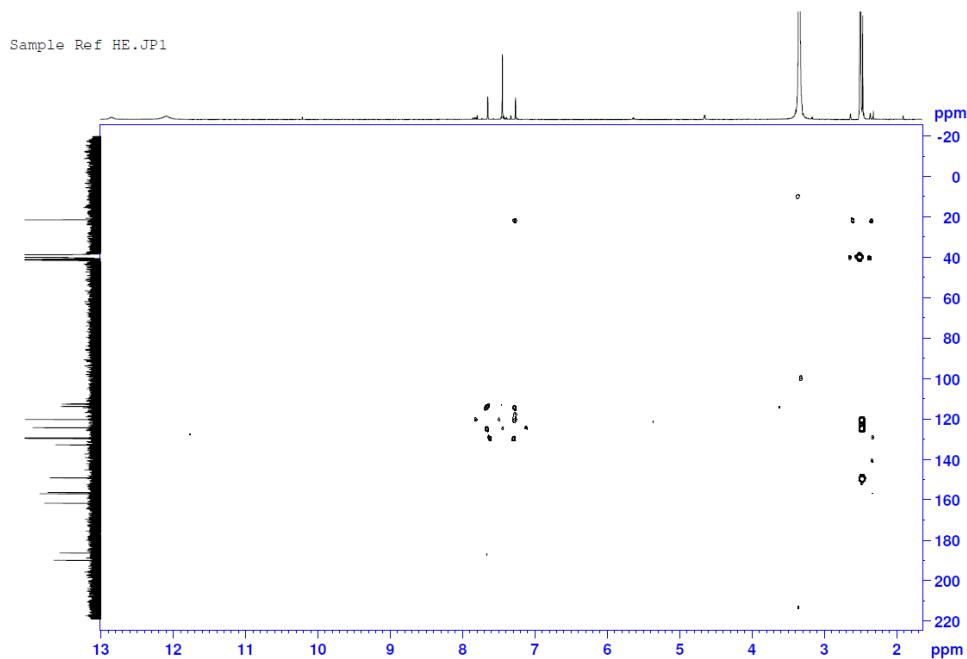
**Figure S0-42 Expand cosy of helminthosporin**



**Figure S0-43 HMQC of helminthosporin**

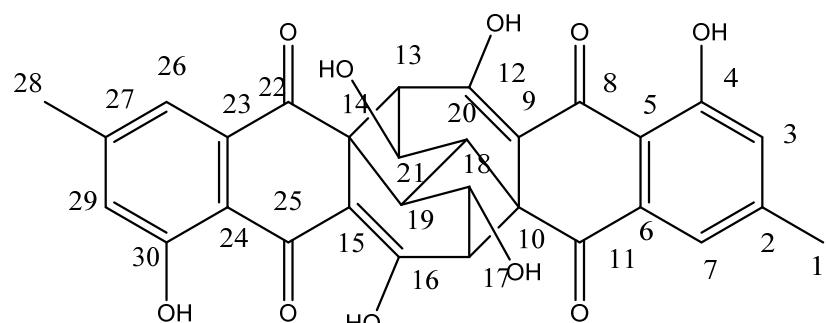


**Figure S0-44 Expand HMQC of helminthosporin**

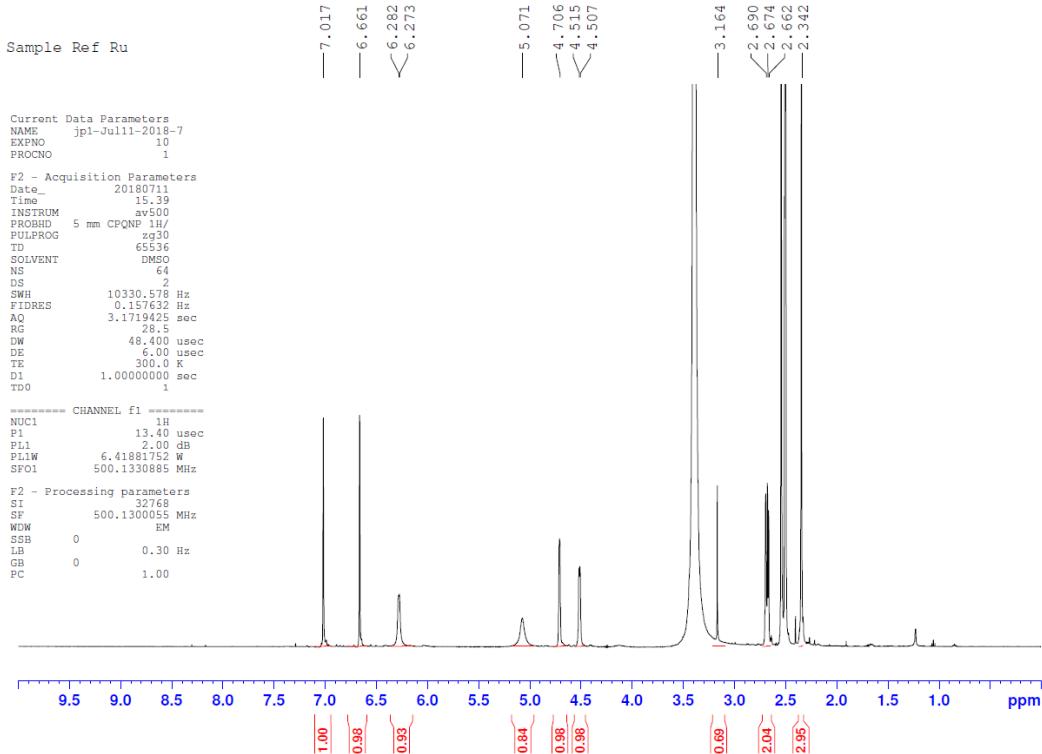


**Figure S0-45 HMBC of helminthosporin**

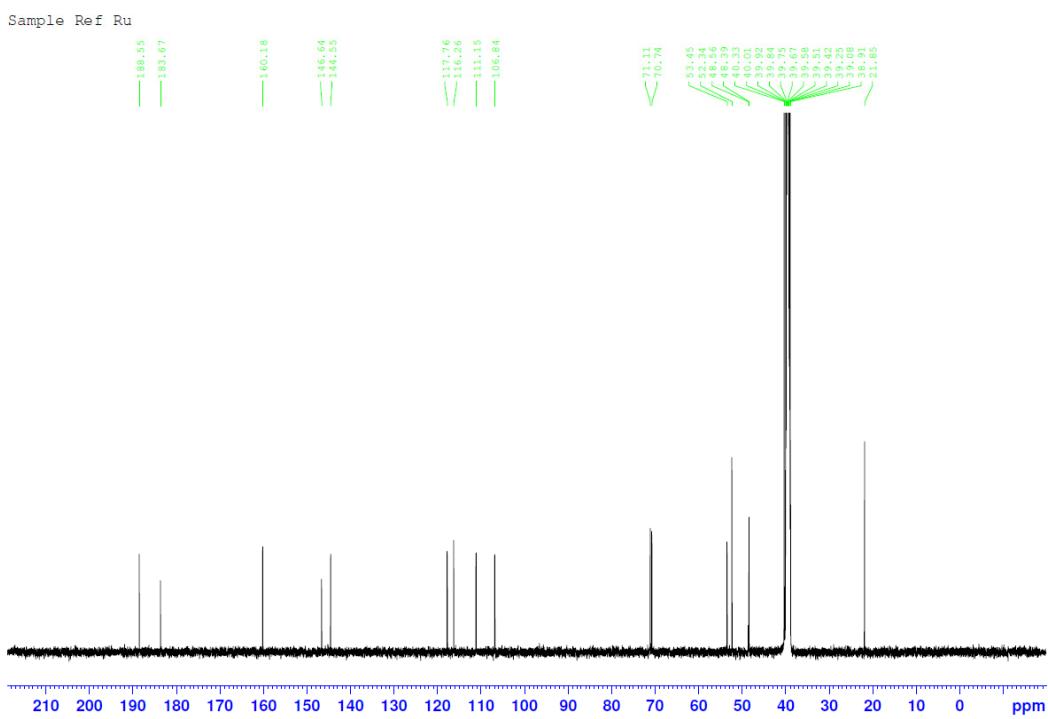
*Rugulosin*



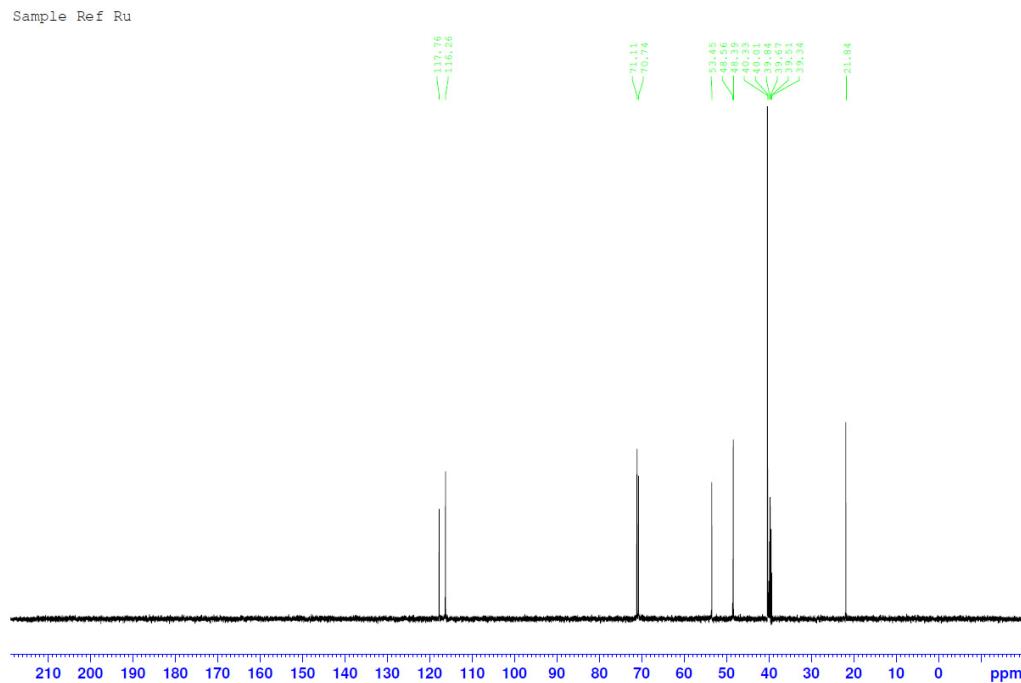
**RUGULOSIN**



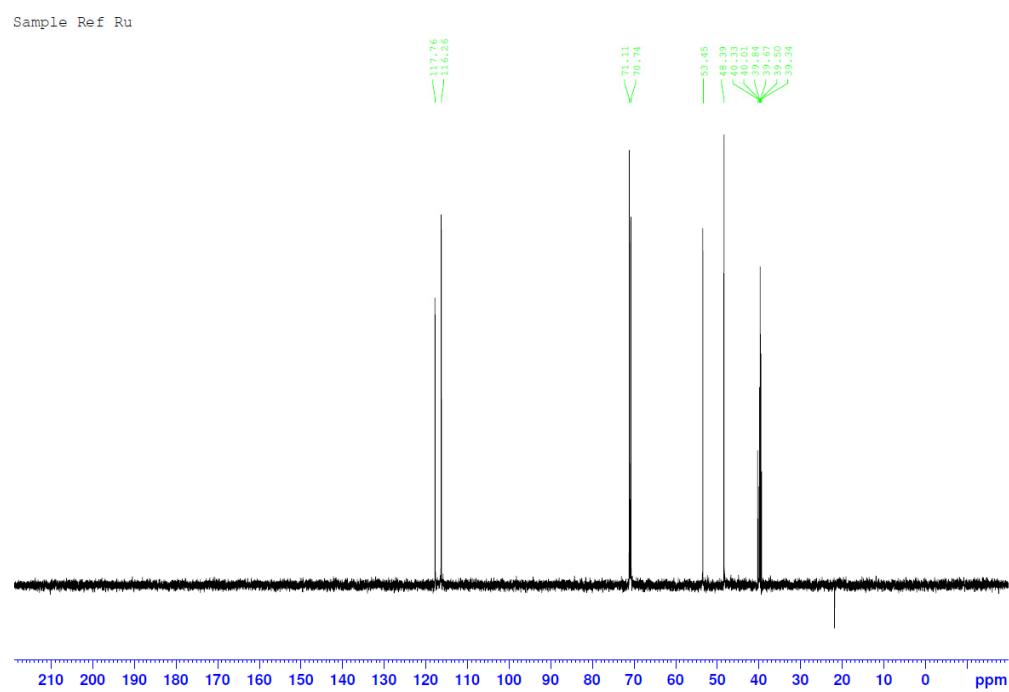
**Figure S0-46**  $^1\text{H}$  NMR Chemical Shift of rugulosin



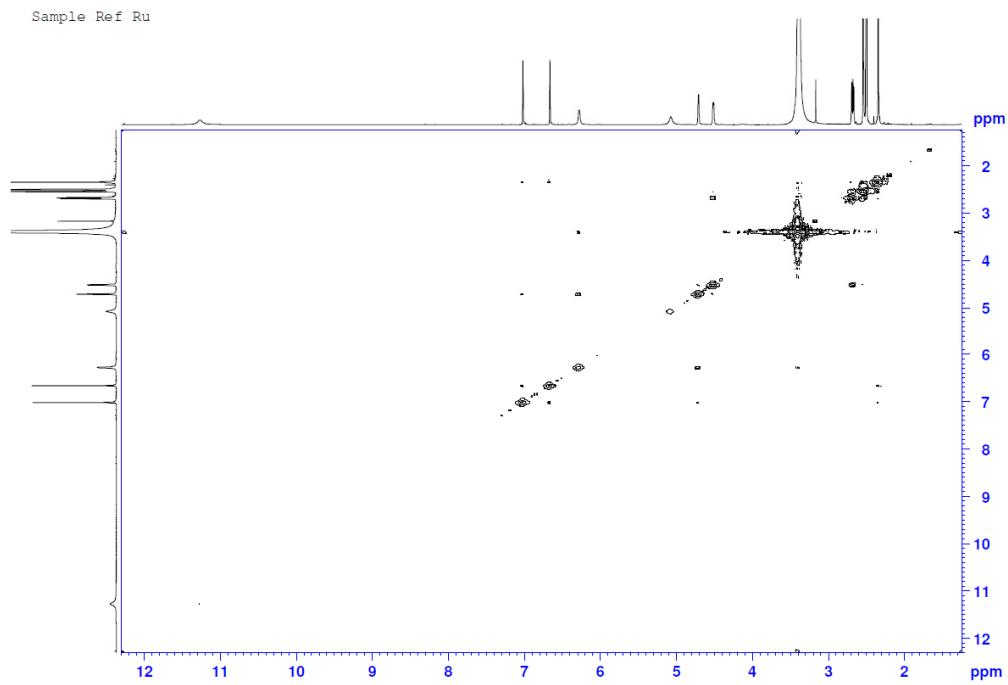
**Figure S0-47**  $^{13}\text{C}$  NMR Chemical Shift of rugulosin



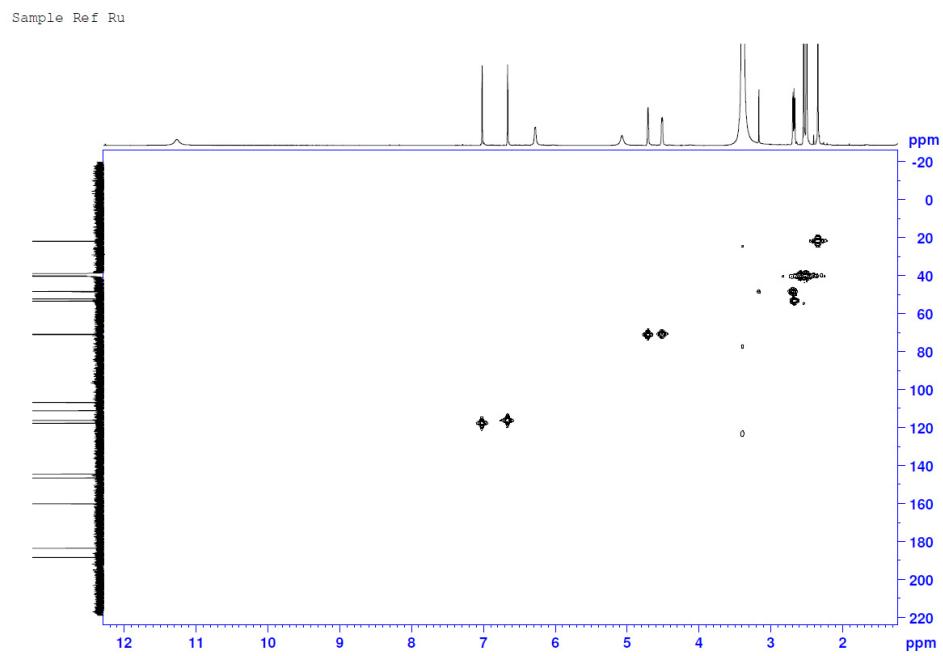
**Figure S0-48 Dept 135 of rugulosin**



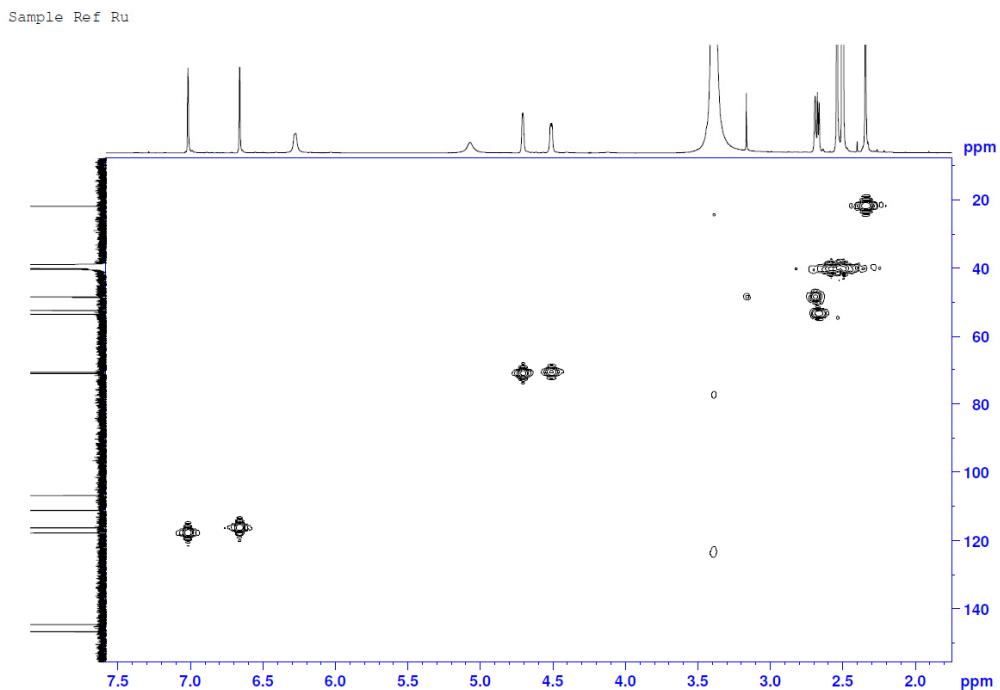
**Figure S0-49 Dept 90 of rugulosin**



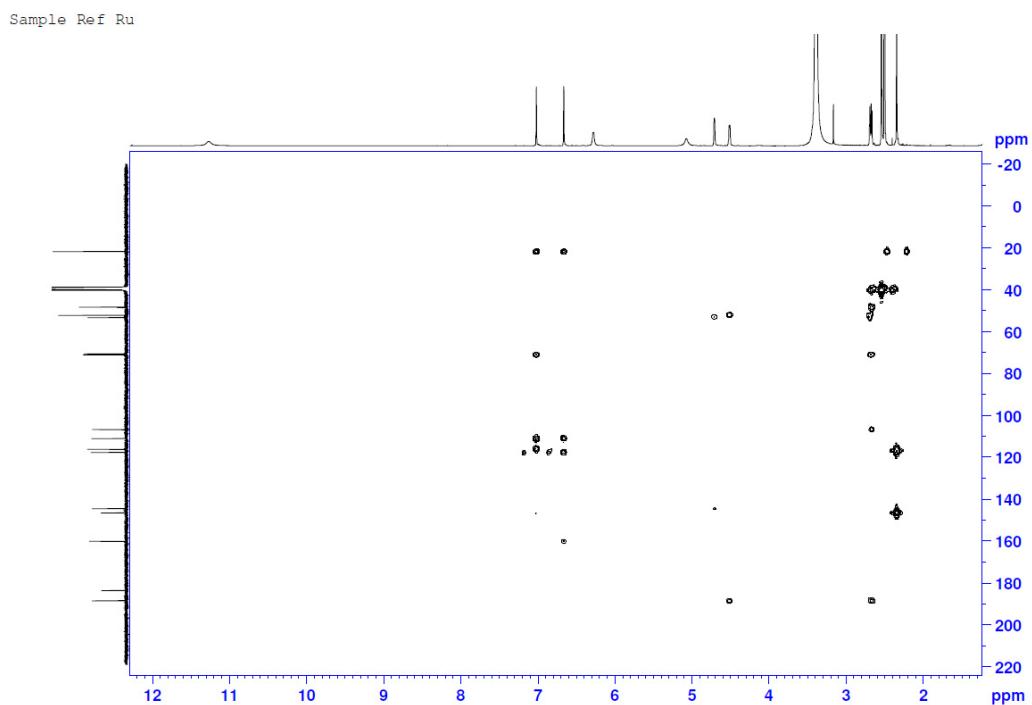
**Figure S0-50 Cosy of rugulosin**



**Figure S0-51 HMQC of rugulosin**



**Figure S0-52 Expand HMQC of rugulosin**



**Figure S0-53 HMBC of rugulosin**

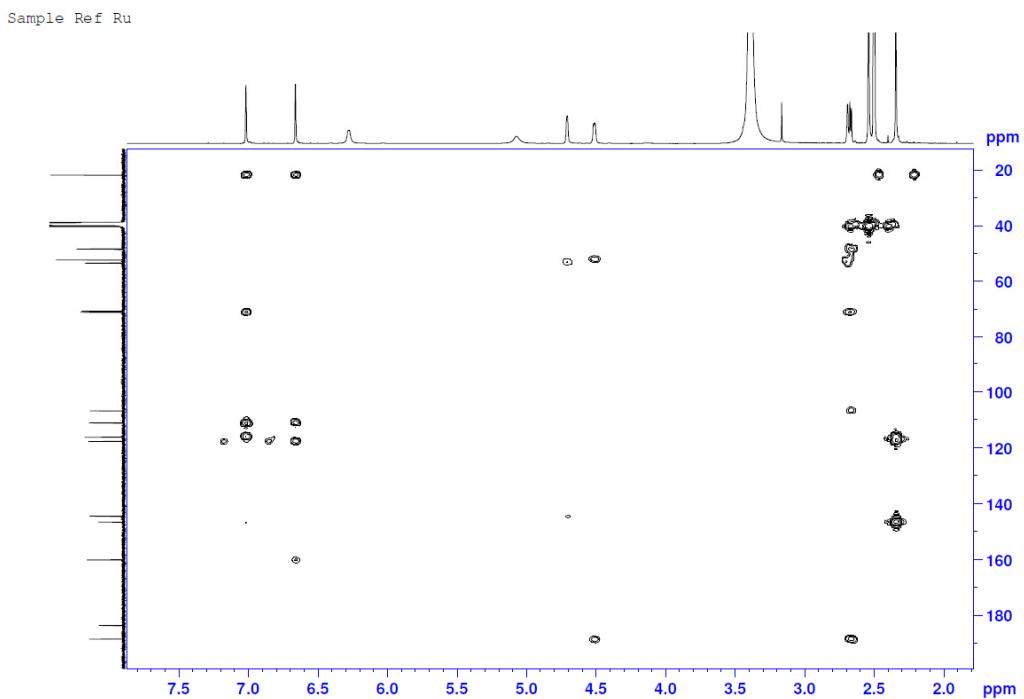
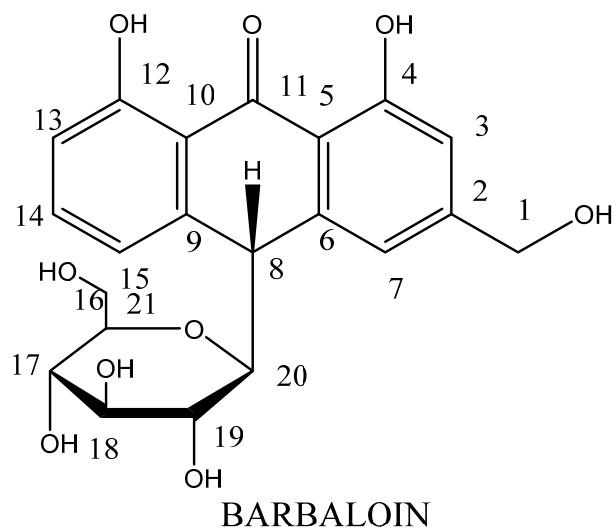
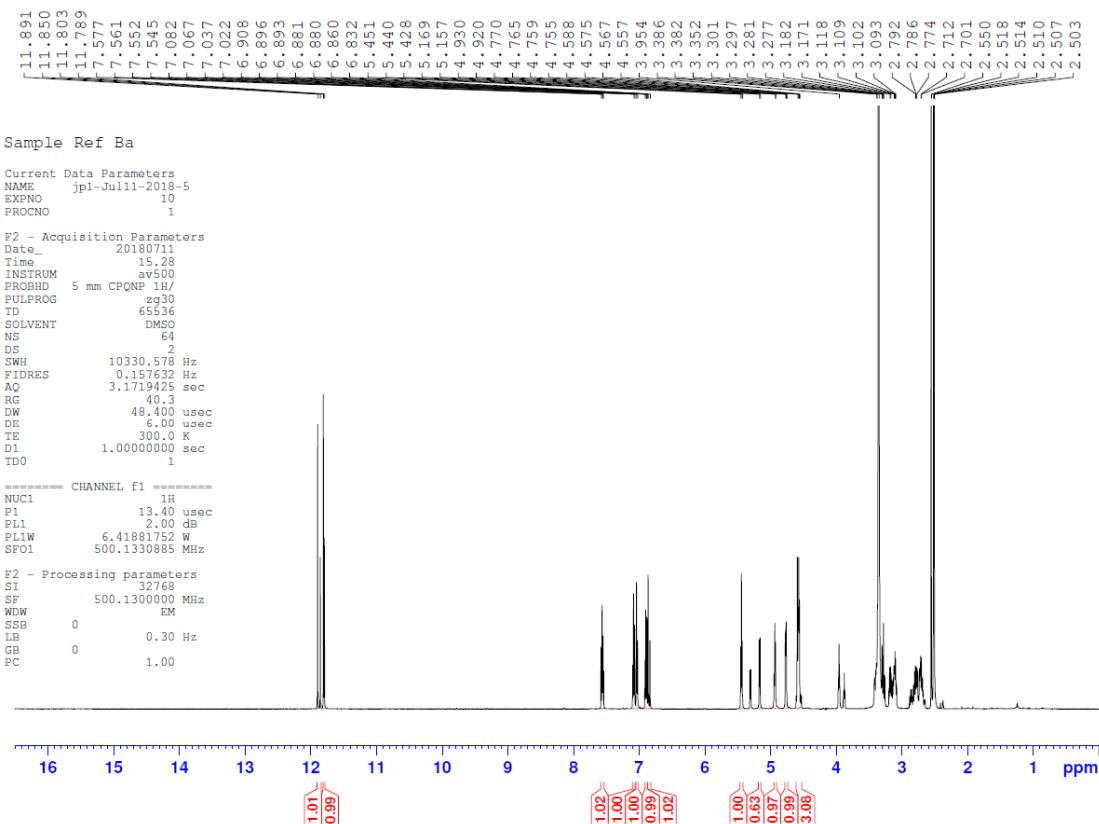


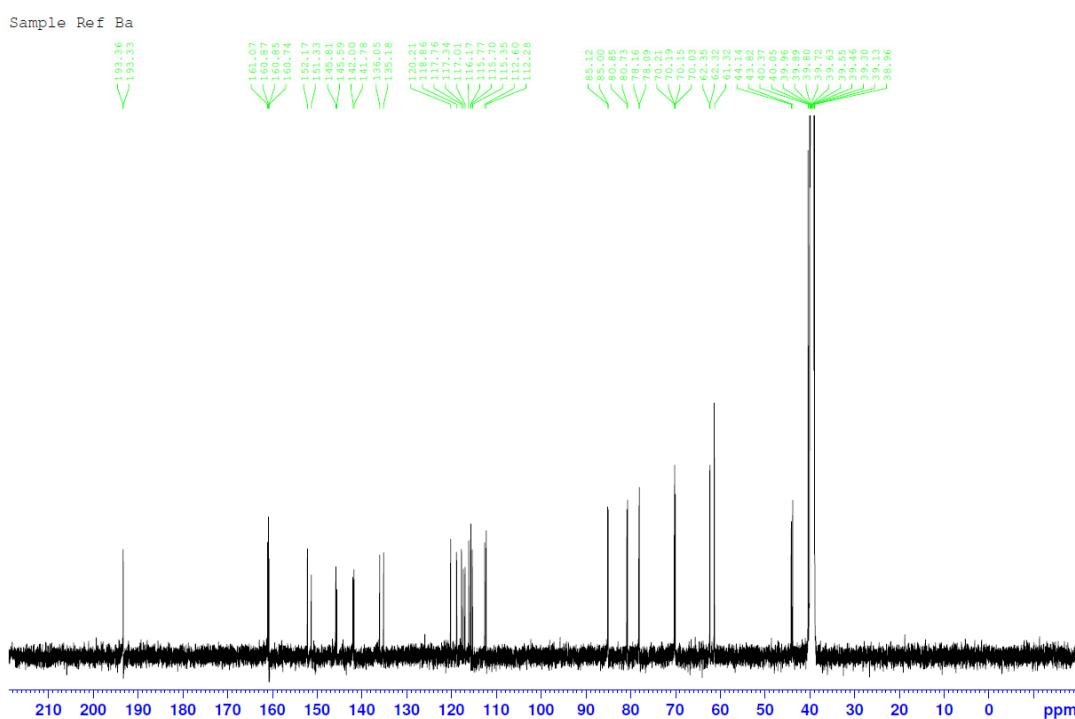
Figure S0-54 Expand HMBC of rugulosin

*Barbaloin*

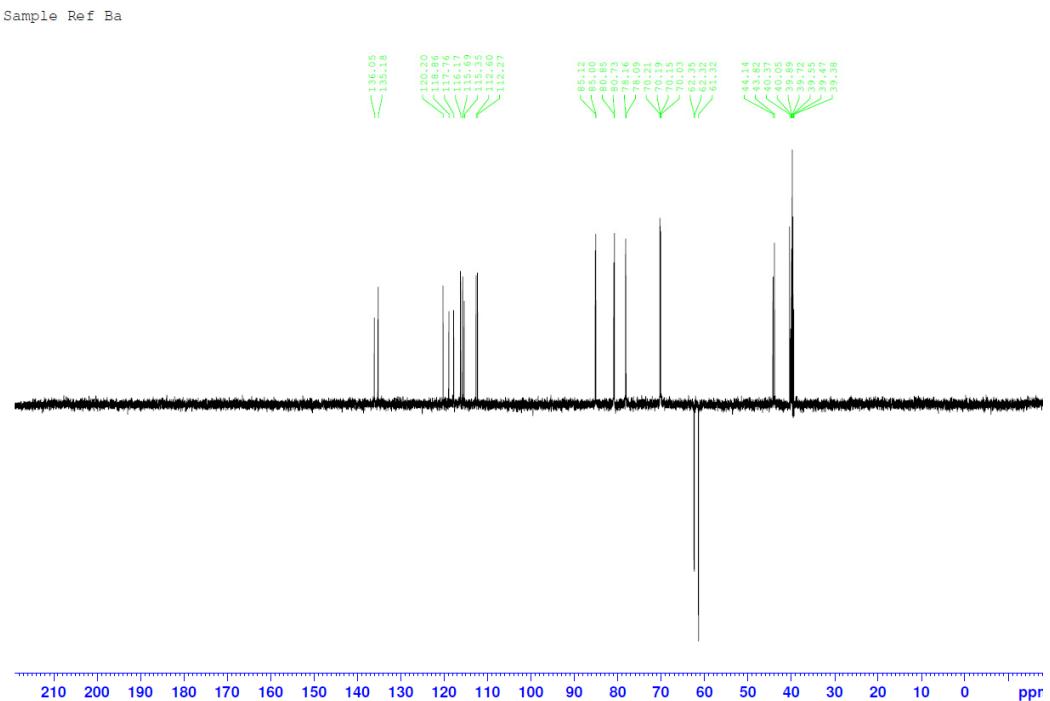




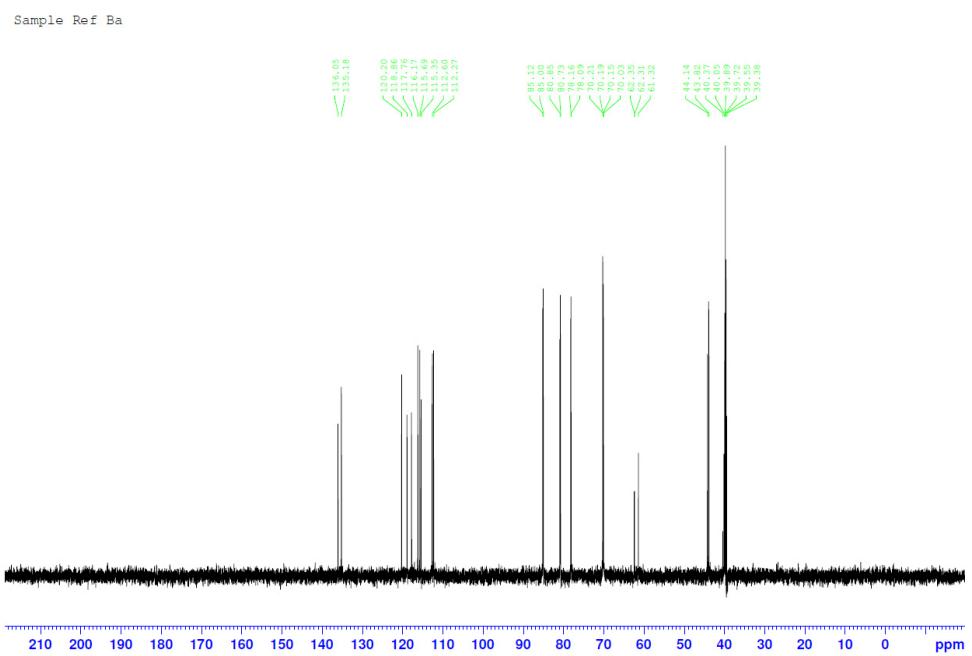
**Figure S0-55**  $^1\text{H}$  NMR Chemical Shift of barbaloin



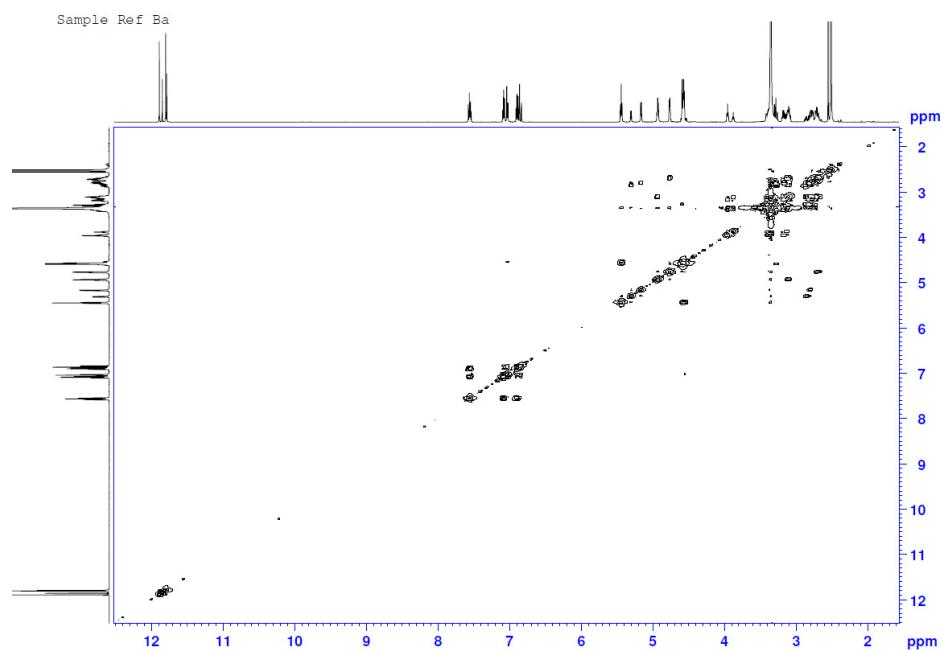
**Figure S0-56**  $^{13}\text{C}$  NMR Chemical Shift of barbaloin



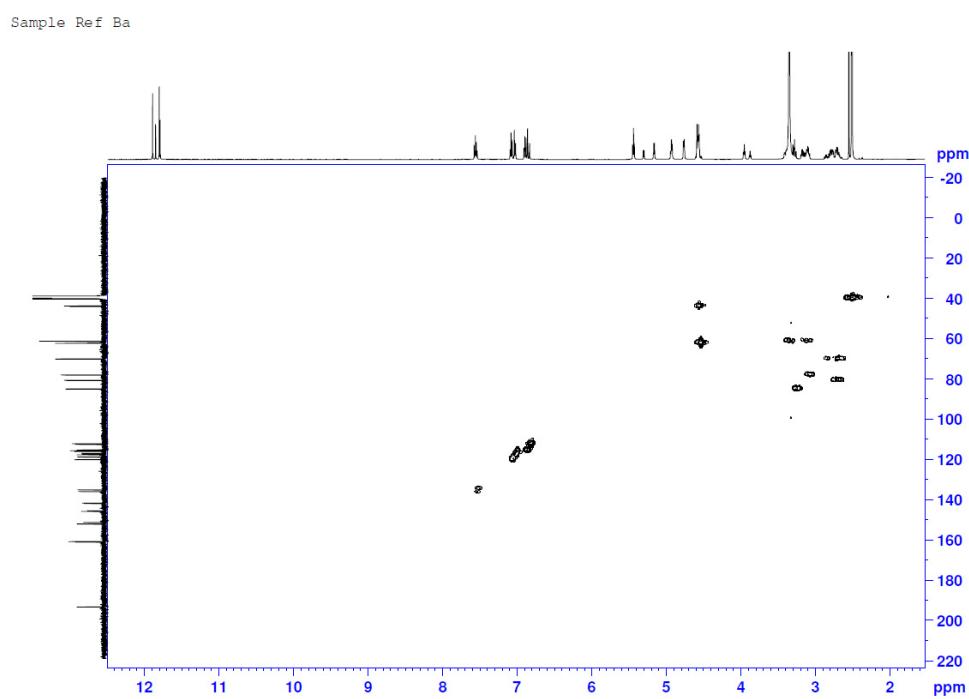
**Figure S0-57 Dept 135 of barbaloin**



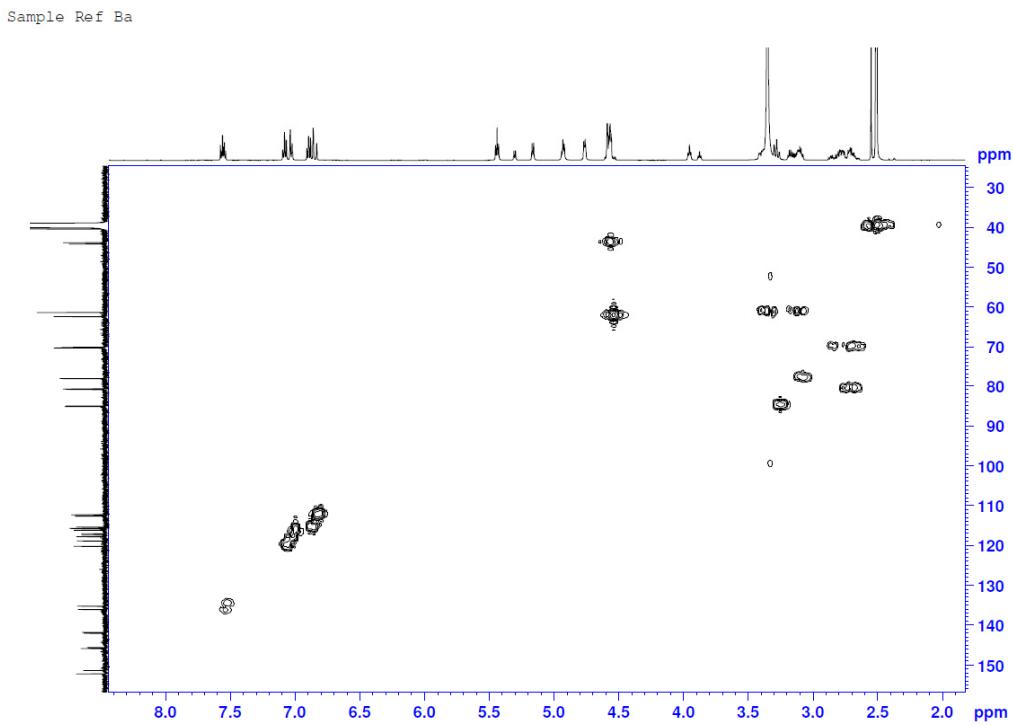
**Figure S0-58 Dept 90 of barbaloin**



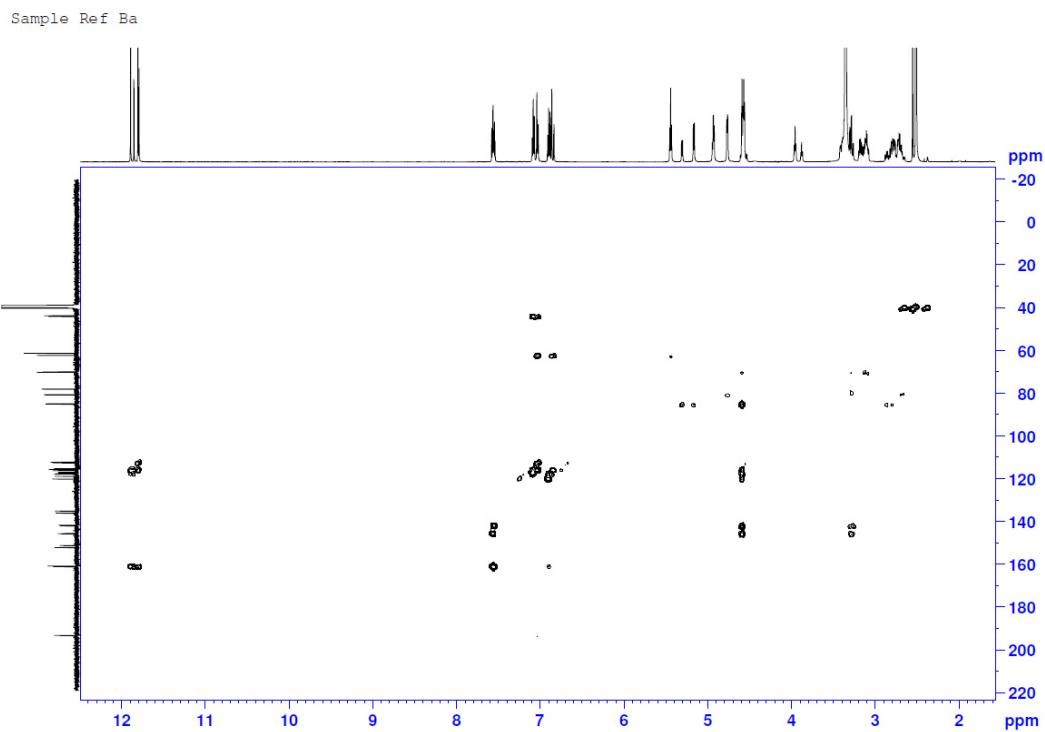
**Figure S0-59 Cosy of barbaloin**



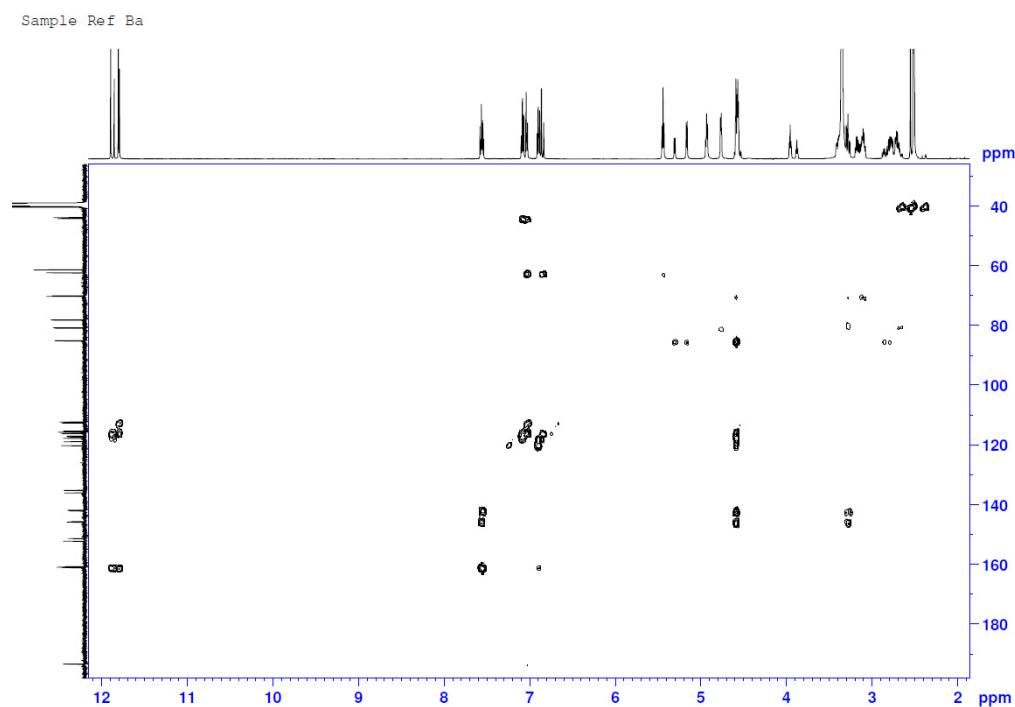
**Figure S0-60 HMQC of barbaloin**



**Figure S0-61 Expand HMQC of barbaloin**



**Figure S0-62 HMBC of barbaloin**



**Figure S0-63 Expand HMBC of barbaloin**