*Supplementary Materials*

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

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# 1. NMR Prediction

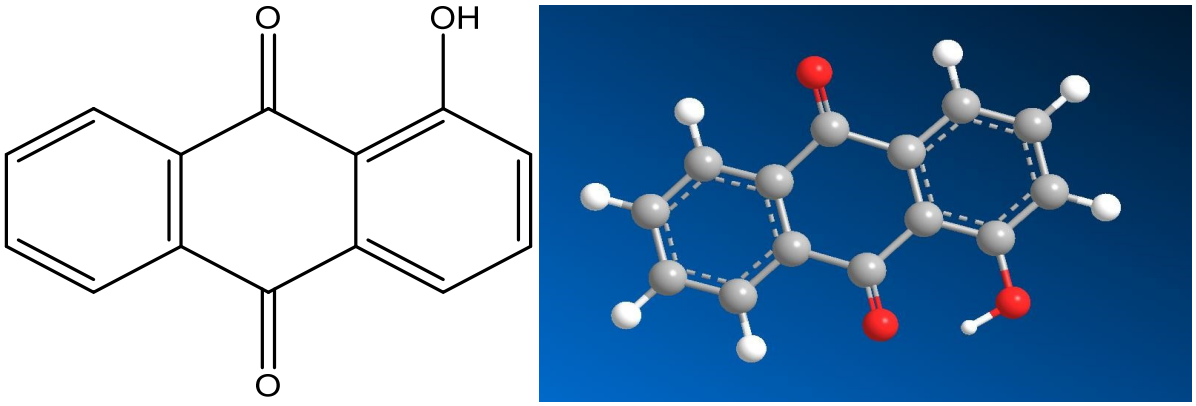



**Figure S1-1 2D and 3D chemical structure of Hydroxyanthraquinones (Source: ChemDraw Professional).**

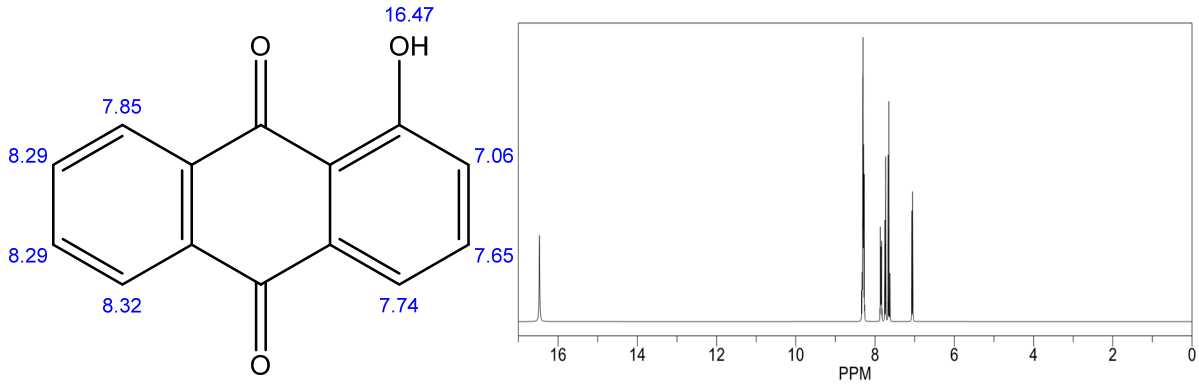



**Figure S0-1 Chem NMR 1H Estimation of Hydroxyanthraquinones (Source: ChemDraw Professional)**

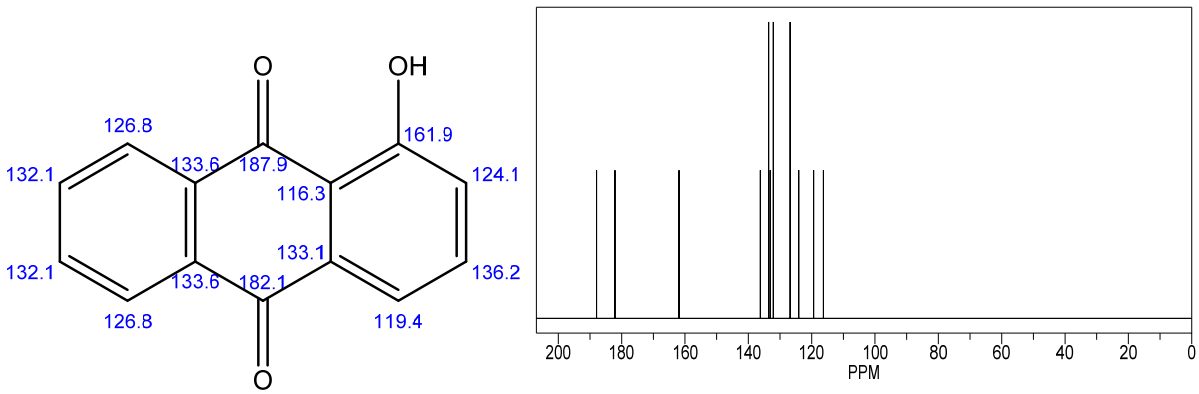



**Figure S0-2 Chem NMR 13C Estimation of Hydroxyanthraquinones (Source: ChemDraw Professional)**

***Aloe-emodin***

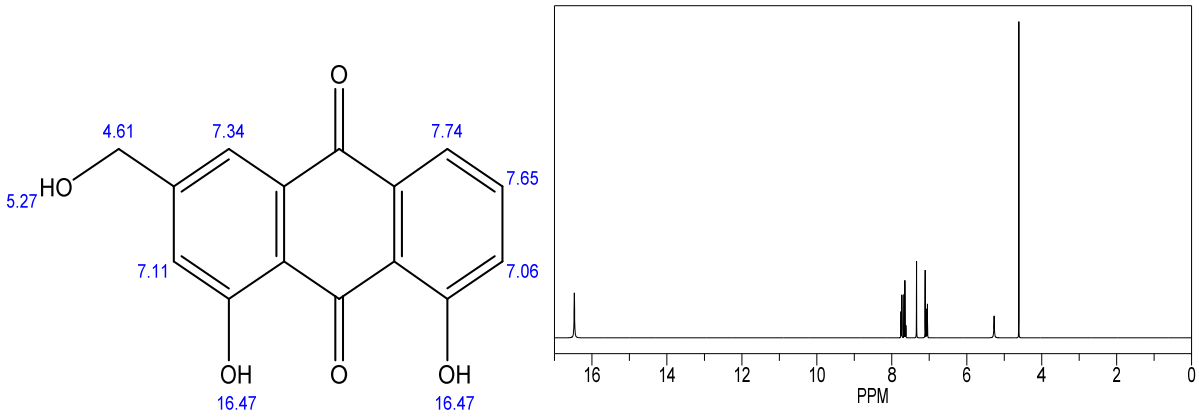



**Figure S0-3 Chem NMR 1H Estimation of Aloe-emodin (Source: ChemDraw Professional)**

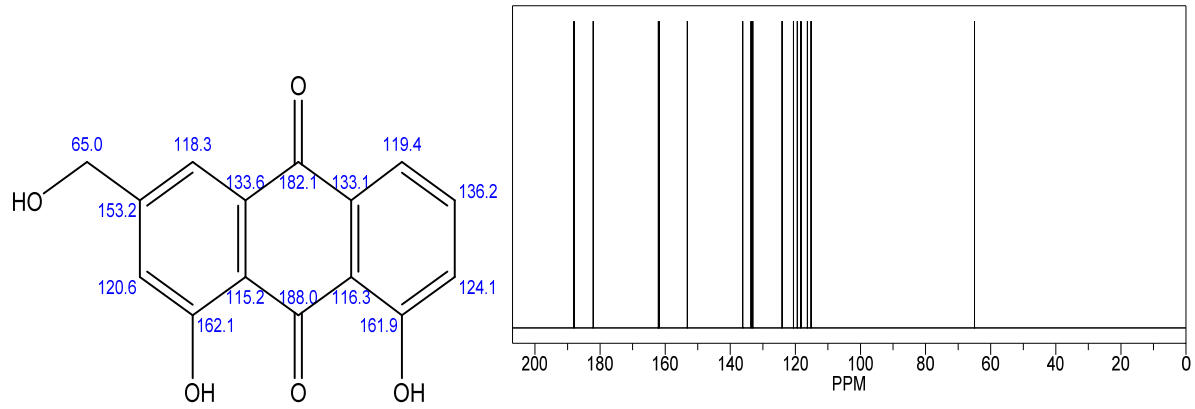



**Figure S0-4 Chem NMR 13C Estimation of Aloe-emodin (Source: ChemDraw Professional)**

As per literature "1H NMR (DMSO-d6): δ = 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);.13C NMR (DMSO-d6): δ = 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***

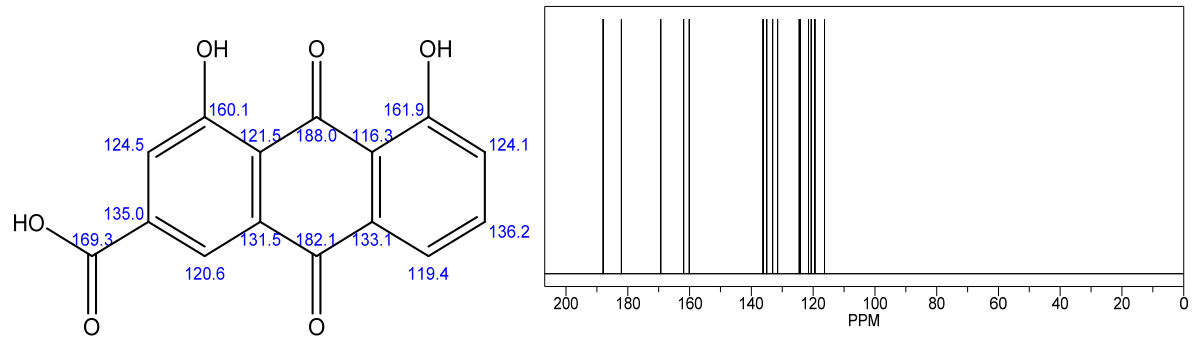



**Figure S0-5 Chem NMR 13C Estimation of Rhein (Source: ChemDraw Professional)**

**Table 1.** $^{1}$H NMR chemical shifts and coupling constants for anthraquinones 1–5

| Proton | Chrysophanol (1) | Physcion (2) | Emodin (3) | Aloe-emodin (4) | Rhein (5) |
|---|---|---|---|---|---|
| H-2 | 7.22 | 6.68 | 6.59 | 7.29 | 7.77 |
| H-4 | 7.55 | 7.36 | 7.12 | 7.69 | 8.14 |
| H-5 | 7.71 | 7.62 | 7.49 | 7.72 | 7.75 |
| H-6 | 7.80 | — | — | 7.80 | 7.84 |
| H-7 | 7.38 | 7.07 | 7.16 | 7.38 | 7.41 |
| OH-1 | 11.87 | 12.30 | 12.08 | 11.91 | |
| OH-8 | 11.97 | 12.11 | 12.01 | 11.97 | |
| OH-3 | — | — | 11.37 | 5.62 | |
| $CH_3$ | 2.44 | 2.44 | 2.41 | — | — |
| $OCH_3$ | — | 3.93 | — | — | — |
| $CH_2$ | — | — | — | 4.63 | — |
| H-2(*m*) | 0.82, 1.15 | 2.57 | 2.46, 0.35 | 1.66 | 1.47 |
| H-4(*m*) | 0.49, 1.15 | 2.57 | 2.28, 0.35 | 1.66 | 1.47 |
| H-5(*m*) | 1.31 | 0.55, 0.92 | 0.35, 0.53 | 1.16 | 1.10 |
| H-5(*o*) | 7.55 | — | — | 7.63 | 7.54 |
| H-6(*o*) | 7.55, 8.37 | — | — | 7.63, 8.29 | 7.54, 8.22 |
| H-7(*m*) | 1.31 | 0.74, 0.92 | 0.35, 0.70 | 1.16 | 1.10 |
| H-7(*o*) | 8.37 | — | — | 8.29 | 8.22 |
| $CH_3$(*m*) | 0.82, 0.49 | 0.55, 0.74 | 0.53, 0.70 | — | — |

**Table 2.** $^{13}$C NMR chemical shifts for anthraquinones 1–5[a]

| Carbon | Chrysophanol (1) | Physcion (2) | Emodin (3) | Aloe-emodin (4) | Rhein (5) |
|---|---|---|---|---|---|
| C-1 | 161.67 | 165.20 | 164.54 | 161.72 | 161.51 |
| C-2 | 124.16 | 106.78 | 108.02 | 120.78 | 124.21 |
| C-3 | 149.26 | 166.56 | 165.64 | 153.80 | 138.20 |
| C-4 | 120.64 | 108.22 | 108.84 | 117.18 | 119.05 |
| C-5 | 119.41 | 121.29 | 120.58 | 119.43 | 119.48 |
| C-6 | 137.41 | 148.44 | 148.35 | 137.42 | 137.63 |
| C-7 | 124.49 | 124.51 | 124.23 | 124.49 | 124.64 |
| C-8 | 161.41 | 162.51 | 161.51 | 161.43 | 161.27 |
| C-9 | 191.72 | 190.82 | 189.83 | 191.74 | 191.49 |
| C-10 | 181.57 | 182.05 | 181.48 | 181.59 | 181.25 |
| C-11 | 133.40 | 133.23 | 132.91 | 133.54 | 133.41 |
| C-12 | 115.94 | 113.69 | 113.46 | 116.01 | 116.33 |
| C-13 | 113.85 | 110.27 | 109.06 | 114.57 | 118.48 |
| C-14 | 133.10 | 135.27 | 135.21 | 133.22 | 133.61 |
| $CH_3$ | 21.71 | 22.15 | 21.60 | — | — |
| $OCH_3$ | — | 56.07 | — | — | — |
| $CH_2$ | — | — | — | 62.15 | — |
| COOH | — | — | — | — | 165.52 |

**Figure S0-6 1H and 13C NMR Chemical Shift of Rhein (Source: Danielsen, Aksnes and Francis, 1992)**

***Catenarin***

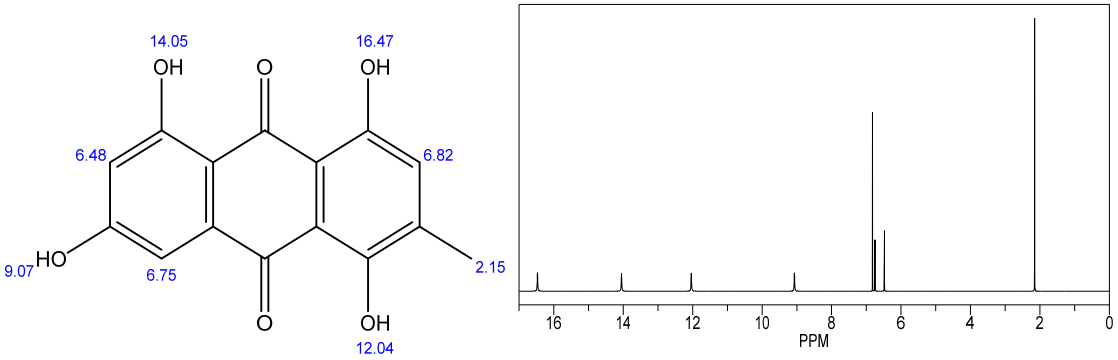



**Figure S0-7 Chem NMR 1H Estimation of Catenarin (Source: ChemDraw Professional)**

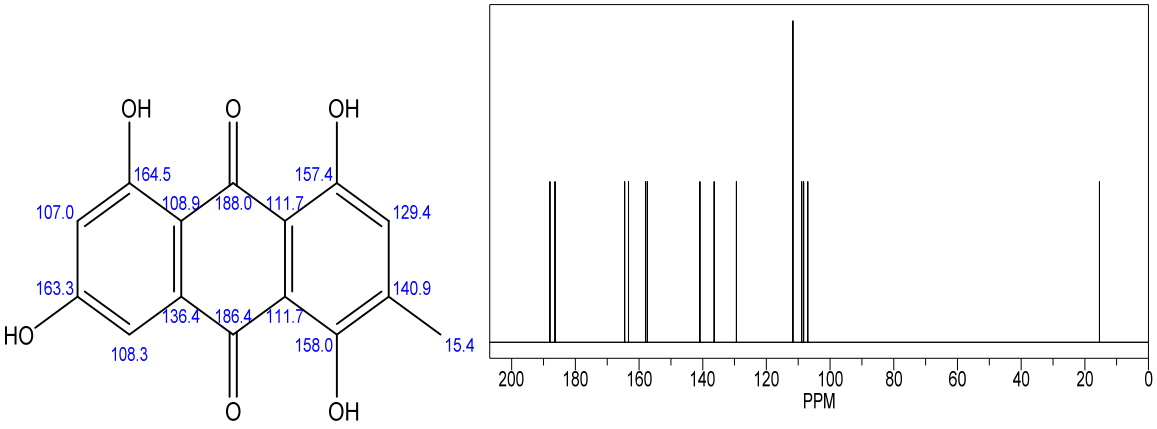



**Figure S0-8 Chem NMR 13C Estimation of Catenarin (Source: ChemDraw Professional)**

As per literature "1H NMR (CDCl3) spectrum was as follows: 6′-CH3: 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: δH12.35, 12.42, 13.34." (Kalidhar, 1989).

***Barbaloin***

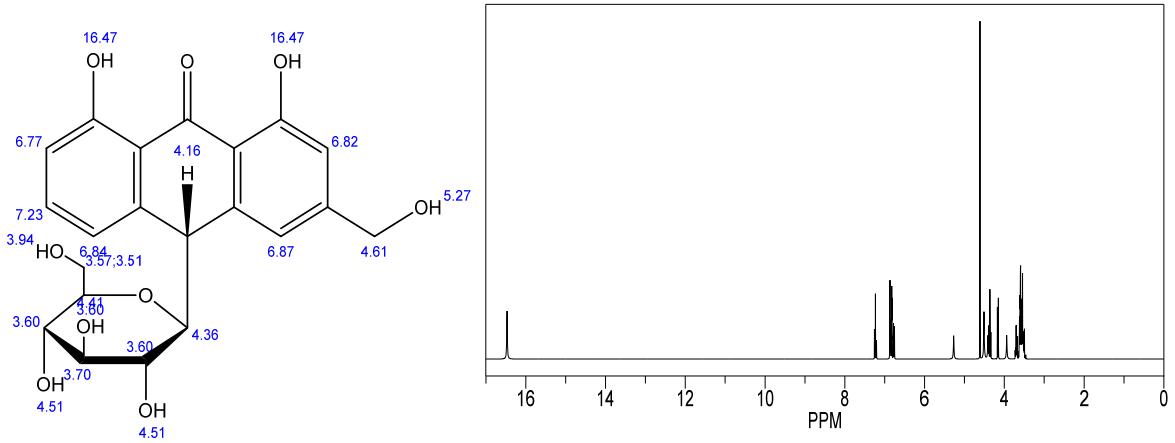



**Figure S0-9 Chem NMR 1H Estimation of Barbaloin (Source: ChemDraw Professional)**

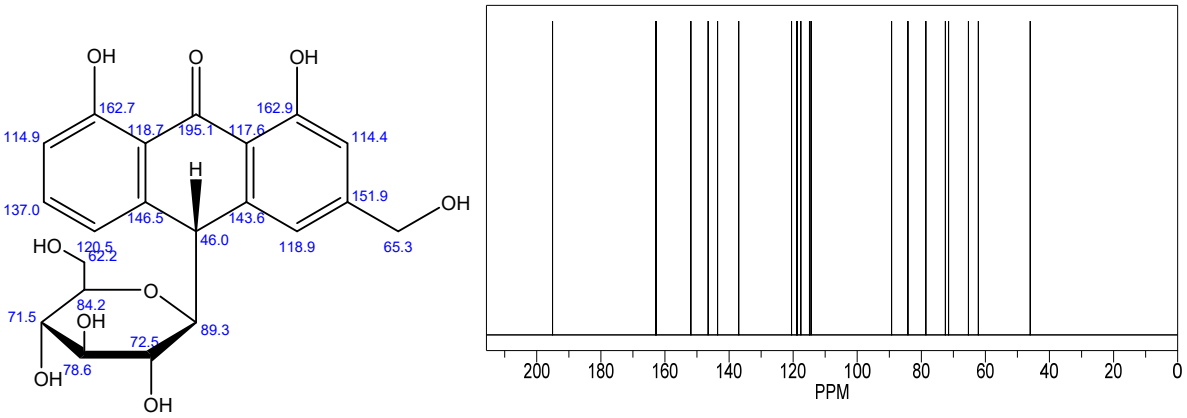



**Figure S0-10 Chem NMR 13C Estimation of Barbaloin (Source: ChemDraw Professional)**

As per literature "1H NMR (400 MHz, MeOH-d4) d 7.49 (1H, t, J¼7.8 Hz, H6), 7.07 (1H, H5), 7.05 (1H, s,H4), 6.88 (1H, s, 8, H2), 6.82(1H, d, J¼8.2 Hz, H7), 4.66 (1H, s, H15b), 4.65 (1H, s, H15a), 4.61 (1H, d, J¼0.9 Hz, H10), 3.56 (1H, dd, J 11.4, 1.6 Hz, H-6b'), 3.41 (1H, dd, J¼9.7, 2.4 Hz, H-6a'), 3.37 (1H,m, H-1'), 3.25 (1H, t, J¼8.7 Hz, H-3'), 3.01 (1H, t, J¼8.7 Hz, H-2'),2.91 (1H, br s, H-5'), 2.90 (1H,br s, H-4')" (Kim et al., 2017).

***Chrysazin***

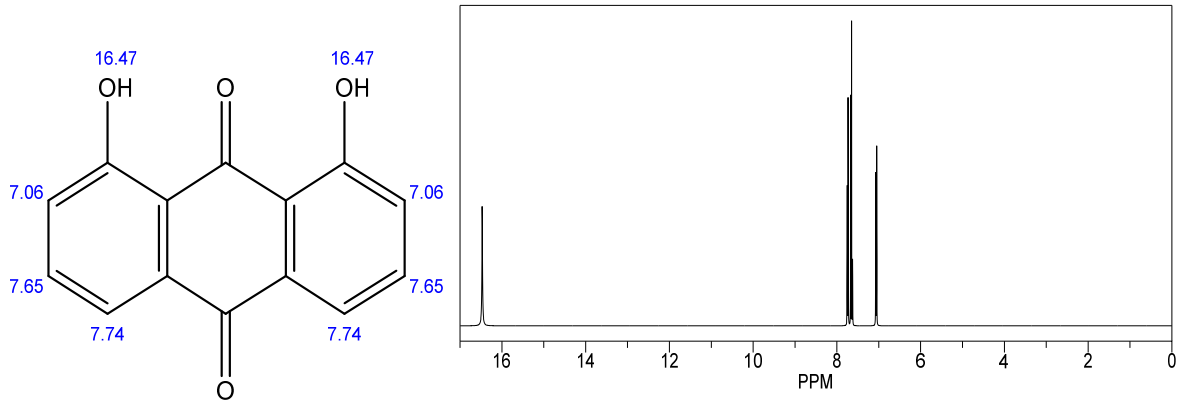



**Figure S0-11 Chem NMR 1H Estimation of Chrysazin (Source: ChemDraw Professional)**

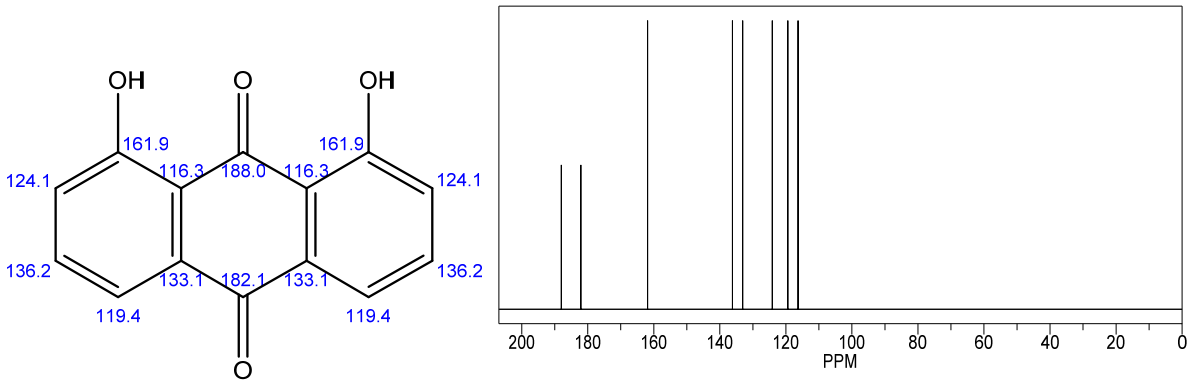



**Figure S0-12 Chem NMR 13C Estimation of Chrysazin (Source: ChemDraw Professional)**

As per literature "1H 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). 1H 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); 13C 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***

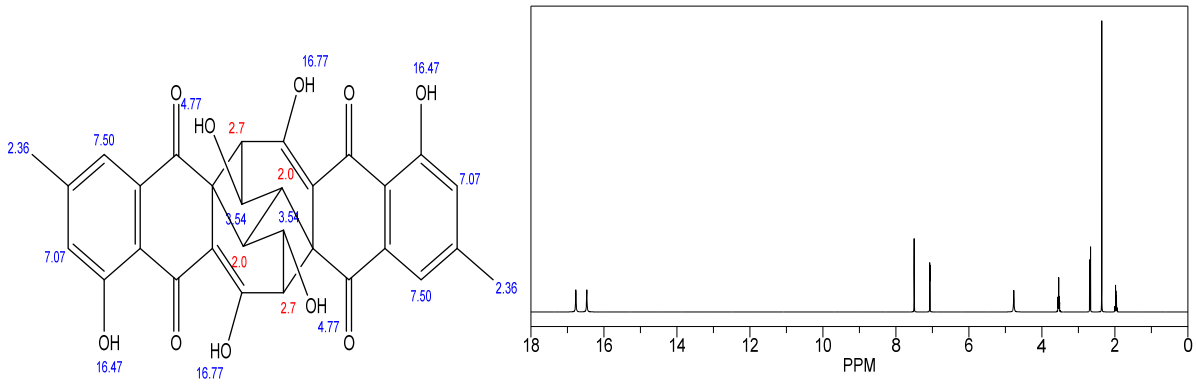
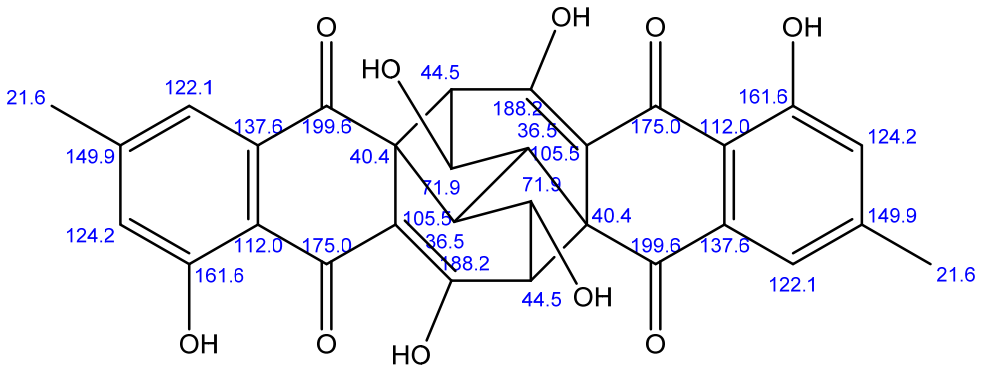



**Figure S0-13 Chem NMR 1H Estimation of Rugulosin (Source: ChemDraw Professional)**



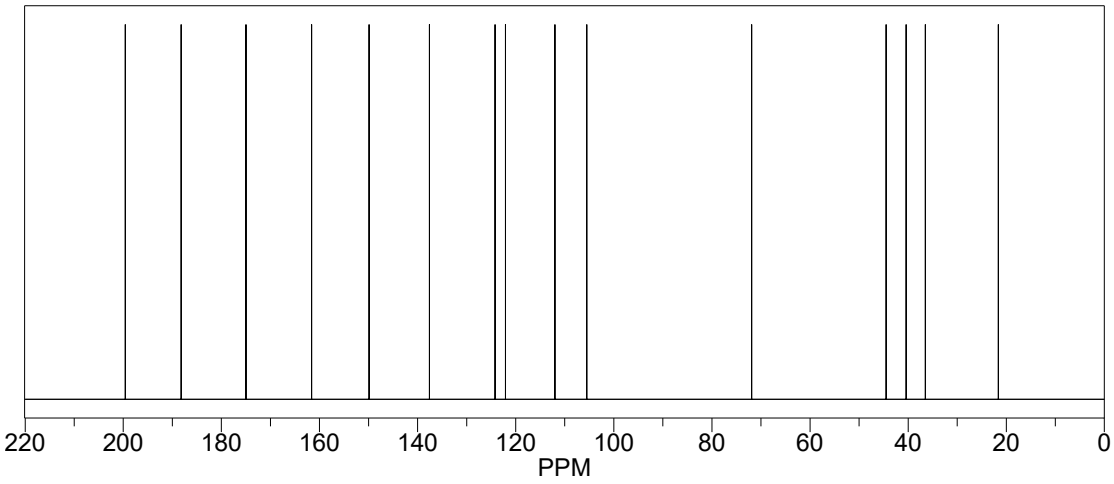



**Figure S0-14 Chem NMR 13C Estimation of Rugulosin (Source: ChemDraw Professional)**

As per literature "1H NMR (DMSO-d6) 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′); 13C 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***

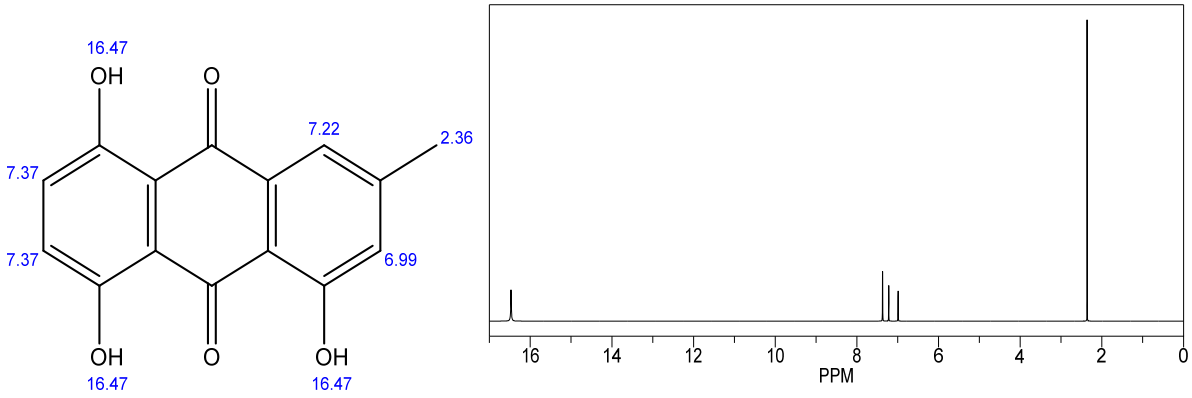



**Figure S0-15 Chem NMR 1H Estimation of Helminthosporin (Source: ChemDraw Professional)**

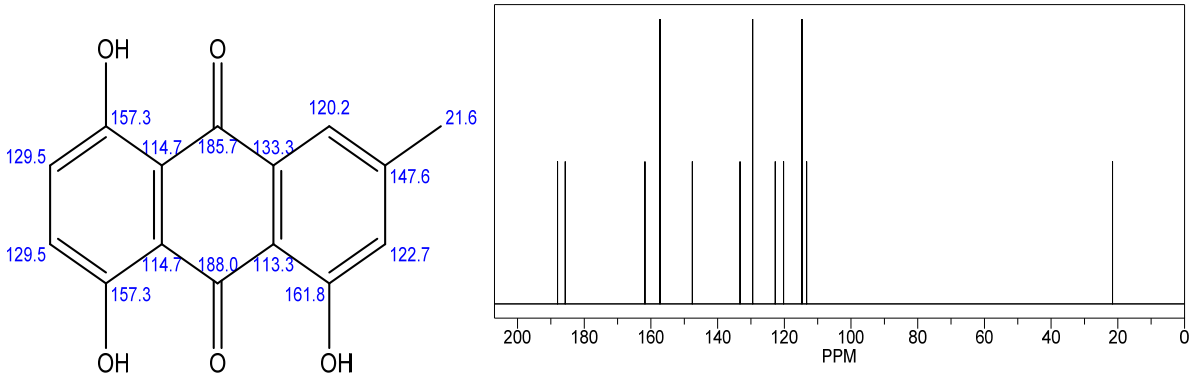
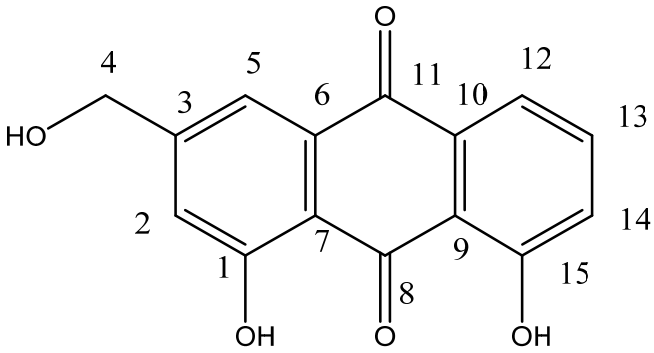



**Figure S0-16 Chem NMR 13C Estimation of Helminthosporin (Source: ChemDraw Professional)**

As per literature "1H-NMR (400 MHz, CDCl Me,Si) 6 2-49 (H-3', 3H, t, I,. = 0.8 Hz, I = 0-7 Hz) 7-13 (H-2, IH, m,] = 0.8 Hz,] = 1.7 Hz) 7.30 (H-6, H-7, 2H, s) 771 (H-4, IH, m, I= 1.7 Hz, I= 0.7 Hz) 12.16, 12.34 (20H, 2H, 2s) 13.03 (OH1, IH, s)" (Engström et al., 1993).

# 2. Experimental NMR

***Aloe-emodin***




ALOE-EMODIN

| Position | (500MHz) (DMSO-*d6*) | Peak shape | C13 | ChemDraw prediction (300 MHz) (DMSO) | C13 | Literature review (500MHz) (DMSO-*d6*) (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 1H and 13C NMR Chemical Shift of Aloe-emodin**

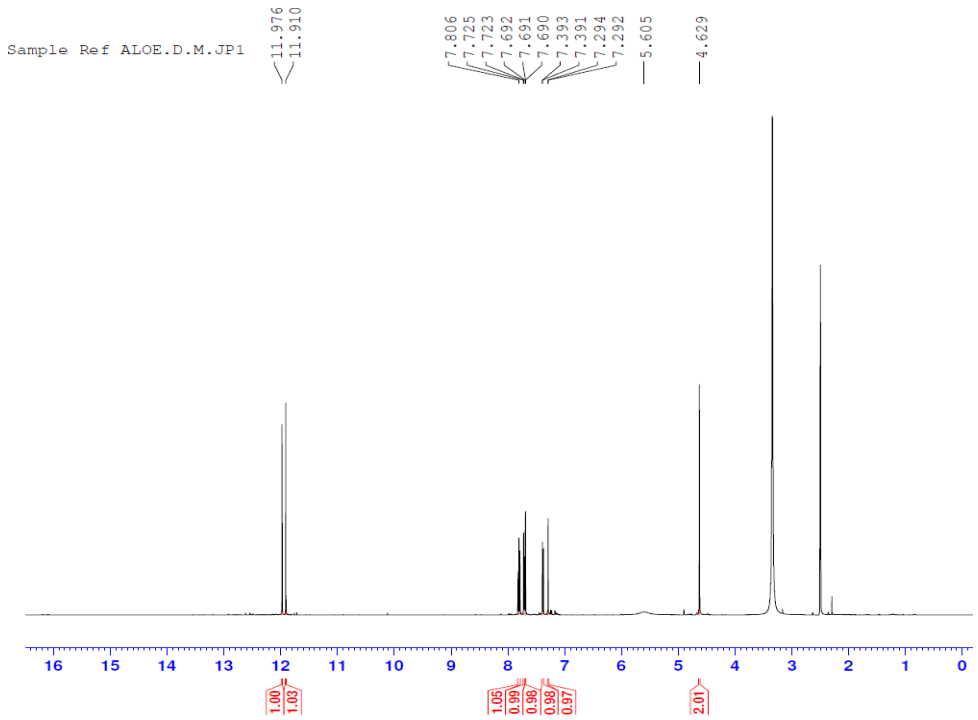



**Figure S0-1 1H NMR Chemical Shift of Aloe-emodin**

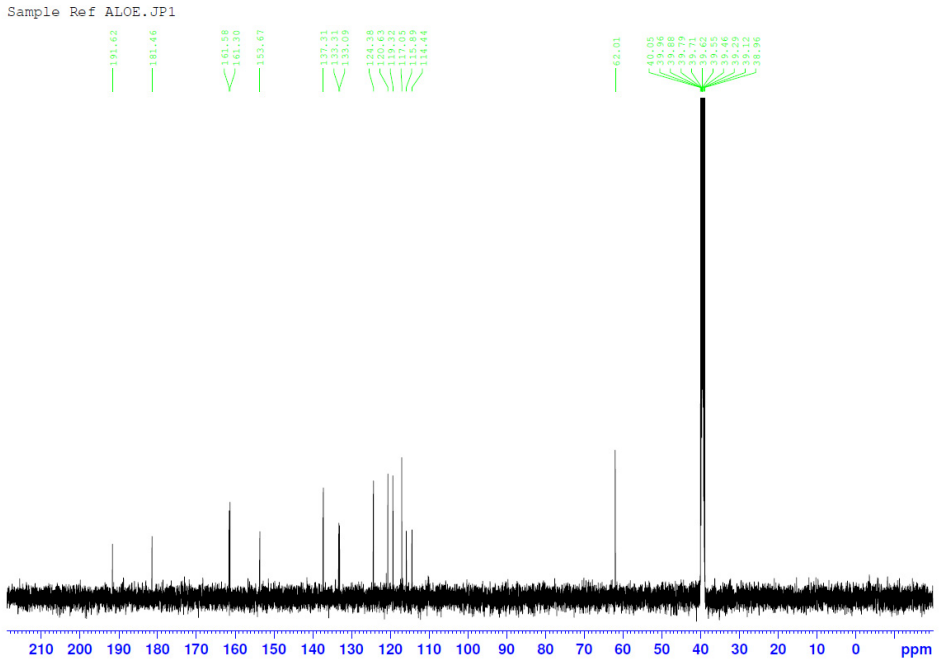



**Figure S0-2 13C NMR Chemical Shift of Aloe-emodin**

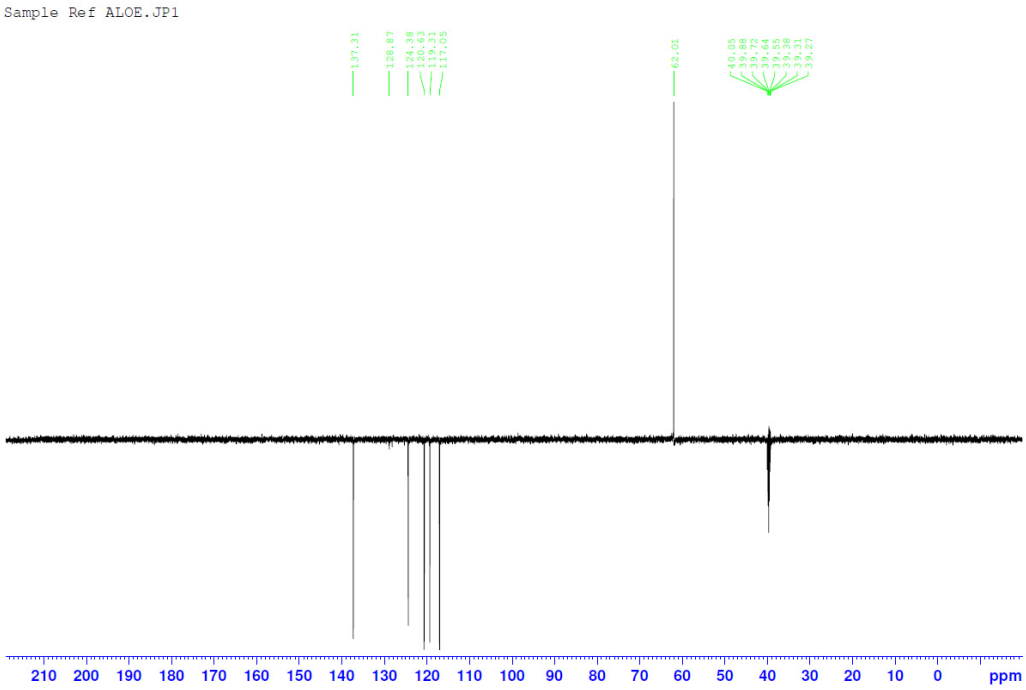



**Figure S0-3 Dept 135 of Aloe-emodin**

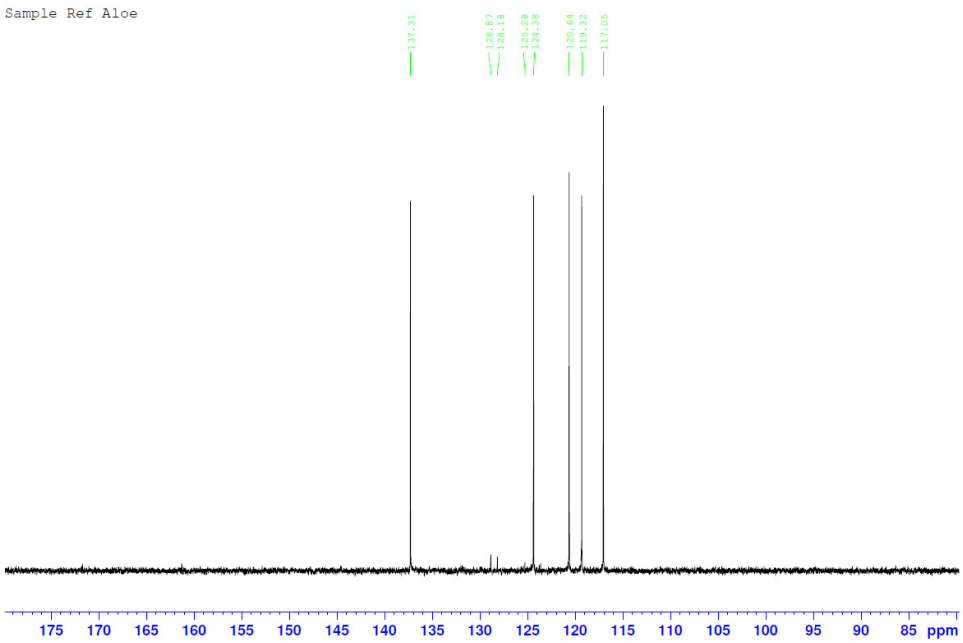



**Figure S0-4 Dept 90 of Aloe-emodin**

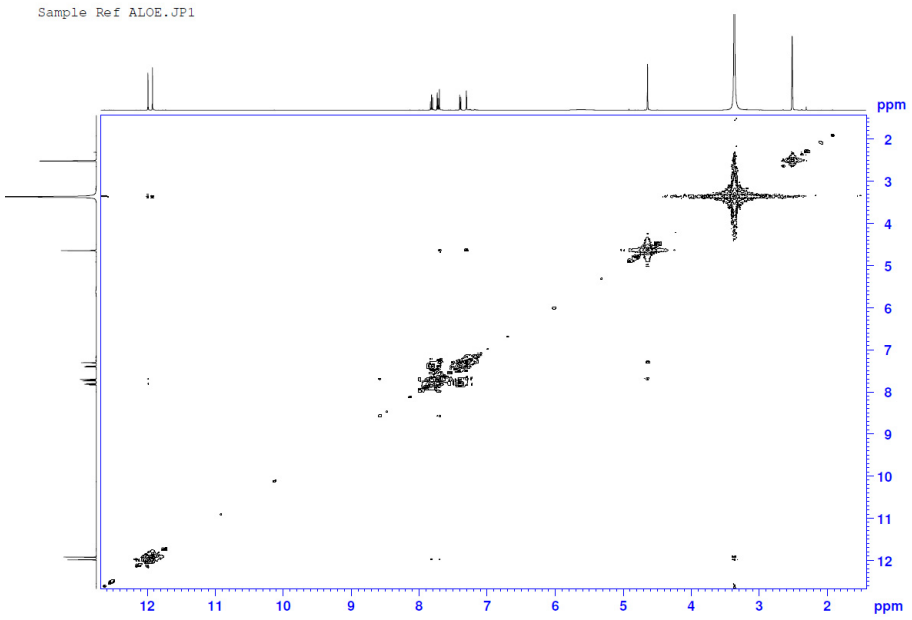



**Figure S0-5 Cosy of Aloe-emodin**

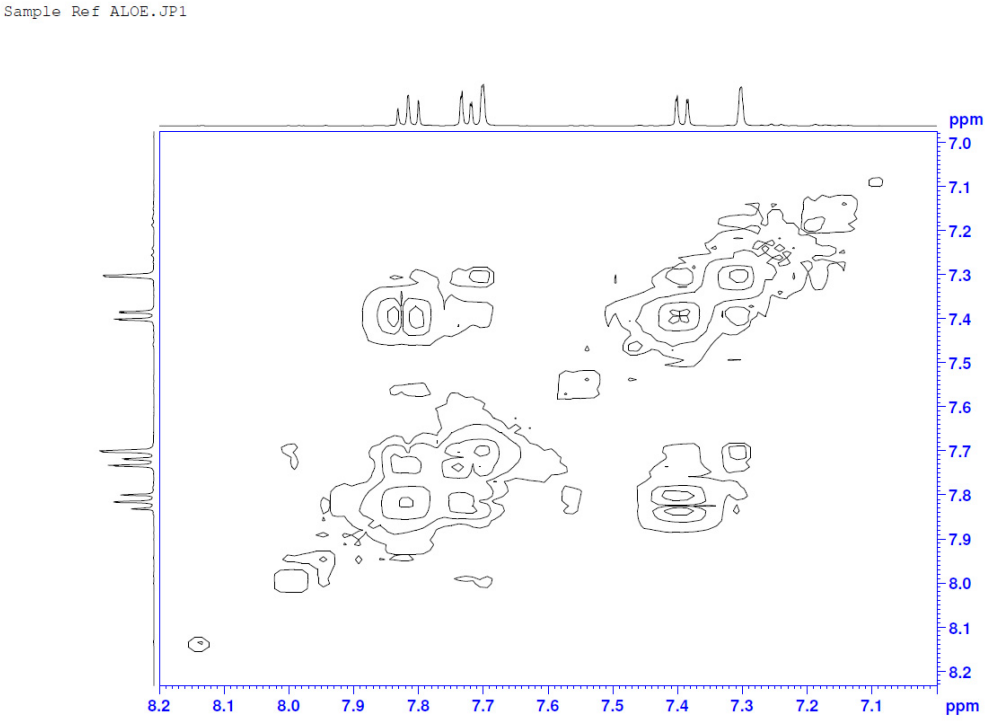



**Figure S0-6 Expand cosy of Aloe-emodin**

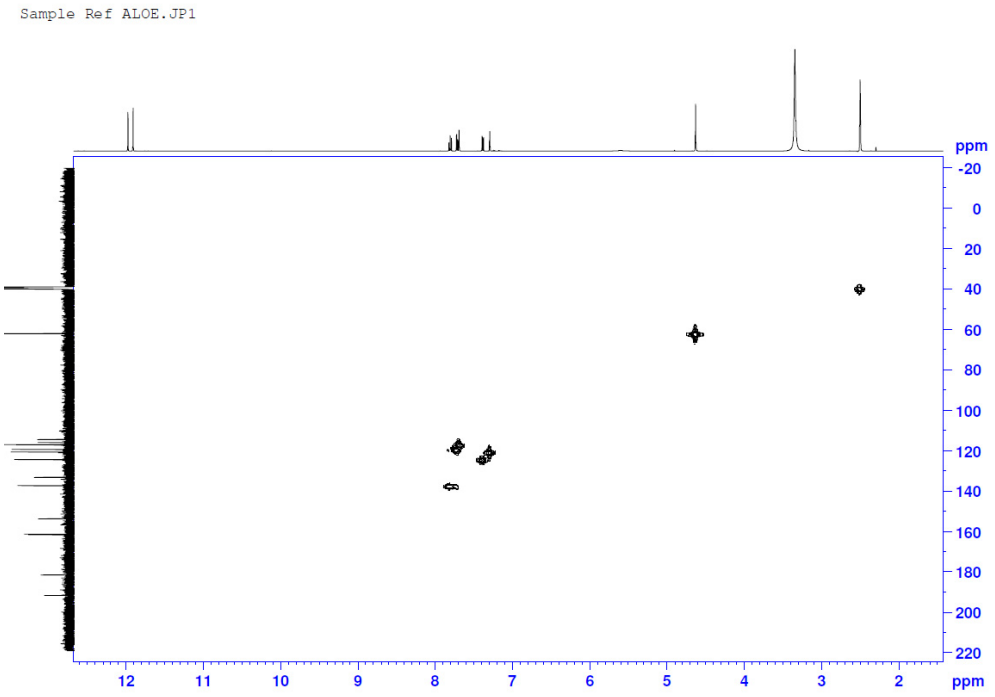



**Figure S0-7 HMQC of Aloe-emodin**

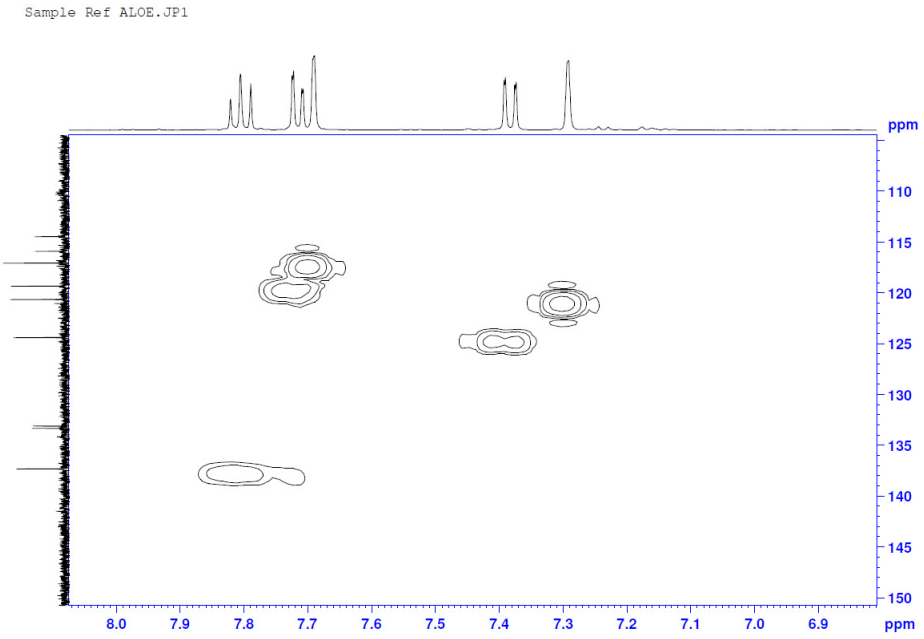



**Figure S0-8 Expand HMQC of Aloe-emodin**

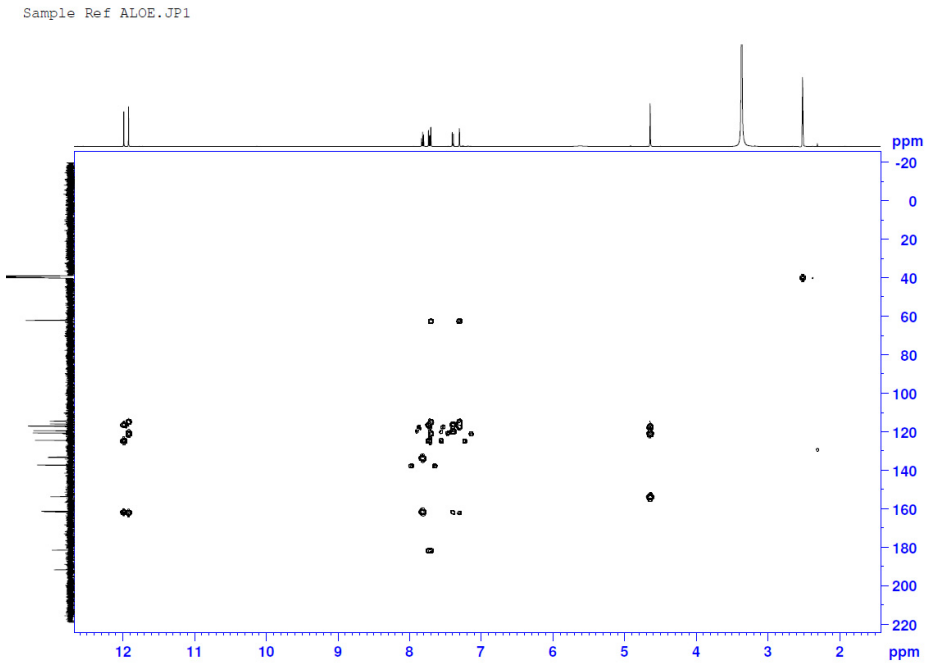
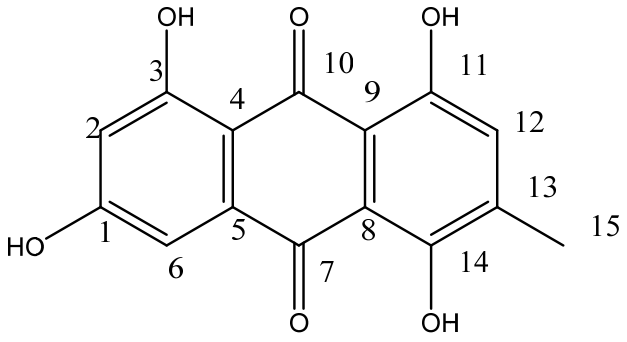



**Figure S0-9 HMBC of Aloe-emodin**

***Catenarin***




CATENARIN

| Position | (500MHz) (DMSO-*d*6) | Peak shape | C13 | ChemDraw Prediction (300MHz) (DMSO) | C13 | Literature review PPM(400MHz) (DMSO-*d*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 1H and 13C NMR Chemical Shift of catenarin**

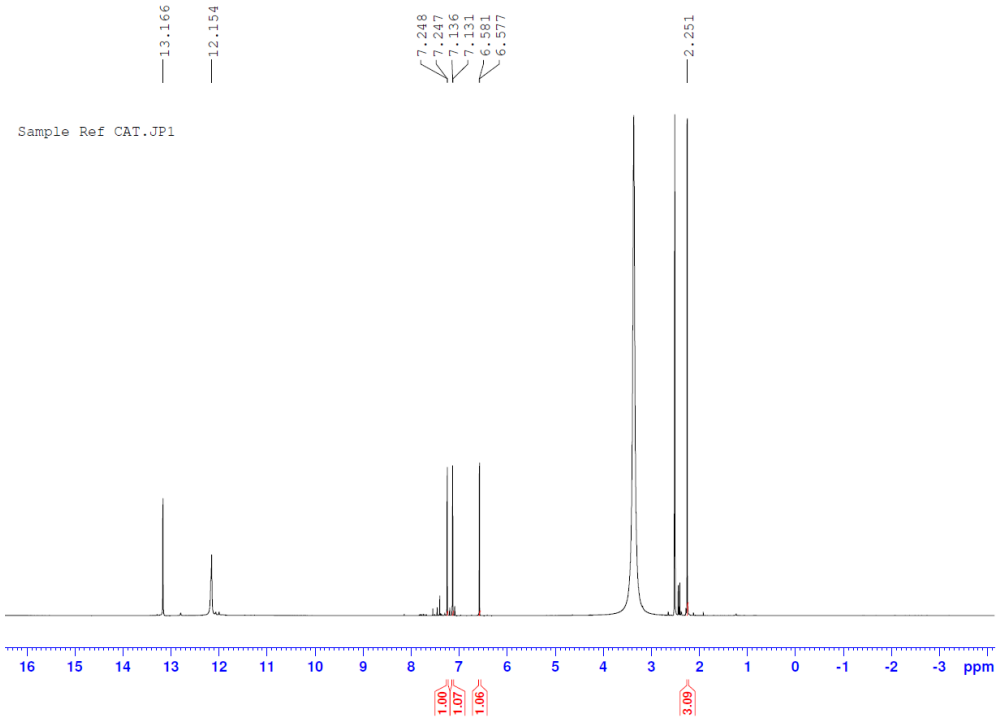



**Figure S0-10 1H NMR Chemical Shift of catenarin**

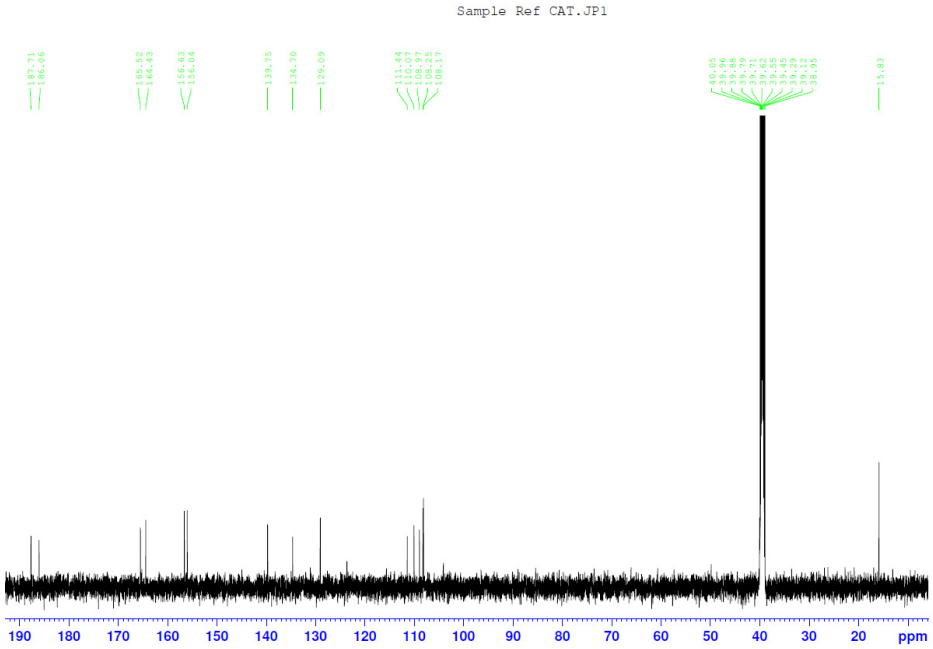



**Figure S0-11 13C NMR Chemical Shift of catenarin**

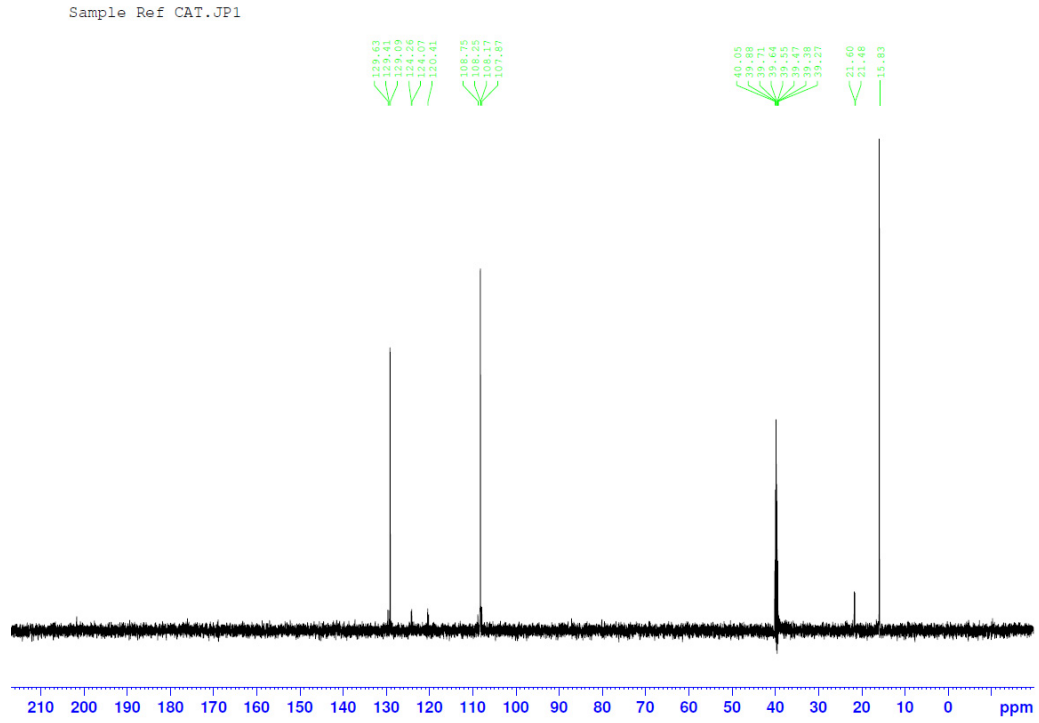



**Figure S0-12 Dept 135 of catenarin**

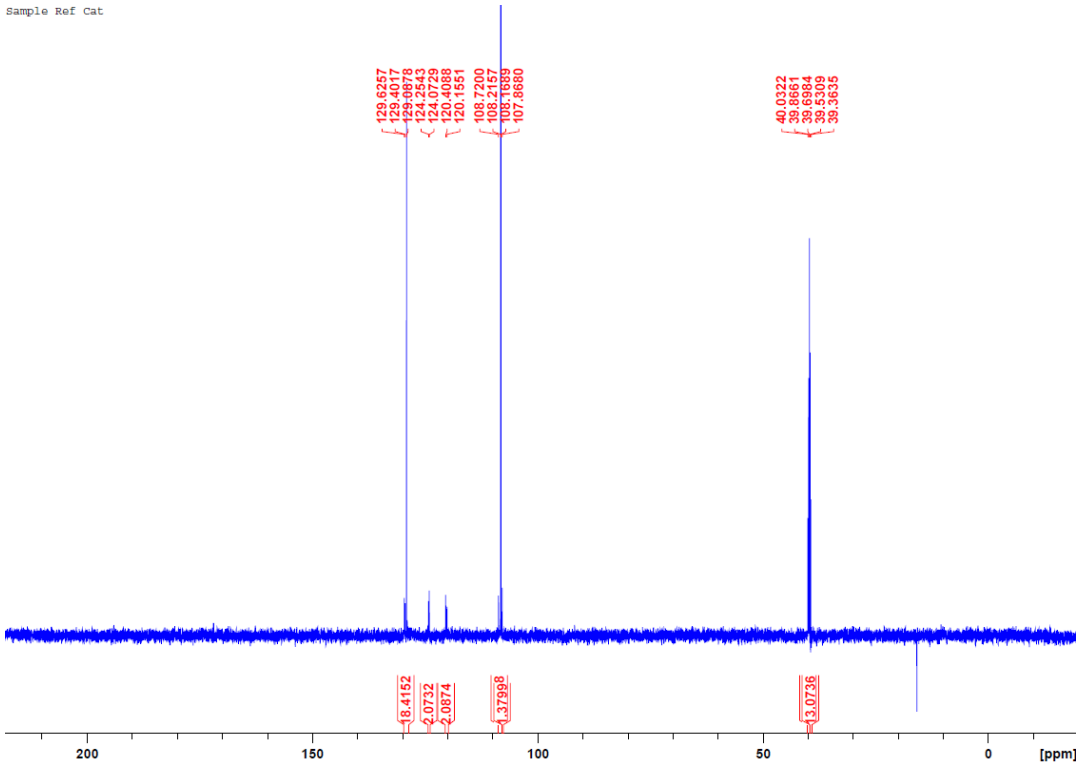



**Figure S0-13 Dept 90 of catenarin**

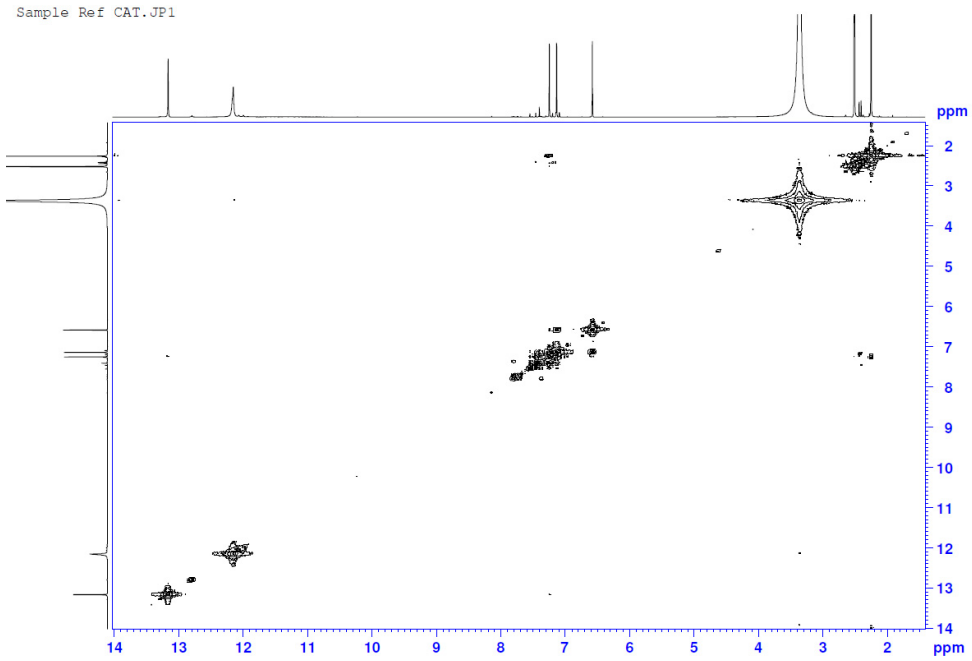



**Figure S0-14 Cosy of catenarin**

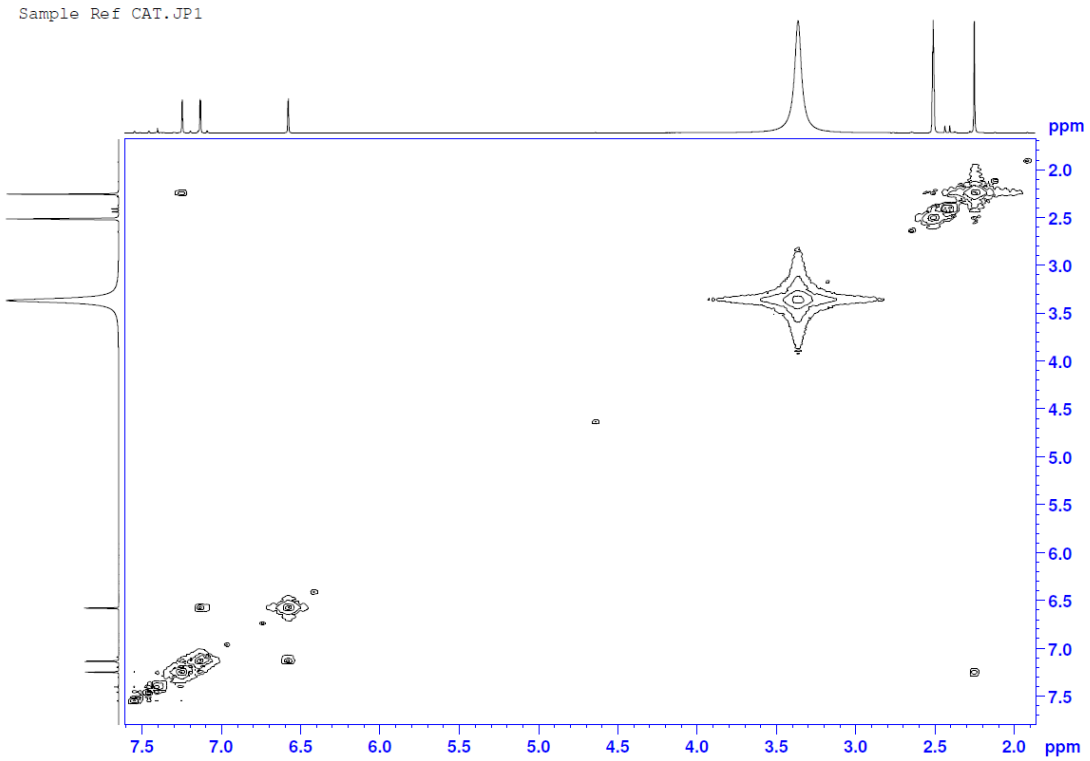



**Figure S0-15 Expand cosy of catenarin**

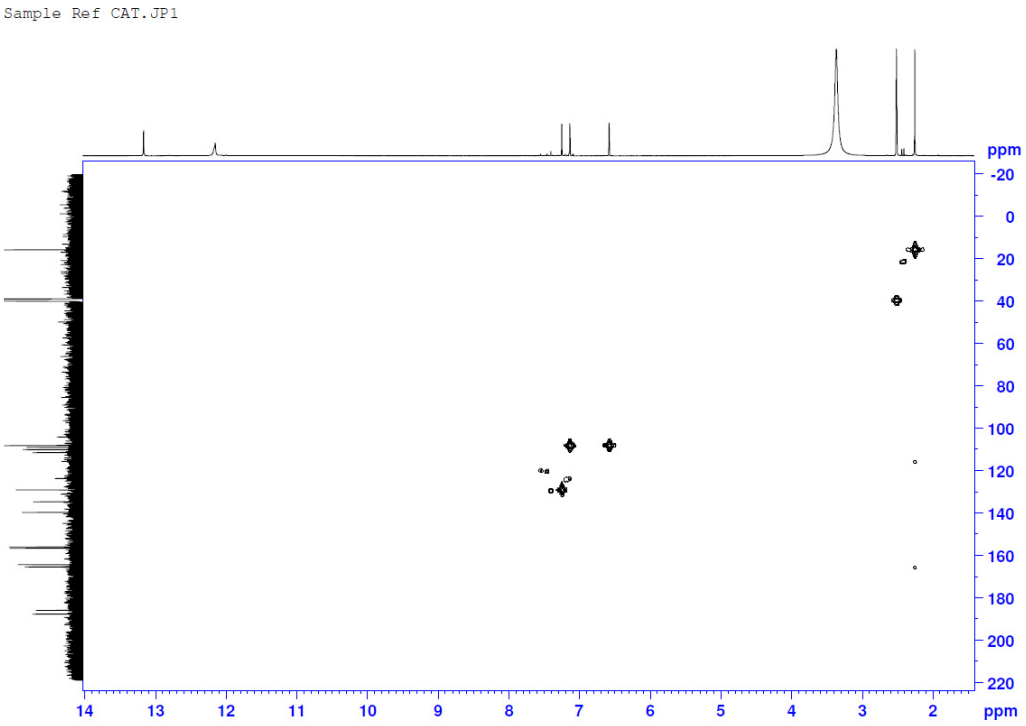



**Figure S0-16 HMQC of catenarin**

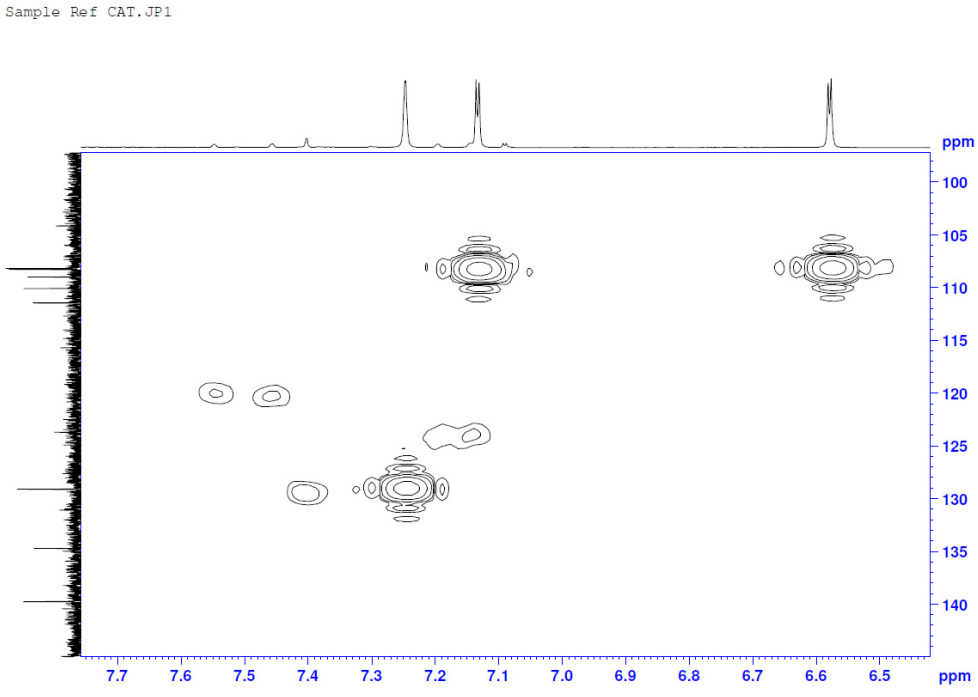



**Figure S0-17 Expand HMQC of catenarin**

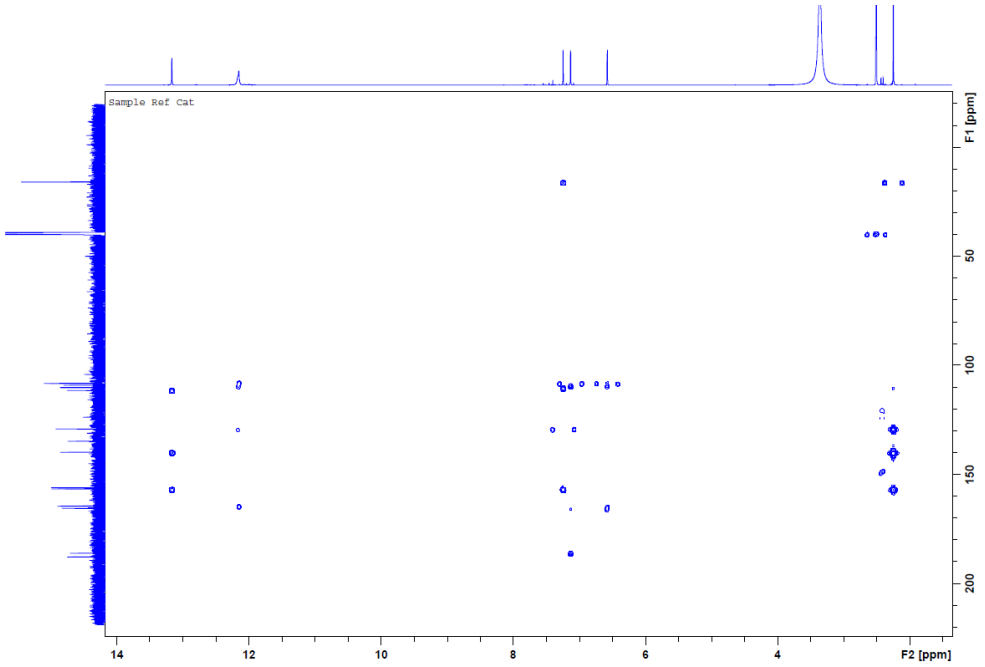
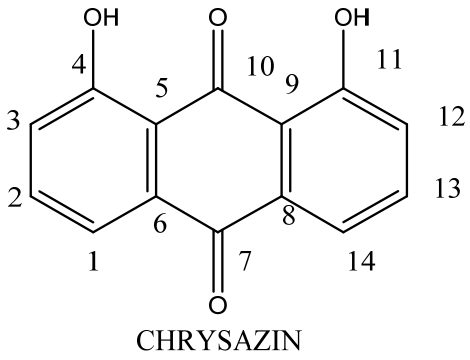



**Figure S0-18 HMBC of catenarin**

***Chrysazin***




| Position | (500MHz) (DMSO-*d*6) | Peak shape | C13 | ChemDraw prediction (300MHz) (DMSO) | C13 | Literature review (500MHz) (DMSO-*d*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**

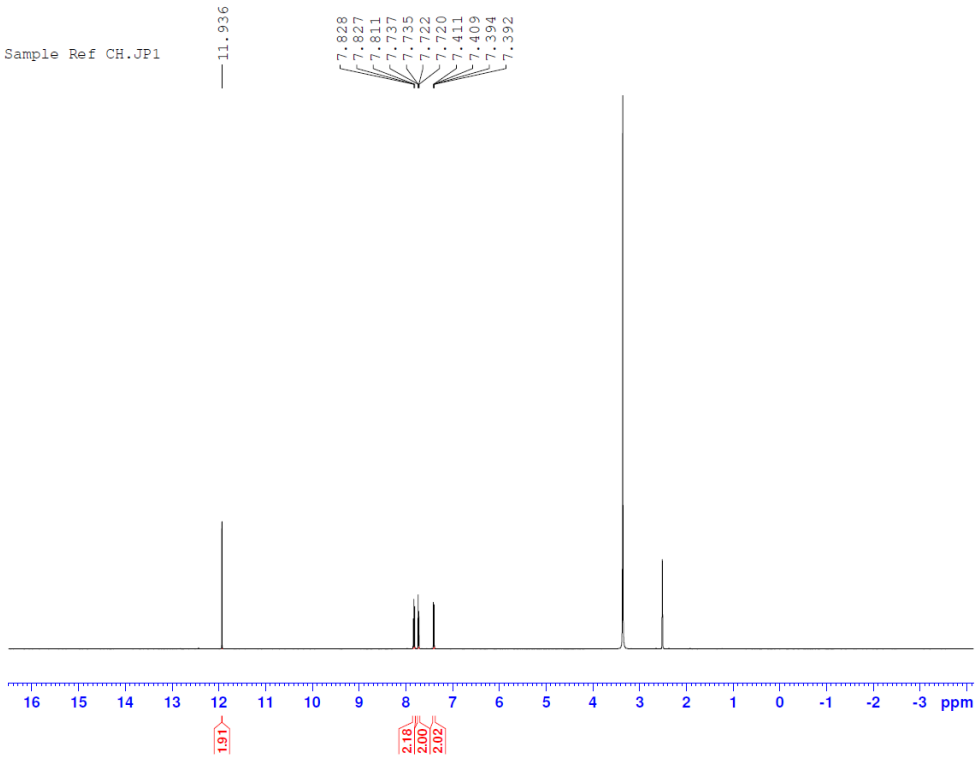



**Figure S0-19 1H NMR Chemical Shift of chrysazin**

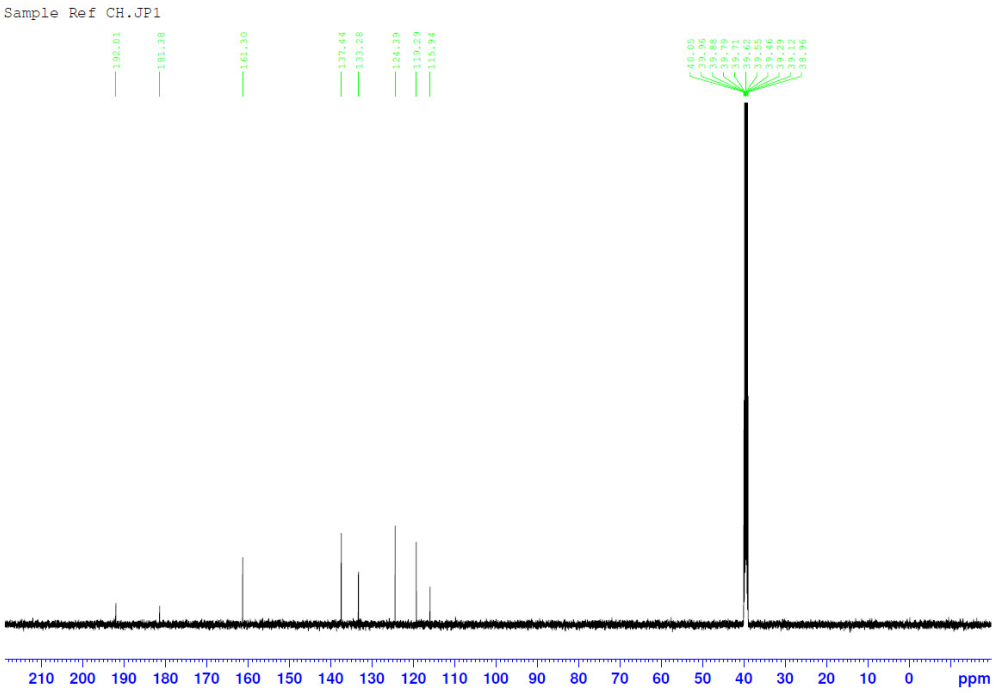



**Figure S0-20 13C NMR Chemical Shift of chrysazin**

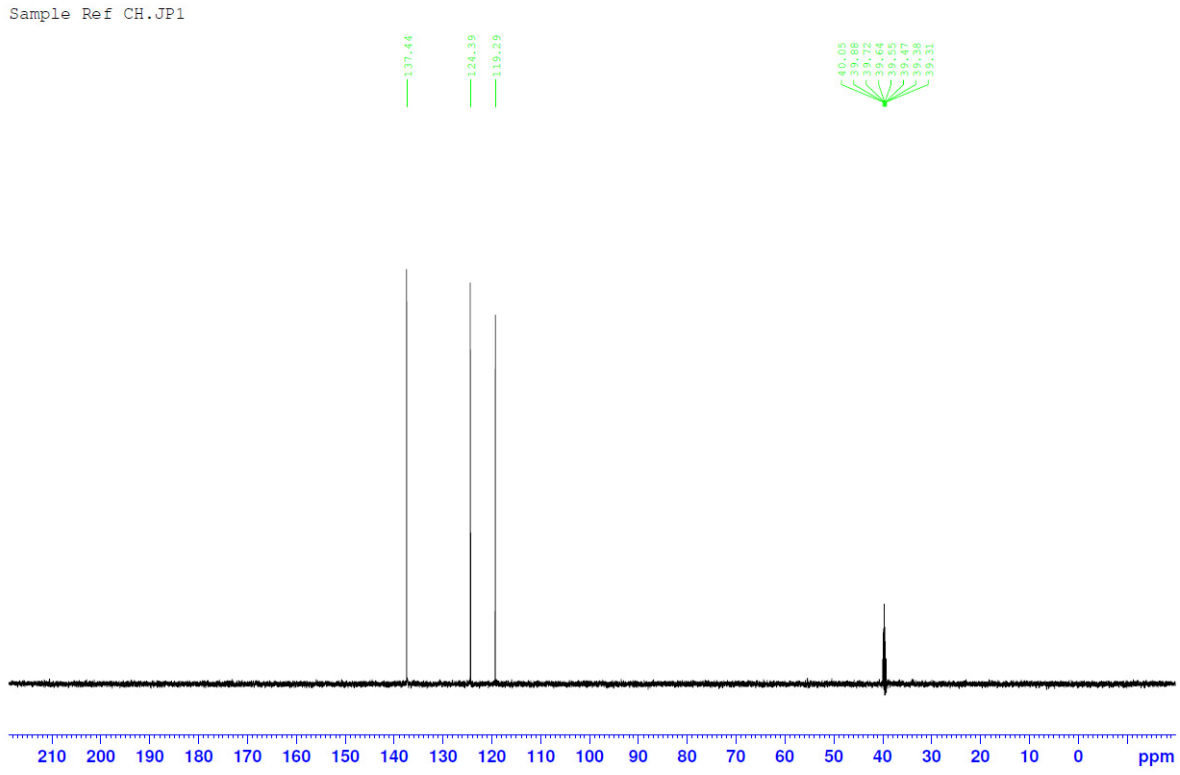



**Figure S0-21 Dept 135 of chrysazin**

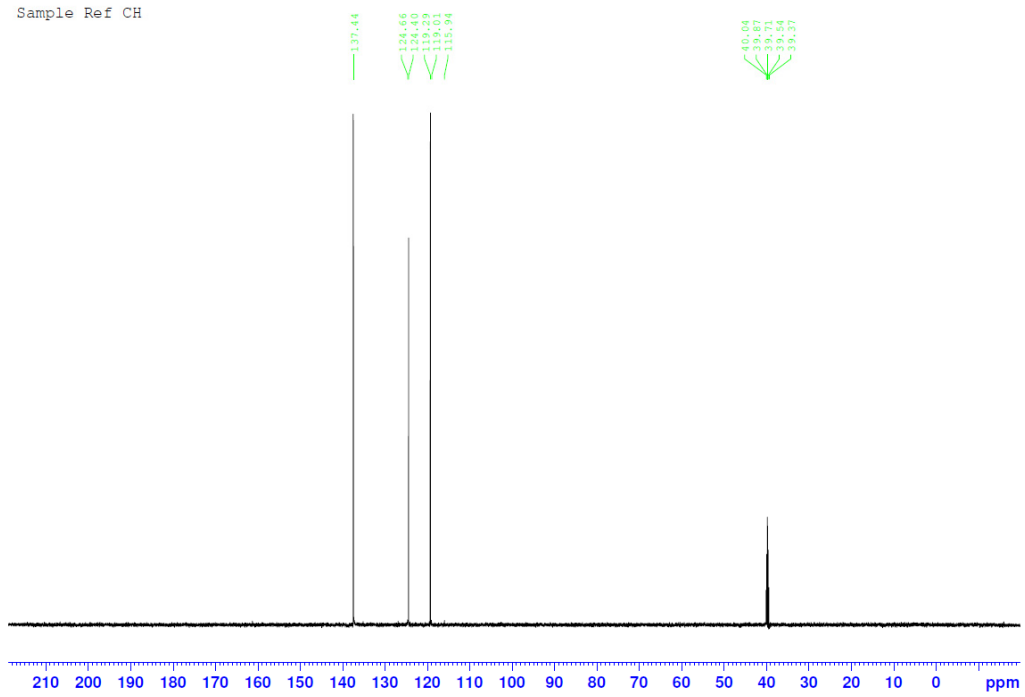



**Figure S0-22 Dept 90 of chrysazin**

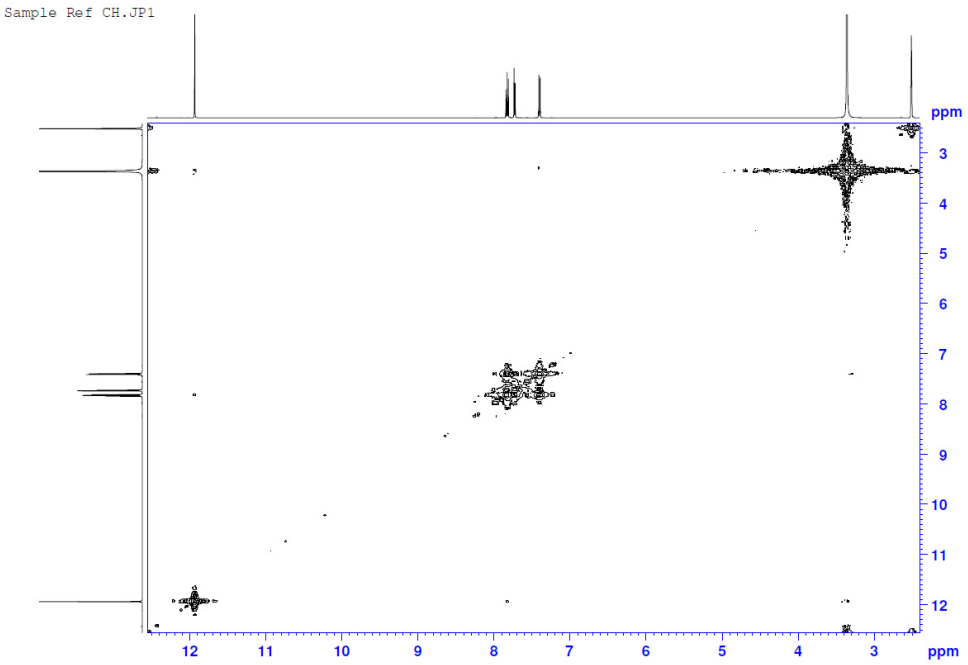



**Figure S0-23 Cosy of chrysazin**

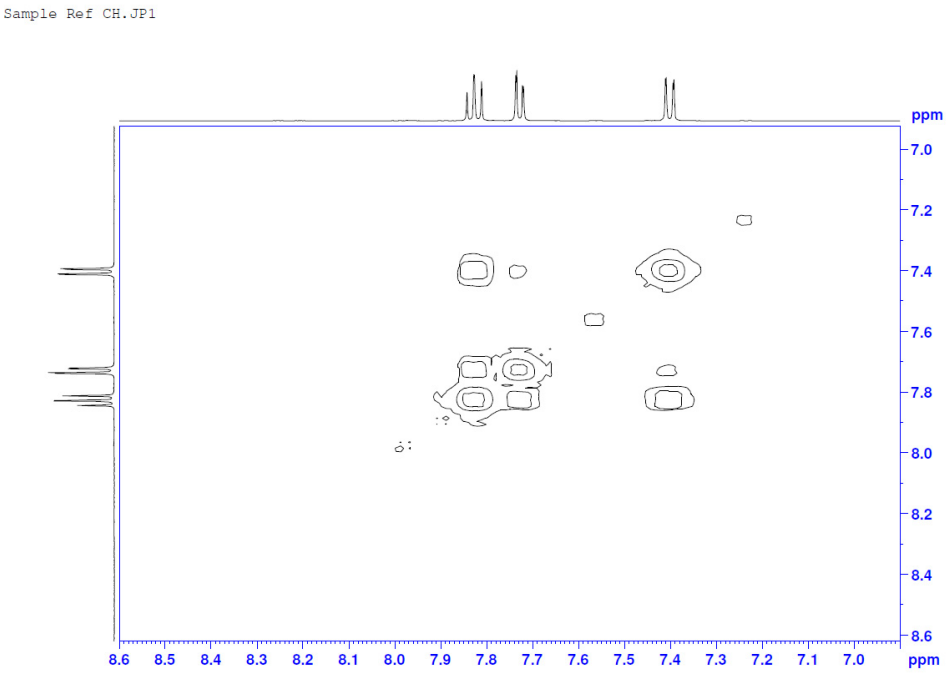



**Figure S0-24 Expand cosy of chrysazin**

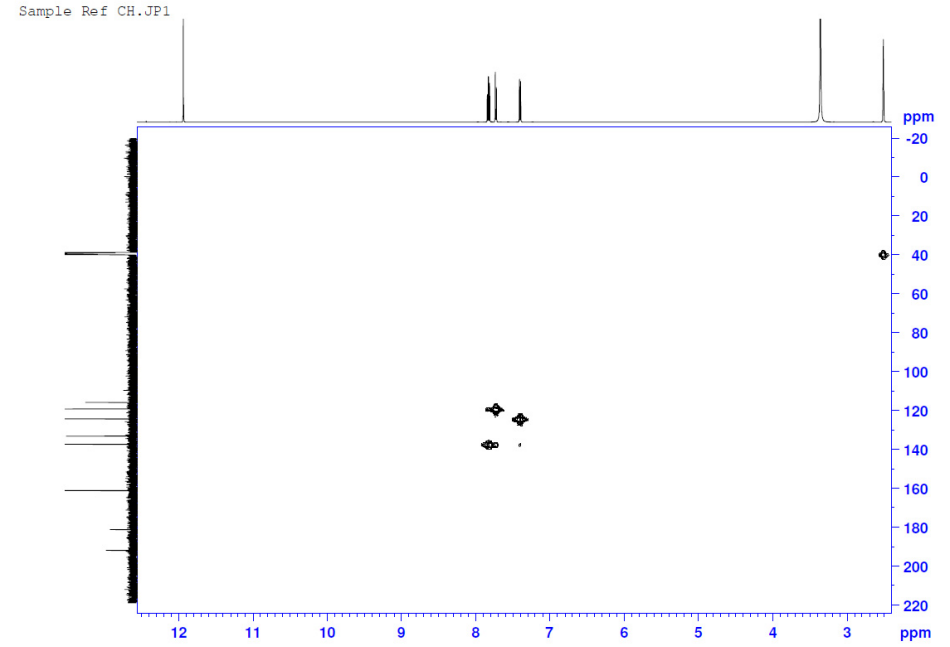



**Figure S0-25 HMQC of chrysazin**

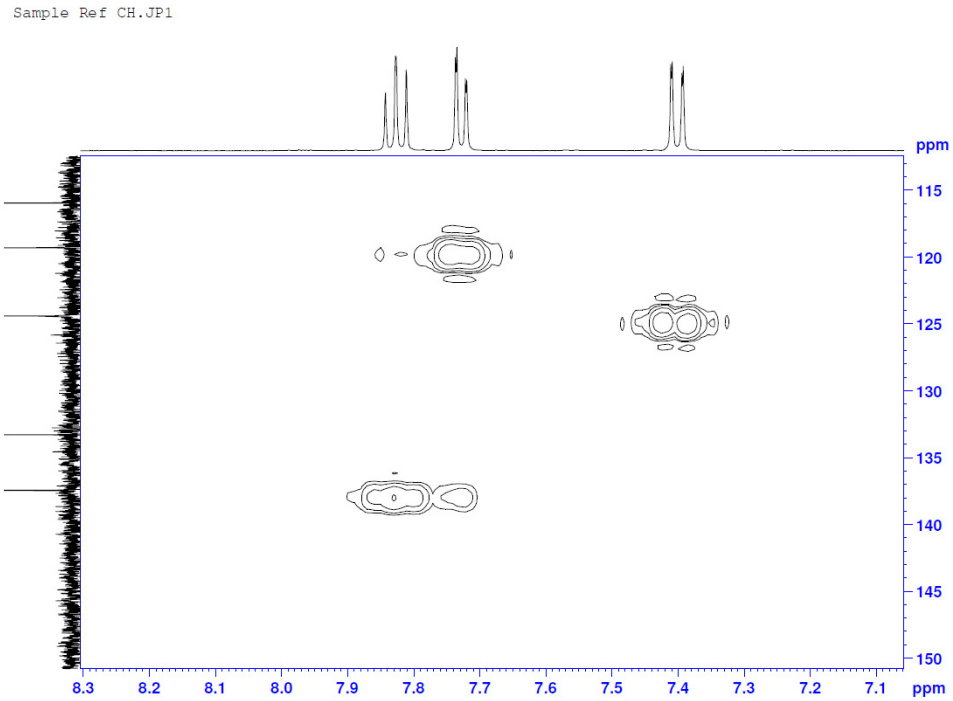



**Figure S0-26 Expand HMQC of chrysazin**

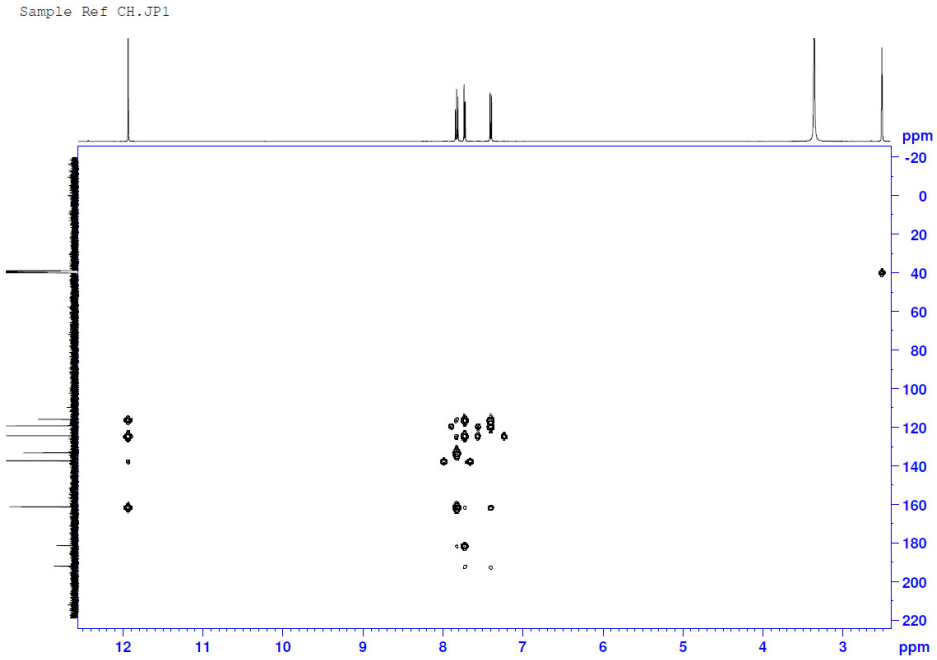
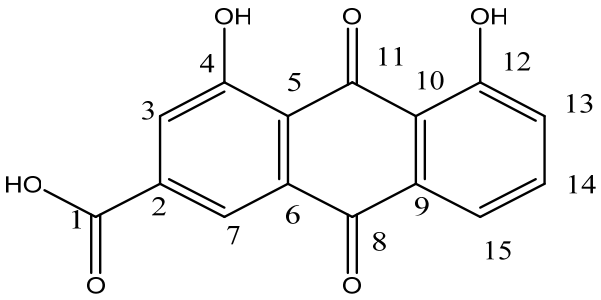



**Figure S0-27 HMBC of chrysazin**

***Rhein***




RHEIN

| Position | (500MHz) (DMSO-*d6*) | Peak shape | C13 | ChemDraw prediction (300MHz) (DMSO) | C13 | Literature review (500MHz) (DMSO-*d6*) Danielsen, Aksnes 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**

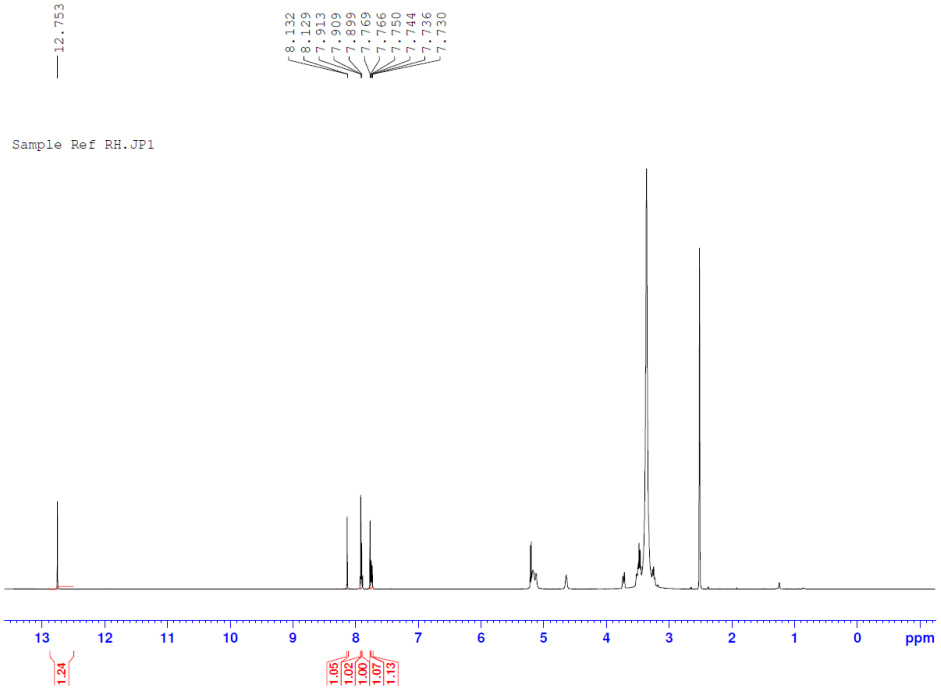



**Figure S0-28 1H NMR Chemical Shift of rhein**

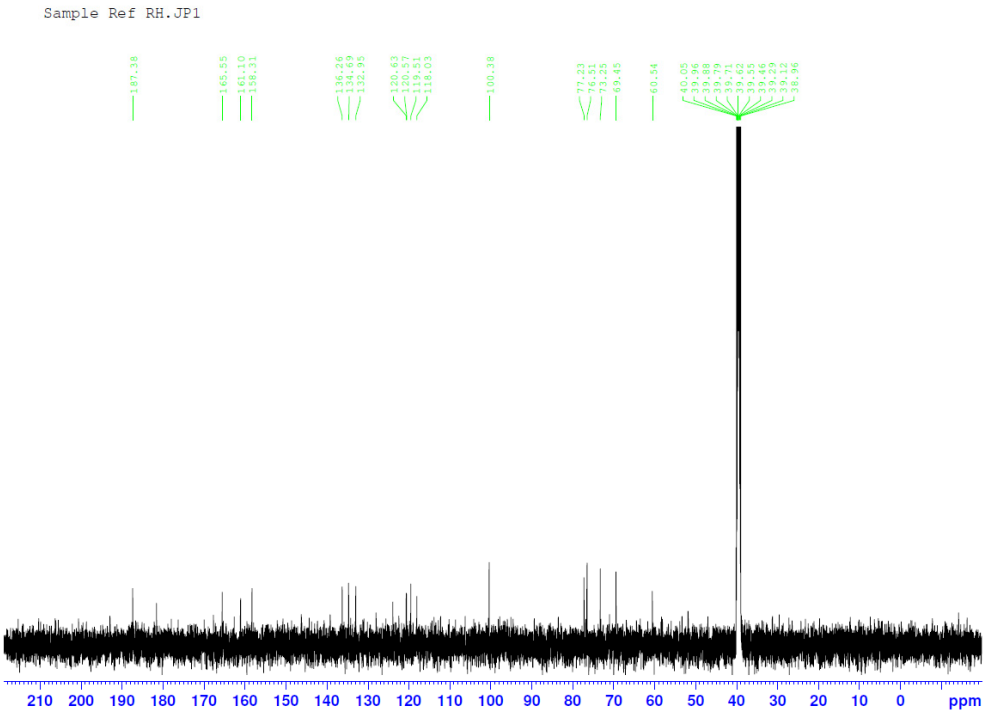



**Figure S0-29 13C NMR Chemical Shift of rhein**

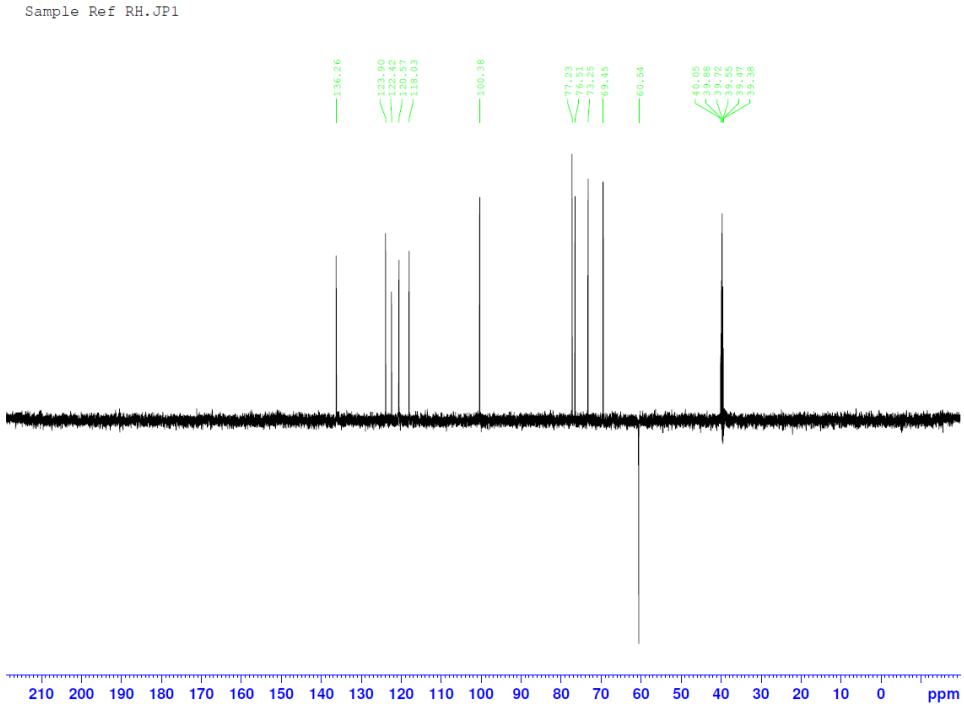



**Figure S0-30 Dept 135 of rhein**

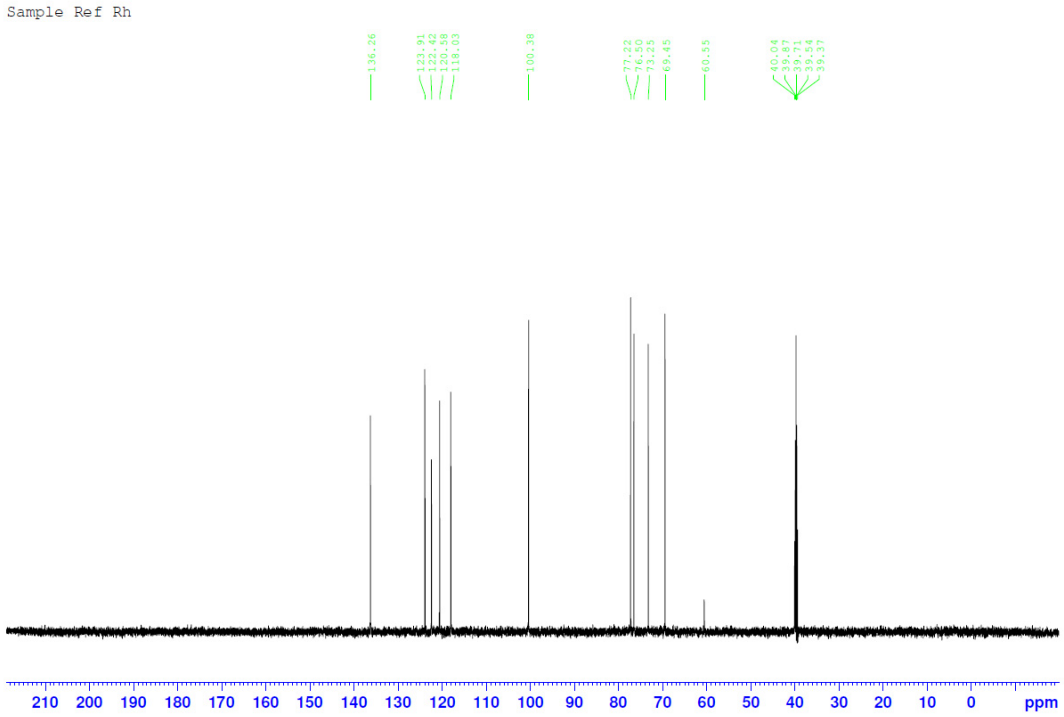



**Figure S0-31 Dept 90 of rhein**

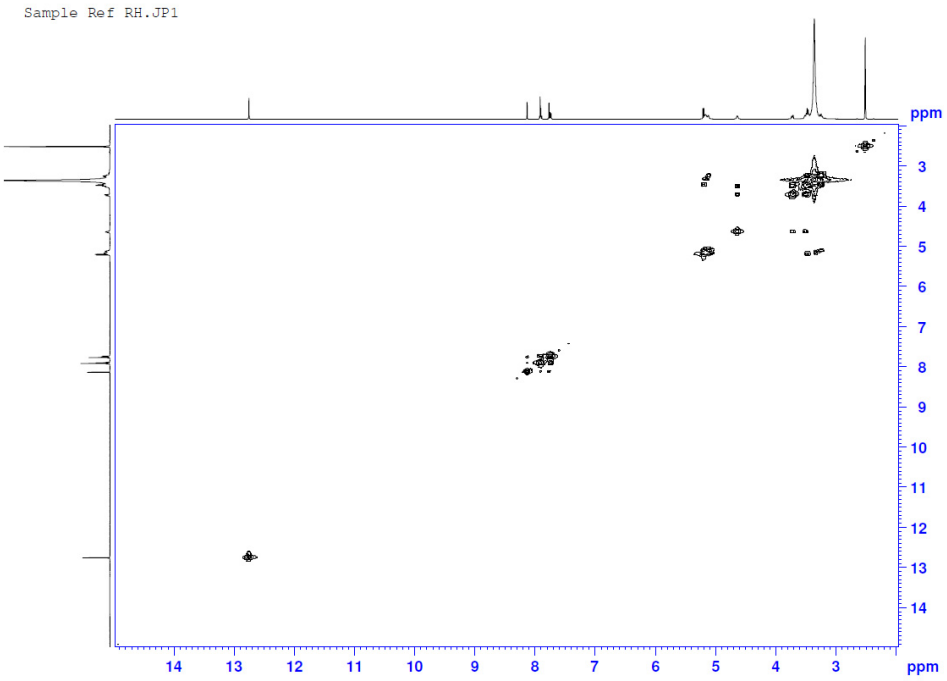



**Figure S0-32 Cosy of rhein**

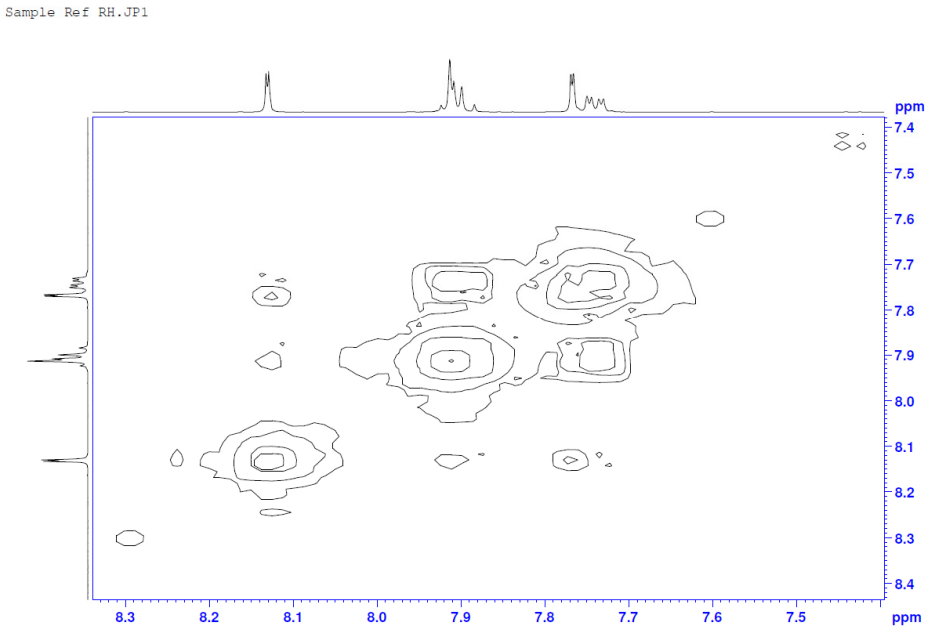



**Figure S0-33 Expand cosy of rhein**

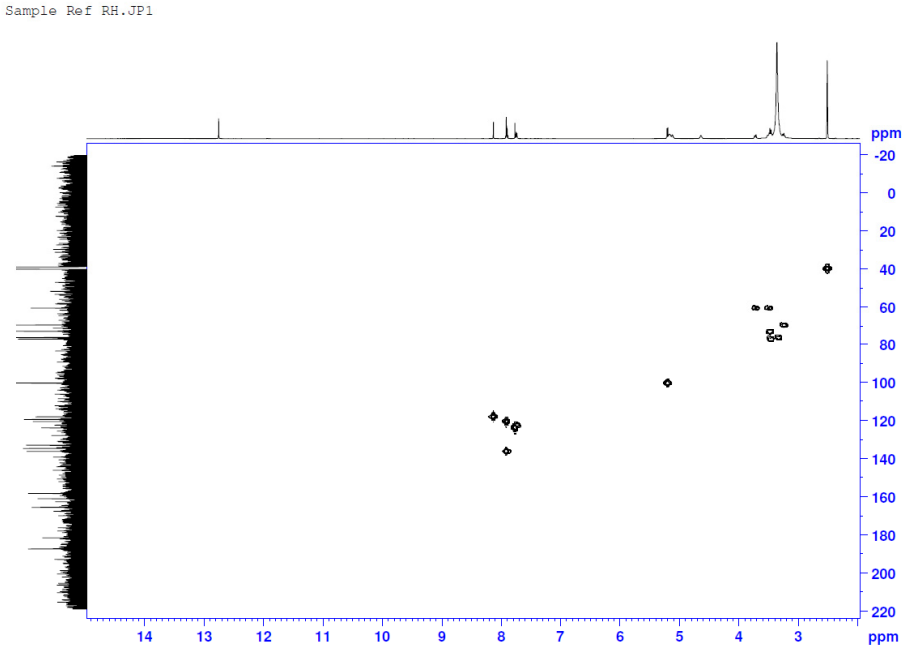



**Figure S0-34 HMQC of rhein**

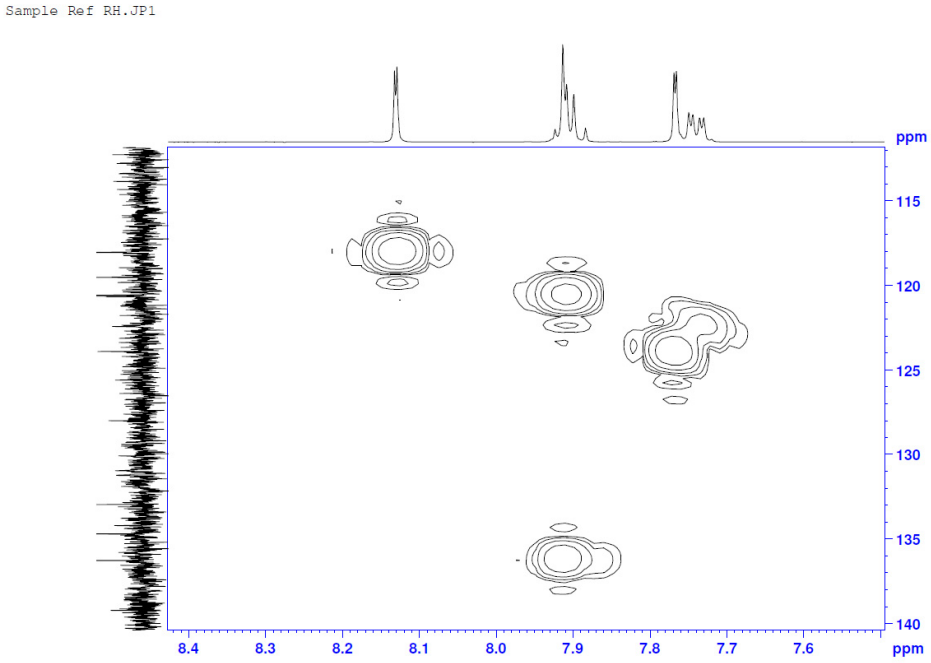



**Figure S0-35 Expand HMQC of rhein**

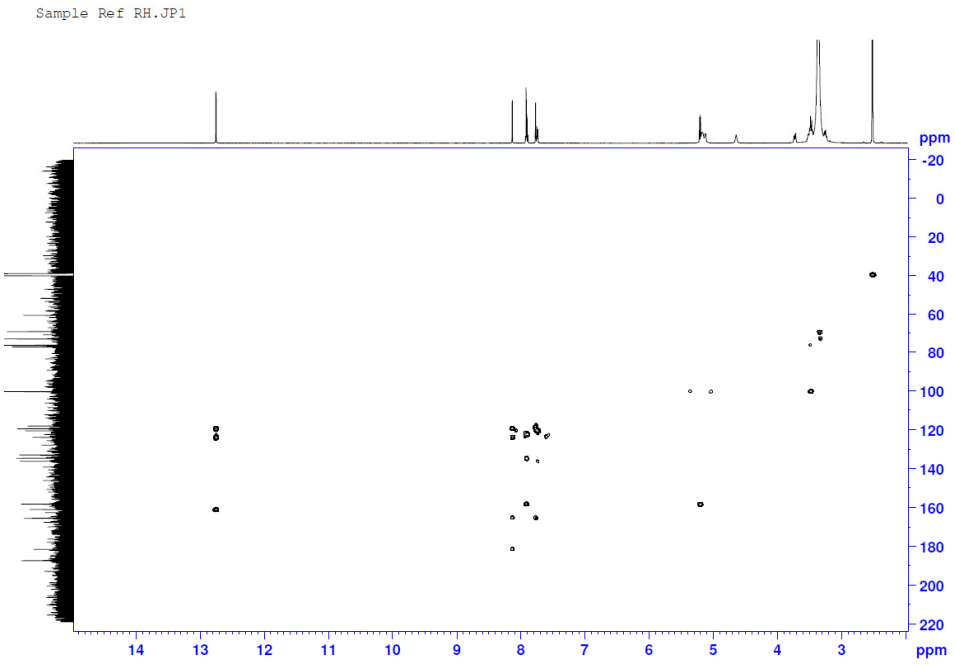
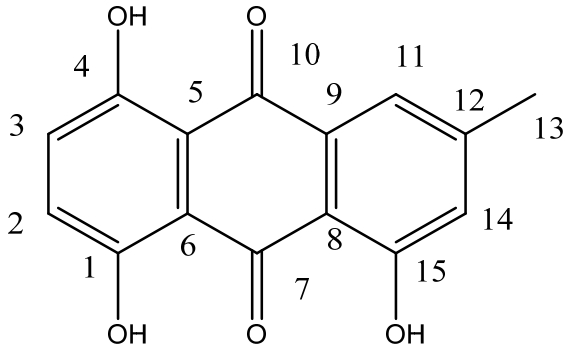



**Figure S0-36 HMBC of rhein**

***Helminthosporin***




HELMINTHOSPORIN

| Position | (500MHz) (DMSO-*d*6) | Peak shape | C13 | ChemDraw prediction (300MHz) (DMSO) | C13 | Literature review (500MHz) (DMSO-*d*6) (Engström 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**

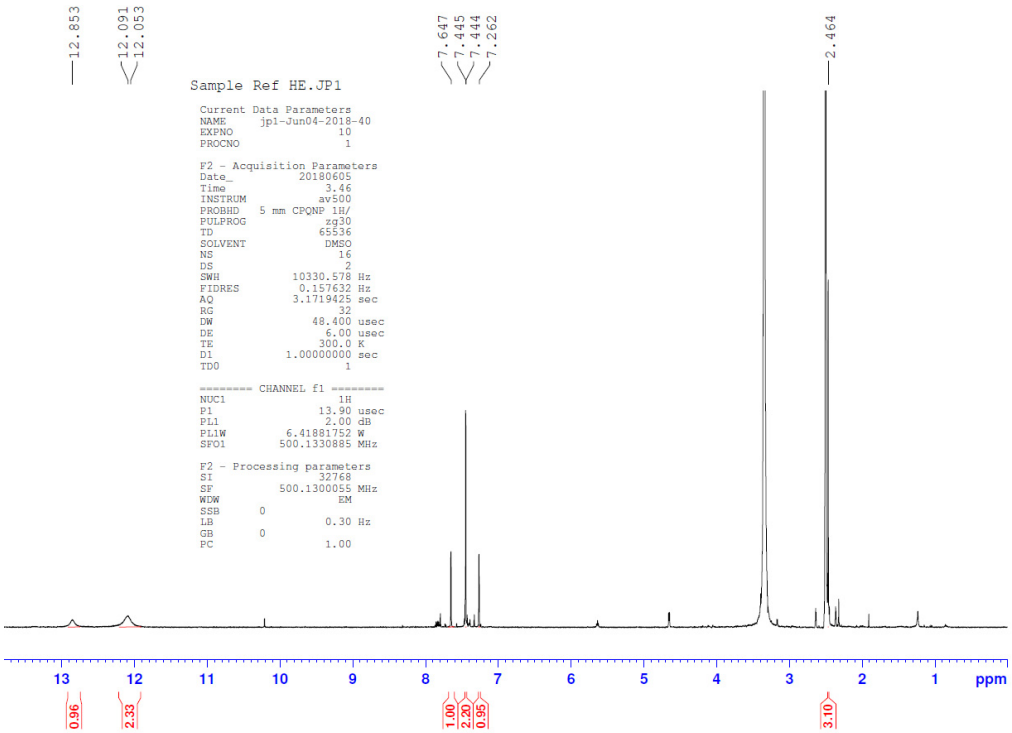



**Figure S0-37 1H NMR Chemical Shift of helminthosporin**

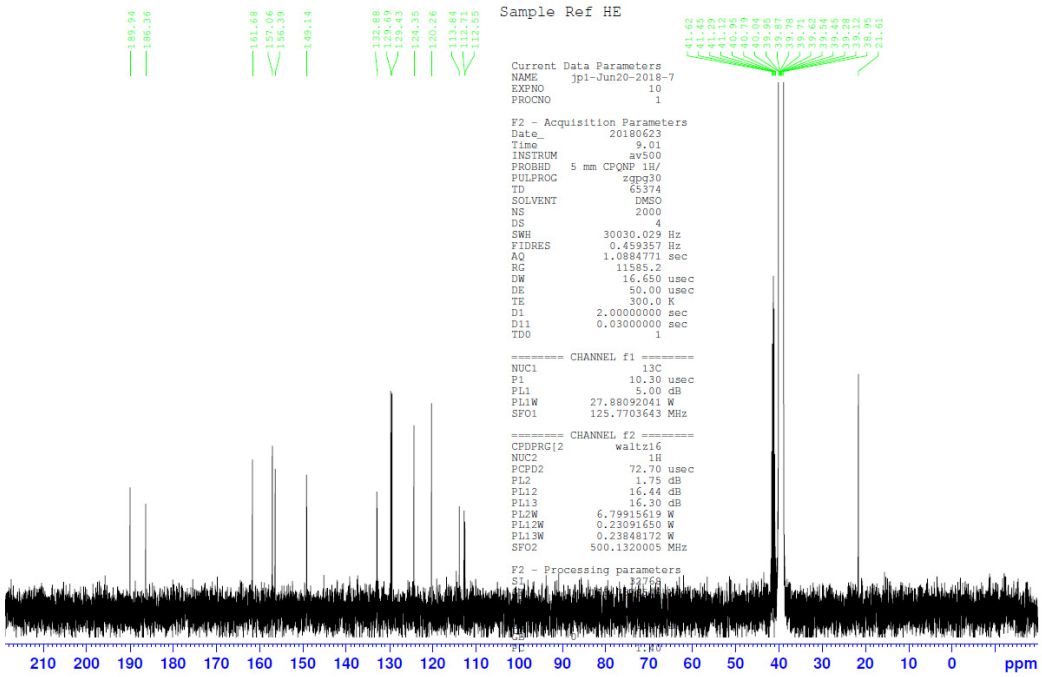



**Figure S0-38 13C NMR Chemical Shift of helminthosporin**

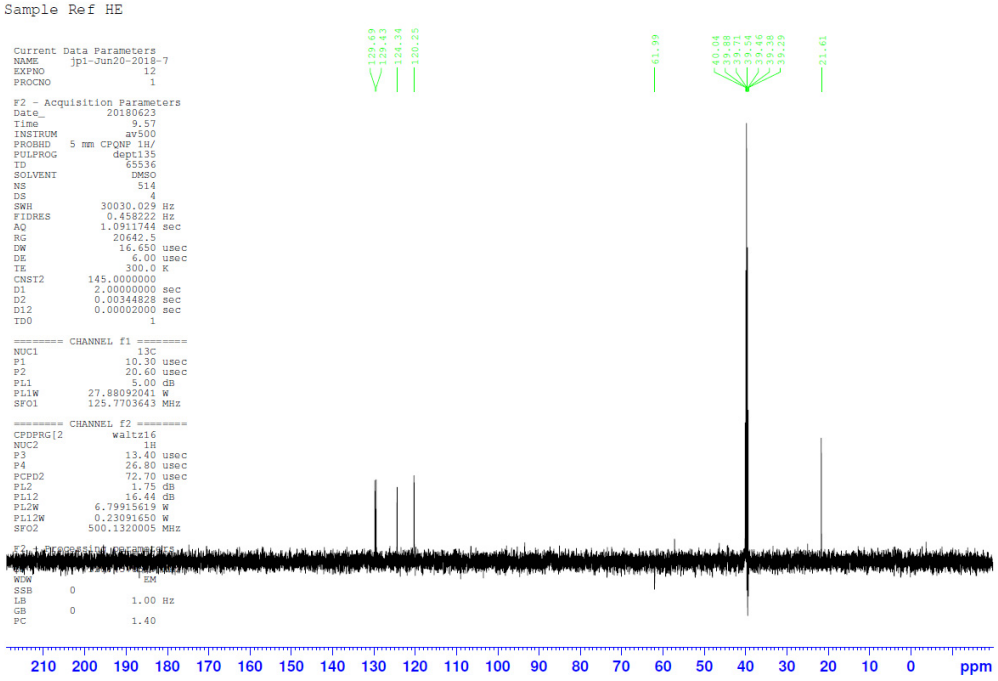



**Figure S0-39 Dept 135 of helminthosporin**

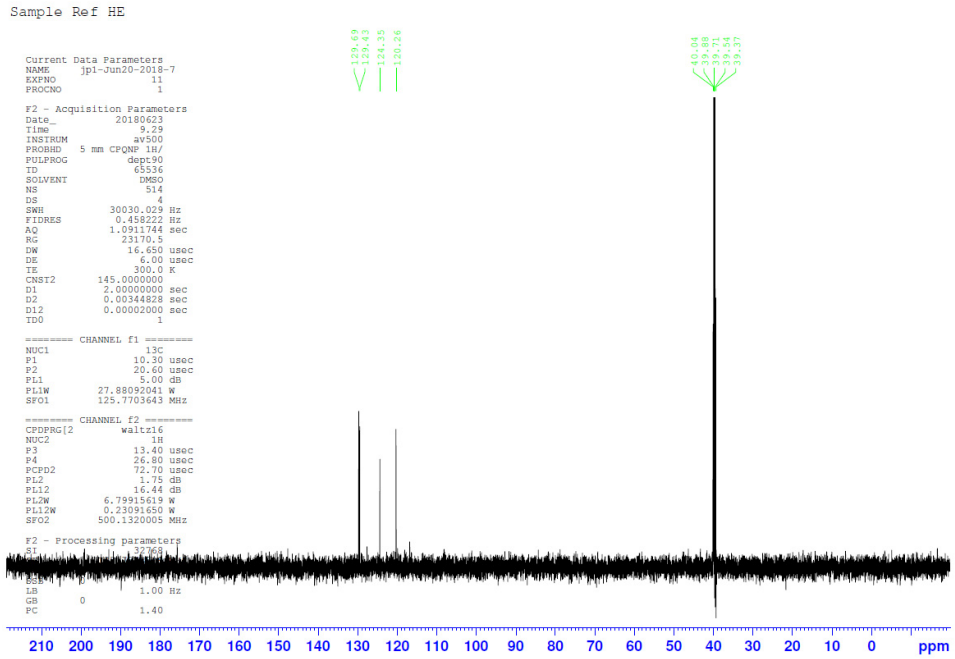



**Figure S0-40 Dept 90 of helminthosporin**

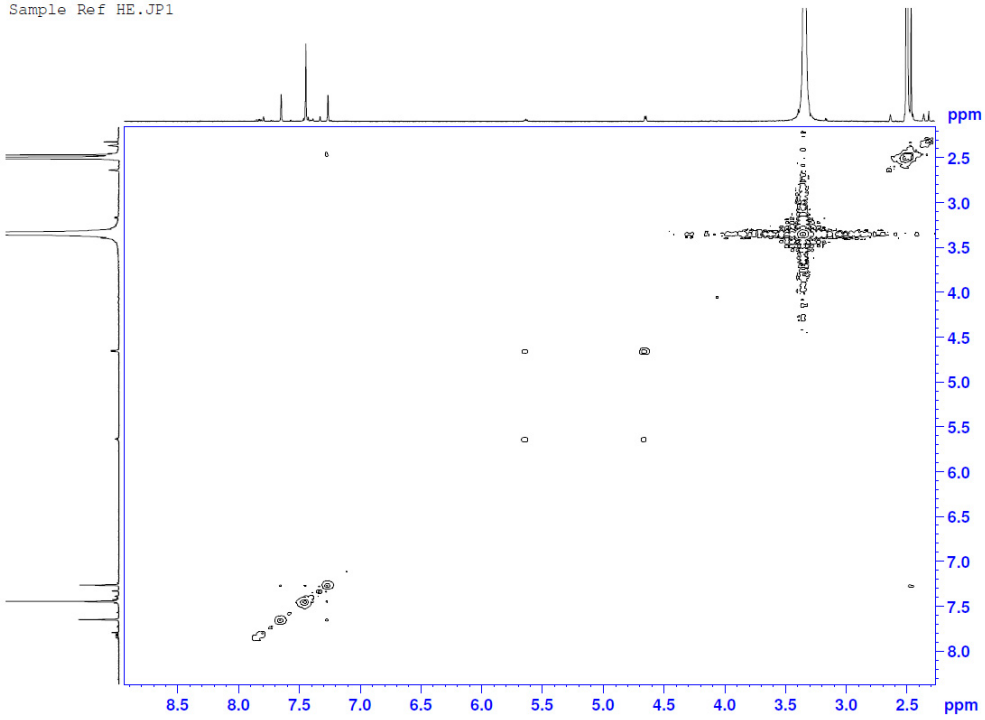



**Figure S0-41 Cosy of helminthosporin**

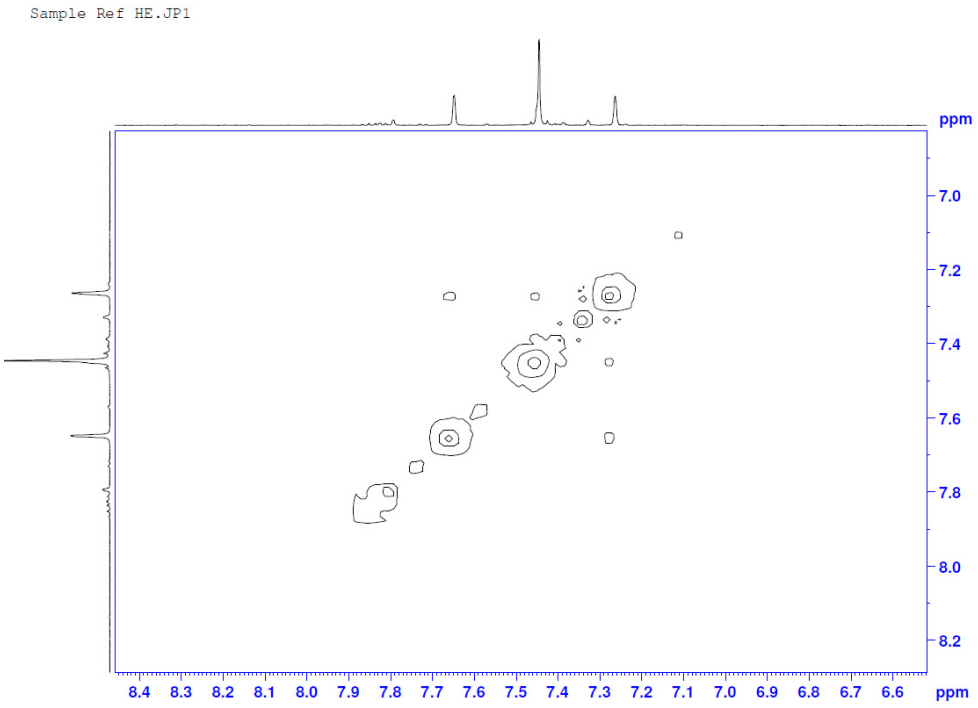



**Figure S0-42 Expand cosy of helminthosporin**

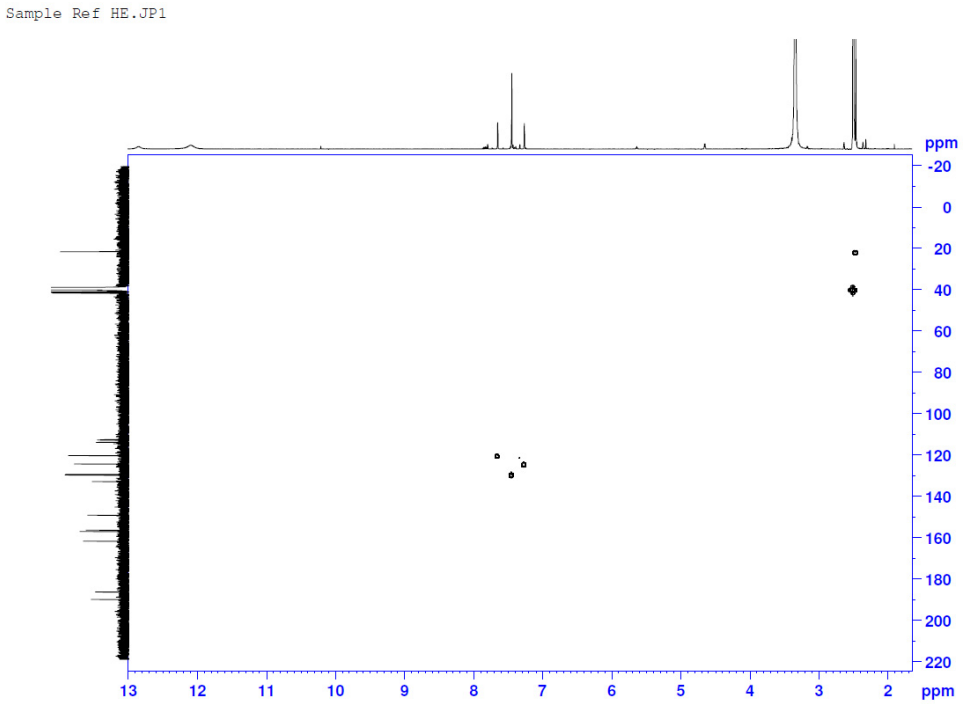



**Figure S0-43 HMQC of helminthosporin**

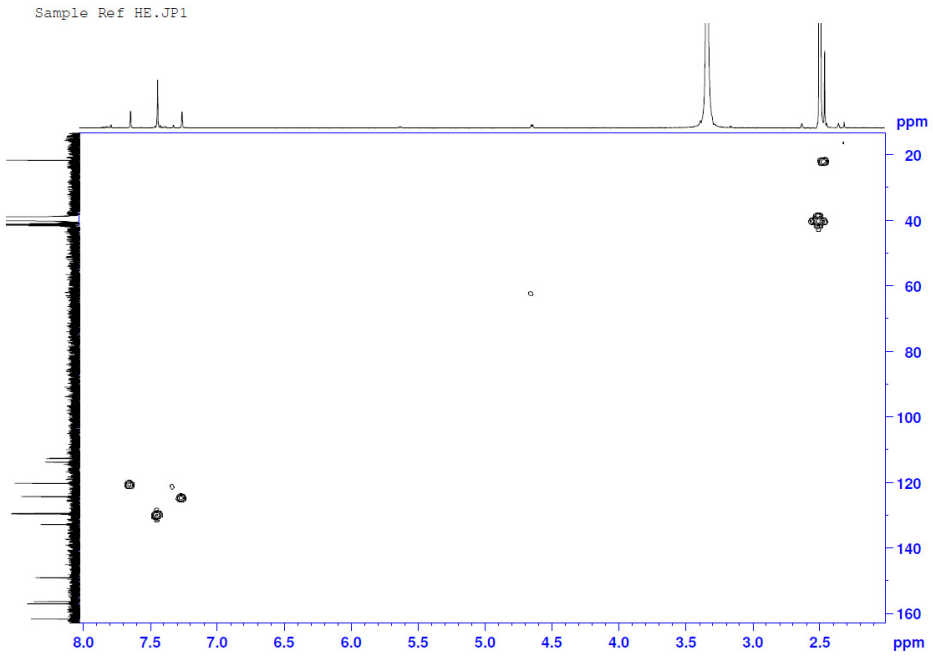



**Figure S0-44 Expand HMQC of helminthosporin**

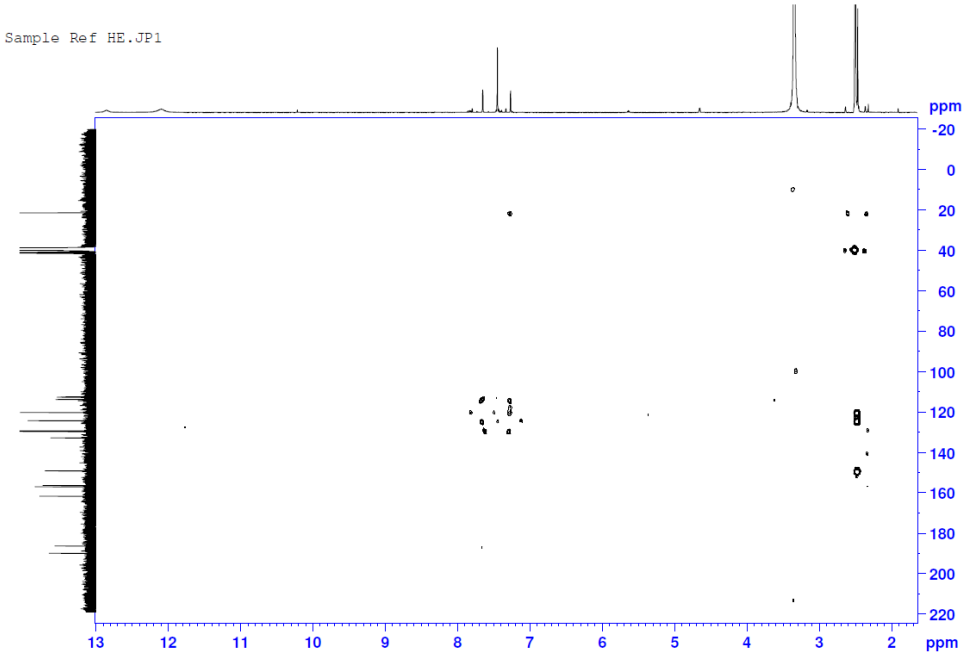
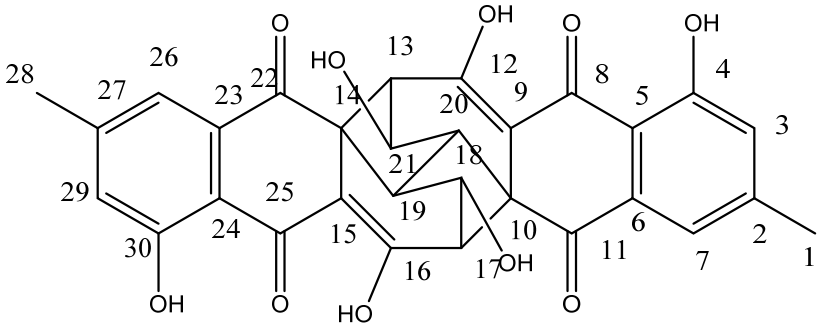



**Figure S0-45 HMBC of helminthosporin**

***Rugulosin***




RUGULOSIN

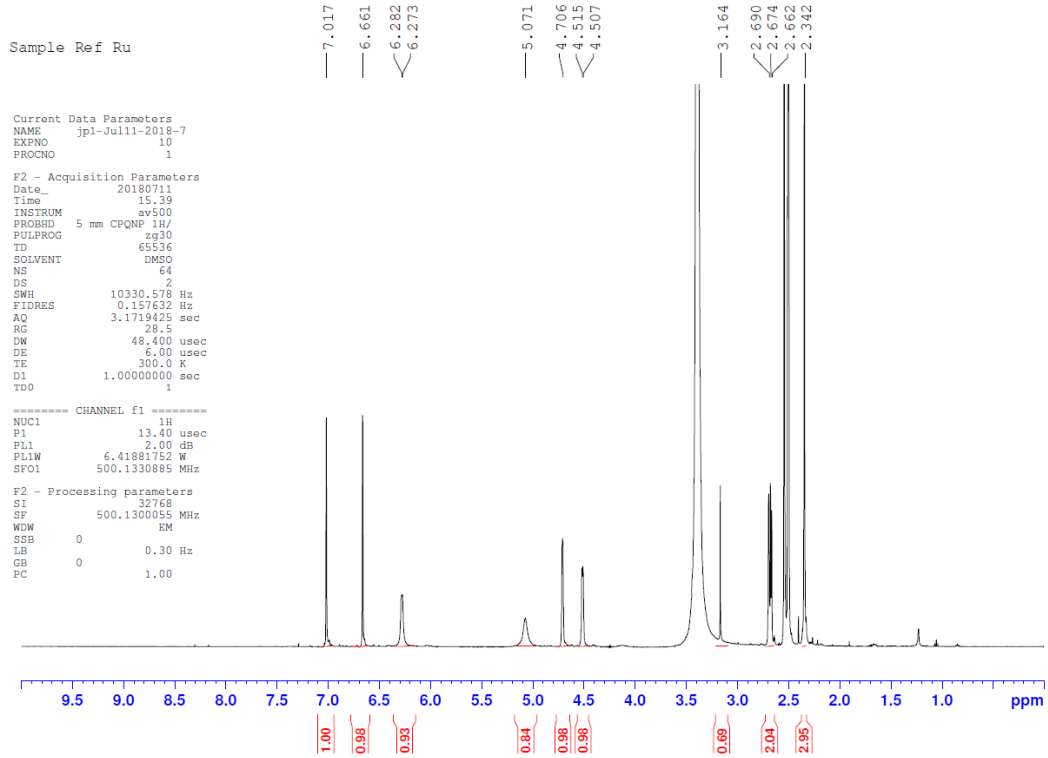



**Figure S0-46 1H NMR Chemical Shift of rugulosin**

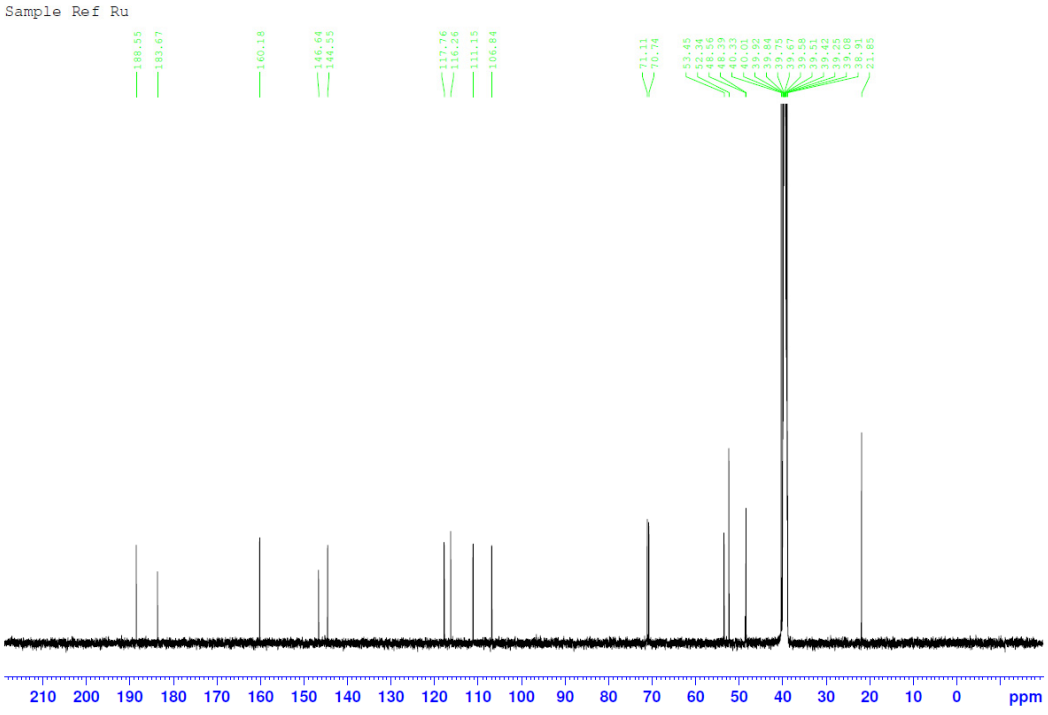



**Figure S0-47 13C NMR Chemical Shift of rugulosin**

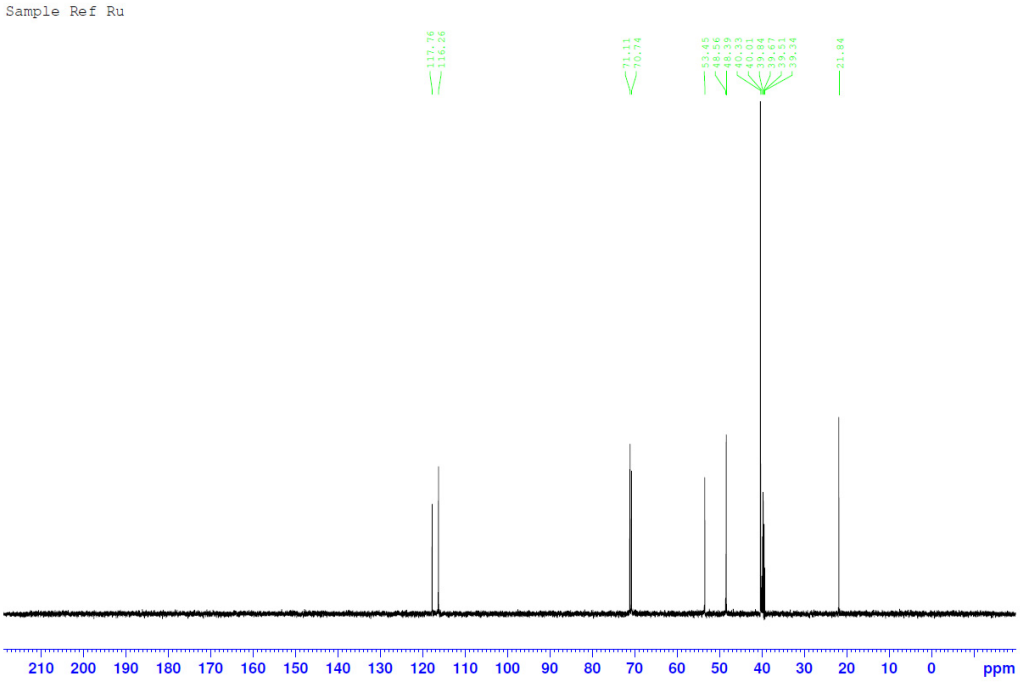



**Figure S0-48 Dept 135 of rugulosin**

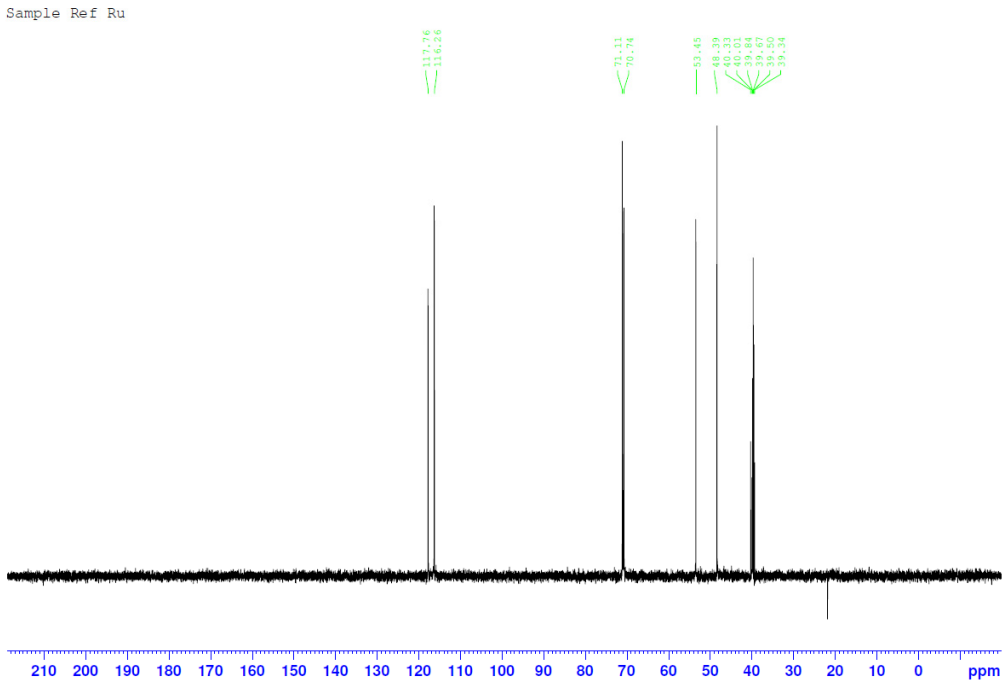



**Figure S0-49 Dept 90 of rugulosin**

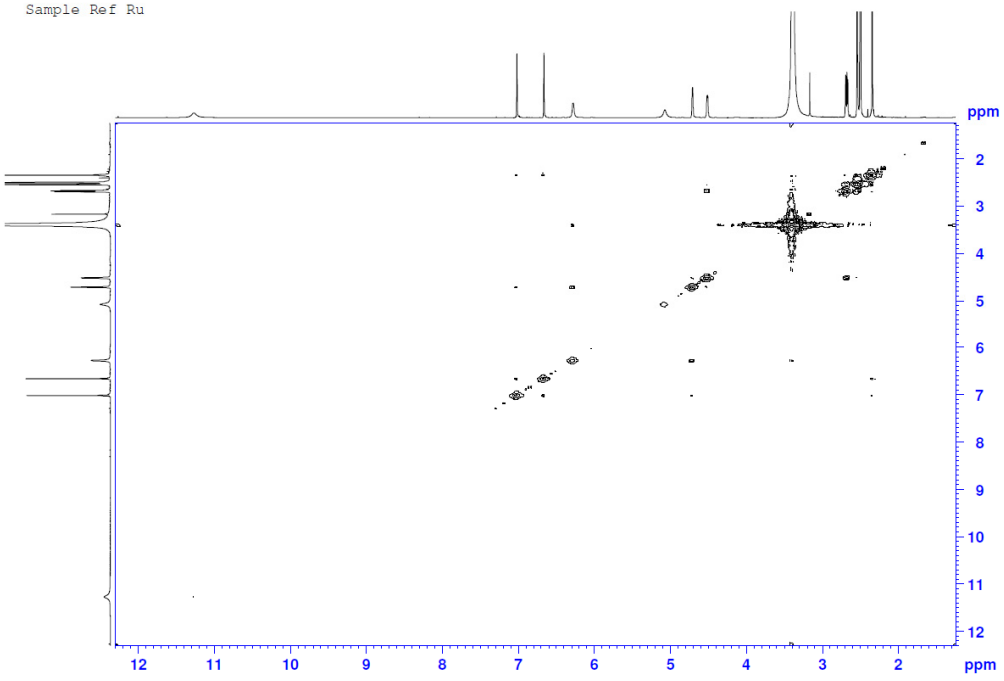



**Figure S0-50 Cosy of rugulosin**

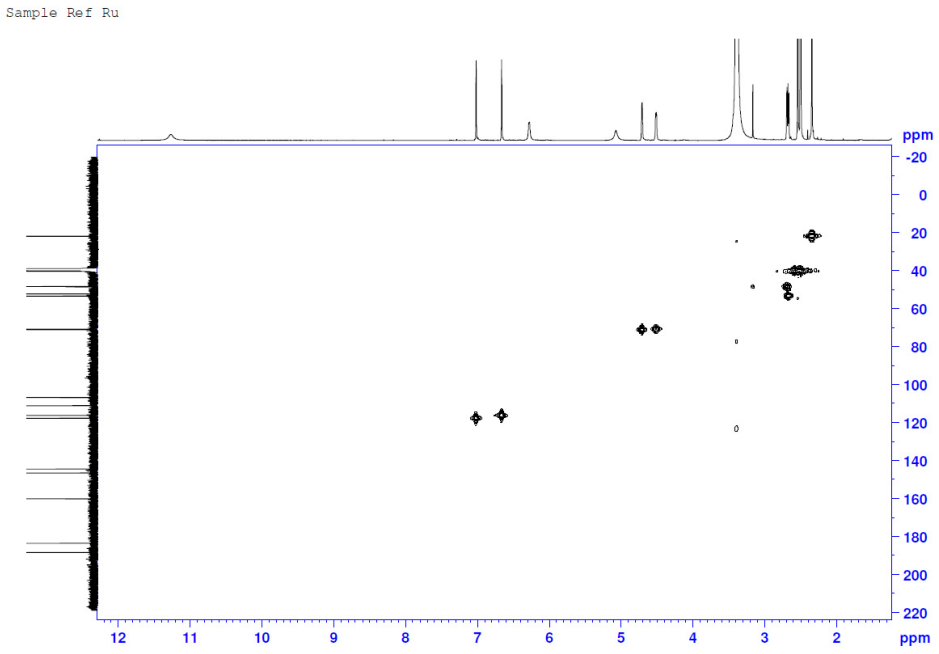



**Figure S0-51 HMQC of rugulosin**

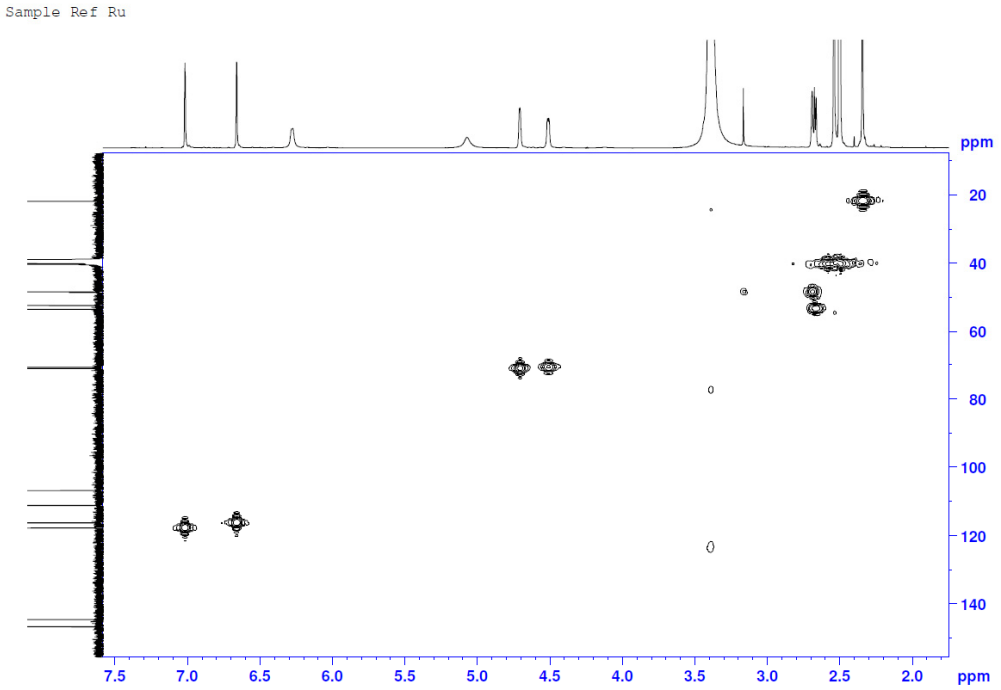



**Figure S0-52 Expand HMQC of rugulosin**

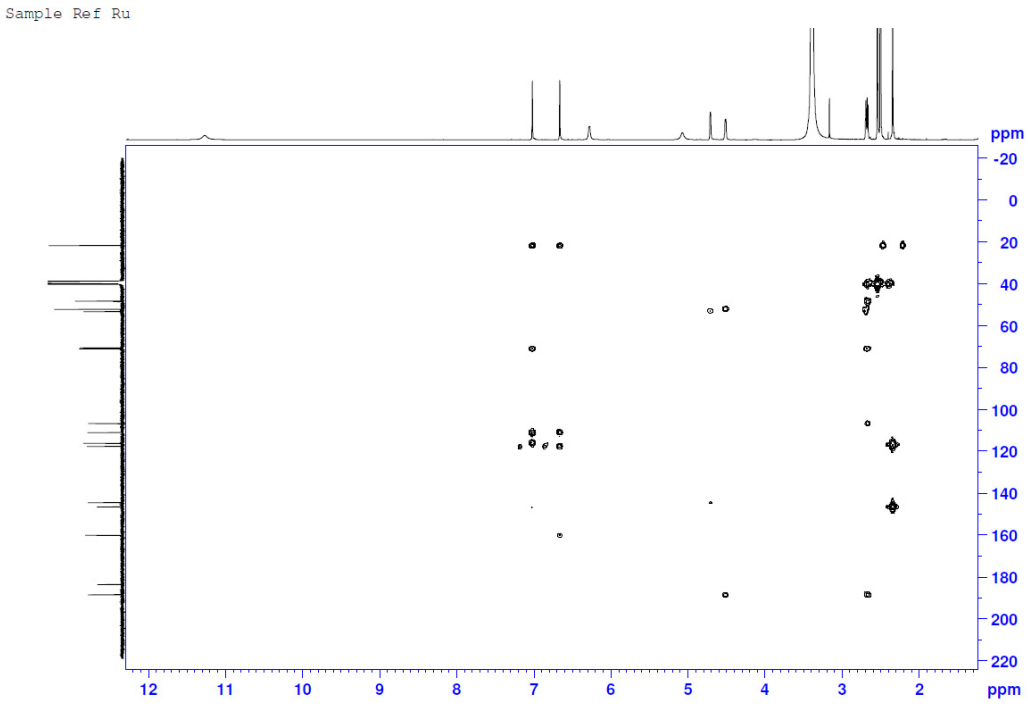



**Figure S0-53 HMBC of rugulosin**

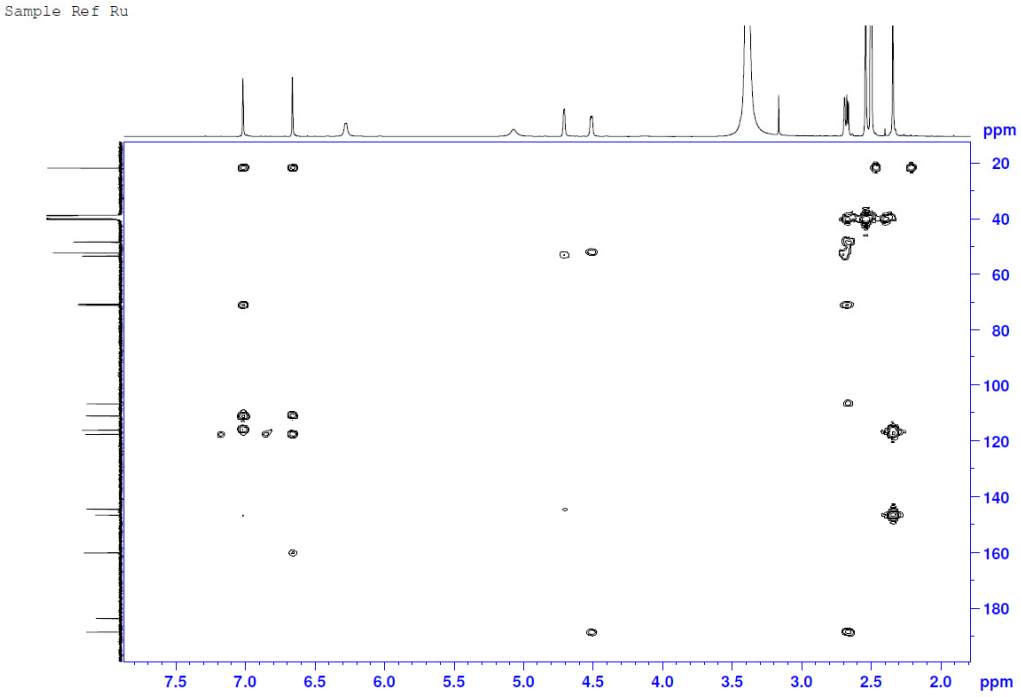
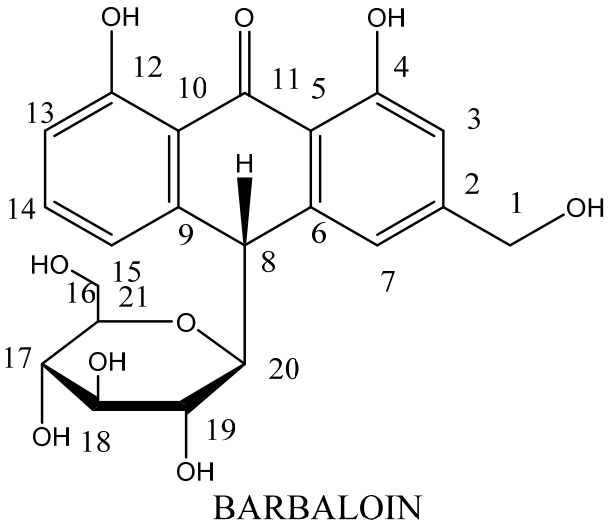



**Figure S0-54 Expand HMBC of rugulosin**

***Barbaloin***




BARBALOIN

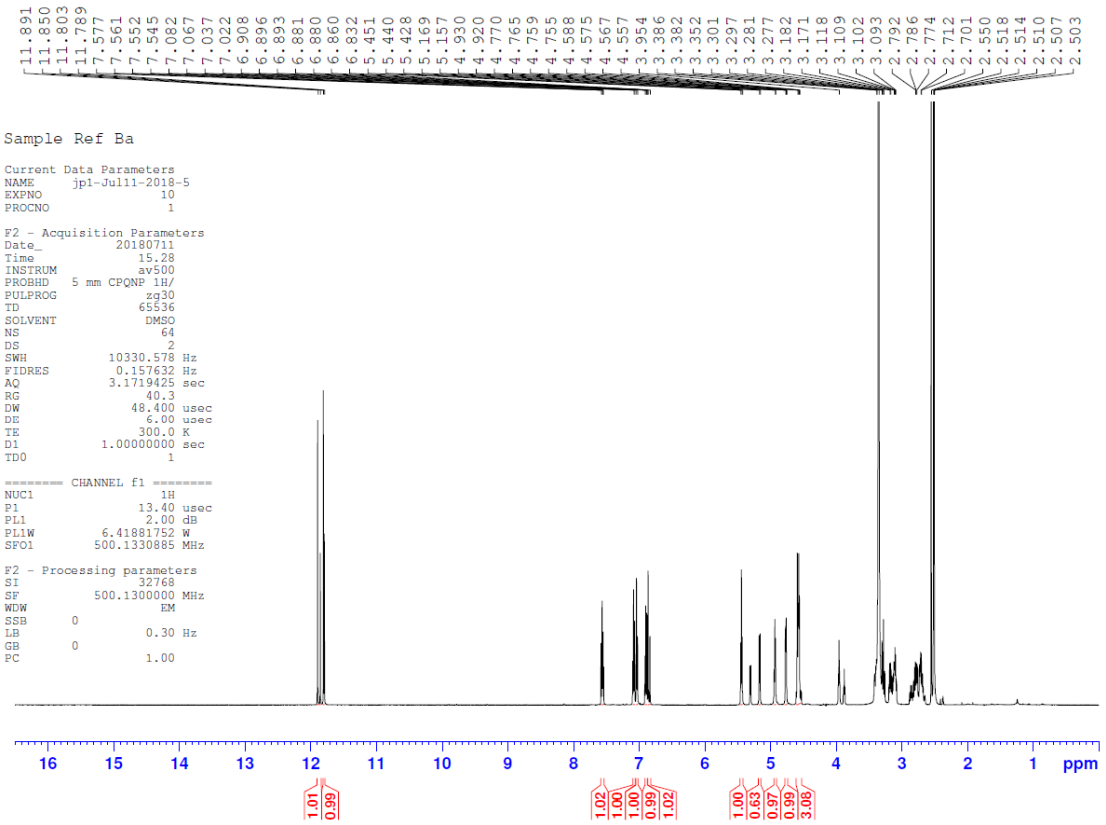



**Figure S0-55 1H NMR Chemical Shift of barbaloin**

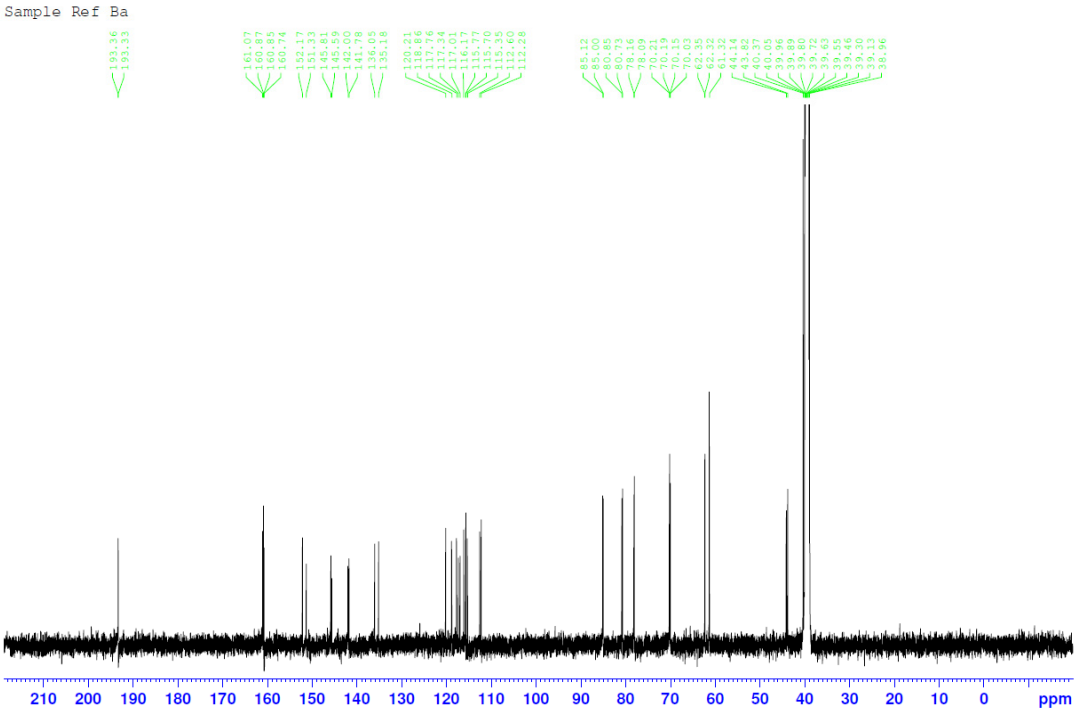



**Figure S0-56 13C NMR Chemical Shift of barbaloin**

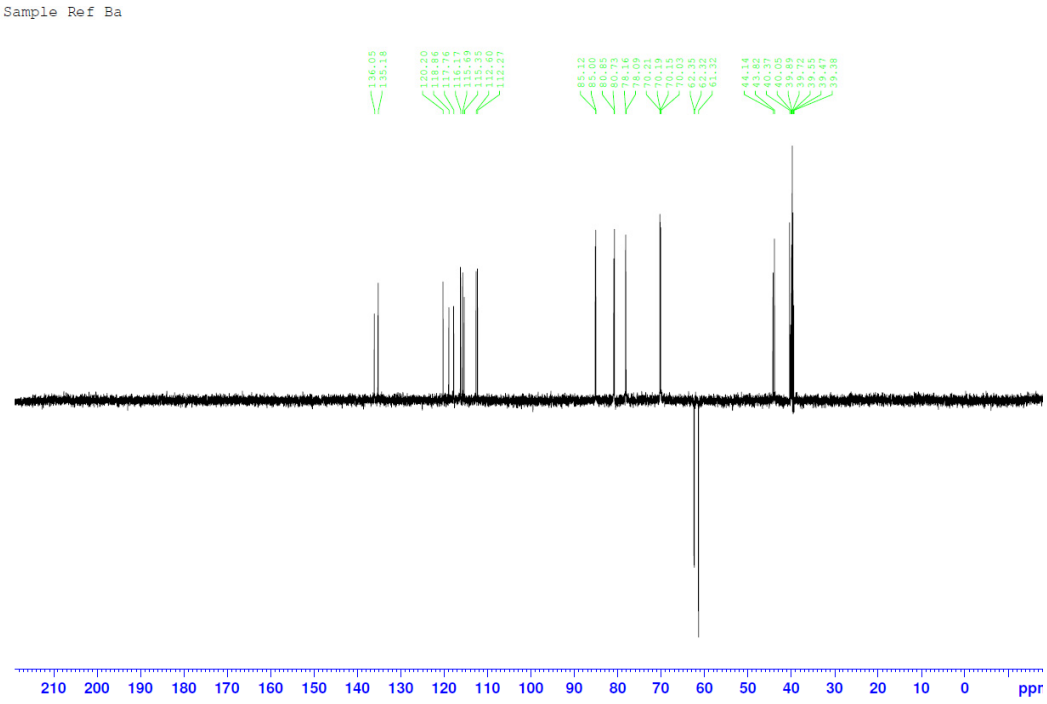



**Figure S0-57 Dept 135 of barbaloin**

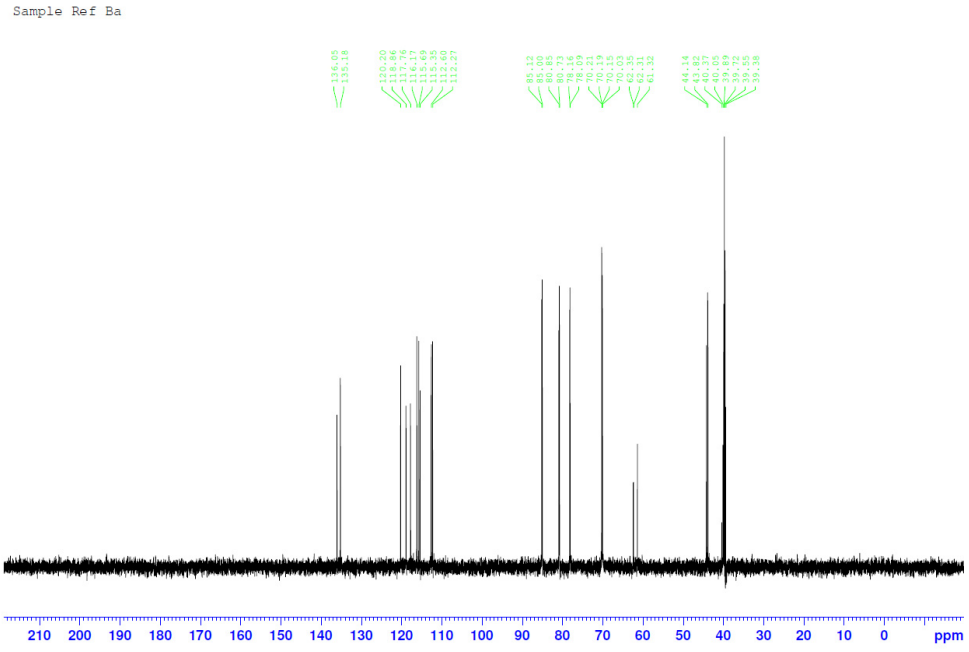



**Figure S0-58 Dept 90 of barbaloin**

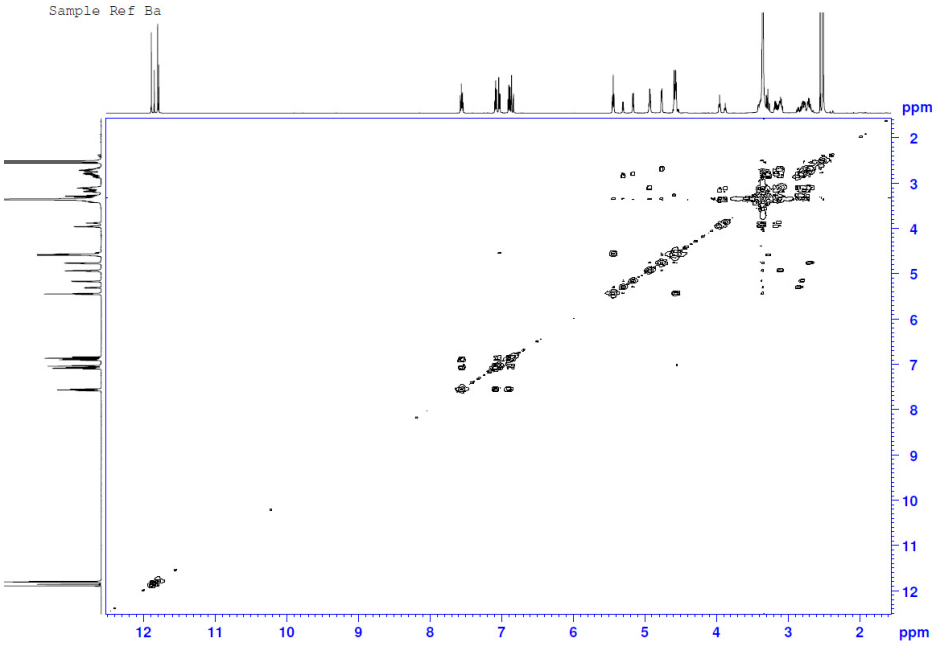



**Figure S0-59 Cosy of barbaloin**

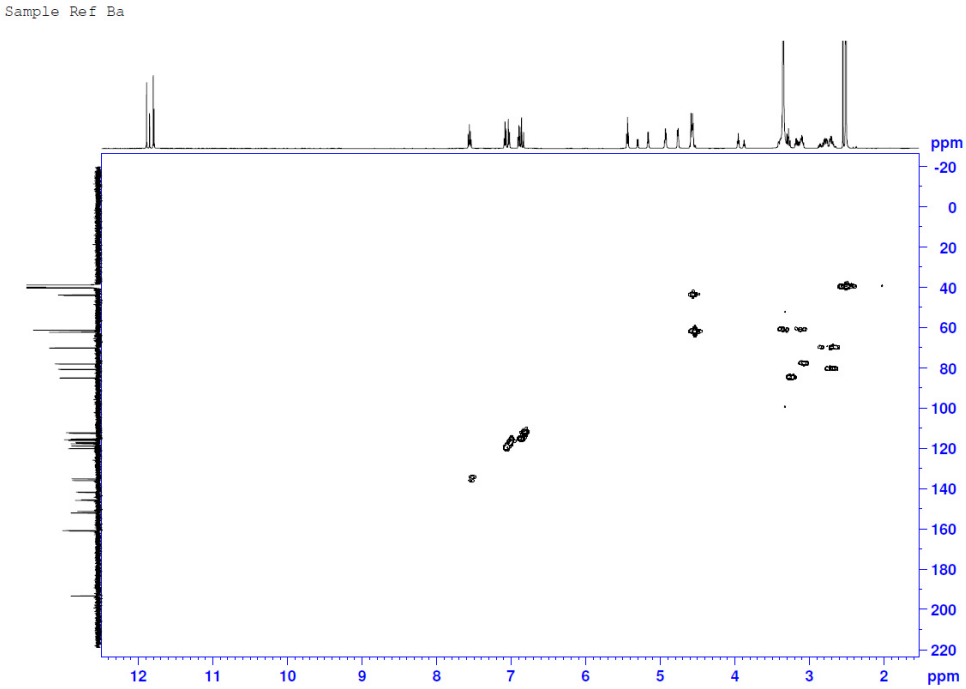



**Figure S0-60 HMQC of barbaloin**

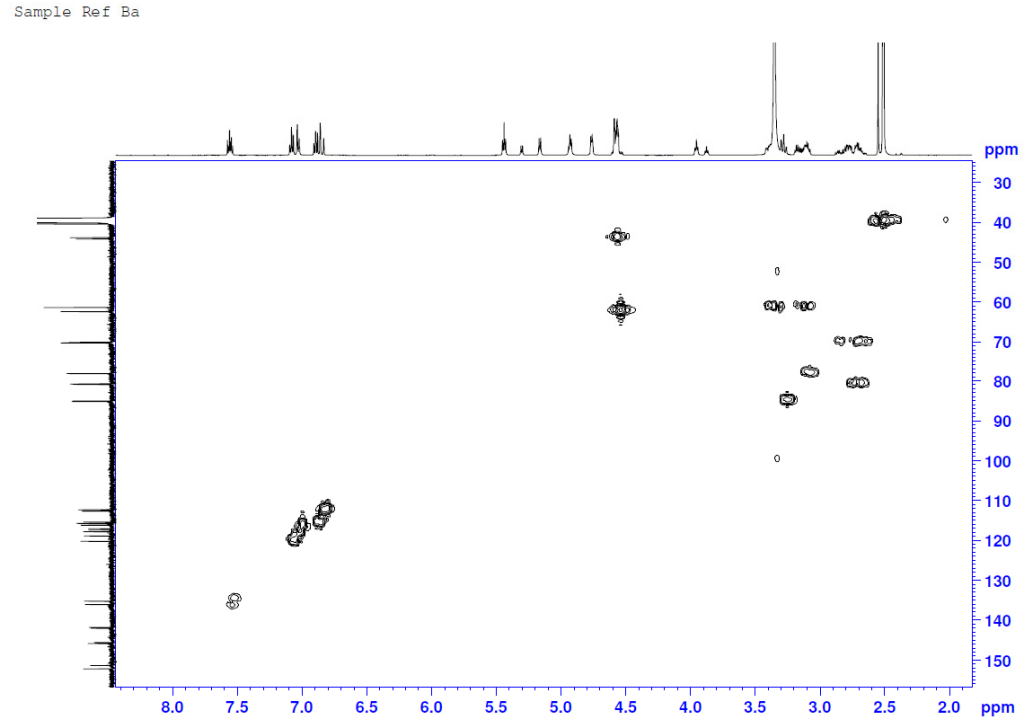



**Figure S0-61 Expand HMQC of barbaloin**

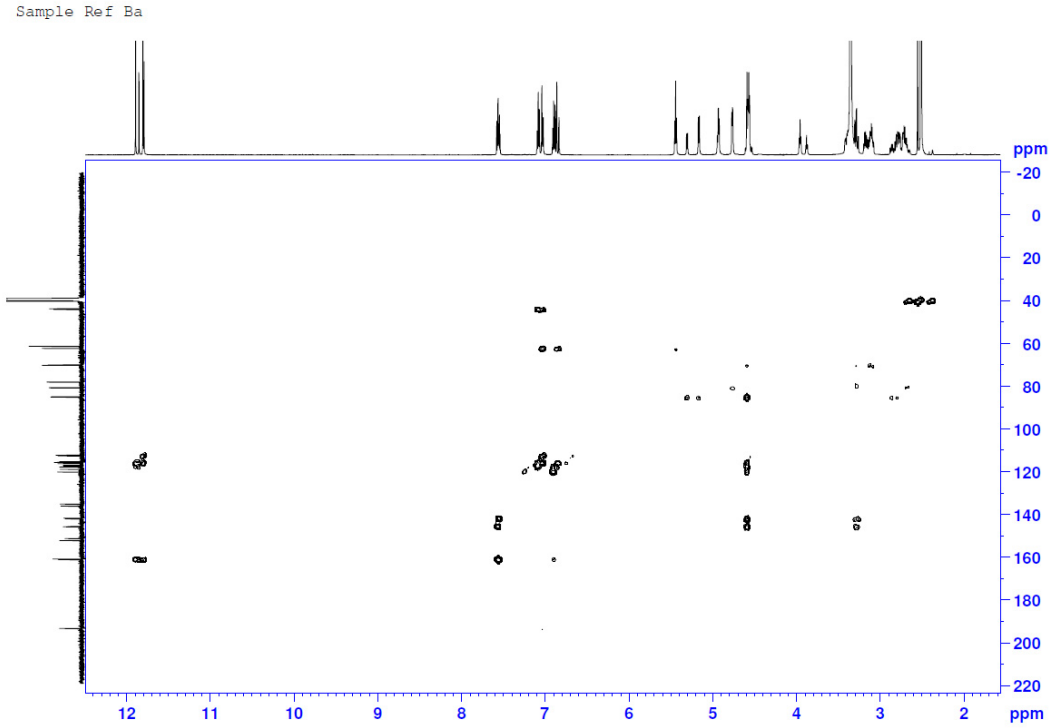



**Figure S0-62 HMBC of barbaloin**

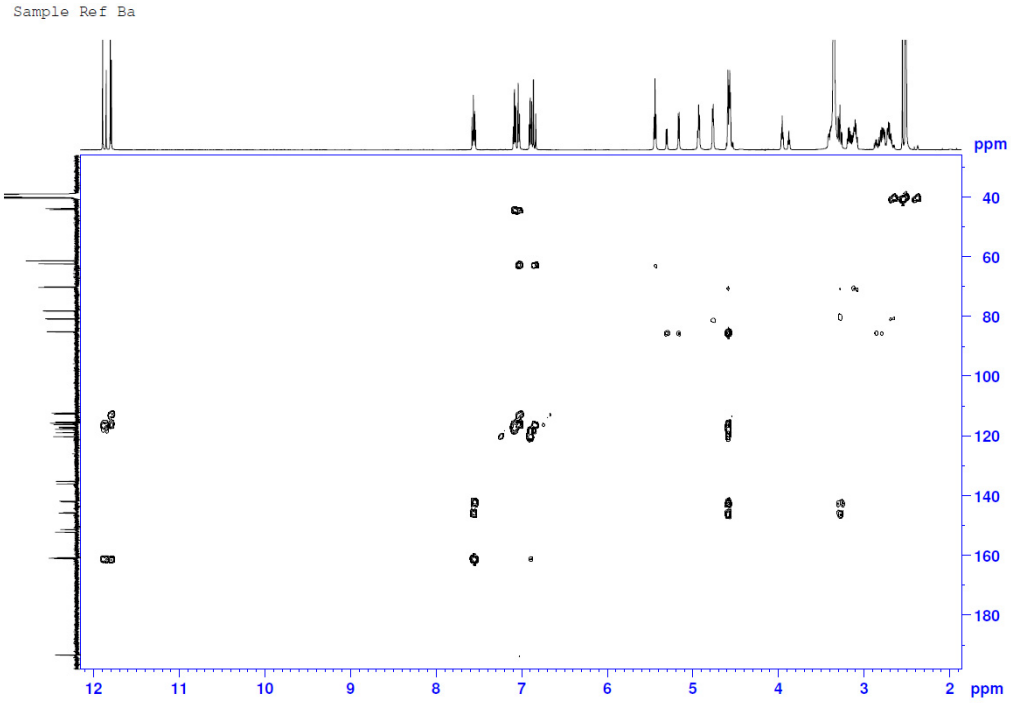



**Figure S0-63 Expand HMBC of barbaloin**