

Figure S1-1  $^1\text{H}$  NMR spectrum of compound 1 in  $\text{CD}_3\text{OD}$  (400 MHz)

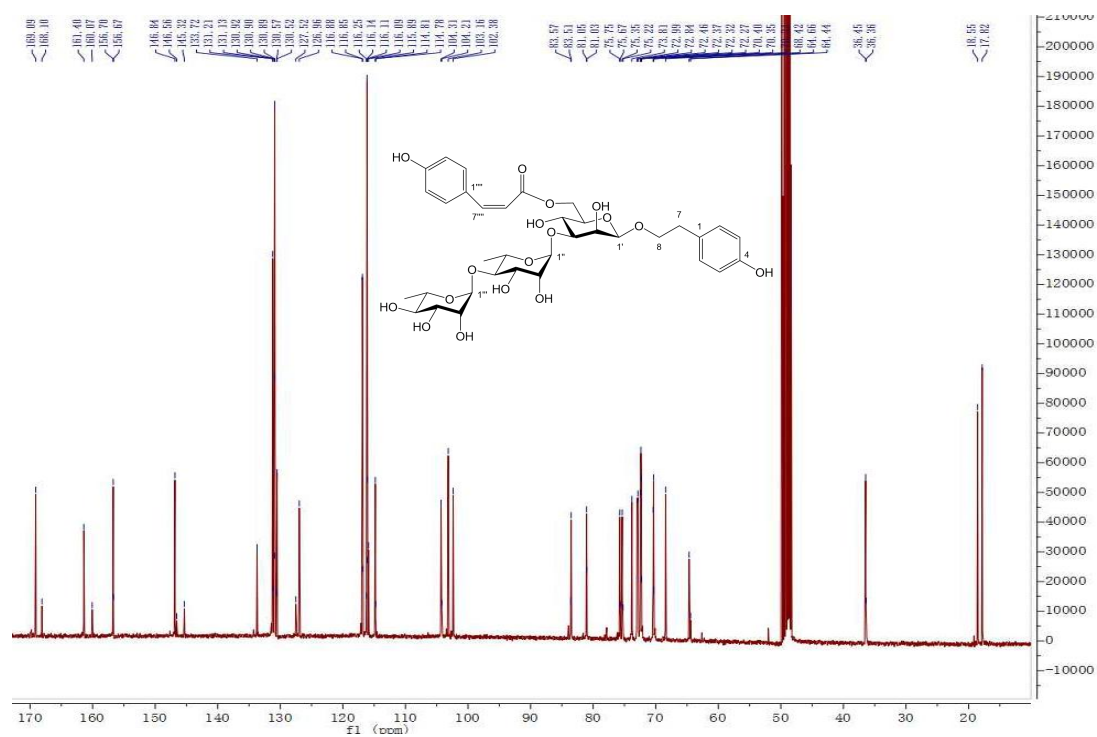


Figure S1-2  $^{13}\text{C}$  NMR spectrum of compound 1 in  $\text{CD}_3\text{OD}$  (100 MHz)

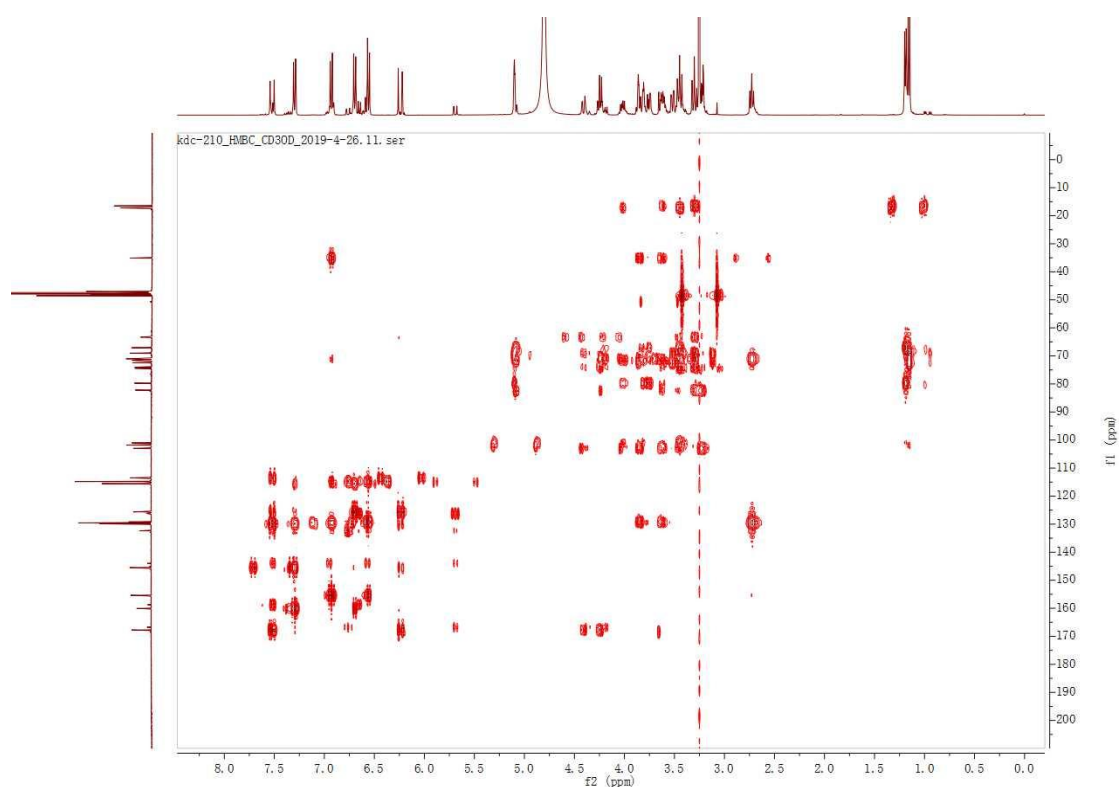


Figure S1-3 HMBC spectrum of compound **1** in CD<sub>3</sub>OD (400 MHz)

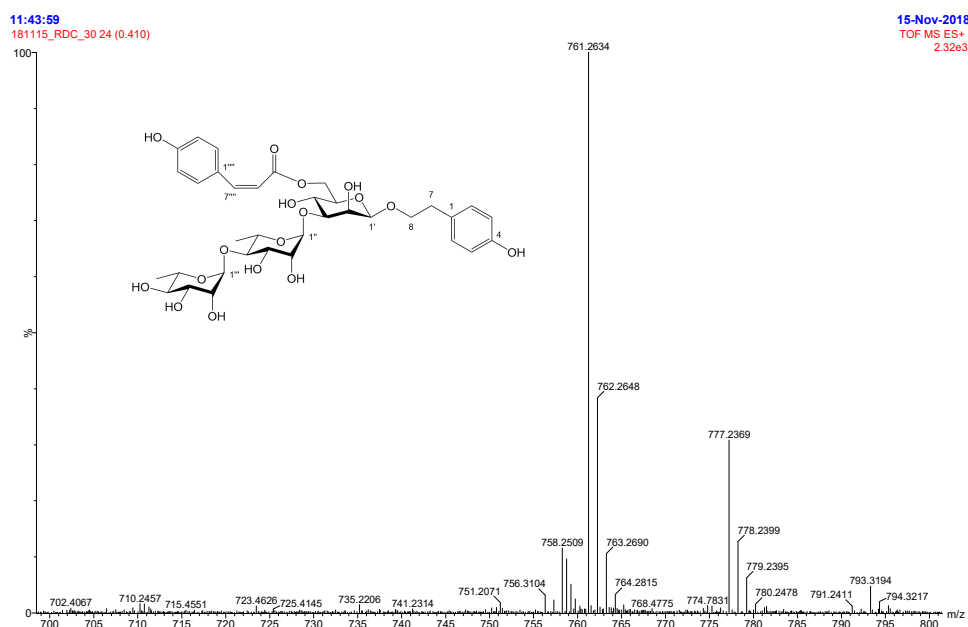


Figure S1-4 HRESIMS spectrum of compound **1**

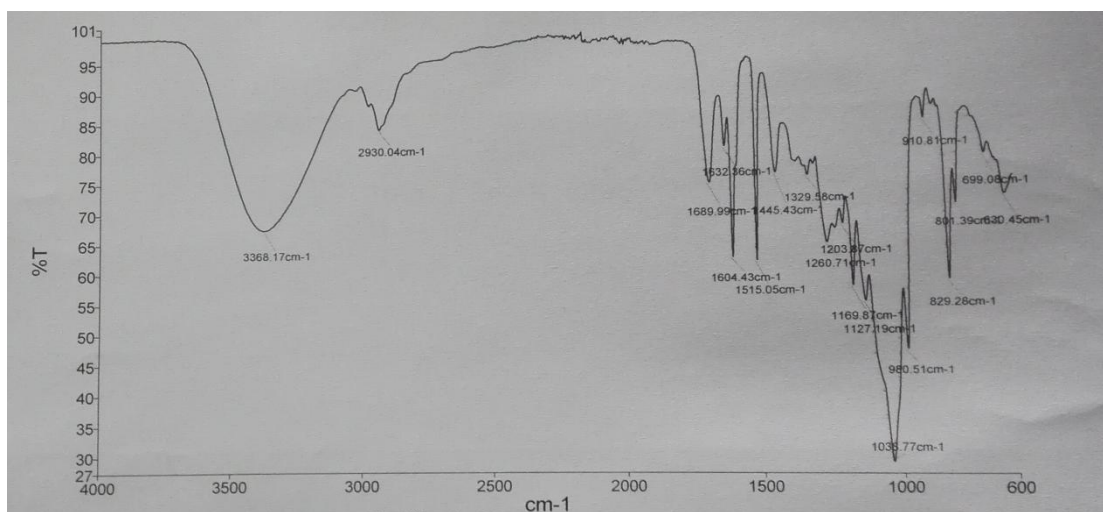


Figure S1-5 IR spectrum of compound 1 (film)

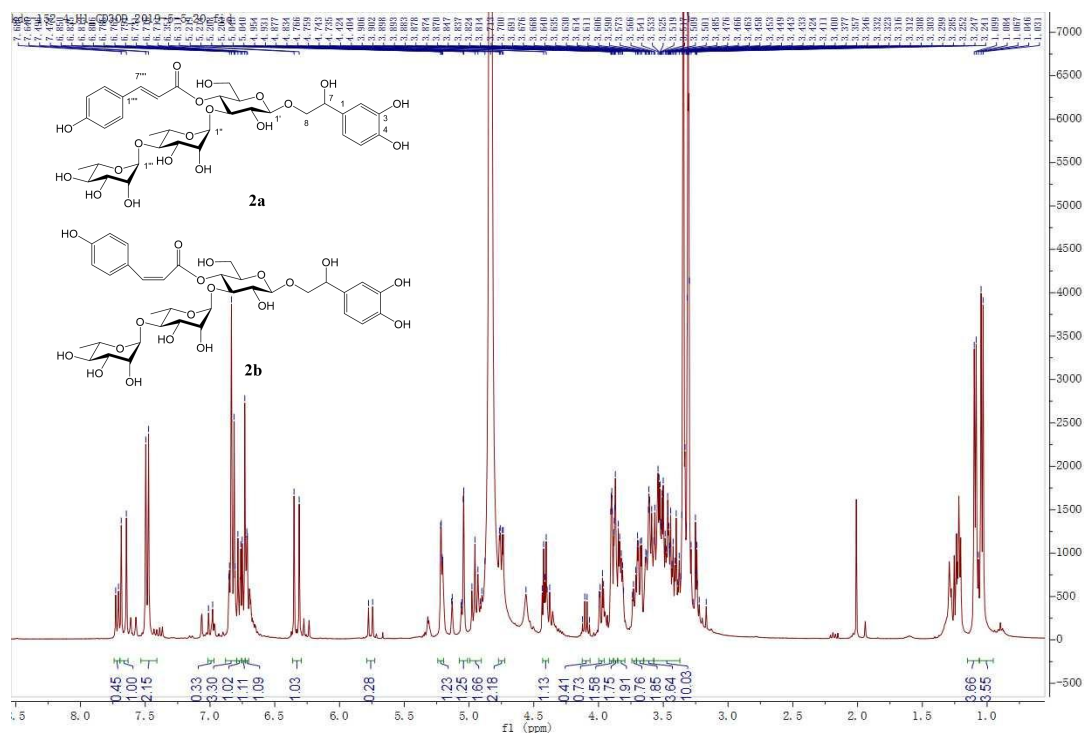


Figure S2-1  $^1\text{H}$  NMR spectrum of mixture 2 in  $\text{CD}_3\text{OD}$  (400 MHz)

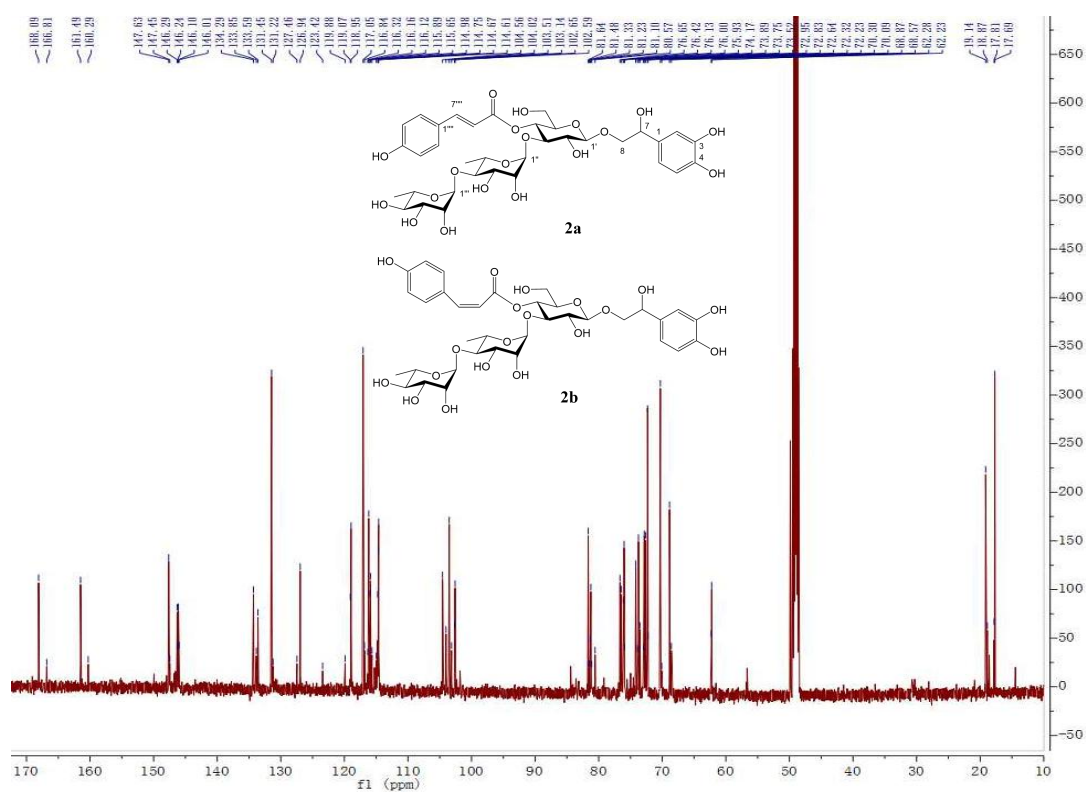


Figure S2-2  $^{13}\text{C}$  NMR spectrum of mixture **2** in  $\text{CD}_3\text{OD}$  (150 MHz)

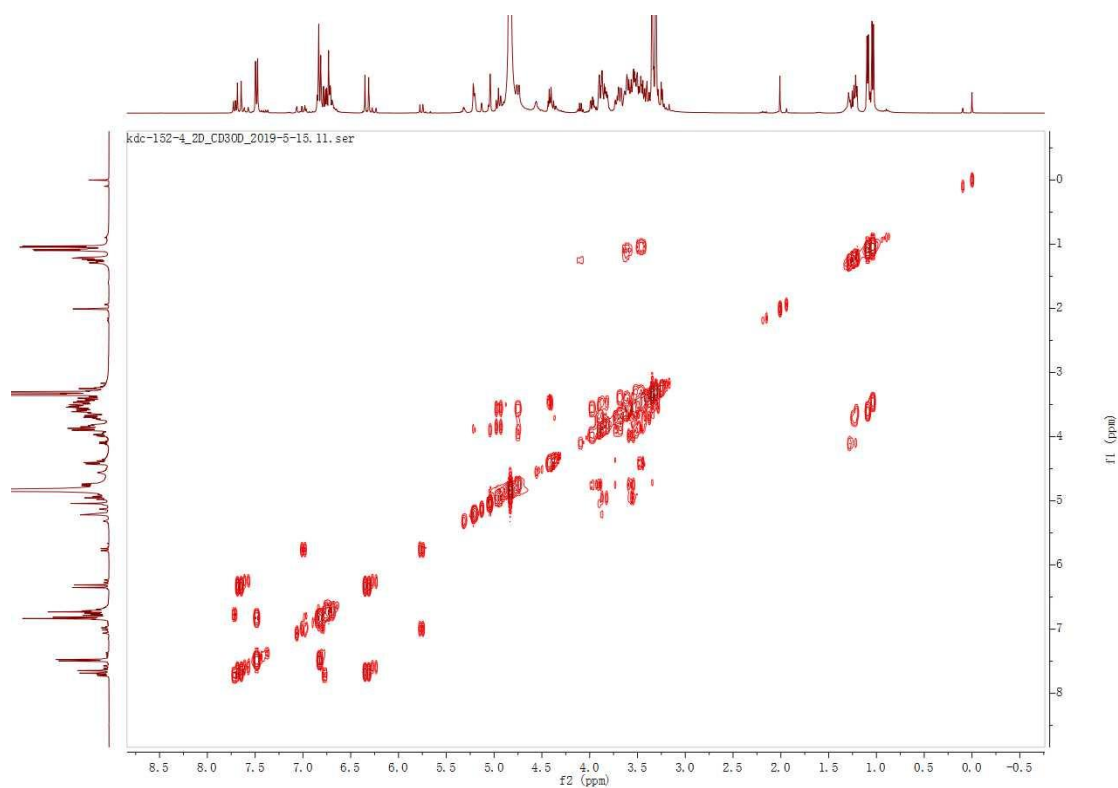


Figure S2-3  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of mixture **2** in  $\text{CD}_3\text{OD}$  (400 MHz)

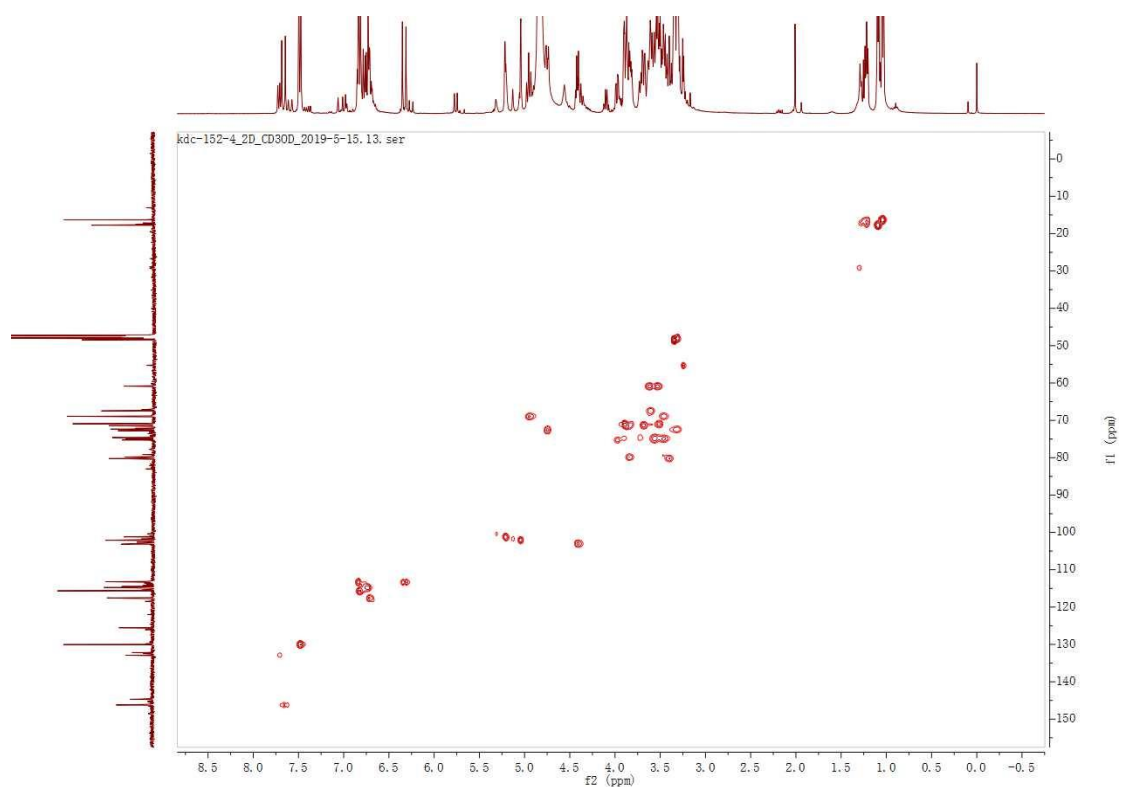


Figure S2-4 HSQC spectrum of mixture **2** in CD<sub>3</sub>OD (400 MHz)

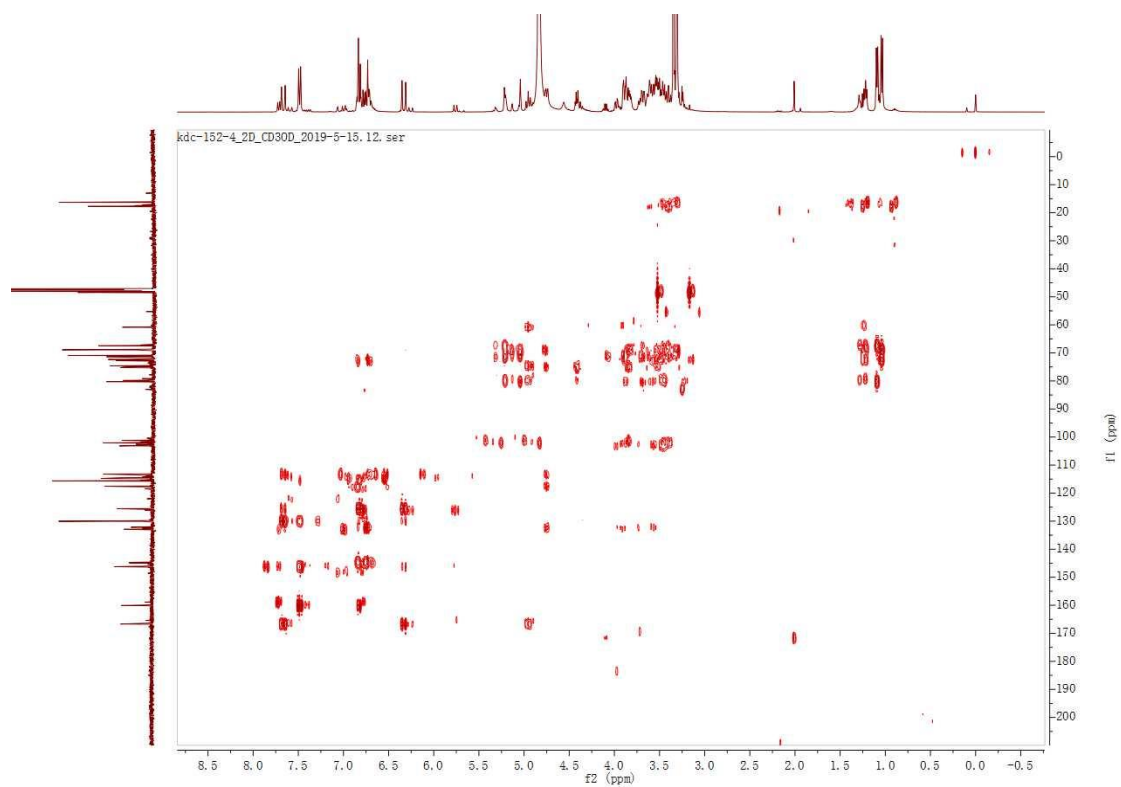


Figure S2-5 HMBC spectrum of mixture **2** in CD<sub>3</sub>OD (400 MHz)

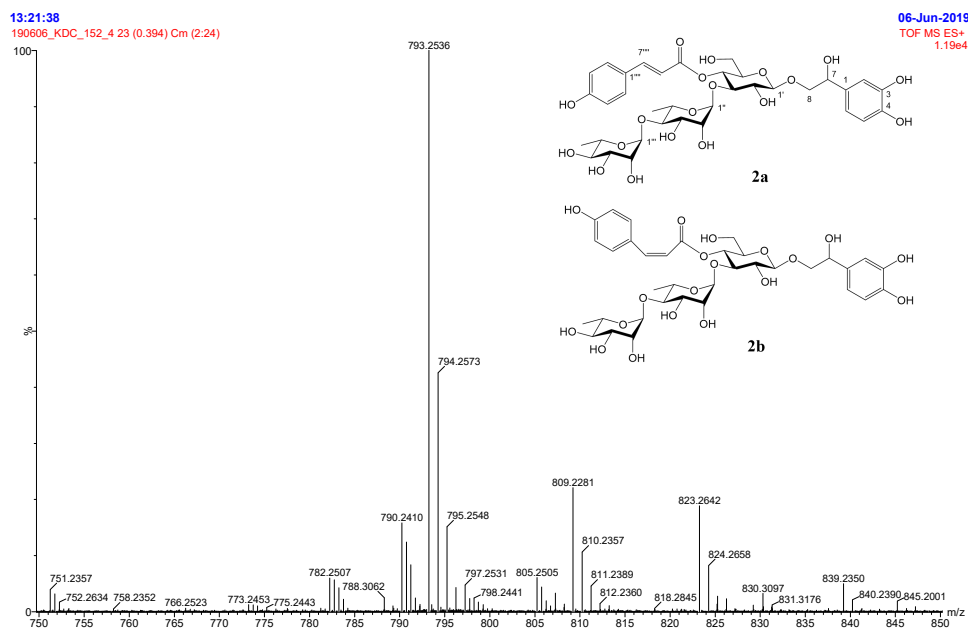


Figure S2-6 HRESIMS spectrum of mixture 2

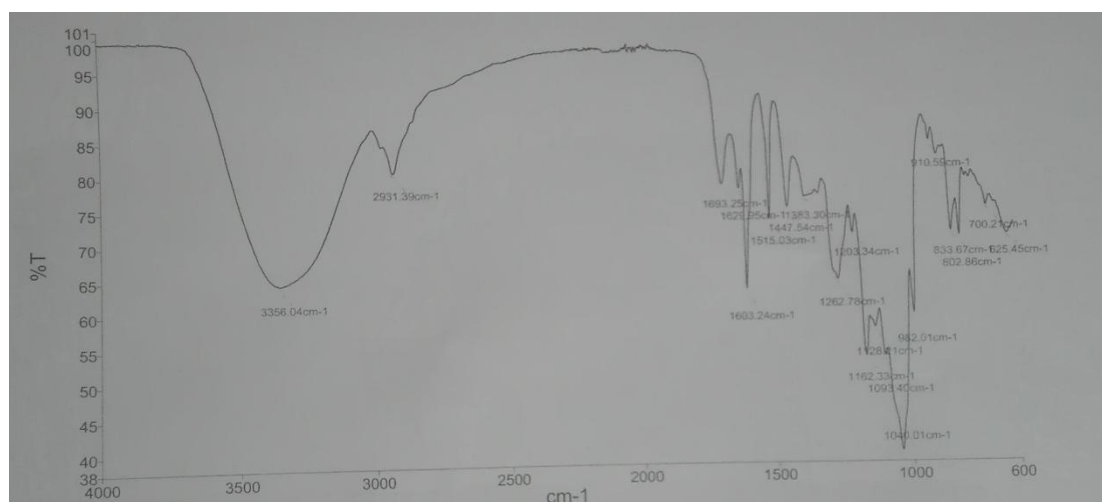


Figure S2-7 IR spectrum of mixture 2 (film)

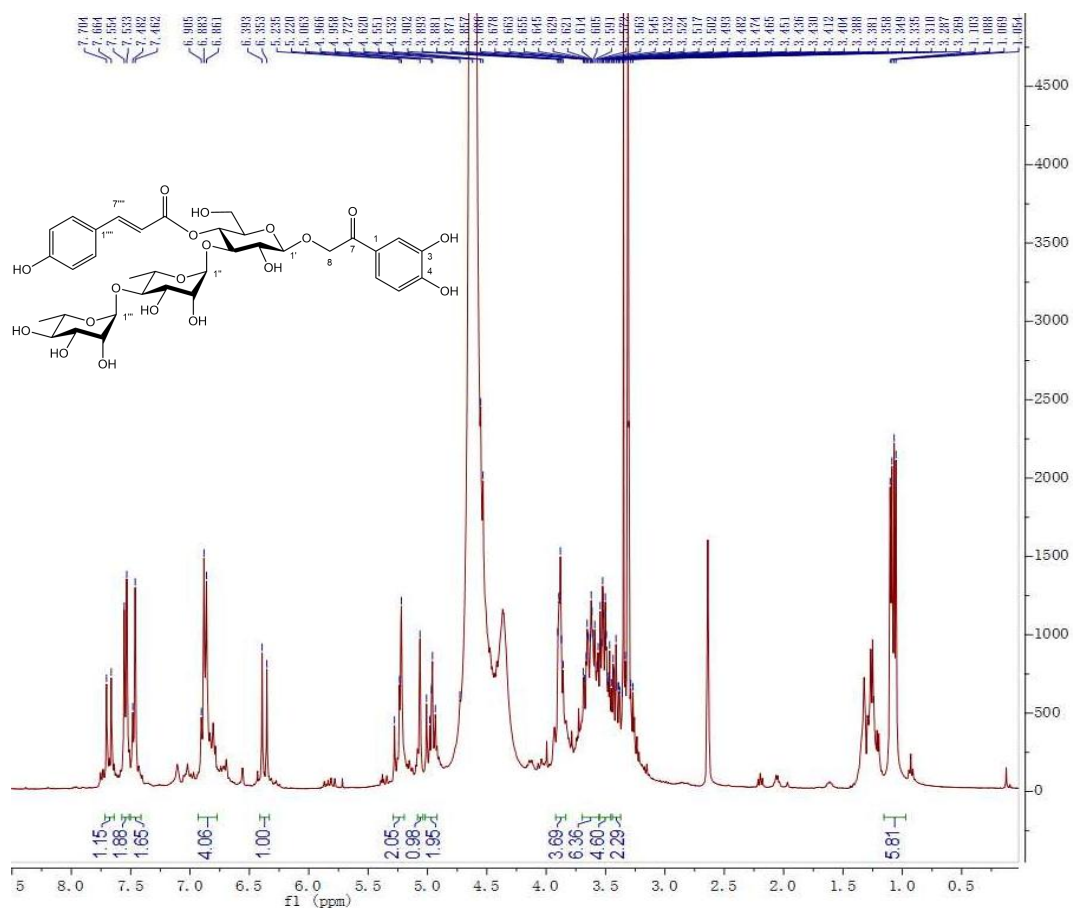


Figure S3-1 <sup>1</sup>H NMR spectrum of compound **3** in (CD<sub>3</sub>OD+DMSO-d<sub>6</sub>) (400 MHz)

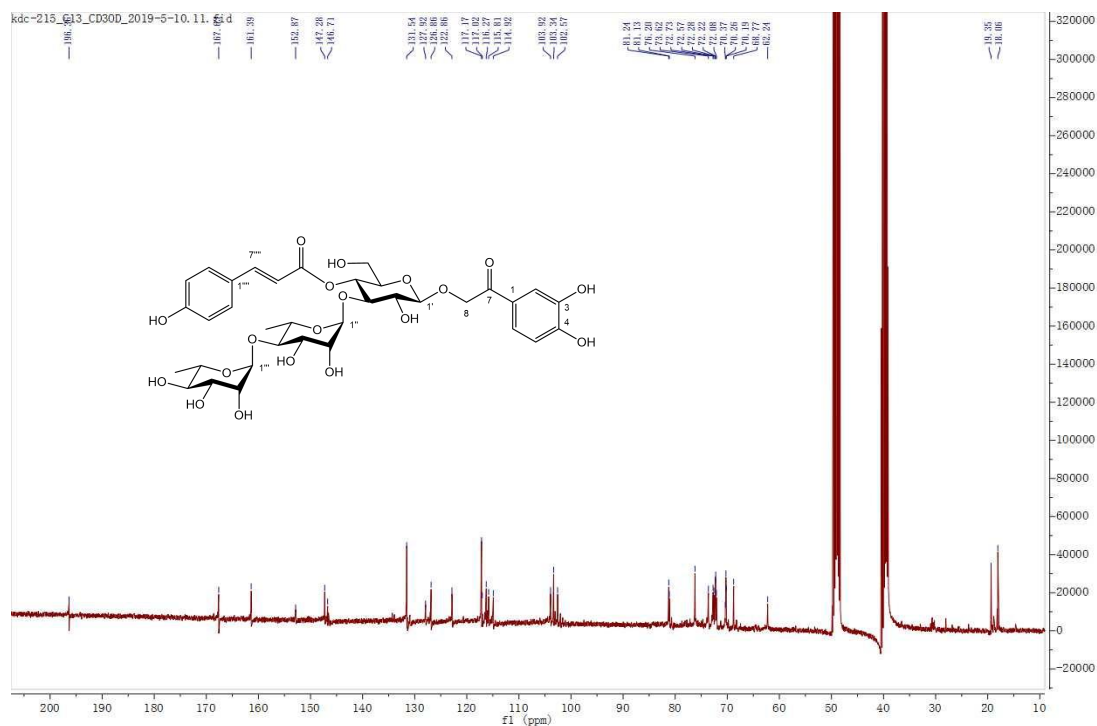


Figure S3-2 <sup>13</sup>C NMR spectrum of compound **3** in (CD<sub>3</sub>OD+DMSO-d<sub>6</sub>) (100 MHz)



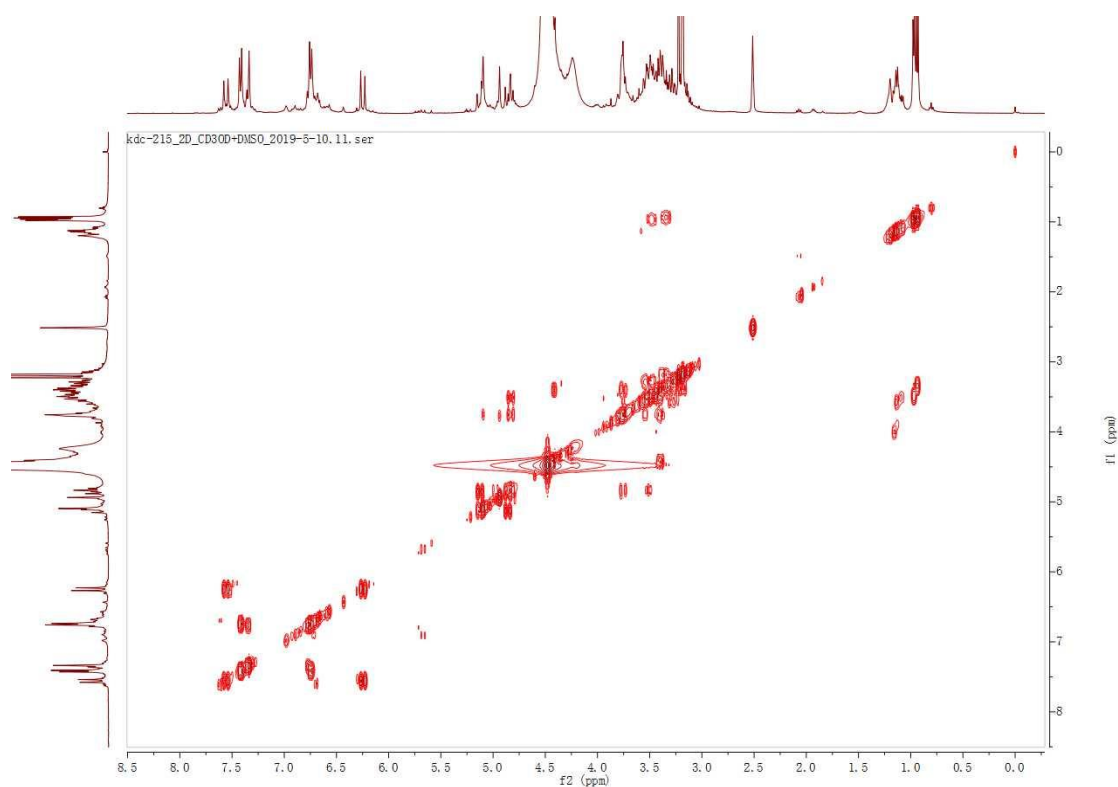


Figure S3-3  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **3** in ( $\text{CD}_3\text{OD}+\text{DMSO}-d_6$ ) (400 MHz)

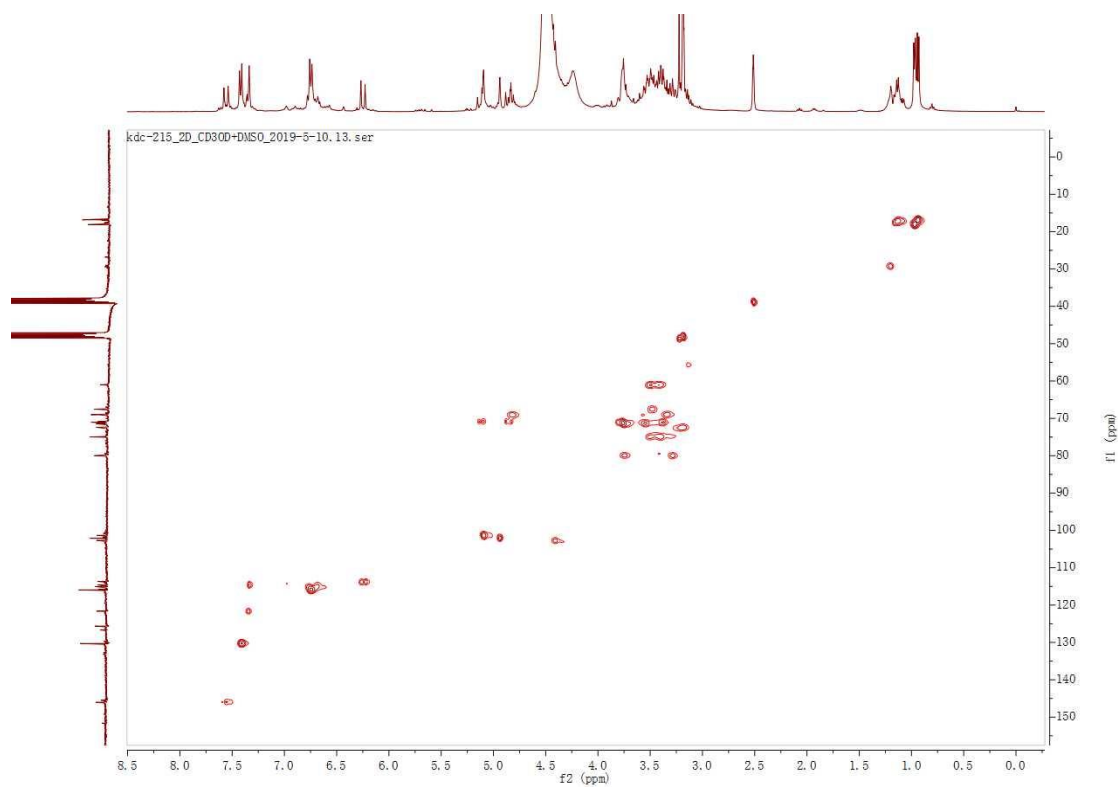


Figure S3-4 HSQC spectrum of compound **3** in ( $\text{CD}_3\text{OD}+\text{DMSO}-d_6$ ) (400 MHz)



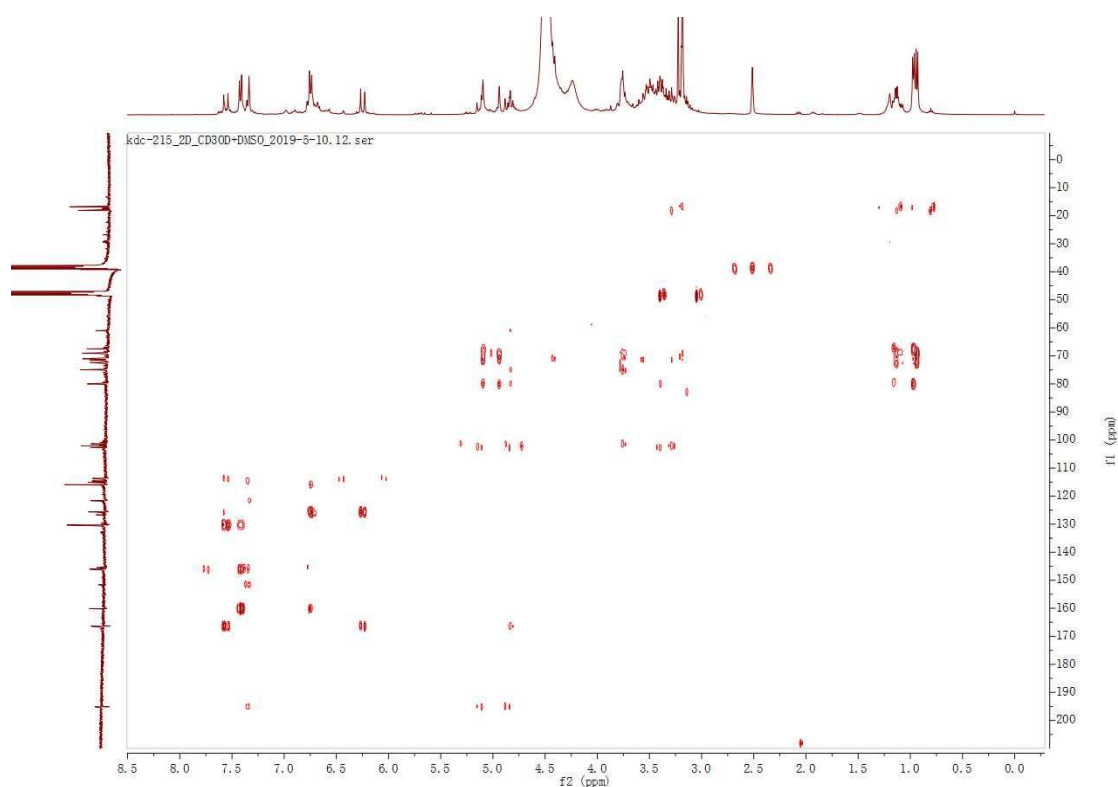


Figure S3-5 HMBC spectrum of compound **3** in (CD<sub>3</sub>OD+DMSO-d<sub>6</sub>) (400 MHz)

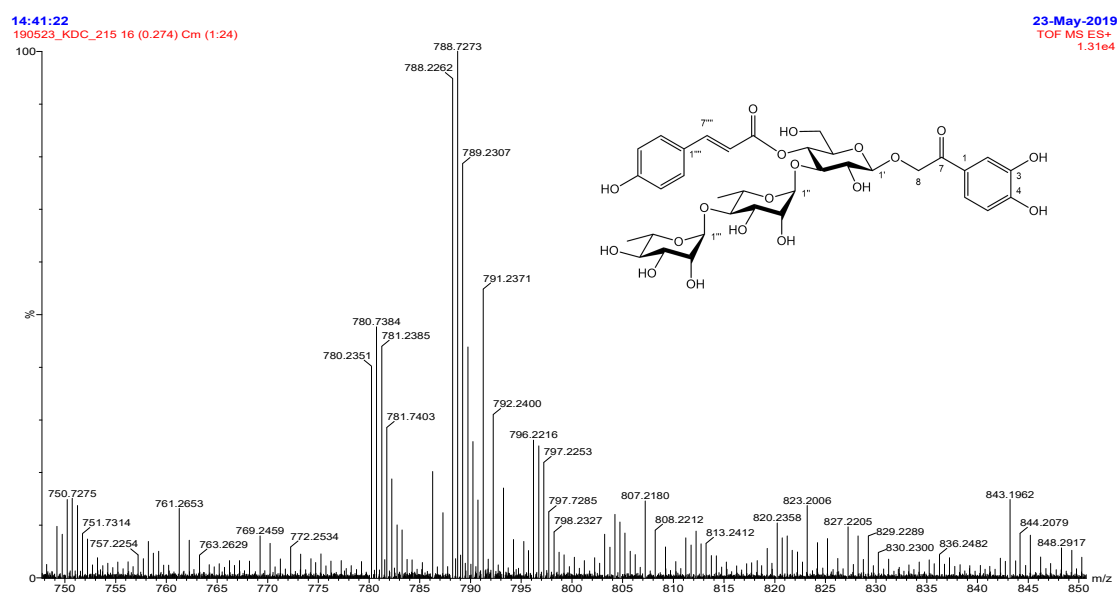


Figure S3-6 HRESIMS spectrum of compound **3**

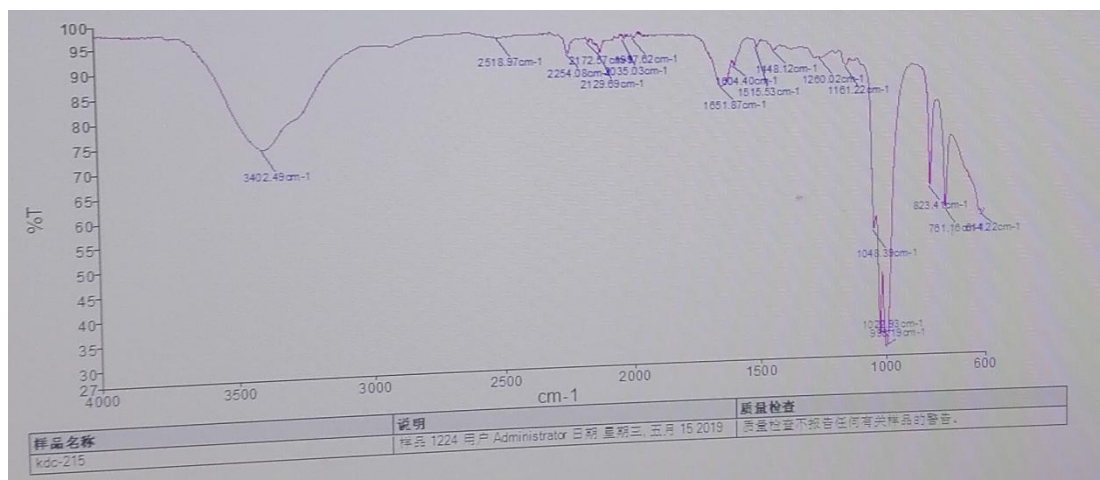


Figure S3-7 IR spectrum of compound **3** (film)

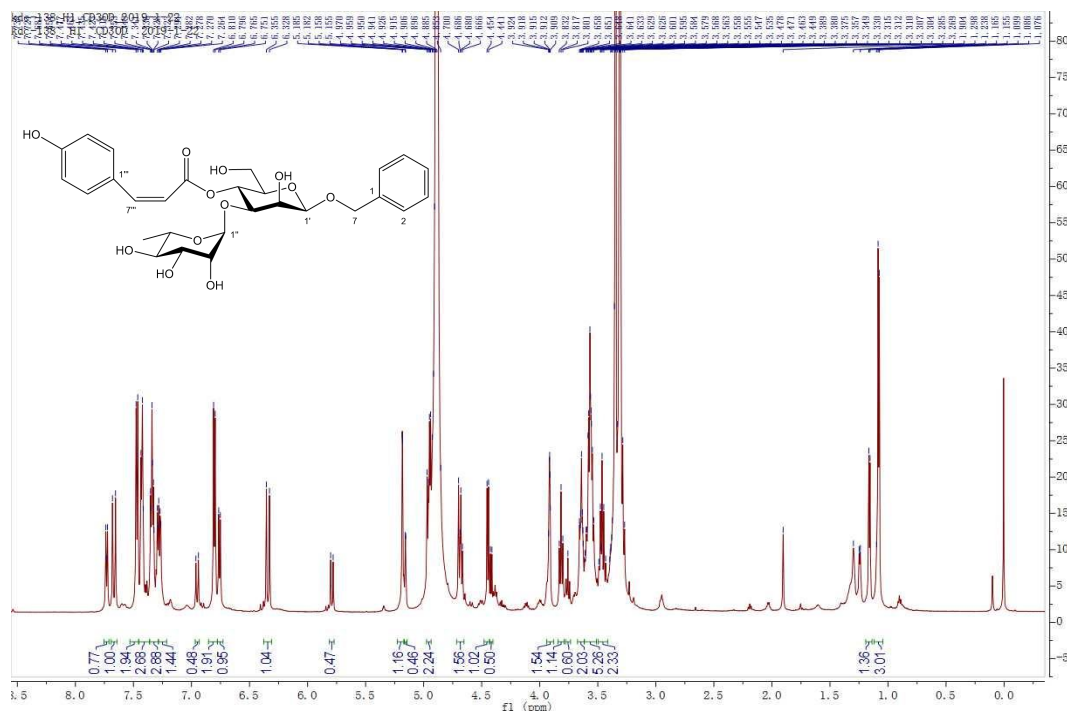


Figure S4-1  $^1\text{H}$  NMR spectrum of compound **4** in  $\text{CD}_3\text{OD}$  (600 MHz)

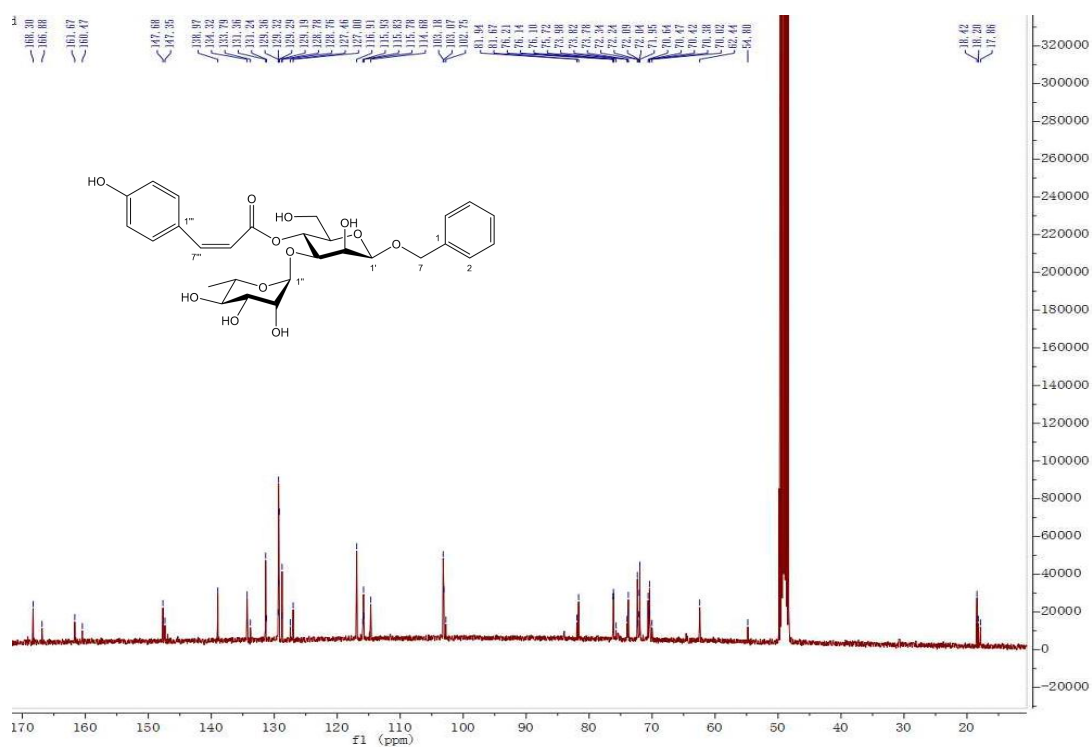


Figure S4-2  $^{13}\text{C}$  NMR spectrum of compound 4 in  $\text{CD}_3\text{OD}$  (100 MHz)

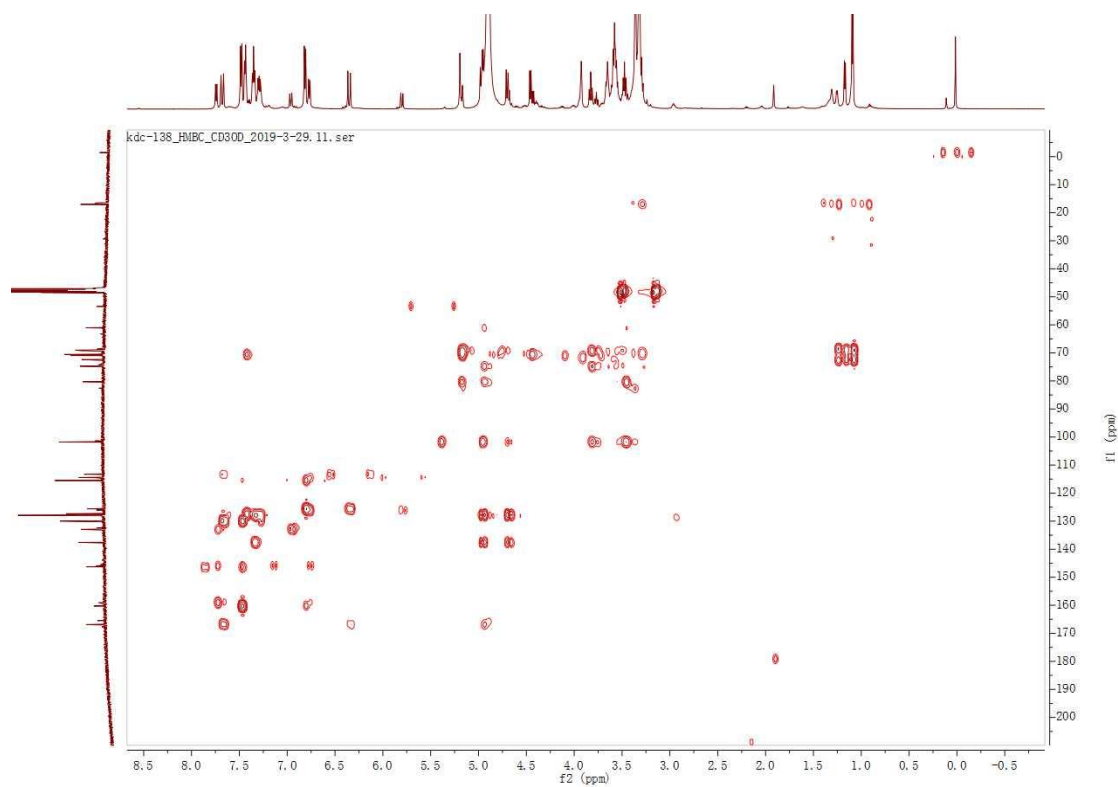


Figure S4-3 HMBC spectrum of compound 4 in  $\text{CD}_3\text{OD}$  (400 MHz)

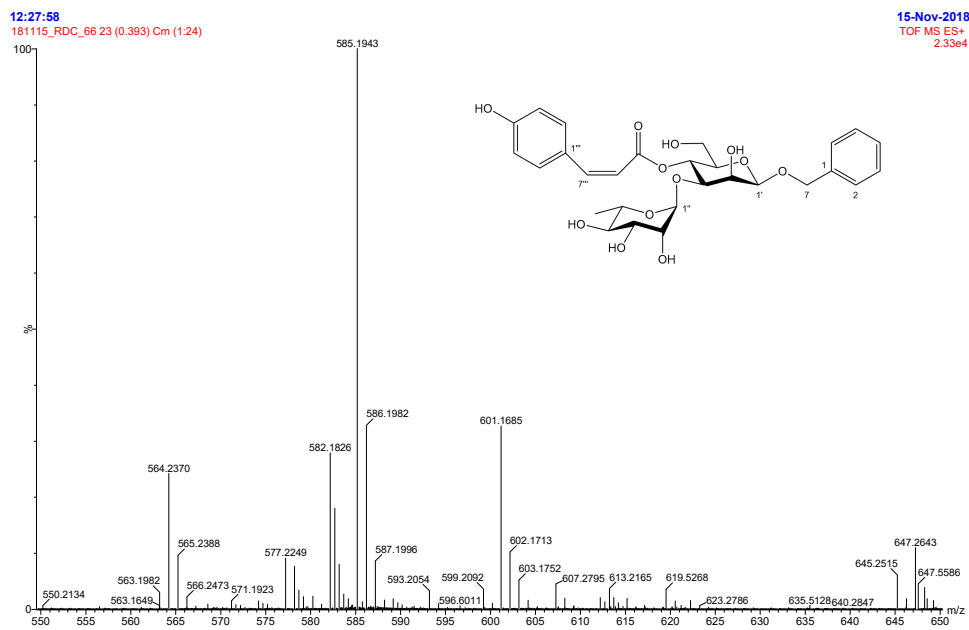


Figure S4-4 HRESIMS spectrum of compound 4

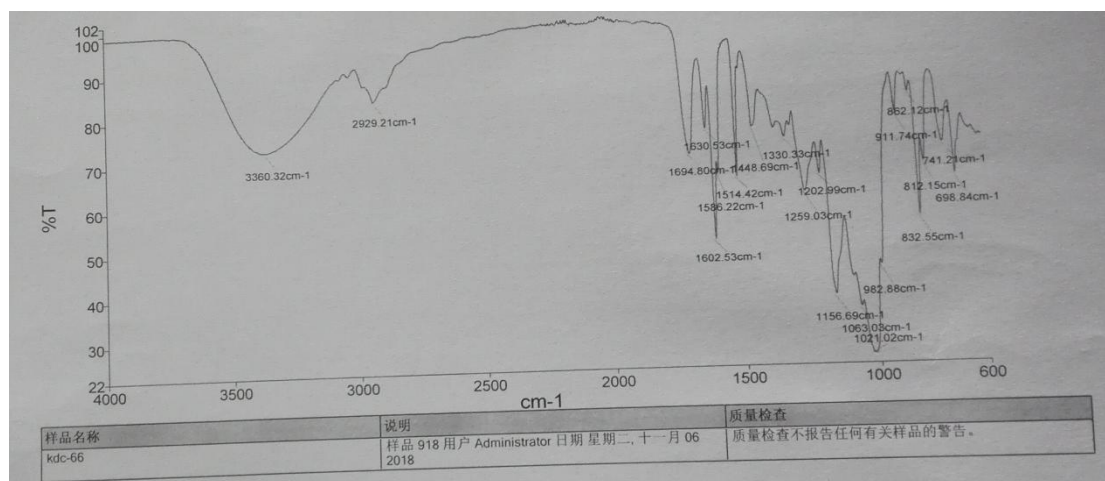


Figure S4-5 IR spectrum of compound 4 (film)

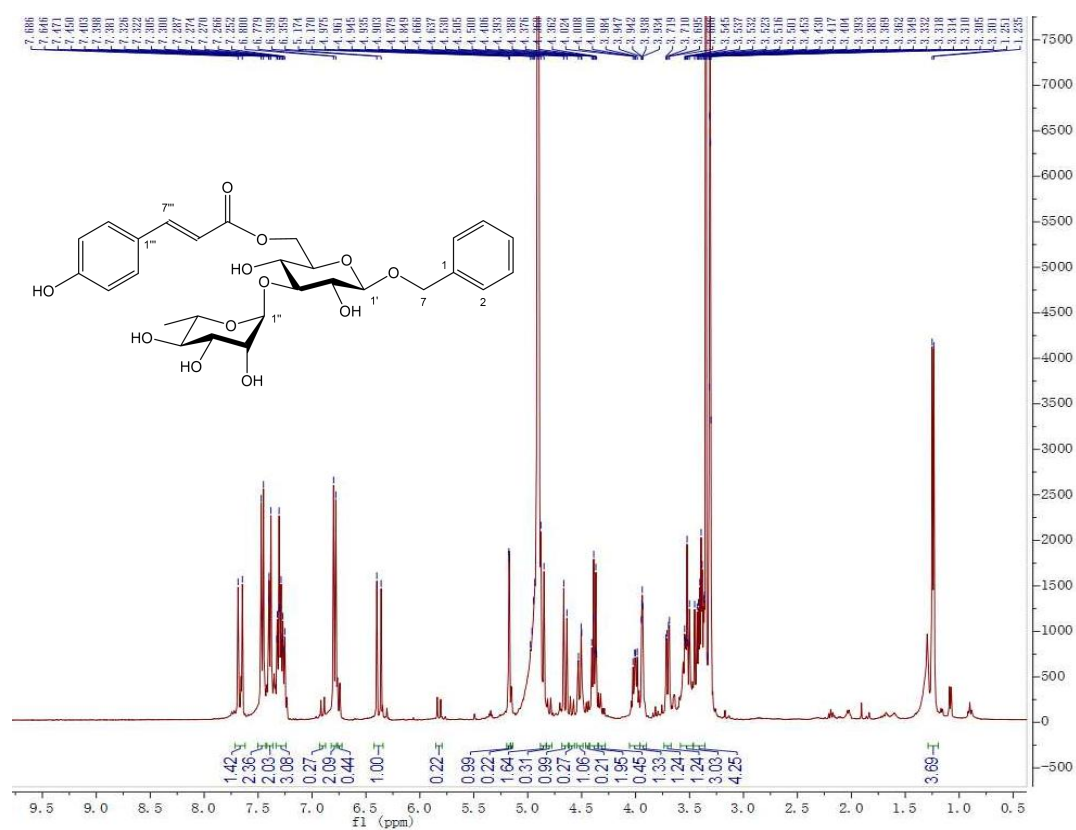


Figure S5-1 <sup>1</sup>H NMR spectrum of compound **5** in CD<sub>3</sub>OD (400 MHz)

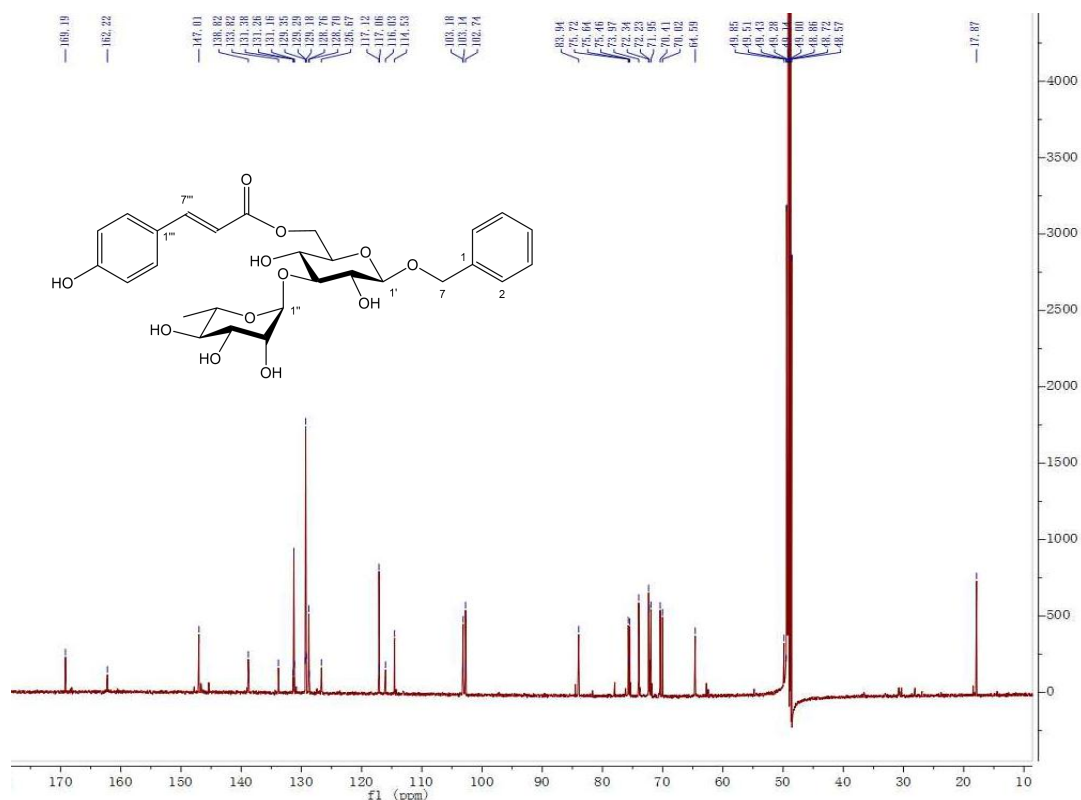


Figure S5-2 <sup>13</sup>C NMR spectrum of compound **5** in CD<sub>3</sub>OD (150 MHz)

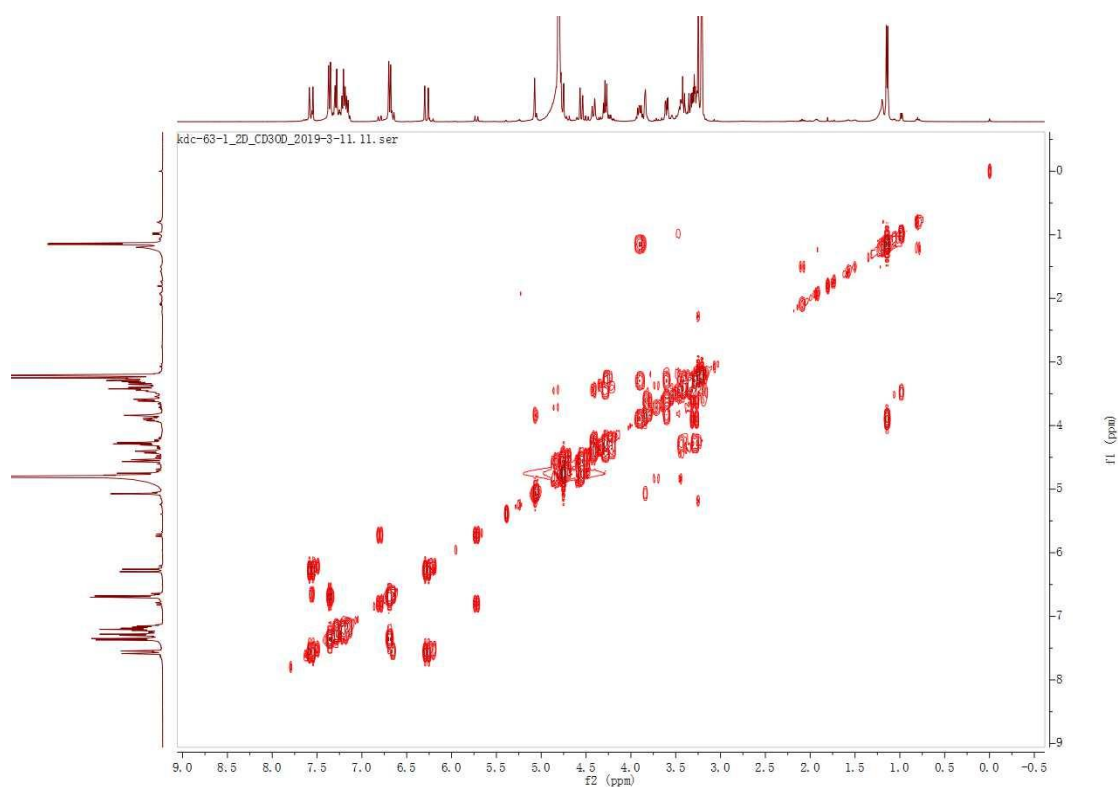


Figure S5-3  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **5** in  $\text{CD}_3\text{OD}$  (400 MHz)

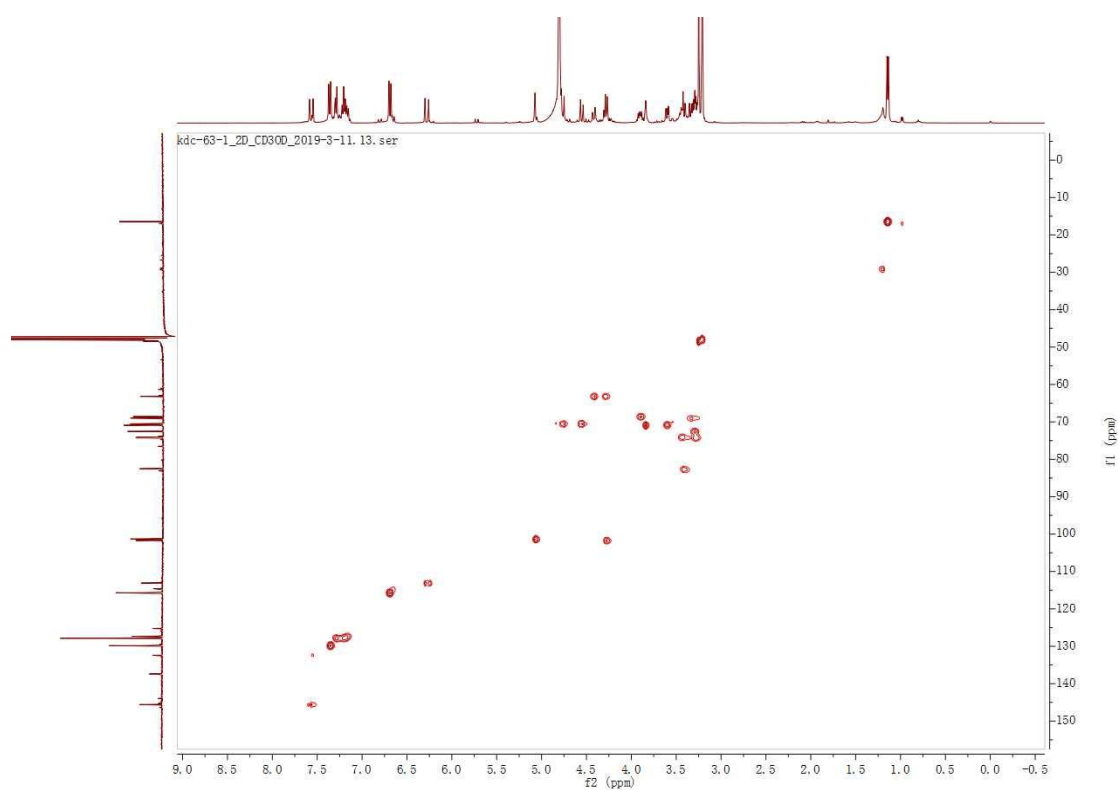


Figure S5-4 HSQC spectrum of compound **5** in  $\text{CD}_3\text{OD}$  (400 MHz)

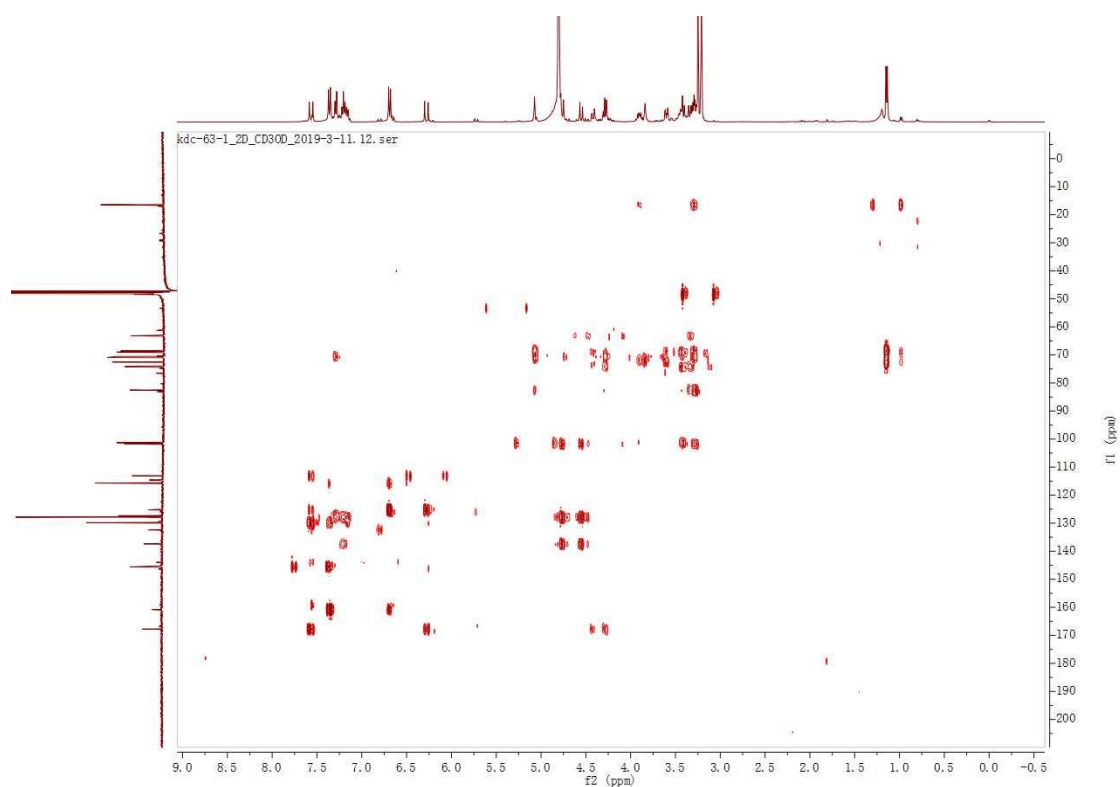


Figure S5-5 HMBC spectrum of compound **5** in CD<sub>3</sub>OD (400 MHz)

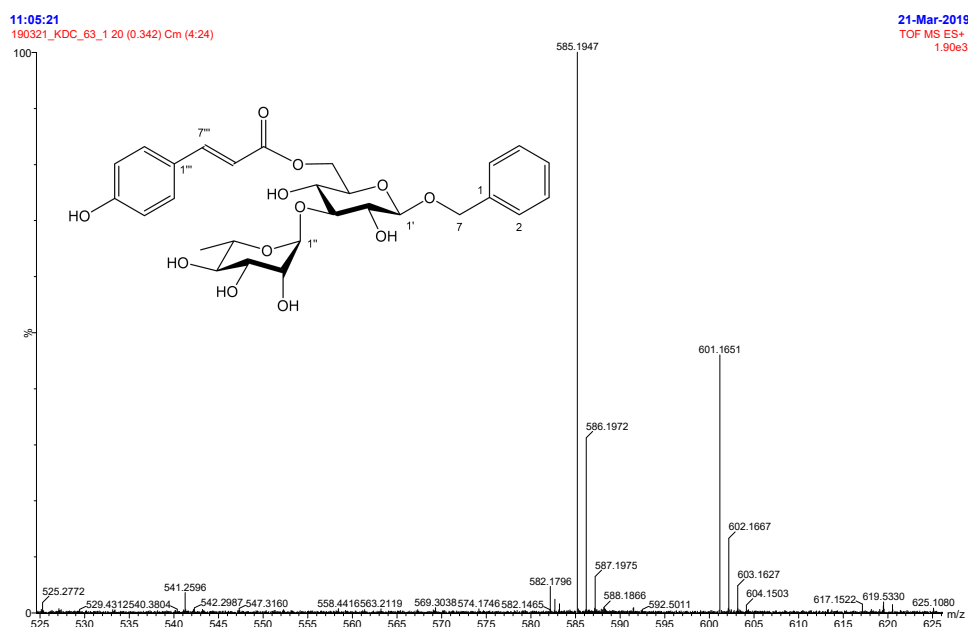


Figure S5-6 HRESIMS spectrum of compound **5**



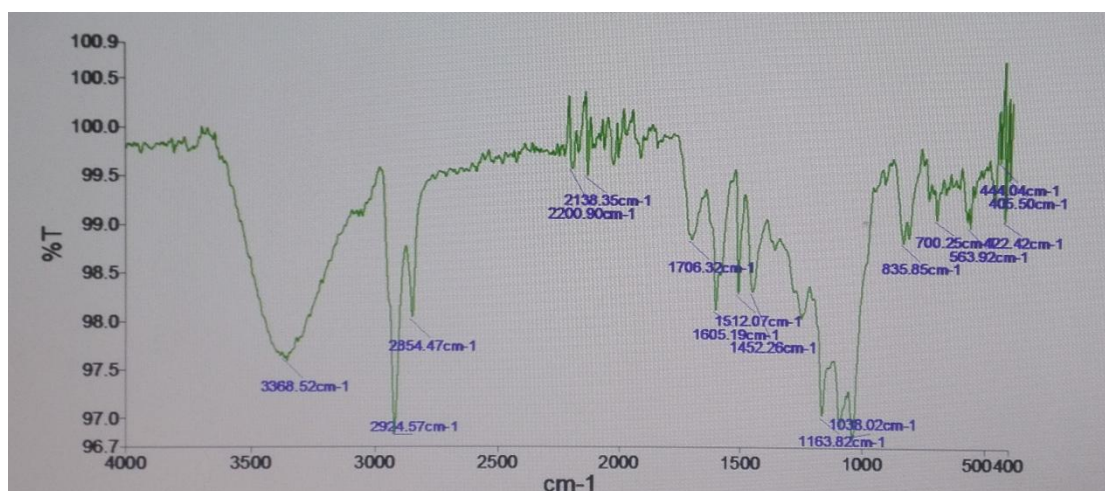


Figure S5-7 IR spectrum of compound **5** (film)

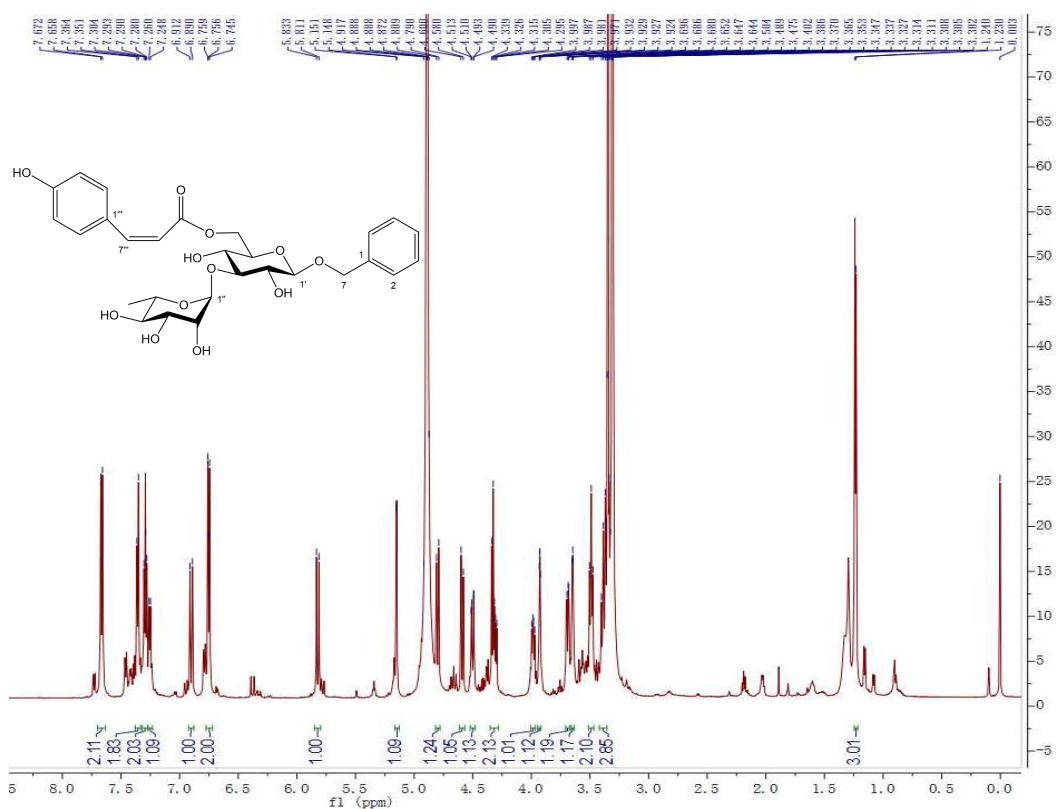


Figure S6-1  $^1\text{H}$  NMR spectrum of compound **6** in  $\text{CD}_3\text{OD}$  (600 MHz)

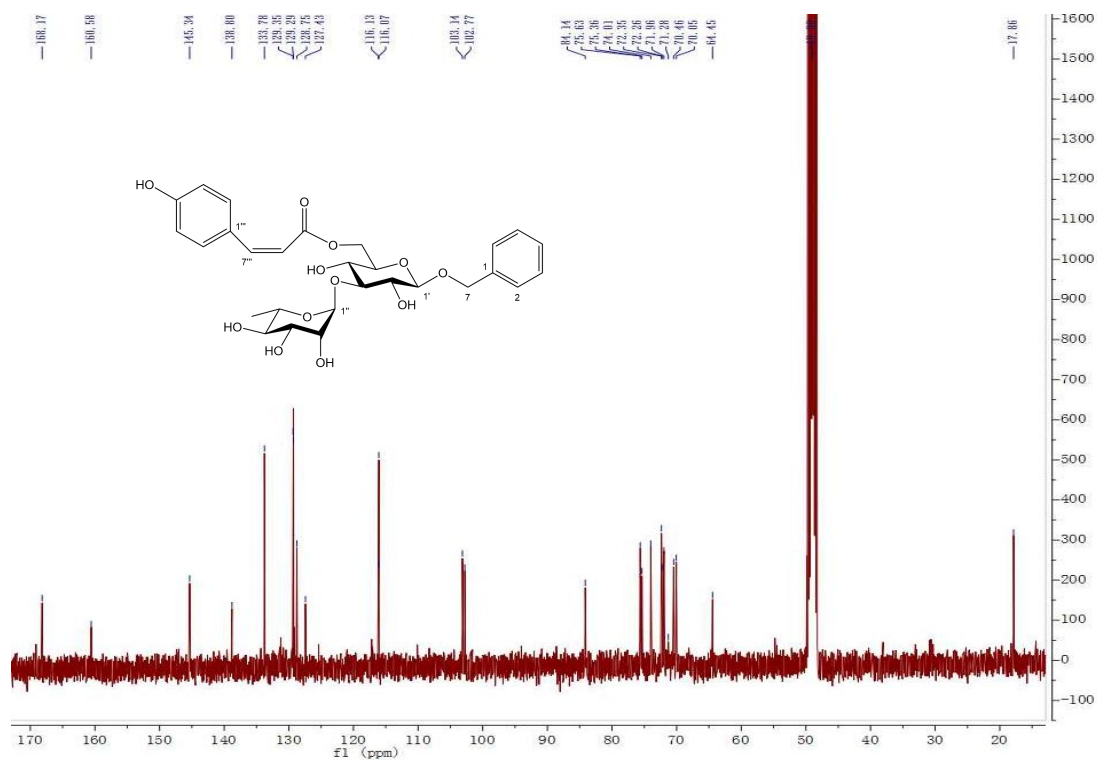


Figure S6-2 <sup>13</sup>C NMR spectrum of compound 6 in CD<sub>3</sub>OD (100 MHz)

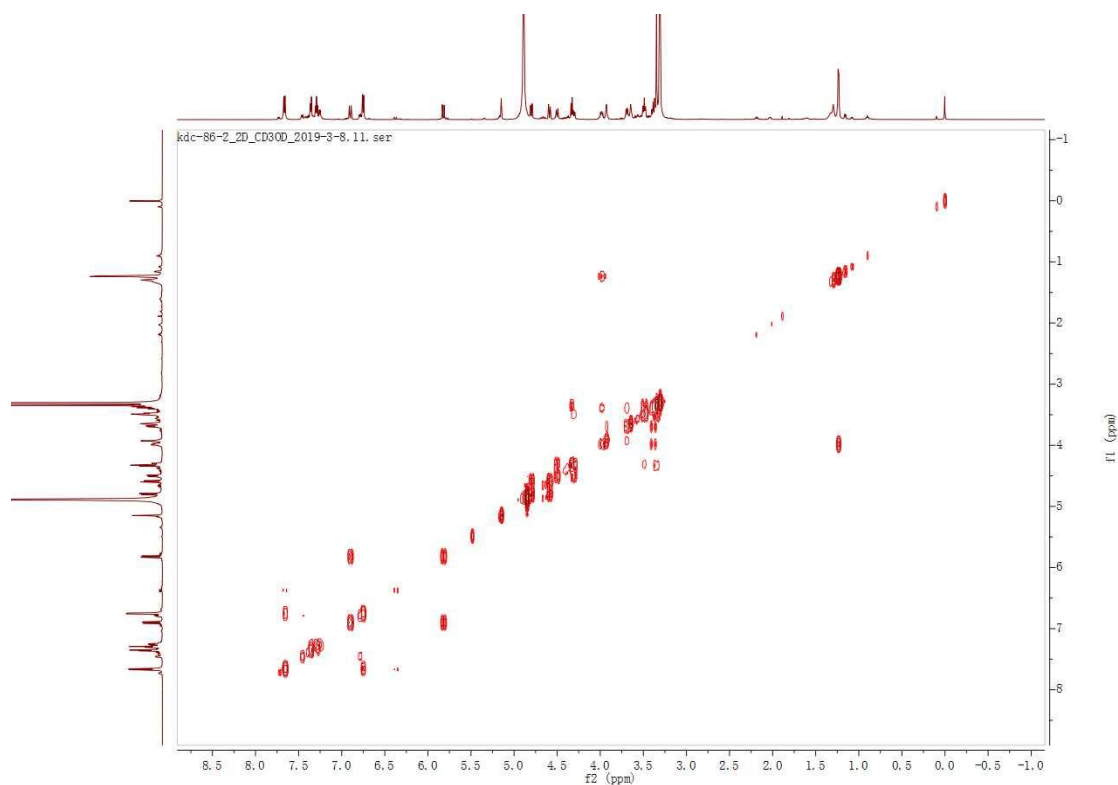


Figure S6-3 <sup>1</sup>H-<sup>1</sup>H NMR spectrum of compound 6 in CD<sub>3</sub>OD (400 MHz)

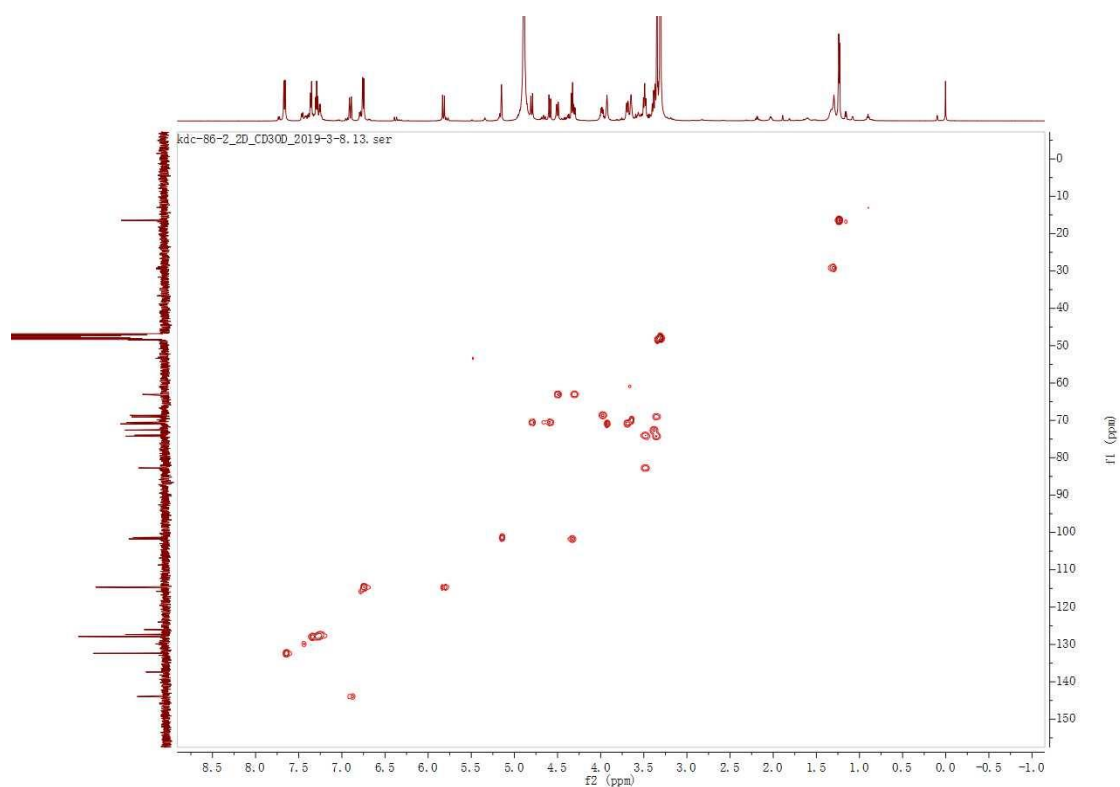


Figure S6-4 HSQC spectrum of compound **6** in CD<sub>3</sub>OD (400 MHz)

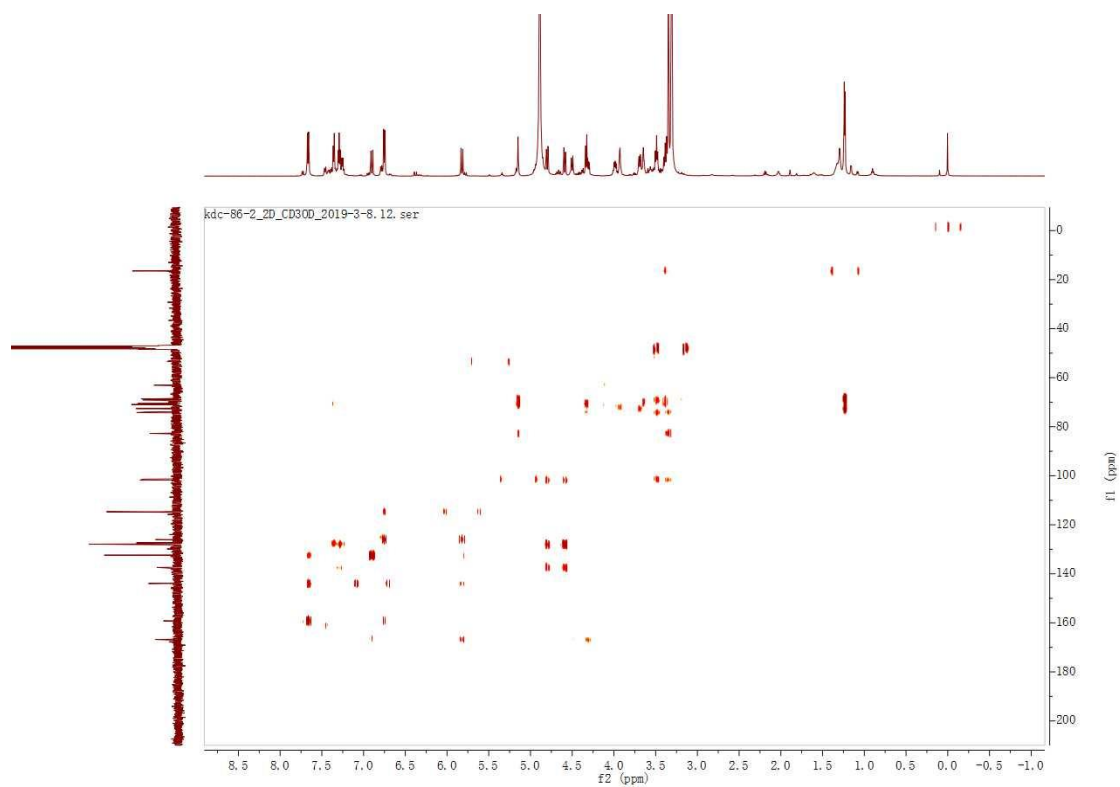


Figure S6-5 HMBC spectrum of compound **6** in CD<sub>3</sub>OD (400 MHz)

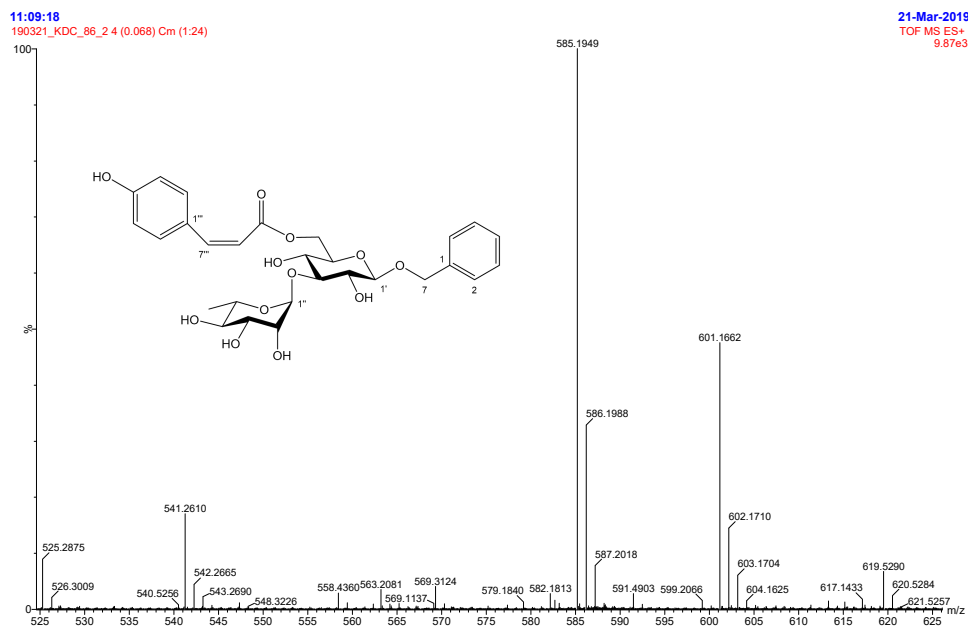


Figure S6-6 HRESIMS spectrum of compound **6**

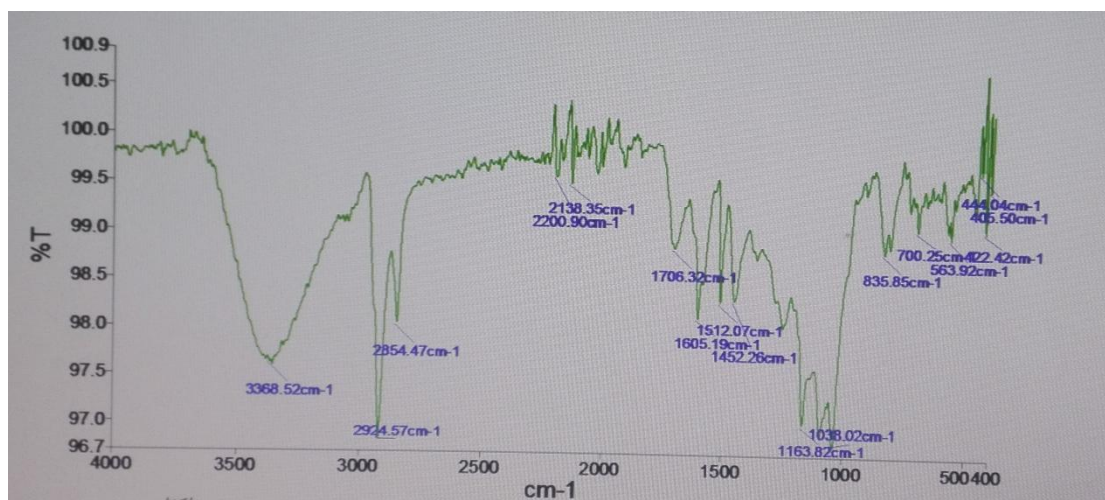


Figure S6-7 IR spectrum of compound **6** (film)

## *S1. Determination of bioactivities*

### **S1.1. Determination of FAS inhibitory activity**

Compounds **1-11** (1.0-1.7 mg) were dissolved in DMSO (100  $\mu$ L) and then diluted with potassium phosphate buffer (0.1 M, pH 7.0). Sample solution (100  $\mu$ L, 20-2000  $\mu$ M, 37  $^{\circ}$ C) and FAS substrates (1.8 mL, 37  $^{\circ}$ C) were mixed in a cuvette, and then FAS solution (100  $\mu$ L, 37  $^{\circ}$ C, isolated from chicken liver and kept in ice-bath before use) was added. The absorbance of reaction mixture was monitored by a UV-vis spectrophotometer at 340 nm in 1 min. The inhibitory effect was calculated by the following equation: FAS inhibition (%) =  $(A_{\text{control}} - A_{\text{sample}})/A_{\text{control}} \times 100\%$ , where  $A_{\text{control}}$  represented the FAS activity in the control group (phosphate buffer instead of sample solution),  $A_{\text{sample}}$  represented the FAS activity in the sample groups. The FAS activity was calculated as  $(A_0 - A_1)/1$  min, in which  $A_0$  was the absorbance of the reaction mixture when the FAS was added, and  $A_1$  was the absorbance of the reaction mixture after reaction 1 min. Orlistat was used as the positive control.

FAS substrates: 0.1 M potassium phosphate buffer (pH 7.0), 1 mM ethylenediaminetetraacetic acid (EDTA), 1 mM dithiothreitol, 3  $\mu$ M acetyl-coenzyme A, 10  $\mu$ M methylmalonyl coenzyme A, 35  $\mu$ M NADPH.

### **S1.2. Determination of $\alpha$ -glucosidase inhibitory activity**

Compounds **1-11** (1.0-1.7 mg) were dissolved in DMSO (100  $\mu$ L) and then diluted with phosphate buffer (0.1 M, pH 6.8). Sample solution (50  $\mu$ L, 0.078-78 nM) and 4-nitrophenyl  $\alpha$ -D-glucopyranoside (pNPG) solution (50  $\mu$ L, 5 mM) were mixed and incubated in a 96-well microplate at 37  $^{\circ}$ C for 5 min.  $\alpha$ -Glucosidase from yeast (50  $\mu$ L, 0.2 U/mL) was added and incubated at 37  $^{\circ}$ C for another 30 min. Finally, 50  $\mu$ L of  $\text{Na}_2\text{CO}_3$  (1M) was added to terminate the reaction. The absorbance of mixture was measured using a microplate reader at a wavelength 405 nm. The background absorbance (phosphate buffer instead of substrate pNPG) of all samples in no more than 20  $\mu$ M at 405 nm was little, therefore the inhibitory effect was calculated by the following equation:  $\alpha$ -glucosidase inhibition (%) =  $(A_{\text{control}} - A_{\text{sample}})/A_{\text{control}} \times 100\%$ , where  $A_{\text{control}}$  represented the absorbance of phosphate buffer control without test samples,  $A_{\text{sample}}$  represented the absorbance of test samples. Acarbose was used as the positive control.

### S1.3. Determination of $\alpha$ -amylase inhibitory activity

Phosphate buffer (20 mM, pH 6.9, containing 6 mM NaCl) was used as the solvent in this assay. Sample solution (50  $\mu$ L, 50-1500  $\mu$ M) and starch solution (50  $\mu$ L, 1%, w/v) were mixed and incubated in a 96-well microplate at 37 °C for 10 min. Then,  $\alpha$ -amylase solution (50  $\mu$ L, 0.2 U/mL) was added and the mixture was incubated at 37 °C for an additional 10 min. The reaction was stopped by addition of 3, 5-dinitrosalicylic acid colour reagent (100  $\mu$ L, 27.6 mM) and the 96-well microplate was immediately heated in 95 °C water bath for 10 min. When the reaction solution cooled to room temperature, all samples were diluted by adding distilled water (50  $\mu$ L), and then their absorbance was measured using a microplate reader at 540 nm. All samples had little background absorbance (phosphate buffer instead of starch solution) at 540 nm, thus the inhibitory activity was calculated as  $(A_{\text{control}} - A_{\text{sample}})/A_{\text{control}} \times 100\%$ , in which  $A_{\text{sample}}$  was the absorbance of the sample and  $A_{\text{control}}$  was the absorbance of the phosphate buffer control without test samples. Acarbose was used as the positive control.

### S1.4. DPPH radical scavenging assay

The DPPH radical scavenging assay was used to evaluate the antioxidant activity of compounds **1-11**. In a 96-well microplate, 100  $\mu$ L of DPPH solution (200  $\mu$ M in ethanol) was added to 100  $\mu$ L sample in ethanol at graded concentrations ranging from 7 to 500  $\mu$ M. The mixture was incubated in the dark at room temperature for 30 min. The absorbance of the reaction mixture was measured at 517 nm using a microplate reader. The DPPH scavenging activity was calculated by the following formula: DPPH scavenging activity (%) =  $(A_{\text{control}} - A_{\text{sample}})/A_{\text{control}} \times 100\%$ , where  $A_{\text{control}}$  was the absorbance of ethanol control without samples,  $A_{\text{sample}}$  was the absorbance of sample. Ascorbic acid was used as the positive control in the experiment.

### S1.5. ABTS radical scavenging assay

The ABTS radical scavenging assay was used also to evaluate the antioxidant activity of compounds **1-11**. The ABTS free radical cation ( $\text{ABTS}^{\bullet+}$ ) was manufactured by reacting ABTS stock solution (7 mM) with potassium persulphate

(2.45 mM) in the dark at room temperature for 12-16 h. The ABTS<sup>•+</sup> solution was diluted with ethanol to an absorbance of 0.7 at 734 nm. Sample solution (100 μL, 2-100 μM in ethanol) was mixed with 150 μL diluted ABTS<sup>•+</sup> solution. After reaction in the dark at room temperature for 20 min, the absorbance of the reaction mixture at 734 nm was recorded. The ABTS<sup>•+</sup> scavenging capability was calculated as  $(A_{\text{control}} - A_{\text{sample}})/A_{\text{control}} \times 100\%$ , in which  $A_{\text{control}}$  was the absorbance of ethanol control without samples,  $A_{\text{sample}}$  was the absorbance of sample. Ascorbic acid was used as the positive control.

## S2. <sup>1</sup>H, <sup>13</sup>C NMR data of **1a**, **4a**, and **7-11**

Compound **1a** (ligurobustoside R): <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ: aglycone 7.03 (2H, d,  $J = 8.4$  Hz, H-2, 6), 6.65 (2H, d,  $J = 8.4$  Hz, H-3, 5), 2.83 (2H, t,  $J = 7.2$  Hz, H-7), 3.72 (1H, m, H-8a), 3.96 (1H, m, H-8b); Man 4.33 (1H, d,  $J = 8.0$  Hz, H-1'), 3.31 (1H, m, H-2'), 3.54 (1H, m, H-3'), 3.38 (1H, m, H-4'), 3.53 (1H, m, H-5'), 4.33 (1H, dd,  $J = 11.6, 6.4$  Hz, H-6a'), 4.50 (1H, dd,  $J = 11.6, 2.0$  Hz, H-6b'); inner Rha 5.18 (1H, d,  $J = 2.0$  Hz, H-1''), 3.89 (1H, m, H-2''), 3.84 (1H, dd,  $J = 9.6, 3.2$  Hz, H-3''), 3.53 (1H, m, H-4''), 4.10 (1H, m, H-5''), 1.28 (3H, d,  $J = 6.0$  Hz, H-6''); outer Rha 5.19 (1H, d,  $J = 1.6$  Hz, H-1'''), 3.94 (1H, m, H-2'''), 3.60 (1H, dd,  $J = 9.6, 3.2$  Hz, H-3'''), 3.39 (1H, m, H-4'''), 3.70 (1H, m, H-5'''), 1.25 (3H, d,  $J = 6.4$  Hz, H-6'''); Cou 7.41 (2H, d,  $J = 8.8$  Hz, H-2''', 6'''), 6.79 (2H, d,  $J = 8.8$  Hz, H-3''', 5'''), 7.62 (1H, d,  $J = 16.0$  Hz, H-7'''), 6.35 (1H, d,  $J = 16.0$  Hz, H-8'''). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ: aglycone 130.6 (C-1), 130.9 (C-2,6), 116.1 (C-3,5), 156.7 (C-4), 36.4 (C-7), 72.3 (C-8); Man 104.2 (C-1'), 75.7 (C-2'), 83.6 (C-3'), 70.4 (C-4'), 75.2 (C-5'), 64.4 (C-6'); inner Rha 103.2 (C-1''), 72.8 (C-2''), 73.0 (C-3''), 81.1 (C-4''), 68.4 (C-5''), 18.6 (C-6''); outer Rha 102.4 (C-1'''), 72.3 (C-2'''), 72.3 (C-3'''), 73.8 (C-4'''), 70.4 (C-5'''), 17.8 (C-6'''); Cou 127.5 (C-1'''), 133.7 (C-2''',6'''), 115.9 (C-3''',5'''), 160.1 (C-4'''), 145.3 (C-7'''), 116.3 (C-8'''), 168.1 (CO).

Compound **4a** (ligurobustoside S): <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ: aglycone 7.43 (2H, br. d,  $J = 7.2$  Hz, H-2, 6), 7.35 (2H, br. t,  $J = 7.2$  Hz, H-3, 5), 7.28 (1H, br. d,  $J = 7.2$  Hz, H-4), 4.69 (1H, d,  $J = 11.6$  Hz, H-7a), 4.96 (1H, d,  $J = 11.6$  Hz, H-7b); Man 4.45 (1H, d,  $J = 8.0$  Hz, H-1'), 3.46 (1H, dd,  $J = 9.2, 8.0$  Hz, H-2'), 3.82 (1H, t,  $J$



= 9.2 Hz, H-3'), 4.94 (1H, m, H-4'), 3.54 (1H, m, H-5'), 3.56 (1H, m, H-6a'), 3.64 (1H, m, H-6b'); Rha 5.18 (1H, d,  $J = 1.6$  Hz, H-1''), 3.92 (1H, dd,  $J = 3.2, 1.6$  Hz, H-2''), 3.58 (1H, m, H-3''), 3.29 (1H, t,  $J = 9.6$  Hz, H-4''), 3.56 (1H, m, H-5''), 1.08 (3H, d,  $J = 6.0$  Hz, H-6''); Cou 7.47 (2H, d,  $J = 8.4$  Hz, H-2''', 6'''), 6.81 (2H, d,  $J = 8.4$  Hz, H-3''', 5'''), 7.67 (1H, d,  $J = 16.0$  Hz, H-7'''), 6.35 (1H, d,  $J = 16.0$  Hz, H-8''').  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : aglycone 139.0 (C-1), 129.3 (C-2,6), 129.1 (C-3,5), 128.7 (C-4), 72.0 (C-7); Man 103.2 (C-1'), 76.2 (C-2'), 81.7 (C-3'), 70.6 (C-4'), 76.1 (C-5'), 62.4 (C-6'); Rha 103.1 (C-1''), 72.3 (C-2''), 72.0 (C-3''), 73.8 (C-4''), 70.4 (C-5''), 18.4 (C-6''); Cou 127.1 (C-1'''), 131.3 (C-2''', 6'''), 116.8 (C-3''', 5'''), 161.4 (C-4'''), 147.6 (C-7'''), 114.8 (C-8'''), 168.3 (CO).

Compound **7** (ligupurpurosides B): white amorphous powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : aglycone 7.07 (2H, d,  $J = 8.4$  Hz, H-2, 6), 6.71 (2H, d,  $J = 8.4$  Hz, H-3, 5), 2.84 (2H, t,  $J = 7.6$  Hz, H-7), 3.90 (1H, m, H-8a), 4.06 (1H, m, H-8b); Glc 4.38 (1H, d,  $J = 7.6$  Hz, H-1'), 3.37 (1H, m, H-2'), 3.77 (1H, t,  $J = 9.6$  Hz, H-3'), 4.91 (1H, t,  $J = 9.6$  Hz, H-4'), 3.46 (1H, m, H-5'), 3.50 (1H, m, H-6a'), 3.57 (1H, m, H-6b'); inner Rha 5.19 (1H, d,  $J = 2.0$  Hz, H-1''), 3.86 (1H, dd,  $J = 3.2, 2.0$  Hz, H-2''), 3.68 (1H, dd,  $J = 9.6, 3.2$  Hz, H-3''), 3.39 (1H, m, H-4''), 3.59 (1H, m, H-5''), 1.09 (3H, d,  $J = 6.0$  Hz, H-6''); outer Rha 5.04 (1H, d,  $J = 2.0$  Hz, H-1'''), 3.90 (1H, dd,  $J = 3.2, 2.0$  Hz, H-2'''), 3.51 (1H, m, H-3'''), 3.32 (1H, m, H-4'''), 3.46 (1H, m, H-5'''), 1.04 (3H, d,  $J = 6.0$  Hz, H-6'''); Cou 7.48 (2H, d,  $J = 8.4$  Hz, H-2''', 6'''), 6.83 (2H, d,  $J = 8.4$  Hz, H-3''', 5'''), 7.66 (1H, d,  $J = 16.0$  Hz, H-7'''), 6.33 (1H, d,  $J = 16.0$  Hz, H-8''').  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : aglycone 130.7 (C-1), 130.9 (C-2,6), 116.2 (C-3,5), 156.8 (C-4), 36.3 (C-7), 72.4 (C-8); Glc 104.2 (C-1'), 76.2 (C-2'), 81.6 (C-3'), 70.5 (C-4'), 75.8 (C-5'), 62.4 (C-6'); inner Rha 102.7 (C-1''), 72.7 (C-2''), 72.9 (C-3''), 81.6 (C-4''), 68.9 (C-5''), 19.2 (C-6''); outer Rha 103.5 (C-1'''), 72.3 (C-2'''), 72.3 (C-3'''), 73.8 (C-4'''), 70.3 (C-5'''), 17.7 (C-6'''); Cou 127.0 (C-1'''), 131.4 (C-2''', 6'''), 117.1 (C-3''', 5'''), 161.3 (C-4'''), 147.6 (C-7'''), 114.7 (C-8'''), 168.1 (CO).

Compound **8** (*cis*-ligupurpurosides B): white amorphous powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : aglycone 7.07 (2H, d,  $J = 8.4$  Hz, H-2, 6), 6.70 (2H, d,  $J = 8.4$  Hz, H-3, 5), 2.84 (2H, t,  $J = 7.6$  Hz, H-7), 3.70 (1H, m, H-8a), 4.03 (1H, m, H-8b); Glc 4.36 (1H, d,  $J = 8.0$  Hz, H-1'), 3.37 (1H, m, H-2'), 3.77 (1H, t,  $J = 9.6$  Hz, H-3'), 4.88 (1H, t,  $J = 9.6$  Hz, H-4'), 3.46 (1H, m, H-5'), 3.50 (1H, m, H-6a'), 3.57 (1H, m, H-6b'); inner Rha 5.29 (1H, d,  $J = 1.6$  Hz, H-1''), 3.82 (1H, dd,  $J = 3.2, 1.6$  Hz, H-2''), 3.68 (1H, dd,  $J = 9.6, 3.2$  Hz, H-3''), 3.45 (1H, m, H-4''), 3.60 (1H, m, H-5''), 1.22 (3H, d,  $J = 6.0$  Hz, H-6''); outer Rha 5.13 (1H, d,  $J = 1.6$  Hz, H-1'''), 3.82 (1H, dd,  $J = 3.2, 1.6$  Hz, H-2'''), 3.51 (1H, m, H-3'''), 3.34 (1H, m, H-4'''),

3.46 (1H, m, H-5'''), 1.21 (3H, d,  $J = 6.4$  Hz, H-6'''); Cou 7.72 (2H, d,  $J = 8.8$  Hz, H-2''', 6'''), 6.77 (2H, d,  $J = 8.8$  Hz, H-3''', 5'''), 6.99 (1H, d,  $J = 12.8$  Hz, H-7'''), 5.76 (1H, d,  $J = 12.8$  Hz, H-8''').  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : aglycone 130.7 (C-1), 130.9 (C-2,6), 116.1 (C-3,5), 156.8 (C-4), 36.3 (C-7), 72.4 (C-8); Glc 104.2 (C-1'), 76.4 (C-2'), 79.6 (C-3'), 70.4 (C-4'), 75.9 (C-5'), 62.4 (C-6'); inner Rha 101.9 (C-1''), 72.9 (C-2''), 73.0 (C-3''), 80.6 (C-4''), 68.6 (C-5''), 18.9 (C-6''); outer Rha 103.2 (C-1'''), 72.3 (C-2'''), 72.3 (C-3'''), 73.9 (C-4'''), 70.3 (C-5'''), 17.8 (C-6'''); Cou 127.5 (C-1'''), 134.3 (C-2''',6'''), 115.9 (C-3''',5'''), 160.3 (C-4'''), 147.4 (C-7'''), 115.8 (C-8'''), 166.9 (CO).

Compound **9** (ligurobustoside N): yellow amorphous powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : aglycone 7.07 (2H, d,  $J = 8.4$  Hz, H-2, 6), 6.70 (2H, d,  $J = 8.4$  Hz, H-3, 5), 2.84 (2H, dt,  $J = 7.2, 2.0$  Hz, H-7), 3.68 (1H, m, H-8a), 3.90 (1H, m, H-8b); Glc 4.38 (1H, d,  $J = 8.0$  Hz, H-1'), 3.37 (1H, m, H-2'), 3.77 (1H, t,  $J = 9.6$  Hz, H-3'), 4.93 (1H, t,  $J = 9.6$  Hz, H-4'), 3.46 (1H, m, H-5'), 3.50 (1H, m, H-6a'), 3.57 (1H, m, H-6b'); inner Rha 5.20 (1H, d,  $J = 2.0$  Hz, H-1''), 3.86 (1H, dd,  $J = 3.2, 2.0$  Hz, H-2''), 3.68 (1H, dd,  $J = 9.6, 3.2$  Hz, H-3''), 3.39 (1H, m, H-4''), 3.59 (1H, m, H-5''), 1.09 (3H, d,  $J = 6.4$  Hz, H-6''); outer Rha 5.05 (1H, d,  $J = 1.6$  Hz, H-1'''), 3.90 (1H, dd,  $J = 3.2, 1.6$  Hz, H-2'''), 3.51 (1H, m, H-3'''), 3.32 (1H, m, H-4'''), 3.46 (1H, m, H-5'''), 1.06 (3H, d,  $J = 6.4$  Hz, H-6'''); Caff 7.07 (1H, d,  $J = 2.0$  Hz, H-2'''), 6.79 (1H, d,  $J = 8.0$  Hz, H-5'''), 6.97 (1H, dd,  $J = 8.0, 2.0$  Hz, H-6'''), 7.60 (1H, d,  $J = 16.0$  Hz, H-7'''), 6.26 (1H, d,  $J = 16.0$  Hz, H-8''').  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : aglycone 130.7 (C-1), 130.9 (C-2,6), 116.1 (C-3,5), 156.8 (C-4), 36.4 (C-7), 72.3 (C-8); Glc 104.2 (C-1'), 76.2 (C-2'), 81.5 (C-3'), 70.3 (C-4'), 76.0 (C-5'), 62.3 (C-6'); inner Rha 103.4 (C-1''), 73.8 (C-2''), 70.4 (C-3''), 81.5 (C-4''), 68.9 (C-5''), 19.2 (C-6''); outer Rha 102.7 (C-1'''), 72.4 (C-2'''), 72.3 (C-3'''), 73.8 (C-4'''), 68.9 (C-5'''), 17.7 (C-6'''); Caff 127.5 (C-1'''), 115.3 (C-2'''), 146.8 (C-3'''), 149.9 (C-4'''), 116.7 (C-5'''), 123.4 (C-6'''), 148.0 (C-7'''), 114.7 (C-8'''), 168.1 (CO).

Compound **10** (osmanthuside D): white amorphous powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : aglycone 7.07 (2H, d,  $J = 8.4$  Hz, H-2, 6), 6.70 (2H, d,  $J = 8.4$  Hz, H-3, 5), 2.85 (2H, dt,  $J = 7.6, 2.0$  Hz, H-7), 3.75 (1H, m, H-8a), 4.05 (1H, m, H-8b); Glc 4.35 (1H, d,  $J = 8.0$  Hz, H-1'), 3.52 (1H, m, H-2'), 3.82 (1H, t,  $J = 9.2$  Hz, H-3'), 4.89 (1H, m, H-4'), 3.58 (1H, m, H-5'), 3.56 (1H, m, H-6a'), 3.64 (1H, m, H-6b'); Rha 5.16 (1H, d,  $J = 1.6$  Hz, H-1''), 3.92 (1H, dd,  $J = 3.2, 1.6$  Hz, H-2''), 3.60 (1H, m, H-3''), 3.29 (1H, m, H-4''), 3.58 (1H, m, H-5''), 1.16 (3H, d,  $J = 6.4$  Hz, H-6''); Cou 7.72 (2H, d,  $J = 8.8$  Hz, H-2''', 6'''), 6.76 (2H, d,  $J = 8.8$  Hz, H-3''', 5'''), 6.95 (1H, d,  $J = 12.8$  Hz, H-7'''), 5.79 (1H, d,  $J = 12.8$  Hz, H-8''').  $^{13}\text{C}$  NMR

(100 MHz, CD<sub>3</sub>OD)  $\delta$ : aglycone 130.7 (C-1), 131.3 (C-2, 6), 116.1 (C-3, 5), 156.8 (C-4), 36.4 (C-7), 72.1 (C-8); Glc 104.2 (C-1'), 76.0 (C-2'), 81.8 (C-3'), 70.5 (C-4'), 76.1 (C-5'), 62.4 (C-6'); Rha 103.1 (C-1''), 72.3 (C-2''), 72.2 (C-3''), 73.9 (C-4''), 70.4 (C-5''), 18.2 (C-6''); Cou 127.5 (C-1'''), 134.3 (C-2''', 6'''), 115.8 (C-3''', 5'''), 160.4 (C-4'''), 147.3 (C-7'''), 115.9 (C-8'''), 166.9 (CO).

Compound **11** [(*Z*)-osmanthuside B<sub>6</sub>]: white amorphous powder. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD)  $\delta$ : aglycone 7.02 (2H, d, *J* = 8.4 Hz, H-2, 6), 6.67 (2H, d, *J* = 8.4 Hz, H-3, 5), 2.83 (2H, t, *J* = 7.8 Hz, H-7), 3.70 (1H, m, H-8a), 3.93 (1H, m, H-8b); Glc 4.28 (1H, d, *J* = 7.8 Hz, H-1'), 3.33 (1H, m, H-2'), 3.53 (1H, t, *J* = 9.0 Hz, H-3'), 3.40 (1H, m, H-4'), 3.55 (1H, m, H-5'), 4.31 (1H, dd, *J* = 12.0, 6.0 Hz, H-6a'), 4.48 (1H, dd, *J* = 12.0, 2.4 Hz, H-6b'); Rha 5.16 (1H, d, *J* = 1.8 Hz, H-1''), 3.94 (1H, m, H-2''), 3.70 (1H, m, H-3''), 3.40 (1H, t, *J* = 9.6 Hz, H-4''), 4.00 (1H, dd, *J* = 9.6, 6.6 Hz, H-5''), 1.24 (3H, d, *J* = 6.6 Hz, H-6''); Cou 7.63 (2H, d, *J* = 8.4 Hz, H-2''', 6'''), 6.74 (2H, d, *J* = 8.4 Hz, H-3''', 5'''), 6.87 (1H, d, *J* = 12.6 Hz, H-7'''), 5.79 (1H, d, *J* = 12.6 Hz, H-8'''). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$ : aglycone 130.6 (C-1), 131.2 (C-2, 6), 116.3 (C-3, 5), 156.8 (C-4), 36.4 (C-7), 72.3 (C-8); Glc 104.3 (C-1'), 75.6 (C-2'), 83.9 (C-3'), 70.4 (C-4'), 75.4 (C-5'), 64.4 (C-6'); Rha 102.7 (C-1''), 72.3 (C-2''), 72.2 (C-3''), 74.0 (C-4''), 70.0 (C-5''), 17.9 (C-6''); Cou 127.6 (C-1'''), 133.7 (C-2''', 6'''), 116.1 (C-3''', 5'''), 160.1 (C-4'''), 145.3 (C-7'''), 115.9 (C-8'''), 168.1 (CO).