SUPPLEMENTARY MATERIAL

Benzophenone glycosides from the pericarps of *Aquilaria yunnanensis* S. C. Huang

Hui Sun, Yun-Feng Zhang, Hui-Xia Huo, Peng-Wei Guan, Chao-Chao Wang, Hui-Na Yao, Yun-Fang Zhao, Peng-Fei Tu and Jun Li*

Modern Research Center for Traditional Chinese Medicine, School of Chinese Materia Medica, Beijing University of Chinese Medicine, Beijing 100029, People'Republic of China

CONTACT
Jun Li, drlj666@163.com

ABSTRACT

Two new benzophenone glycosides, aquilarisides A (**1**) and B (**2**), together with six known analogues (**3**−**8**) were isolated from the pericarps of *Aquilaria yunnanensis* S. C. Huang. Their structures were elucidated on the basis of 1D and 2D NMR and mass spectroscopic analyses, and the absolute configuration of compound **1** was determined by experimental and calculated electronic circular dichroism (ECD) spectra. Anti-inflammatory activities of all compounds **1**–**8** were evaluated for their inhibitory activities against lipopolysaccharide (LPS)-stimulated induced nitric oxide (NO) production in RAW 264.7 cells using the Griess assay. Compound **2** indicated a weak inhibition of NO production.

KEYWORDS

Aquilaria yunnanensis; aquilarisides A and B; benzophenone glycoside; anti-inflammatory; nitric oxide; Griess assay

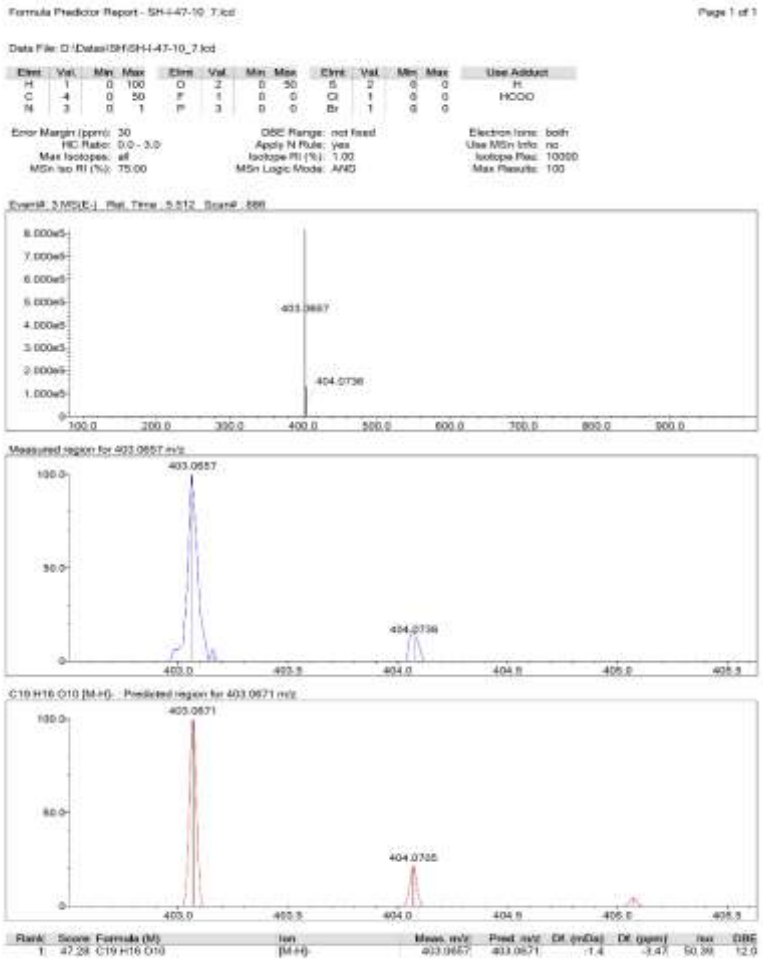

Figure S1 HRESIMS spectrum of compound **1**

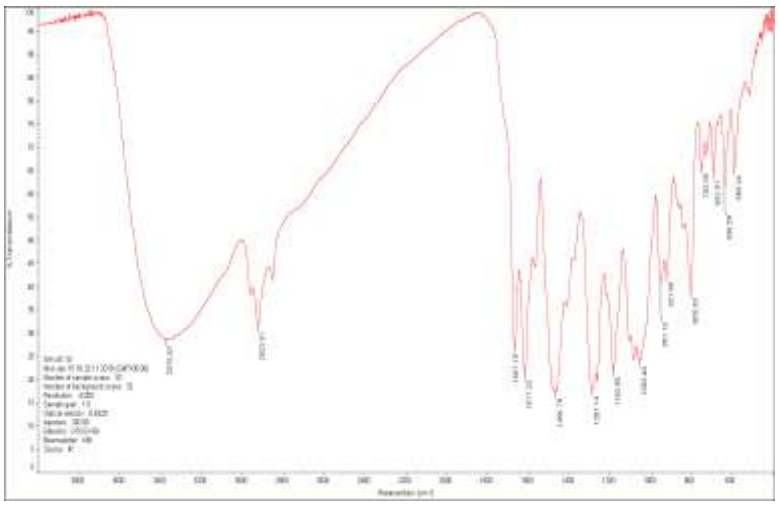

Figure S2 IR spectrum of compound **1**

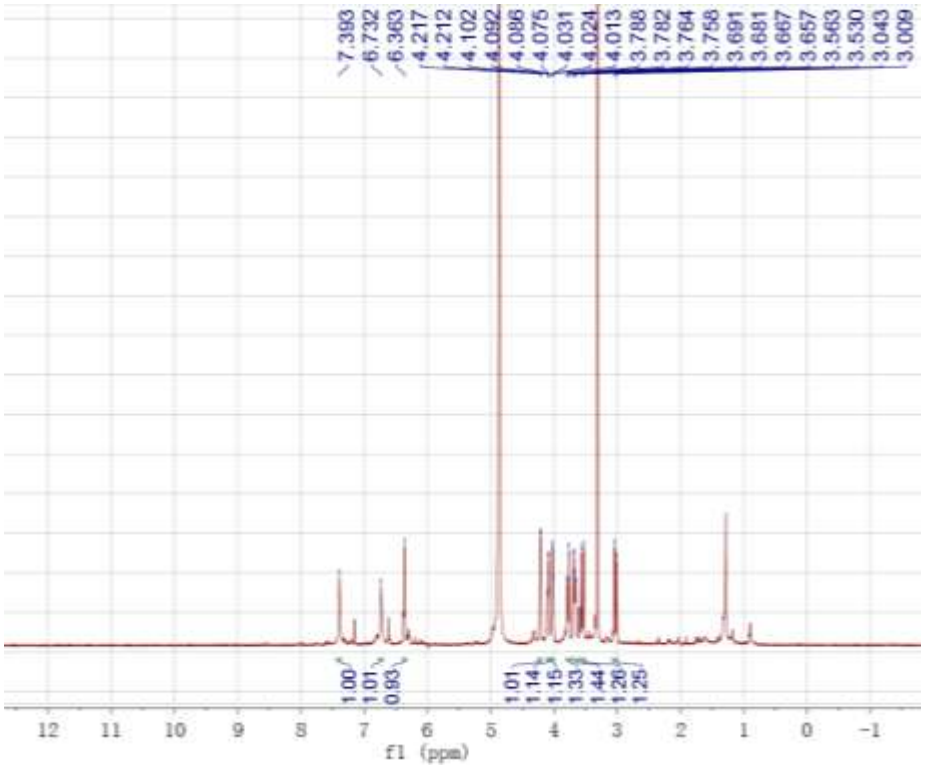

Figure S3 ^{1}H NMR spectrum of compound **1** (500 MHz, methanol-d_4)

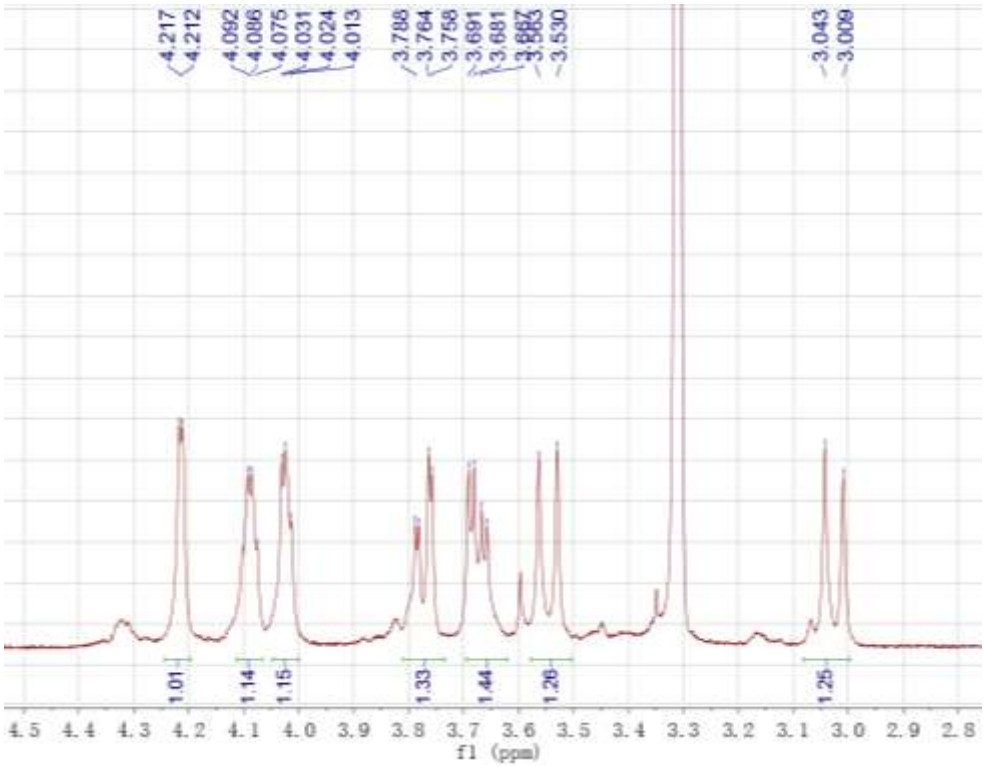

Figure S4 Enlarged (δ 2.8-4.5) ^{1}H NMR spectrum of compound **1** (500 MHz, methanol-d_4)

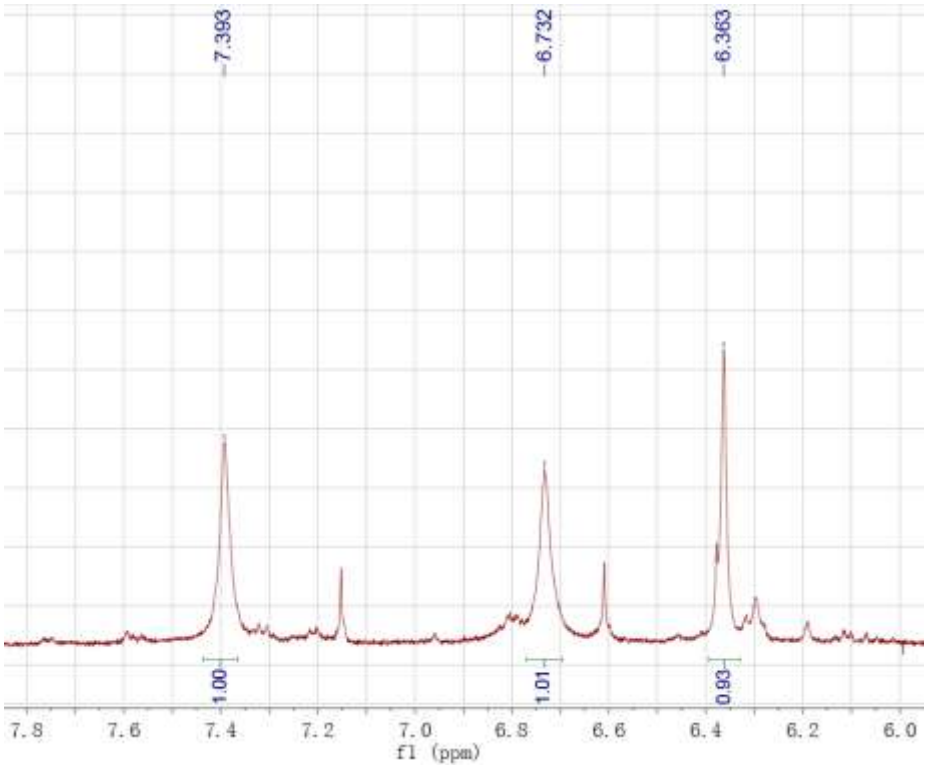

Figure S5 Enlarged (δ 6.0-7.8) ^{1}H NMR spectrum of compound **1** (500 MHz, methanol-d_4)

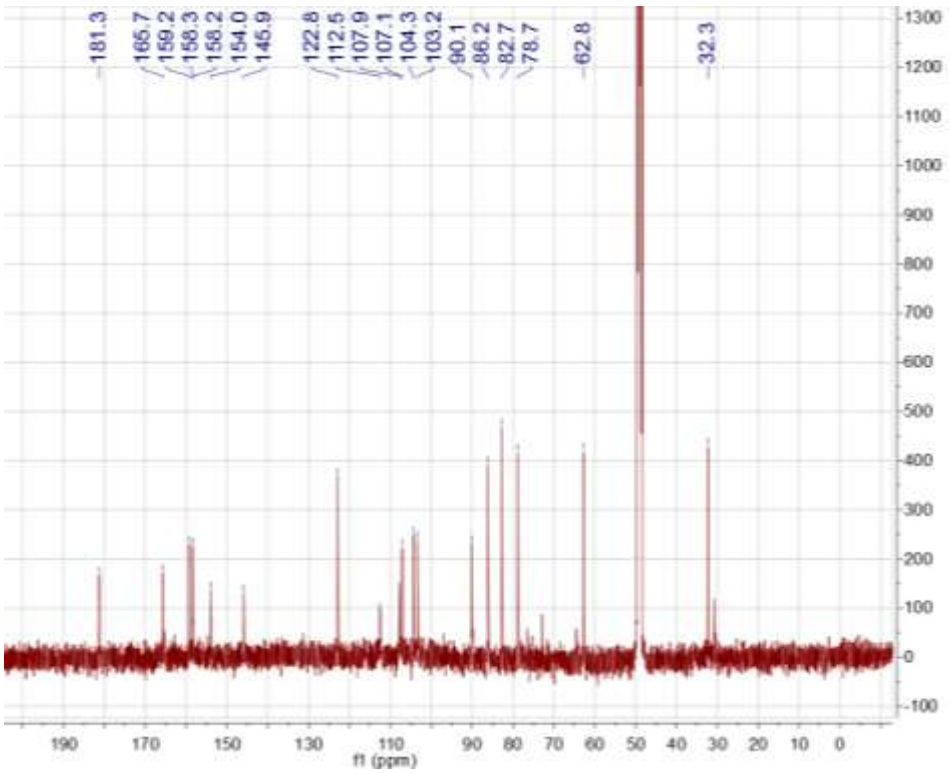

Figure S6 ^{13}C NMR spectrum of compound **1** (125 MHz, methanol-d_4)

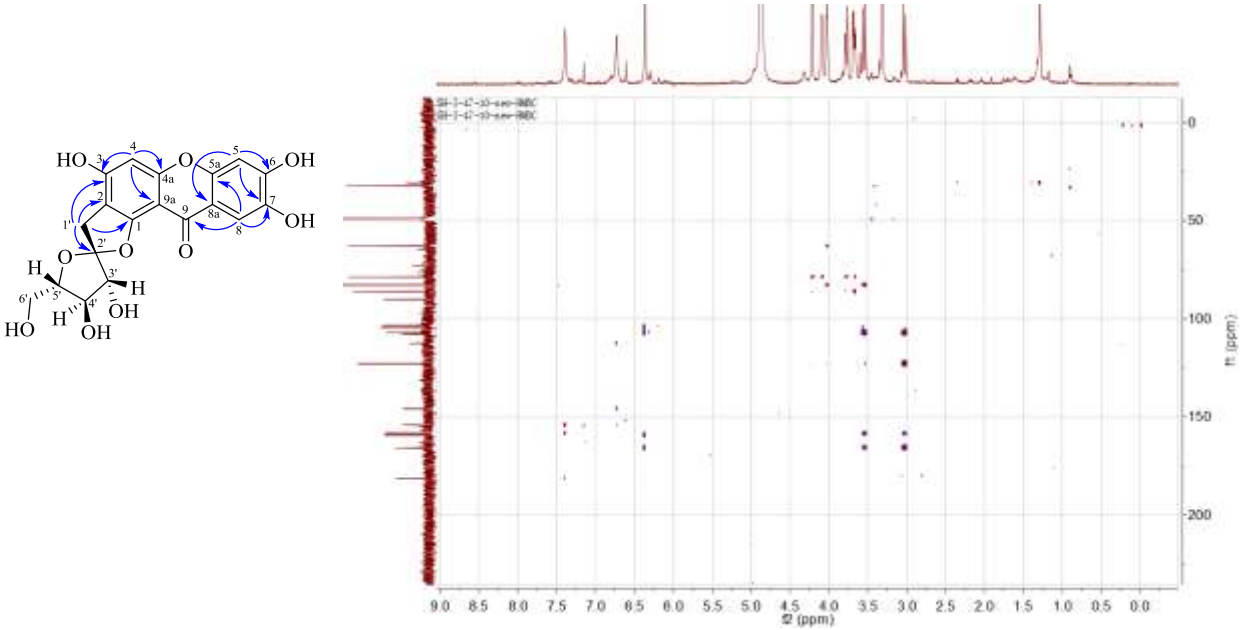

Figure S7 HMBC spectrum of compound **1** (500 MHz, methanol-d_4)

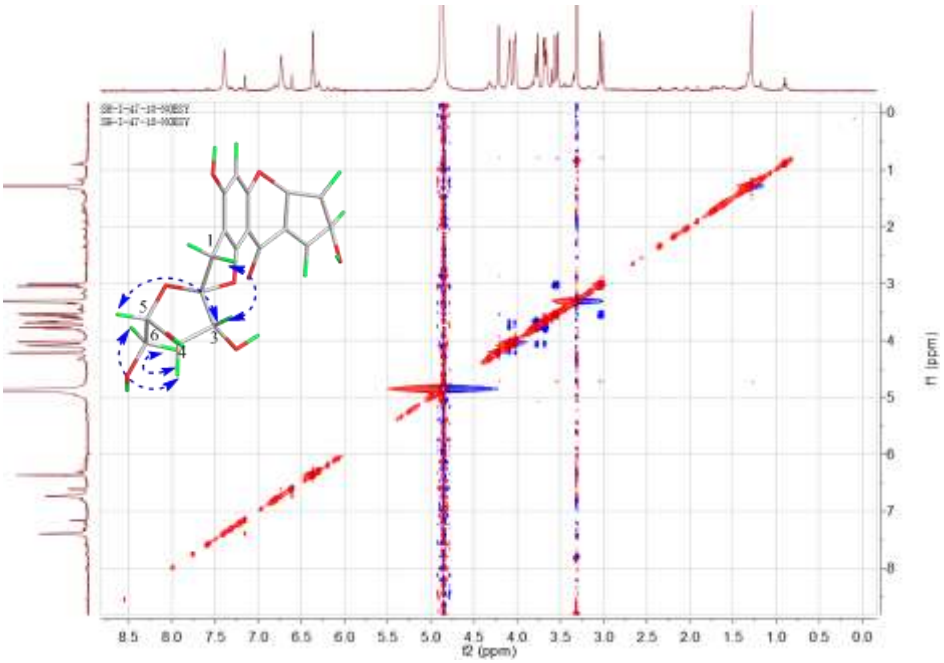

Figure S8 NOESY spectrum of compound **1** (500 MHz, methanol-d_4)

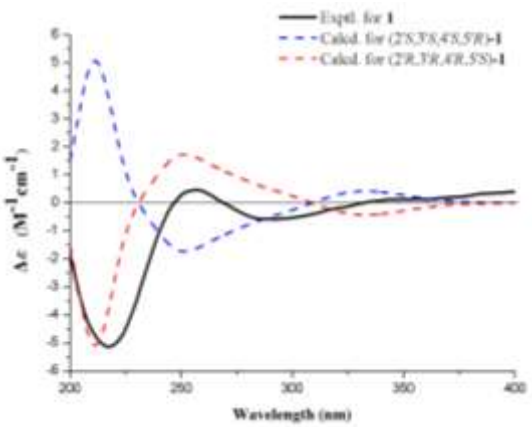

Figure S9 Experimental, calculated ECD spectra (in MeOH) of compound **1**

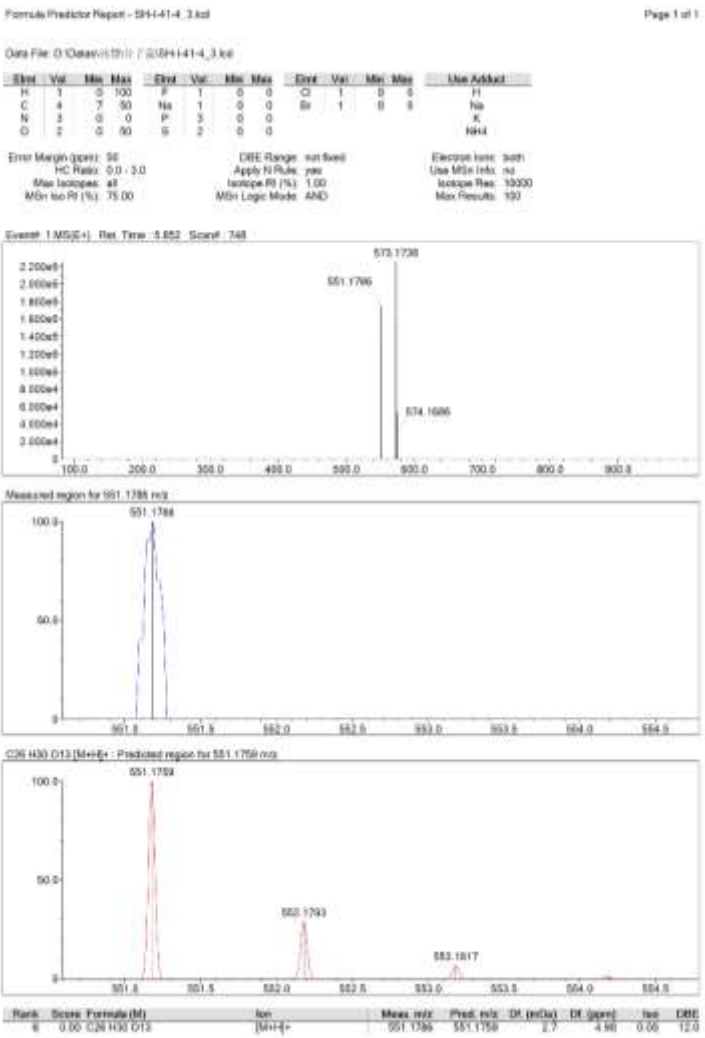

Figure S10 HRESIMS spectrum of compound **2**

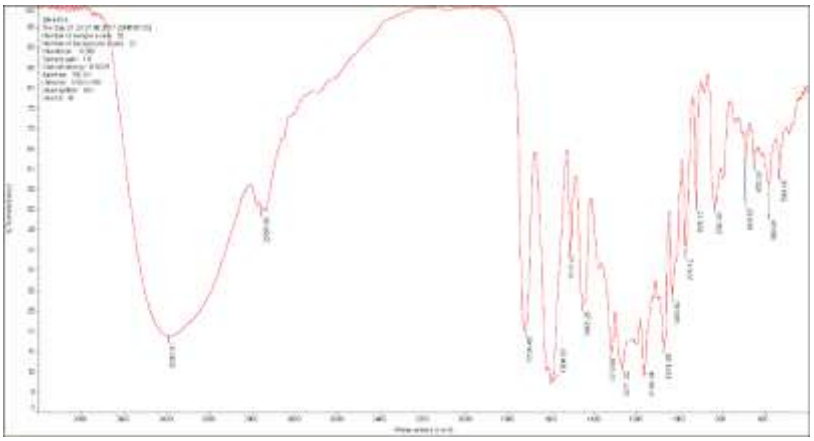

Figure S11 IR spectrum of compound **2**

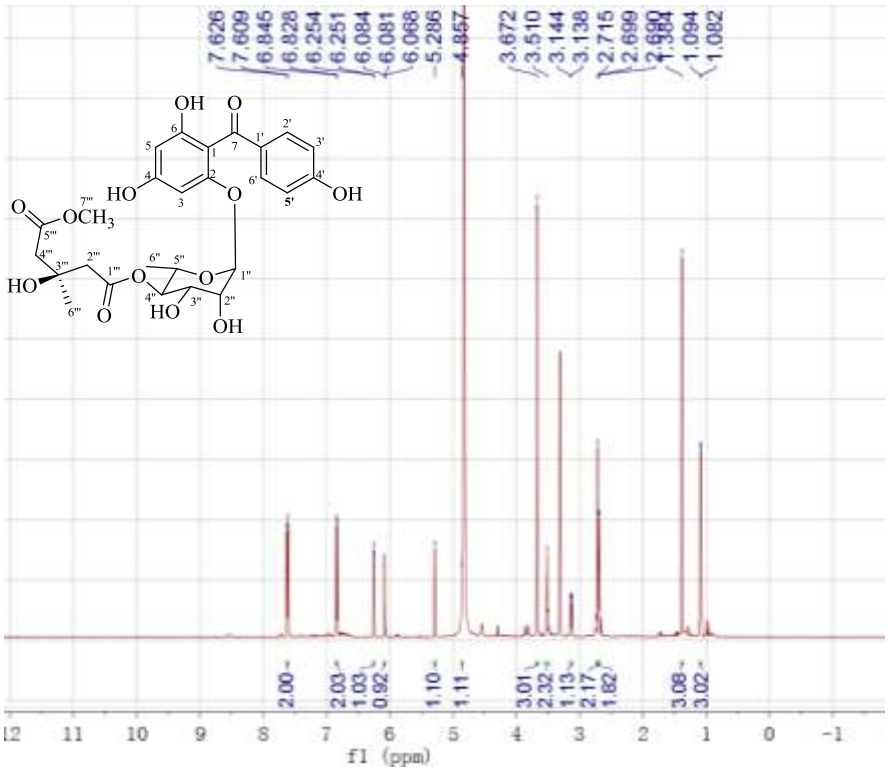

Figure S12 ^{1}H NMR spectrum of compound **2** (500 MHz, methanol-d_4)

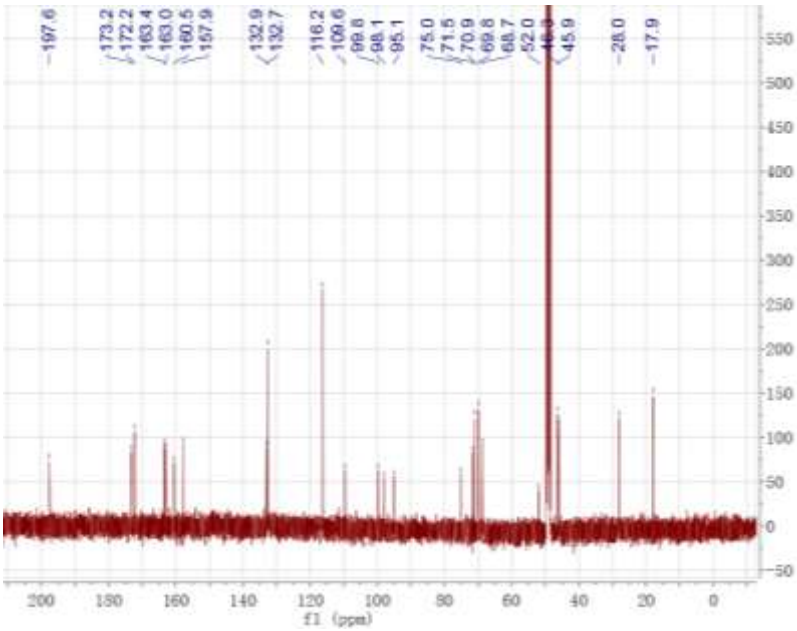

Figure S13 ^{13}C NMR spectrum of compound **2** (125 MHz, methanol-d_4)

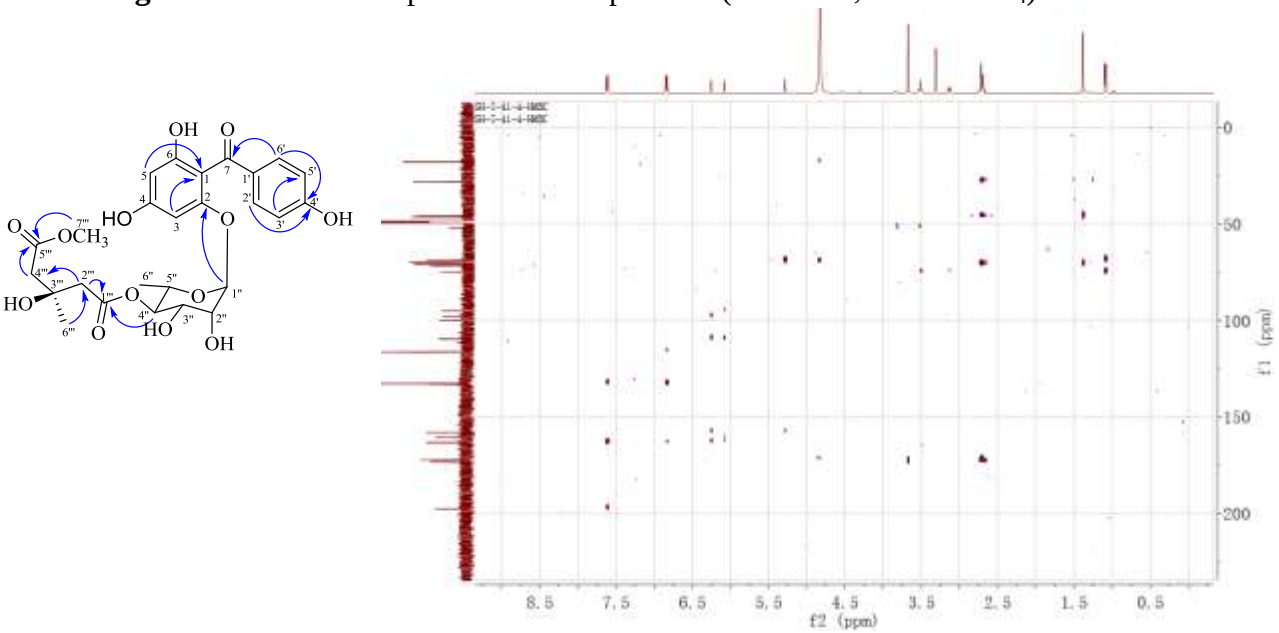

Figure S14 HMBC spectrum of compound **2** (500 MHz, methanol-d_4)

Table S1 ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectroscopic data (δ in ppm) of compounds **1** and **2** (in methanol-d_4))

position	**1**		**2**	
	δ_H mult. (J in Hz)	δ_C	δ_H mult. (J in Hz)	δ_C
1		158.2		109.6
2		107.1		157.9
3		165.7	6.25 d (2.0)	95.1
4	6.36 s	90.1		163.0
4a		159.2		
5	6.73 s	103.2	6.08 d (2.0)	98.1
5a		158.2		
6		145.9		160.5
7	7.39 s	154.0		197.6
8		107.9		
8a		112.5		
9		181.3		
9a		104.3		
1′a	3.55 d (17.0)	32.3		132.9
1′b	3.03 d (17.0)			
2′		122.8	7.62 d (8.5)	132.7
3′	4.21 d (2.5)	82.7	6.84 d (8.5)	116.2
4′	4.03 m	78.7		163.4
5′	4.09 m	86.2	6.84 d (8.5)	116.2
6′a	3.77 m	62.8	7.62 d (8.5)	132.7
6′b	3.67 m			
1″			5.29 s	99.8
2″			3.51 m	71.5
3″			3.13 dd (9.5,3.0)	69.8
4″			4.86 m	75.0
5″			3.51 m	68.7
6″			1.09 d (6.0)	17.9
1‴				172.2
2‴			2.72 s	46.3
3‴				70.9
4‴			2.69 d (4.5)	45.9
5‴				173.2
6‴			1.38 s	28.0
7‴			3.67 s	52.0

Table S2 ^{1}H and ^{13}C NMR spectroscopic data (δ in ppm) of iriflophenone 2-*O*-α-L-[4″-*O*-[3‴(*S*)-hydroxy-methylglutaryl]]-rhamnopyranoside and compound **3**

position	iriflophenone 2-*O*-α-L-[4″-*O*-[3‴(*S*)-hydroxy-methylglutaryl]] -rhamnopyranside (500 and 125 MHz, methanol-d_4) (Yuan et al. 2017)		**3** (500 and 125 MHz, methanol-d_4)	
	δ_H mult. (*J* in Hz)	δ_C	δ_H mult. (*J* in Hz)	δ_C
1		108.1		109.5
2		156.5		158.0
3	6.25 d (2.0)	93.6	6.25 d (2.0)	95.0
4		161.5		163.0
5	6.08 d (2.0)	96.6	6.09 d (2.0)	98.1
6		159.1		160.6
7		196.2		197.7
1′		131.5		132.9
2′,6′	7.61 d (8.8)	131.2	7.61 d (8.5)	132.6
3′,5′	6.84 d (8.8)	114.8	6.86 d (8.5)	116.2
4′		161.9		163.4
1″	5.28 d (1.6)	98.3	5.28 d (1.6)	99.7
2″	3.51 m	70.1	3.52 m	71.5
3″	3.11 dd (9.8,3.4)	68.4	3.09 dd (9.5,3.0)	69.8
4″	4.84 m	73.6	4.84 m	75.1
5″	3.51 m	67.3	3.49 m	68.7
6″	1.08 d (6.2)	16.5	1.09 d (6.0)	17.9
1‴		170.9		172.4
2‴	2.72 s	44.9	2.68 s	46.9
3‴		69.4		71.1
4‴	2.63 d (15.2)	44.4	2.53 d (15.0)	46.7
	2.68 d (15.2)		2.61 d (15.0)	
5‴		173.3		173.8
6‴	1.39 s	26.5	1.37 s	27.9

Table S3 ^{1}H and ^{13}C NMR spectroscopic data (δ in ppm) of iriflophenone 2-*O*-β-D-xylopyranoside and compound **4**

position	iriflophenone 2-*O*-β-D-xylopyranoside (500 and 125 MHz, methanol-d_4) (Yuan et al. 2017)		**4** (500 and 125 MHz, methanol-d_4)	
	δ_H mult. (*J* in Hz)	δ_C	δ_H mult. (*J* in Hz)	δ_C
1		108.7		110.0
2		157.2		158.7
3	6.17 d (2.0)	94.3	6.16 d (2.0)	95.8
4		161.2		163.1
5	6.06 d (2.0)	96.8	6.06 d (2.0)	98.3
6		158.6		160.2
7		196.0		197.4
1′		130.9		132.3
2′,6′	7.65 d (8.8)	131.9	7.65 d (8.0)	133.4
3′,5′	6.78 d (8.8)	114.3	6.77 d (8.0)	115.8
4′		162.1		163.8
1″	4.79 d (7.3)	101.2	4.79 d (7.5)	102.6
2″	3.04 dd (8.9,7.3)	73.0	3.04 m	74.4
3″	3.30 m	75.9	3.30 m	77.4
4″	3.44 m	69.4	3.43 m	70.8
5″	3.27 dd (11.4,9.8)	65.4	3.26 m	66.9
	3.85 dd (11.4,5.2)		3.85 dd (11.5,5.0)	

Table S4 ^{1}H and ^{13}C NMR spectroscopic data (δ in ppm) of iriflophenone 2-*O*-α-L-rhamnoside and compound **5**

position	iriflophenone 2-*O*-α-L-rhamnoside (500 and 125 MHz, methanol-d_4) (Xia et al. 2013)		**5** (500 and 125 MHz, methanol-d_4)	
	δ_H mult. (*J* in Hz)	δ_C	δ_H mult. (*J* in Hz)	δ_C
1		109.6		109.5
2		160.5		158.4
3	6.34 d (2.0)	95.6	6.29 d (2.0)	95.7
4		163.4		163.5
5	6.11 d (2.0)	98.0	6.07 d (2.0)	98.1
6		158.4		158.4
7		197.6		197.6
1′		128.8		130.9
2′,6′	7.65 d (8.5)	132.7	7.61 d (8.5)	132.7
3′,5′	6.85 d (8.5)	116.1	6.81 d (8.5)	116.1
4′		163.0		163.3
1″	5.26 d (1.0)	100.5	5.22 d (1.0)	100.5
2″	3.45-3.50 m	71.6	3.43 m	71.6
3″	3.16 dd (9.5,3.0)	71.9	3.12 dd (9.5,3.5)	71.9
4″	3.32 dd (9.5,3.0)	73.6	3.28 dd (9.5,3.5)	73.6
5″	3.45-3.50 m	70.8	3.40 m	70.8
6″	1.23 d (6.0)	18.0	1.19 d (6.0)	18.0

Table S5 ^{1}H and ^{13}C NMR spectroscopic data (δ in ppm) of iriflophenone 2-*O*-*β*-D-glucopyranoside and compound **6**

	iriflophenone 2-*O*-*β*-D-glucopyranoside (400 and 100 MHz, methanol-d_4) (Lee et al. 2010)		**6** (600 and 150 MHz, methanol-d_4)	
position	δ_H mult. (*J* in Hz)	δ_C	δ_H mult. (*J* in Hz)	δ_C
1		110.3		110.2
2		158.7		158.8
3	6.24 d (1.8)	95.8	6.24 d (1.8)	96.0
4		162.4		162.9
5	6.06 d (1.8)	98.1	6.06 d (1.8)	98.0
6		159.6		159.9
7		197.5		197.4
1′		132.1		132.2
2′,6′	7.68 d (8.8)	133.5	7.67 d (8.4)	133.5
3′,5′	6.78 d (8.8)	115.8	6.78 d (8.4)	115.9
4′		163.6		163.9
1″	4.82 d (7.6)	102.2	4.82 d (7.8)	102.3
2″	3.09 dd (8.8,7.6)	74.6	3.08 t (9.0)	74.7
3″	3.37 dd (9.3,8.8)	77.7	3.36 m	77.8
4″	3.27 t (9.3)	71.0	3.27 t (9.6)	71.1
5″	3.33-3.37 m	78.1	3.35 m	78.2
6″	3.86 dd (12.3,2.3)	62.4	3.86 dd (12.0,5.4)	62.5
	3.67 dd (12.3,5.3)		3.67 dd (12.0,5.4)	

Table S6 ^{1}H and ^{13}C NMR spectroscopic data (δ in ppm) of iriflophenone 2-*O*-α-L-(4″-acetyl)-rhamnopyranoside and compound **7**

position	iriflophenone 2-*O*-α-L-(4″-acetyl)-rhamnopyranoside (500 and 125 MHz, methanol-d_4) (Sun et al. 2014)		**7** (500 and 125 MHz, methanol-d_4)	
	δ_H mult. (*J* in Hz)	δ_C	δ_H mult. (*J* in Hz)	δ_C
1		109.7		109.5
2		158.0		157.8
3	6.25 d (2.0)	95.1	6.22 d (2.0)	94.9
4		163.1		162.9
5	6.08 d (2.0)	98.1	6.06 d (2.0)	97.9
6		160.6		160.3
7		197.7		197.6
1′		133.1		132.8
2′,6′	7.60 d (8.7)	132.8	7.60 d (8.5)	132.7
3′,5′	6.80 d (8.7)	116.3	6.81 d (8.5)	116.1
4′		163.1		163.4
1″	5.29 d (1.4)	99.8	5.26 d (1.4)	99.6
2″	3.52 m	71.6	3.49 m	71.5
3″	3.09 m	69.9	3.07 m	69.7
4″	3.79 m	79.2	4.78 m	75.0
5″	3.48 m	68.8	3.45 m	68.7
6″	1.05 d (6.0)	17.9	1.03 d (6.0)	17.8
CH_3	2.0 s	21.1	2.0 s	21.0
CO		172.7		172.5

Table S7 ^{1}H and ^{13}C NMR spectroscopic data (δ in ppm) of iriflophenone 2-*O*-*α*-L-[4″-*O*-(*p*-hydroxy-*β*-oxo-benzenepropanoyl)]-rhamnopyranoside and compound **8**

position	iriflophenone 2-*O*-*α*-L-[4″-*O*-(*p*-hydroxy-*β*-oxo-benzenepropanoyl)]-rhamnopyranoside (500 and 125 MHz, methanol-d_4) (Yuan et al. 2017)		**8** (500 and 125 MHz, methanol-d_4)	
	δ_H mult. (*J* in Hz)	δ_C	δ_H mult. (*J* in Hz)	δ_C
1		107.9		109.2
2		156.6		158.1
3	6.23 d (1.9)	93.5	6.23 d (1.5)	95.0
4		161.9		163.5
5	6.07 d (1.9)	96.6	6.07 d (1.5)	98.1
6		159.3		160.9
7		196.3		197.7
1′		131.7		133.0
2′,6′	7.58 d (8.7)	131.1	7.58 d (9.0)	132.5
3′,5′	6.81 d (8.7)	115.1	6.81 d (8.5)	116.3
4′		161.7		163.5
1″	5.27 br s (d, 1.4)[a]	98.2	5.27 br s	99.7
2″	3.51 m	70.0	3.51 m	71.4
3″	3.02 dd (9.8,3.4)	68.3	3.03 dd (9.5,3.0)	69.7
4″	4.86 m	74.5	4.84 m	75.9
5″	3.48 m	67.2	3.48 m	68.7
6″	1.08 d (6.2)	16.3	1.09 d (6.0)	17.8
1‴		168.0		169.4
2‴	4.02 d (15.7)[a] 4.11 d (15.7)[a]	45.8[a]		
3‴		192.3		193.7
4‴		127.7		128.9
5‴	7.89 d (8.7)	131.1	7.90 d (8.5)	132.5
6‴	6.87 d (8,7)	114.8	6.86 d (8.5)	116.6
7‴		163.1		165.0
8‴	6.87 d (8.7)	114.8	6.86 d (8.5)	116.6
9‴	7.89 d (8.7)	131.1	7.90 d (8.5)	132.5

Note: [a]Observed in acetonitrile-d_3

Reference:

Lee SS. Tseng CC, Chen CK. 2010. Three new benzophenone glucosides from the leaves of *Planchonella obovata*. Helv Chim Acta. 93:522–529.

Sun J, Wang S, Xia F, Wang KY, Chen JM, Tu PF. 2014. Five new benzophenone glycosides from the leaves of *Aquilaria sinensis* (Lour.) Gilg. Chin Chem Lett. 25:1573–1576.

Xia F, Sun J, Jiang Y, Tu PF. 2013. Further chemical investigation of leaves of *Aquilaria sinensis*. Chin J Chin Mater Med. 38:3299–3303.

Yuan HW, Zhao JP, Wang M, Khan SI, Zhai CM, Xu QM, Huang JH, Peng GY, Xiong GH, Wang M, et al. 2017. Benzophenone glycosides from the flower buds of *Aquilaria sinensis*. Fitoterapia. 121:170–174.