Supporting Information

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A New Megastigmane Glycoside And Anti-Inflammatory Bibenzyls And From The Stems of *Dendrobium henanense* Siyu Wu ¹, Shihui Qin¹, Chuihao Kong ¹, Renzhong Wang ^{1*}, Deling Wu ^{1,2}

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P. R.China

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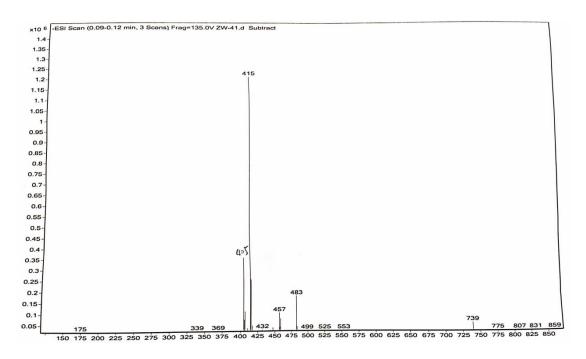


Figure S1: ESI-MS Spectrum of **1** ((9S)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one)

Fragmentor Voltage 135 Collision Energy 0 Ionization Mode ESI x10 4 -ESI Scan (0.08-0.10 min, 2 Scans) Frag=135.0V ZW-41.d Subtract (2) 369,1924 ([C19 H30 O7]-H)66 57 44 33 22 11 370,1953 ([C19 H30 O7]-H)1371,1991 ([C19 H30 O7]-H)140 388.4 368.6 368.8 369 369.2 369.4 369.6 369.8 370 370.2 370.4 370.6 370.8 371 371.2 371.4 371.6 371.8

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5-										
4-										
3-										
2-				370.19 ([C19 H30 (
1-					37] 11)		.1991			
0							30 O7]-H)-			
36	58.4 3	68.6 368.8 369	369.2 369	0.4 369.6 369.8 370 370.2 Counts vs. Mass-to-Cha		0.8 371 37	71.2 371.4	371.6 371.8		
Peak List										
m/z	Z	Abund	Formula	Ior	1					
112.9855	1	16070.53								
369.1924	1	71310.68	C19 H30	O7 (M-	·H)-					
405.1689	1	22914.64								
415.1981	1	83379.62								
416.2011	1	18338.2								
432.1879	1	15022.06								
483.1858	1	149955.14								
484.1889	1	34733.03								
739.3917	1	40807.55								
740.3954	1	17841.75								
Formula Cal Element	culat IMin	or Element L	imits ¬							
	MIII		4							
<u>C</u>	+	3 120	4							
H	+	0 300	4							
O Formula Cal	 culat	0 30	┙							
Formula	cuiat	Calculated	lass	CalculatedMz	Mz	Diff. (mD	a)	Diff. (ppm)		DBE
C19 H30 O7			370 1992	369 1919	9 369 1924	<u> </u>	-0.50		-1.35	5,0000

C19 H30 O7 370.1992 369.1919 369.1924 -0.50 -1.35 5.0000

Figure S2: HR-ESI-MS Spectrum of **1** ((9*S*)-O-*β*-D-glucopyranosyl-2,5-megastigmen-4- one)

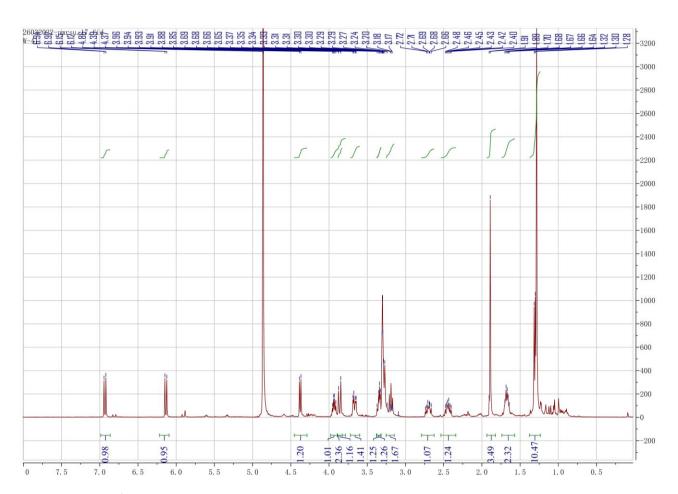


Figure S3: 1 H-NMR (400 MHz, CD₃OD) Spectrum of **1** (((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one)

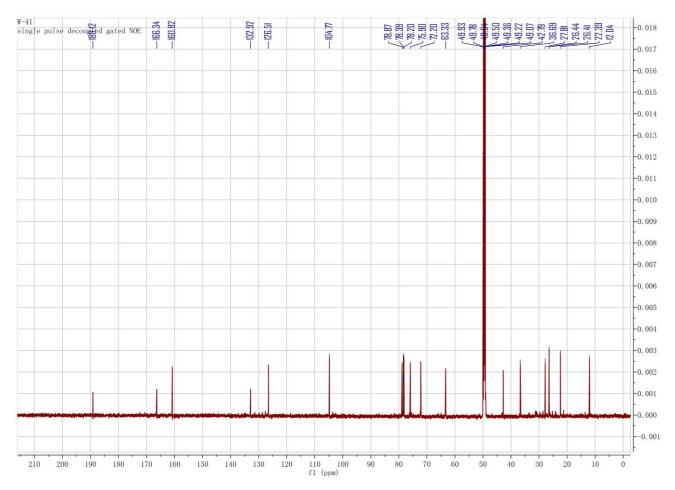


Figure S4: 13 C-NMR (150 MHz, CD₃OD) Spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one)

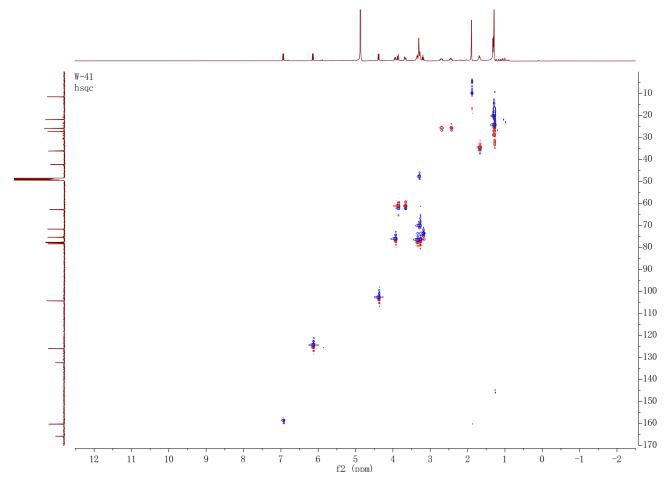


Figure S5: HSQC Spectrum of **1** ((9*S*)-O-*β*-D-glucopyranosyl-2,5-megastigmen-4- one)

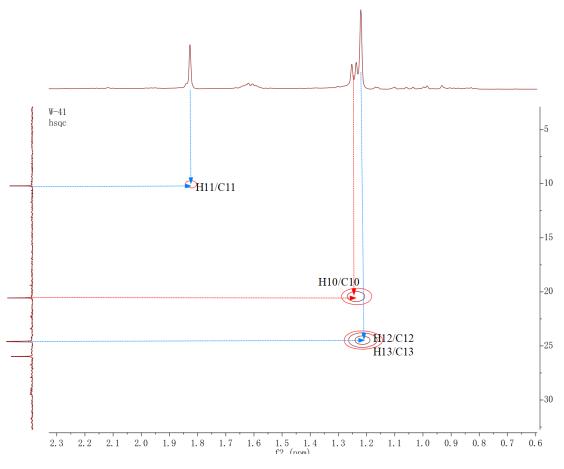


Figure S6: HSQC spectrum of **1** ((9S)-O-β-D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 0.6 ppm to $\delta_{\rm H}$ 2.3 ppm)

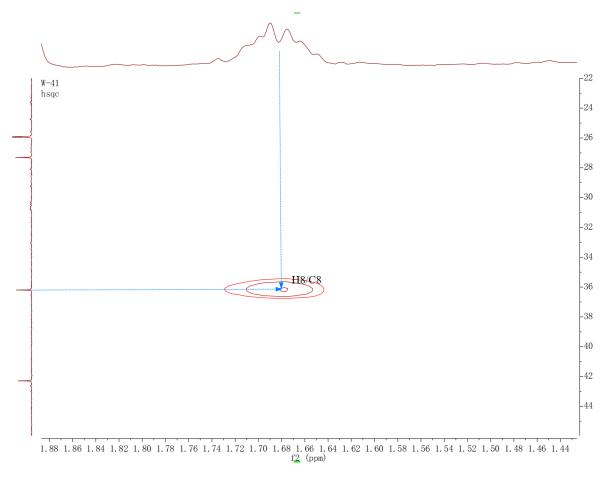


Figure S7: HSQC spectrum of **1** ((9S)-O-β-D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 1.44 ppm to $\delta_{\rm H}$ 1.88 ppm)

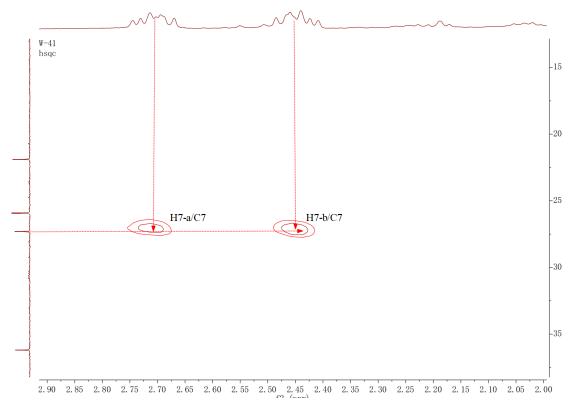


Figure S8: HSQC spectrum of **1** ((9S)-O-β-D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 2.0 ppm to $\delta_{\rm H}$ 2.9 ppm)

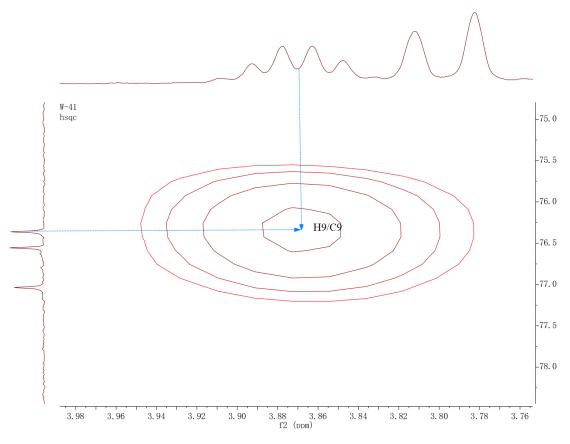


Figure S9: HSQC spectrum of **1** ((9S)-O-β-D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 3.76 ppm to $\delta_{\rm H}$ 3.98 ppm)

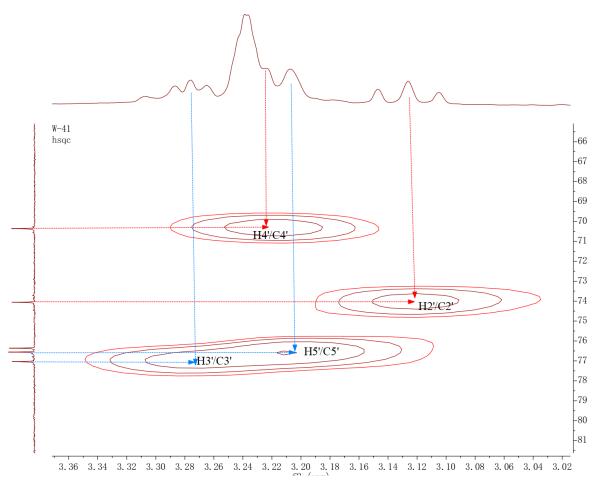


Figure S10: HSQC spectrum of **1** ((9S)-O-β-D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 3.02 ppm to $\delta_{\rm H}$ 3.36 ppm)

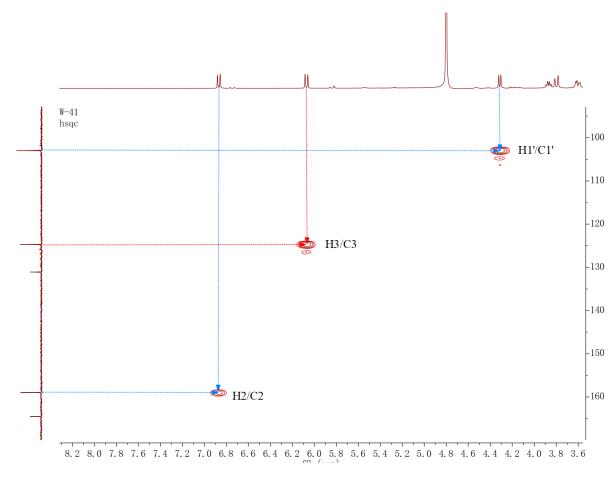


Figure S11: HSQC spectrum of **1** ((9S)-O-β-D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 3.6 ppm to $\delta_{\rm H}$ 8.2 ppm)

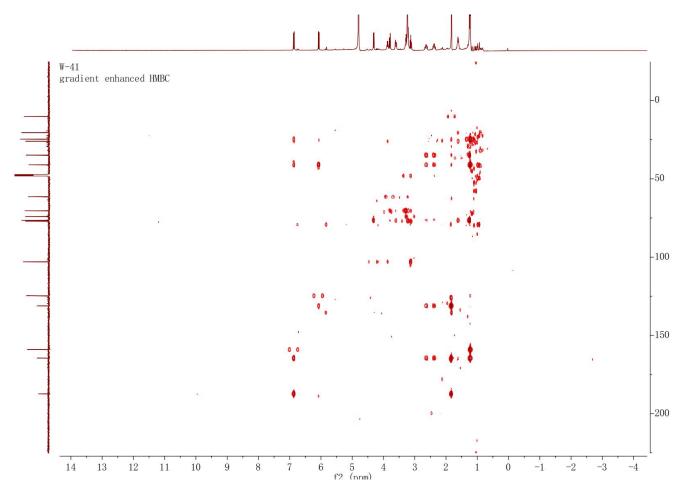


Figure S12: HMBC Spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one)

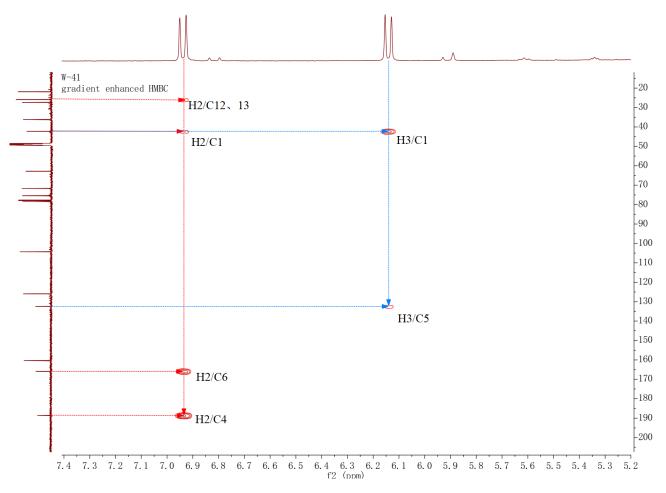


Figure S13: HMBC spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From δ_H 5.2 ppm to δ_H 7.4 ppm)

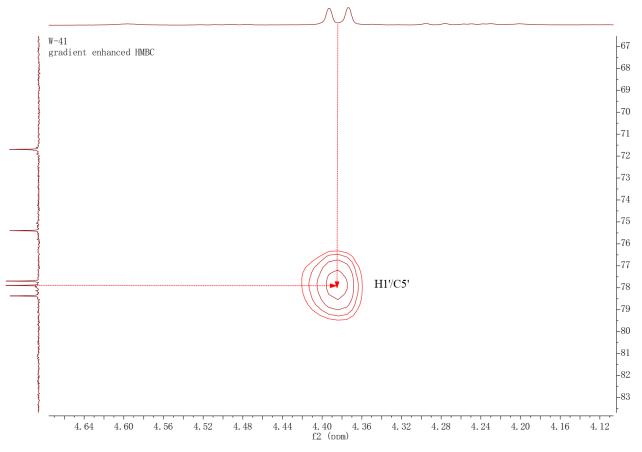


Figure S14: HMBC spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 4.12 ppm to $\delta_{\rm H}$ 4.64 ppm)

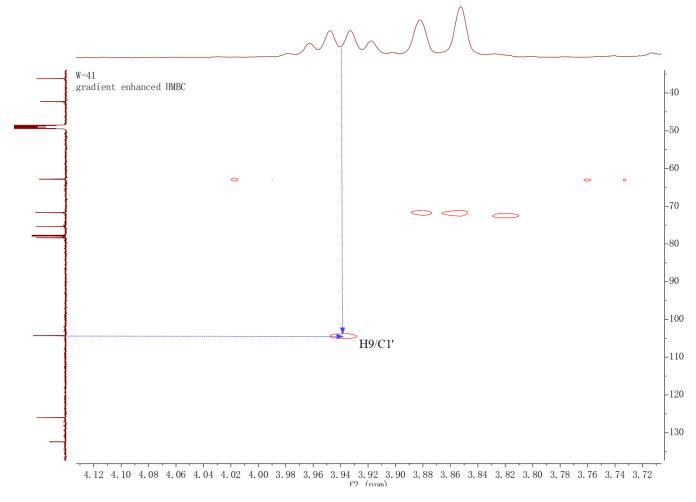


Figure S15: HMBC spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From δ_H 3.72 ppm to δ_H 4.12 ppm)



Figure S16: HMBC spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From δ_H 3.48 ppm to δ_H 3.72 ppm)

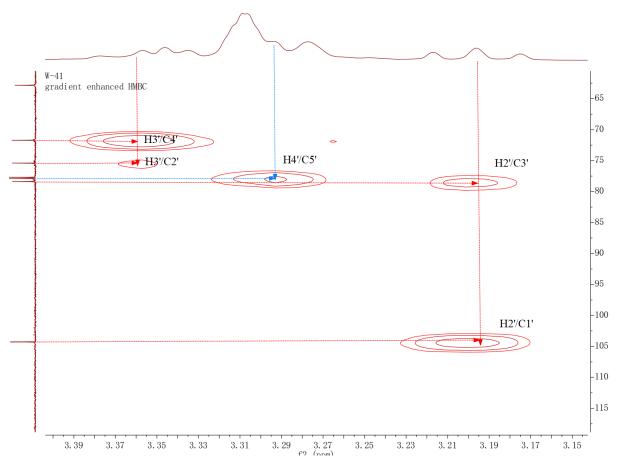


Figure S17: HMBC spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From δ_H 3.15 ppm to δ_H 3.39 ppm)

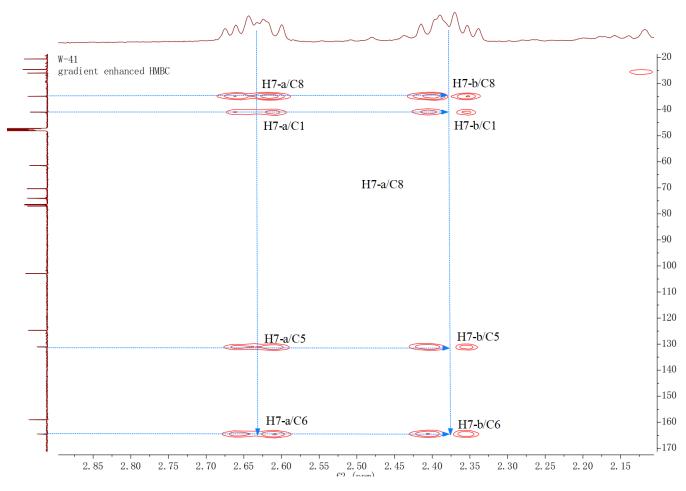


Figure S18: HMBC spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 2.15 ppm to $\delta_{\rm H}$ 2.85 ppm)

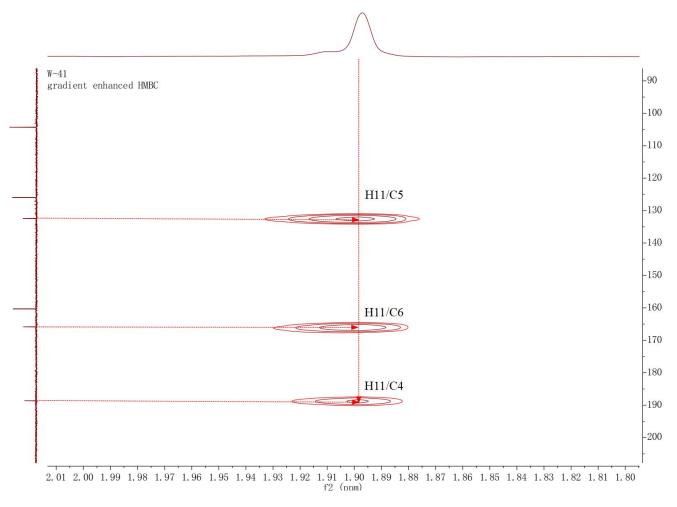


Figure S19: HMBC spectrum of **1** ((9*S*)-O-*β*-D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 1.80 ppm to $\delta_{\rm H}$ 2.01 ppm)

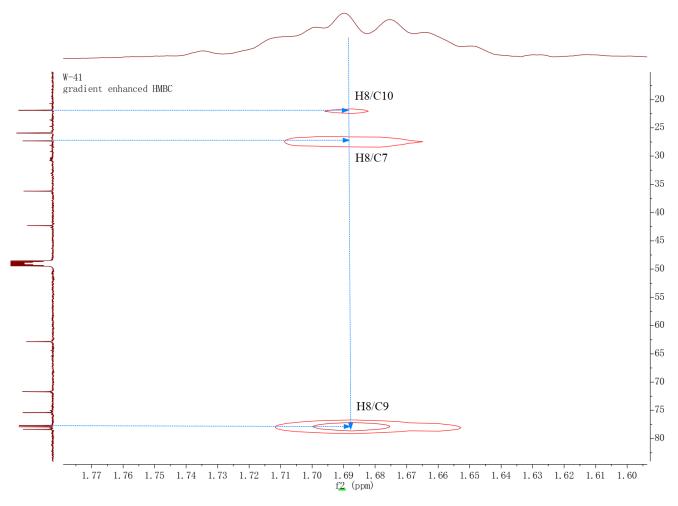


Figure S20: HMBC spectrum of **1** ((9*S*)-O-*β*-D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 1.60 ppm to $\delta_{\rm H}$ 1.77 ppm)

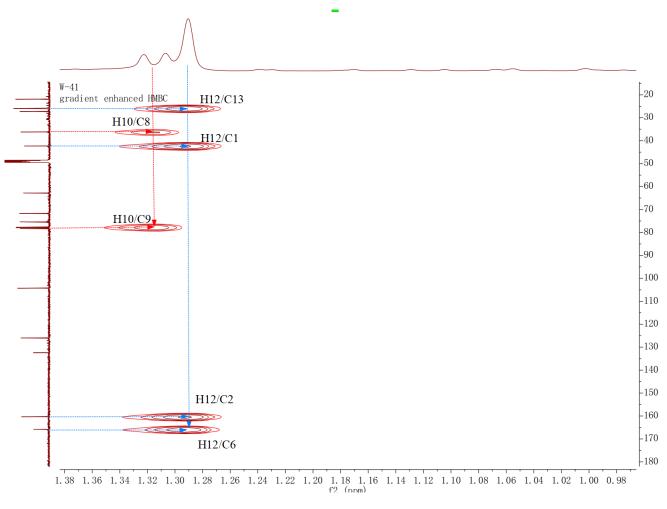


Figure S21: HMBC spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From $\delta_{\rm H}$ 0.98 ppm to $\delta_{\rm H}$ 1.38 ppm)

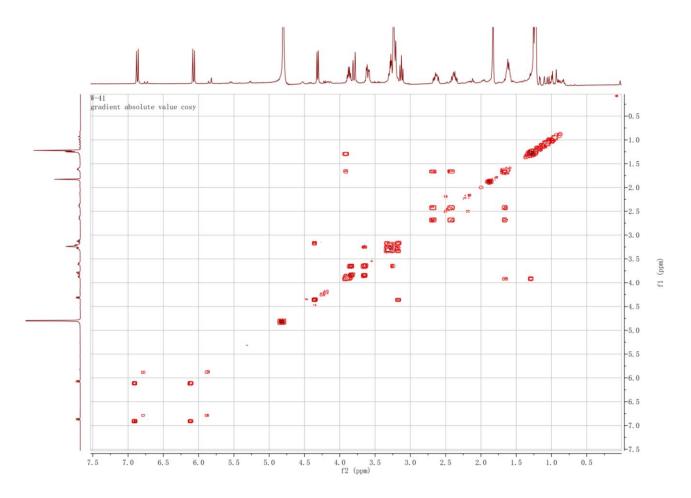


Figure S22: ${}^{1}\text{H-}{}^{1}\text{H COSY Spectrum of } \mathbf{1}$ ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one)

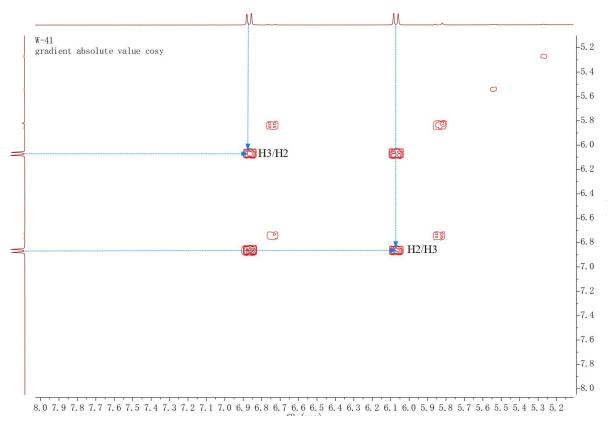


Figure S23: ${}^{1}\text{H}$ - ${}^{1}\text{H}$ COSY Spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From δ_{H} 5.2 ppm to δ_{H} 8.0 ppm)

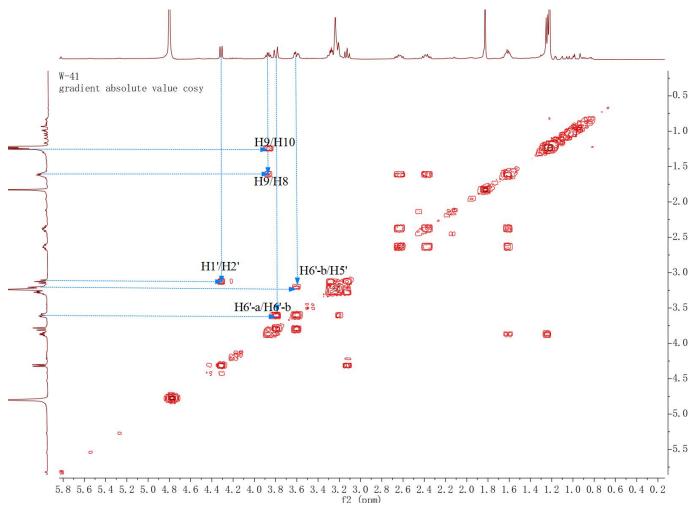


Figure S24: ^{1}H - ^{1}H COSY Spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From δ_{H} 0.2 ppm to δ_{H} 5.8 ppm)

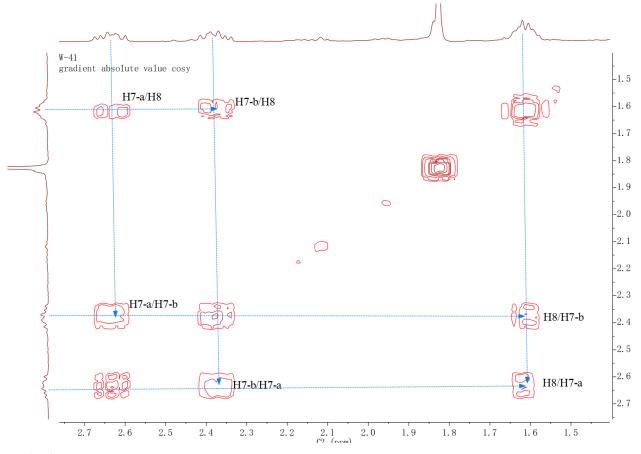


Figure S25: ${}^{1}\text{H}$ - ${}^{1}\text{H}$ COSY Spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one) (From δ_{H} 1.5 ppm to δ_{H} 2.7 ppm)

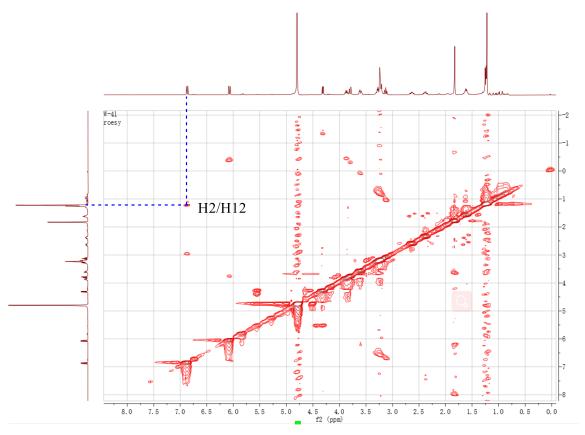
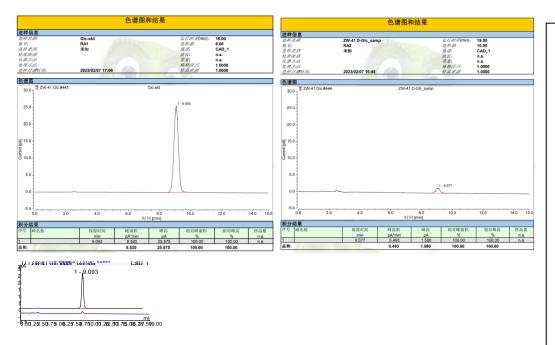


Figure S26: ROESY spectrum of **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one)



a hydrolysis experiment to determine the absolute configuration of sugar moiety in 1.

Compound 1 was acid hydrolyzed according to the method described in the literature. Compound 1 (3 mg) was individually refluxed with 5 % HCl in MeOH (5 mL) for 2 hrs. The solution was diluted with H₂O (5 mL) and extracted with EtOAc (10 mL) for 3 times. The aqueous layer was neutralized with NaHCO3 and concentrated in vacumn to give a residue. Purification of the residue was performed by RP-18 column, eluted with 20% MeOH-H₂O, to afford the purified sugar. The optical rotation was determined after dissolving the sugar in MeOH: $[\alpha]22.3$ D: +40.1 (c 0.09, MeOH). And the sugar molecule were determined to be D-glc using HPLC-CAD, in contrast with the reference D-glc. Chromatographic analyses were performed on a Ulimate 3000 HPLC system equipped with a CAD detector. Chromatographic separation was carried out at 30 °C on a Shodex Asahipak NH₂-P-50 4E column (250 mm \times 4.6 mm, 5 μ m, USA). The mobile phase was composed of acetonitrile-water (25:75, v/v) at 1.0 ml·min⁻¹, every 3 μL sample solution was injected for each run and the CAD spectra were recorded at the frequency was 5 Hz, the filter was 3.6F, the atomizer temperature was 35 °C, the air source was N_2 , and the pressure was 4.328×10^5 Pa.

Figure S27: The HPLC of sugar in compound 1 ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one)

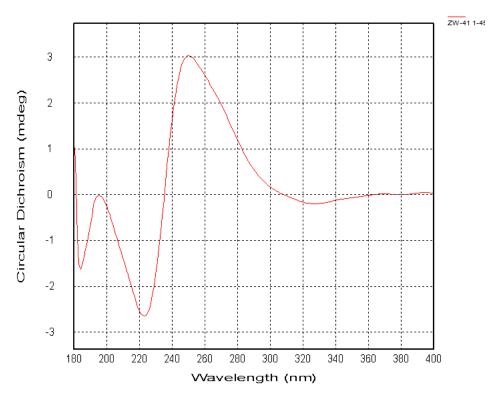


Figure S28: The circular dichroism spectrum of compound **1** ((9*S*)-O- β -D-glucopyranosyl-2,5-megastigmen-4- one)

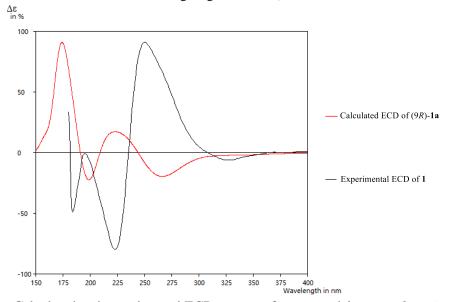
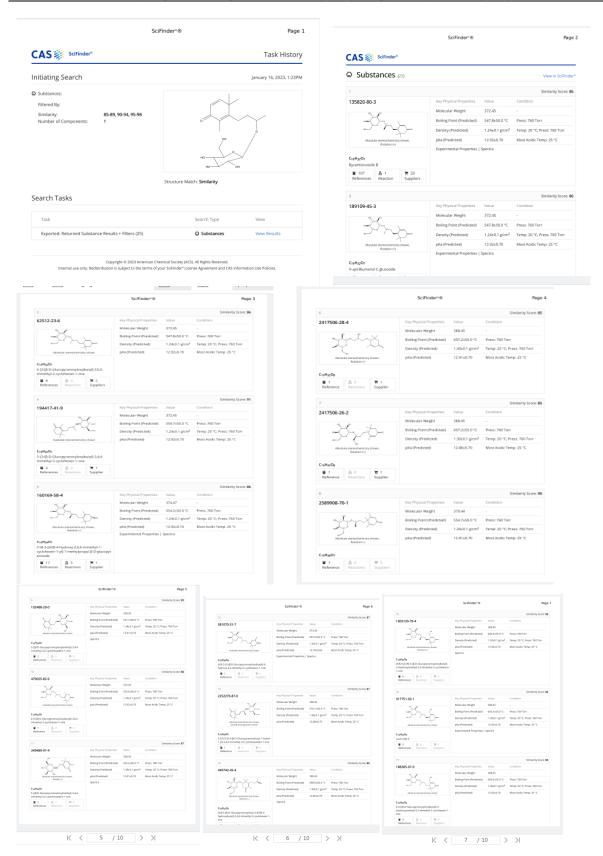


Figure S29: Calculated and experimental ECD spectra of compound $\mathbf{1}((9S)\text{-O-}\beta\text{-D-glucopyranosyl-}2,5\text{-megastigmen-4-one})$

Figure S30: Similarity report of compound $1((9S)-O-\beta-D-glucopyranosyl-2,5-megastigmen-4-one)$



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Figure S30: Similarity report of compound $\mathbf{1}((9S)\text{-O-}\beta\text{-D-glucopyranosyl-2,5-megastigmen-4-one)}$

