

## Supplementary data

### The influence of glycosylation of natural and synthetic prenylated flavonoids on binding to human serum albumin and inhibition of cyclooxygenases COX-1 and COX-2

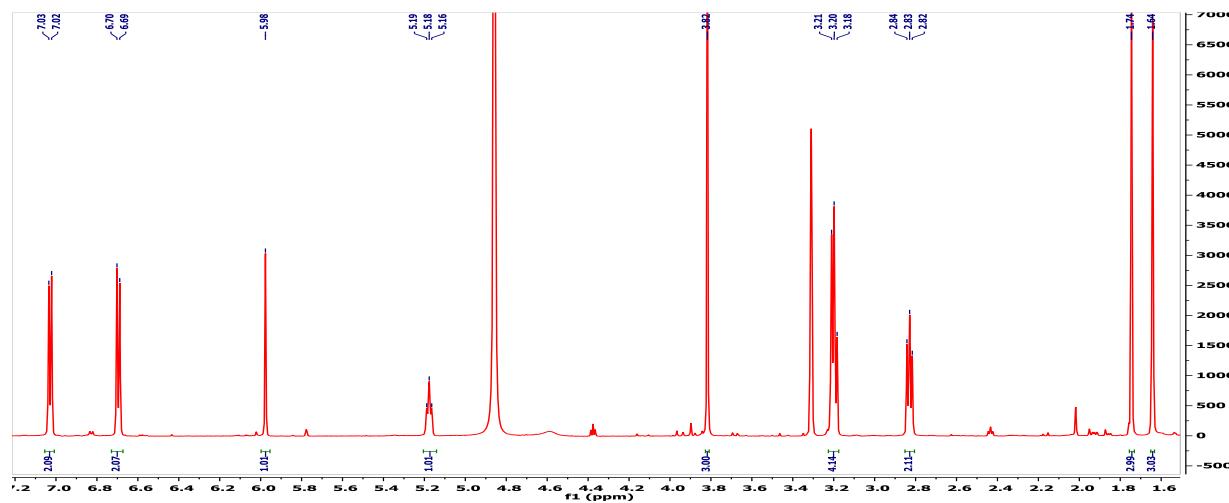
Tomasz Tronina<sup>\*1</sup>, Paulina Strugała<sup>2</sup>, Jarosław Popłoński<sup>1</sup>, Aleksandra Włoch<sup>2</sup>, Sandra Sordon<sup>1</sup>, Agnieszka Bartmańska<sup>1</sup> and Ewa Huszcza<sup>1</sup>

<sup>1</sup>Department of Chemistry, Wrocław University of Environmental and Life Sciences, Norwida 25, 50-375 Wrocław, Poland.<sup>2</sup>Department of Physics and Biophysics, Wrocław University of Environmental and Life Sciences, Norwida 25, 50-375 Wrocław, Poland.

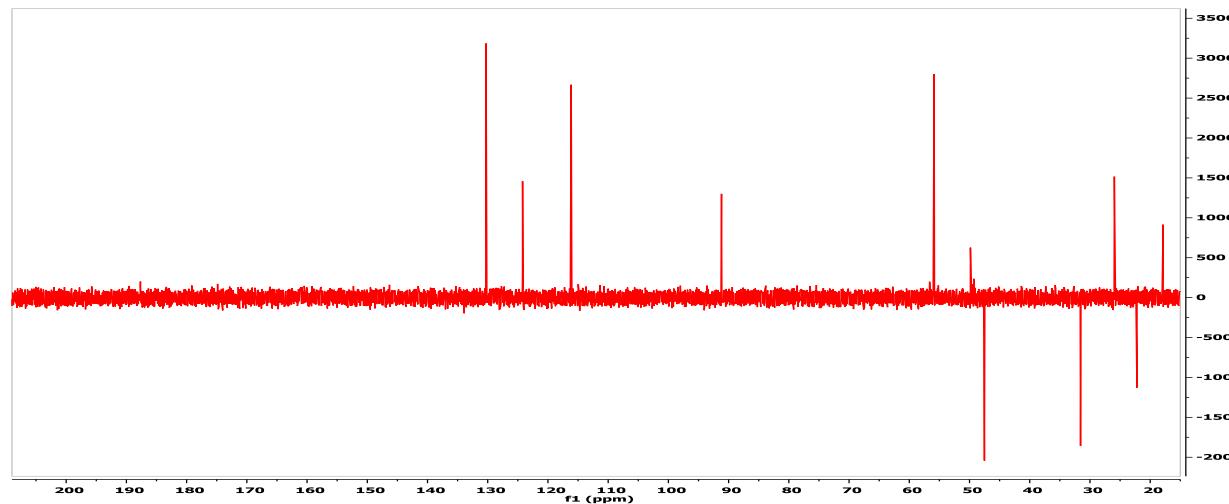
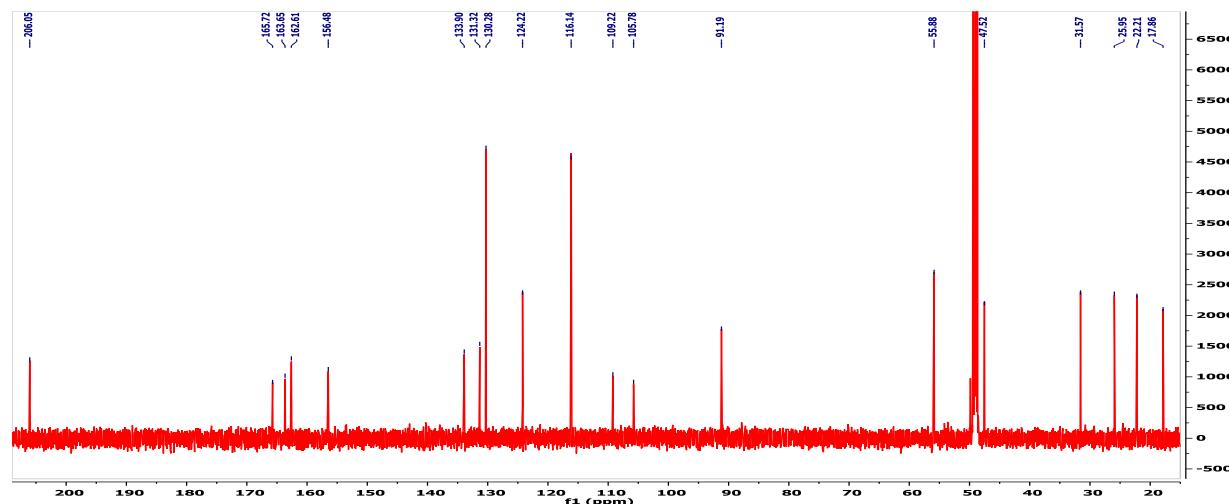
\*Corresponding Author: E-mail address: tomasz.tronina@upwr.edu.pl, Phone: +48 713205197; fax: +48 3207744

<b>Table of Contents:</b>	<b>Page</b>
<sup>1</sup> H NMR spectrum of $\alpha,\beta$ -dihydroxanthohumol ( <b>2</b> )	S2
<sup>13</sup> C NMR and DEPT 135° spectra of $\alpha,\beta$ -dihydroxanthohumol ( <b>2</b> )	S2
UV spectra of xanthohumol ( <b>1</b> ) and (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone ( <b>3</b> )	S3
HRMS spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone ( <b>3</b> )	S3
<sup>1</sup> H NMR spectra of xanthohumol ( <b>1</b> ) and (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone ( <b>3</b> )	S4
Fragments of <sup>1</sup> H NMR spectra of xanthohumol ( <b>1</b> ) and (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone ( <b>3</b> )	S5
<sup>13</sup> C NMR spectra of xanthohumol ( <b>1</b> ) and (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone ( <b>3</b> )	S6
<sup>1</sup> H- <sup>1</sup> H NMR (COSY) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone ( <b>3</b> )	S7
<sup>1</sup> H- <sup>13</sup> C NMR (HSQC) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone ( <b>3</b> )	S7
UV spectrum of $\alpha,\beta$ -dihydroxanthohumol 4'-O- $\beta$ -D-glucopyranoside ( <b>6</b> )	S8
HRMS spectrum of $\alpha,\beta$ -dihydroxanthohumol 4'-O- $\beta$ -D-glucopyranoside ( <b>6</b> )	S8
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-glucopyranoside ( <b>6</b> )	S9
<sup>1</sup> H NMR - <sup>1</sup> H NMR (COSY) spectrum of $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-glucopyranoside ( <b>6</b> )	S10
<sup>1</sup> H NMR - <sup>13</sup> C NMR (HSQC) spectrum of $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-glucopyranoside ( <b>6</b> )	S10
UV spectrum of $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>7</b> )	S11
HRMS spectrum of $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>7</b> )	S11
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>7</b> )	S12
<sup>1</sup> H NMR - <sup>1</sup> H NMR (COSY) spectrum of $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>7</b> )	S13
<sup>1</sup> H NMR - <sup>13</sup> C NMR (HSQC) spectrum of $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>7</b> )	S13
UV spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside ( <b>8</b> )	S14
HRMS spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside ( <b>8</b> )	S14
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside ( <b>8</b> )	S15
<sup>1</sup> H NMR - <sup>1</sup> H NMR (COSY) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside ( <b>8</b> )	S16
<sup>1</sup> H NMR - <sup>13</sup> C NMR (HSQC) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside ( <b>8</b> )	S16
UV spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>9</b> )	S17
HRMS spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>9</b> )	S17
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>9</b> )	S18
<sup>1</sup> H NMR - <sup>1</sup> H NMR (COSY) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>9</b> )	S19
<sup>1</sup> H NMR - <sup>13</sup> C NMR (HSQC) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside ( <b>9</b> )	S19

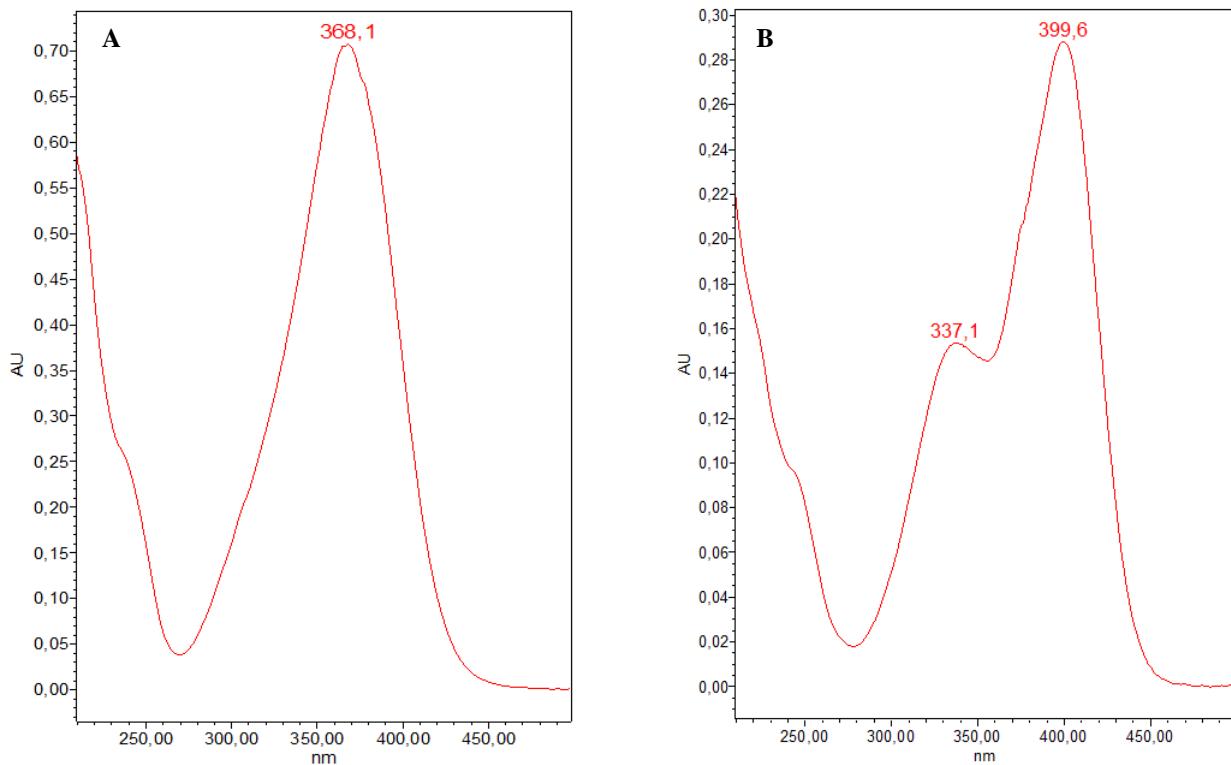
**Figure S1.**  $^1H$  NMR spectrum of  $\alpha,\beta$ -dihydroxanthohumol (**2**) (600 MHz,  $CD_3OD$ , Temp. 25 °C)



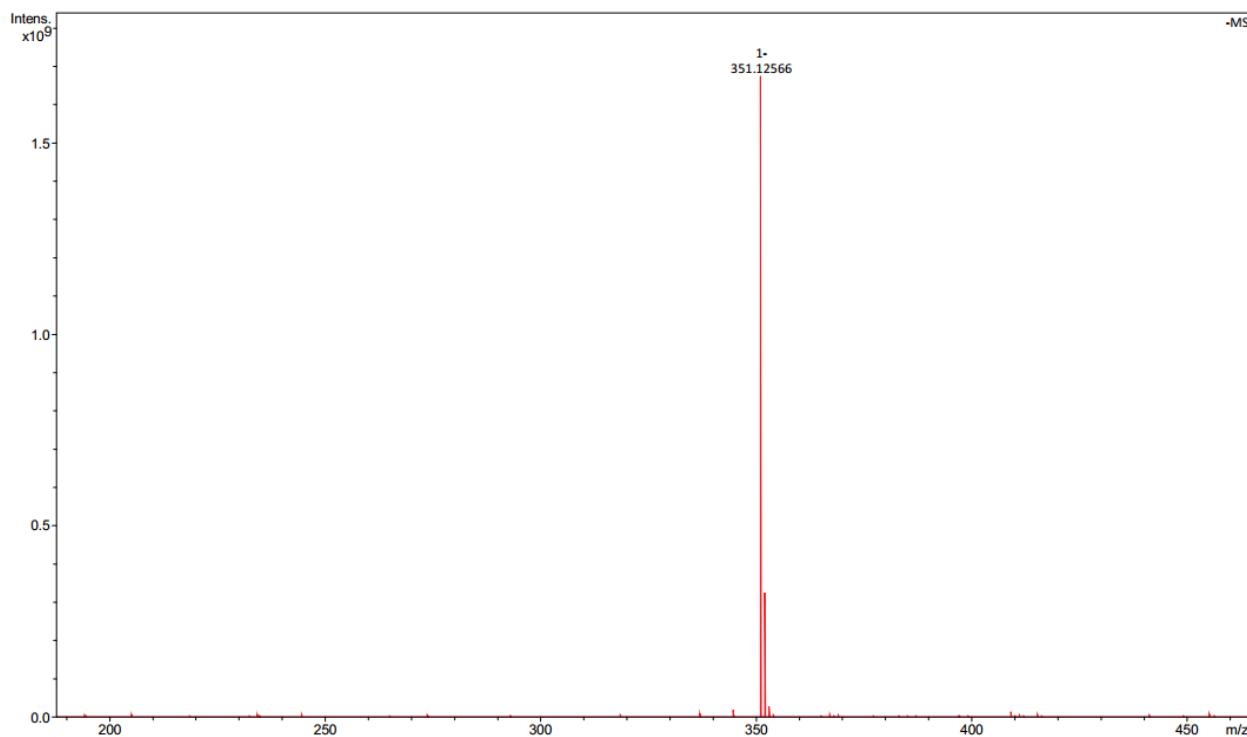
**Figure S2.**  $^{13}\text{C}$  NMR and DEPT 135° spectra of  $\alpha,\beta$ -dihydroxanthohumol (**2**) (151 MHz,  $\text{CD}_3\text{OD}$ , Temp. 25 °C)



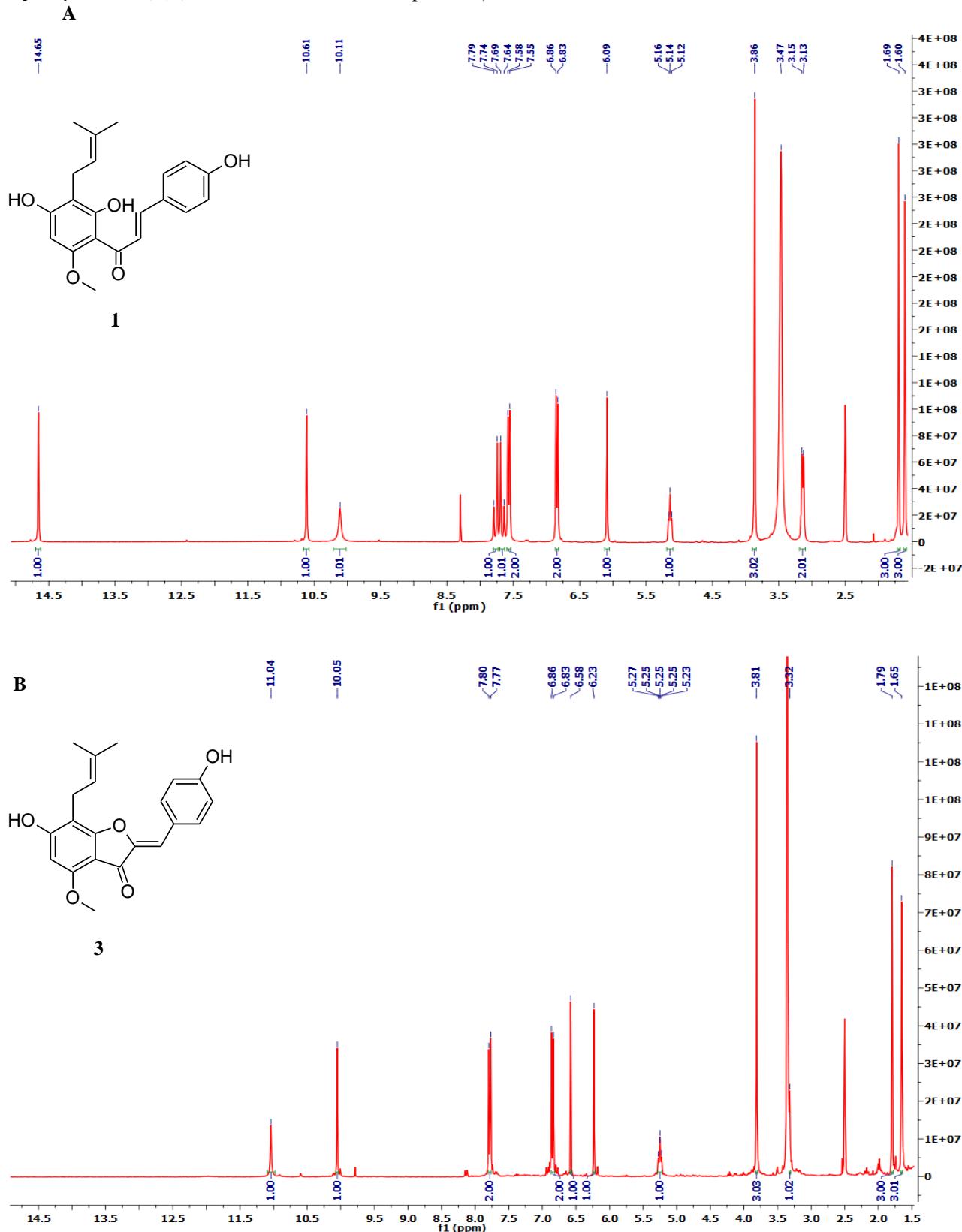
**Figure S3:** UV spectra of: A xanthohumol (**1**), B (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone (**3**) (MeOH, Temp. 20 °C)



**Figure S4.** HRMS spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone (**3**)

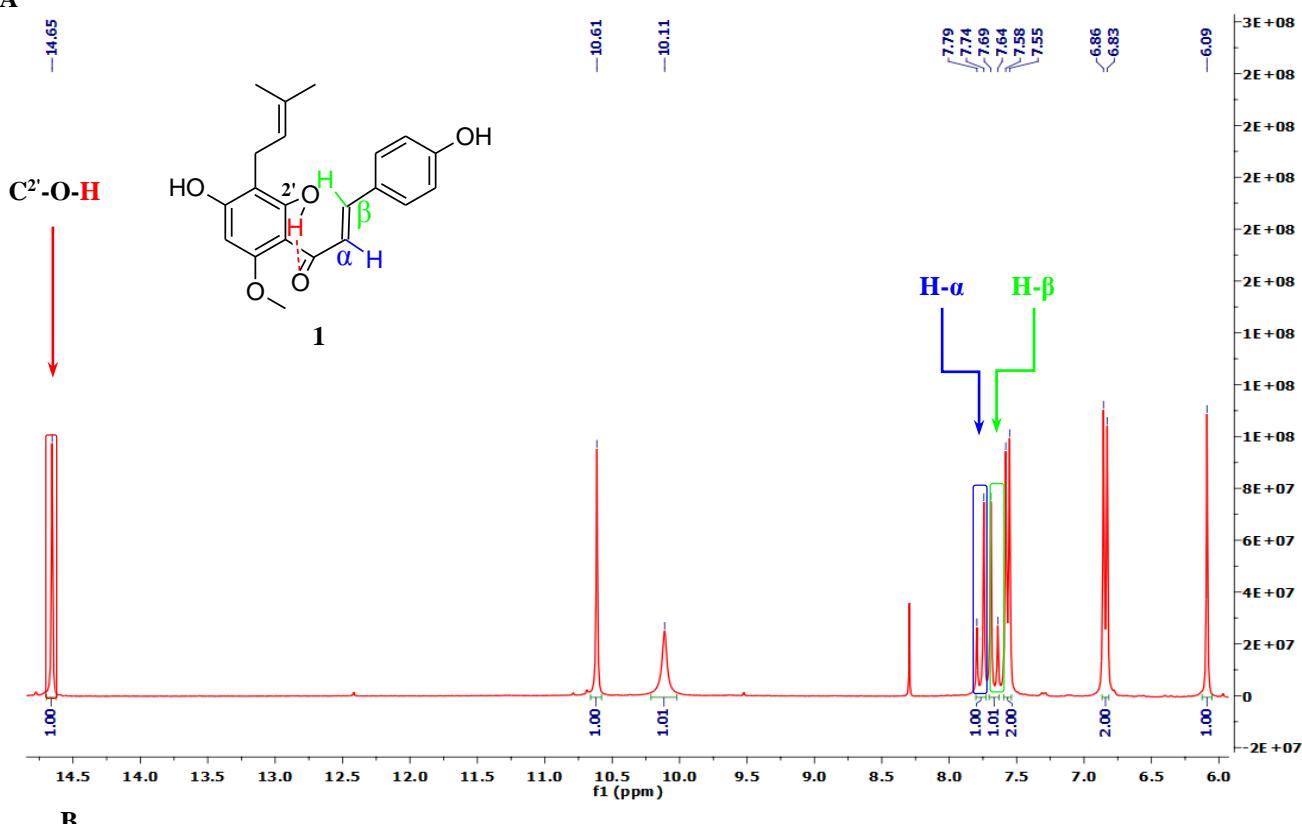


**Figure S5.**  $^1\text{H}$  NMR spectra of: A xanthohumol (**1**) (600 MHz,  $\text{DMSO}-d_6$ ), B (Z)-6,4'-dihydroxy-4-methoxy-7-prenyllaurone (**3**) (300 MHz,  $\text{DMSO}-d_6$ , Temp. 25 °C)

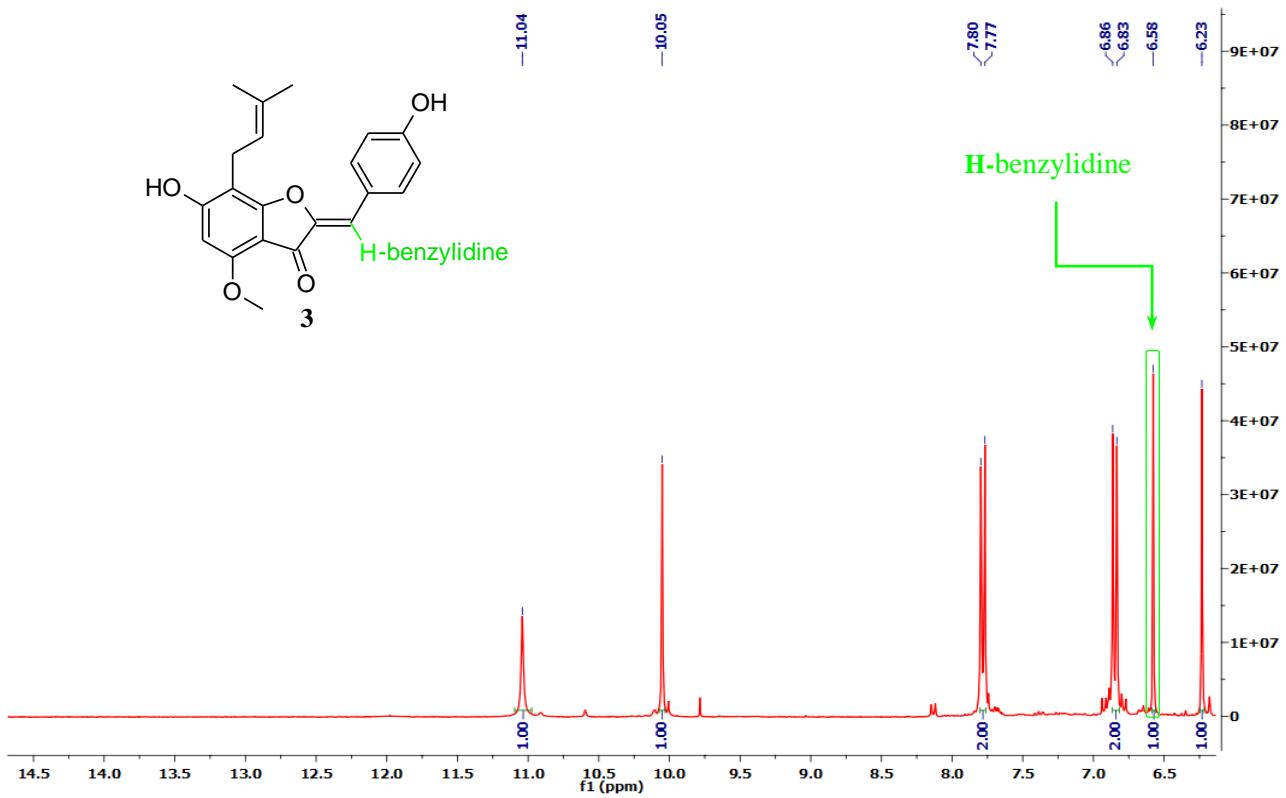


**Figure S6.** Fragments of  $^1\text{H}$  NMR spectra of: A xanthohumol (**1**) (600 MHz,  $\text{DMSO}-d_6$ ), B aurone (**3**) (300 MHz,  $\text{DMSO}-d_6$ , Temp. 25 °C)

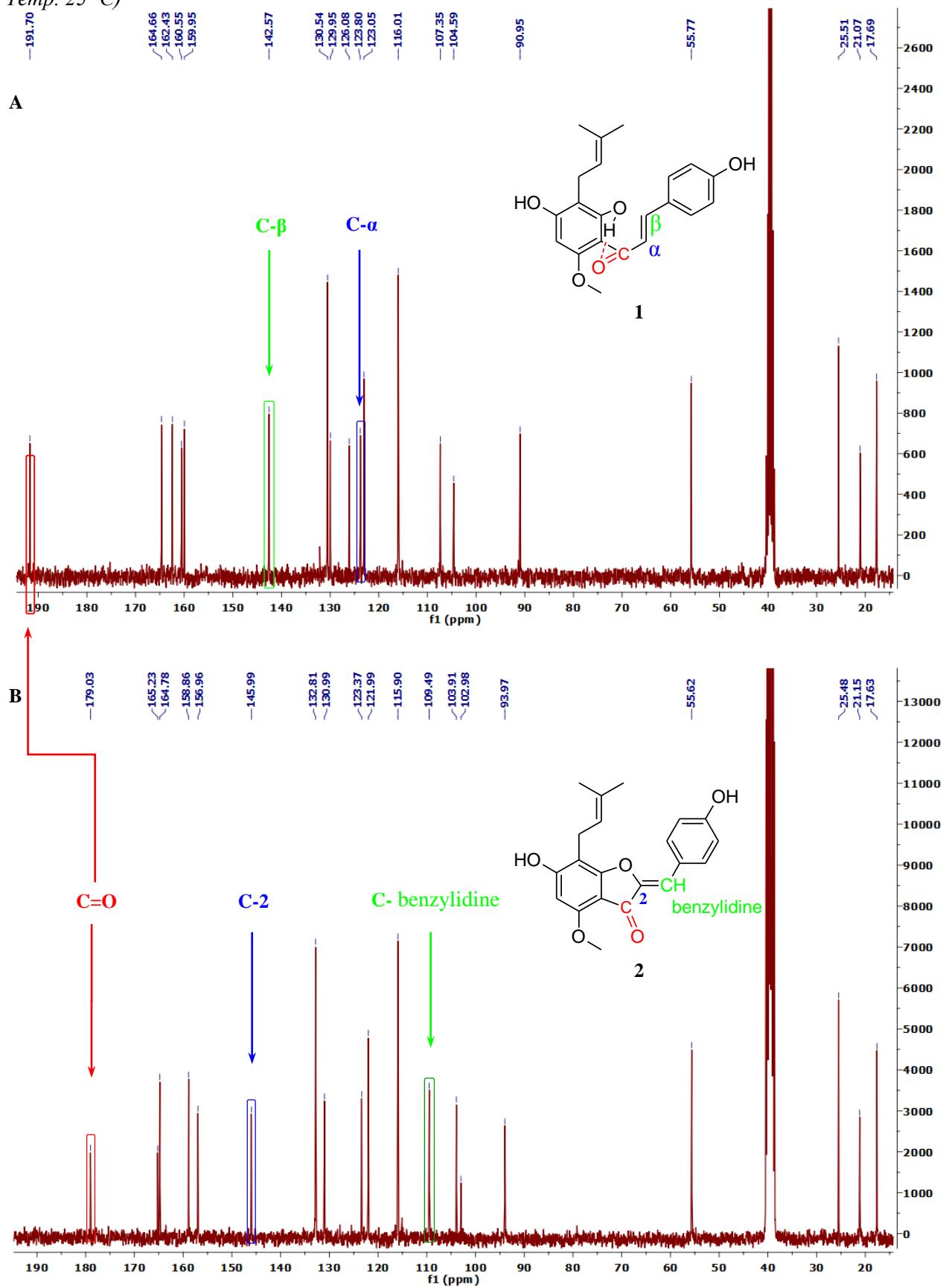
A



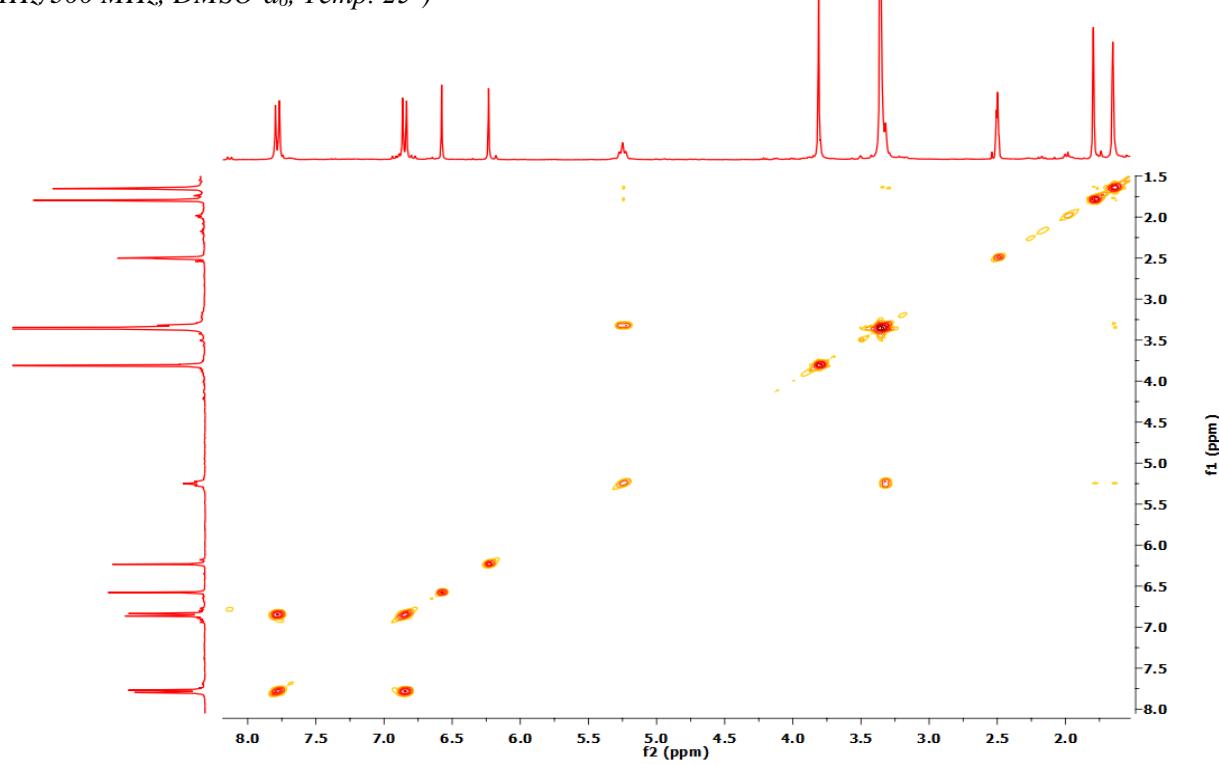
B



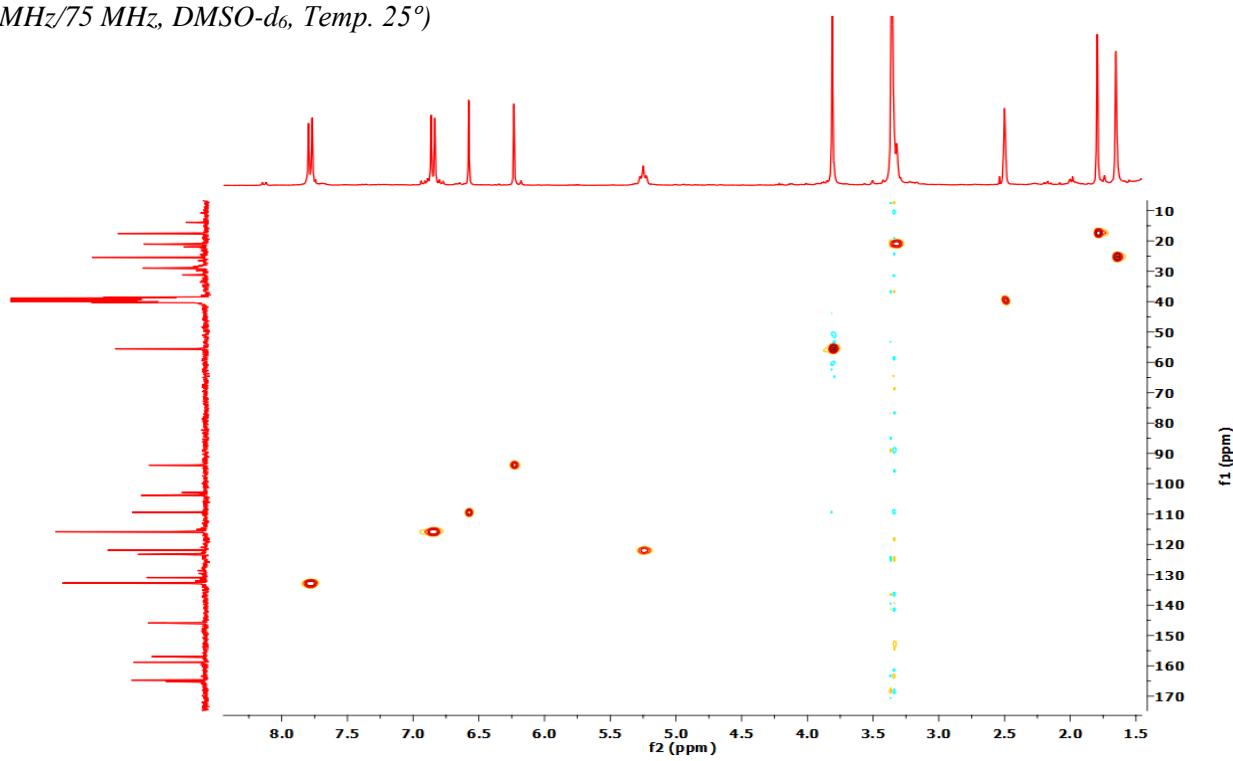
**Figure S7.**  $^{13}\text{C}$  NMR spectra of: **A** xanthohumol (**1**) (151 MHz,  $\text{DMSO-d}_6$ ), **B** auron (**3**) (75 MHz,  $\text{DMSO-d}_6$ , Temp. 25 °C)



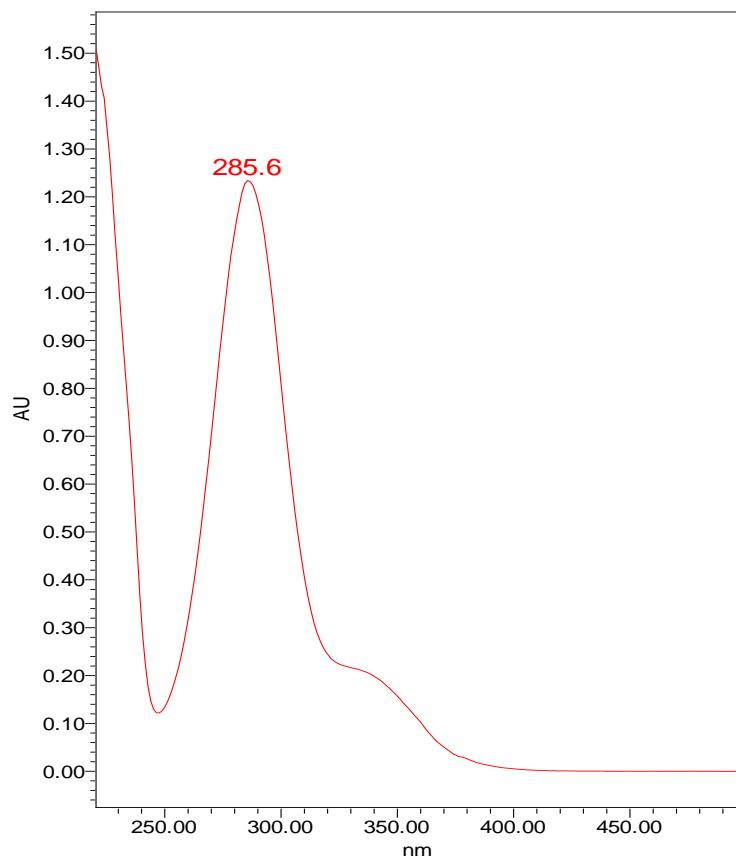
**Figure S8.**  $^1\text{H}$ - $^1\text{H}$  NMR (COSY) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone (**3**) (300 MHz/300 MHz, DMSO- $d_6$ , Temp. 25°)



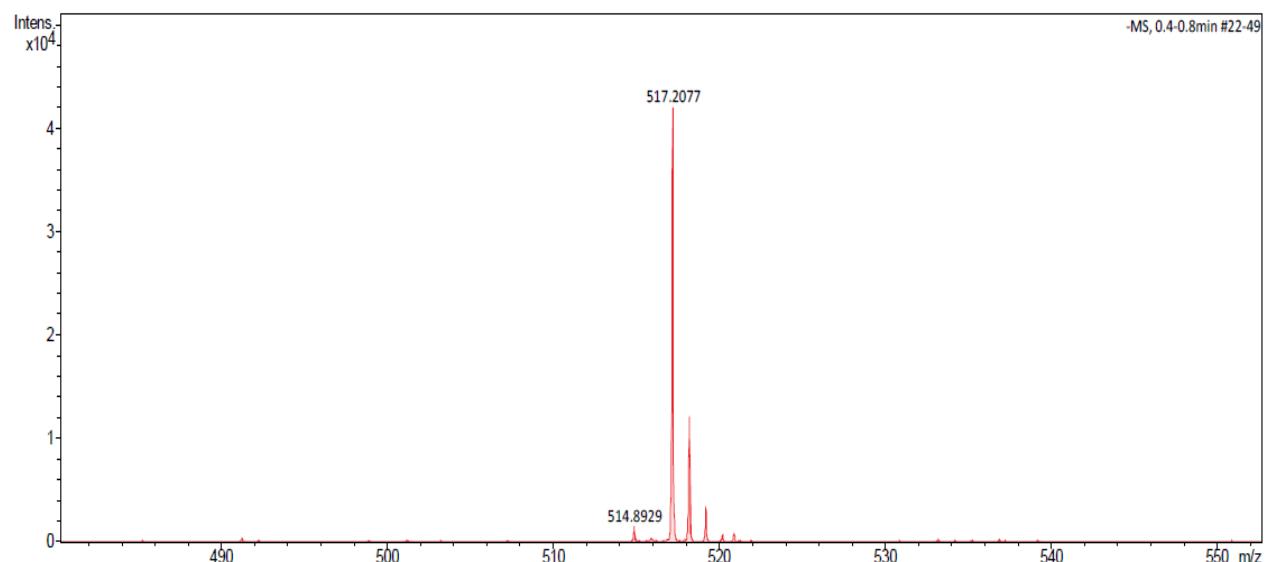
**Figure S9.**  $^1\text{H}$ - $^{13}\text{C}$  NMR (HSQC) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone (**3**) (300 MHz/75 MHz, DMSO- $d_6$ , Temp. 25°)



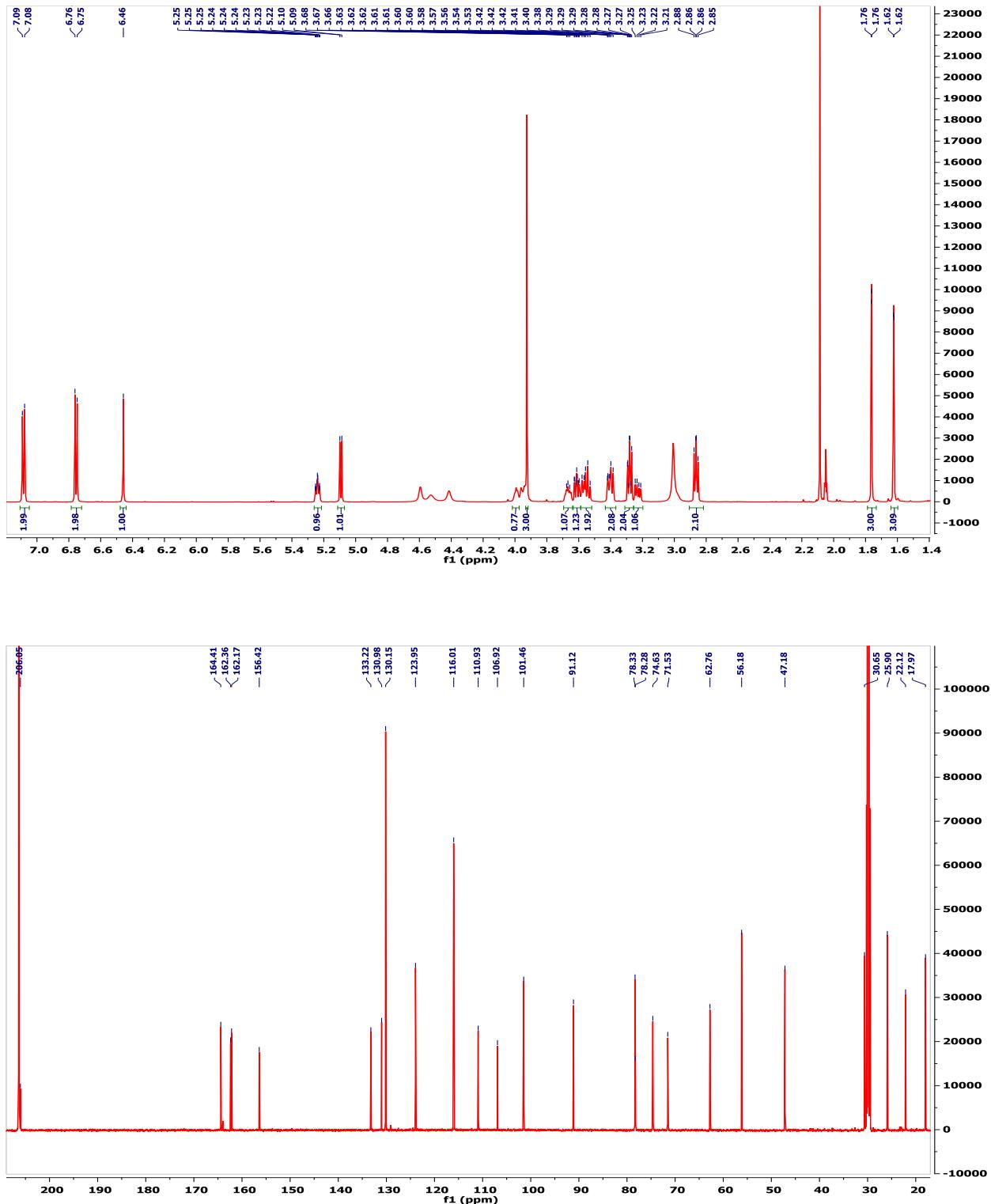
**Figure S10.** UV spectrum of  $\alpha,\beta$ -dihydroxanthohumol 4' -O- $\beta$ -D-glucopyranoside (**6**) (MeOH, Temp. 20 °C)



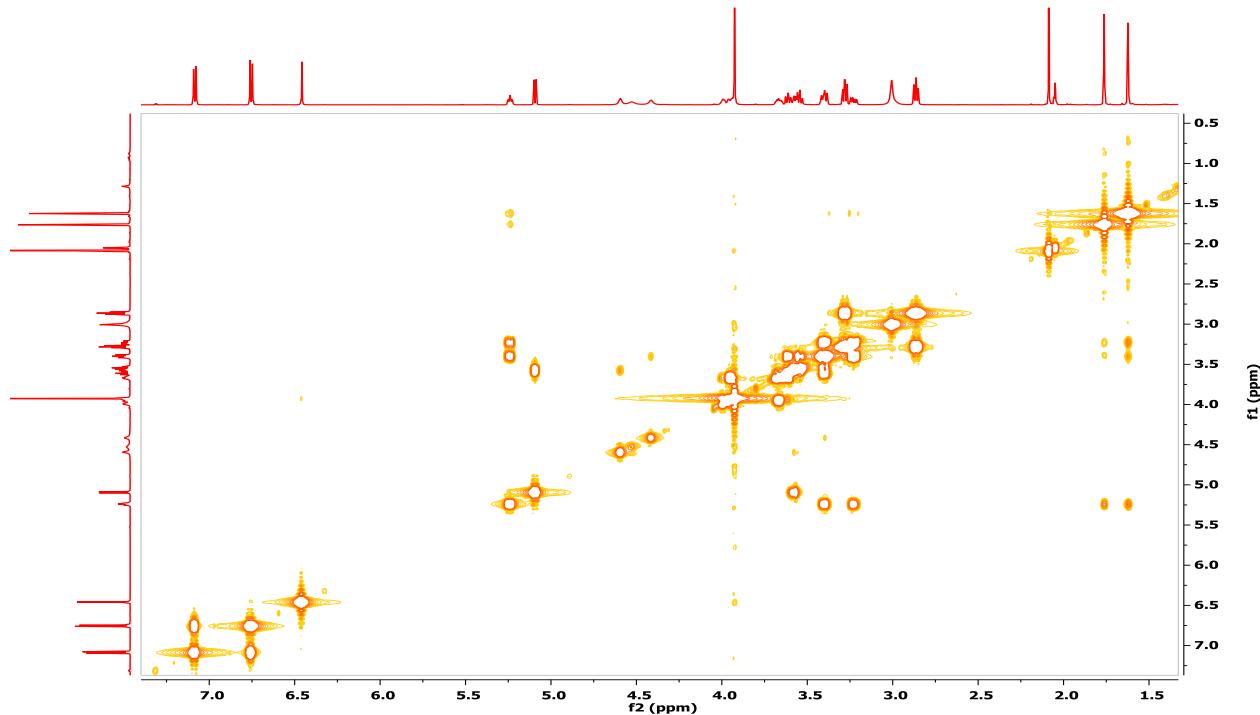
**Figure S11.** HRMS spectrum of  $\alpha,\beta$ -dihydroxanthohumol 4' -O- $\beta$ -D-glucopyranoside (**6**)



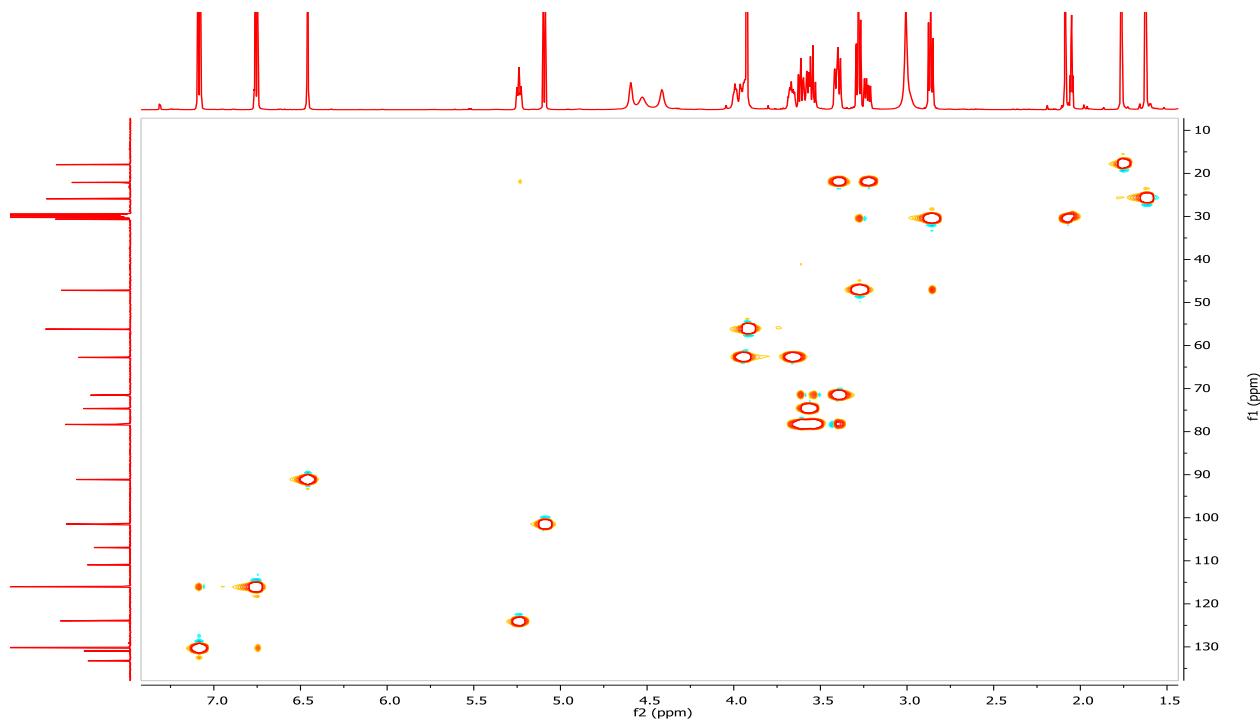
**Figure S12.**  $^1\text{H}$  NMR (600 MHz) and  $^{13}\text{C}$  NMR (151 MHz) spectra of  $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-glucopyranoside (**6**) (Acetone- $d_6$ , Temp. 25 °C)



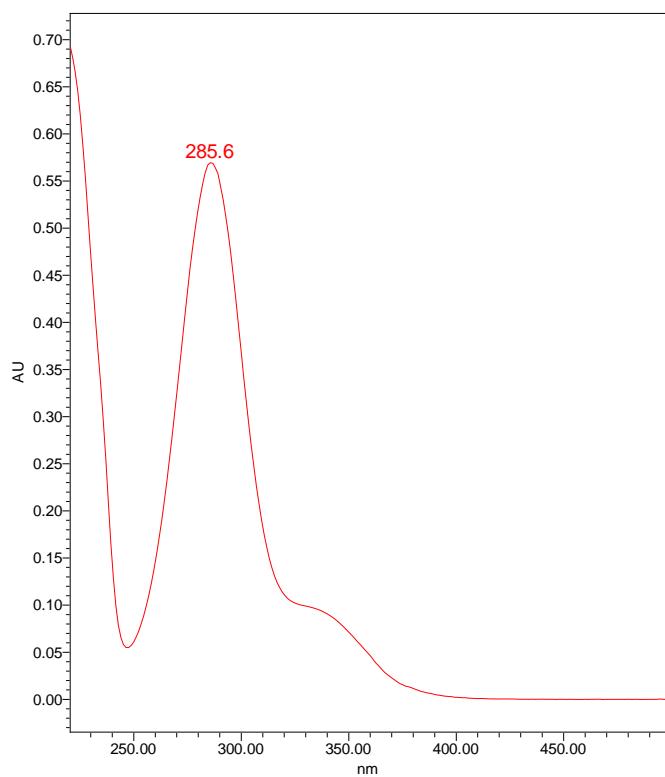
**Figure S13.**  $^1\text{H}$  NMR -  $^1\text{H}$  NMR (COSY) spectrum of  $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-glucopyranoside (**6**) (600 MHz/600 MHz, Acetone- $d_6$ , Temp. 25°)



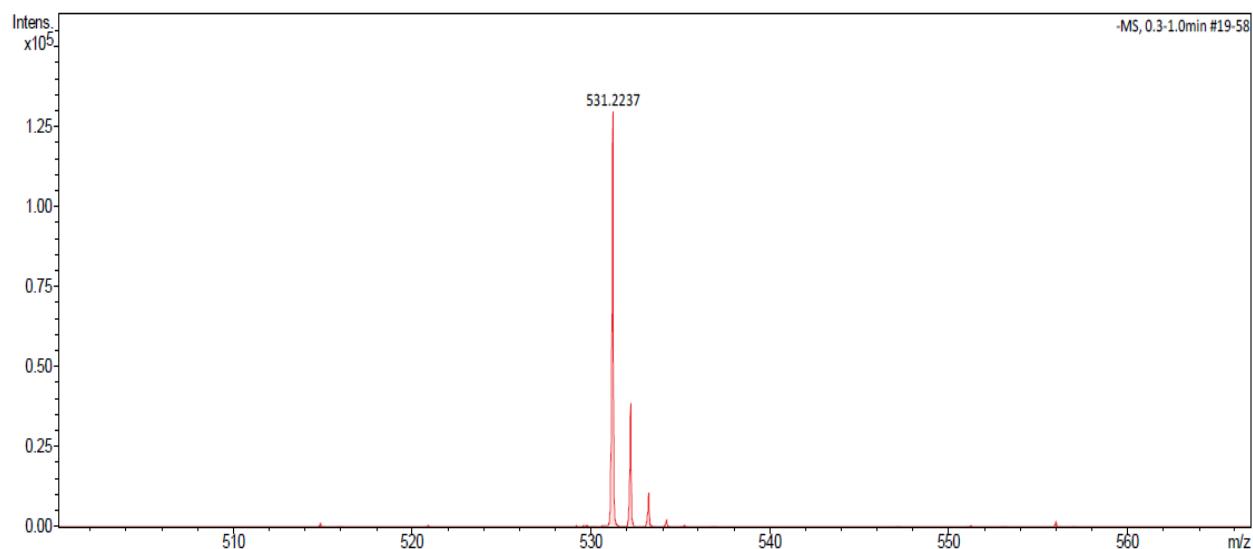
**Figure S14.**  $^1\text{H}$  NMR -  $^{13}\text{C}$  NMR (HSQC) spectrum of  $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-glucopyranoside (**6**) (600 MHz/151 MHz, Acetone- $d_6$ , Temp. 25°)



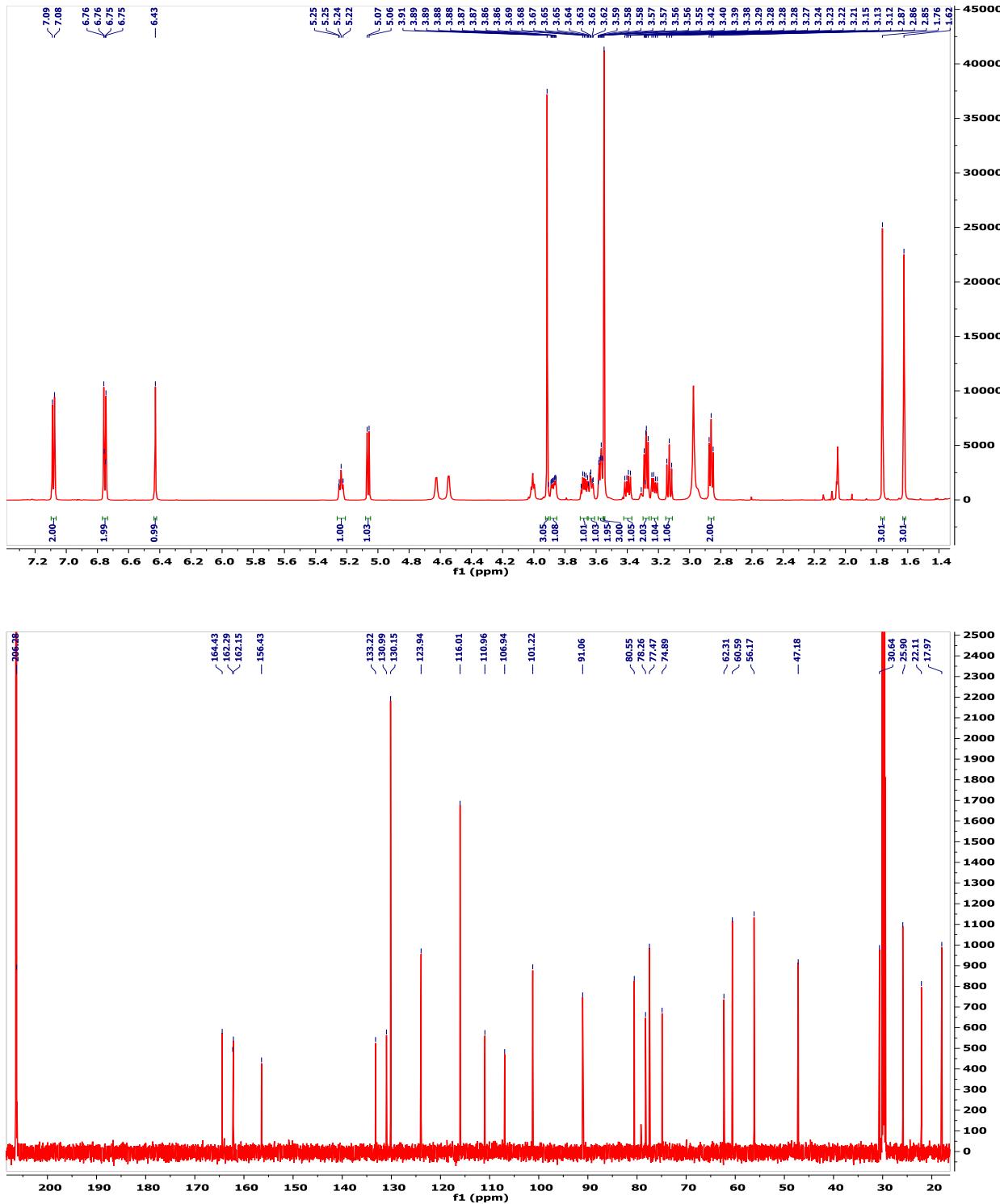
**Figure S15.** UV spectrum of  $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4''-O-methyl)glucopyranoside (**7**) (MeOH, Temp. 20 °C)



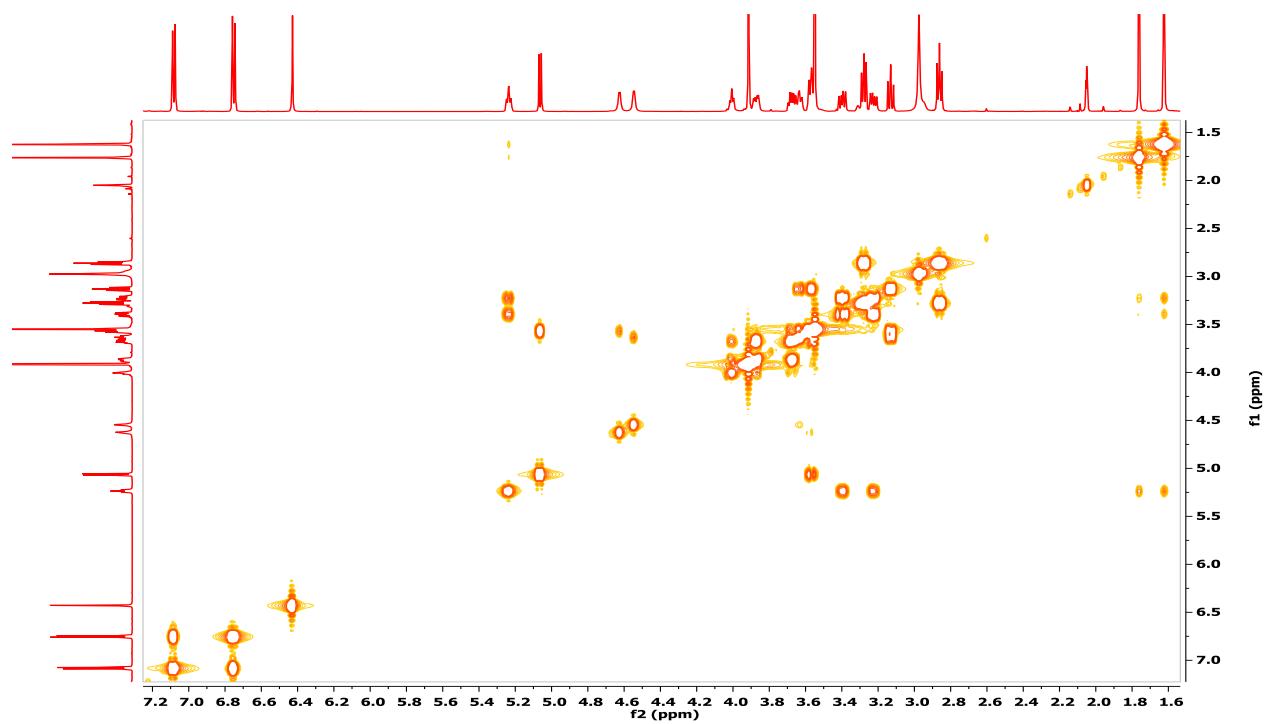
**Figure S16.** HRMS spectrum of  $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4''-O-methyl)glucopyranoside (**7**)



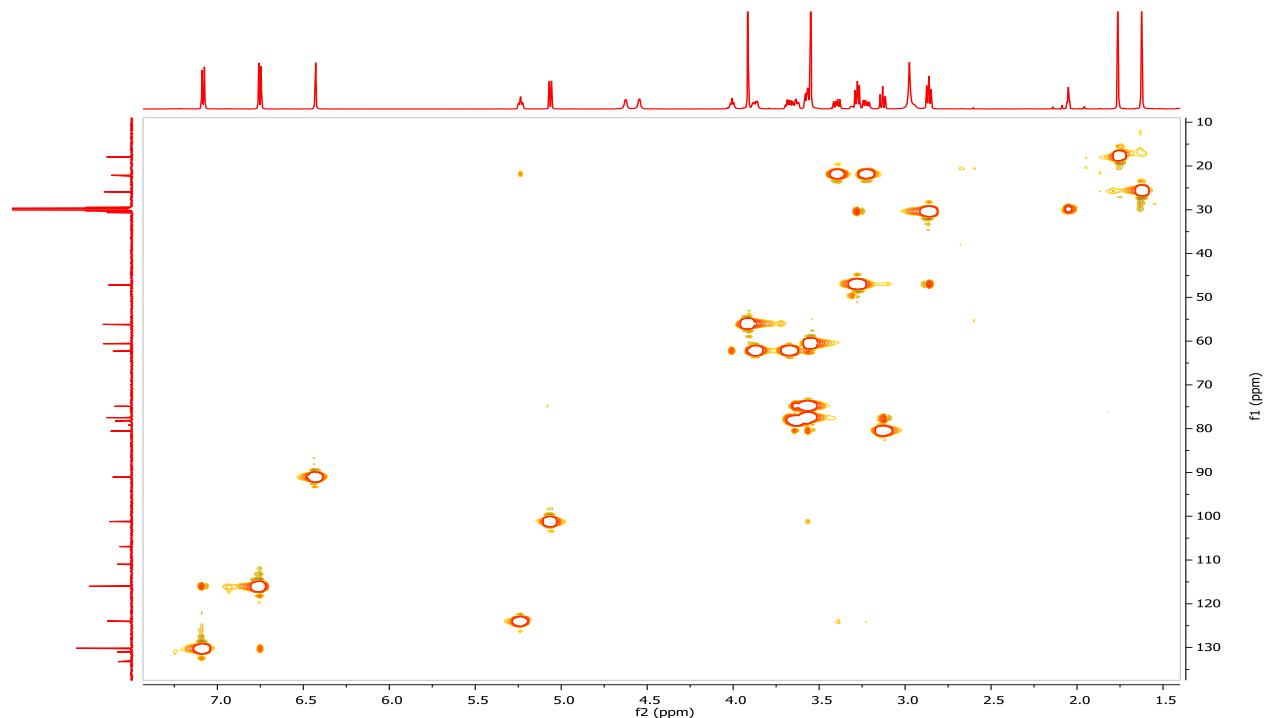
**Figure S17.**  $^1\text{H}$  NMR (600 MHz) and  $^{13}\text{C}$  NMR (151 MHz) spectra of  $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4''-O-methyl)glucopyranoside (**7**) (Acetone- $d_6$ , Temp. 25 °C).



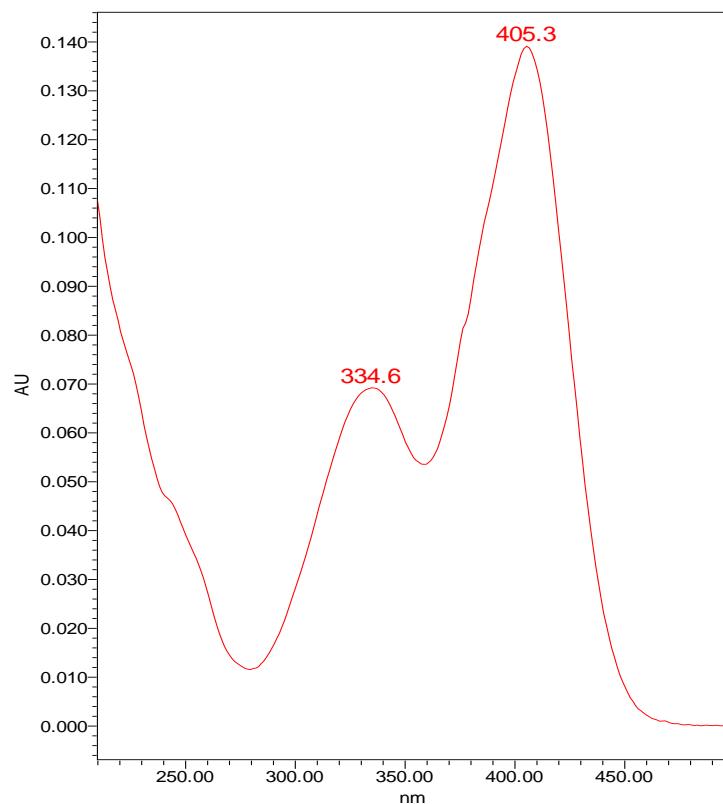
**Figure S18.**  $^1\text{H}$  NMR -  $^1\text{H}$  NMR (COSY) spectrum of  $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4''-O-methyl)glucopyranoside (**7**) (600 MHz/600 MHz, Acetone- $d_6$ , Temp. 25°)



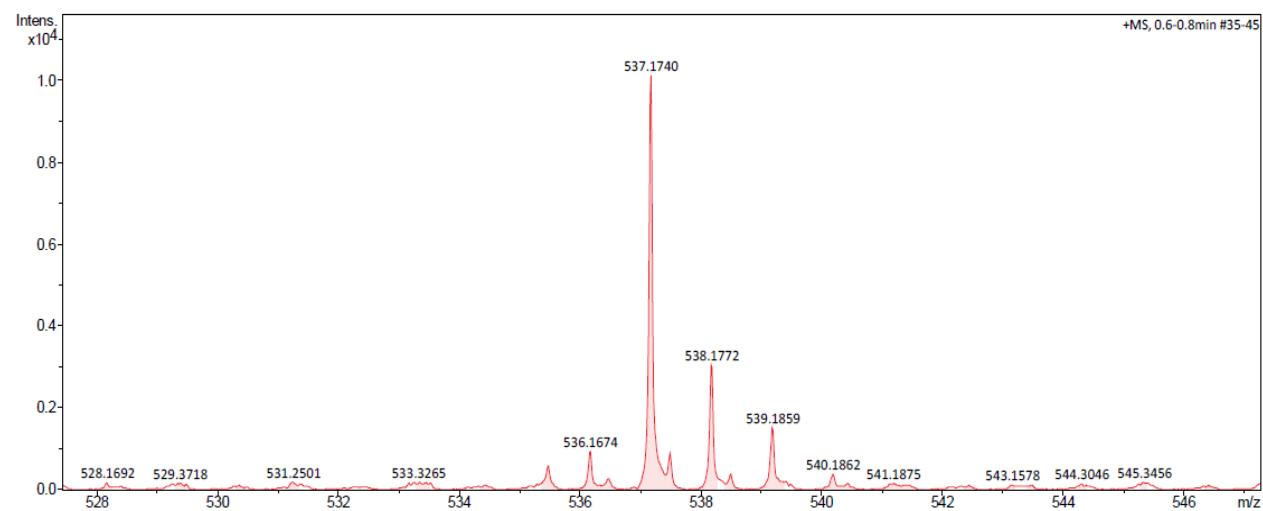
**Figure S19.**  $^1\text{H}$  NMR -  $^{13}\text{C}$  NMR (HSQC) spectrum of  $\alpha,\beta$ -dihydroxanthohumol 7-O- $\beta$ -D-(4''-O-methyl)glucopyranoside (**7**) (600 MHz/151 MHz, Acetone- $d_6$ , Temp. 25°)



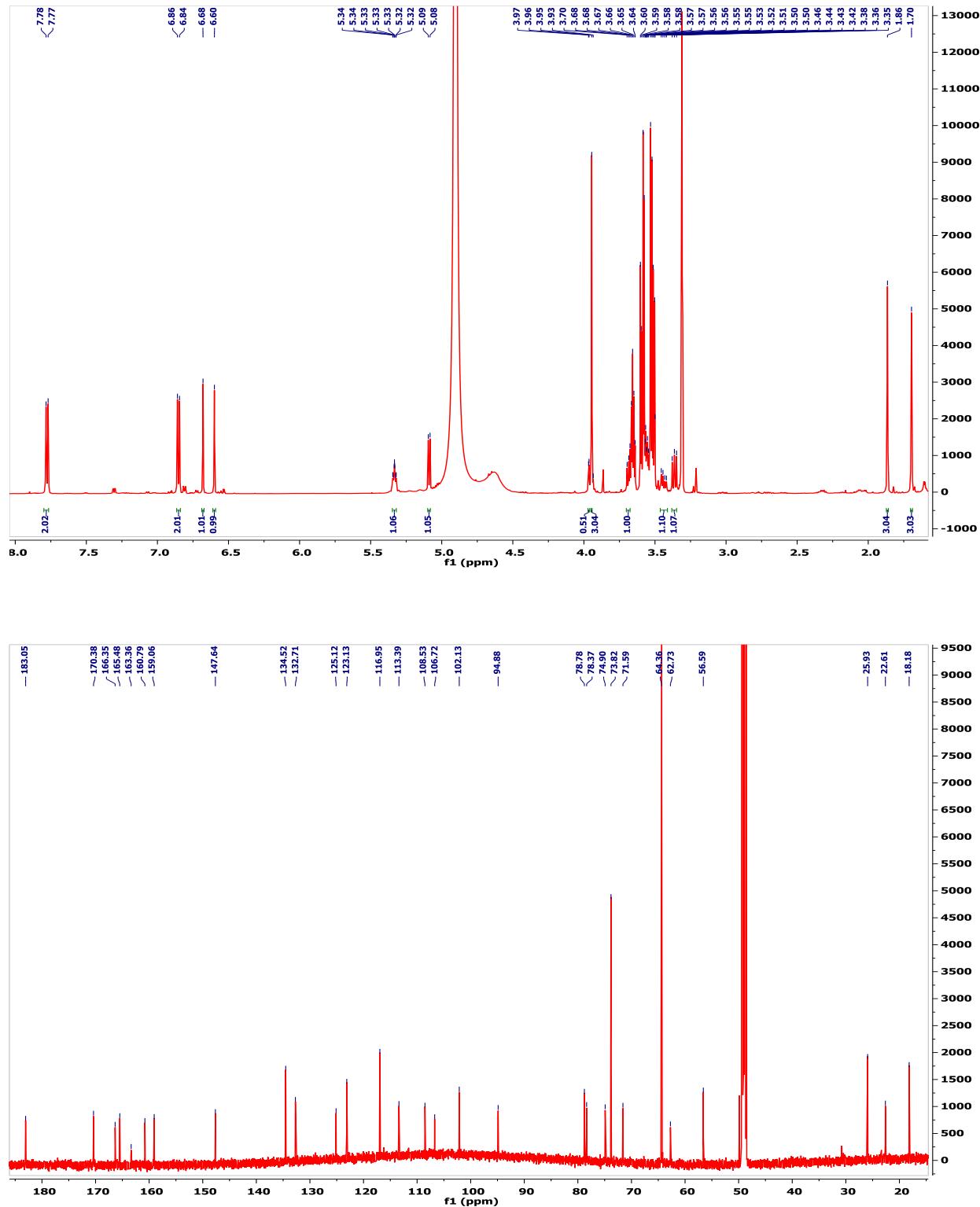
**Figure S20.** UV spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside (**8**) (MeOH, Temp. 20 °C)



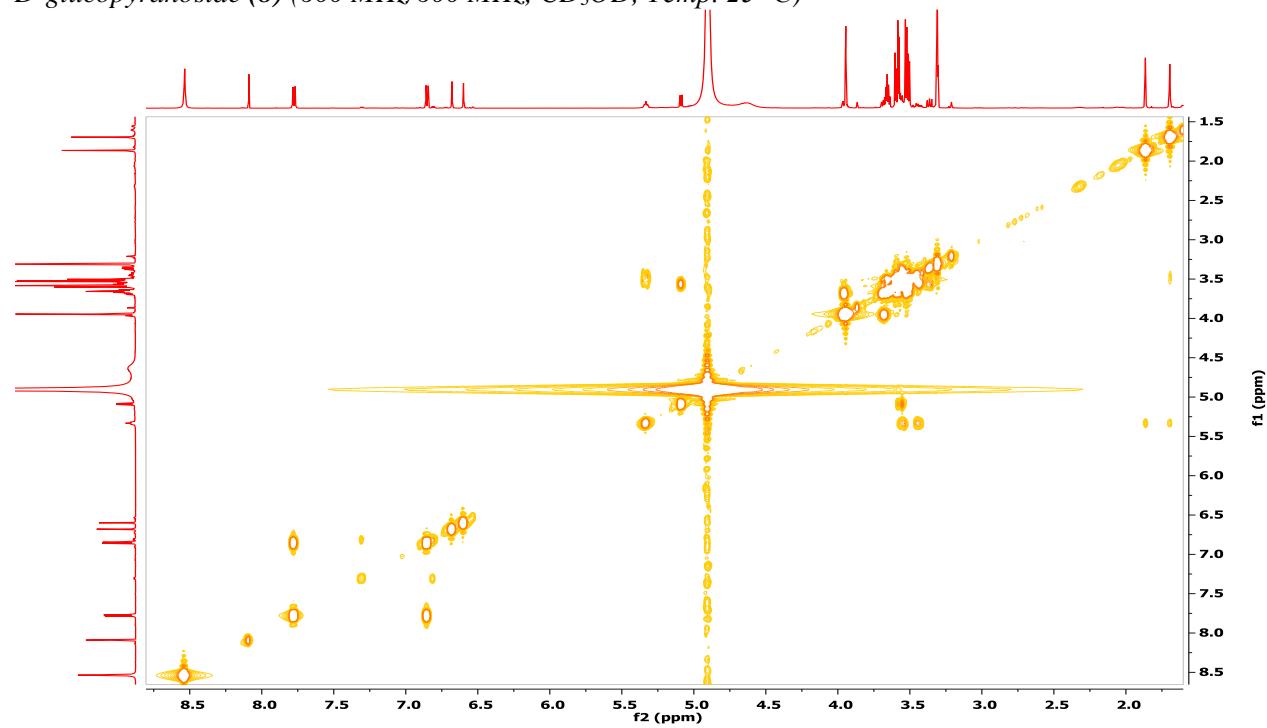
**Figure S21.** HRMS spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside (**8**)



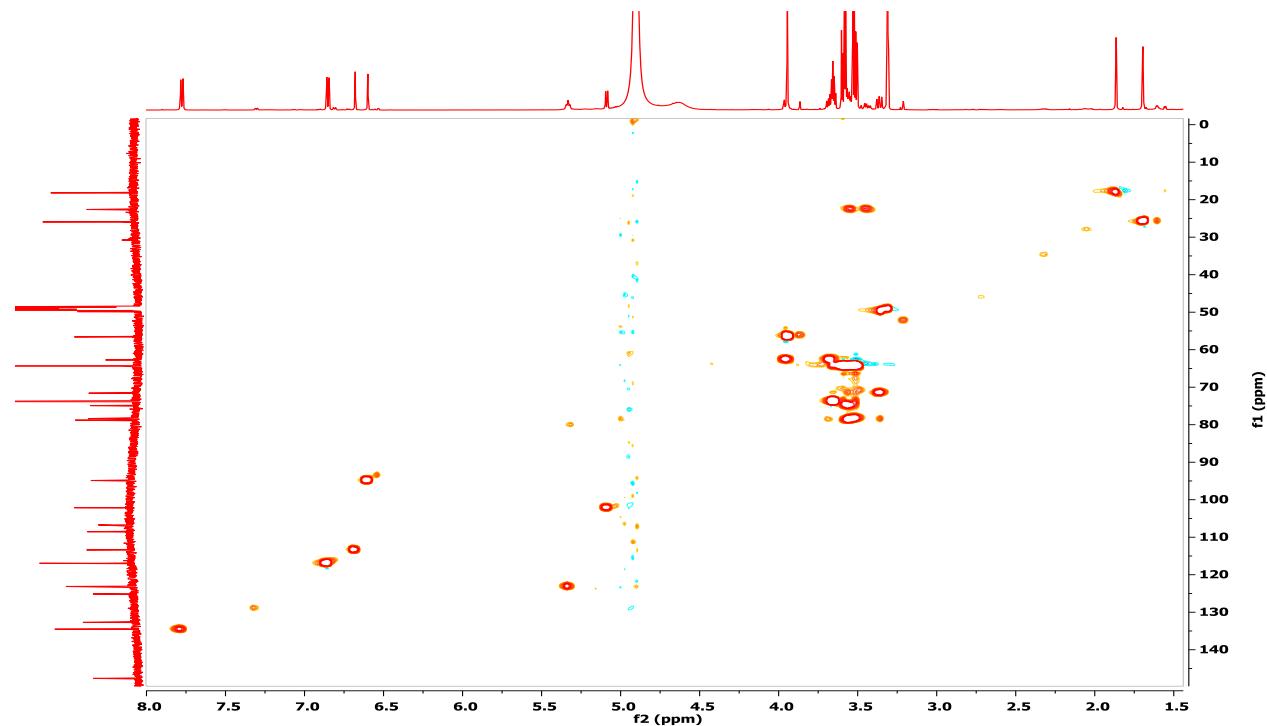
**Figure S22.**  $^1\text{H}$  NMR (600 MHz) and  $^{13}\text{C}$  NMR (151 MHz) spectra of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside (**8**)  $\text{CD}_3\text{OD}$ , Temp. 25 °C



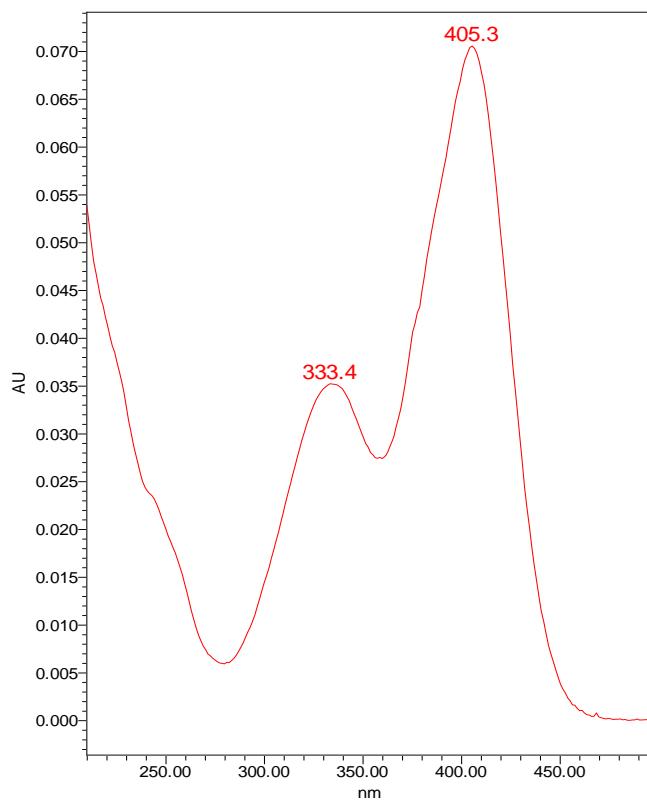
**Figure S23.**  $^1\text{H}$  NMR -  $^1\text{H}$  NMR (COSY) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside (**8**) (600 MHz/600 MHz,  $\text{CD}_3\text{OD}$ , Temp. 25 °C)



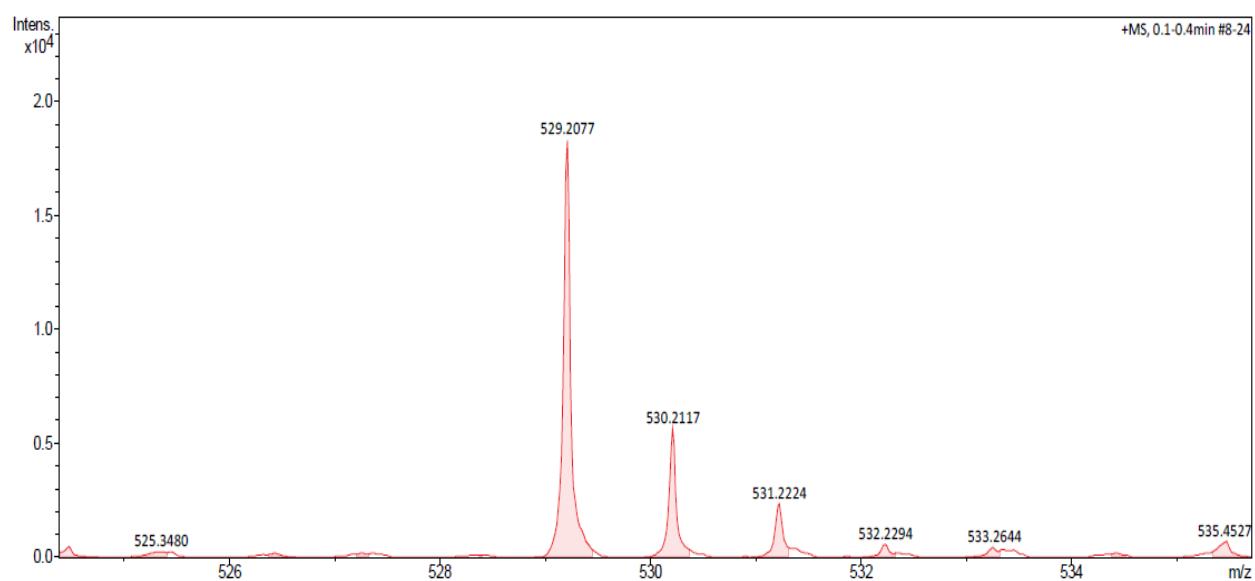
**Figure S24.**  $^1\text{H}$  NMR -  $^{13}\text{C}$  NMR (HSQC) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-glucopyranoside (**8**) (600 MHz/151 MHz,  $\text{CD}_3\text{OD}$ , Temp. 25 °C)



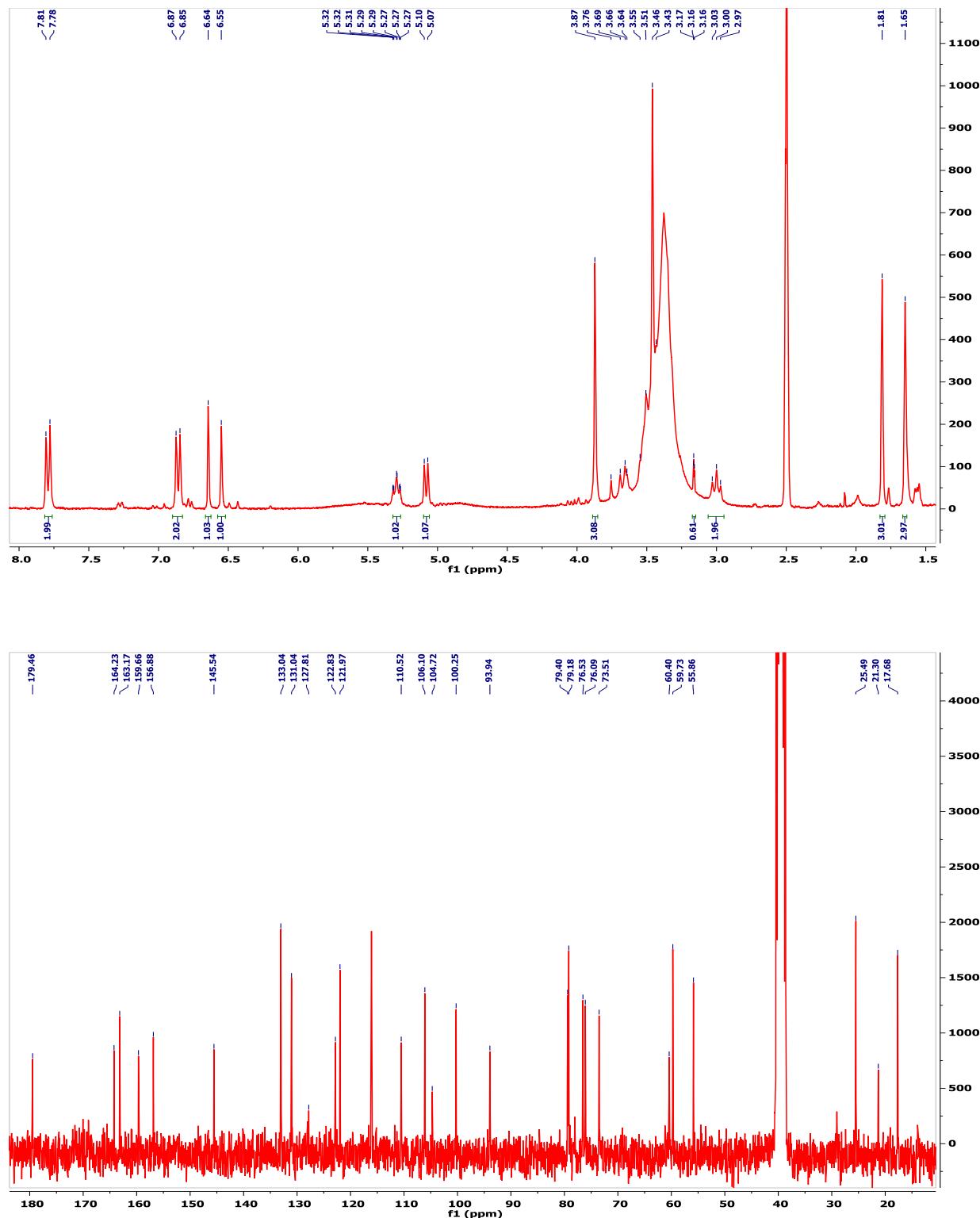
**Figure S25.** UV spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside (**9**) (MeOH, Temp. 20 °C)



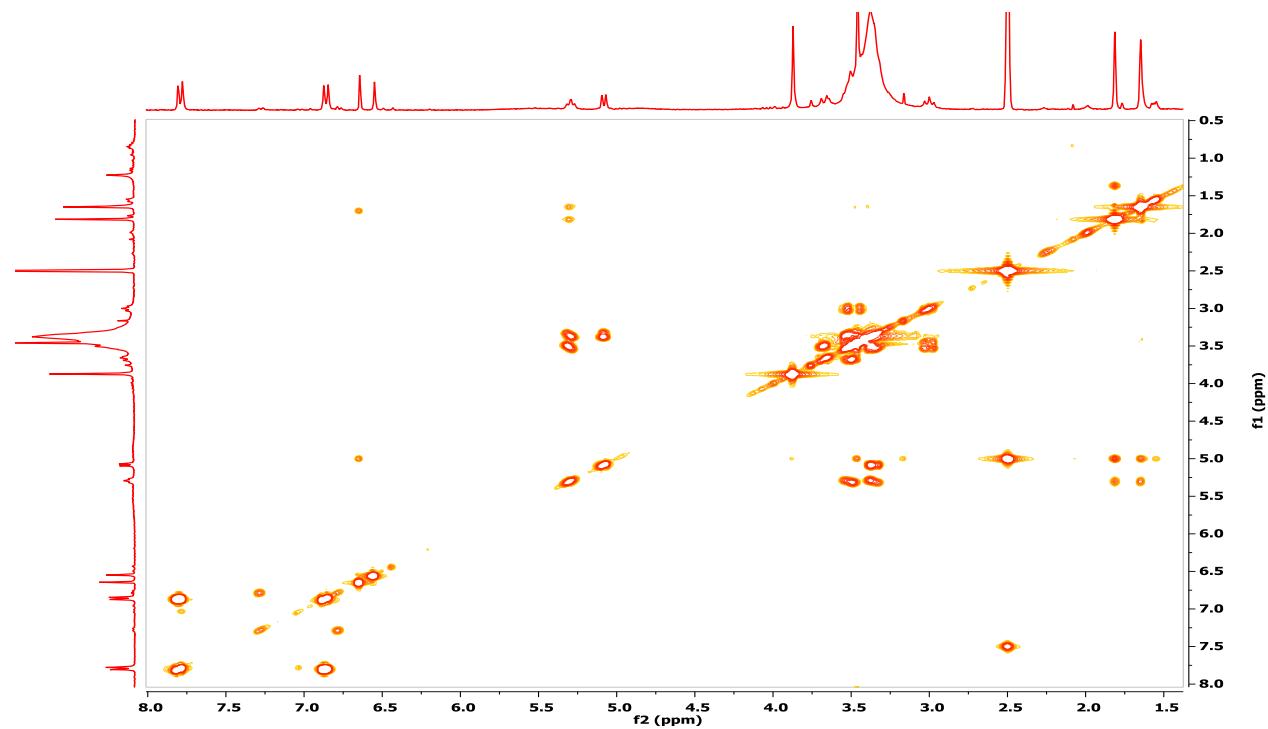
**Figure S26.** HRMS spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside (**9**)



**Figure S27.**  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz,) spectra of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside (**9**) (DMSO- $d_6$ , Temp. 25 °C)



**Figure S28.**  $^1\text{H}$  NMR -  $^1\text{H}$  NMR (COSY) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside (**9**) (600 MHz/600 MHz,  $\text{DMSO}-d_6$ , Temp. 25 °C)



**Figure S29.**  $^1\text{H}$  NMR -  $^{13}\text{C}$  NMR (HSQC) spectrum of (Z)-6,4'-dihydroxy-4-methoxy-7-prenylaurone 6-O- $\beta$ -D-(4'''-O-methyl)glucopyranoside (**9**) (600 MHz/151 MHz,  $\text{DMSO}-d_6$ , Temp. 25 °C)

