

## Supporting Information

*Rec. Nat. Prod.* **14:1** (2020) 83-88

### Natural Glycosides from *Indigofera stachyoides radix*

Wei Zhou<sup>1#</sup>, Zhong Lei<sup>1,2#</sup>, Donna Lai<sup>3</sup>, George Q. Li<sup>3</sup>, Yan Liang<sup>1</sup>,  
Xiaoyan Zhang<sup>2</sup>, Junlae Cho<sup>3\*</sup> and Xiaoyan Hao<sup>1\*</sup>

<sup>1</sup> School of Pharmacy, Guizhou Medical University, Guiyang 550025, Guizhou, China

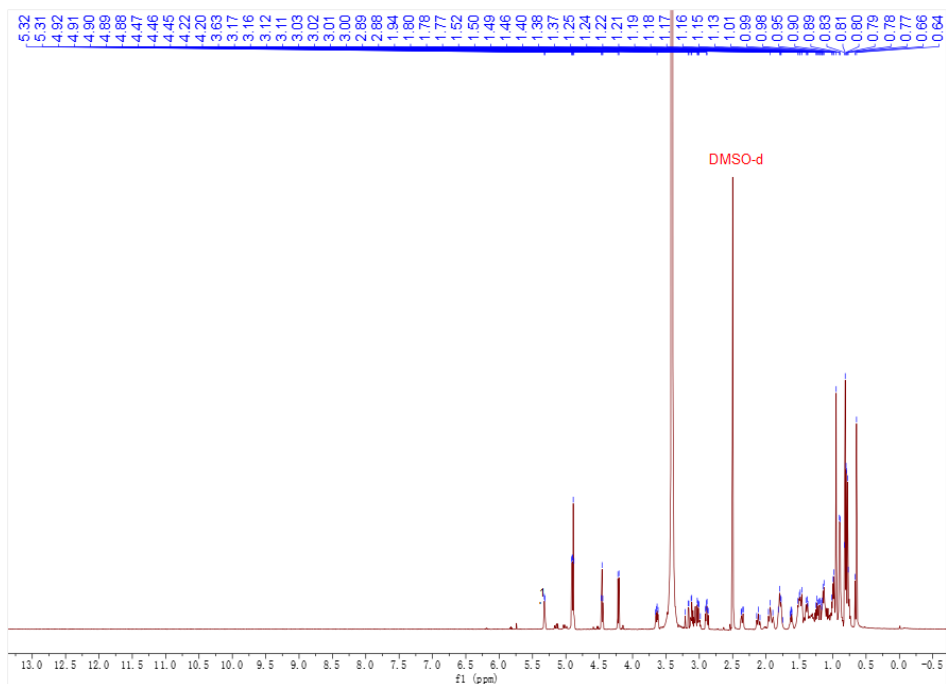
<sup>2</sup> School of Basic Medical Sciences, Guizhou Medical University, Guiyang 550025, Guizhou,  
China

<sup>3</sup> Faculty of Medicine and Life Science, The University of Sydney, NSW, 2006, Australia

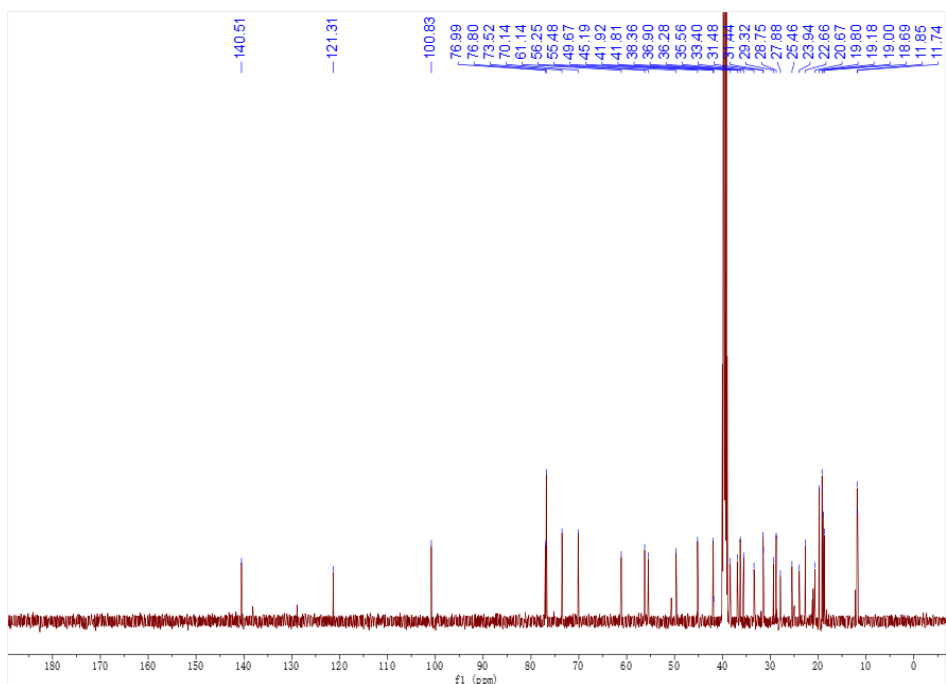
Table of Contents	Page
<b>Figure S1:</b> <sup>1</sup> H-NMR (500 MHz, DMSO- <i>d</i> <sub>6</sub> ) spectrum of compound <b>1</b> (β-sitosterol-D-glucoside)	3
<b>Figure S2:</b> <sup>13</sup> C NMR (126 MHz, DMSO- <i>d</i> <sub>6</sub> ) spectrum of compound <b>1</b> (β-sitosterol-D-glucoside)	3
<b>Figure S3:</b> <sup>1</sup> H NMR (500 MHz, CD <sub>3</sub> OD) spectrum of compound <b>2</b> (schizandriside)	4
<b>Figure S4:</b> <sup>13</sup> C NMR (126 MHz, CD <sub>3</sub> OD) spectrum of compound <b>2</b> (schizandriside)	4
<b>Figure S5:</b> <sup>1</sup> H NMR (600 MHz, CD <sub>3</sub> OD) spectrum of compound <b>3</b> (kaempferol-7-O-β-D-glucopyranoside)	5
<b>Figure S6:</b> <sup>13</sup> C NMR (151 MHz, CD <sub>3</sub> OD) spectrum of compound <b>3</b> (kaempferol-7-O-β-D-glucopyranoside)	5
<b>Figure S7:</b> <sup>1</sup> H NMR (600 MHz, CH <sub>3</sub> OD) spectrum of compound <b>4</b> (3,4,5-trimethoxyphenyl-O-β-D-glucopyranoside)	6
<b>Figure S8:</b> <sup>13</sup> C NMR (151 MHz, CH <sub>3</sub> OD) spectrum of compound <b>4</b> (3,4,5-trimethoxyphenyl-O-β-D-glucopyranoside)	6
<b>Figure S9:</b> <sup>1</sup> H-NMR (600 MHz, CH <sub>3</sub> OD) spectrum of compound <b>5</b> (2-methoxy-4-(2'-hydroxyethyl)-phenol-1-O-β-D-glucopyranoside)	7
<b>Figure S10:</b> <sup>13</sup> C NMR (151 MHz, CH <sub>3</sub> OD) spectrum of compound <b>5</b> (2-methoxy-4-(2'-hydroxyethyl)-phenol-1-O-β-D-glucopyranoside)	7
<b>Figure S11:</b> <sup>1</sup> H-NMR (600 MHz, CH <sub>3</sub> OD) spectrum of compound <b>6</b> (2-(3-hydroxy-4-methoxyphenyl) ethyl 1-O-β-D-glucopyranoside)	8
<b>Figure S12:</b> <sup>13</sup> C NMR (151 MHz, CH <sub>3</sub> OD) spectrum of compound <b>6</b> (2-(3-hydroxy-4-methoxyphenyl) ethyl 1-O-β-D-glucopyranoside)	8
<b>Figure S13:</b> (-)ESI-MS spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone)	9
<b>Figure S14:</b> <sup>1</sup> H-NMR (600 MHz, CH <sub>3</sub> OD) spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone)	9
<b>Figure S15:</b> Expansion of the <sup>1</sup> H-NMR (600 MHz, CH <sub>3</sub> OD) spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone) (From 6.50 to 8.50 ppm)	10

<b>Figure S16:</b> $^{13}\text{C}$ -NMR (151 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone)	10
<b>Figure S17:</b> DEPT90 (151 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone)	11
<b>Figure S18:</b> DEPT135 (151 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone)	11
<b>Figure S19:</b> H-H COSY (600 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone)	12
<b>Figure S20:</b> HMBC (600 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone)	12
<b>Figure S21:</b> Expansion of the HMBC (600 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone) (From 6.50 to 9.50 in $^1\text{H}$ -NMR, 100.0 to 180.0 in $^{13}\text{C}$ -NMR)	13
<b>Figure S22:</b> HSQC (600 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>7</b> (7, 4'-dihydroxyl-3'-methoxyisoflavone)	13
<b>Figure S23:</b> $^1\text{H}$ NMR (600 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>8</b> (calycosin)	14
<b>Figure S24:</b> $^{13}\text{C}$ NMR (151 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>8</b> (calycosin)	14
<b>Figure S25:</b> $^1\text{H}$ -NMR (600 MHz, $\text{CH}_3\text{OD}$ ) spectrum of compound <b>9</b> (7-hydroxyl-4'-methoxyflavanone)	15
<b>Figure S26:</b> $^{13}\text{C}$ NMR (151 MHz) spectrum of compound <b>9</b> (7-hydroxyl-4'-methoxyflavanone)	15
<b>Figure S27:</b> $^1\text{H}$ -NMR (500 MHz, $\text{CD}_3\text{COCD}_3$ ) spectrum of compound <b>10</b> (maackiain)	16
<b>Figure S28:</b> $^{13}\text{C}$ NMR (126 MHz, $\text{CD}_3\text{COCD}_3$ ) spectrum of compound <b>10</b> (maackiain)	16
<b>Figure S29:</b> $^1\text{H}$ -NMR (500 MHz, $\text{CDCl}_3$ ) spectrum of compound <b>11</b> (stigmasterol)	18
<b>Figure S30:</b> $^{13}\text{C}$ NMR (126 MHz, $\text{CDCl}_3$ ) spectrum of compound <b>11</b> (stigmasterol)	18
<b>Figure S31:</b> Key $^1\text{H}$ - $^1\text{H}$ COSY and HMBC correlations of compound <b>7</b>	20

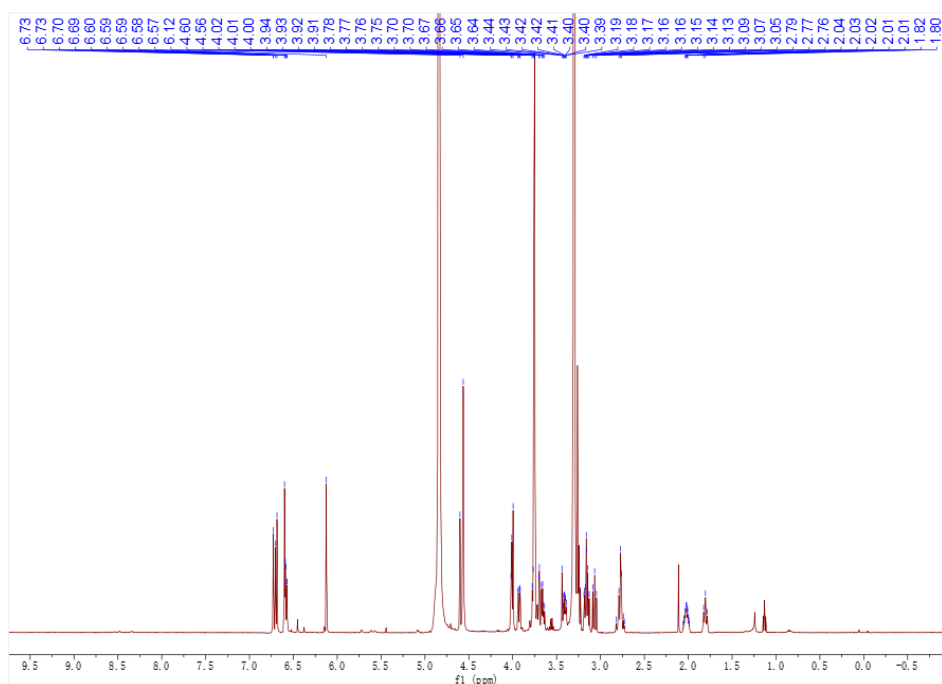
---



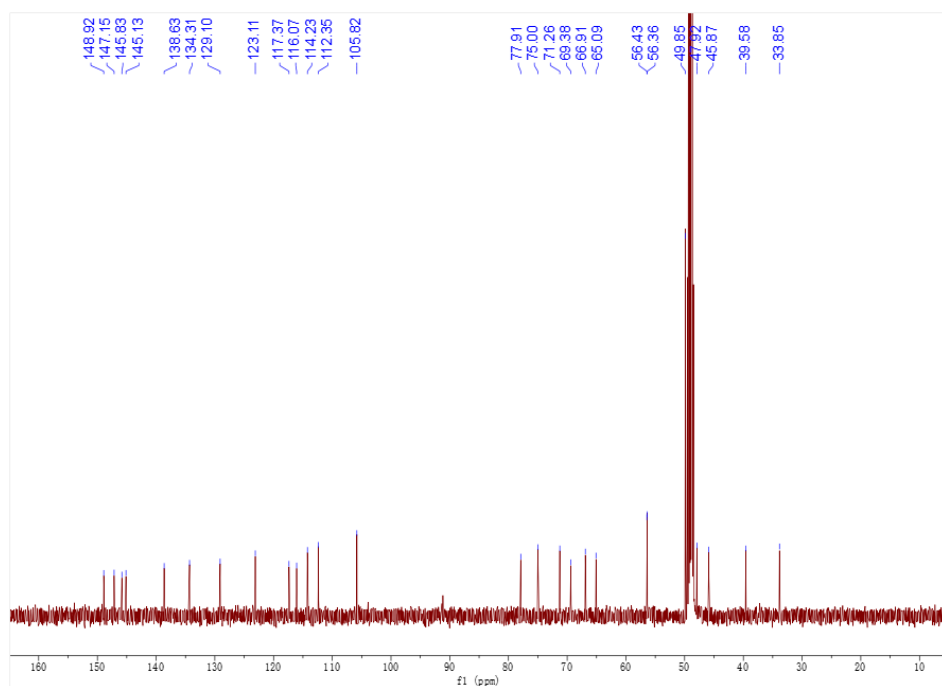
**Figure S1:**  $^1\text{H}$ -NMR (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound **1** ( $\beta$ -sitosterol-D-glucoside)



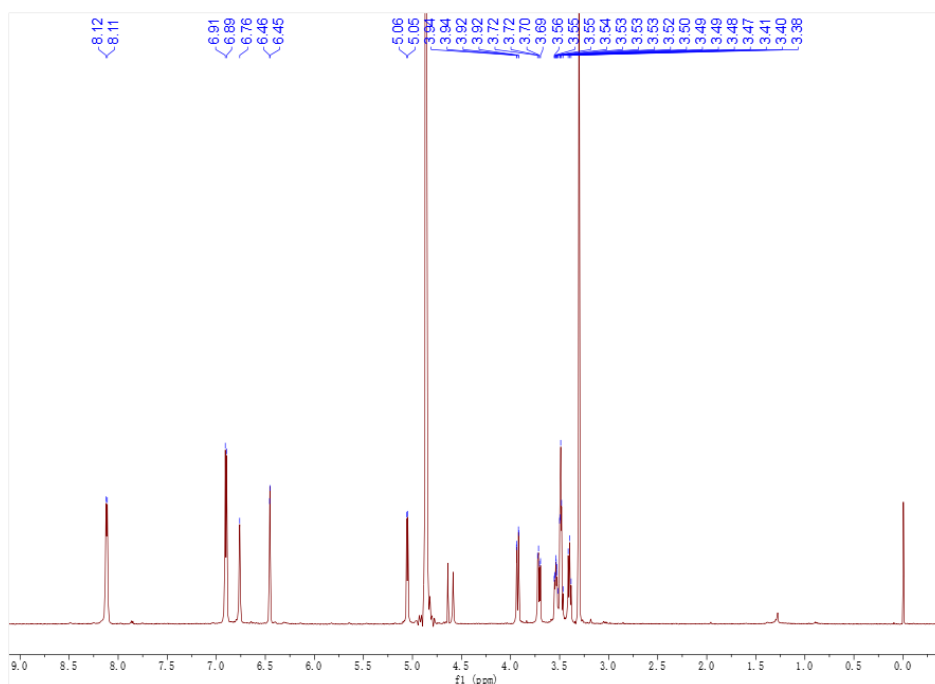
**Figure S2:**  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound **1** ( $\beta$ -sitosterol-D-glucoside)



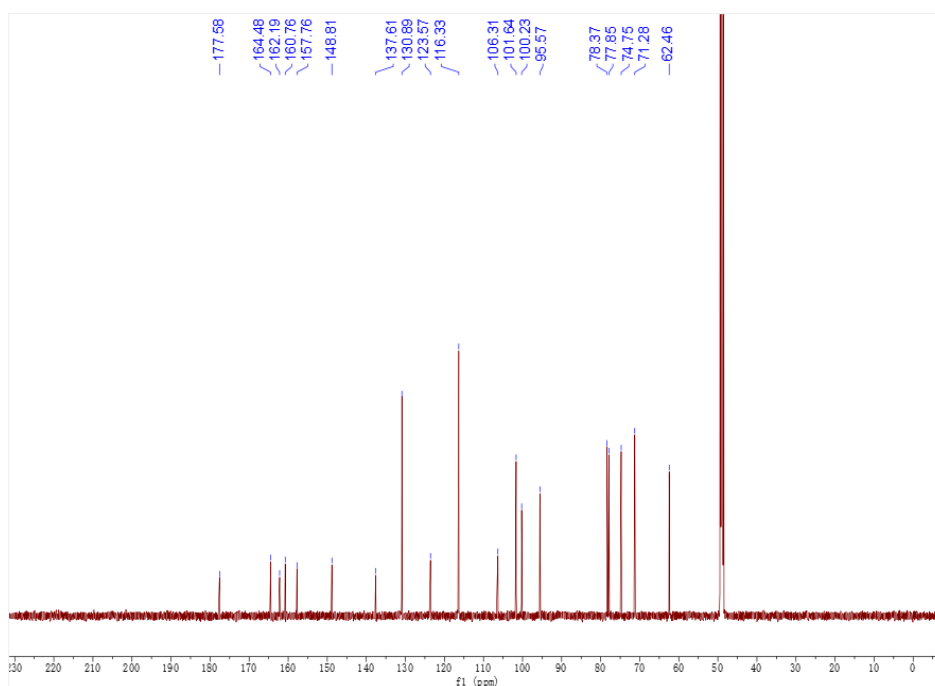
**Figure S3:**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **2** (schizandriside)



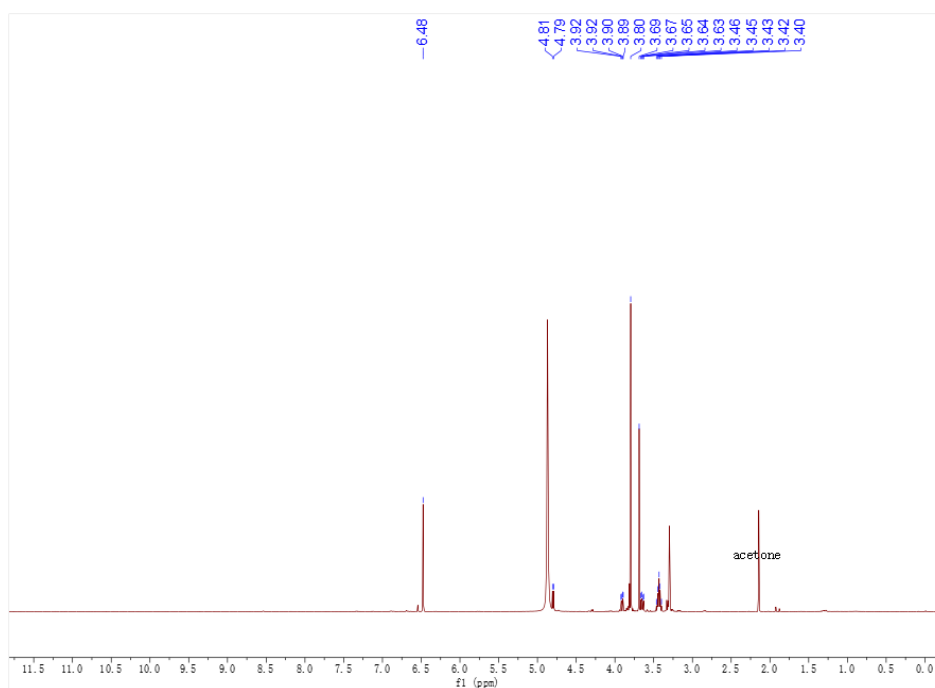
**Figure S4:**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **2** (schizandriside)



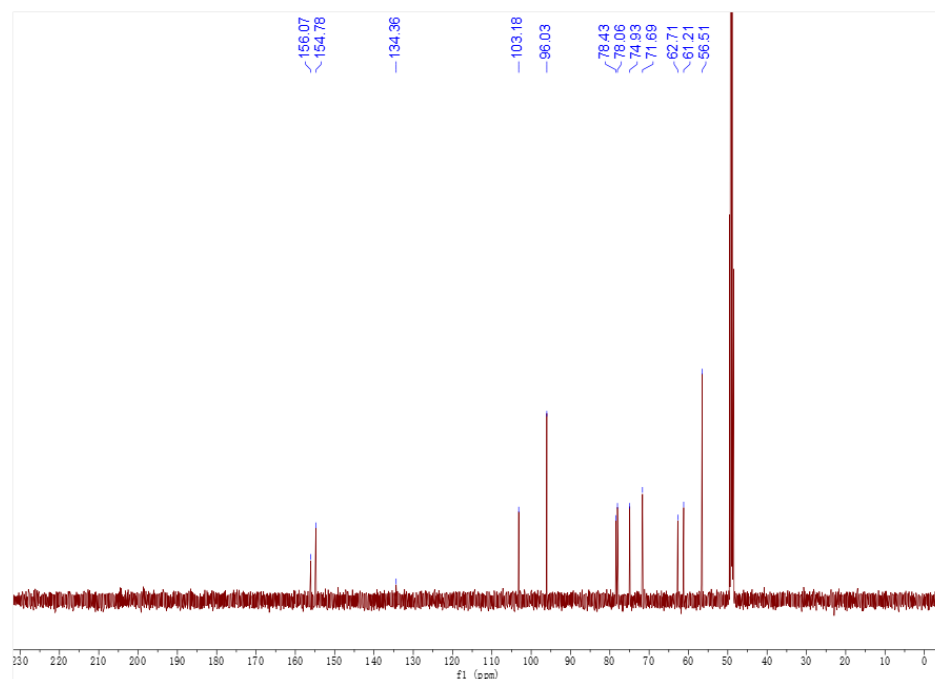
**Figure S5:**  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **3** (kaempferol-7-O- $\beta$ -D-glucopyranoside)



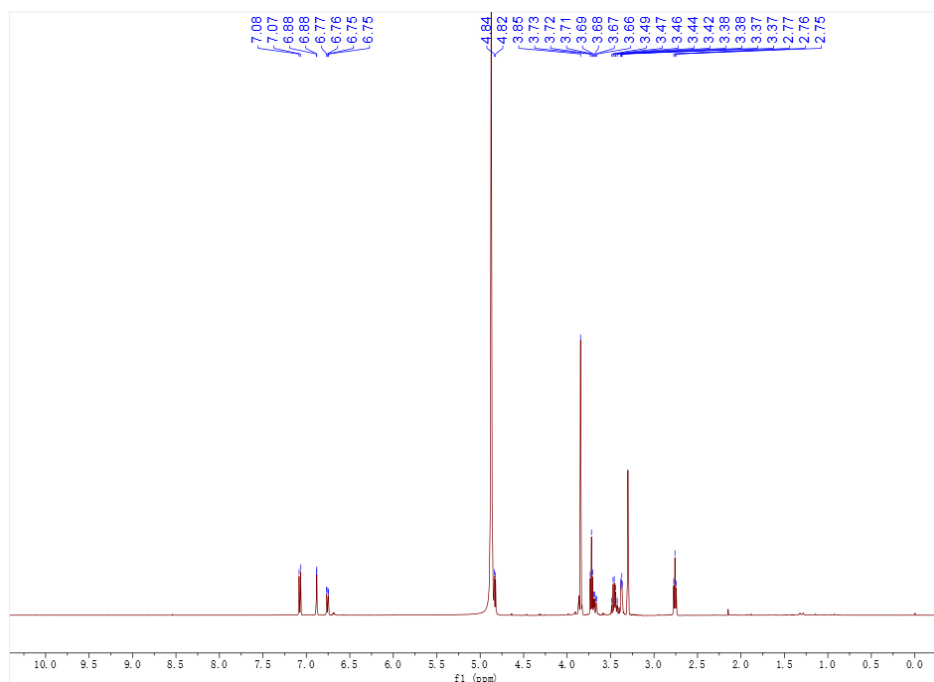
**Figure S6:**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **3** (kaempferol-7-O- $\beta$ -D-glucopyranoside)



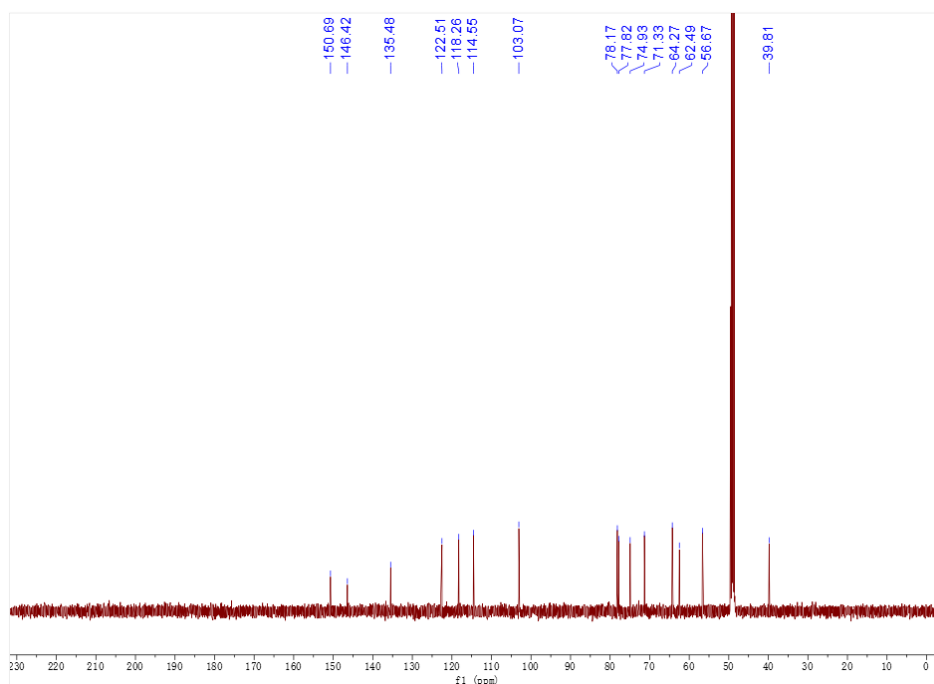
**Figure S7:**  $^1\text{H}$  NMR (600 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **4** (3,4,5-trimethoxyphenyl-O- $\beta$ -D-glucopyranoside)



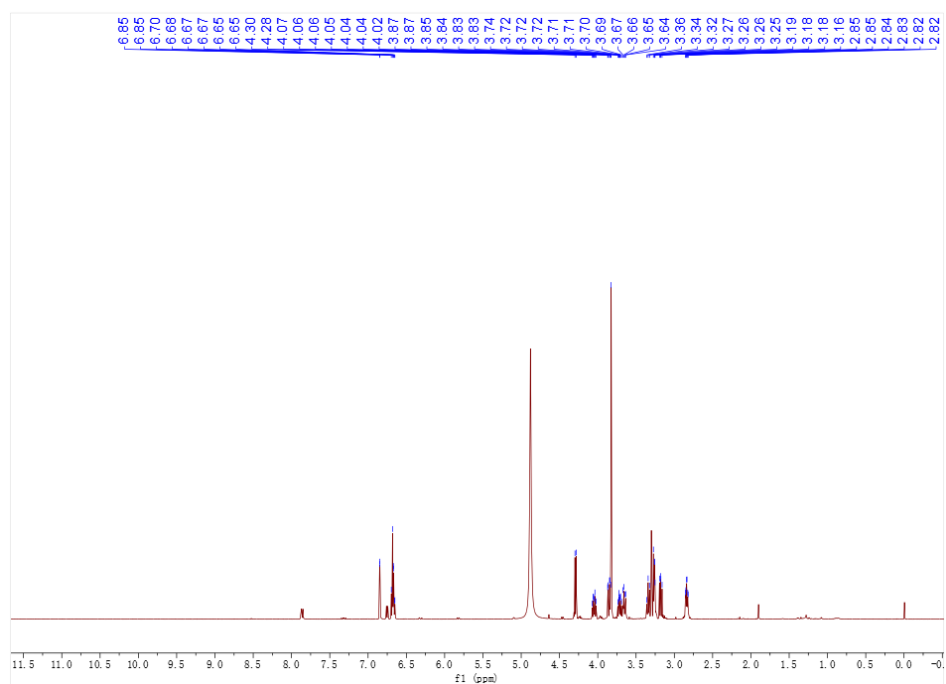
**Figure S8:**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **4** (3,4,5-trimethoxyphenyl-O- $\beta$ -D-glucopyranoside)



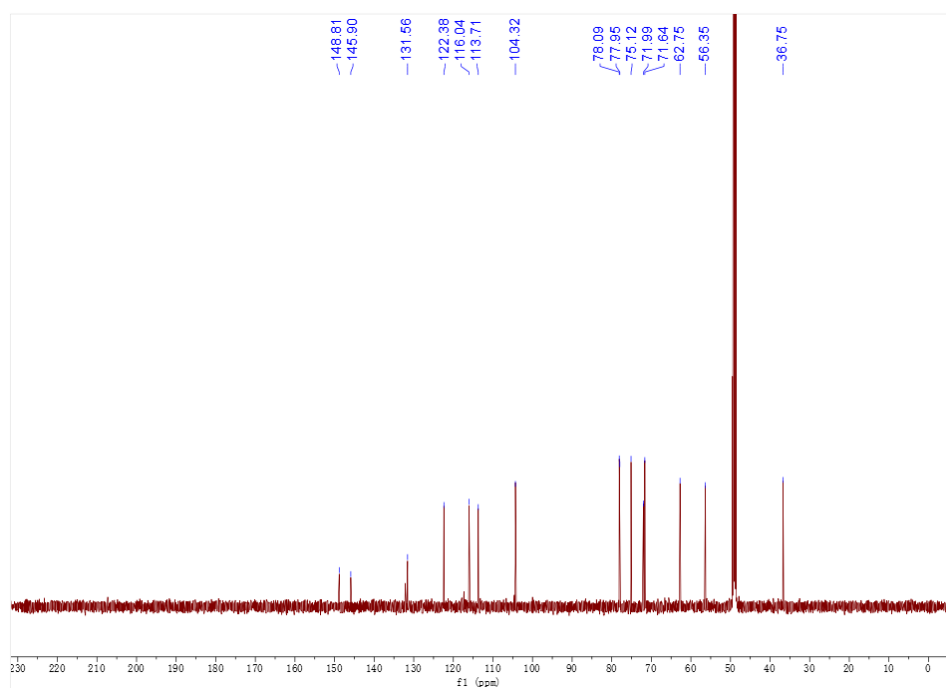
**Figure S9:**  $^1\text{H-NMR}$  (600 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **5** (2-methoxy-4-(2'-hydroxyethyl)-phenol-1-O- $\beta$ -D-glucopyranoside)



**Figure S10:**  $^{13}\text{C NMR}$  (151 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **5** (2-methoxy-4-(2'-hydroxyethyl)-phenol-1-O- $\beta$ -D-glucopyranoside)



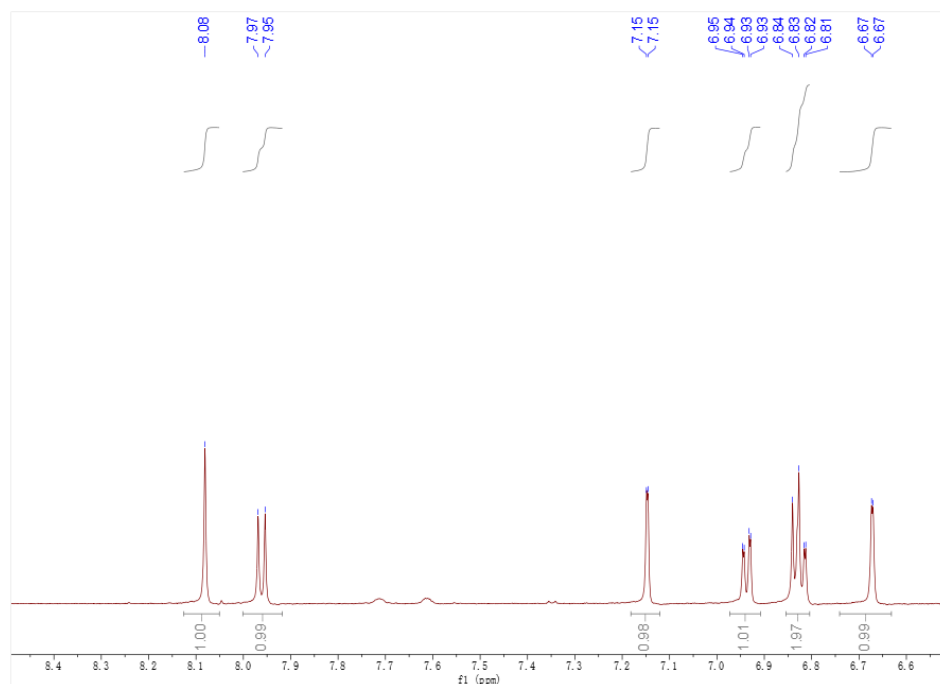
**Figure S11:**  $^1\text{H-NMR}$  (600 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **6** (2-(3-hydroxy-4-methoxyphenyl) ethyl 1-O- $\beta$ -D-glucopyranoside)



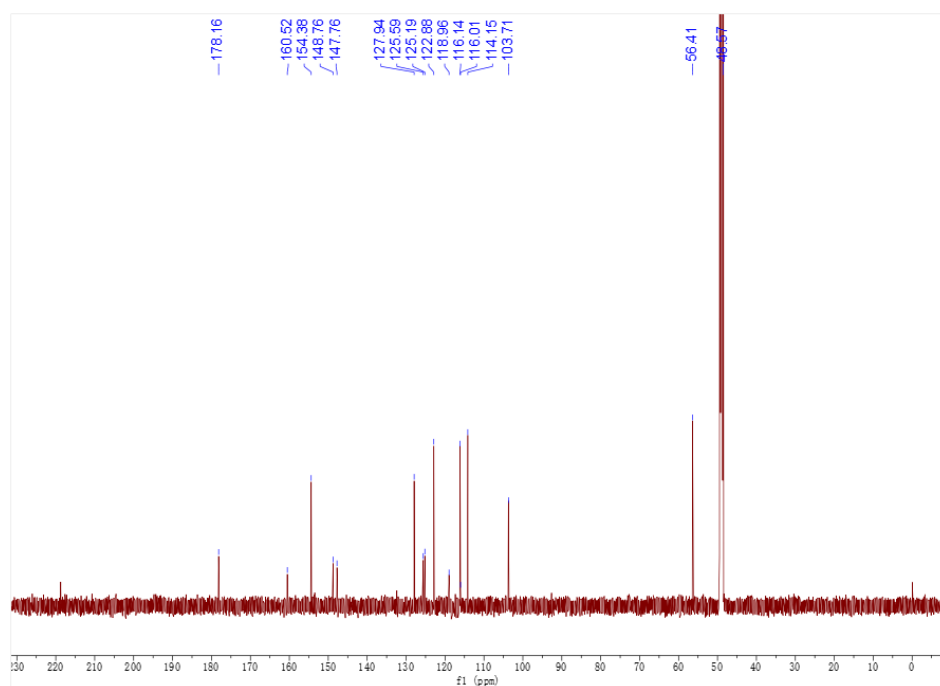
**Figure S12:**  $^{13}\text{C-NMR}$  (151 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **6** (2-(3-hydroxy-4-methoxyphenyl) ethyl 1-O- $\beta$ -D-glucopyranoside)



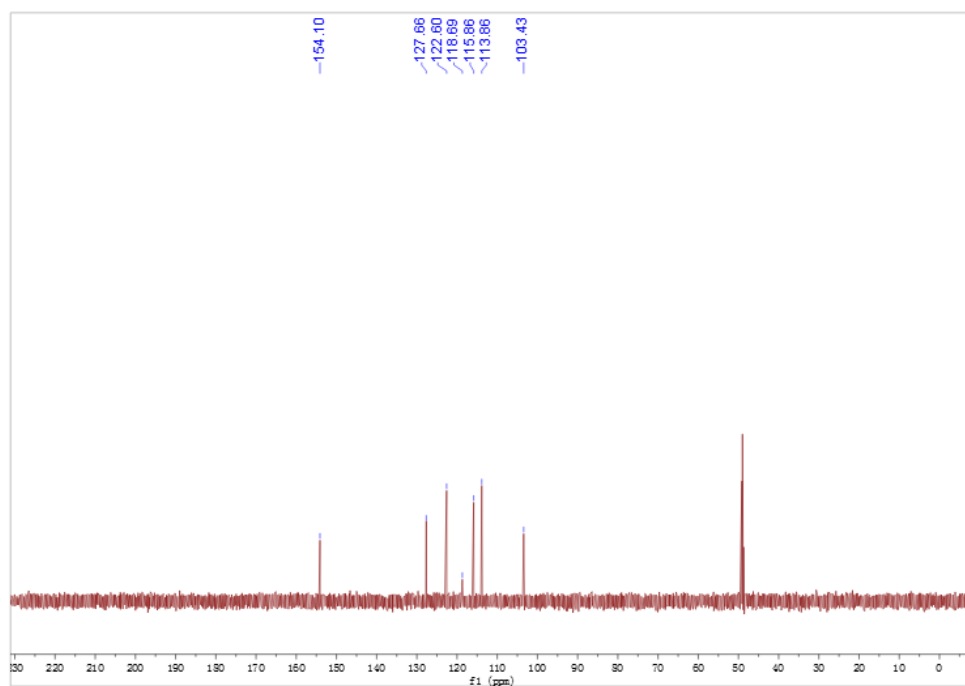




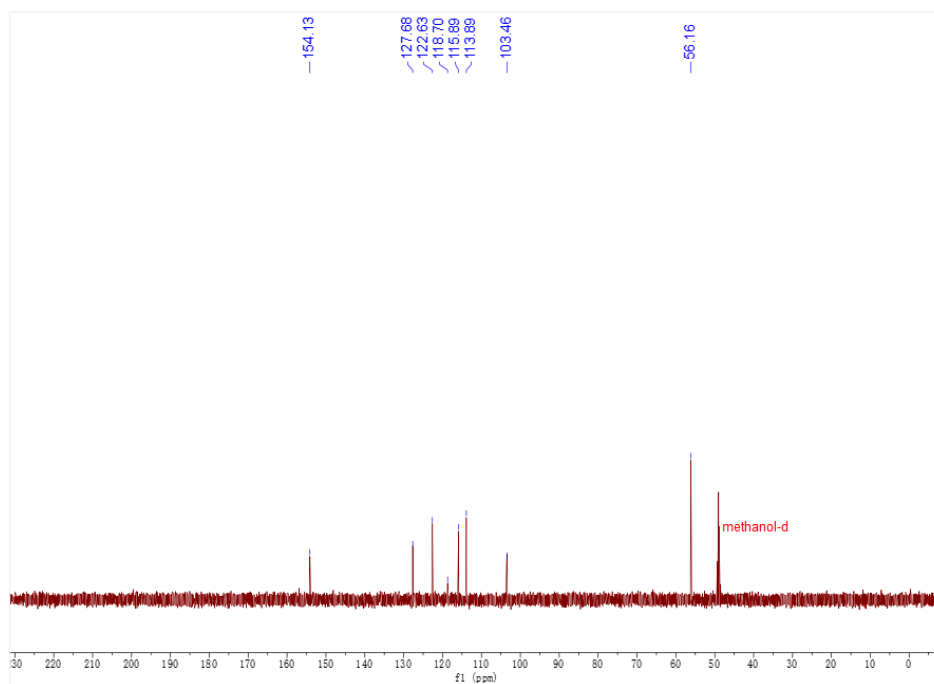
**Figure S15:** Expansion of the  $^1\text{H-NMR}$  (600 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **7** (7, 4'-dihydroxy-3'-methoxyisoflavone) (From 6.50 to 8.50 ppm)



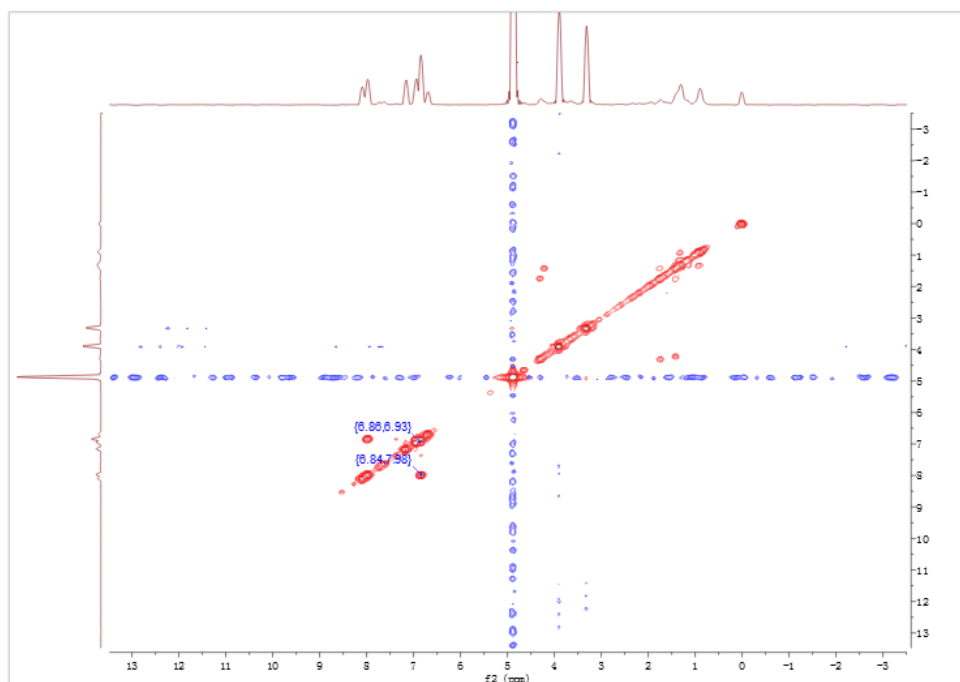
**Figure S16:**  $^{13}\text{C-NMR}$  (151 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **7** (7, 4'-dihydroxy-3'-methoxyisoflavone)



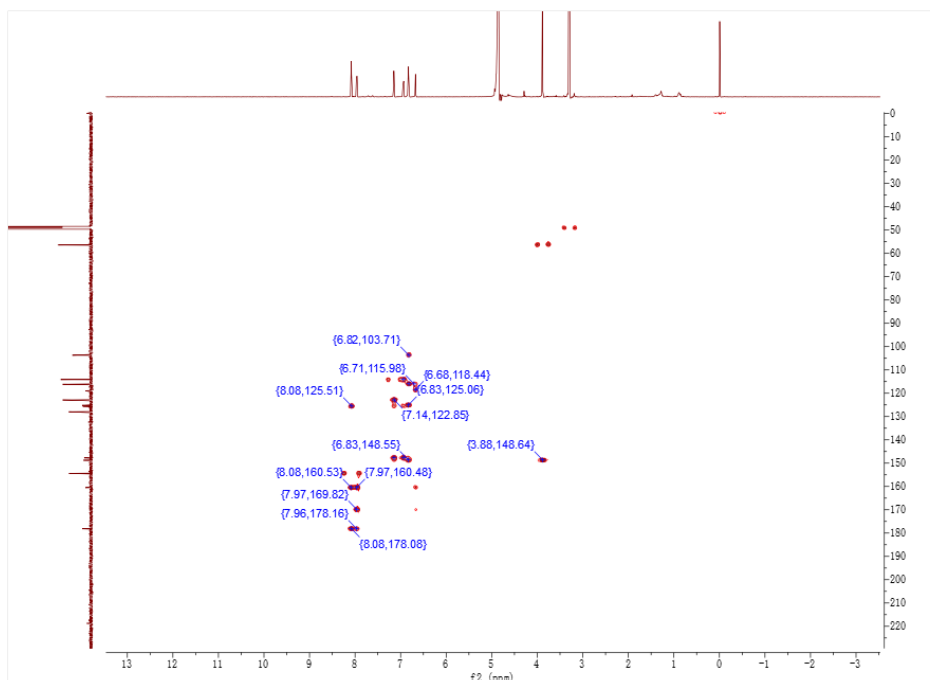
**Figure S17:** DEPT90 (151 MHz, CH<sub>3</sub>OD) spectrum of compound **7** (7, 4'-dihydroxyl-3'-methoxyisoflavone)



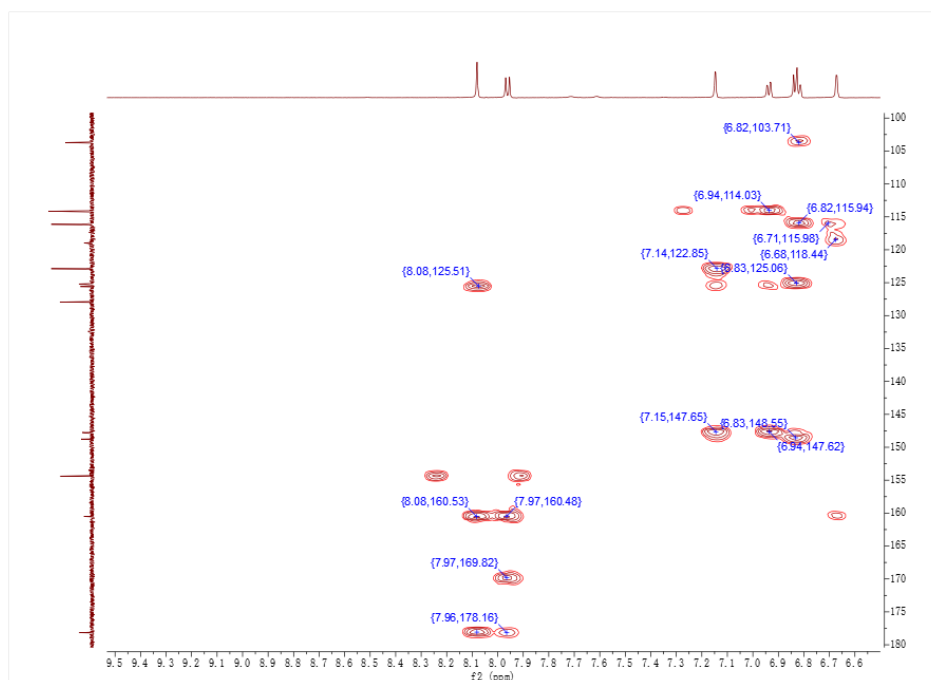
**Figure S18:** DEPT135 (151 MHz, CH<sub>3</sub>OD) spectrum of compound **7** (7, 4'-dihydroxyl-3'-methoxyisoflavone)



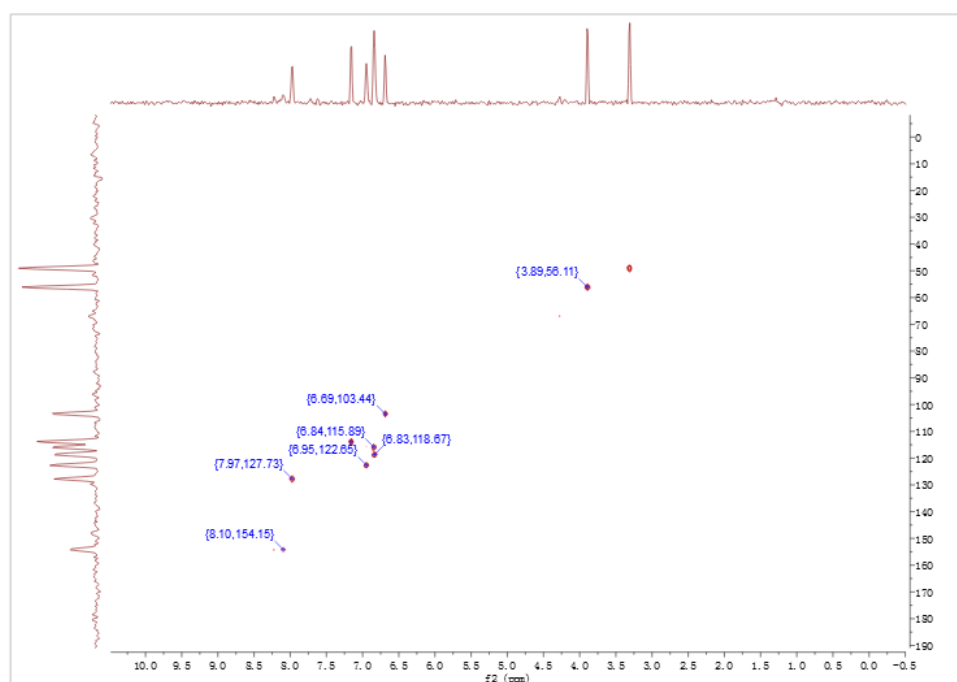
**Figure S19:** H-H COSY (600 MHz, CH<sub>3</sub>OD) spectrum of compound **7** (7, 4'-dihydroxyl-3'-methoxyisoflavone)



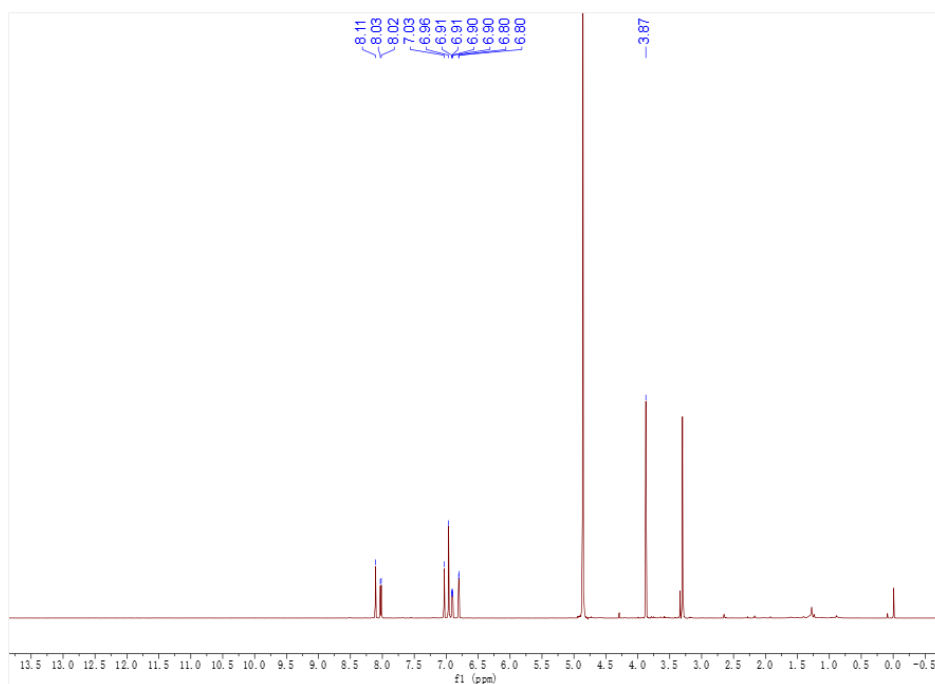
**Figure S20:** HMBC (600 MHz, CH<sub>3</sub>OD) spectrum of compound **7** (7, 4'-dihydroxyl-3'-methoxyisoflavone)



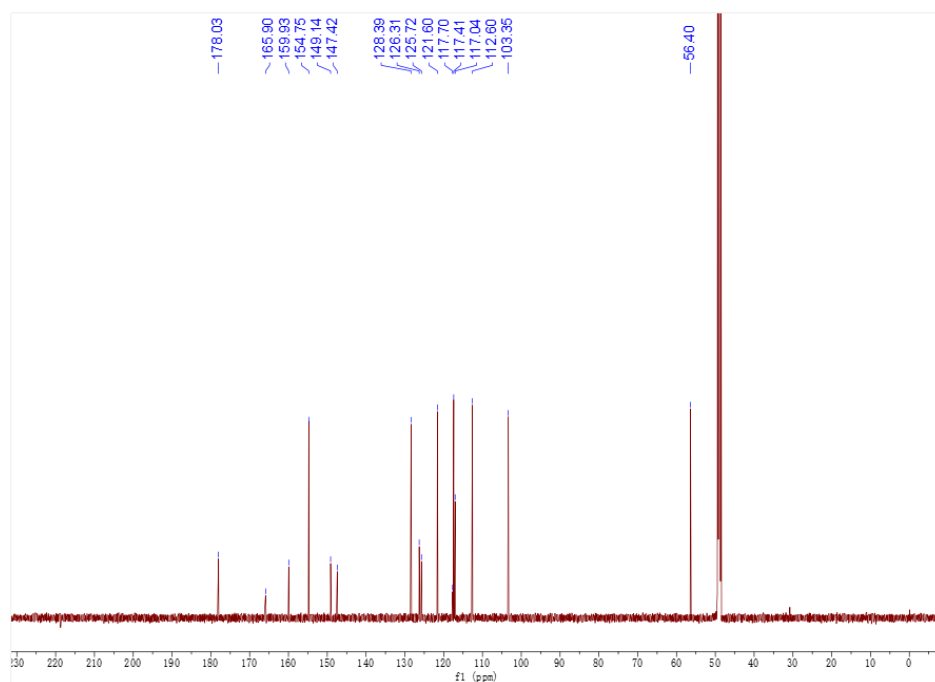
**Figure S21:** Expansion of the HMBC (600 MHz, CH<sub>3</sub>OD) spectrum of compound **7** (7, 4'-dihydroxyl-3'-methoxyisoflavone) (From 6.50 to 9.50 in <sup>1</sup>H-NMR, 100.0 to 180.0 in <sup>13</sup>C-NMR)



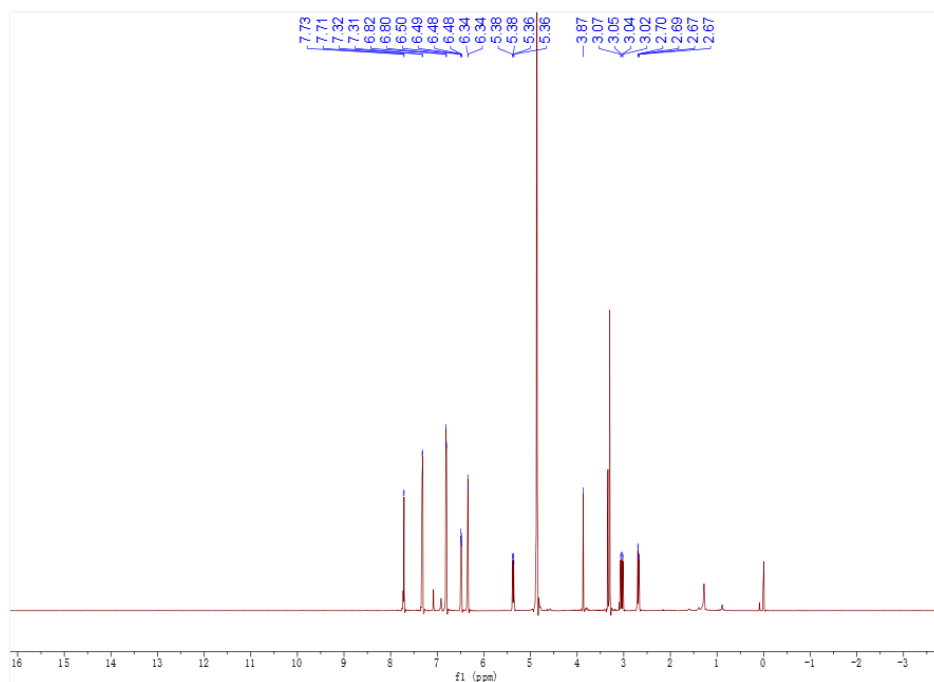
**Figure S22:** HSQC (600 MHz, CH<sub>3</sub>OD) spectrum of compound **7** (7, 4'-dihydroxyl-3'-methoxyisoflavone)



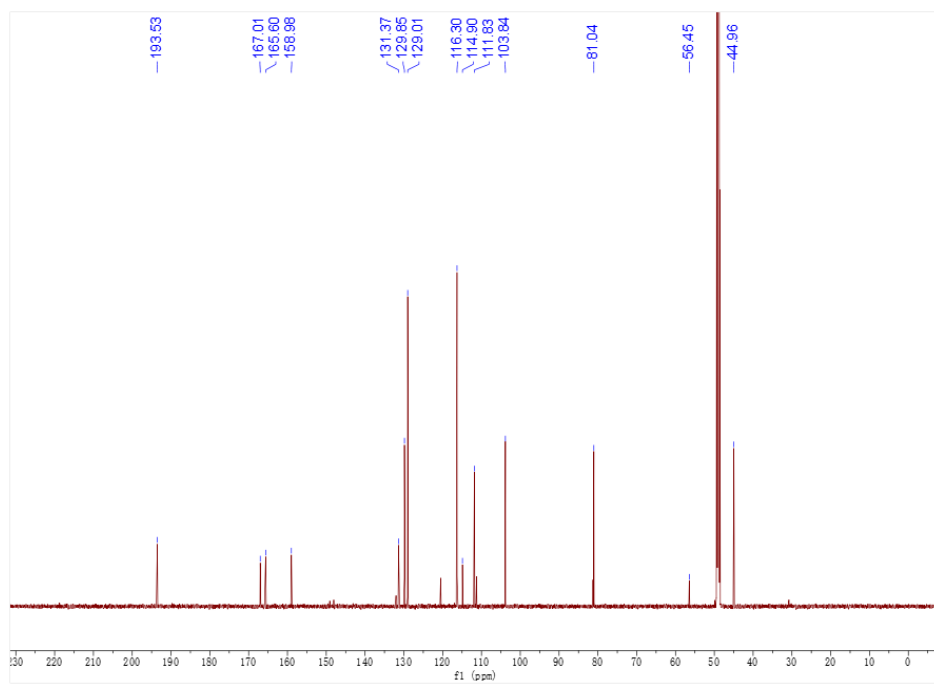
**Figure S23:**  $^1\text{H}$  NMR (600 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **8** (calycosin)



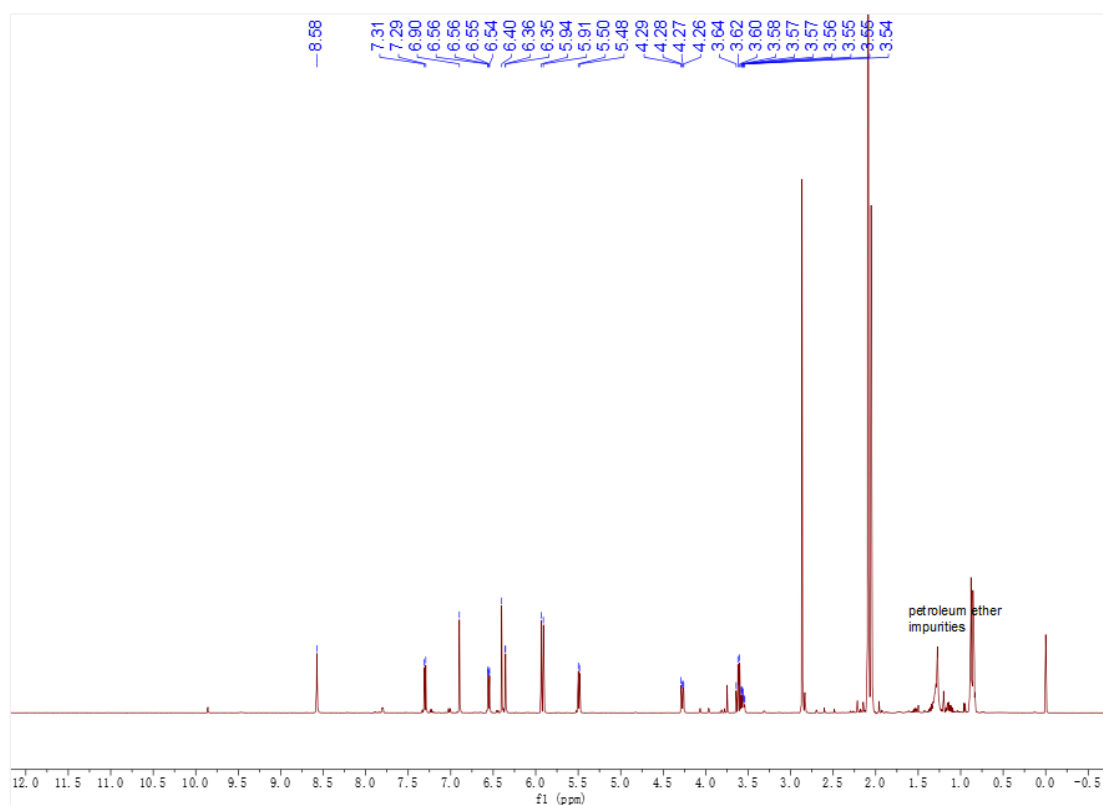
**Figure S24:**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **8** (calycosin)



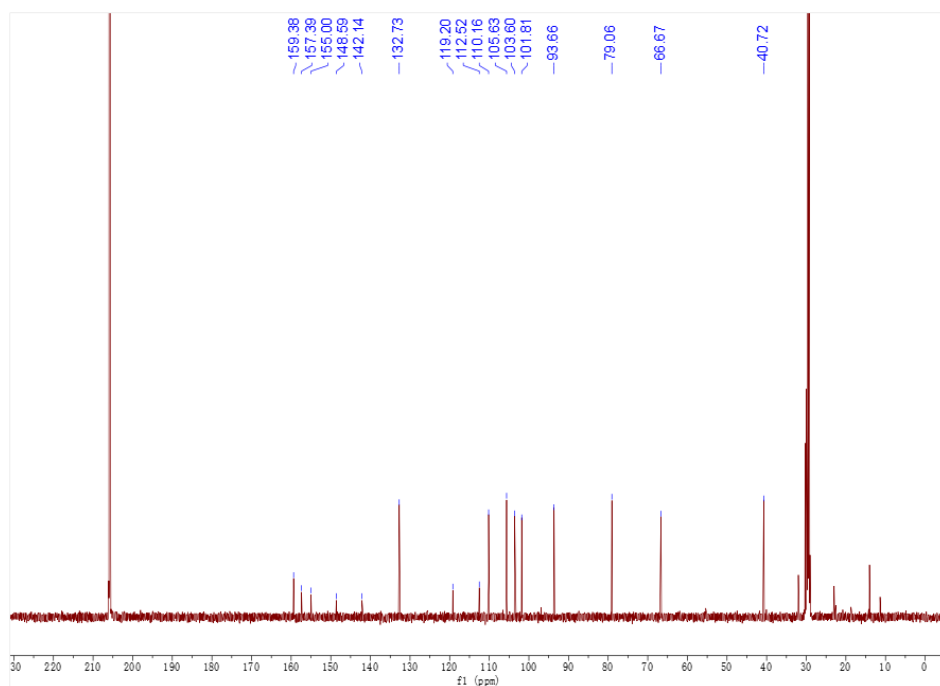
**Figure S25:**  $^1\text{H-NMR}$  (600 MHz,  $\text{CH}_3\text{OD}$ ) spectrum of compound **9** (7-hydroxyl-4'-methoxyflavanone)



**Figure S26:**  $^{13}\text{C-NMR}$  (151 MHz) spectrum of compound **9** (7-hydroxyl-4'-methoxyflavanone)



**Figure S27:**  $^1\text{H-NMR}$  (500 MHz,  $\text{CD}_3\text{COCD}_3$ ) spectrum of compound **10** (maackiain)



**Figure S28:**  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_3\text{COCD}_3$ ) spectrum of compound **10** (maackiain)



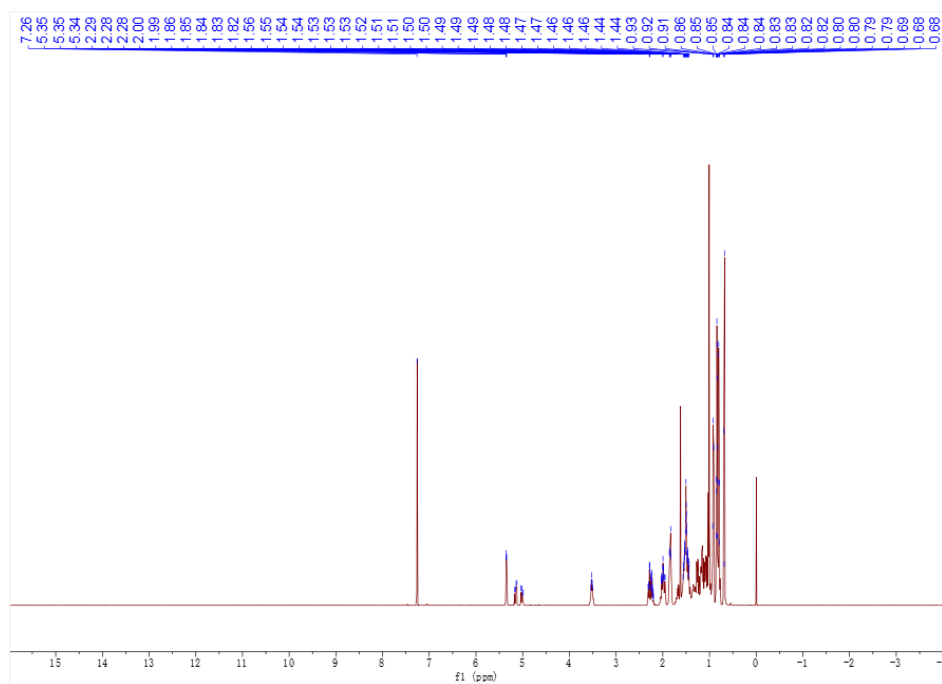
Compound **10** was colorless needle-like crystals.

Its ESI-MS peak at  $m/z$  285  $[M+H]^+$ .

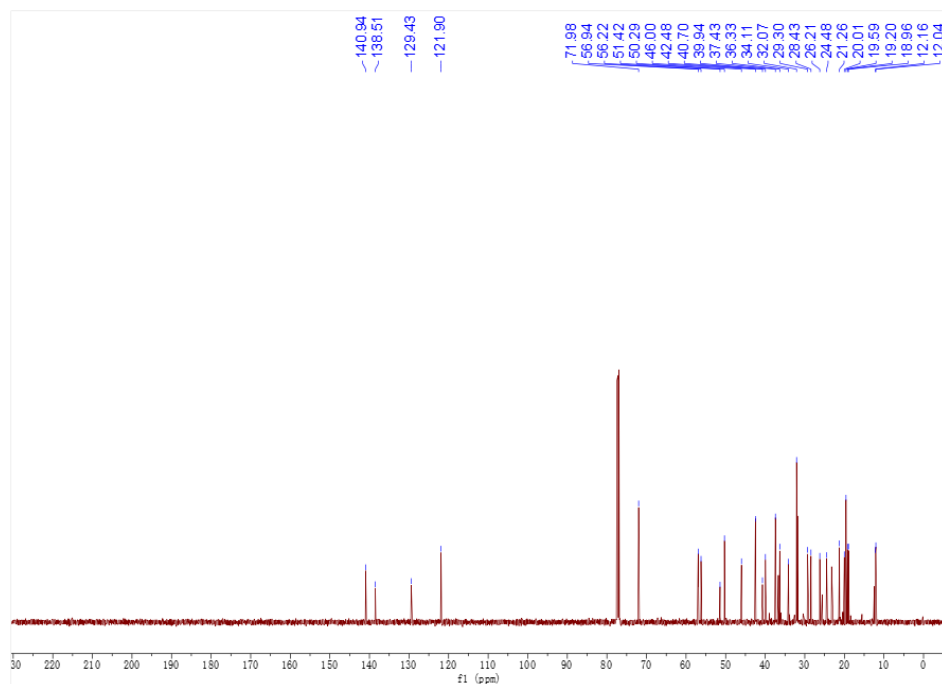
$^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta$ : 8.58 (s, 1H, 3-OH), 7.30 (d,  $J = 8.5$  Hz, 1H, H-1), 6.90 (s, 1H, H-7), 6.55 (dd,  $J = 8.5, 2.4$  Hz, 1H, H-2), 6.40 (s, 1H, H-11), 6.36 (d,  $J = 2.4$  Hz, 1H, H-4), 5.92 (d,  $J = 12.6$  Hz, 2H, H-9), 5.49 (d,  $J = 6.9$  Hz, 1H, H-12a), 4.27 (m, 1H, H-6), 3.62 (m, 1H, H-6a), 3.56 (m, 1H, H-6).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta$ : 159.38 (C-3), 157.39 (C-4a), 155.00 (C-11a), 148.59 (C-10a), 142.14 (C-7a), 132.73 (C-1), 119.20 (C-6b), 112.52 (C-12b), 110.16 (C-2), 105.63 (C-7), 103.60 (C-4), 101.81 (C-9), 93.66 (C-11), 79.06 (C-12a), 66.67 (C-6), 40.72 (C-6a).

The above NMR data are consistent with the reference[15], this compound was eventually identified as maackiain (RN 2035-15-6).



**Figure S29:**  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **11** (stigmasterol)



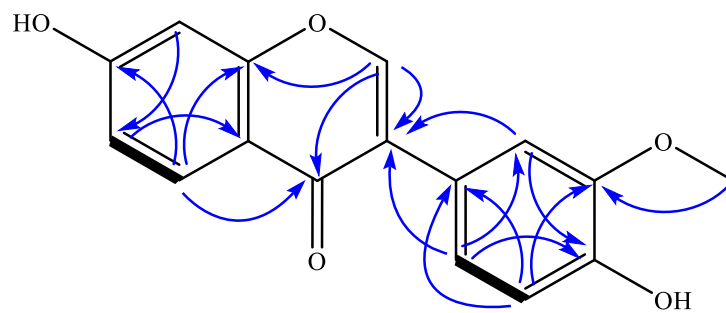
**Figure S30:**  $^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **11** (stigmasterol)

Compound **11** was colorless needle-like crystals.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.35 (m, 2H, H-22, 23), 5.08 (m, 1H, H-6), 3.52 (m, 1H, H-3), 2.26 (m, 4H, H-4, 7), 1.84 (m, 4H, H-15, 16, 20, 24), 1.49 (m, 17H, H-1, 1, 2, 2, 8, 9, 11, 11, 12, 12, 14, 15, 16, 17, 25, 28, 28), 0.82 (m, 12H, 19, 26, 27, 29- $\text{CH}_3$ ), 0.69 (m, 6H, 18, 21- $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.94 (C-5), 138.51 (C-22), 129.43 (C-23), 121.90 (C-6), 71.98 (C-3), 56.94 (C-14), 56.22 (C-17), 51.42 (C-24), 50.29 (C-9), 46.00 (C-13), 42.48 (C-4), 40.70 (C-20), 39.94 (C-12), 37.43 (C-1), 36.32 (C-10), 34.11 (C-7), 32.09 (C-2), 32.07 (C-8), 29.30 (C-25), 28.43 (C-16), 26.21 (C-15), 24.48 (C-28), 21.26 (C-11), 20.01 (C-26), 19.59 (C-27), 19.20 (C-21), 18.96 (C-19), 12.16 (C-29), 12.04 (C-18).

The above NMR data are consistent with the reference[16], this compound was eventually identified as stigmasterol (RN 83-48-7).



**Figure S31:** Key  $^1\text{H}$ - $^1\text{H}$  COSY and HMBC correlations of compound 7