

# Supplementary data

## Glycosylation of 3-hydroxyflavone, 3-methoxyflavone, quercetin and baicalein in fungal cultures of the genus *Isaria*

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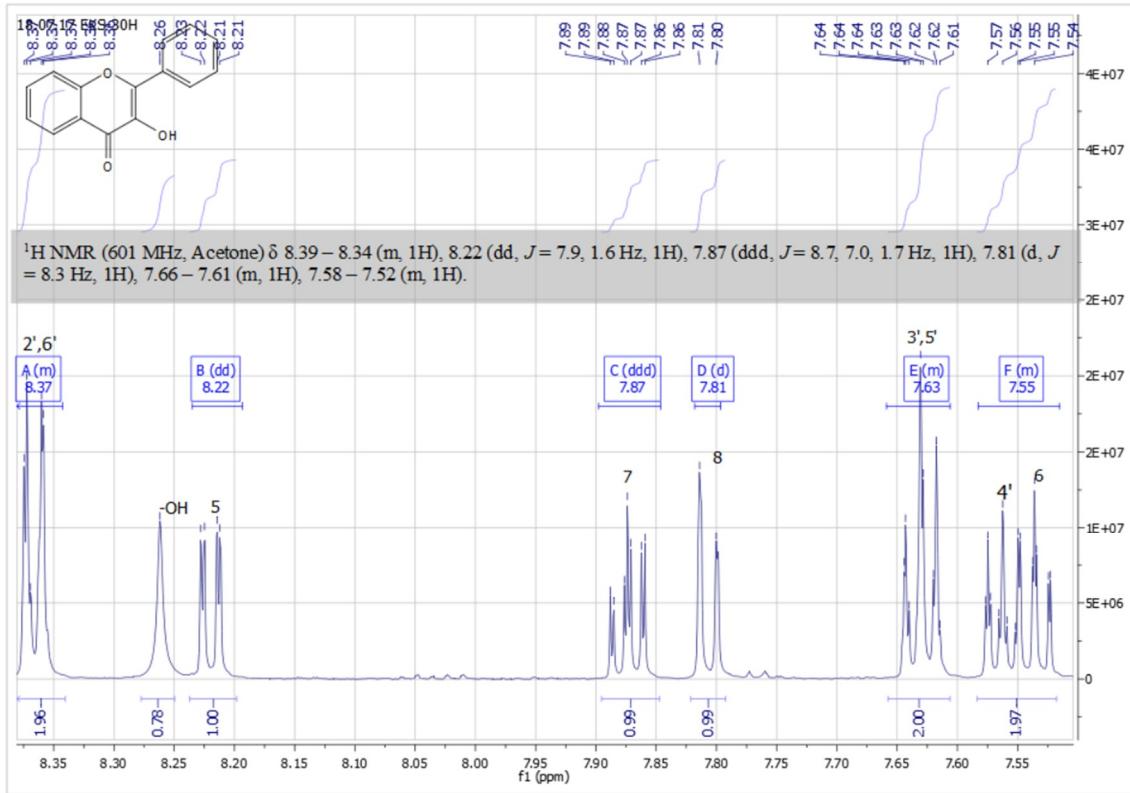
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### Content

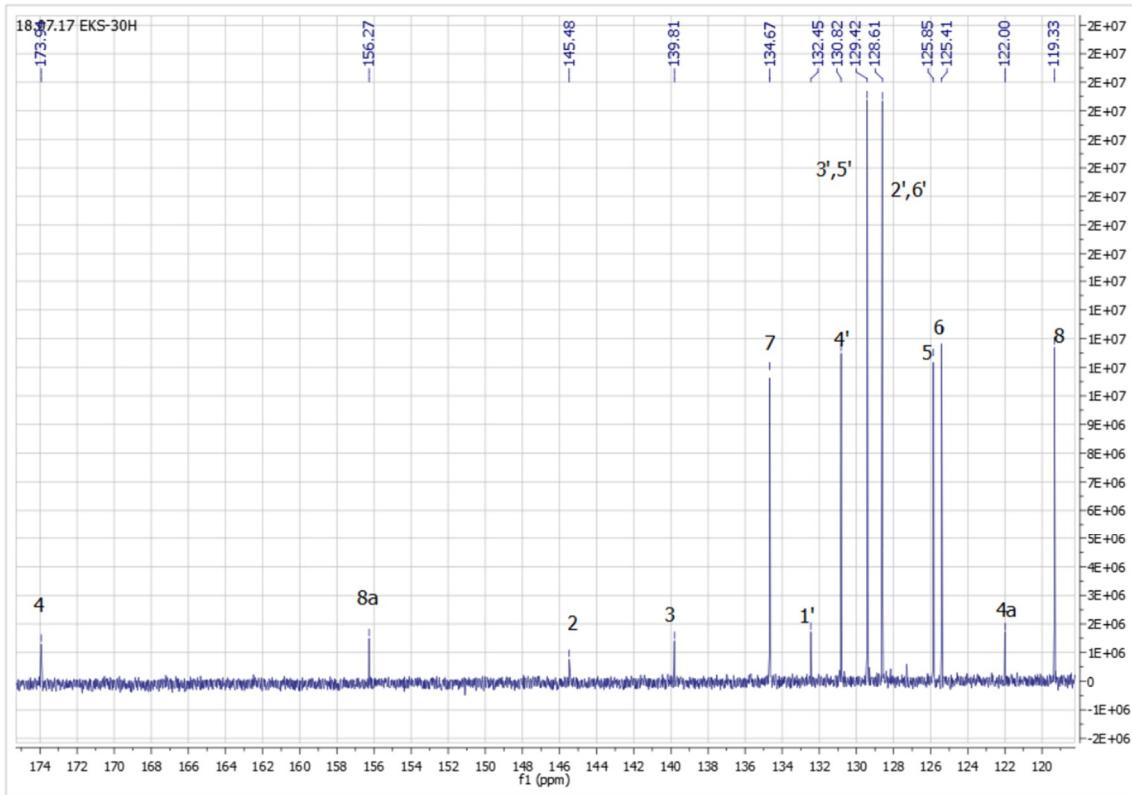
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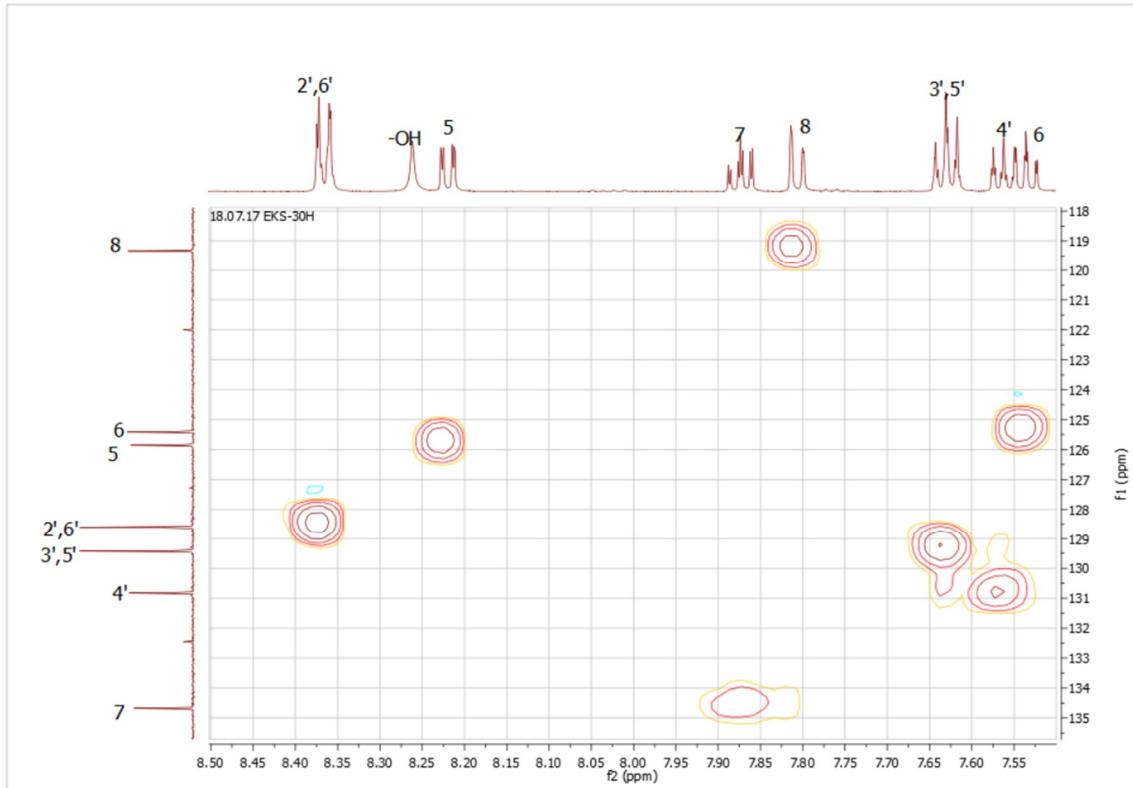
- Figure S36.**  $^{13}\text{C}$  NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (3a) (Acetone-d<sub>6</sub>, 151 MHz)
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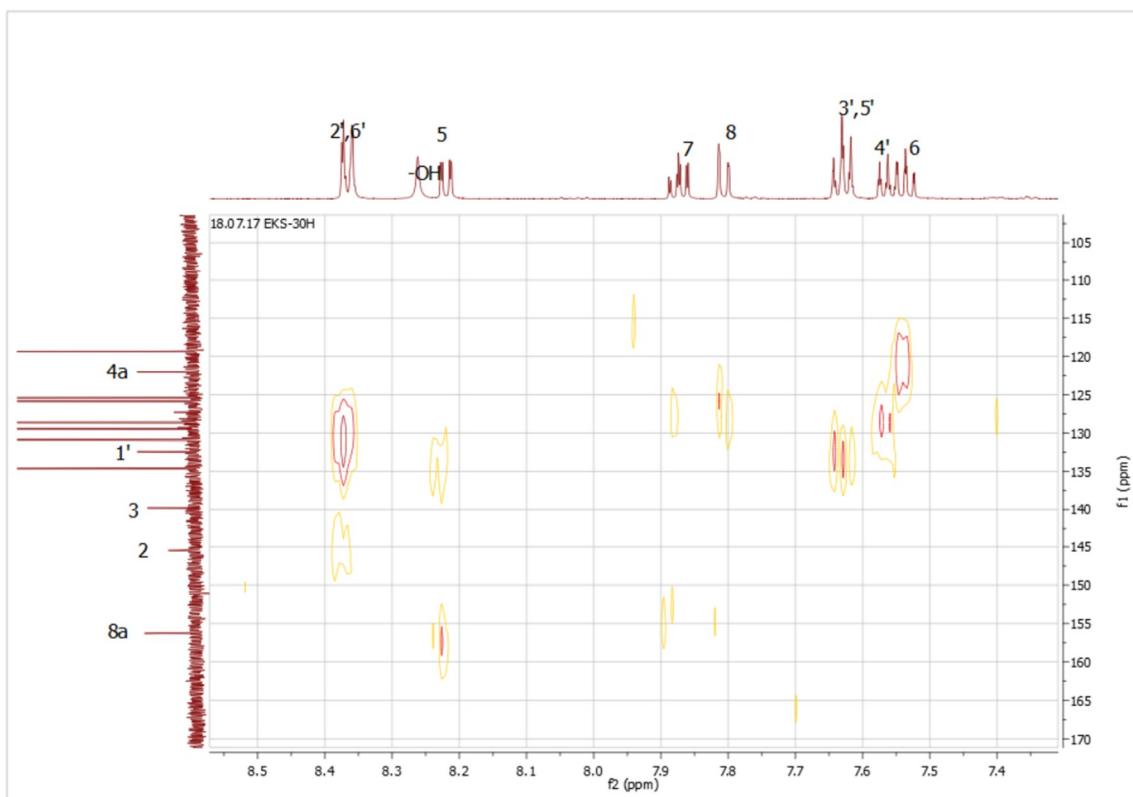
**Figure S1.** <sup>1</sup>H NMR spectrum of 3-hydroxyflavone (1) (Acetone-d<sub>6</sub>, 600 MHz)



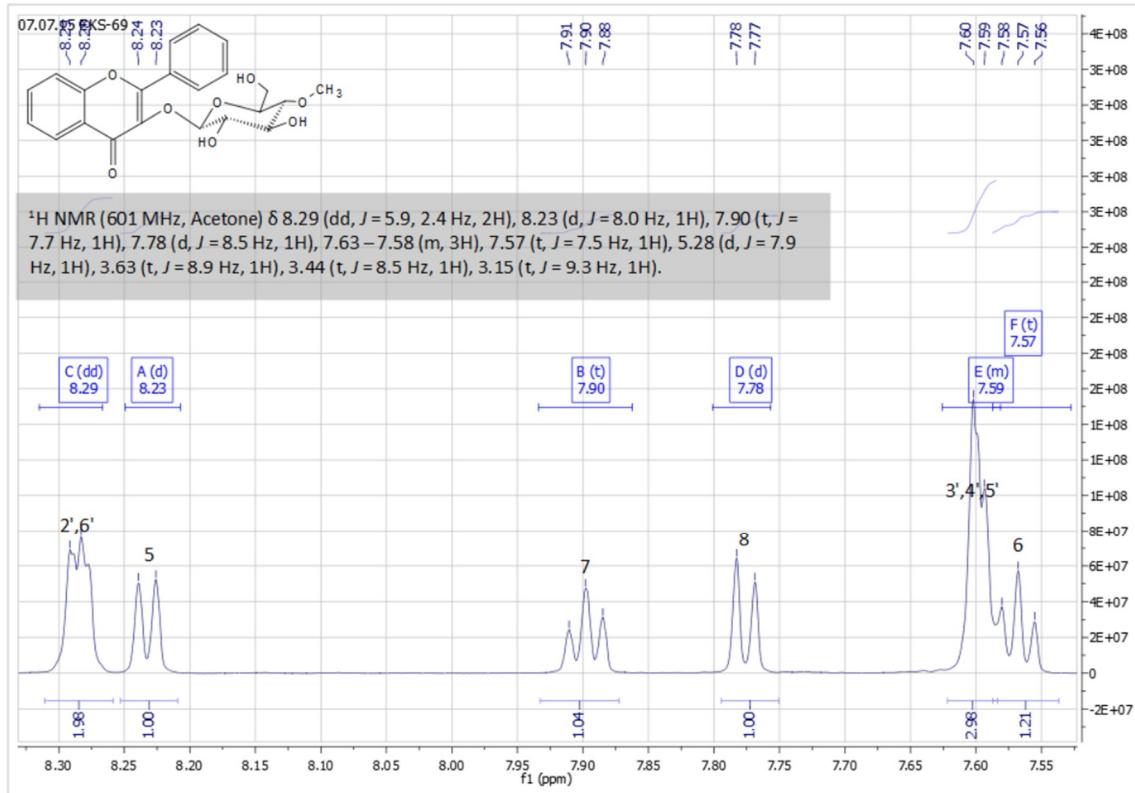
**Figure S2.** <sup>13</sup>C NMR spectrum of 3-hydroxyflavone (1) (Acetone-d<sub>6</sub>, 151 MHz)



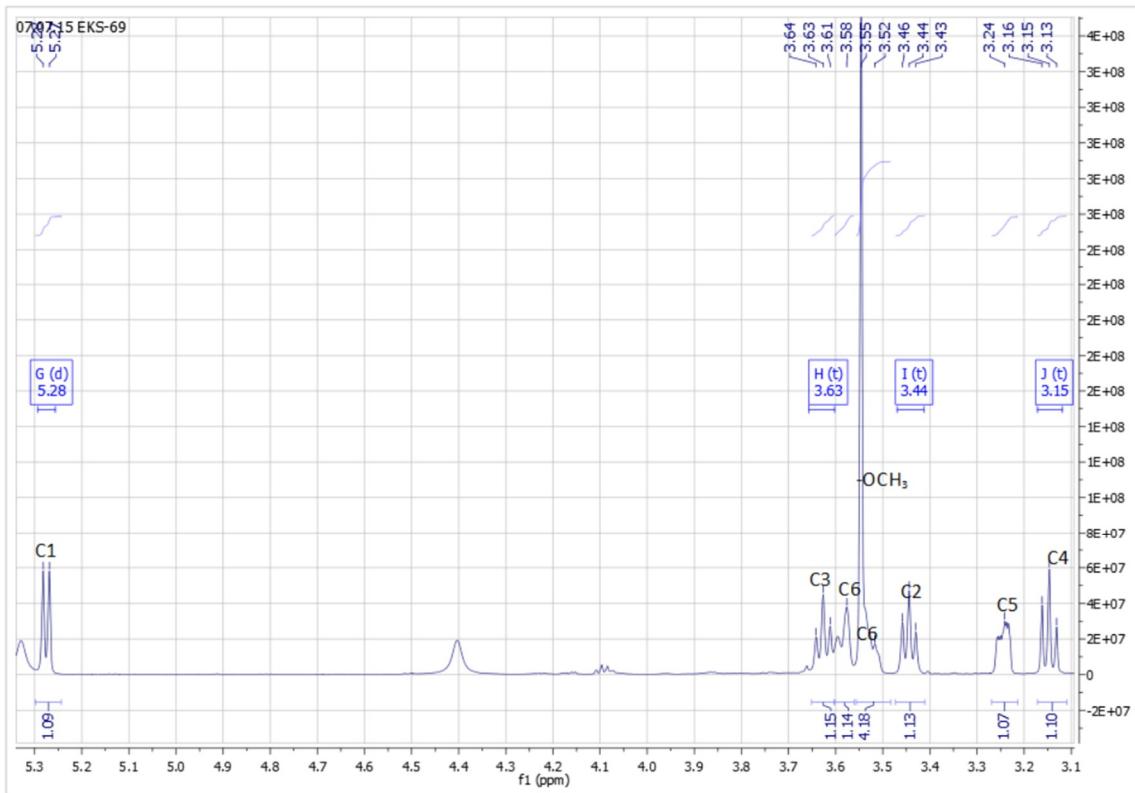
**Figure S3.** HSQC NMR spectrum of 3-hydroxyflavone (1) (Acetone-d<sub>6</sub>, 151 MHz)



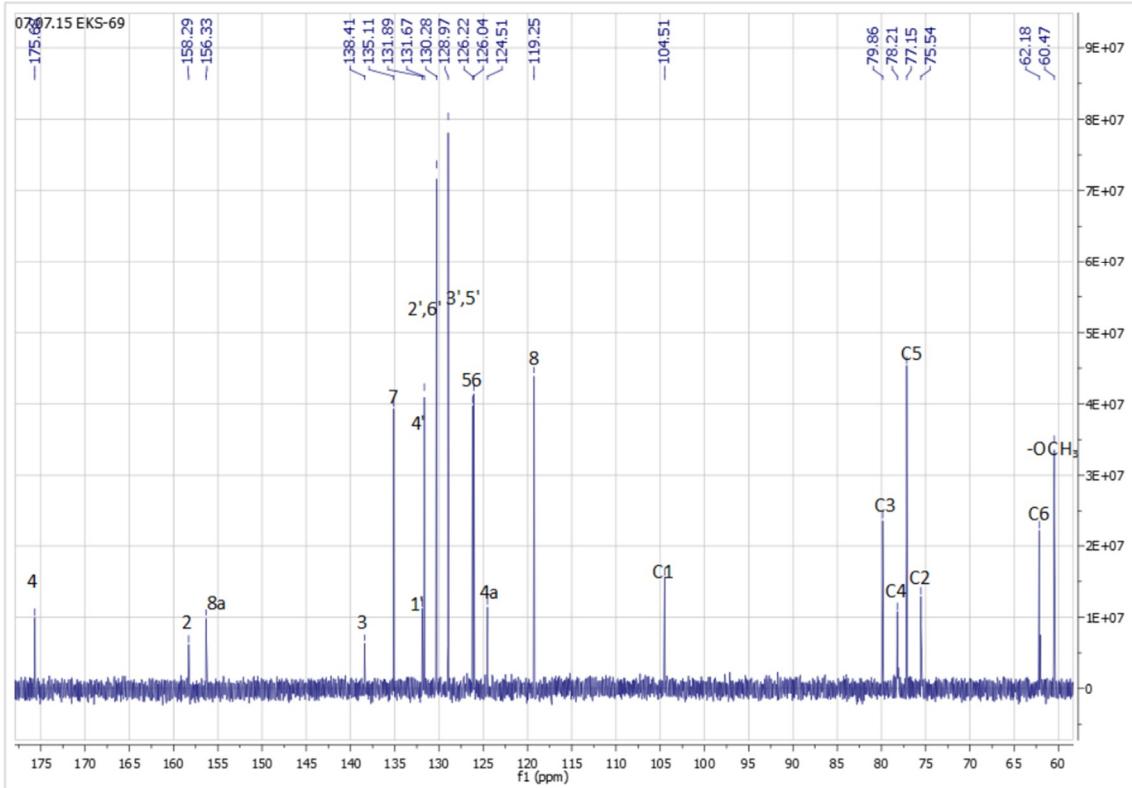
**Figure S4.** HMBC NMR spectrum of 3-hydroxyflavone (1) (Acetone-d<sub>6</sub>, 151 MHz)



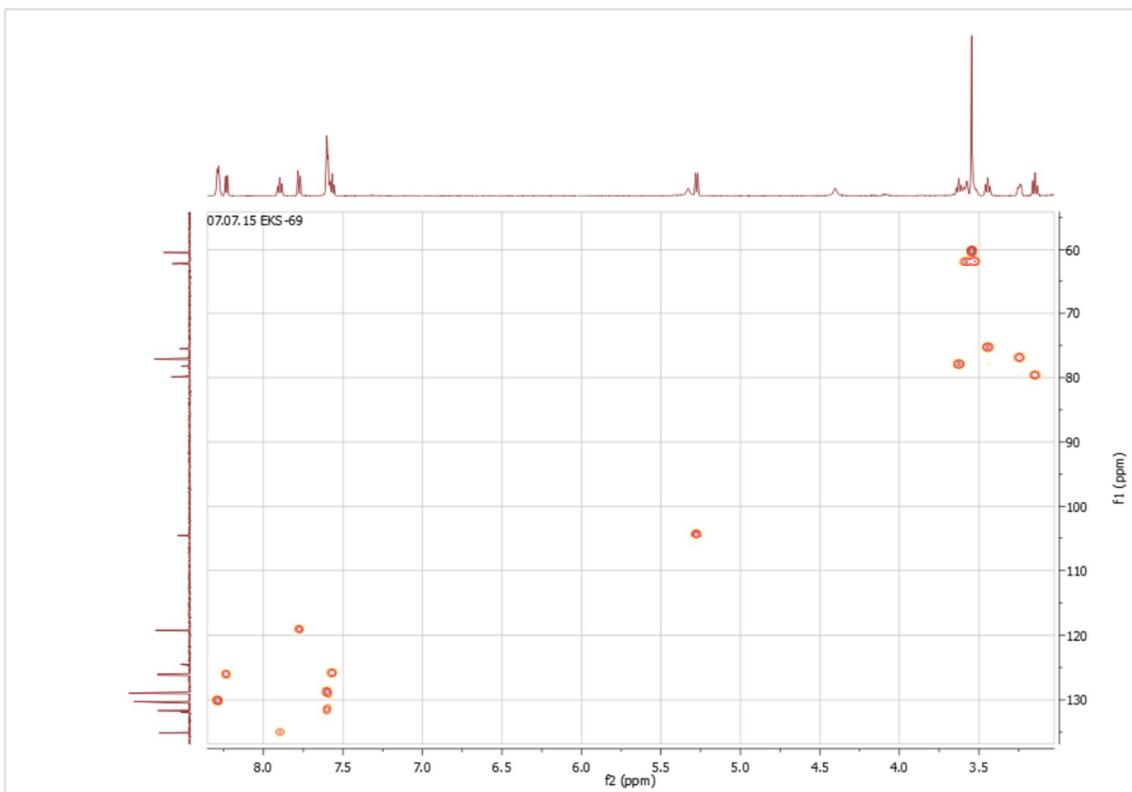
**Figure S5.** <sup>1</sup>H NMR spectrum of flavone 3-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (1a) (Acetone-d<sub>6</sub>, 600 MHz)



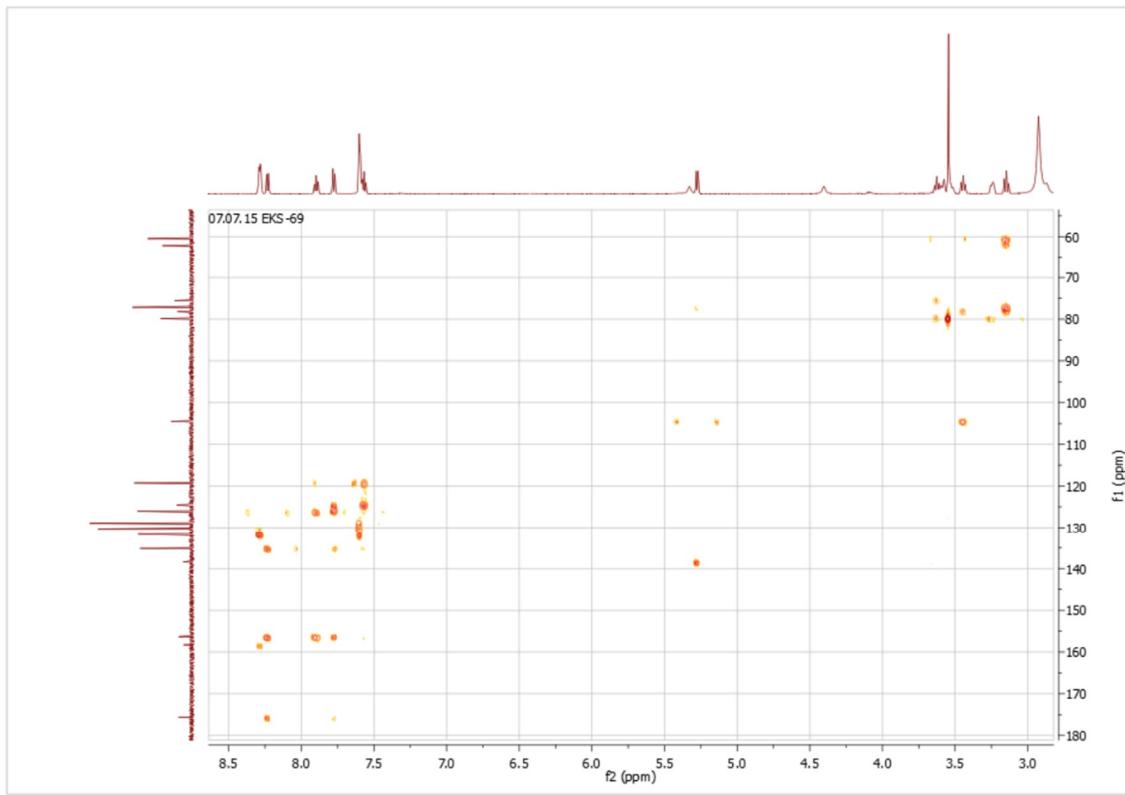
**Figure S6.** <sup>1</sup>H NMR spectrum of flavone 3-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (1a) (Acetone-d<sub>6</sub>, 600 MHz)



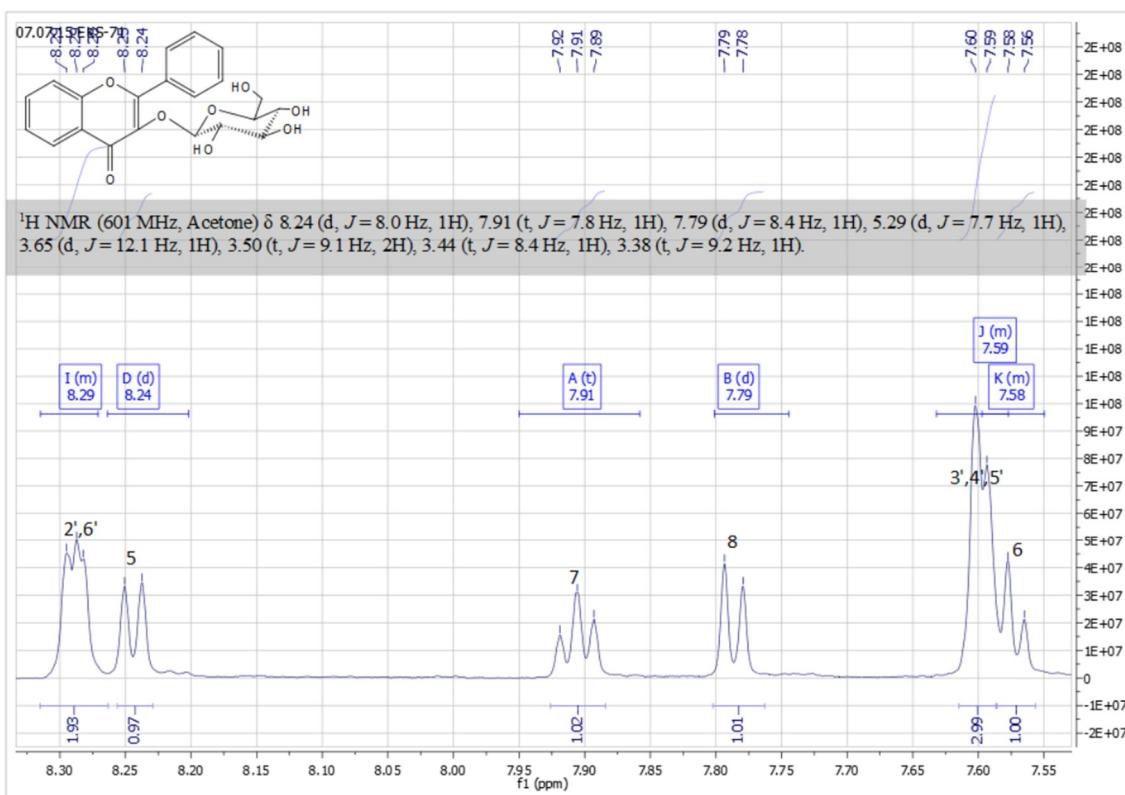
**Figure S7.**  $^{13}\text{C}$  NMR spectrum of flavone 3- $O$ - $\beta$ -D-(4''- $O$ -methyl)-glucopyranoside (1a) (Acetone- $d_6$ , 151 MHz)



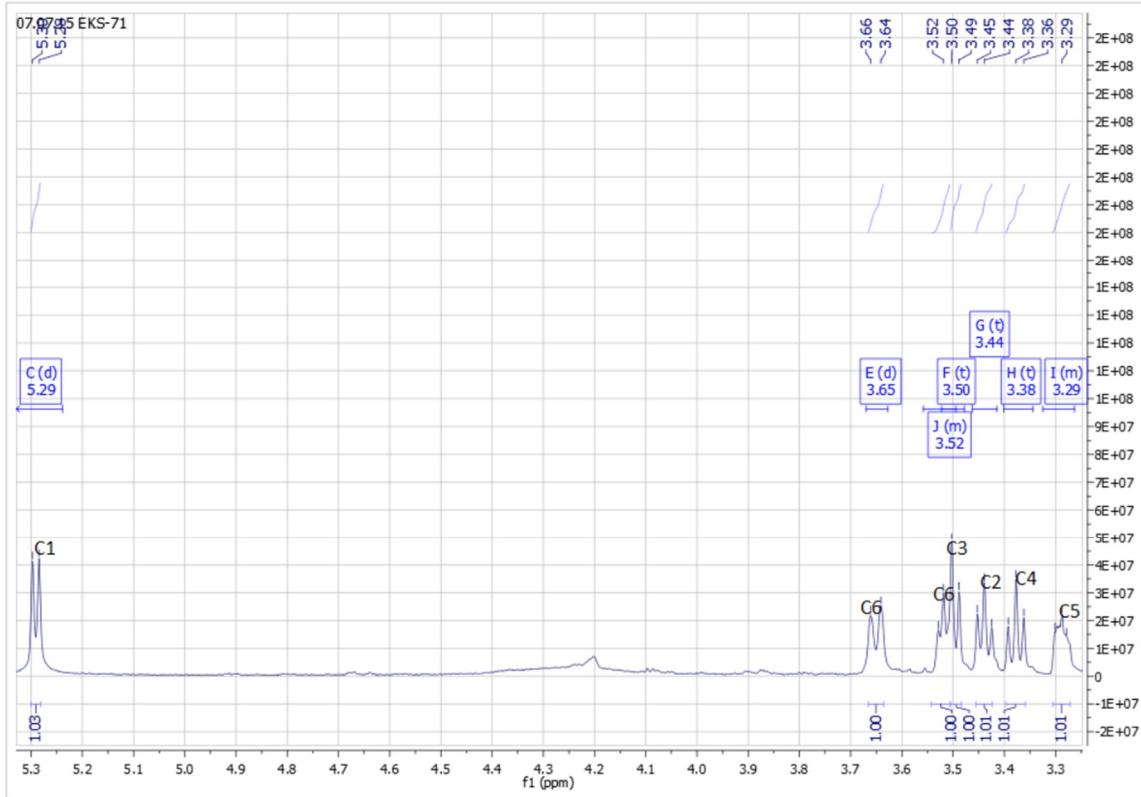
**Figure S8.** HSQC NMR spectrum of flavone 3- $O$ - $\beta$ -D-(4''- $O$ -methyl)-glucopyranoside (1a) (Acetone- $d_6$ , 151 MHz)



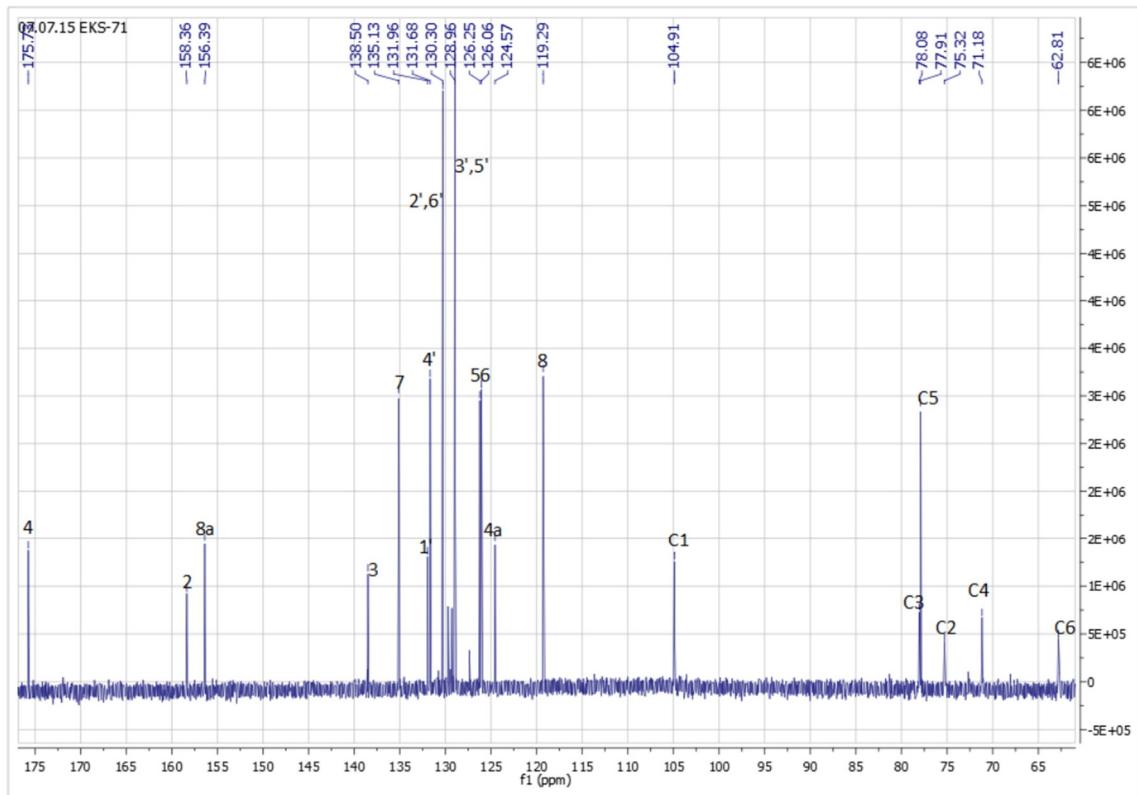
**Figure S9.** HMBC NMR spectrum of flavone 3-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (1a) (Acetone-d<sub>6</sub>, 151 MHz)



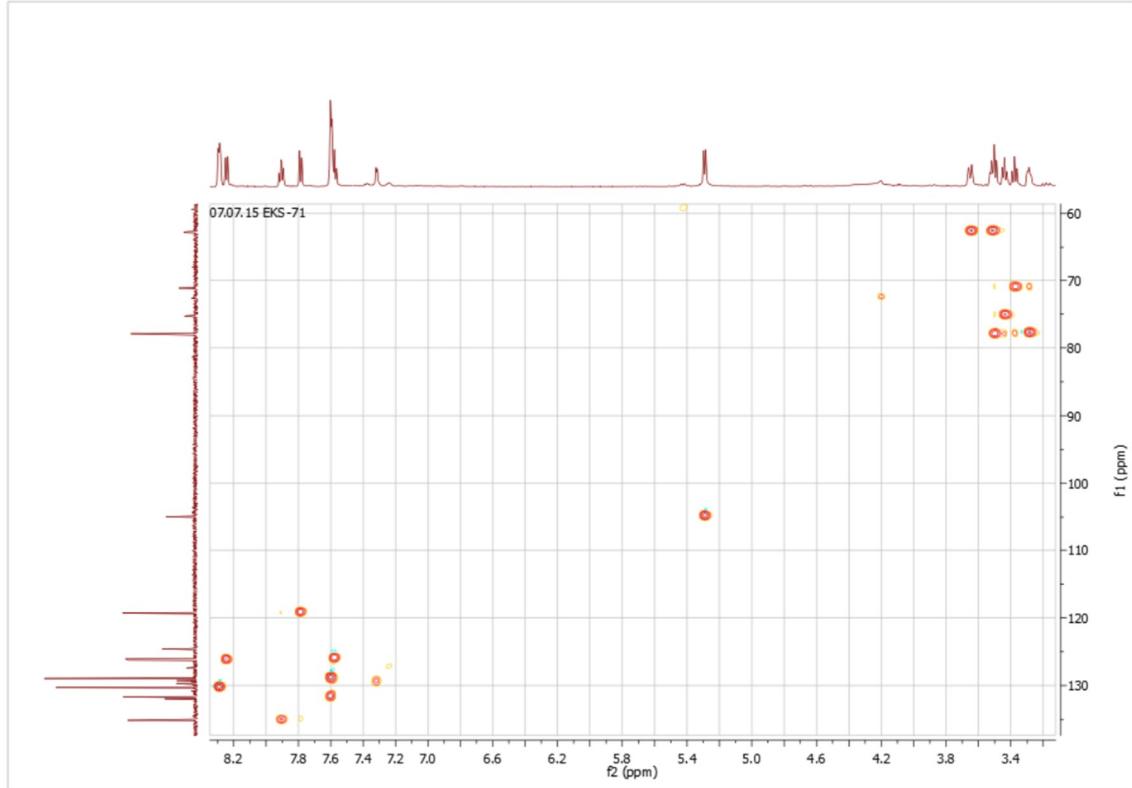
**Figure S10.** <sup>1</sup>H NMR spectrum of flavone 3-O- $\beta$ -D-glucopyranoside (1b) (Acetone-d<sub>6</sub>, 600 MHz)



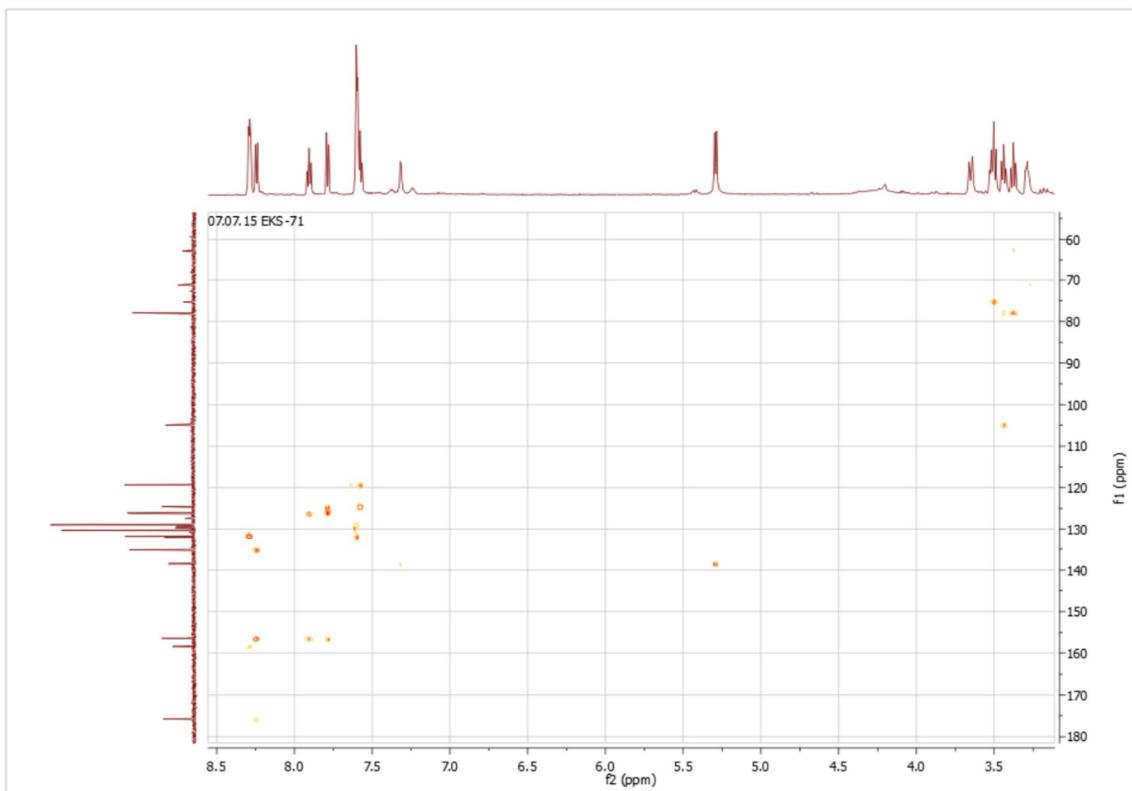
**Figure S11.**  $^1\text{H}$  NMR spectrum of flavone 3- $O$ - $\beta$ -D-glucopyranoside (1b) (Acetone- $d_6$ , 600 MHz)



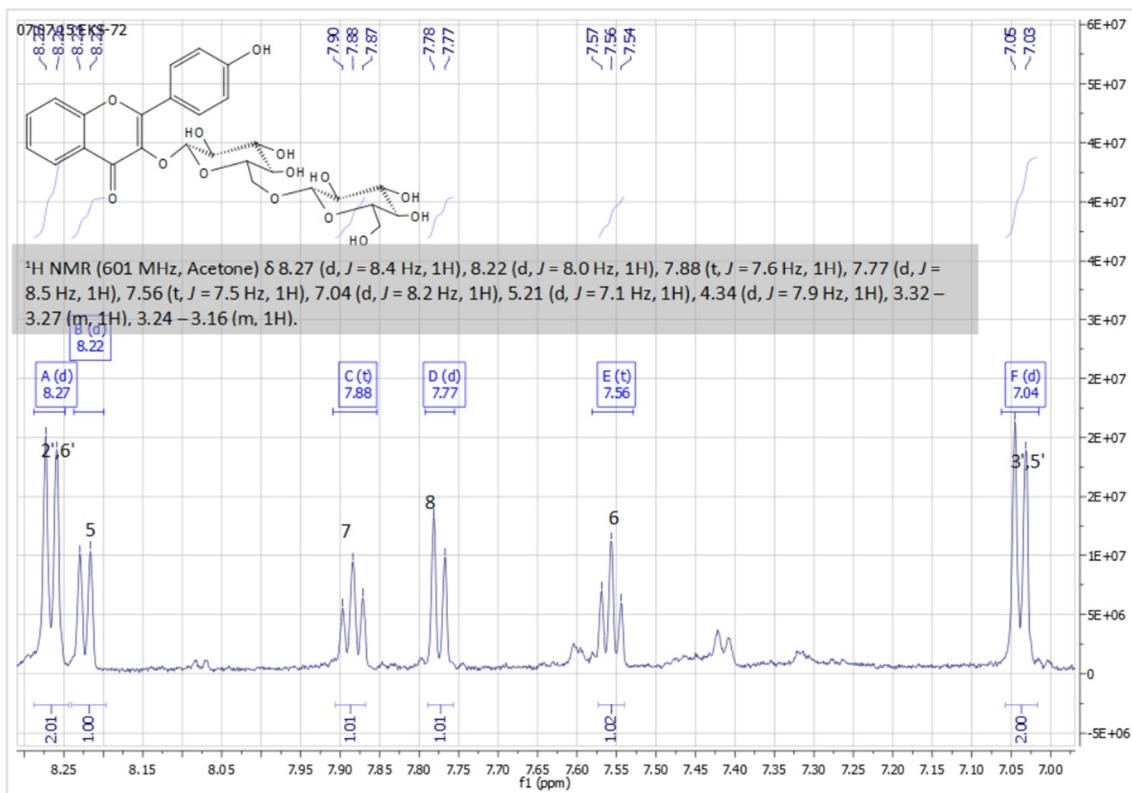
**Figure S12.**  $^{13}\text{C}$  NMR spectrum of flavone 3- $O$ - $\beta$ -D-glucopyranoside (1b) (Acetone- $d_6$ , 151 MHz)



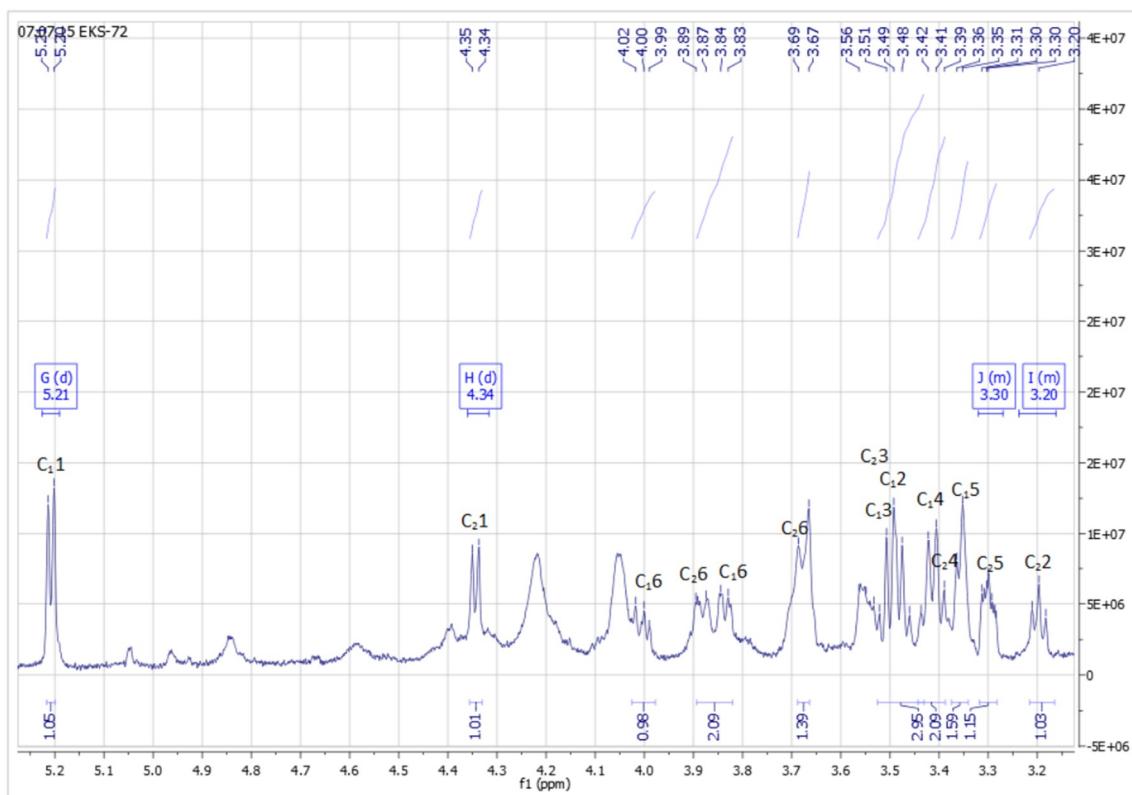
**Figure S13.** HSQC NMR spectrum of flavone 3- $O$ - $\beta$ -D-glucopyranoside (1b) (Acetone-d<sub>6</sub>, 151 MHz)



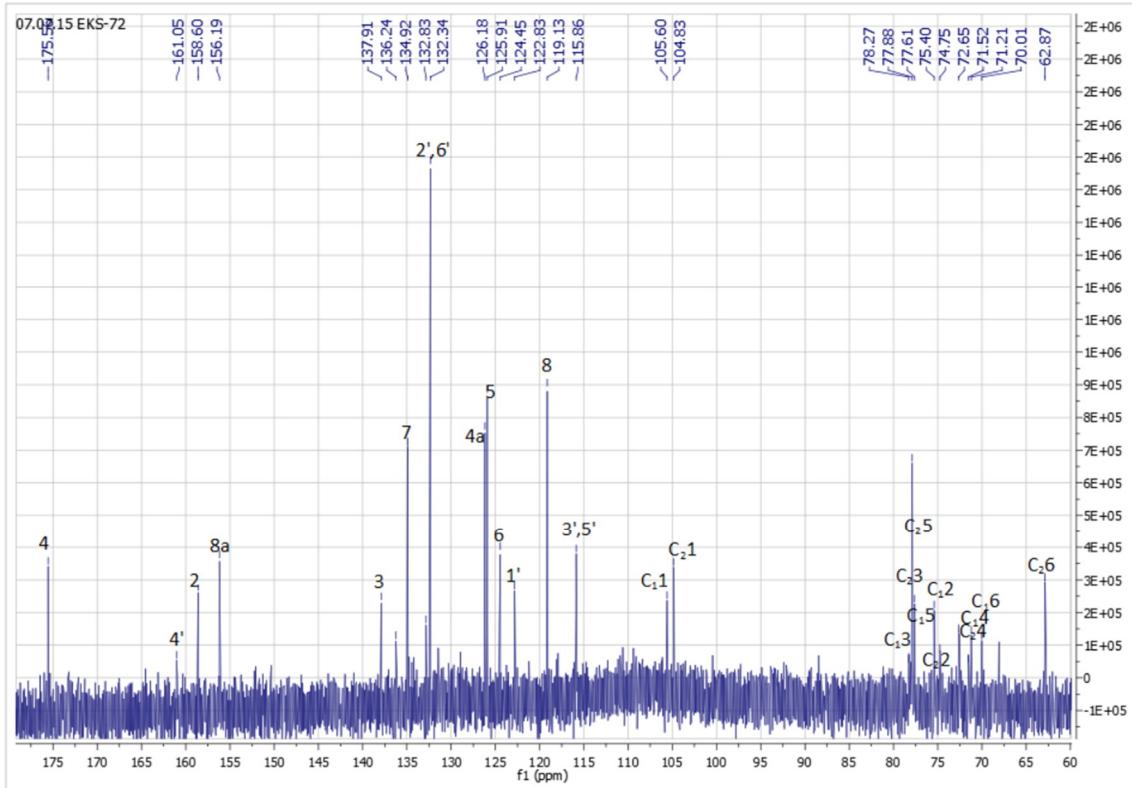
**Figure S14.** HMBC NMR spectrum of flavone 3- $O$ - $\beta$ -D-glucopyranoside (1b) (Acetone-d<sub>6</sub>, 151 MHz)



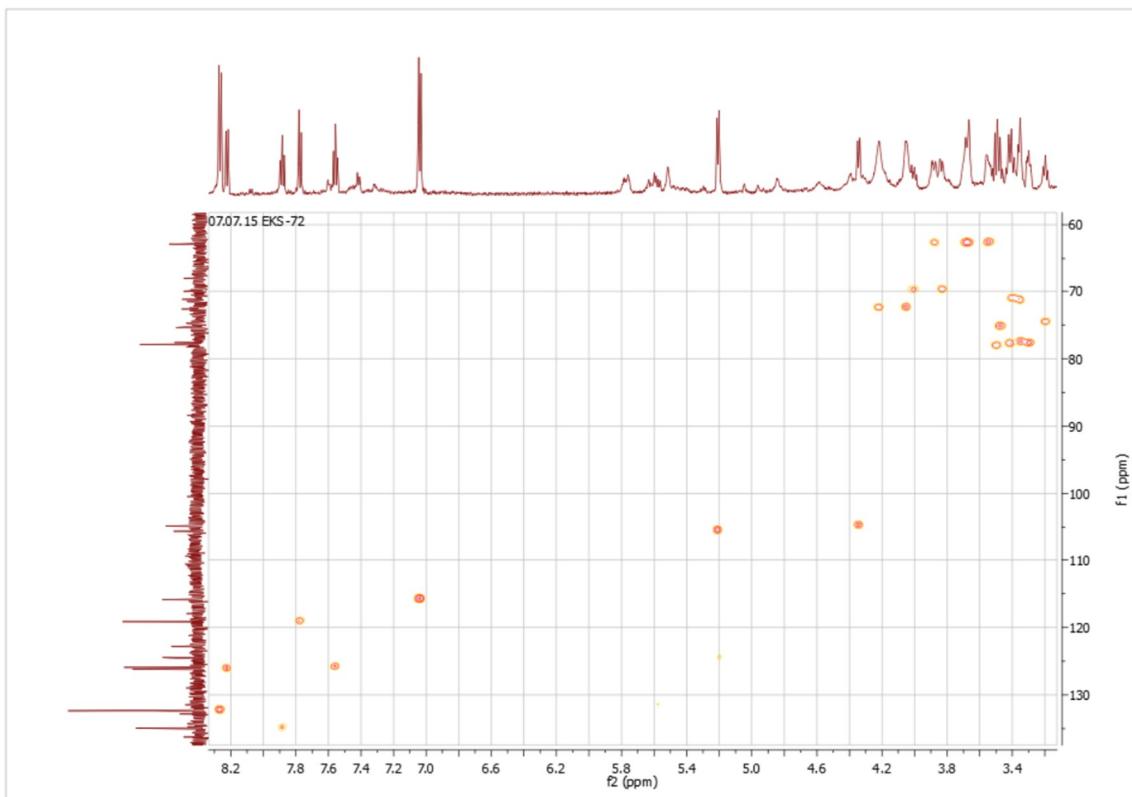
**Figure S15.** <sup>1</sup>H NMR spectrum of 3-O-[β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl]-4'-hydroxyflavone (1c) (Acetone-d<sub>6</sub>, 600 MHz)



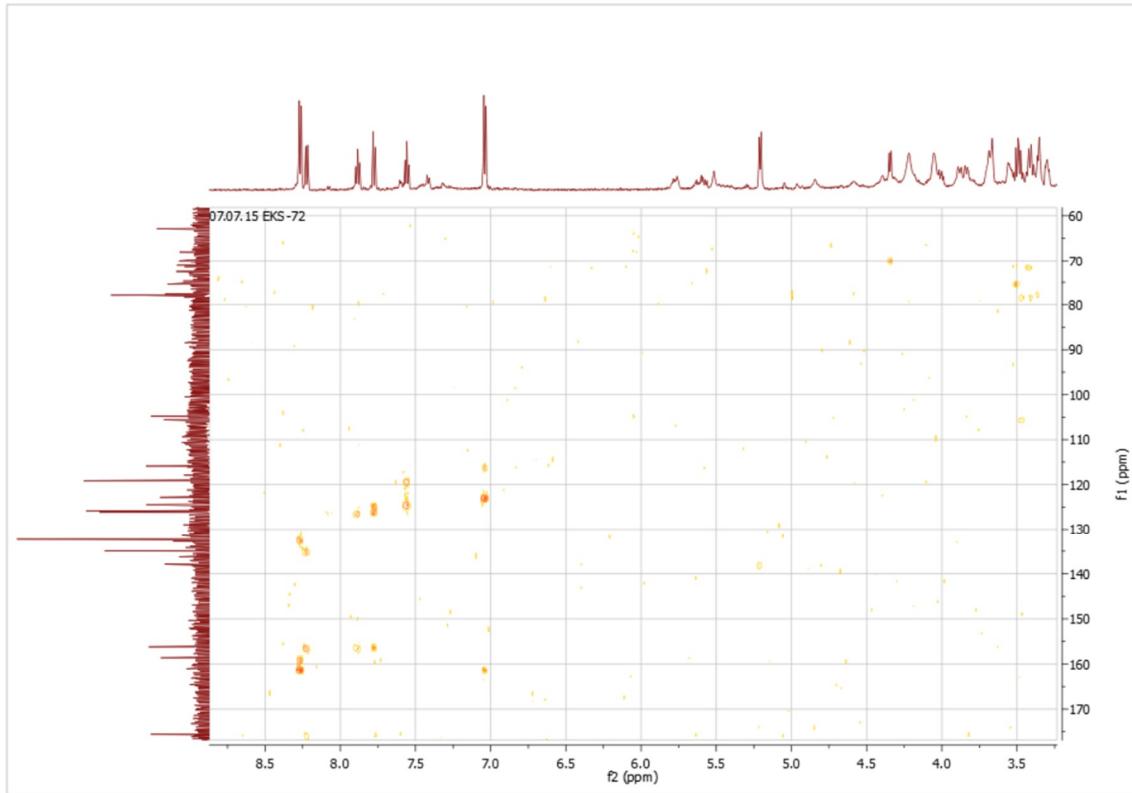
**Figure S16.** <sup>1</sup>H NMR spectrum of 3-O-[β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl]-4'-hydroxyflavone (Acetone-d<sub>6</sub>, 600 MHz)



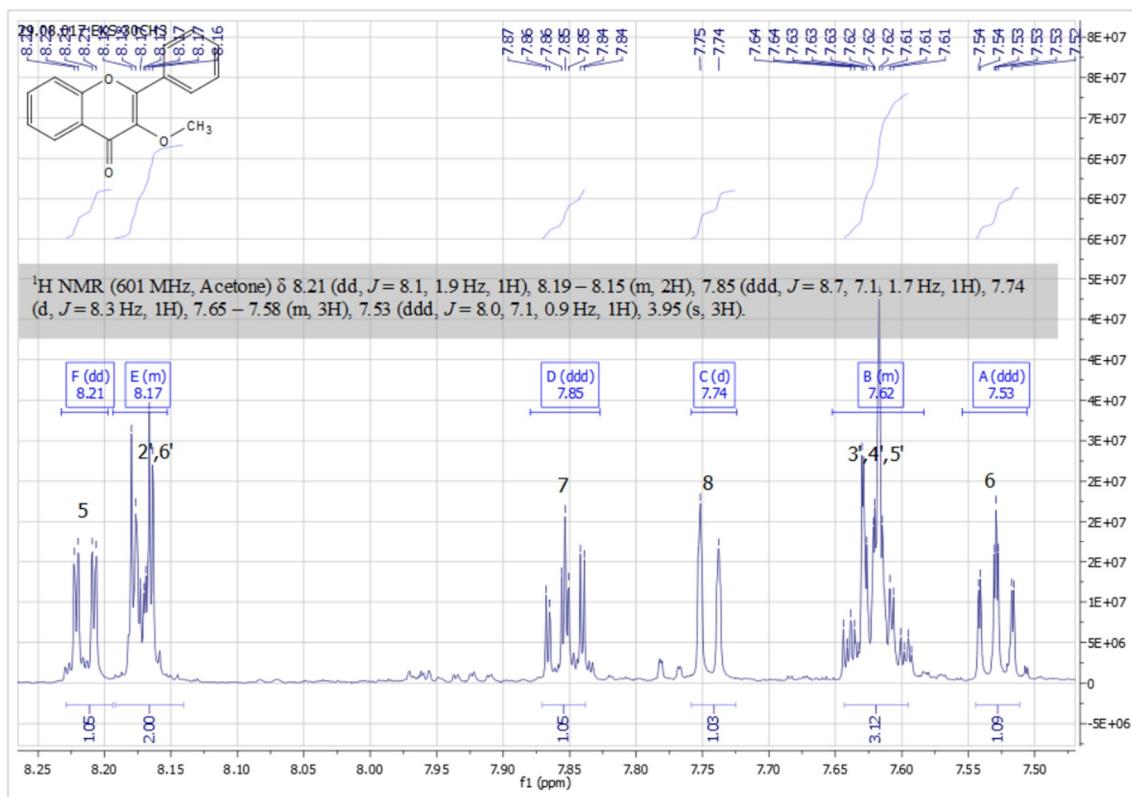
**Figure S17.**  $^{13}\text{C}$  NMR spectrum of 3-O-[ $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranosyl]-4'-hydroxyflavone (Acetone-d<sub>6</sub>, 151 MHz)



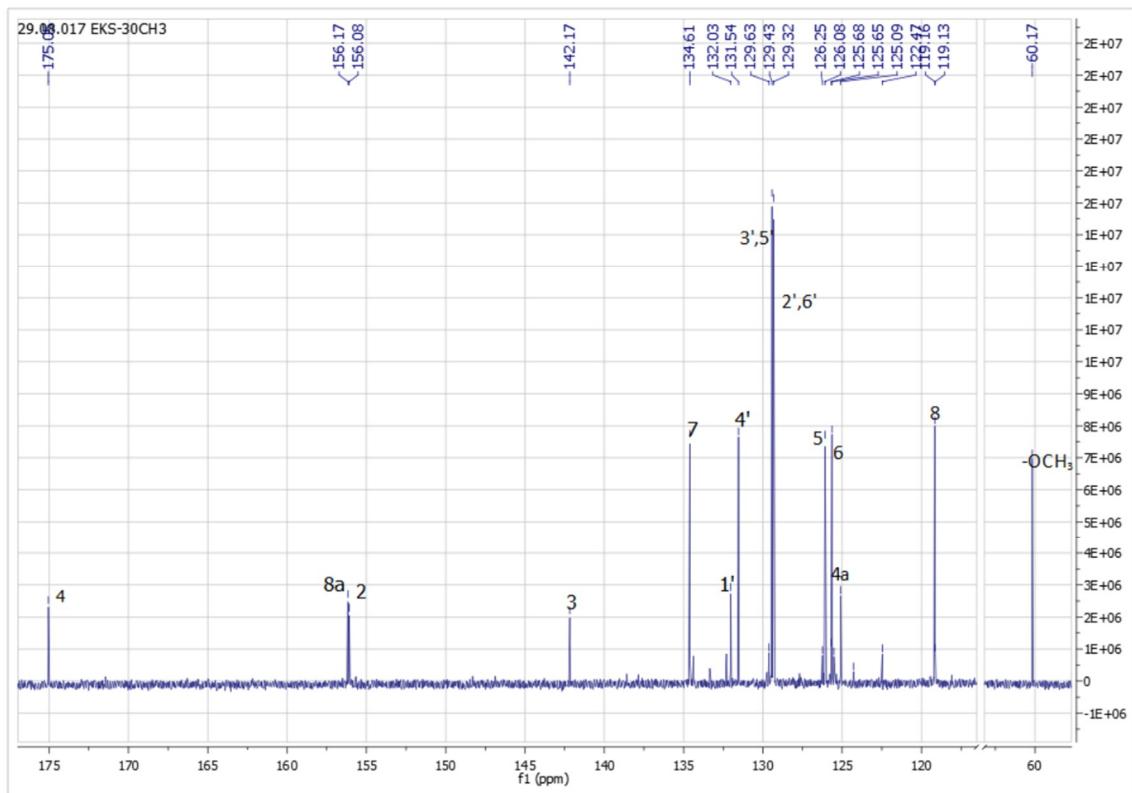
**Figure S18.** HSQC NMR spectrum of 3-O-[ $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranosyl]-4'-hydroxyflavone (Acetone-d<sub>6</sub>, 151 MHz)



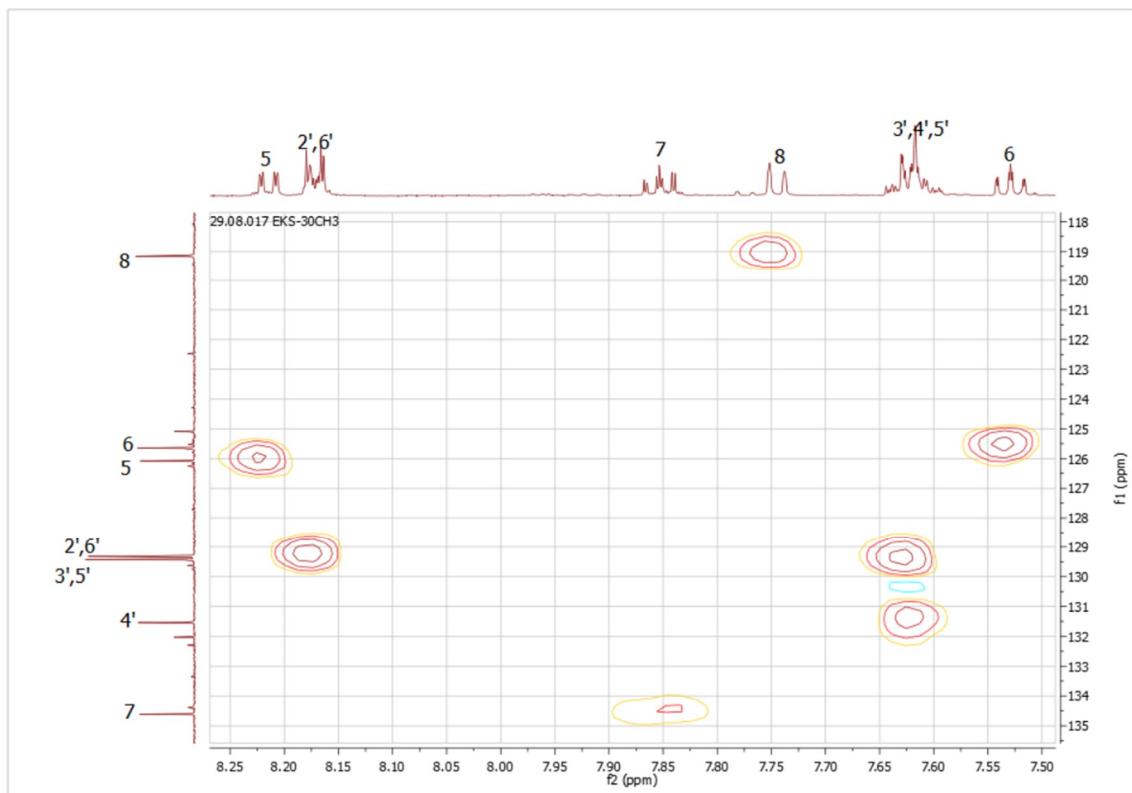
**Figure S19.** HMBC NMR spectrum of 3-O-[ $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranosyl]-4'-hydroxyflavone (Acetone-d<sub>6</sub>, 151 MHz)



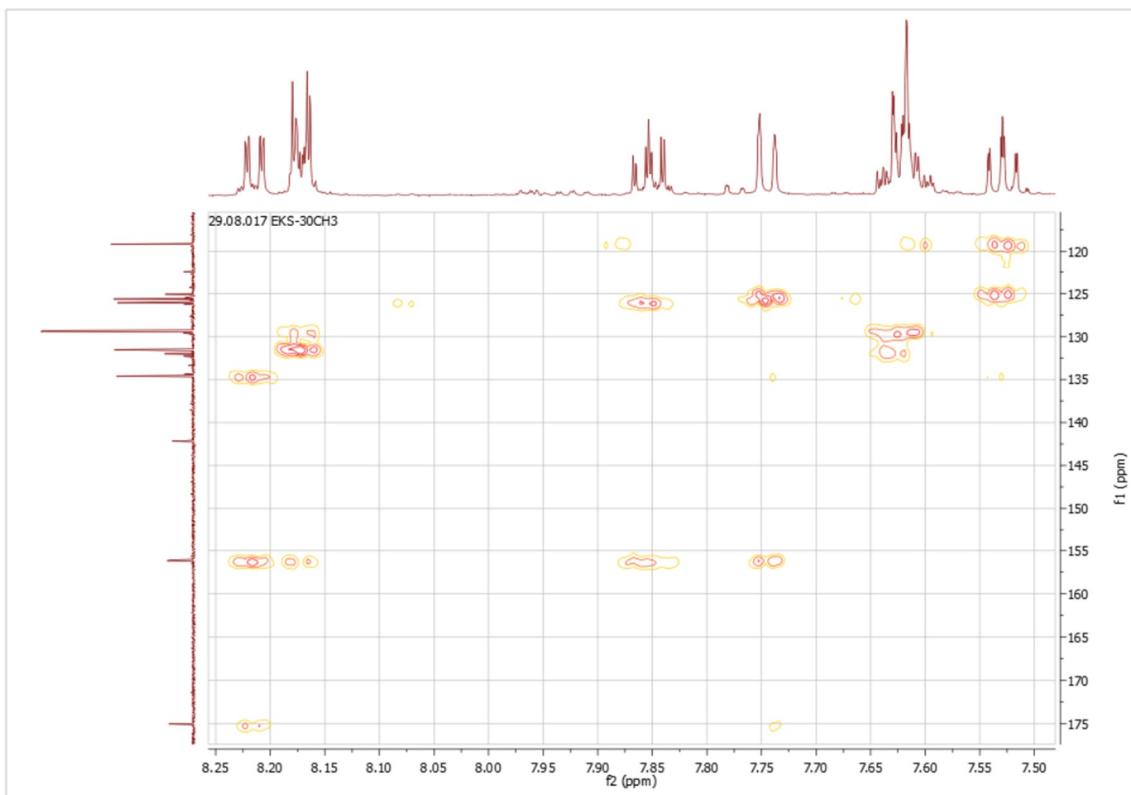
**Figure S20.** <sup>1</sup>H NMR spectrum of 3-methoxyflavone (2) (Acetone-d<sub>6</sub>, 600 MHz)



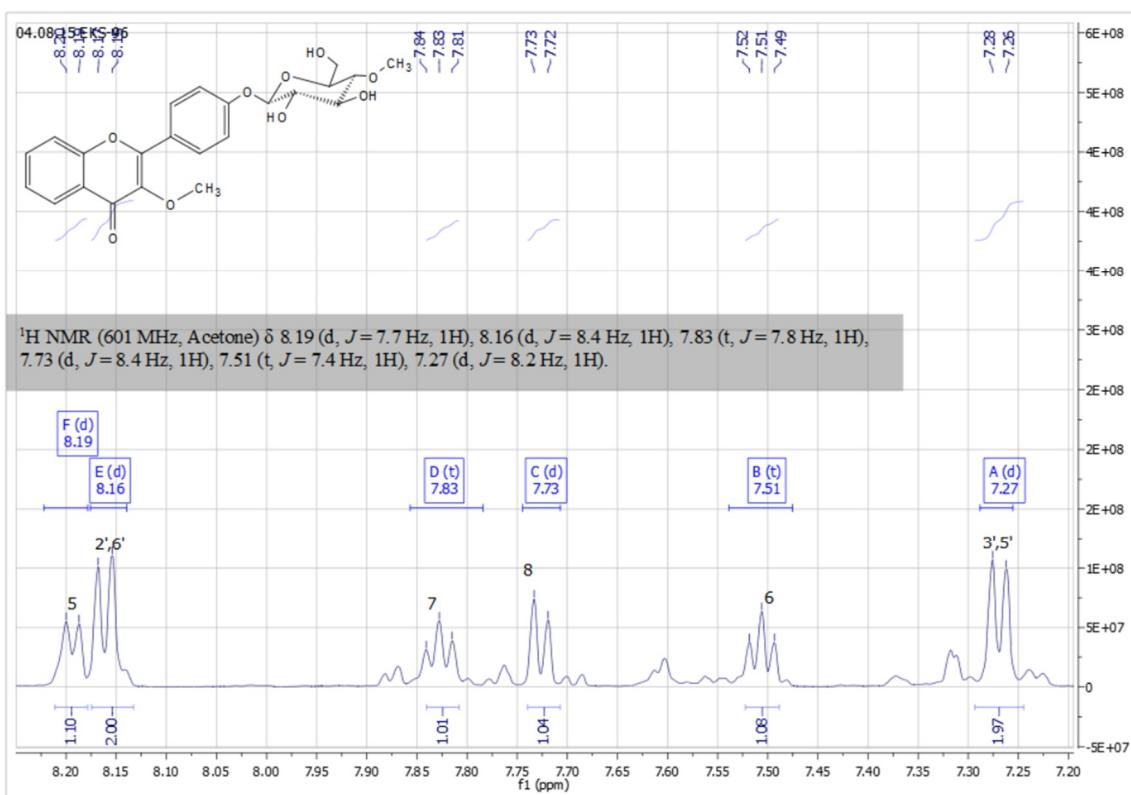
**Figure S21.**  $^{13}\text{C}$  NMR spectrum of 3-methoxyflavone (2) (Acetone- $\text{d}_6$ , 151 MHz)



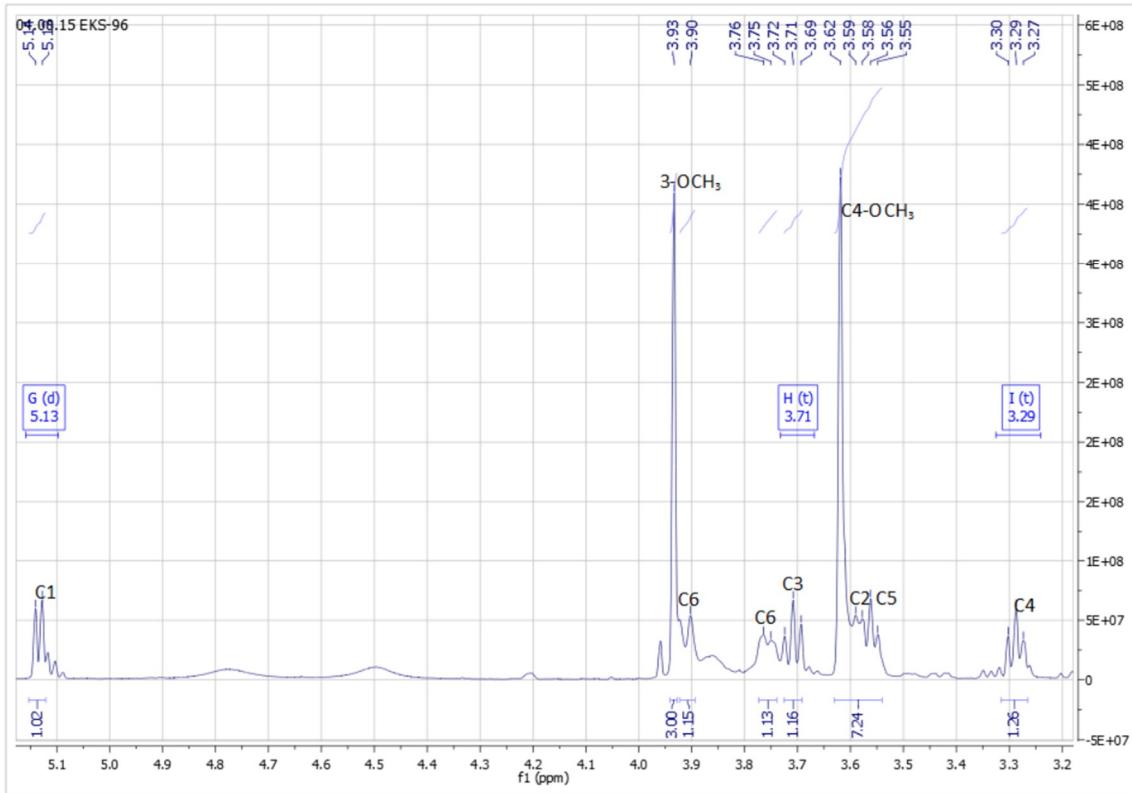
**Figure S22.** HSQC NMR spectrum of 3-methoxyflavone (2) (Acetone- $\text{d}_6$ , 151 MHz)



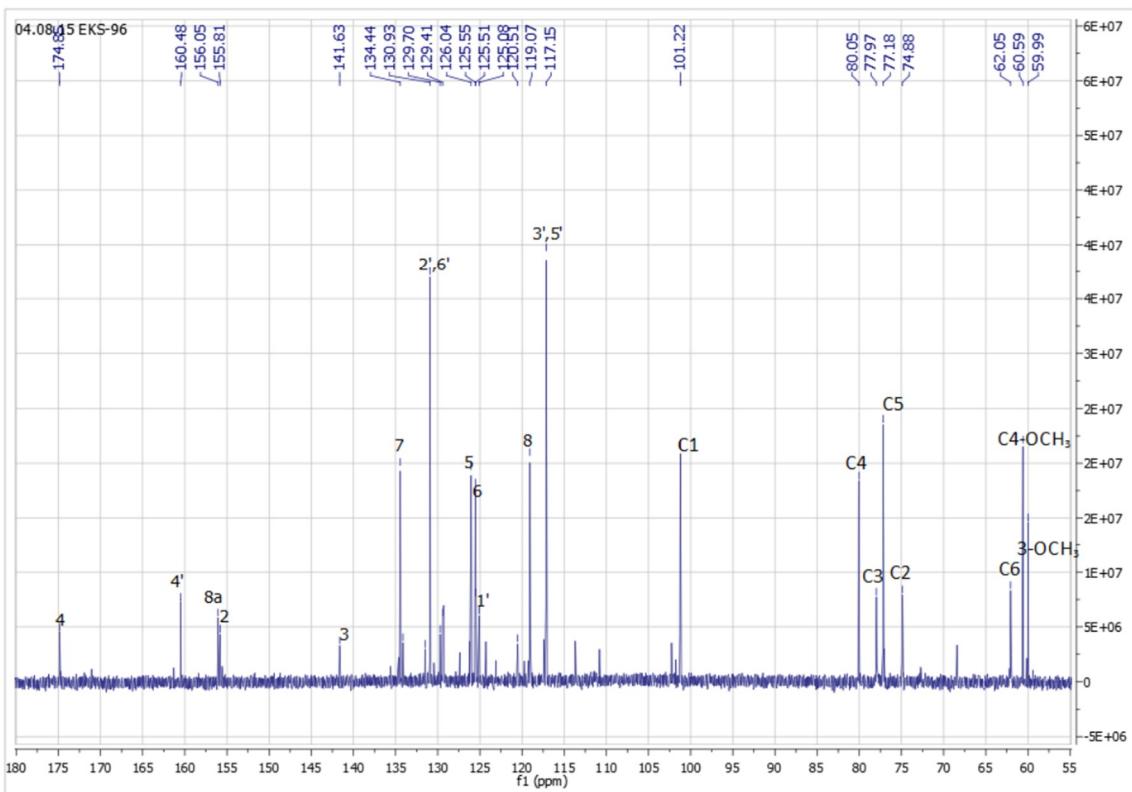
**Figure S23.** HMBC NMR spectrum of 3-methoxyflavone (2) (Acetone-d<sub>6</sub>, 151 MHz)



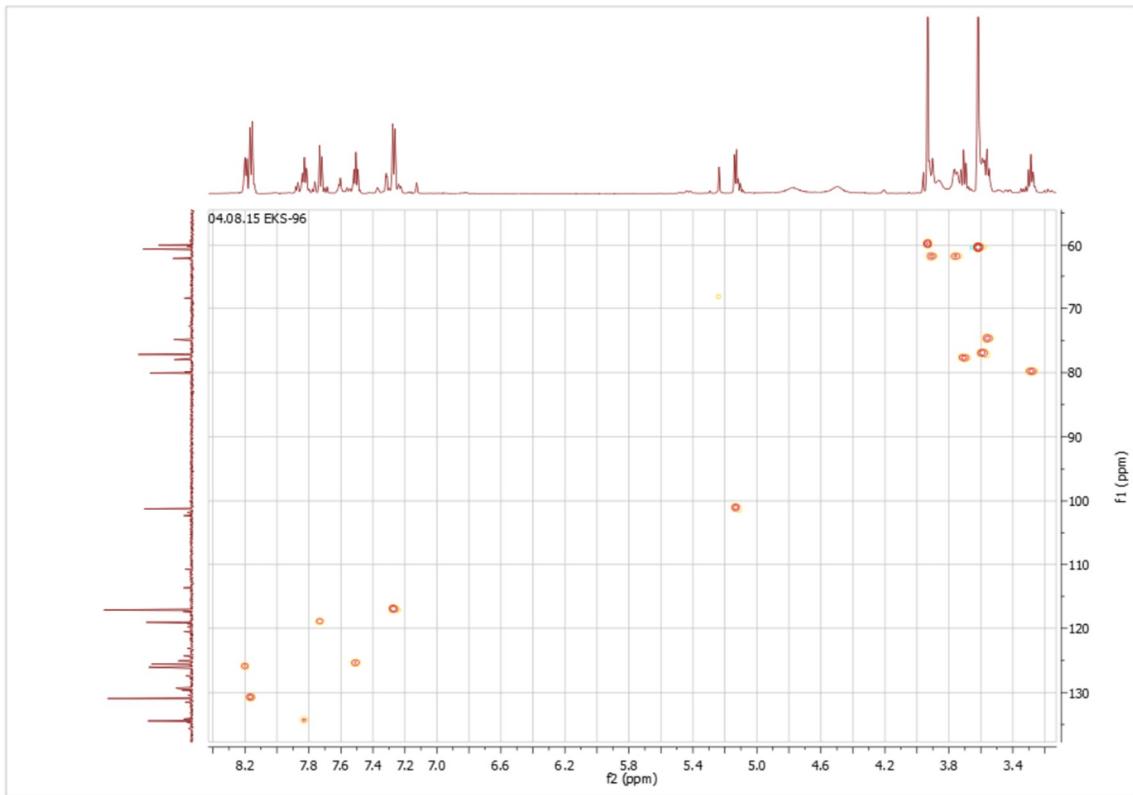
**Figure S24.** <sup>1</sup>H NMR spectrum of 3-methoxyflavone 4'-O-β-D-(4''-O-methyl)-glucopyranoside (2a) (Acetone-d<sub>6</sub>, 600 MHz)



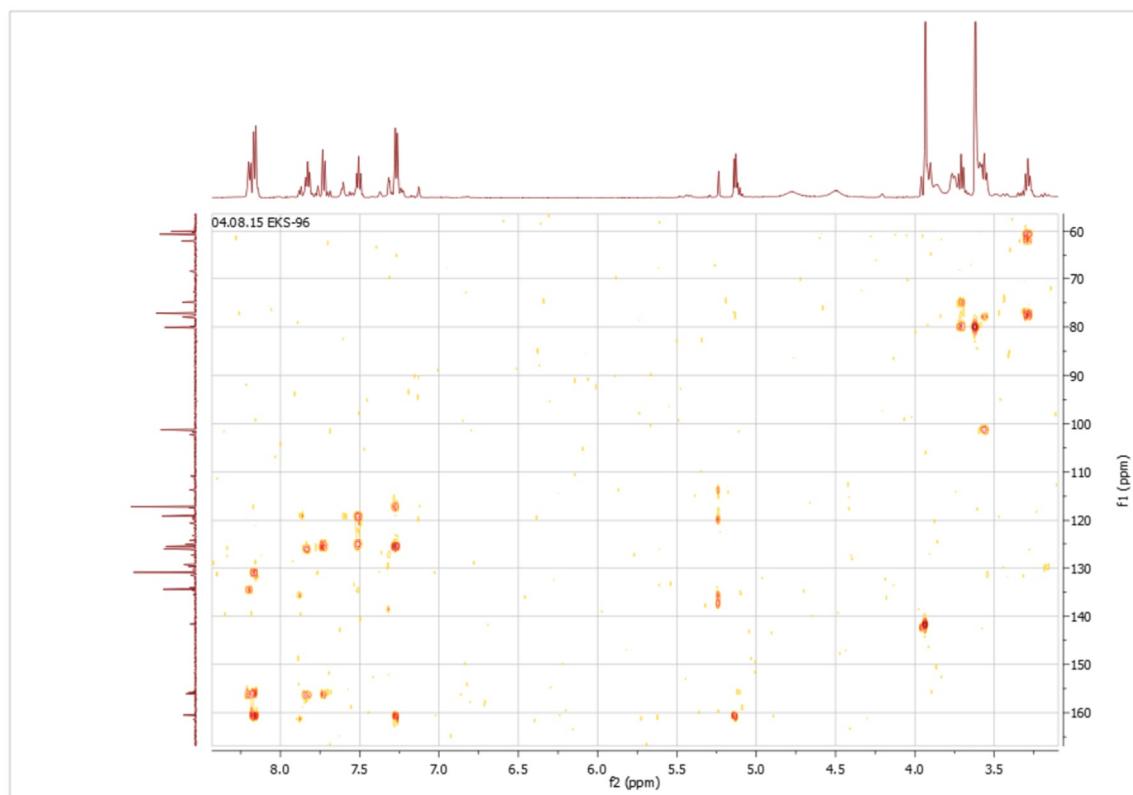
**Figure S25.**  $^1\text{H}$  NMR spectrum of 3-methoxyflavone 4'-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (2a) (Acetone- $d_6$ , 600 MHz)



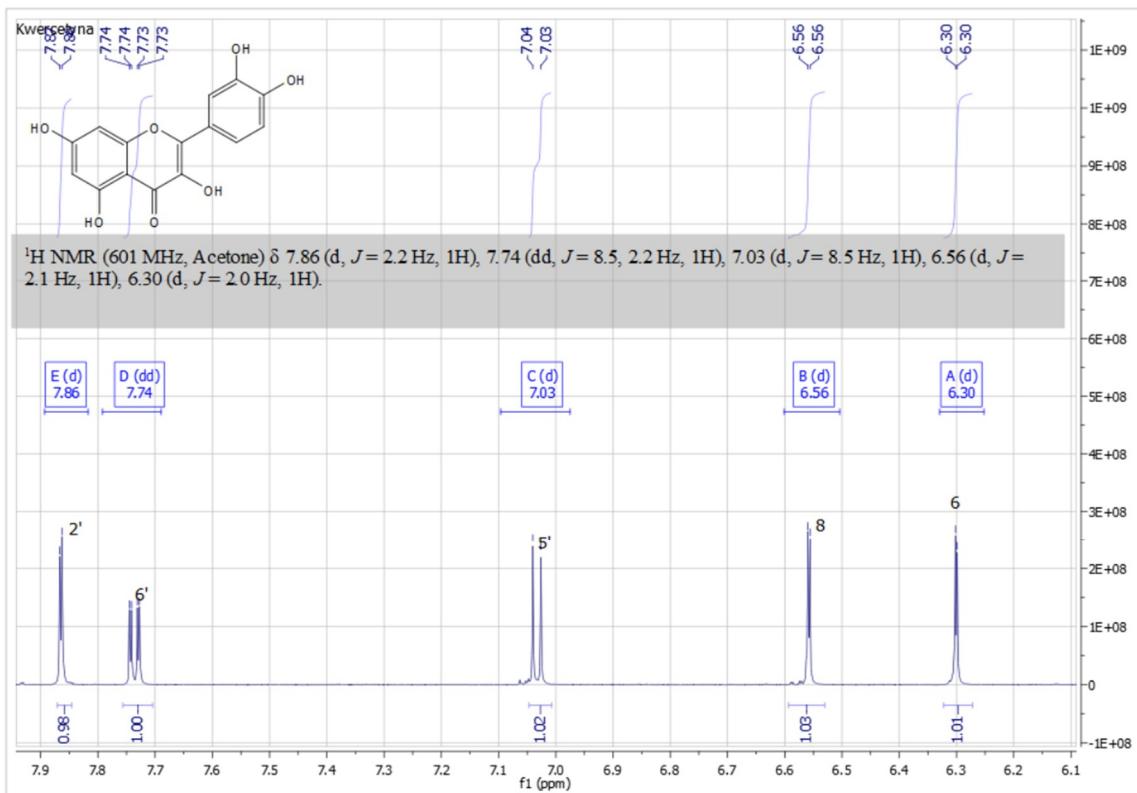
**Figure S26.**  $^{13}\text{C}$  NMR spectrum of 3-methoxyflavone 4'-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (2a) (Acetone- $d_6$ , 151 MHz)



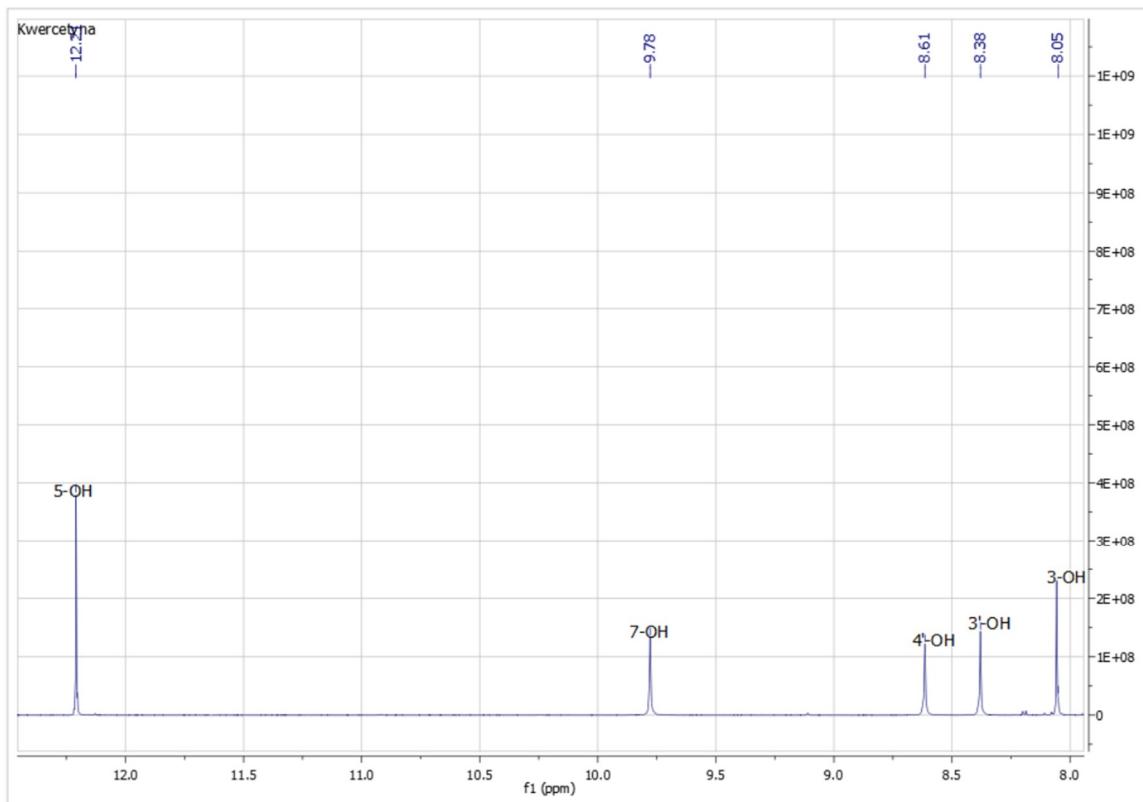
**Figure S27.** HSQC NMR spectrum of 3-methoxyflavone 4'-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (2a) (Acetone-d<sub>6</sub>, 151 MHz)



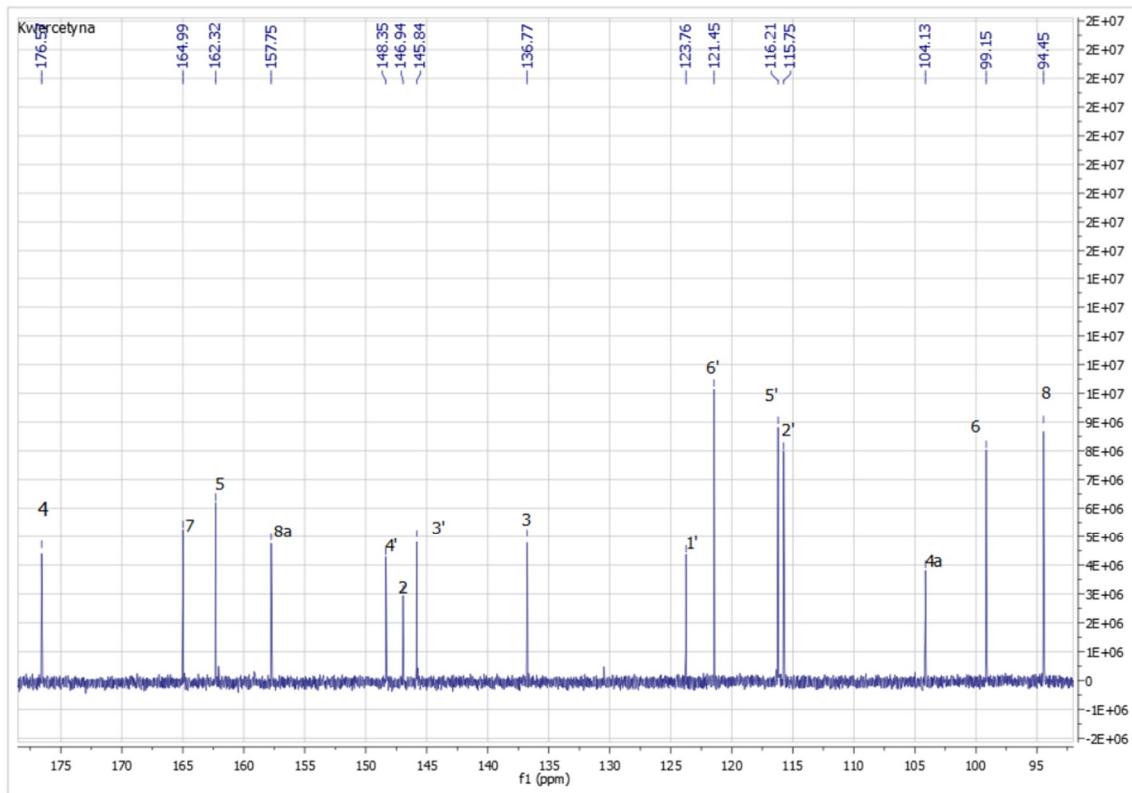
**Figure S28.** HMBC NMR spectrum of 3-methoxyflavone 4'-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (2a) (Acetone-d<sub>6</sub>, 151 MHz)



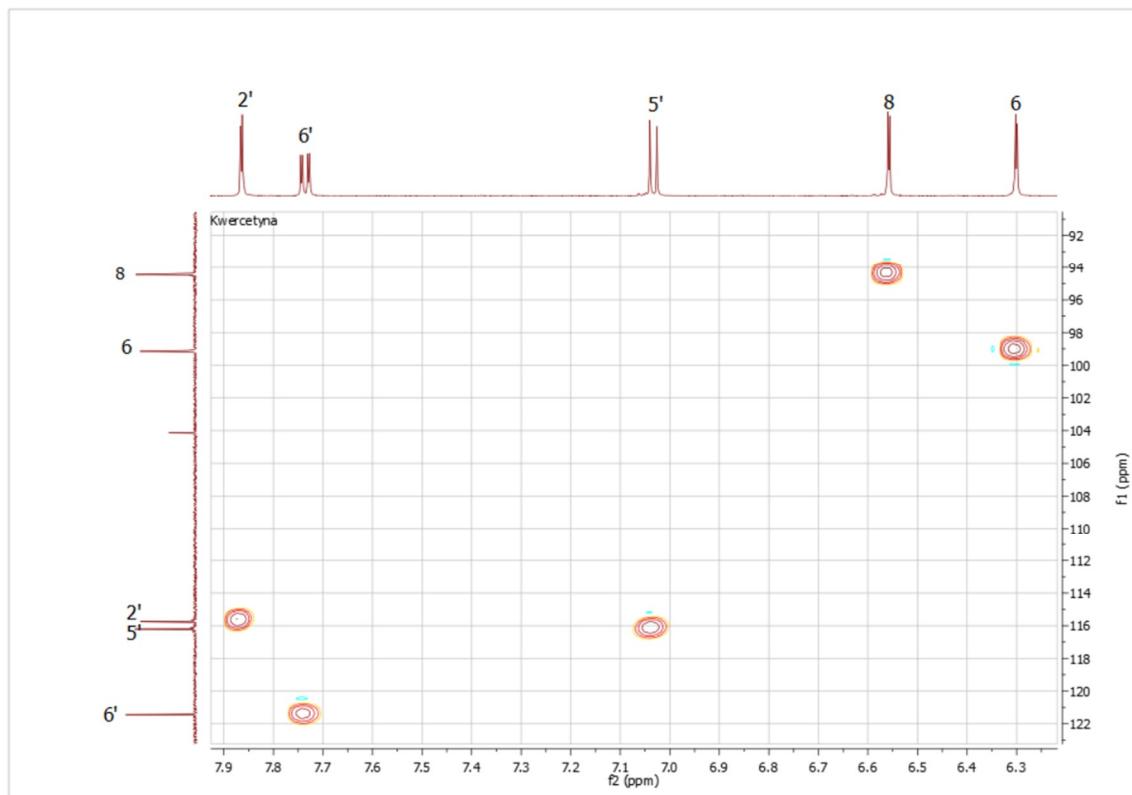
**Figure S29.** <sup>1</sup>H NMR spectrum of 3,3',4',5,7-Pentahydroxyflavone (Quercetin) (3) (Acetone-d<sub>6</sub>, 600 MHz)



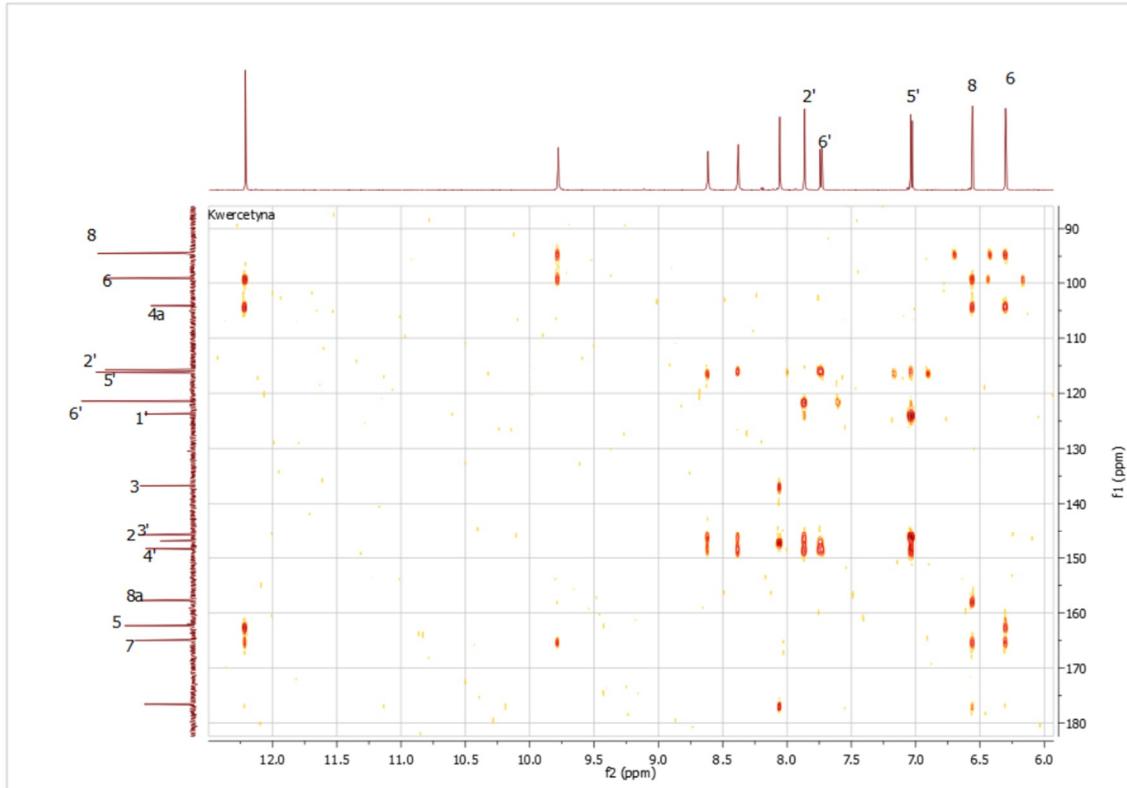
**Figure S30.** <sup>1</sup>H NMR spectrum of 3,3',4',5,7-Pentahydroxyflavone (Quercetin) (3) (Acetone-d<sub>6</sub>, 600 MHz)



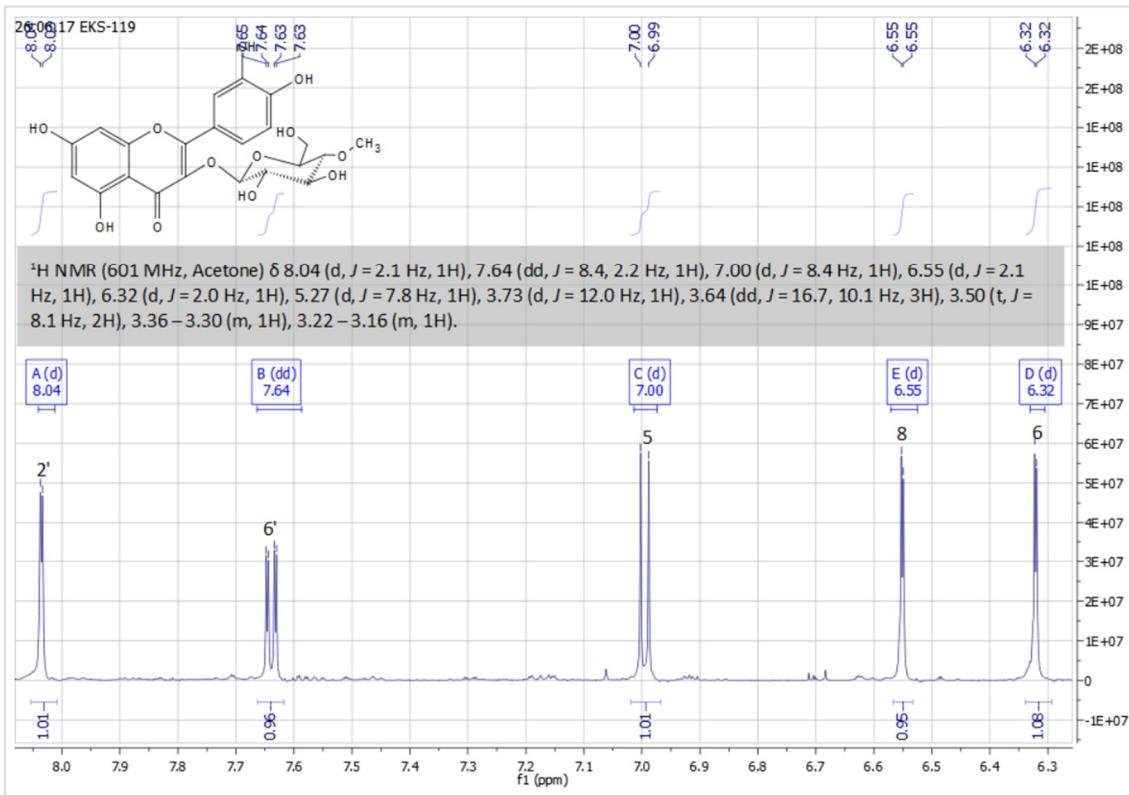
**Figure S31.**  $^{13}\text{C}$  NMR spectrum of 3,3',4',5,7-Pentahydroxyflavone (Quercetin) (3) (Acetone-d<sub>6</sub>, 151 MHz)



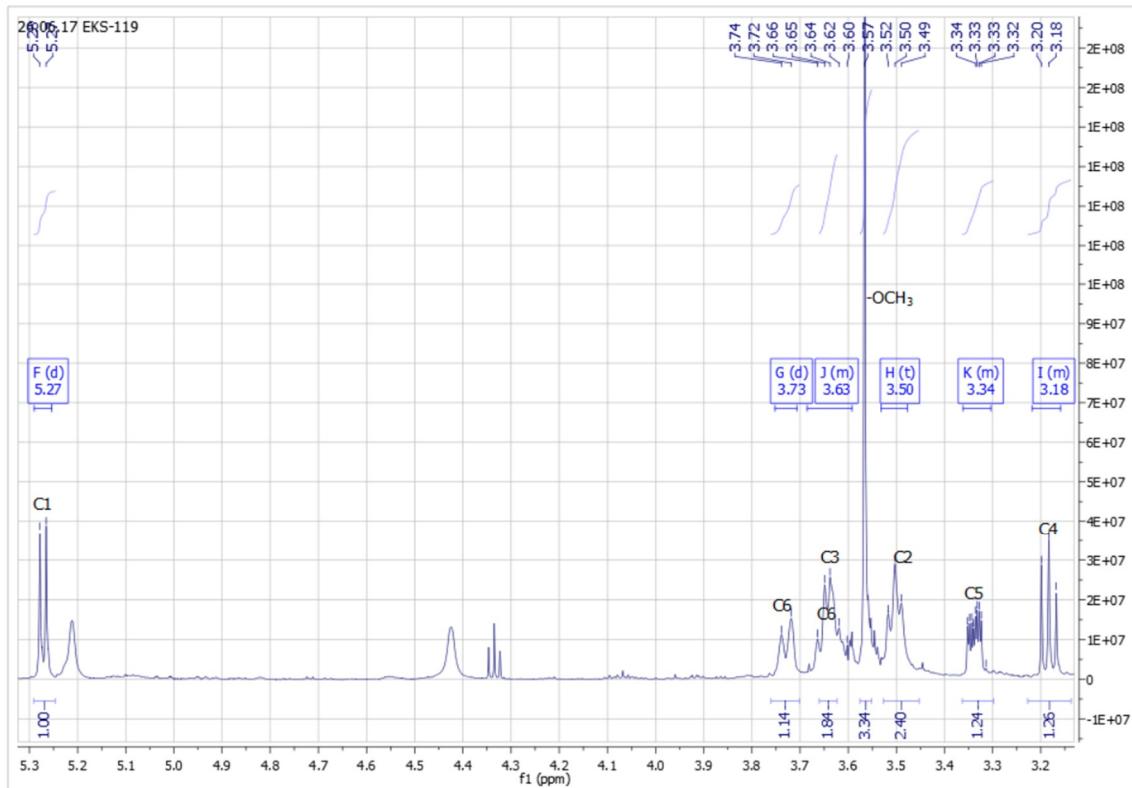
**Figure S32.** HSQC NMR spectrum of 3,3',4',5,7-Pentahydroxyflavone (Quercetin) (3) (Acetone-d<sub>6</sub>, 151 MHz)



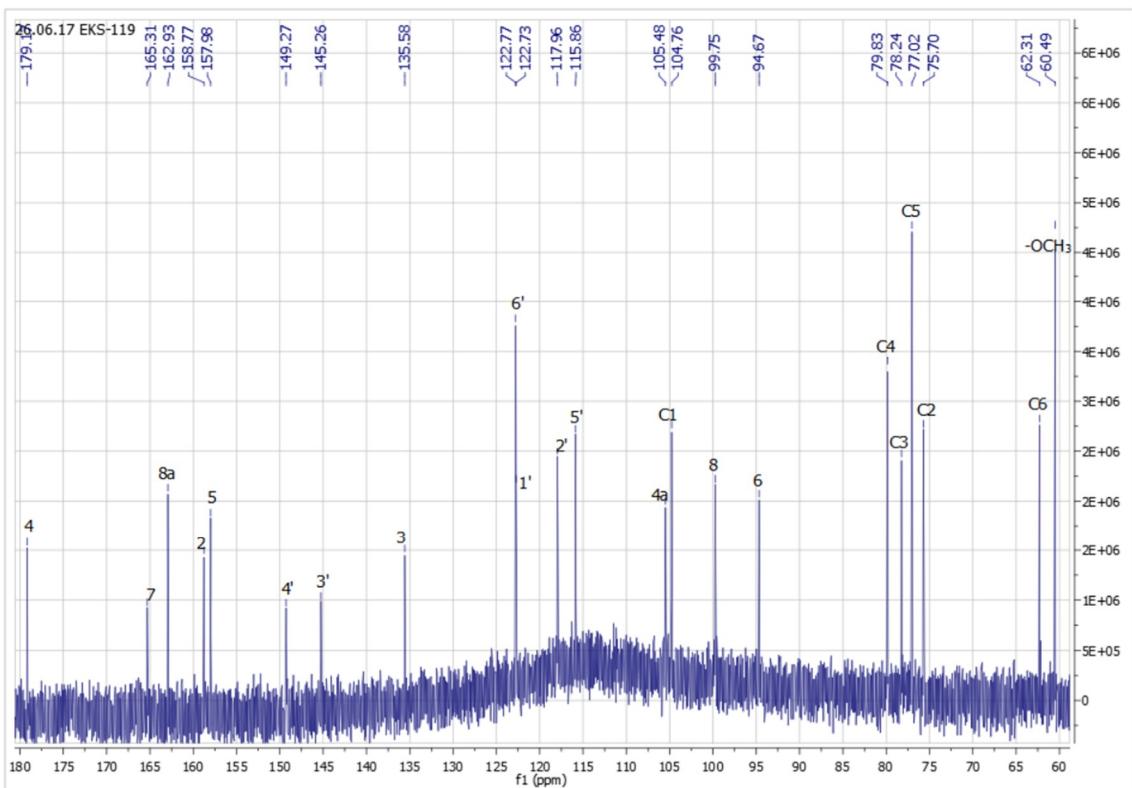
**Figure S33.** HMBC NMR spectrum of 3,3',4',5,7-Pentahydroxyflavone (Quercetin) (3) (Acetone-d<sub>6</sub>, 151 MHz)



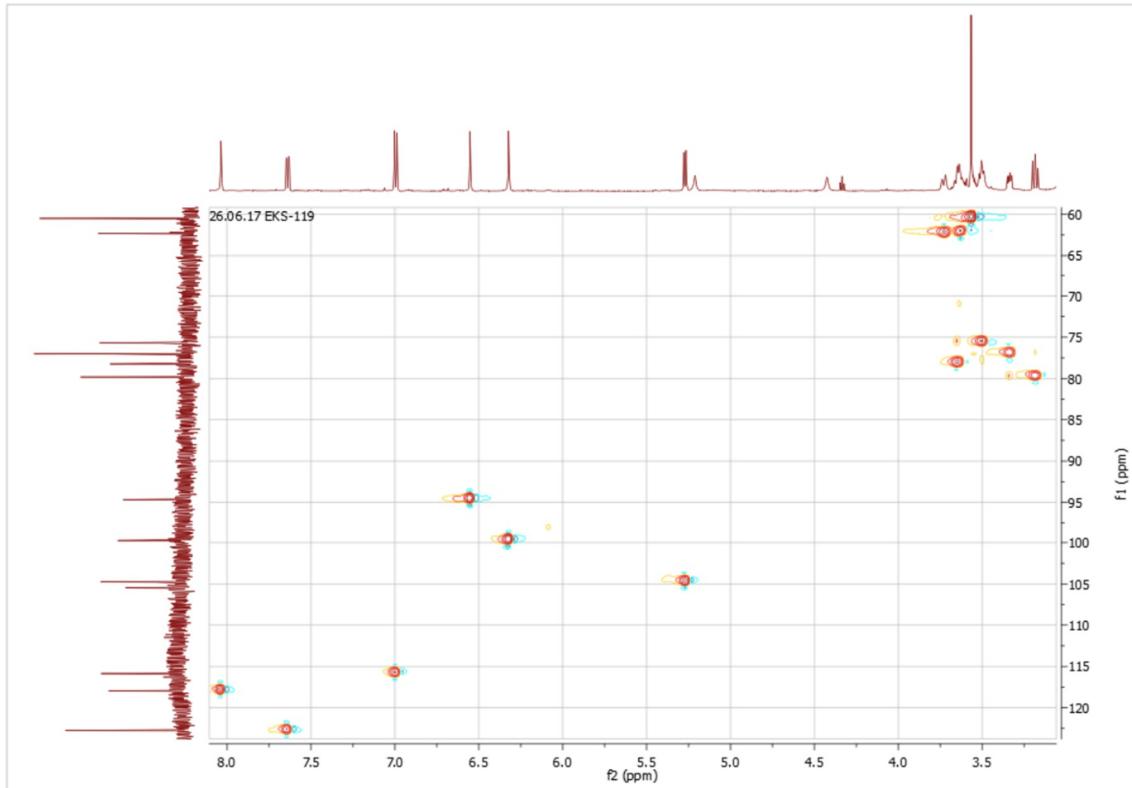
**Figure S34.** <sup>1</sup>H NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3-O-β-D-(4''-O-methyl)-glucopyranoside (3a) (Acetone-d<sub>6</sub>, 600 MHz)



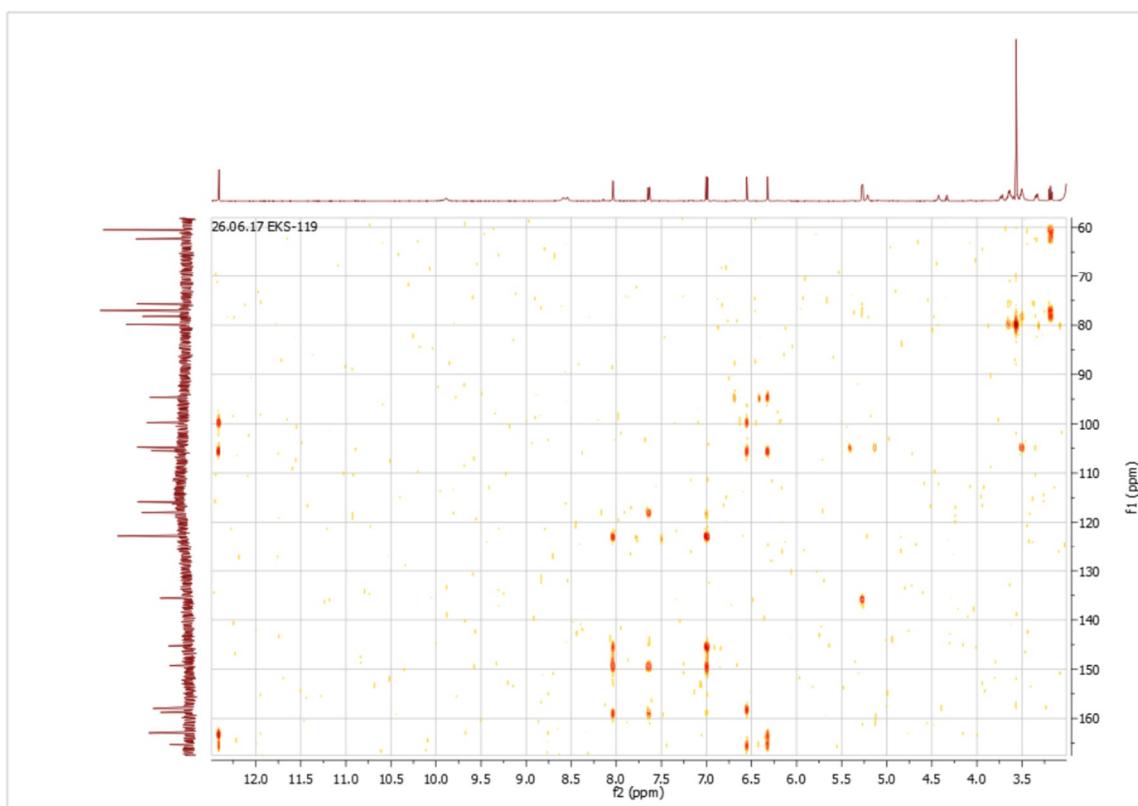
**Figure S35.**  $^1\text{H}$  NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (3a) (Acetone-d<sub>6</sub>, 600 MHz)



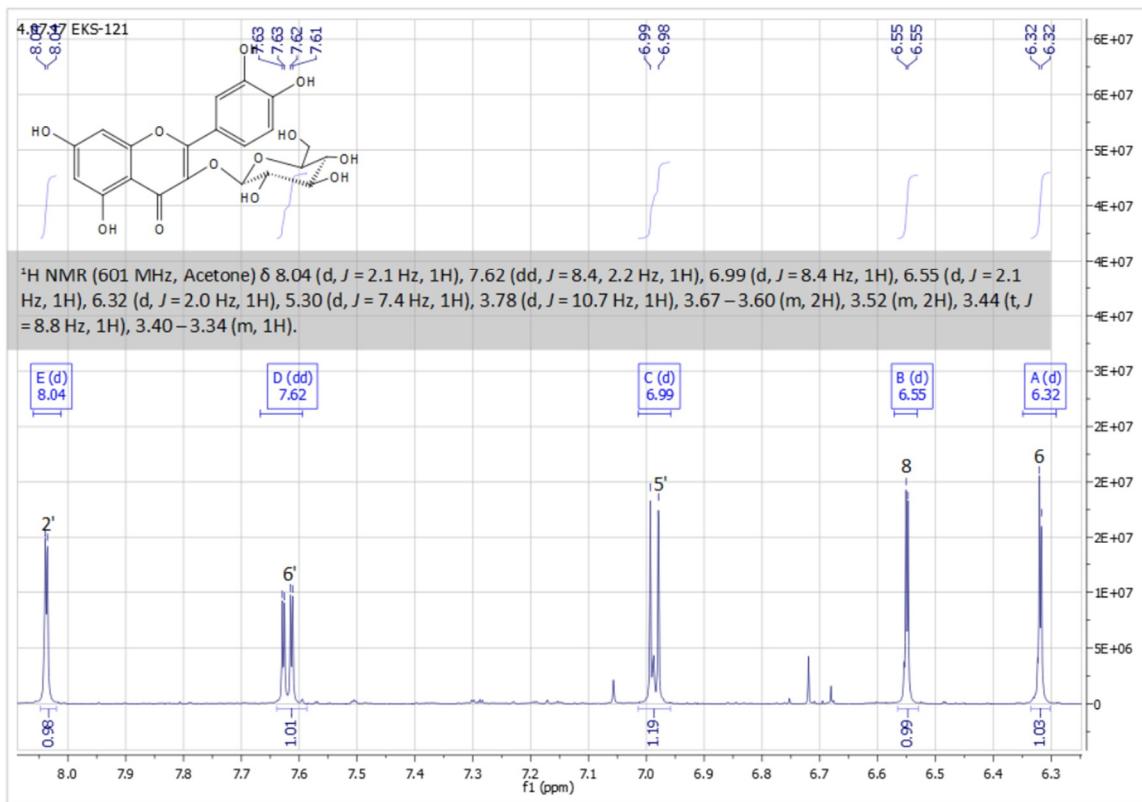
**Figure S36.**  $^{13}\text{C}$  NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (3a) (Acetone-d<sub>6</sub>, 151 MHz)



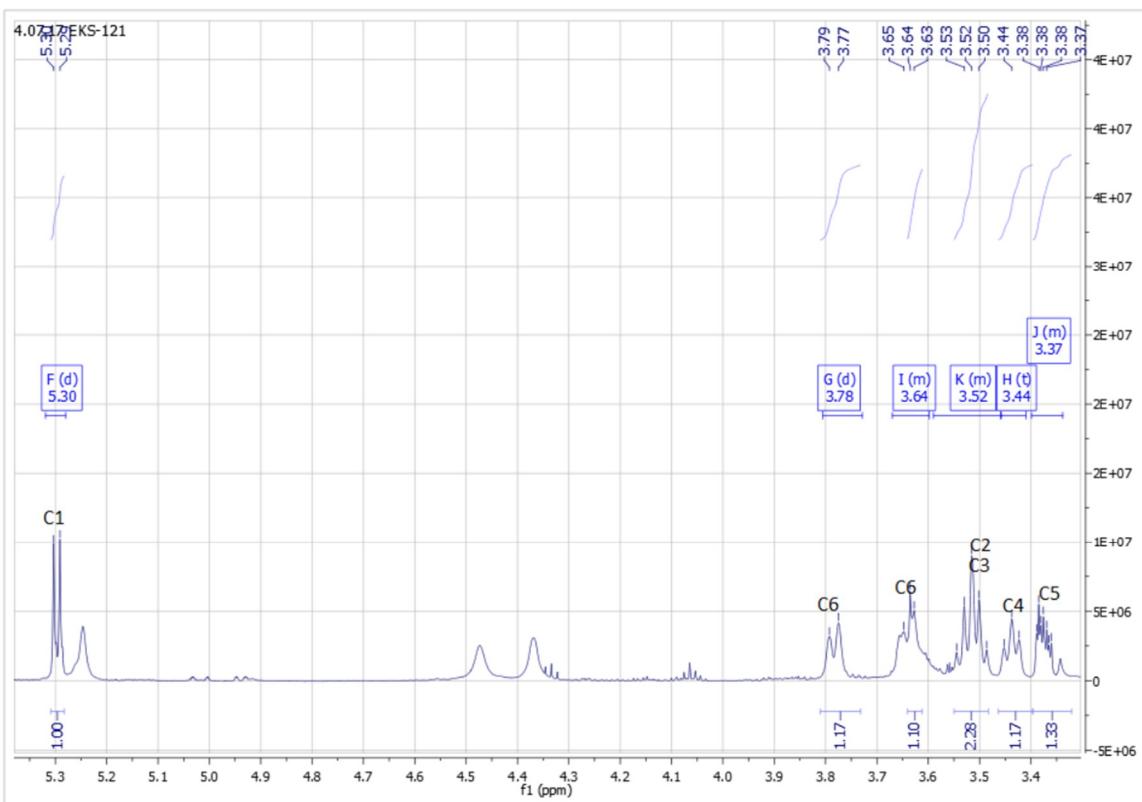
**Figure S37.** HSQC NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (3a) (Acetone-d<sub>6</sub>, 151 MHz)



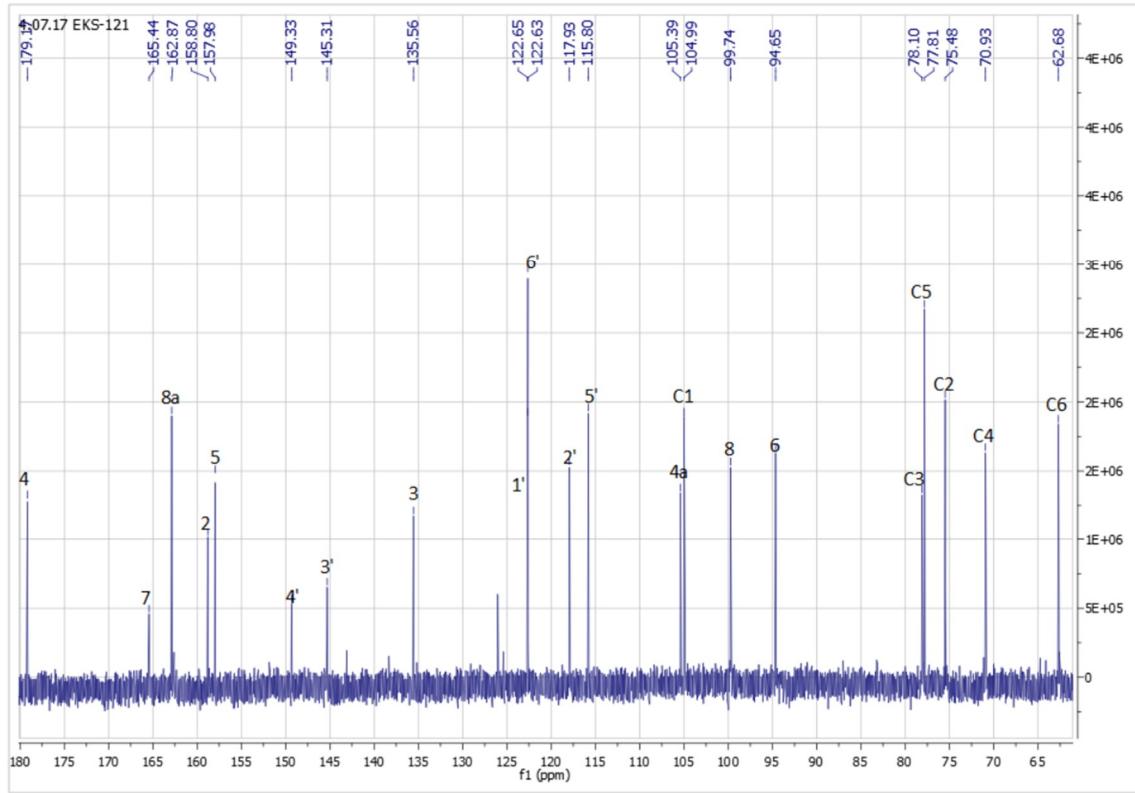
**Figure S38.** HMBC NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (3a) (Acetone-d<sub>6</sub>, 151 MHz)



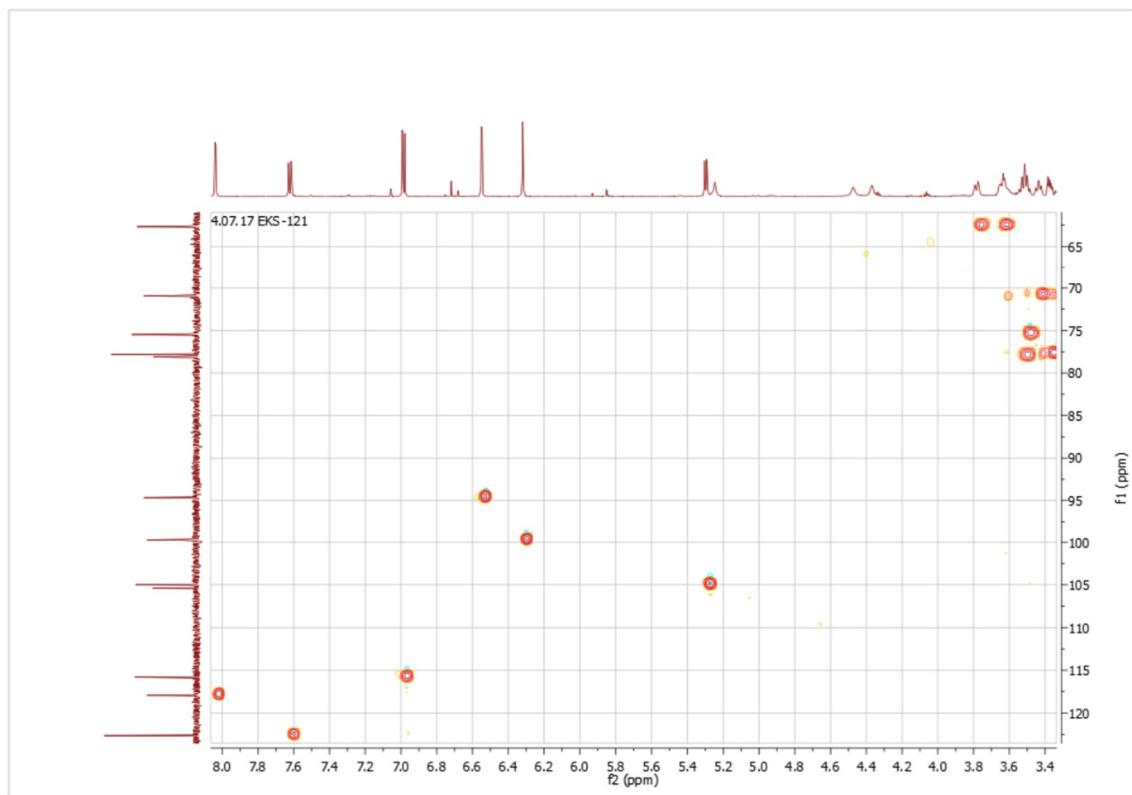
**Figure S39.** <sup>1</sup>H NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3-O-β-D-glucopyranoside (isoquercetin) (3b) (Acetone-d<sub>6</sub>, 600 MHz)



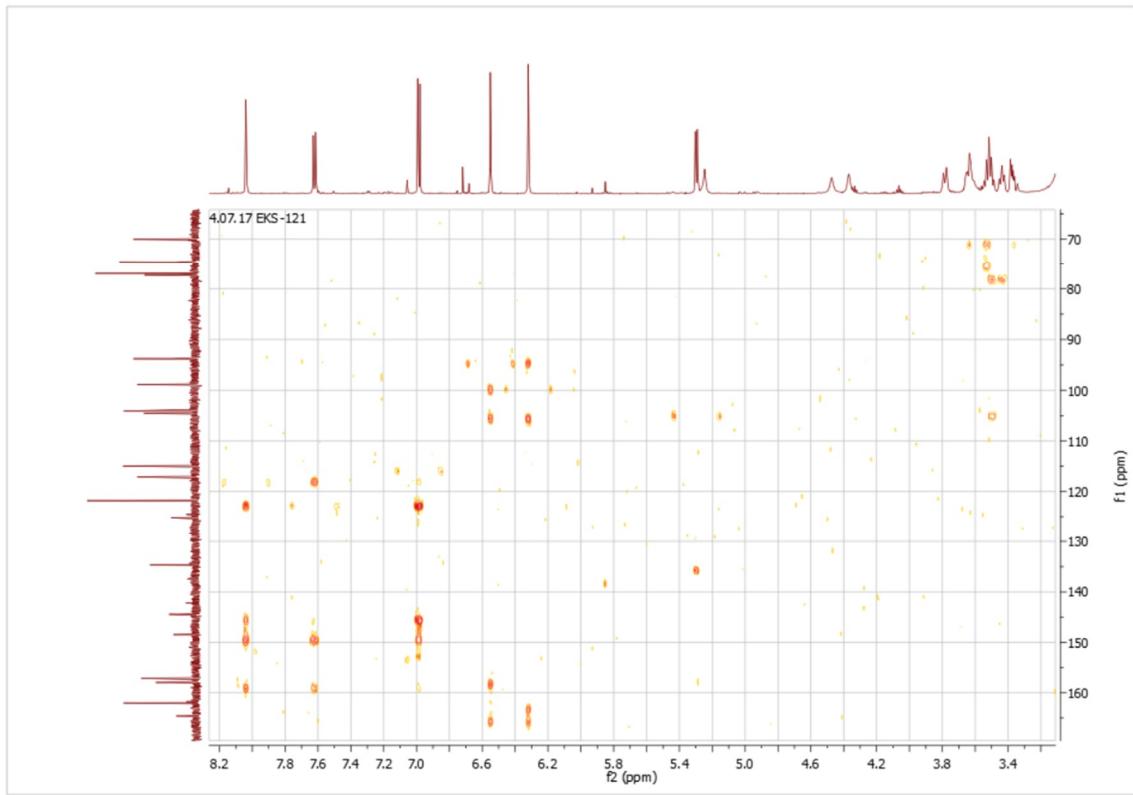
**Figure S40.** <sup>1</sup>H NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3-O-β-D-glucopyranoside (isoquercetin) (3b) (Acetone-d<sub>6</sub>, 600 MHz)



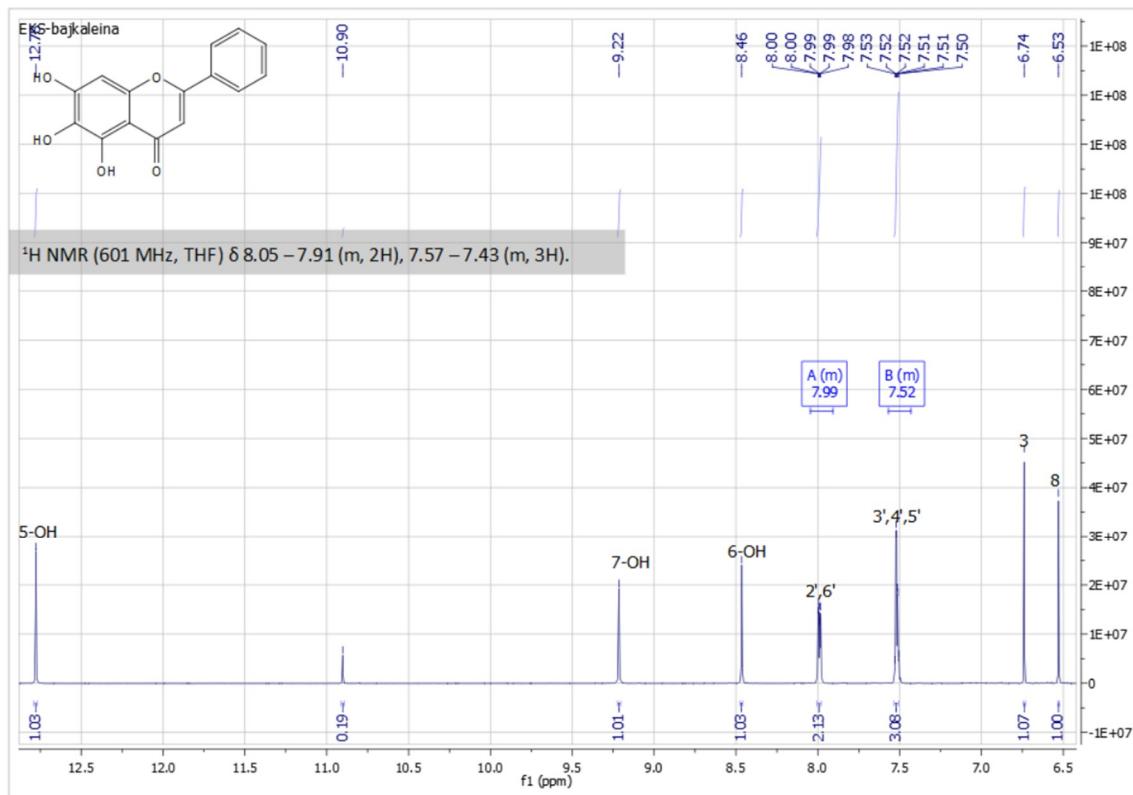
**Figure S41.**  $^{13}\text{C}$  NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3- $O$ - $\beta$ -D-glucopyranoside (isoquercetin) (3b) (Acetone-d<sub>6</sub>, 151 MHz)



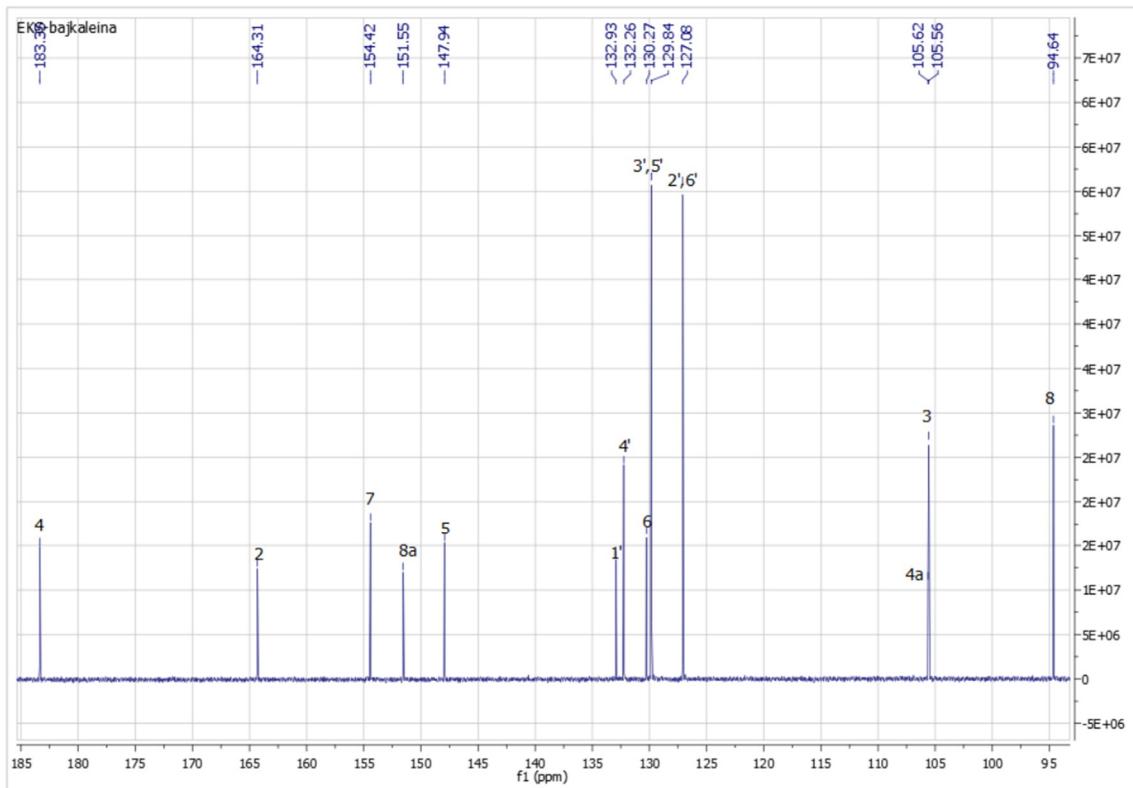
**Figure S42.** HSQC NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3- $O$ - $\beta$ -D-glucopyranoside (isoquercetin) (3b) (Acetone-d<sub>6</sub>, 151 MHz)



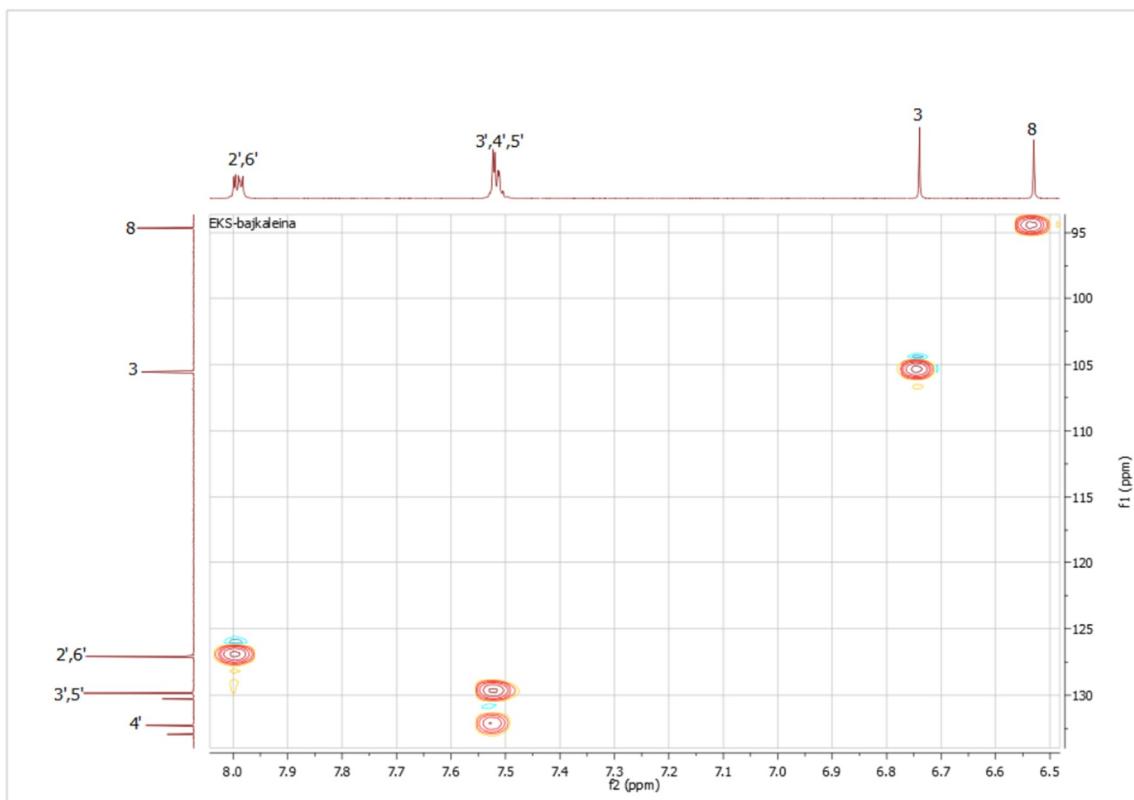
**Figure S43.** HMBC NMR spectrum of 3',4',5,7-tetrahydroxyflavone 3-O- $\beta$ -D-glucopyranoside (isoquercetin) (3b) (Acetone-d<sub>6</sub>, 151 MHz)



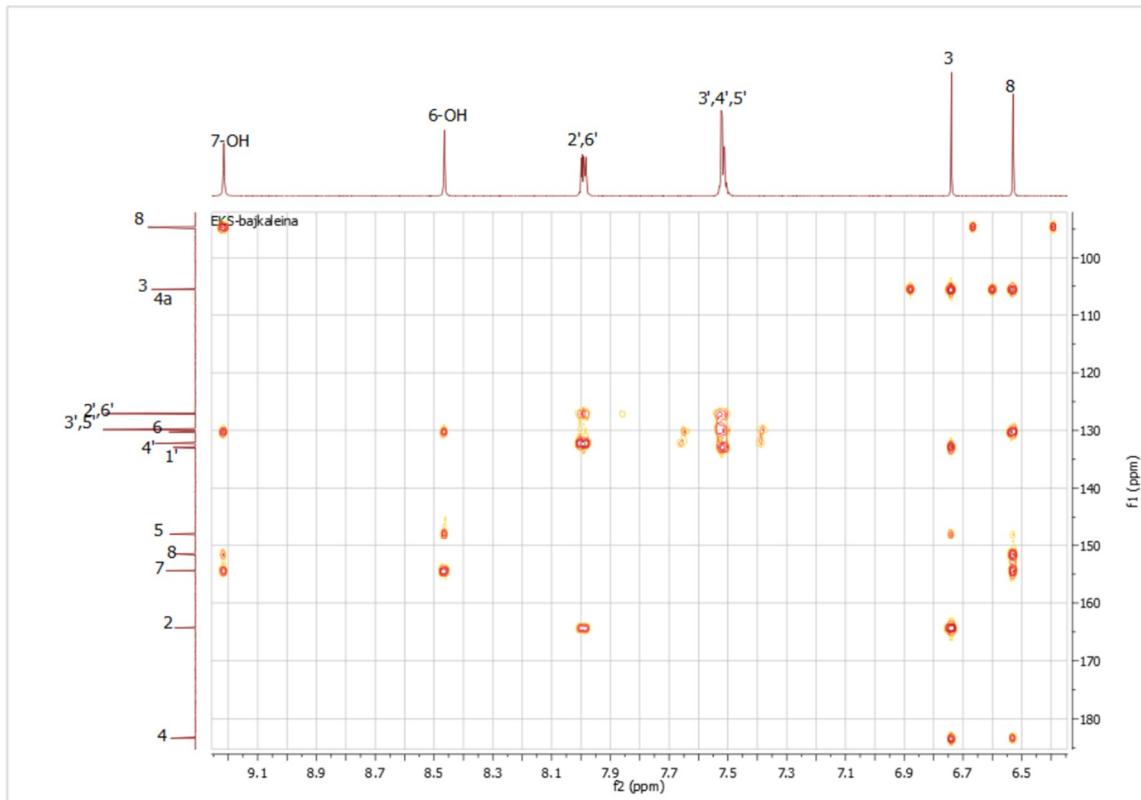
**Figure S44.**  $^1\text{H}$  NMR spectrum of 5,6,7-Trihydroxyflavone (Baicalein) (4) (Tetrahydrofuran-d<sub>8</sub>, 600 MHz)



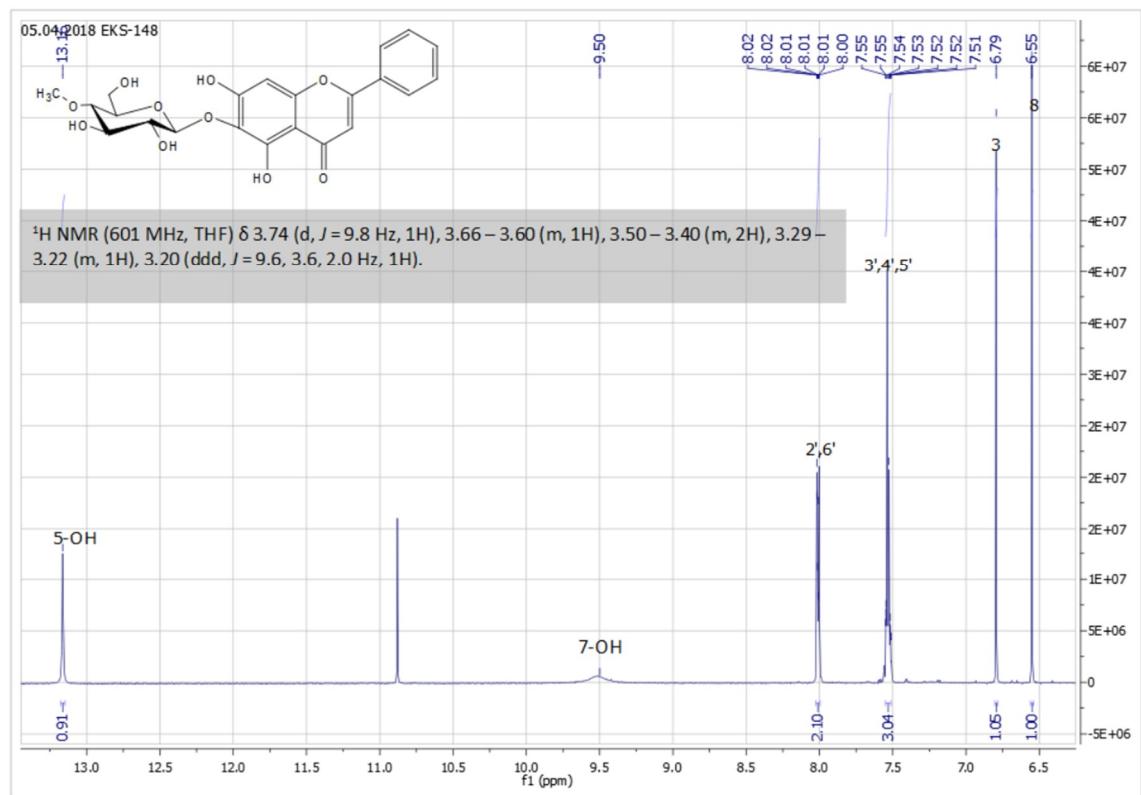
**Figure S45.**  $^{13}\text{C}$  NMR spectrum of 5,6,7-Trihydroxyflavone (Baicalein) (4) (Tetrahydrofuran-d<sub>8</sub>, 151 MHz)



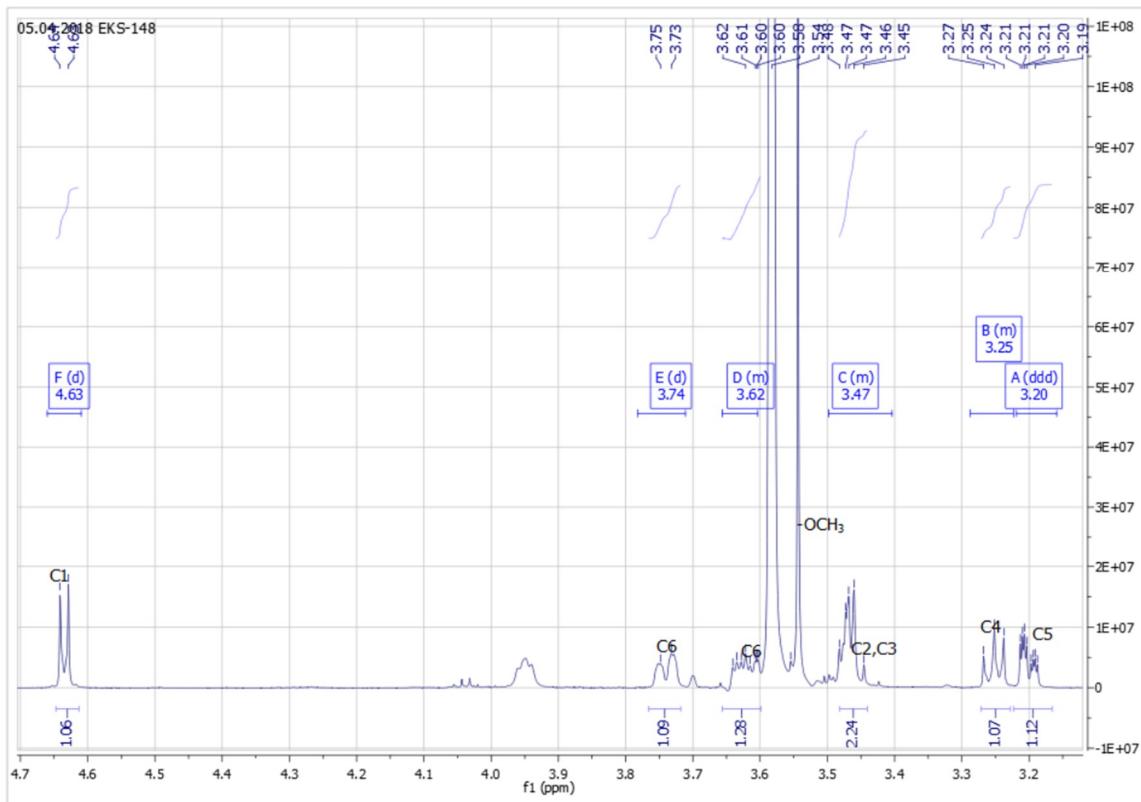
**Figure S46.** HSQC NMR spectrum of 5,6,7-Trihydroxyflavone (Baicalein) (4) (Tetrahydrofuran-d<sub>8</sub>, 151 MHz)



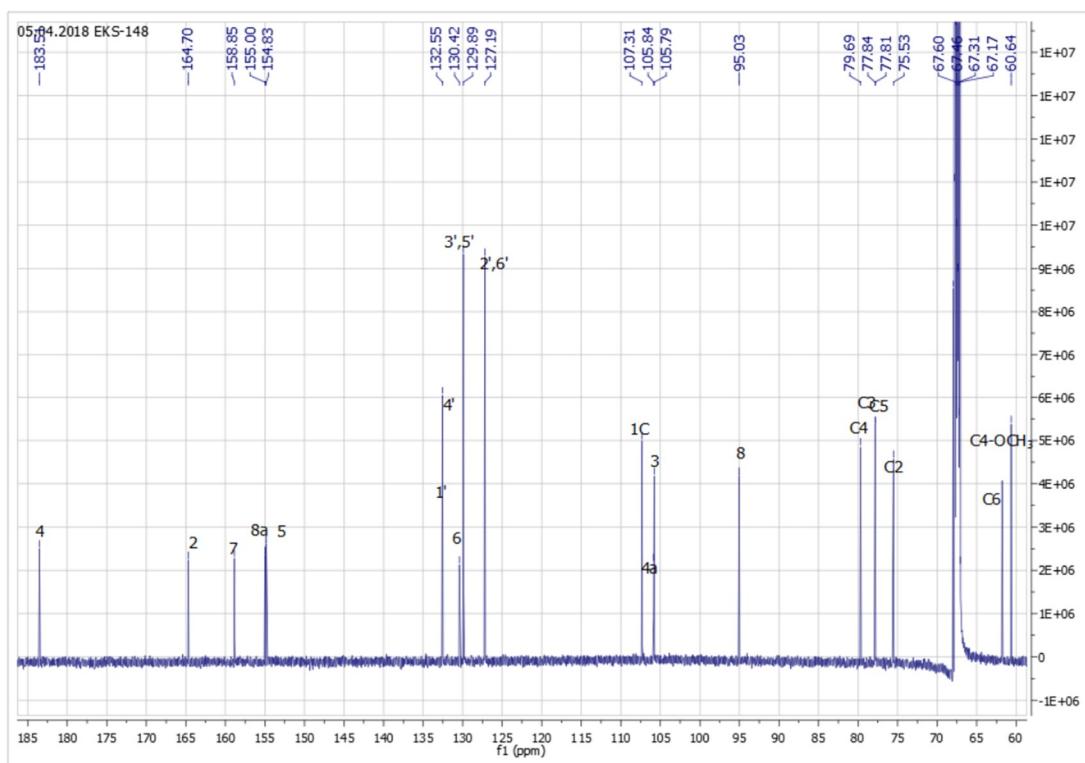
**Figure S47.** HMBC NMR spectrum of 5,6,7-Trihydroxyflavone (Baicalein) (4) (Tetrahydrofuran-d<sub>8</sub>, 151 MHz)



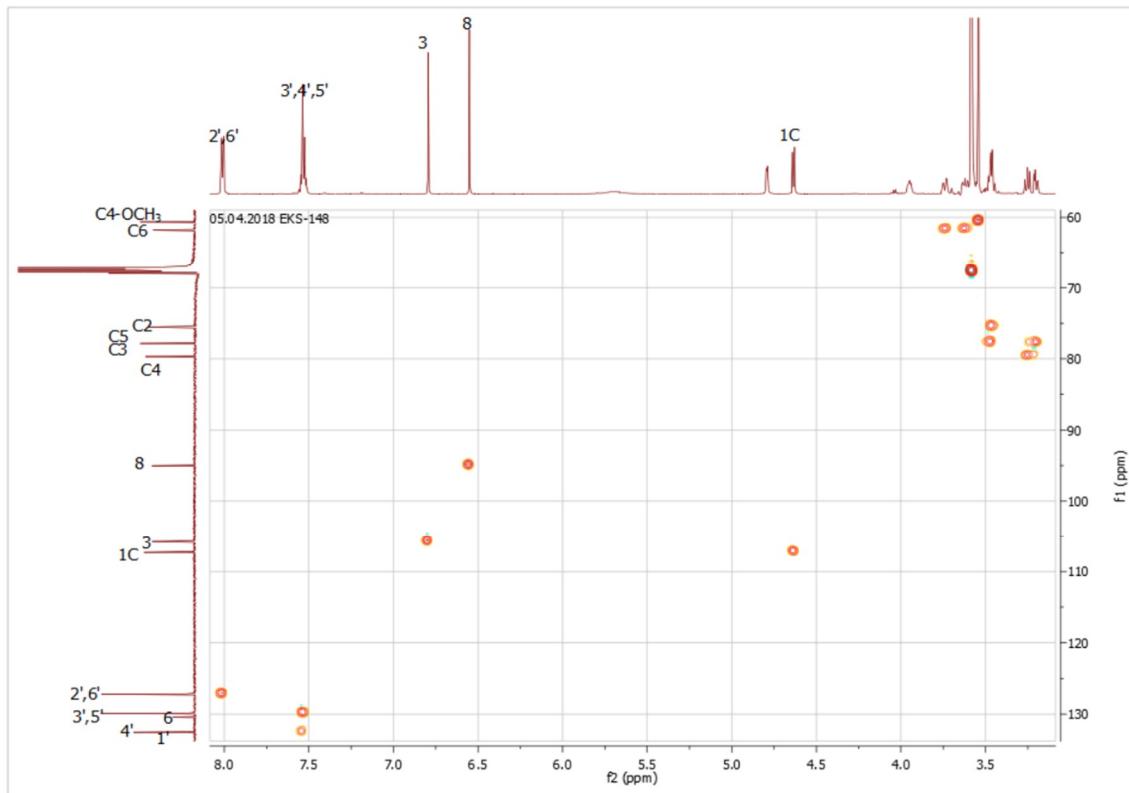
**Figure S48.** <sup>1</sup>H NMR spectrum of 5,7-dihydroxyflavone 6-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (4a) (Tetrahydrofuran-d<sub>8</sub>, 600 MHz)



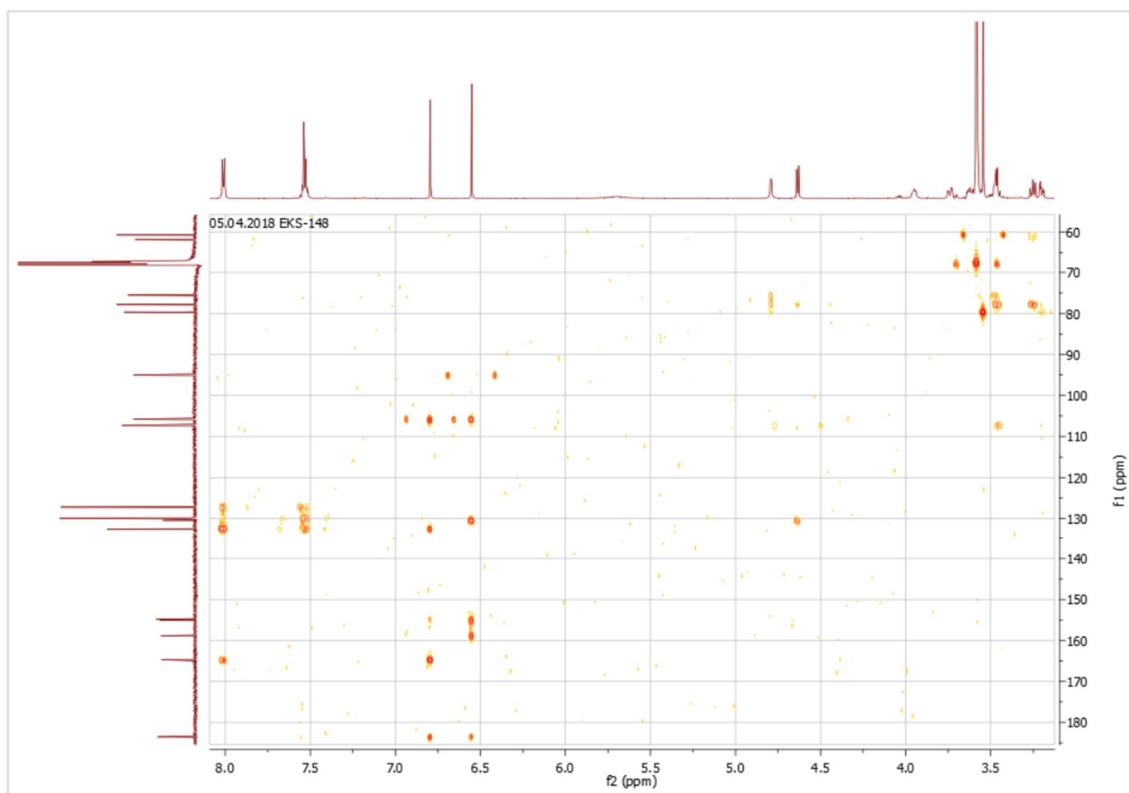
**Figure S49.**  $^1\text{H}$  NMR spectrum of 5,7-dihydroxyflavone 6-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (4a) (Tetrahydrofuran-d<sub>8</sub>, 600 MHz)



**Figure S50.**  $^{13}\text{C}$  NMR spectrum of 5,7-dihydroxyflavone 6-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (4a) (Tetrahydrofuran-d<sub>8</sub>, 151 MHz)



**Figure S51.** HSQC NMR spectrum of 5,7-dihydroxyflavone 6-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (4a) (Tetrahydrofuran-d<sub>8</sub>, 151 MHz)



**Figure S52.** HMBC NMR spectrum of 5,7-dihydroxyflavone 6-O- $\beta$ -D-(4''-O-methyl)-glucopyranoside (4a) (Tetrahydrofuran-d<sub>8</sub>, 151 MHz)