

1 Article

2 **Acylated flavonoid glycosides are the main pigments  
3 that determine the flower colour of the Brazilian  
4 native tree *Tibouchina pulchra* (Cham.) Cogn.**5 Fernanda Mendes Rezende <sup>1,\*</sup>, Marcelo José Pena Ferreira <sup>1</sup>, Mads Hartvig Clausen <sup>2</sup>,  
6 Magdalena Rossi <sup>1</sup> and Claudia Maria Furlan <sup>1,\*</sup>7 <sup>1</sup> Botany Department, Institute of Bioscience, University of São Paulo (USP), São Paulo, Brazil;  
8 marcelopena@ib.usp.br (M.J.P.F.); magdarossirocco@gmail.com (M.R.)9 <sup>2</sup> Center for Nanomedicine and Theranostics, Department of Chemistry, Technical University of Denmark,  
10 Kgs. Lyngby, Denmark; mhc@kemi.dtu.dk

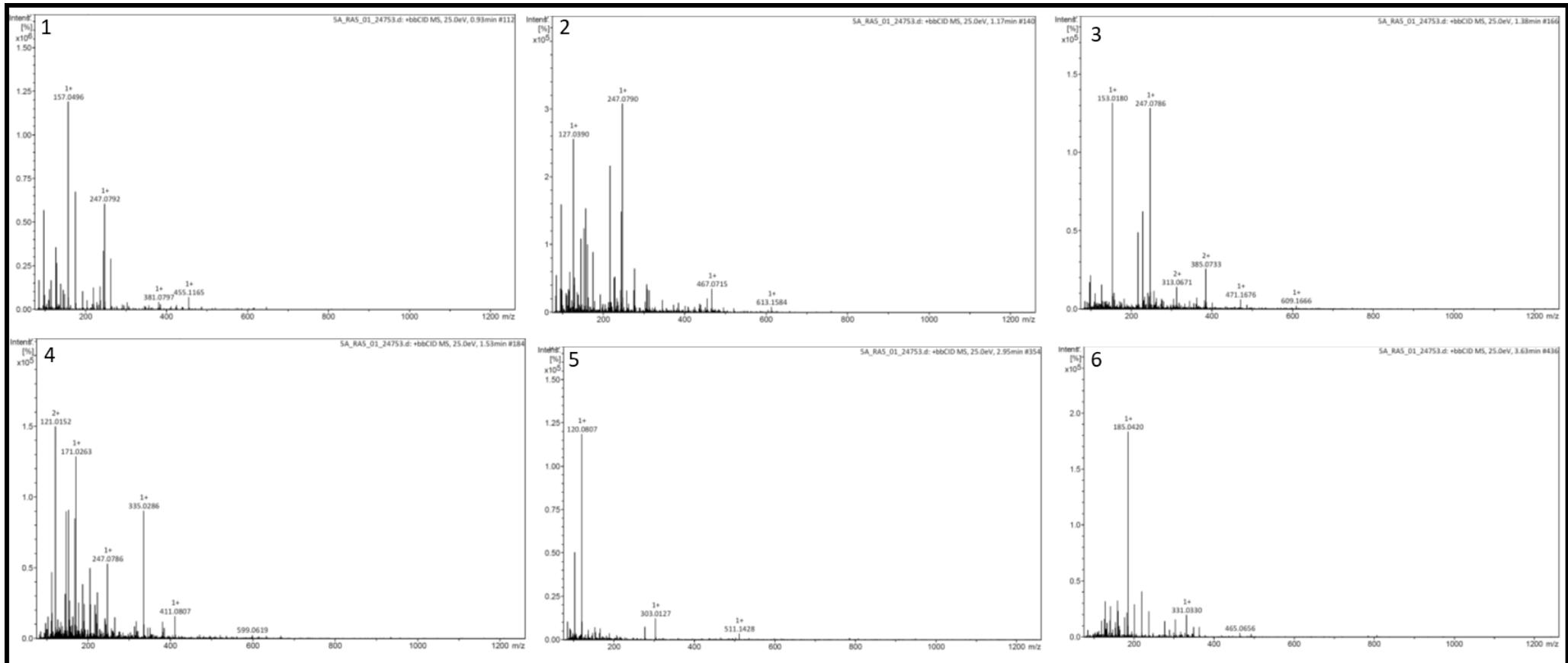
11 \* Correspondence: rezendefm@usp.br (F.M.R.); furlancm@ib.usp.br (C.M.F.); Tel.: +55-011-3091-8065

12 **SUPPLEMENTARY MATERIAL**

13 <b>Figure S1.</b> MS <sup>+</sup> spectra of compounds <b>1</b> to <b>30</b> . Structures represent the proposed compound and its main 14 fragmentation.....	1
15 <b>Figure S2.</b> <sup>1</sup> H NMR spectrum (DMSO-d6) of kaempferol 3-O-(2''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or 16 <b>19</b> ).....	8
17 <b>Figure S3.</b> Zoom from 5.2 to 8.5 ppm, <sup>1</sup> H NMR spectrum (DMSO-d6) of kaempferol 18 3-O-(2''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or <b>19</b> ) .....	8
19 <b>Figure S4.</b> HSQC NMR spectrum (DMSO-d6) of kaempferol 3-O-(2''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or 20 <b>19</b> ).....	9
21 <b>Figure S5.</b> Zoom from 2.7 to 3.8 ppm, HSQC NMR spectrum (DMSO-d6) of kaempferol 22 3-O-(2''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or <b>19</b> ).....	9
23 <b>Figure S6.</b> HMBC NMR spectrum (DMSO-d6) of kaempferol 3-O-(2''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or 24 <b>19</b> ).....	10
25 <b>Figure S7.</b> Zoom from 2.7 to 3.9 ppm, HMBC NMR spectrum (DMSO-d6) of kaempferol 26 3-O-(2''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or <b>19</b> ) .....	10
27 <b>Figure S8.</b> Zoom from 5.2 to 8.6 ppm, HMBC NMR spectrum (DMSO-d6) of kaempferol 28 3-O-(2''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or <b>19</b> ) .....	11
29 <b>Figure S9.</b> <sup>1</sup> H NMR spectrum (DMSO-d6) of kaempferol 3-O-(6''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or 30 <b>19</b> ).....	11
31 <b>Figure S10.</b> Zoom from 5.1 to 8.1 ppm, <sup>1</sup> H NMR spectrum (DMSO-d6) of kaempferol 32 3-O-(6''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or <b>19</b> ). ....	12
33 <b>Figure S11.</b> HSQC NMR spectrum (DMSO-d6) of kaempferol 3-O-(6''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or 34 <b>19</b> ).....	12
35 <b>Figure S12.</b> Zoom from 3.0 to 4.6 ppm, HSQC NMR spectrum (DMSO-d6) of kaempferol 36 3-O-(6''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or <b>19</b> ).....	13
37 <b>Figure S13.</b> HMBC NMR spectrum (DMSO-d6) of kaempferol 3-O-(6''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or 38 <b>19</b> ).....	13
39 <b>Figure S14.</b> Zoom from 2.8 to 4.9 ppm, HMBC NMR spectrum (DMSO-d6) of kaempferol 40 3-O-(6''-galloyl)-β-D-glucopyranoside ( <b>13</b> , <b>16</b> or <b>19</b> ).....	14

41	<b>Figure S15.</b> Zoom from 5.2 to 8.4 ppm, HMBC NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 42 3-O-(6''-galloyl)- $\beta$ -D-glucopyranoside ( <b>13, 16 or 19</b> ).....	14
43	<b>Figure S16.</b> $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of mixture 44 ( <b>17</b> ).....	15
45	<b>Figure S17.</b> Zoom from 5.2 to 8.2 ppm, $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of mixture 46 ( <b>17</b> ).....	15
47	<b>Figure S18.</b> $^{13}\text{C}$ NMR spectrum (DMSO- <i>d</i> 6) of mixture 48 ( <b>17</b> ).....	16
49	<b>Figure S19.</b> HMBC NMR spectrum (DMSO- <i>d</i> 6) of mixture 50 ( <b>17</b> ).....	16
51	<b>Figure S20.</b> Zoom from 2.4 to 4.5 ppm, HMBC NMR spectrum (DMSO- <i>d</i> 6) of mixture 52 ( <b>17</b> ).....	17
53	<b>Figure S21.</b> Zoom from 4.8 to 8.6 ppm, HMBC NMR spectrum (DMSO- <i>d</i> 6) of mixture 54 ( <b>17</b> ).....	17
55	<b>Figure S22.</b> $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 3-O-glucoronide-6''-O-methylester 56 ( <b>23</b> ).....	18
57	<b>Figure S23.</b> Zoom from 5.1 to 8.1 ppm, $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 58 3-O-glucoronide-6''-O-methylester ( <b>23</b> ).....	18
59	<b>Figure S24.</b> HSQC NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 3-O-glucoronide-6''-O-methylester 60 ( <b>23</b> ).....	19
61	<b>Figure S25.</b> Zoom from 2.9 to 4.5 ppm, HSQC NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 62 3-O-glucoronide-6''-O-methylester ( <b>23</b> ).....	19
63	<b>Figure S26.</b> Zoom from 5.0 to 8.6 ppm, HMBC NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 64 3-O-glucoronide-6''-O-methylester ( <b>23</b> ).....	20
65	<b>Figure S27.</b> $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of quercetin 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside 66 ( <b>25</b> ).....	20
67	<b>Figure S28.</b> Zoom from 5.1 to 8.1 ppm, $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of quercetin 68 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside ( <b>25</b> ).....	21
69	<b>Figure S29.</b> HSQC NMR spectrum (DMSO- <i>d</i> 6) of quercetin 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside 70 ( <b>25</b> ).....	21
71	<b>Figure S30.</b> Zoom from 2.7 to 4.7 ppm, HSQC NMR spectrum (DMSO- <i>d</i> 6) of quercetin 72 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside ( <b>25</b> ).....	22
73	<b>Figure S31.</b> Zoom from 5.0 to 8.8 ppm, HSQC NMR spectrum (DMSO- <i>d</i> 6) of quercetin 74 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside ( <b>25</b> ).....	22
75	<b>Figure S32.</b> $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside 76 ( <b>27</b> ).....	23
77	<b>Figure S33.</b> Zoom from 5.1 to 8.1 ppm, $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 78 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside ( <b>27</b> ).....	23
79	<b>Figure S34.</b> HSQC NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside 80 ( <b>27</b> ).....	24
81	<b>Figure S35.</b> Zoom from 3.0 to 4.6 ppm, HSQC NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 82 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside ( <b>27</b> ).....	24

83	<b>Figure S36.</b> HMBC NMR spectrum (DMSO- <i>d</i> 6) of kaempferol 3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside	25
84	(27).....	
85	<b>Figure S37.</b> Zoom from 2.9 to 4.8 ppm, HMBC NMR spectrum (DMSO- <i>d</i> 6) of kaempferol	25
86	3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside (27).....	
87	<b>Figure S38.</b> Zoom from 5.2 to 8.4 ppm, HMBC NMR spectrum (DMSO- <i>d</i> 6) of kaempferol	26
88	3-O-(6''- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside (27).....	
89	<b>Figure S39.</b> $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of kaempferol	26
90	(29).....	
91	<b>Figure S40.</b> Zoom from 6.1 to 8.2 ppm, $^1\text{H}$ NMR spectrum (DMSO- <i>d</i> 6) of kaempferol	27
92	(29).....	
93	<b>Figure S41.</b> $^{13}\text{C}$ NMR spectrum (DMSO- <i>d</i> 6) of kaempferol	27
94	(29).....	
95	<b>Table S1.</b> NMR data of $^1\text{H}$ , $^{13}\text{C}$ and HMBC for kaempferol 3-O-(6''-O-galloyl)- $\beta$ -D-glucopyranoside and	28
96	Kaempferol 3-O-(2''-O-galloyl)- $\beta$ -D-glucopyranoside (13, 16 or 19).....	
97	<b>Table S2.</b> NMR data of $^1\text{H}$ , $^{13}\text{C}$ and HMBC for kaempferol 3-O-glucuronide-6''-O-methylester (23).....	29
98	<b>Table S3.</b> NMR data of $^1\text{H}$ , $^{13}\text{C}$ and HMBC for quercetin 3-O-(6''-O- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside (25) and	30
99	Kaempferol 3-O-(6''-O- <i>p</i> -coumaroyl)- $\beta$ -D-glucopyranoside (27).....	
100	<b>Table S4.</b> NMR data of $^1\text{H}$ and $^{13}\text{C}$ for kaempferol (29).....	31
101		



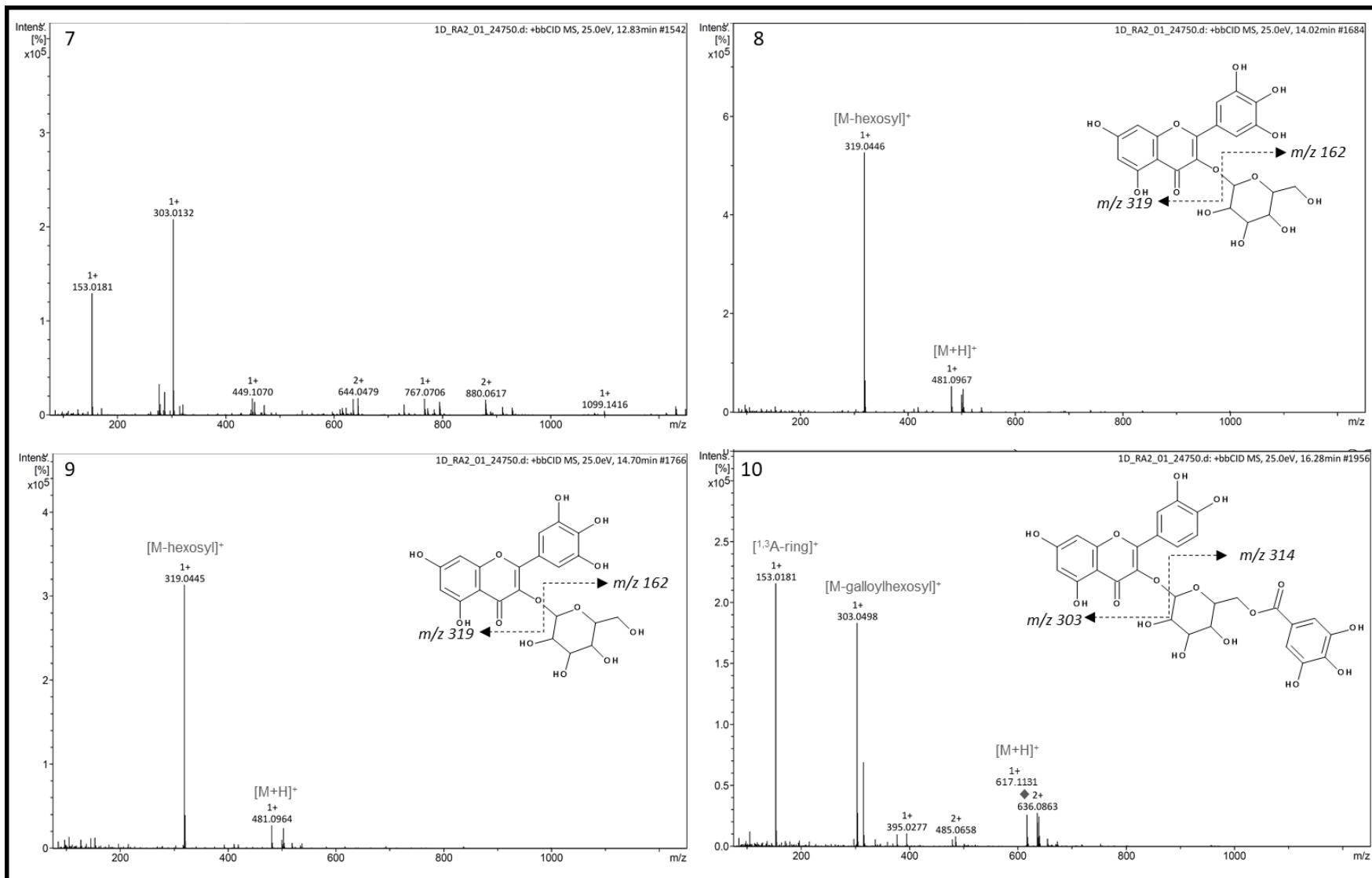
102

103 **Figure S1.**  $\text{MS}^+$  spectra of compounds 1 to 30. Structures represent the proposed compound and its main fragmentation.

104

105

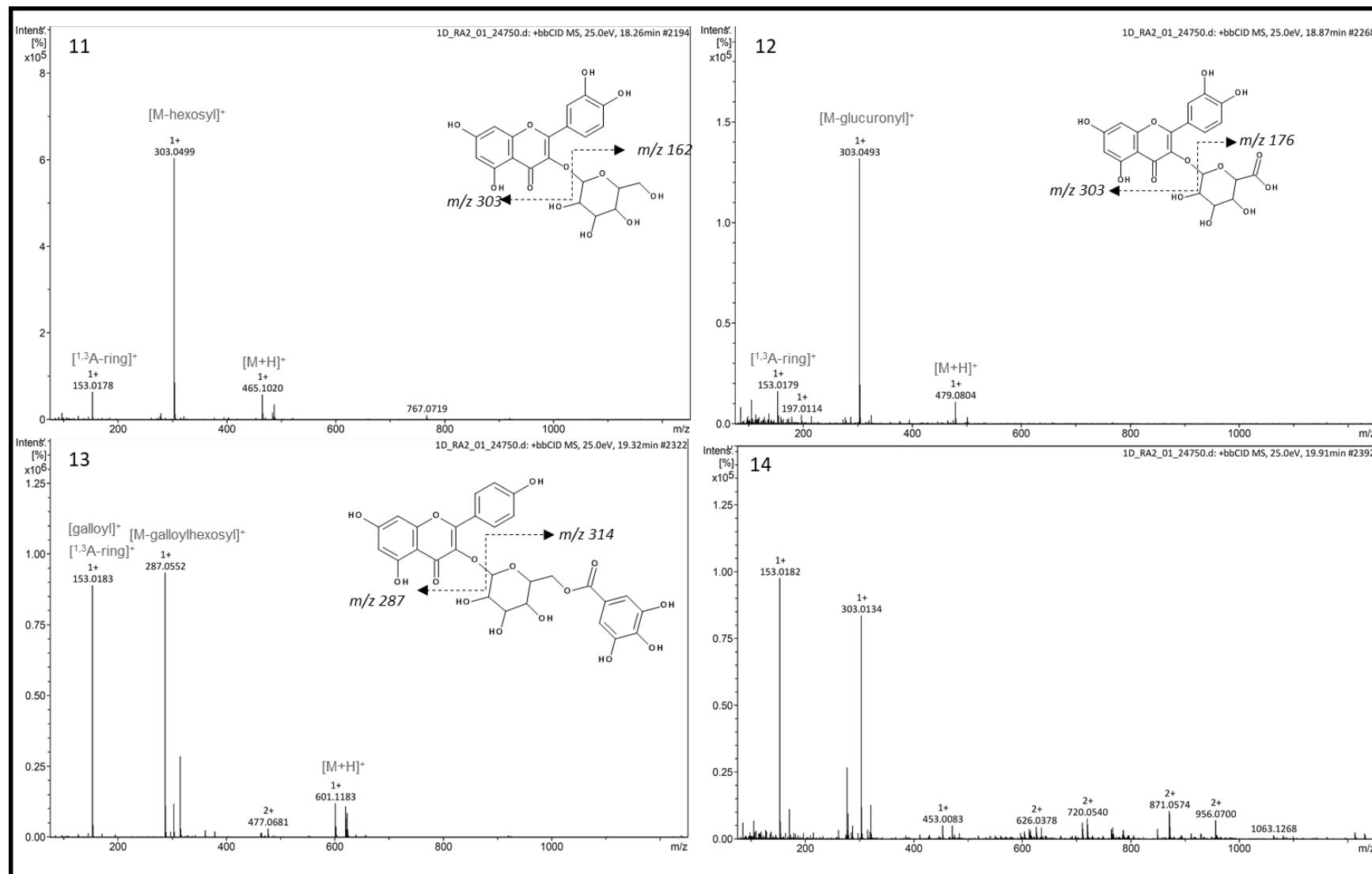
Figure S1 (continue).



106

107

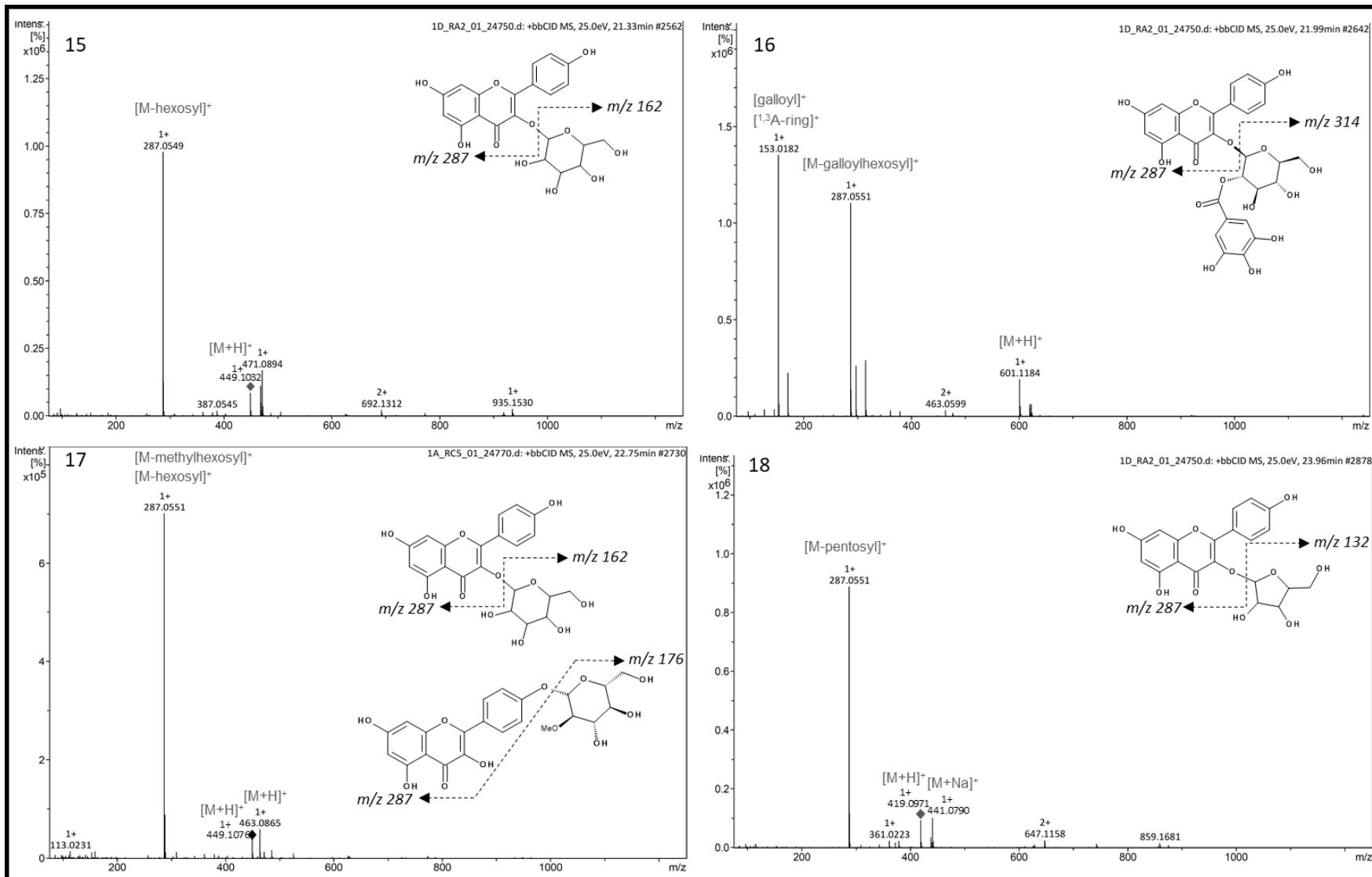
Figure S1 (continue).



108

109

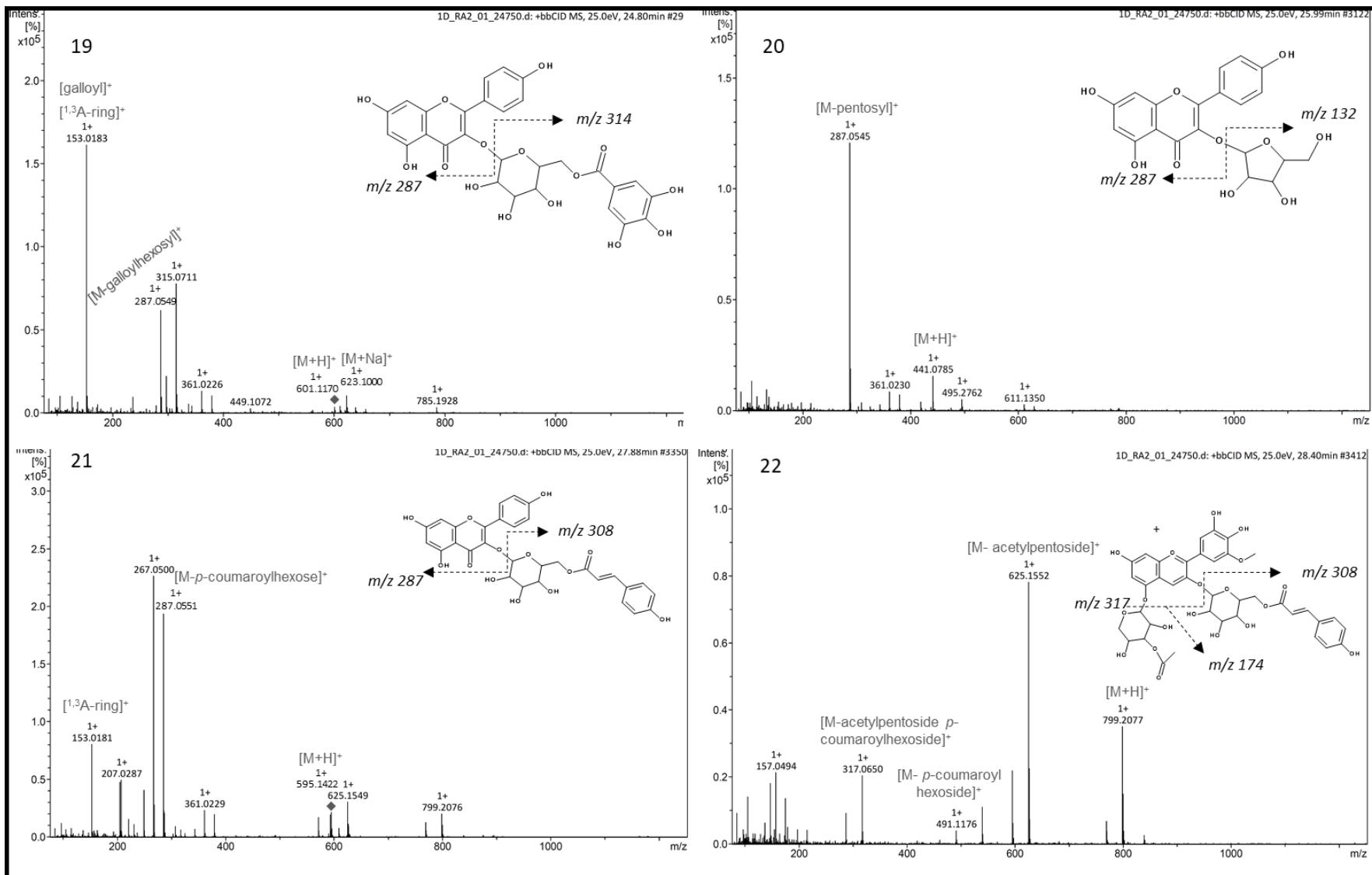
Figure S1 (continue).



110

111

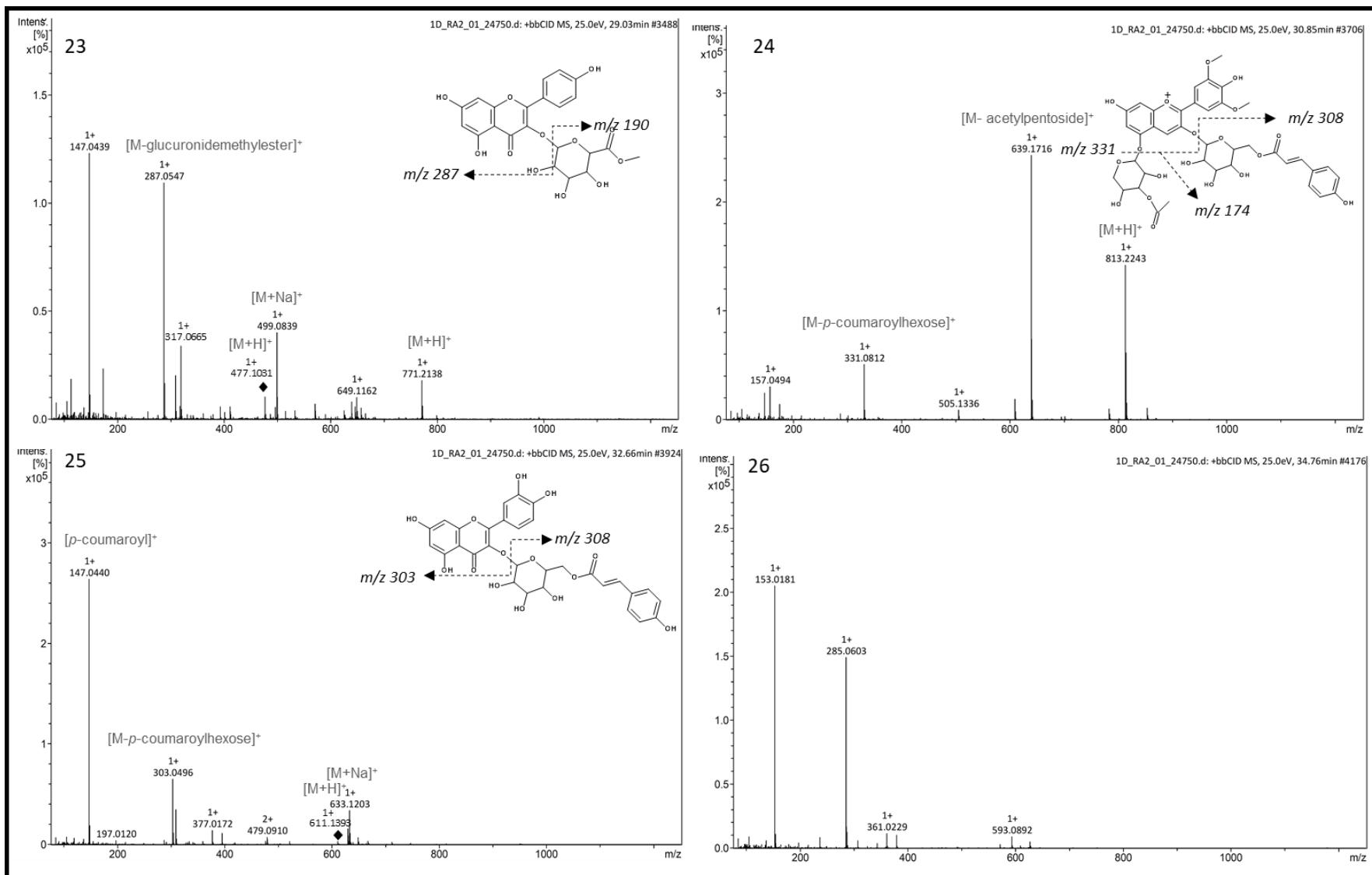
Figure S1 (continue).



112

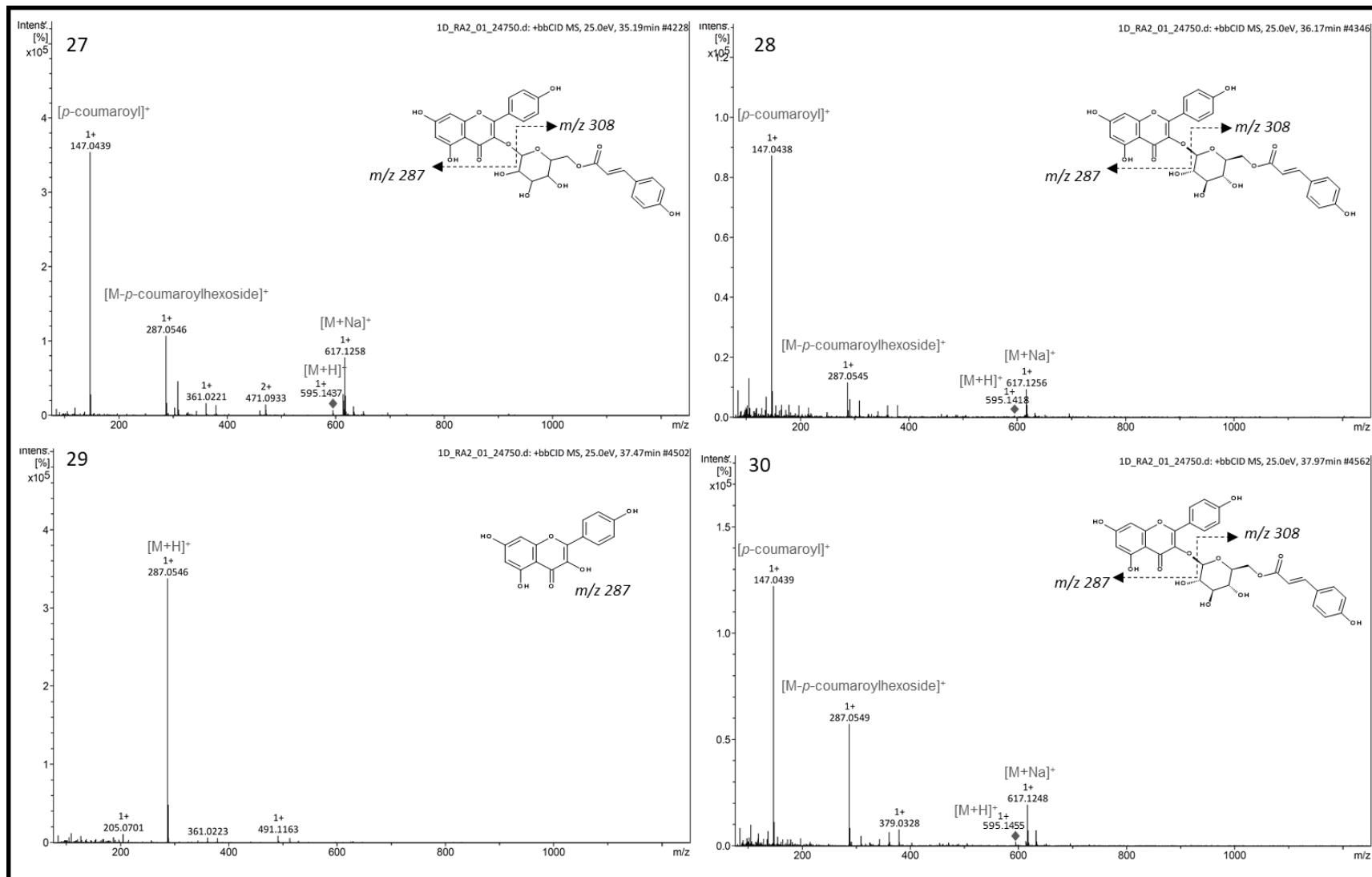
113

Figure S1 (continue).

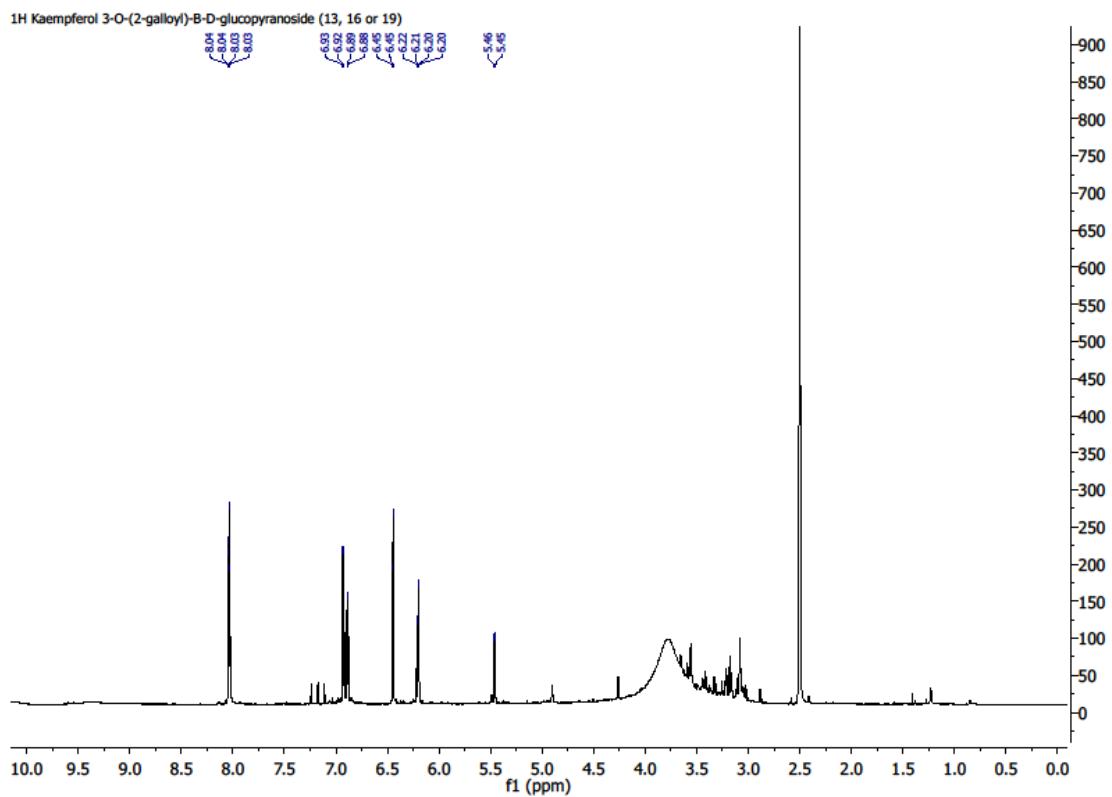


114

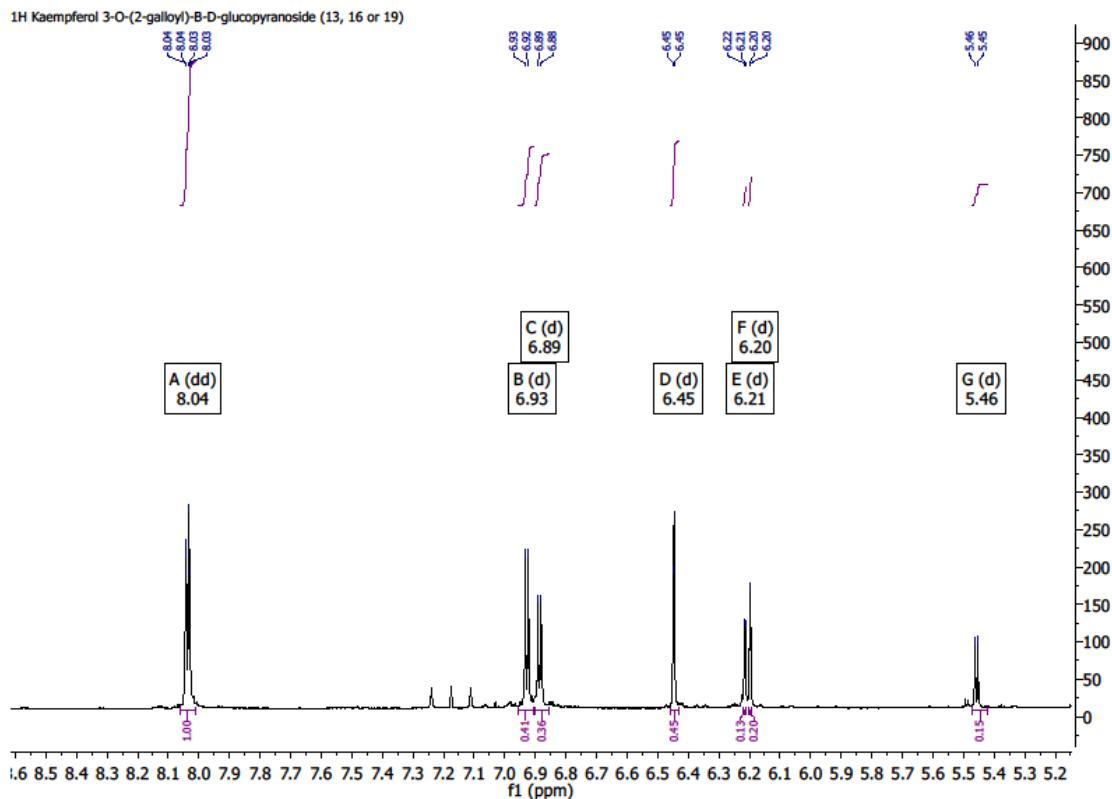
115 Figure S1 (continue).



116

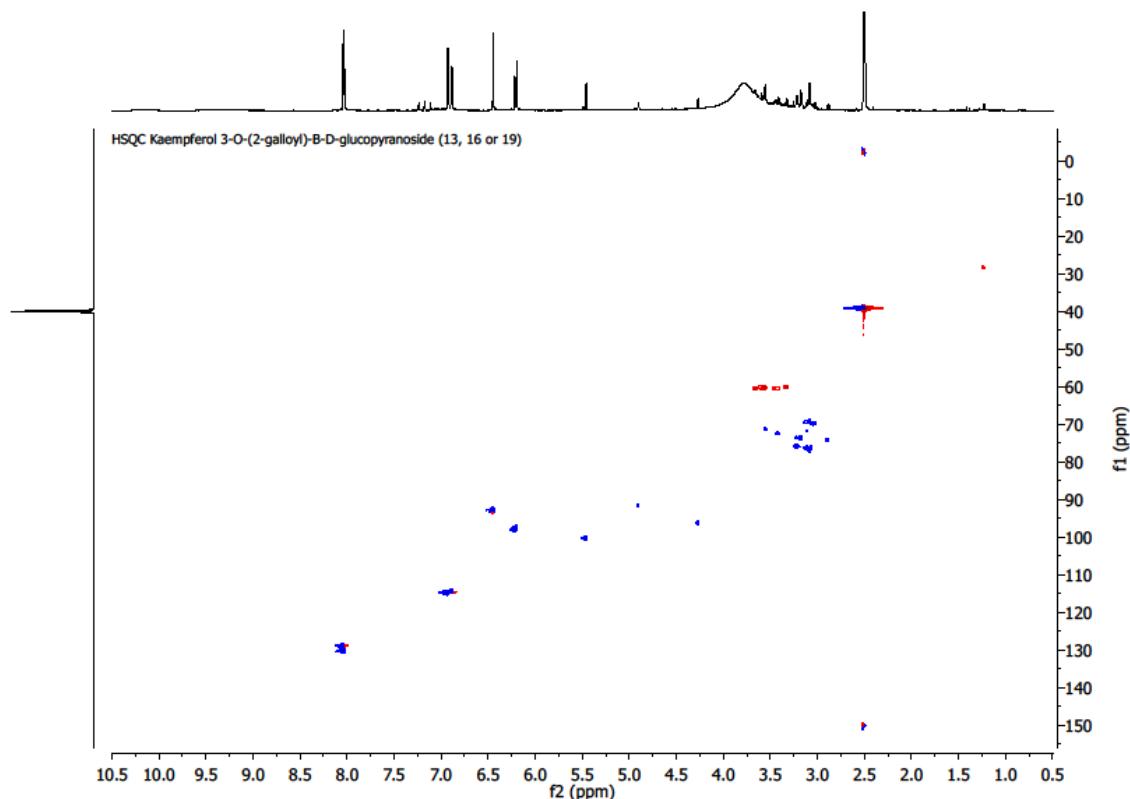


117

118 **Figure S2.**  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of kaempferol 3-O-(2''-galloyl)- $\beta$ -D-glucopyranoside (13, 16 or 19).

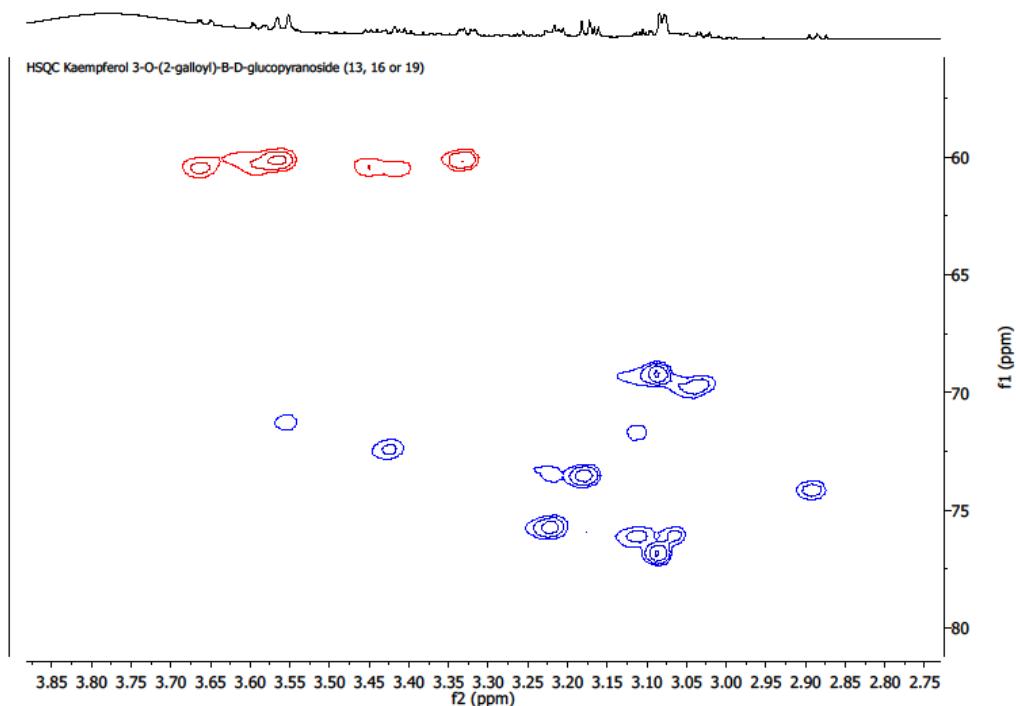
119

120 **Figure S3.** Zoom from 5.2 to 8.5 ppm,  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of kaempferol  
121 3-O-(2''-galloyl)- $\beta$ -D-glucopyranoside (13, 16 or 19).  
122



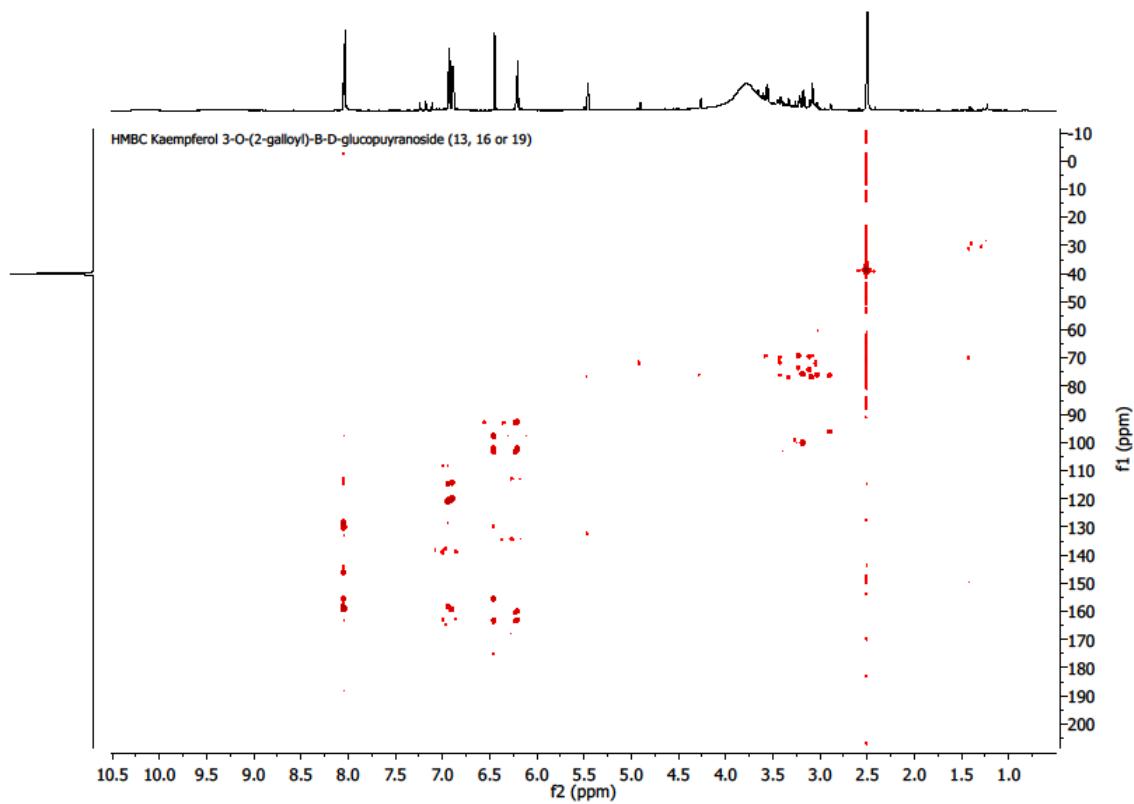
123

124 **Figure S4.** HSQC NMR spectrum (DMSO-*d*6) of kaempferol 3-O-(2''-galloyl)-β-D-glucopyranoside (**13**, **16** or  
125 **19**).

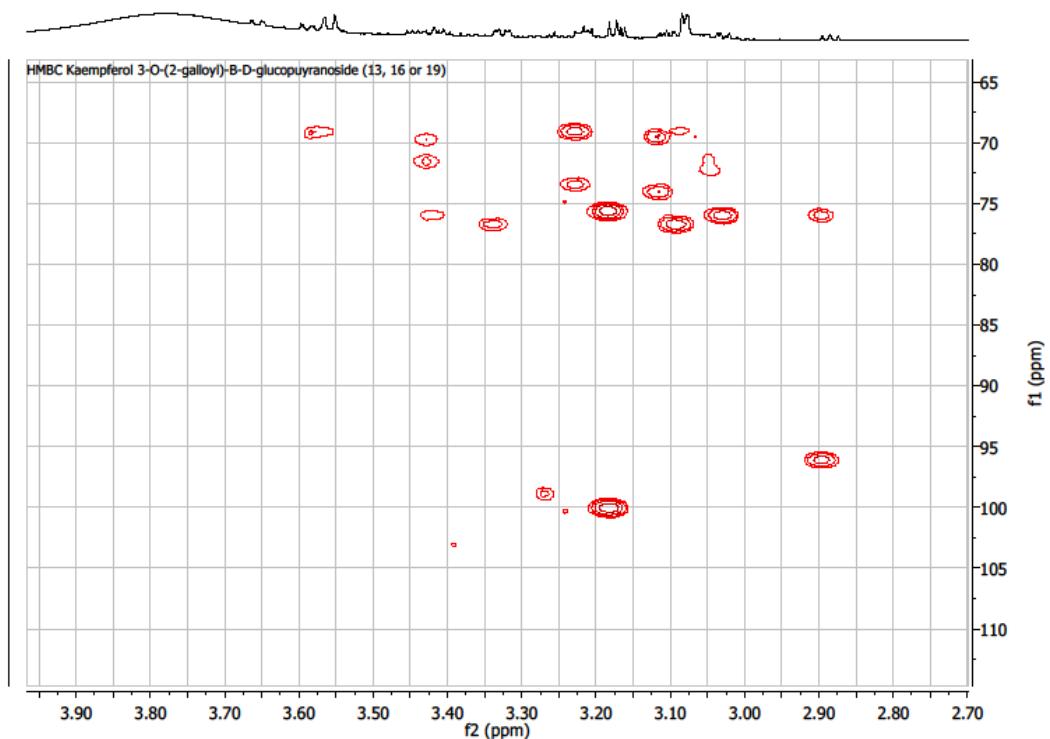


126

127 **Figure S5.** Zoom from 2.7 to 3.8 ppm, HSQC NMR spectrum (DMSO-*d*6) of kaempferol  
128 3-O-(2''-galloyl)-β-D-glucopyranoside (**13**, **16** or **19**).  
129

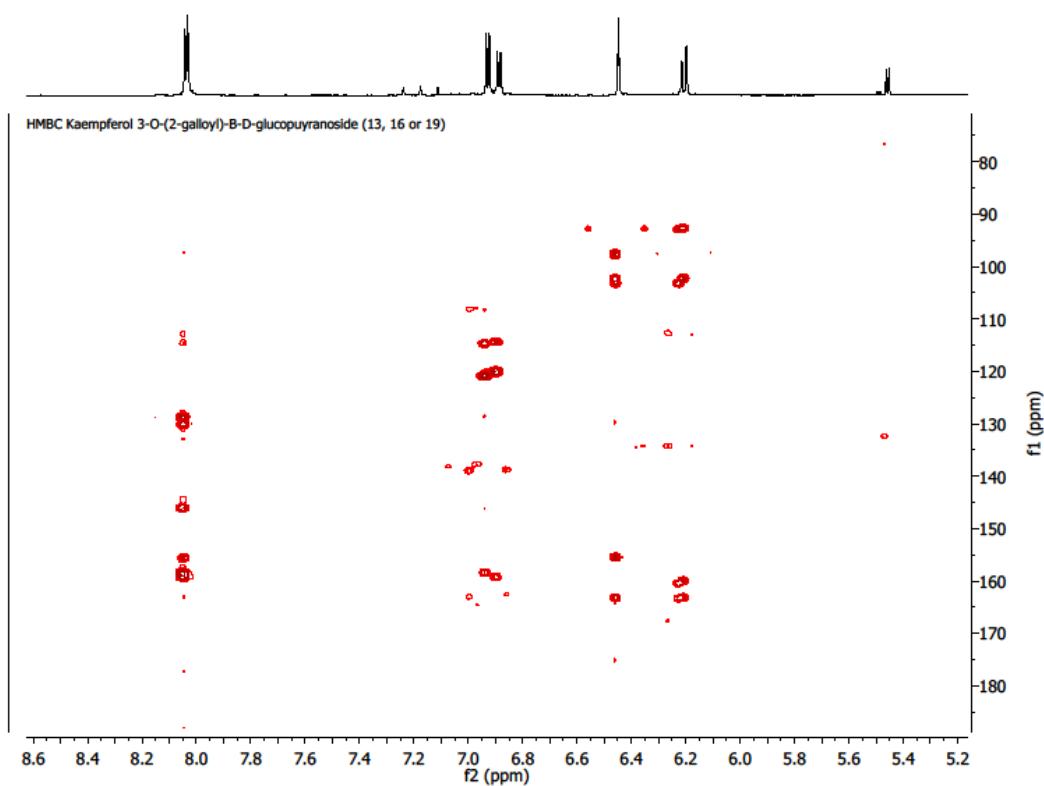


130

131 **Figure S6.** HMBC NMR spectrum (DMSO-*d*6) of kaempferol 3-O-(2''-galloyl)-β-D-glucopyranoside (13, 16 or 19).

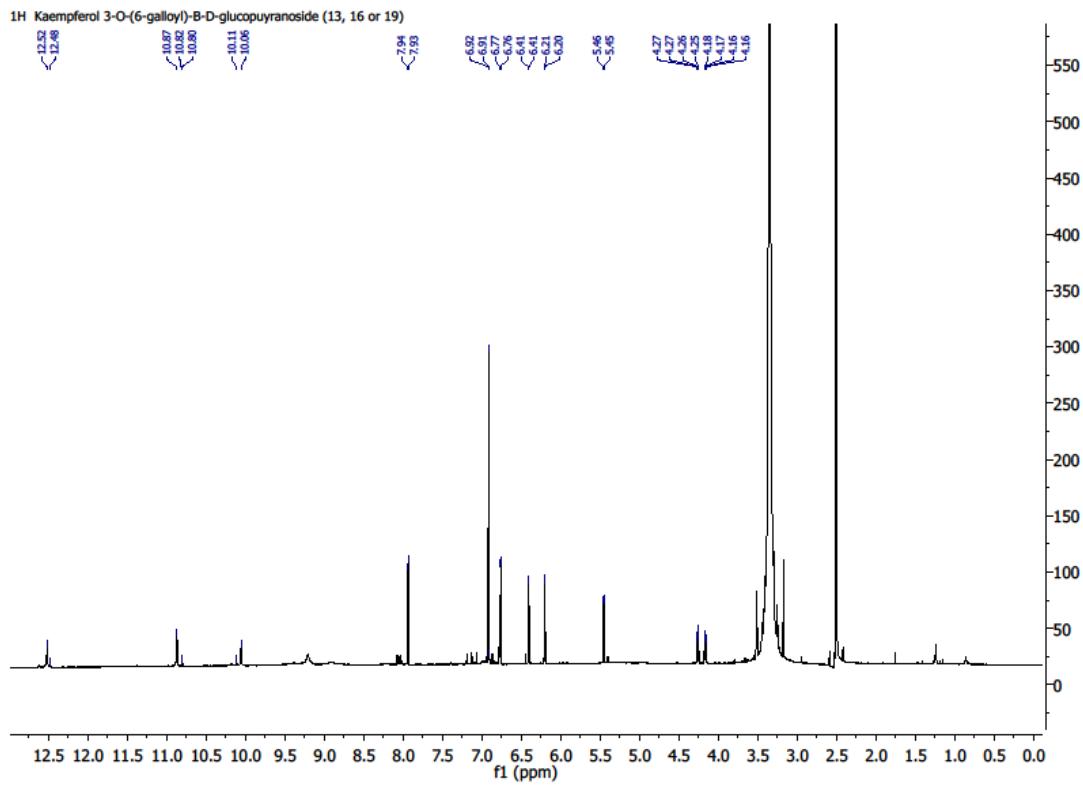
132

133 **Figure S7.** Zoom from 2.7 to 3.9 ppm, HMBC NMR spectrum (DMSO-*d*6) of kaempferol  
134 3-O-(2''-galloyl)-β-D-glucopyranoside (13, 16 or 19).  
135



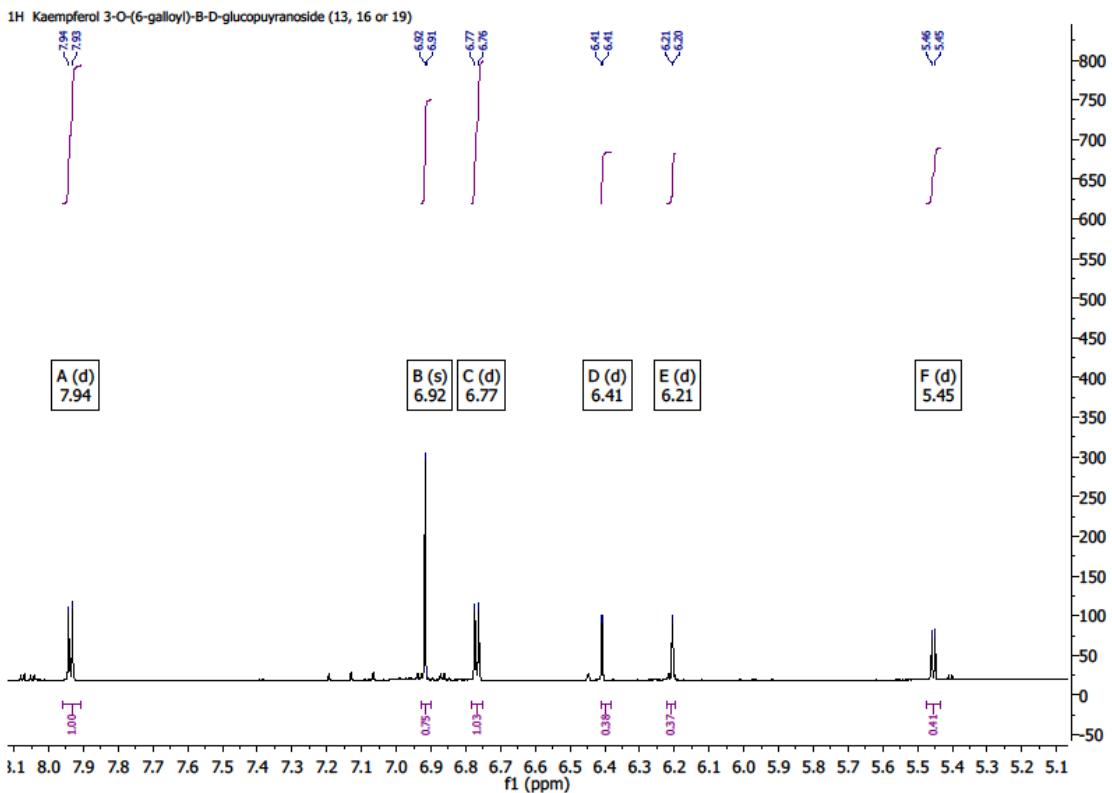
136

137      **Figure S8.** Zoom from 5.2 to 8.6 ppm, HMBC NMR spectrum (DMSO-*d*6) of kaempferol  
 138      3-O-(2''-galloyl)- $\beta$ -D-glucopyranoside (**13, 16 or 19**).



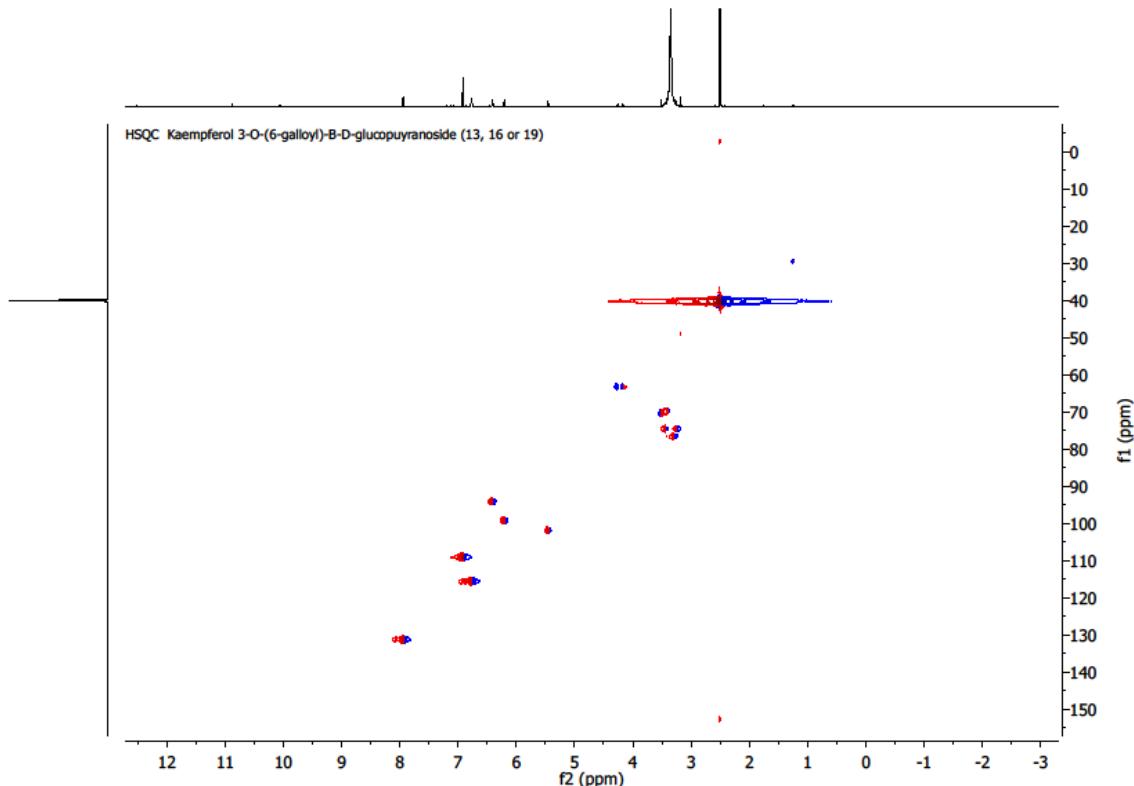
139

140      **Figure S9.**  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of kaempferol 3-O-(6''-galloyl)- $\beta$ -D-glucopyranoside (**13, 16 or 19**).



141

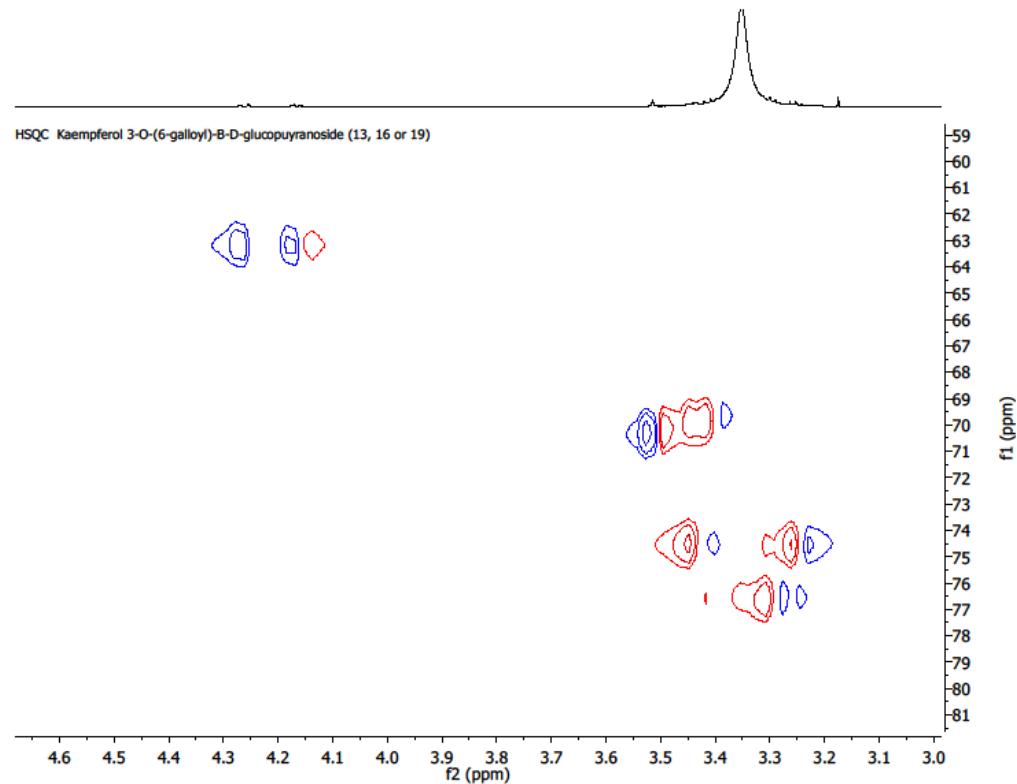
142 Figure S10. Zoom from 5.1 to 8.1 ppm,  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of kaempferol  
143 3-O-(6''-galloyl)- $\beta$ -D-glucopyranoside (**13, 16 or 19**).



144

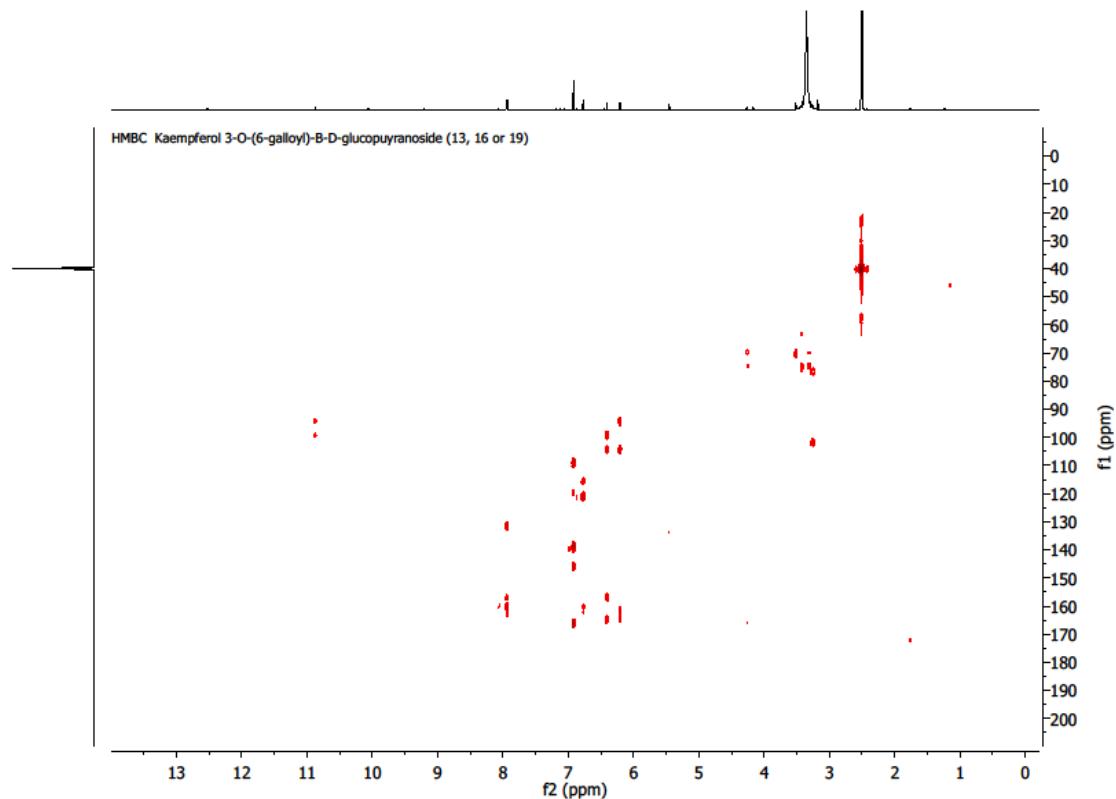
145 Figure S11. HSQC NMR spectrum (DMSO-*d*6) of kaempferol 3-O-(6''-galloyl)- $\beta$ -D-glucopyranoside (**13, 16 or**  
146 **19**).

147



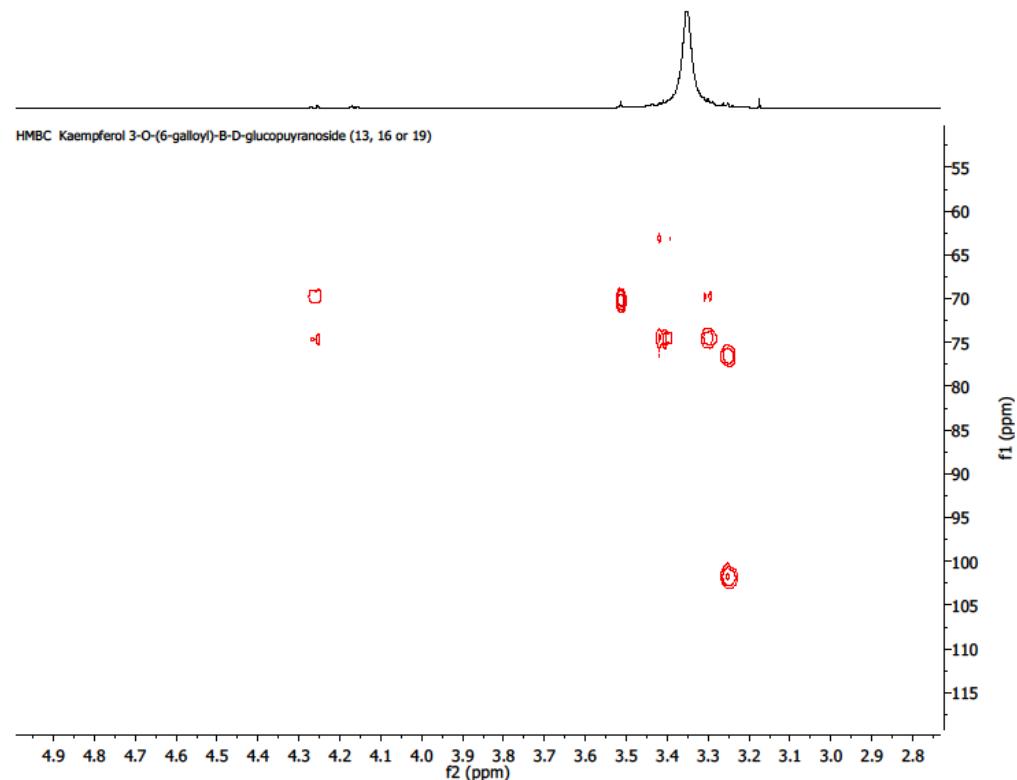
148

149 **Figure S12.** Zoom from 3.0 to 4.6 ppm, HSQC NMR spectrum (DMSO-*d*6) of kaempferol  
 150 3-O-(6''-galloyl)- $\beta$ -D-glucopyranoside (**13, 16 or 19**).



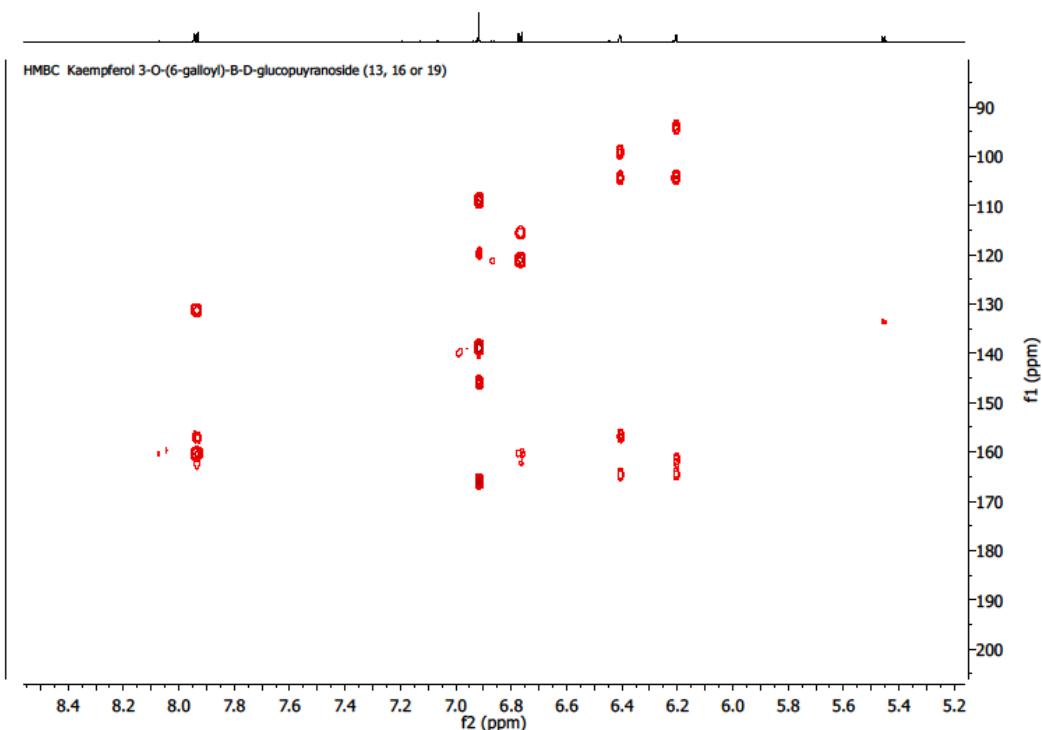
151

152 **Figure S13.** HMBC NMR spectrum (DMSO-*d*6) of kaempferol 3-O-(6''-galloyl)- $\beta$ -D-glucopyranoside (**13, 16 or**  
 153 **19**).



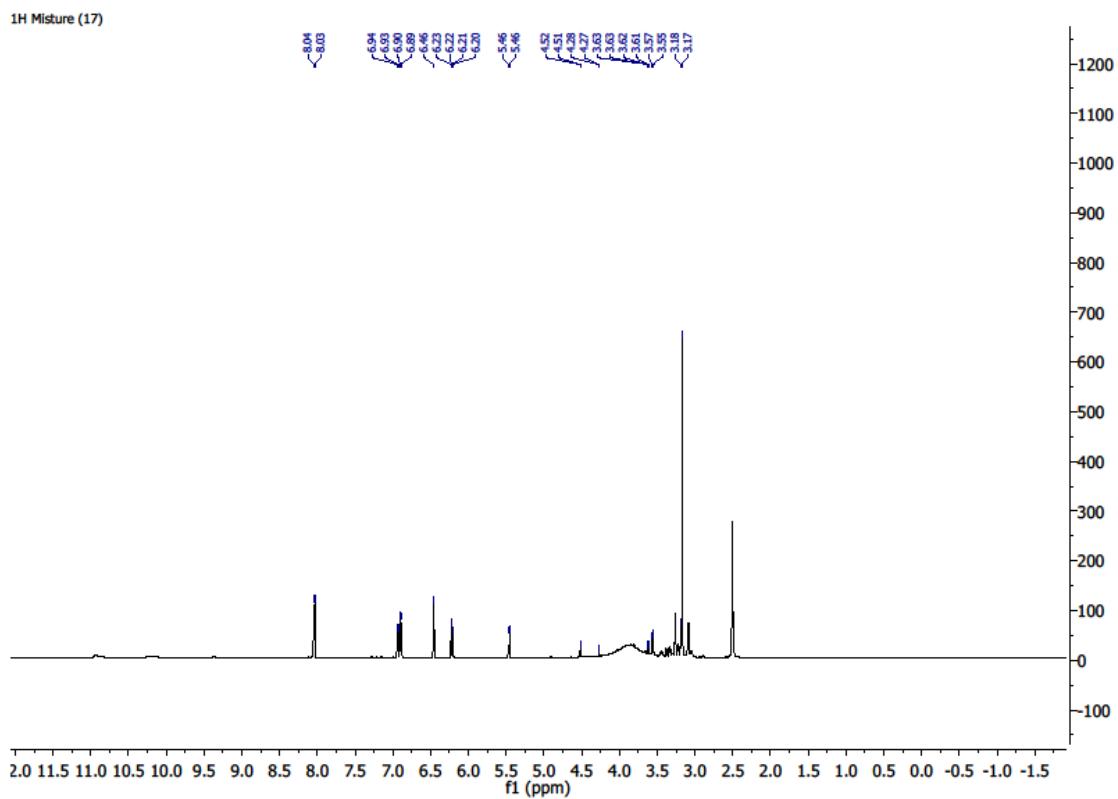
154

155 Figure S14. Zoom from 2.8 to 4.9 ppm, HMBC NMR spectrum (DMSO-*d*6) of kaempferol  
156 3-O-(6''-galloyl)- $\beta$ -D-glucopyranoside (**13, 16 or 19**).



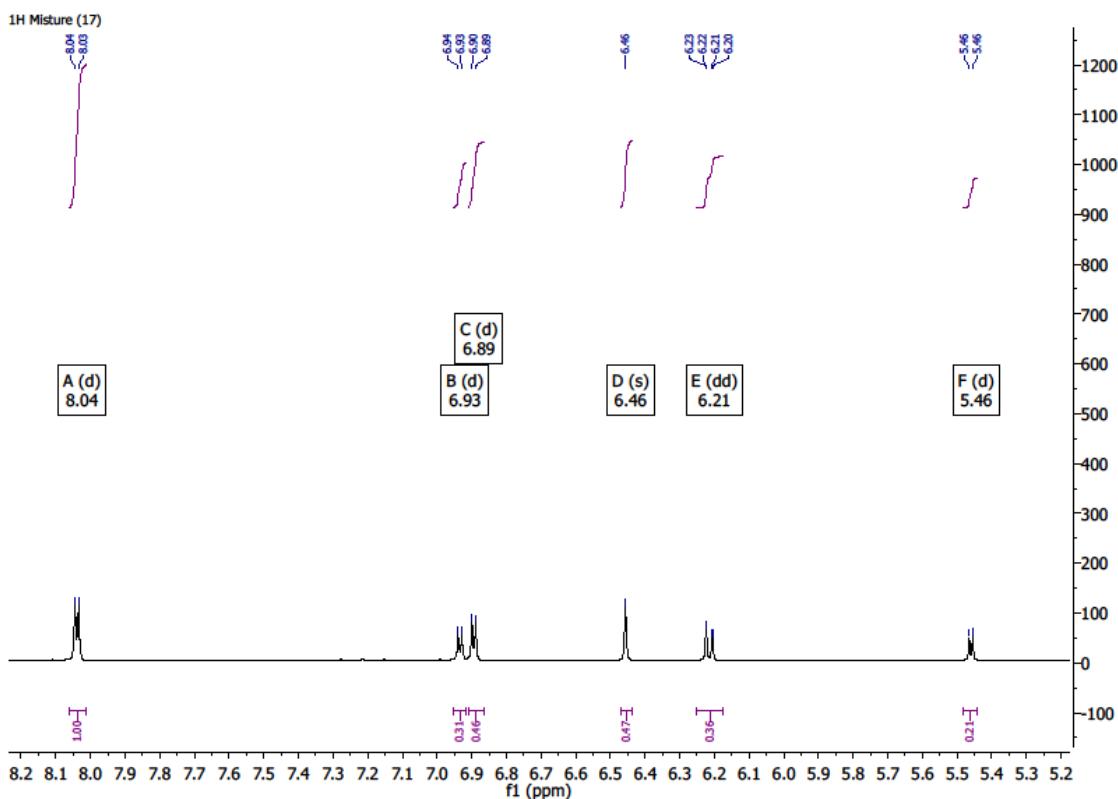
157

158 Figure S15. Zoom from 5.2 to 8.4 ppm, HMBC NMR spectrum (DMSO-*d*6) of kaempferol  
159 3-O-(6''-galloyl)- $\beta$ -D-glucopyranoside (**13, 16 or 19**).



160

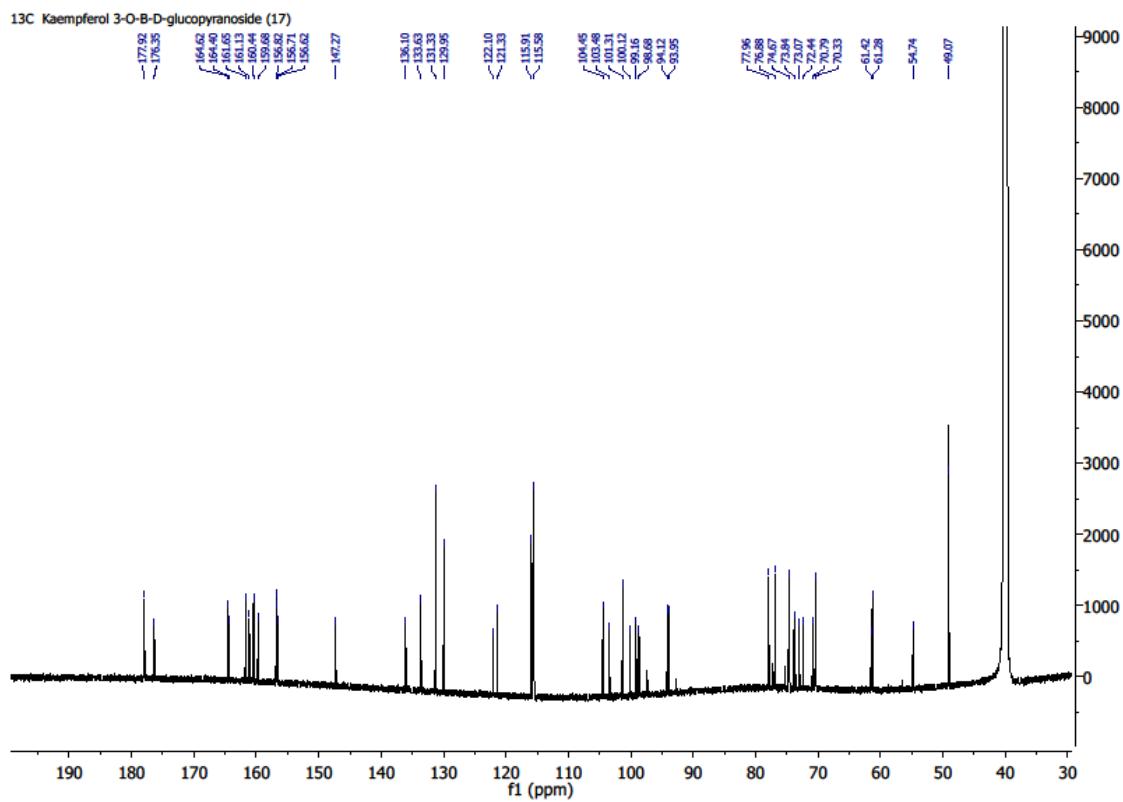
161

**Figure S16.**  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of mixture (17).

162

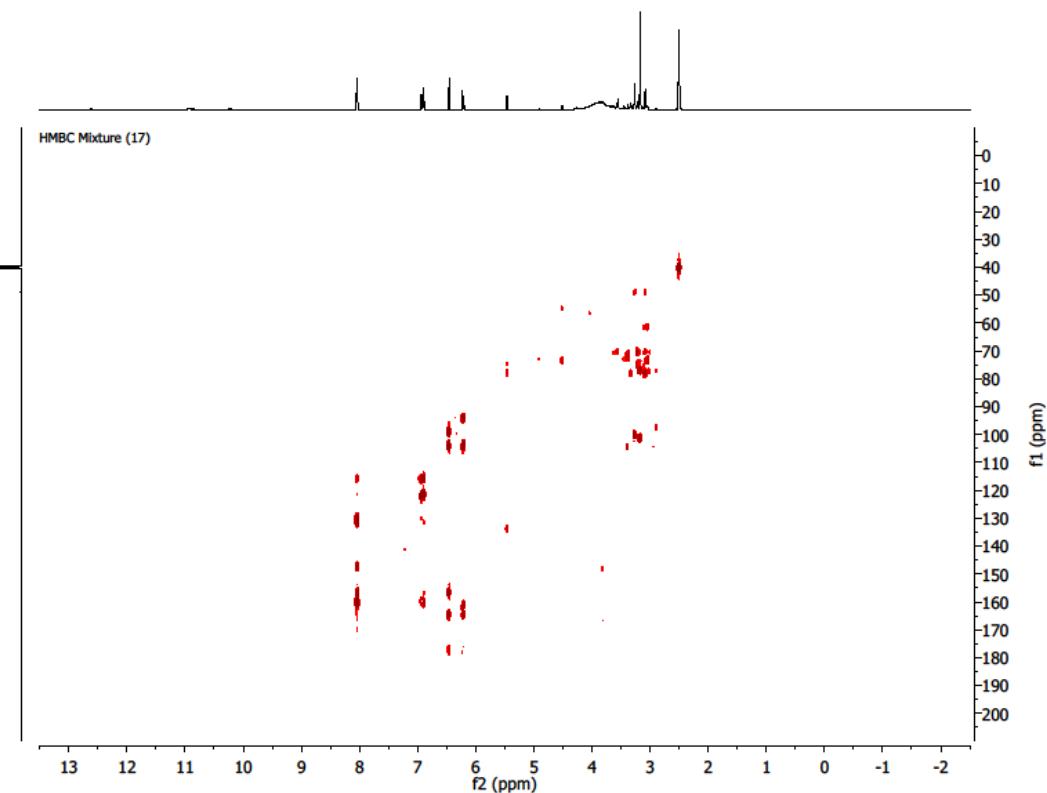
163

**Figure S17.** Zoom from 5.2 to 8.2 ppm,  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of mixture (17).



164

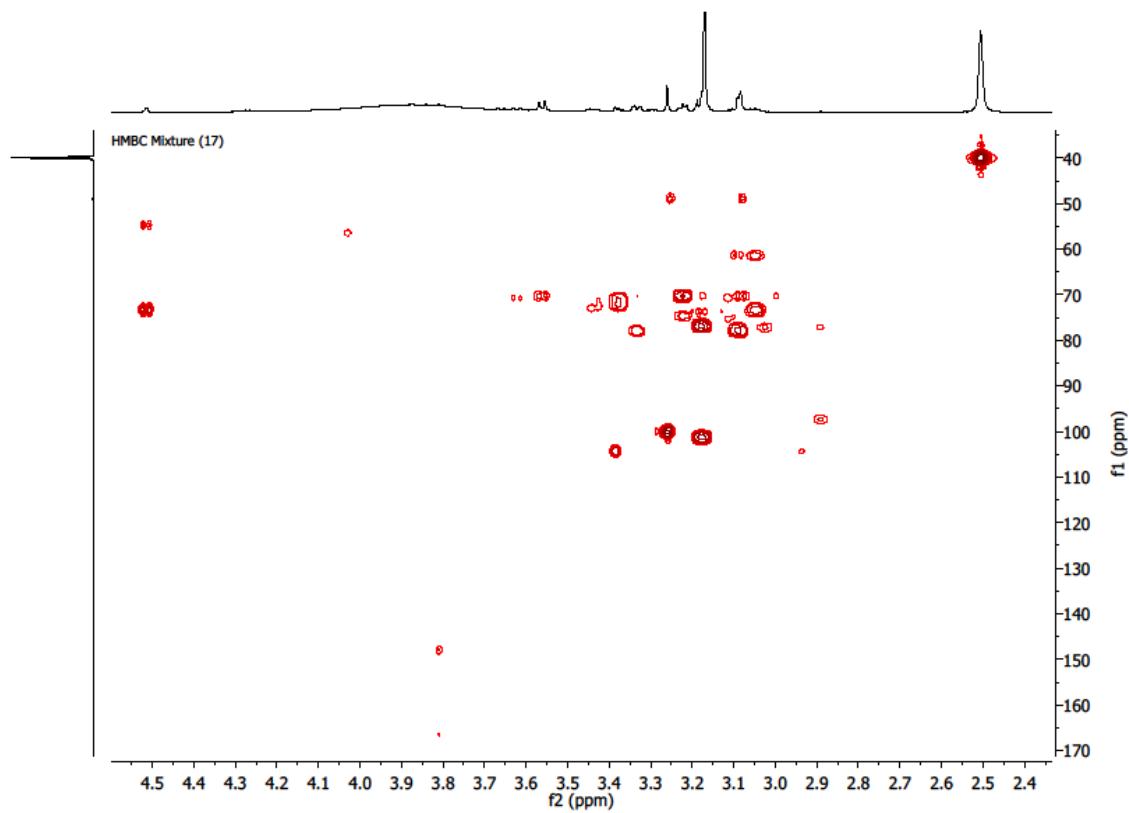
165

**Figure S18.** <sup>13</sup>C NMR spectrum (DMSO-*d*6) of mixture (17).

166

167

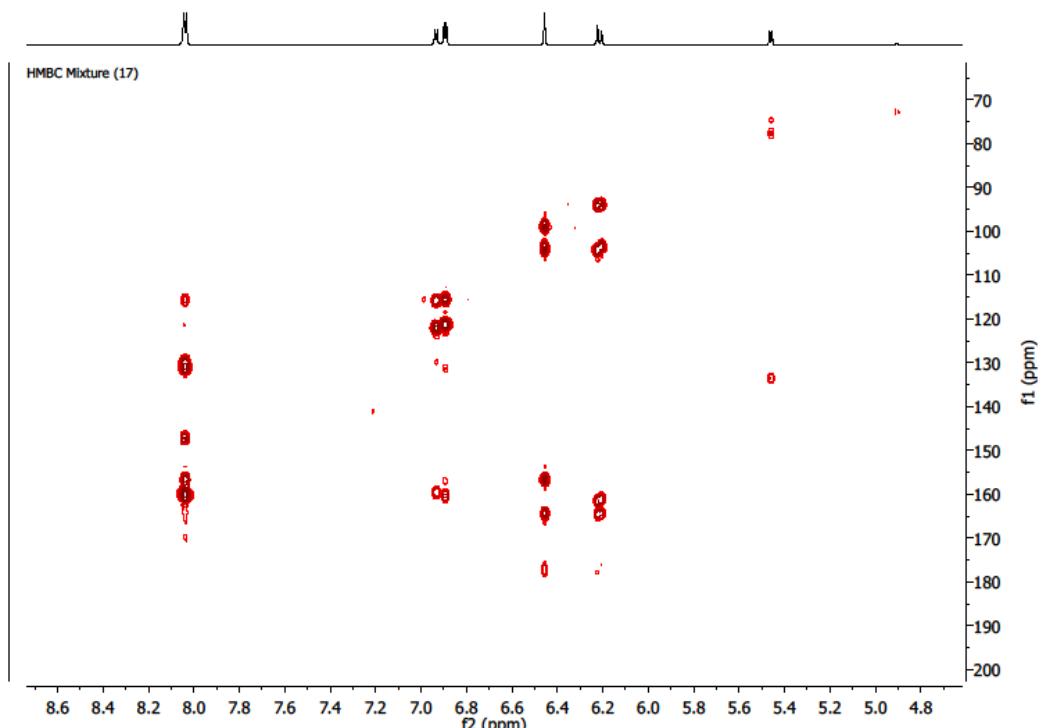
**Figure S19.** HMBC NMR spectrum (DMSO-*d*6) of mixture (17).



168

169

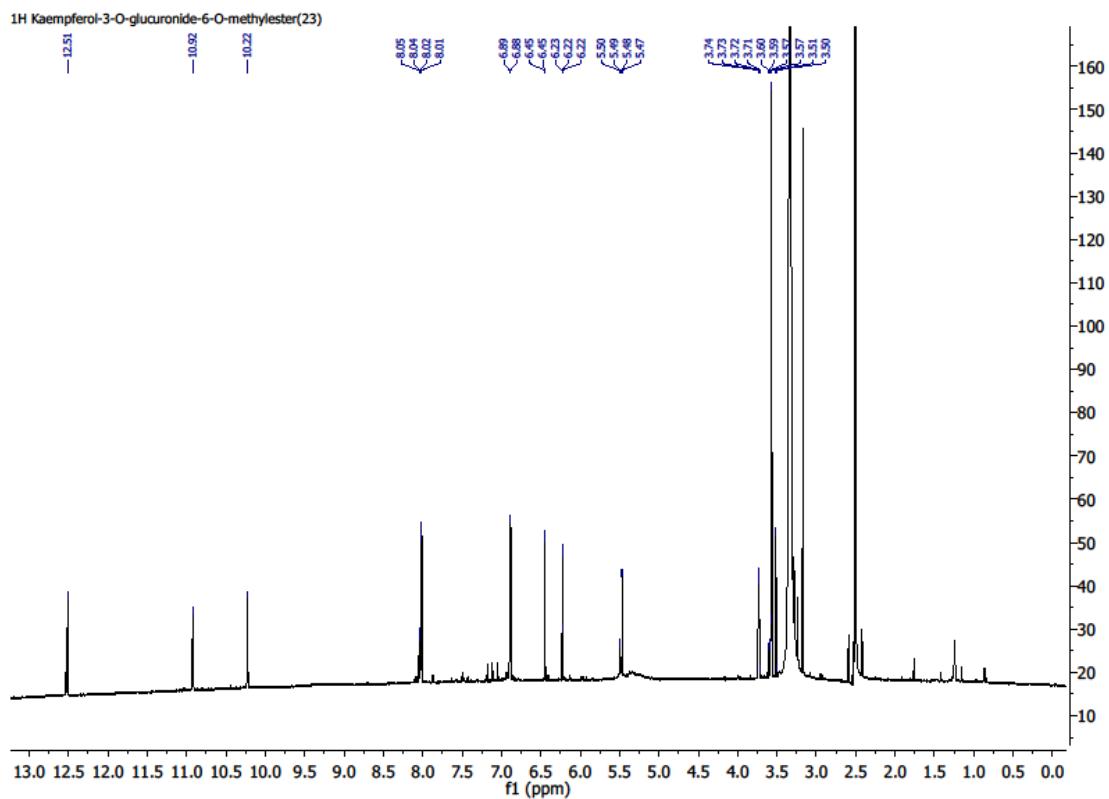
**Figure S20.** Zoom from 2.4 to 4.5 ppm, HMBC NMR spectrum (DMSO-*d*6) of mixture (17).



170

171

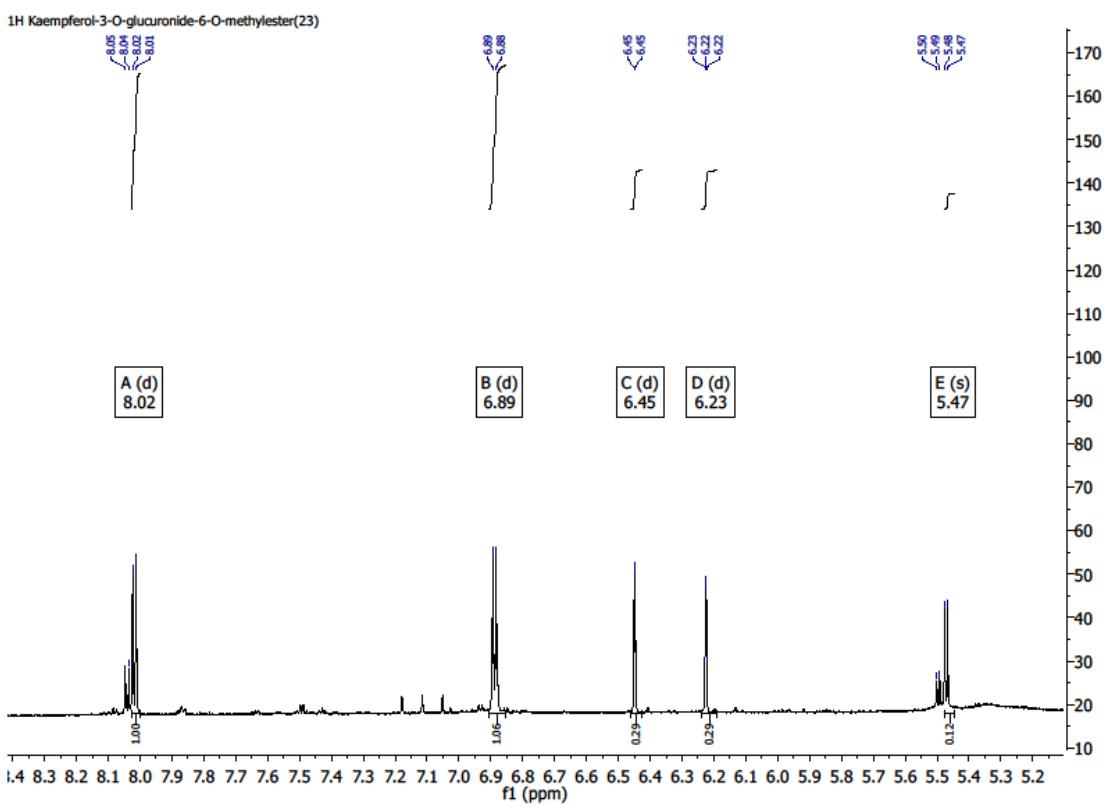
**Figure S21.** Zoom from 4.8 to 8.6 ppm, HMBC NMR spectrum (DMSO-*d*6) of mixture (17).



172

173

**Figure S22.**  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ) of kaempferol 3-O-glucuronide-6''-O-methylester (23).

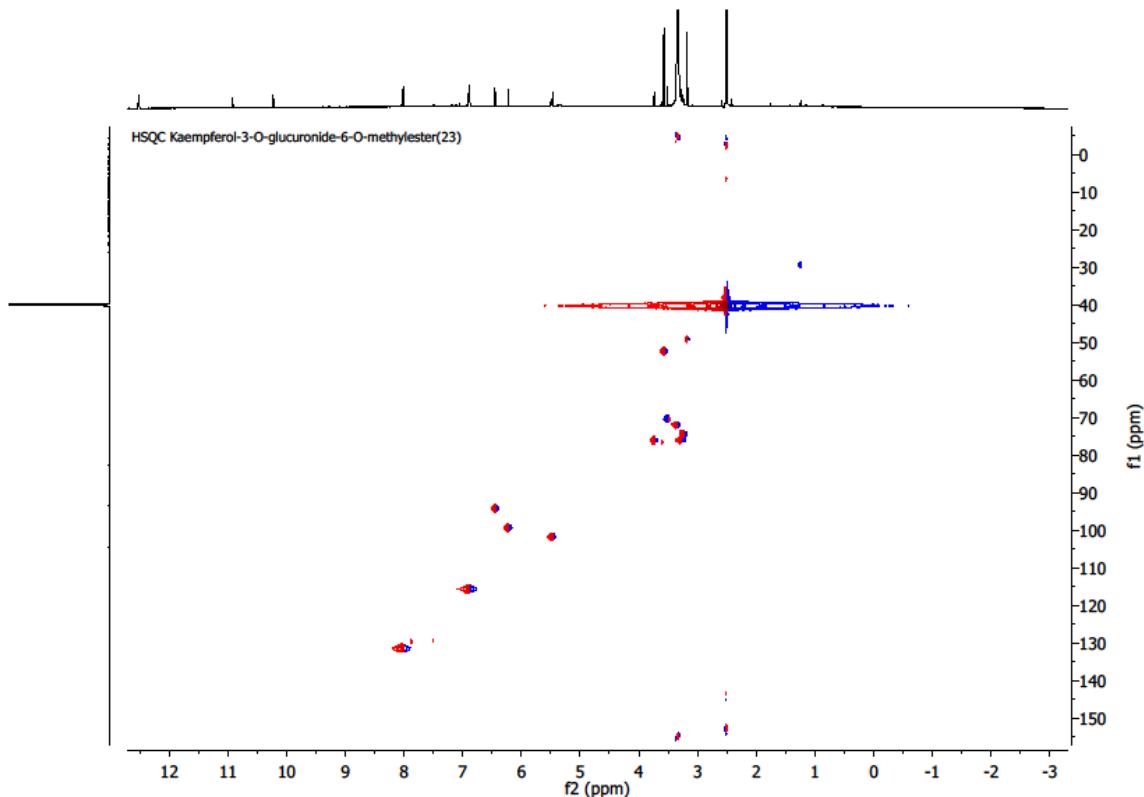


174

175

**Figure S23.** Zoom from 5.1 to 8.1 ppm,  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ) of kaempferol 3-O-glucuronide-6''-O-methylester (23).

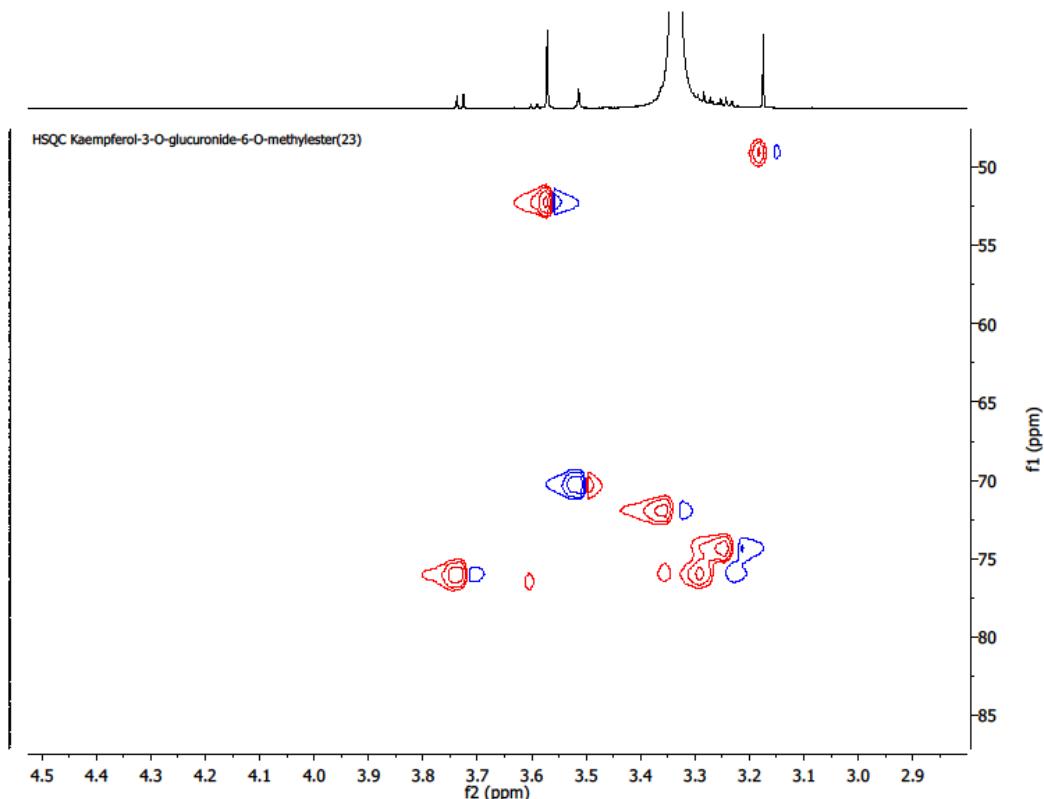
176



177

178

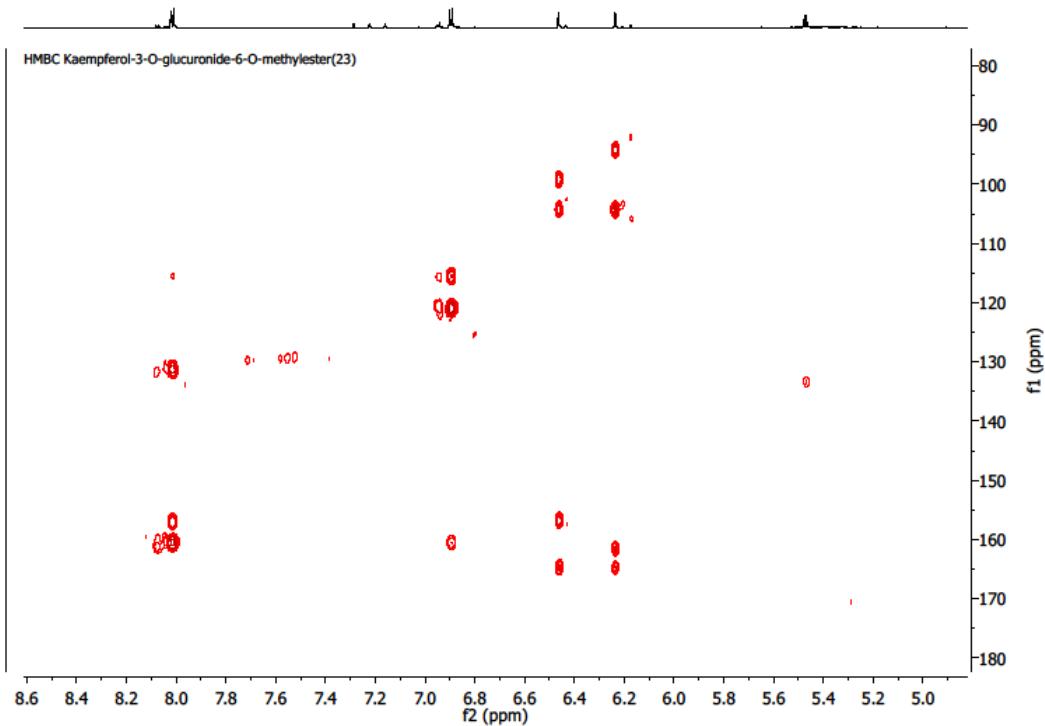
**Figure S24.** HSQC NMR spectrum (DMSO-*d*6) of kaempferol 3-*O*-glucuronide-6''-*O*-methylester (23).



179

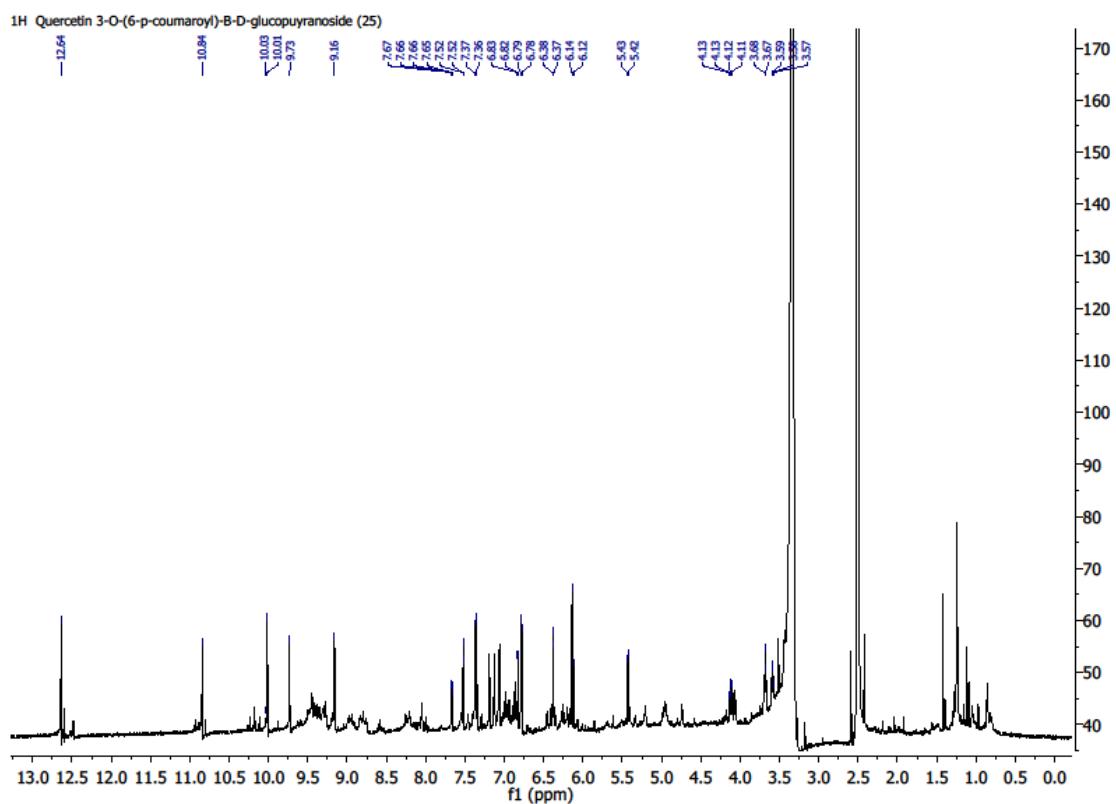
180  
181

**Figure S25.** Zoom from 2.9 to 4.5 ppm, HSQC NMR spectrum (DMSO-*d*6) of kaempferol 3-*O*-glucuronide-6''-*O*-methylester (23).



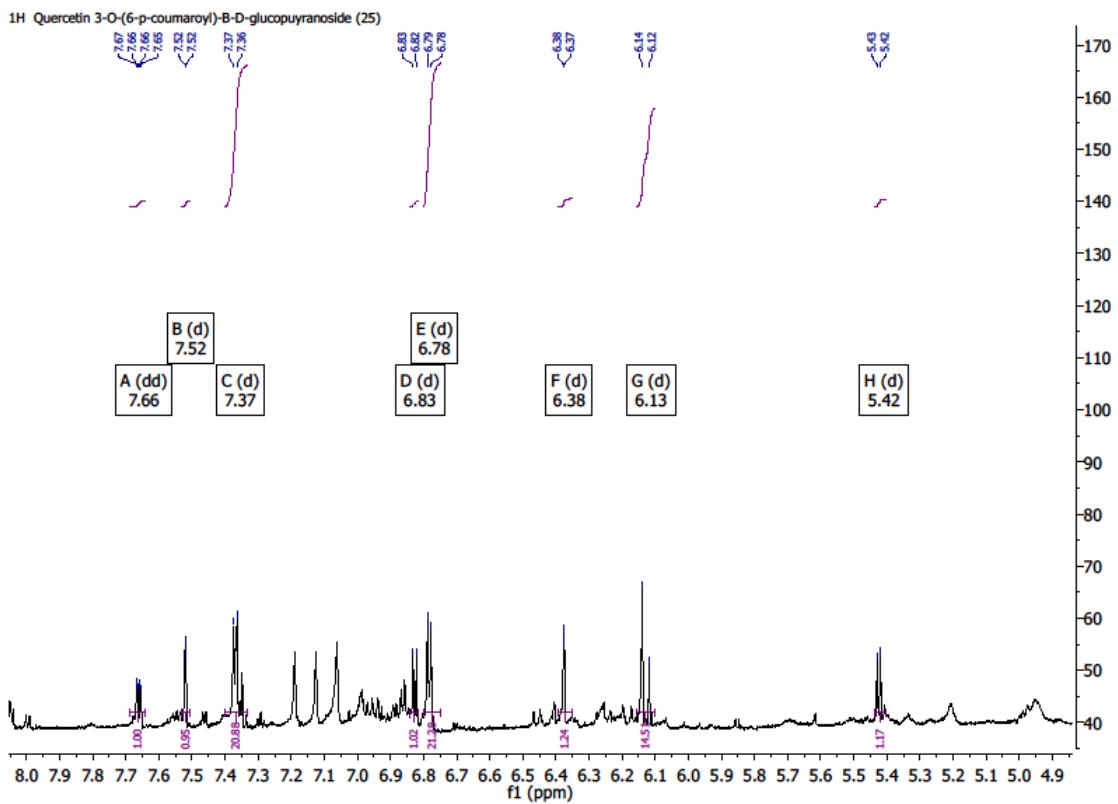
182

183 **Figure S26.** Zoom from 5.0 to 8.6 ppm, HMBC NMR spectrum (DMSO-*d*6) of kaempferol  
184 3-O-glucuronide-6''-O-methylester (23).



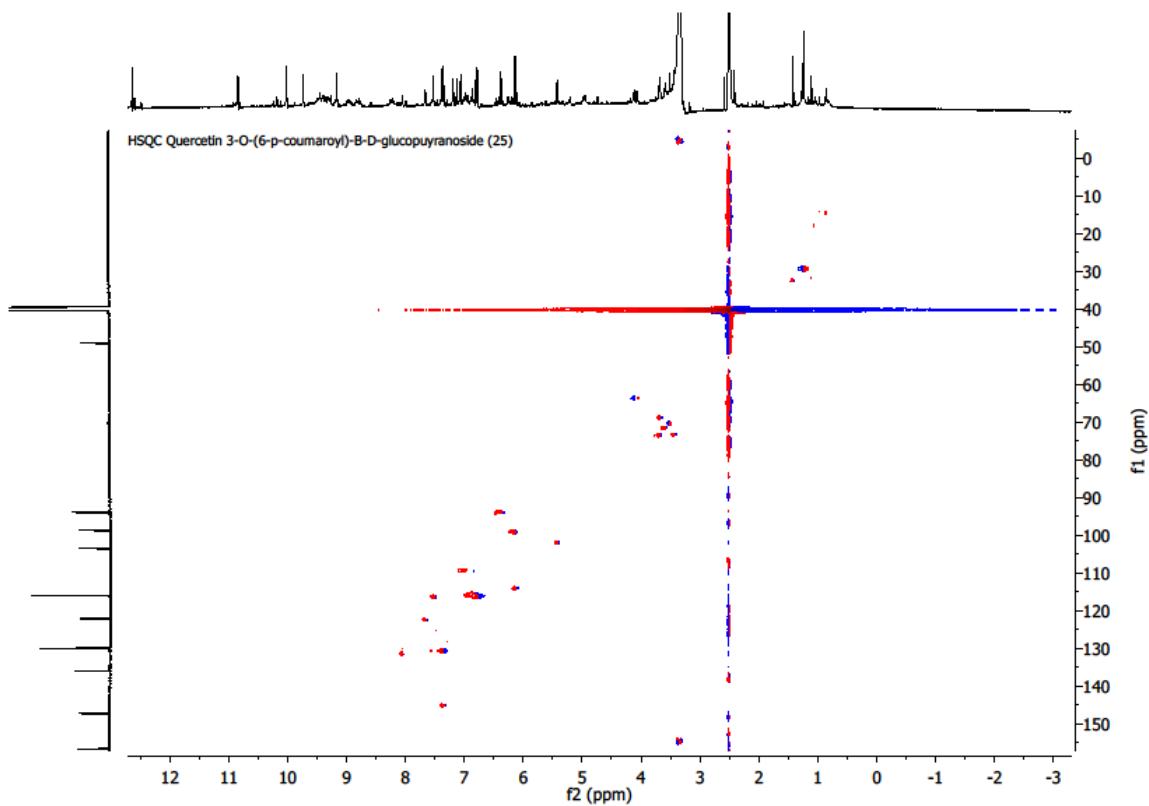
185

186 **Figure S27.** <sup>1</sup>H NMR spectrum (DMSO-*d*6) of Quercetin 3-O-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (25).



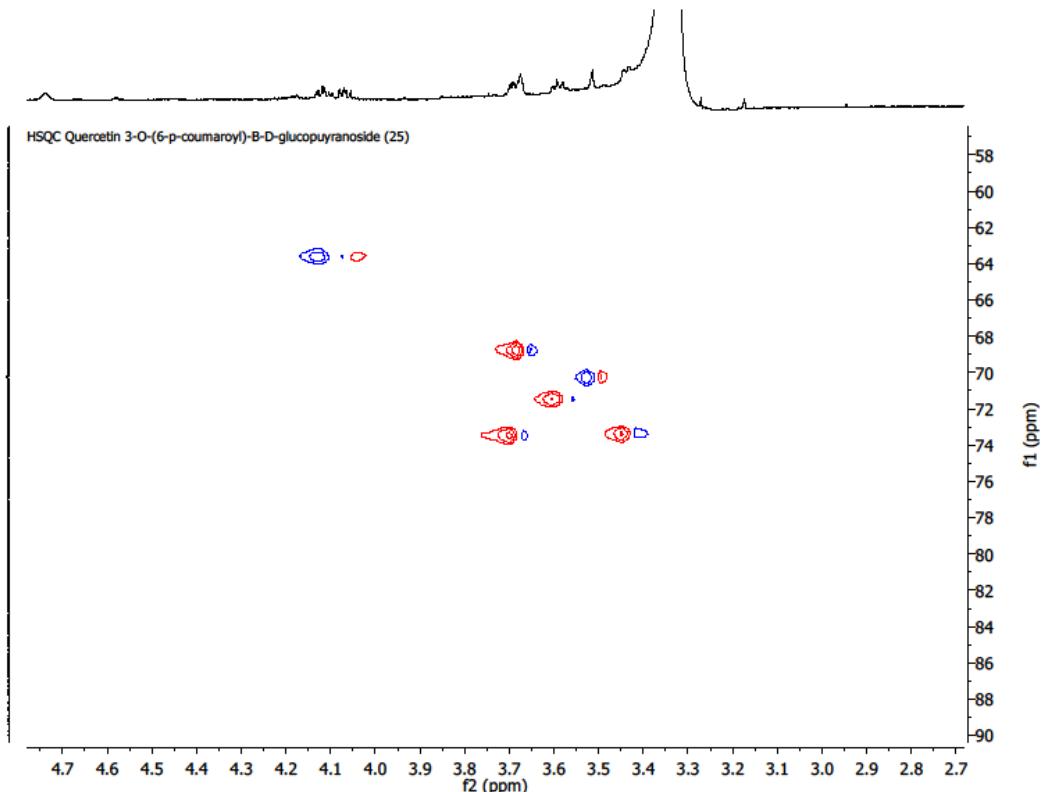
187

188 **Figure S28.** Zoom from 5.1 to 8.1 ppm,  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of Quercetin  
 189 3-*O*-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (**25**).



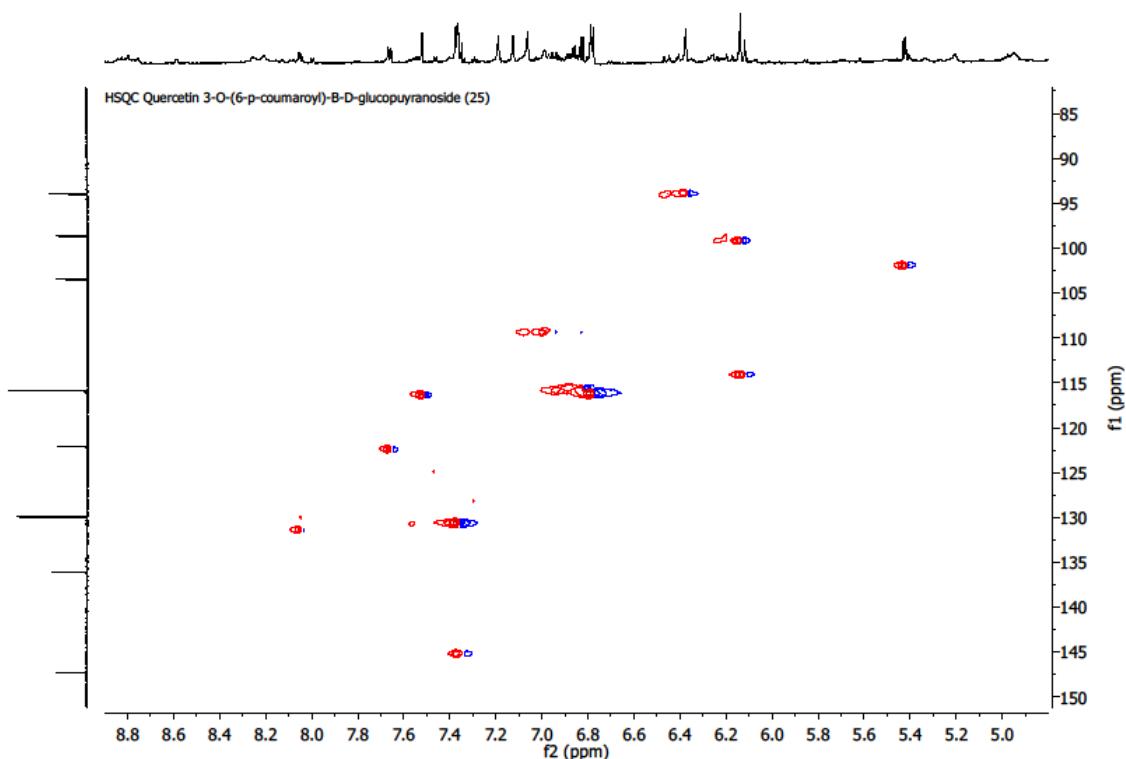
190

191 Figure S29. HSQC NMR spectrum ( $\text{DMSO}-d_6$ ) of Quercetin 3-O-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (**25**).



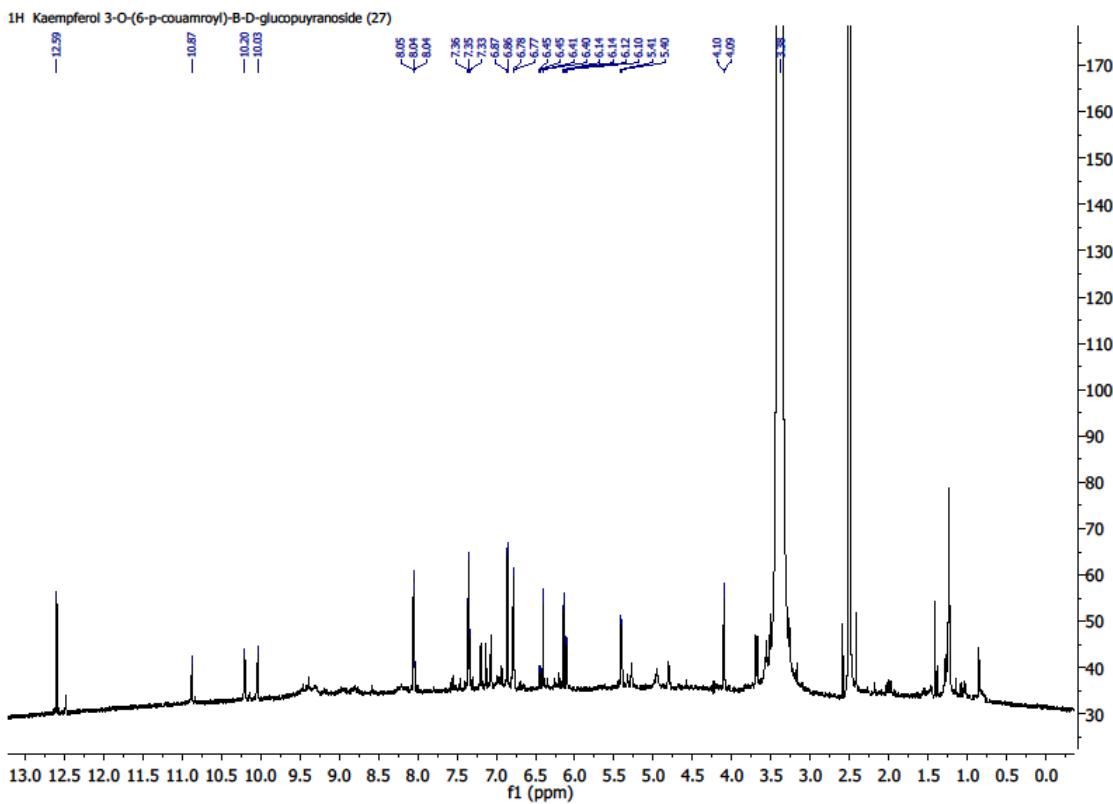
192

193 **Figure S30.** Zoom from 2.7 to 4.7 ppm, HSQC NMR spectrum (DMSO-*d*6) of Quercetin  
194 3-O-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (25).

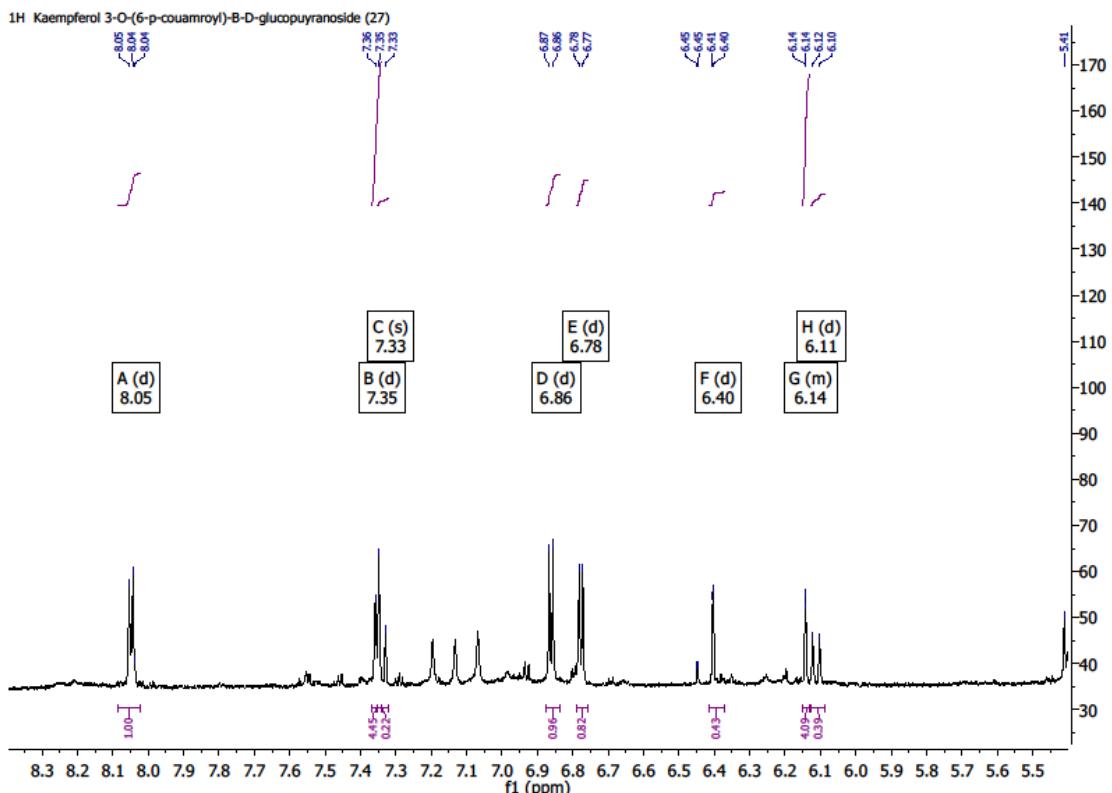


195

196 **Figure S31.** Zoom from 5.0 to 8.8 ppm, HSQC NMR spectrum (DMSO-*d*6) of Quercetin  
197 3-O-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (25).

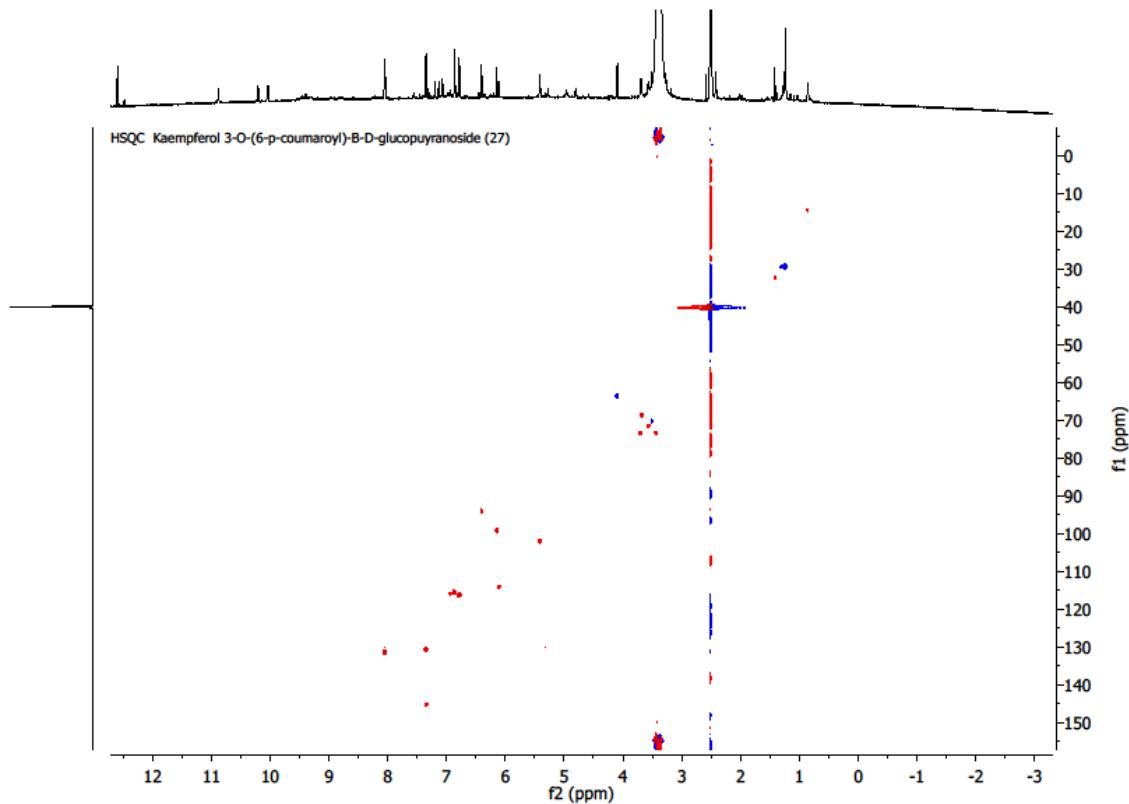


198

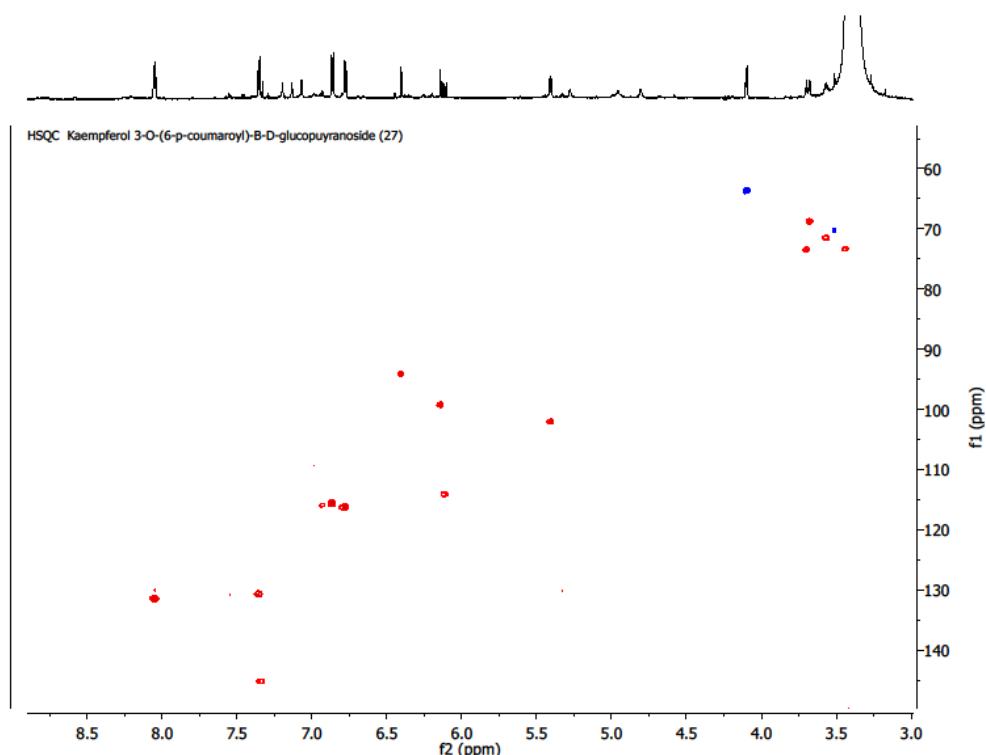
199 Figure S32.  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of Kaempferol 3-O-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (27).

200

201 Figure S33. Zoom from 5.1 to 8.1 ppm,  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of Kaempferol  
202 3-O-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (27).



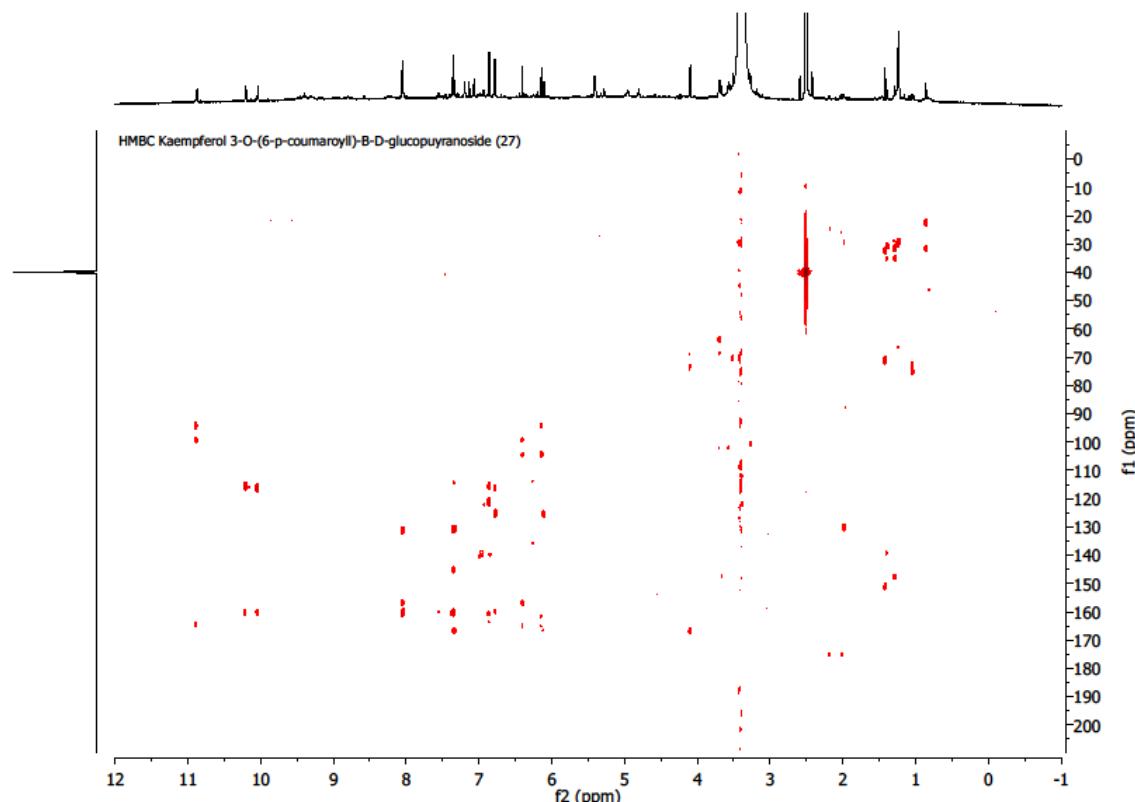
203

204 **Figure S34.** HSQC NMR spectrum (DMSO-*d*6) of Kaempferol 3-O-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (27).

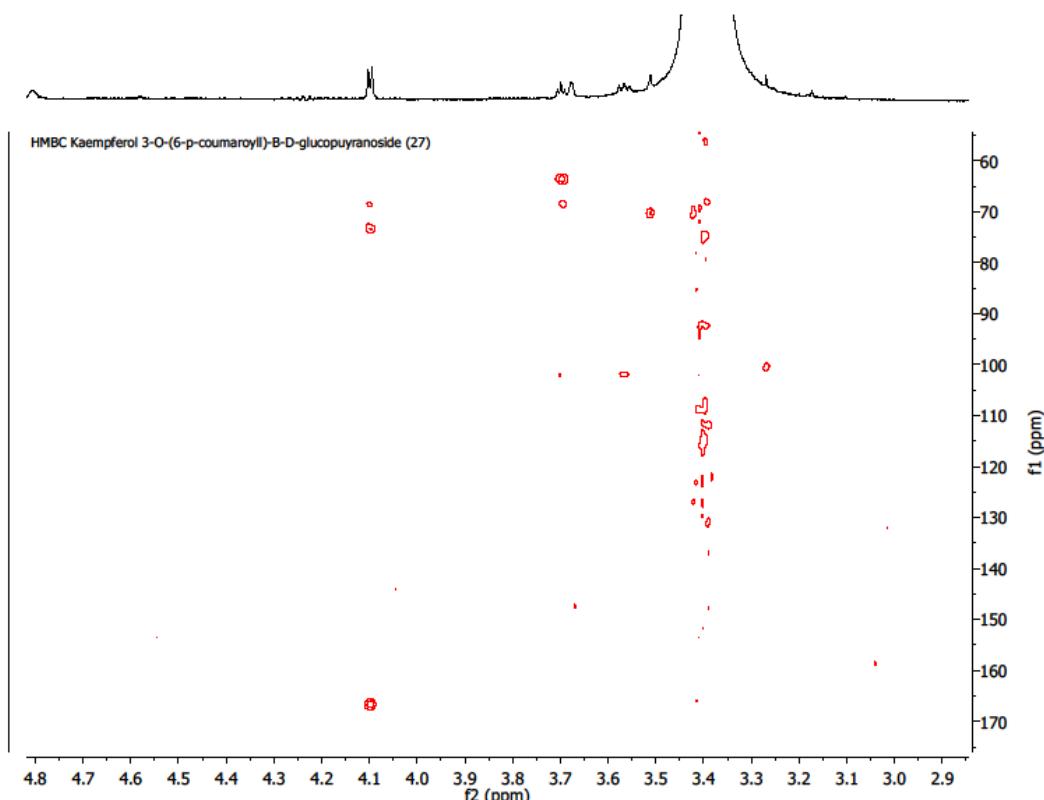
205

206 **Figure S35.** Zoom from 3.0 to 4.6 ppm, HSQC NMR spectrum (DMSO-*d*6) of Kaempferol  
207 3-O-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (27).

208

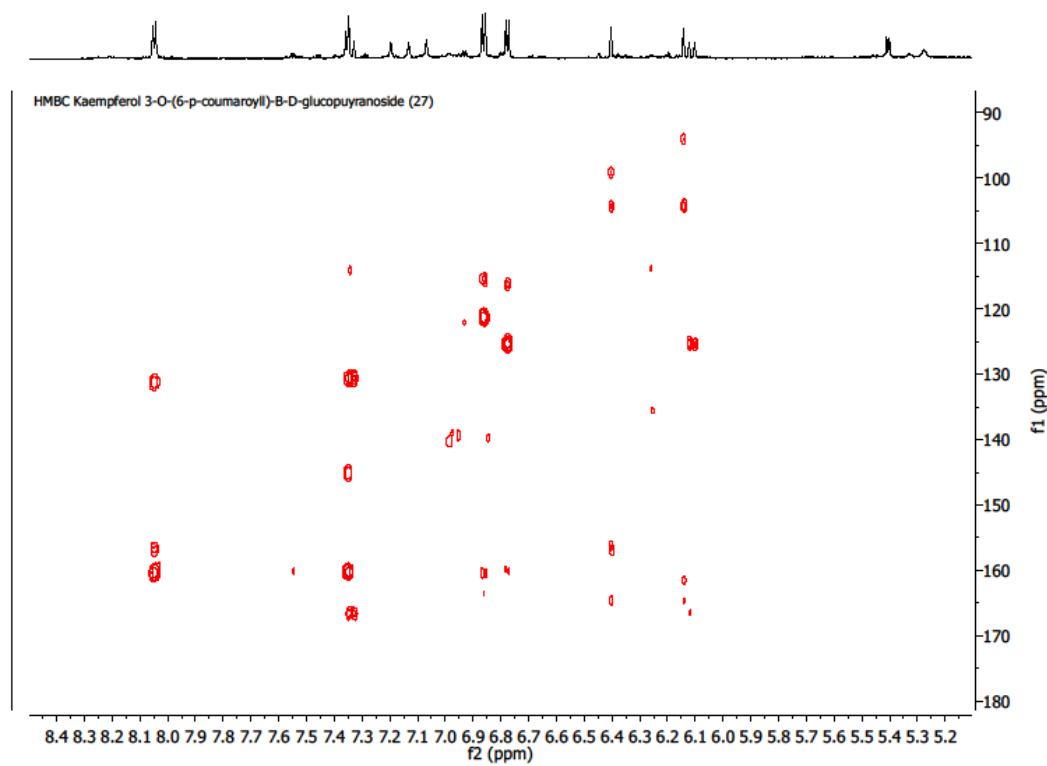


209

210 **Figure S36.** HMBC NMR spectrum (DMSO-*d*6) of Kaempferol 3-*O*-(6''-*p*-coumaroyl)-β-D-glucopyranoside (27).

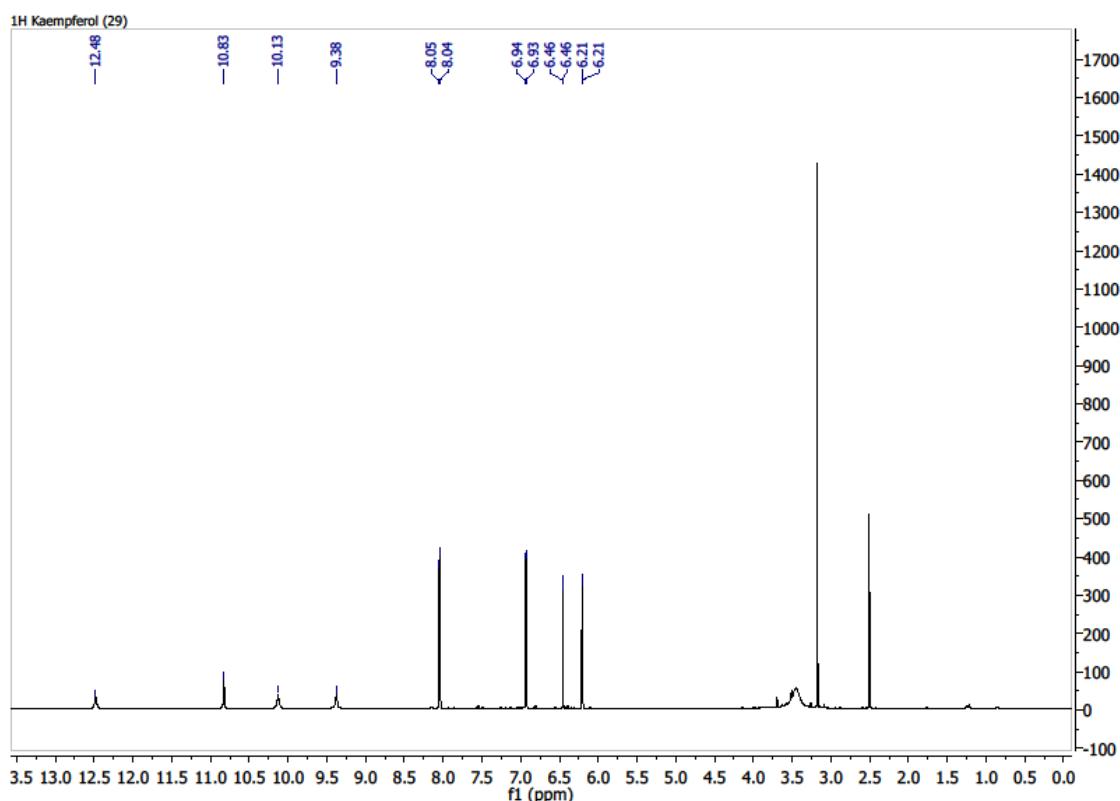
211

212 **Figure S37.** Zoom from 2.9 to 4.8 ppm, HMBC NMR spectrum (DMSO-*d*6) of Kaempferol  
213 3-*O*-(6''-*p*-coumaroyl)-β-D-glucopyranoside (27).



214

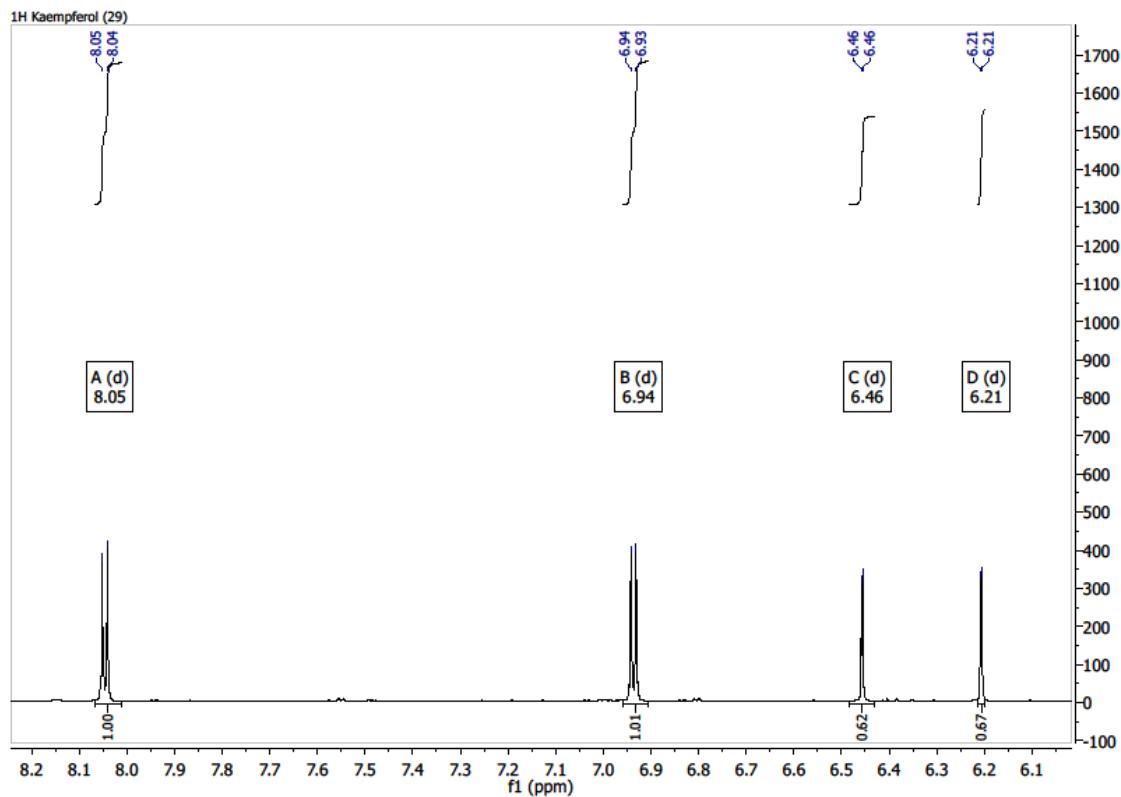
215 Figure S38. Zoom from 5.2 to 8.4 ppm, HMBC NMR spectrum (DMSO-*d*6) of Kaempferol  
 216 3-O-(6''-*p*-coumaroyl)- $\beta$ -D-glucopyranoside (27).



217

218

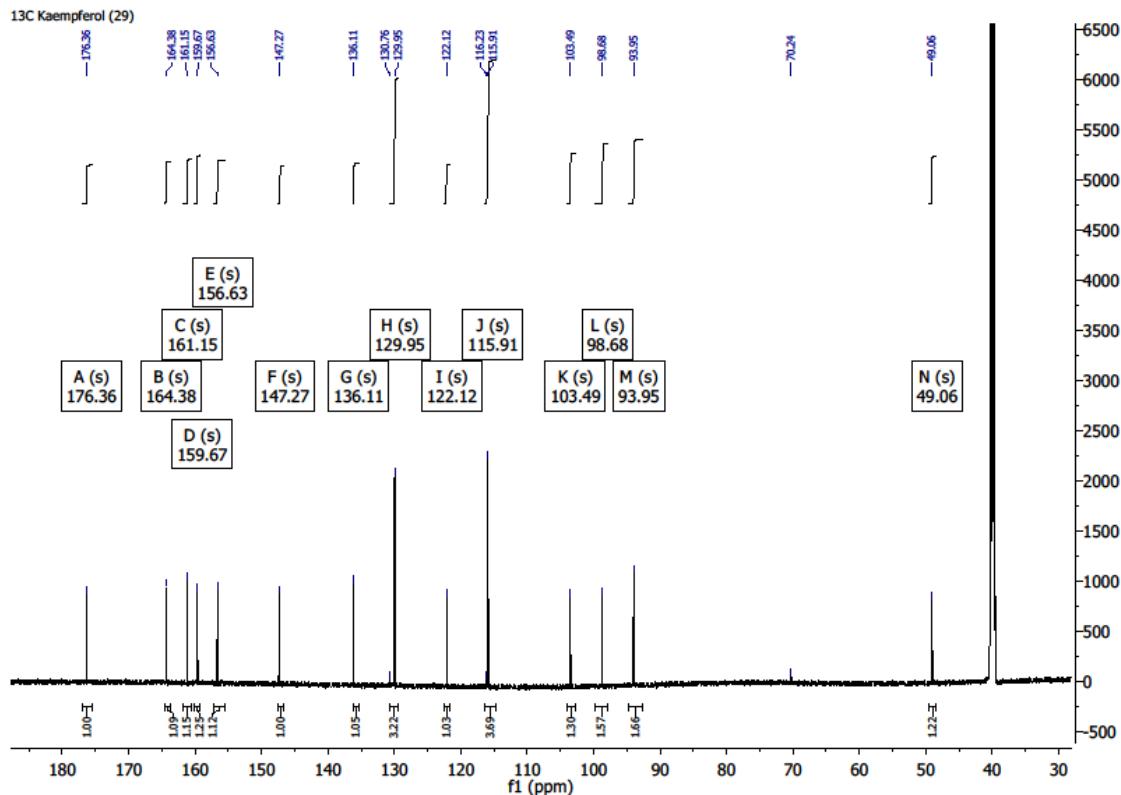
Figure S39. <sup>1</sup>H NMR spectrum (DMSO-*d*6) of kaempferol (29).



219

220

**Figure S40.** Zoom from 6.1 to 8.2 ppm,  $^1\text{H}$  NMR spectrum (DMSO-*d*6) of kaempferol (29).



221

222

223

**Figure S41.**  $^{13}\text{C}$  NMR spectrum (DMSO-*d*6) of kaempferol (29).

224      **Table S1.** NMR data of <sup>1</sup>H, <sup>13</sup>C and HMBC for kaempferol 3-O-(6''-O-galloyl)- $\beta$ -D-glucopyranoside and  
225      kaempferol 3-O-(2''-O-galloyl)- $\beta$ -D-glucopyranoside (**13**, **16** or **19**).

Carbon number	Kaempferol 3-O-(6''-O-galloyl)- $\beta$ -D-glucopyranoside			Kaempferol 3-O-(2''-O-galloyl)- $\beta$ -D-glucopyranoside		
	<sup>1</sup> H	<sup>13</sup> C*	HMBC	<sup>1</sup> H	<sup>13</sup> C*	HMBC
2	-	157.15	-	-	155.46	-
3	-	133.52	-	-	133.22	-
4	-	-	-	-	-	-
5	-	161.90	-	-	160.00	-
6	6.21 d ( <i>J</i> = 2.0 Hz)	99.58	C8, C10, C7, C5	6.21 d ( <i>J</i> = 2.0 Hz)	98.02	C8, C10, C7, C5
7	-	164.50	-	-	163.30	-
8	6.45 d ( <i>J</i> = 2.0 Hz)	94.91	C10, C9, C7, C6	6.45 d ( <i>J</i> = 2.0 Hz)	93.05	C10, C6, C7, C9
9	-	157.26	-	-	155.50	-
10	-	104.66	-	-	102.70	-
1'	-	121.04	-	-	120.90	-
2',6'	7.94 d ( <i>J</i> = 8.8 Hz)	131.19	C2, C4', C6' or 2'	8.04 d ( <i>J</i> = 8.8 Hz)	129.54	C2' or 6', C4', C2, C3''' or 5'''
3',5'	6.77 d ( <i>J</i> = 8.8 Hz)	116.46	C4', C1', C5' or 3'	6.89/6.93 d ( <i>J</i> = 8.8 Hz)	114.66	C3''' or 5''', C4', C1'
4'	-	150.58	-	-	158.40	-
1''	5.45 d ( <i>J</i> = 7.6 Hz)	102.17	C3	5.47 d ( <i>J</i> = 7.6 Hz)	100.38	C3
2''	{}	74.52	C1'', C3''		73.68	C1, C3
3''		76.51	C2'', C4''		75.87	C2, C4
4''		3.24 - 3.50*	69.89	C2'', C6''	3.09 - 3.22*	69.48
5''		74.60	-		76.74	C5
6''	4.17 dd ( <i>J</i> = 12 and 3.8 Hz), 4.26 dd ( <i>J</i> = 12 and 2.0 Hz)	63.15	C5'', C4'', C7'''	3.62 and 3.38*	60.68	C3, C4
1'''	-	120.00	-	-	124.00	-
2''',6'''	6.92 s	109.70	C7''', C2''' or 6''', C3''' or 5''', C4'''	6.90 s	108.45	C7''', C4''', C3''' ou 5''', C1''', C2''' or 6'''
			C1'''			
3''',5'''	-	146.11	-	-	145.96	-
4'''	-	138.94	-	-	138.86	-
7'''	-	165.36	-	-	162.11	-
OH-C5	12.52 s	-	-			
OH-C7	10.87 s	-	-			
OH-C4'	10.06 s	-	-			

226      \*Chemical shifts of <sup>13</sup>C NMR were obtained by correlations in HSQC and HMBC.

227

228 **Table S2.** NMR data of  $^1\text{H}$ ,  $^{13}\text{C}$  and HMBC for kaempferol 3-*O*-glucuronide-6"-*O*-methyl ester (23).

Carbon number	$^1\text{H}$	$^{13}\text{C}^*$	HMBC
2	-	157.17	-
3	-	133.58	-
4	-	-	-
5	-	161.58	-
6	6.23 d ( $J=2.0$ Hz)	99.53	C8, C10, C7
7	-	164.78	-
8	6.45 d ( $J=2.0$ Hz)	94.10	C6, C10, C7, C9
9	-	156.94	-
10	-	104.46	-
1'	-	121.05	-
2',6'	8.02 d ( $J=8.9$ Hz)	131.73	C3, C2' or 6', C4'
3',5'	6.89 d ( $J=8.9$ Hz)	115.50	C1', C3' or 5', C4'
4'	-	160.62	-
1''	5.47 d ( $J=7.7$ Hz)	101.74	C3
2''	3.24-3.36*	74.60	C1'', C3'',
3''		75.92	C2'', C4''
4''		71.95	C5'', C6''
5''	3.73 d ( $J=9.7$ Hz)	76.13	C1'', C6'', C4''
6''	-	169.52	-
MeO-C6''	3.57 s	52.32	C6''
OH-C5	12.51 s	-	-
OH-C7	10.97 s	-	-
OH-C4'	10.22 s	-	-

229 \*Chemical shifts of  $^{13}\text{C}$  NMR were obtained by correlations in HSQC and HMBC.  
230

231      **Table S3.** NMR data of <sup>1</sup>H, <sup>13</sup>C and HMBC for quercetin 3-O-(6''-O-p-coumaroyl)-β-D-glucopyranoside (**25**) and  
232      kaempferol 3-O-(6''-O-p-coumaroyl)-β-D-glucopyranoside (**27**).

Carbon number	Quercetin 3-O-(6''-O-p-coumaroyl)-β-D-glucopyranoside		Kaempferol 3-O-(6''-O-p-coumaroyl)-β-D-glucopyranoside		
	<sup>1</sup> H	<sup>13</sup> C*	<sup>1</sup> H	<sup>13</sup> C*	HMBC
2	-	-	-	156.96	-
3	-	-	-	-	-
4	-	-	-	-	-
5	-	-	-	161.69	-
6	6.14 d ( <i>J</i> = 2.1 Hz)	99.19	6.14 d ( <i>J</i> = 2.1 Hz)	99.30	C8, C10, C5
7	-	-	-	164.56	-
8	6.38 d ( <i>J</i> = 2.1 Hz)	93.90	6.40 d ( <i>J</i> = 2.1 Hz)	94.19	C10, C9, C7, C6
9	-	-	-	156.55	-
10	-	-	-	104.20	-
1'	-	-	-	125.58	-
2'	7.52 d ( <i>J</i> = 2.3 Hz)	116.42	8.05 d ( <i>J</i> = 8.4 Hz)	131.47	C2, C4', C6' or 2'
3'	-	-	6.78 d ( <i>J</i> = 8.4 Hz)	116.35	C1', C5' or 3'
4'	-	-	-	160.38	-
5'	6.78 d ( <i>J</i> = 8.4 Hz)	116.01	6.78 d ( <i>J</i> = 8.4 Hz)	116.35	
6'	7.66 dd ( <i>J</i> = 8.4 Hz and 2.3 Hz)	122.38	8.05 d ( <i>J</i> = 8.4 Hz)	131.47	
1''	5.42 d ( <i>J</i> = 7.8 Hz)	102.03	5.41 d ( <i>J</i> = 7.7 Hz)	102.04	-
2''	-	-	3.51 - 3.70	71.47	C1
3''	-	-	-	70.32	-
4''	-	-	-	73.40	C5" ou C3", C1", C6" or C2"
5''	-	-	-	69.05	-
6''	4.12 dd ( <i>J</i> = 11.5 Hz and 4.6Hz)	63.62	4.10 d ( <i>J</i> = 6.2 Hz)	63.71	C9", C4", C5" or C3"
1'''	-	-	-	121.33 or 125.05	-
2'',6'''	7.37 d ( <i>J</i> = 8.4 Hz)	130.62	7.35 d ( <i>J</i> = 8.7 Hz)	130.66	C7", C4""
3'',5'''	6.83 d ( <i>J</i> = 8.4 Hz)	115.61	6.86 d ( <i>J</i> = 8.7 Hz)	115.52	C1'', C5" or C3", C4"
4'''	-	-	-	160.53	-
7'''	7.36 d ( <i>J</i> = 15.7 Hz)	145.31	7.34 d ( <i>J</i> = 15.9 Hz)	145.24	C9", C2" or C6""
8'''	6.13 d ( <i>J</i> = 15.7 Hz)	114.10	6.11 d ( <i>J</i> = 15.9 Hz)	114.29	-
9'''	-	-	-	166.85	-
OH-C5	12.64 s	-	12.59 s	-	-
OH-C7	10.84 s	-	10.87 s	-	C7, C6, C8
OH-C3'	9.16 s	-	-	-	-
OH-C4'	9.73 s	-	10.03 s	-	-
OH-C4'''	10.01 s	-	10.20 s	-	-

233      \*Chemical shifts of <sup>13</sup>C NMR were obtained by correlations in HSQC.

234 **Table S4.** NMR data of  $^1\text{H}$  and  $^{13}\text{C}$  for Kaempferol (**29**).

Carbon number	$^1\text{H}$	$^{13}\text{C}$
2	-	147.27
3	-	136.11
4	-	176.36
5	-	161.15
6	6.21 d ( $J= 2.0$ Hz)	96.68
7	-	164.38
8	6.46 d ( $J= 2.0$ Hz)	93.95
9	-	156.63
10	-	103.49
1'	-	122.12
2',6'	8.05 d ( $J= 8.9$ Hz)	129.95
4'		159.67
3',5'	6.94 d ( $J= 8.9$ Hz)	115.91
OH-C3	9.38 s	
OH-C5	12.48 s	-
OH-C7	10.83 s	-
OH-C4'	10.13 s	-

235