Supporting Information

Identification and Characterisation of the Phenolic Glycosides of *Lagenaria siceraria* Stand. (Bottle Gourd) Fruit by Liquid Chromatography Tandem Mass Spectrometry

RAKESH JAISWAL[*1] AND NIKOLAI KUHNERT[*2]

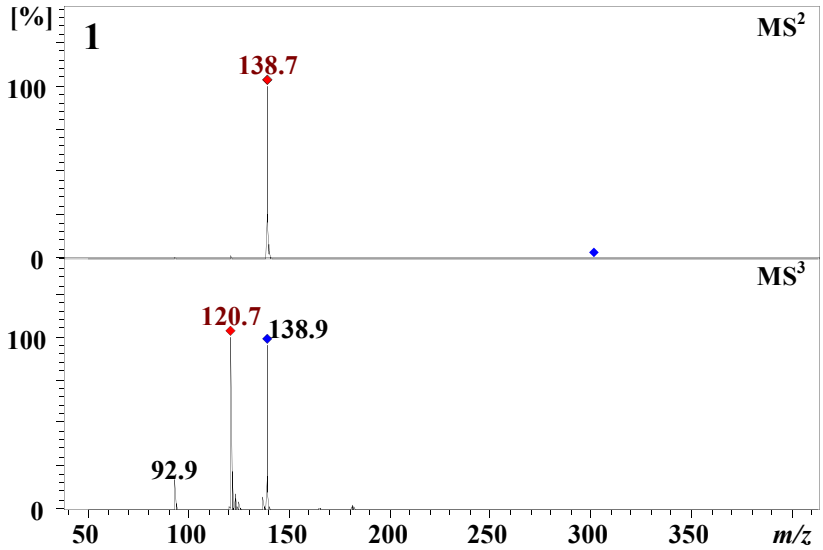


Figure S1. MS^4 spectra of 4-*O*-glucosyl-3,4-dihydroxybenzyl alcohol **1** at *m/z* 301 in negative ion mode.

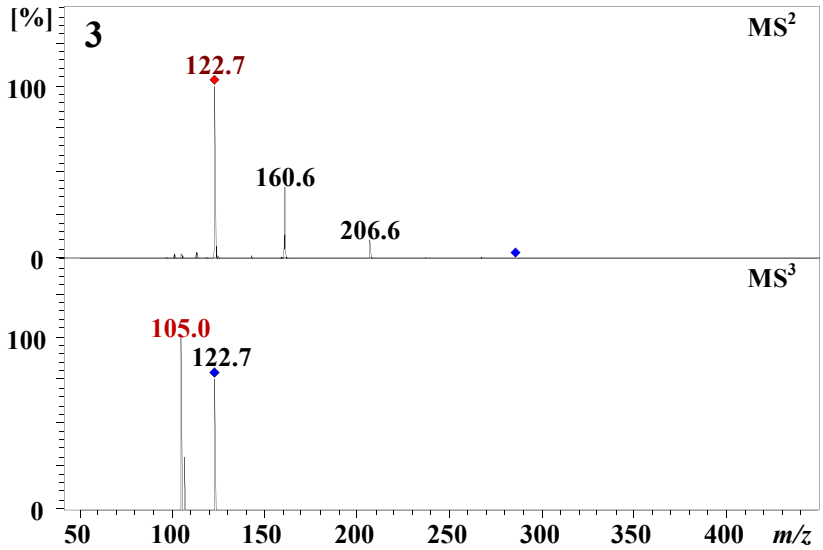


Figure S2. MS^3 spectra 4-*O*-glucosyl-4-hydroxybenzyl alcohol **3** at *m/z* 285 in negative ion mode.

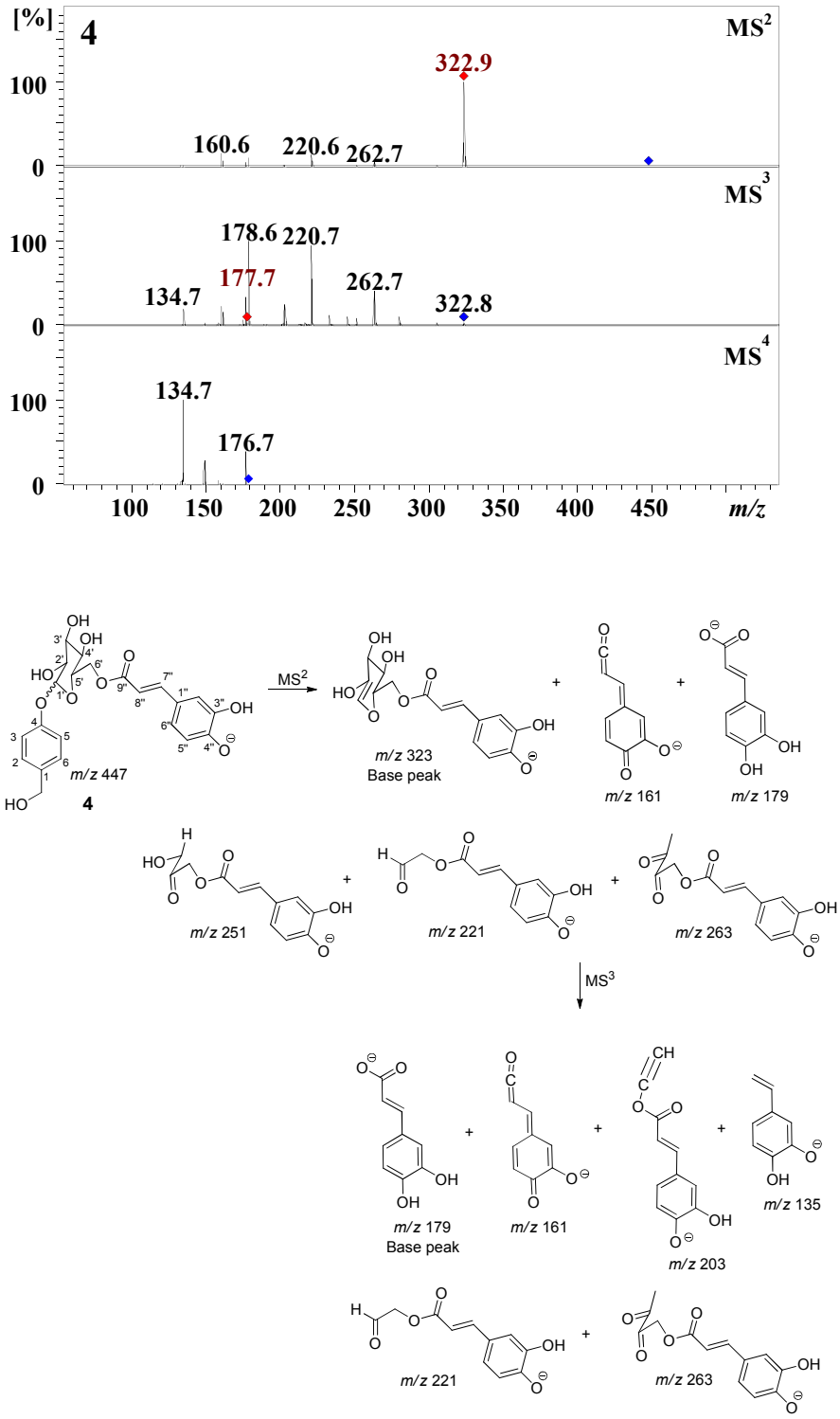
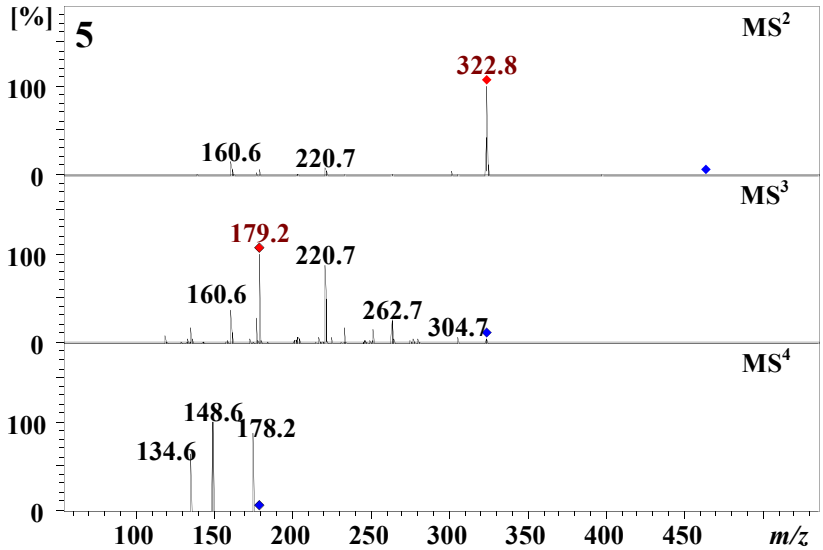


Figure S3. MS^4 spectra of 4-*O*-(6'-*O*-glucosyl caffeoyl)-4-hydroxybenzyl alcohol **4** at *m/z* 447 in negative ion mode.


[%]
5
MS2
322.8
160.6
220.7
MS3
179.2
220.7
160.6
262.7
304.7
MS4
148.6
178.2
134.6
100
0
100
150
200
250
300
350
400
450
m/z

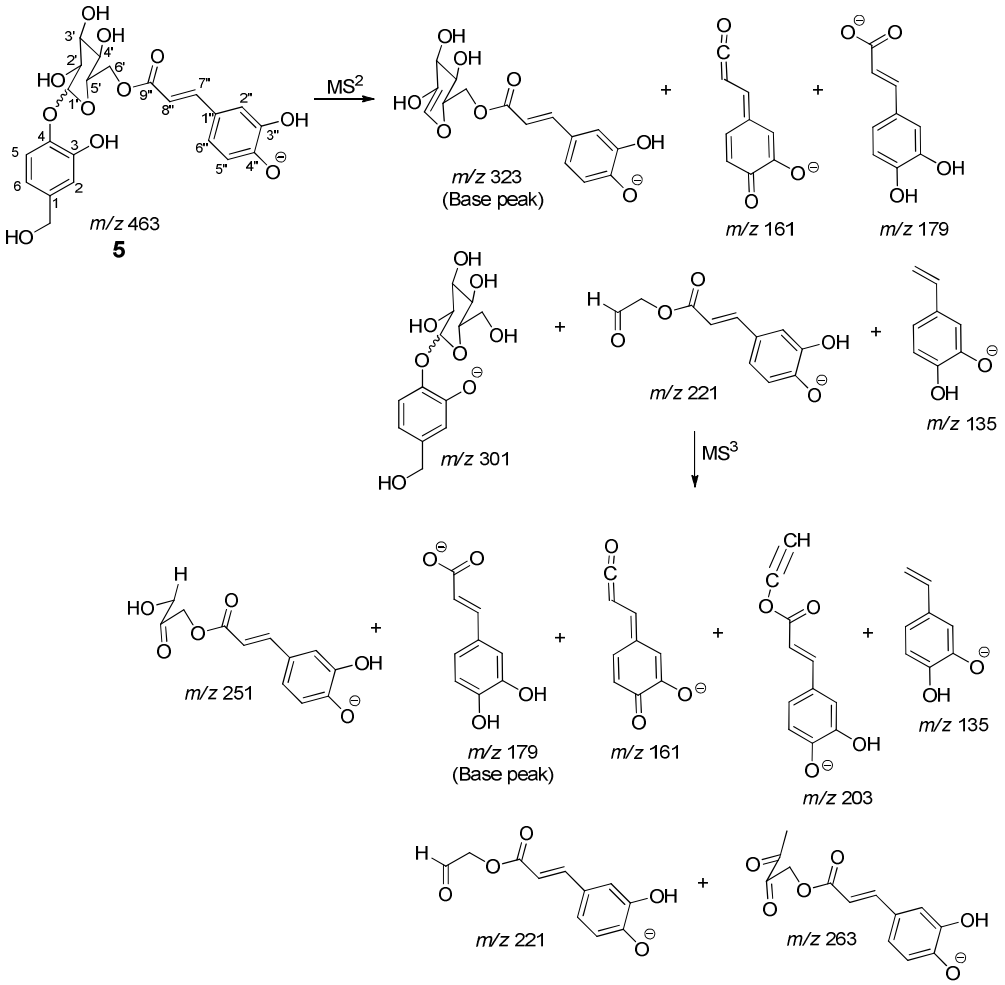

m/z 463
5
MS2
m/z 323
(Base peak)
m/z 161
m/z 179
m/z 301
m/z 221
m/z 135
MS3
m/z 251
m/z 179
(Base peak)
m/z 161
m/z 203
m/z 135
m/z 221
m/z 263

Figure S4. A fragmentation pathway and MS^4 spectra of 4-*O*-(6'-*O*-glucosyl caffeoyl)-3,4-dihydroxybenzyl alcohol **5** at *m/z* 463 in negative ion mode.

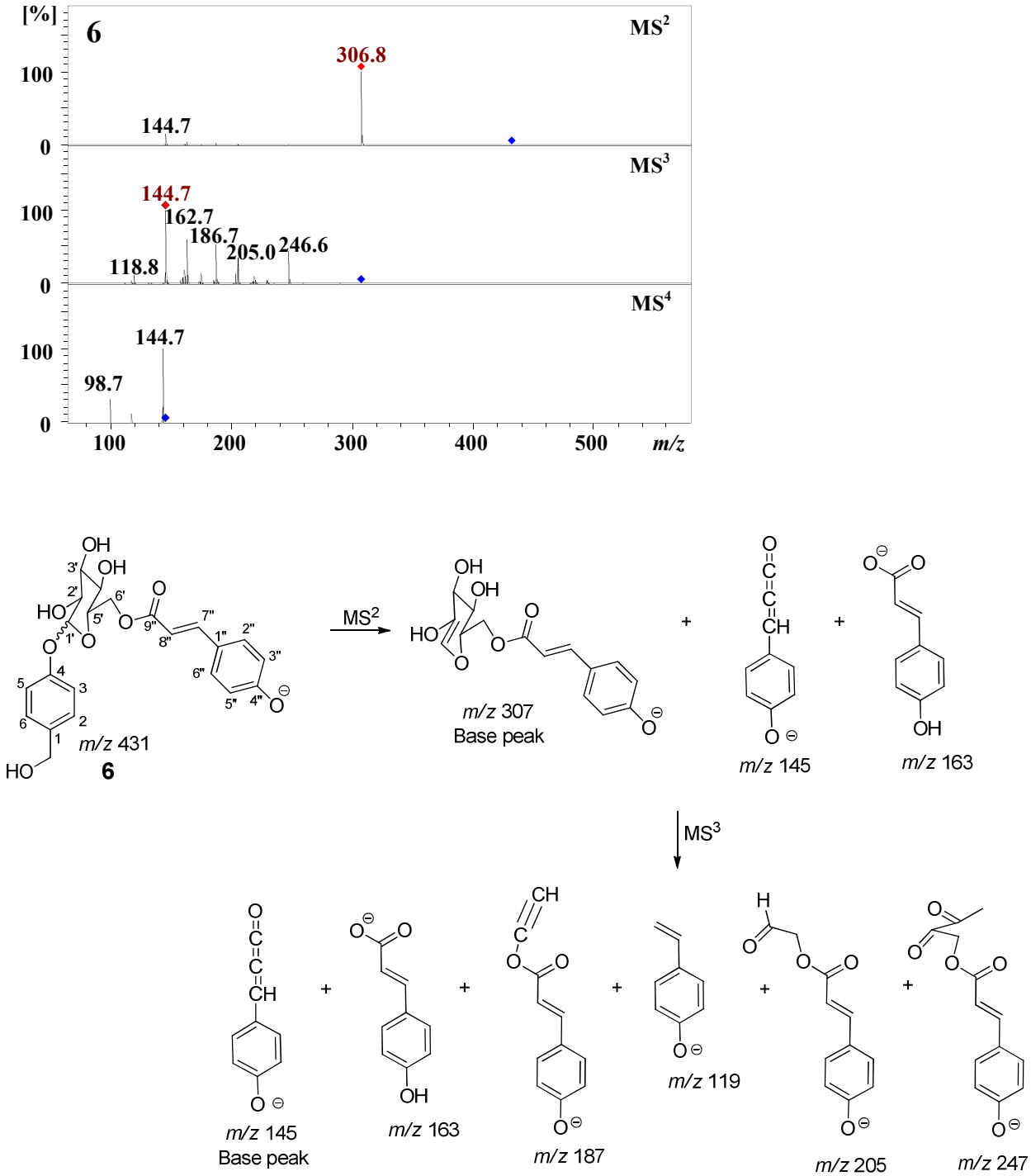


Figure S5. MS^4 spectra of 4-*O*-(6'-*O*-glucosyl *p*-coumaroyl)-4-hydroxybenzyl alcohol **6** at *m/z* 431 in negative ion.

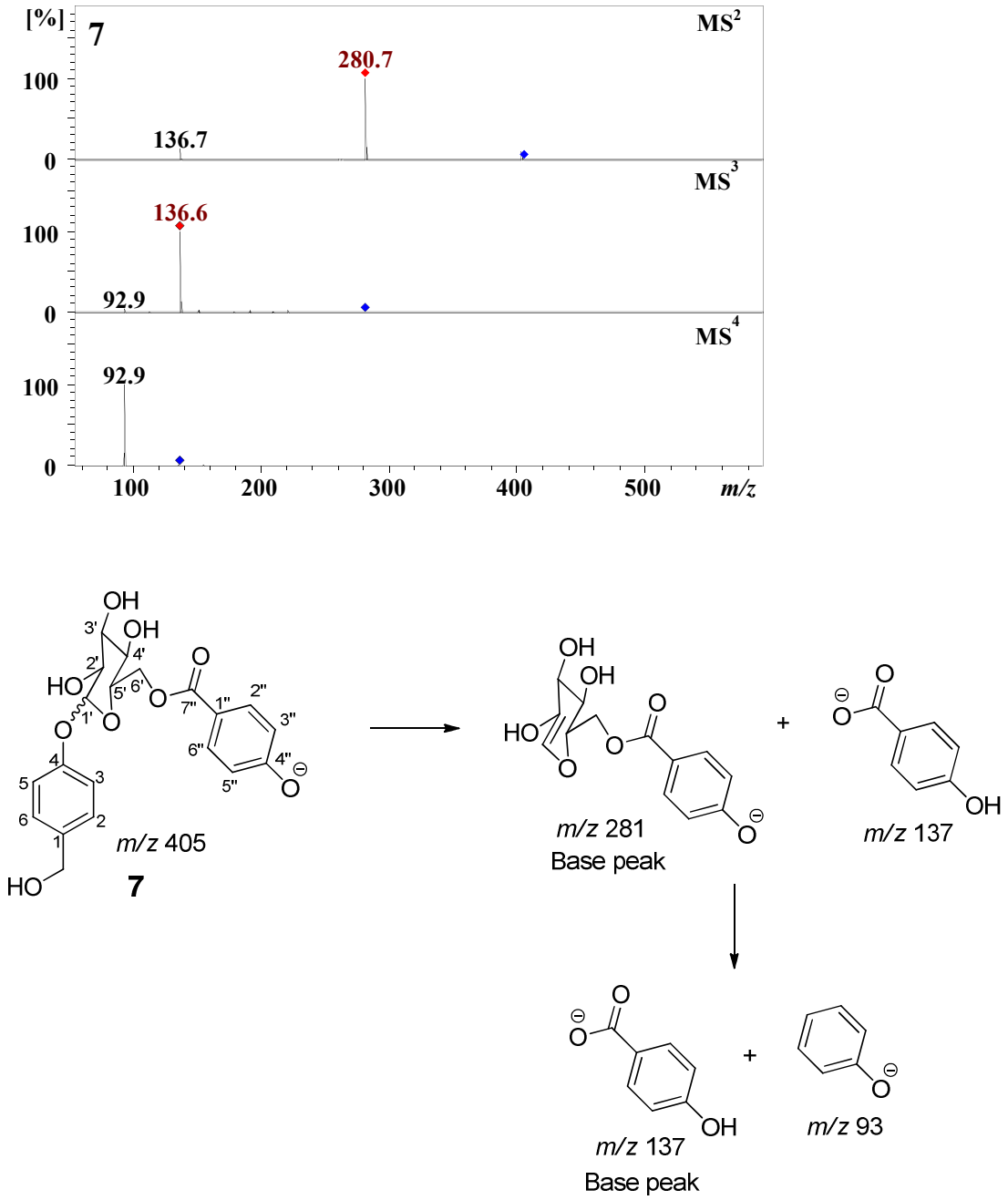
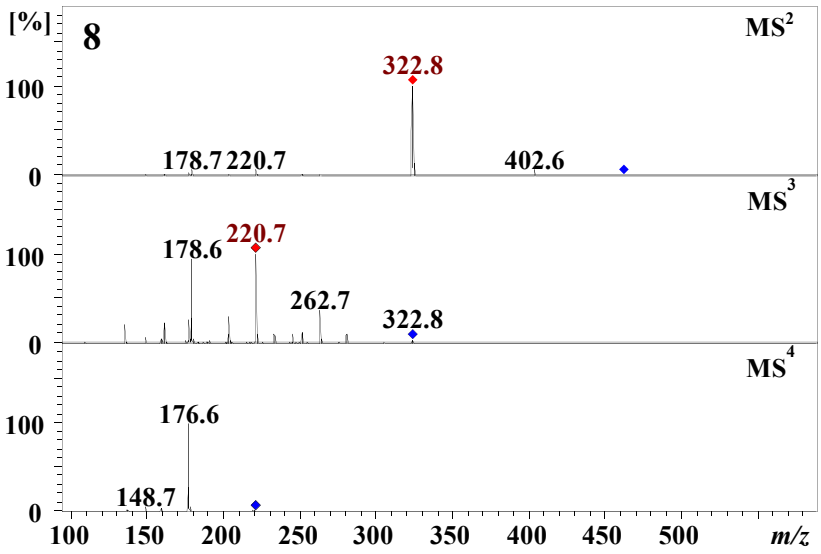


Figure S6. MS^4 spectra of 4-*O*-(6'-*O*-glucosyl 4"-hydroxybenzoyl)-4-hydroxybenzyl alcohol **7** at *m/z* 405 in negative ion mode.


[%]
8
MS2
322.8
178.7
220.7
402.6
MS3
178.6
220.7
262.7
322.8
MS4
176.6
148.7
100
0
100
150
200
250
300
350
400
450
500
m/z

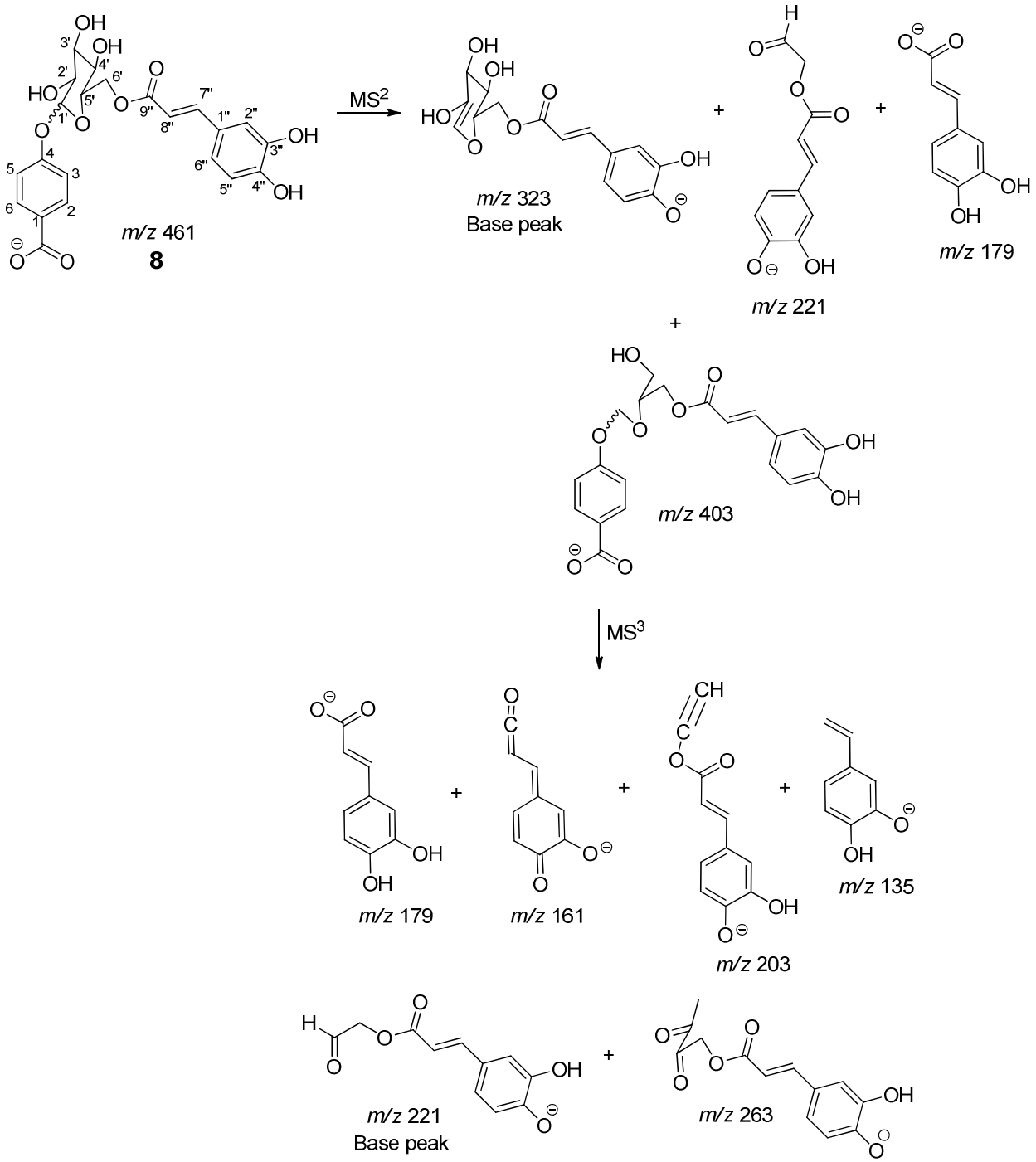


Figure S7. MS^4 spectra of 4-*O*-(6'-*O*-glucosyl caffeoyl)-4-hydroxybenzoic acid **8** at *m/z* 461 in negative ion mode.

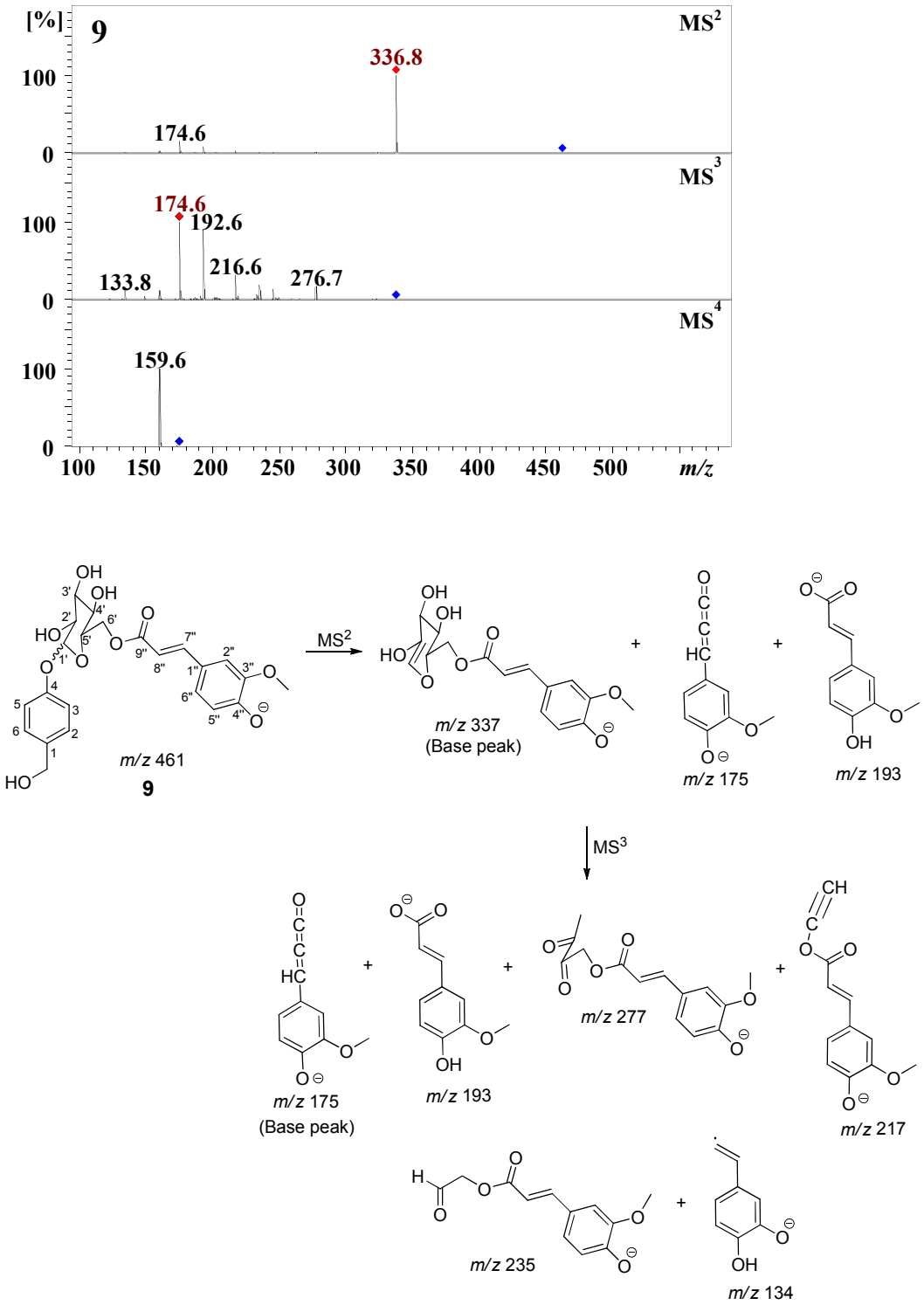
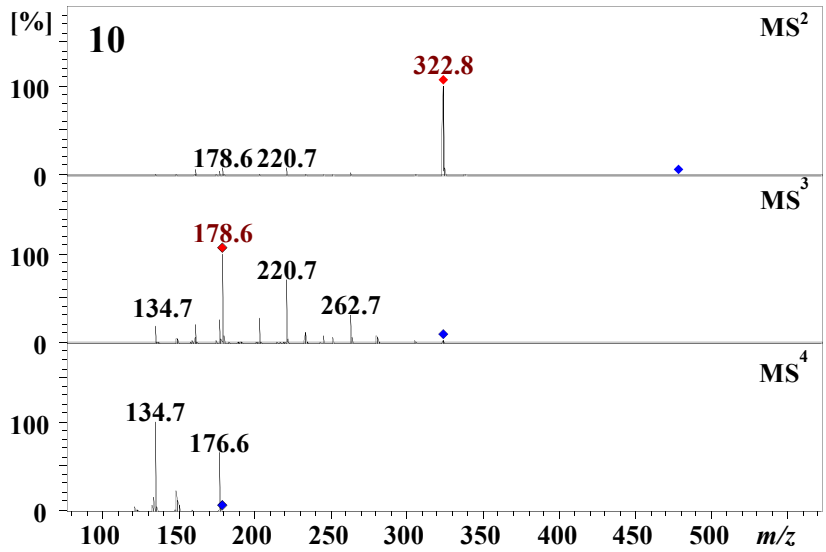


Figure S8. MS^4 spectra of 4-*O*-(6'-*O*-glucosyl feruloyl)-4-hydroxybenzyl alcohol **9** at *m/z* 461 in negative ion mode.


[%]
10
MS2
322.8
178.6 220.7
MS3
178.6
220.7
134.7
262.7
MS4
134.7
176.6
100
0
100 150 200 250 300 350 400 450 500 m/z

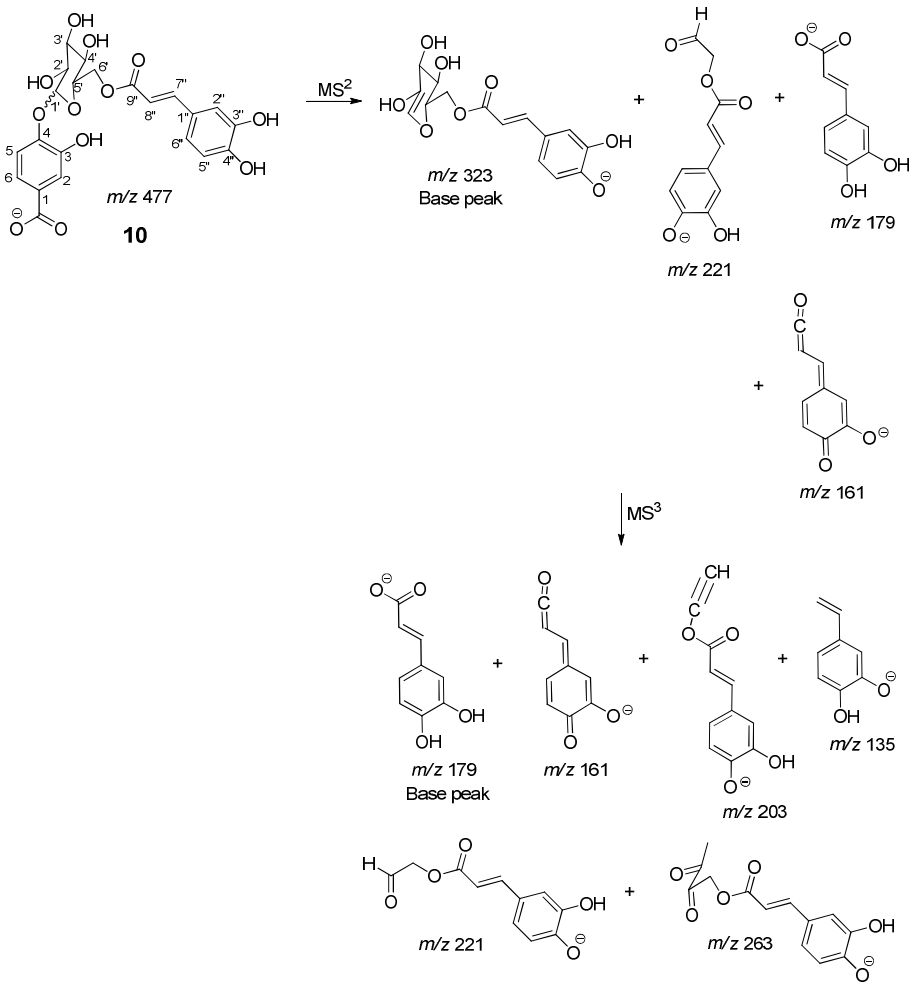

m/z 477
10
MS2
m/z 323
Base peak
m/z 221
m/z 179
m/z 161
MS3
m/z 179
Base peak
m/z 161
m/z 203
m/z 135
m/z 221
m/z 263

Figure S9. MS^4 spectra of 4-*O*-(6'-*O*-glucosyl caffeoyl)-3,4-dihydroxybenzoic acid **10** at *m/z* 477 in negative ion mode.

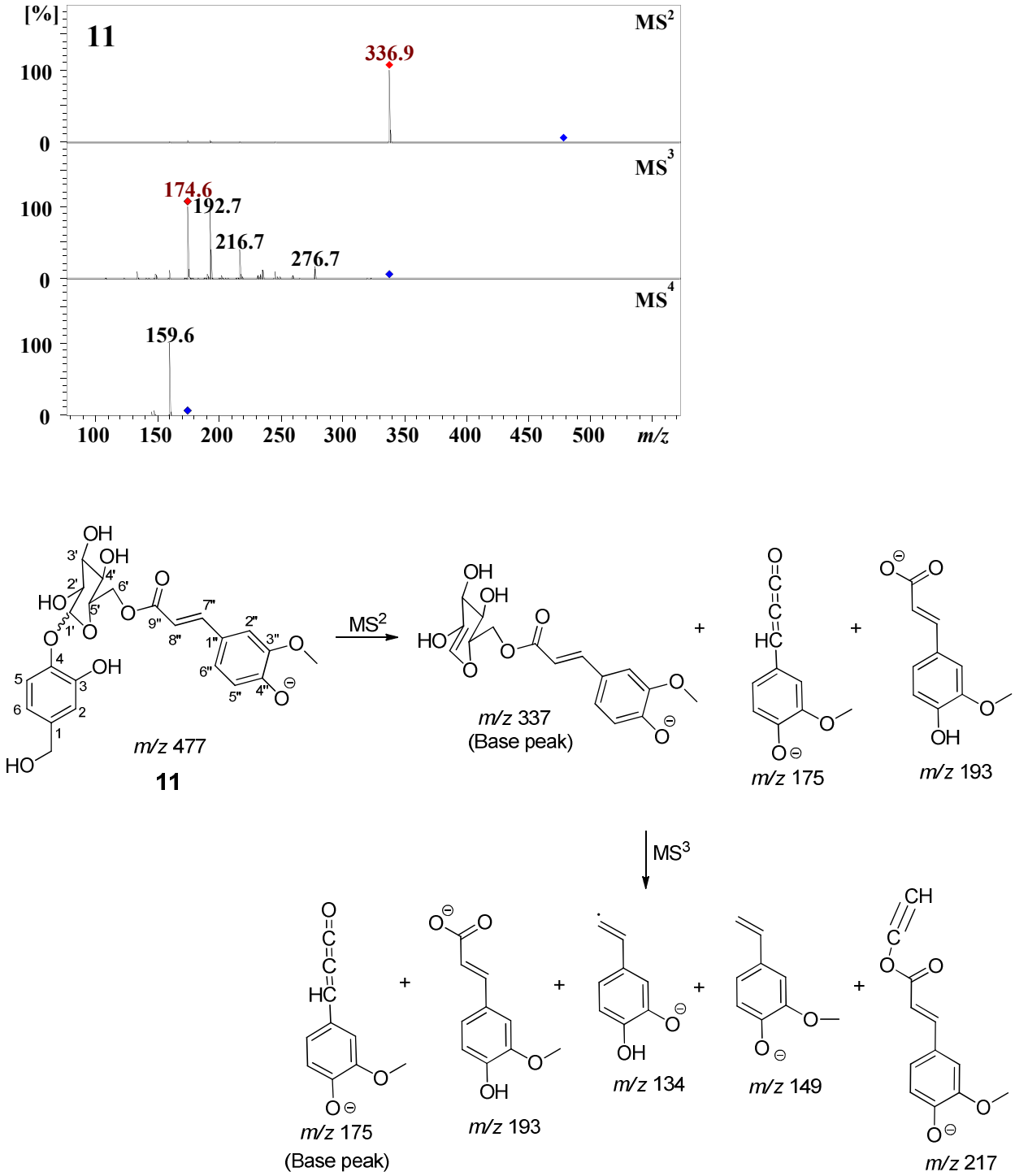
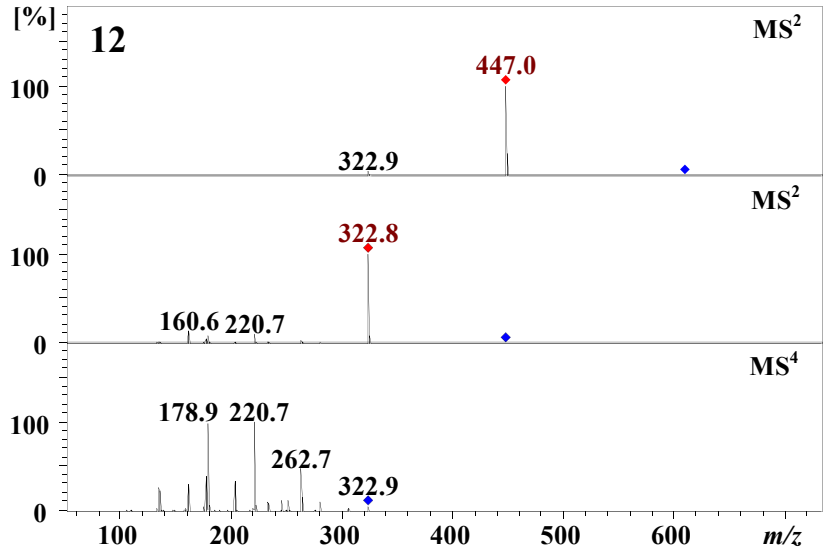


Figure S10. MS^4 spectra of 4-*O*-(6'-*O*-glucosyl feruloyl)-3,4-dihydroxybenzyl alcohol **11** at *m/z* 477 in negative ion mode.


[%]
12
MS2
447.0
322.9
MS2
322.8
160.6
220.7
MS4
178.9
220.7
262.7
322.9
100
0
100
200
300
400
500
600
m/z

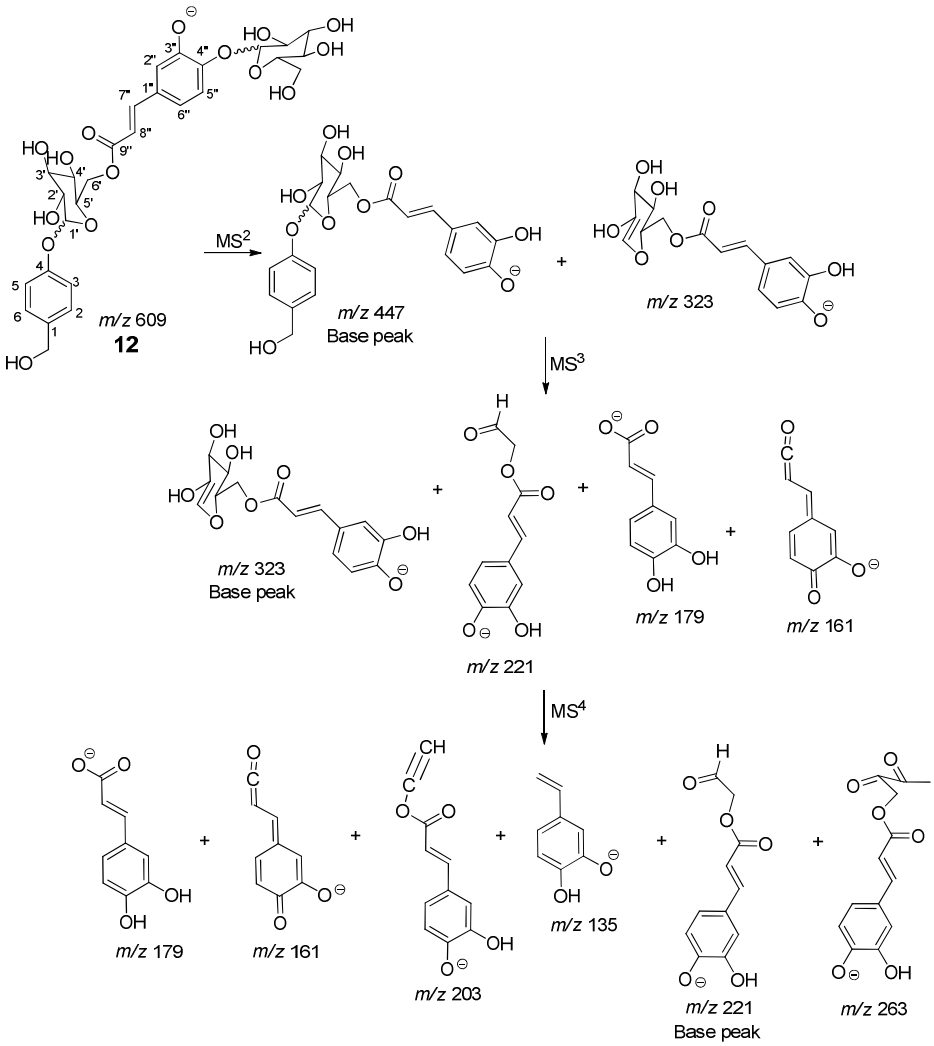
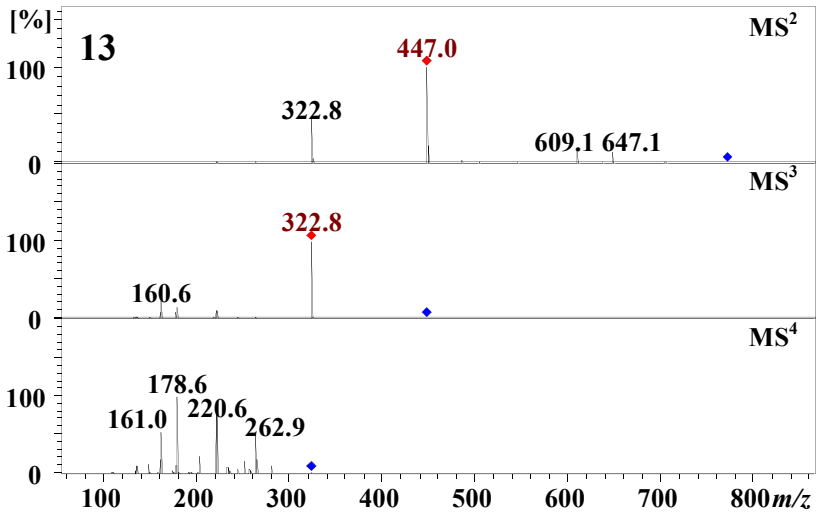

m/z 609
12
MS2
m/z 447
Base peak
m/z 323
MS3
m/z 323
Base peak
m/z 221
m/z 179
m/z 161
MS4
m/z 179
m/z 161
m/z 203
m/z 135
m/z 221
Base peak
m/z 263

Figure S11. MS^4 spectra of 4-*O*-(6'-*O*-glucosyl caffeoyl-glucosyl)-4-hydroxybenzyl alcohol **12** at *m/z* 609 in negative ion mode.


[%]
13
MS2
447.0
322.8
609.1
647.1
MS3
322.8
160.6
MS4
178.6
161.0
220.6
262.9
100
0
100
0
100
0
100
200
300
400
500
600
700
800
m/z

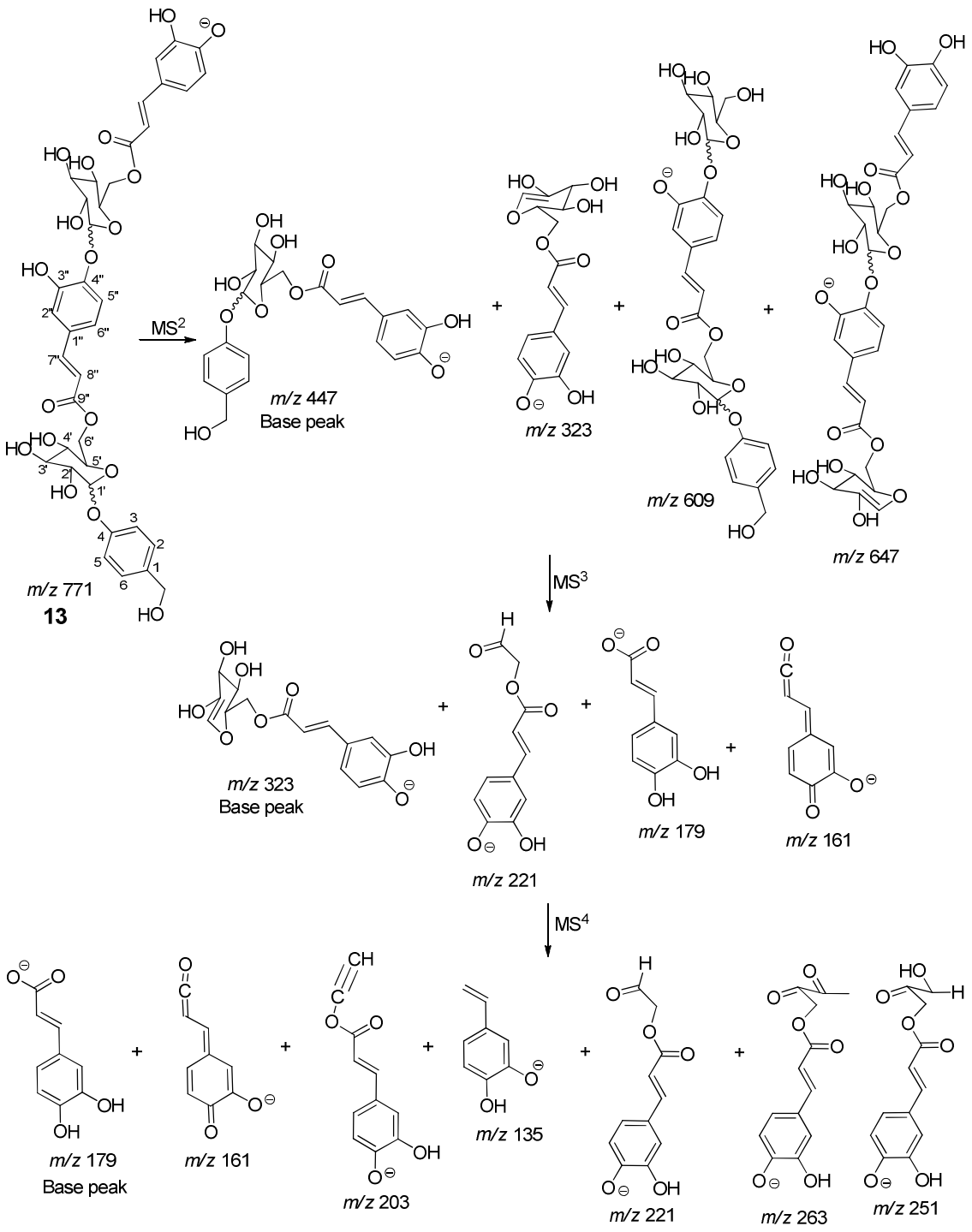
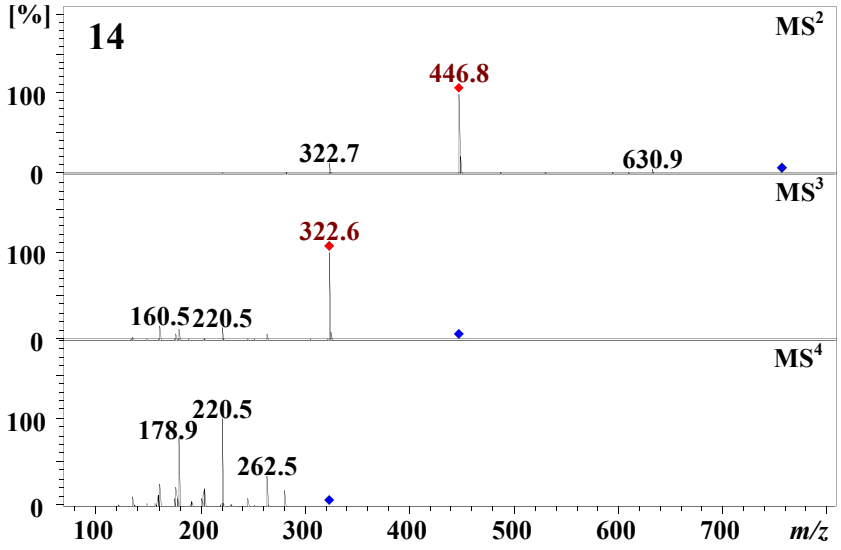


Figure S12. A fragmentation pathway and MS^4 spectra of 4-*O*-(6'-*O*-glucosyl caffeoyl-glucosyl-caffeoyl)-4-hydroxybenzyl alcohol **13** at *m/z* 771 in negative ion mode.


14
[%]
MS2
446.8
322.7
630.9
MS3
322.6
160.5
220.5
MS4
220.5
178.9
262.5
100
0
100
200
300
400
500
600
700
m/z

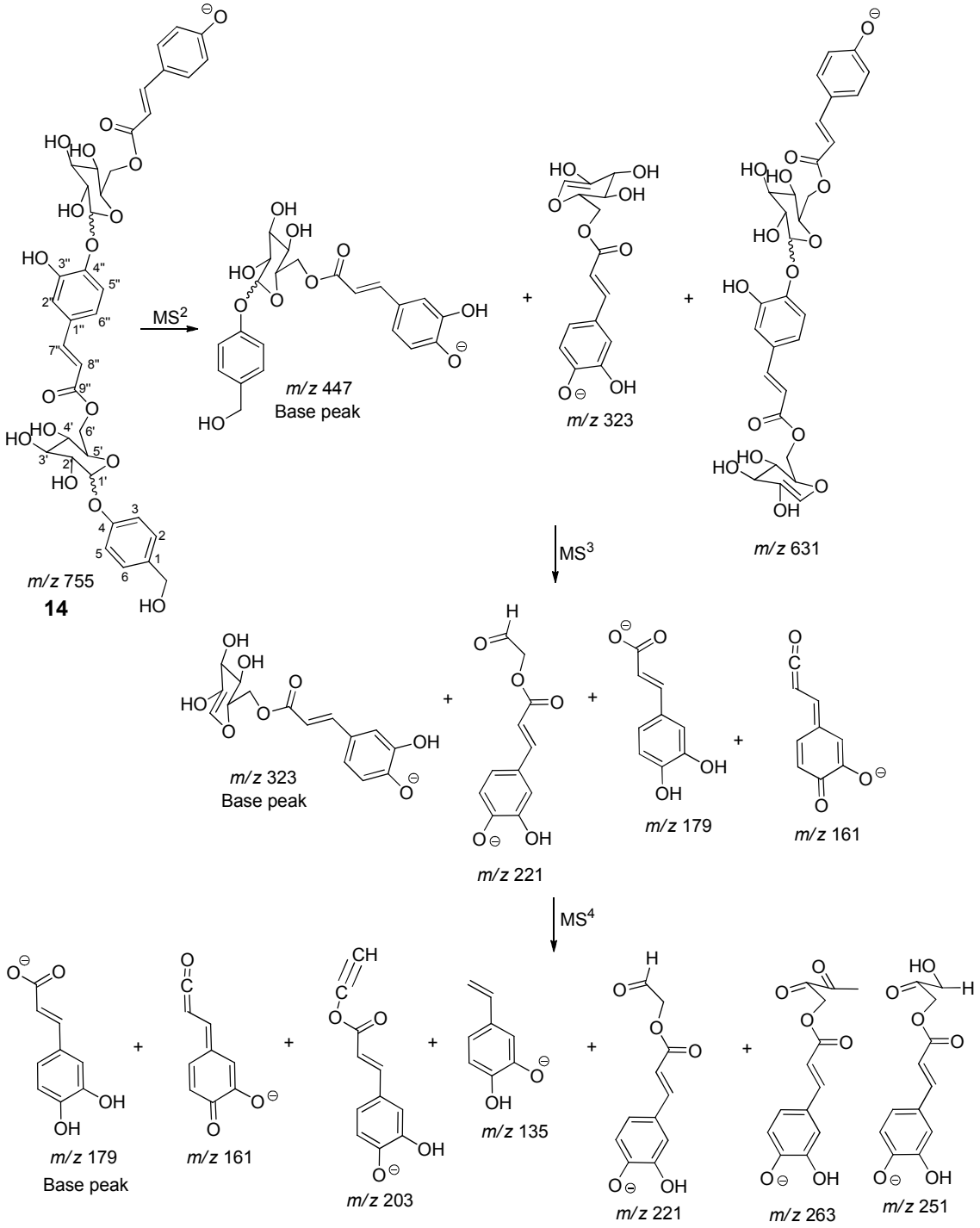
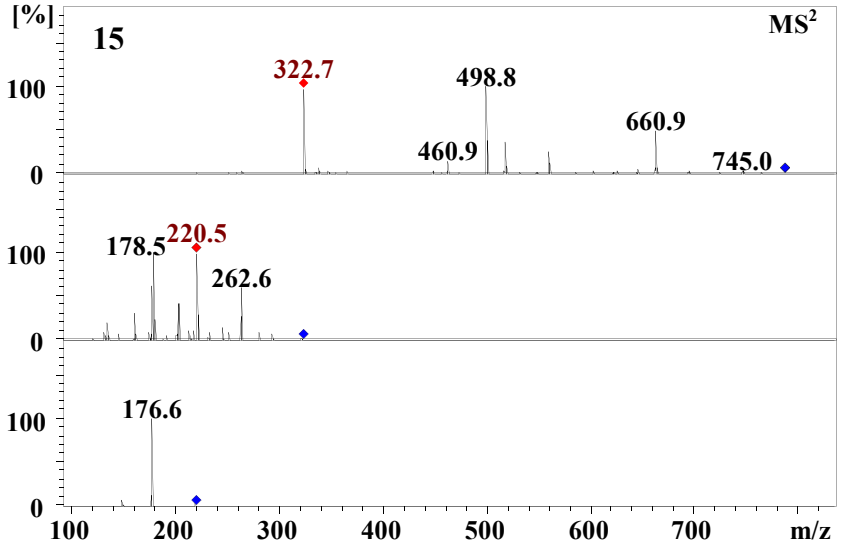


Figure S13. A fragmentation pathway and MS^4 spectra of 4-*O*-(6'-*O*-glucosyl caffeoyl-glucosyl-*p*-coumaroyl)-4-hydroxybenzyl alcohol **14** at *m/z* 755 in negative ion mode.


[%]
15
MS2
322.7
498.8
660.9
460.9
745.0
178.5
220.5
262.6
176.6
100
0
100
0
100
0
100
200
300
400
500
600
700
m/z

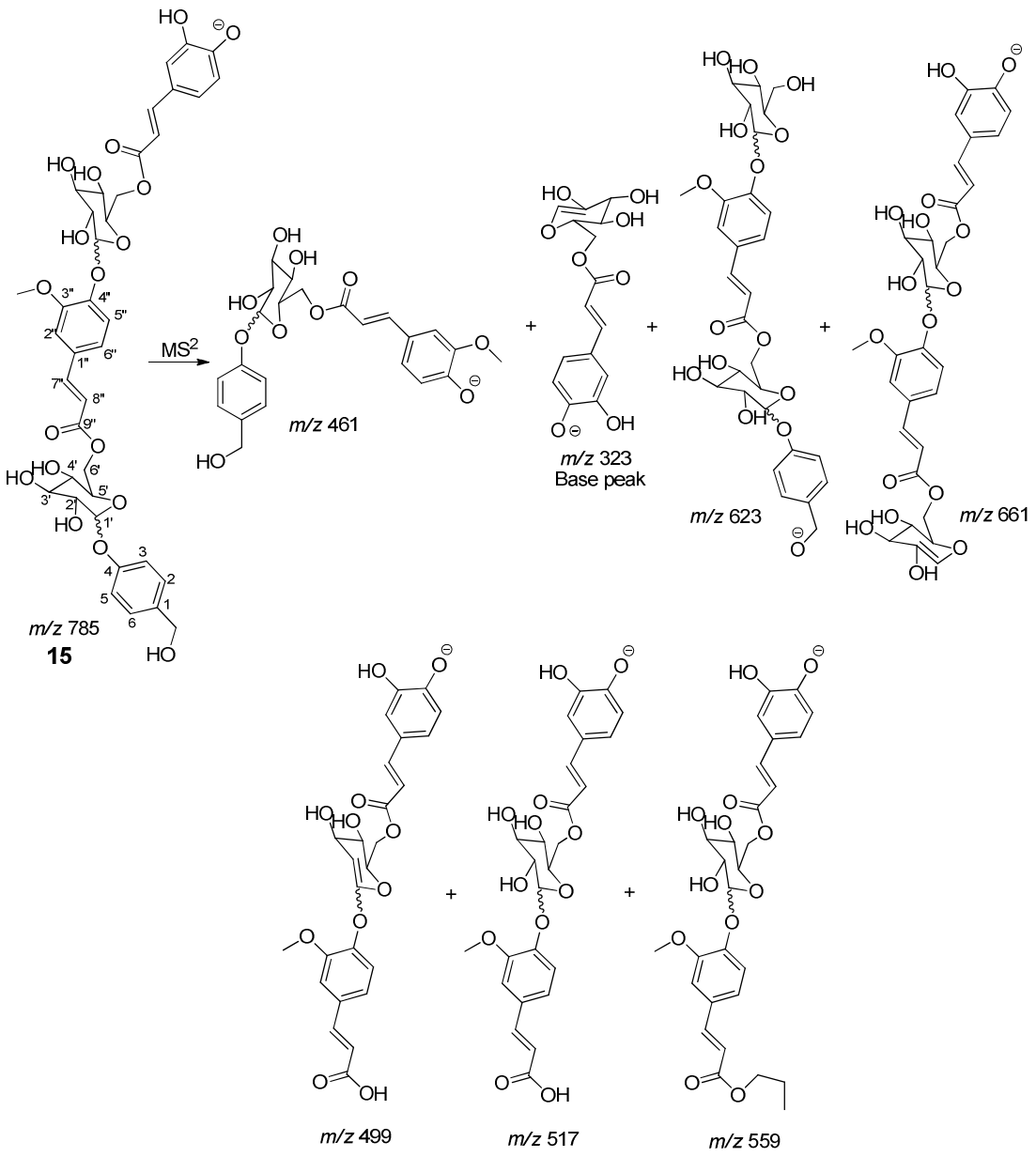
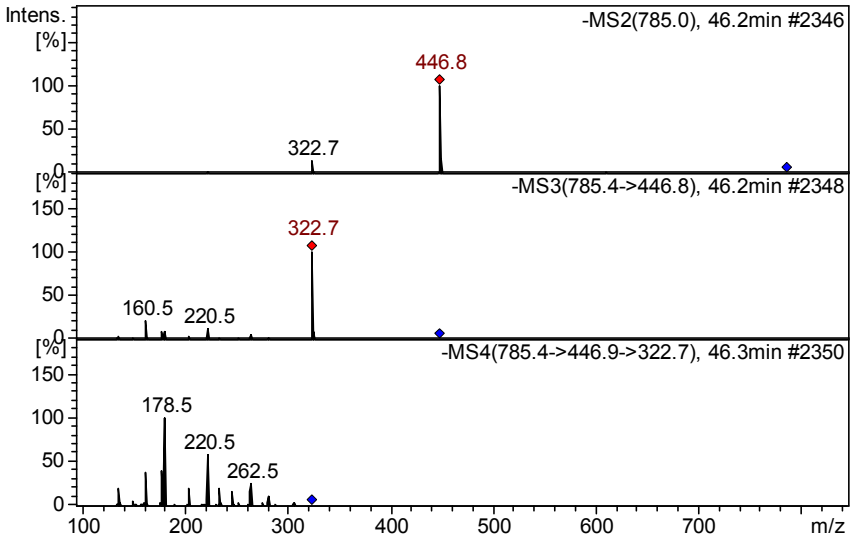


Figure S14. A fragmentation pathway and MS^4 spectra of 4-*O*-(6'-*O*-glucosyl feruloyl-glucosyl-caffeoyl)-4-hydroxybenzyl alcohol **15** at *m/z* 785 in negative ion mode.


Intens.
[%]
-MS2(785.0), 46.2min #2346
446.8
322.7
-MS3(785.4->446.8), 46.2min #2348
322.7
160.5
220.5
-MS4(785.4->446.9->322.7), 46.3min #2350
178.5
220.5
262.5
m/z

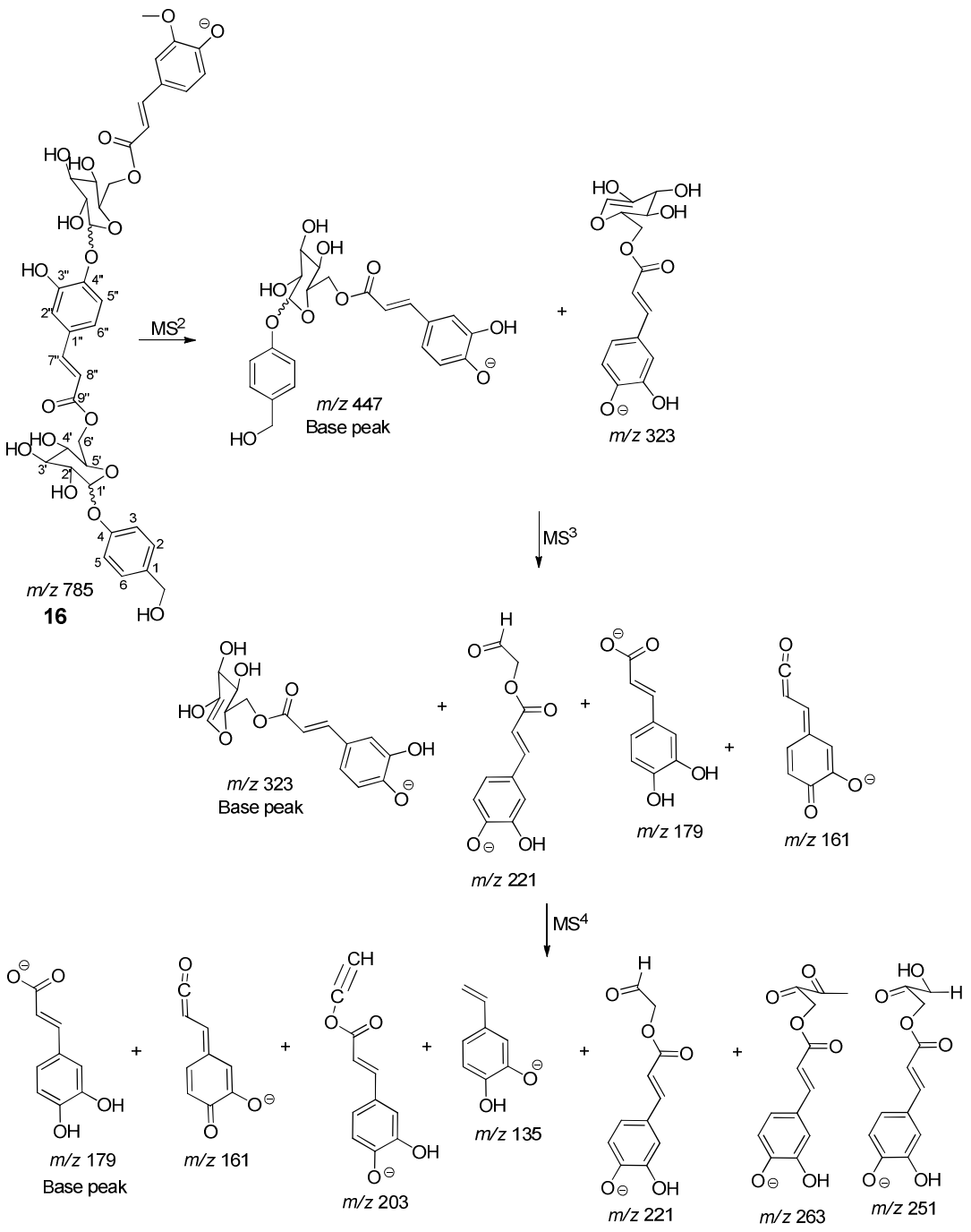
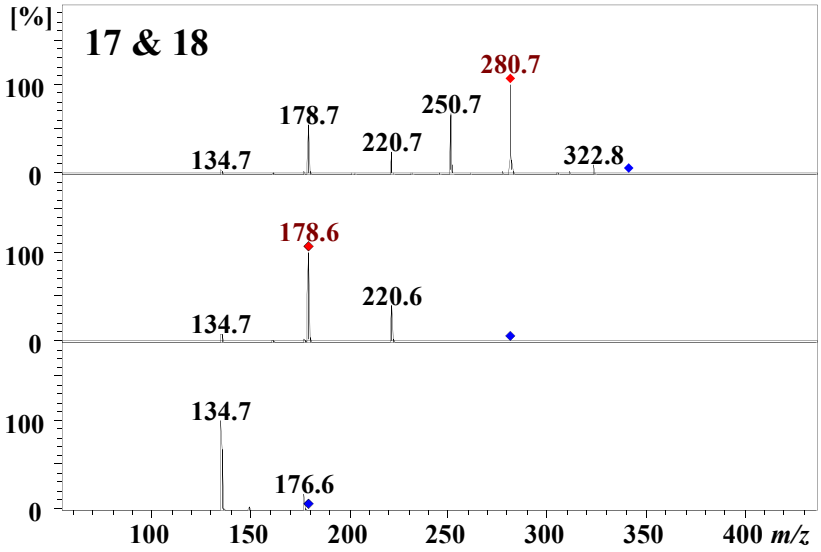
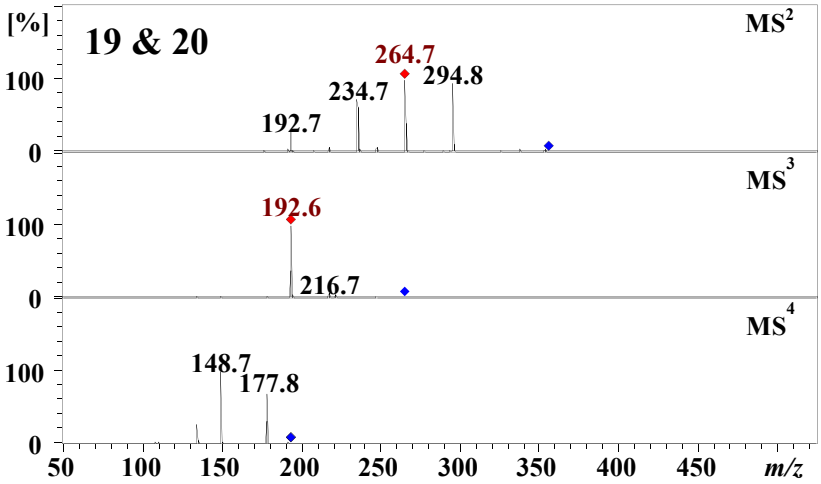


Figure S15. A fragmentation pathway and MS^4 spectra of 4-*O*-(6'-*O*-glucosyl caffeoyl-glucosyl-feruloyl)-4-hydroxybenzyl alcohol **16** at *m/z* 785 in negative ion mode.


[%]
17 & 18
280.7
250.7
178.7
220.7
134.7
322.8
178.6
220.6
134.7
134.7
176.6
100
0
100
150
200
250
300
350
400
m/z


[%]
19 & 20
MS2
264.7
294.8
234.7
192.7
MS3
192.6
216.7
MS4
148.7
177.8
100
0
50
100
150
200
250
300
350
400
450
m/z

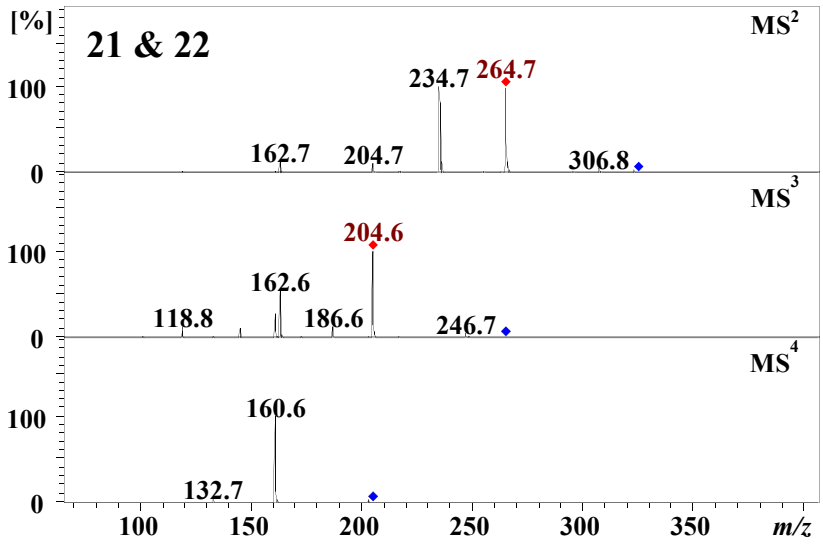


Figure S16. MS^4 spectra of 6-*O*-caffeoyl glucoses (**17** and **18**), 6-*O*-feruloyl glucoses (**19** and **20**) and 6-*O*-*p*-coumaroyl glucoses (**21** and **22**) in negative ion mode.

Table S1. High Resolution MS Data of Bottle Gourd Phenolics in Negative Ion Mode

No.	Compound	Molecular formula	Theoretical *m/z* (M-H)	Experimental *m/z* (M-H)	Error (ppm)
1	4-*O*-Glucosyl-3,4-dihydroxybenzyl alcohol	$C_{13}H_{18}O_8$	301.0929	301.0929	-4.3
2	4-*O*-Glucosyl-4-hydroxybenzoic acid	$C_{13}H_{16}O_8$	299.0772	299.0770	0.9
3	4-*O*-Glucosyl-4-hydroxybenzyl alcohol	$C_{13}H_{18}O_7$	285.0980	285.0976	1.3
4	4-*O*-(6'-*O*-Glucosyl caffeoyl)-4-hydroxybenzyl alcohol	$C_{22}H_{24}O_{10}$	447.1297	447.1311	-3.2
5	4-*O*-(6'-*O*-Glucosyl caffeoyl)-3,4-dihydroxybenzyl alcohol	$C_{22}H_{23}O_{11}$	463.1246	463.1255	-2.0
6	4-*O*-(6'-*O*-Glucosyl *p*-coumaroyl)-4-hydroxybenzyl alcohol	$C_{22}H_{24}O_9$	431.1348	431.1366	-4.2
7	4-*O*-(6'-*O*-Glucosyl 4"-hydroxybenzoyl)-4-hydroxybenzyl alcohol	$C_{20}H_{22}O_9$	405.1191	405.1198	-1.8
8	4-*O*-(6'-*O*-Glucosyl caffeoyl)-4-hydroxybenzoic acid	$C_{22}H_{22}O_{11}$	461.1089	461.1113	-5.0
9	4-*O*-(6'-*O*-Glucosyl feruloyl)-4-hydroxybenzyl alcohol	$C_{23}H_{26}O_{10}$	461.1453	461.1474	-4.4
10	4-*O*-(6'-*O*-Glucosyl caffeoyl)-3,4-dihydroxybenzoic acid	$C_{22}H_{22}O_{12}$	477.1038	477.1040	-0.2
11	4-*O*-(6'-*O*-Glucosyl feruloyl)-3,4-dihydroxybenzyl alcohol	$C_{23}H_{26}O_{11}$	477.1402	477.1422	-4.1
12	4-*O*-(6'-*O*-Glucosyl caffeoyl-glucosyl)-4-hydroxybenzyl alcohol	$C_{28}H_{34}O_{15}$	609.1825	609.1845	-3.3
13	4-*O*-(6'-*O*-Glucosyl caffeoyl-glucosyl-caffeoyl)-4-hydroxybenzyl alcohol	$C_{37}H_{40}O_{18}$	771.2142	771.2145	-0.5

14	4-*O*-(6'-*O*-Glucosyl caffeoyl-glucosyl-*p*-coumaroyl)-4-hydroxybenzyl alcohol	$C_{37}H_{40}O_{17}$	755.2193	755.2197	0.5
15	4-*O*-(6'-*O*-Glucosyl feruloyl-glucosyl-caffeoyl)-4-hydroxybenzyl alcohol	$C_{38}H_{42}O_{18}$	785.2298	785.2291	-0.9
16	4-*O*-(6'-*O*-Glucosyl caffeoyl-glucosyl-feruloyl)-4-hydroxybenzyl alcohol	$C_{38}H_{42}O_{18}$	785.2298	785.2294	-0.5
17	6-*O*-Caffeoyl-α-glucose	$C_{15}H_{18}O_9$	341.0878	341.0881	-0.9
18	6-*O*-Caffeoyl-β-glucose	$C_{15}H_{18}O_9$	341.0878	341.0888	-2.9
19	6-*O*-Feruloyl-α-glucose	$C_{16}H_{14}O_6$	355.1035	355.1038	-1.1
20	6-*O*-Feruloyl-β-glucose	$C_{22}H_{28}O_{14}$	355.1035	355.1030	1.3
21	6-*O*-*p*-Coumaroyl-α-glucose	$C_{15}H_{18}O_8$	325.0929	325.0922	2.2
22	6-*O*-*p*-Coumaroyl-β-glucose	$C_{15}H_{18}O_8$	325.0929	325.0933	-1.3