Supplementary Materials: Screening for Triterpenoid Saponins in Plants Using Hyphenated Analytical Platforms

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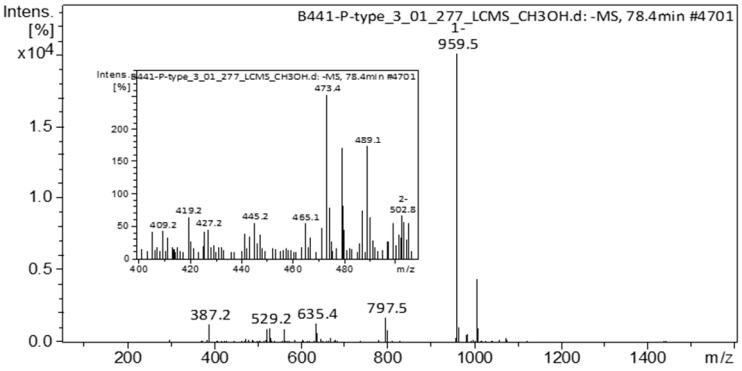
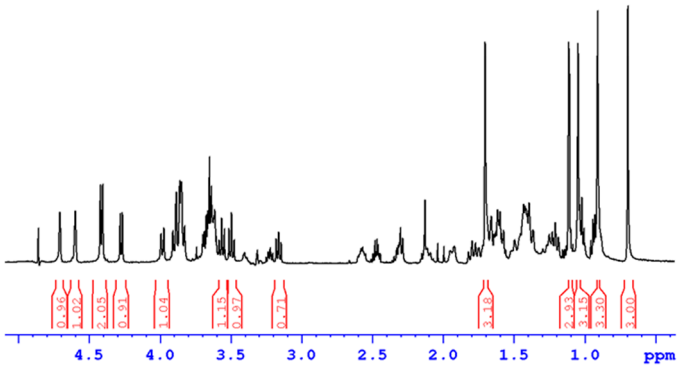
A

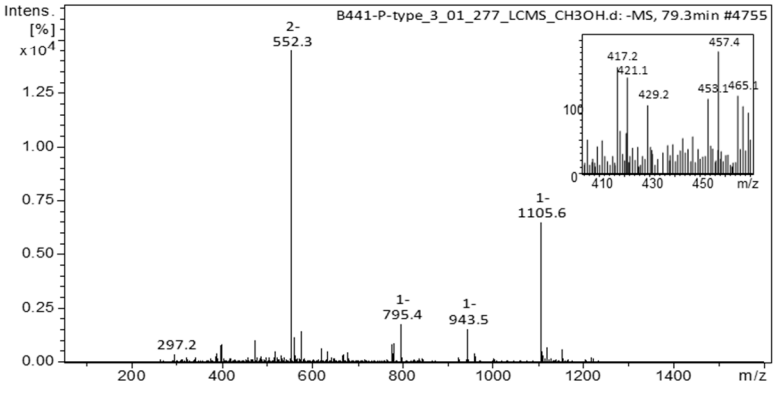
№	RT (min)	Aglycone (Da)	Sugar Moieties	Fragmentation pattern in mass spectra	Anomeric protons (ppm)
P-type Peak 17	78.4	474	3 × Hexose	$[M_{959} - H - 162 - 162 - 162]^-$ = 473	4.27 (d, J = 7.8) 4.41 (d, J = 7.8) 4.41 (d, J = 7.8)

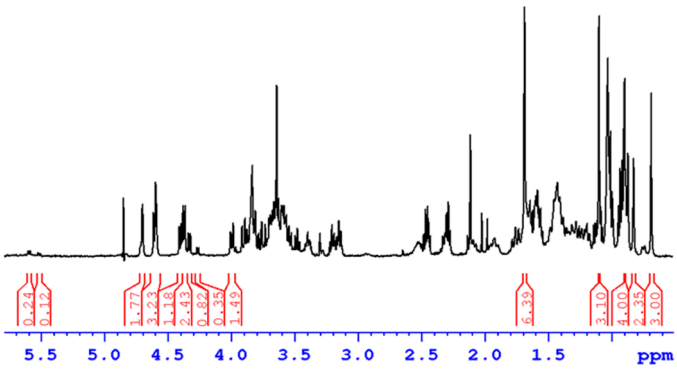




B

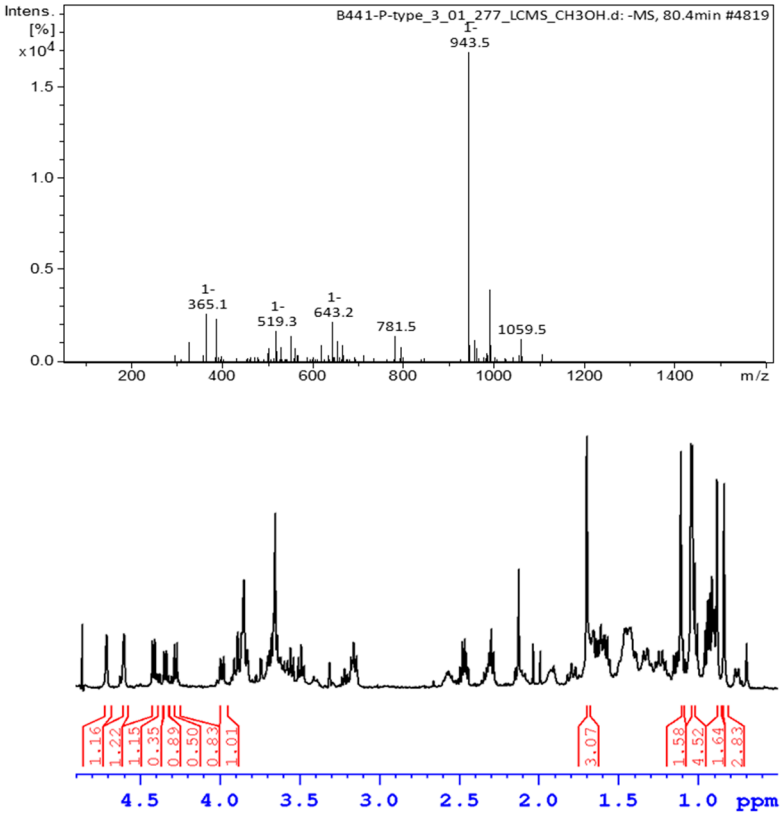
№	RT (min)	Aglycone (Da)	Sugar Moieties	Fragmentation pattern in mass spectra	Anomeric protons (ppm)
P-type Peak 18	79.1	458	4 × Hexose	$[M_{1105} - H - 162 - 162 - 162 - 162]^-$ = 457	4.27 (d, J = 7.8) 4.34 (d, J = 7.8)
P-type Peak 20	79.8	474	1 × Methylpentose 3 × Hexose	$[M_{1105} - H - 146 - 162 - 162 - 162]^-$ = 473	4.382 (d, J = 7.8) 4.386 (d, J = 7.8) 4.41(d, J = 7.8) 4.61 (d, J = 7.8) 5.53 (d, J = 8.2) 5.60 (d, J = 8.2)





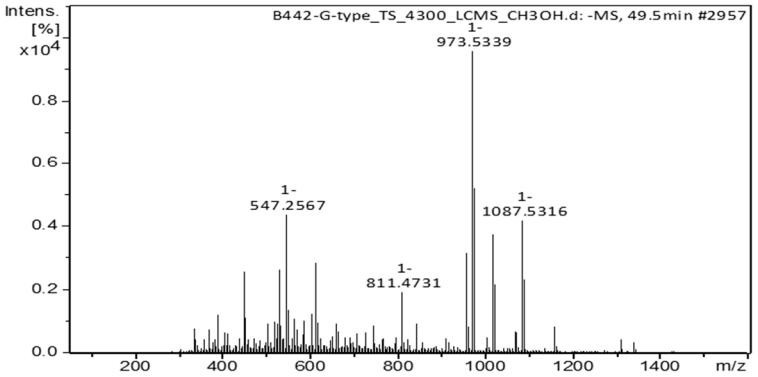
C

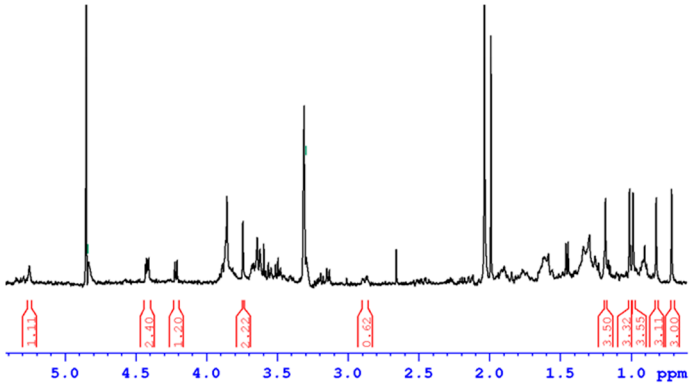
№	RT (min)	Aglycone (Da)	Sugar Moieties	Fragmentation pattern in mass spectra	Anomeric protons (ppm)
P-type Peak 21	80.4	458	4 × Hexose	$[M_{943} - H - 162 - 162 - 162]^- = 457$	4.27 (d, J = 7.8) 4.34 (d, J = 7.8) 4.41(d, J = 7.8)



D

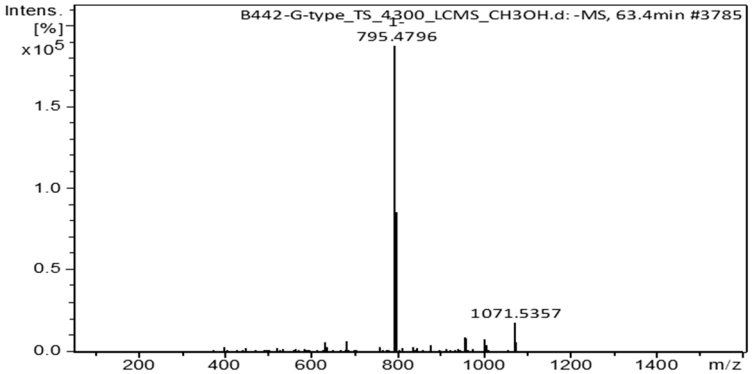
№	RT (min)	Aglycone (Da)	Sugar Moieties	Fragmentation pattern in mass spectra	Anomeric protons (ppm)
G-type Peak 3	49.5	504	1 × Methylpentose 2 × Hexose	$[M_{973} - H - 146 - 162 - 162]^-$ = 503	4.21 (d, J = 7.8) 4.41 (d, J = 7.8) 4.42 (d, J = 7.8) 5.25* (t, J = 3.4)

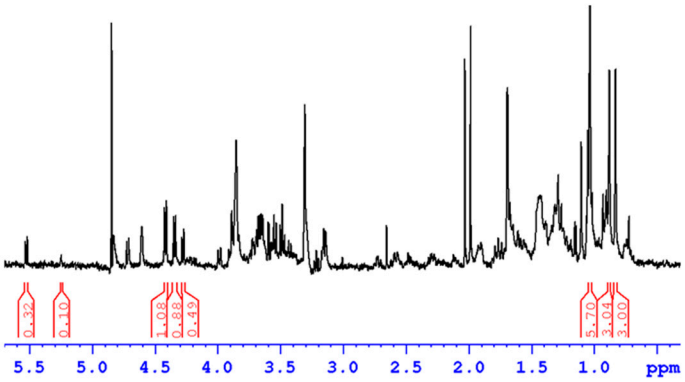




E

№	RT (min)	Aglycone (Da)	Sugar Moieties	Fragmentation pattern in mass spectra	Anomeric protons (ppm)
G-type Peak 11	63.4	472	3 × Hexose	$[M_{957} - H - 162 - 162 - 162]^-$ = 471	4.27 (d, J = 7.8) 4.34 (d, J = 7.8) 4.41 (d, J = 7.8) 5.24* (t, J = 3.4) 5.53 (d, J = 8.0)





F

№	RT (min)	Aglycone (Da)	Sugar Moieties	Fragmentation pattern in mass spectra	Anomeric protons (ppm)
G-type Peak 12	64.0	458	3 × Hexose	$[M_{943} - H - 162 - 162 - 162]^- = 457$	4.27 (d, J = 7.8) 4.34 (d, J = 7.8) 4.41 (d, J = 7.8)

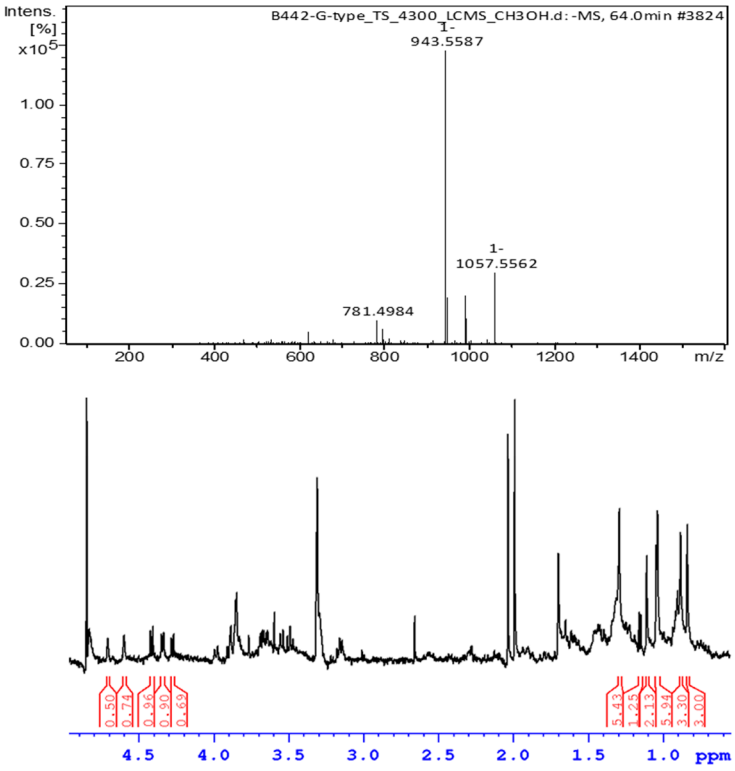
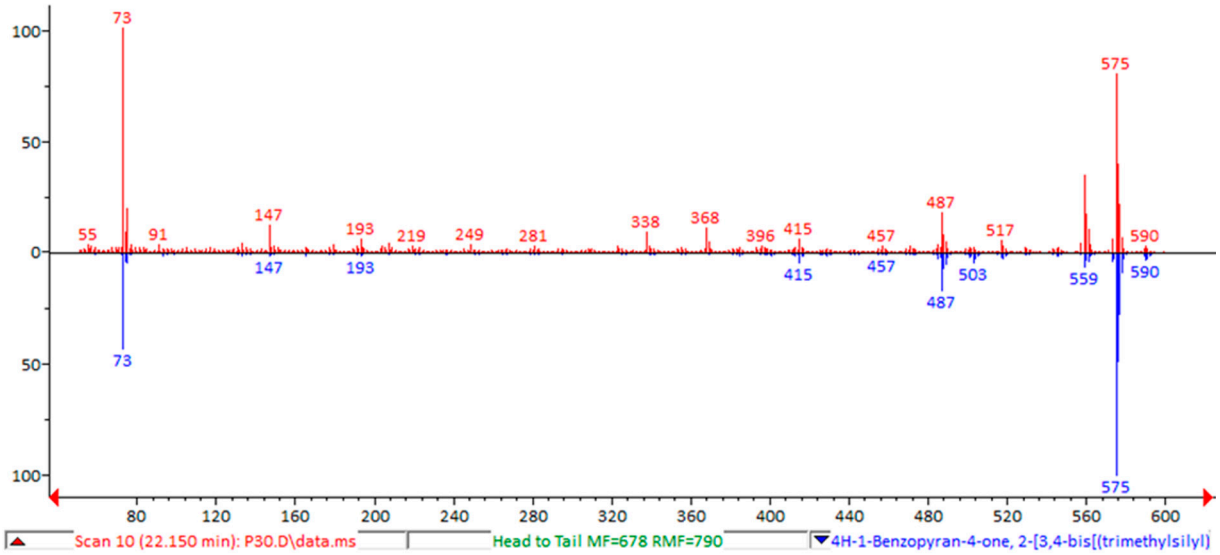
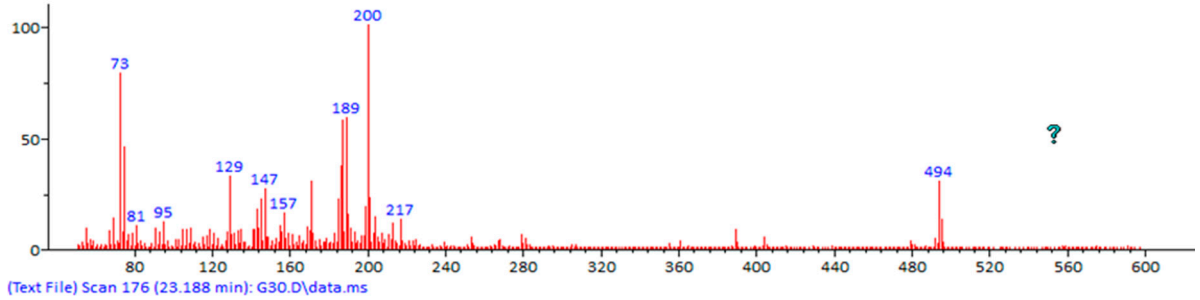


Figure S1. Mass spectral fragmentation pattern and 1D proton NMR spectrum of tentatively identified saponins measured in LC-SPE-NMR/MS experiment performed on saponin enriched extract of the G-type *B. vulgaris*. Tentatively identified P-type saponins correspond to peaks 17 (**A**), 18 and 20 (**B**), and 1 (**C**) in Table 2. Tentatively identified G-type saponins correspond to peaks 3 (**D**), 11 (**E**), and 12 (**F**) in Table 1.

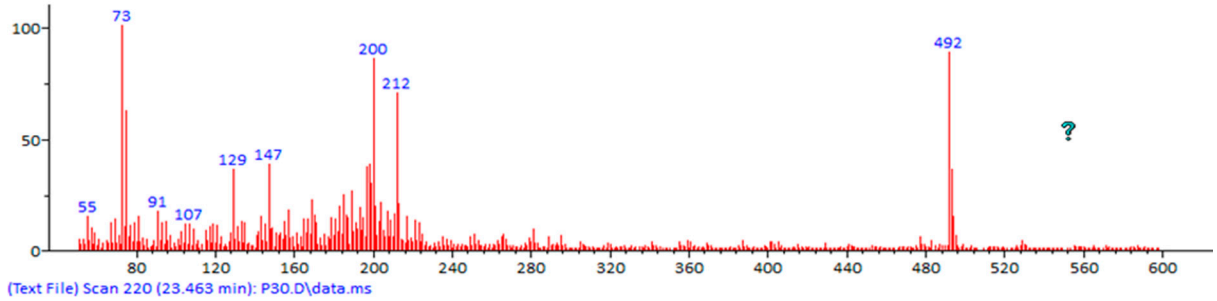
U1: Quercetin-nTMS



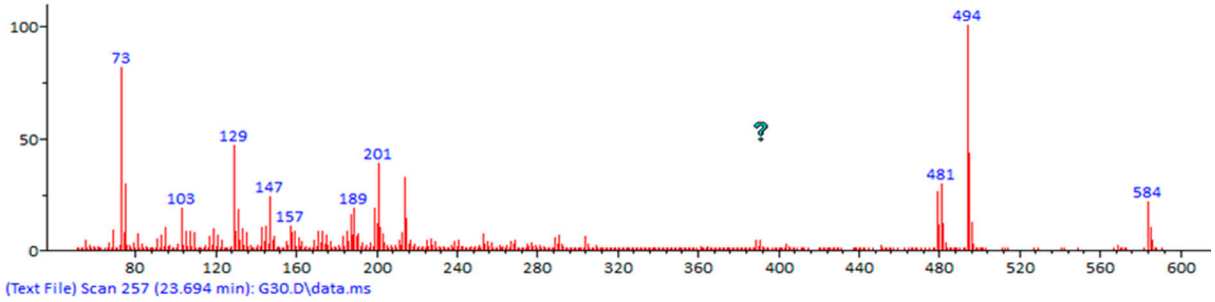
U2



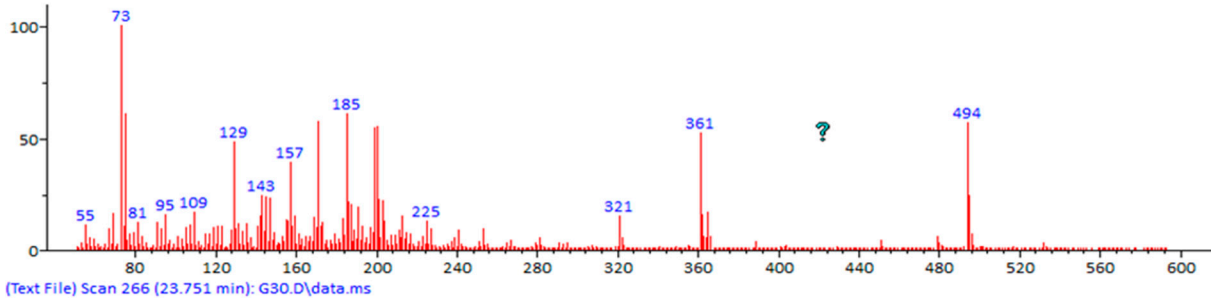
U3



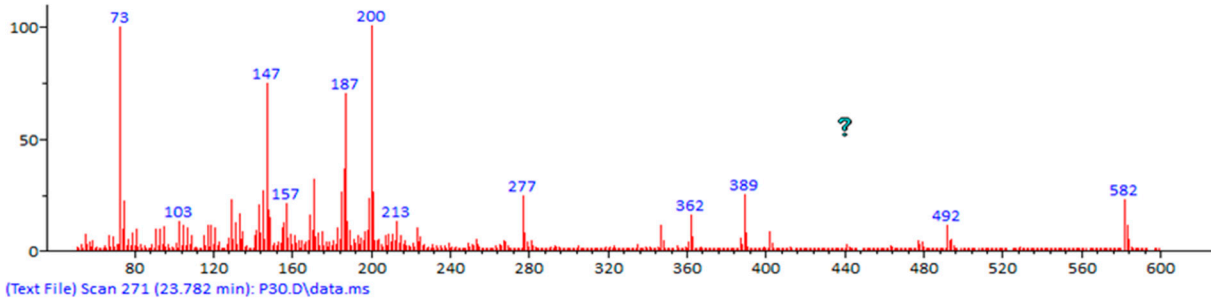
U4


73
129
103
147
157
189
201
494
481
584
(Text File) Scan 257 (23.694 min): G30.D\data.ms

U5


73
55
81
95
109
129
143
157
185
225
321
361
494
(Text File) Scan 266 (23.751 min): G30.D\data.ms

U6


73
103
147
157
187
200
213
277
362
389
492
582
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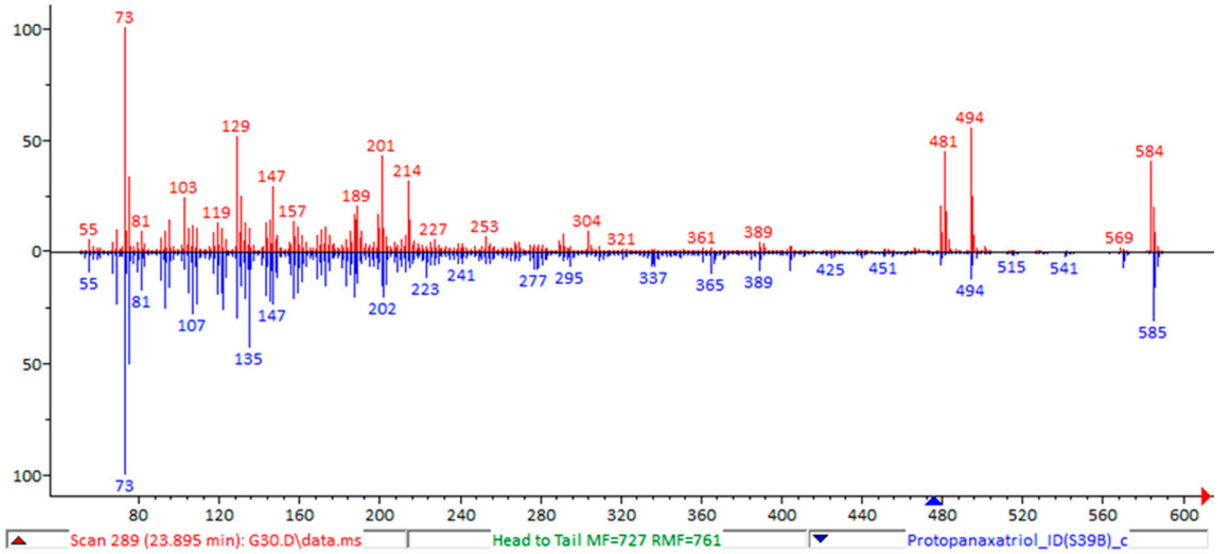
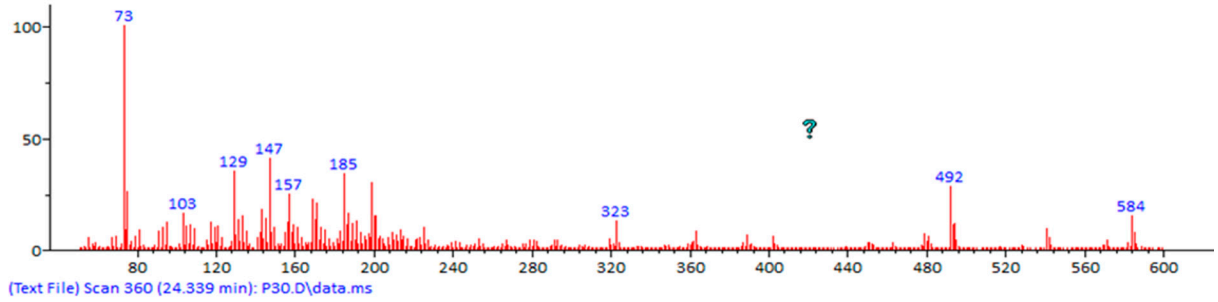
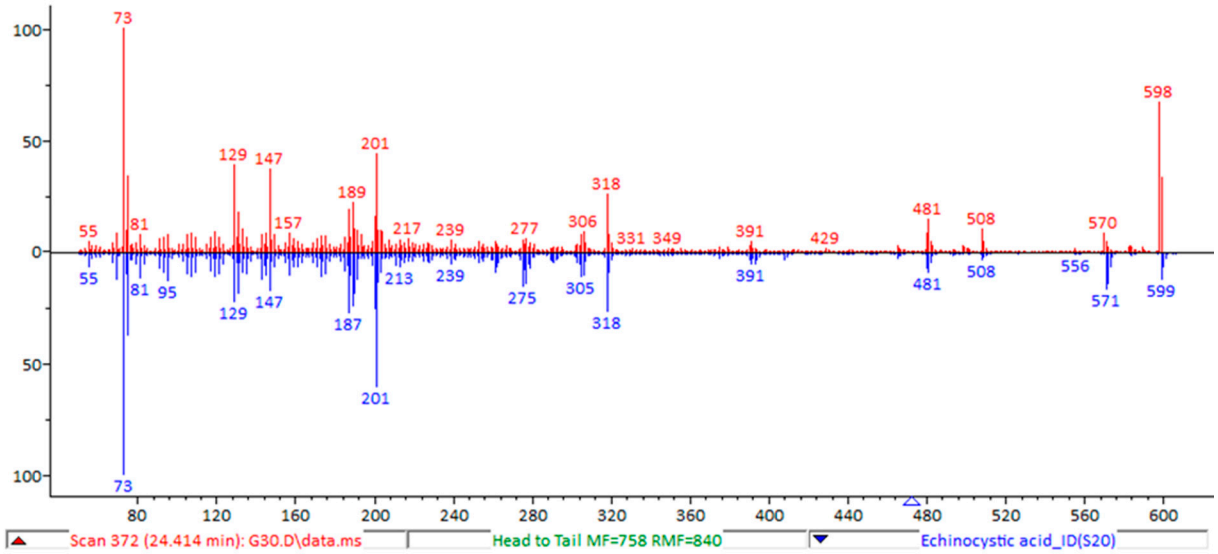
U7: Protopanaxatriol-nTMS



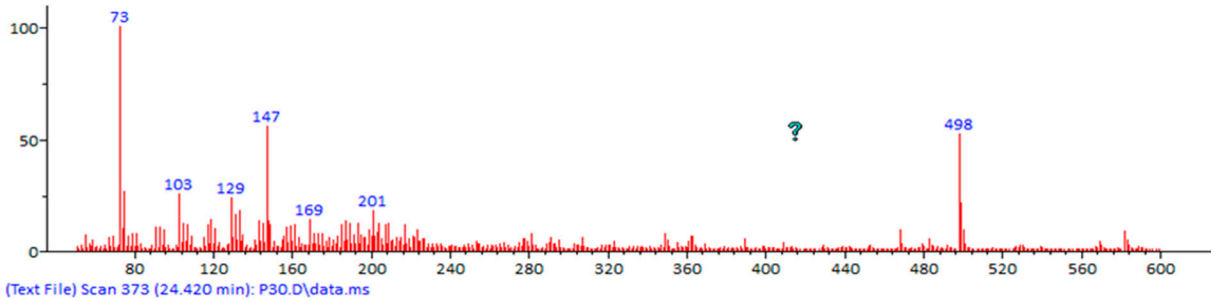
U8



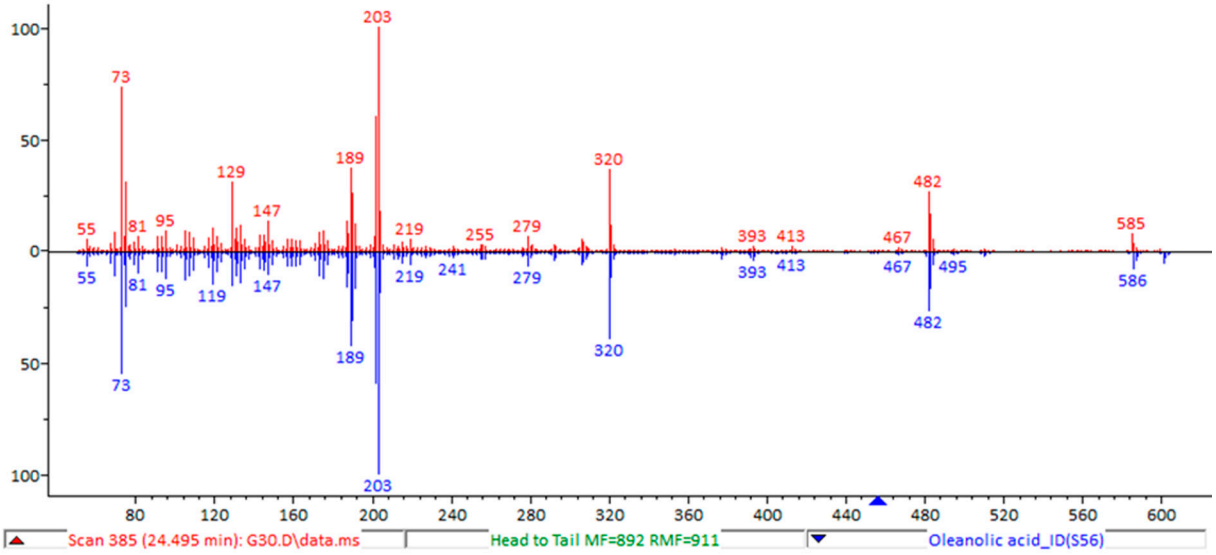
U9: Echinocystic acid-nTMS



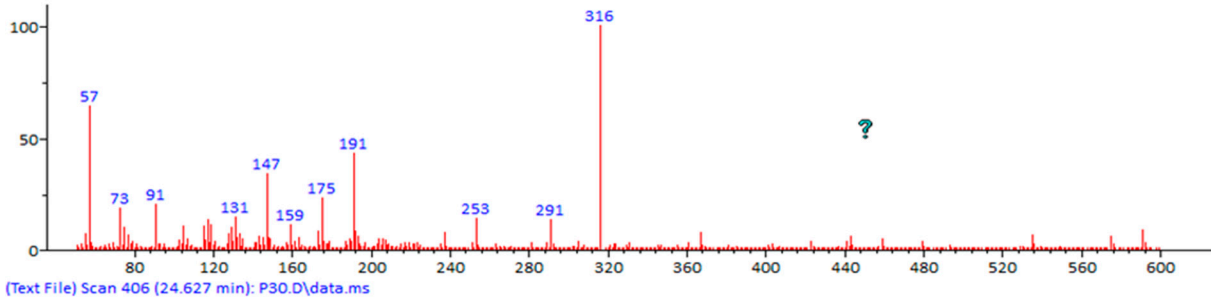
U10



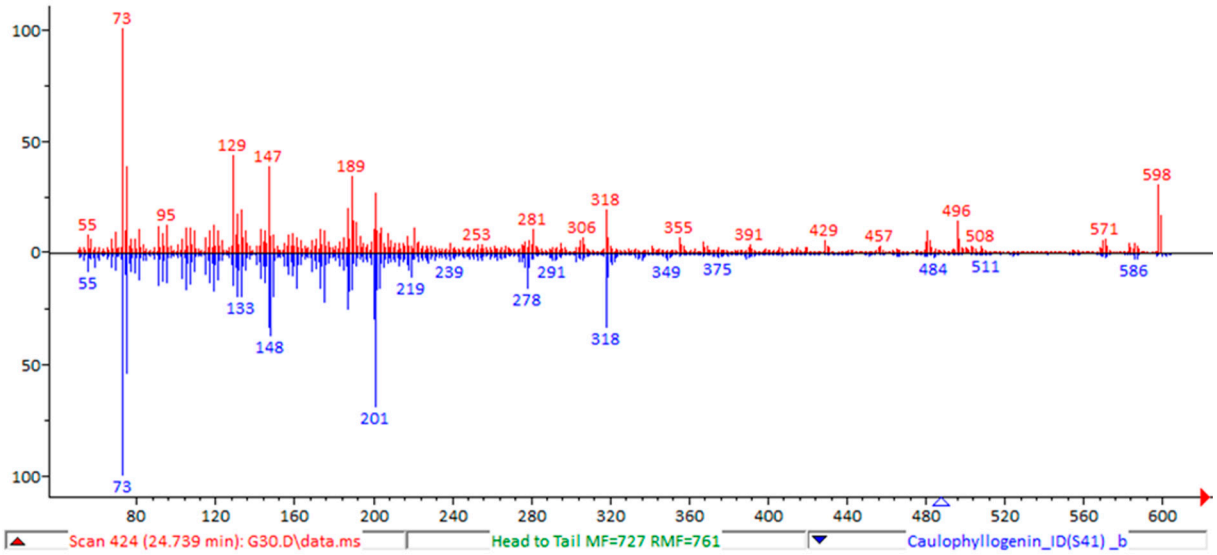
11: Oleanolic acid-2TMS



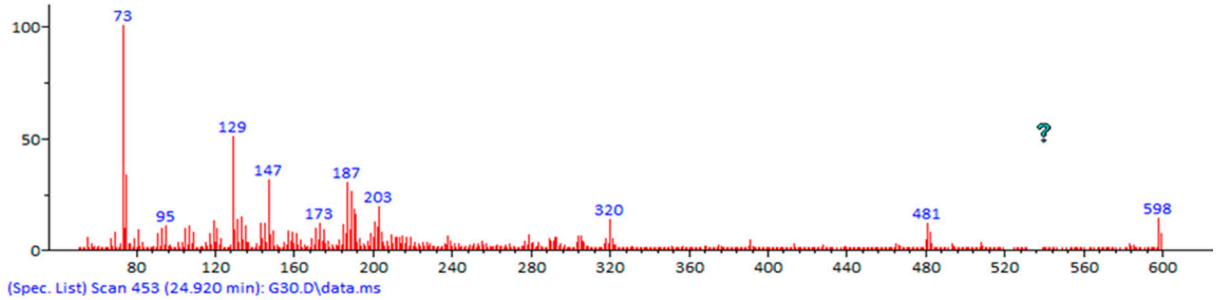
U12



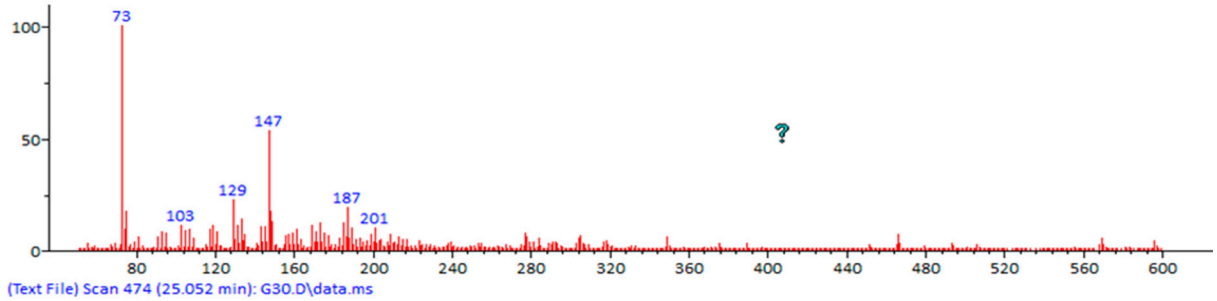
U13: Caulophyllogenin-nTMS



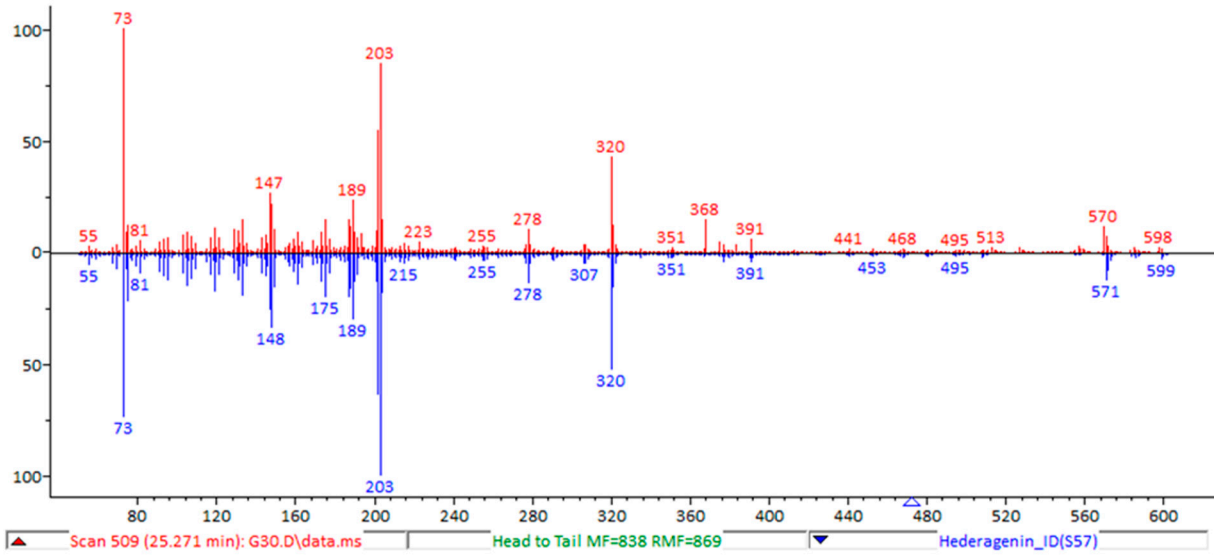
U14



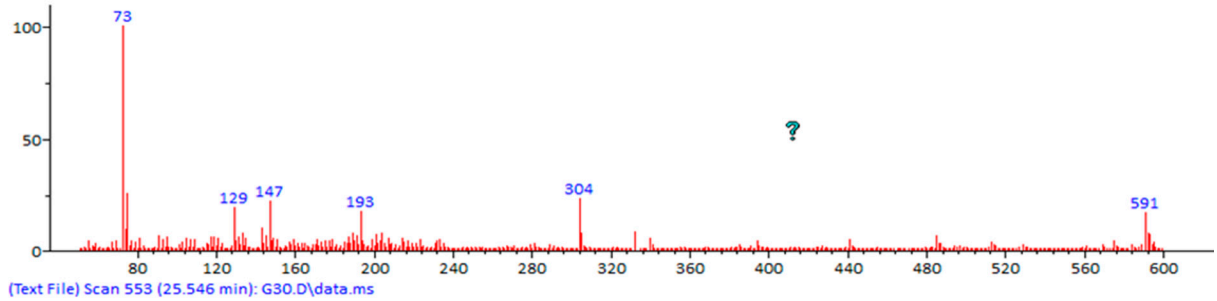
U15



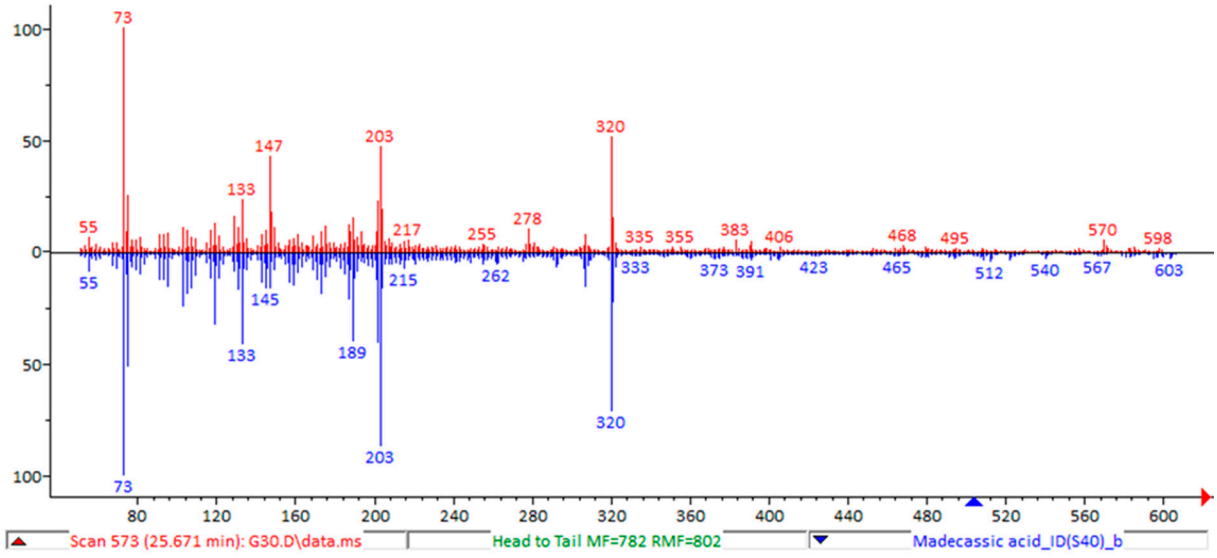
U16: Hederagenin-3TMS



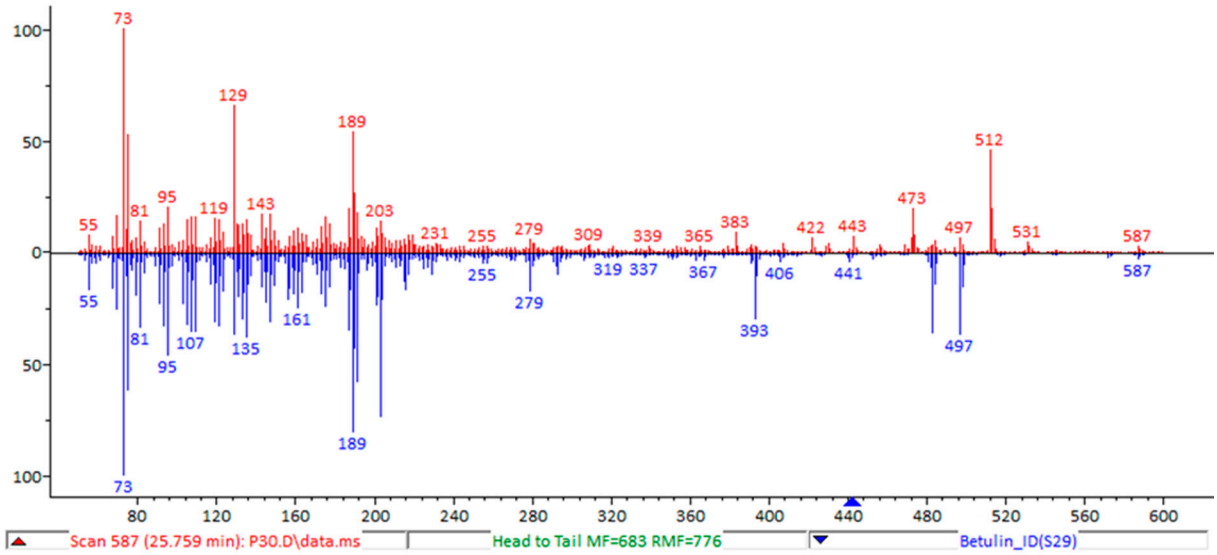
U17



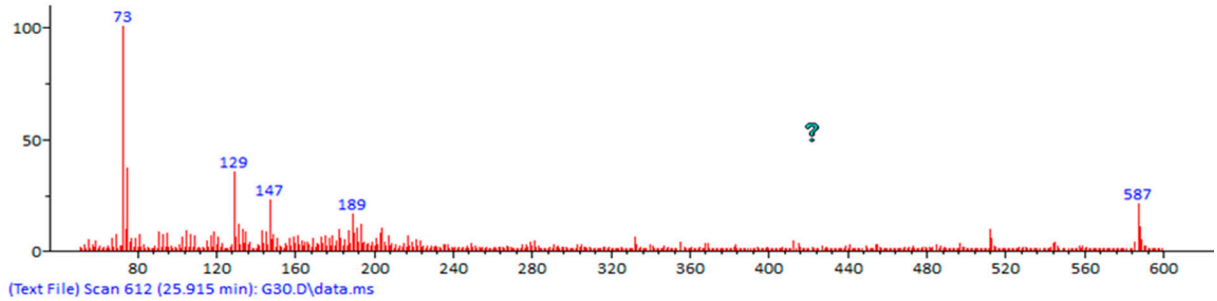
U18: Madecassic acid-nTMS



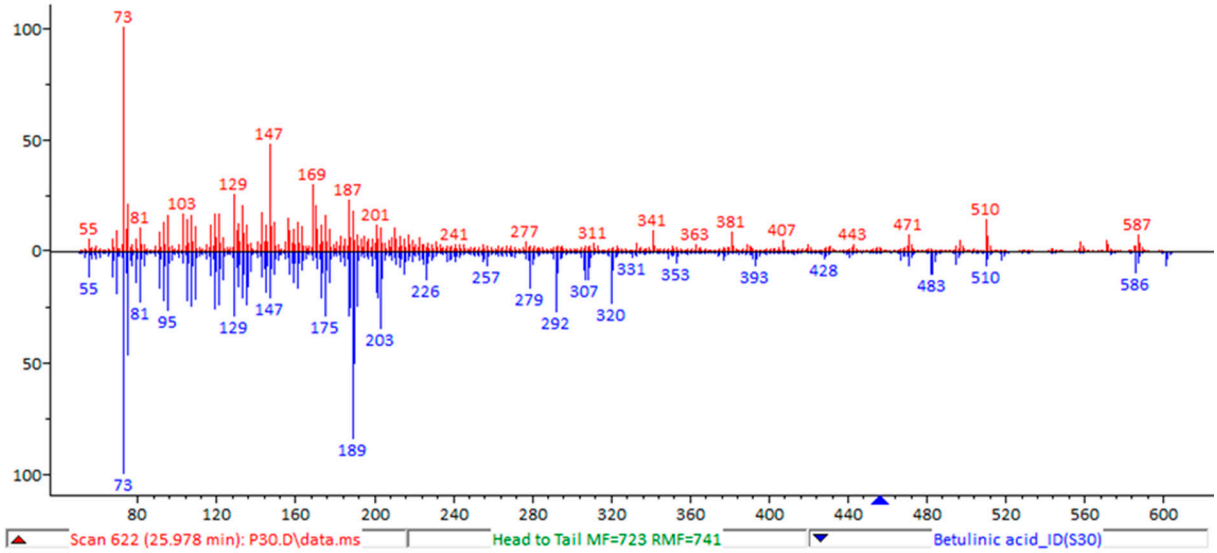
U19: Betulin-nTMS



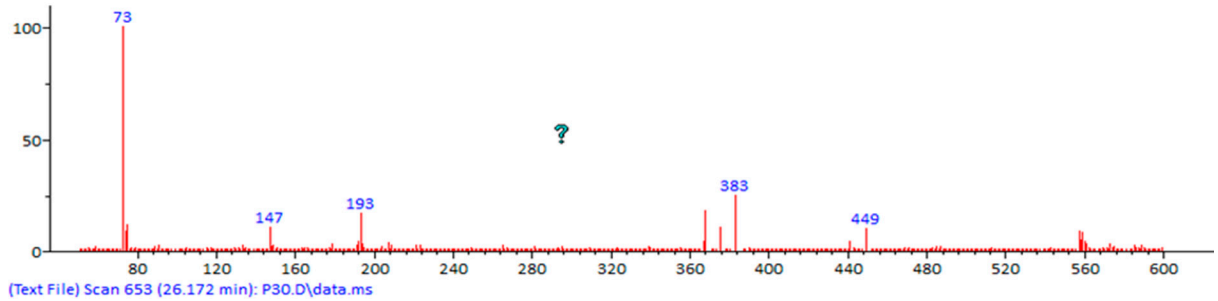
U20



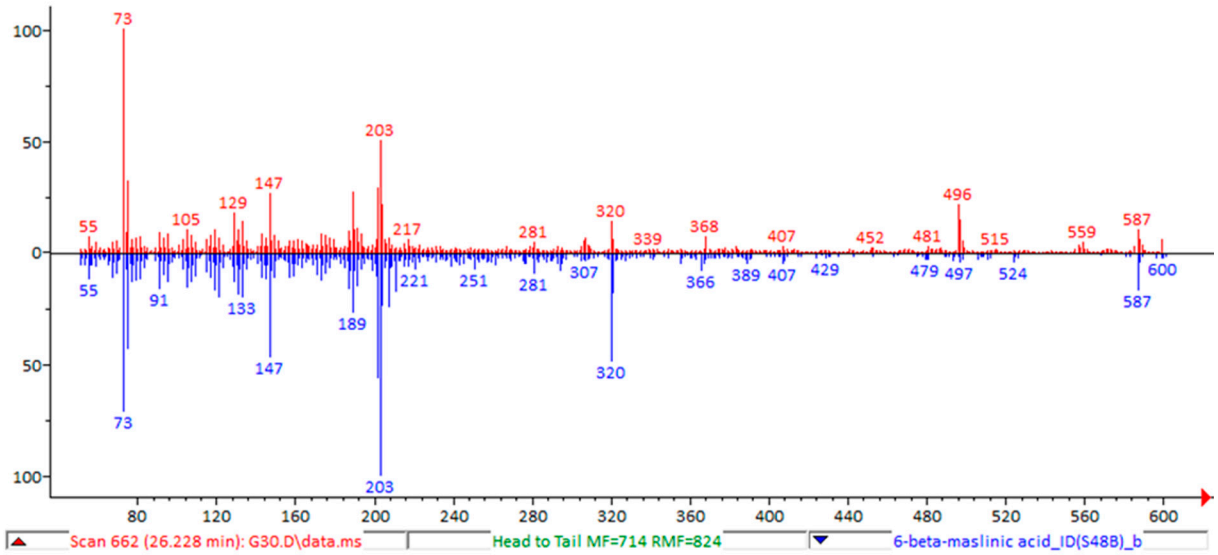
U21: Betulinic acid-nTMS



U22



U23: 6-beta-maslinic acid-nTMS



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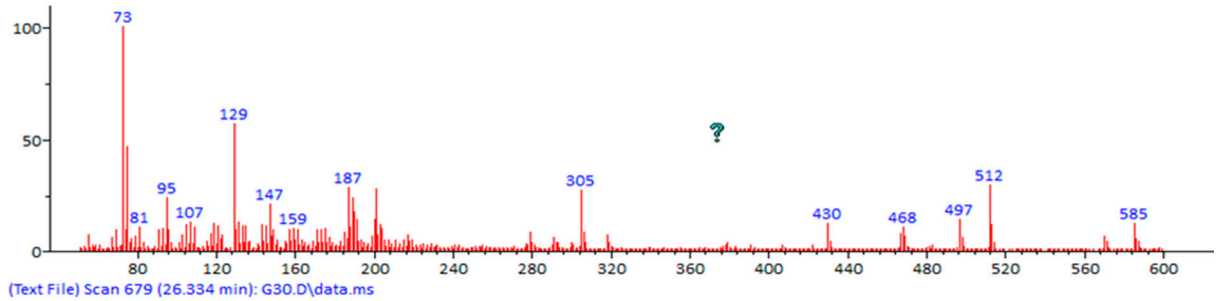
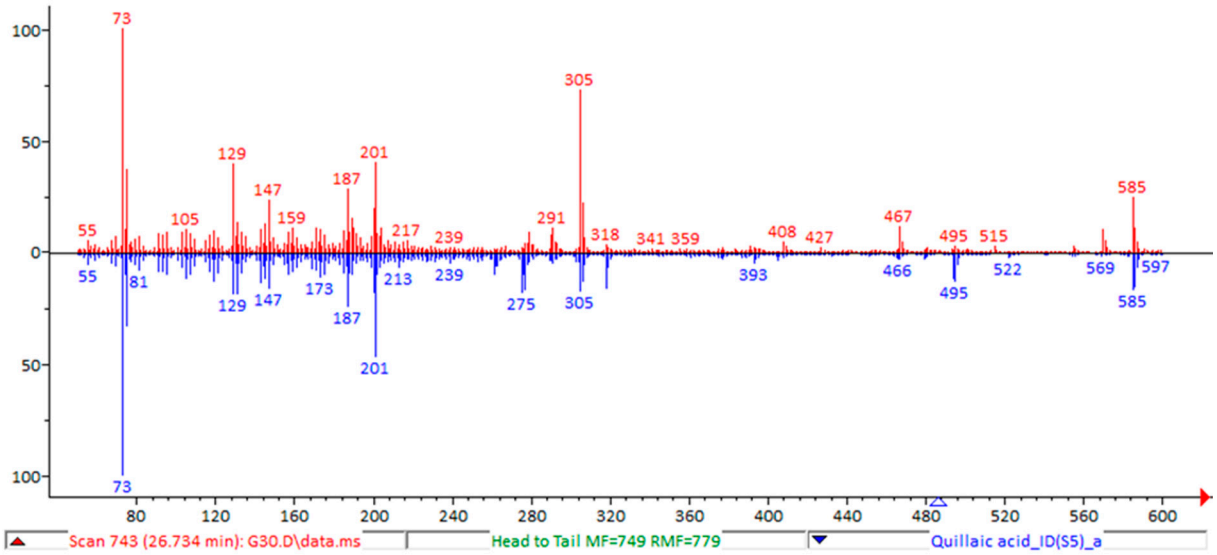
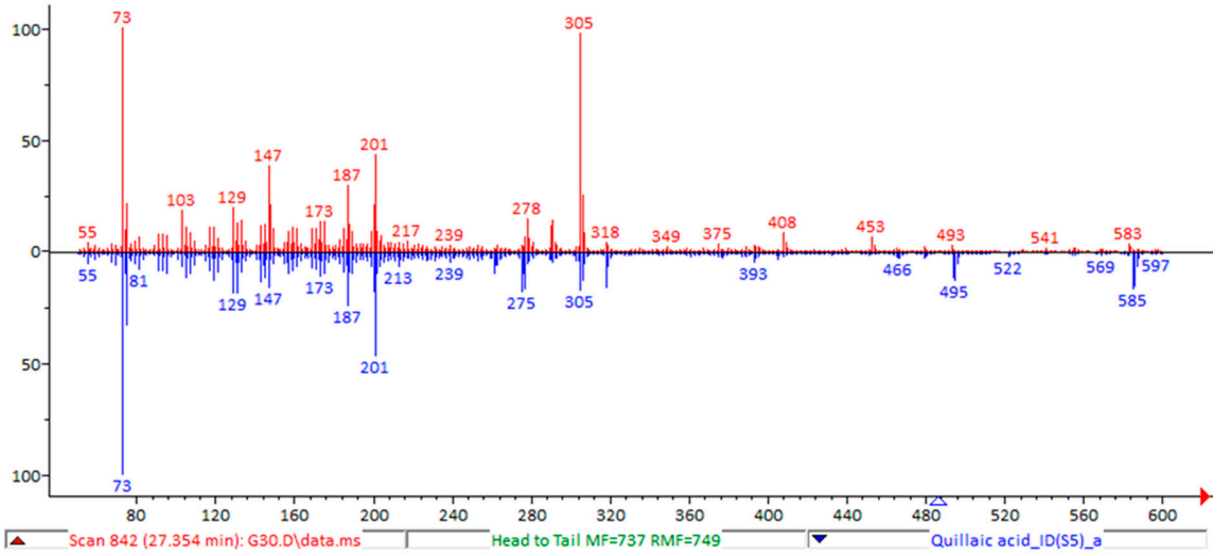


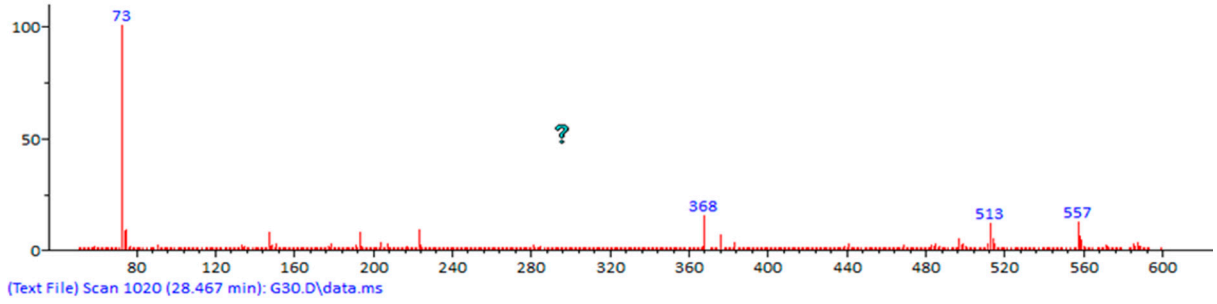
U25: Quillaic acid-nTMS



U26: Quillaic acid-nTMS



U27



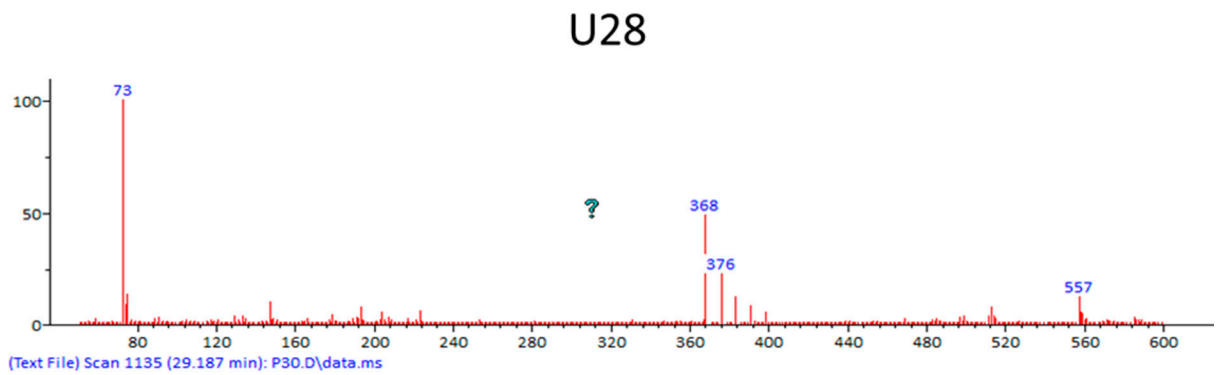


Figure S2. Electron impact-mass spectrum (EI-MS) fragmentation patterns of 28 peaks detected saponin enriched extracts of the G- and P-type *B. vulgaris* after acidic hydrolysis of the extracts which allowed cleave off sugar moieties attached to aglycones. GC-MS total ion current (TIC) chromatograms are illustrated in Figure 7.