**HPLC-qTOF-MS/MS based profiling reveals anthocyanin profile alterations in berries of hybrid muscadine variety FLH 13-11 in two continuous cropping seasons**

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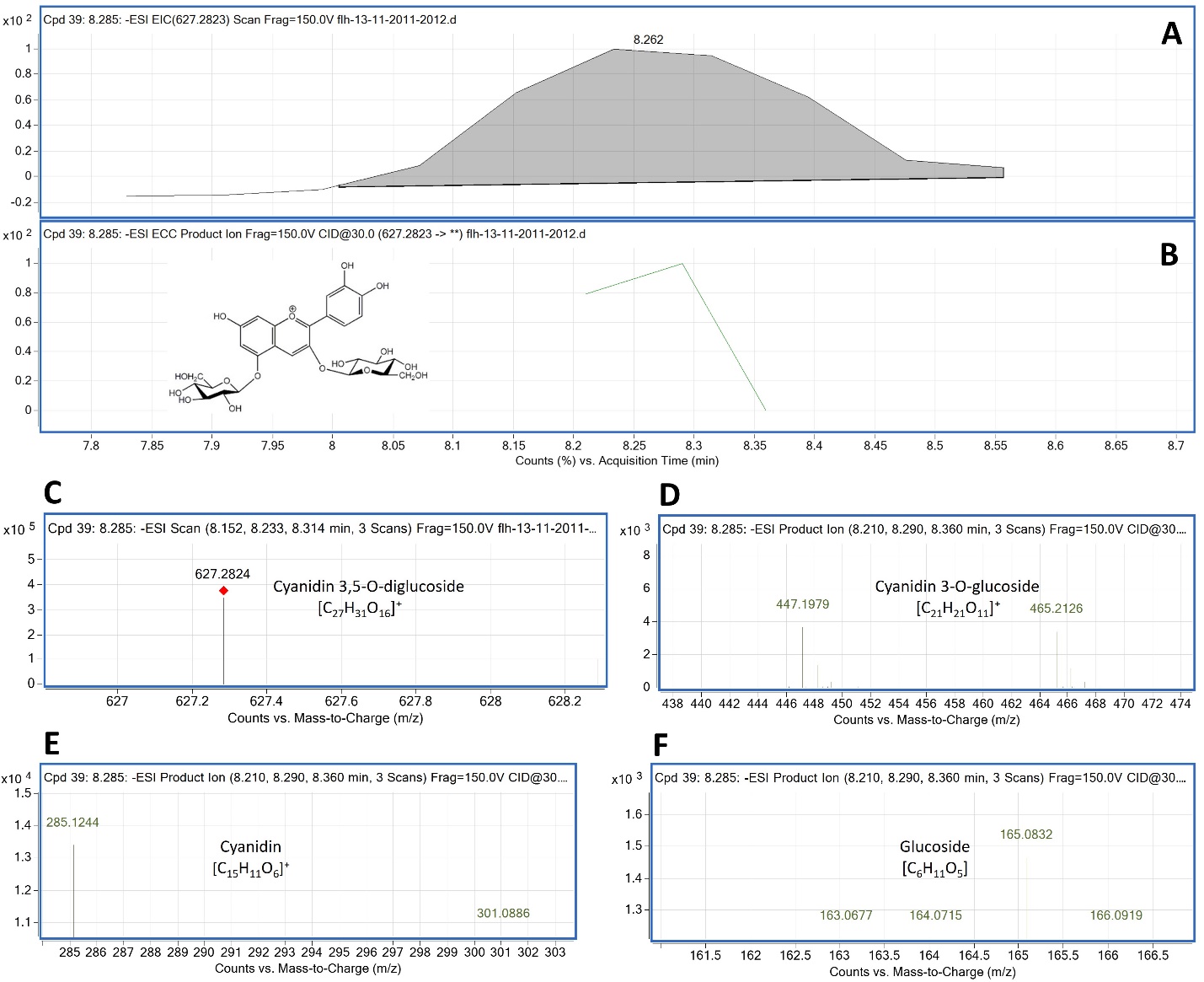
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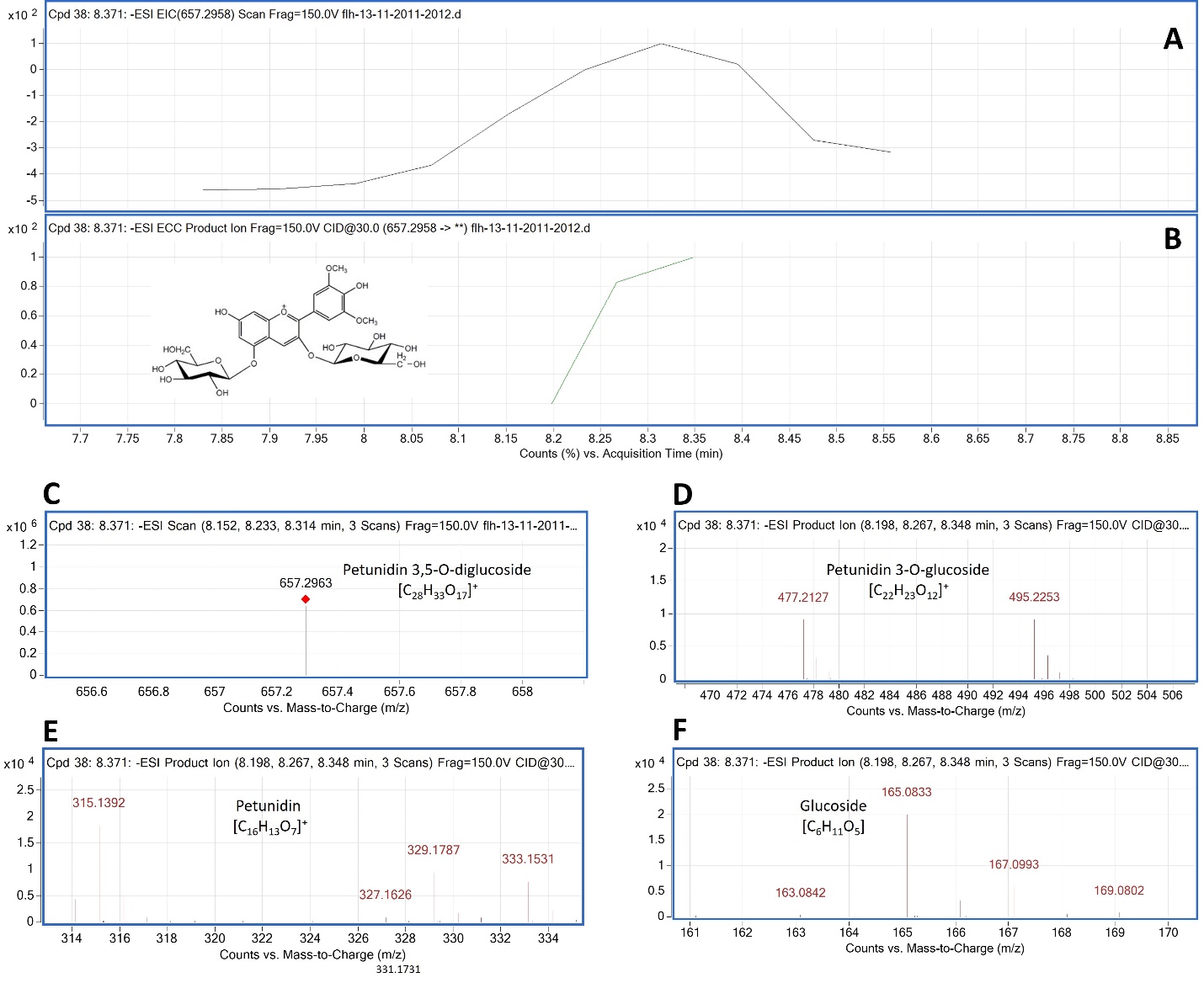
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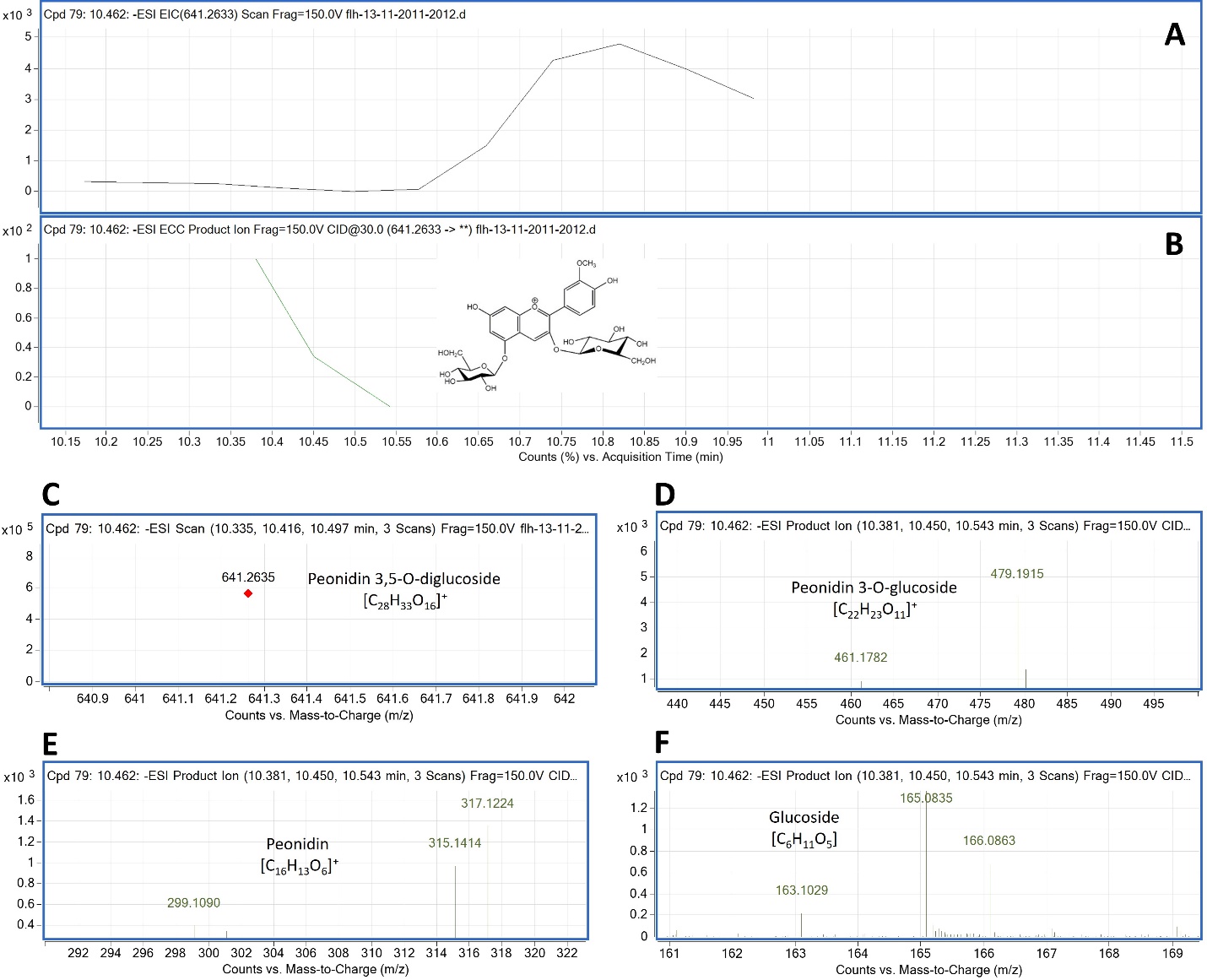
**Supplementary Figures 1-12**



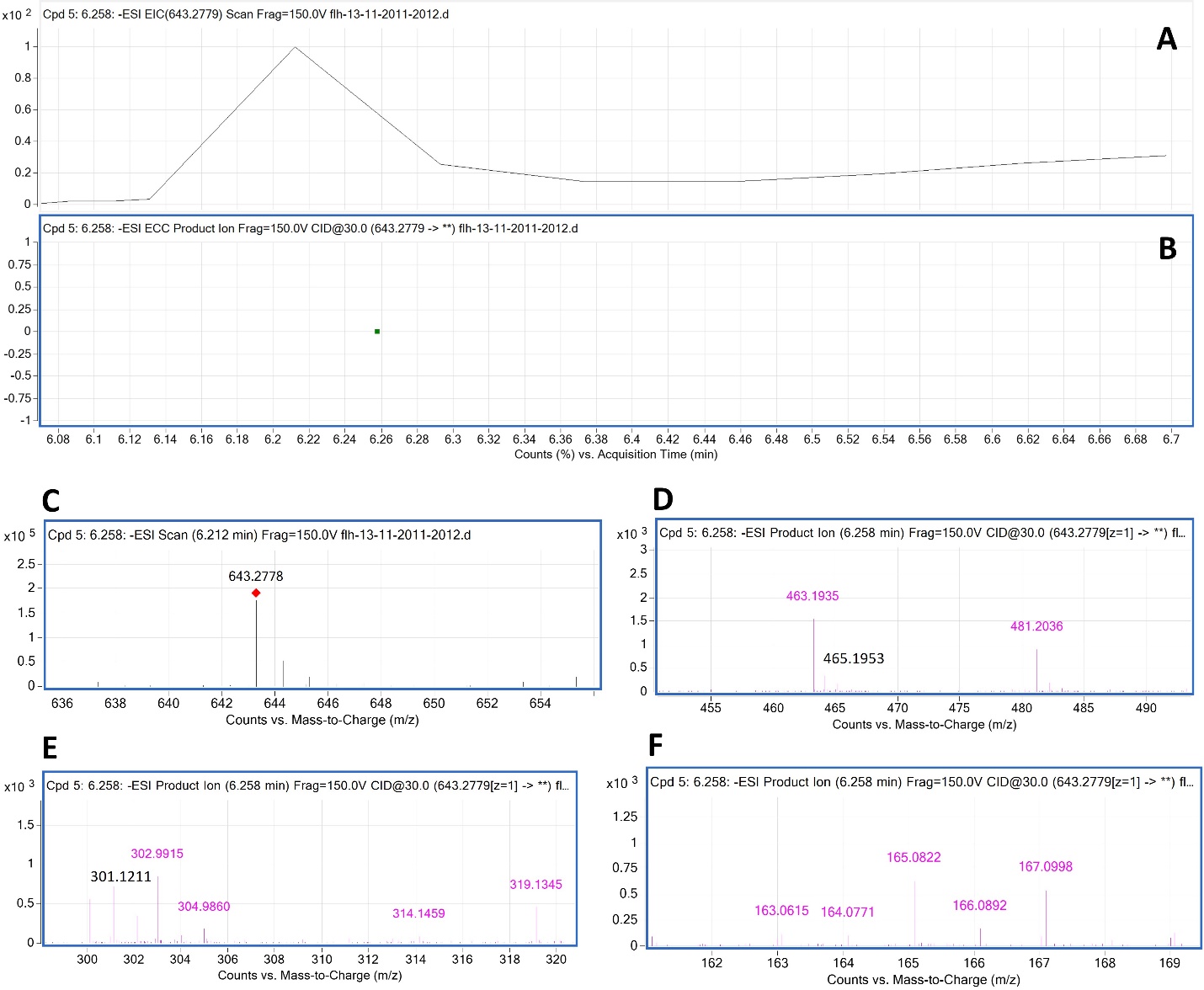
**Supplementary Figure 1** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN7. These data annotate this peak to be cyanidin 3, 5-digluosides (Cy-3,5-dG, molecular weight: 611.529). A: EIC of primary ion 627.2824 [m/z]¯, [M+18-2H], B: enhanced charge capacity (ECC) ion product for 627.2824 [m/z]¯, C: a MS profile showing an extracted m/z value, 627.2824 [m/z]¯, [M+18-2H], D-F: fragments from CID of 627.2824 showing 447.1979 and 448.1953 [m/z]¯ relating to Cy-3-G (D), 285.1244 [m/z]¯ relating to cyanidin aglycone (E), and 163.0677-166.0919 relating to glucose (F).



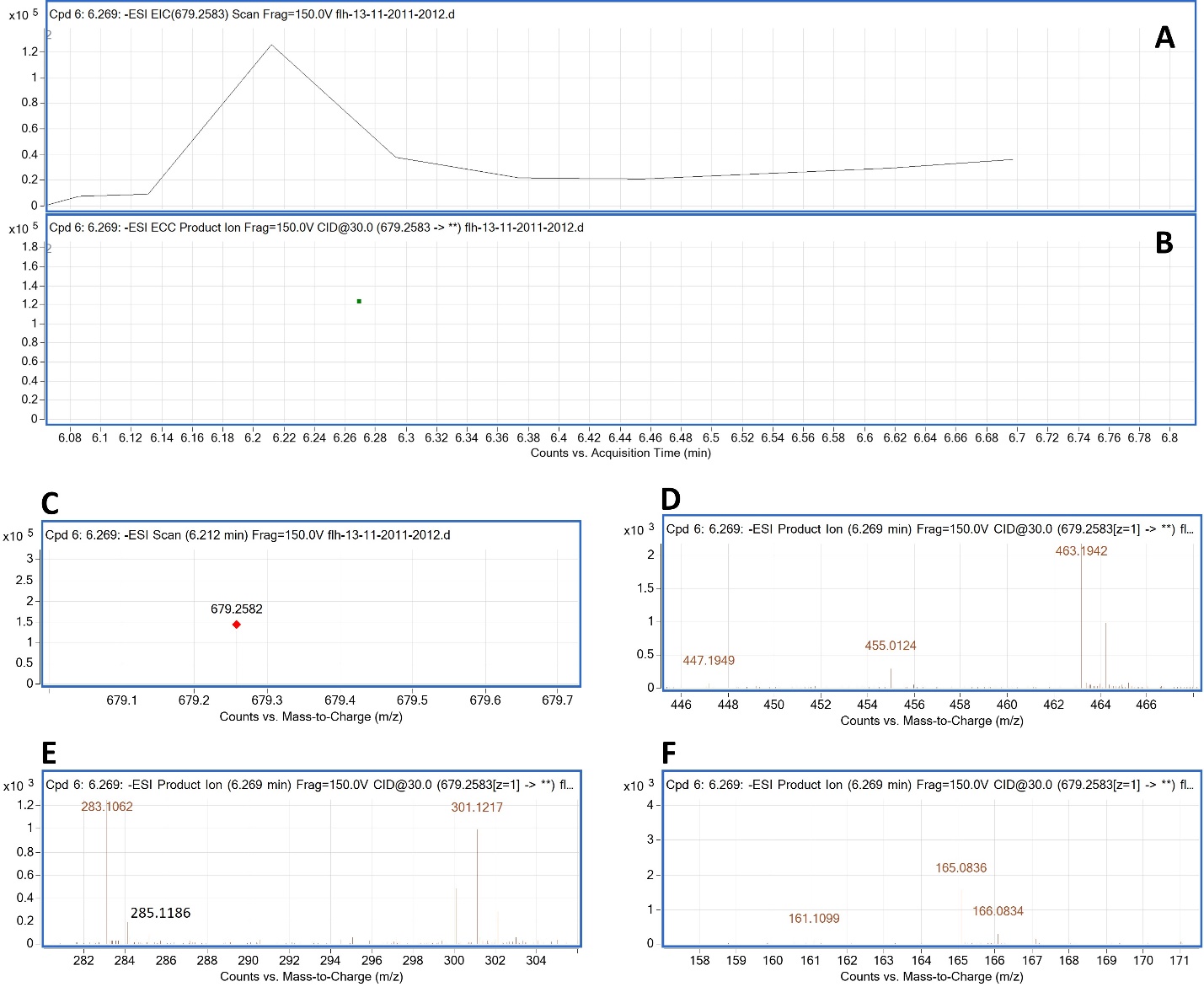
**Supplementary Figure 2** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN8. These data annotate this peak to be petunidin 3, 5-digluosides (Pt-3,5-dG, molecular weight: 641.282). A: EIC of primary ion 657.2963 [m/z]¯, [M+18-2H], B: enhanced charge capacity (ECC) ion product for 657.2963 [m/z]¯, C: a MS profile showing an extracted m/z value, 657.2963 [m/z]¯, [M+18-2H], D-F: fragments from CID of 657.2963 showing 477.2a MS profile27 and 478.2127 [m/z]¯ relating to Pt-3-G (D), 314.1391, 315.1392, and 316.1389 [m/z]¯ relating to petunidin aglycone (E), and 163.0842-169.0802 relating to glucose (F).



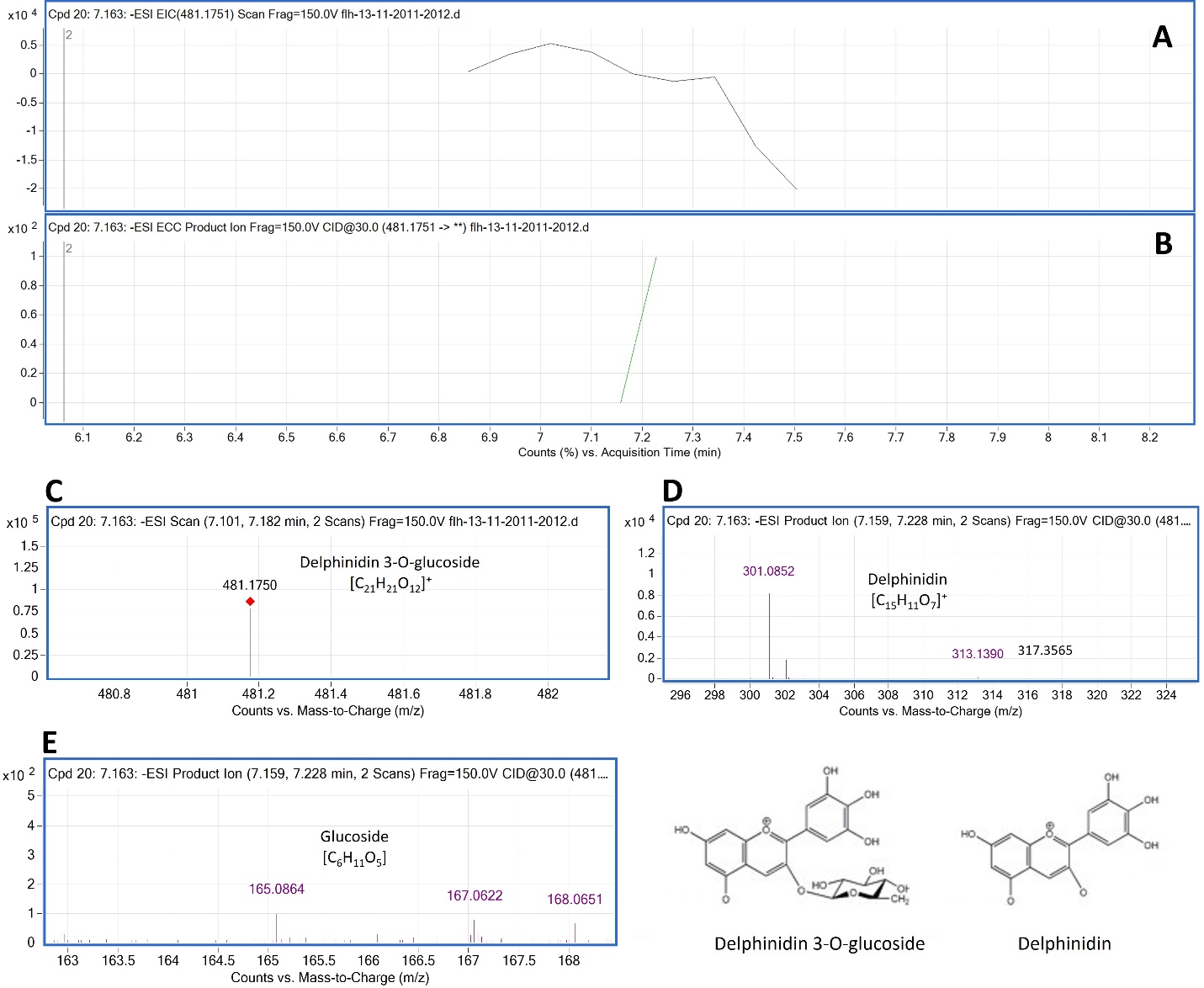
**Supplementary Figure 3** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN10. These data annotate this peak to be peonidin 3, 5-digluosides (Pn-3,5-dG, molecular weight: 625.556). A: EIC of primary ion 641.2635 [m/z]¯, [M+18-2H], B: enhanced charge capacity (ECC) ion product for 641.2635 [m/z]¯, C: a MS profile showing an extracted m/z value, 641.2635 [m/z]¯, [M+18-2H], D-F: fragments from CID of 641.2635 showing 461.1782 and 479.1915 [m/z]¯ relating to Pn-3-G (D), 299.1090 and 301.1093 [m/z]¯ relating to petunidin aglycone (E), and 163.1029-166.0863 relating to glucose (F).



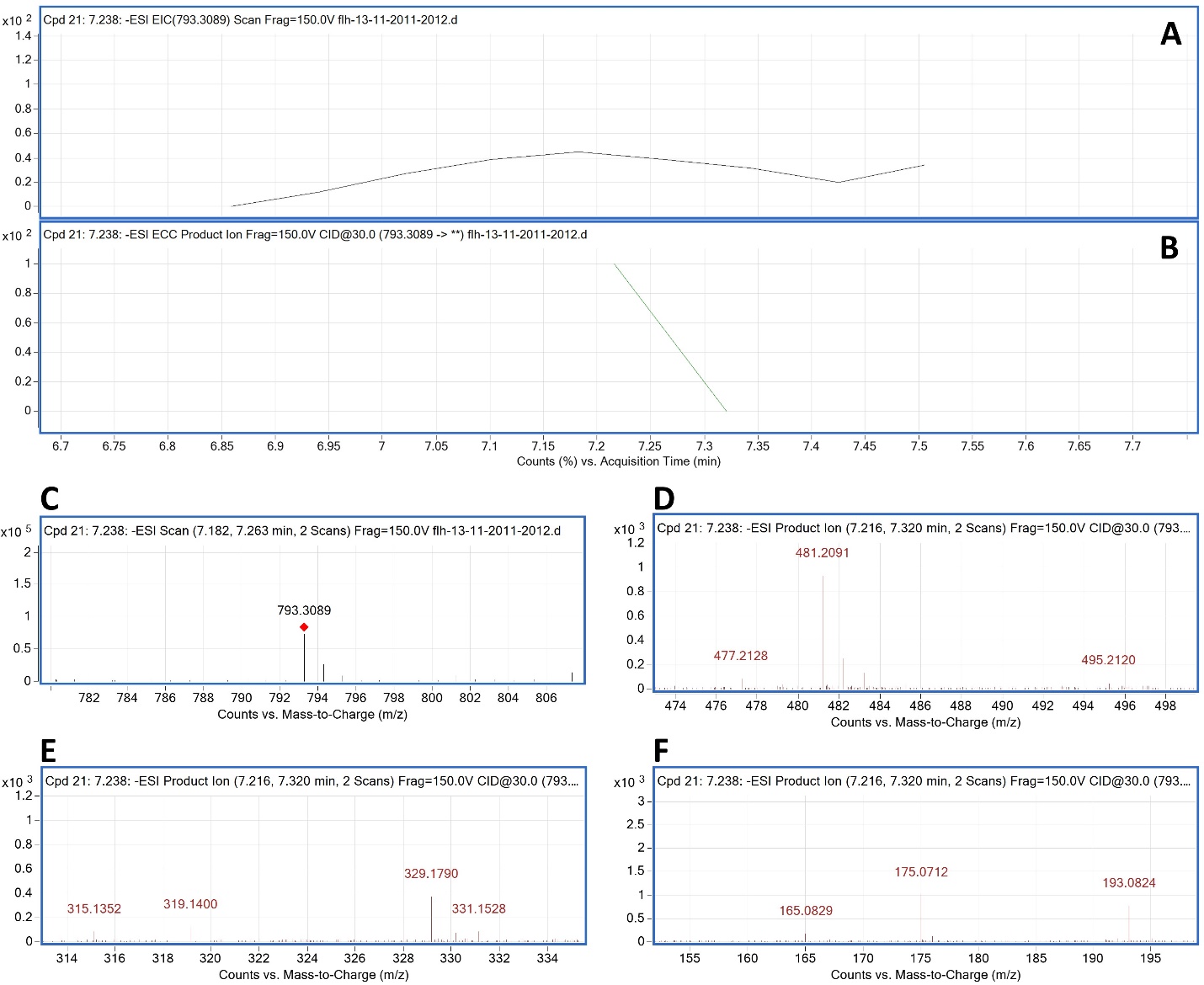
**Supplementary Figure 4** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN1. These data annotate this peak to be a delphinidin 3, 5-digluosides-like anthocyanin. A: EIC of primary ion 643.2778 [m/z]¯, B: enhanced charge capacity (ECC) ion product for 643.2778 [m/z]¯; C: a MS profile showing an extracted m/z value, 643.2778 [m/z]¯, D-F: fragments from CID of 643.2778 showing 463.1936 and 481.2036 [m/z]¯ relating to Del-3-G like structure (D), 300.1235 and 301.1211, and 302.9960 [m/z]¯ relating to delphinidin aglycone (E), and 163.0615-167.0998 relating to glucose (F).



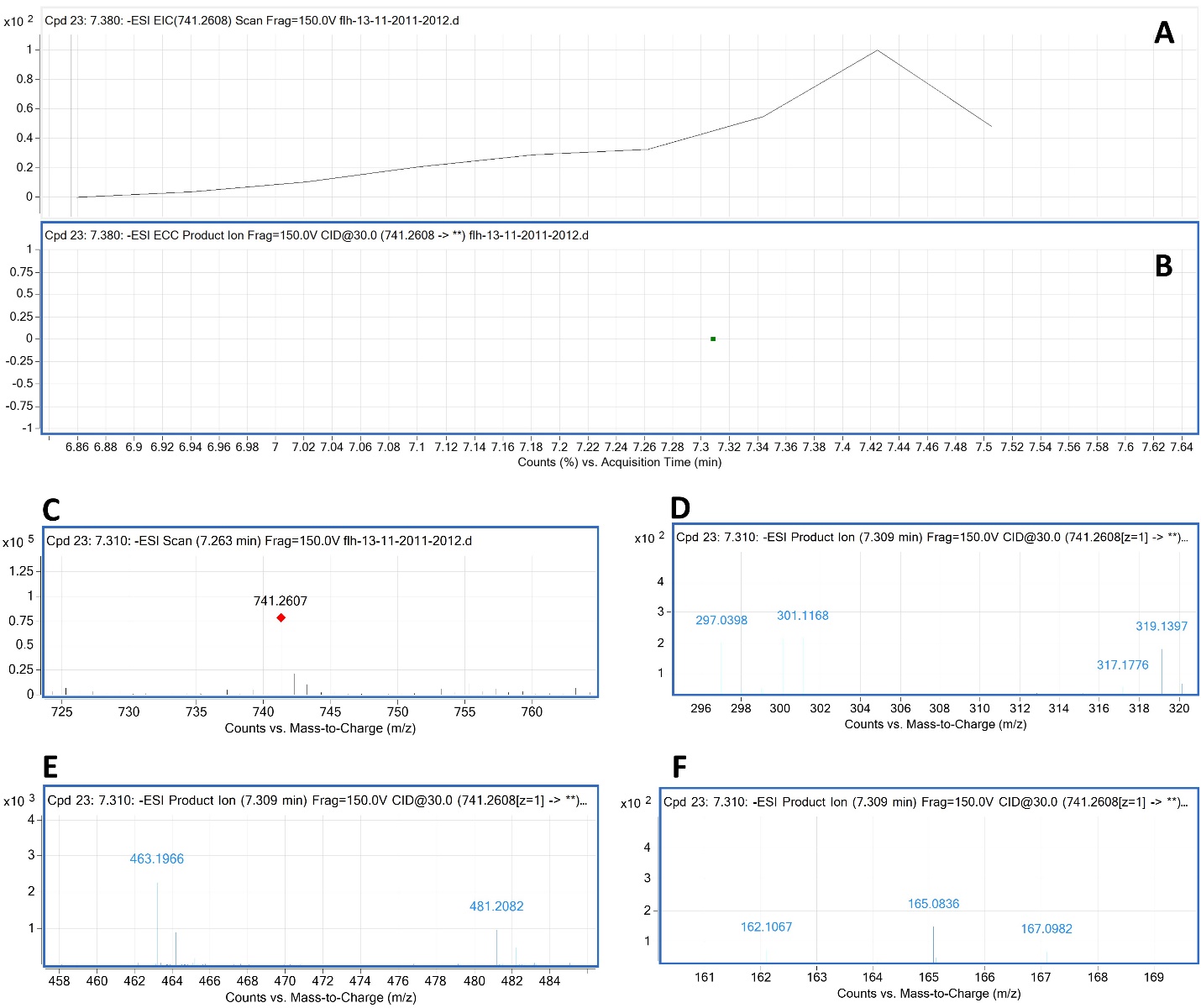
**Supplementary Figure 5** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN2. These data annotate this peak to be a cyanidin 3, 5-digluosides like anthocyanin. A: EIC of primary ion 679.2583 [m/z]¯, B: enhanced charge capacity (ECC) ion product for 679.2583 [m/z]¯; C: a MS profile showing an extracted m/z value, 679.2583 [m/z]¯, D-F: fragments from CID of 679.2583 showing 447.1979, 455.0124, and 463.1942 [m/z]¯ relating to a Cy-3-G like structure (D), 283.1062, 285.1186, and 301.1217 [equals 285+18-2H] [m/z]¯ relating to cyanidin aglycone (E), and 161.1099-166.0834 relating to glucose (F).



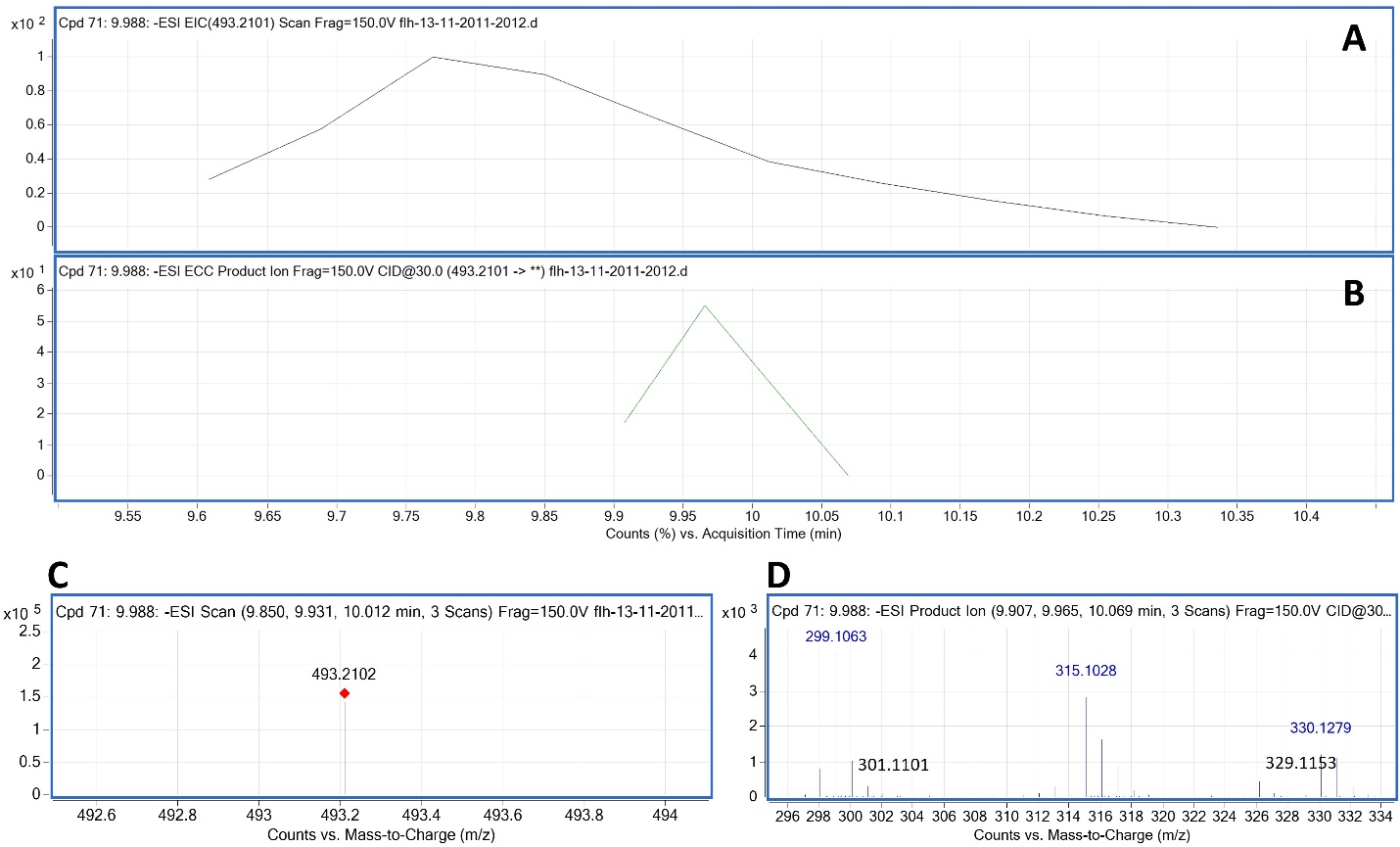
**Supplementary Figure 6** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN3. These data annotate this peak to be a delphinidin a 3-gluoside (Del-3-G) like anthocyanin. A: EIC of primary ion 481.1750 [m/z]¯, B: enhanced charge capacity (ECC) ion product for 481.1750 [m/z]¯; C: a MS profile showing an extracted m/z value, 481.1750 [m/z]¯, D-F: fragments from CID of 481.1750 showing 301.0852 [m/z]¯ relating to delphinidin aglycone (D), 163.0854-168.0651relating to glucose (E), and structures of Del-3-G and delphinidin (F)



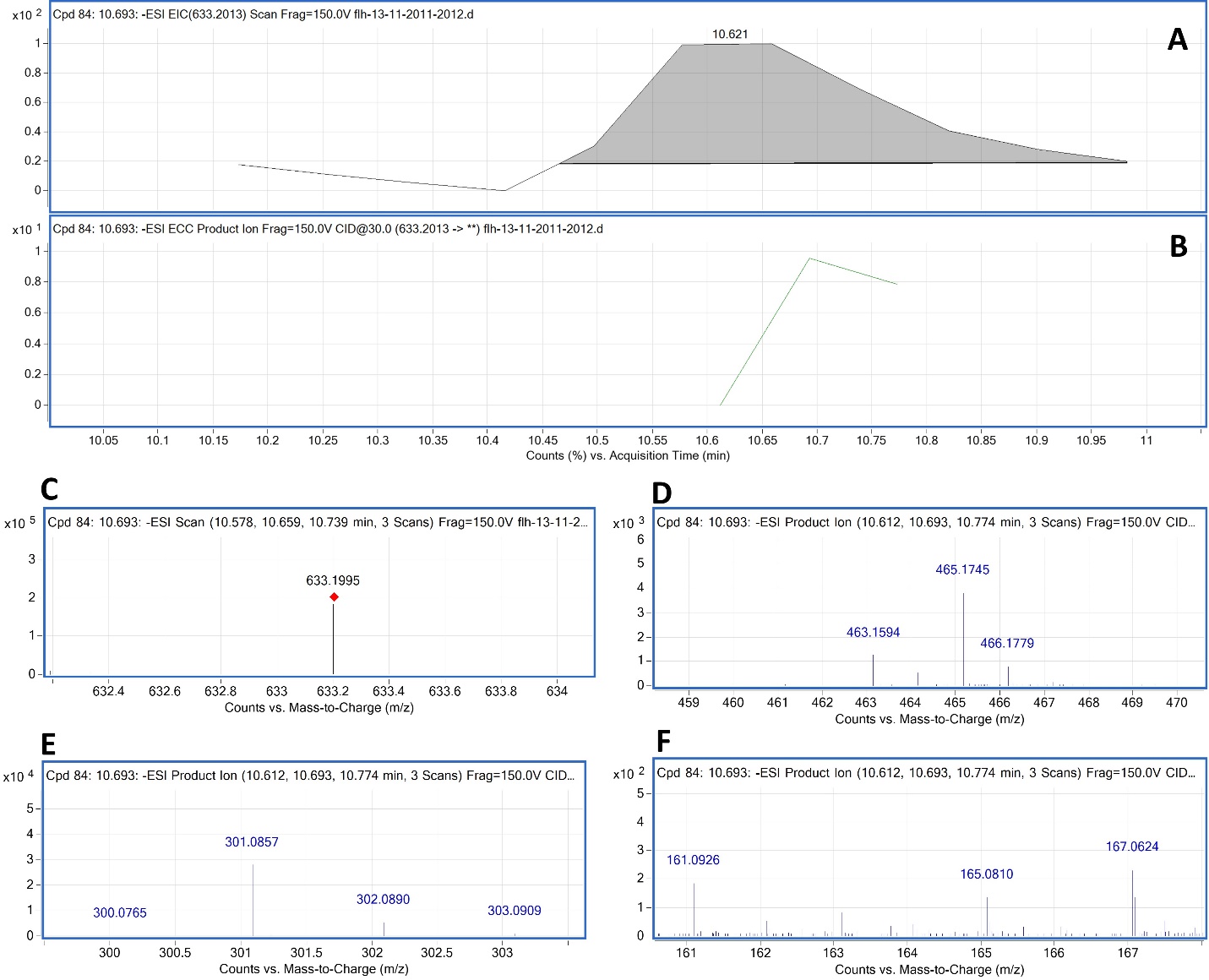
**Supplementary Figure 7** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN4. These data annotate this peak to be a petunidin 3, 5-digluosides (Pt-3, 5-dG) like anthocyanin. A: EIC of primary ion 793.3089 [m/z]¯, B: enhanced charge capacity (ECC) ion product for 793.3089 [m/z]¯; C: a MS profile showing an extracted m/z value, 793.3089 [m/z]¯, D-F: fragments from CID of 793.3089 showing 477.2128, 481.2091, 495.2120 [m/z]¯ relating to a Pt-3-dG like structure (D), 315.52, 319.14, 329.1790, and 331.1528 [equals 315+18-2H] [m/z]¯ relating to petunidin aglycone (E), and 165.0829 relating to glucose (F).



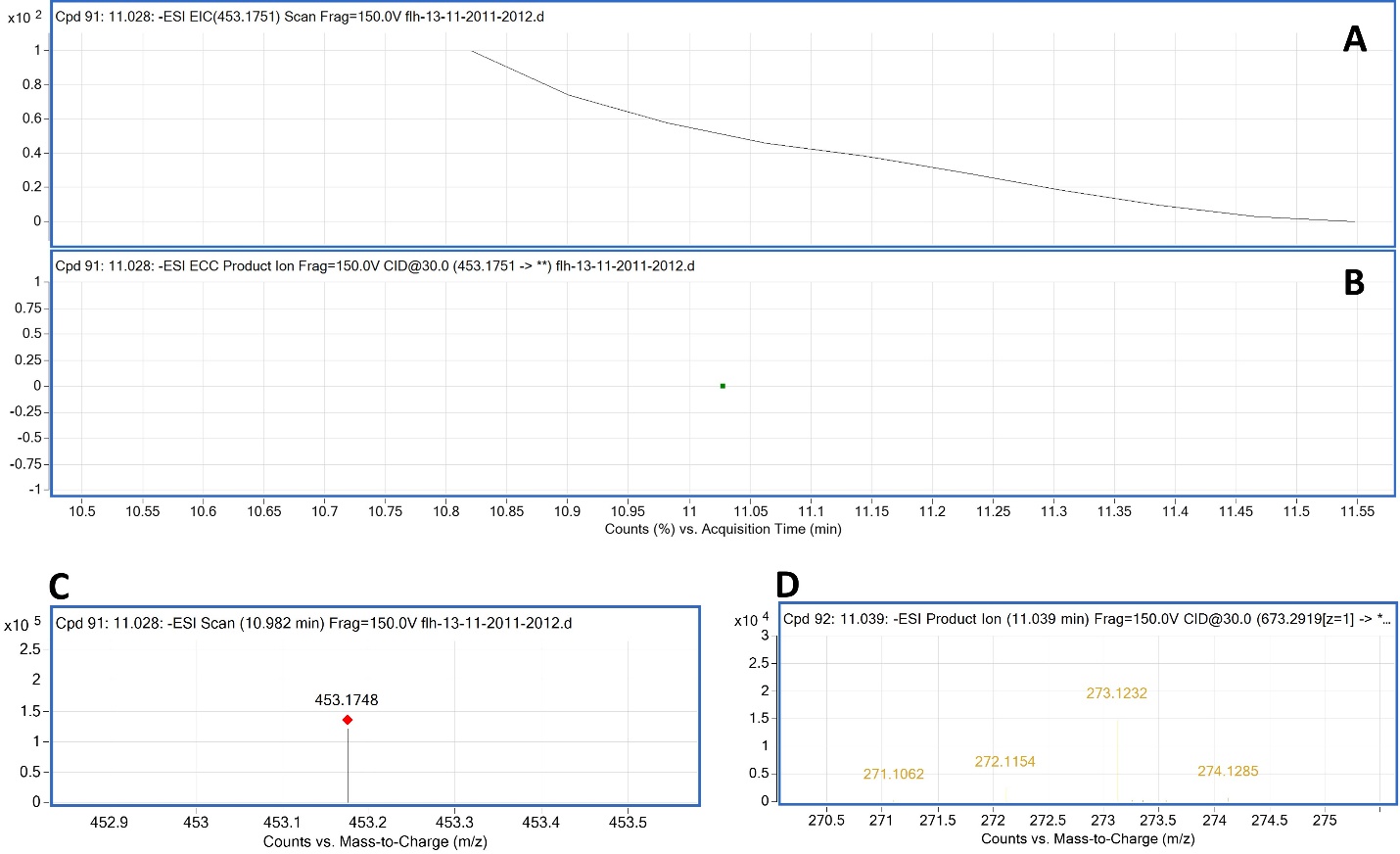
**Supplementary Figure 8** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN5. These data annotate this peak to be a peonidin 3, 5-digluosides (Pn-3, 5-dG) like anthocyanin. A: EIC of primary ion 741.2607 [m/z]¯, B: enhanced charge capacity (ECC) ion product for 741.2607 [m/z]¯; C: a MS profile showing an extracted m/z value, 741.2607 [m/z]¯, D-F: fragments from CID of 741.2607 showing 463.1936 and 481.2082 [equals 463+18-2H] [m/z]¯ relating to Pn-3-G like structure (E), 297.0398-301.1168, 317.1776 and 319.1397 [m/z]¯ relating to peonidin aglycone (E), and 162.1067, 165.0836, and 167.0982 relating to glucose (F).



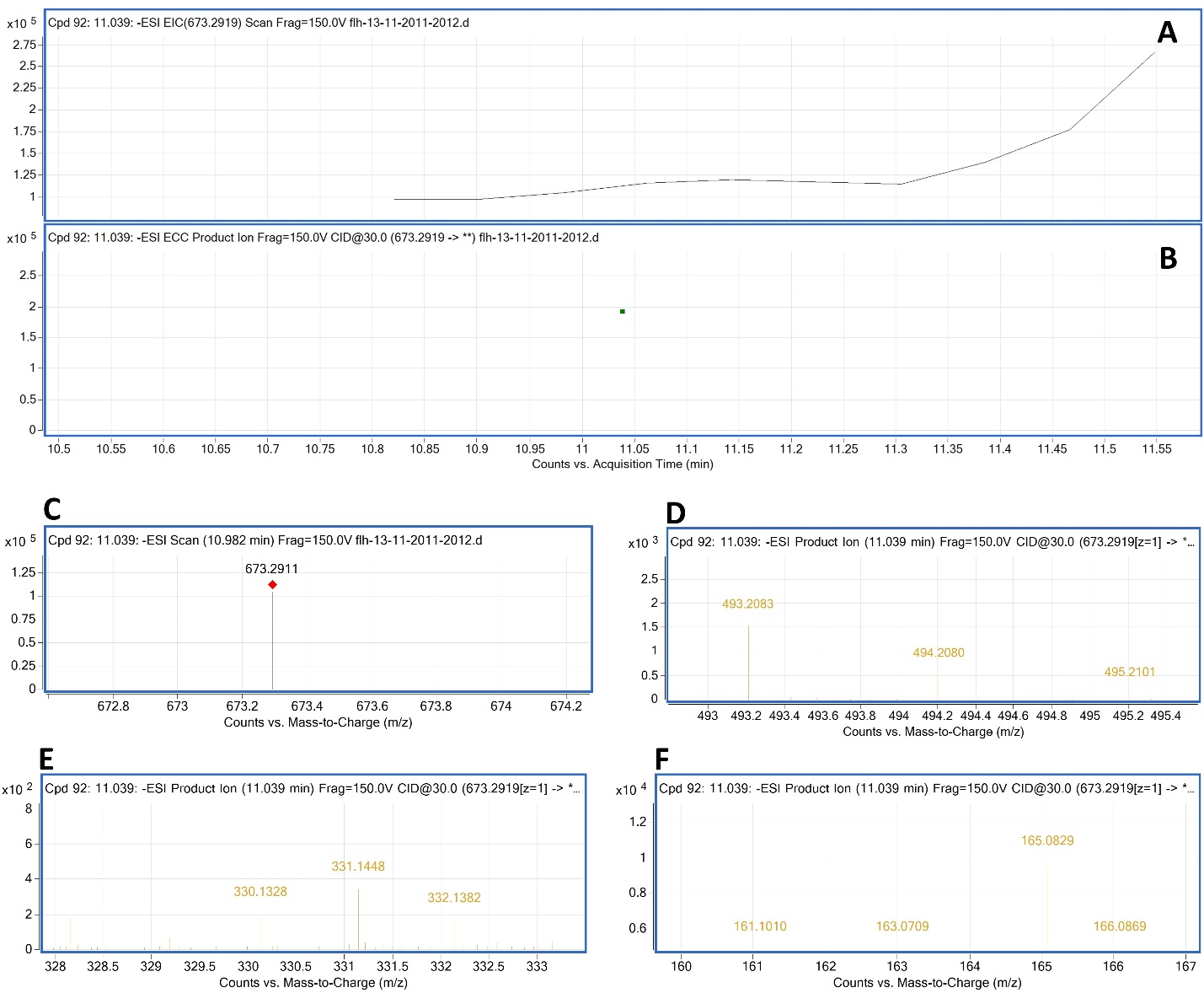
**Supplementary Figure 9** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN9. These data annotate this peak to be a peonidin 3-gluoside (Pn-3-G) like anthocyanin. A: EIC of primary ion 493.2102 [m/z]¯, B: enhanced charge capacity (ECC) ion product for 493.2102 [m/z]¯; C: a MS profile showing an extracted m/z value, 493.2102 [m/z]¯, D: fragments from CID of 741.2607 showing 299.1063 and 301.1101[m/z]¯ relating to peonidin aglycone. Its fragments for glucose include 163.0836, 165.0836, 166.0824, and 167.0988 (Table 1).



**Supplementary Figure 10** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN11. These data annotate this peak to be a delphinidin-related anthocyanin. A: EIC of primary ion 633.1995 [m/z]¯, B: enhanced charge capacity (ECC) ion product for 633.1995 [m/z]¯, C: a MS profile showing an extracted m/z value, 633.1995 [m/z]¯, D-F: fragments from CID of 633.1995 showing 463.1594-166.1779 [m/z]¯ relating to a glycosylated delphinidin structure (D), 300.0765-303.0909 [m/z]¯ relating to delphinidin aglycone (E), and 161.0926-167.0624 relating to glucose.



**Supplementary Figure 11** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN12. These data annotate this peak to be a pelargonidin-related anthocyanin. A: EIC of primary ion 453.1751 [m/z]¯, B: enhanced charge capacity (ECC) ion product for 453.1751 [m/z]¯, C: a MS profile showing an extracted m/z value, 453.1751 [m/z]¯, D: fragments from CID of 453.1751 showing 271.1062-274.1285 [m/z]¯ relating to pelargonidin. Its fragments for glucose include 163.1029, 165.0829, and 166.0863 (Table 1).



**Supplementary Figure 12** Extracted ion chromatogram (EIC) of primary mass spectrum and m/z features of secondary ion fragments derived from LC-MC/MS of peak F13-AN13. These data annotate this peak to be a malvidin 3, 5-digluoside (Mal-3, 5-dG). A: EIC of primary ion 673.2911 [M+18] [m/z]¯, B: enhanced charge capacity (ECC) ion product for 673.2911 [m/z]¯, C: a MS profile showing an extracted m/z value, 673.2911 [m/z]¯, D-F: fragments from CID of 673.2911 showing 493.2083-495.2101 [m/z]¯ relating to a Mal-3-glocuside structure (D), 330.1328, 331.1448, and 332.1382 [m/z]¯ relating to malvidin aglycone (E), and 161.1010-167.0809 relating to glucose (F).