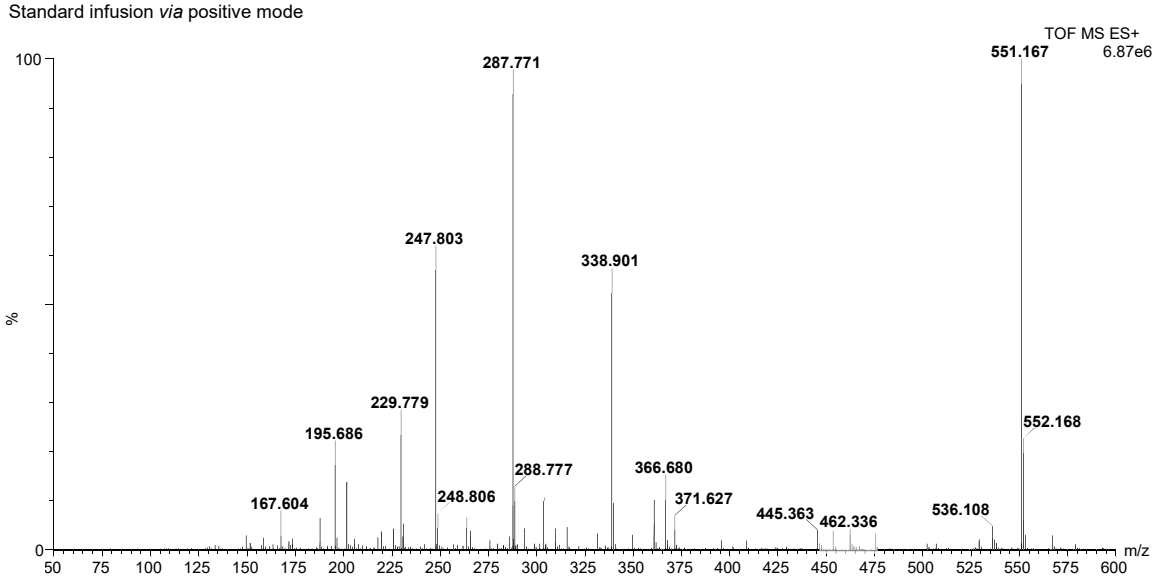
Electronic Supplementary Material (ESI) for Analyst.

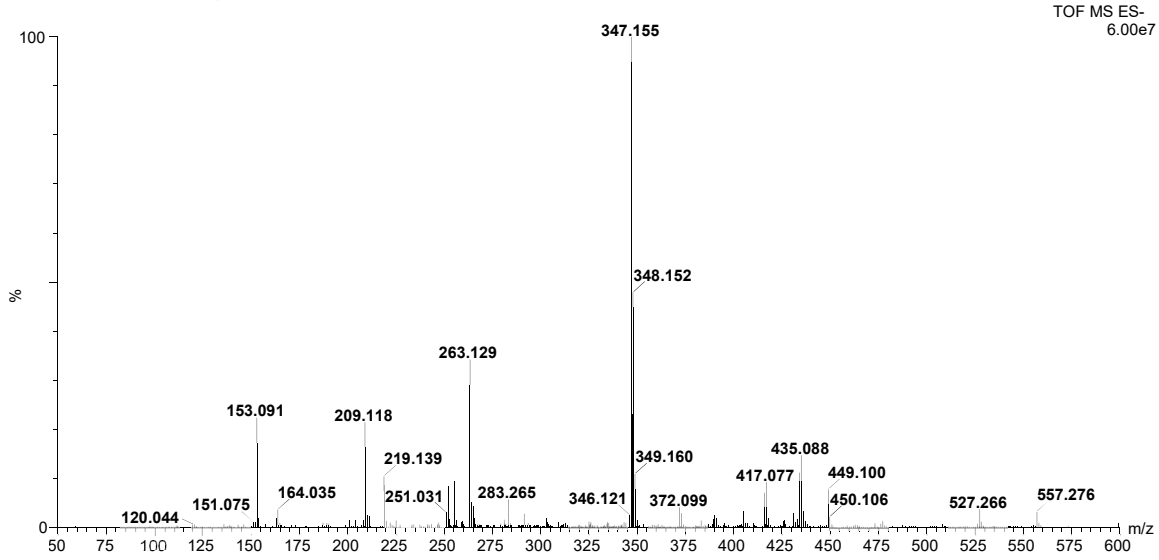
Representative DESI-MS spectra of the infusion standard phytohormone compounds in the positive mode and the negative mode.

The standard compounds were diluted to 1 µM in the 95% methanol (v/v) and delivered at 3 µL/min into DESI source.

Standard infusion *via* positive mode



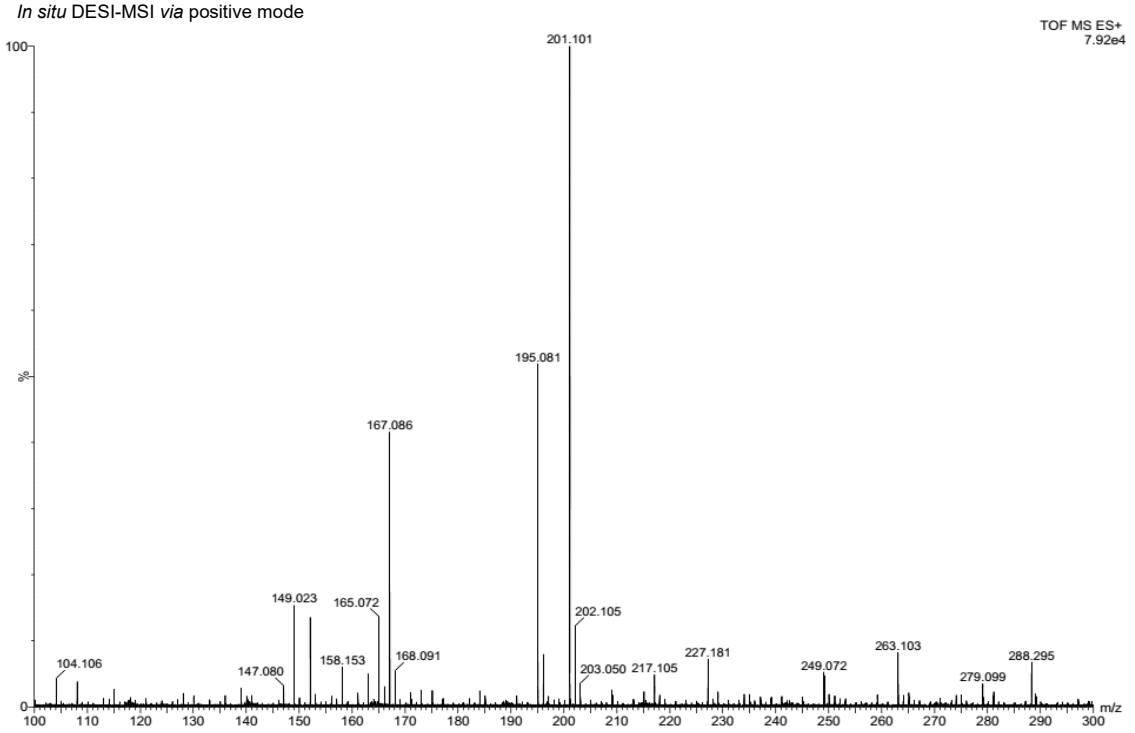
Standard infusion *via* negative mode



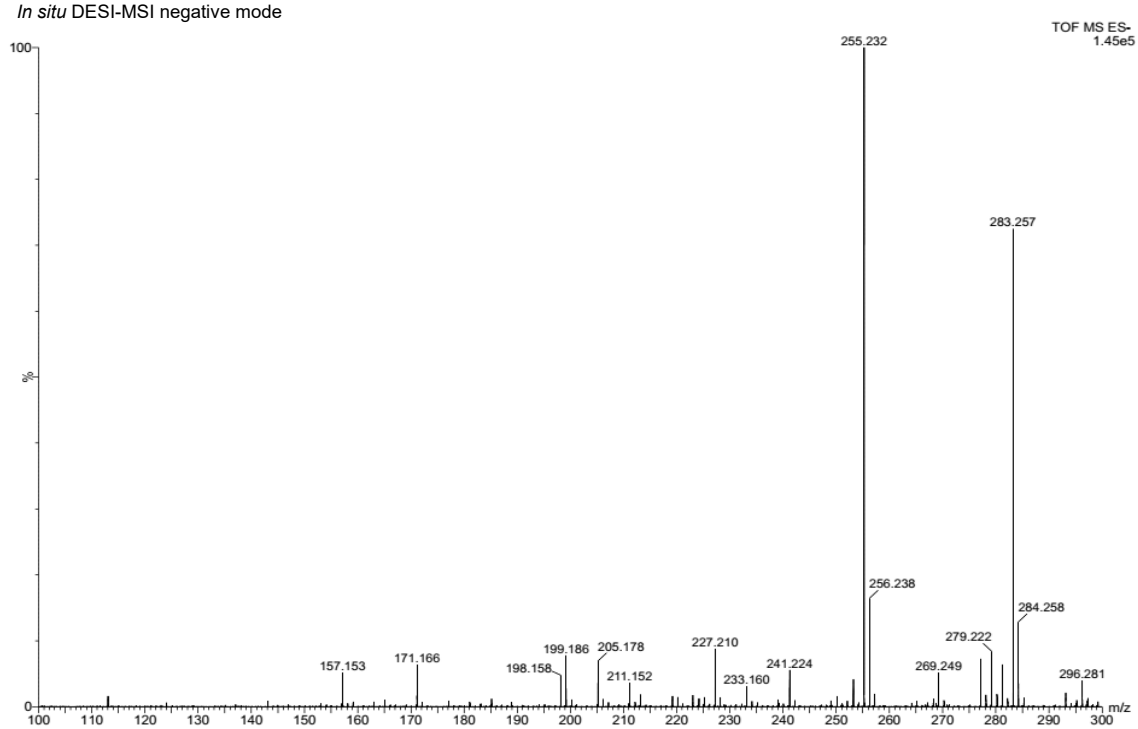
Representative *in situ* DESI-MS spectra of the phytohormone compounds in the positive mode and the negative mode.

The 95% methanol (v/v) was performed as spray solvent and delivered at 3 μL/min into DESI source.

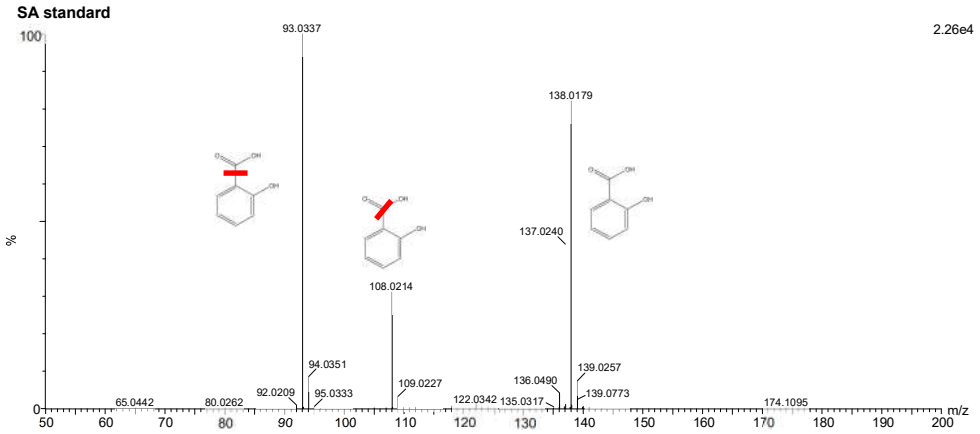
In situ DESI-MSI *via* positive mode

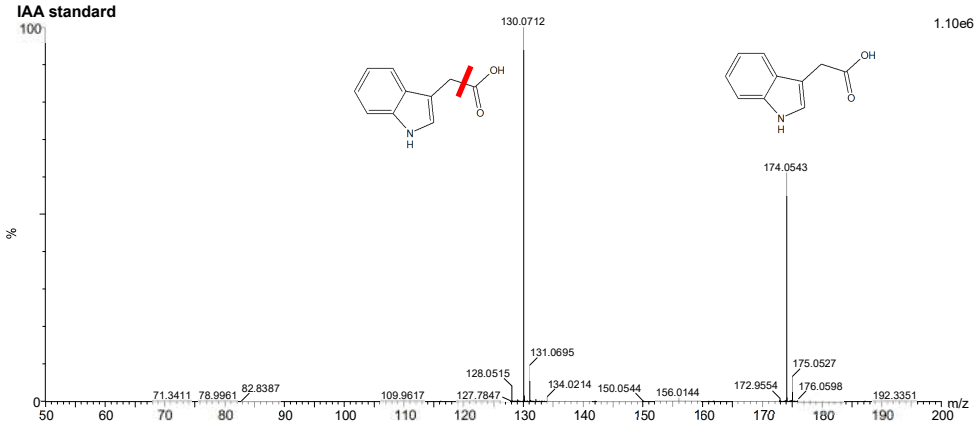


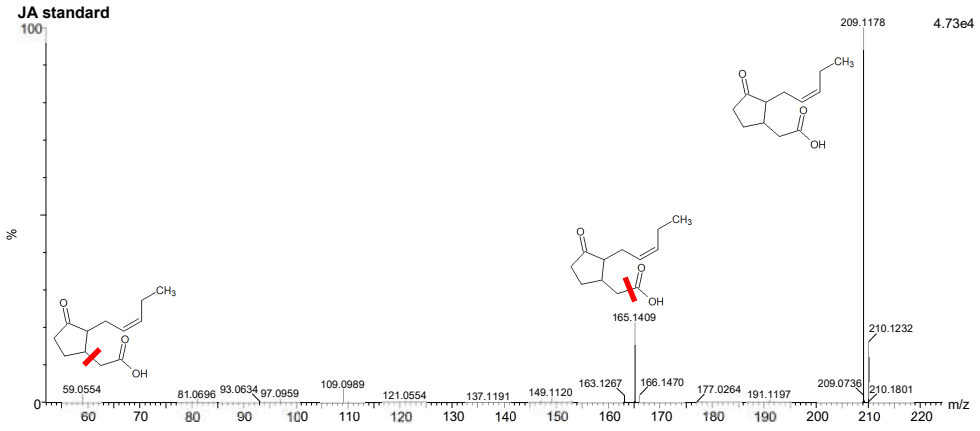
In situ DESI-MSI negative mode



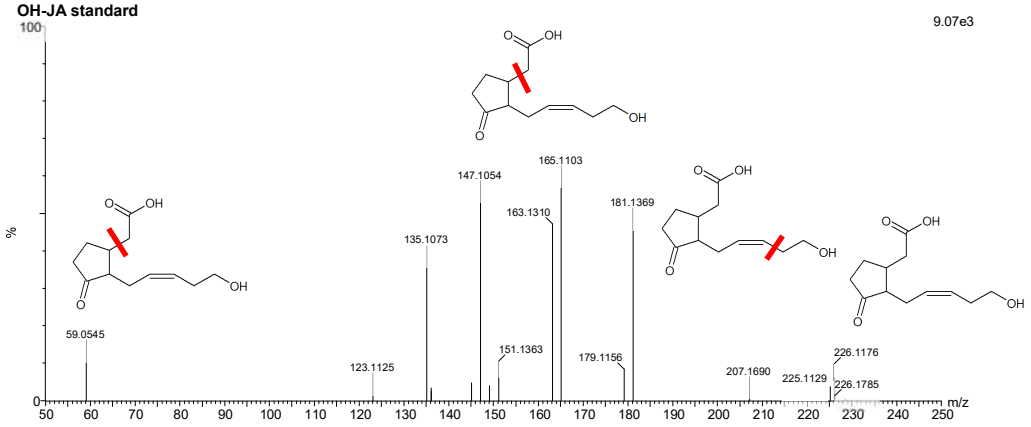
Representative DESI-MS/MS fragmentation spectra of the standard phytohormone compounds



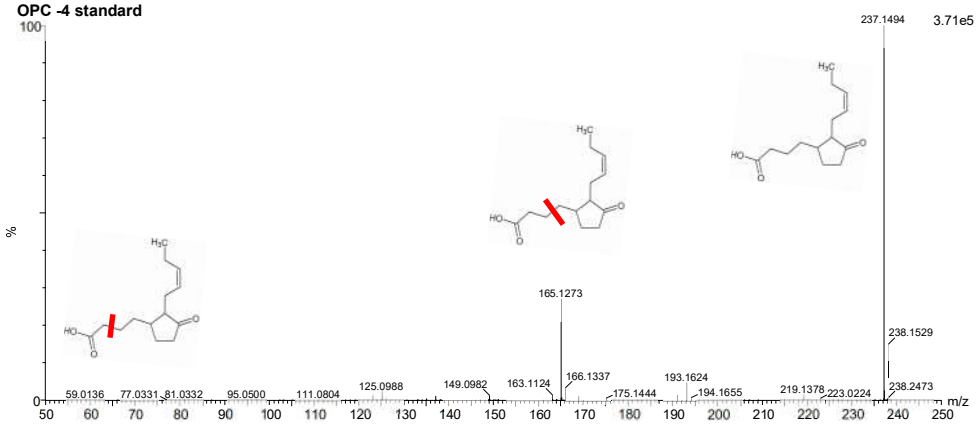




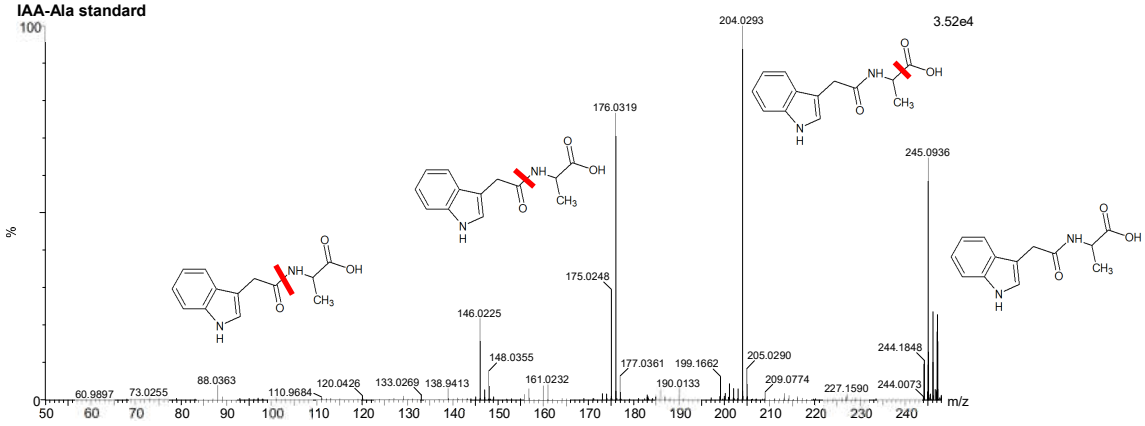
OH-JA standard



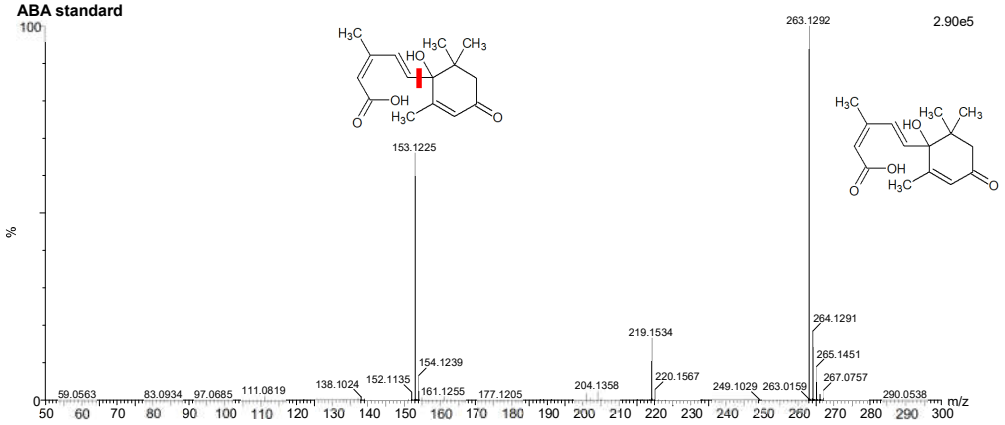
OPC -4 standard



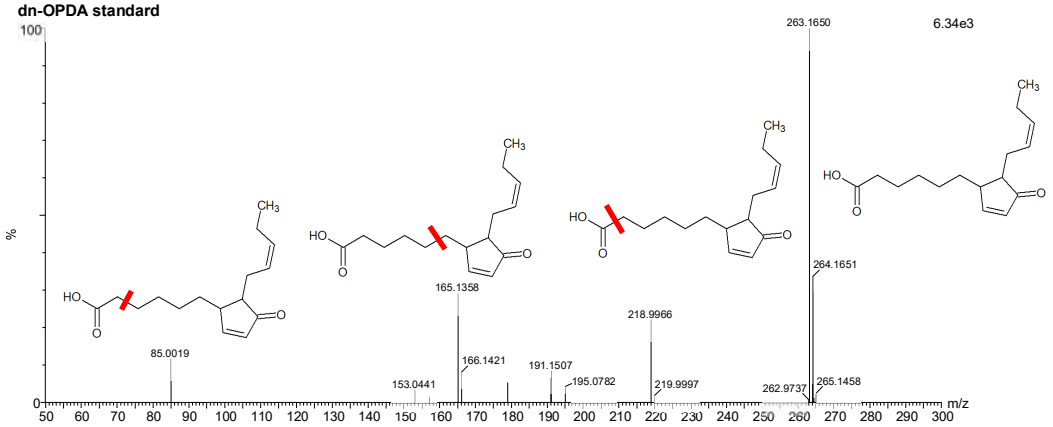
IAA-Ala standard



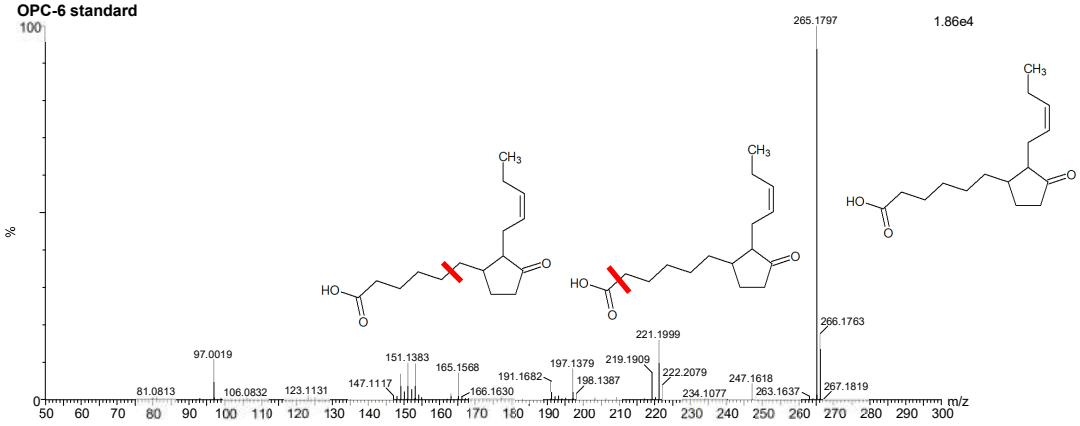
ABA standard



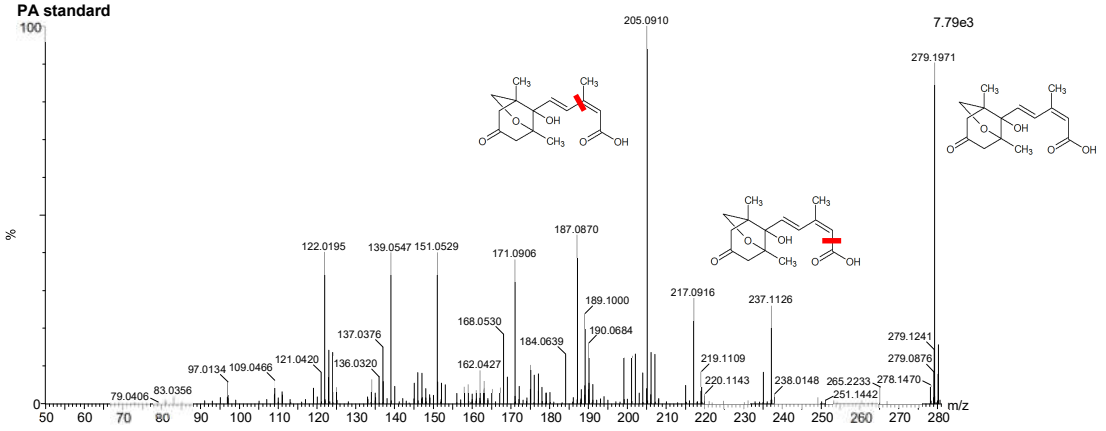
dn-OPDA standard



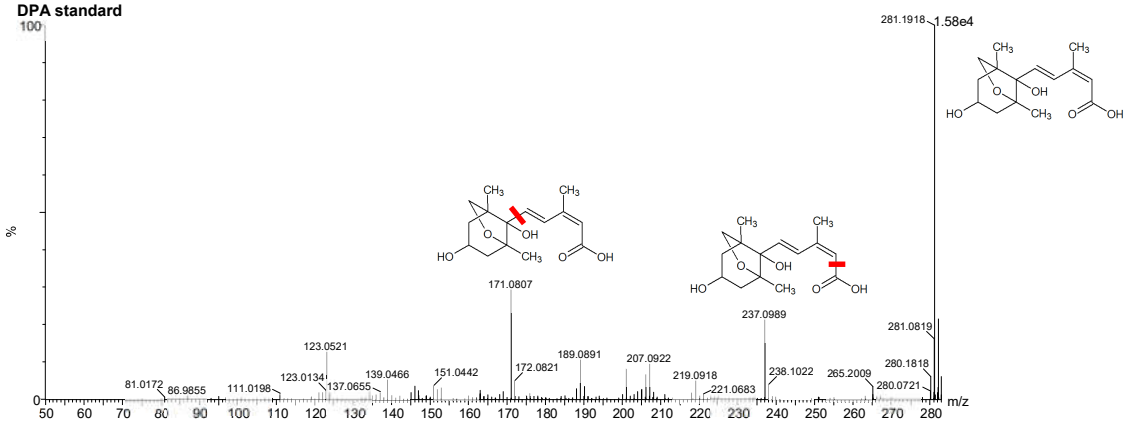
OPC-6 standard



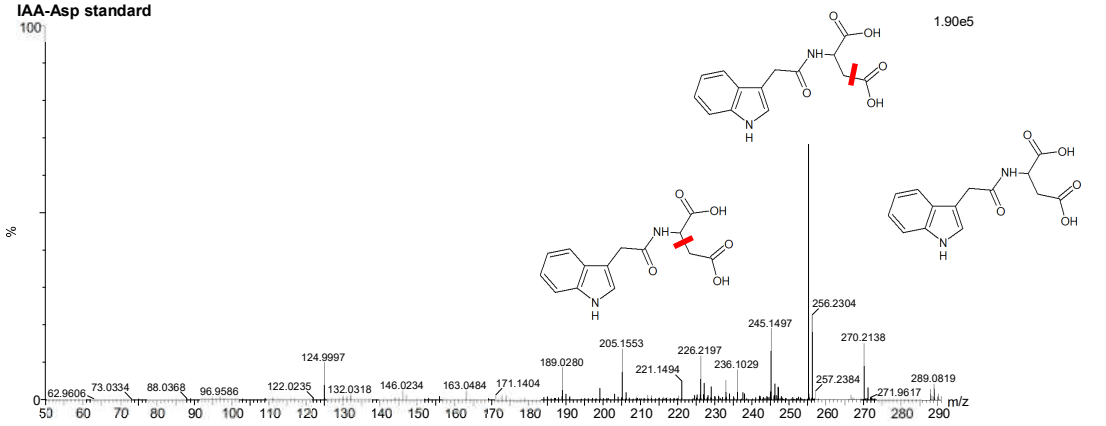
PA standard



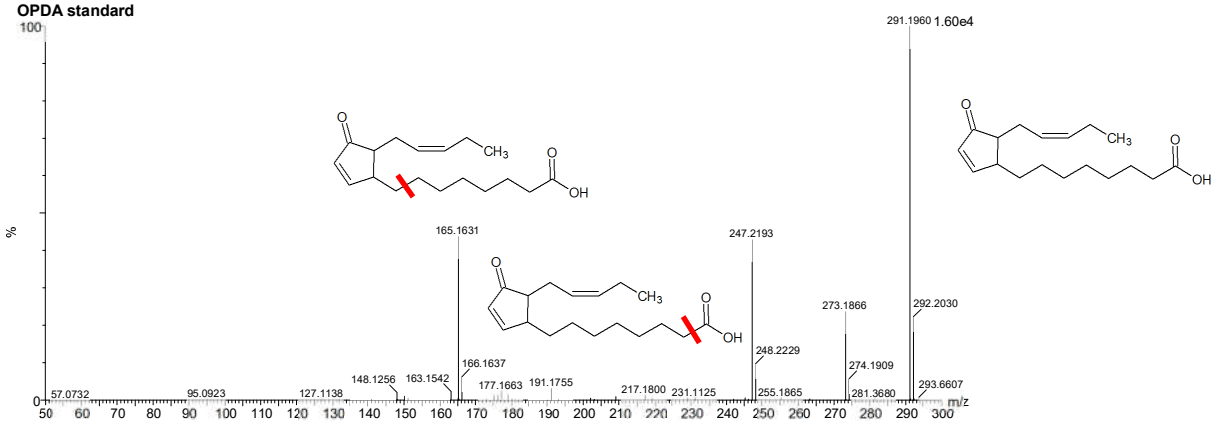
DPA standard



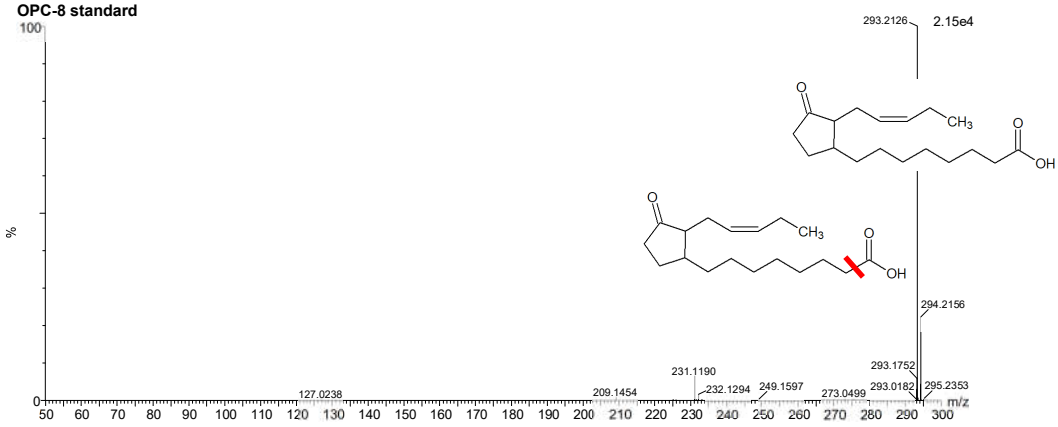
IAA-Asp standard



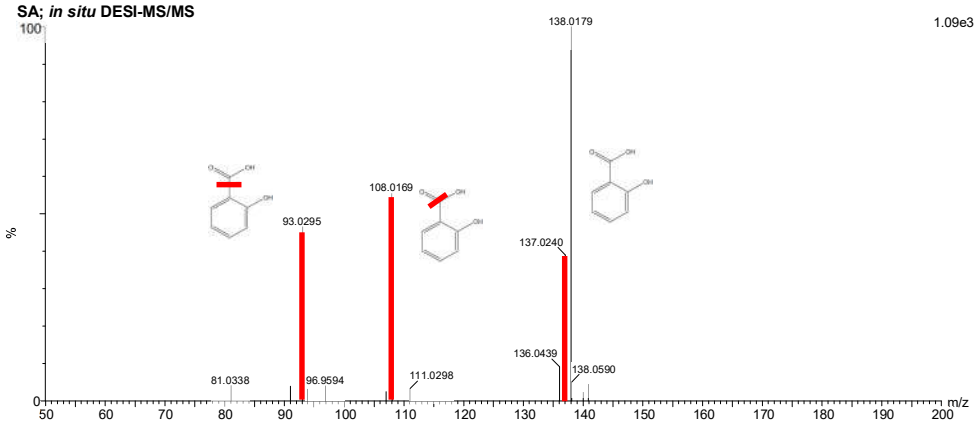
OPDA standard

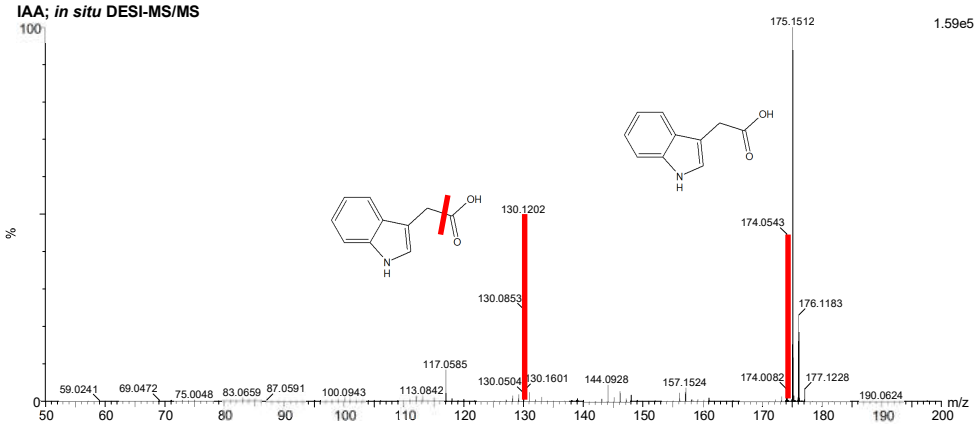


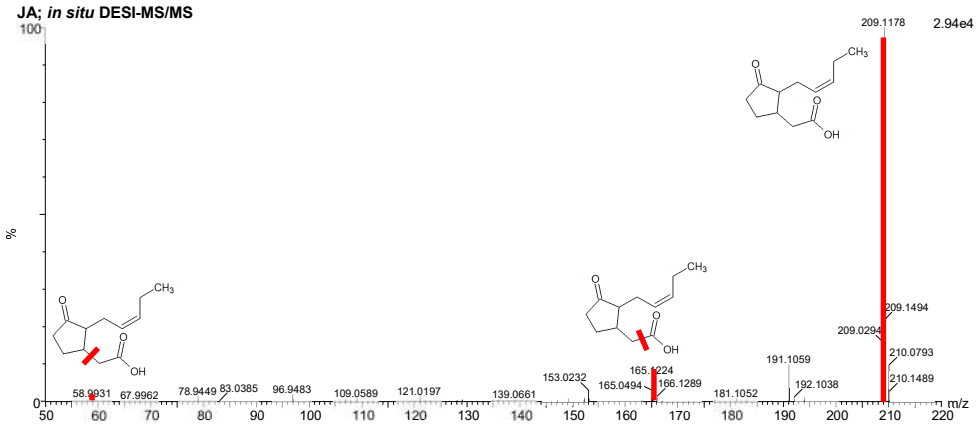
OPC-8 standard



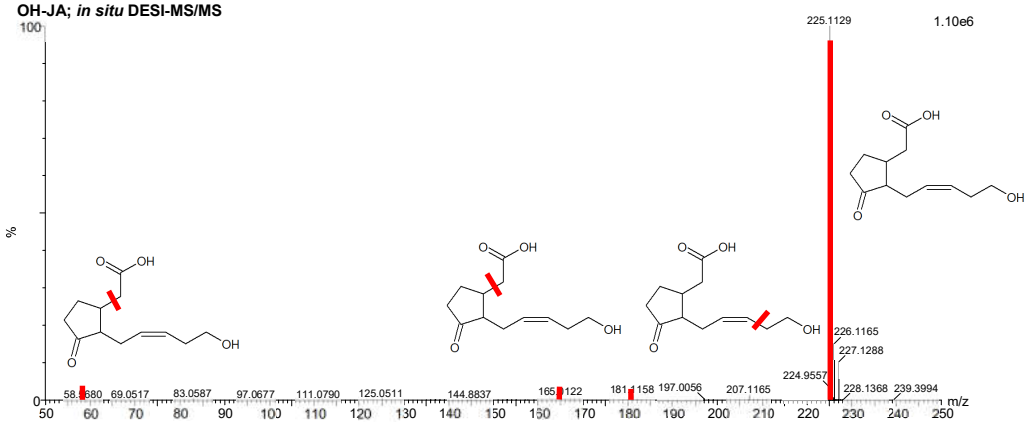
Representative *in situ* DESI-MS/MS fragmentation spectra of the targeted phytohormone compounds



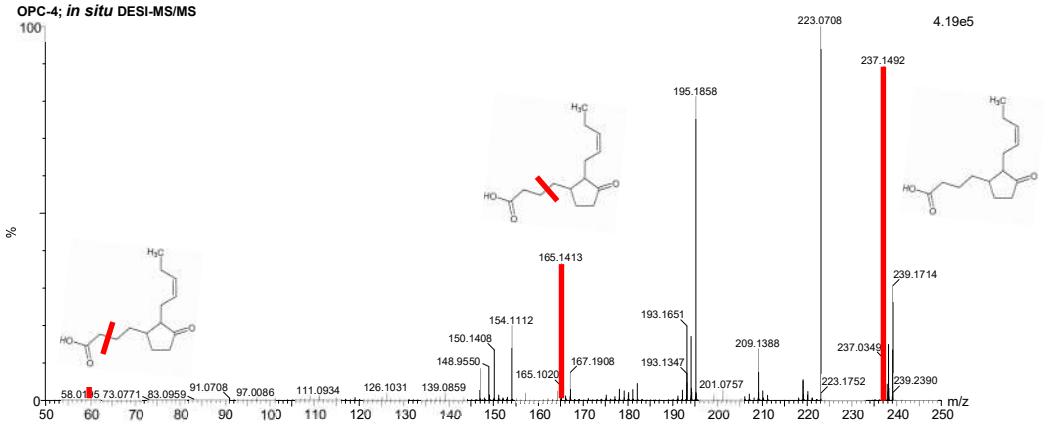




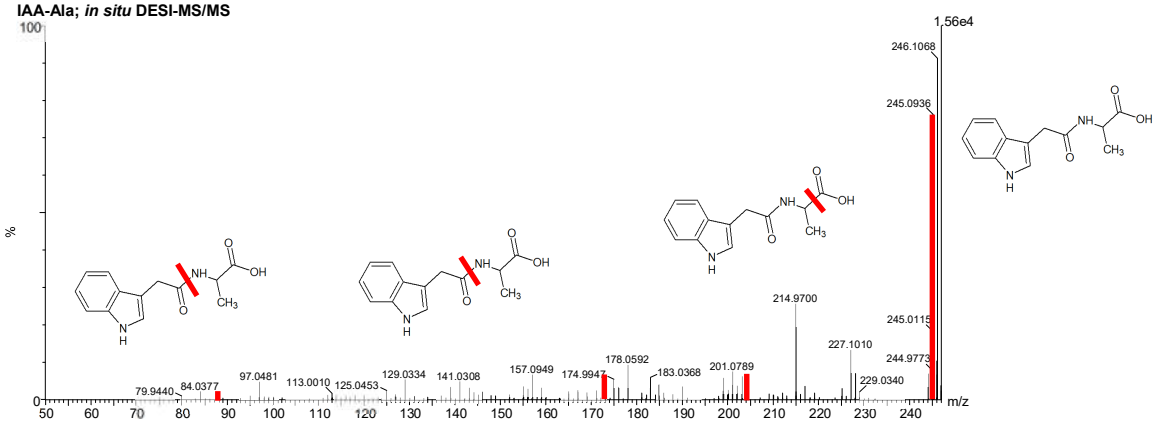
OH-JA; *in situ* DESI-MS/MS



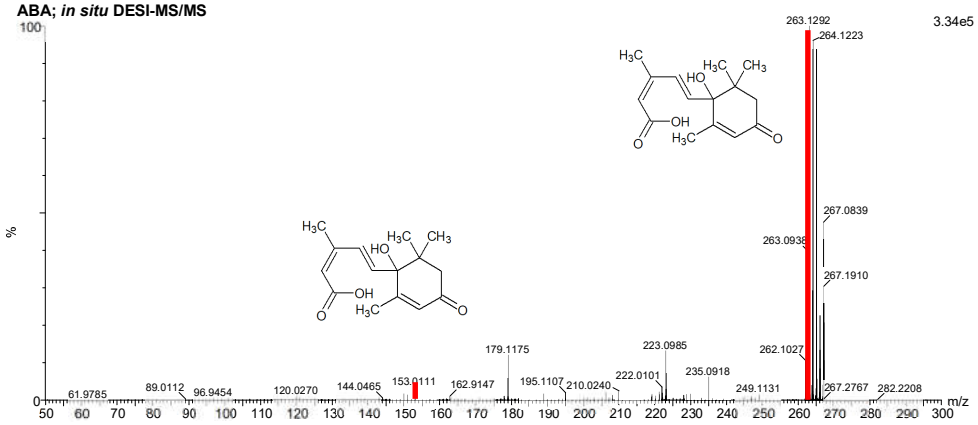
OPC-4; *in situ* DESI-MS/MS



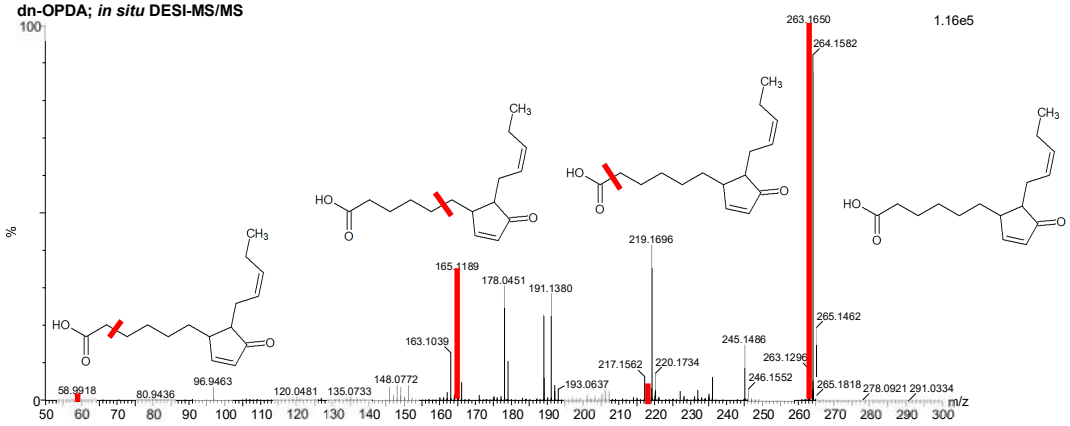
IAA-Ala; *in situ* DESI-MS/MS



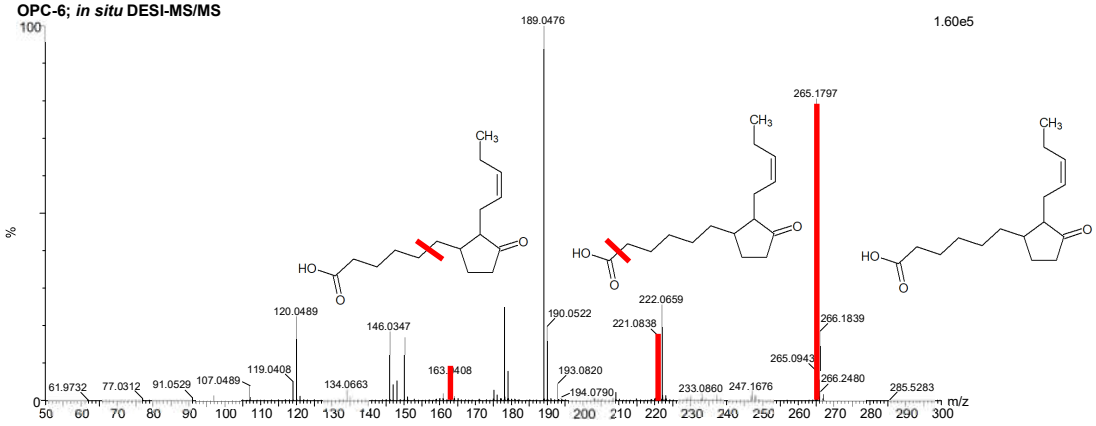
ABA; *in situ* DESI-MS/MS



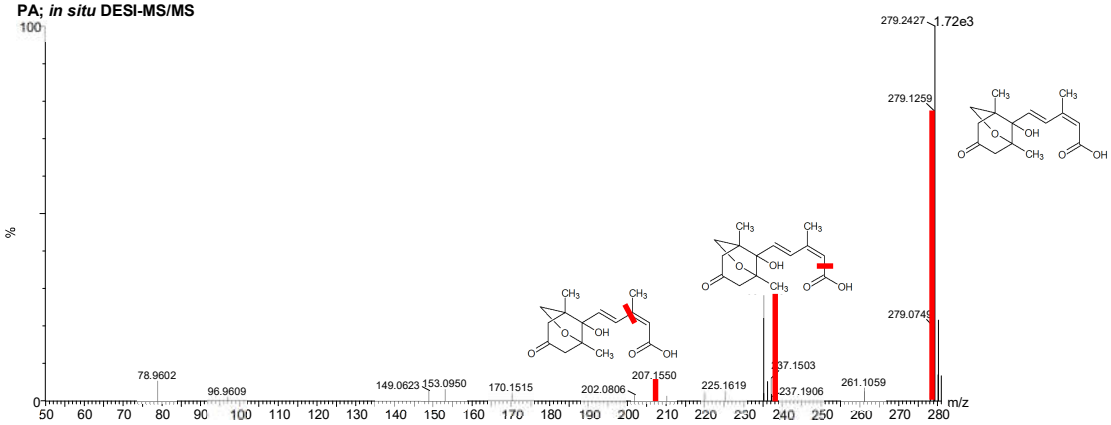
dn-OPDA; *in situ* DESI-MS/MS



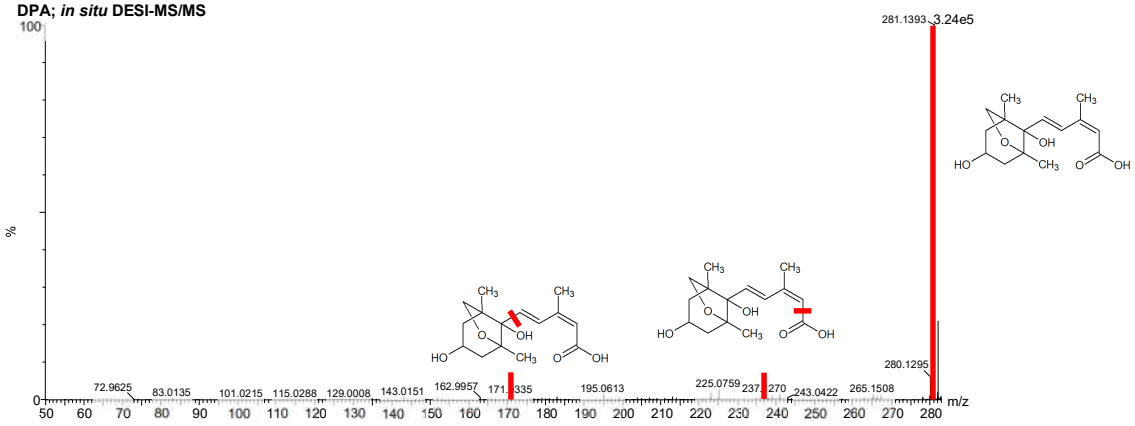
OPC-6; *in situ* DESI-MS/MS



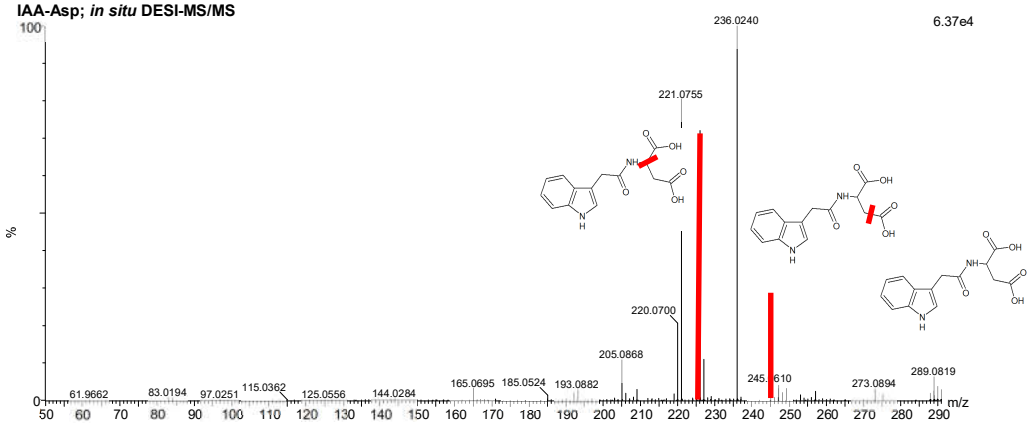
PA; *in situ* DESI-MS/MS



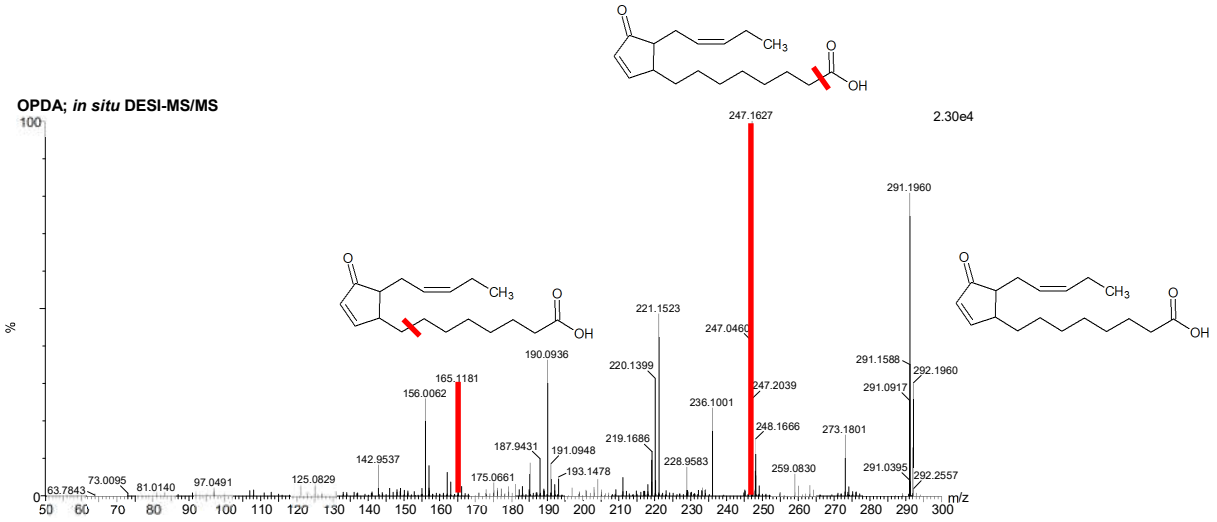
DPA; *in situ* DESI-MS/MS



IAA-Asp; *in situ* DESI-MS/MS



OPDA; *in situ* DESI-MS/MS



OPC-8; *in situ* DESI-MS/MS