On flow injection (routine service)

High-resolution mass spectra were acquired on a *QExactive* instrument (*ThermoFisher Scientific*, Bremen, Germany) equipped with a heated electrospray (ESI) ionization source and connected to a *Dionex Ultimate 3000* UHPLC system (*ThermoFischer Scientifics*, Germering, Germany). The samples were dissolved in MeOH, MeOH/CH_2Cl_2 3:1, MeOH/H_2O 1:1, DMSO/H_2O 1:10, or H_2O at a concentration of ca. 50 µg•ml^{-1} thereof 1 µl was injected on-flow with a XRS auto-sampler (*CTC*, Zwingen, Switzerland). The mobile phase (120 µl ml^{-1} flow rate) consisting of MeOH + 0.1 % HCOOH or acetonitrile/H_2O 2:8 + 0.1% HCOOH was chosen according to the solubility. Ion source parameters were set as follow: spray voltage 3.0 kV; capillary temperature 280°C; sheath gas 30 l min^{-1}; aux gas 8 30 l min^{-1}; s-lens RF level 55.0; and aux gas temperature 250°C.

Full scan MS were acquired in the alternating (+)/(–)-ESI mode and over the ranges *m/z* 80-1'200, 133-2'000, or 200-3'000 at 70'000 resolution (full width half-maximum) and with automatic gain control (AGC) target of 3.00E +06. The maximum allowed ion transfer time (IT) was 30 ms. Masses were calibrated below 2 ppm accuracy between *m/z* 130.06619 and 1621.96509 in the positive and between 265.14790 and 1779.96528 in the negative ESI mode using the Pierce® ESI calibration solutions (ThermoFisher Scientific, Rockford, USA). Additionally, contaminations of erucamide (*m/z* 338.34174, (+)-ESI) and palmitic acid (*m/z* 255.23295, (–)-ESI) were used as lock masses in (+)- and (–)-ESI, respectively.

LC-MS

Samples (1 µl injection) were analyzed with a *Dionex Ultimate 3000* UHPLC system (*ThermoFischer Scientifics*, Germering, Germany) connected to an *Acquity* eλ detector and a *QExactive* high-resolution mass spectrometer (*ThermoFisher Scientific*, Bremen, Germany) equipped with a heated electrospray (ESI) ionization source. Separation was performed with an *Acquity BEH C18* HPLC column (1.7 µm particle size, 2x100 mm, *Waters*) kept at 30 °C. The mobile phase was consisting of A: H_2O + 0.1% HCOOH and B: CH_3CN + 0.1% HCOOH. A linear gradient was run from 5 to 98% B within 5 min followed by flushing with 98% B for 1 min at 400 µl min^{-1} flow rate. UV spectra were recorded between 200 and 600 nm at 1.2 nm resolution and 20 points s^{-1}. MS ion source parameters were set as follows: spray voltage, 3.5 kV; capillary temperature, 260°C; sheath gas 45 l min^{-1}; aux gas 15 l•min^{-}1; sweep gas 2 l min^{-}1; s-lens RF level 450.0, and aux gas temperature 250°C.

Full scan MS were acquired in the (+) ESI mode and over the ranges *m/z* 80-1'200, 133-2'000, or 200-3'000 at 70'000 resolution (full width half-maximum) and with automatic gain control (AGC) target of 3.00E +06. The maximum allowed ion transfer time (IT) was 30 ms. Masses were calibrated below 2 ppm accuracy between *m/z* 130.06619 and 1621.96509 in the positive and between 265.14790 and 1779.96528 in the negative ESI mode using the Pierce® ESI calibration solutions (ThermoFisher Scientific, Rockford, USA). Additionally, contaminations of erucamide (*m/z* 338.34174, (+)-ESI) and palmitic acid (*m/z* 255.23295, (-)ESI) were used as lock masses in (+)- and (-)-ESI, respectively.