Continuous flow injection

High-resolution electrospray mass spectra (HR-ESI-MS) were recorded on a *maXis* QTOF-MS instrument (*Bruker Daltonics* GmbH, Bremen, Germany). The samples were dissolved in (e.g. MeOH) at a concentration of ca. 50 µg/ml and analyzed via continuous flow injection (2 µL/min). The mass spectrometer was operated in the positive (or negative) electrospray ionization mode at 4'000 V (-4'000 V) capillary voltage, -500 V (500 V) endplate offset, with a N_2 nebulizer pressure of 0.8 bar and dry gas flow of 4 l min^{-1} at 180°C. Mass spectra were acquired in the mass range from *m/z* 50 to 2'000 at 20'000 resolution (full width at half maximum) and 1.0 Hz rate. The mass analyzer was calibrated between *m/z* 118 and 2721 using an *Agilent* ESI-L low concentration tuning mix solution (*Agilent*, USA) at a resolution of 20'000 and a mass accuracy below 2 ppm. All solvent used were purchased in best LC-MS qualities.

LC-MS

Samples (1 µl injection) were analyzed with an *Acquity UPLC* (*Waters*, Milford, USA) connected to an *Acquity* eλ detector and a *maXis* QTof high-resolution mass spectrometer (*Bruker Daltonics*, Bremen, Germany). 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}. The mass spectrometer was operated in the positive (negative) electrospray ionization mode at 4'000 V (-4'000 V) capillary voltage, -500 V (500 V) endplate offset, with a N_2 nebulizer pressure of 1.6 bar and dry gas flow of 8 l min^{-1} at 200°C. Spectra were acquired in the mass range from *m/z* 50 to 2'000 at 20'000 resolution (full width at half maximum) and 1.5 Hz rate. The mass analyzer was calibrated prior analysis between *m/z* 158 and 1450 using a 2 mM solution of sodium formate at a resolution of 20'000 and a mass accuracy below 2 ppm.

LC-MS/MS

Samples (1 µl injection) were analyzed with an *Acquity UPLC* (*Waters*, Milford, USA) connected to an *Acquity* eλ detector and a *maXis* QTof high-resolution mass spectrometer (*Bruker Daltonics*, Bremen, Germany). 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}. The mass spectrometer was operated in the positive (negative) electrospray ionization mode at 4'000 V (-4'000 V) capillary voltage, -500 V (500 V) endplate offset, with a N_2 nebulizer pressure of 1.6 bar and dry gas flow of 8 l min^{-1} at 200°C. Spectra were acquired in the mass range from *m/z* 50 to 2'000 at 20'000 resolution (full width at half maximum) and 1.5 Hz rate. The mass analyzer was calibrated prior analysis between *m/z* 158 and 1450 using a 2 mM solution of sodium formate at a resolution of 20'000 and a mass accuracy below 2 ppm. MS/MS spectra were acquired at (35 eV) collision energy with 3 *m/z* isolation width, N_2 as collision gas, in the mass range from *m/z* 50 to 600, and at 2.0 Hz rate.