Electronic Supplementary Information for the study entitled

Water soluble selenometabolome of *Cardamine violifolia*

by

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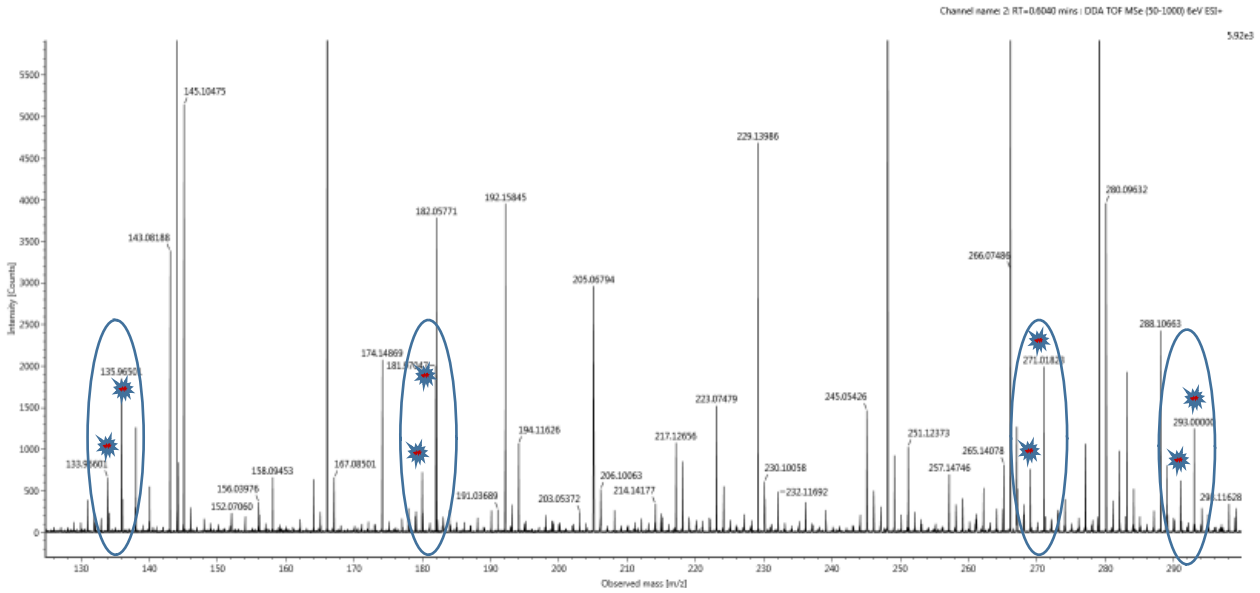


Fig. S1: Full scan spectrum from Fr4, showing the selenocystathionine related selenium patterns (in-source fragments, parent molecule and sodium adduct). Stars indicate the ^{78}Se-^{80}Se isotopologues.

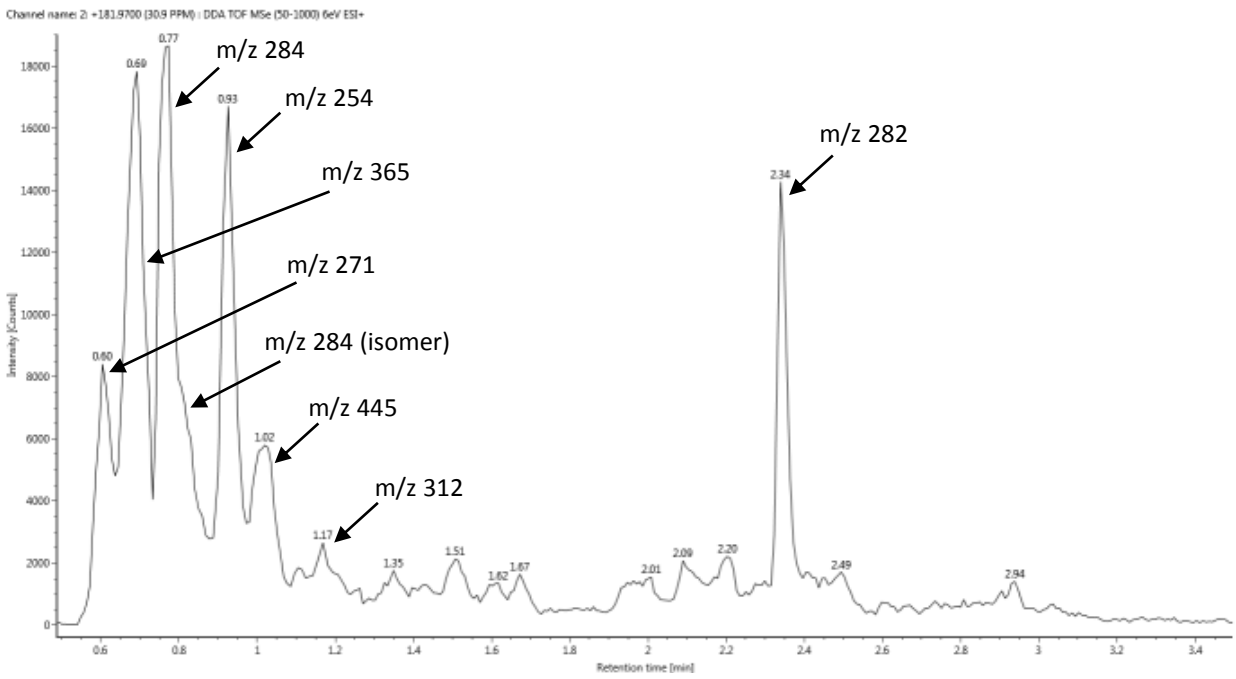
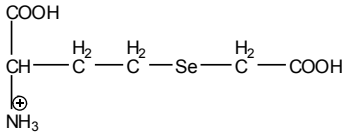
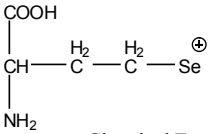


Fig. S2: Extracted ion chromatogram of selenohomocysteine ion-source fragment (m/z 181.97). Arrows and values indicate the corresponding and detected selenium species (see Table 1 for further information).

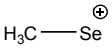


Chemical Formula: $C_6H_{12}NO_4Se^+$
Exact Mass: 241.9926

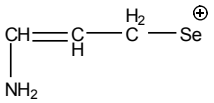
Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
181.97069	C4H8NO2Se+	181.97150	-4.45
135.96558	C3H6NSe+	135.96600	-3.09
108.95336	C2H5Se+	108.95510	-15.97
94.93872	CH3Se+	94.93940	-7.16



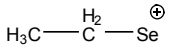
Chemical Formula: $C_4H_8NO_2Se^+$
Exact Mass: 181.9715



Chemical Formula: CH_3Se^+
Exact Mass: 94.9394

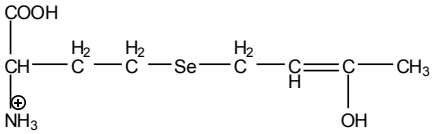


Chemical Formula: $C_3H_6NSe^+$
Exact Mass: 135.9660



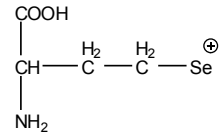
Chemical Formula: $C_2H_5Se^+$
Exact Mass: 108.9551

Fig. S3: Proposed structures of the m/z 241.9926 compound and its MS/MS fragments, together with mass accuracy data of the fragments (see Fig. 2).

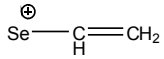


Chemical Formula: $C_8H_{16}NO_3Se^+$
Exact Mass: 254.0290

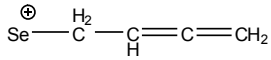
Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
181.97047	C4H8NO2Se+	181.9715	-5.66
135.96649	C3H6NSe+	135.966	3.60
134.96881	C4H7Se+	134.97070	-14.00
132.95525	C4H5Se+	132.95510	1.13
106.93961	C2H3Se+	106.93940	1.96



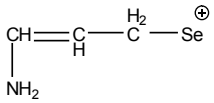
Chemical Formula: $C_4H_8NO_2Se^+$
Exact Mass: 181.9715



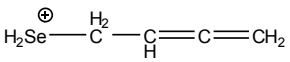
Chemical Formula: $C_2H_3Se^+$
Exact Mass: 106.9394



Chemical Formula: $C_4H_5Se^+$
Exact Mass: 132.9551

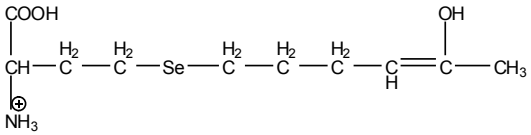


Chemical Formula: $C_3H_6NSe^+$
Exact Mass: 135.9660



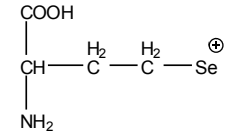
Chemical Formula: $C_4H_7Se^+$
Exact Mass: 134.9707

Fig. S4: Proposed structures of the m/z 254.0289 compound and its MS/MS fragments, together with mass accuracy data of the fragments (see Fig. 3).

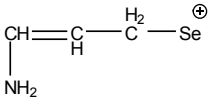


Chemical Formula: $C_{10}H_{20}NO_3Se^+$
Exact Mass: 282.0603

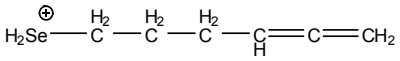
Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
181.97079	C4H8NO2Se+	181.97150	-3.90
163.00156	C6H11Se+	163.00200	-2.70
135.96549	C3H6NSe+	135.96600	-3.75



Chemical Formula: $C_4H_8NO_2Se^+$
Exact Mass: 181.9715

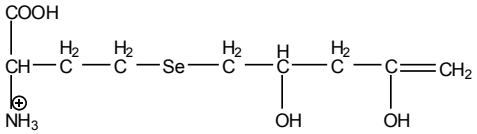


Chemical Formula: $C_3H_6NSe^+$
Exact Mass: 135.9660

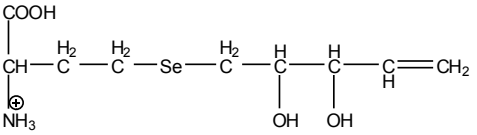


Chemical Formula: $C_6H_{11}Se^+$
Exact Mass: 163.0020

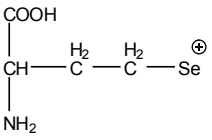
Fig. S5: Proposed structures of the m/z 282.0603 compound and its MS/MS fragments, together with mass accuracy data of the fragments (see Fig. 4).



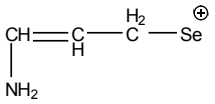
Chemical Formula: $C_9H_{18}NO_4Se^+$
Exact Mass: 284.0396



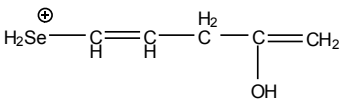
Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
181.97079	C4H8NO2Se+	181.97150	-3.90
164.98097	C5H9OSe+	164.98130	-2.00
146.97314	C5H7Se+	146.97070	16.60
135.96549	C3H6NSe+	135.96600	-3.75
102.05505	C4H8NO2+	102.05500	0.49



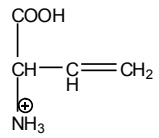
Chemical Formula: $C_4H_8NO_2Se^+$
Exact Mass: 181.9715



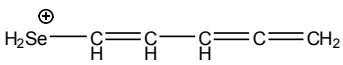
Chemical Formula: $C_3H_6NSe^+$
Exact Mass: 135.9660



Chemical Formula: $C_5H_9OSe^+$
Exact Mass: 164.9813

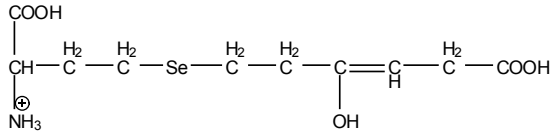


Chemical Formula: $C_4H_8NO_2^+$
Exact Mass: 102.0550



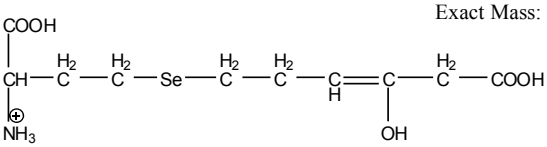
Chemical Formula: $C_5H_7Se^+$
Exact Mass: 146.9707

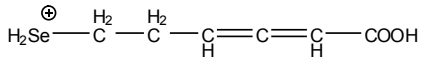
Fig. S6: Proposed structures of the m/z 284.0396 compounds and their MS/MS fragments, together with mass accuracy data of the fragments (see Fig. 5).



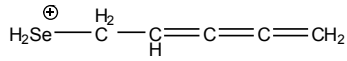
Chemical Formula: $C_{10}H_{18}NO_5Se^+$
Exact Mass: 312.0345

Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
192.98019	C6H9O2Se+	192.97620	20.68
181.97047	C4H8NO2Se+	181.97150	-5.66
164.98220	C5H9OSe+	164.98130	5.46
146.97114	C5H7Se+	146.97070	2.99
135.96501	C3H6NSe+	135.96600	-7.28

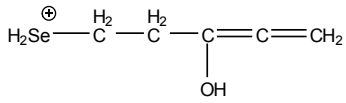




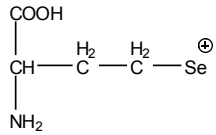
Chemical Formula: $C_6H_9O_2Se^+$
Exact Mass: 192.9762



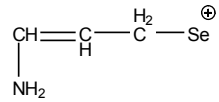
Chemical Formula: $C_5H_7Se^+$
Exact Mass: 146.9707



Chemical Formula: $C_5H_9OSe^+$
Exact Mass: 164.9813

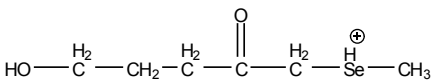


Chemical Formula: $C_4H_8NO_2Se^+$
Exact Mass: 181.9715



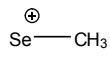
Chemical Formula: $C_3H_6NSe^+$
Exact Mass: 135.9660

Fig. S7: Proposed structures of the m/z 312.0345 compounds and their MS/MS fragments, together with mass accuracy data of the fragments (see Fig. 6).

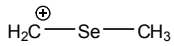


Chemical Formula: $C_6H_{13}O_2Se^+$
Exact Mass: 197.0075

Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
108.95479	C2H5Se+	108.9551	-2.85
94.93865	CH3Se+	94.9394	-7.90

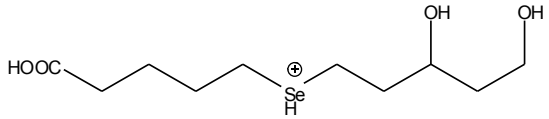


Chemical Formula: CH_3Se^+
Exact Mass: 94.9394

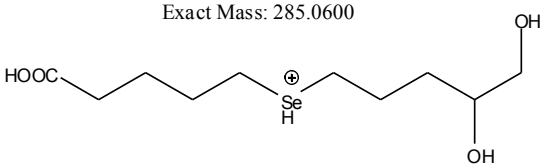


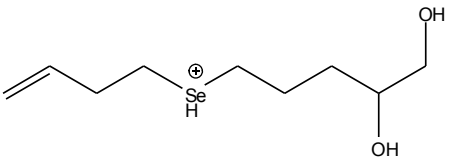
Chemical Formula: $C_2H_5Se^+$
Exact Mass: 108.9551

Fig. S8: Proposed structures of the m/z 197.0075 compound and its MS/MS fragments, together with mass accuracy data of the fragments (see Fig. 7).



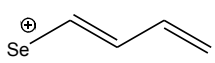
Chemical Formula: $C_{10}H_{21}O_4Se^+$
Exact Mass: 285.0600



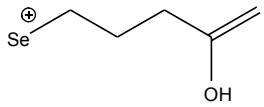


Chemical Formula: $C_9H_{19}O_2Se^+$
Exact Mass: 239.0545

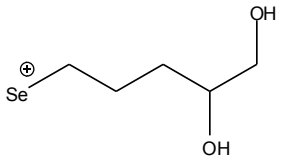
Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
239.05915	C9H19O2Se+	239.05450	19.45
182.99294	C5H11O2Se+	182.99190	5.68
164.98200	C5H9OSe+	164.98130	4.24
134.96998	C4H7Se+	134.97070	-5.33
132.95493	C4H5Se+	132.95510	-1.28
106.93922	C2H3Se+	106.93940	-1.68
85.06494	C5H9O+	85.06480	1.65



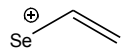
Chemical Formula: $C_4H_5Se^+$
Exact Mass: 132.9551



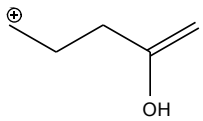
Chemical Formula: $C_5H_9OSe^+$
Exact Mass: 164.9813



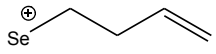
Chemical Formula: $C_5H_{11}O_2Se^+$
Exact Mass: 182.9919



Chemical Formula: $C_2H_3Se^+$
Exact Mass: 106.9394



Chemical Formula: $C_5H_9O^+$
Exact Mass: 85.0648



Chemical Formula: $C_4H_7Se^+$
Exact Mass: 134.9707

Fig. S9: Proposed structures of the m/z 285.0600 compounds and their MS/MS fragments, together with mass accuracy data of the fragments (see Fig. 8).

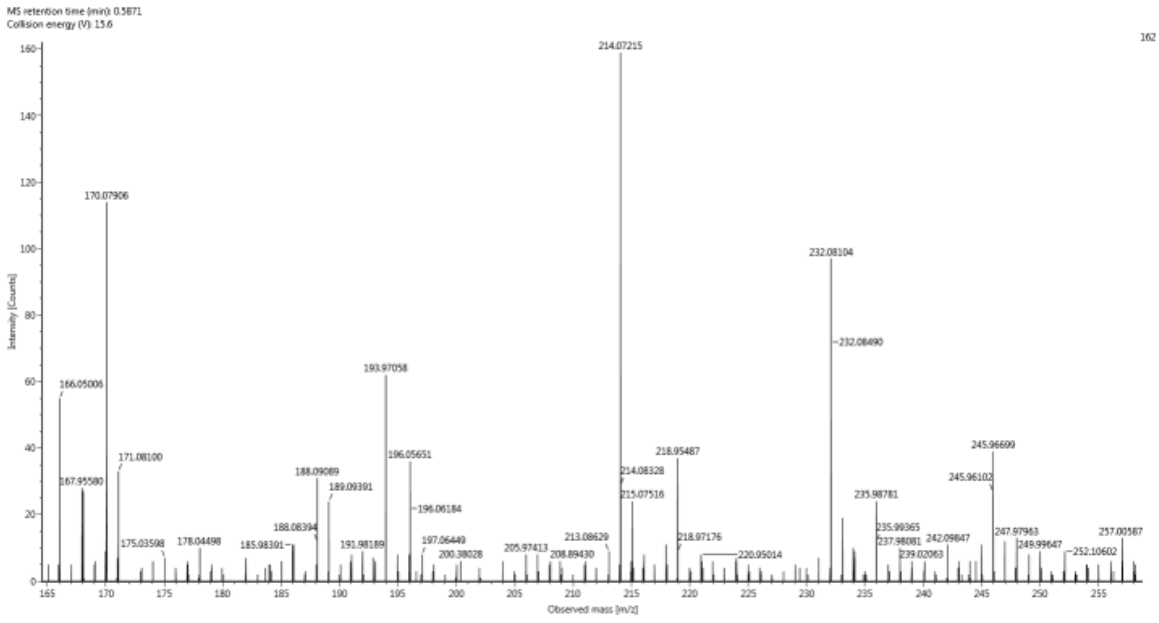
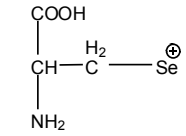
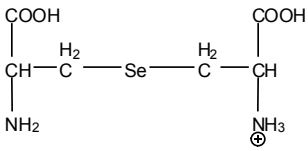


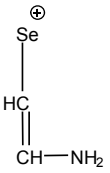
Fig. S10: Additional (zoomed) MS/MS spectrum of the m/z 581.1092 compound (see Fig. 9 and S11).



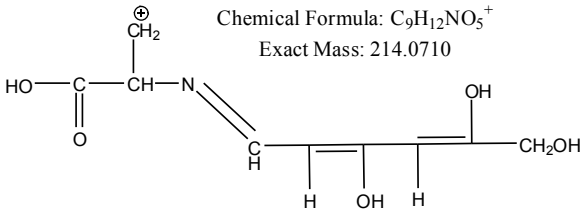
Chemical Formula: $C_3H_6NO_2Se^+$
Exact Mass: 167.9558



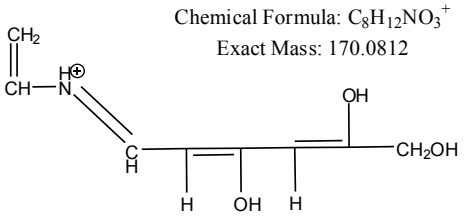
Chemical Formula: $C_6H_{13}N_2O_4Se^+$
Exact Mass: 257.0035



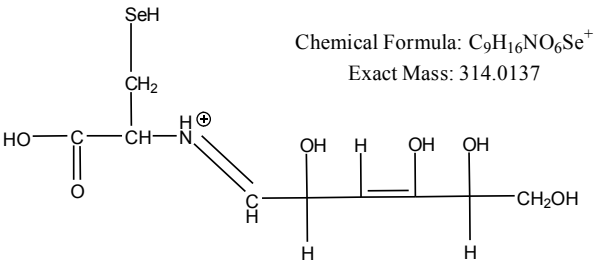
Chemical Formula: $C_2H_4NSe^+$
Exact Mass: 121.9503



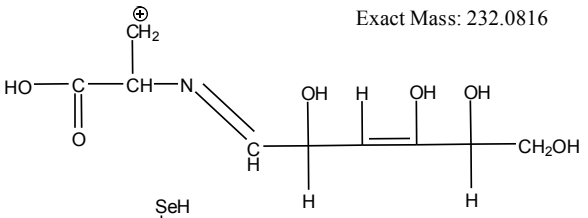
Chemical Formula: $C_9H_{12}NO_5^+$
Exact Mass: 214.0710



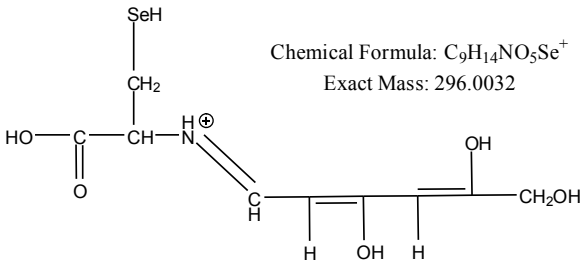
Chemical Formula: $C_8H_{12}NO_3^+$
Exact Mass: 170.0812



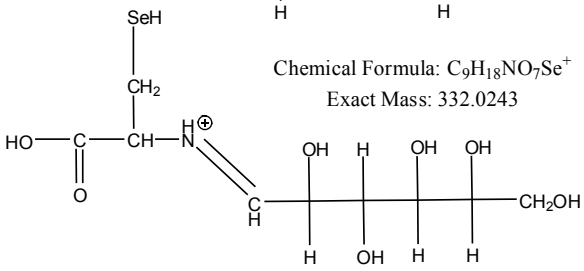
Chemical Formula: $C_9H_{16}NO_6Se^+$
Exact Mass: 314.0137



Chemical Formula: $C_9H_{14}NO_6^+$
Exact Mass: 232.0816

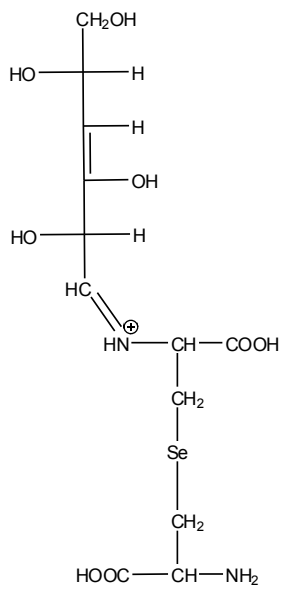


Chemical Formula: $C_9H_{14}NO_5Se^+$
Exact Mass: 296.0032

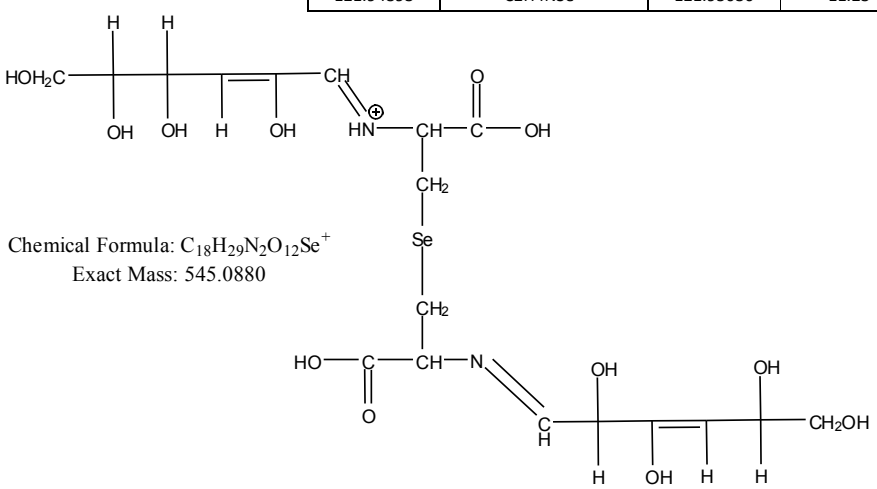


Chemical Formula: $C_9H_{18}NO_7Se^+$
Exact Mass: 332.0243

Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
545.08614	C18H29N2O12Se+	545.08800	-3.41
401.04552	C12H21N2O8Se+	401.04580	-0.70
332.03000	C9H18NO7Se+	332.02430	17.17
314.00981	C9H16NO6Se+	314.01370	-12.39
296.00129	C9H14NO5Se+	296.00320	-6.45
257.0079	C6H13N2O4Se+	257.00350	17.12
232.08104	C9H14NO6+	232.08160	-2.41
214.07215	C9H12NO5+	214.07100	5.37
170.07906	C8H12NO3+	170.08120	-12.58
167.95415	C3H6NO2Se+	167.95580	-9.82
121.94893	C2H4NSe+	121.95030	-11.23

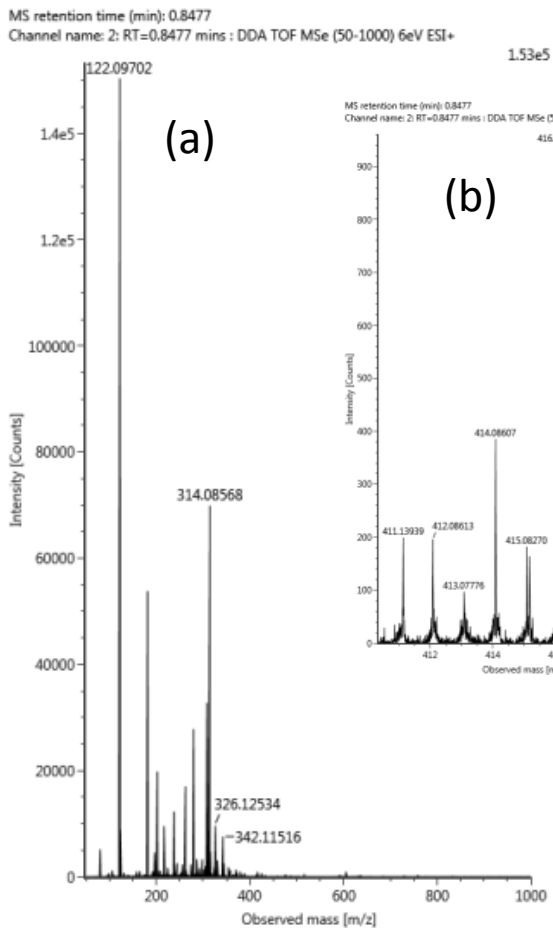


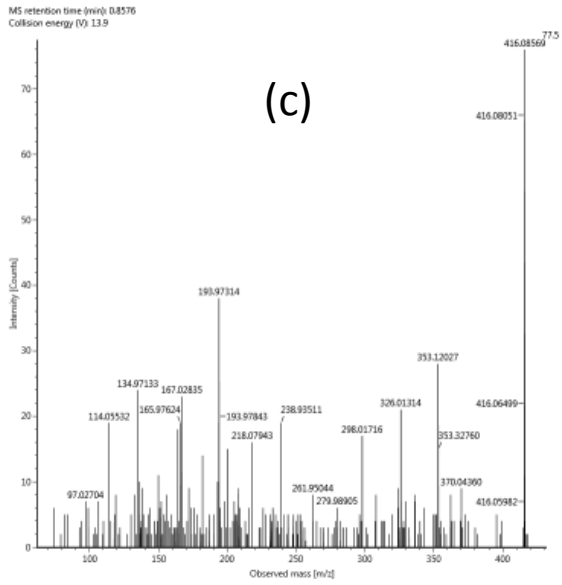
Chemical Formula: $C_{12}H_{21}N_2O_8Se^+$
Exact Mass: 401.0458

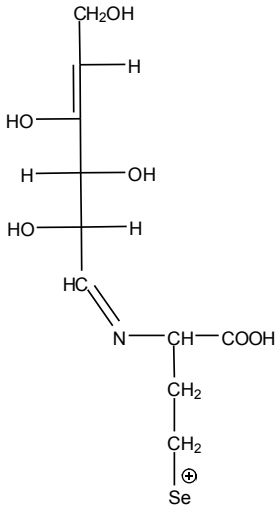


Chemical Formula: $C_{18}H_{29}N_2O_{12}Se^+$
Exact Mass: 545.0880

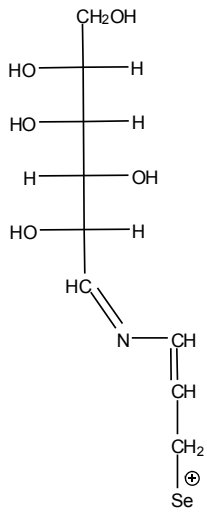
Fig. S11: Proposed structures of the MS/MS fragments of the m/z 419.0568 and 581.1092 compounds, together with mass accuracy data of the fragments (see Fig. 9).



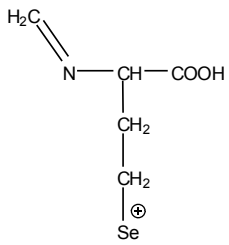




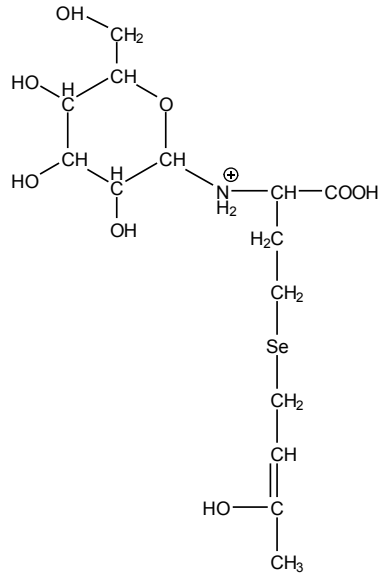
Chemical Formula: $C_{10}H_{16}NO_6Se^+$
Exact Mass: 326.0137



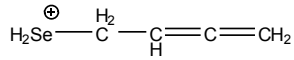
Chemical Formula: $C_9H_{16}NO_5Se^+$
Exact Mass: 298.0188



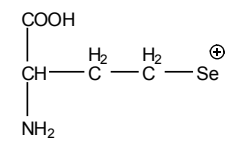
Chemical Formula: $C_5H_8NO_2Se^+$
Exact Mass: 193.9715



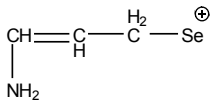
Chemical Formula: $C_{14}H_{26}NO_8Se^+$
Exact Mass: 416.0818



Chemical Formula: $C_4H_7Se^+$
Exact Mass: 134.9707



Chemical Formula: $C_4H_8NO_2Se^+$
Exact Mass: 181.9715



Chemical Formula: $C_3H_6NSe^+$
Exact Mass: 135.9660

Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
326.01314	C10H16NO6Se+	326.01370	-1.72
298.01716	C9H16NO5Se+	298.01880	-5.50
193.97314	C5H8NO2Se+	193.97150	8.45
181.97515	C4H8NO2Se+	181.97150	20.06
135.96461	C3H6NSe+	135.96600	-10.2
134.97133	C4H7Se+	134.97070	4.67

Fig. S12: Compound at the experimental m/z 416.08051 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum, together with the proposed structures and the mass accuracy data of the MS/MS fragments.

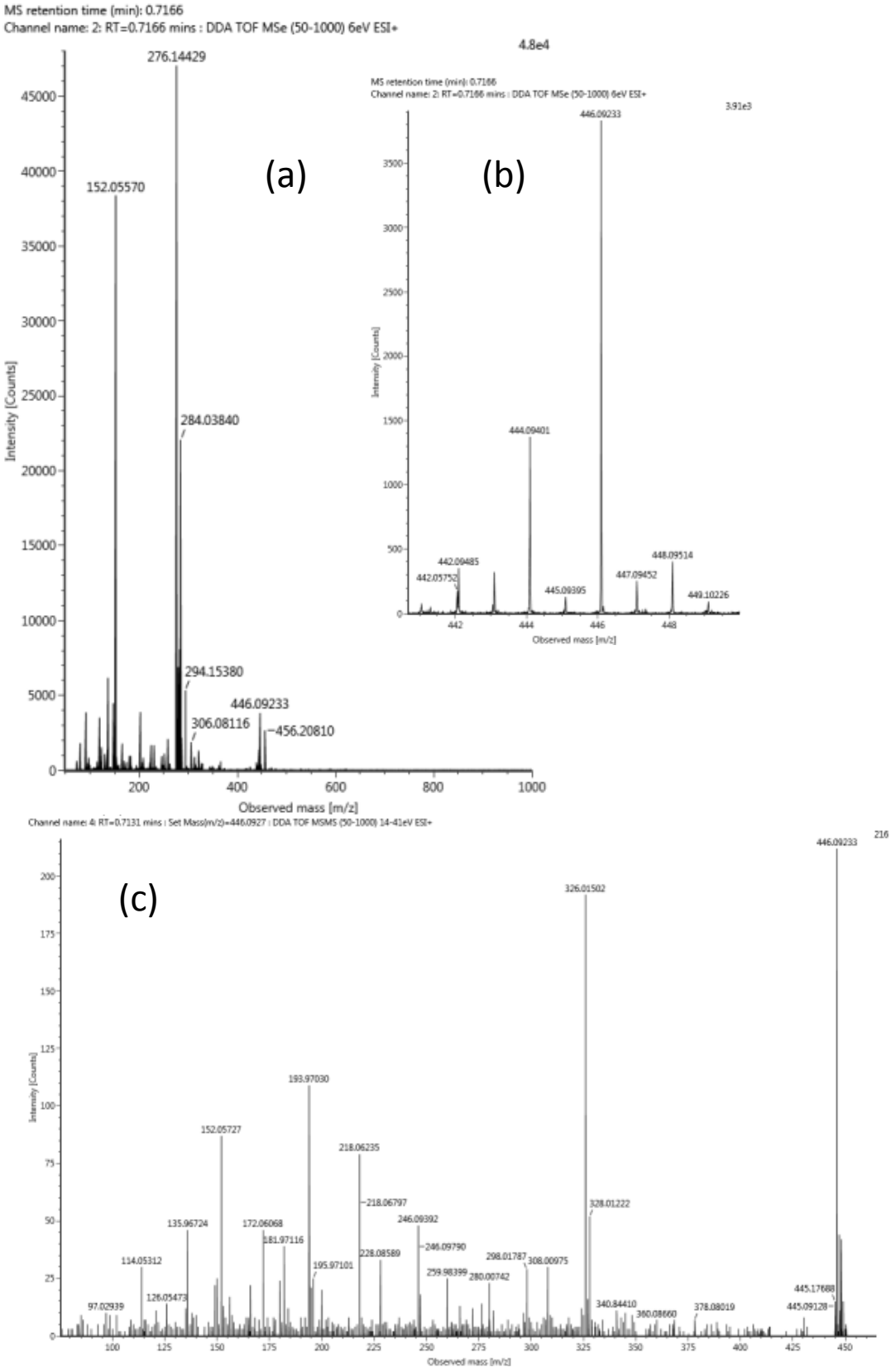
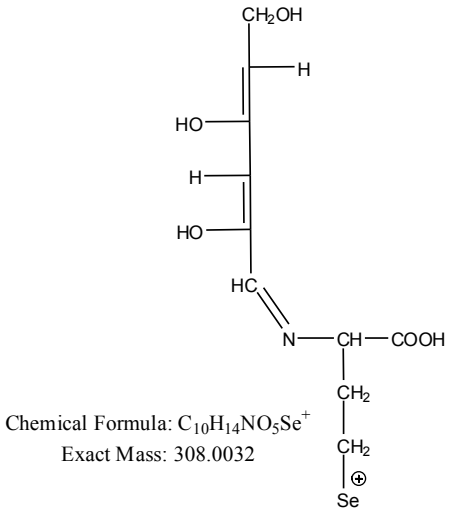
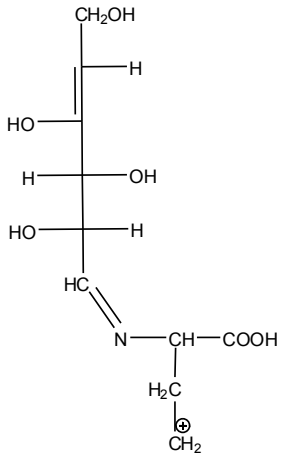


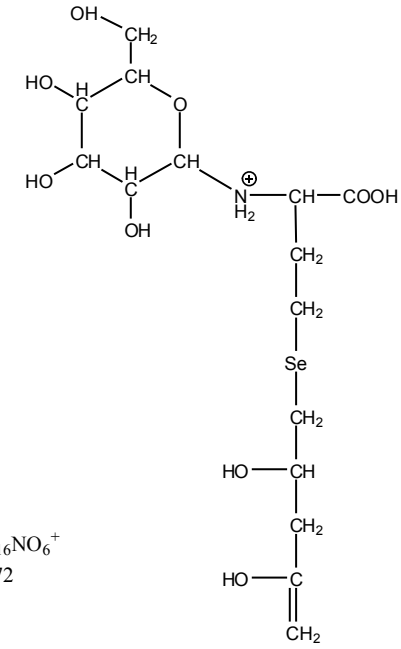
Fig. S13: Compound at the experimental m/z 446.09233 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum, together with the proposed structures and the mass accuracy data of the MS/MS fragments.



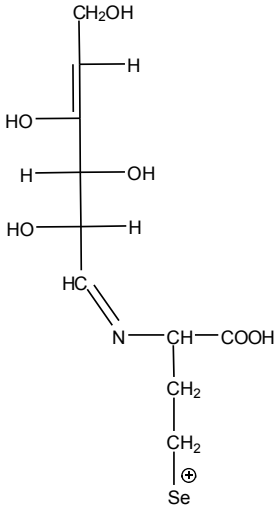
Chemical Formula: $C_{10}H_{14}NO_5Se^+$
Exact Mass: 308.0032



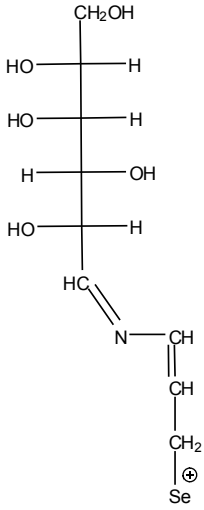
Chemical Formula: $C_{10}H_{16}NO_6^+$
Exact Mass: 246.0972



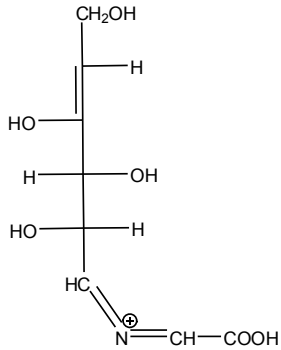
Chemical Formula: $C_{15}H_{28}NO_9Se^+$
Exact Mass: 446.0924



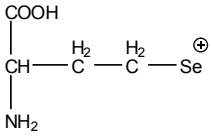
Chemical Formula: $C_{10}H_{16}NO_6Se^+$
Exact Mass: 326.0137



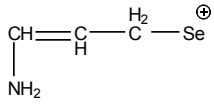
Chemical Formula: $C_9H_{16}NO_5Se^+$
Exact Mass: 298.0188



Chemical Formula: $C_8H_{12}NO_6^+$
Exact Mass: 218.0659



Chemical Formula: $C_4H_8NO_2Se^+$
Exact Mass: 181.9715



Chemical Formula: $C_3H_6NSe^+$
Exact Mass: 135.9660

Experimental m/z	Elemental composition, [M+H]+	Theoretical m/z	Difference, ppm
326.01314	C10H16NO6Se+	326.01370	-1.72
308.00975	C10H14NO5Se+	308.00320	21.27
298.01787	C9H16NO5Se+	298.01880	-3.12
246.09392	C10H16NO6+	246.09720	-13.33
218.06235	C8H12NO6+	218.06590	-16.28
181.97116	C4H8NO2Se+	181.97150	-1.87
135.96724	C3H6NSe+	135.96600	9.12

Fig. S14: Compound at the experimental m/z 446.09233 (for details, see Table 1); proposed structures and the mass accuracy data of the MS/MS fragments.

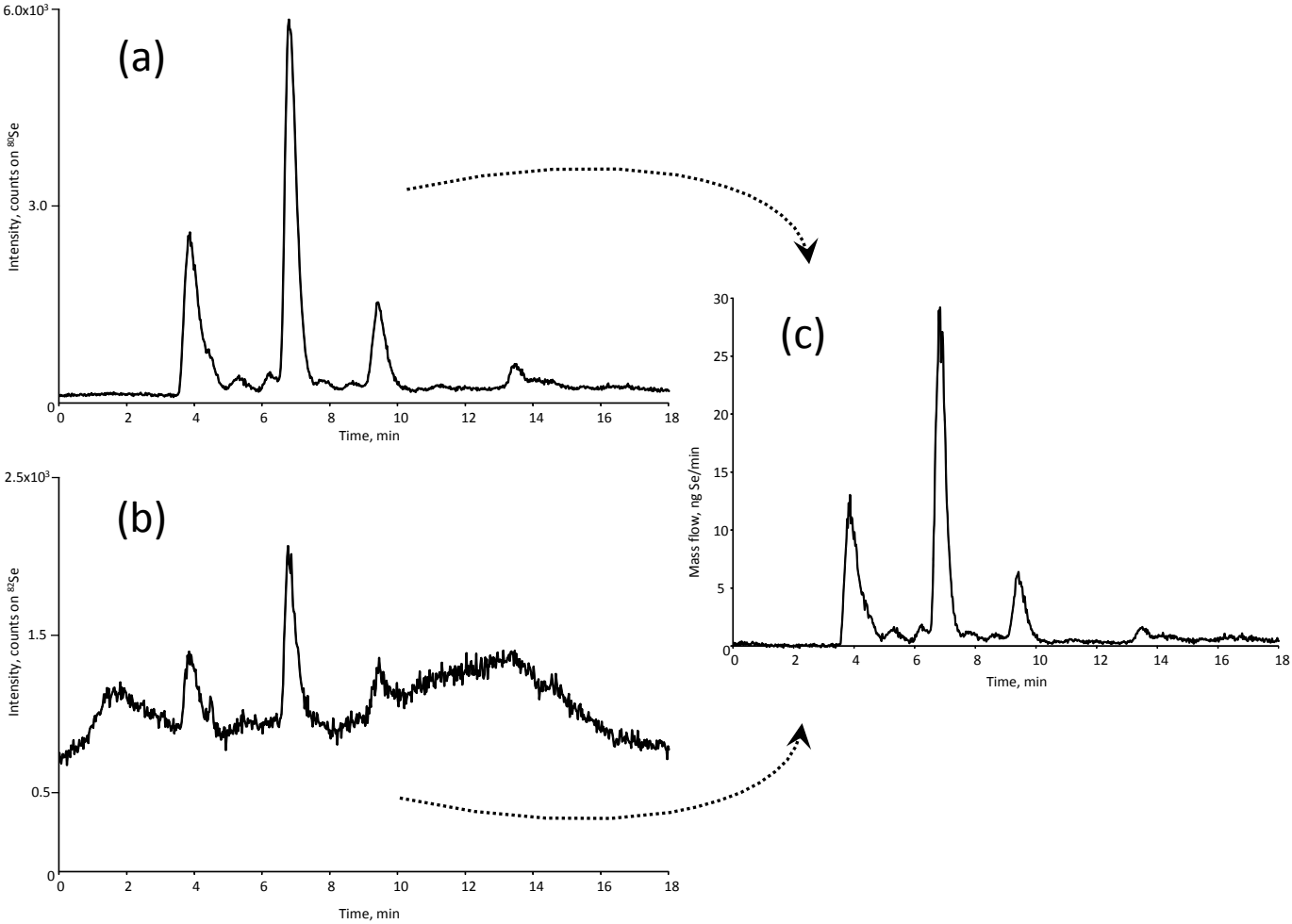


Fig. S15: IP-RP-IDA-ICP-MS based quantification of selenolanthionine (eluting at 6.8 min) extracted from C. violifolia leaves. (a) LC-ICP-MS chromatogram recorded on ^{80}Se; (b) LC-ICP-MS chromatogram recorded on ^{82}Se used for isotope dilution; (c) selenium mass flow calculated from the $^{80}Se/^{82}Se$ data.

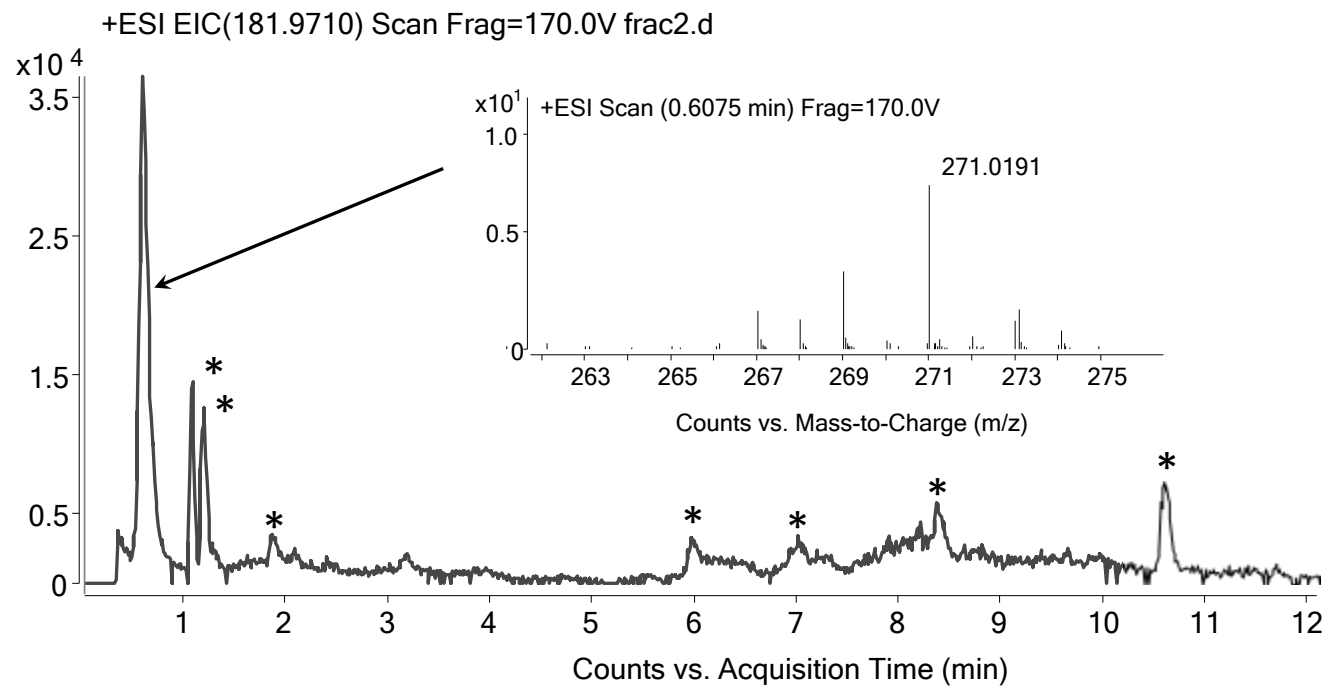


Fig. S16: In-source selenohomocysteine fragment (m/z 181.971) of selenocystathionine from Fraction #4, together with several other minor appearance of this fragment (indicated with '*'). Data were recorded on an Agilent 6530 ESI-QTOFMS instrument.

Known selenium species (other than selenolanthionine) detected in the water soluble selenometabolome of C. violifolia

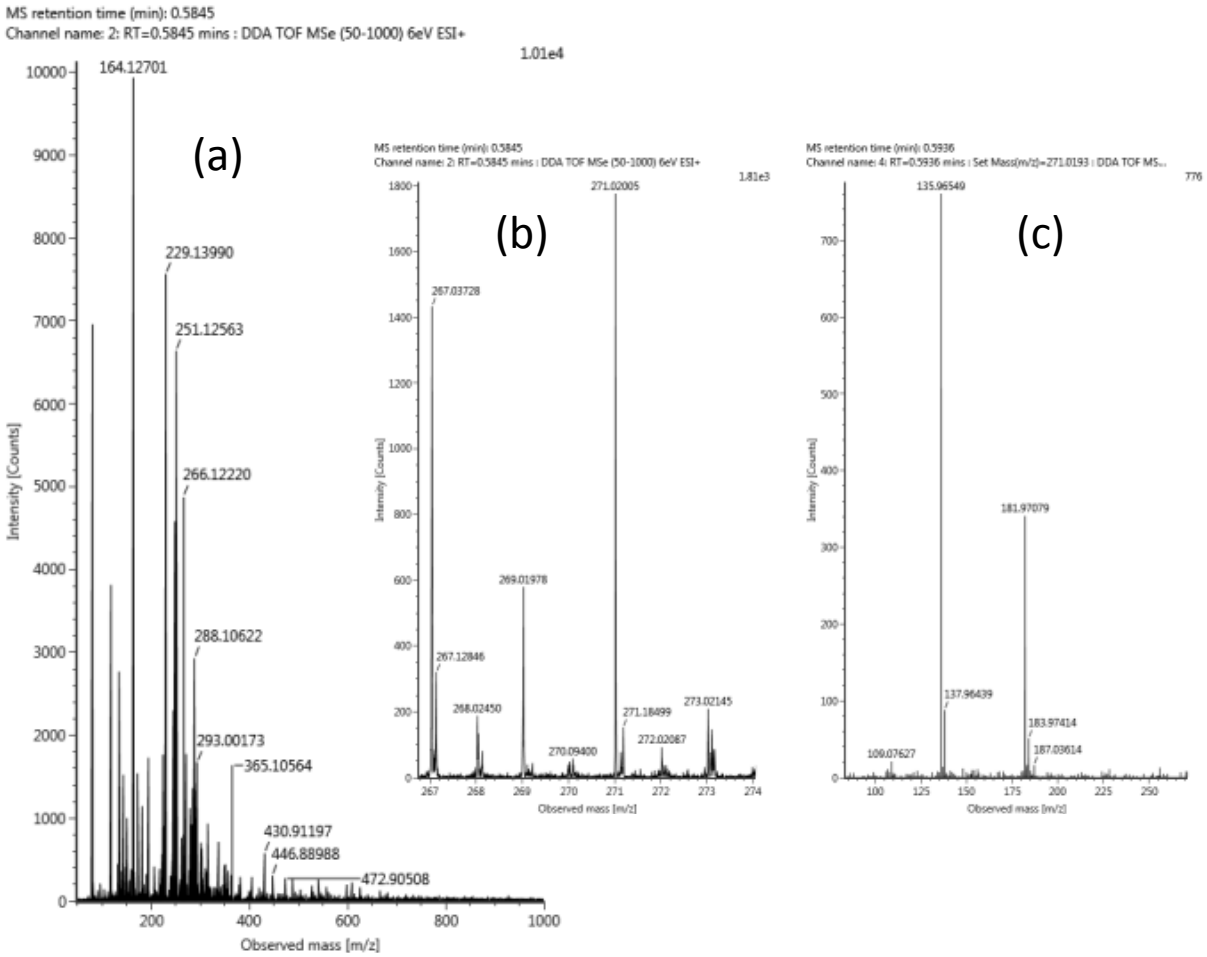


Fig. S17: Selenocystathionine (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

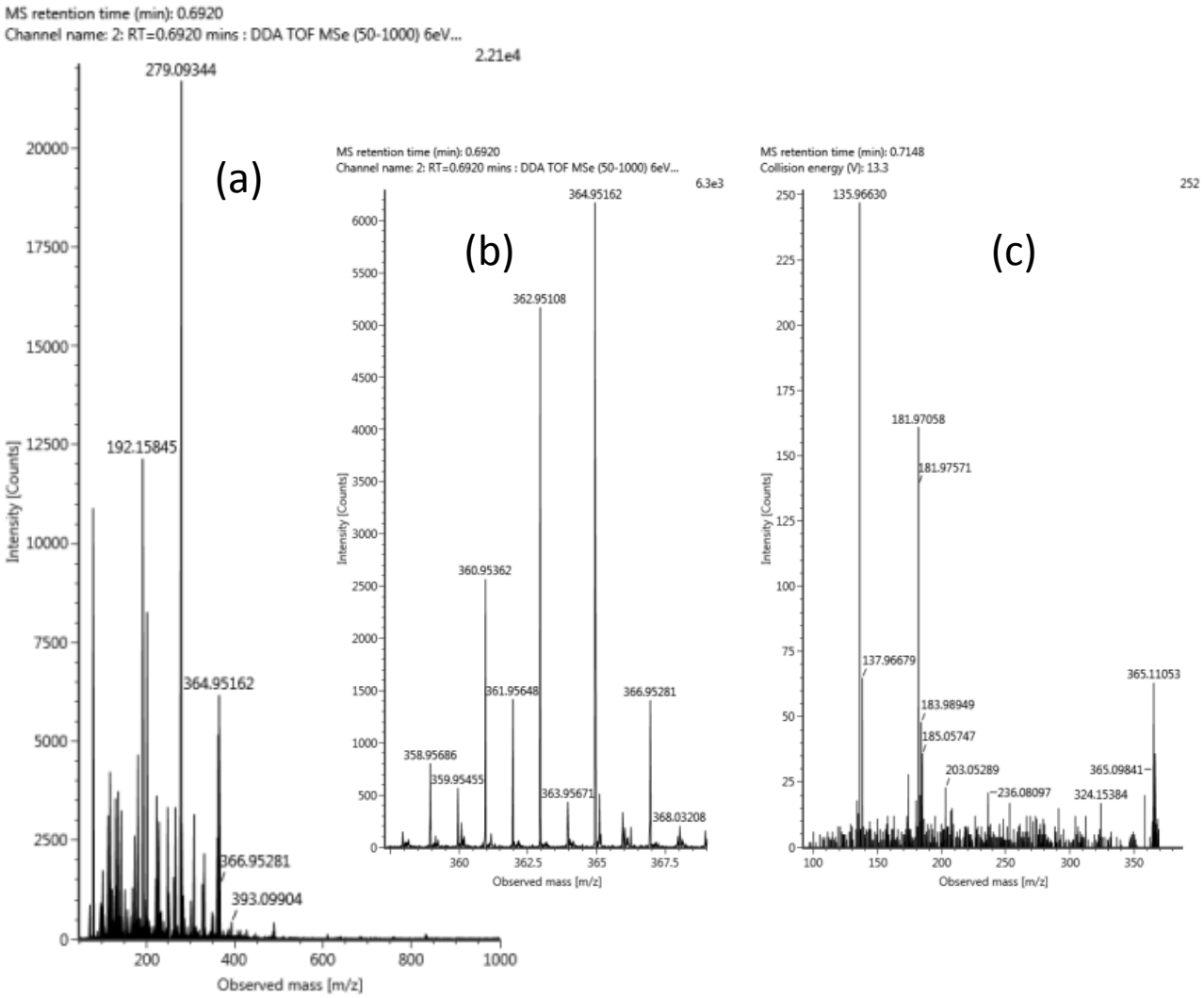


Fig. S18: Selenohomocystine (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

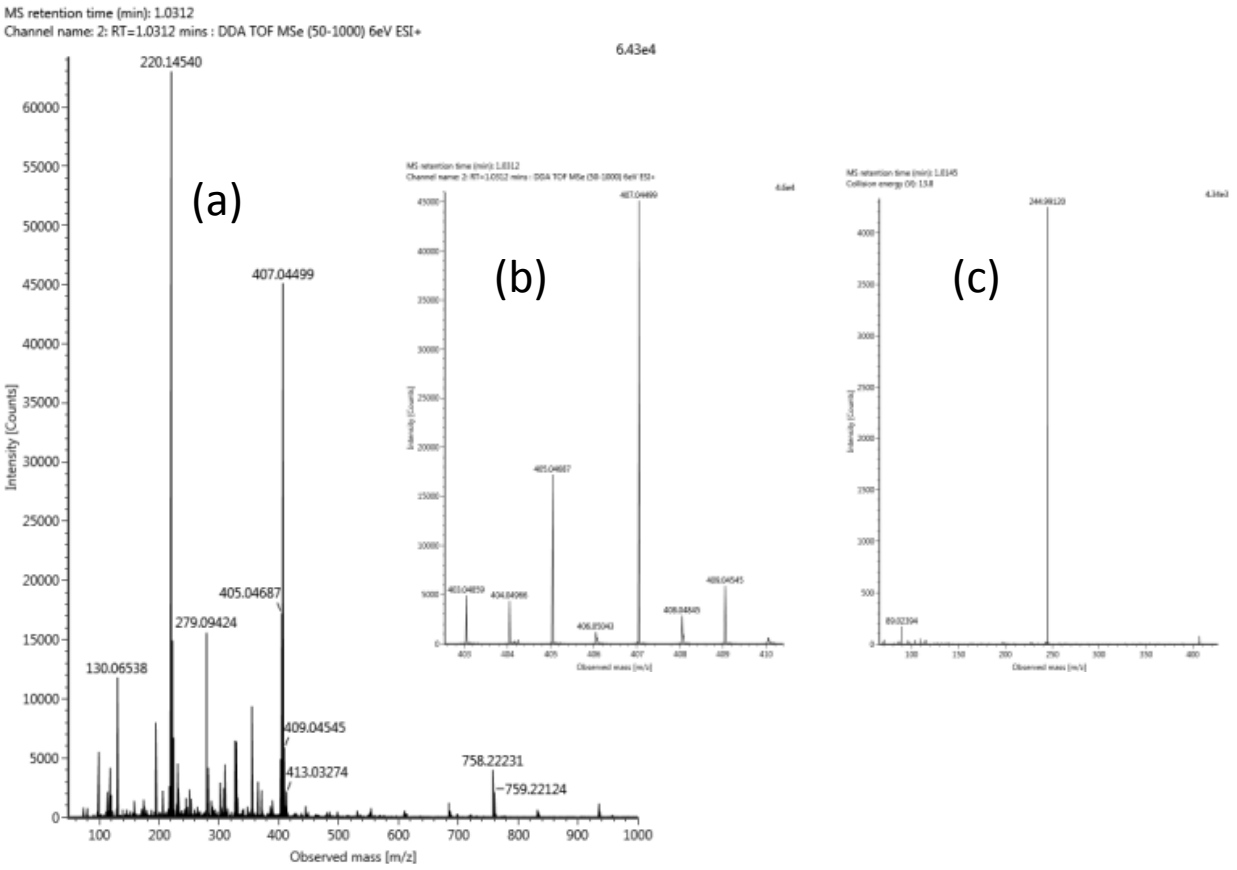


Fig. S19: Selenosugar at m/z 407 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

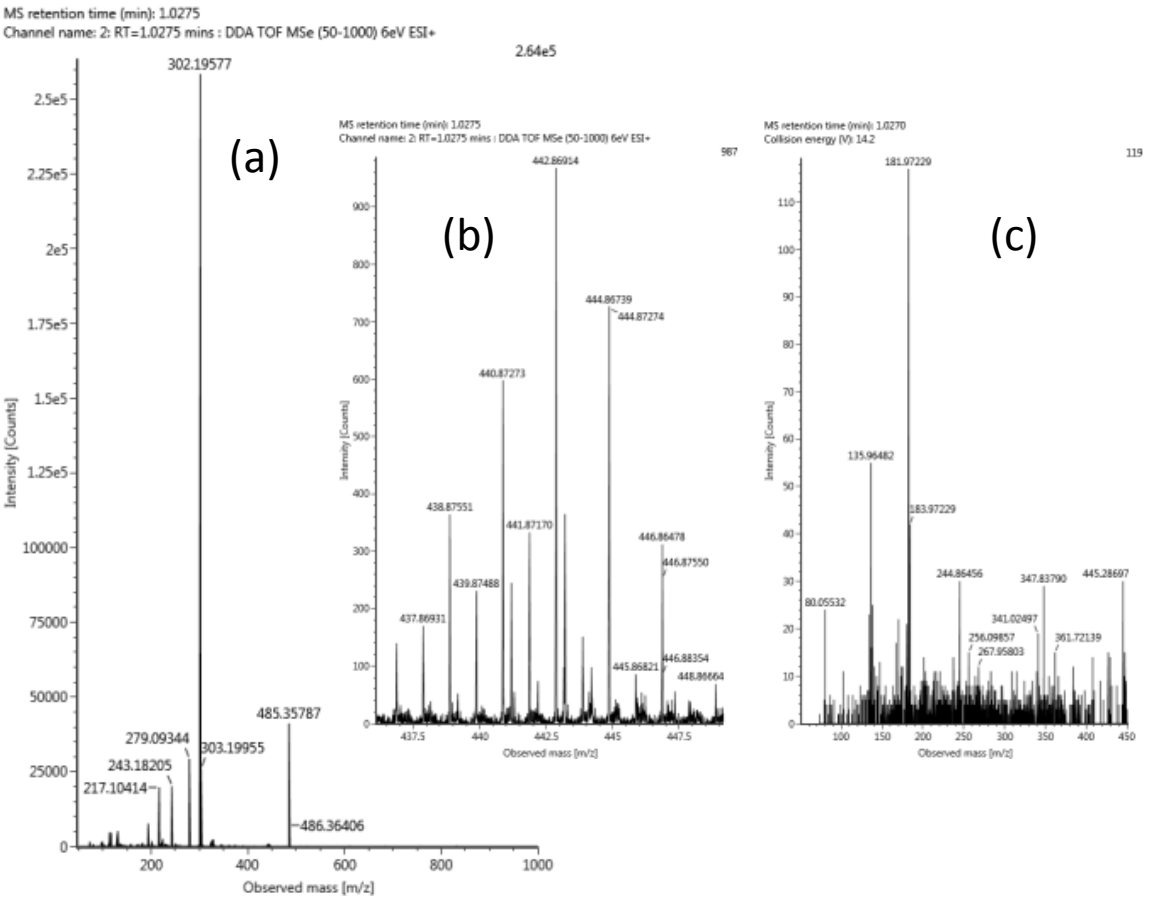


Fig. S20: Se-selenohomocysteinyl-diseleno-homocysteine (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

Unknown selenium species detected in the water soluble selenometabolome of C. violifolia without structure assignment (in the order of m/z values; see Table 1)

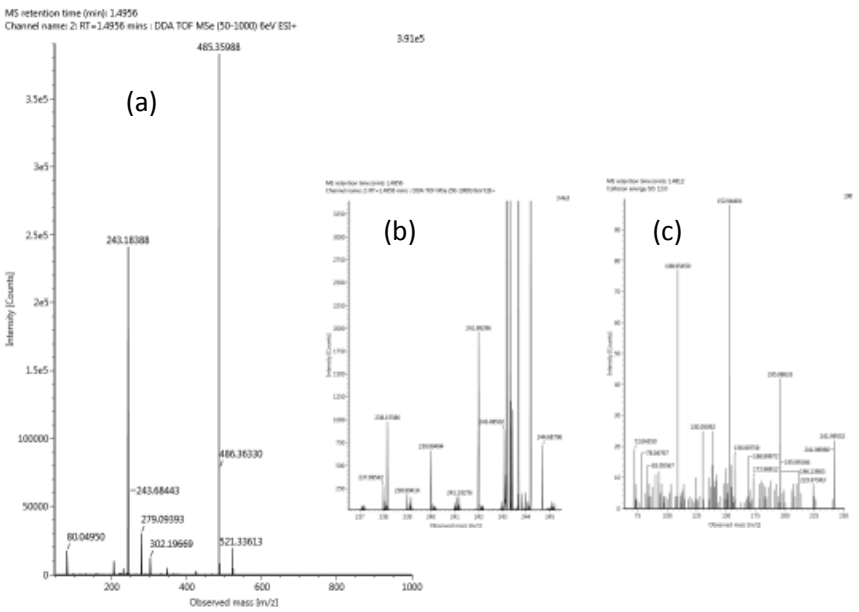


Fig. S21: Compound at the experimental m/z 241.99296 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

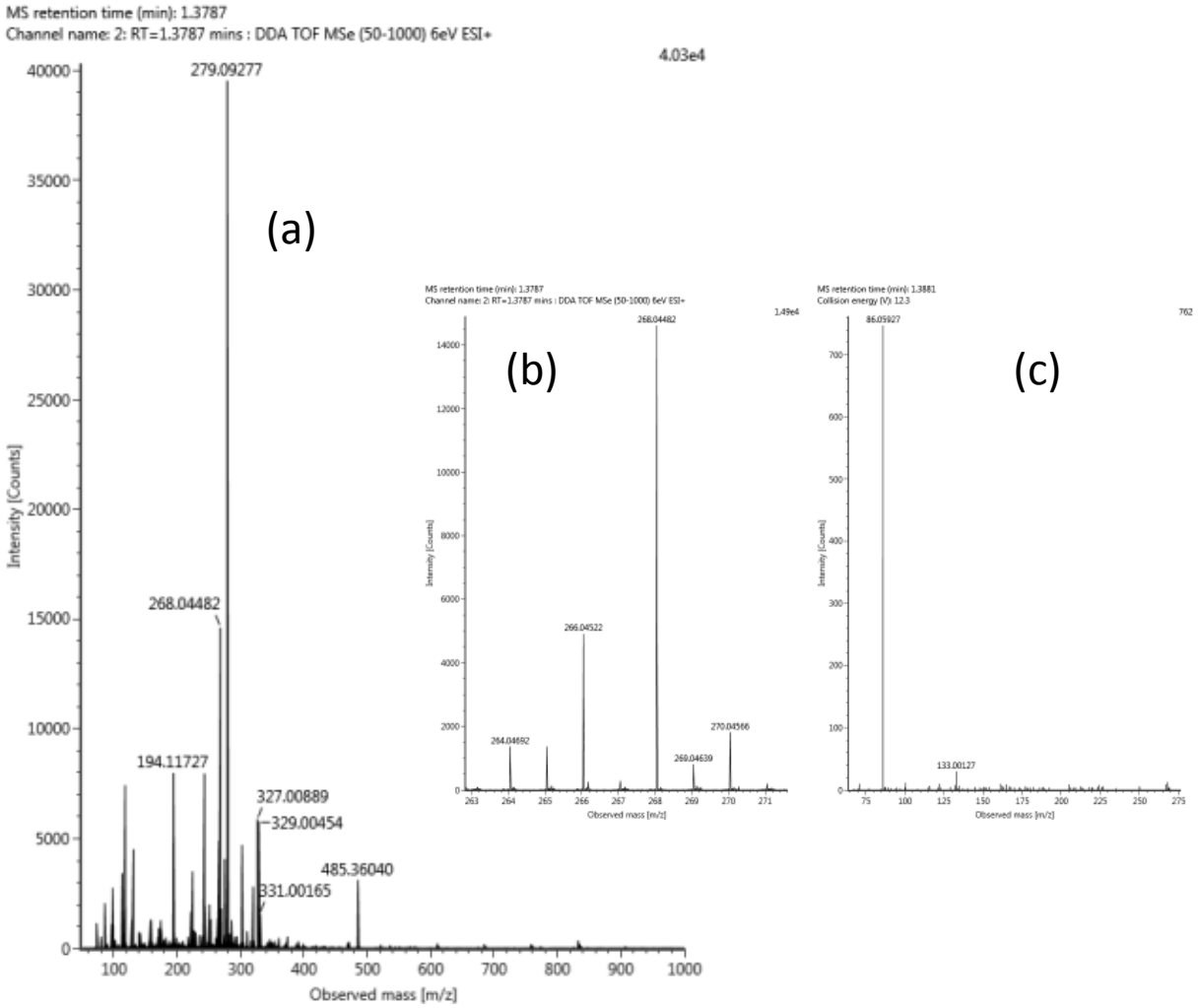


Fig. S22: Compound at the experimental m/z 268.04482 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

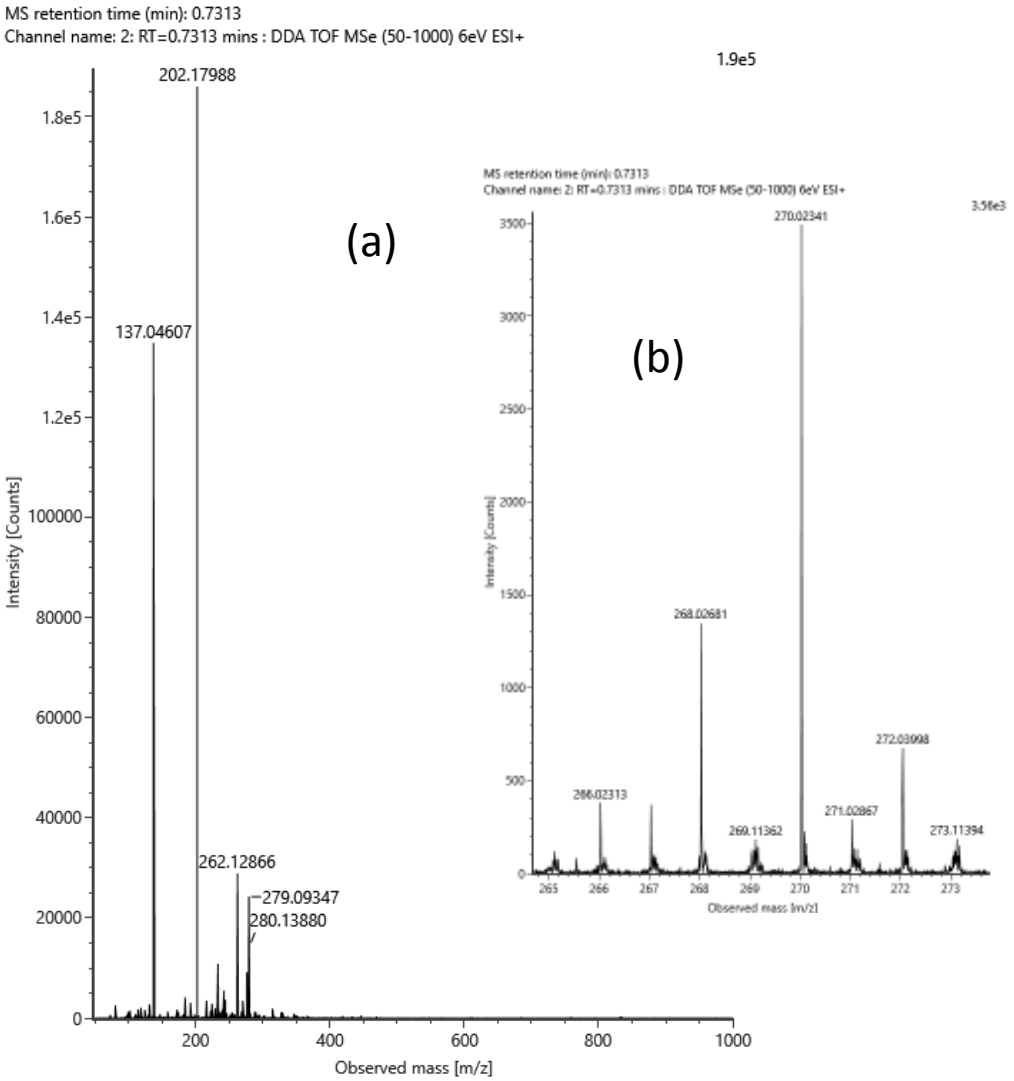


Fig. S23: Compound at the experimental m/z 270.02341 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/. MS/MS spectrum couldn't be recorded because of low abundance.

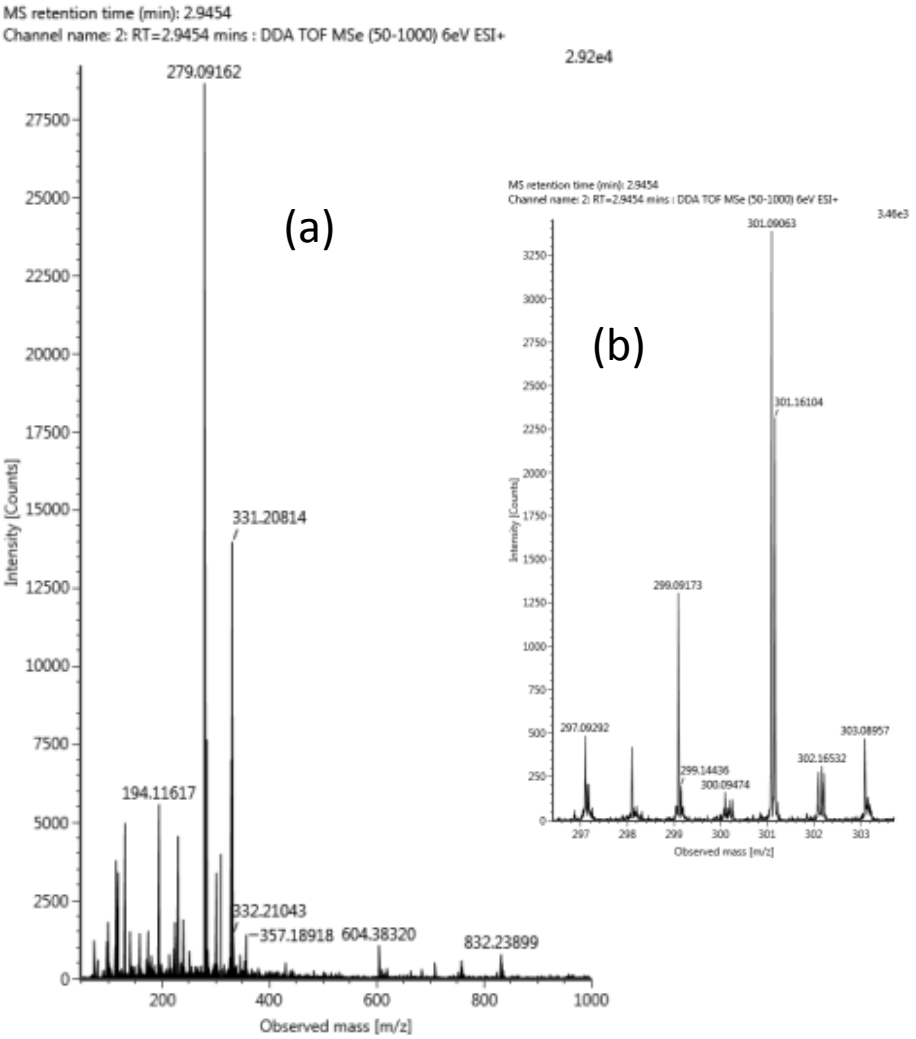


Fig. S24: Compound at the experimental m/z 301.09063 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/. MS/MS spectrum couldn't be recorded because of spectral interference.

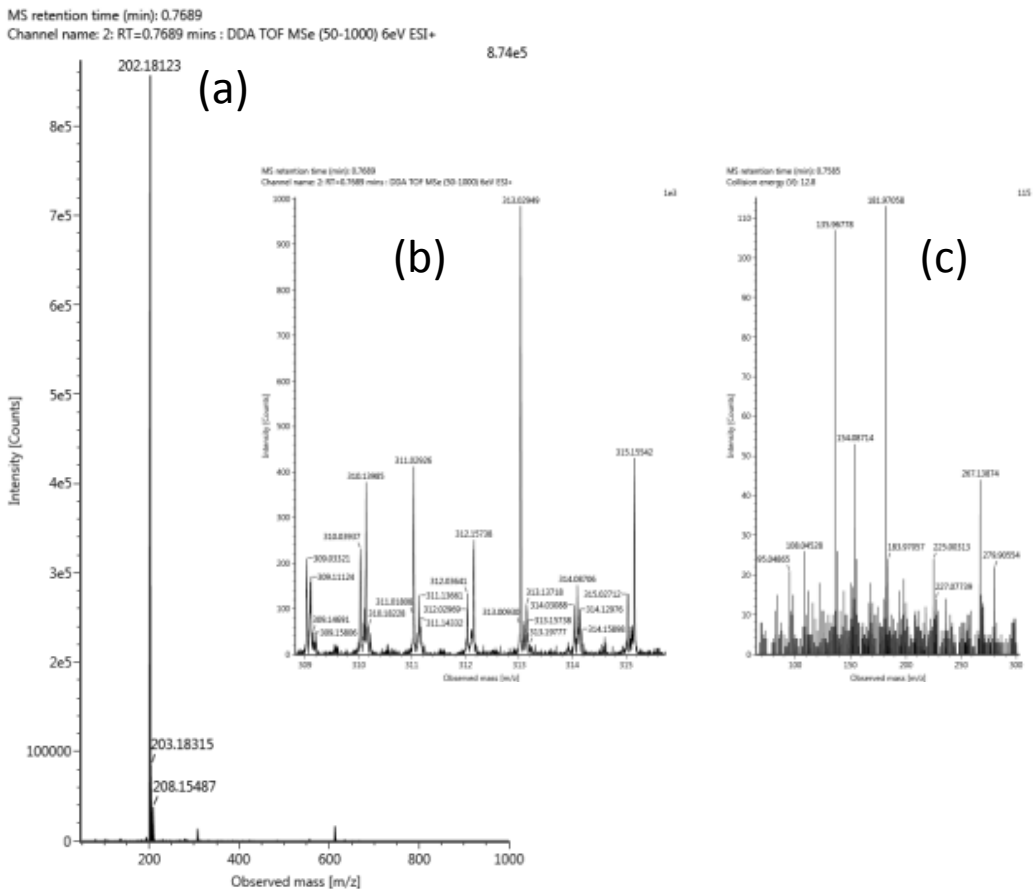


Fig. S25: Compound at the experimental m/z 313.02949 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

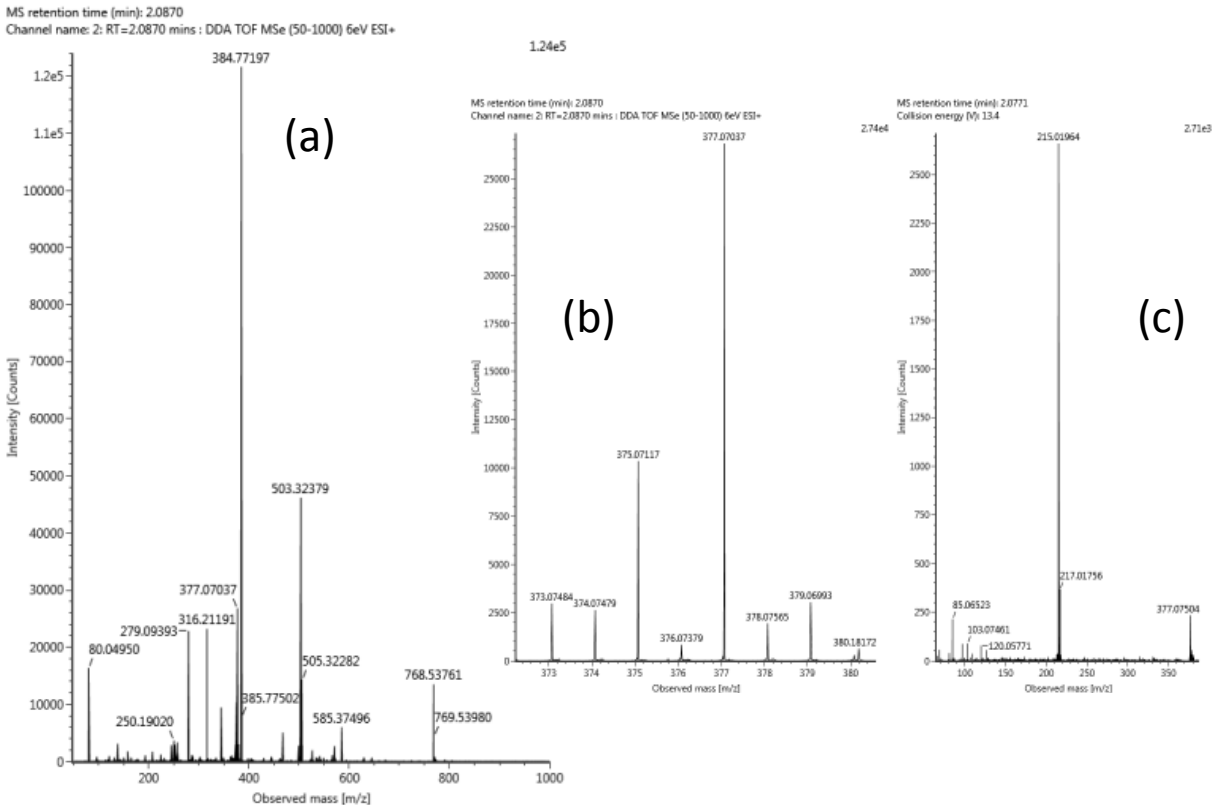


Fig. S26: Compound at the experimental m/z 377.07037 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

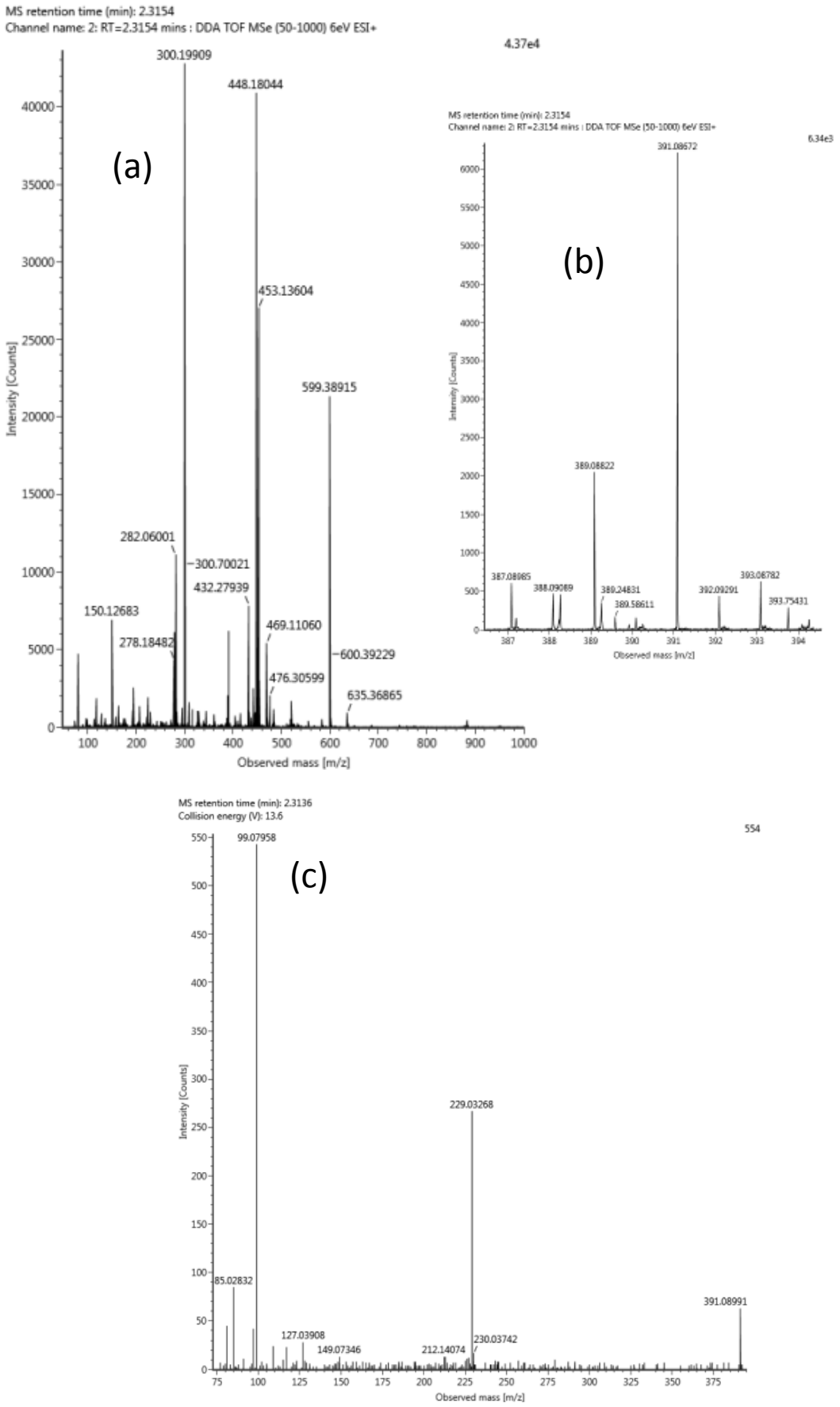


Fig. S27: Compound at the experimental m/z 391.08672 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

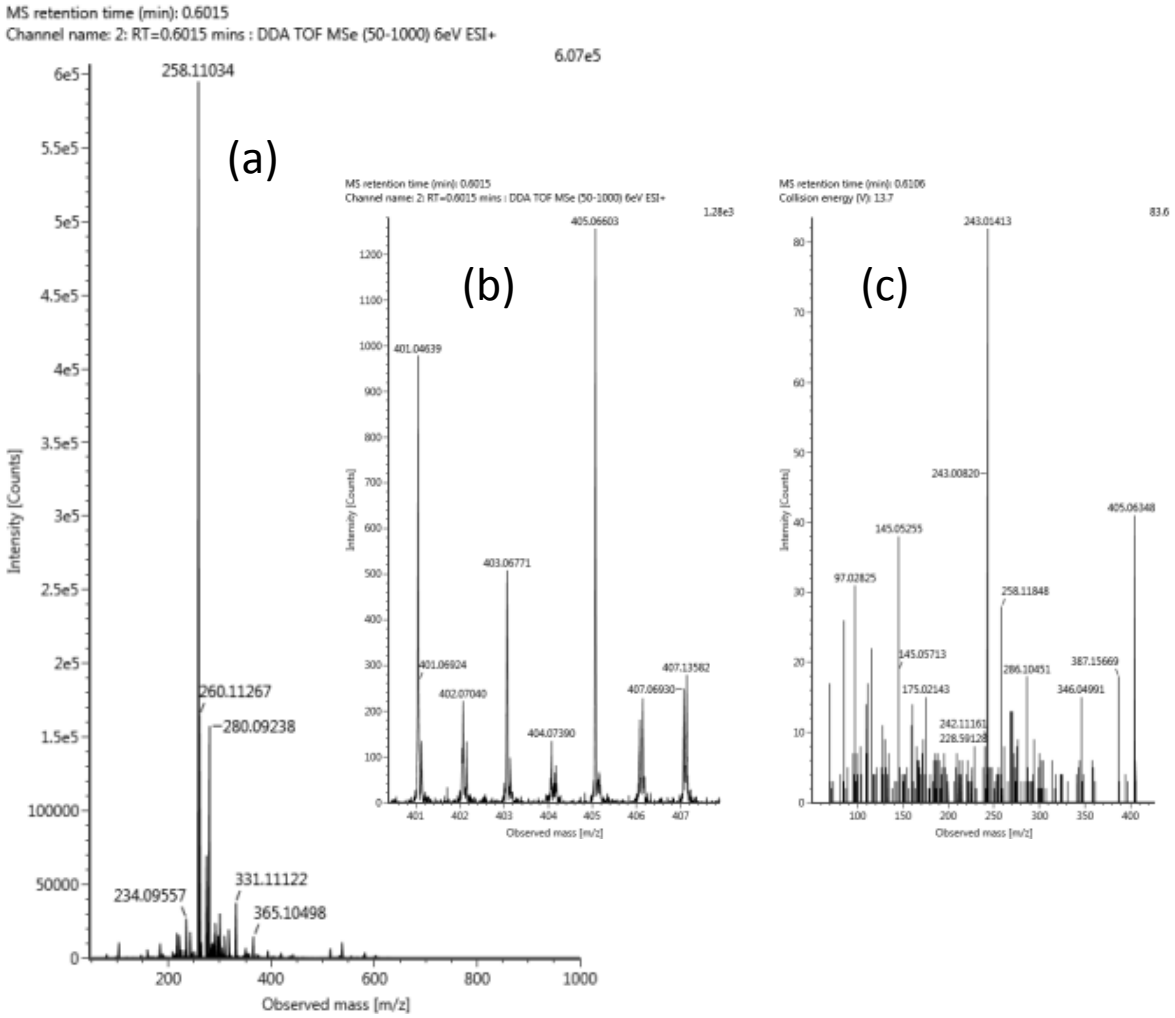


Fig. S28: Compound at the experimental m/z 405.06603 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

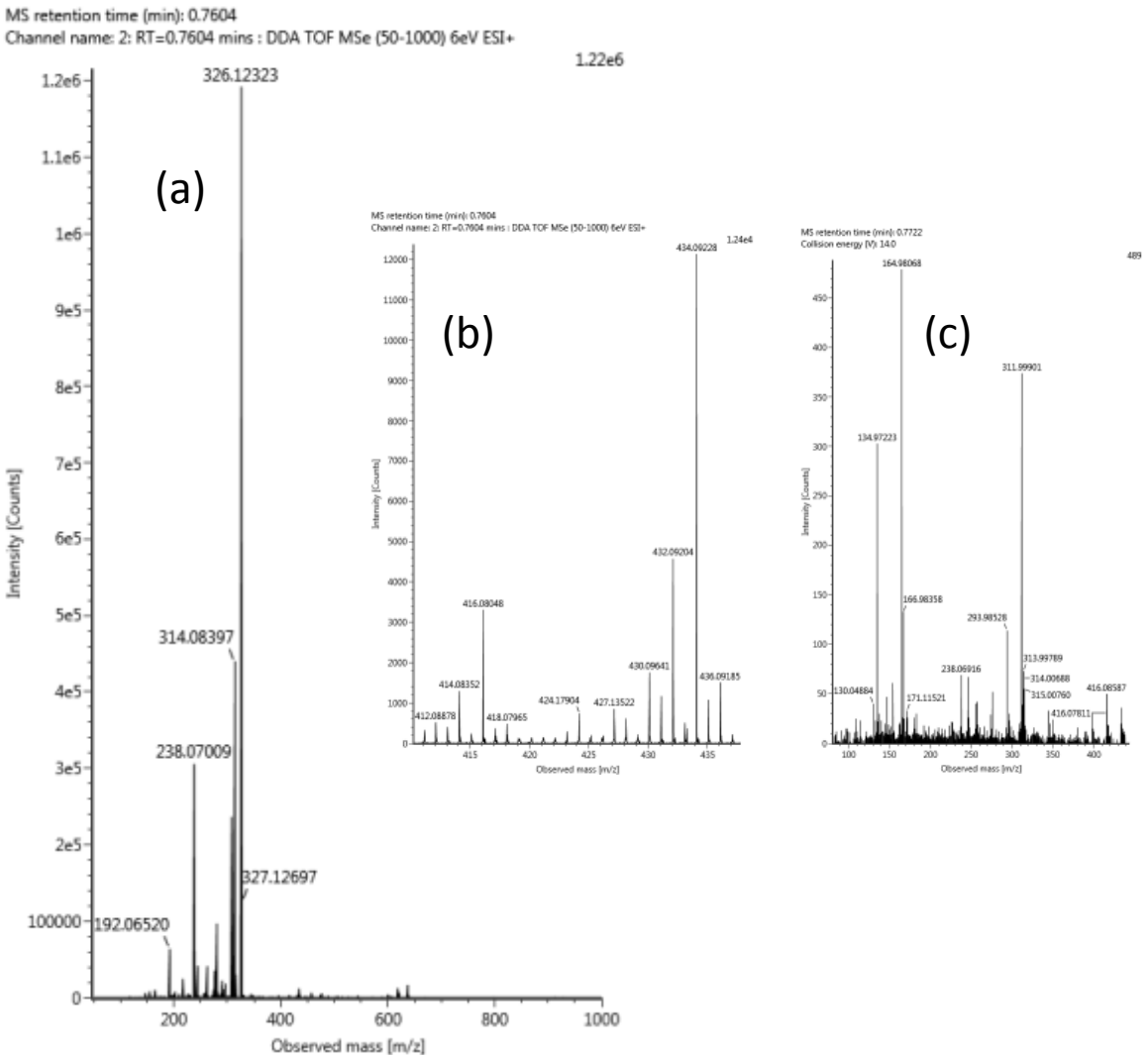


Fig. S29: Compound at the experimental m/z 434.09228 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

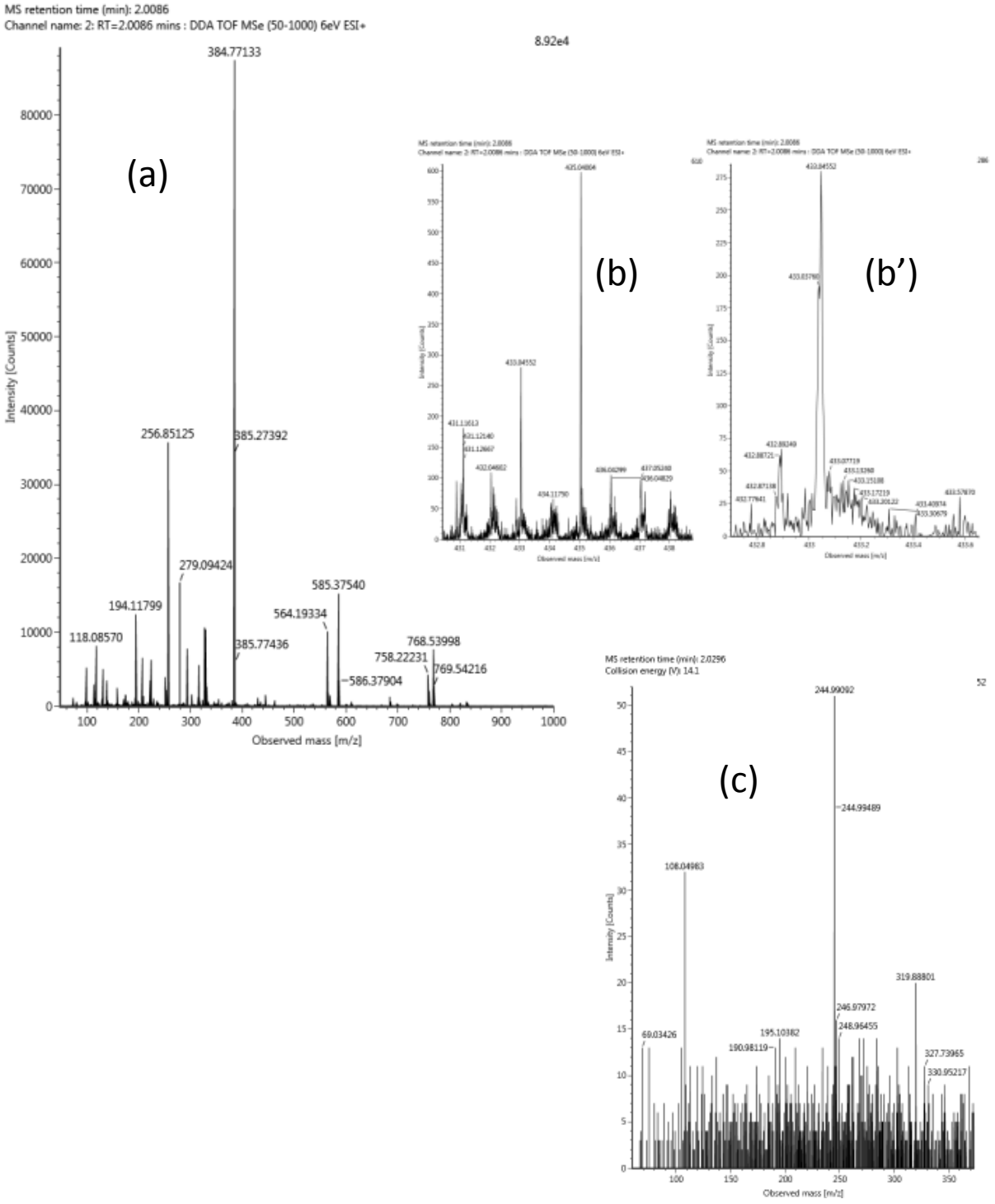


Fig. S30: Compound at the experimental m/z 435.04004 (for details, see Table 1); (a) full scan spectrum; (b) and (b') full scan spectra /zoomed/; (c) MS/MS spectrum.

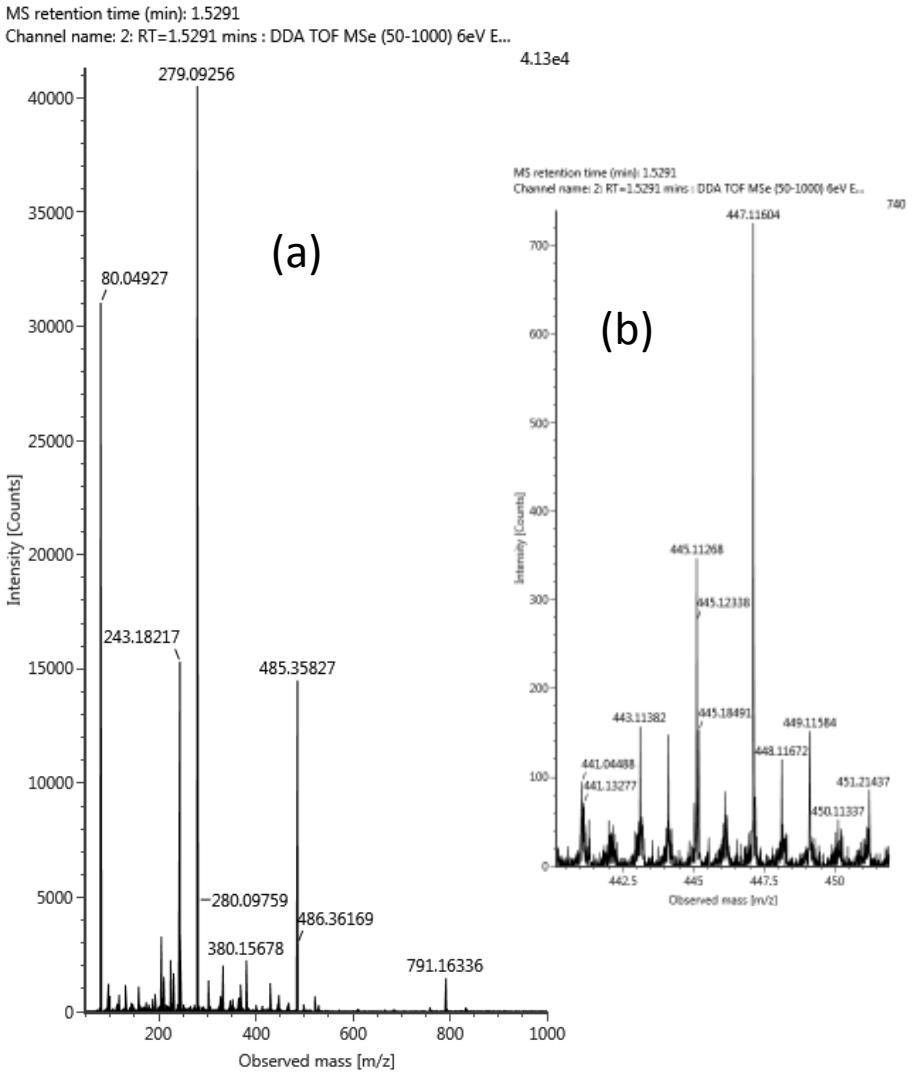


Fig. S31: Compound at the experimental m/z 447.11604 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/. MS/MS spectrum couldn't be recorded because of low abundance.

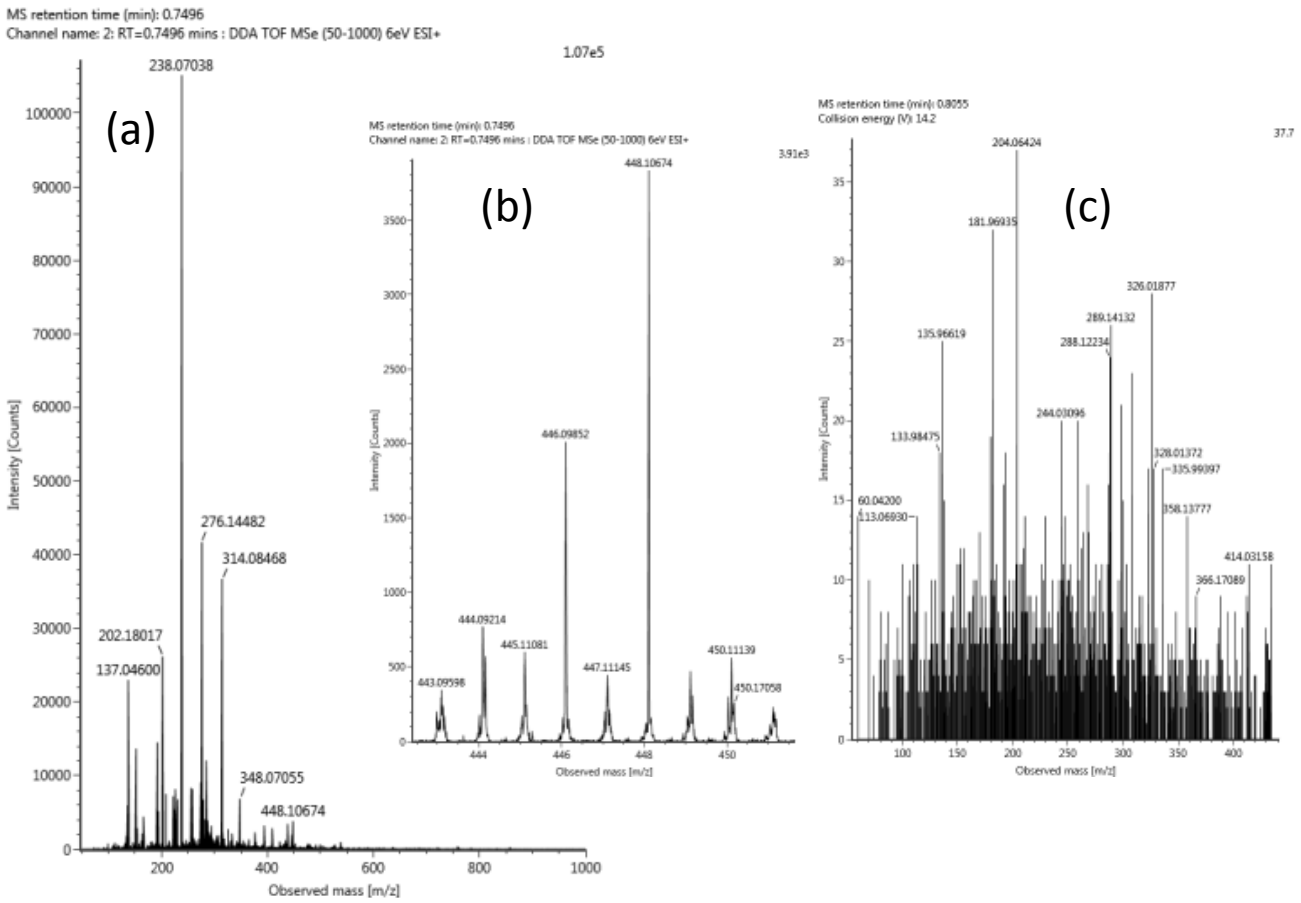


Fig. S32: Compound at the experimental m/z 448.10674 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

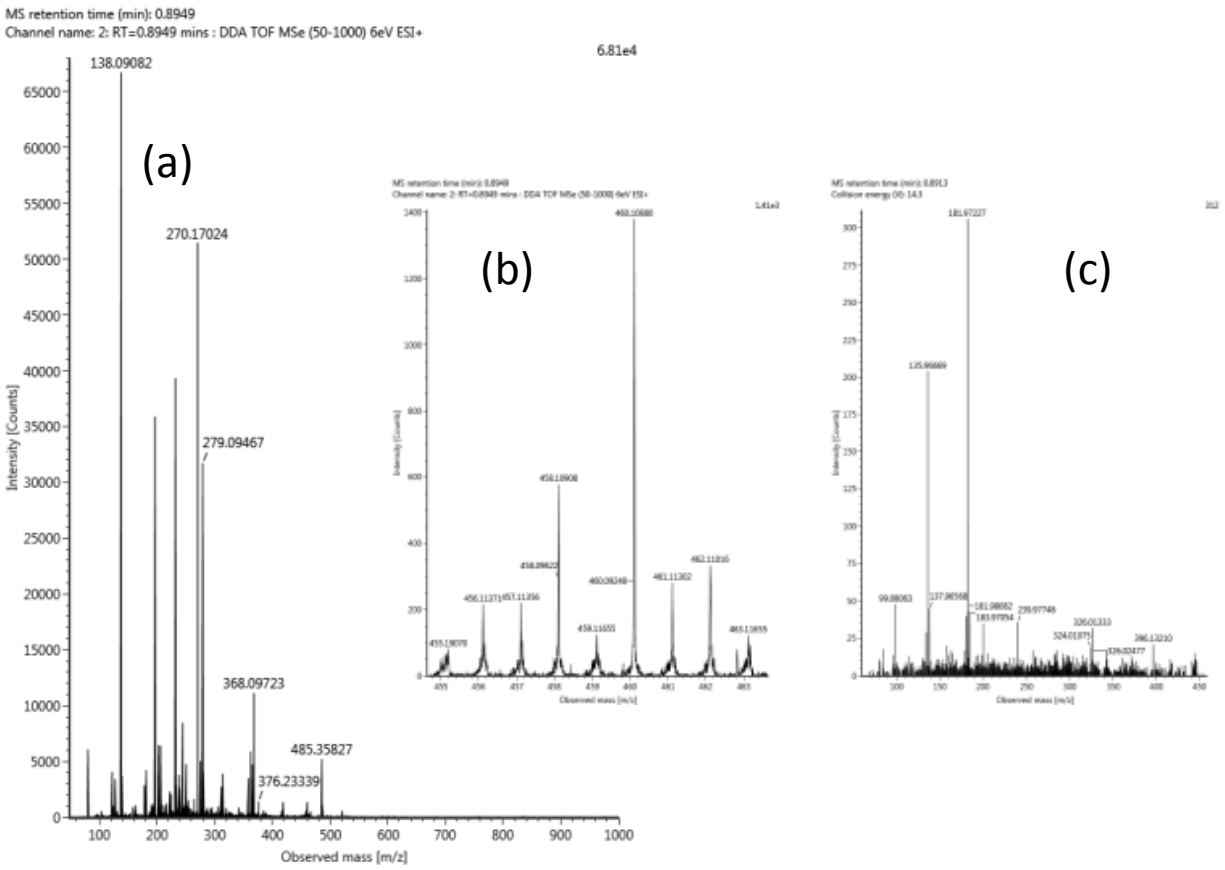


Fig. S33: Compound at the experimental m/z 460.10880 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

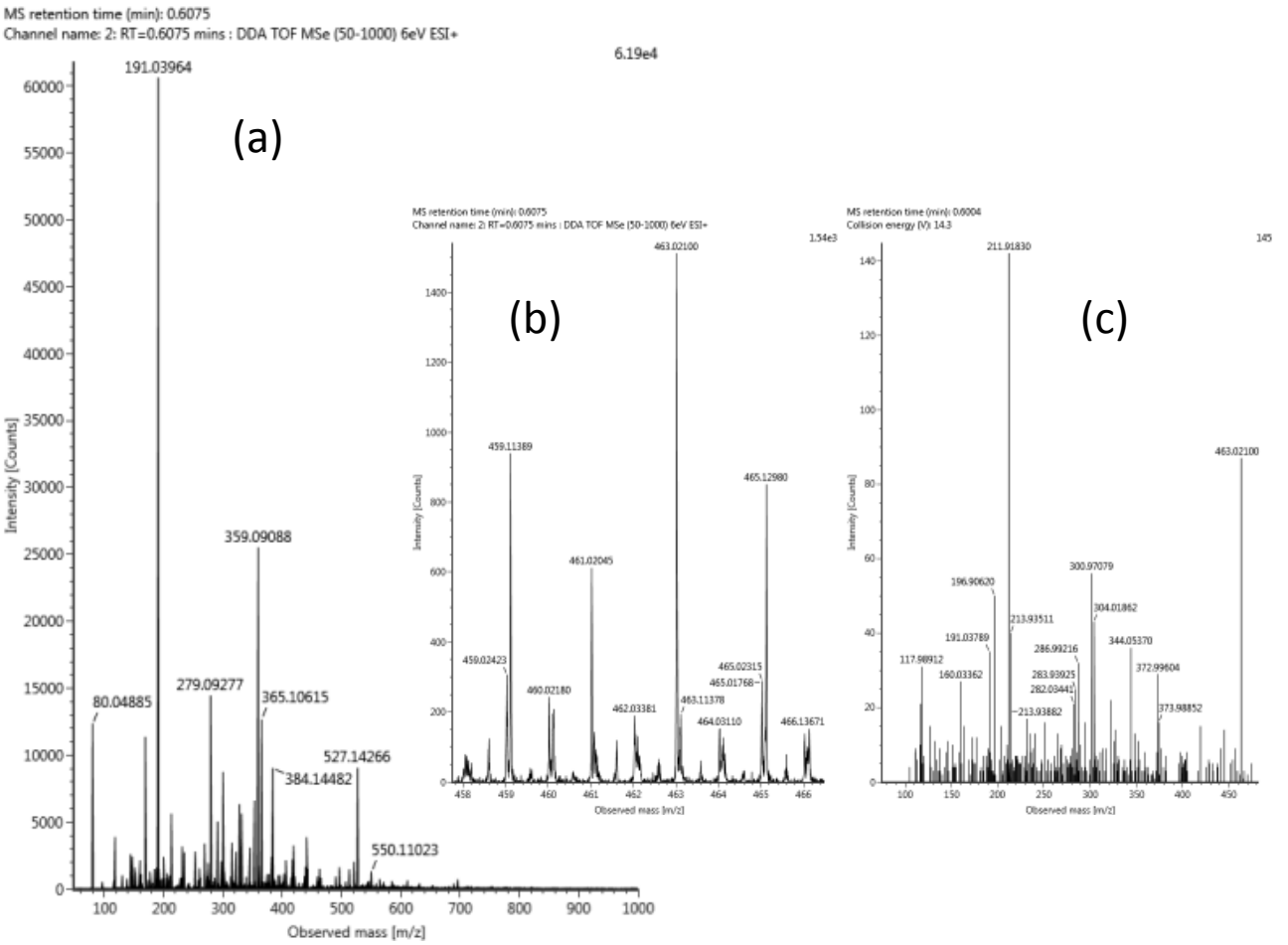


Fig. S34: Compound at the experimental m/z 463.02100 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

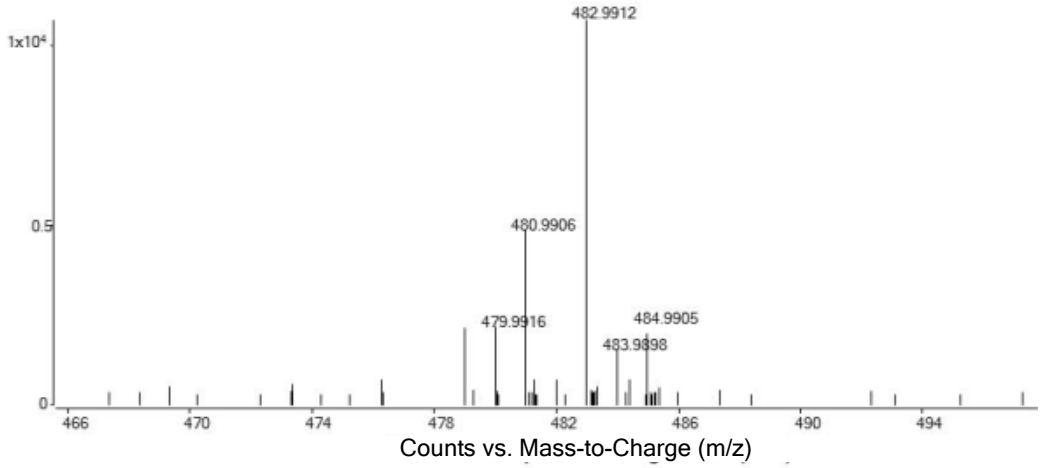


Fig. S35: Compound at the experimental m/z 482.9912 (for details, see Table 1). MS/MS spectrum couldn't be recorded because of low abundance. Data obtained with an Agilent 6530 ESI-QTOFMS system.

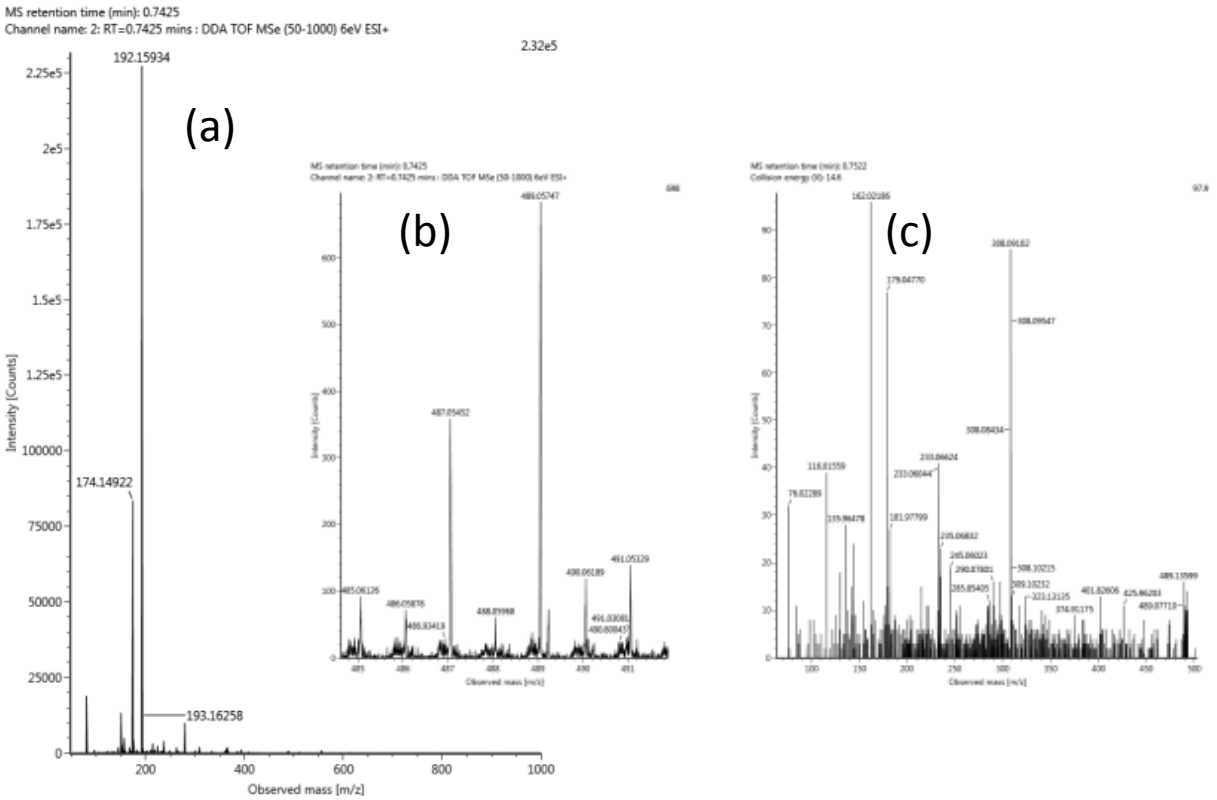


Fig. S36: Compound at the experimental m/z 489.05747 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

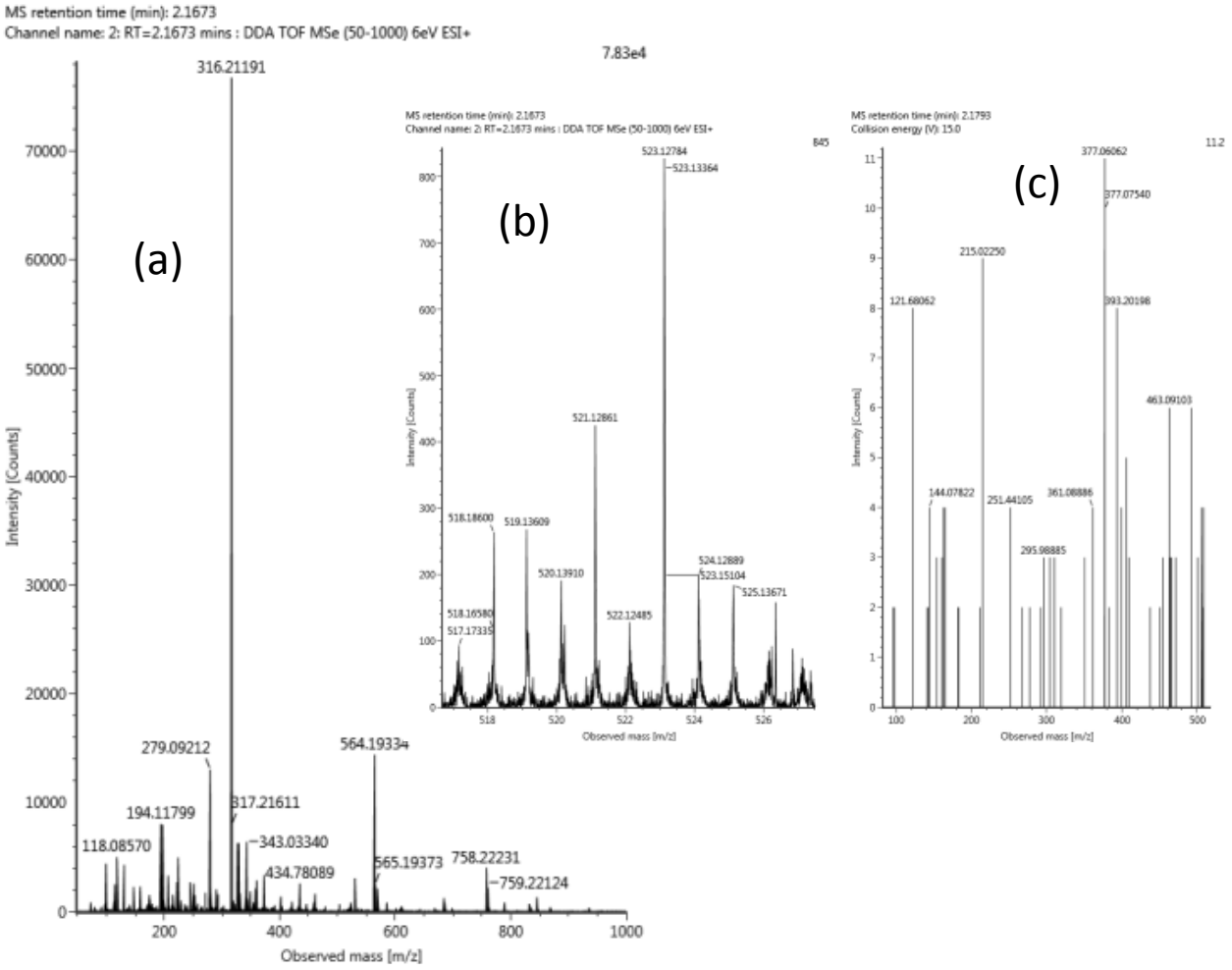


Fig. S37: Compound at the experimental m/z 523.12784 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

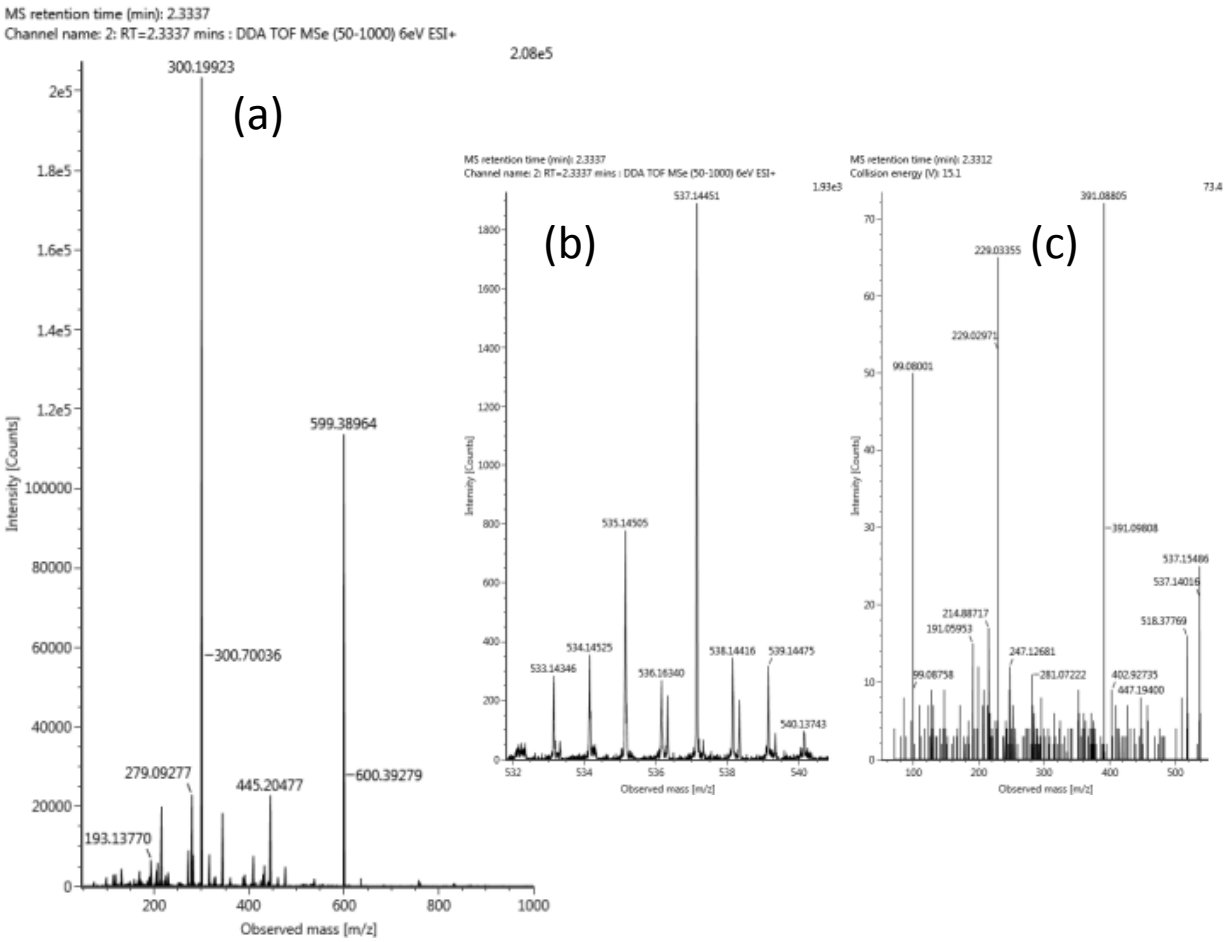


Fig. S38: Compound at the experimental m/z 537.14451 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.

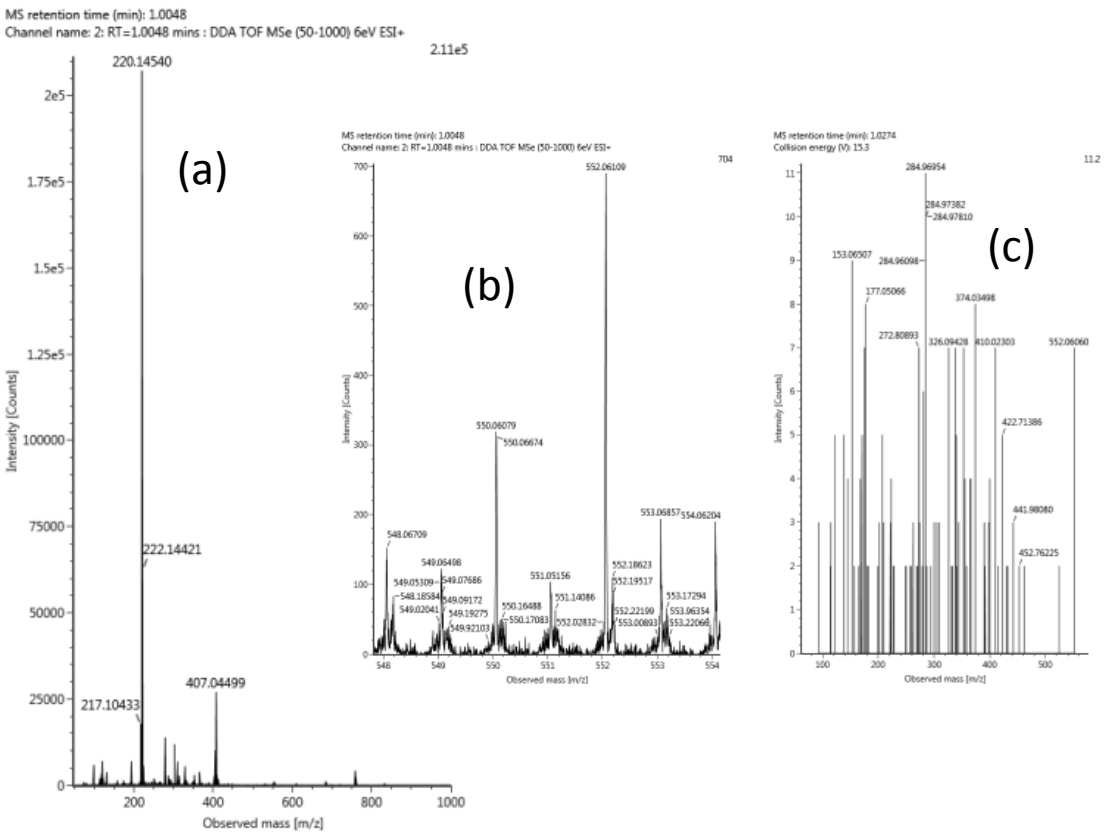
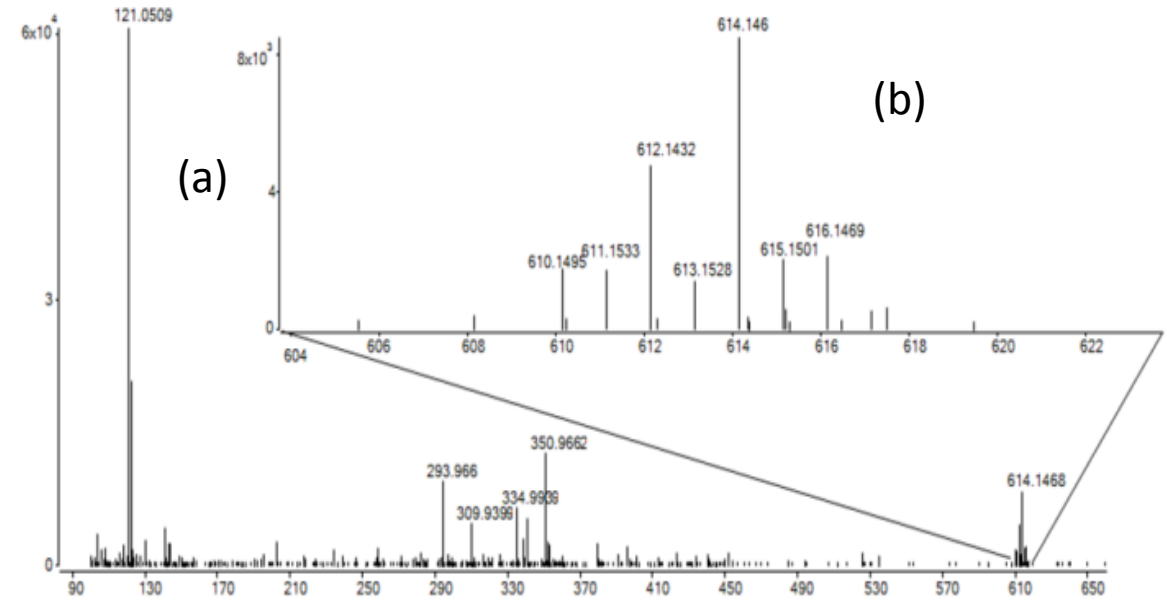


Fig. S39: Compound at the experimental m/z 552.06109 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum.



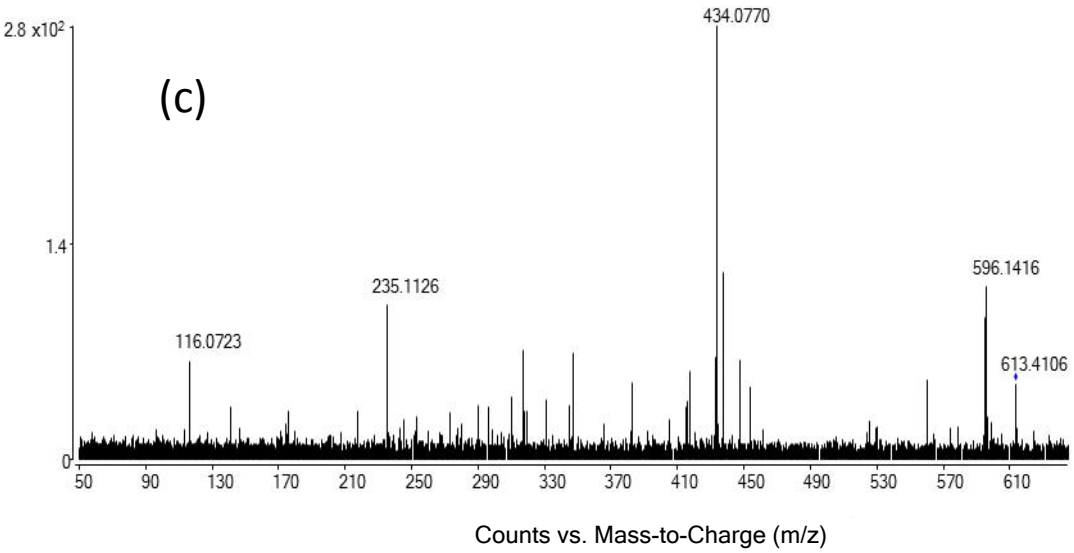


Fig. S40: Compound at the experimental m/z 614.1468 (for details, see Table 1); (a) full scan spectrum; (b) full scan spectrum /zoomed/; (c) MS/MS spectrum. Data obtained with an Agilent 6530 ESI-QTOFMS system.