Supplementary material

Chemical Investigation of the Mediterranean Sponge *Crambe crambe* by UHPLC-HRMS/MS via manual and computational dereplication approaches

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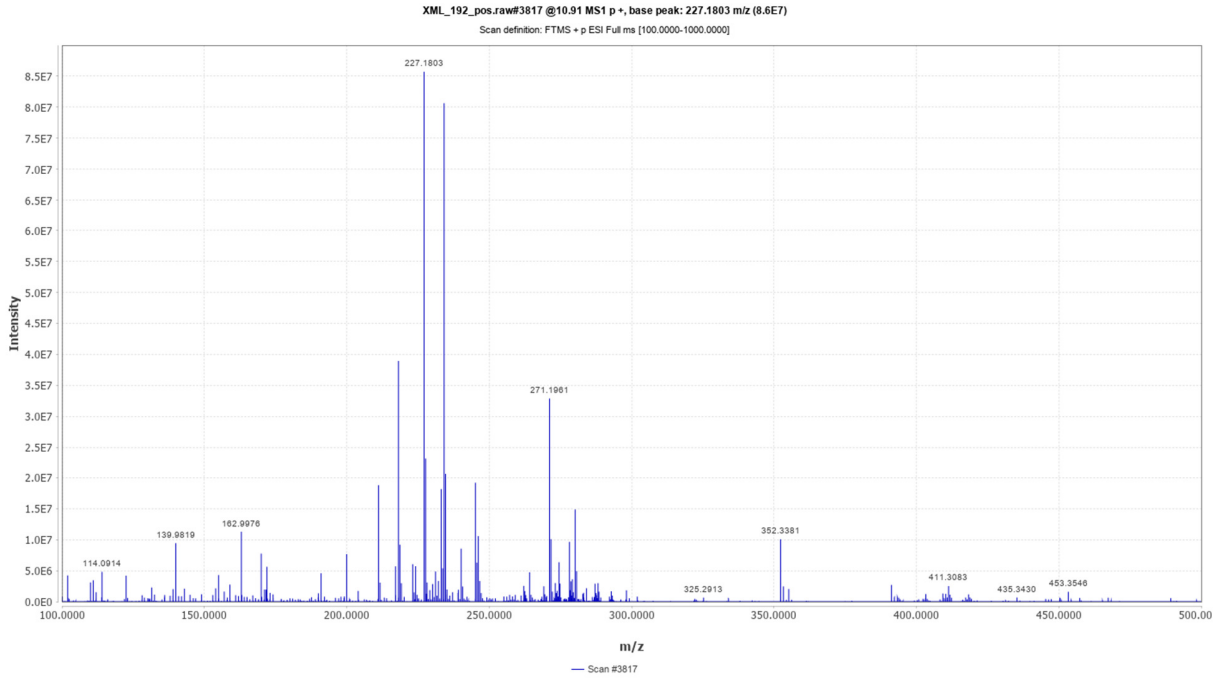
- **Crambescin B 452 homologue (m=5, n=4), Compound 9**

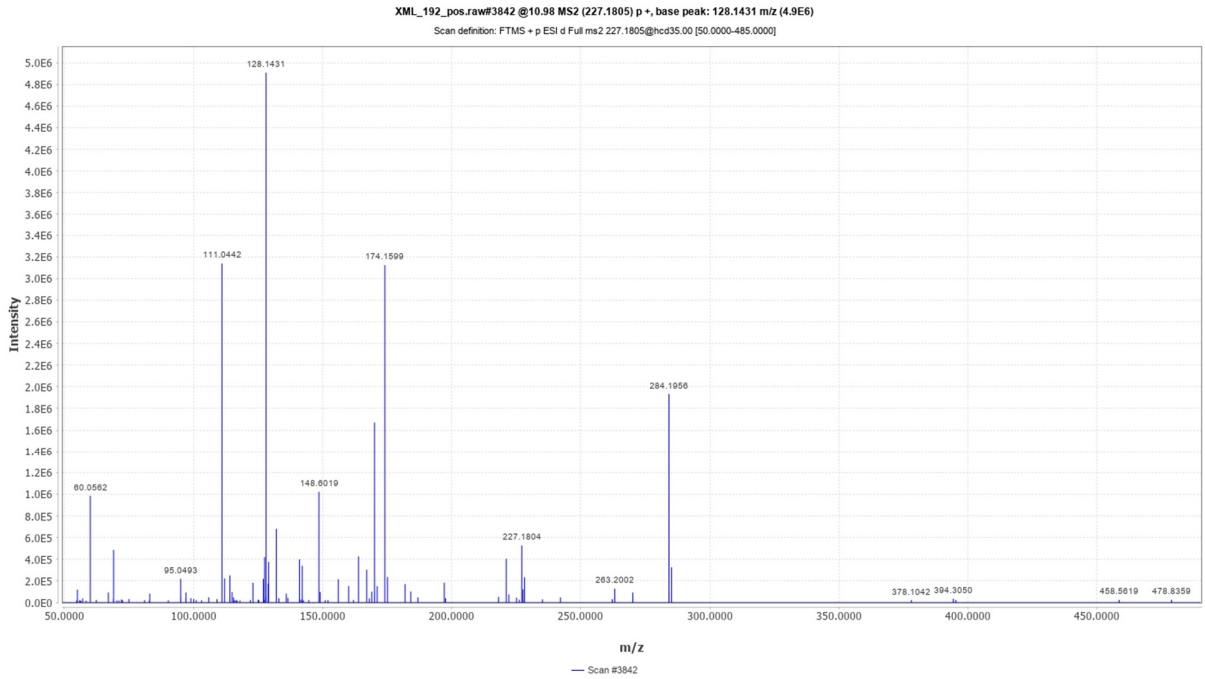
MS spectrum



m/z	Rt	Charge state, *z*	M_w exp.*	Proposed Formula*	Δ(ppm)*	Proposed Structure $[M+2H]^{2+}$
227.1803	10.88	2	452.3450	$C_{23}H_{44}N_6O_3$	-3.32	

** corresponding to the non-charged species, calculation of the experimental M_w and mass error are detailed in the note to **Table 1**.*

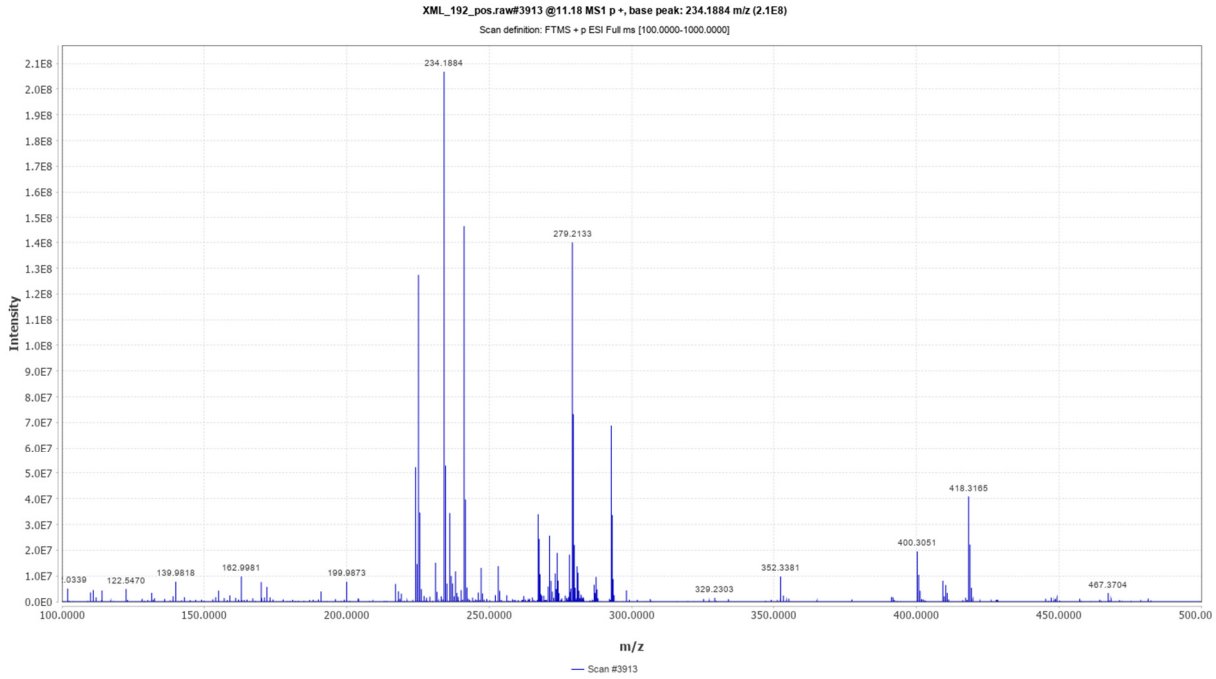
MS/MS spectrum



MS/MS fragment m/z	Charge state, *z*	Proposed Formula	Δ(ppm)	Proposed Structure
128.1431	1	$C_8H_{18}N^+$	-3.12	
174.1599	1	$C_8H_{20}N_3O^+$	-1.72	
111.0442	1	$C_6H_7O_2^+$	-1.80	
284.1956	1	$C_{14}H_{26}N_3O_3^+$	-4.22	
170.1649	1	$C_9H_{20}N_3^+$	-2.35	

- **Crambescin B 466 homologue (m=6, n=4), Compound 14**

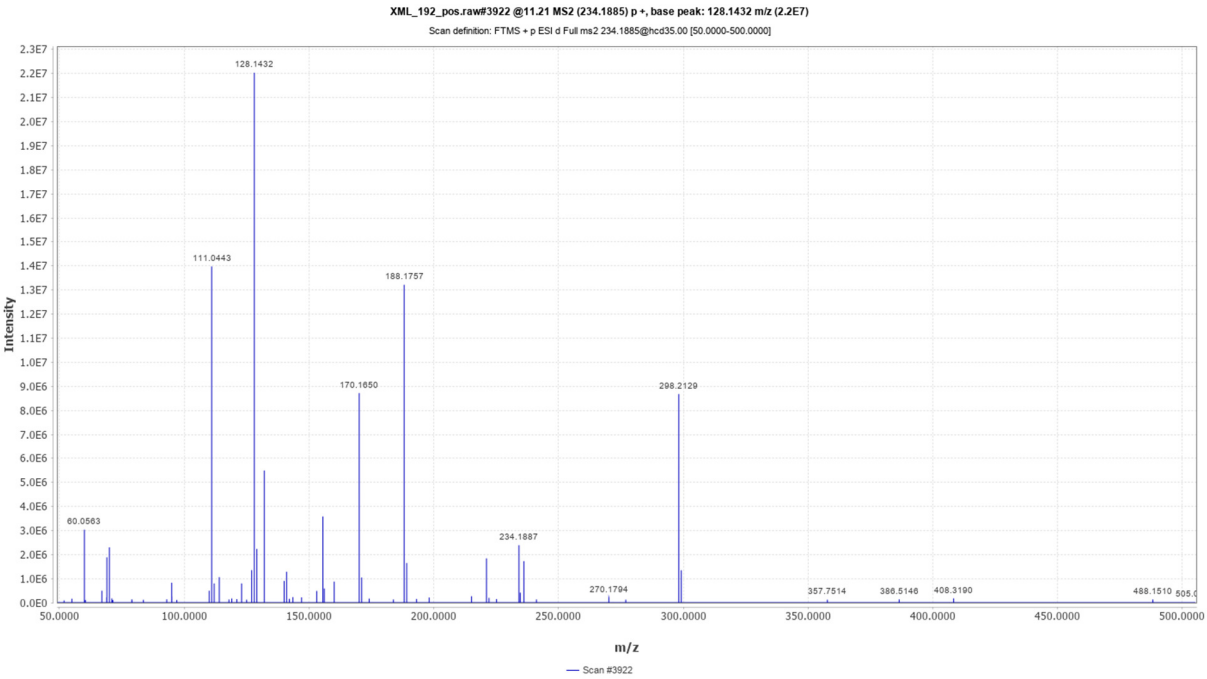
MS spectrum



m/z	Rt	Charge state, *z*	M_w exp.*	Proposed Formula*	Δ(ppm)*	Proposed Structure $[M+2H]^{2+}$
234.1884	11.18	2	466.3612	$C_{24}H_{46}N_6O_3$	-1.93	

** corresponding to the non-charged species, calculation of the experimental M_w and mass error are detailed in the note to* ***Table 1****.*

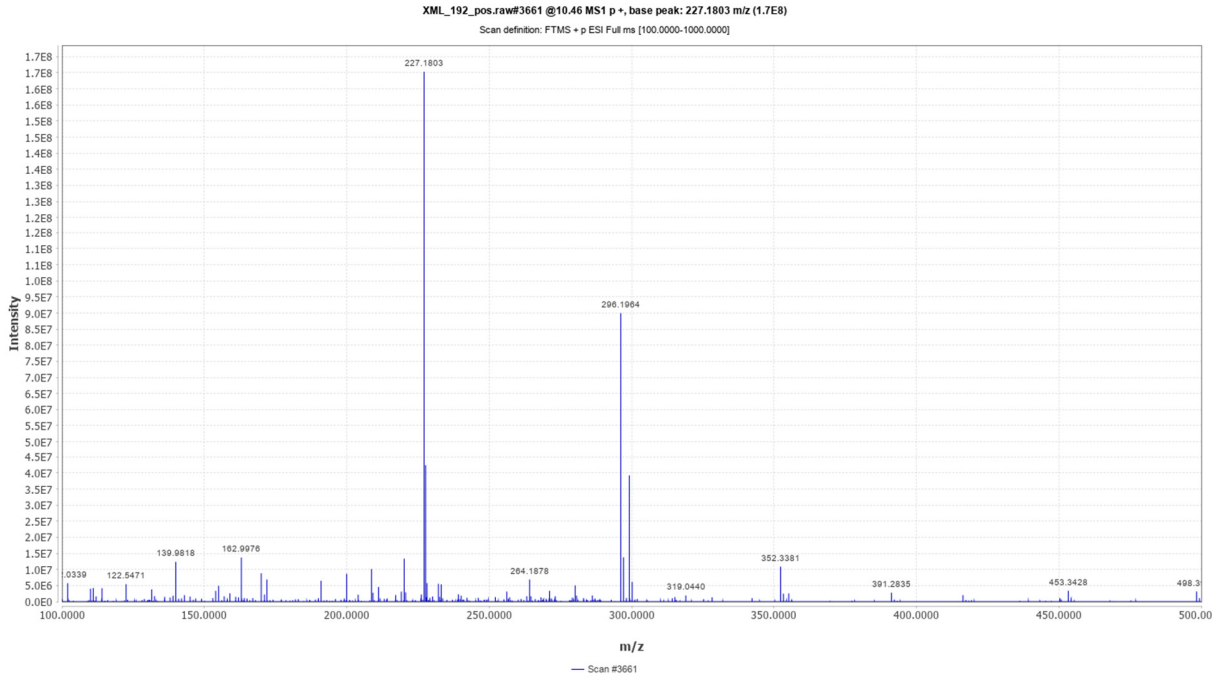
MS/MS spectrum



MS/MS fragment m/z	Charge state, *z*	Proposed Formula	Δ(ppm)	Proposed Structure
128.1432	1	$C_8H_{18}N^+$	-2.34	
111.0443	1	$C_6H_7O_2^+$	-0.90	
188.1757	1	$C_9H_{22}N_3O^+$	-0.53	
298.2129	1	$C_{15}H_{28}N_3O_3^+$	-1.68	
170.1650	1	$C_9H_{20}N_3^+$	-1.76	

- **Crambescin C 452 homologue (m=5, n=4), Compound 5**

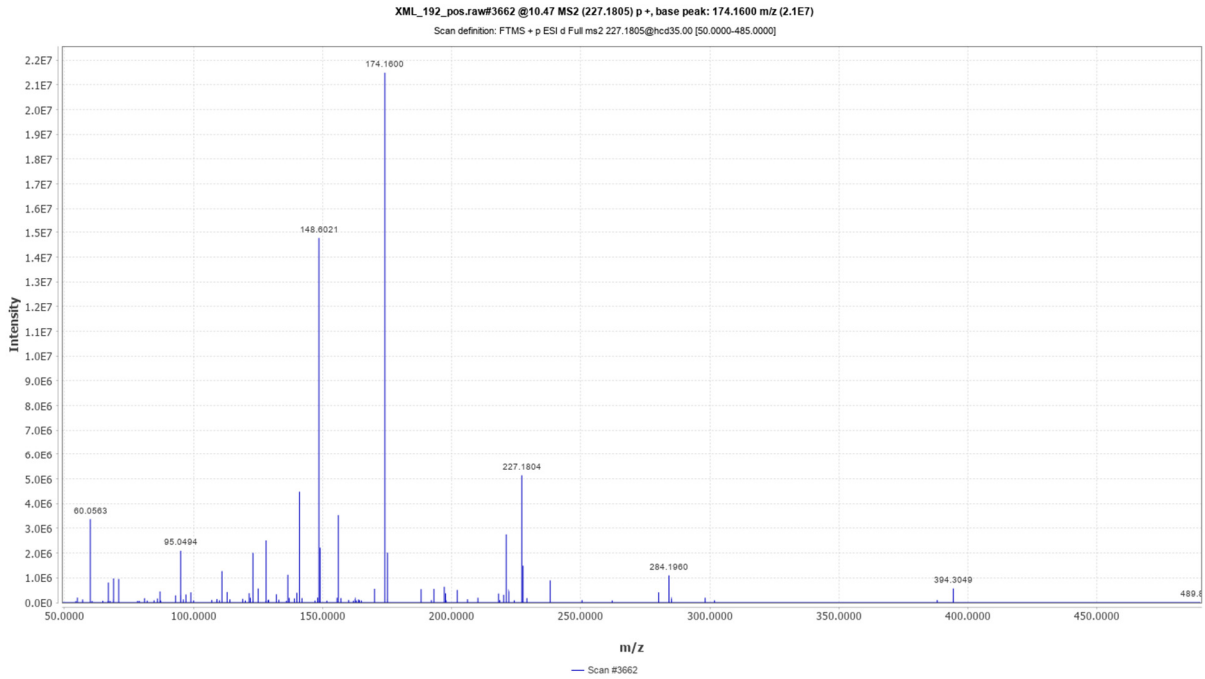
MS spectrum



m/z	Rt	Charge state, *z*	M_w exp.*	Proposed Formula*	Δ(ppm)*	Proposed Structure $[M+2H]^{2+}$
227.1803	10.46	2	452.3450	$C_{23}H_{44}N_6O_3$	-3.32	

** corresponding to the non-charged species, calculation of the experimental M_w and mass error are detailed in the note to* ***Table 1****.*

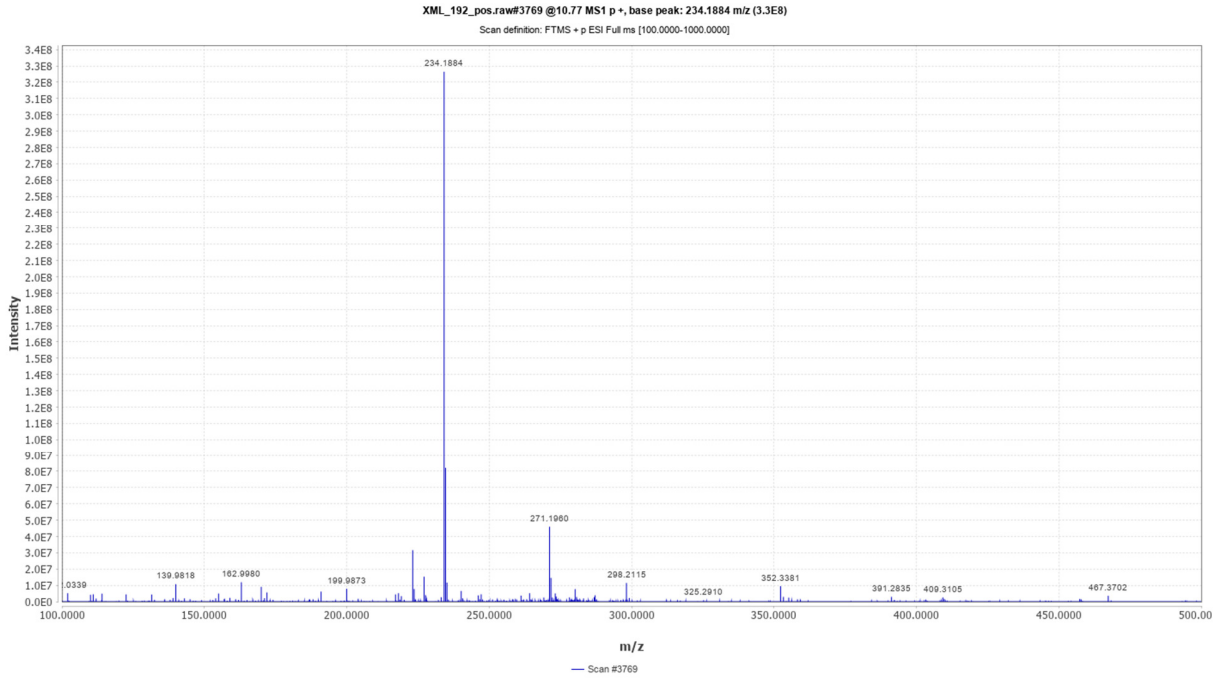
MS/MS spectrum



MS/MS fragment m/z	Charge state, *z*	Proposed Formula	Δ(ppm)	Proposed Structure
174.1600	1	$C_8H_{20}N_3O^+$	-1.15	
148.6021	2	$C_{15}H_{27}N_3O_3^{2+}$	-0.67	

- **Crambescin C 466 homologue (m=6, n=4), Compound 6**

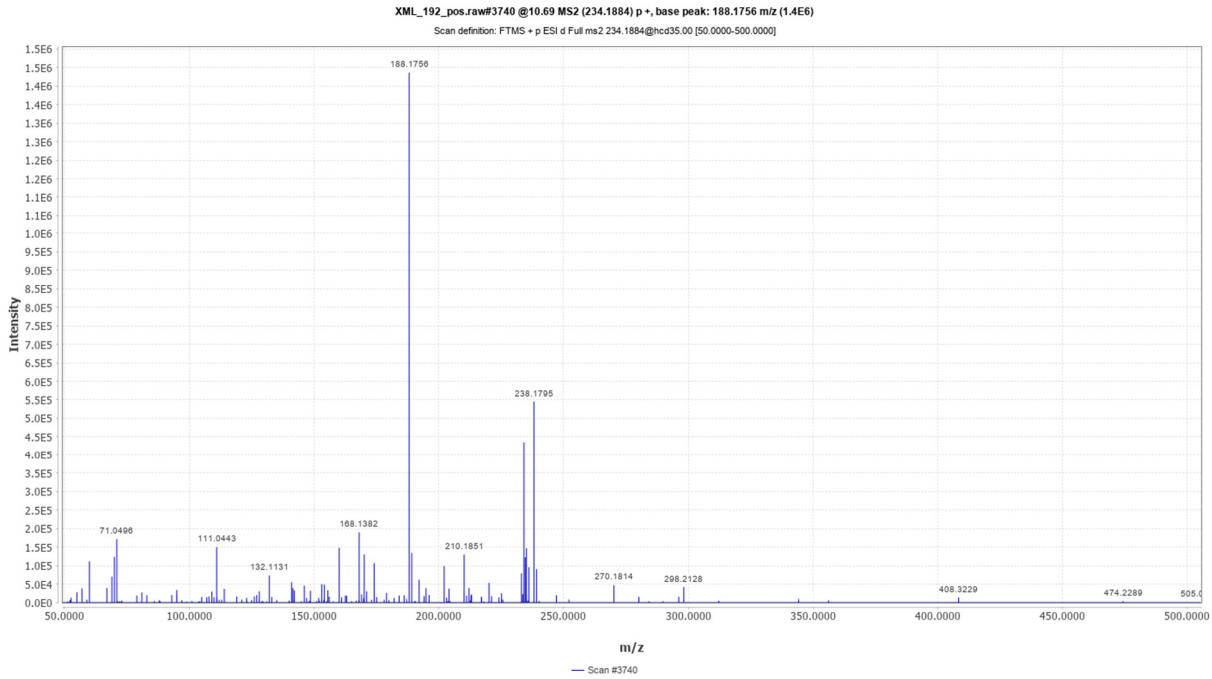
MS spectrum



m/z	Rt	Charge state, *z*	M_w exp.*	Proposed Formula*	Δ(ppm)*	Proposed Structure $[M+2H]^{2+}$
234.1884	10.77	2	466.3612	$C_{24}H_{46}N_6O_3$	-1.93	

** corresponding to the non-charged species, calculation of the experimental M_w and mass error are detailed in the note to* ***Table 1****.*

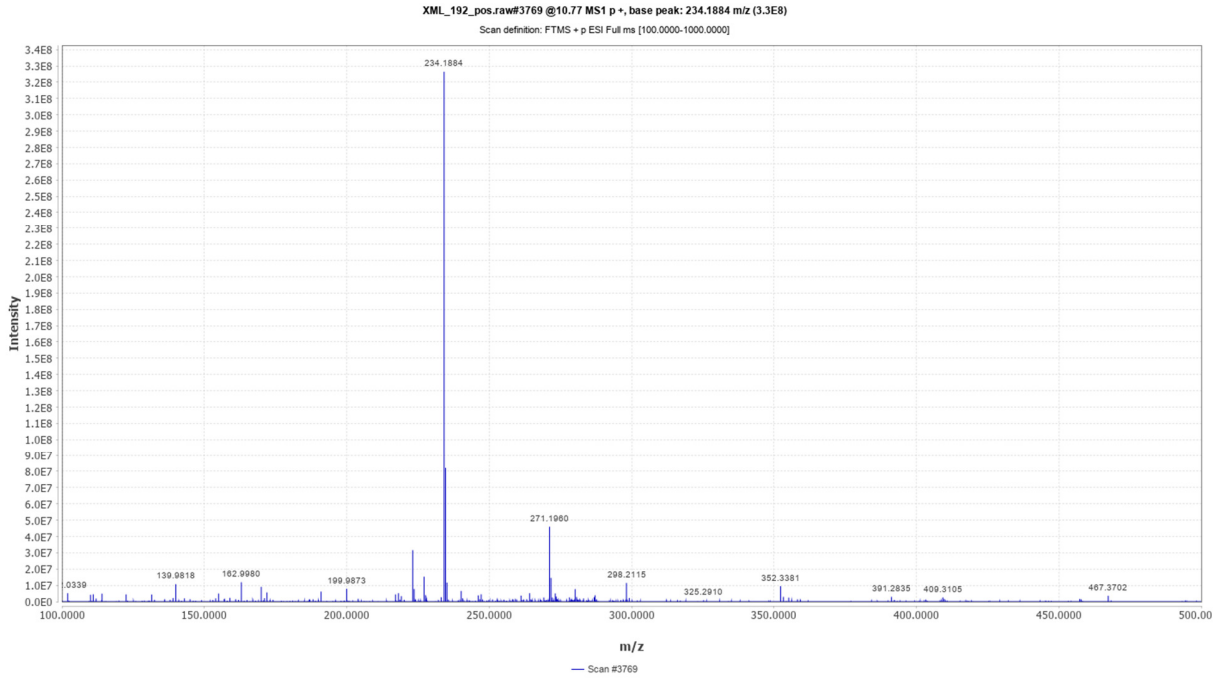
MS/MS spectrum



MS/MS fragment m/z	Charge state, *z*	Proposed Formula	Δ(ppm)	Proposed Structure
188.1756	1	$C_9H_{22}N_3O^+$	-1.06	
155.6100	2	$C_{16}H_{29}N_3O_3^{2+}$	-0.32	

- **Crambescin C 466 homologue (m=5, n=5), Compound 7**

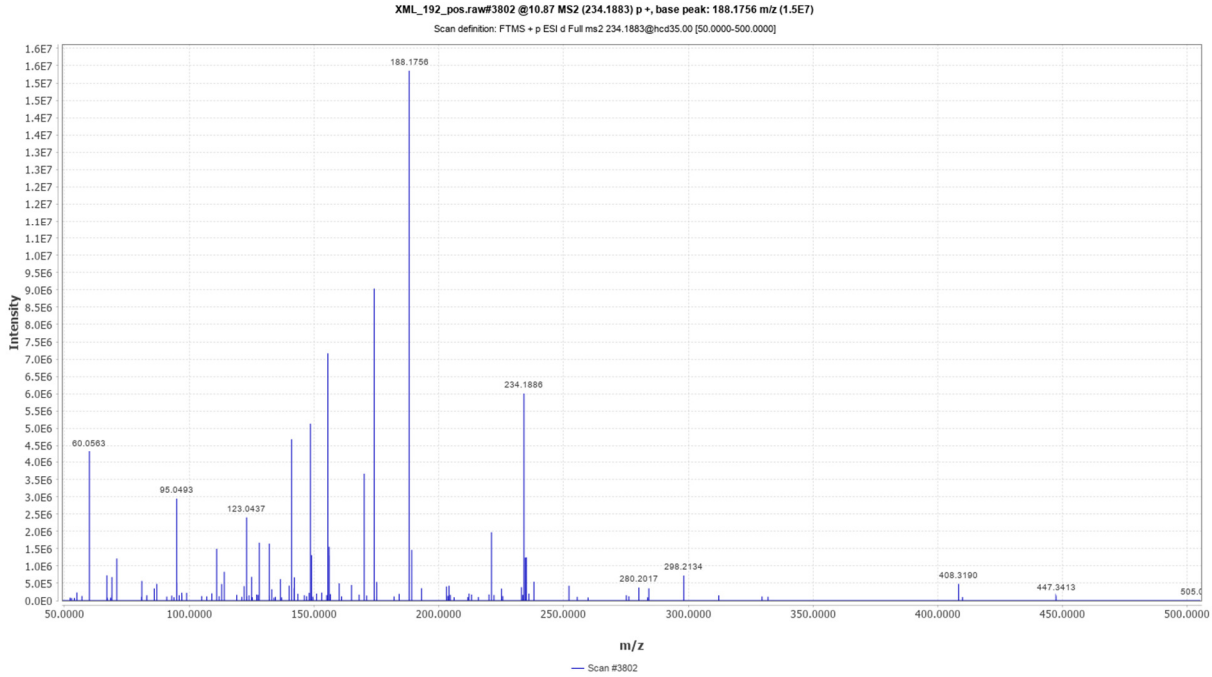
MS spectrum



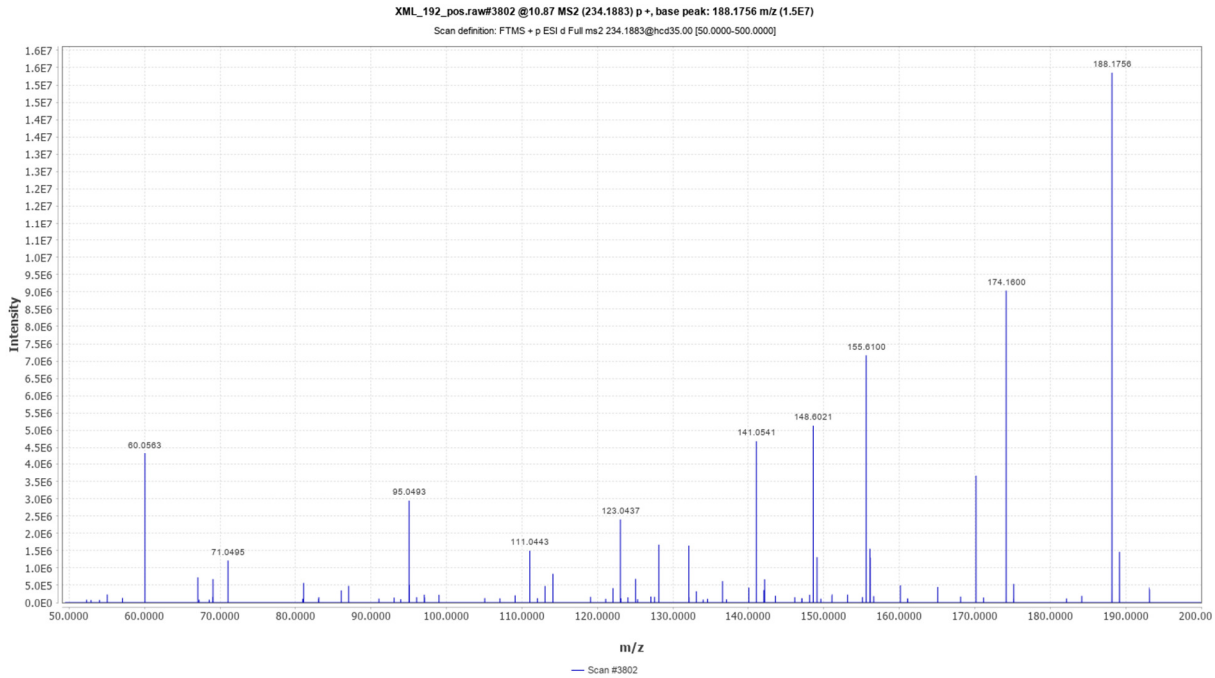
m/z	Rt	Charge state, *z*	M_w exp.*	Proposed Formula*	Δ(ppm)*	Proposed Structure $[M+2H]^{2+}$
234.1884	10.77	2	466.3612	$C_{24}H_{46}N_6O_3$	-1.93	

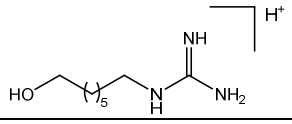
** corresponding to the non-charged species, calculation of the experimental M_w and mass error are detailed in the note to* ***Table 1****.*

MS/MS spectrum



zoom m/z range 50-200



MS/MS fragment m/z	**Charge state, *z***	**Proposed Formula**	**Δ(ppm)**	**Proposed Structure**
174.1600	1	$C_8H_{20}N_3O^+$	-1.15	
148.6021	2	$C_{15}H_{27}N_3O_3^{2+}$	-0.67