

Supplementary Material: Eighteen new aeruginosamide variants produced by the Baltic cyanobacterium *Limnoraphis* CCNP1324

Marta Ceglowska¹, Karolia Szubert², Ewa Wieczerek³, Alicja Kosakowska¹ and Hanna Mazur-Marzec^{2*}

¹ Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, PL-81712 Sopot, Poland; mceglowska@iopan.pl (M.C.), akosak@iopan.gda.pl (A.K.)

² Division of Marine Biotechnology, Faculty of Oceanography and Geography, University of Gdańsk, Marszałka J. Piłsudskiego 46, PL-81378 Gdynia, Poland; karolina.szubert@phdstud.ug.edu.pl

³ Department of Biomedical Chemistry, Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, PL-80308 Gdańsk, Poland; ewa.wieczerek@ug.edu.pl

* Correspondence: hanna.mazur-marzec@ug.edu.pl

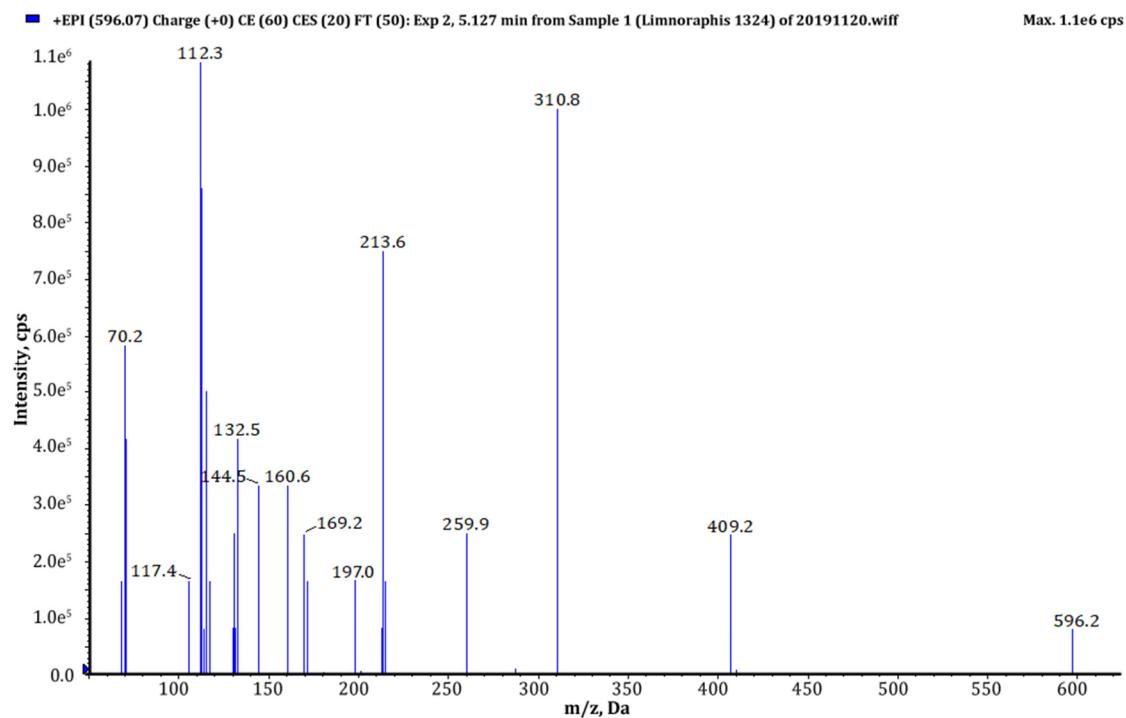


Figure S1. Enhanced product ion mass spectrum of aeruginosamide AER595 with general structure 187+Val+Pro+Pyr+TzlCOOMe identified based on the following fragment ions: 596 [M+H], 409 [Val+Pro+Pyr+TzlCOOMe], 310 [Pro+Pyr+TzlCOOMe+H], 259 [187+Val+H-CO], 213 [Pyr+TzlCOOMe+H], 197 [Val+Pro+H], 169 [Val+Pro+H-CO], 160 [187+H-CO], 144 [TzlCOOMe], 112 TzlCO, 70 Pro immonium ion.

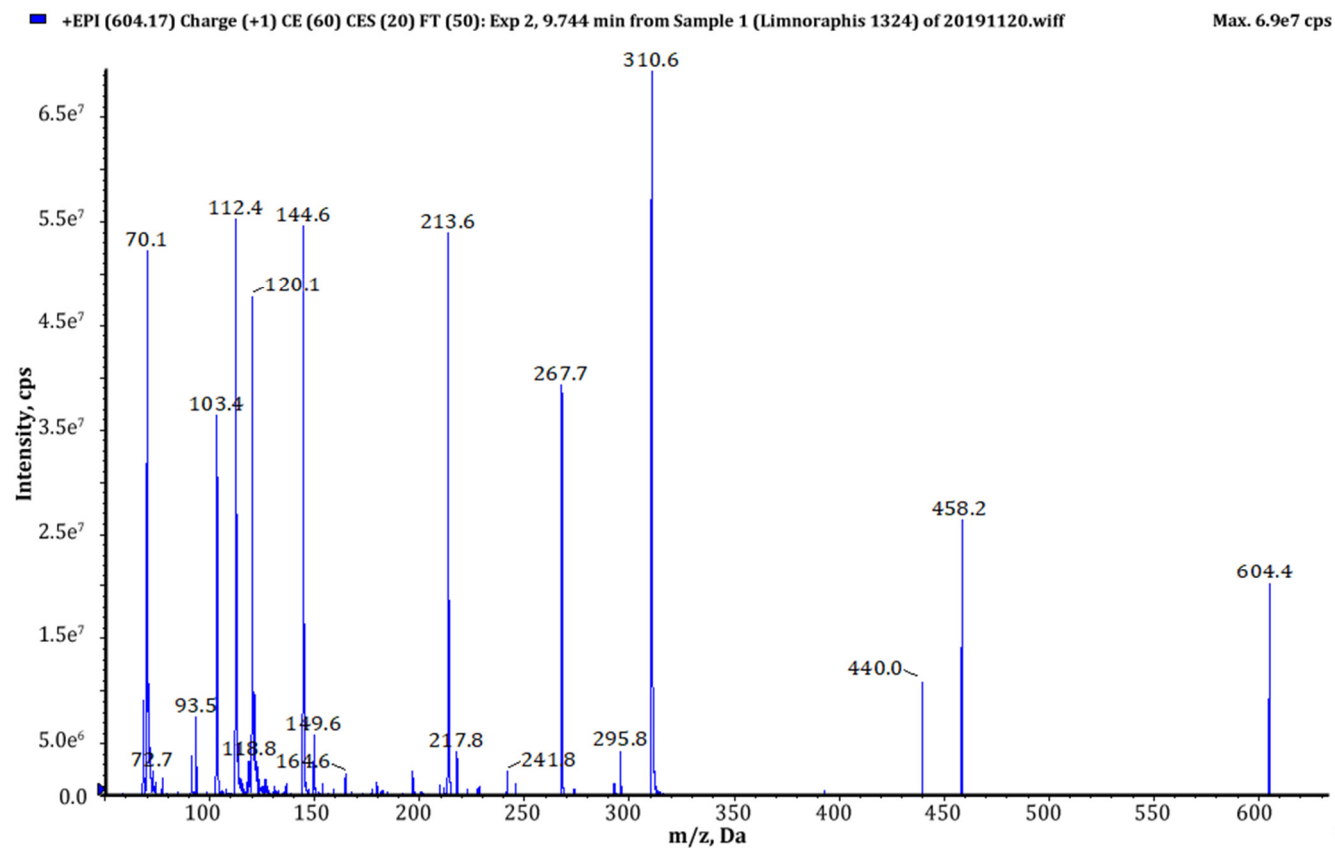


Figure S2. Enhanced product ion mass spectrum of aeruginosamide AEG603 with general structure Phe+Phe+Pro+Pyr+TzlCOOMe identified based on the following fragment ions: 604 [M+H], 458 [M+H-Phe], 310 [Pro+Pyr+TzlCOOMe+H], 295 [Phe+Phe+H], 267 [Phe+Phe+H-CO], 217 [Phe+Pro+H-CO], 213 [Pyr+TzlCOOMe+H], 144 [TzlCOOMe], 120 Phe immonium ion, 112 TzlCO, 70 Pro immonium ion.

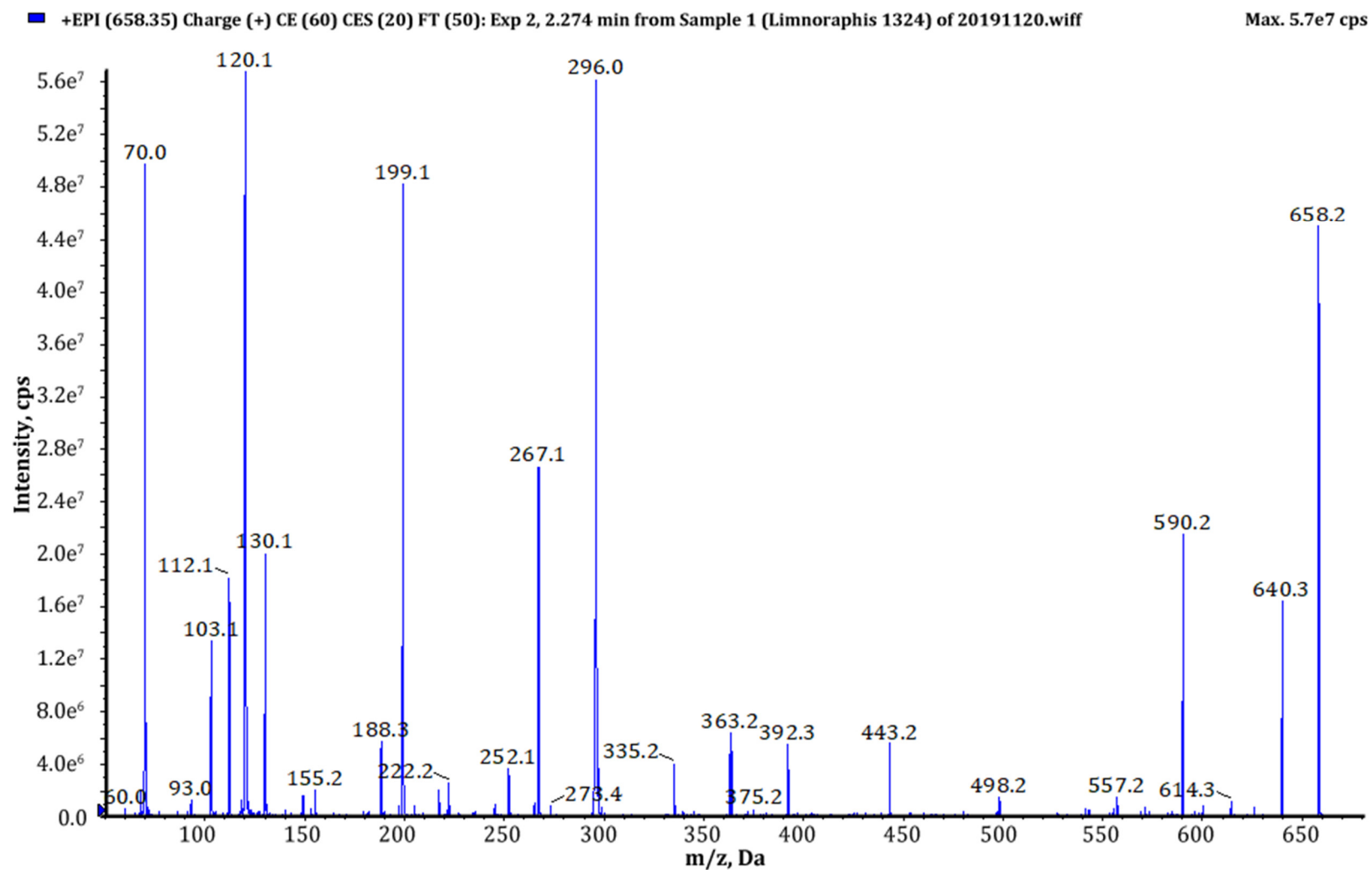


Figure S3. Enhanced product ion mass spectrum of aeruginosamide AEG657 with general structure Pre+Phe+Phe+Pro+Pyr+TzlCOOH identified based on the following fragment ions: 658 [M+H], 640 [M+H-H₂O], 590 [M+H-Pre], 443 [M+H-(Pre+Phe)], 392 [Phe+Phe+Pro+H], 363 [Pre+Phe+Phe+H], 335 [Pre+Phe+Phe+H-CO], 296 [Pro+Pyr+TzlCOOH], 267 [Phe+Phe+H-CO], 199 [Pyr+TzlCOOH+H], 188 [Pre+Phe+H-CO], 130 [TzlCOOH], 120 Phe immonium ion, 112 TzlCO, 70 Pro immonium ion.

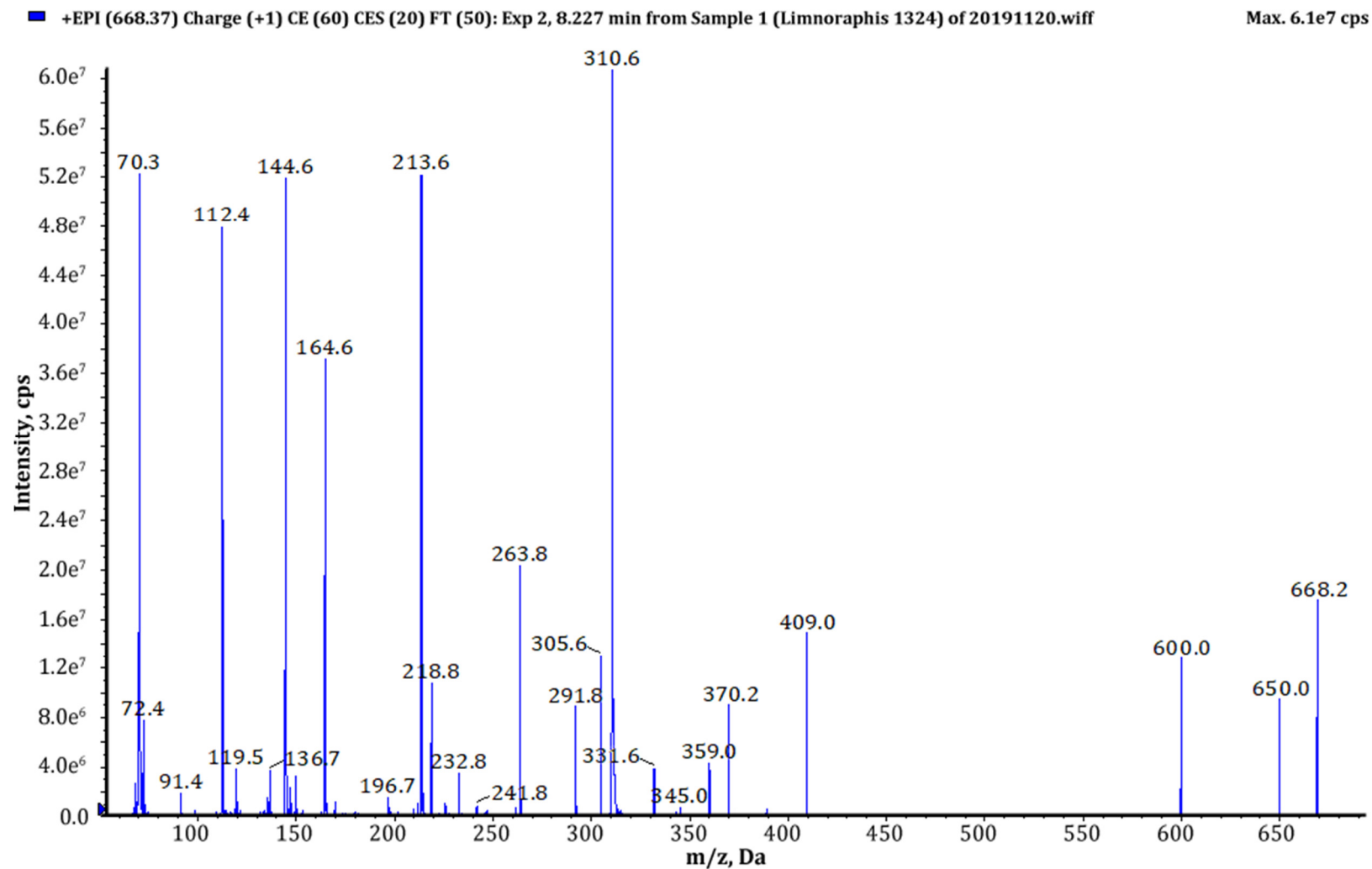


Figure S4. Enhanced product ion mass spectrum of aeruginosamide AER667 with general structure Pre+MeHTyr+Val+Pro+Pyr+TzlCOOMe identified based on the following fragment ions: 668 [M+H], 650 [M+H-H₂O], 600 [M+H-Pre], 409 [Val+Pro+Pyr+TzlCOOMe], 370 [MeHTyr+Val+Pro+H-H₂O], 359 [Pre+MeHTyr+Val+H], 331 [Pre+MeHTyr+Val+H-CO], 310 [Pro+Pyr+TzlCOOMe+H], 291 [MeHTyr+Val+H], 263 [MeHTyr+Val+H-CO], 213 [Pyr+TzlCOOMe+H], 164 MeHTyr immonium ion, 144 [TzlCOOMe], 112 TzlCO, 72 Val immonium ion, 70 Pro immonium ion.

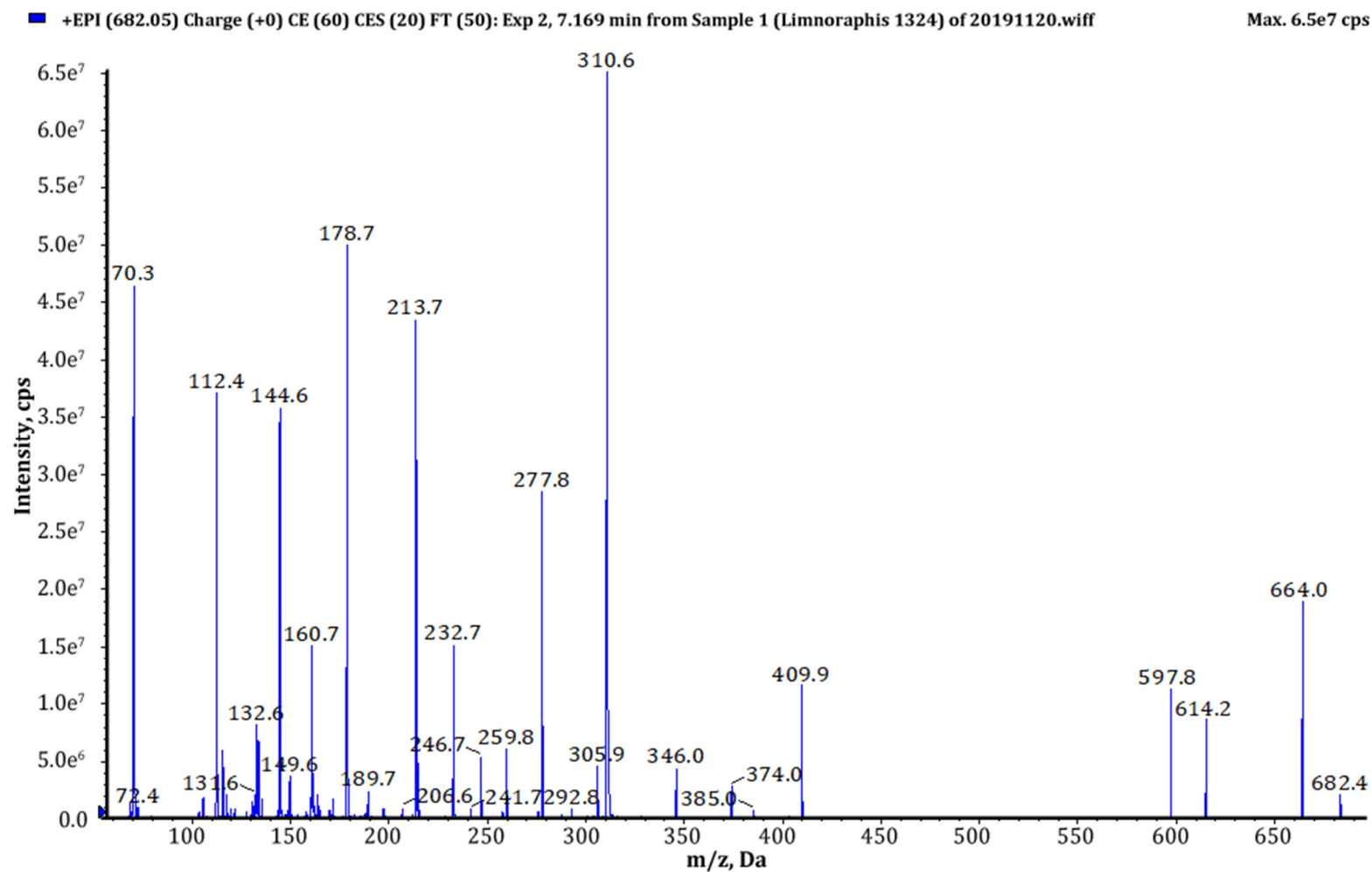


Figure S5. Enhanced product ion mass spectrum of aeruginosamide AER681a with general structure Pre+205+Val+Pro+Pyr+TzlCOOMe identified based on the following fragment ions: 682 [M+H], 664 [M+H-H₂O], 614 [M+H-Pre], 409 [M+H-(Pre+205)], 374 [205+Val+Pro+H-CO], 310 [Pro+Pyr+TzlOMe+H], 305 [205+Val+H], 277 [205+Val+H-CO], 259 [205+Val+H-CO-H₂O], 213 [Pyr+TzlCOOMe+H], 178 [205+H-CO], 144 [TzlCOOMe], 112 TzlCO, 72 Val immonium ion, 70 Pro immonium ion.

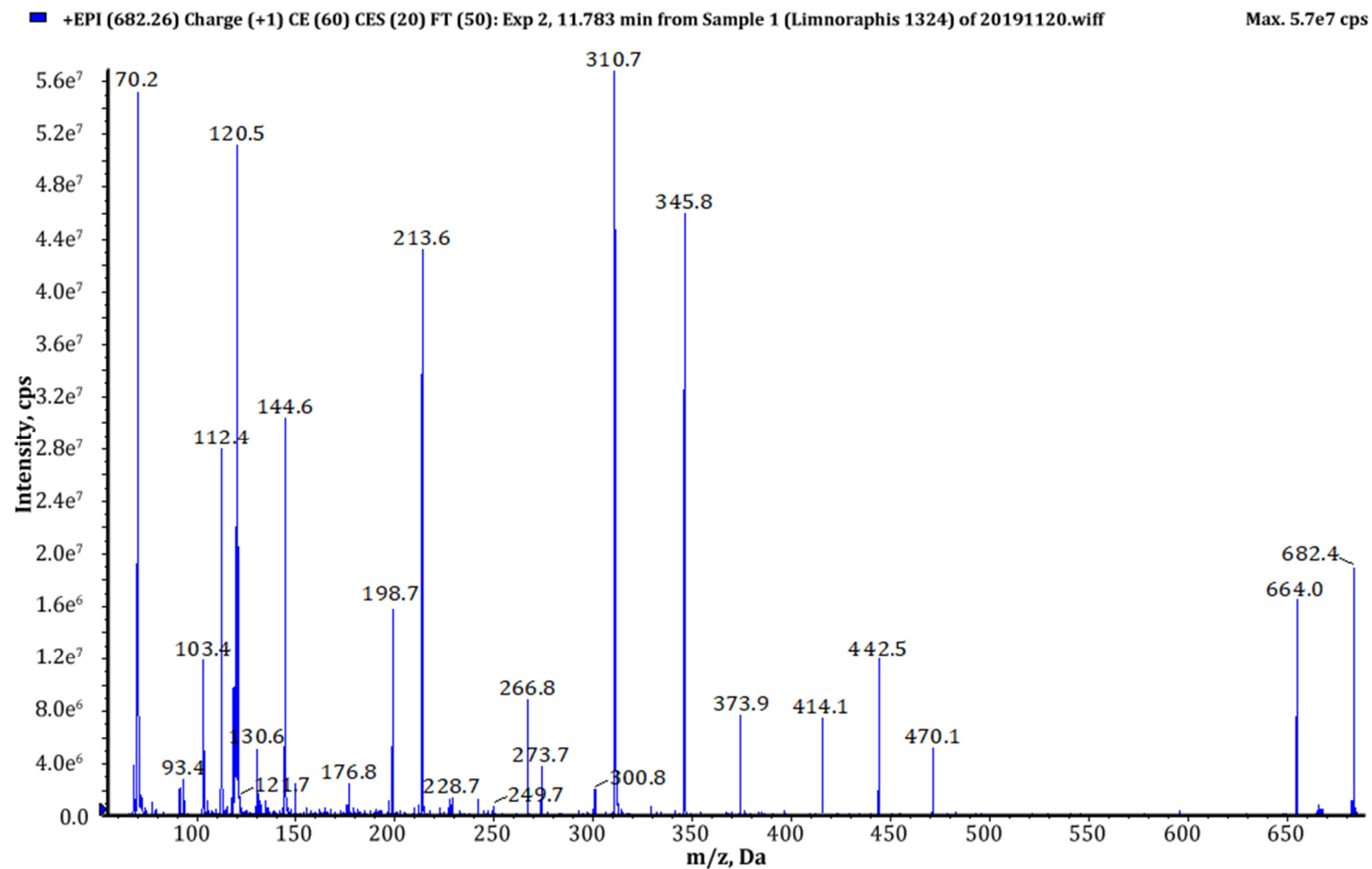


Figure S6. Enhanced product ion mass spectrum of aeruginosamide AER681b with general structure 225+Phe+Pro+Pyr+TzlCOOMe identified based on the following fragment ions: 682 [M+H], 664 [M+H-H₂O], 470 [225+Phe+Pro+H], 442 [225+Phe+Pro+H-CO], 373 [225+Phe+H], 345 [225+Phe+H-CO], 310 [Pro+Pyr+TzlCOOMe+H], 228 [Pre+187+H-CO], 213 [Pyr+TzlOMe+H], 198 [225+H-CO], 144 [TzlCOOMe], 120 Phe immonium ion, 112 TzlCO, 70 Pro immonium ion.

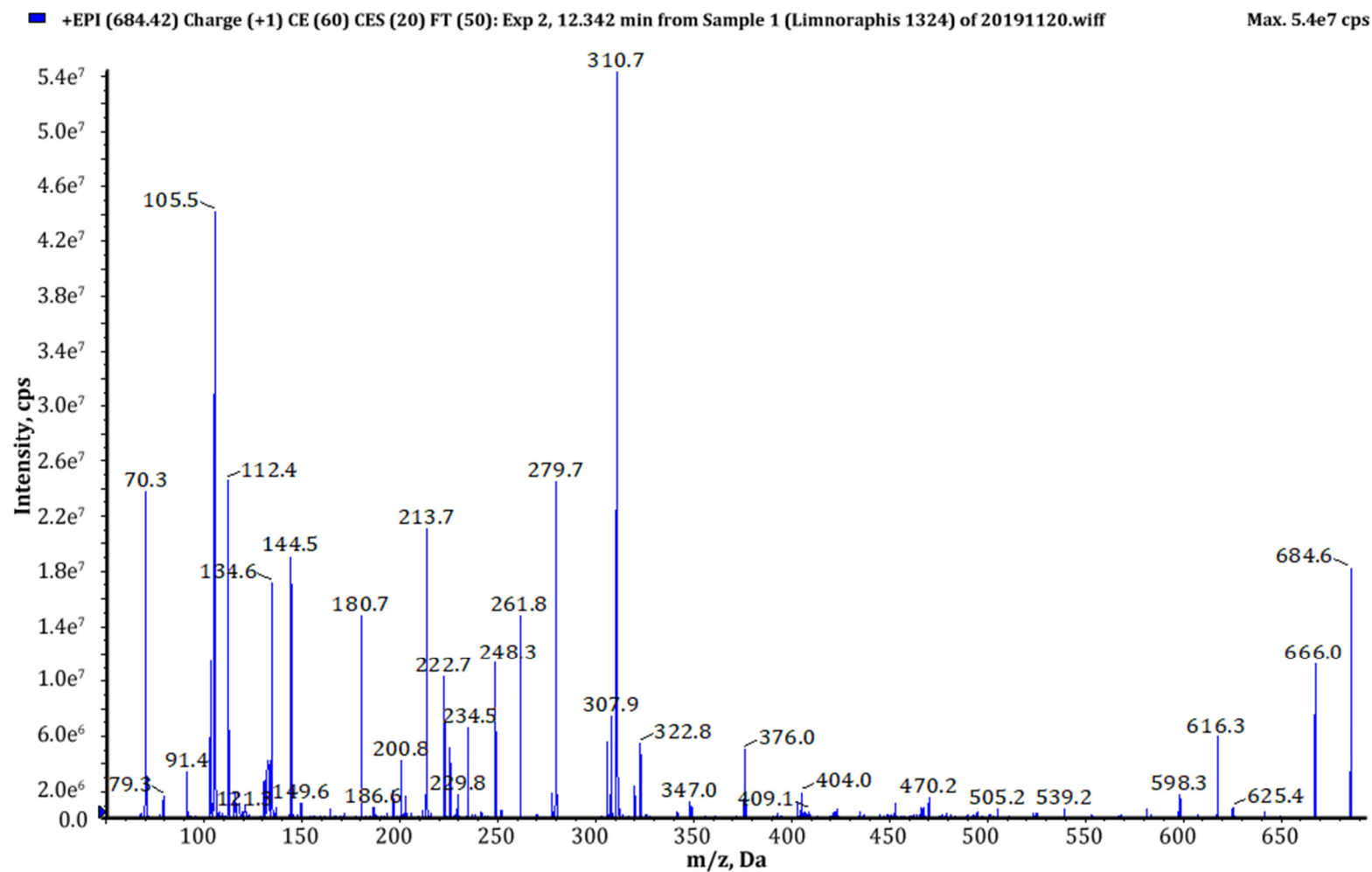


Figure S7. Enhanced product ion mass spectrum of aeruginosamide AER683 with general structure Pre+207+Val+Pro+Pyr+TzlCOOMe identified based on the following fragment ions: 684 [M+H], 666 [M+H-H₂O], 616 [M+H-Pre], 598 [M+H-Pre-H₂O], 409 [Val+Pro+Pyr+TzlCOOMe], 404 [207+Val+Pro+H], 376 [207+Val+Pro+H-CO], 310 [Pro+Pyr+TzlCOOMe+H], 307 [207+Val+H], 279 [207+Val+H-CO], 261 [207+Val+H-CO-H₂O], 213 [Pyr+TzlCOOMe+H], 180 [207+H-CO], 144 [TzlCOOMe], 112 TzlCO, 70 Pro immonium ion.

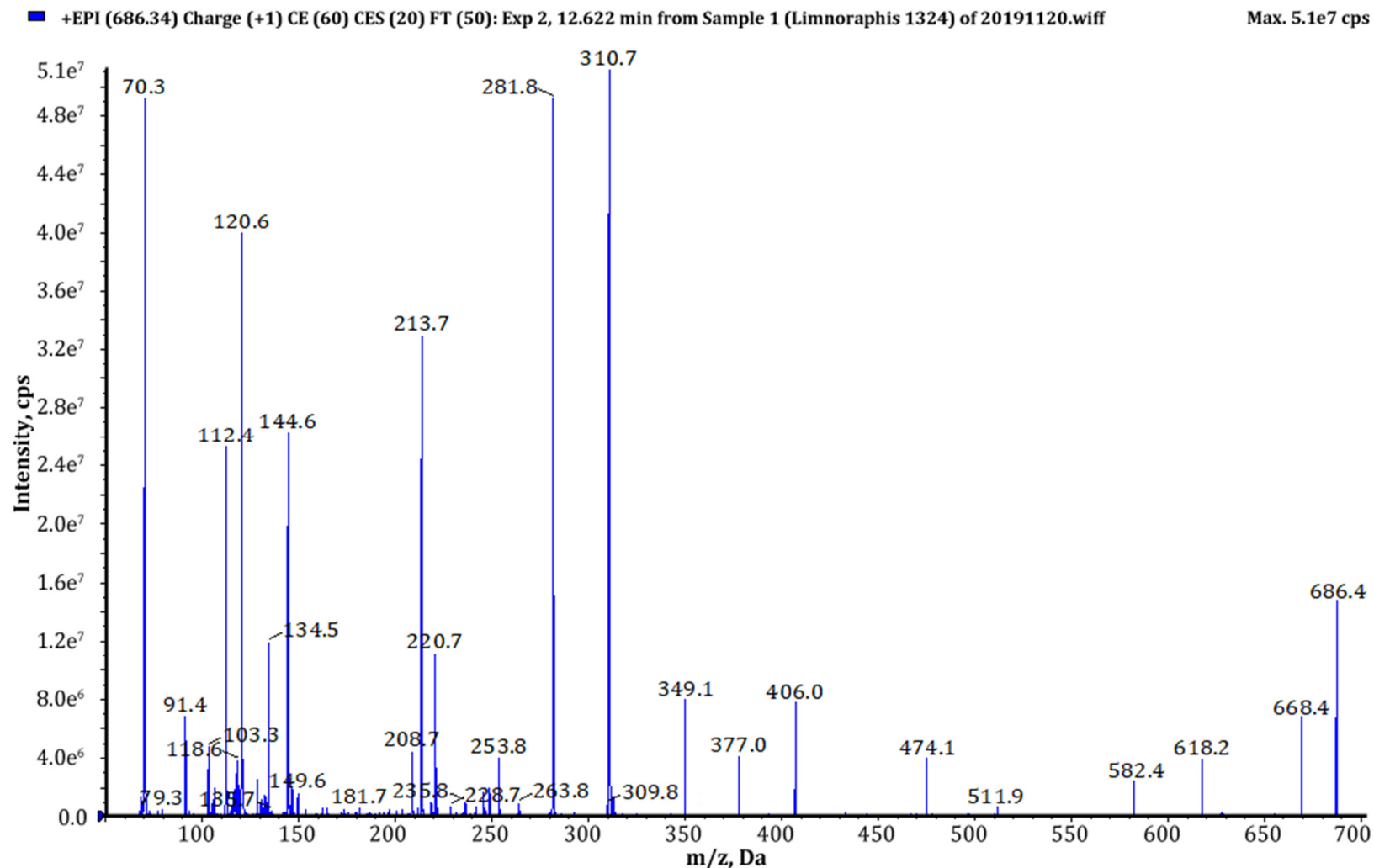


Figure S8. Enhanced product ion mass spectrum of aeruginosamide AER685 with general structure Pre+Phe+Hph/MeHph+Pro+Pyr+TzlCOOMe identified based on the following fragment ions: 686 [M+H], 668 [M+H-H₂O], 618 [M+H-Pre], 474 [Pre+Phe+Hph/MeHph+Pro+H], 406 [Phe+Hph/MeHph+Pro+H], 377 [Pre+Phe+Hph/MeHph+H], 349 [Pre+Phe+Hph/MeHph+H-CO], 310 [Pro+Pyr+TzlCOOMe+H], 309 [Phe+Hph/MeHph+H], 281 [Phe+Hph/MeHph+H-CO], 213 [Pyr+TzlCOOMe+H], 144 [TzlCOOMe], 134 Hph/MeHph immonium ion, 120 Phe immonium ion, 112 TzlCO, 70 Pro immonium ion.

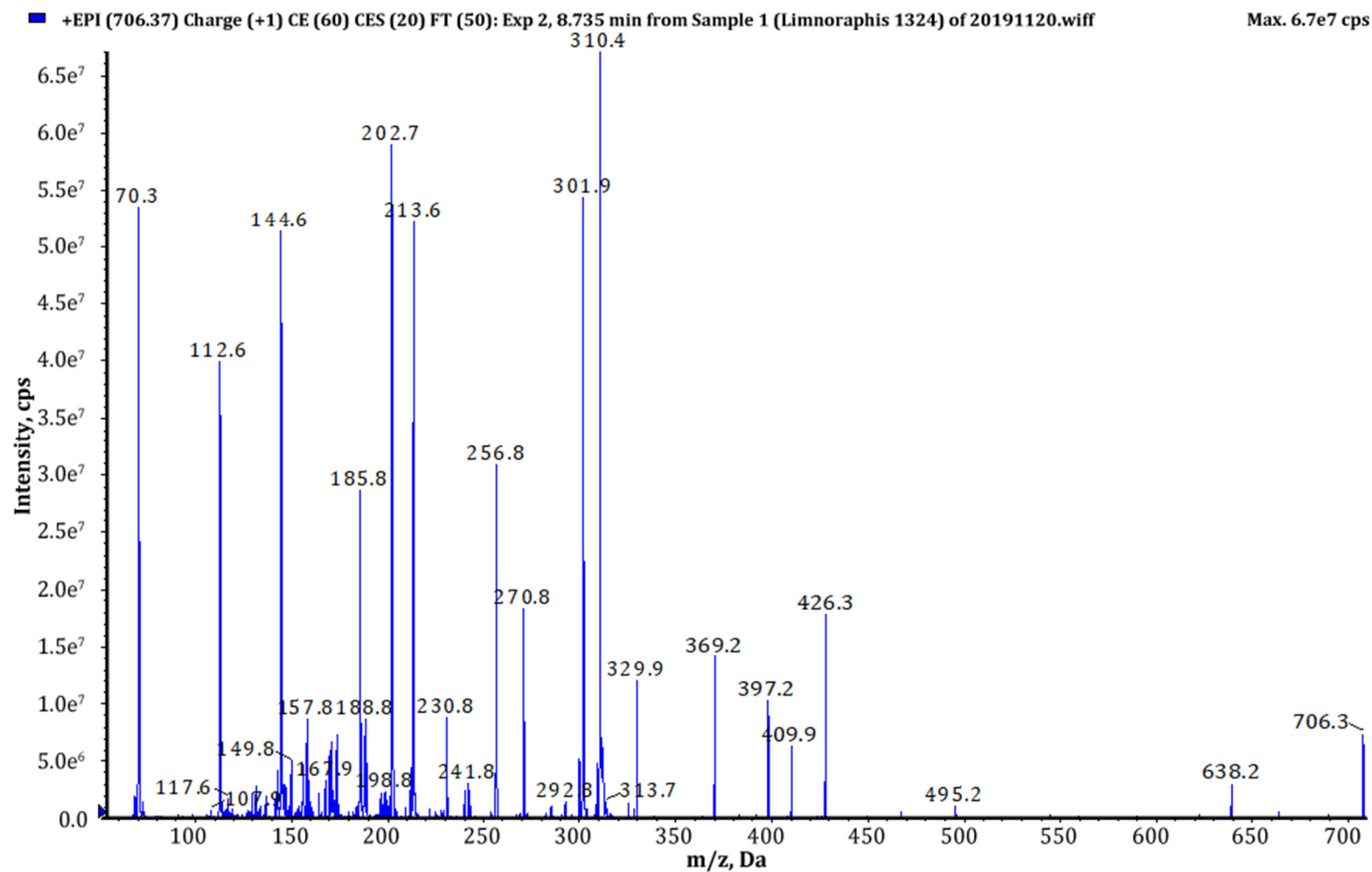


Figure S9. Enhanced product ion mass spectrum of aeruginosamide AEG705 with general structure $(\text{Pre})_2+\text{Hph}/\text{MeHph}+\text{Val}+\text{Pro}+\text{Pyr}+\text{TzI}(\text{COOMe})$ identified based on the following fragment ions: 706 [M+H], 638 [M+H-Pre], 495 [Pre+Hph/MeHph+Val+Pro+Pyr+H], 426 [Pre+Hph/MeHph+Val+Pro+H], 409 [Val+Pro+Pyr+TzI(COOMe)], 397 [(Pre)₂+Hph/MeHph+Val+H], 369 [(Pre)₂+Hph/MeHph+Val+H-CO], 329 [Pre+Hph/MeHph+Val+H], 310 [Pro+Pyr+TzI(COOMe)+H], 301 [Pre+Hph/MeHph+Val+H-CO], 270 [(Pre)₂+Hph/MeHph+H-CO], 230 [Pre+Hph/MeHph+H], 213 [Pyr+TzI(COOMe)+H], 202 [Pre+Hph/MeHph+H-CO], 144 [TzI(COOMe)], 112 TzI(CO), 70 Pro immonium ion.

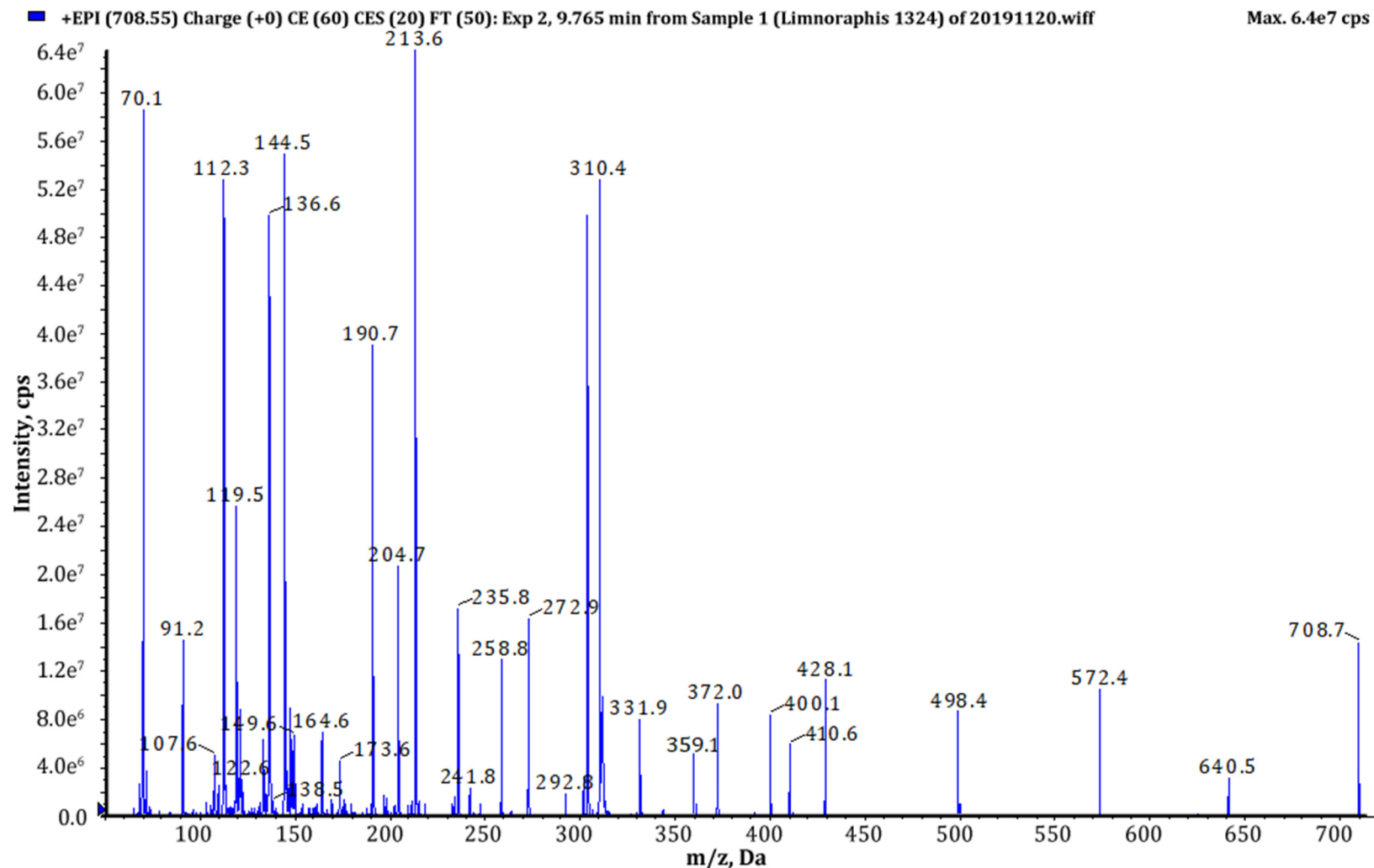


Figure S10. Enhanced product ion mass spectrum of aeruginosamide AEG707 with general structure $(\text{Pre})_2\text{Tyr+Val+Pro+Pyr+TzlCOOMe}$ identified based on the following fragment ions: 708 [M+H], 640 [M+H-Pre], 572 [M+H-(Pre)₂], 498 [M+H-Pre-TzlCOOMe], 429 [Tyr+Val+Pro+Pyr+H], 409 [Val+Pro+Pyr+TzlCOOMe], 400 [Pre+Tyr+Val+Pro+H-CO], 370 [(Pre)₂+Tyr+Val+H-CO], 360 [Tyr+Val+Pro+H], 331 [Pre+Tyr+Val+H], 310 [Pro+Pyr+TzlCOOMe+H], 271 [(Pre)₂+Tyr+H-CO], 235 [Tyr+Val+H-CO], 213 [Pyr+TzlCOOMe+H], 204 [Pre+Tyr+H-CO], 144 [TzlCOOMe], 136 Tyr immonium ion, 112 TzlCO, 70 Pro immonium ion.

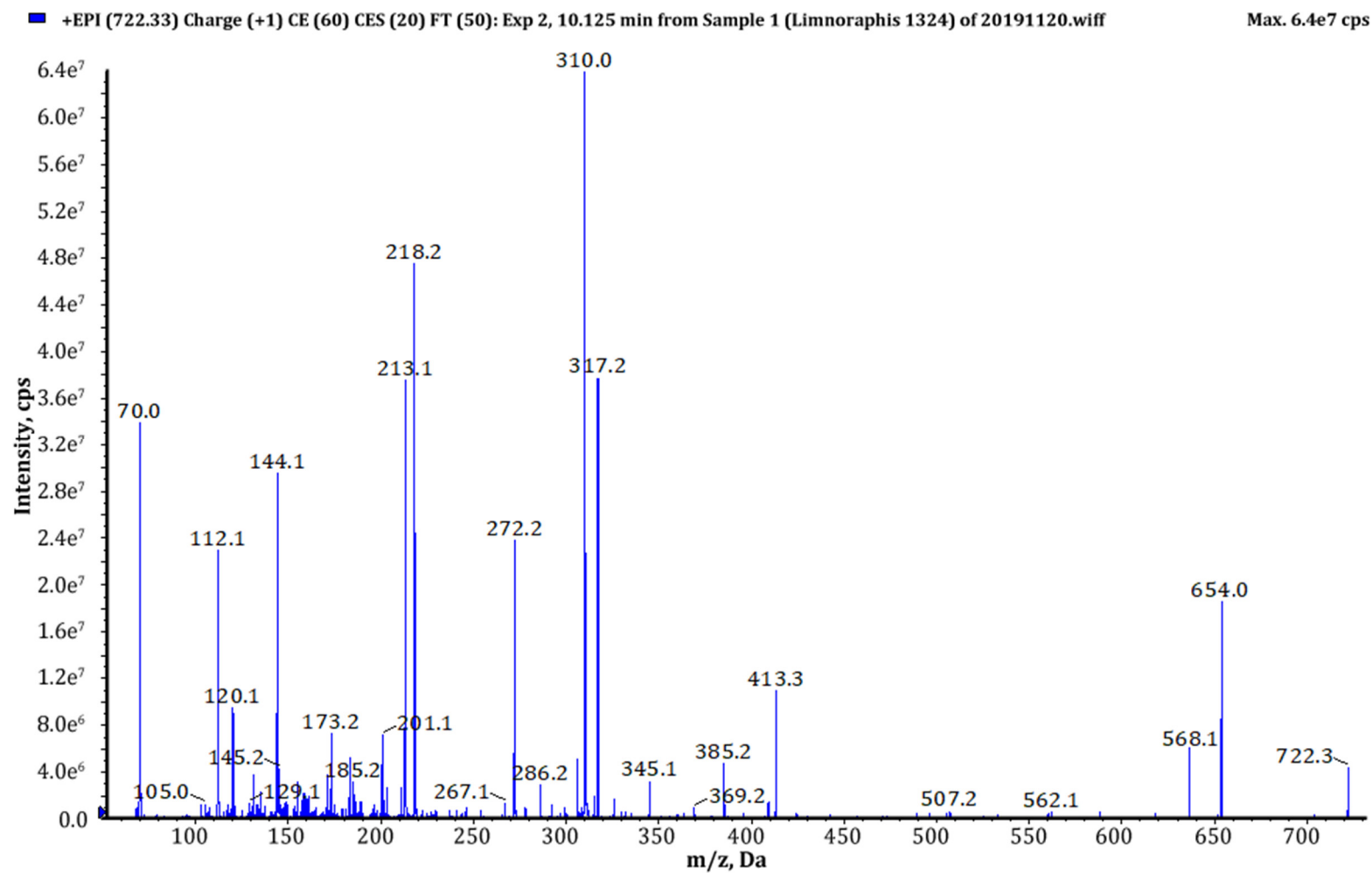


Figure S11. Enhanced product ion mass spectrum of aeruginosamide AEG721 with general structure $(\text{Pre})_2+\text{Tyr}+\text{Ile}/\text{Leu}+\text{Pro}+\text{Pyr}+\text{TzlCOOMe}$ identified based on the following fragment ions: 722 $[\text{M}+\text{H}]$, 654 $[\text{M}+\text{H}-\text{Pre}]$, 586 $[\text{M}+\text{H}-(\text{Pre})_2]$, 413 $[(\text{Pre})_2+\text{Tyr}+\text{Ile}/\text{Leu}+\text{H}]$, 385 $[(\text{Pre})_2+\text{Tyr}+\text{Ile}/\text{Leu}+\text{H}-\text{CO}]$, 345 $[\text{Pre}+\text{Tyr}+\text{Ile}/\text{Leu}+\text{H}]$, 317 $[\text{Pre}+\text{Tyr}+\text{Ile}/\text{Leu}+\text{H}-\text{CO}]$, 310 $[\text{Pro}+\text{Pyr}+\text{TzlOMe}+\text{H}]$, 272 $[(\text{Pre})_2+\text{Tyr}+\text{H}-\text{CO}]$, 213 $[\text{Pyr}+\text{TzlCOOMe}+\text{H}]$, 144 $[\text{TzlCOOMe}]$, 112 TzlCO , 70 Pro immonium ion.

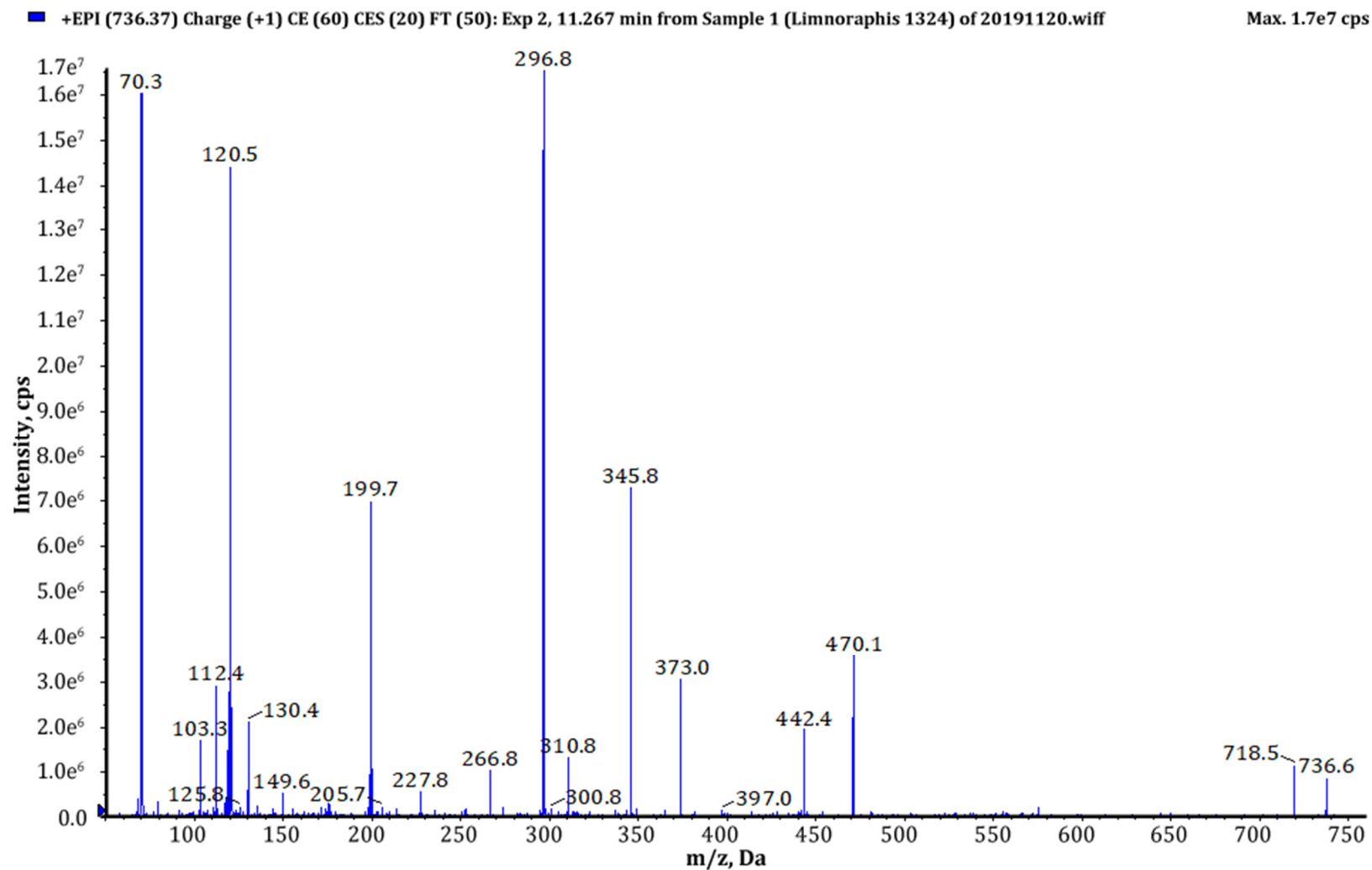


Figure S12. Enhanced product ion mass spectrum of aeruginosamide AER735 with general structure Pre+225+Phe+Pro+Pyr+TzlCOOH identified based on the following fragment ions: 736 [M+H], 718 [M+H-H₂O], 470 [225+Phe+Pro+H], 442 [225+Phe+Pro+H-CO], 373 [225+Phe+H], 345 [225+Phe+H-CO], 296 [Pro+Pyr+TzlCOOH+H], 266 [Pre+225+H-CO], 199 [Pyr+TzlCOOH+H], 130 [TzlCOOH], 120 Phe immonium ion, 112 TzlCO, 70 Pro immonium ion.

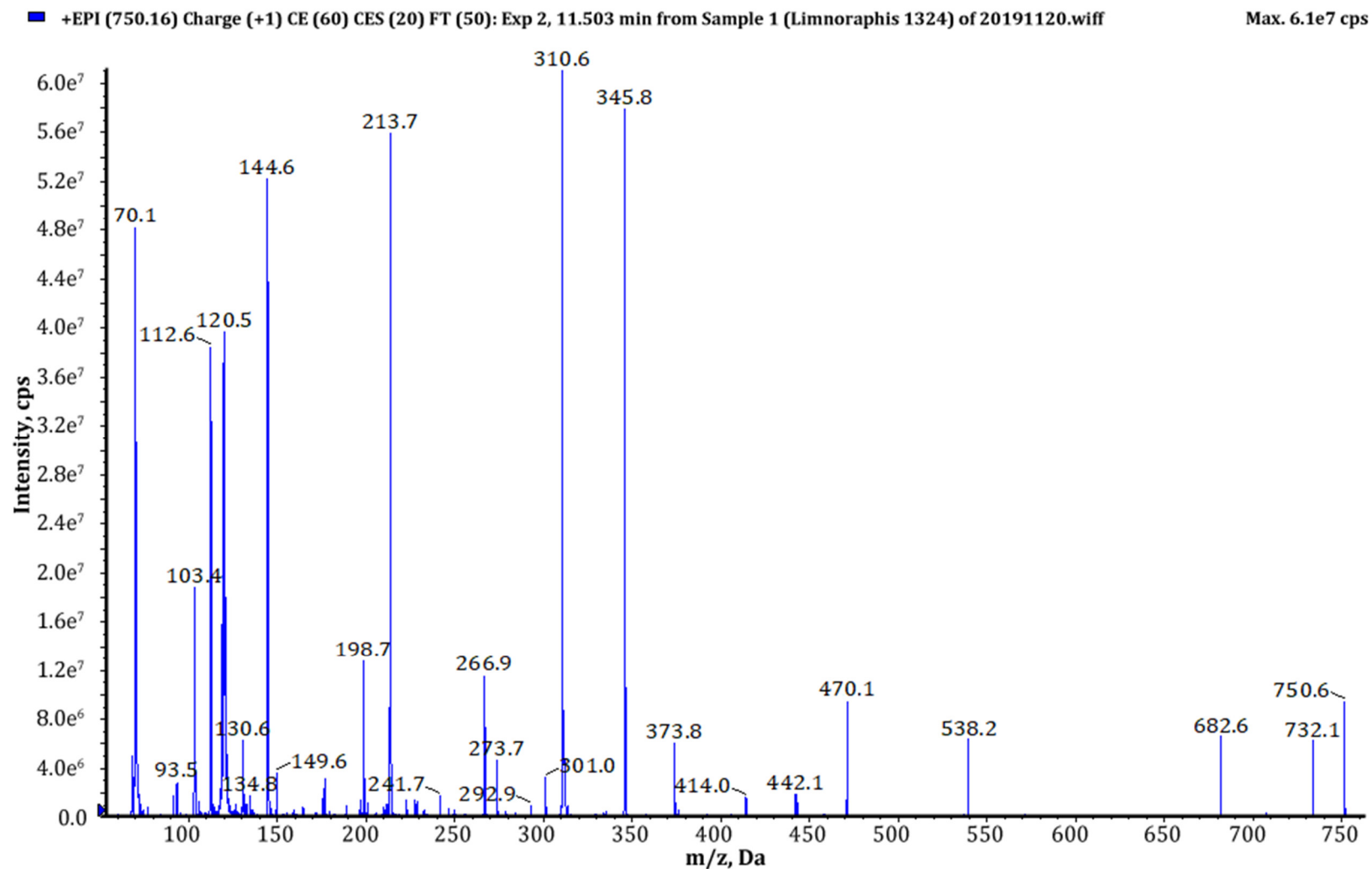


Figure S13. Enhanced product ion mass spectrum of aeruginosamide AER749 with general structure Pre+225+Phe+Pro+Pro+TzlCOOMe identified based on the following fragment ions: 750 [M+H], 732 [M+H-H₂O], 538 [M+H-(Pyr+TzlCOOMe)], 470 [225+Phe+Pro+H], 442 [225+Phe+Pro+H-CO], 373 [225+Phe+H], 345 [225+Phe+H-CO], 310 [Pro+Pyr+TzlCOOMe+H], 266 [Pre+225+H-CO], 213 [Pyr+TzlCOOMe+H], 198 [225+H-CO], 144 [TzlCOOMe], 120 Phe immonium ion, 112 TzlCO, 70 Pro immonium ion.

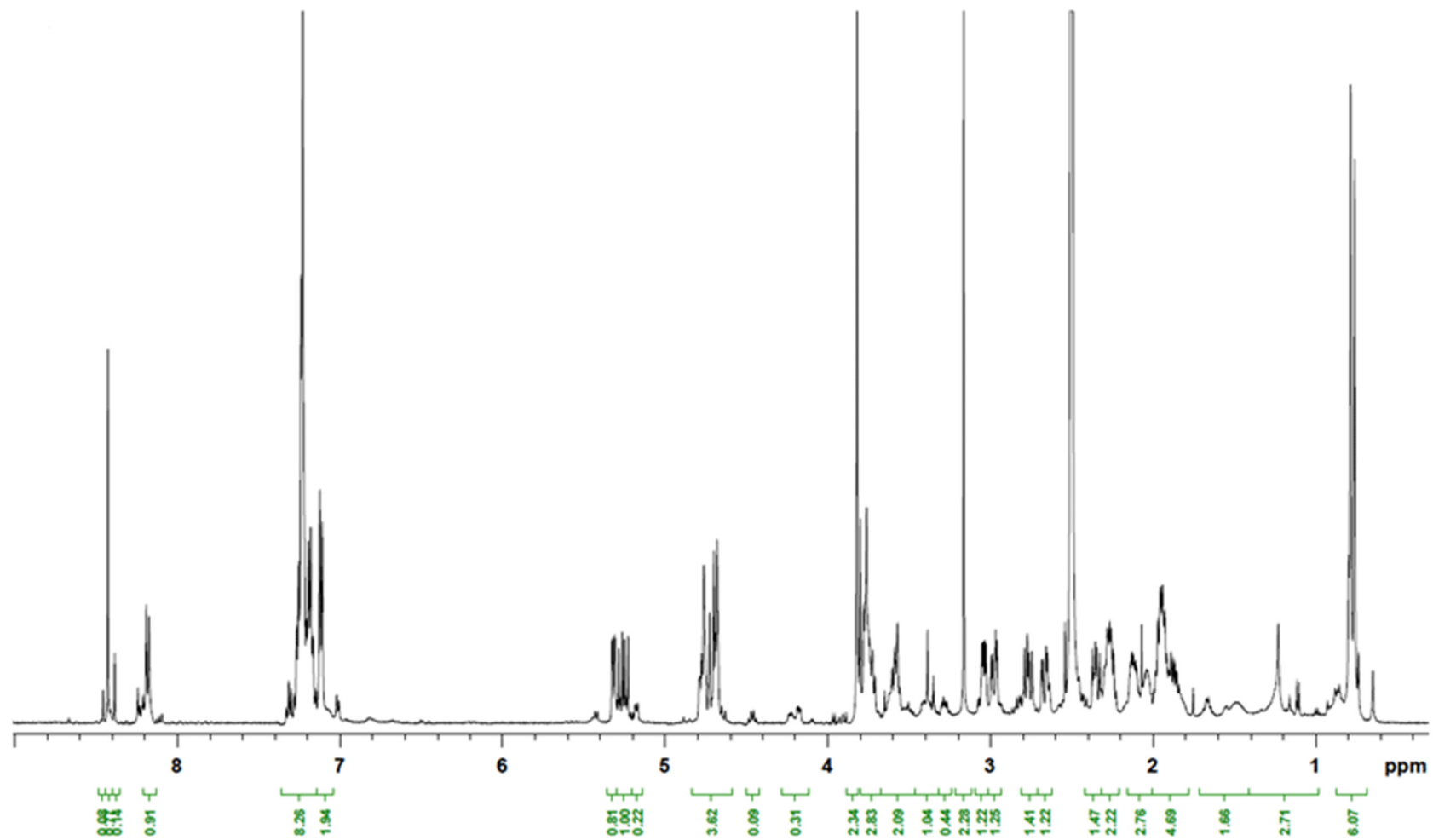


Figure 14. ¹H NMR Spectrum of aeruginosamide AEG671 in DMSO-d₆.

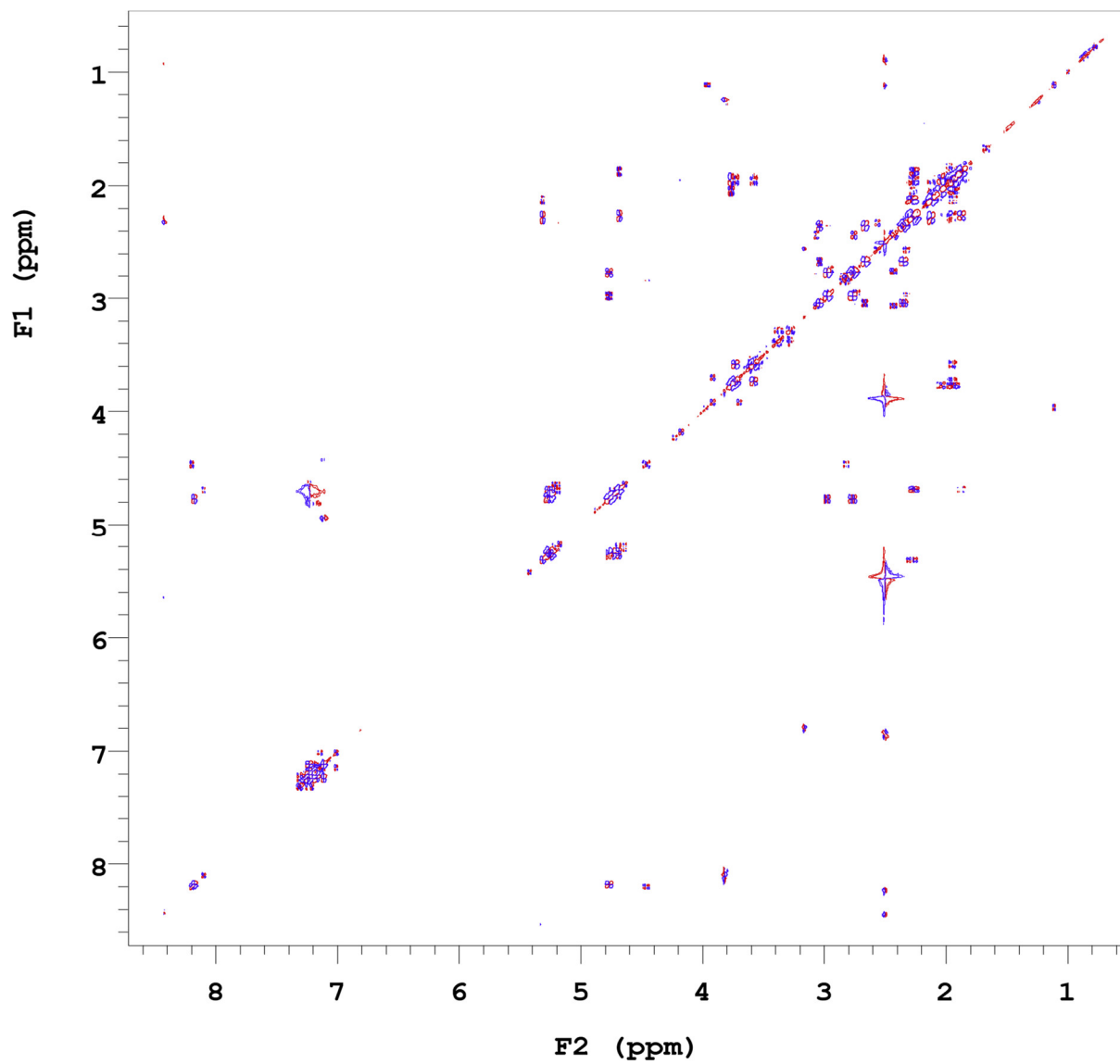


Figure 15. COSY Spectrum of aeruginosamide AEG671 in DMSO-d₆.

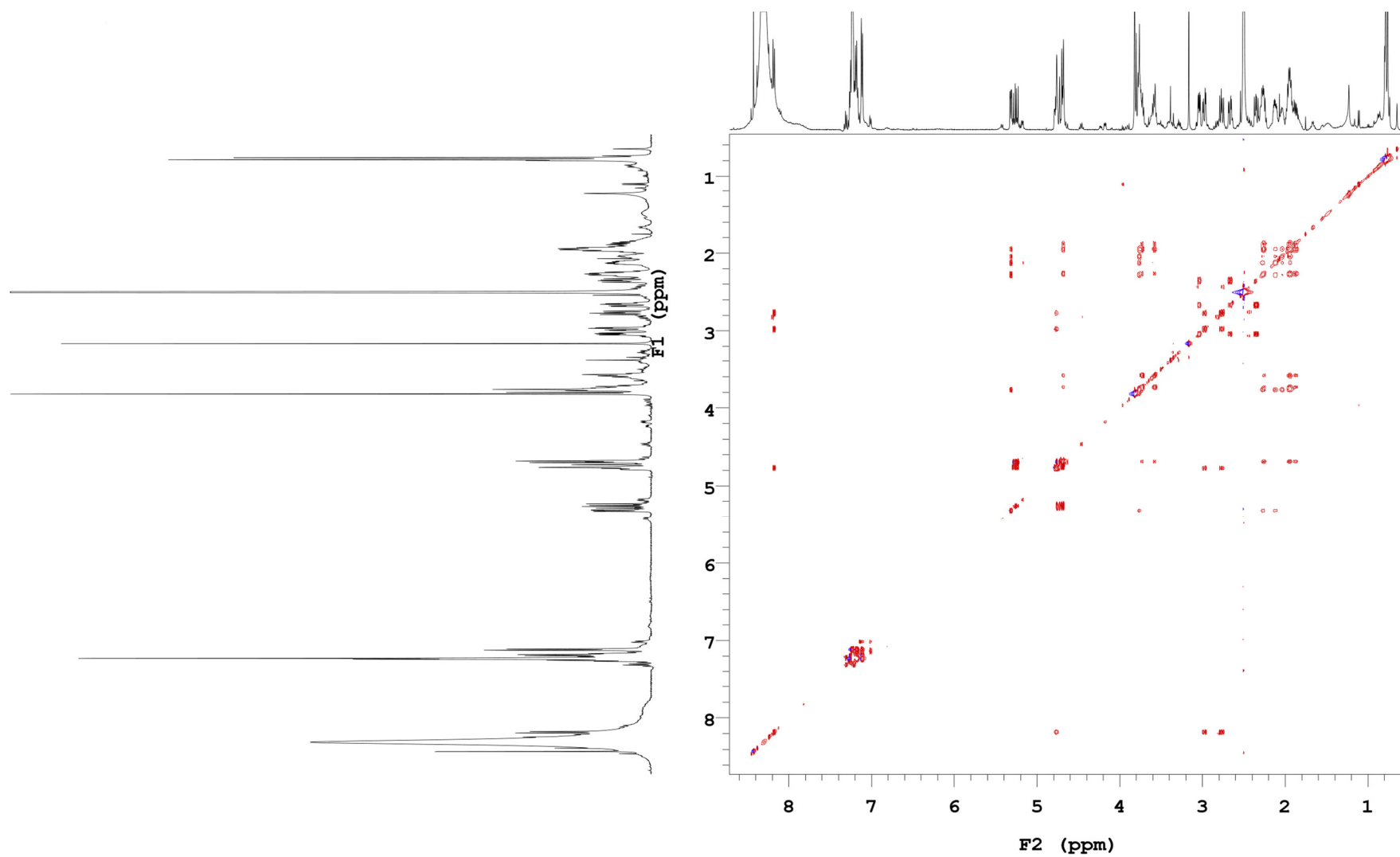


Figure 16. TOCSY Spectrum of aeruginosamide AEG671 in DMSO-d₆.

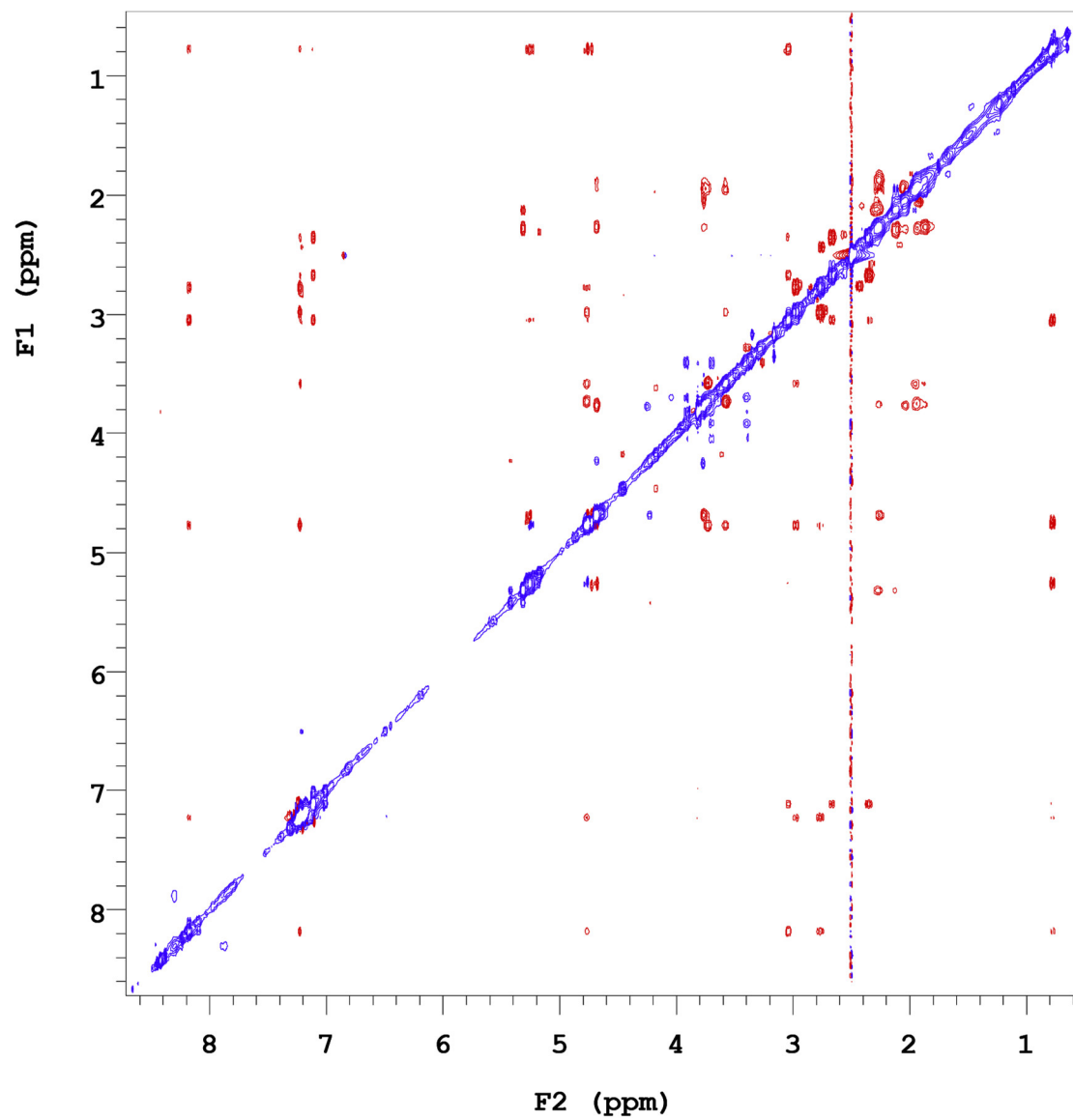


Figure 17. ROESY Spectrum of aeruginosamide AEG671 in DMSO-d₆.

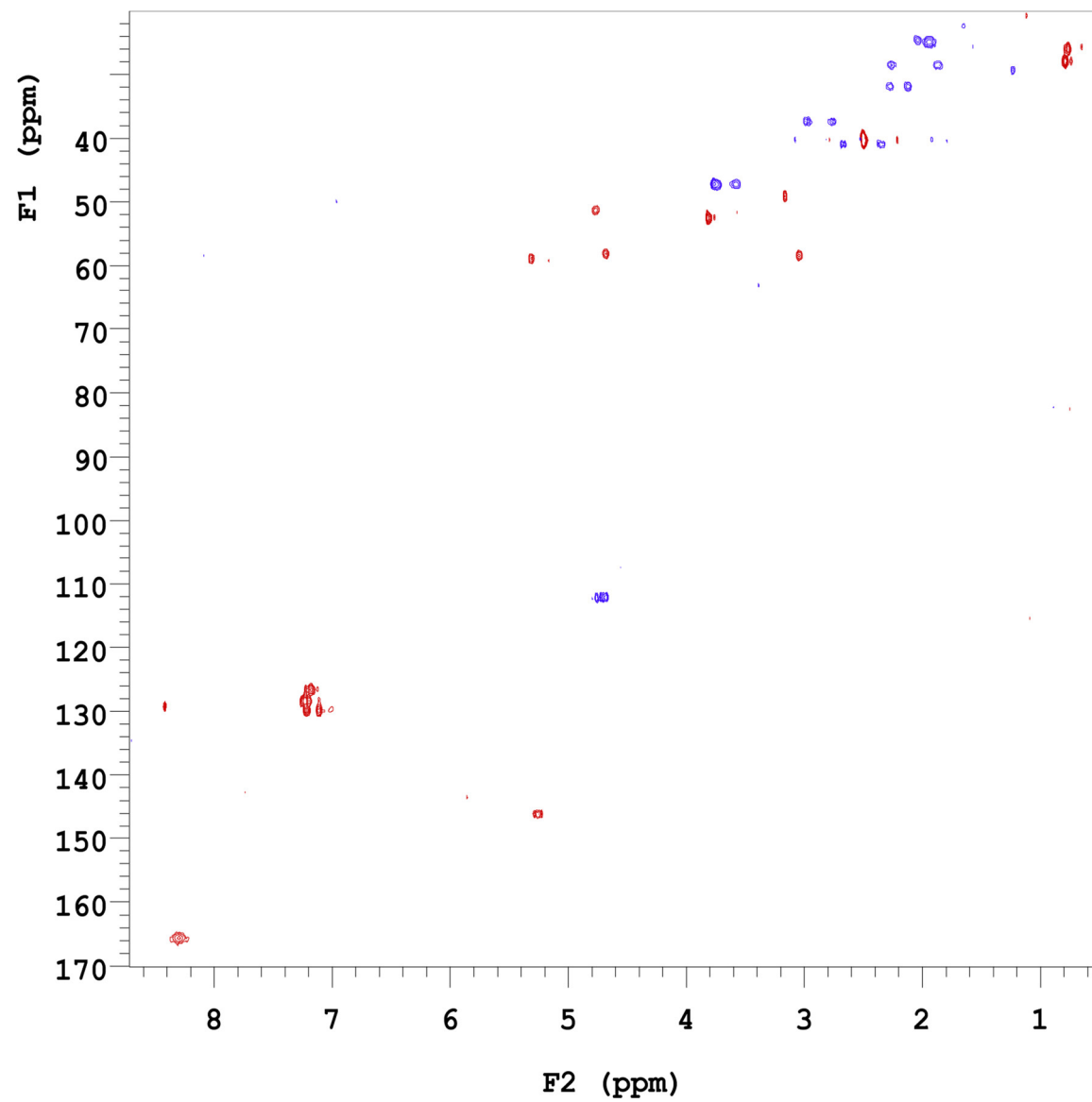


Figure 18. HSQC Spectrum of aeruginosamide AEG671 in DMSO-d₆.

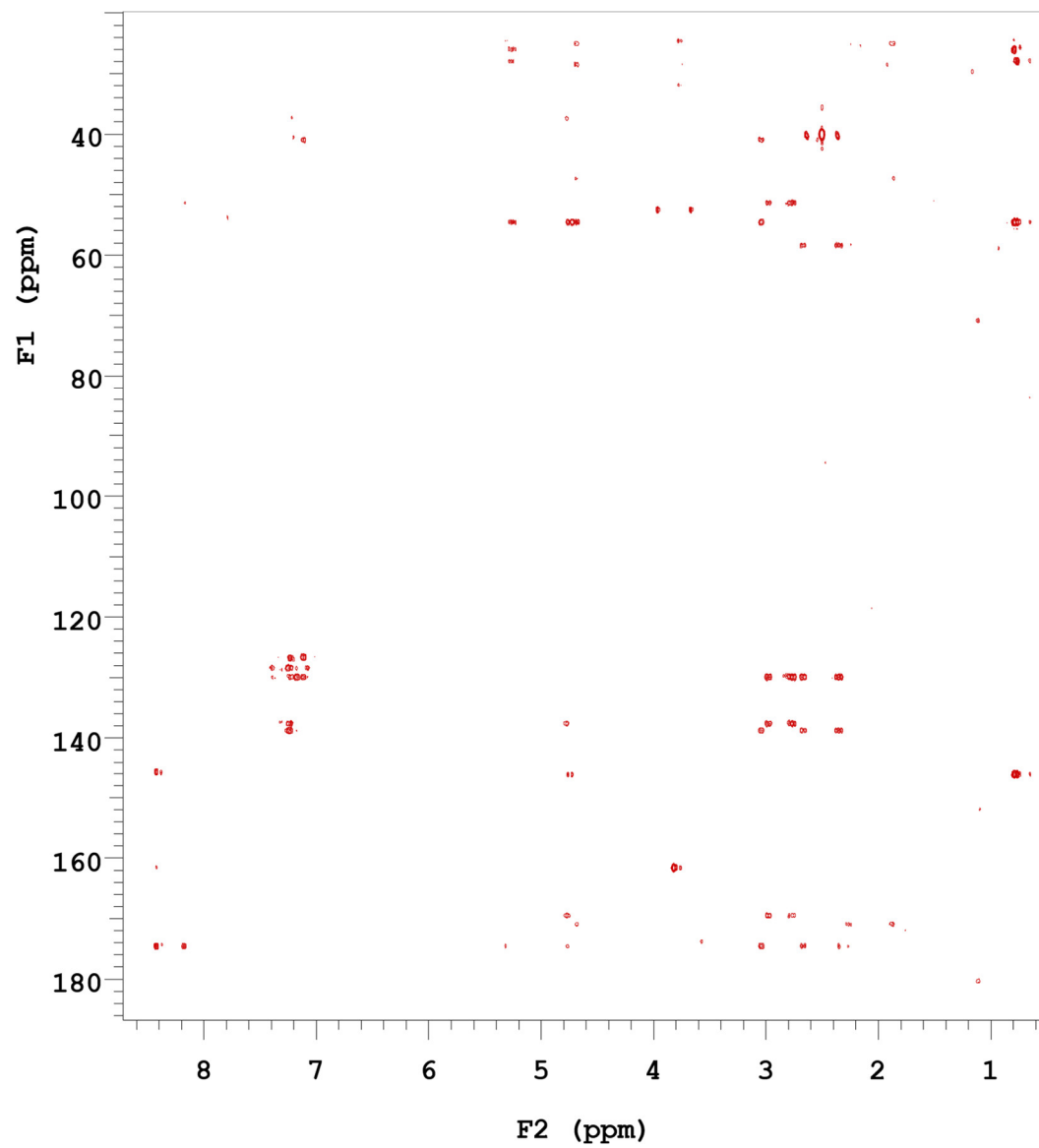


Figure 19. HMBC Spectrum of aeruginosamide AEG671 in DMSO-d₆.



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