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Supporting Information

for

Genomics-inspired discovery of massiliachelin, an agrochelin epimer from *Massilia* sp. NR 4-1

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Additional tables and copies of NMR spectra

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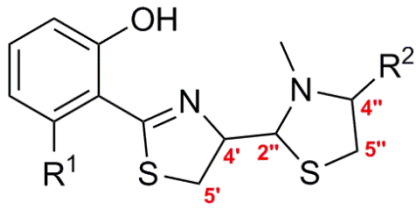
Table S1: Epimerization domains in pyochelin-type synthetases and configuration of the generated thiazoline ring.

	Protein accession # of PchE homolog	Methyltransferase-like epimerization domain in PchE homolog	Configuration of thiazoline ring (proposed)
Pyochelin	AAD55800	Yes	D
Enantio-pyochelin	ABW70809	No	L
Yersiniabactin	P48633	Yes	D
Micacocidin	CAD15508	Yes	D
Massiliachelin (**1**)	AKU20507	Yes	(D)

Table S2: Alignment of the residue 88–103 and 134–148 regions of the ketoreductase (KR) domains in MicG from *Ralstonia solanacearum* GMI1000, HMWP1 from *Yersinia pestis* KIM6+, and ACZ_RS02195 from *Massilia* sp. NR 4-1.

	Protein accession #	88–103 region	134–149 region	KR-type	Configuration (proposed)
MicG	CAD15512	HLAGIVR**D**APLAAADWR	FSSAASACGA**P**GQGAH	B	*S*
HMWP1	AAC69588	HAAGVLA**D**APLQELDDH	YSSAAATLGA**P**GQSAH	B	*S*
RS02195	WP_050407226	HLAAVVR**D**ATLAAINTE	FSSAATAFGA**P**GQGAY	B	(*S*)

Table S3: Stereochemistry of siderophores with a thiazoline-thiazolidine motif.



Natural product	Configuration	δ(H-4'), m (*J* in Hz) measured in $CDCl_3$	Reference in main manuscript
Pyochelin I	4'*R*, 2''*R*, 4''*R*	5.08, td (8.8, 5.0)	[19]
Yersiniabactin I	4'*R*, 2''*R*, 4''*R*	5.15, td (9.2, 4.8)	[26]
Massiliachelin (**1**)	4'*R*, 2''*R*, 4''*R*	5.09, td (9.9, 6.4)	This study
Neopyochelin I	4'*S*, 2''S, 4''*R*	5.12, td (9.1, 4.6)	[19]
Pyochelin II	4'*R*, 2''*S*, 4''*R*	4.92, q (8.2)	[19]
Yersiniabactin II	4'*R*, 2''*S*, 4''*R*	4.78, q (n.d.)	[21]
Agrochelin (**2**)	4'*R*, 2''*S*, 4''*R*	4.72, q (8.7)	[17]
Neopyochelin II	4'*S*, 2''*R*, 4''*R*	4.79, q (8.0)	[19]

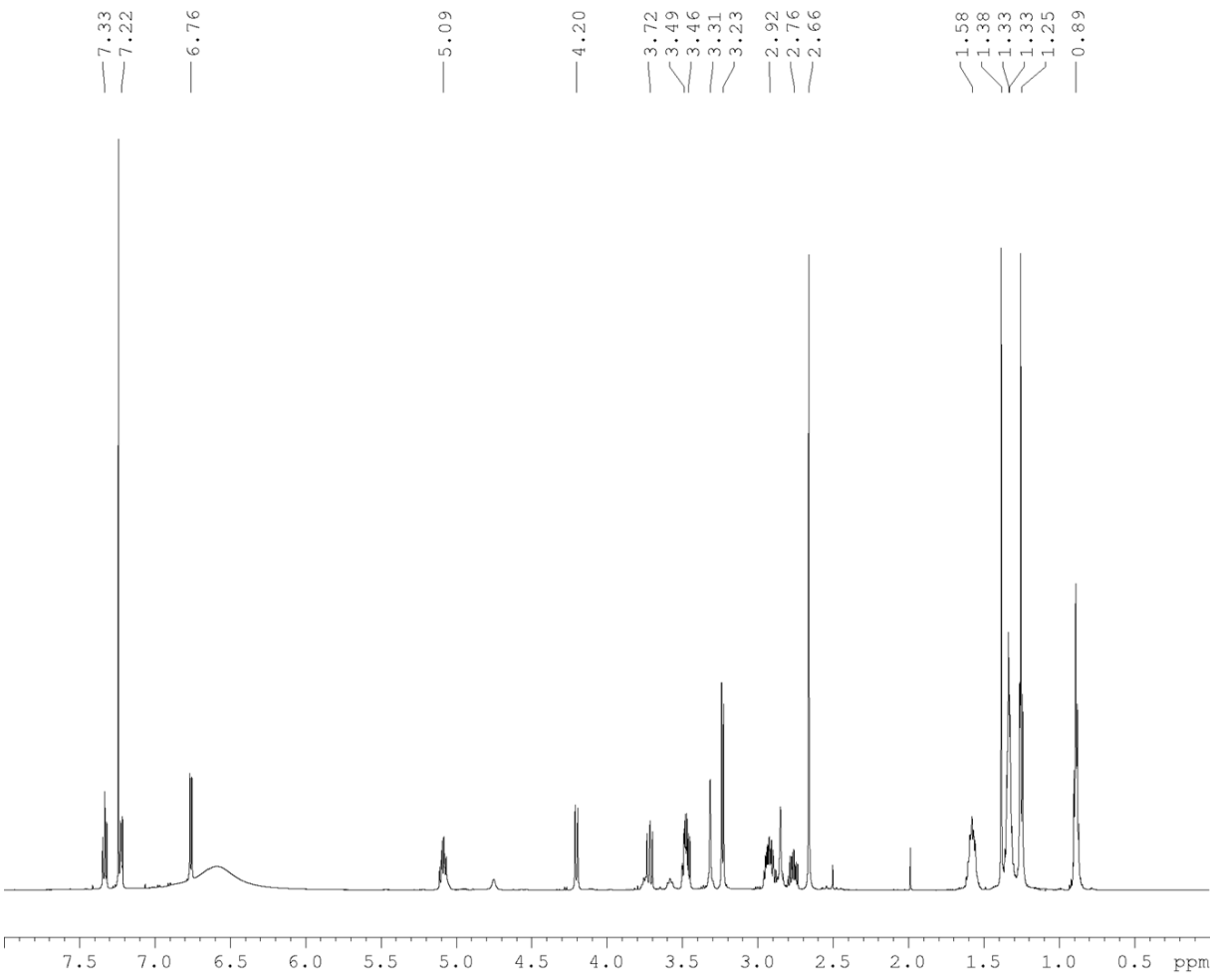


Figure S1: ^{1}H NMR spectrum of massiliachelin (**1**) in chloroform-*d*.

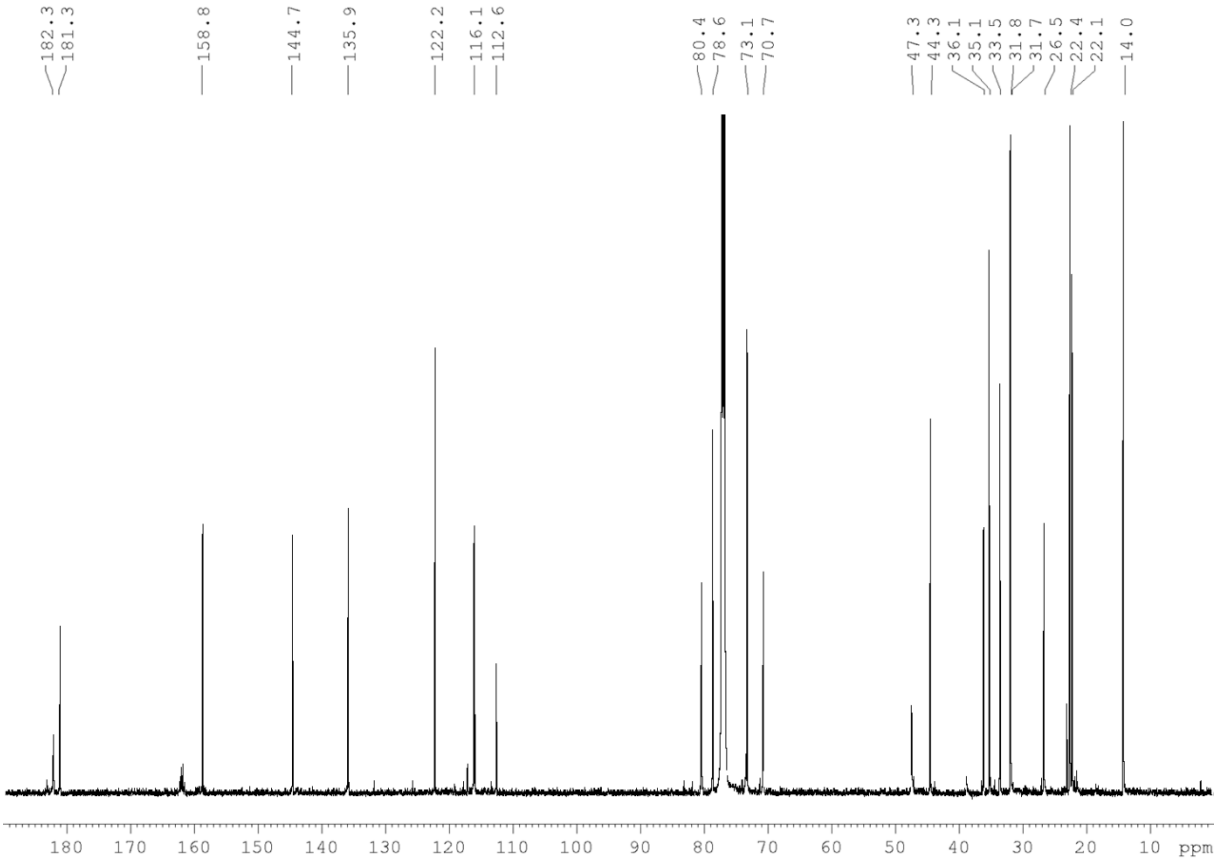


Figure S2: ^{1}H-decoupled ^{13}C NMR spectrum of massiliachelin (**1**) in chloroform-*d*.

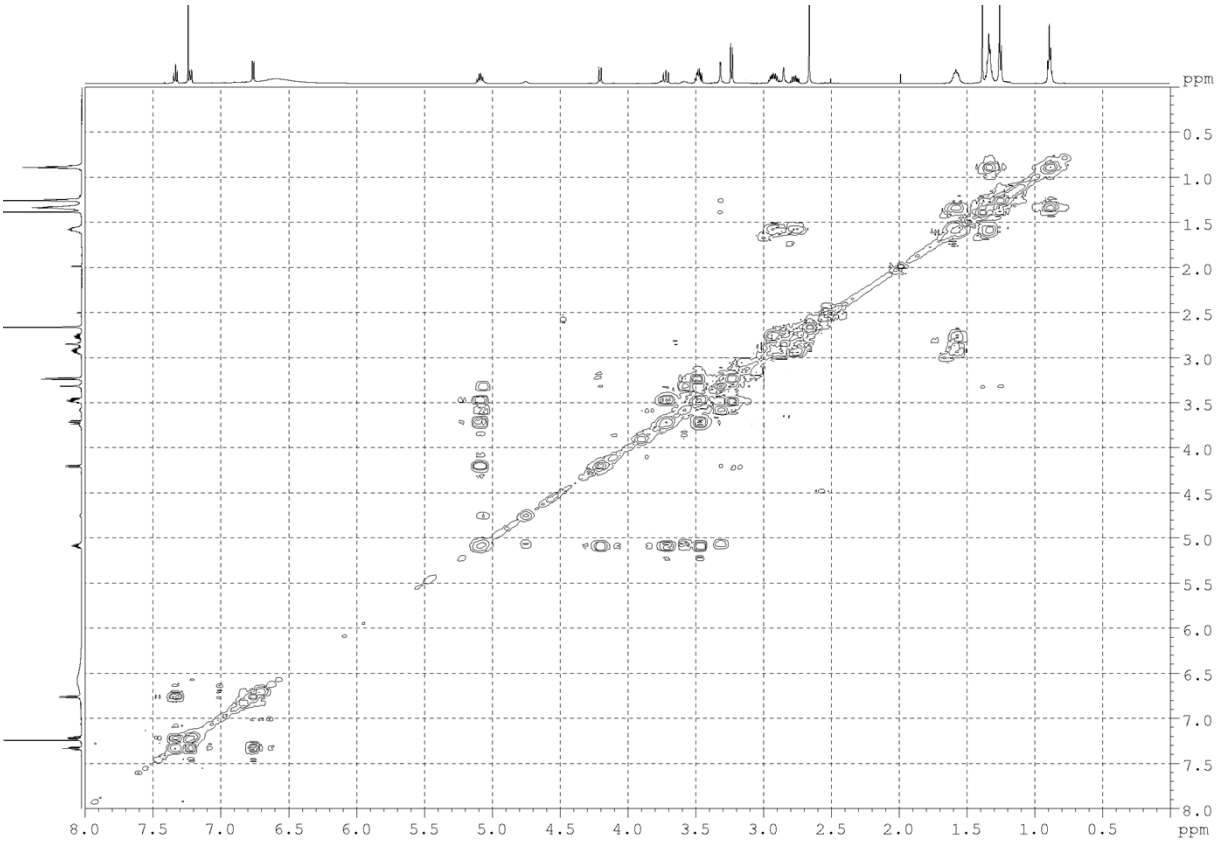


Figure S3: ^{1}H,^{1}H COSY spectrum of massiliachelin (**1**) in chloroform-*d*.

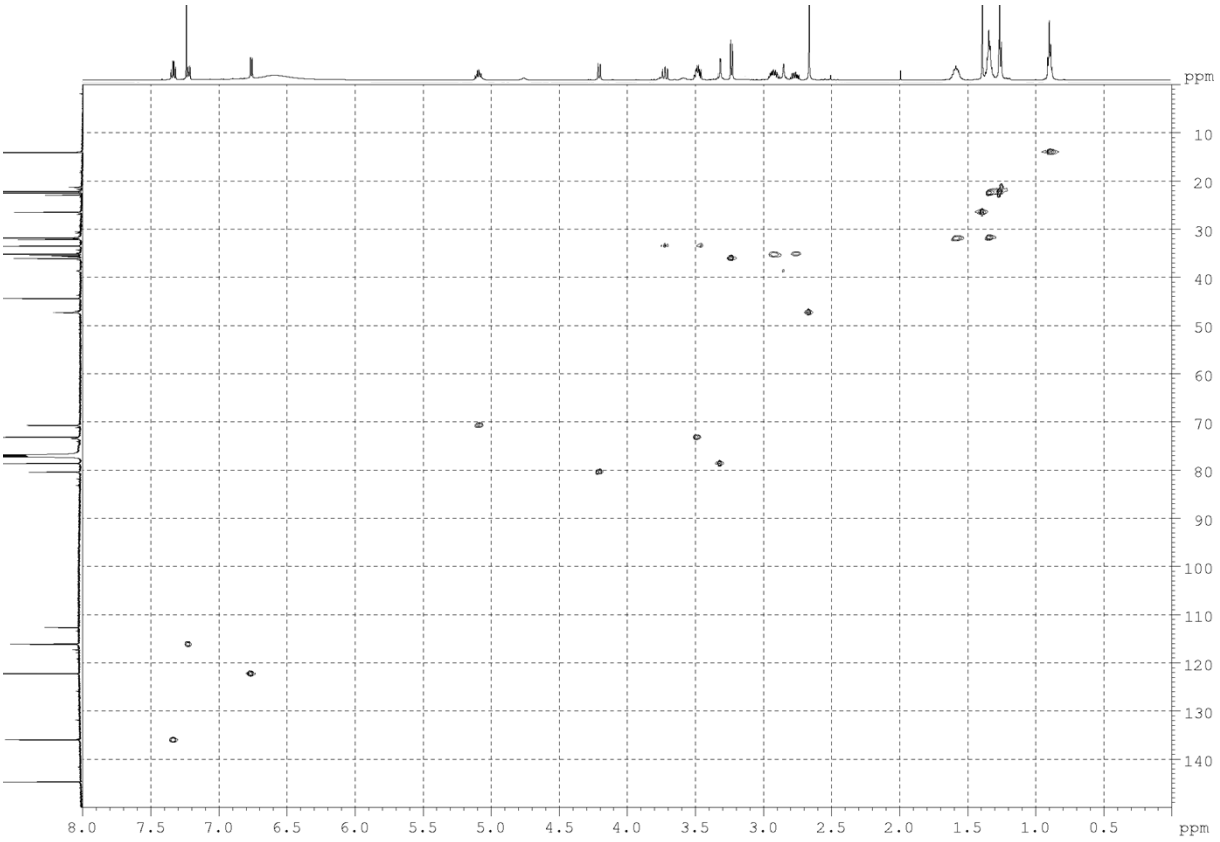


Figure S4: $^{1}H,^{13}C$ HSQC spectrum of massiliachelin (**1**) in chloroform-*d*.

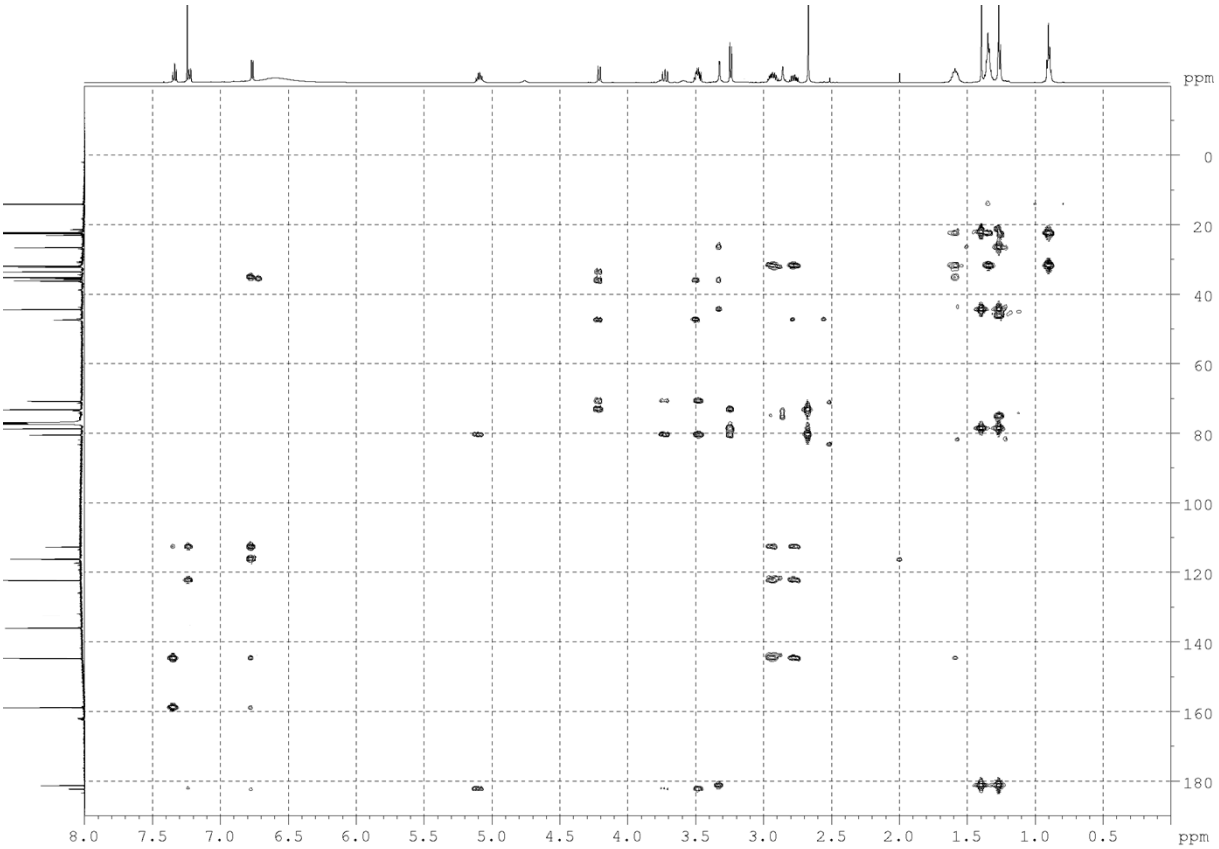


Figure S5: $^{1}H,^{13}C$ HMBC spectrum of massiliachelin (**1**) in chloroform-*d*.

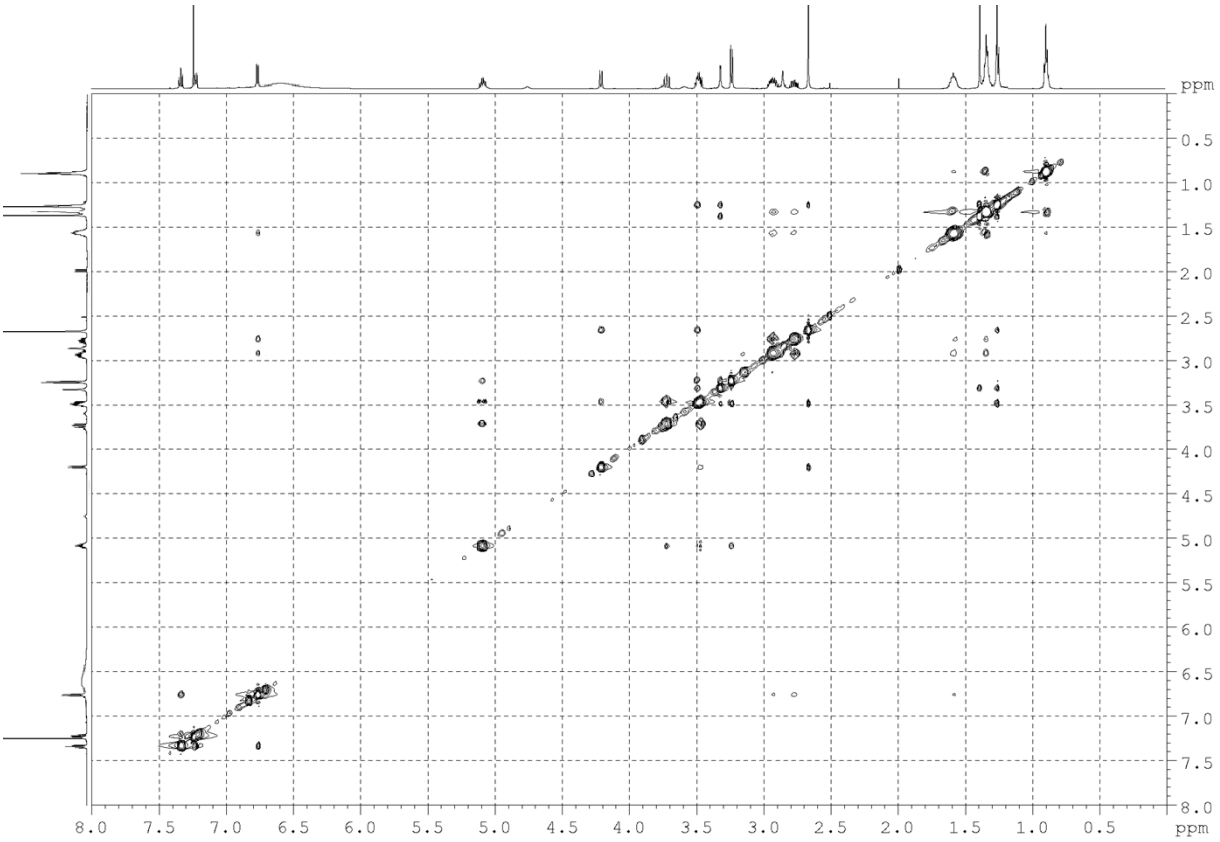


Figure S6: ^{1}H,^{1}H NOESY spectrum of massiliachelin (**1**) in chloroform-*d*.

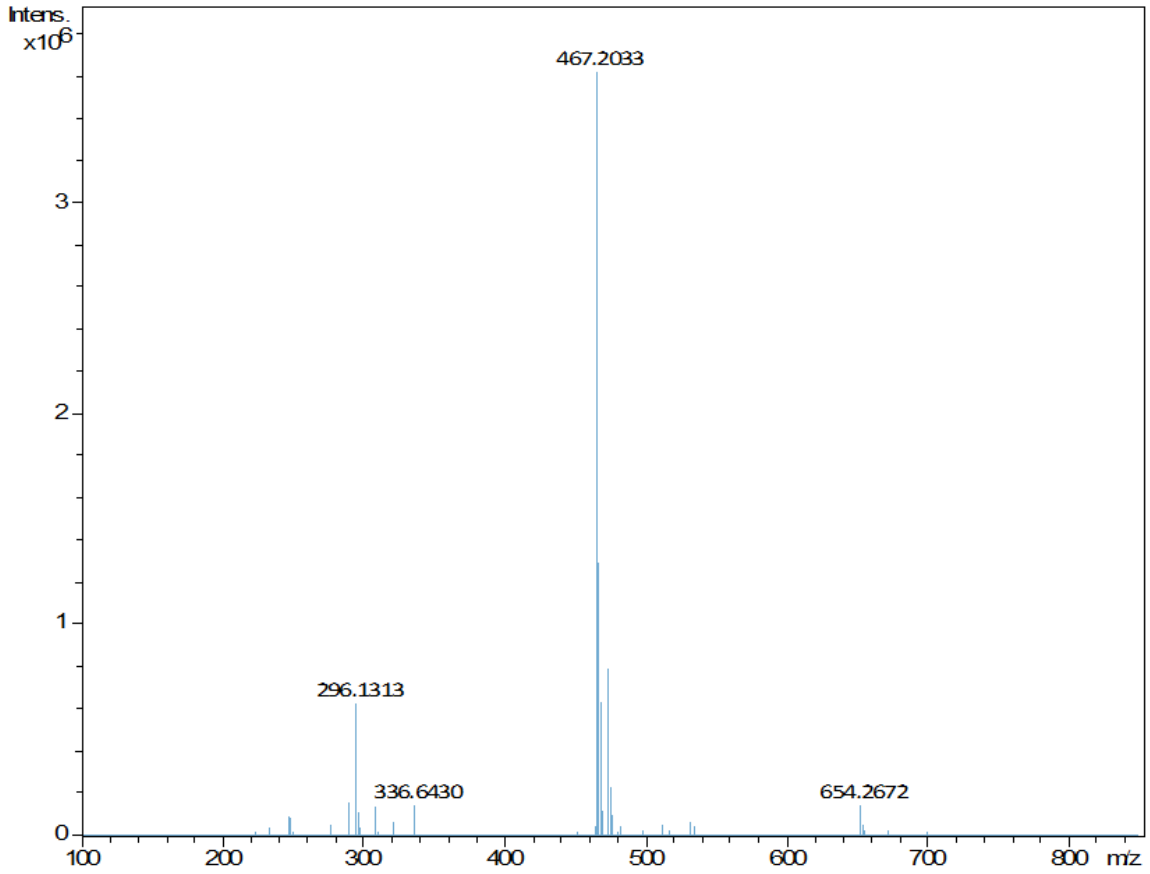


Figure S7: HRESIMS spectrum of massiliachelin (**1**).