# SUPPLEMENTARY MATERIAL

**Figure S1.** The HRMS spectra of compounds **1 – 4**.

**Figure S2-S5.** Mirror-match of compounds **1 – 4** with valinomycin from the MASST GNPS database.

**Figure S6-S10.** $MS^2$ spectra of the compounds **1 – 4.**

**Table S1-S4.** $^1$H-NMR from the reference Ye et al. Phytochemistry 135 (2017), 151-159.

**Figure S11-S15**. $^1$H-NMR of compounds **1 – 4** in $CDCl_3$.

**Figure S16.** Full $^{13}$C-NMR spectrum of streptodepsipeptide SV21 (**4**) in $CDCl_3$.

**Figure S17.** Full $^1$H-NMR spectrum of streptodepsipeptide SV21 (**4**) in $CDCl_3$.

**Figure S18.** Full HSQC spectrum of streptodepsipeptide SV21 (**4**)**.**

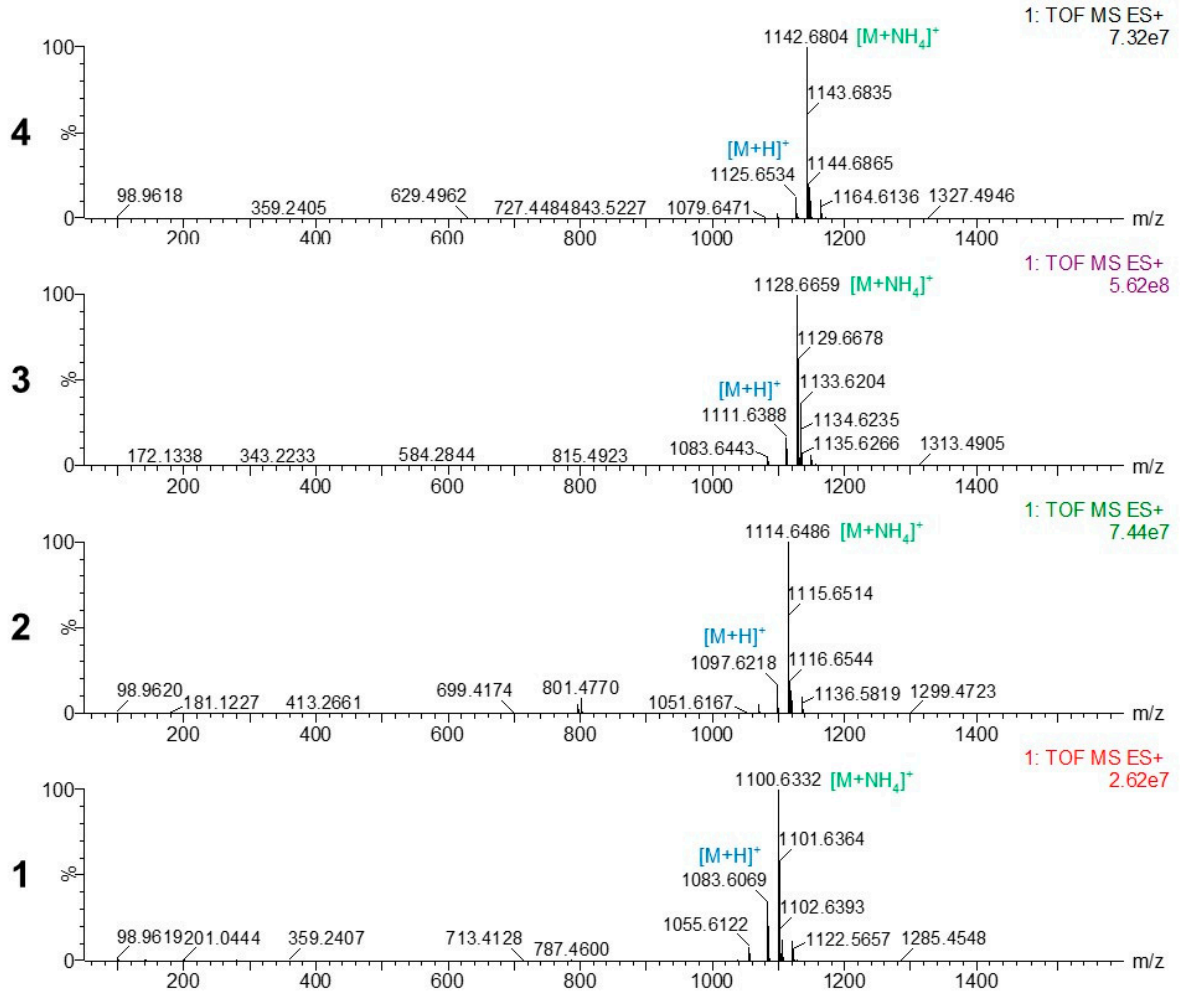


**Figure S1.** The HRMS spectra of compounds **1 - 4**.

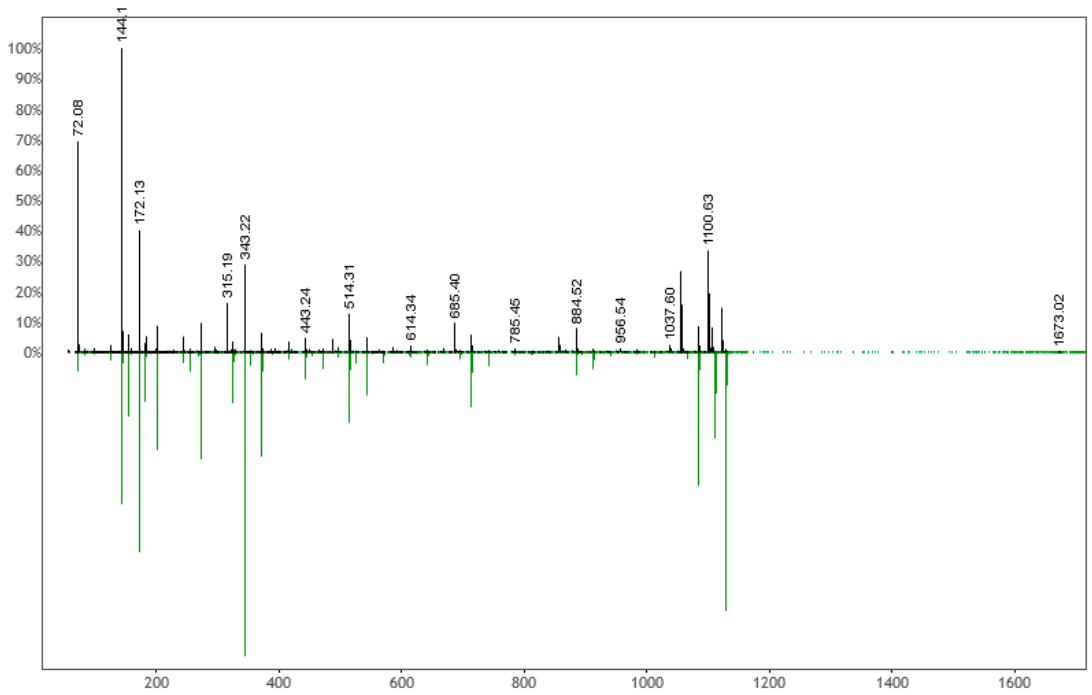


**Figure S2.** Mirror-match of compound **1** with valinomycin from the MASST GNPS database (library class: gold; cosine-score: 0.76; shared peaks: 44; mass-diff: 28.03; specMZ: 1100.63; libMZ: 1128.66).

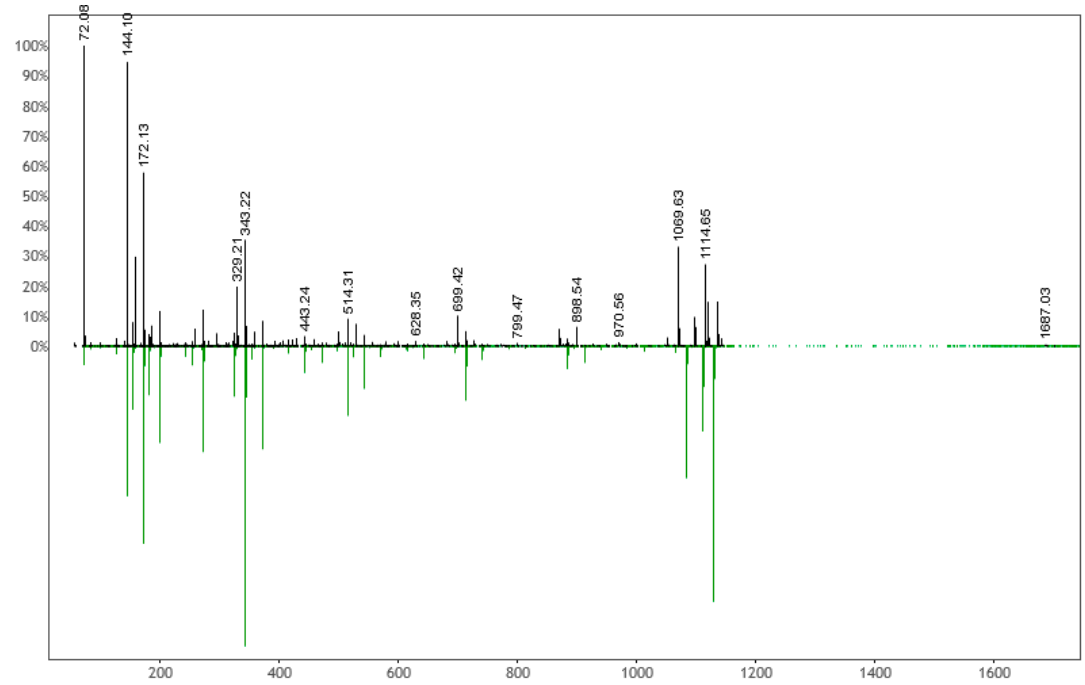


**Figure S3.** Mirror-match of compound **2** with valinomycin from the database (library class: gold; cosine-score: 0.77; shared peaks: 42; mass-diff: 14.01; specMZ: 1114.54; libMZ: 1128.66).

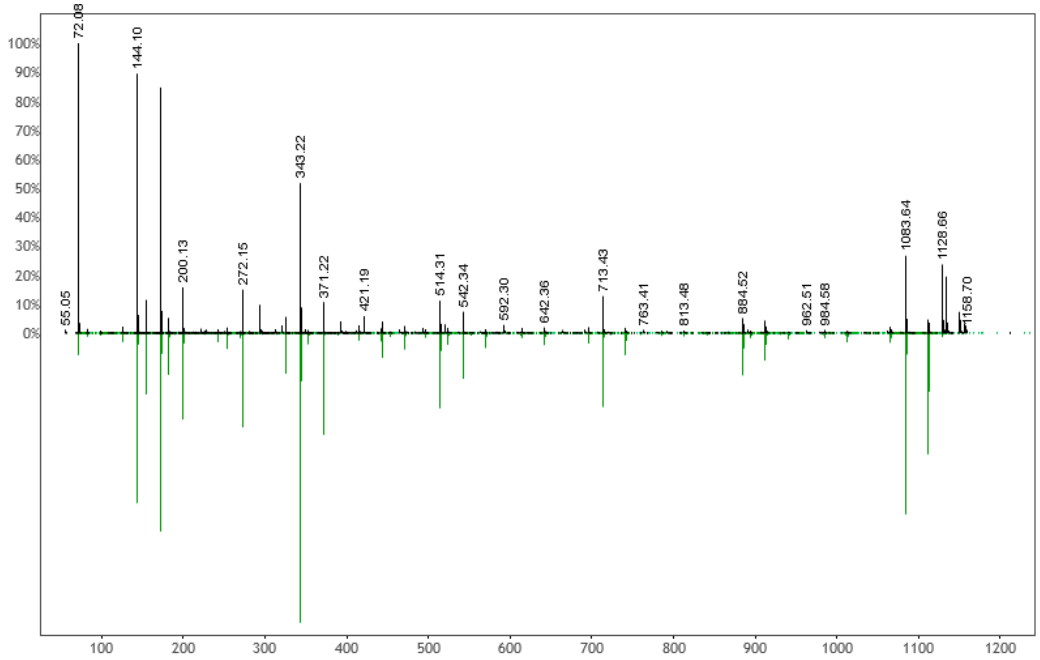


**Figure S4.** Mirror-match of valinomycin **(3)** with valinomycin from the database (library class: gold; cosine-score: 0.83; shared peaks: 49; mass-diff: 0.01; specMZ: 1128.67; libMZ: 1128.66).

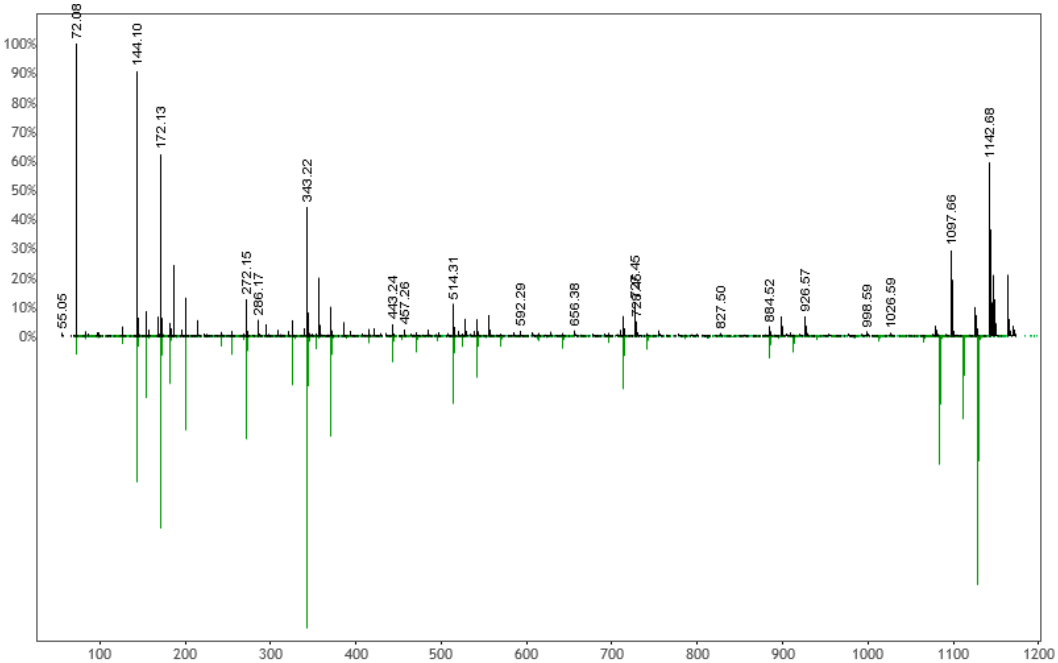


**Figure S5.** Mirror-match of compound **4** with valinomycin from the database (library class: gold; cosine-score: 0.77; shared peaks: 42; mass-diff: 14.02; specMZ: 1142.68; libMZ: 1128.66).

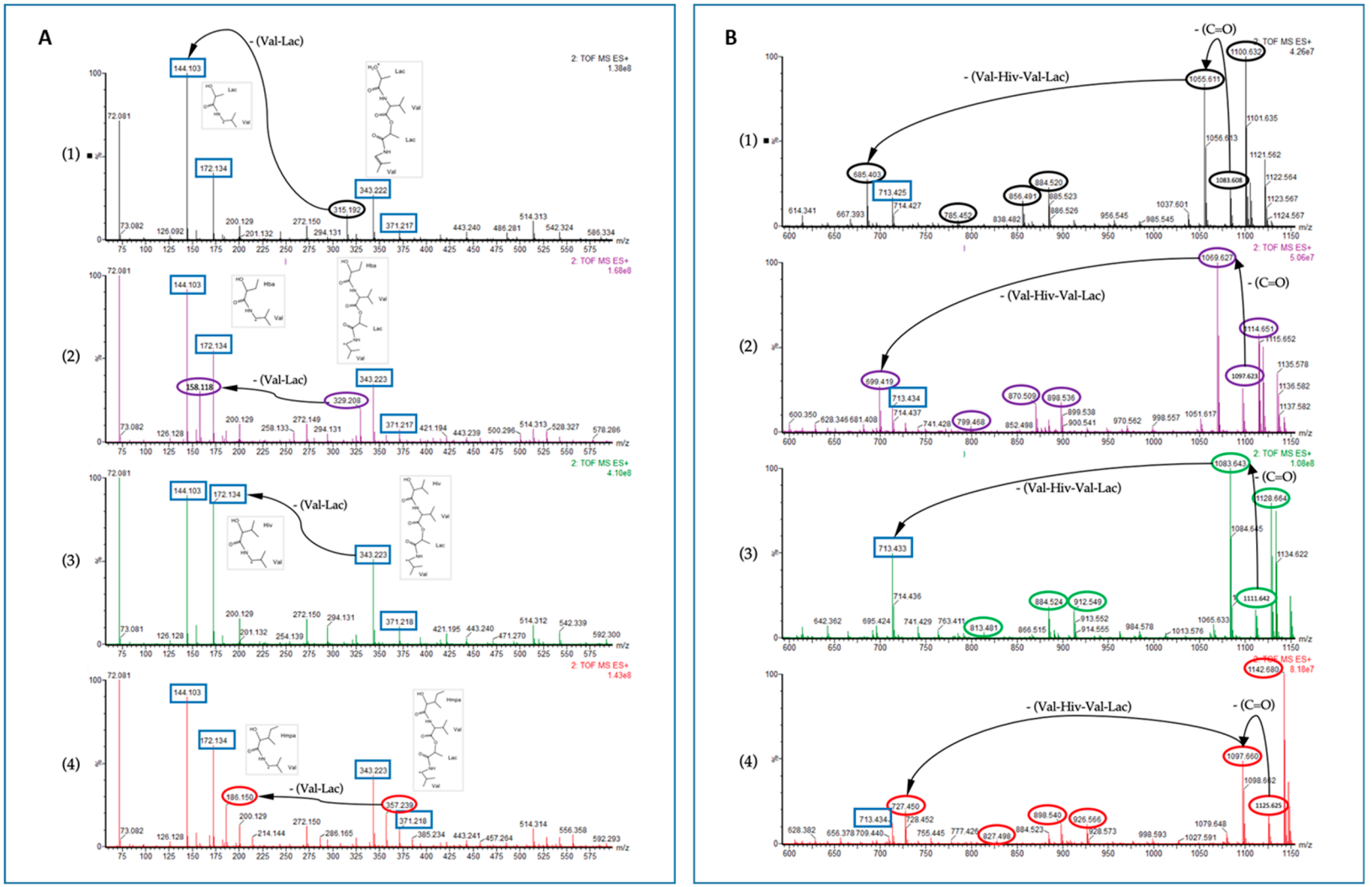


**Figure S6.** $MS^2$ spectra of the compounds **1 – 4**: (A)The mass window magnifies on the range between *m/z* 50 – *m/z* 600; and (B) on the range between *m/z* 600 – *m/z* 1150. Identical masses that occurred in all four spectra of the derivates of valinomycin were marked with a blue box, while the compound specific masses were highlighted in circles.

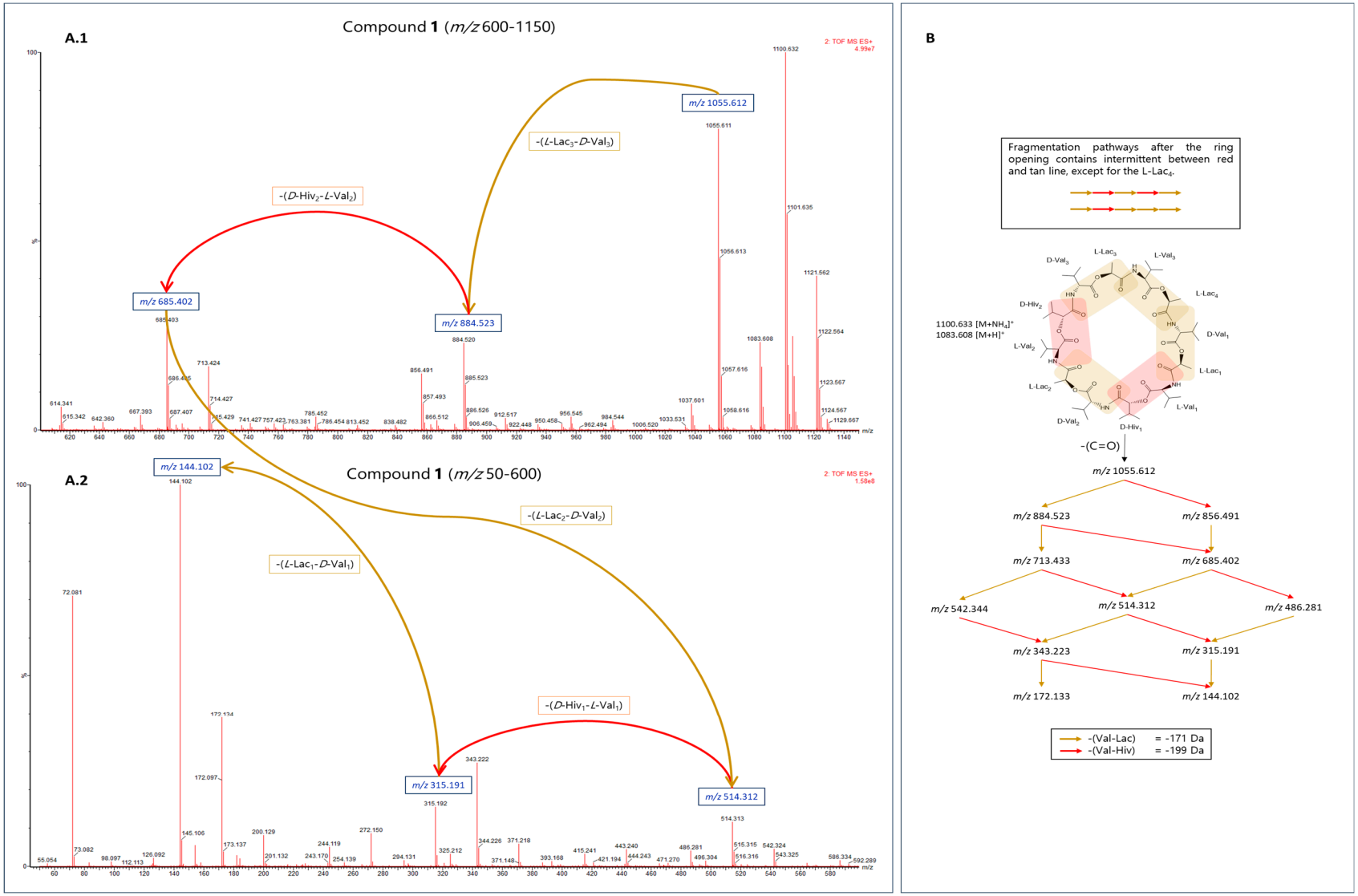


**Figure S7.** $MS^2$ spectra of compound **1**. (A.1) from *m/z* 600 – *m/z* 1150, (A.2) *m/z* 50 – *m/z* 600, and (B) the possible fragmentation pathways.

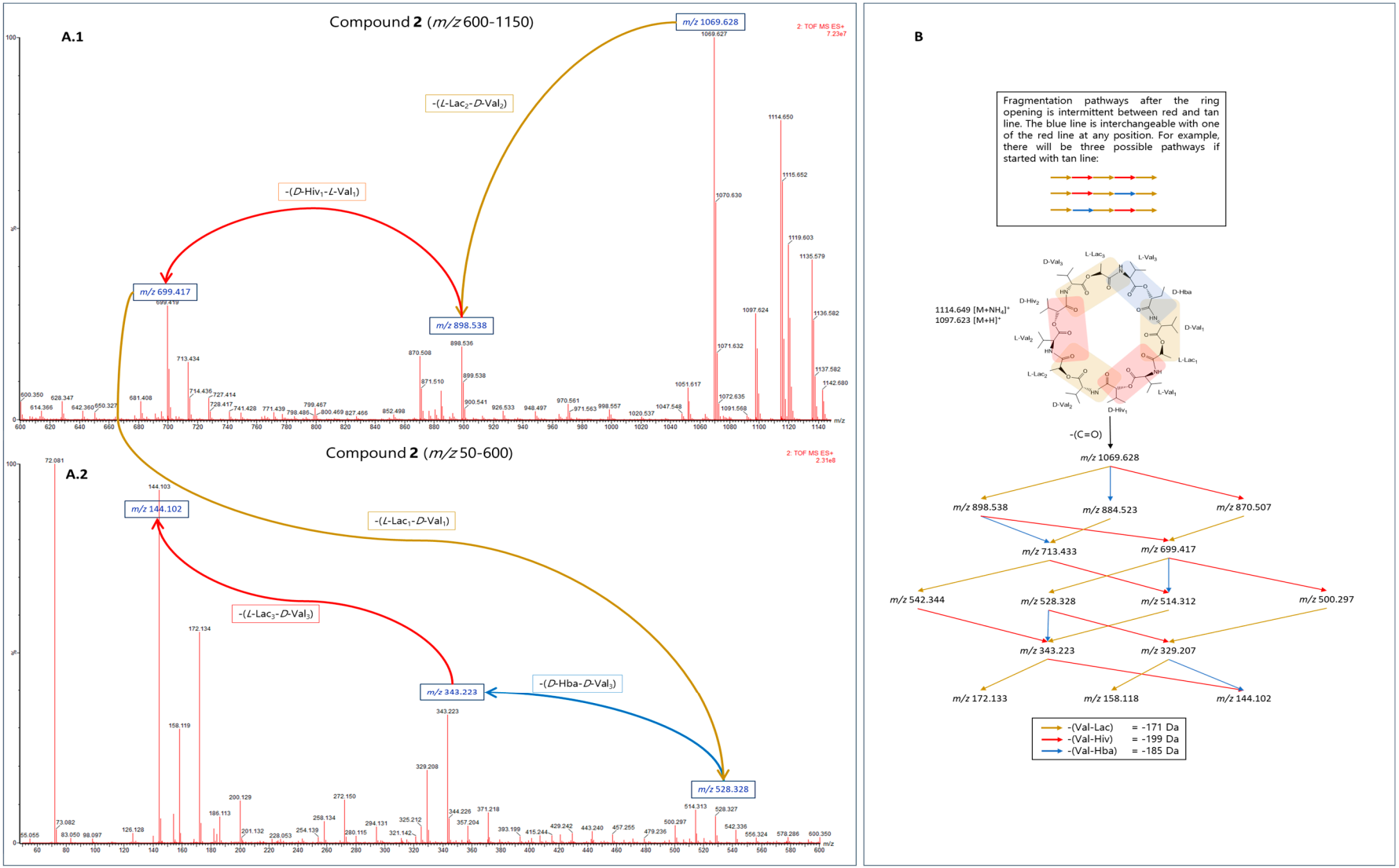


**Figure S8**. MS$^2$ spectra of compound **2**. (A.1) from *m/z* 600 – *m/z* 1150, (A.2) *m/z* 50 – *m/z* 600, and (B) the possible fragmentation pathways.

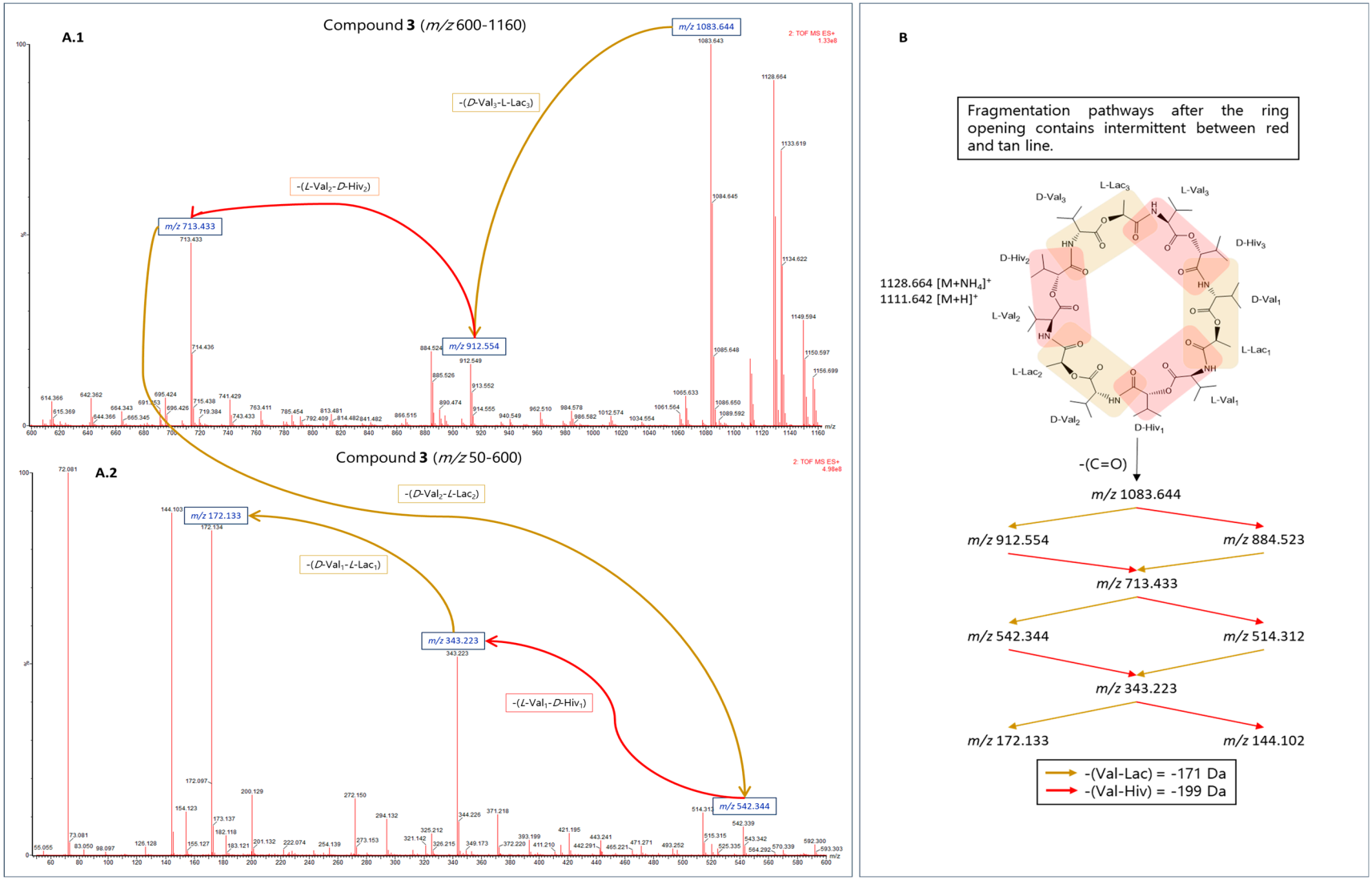


**Figure S9**. MS$^2$ spectra of valinomycin (**3**). (A.1) from *m/z* 600 – *m/z* 1150, (A.2) *m/z* 50 – *m/z* 600, and (B) the possible fragmentation pathways.

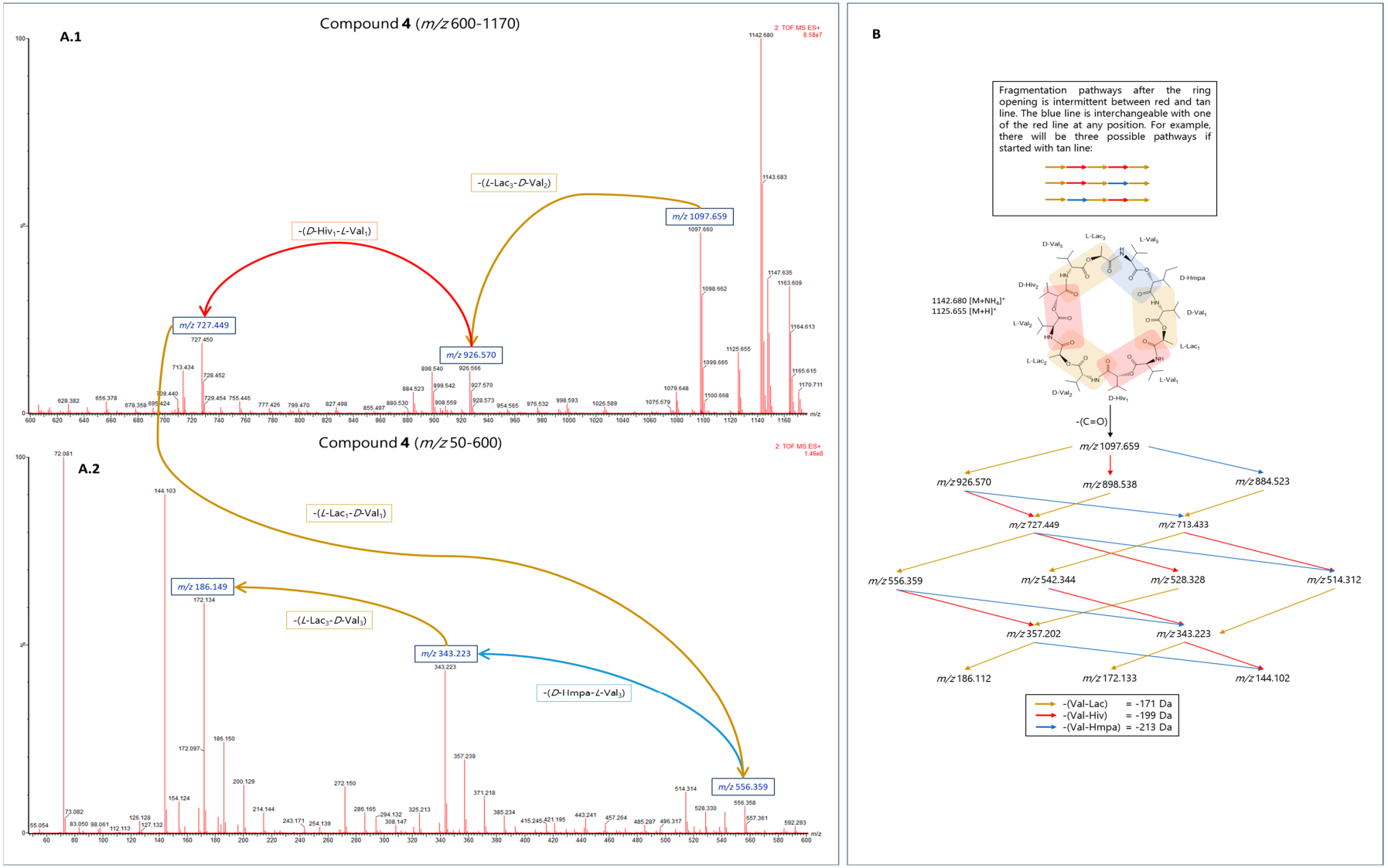


**Figure S10.** $MS^2$ spectra of compound **4**. (A.1) from *m/z* 600 – *m/z* 1150, (A.2) *m/z* 50 – *m/z* 600, and (B) the possible fragmentation pathways.

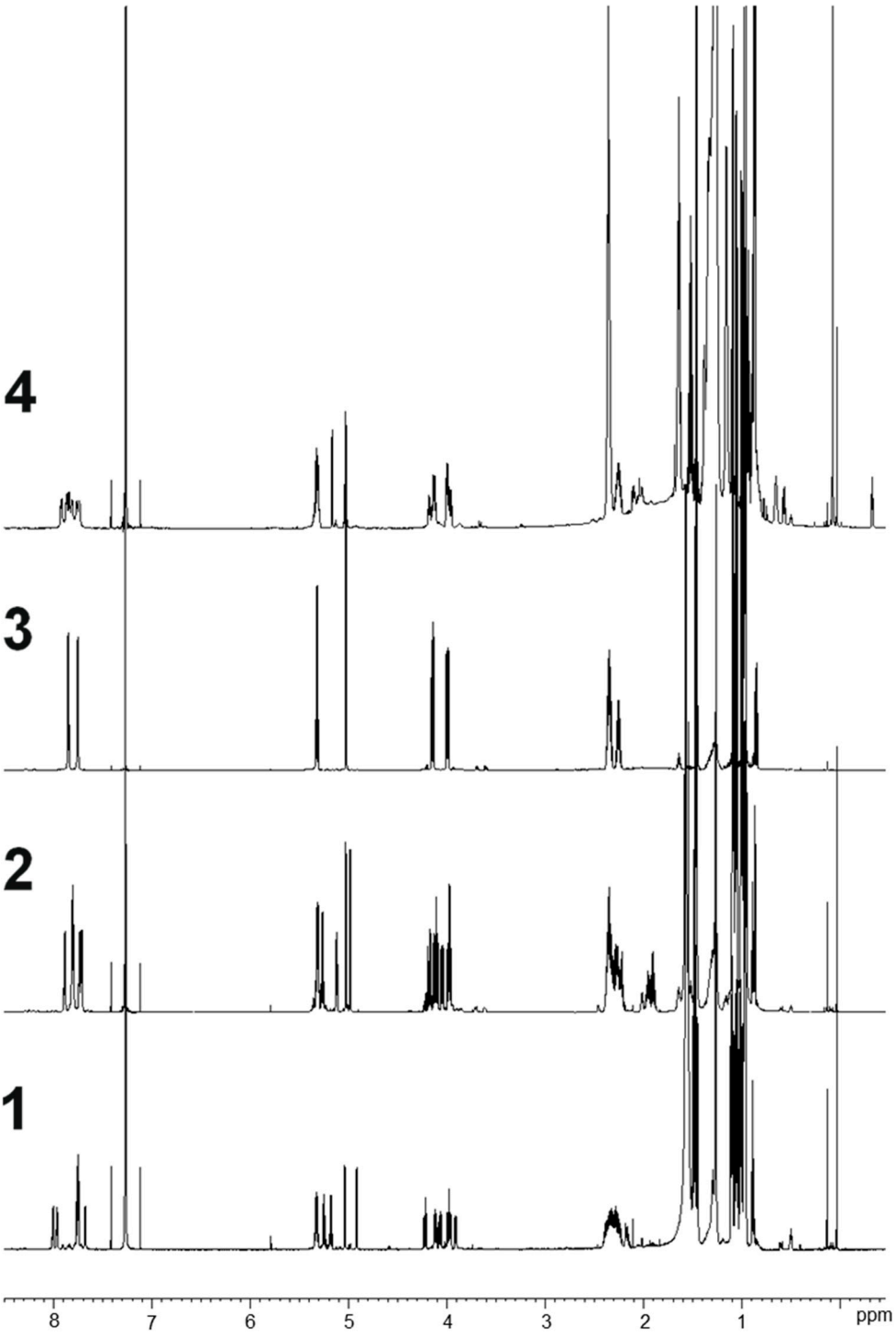


**Figure S11.** Full $^{1}$H-NMR spectra of compounds **1** to **4.**

**Table S1.** $^{1}$H-NMR at amide regions from the reference Ye et al. Phytochemistry 135 (2017), 151-159.

| | Streptodepsipeptide P11B | | Streptodepsipeptide P11A | | Valinomycin | |
|---|---|---|---|---|---|---|
| | | **$\delta_H$, (*J* in Hz)** | | **$\delta_H$, (*J* in Hz)** | | **$\delta_H$, (*J* in Hz)** |
| NH | L-Val | 7.74, d (5.9) | L-Val1 | 7.76, d (5.8) | L-Val | 7.80, d (6.2) |
| | | 7.78, d (6.3) | L-Val2 | 7.84, d (6.0) | D-Val | 7.88, d (8.1) |
| | | 7.96, d (8.2) | L-Val3 | 7.77, d (6.2) | | |
| | D-Val | 7.79, d (8.2) | D-Val1 | 7.83, d (8.0) | | |
| | | 7.79, d (8.2) | D-Val2 | 7.83, d (8.0) | | |
| | | 8.00, d (7.6) | D-Val3 | 7.89,d (7.9) | | |

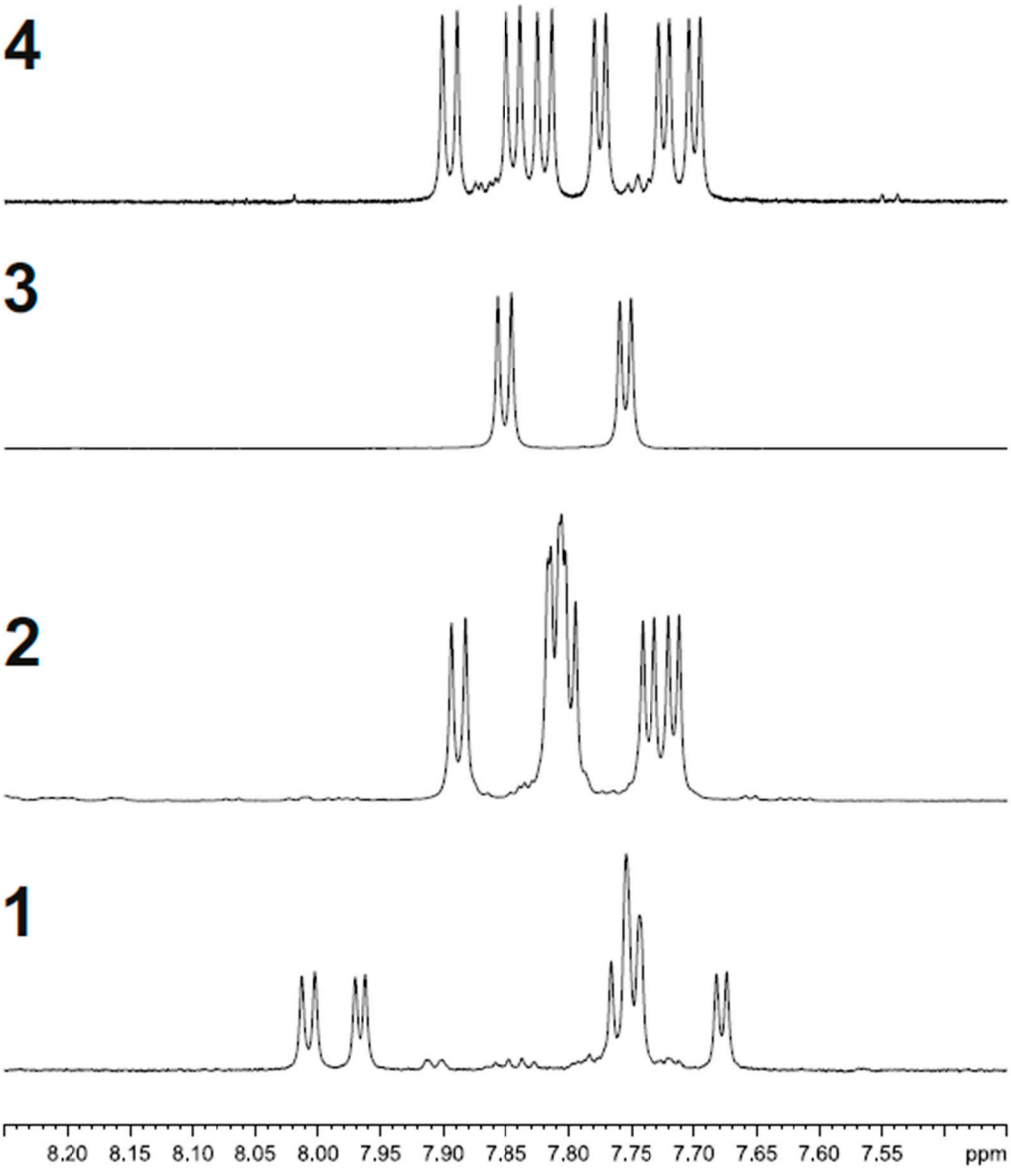


**Figure S12**. $^{1}$H-NMR spectra at amide regions of compounds **1-4** in $CDCl_3$.

**Table S2.** $^{1}$H-NMR at Hα regions from the reference Ye et al. Phytochemistry 135 (2017), 151-159.

| | Streptodepsipeptide P11B | | Streptodepsipeptide P11A | | Valinomycin | |
|---|---|---|---|---|---|---|
| | | **$\delta_H$, (*J* in Hz)** | | **$\delta_H$, (*J* in Hz)** | | **$\delta_H$, (*J* in Hz)** |
| α-CH-O | D-Hiv | 4.94, d (3.2) | D-Hiv$_1$ | 4.99, d (3.2) | D-Hiv | 5.02, d (3.1) |
| | | 5.04, d (3.0) | D-Hiv$_2$ | 5.02, d (3.2) | | |
| | L-Lac | 5.22, q (7.0) | D-Hba | 5.11, dd (6.6, 4.3) | | |
| | | 5.20, q (7.0) | L-Lac$_1$ | 5.33, q (6.8) | L-Lac | 5.32, q (7.0) |
| | | 5.32, q (7.0) | L-Lac$_2$ | 5.27, q (6.8) | | |
| | | 5.31, q (7.0) | L-Lac$_3$ | 5.33, q (6.8) | | |
| α-CH-N | L-Val | 3.91, dd (10.0, 5.9) | L-Val$_1$ | 3.96, dd (10.0, 5.8) | L-Val | 3.96, dd (10.2, 6.2) |
| | | 3.96, dd (10.0, 6.3) | L-Val$_2$ | 3.97, dd (10.0, 6.0) | | |
| | | 4.01, dd (9.8, 6.0) | L-Val$_3$ | 4.01, dd (10.0, 6.2) | | |
| | D-Val | 4.05, dd (10.0, 7.6) | D-Val$_1$ | 4.13, dd (9.2, 8.0) | D-Val | 4.10, dd (10.0, 8.1) |
| | | 4.07, dd (10.0, 8.2) | D-Val$_2$ | 4.08, dd(9.2, 8.0) | | |
| | | 4.16, dd (9.8, 8.2) | D-Val$_3$ | 4.08, dd(9.2, 7.9) | | |

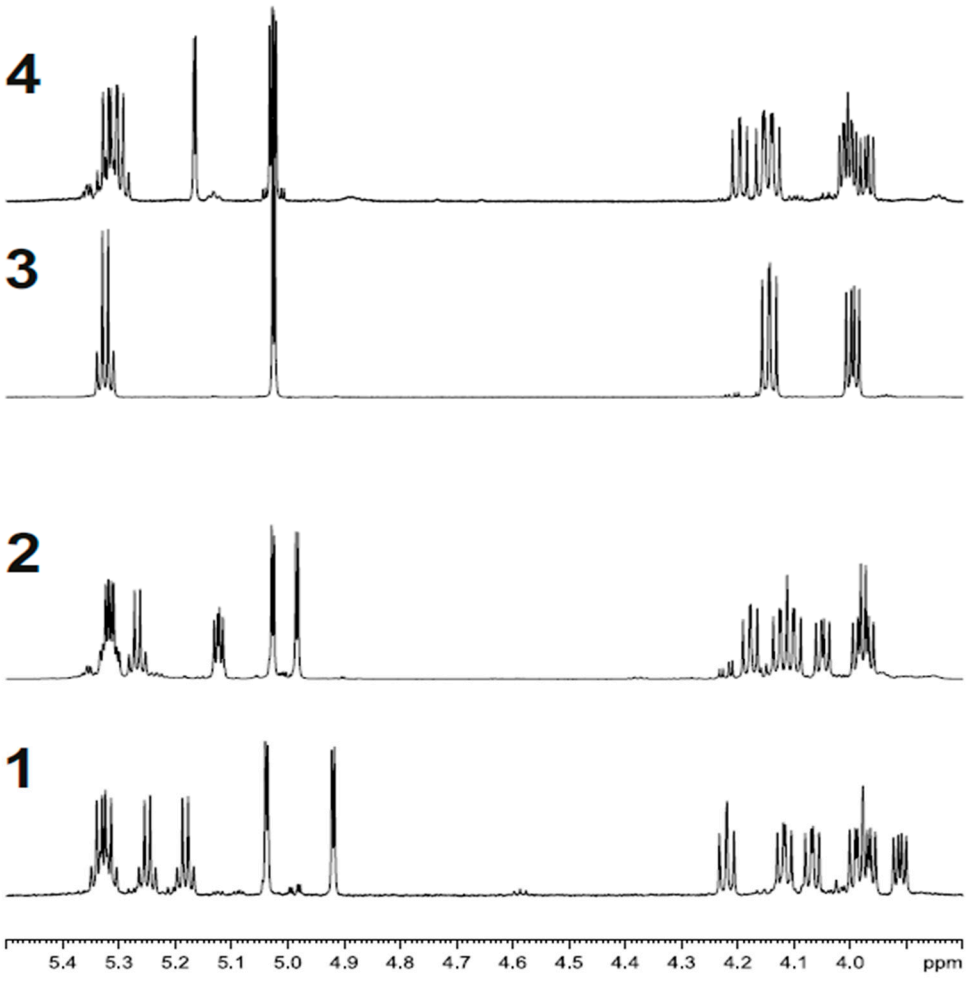


**Figure S13**. $^{1}$H-NMR spectra at Hα regions of compounds **1-4** in $CDCl_3$.

**Table S3.** $^{1}$H-NMR at Hβ regions from the reference Ye et al. Phytochemistry 135 (2017), 151-159.

| | Streptodepsipeptide P11B | | Streptodepsipeptide P11A | | Valinomycin | |
|---|---|---|---|---|---|---|
| | | **$\delta_H$, (*J* in Hz)** | | **$\delta_H$, (*J* in Hz)** | | **$\delta_H$, (*J* in Hz)** |
| β-$CH_2$ | | | D-Hba | 1.91, m | | |
| β-CH | D-Hiv | 2.36, m | D-Hiv | 2.37, m | D-Hiv | 2.33, m |
| | Val | 2.17-2.40 | Val | 2.27-2.35 | L-Val | 2.23, m |
| | | | | | D-Val | 2.36, m |

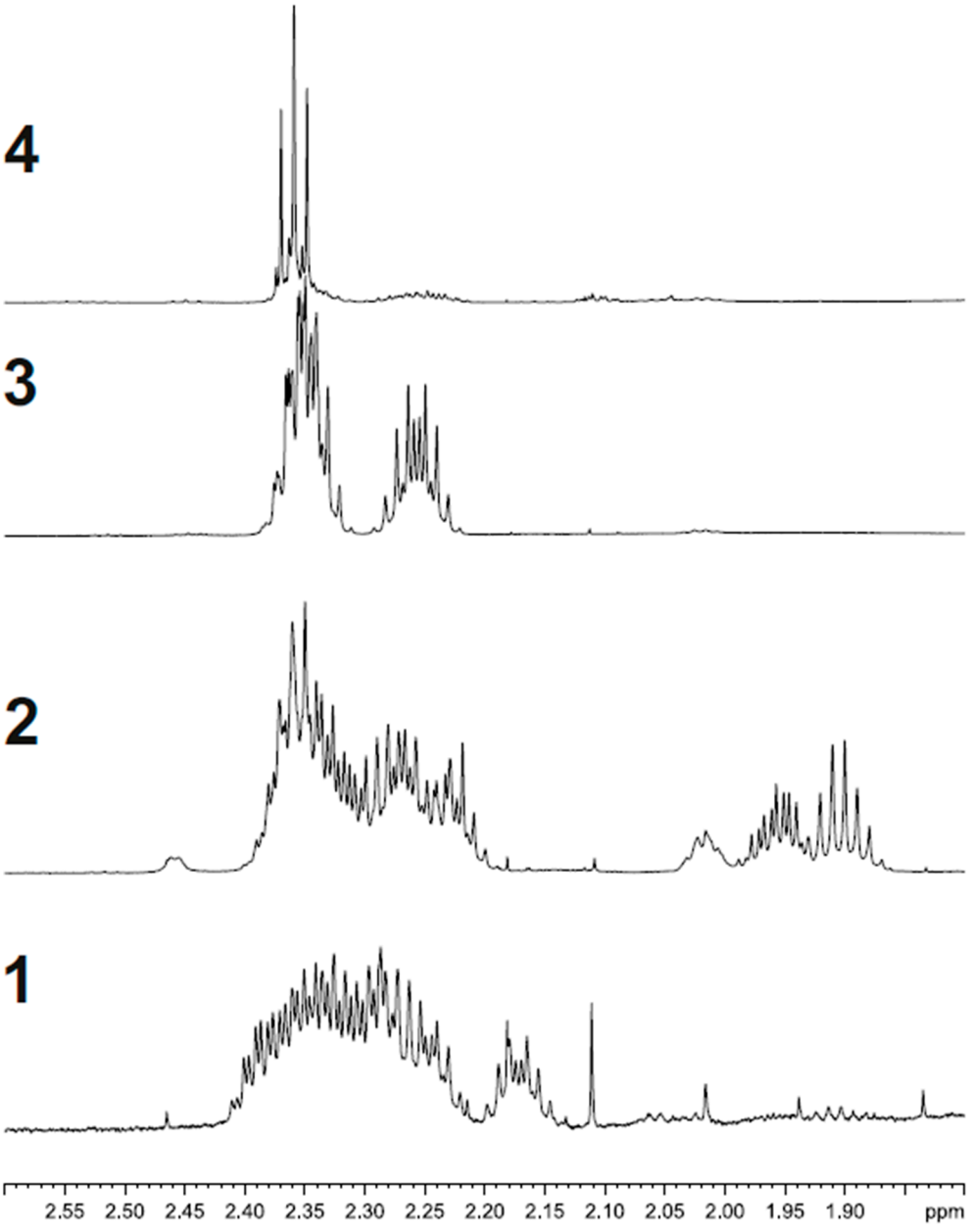


**Figure S14**. $^{1}$H-NMR spectra at Hβ regions of compounds **1-4** in $CDCl_3$.

**Table S4.** $^{1}$H-NMR at methyl regions from the reference Ye et al. Phytochemistry 135 (2017), 151-159.

| | Streptodepsipeptide P11B | | Streptodepsipeptide P11A | | Valinomycin | |
|---|---|---|---|---|---|---|
| | | **$\delta_H$, (*J* in Hz)** | | **$\delta_H$, (*J* in Hz)** | | **$\delta_H$, (*J* in Hz)** |
| β-$CH_3$ | L-Lac | 1.44-1.49 | L-Lac | 1.44-1.47 | L-Lac | 1.44, d (7.0) |
| γ-$CH_3$ | Val, D-Hiv | 0.95-1.10 | Val, D-Hiv | 0.95-1.10 | L-Val | 1.08, d (6.6) |
| | | | | | | 0.95, d (6.6) |
| | | | | | D-Val | 0.95, d (6.6) |
| | | | | | | 1.04, d 6.6) |
| | D-Hiv | 0.98 | D-Hiv | 0.98 | D-Hiv | 0.98, d (6.6) |
| | | | D-Hba | 0.95 | | 0.96, d (6.6) |

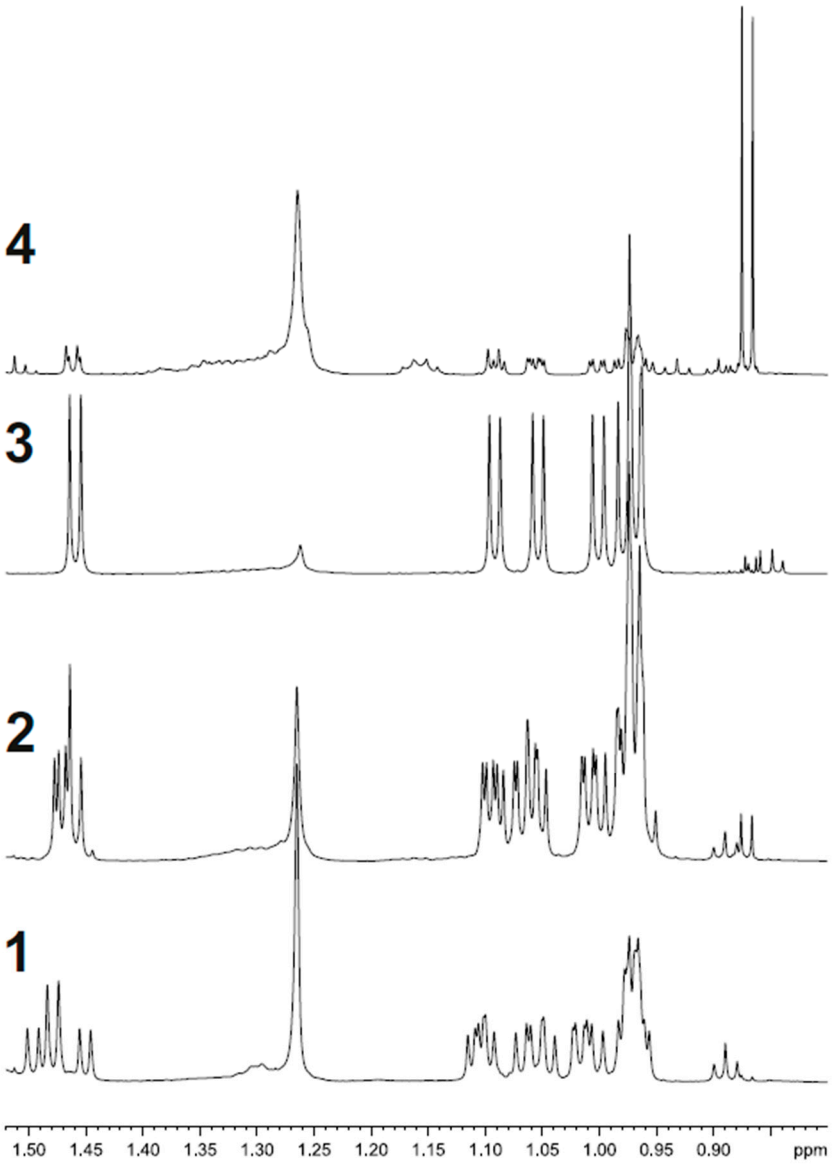


**Figure S15**. $^{1}$H-NMR spectra at methyl regions of compounds **1-4** in $CDCl_3$.

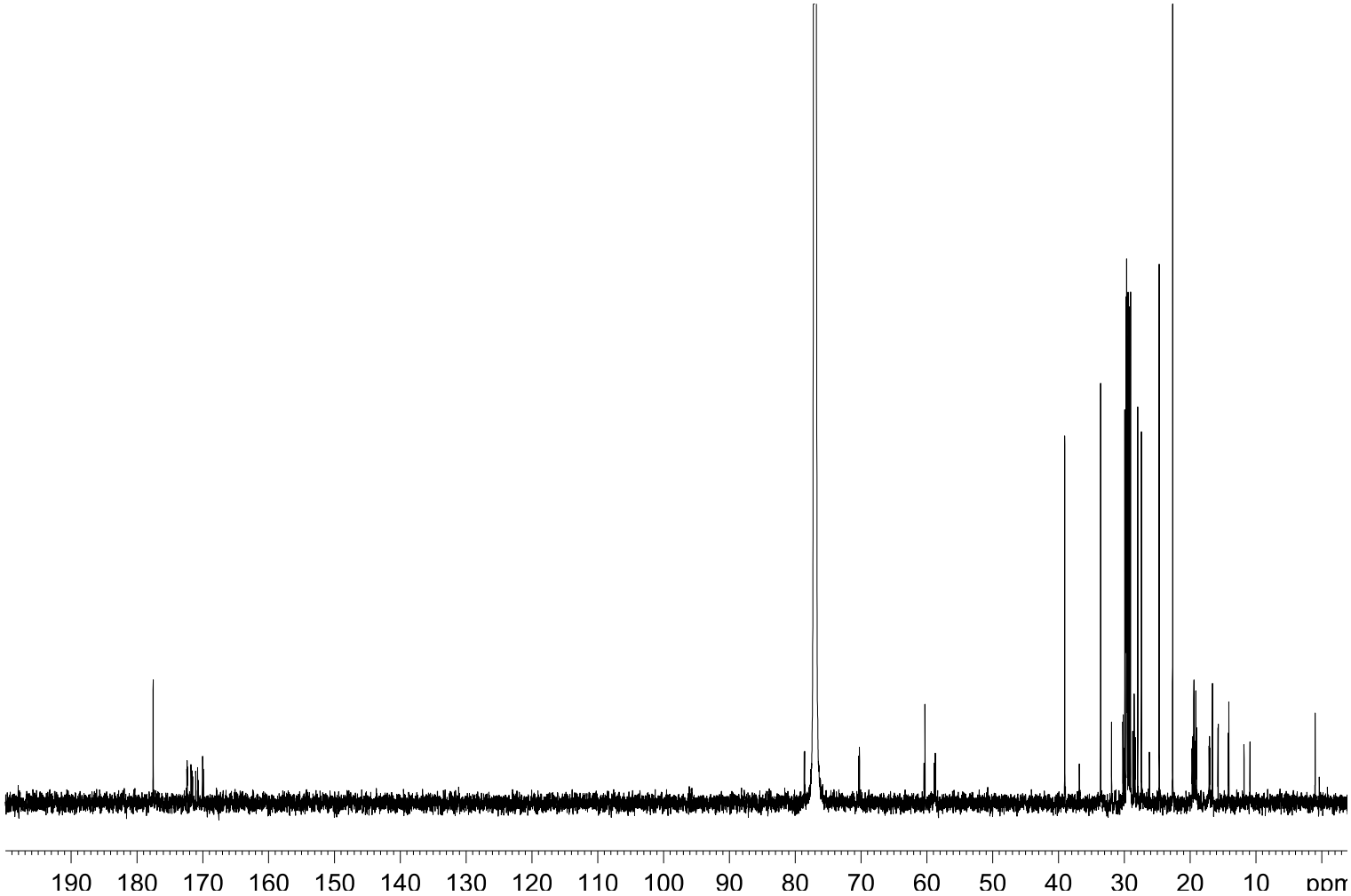


**Figure S16.** Full $^{13}$C-NMR spectrum of streptodepsipeptide SV21 (**4**) in $CDCl_3$.

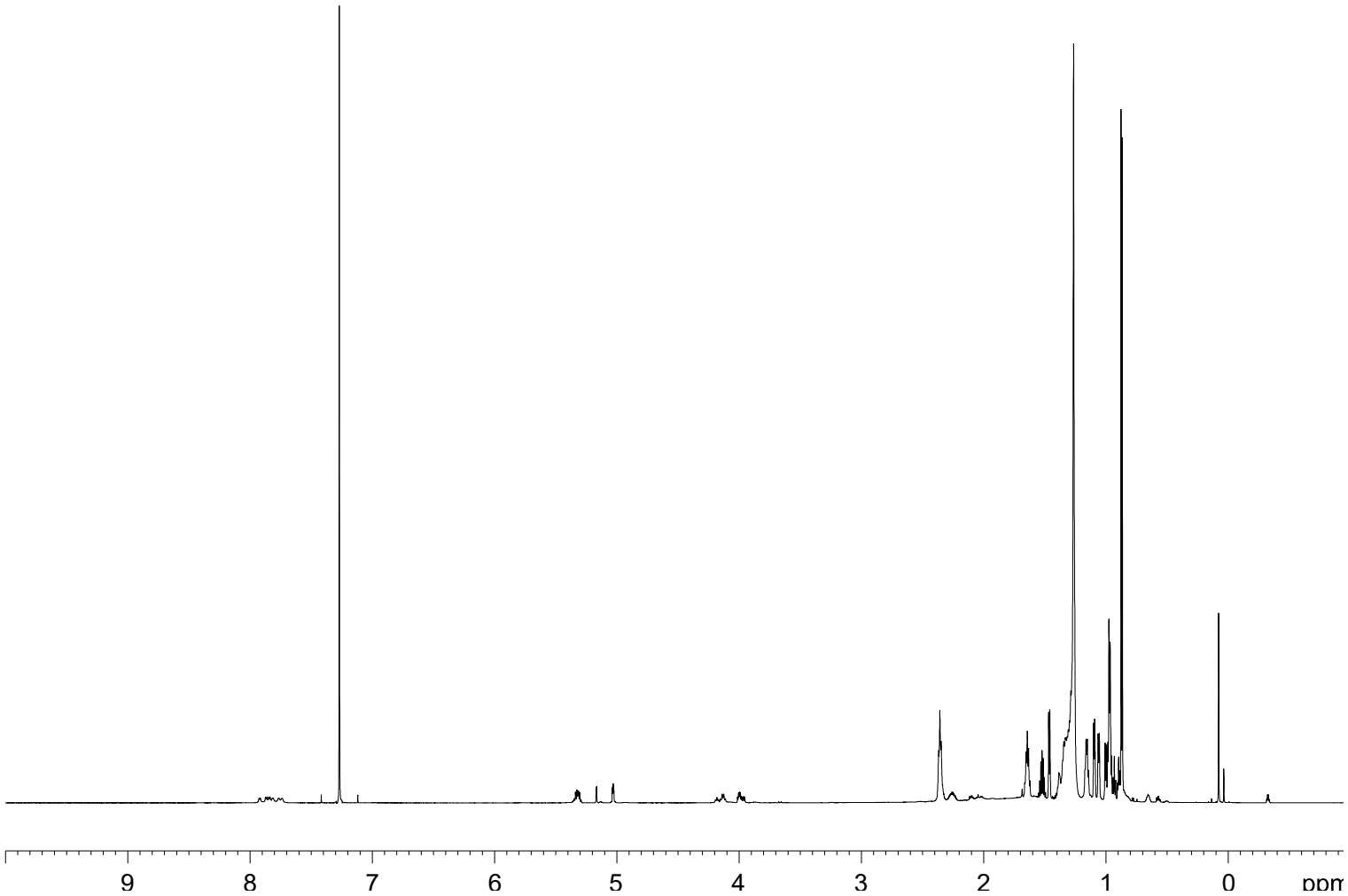


**Figure S17.** Full $^{1}$H-NMR spectrum of streptodepsipeptide SV21 (**4**) in $CDCl_3$.

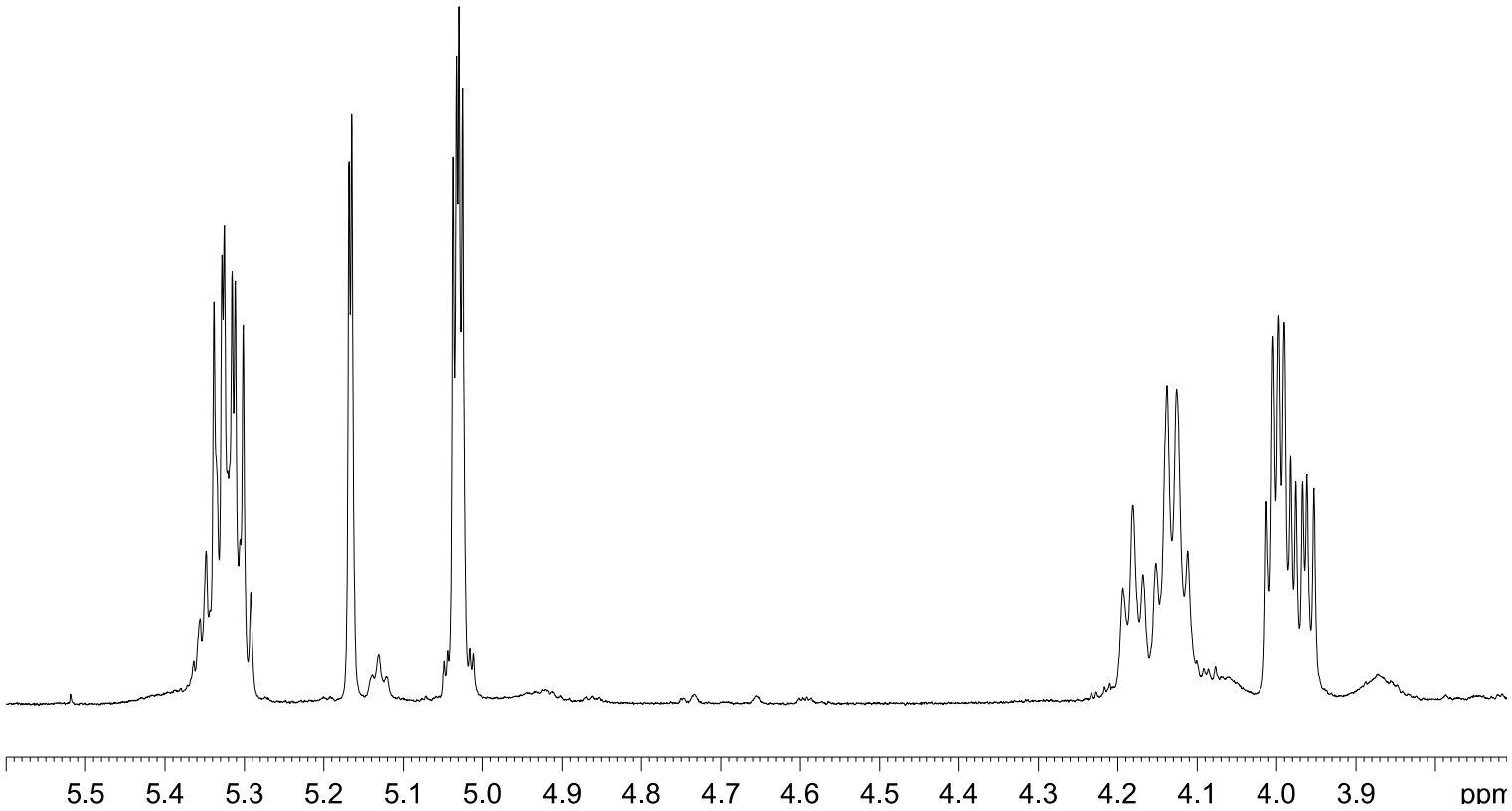


**Figure S17.1:** Hα region of the 1D $^{1}$H-NMR spectrum of streptodepsipeptide SV21 (**4**) in $CDCl_3$.

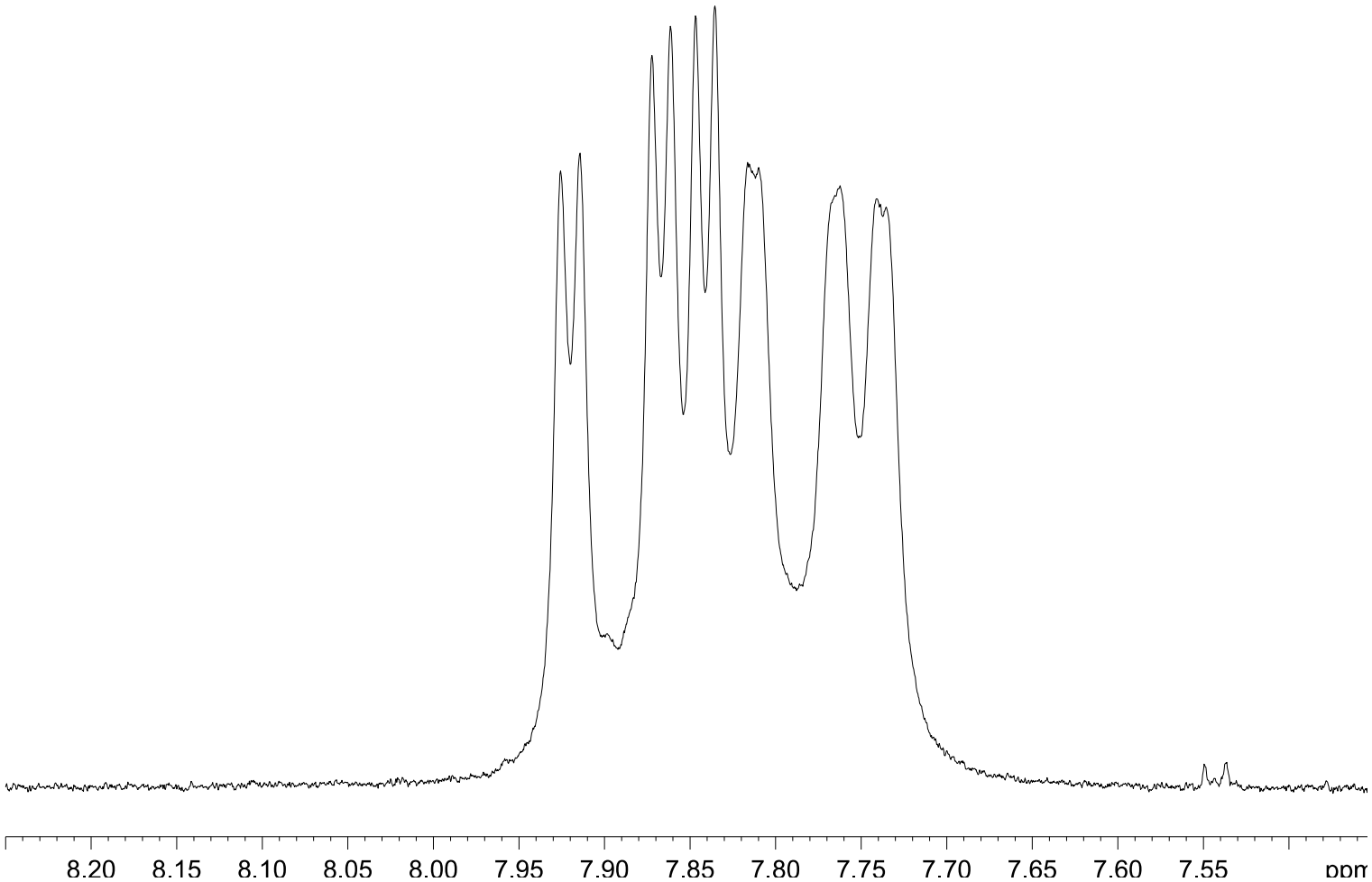


**Figure S17.2.** Amide regions of the 1D $^{1}$H-NMR spectrum of streptodepsipeptide SV21 (**4**) in $CDCl_3$.

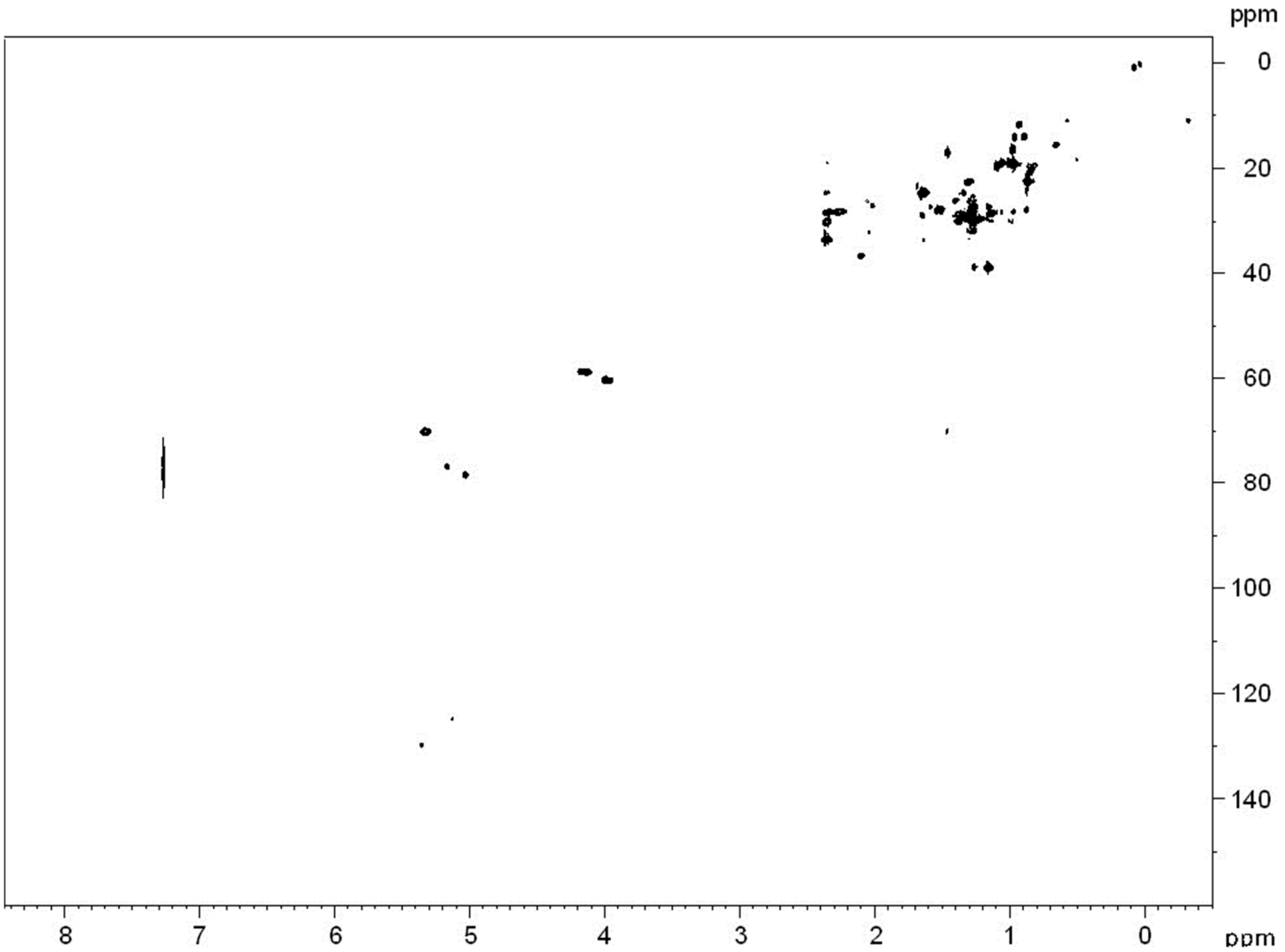


**Figure S18.** Full HSQC spectrum of streptodepsipeptide SV21 (**4**).