Totopotensamides, Polyketide-Cyclic Peptide Hybrids from a Mollusk-Associated Bacterium *Streptomyces* sp.

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Figure S1. ^{1}H NMR spectrum of compound 1 in DMSO- d_6.

Figure S2. ^{1}H NMR spectrum of compound 1 in CD_3OD.

Figure S3. ^{13}C NMR spectrum of compound 1 in DMSO- d_6.

Figure S4. HSQC spectrum of compound 1 in DMSO- d_6.

Figure S5. HMBC spectrum of compound 1 in DMSO- d_6.

Figure S6. ^{1}H-^{1}H COSY spectrum of compound 1 in DMSO- d_6.

Figure S7. NOESY spectrum of compound 1 in DMSO- d_6.

Figure S8. 1D TOCSY spectrum of compound 1 in CD_3OD.

Figure S9. ^{1}H NMR spectrum of compound 2 in DMSO- d_6.

Figure S10. HSQC spectrum of compound 2 in DMSO- d_6.

Figure S11. HMBC spectrum of compound 2 in DMSO- d_6.

Figure S12. ^{1}H-^{1}H COSY spectrum of compound 2 in DMSO- d_6.

Figure S13. LC-MS Analysis of D/L-FDLA Derivatives.

Figure S14. LC-MS Analysis of L-FDAA Derivatives.

Figure S15. HRESIMS spectra of compounds 1 and 2.

Figure S16. ^{1}H NMR spectrum of FDLA derivatives of Phg and DHPhg in CD3OD- d_4.

Table S1. The chemical differences of the α protons of the Leu and Phgs.

Figure S1. ^{1}H NMR spectrum of compound 1 in DMSO-d_6.

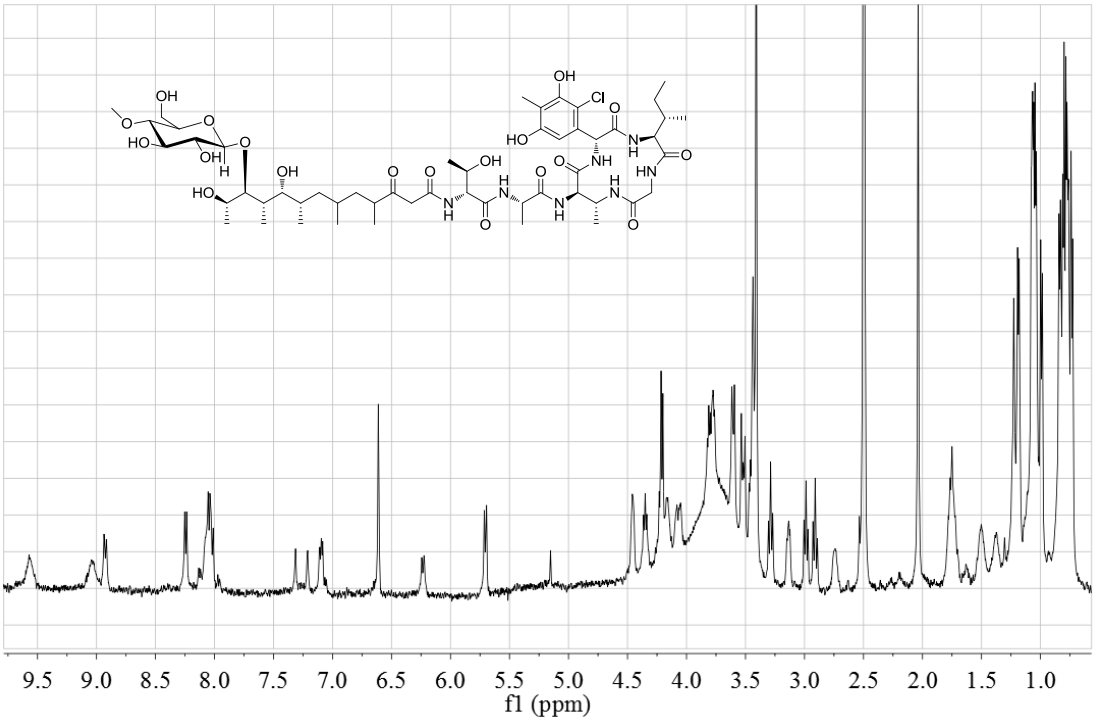


Figure S2. ^{1}H NMR spectrum of compound 1 in CD_3OD.

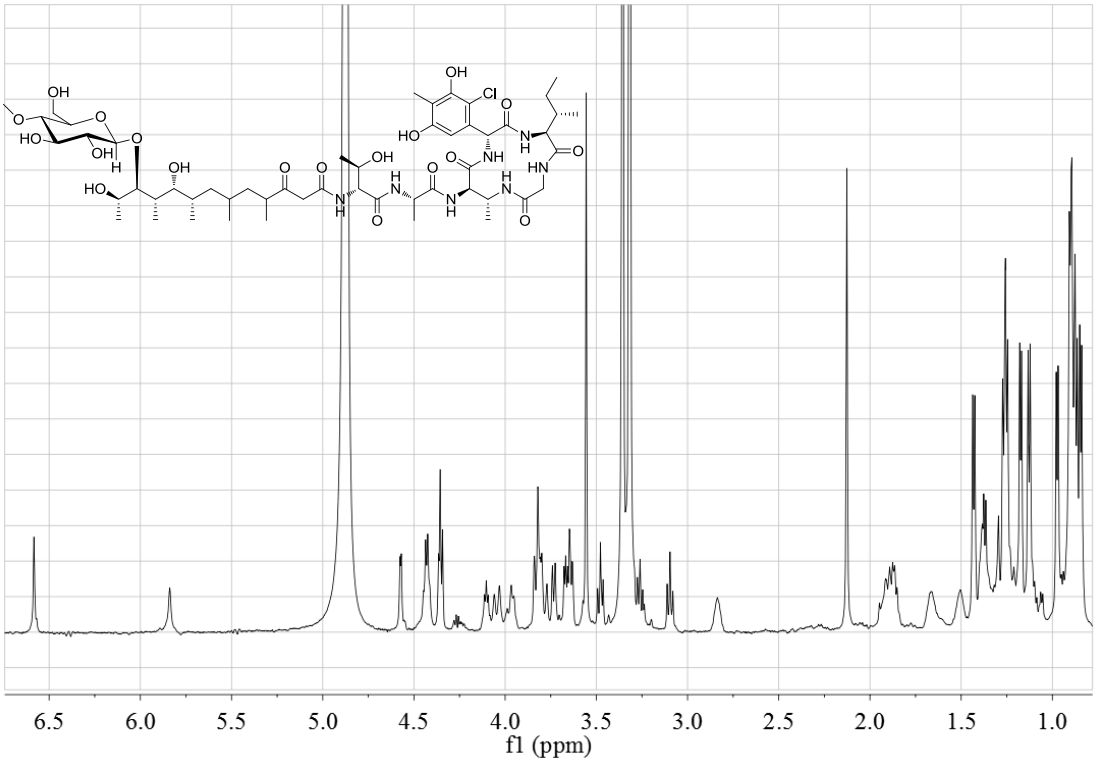


Figure S3. ^{13}C NMR spectrum of compound 1 in DMSO- d_6.

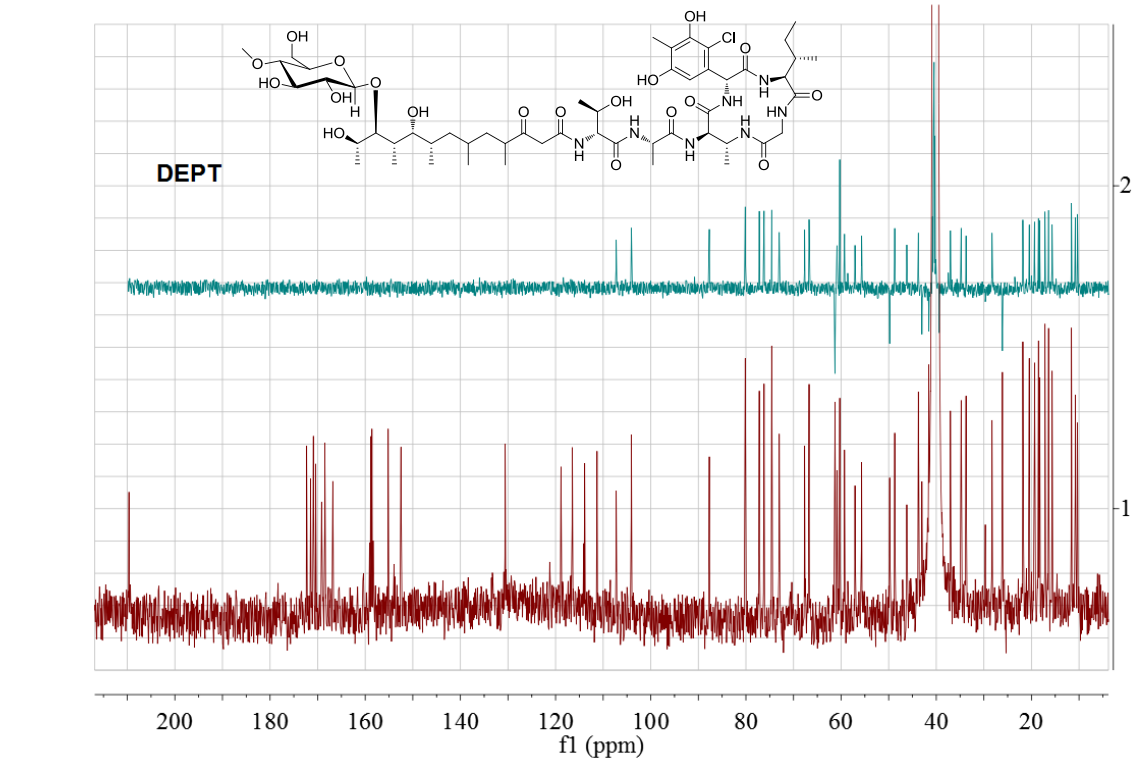
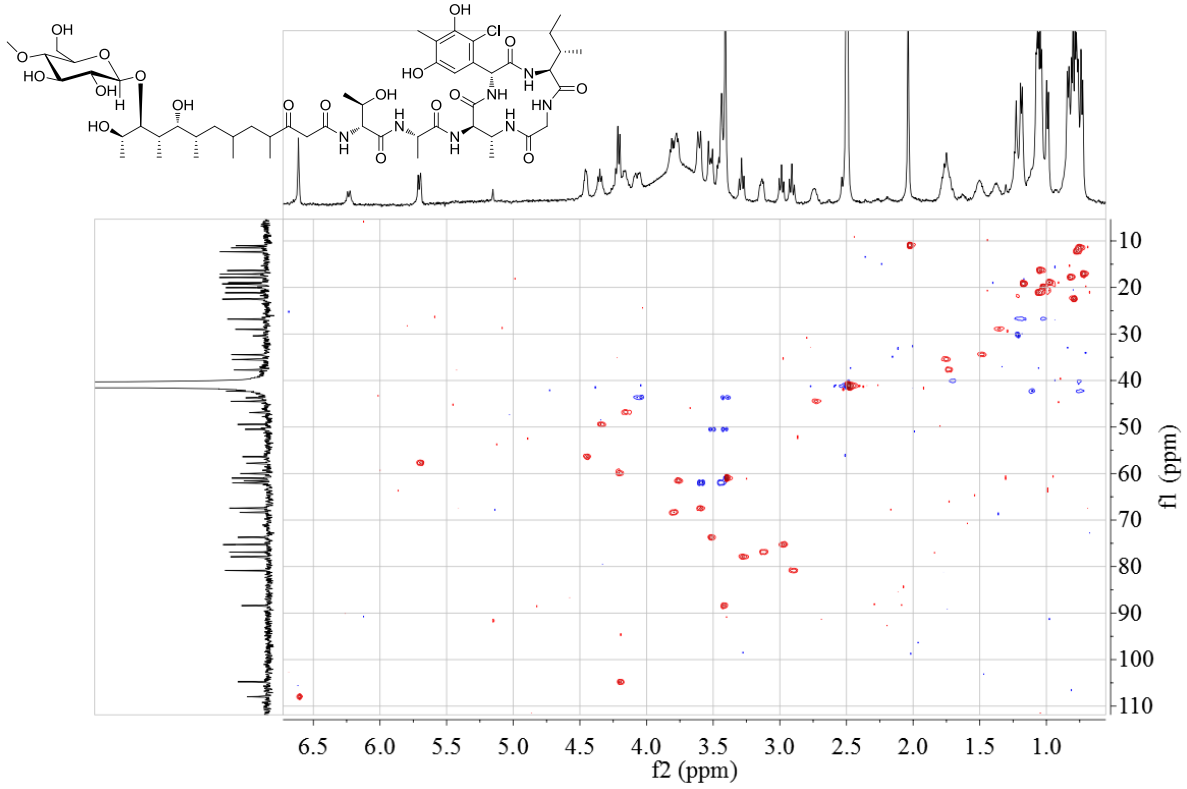


Figure S4. HSQC spectrum of compound 1 in DMSO- d_6.



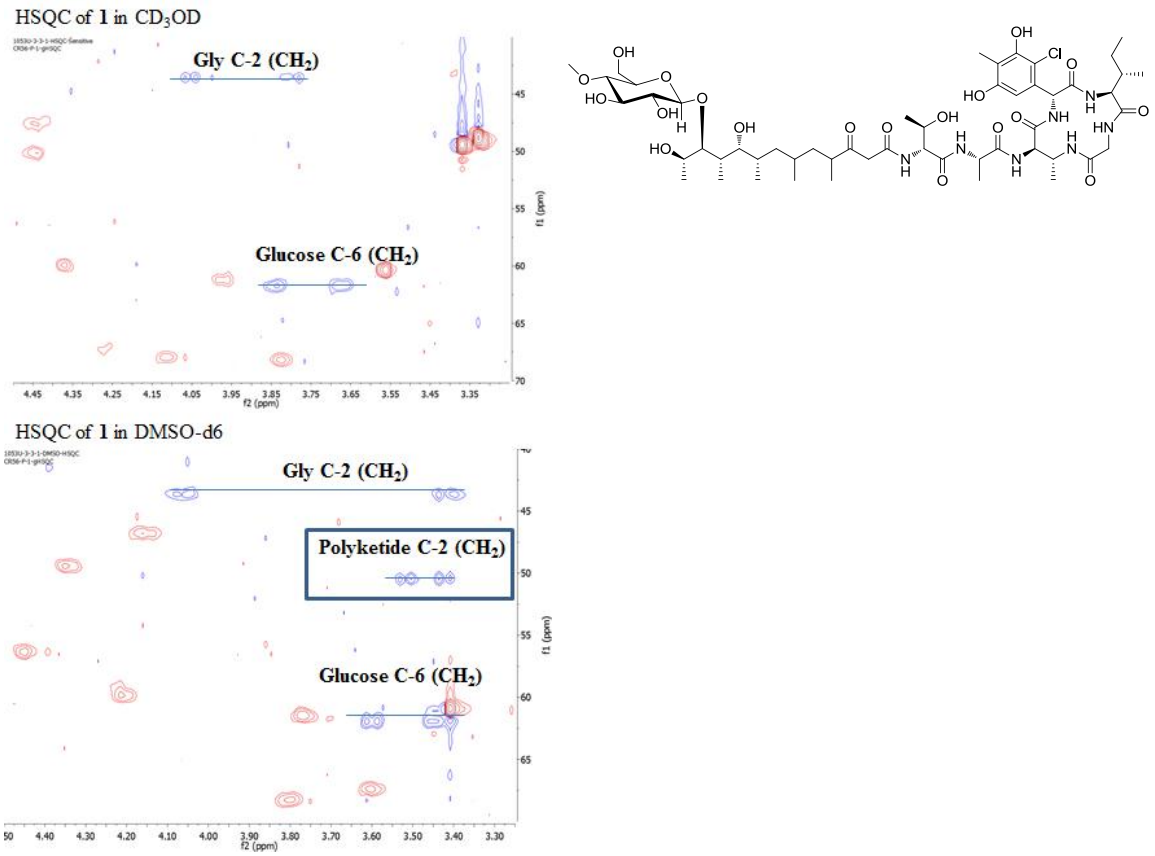


Figure S5. HMBC spectrum of compound 1 in DMSO- d_6.

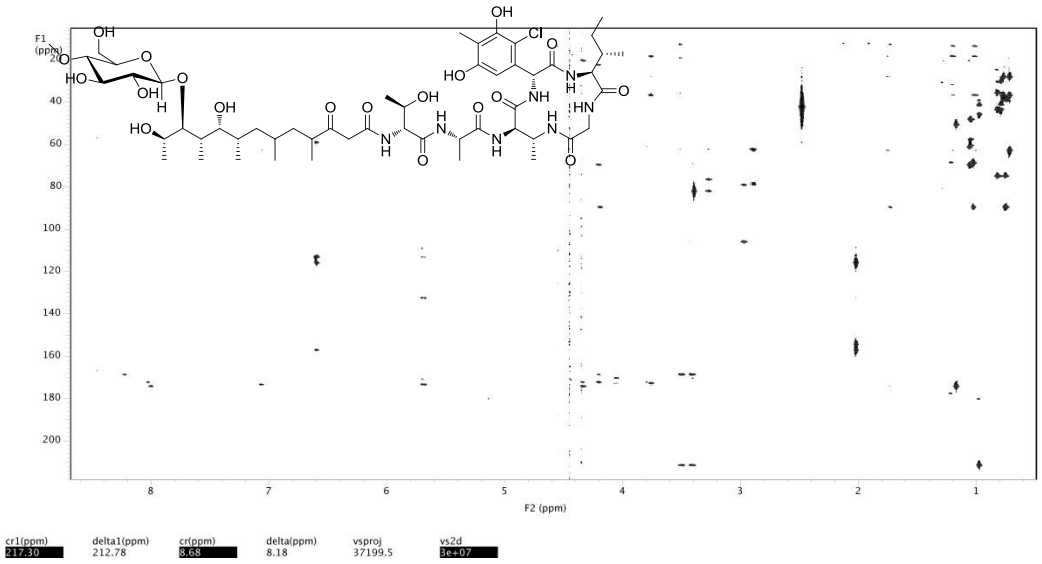


Figure S6. ^{1}H-^{1}H COSY spectrum of compound 1 in DMSO- d_6.

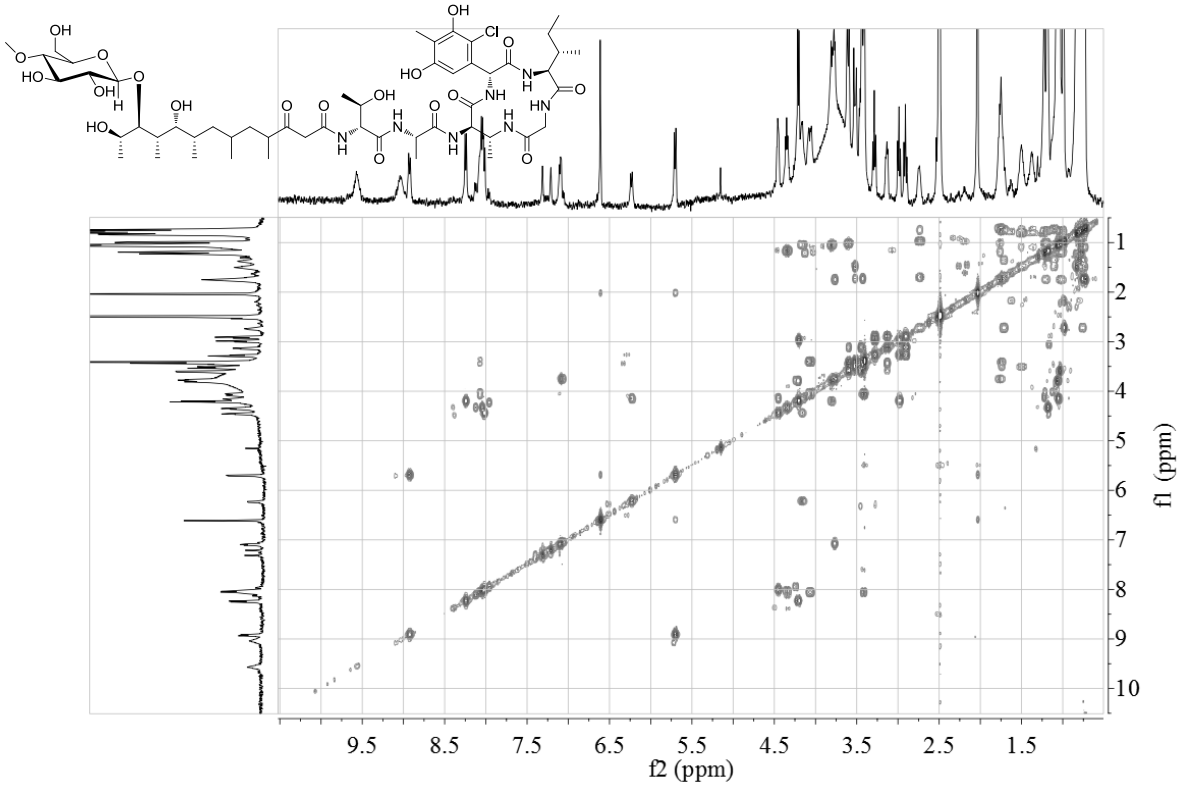


Figure S7. NOESY spectrum of compound 1 in DMSO- d_6.

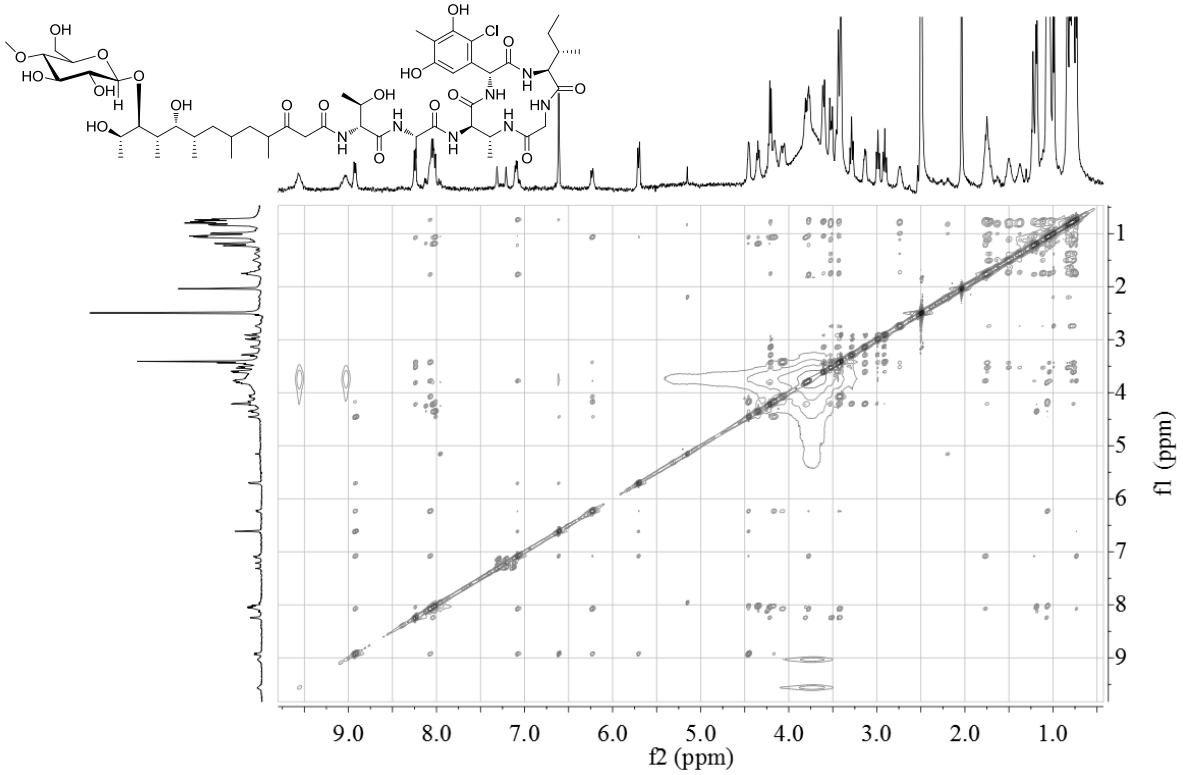


Figure S8. 1D TOCSY spectrum of compound 1 in CD_3OD.

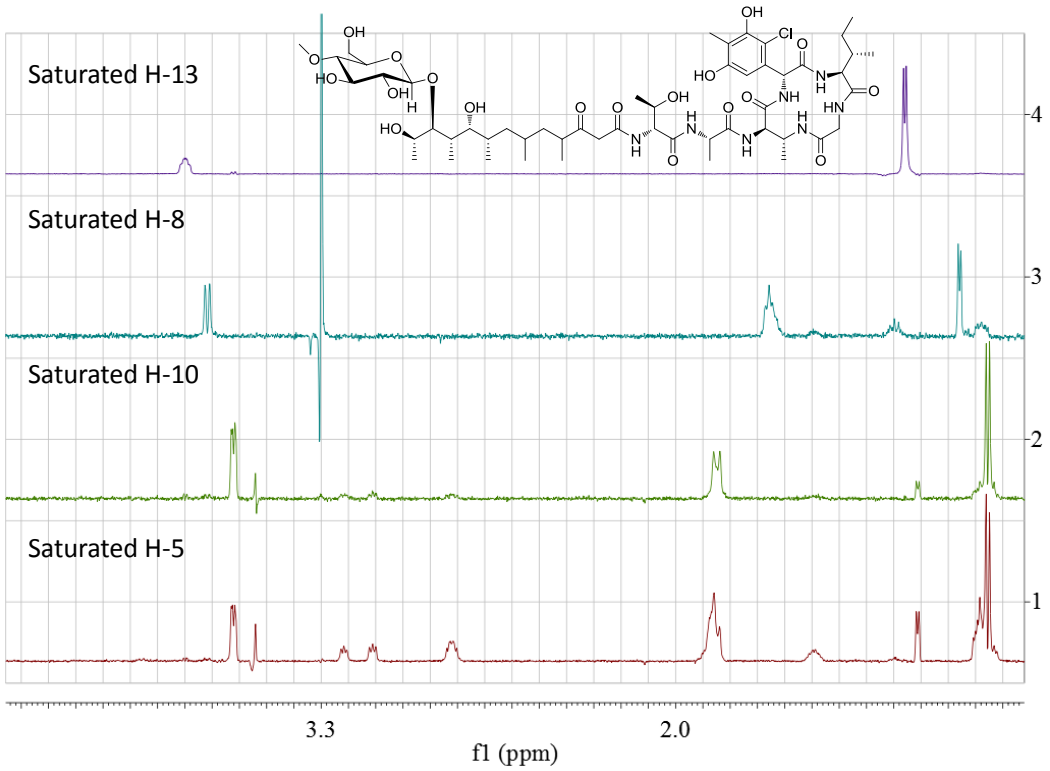


Figure S9. ^{1}H NMR spectrum of compound 2 in DMSO- d_6.

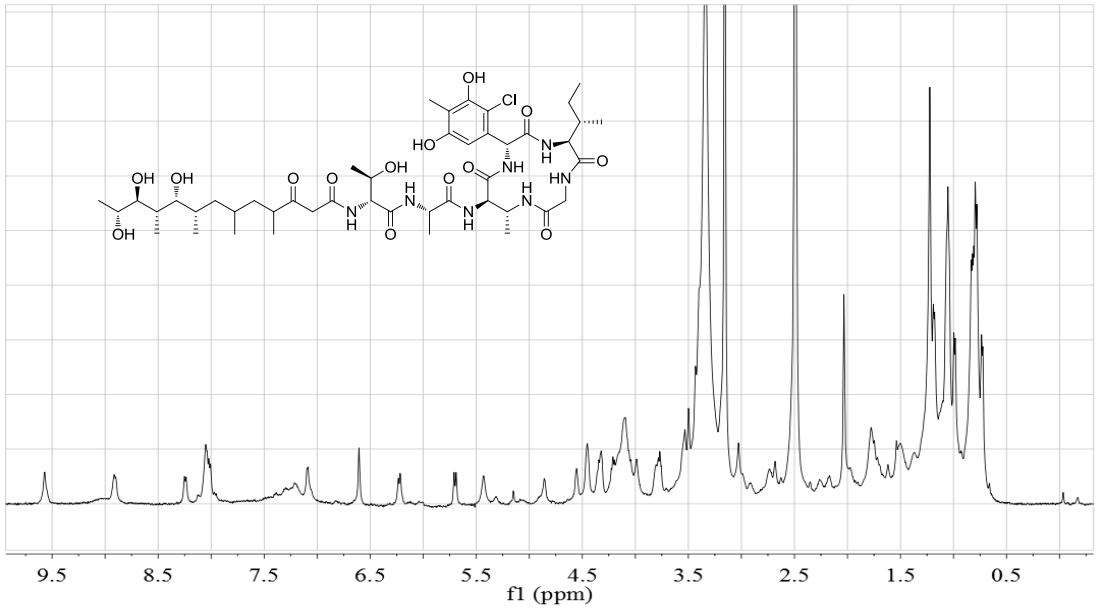


Figure S10. HSQC spectrum of compound 2 in DMSO- d_6.

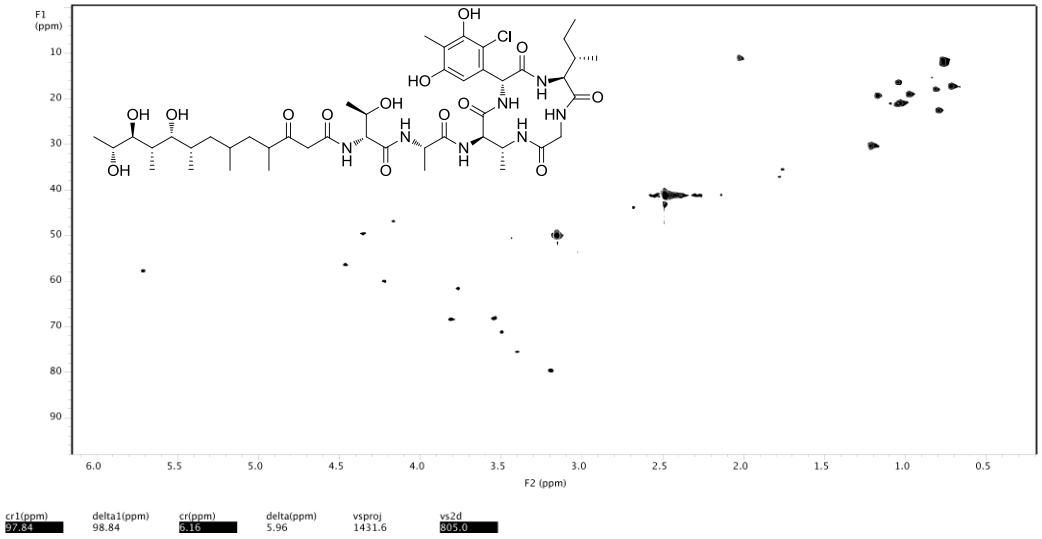


Figure S11. HMBC spectrum of compound 2 in DMSO- d_6.

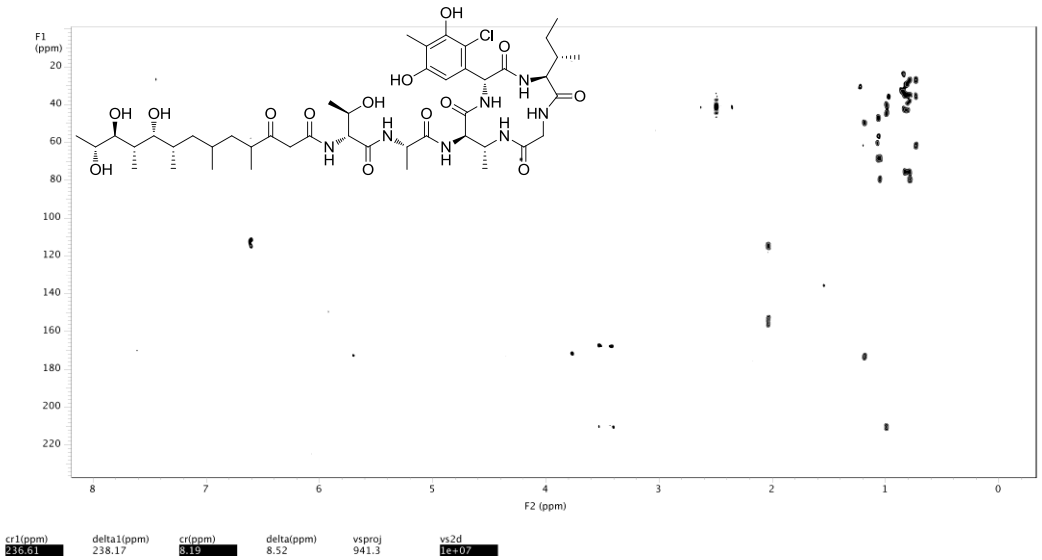


Figure S12. ^{1}H-^{1}H COSY spectrum of compound 2 in DMSO- d_6.

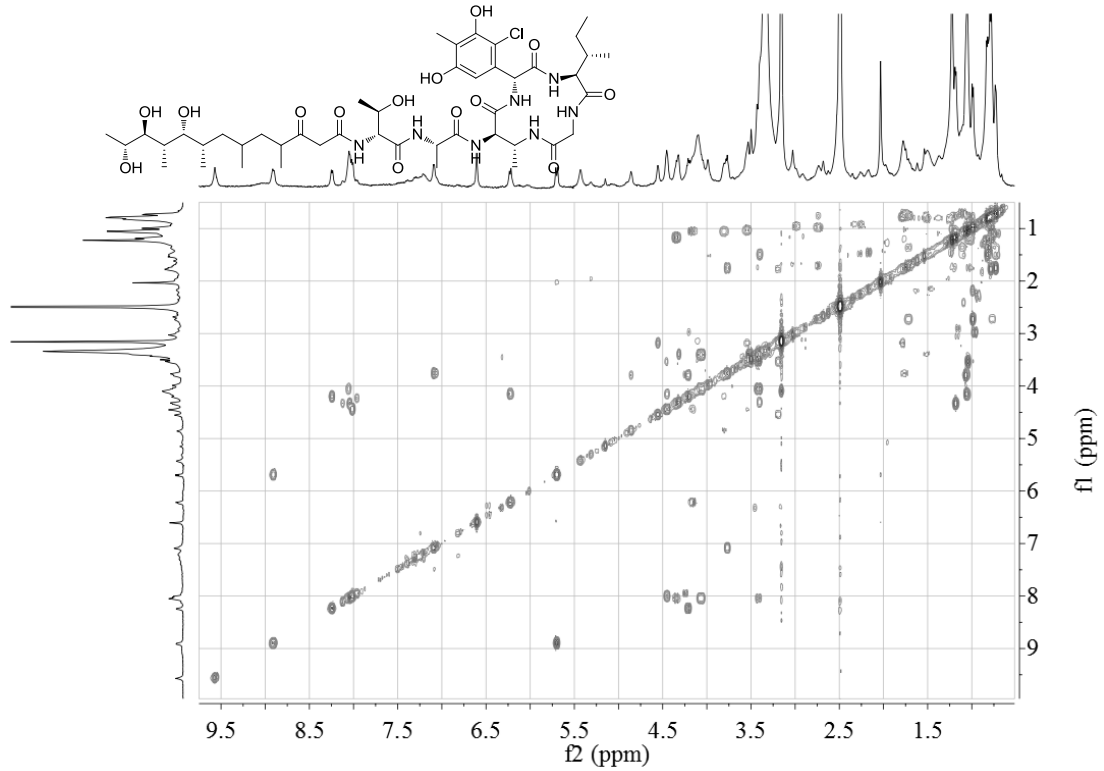
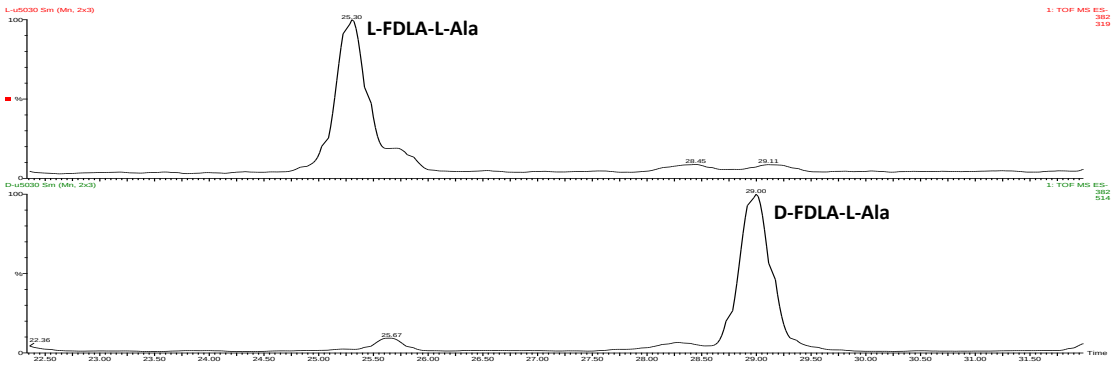


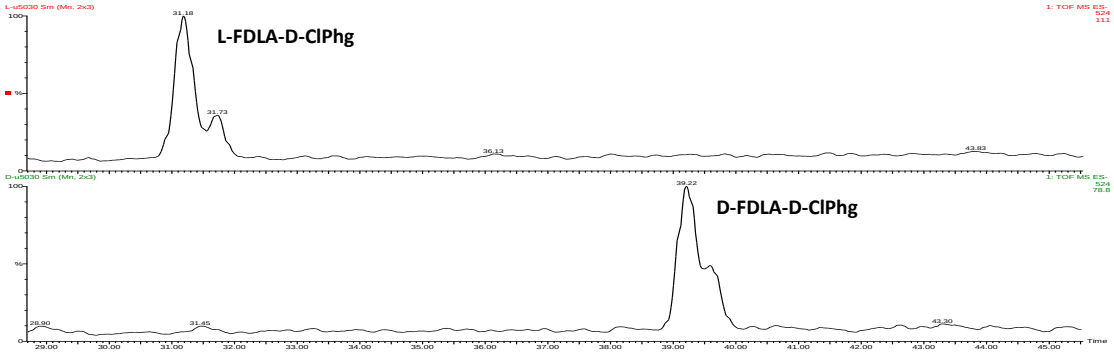
Figure S13. LC-MS Analysis of D/L-FDLA Derivatives.

Hydrolysate of **1** was reacted with L-FDLA (top) and D-FDLA (bottom), showing are extracted ion chromatographs.

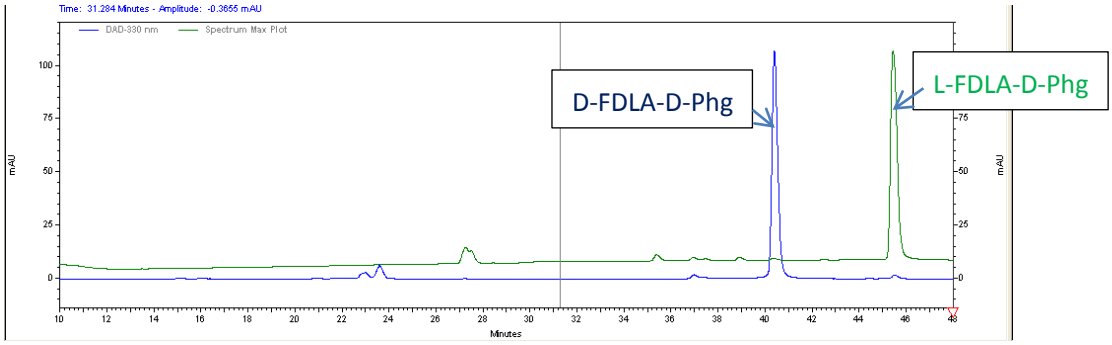
A) L-Ala in **1**: *m/z* 382 $[M - H]^-$



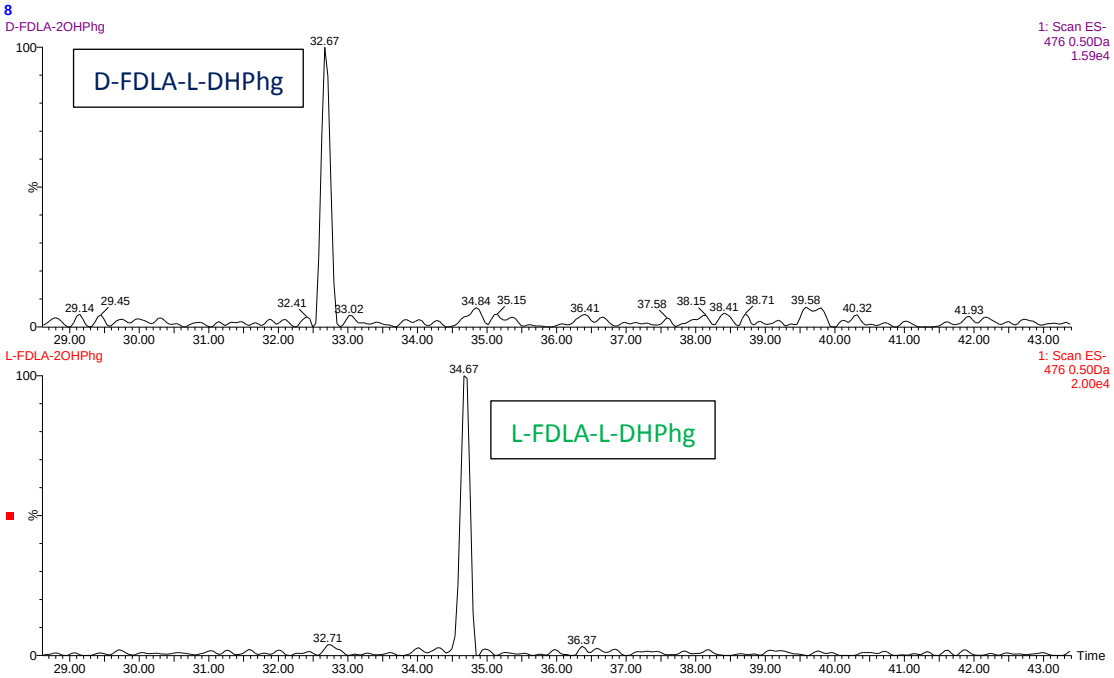
B) D-ClPhg in **1**: *m/z* 524 $[M - H]^-$



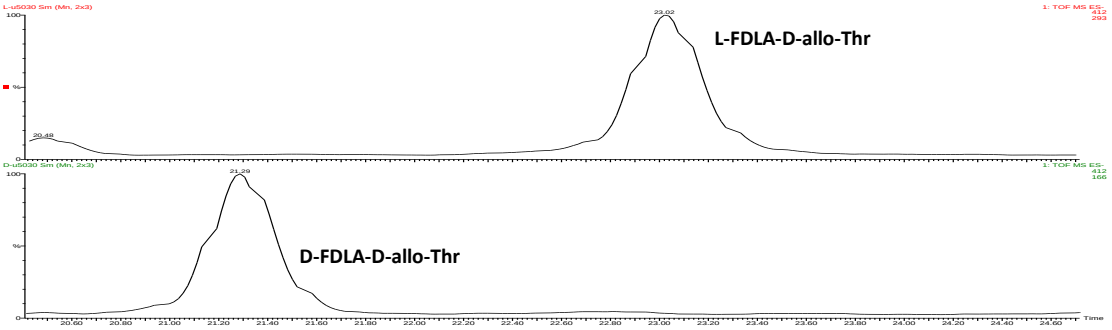
C) HPLC analysis of D/L-FDLA Derivatives for standard D-Phg



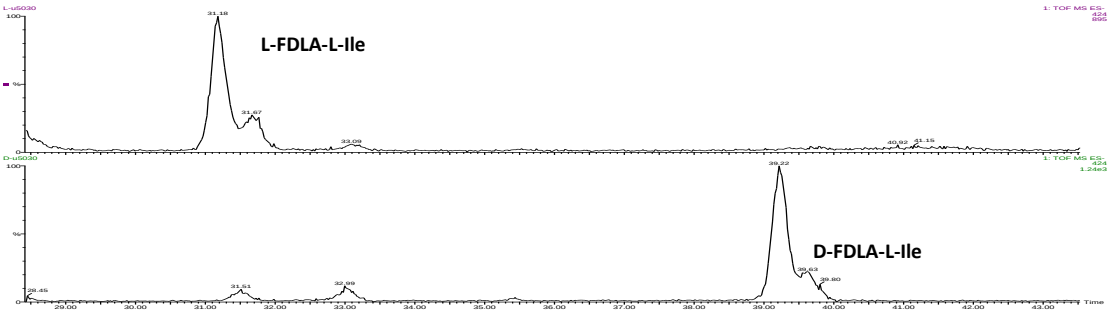
D) LC-MS analysis of D/L-FDLA Derivatives for standard L-3,5-Dihydroxyphenylglycine (DHPhg)



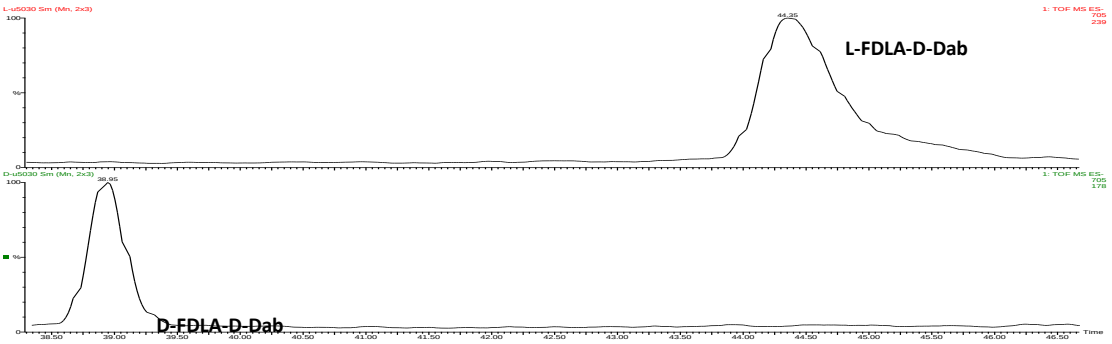
E) D-allo-Thr in **1**: *m/z* 412 $[M - H]^-$



F) L-Ile in **1**: *m/z* 424 $[M - H]^-$



G) D-Dab in **1**: *m/z* 705 $[M - H]^-$



H) LC-MS analysis of D/L-FDLA Derivatives for standard 2*S*,3*S*-Dab and 2*S* 3*R*-Dab.

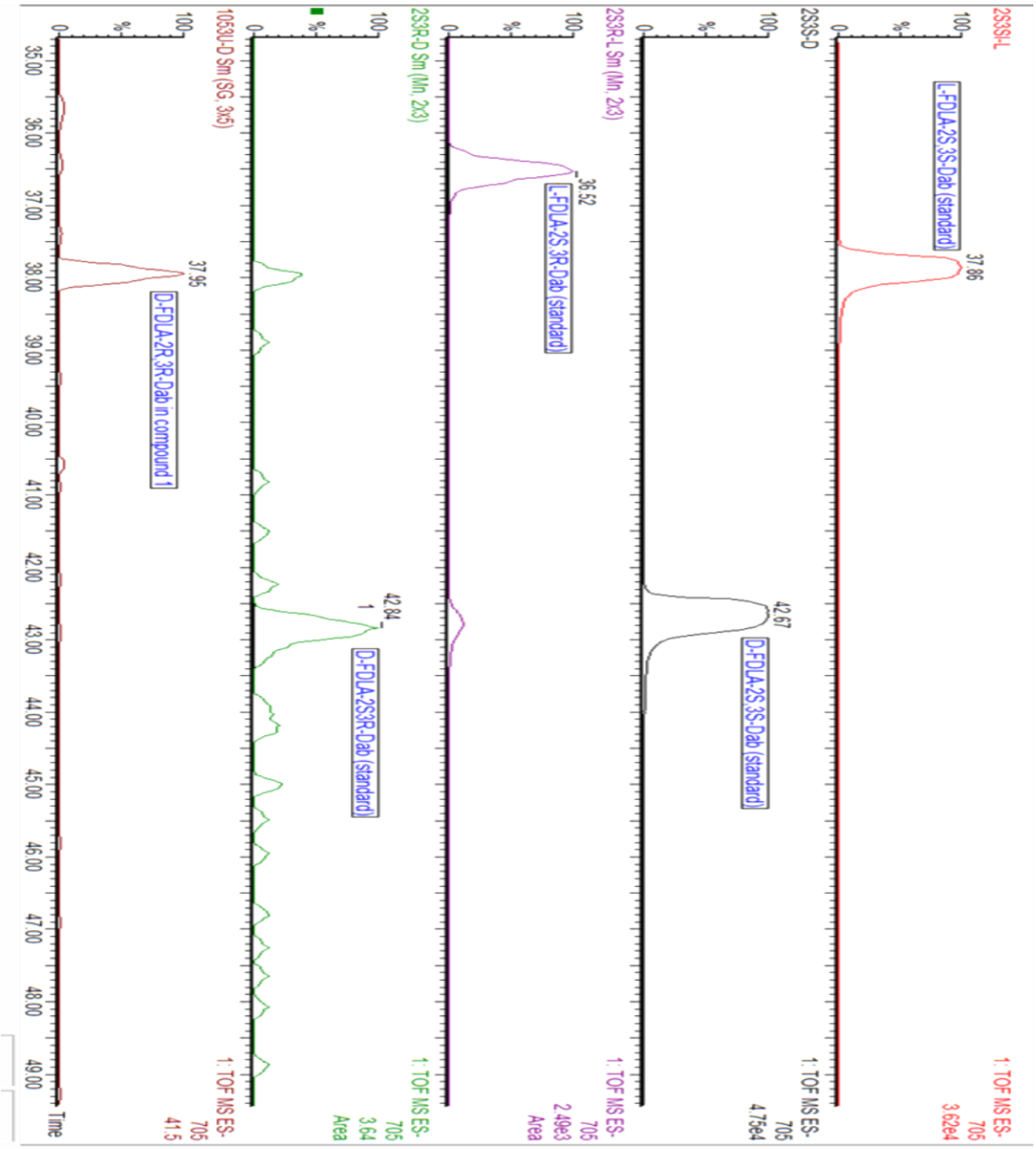

2S3S-L
1: TOF MS ES-
705
3.62e4
L-FDLA-2S,3S-Dab (standard)
37.86
2S3S-D
1: TOF MS ES-
705
4.75e4
42.67
D-FDLA-2S,3S-Dab (standard)
2S3R-L Sm (Mn, 2x3)
1: TOF MS ES-
705
2.49e3
Area
36.52
L-FDLA-2S,3R-Dab (standard)
2S3R-D Sm (Mn, 2x3)
1: TOF MS ES-
705
3.64
Area
42.84
1
D-FDLA-2S3R-Dab (standard)
1053U-D Sm (SG, 3x5)
1: TOF MS ES-
705
41.5
37.95
D-FDLA-2R,3R-Dab in compound 1
%
100
0
35.00
36.00
37.00
38.00
39.00
40.00
41.00
42.00
43.00
44.00
45.00
46.00
47.00
48.00
49.00
Time

Figure S14. LC-MS Analysis of L-FDAA Derivatives.

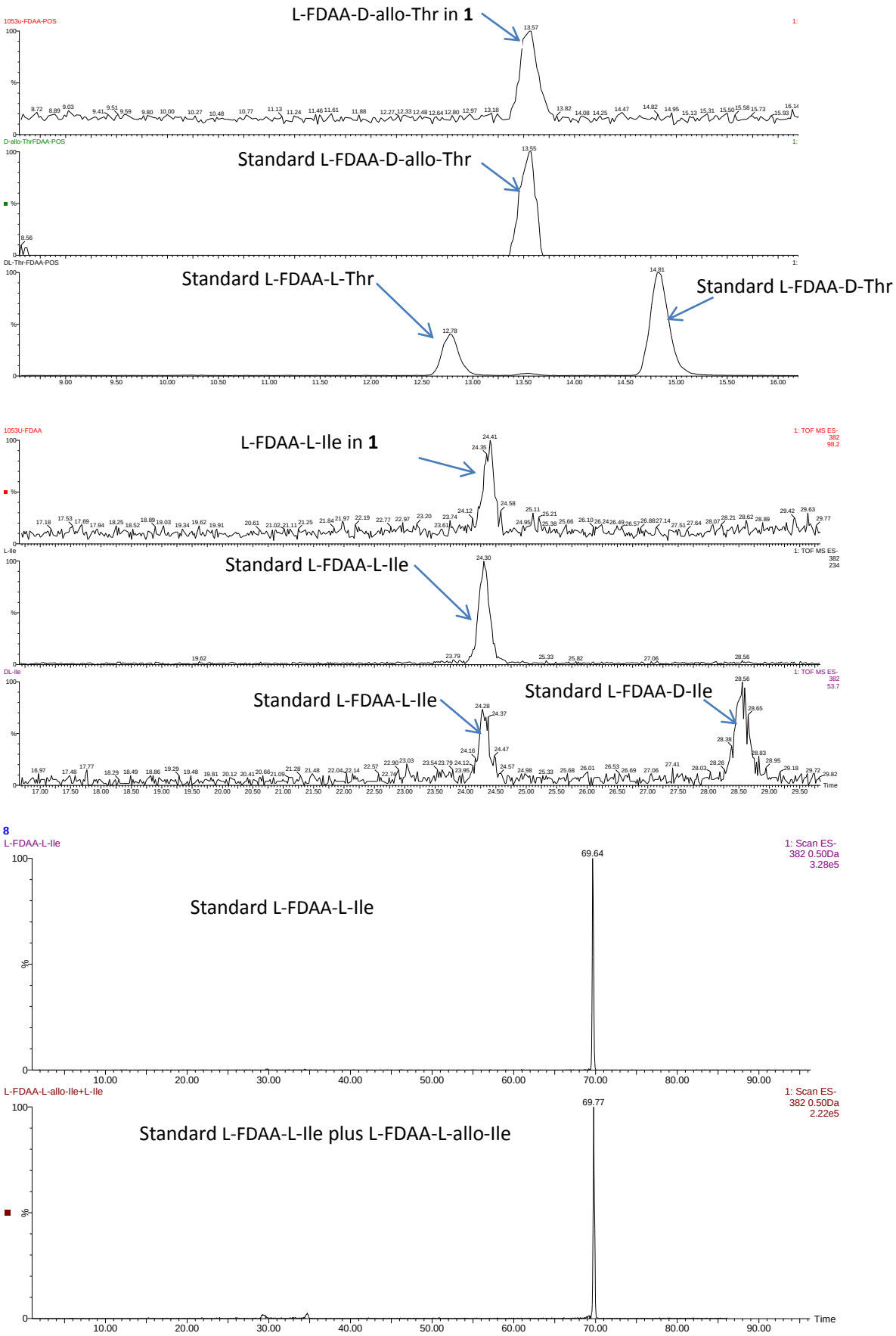
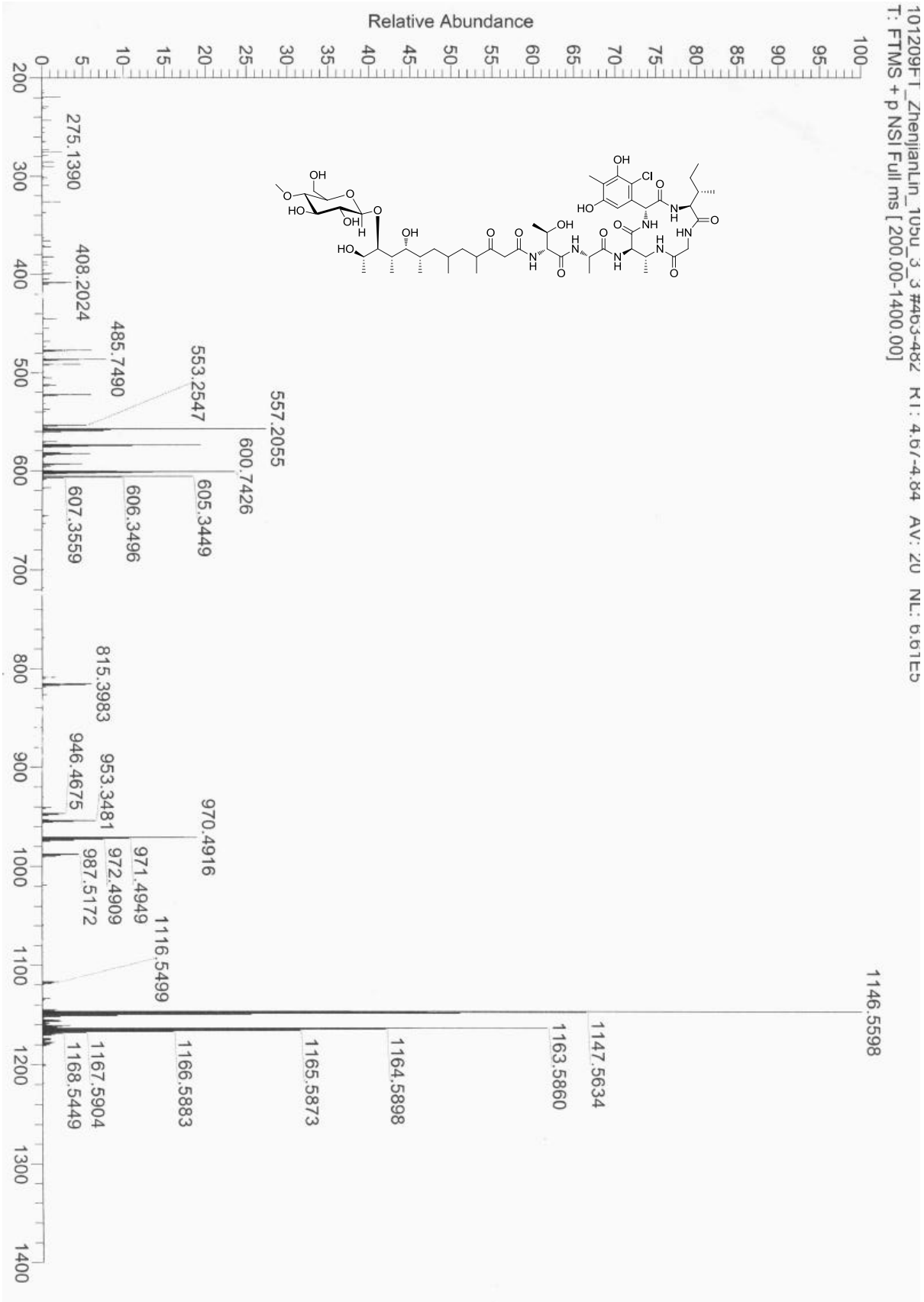
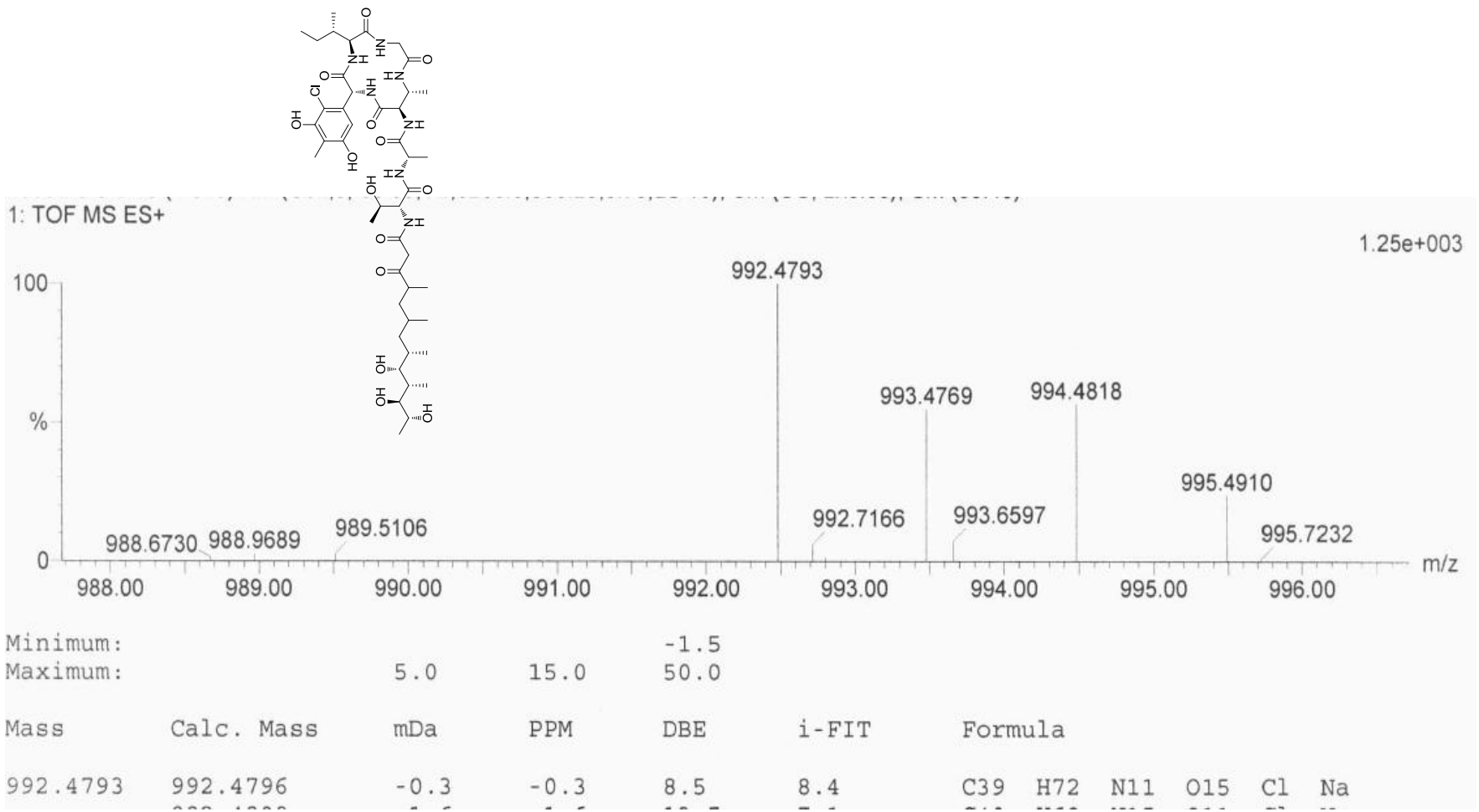


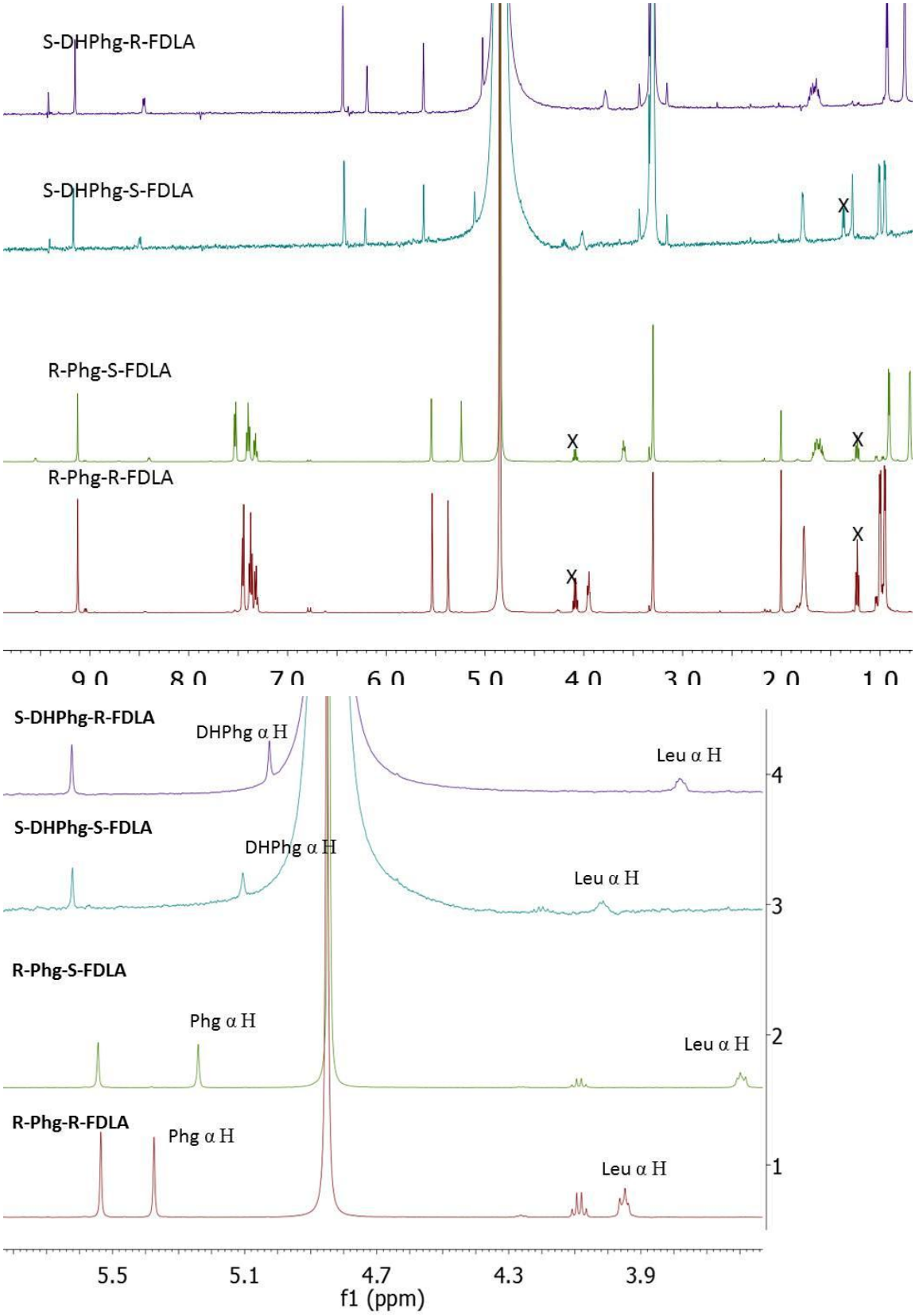
Figure S15. HRESIMS spectra of compounds 1 and 2.





Minimum:				-1.5		
Maximum:		5.0	15.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
992.4793	992.4796	-0.3	-0.3	8.5	8.4	C39 H72 N11 O15 Cl Na

Figure S16. ^{1}H NMR spectrum of FDLA derivatives of Phg and DHPhg in CD3OD- d_4.



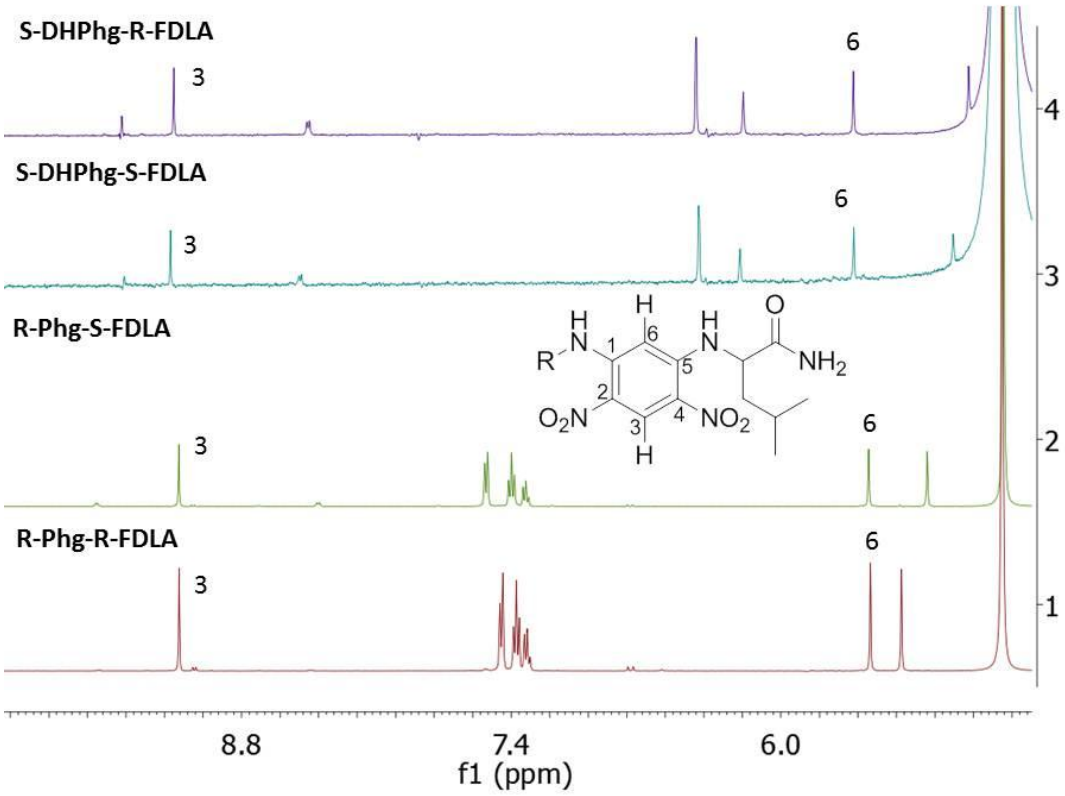


Table S1. The chemical difference of the *α* protons of the Leu and Phgs.

	S-DHPhg-R-FDLA	S-DHPhg-S-FDLA	Δδ1	R-Phg-S-FDLA	R-Phg-R-FDLA	Δδ2
*α*H-Leu (ppm)	3.7794	4.0153	-0.2359	3.5955	3.9494	-0.3539
*α*H-Phgs (ppm)	5.0252	5.1045	-0.0793	5.2400	5.3738	-0.1338