

Supplementary Materials for

Dianthiamides A–E, Proline-Containing Orbitides
from *Dianthus Chinensis*

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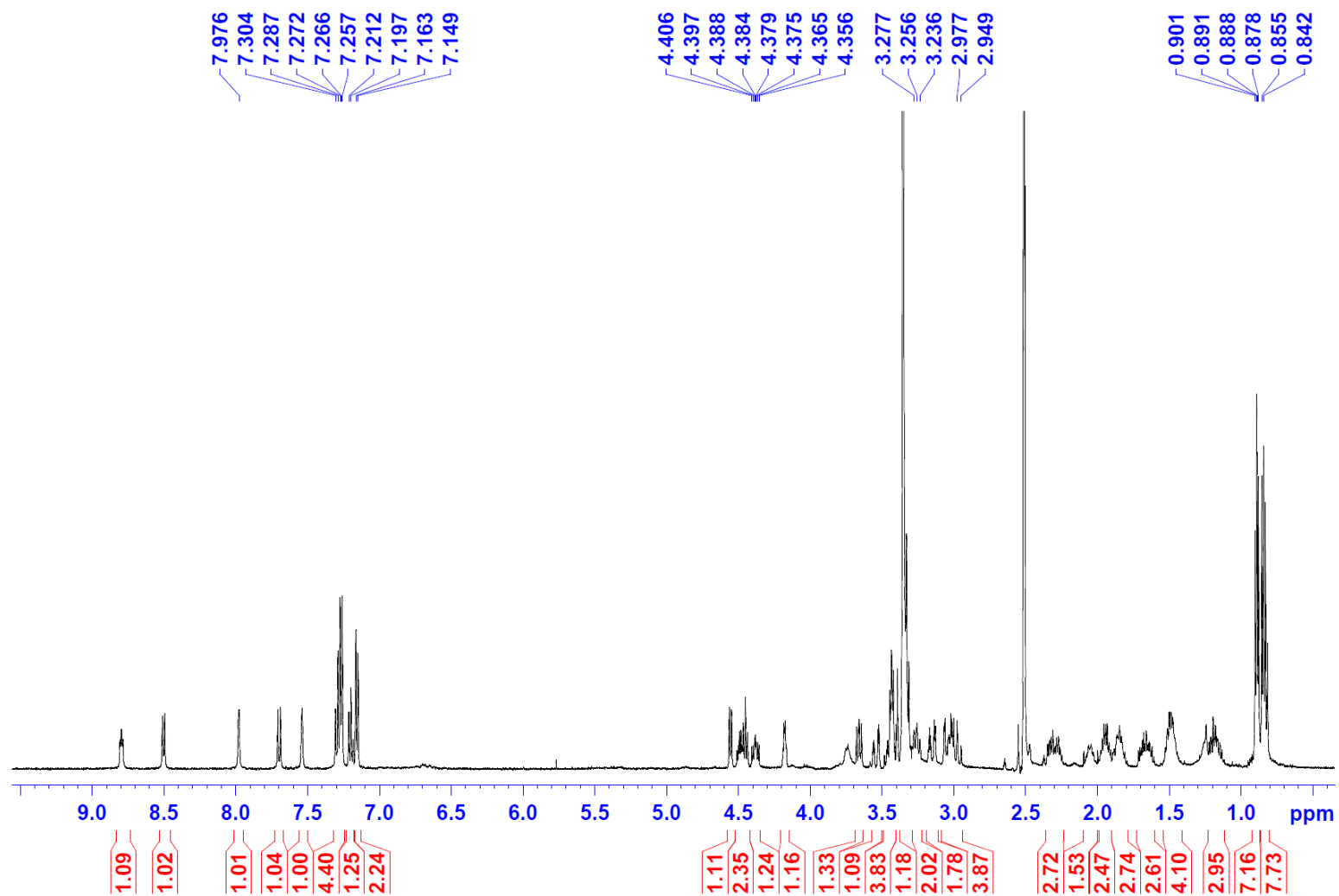


Figure S1. ¹H NMR spectrum of compound 1 (DMSO-*d*₆, 700 MHz)

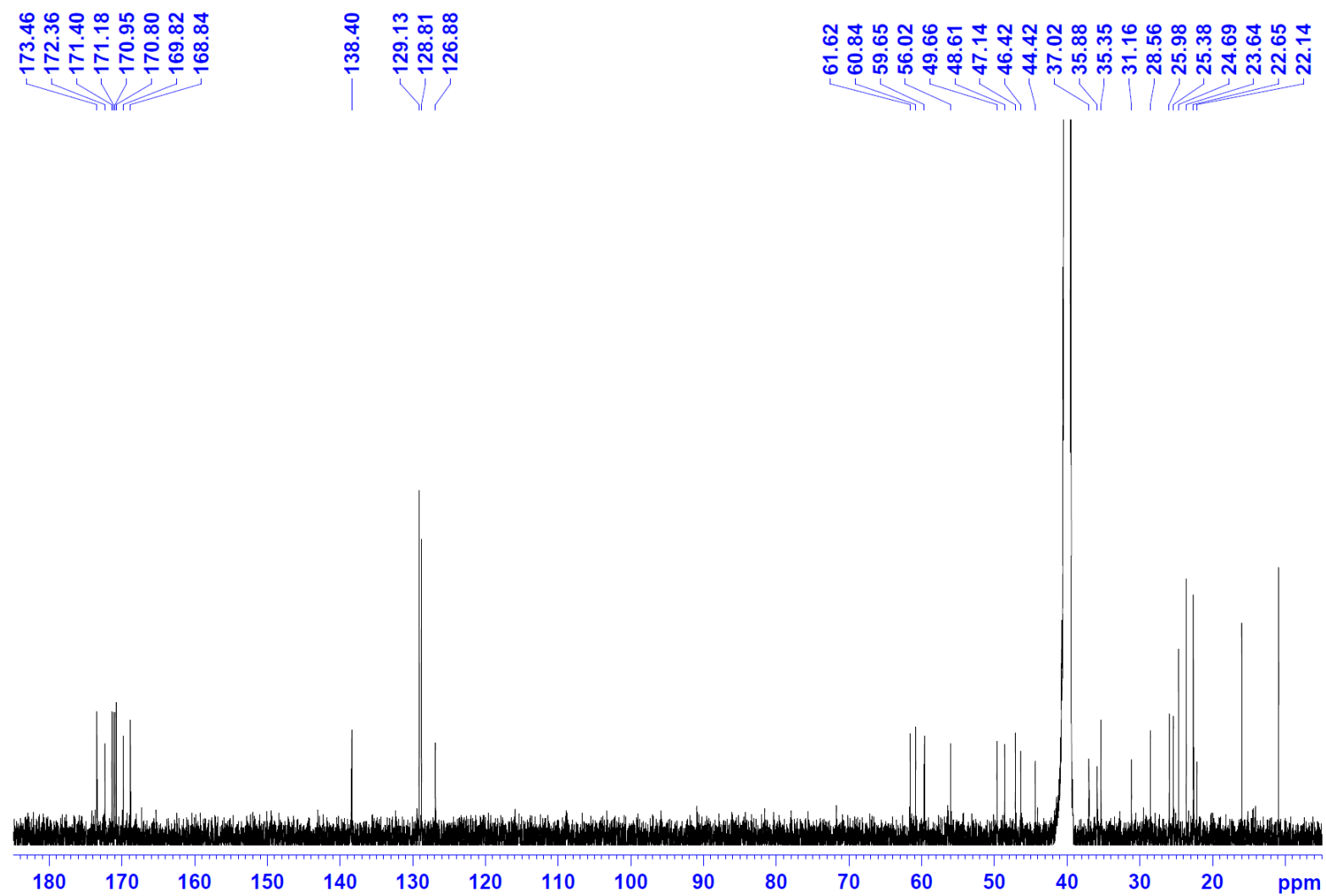


Figure S2. ¹³C NMR spectrum of compound **1** (DMSO-*d*₆, 175 MHz)

COSY of DSC141 in DMSO

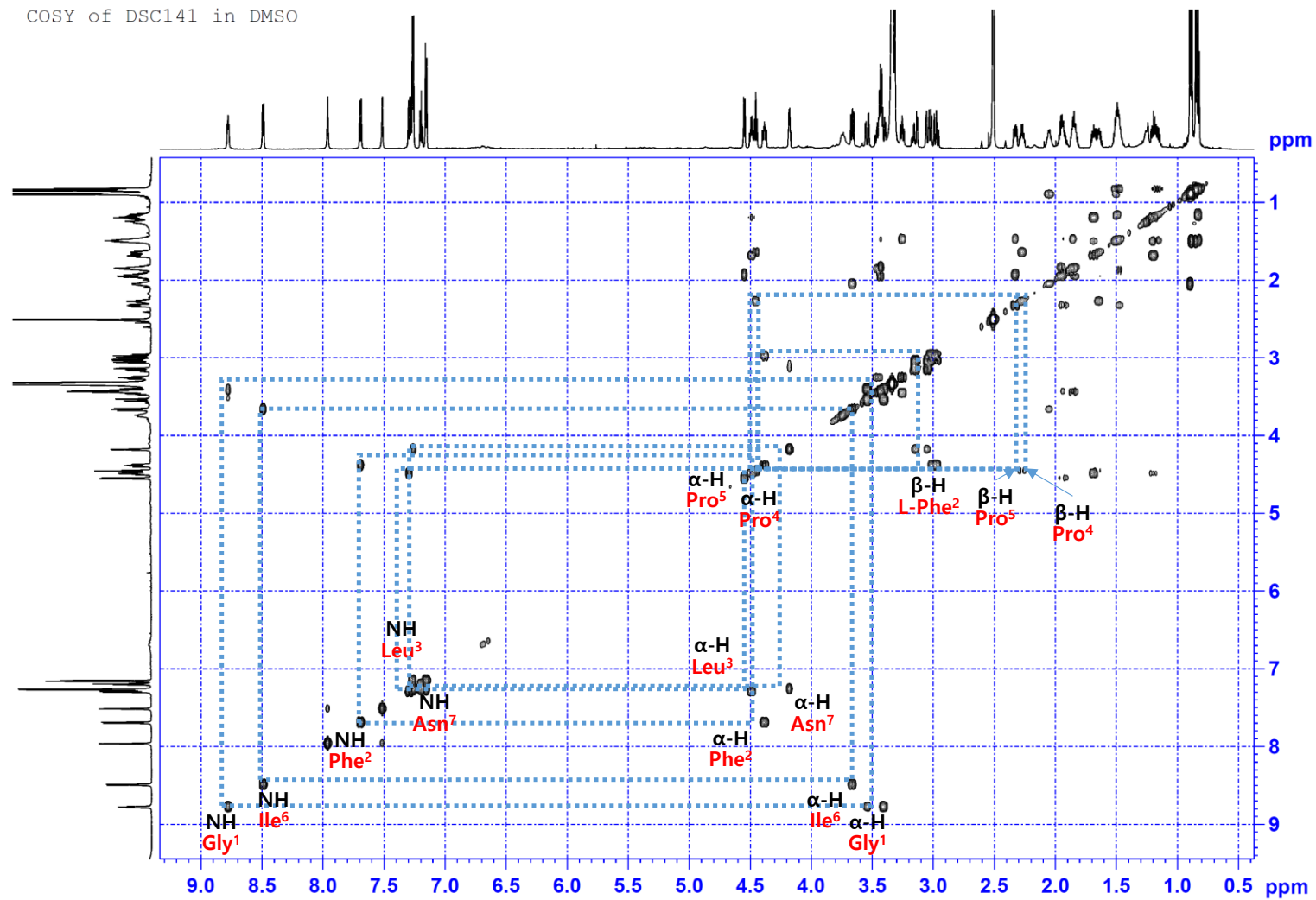


Figure S3. COSY spectrum of compound 1

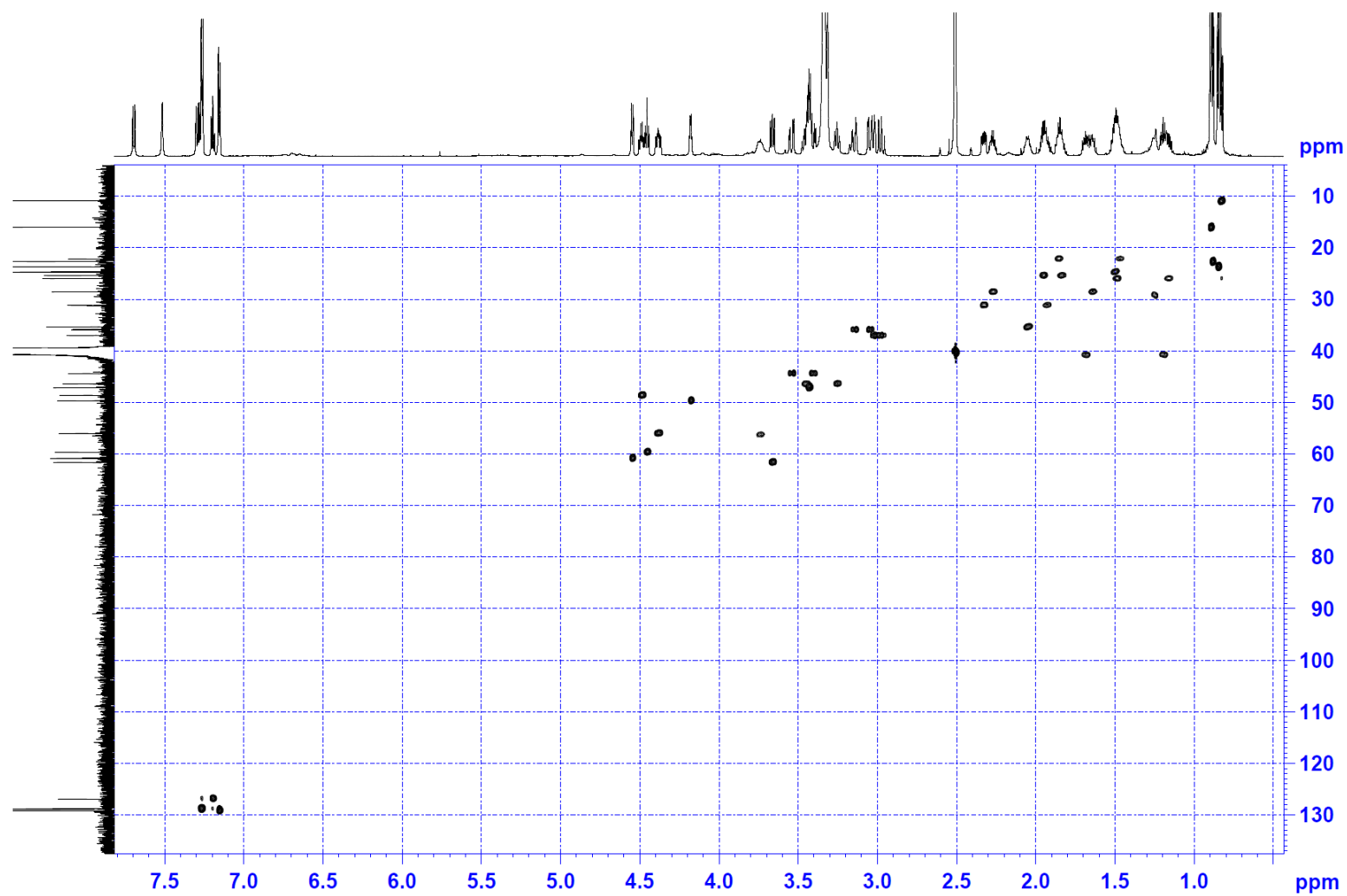


Figure S4. HSQC spectrum of compound **1**

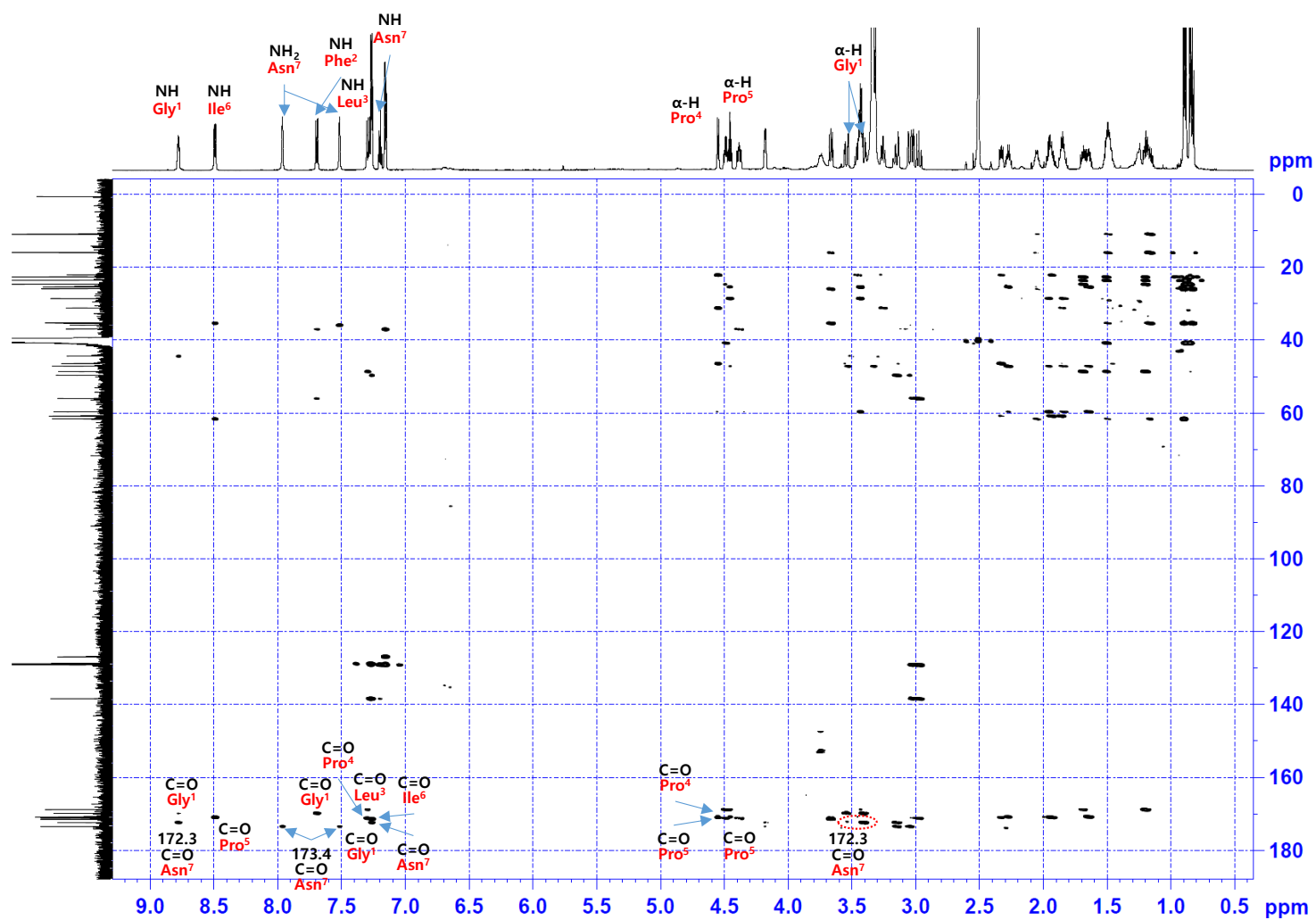


Figure S5. HMBC spectrum of compound 1

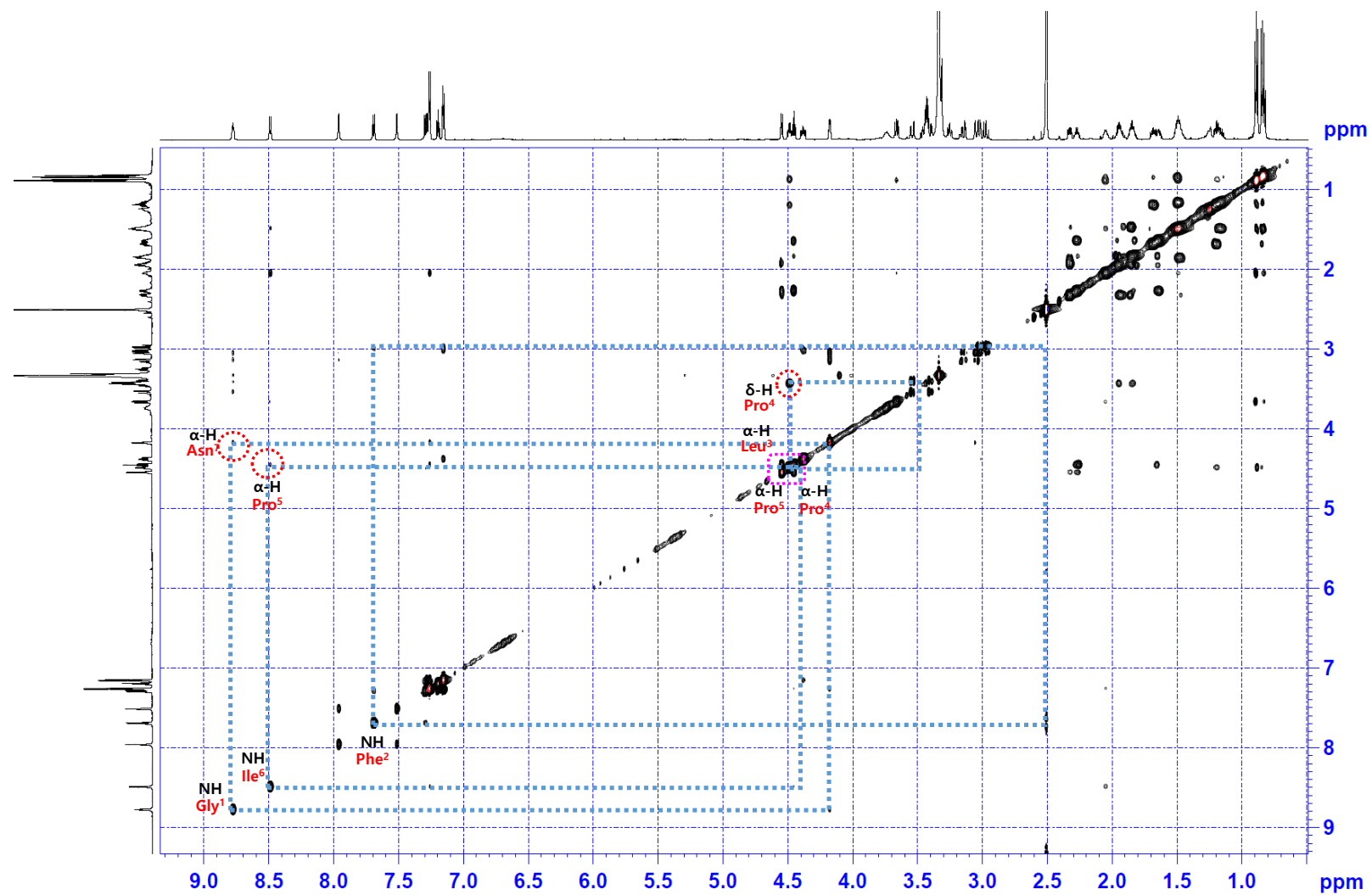


Figure S6. ROESY spectrum of compound 1

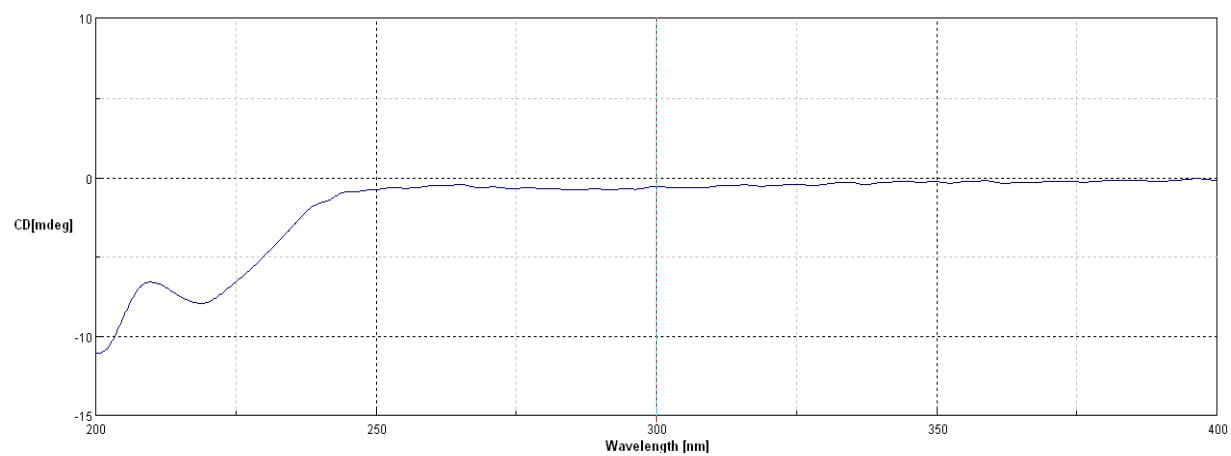


Figure S7. ECD spectrum of compound **1**

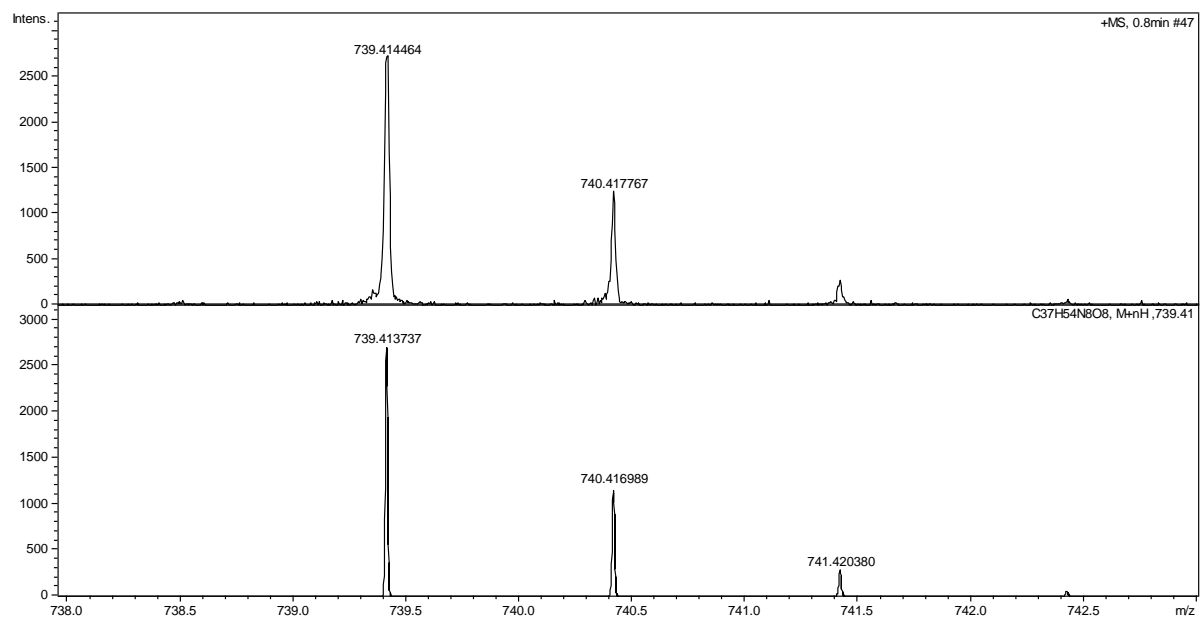


Figure S8. HRESI-MS spectrum of compound **1**

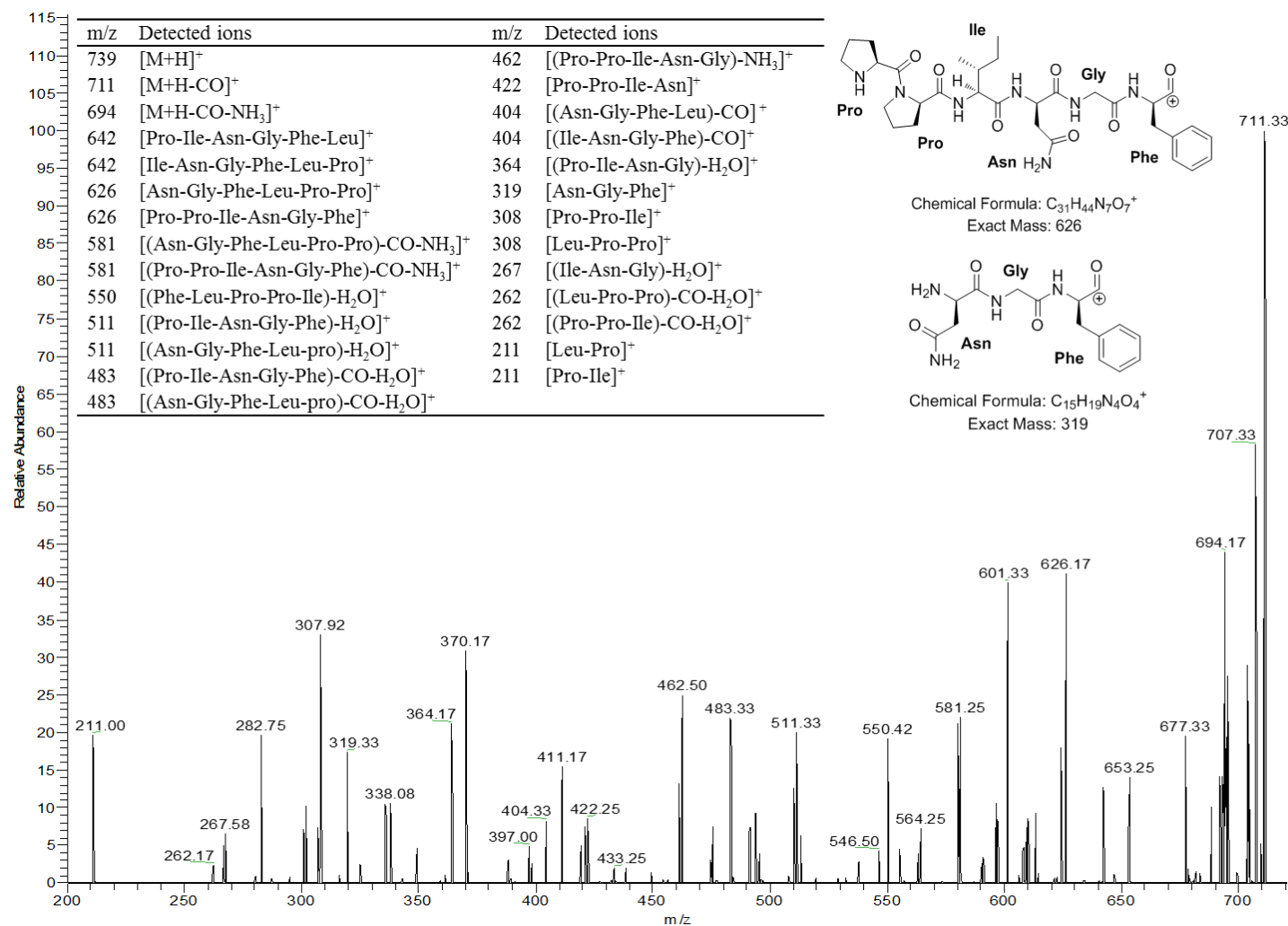


Figure S9. ESI-MS/MS spectrum of compound **1**

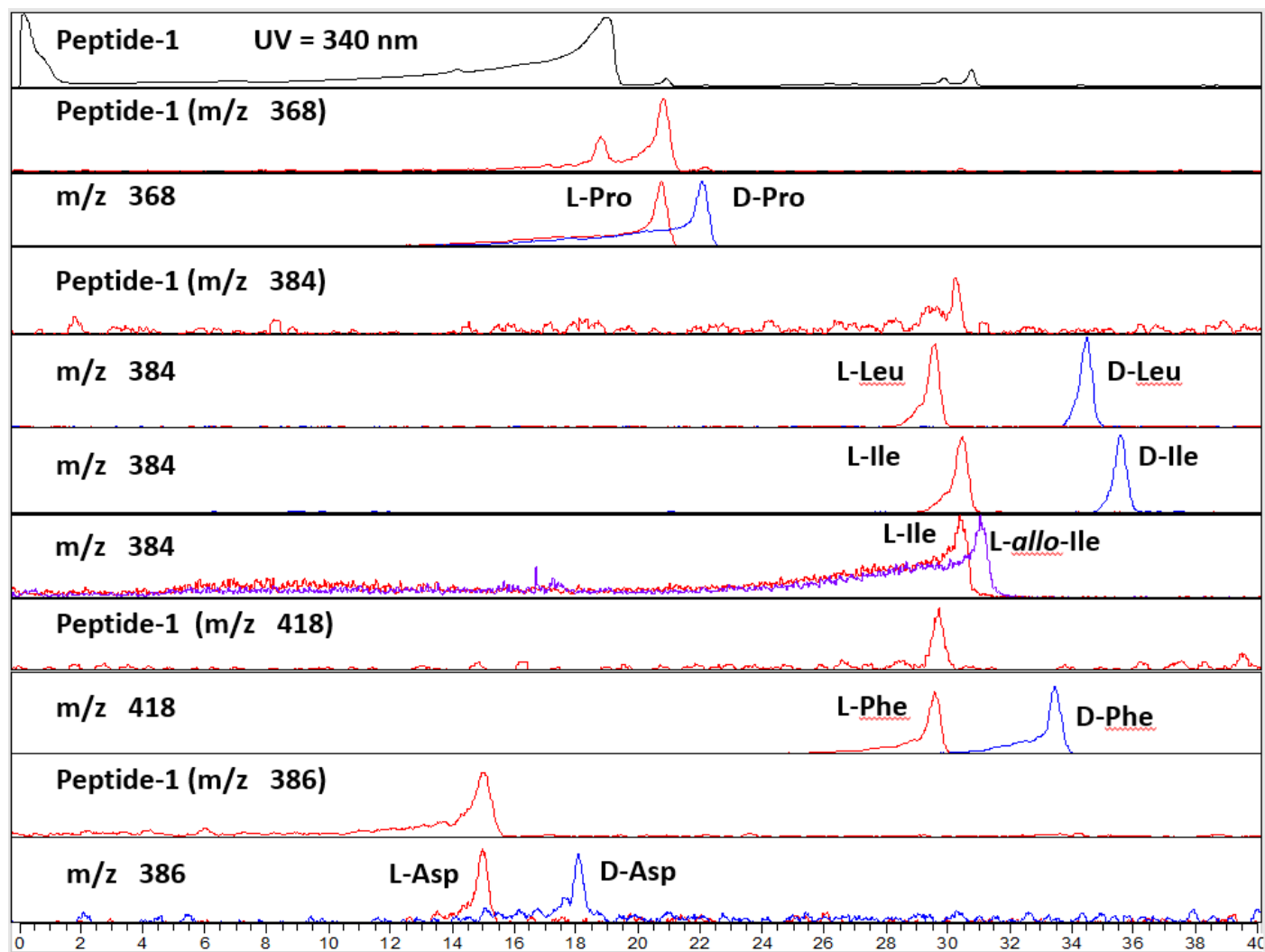


Figure S10. Marfey's analysis of compound 1

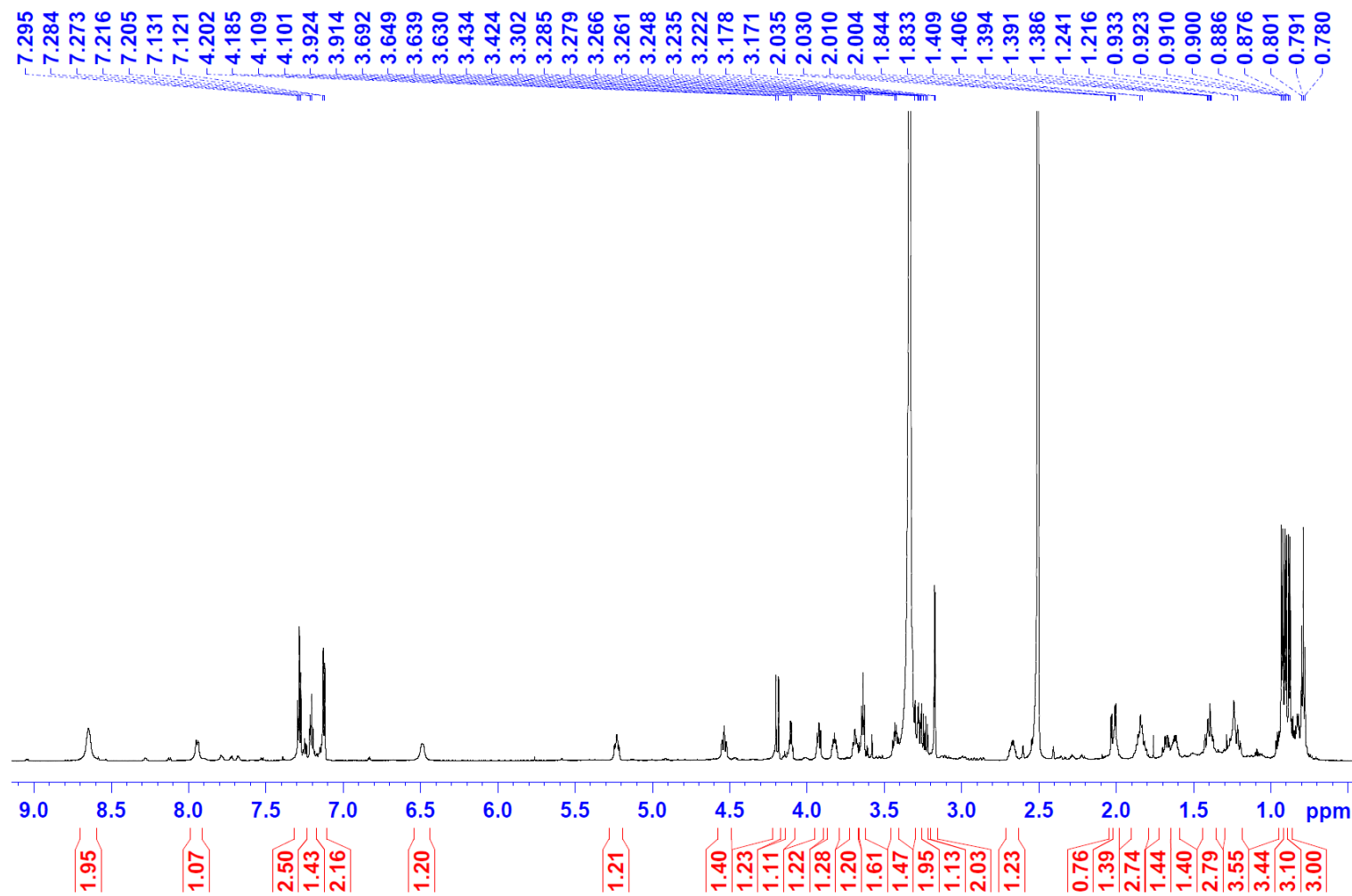


Figure S11. ¹H NMR spectrum of compound 2 (DMSO-*d*₆, 700 MHz)

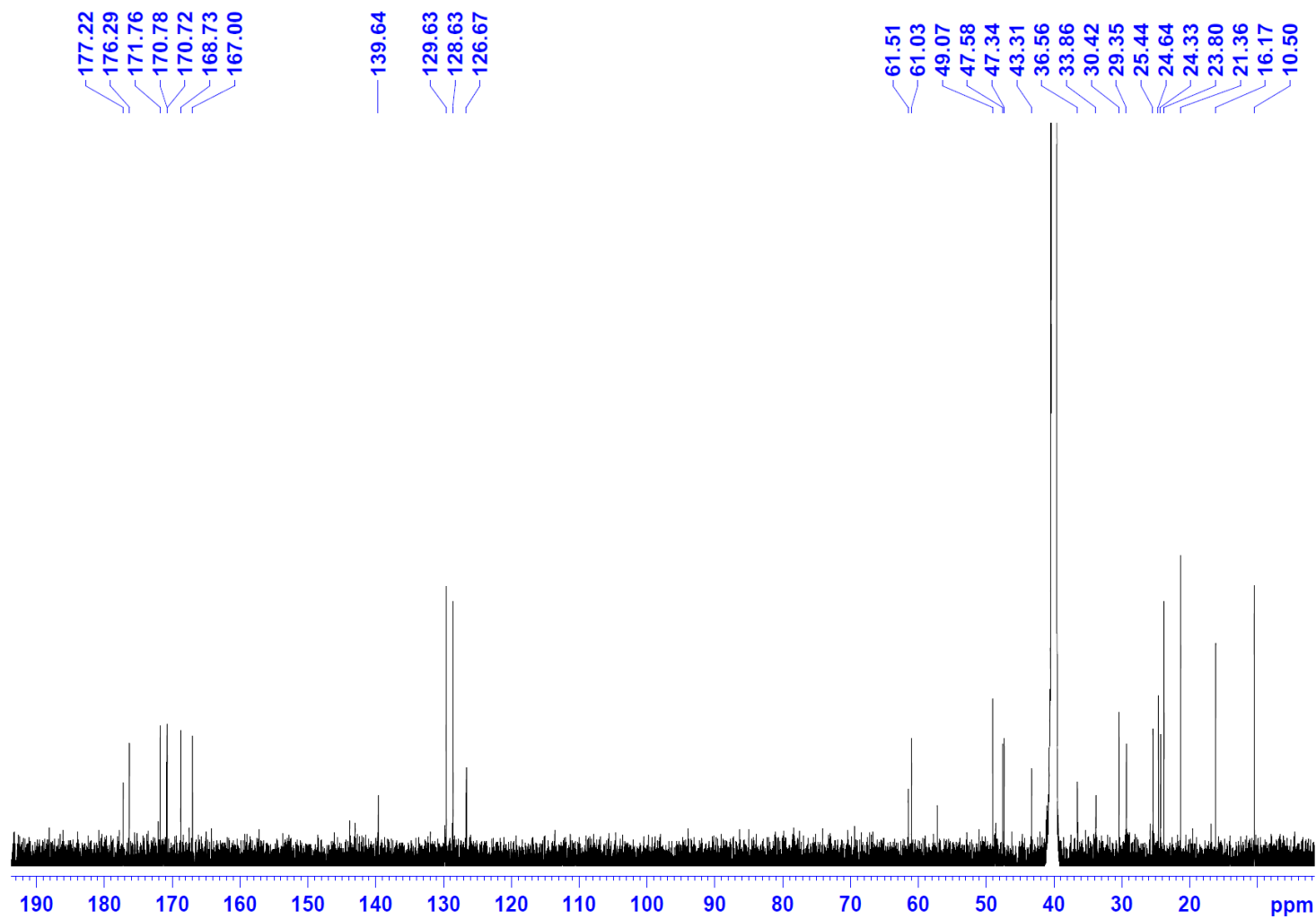


Figure S12. ¹³C NMR spectrum of compound **2** (DMSO-*d*₆, 175 MHz)

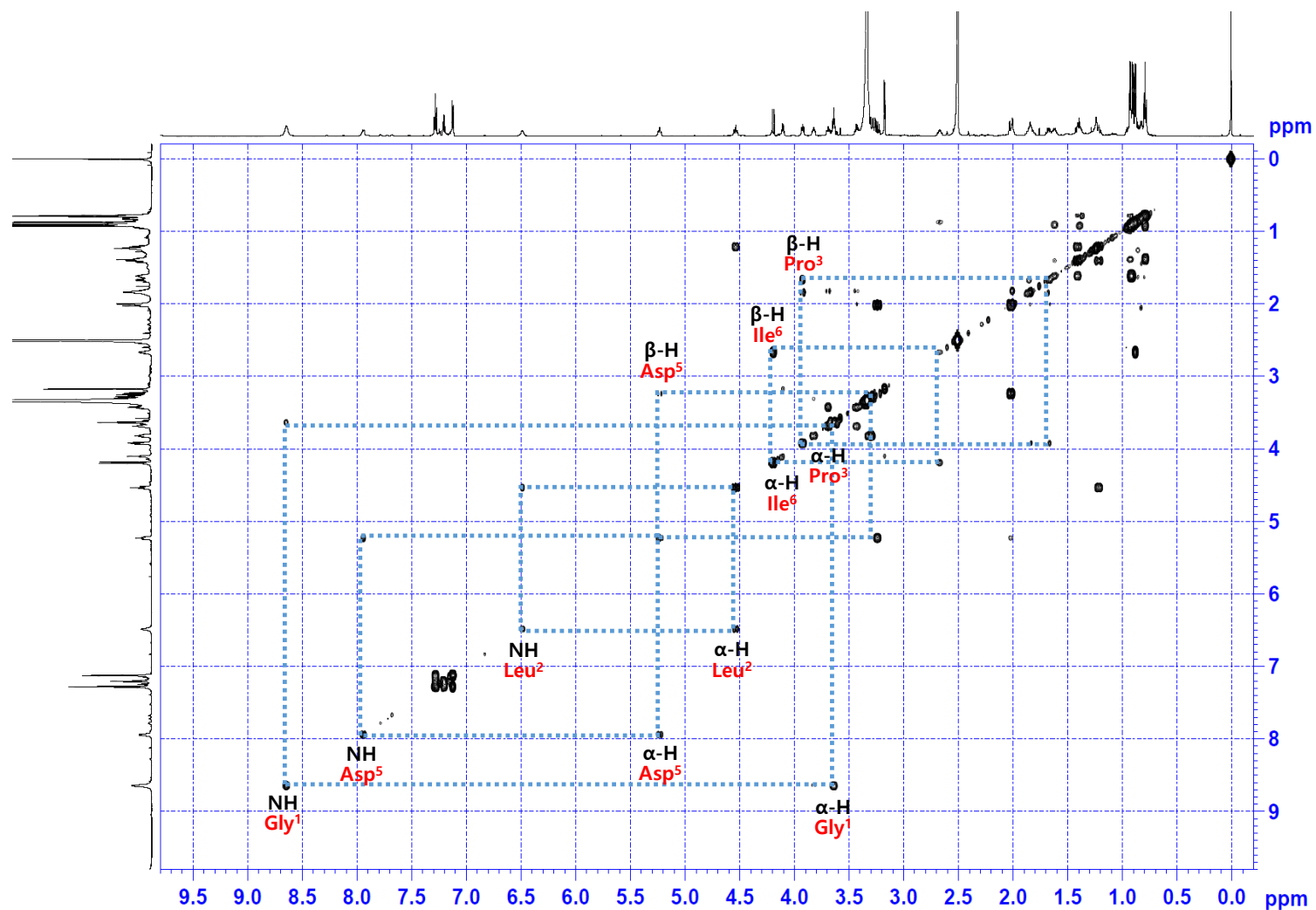


Figure S13. COSY spectrum of compound 2

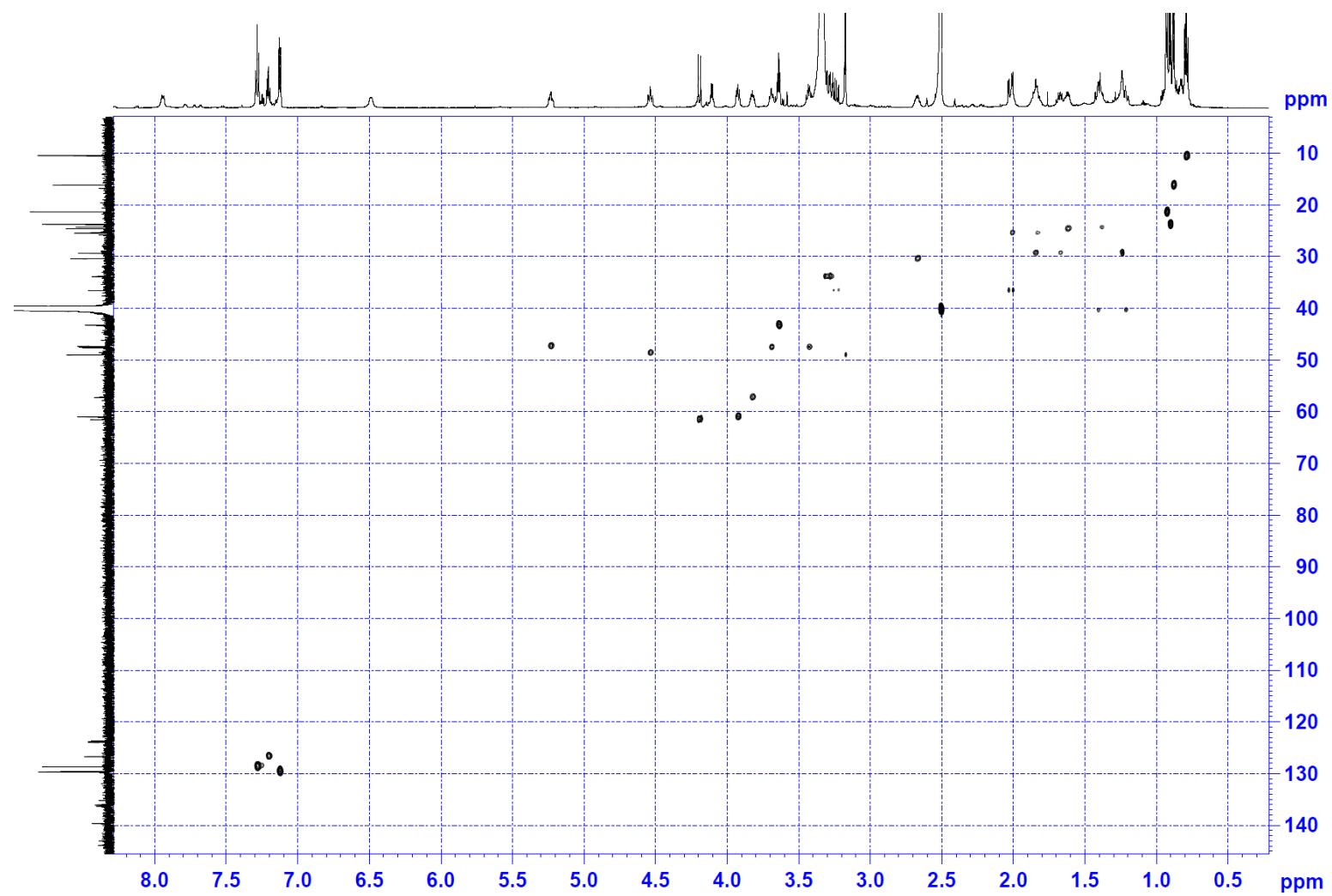


Figure S14. HSQC spectrum of compound 2

S17

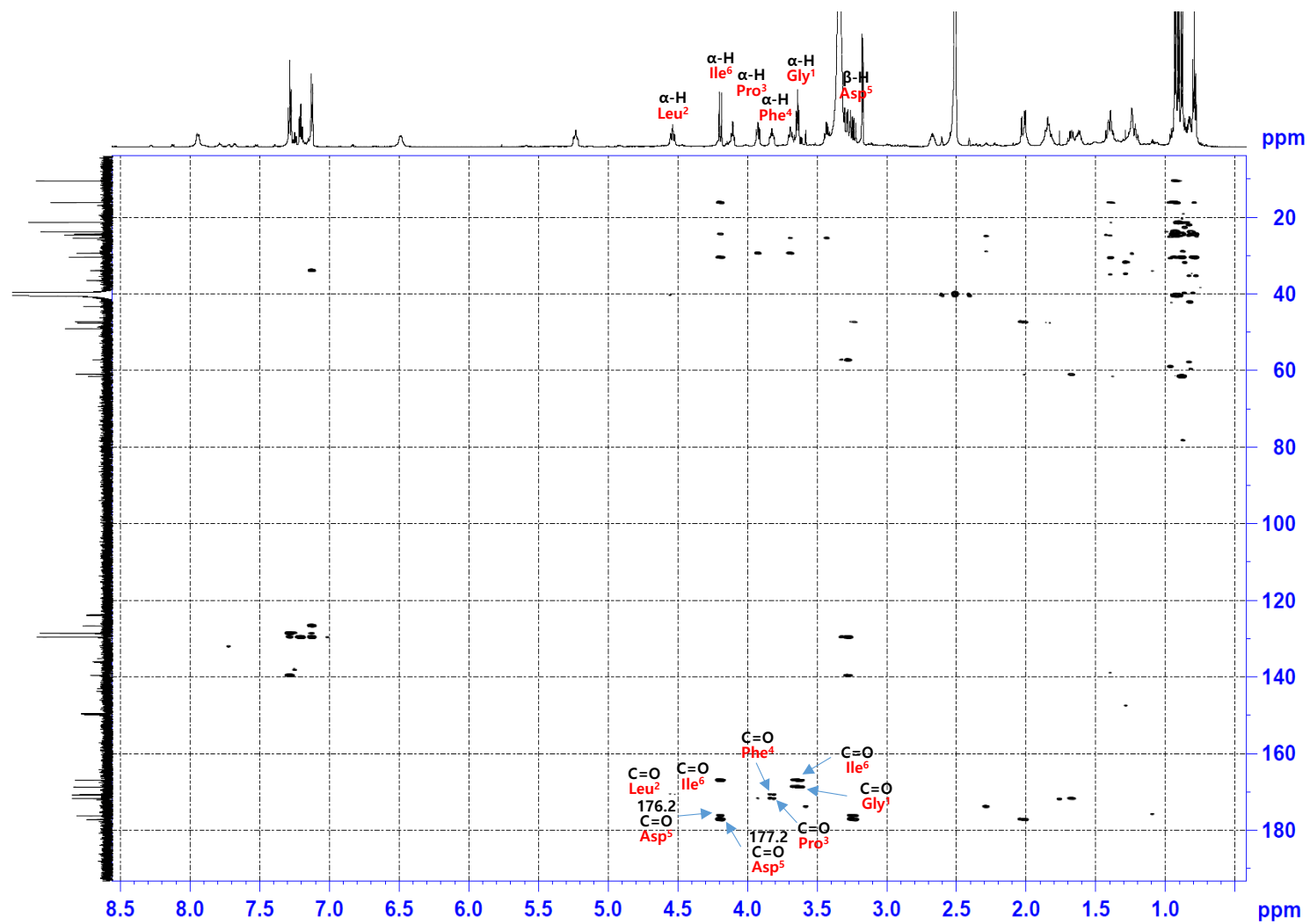


Figure S15. HMBC spectrum of compound 2
S18

ROESY of DSC741 in DMSO

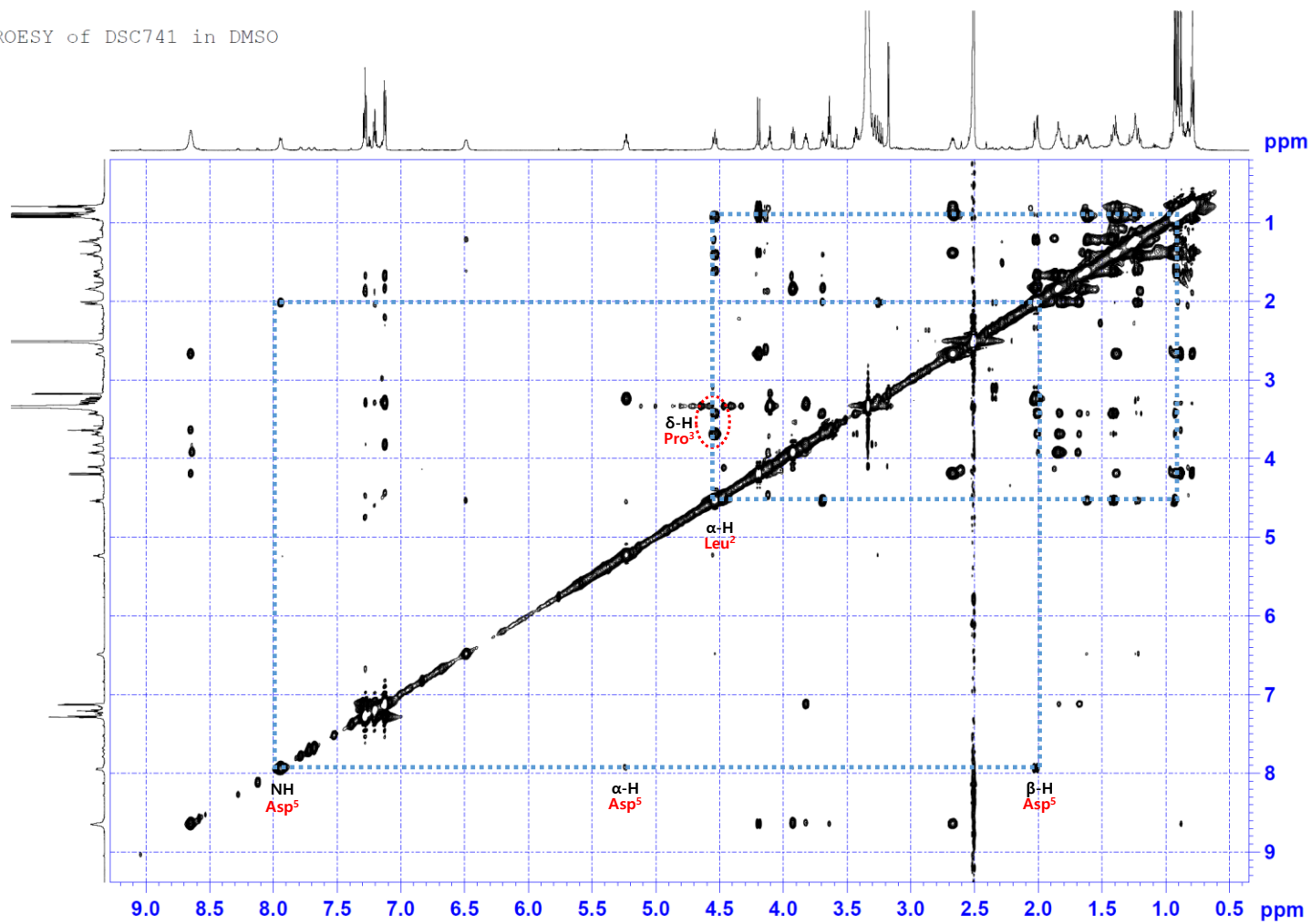


Figure S16. ROESY spectrum of compound 2

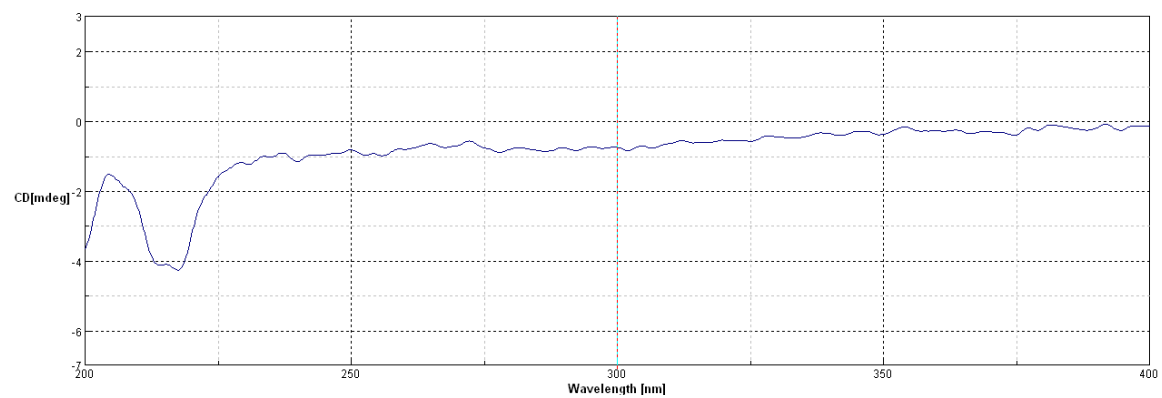


Figure S17. ECD spectrum of compound **2**

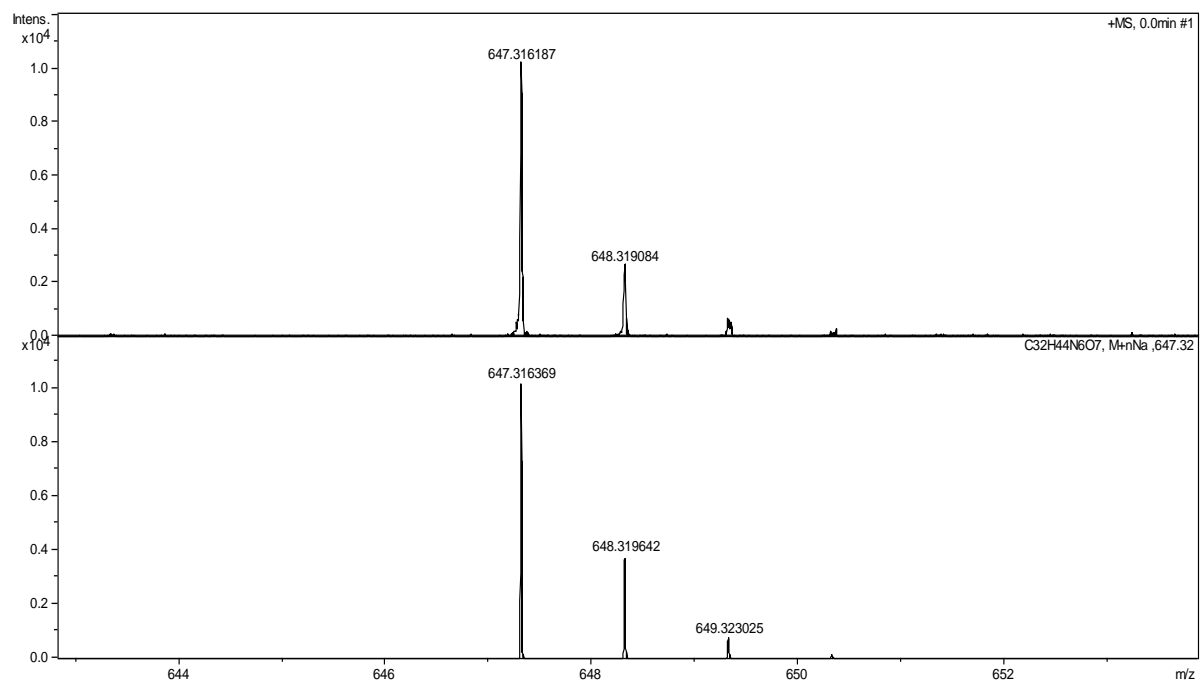


Figure S18. HRESI-MS spectrum of compound **2**

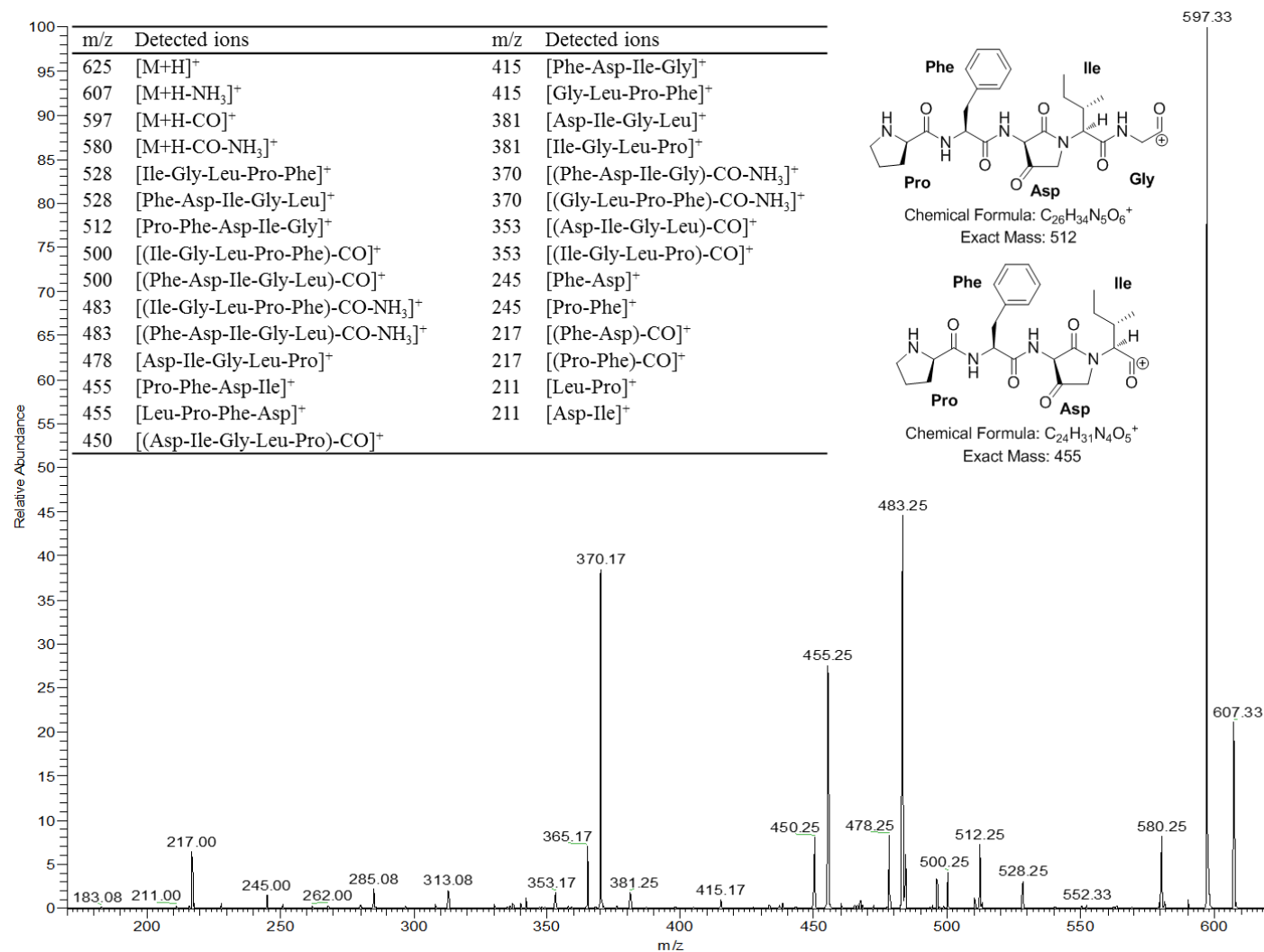


Figure S19. ESI-MS/MS spectrum of compound **2**

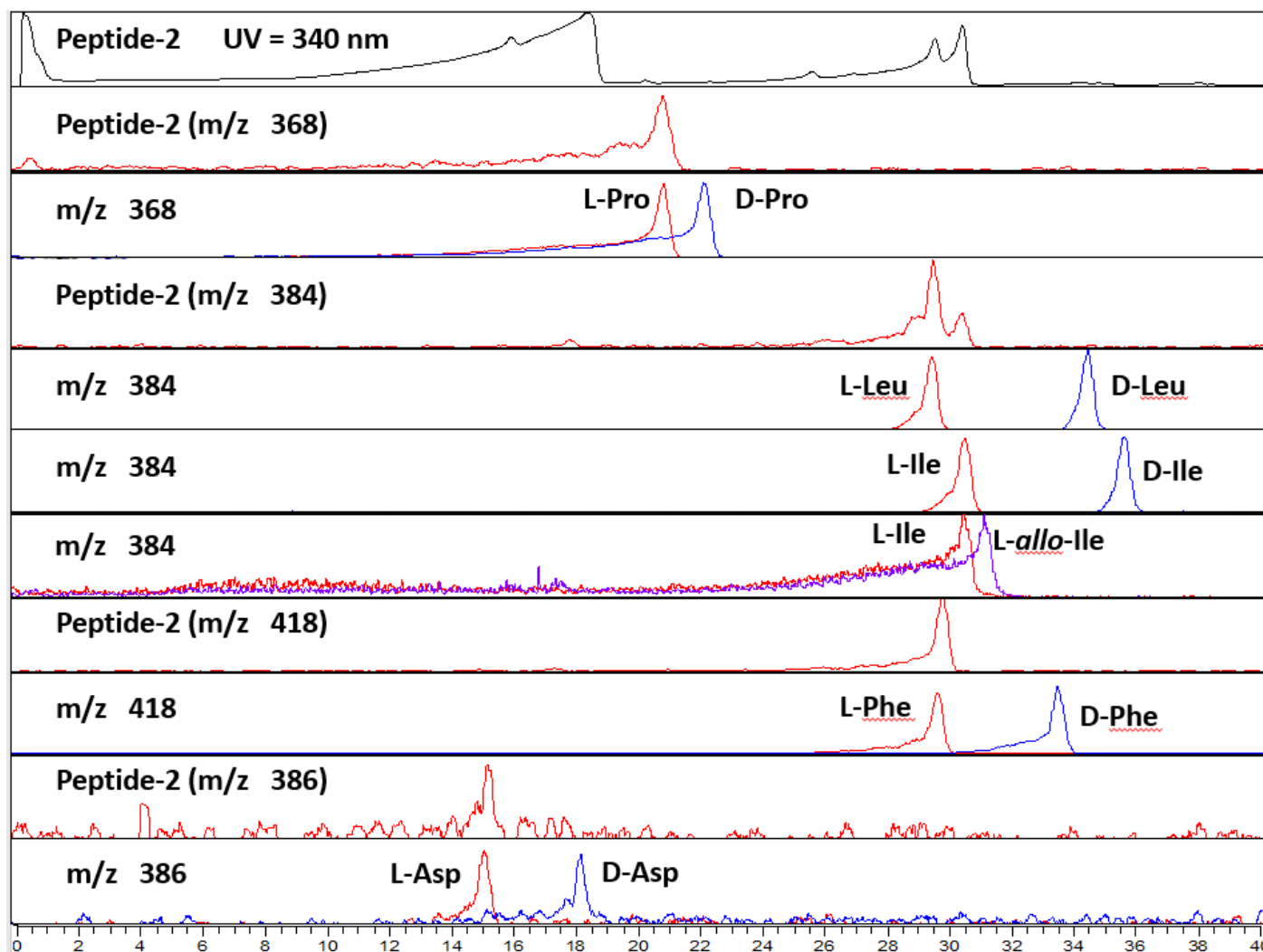


Figure S20. Marfey's analysis of compound 2

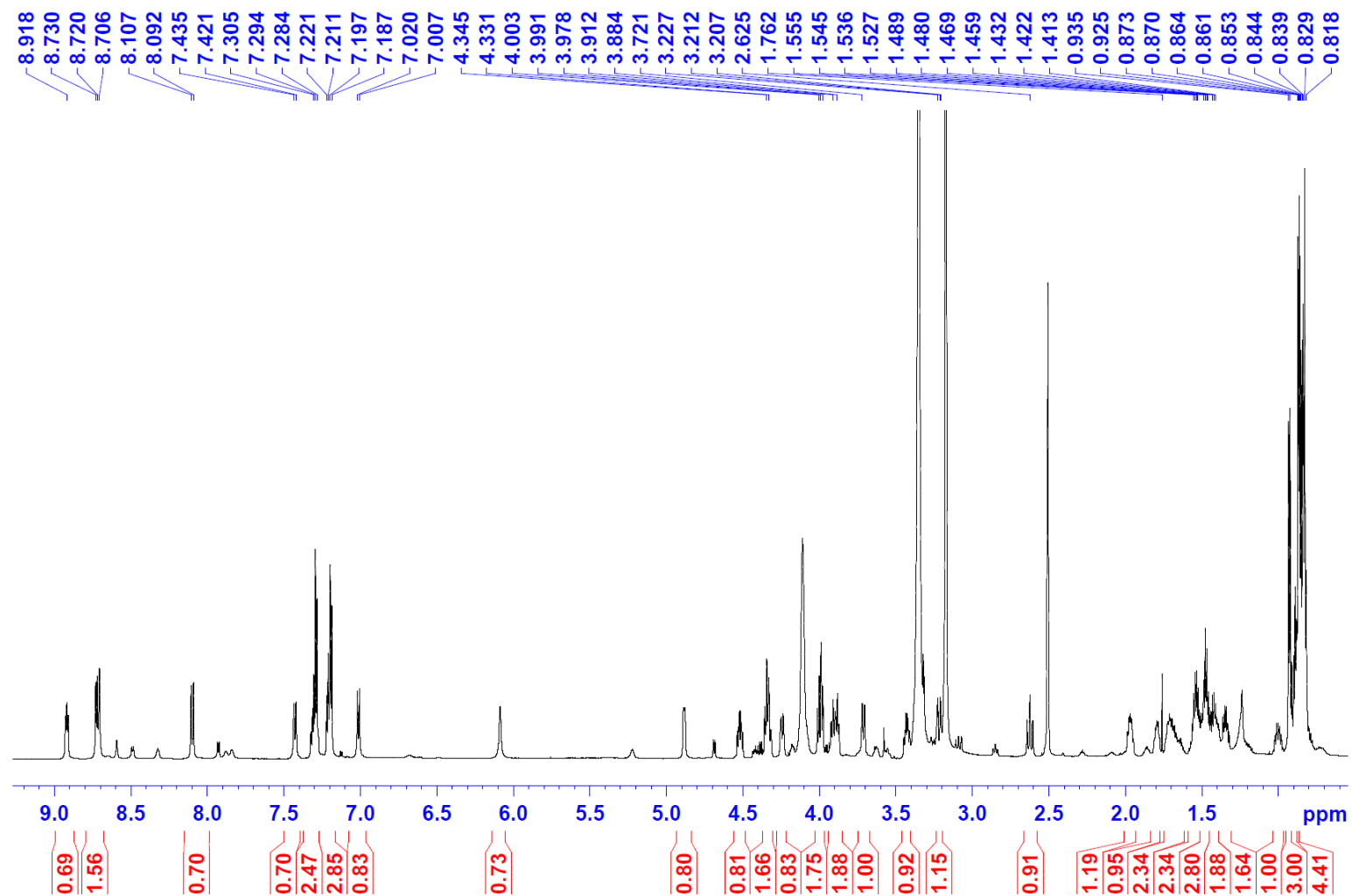


Figure S21. ^1H NMR spectrum of compound **3** ($\text{DMSO}-d_6$, 700 MHz)

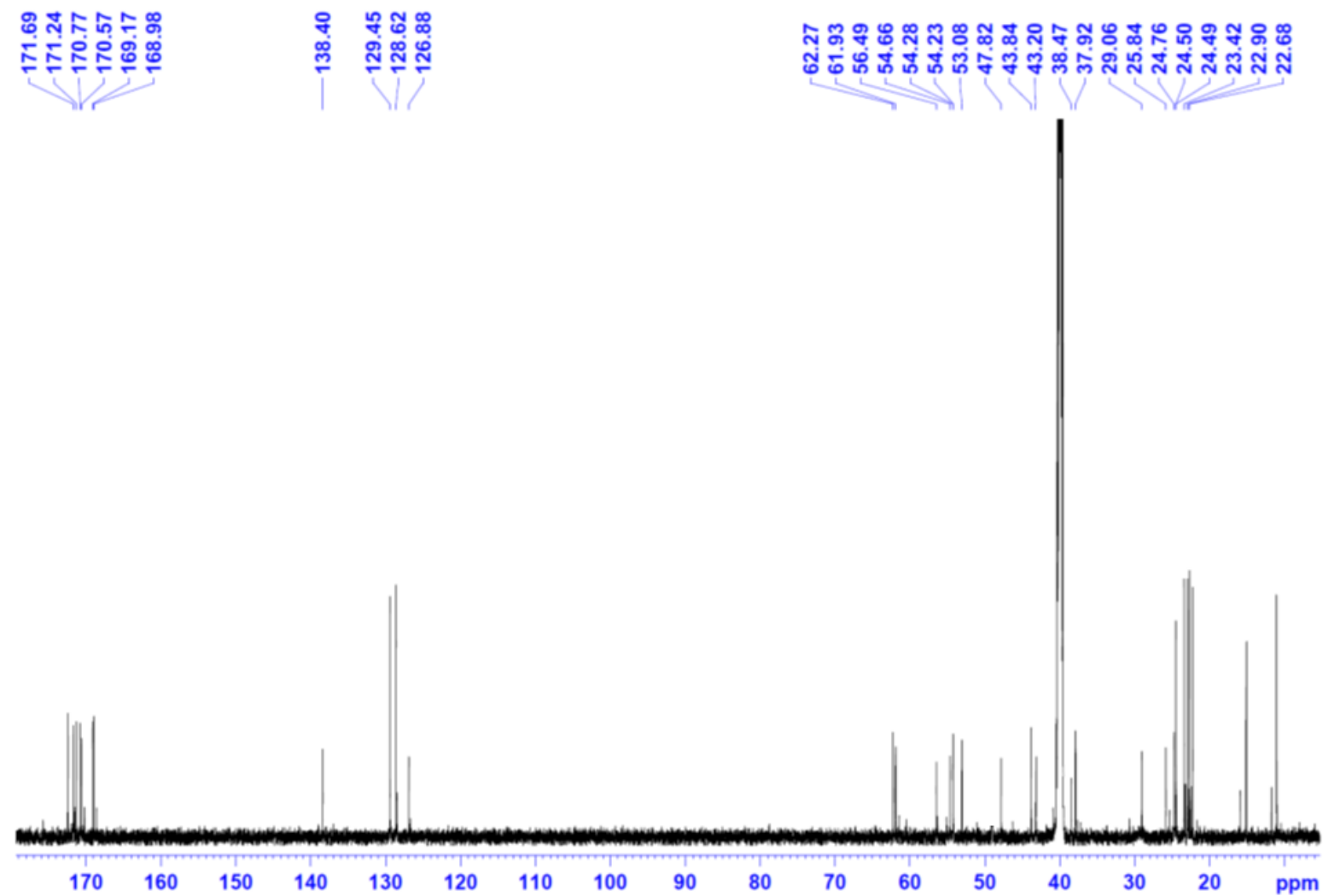


Figure S22. ¹³C NMR spectrum of compound **3** (DMSO-*d*₆, 175 MHz)

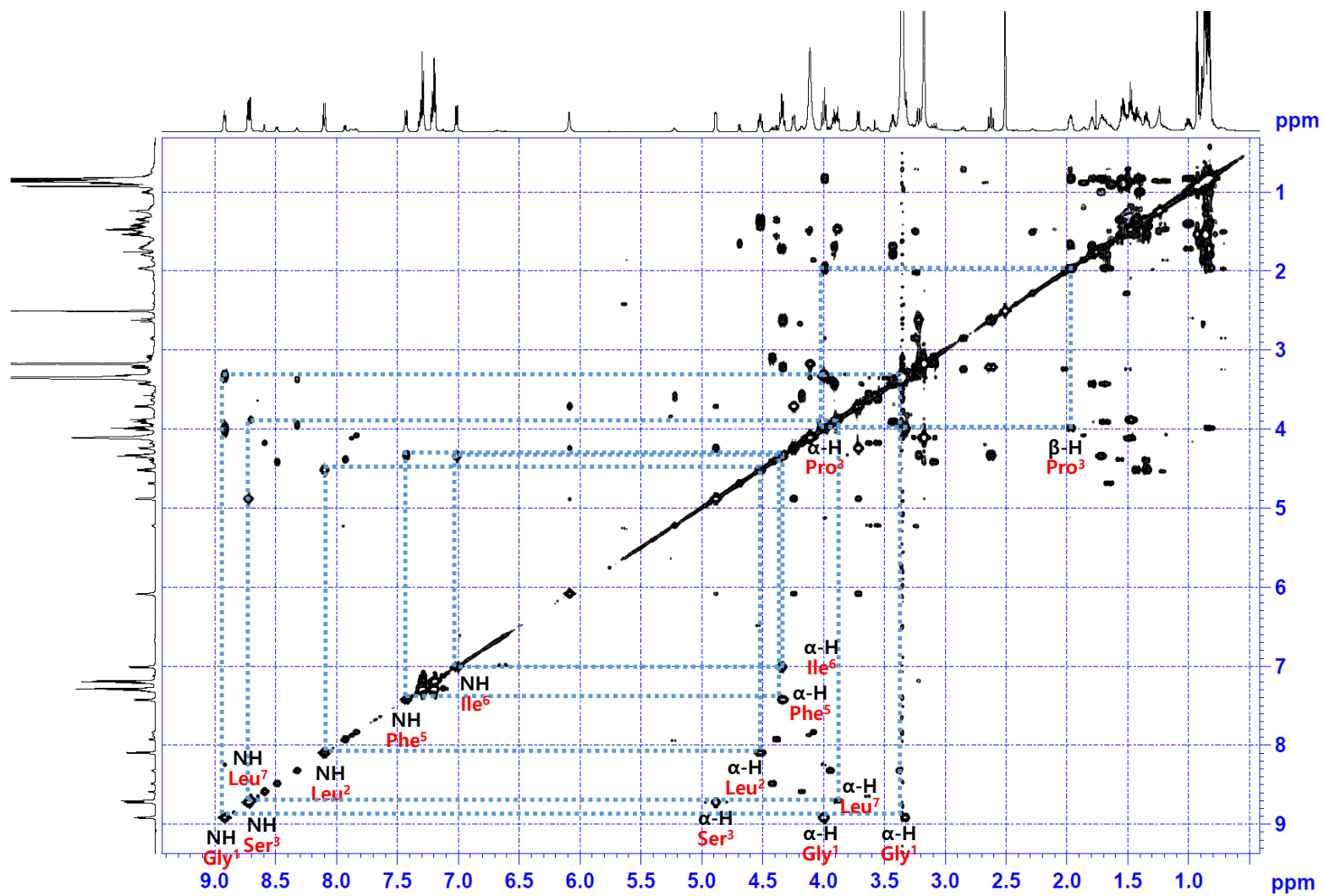


Figure S23. COSY spectrum of compound 3

S26

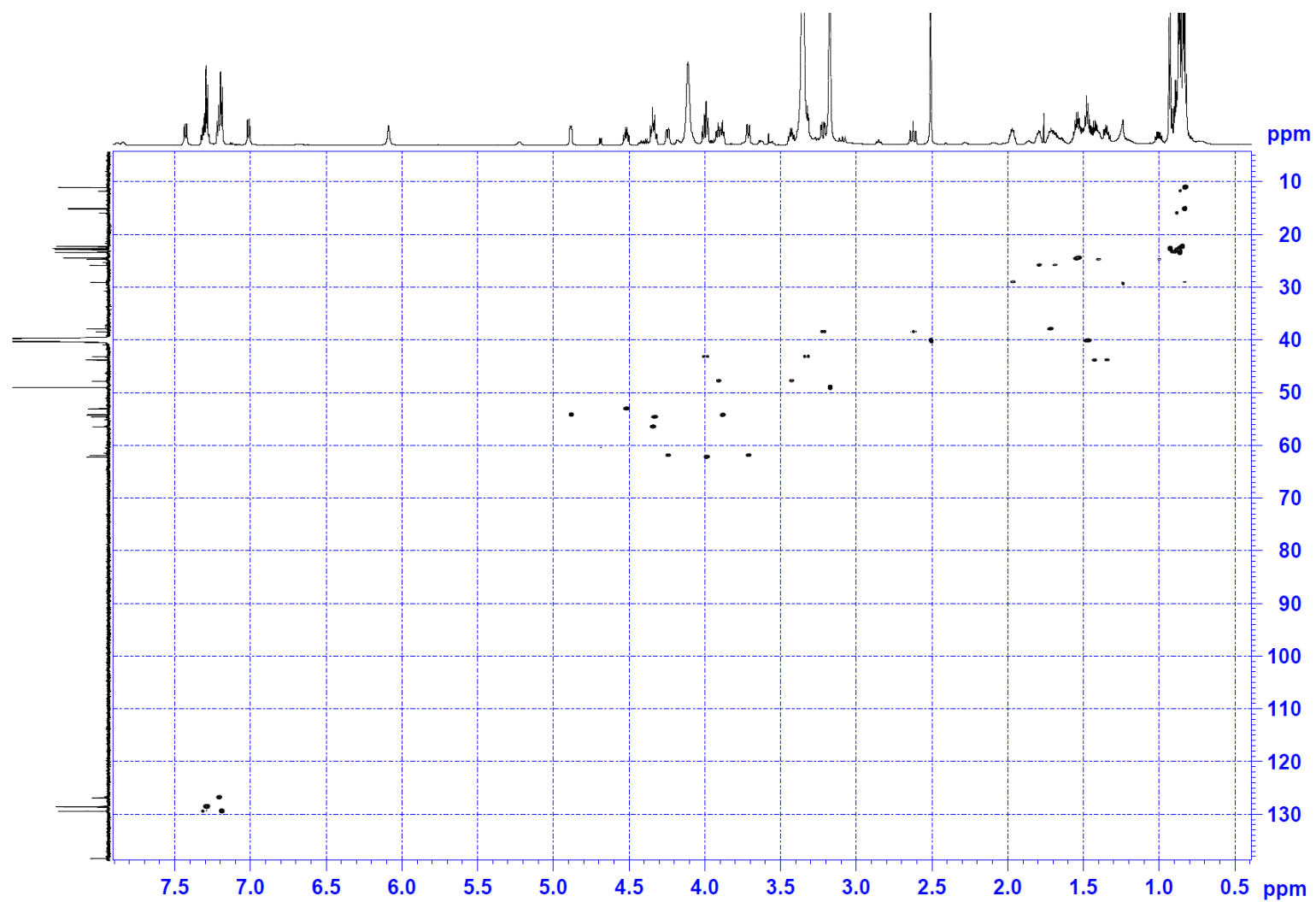


Figure S24. HSQC spectrum of compound **3**

S27

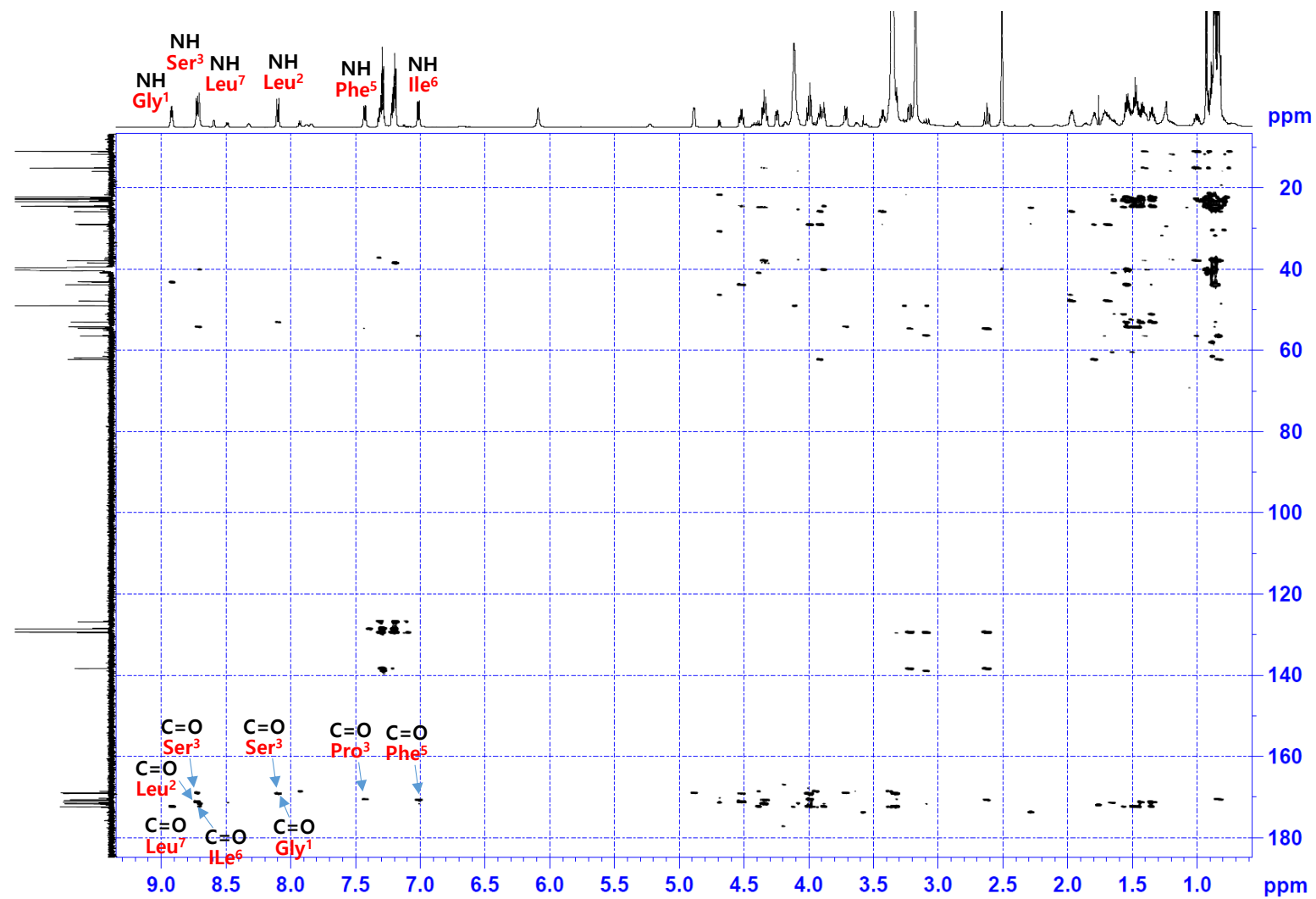


Figure S25. HMBC spectrum of compound 3
S28

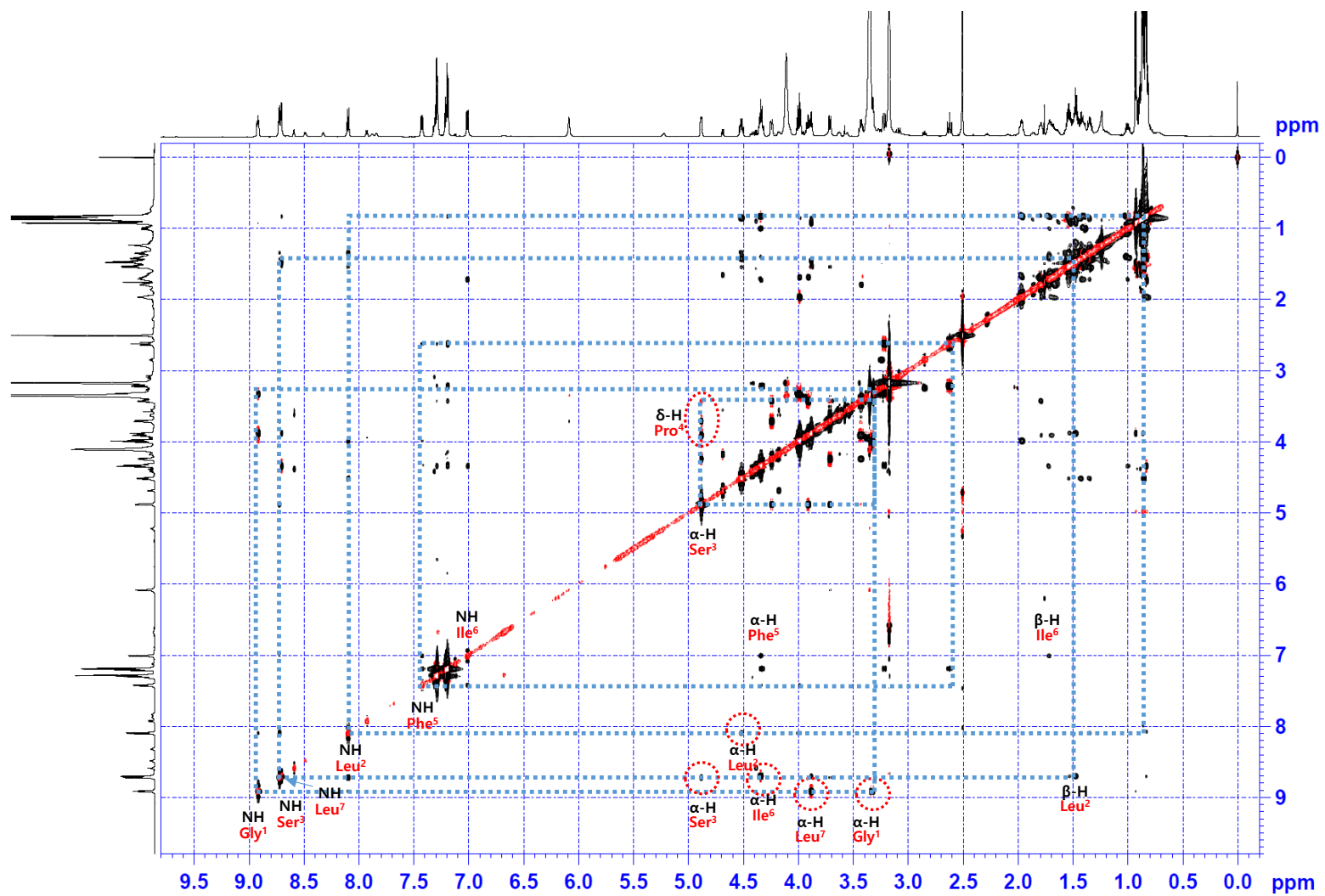


Figure S26. ROESY spectrum of compound 3

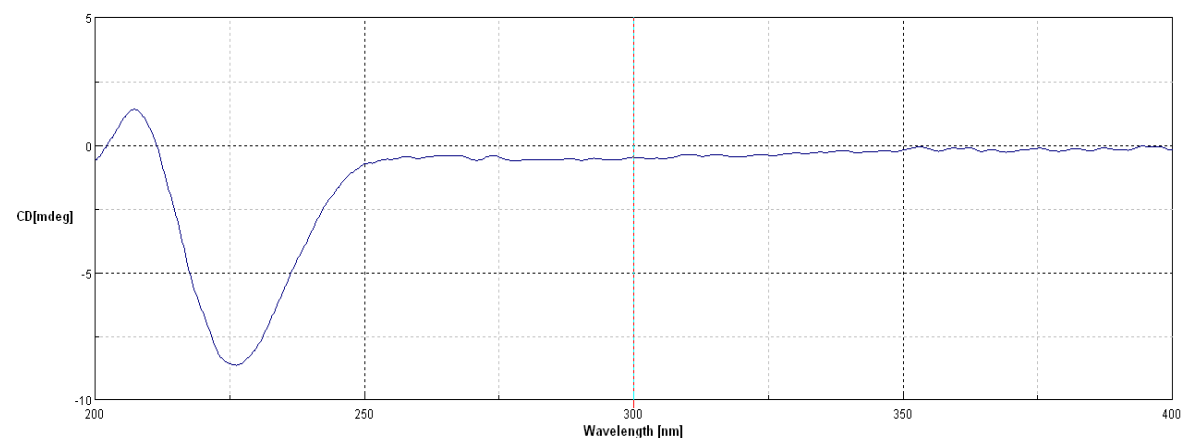


Figure S27. ECD spectrum of compound **3**

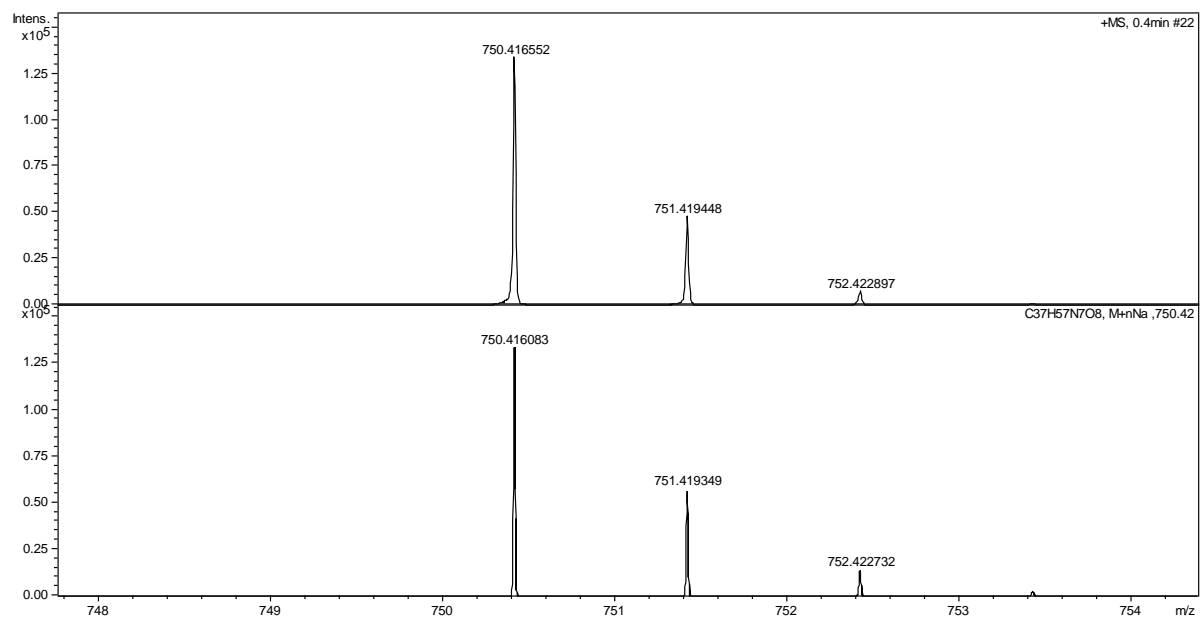


Figure S28. HRESI-MS spectrum of compound **3**

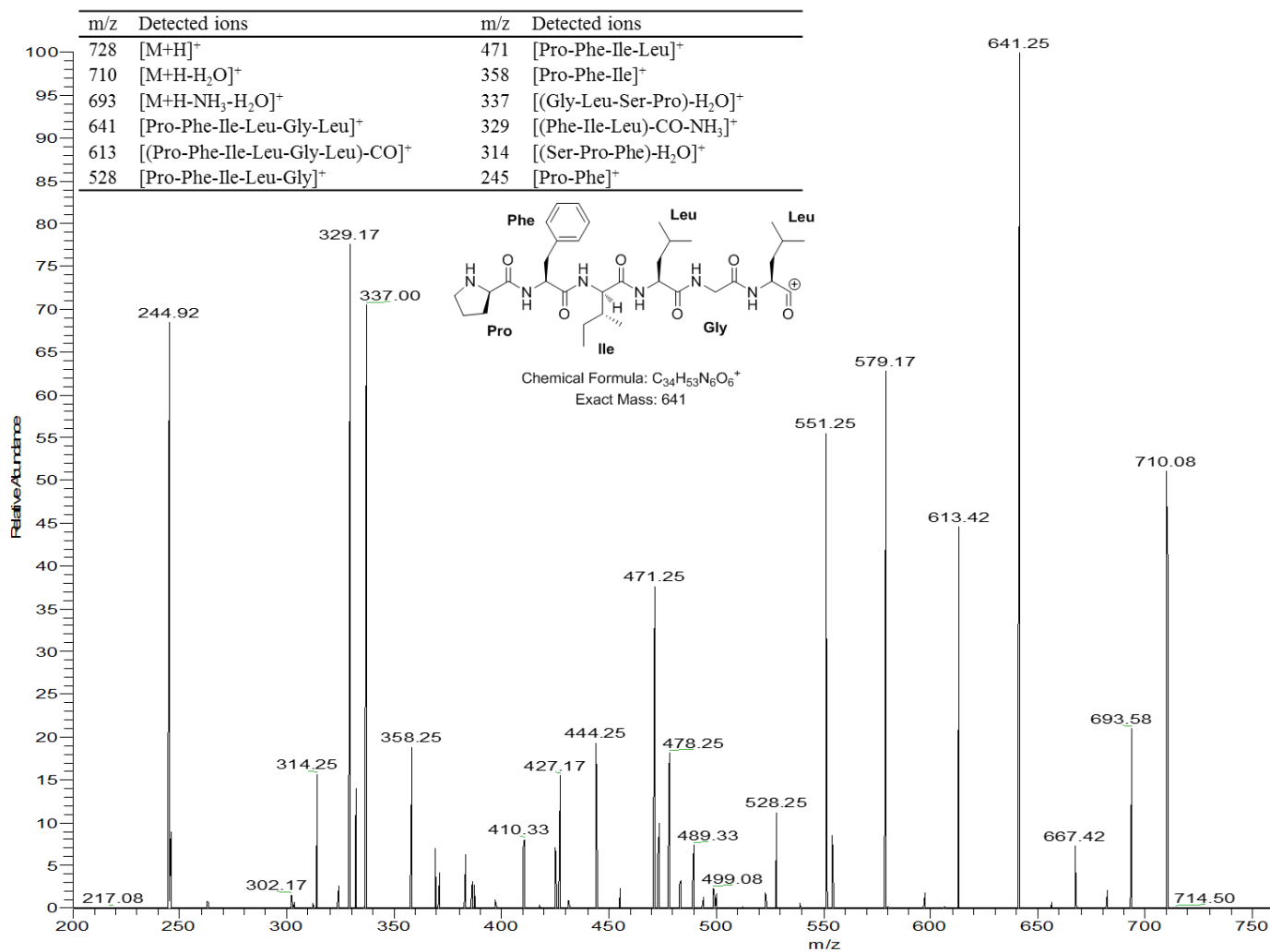


Figure S29. ESI-MS/MS spectrum of compound **3**

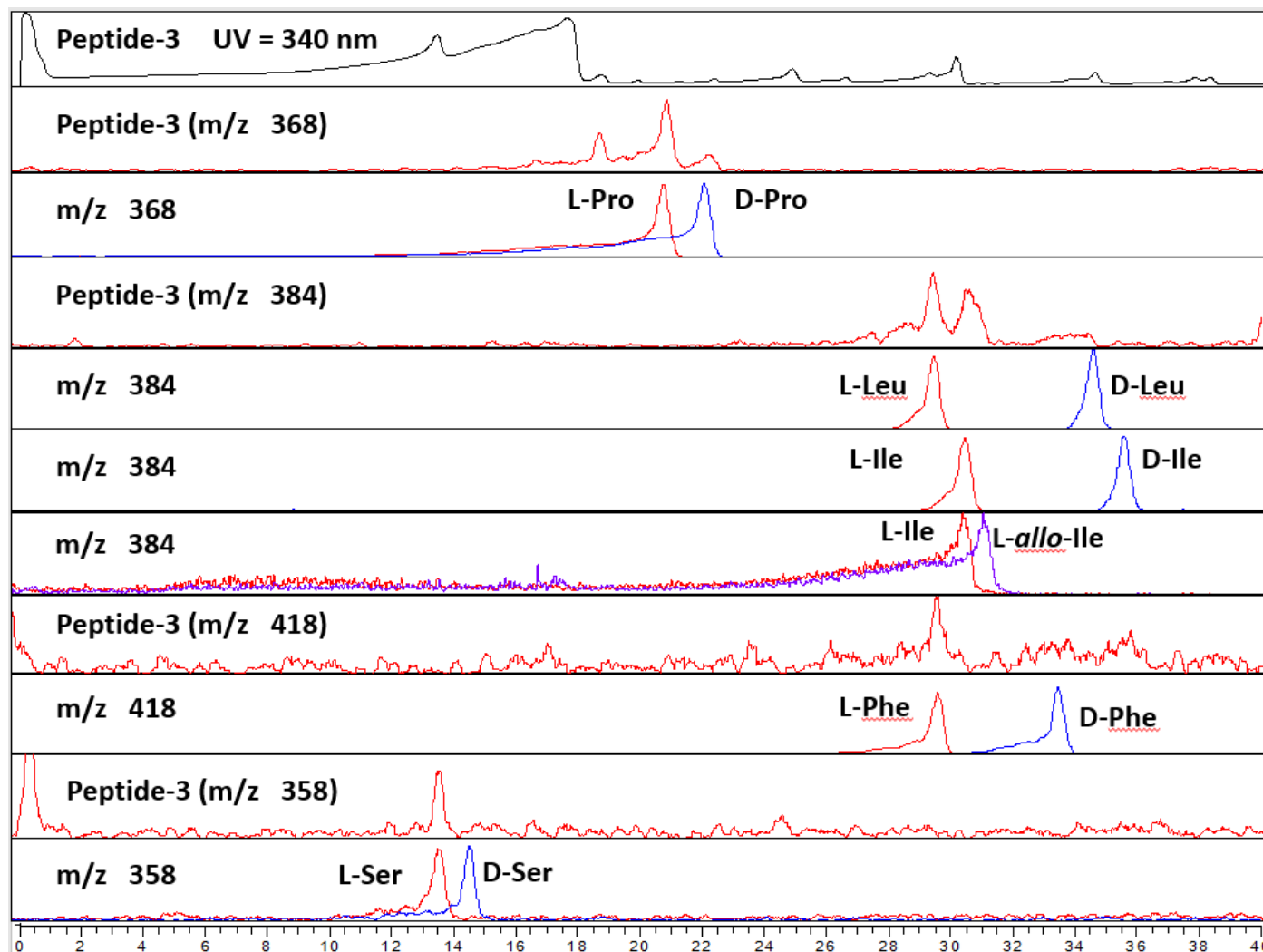


Figure S30. Marfey's analysis of compound 3

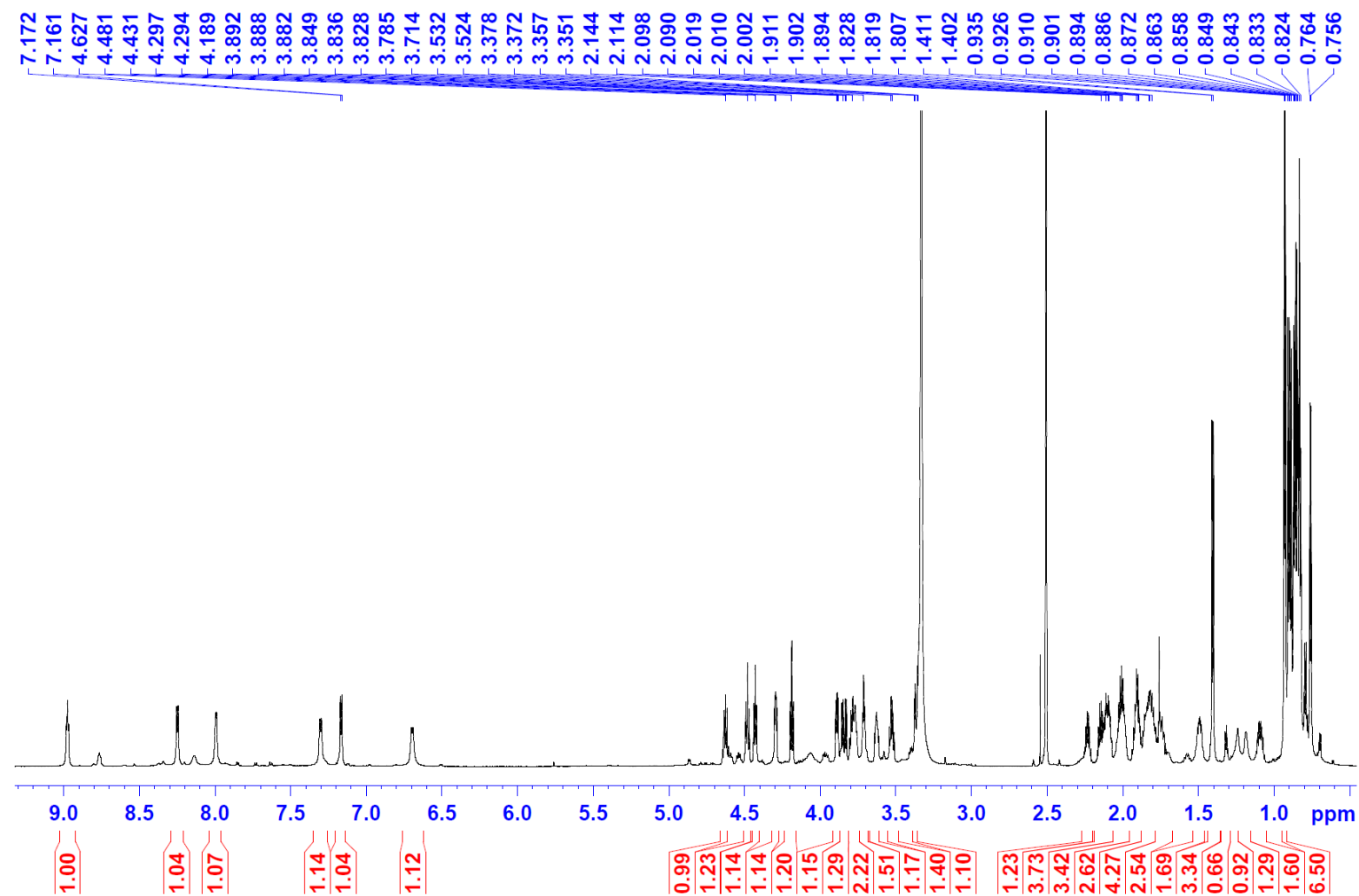


Figure S31. ^1H NMR spectrum of compound **4** ($\text{DMSO-}d_6$, 700 MHz)

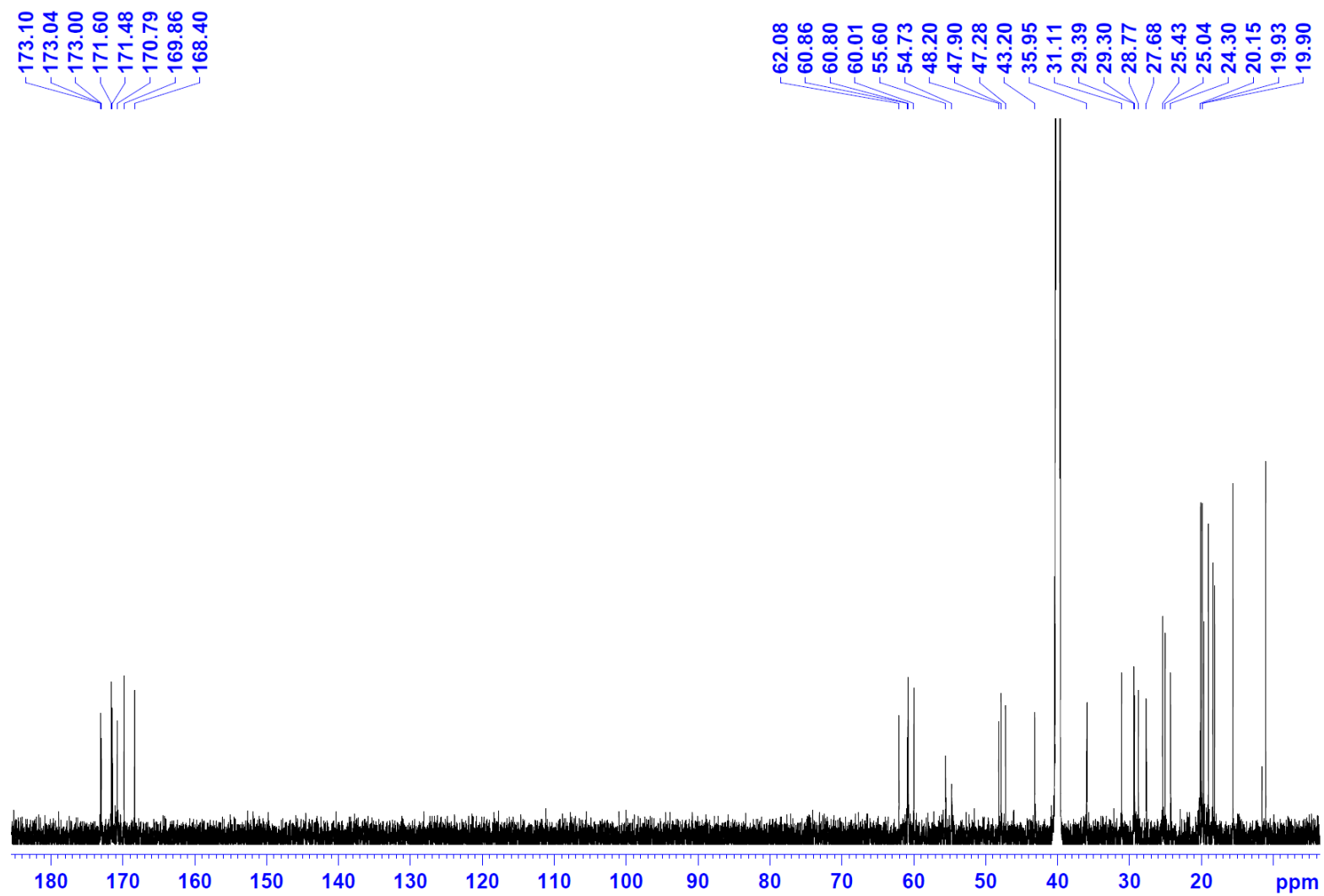


Figure S32. ¹³C NMR spectrum of compound **4** (DMSO-*d*₆, 175 MHz)

COSY of DSC992 in DMSO

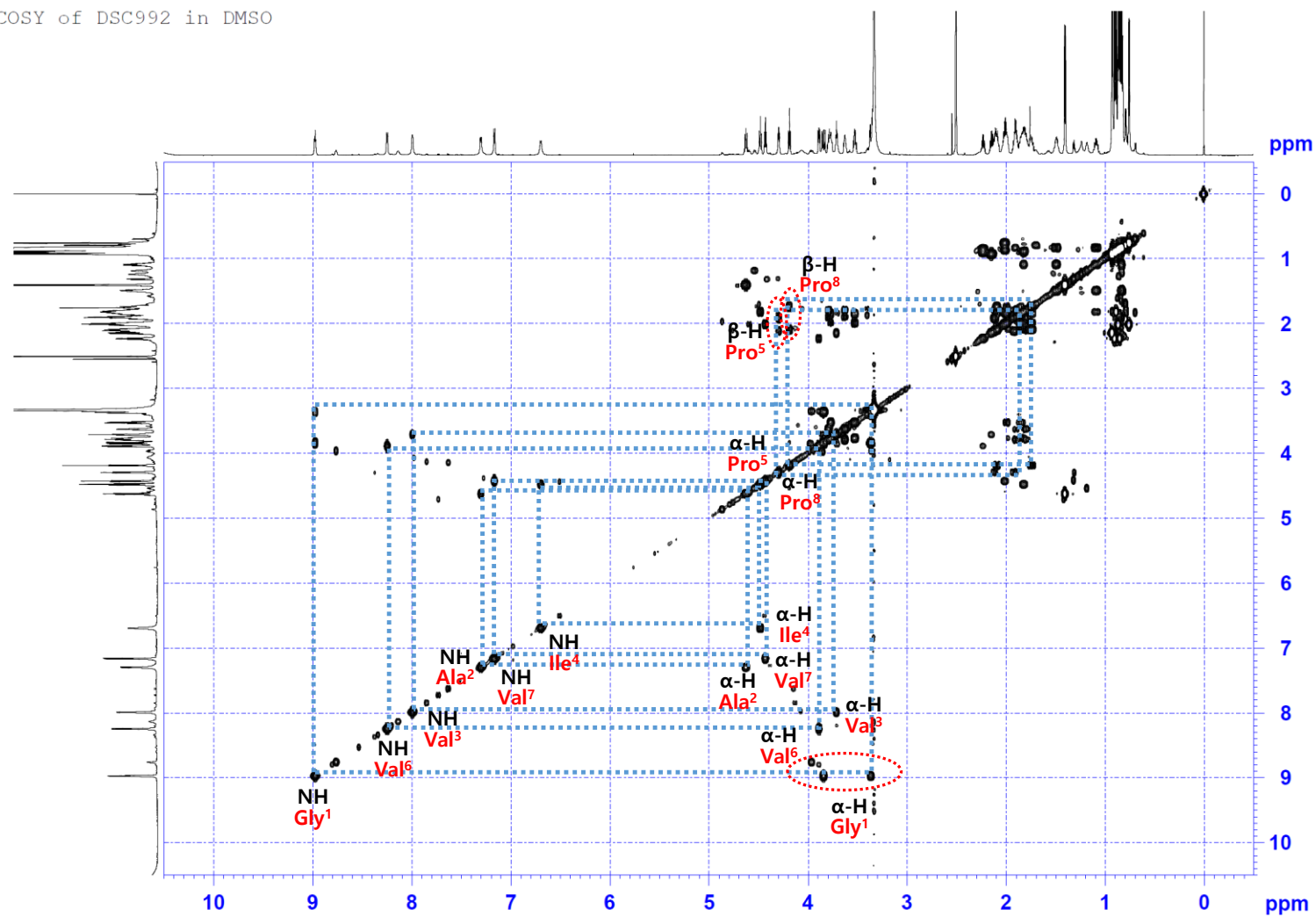


Figure S33. COSY spectrum of compound 4

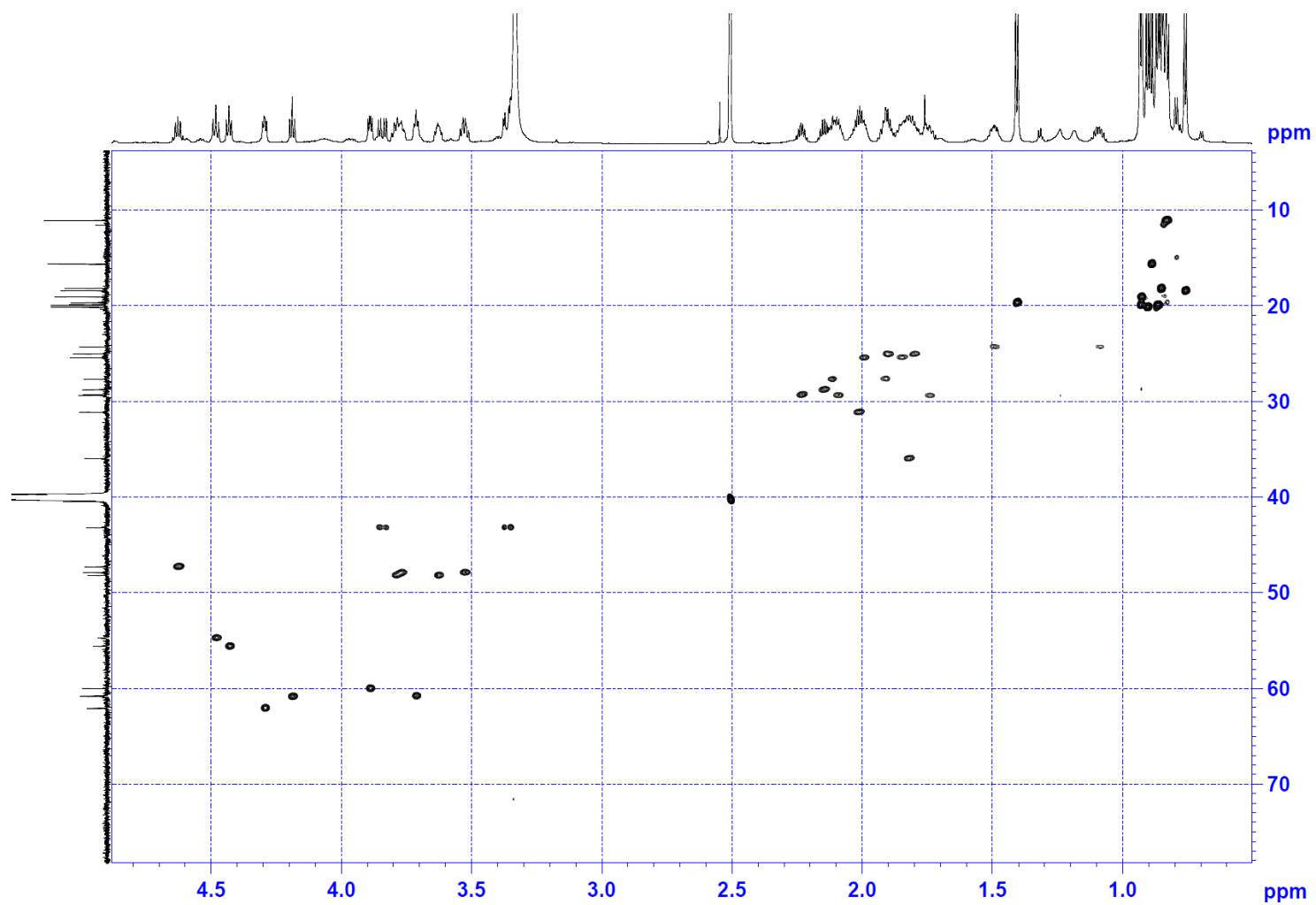


Figure S34. HSQC spectrum of compound **4**

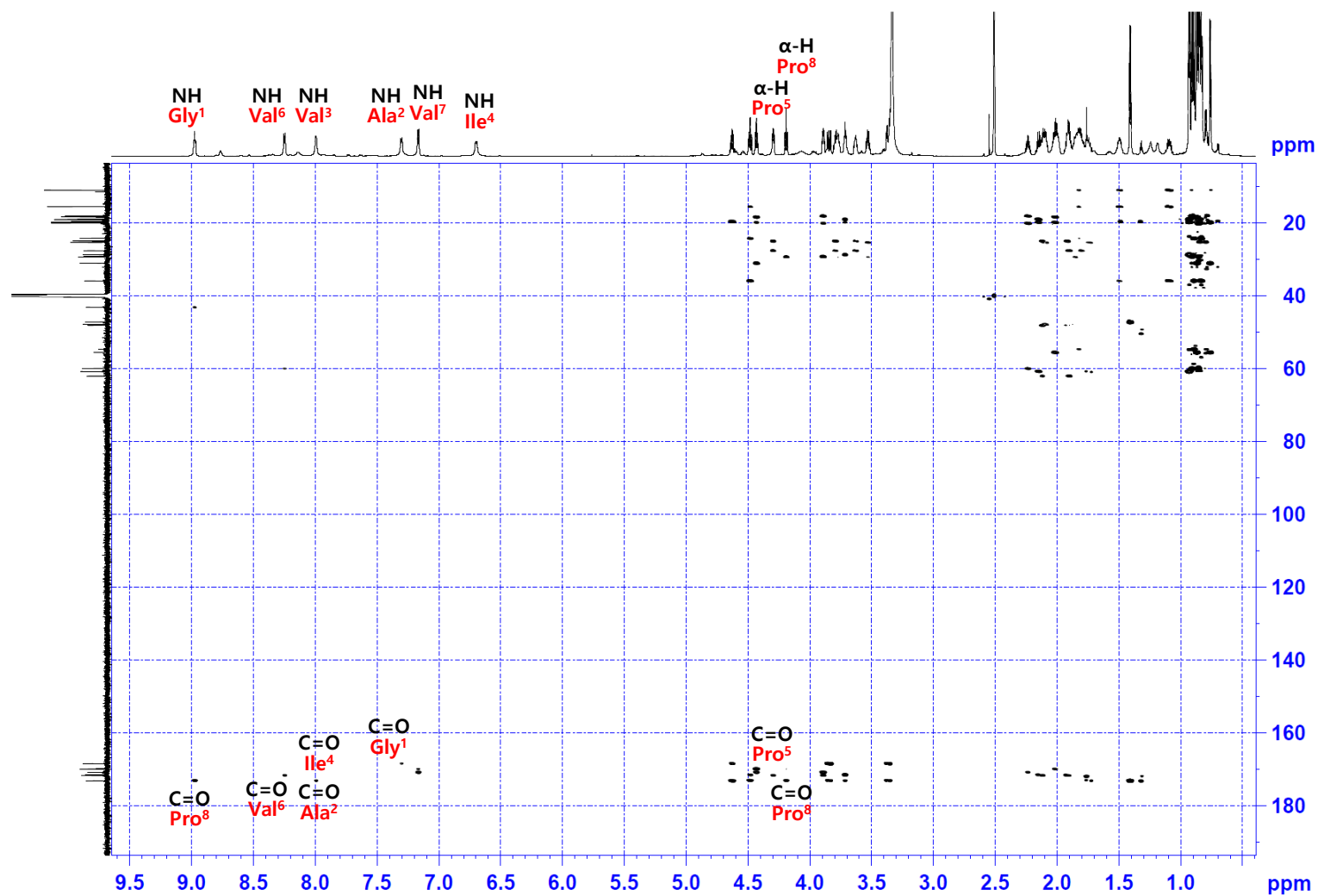


Figure S35. HMBC spectrum of compound 4

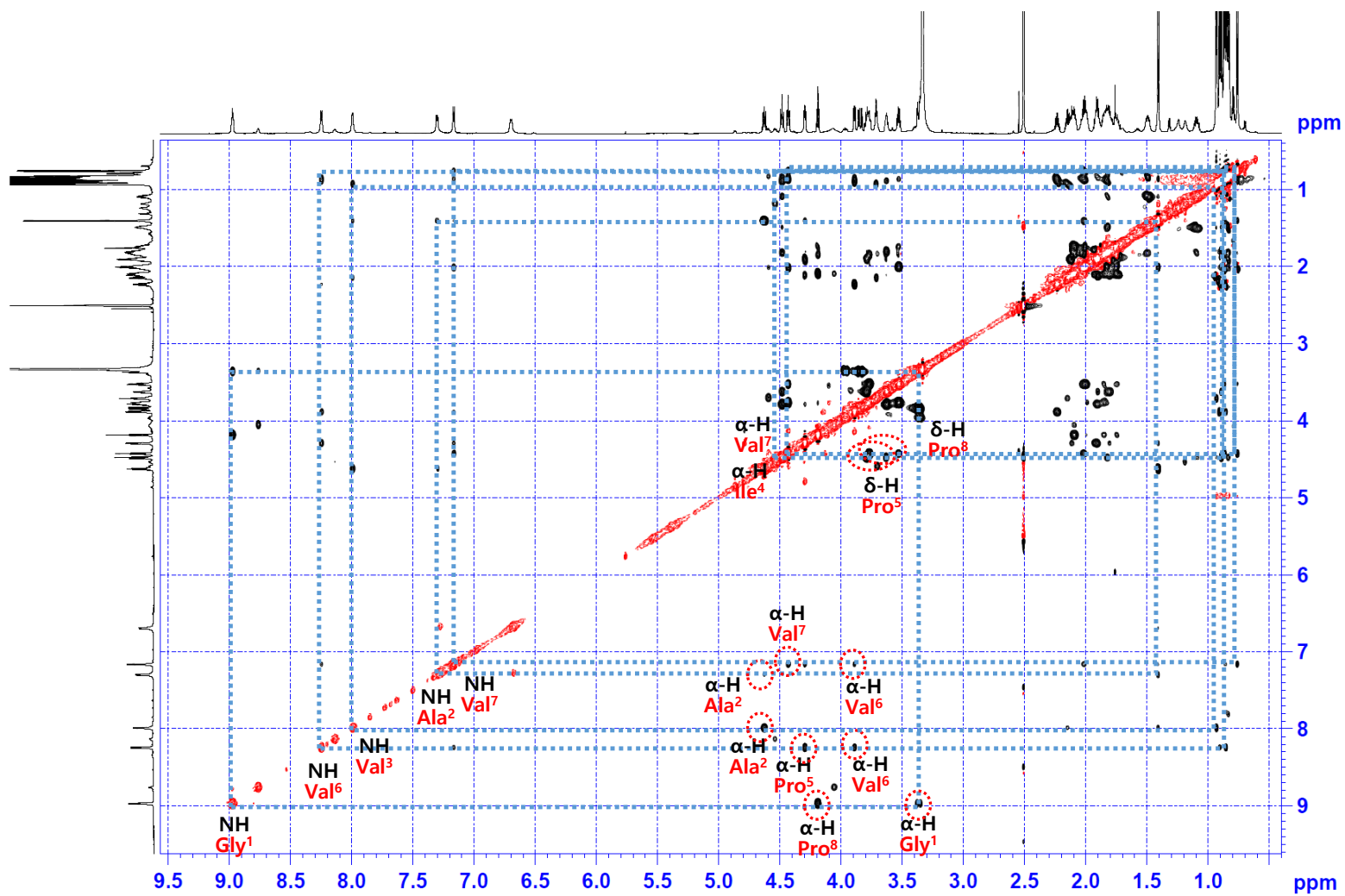


Figure S36. ROESY spectrum of compound 4

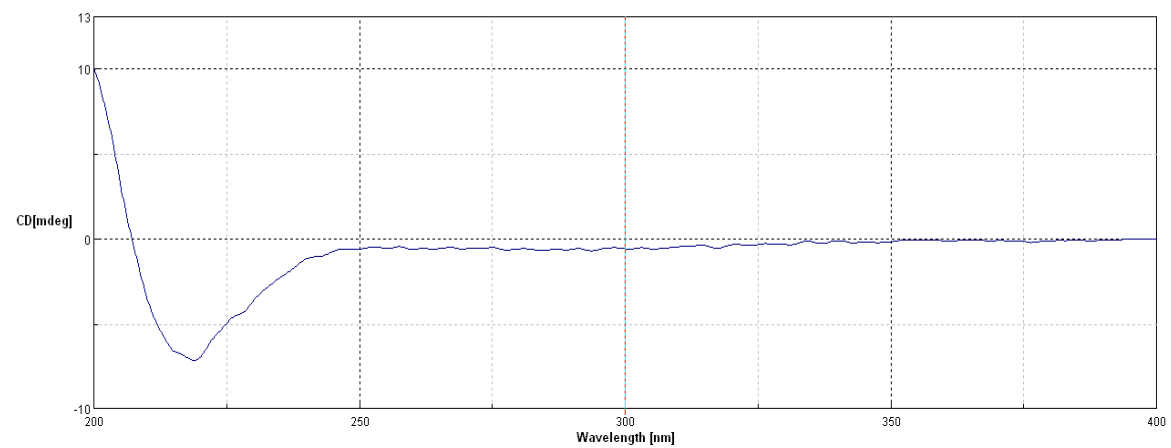


Figure S37. ECD spectrum of compound **4**

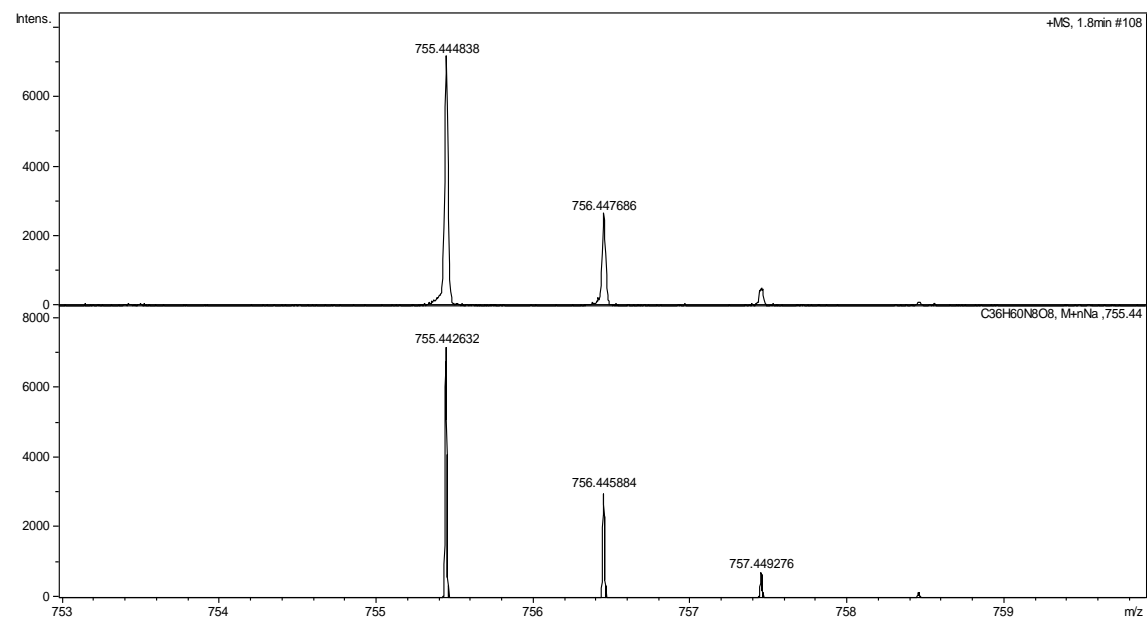
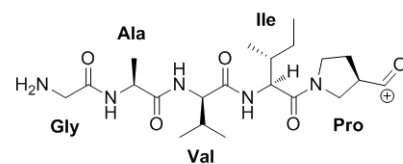
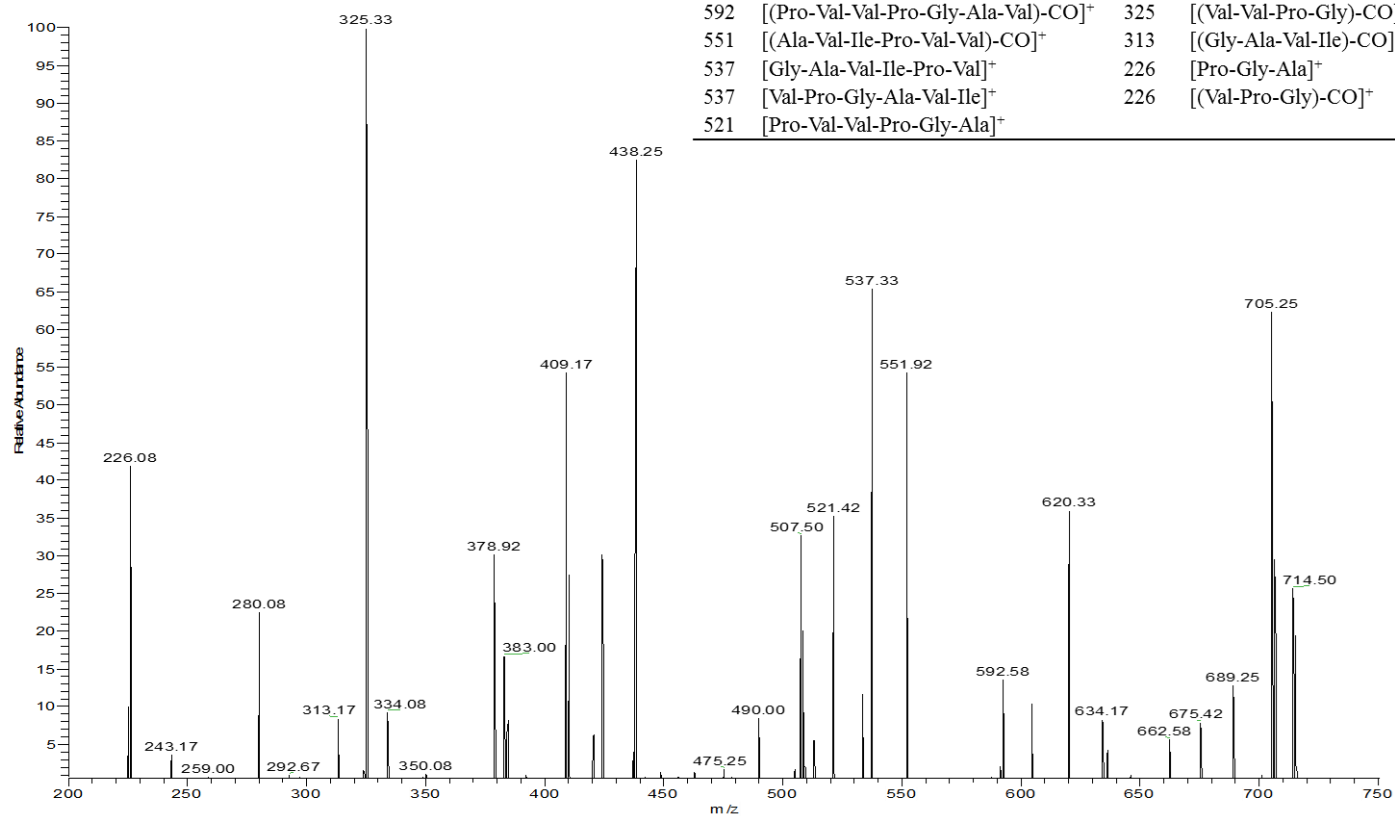


Figure S38. HRESI-MS spectrum of compound **4**



Chemical Formula: $C_{21}H_{36}N_5O_5^+$
Exact Mass: 438



m/z	Detected ions	m/z	Detected ions
733	$[M+H]^+$	508	$[\text{Val-Ile-Pro-Val-Val}]^+$
705	$[M+H-CO]^+$	438	$[\text{Gly-Ala-Val-Ile-Pro}]^+$
662	$[\text{Val-Ile-Pro-Val-Val-Pro-Gly}]^+$	438	$[\text{Pro-Gly-Ala-Val-Ile}]^+$
634	$[\text{Ile-Pro-Val-Val-Pro-Gly-Ala}]^+$	409	$[\text{Val-Ile-Pro-Val}]^+$
634	$[\text{Val-Pro-Gly-Ala-Val-Ile-Pro}]^+$	409	$[\text{Ile-Pro-Val-Val}]^+$
634	$[\text{Pro-Gly-Ala-Val-Ile-Pro-Val}]^+$	325	$[\text{Val-Pro-Gly-Ala}]^+$
620	$[\text{Pro-Val-Val-Pro-Gly-Ala-Val}]^+$	325	$[\text{Pro-Gly-Ala-Val}]^+$
592	$[(\text{Pro-Val-Val-Pro-Gly-Ala-Val})-CO]^+$	325	$[(\text{Val-Val-Pro-Gly})-CO]^+$
551	$[(\text{Ala-Val-Ile-Pro-Val-Val})-CO]^+$	313	$[(\text{Gly-Ala-Val-Ile})-CO]^+$
537	$[\text{Gly-Ala-Val-Ile-Pro-Val}]^+$	226	$[\text{Pro-Gly-Ala}]^+$
537	$[\text{Val-Pro-Gly-Ala-Val-Ile}]^+$	226	$[(\text{Val-Pro-Gly})-CO]^+$
521	$[\text{Pro-Val-Val-Pro-Gly-Ala}]^+$		

Figure S39. ESI-MS/MS spectrum of compound 4
S42

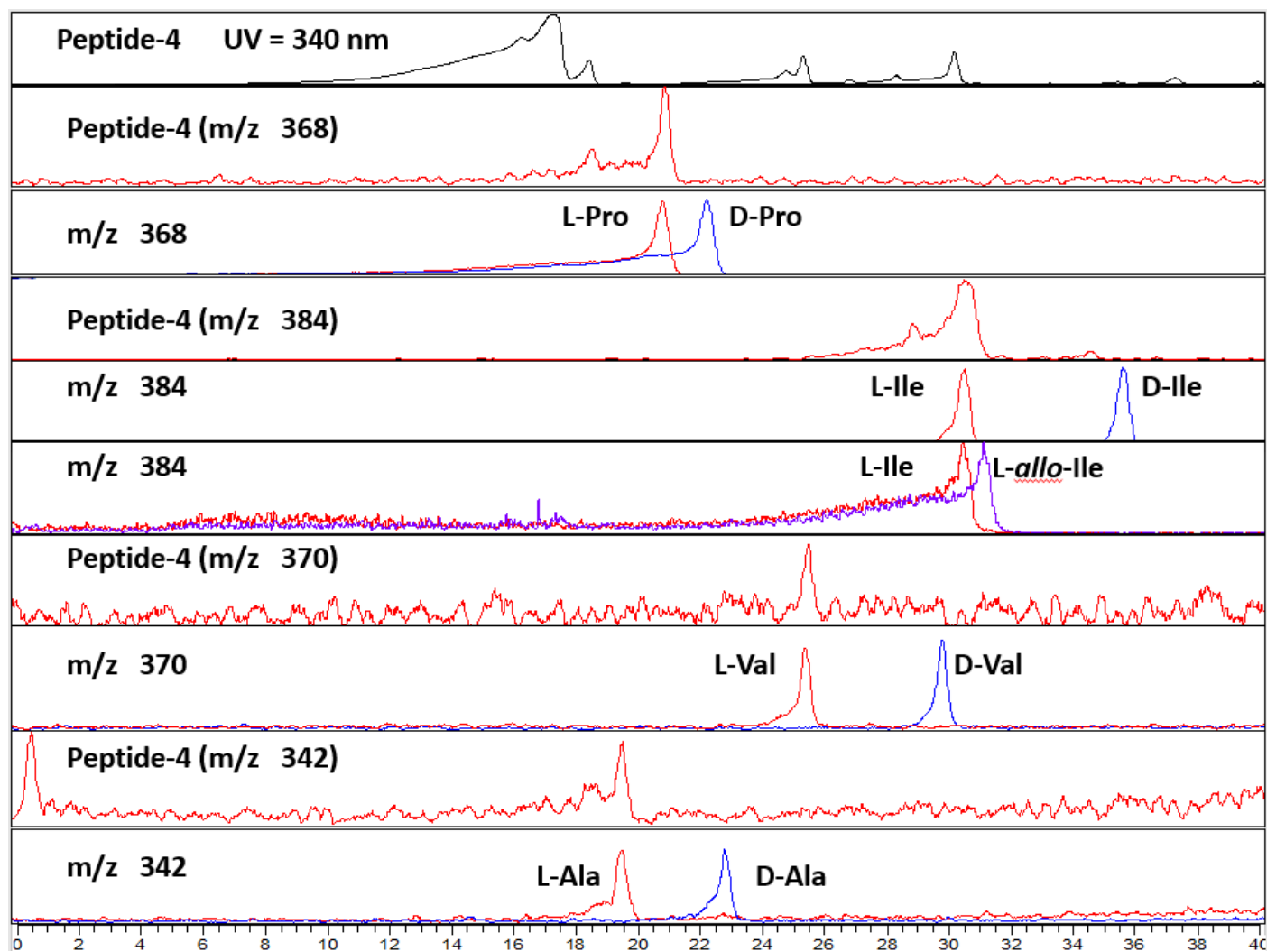


Figure S40. Marfey's analysis of compound 4

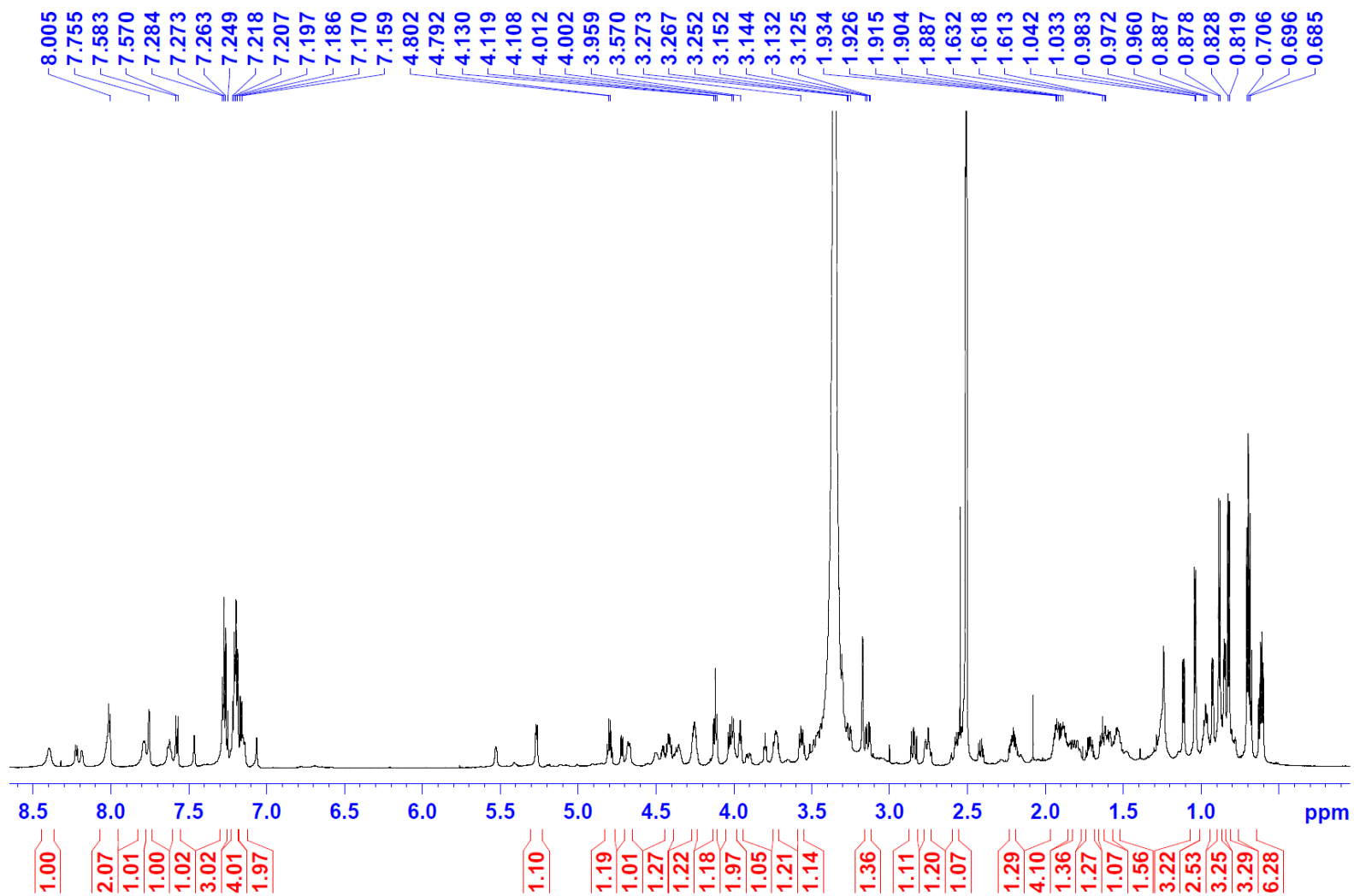


Figure S41. ^1H NMR spectrum of compound **5** ($\text{DMSO}-d_6$, 700 MHz)

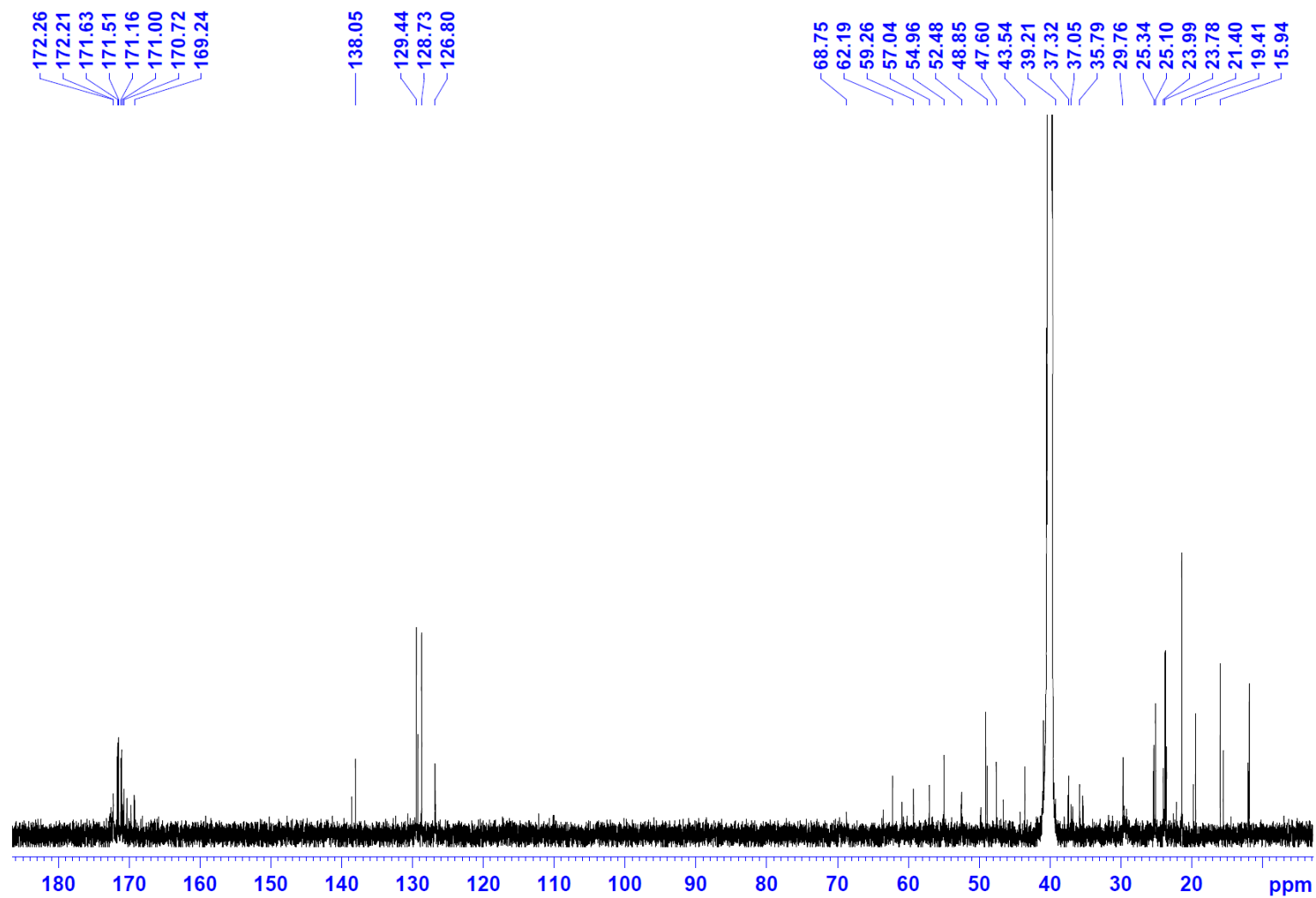


Figure S42. ^{13}C NMR spectrum of compound **5** ($\text{DMSO-}d_6$, 175 MHz)

S45

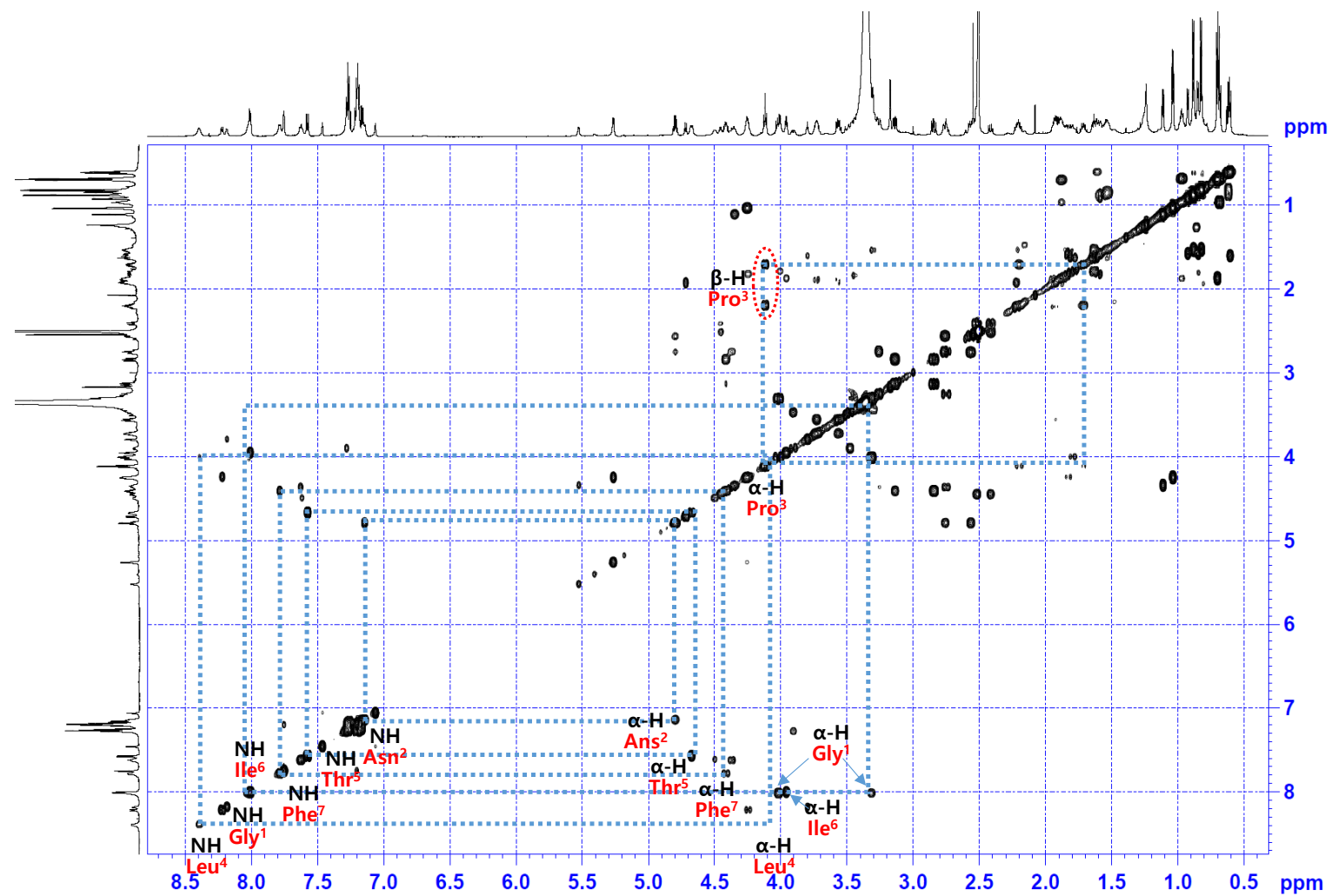


Figure S43. COSY spectrum of compound 5

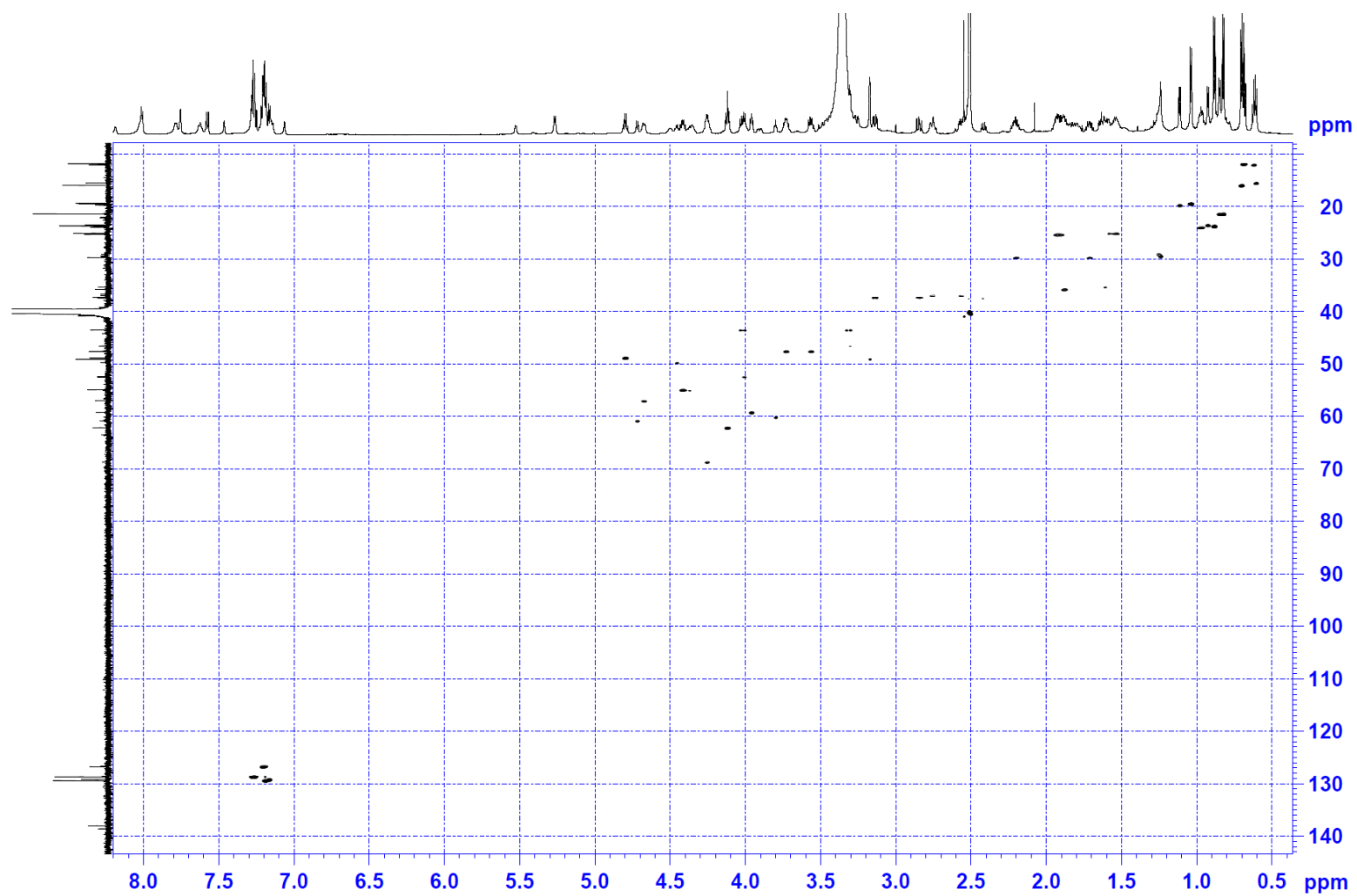


Figure S44. HSQC spectrum of compound **5**

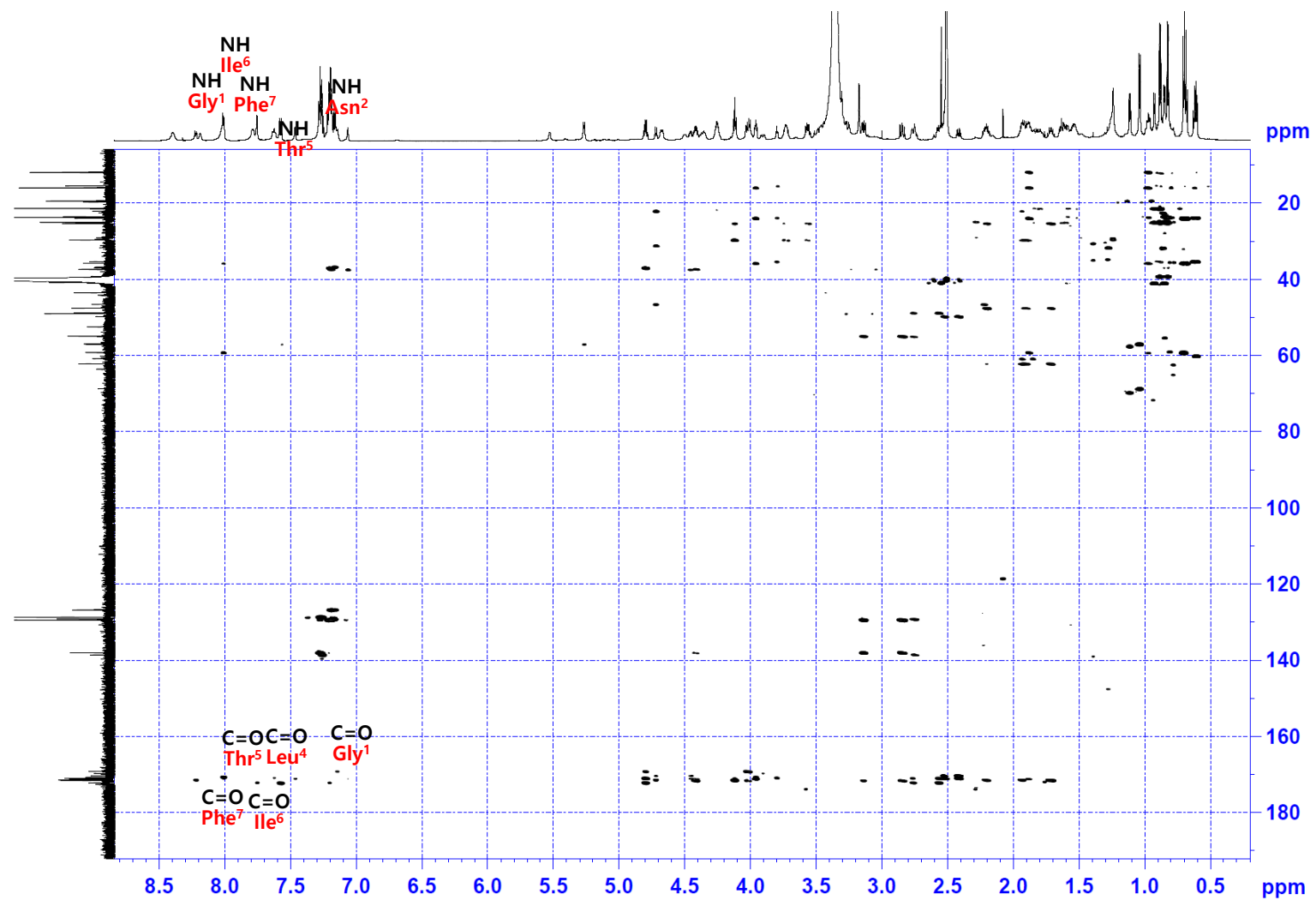


Figure S45. HMBC spectrum of compound 5

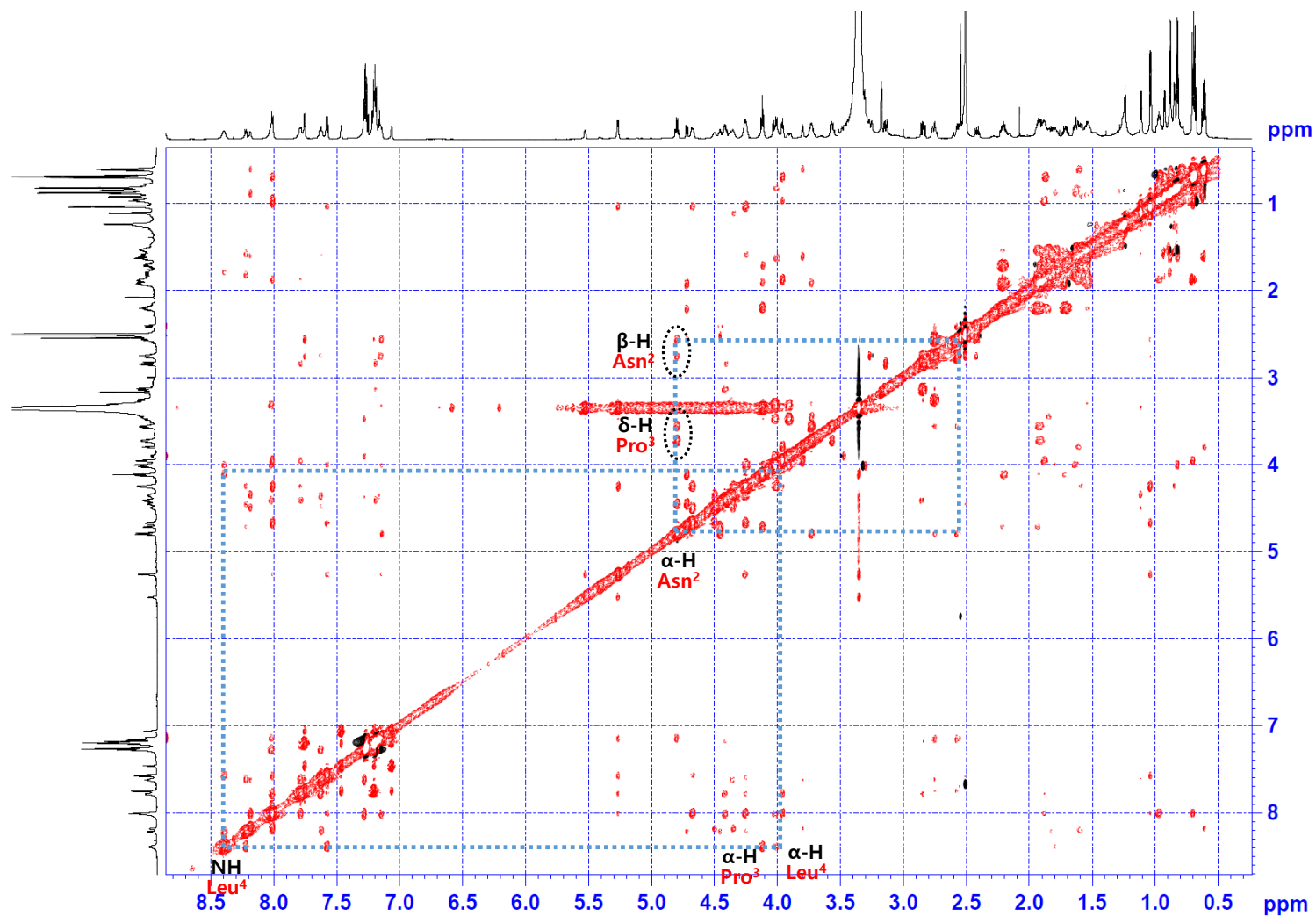


Figure S46. ROESY spectrum of compound **5**

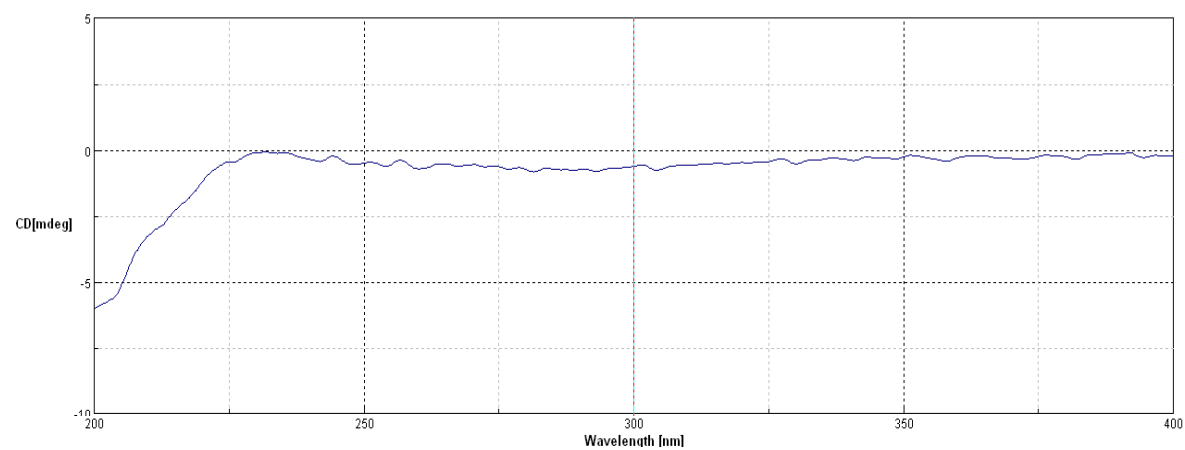


Figure S47. ECD spectrum of compound **5**

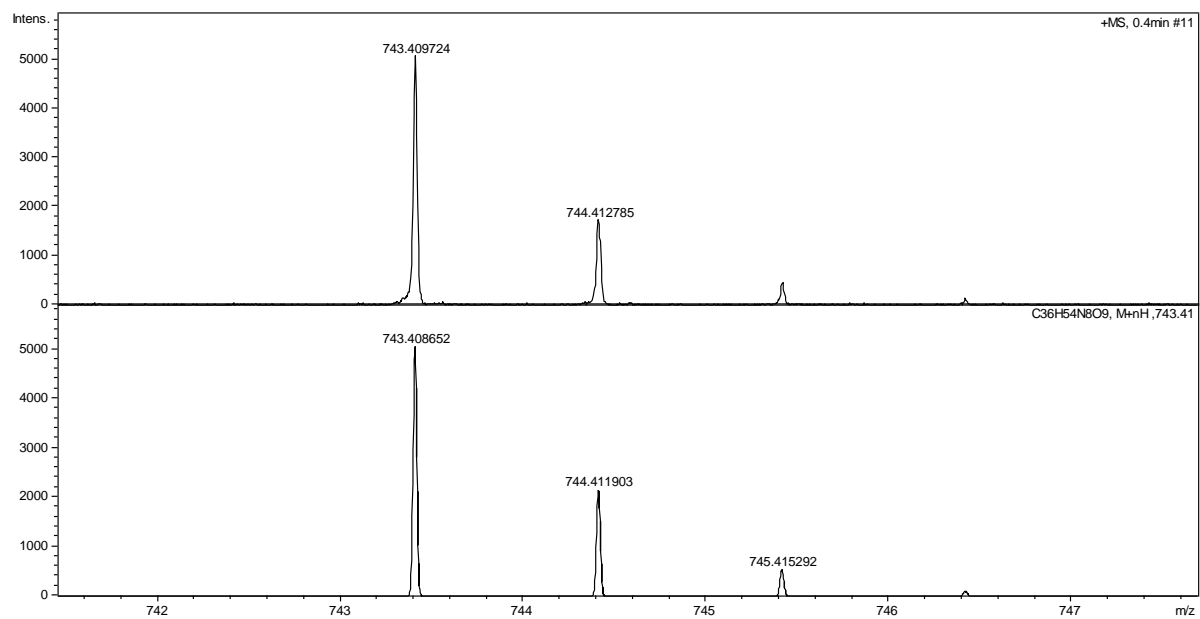


Figure S48. HRESI-MS spectrum of compound **5**

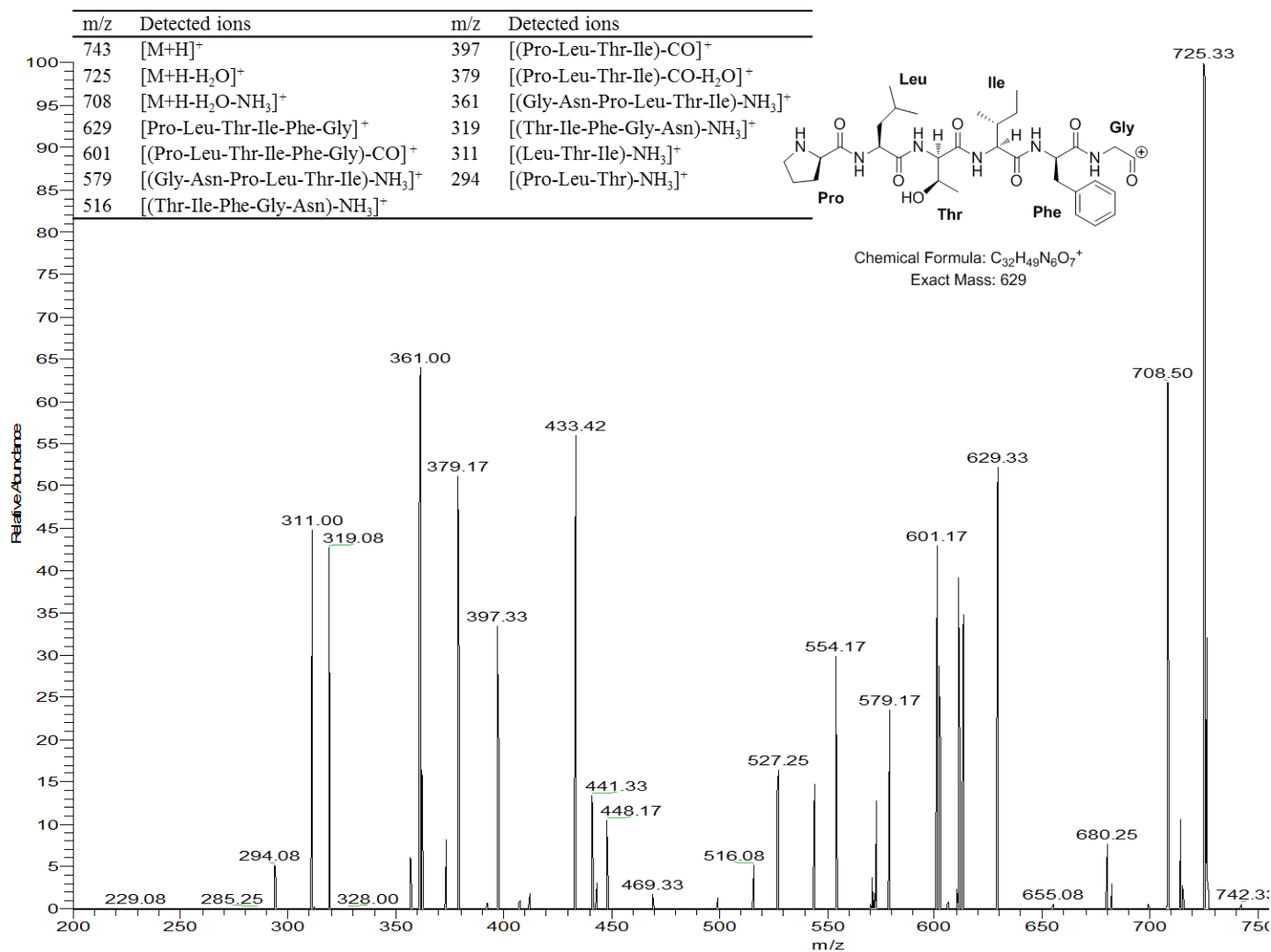


Figure S49. ESI-MS/MS spectrum of compound 5

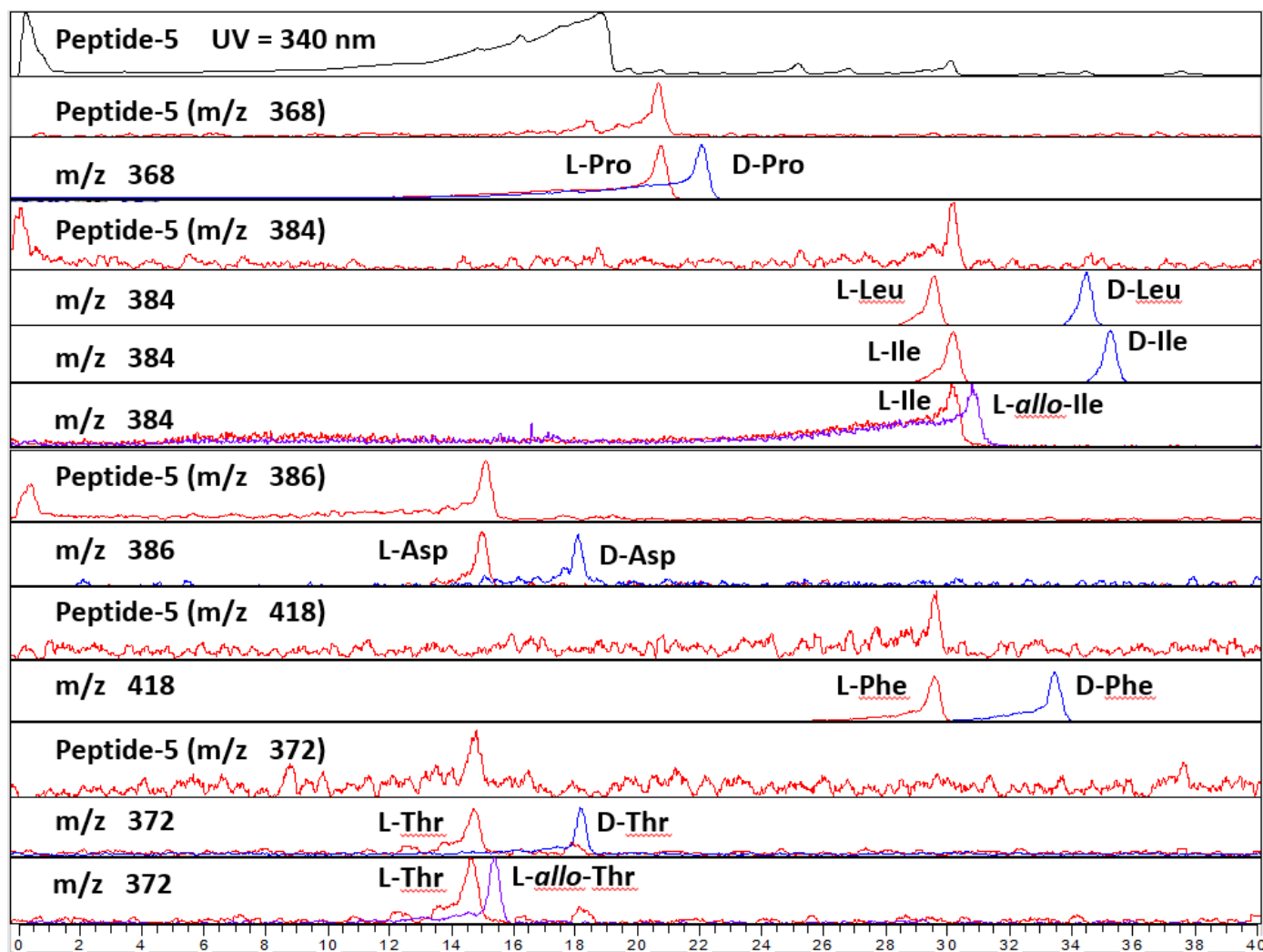


Figure S50. Marfey's analysis of compound 5