Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Cytotoxic Alkaloids from Marine Shellfish-Associated Fungus *Aspergillus* sp. XBB-4 Induced by Amino Acid-directed Strategy

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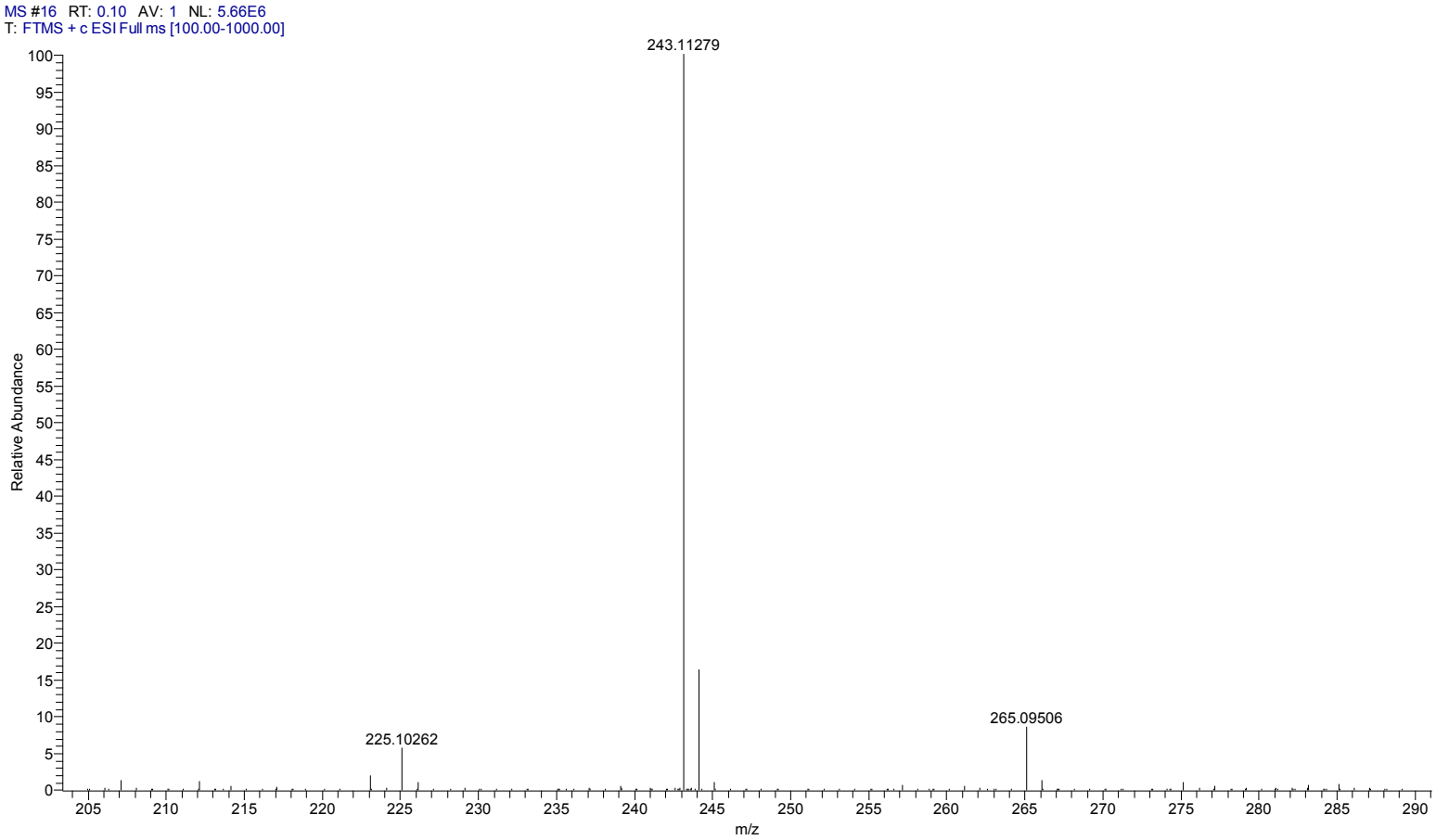


SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
243.11279	243.11280	-0.06	8.5	C14 H15 N2 O2

Figure S1. HR-ESI-MS spectrum of aspercarboline A (**1**).

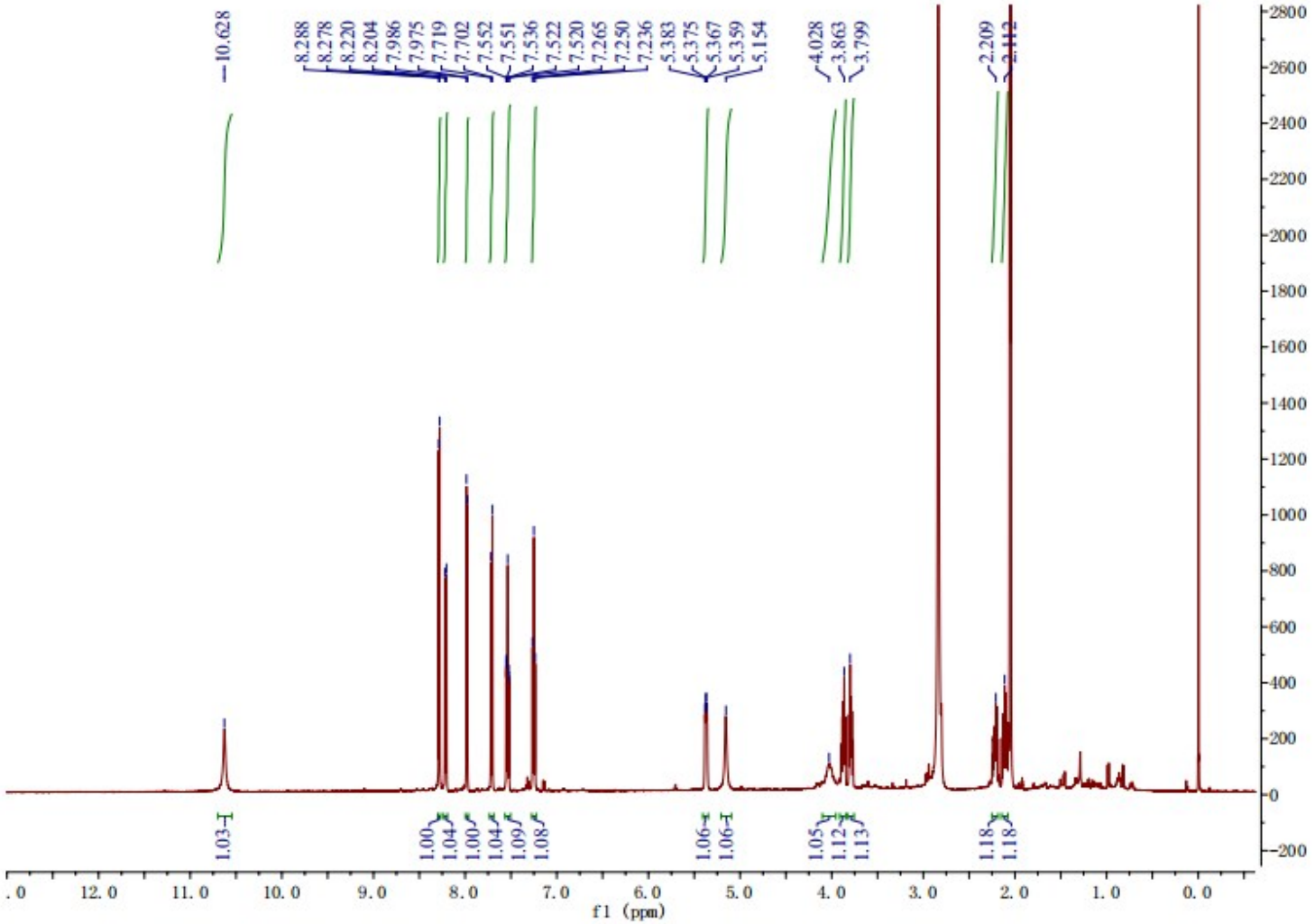


Figure S2. ^{1}H NMR spectrum (500 MHz, acetone-d_6) spectrum of aspercarboline A (**1**)

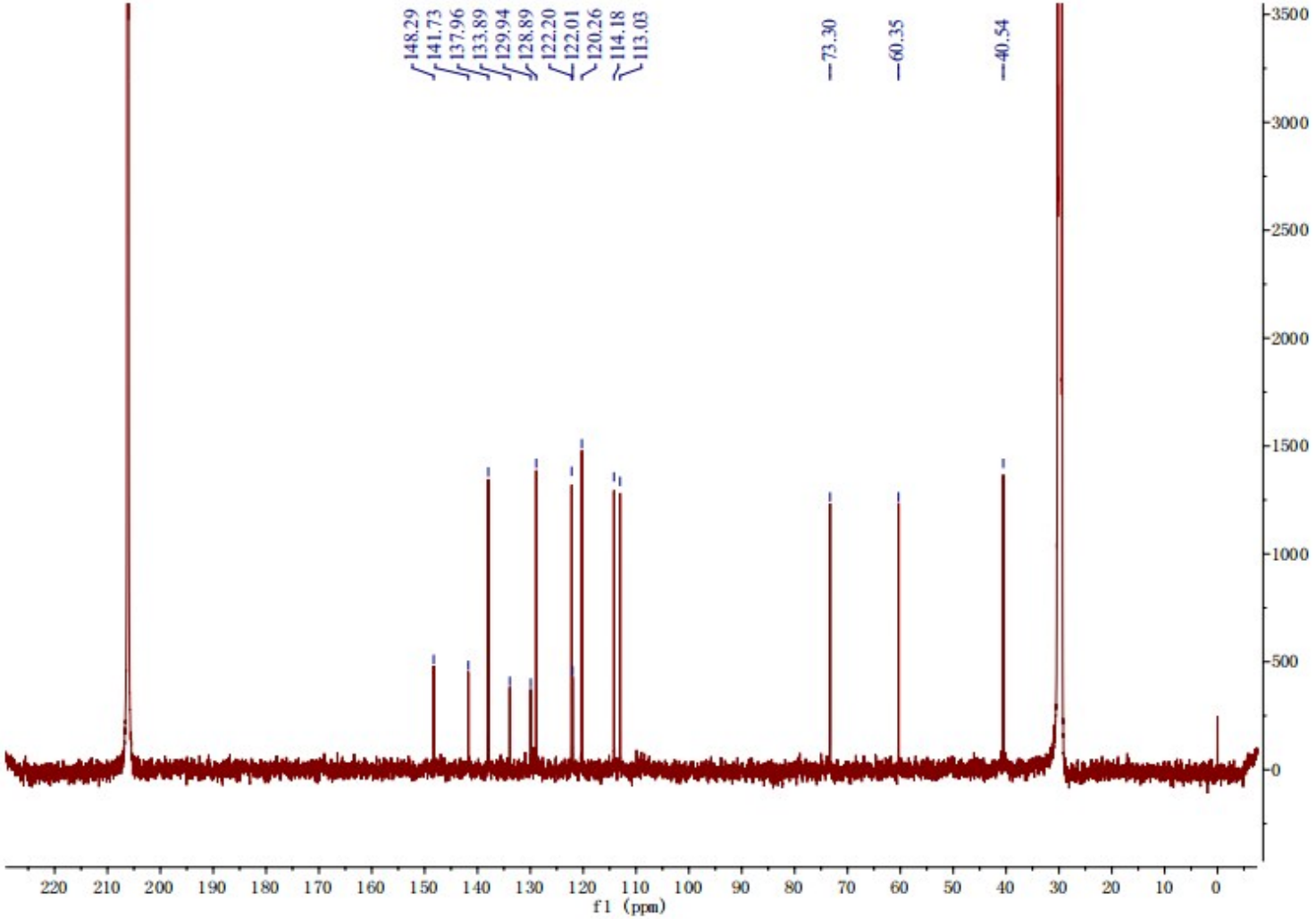


Figure S3. ^{13}C NMR spectrum (125 MHz, acetone-d_6) of aspercarboline A (**1**)

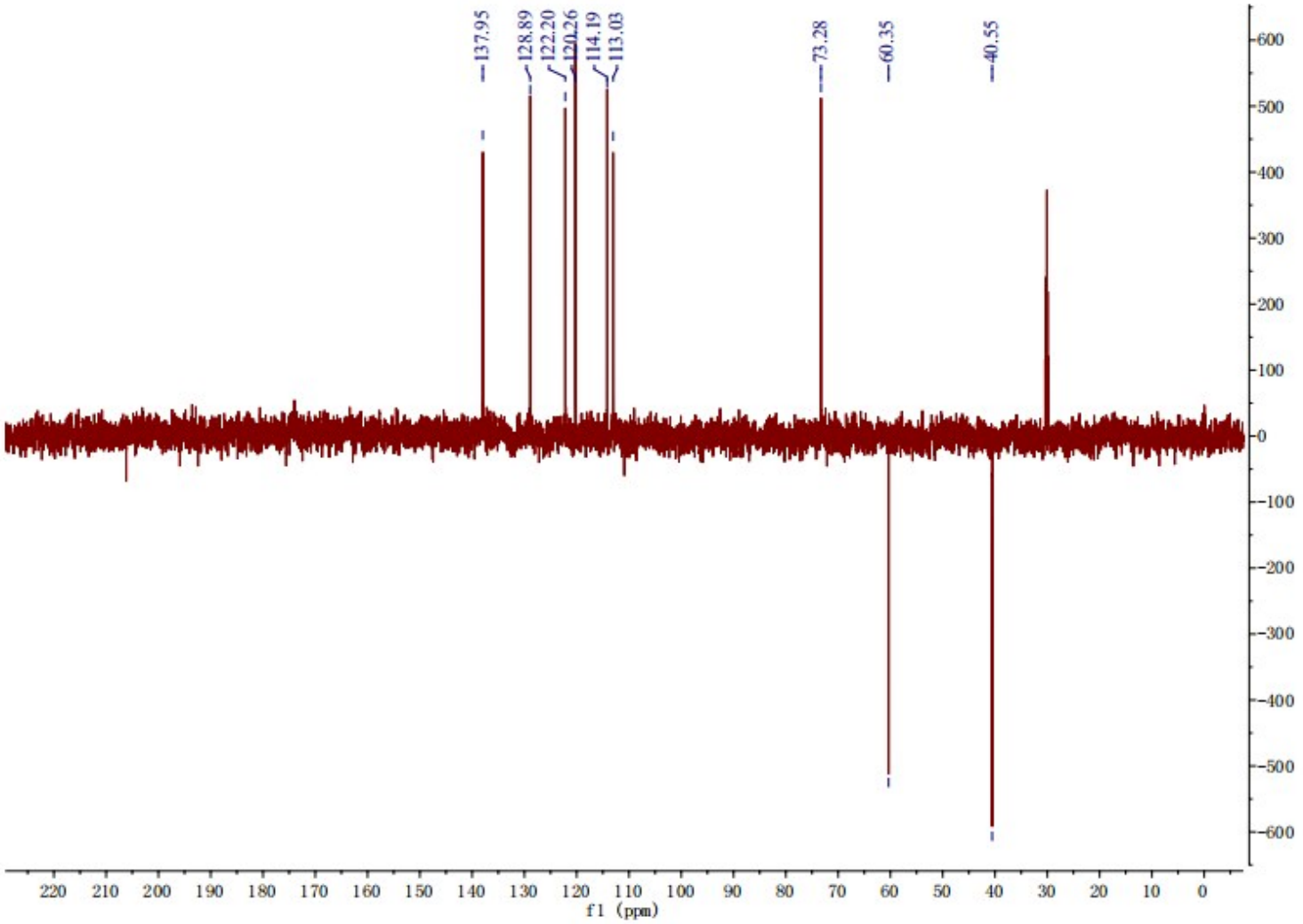


Figure S4. DEPT 135 spectrum (125 MHz, acetone-d_6) of aspercarboline A (**1**)

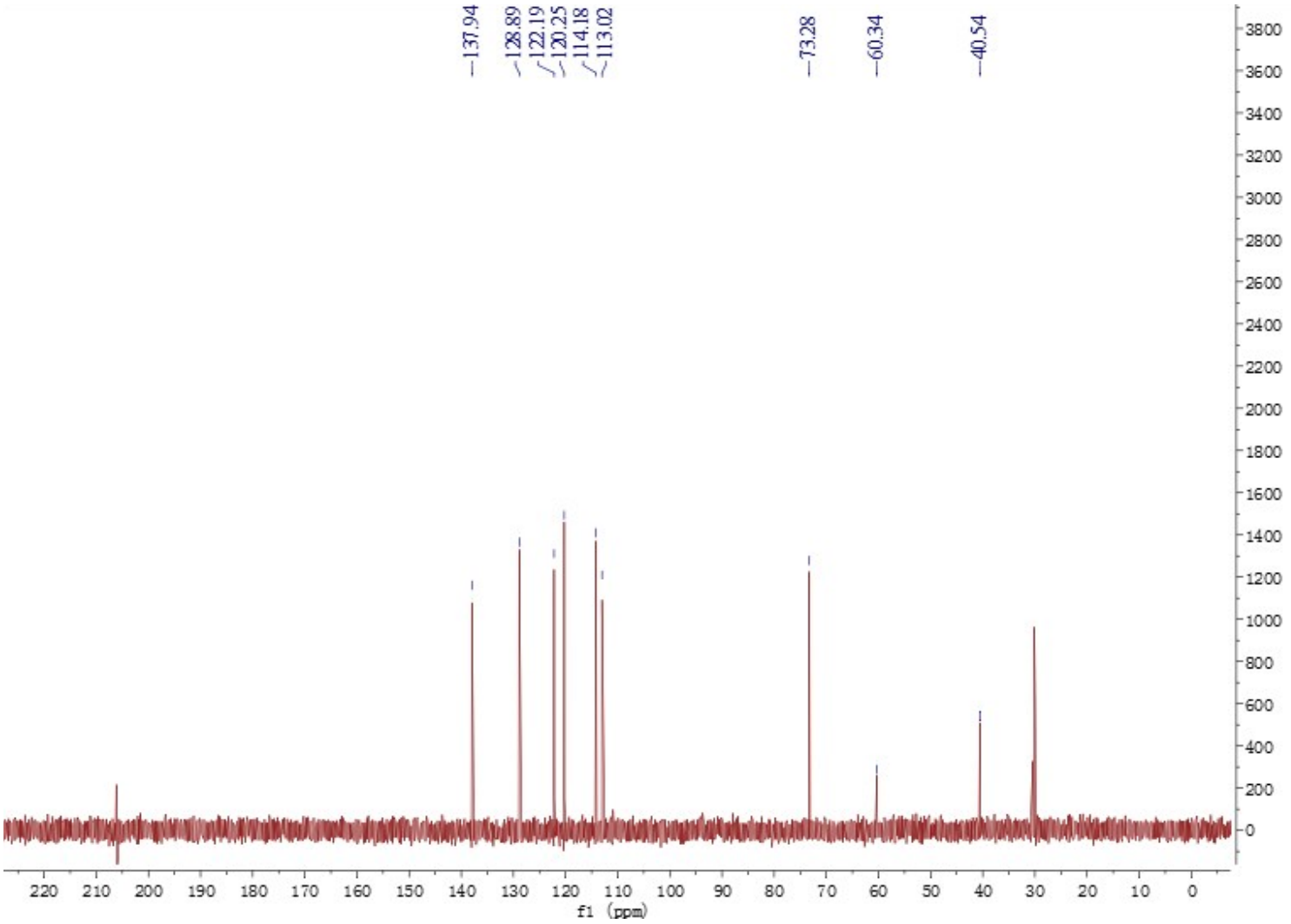


Figure S5. DEPT 90 spectrum (125 MHz, acetone-d_6) of aspercarboline A (**1**)

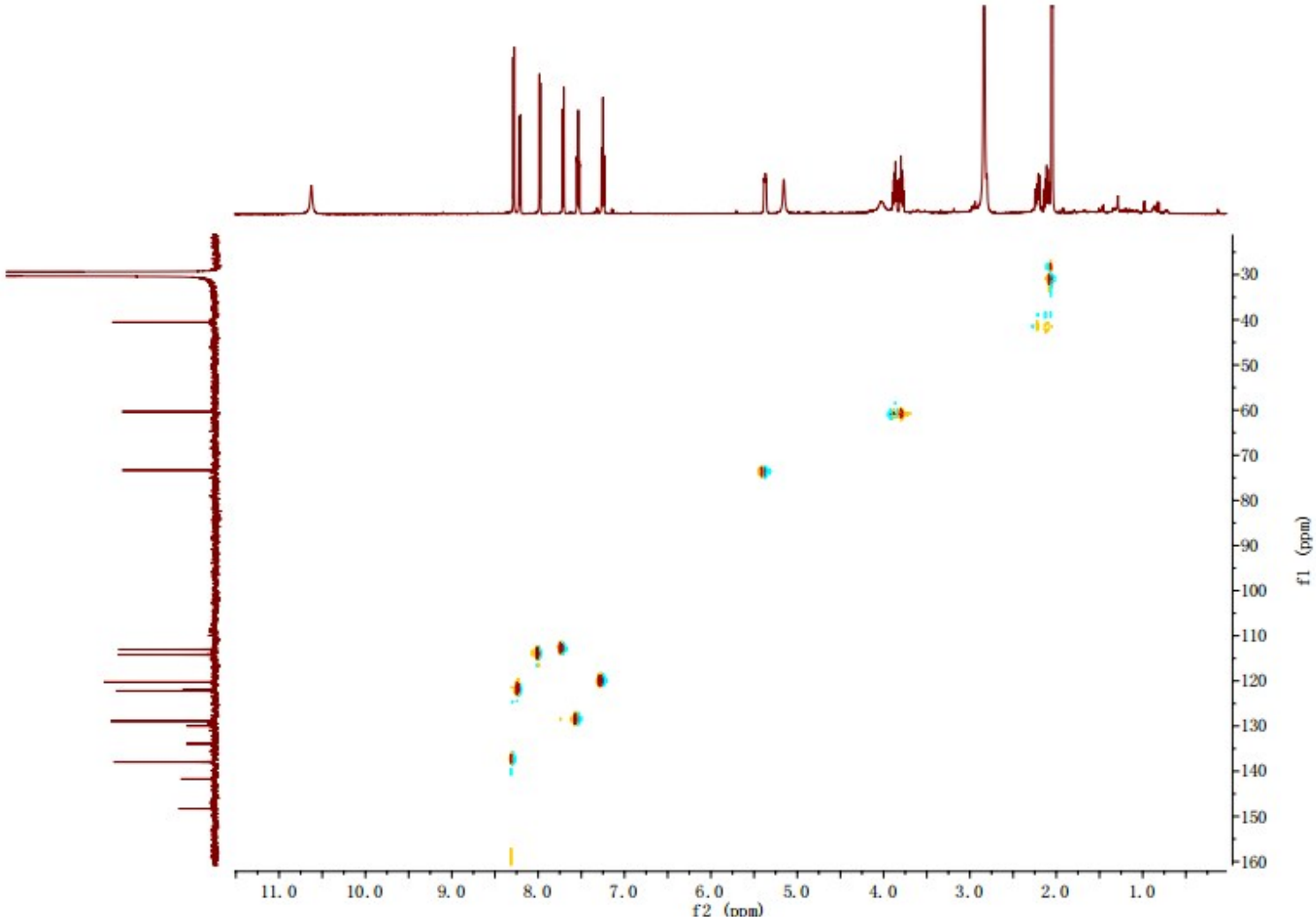


Figure S6. HSQC spectrum of aspercarboline A (**1**)

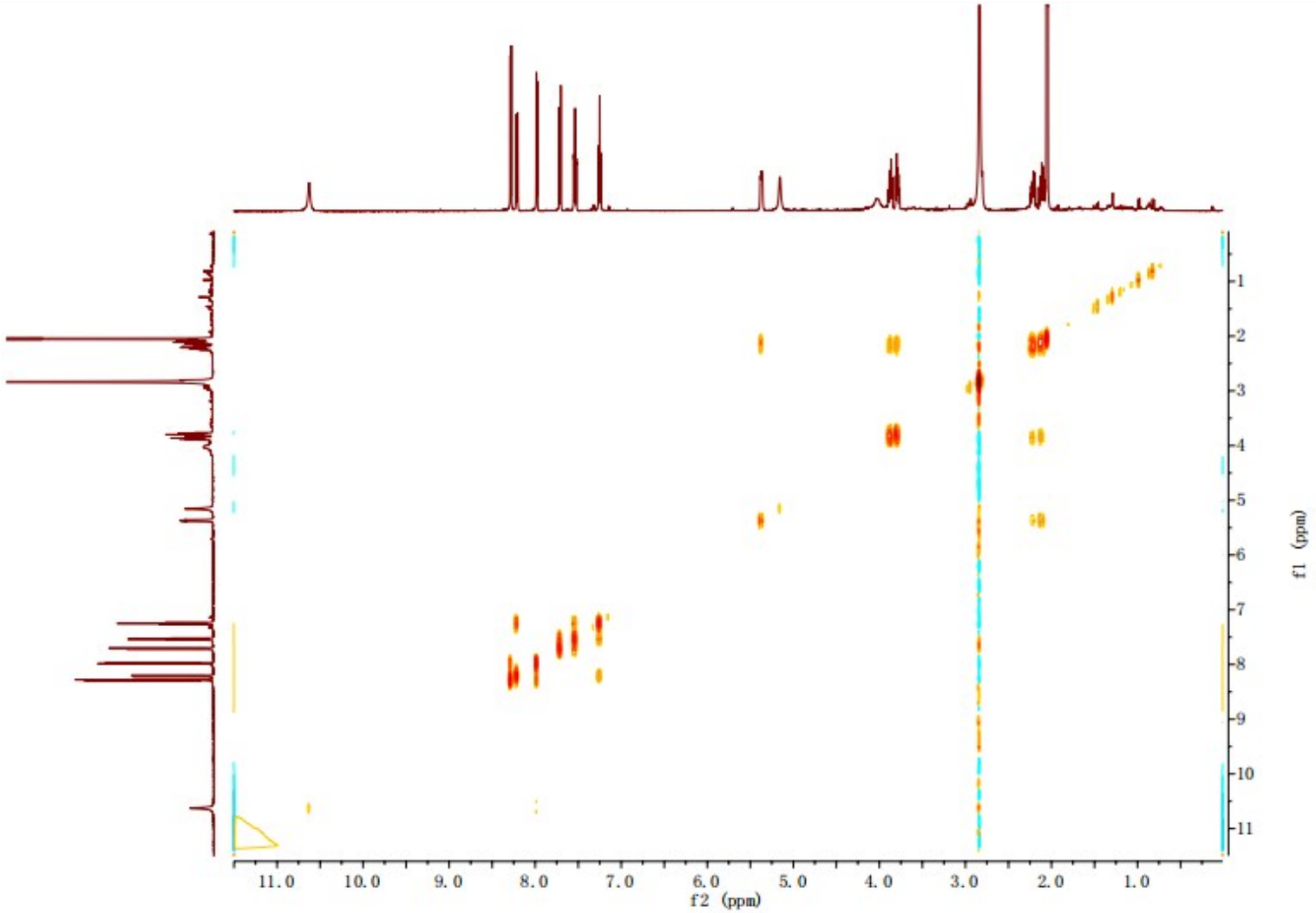


Figure S7. $^{1}H-^{1}H$ COSY spectrum of aspercarboline A (**1**)

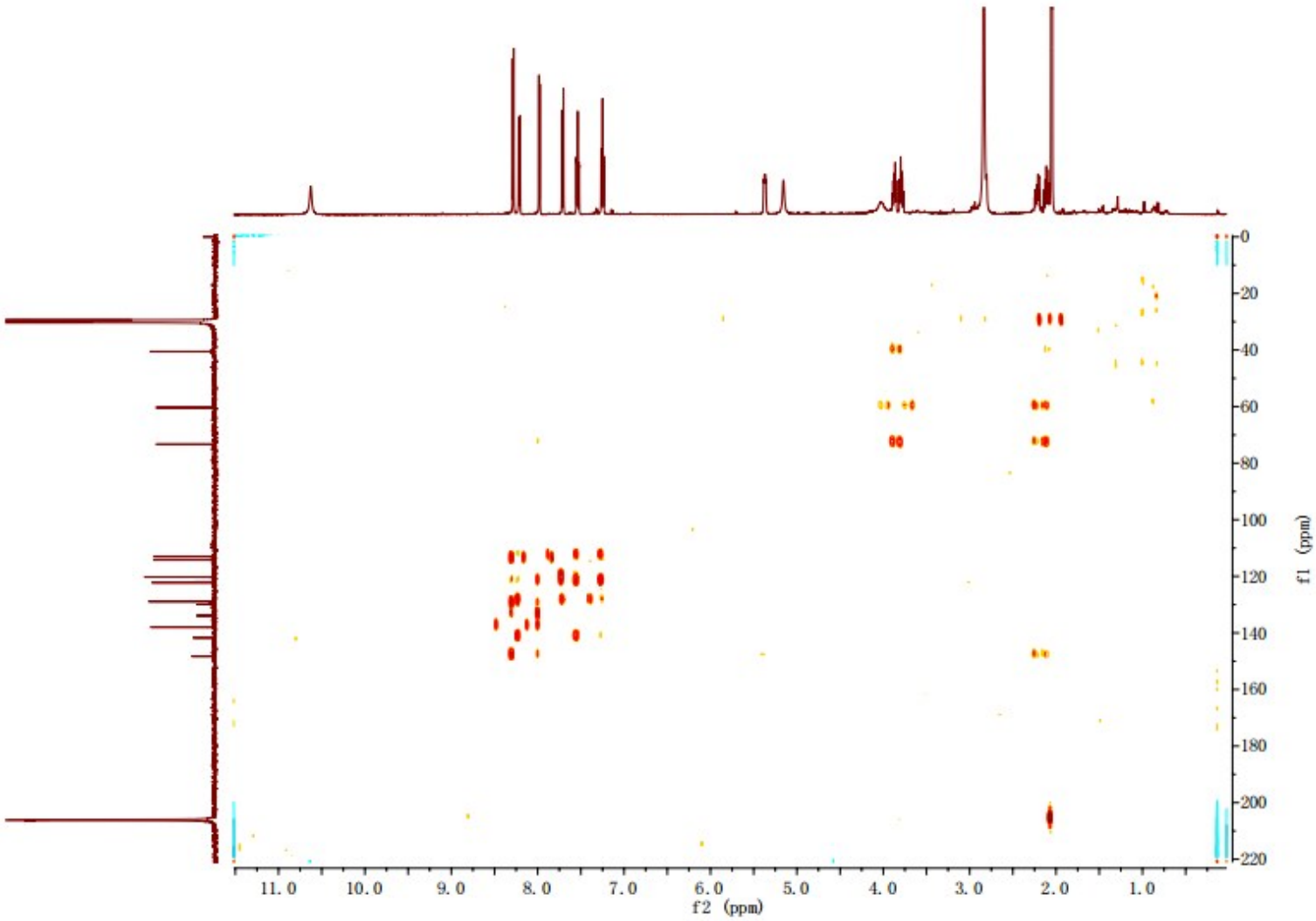
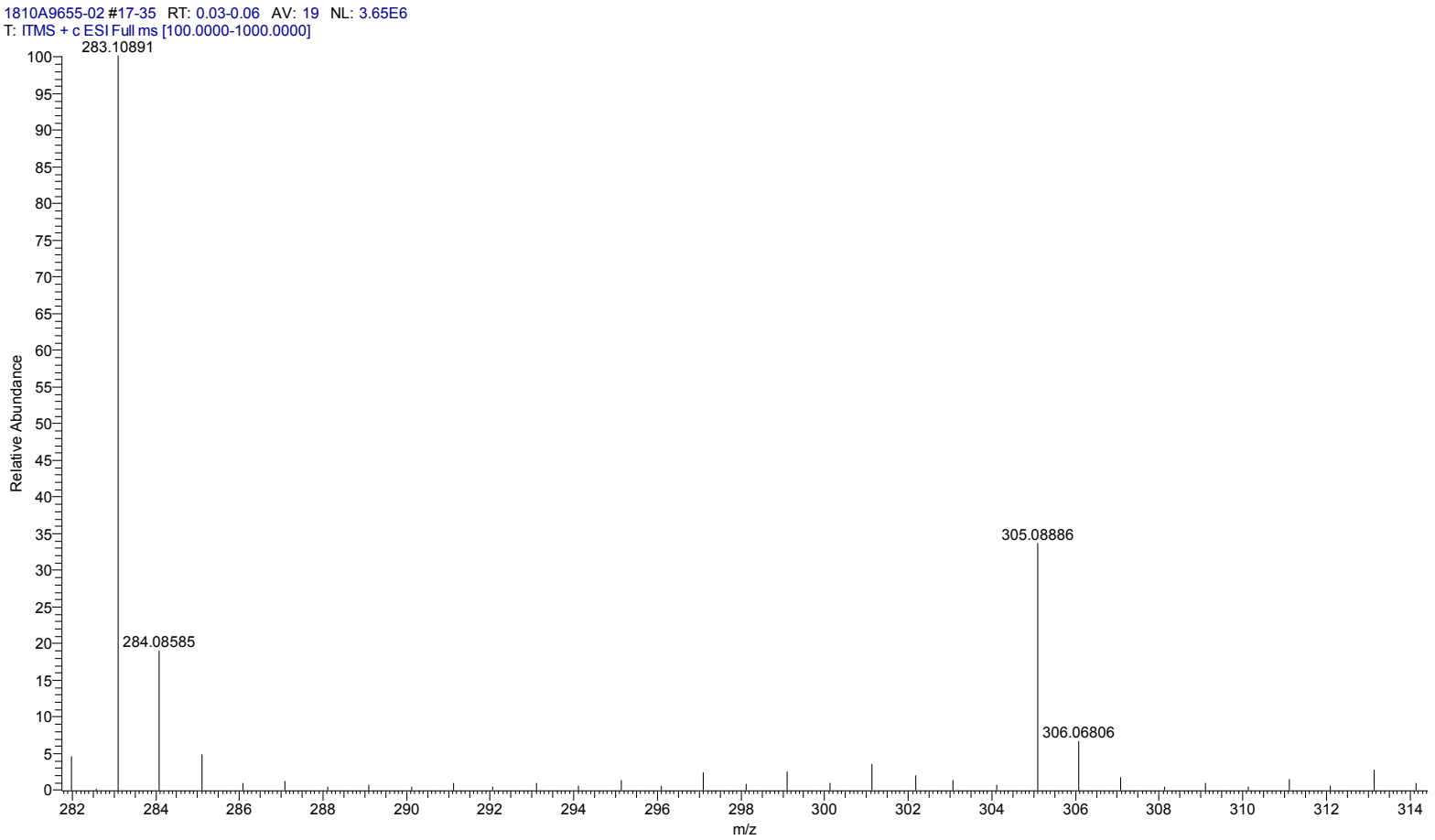


Figure S8. HMBC spectrum of aspercarboline A (**1**)



SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
283.10891	283.10772	4.21	10.5	C16H15O3N2

Figure S9. HR-ESI-MS spectrum of aspercarboline B (**2**).

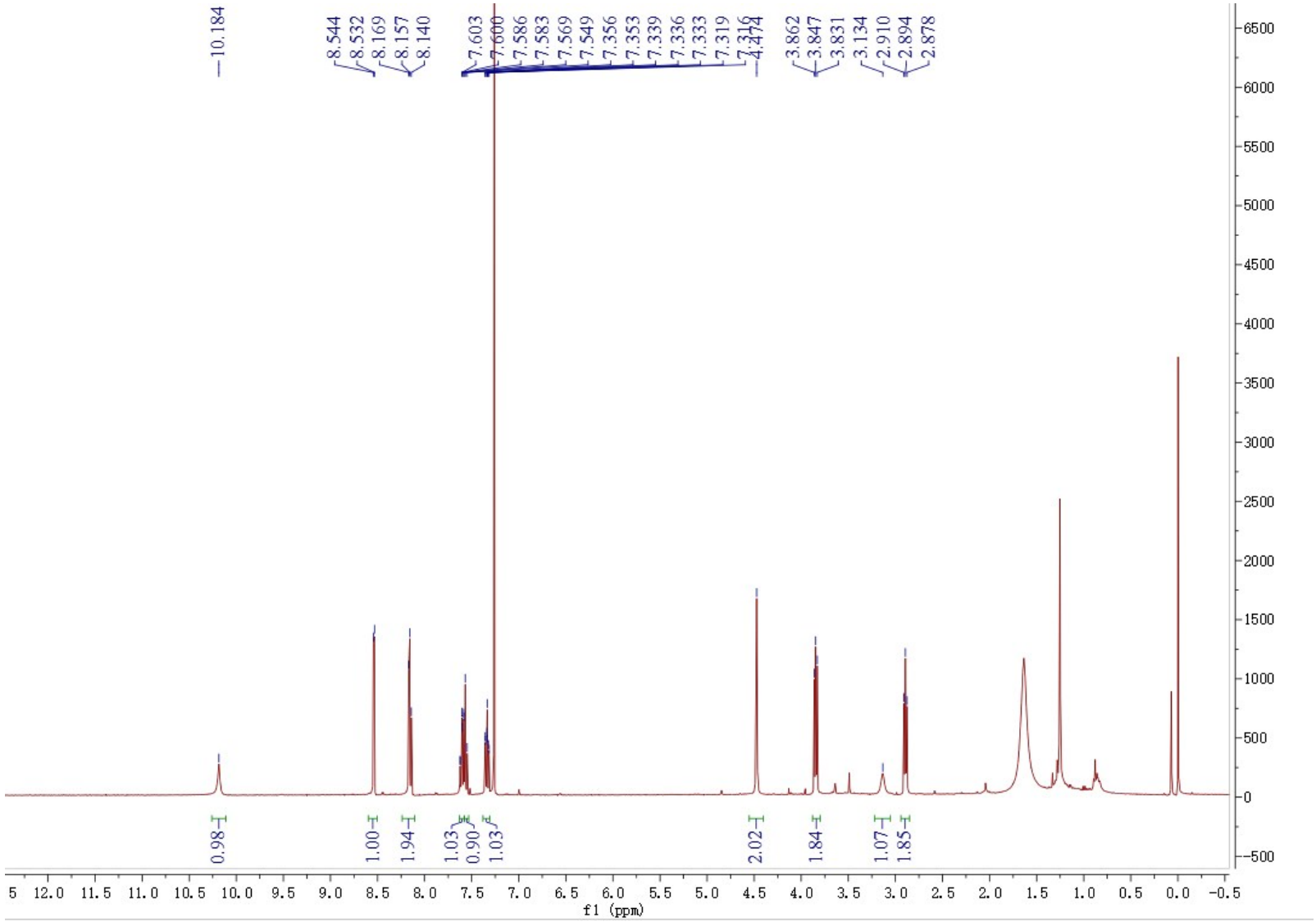


Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of aspercarboline B (**2**)

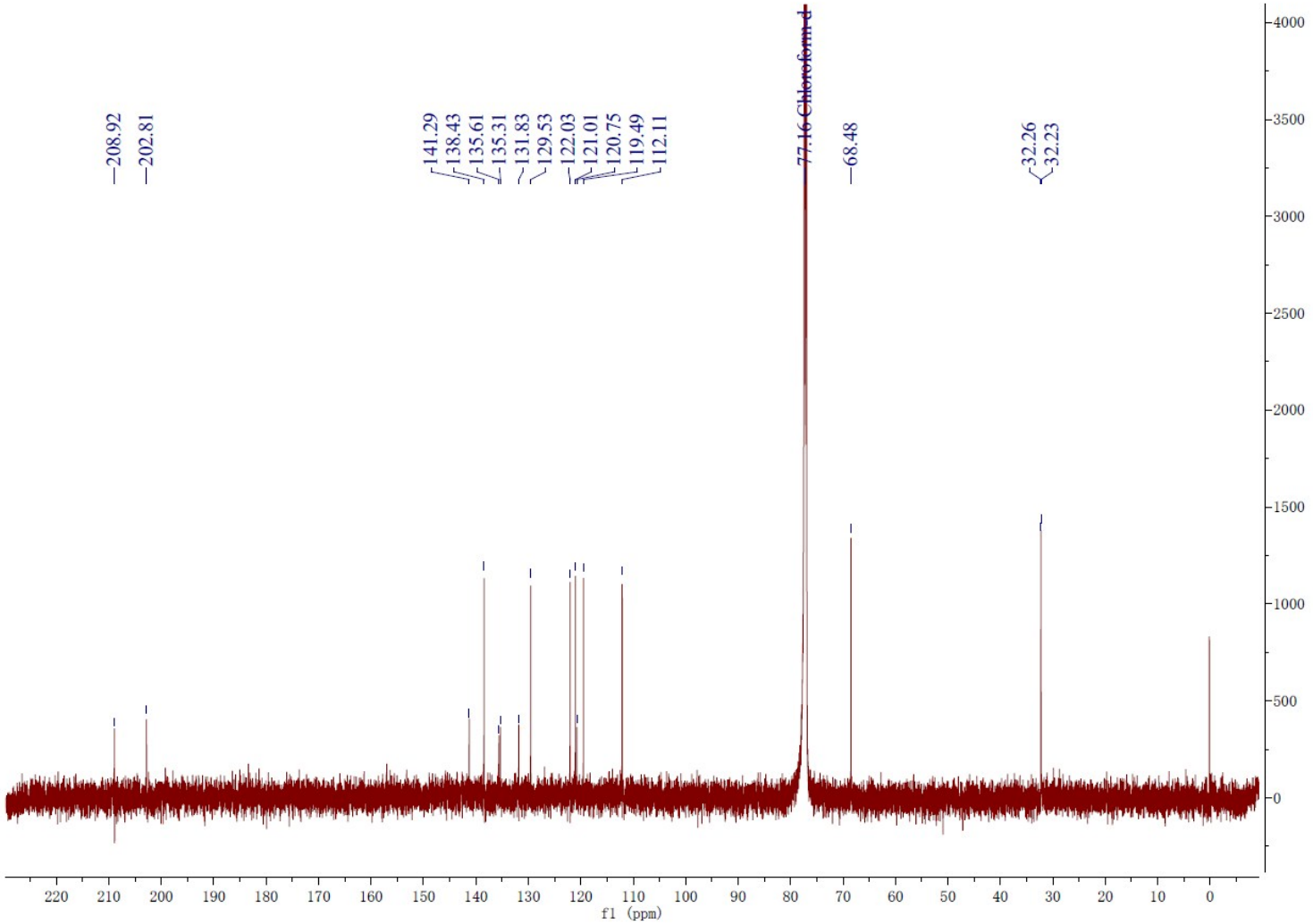


Figure S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of aspercarboline B (**2**)

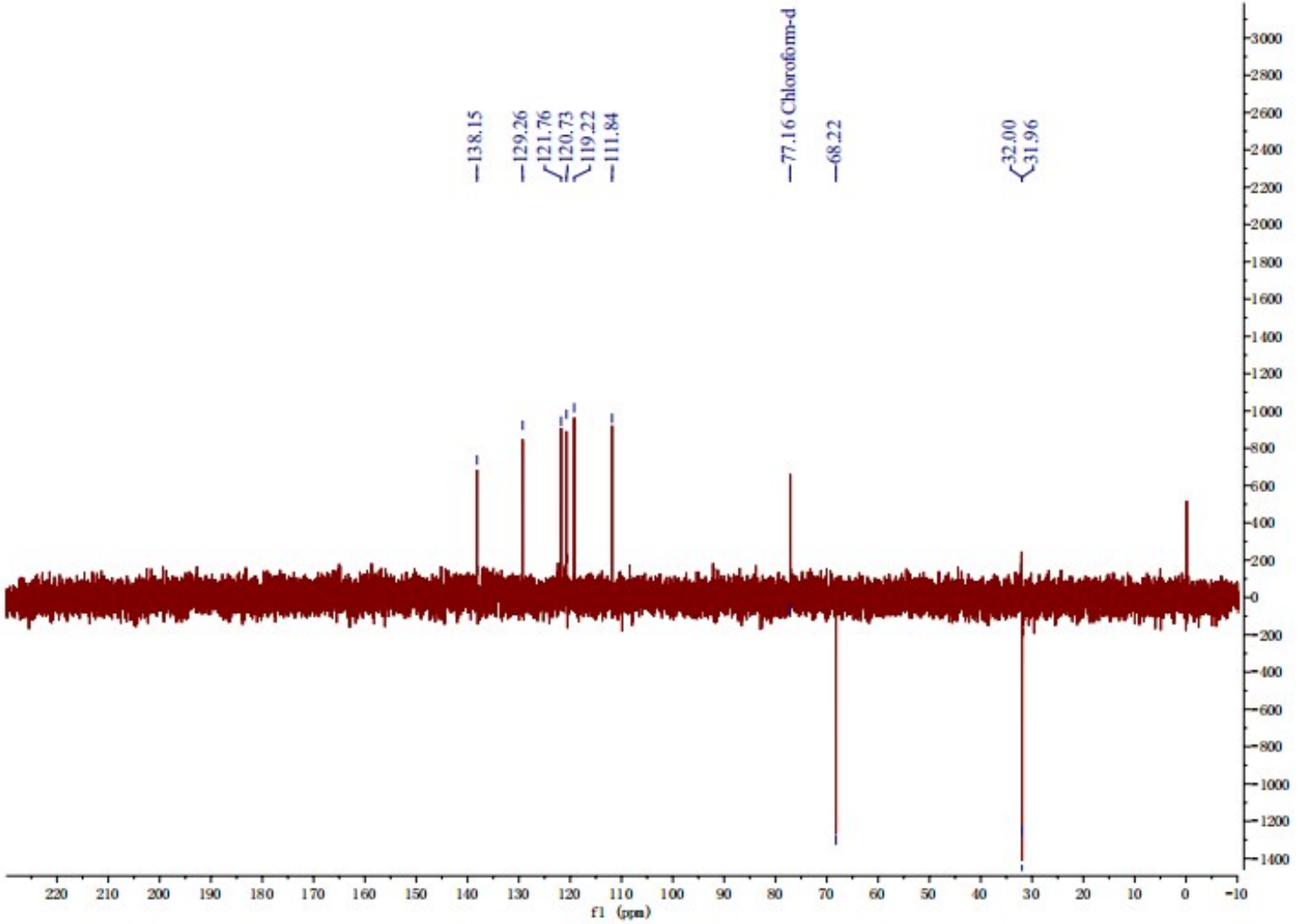


Figure S12. DEPT 135 spectrum (100 MHz, $CDCl_3$) of aspercarboline B (**2**)

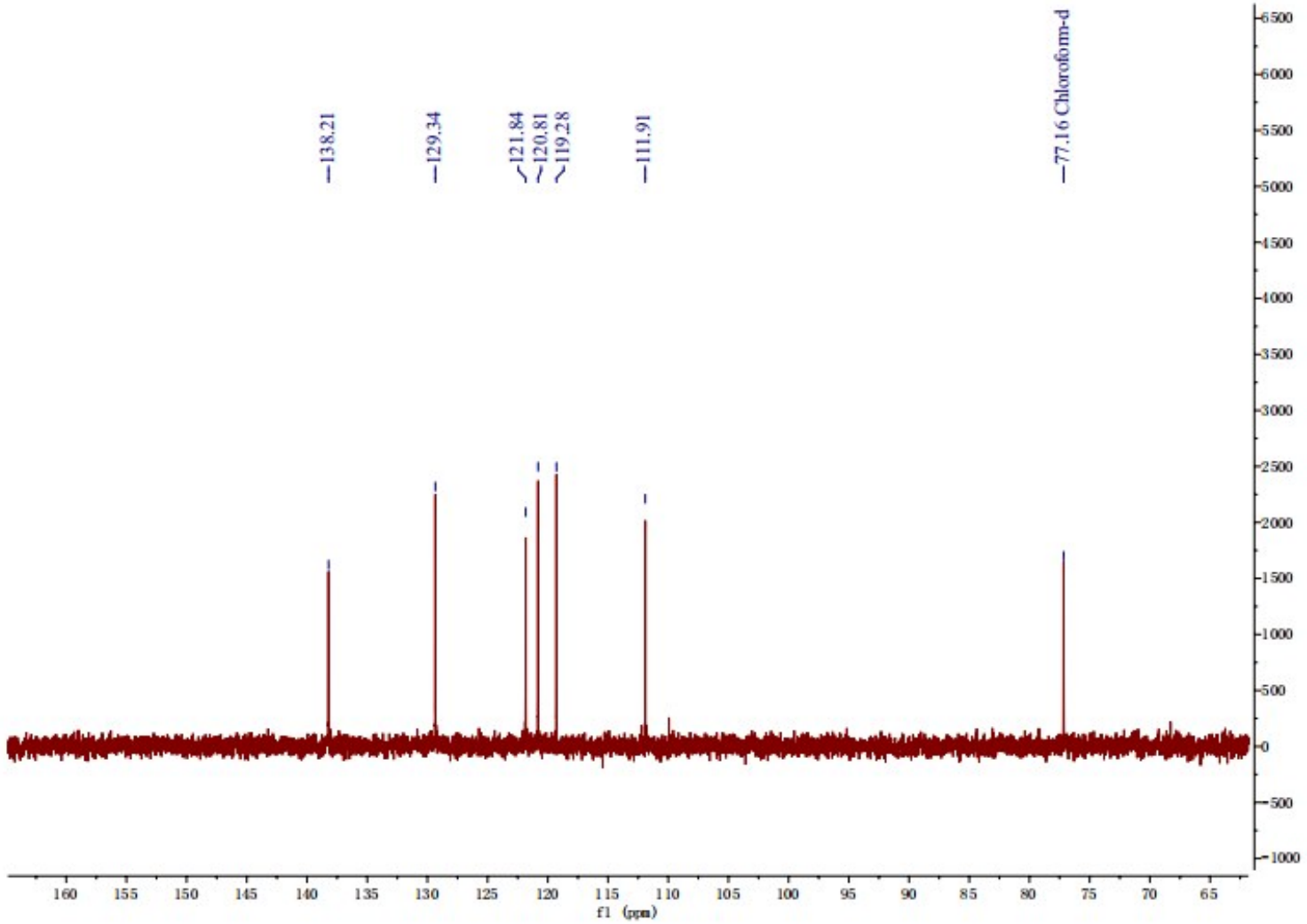


Figure S13. DEPT 90 spectrum (100 MHz, $CDCl_3$) of aspercarboline B (**2**)

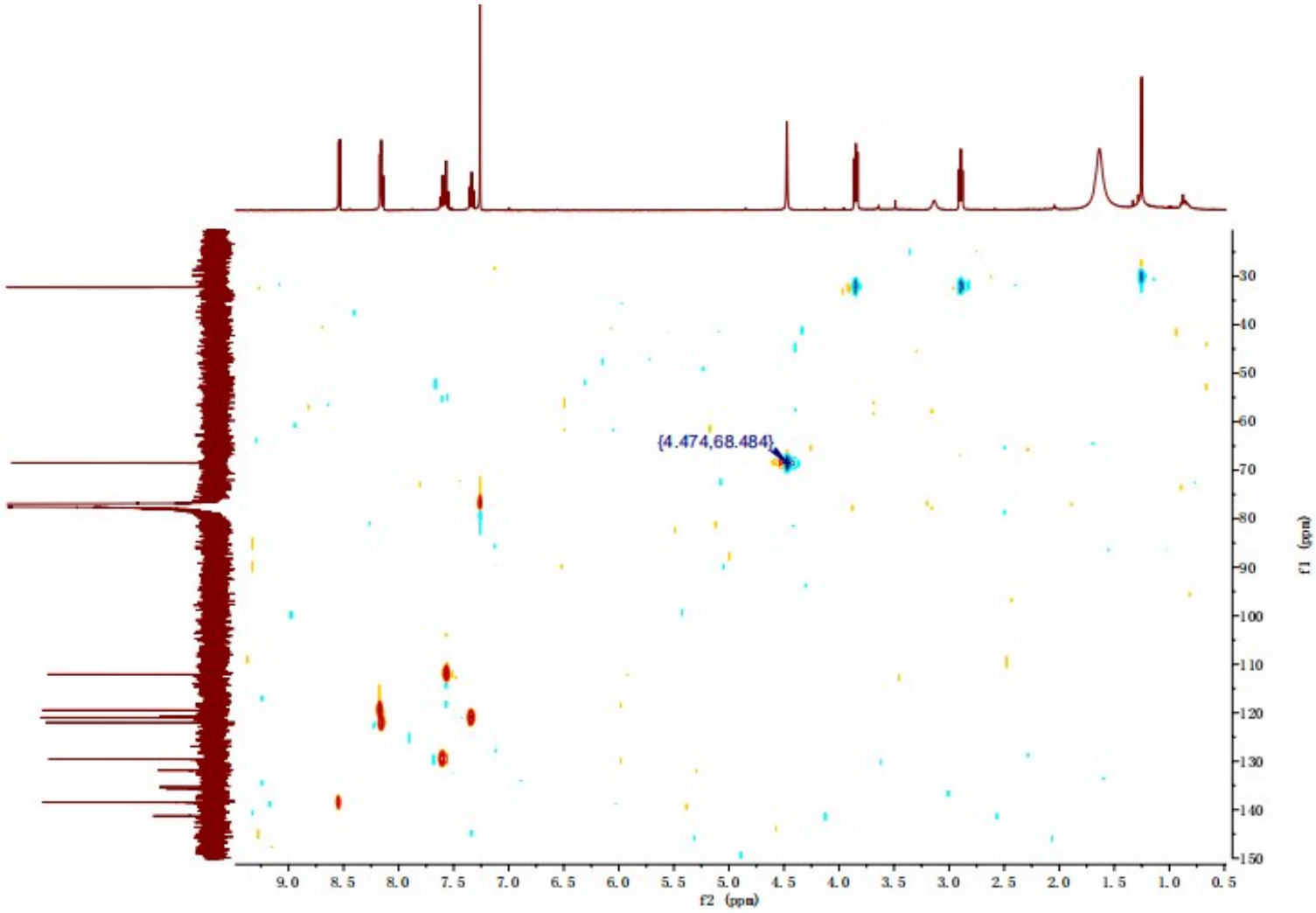


Figure S14. HSQC spectrum of aspercarboline B (**2**)

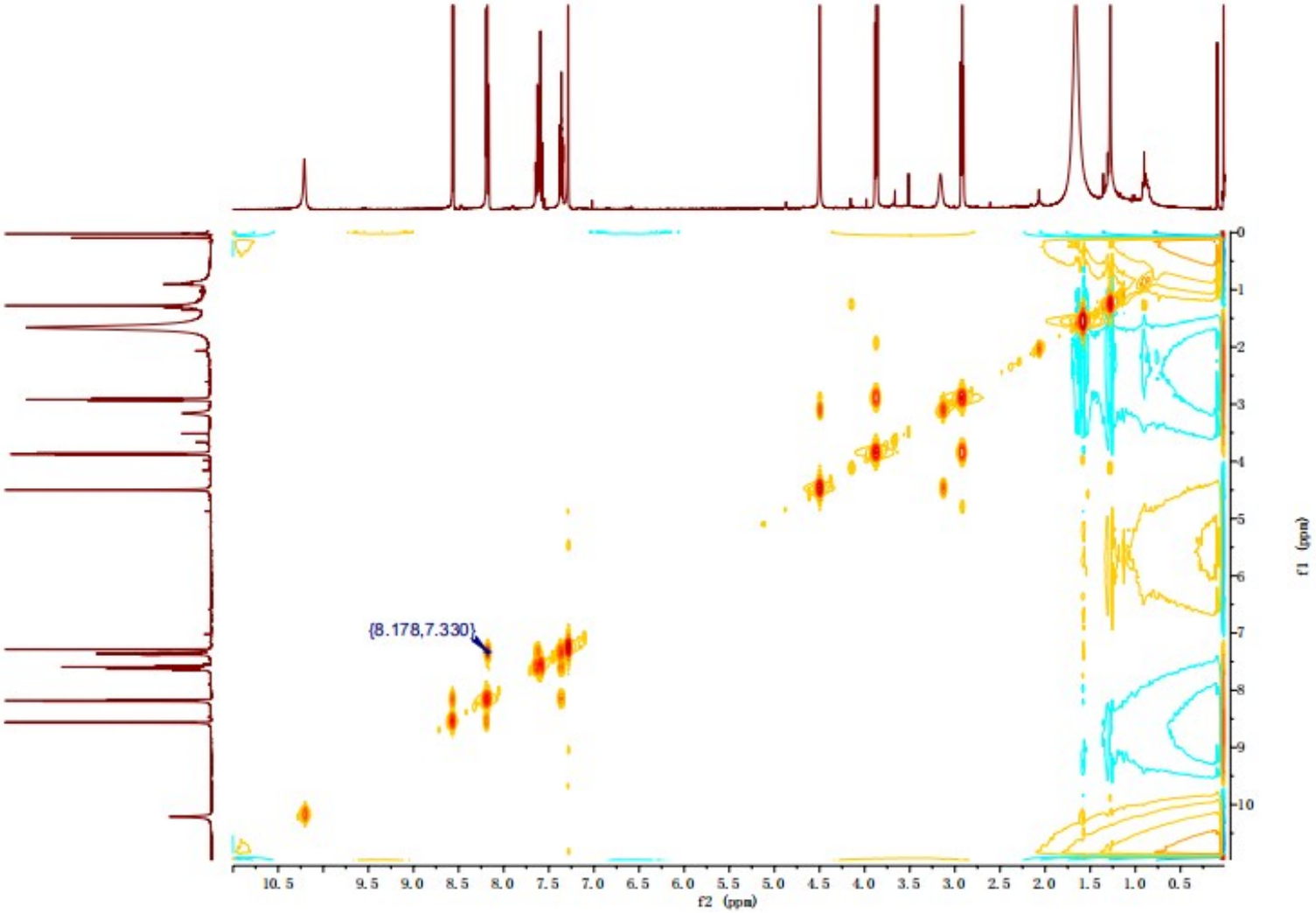


Figure S15. $^{1}H-^{1}H$ COSY spectrum of aspercarboline B (**2**)

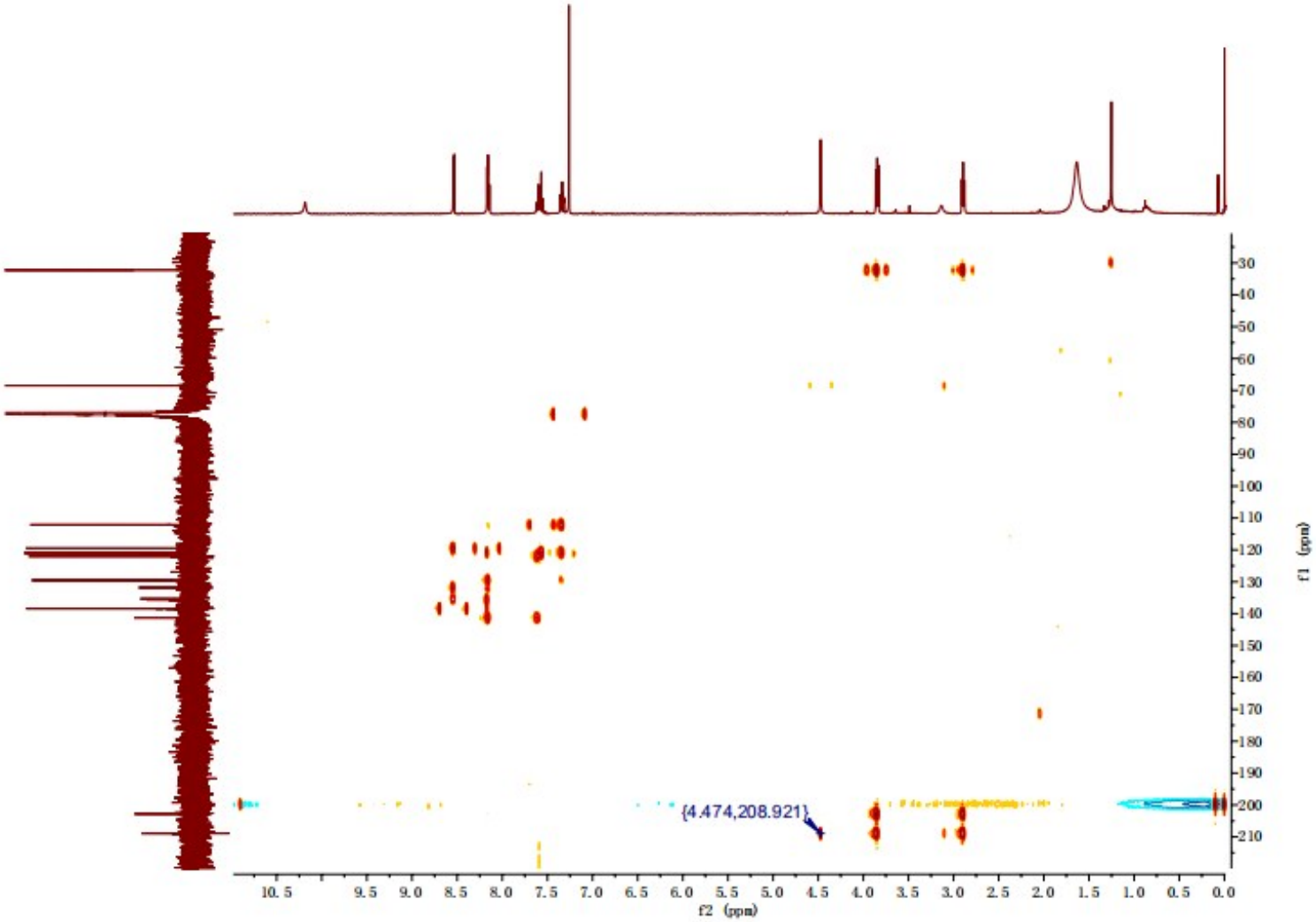
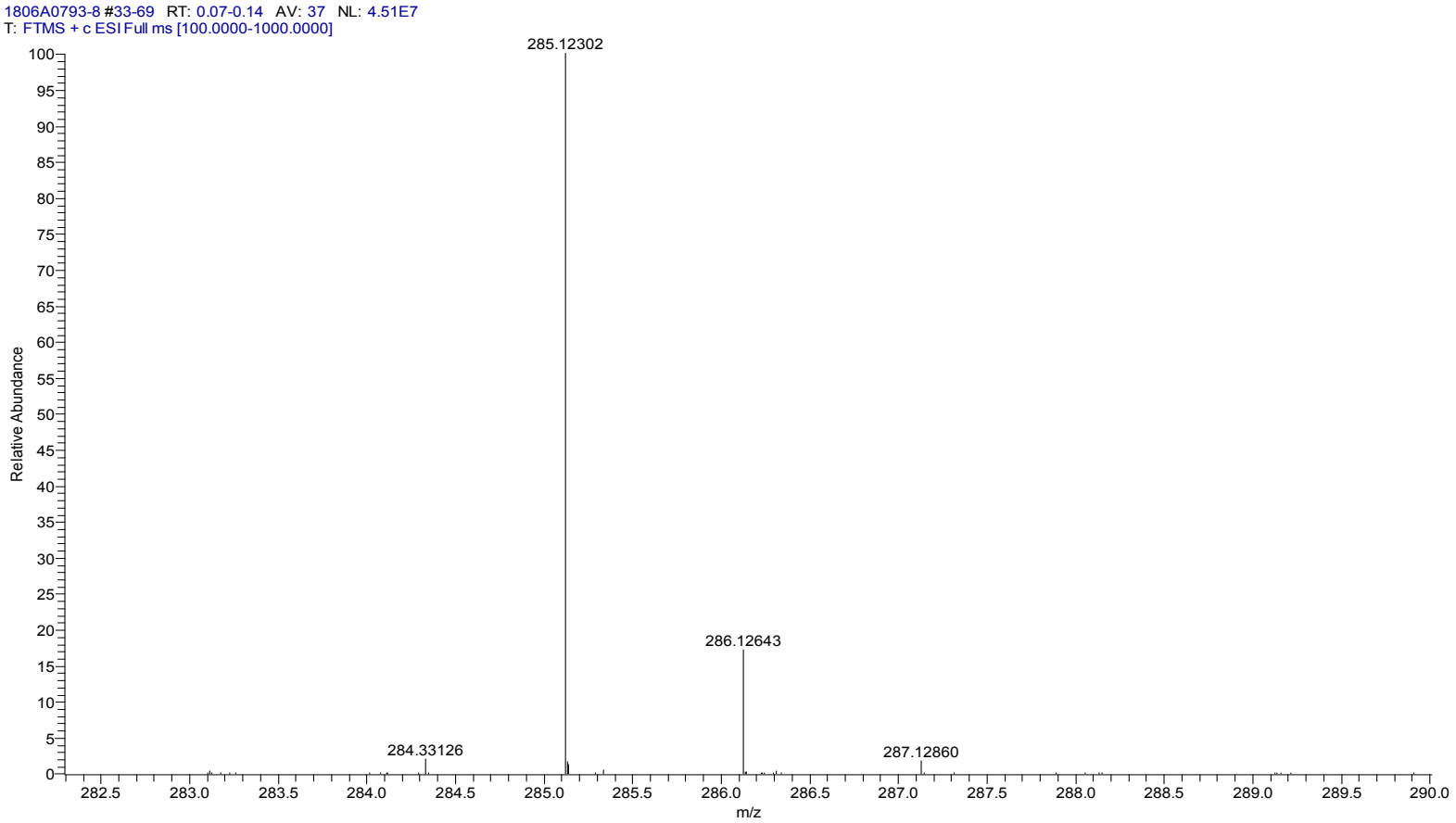


Figure S16. HMBC spectrum of aspercarboline B (**2**)



SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
285.12302	285.12337	-1.22	9.5	C16 H17 N2 O3

Figure S17. HR-ESI-MS spectrum of aspercarboline C (**3**).

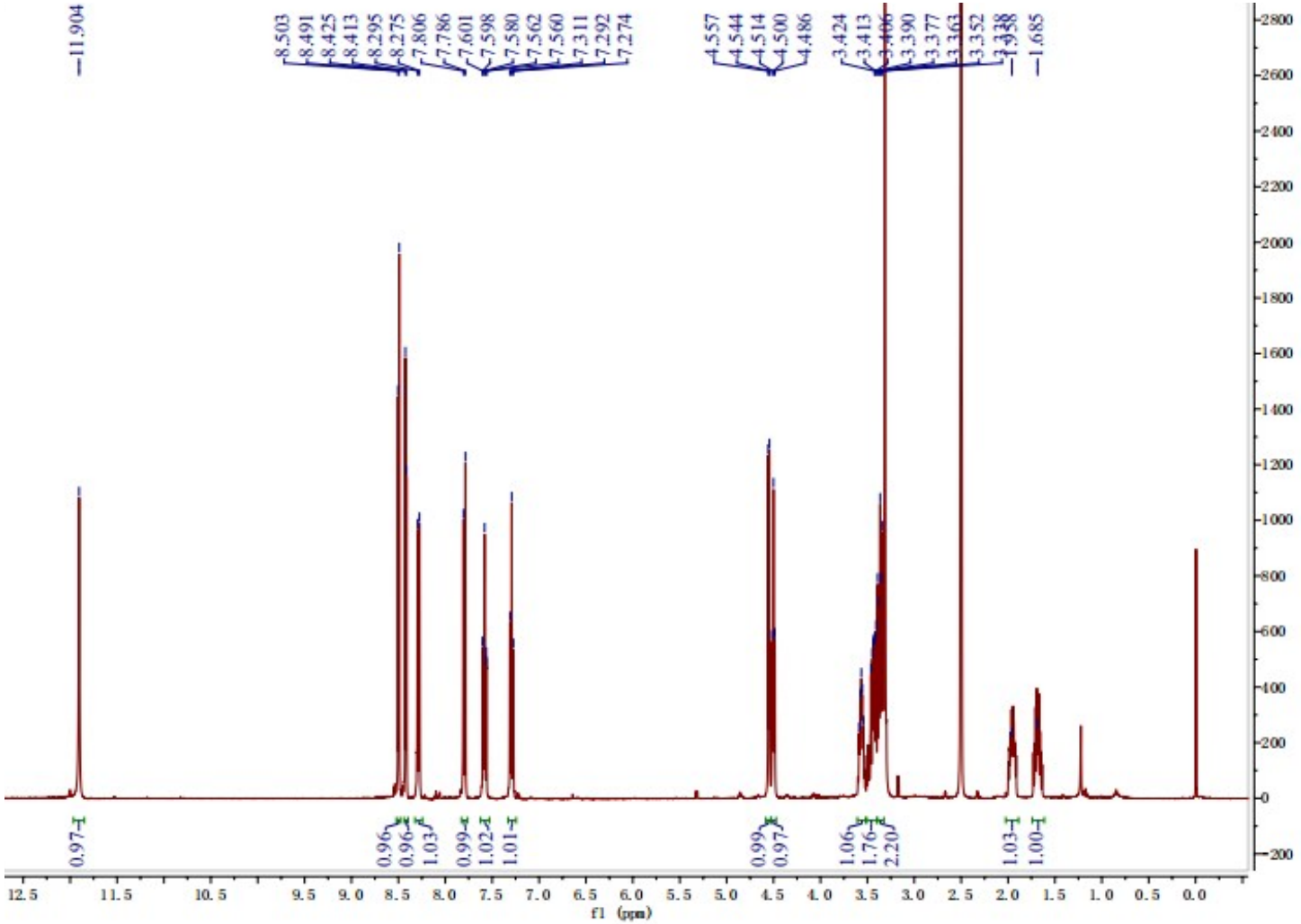


Figure S18. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of aspercarboline C (**3**)

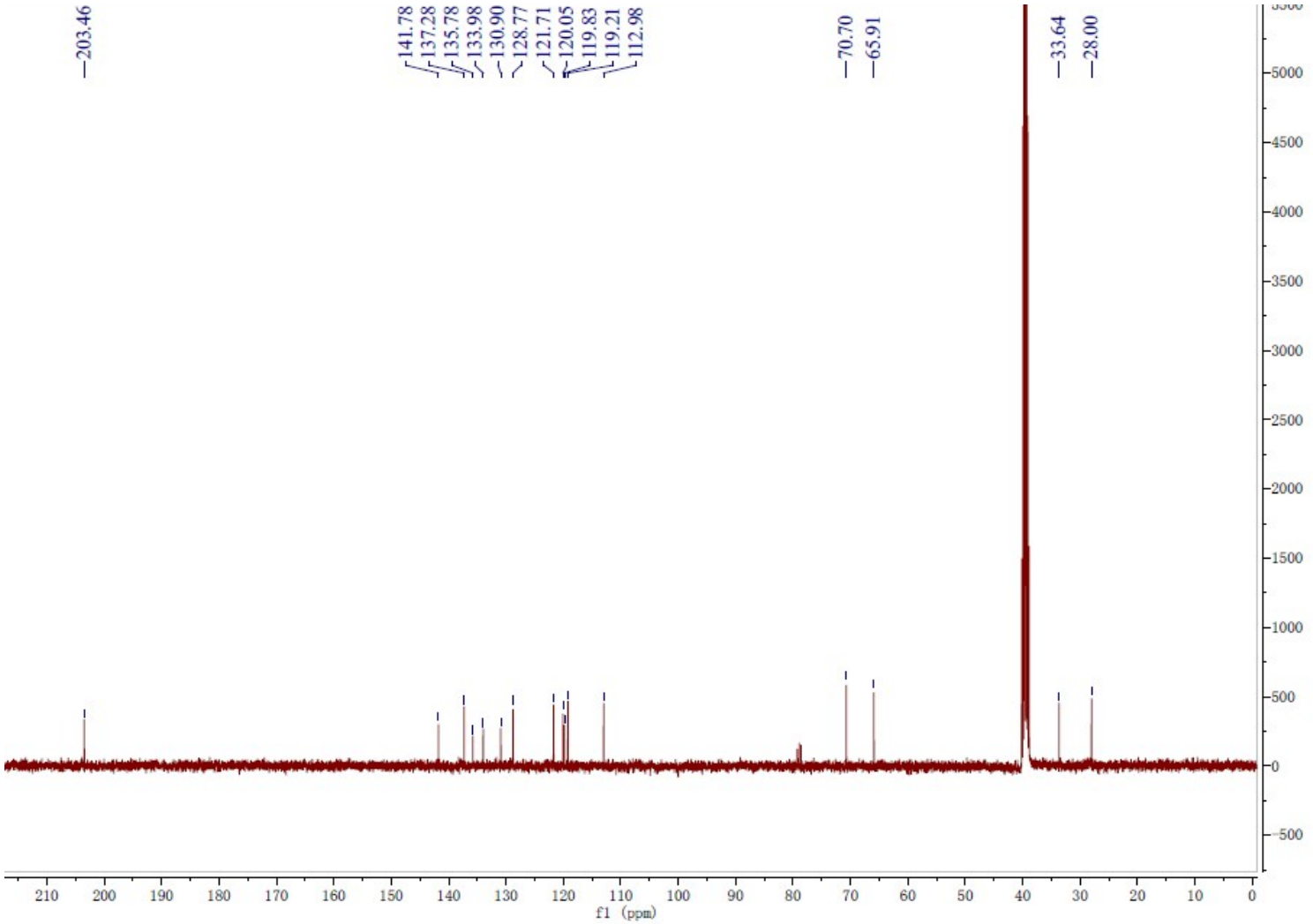


Figure S19. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of aspercarboline C (**3**)

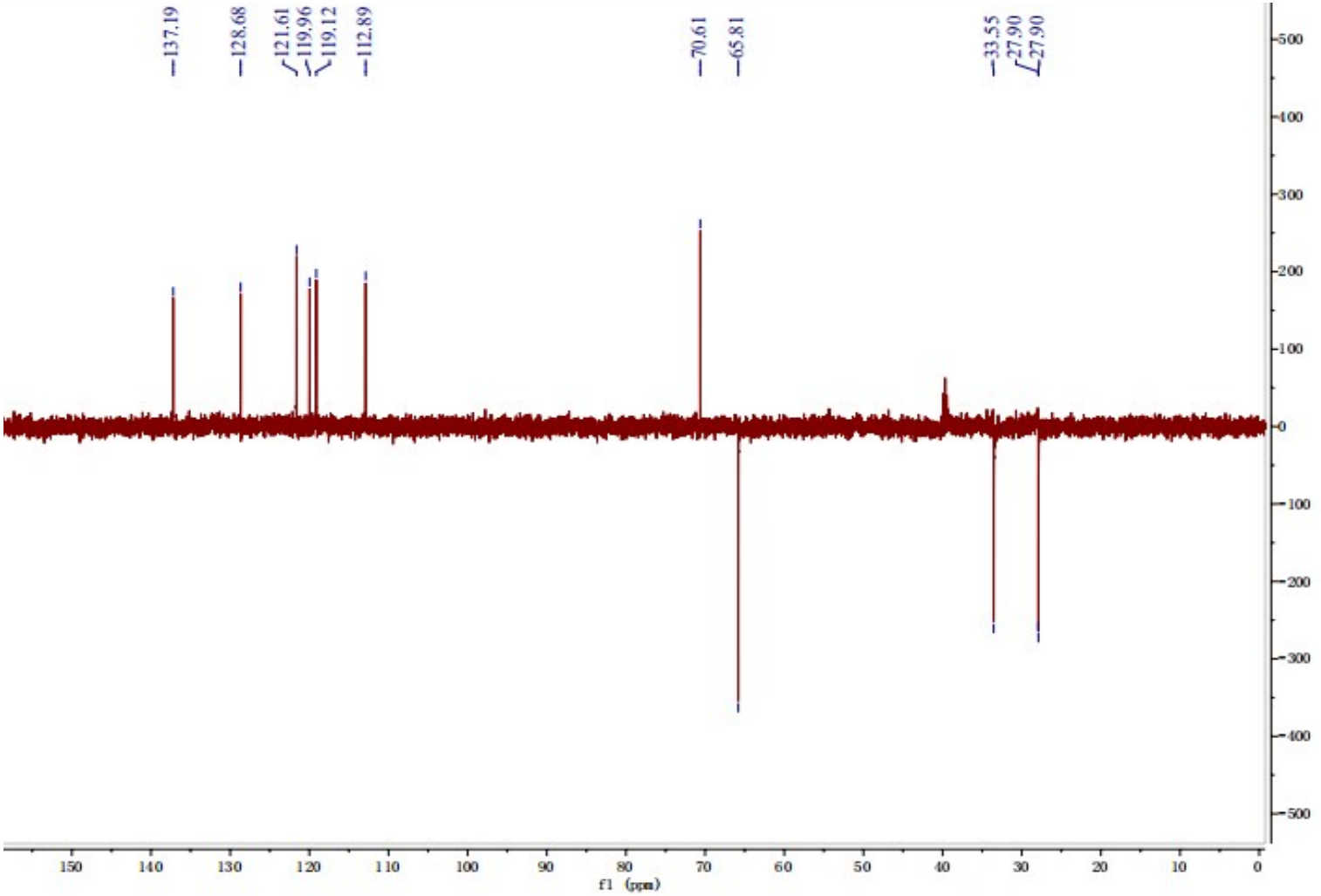


Figure S20. DEPT 135 spectrum (100 MHz, DMSO-d_6) of aspercarboline C (**3**)

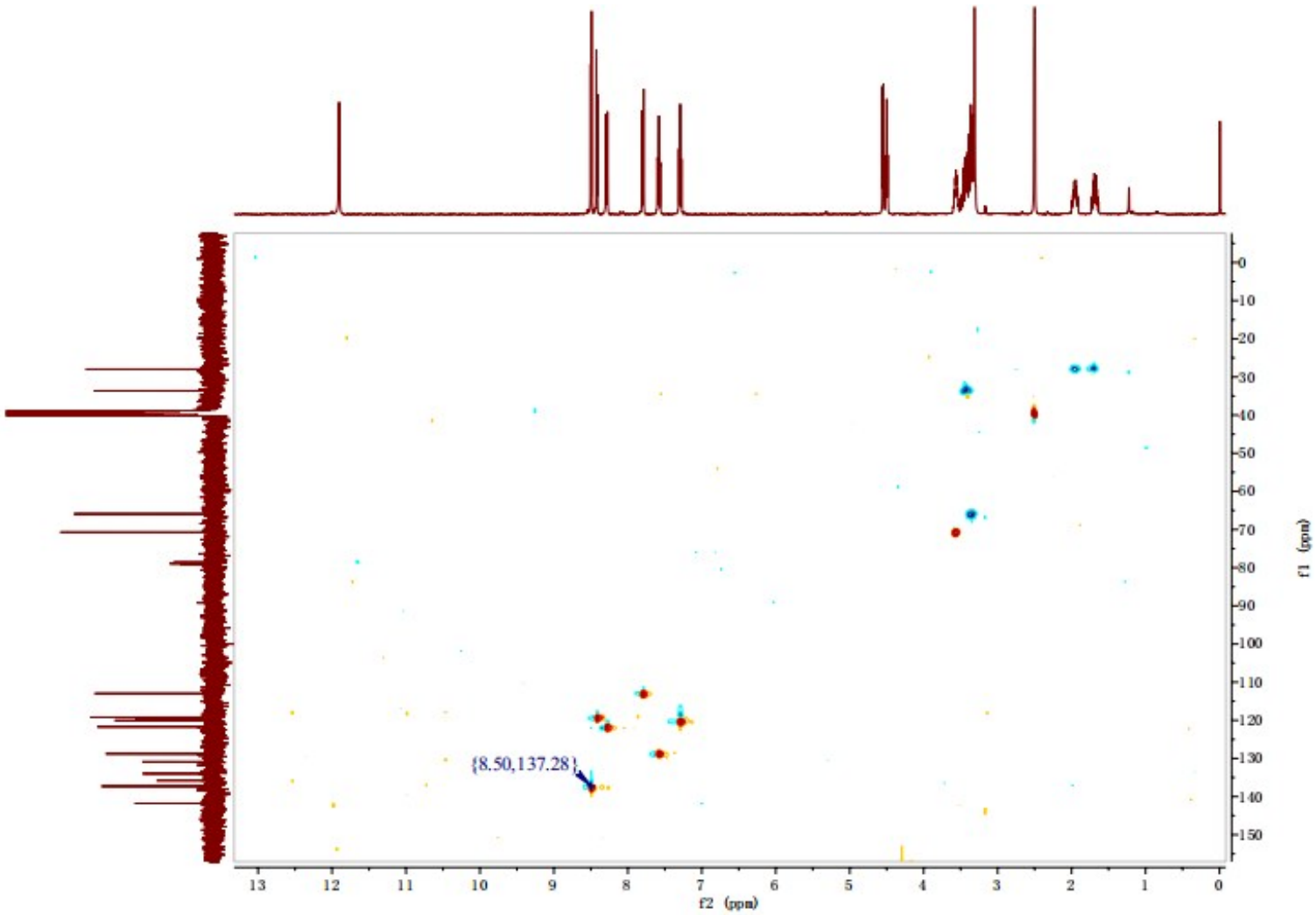


Figure S21. HSQC spectrum of aspercarboline C (**3**)

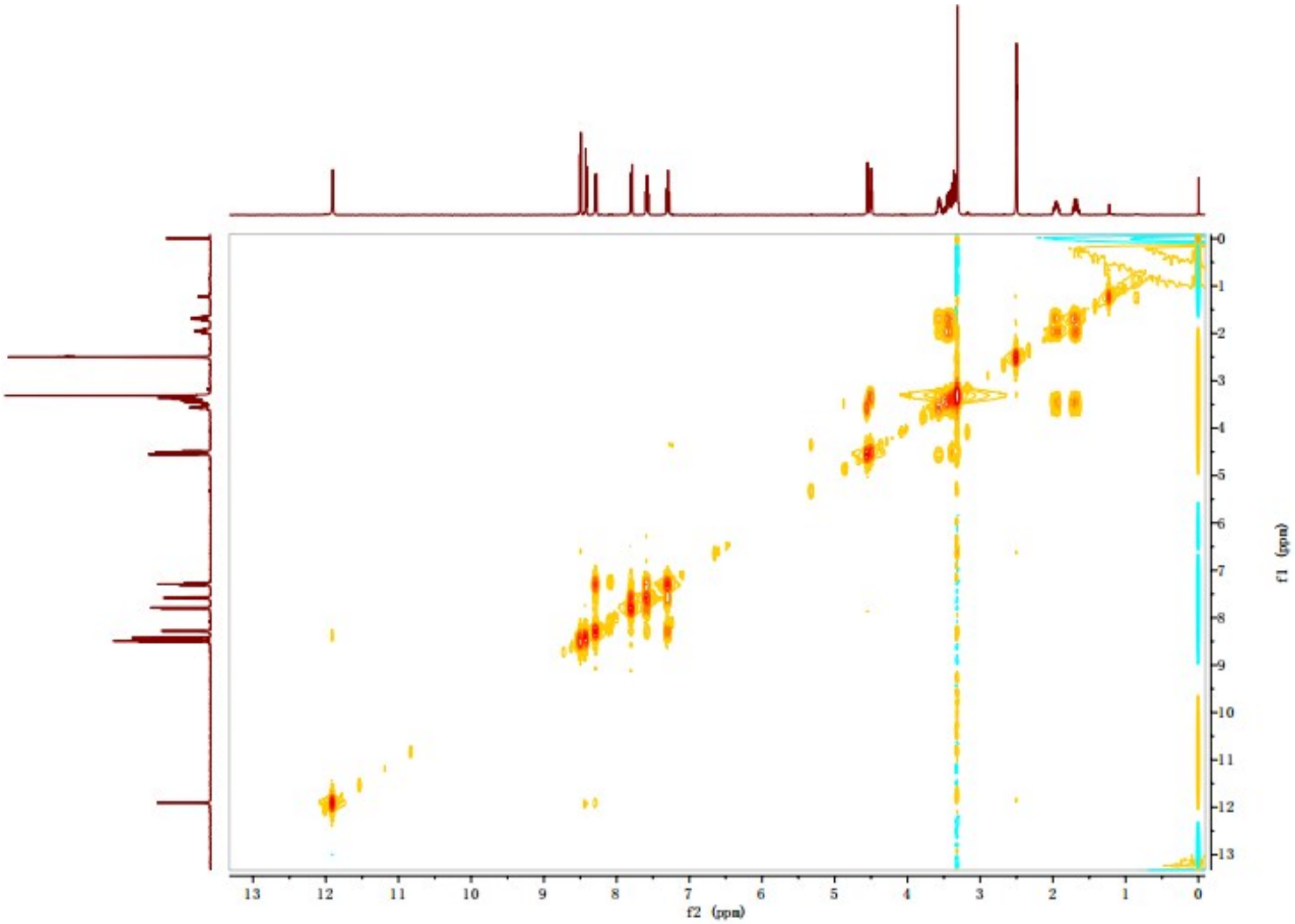


Figure S22. $^{1}H–^{1}H$ COSY spectrum of aspercarboline C (**3**)

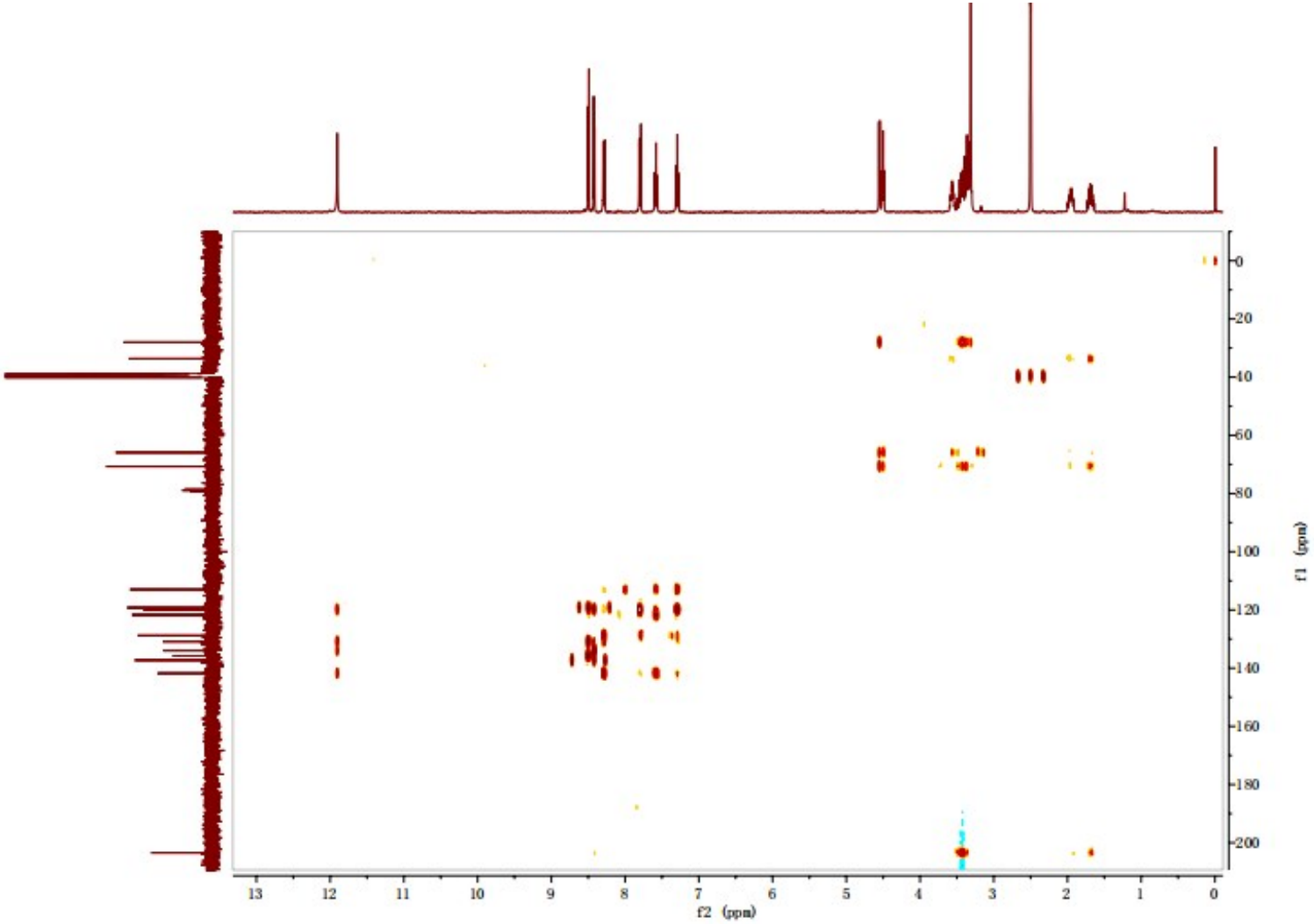
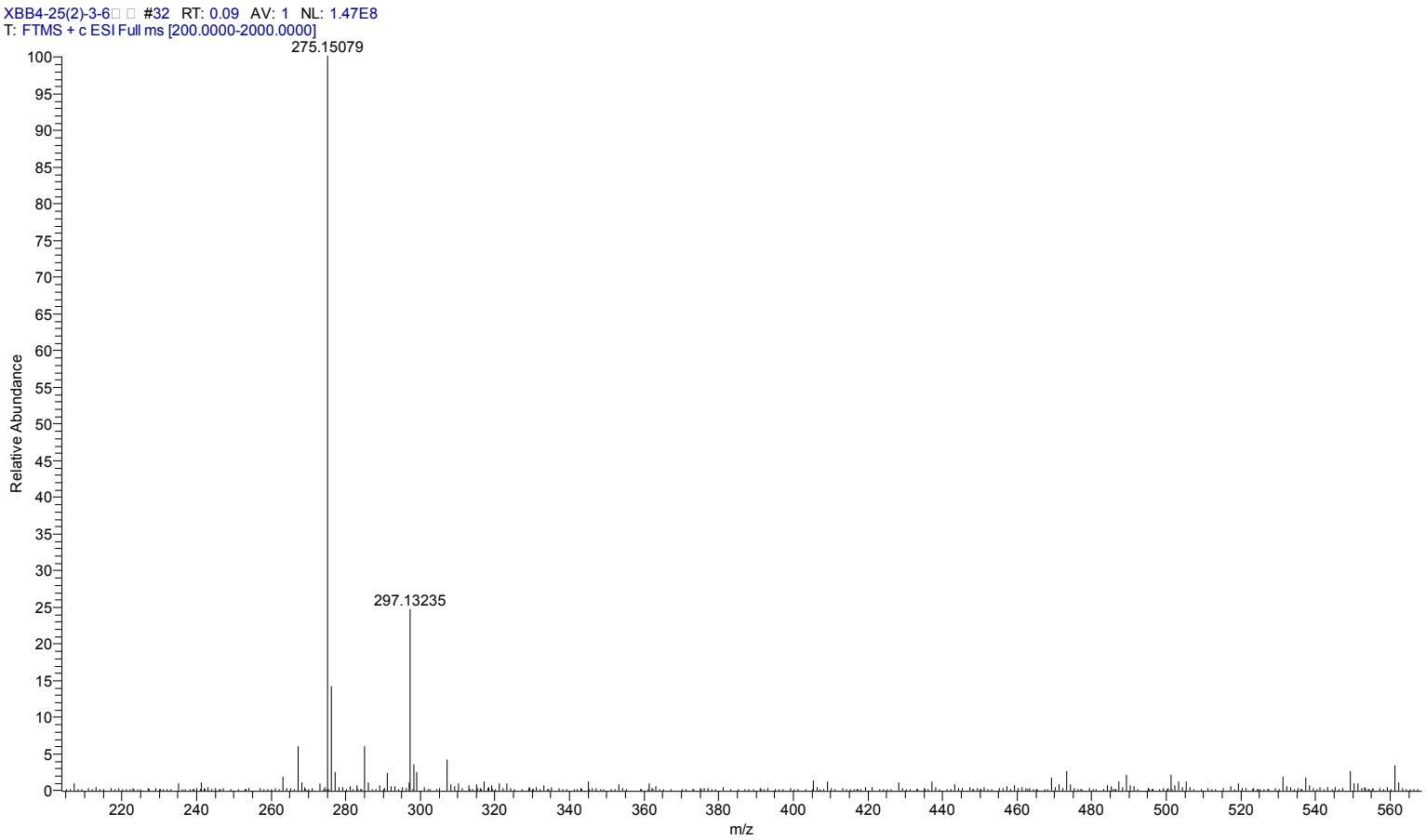


Figure S23. HMBC spectrum of aspercarboline C (**3**)



SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
275.15079	275.15025	0.54	7.5	C14 H19 O2 N4

Figure S24. HR-ESI-MS spectrum of asperdione A (**13**).

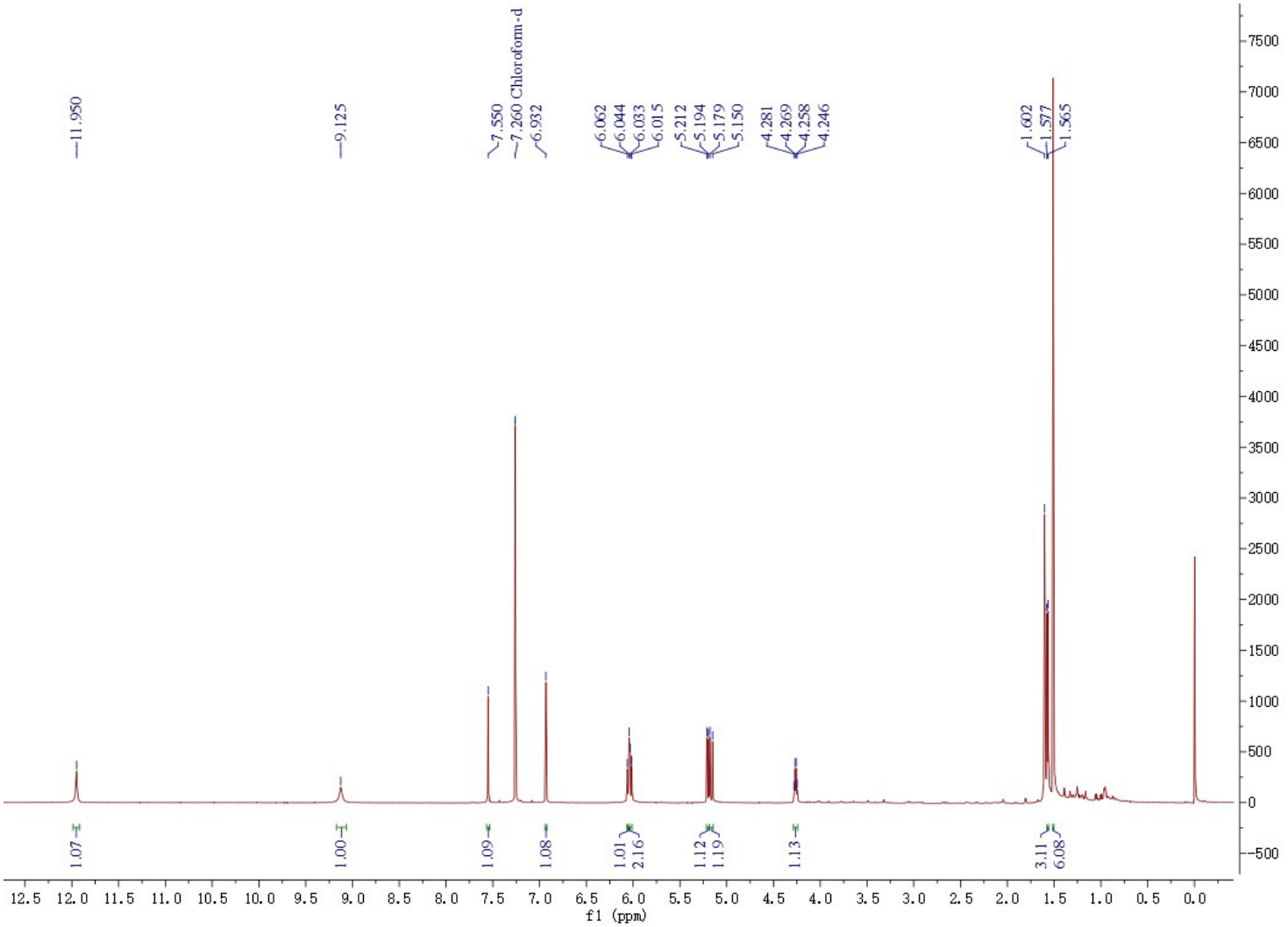


Figure S25. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of asperdione A (**13**)

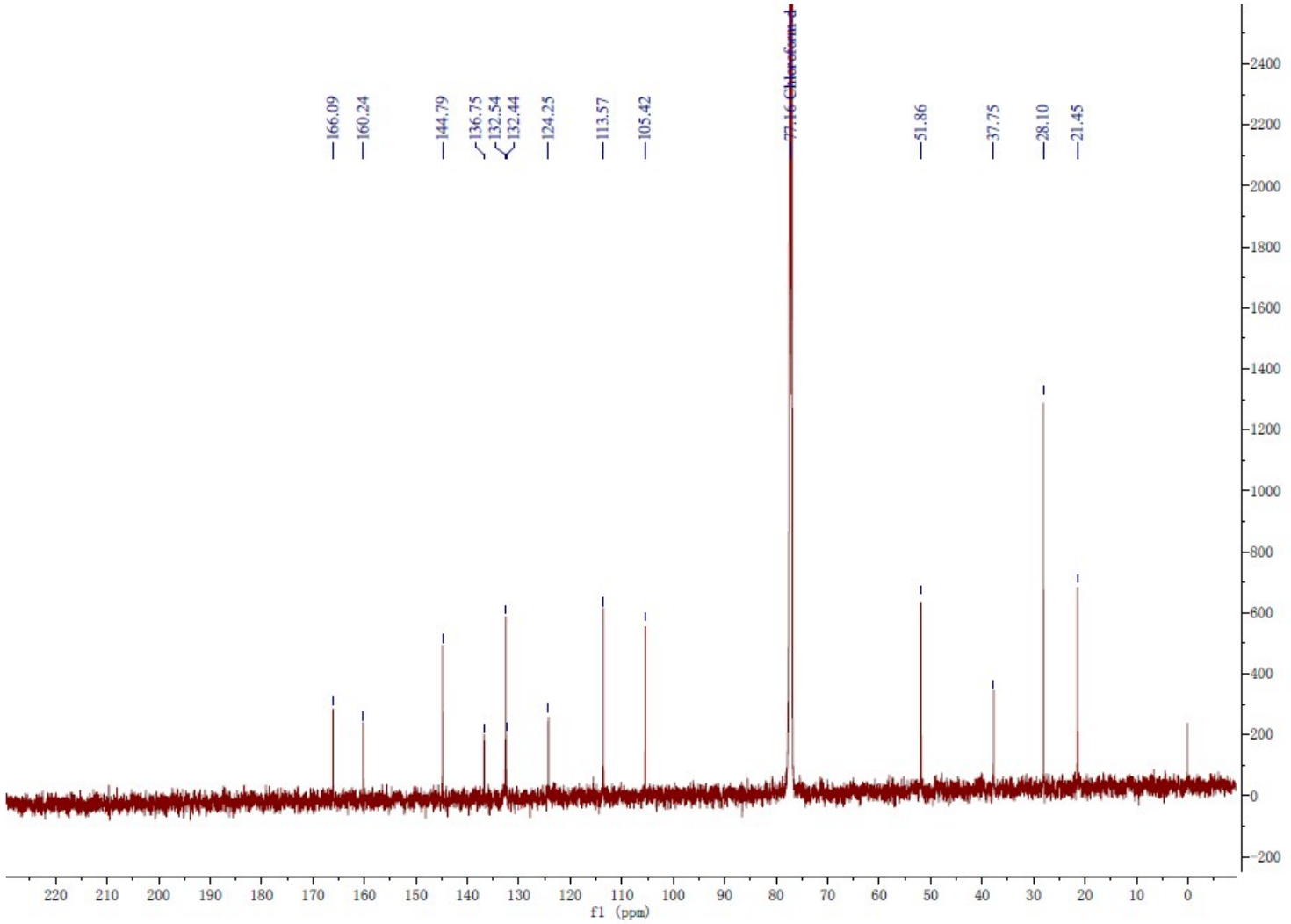


Figure S26. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of asperdione A (**13**)

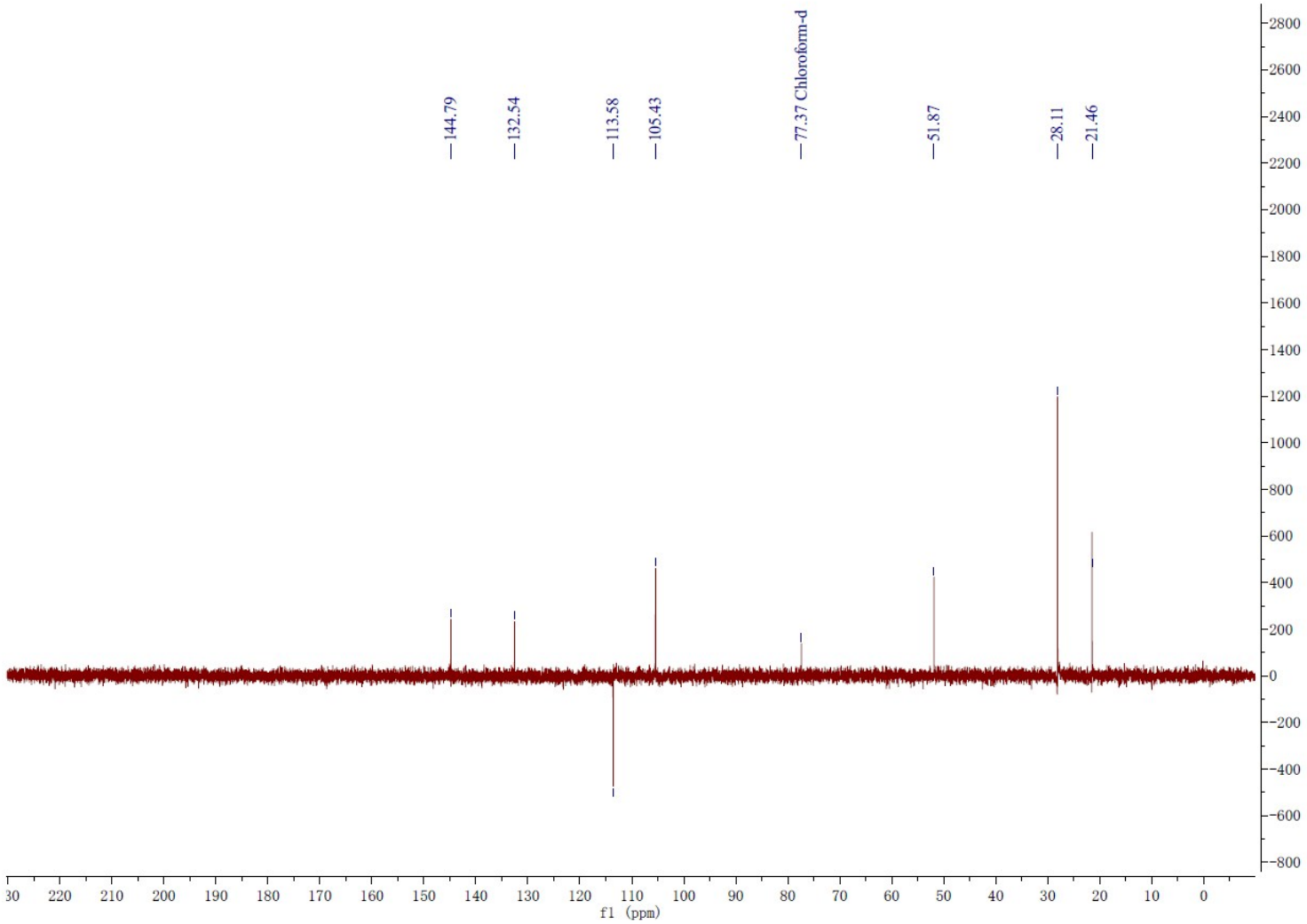


Figure S27. DEPT 135 spectrum (150 MHz, $CDCl_3$) of asperdione A (**13**)

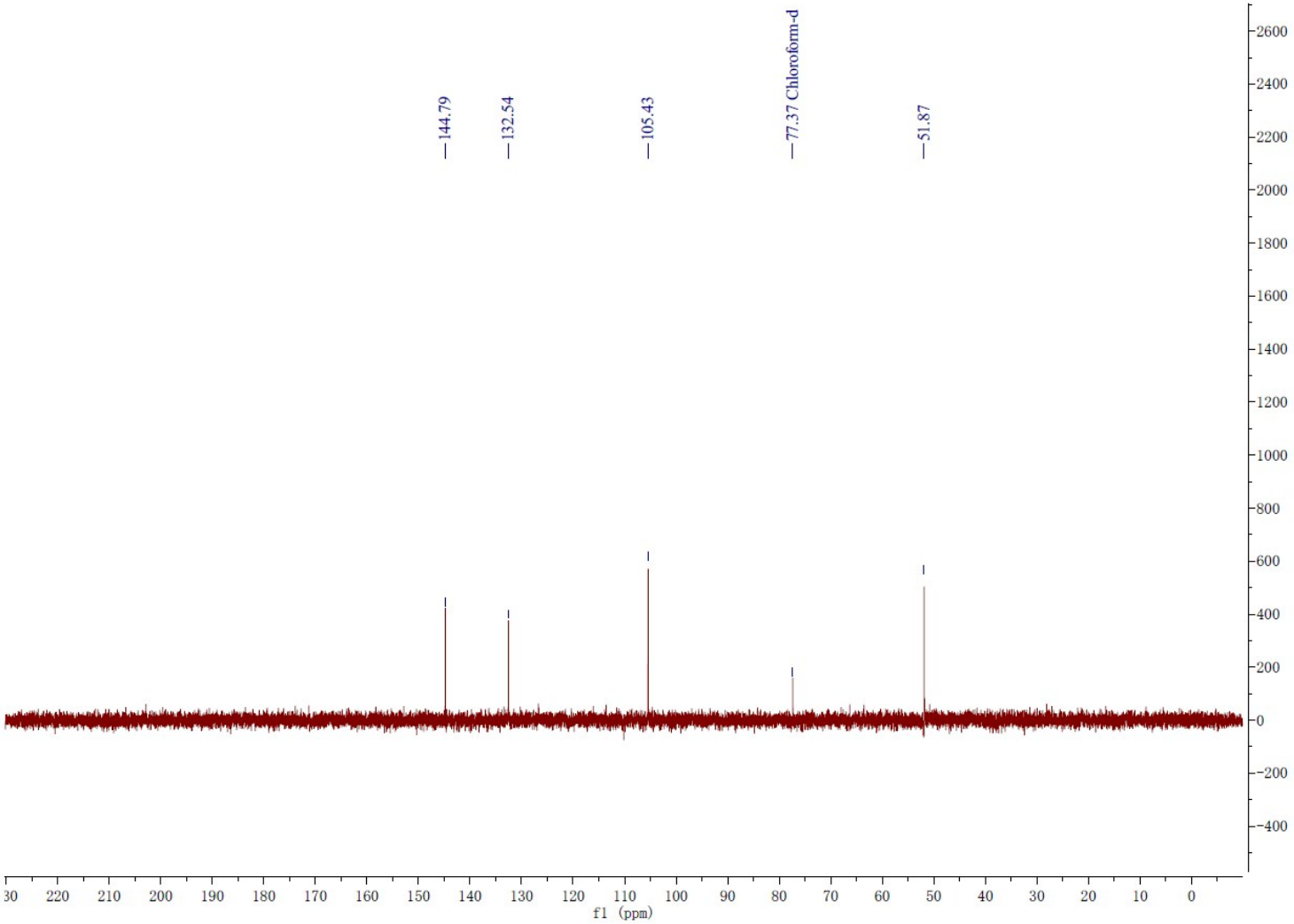


Figure S28. DEPT 90 spectrum (150 MHz, $CDCl_3$) of asperdione A (**13**)

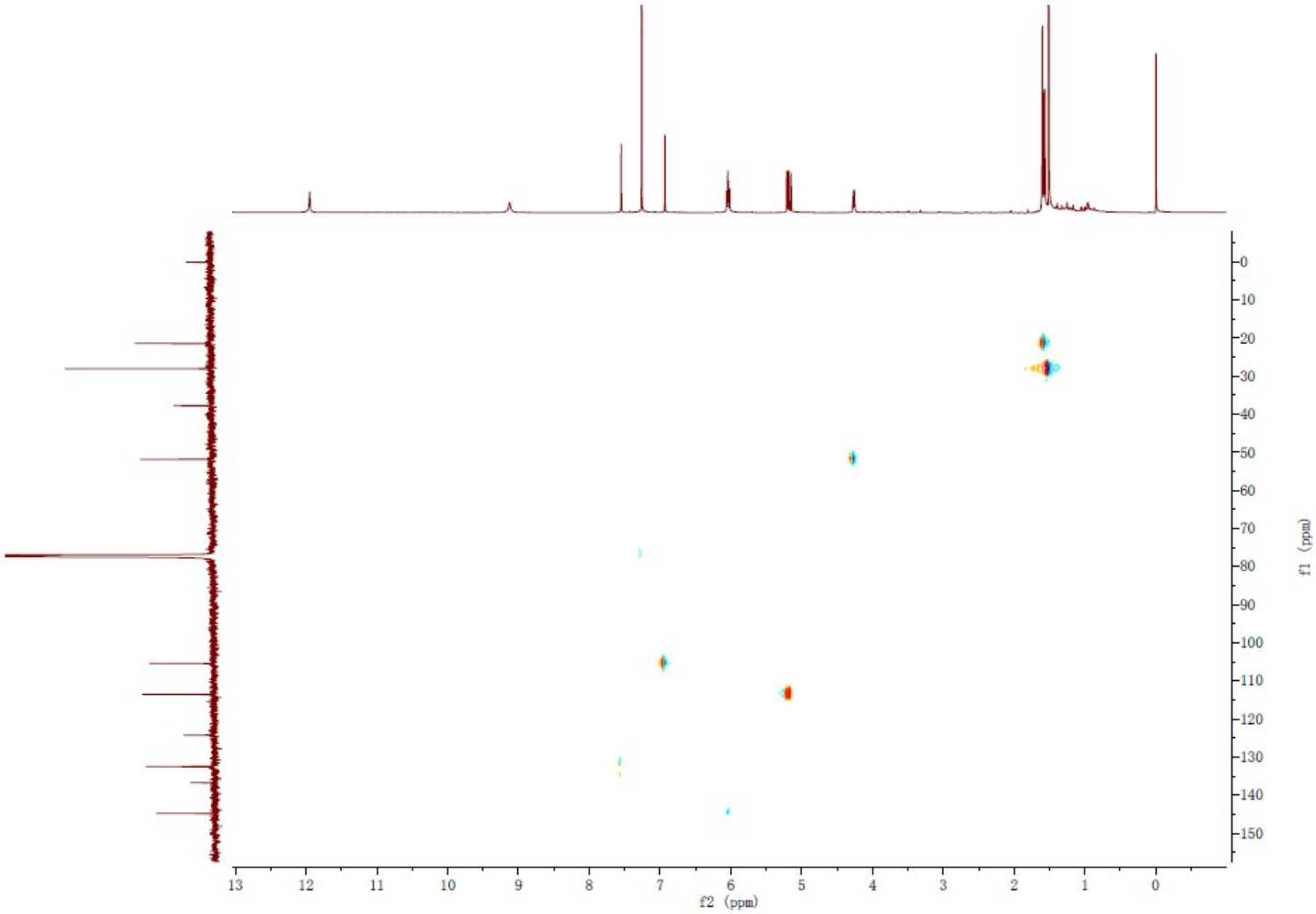


Figure S29. HSQC spectrum of asperdione A (**13**)

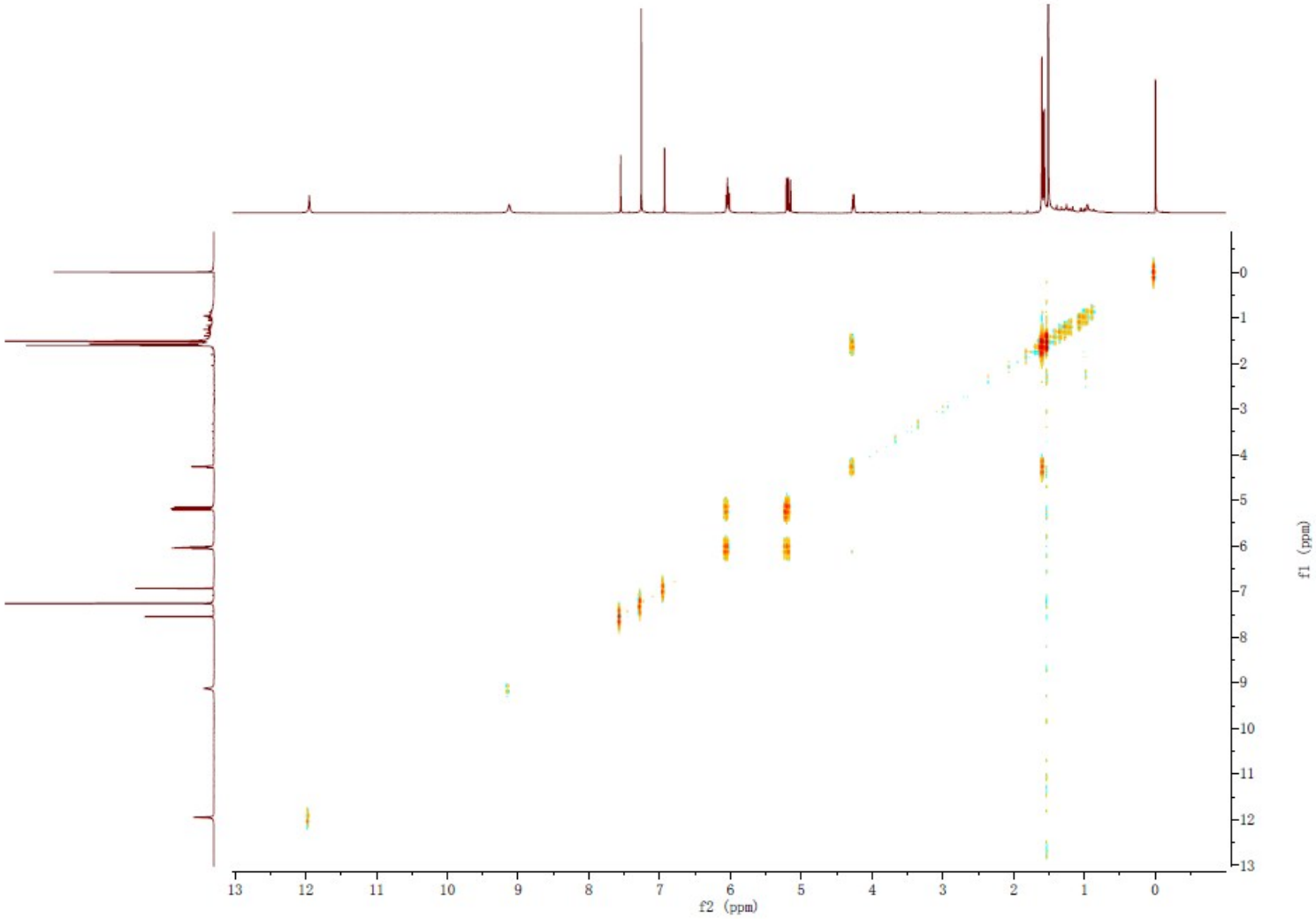


Figure S30. $^{1}H–^{1}H$ COSY spectrum of asperdione A (**13**)

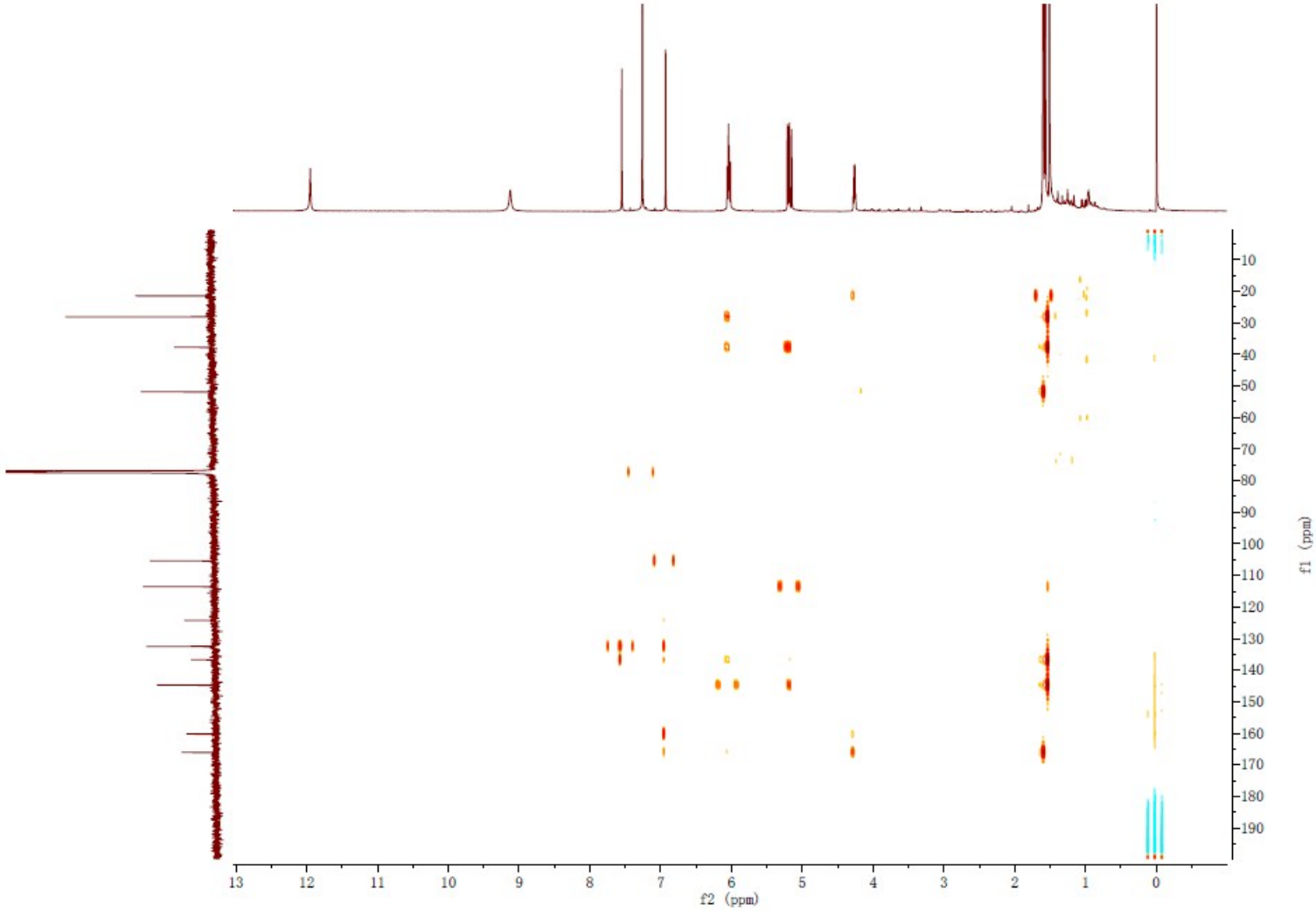


Figure S31. HMBC spectrum of asperdione A (**13**)

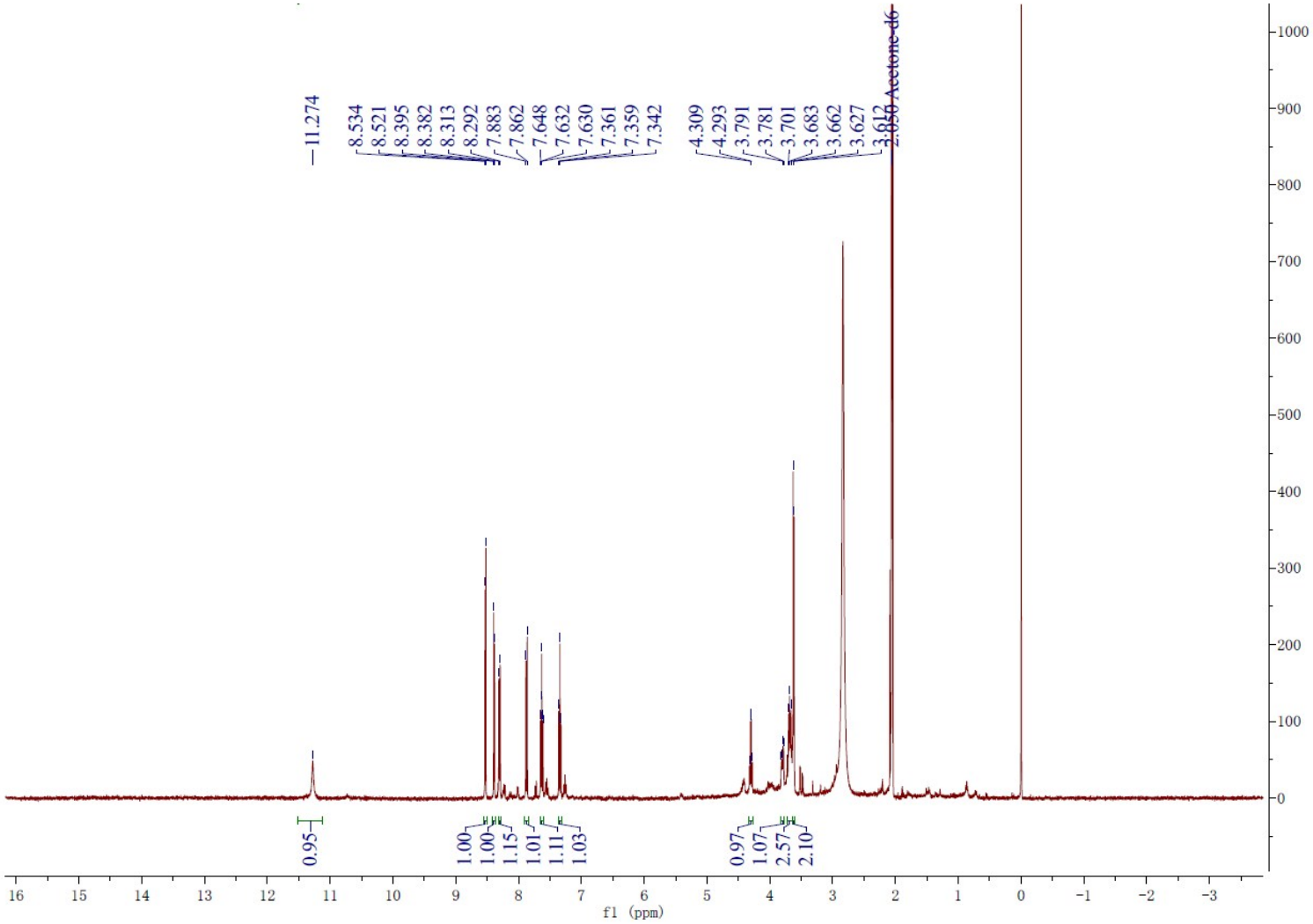


Figure S32. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of 1-(1-oxo-3,4,5-trihydroxy-1-pentyl)-β-carboline (**4**)

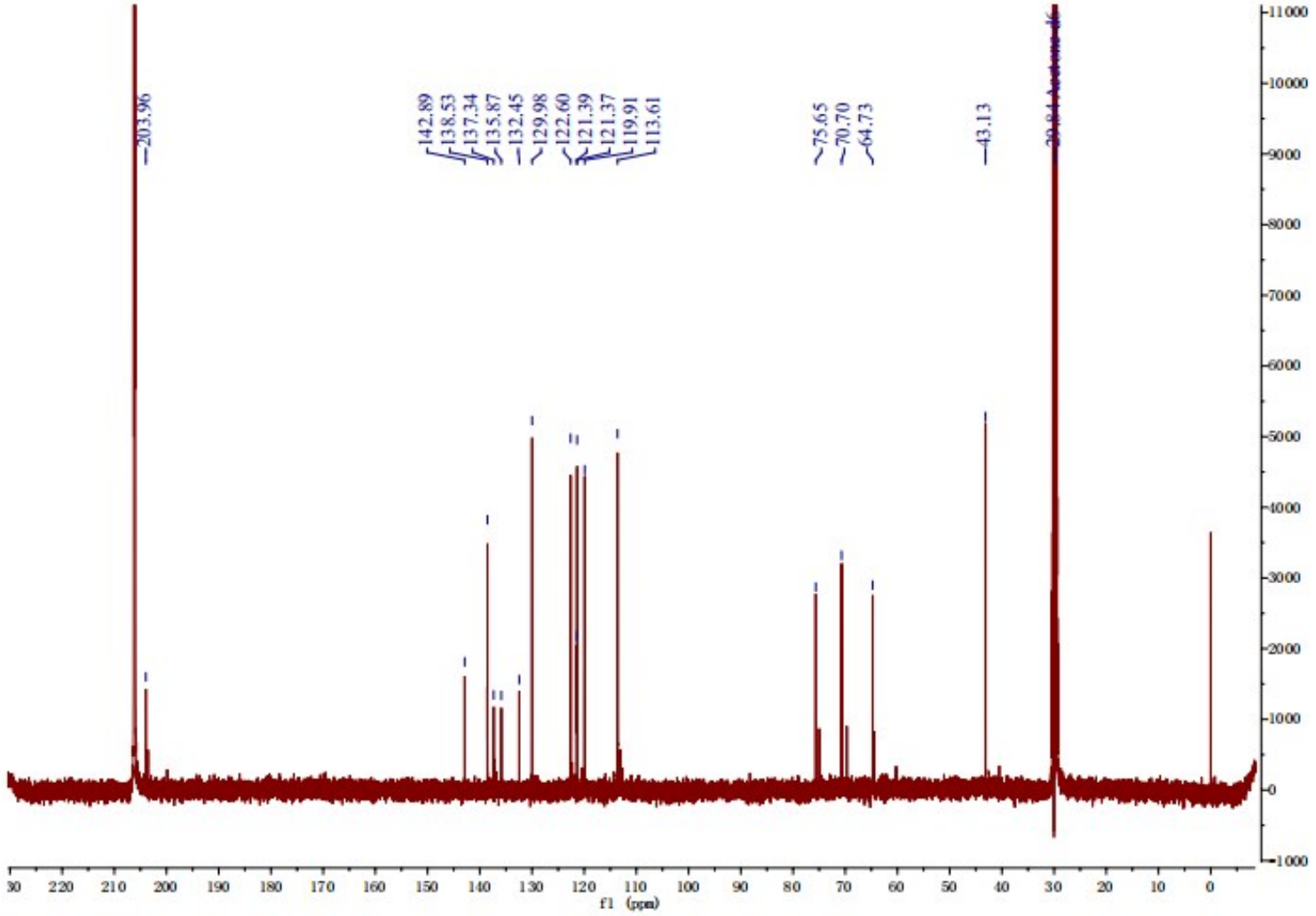
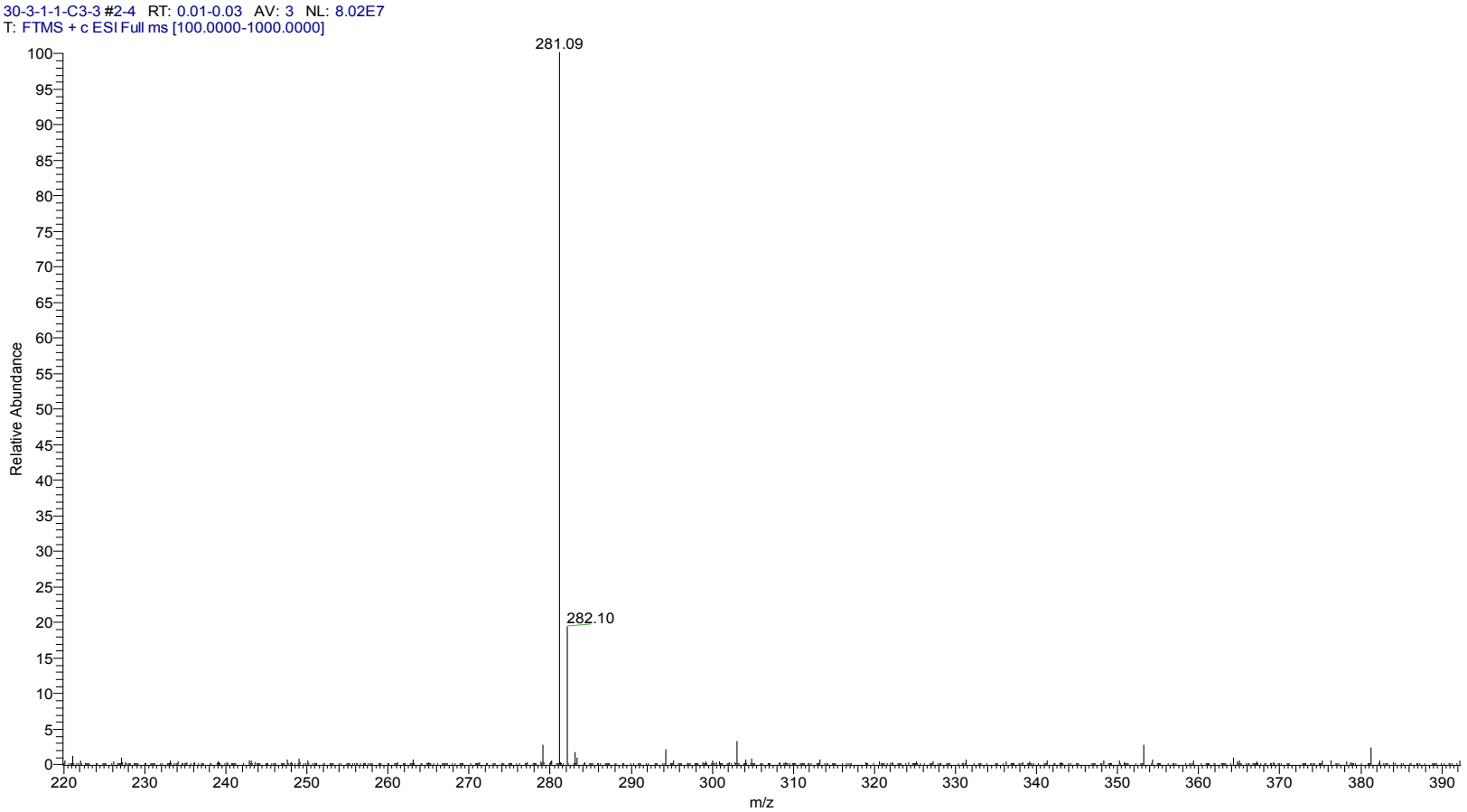


Figure S33. ^{13}C NMR spectrum (100 MHz, acetone-d_6) of 1-(1-oxo-3,4,5-trihydroxy-1-pentyl)-β-carboline (**4**)



SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
281.09241	281.09207	1.21	11.5	C16 H13 O3 N2

Figure S34. HR-ESI-MS spectrum of 4-(9*H*-β-Carbolin-1-yl)-4-oxobut-2-enoic acid methyl ester (**5**).

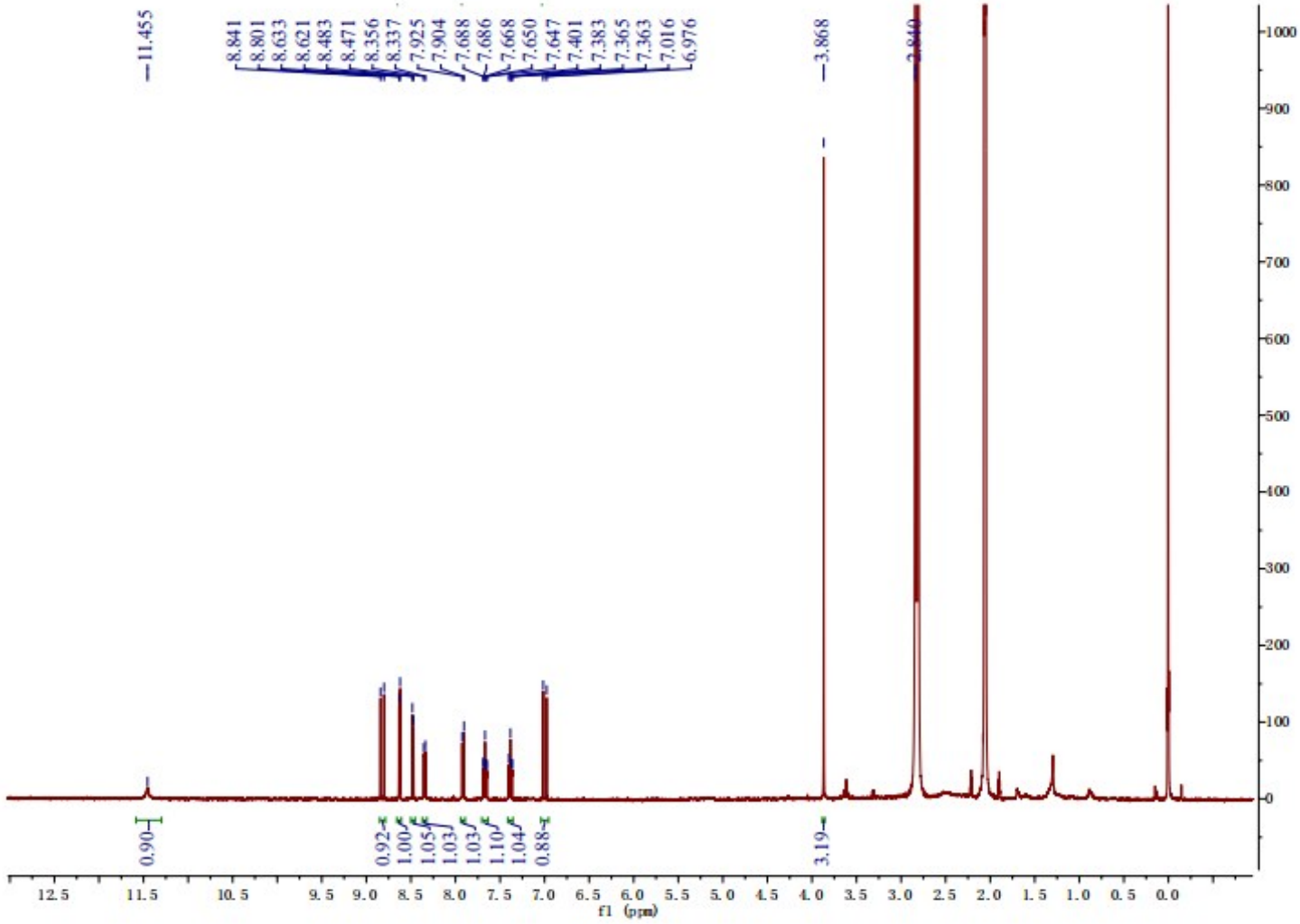


Figure S35. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of 4-(9*H*-β-Carbolin-1-yl)-4-oxobut-2-enoic acid methyl ester (**5**)

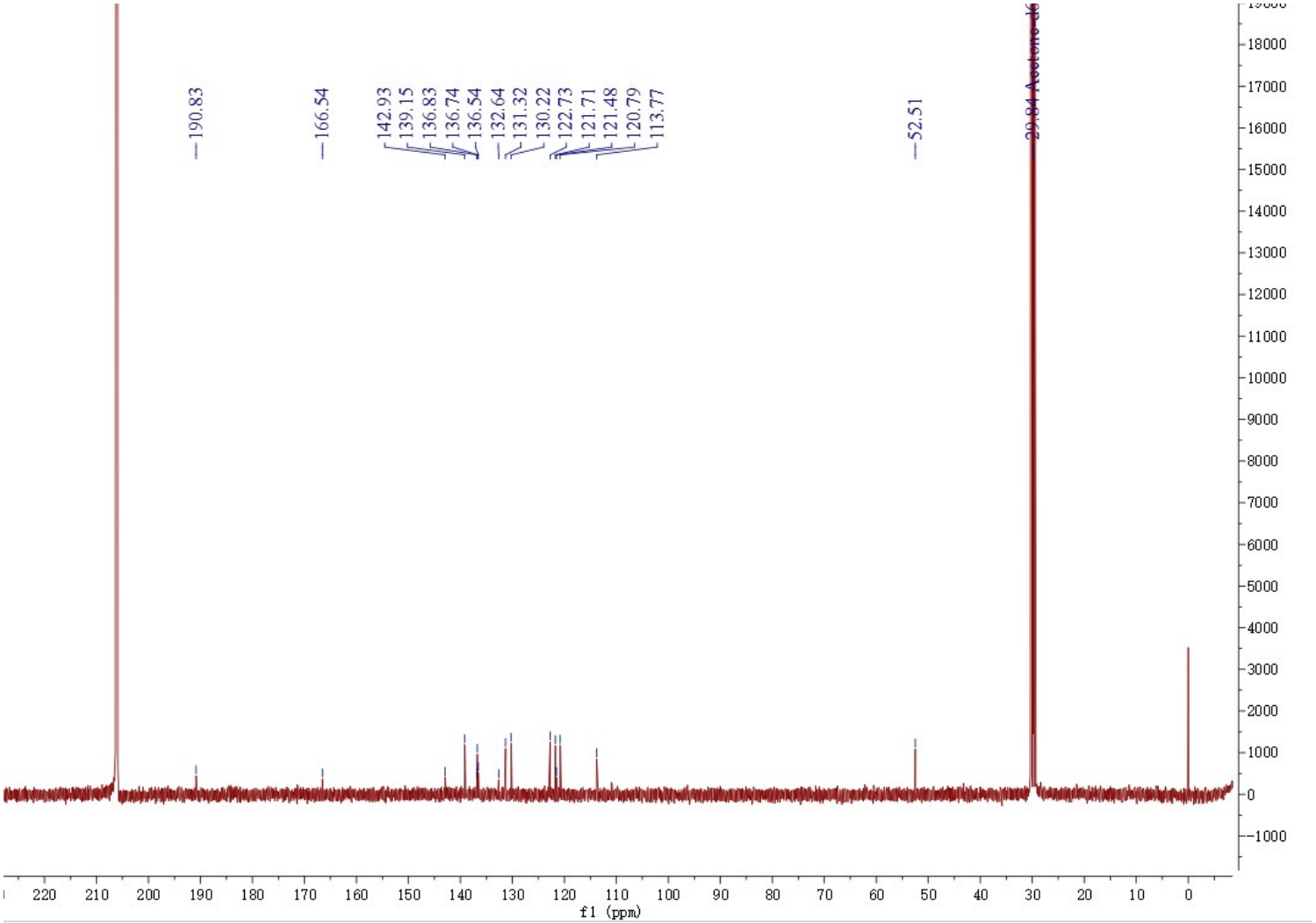


Figure S36. ^{13}C NMR spectrum (100 MHz, acetone-d_6) of 4-(9*H*-β-Carbolin-1-yl)-4-oxobut-2-enoic acid methyl ester (**5**)

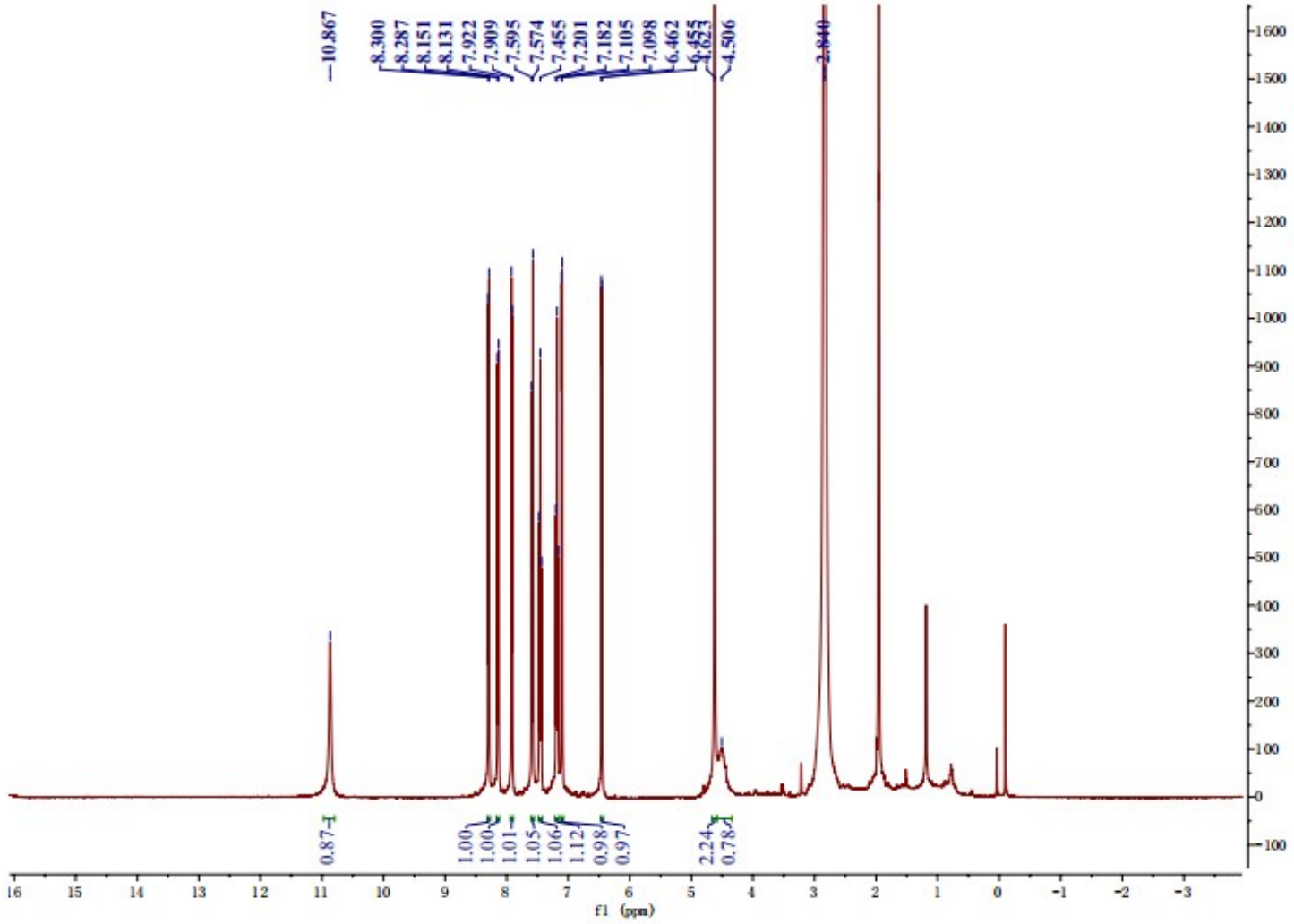


Figure S37. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of perlolyrin (**6**)

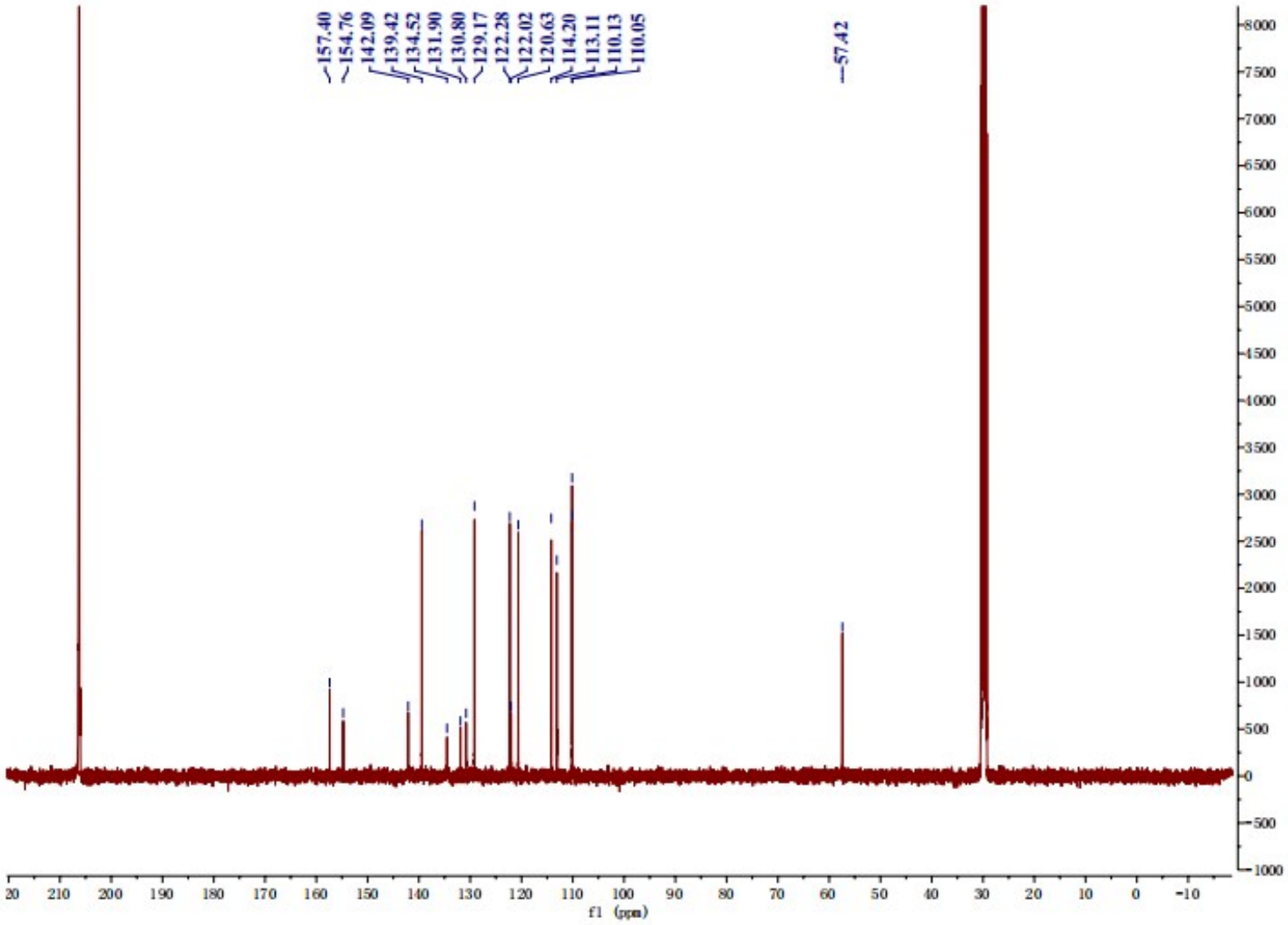


Figure S38. ^{13}C NMR spectrum (100 MHz, acetone-d_6) of perlolyrin (**6**)

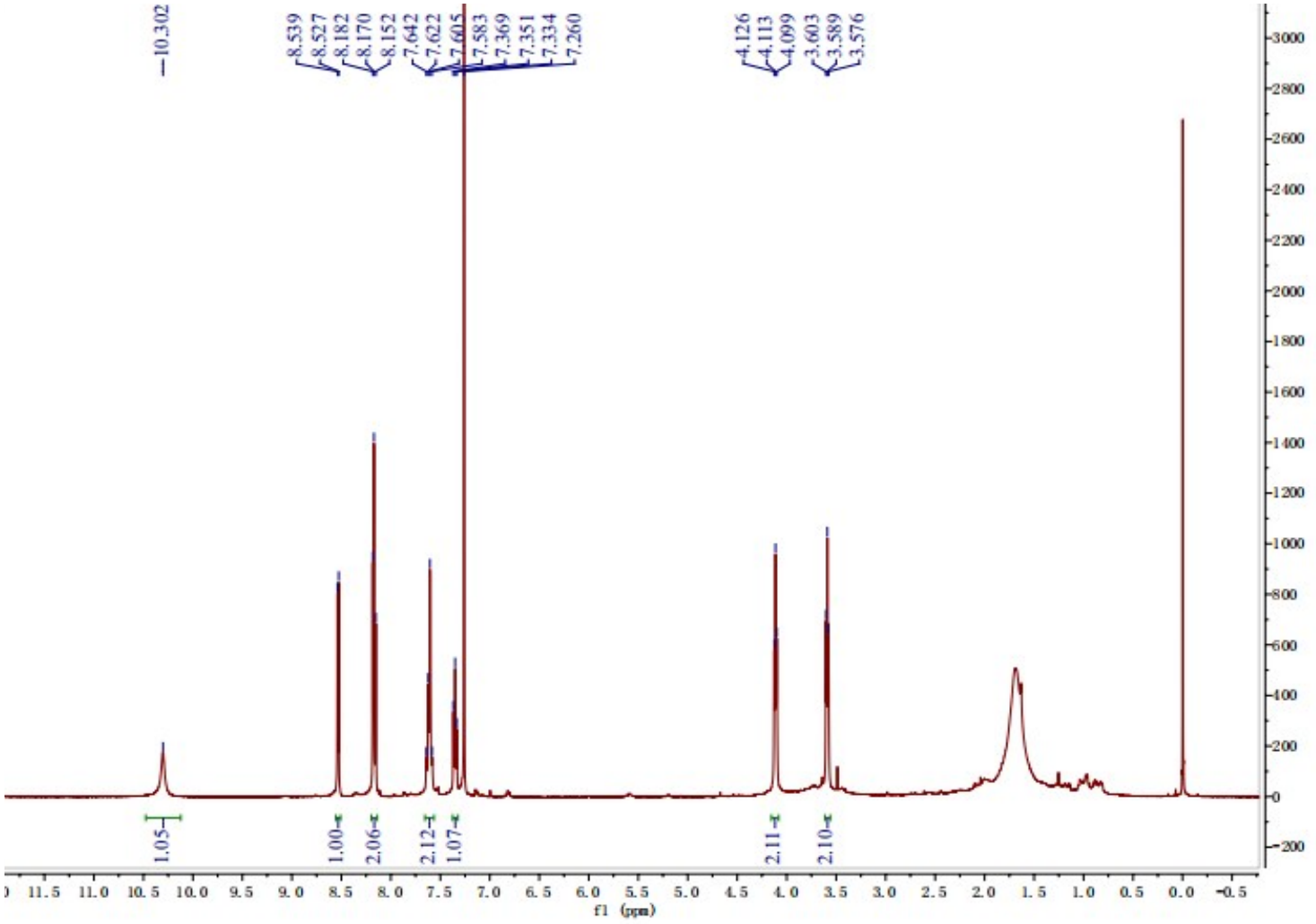


Figure S39. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-(9*H*-β-carbolin-1-yl)-3-hydroxy-propan-1-one (**7**)

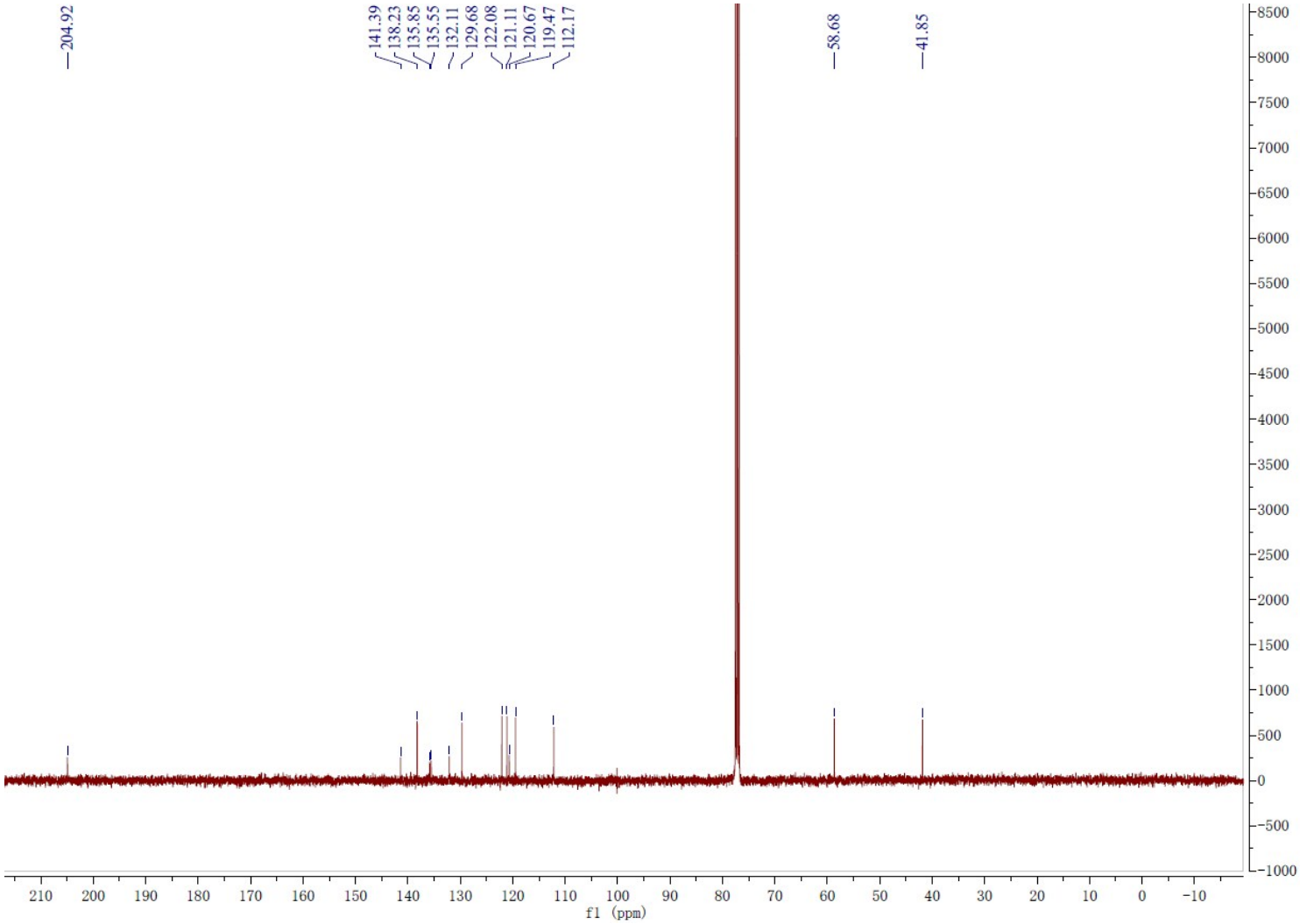


Figure S40. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1-(9*H*-β-carbolin-1-yl)-3-hydroxy-propan-1-one (**7**)

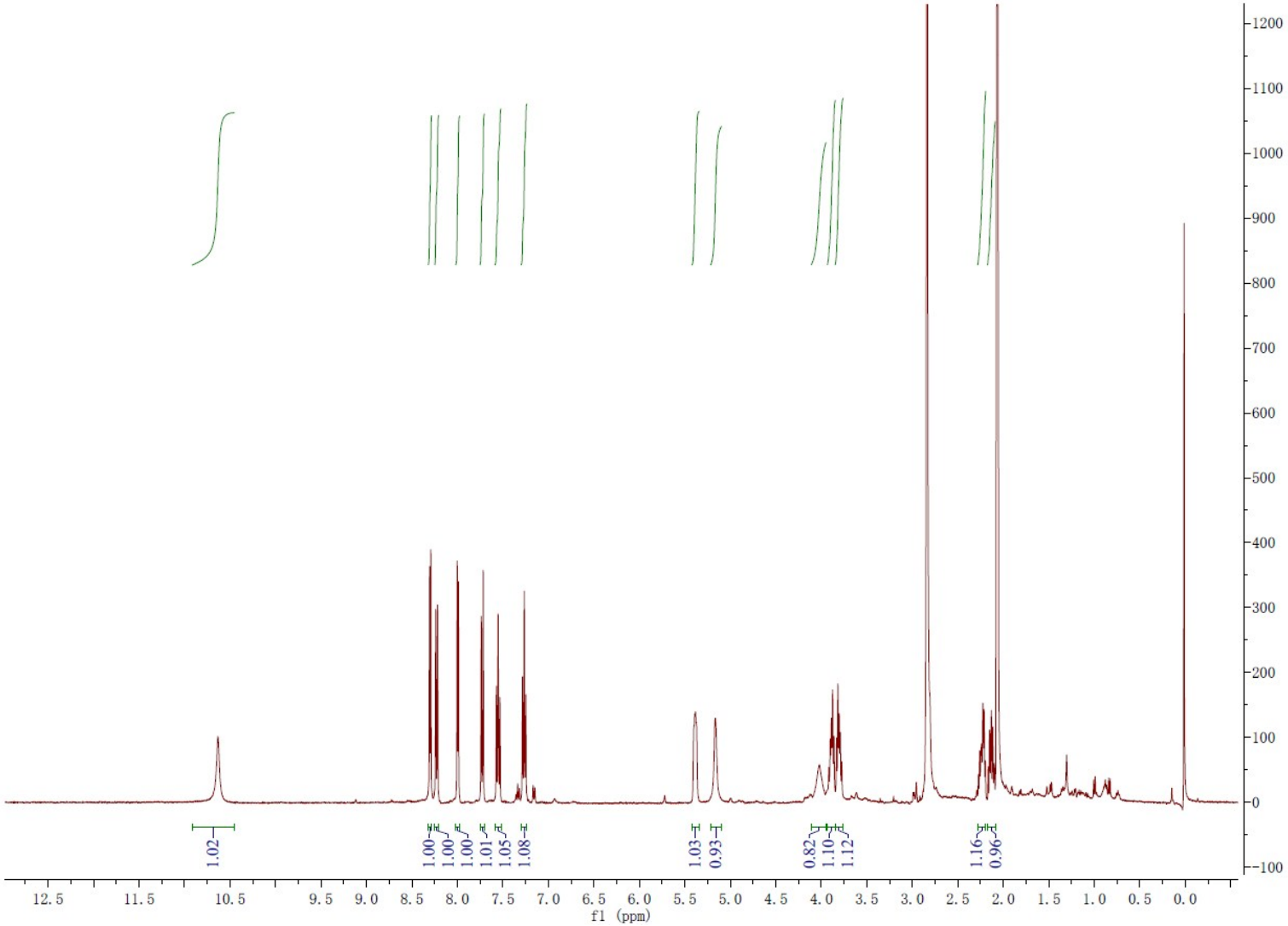


Figure S41. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of cordysinin E (**8**)

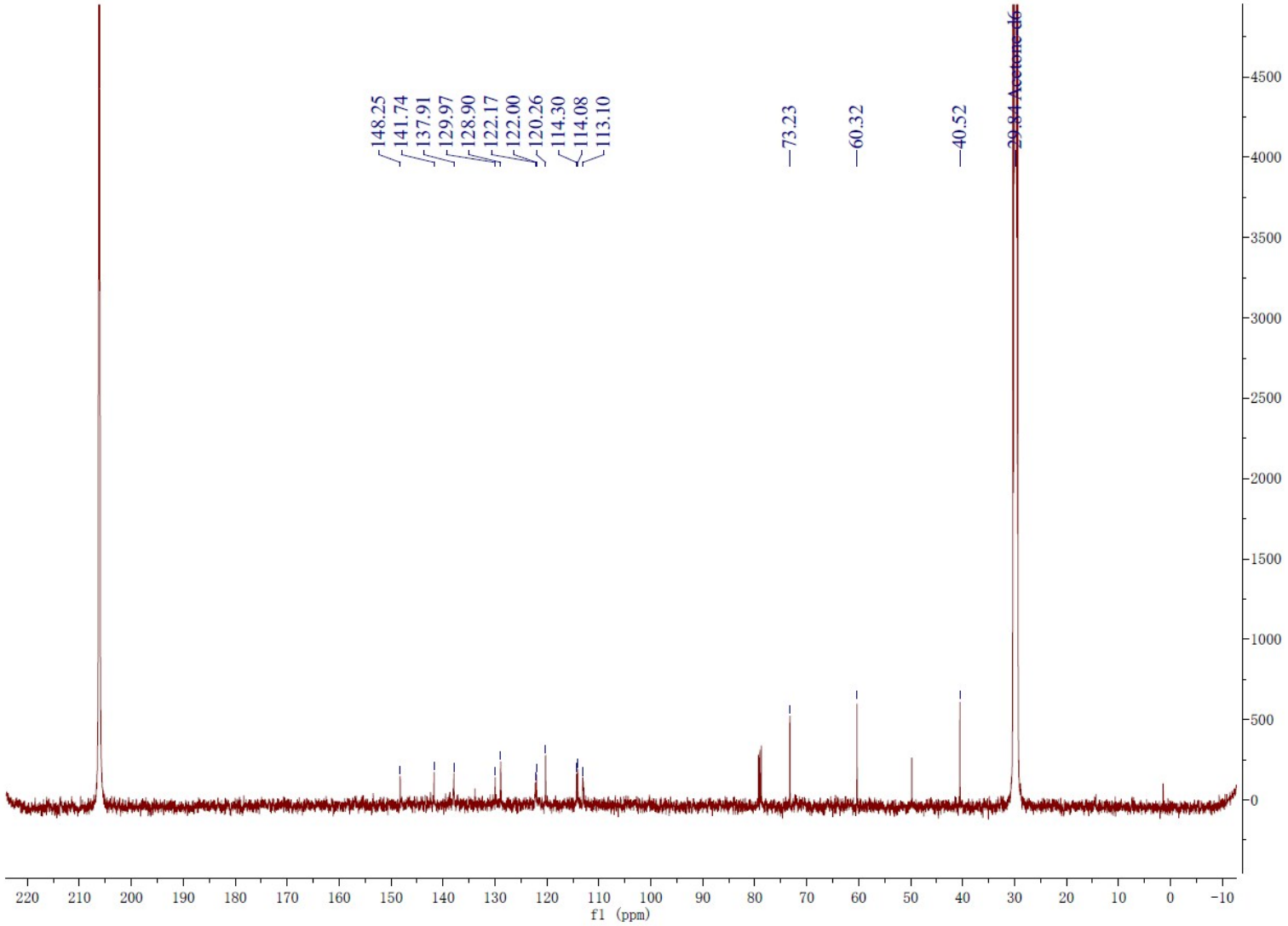


Figure S42. ^{13}C NMR spectrum (100 MHz, acetone-d_6) of cordysinin E (**8**)

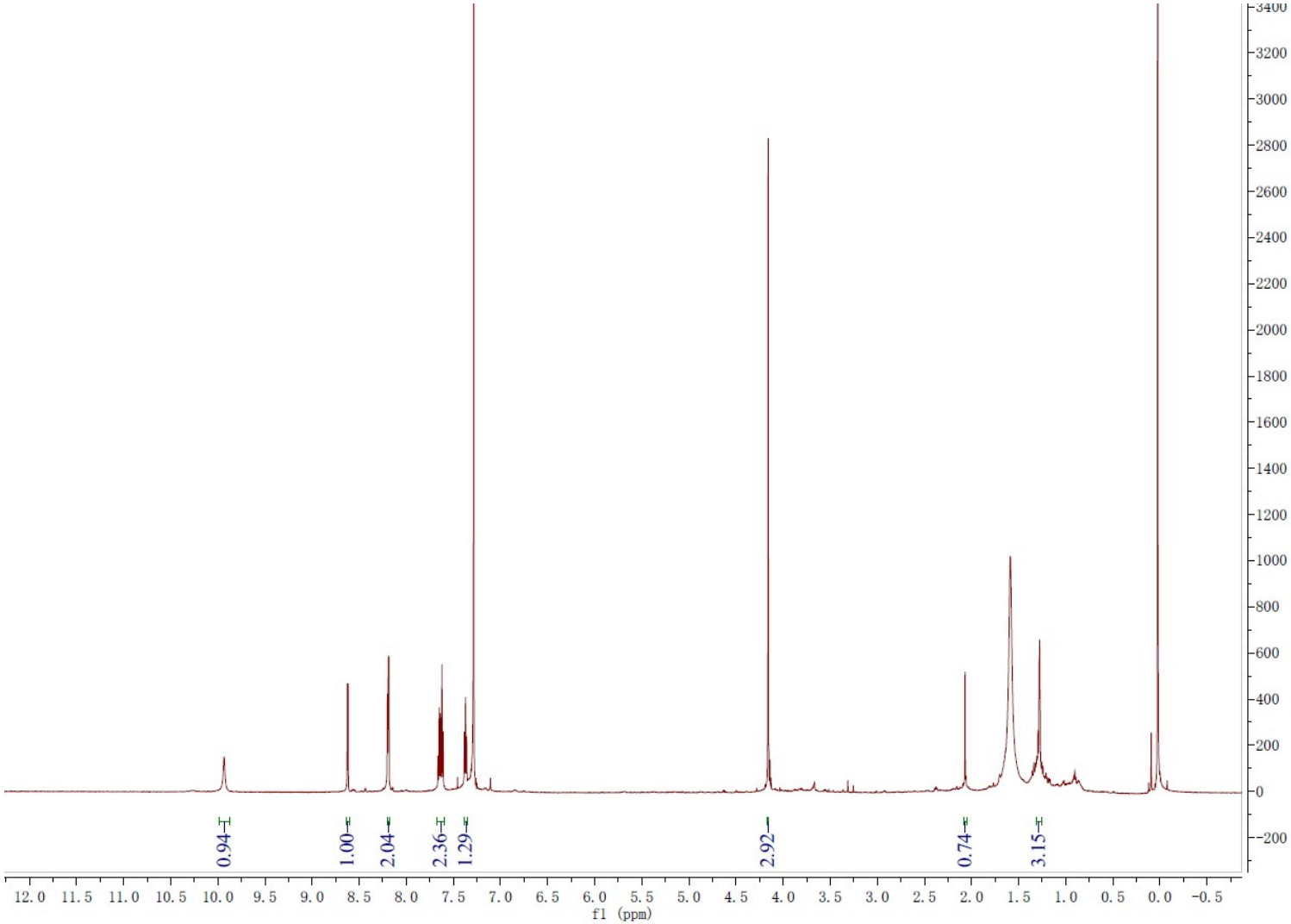


Figure S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-methoxycarbonyl-β-carboline (**9**)

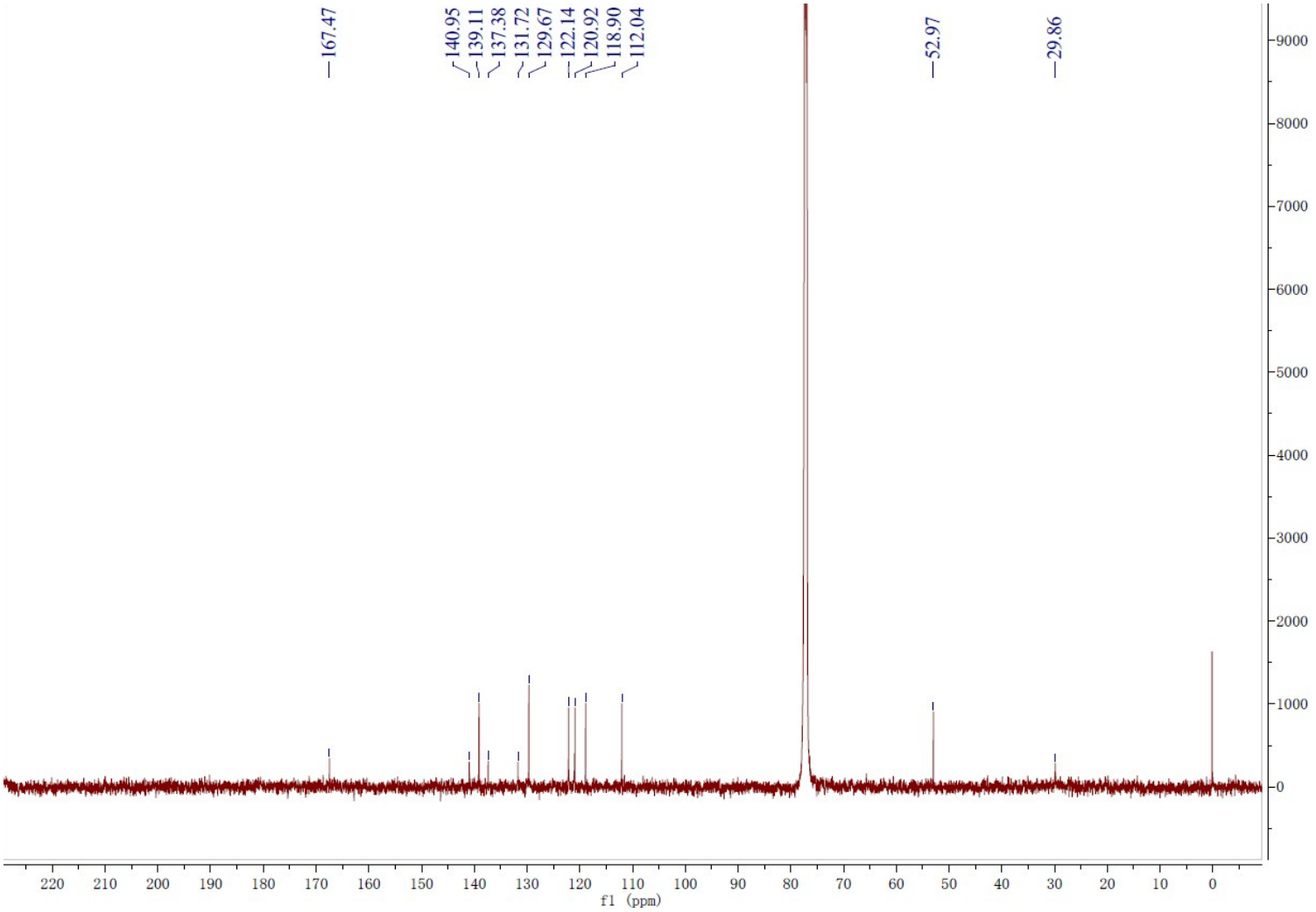


Figure S44. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1-methoxycarbonyl-β-carboline (**9**)

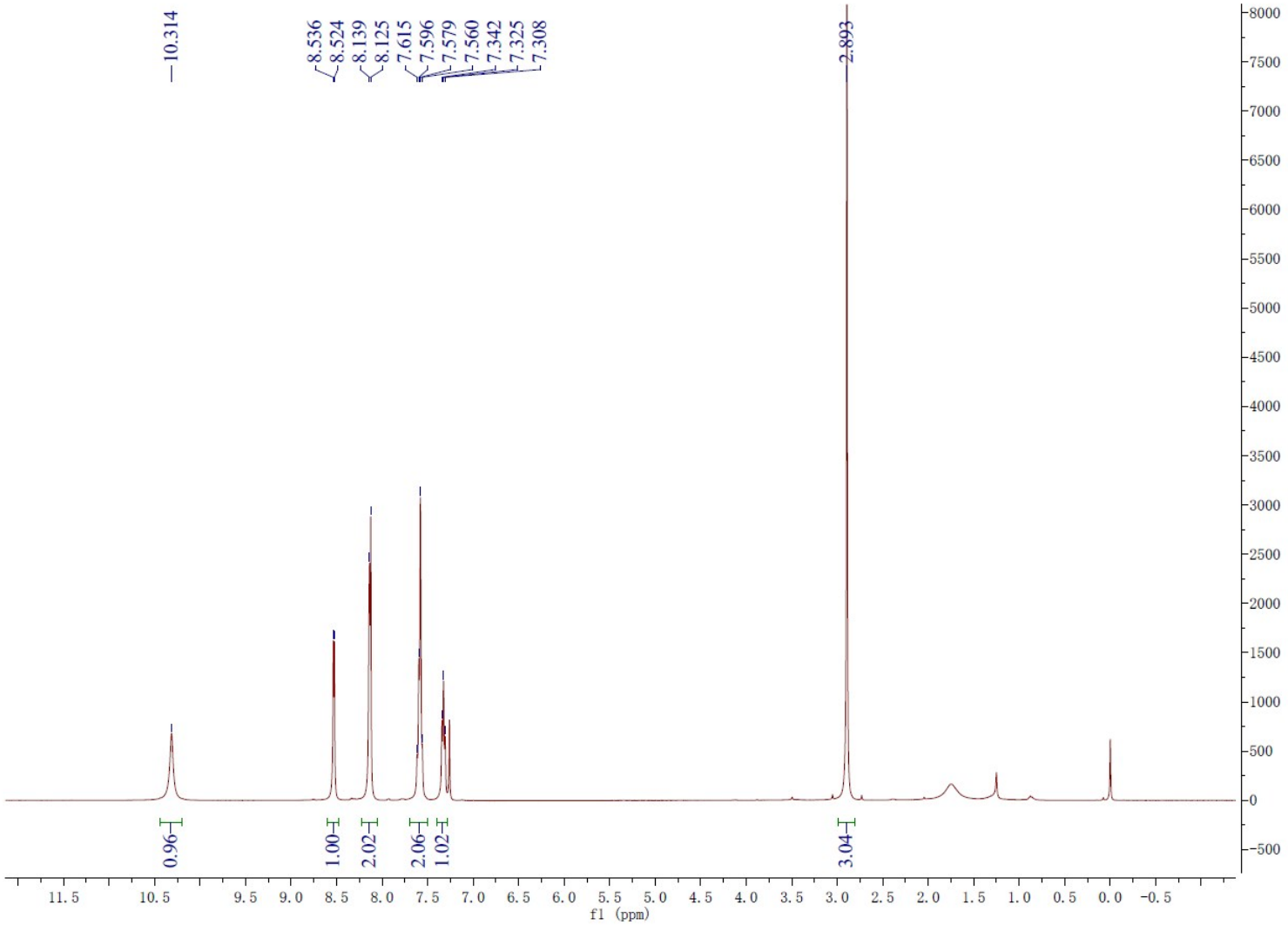


Figure S45. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-acetyl-β-carboline (**10**)

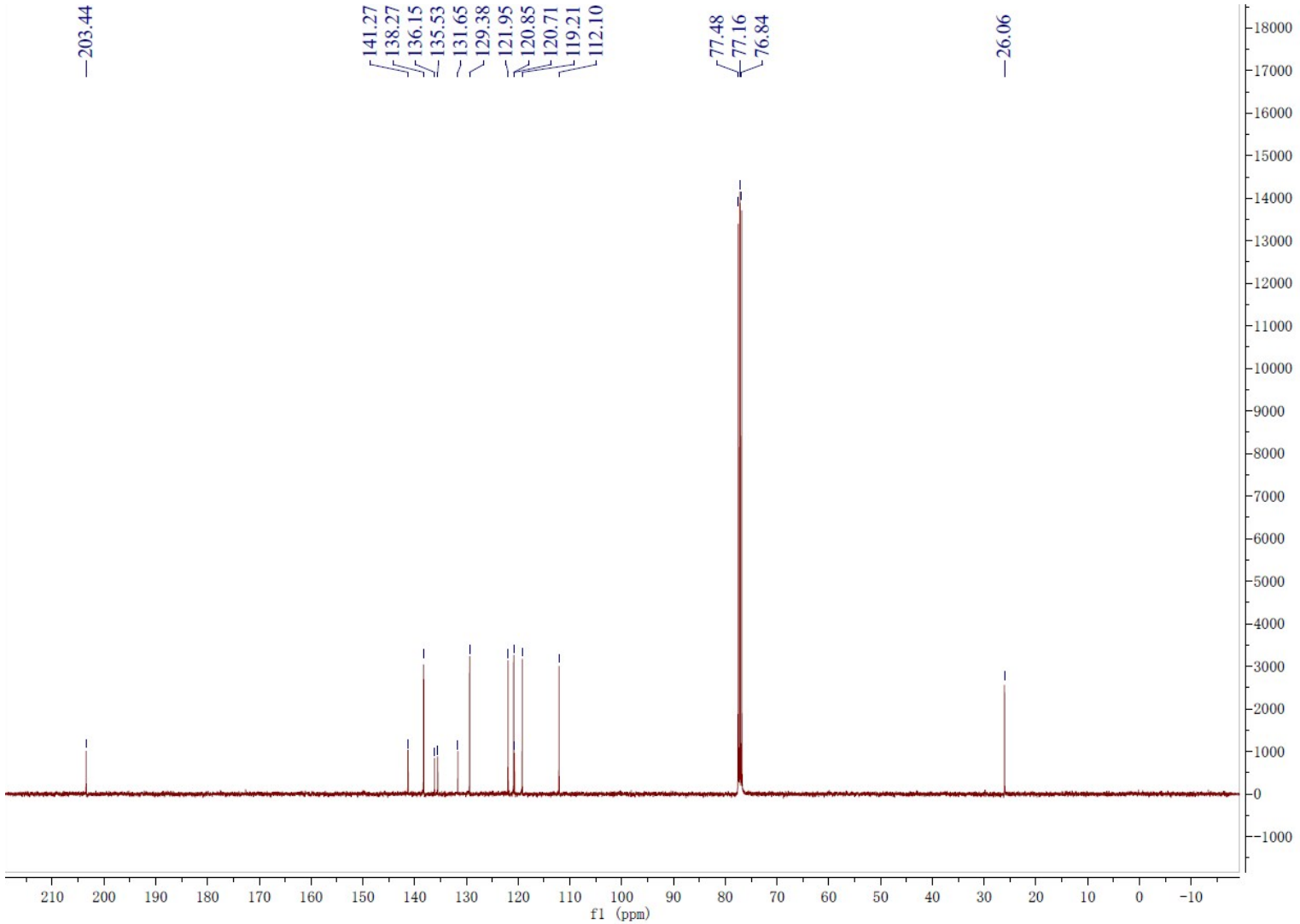


Figure S46. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1-acetyl-β-carboline (**10**)

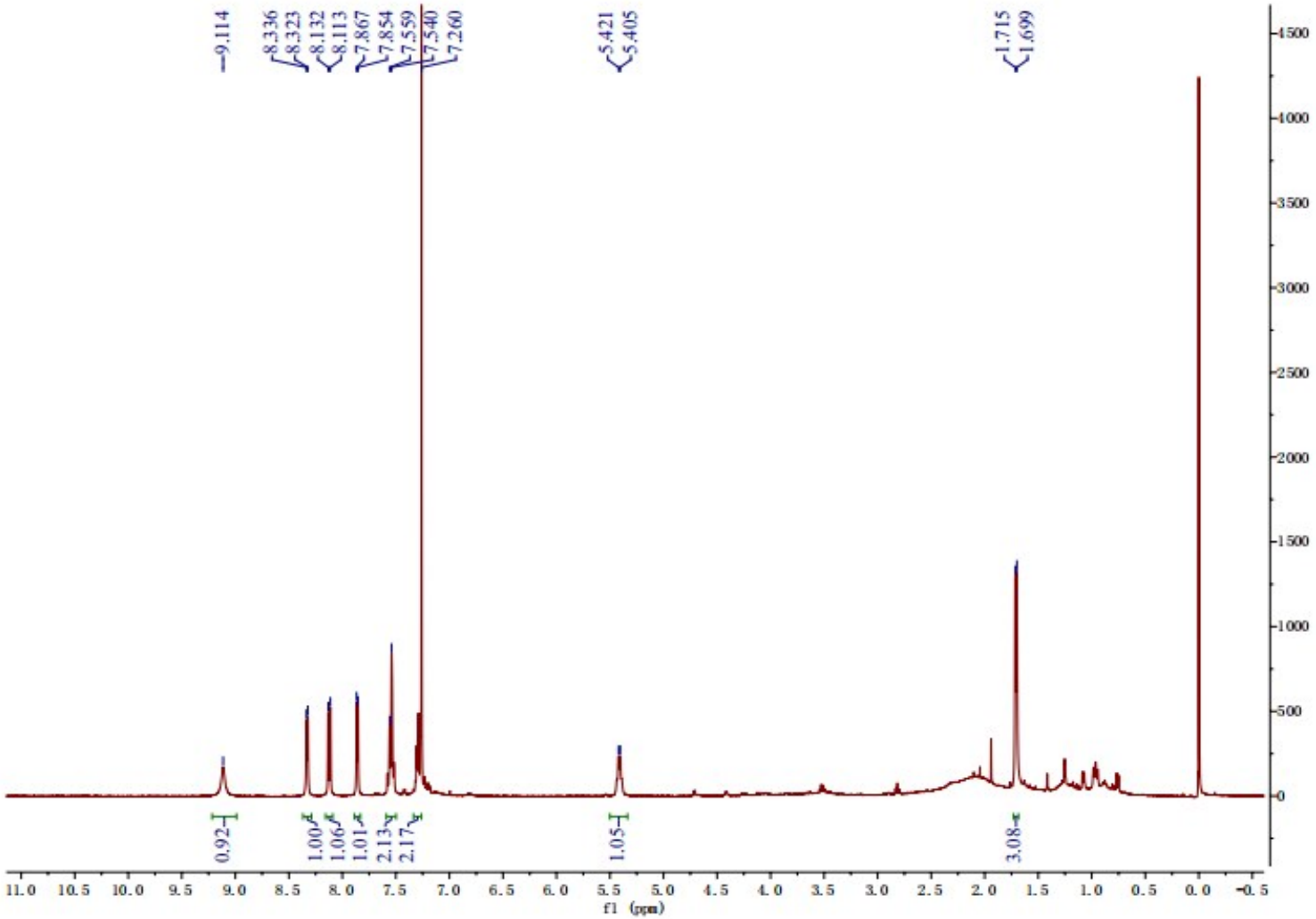


Figure S47. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of cordysinin C (**11**)

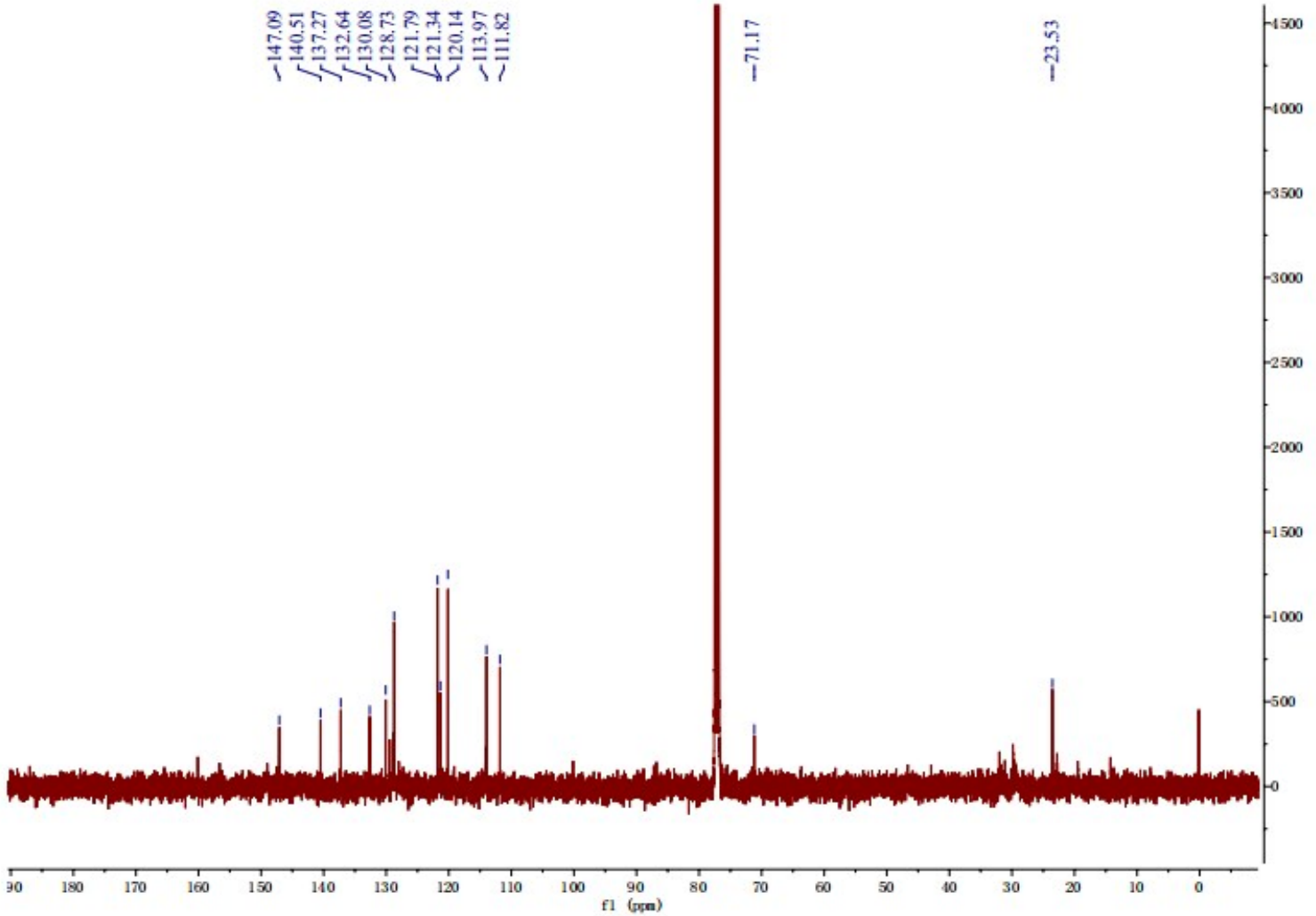


Figure S48. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of cordysinin C (**11**)

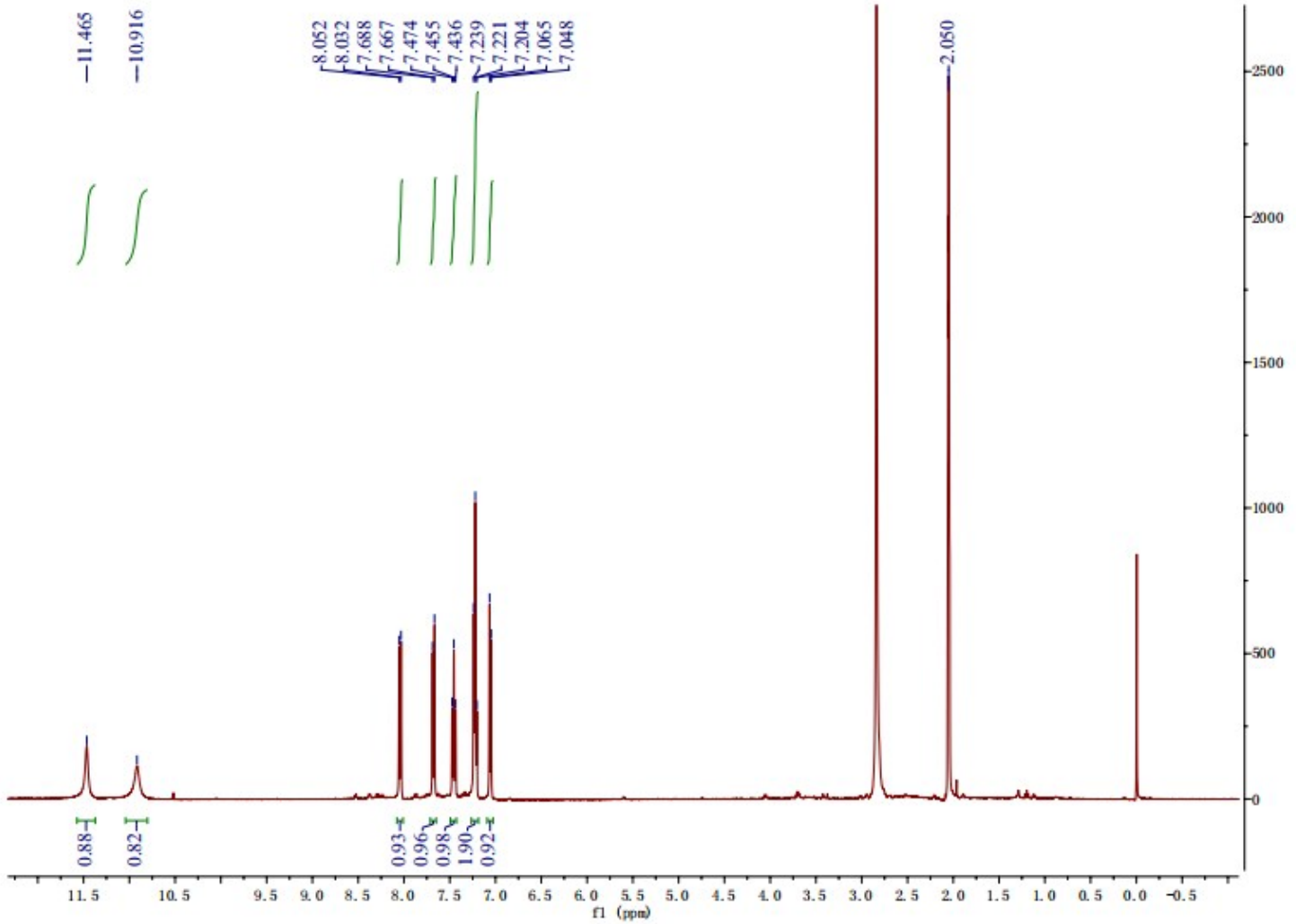


Figure S49. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of 3-hydroxy-β-carboline (**12**)

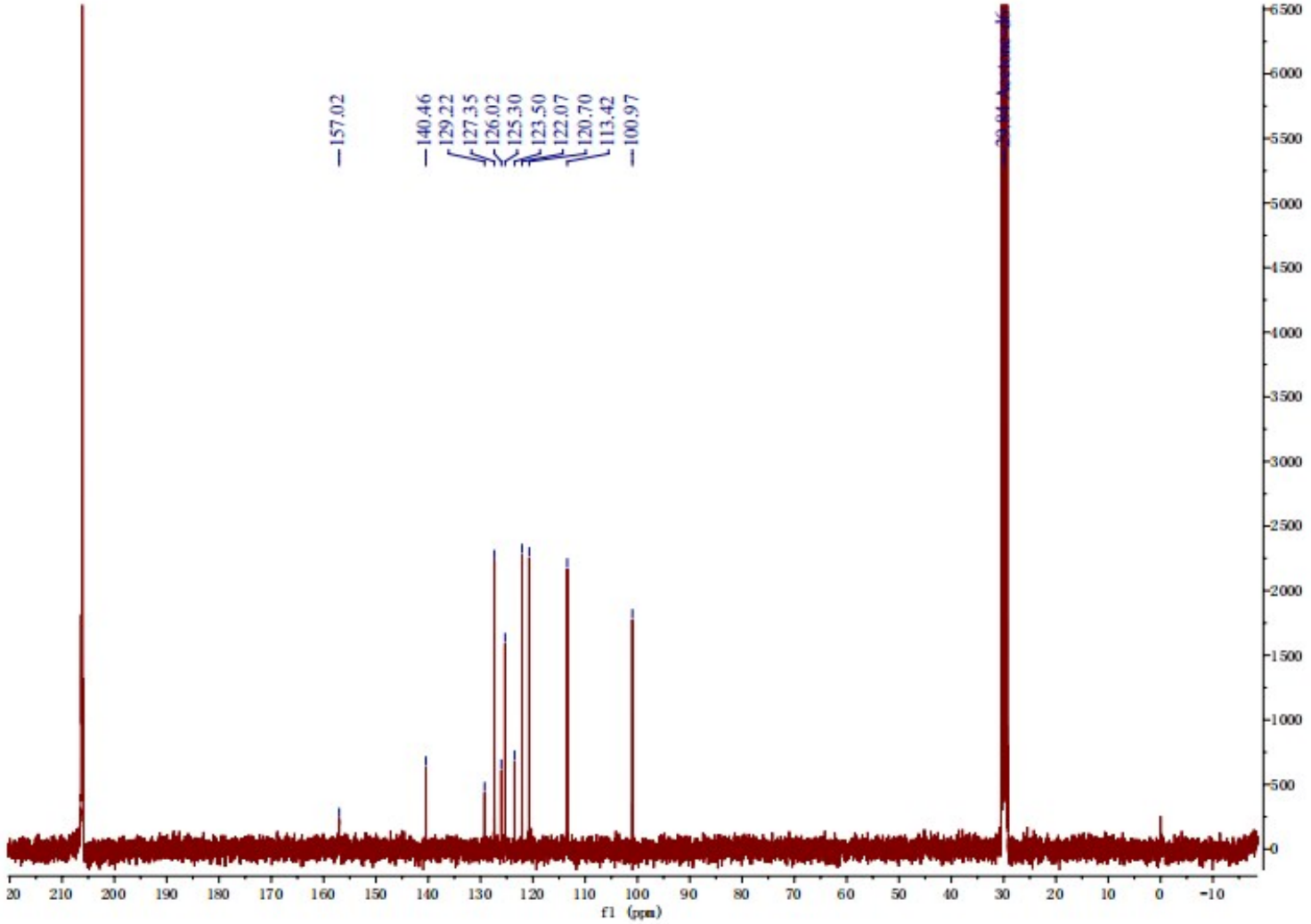


Figure S50. ^{13}C NMR spectrum (100 MHz, acetone-d_6) of 3-hydroxy-β-carboline (**12**)

Table S1. Composition of each nutrient source in different culture media

Composition of Nutrient Sources*	Culture Media (g/L)							
	A	B	C	D	E	F	G	H
salt	0.0	0.0	30.0	30.0	0.0	0.0	30.0	30.0
glucose	15.0	15.0	15.0	15.0	0.0	0.0	0.0	0.0
peptone	10.0	10.0	10.0	10.0	0.0	0.0	0.0	0.0
yeast extract	2.0	2.0	2.0	2.0	0.0	0.0	0.0	0.0
L-lysine	0.0	2.0	0.0	2.0	0.0	2.0	0.0	2.0
phenylalanine	0.0	2.0	0.0	2.0	0.0	2.0	0.0	2.0
L-threonine	0.0	2.0	0.0	2.0	0.0	2.0	0.0	2.0
L-tryptophan	0.0	2.0	0.0	2.0	0.0	2.0	0.0	2.0
L-methionine	0.0	2.0	0.0	2.0	0.0	2.0	0.0	2.0
nicotinamide	0.0	1.0	0.0	1.0	0.0	1.0	0.0	1.0
folic acid	0.0	1.0	0.0	1.0	0.0	1.0	0.0	1.0

* In the solid culture medium, the ratio of rice to the solution containing above composition is 60 g: 100 mL

Each kind of liquid culture medium contained 2 L materials in total while the solid one contained 300 g. All the media were sterilized at 120 °C for 30 min. After the fermentation media were cold, fungal mycelia were cut and transferred aseptically into them. The fungi were incubated at 28 ℃ for 30 days. Then fungi cultured in liquid media were extracted by EtOAc for three times while the solid ones were extracted by MeOH. After concentrated by low-temperature rotary evaporation crude extracts were obtained and the yields of each culture medium were showed in Table S1.

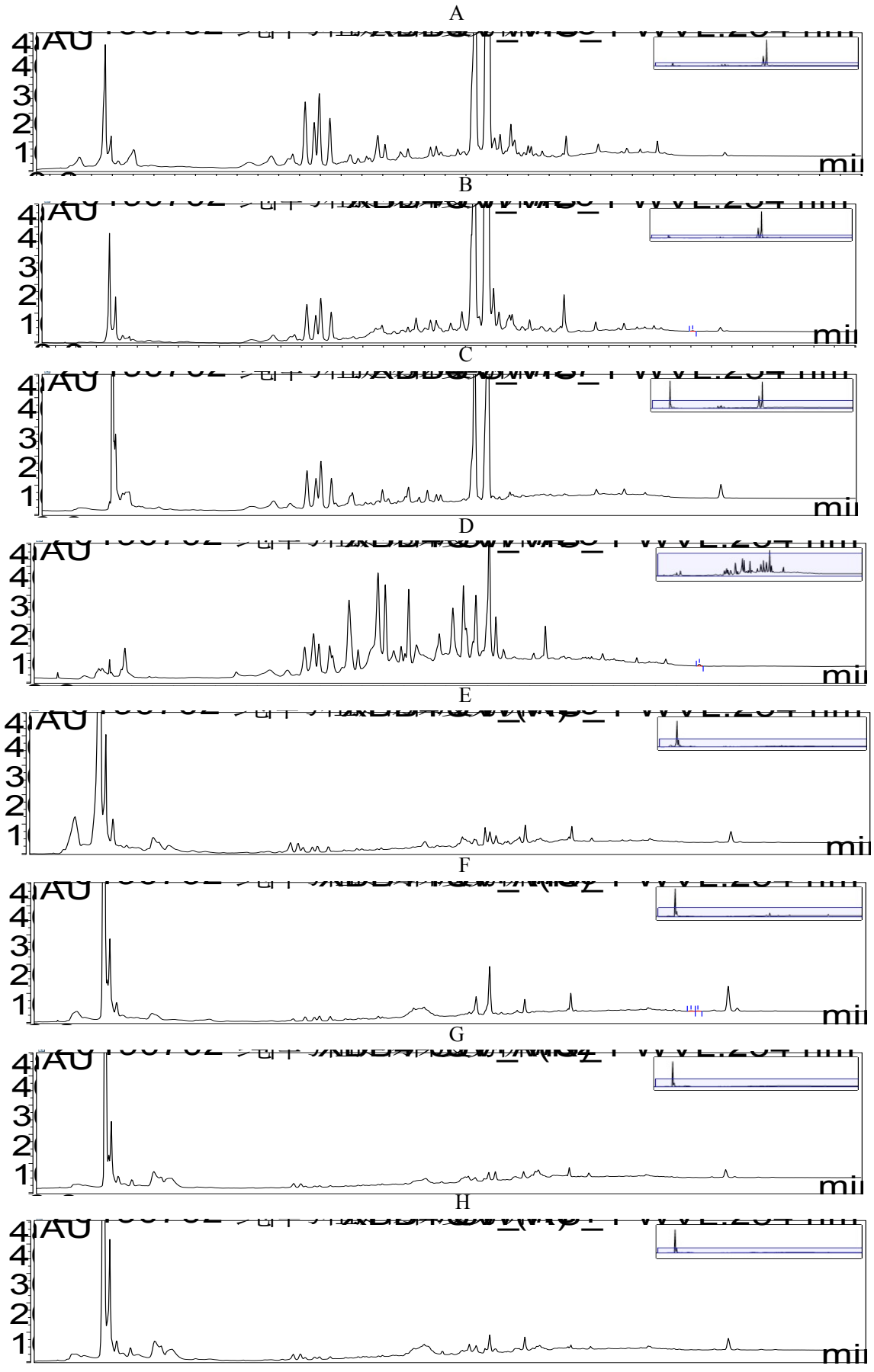


Figure S51. HPLC spectra of eight extracts from eight culture media.

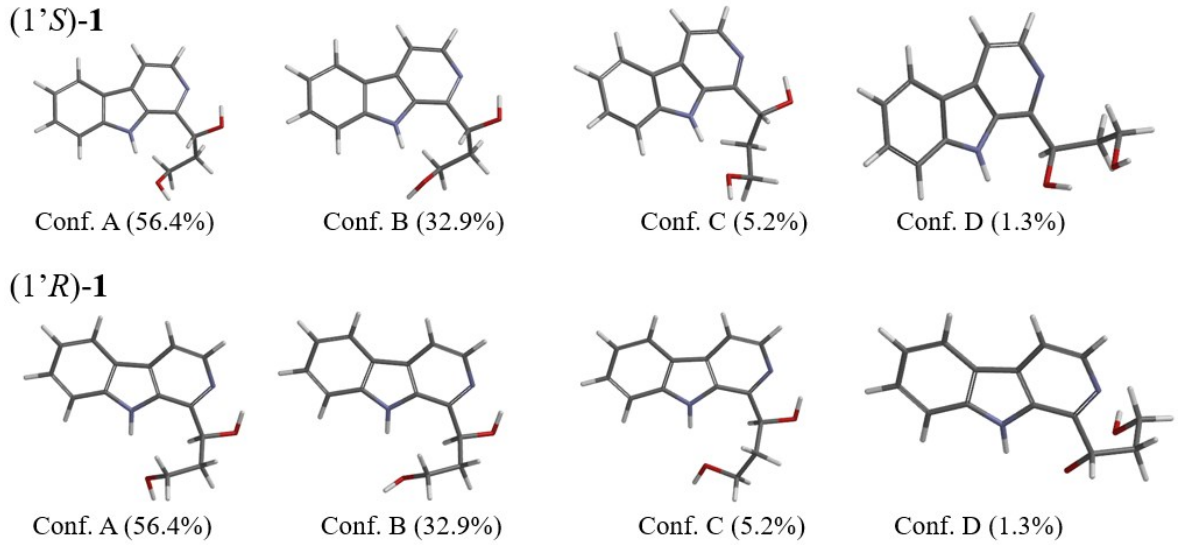


Figure S52. The most stable conformers of compound **1** calculated at the B3LYP/6-31+G(d) level. Relative populations are in parentheses.

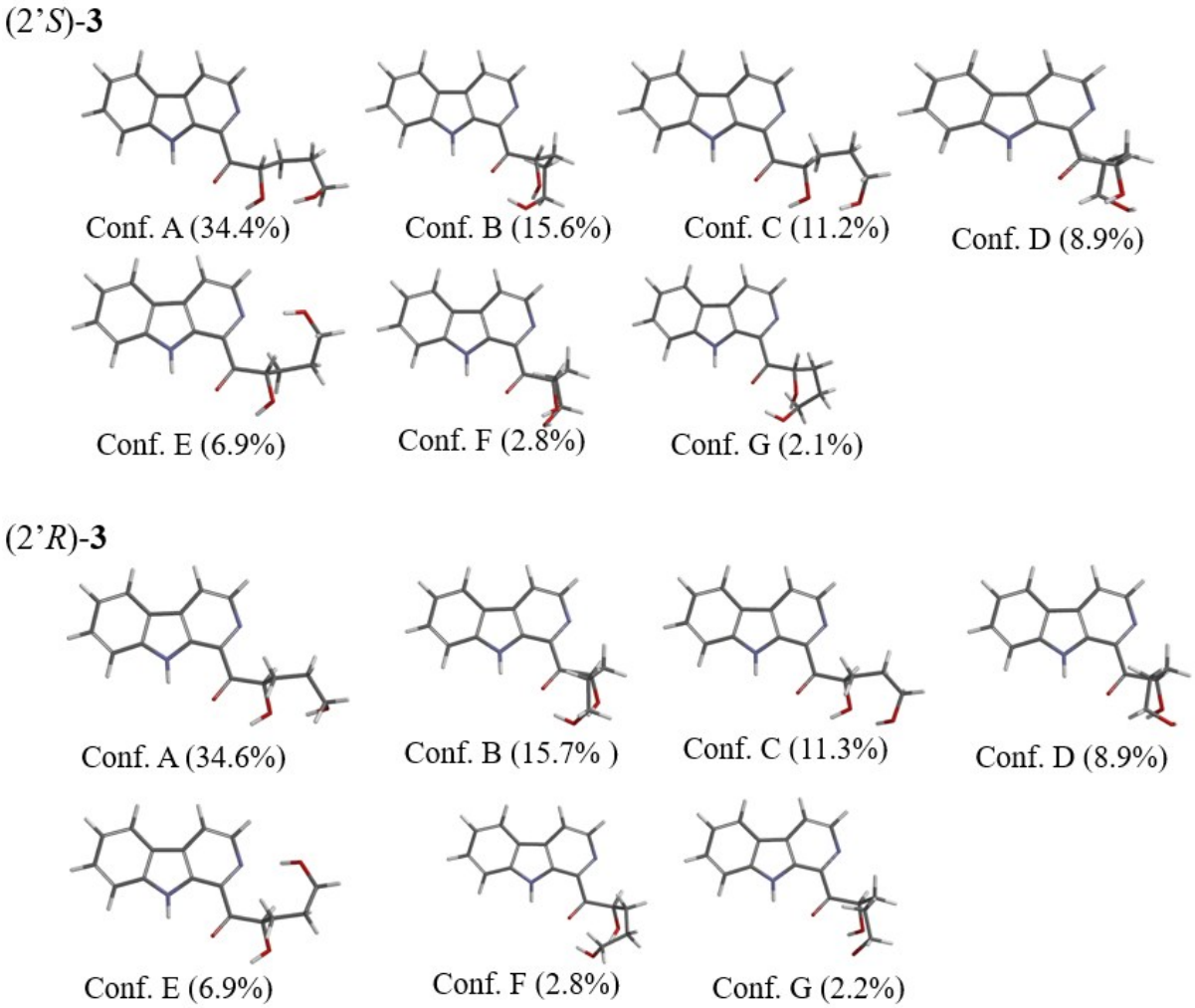


Figure S53. The most stable conformers of compound **3** calculated at the B3LYP/6-31+G(d) level. Relative populations are in parentheses.

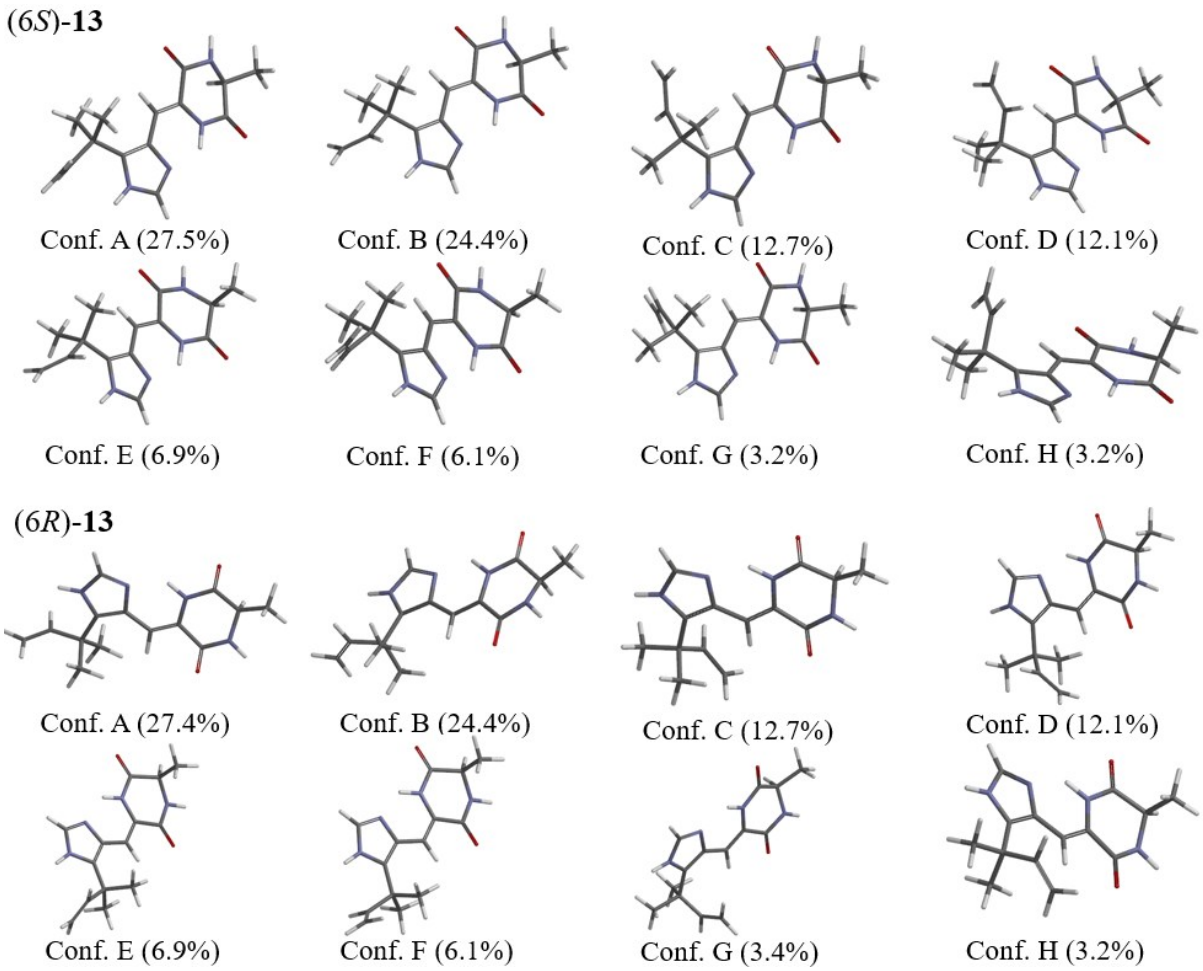


Figure S54. The most stable conformers of compound **13** calculated at the B3LYP/6-31+G(d) level. Relative populations are in parentheses.