

Supporting Information

Shearinines U–Y, indole diterpenoids from an entomogenous fungus *Penicillium* sp.

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Contents	Page
1) Figure S1. ^1H NMR spectrum of shearinine U (2); 600 MHz, $\text{DMSO-}d_6$)	5
2) Figure S2. ^{13}C NMR spectrum of shearinine U (2); 150 MHz, $\text{DMSO-}d_6$)	6
3) Figure S3. HSQC spectrum of shearinine U (2); 600 MHz, $\text{DMSO-}d_6$)	7
4) Figure S4. $^1\text{H-}^1\text{H}$ COSY spectrum of shearinine U (2); 600 MHz, $\text{DMSO-}d_6$)	8
5) Figure S5. HMBC spectrum of shearinine U (2); 600 MHz, $\text{DMSO-}d_6$)	9
6) Figure S6. NOESY spectrum of shearinine U (2); 600 MHz, $\text{DMSO-}d_6$)	10
7) Figure S7. HRESIMS spectrum of shearinine U (2)	11
8) Figure S8. IR spectrum of shearinine U (2)	12
9) Figure S9. UV spectrum of shearinine U (2) in MeOH	13
10) Figure S10. ECD spectrum of 2 in MeOH	13
11) Figure S11. Relative configurations and the optimized conformers for 2	14
12) Figure S12. ^1H NMR spectrum of shearinine V (3); 600 MHz, $\text{DMSO-}d_6$)	15
13) Figure S13. ^{13}C NMR spectrum of shearinine V (3); 150 MHz, $\text{DMSO-}d_6$)	16
14) Figure S14. HSQC spectrum of shearinine V (3); 600 MHz, $\text{DMSO-}d_6$)	17
15) Figure S15. $^1\text{H-}^1\text{H}$ COSY spectrum of shearinine V (3); (2); 600 MHz, $\text{DMSO-}d_6$)	18
16) Figure S16. HMBC spectrum of shearinine V (3); 600 MHz, $\text{DMSO-}d_6$)	19
17) Figure S17. NOESY spectrum of shearinine V (3); 600 MHz, $\text{DMSO-}d_6$)	20
18) Figure S18. HRESIMS spectrum of shearinine V (3)	21
19) Figure S19. IR spectrum of shearinine V (3)	22

20) Figure S20. UV spectrum of shearinine V (3) in MeOH	23
21) Figure S21. ECD spectrum of 3 in MeOH	23
22) Figure S22. ¹ H NMR spectrum of shearinine W (4; 600 MHz, DMSO- <i>d</i> ₆)	24
23) Figure S23. ¹³ C NMR spectrum of shearinine W (4; 150 MHz, DMSO- <i>d</i> ₆)	25
24) Figure S24. HSQC spectrum of shearinine W (4; 600 MHz, DMSO- <i>d</i> ₆)	26
25) Figure S25. ¹ H- ¹ H COSY spectrum of shearinine W (4; 600 MHz, DMSO- <i>d</i> ₆)	27
26) Figure S26. HMBC spectrum of shearinine W (4; 600 MHz, DMSO- <i>d</i> ₆)	28
27) Figure S27. NOESY spectrum of shearinine W (4; 600 MHz, DMSO- <i>d</i> ₆)	29
28) Figure S28. HRESIMS spectrum of shearinine W (4)	30
29) Figure S29. IR spectrum of shearinine W (4)	31
30) Figure S30. UV spectrum of shearinine W (4) in MeOH	32
31) Figure S31. ECD spectrum of 4 in MeOH	32
32) Figure S32. Relative configurations and the optimized conformers for 4	33
33) Figure S33. ¹ H NMR spectrum of shearinine X (5; 600 MHz, DMSO- <i>d</i> ₆)	34
34) Figure S34. ¹³ C NMR spectrum of shearinine X (5; 150 MHz, DMSO- <i>d</i> ₆)	35
35) Figure S35. HSQC spectrum of shearinine X (5; 600 MHz, DMSO- <i>d</i> ₆)	36
36) Figure S36. ¹ H- ¹ H COSY spectrum of shearinine X (5; 600 MHz, DMSO- <i>d</i> ₆)	37
37) Figure S37. HMBC spectrum of shearinine X (5; 600 MHz, DMSO- <i>d</i> ₆)	38
38) Figure S38. NOESY spectrum of shearinine X (5; 600 MHz, DMSO- <i>d</i> ₆)	39
39) Figure S39. HRESIMS spectrum of shearinine X (5)	40

40) Figure S40. IR spectrum of shearinine X (5)	41
41) Figure S41. UV spectrum of shearinine X (5) in MeOH	42
42) Figure S42. ECD spectrum of 5 in MeOH	42
43) Figure S43. Relative configurations and the optimized conformers for 5	43
44) Figure S44. ^1H NMR spectrum of shearinine Y (6 ; 600 MHz, $\text{DMSO-}d_6$)	44
45) Figure S45. ^{13}C NMR spectrum of shearinine Y (6 ; 150 MHz, $\text{DMSO-}d_6$)	45
46) Figure S46. HSQC spectrum of shearinine Y (6 ; 600 MHz, $\text{DMSO-}d_6$)	46
47) Figure S47. $^1\text{H-}^1\text{H}$ COSY spectrum of shearinine Y (6 ; 600 MHz, $\text{DMSO-}d_6$)	47
48) Figure S48. HMBC spectrum of shearinine Y (6 ; 600 MHz, $\text{DMSO-}d_6$)	48
49) Figure S49. NOESY spectrum of shearinine Y (6 ; 600 MHz, $\text{DMSO-}d_6$)	49
50) Figure S50. HRESIMS spectrum of shearinine Y (6)	50
51) Figure S51. IR spectrum of shearinine Y (6)	51
52) Figure S52. UV spectrum of shearinine Y (6) in MeOH	52
53) Figure S53. ECD spectrum of 6 in MeOH	52
54) Figure S54. Relative configurations and the optimized conformers for 6	53
55) Figure S55. ^1H NMR spectrum of 22,23-dehydro-shearinine A (1 ; 600 MHz, CDCl_3)	54
56) Figure S56. ^{13}C NMR spectrum of 22,23-dehydro-shearinine A (1 ; 150 MHz, CDCl_3)	55
57) Scheme S1. Hypothetical biosynthetic pathways for 1-6	56

Figure S1. ^1H NMR Spectrum of Shearinine U (**2**; 600 MHz, $\text{DMSO-}d_6$)

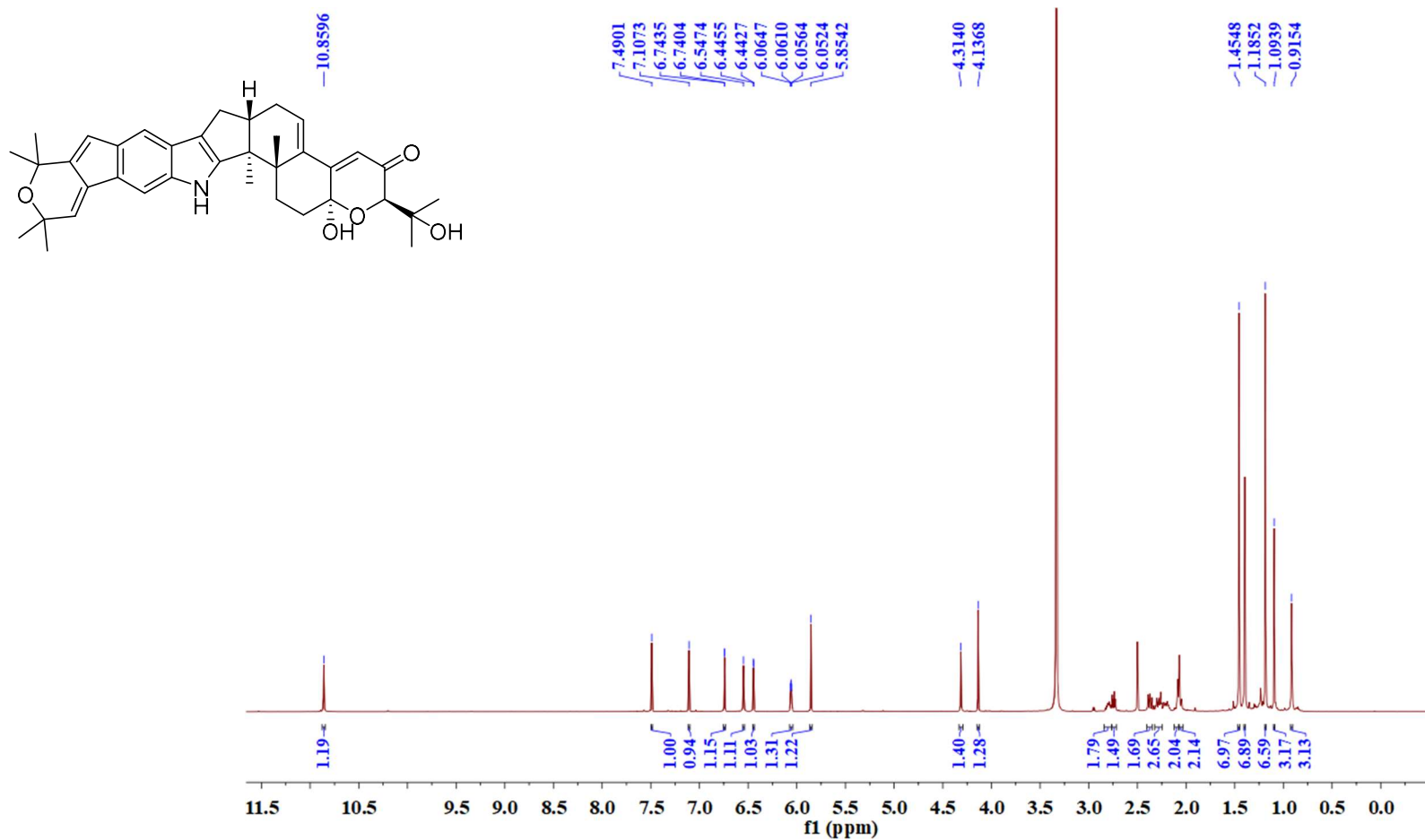


Figure S2. ^{13}C NMR Spectrum of Shearinine U (2; 150 MHz, DMSO- d_6)

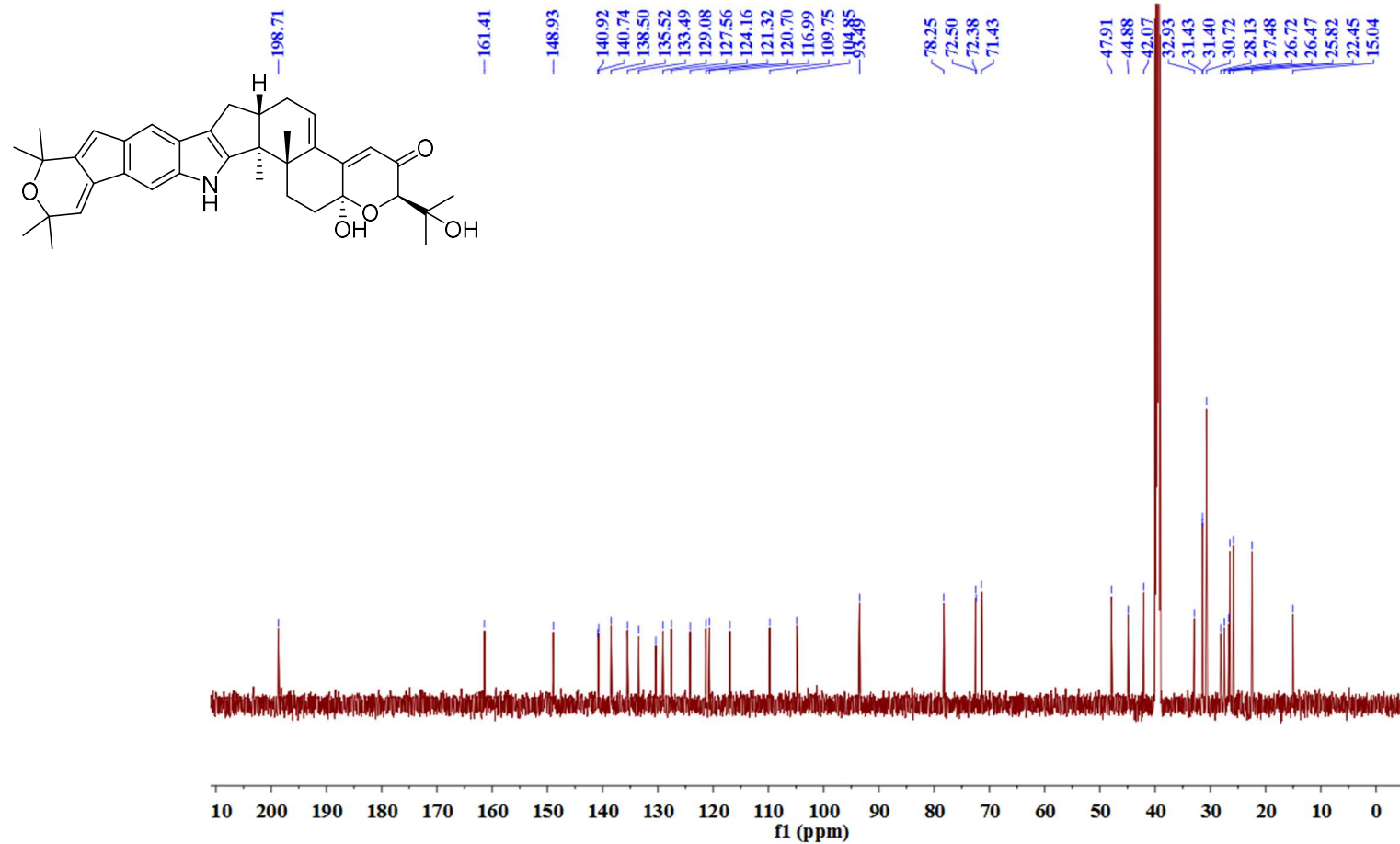


Figure S3. HSQC Spectrum of Shearinine U (**2**; 600 MHz, DMSO-*d*₆)

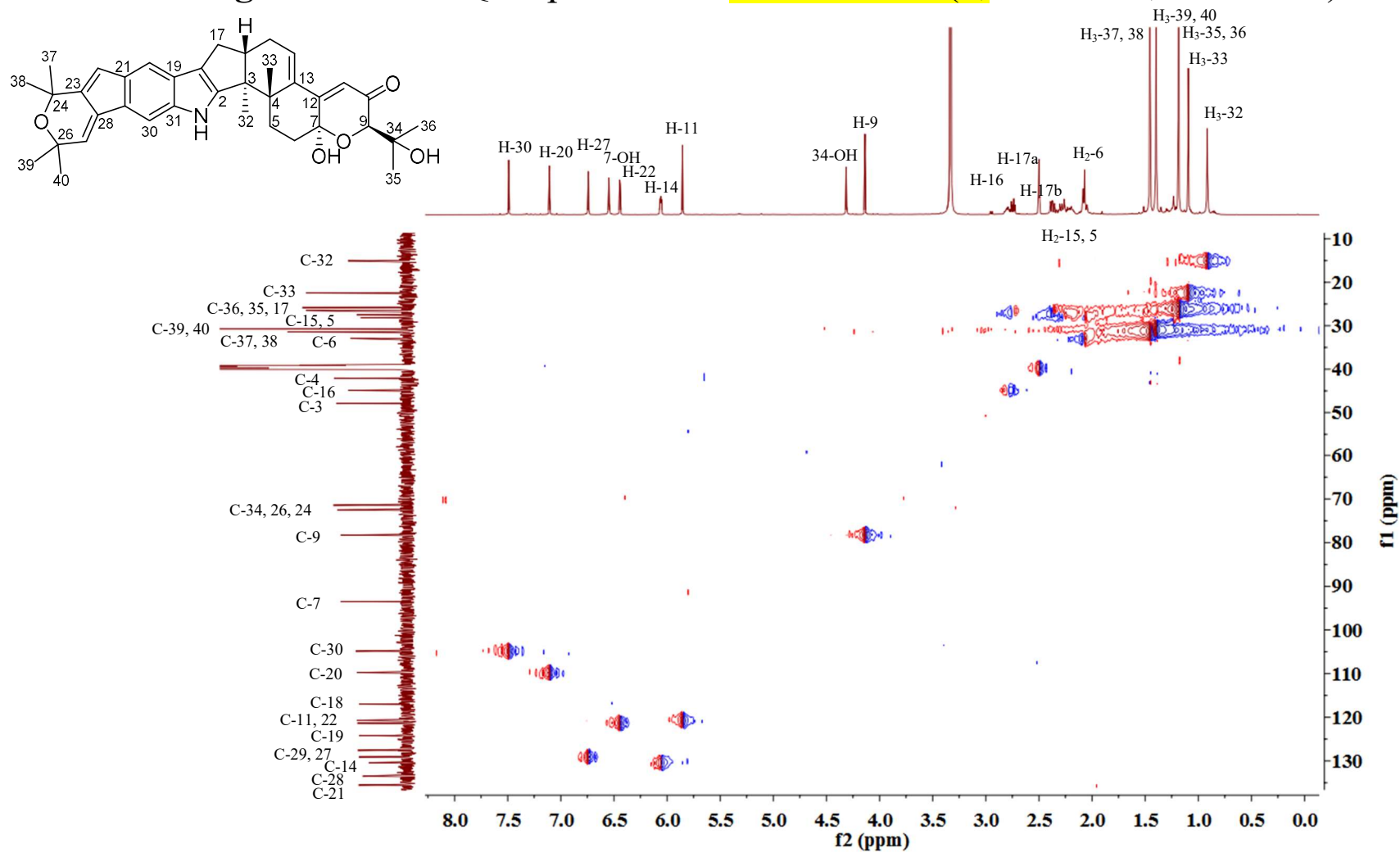


Figure S4. ^1H - ^1H COSY Spectrum of Shearinine U (**2**; 600 MHz, $\text{DMSO-}d_6$)

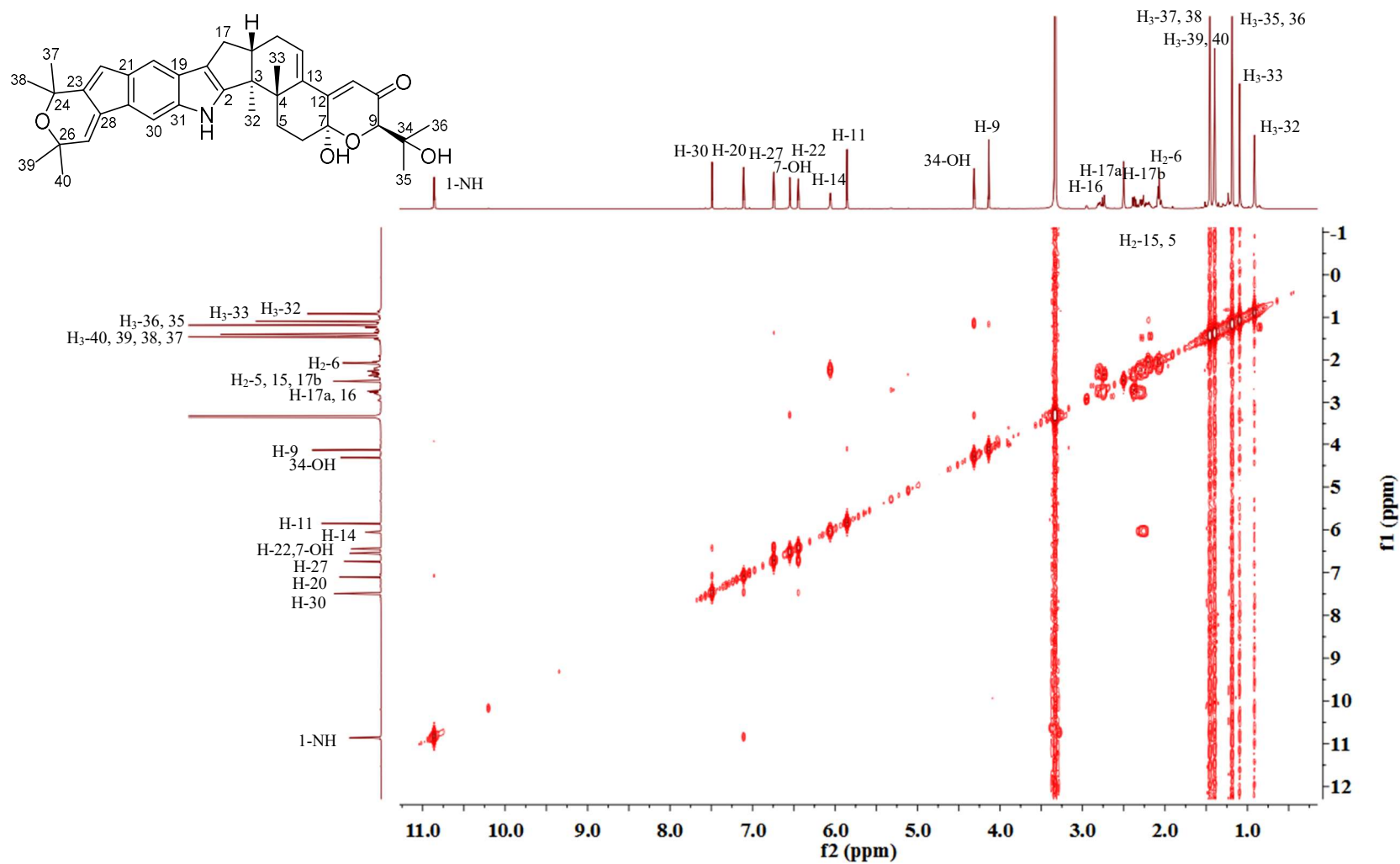


Figure S5. HMBC Spectrum of Shearinine U (2; 600 MHz, DMSO-*d*₆)

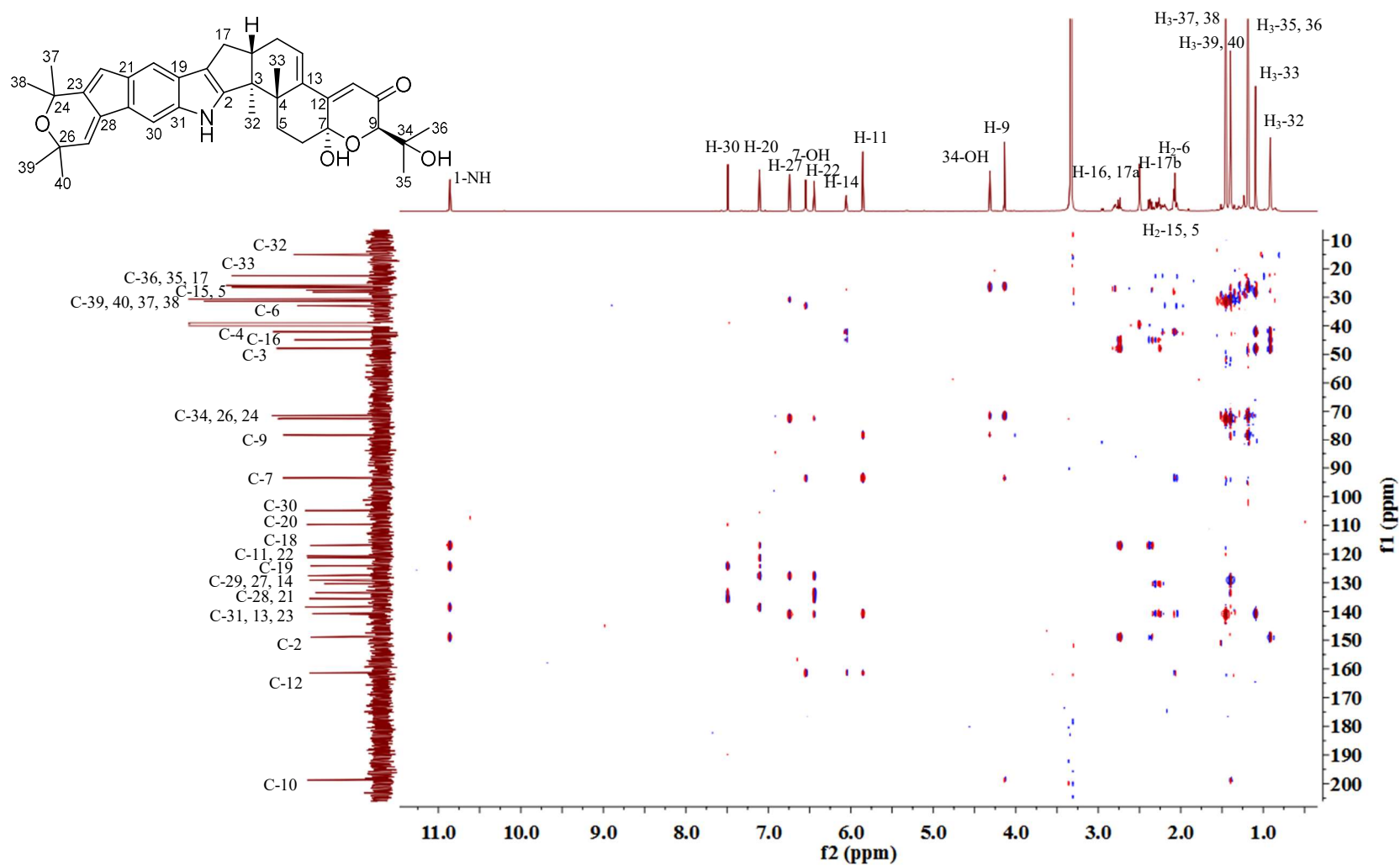


Figure S6. NOESY Spectrum of **Shearinine U (2)**; 600 MHz, DMSO-*d*₆)

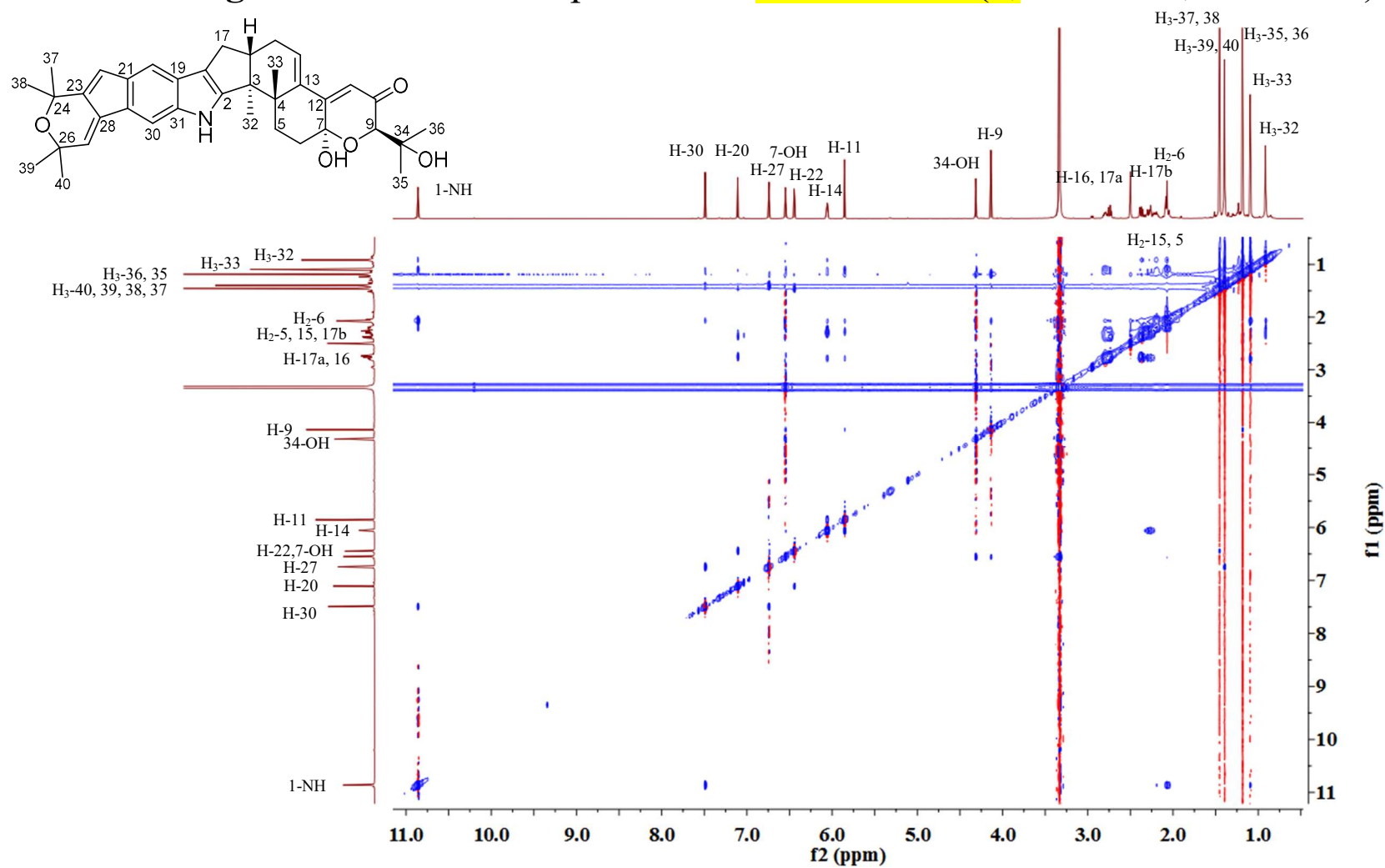


Figure S7. HRESIMS Spectrum of Shearinine U (2)

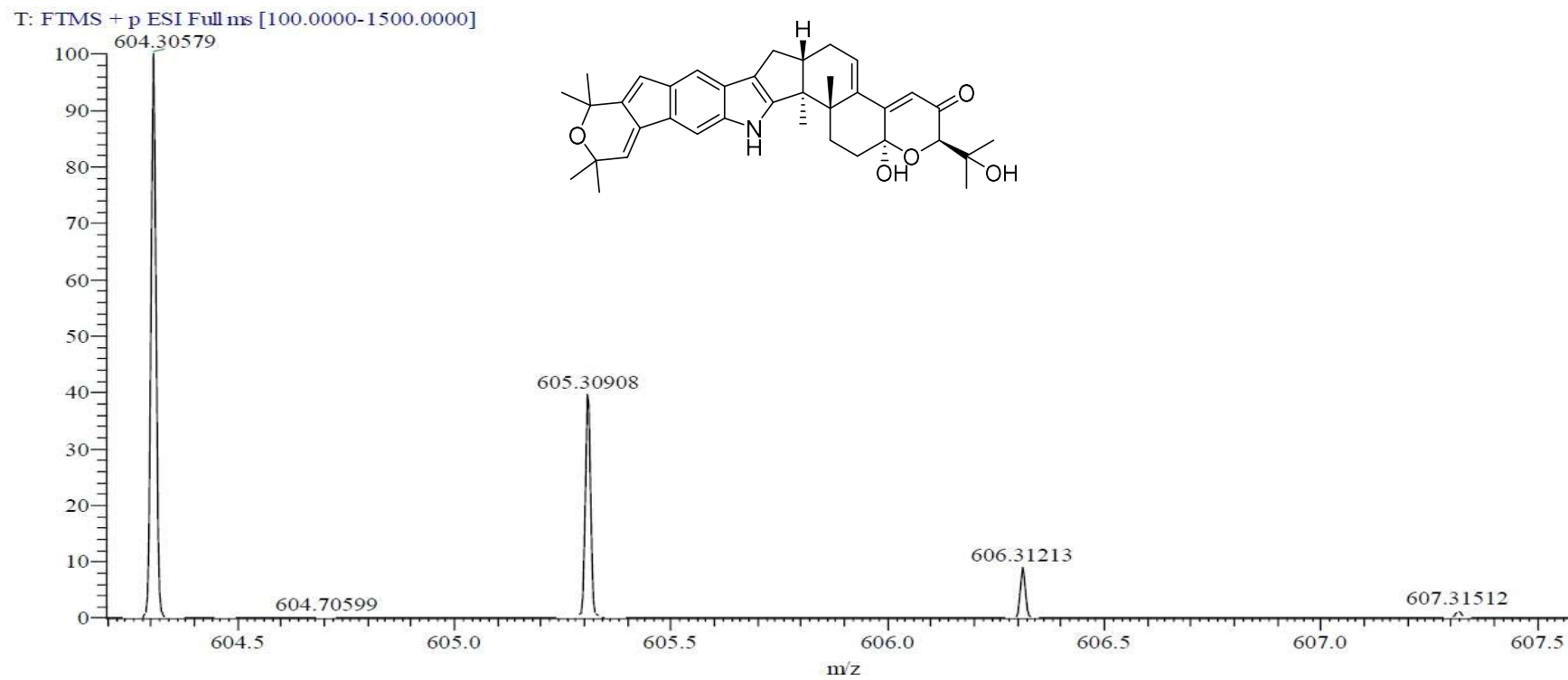


Figure S8. IR Spectrum of Shearinine U (2)

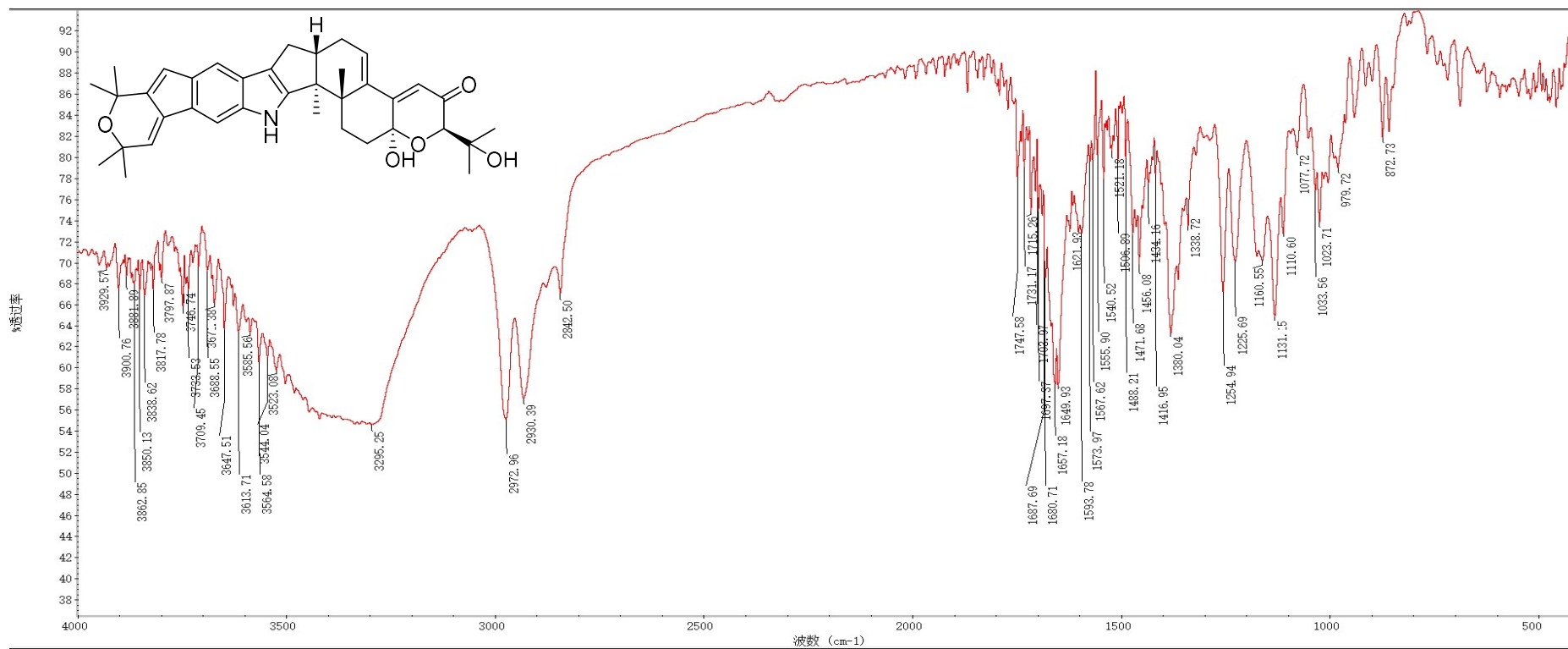


Figure S9. UV Spectrum of Shearinine U (2) in MeOH

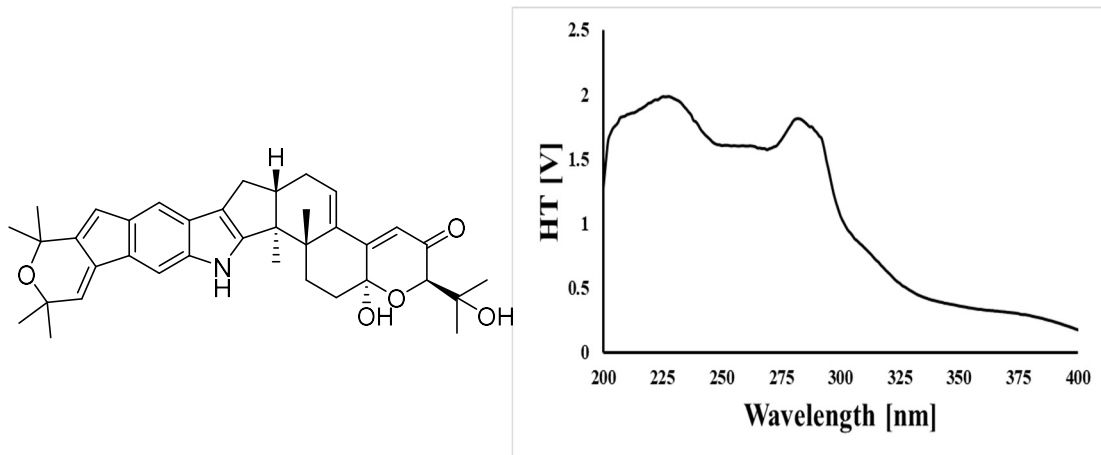


Figure S10. ECD Spectrum of Shearinine U (2) in MeOH

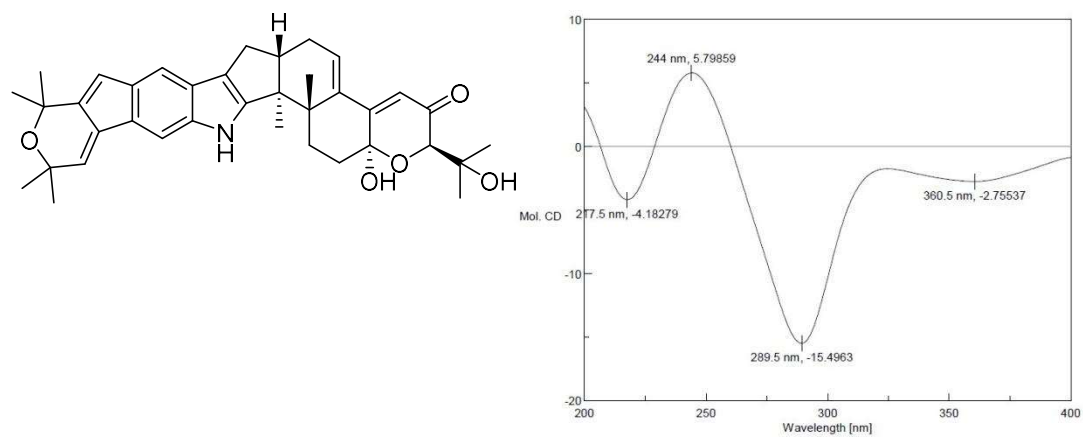
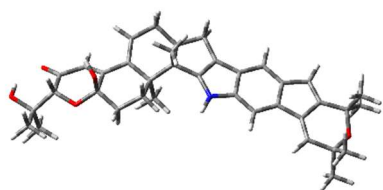
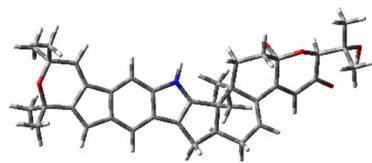


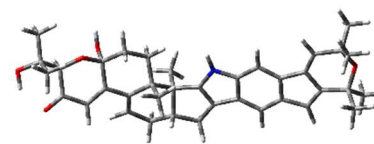
Figure S11. Relative Configurations and the Optimized Conformers for **2**



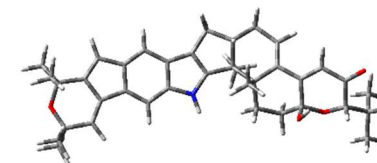
2a



2b



2c



2d

Figure S12. ¹H NMR Spectrum of Shearinine V (**3**; 600 MHz, DMSO-*d*₆)

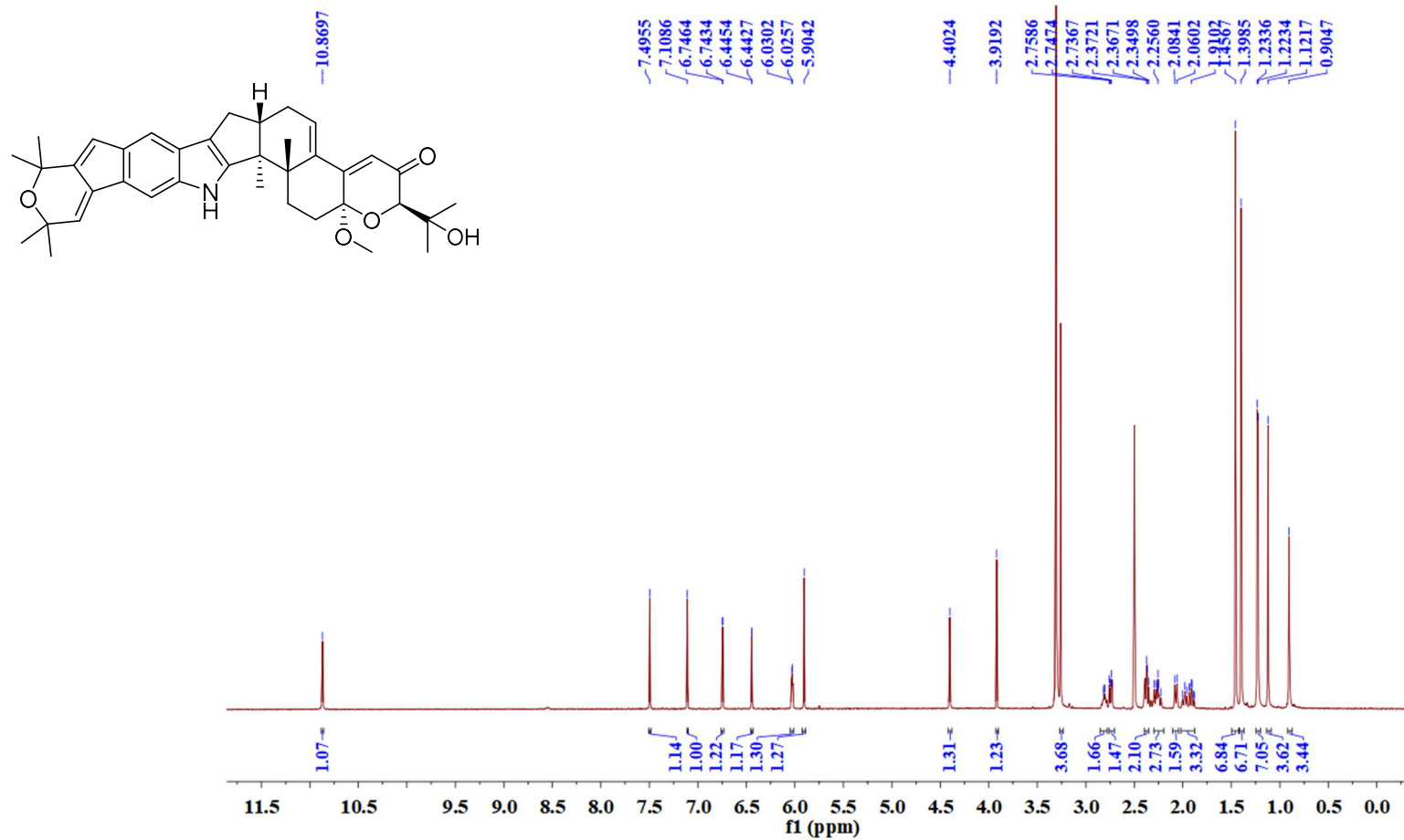


Figure S13. ^{13}C NMR Spectrum of Shearinine V (3; 150 MHz, DMSO- d_6)

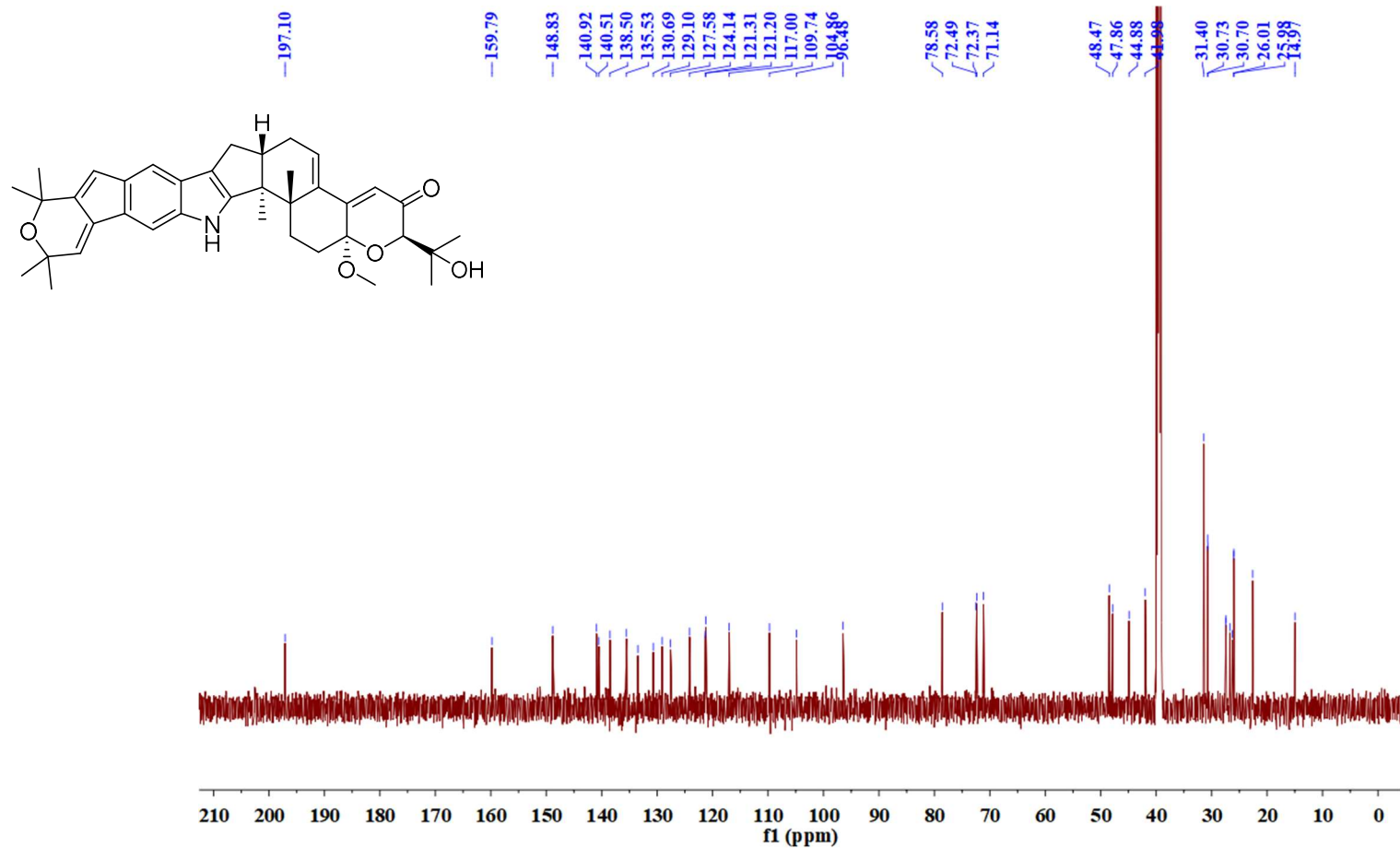


Figure S14. HSQC Spectrum of Shearinine V (**3**; 600 MHz, DMSO-*d*₆)

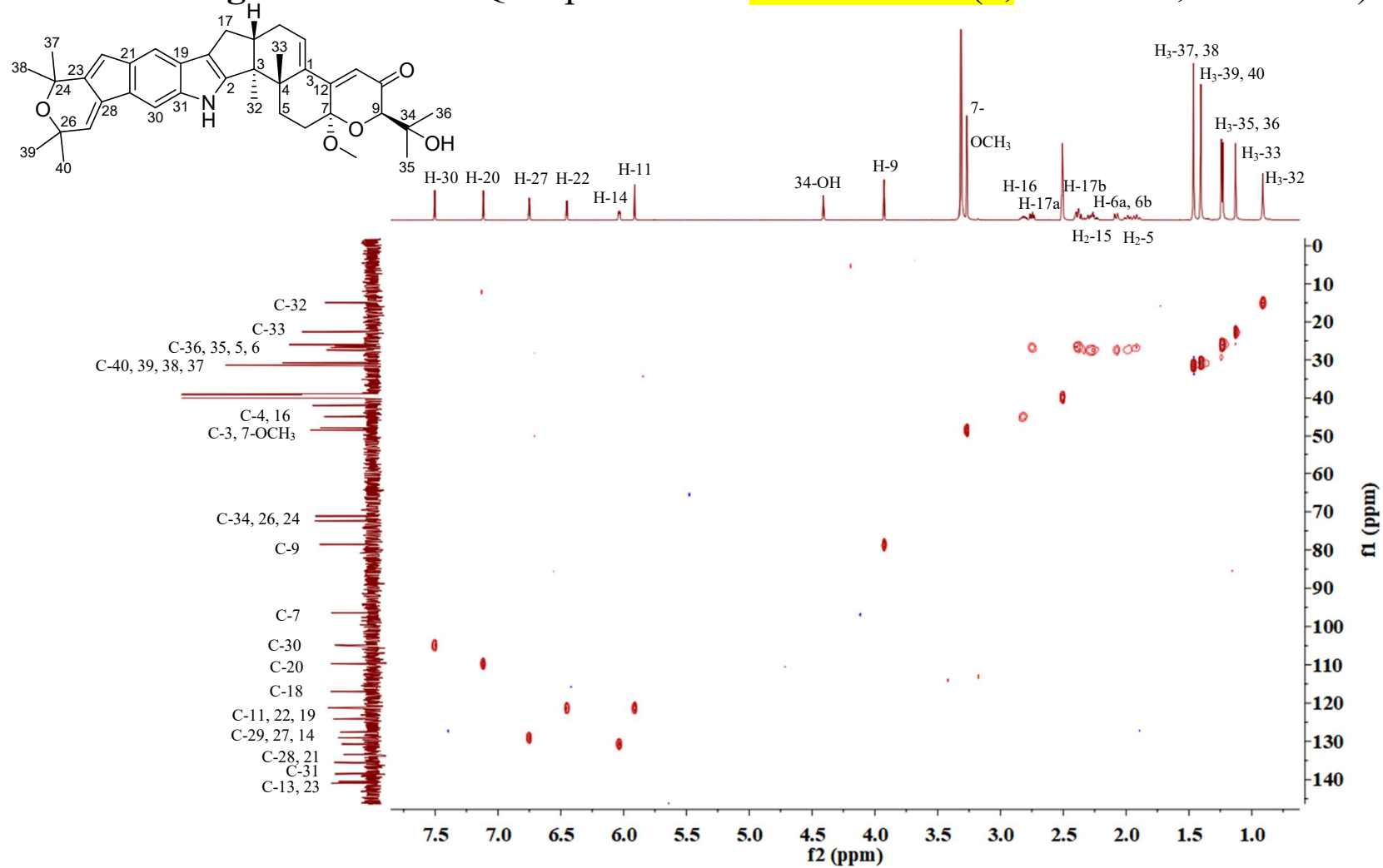


Figure S15. ^1H - ^1H COSY Spectrum of Shearinine V (**3**; 600 MHz, $\text{DMSO-}d_6$)

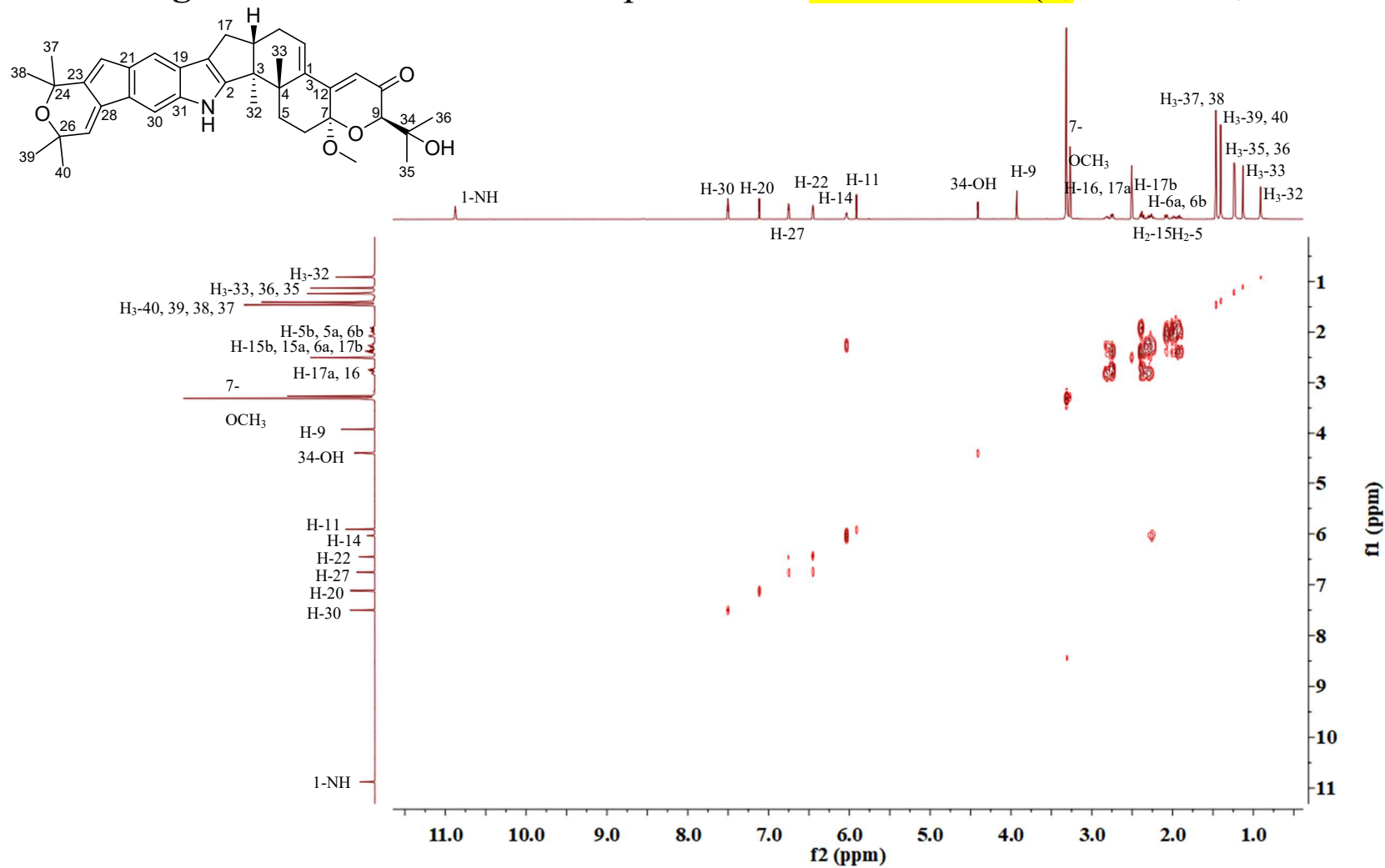


Figure S16. HMBC Spectrum of **Shearinine V (3)**; 600 MHz, DMSO-*d*₆)

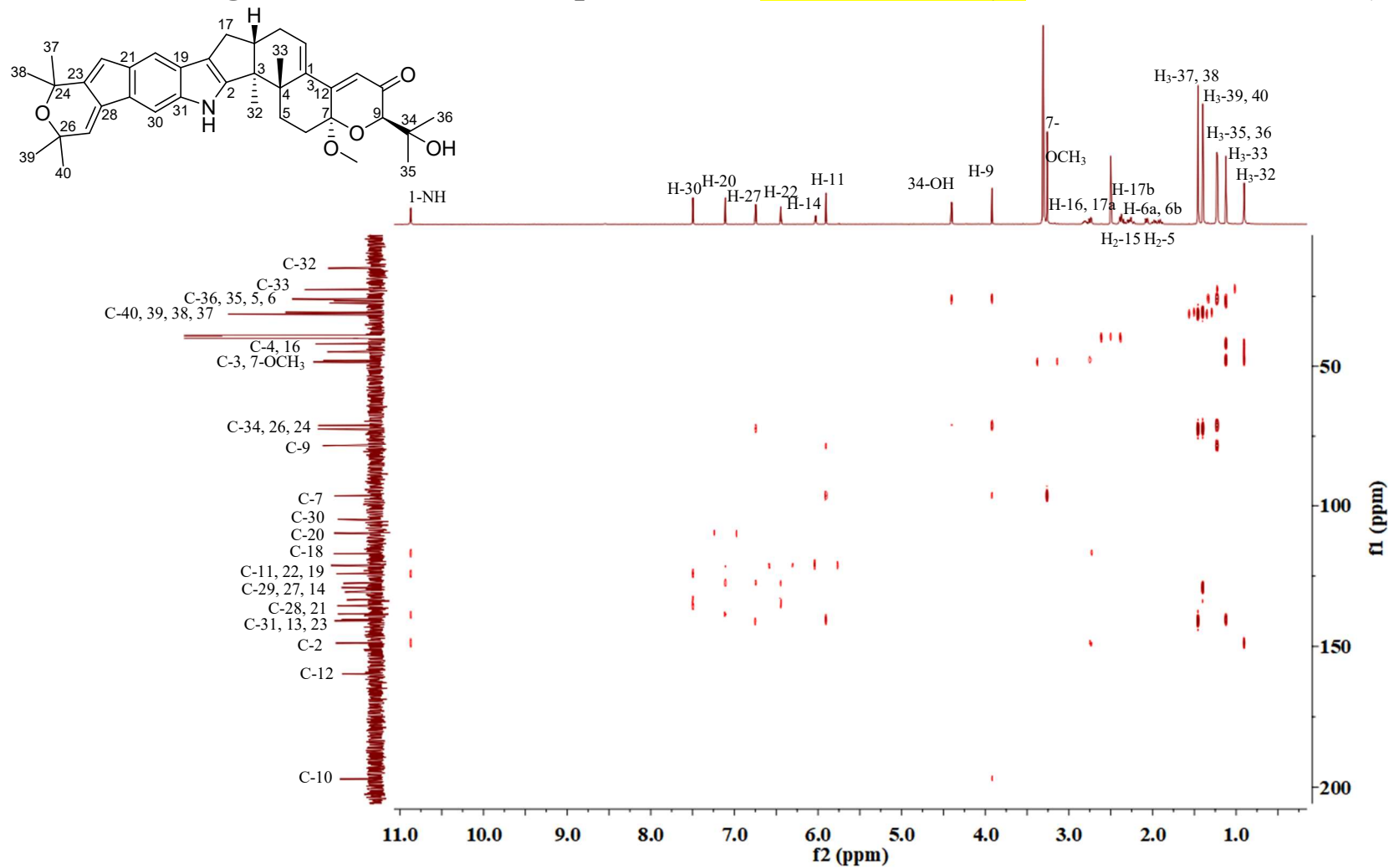


Figure S17. NOESY Spectrum of Shearinine V (**3**; 600 MHz, DMSO-*d*₆)

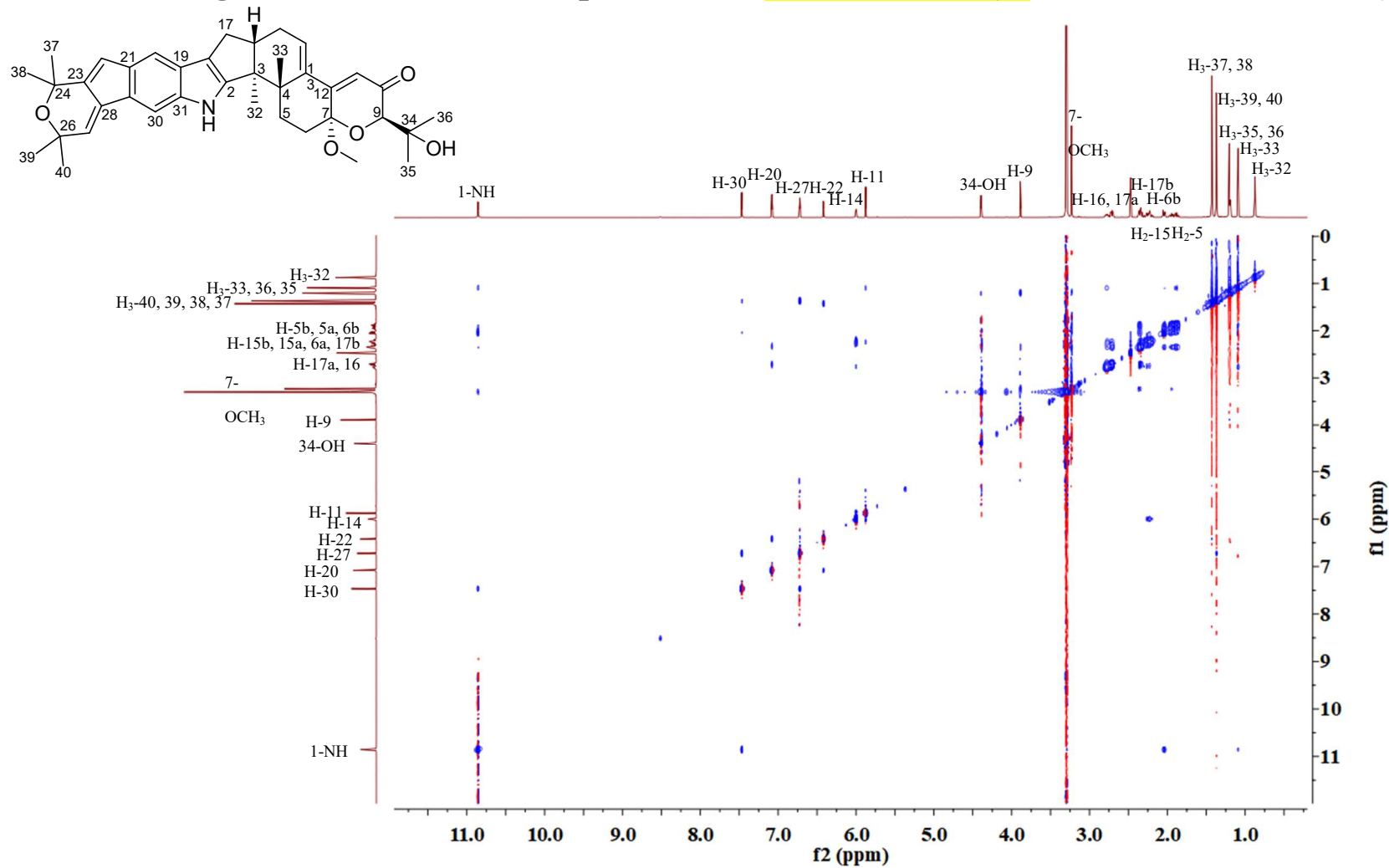


Figure S18. HRESIMS Spectrum of Shearinine V (3)

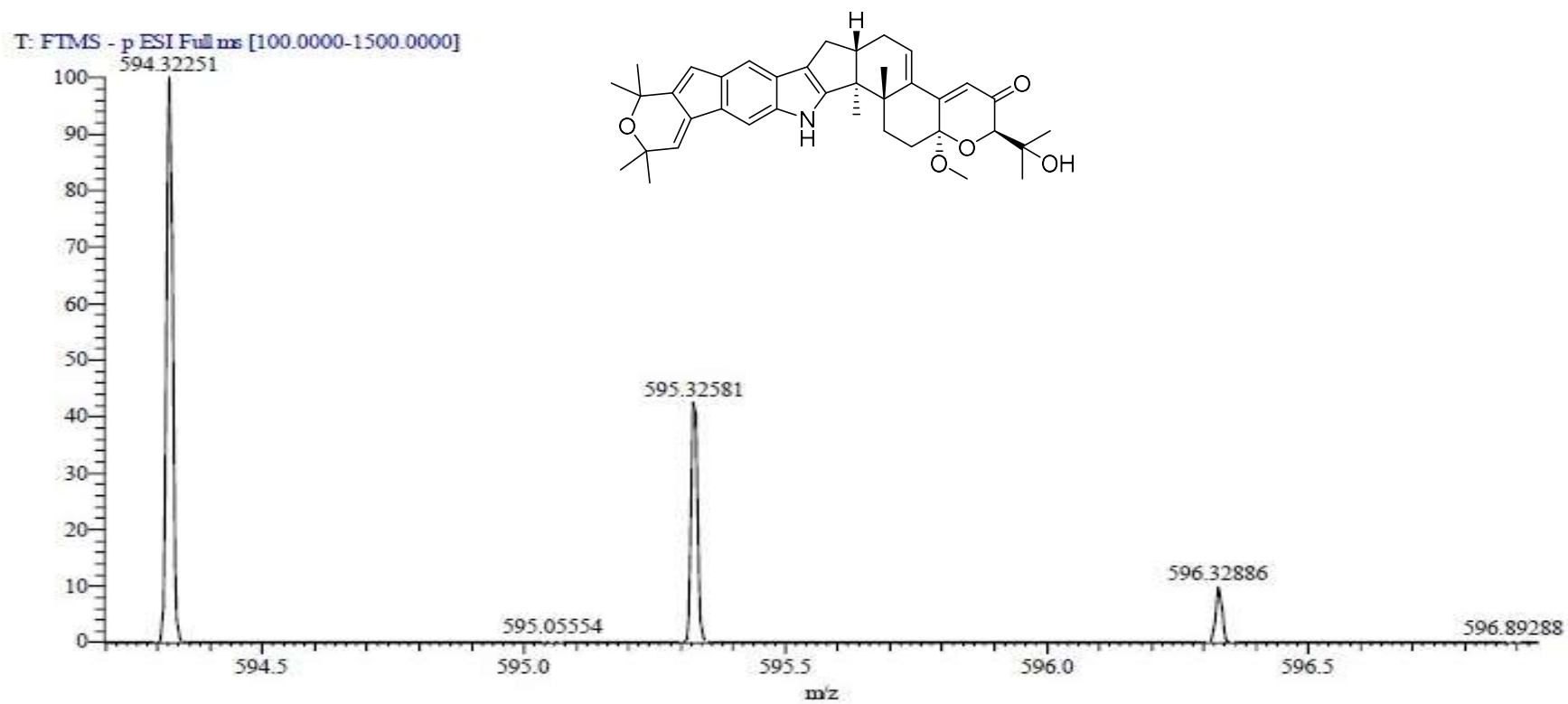


Figure S19. IR Spectrum of Shearinine V (3)

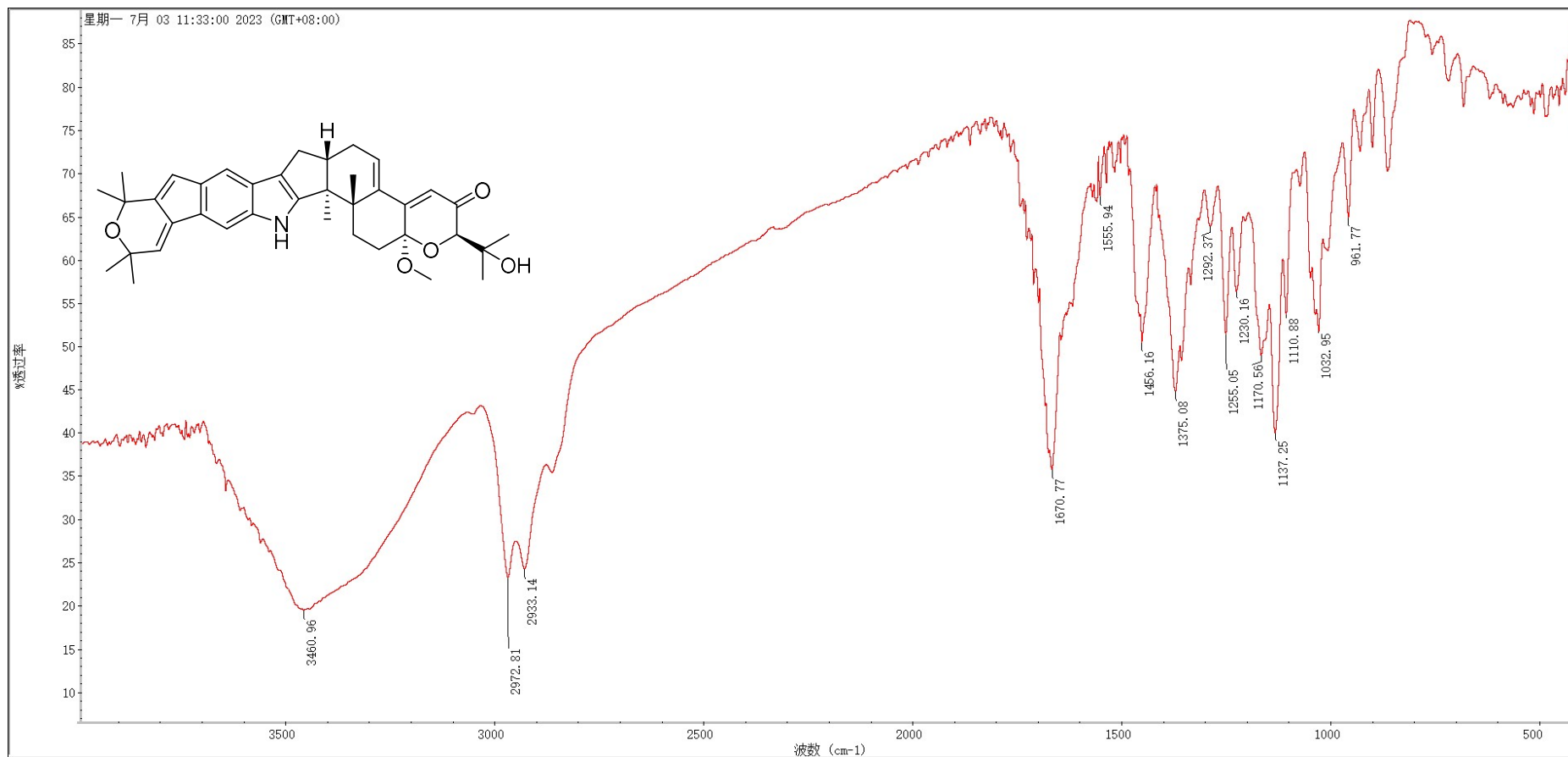


Figure S20. UV Spectrum of Shearinine V (3) in MeOH

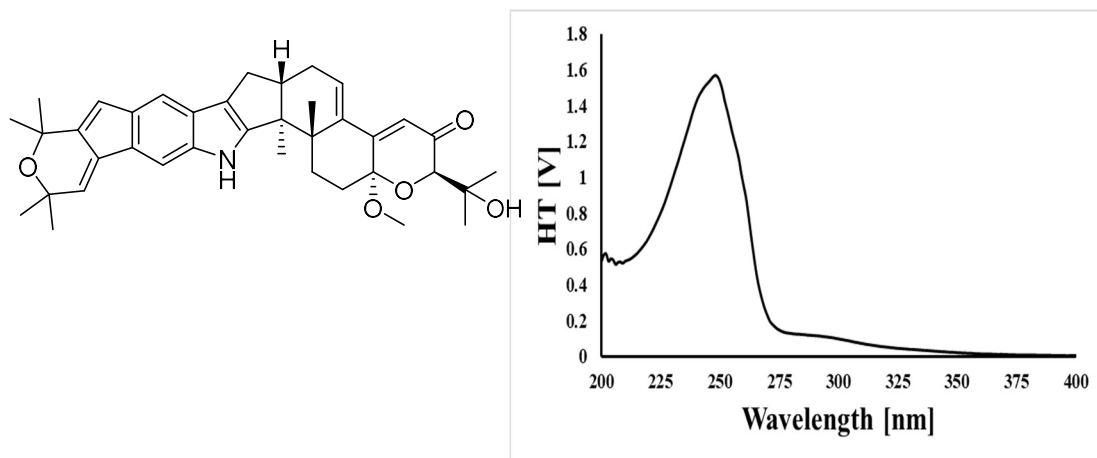


Figure S21. ECD Spectrum of Shearinine V (3) in MeOH

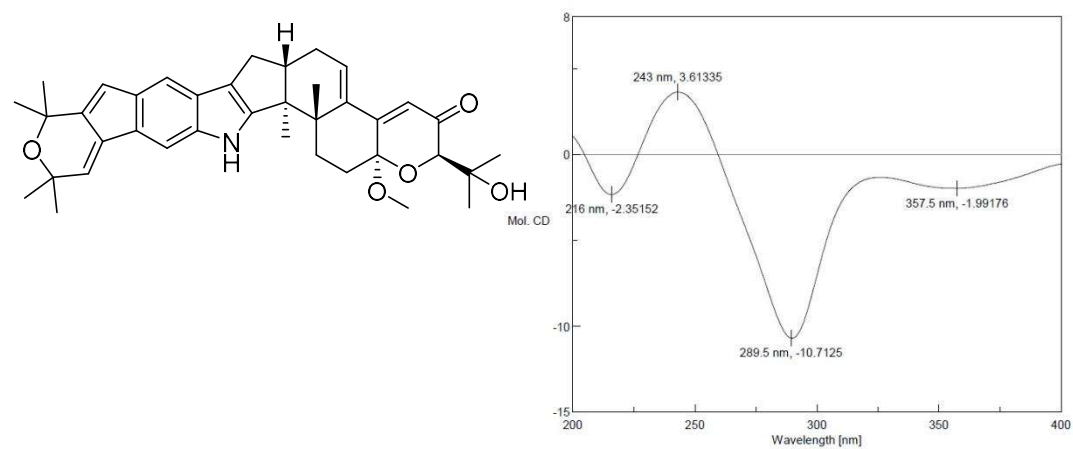


Figure S22. ¹H NMR Spectrum of Shearinine W (4; 600 MHz, DMSO-*d*₆)

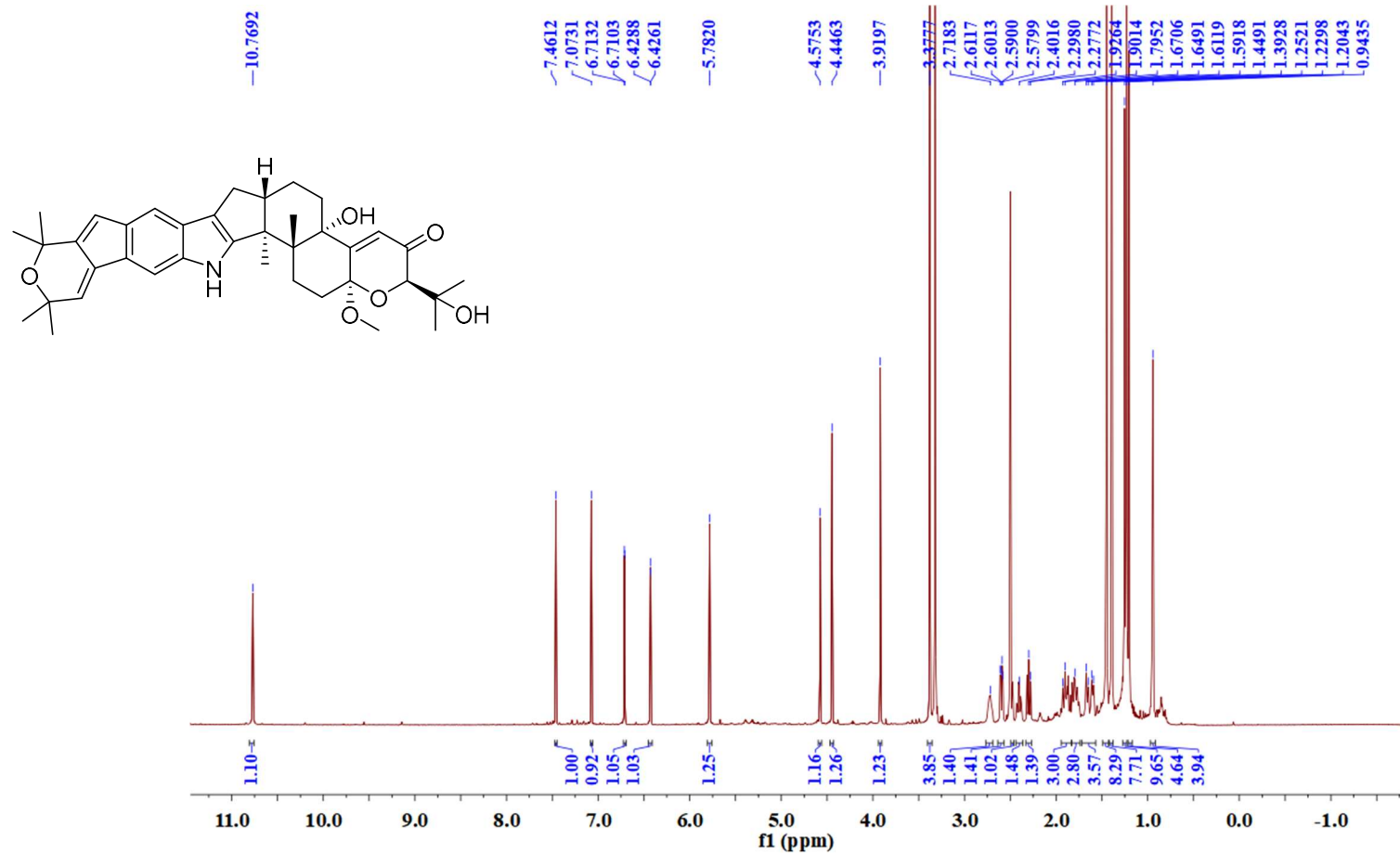


Figure S23. ¹³C NMR Spectrum of Shearinine W (4; 150 MHz, DMSO-*d*₆)

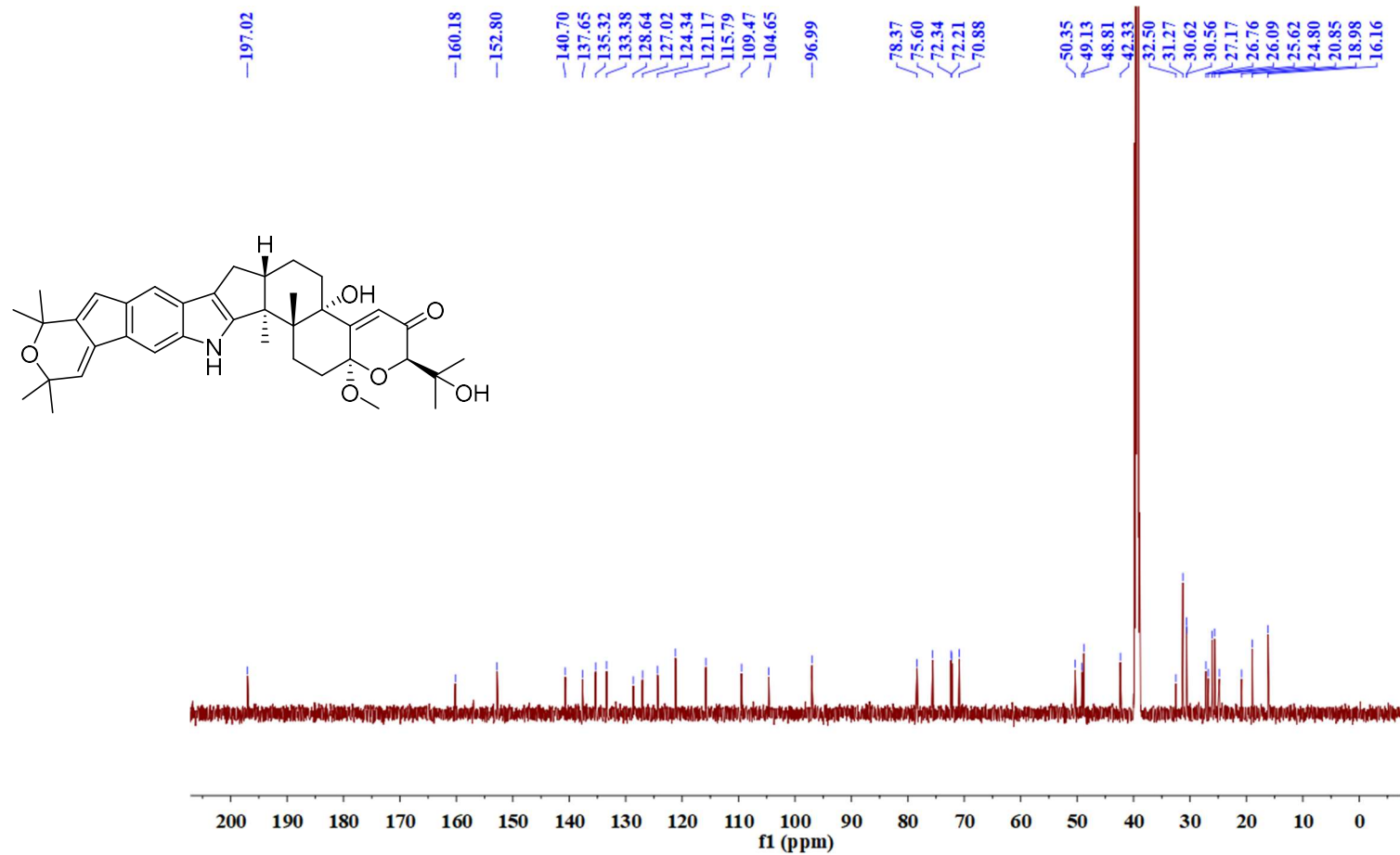


Figure S24. HSQC Spectrum of Shearinine W (4; 600 MHz, DMSO-*d*₆)

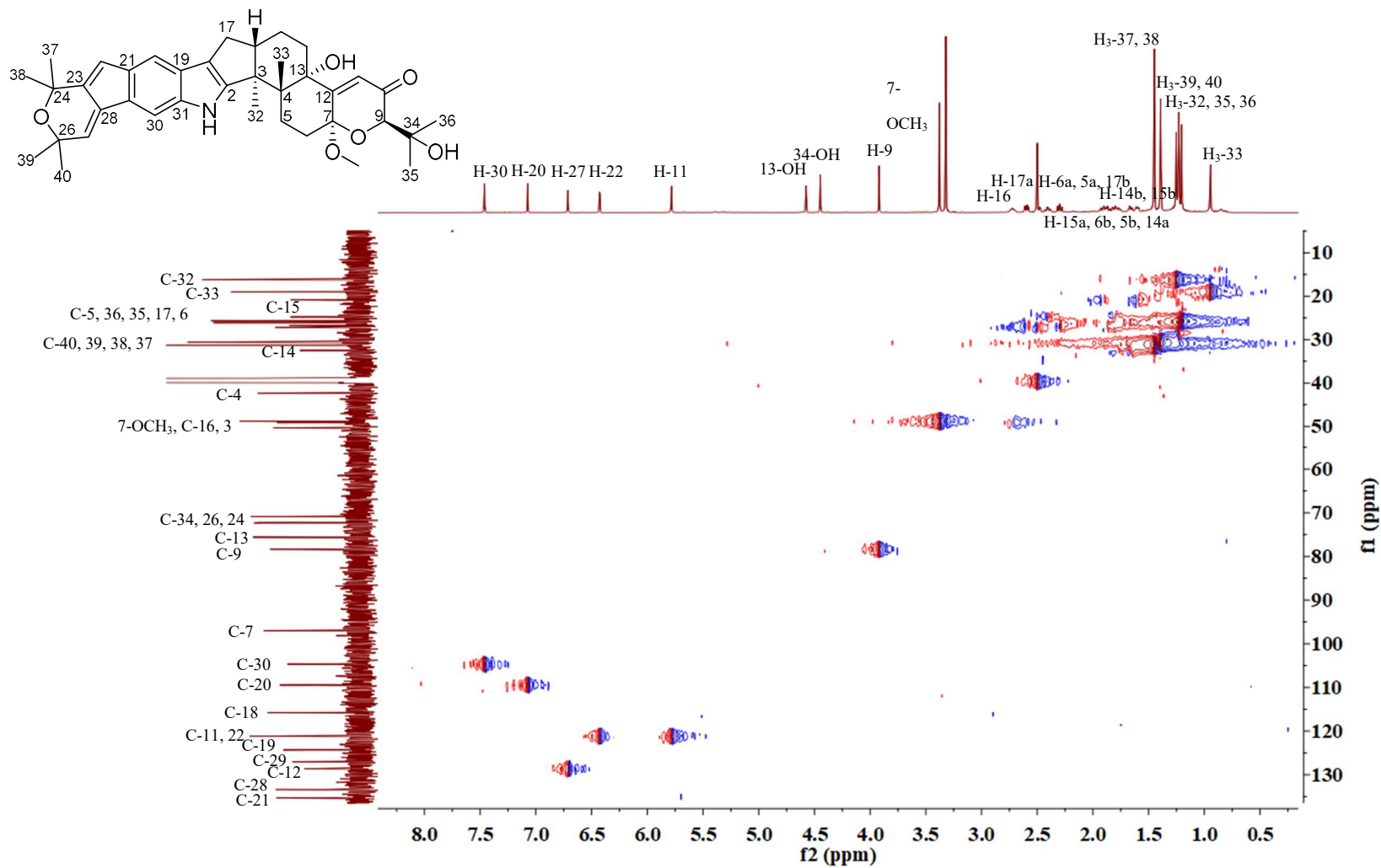


Figure S25. ^1H - ^1H COSY Spectrum of Shearinine W (**4**; 600 MHz, $\text{DMSO-}d_6$)

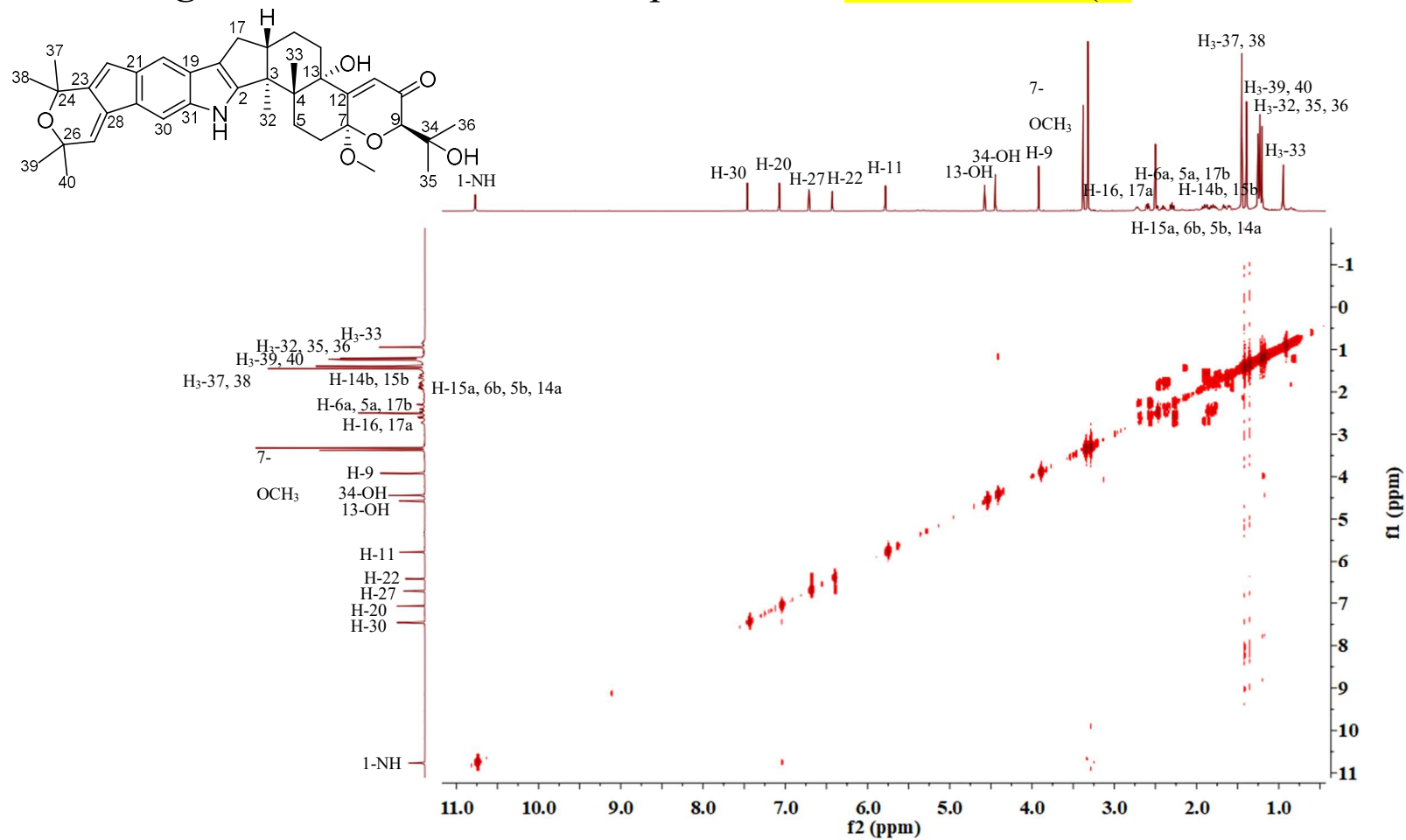


Figure S26. HMBC Spectrum of Shearinine W (**4**; 600 MHz, DMSO-*d*₆)

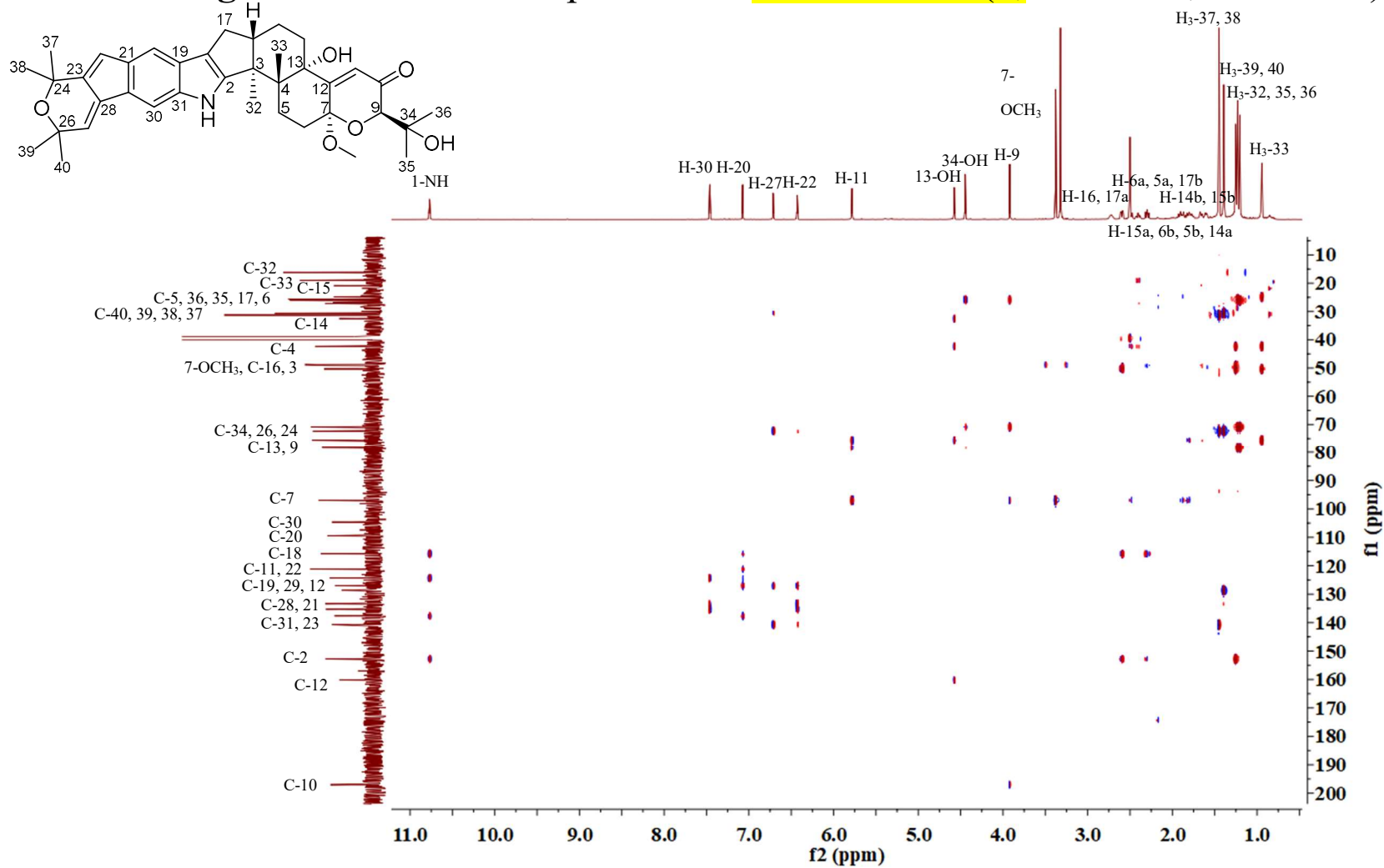


Figure S27. NOESY Spectrum of Shearinine W (4; 600 MHz, DMSO-*d*₆)

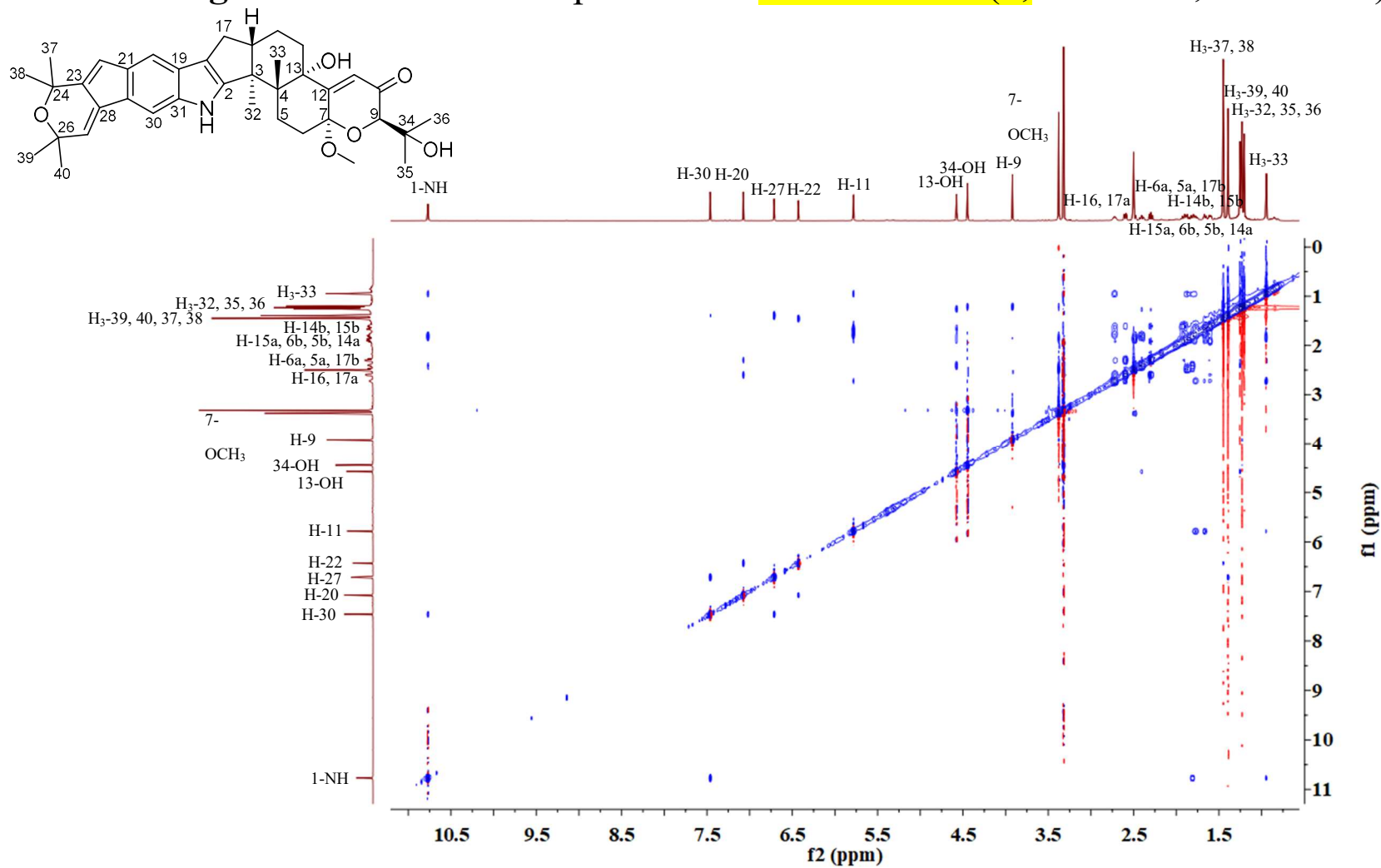


Figure S28. HRESIMS Spectrum of Shearinine W (4)

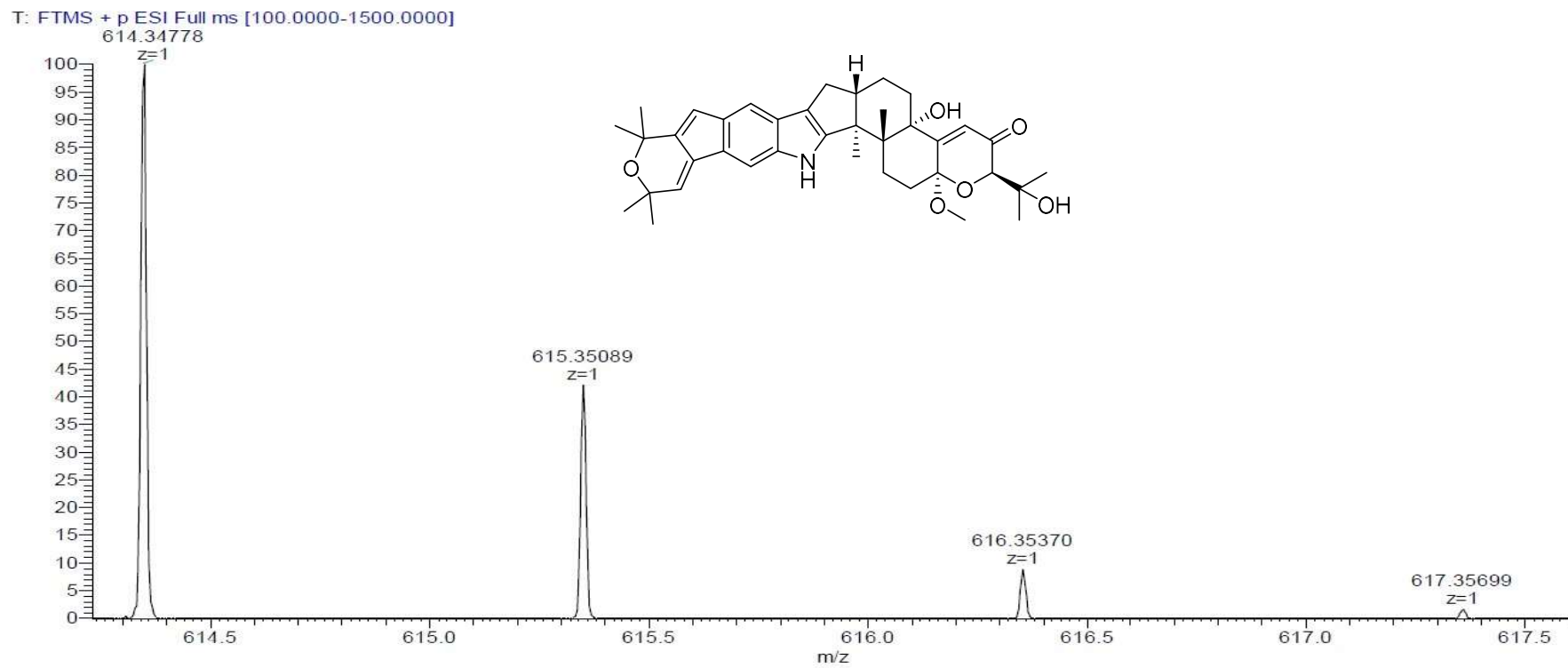


Figure S29. IR Spectrum of Shearinine W (4)

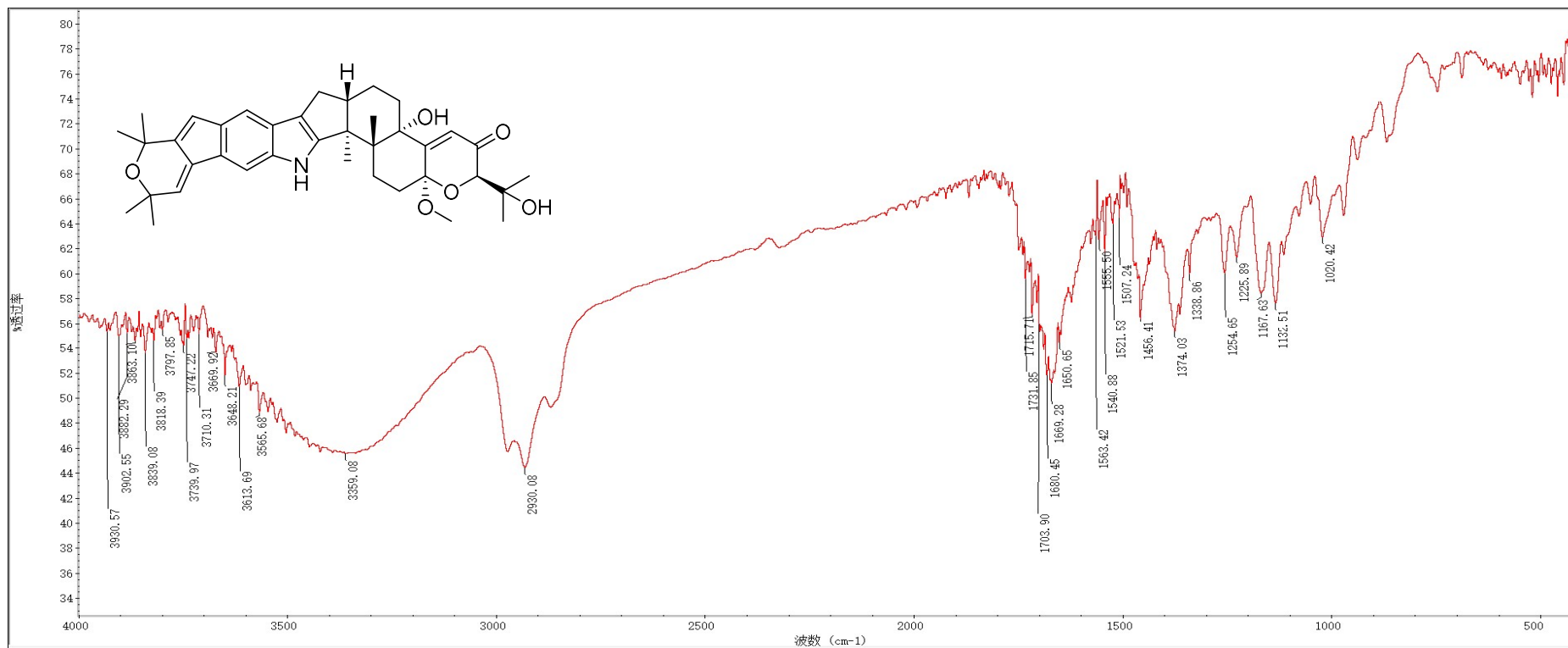


Figure S30. UV Spectrum of Shearinine W (4) in MeOH

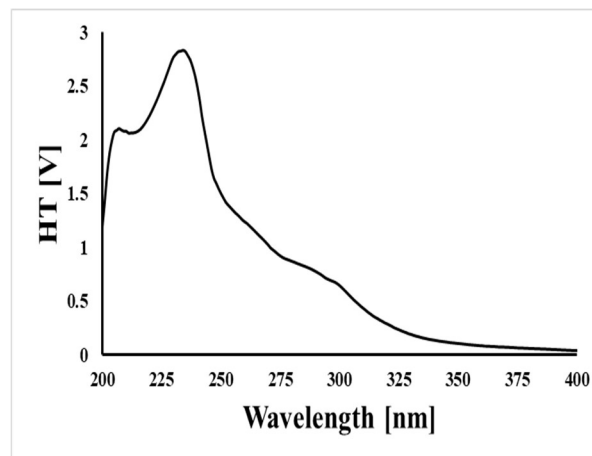
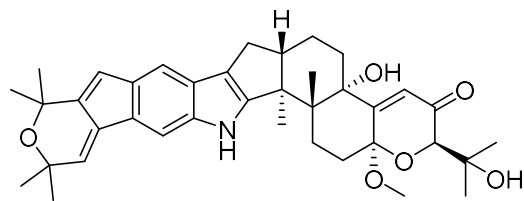


Figure S31. ECD Spectrum of Shearinine W (4) in MeOH

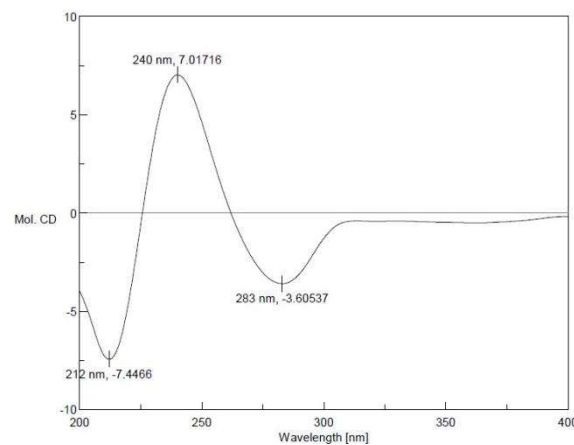
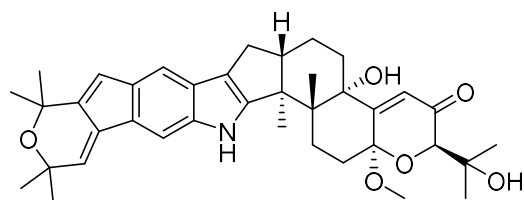


Figure S32. Relative Configurations and the Optimized Conformers for **4**

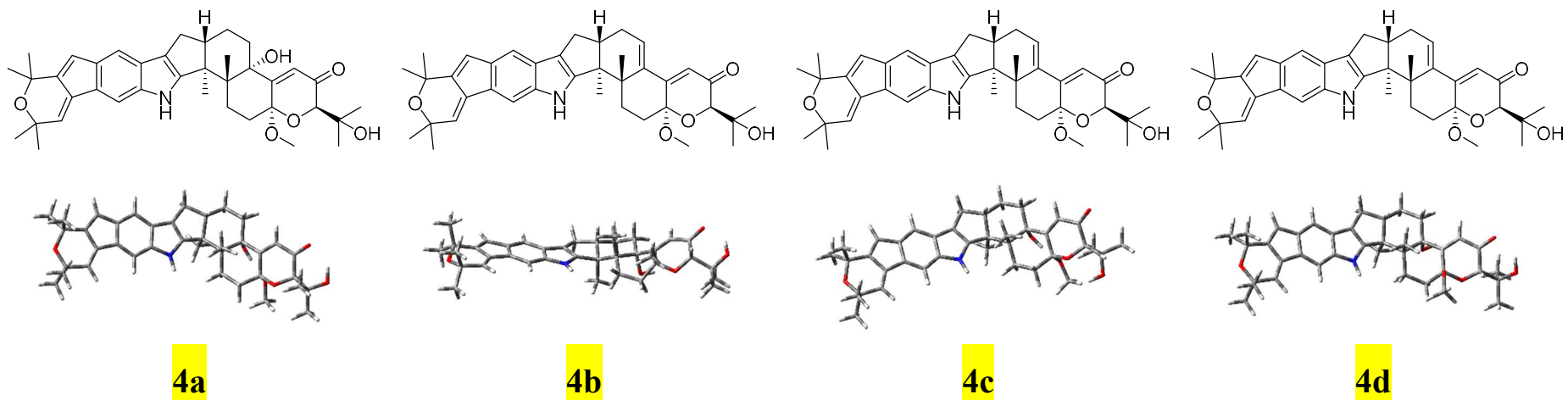


Figure S33. ^1H NMR Spectrum of Shearinine X (5; 600 MHz, $\text{DMSO-}d_6$)

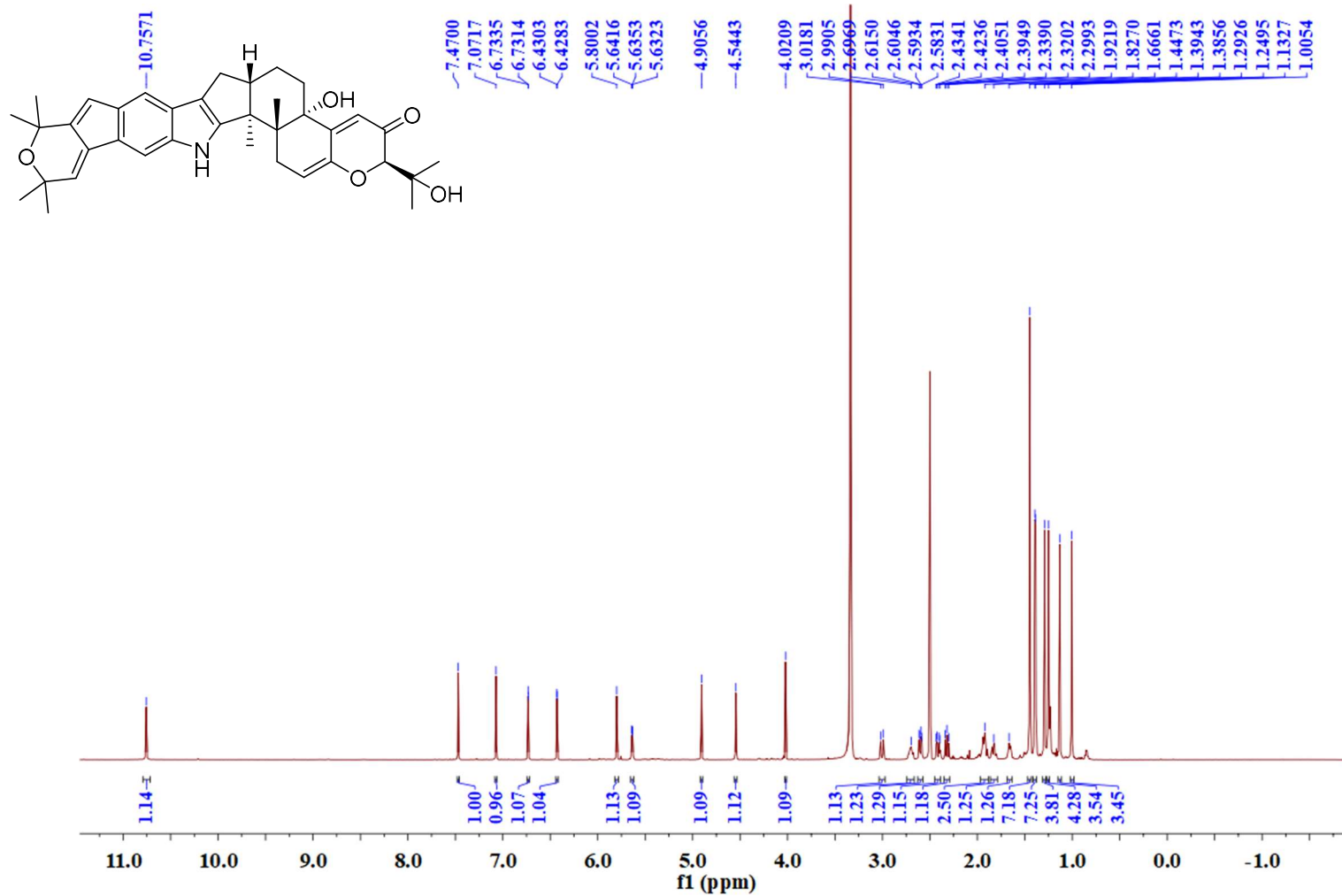


Figure S34. ¹³C NMR Spectrum of Shearinine X (5; 150 MHz, DMSO-*d*₆)

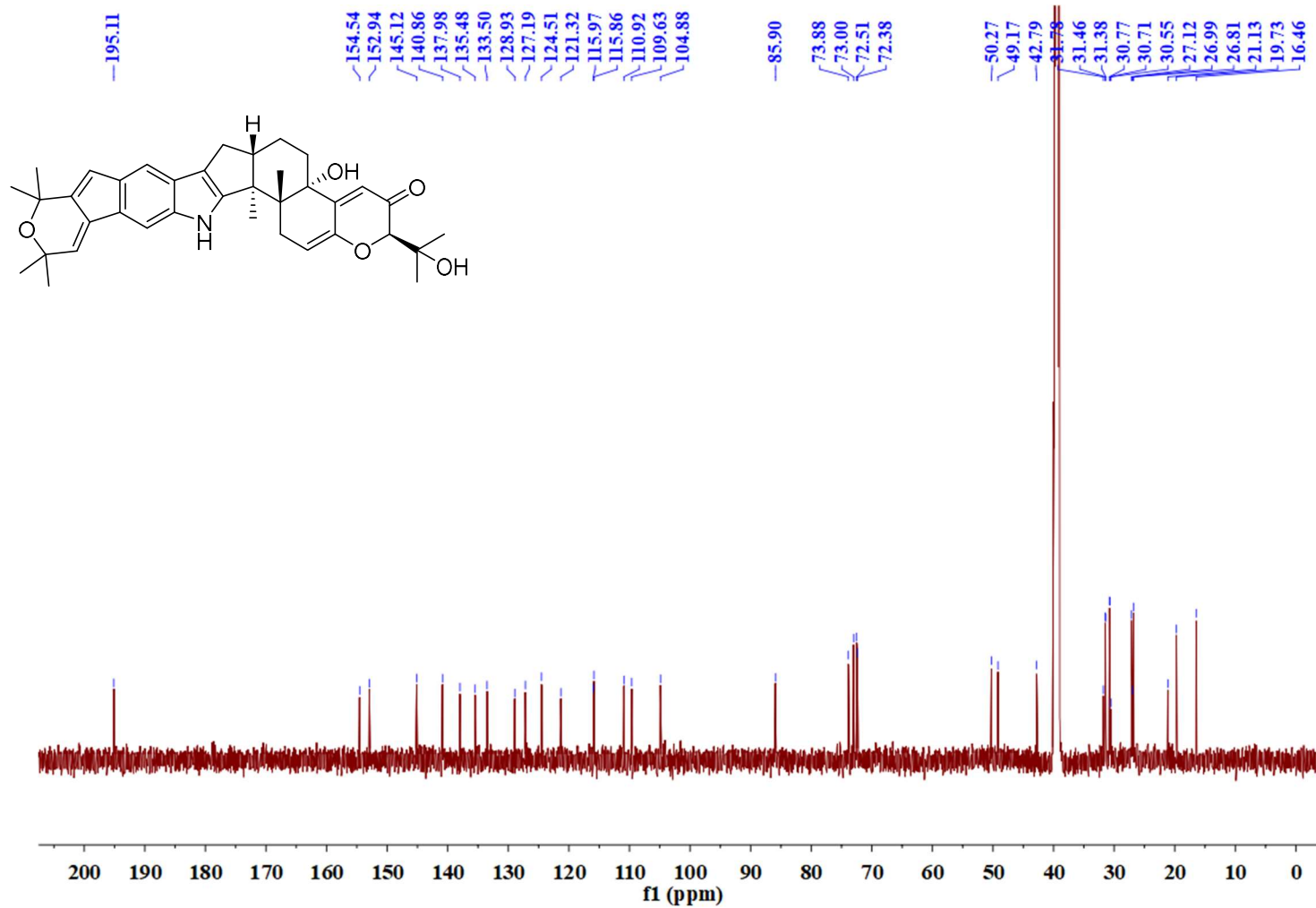


Figure S35. HSQC Spectrum of Shearinine X (5; 600 MHz, DMSO-*d*₆)

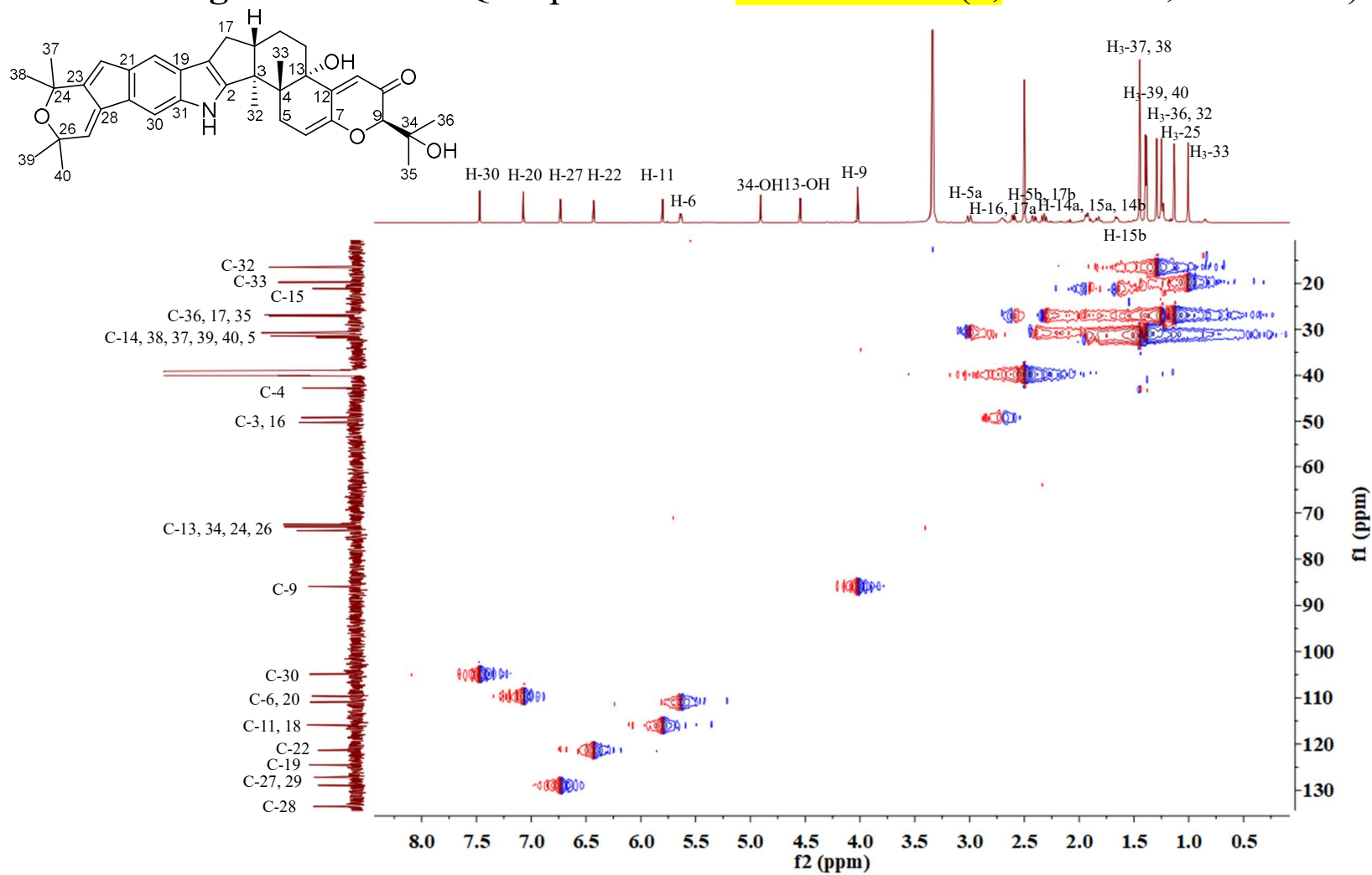


Figure S36. ^1H - ^1H COSY Spectrum of Shearinine X (5; 600 MHz, $\text{DMSO-}d_6$)

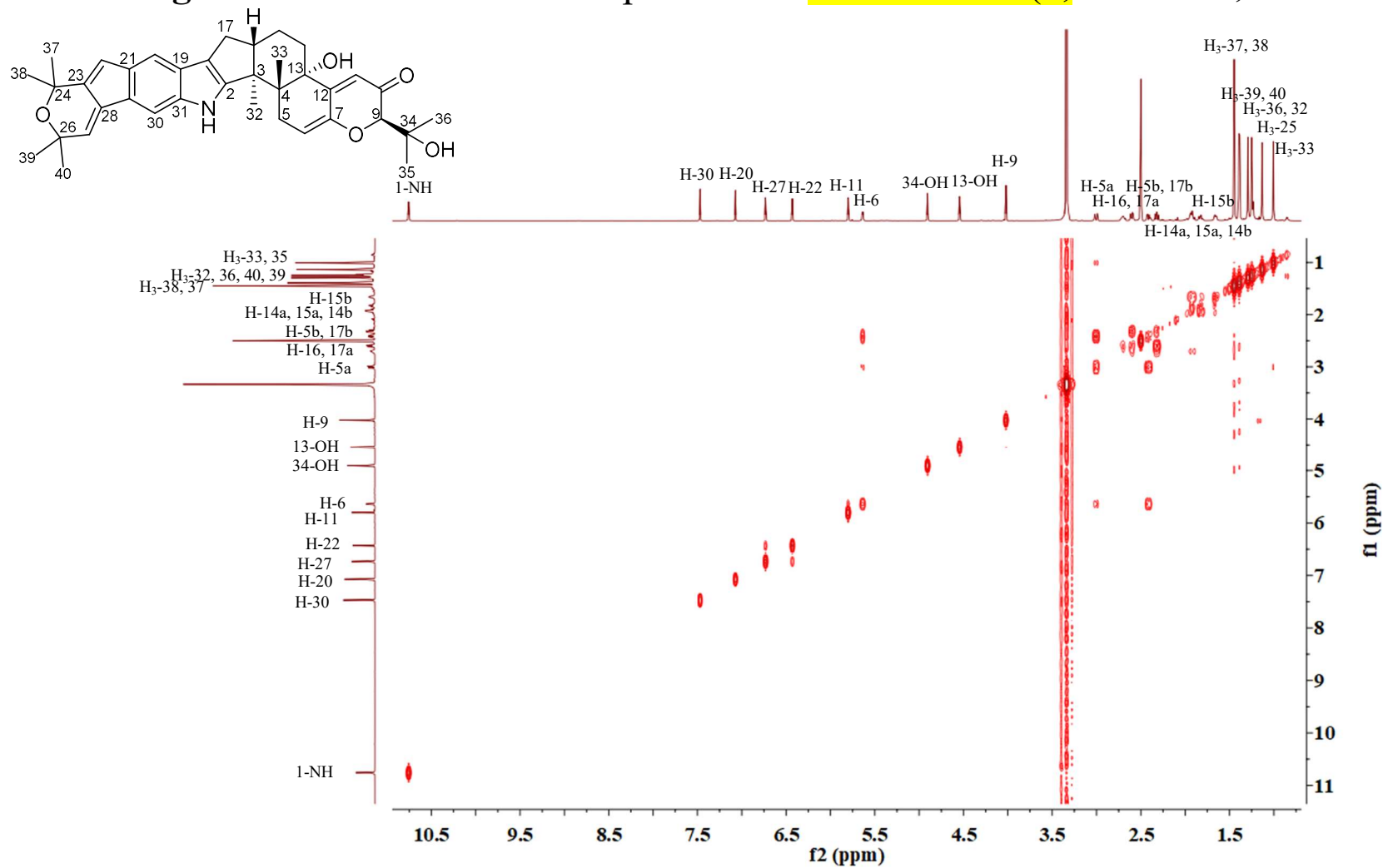


Figure S37. HMBC Spectrum of **Shearinine X (5)**; 600 MHz, DMSO-*d*₆

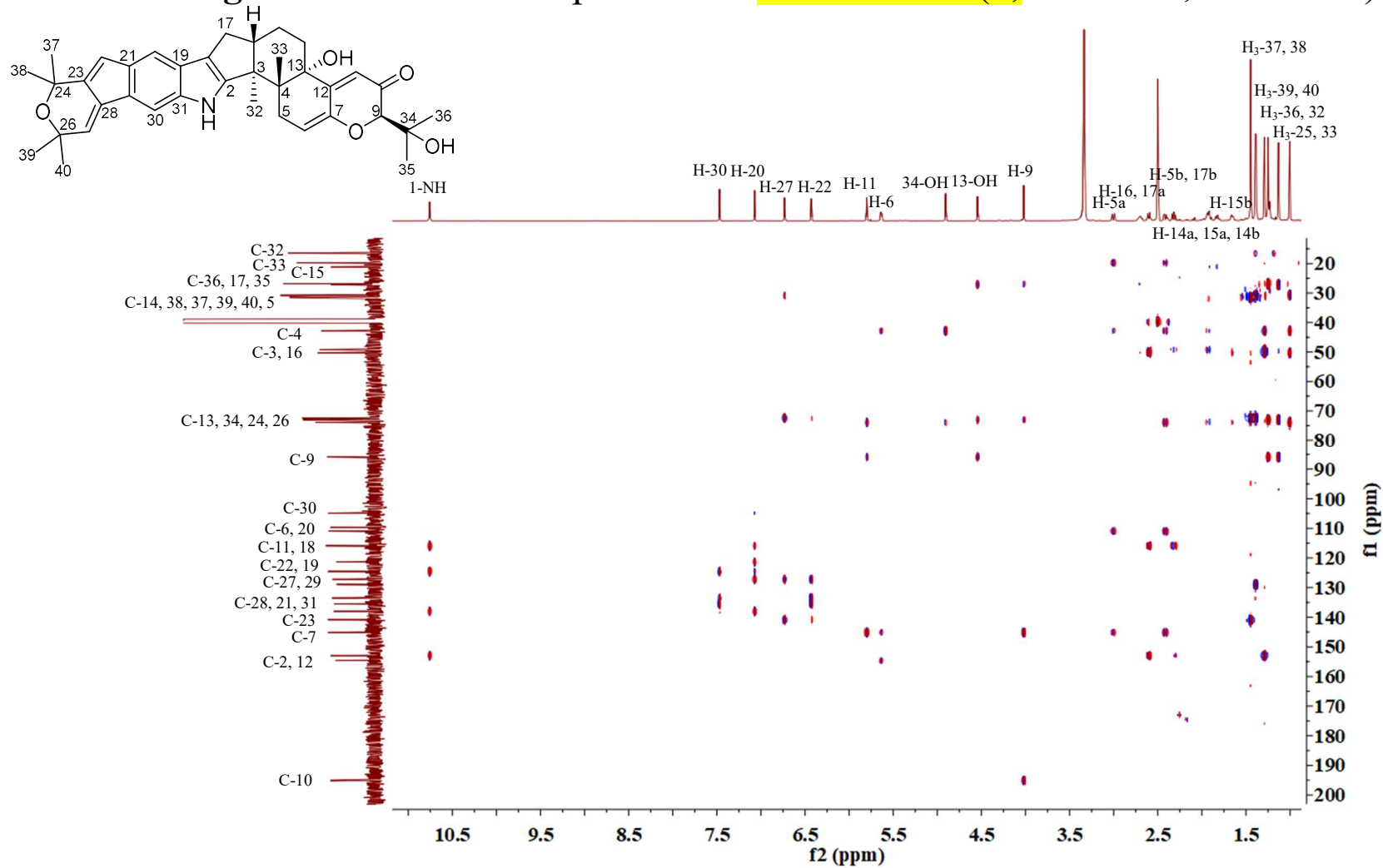


Figure S38. NOESY Spectrum of Shearinine X (**5**; 600 MHz, DMSO-*d*₆)

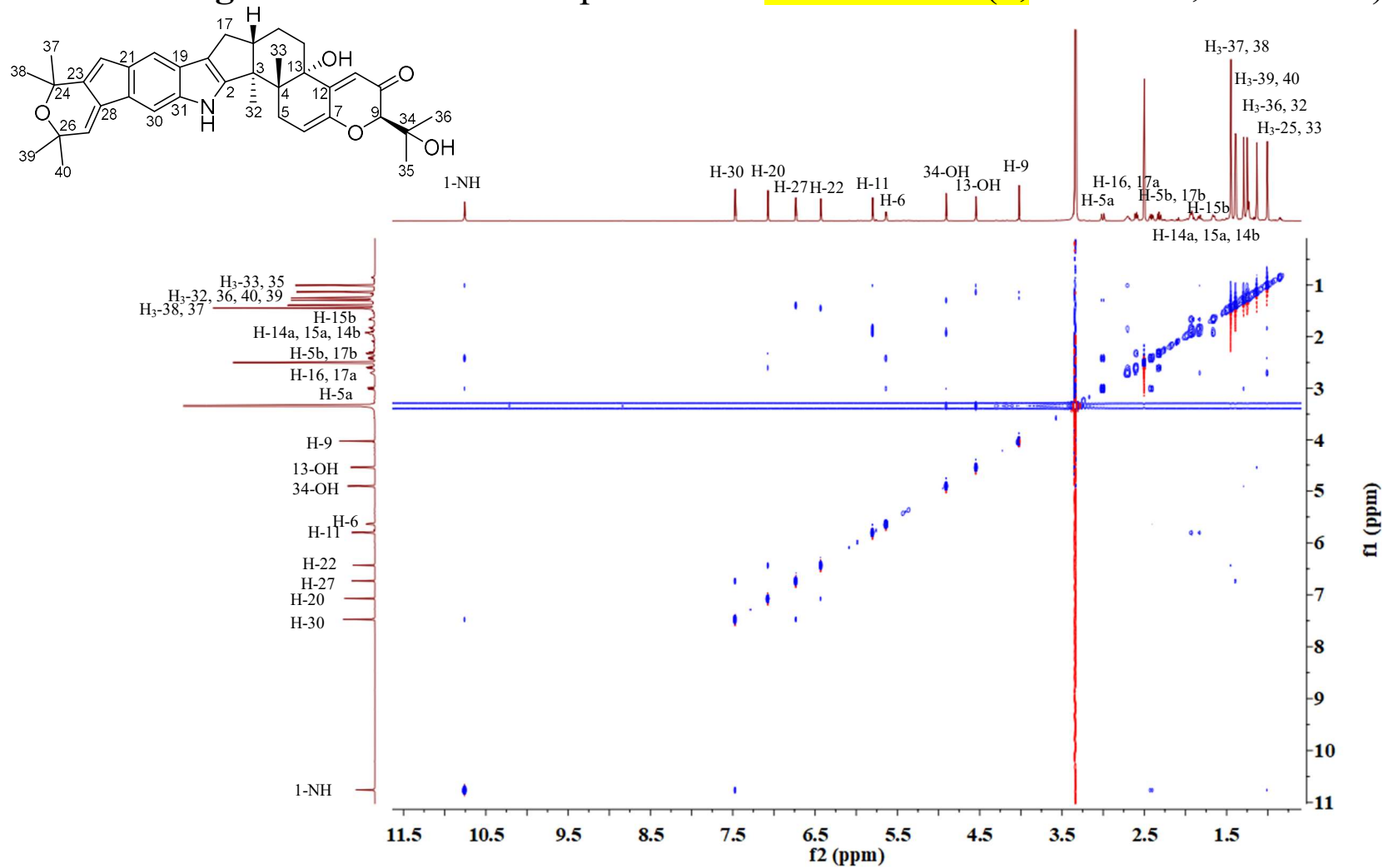


Figure S39. HRESIMS Spectrum of Shearinine X (5)

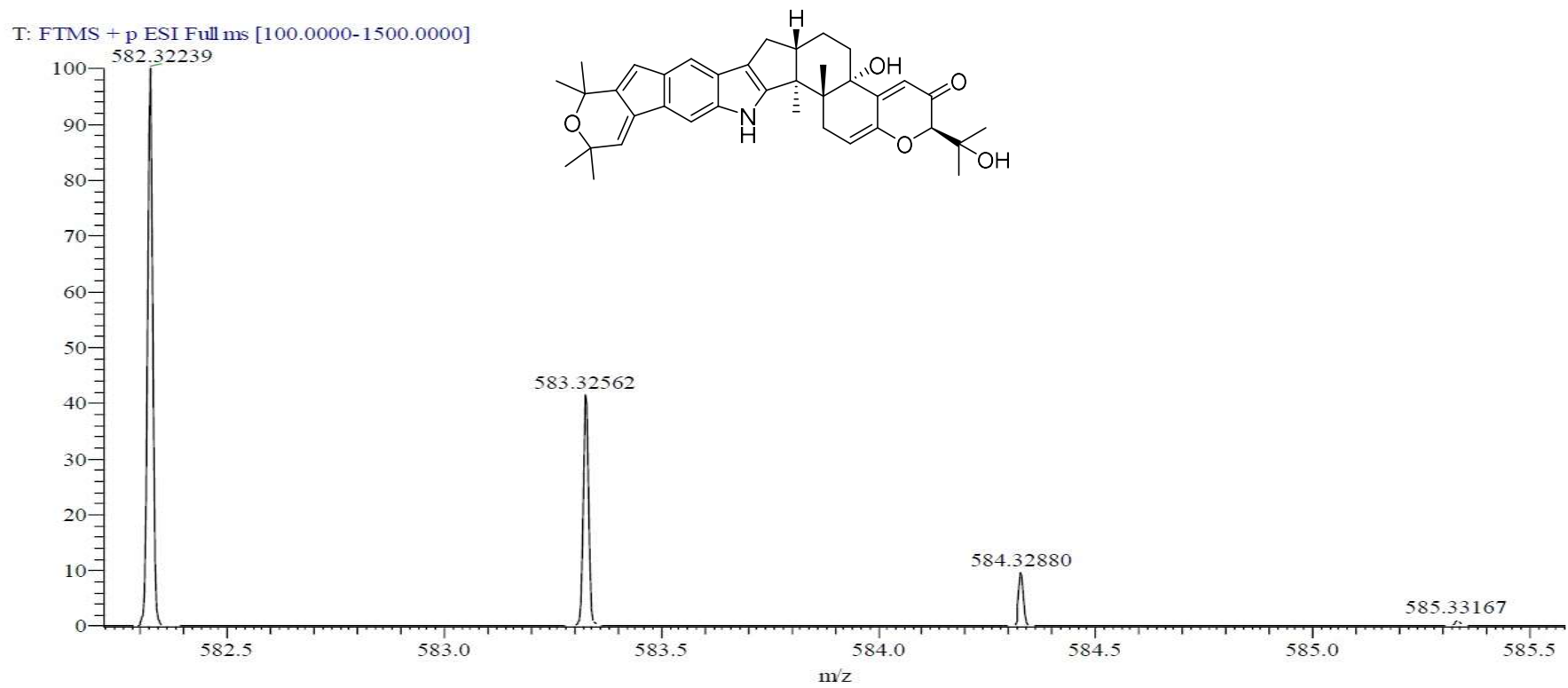


Figure S40. IR Spectrum of Shearinine X (5)

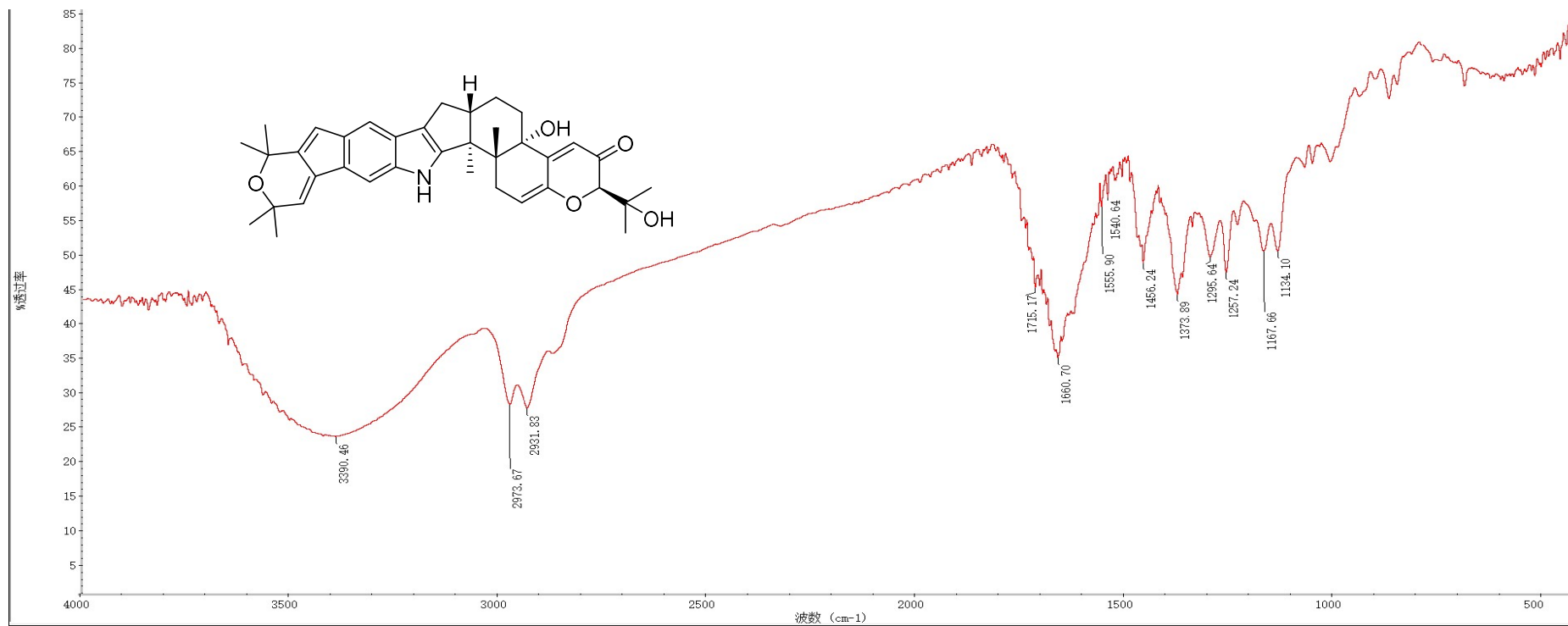


Figure S41. UV Spectrum of Shearinine X (5) in MeOH

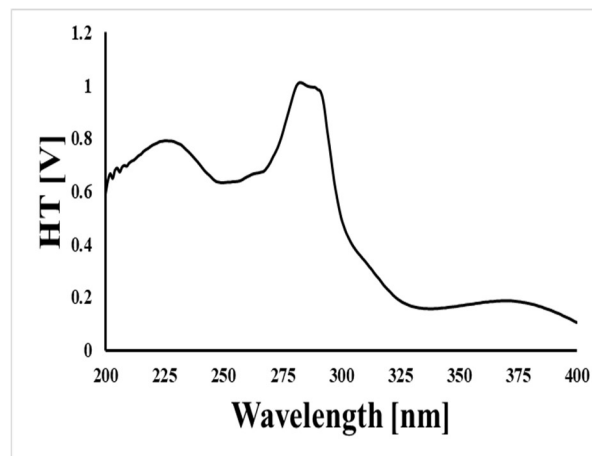
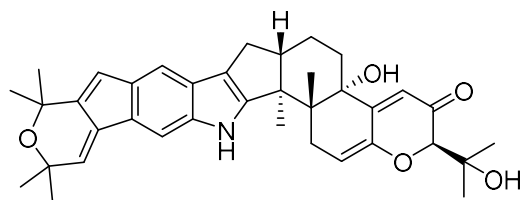


Figure S42. ECD Spectrum of Shearinine X (5) in MeOH

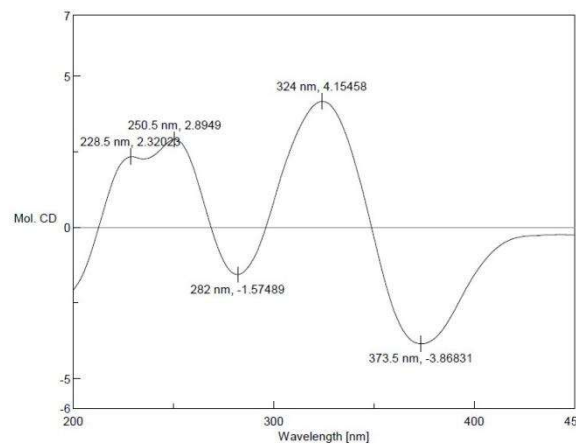
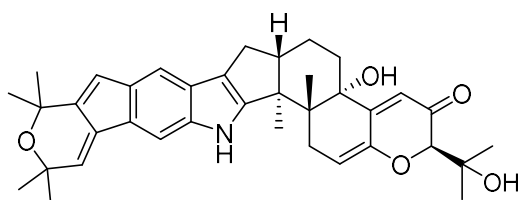


Figure S43. Relative Configurations and the Optimized Conformers for **5**

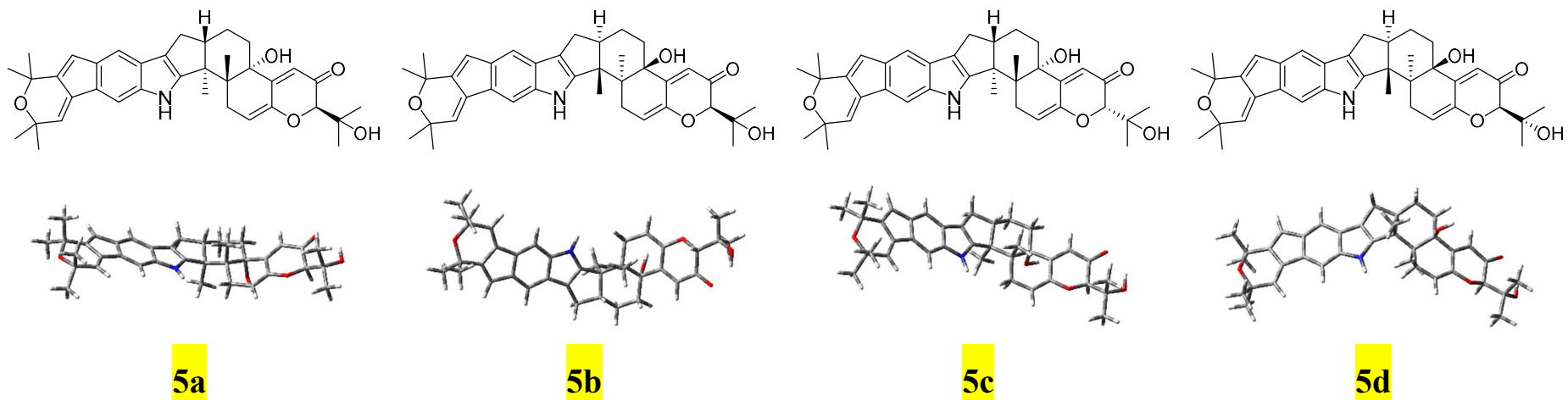


Figure S44. ¹H NMR Spectrum of Shearinine Y (6; 600 MHz, DMSO-*d*₆)

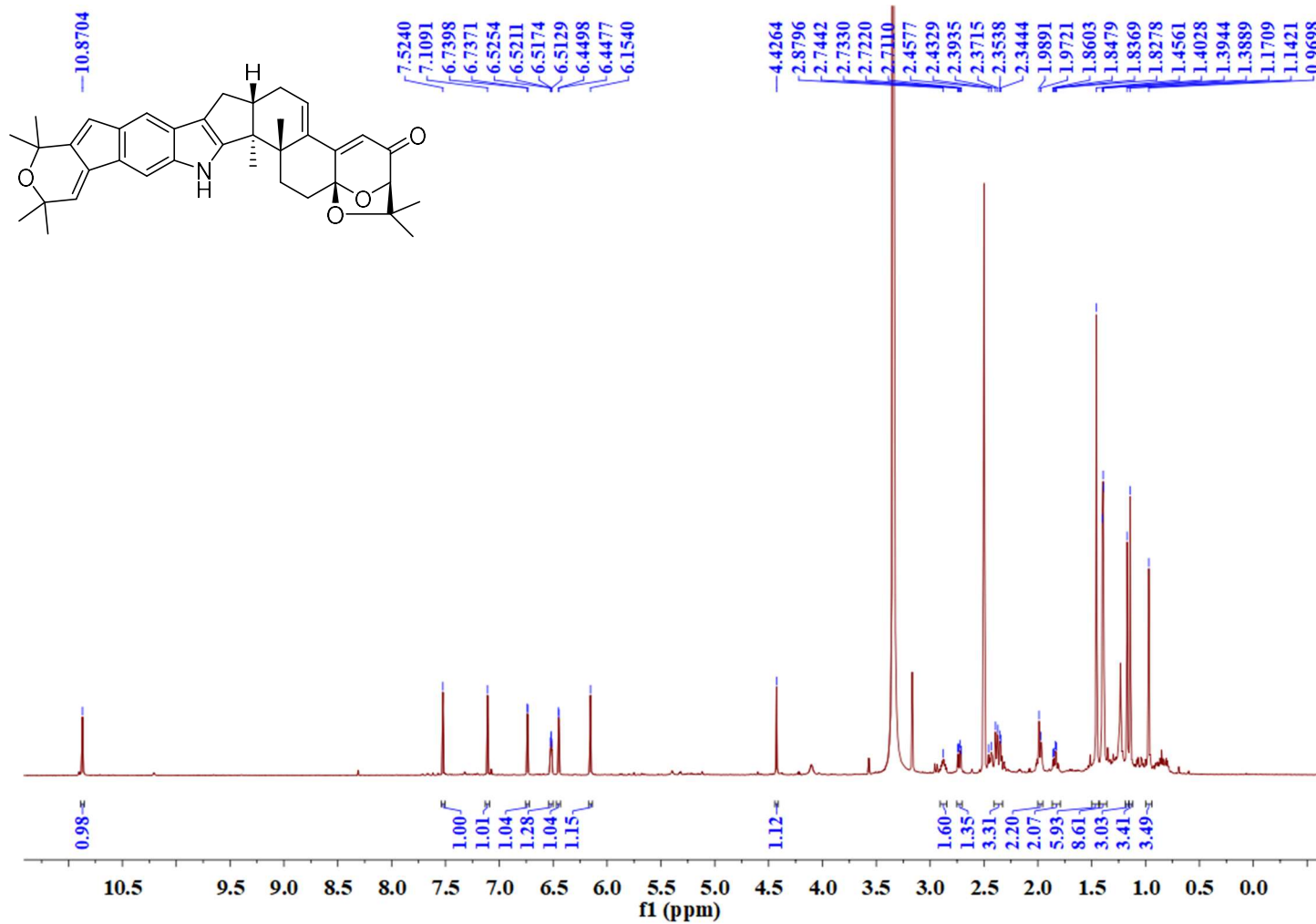


Figure S45. ^{13}C NMR Spectrum of Shearinine Y (**6**; 150 MHz, $\text{DMSO-}d_6$)

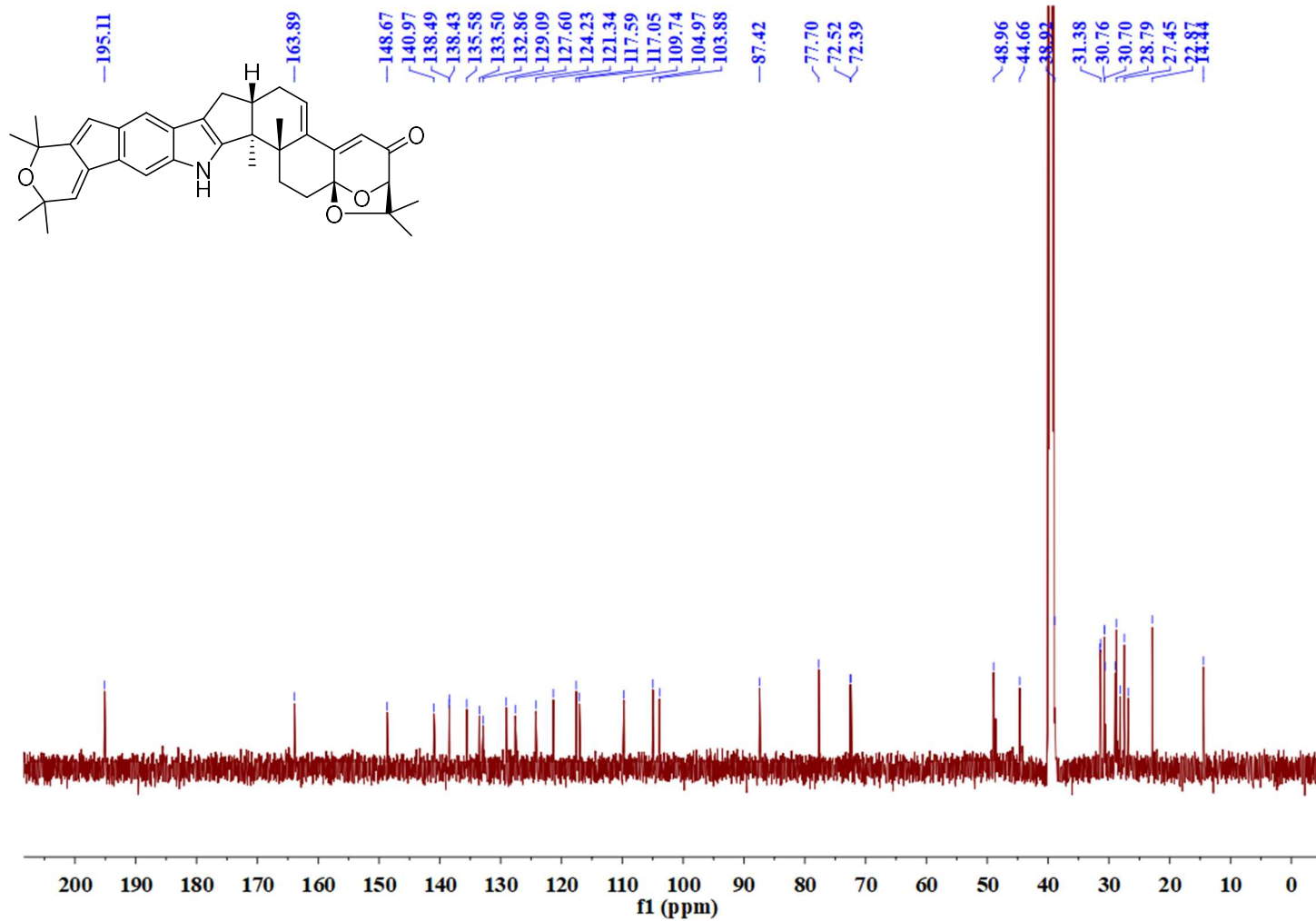


Figure S46. HSQC Spectrum of Shearinine Y (6; 600 MHz, DMSO-*d*₆)

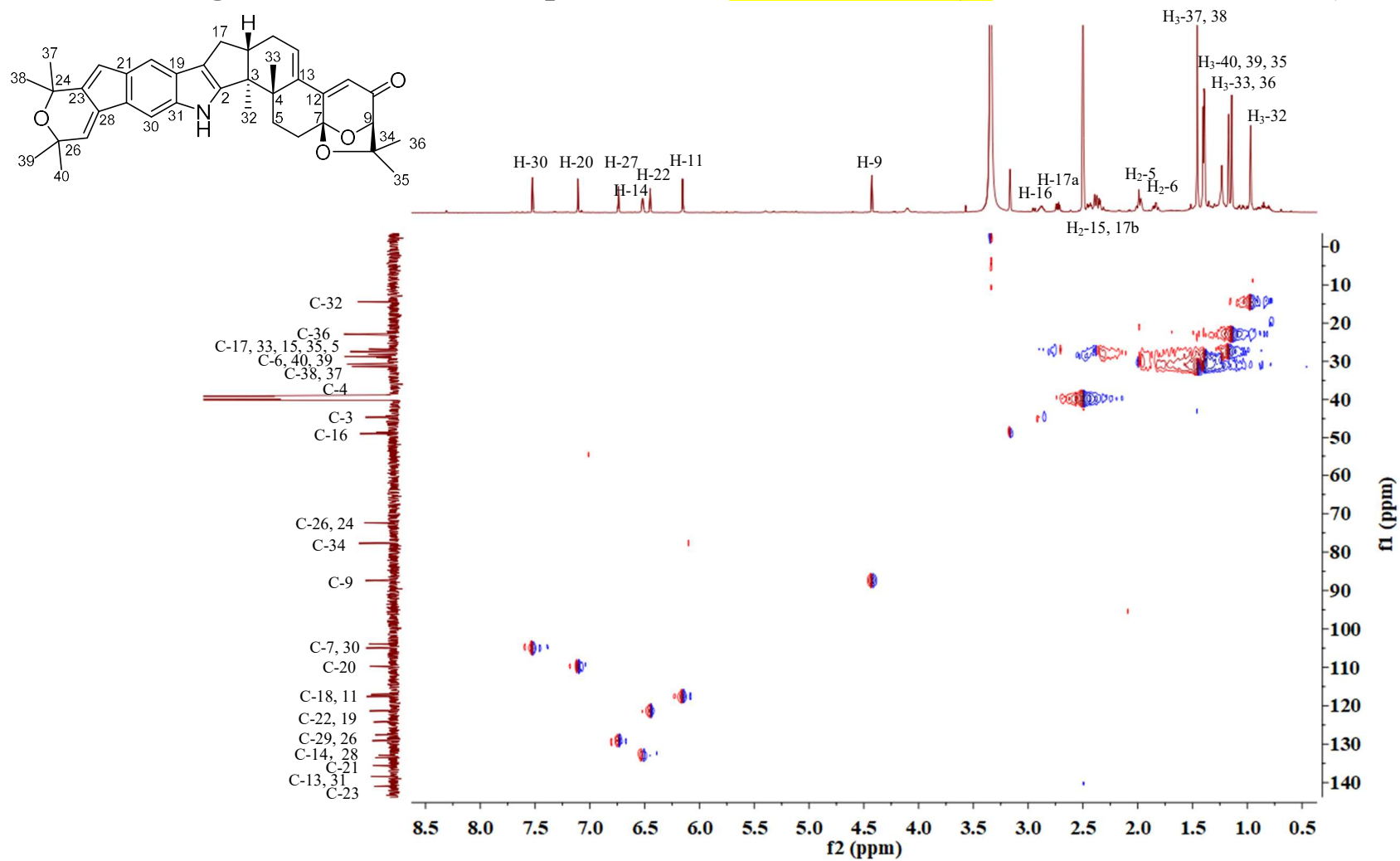


Figure S47. ^1H - ^1H COSY Spectrum of Shearinine Y (6; 600 MHz, $\text{DMSO-}d_6$)

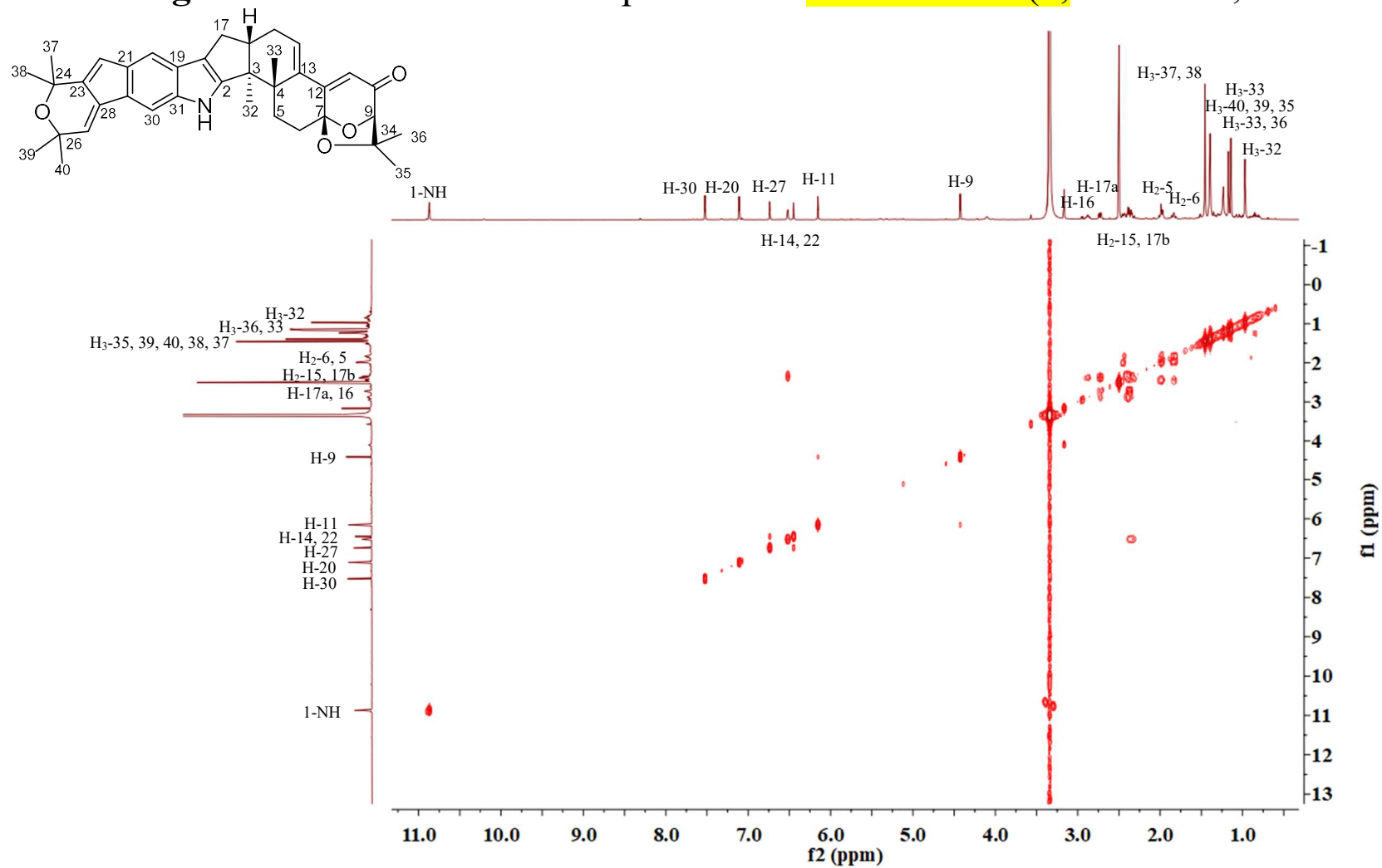


Figure S48. HMBC Spectrum of **Shearinine Y (6)**; 600 MHz, DMSO-*d*₆)

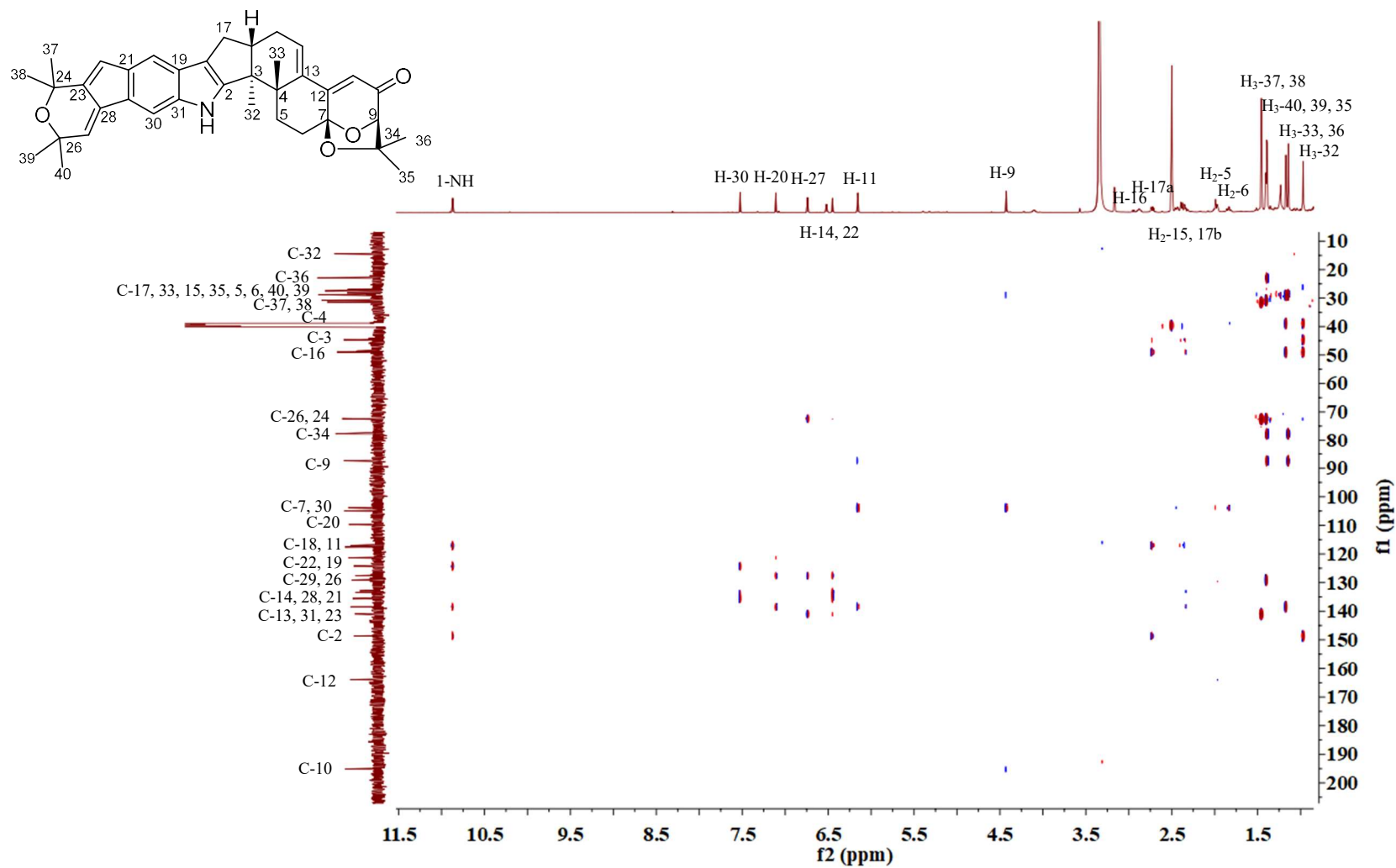


Figure S49. NOESY Spectrum of Shearinine Y (**6**; 600 MHz, DMSO-*d*₆)

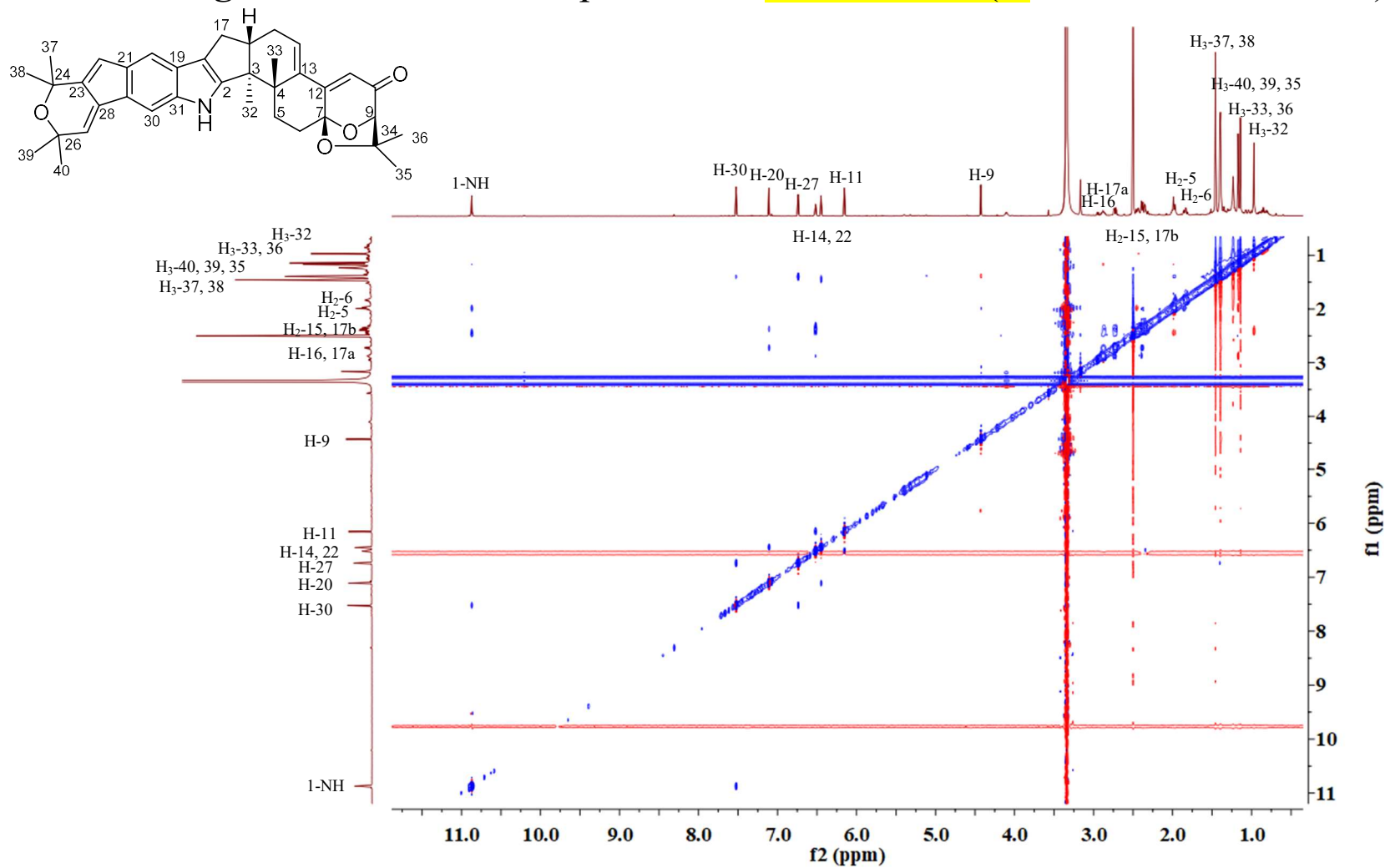


Figure S50. HRESIMS Spectrum of Shearinine Y (6)

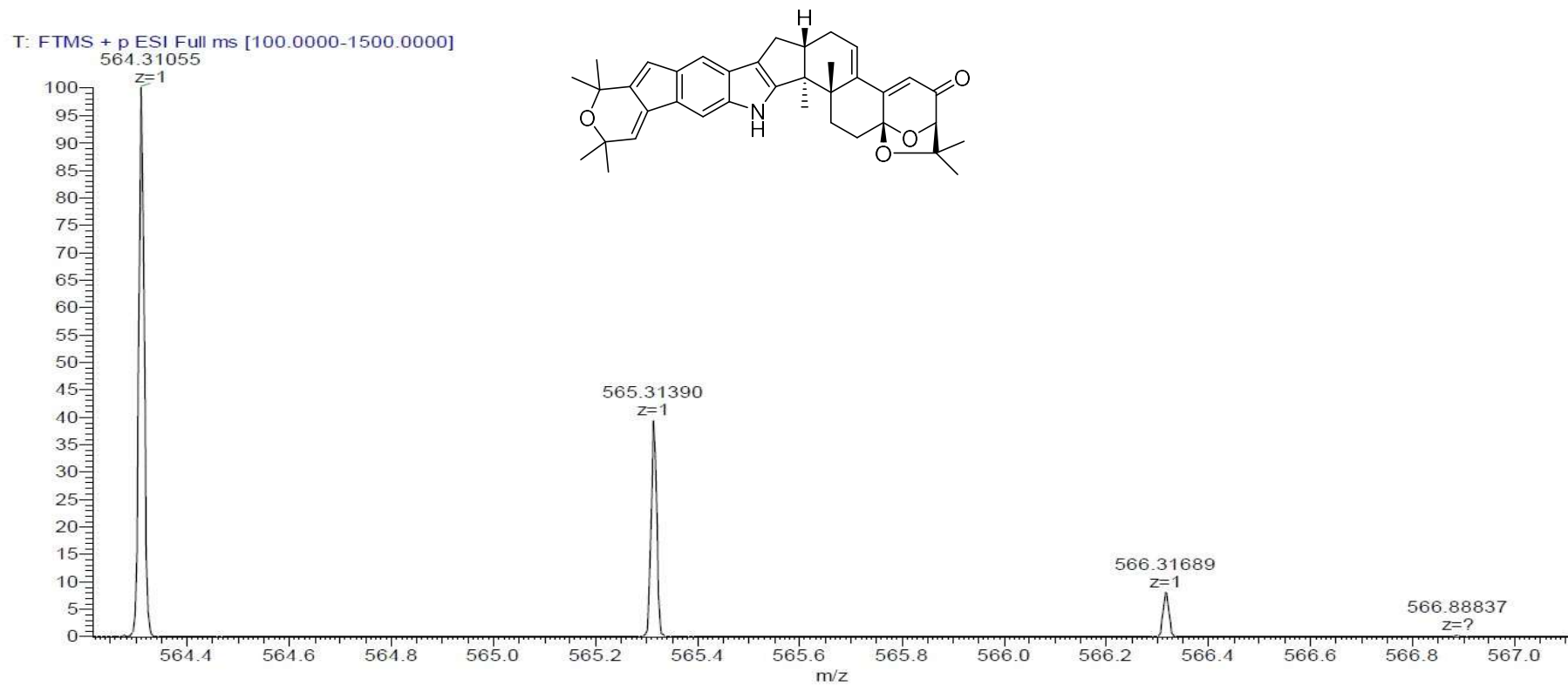


Figure S51. IR Spectrum of Shearinine Y (6)

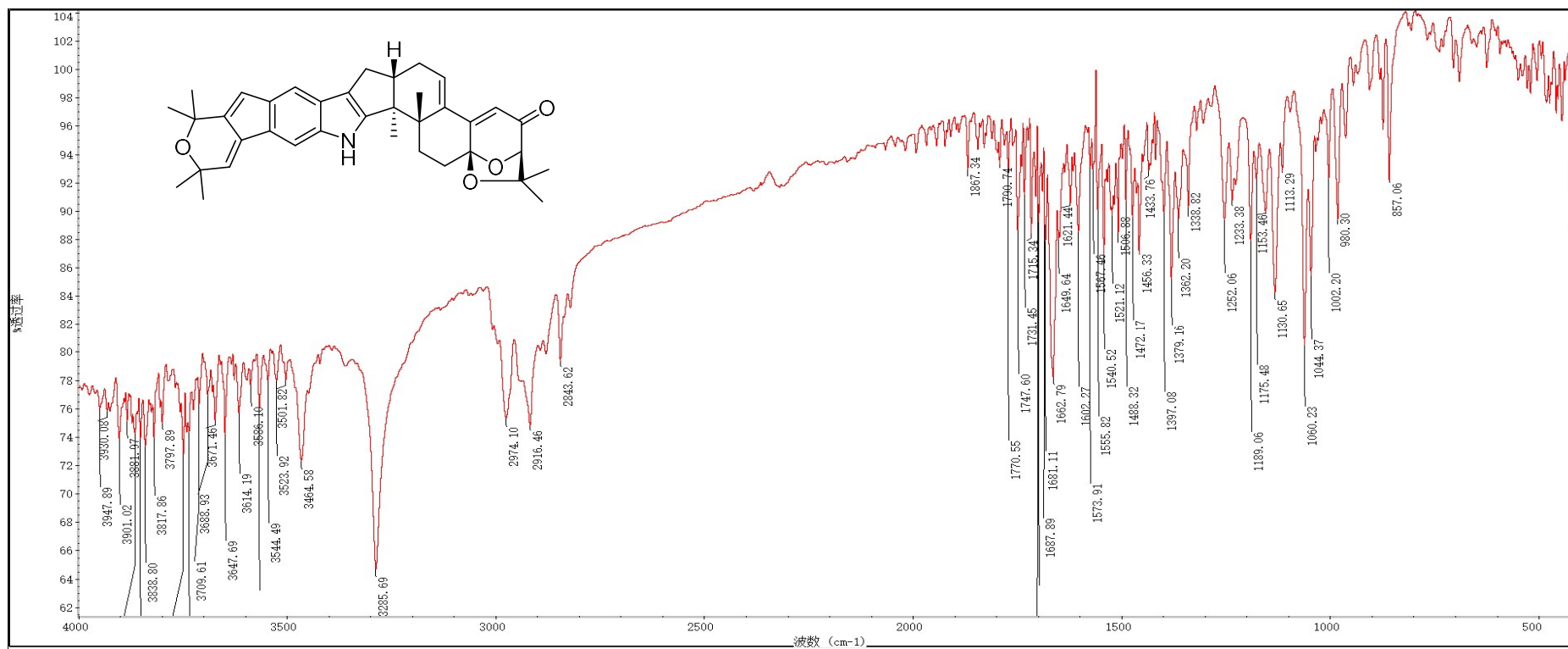


Figure S52. UV Spectrum of Shearinine Y (6) in MeOH

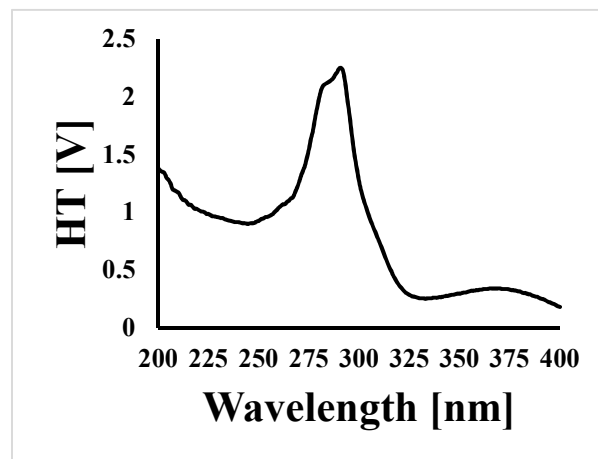
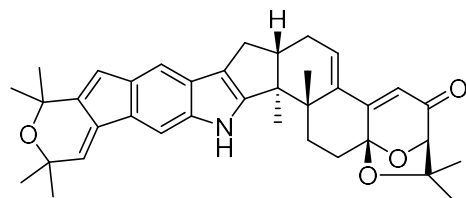


Figure S53. ECD Spectrum of Shearinine Y (6) in MeOH

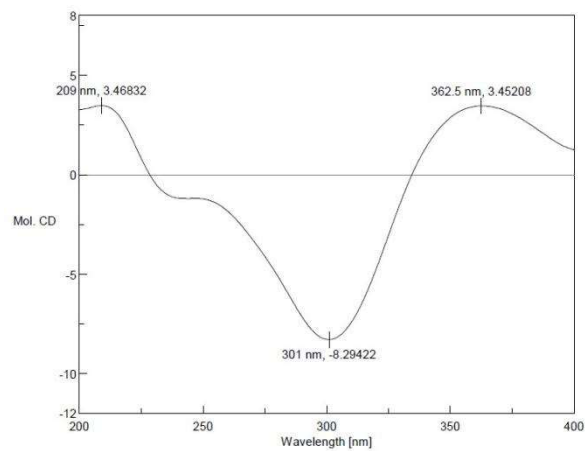
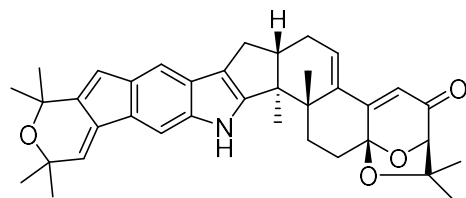
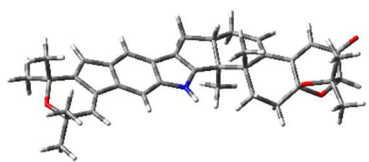
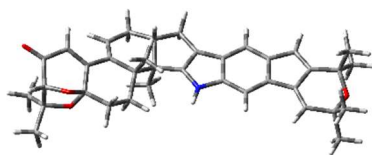


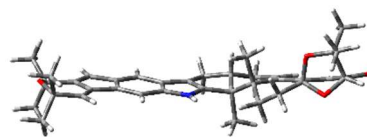
Figure S54. Relative Configurations and the Optimized Conformers for **6**



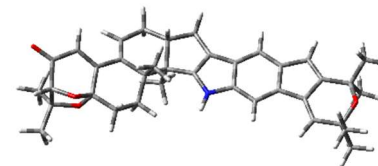
6a



6b



6c



6d

Figure S55. ¹H NMR Spectrum of 22,23-Dehydro-shearinine A (1); 600 MHz, CDCl₃

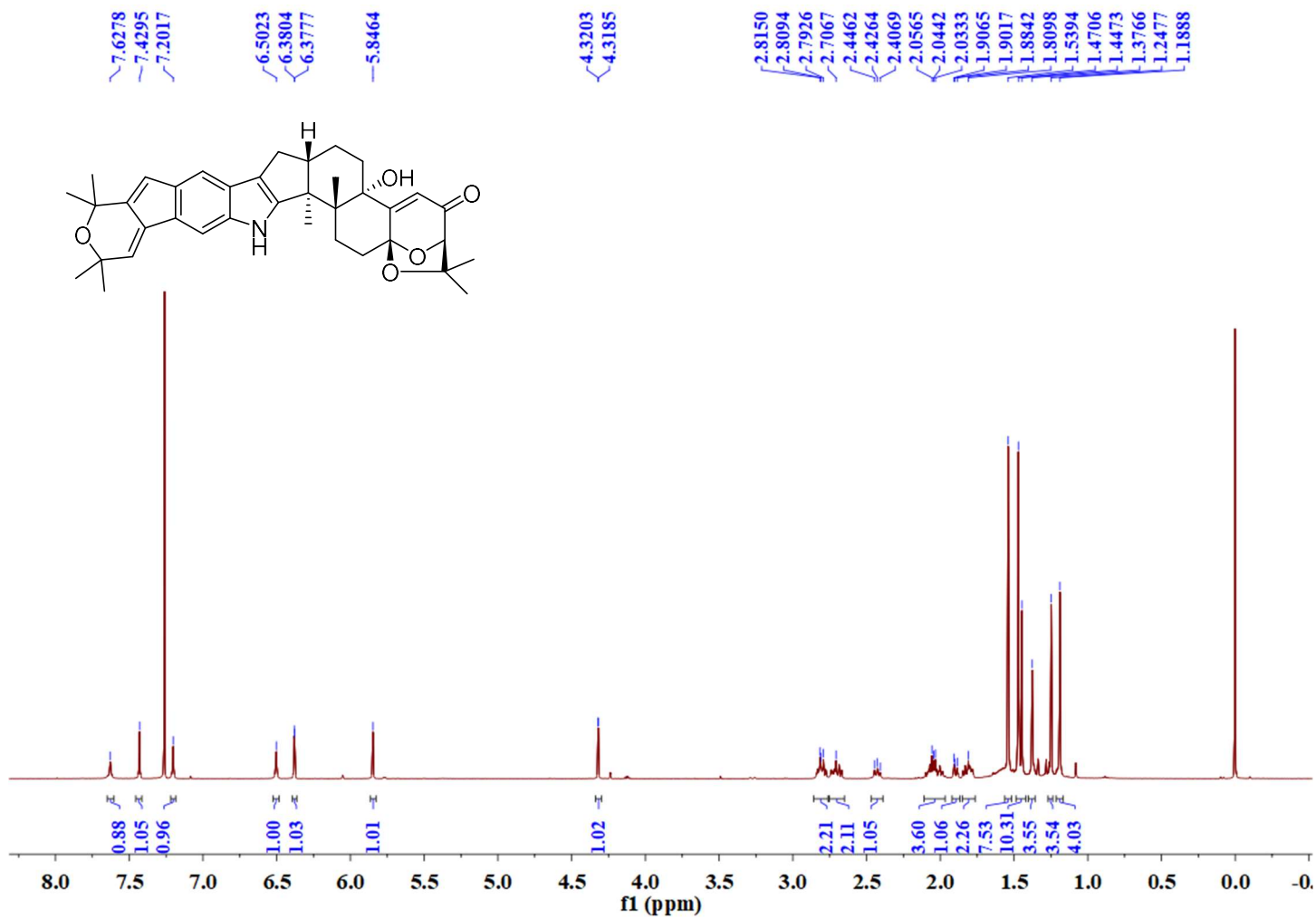
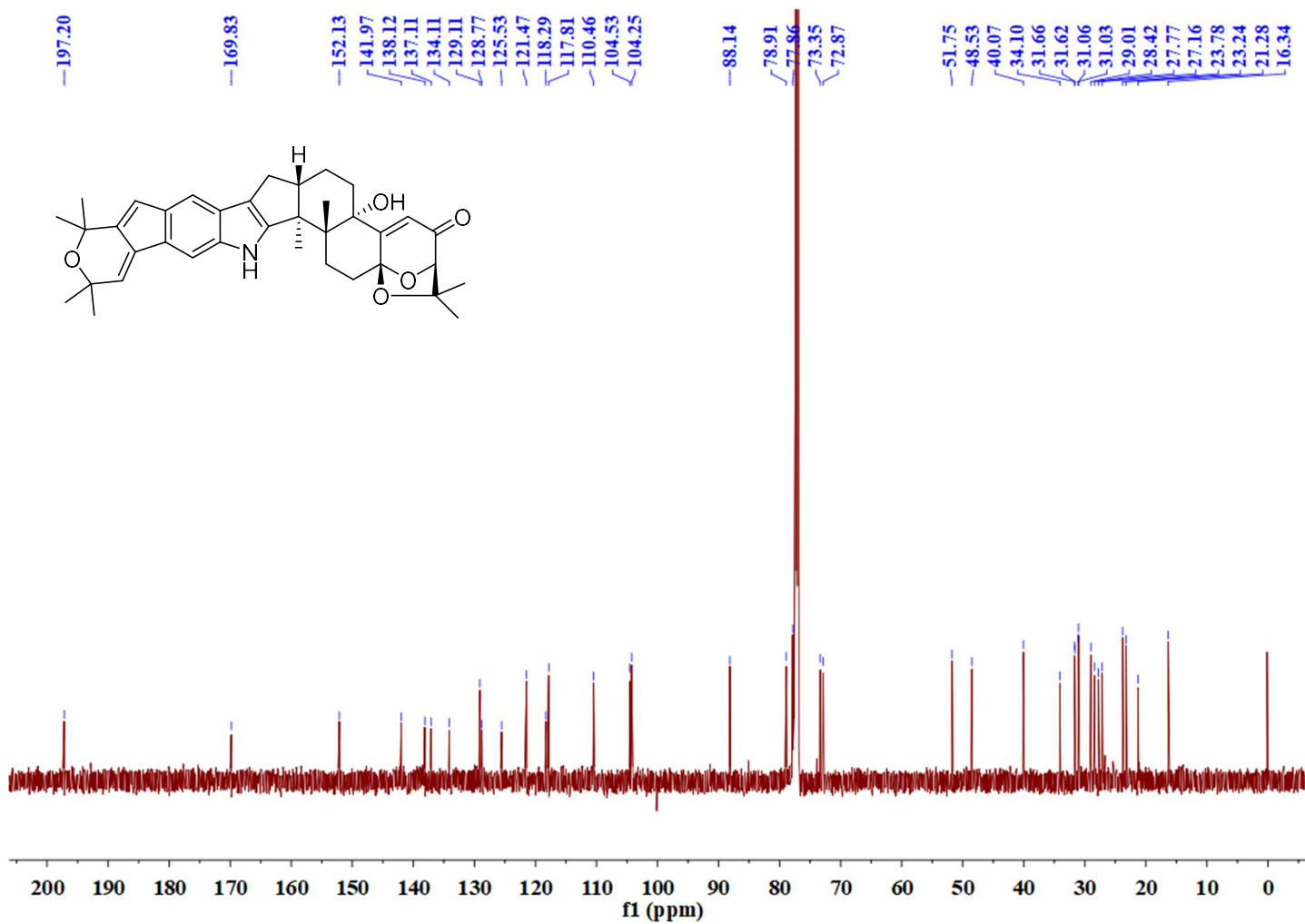


Figure S56. ¹C NMR Spectrum of 22,23-Dehydro-shearinine A (1; 150 MHz, CDCl₃)



Scheme S1. Hypothetical Biosynthetic Pathways for 1–6

