

Supporting Information

Pseudonectrins A–D, heptaketides from an endophytic fungus *Nectria pseudotrichia*

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Figure S1. ^1H NMR Spectrum of Pseudonectrin A (**1**; 600 MHz, CDCl_3)

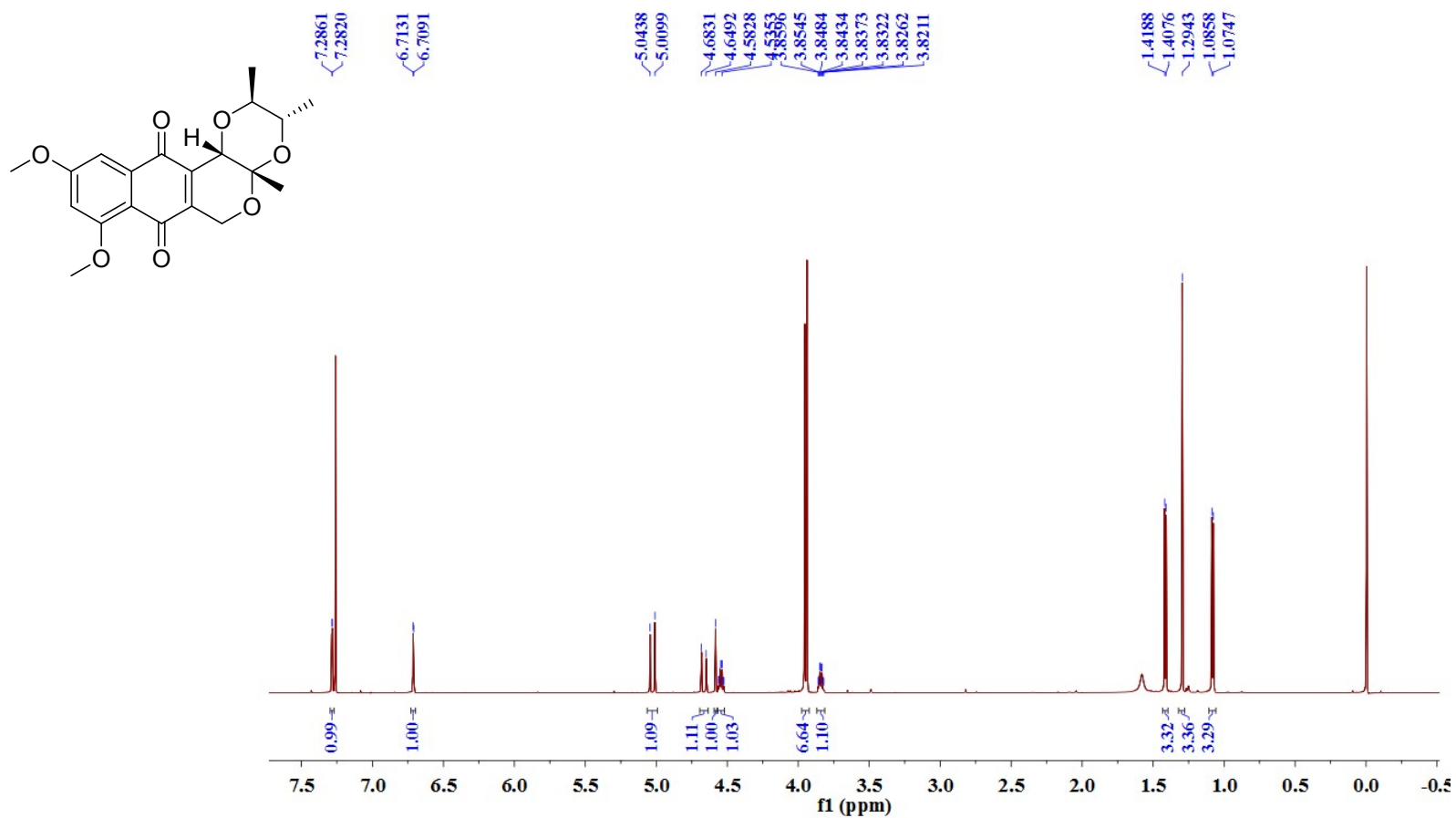
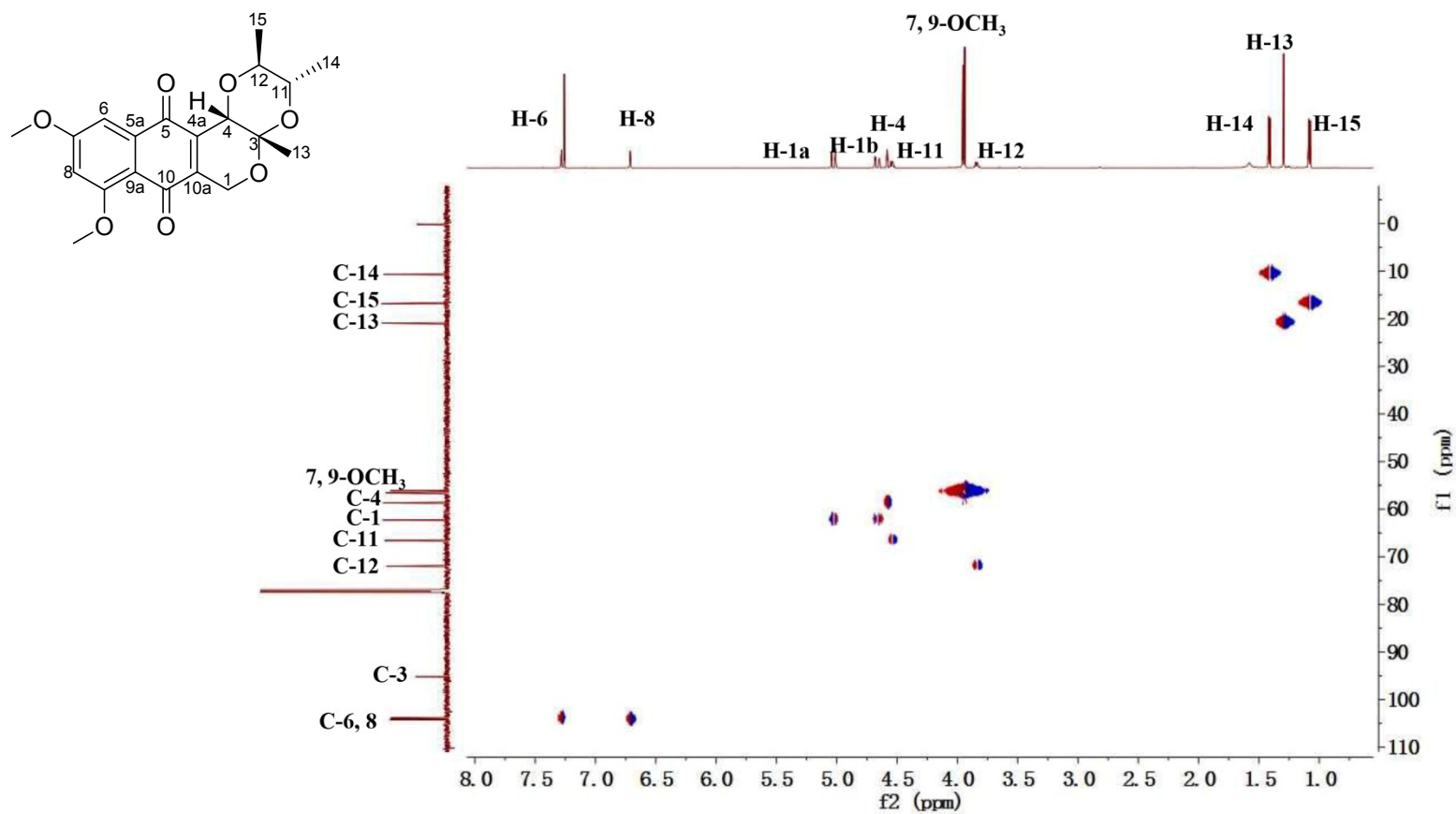


Figure S3. HSQC Spectrum of Pseudonectrin A (**1**; 600 MHz, CDCl₃)



C

Figure S4. ^1H - ^1H COSY Spectrum of Pseudonectrin A (**1**; 600 MHz, CDCl_3)

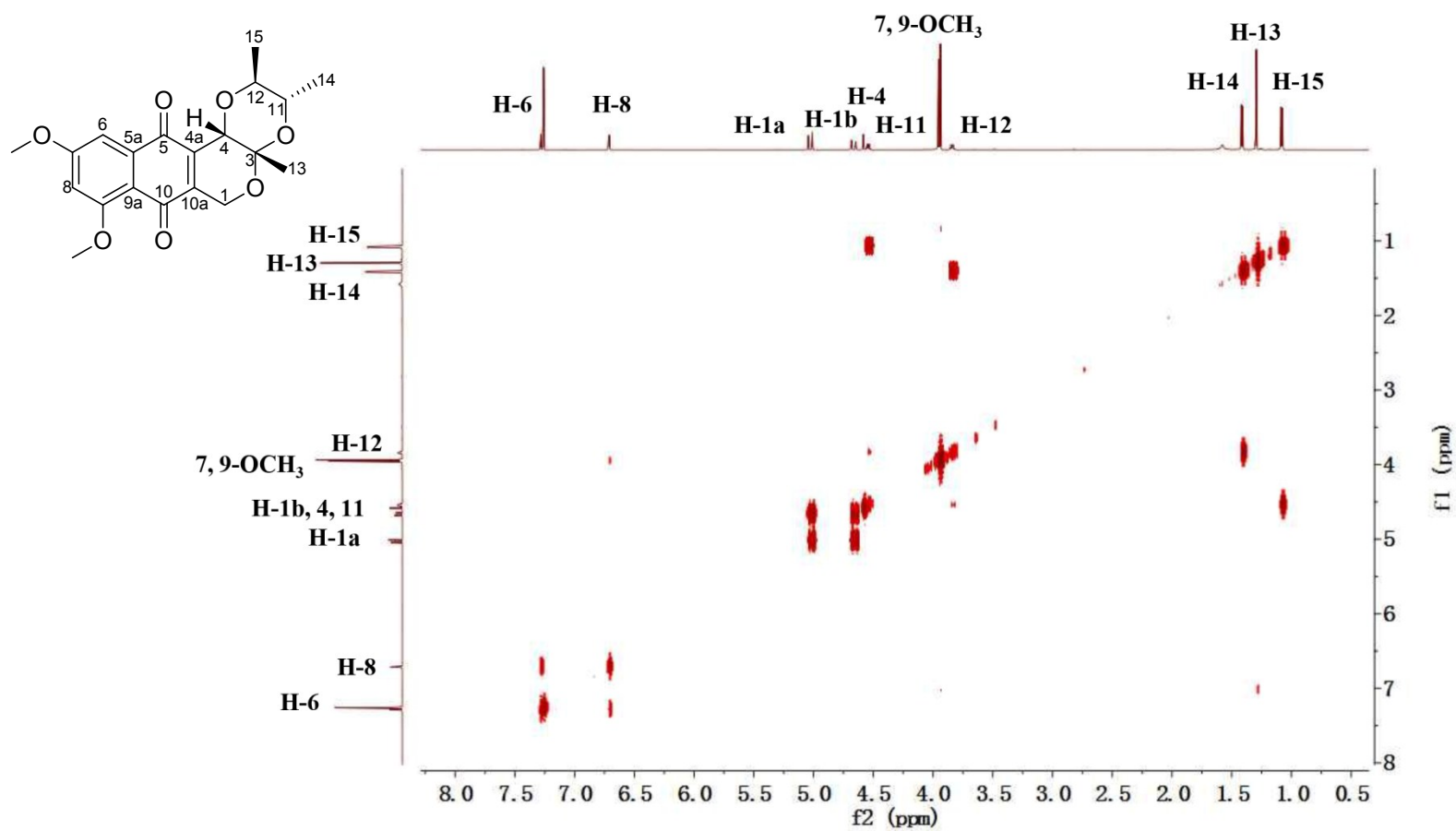


Figure S5. HMBC Spectrum of Pseudonectrin A (1; 600 MHz, CDCl₃)

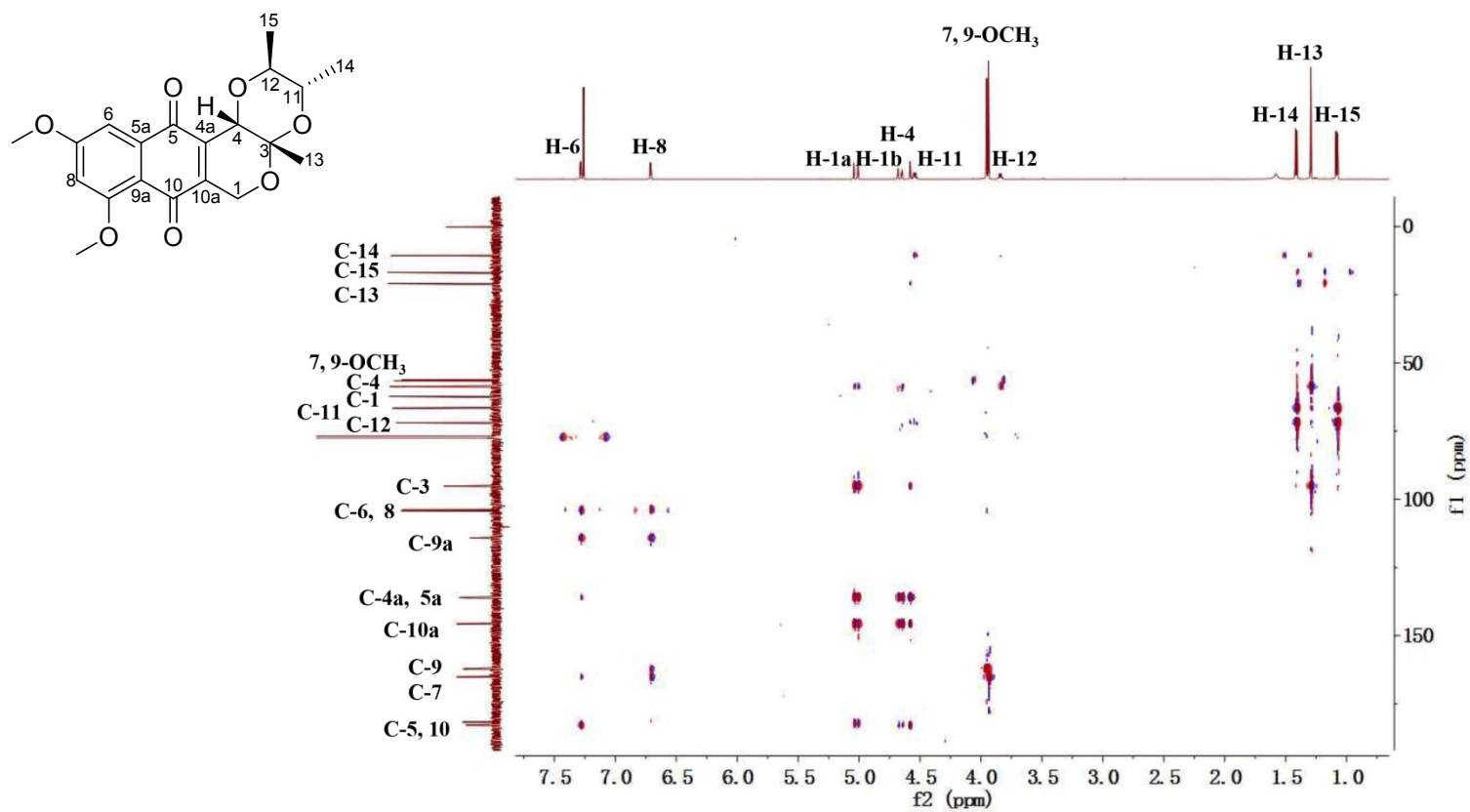


Figure S6. NOESY Spectrum of Pseudonectrin A (**1**; 600 MHz, CDCl₃)

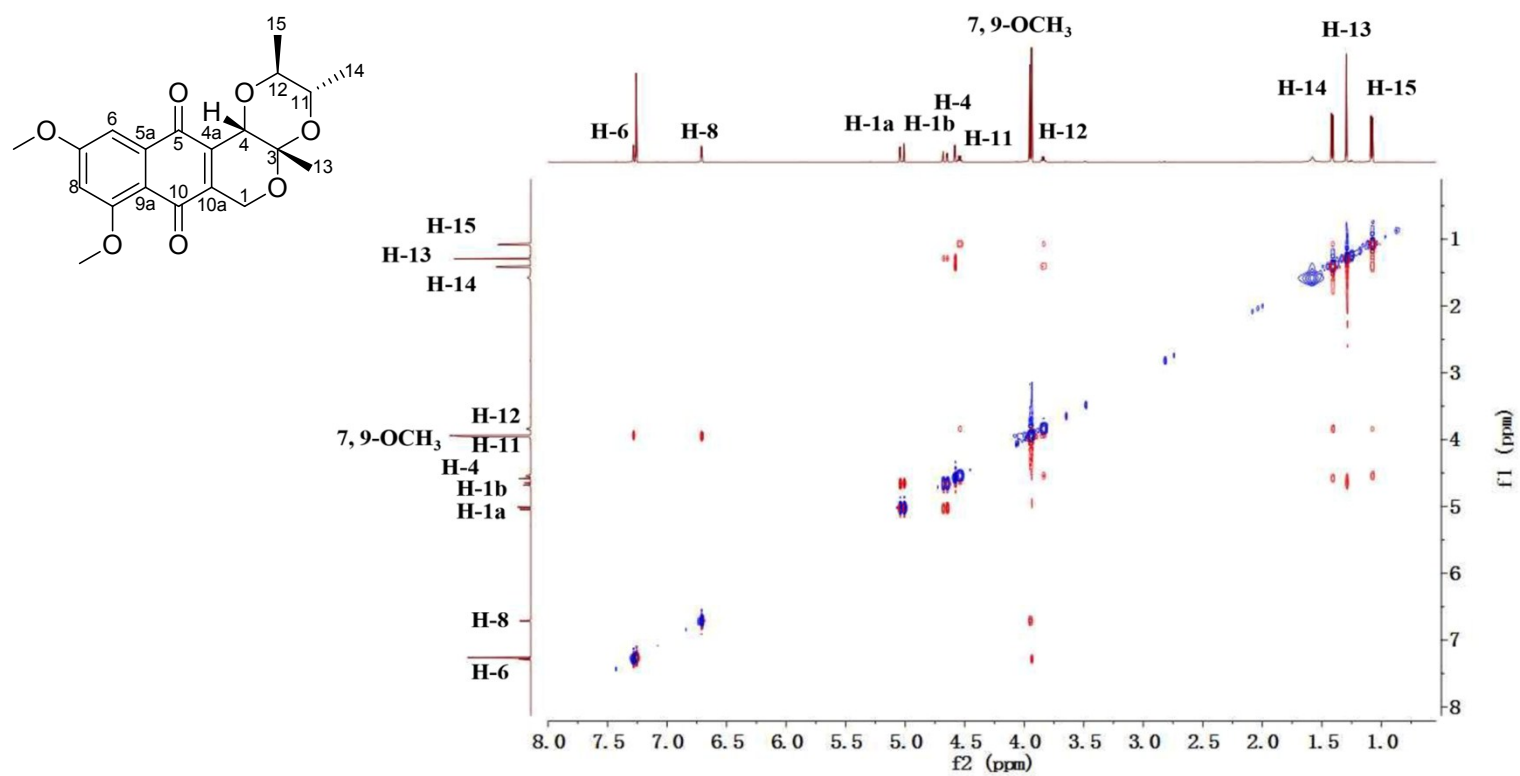


Figure S7. ^1H NMR Spectrum of Pseudonectrin B (**2**; 600 MHz, CDCl_3)

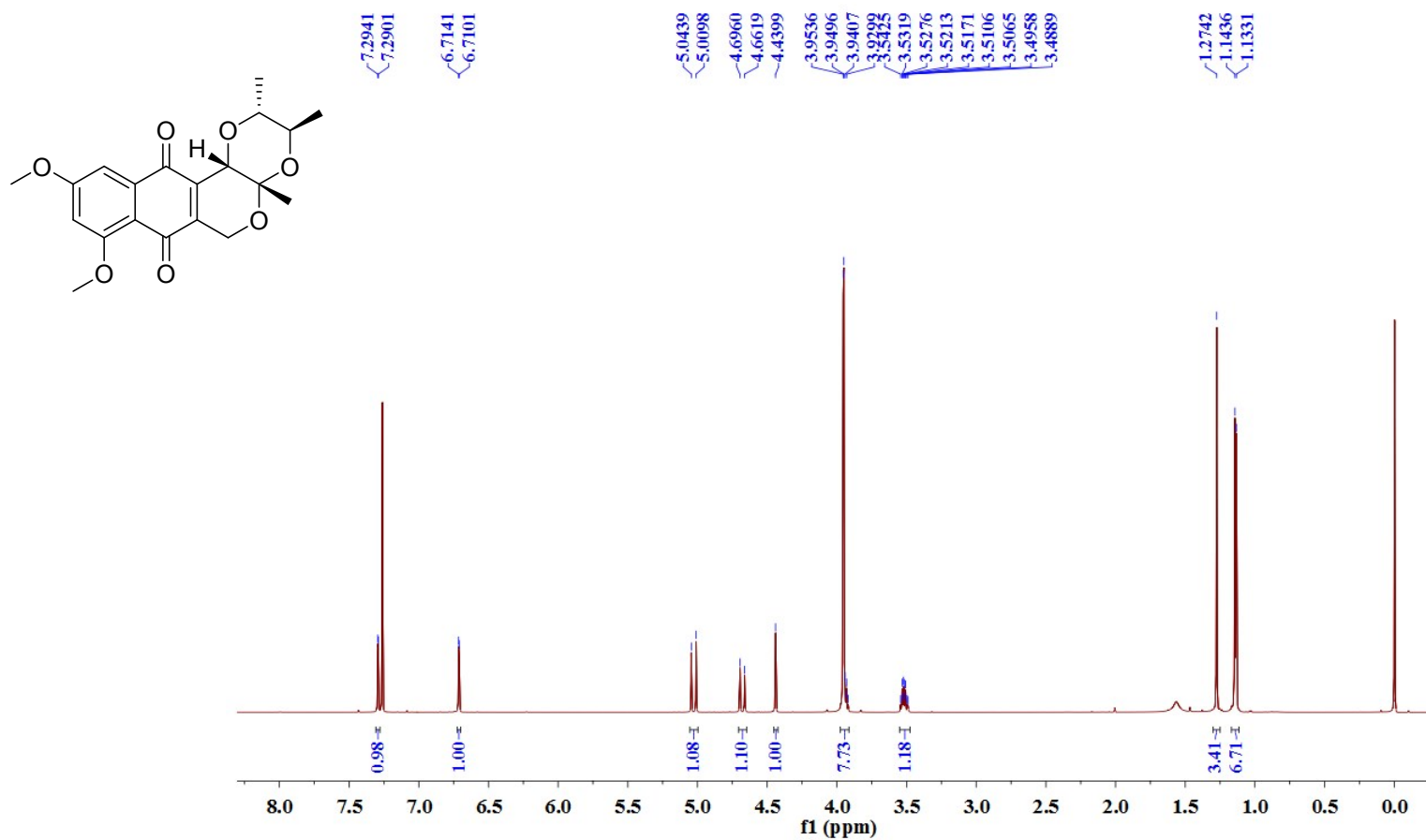


Figure S8. ^{13}C NMR Spectrum of Pseudonectrin B (**2**; 150 MHz, CDCl_3)

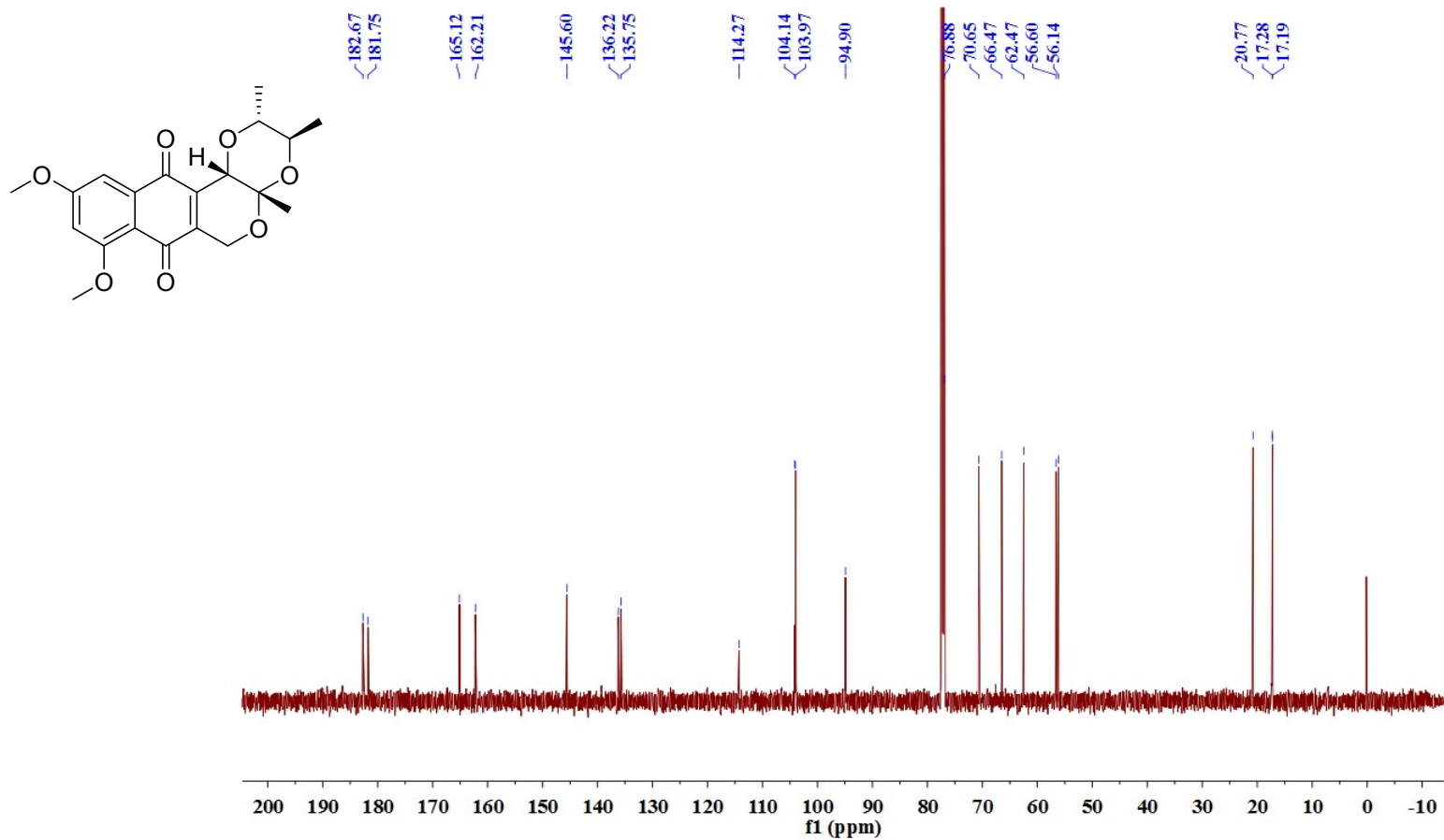


Figure S9. HSQC Spectrum of Pseudonectrin B (**2**; 600 MHz, CDCl₃)

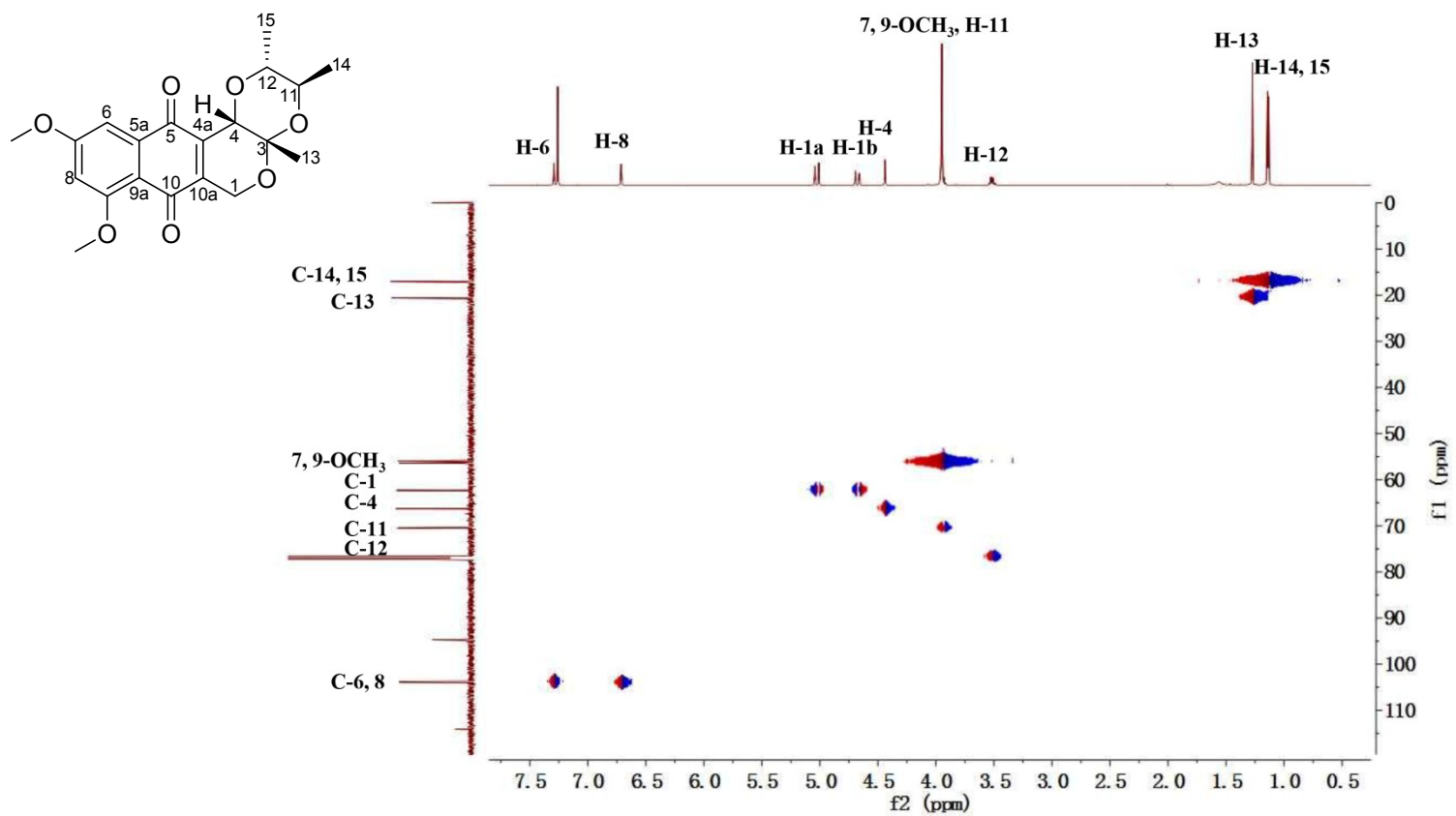


Figure S10. ^1H - ^1H COSY Spectrum of Pseudonectrin B (**2**; 600 MHz, CDCl_3)

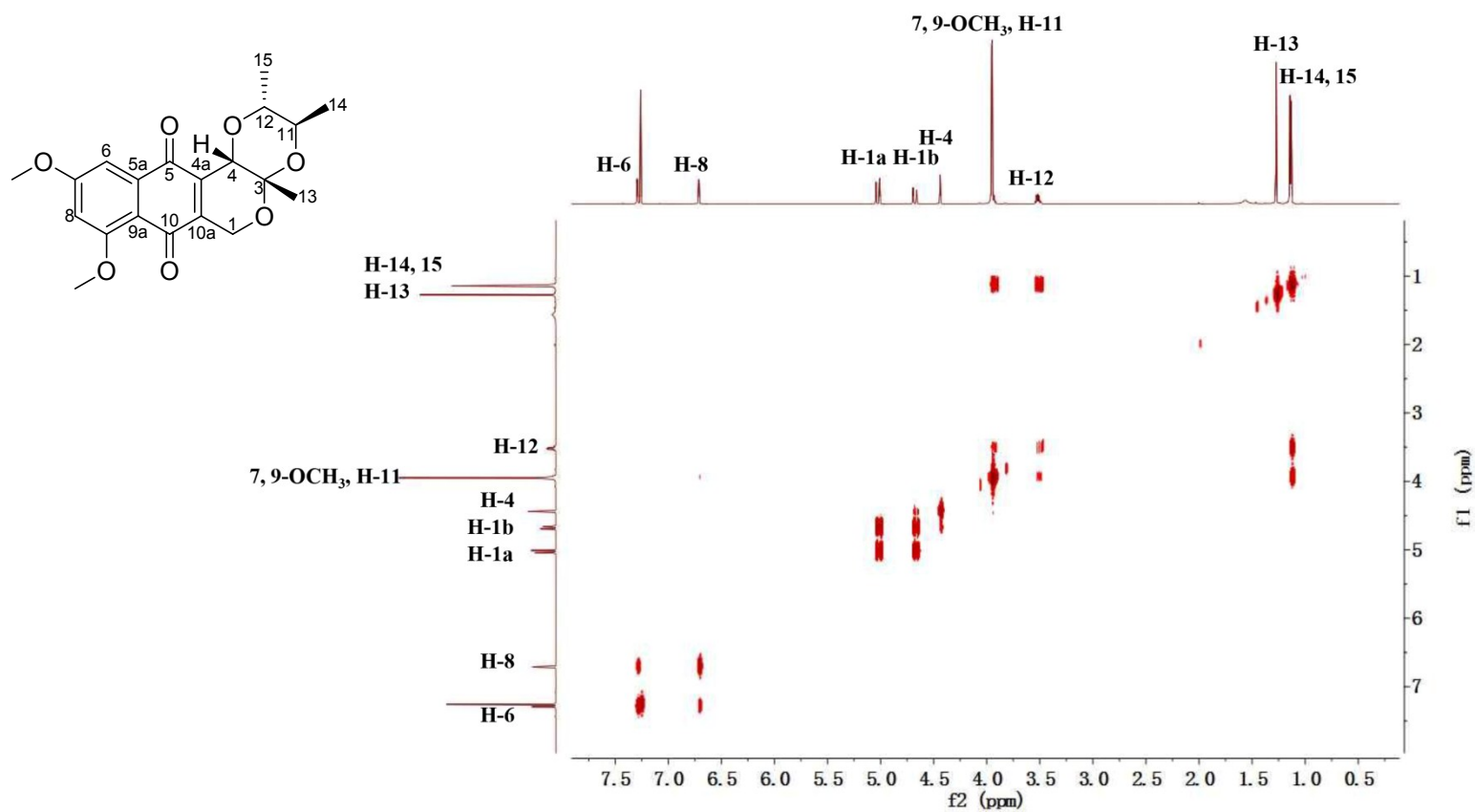


Figure S11. HMBC Spectrum of Pseudonectrin B (**2**; 600 MHz, CDCl₃)

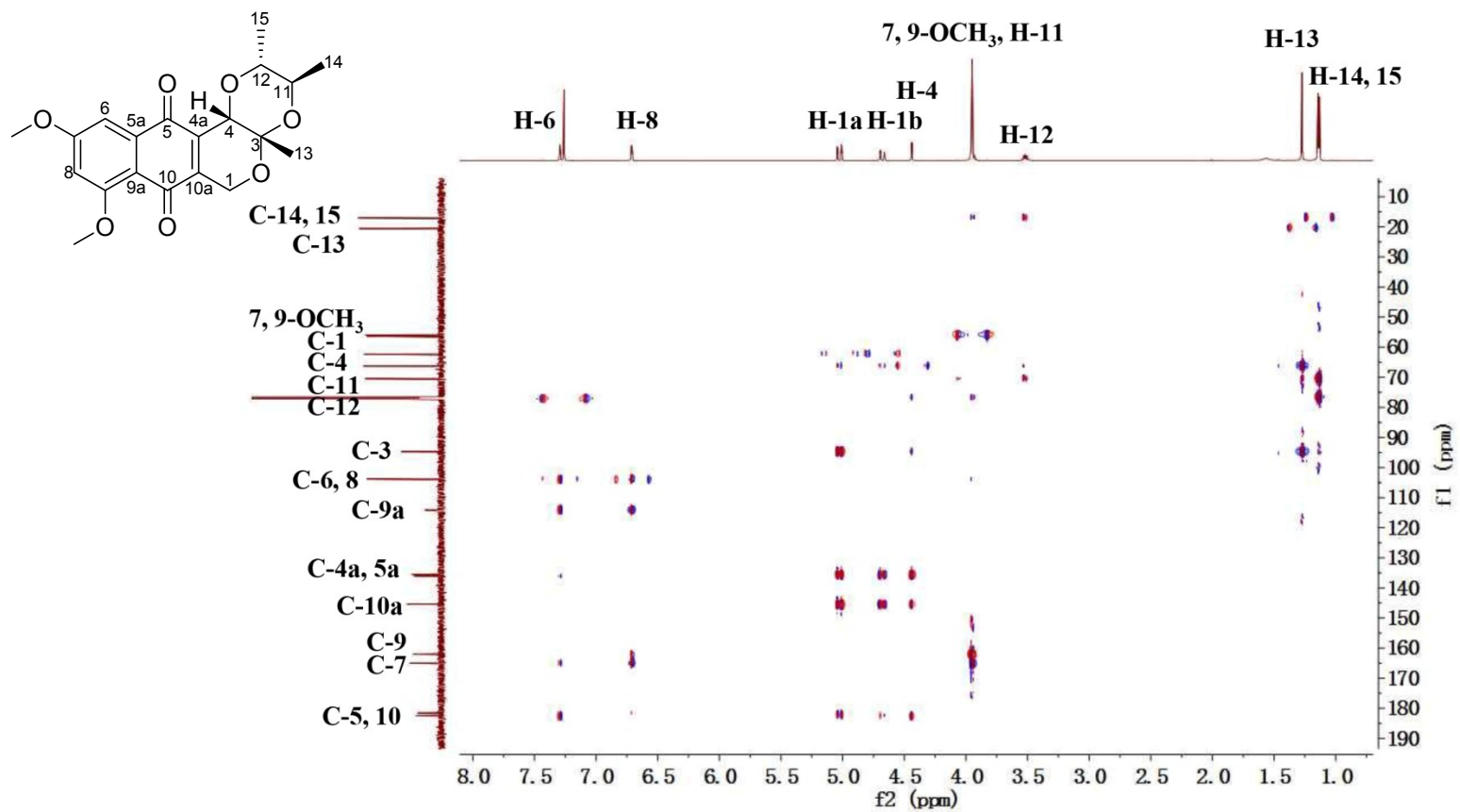


Figure S12. NOESY Spectrum of Pseudonectrin B (**2**; 600 MHz, CDCl₃)

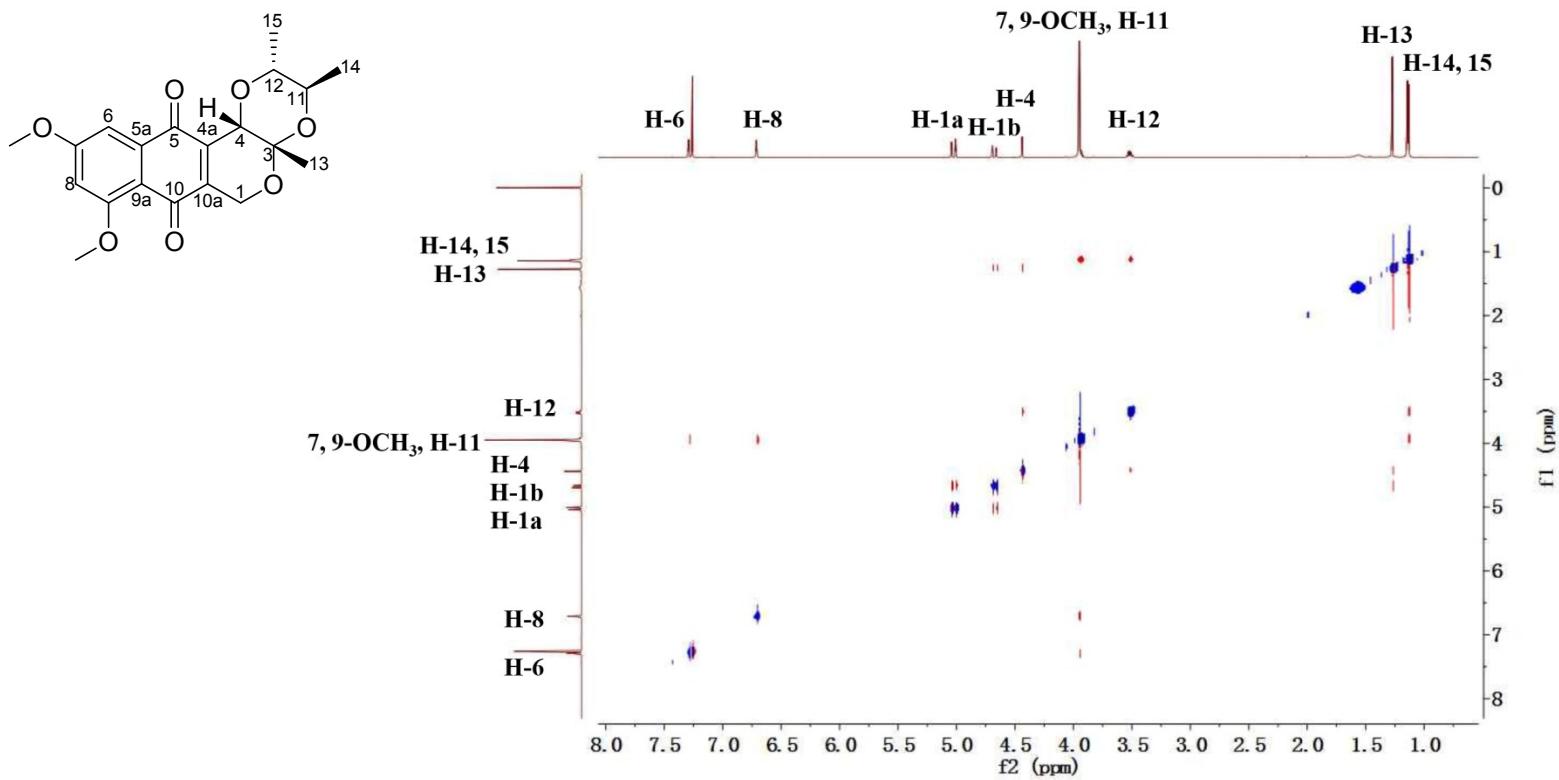


Figure S13. ^1H NMR Spectrum of Pseudonectrin C (**3**; 600 MHz, CDCl_3)

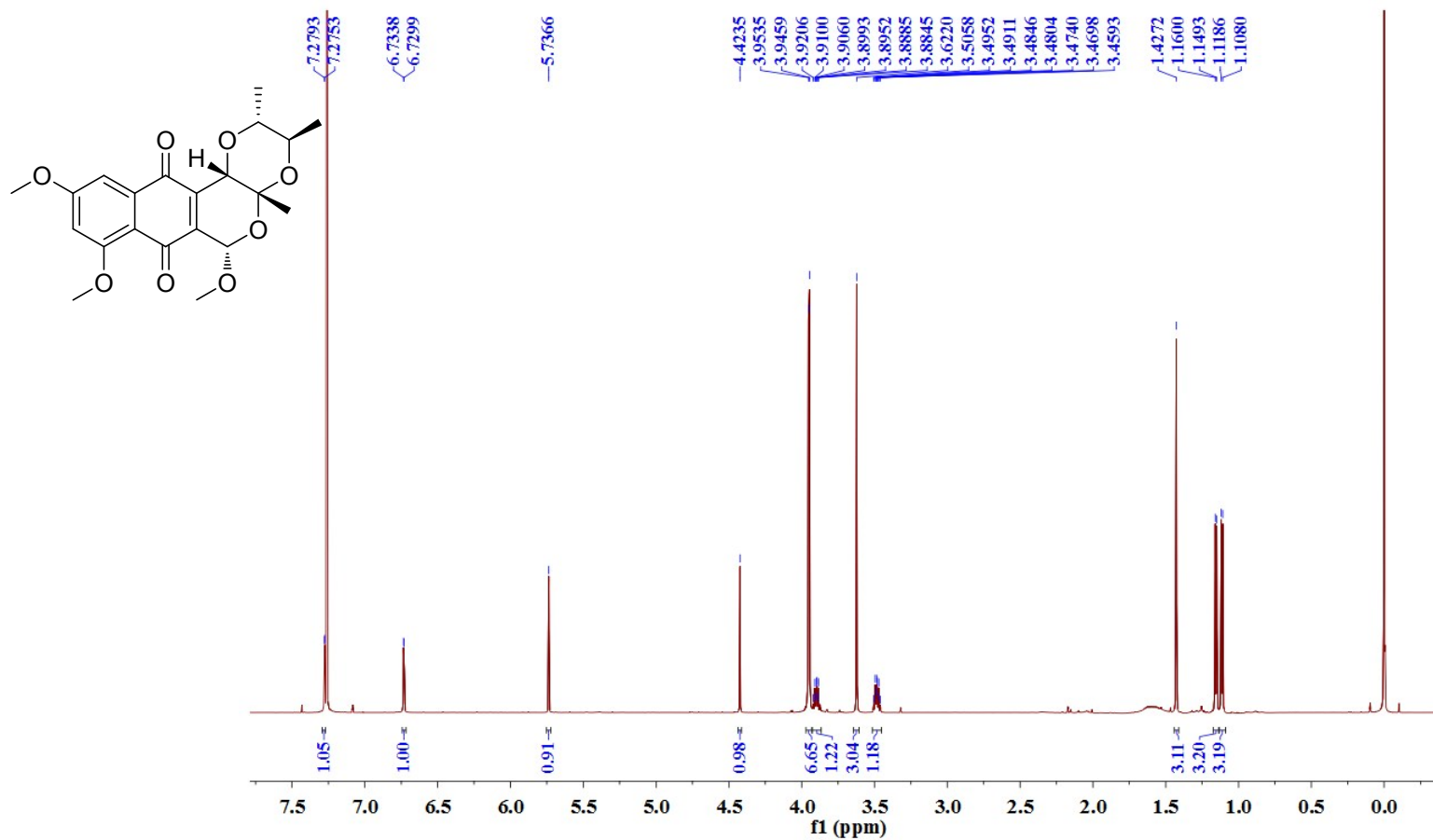


Figure S14. ^{13}C NMR Spectrum of Pseudonectrin C (**3**; 150 MHz, CDCl_3)

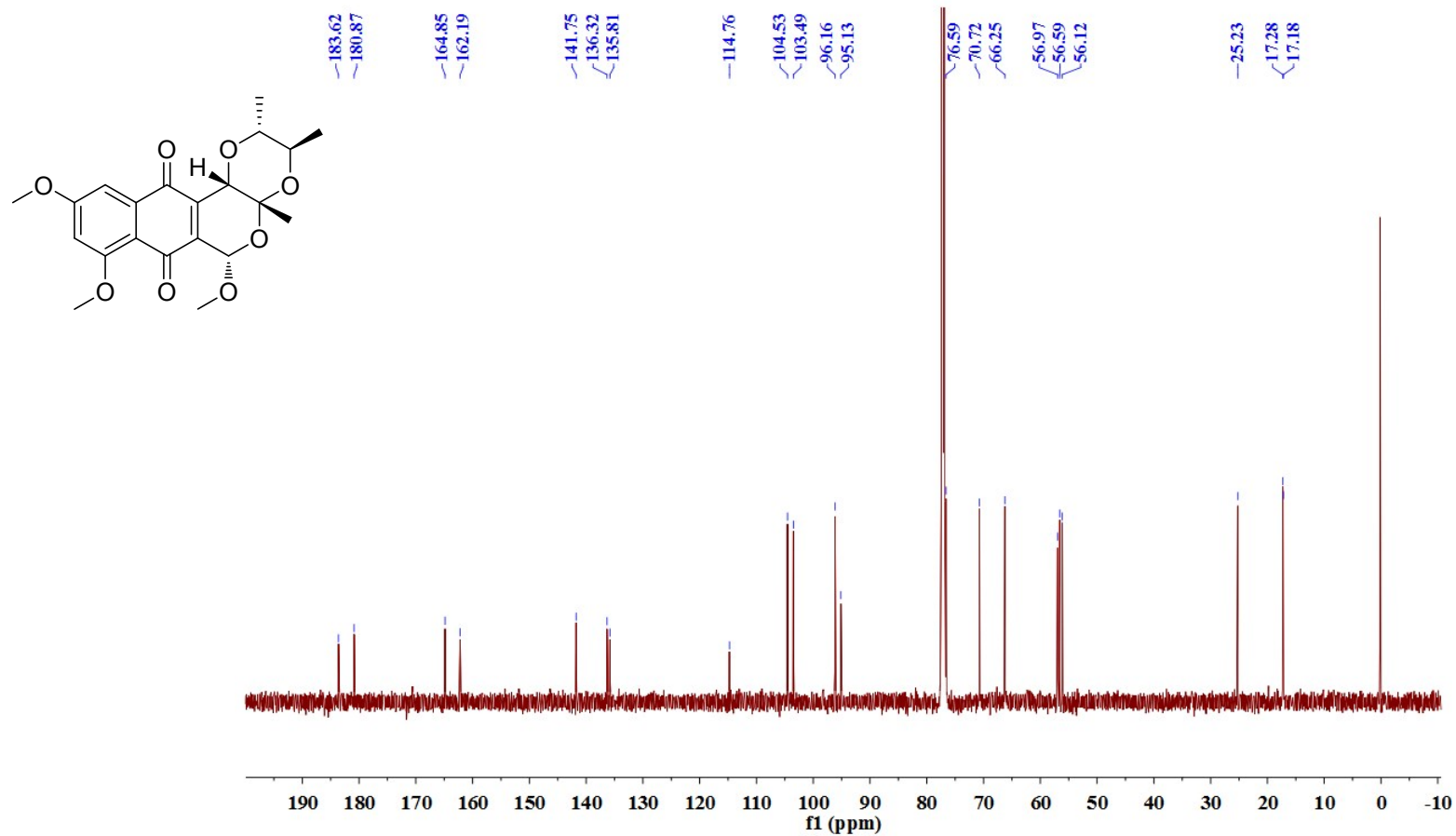


Figure S15. HSQC Spectrum of Pseudonectrin C (**3**; 600 MHz, CDCl₃)

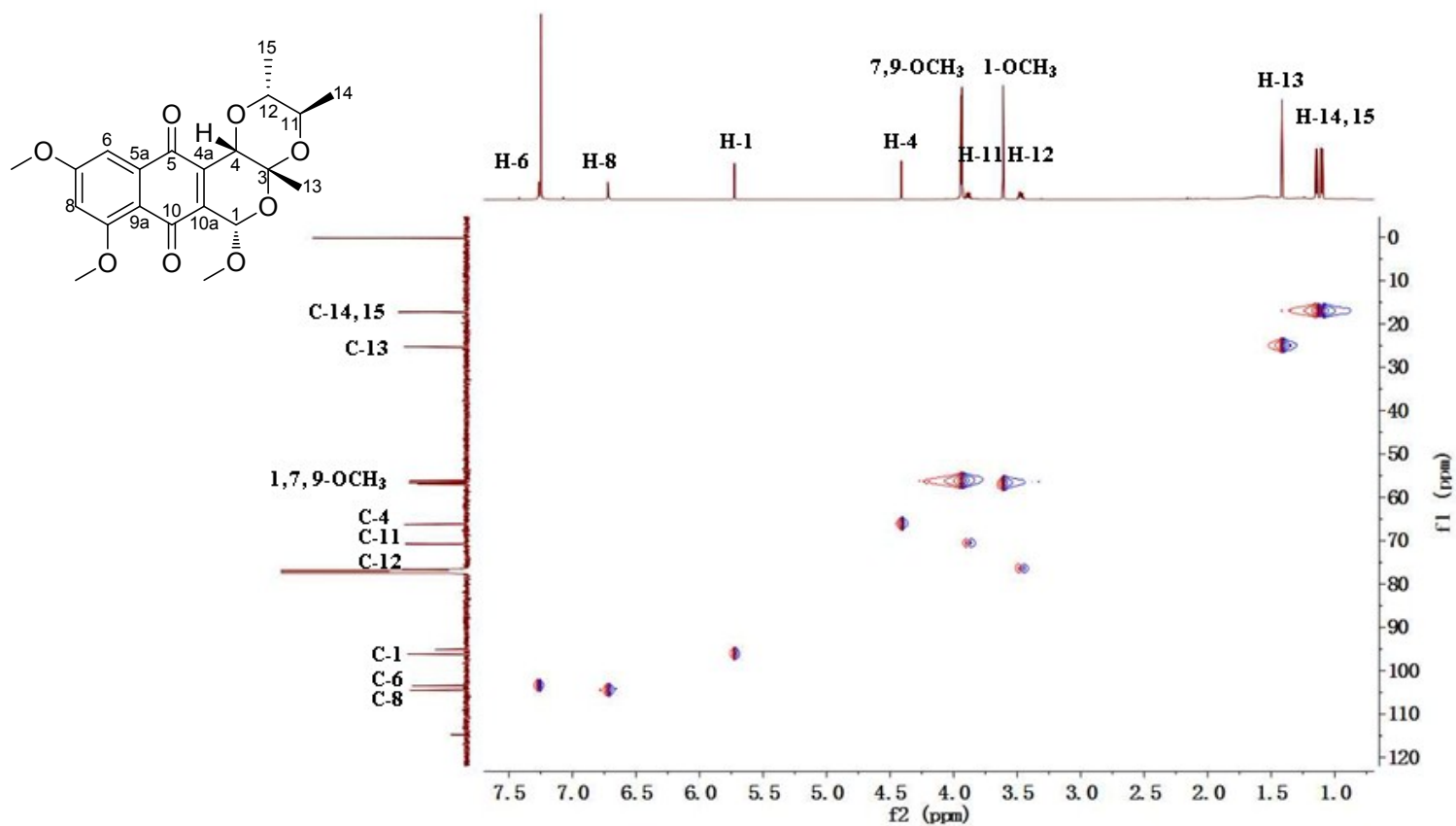


Figure S16. ^1H - ^1H COSY Spectrum of Pseudonectrin C (**3**; 600 MHz, CDCl_3)

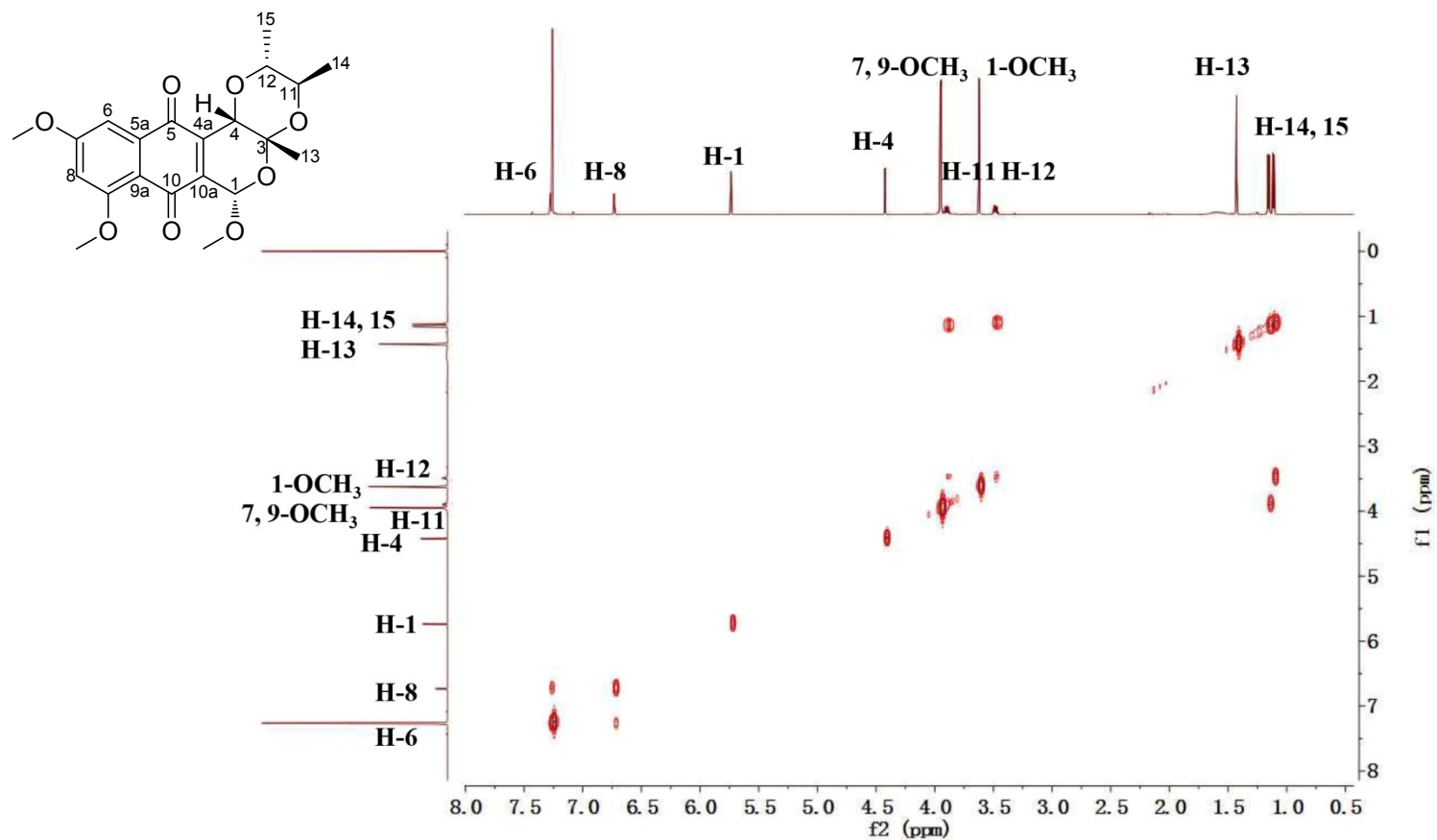


Figure S17. HMBC Spectrum of Pseudonectrin C (**3**; 600 MHz, CDCl₃)

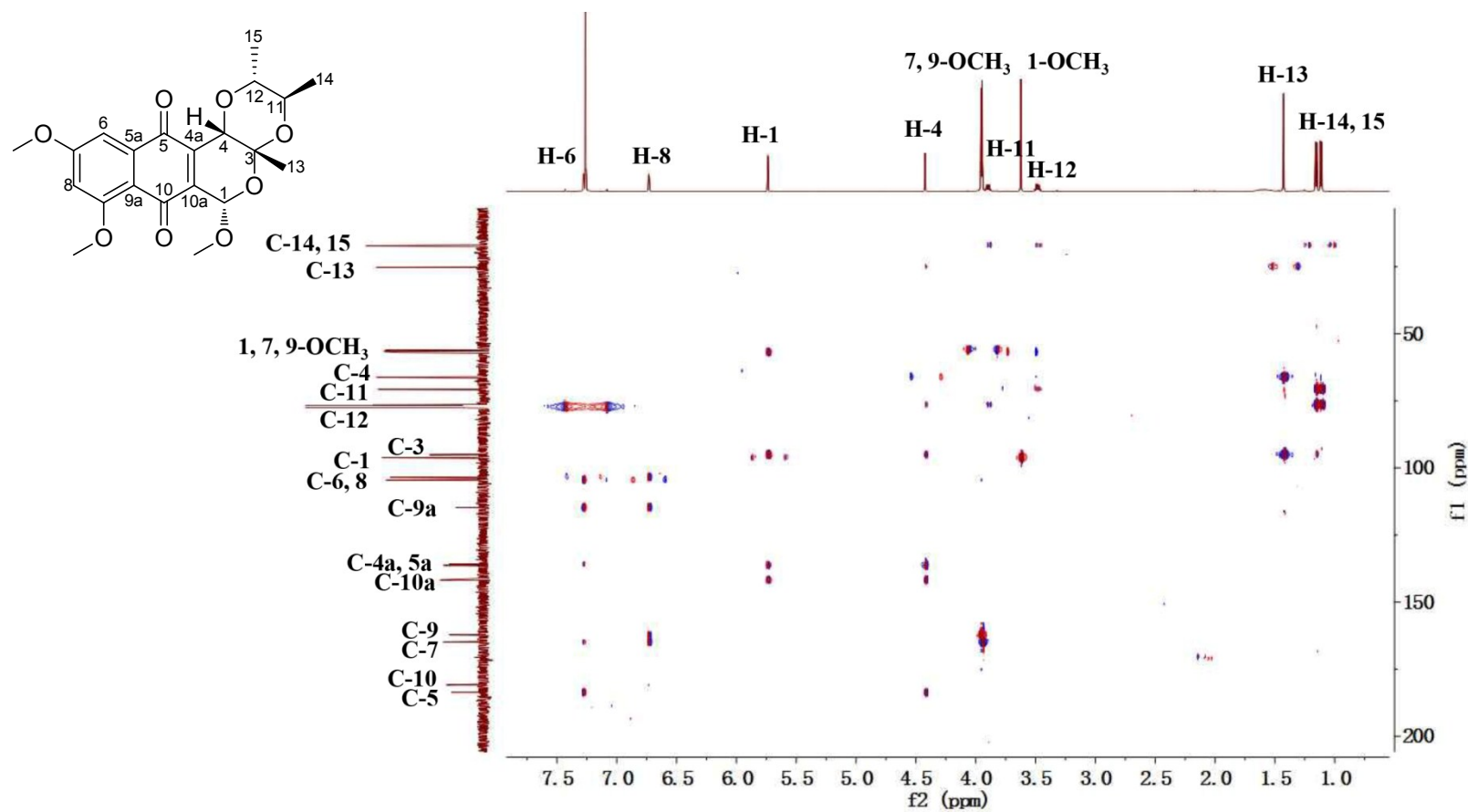


Figure S18. NOESY Spectrum of Pseudonectrin C (**3**; 600 MHz, CDCl₃)

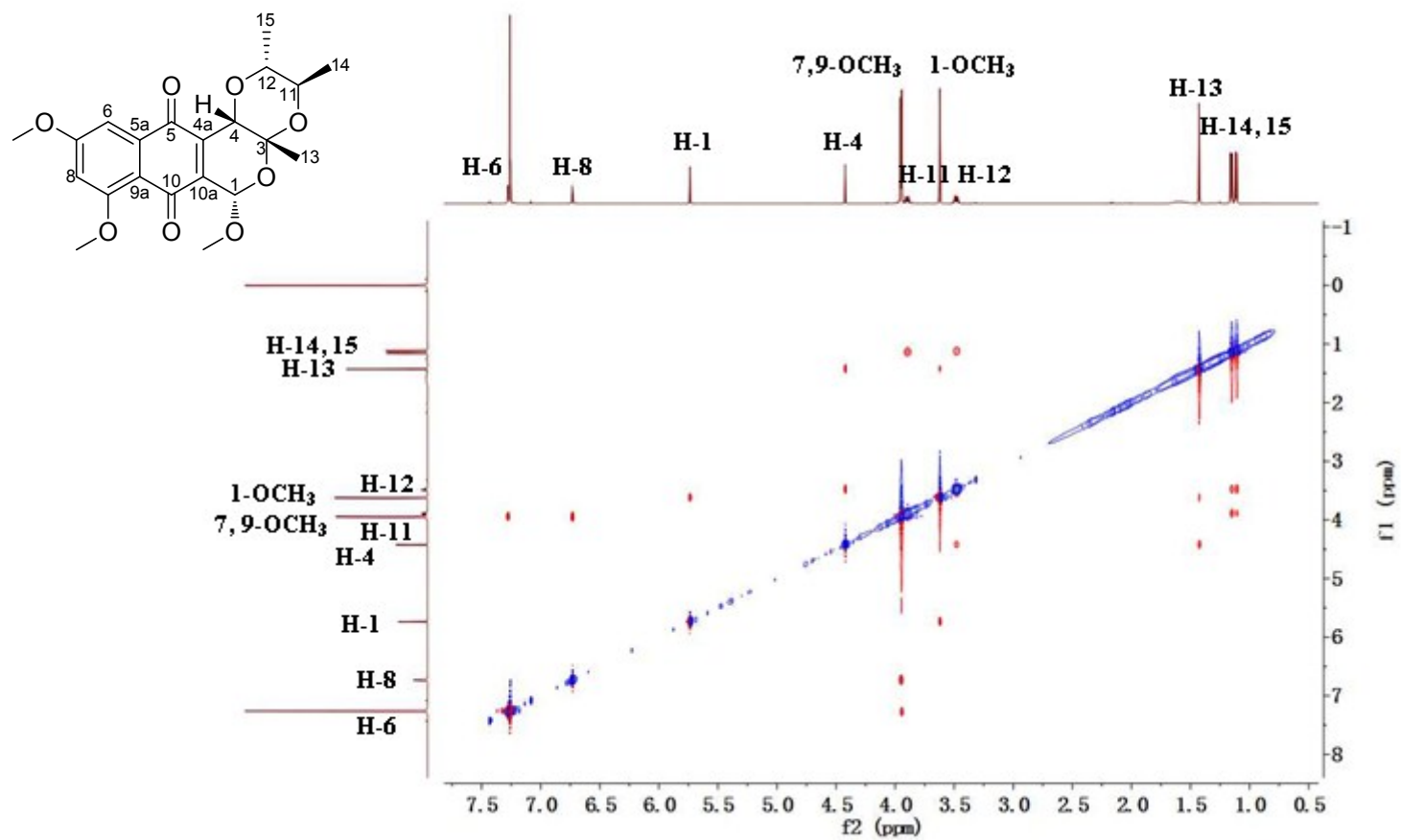


Figure S19. ^1H NMR Spectrum of Pseudonectrin D (**4**; 600 MHz, CDCl_3)

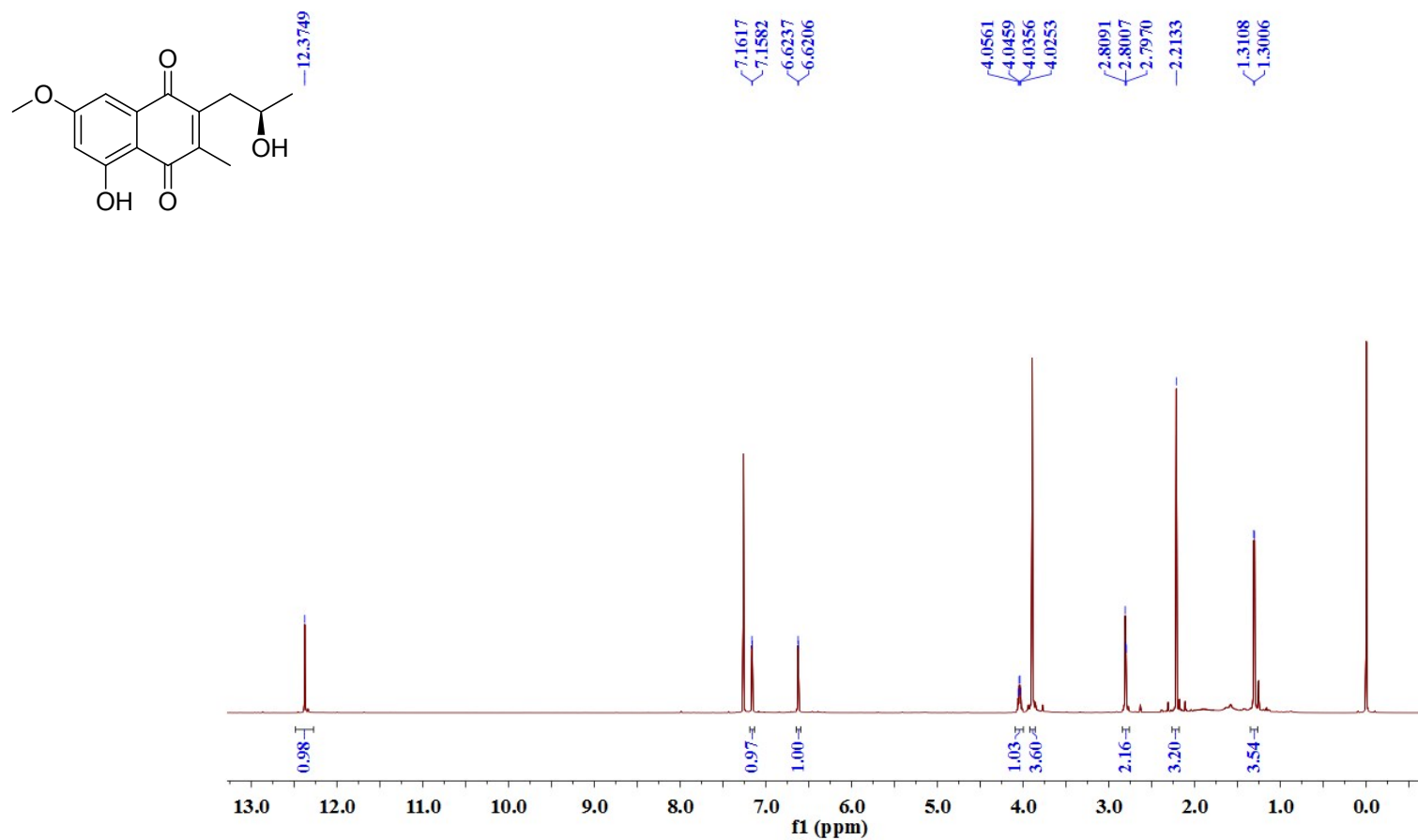


Figure S20. ^{13}C NMR Spectrum of Pseudonectrin D (**4**; 150 MHz, CDCl_3)

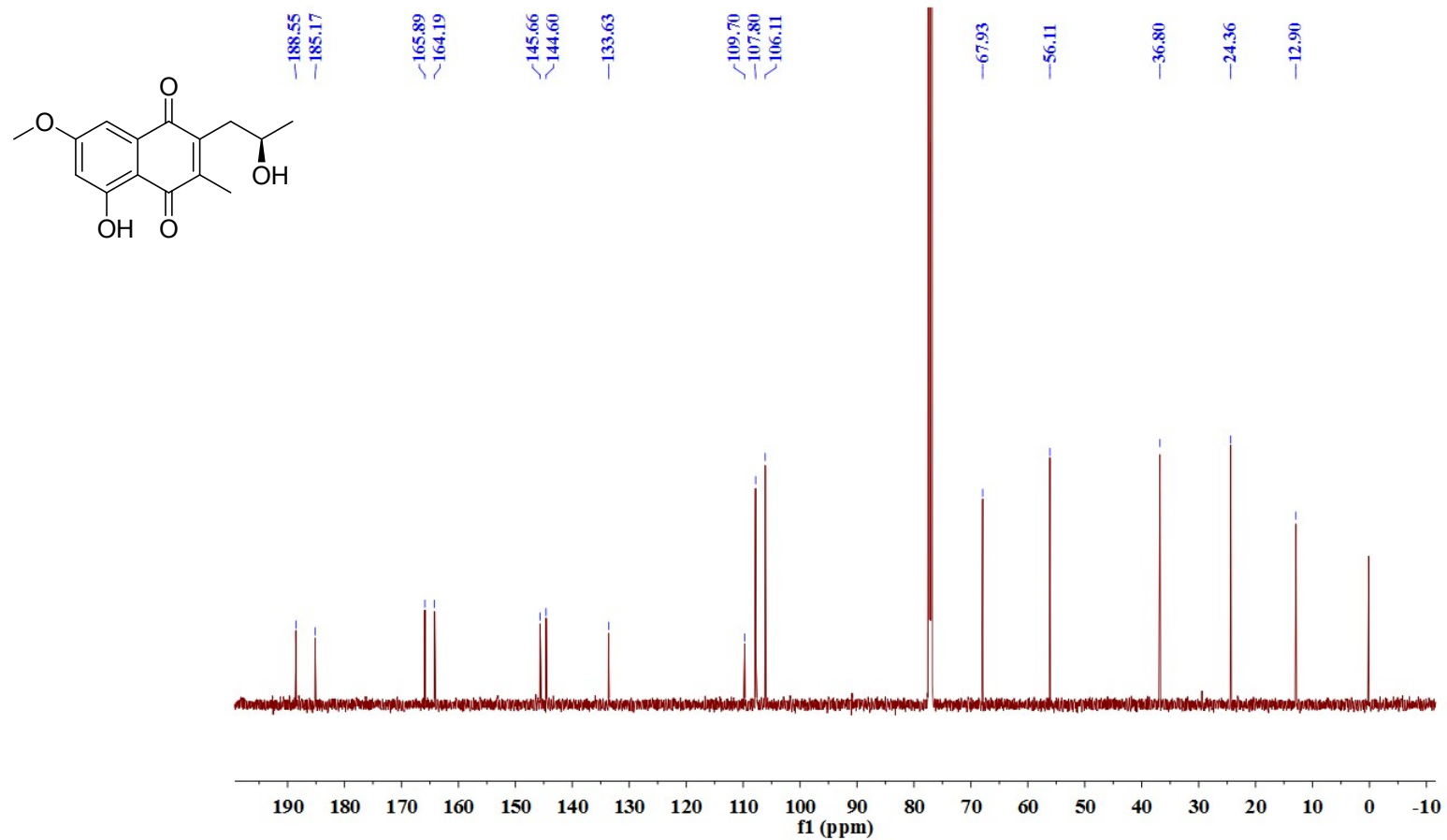


Figure S21. HSQC Spectrum of Pseudonectrin C (4; 600 MHz, CDCl₃)

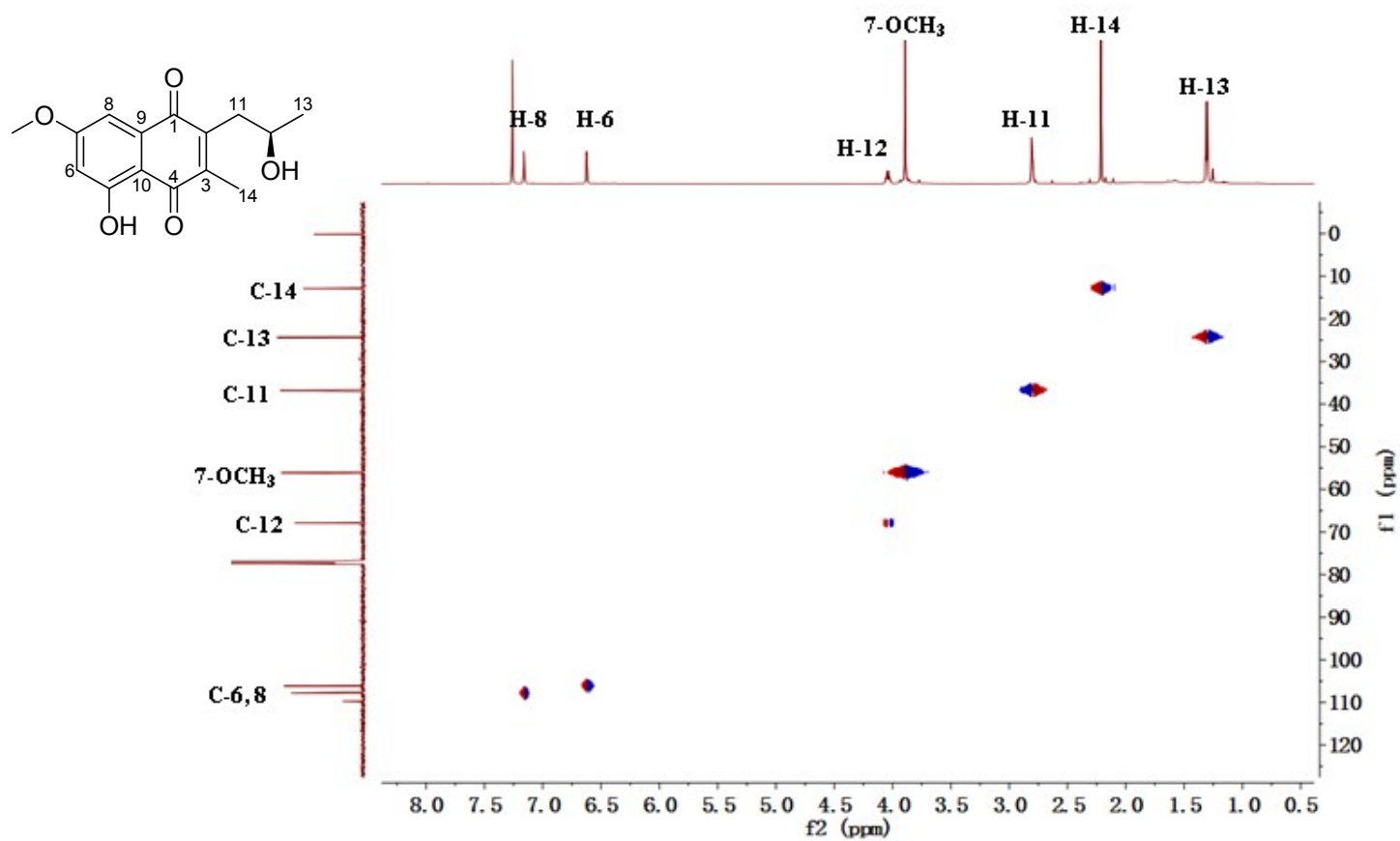


Figure S22. ^1H - ^1H COSY Spectrum of Pseudonectrin D (**4**; 600 MHz, CDCl_3)

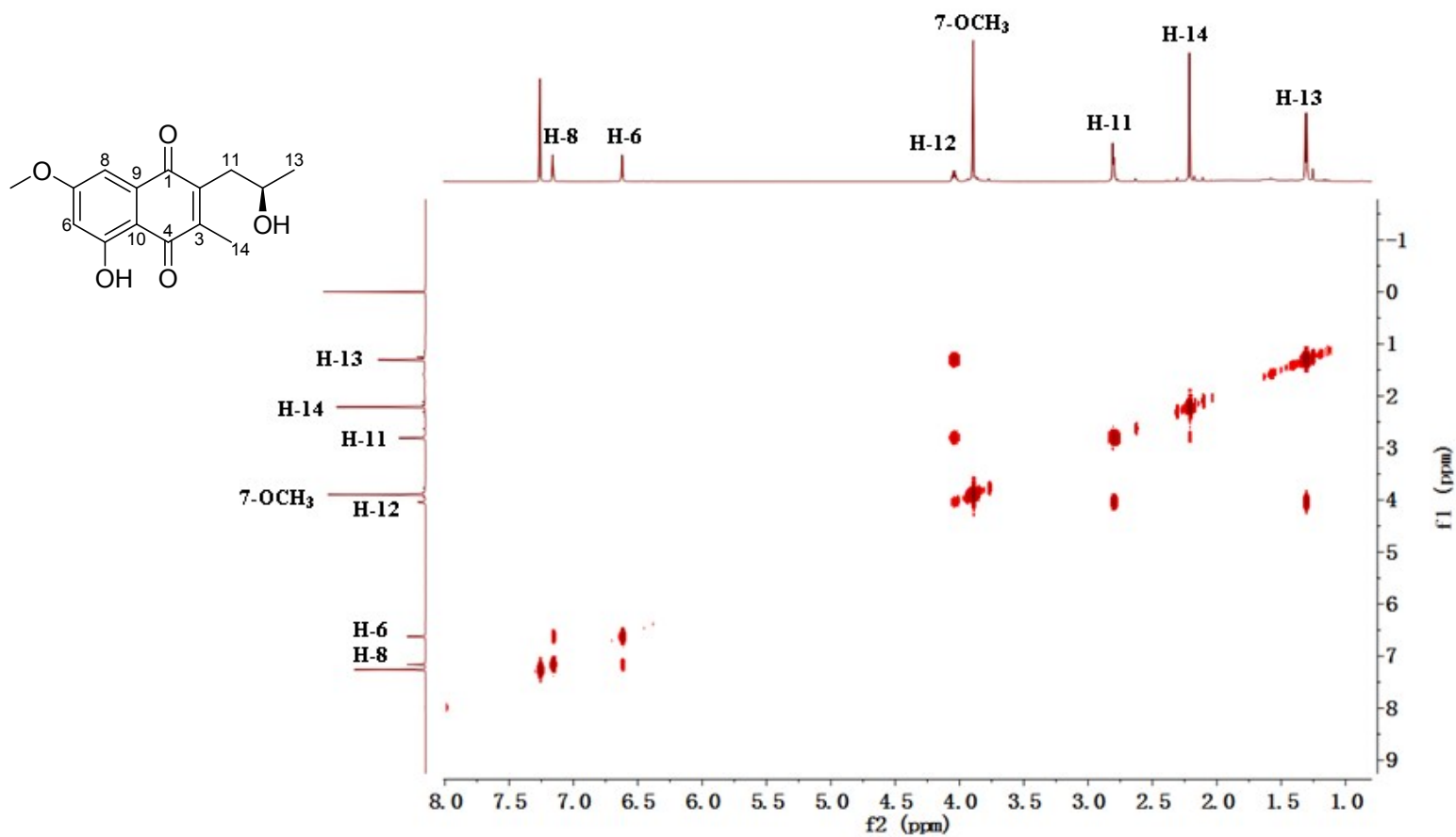


Figure S23. HMBC Spectrum of Pseudonectrin D (**4**; 600 MHz, CDCl₃)

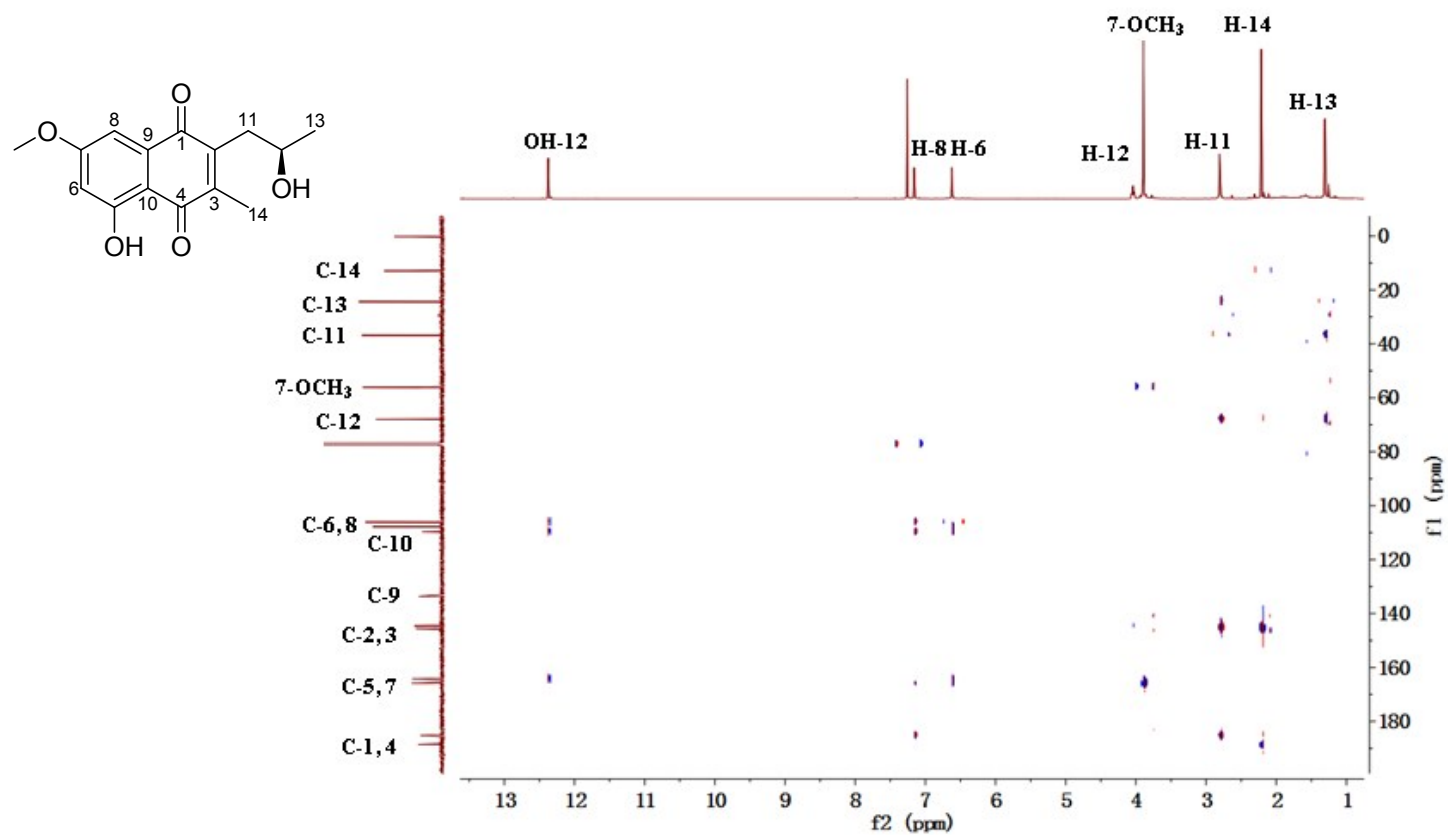


Figure S24. NOESY Spectrum of Pseudonectrin D (4; 600 MHz, CDCl₃)

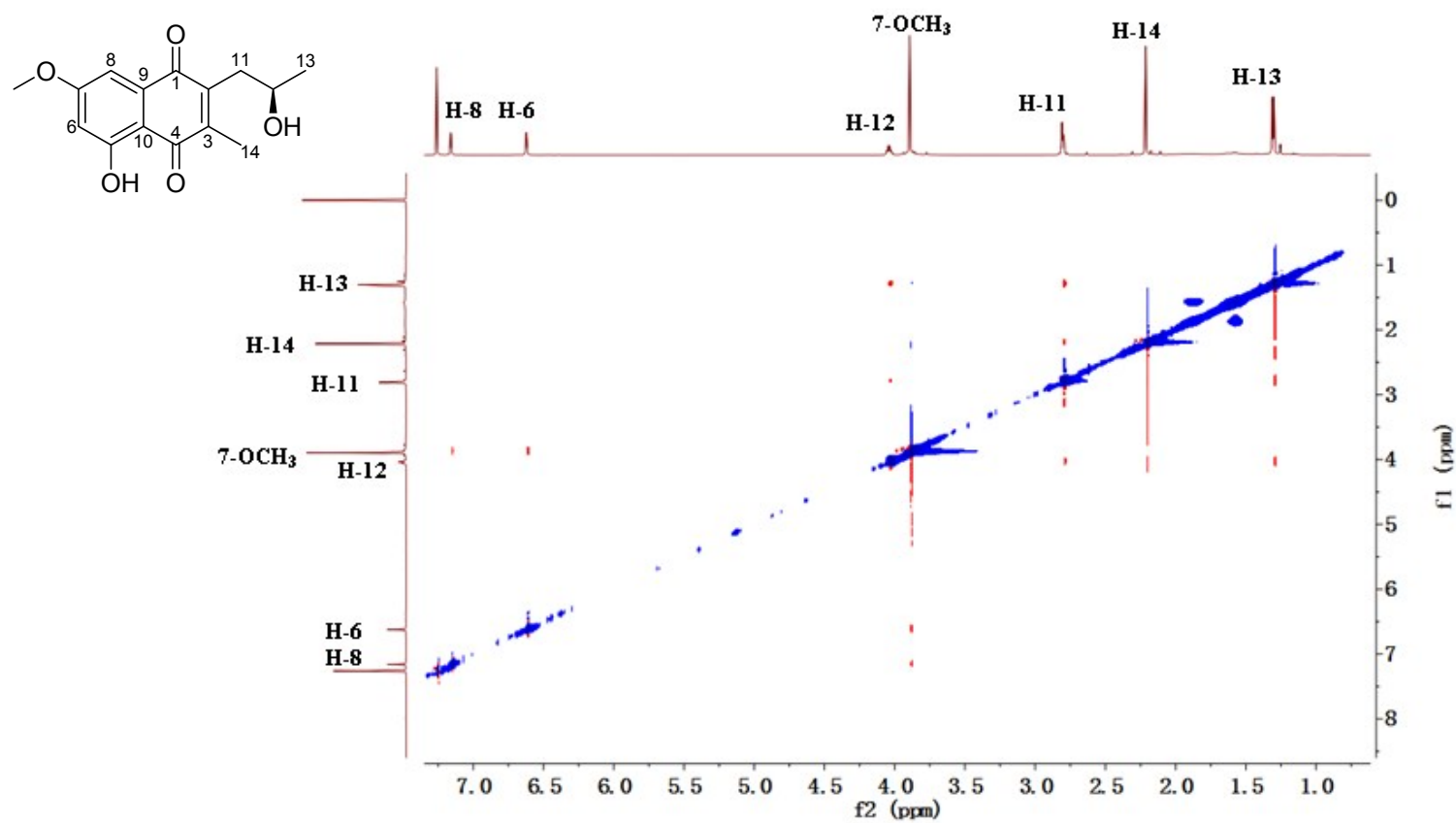
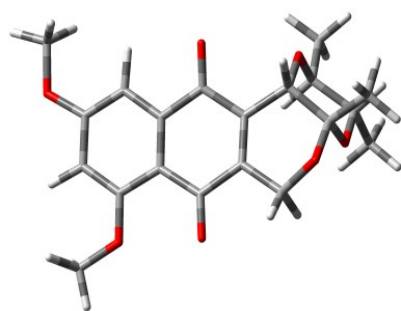
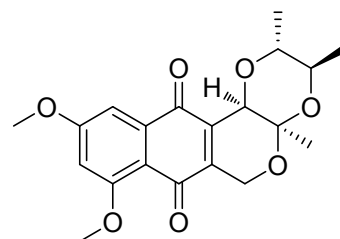
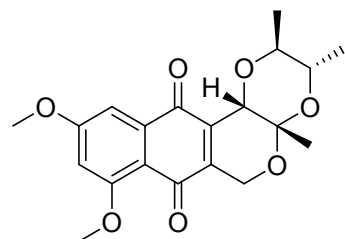
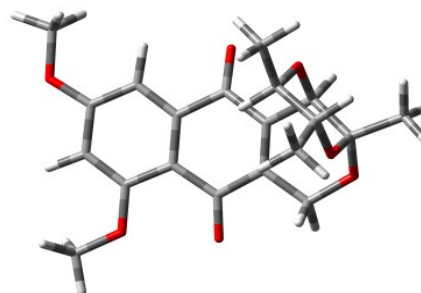


Figure S25. Relative Configurations and the Optimized Conformers for **1**



1a



1b

Figure S26. Relative Configurations and the Optimized Conformers for **2**

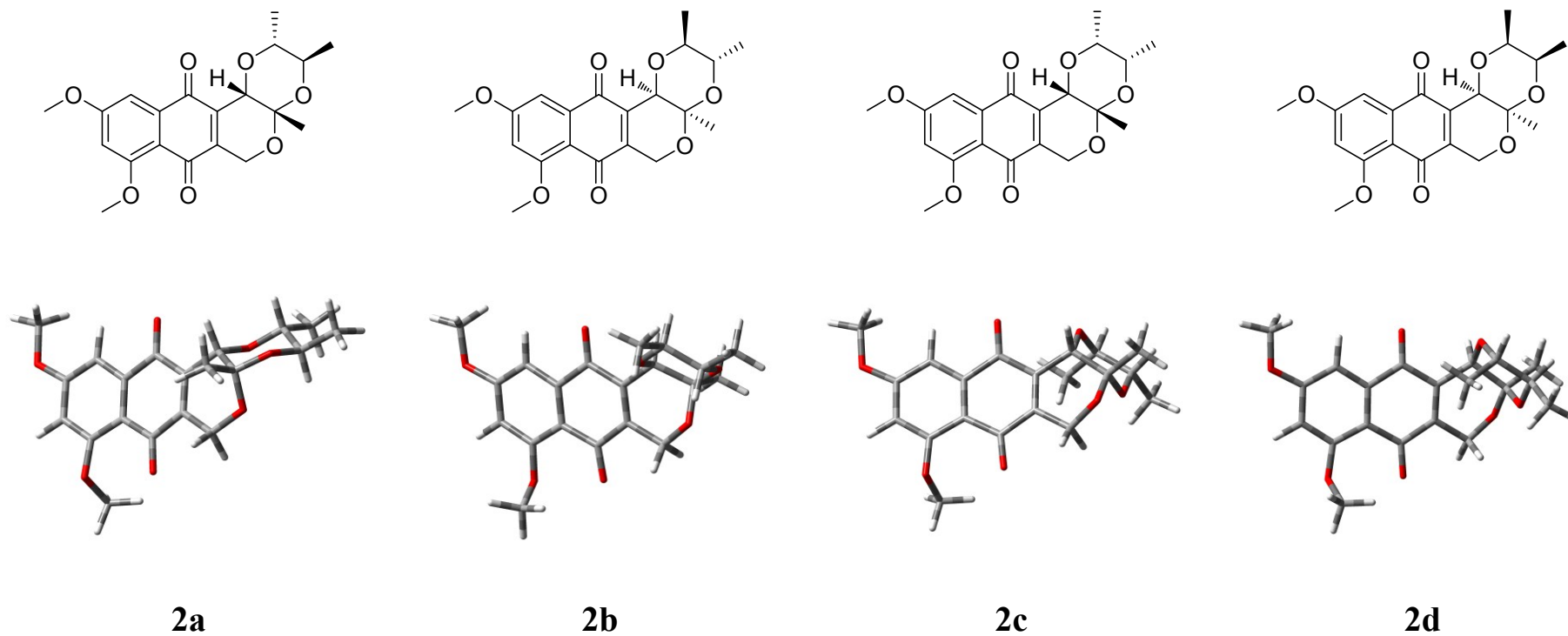
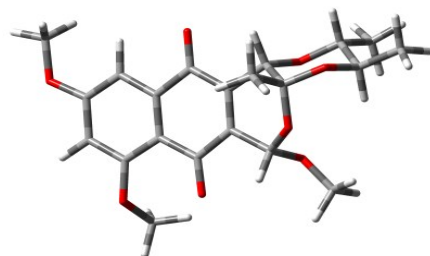
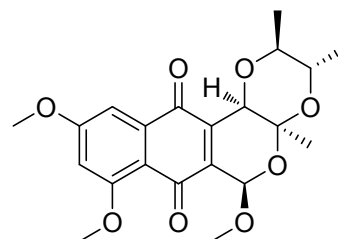
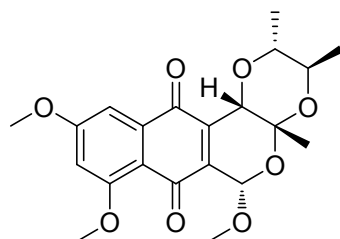
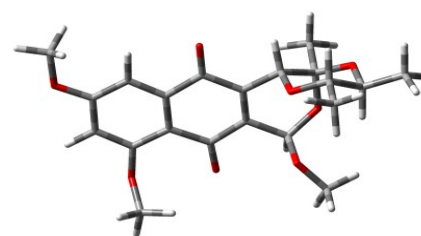


Figure S27. Relative Configurations and the Optimized Conformers for **3**



3a



3b

Figure S28. UV Spectrum of Pseudonectrin A (1) in MeOH

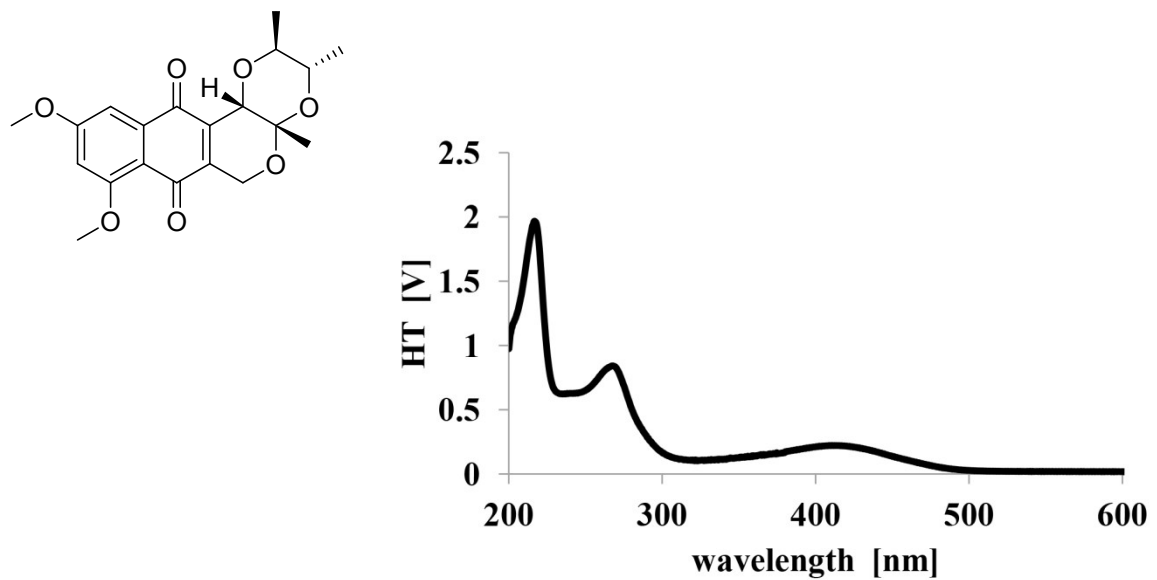


Figure S29. UV Spectrum of Pseudonectrin B (2) in MeOH

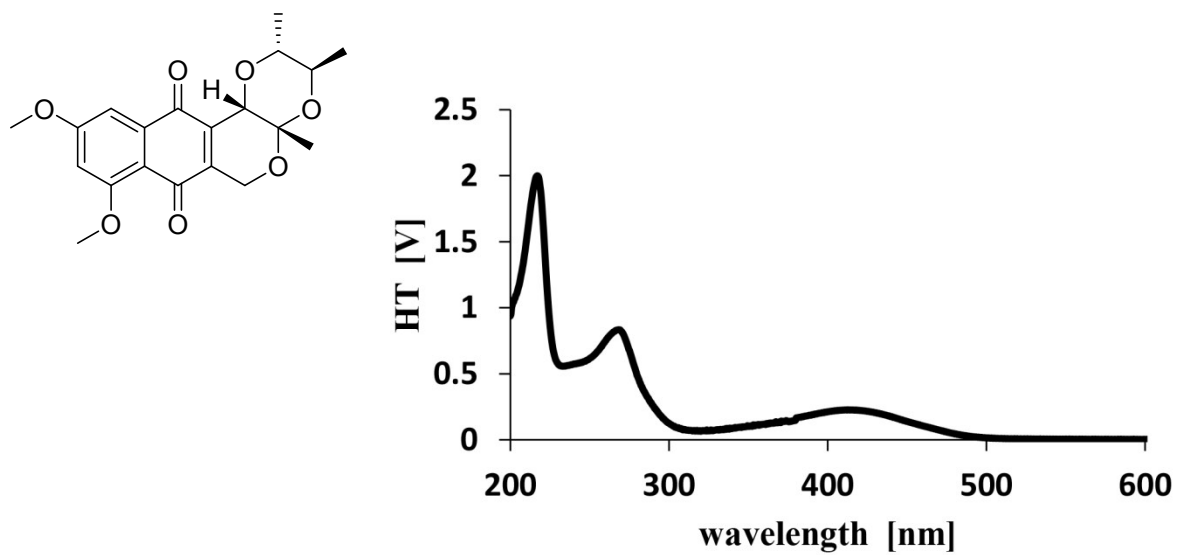


Figure S30. UV Spectrum of Pseudonectrin C (**3**) in MeOH

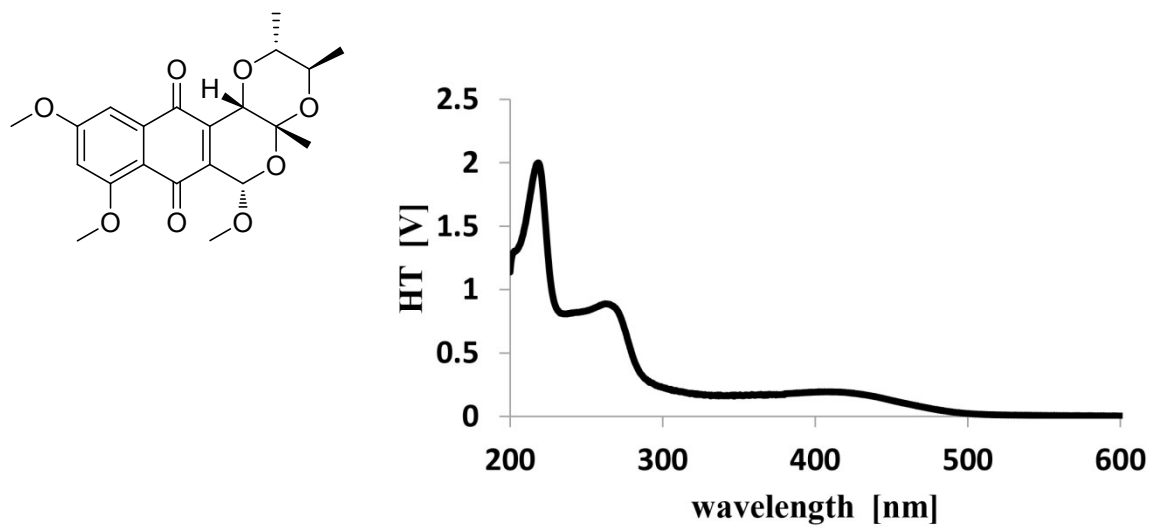


Figure S31. UV Spectrum of Pseudonectrin D (4) in MeOH

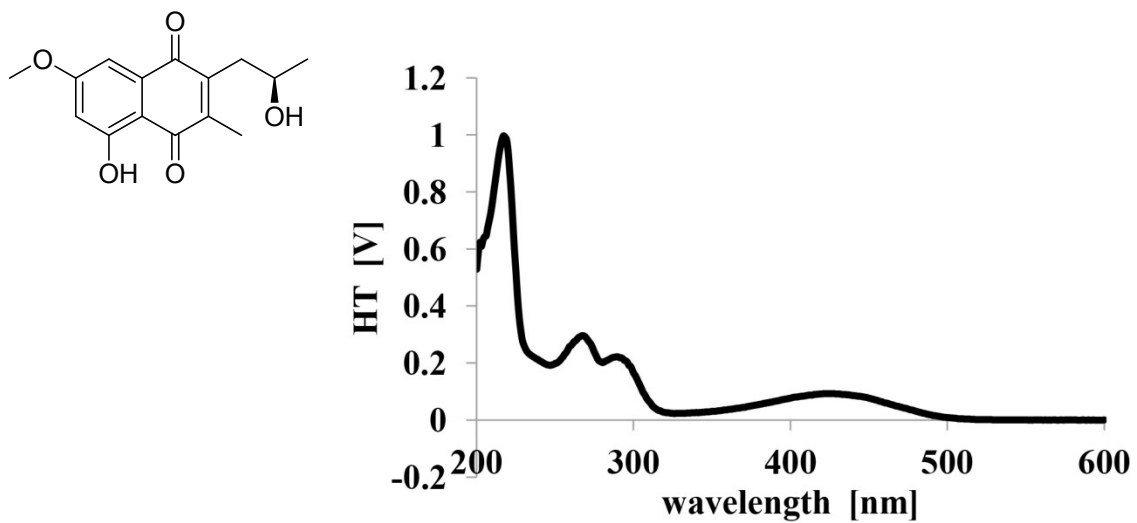


Figure S32. CD Spectrum of Pseudonectrin A (1) in MeOH

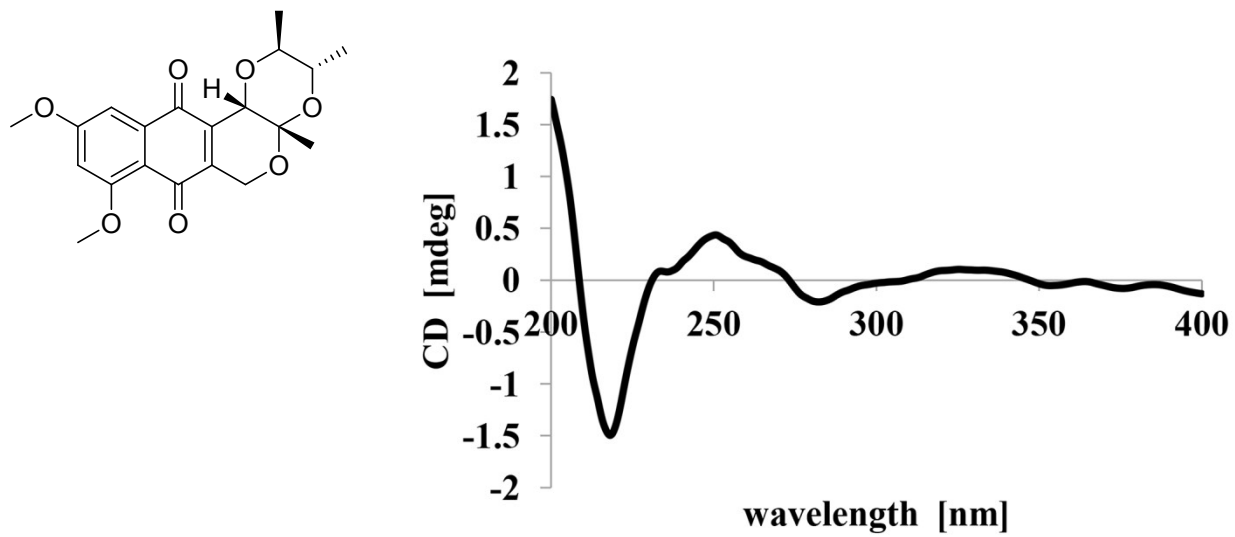


Figure S33. CD Spectrum of Pseudonectrin B (2) in MeOH

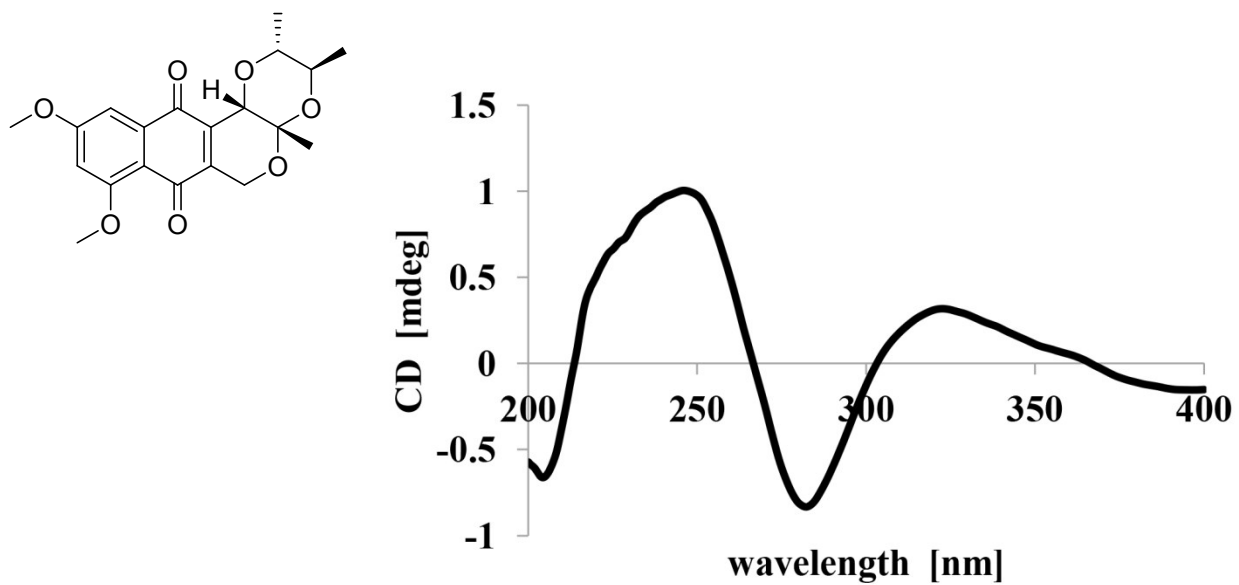


Figure S34. CD Spectrum of Pseudonectrin C (**3**) in MeOH

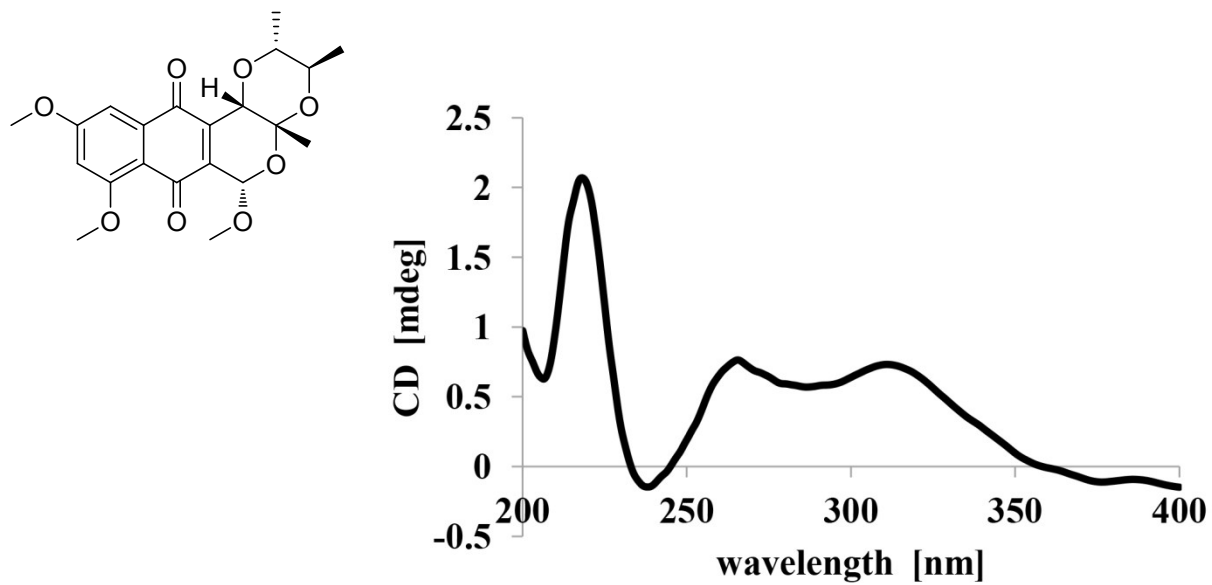


Figure S35. CD Spectrum of Pseudonectrin D (4) in MeOH

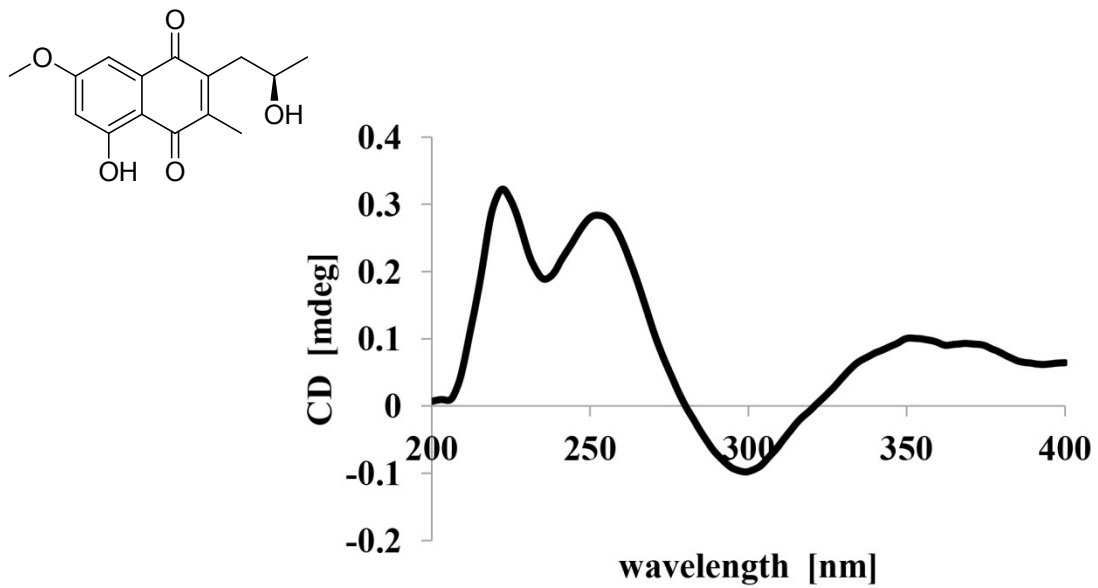


Figure S36. IR Spectrum of Pseudonectrin A (1)

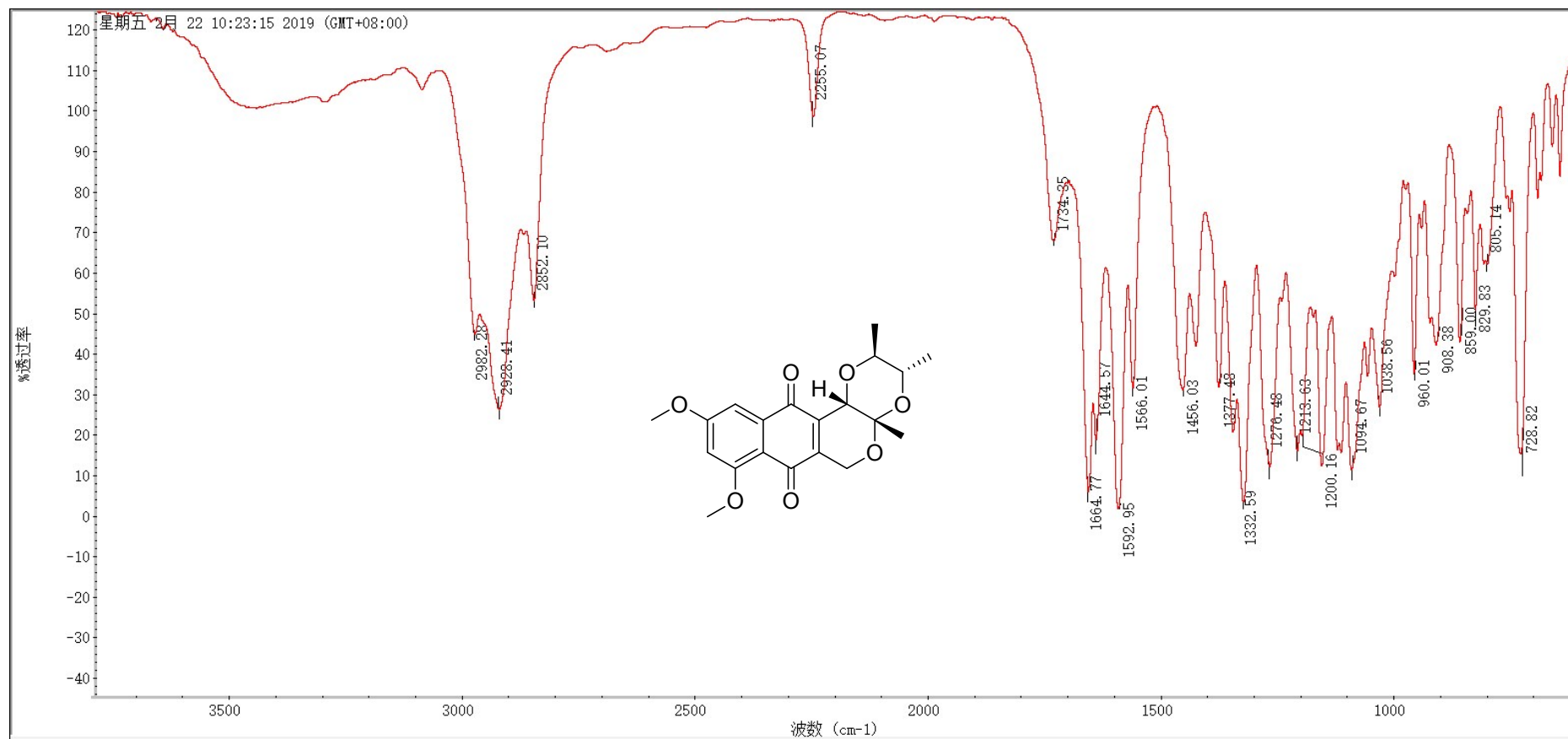


Figure S37. IR Spectrum of Pseudonectrin B (2)

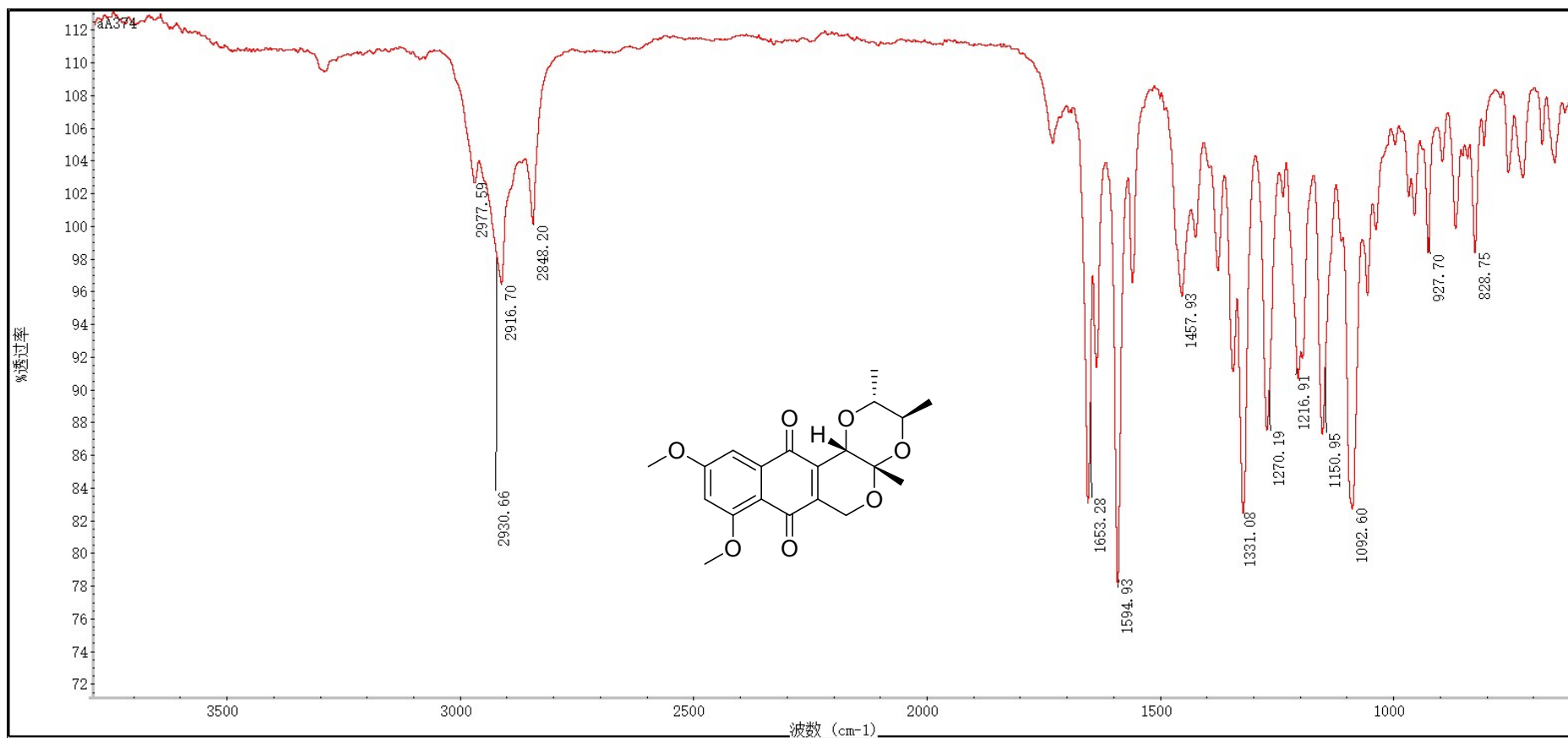


Figure S38. IR Spectrum of Pseudonectrin C (3)

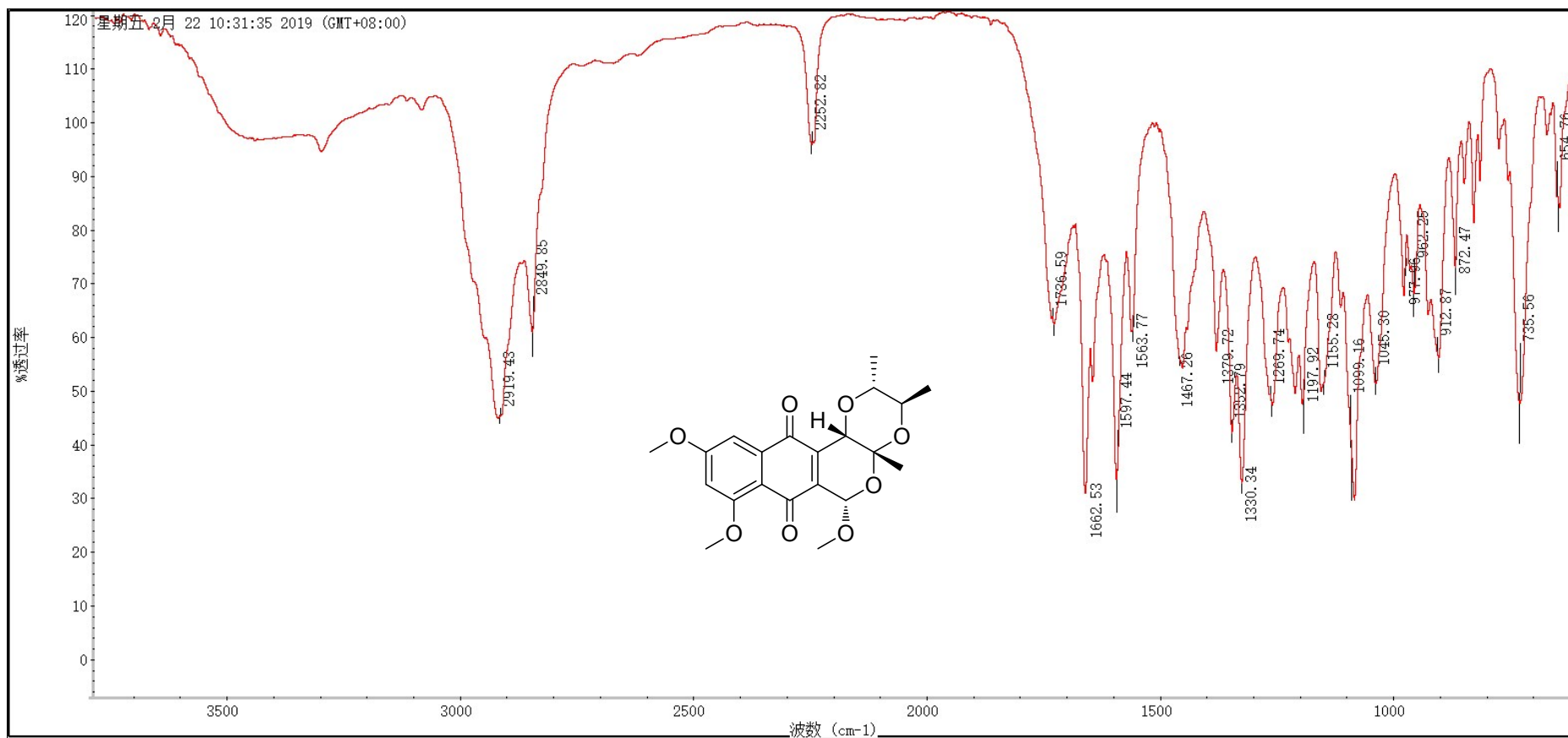


Figure S39. IR Spectrum of Pseudonecetrin D (4)

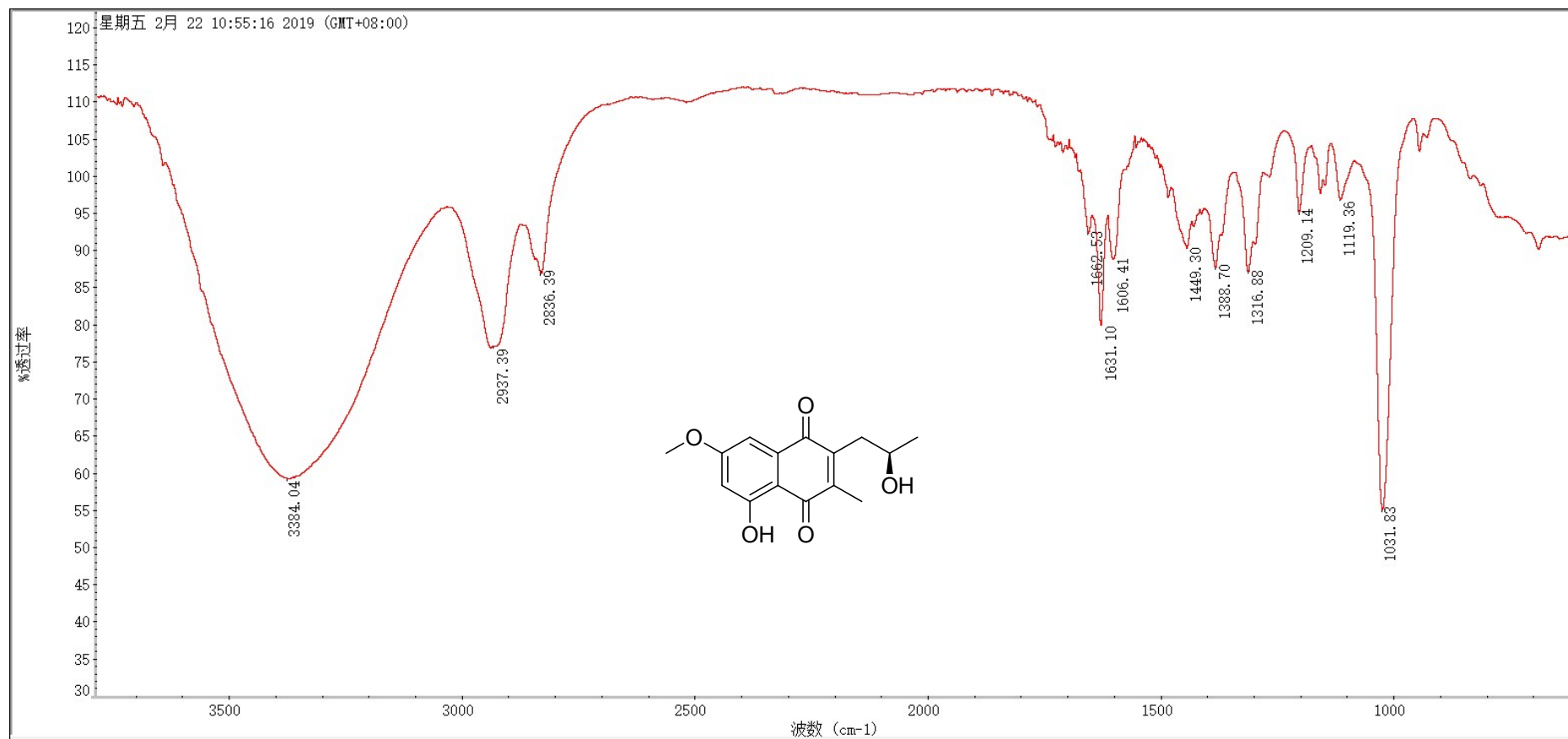


Figure S40. HRESIMS Spectrum of Pseudonectrin A (1)

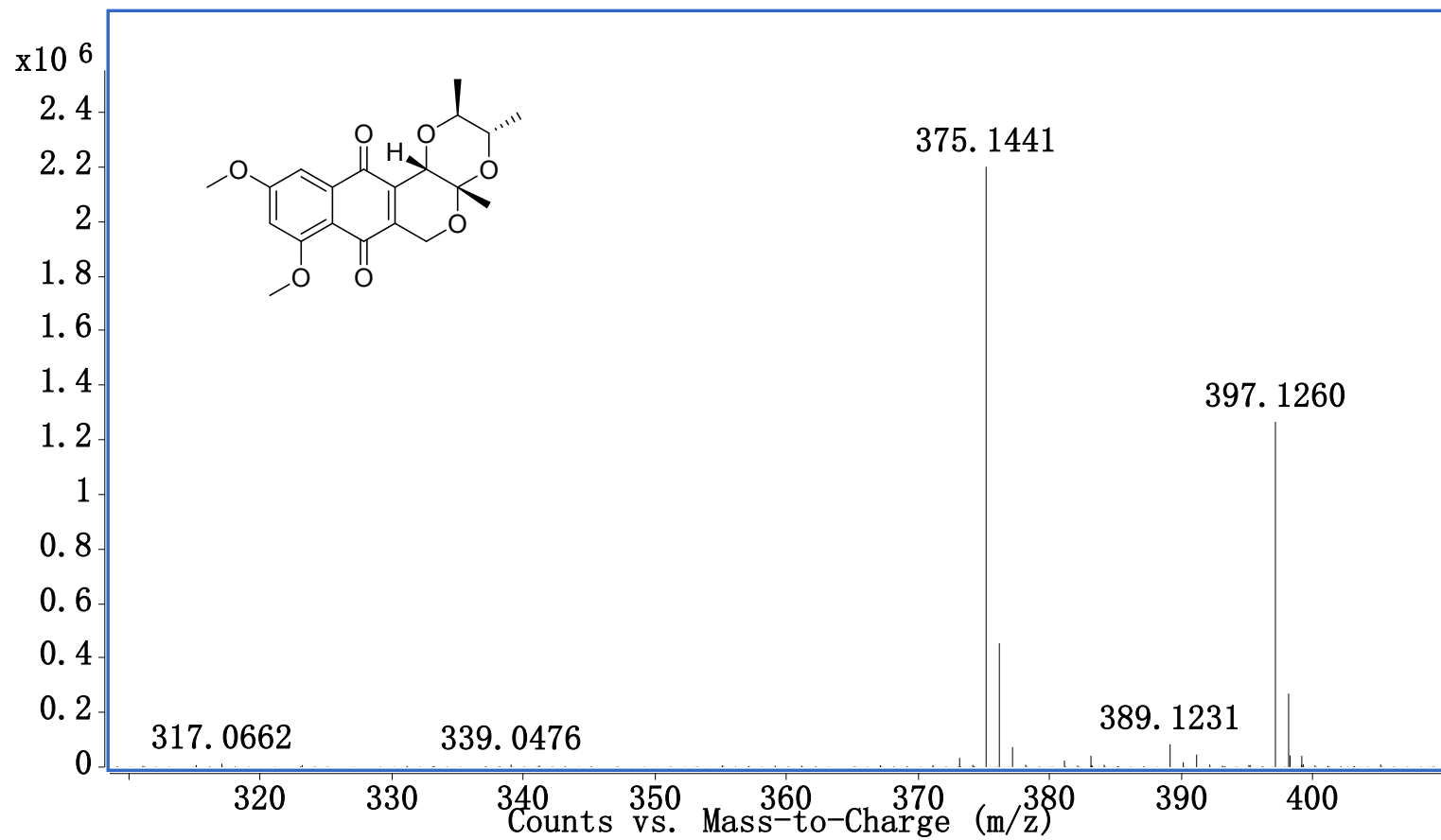


Figure S41. HRESIMS Spectrum of Pseudonectrin B (2)

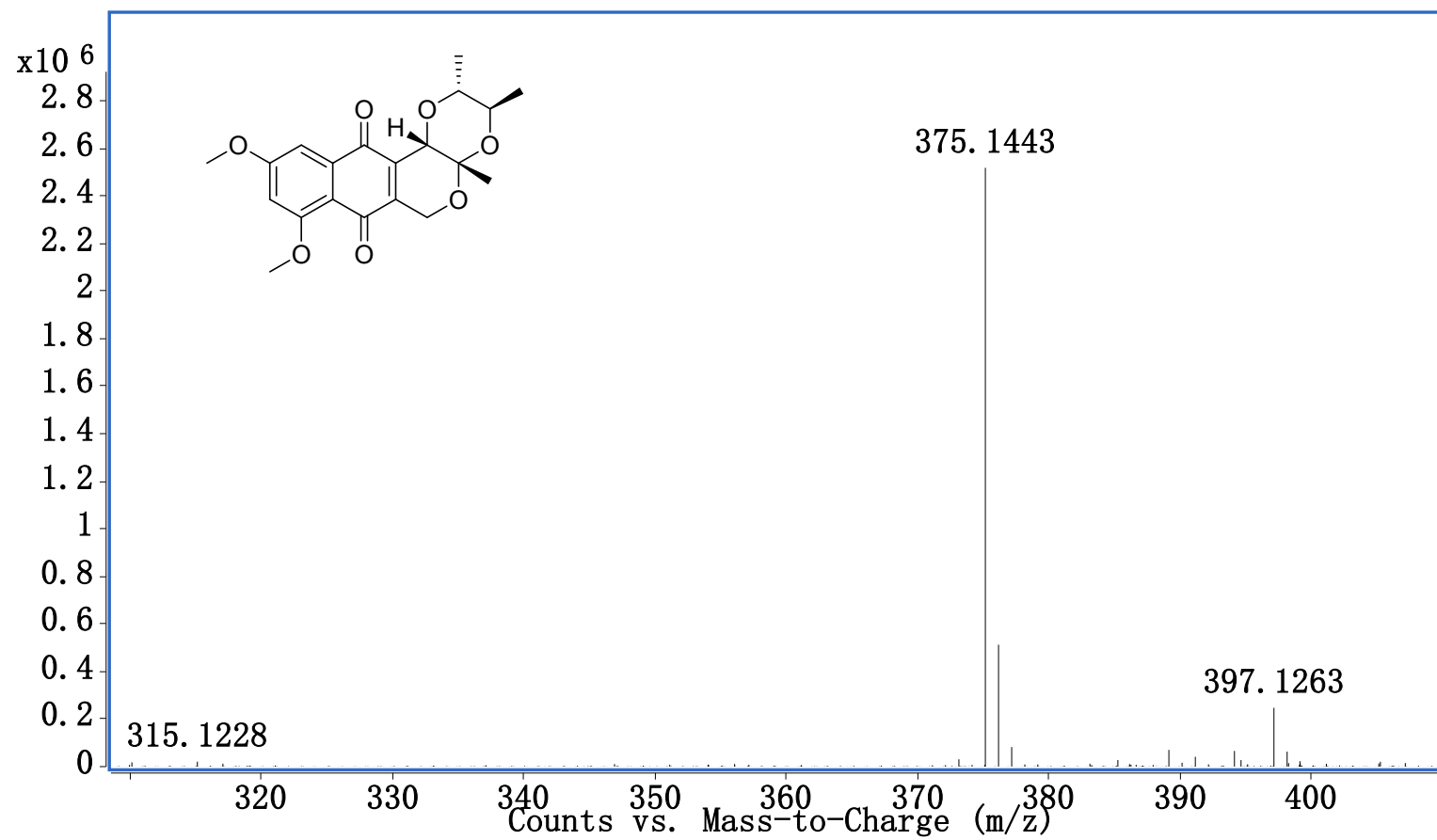


Figure S42. HRESIMS Spectrum of Pseudonectrin C (3)

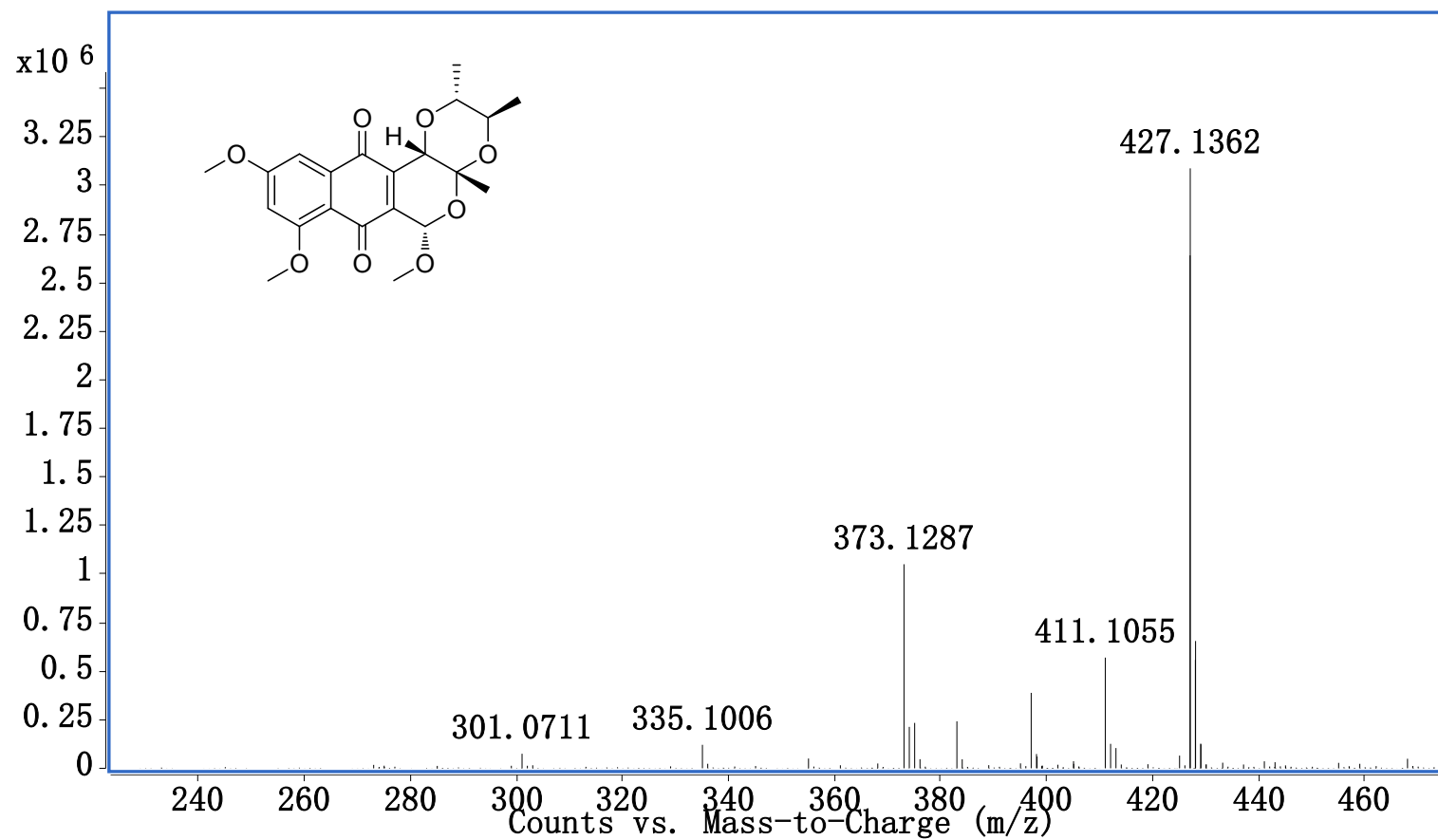


Figure S43 . HRESIMS Spectrum of Pseudonectrin D (4)

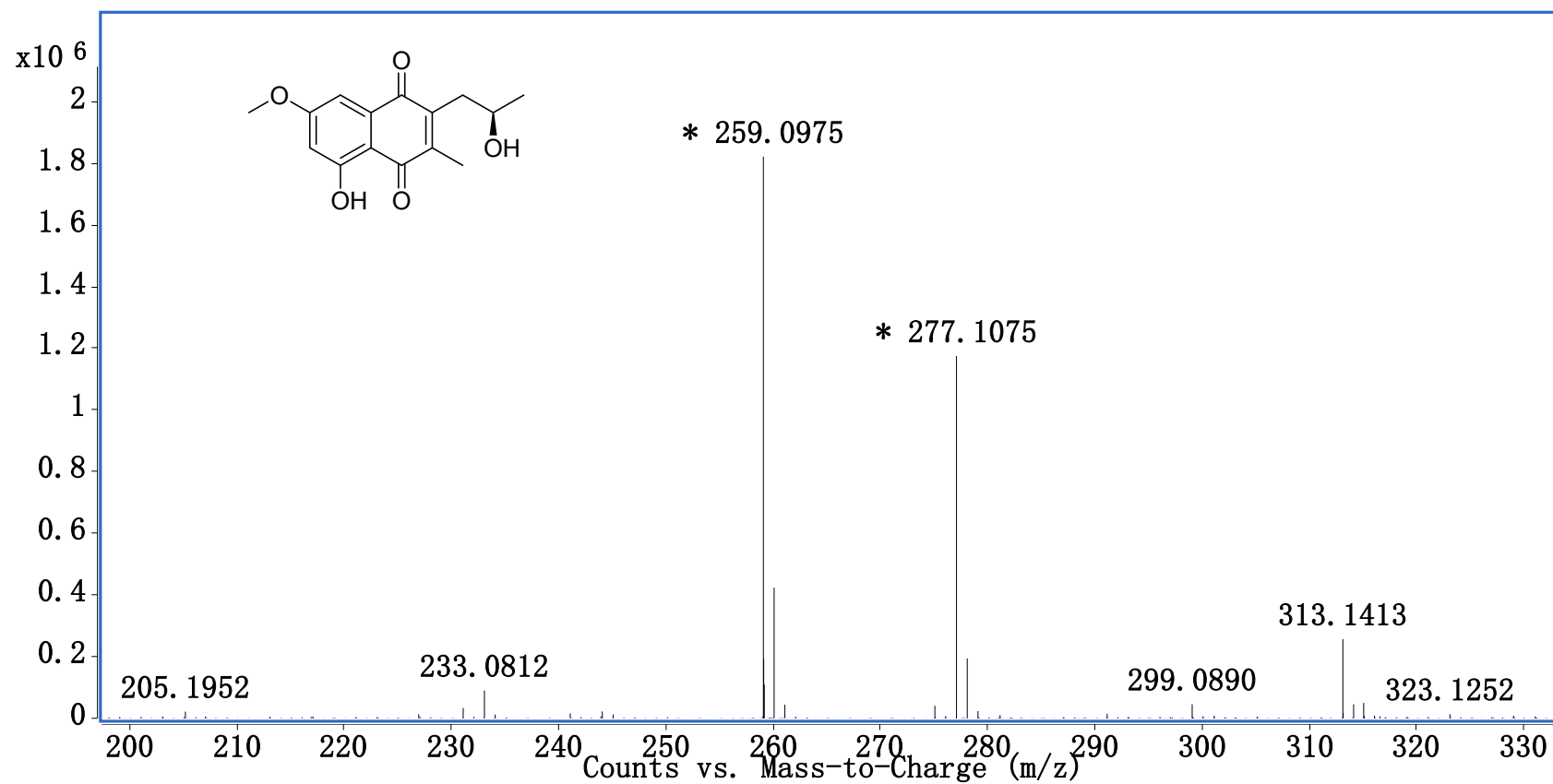


Figure S44. ^1H NMR Spectrum of 2-Acetyl-5,7-dimethoxy-3-methyl-1,4-naphthoquinone (**5**; 400 MHz, CDCl_3)

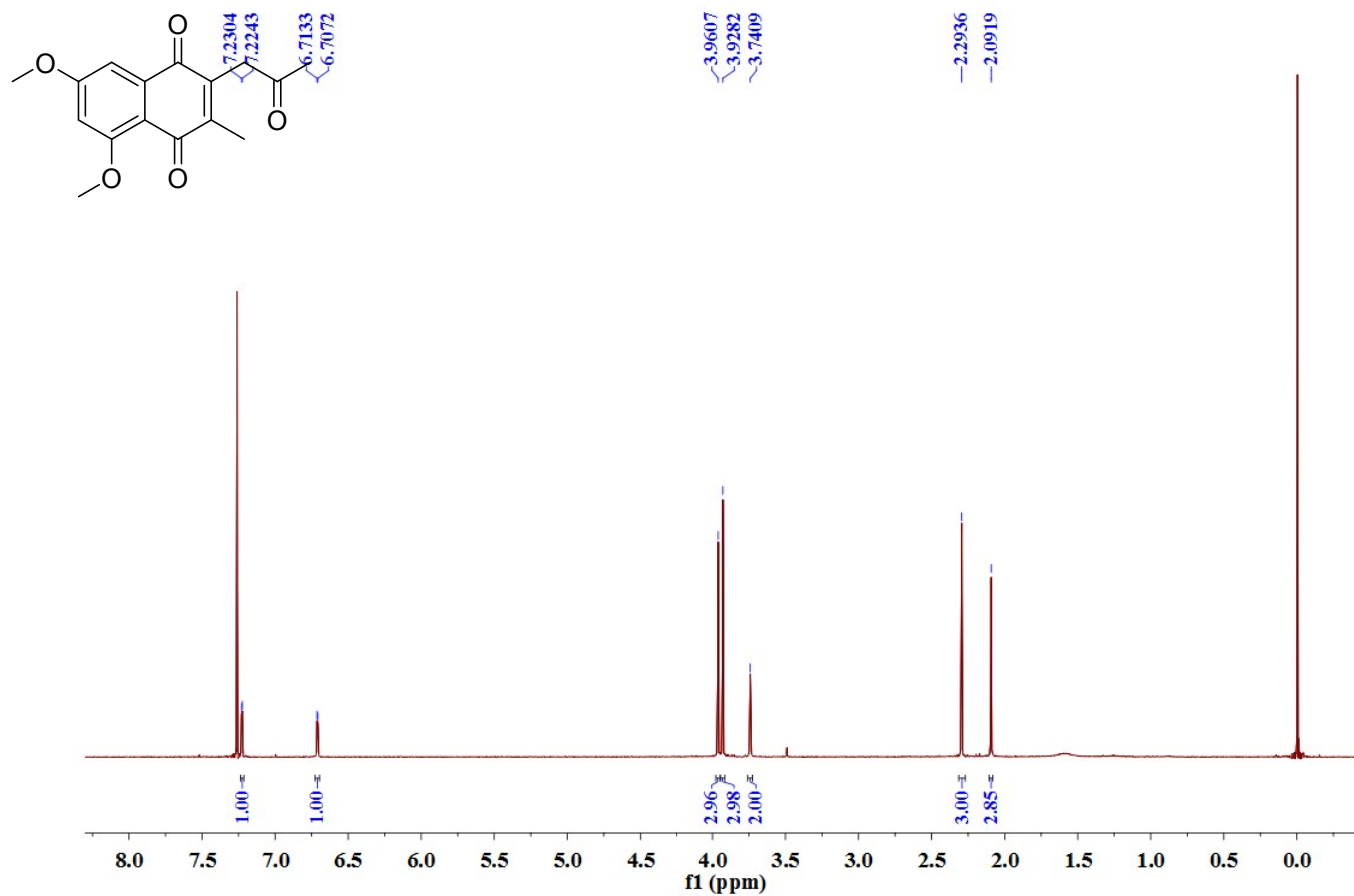


Figure S45. ^{13}C NMR Spectrum of 2-Acetyl-5,7-dimethoxy-3-methyl-1,4-naphthoquinone (**5**; 150 MHz, CDCl_3)

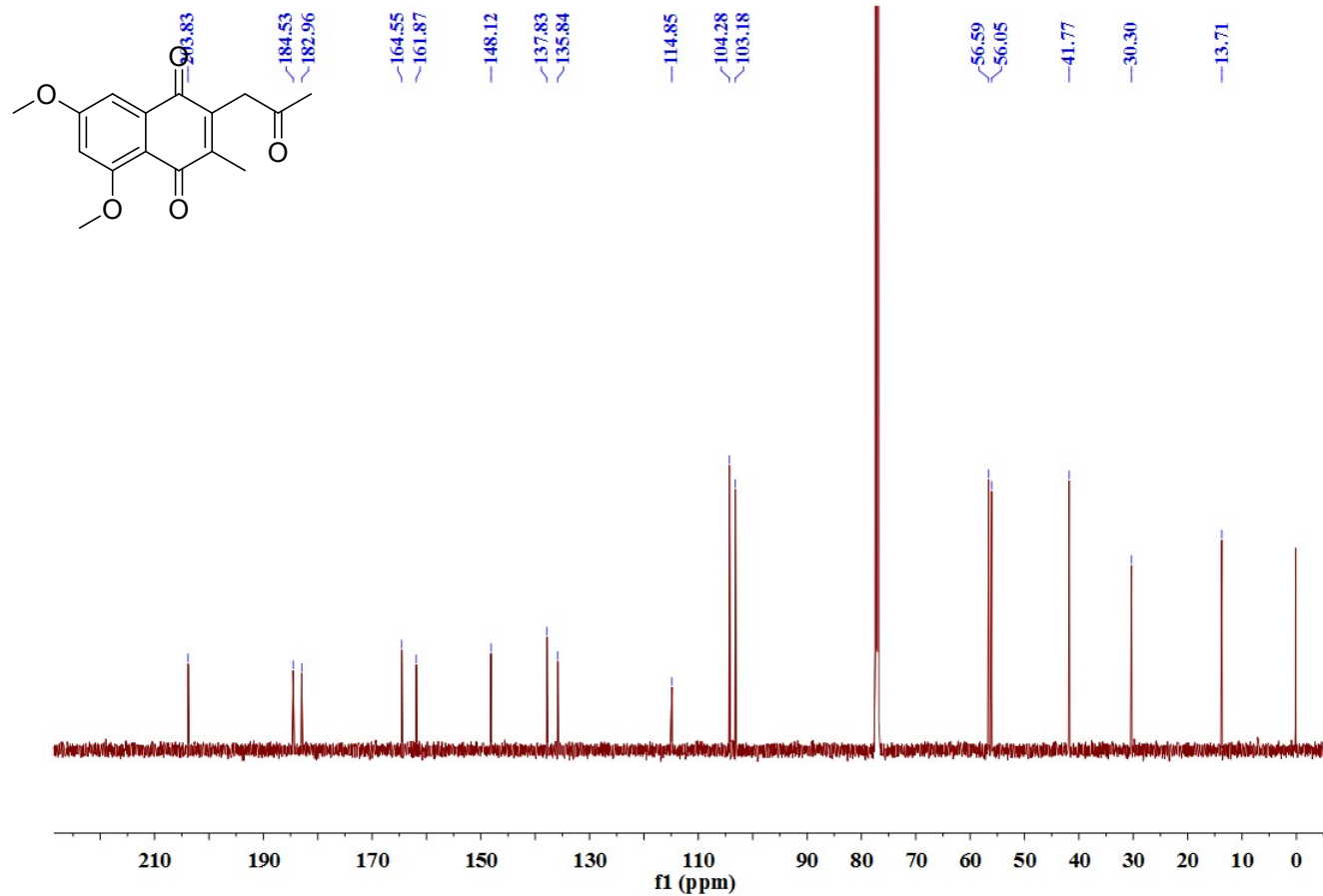


Figure S46. ^1H NMR Spectrum of Herbarin (**6**; 600 MHz, CDCl_3)

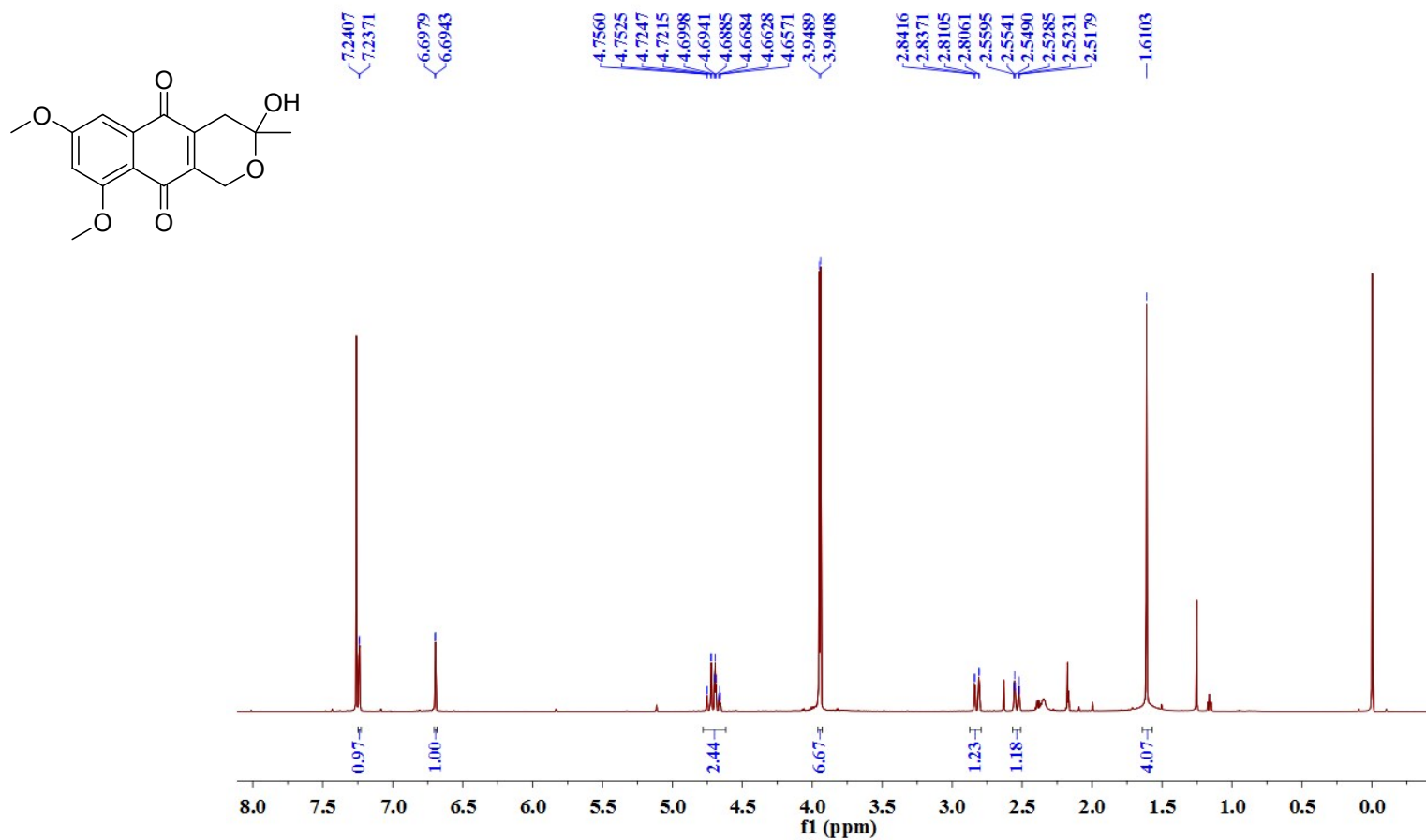


Figure S47. ^{13}C NMR Spectrum of Herbarin (**6**; 150 MHz, CDCl_3)

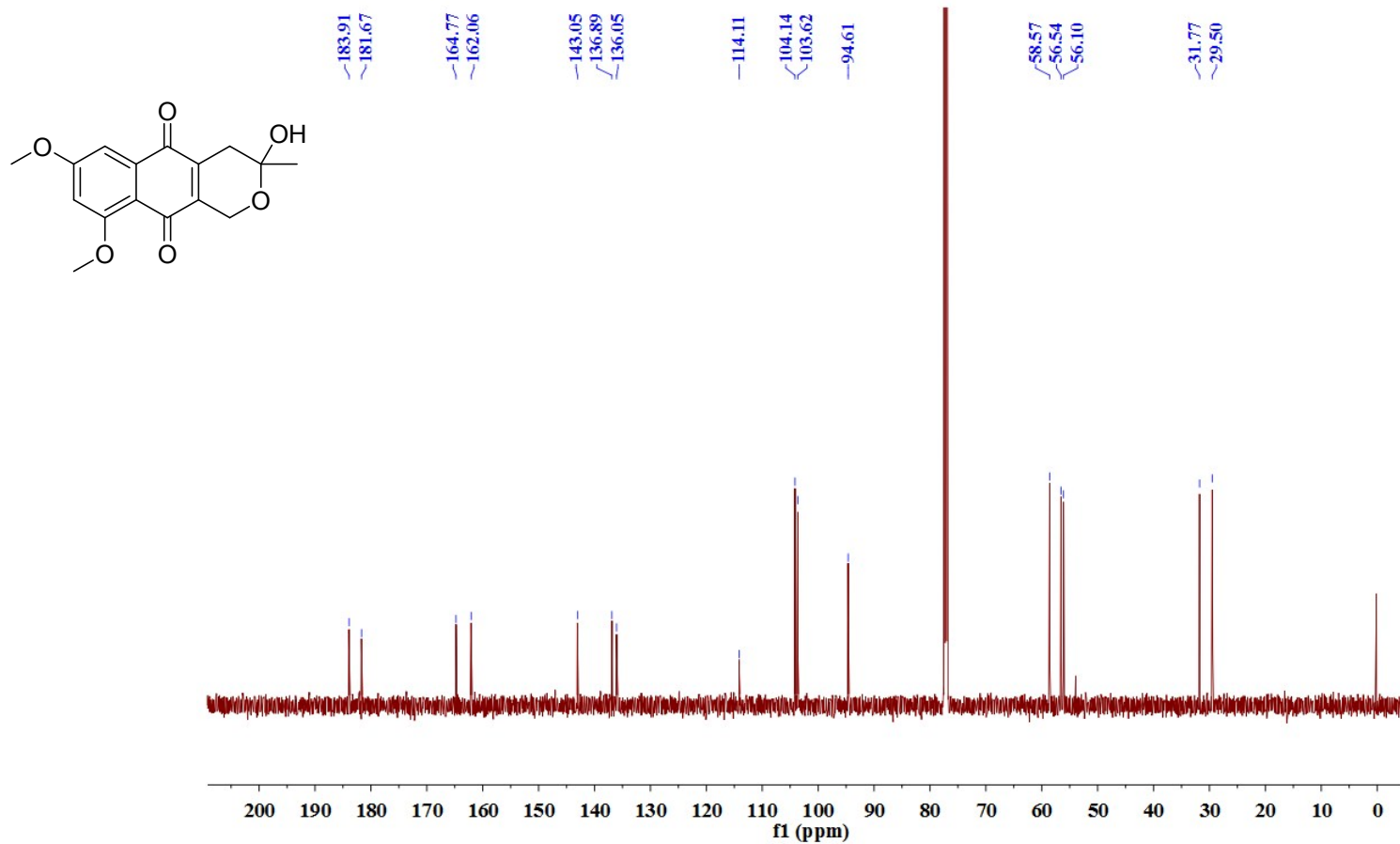


Figure S48. ^1H NMR Spectrum of Dehydroherbarin (**7**; 400 MHz, CDCl_3)

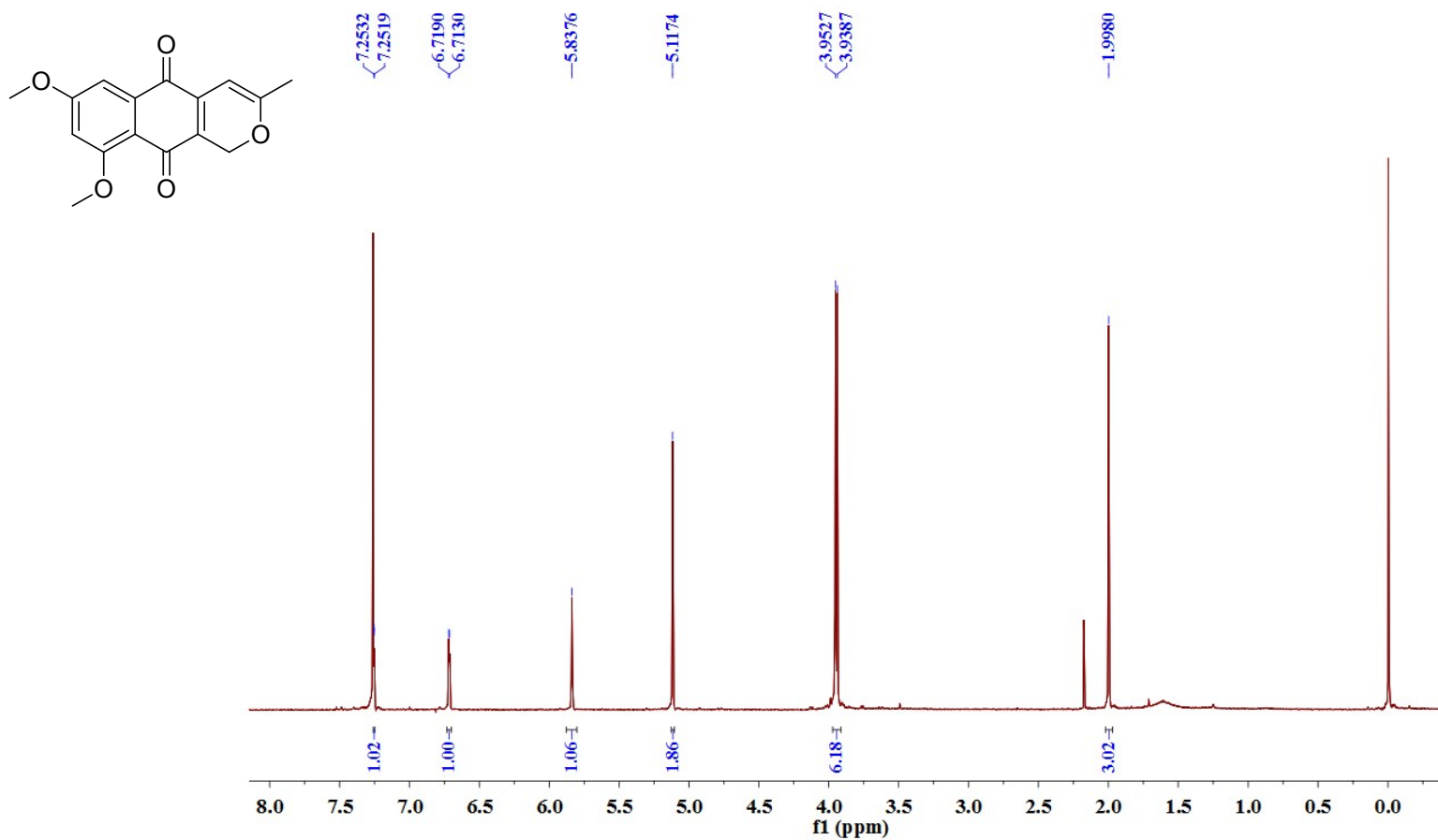


Figure S49. ^{13}C NMR Spectrum of Dehydroherbarin (**7**; 150 MHz, CDCl_3)

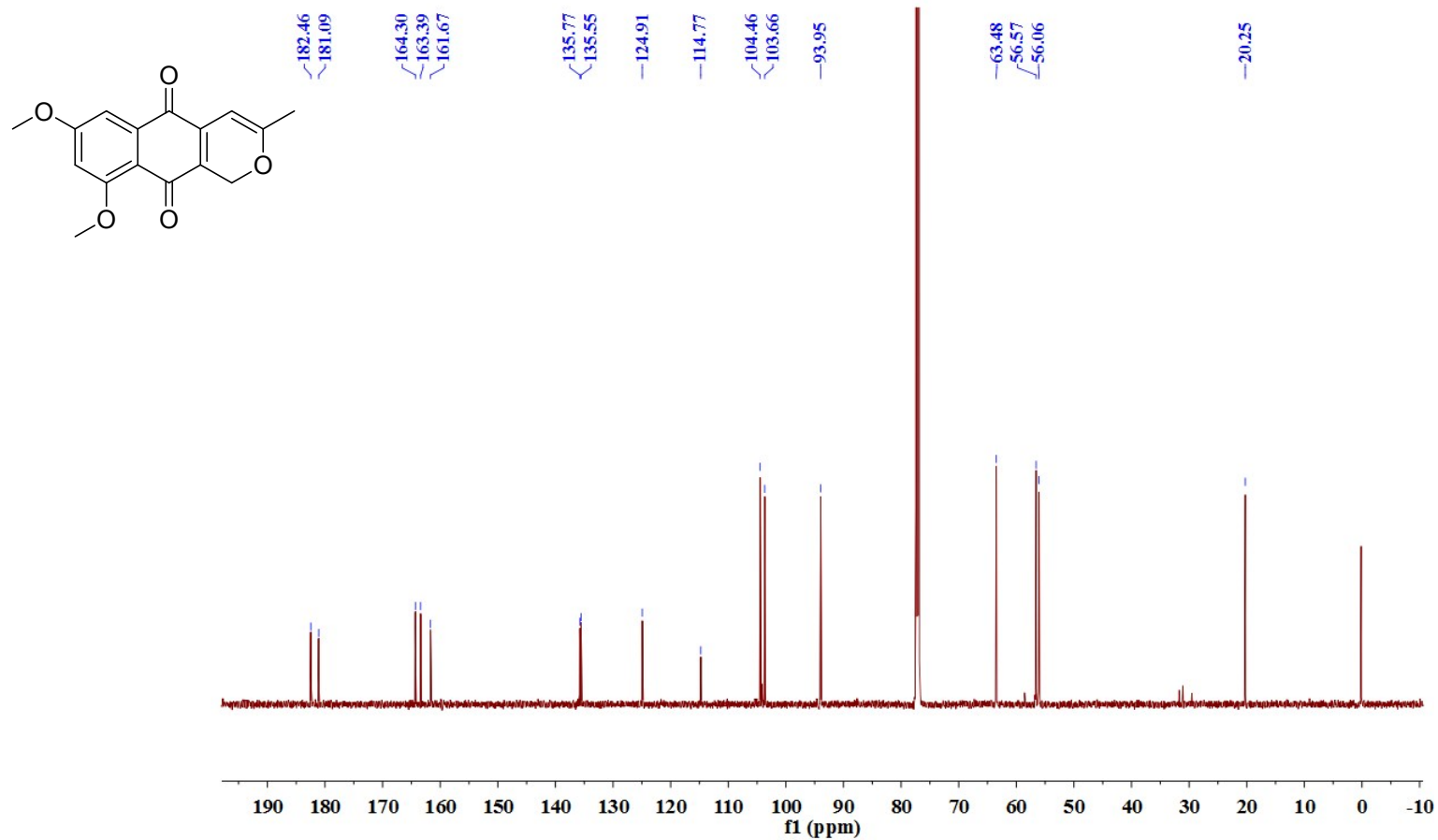


Figure S50. ¹H NMR Spectrum of Scorpionone (**8**; 400 MHz, CDCl₃)

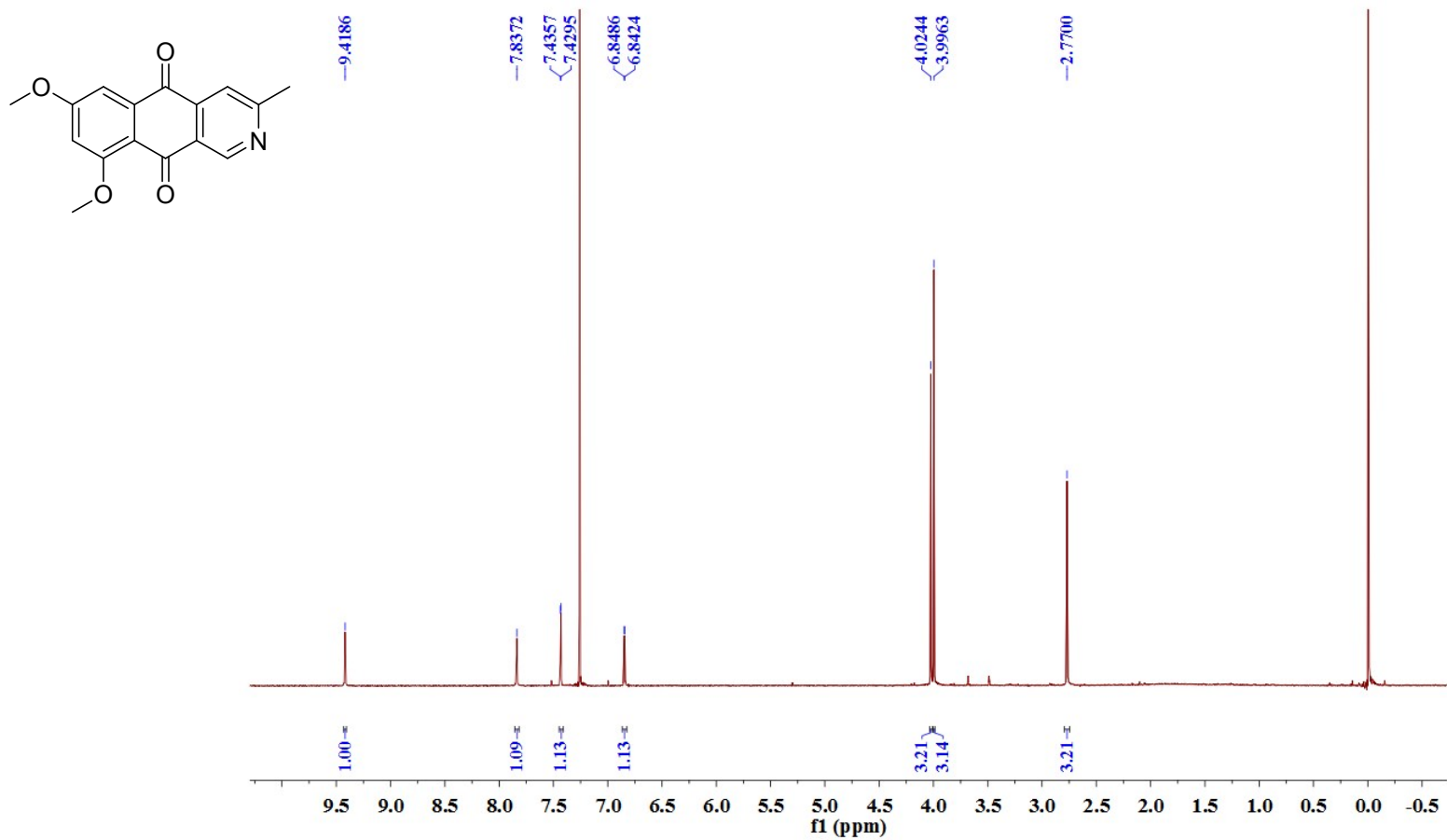
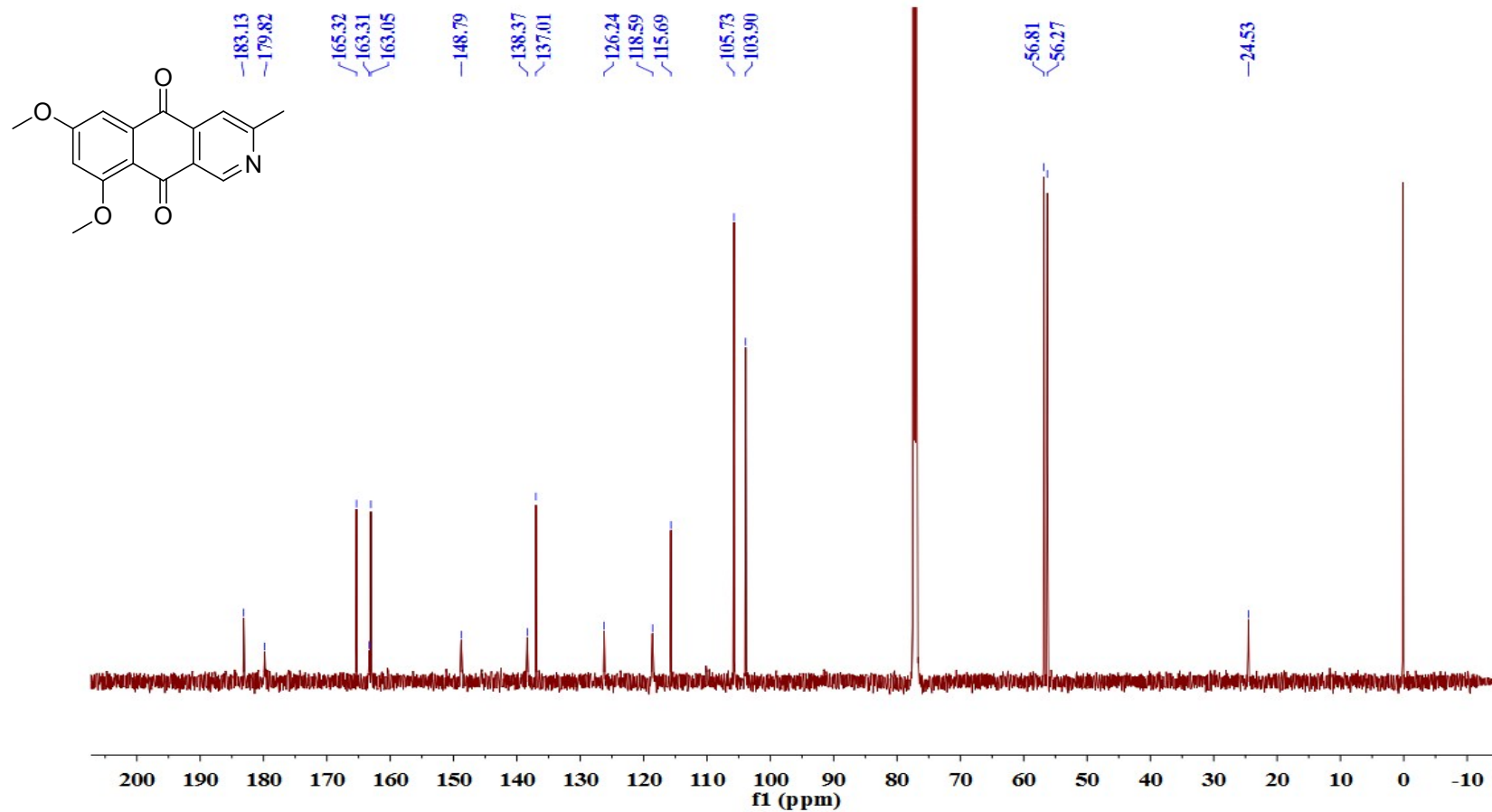
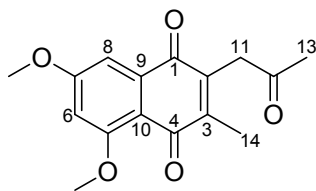


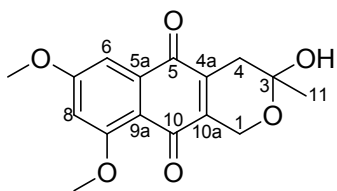
Figure S51. ^{13}C NMR Spectrum of Scorpionone (**8**; 150 MHz, CDCl_3)



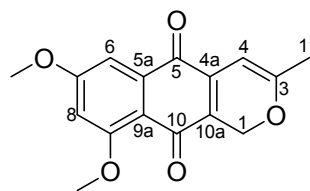
Melting points and spectroscopic data of compounds 5–8



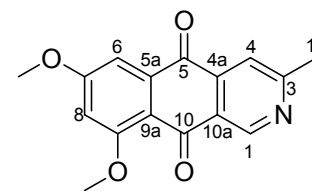
2-Acetyl-5,7-dimethoxy-3-methyl-1,4-naphthoquinone (**5**)



Herbarin (**6**)



Dehydroherbarin (**7**)



Scorpinone (**8**)

2-Acetyl-5,7-dimethoxy-3-methyl-1,4-naphthoquinone (5). mp 184–185 °C ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.22 (1H, d, $J = 2.4$ Hz, H-8), 6.71 (1H, d, $J = 2.4$ Hz, H-6), 3.96 (3H, s, 7-OCH₃), 3.92 (3H, s, 5-OCH₃), 3.74 (2H, s, H-11), 2.29 (3H, s, H-14), 2.09 (3H, s, H-13); ^{13}C NMR (150 MHz, CDCl_3) δ_{C} 203.8 (C-12), 184.5 (C-1), 183.0 (C-4), 164.6 (C-7), 161.9 (C-9), 148.1 (C-2), 137.8 (C-3), 135.8 (C-9), 114.9 (C-10), 104.3 (C-8), 103.2 (C-6), 56.6 (7-OCH₃), 56.1 (5-OCH₃), 41.8 (C-11), 30.3 (C-13), 13.7 (C-14).

Herbarin (6). mp 190–191 °C $[\alpha]_{\text{D}}^{25} +3.7$ (c 0.10, MeOH); ^1H NMR (600 MHz, CDCl_3) δ_{H} 7.24 (1H, d, $J = 2.2$ Hz, H-6), 6.70 (1H, d, $J = 2.2$ Hz, H-8), 4.74 (1H, d, $J = 18.8$ Hz, H-1a), 4.68 (1H, dt, $J = 18.8, 3.4$ Hz, H-1b), 3.95 (3H, s, 7-OCH₃), 3.94 (3H, s, 9-OCH₃), 2.81 (1H, dd, $J = 18.6, 2.7$ Hz, H-4a), 2.52 (1H, dd, $J = 18.6, 3.2$ Hz, H-4b), 1.61 (3H, s, H₃-11); ^{13}C NMR (150 MHz, CDCl_3) δ_{C} 183.9 (C-10), 181.7 (C-5), 164.2 (C-7), 162.1 (C-9), 143.1 (C-5a), 136.9 (C-4a), 136.1 (C-10a), 114.1 (C-9a), 104.1 (C-6), 103.6 (C-8), 94.6 (C-3), 58.6 (C-1), 56.4 (7-OCH₃), 56.1 (9-OCH₃), 31.8 (C-4), 29.5 (C-11).

Dehydroherbarin (7). mp 186–187 °C ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.25 (1H, d, $J = 2.4$ Hz, H-6), 6.72 (1H, d, $J = 2.4$ Hz, H-8), 5.84 (1H, s, H-4), 5.12 (2H, s, H₂-1), 3.95 (3H, s, 7-OCH₃), 3.94 (3H, s, 9-OCH₃), 2.00 (3H, s, H₃-11); ^{13}C NMR (150 MHz, CDCl_3) δ_{C} 182.5 (C-10), 181.1 (C-5), 164.3 (C-7), 163.4 (C-9), 161.7 (C-3), 135.8 (C-4a), 135.6 (C-5a), 124.9 (C-10a), 114.8 (C-9a), 104.5 (C-6), 103.7 (C-8), 94.0 (C-4), 63.5 (C-1), 56.6 (7-OCH₃), 56.1 (9-OCH₃), 20.2 (C-11).

Scorpinone (8). mp 195–196 °C ^1H NMR (400 MHz, CDCl_3) δ_{H} 9.42 (1H, s, H-1), 7.84 (1H, s, H-4), 7.43 (1H, d, $J = 2.4$ Hz, H-6), 6.84 (1H, d, $J = 2.4$ Hz, H-8), 4.02 (3H, s, 9-OCH₃), 4.00 (3H, s, 7-OCH₃), 2.77 (3H, s, H-11); ^{13}C NMR (150 MHz, CDCl_3) δ_{C} 183.1 (C-5), 179.8 (C-10), 165.3 (C-7), 163.3 (C-3), 163.1 (C-9), 148.8 (C-1), 138.4 (C-10a), 137.0 (C-5a), 126.2 (C-4a), 118.6 (C-4), 115.7 (C-9a), 105.7 (C-8), 103.9 (C-6), 56.8 (9-OCH₃), 56.3 (7-OCH₃), 24.5 (C-11).

Scheme S1. Hypothetical Biosynthetic Pathways for 1–8

