

Rufomycins or Ilamycins: Naming Clarifications and Definitive Structural Assignments

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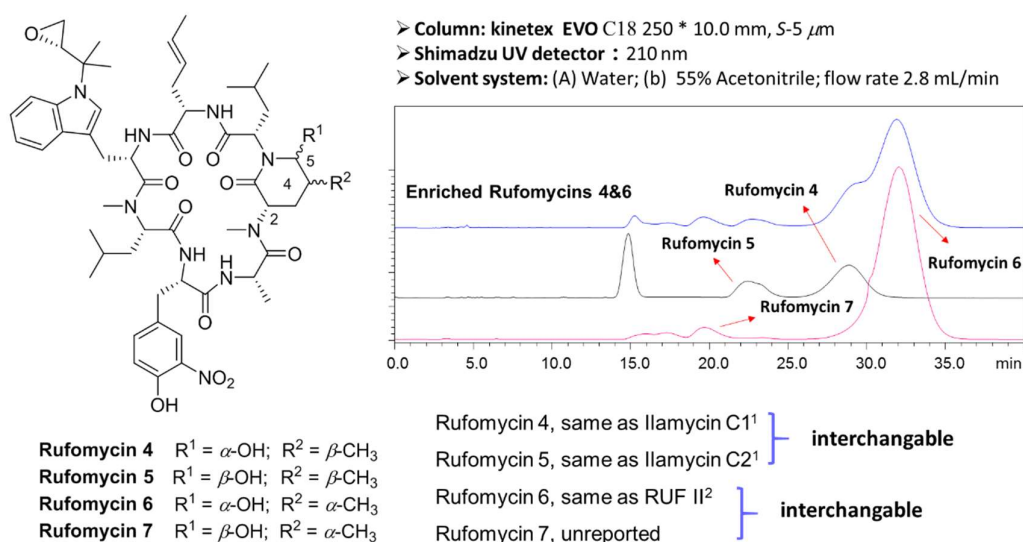
■ SUPPORTING INFORMATION

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Chart S1. Clarification of rufomycin 4 and its related three diastereomers (rufomycins 5–7)



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- [2] Choules, M. P.; Wolf, N. M.; Lee, H.; Anderson, J. R.; Grzelak, E. M.; Wang, Y.; Ma, R.; Gao, W.; McAlpine, J. B.; Jin, Y. Y.; Cheng, J.; Lee, H.; Suh, J. W.; Duc, N. M.; Paik, S.; Choe, J. H.; Jo, E. K.; Chang, C. L.; Lee, J. S.; Jaki, B. U.; Pauli, G. F.; Franzblau, S. G.; Cho, S. rufomycin Targets ClpC1 Proteolysis in Mycobacterium tuberculosis and M. abscessus. *Antimicrob Agents Chemother* **2019**, *63*, e02204–e02218.

Figure S1. ^1H NMR spectrum of rufomycin 4 in CD_3OD at 600 MHz

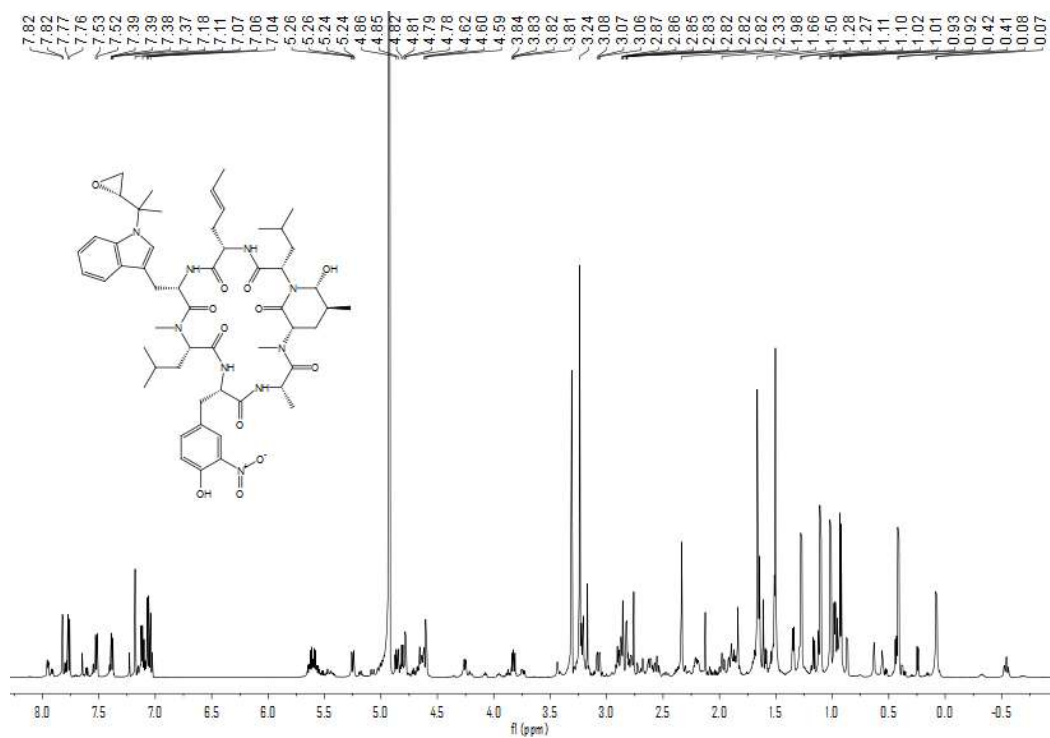


Figure S2. ^{13}C NMR spectrum of rufomycin 4 in CD_3OD at 150 MHz

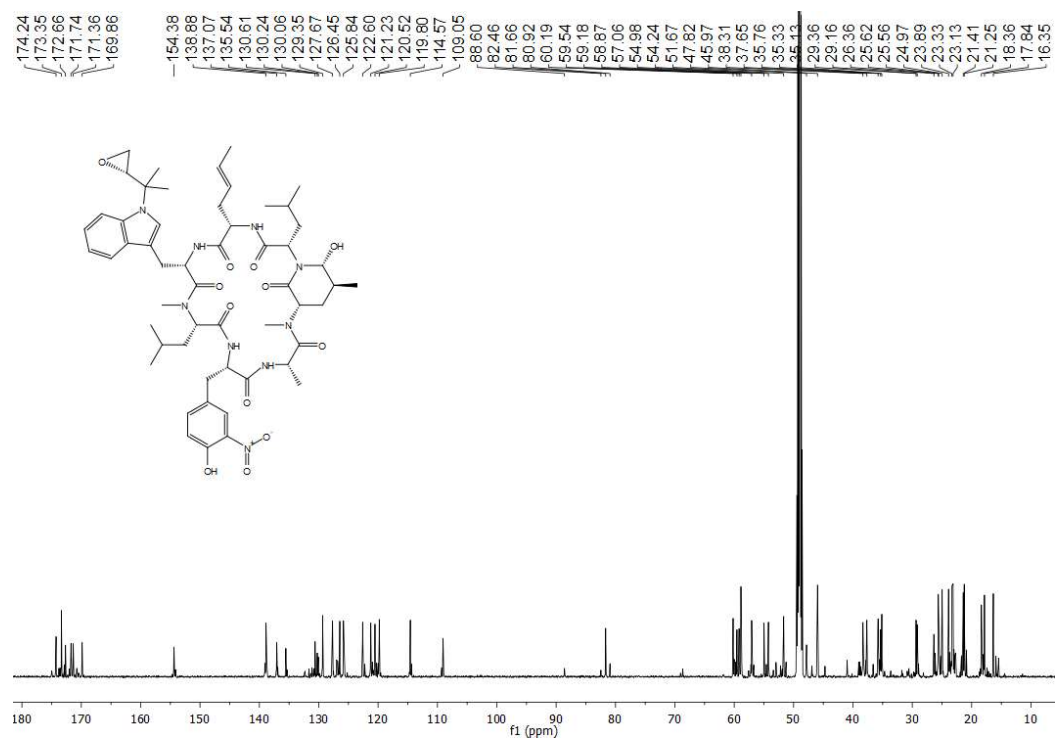


Figure S3. TOCSY spectrum of rufomycin 4 in CD₃OD

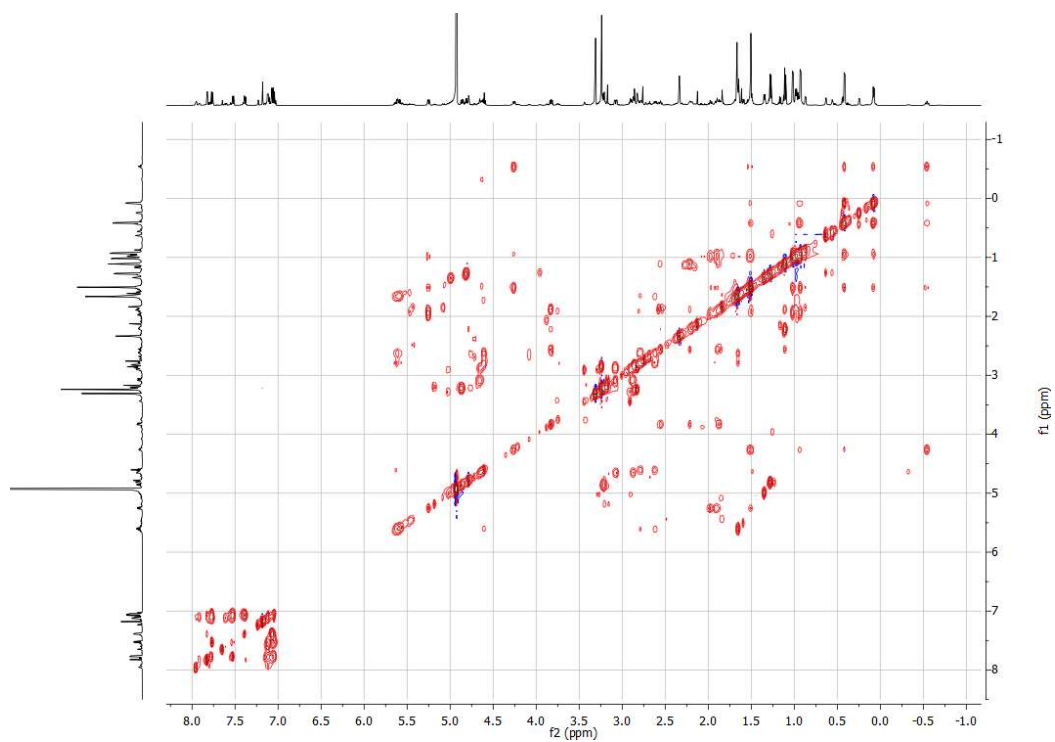


Figure S4. HSQC spectrum of rufomycin 4 in CD₃OD

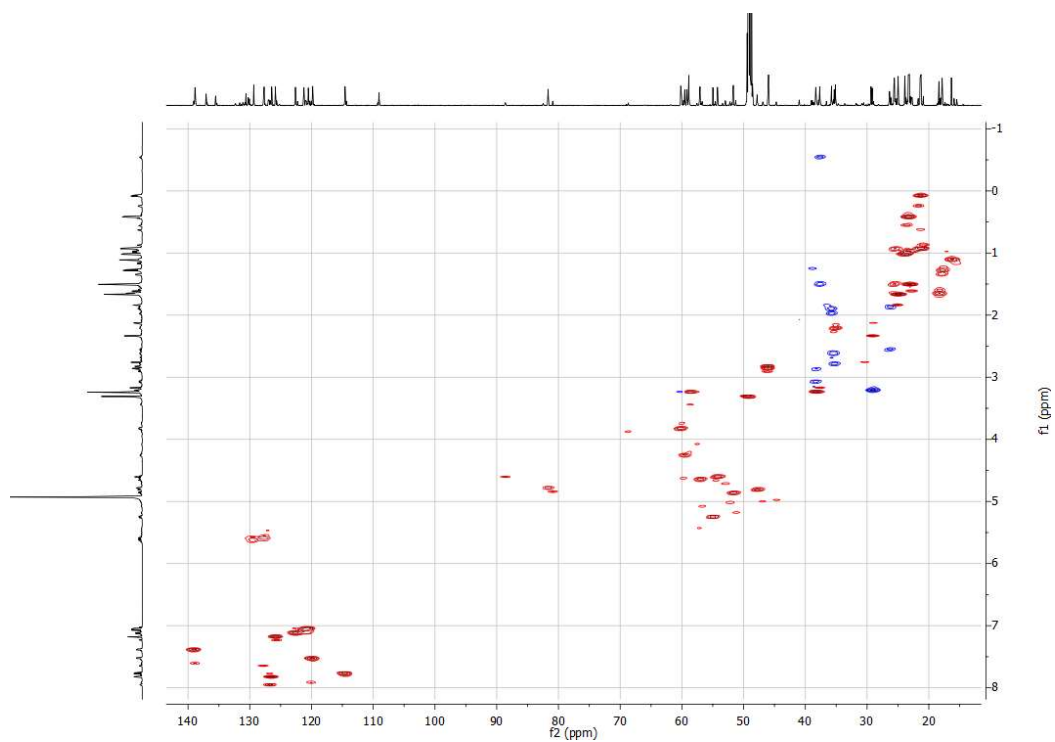


Figure S5. HMBC spectrum of rufomycin 4 in CD₃OD at (600 MHz, ¹H)

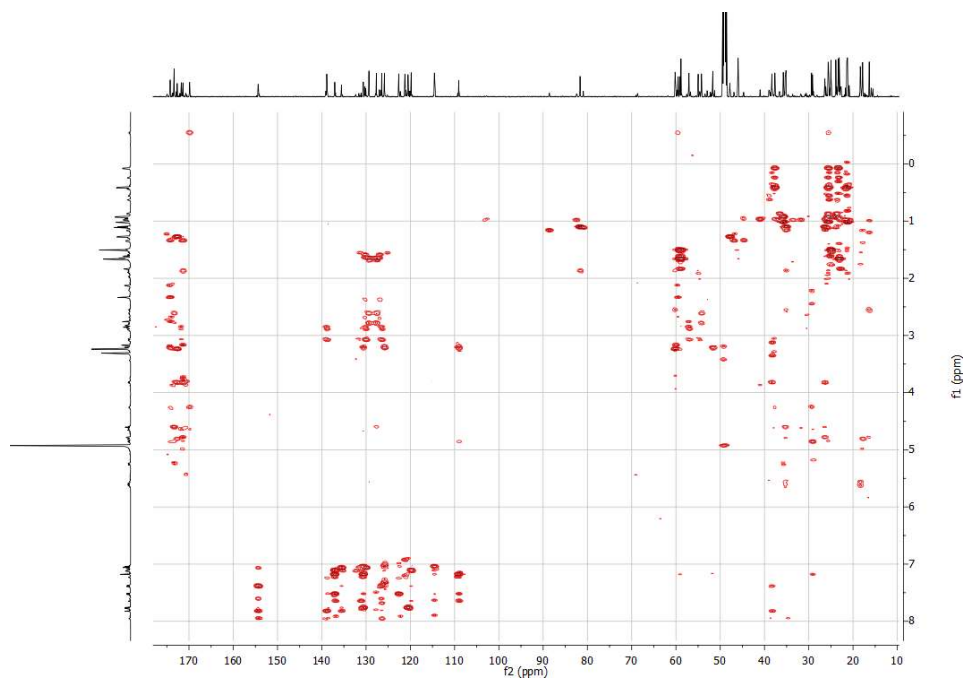


Figure S6. ROESY spectrum of rufomycin 4 in CD₃OD

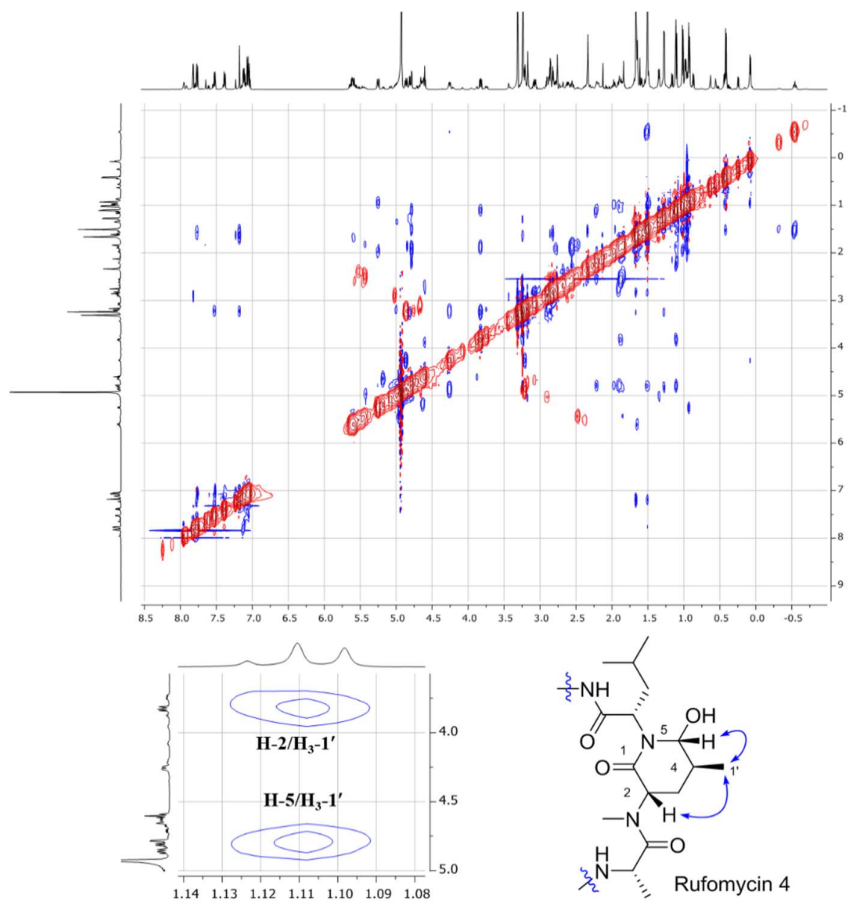


Figure S7. HRMS (ESI) spectrum of rufomycin 4

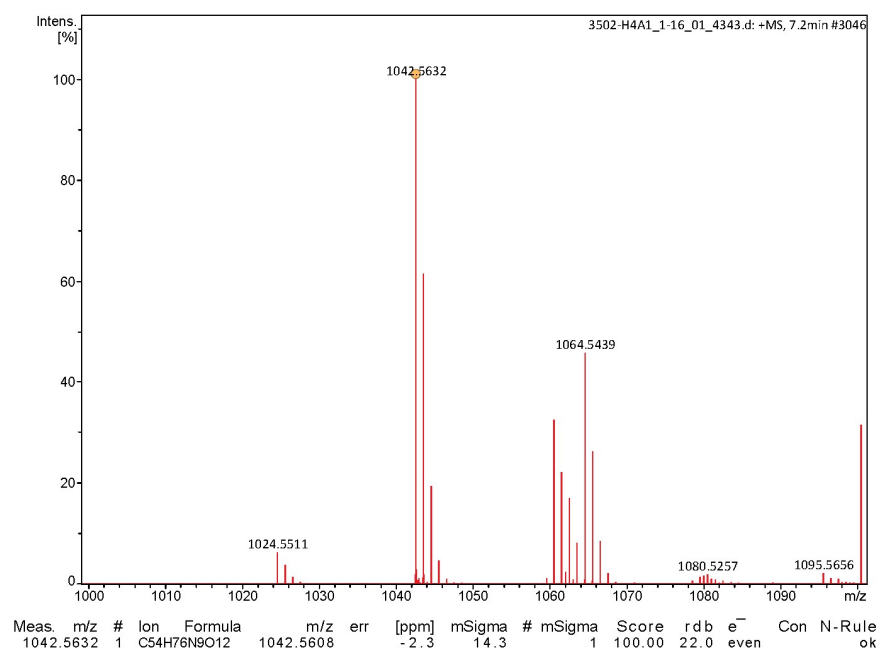


Figure S8. ¹H NMR spectrum of rufomycin 5 in CD₃OD at 600 MHz

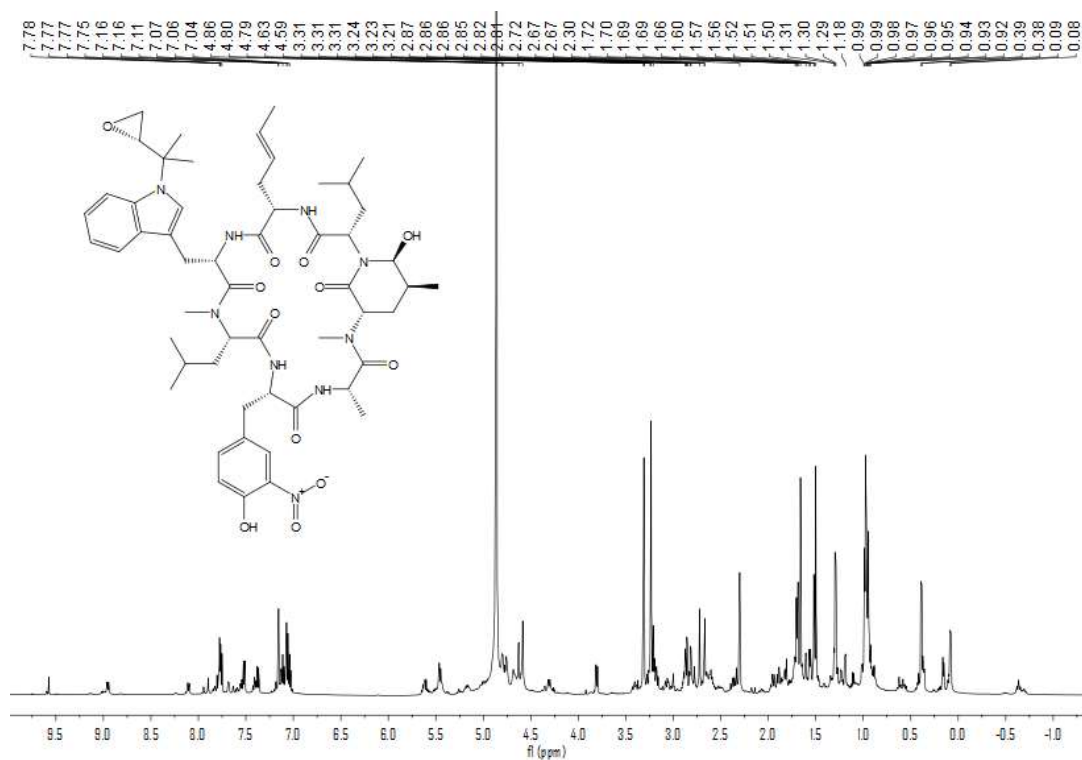


Figure S9. ^{13}C NMR spectrum of rufomycin 5 in CD_3OD at 150 MHz

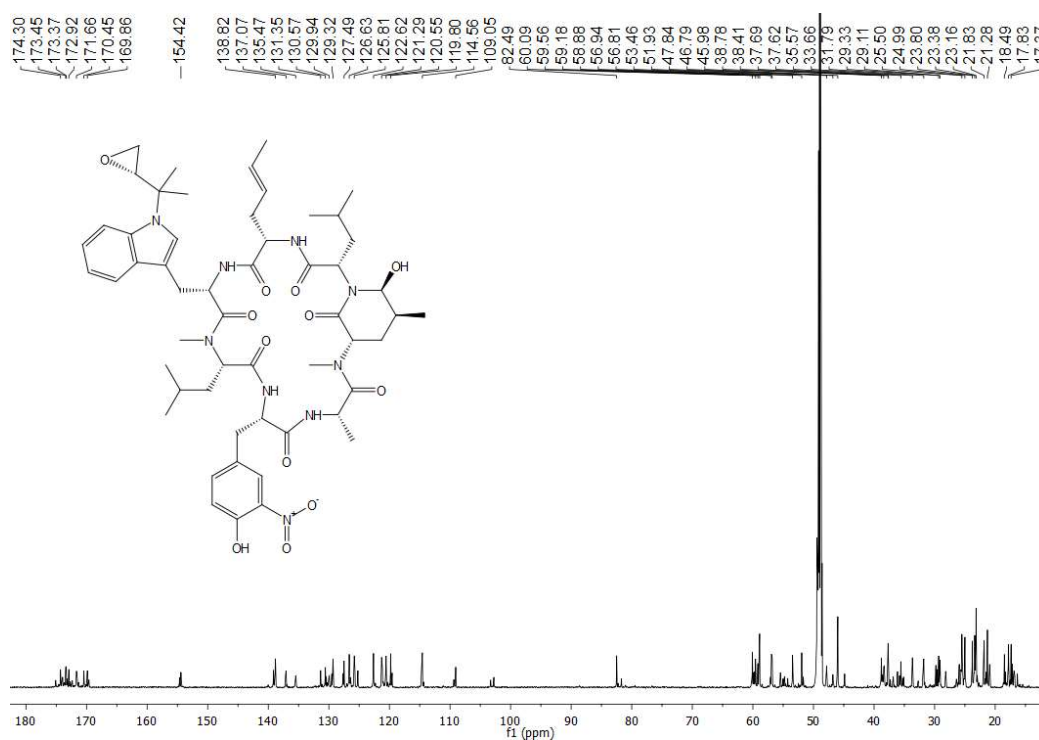


Figure S10. TOCSY spectrum of rufomycin 5 in CD_3OD (400 MHz)

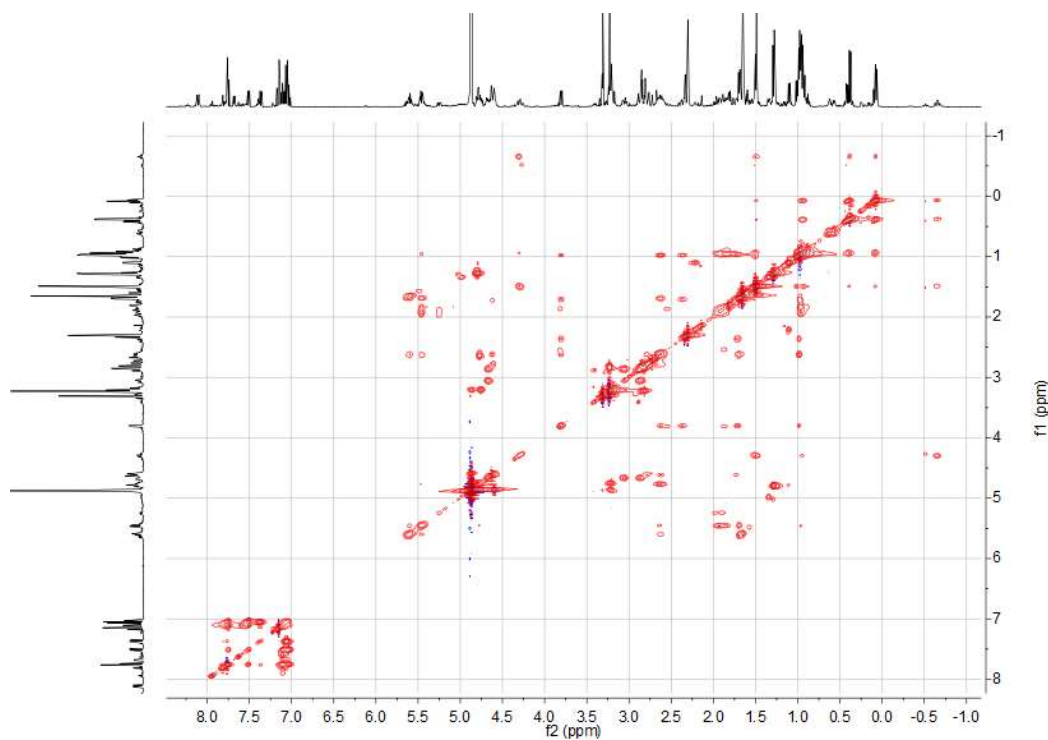


Figure S11. HSQC spectrum of rufomyacin 5 in CD₃OD

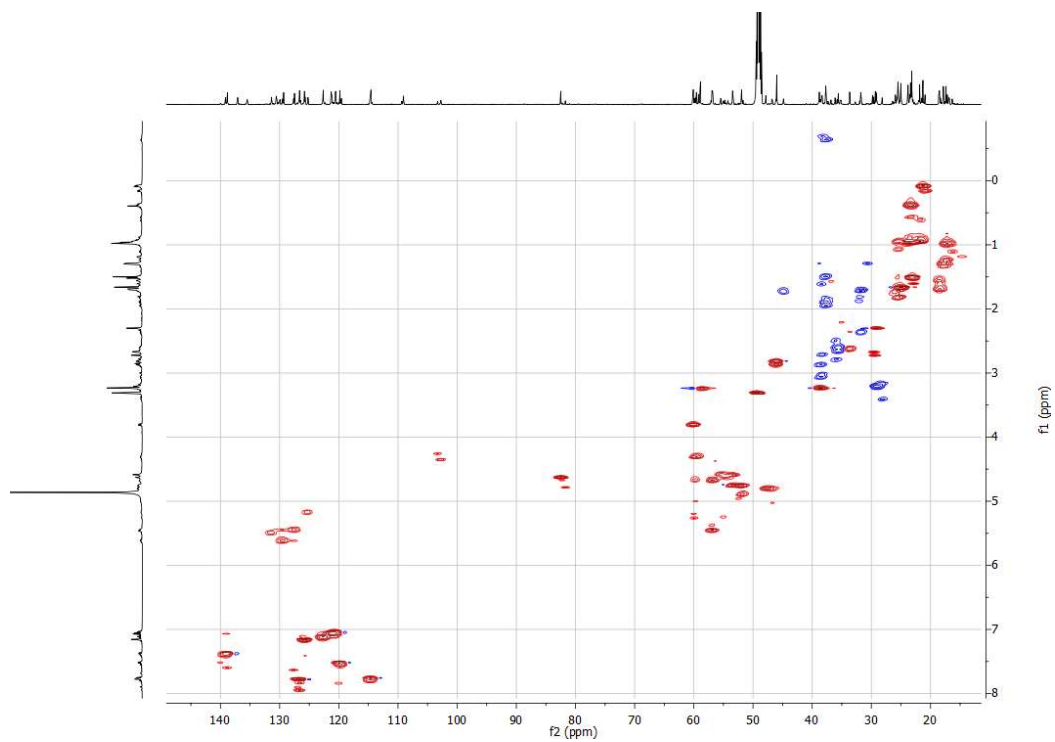


Figure S12. HMBC spectrum of rufomyacin 5 in CD₃OD (400 MHz, ¹H)

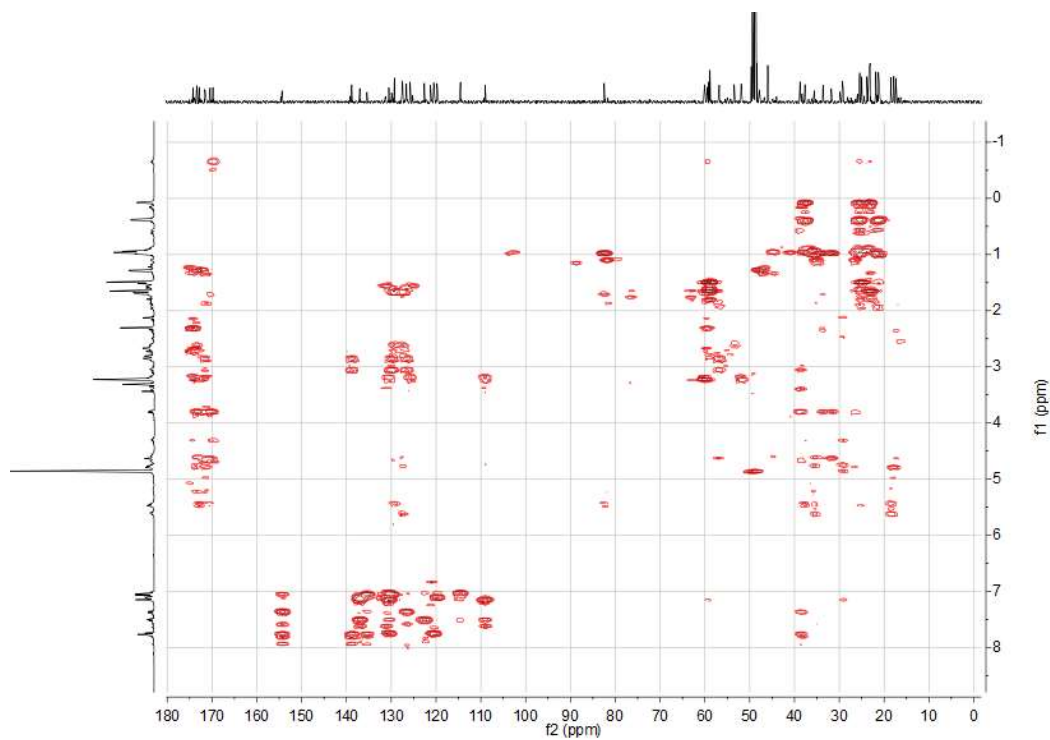


Figure S13. ROESY spectrum of rufomycin 5 in CD₃OD

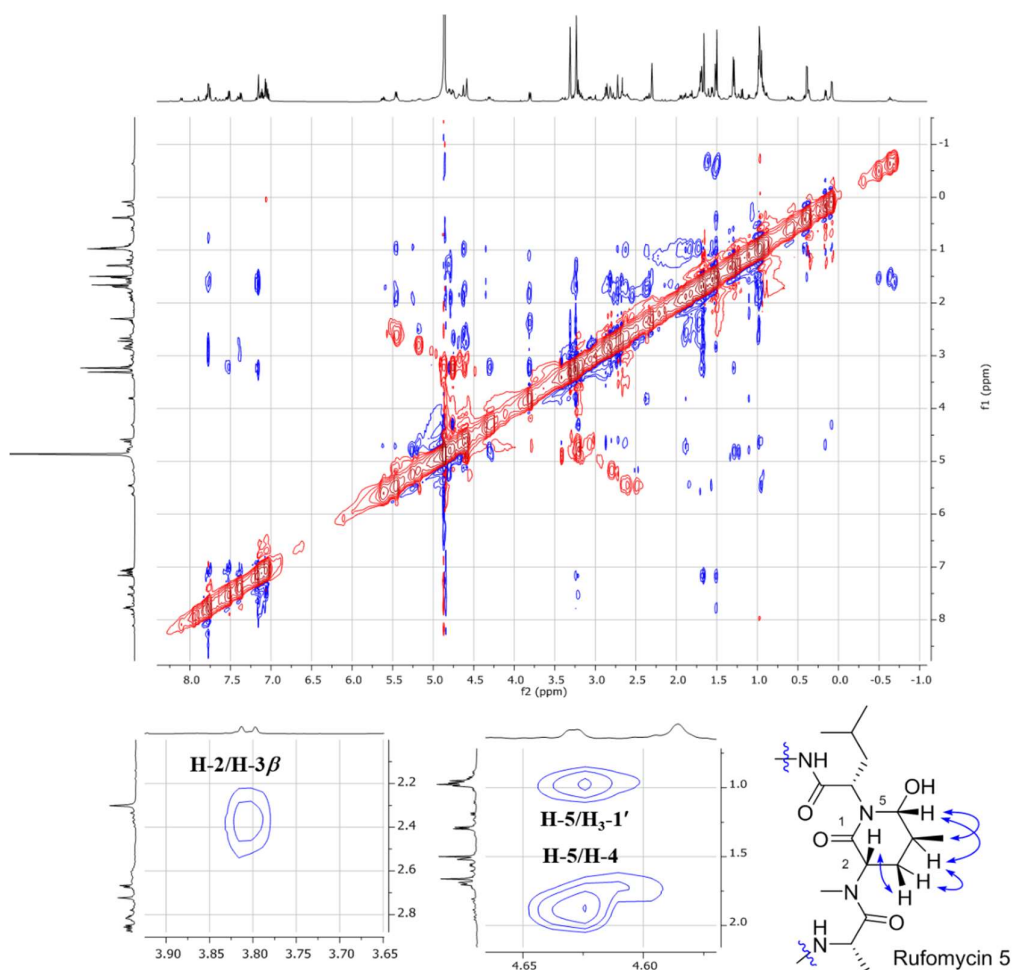


Figure S14. HRMS (ESI) spectrum of rufomycin 5

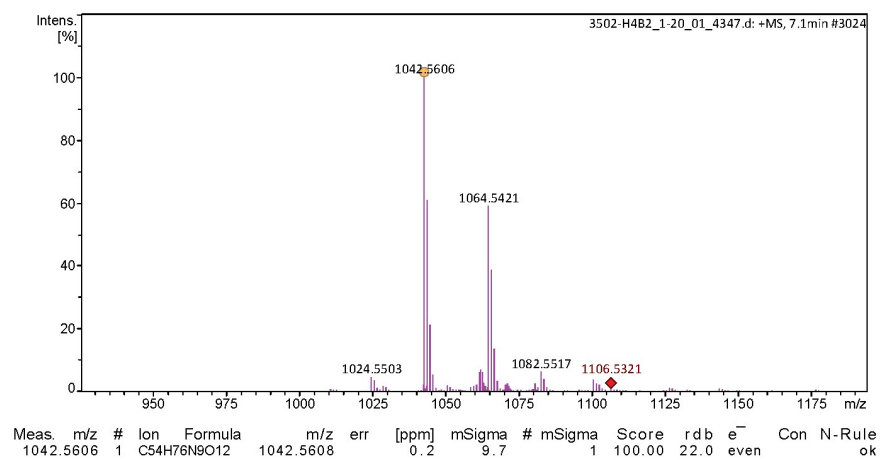


Figure S15. ^1H NMR spectrum of rufomycin 6 in CD_3OD at 600 MHz

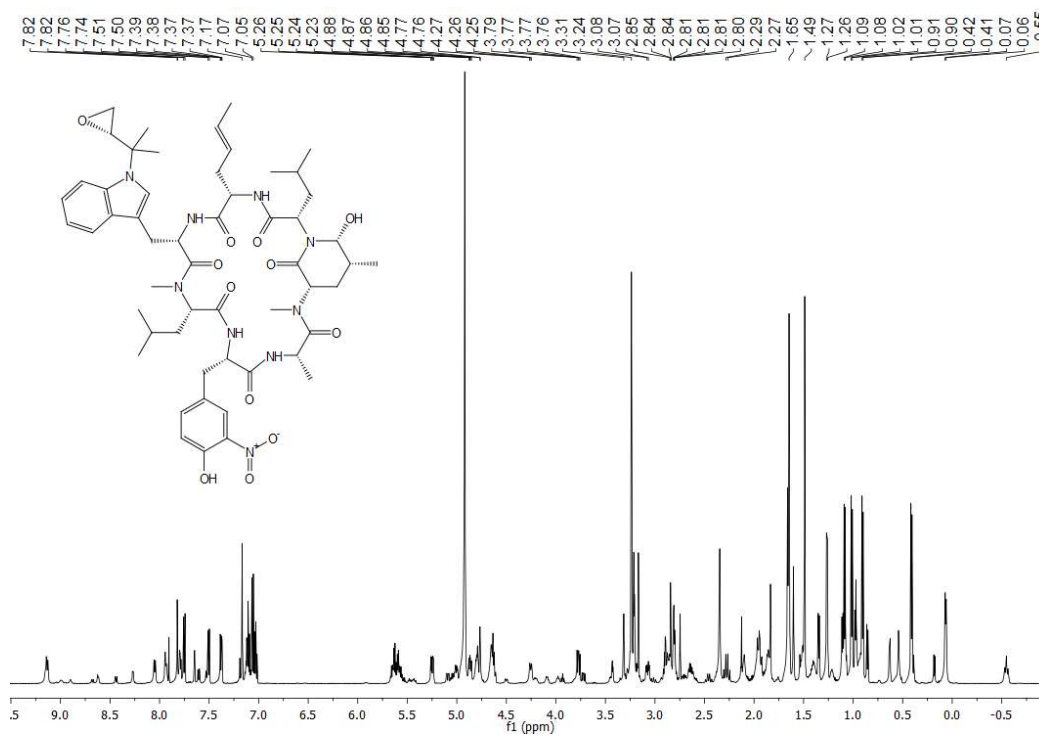


Figure S16. ^{13}C NMR spectrum of rufomycin 6 in CD_3OD at 150 MHz

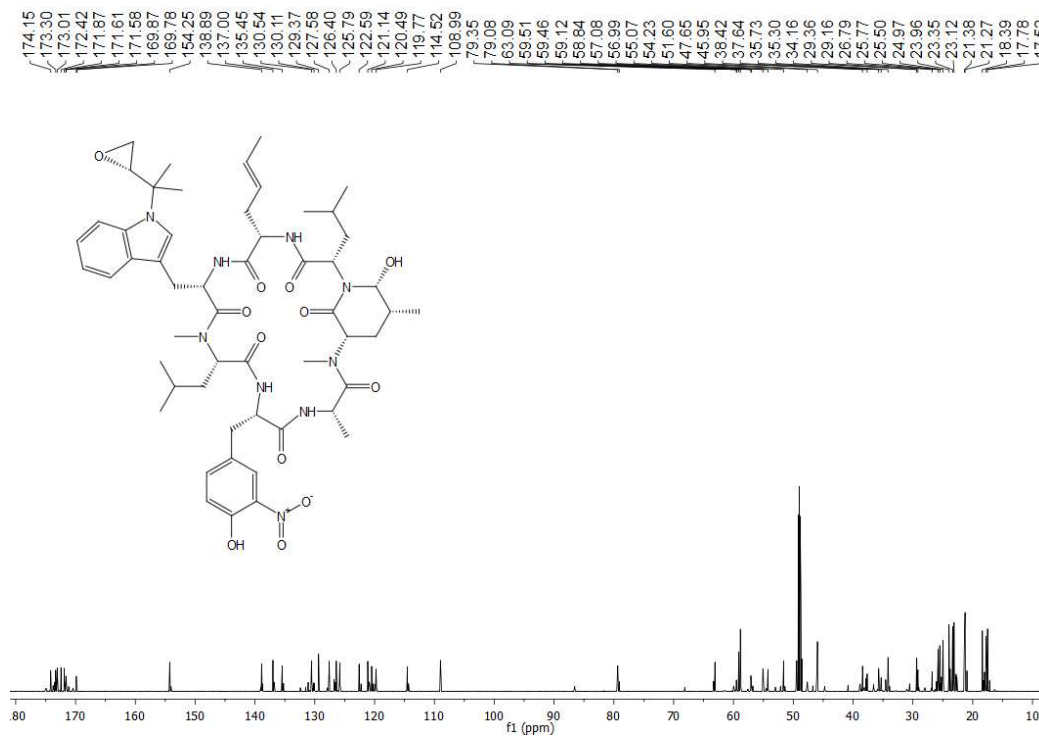


Figure S17. TOCSY spectrum of rufomycin 6 in CD₃OD

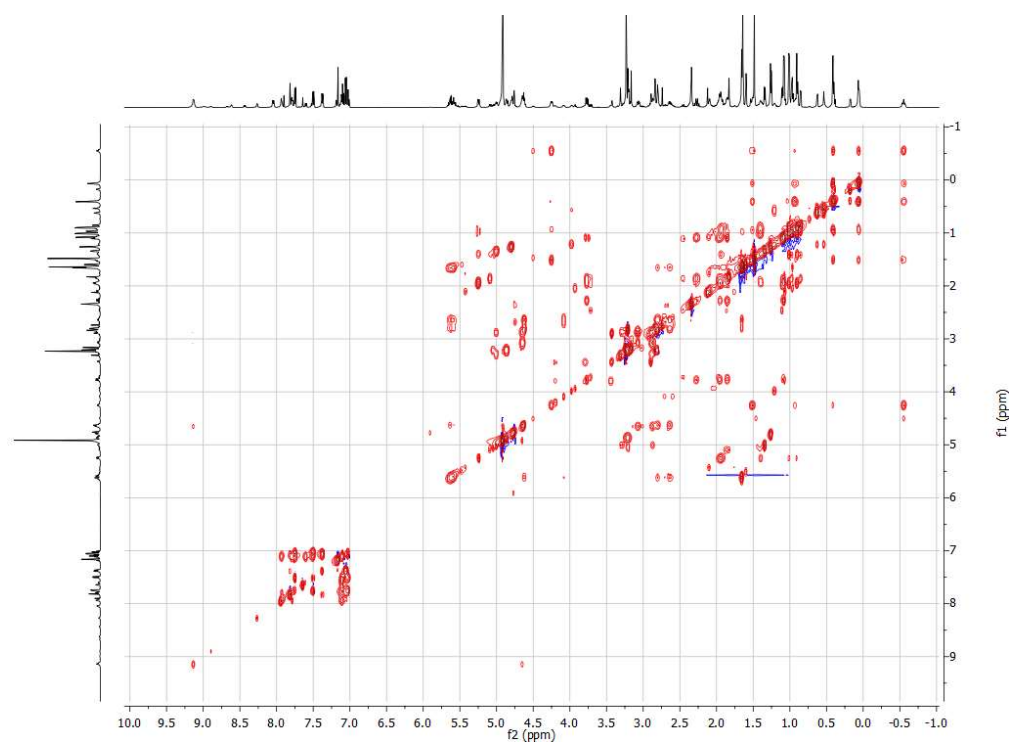


Figure S18. HSQC spectrum of rufomycin 6 in CD₃OD

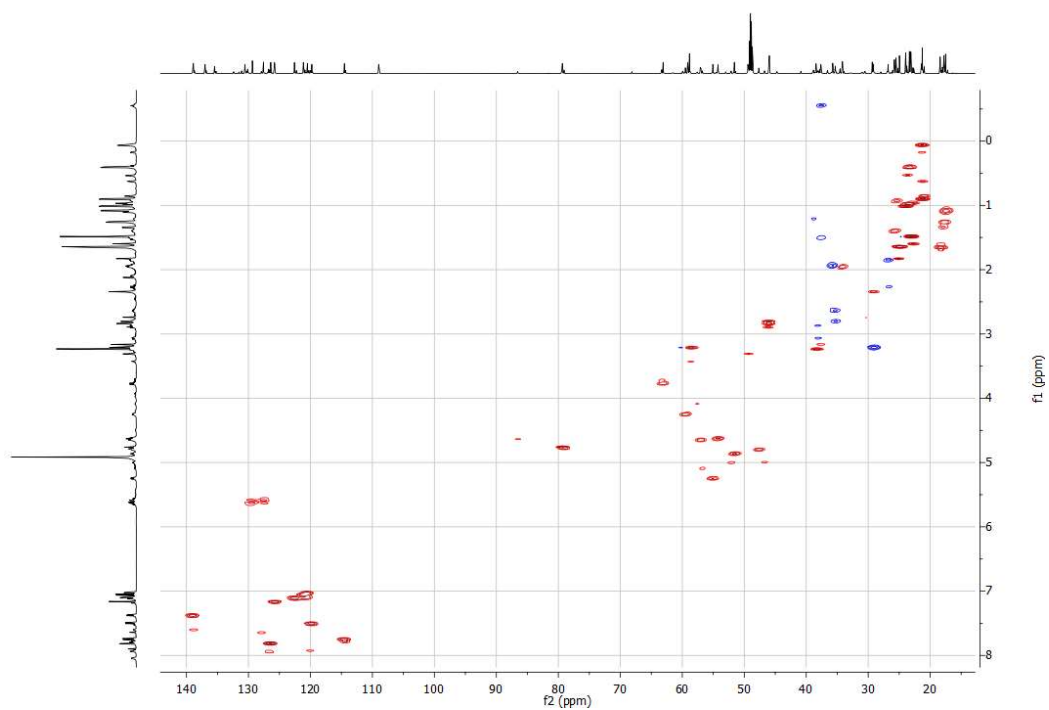


Figure S19. HMBC spectrum of rufomycin 6 in CD₃OD

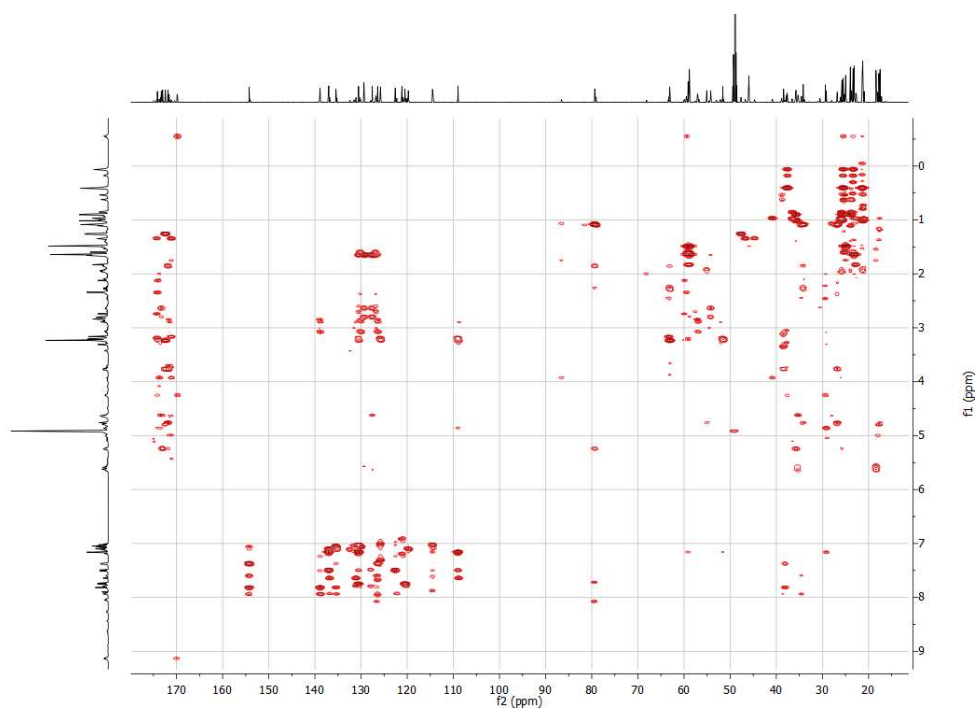


Figure S20. ROESY spectrum of rufomycin 6 in CD₃OD

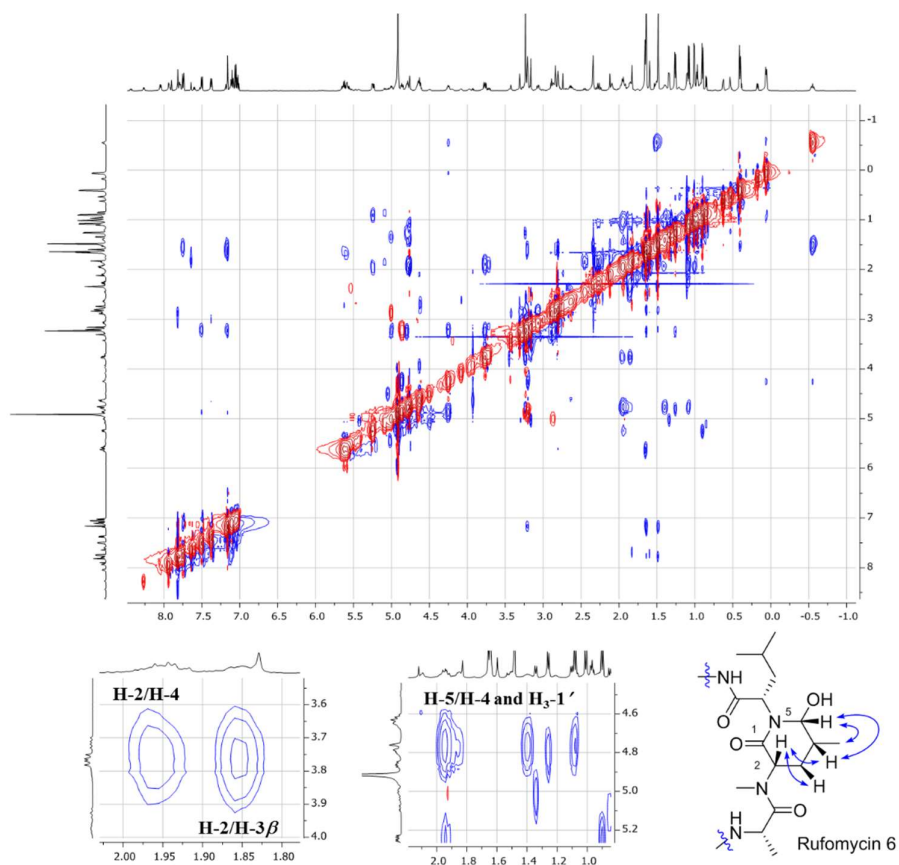


Figure S21. HRMS (ESI) spectrum of rufomycin 6

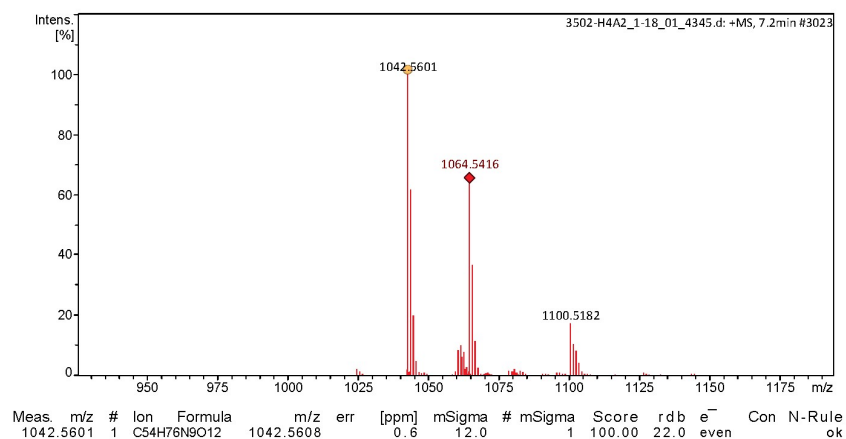


Figure S22. ¹H NMR spectrum of rufomycin 7 in CD₃OD at 600 MHz

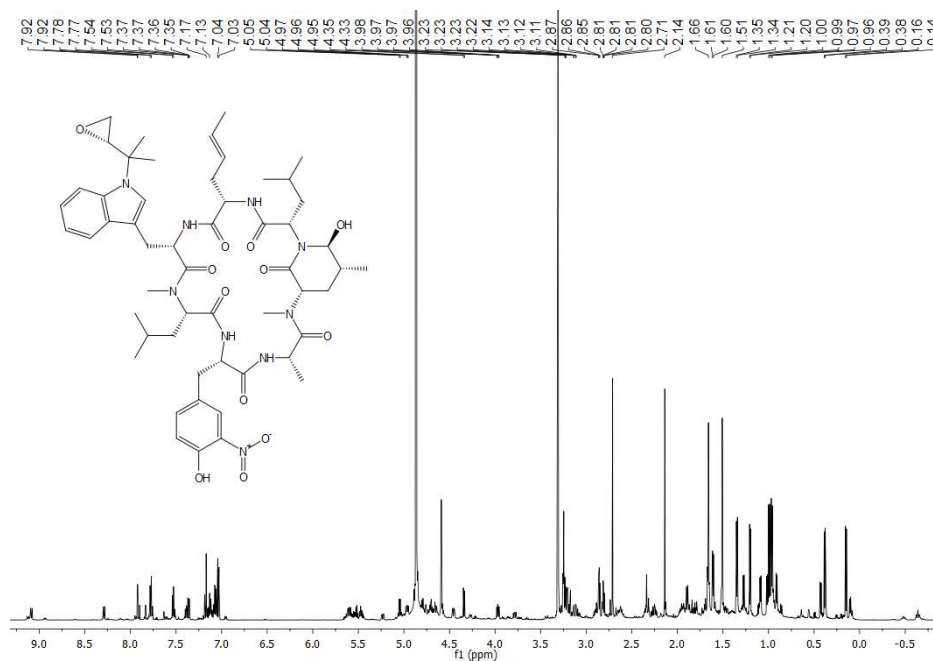


Figure S22-1. Selected ¹H NMR peak of rufomycin 7

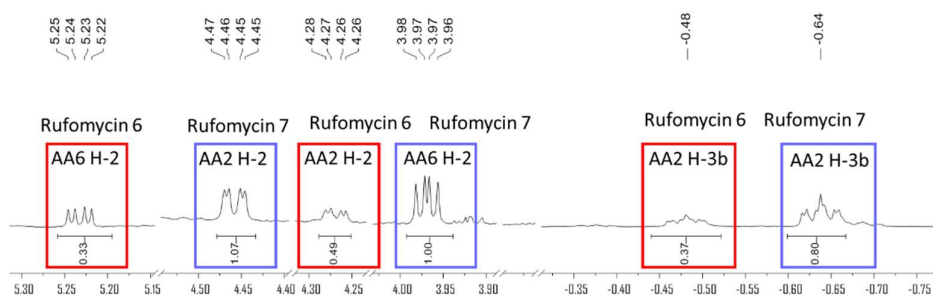


Figure S23. ^{13}C NMR spectrum of rufomycin 7 in CD_3OD at 150 MHz

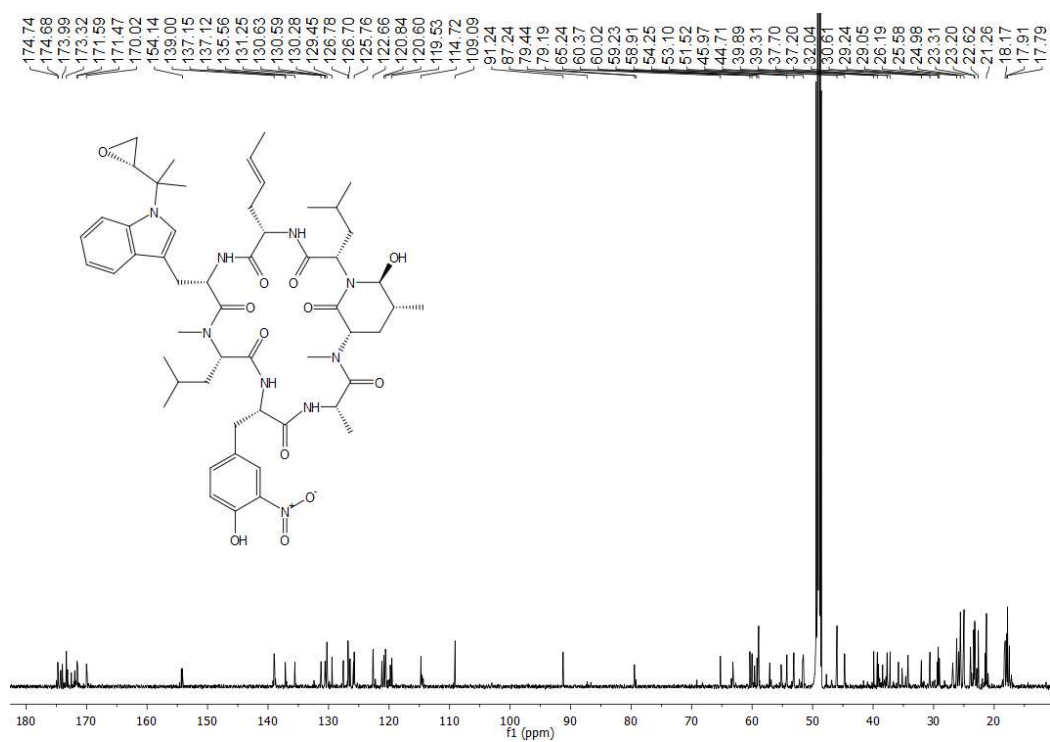


Figure S24. TOCSY spectrum of rufomycin 7 in CD_3OD (400 MHz)

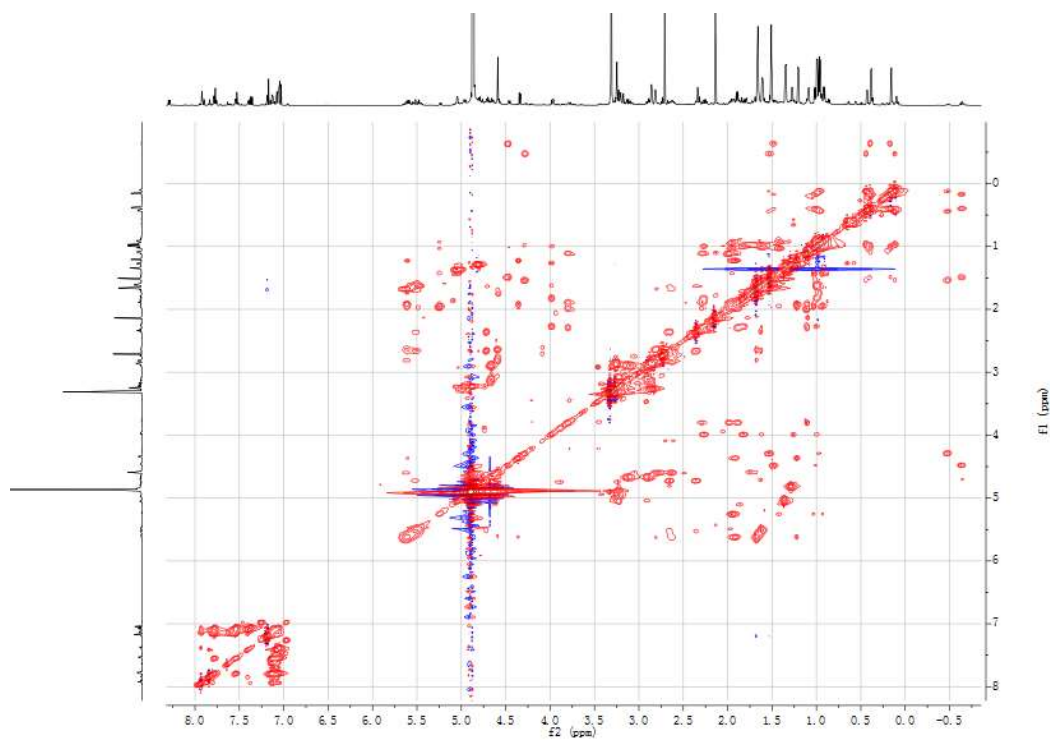


Figure S25. HSQC spectrum of rufomycin 7 in CD₃OD (400 MHz, ¹H)

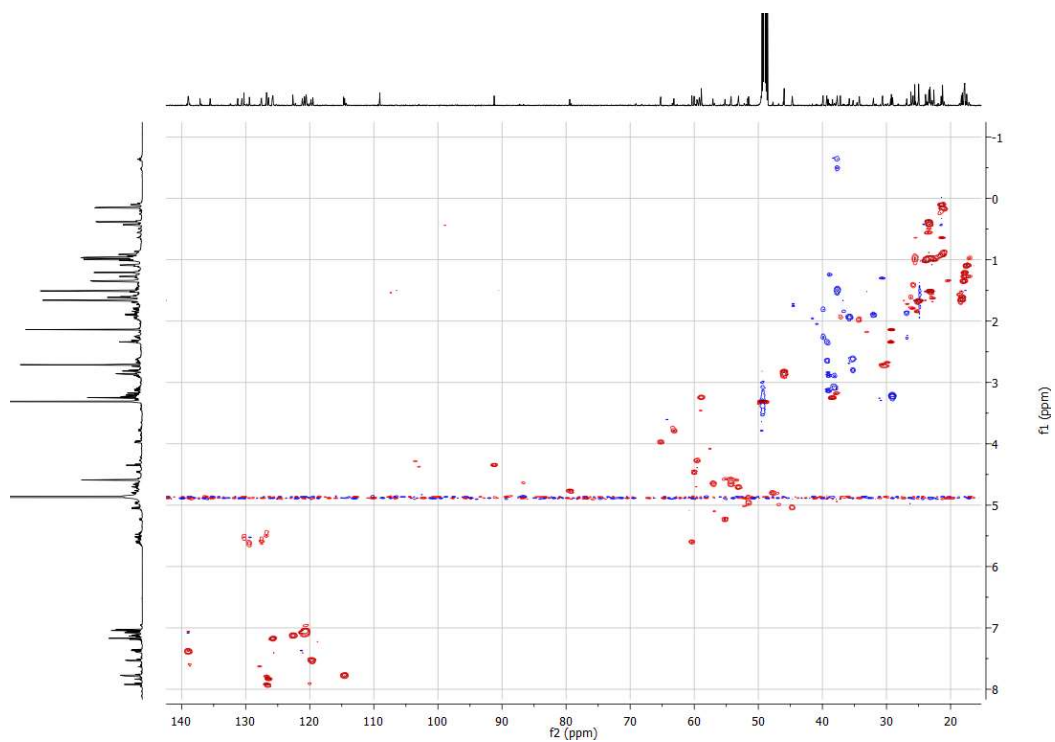


Figure S26. HMBC spectrum of rufomycin 7 in CD₃OD (400 MHz, ¹H)

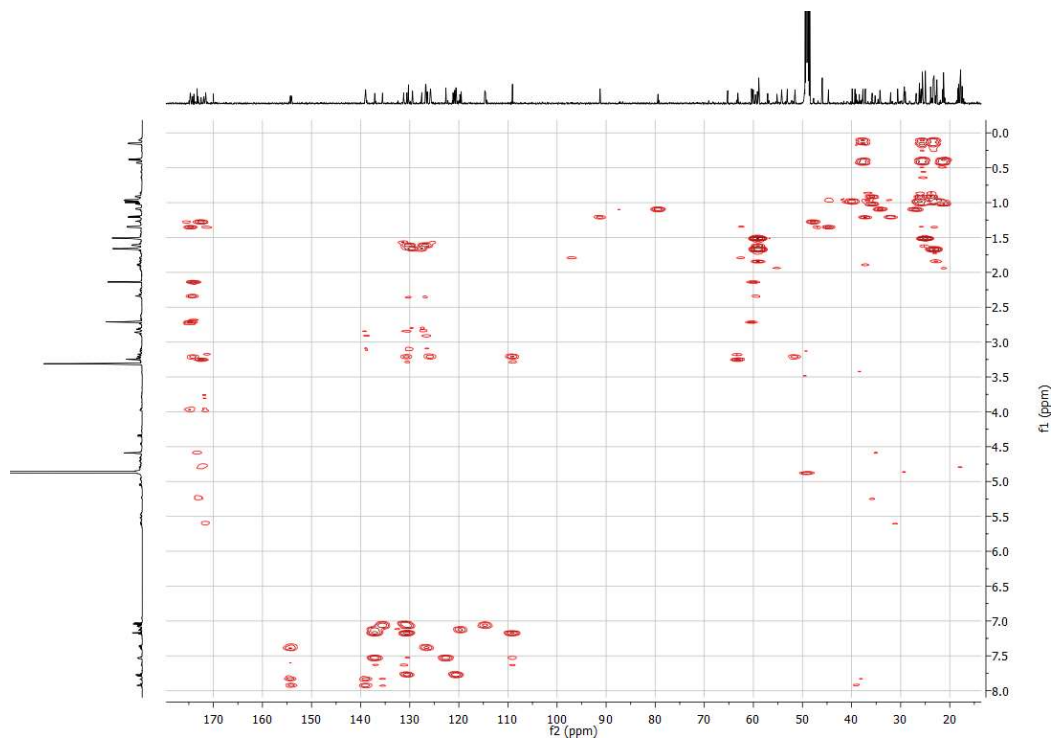


Figure S27. ROESY spectrum of rufomycin 7 in CD₃OD

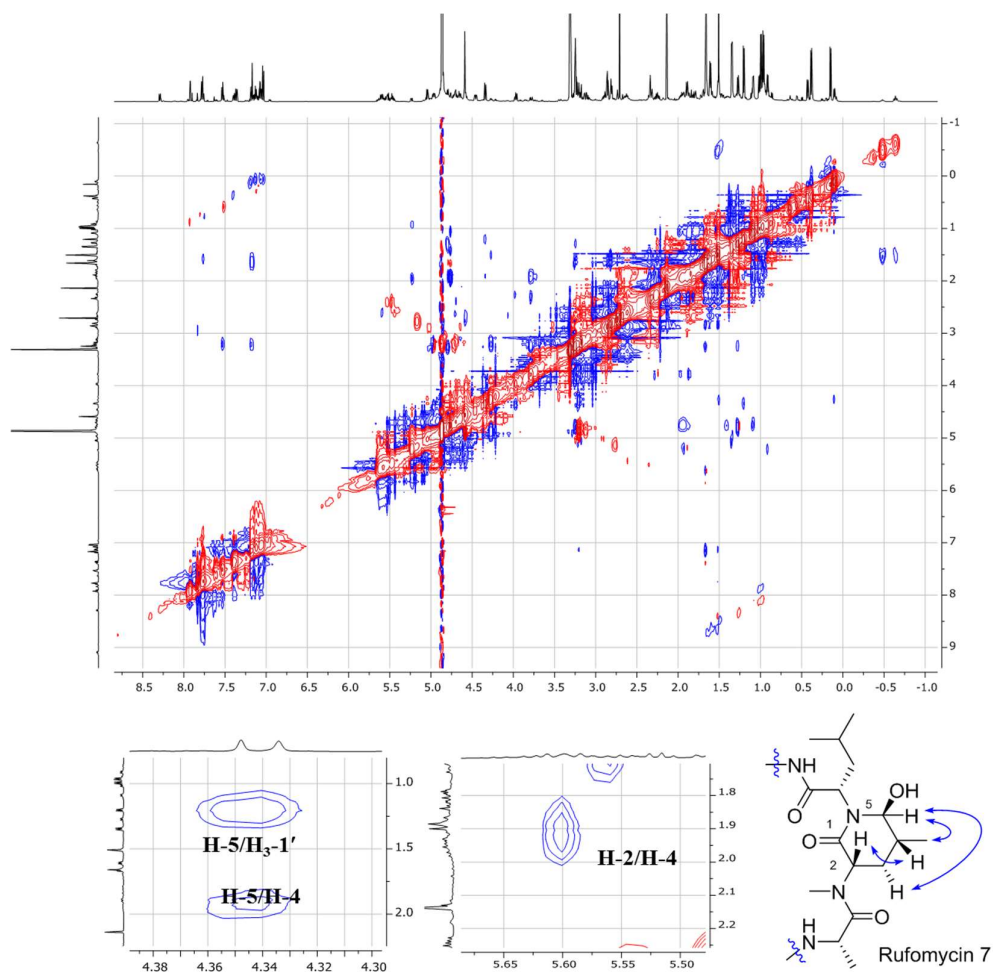


Figure S28. HRMS (ESI) spectrum of rufomycin 7

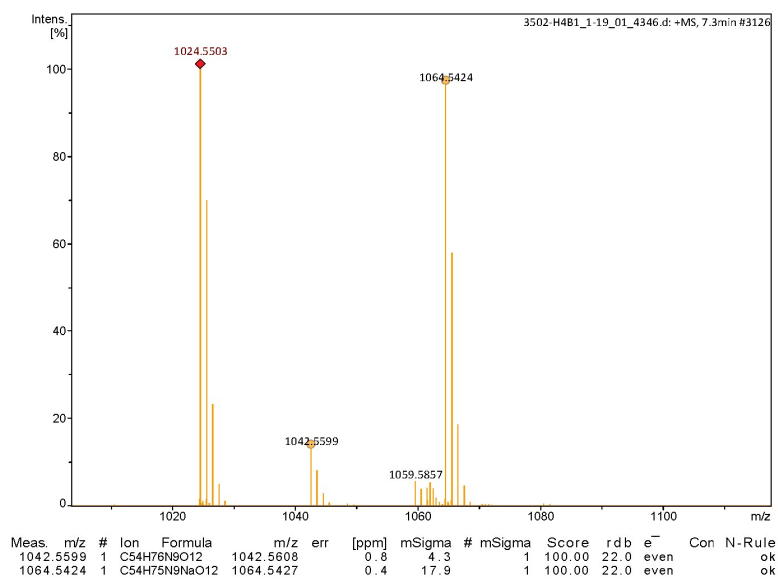


Figure S29. ^1H NMR spectrum of rufomycinSS 1 in CD_3OD at 600 MHz

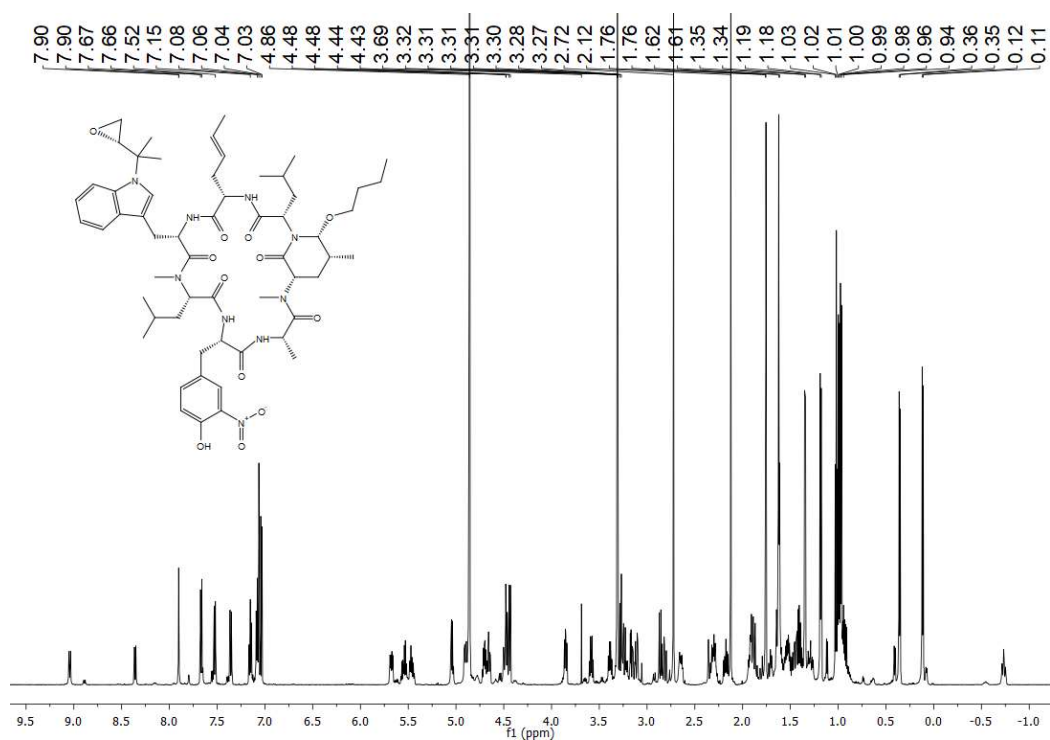


Figure S30. ^{13}C NMR spectrum of rufomycinSS 1 in CD_3OD at 150 MHz

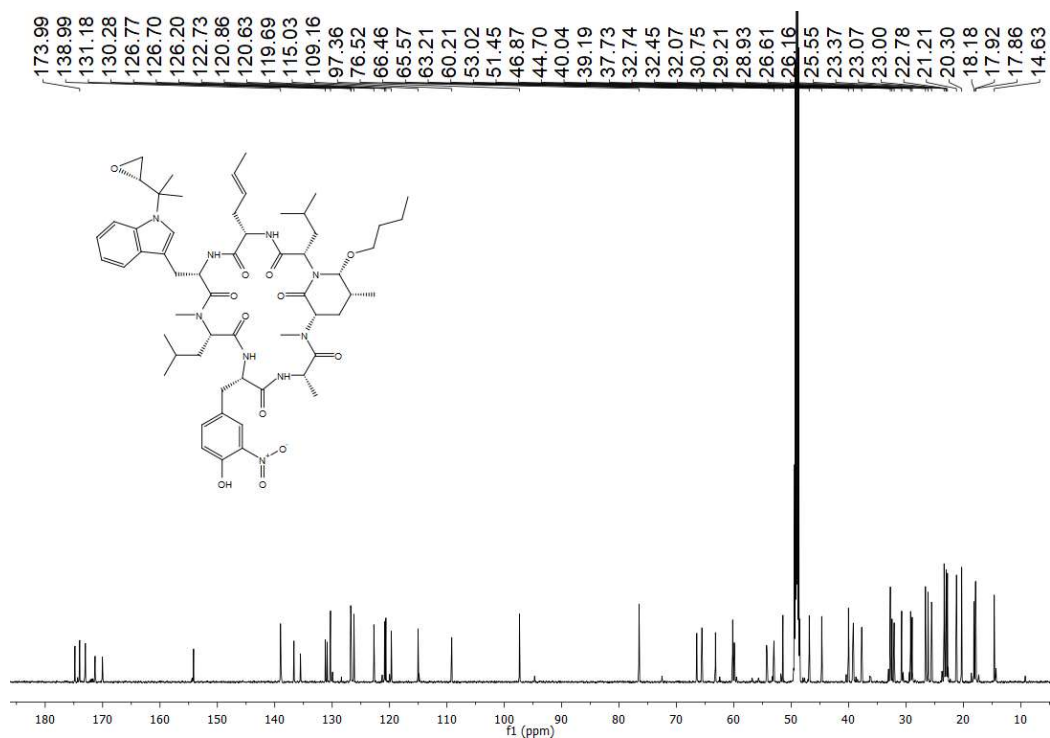


Figure S31. TOCSY spectrum of rufomycinSS 1 in CD₃OD

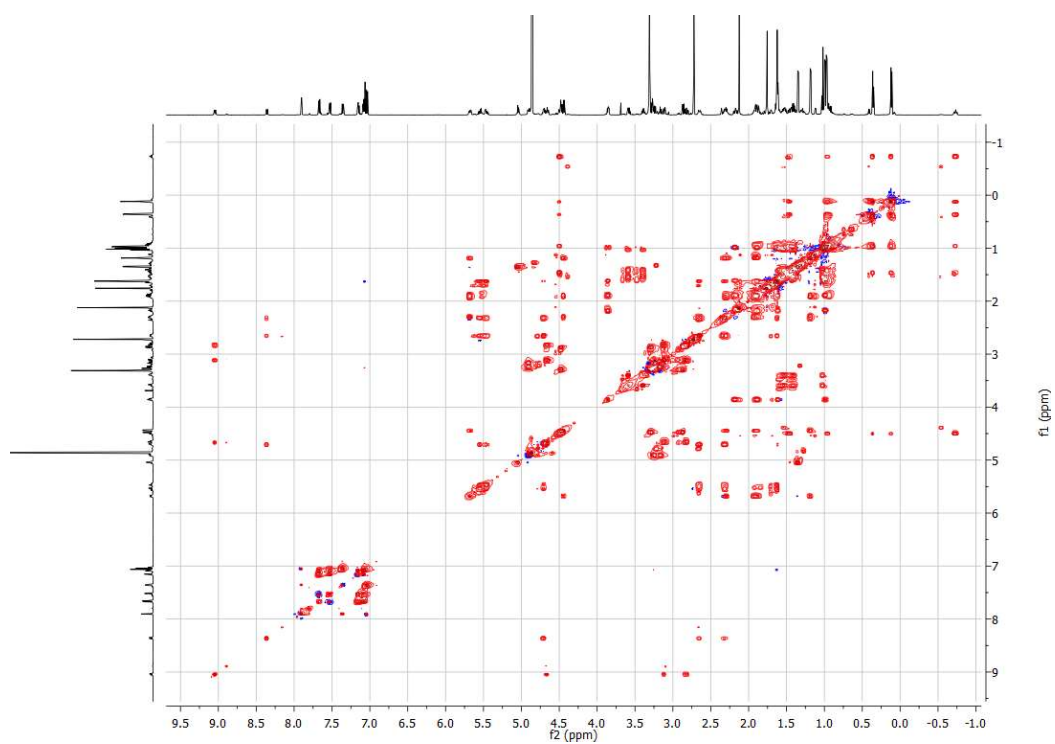


Figure S32. HSQC spectrum of rufomycinSS 1 in CD₃OD

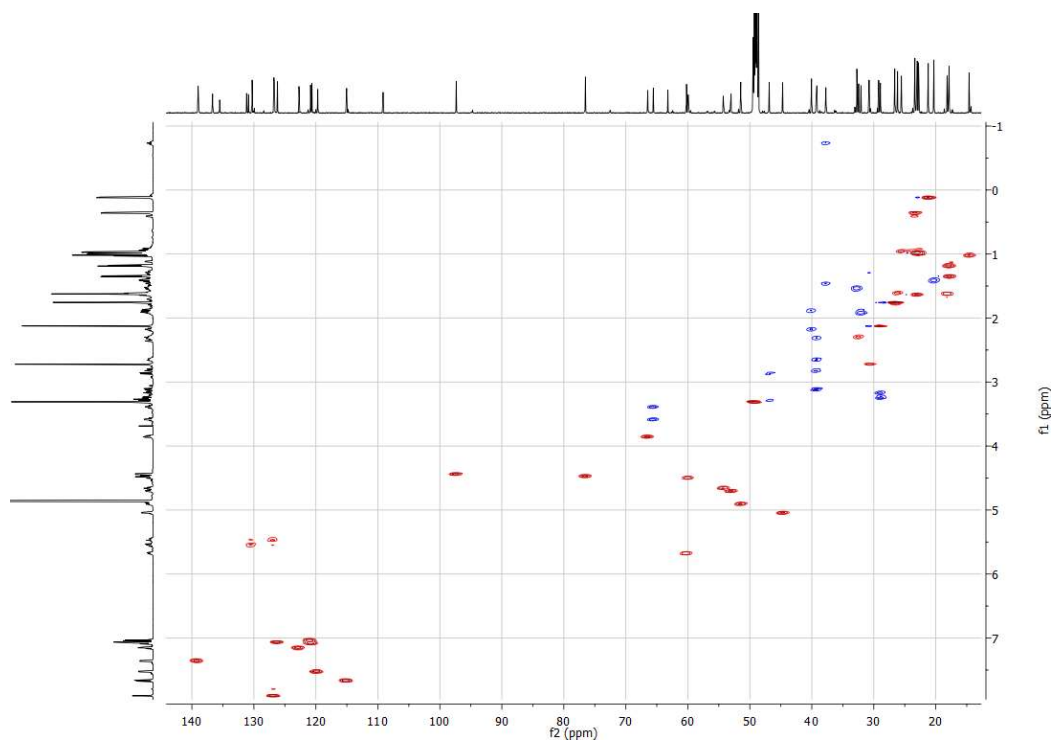


Figure S33. HMBC spectrum of rufomycinSS 1 in CD₃OD

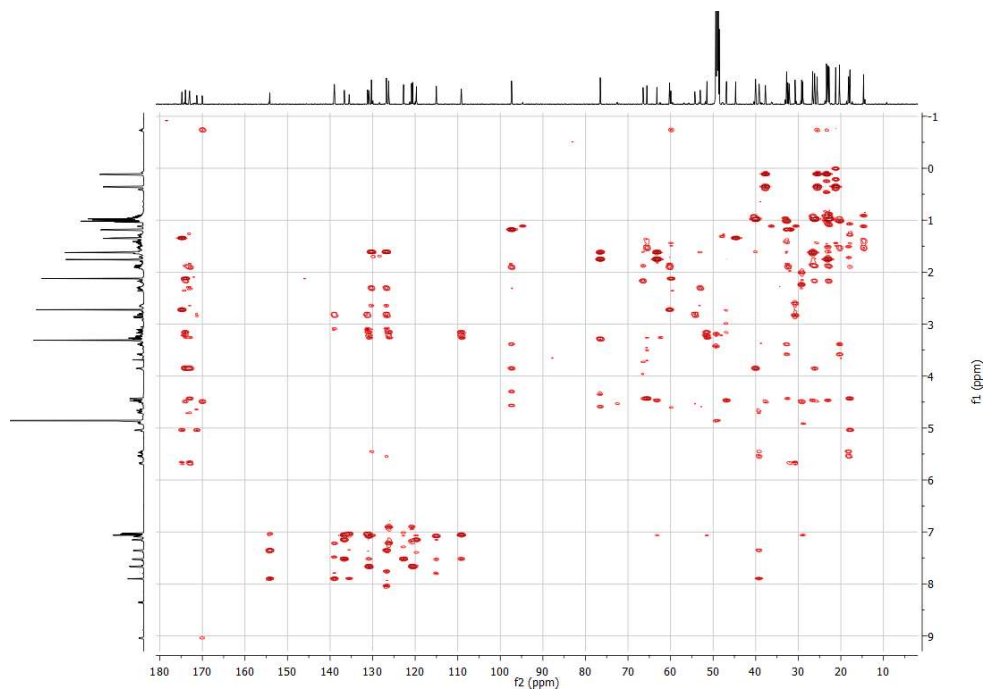


Figure S34. ROESY spectrum of rufomycinSS 1 in CD₃OD

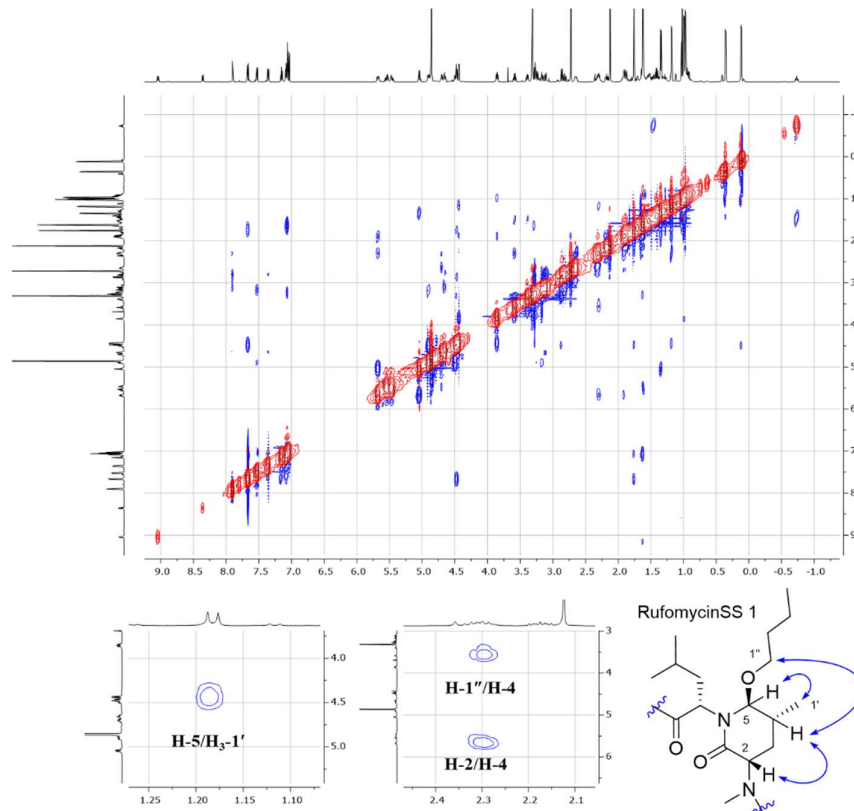


Figure S35. HRMS (ESI) spectrum of rufomycinSS 1

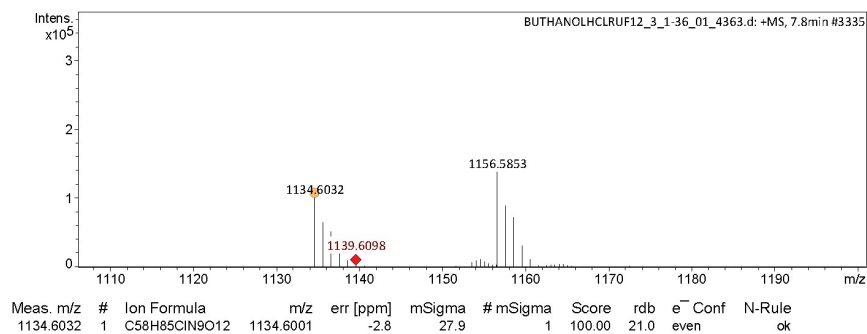


Figure S36. ¹H NMR spectrum of rufomycinSS 2 in CD₃OD at 600 MHz

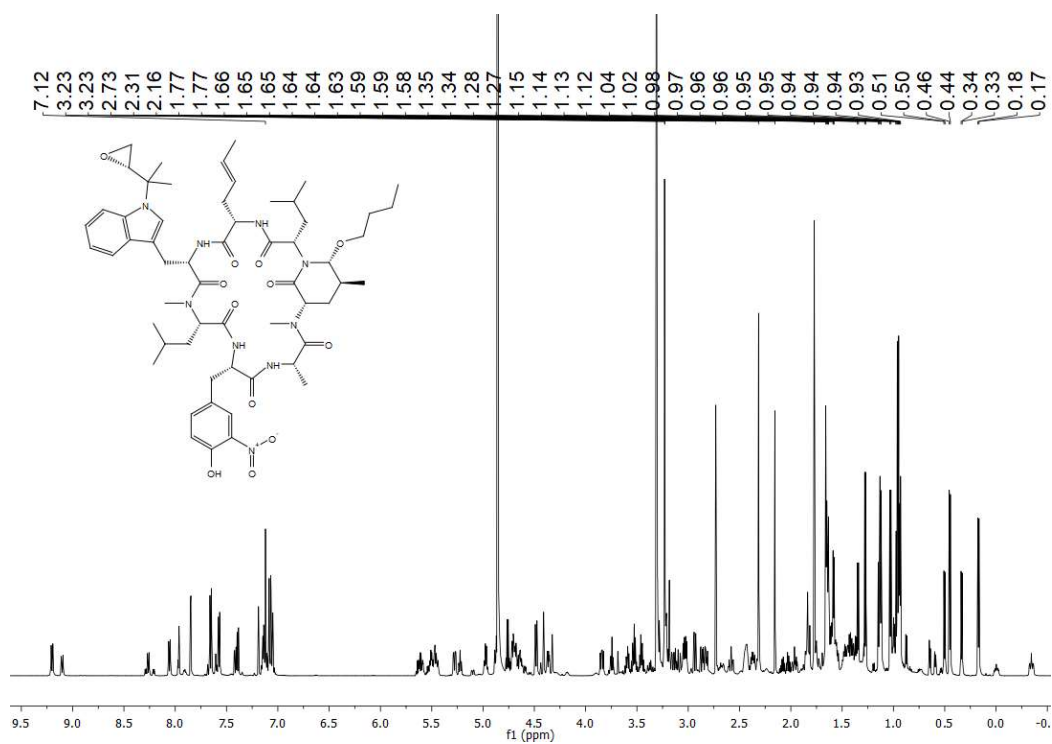


Figure S37. ^{13}C NMR spectrum of rufomycinSS 2 in CD_3OD at 150 MHz

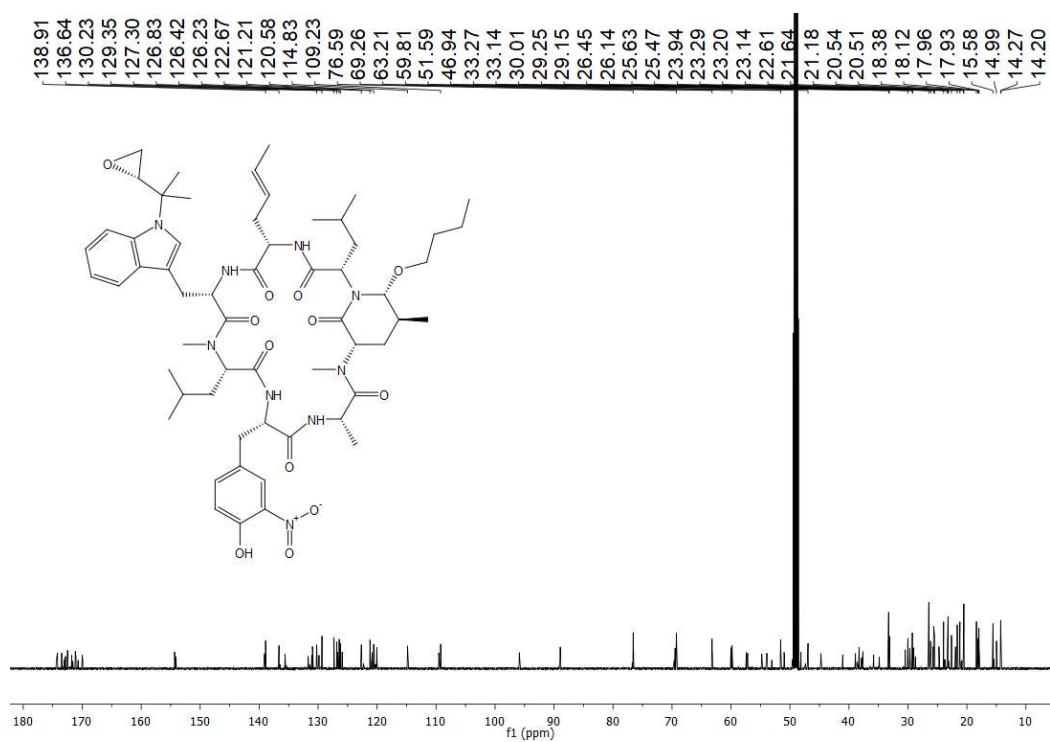


Figure S38. TOCSY NMR spectrum of rufomycinSS 2 in CD_3OD

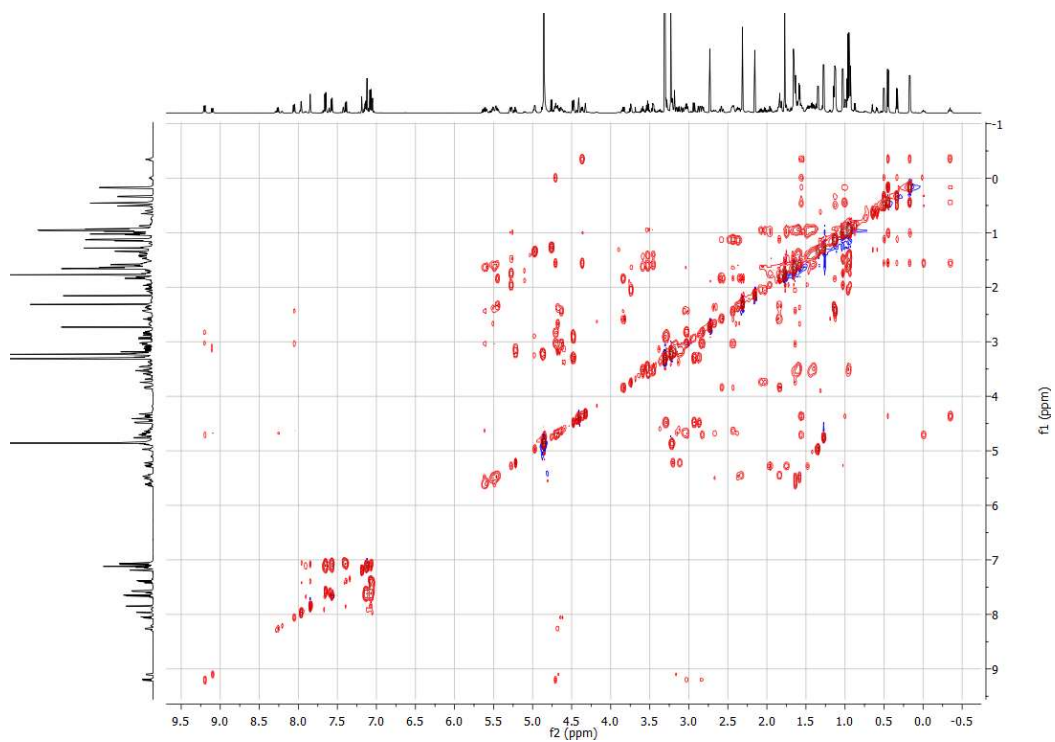


Figure S39. HSQC spectrum of rufomycinSS 2 in CD₃OD

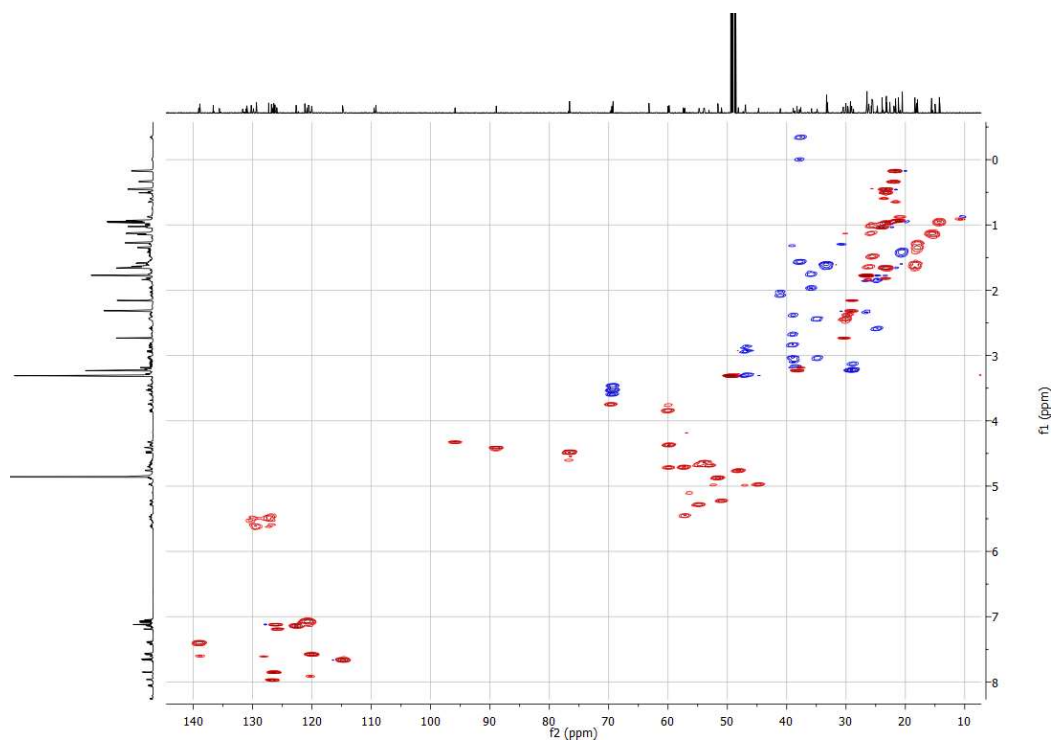


Figure S40. HMBC spectrum of rufomycinSS 2 in CD₃OD

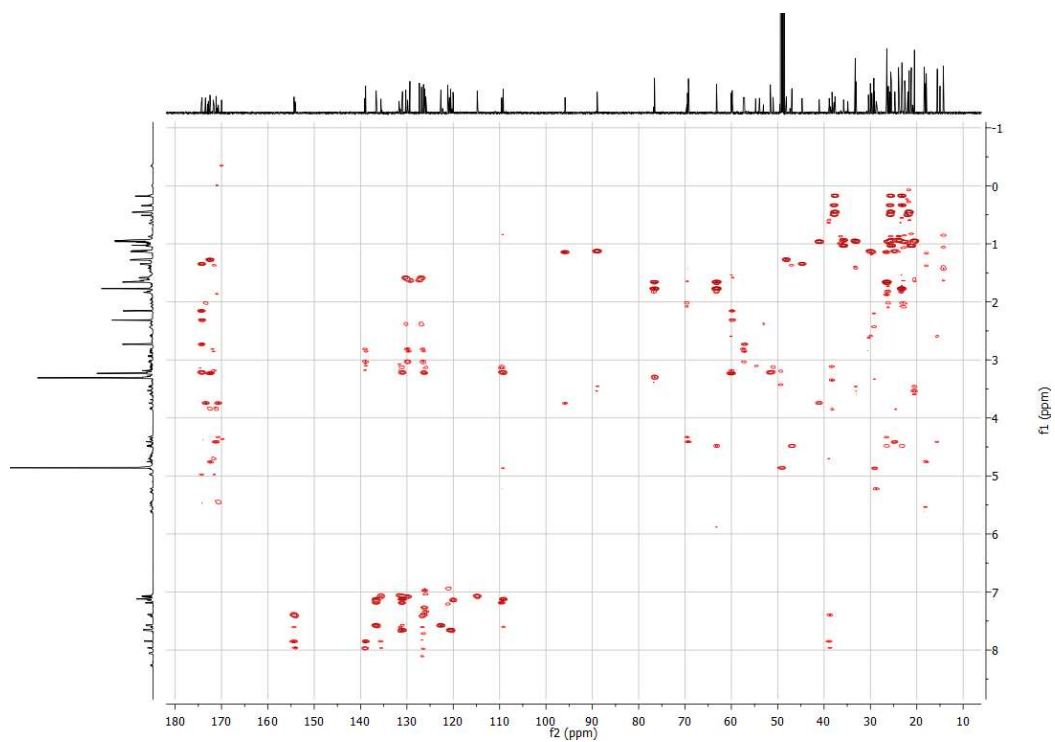


Figure S41. ROESY spectrum of rufomycinSS 2 in CD₃OD

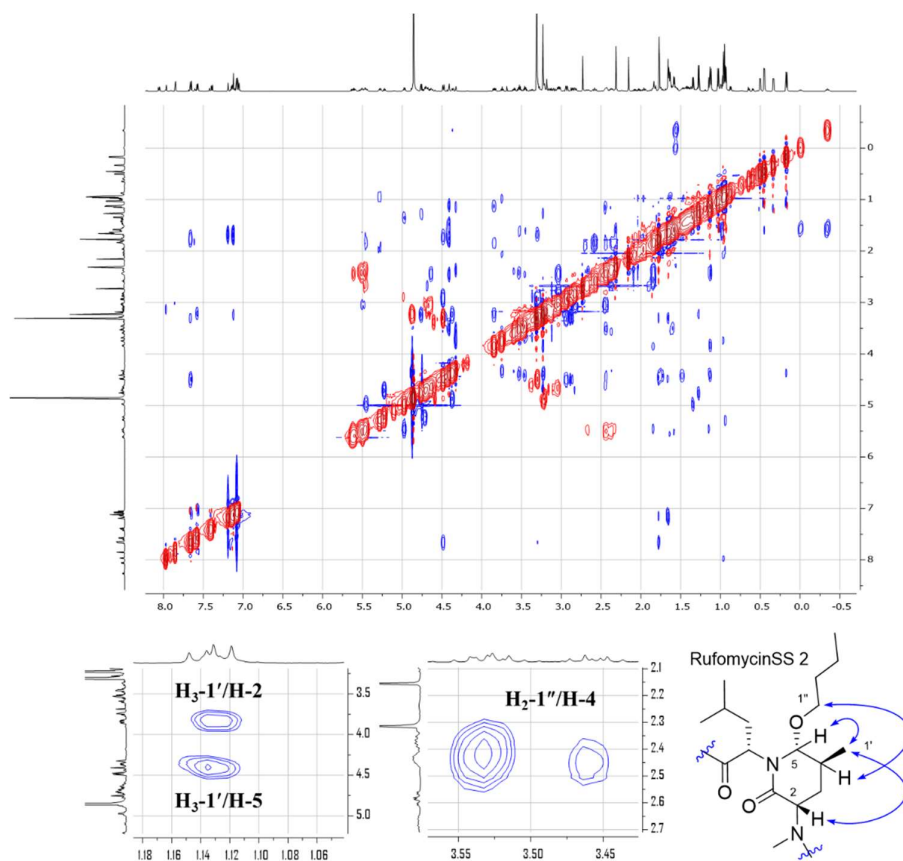


Figure S42. HRMS (ESI) spectrum of rufomycinSS 2

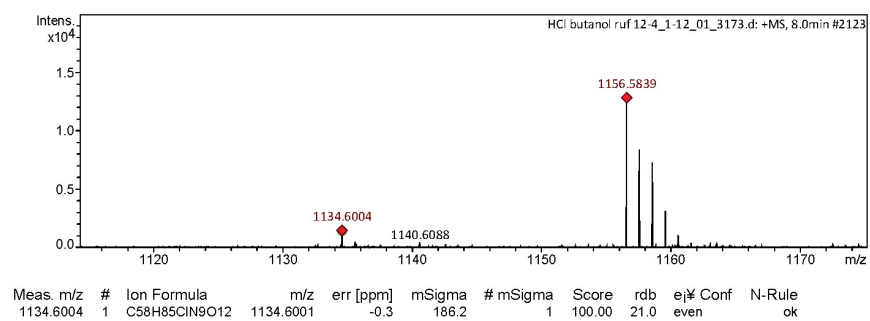


Figure S43. ^1H NMR spectrum of rufomycinSS 3 in CD_3OD at 600 MHz

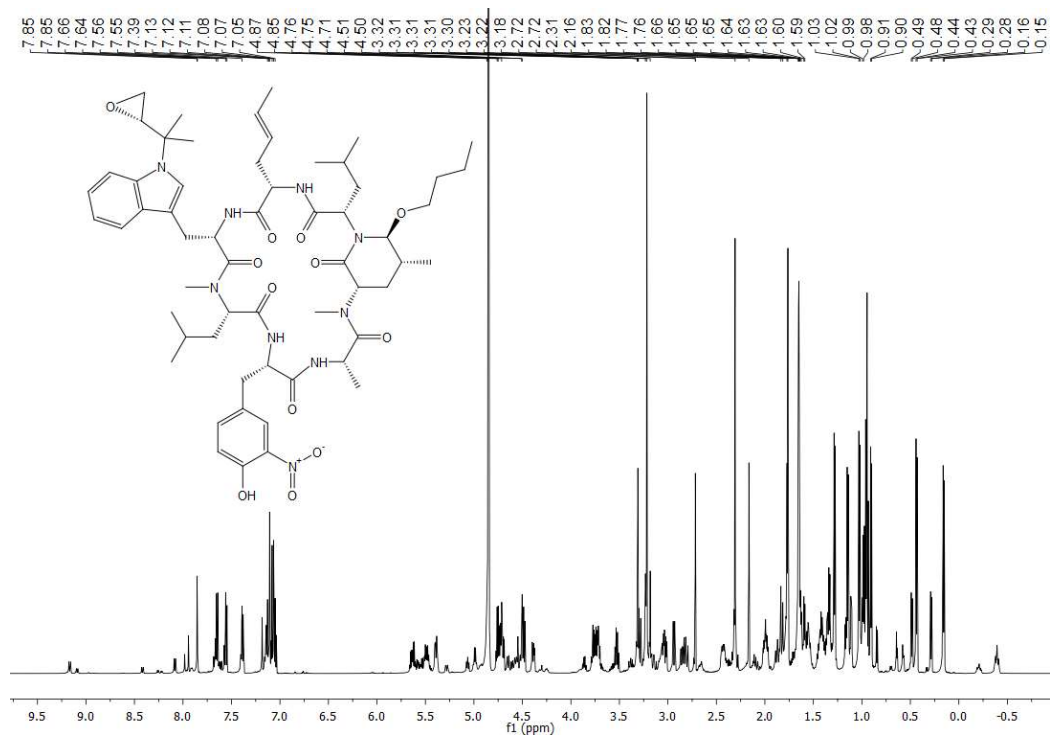


Figure S44. ^{13}C NMR spectrum of rufomycinSS 3 in CD_3OD at 150 MHz

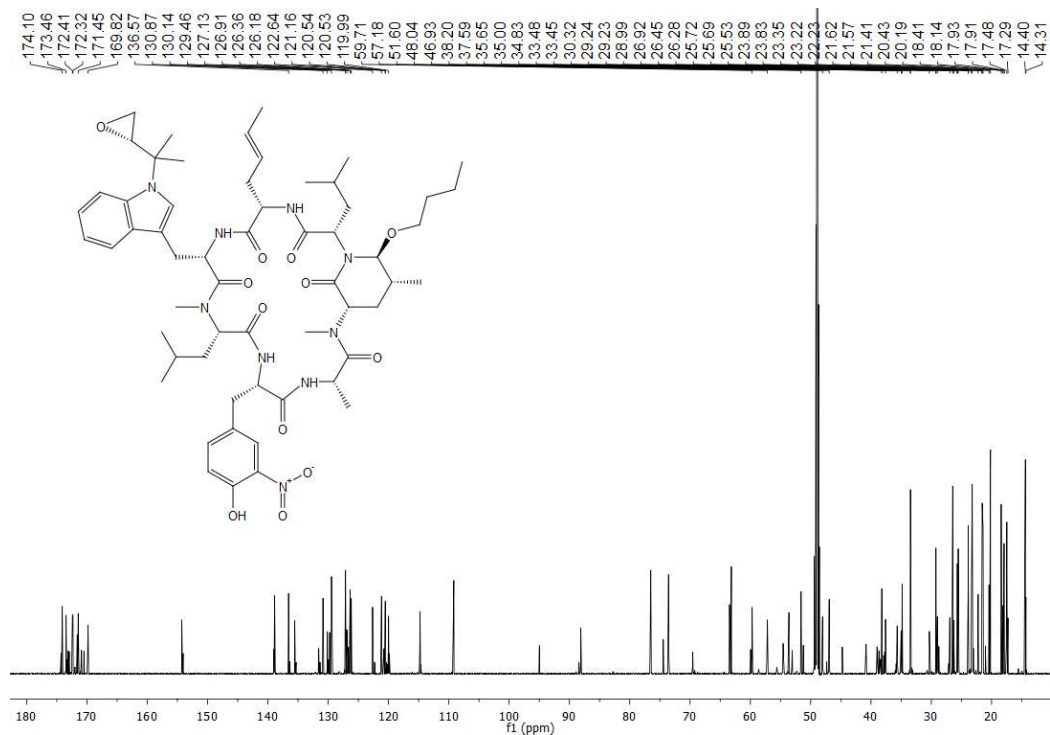


Figure S45. TOCSY NMR spectrum of rufomycinSS 3 in CD₃OD

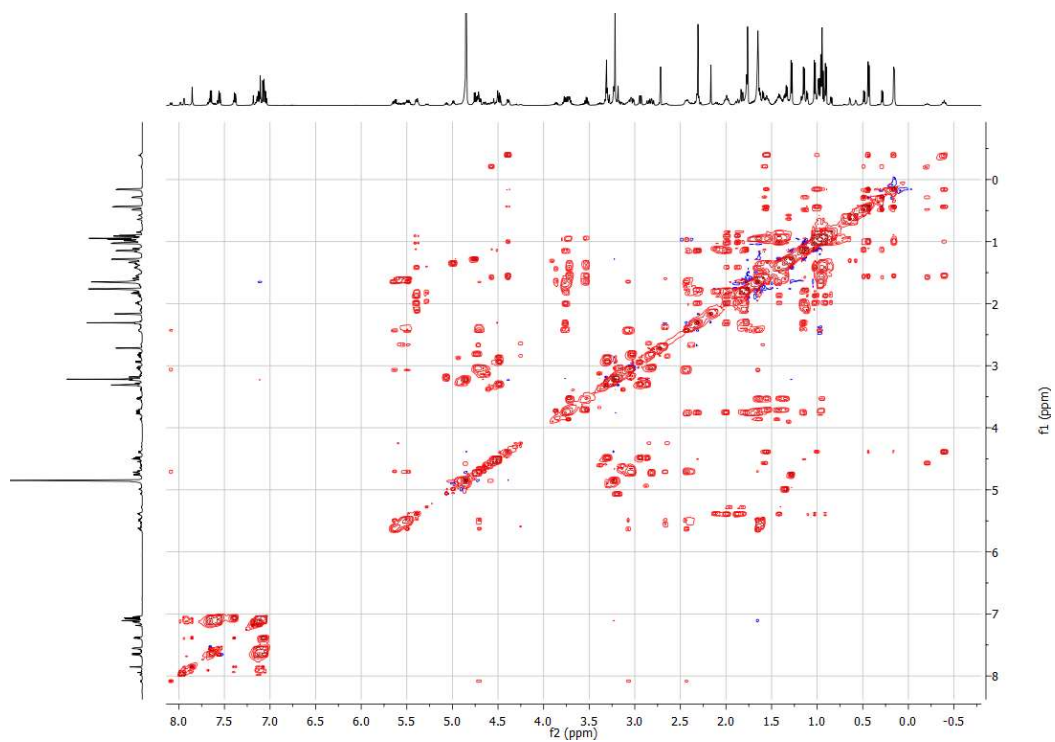


Figure S46. HSQC spectrum of rufomycinSS 3 in CD₃OD

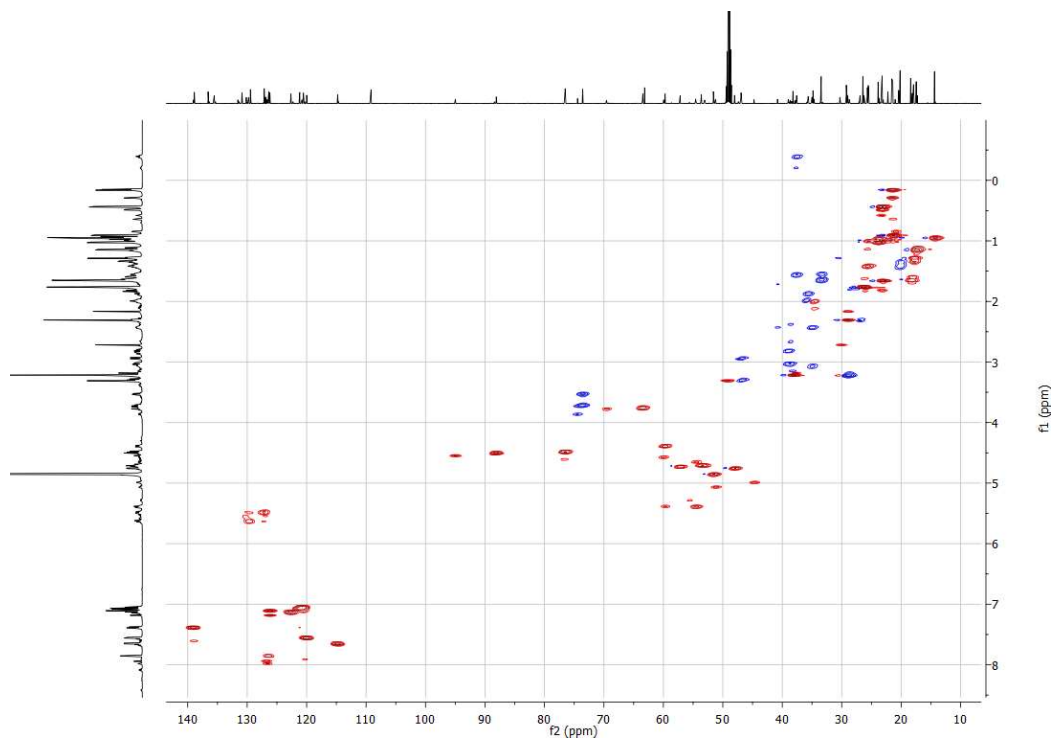


Figure S47. HMBC spectrum of rufomycinSS 3 in CD₃OD

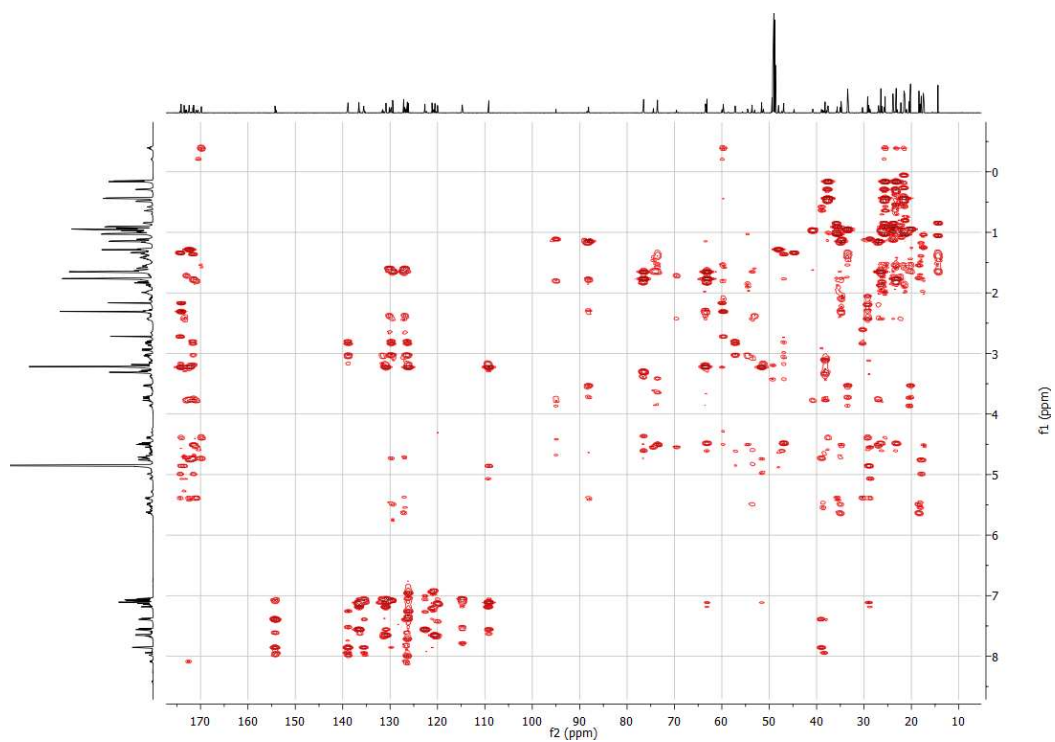


Figure S48. HRMS (ESI) spectrum of rufomycinSS 3

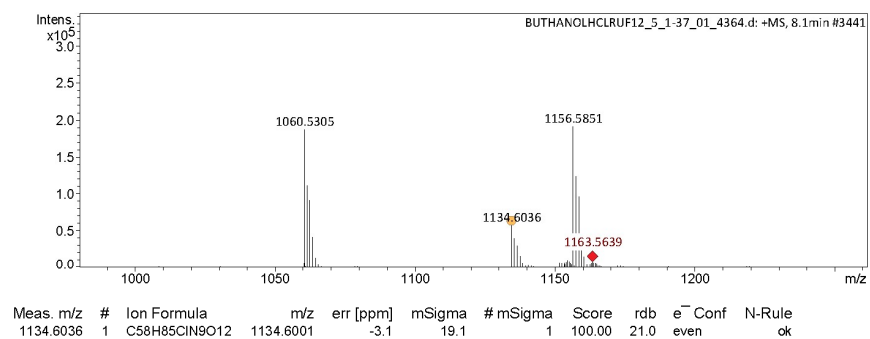


Figure S49. ROESY spectrum of rufomycinSS 3 in CD₃OD

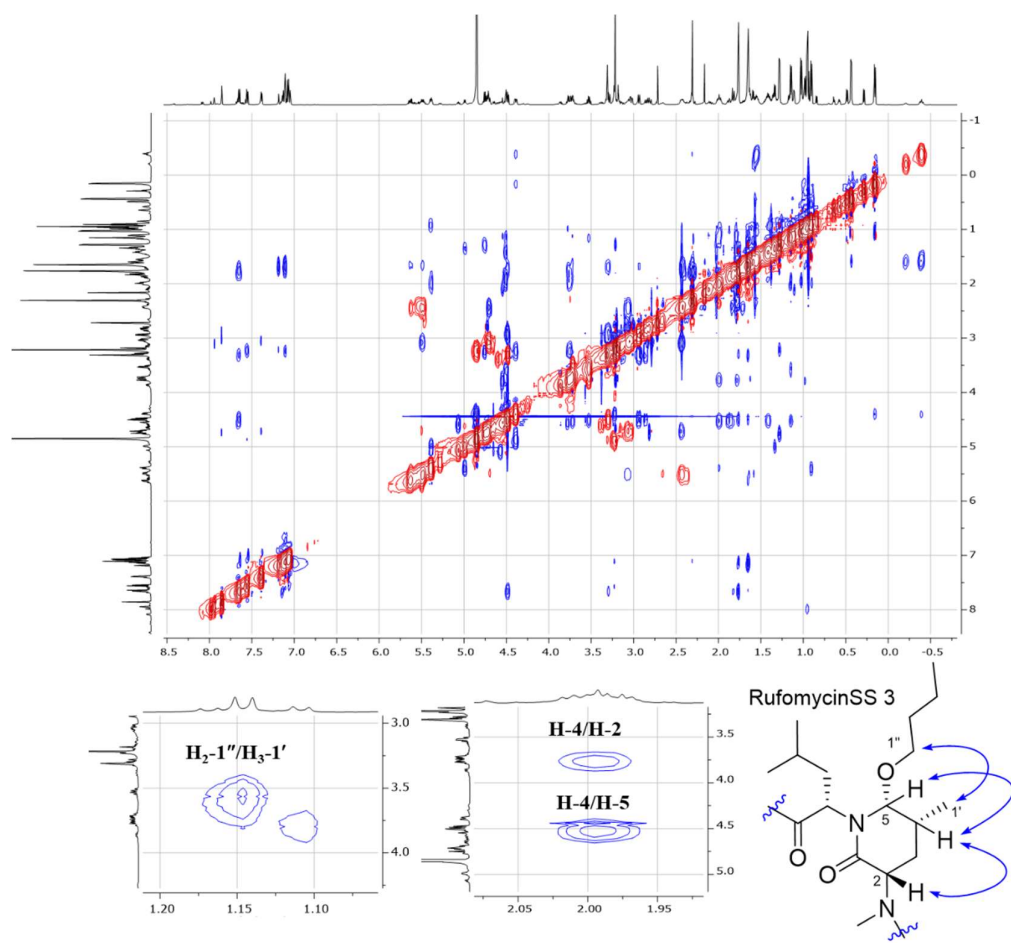


Figure S50. Selected HSQC data of rufomycins 6 and 7

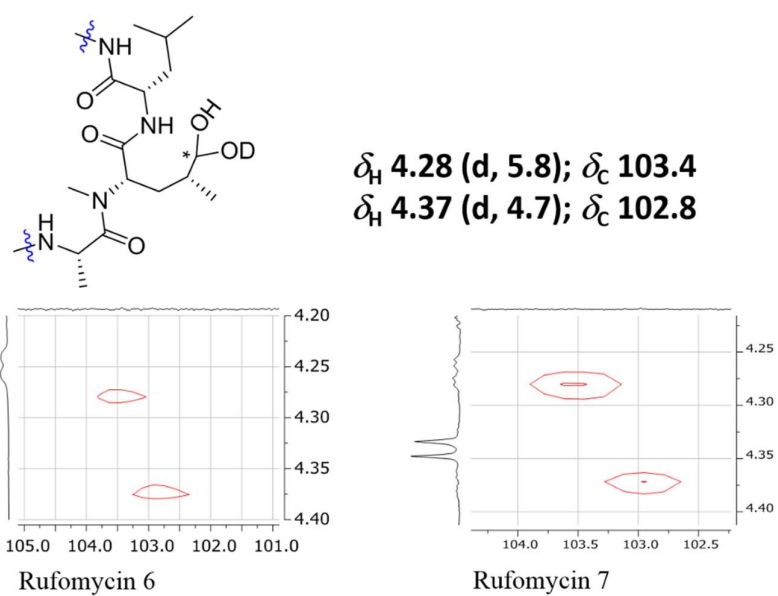


Figure S51. ^1H NMR spectrum of rufomycin 21 in CD_3OD at 400 MHz

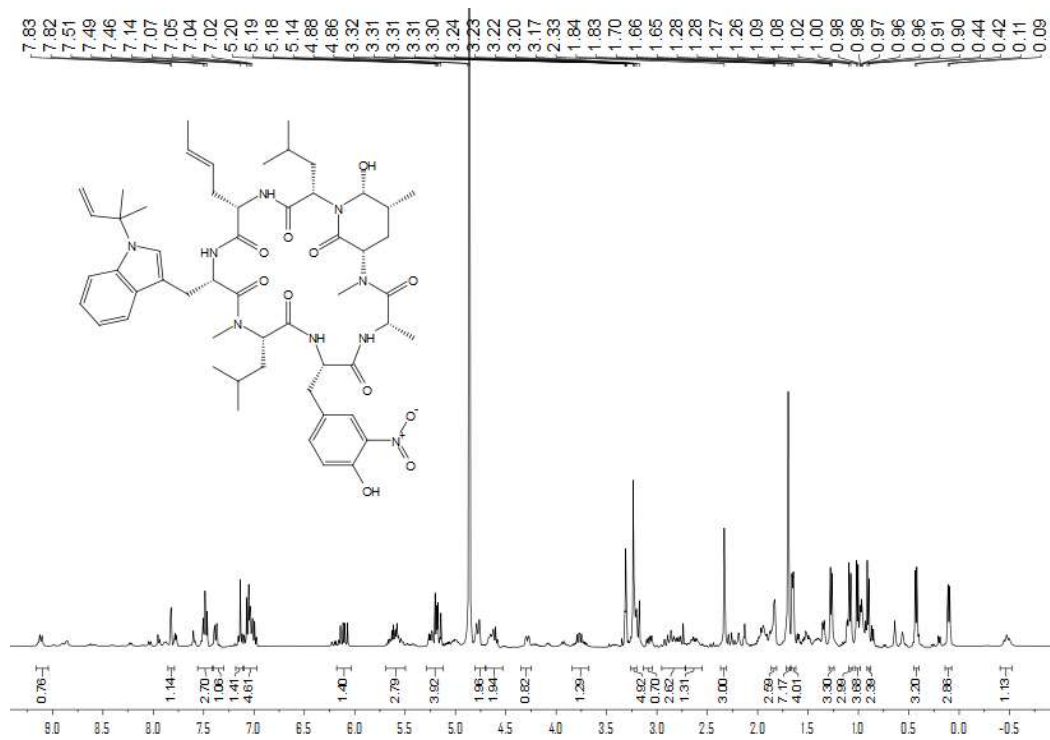


Figure S52. ^{13}C NMR spectrum of rufomycin 21 in CD_3OD at 100 MHz

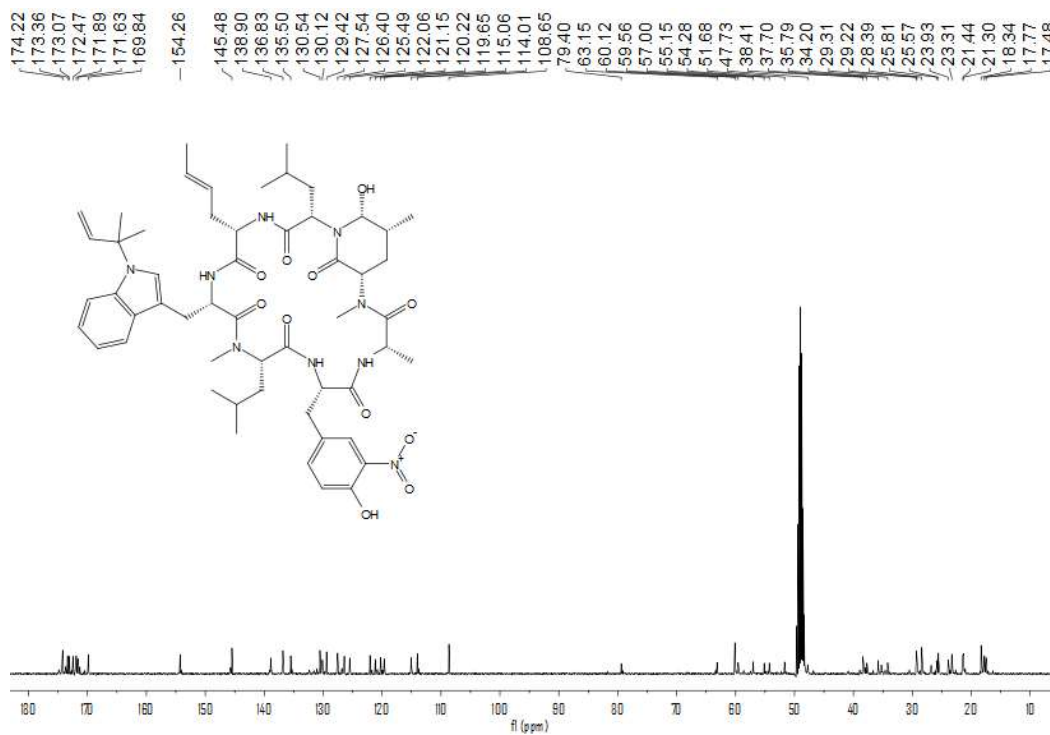


Figure S53. TOCSY NMR spectrum of rufomycin 21 in CD₃OD

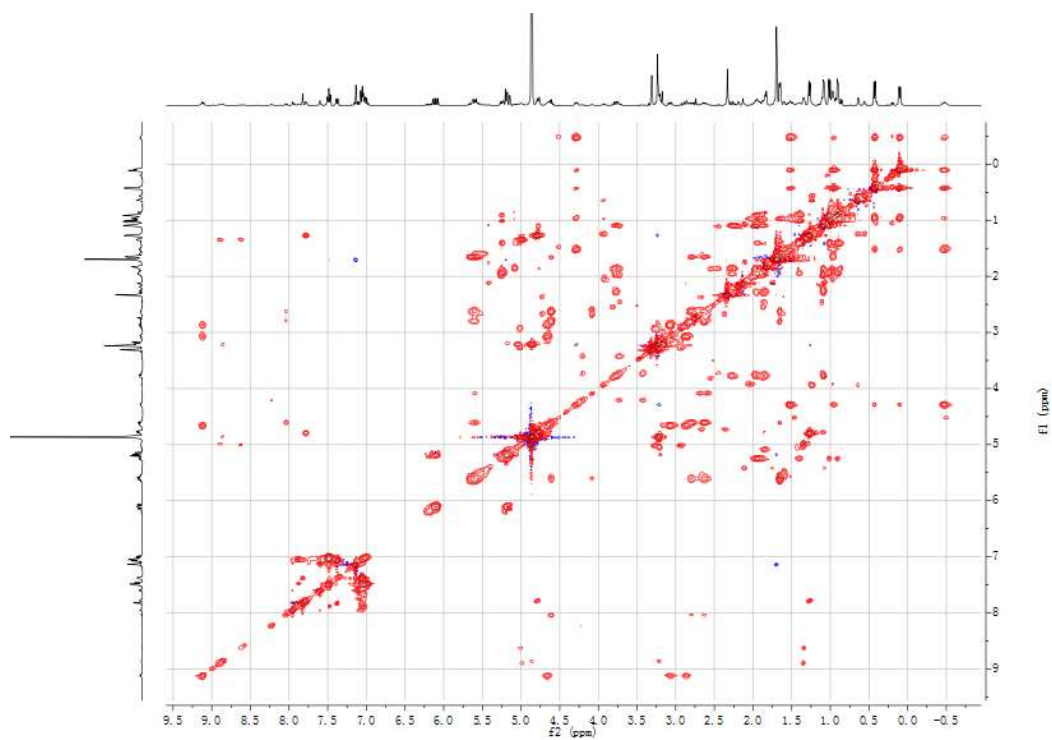


Figure S54. HSQC spectrum of rufomycin 21 in CD₃OD

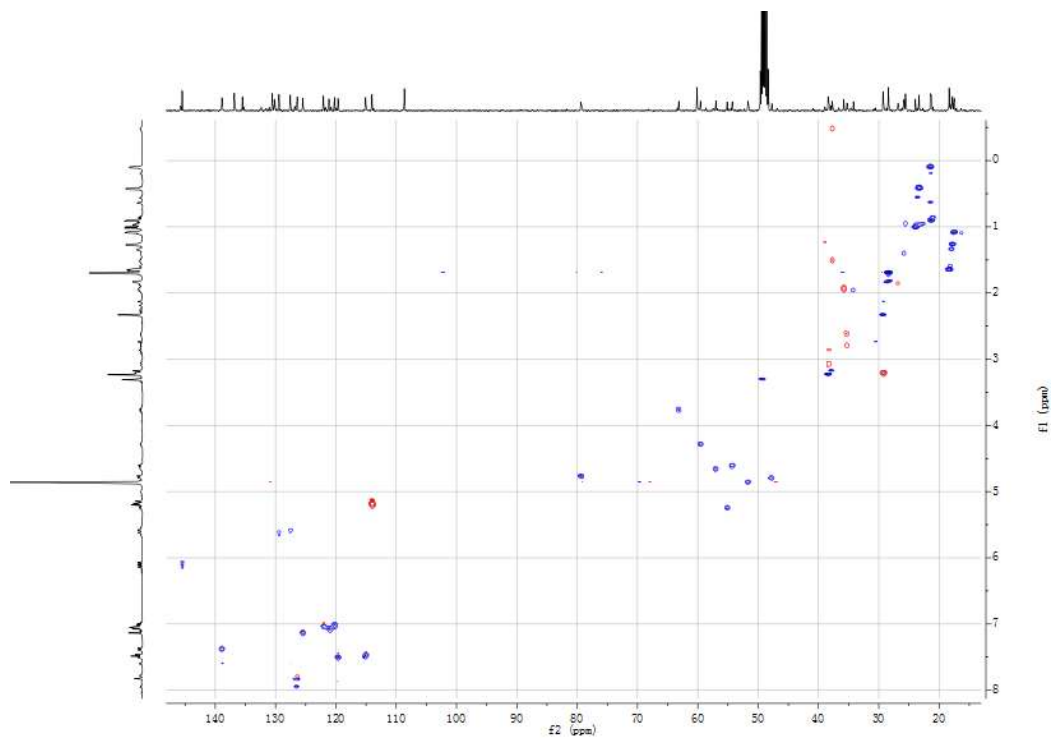


Figure S55. HMBC spectrum of rufomycin 21 in CD₃OD

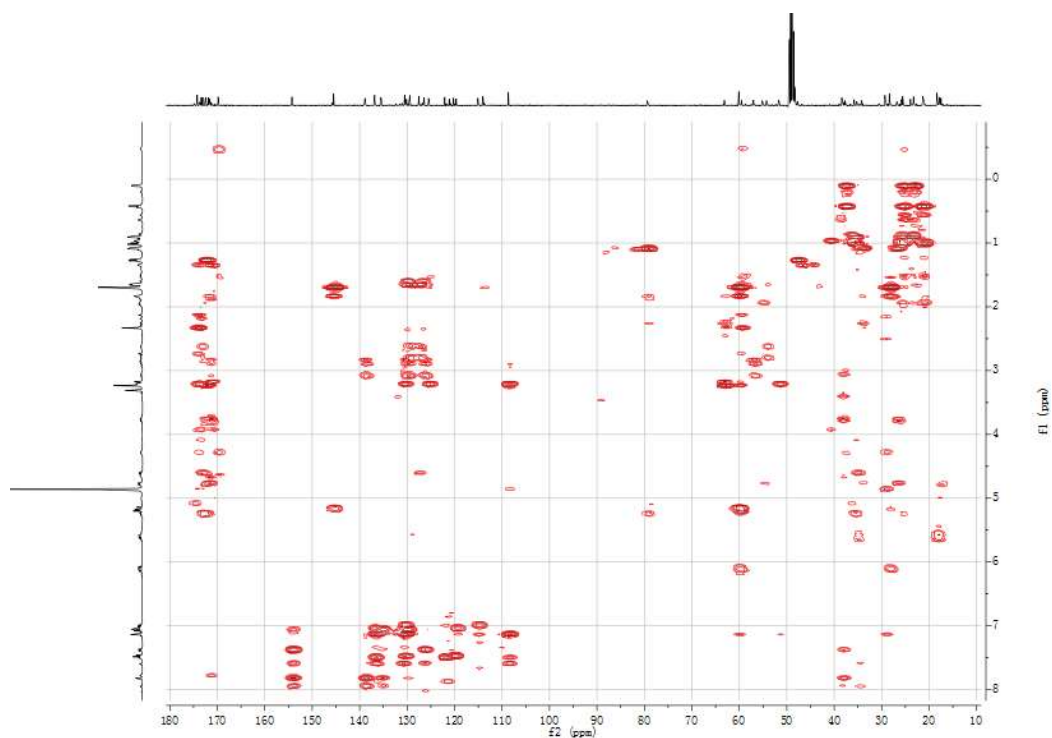


Figure S56. HRMS (ESI) spectrum of rufomycin 21

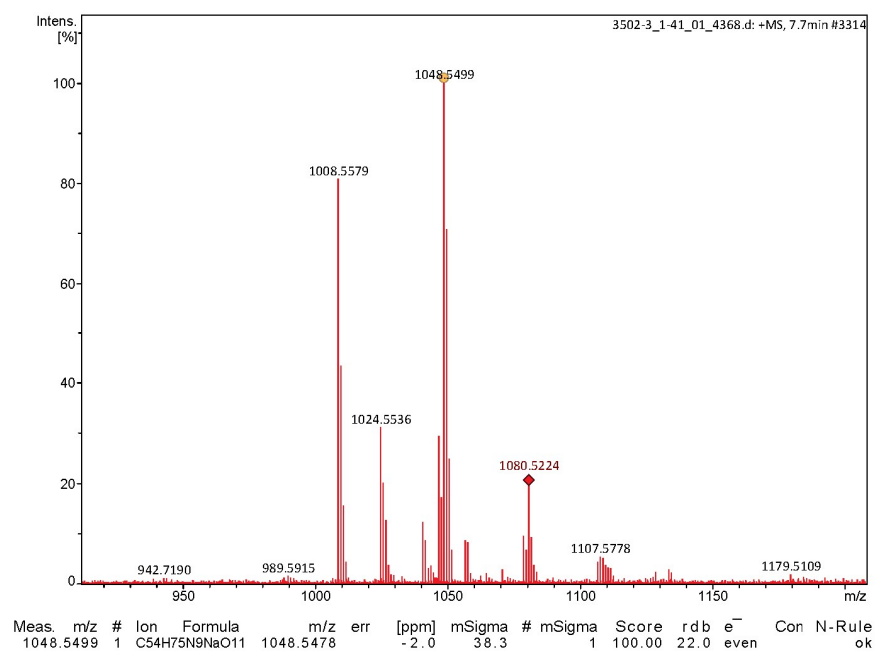


Figure S57. NOESY spectrum of rufomycin 21 in CD₃OD

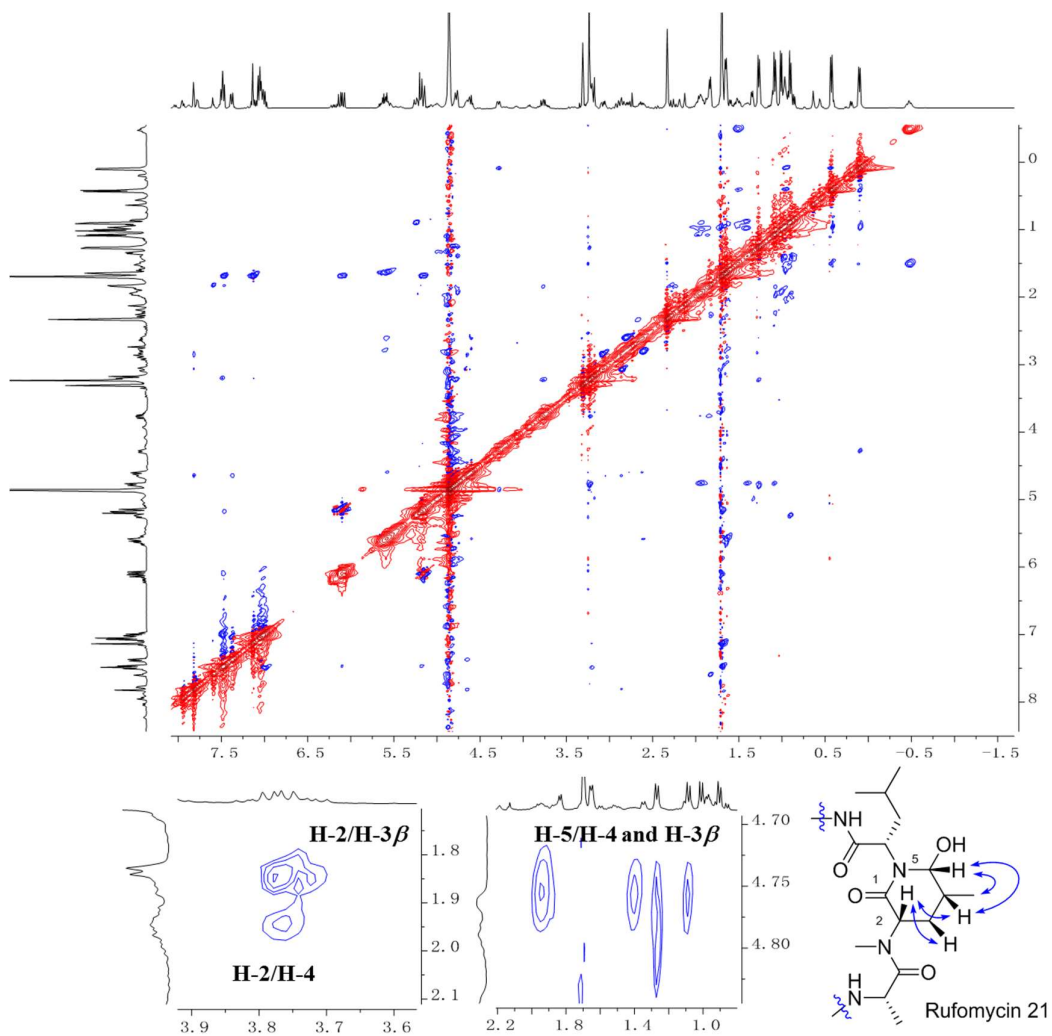
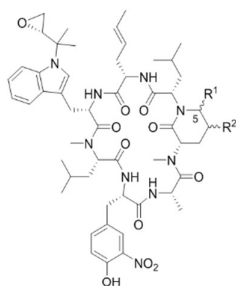


Chart S2. Structure verification of ilamycin E1 and E2

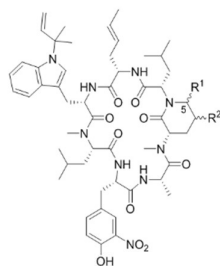


Rufomycin 4 $R^1 = \alpha\text{-OH}$; $R^2 = \beta\text{-CH}_3$
CH-5 δ_C 81.7 and δ_H 4.76, brd, $J = 3.7$ Hz

Rufomycin 5 $R^1 = \beta\text{-OH}$; $R^2 = \beta\text{-CH}_3$
CH-5 δ_C 82.5 and δ_H 4.63, brd, $J = 2.6$ Hz

Rufomycin 6 $R^1 = \alpha\text{-OH}$; $R^2 = \alpha\text{-CH}_3$
CH-5 δ_C 79.4 and δ_H 4.76, brd, $J = 2.1$ Hz

Rufomycin 7 $R^1 = \beta\text{-OH}$; $R^2 = \alpha\text{-CH}_3$
CH-5 δ_C 91.2 and δ_H 4.34, brd, $J = 7.9$ Hz



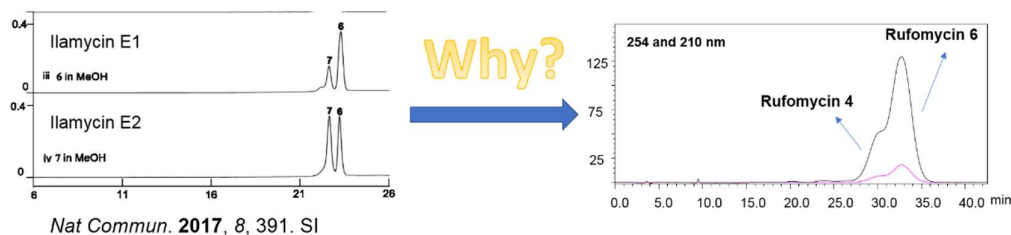
Rufomycin 21=Ilamycin E1 ($R^1 = \alpha\text{-OH}$; $R^2 = \beta\text{-CH}_3$)

CH-5 δ_C 79.4 and δ_H 4.76, brd, $J = 2.6$ Hz
 To be $R^1 = \alpha\text{-OH}$; $R^2 = \alpha\text{-CH}_3$

Ilamycin E2 ($R^1 = \beta\text{-OH}$; $R^2 = \beta\text{-CH}_3$)

CH-5 δ_C 82.5 and δ_H 4.65, brd, $J = 1.6$ Hz
 To be $R^1 = \beta\text{-OH}$; $R^2 = \beta\text{-CH}_3$

Accordingly, the structure assigned to ilamycin E1 should be revised to show the (4*R*,5*R*, α -OH, α -CH₃, AA5) absolute configuration.



Based on our experiences, rufomycins 4 and 6 are hard to separate. Thus, the “peaks” for ilamycin E1, may not only contain part of the interconverted component from ilamycin E2 (4*R*,5*S*; α -OH, β -CH₃), but also contain the main component with (4*R*,5*R*; α -OH, α -CH₃)

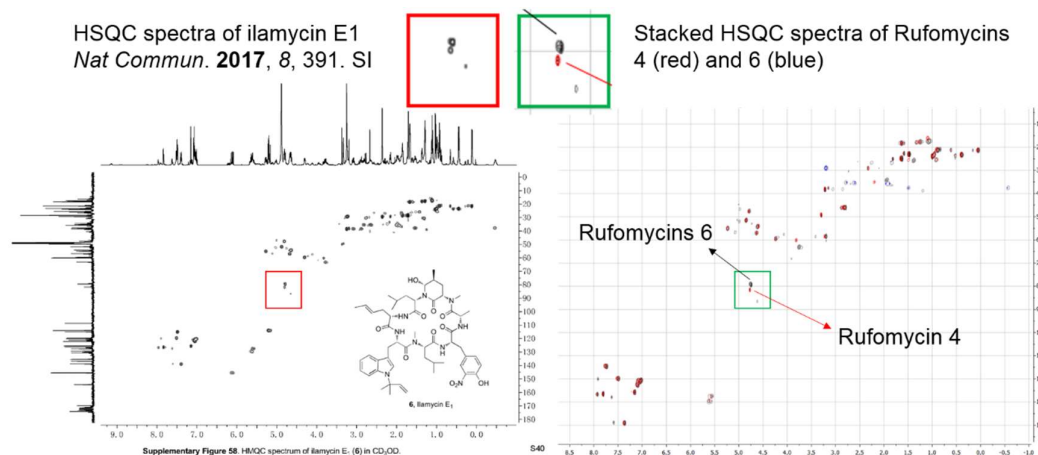


Figure S58. RufomycinSS 2 and 3 showed distinct conformers based on the ^{13}C NMR data

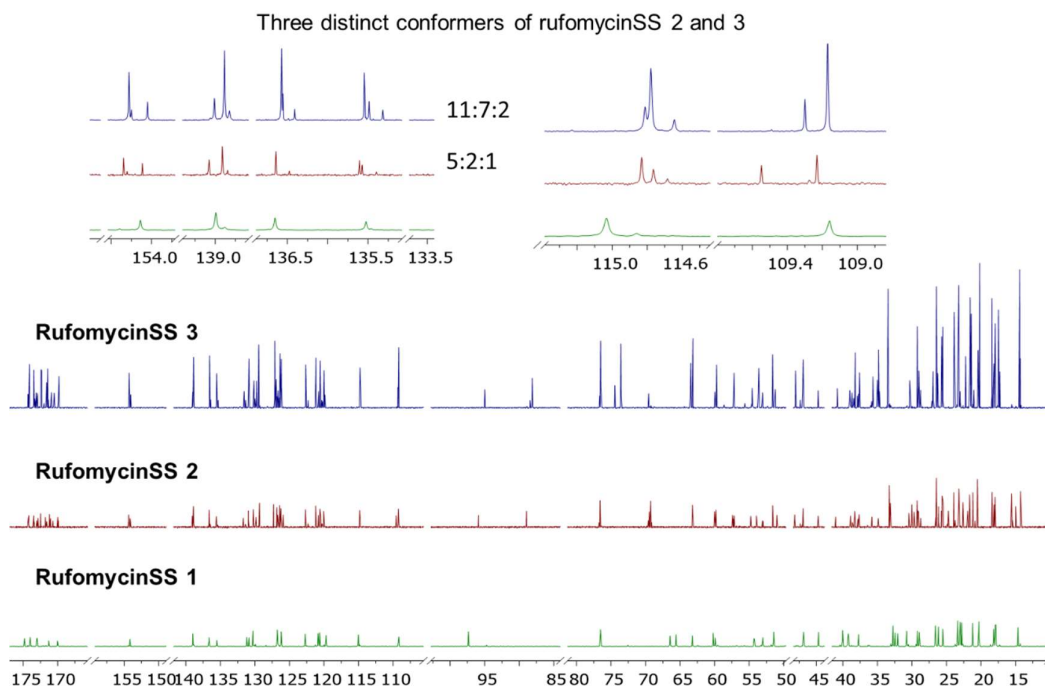


Figure S59. ^{13}C NMR differences ($\Delta\delta_{\text{C}}$) between compound pairs of rufomycins 4/5, 4/6, and 4/7

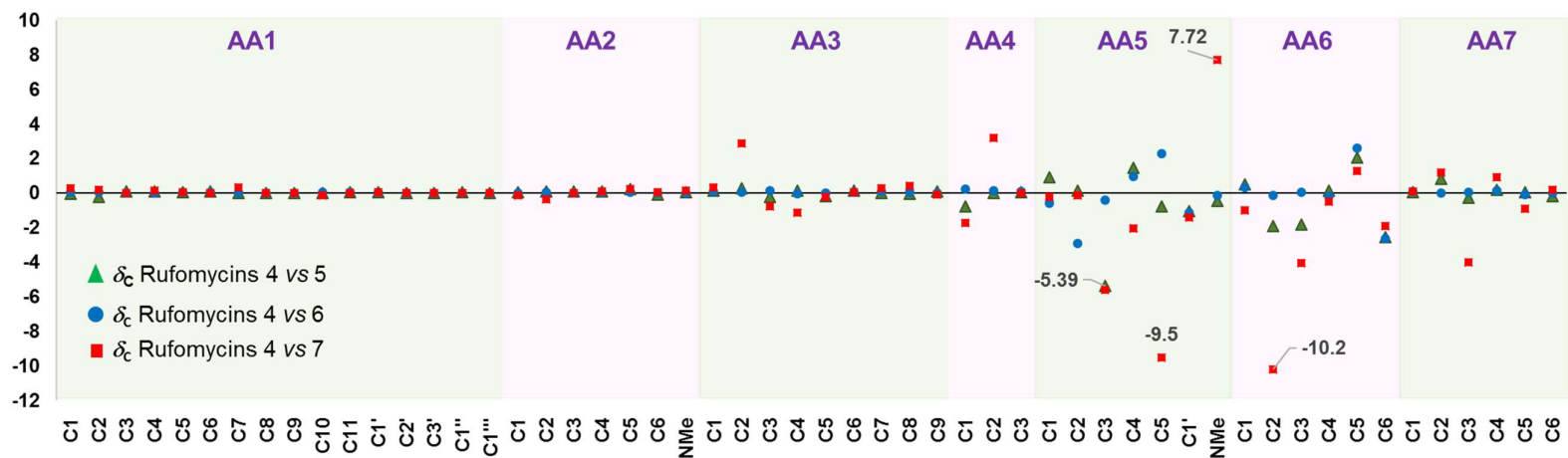


Figure S60. ^1H NMR differences ($\Delta\delta_{\text{H}}$) between compound pairs of rufomycins 4/5, 4/6, and 4/7



Figure S61. Extracted UV data of rufomyicins 4–7

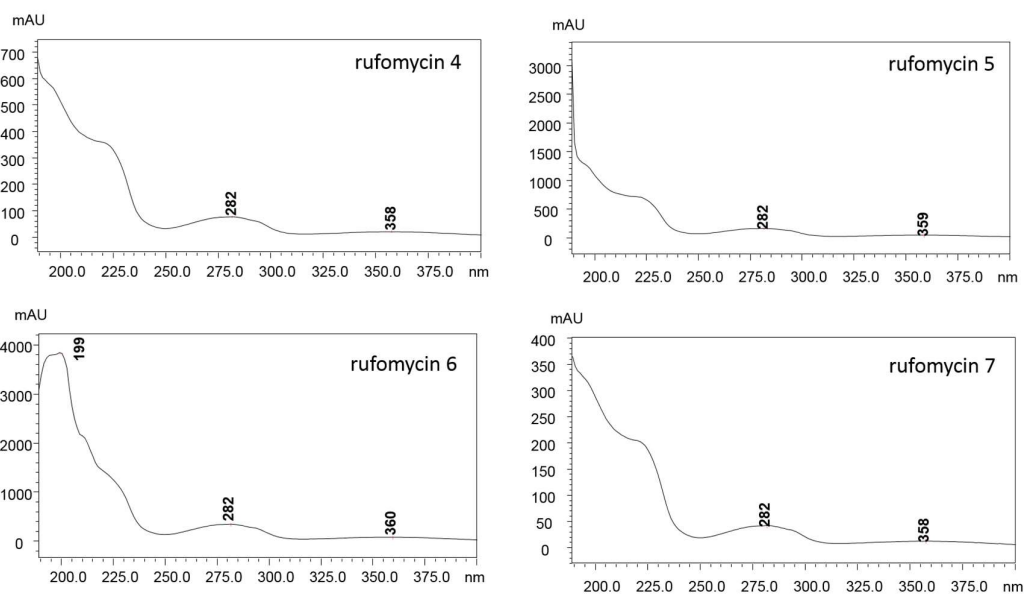


Figure S62. UV spectra of rufomycinSS 1–3 in methanol

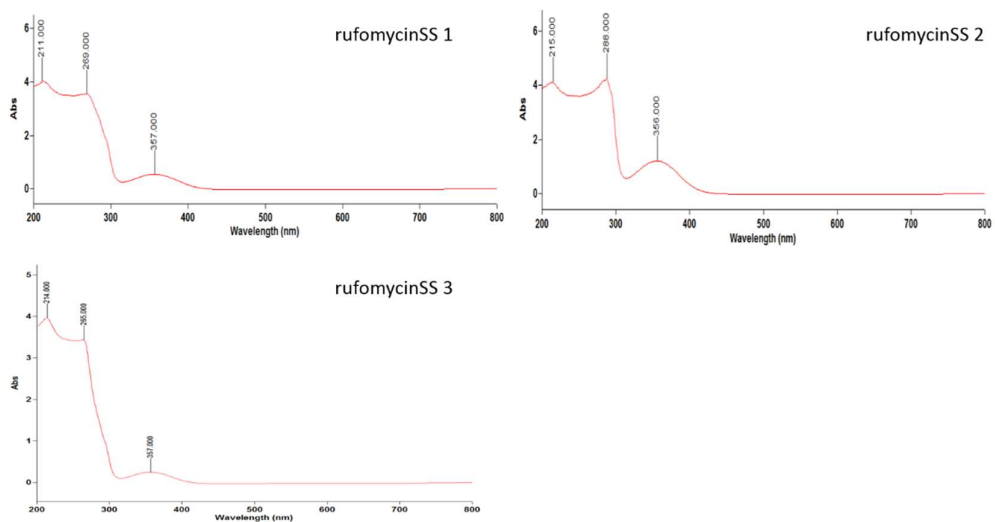


Figure S63. IR spectrum of rufomycin 4

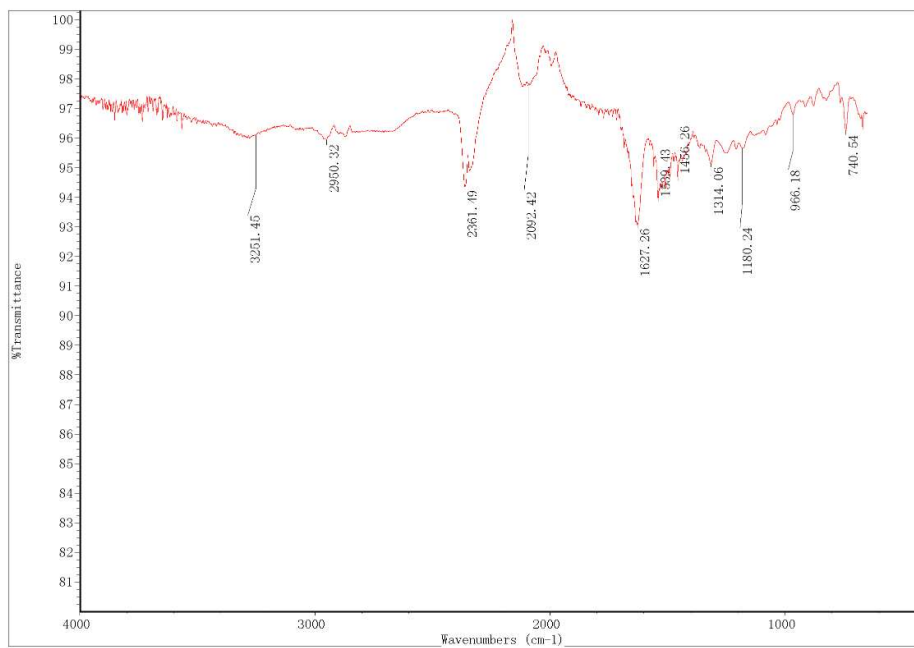


Figure S64. IR spectrum of rufomycin 5

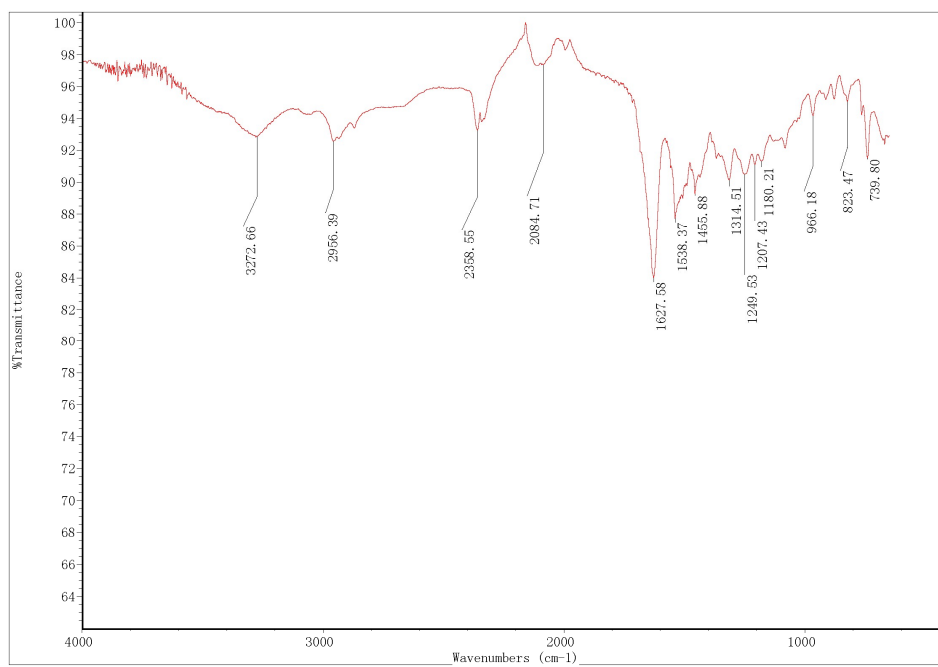


Figure S65. IR spectrum of rufomycin 6

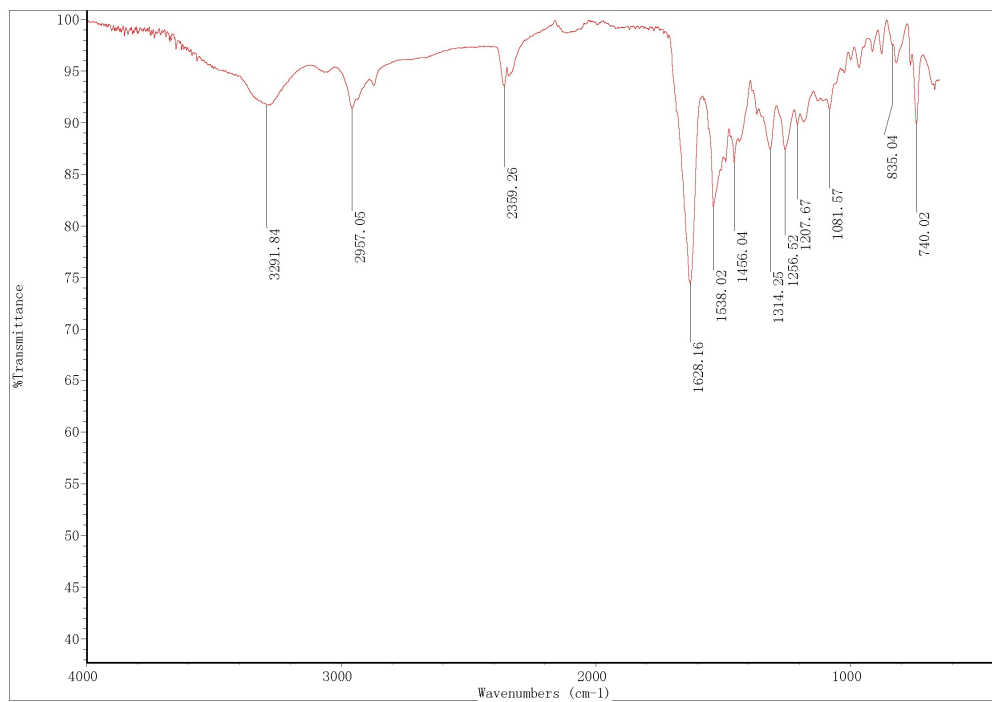


Figure S66. IR spectrum of rufomycinSS 1

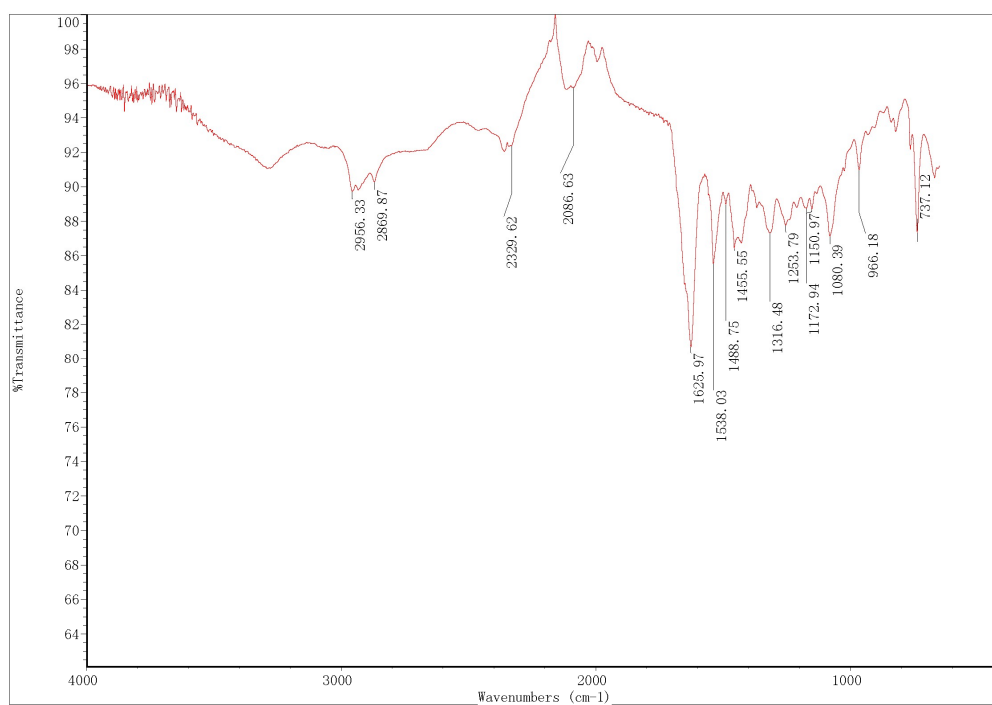


Figure S67. IR spectrum of rufomycinSS 2

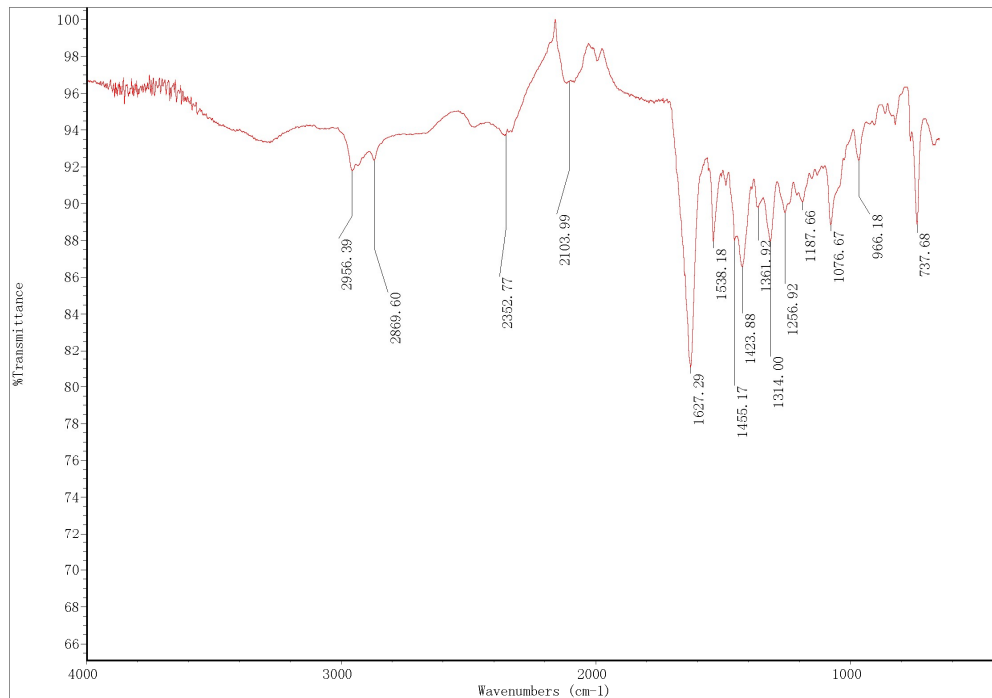


Figure S68. IR spectrum of rufomycinSS 3

