SUPPORTING INFORMATION

Cytotoxic Pregnane Steroidal Glycosides from *Chonemorpha megacalyx*

Fang-Yu Yuan,[†] Xiao-Ling Wang,[‡] Tian Wang,[†] Tao Shen,[†] Dongmei Ren,[†] Hong-Xiang Lou,[†] and Xiao-Ning Wang[*,†]

[†]Department of Natural Product Chemistry, Key Laboratory of Chemical Biology (Ministry of Education), School of Pharmaceutical Sciences, Shandong University, 44 West Wen-Hua Road, Jinan 250012, P. R. China

[‡]The Second Hospital of Shandong University, 247 Bei-Yuan Street, Jinan 250033, P. R. China

[*]**Corresponding author**

Tel.: +86 531 88382012; fax: +86 531 88382548

E-mail address: wangxn@sdu.edu.cn

Contents

Experimental section

X-ray Crystallographic Analysis of Compounds 1 and 3: Two suitable crystals of compounds **1** and **3** were obtained by recrystallization in MeOH and were measured on a Bruker D8 venture diffractometer equipped with an APEXII CCD using Cu Kα radiation (λ = 1.54178 Å) at 296(2) K. The APEX2 Software Suite was used for cell refinement and data reduction. The structure was refined with full-matrix least-squares calculations on F^2 using SHELXL-2014/7.[1]

*Crystal data for **1***: $C_{21}H_{28}O_5$, M = 360.43, triclinic, space group P_1, a = 6.2053(2) Å, b = 8.5119(2) Å, c = 9.3471(3) Å, α = 84.014(2)°, β = 76.948(2)°, γ = 71.401(2)°, V = 455.55(2) Å^3, Z = 1, D_{calcd} = 1.314 g/cm^3, μ (Cu Kα) = 1.542 mm^{-1}, F(000) = 194, 9181 reflections measured (4.859° ≤ θ ≤ 66.572°), 3054 unique, which were used in all calculations. The final stage converged to R_1 = 0.0445 (wR_2 = 0.1017) for 2677 observed reflections [with $I > 2\sigma(I)$] and 239 variable parameters, and R_1 = 0.0571 (wR_2 = 0.1050) for all unique reflections and GOF = 1.104. The flack parameter was 0.08(18).

*Crystal data of **3***: $C_{21}H_{30}O_5$, M = 362.45, monoclinic, space group $P2_1$, a = 5.8958(2) Å, b = 14.3918(5) Å, c = 11.1399(4) Å, β = 103.3550(10)°, V = 919.67(6) Å^3, Z = 2, D_{calcd} = 1.309 g/cm^3, μ (Cu Kα) = 1.542mm^{-1}, F(000) = 392, 11396 reflections measured (4.079° ≤ θ ≤ 72.309°), 3500 unique, which were used in all calculations. The final stage converged to R_1 = 0.0618 (wR_2 = 0.1552) for 3322 observed reflections [with $I > 2\sigma(I)$] and 240 variable parameters, and R_1 = 0.0647 (wR_2 = 0.1592) for all unique reflections and GOF = 1.083. The flack parameter was 0.19(12).

Crystallographic data of **1** and **3** have been deposited with the Cambridge Crystallographic Data Centre with the deposition numbers CCDC 1881130 and 1881135, respectively. The data can be obtained free of charge via www.ccdc.cam.ac.uk/products/csd/request.

1. Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr*. **2015**, *71*, 3–8.

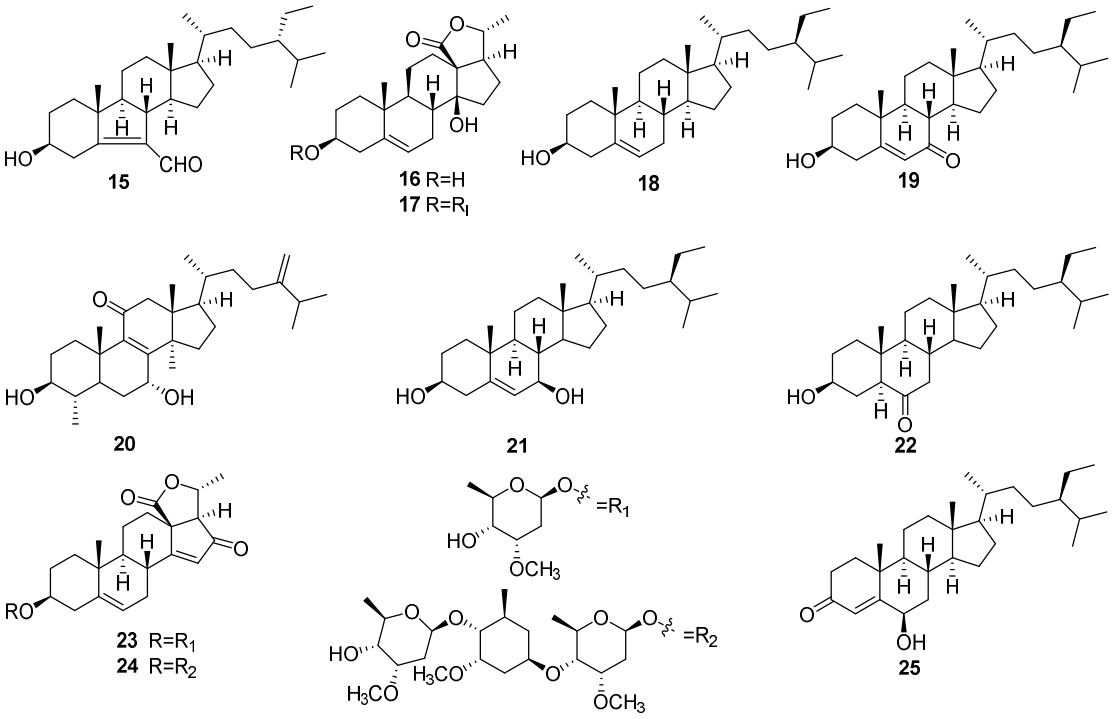
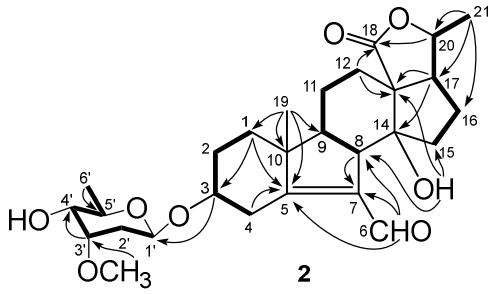


Figure S1. Structure of the known compounds.

Figure S2. Key HMBC (H→C) and ^{1}H–^{1}H COSY (H—H) correlations of **2**, **4**–**8**, and **10**–**14**.



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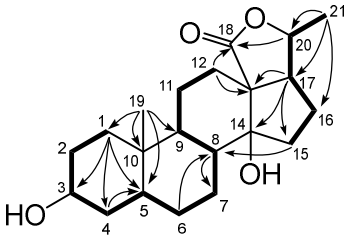

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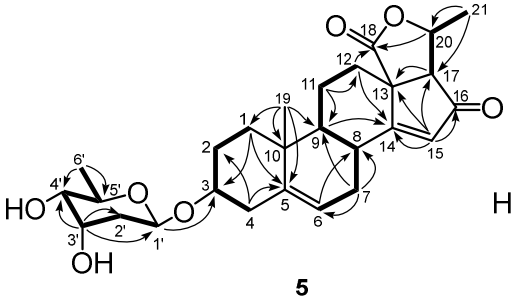

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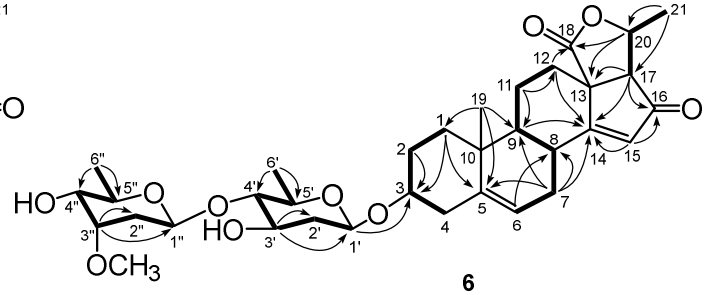

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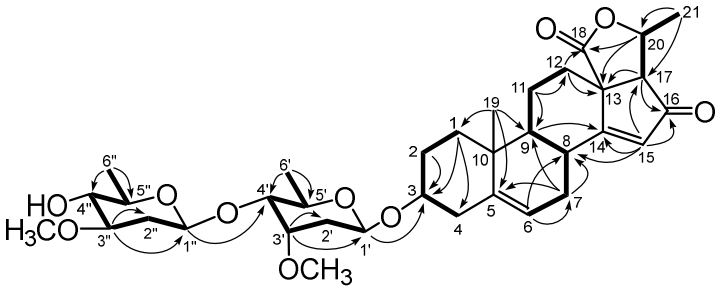

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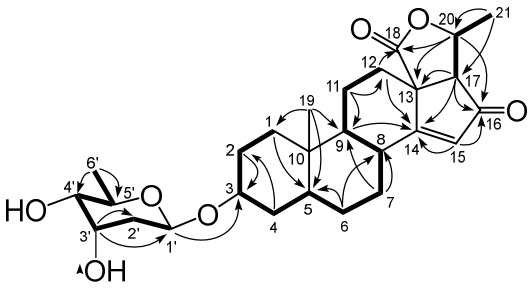

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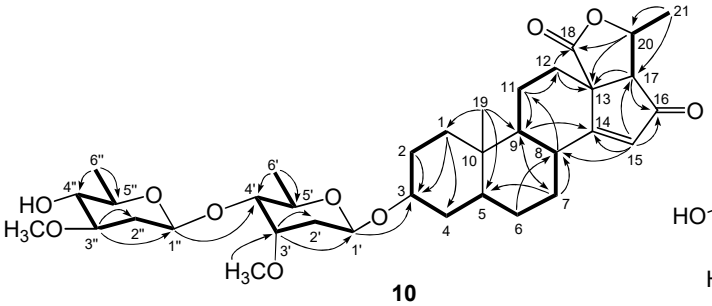

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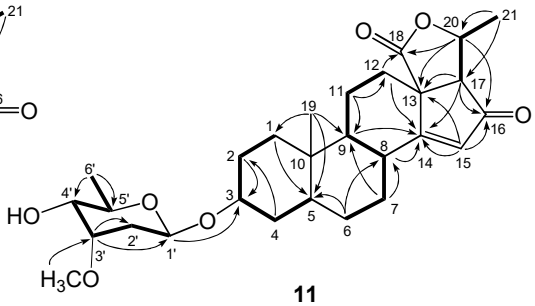

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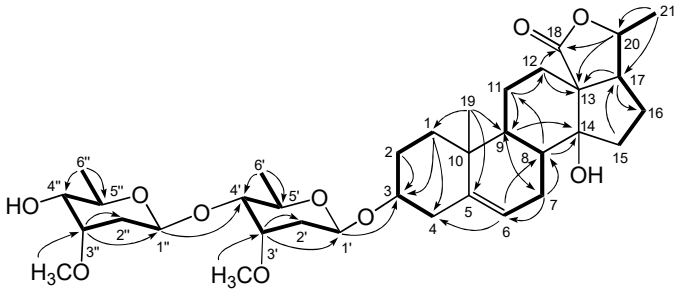

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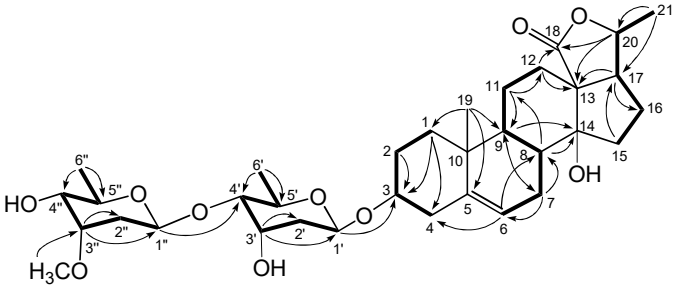

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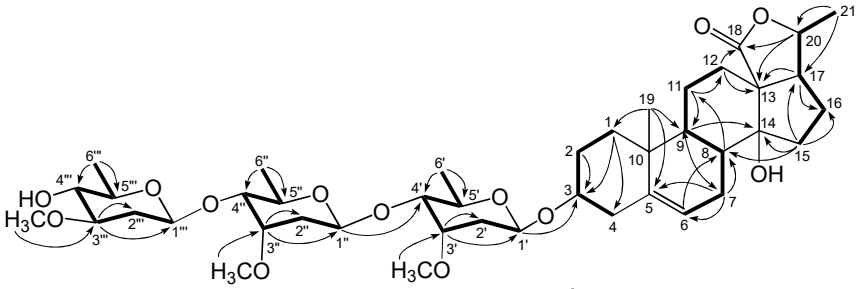

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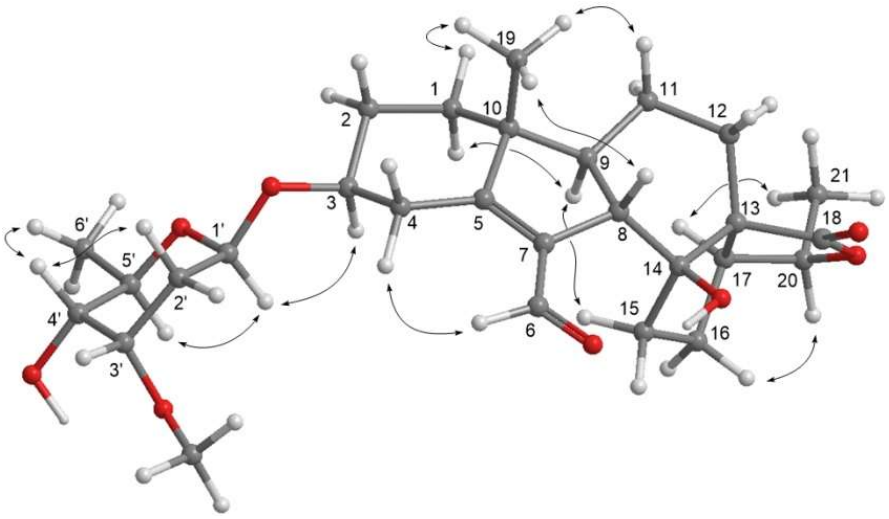
Figure S3. Key NOESY correlations (H↔H) of **2** and **4**–**14**.



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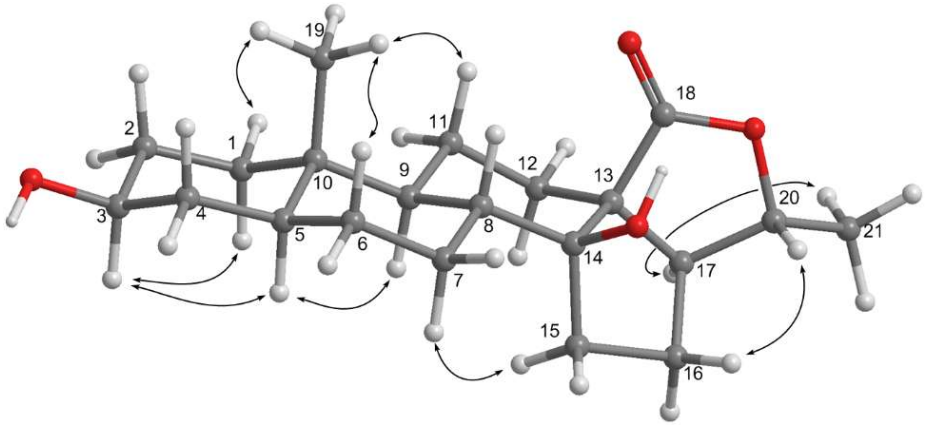

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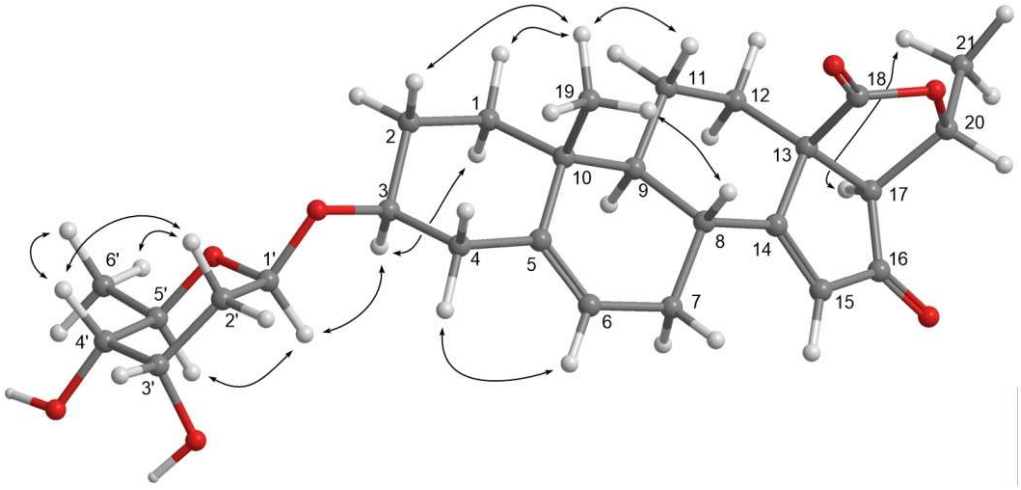

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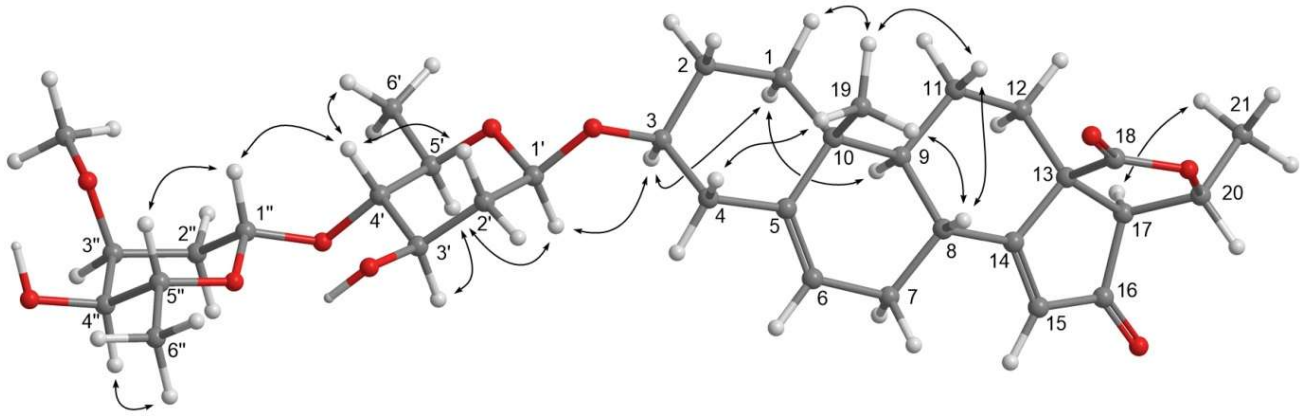
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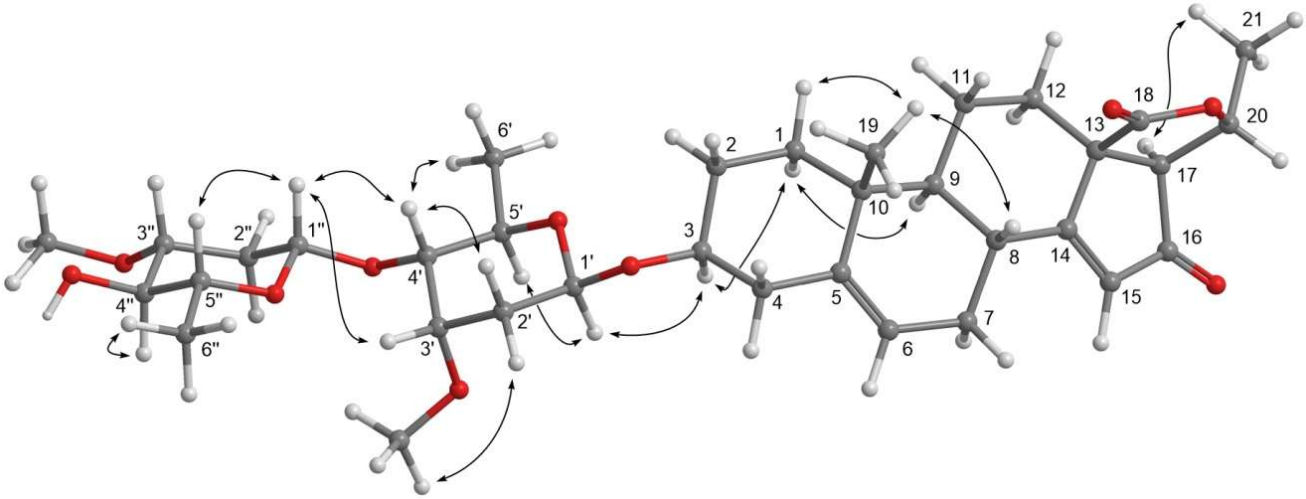
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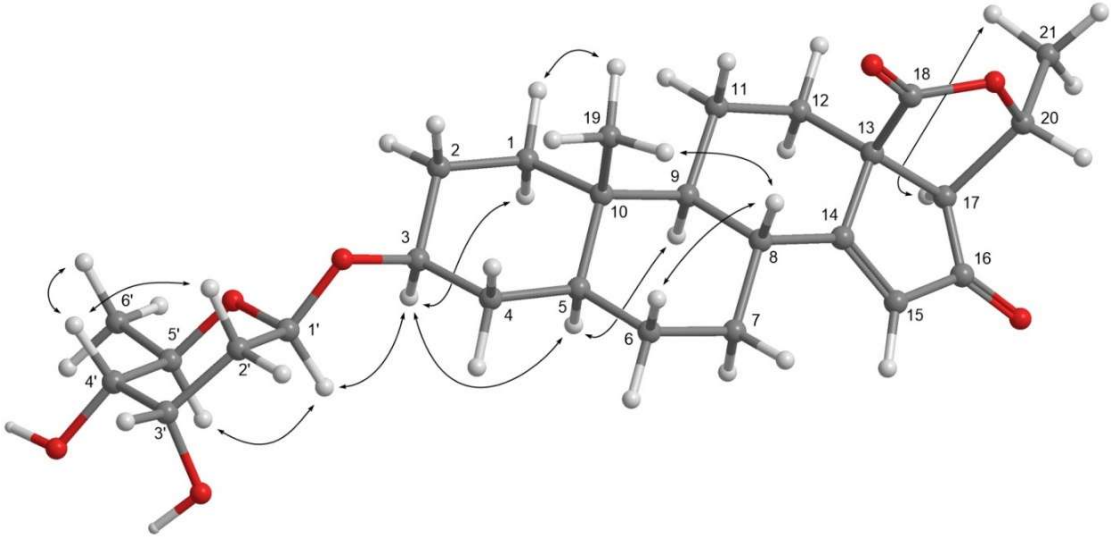
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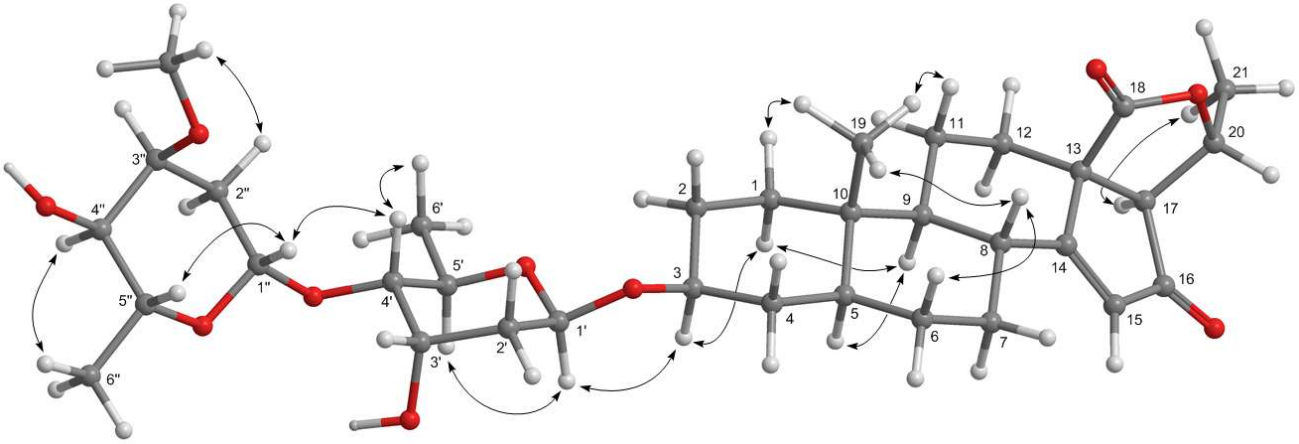
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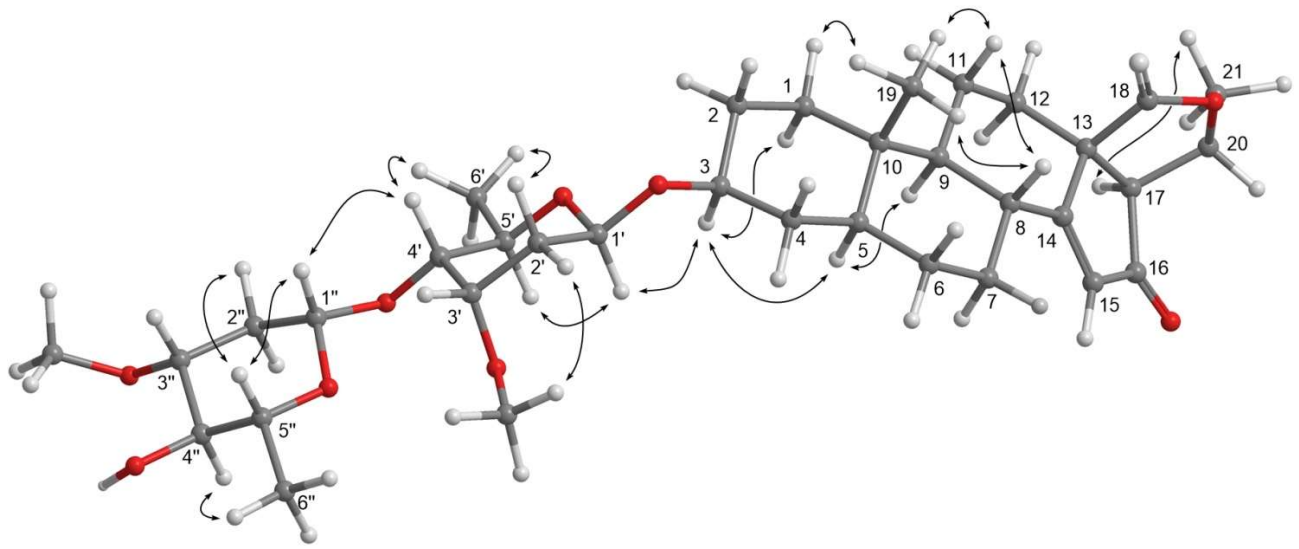
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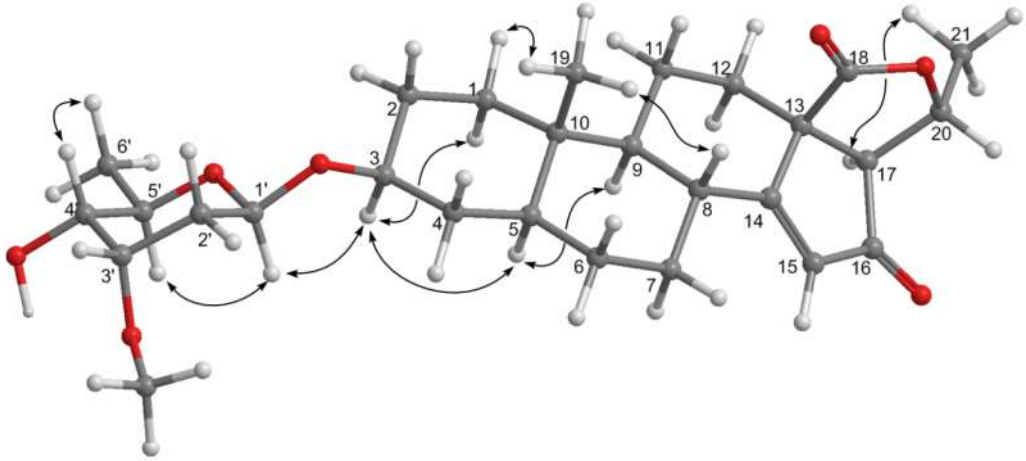
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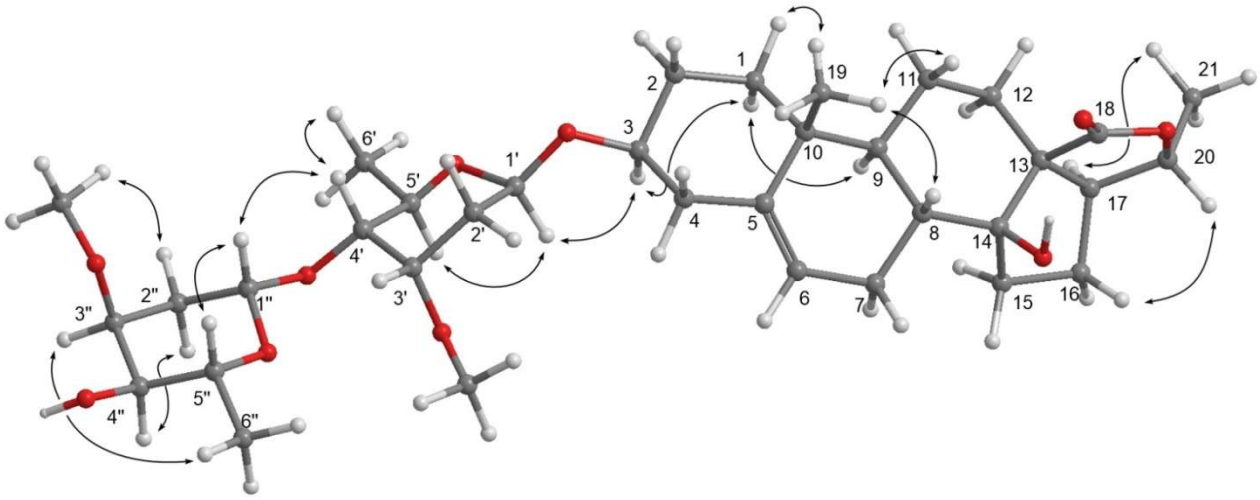
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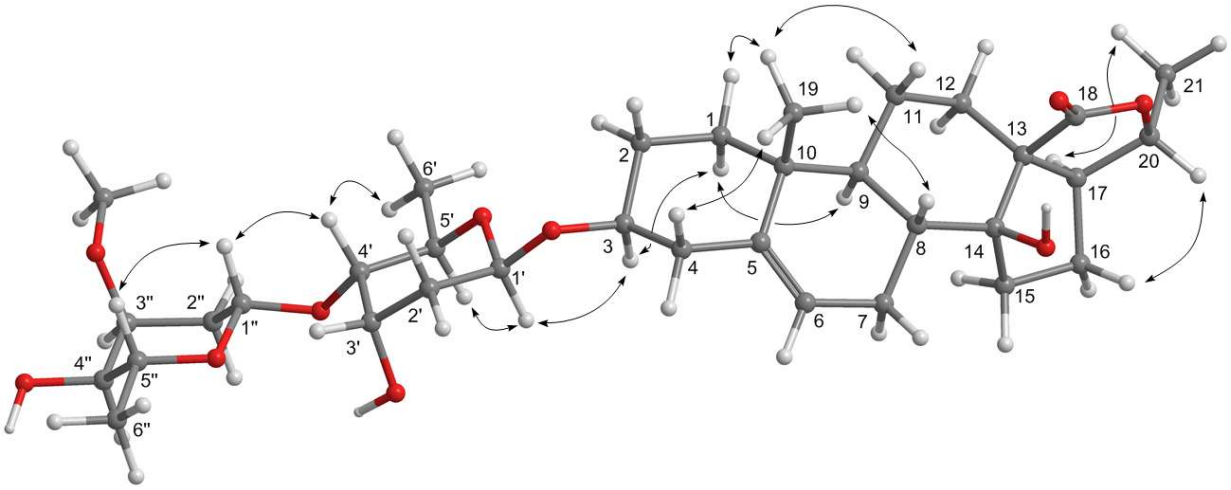
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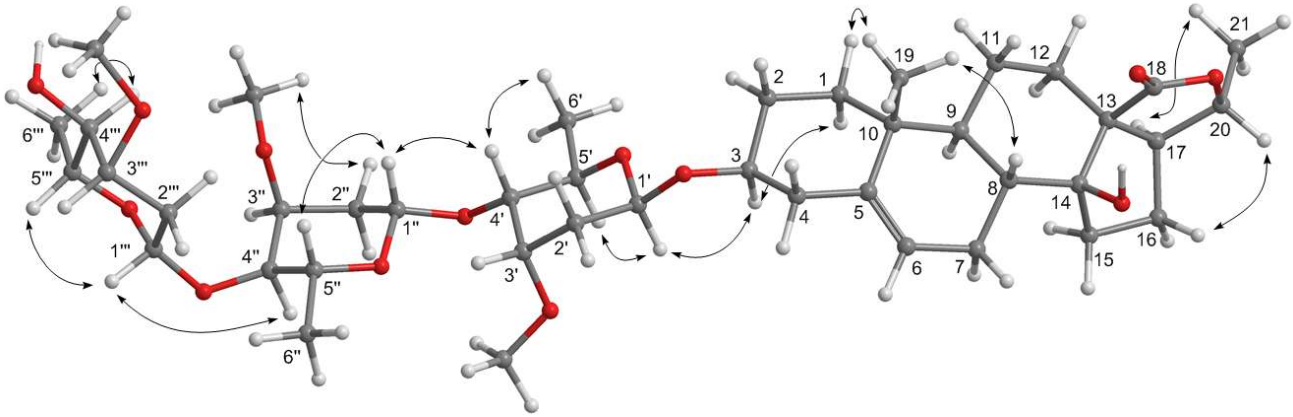
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Figure S4. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1**.

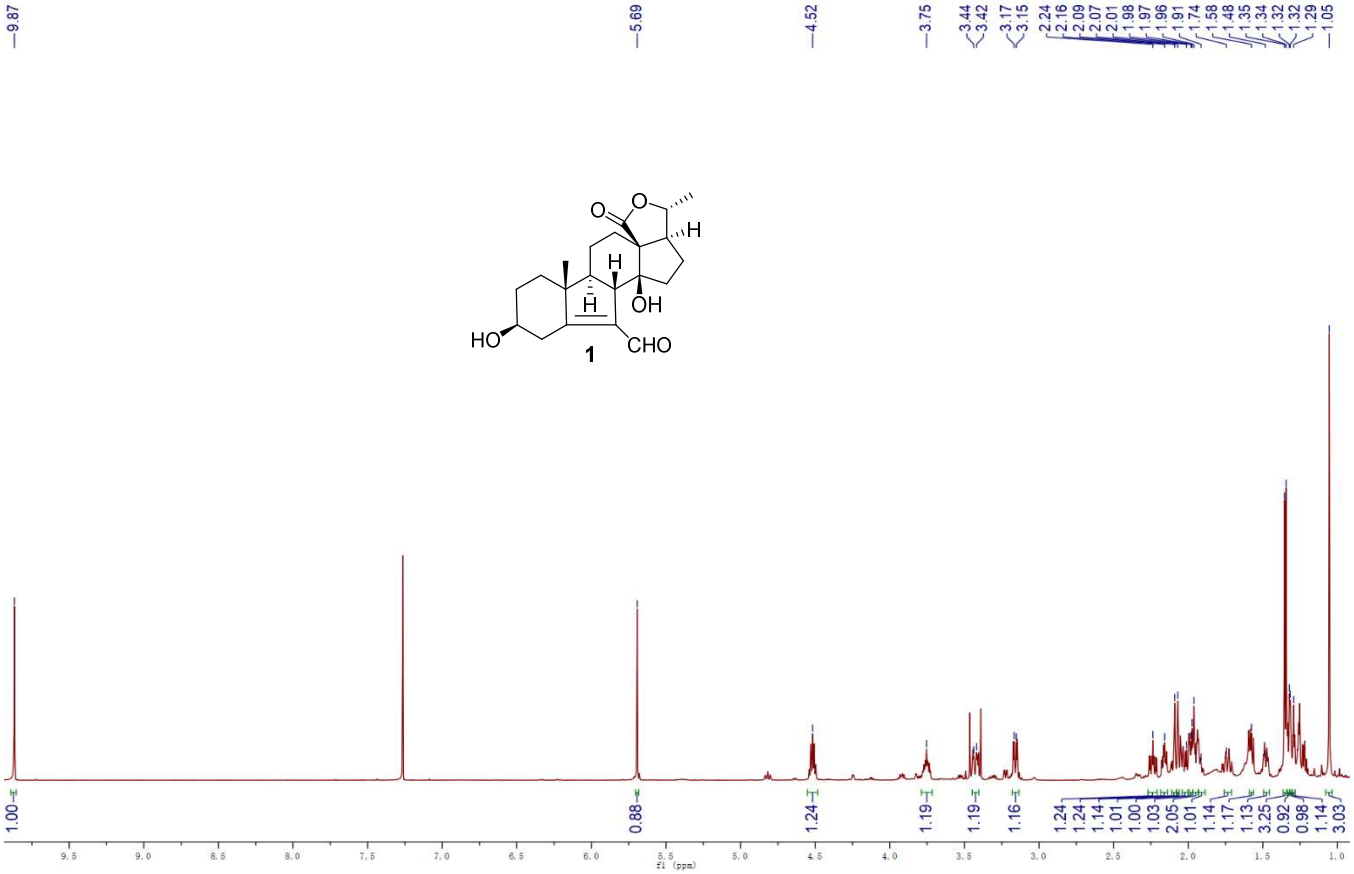

Figure S5. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **1**.

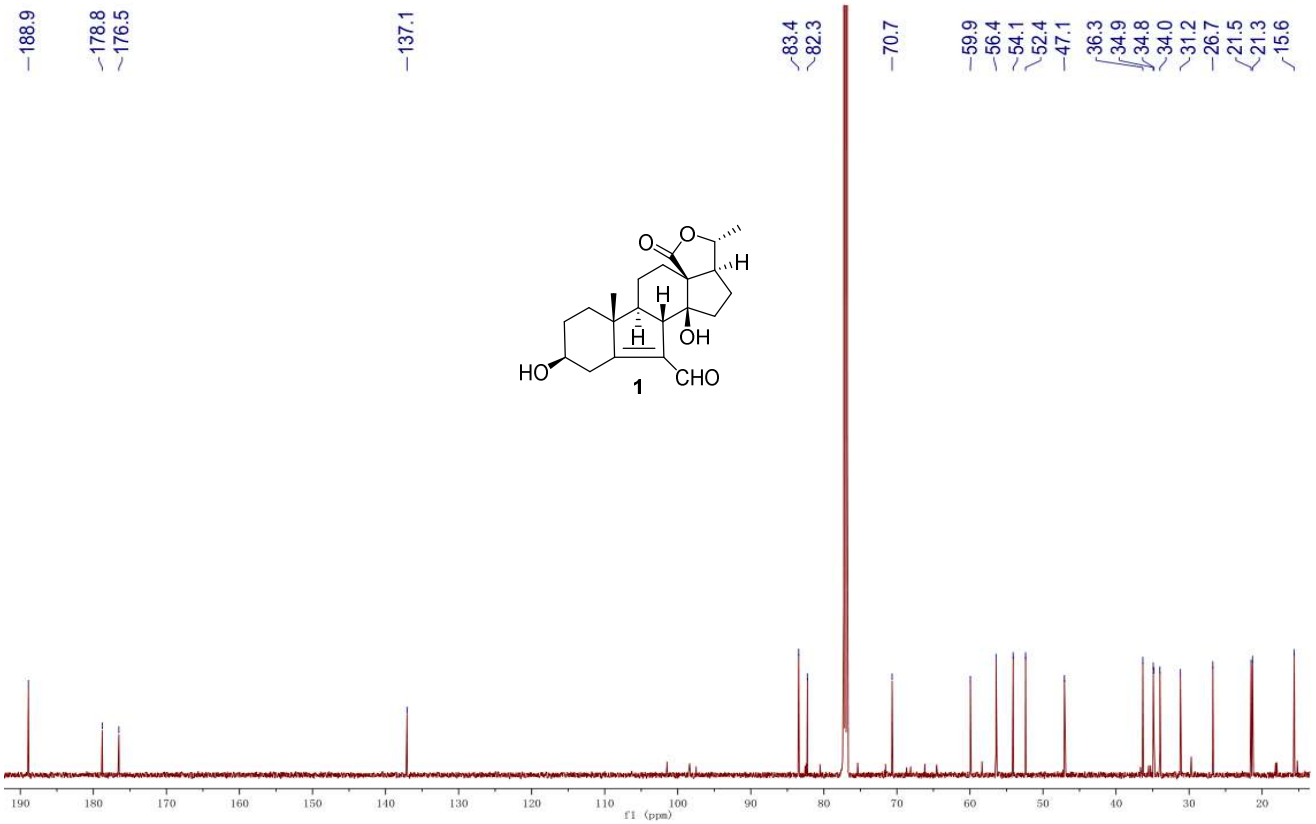

Figure S6. HSQC (600 MHz, $CDCl_3$) spectrum of **1**.

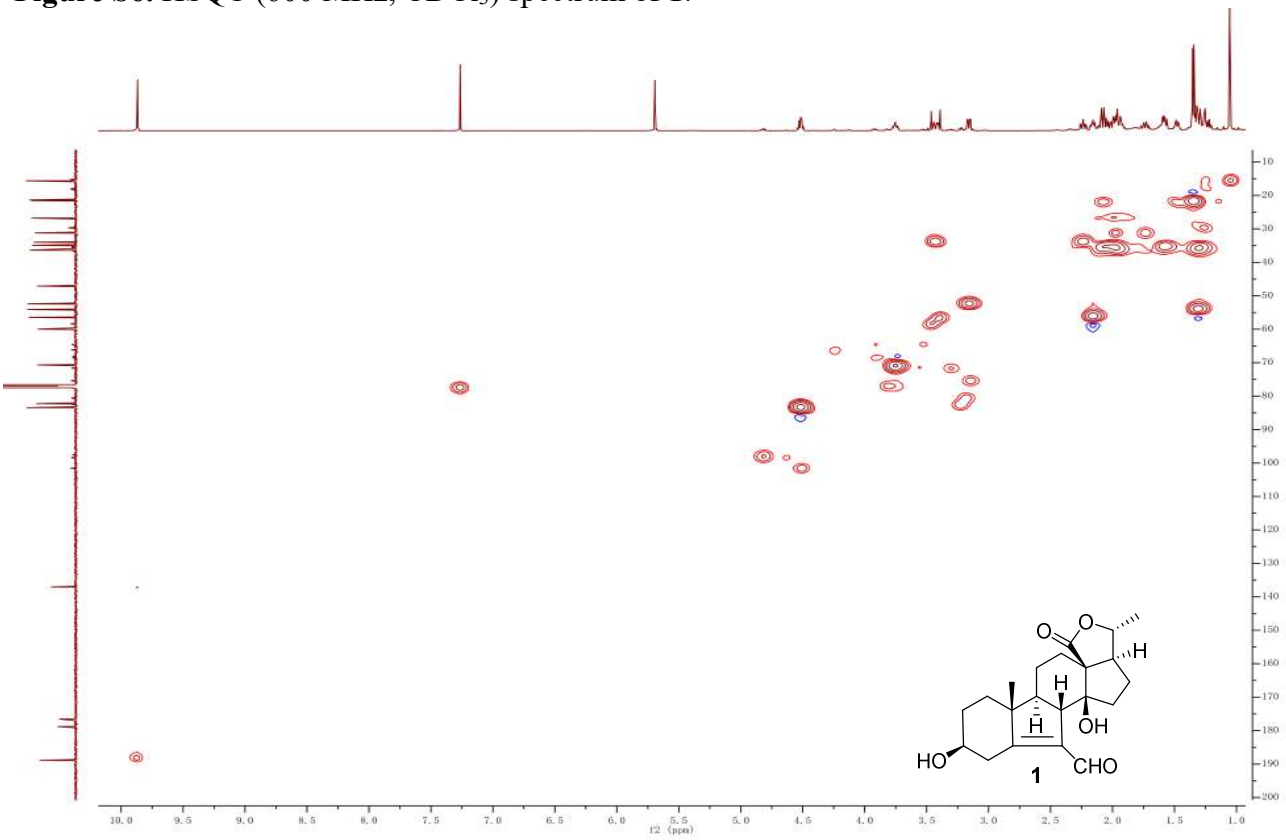

Figure S7. HMBC (600 MHz, $CDCl_{34}$) spectrum of **1**.

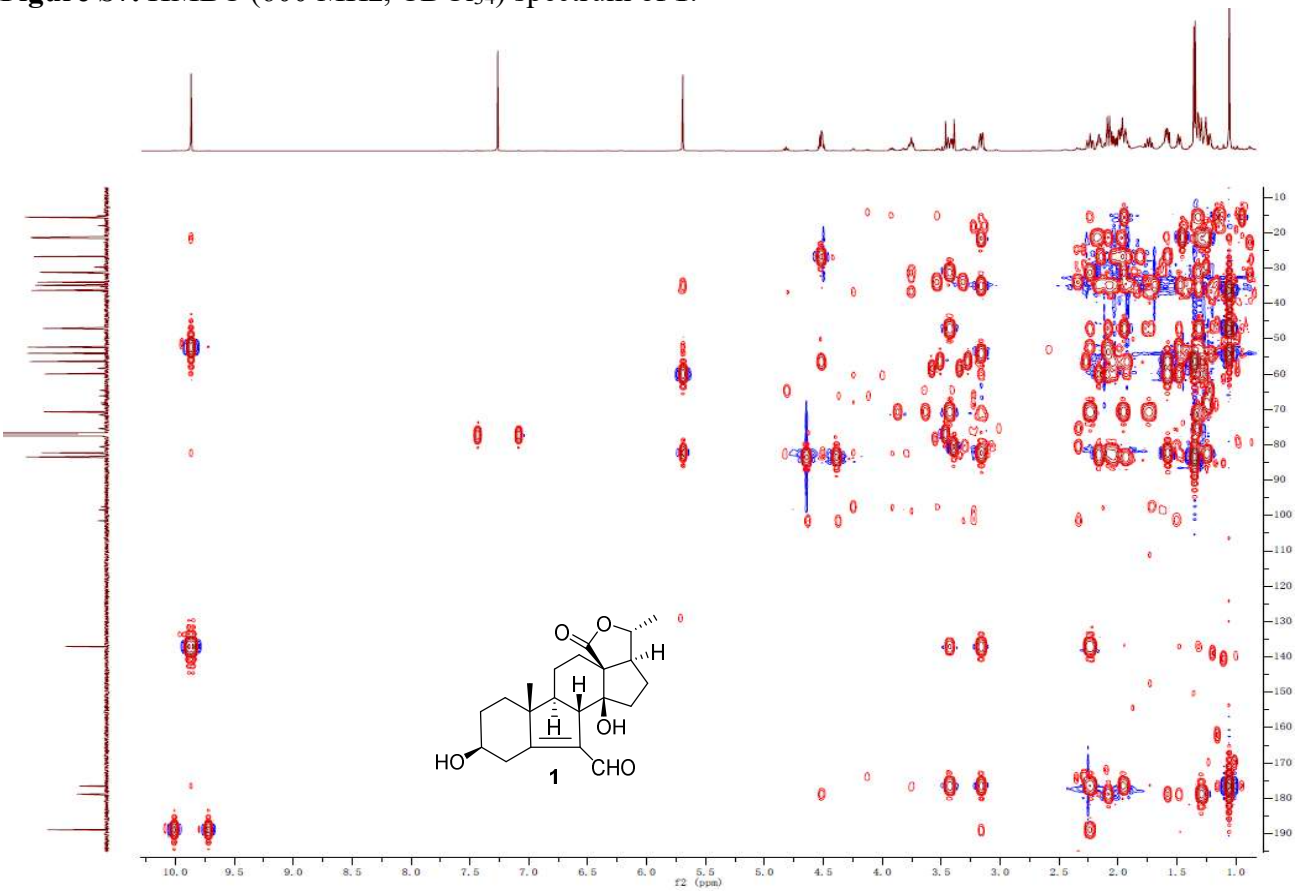

Figure S8. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **1**.

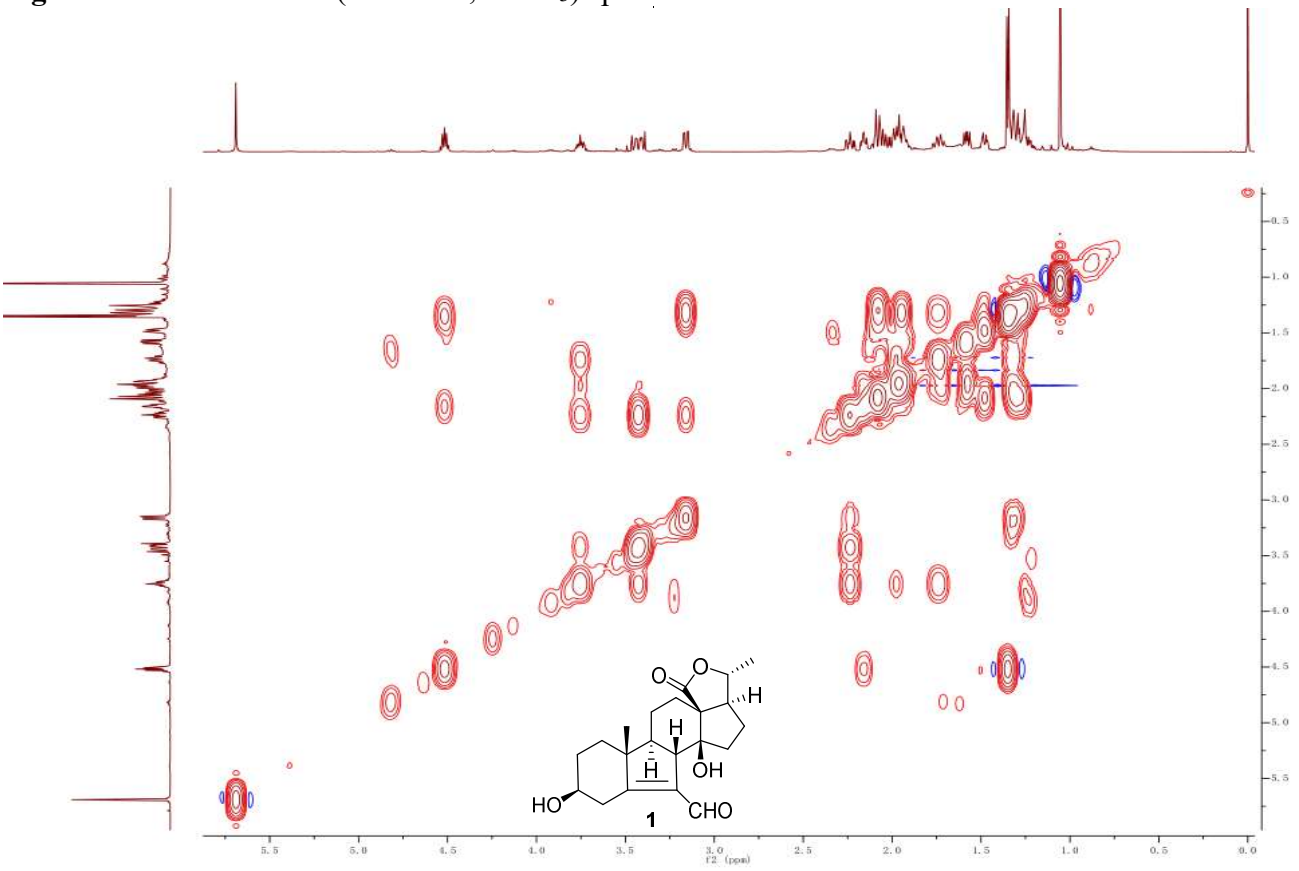

Figure S9. NOESY (600 MHz, $CDCl_3$) spectrum of **1**.

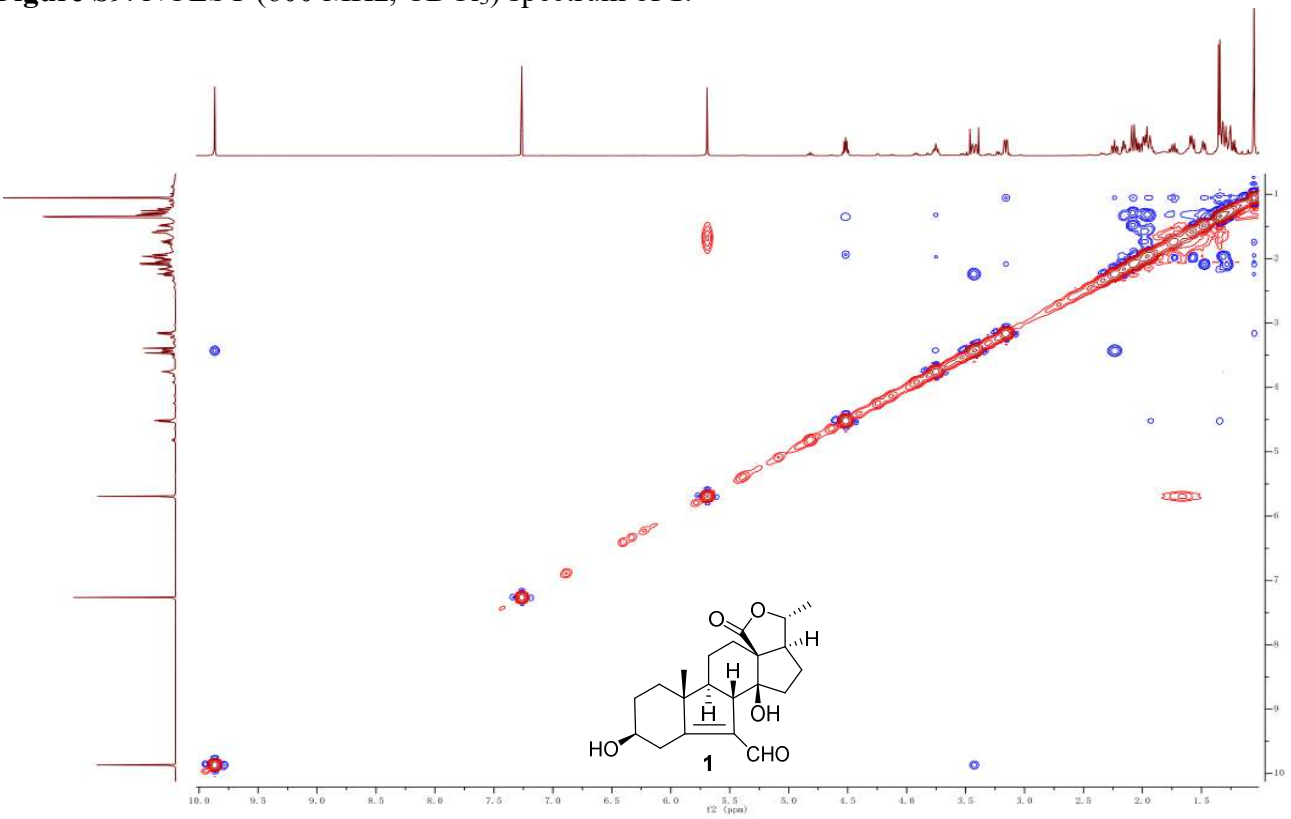

Figure S10. HRESIMS spectrum of **1**.

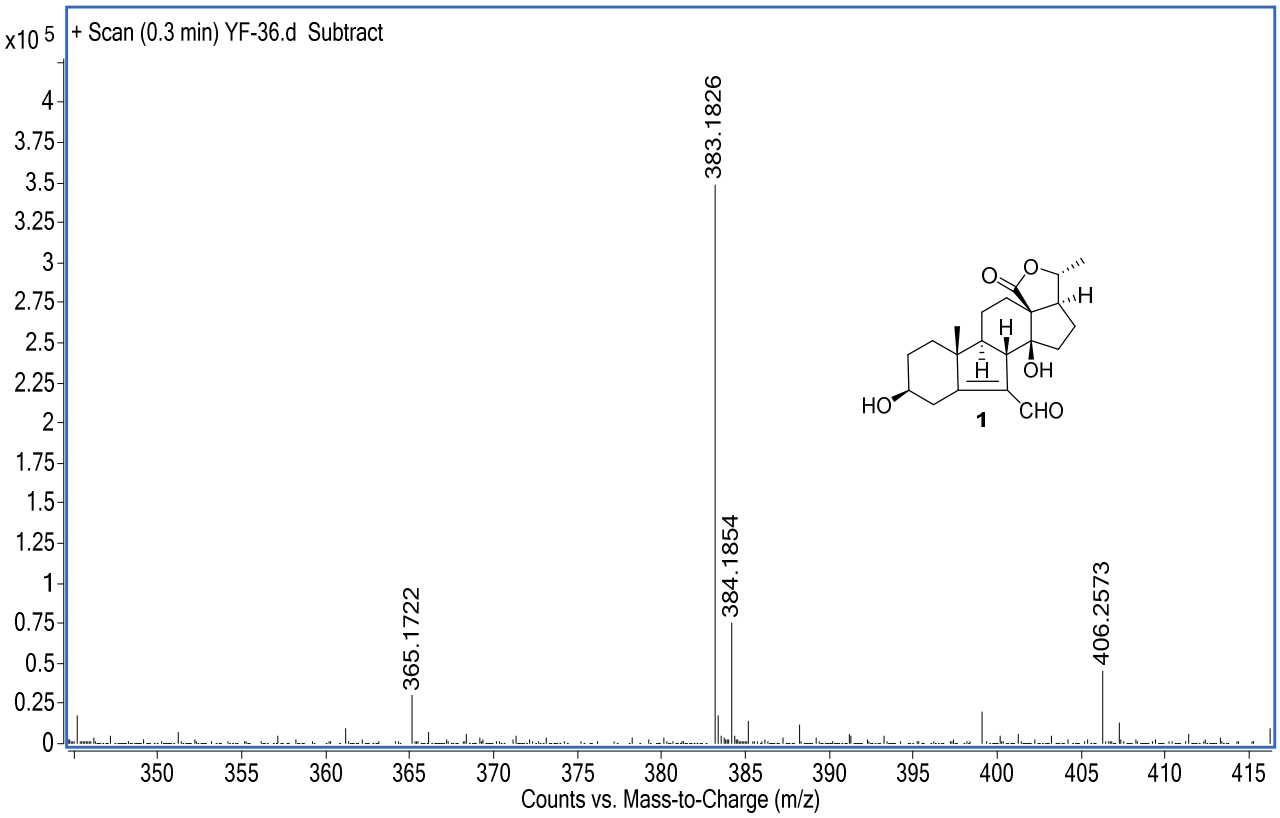

Figure S11. IR spectrum of **1**.

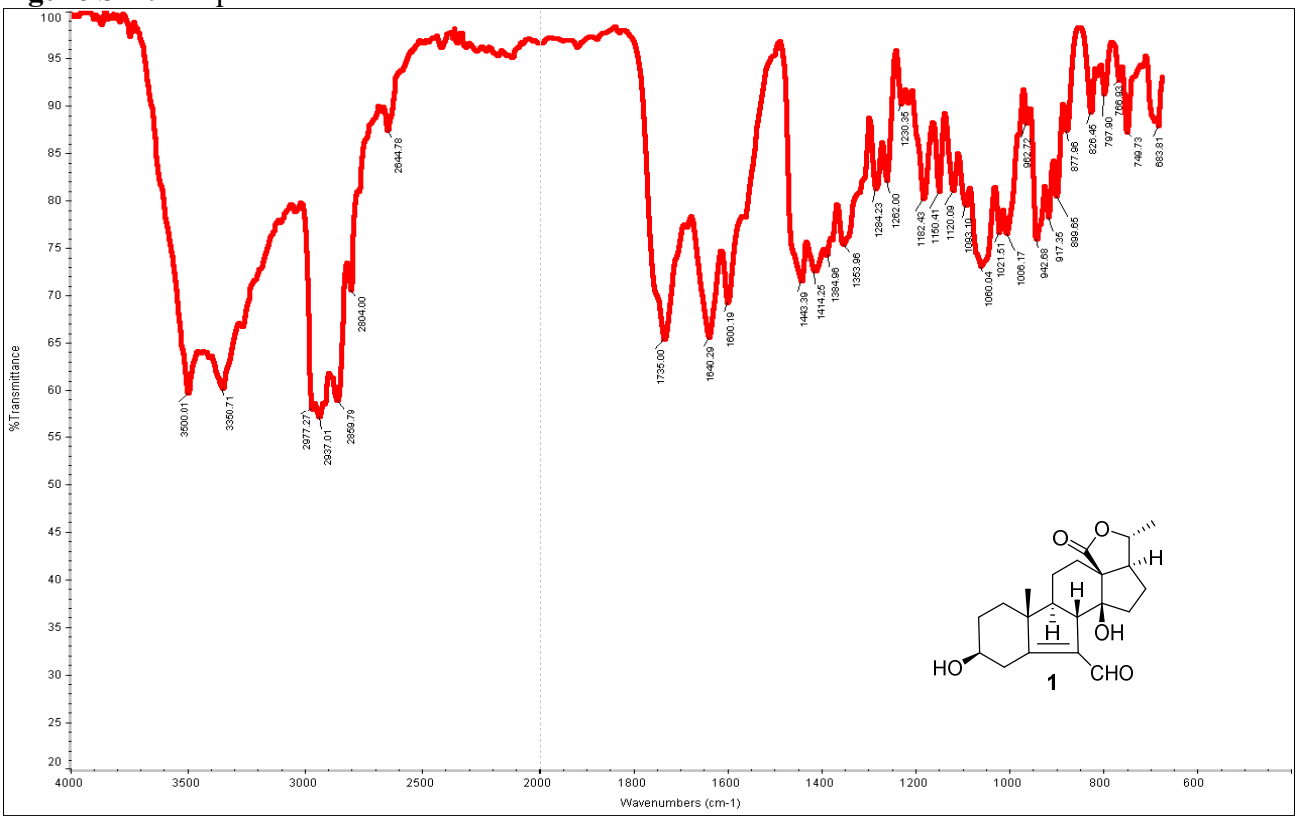

Figure S12. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2**.

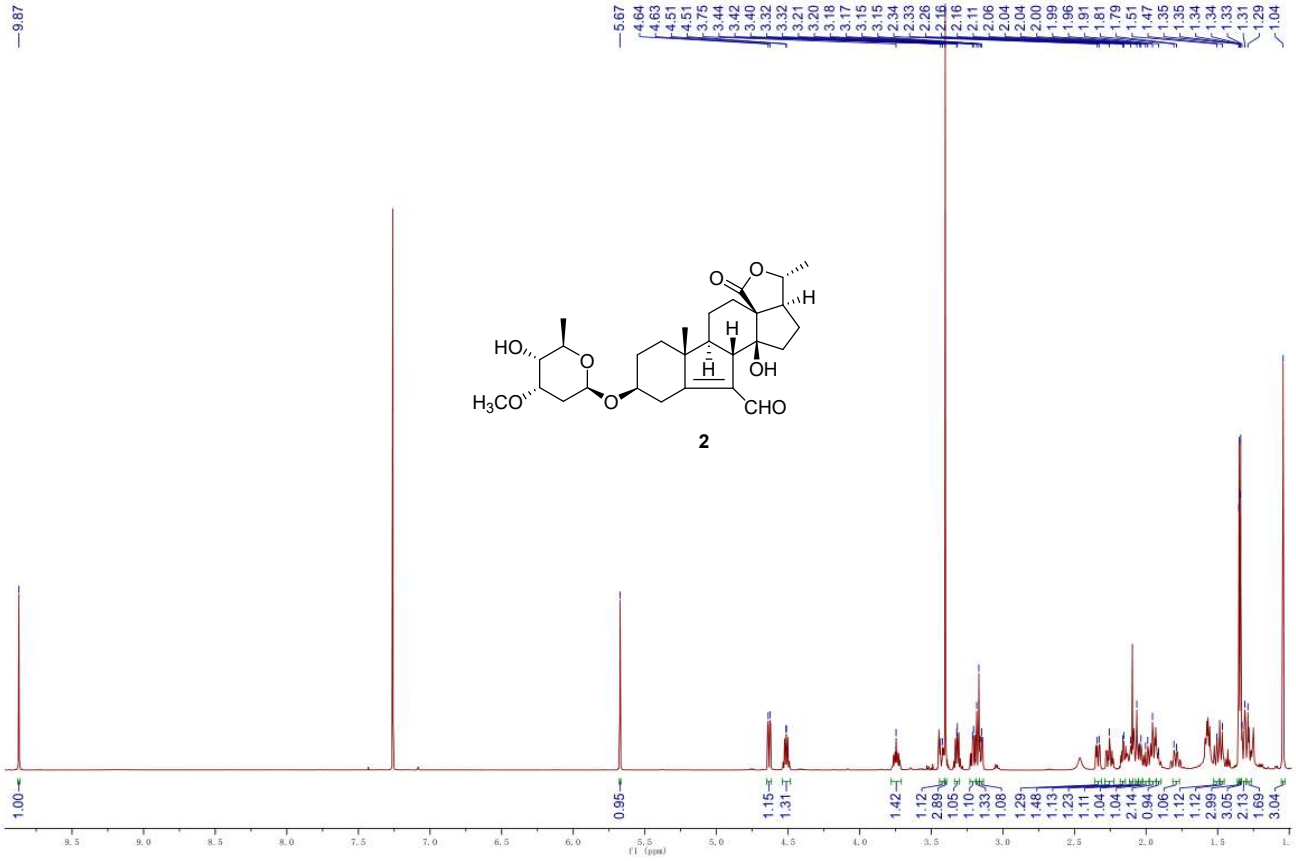

Figure S13. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2**.

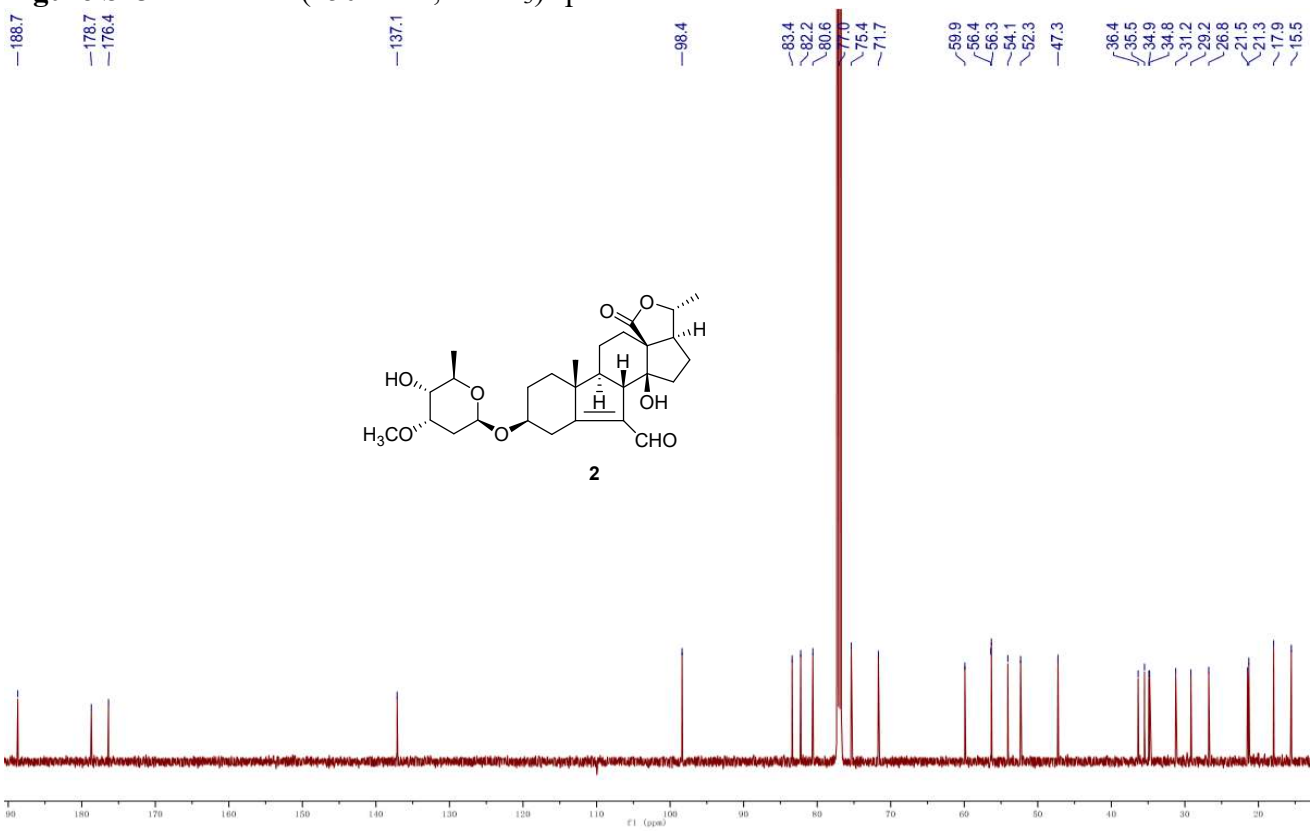

Figure S14. HSQC (600 MHz, $CDCl_3$) spectrum of **2**.

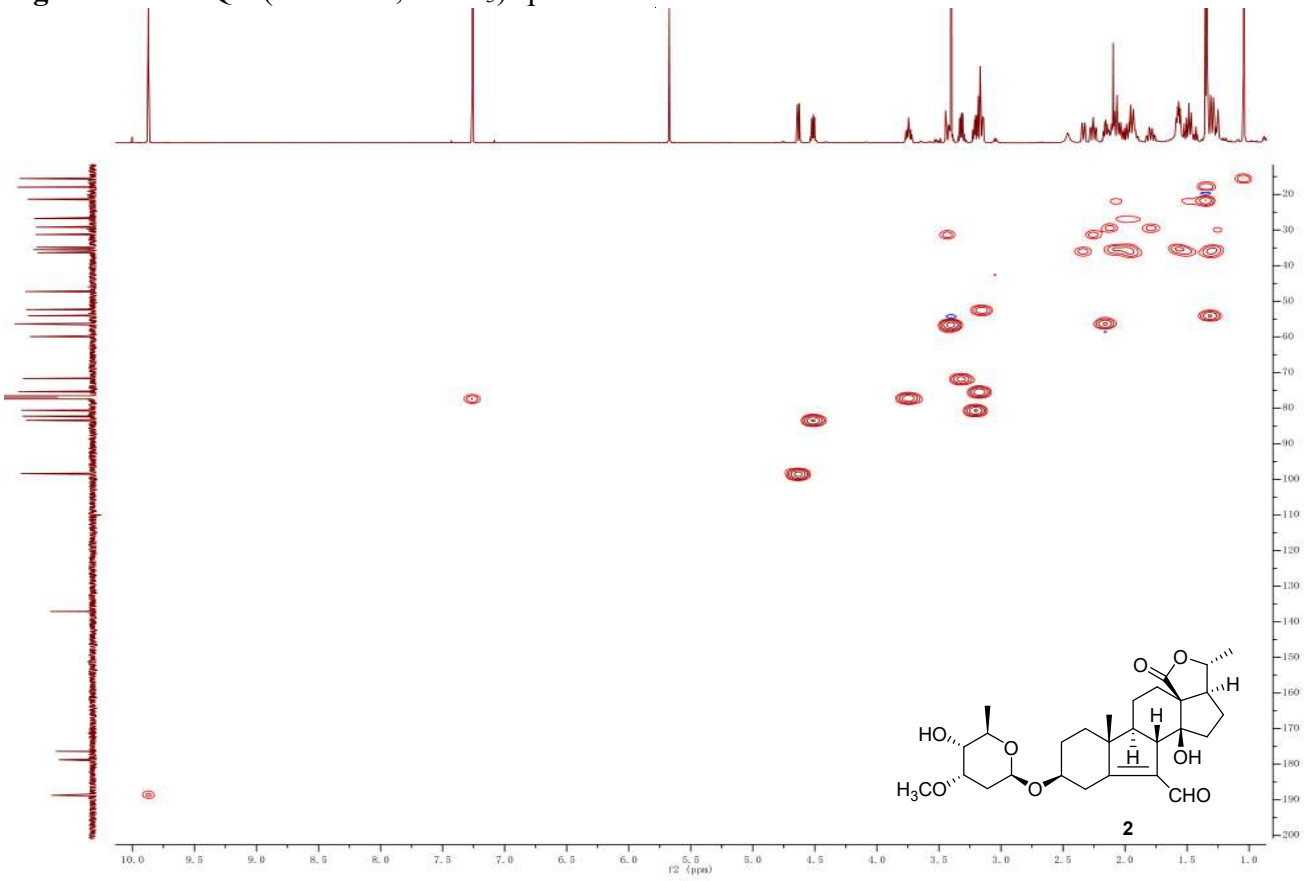

Figure S15. HMBC (600 MHz, $CDCl_3$) spectrum of **2**.

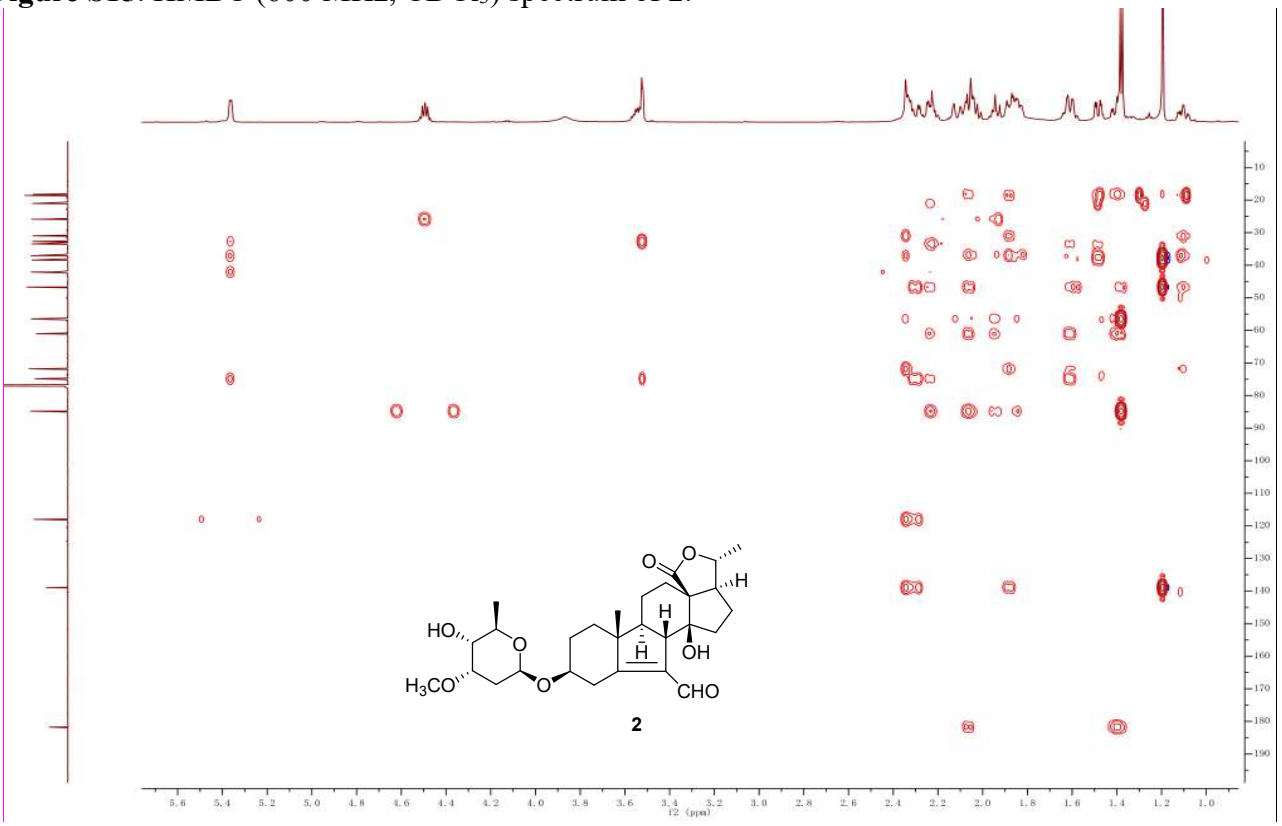

Figure S16. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **2**.

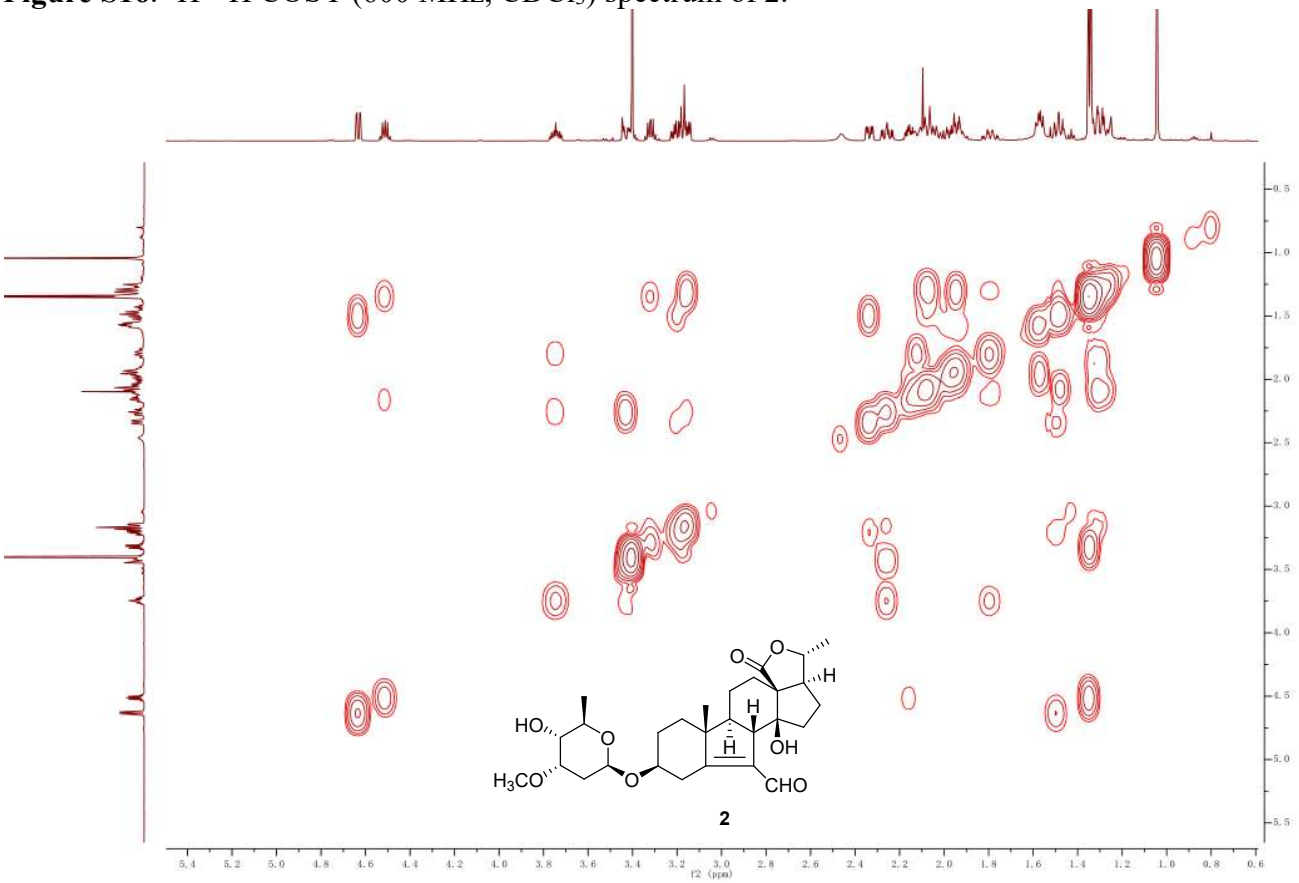

Figure S17. NOESY (600 MHz, $CDCl_3$) spectrum of **2**.

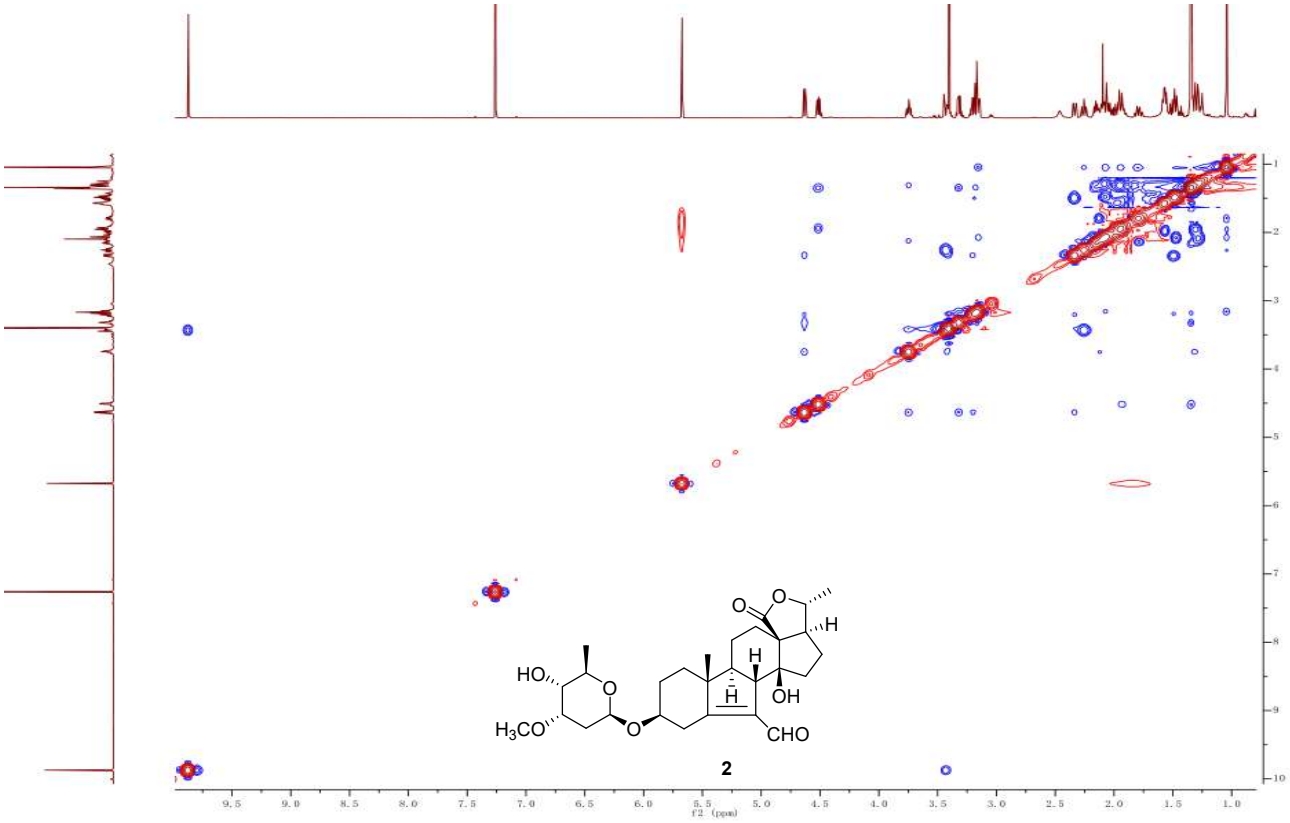

Figure S18. HRESIMS spectrum of **2**.

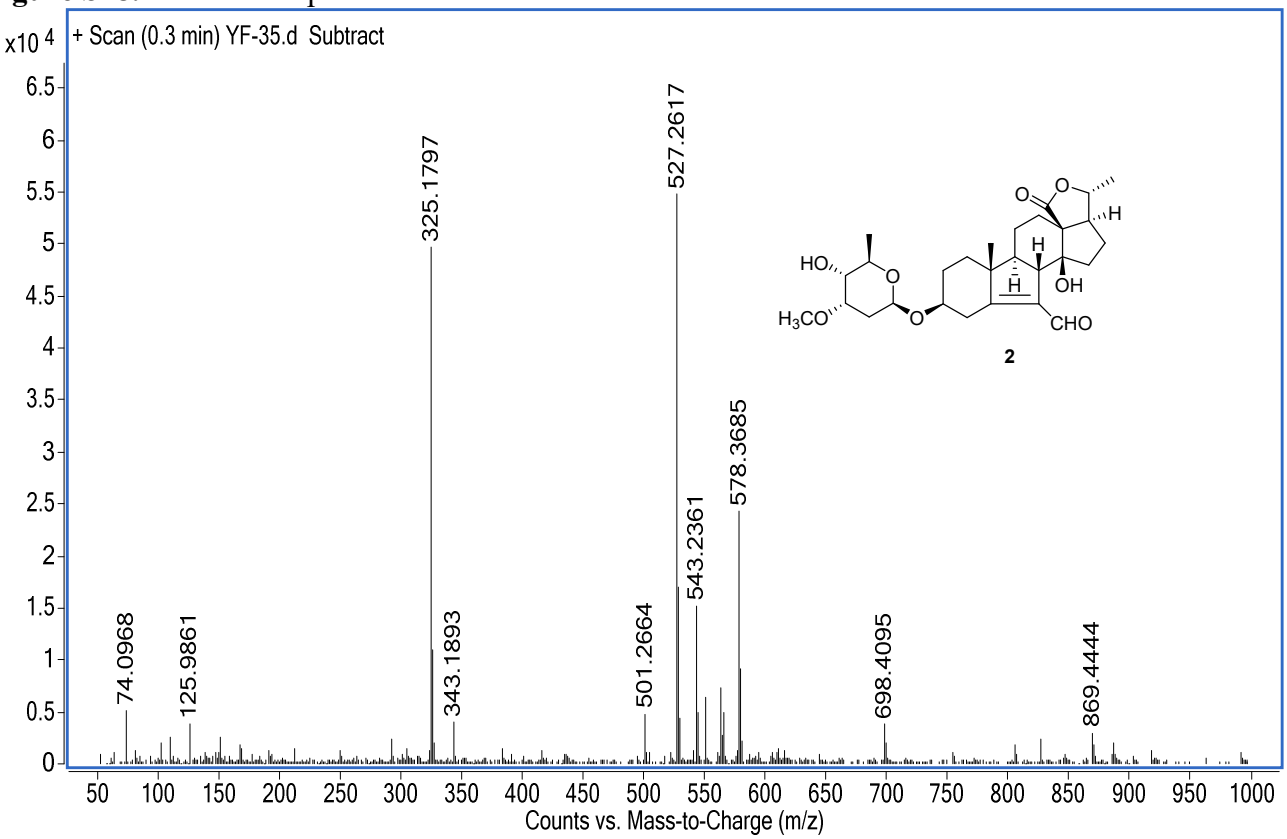

Figure S19. IR spectrum of **2**.

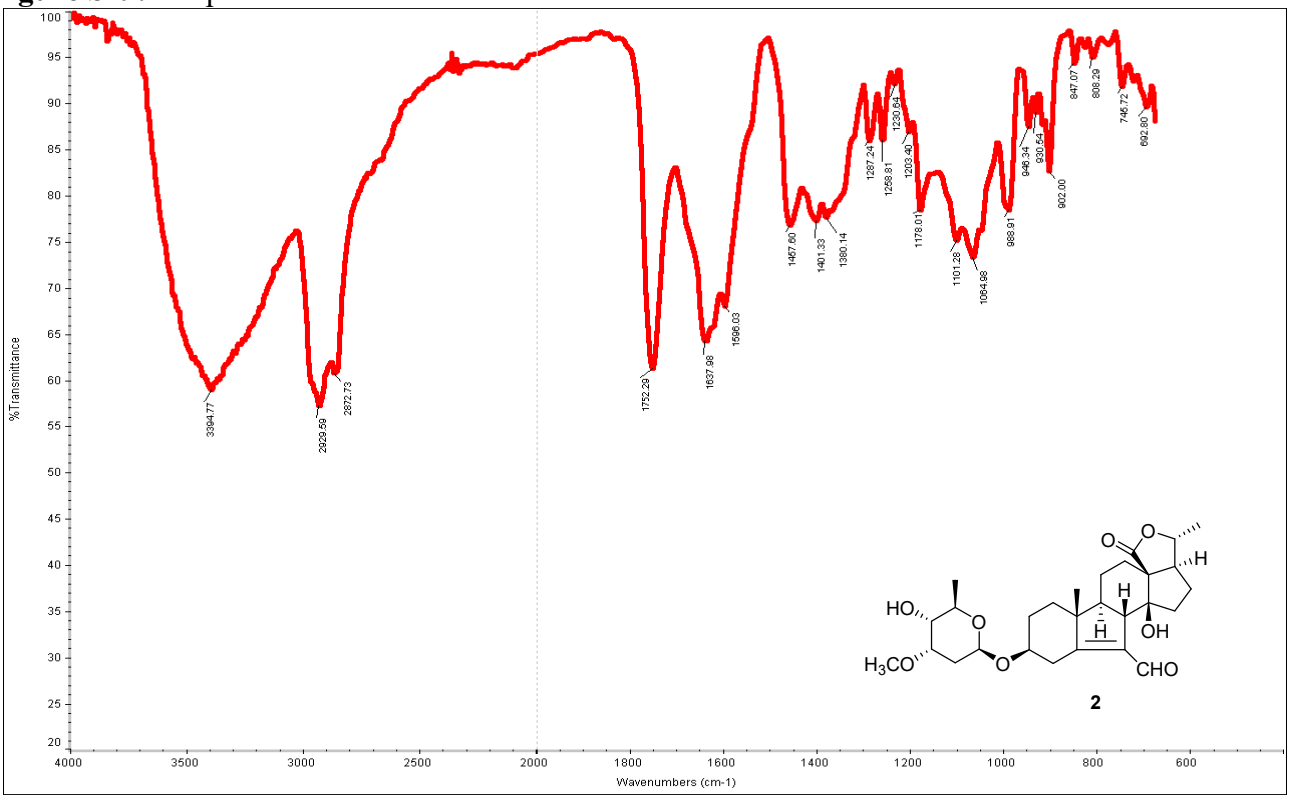

Figure S20. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3**.

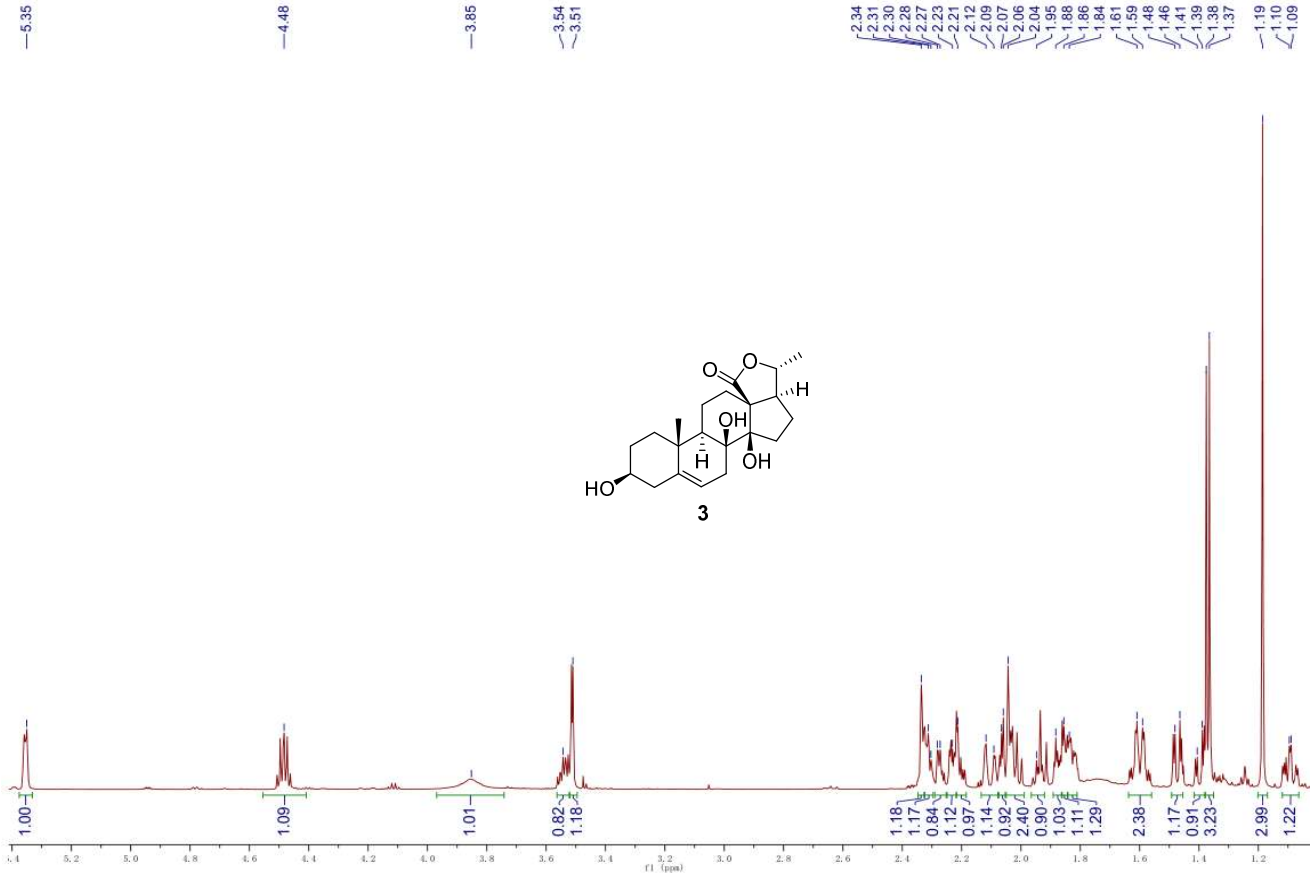

Figure S21. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **3**.

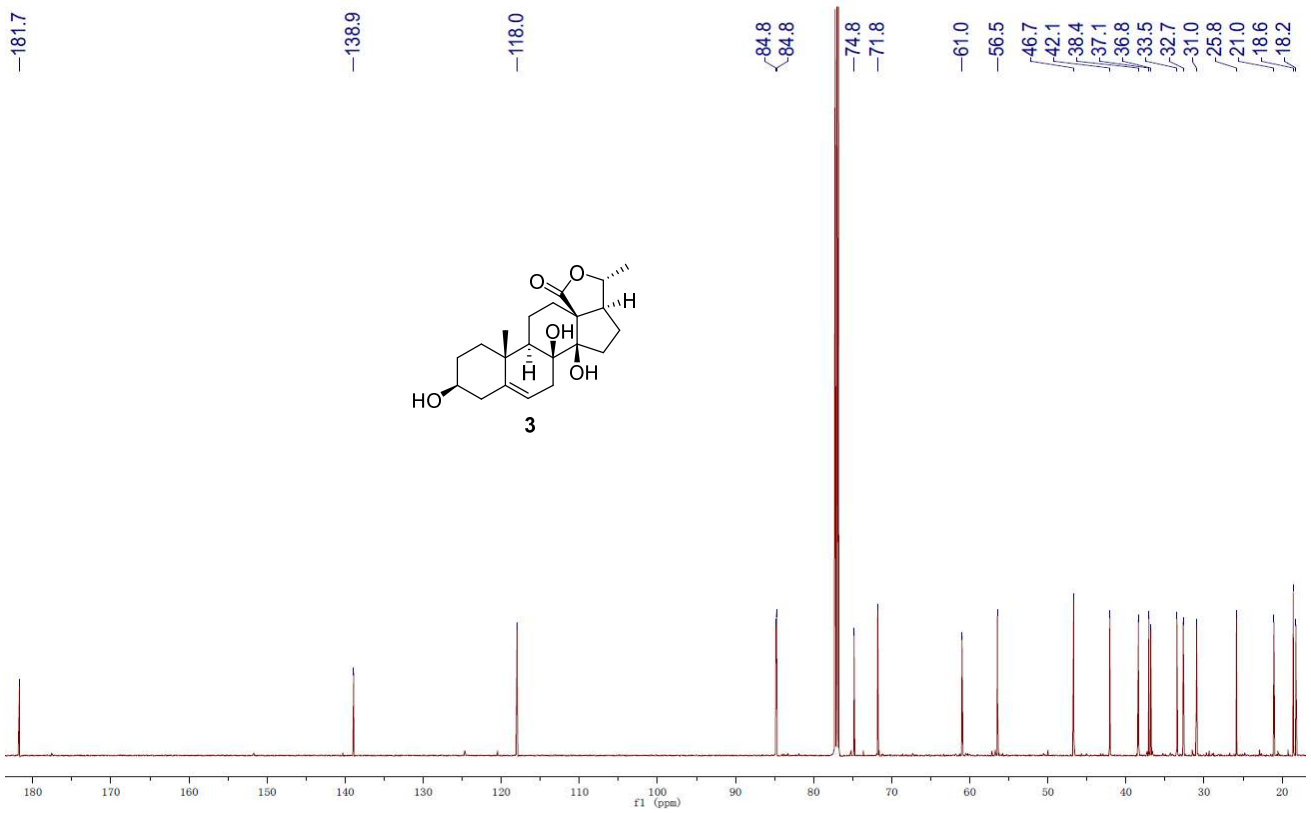

Figure S22. HSQC (600 MHz, $CDCl_3$) spectrum of **3**.

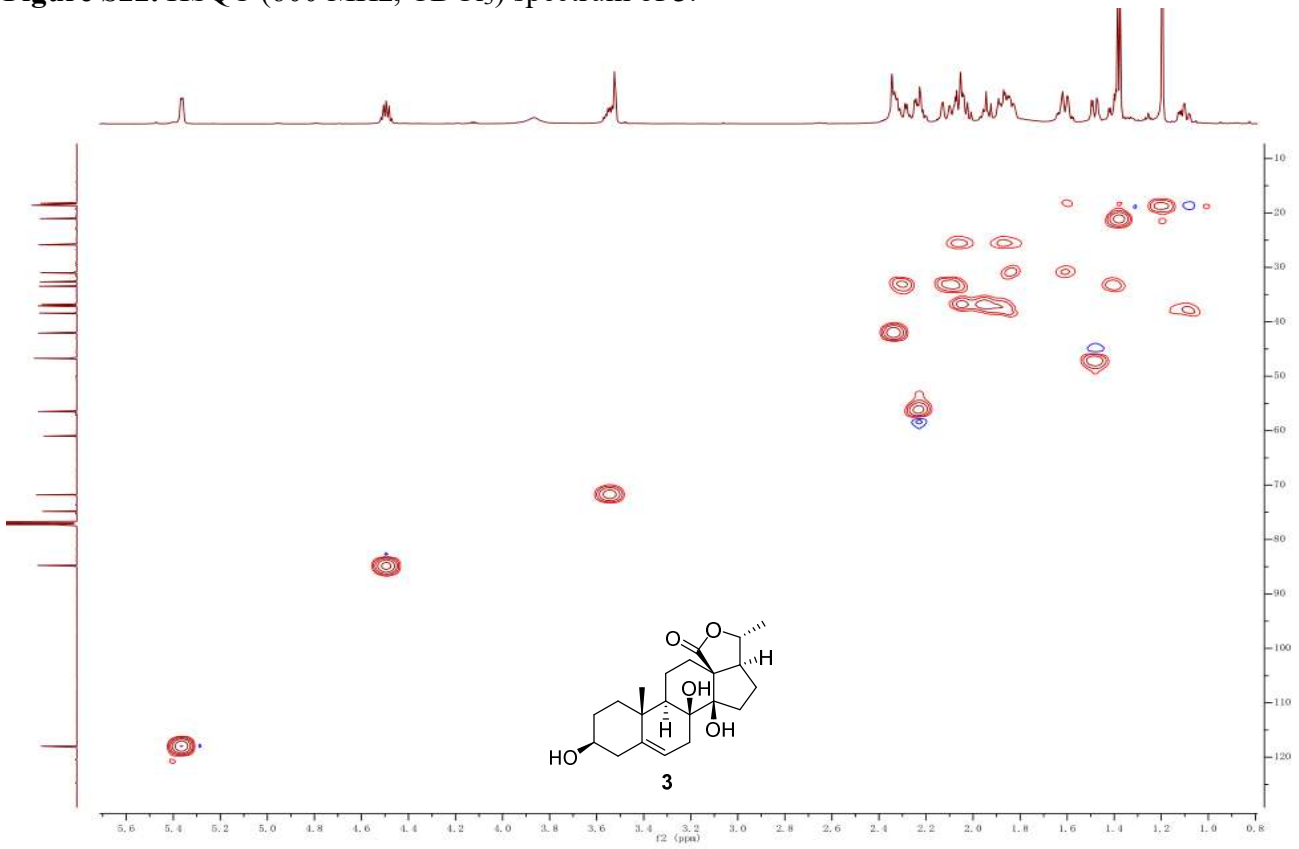

Figure S23. HMBC (600 MHz, $CDCl_3$) spectrum of **3**.

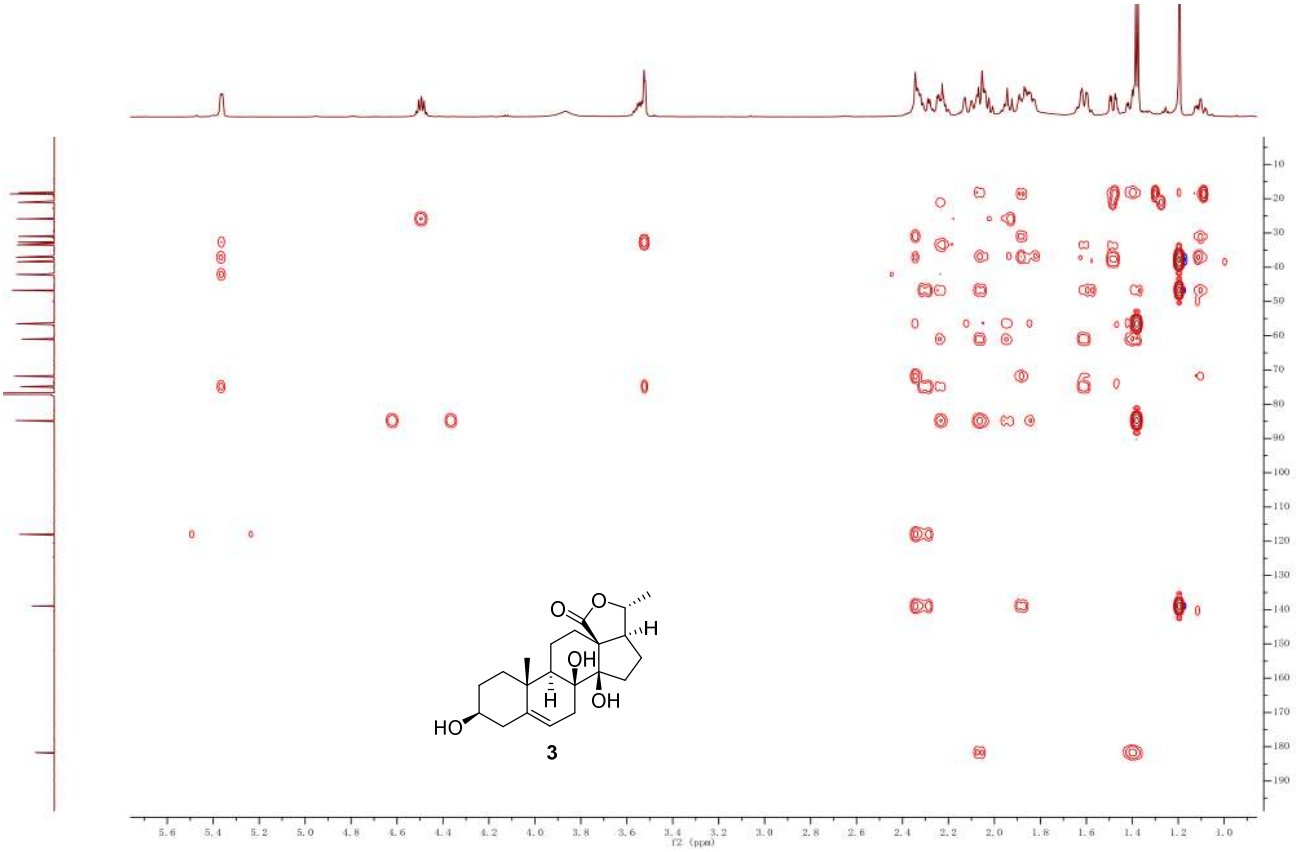

Figure S24. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **3**.

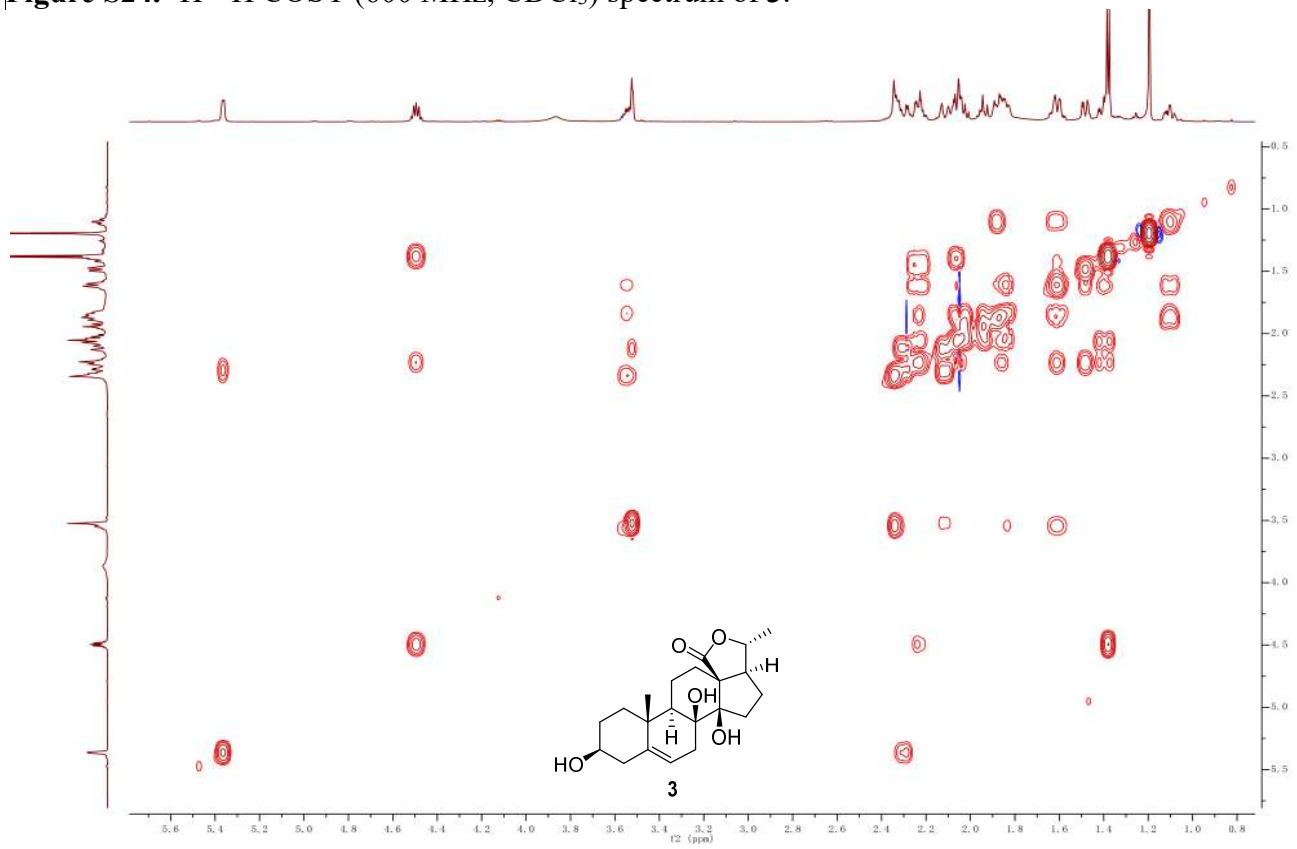

Figure S25. NOESY (600 MHz, $CDCl_3$) spectrum of **3**.

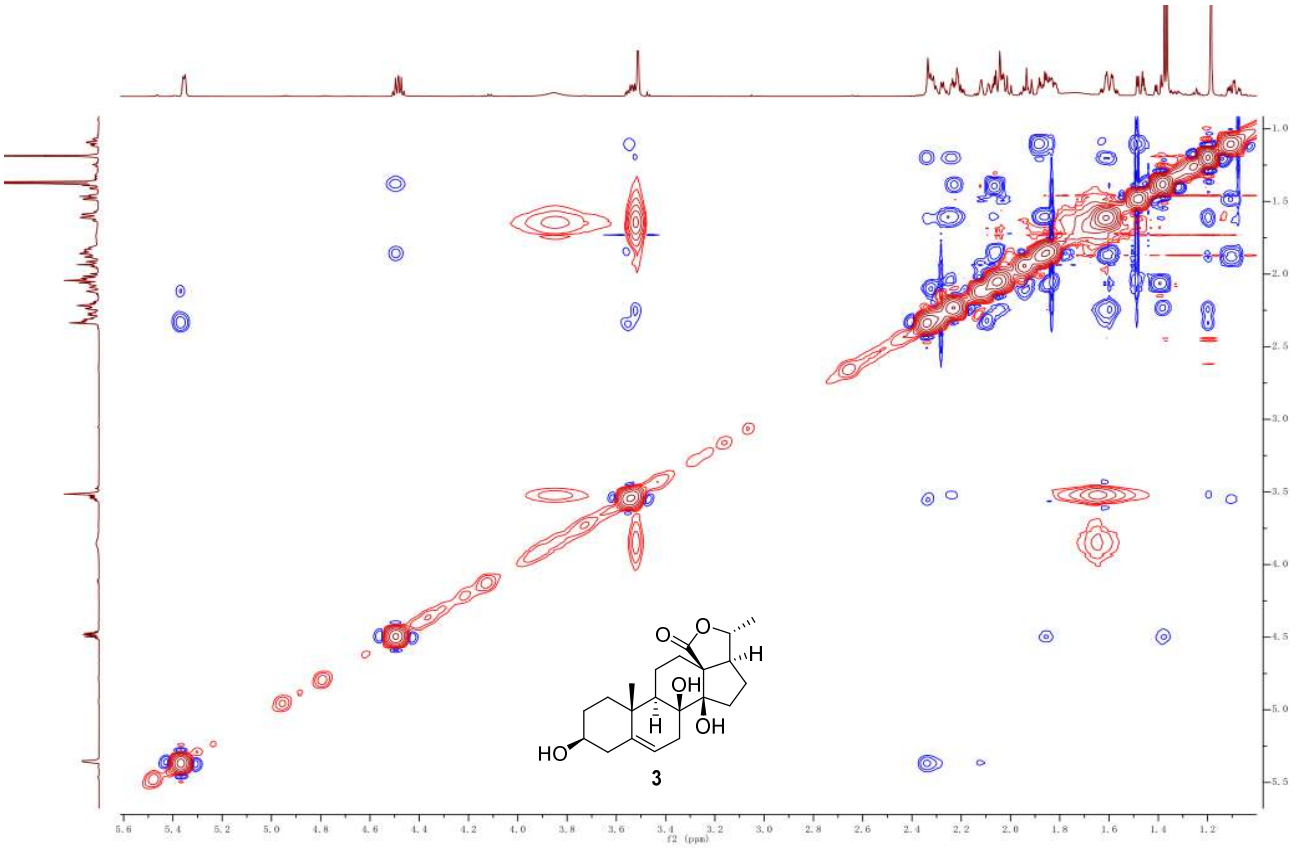

Figure S26. HRESIMS spectrum of **3.**

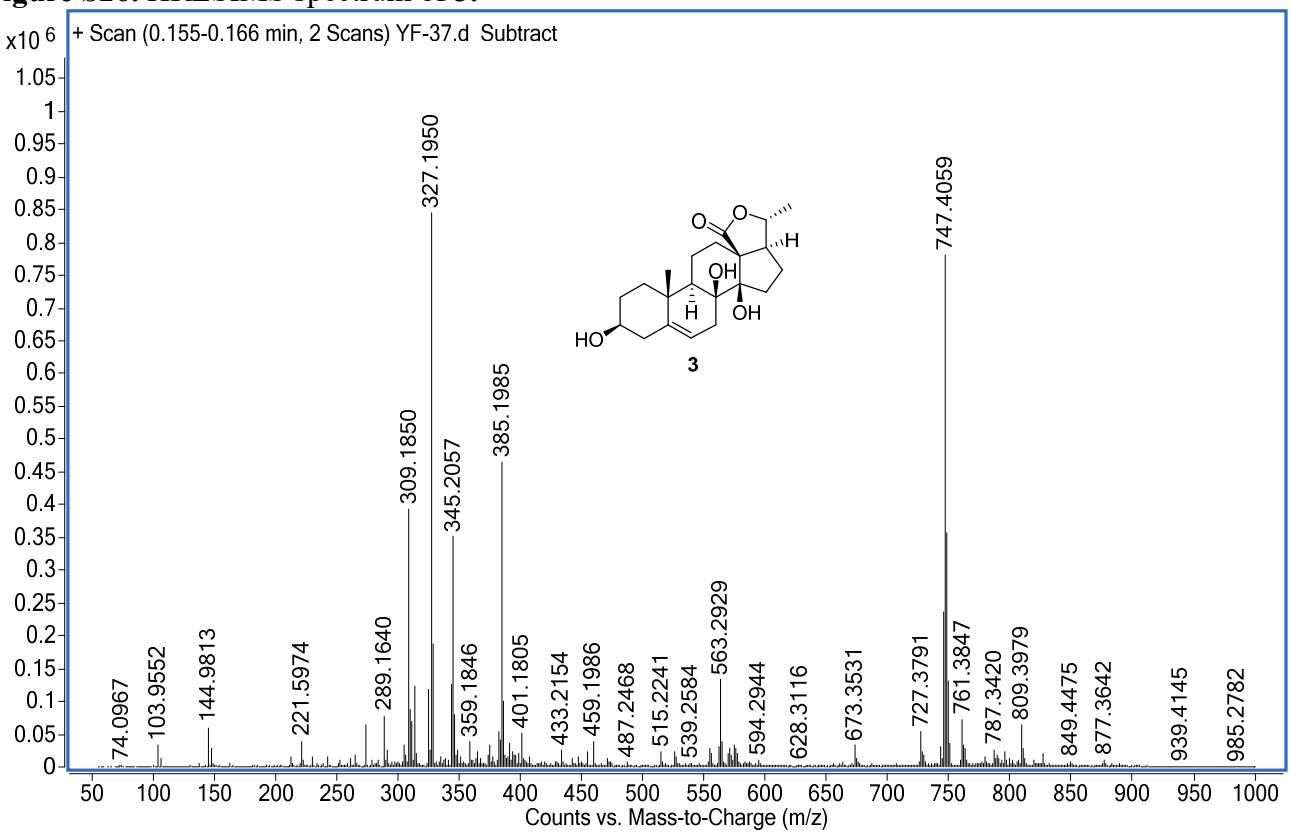

Figure S27. IR spectrum of **3**.

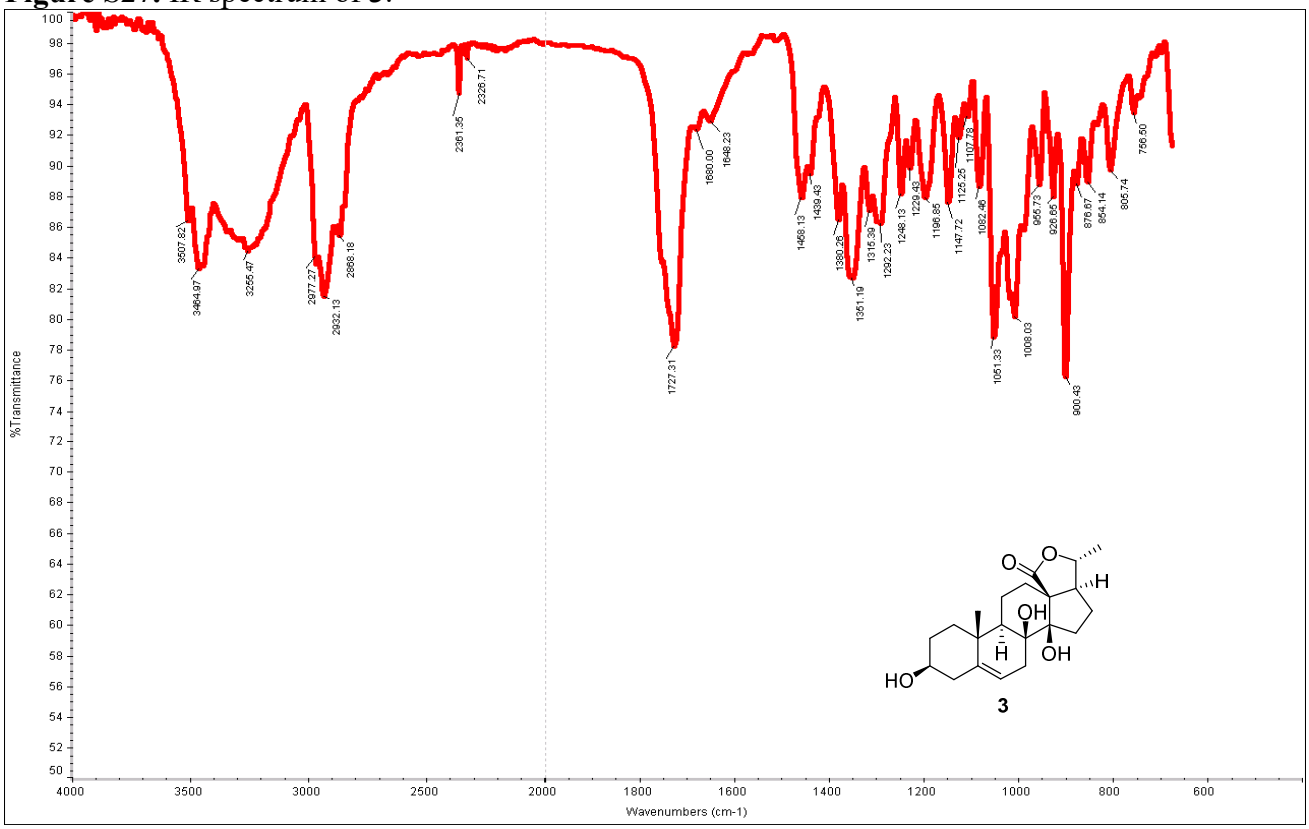

Figure S28. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4**.

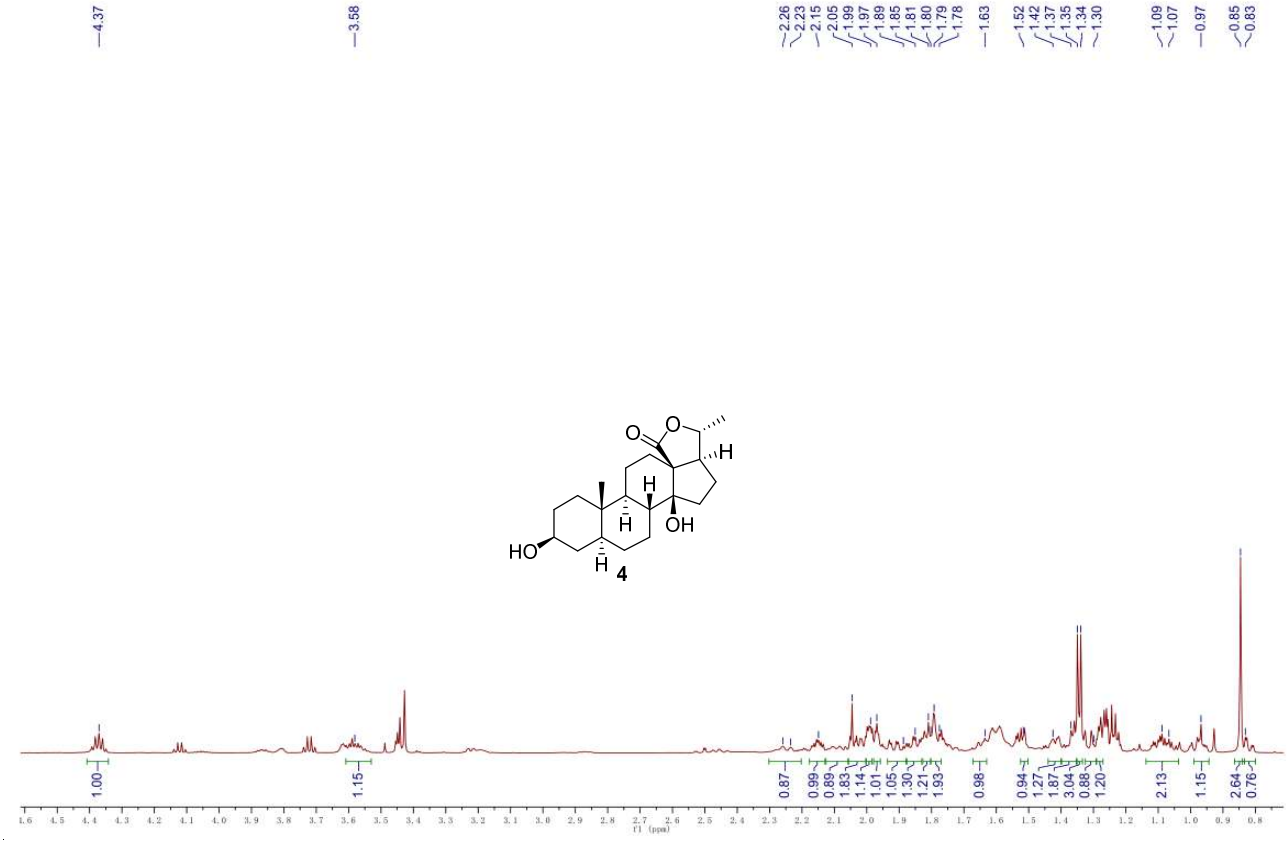

Figure S29. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **4**.

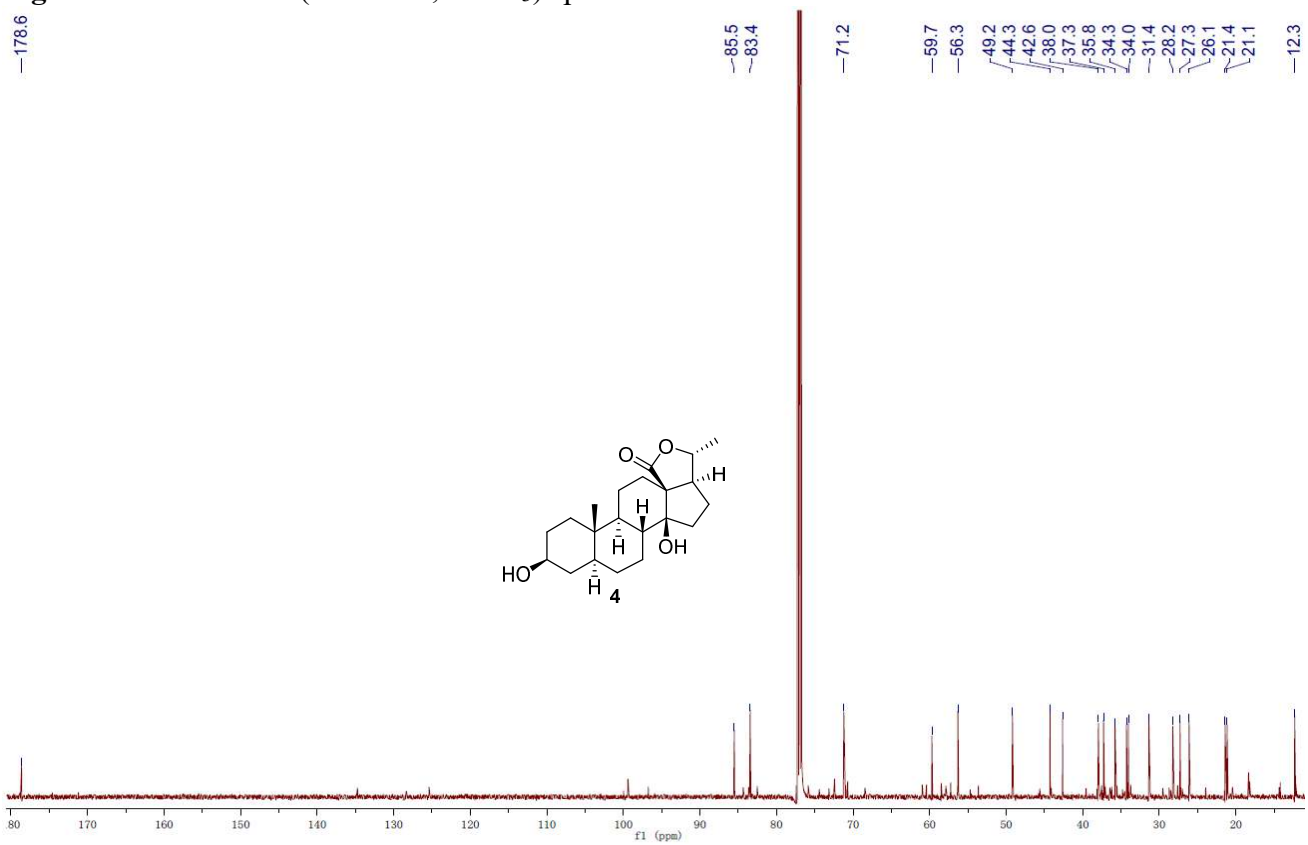

Figure S30. HSQC (600 MHz, $CDCl_3$) spectrum of **4**.

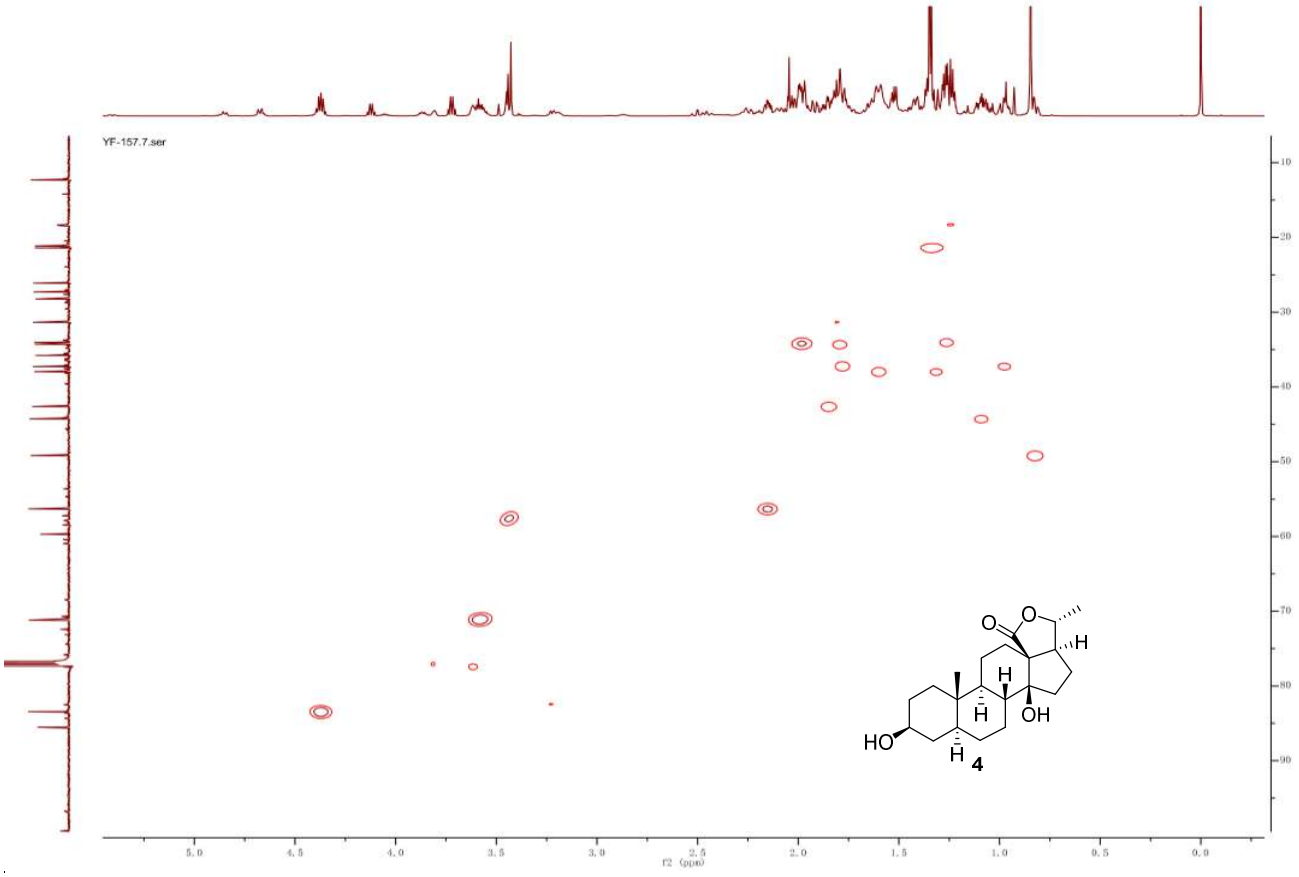

Figure S31. HMBC (600 MHz, $CDCl_3$) spectrum of **4**.

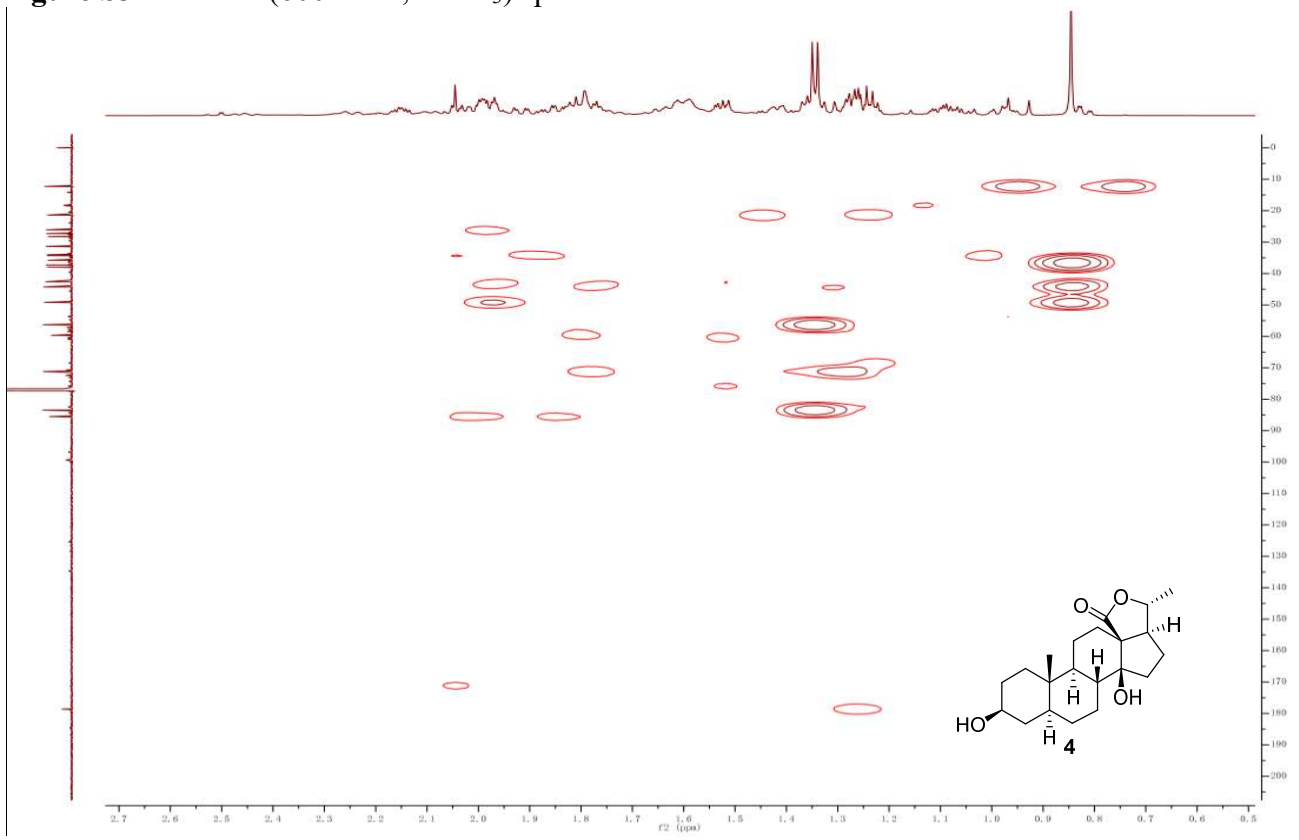

Figure S32. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **4**.

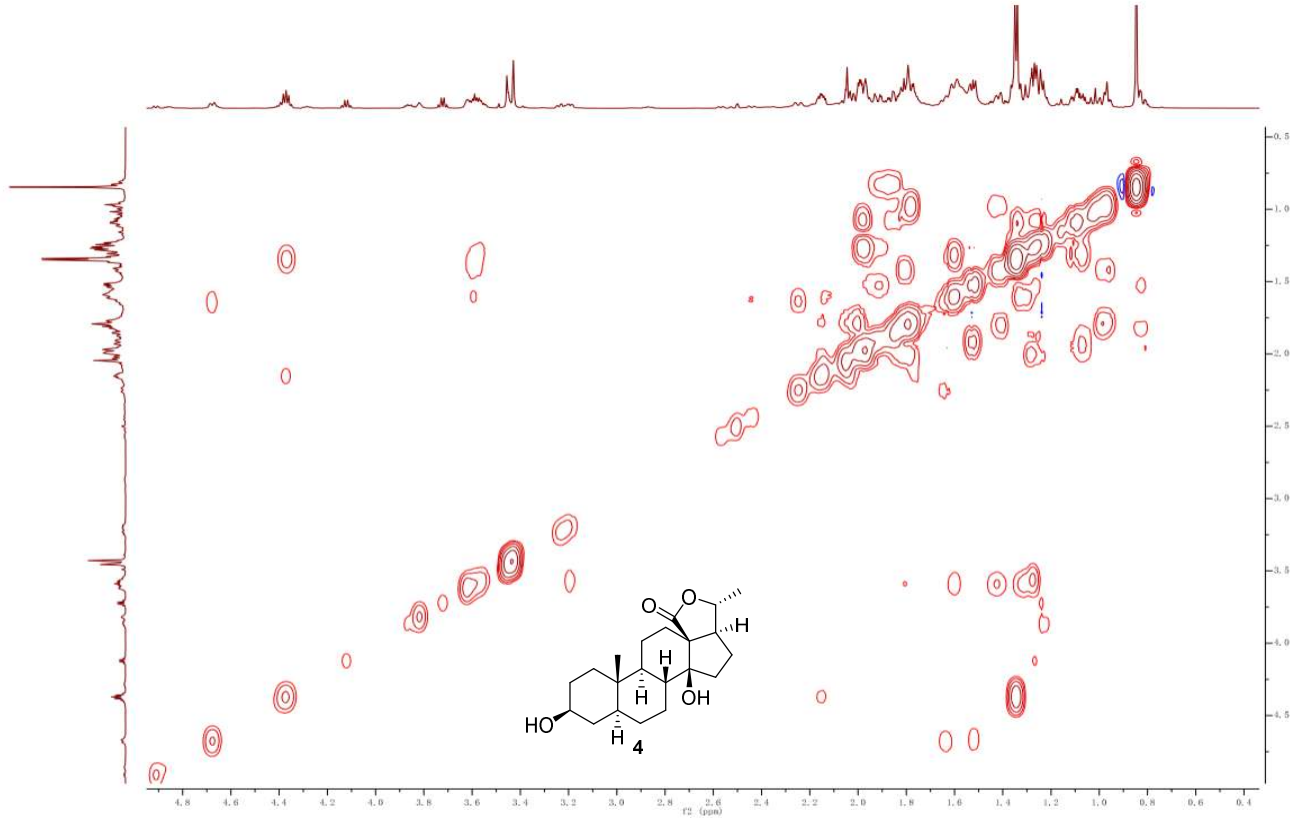

Figure S33. NOESY (600 MHz, $CDCl_3$) spectrum of **4**.

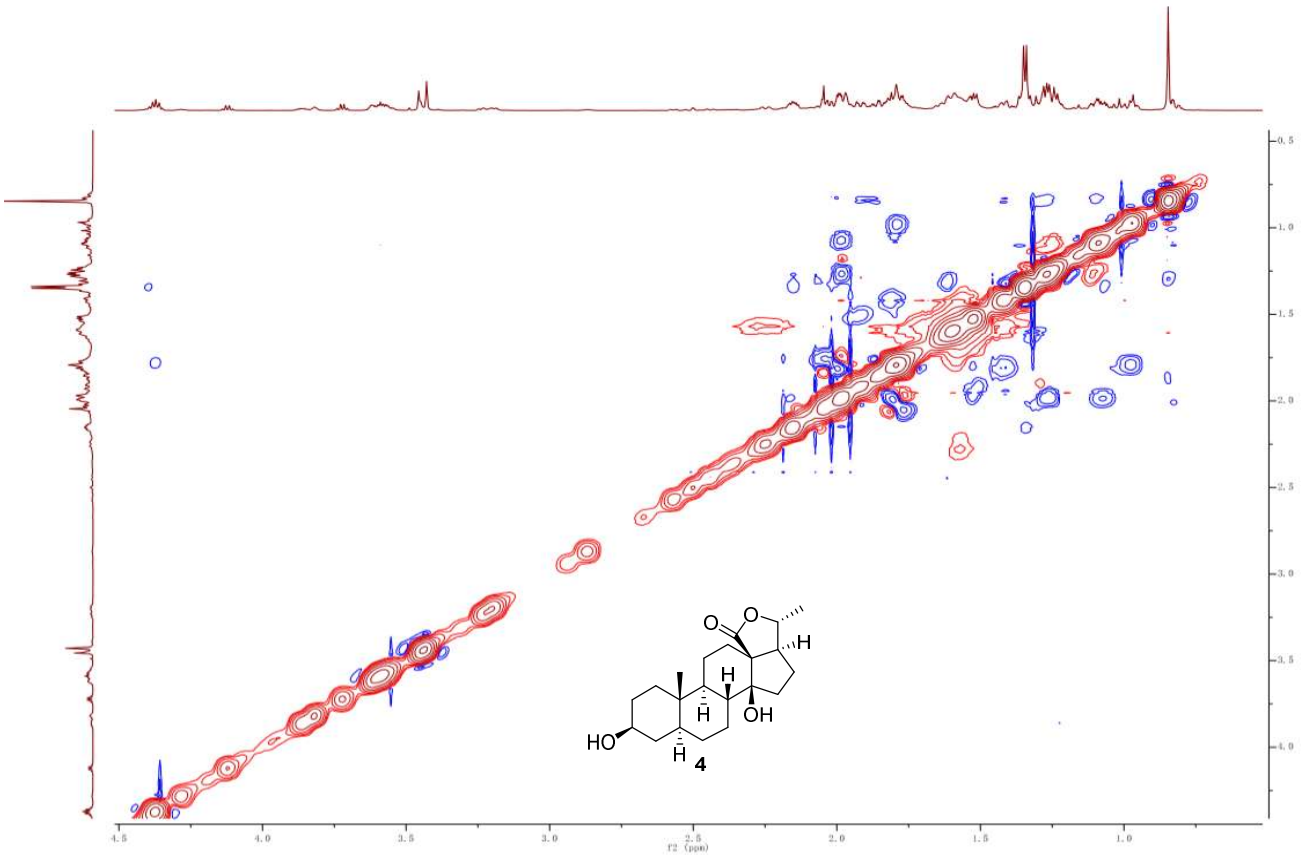

Figure S34. HRESIMS spectrum of **4**.

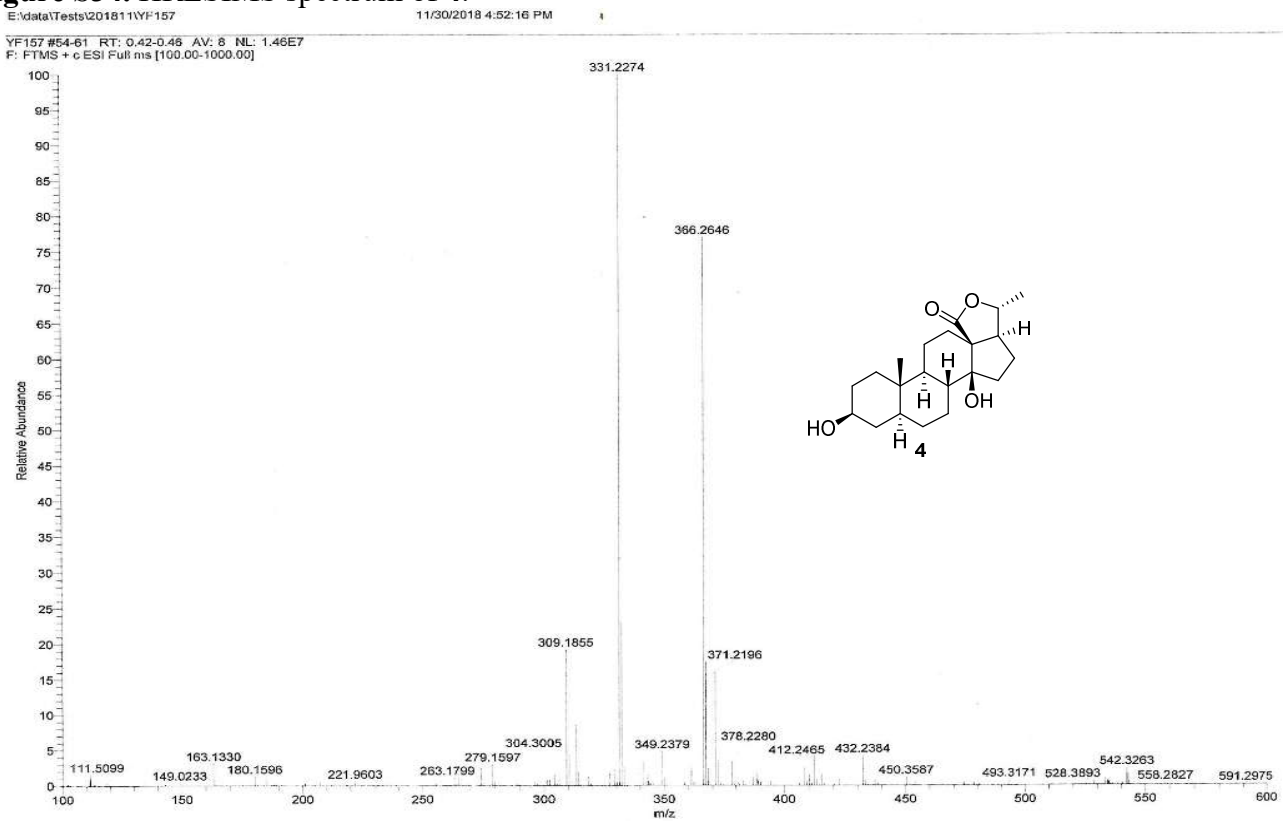

Figure S35. IR spectrum of **4**.

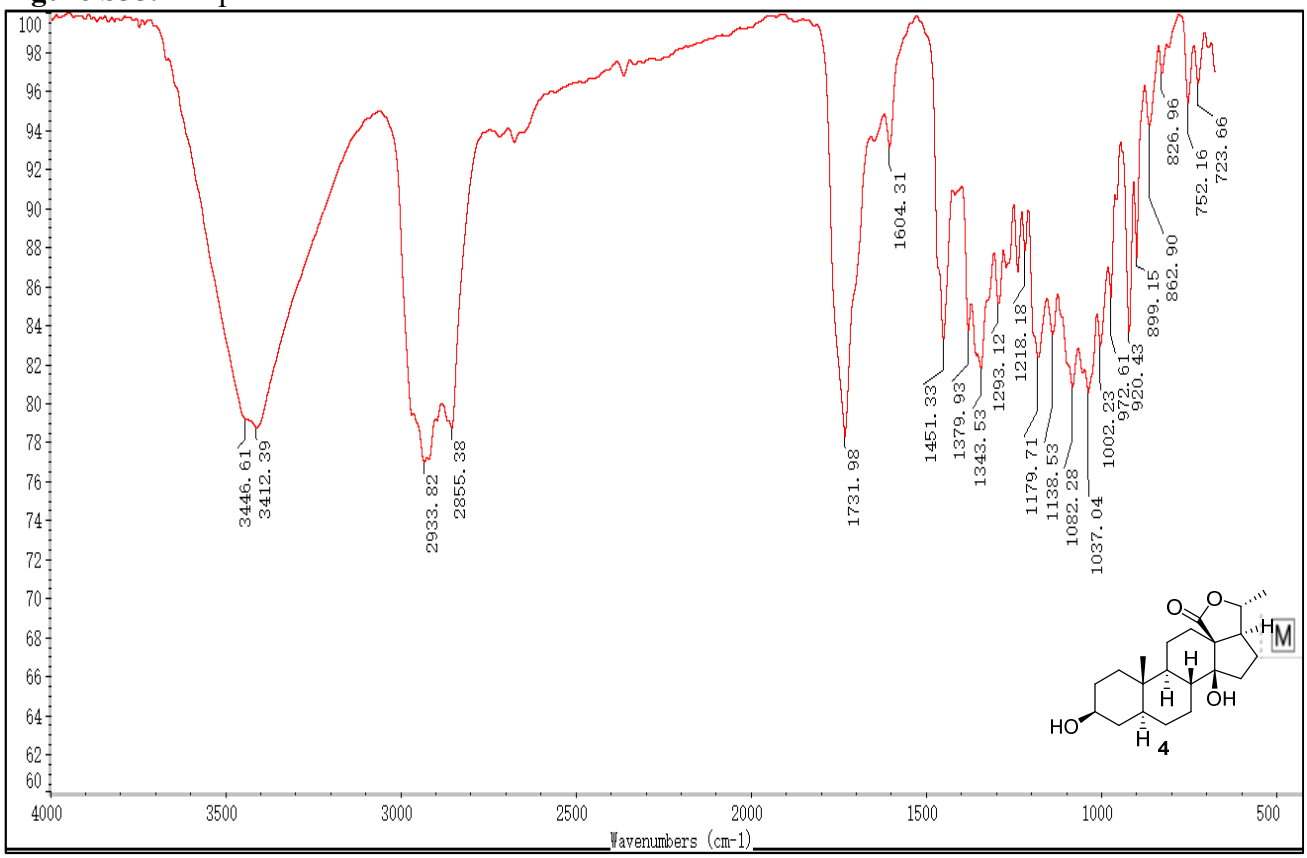

Figure S36. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5**.

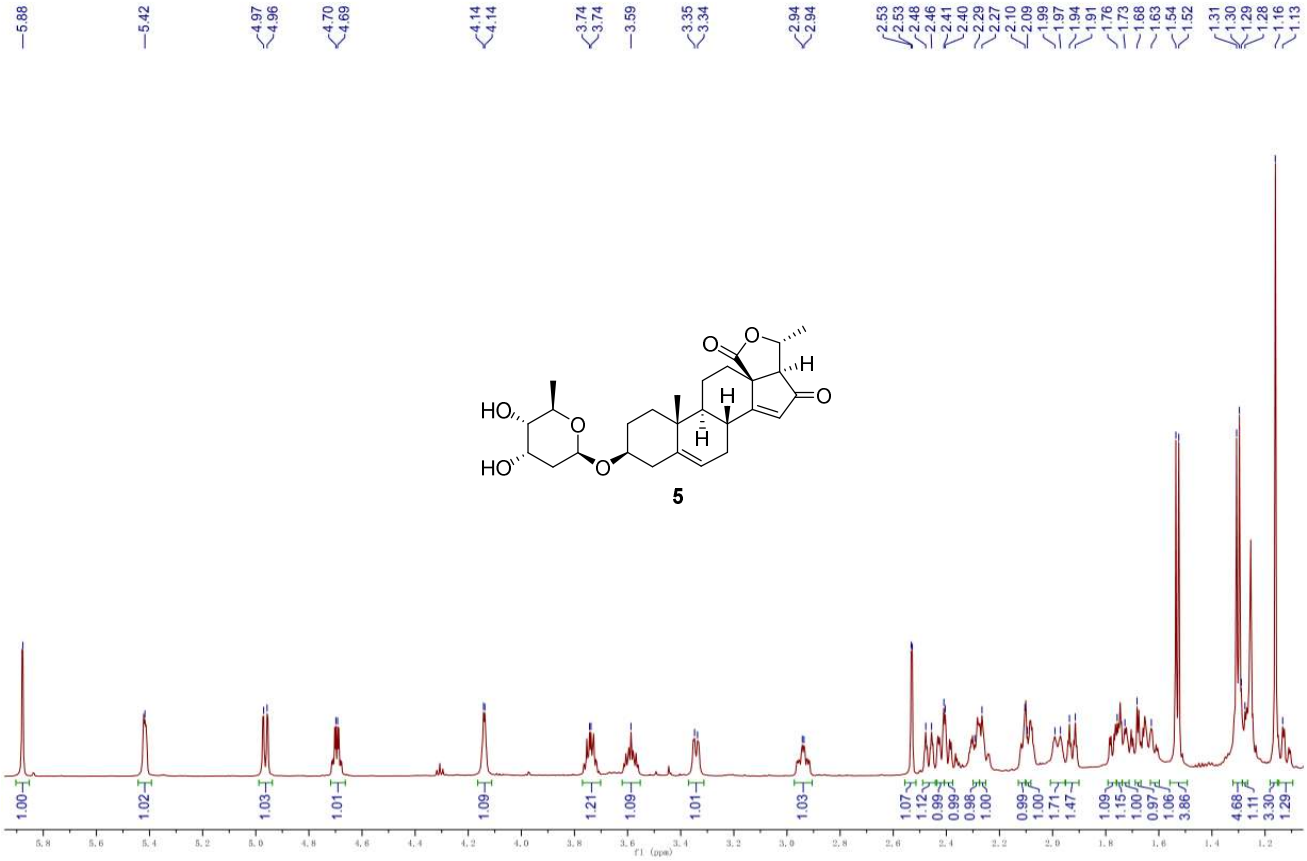

Figure S37. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **5**.

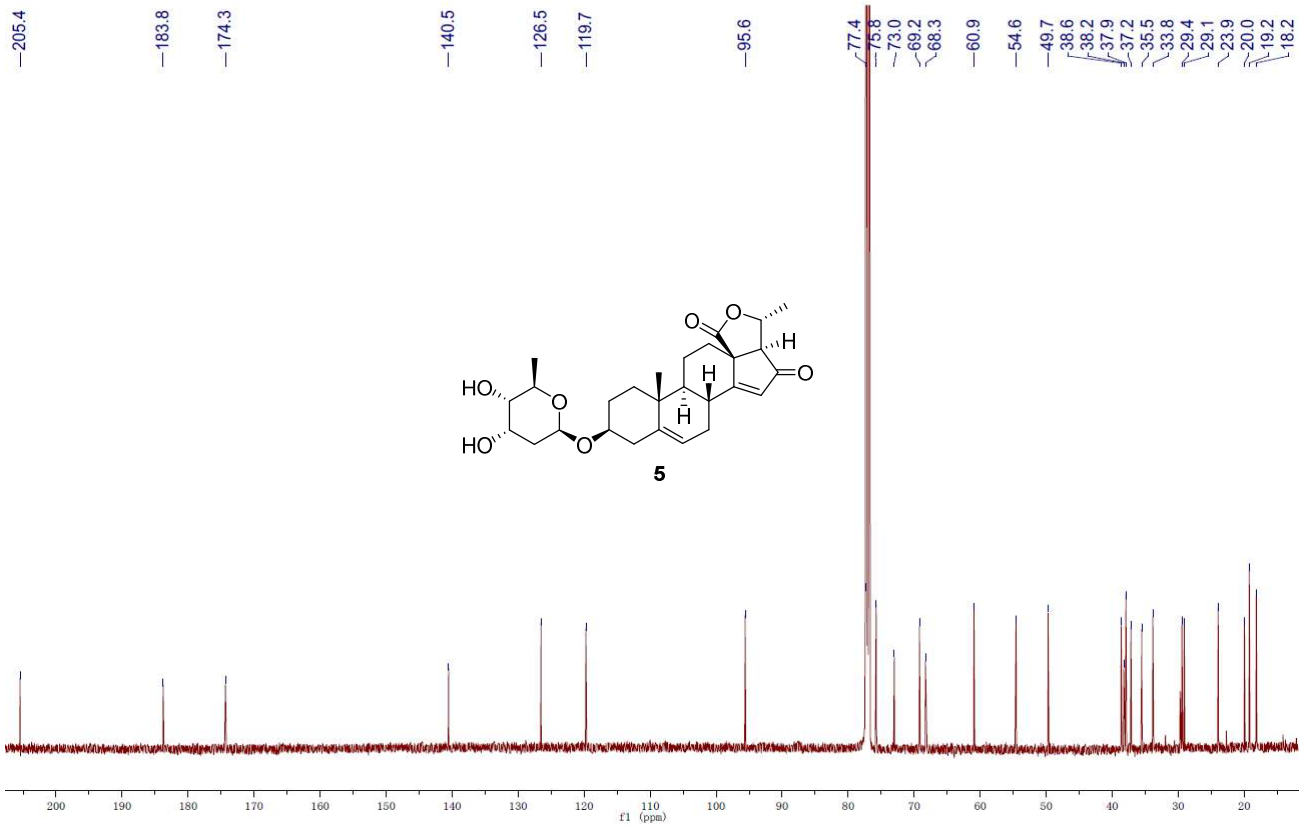

Figure S38. HSQC (600 MHz, $CDCl_3$) spectrum of **5**.

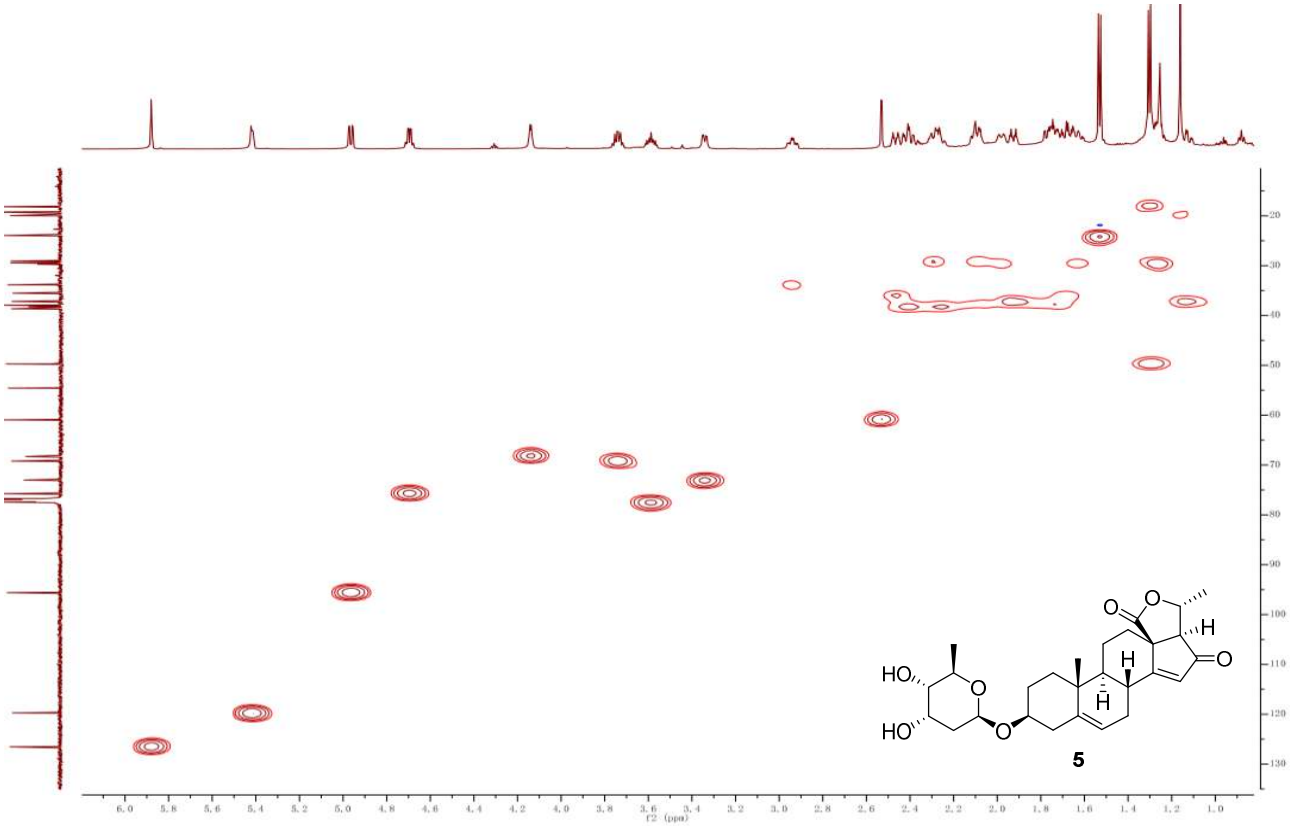

Figure S39. HMBC (600 MHz, $CDCl_3$) spectrum of **5**.

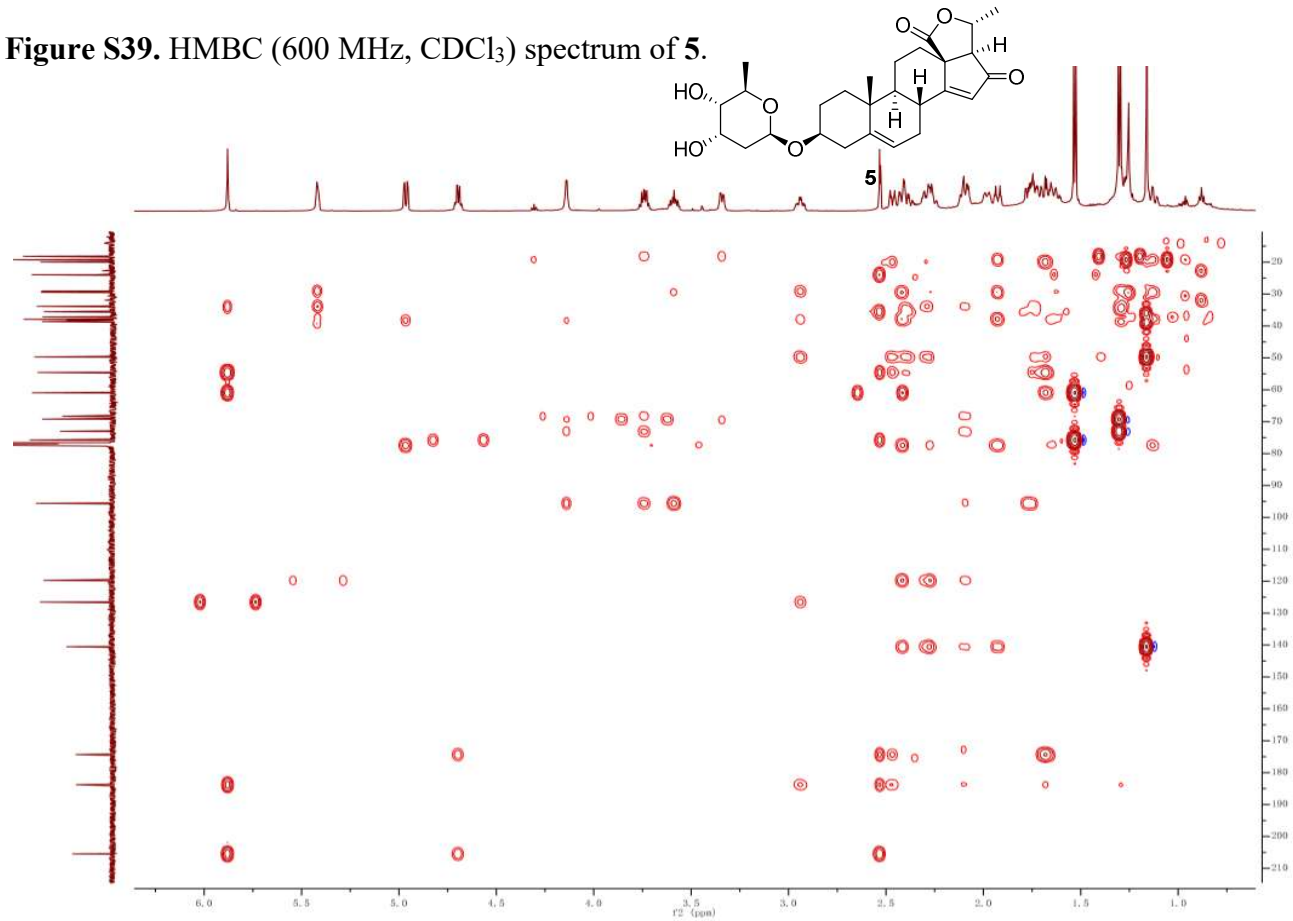

Figure S40. ^{1}H–^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **5**.

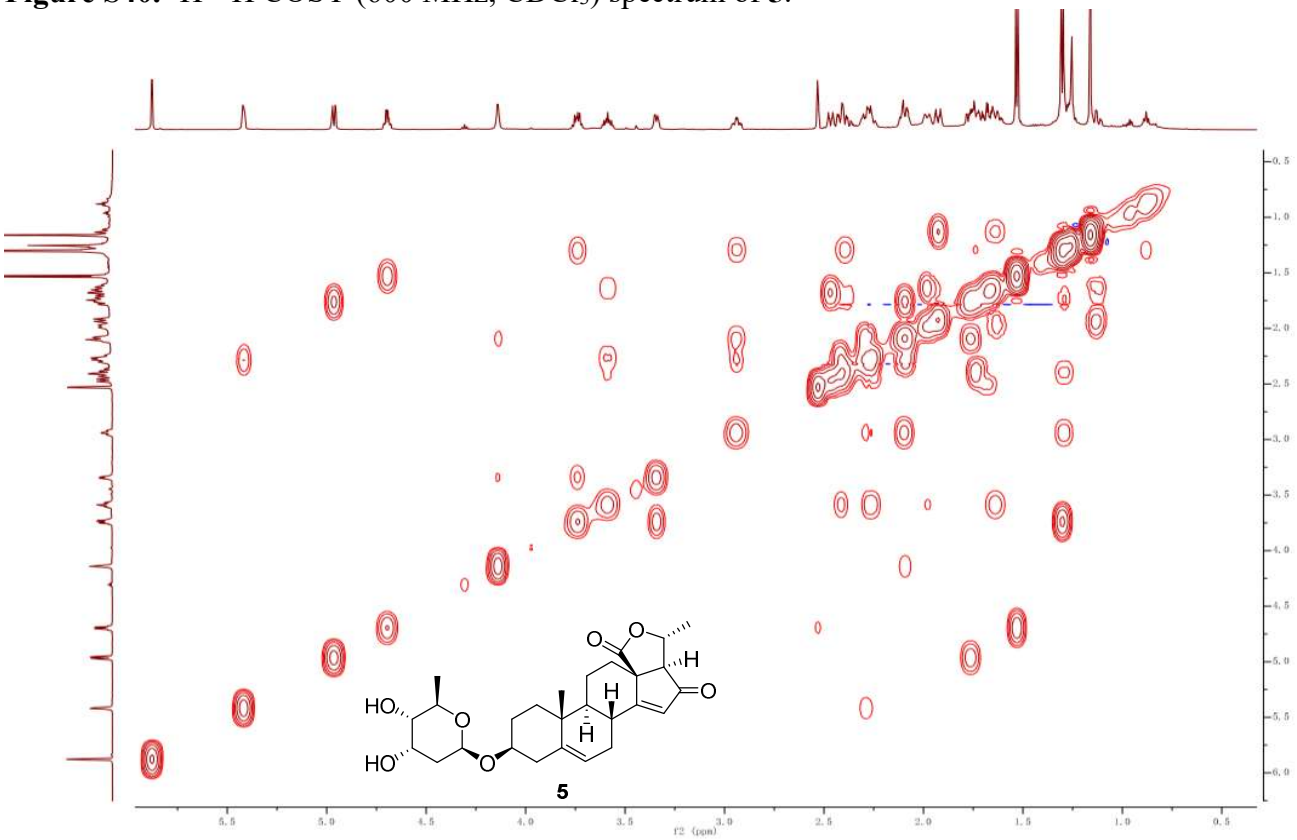

Figure S41. NOESY (600 MHz, $CDCl_3$) spectrum of **5**.

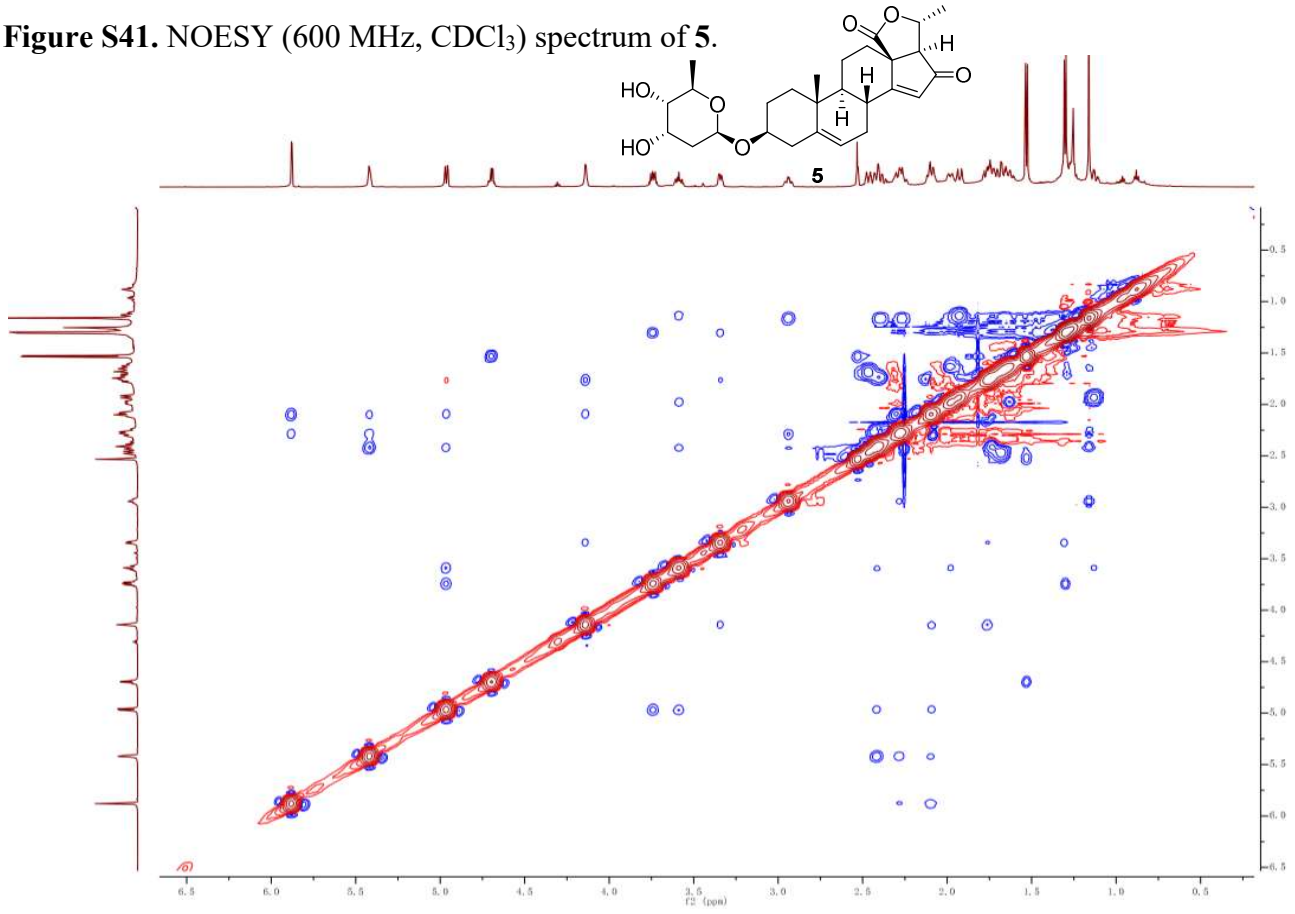

Figure S42. HRESIMS spectrum of **5**.

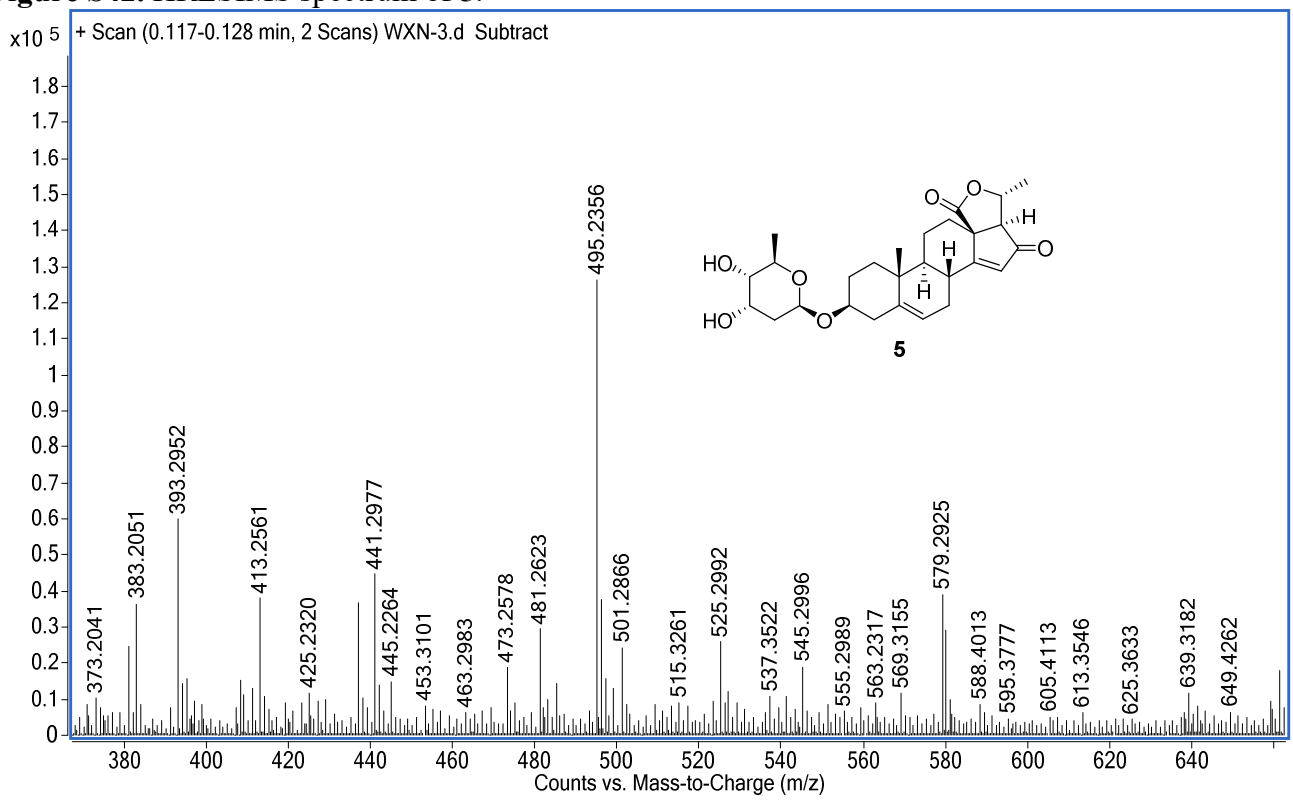

Figure S43. IR spectrum of **5**.

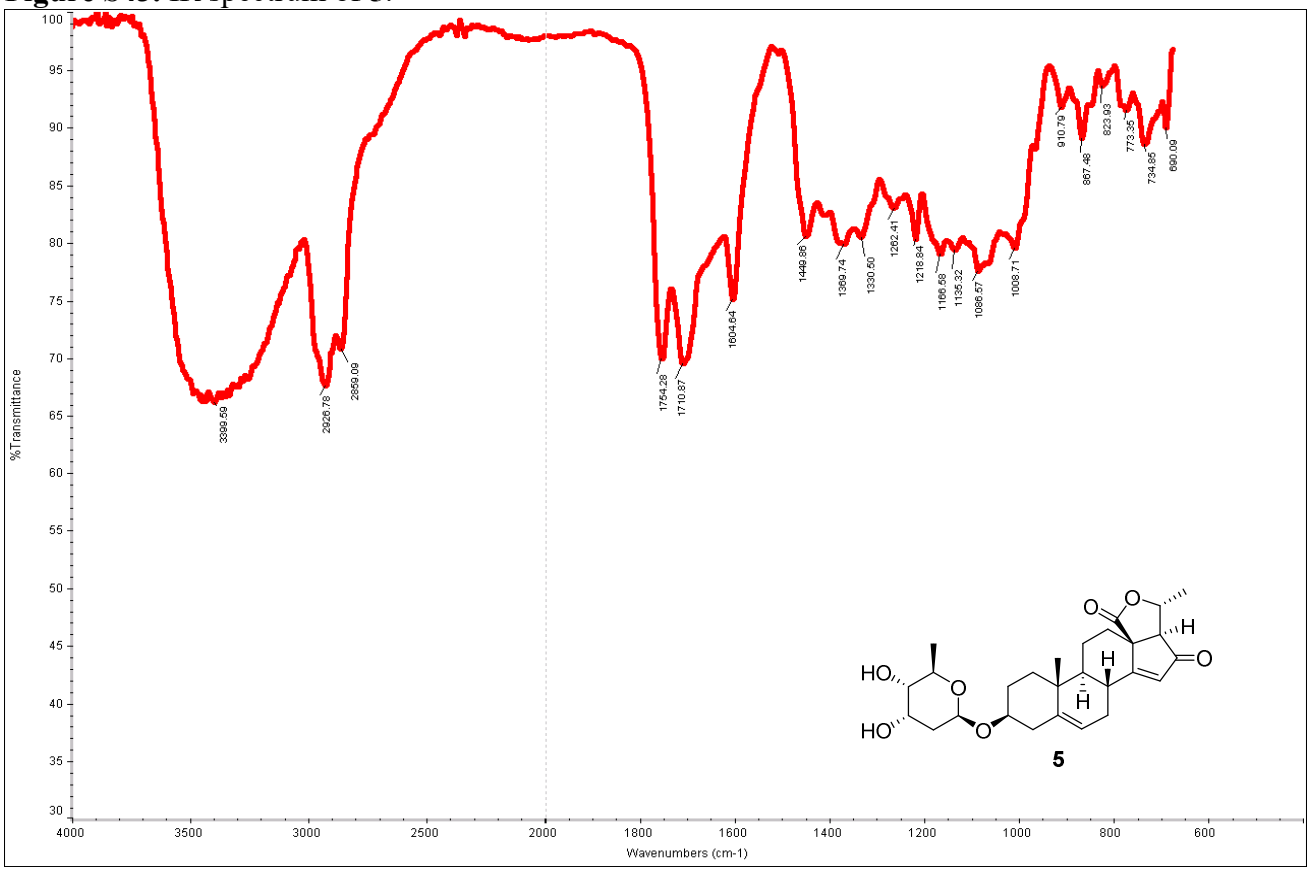

Figure S44. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6**.

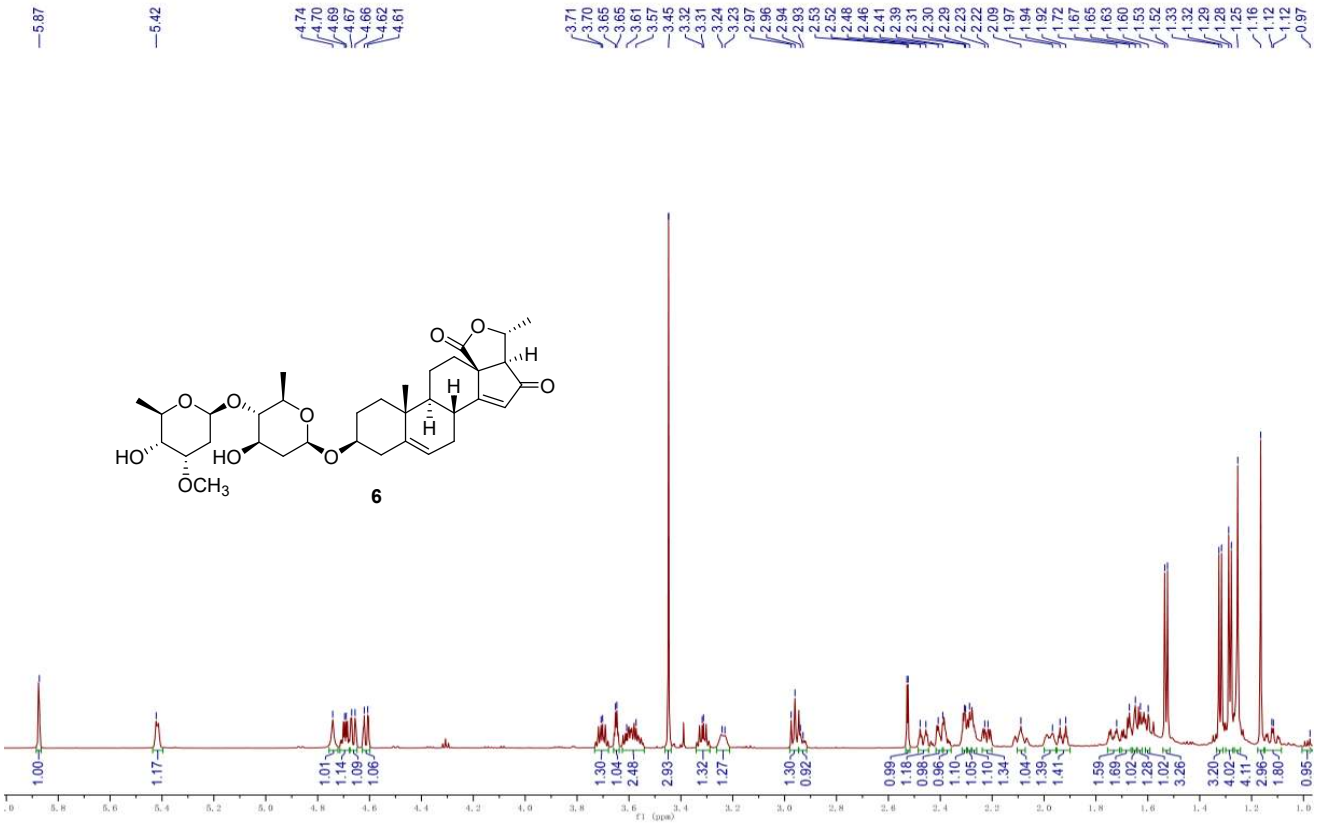

Figure S45. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **6**.

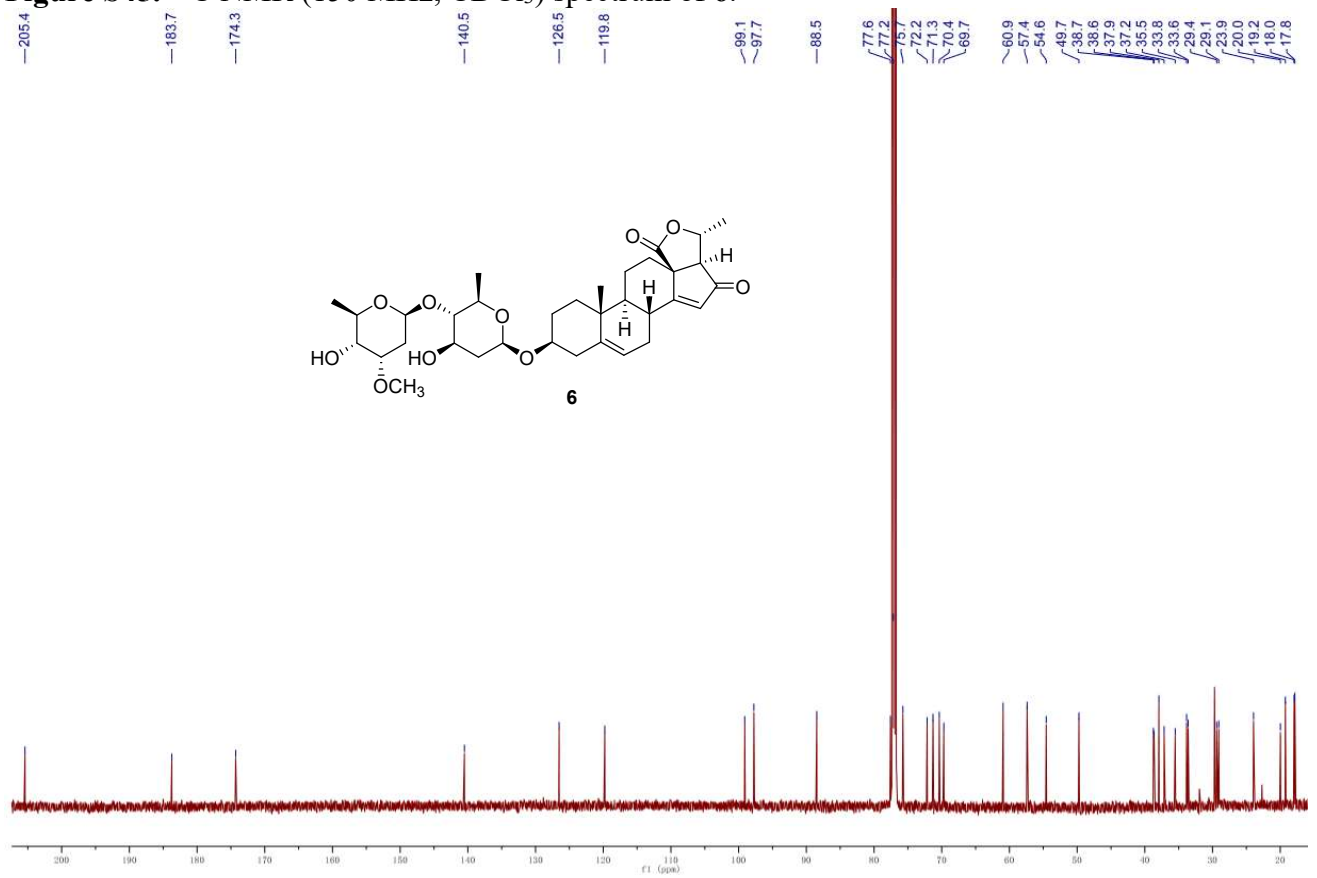

Figure S46. HSQC (600 MHz, $CDCl_3$) spectrum of **6**.

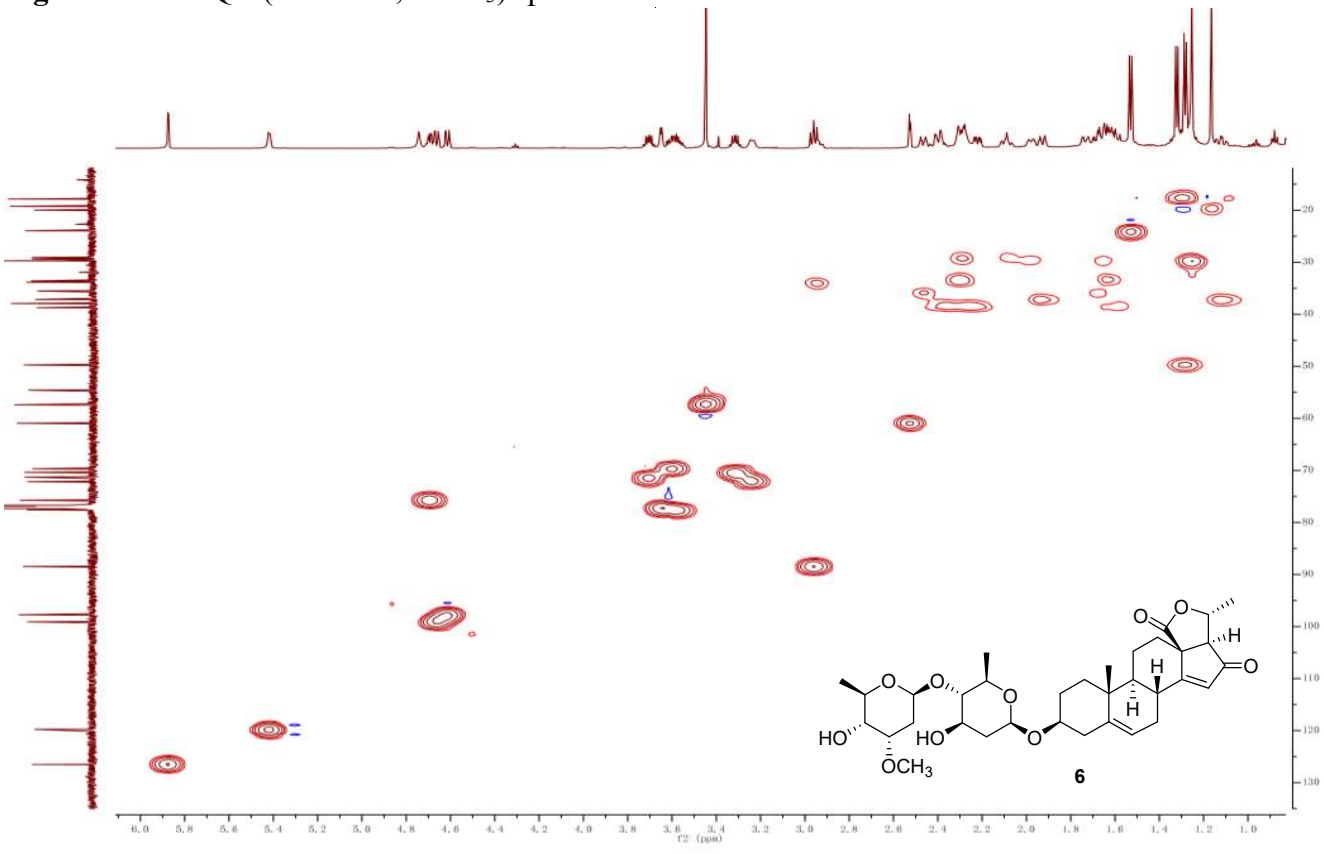

Figure S47. HMBC (600 MHz, $CDCl_3$) spectrum of **6**.

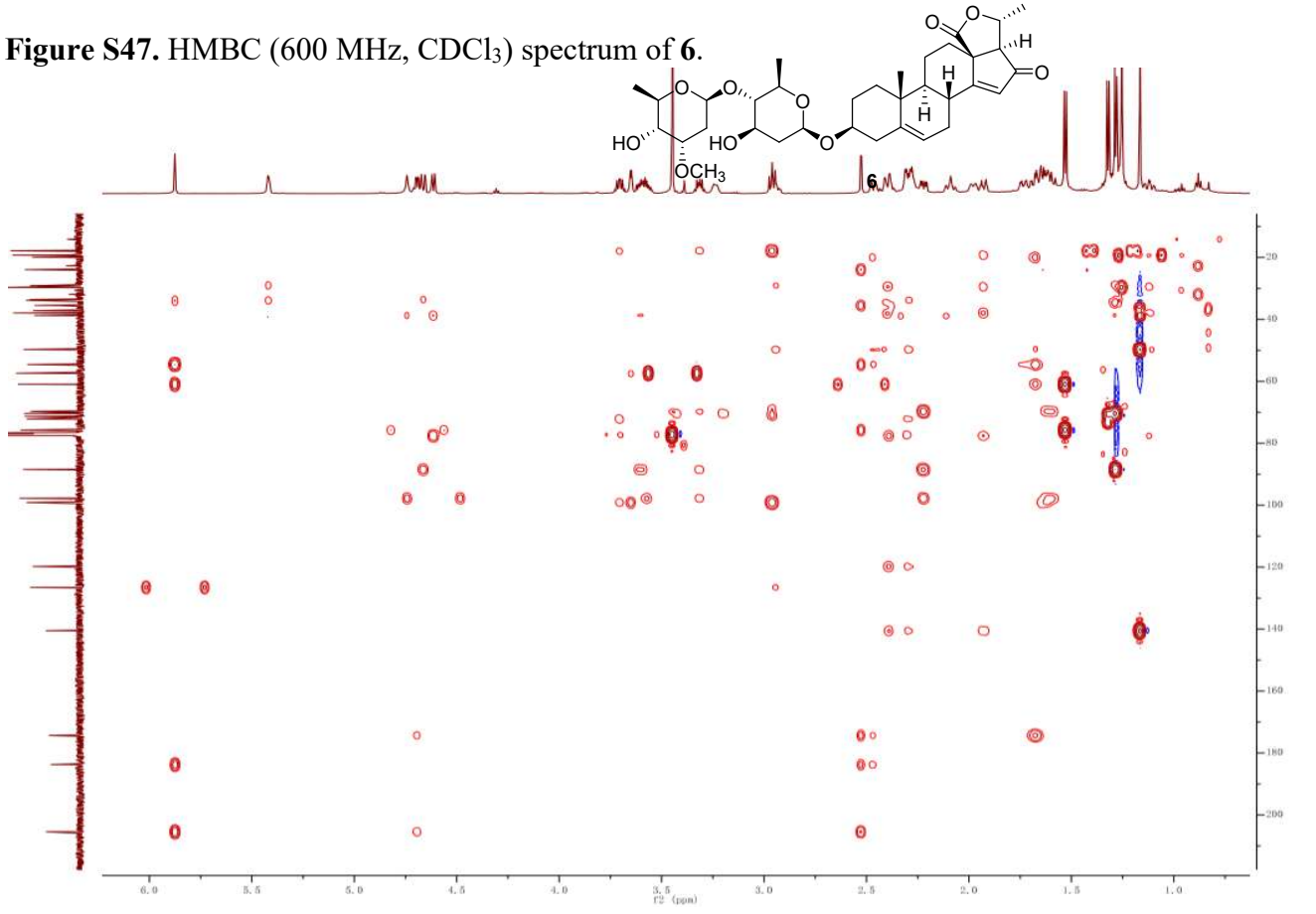

Figure S48. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **6**.

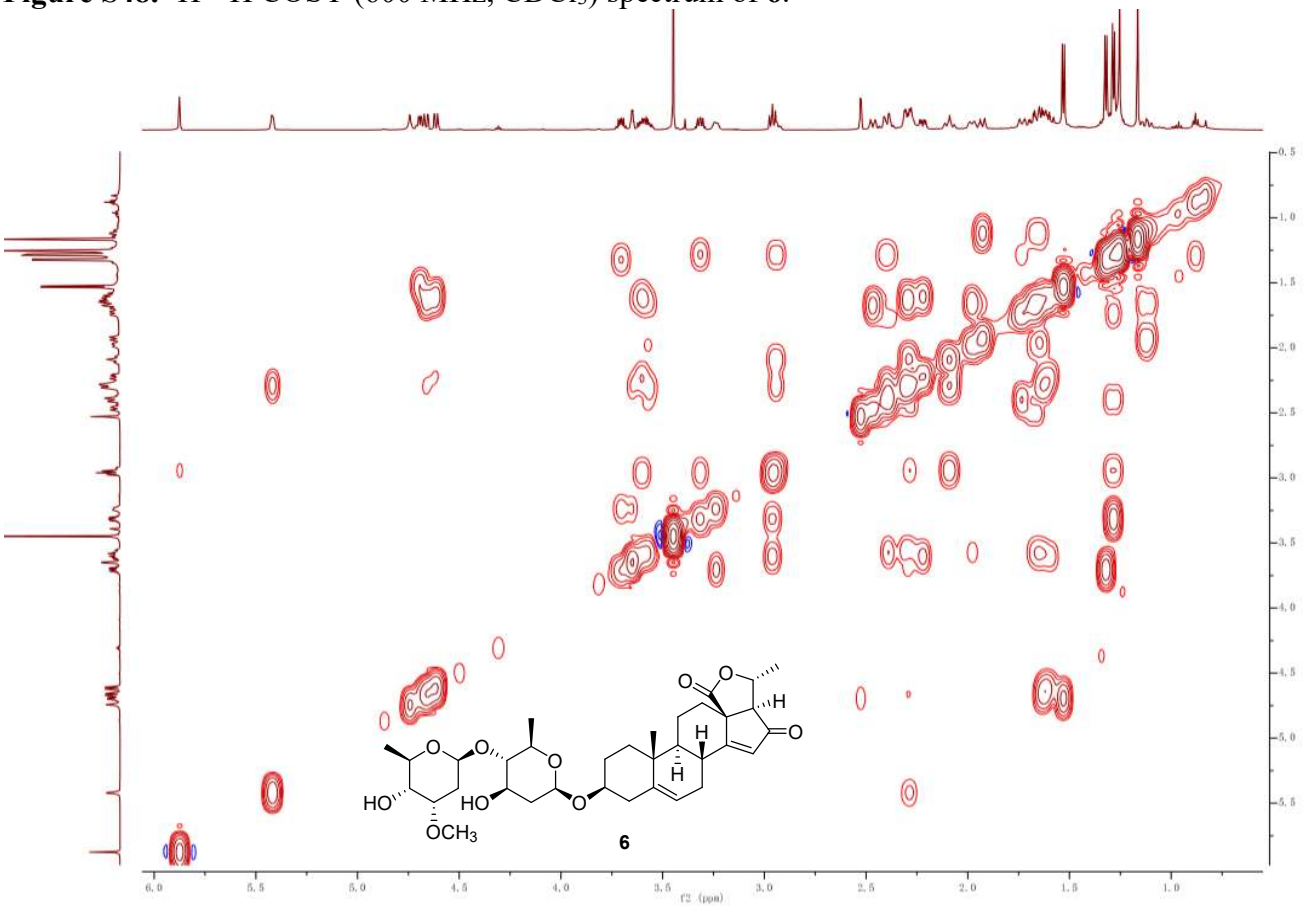

Figure S49. NOESY (600 MHz, $CDCl_3$) spectrum of **6**.

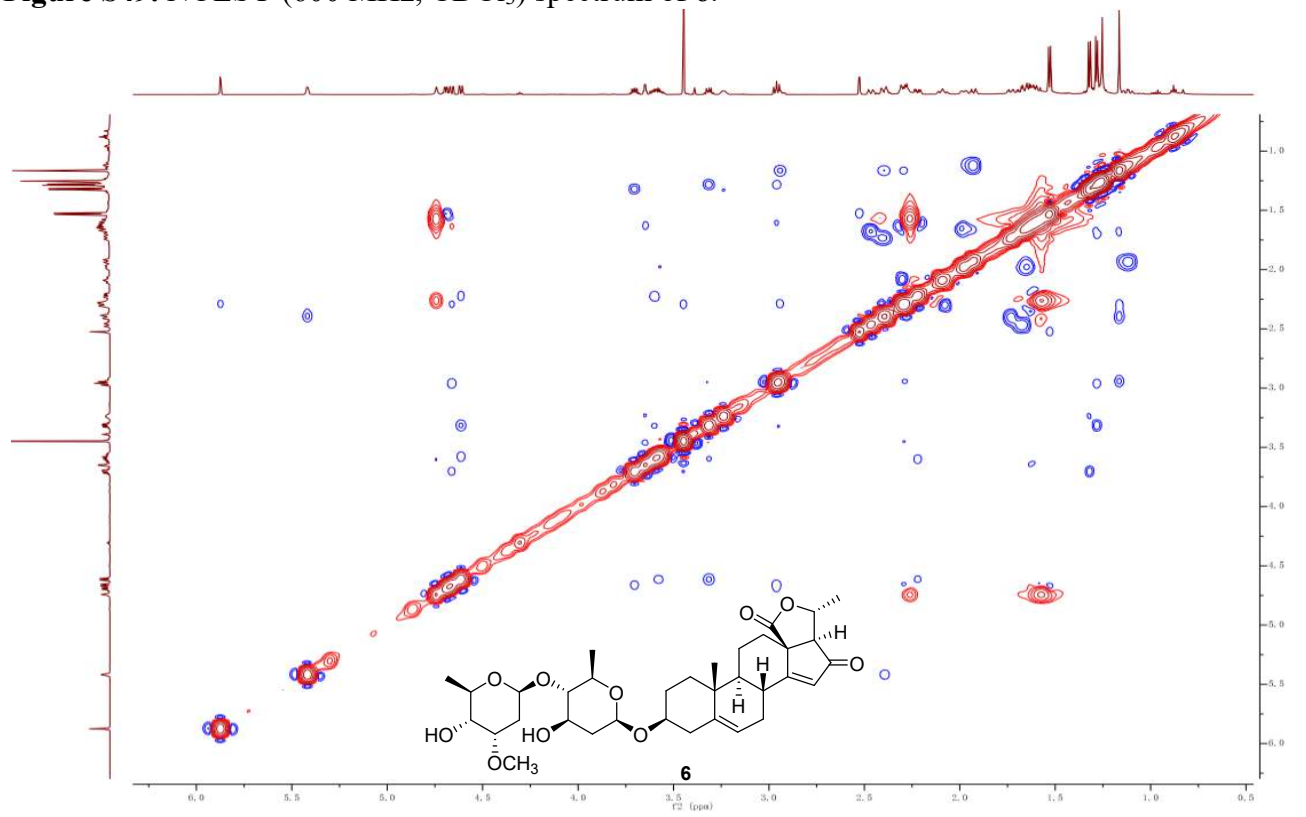

Figure S50. HRESIMS spectrum of **6**.

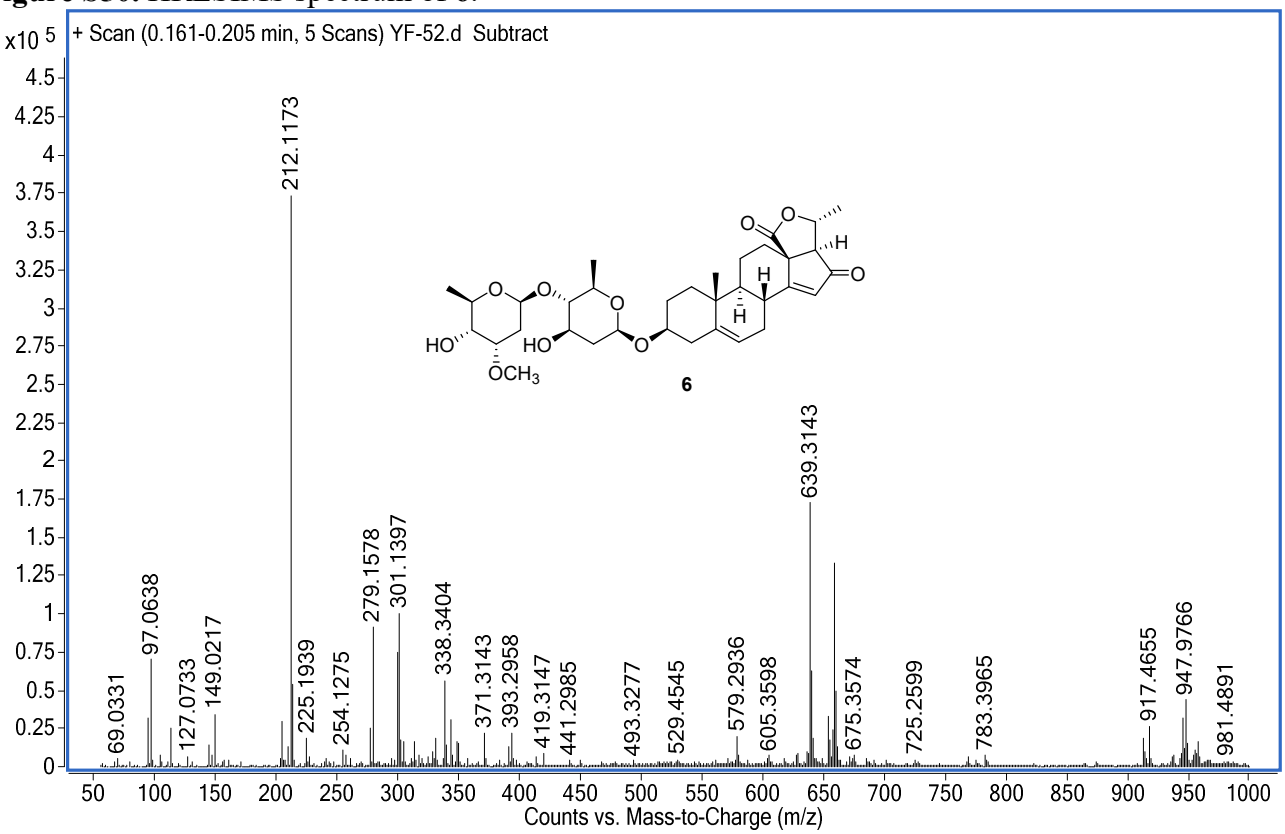

Figure S51. IR spectrum of **6**.

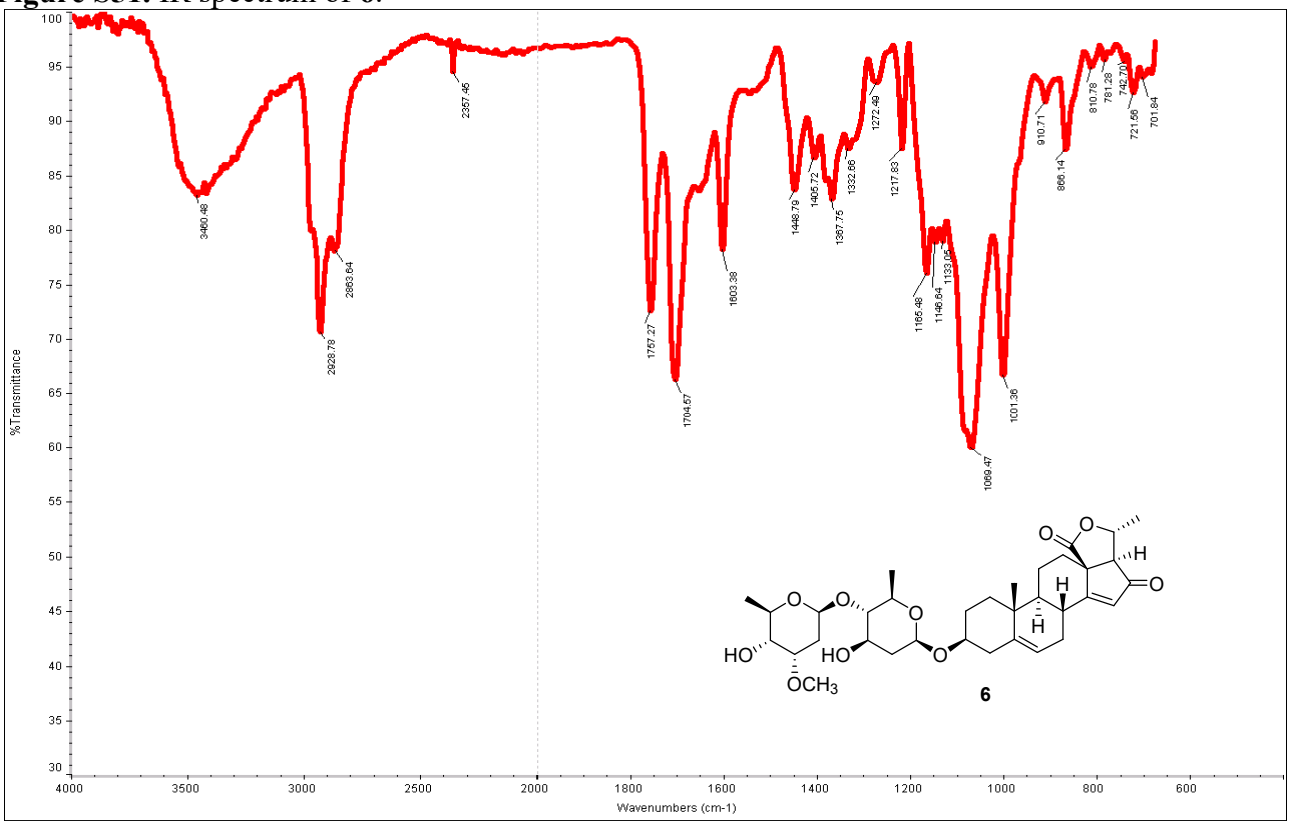

Figure S52. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **7**.

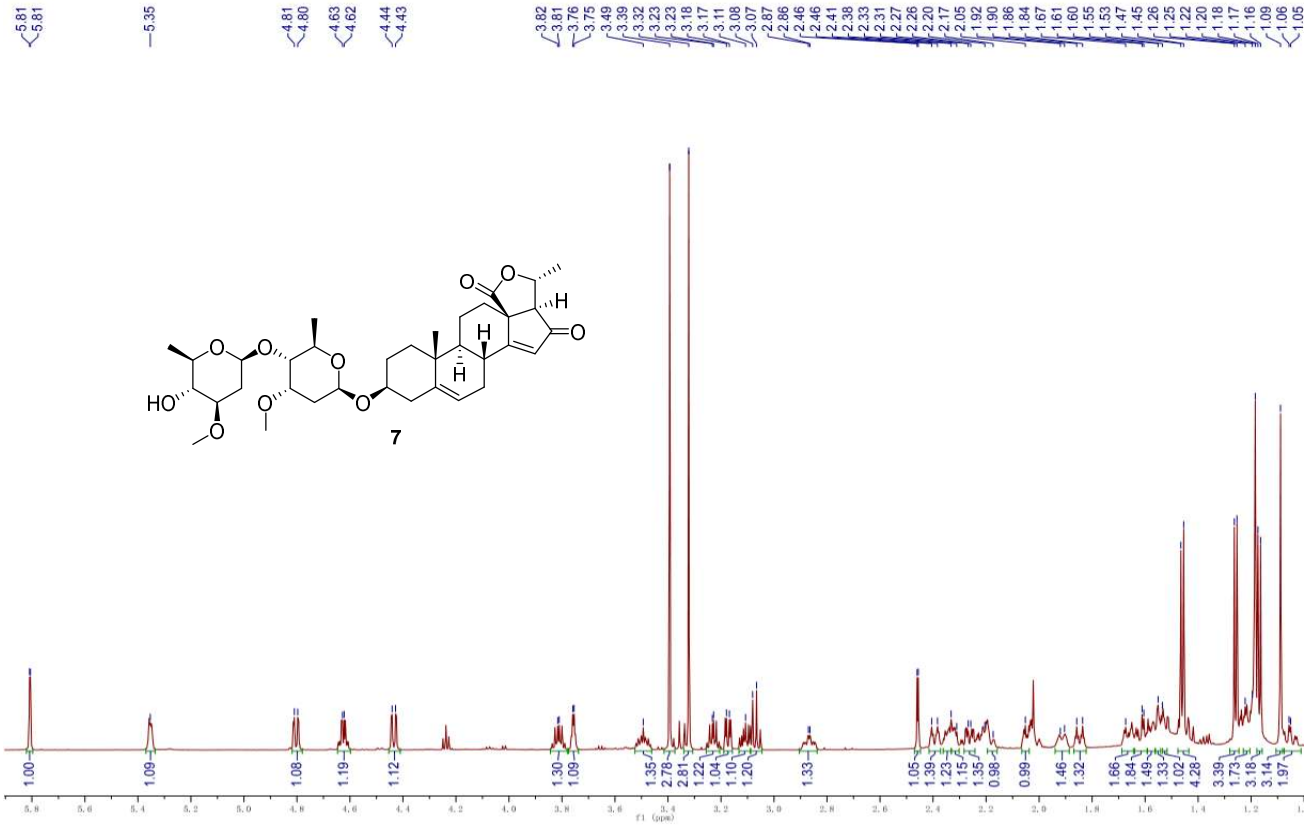

Figure S53. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **7**.

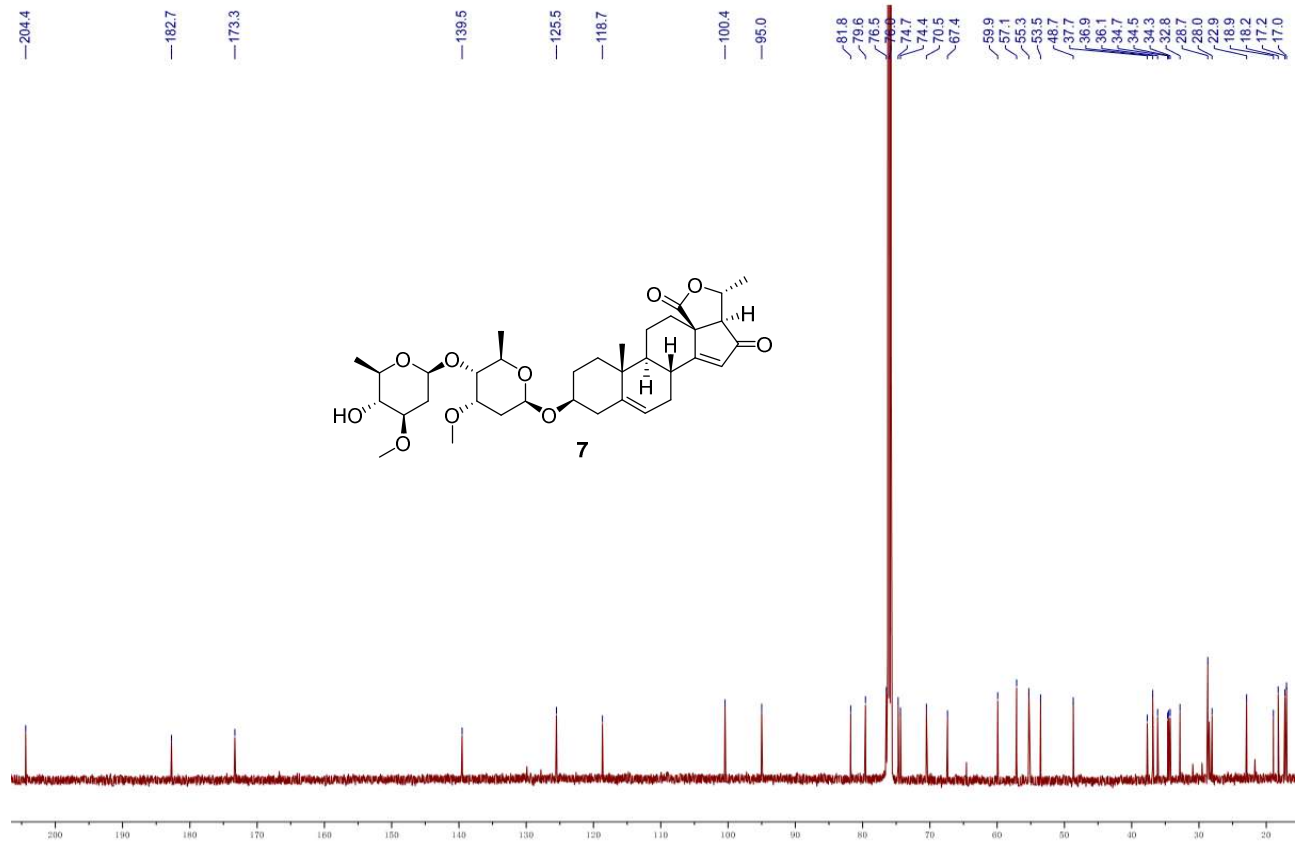

Figure S54. HSQC (600 MHz, $CDCl_3$) spectrum of **7**.

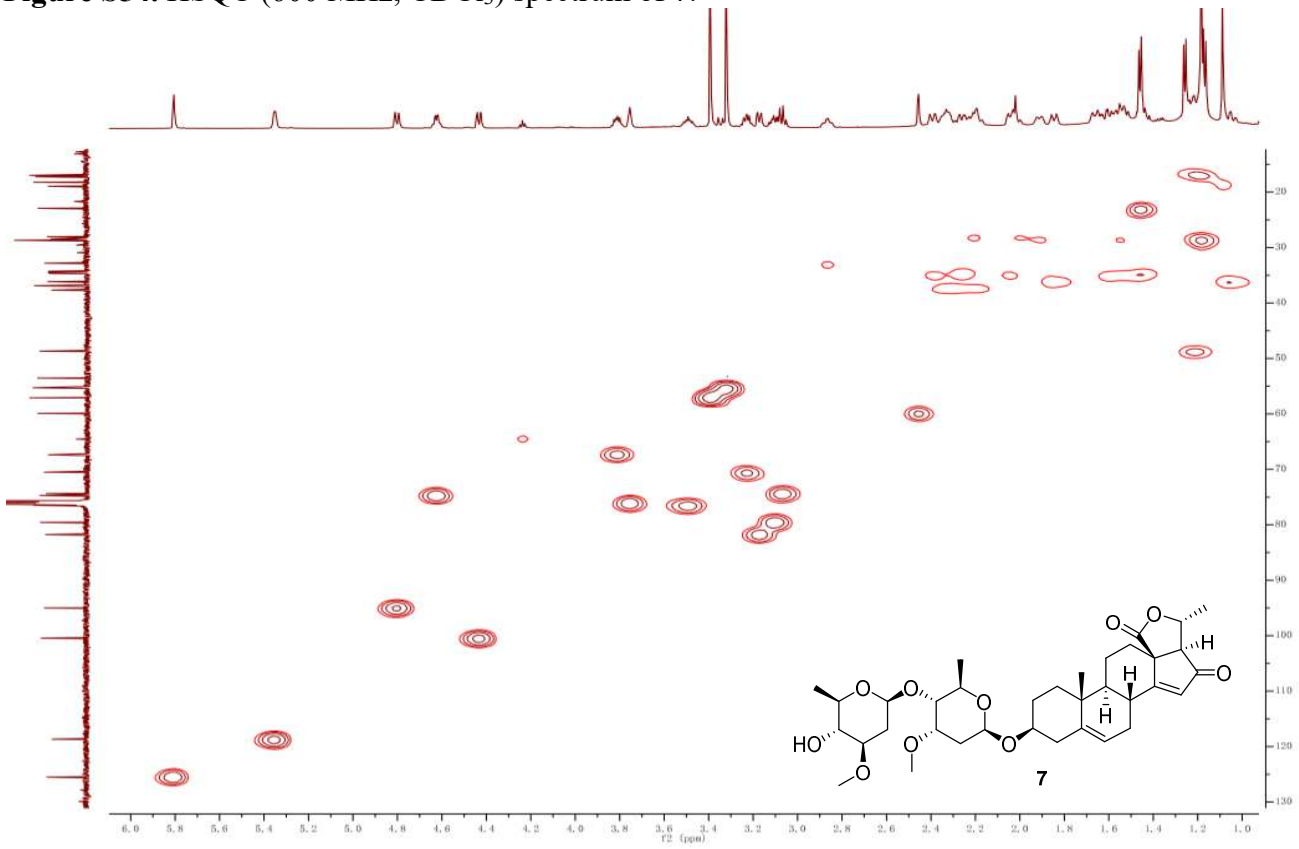

Figure S55. HMBC (600 MHz, $CDCl_3$) spectrum of **7**.

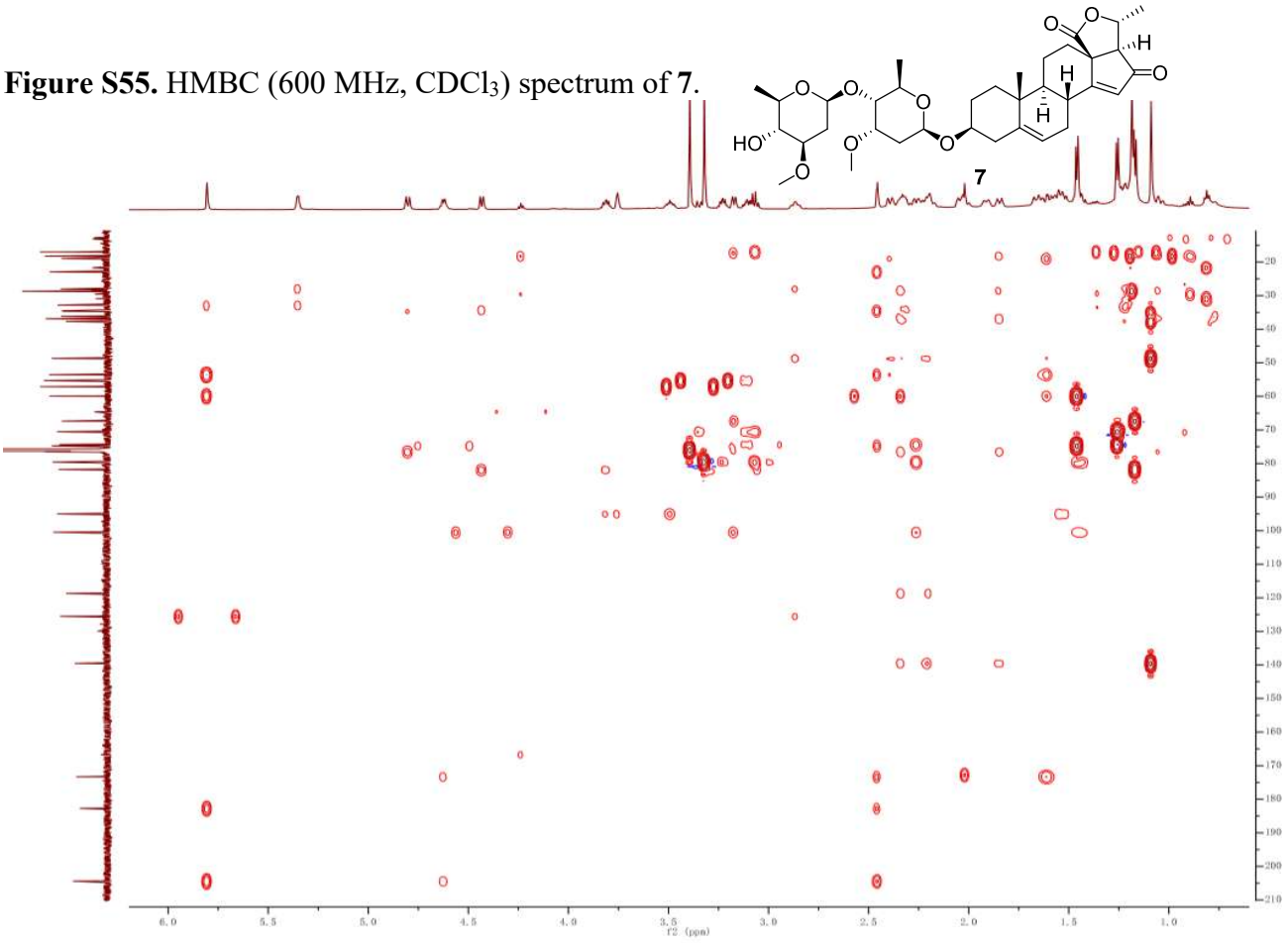

Figure S56. ^{1}H–^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **7**.

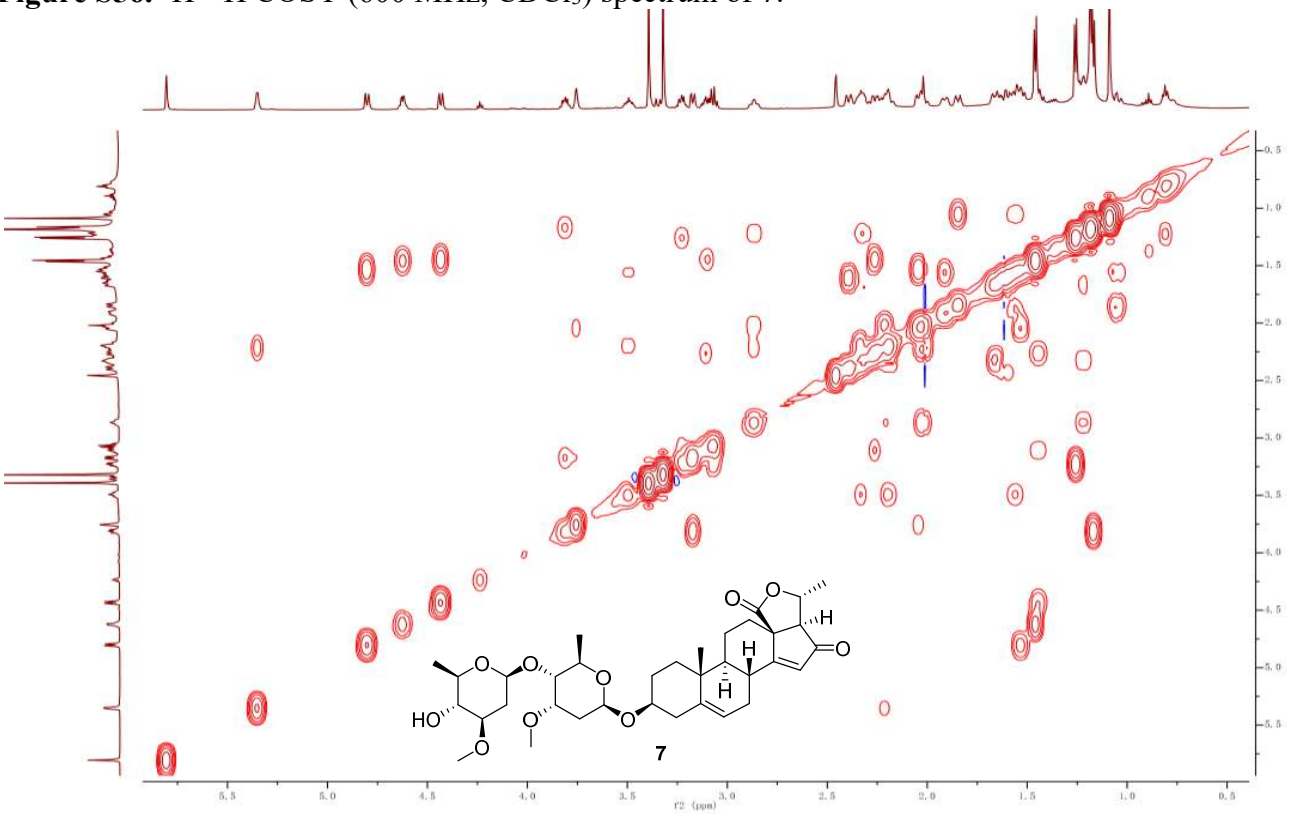

Figure S57. NOESY (600 MHz, $CDCl_3$) spectrum of **7**.

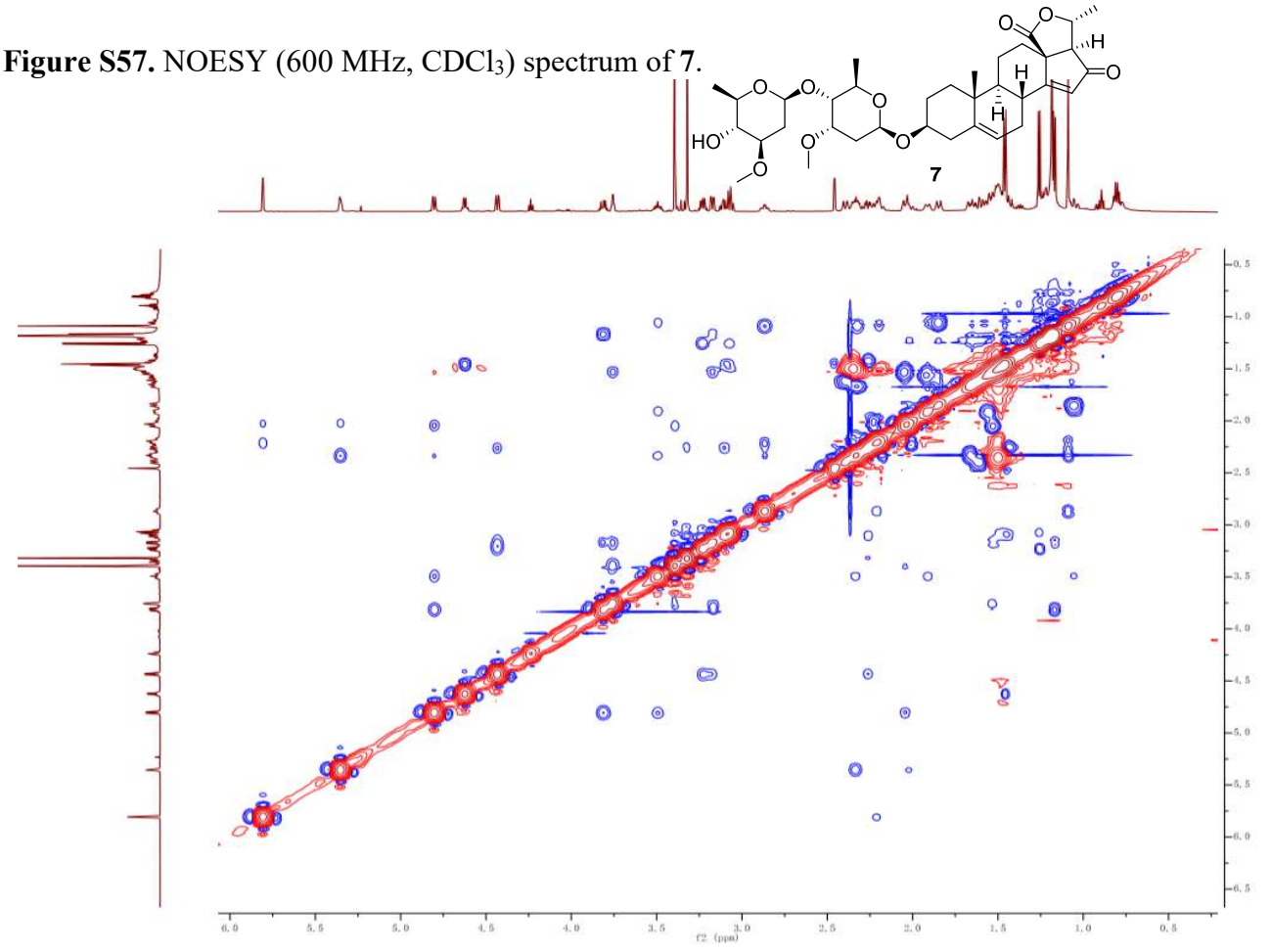

Figure S58. HRESIMS spectrum of **7**.

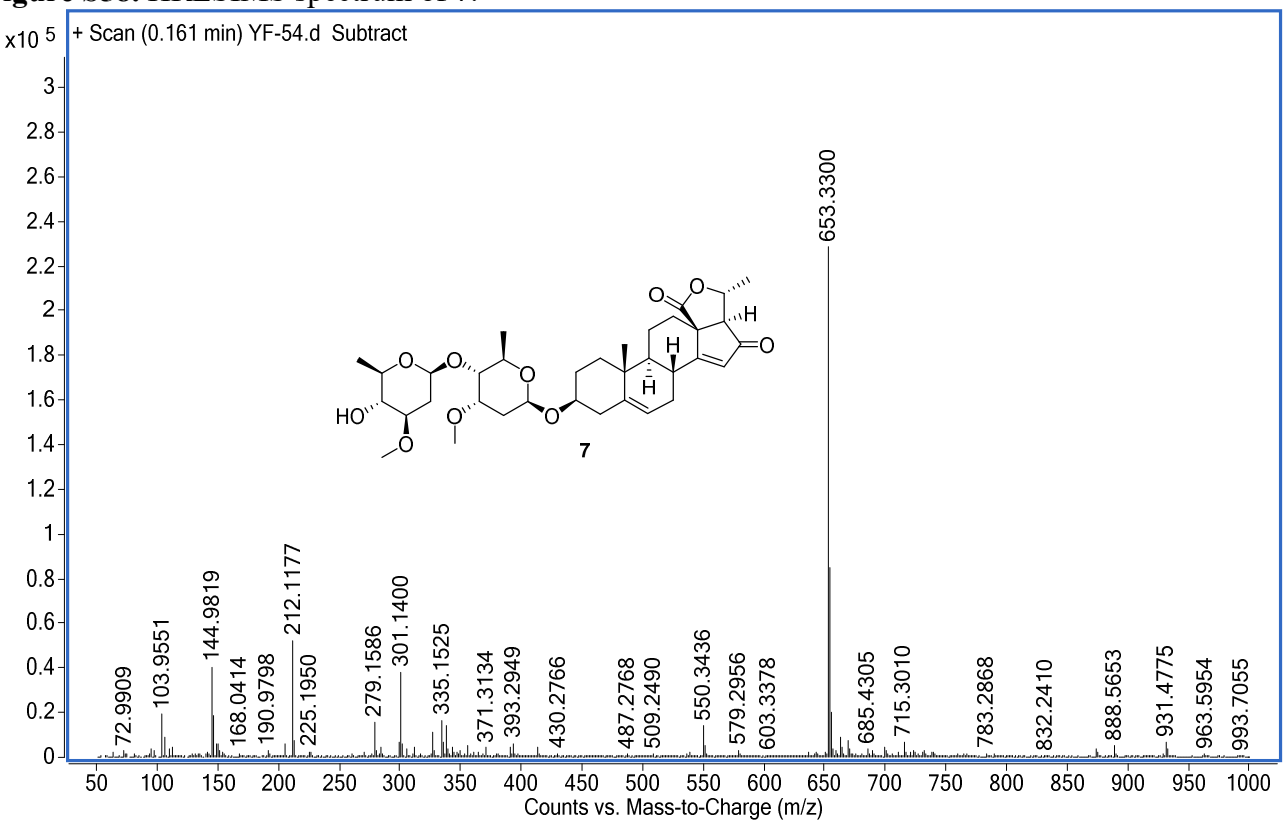

Figure S59. IR spectrum of **7**.

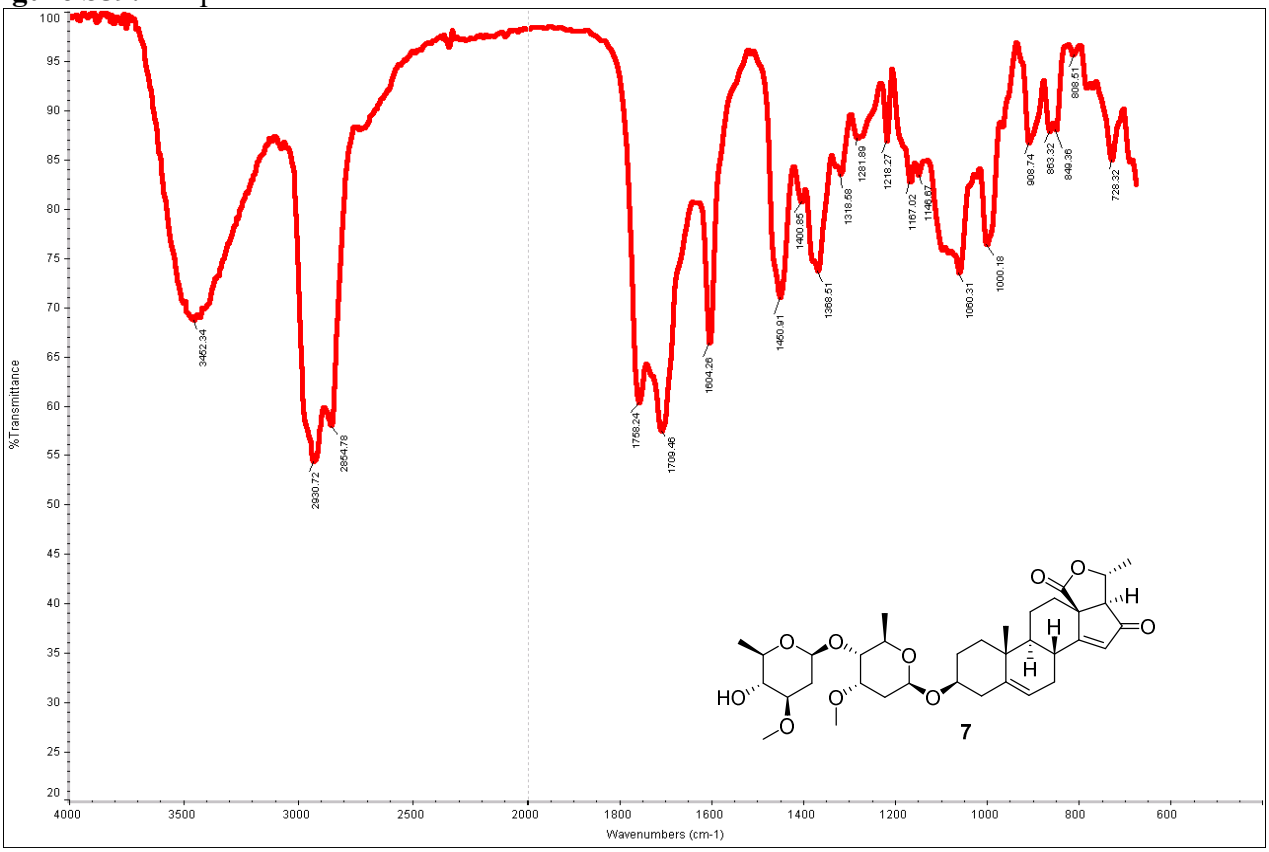

Figure S60. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **8**.

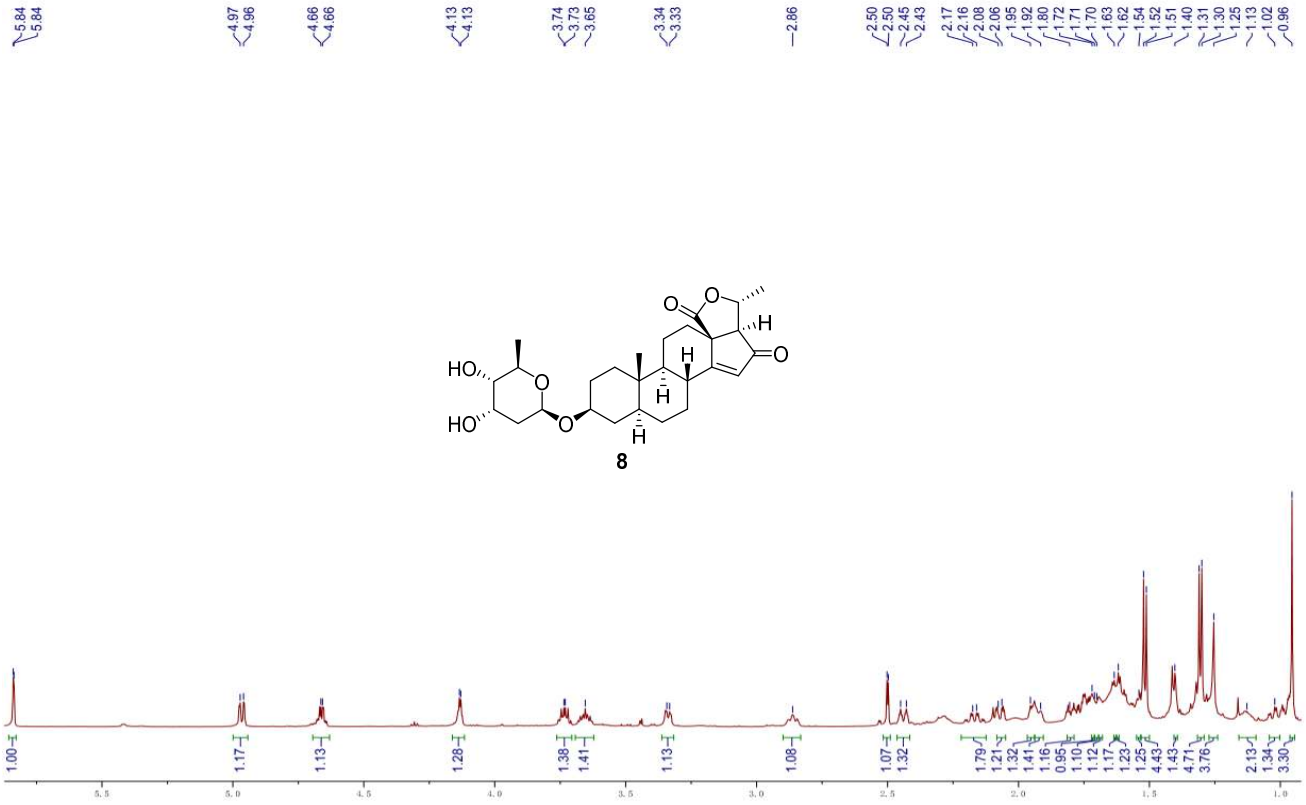

Figure S61. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **8**.

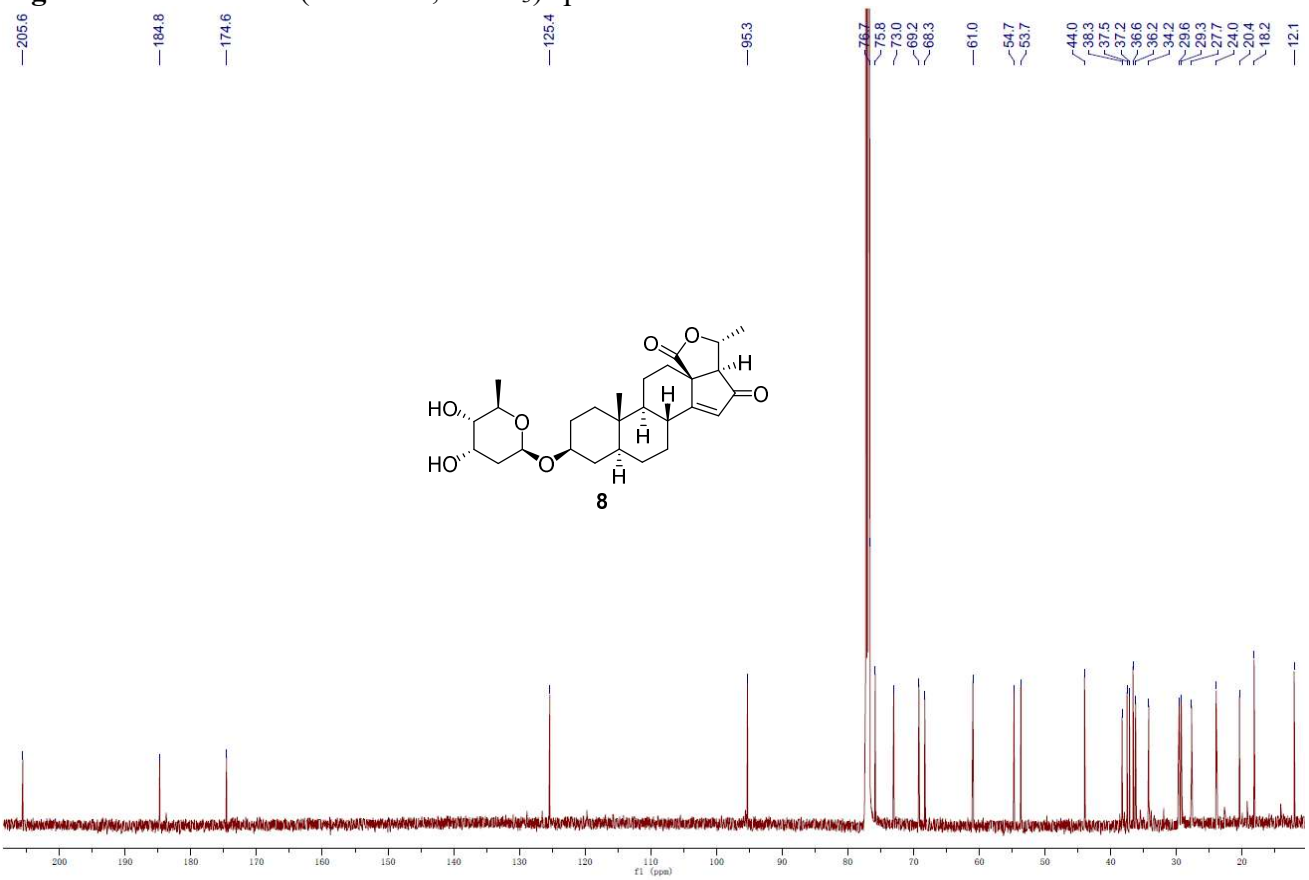

Figure S62. HSQC (600 MHz, $CDCl_3$) spectrum of **8**.

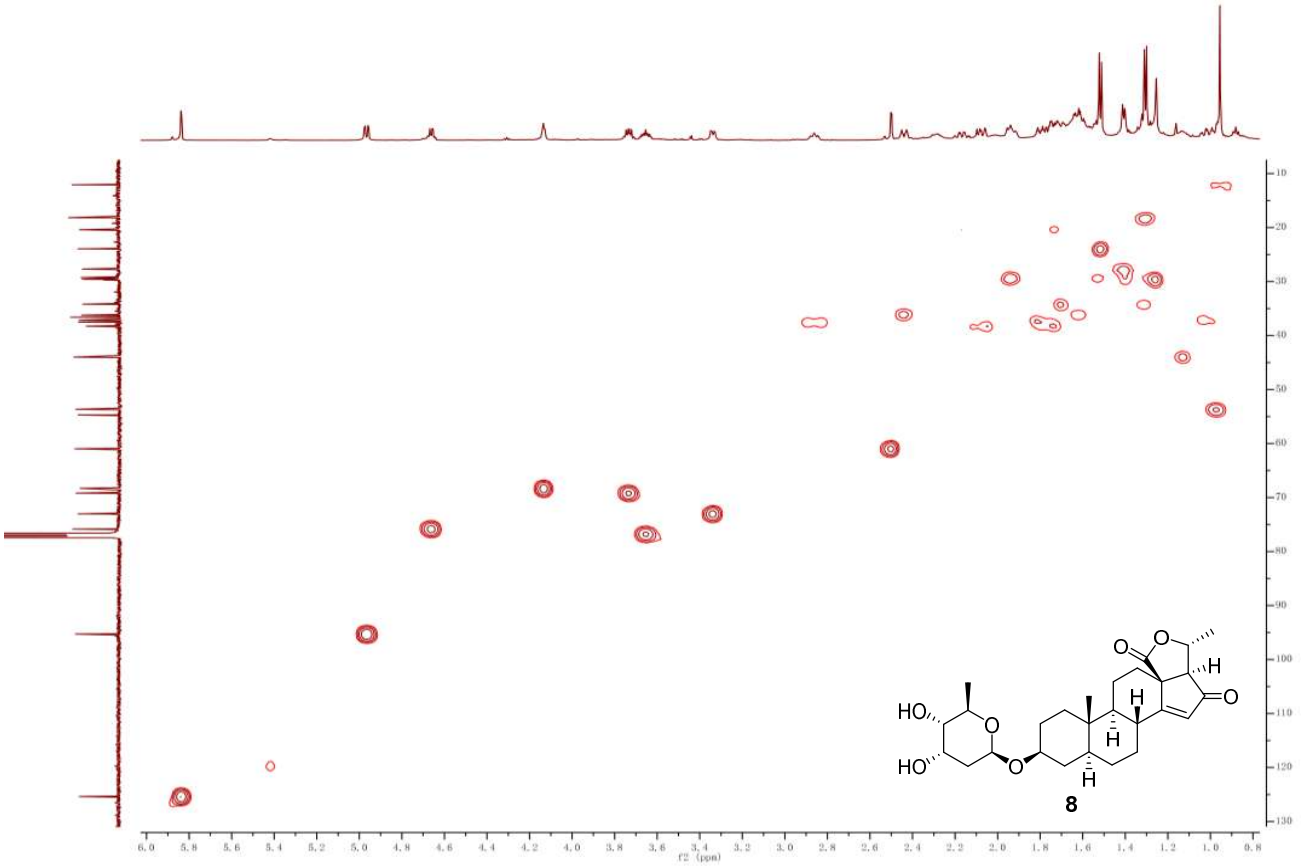

Figure S63. HMBC (600 MHz, $CDCl_3$) spectrum of **8**.

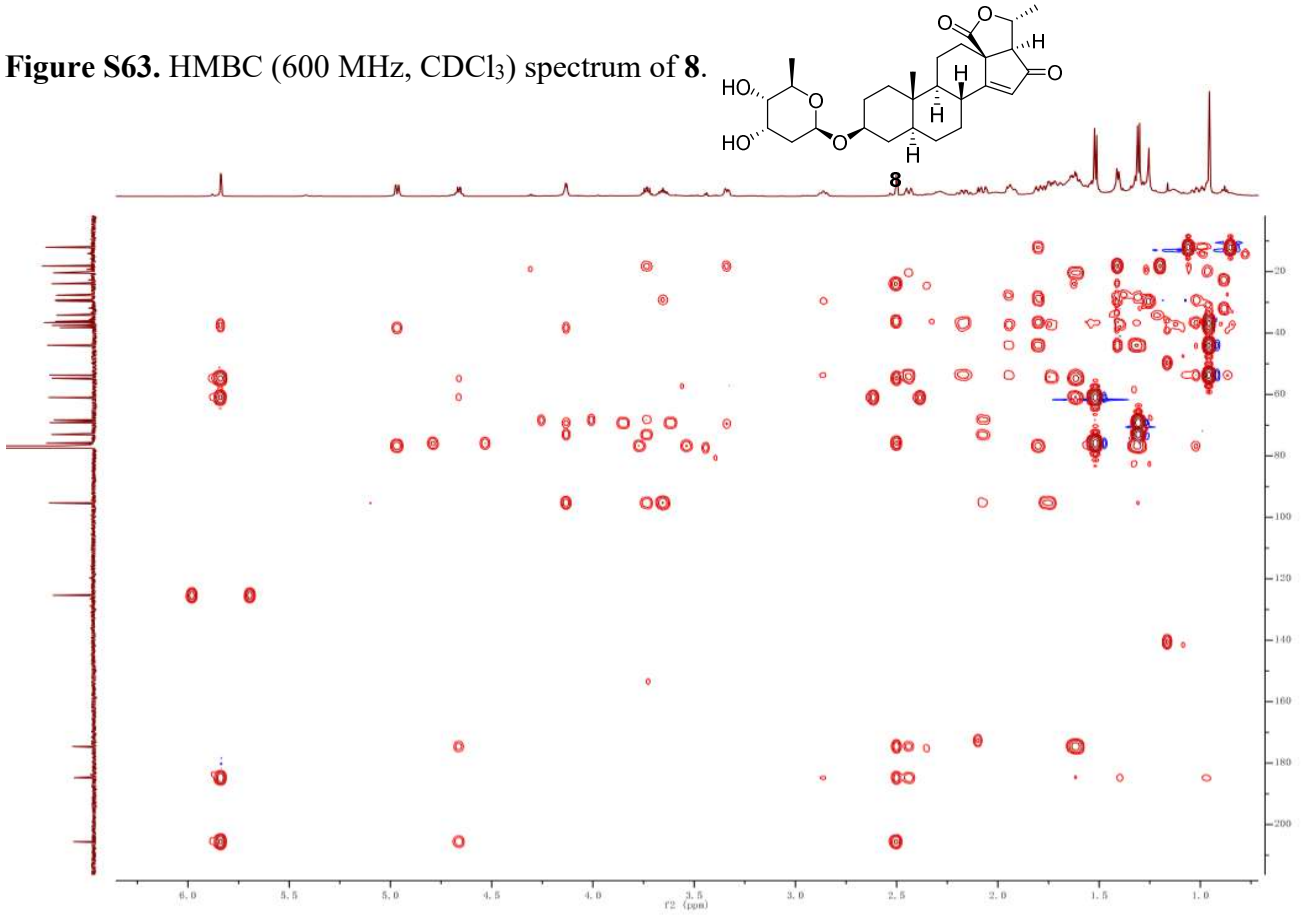

Figure S64. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **8**.

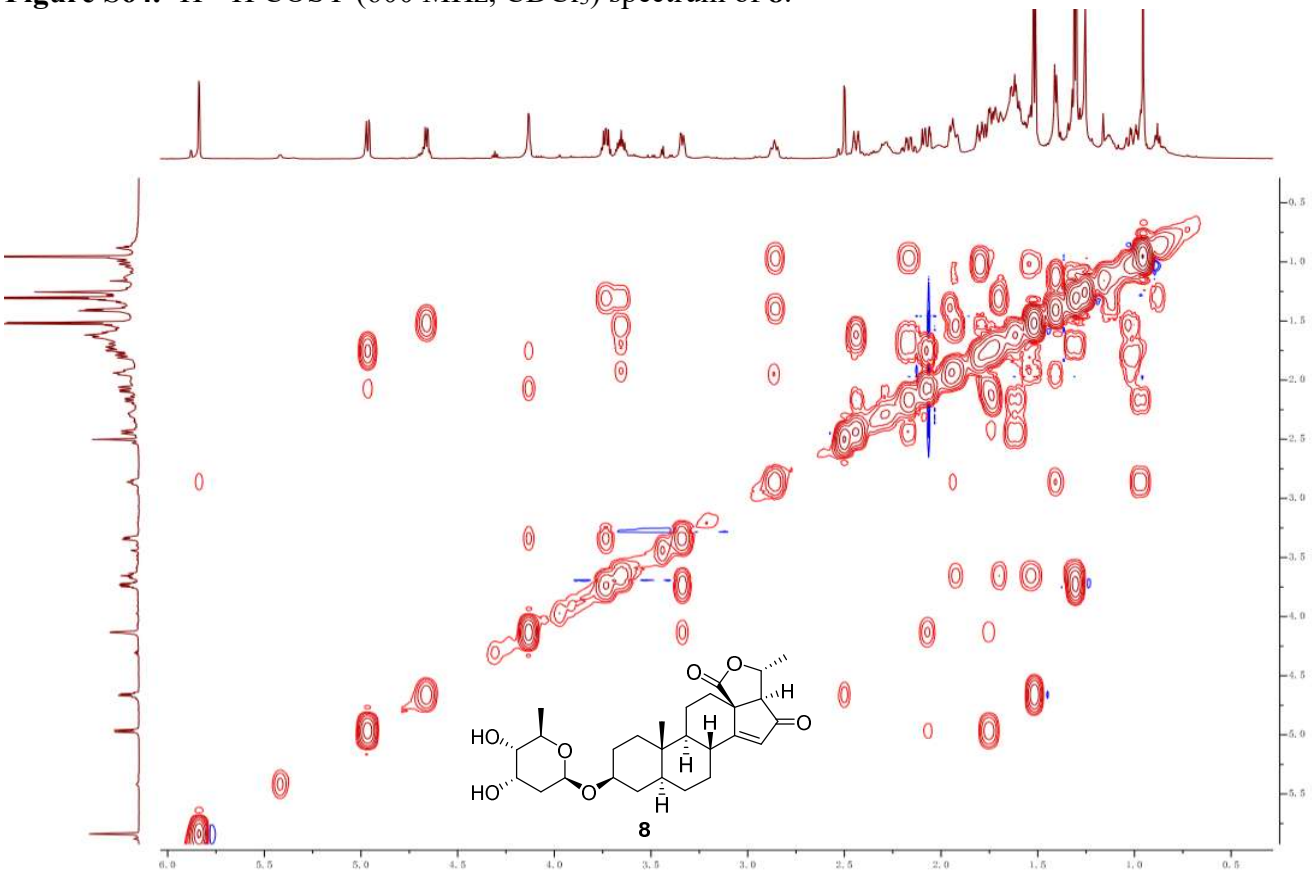

Figure S65. NOESY (600 MHz, $CDCl_3$) spectrum of **8**.

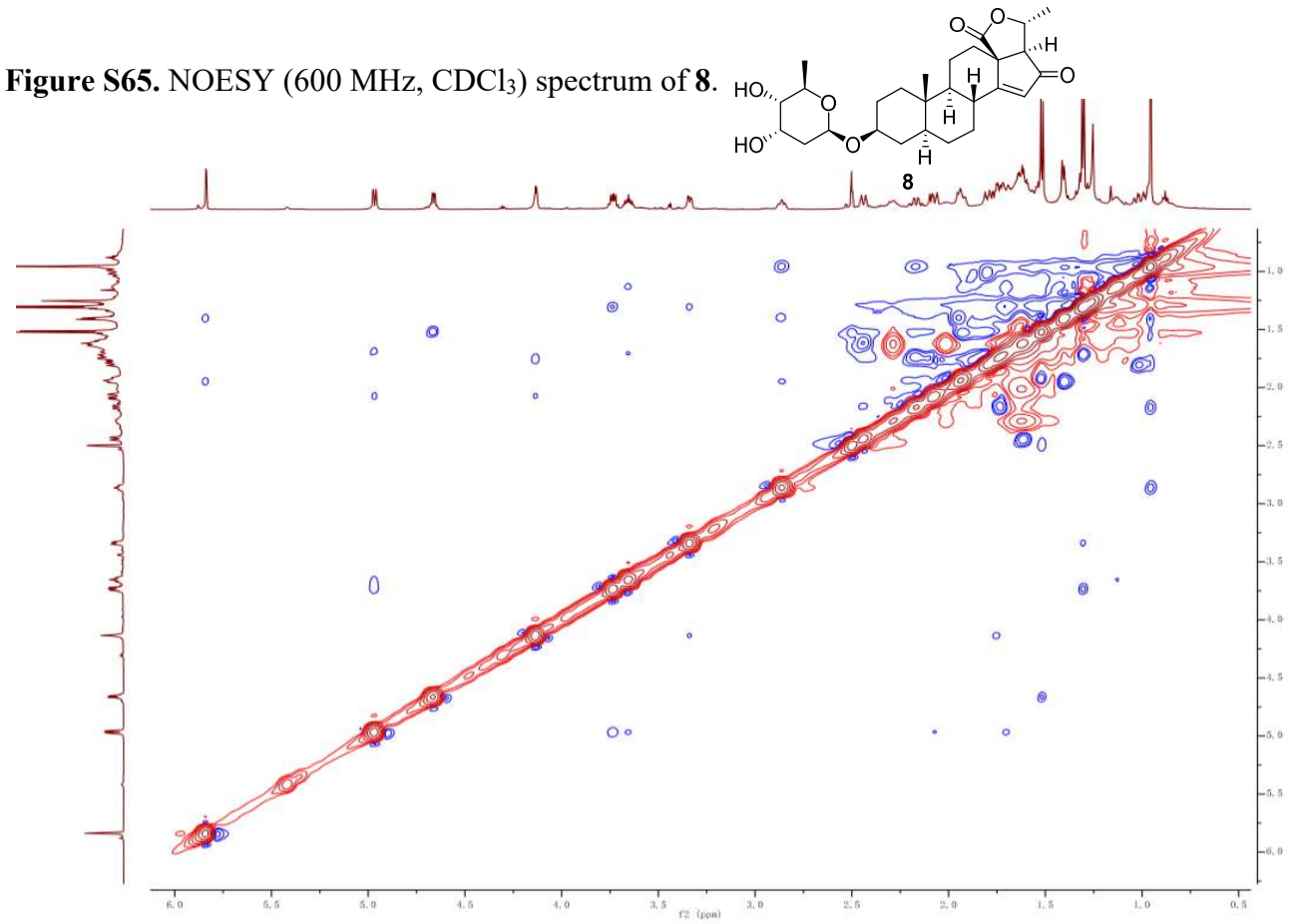

Figure S66. HRESIMS spectrum of **8**.

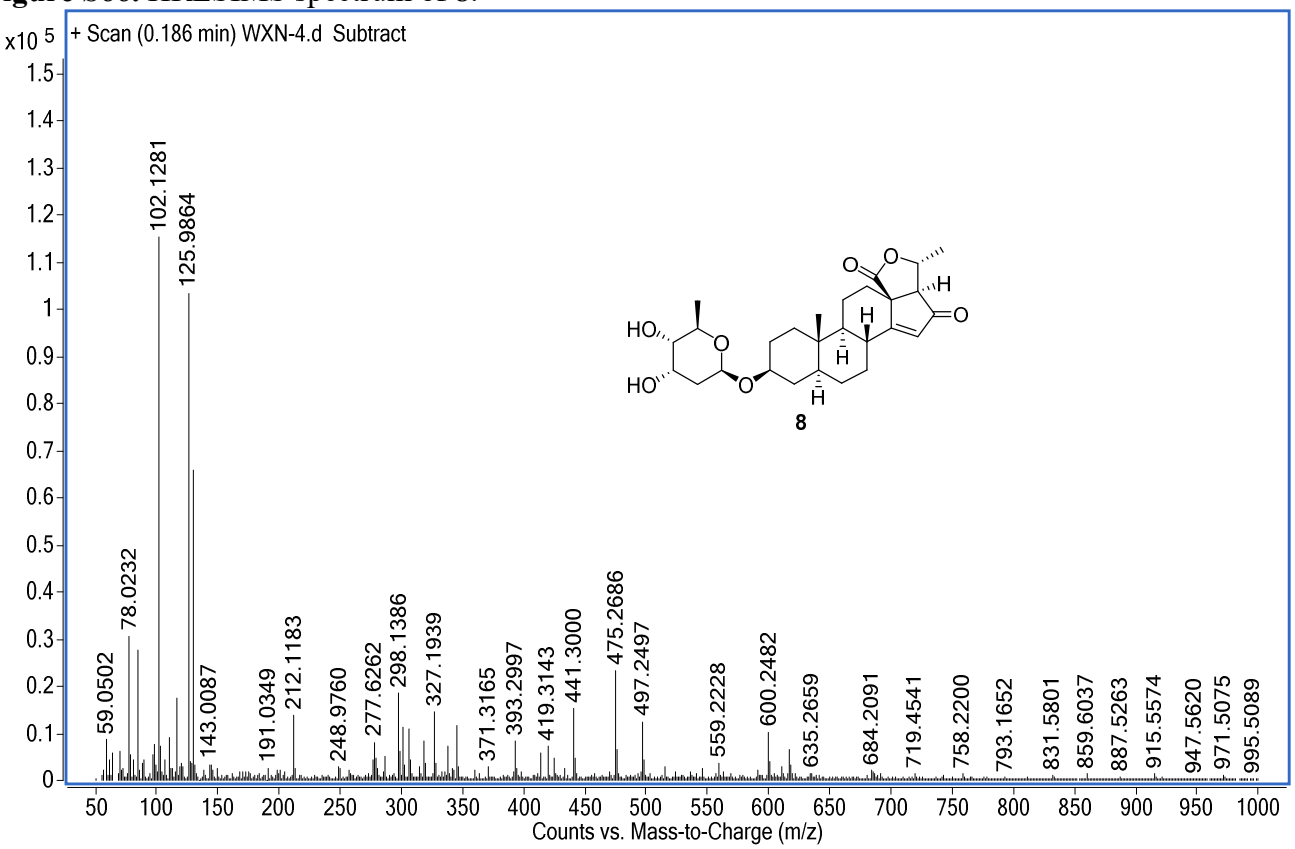

Figure S67. IR spectrum of **8**.

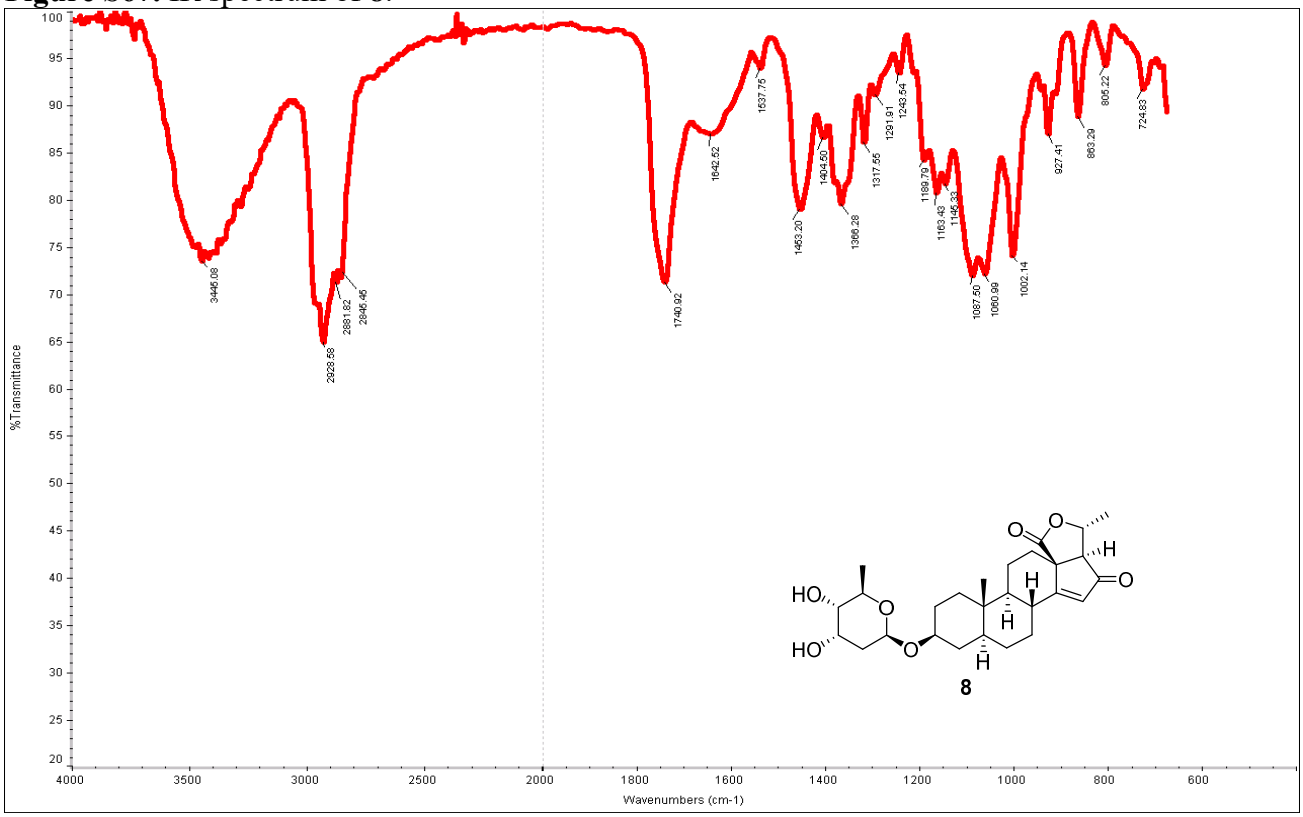

Figure S68. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **9**.

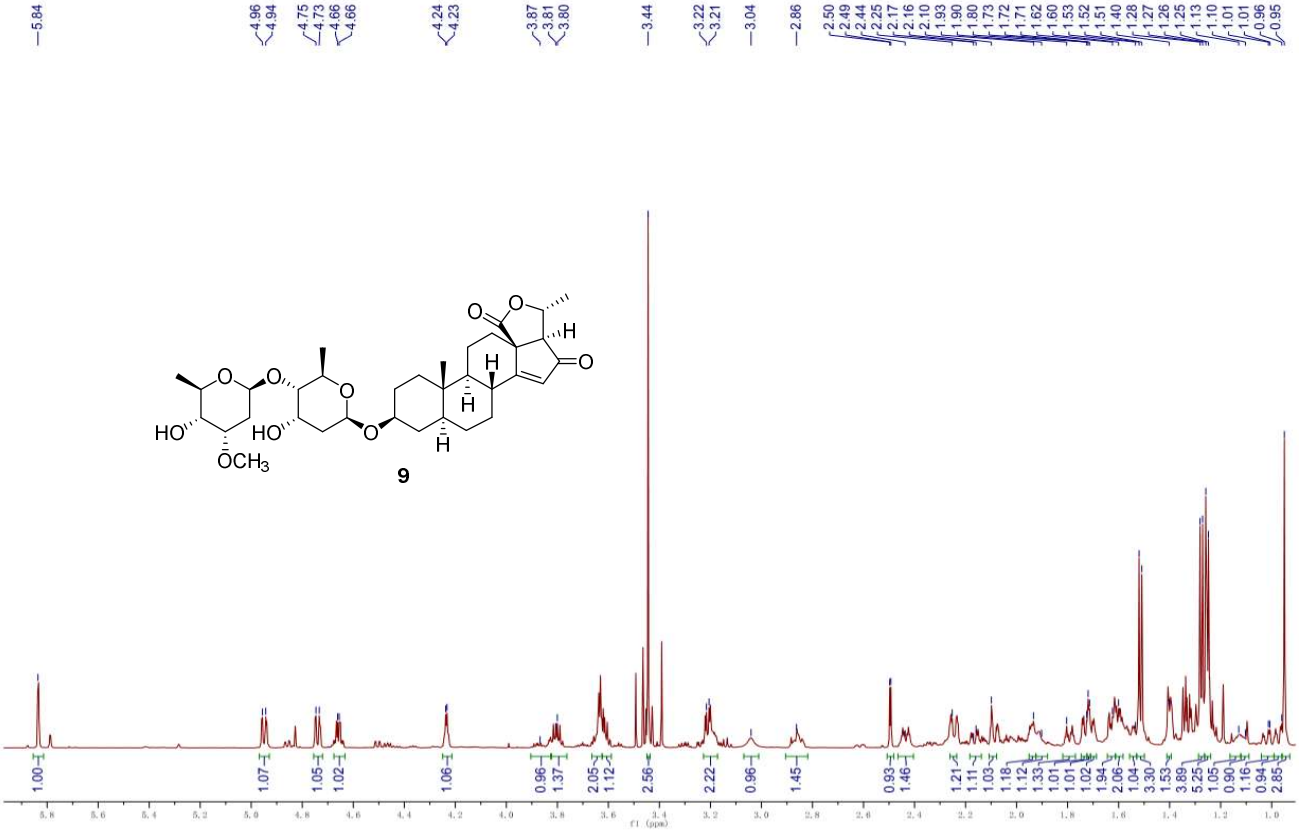

Figure S69. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **9**.

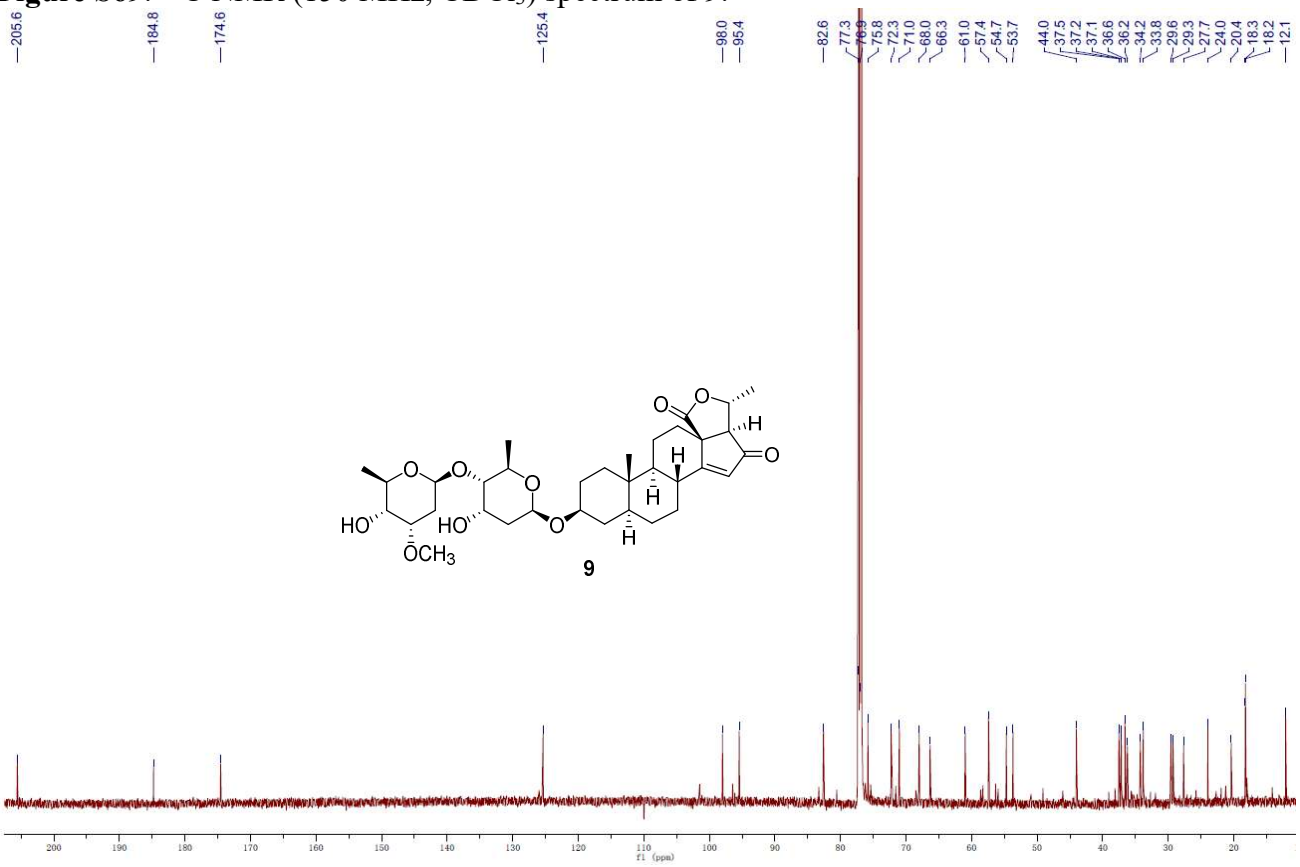

Figure S70. HSQC (600 MHz, $CDCl_3$) spectrum of **9**.

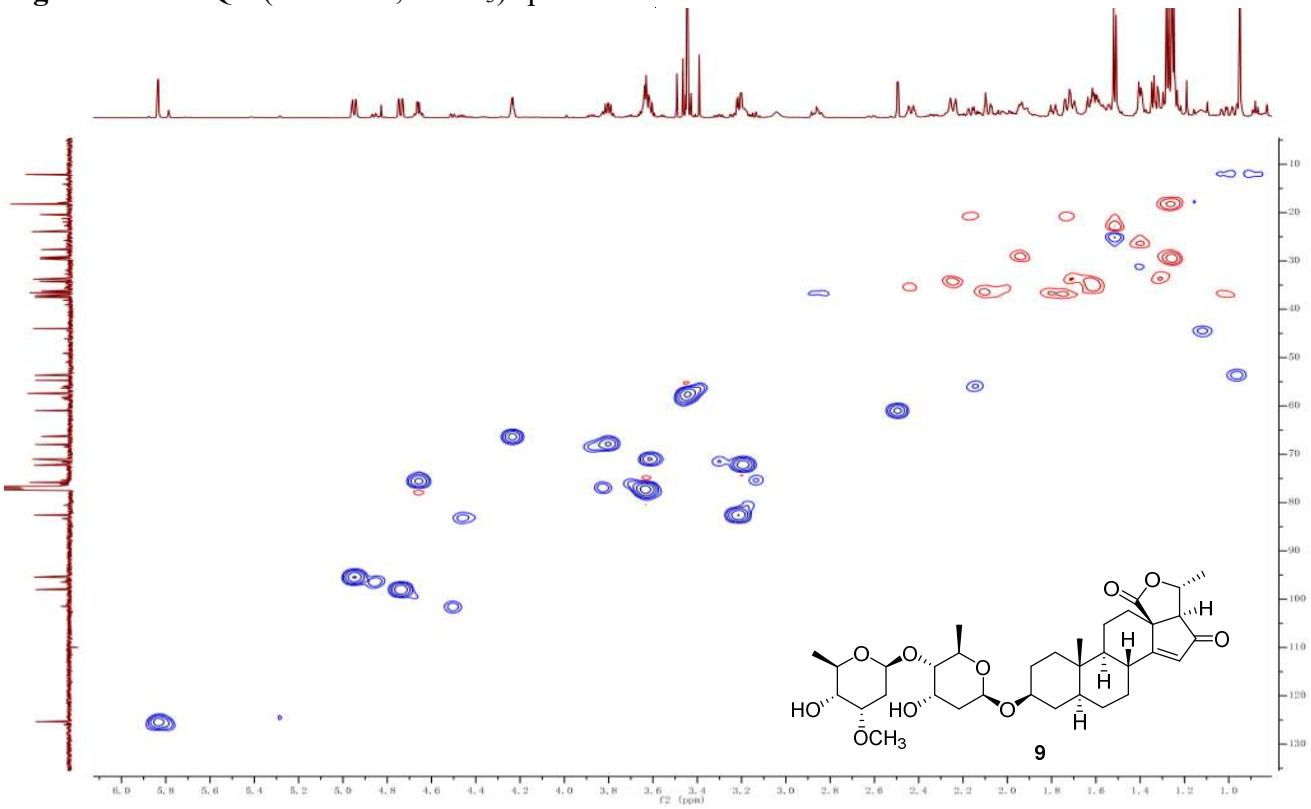

Figure S71. HMBC (600 MHz, $CDCl_3$) spectrum of **9**.

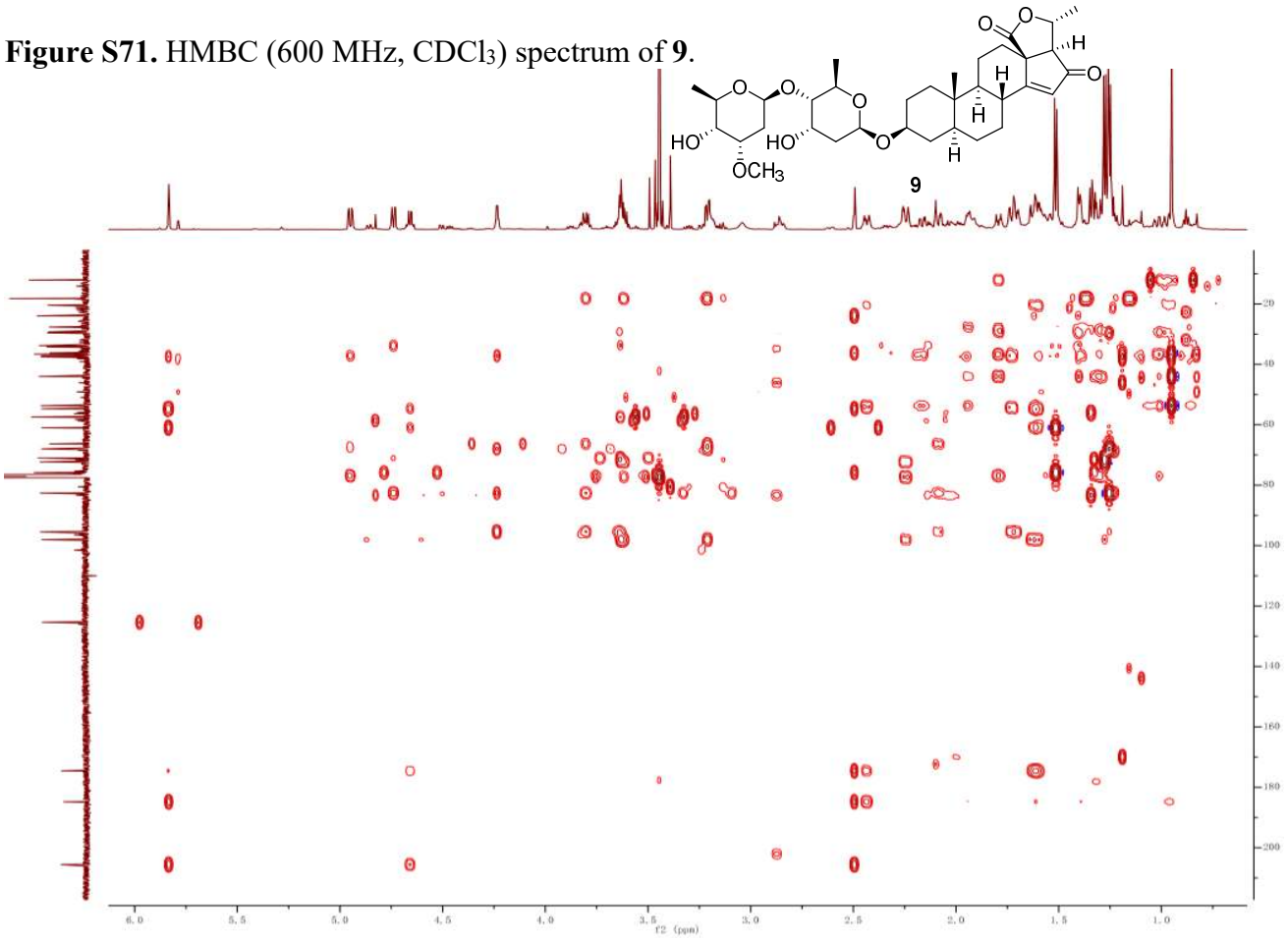

Figure S72. ^{1}H–^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **9**.

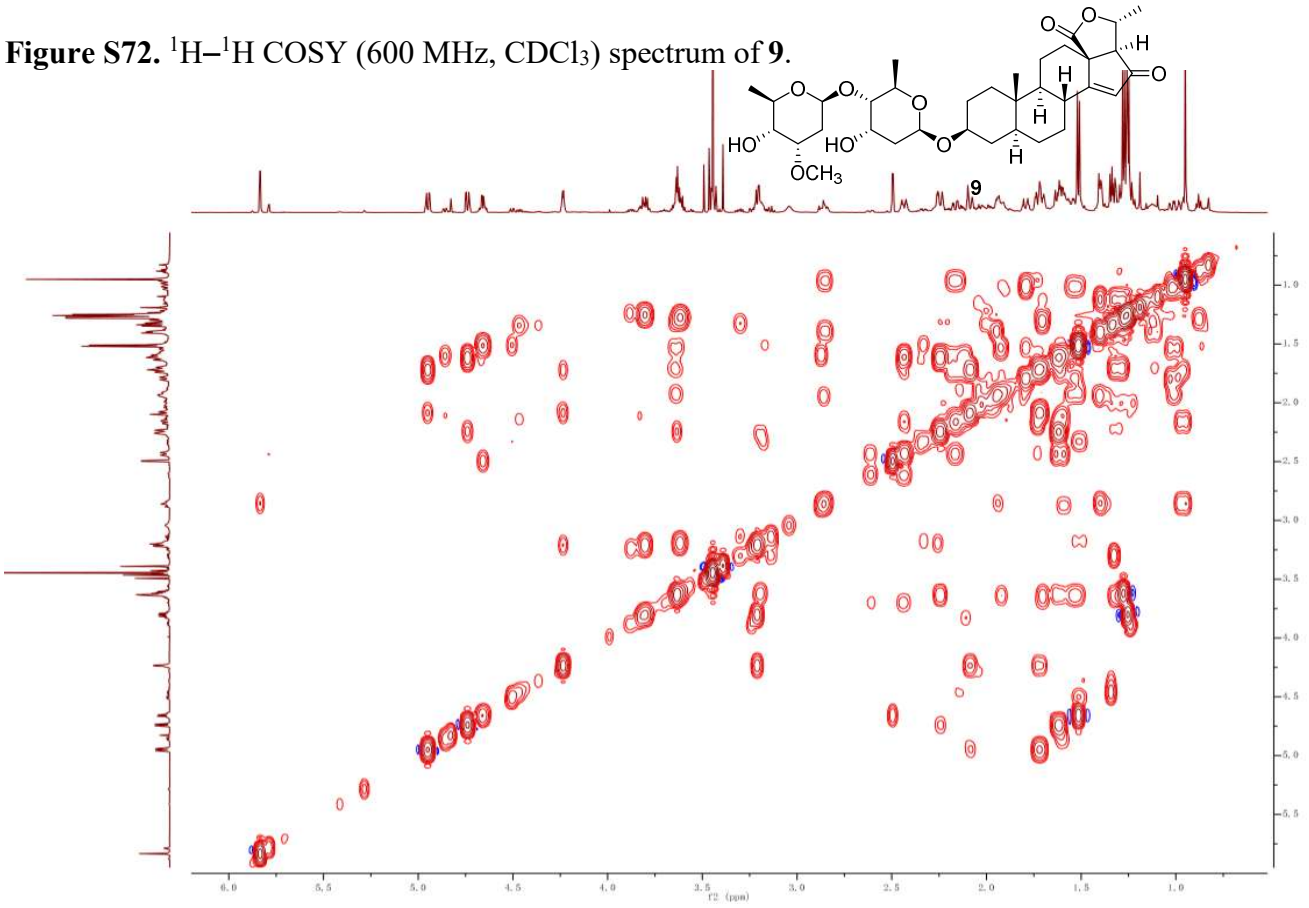

Figure S73. NOESY (600 MHz, $CDCl_3$) spectrum of **9**.

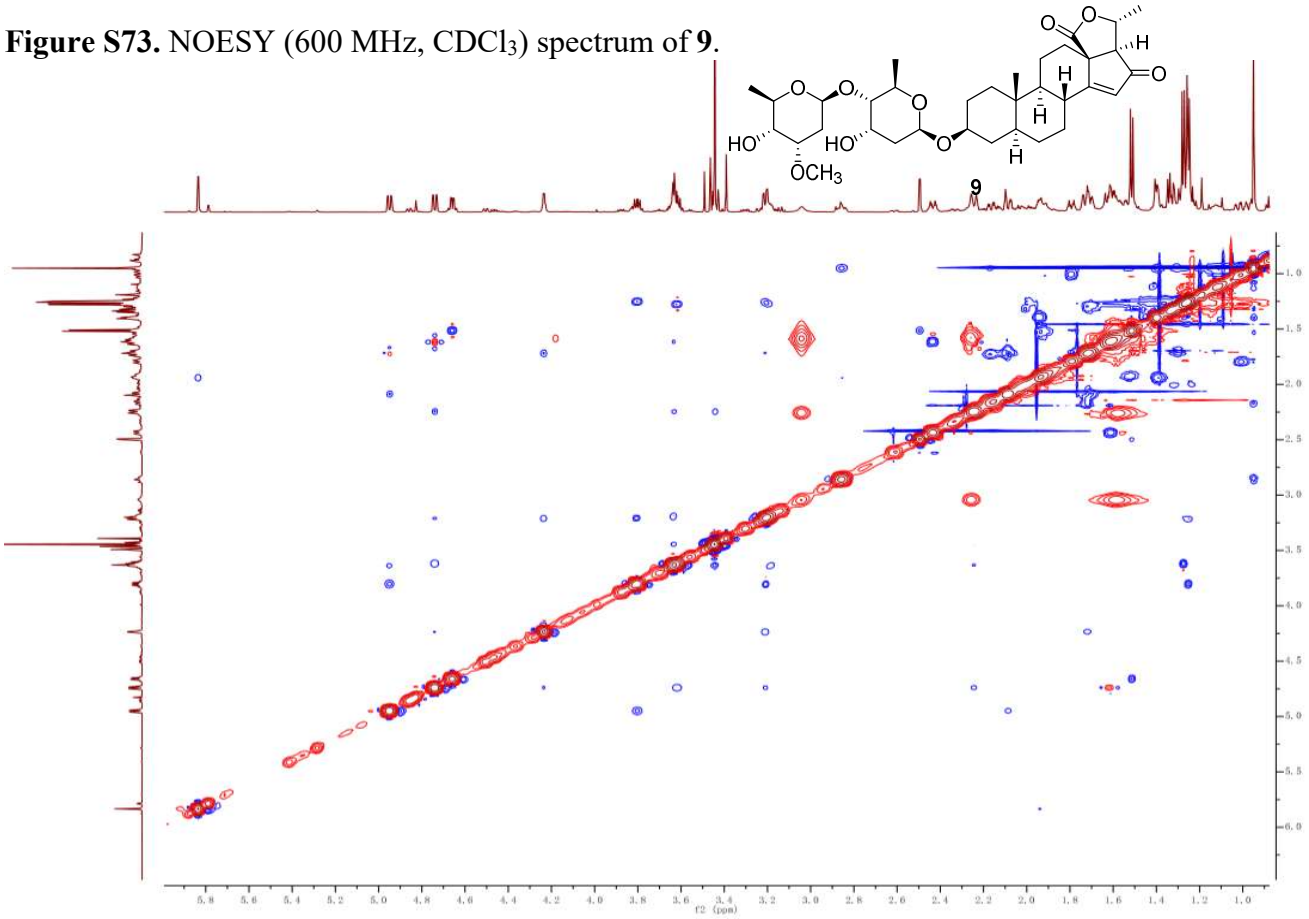

Figure S74. HRESIMS spectrum of **9**.

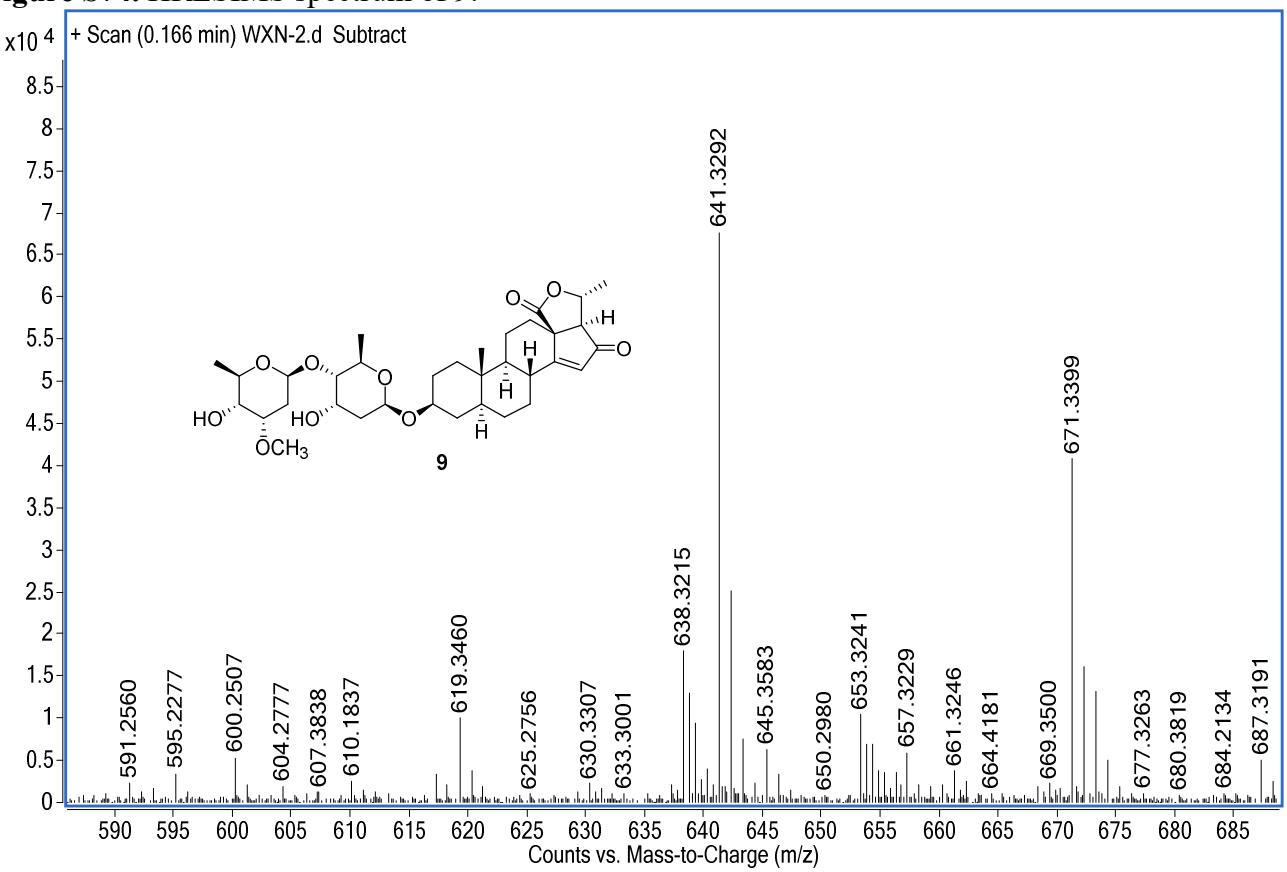

Figure S75. IR spectrum of **9**.

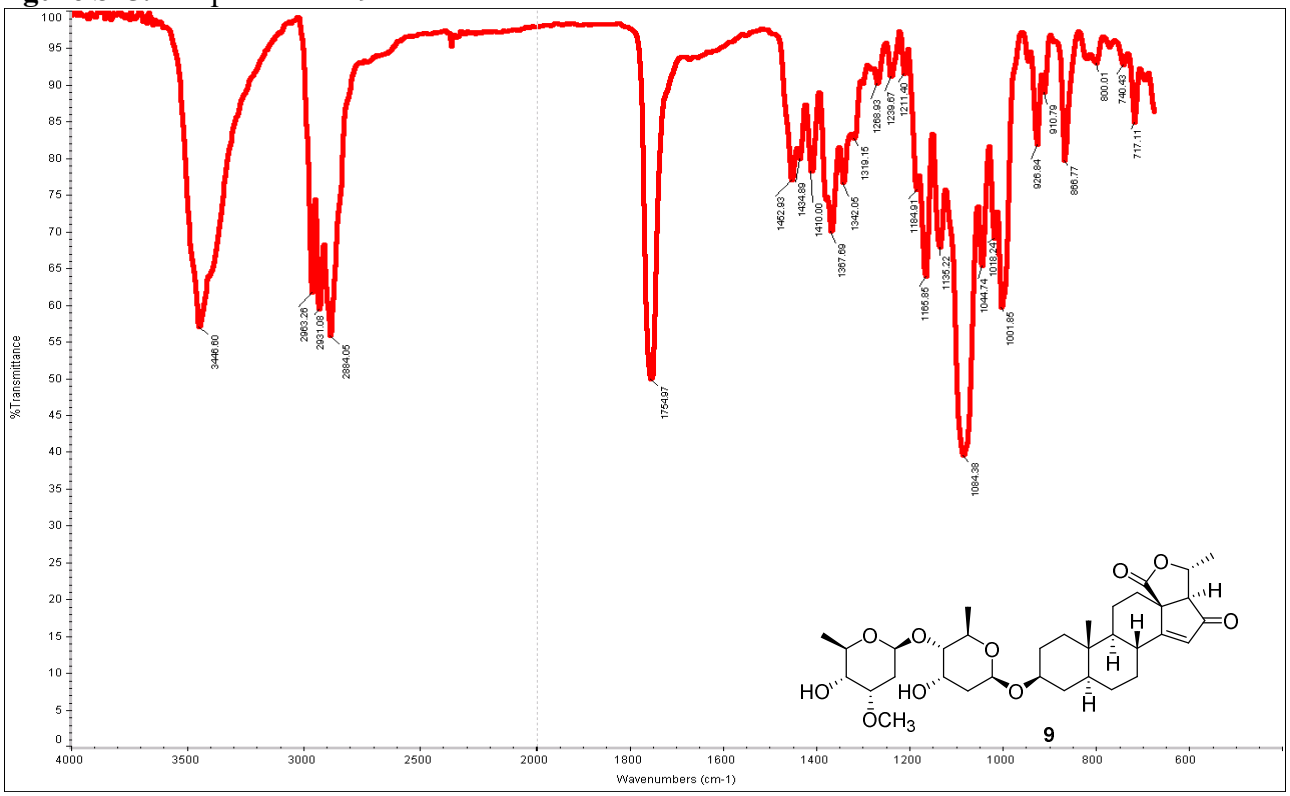

Figure S76. ^{1}H NMR (600 MHz, methanol-d_4) spectrum of **10**.

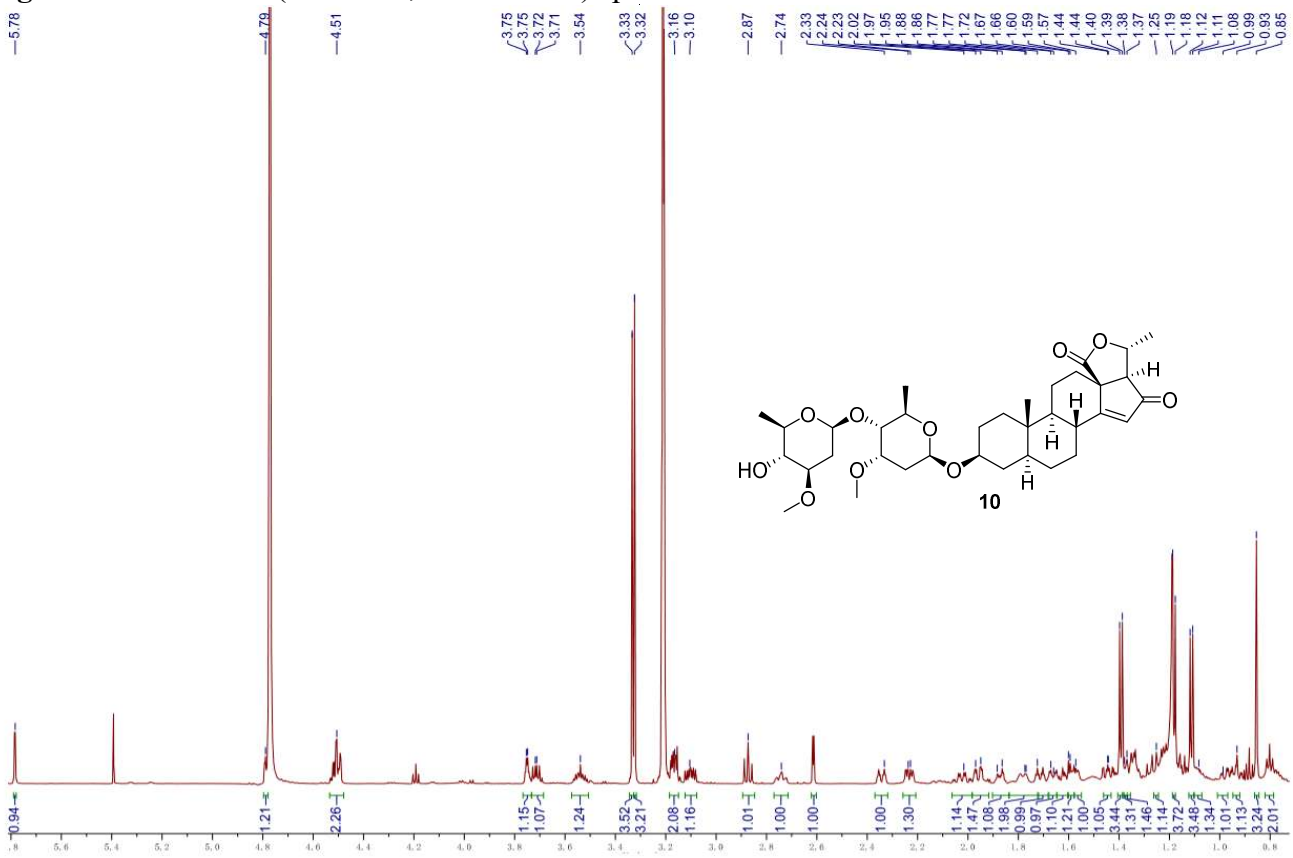

Figure S77. ^{13}C NMR (150 MHz, methanol-d_4) spectrum of **10**.

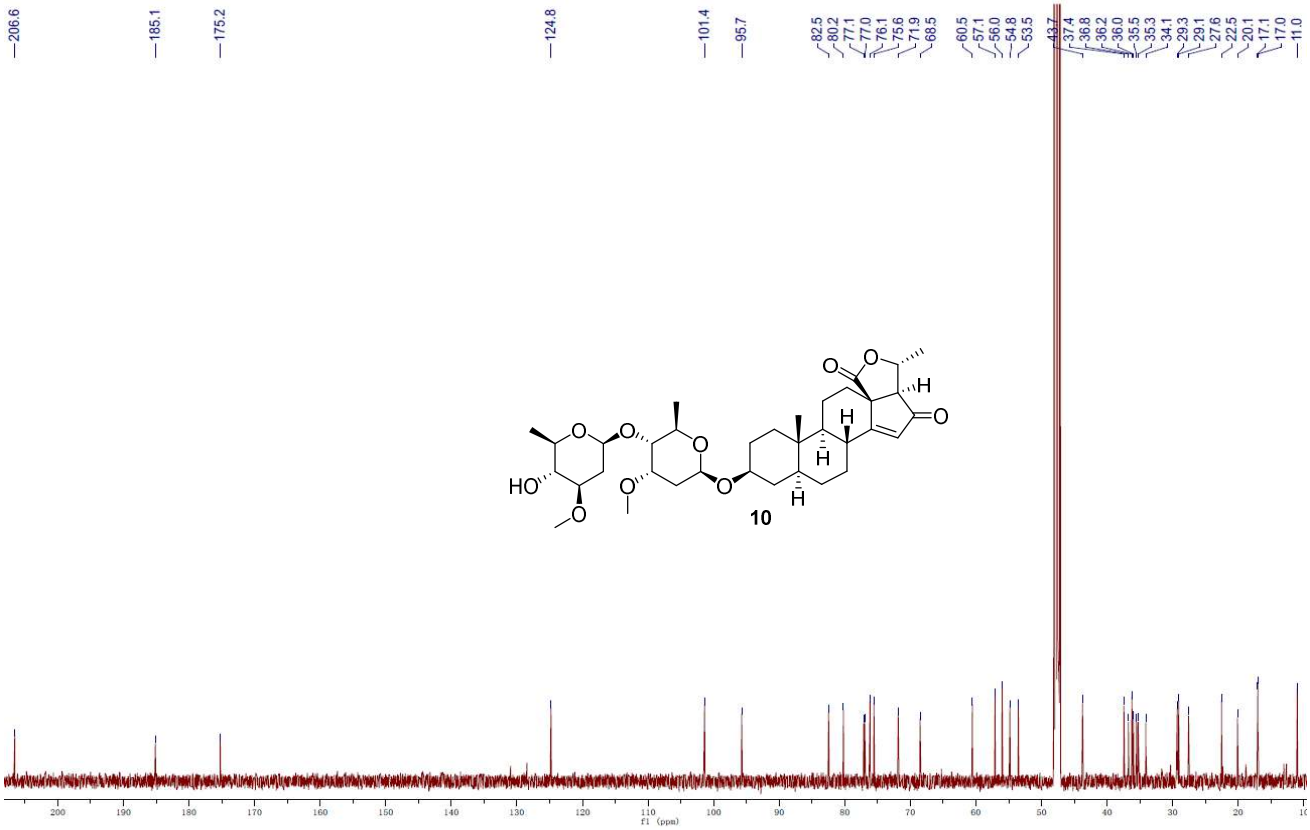

Figure S78. HSQC (600 MHz, methanol-d_4) spectrum of **10**.

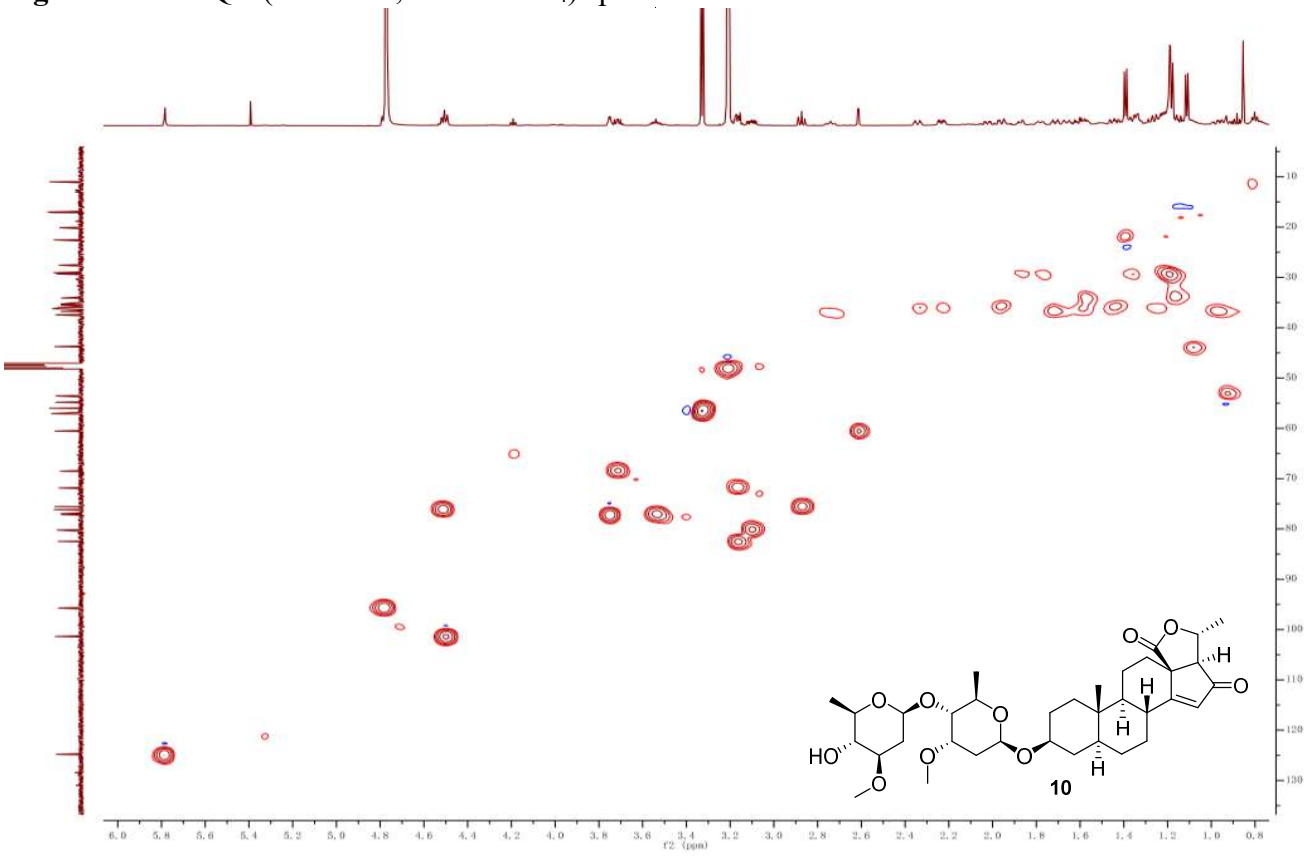

Figure S79. HMBC (600 MHz, methanol-d_4) spectrum of **10**.

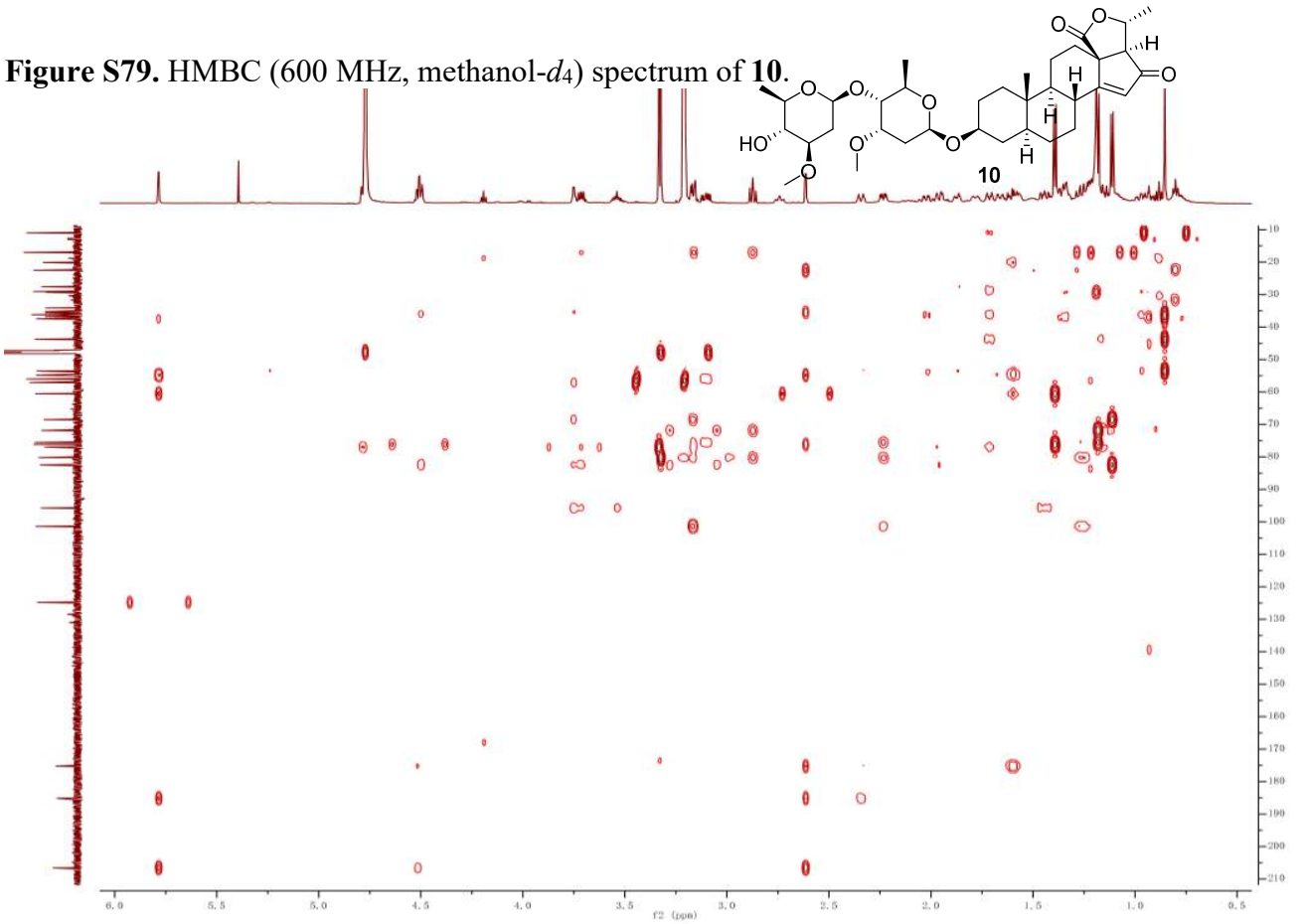

Figure S80. ^{1}H–^{1}H COSY HSQC (600 MHz, methanol-d_4) spectrum of **10**.

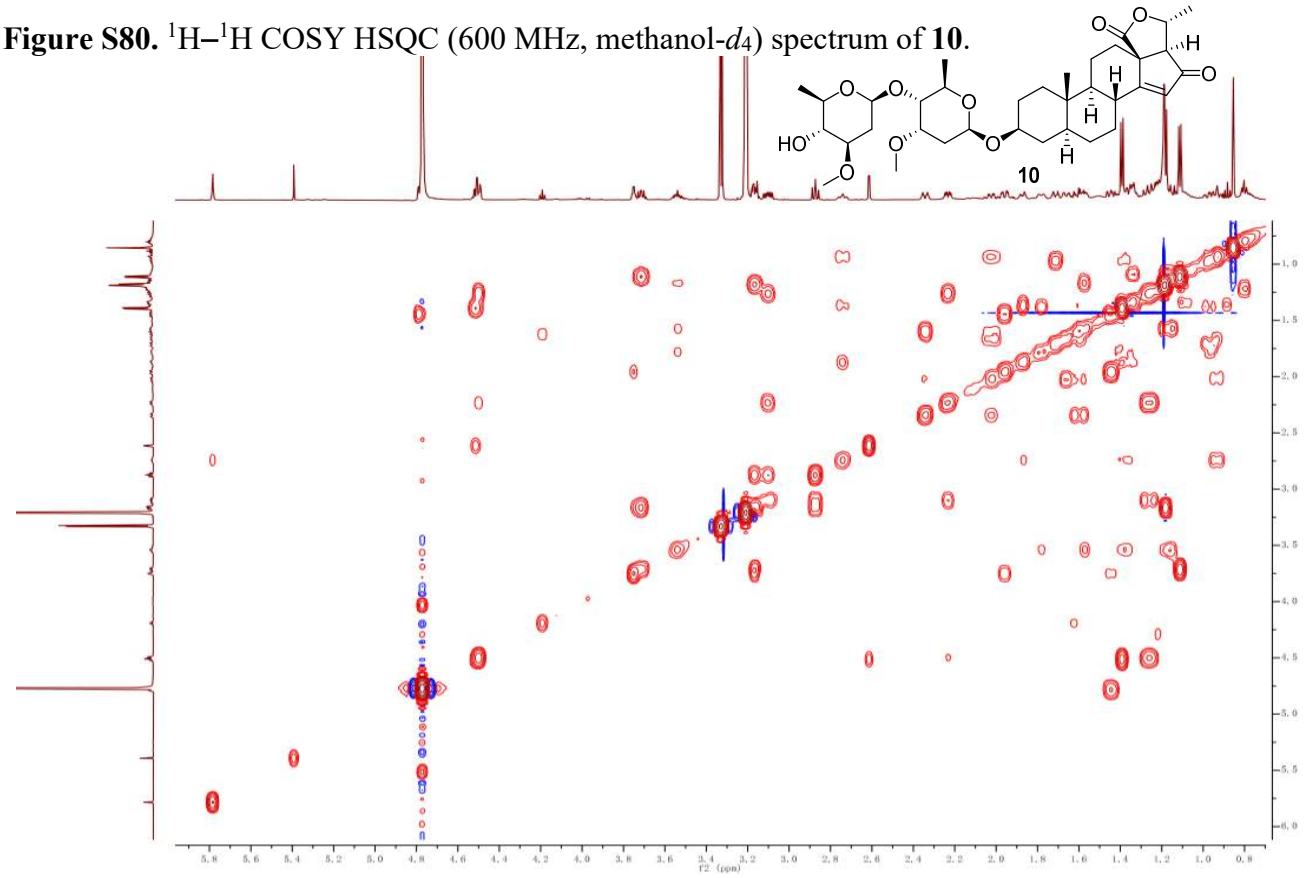

Figure S81. NOESY (600 MHz, methanol-d_4) spectrum of **10**.

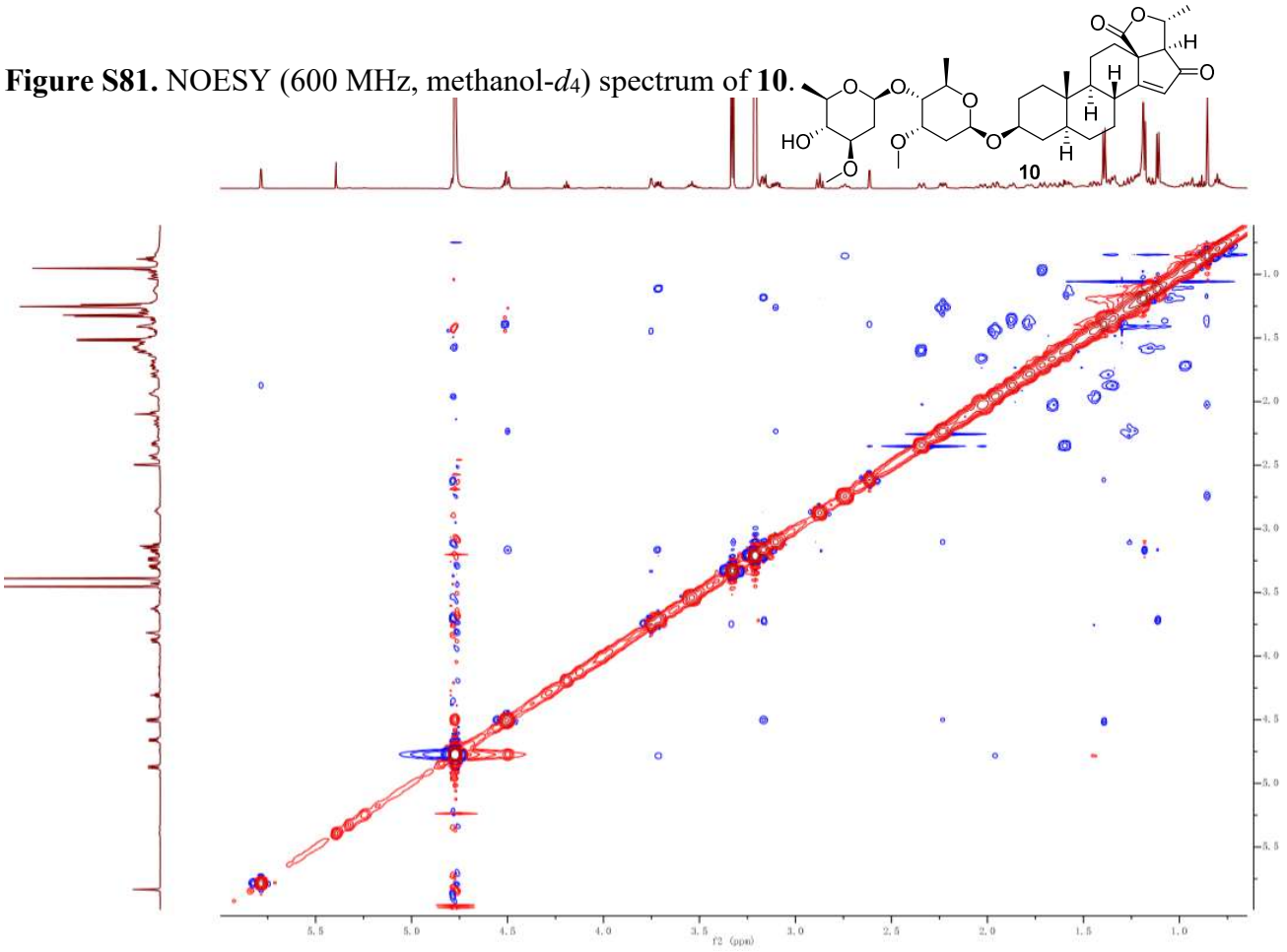

Figure S82. HRESIMS spectrum of **10**.

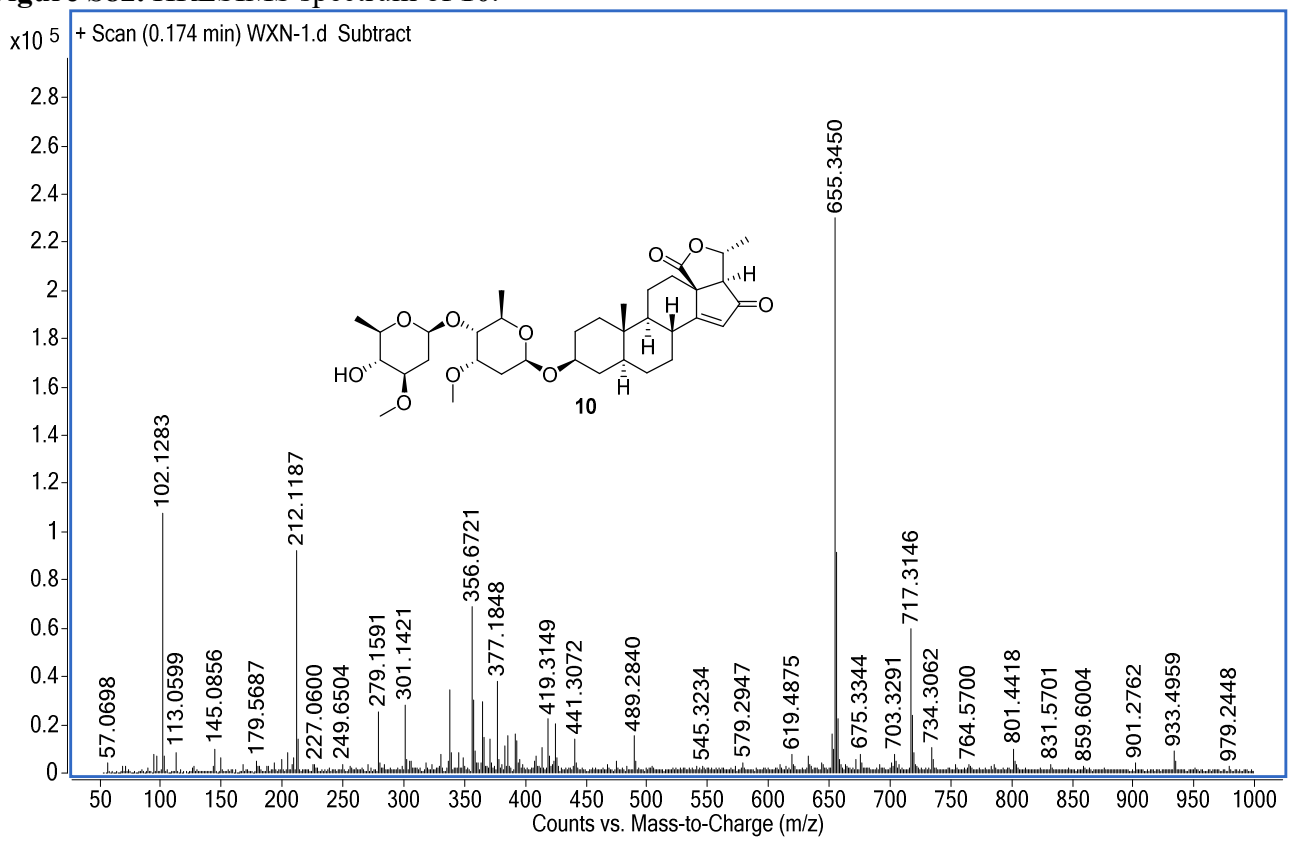

Figure S83. IR spectrum of **10**.

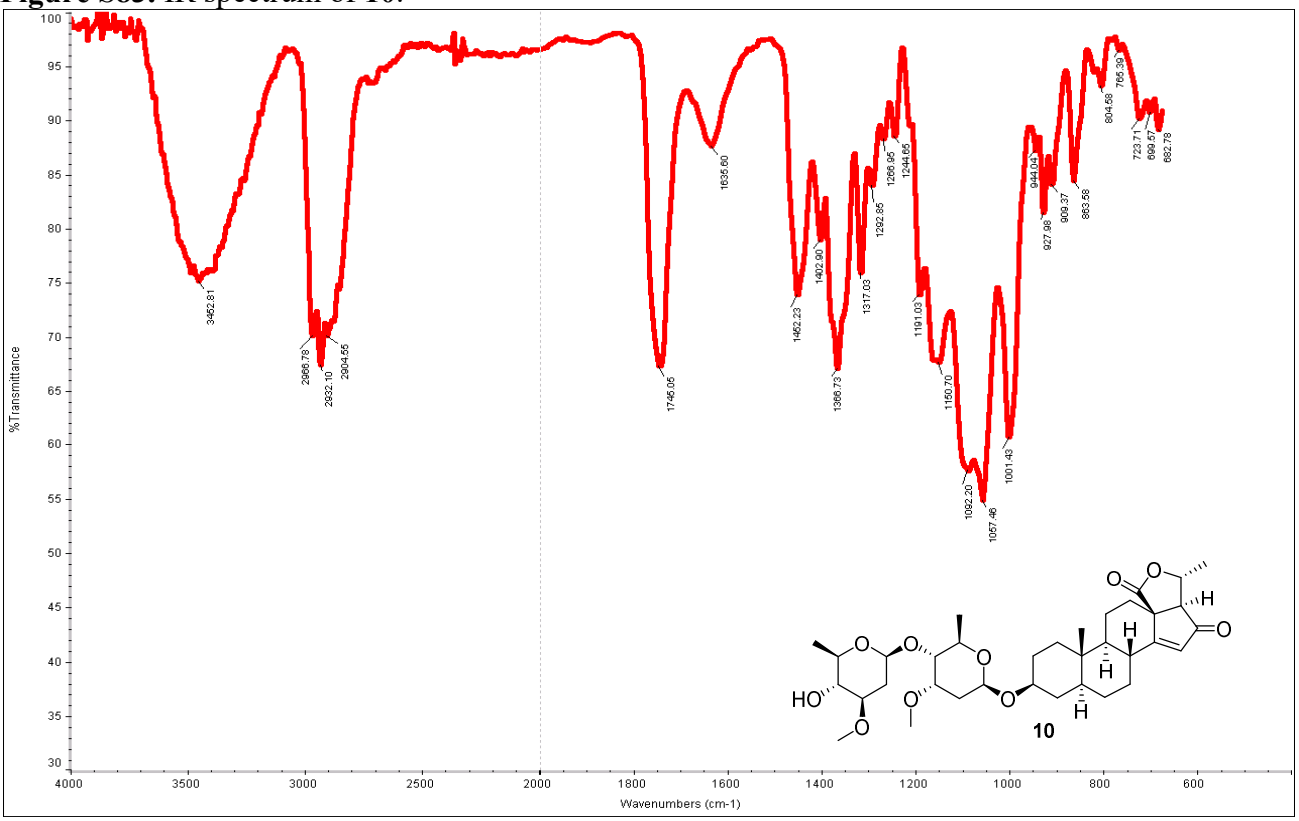

Figure S84. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **11**.

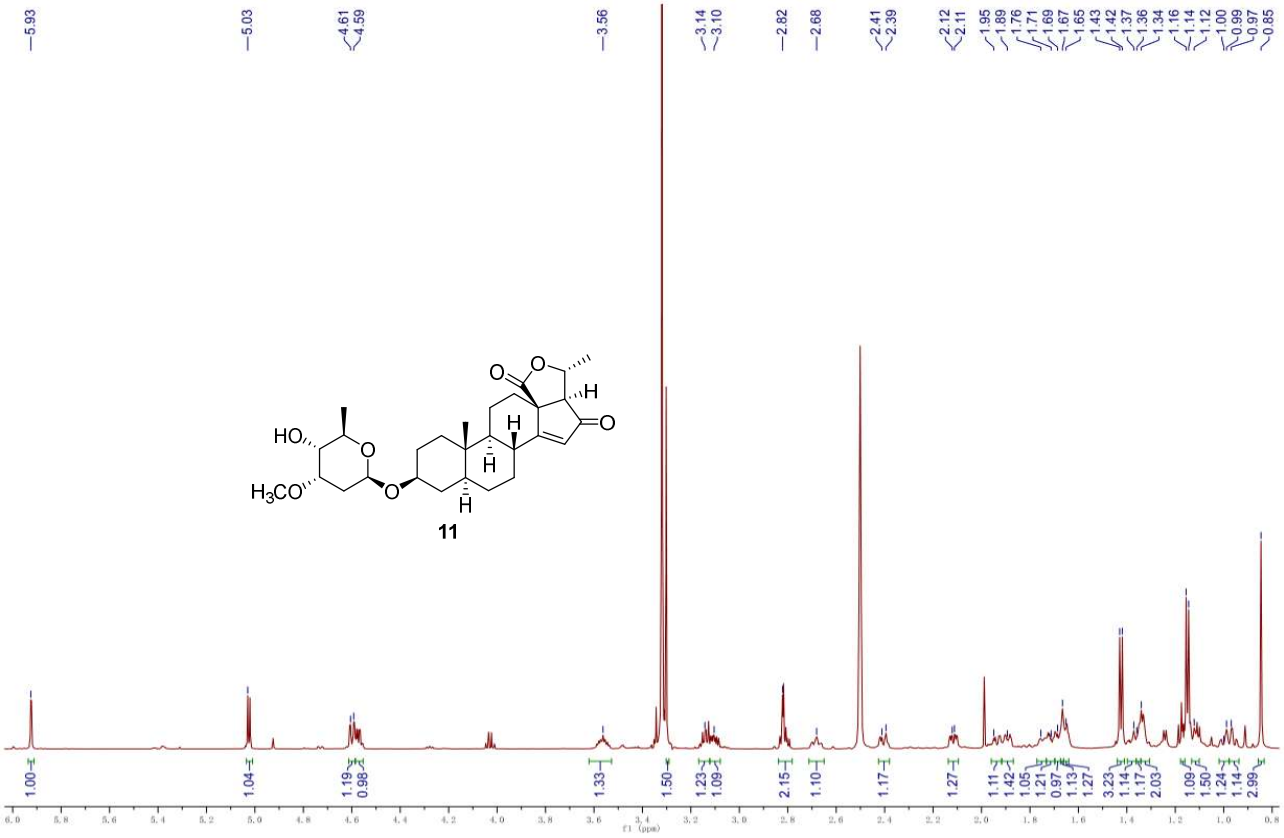

Figure S85. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **11**.

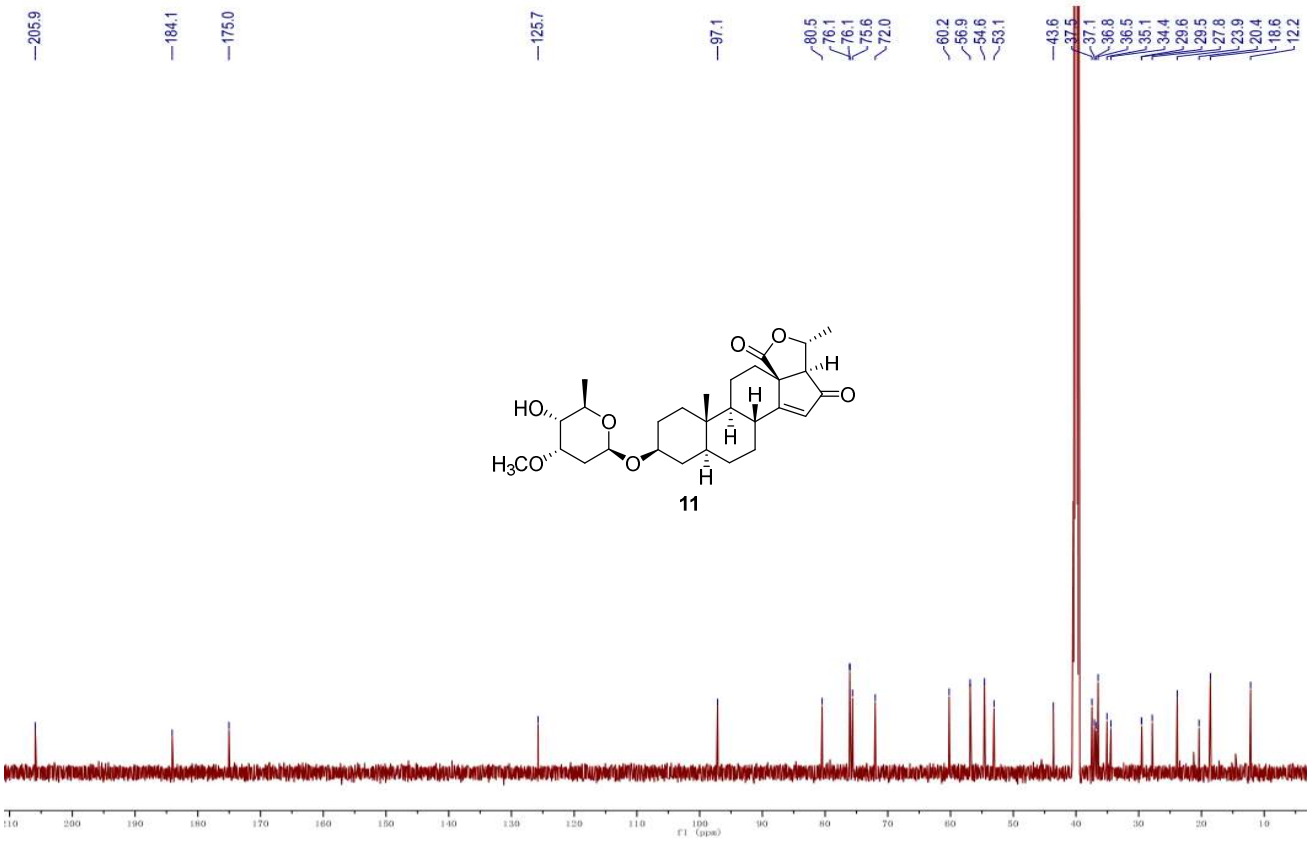

Figure S86. HSQC (600 MHz, $CDCl_3$) spectrum of **11**.

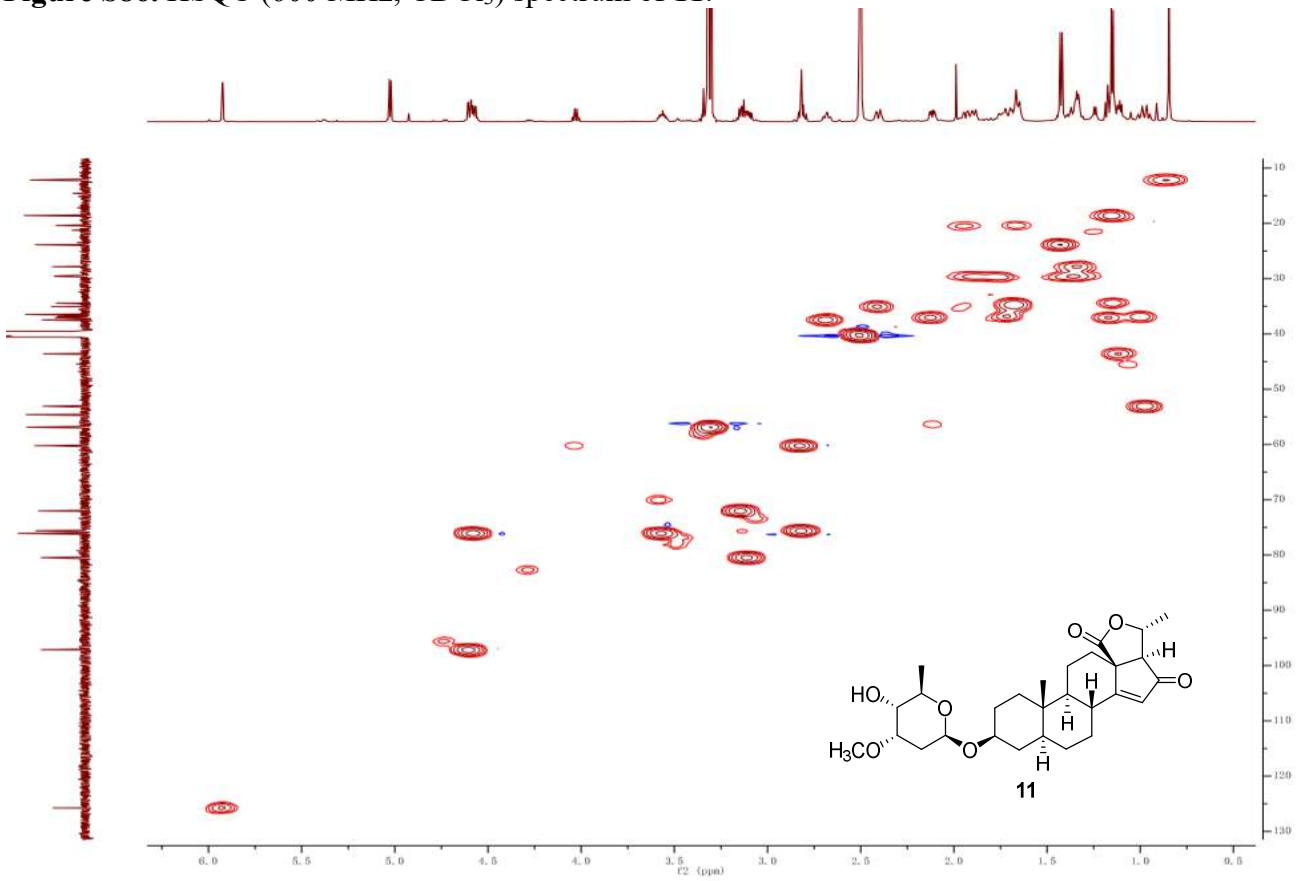

Figure S87. HMBC (600 MHz, $CDCl_3$) spectrum of **11**.

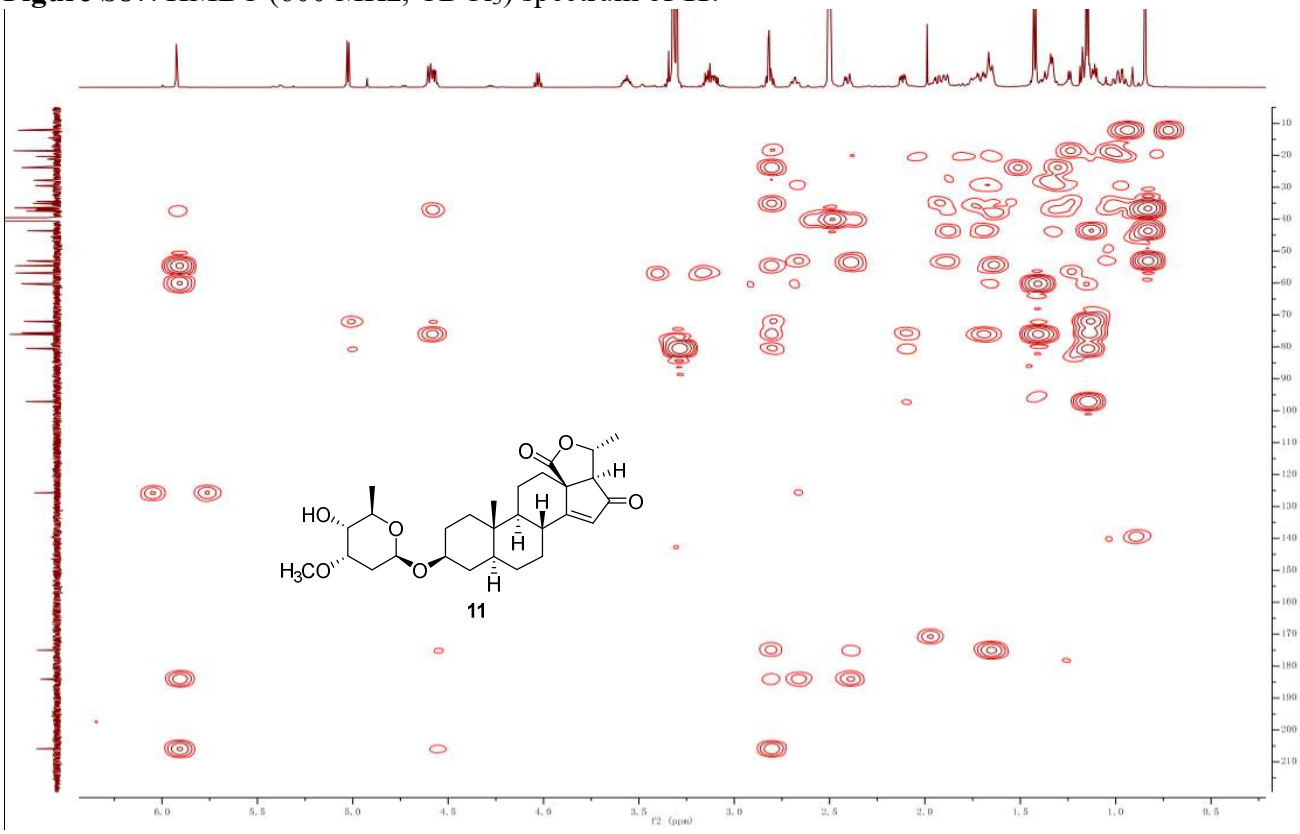

Figure S88. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **11**.

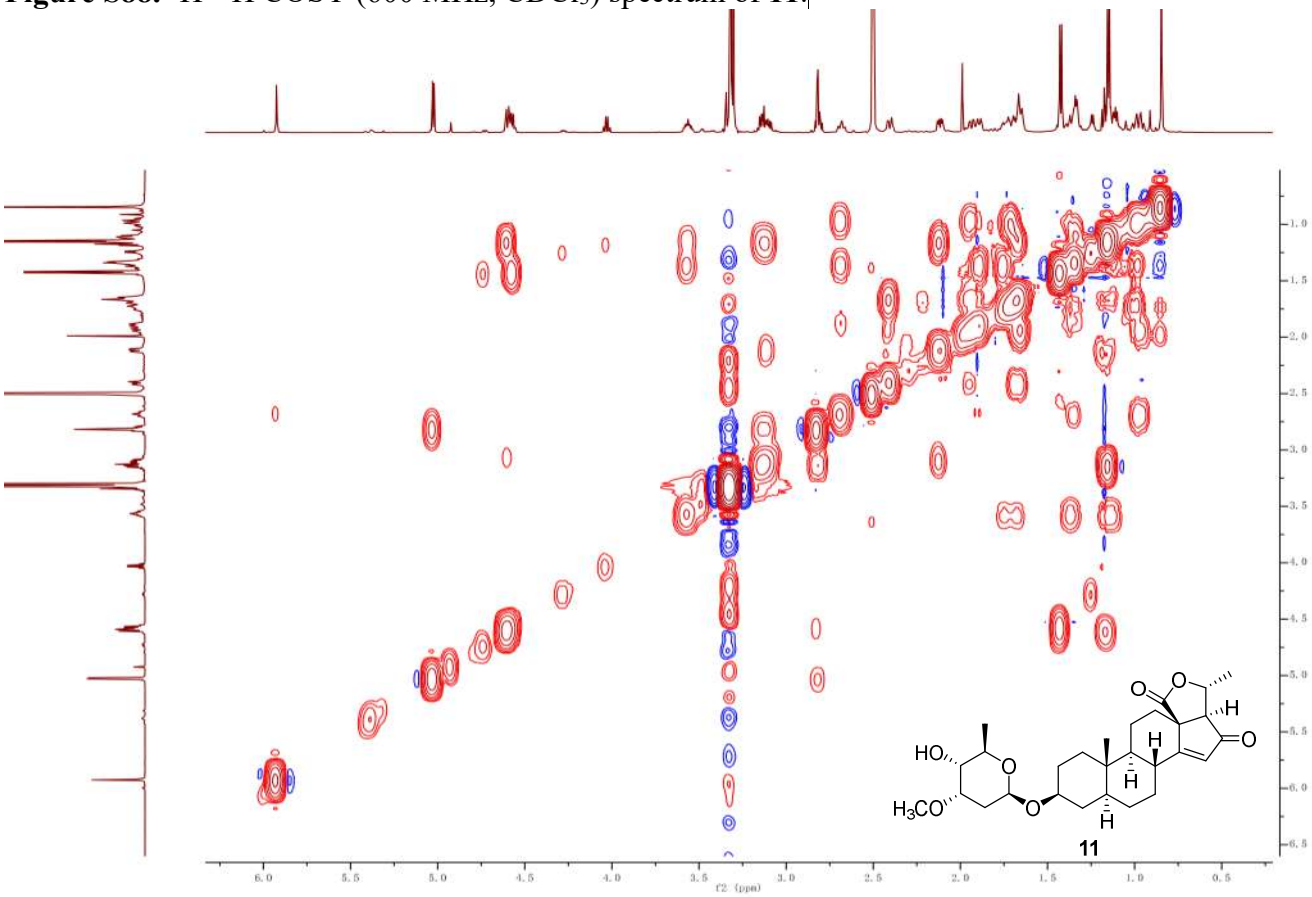

Figure S89. NOESY (600 MHz, $CDCl_3$) spectrum of **11**.

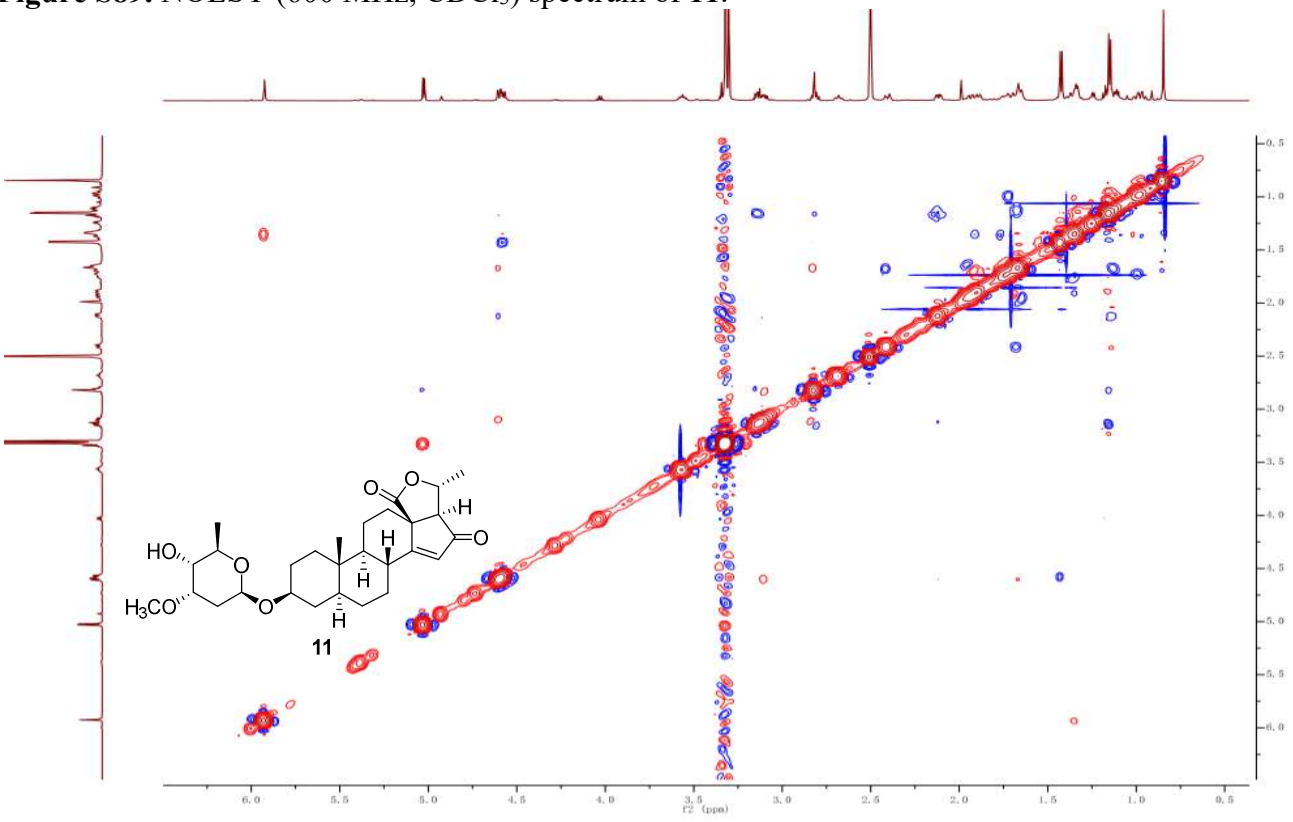

Figure S90. HRESIMS spectrum of **11**.

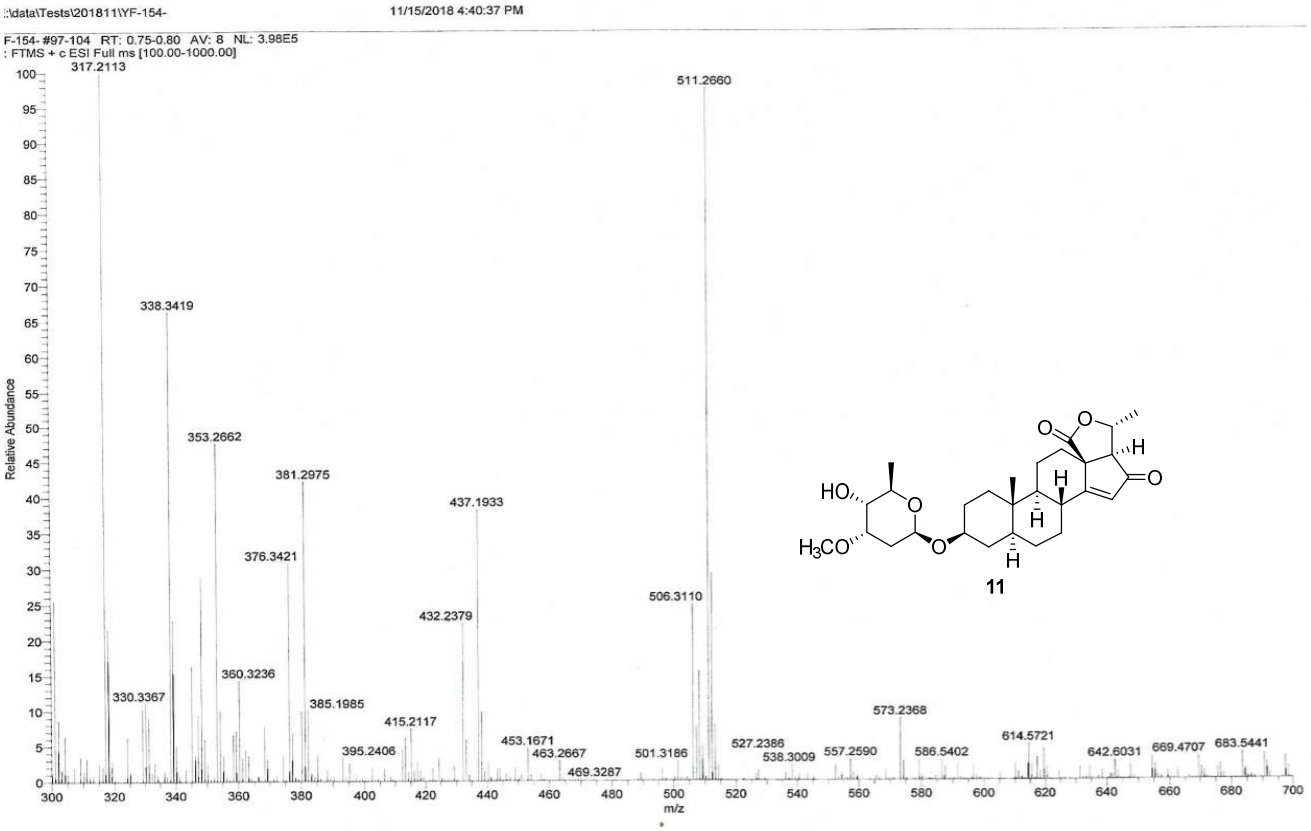

Figure S91. IR spectrum of **11**.

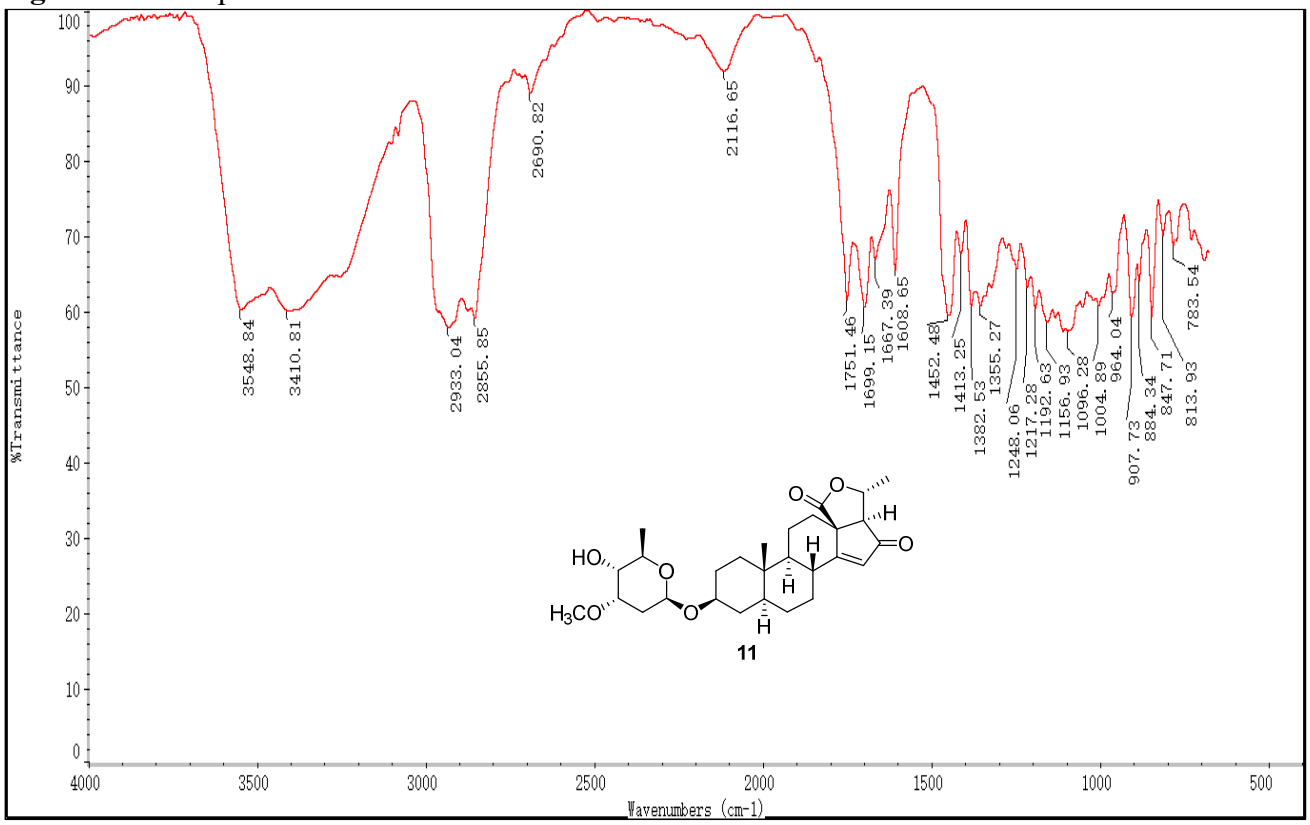

Figure S92. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **12**.

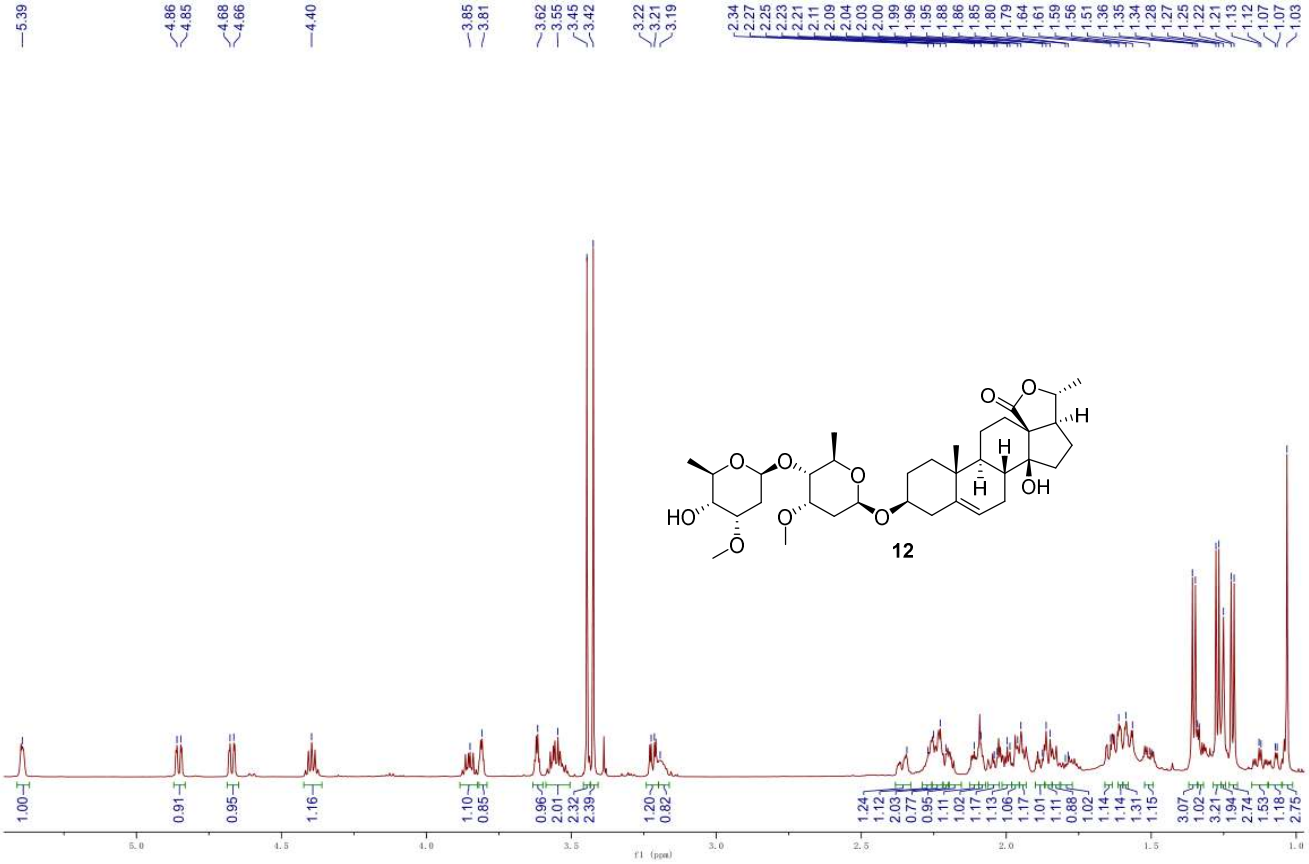

Figure S93. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **12**.

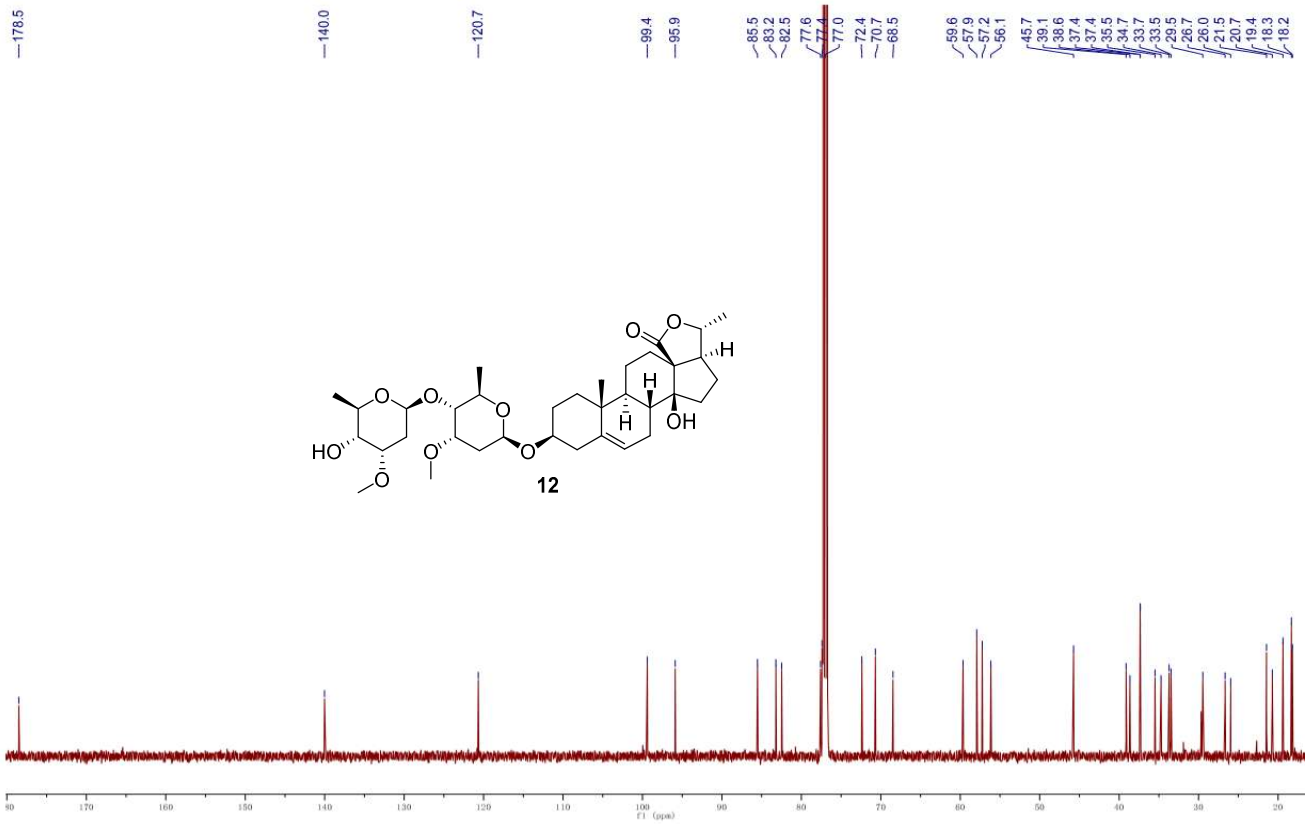

Figure S94. HSQC (600 MHz, $CDCl_3$) spectrum of **12**.

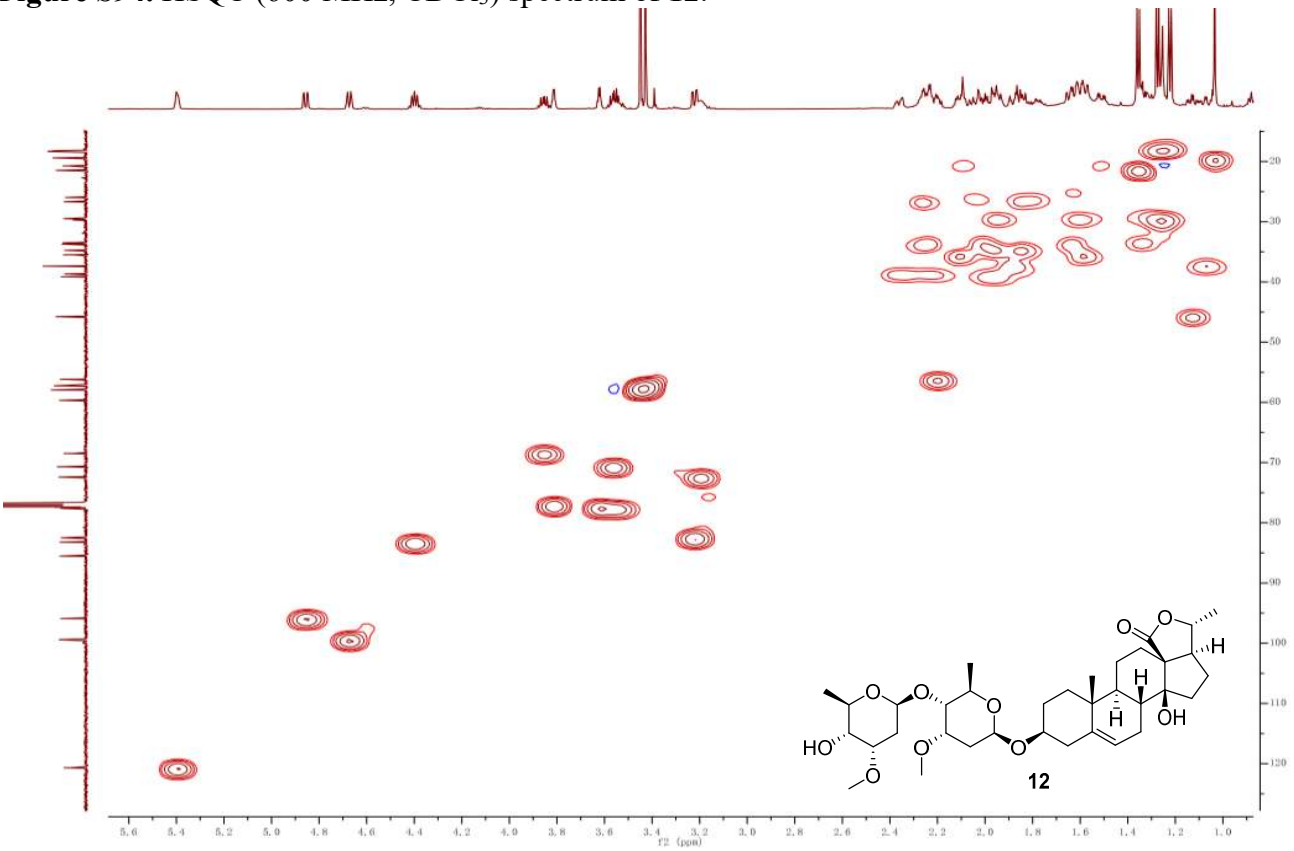

Figure S95. HMBC (600 MHz, $CDCl_3$) spectrum of **12**.

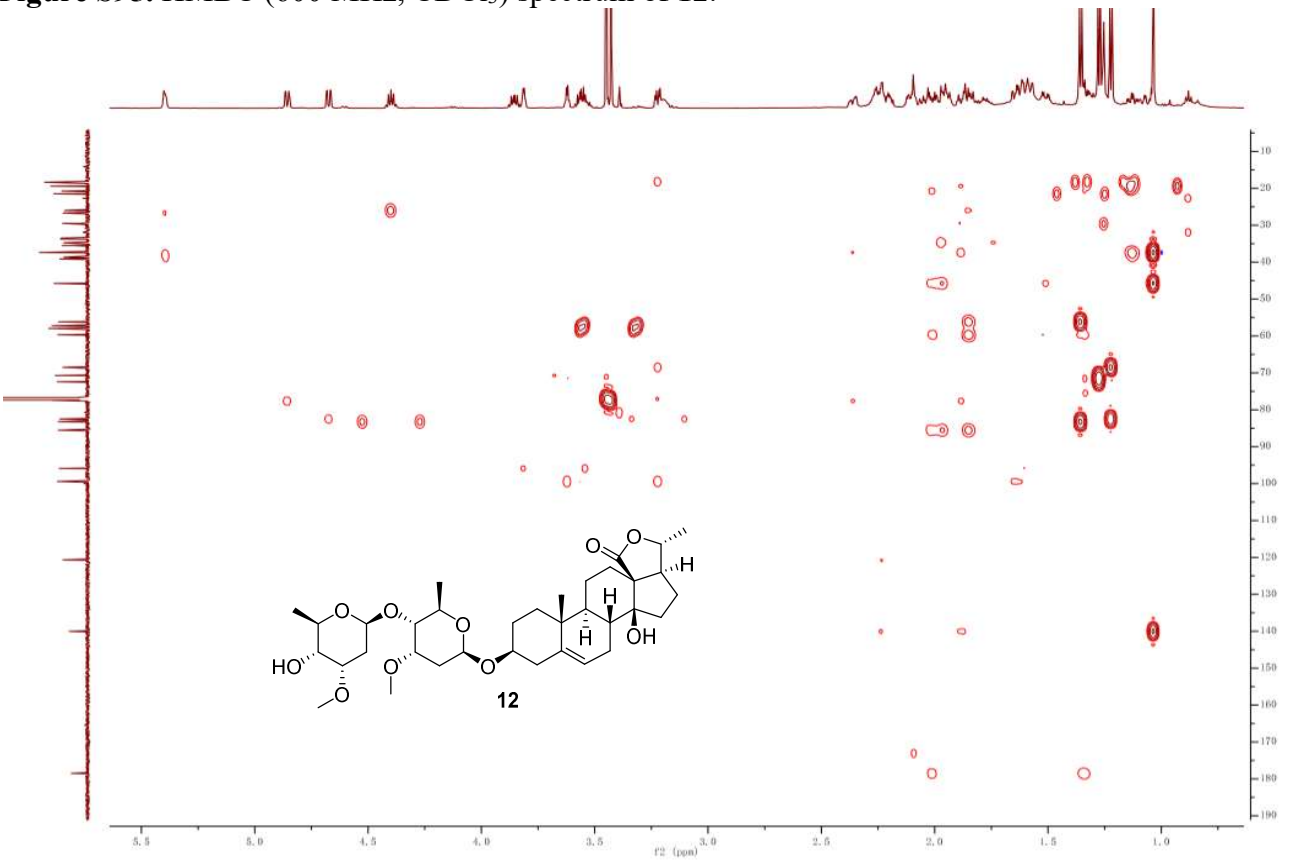

Figure S96. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **12**.

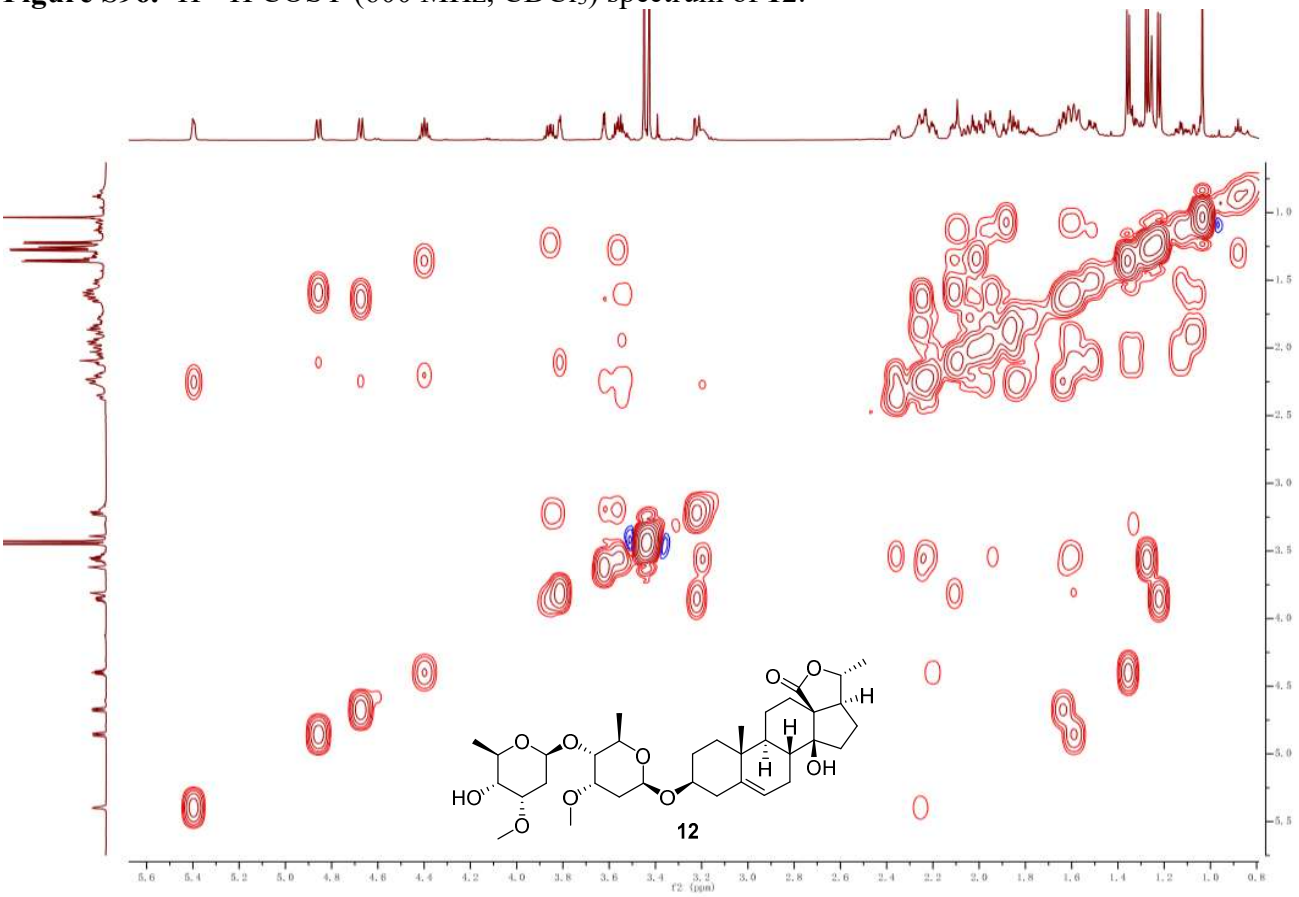

Figure S97. NOESY (600 MHz, $CDCl_3$) spectrum of **12**.

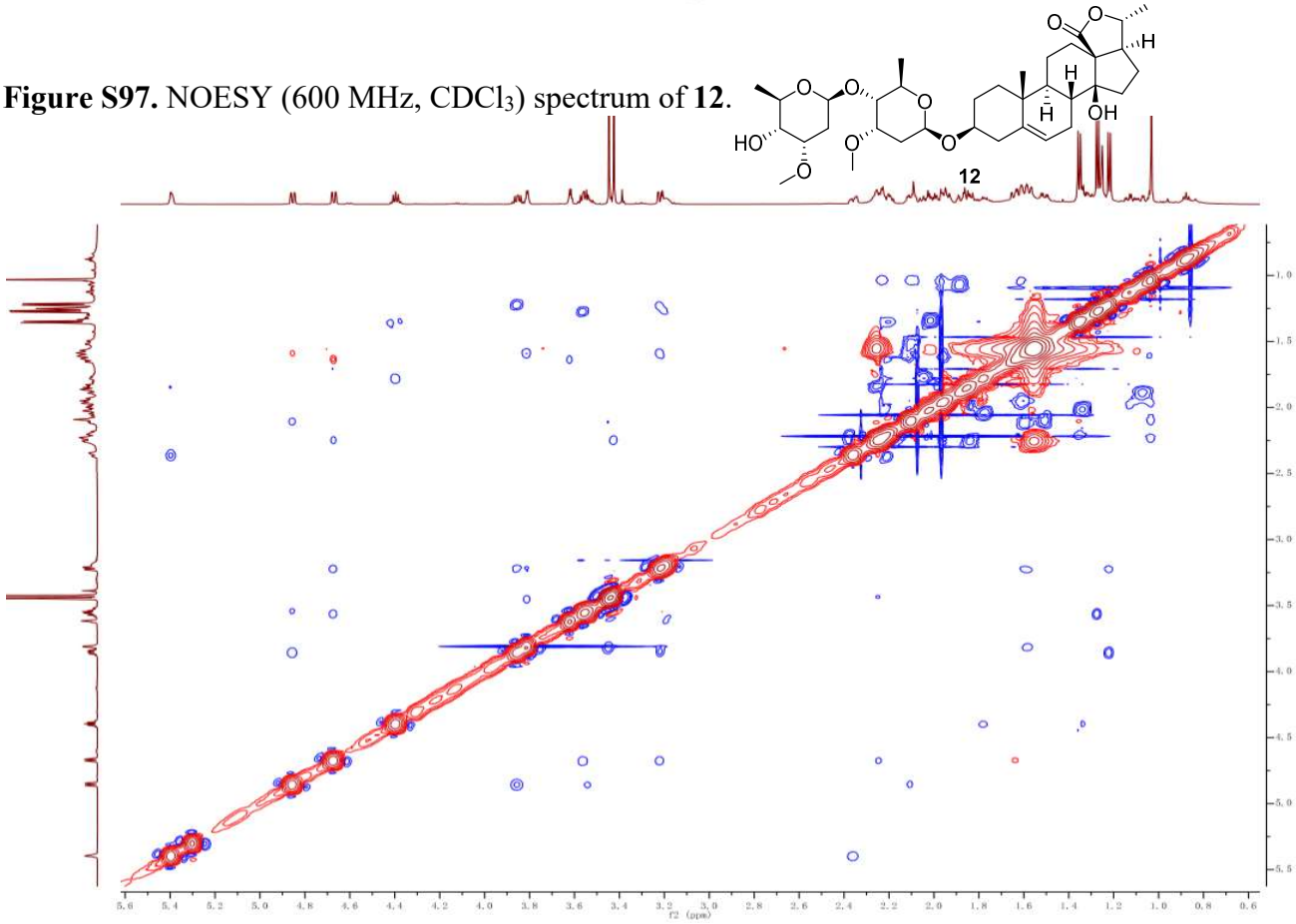

Figure S98. HRESIMS spectrum of **12**.

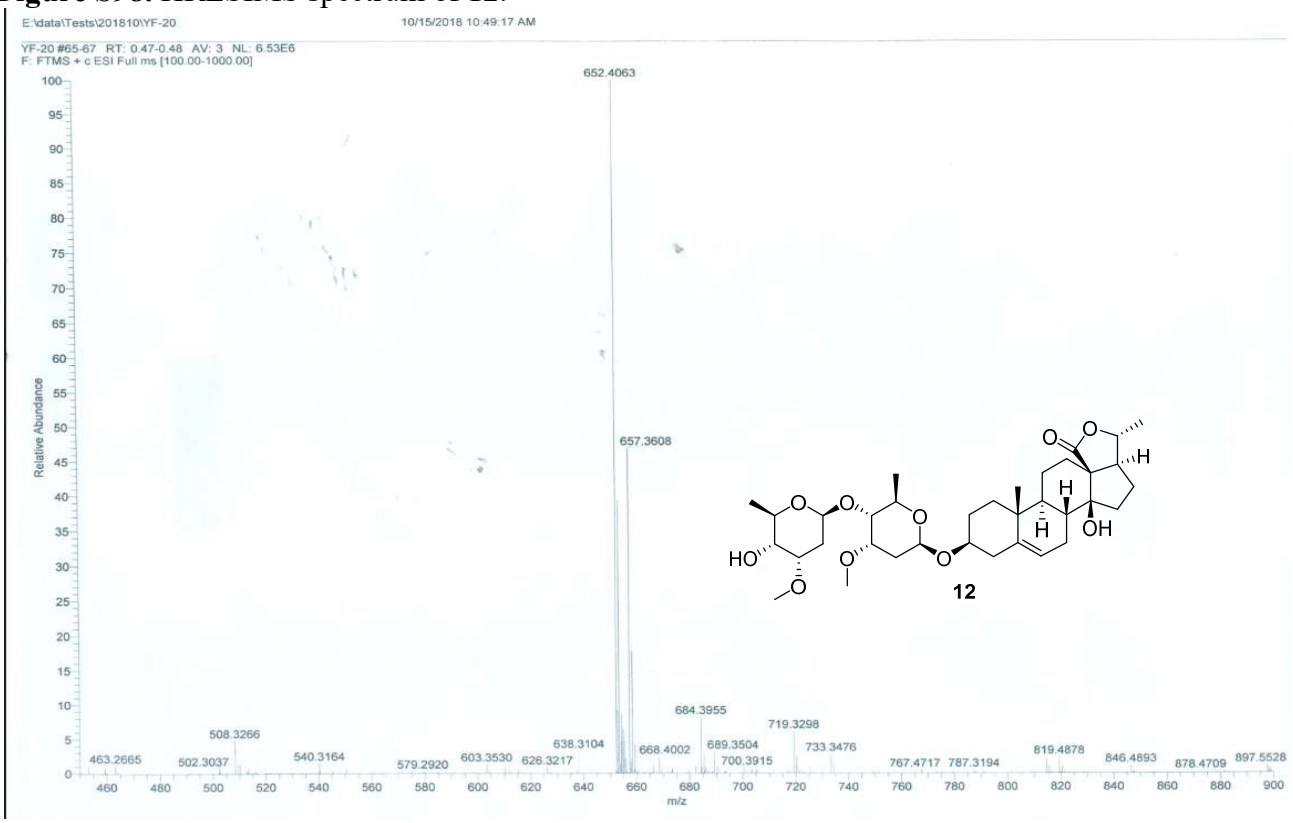

Figure S99. IR spectrum of **12**.

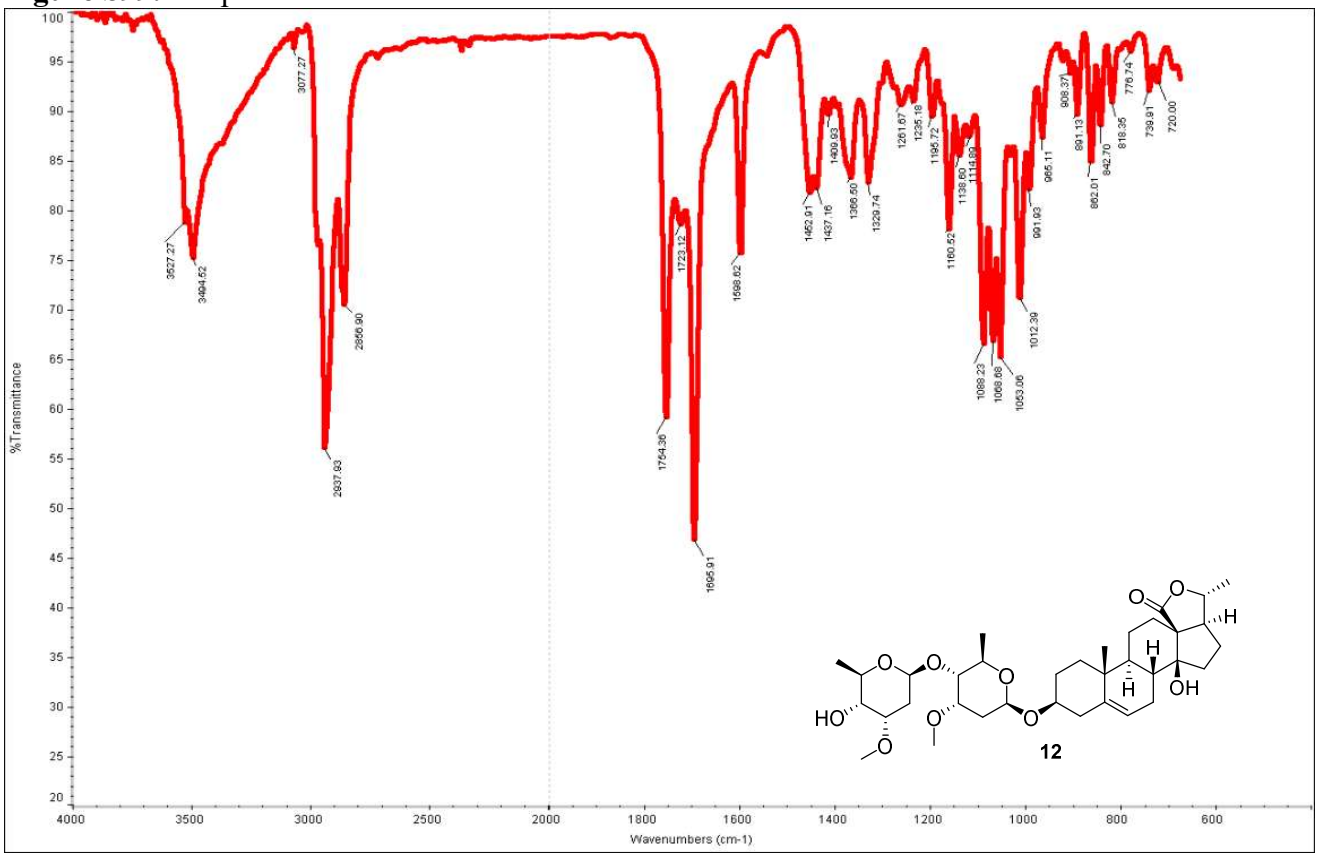

Figure S100. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **13**.

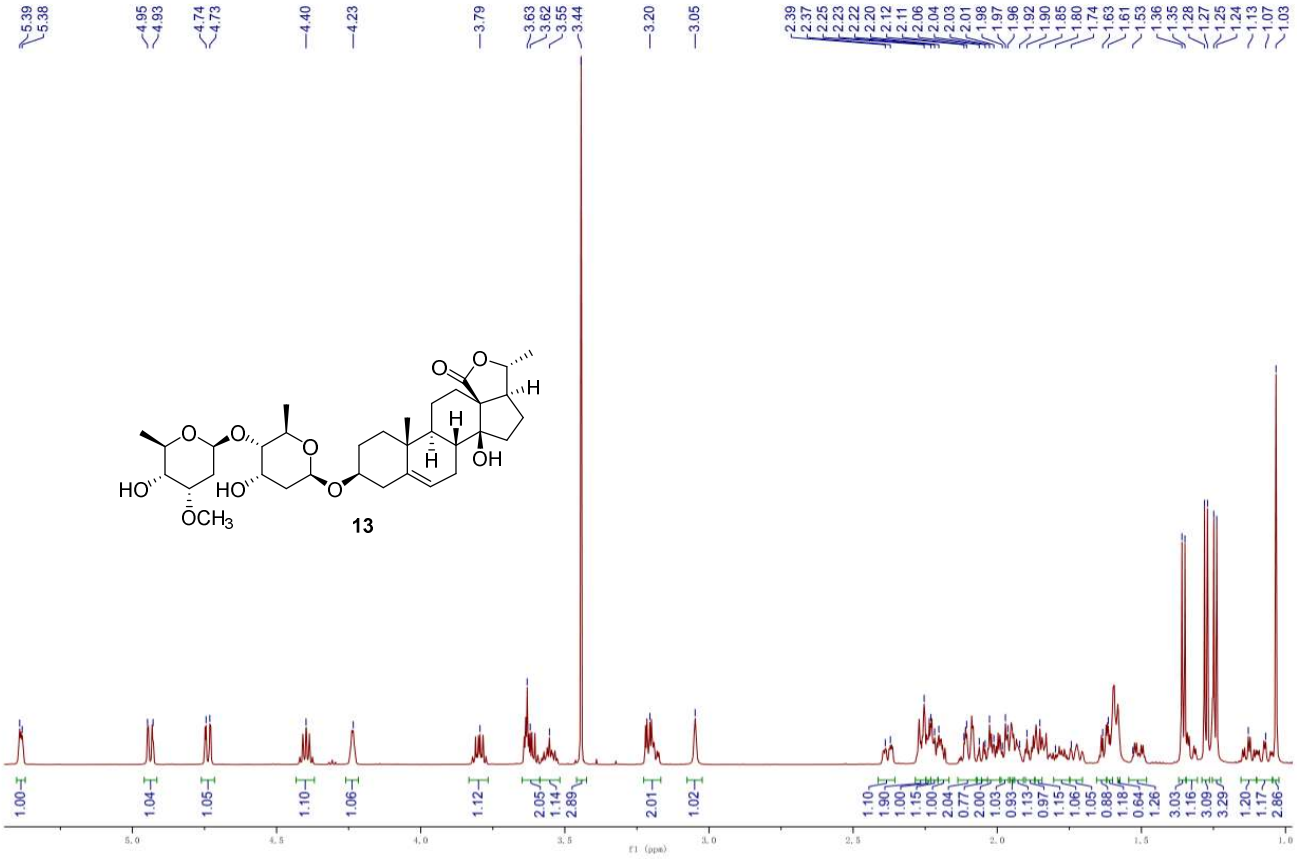

Figure S101. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **13**.

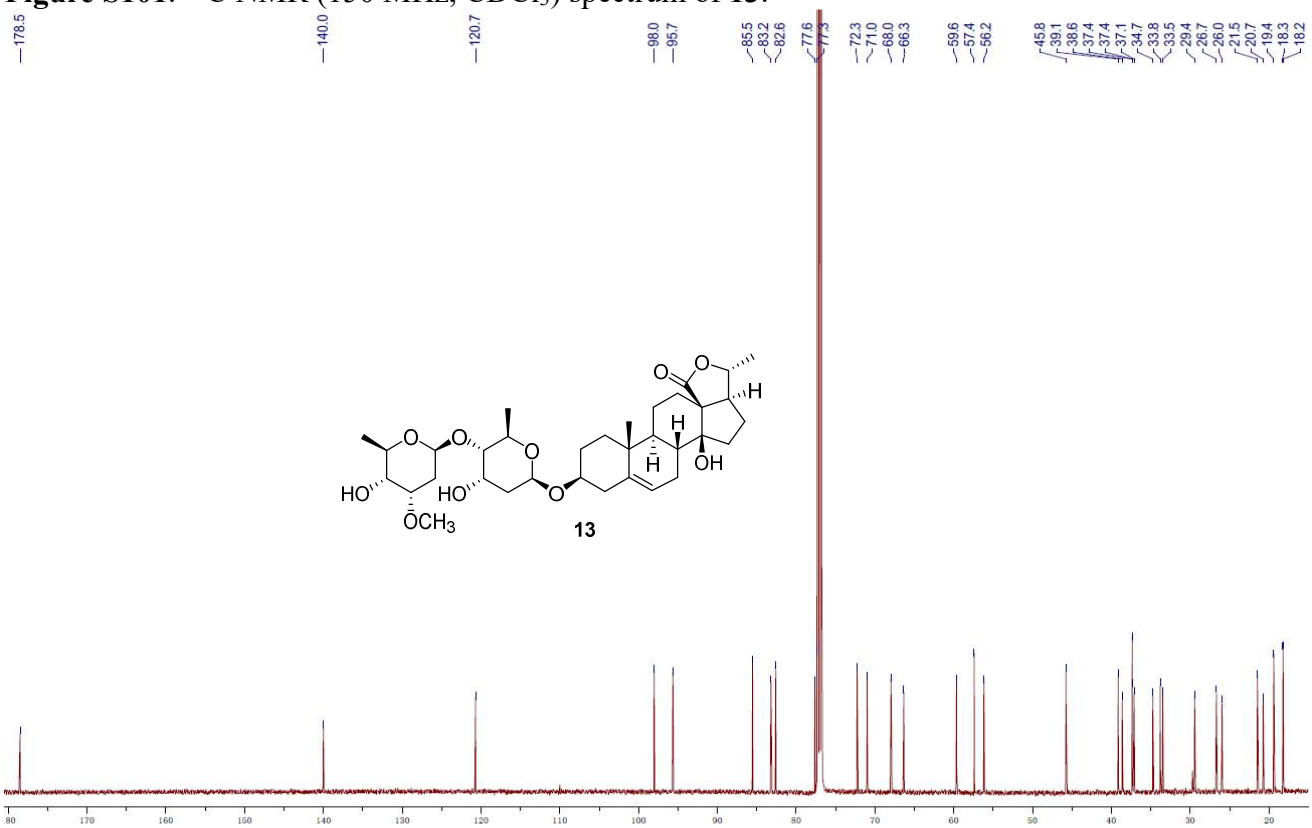

Figure S102. HSQC (600 MHz, $CDCl_3$) spectrum of **13**.

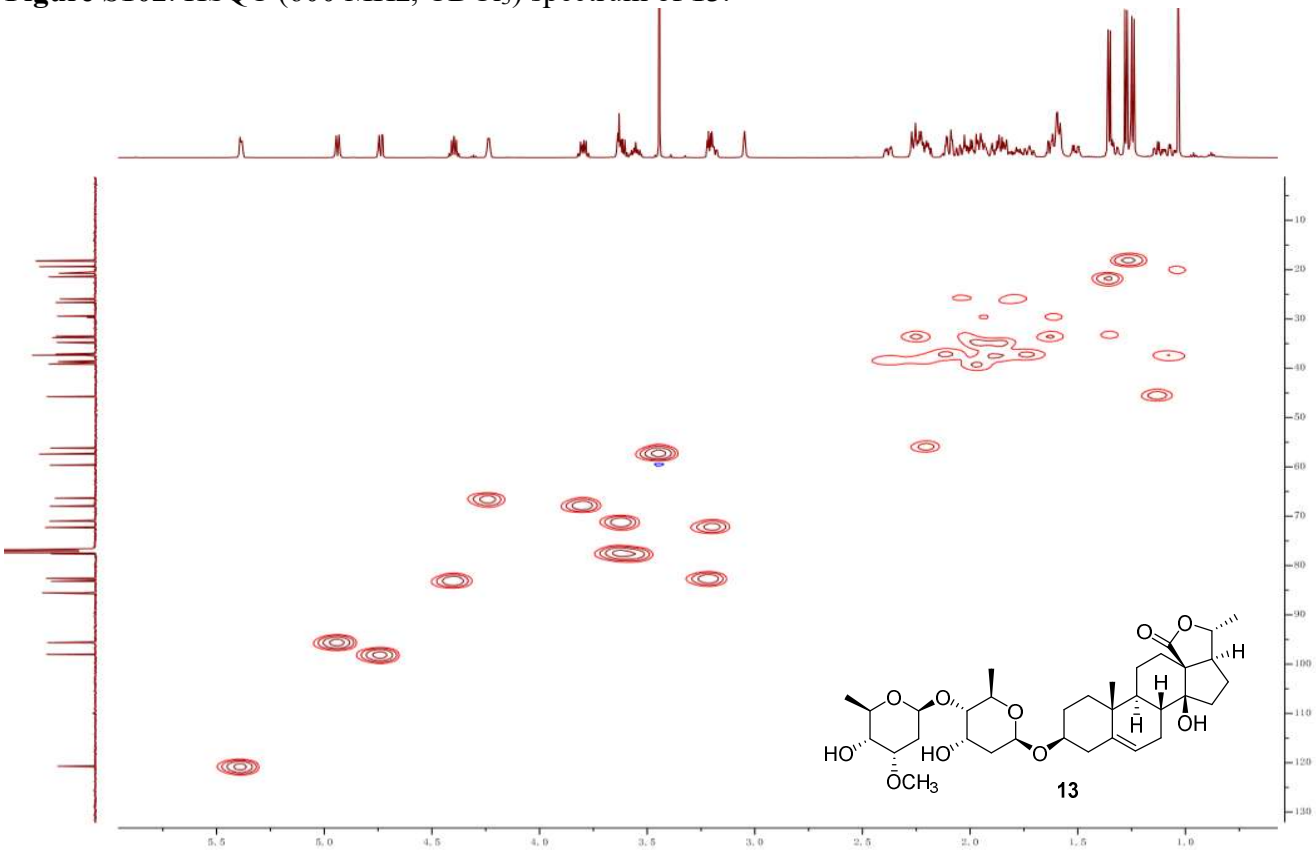

Figure S103. HMBC (600 MHz, $CDCl_3$) spectrum of **13**.

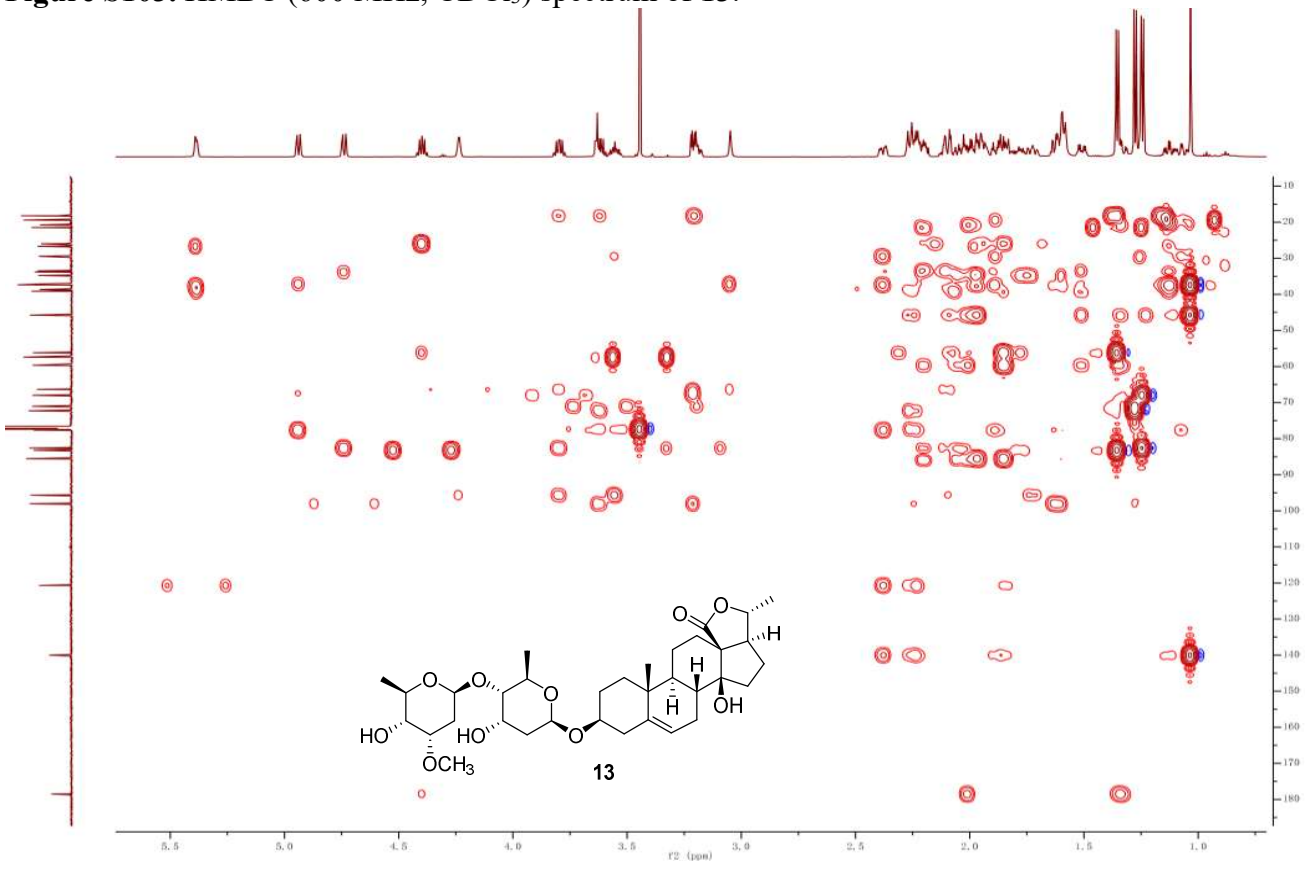

Figure S104. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **13**.

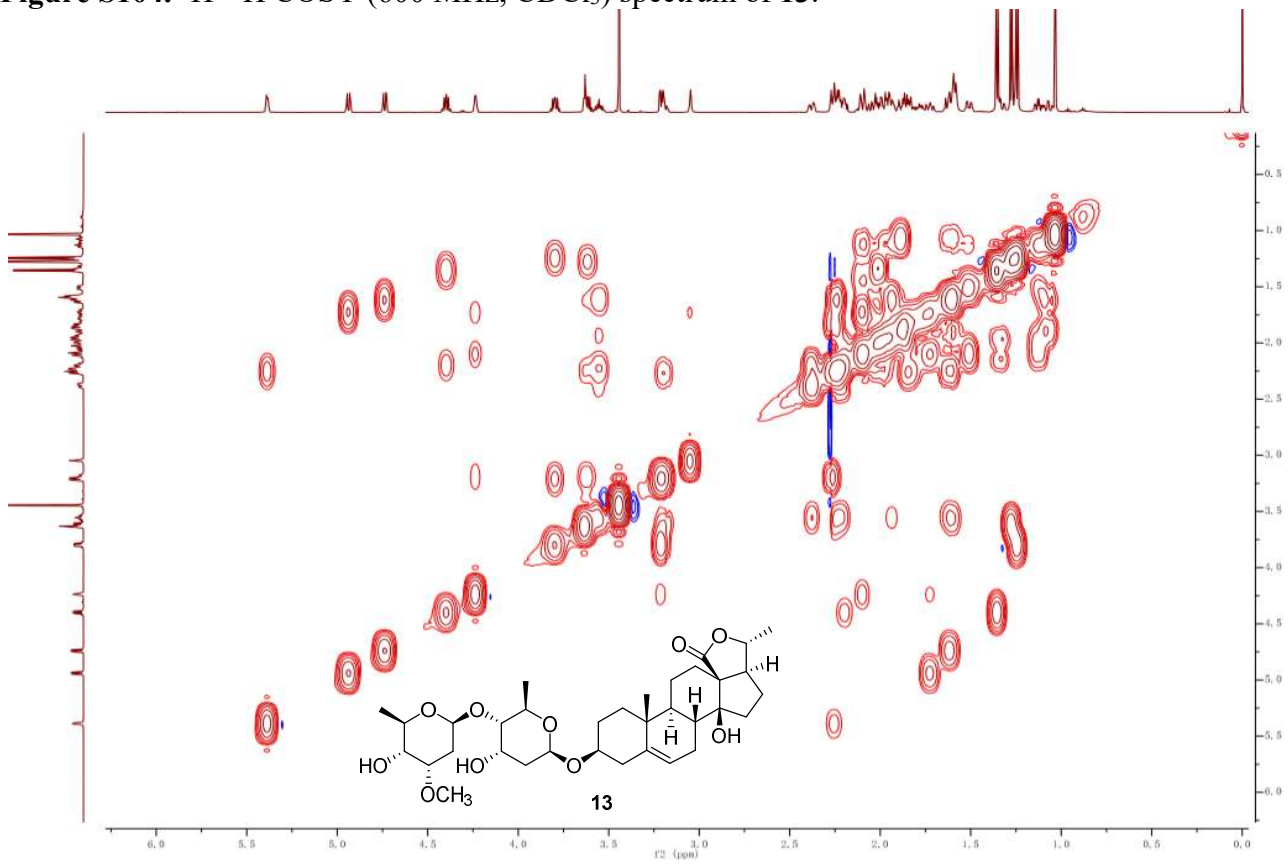

Figure S105. NOESY (600 MHz, $CDCl_3$) spectrum of **13**.

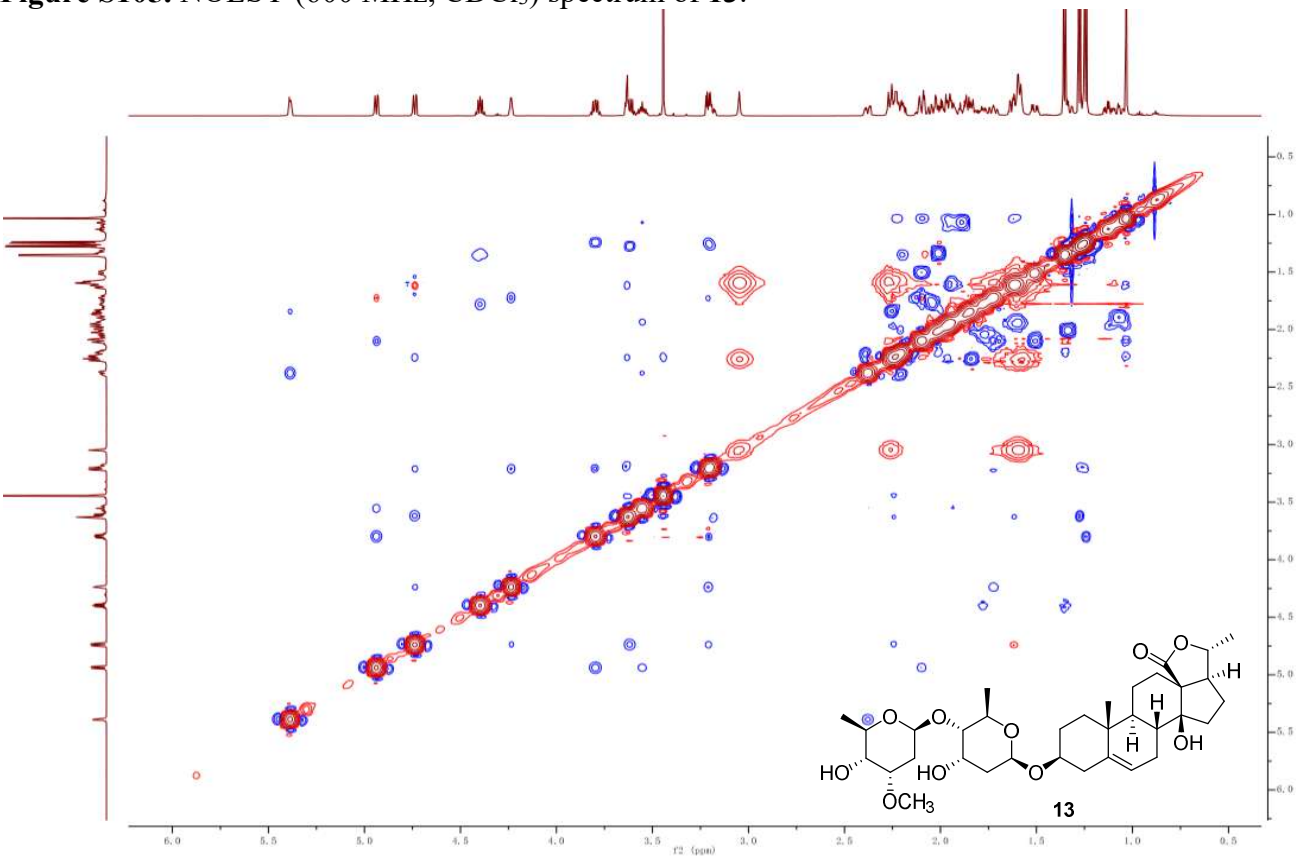

Figure S106. HRESIMS spectrum of **13**.

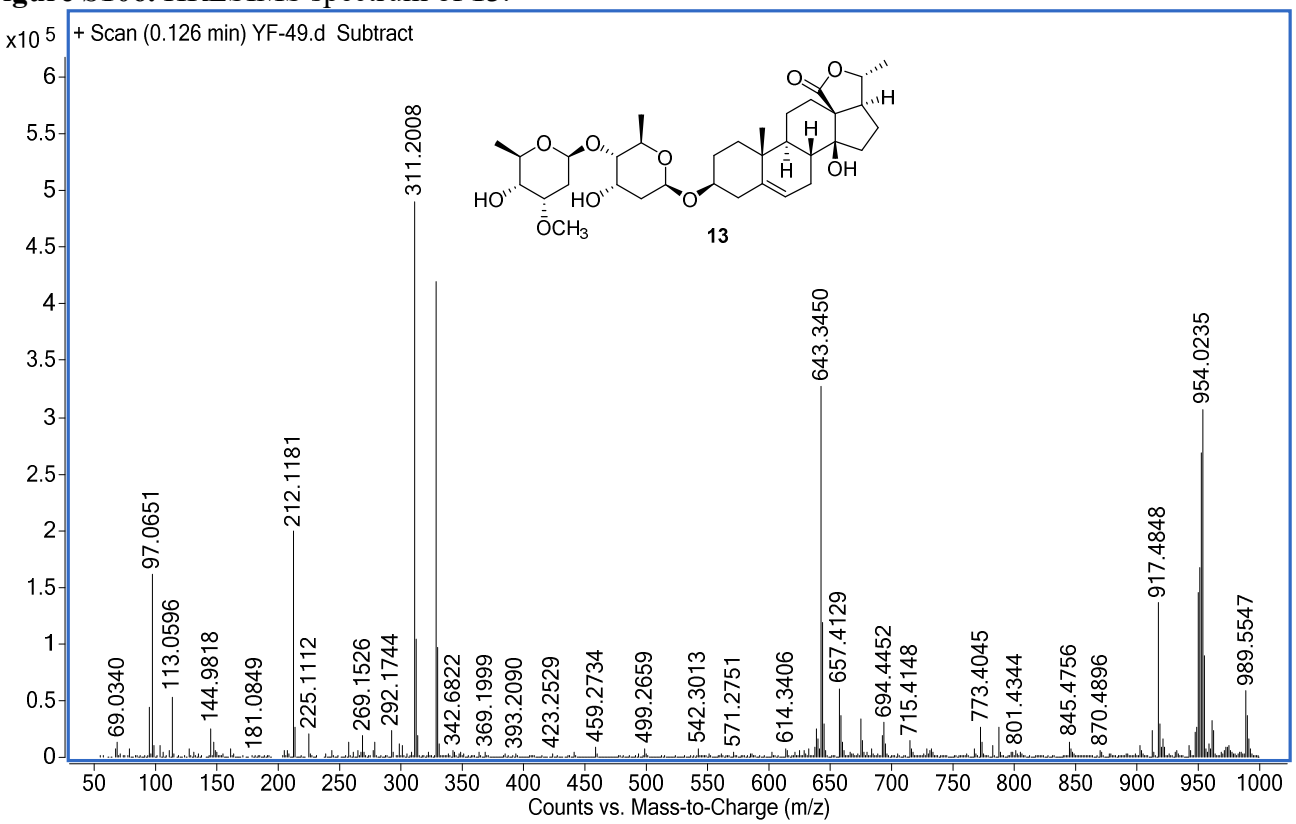

Figure S107. IR spectrum of **13**.

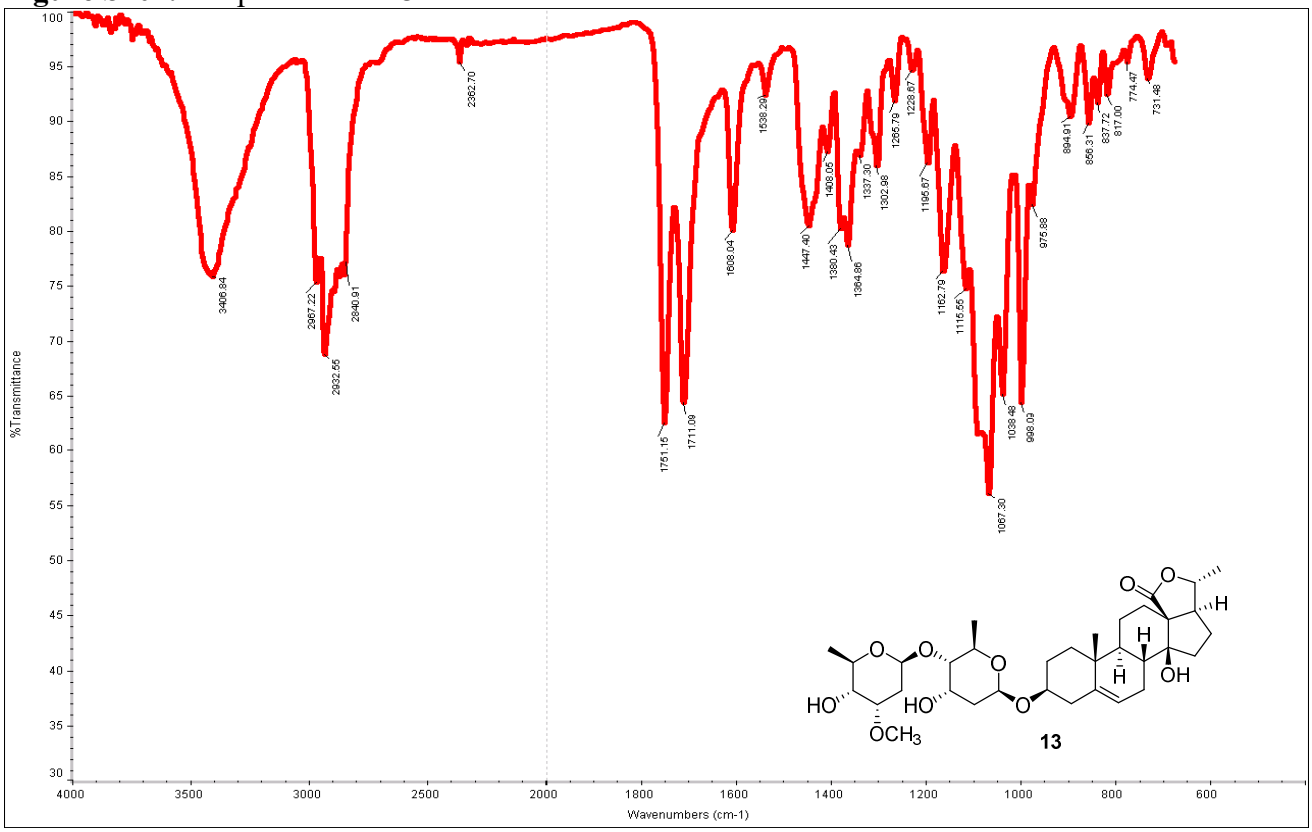

Figure S108. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **14**.

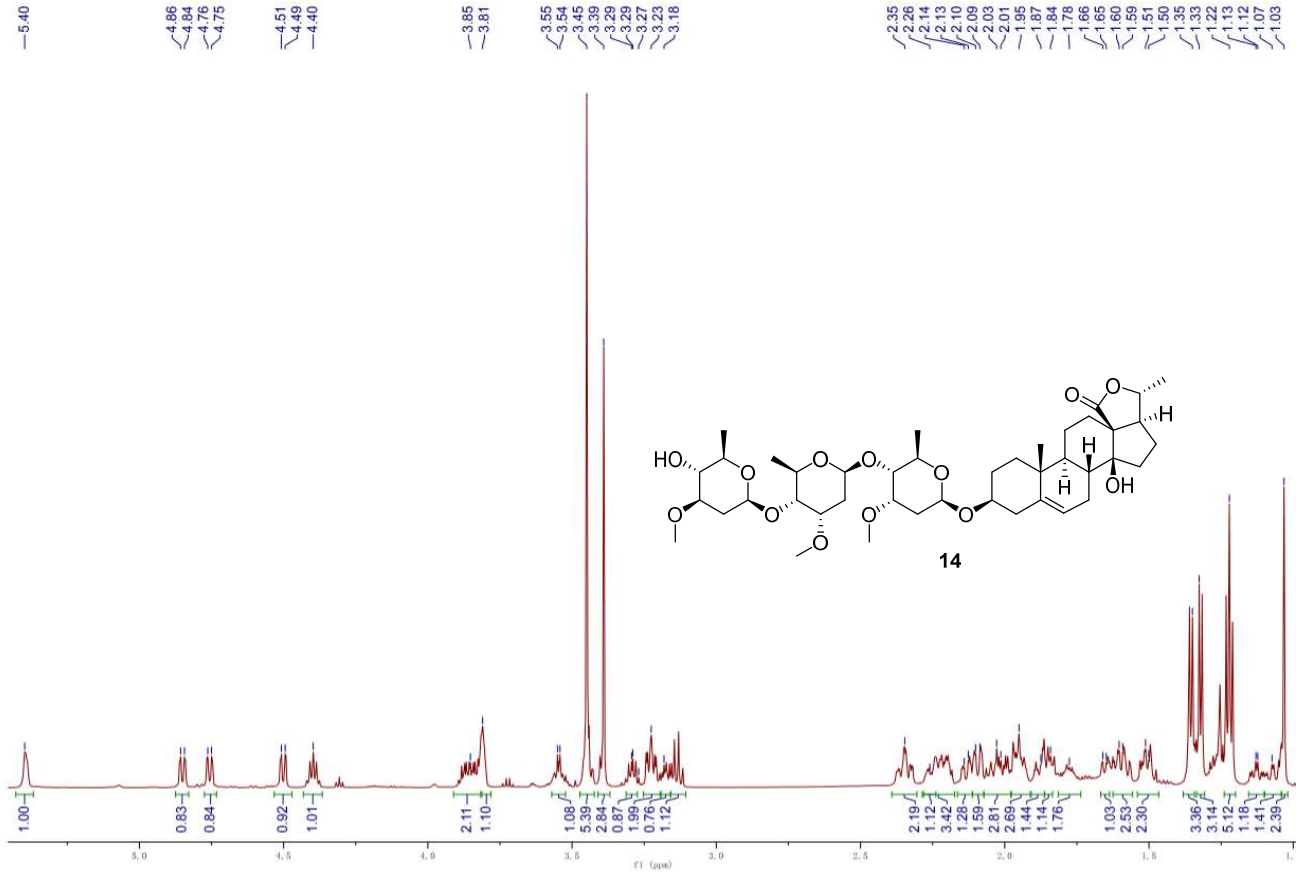

Figure S109. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **14**.

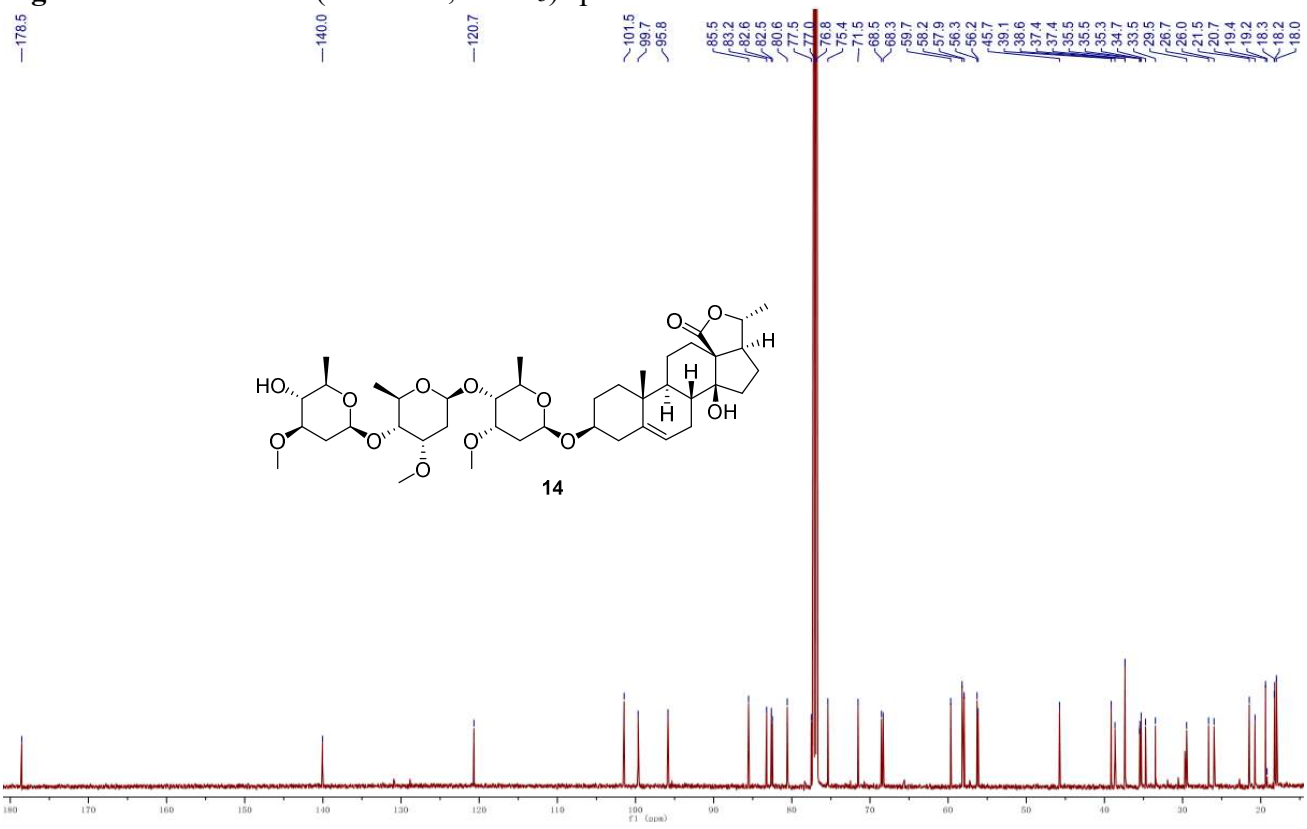

Figure S110. HSQC (600 MHz, $CDCl_3$) spectrum of **14**.

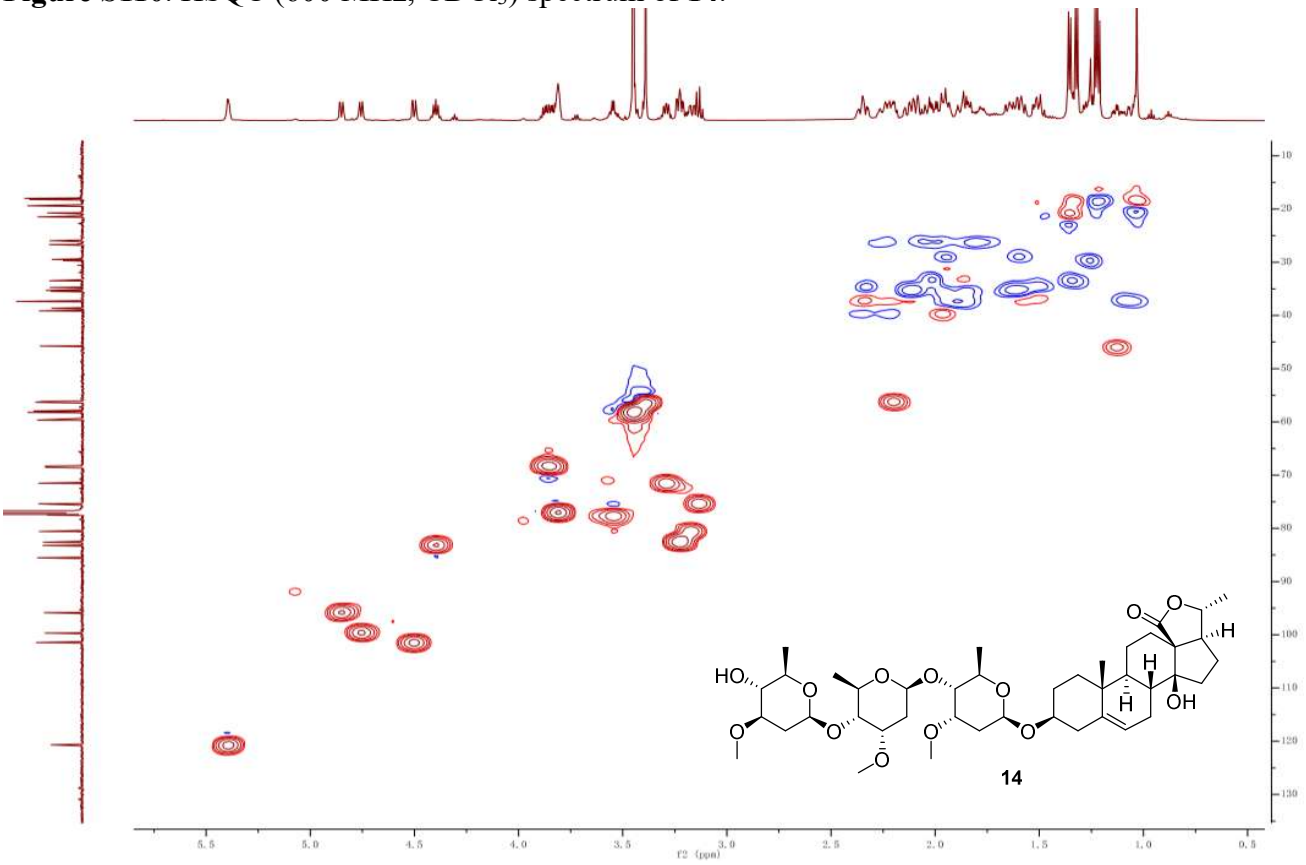

Figure S111. HMBC (600 MHz, $CDCl_3$) spectrum of **14**.

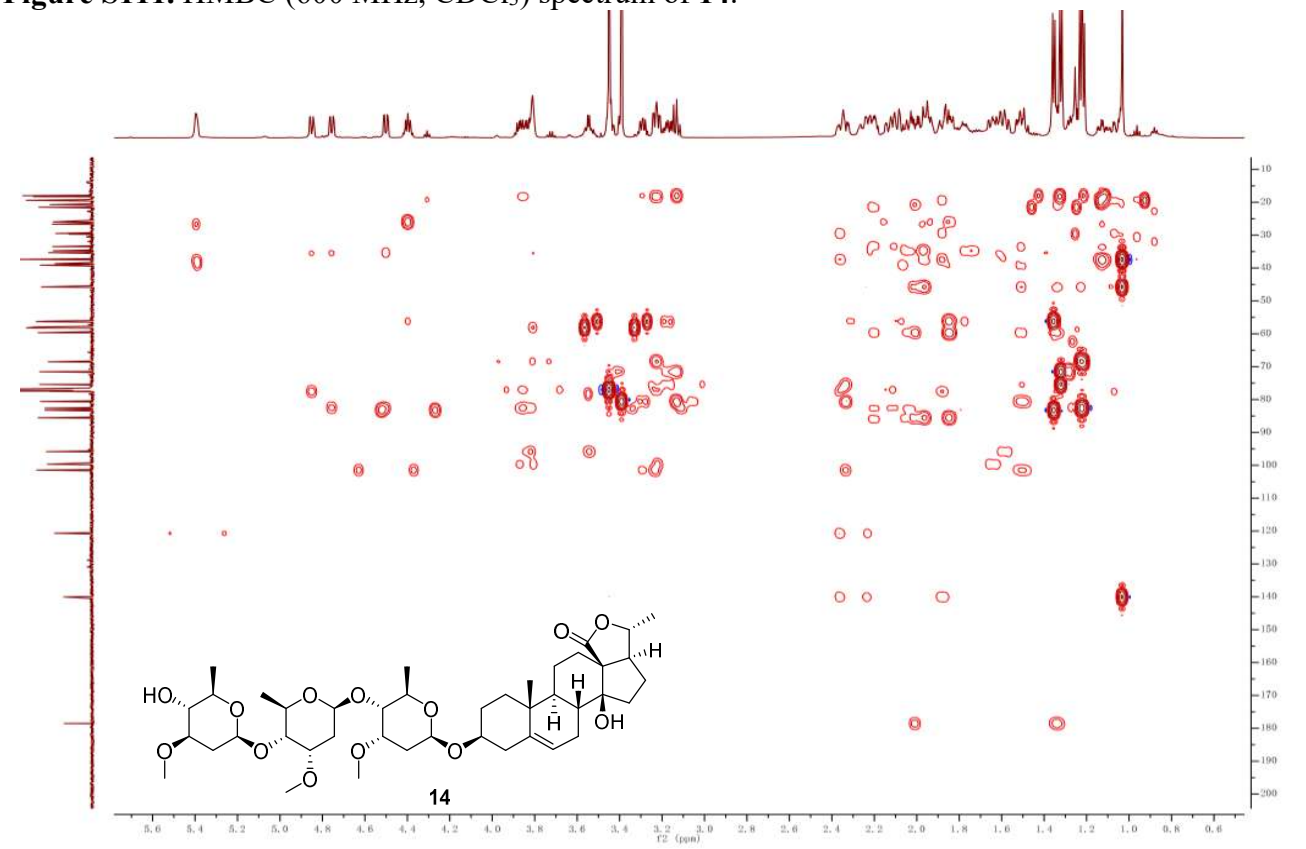

Figure S112. $^{1}H–^{1}H$ COSY (600 MHz, $CDCl_3$) spectrum of **14**.

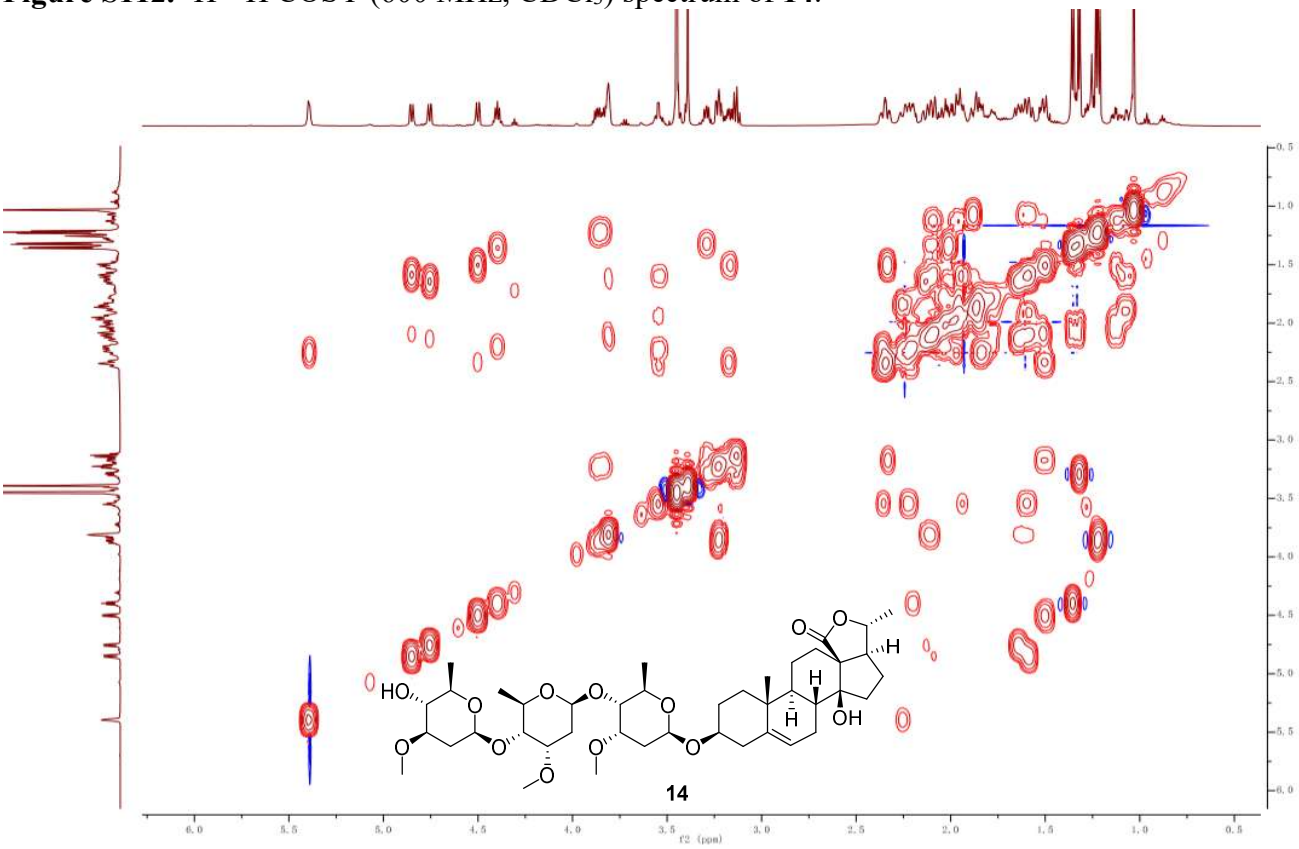

Figure S113. NOESY (600 MHz, $CDCl_3$) spectrum of **14**.

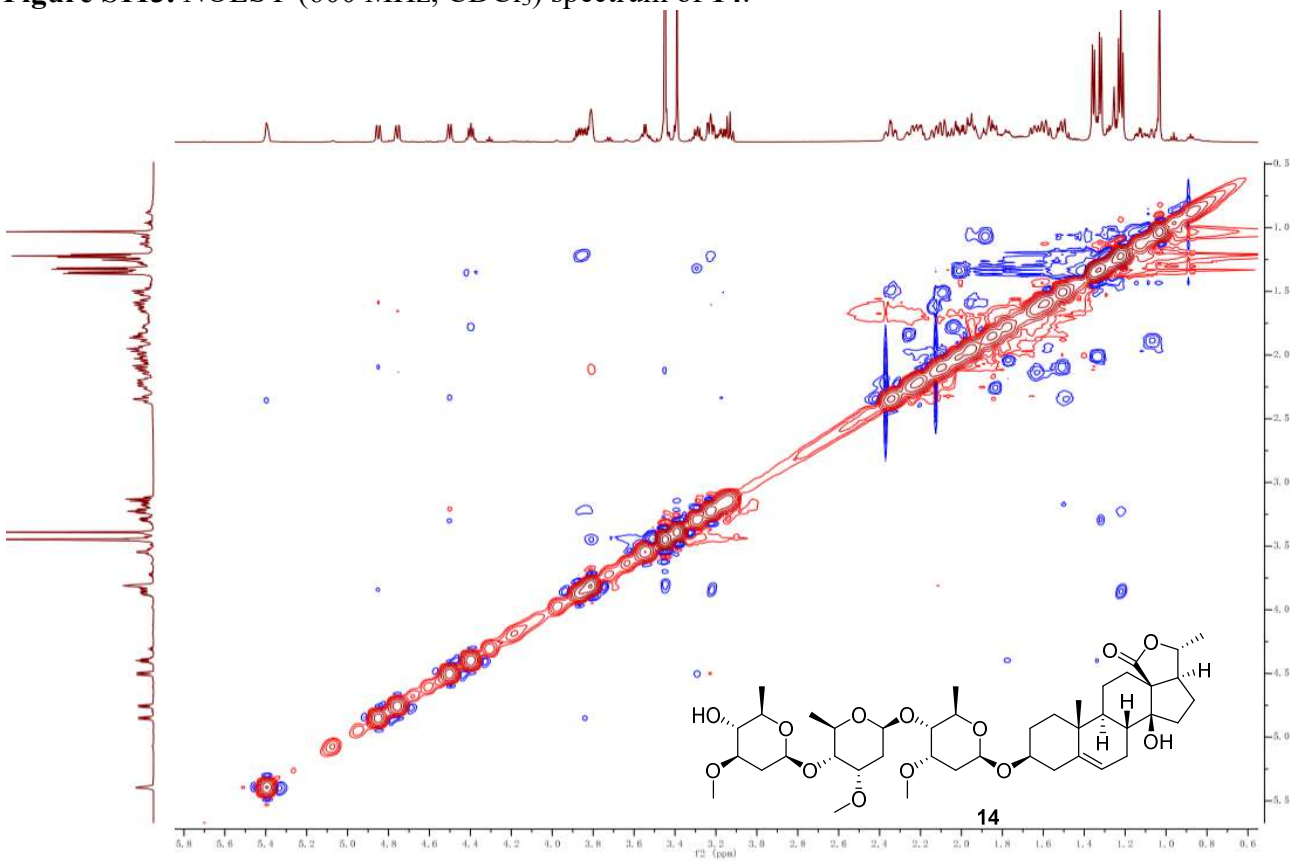

Figure S114. HRESIMS spectrum of **14**.

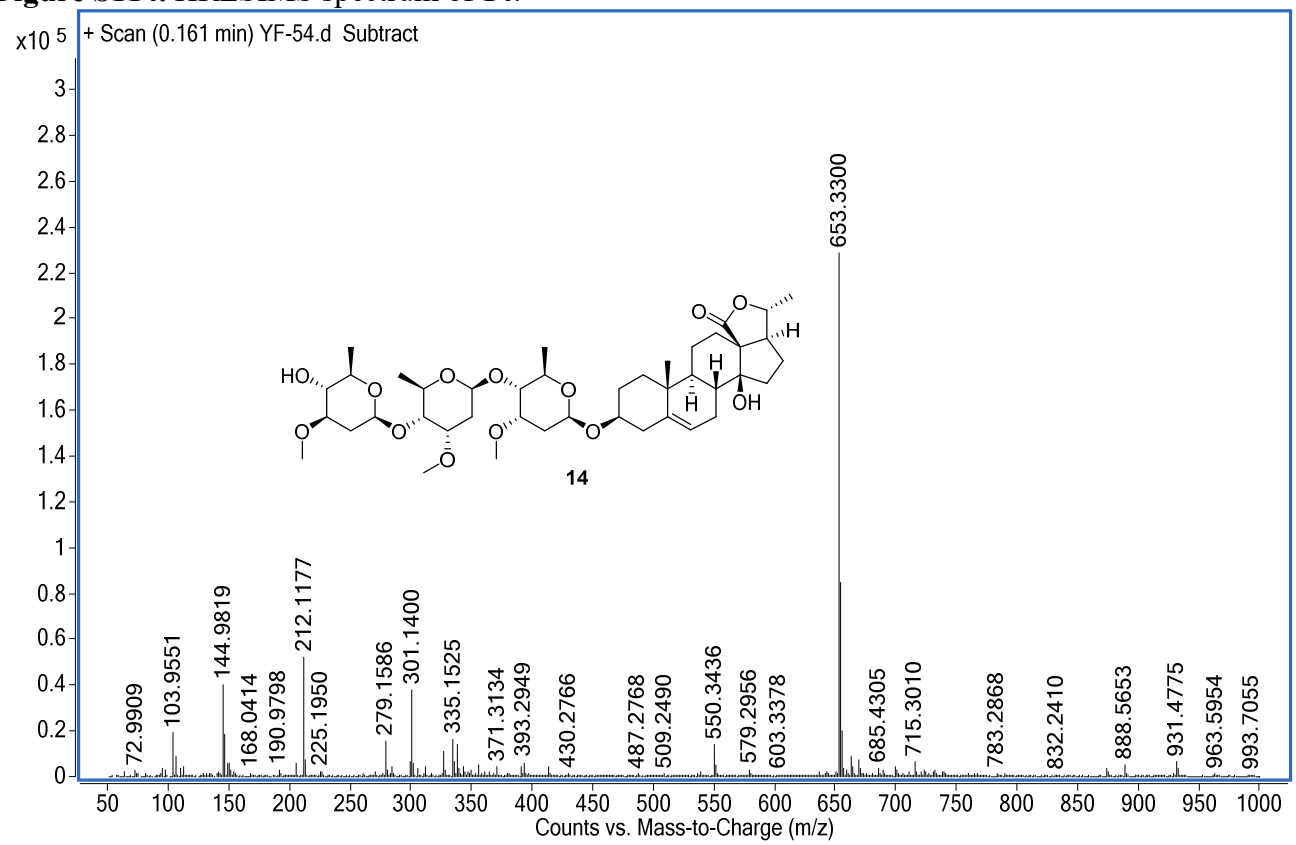

Figure S115. IR spectrum of **14**.