

Supporting Information

Tersone A-G, new pyridone alkaloids from the deep-sea fungus *Phomopsis tersa*

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1. Experimental Section

1.1 X-ray crystallographic analysis of compounds **1a** and **3**.

Table S1. X-ray crystallographic data for (–)-tersone A (**1a**).

Empirical formula	C ₁₉ H ₁₉ NO ₃
Formula weight	309.34
Temperature	99.9(8) K
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	12
Unit cell dimensions	a = 15.4694(2) Å $\alpha = 90^\circ$ b = 11.28363(15) Å $\beta = 101.9564(15)^\circ$ c = 21.3051(3) Å $\gamma = 90^\circ$
Volume	3638.15(9) Å ³
Z	8
Density (calculated)	1.126 Mg/m ³
Absorption coefficient	0.617 mm ⁻¹
F(000)	1304.0
Crystal size	0.08 x 0.06 x 0.05 mm ³
Theta range for data collection	8.484 to 148.346 °
Index ranges	-18 ≤ h ≤ 19, -13 ≤ k ≤ 13, -26 ≤ l ≤ 26
Reflections collected	18985
Independent reflections	7142 [R(int) = 0.0489]
Completeness to theta = 66.97 °	99.94 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7142 / 1 / 423
Goodness-of-fit on F ²	1.062
Final R indices [I > 2σ(I)]	R1 = 0.0404, wR2 = 0.1055
R indices (all data)	R1 = 0.0483, wR2 = 0.1101
Absolute structure parameter	0.09(10)
Largest diff. peak and hole	0.23 and -0.19 e.Å ⁻³

Table S2. X-ray crystallographic data for (\pm)-tersone C (**3**).

Empirical formula	C ₁₉ H ₁₉ NO ₃
Formula weight	309.35
Temperature	103(6) K
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 8.94020(10) Å α = 90 ° b = 17.2446(2) Å β = 98.8880(10) ° c = 10.33770(10) Å γ = 90 °
Volume	1574.63(3) Å ³
Z	4
Density (calculated)	1.305 Mg/m ³
Absorption coefficient	0.713 mm ⁻¹
F(000)	656.0
Crystal size	0.08 x 0.07 x 0.05 mm ³
Theta range for data collection	10.066 to 148.01 °
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 21, -12 ≤ l ≤ 11
Reflections collected	8528
Independent reflections	3083 [R(int) = 0.0280]
Completeness to theta = 67.97 °	99.76 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3083 / 0 / 211
Goodness-of-fit on F ²	1.044
Final R indices [I > 2σ(I)]	R1 = 0.0368, wR2 = 0.0964
R indices (all data)	R1 = 0.0429, wR2 = 0.1002
Largest diff. peak and hole	0.20 and -0.23 e.Å ⁻³

1.2 Computational details

Methods. Merck molecular force field (MMFF) and DFT/TD-DFT calculations were carried out with the Spartan'14 software (Wavefunction Inc., Irvine, CA, USA) and the Gaussian 09 program, respectively [1]. Conformers within the 10 kcal mol⁻¹ energy window were generated and optimized using DFT calculations at the b3lyp/6-31+g(d,p) level. Frequency calculations were performed at the same level to confirm that each optimized conformer was true minimum and to estimate their relative thermal free energy (ΔG) at 298.15 K. Conformers with the Boltzmann distribution over 5% were chosen for ECD calculations in methanol at the b3lyp/6-311+g(d,p) level. Solvent effects were taken into consideration using the self-consistent reaction field (SCRF) method with the polarizable continuum model (PCM) [2]. The ECD spectrum was generated by the

SpecDis program [3] using a Gaussian band shape with 0.26 eV exponential half-width from dipole-length dipolar and rotational strengths.

Results.

Table S3. Energy analysis for the conformers of **4**.

compounds	conformation	G (Hartree)	G (Kcal/mol)	ΔG (Kcal/mol)	Boltzma nn Dist (%)
4	a	-940.73426083	-590313.4768	0	74.82%
	b	-940.73323300	-590312.8319	0.644901673	25.18%

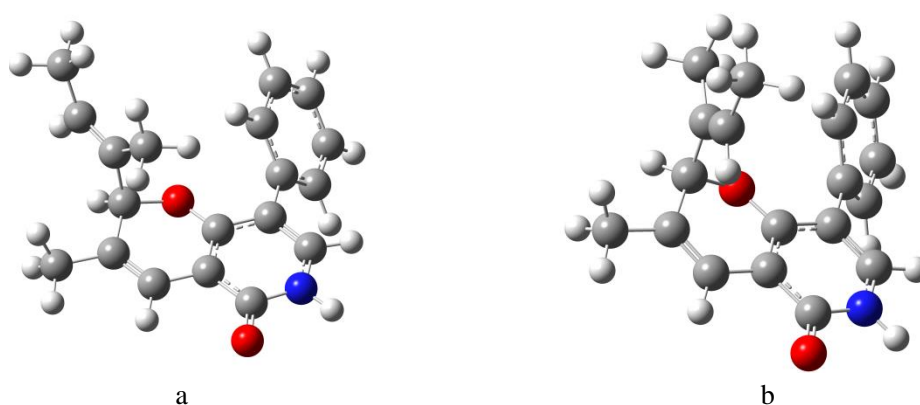


Figure S1. B3LYP/6-31G(d) optimized low-energy conformers of **4**

References

1. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G. A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, Ö.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J. Gaussian 09, revision D.01, Gaussian, Inc., Wallingford, CT, **2013**.
2. Wu, P.; Xue, J.; Yao, L.; Xu, L.; Li, H.; Wei, X. Bisacremine E-G, three polycyclic dimeric acemine produced by *Acremonium persicinum* SC0105. *Org. Lett.*, **2015**, *17*, 4922.
3. Bruhn, T.; Schaumlöffel, A.; Hemberger, Y.; Bringmann, G. SpecDis: Quantifying the comparison of calculated and experimental electronic circular dichroism spectra. *Chirality*, **2013**, *25*, 243.

2. NMR, HRESIMS, CD, UV and IR spectrum of compounds 1-9

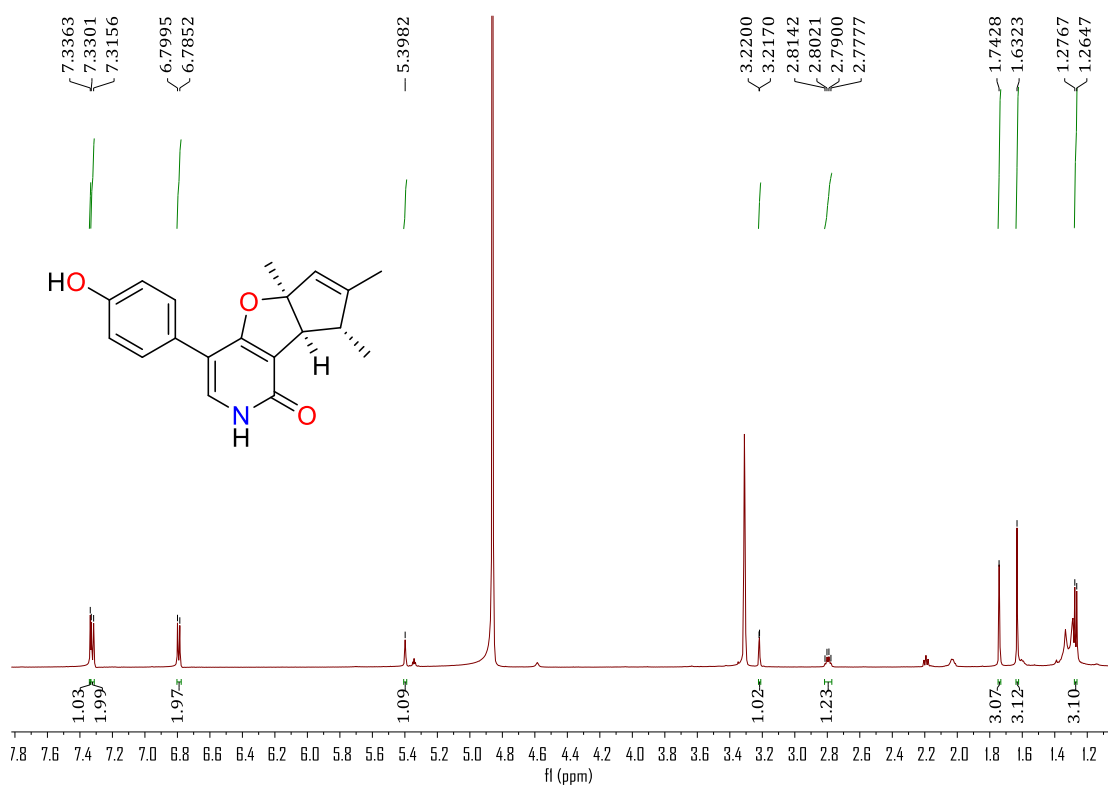


Figure S1. ^1H NMR spectrum (600 MHz, CD_3OD) of **1a**

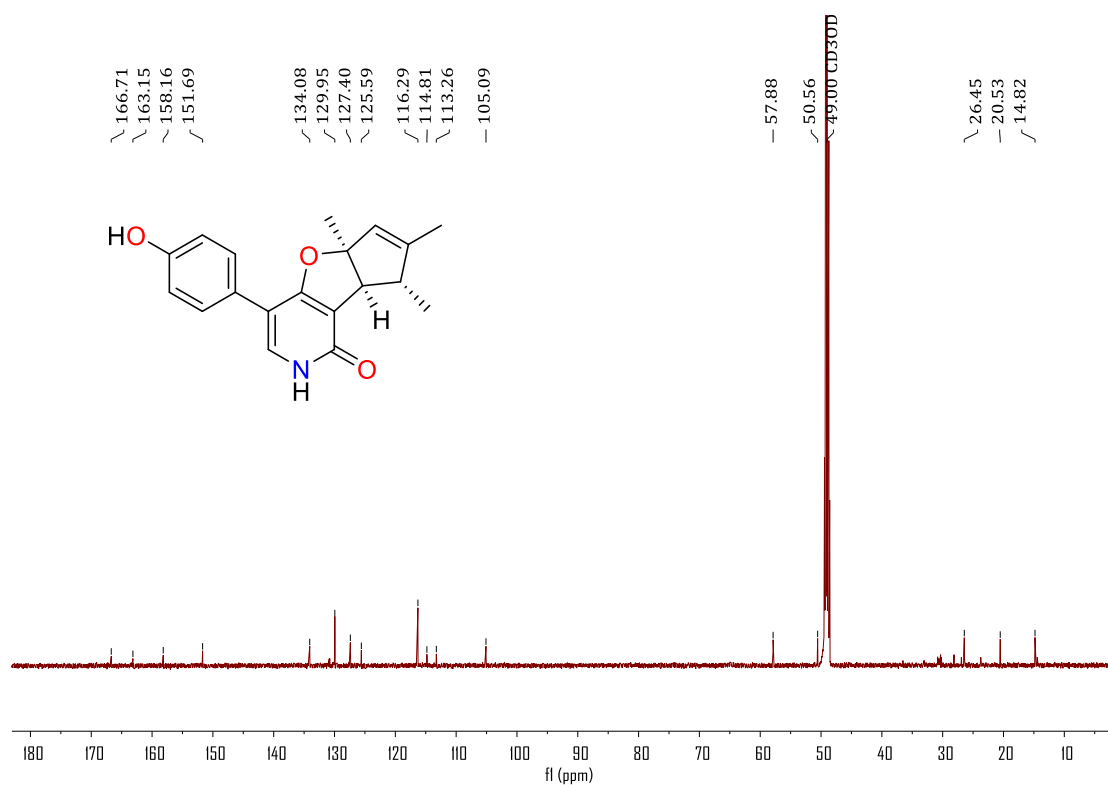


Figure S2. ^{13}C NMR spectrum (150 MHz, CD_3OD) of **1a**

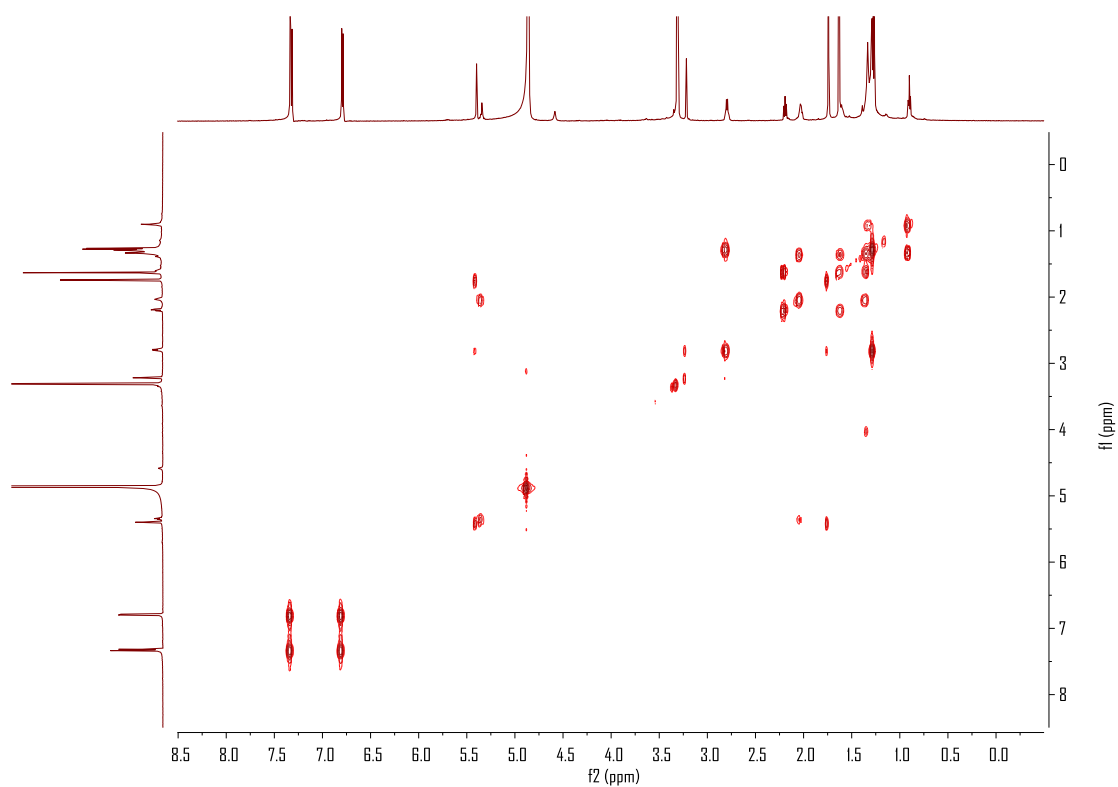


Figure S3. ^1H - ^1H COSY spectrum of **1a** in CD_3OD

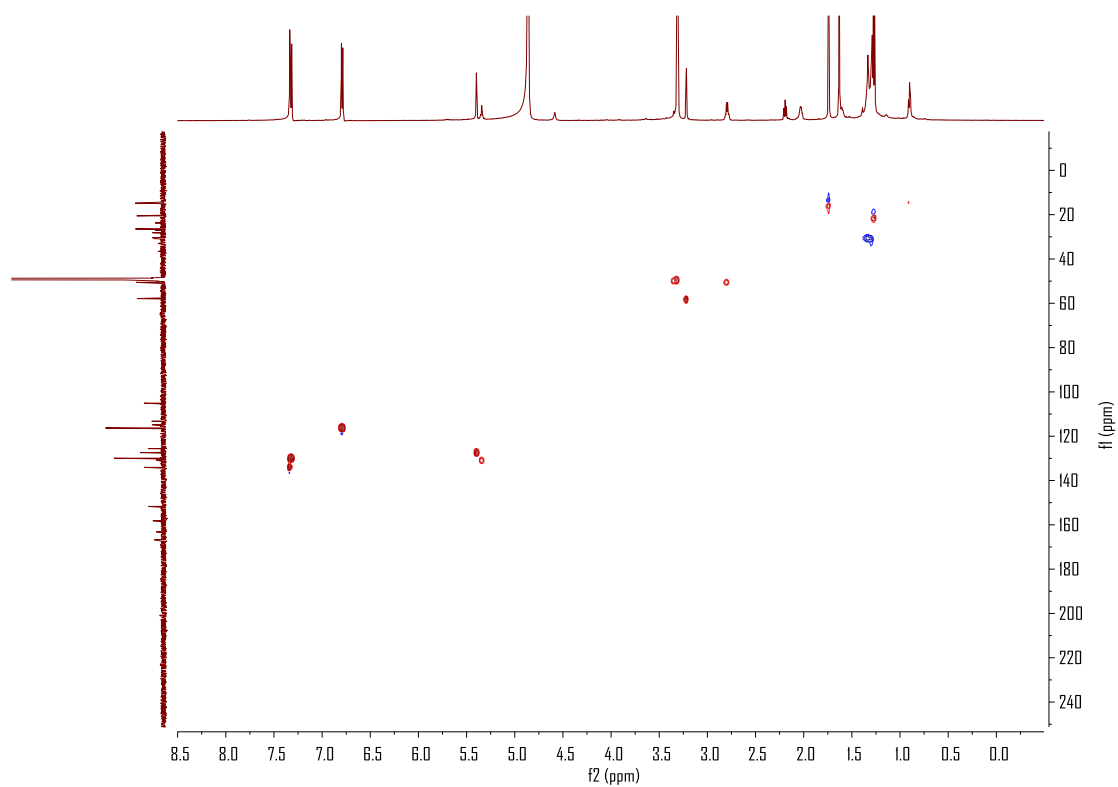


Figure S4. HSQC spectrum of **1a** in CD_3OD

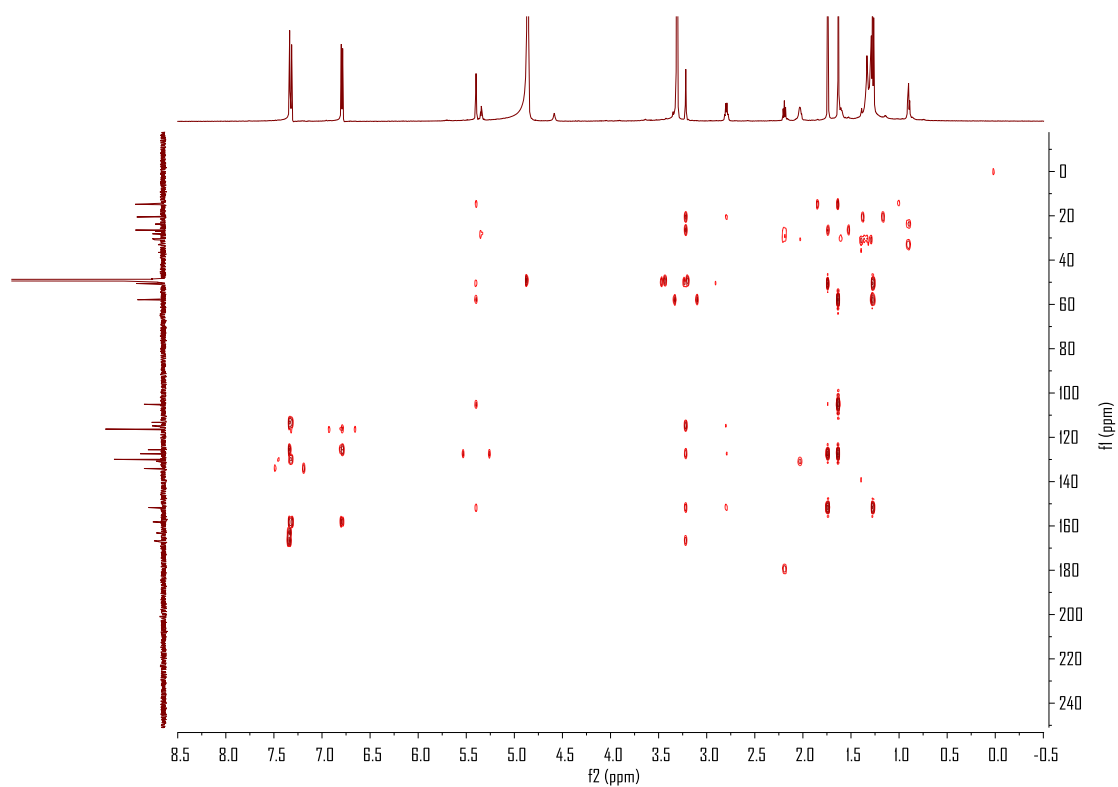


Figure S5. HMBC spectrum of **1a** in CD₃OD

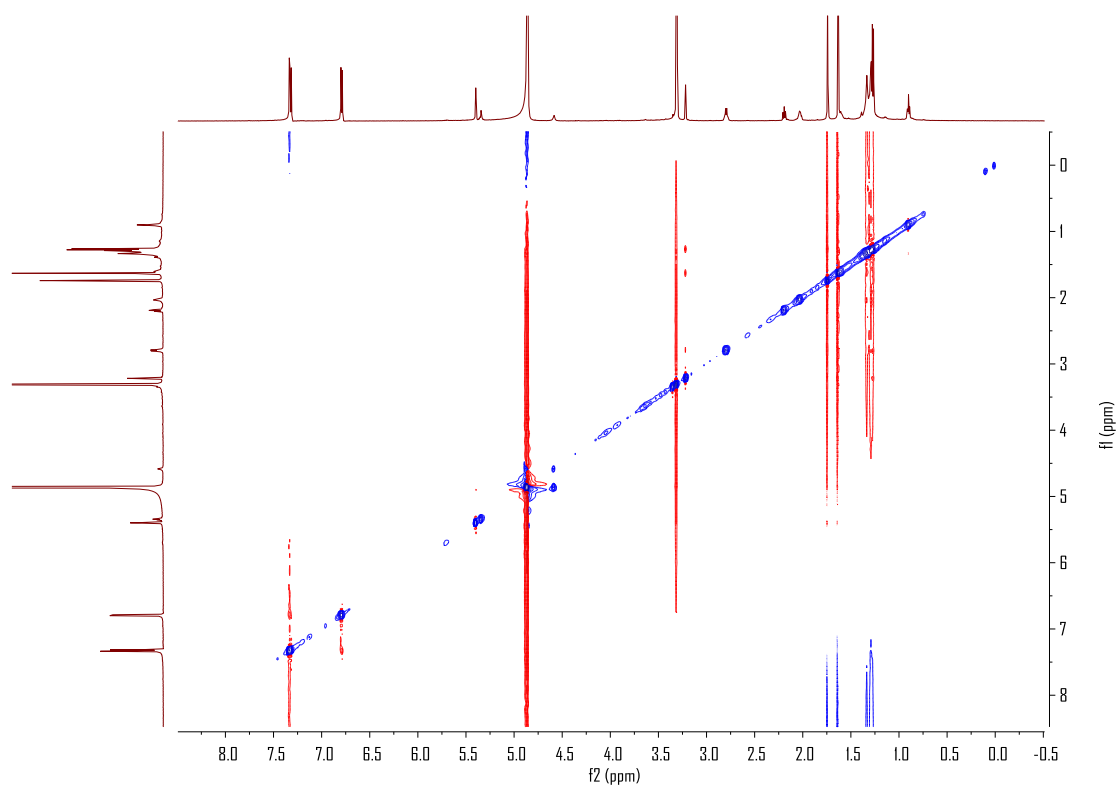


Figure S6. NOESY spectrum of **1a** in CD₃OD

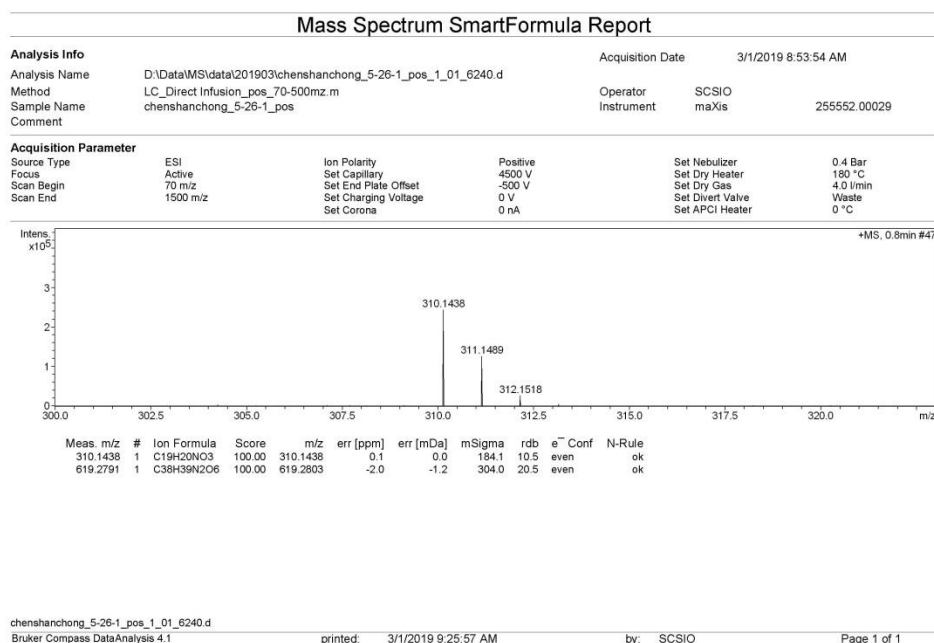


Figure S7. HRESIMS spectrum of **1a**

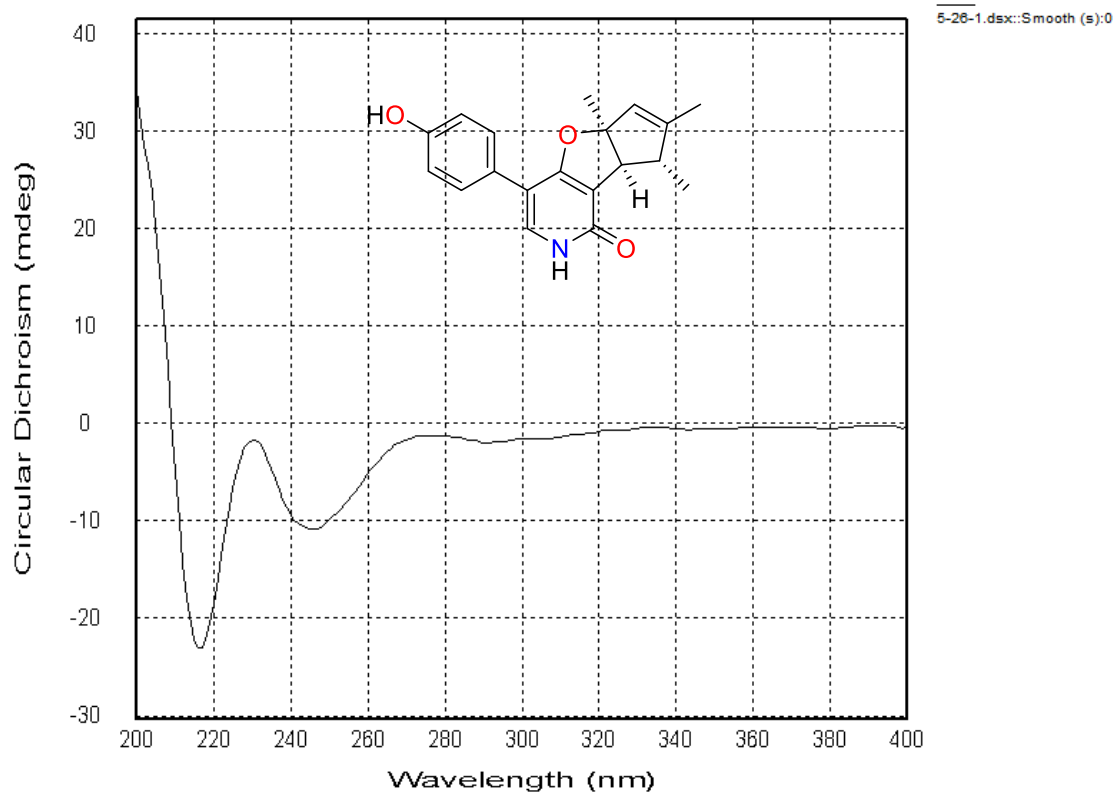


Figure S8. CD spectrum of **1a**

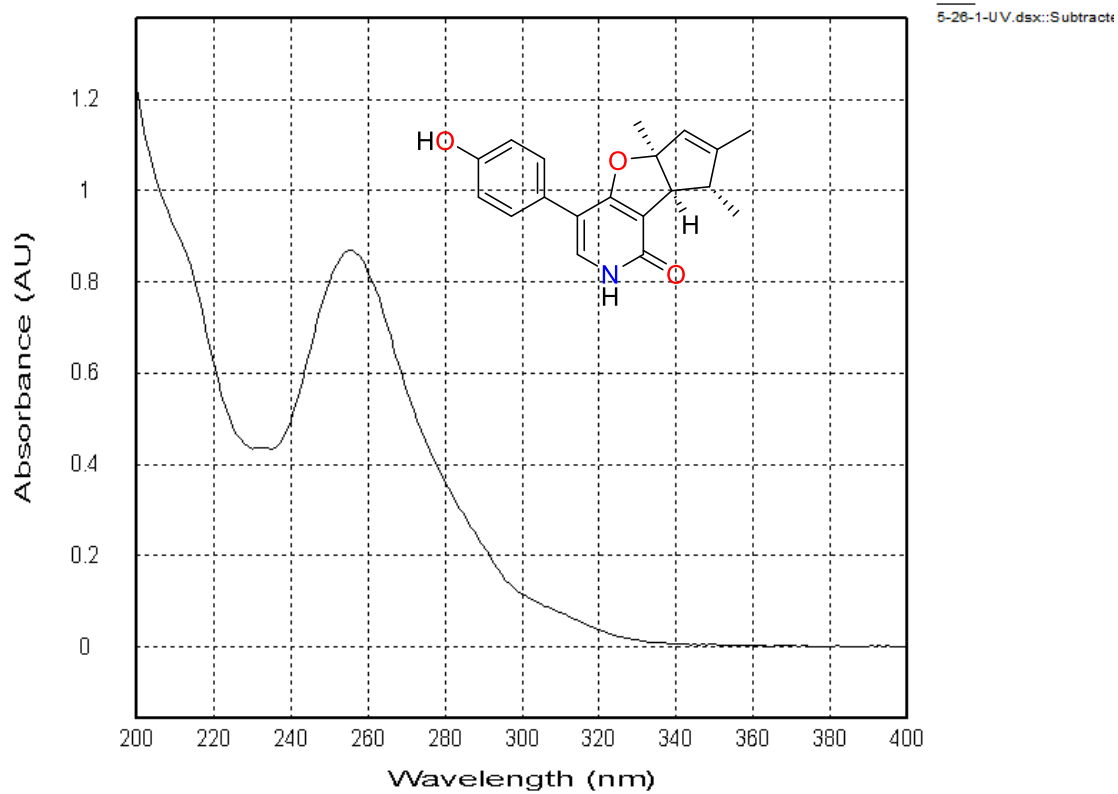


Figure S9. UV spectrum of **1a**

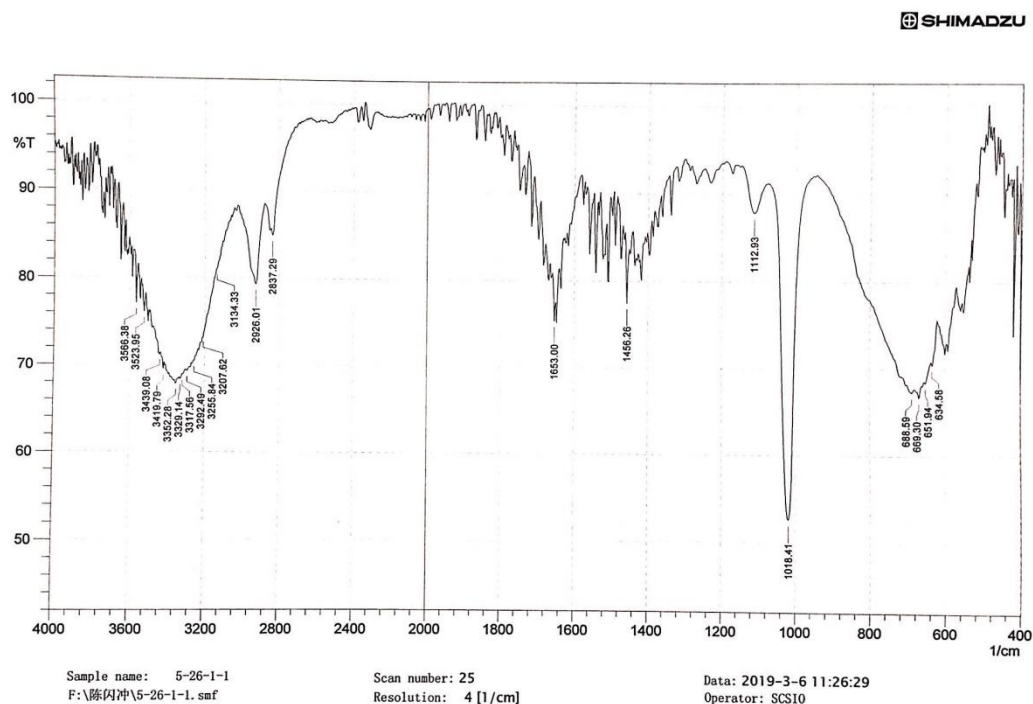


Figure S10. IR spectrum of **1a**

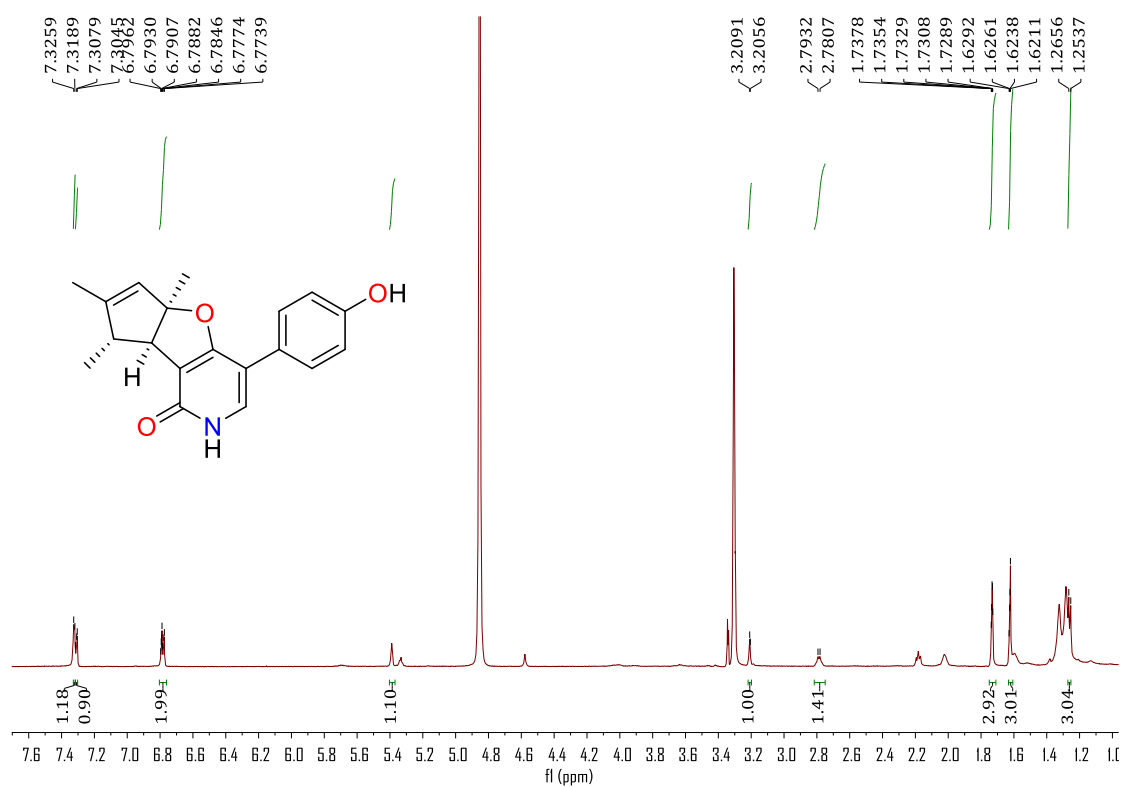


Figure S11. ¹H NMR spectrum (600 MHz, CD₃OD) of **1b**

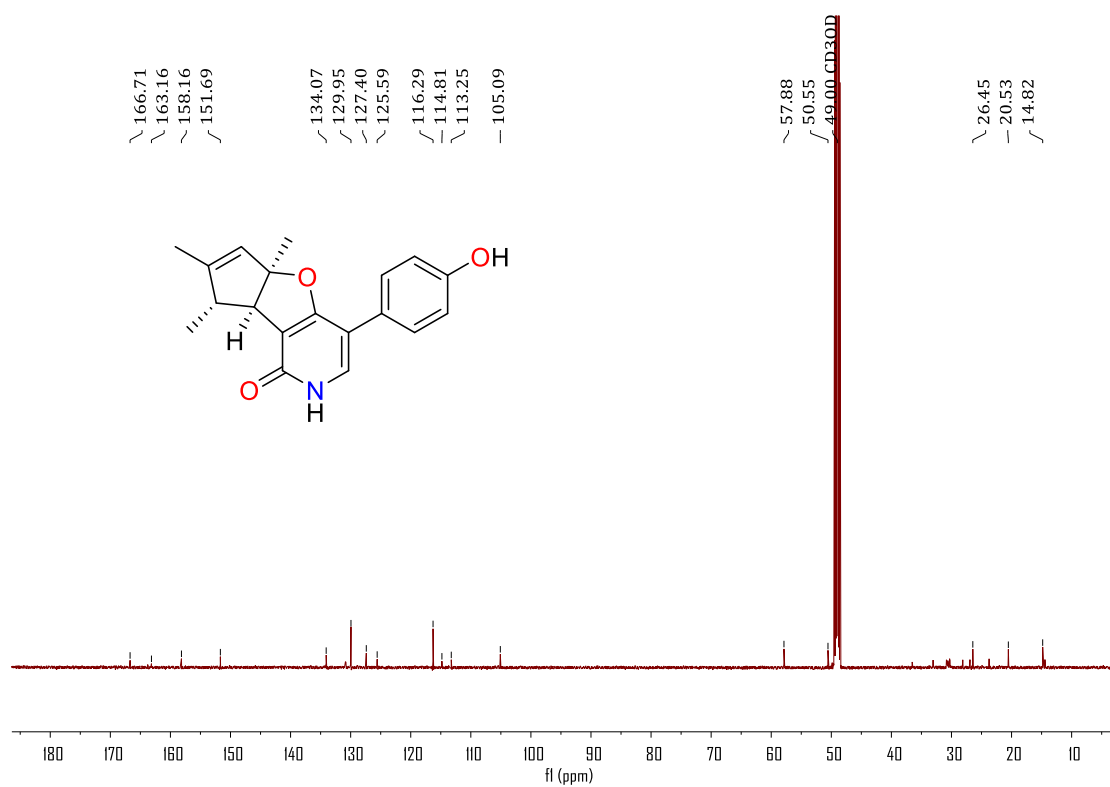


Figure S12. ¹³C NMR spectrum (150 MHz, CD₃OD) of **1b**

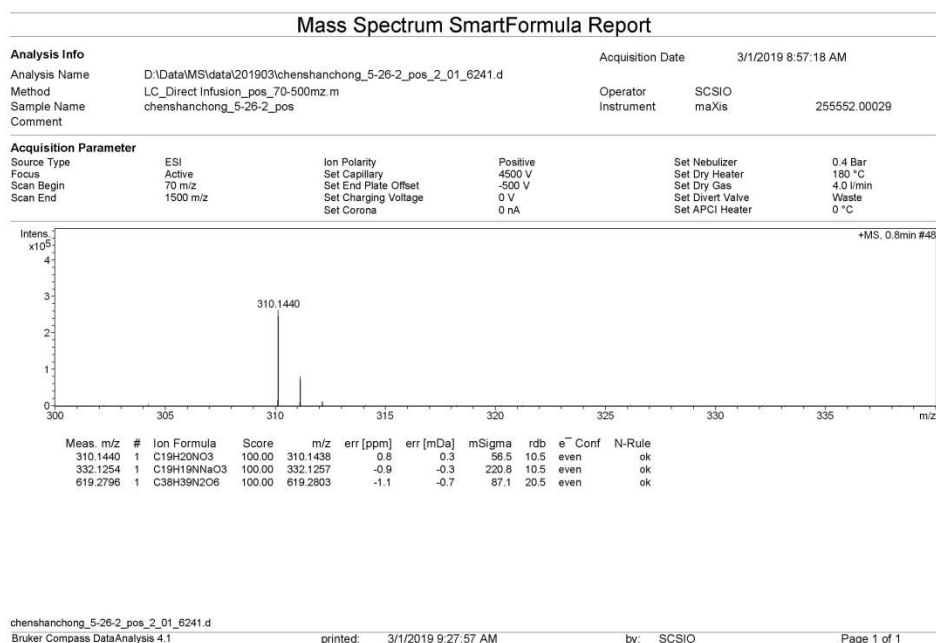


Figure S13. HRESIMS spectrum of **1b**

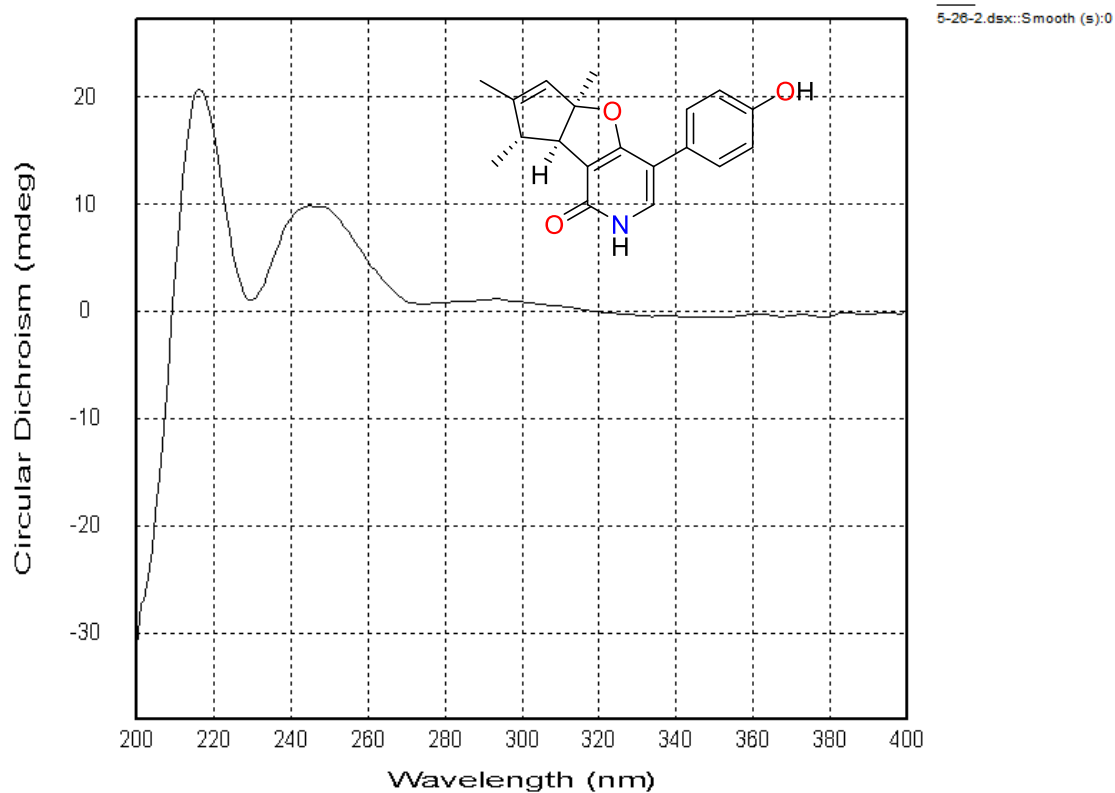


Figure S14. CD spectrum of **1b**

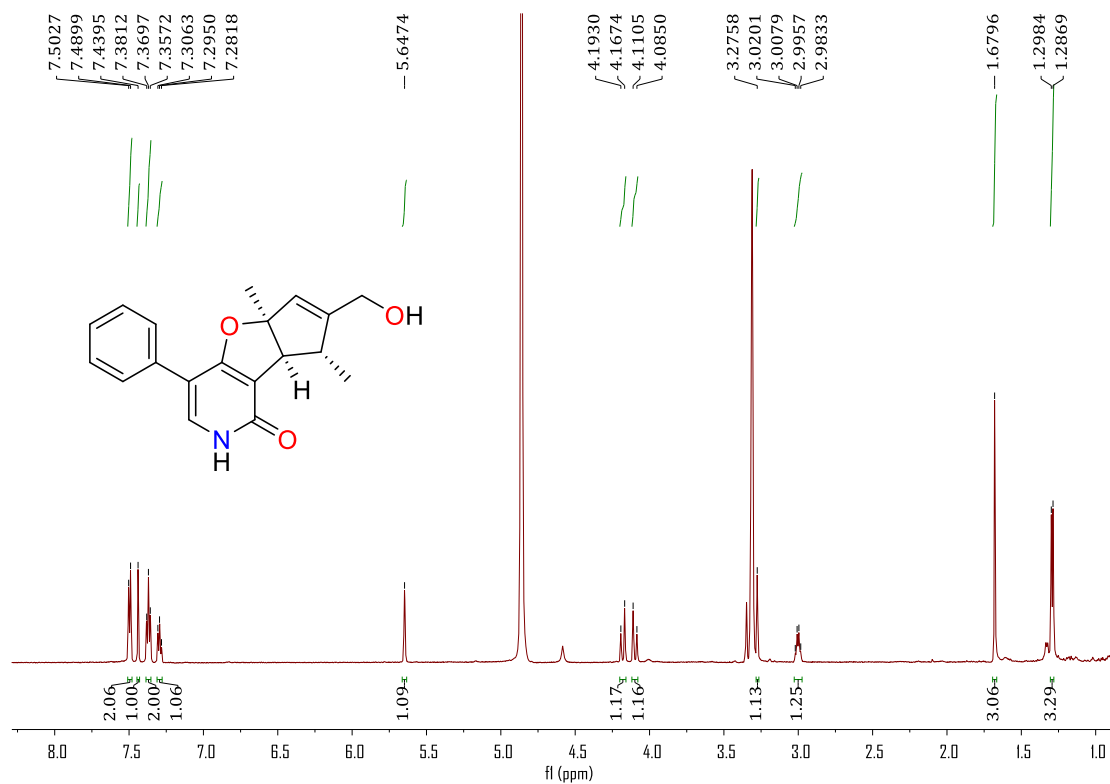


Figure S15. ^1H NMR spectrum (600 MHz, CD_3OD) of **2a**

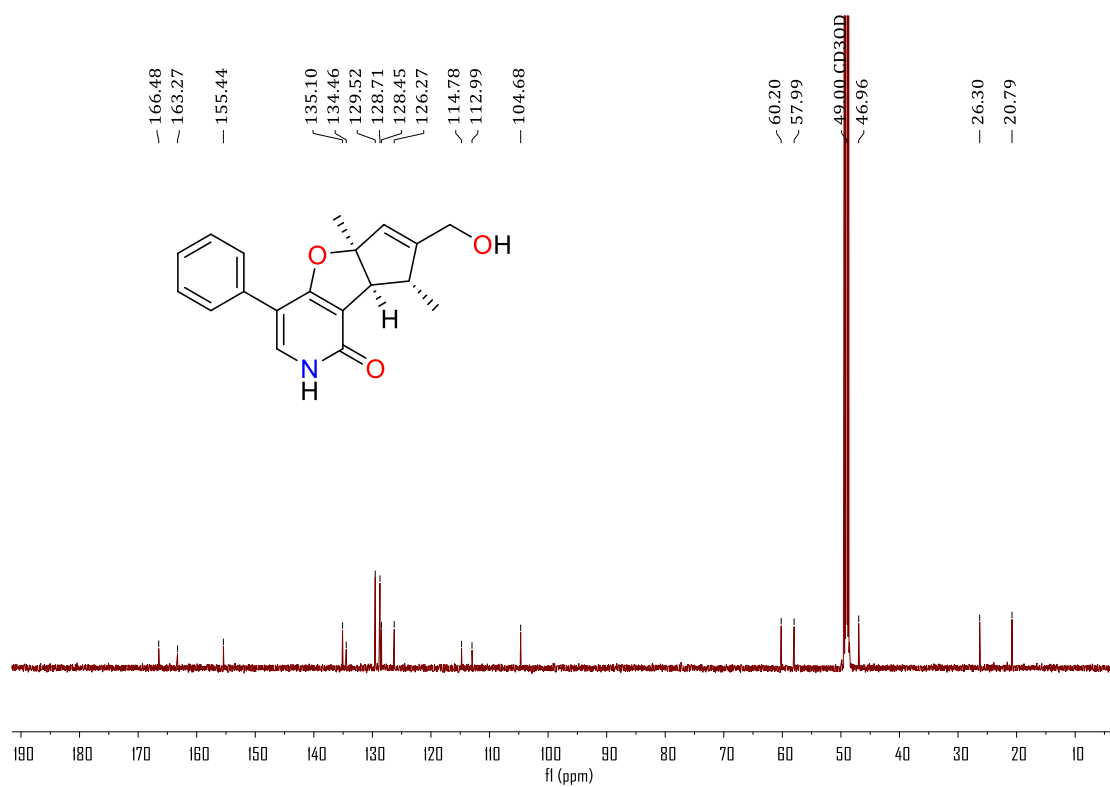


Figure S16. ^{13}C NMR spectrum (150 MHz, CD_3OD) of **2a**

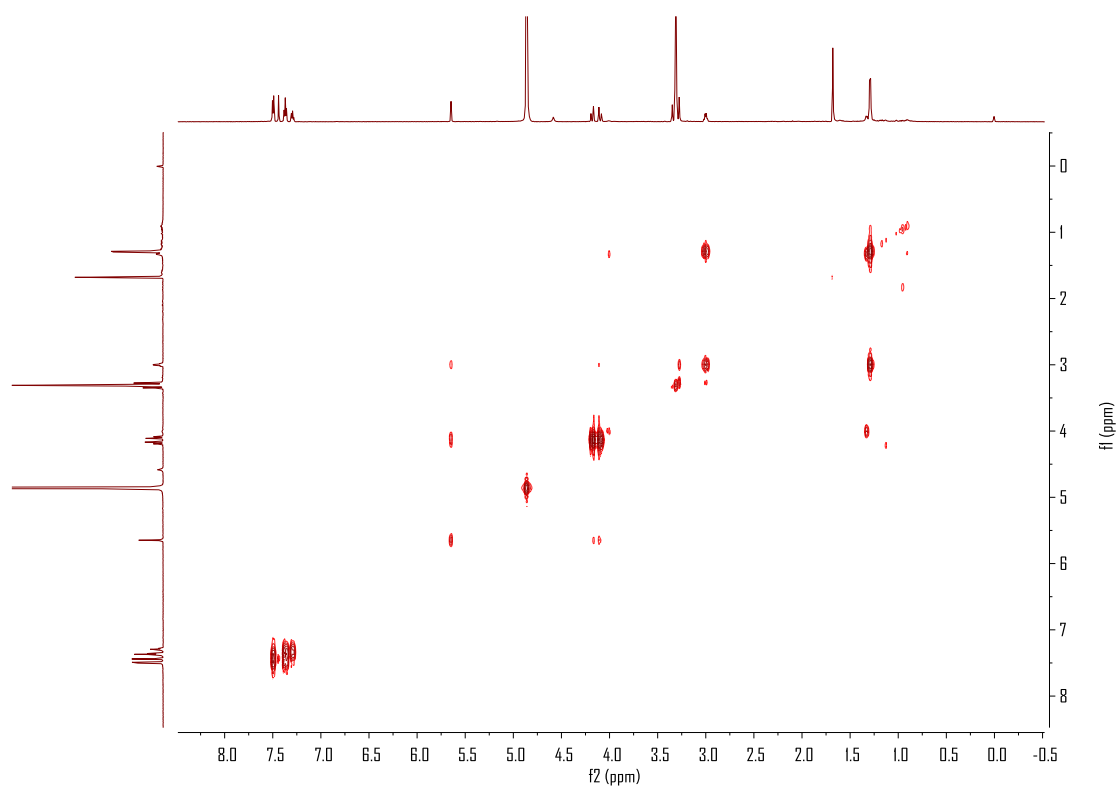


Figure S17. ^1H - ^1H COSY spectrum of **2a** in CD_3OD

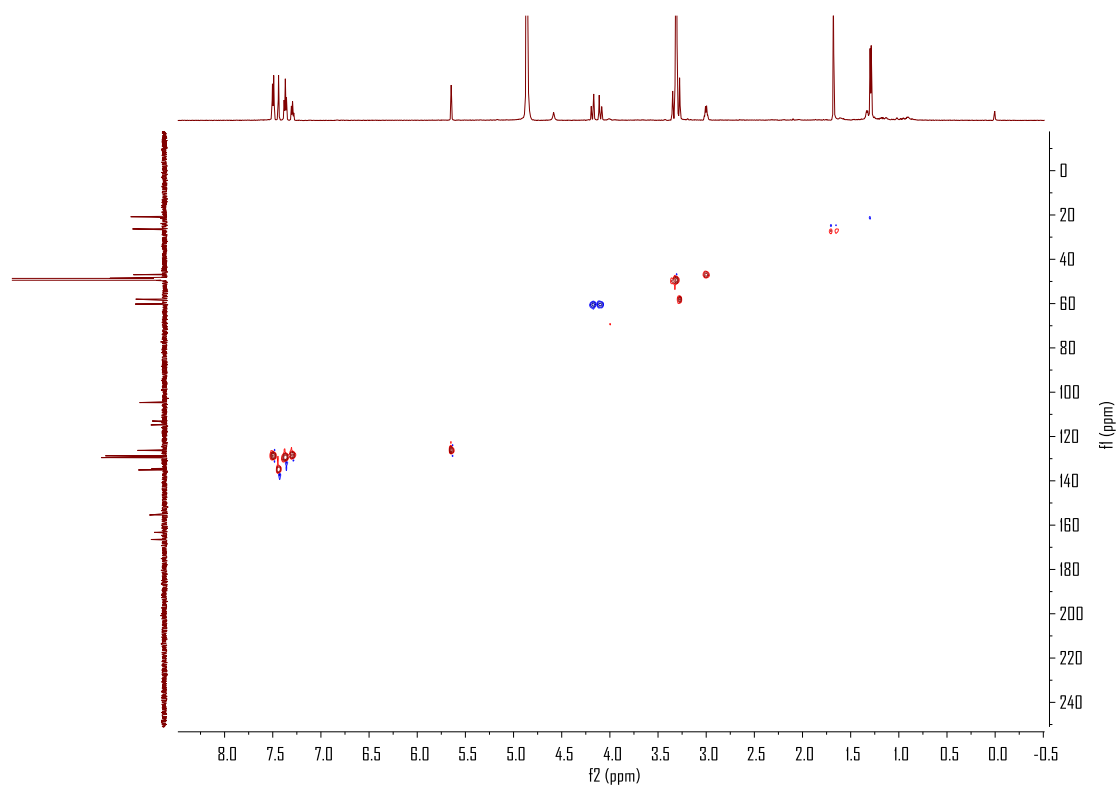


Figure S18. HSQC spectrum of **2a** in CD_3OD

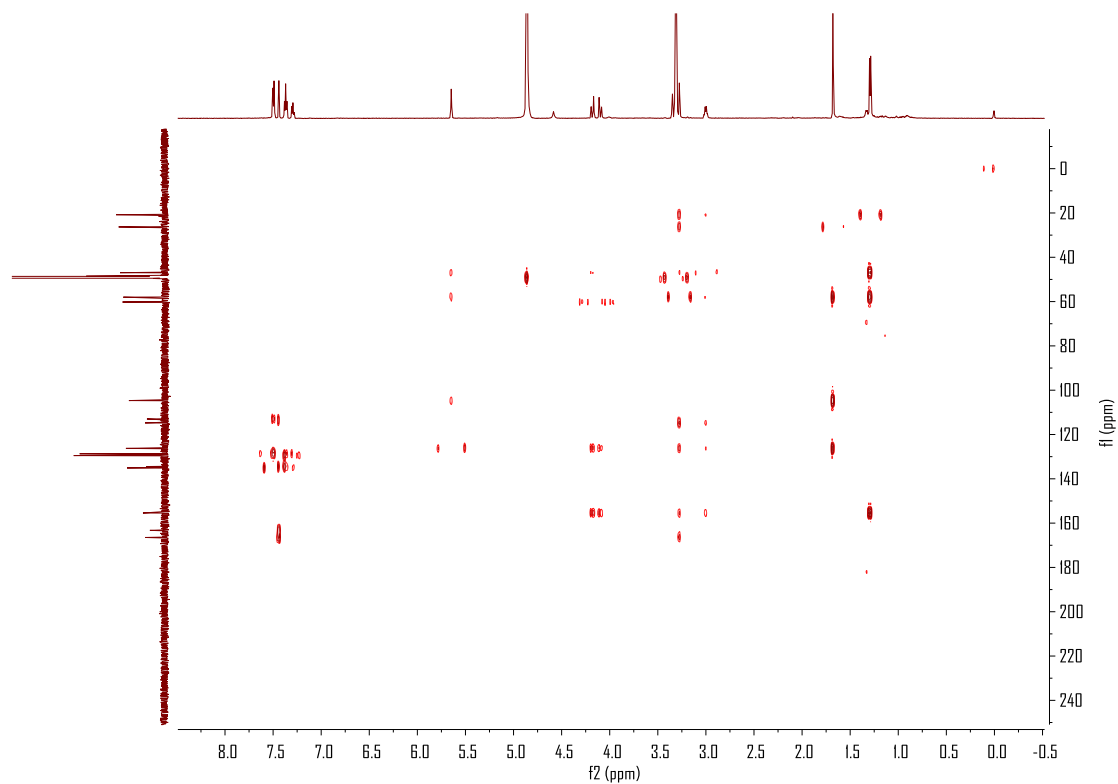


Figure S19. HMBC spectrum of **2a** in CD₃OD

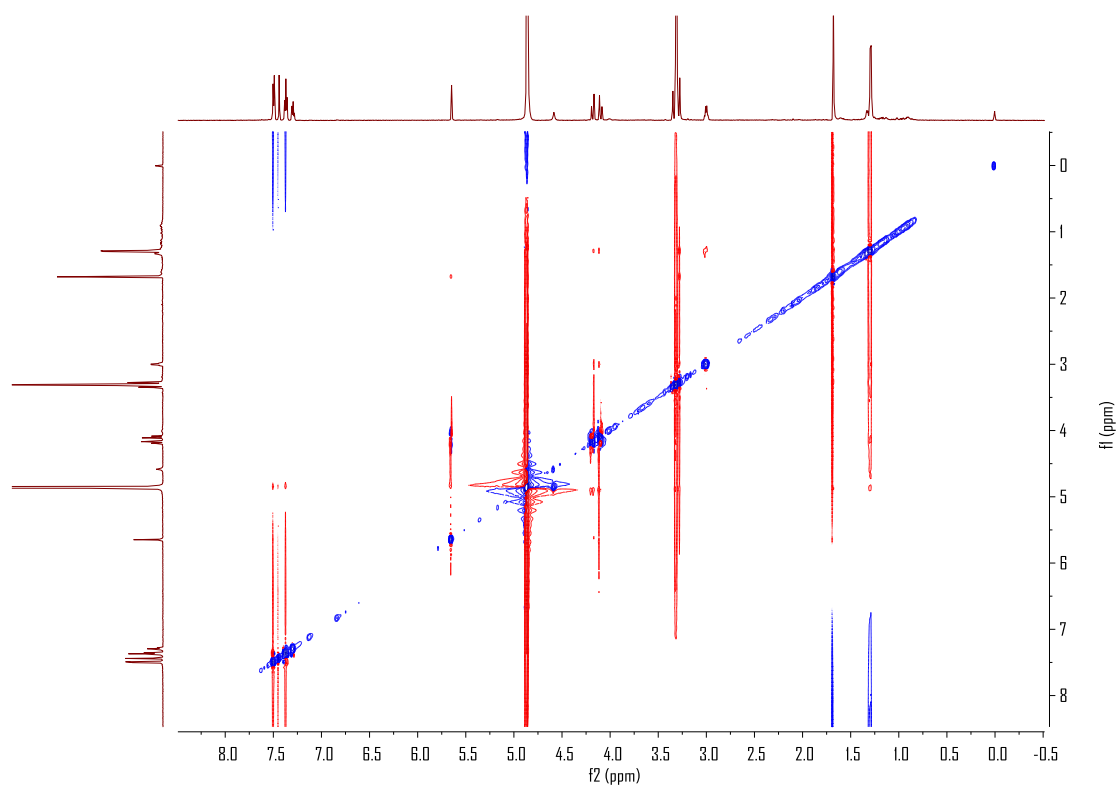


Figure S20. NOESY spectrum of **2a** in CD₃OD

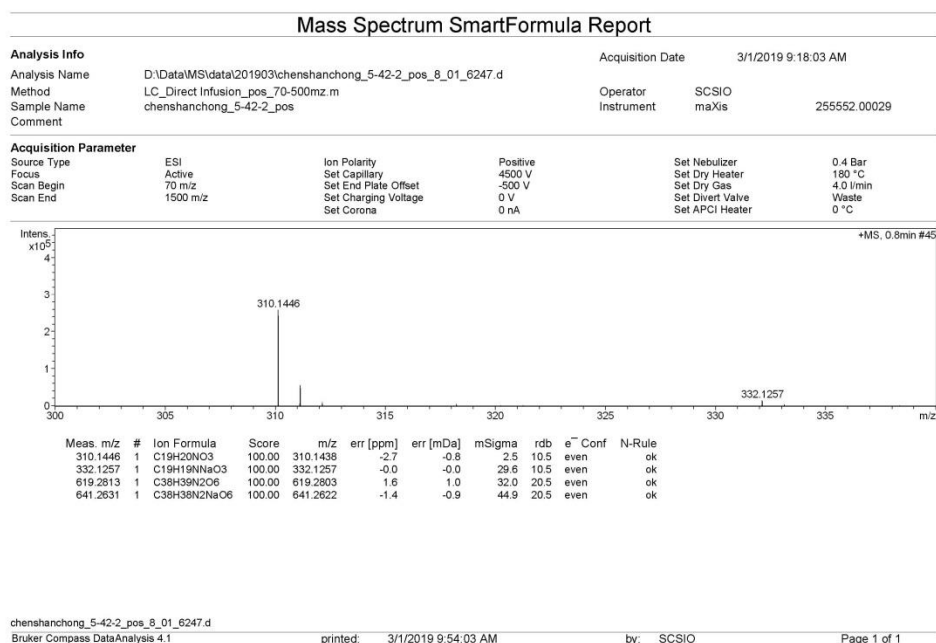


Figure S21. HRESIMS spectrum of **2a**

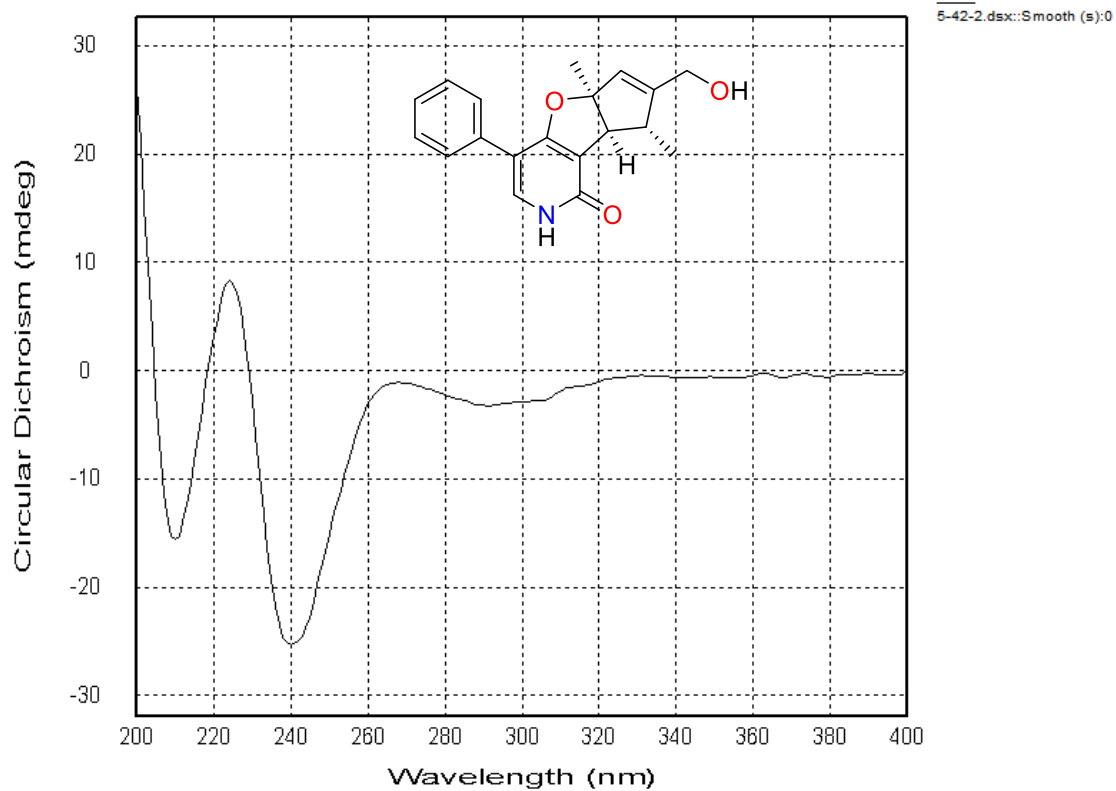


Figure S22. CD spectrum of **2a**

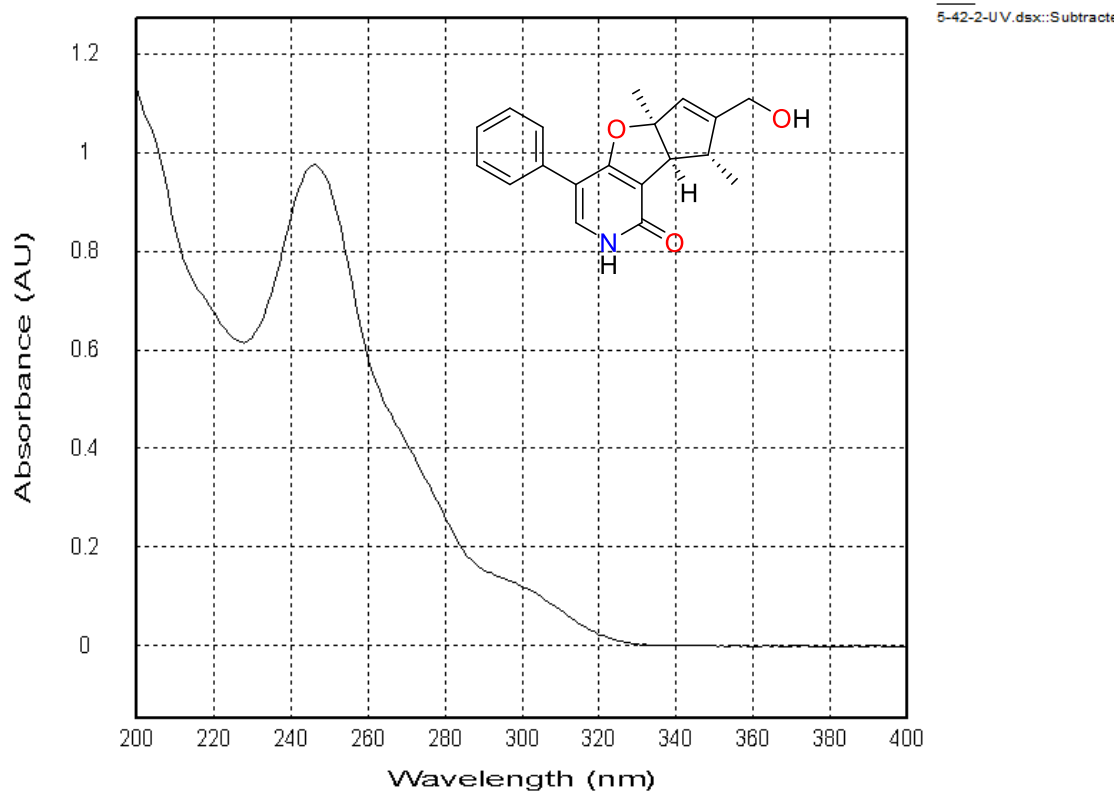


Figure S23. UV spectrum of **2a**

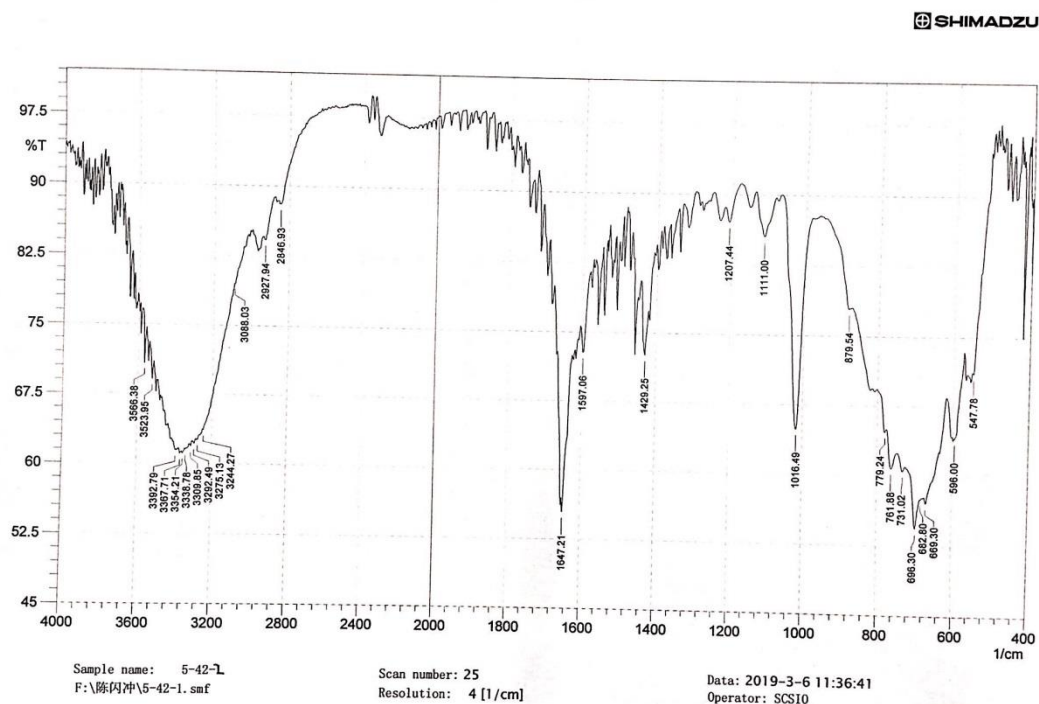


Figure S24. IR spectrum of **2a**

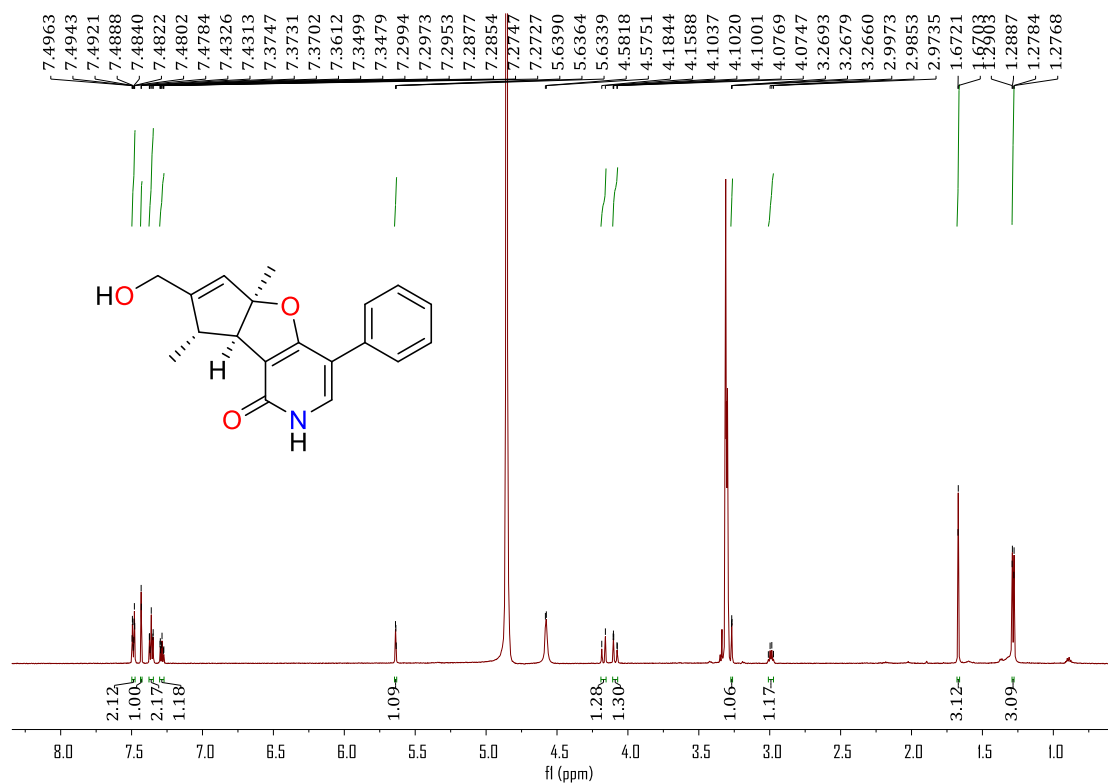


Figure S25. ¹H NMR spectrum (600 MHz, CD₃OD) of **2b**

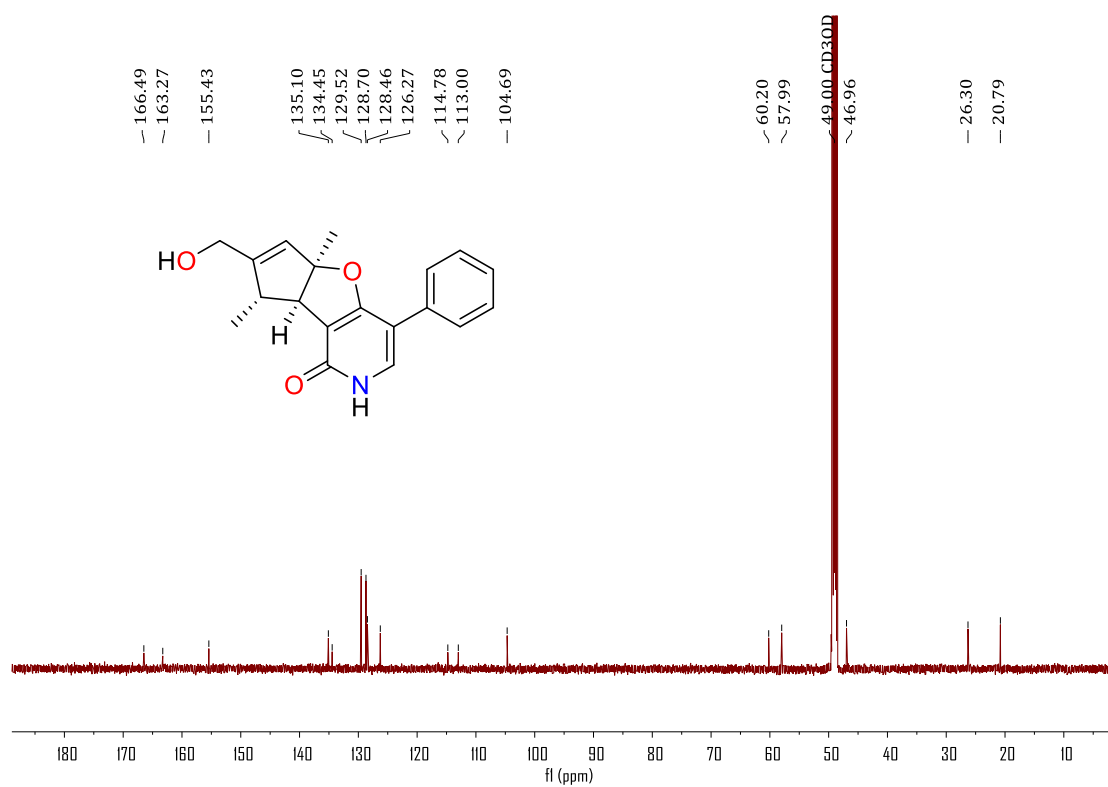


Figure S26. ¹³C NMR spectrum (150 MHz, CD₃OD) of **2b**

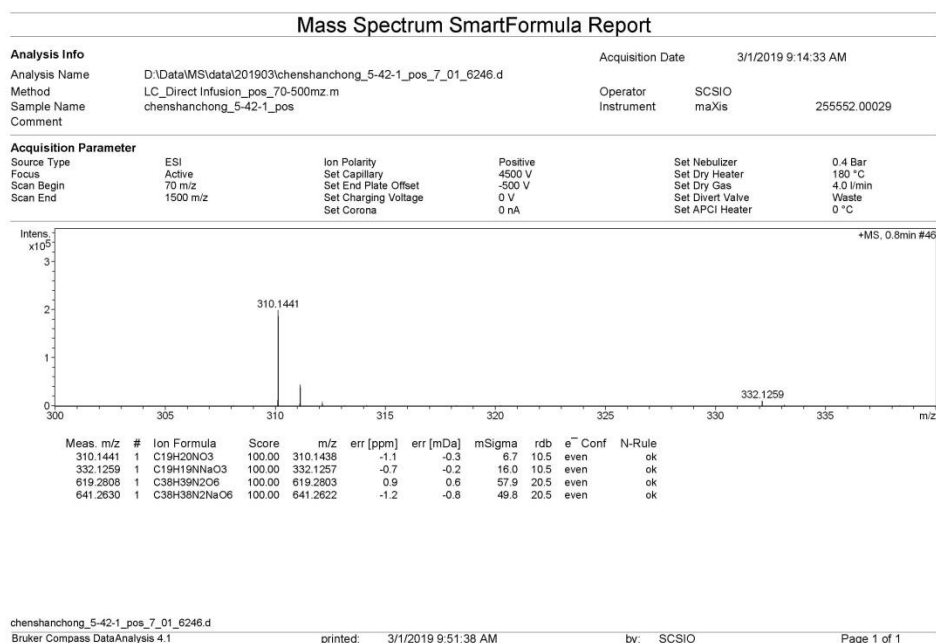


Figure S27. HRESIMS spectrum of **2b**

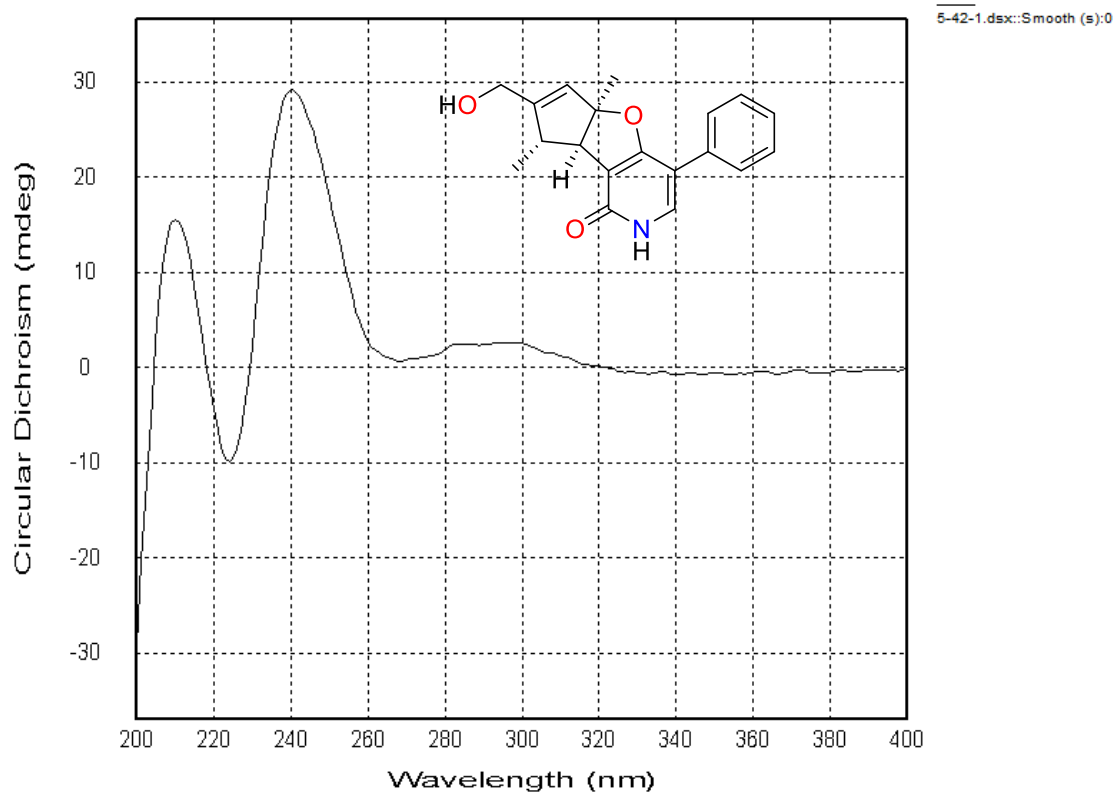


Figure S28. CD spectrum of **2b**

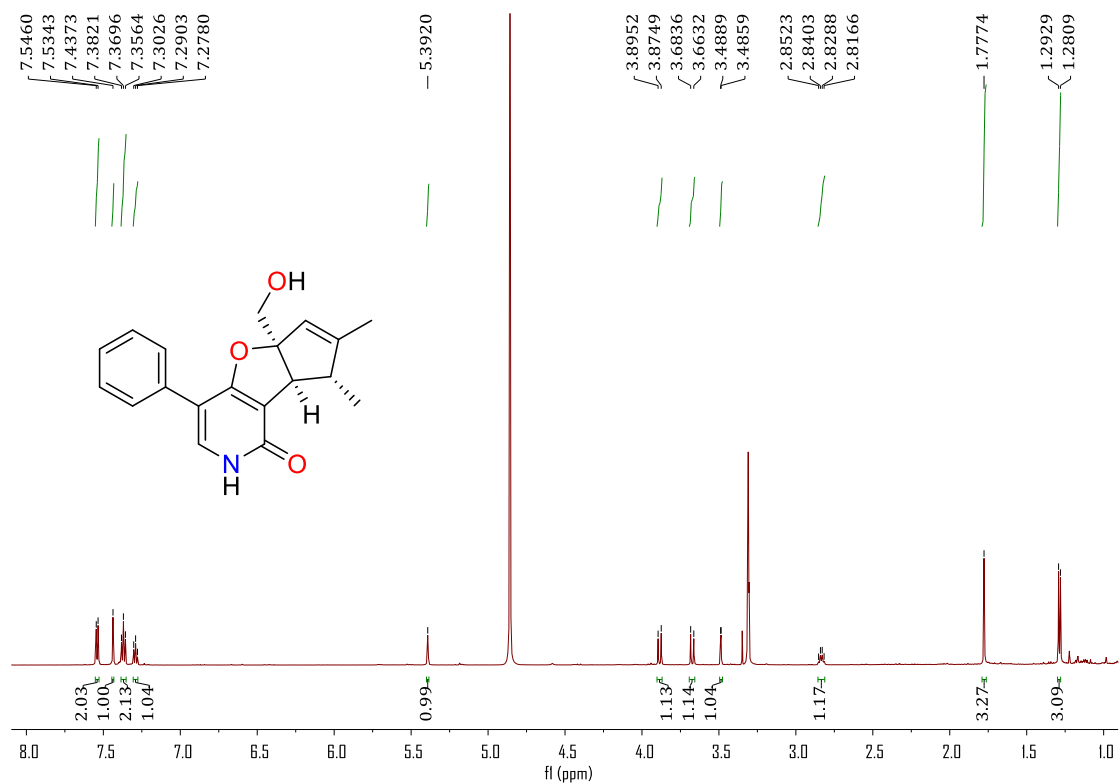


Figure S29. ¹H NMR spectrum (600 MHz, CD₃OD) of **3a**

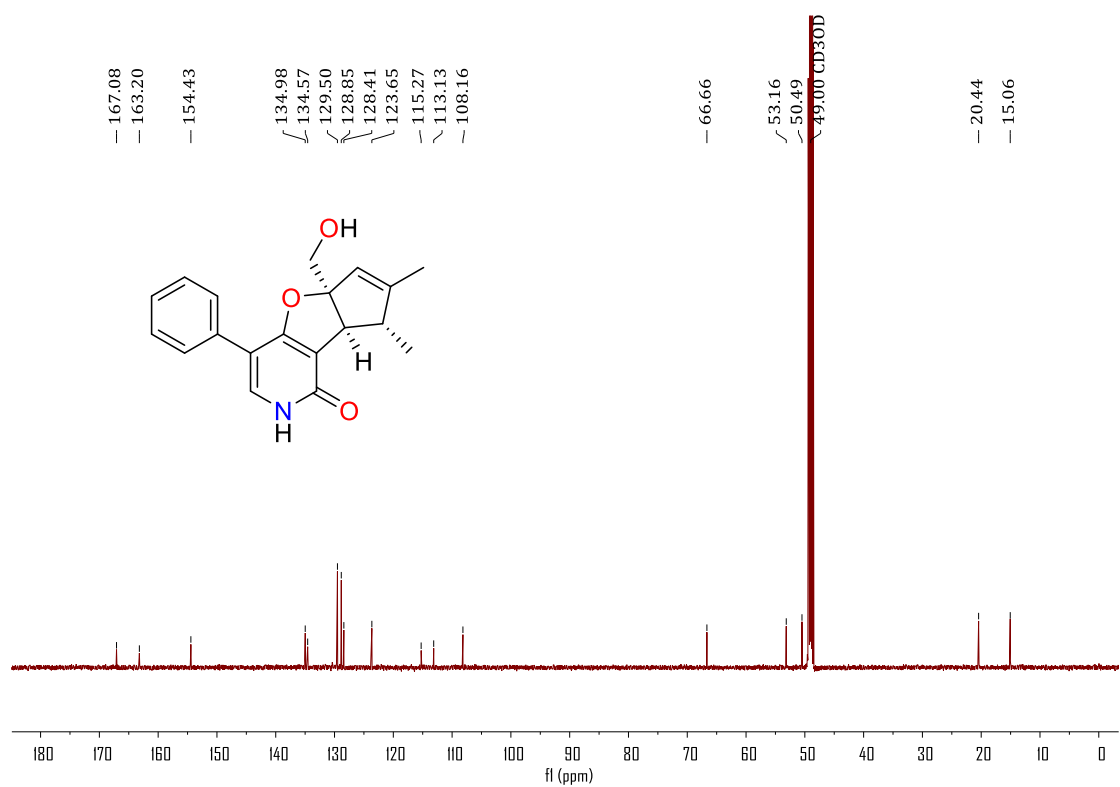


Figure S30. ¹³C NMR spectrum (150 MHz, CD₃OD) of **3a**

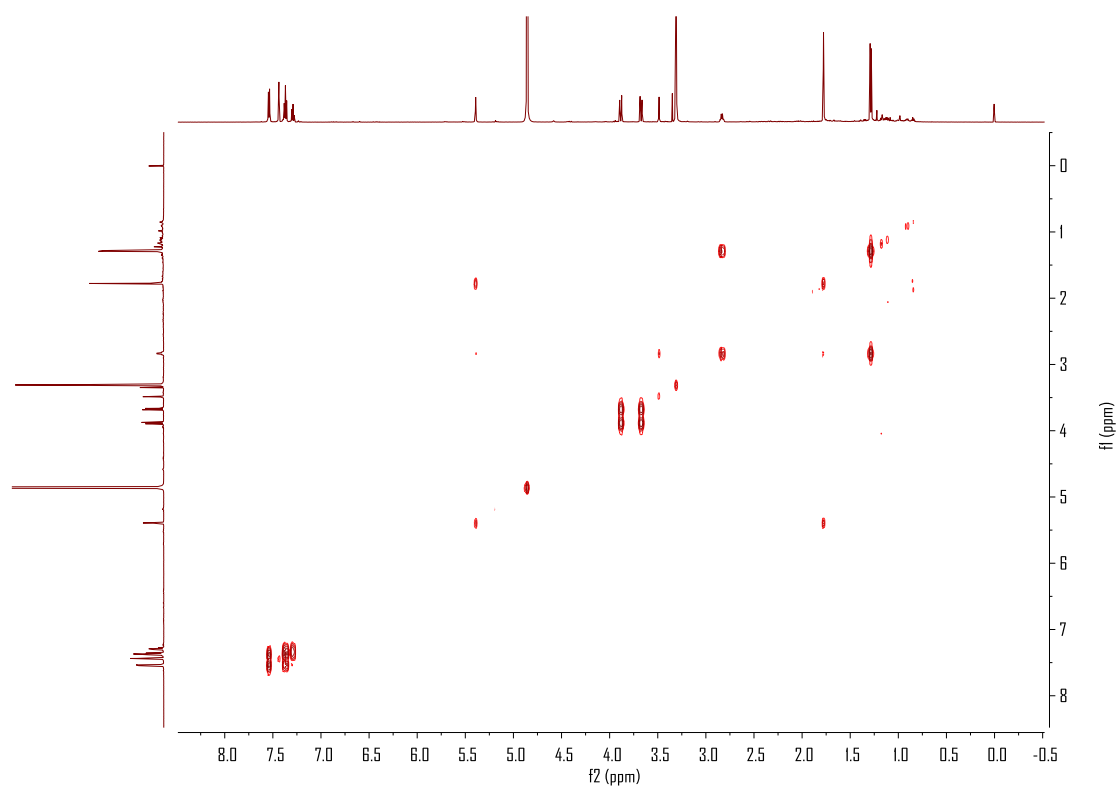


Figure S31. ^1H - ^1H COSY spectrum of **3a** in CD_3OD

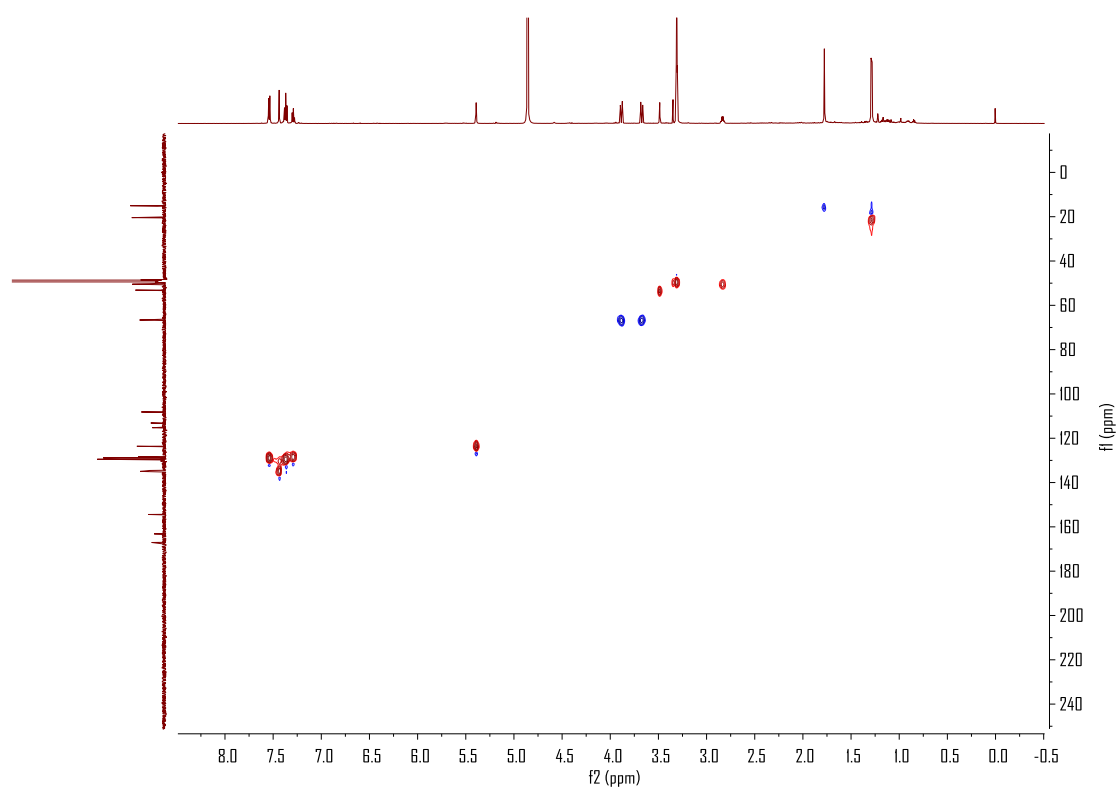


Figure S32. HSQC spectrum of **3a** in CD_3OD

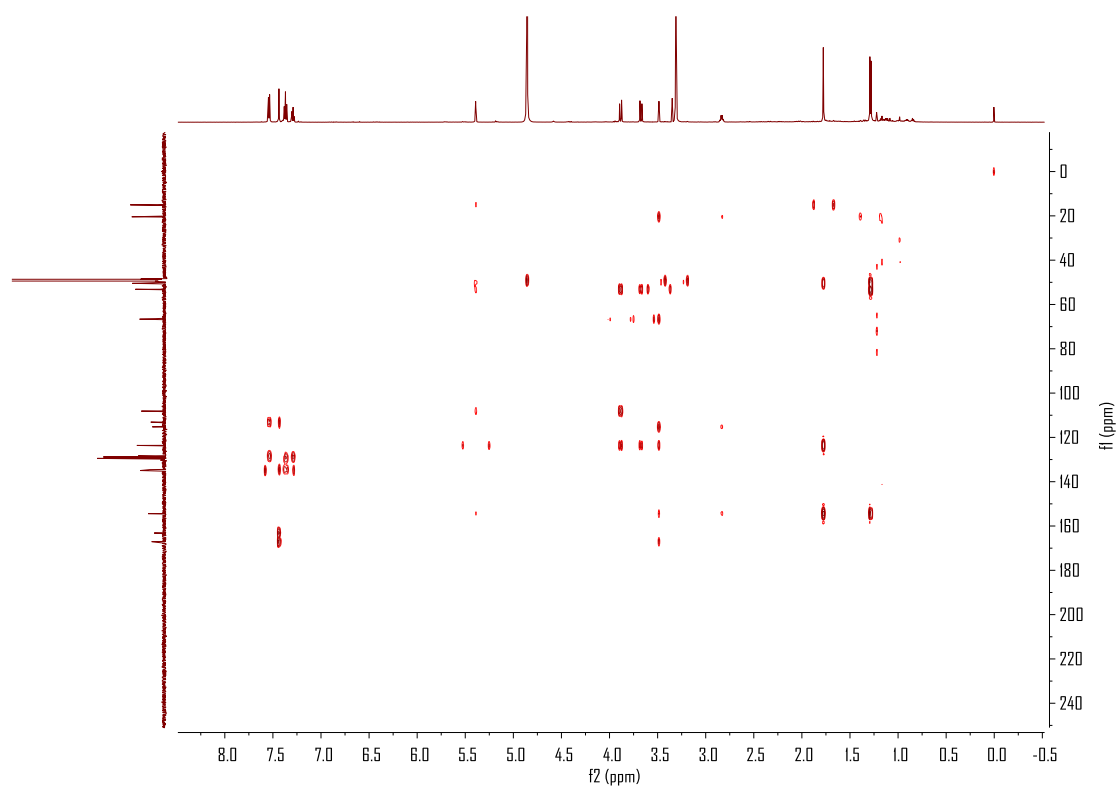


Figure S33. HMBC spectrum of **3a** in CD₃OD

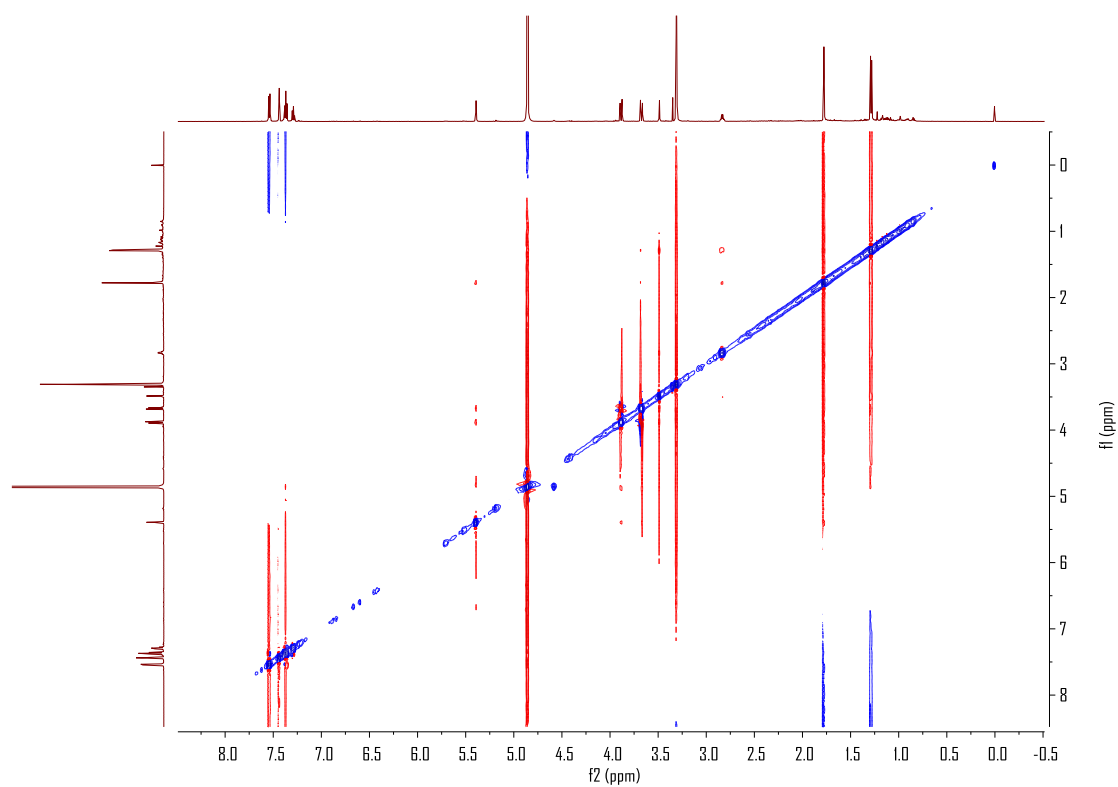


Figure S34. NOESY spectrum of **3a** in CD₃OD

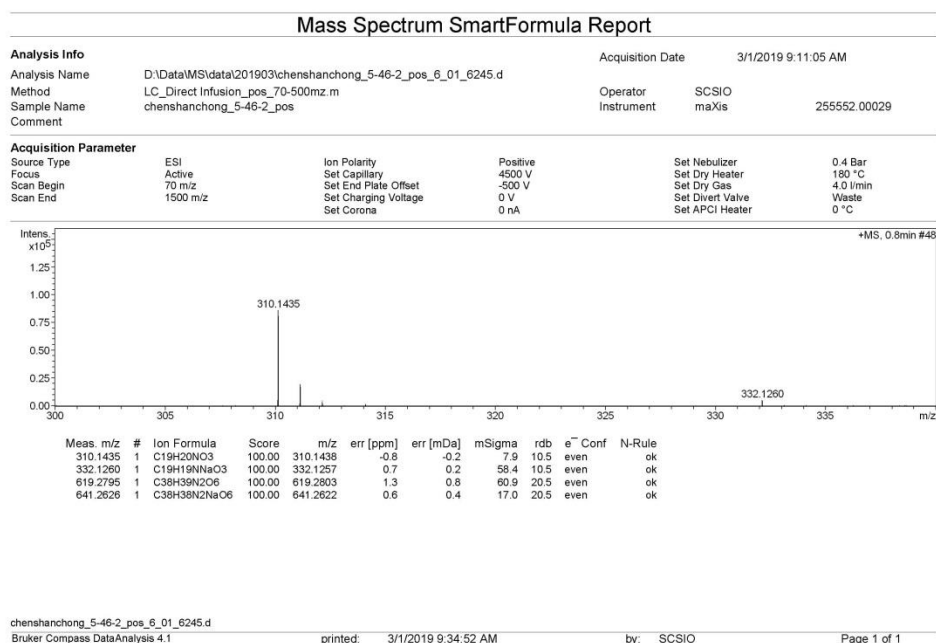
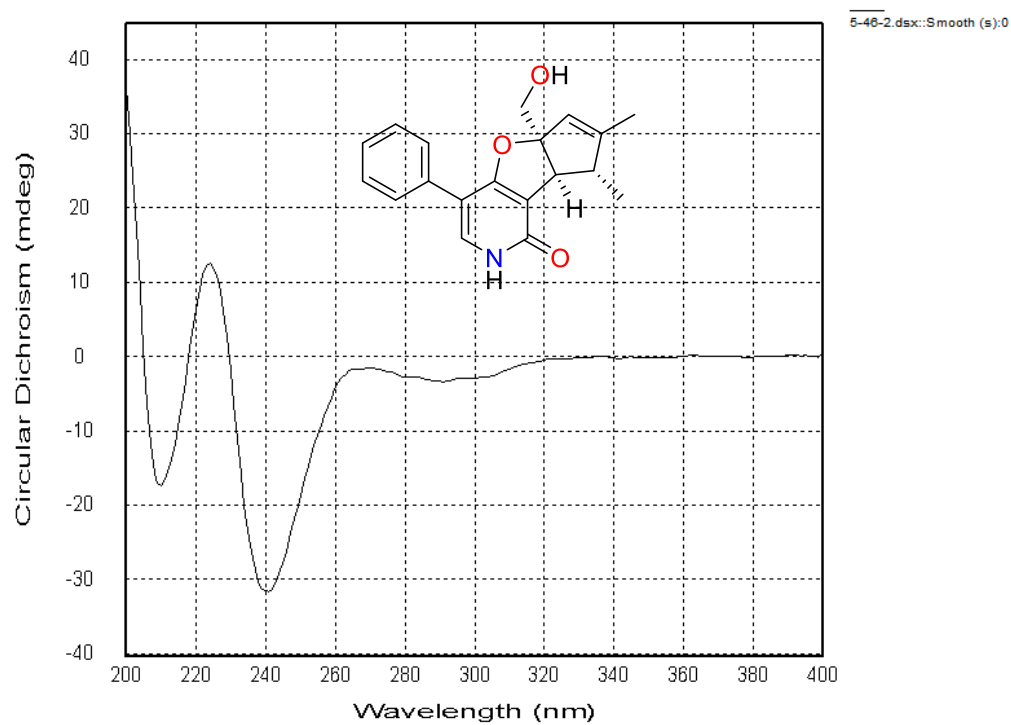


Figure S35. HRESIMS spectrum of **3a**



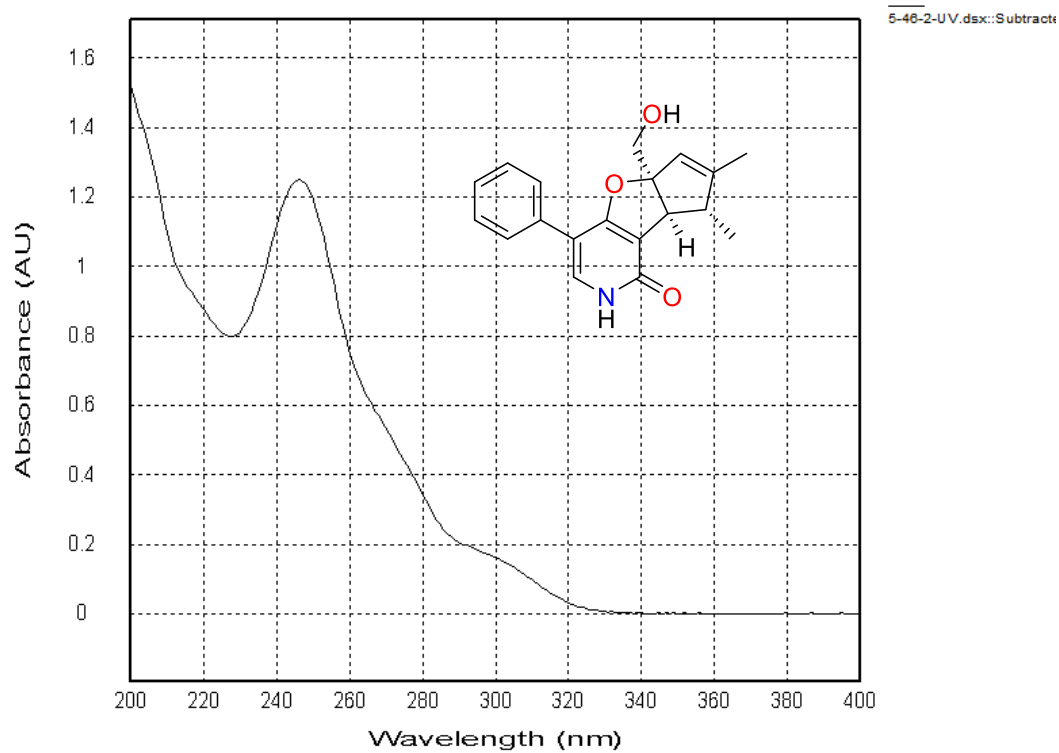


Figure S37. UV spectrum of **3a**

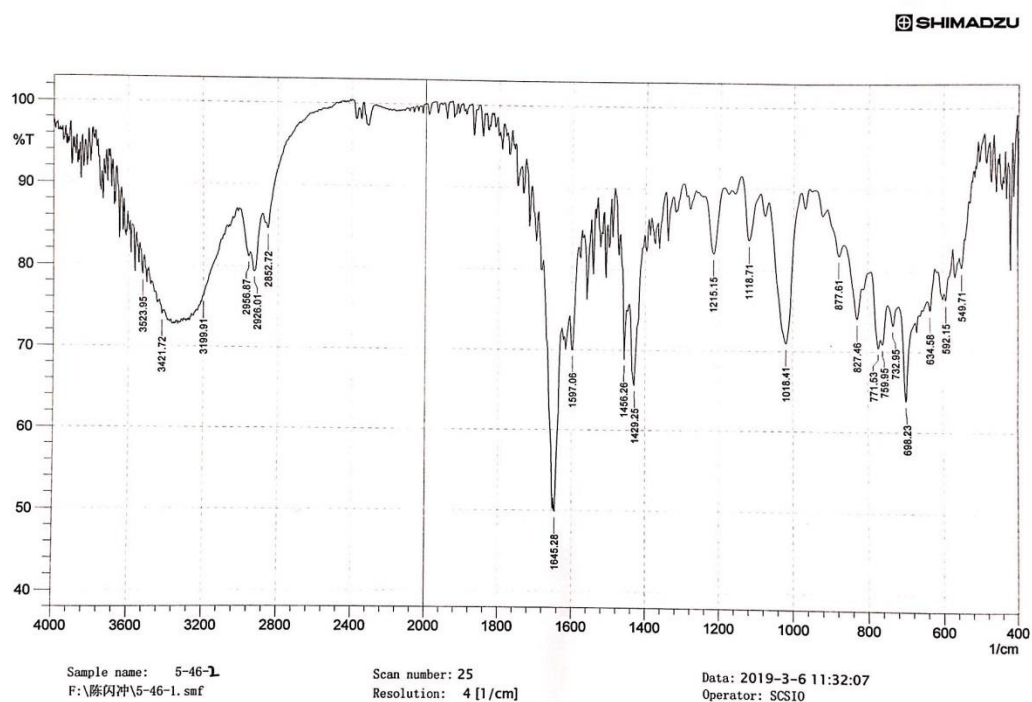


Figure S38. IR spectrum of **3a**

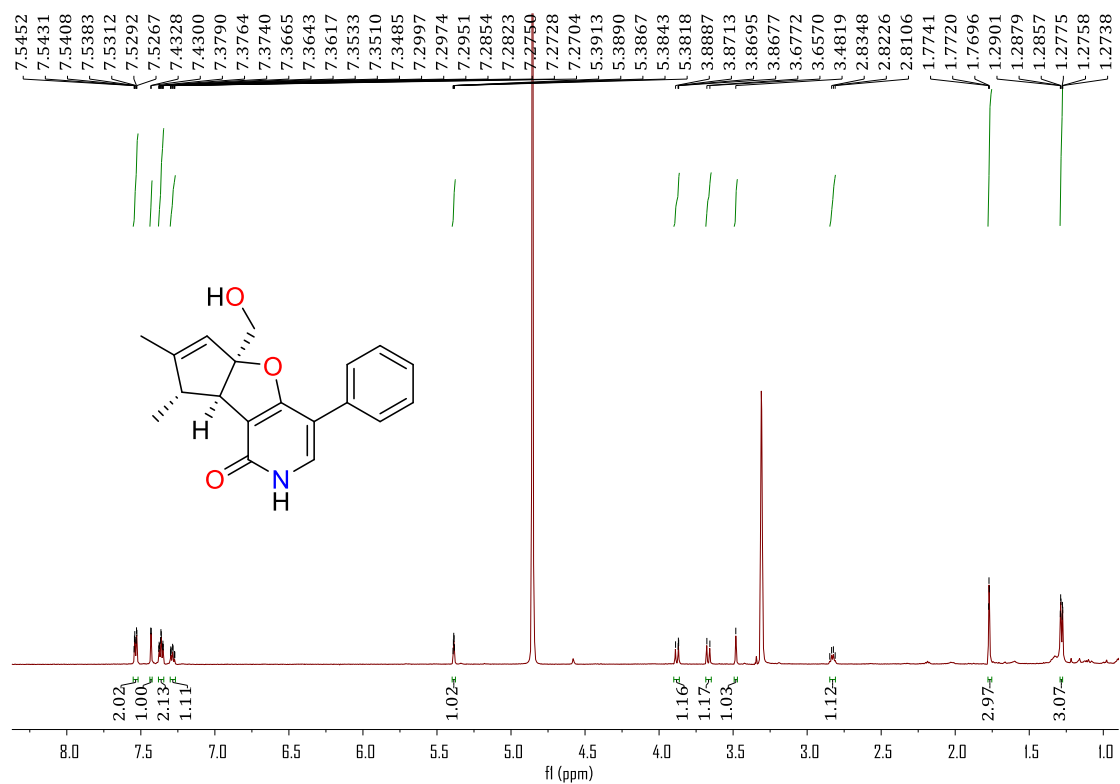


Figure S39. ¹H NMR spectrum (600 MHz, CD₃OD) of **3b**

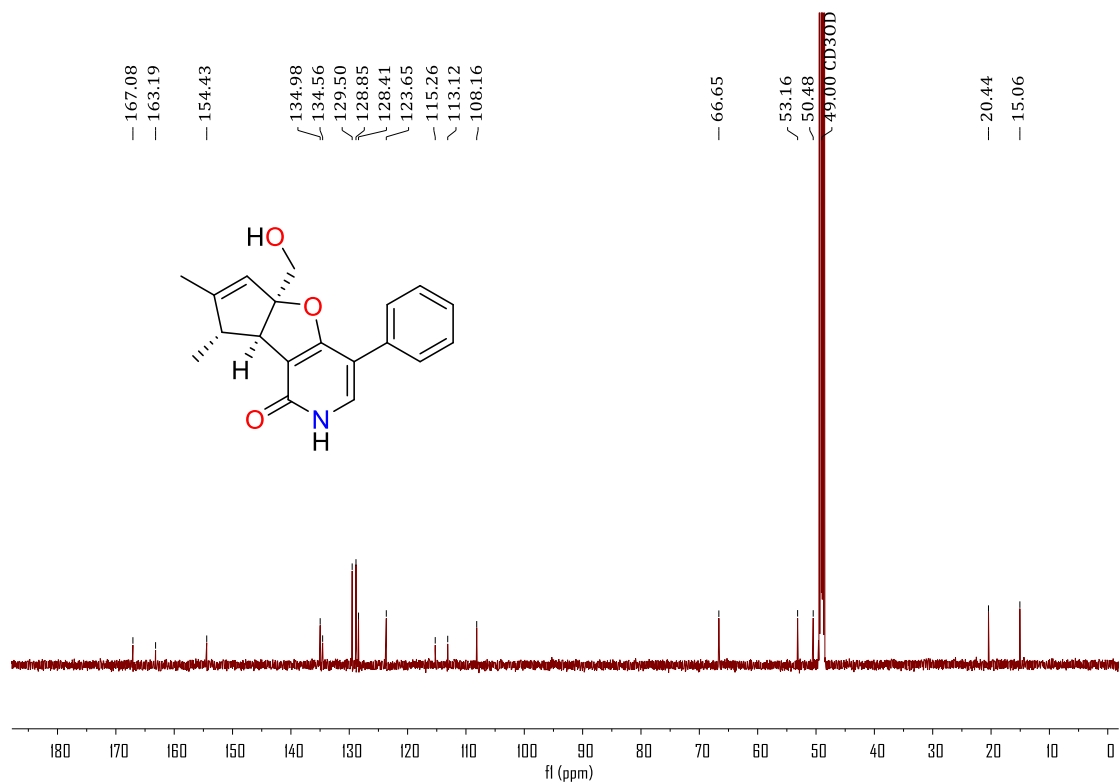


Figure S40. ¹³C NMR spectrum (150 MHz, CD₃OD) of **3b**

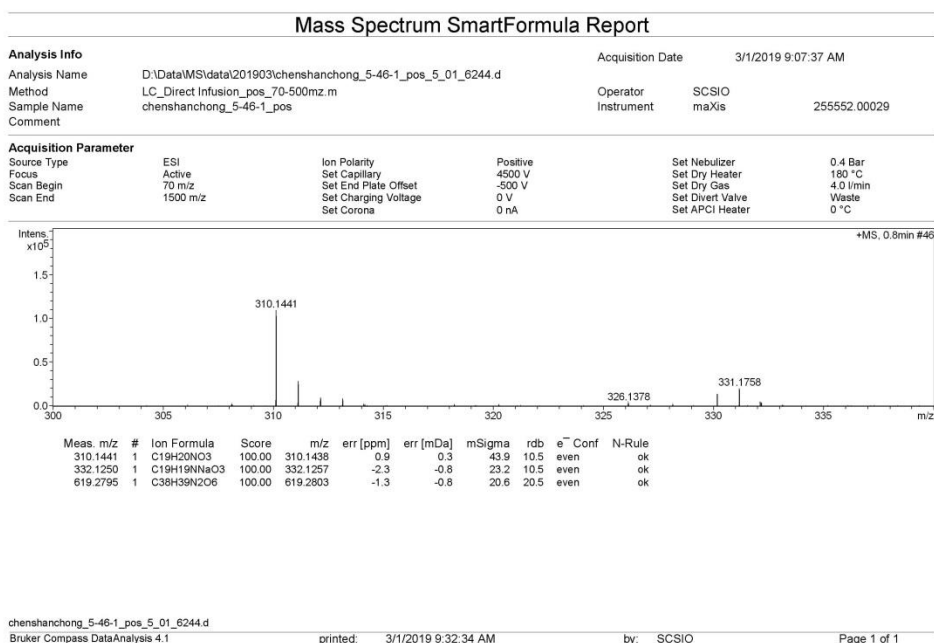


Figure S41. HRESIMS spectrum of **3b**

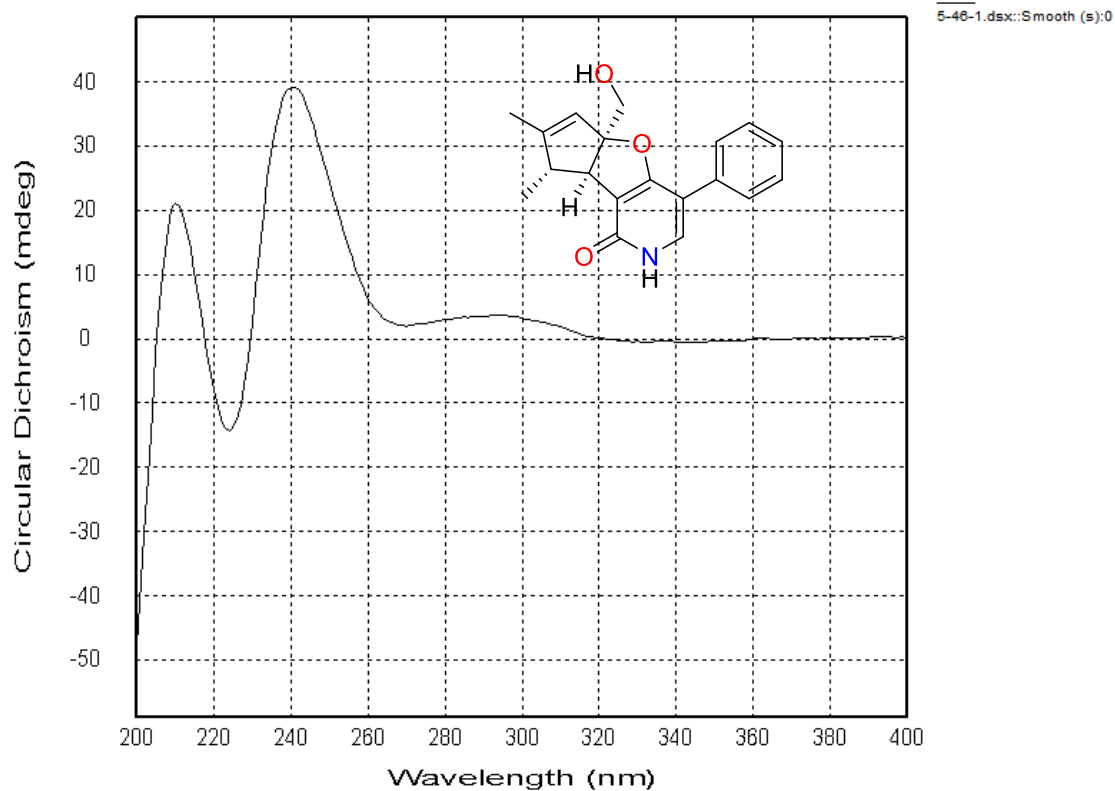


Figure S42. CD spectrum of **3b**

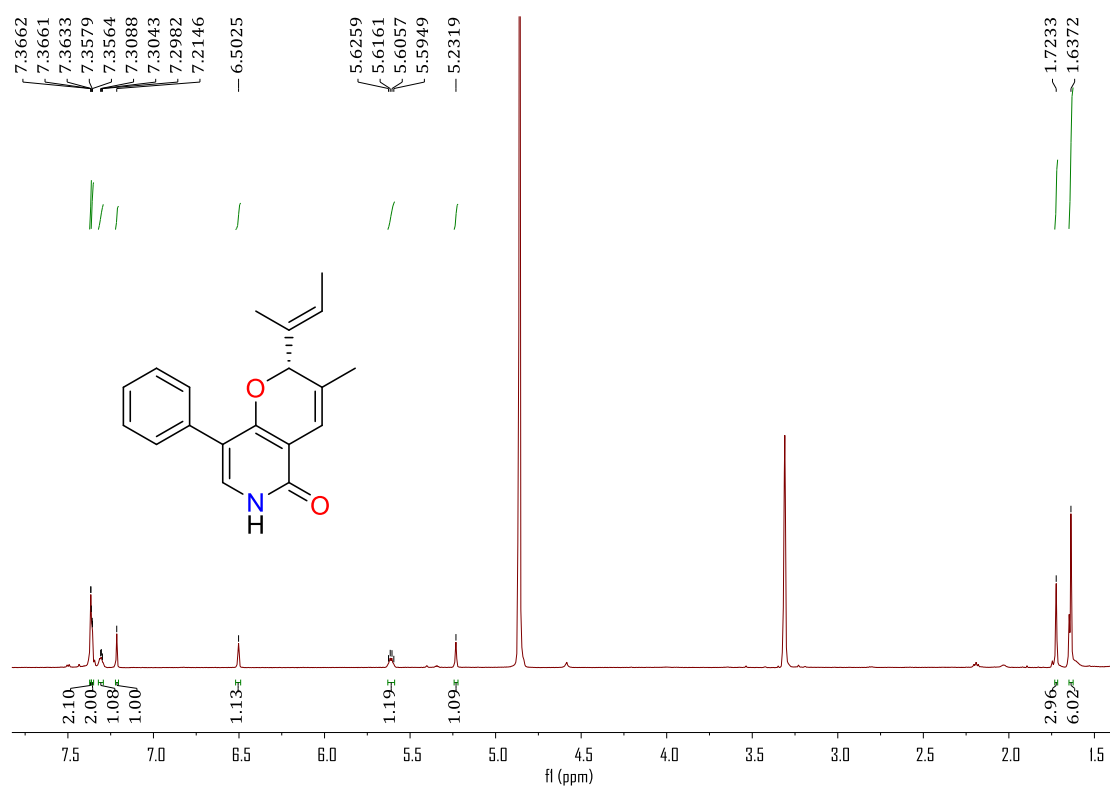


Figure S43. ¹H NMR spectrum (600 MHz, CD₃OD) of 4a

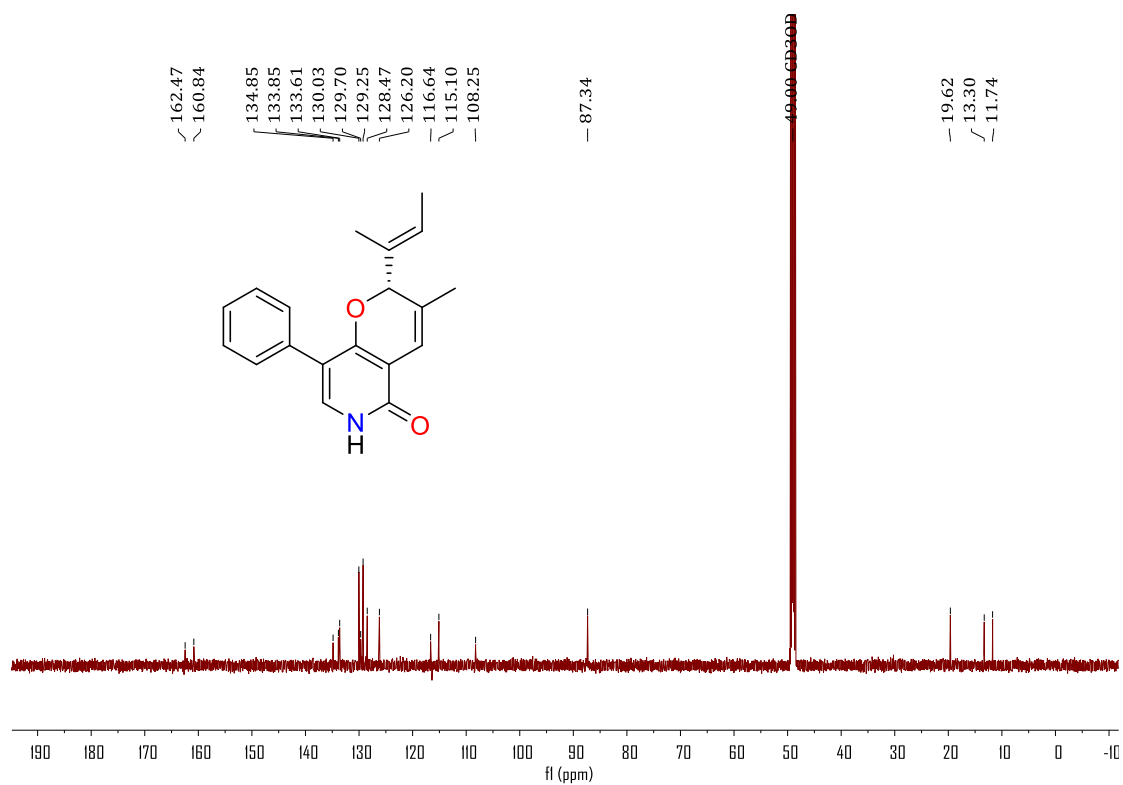


Figure S44. ¹³C NMR spectrum (150 MHz, CD₃OD) of 4a

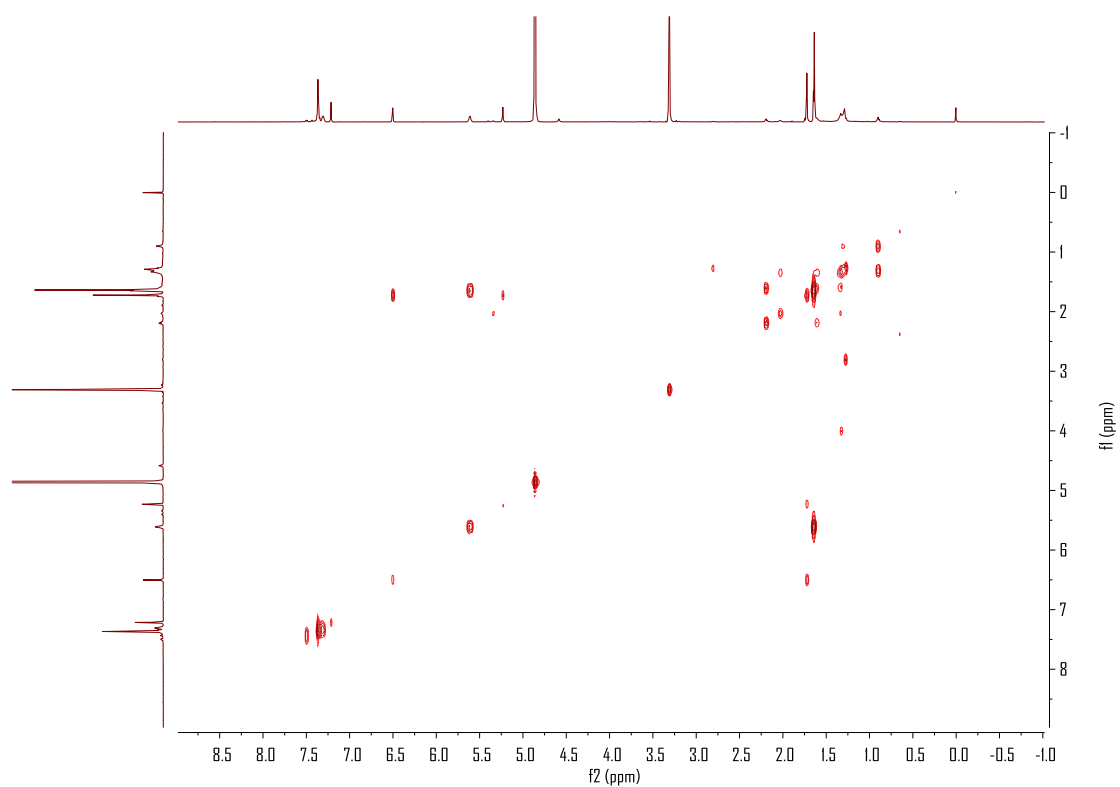


Figure S45. ^1H - ^1H COSY spectrum of **4a** in CD_3OD

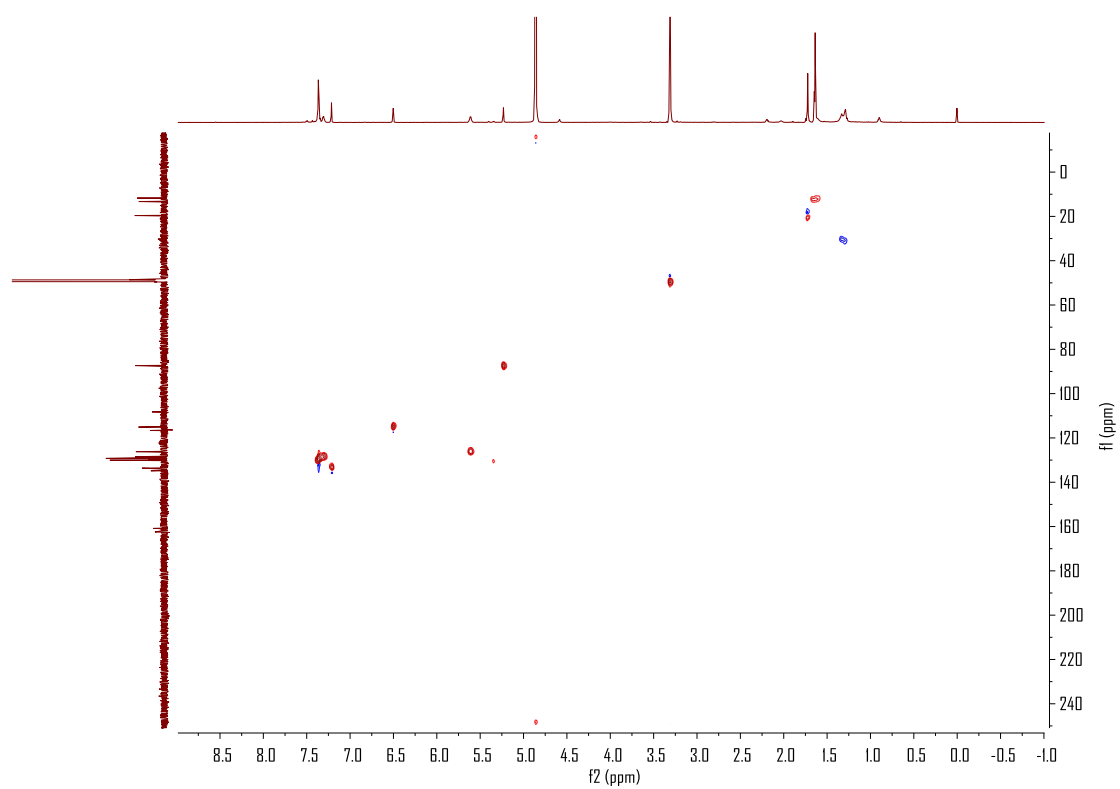


Figure S46. HSQC spectrum of **4a** in CD_3OD

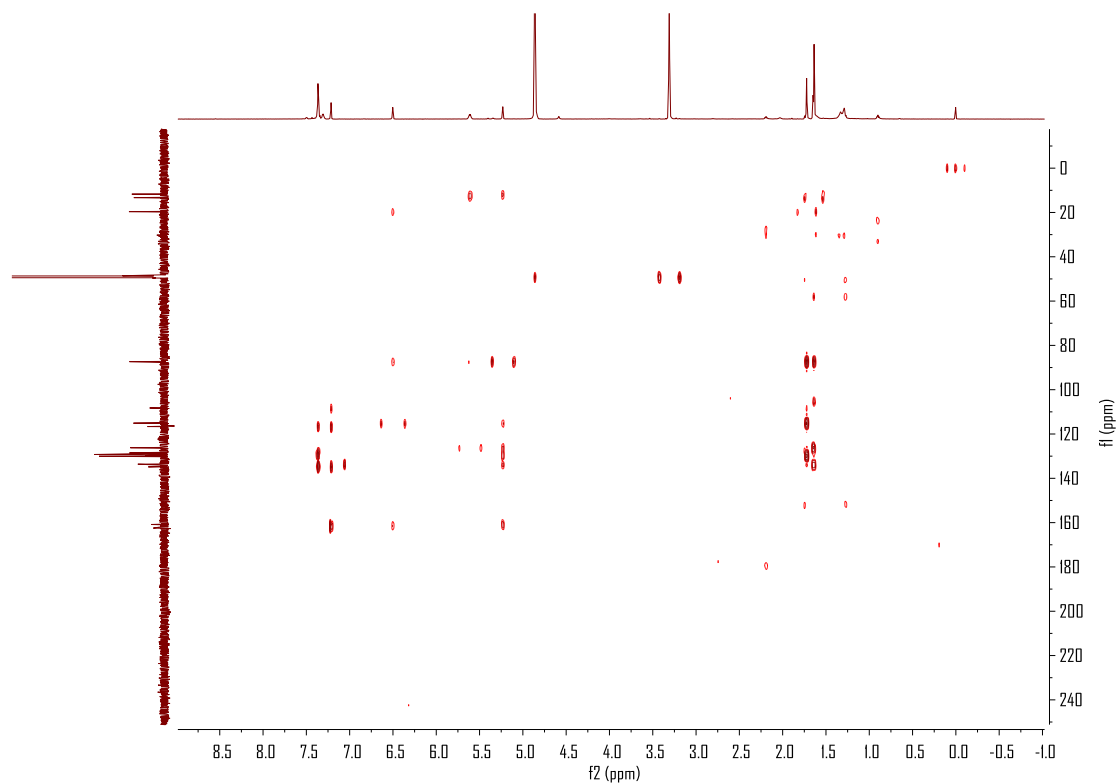


Figure S47. HMBC spectrum of **4a** in CD₃OD

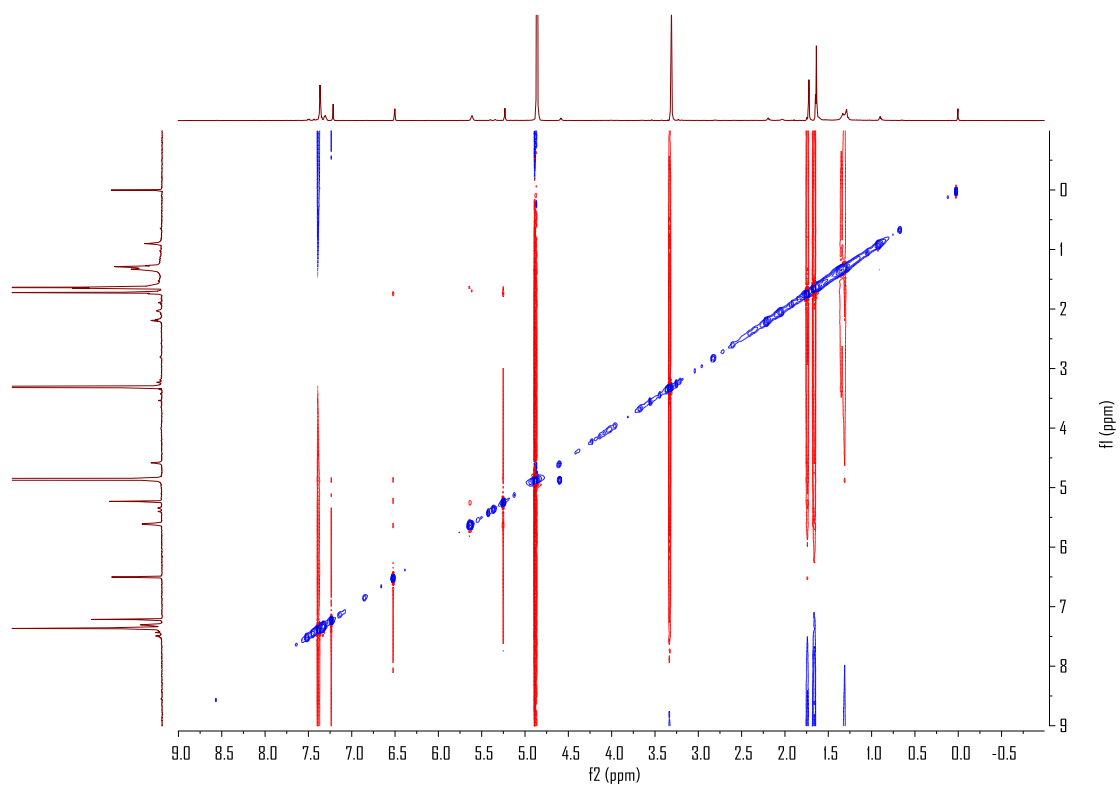


Figure S48. NOESY spectrum of **4a** in CD₃OD

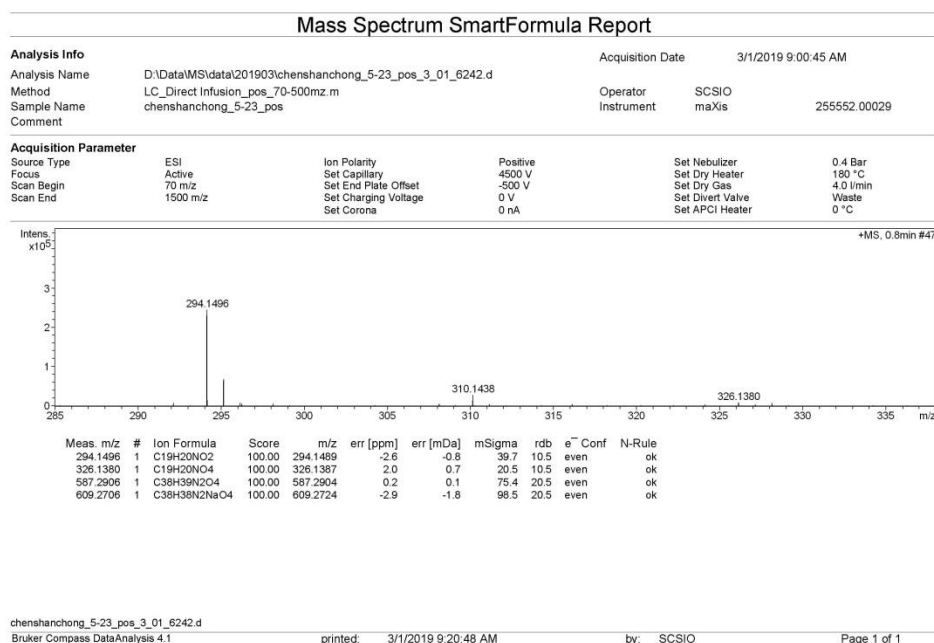


Figure S49. HRESIMS spectrum of **4a**

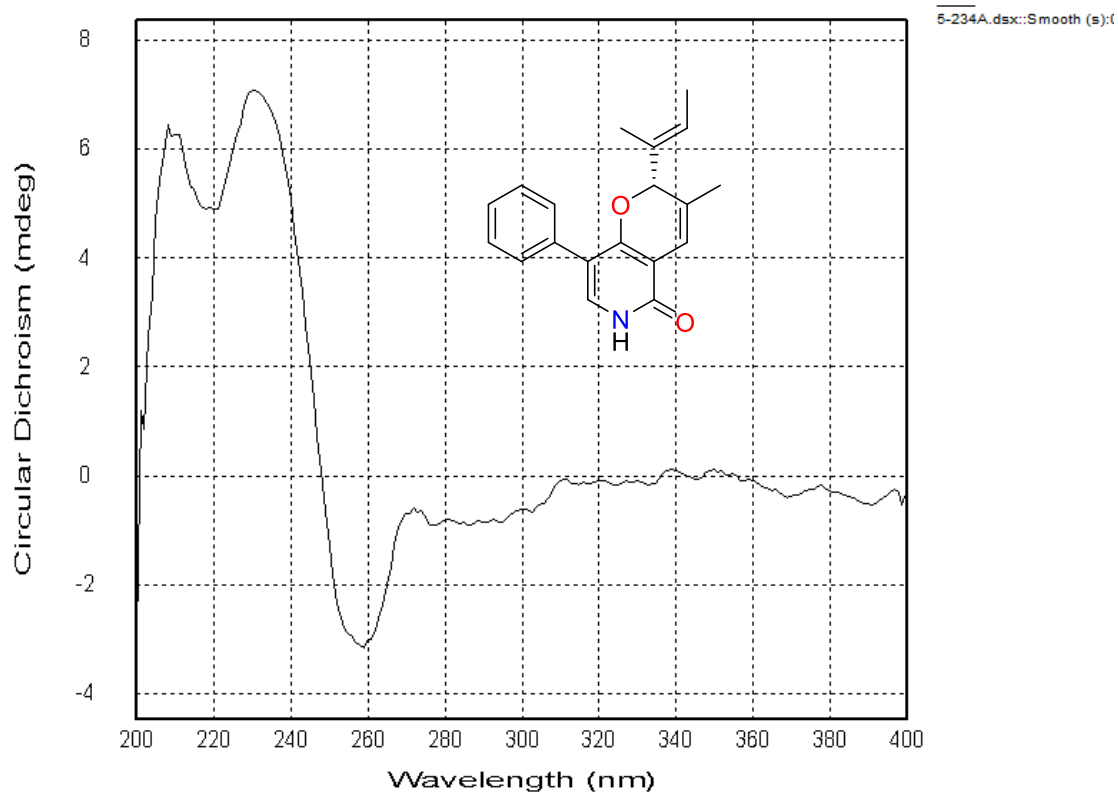
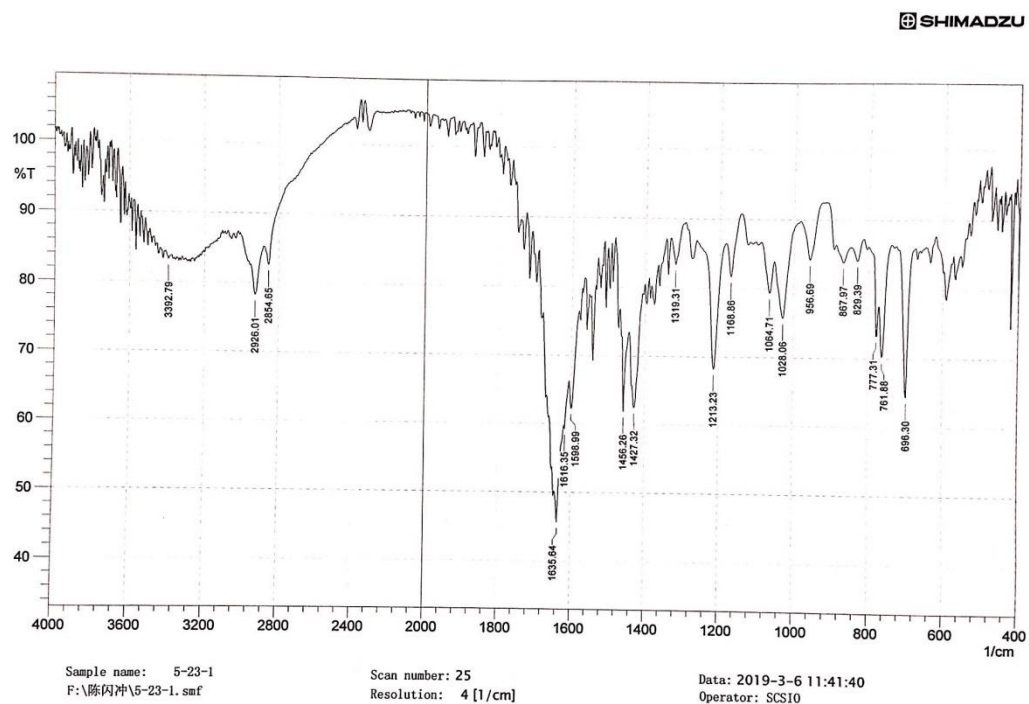
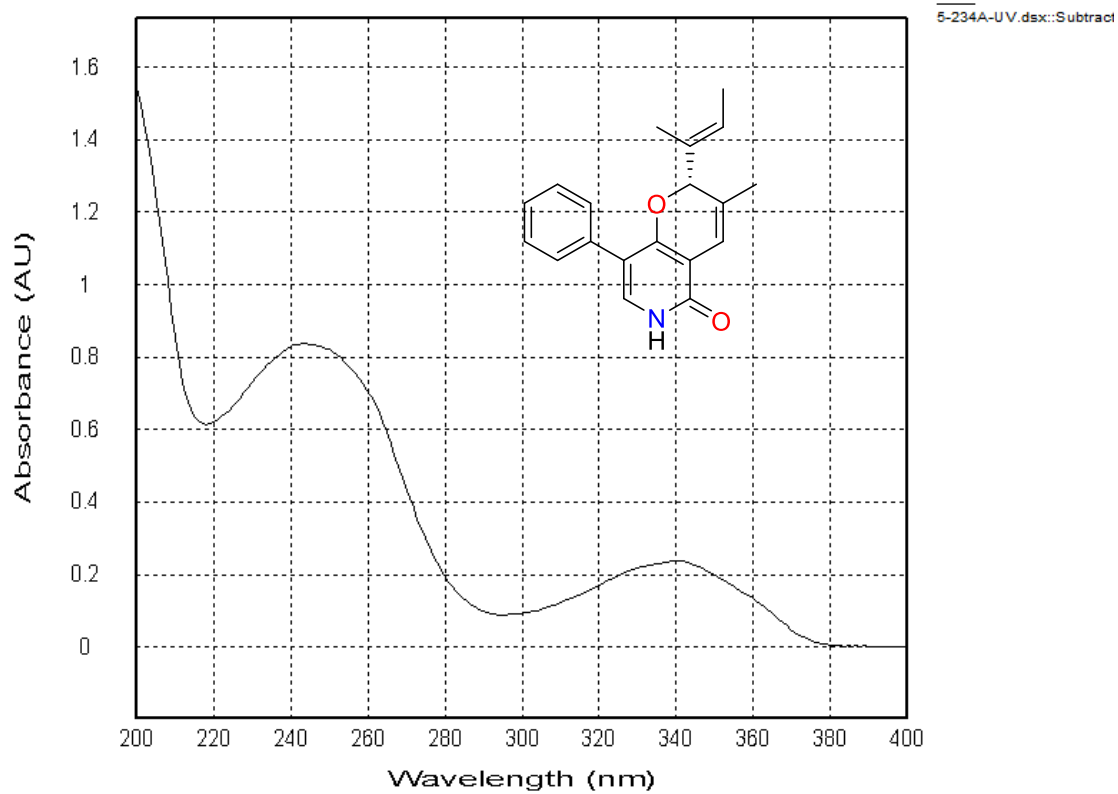


Figure S50. CD spectrum of **4a**



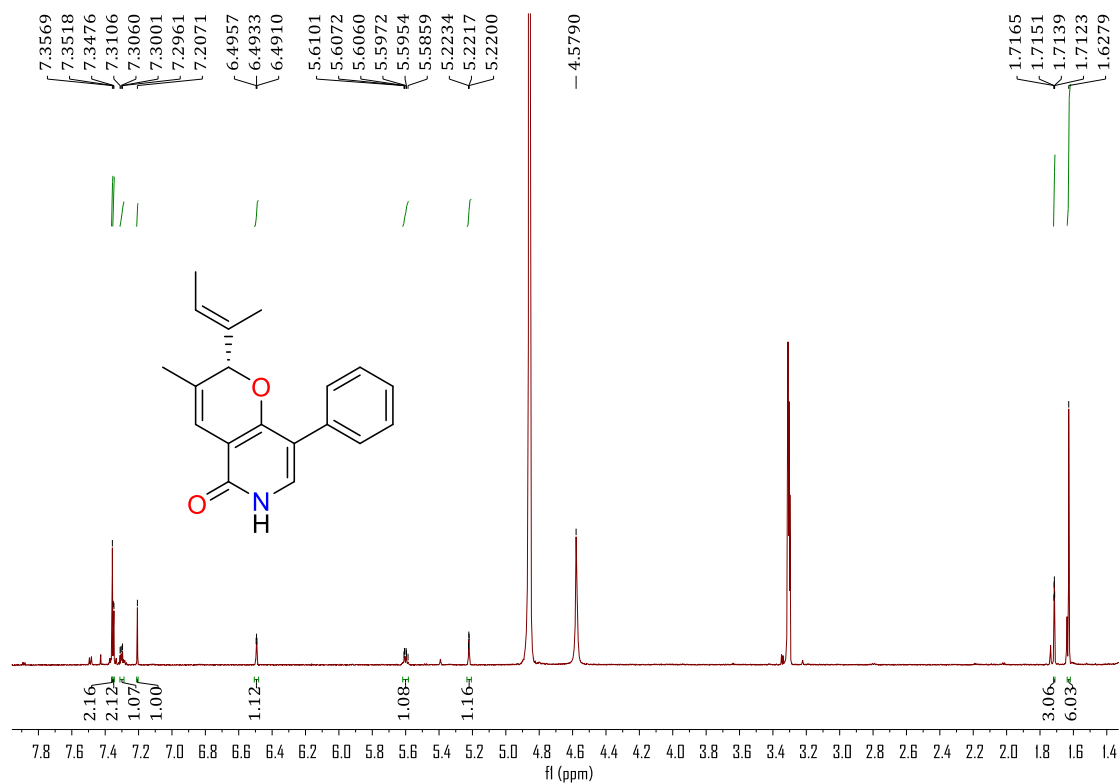


Figure S53. ¹H NMR spectrum (600 MHz, CD₃OD) of **4b**

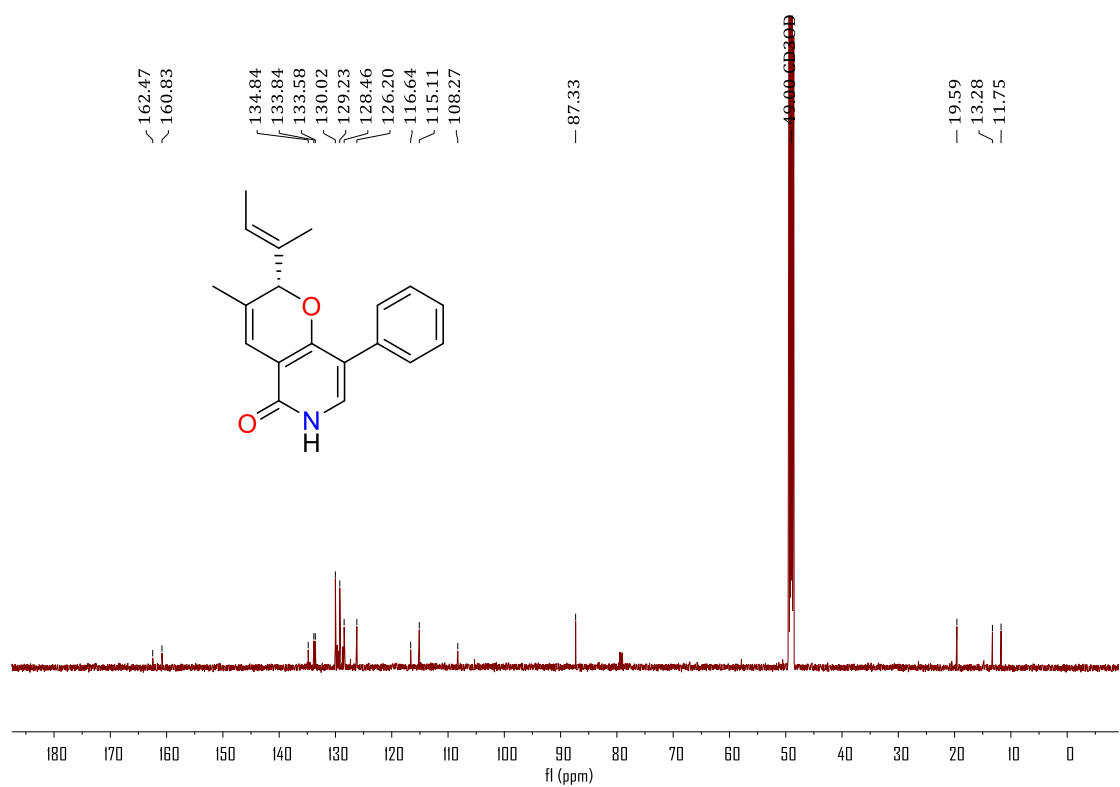


Figure S54. ¹³C NMR spectrum (150 MHz, CD₃OD) of **4b**

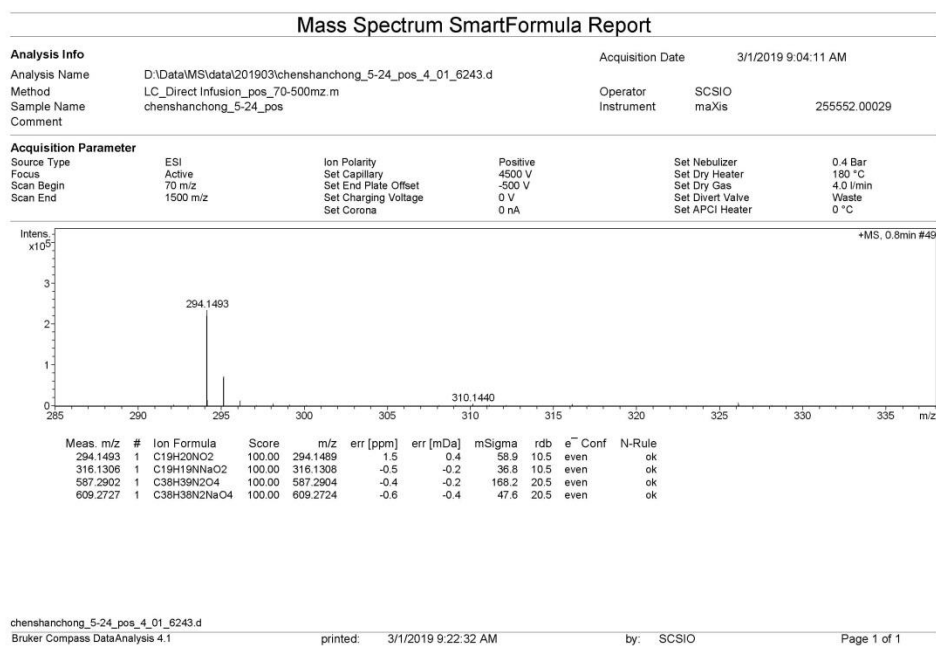


Figure S55. HRESIMS spectrum of **4b**

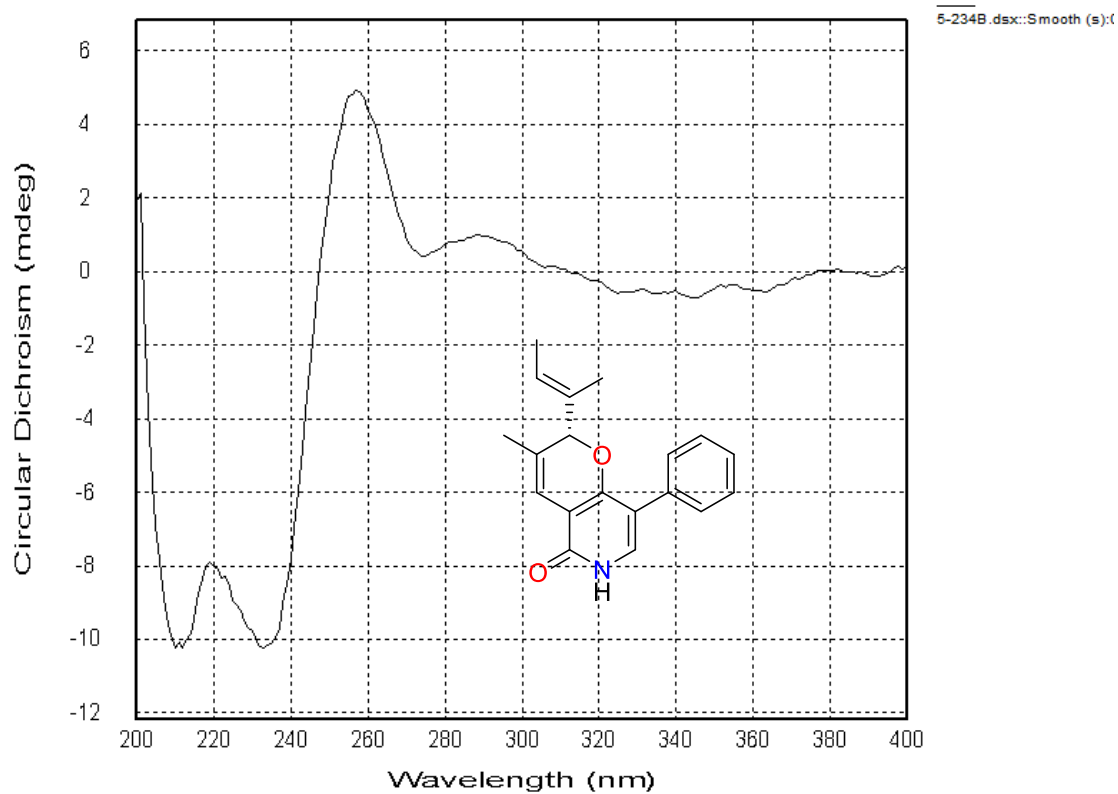


Figure S56. CD spectrum of **4b**

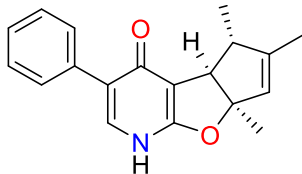


Figure S57. ^1H NMR spectrum (600 MHz, CD_3OD) of **5a**

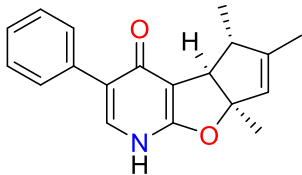


Figure S58. ^{13}C NMR spectrum (150 MHz, CD_3OD) of **5a**

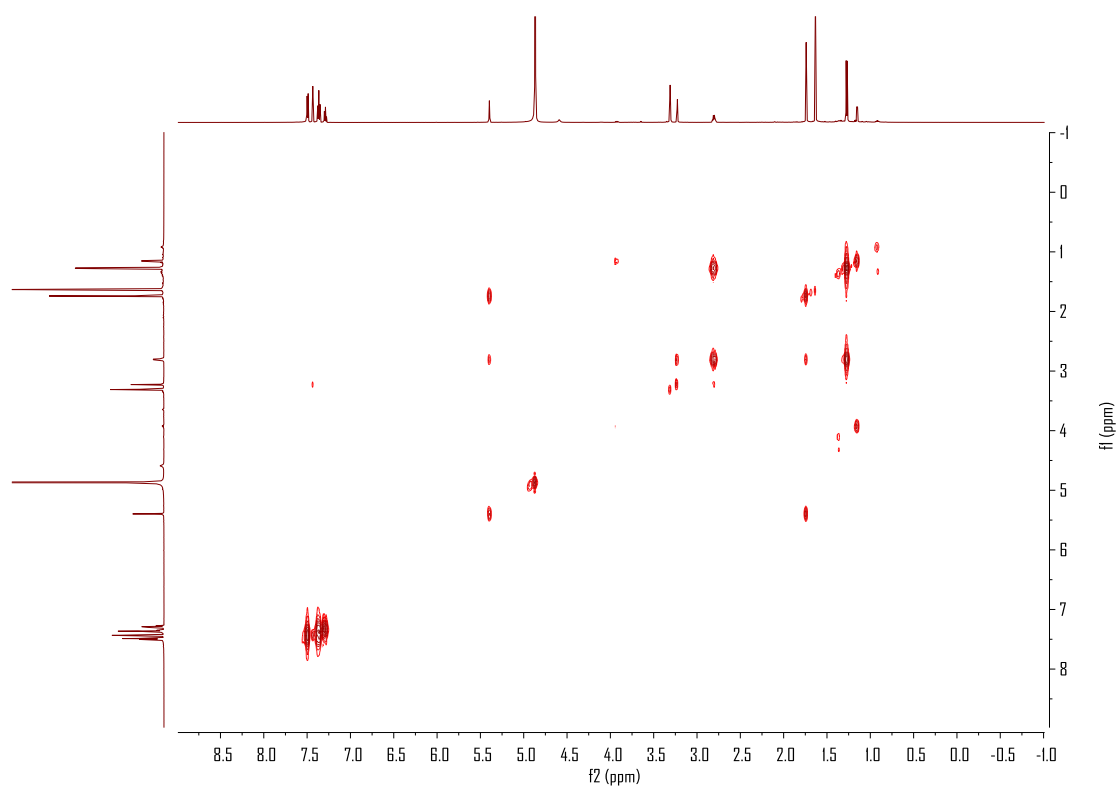


Figure S59. ^1H - ^1H COSY spectrum of **5a** in CD_3OD

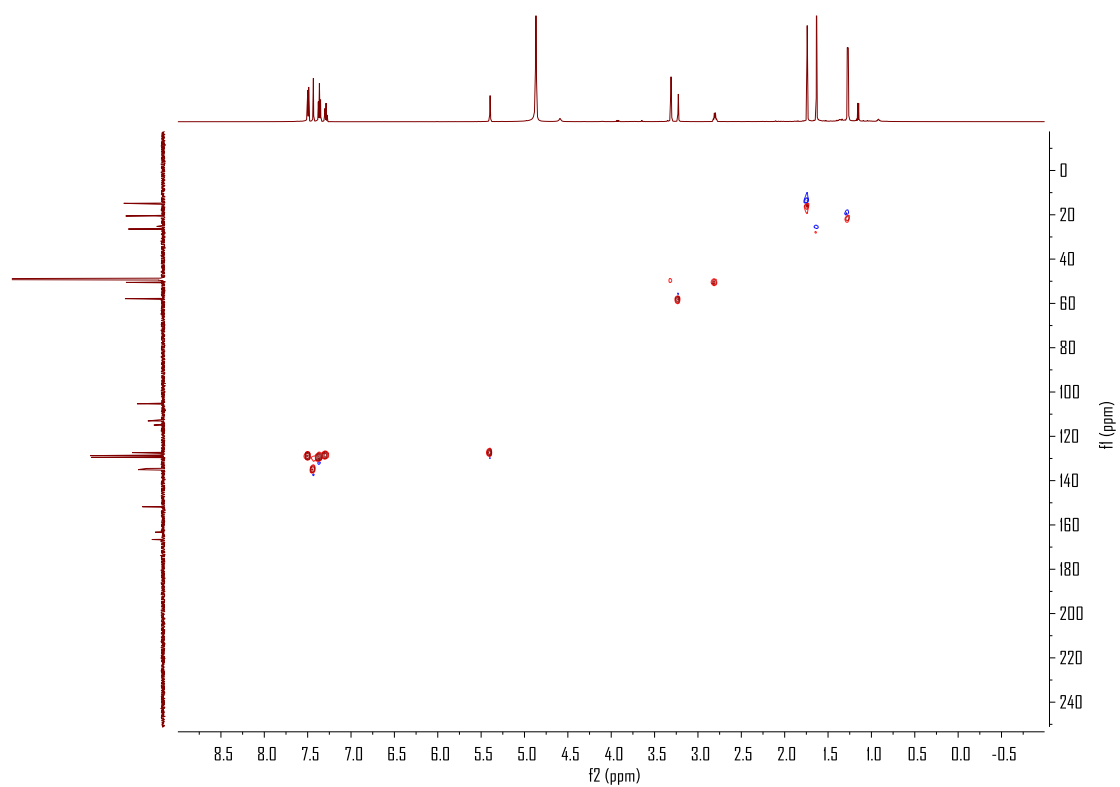


Figure S60. HSQC spectrum of **5a** in CD_3OD

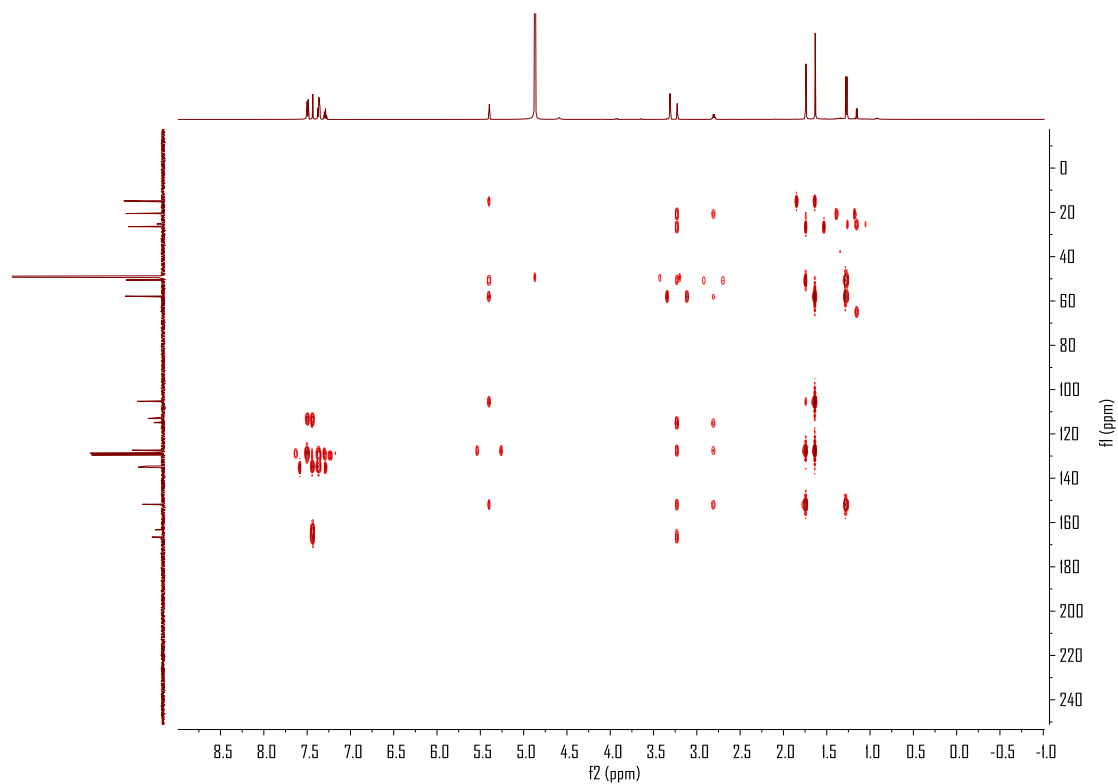


Figure S61. HMBC spectrum of **5a** in CD₃OD

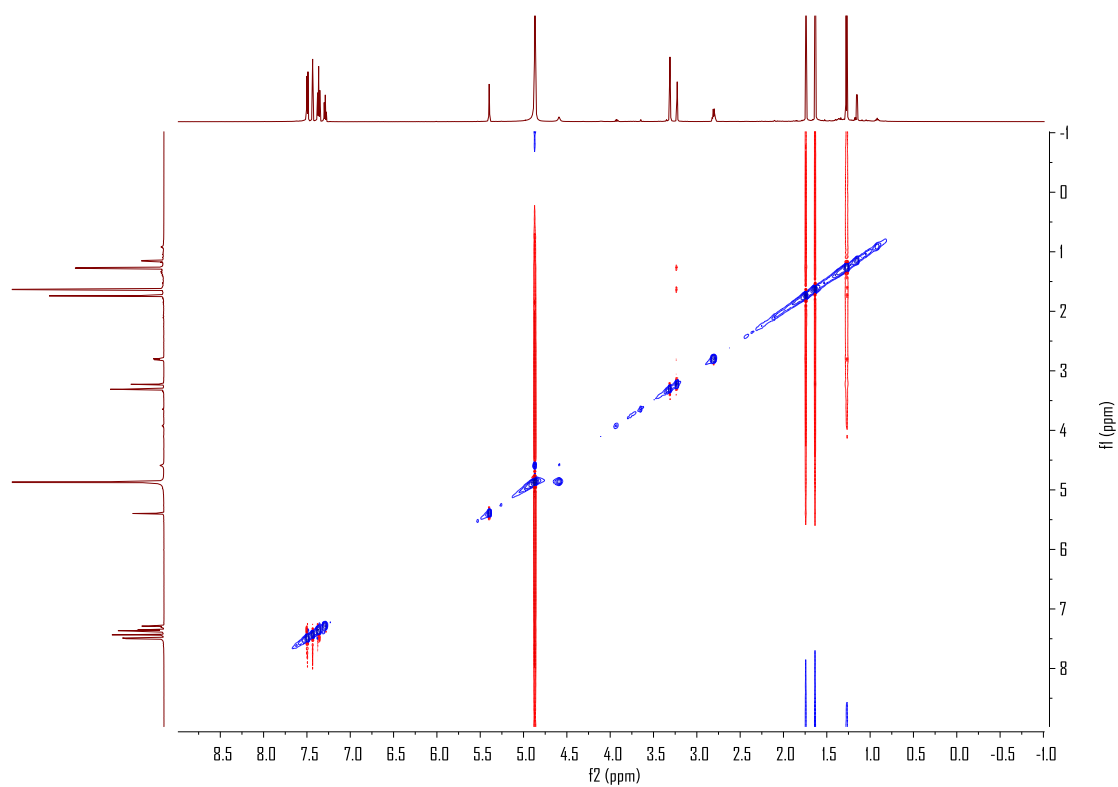


Figure S62. NOESY spectrum of **5a** in CD₃OD

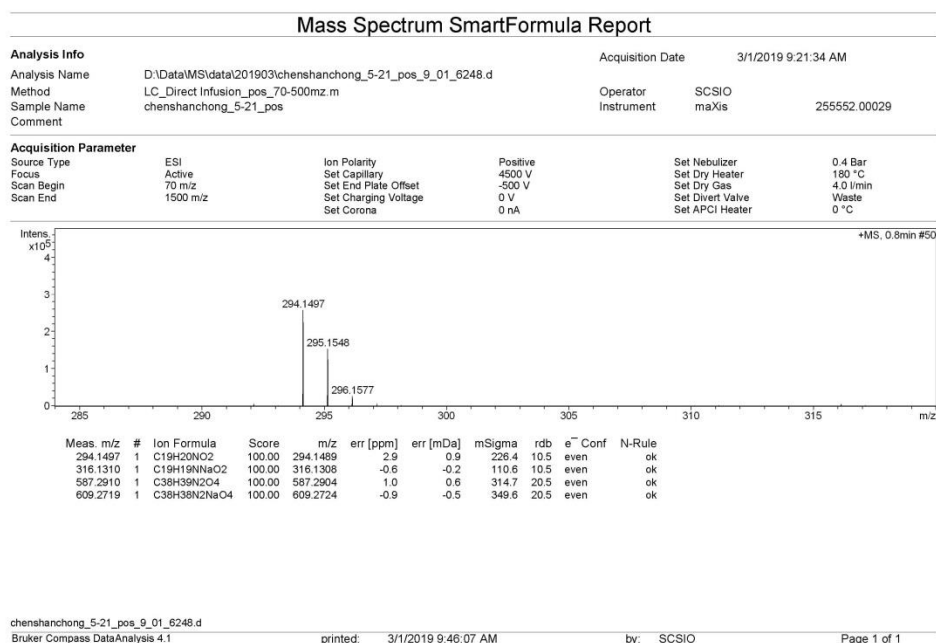


Figure S63. HRESIMS spectrum of **5a**

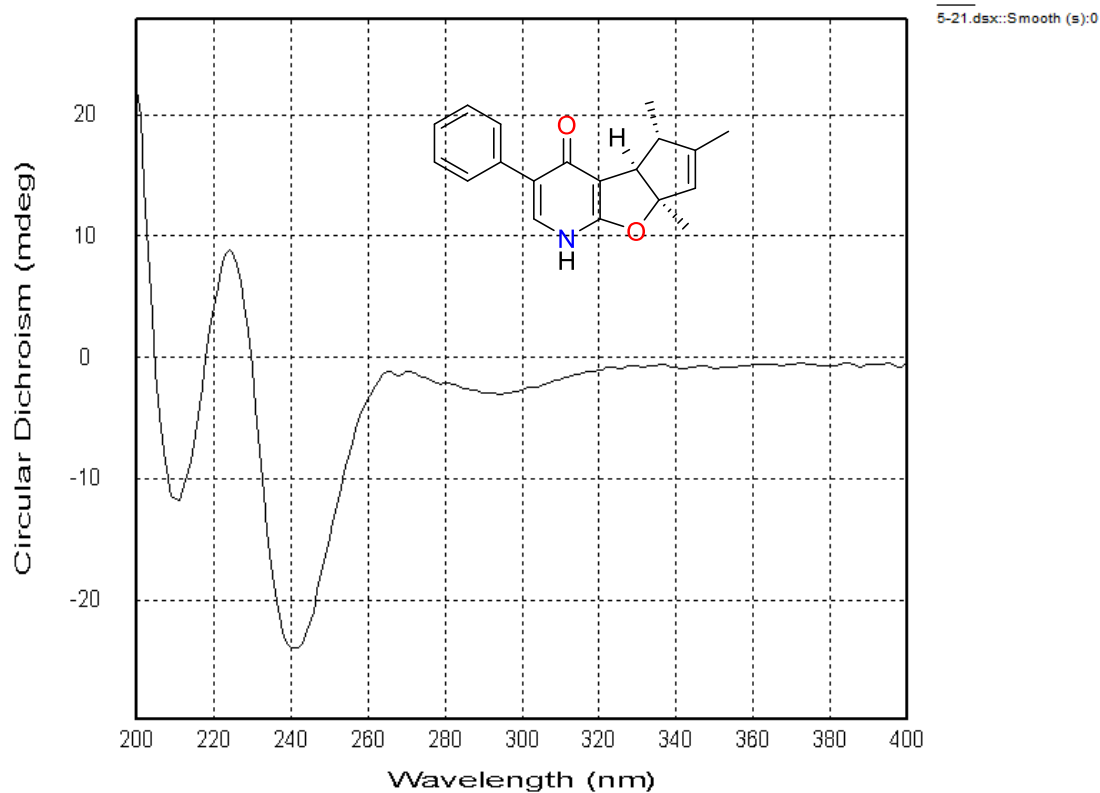


Figure S64. CD spectrum of **5a**

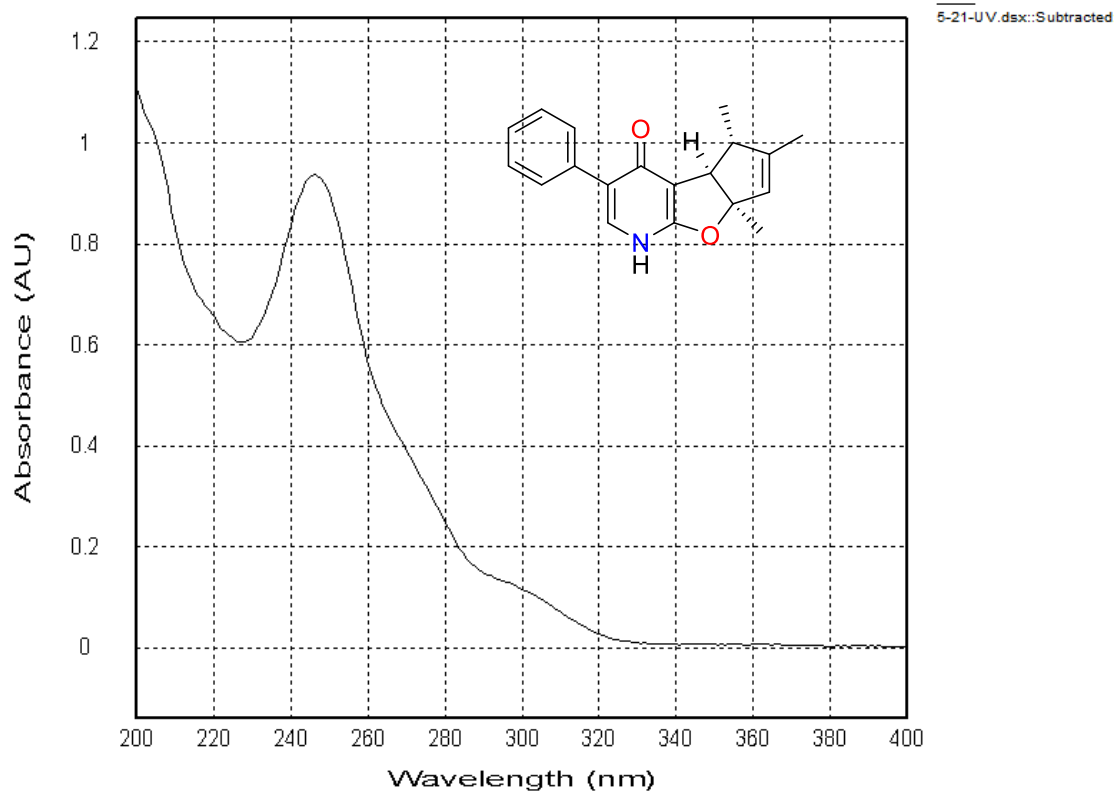


Figure S65. UV spectrum of **5a**

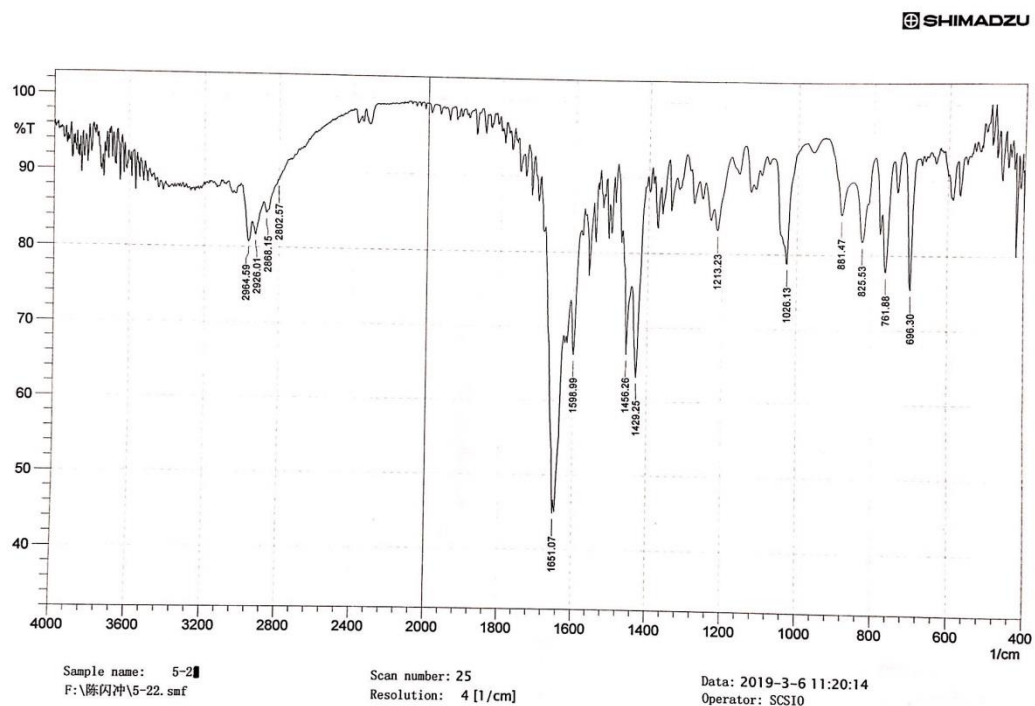


Figure S66. IR spectrum of **5a**

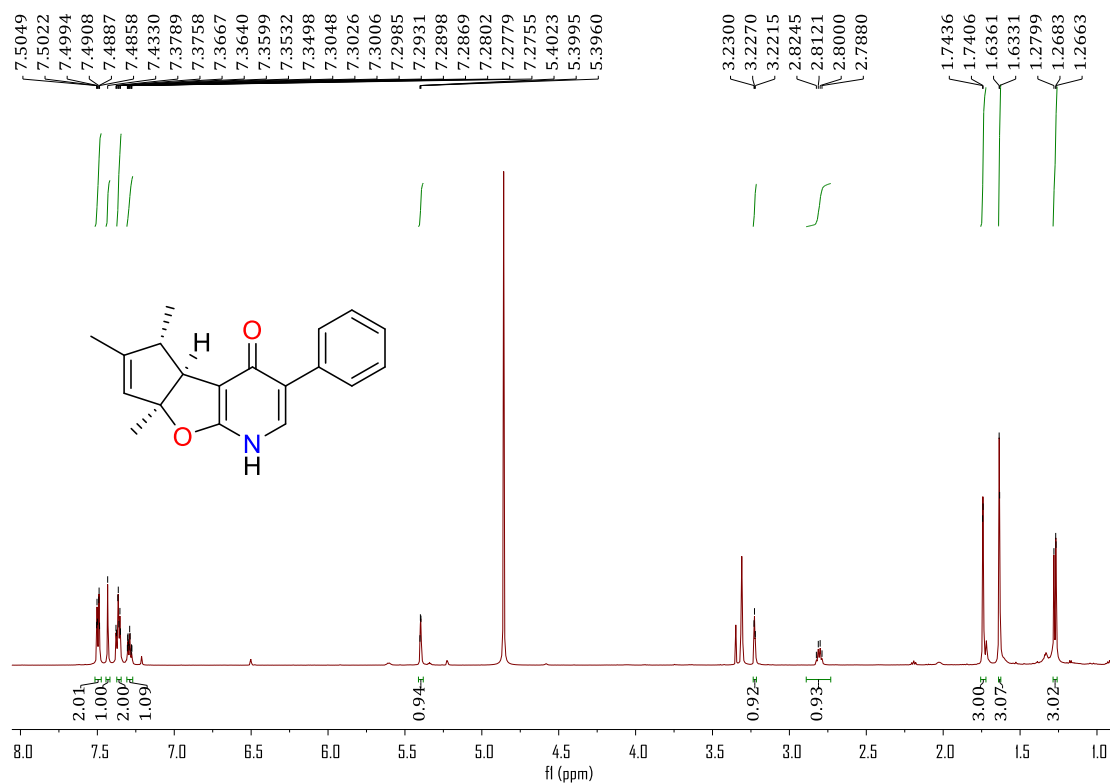


Figure S67. ¹H NMR spectrum (600 MHz, CD₃OD) of **5b**

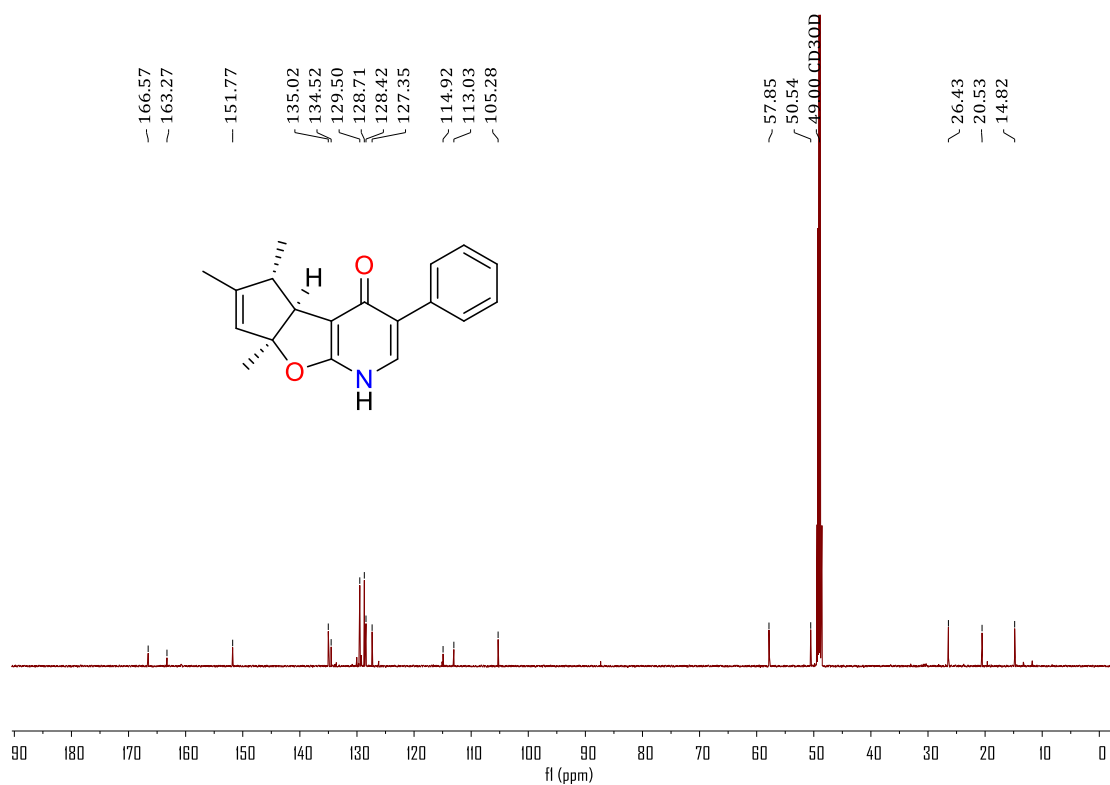


Figure S68. ¹³C NMR spectrum (150 MHz, CD₃OD) of **5b**

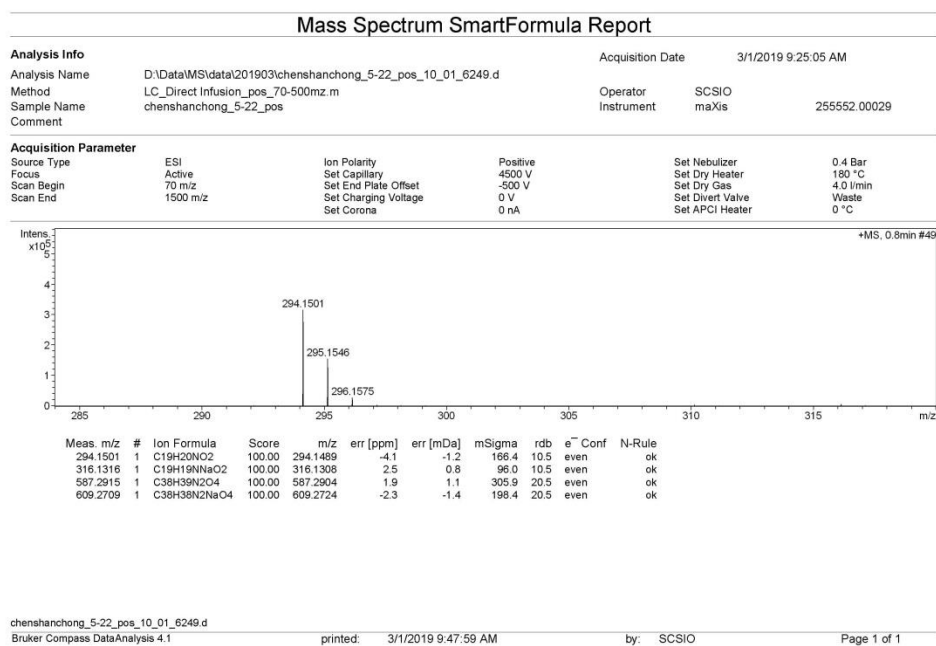


Figure S69. HRESIMS spectrum of **5b**

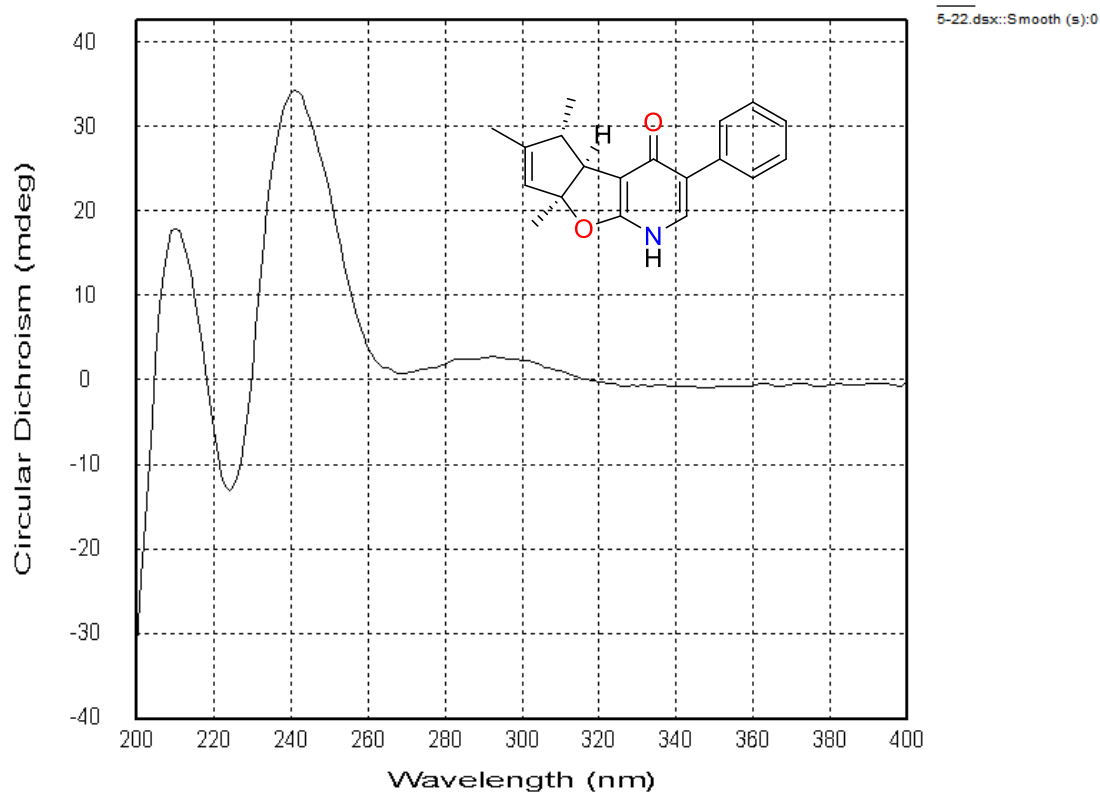


Figure S70. CD spectrum of **5b**

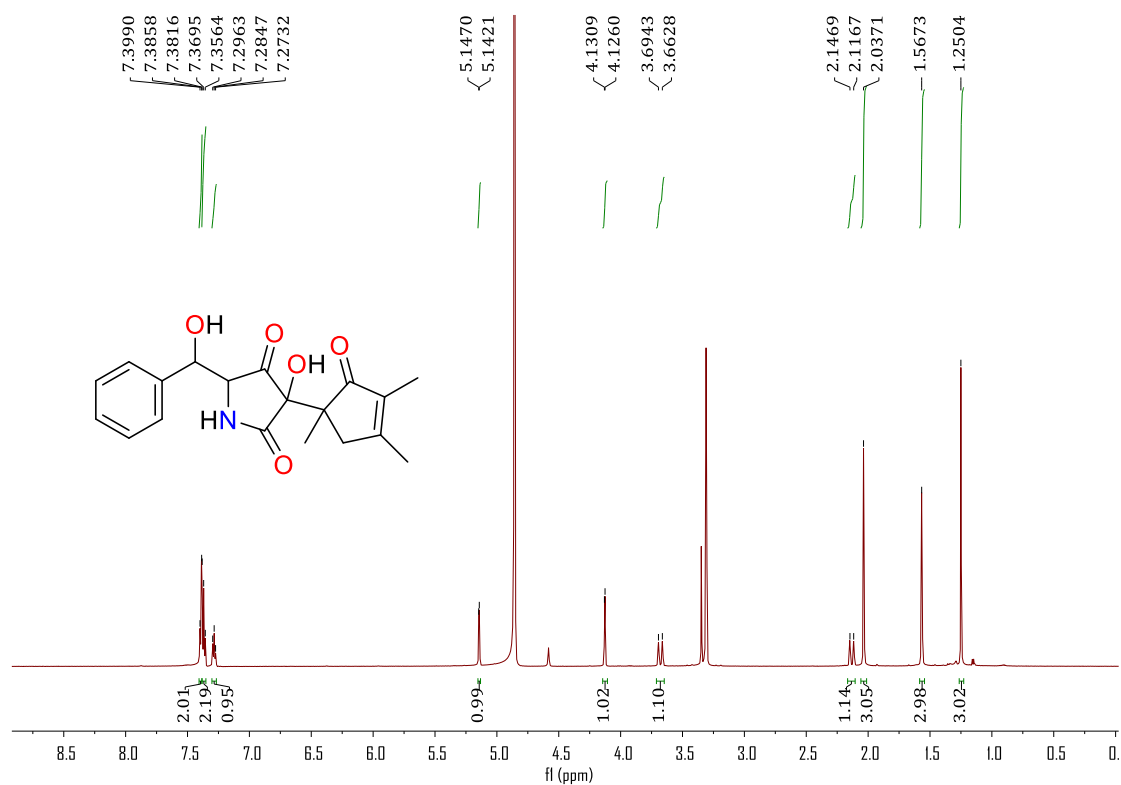


Figure S71. ¹H NMR spectrum (600 MHz, CD₃OD) of **6**

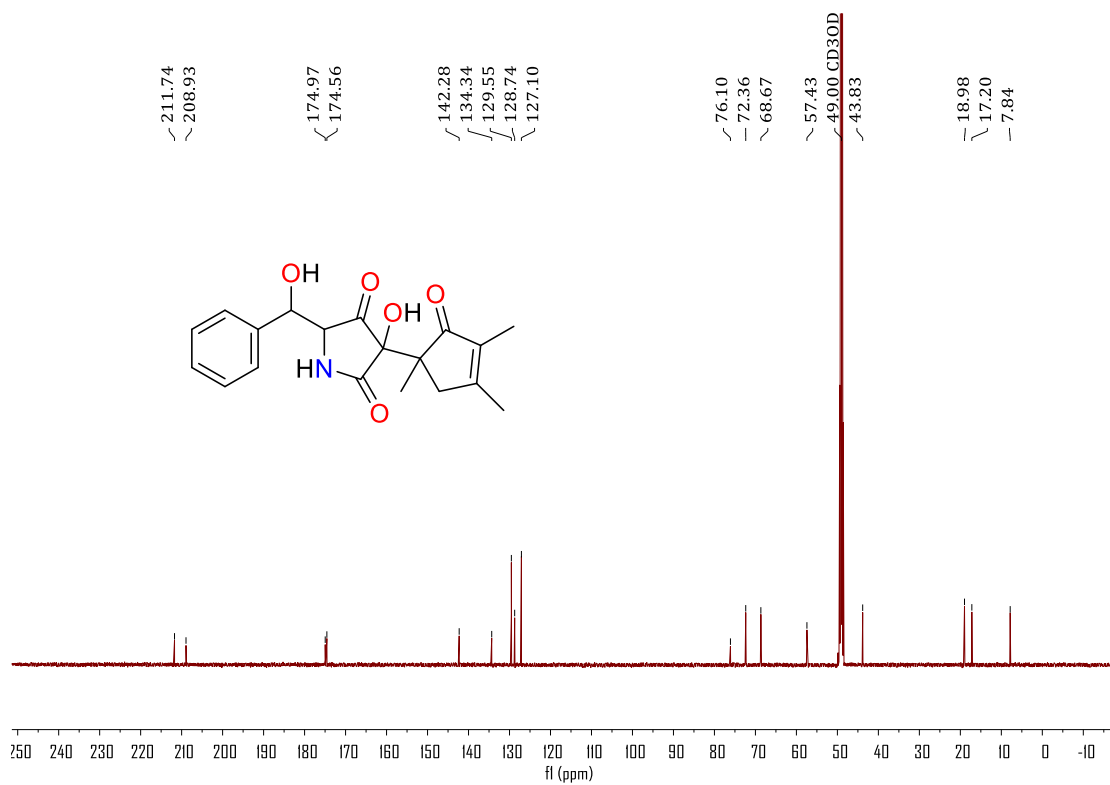


Figure S72. ¹³C NMR spectrum (150 MHz, CD₃OD) of **6**

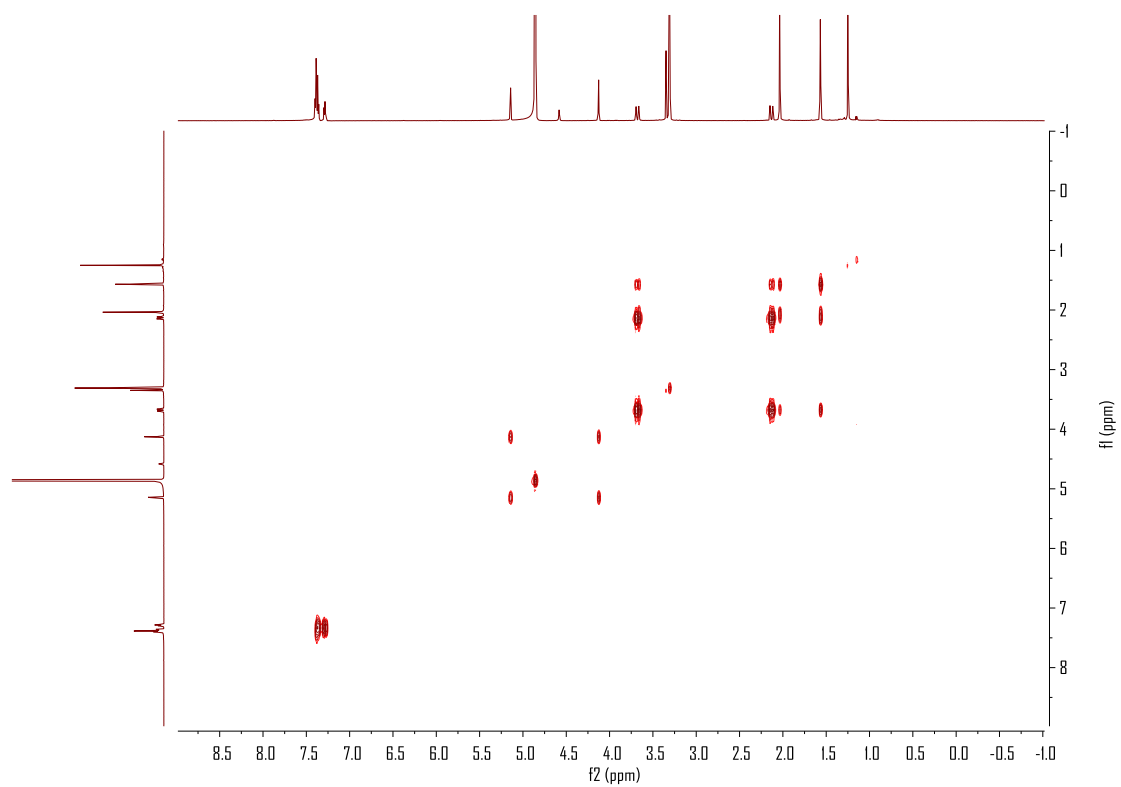


Figure S73. ^1H - ^1H COSY spectrum of **6** in CD_3OD

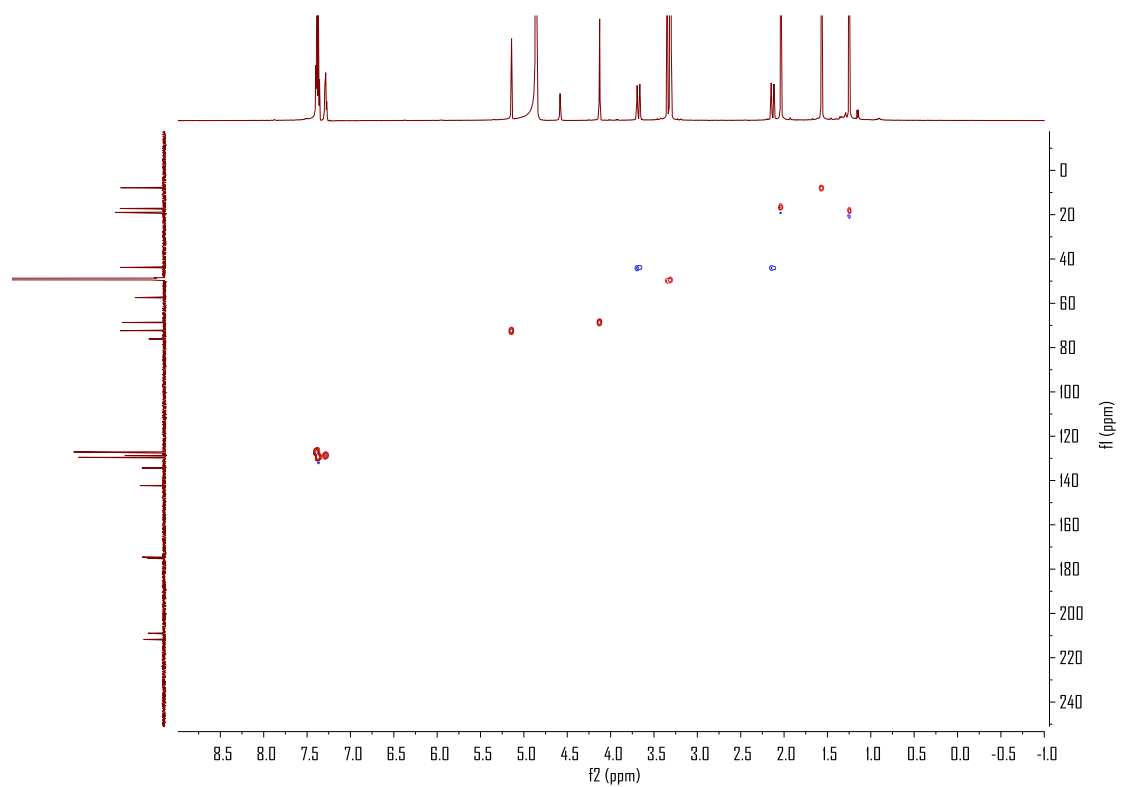


Figure S74. HSQC spectrum of **6** in CD_3OD

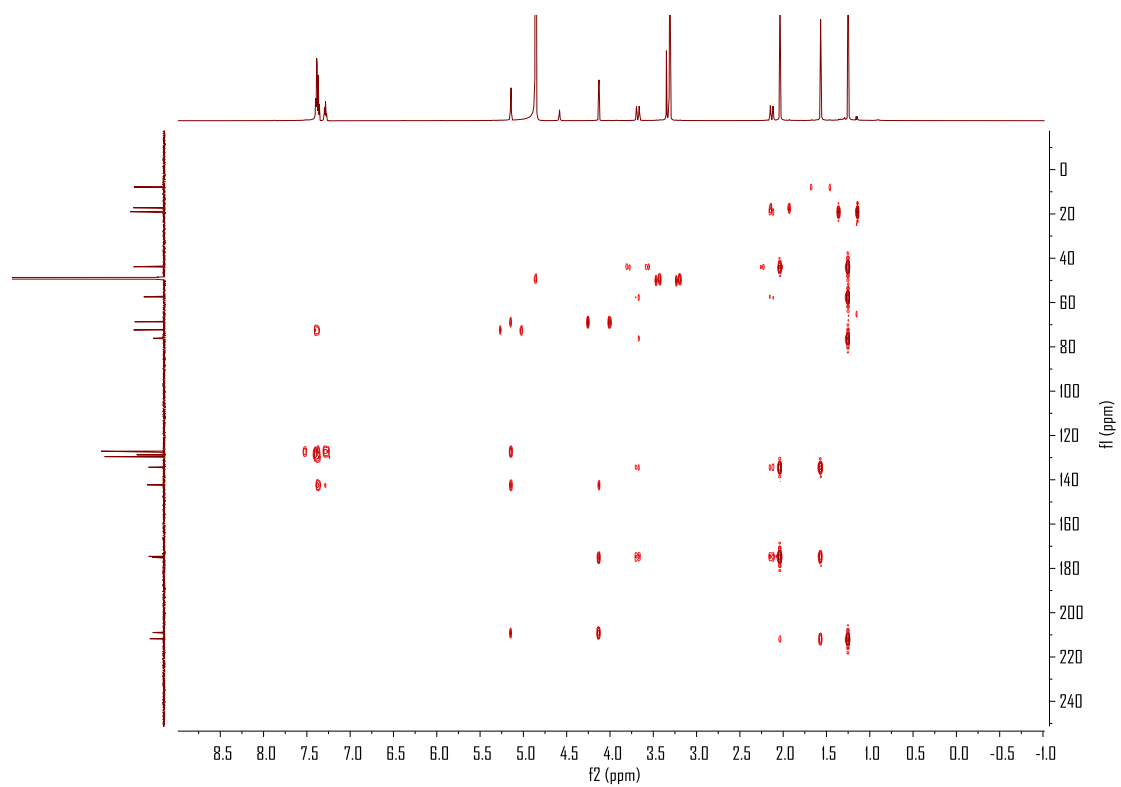


Figure S75. HMBC spectrum of **6** in CD₃OD

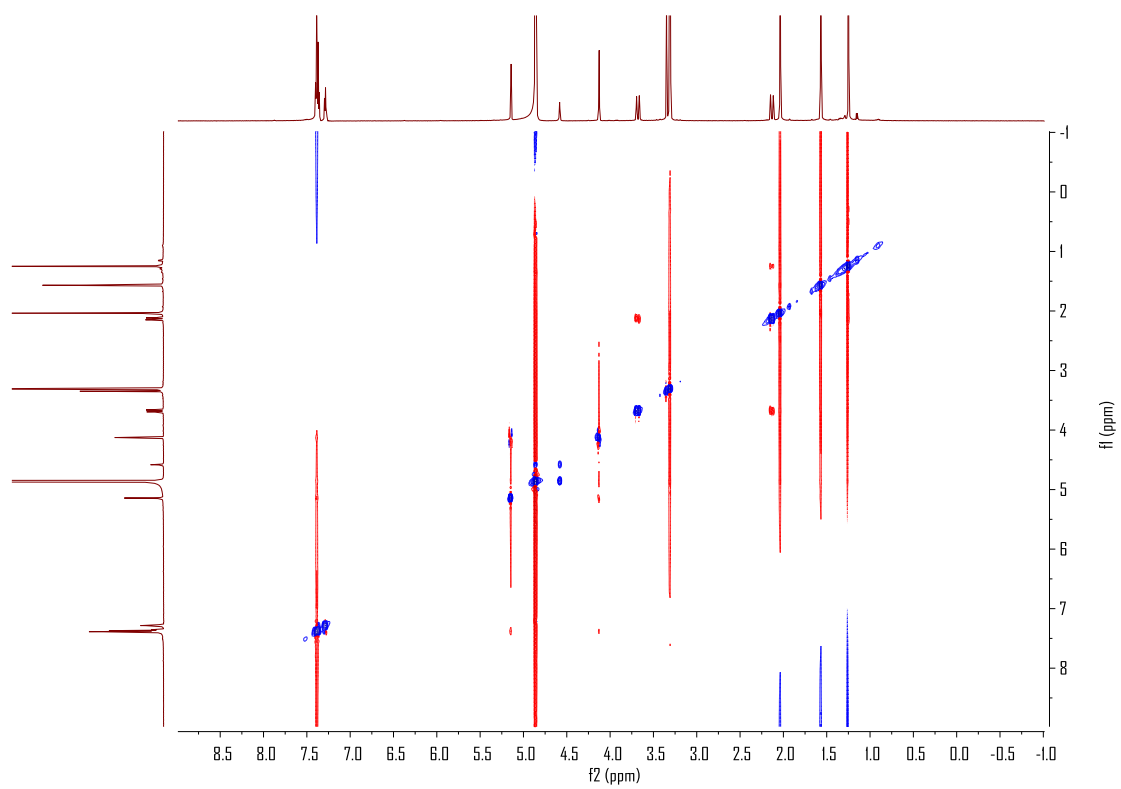


Figure S76. NOESY spectrum of **6** in CD₃OD

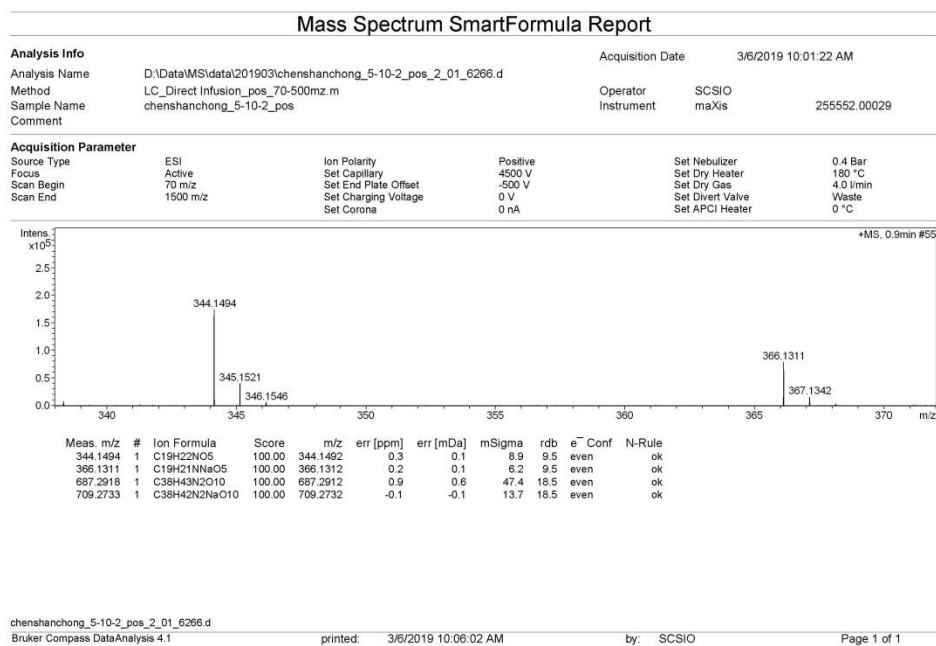


Figure S77. HRESIMS spectrum of **6**

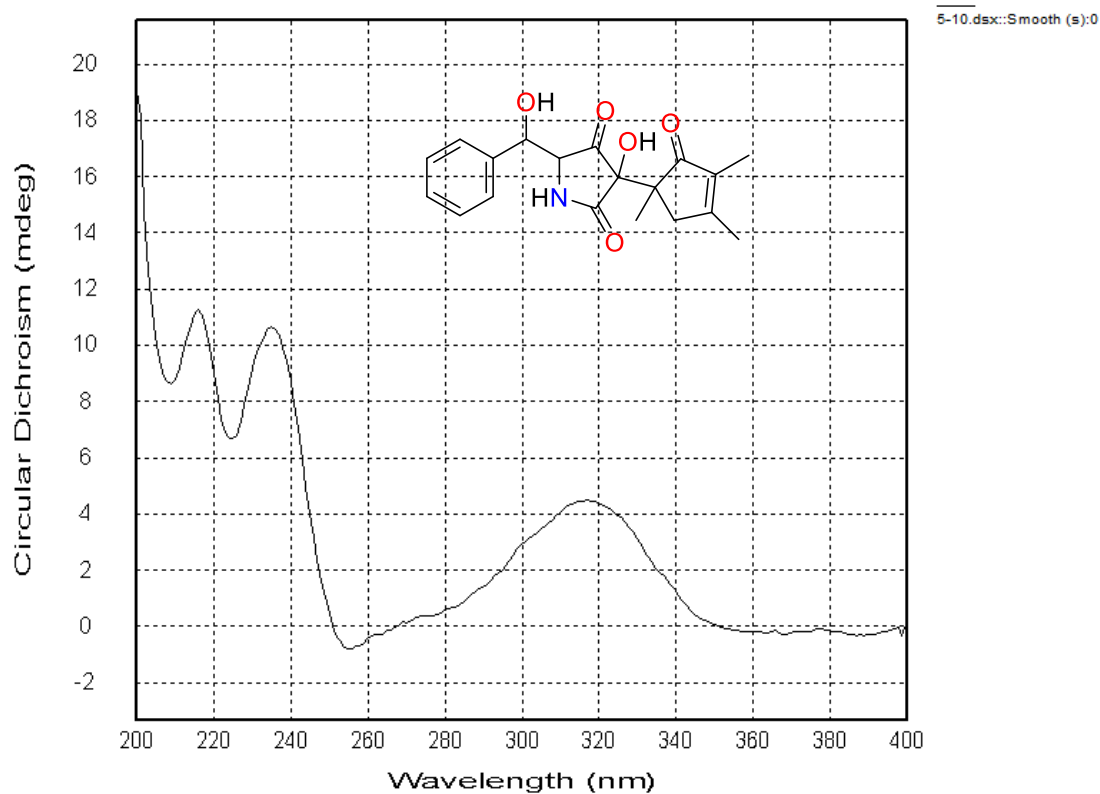


Figure S78. CD spectrum of **6**

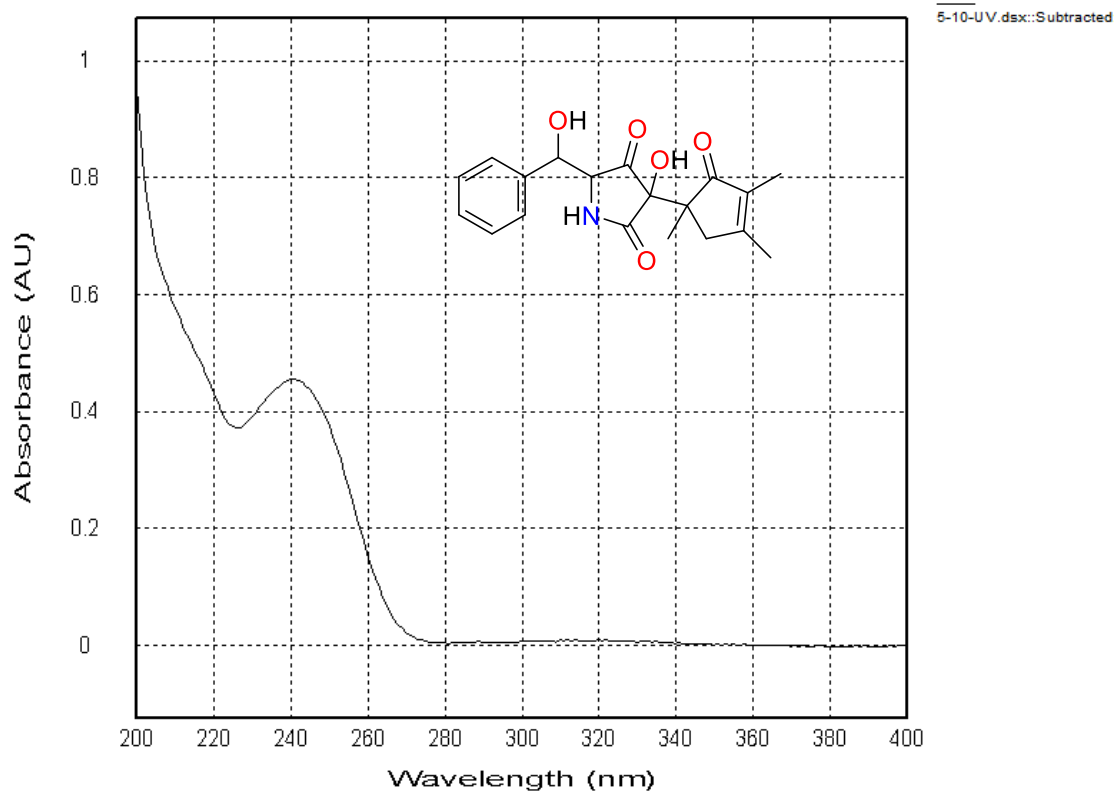


Figure S79. UV spectrum of **6**

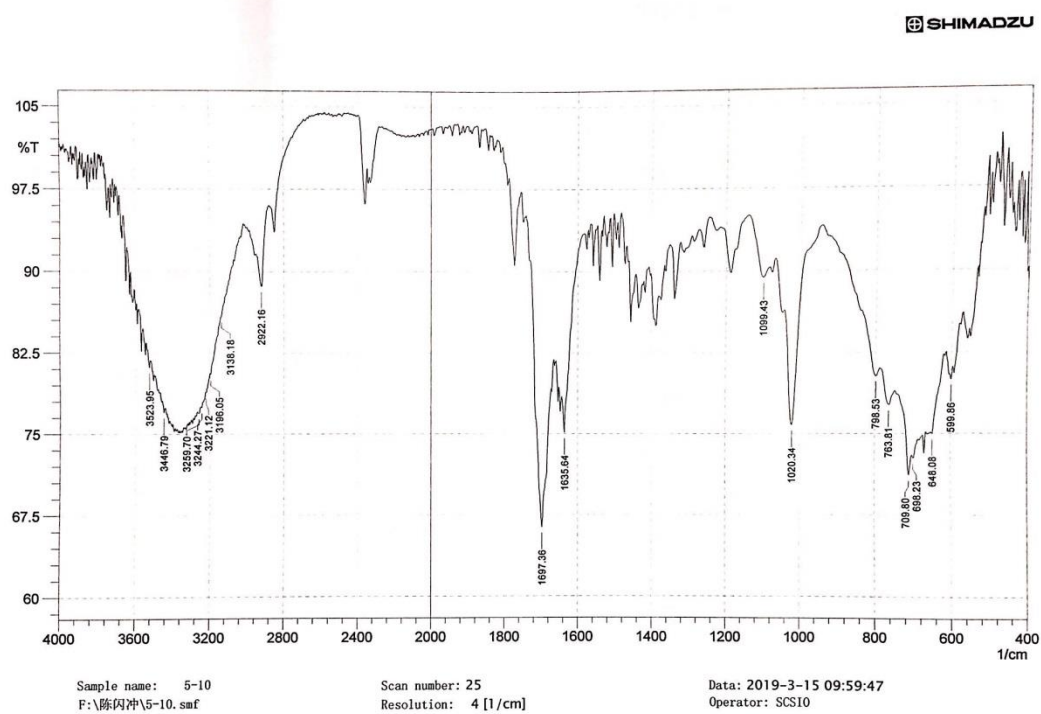


Figure S80. IR spectrum of **6**

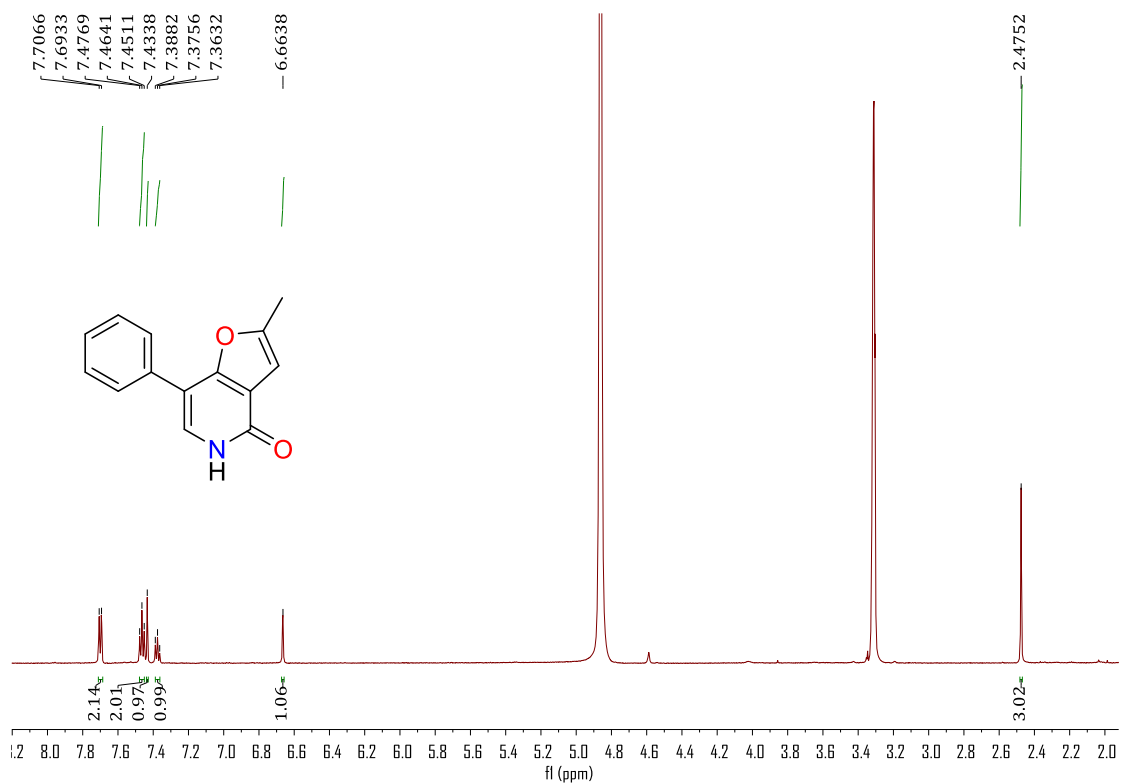


Figure S81. ¹H NMR spectrum (600 MHz, CD₃OD) of **7**

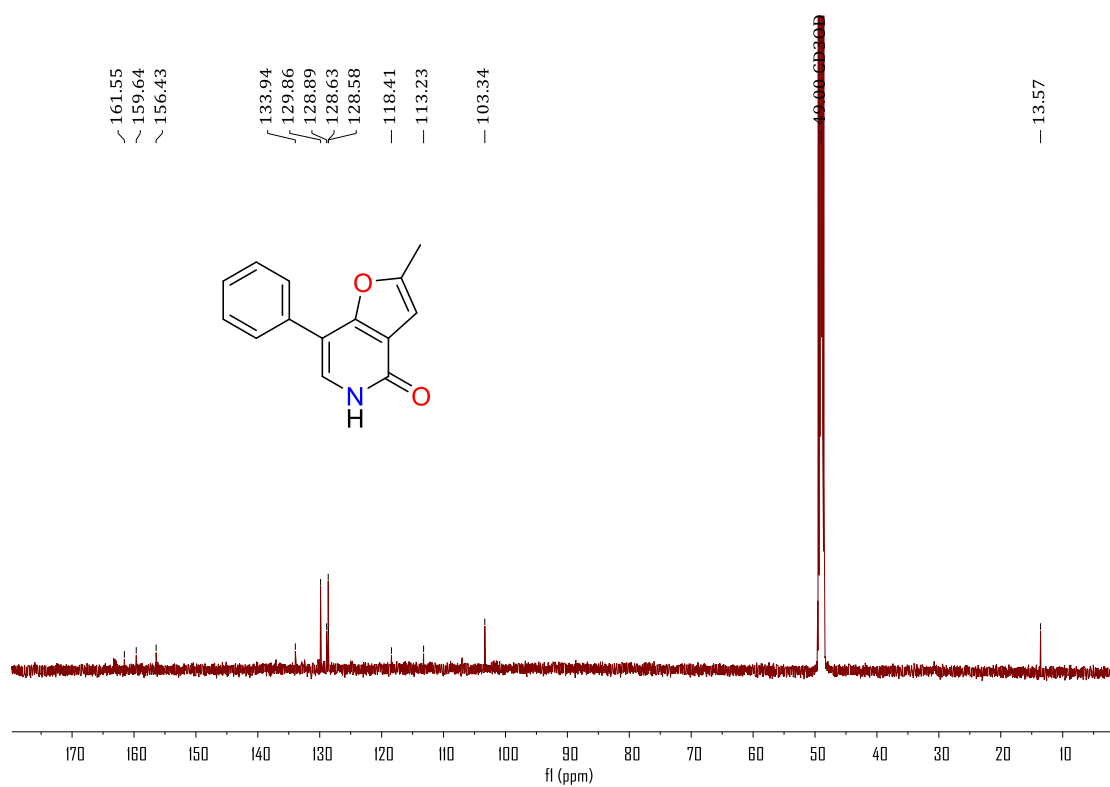


Figure S82. ¹³C NMR spectrum (150 MHz, CD₃OD) of **7**

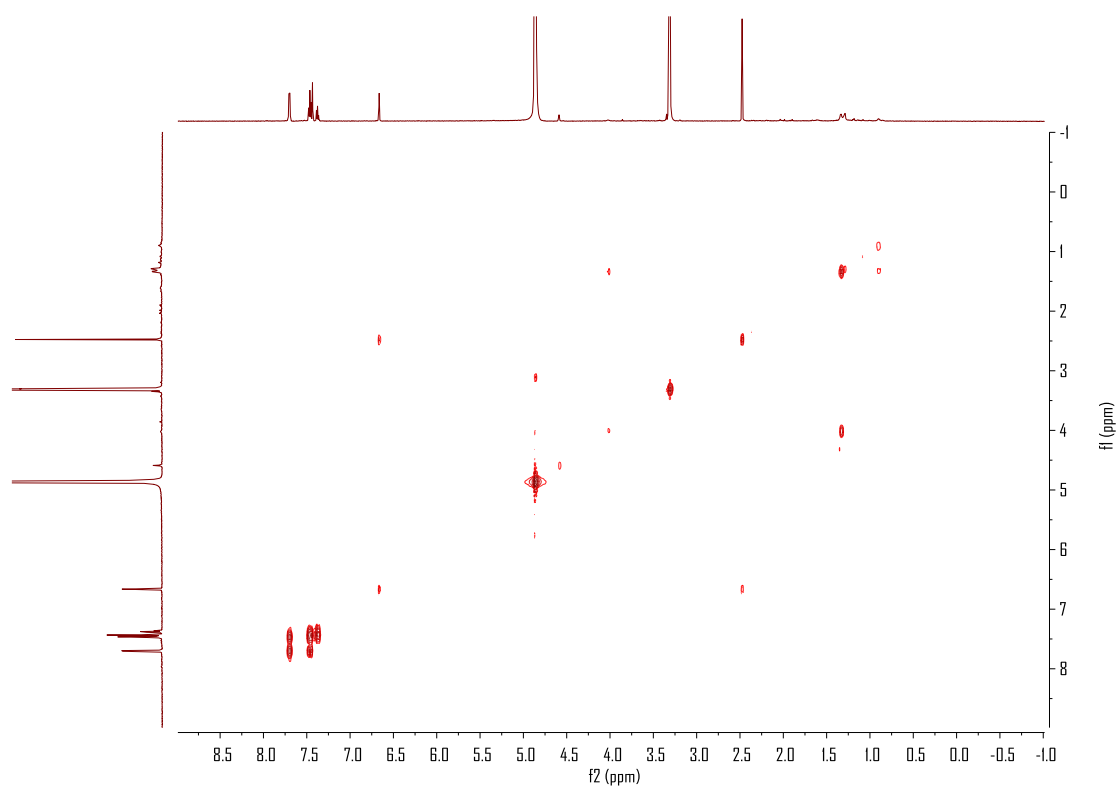


Figure S83. ^1H - ^1H COSY spectrum of **7** in CD_3OD

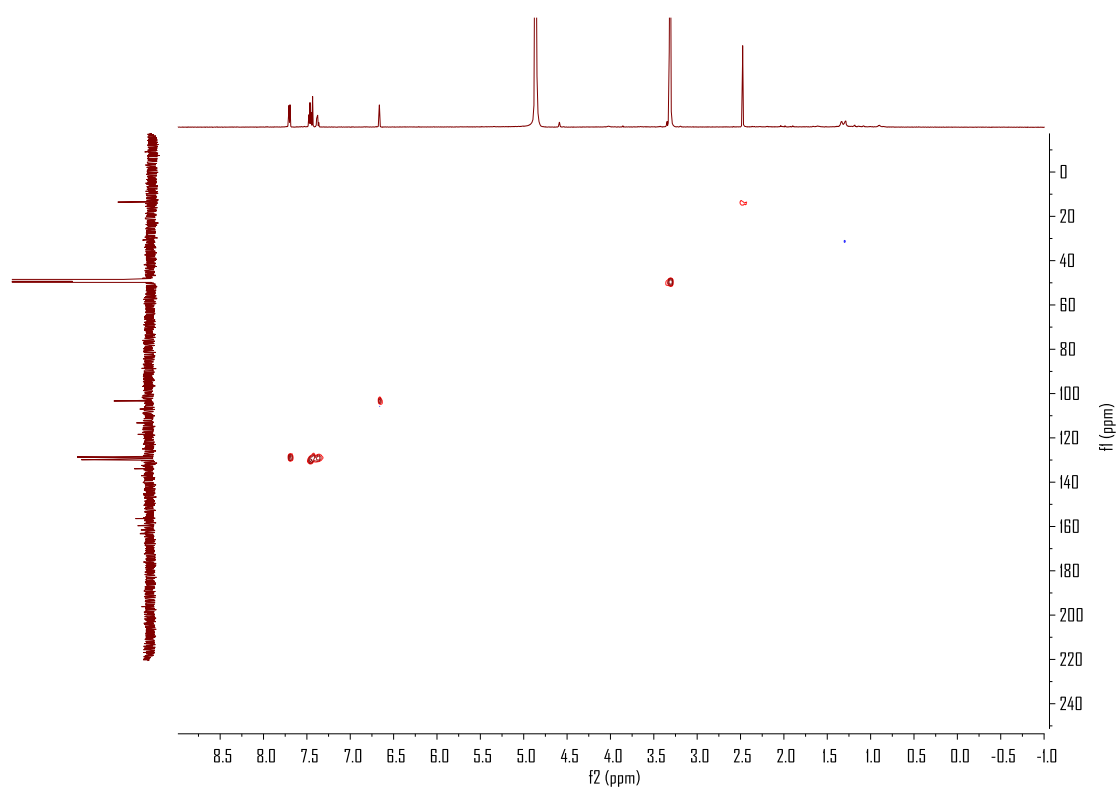


Figure S84. HSQC spectrum of **7** in CD_3OD

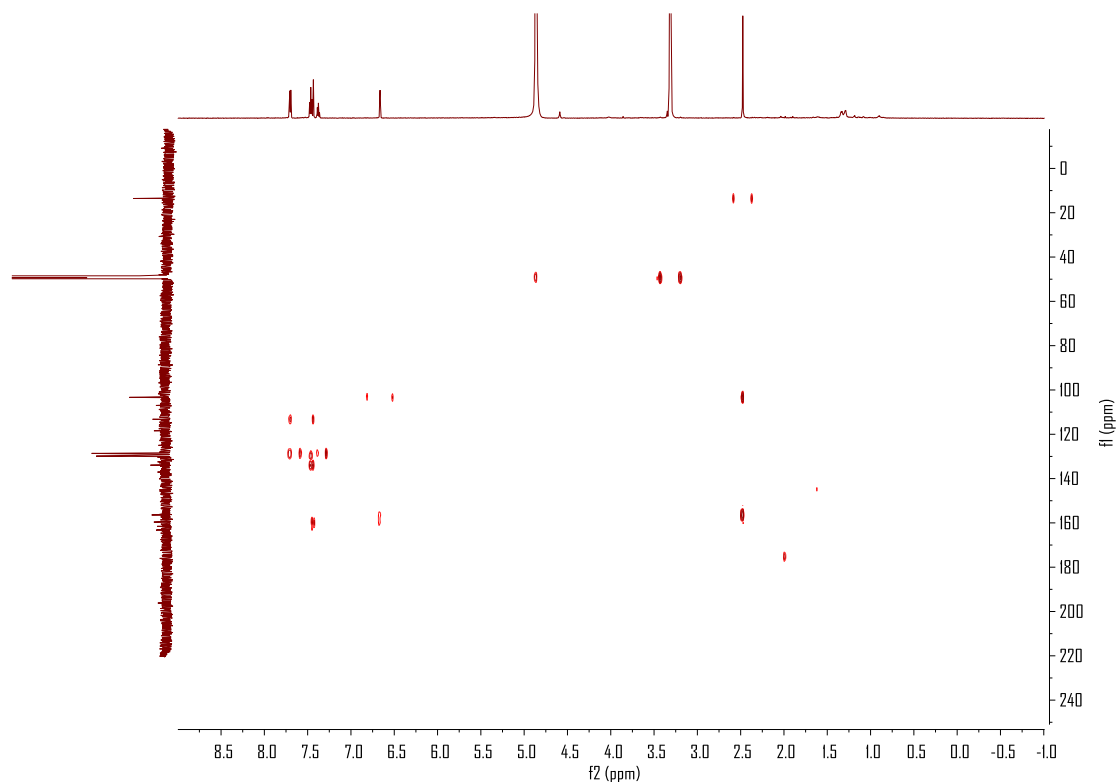
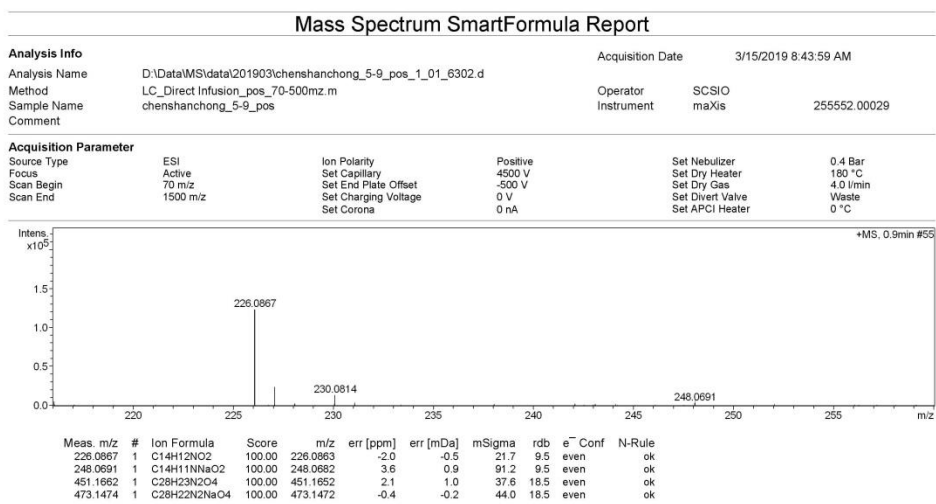


Figure S85. HMBC spectrum of **7** in CD₃OD



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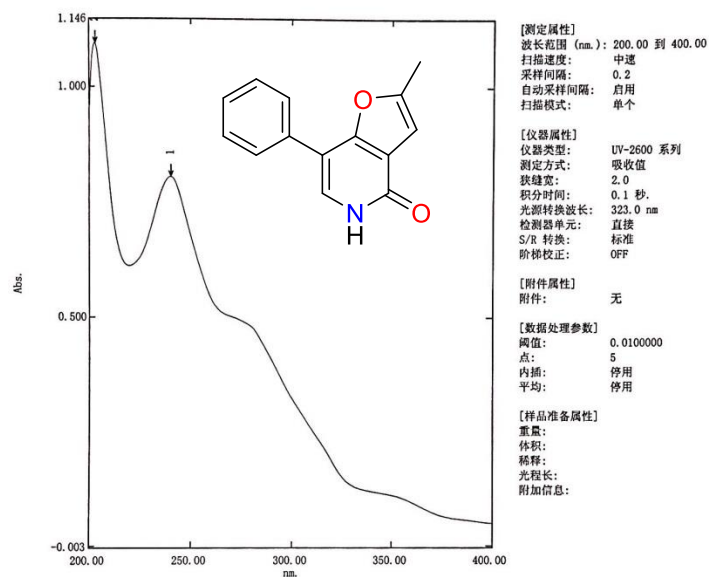
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Figure S86. HRESIMS spectrum of **7**

光谱峰值检测报告

2019-03-15 10:37:14

数据集: FS441 5-9 - RawData



No.	P/V	波长 (nm)	吸收值	描述
1	①	240.20	0.808	
2	①	203.00	1.093	

Figure S87. UV spectrum of 7

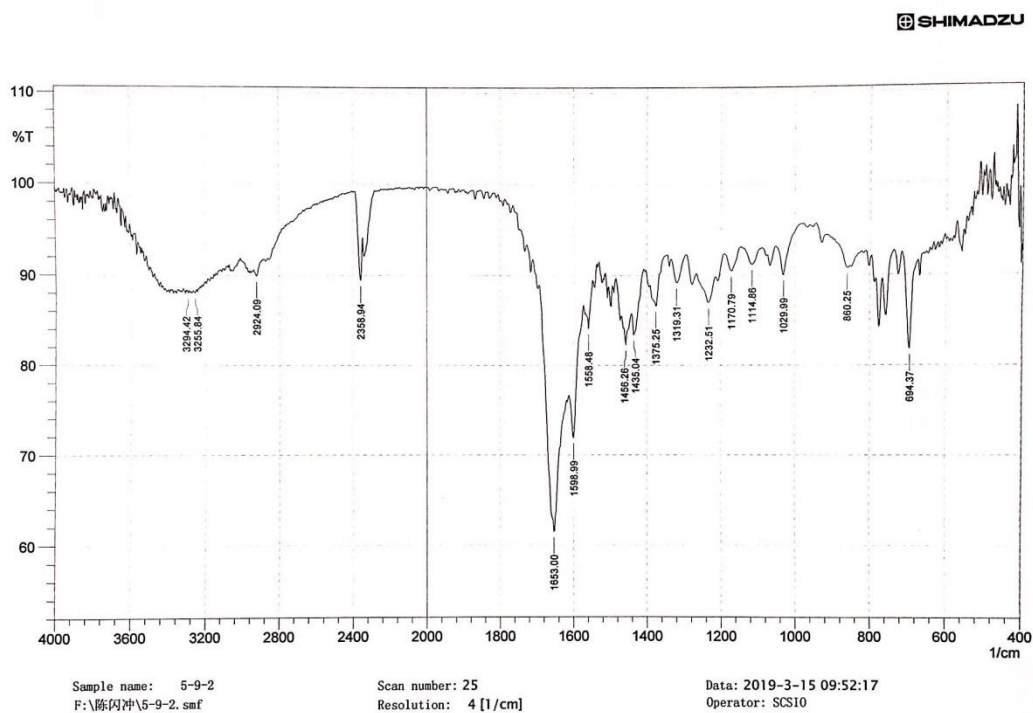


Figure S88. IR spectrum of 7

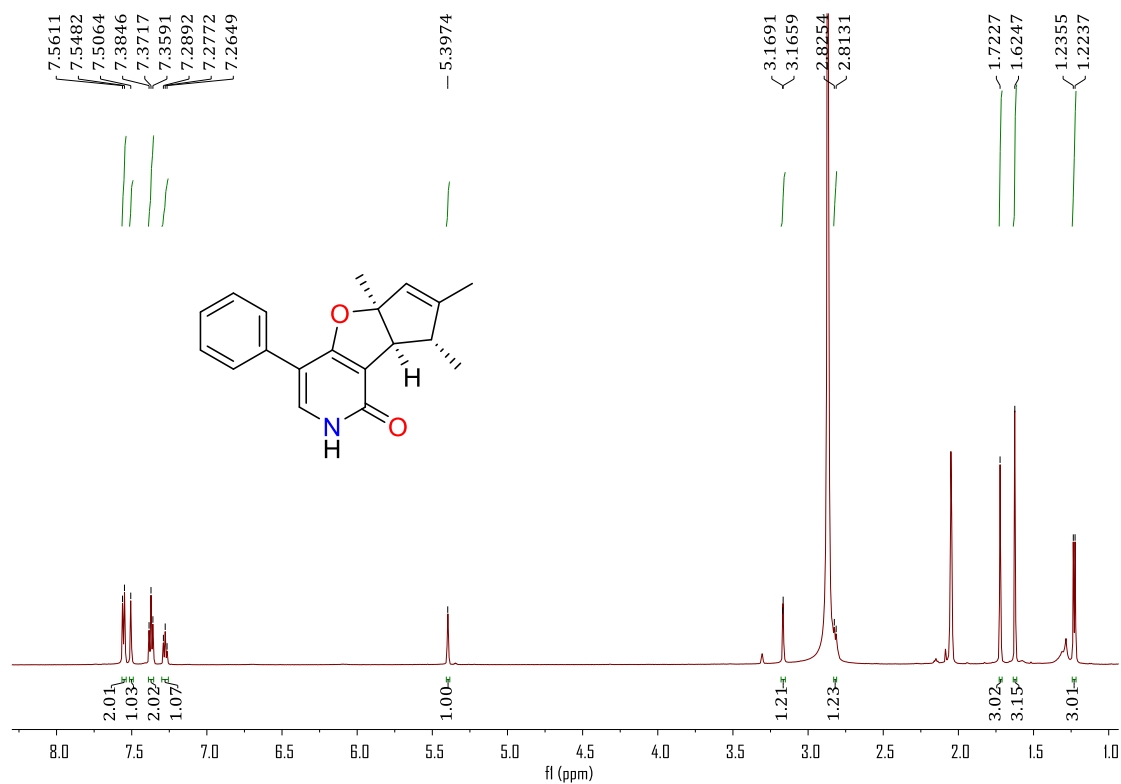


Figure S89. ¹H NMR spectrum (600 MHz, CD₃OD) of **8a**

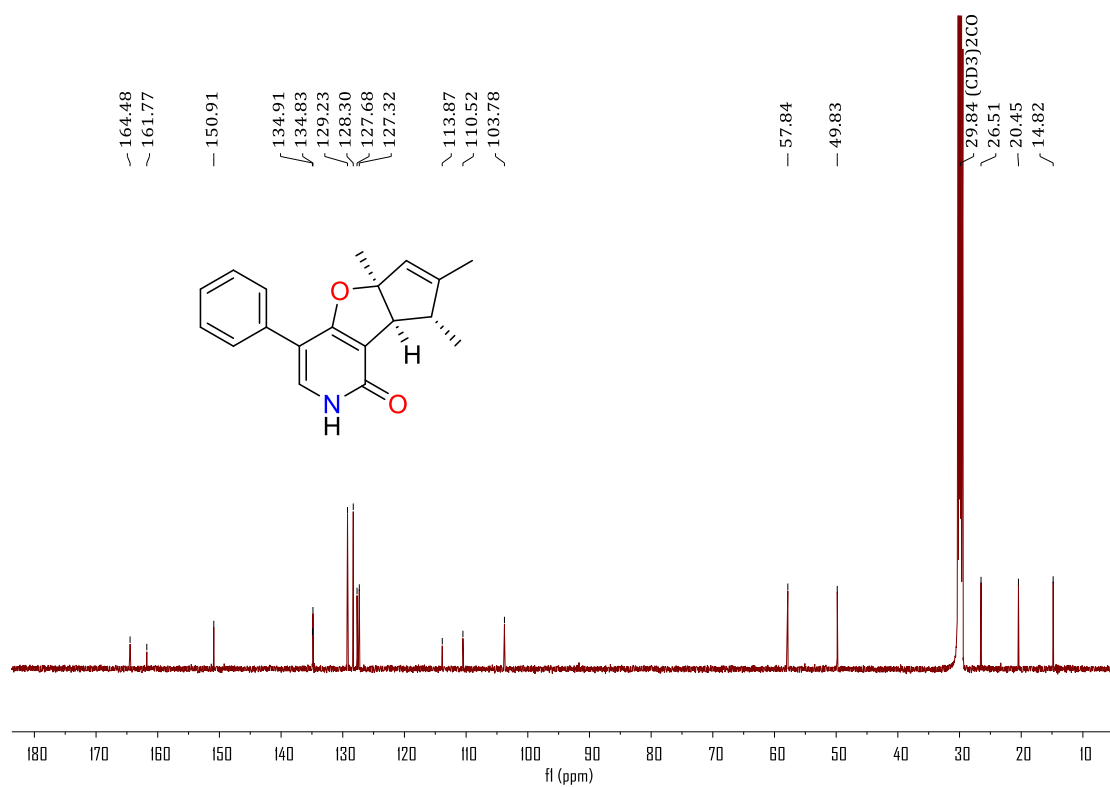


Figure S90. ¹³C NMR spectrum (150 MHz, CD₃OD) of **8a**

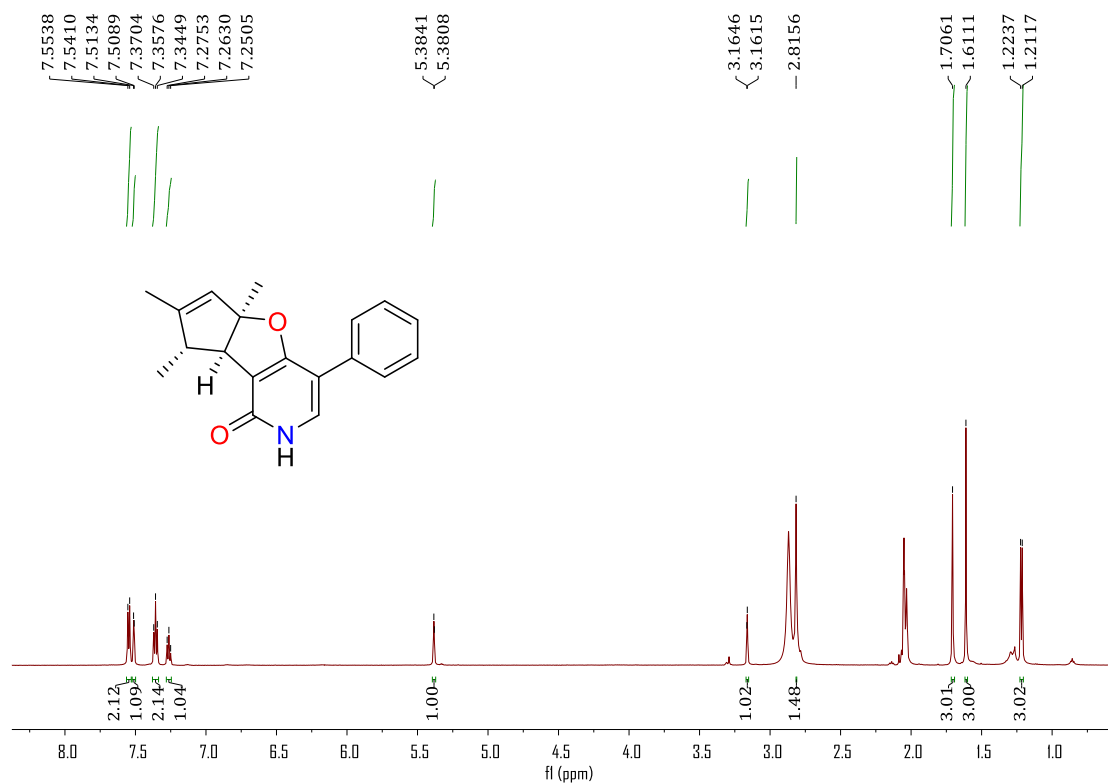


Figure S91. ¹H NMR spectrum (600 MHz, CD₃OD) of **8b**

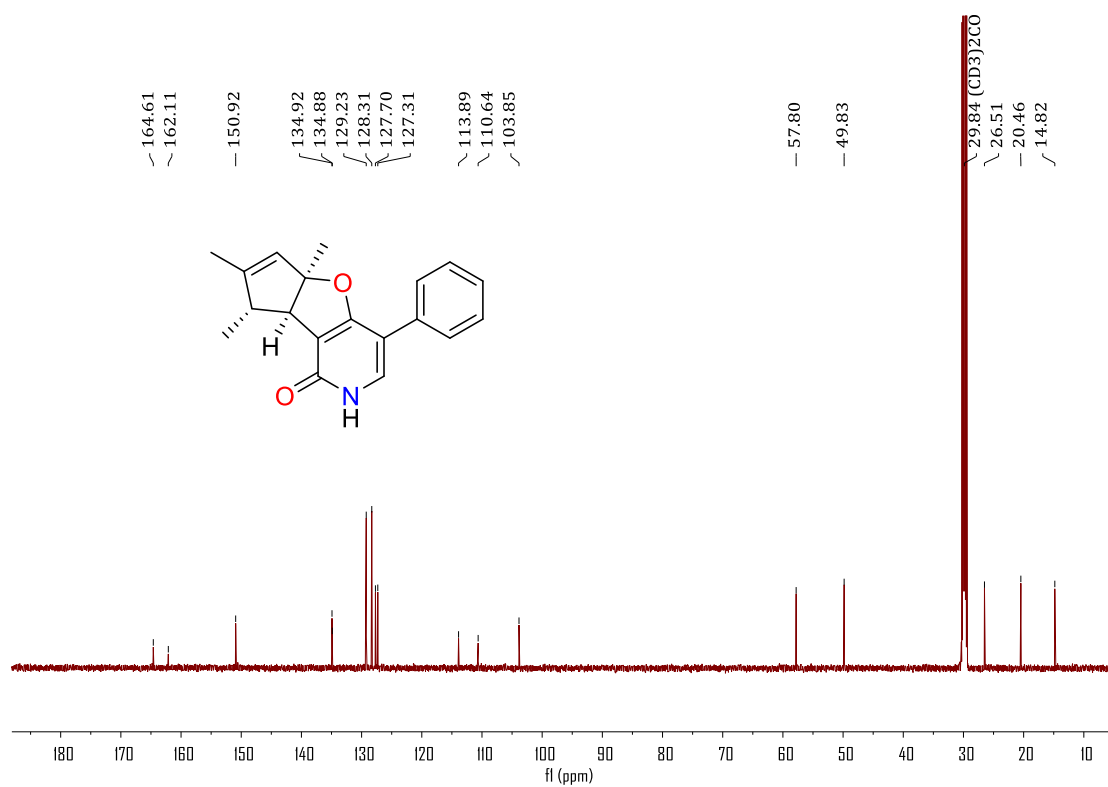


Figure S92. ¹³C NMR spectrum (150 MHz, CD₃OD) of **8b**

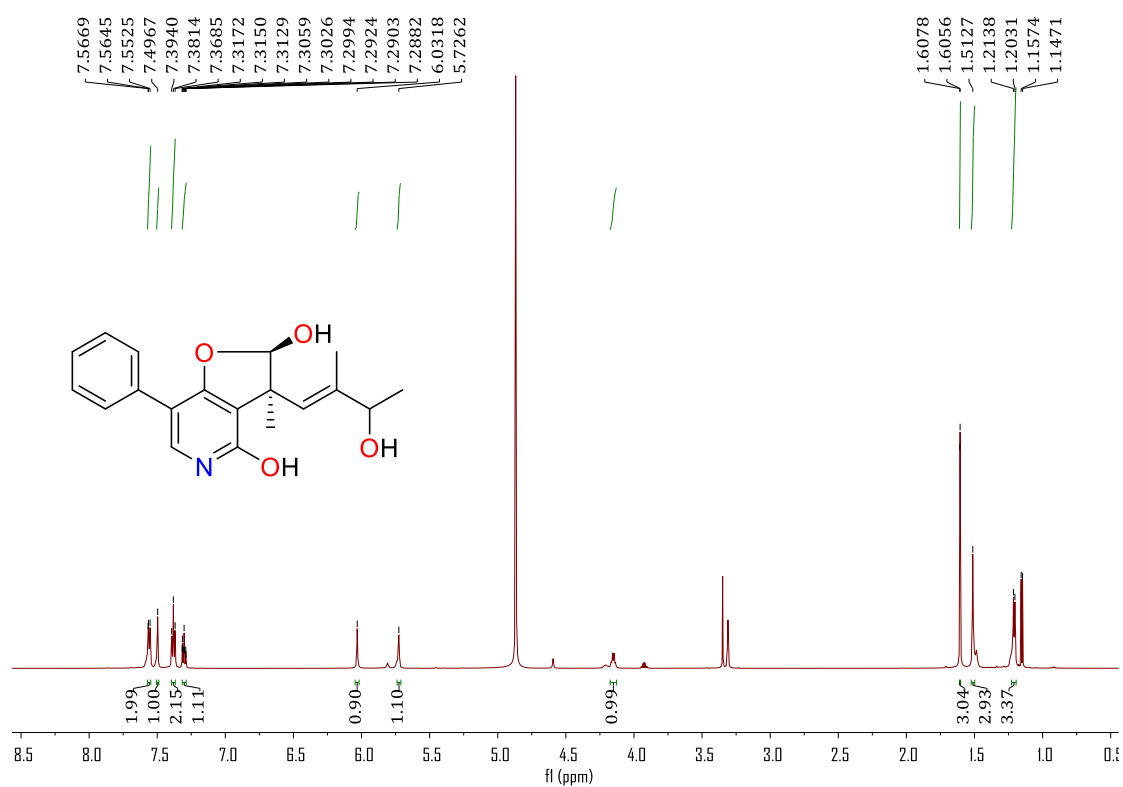


Figure S93. ¹H NMR spectrum (600 MHz, CD₃OD) of **9**

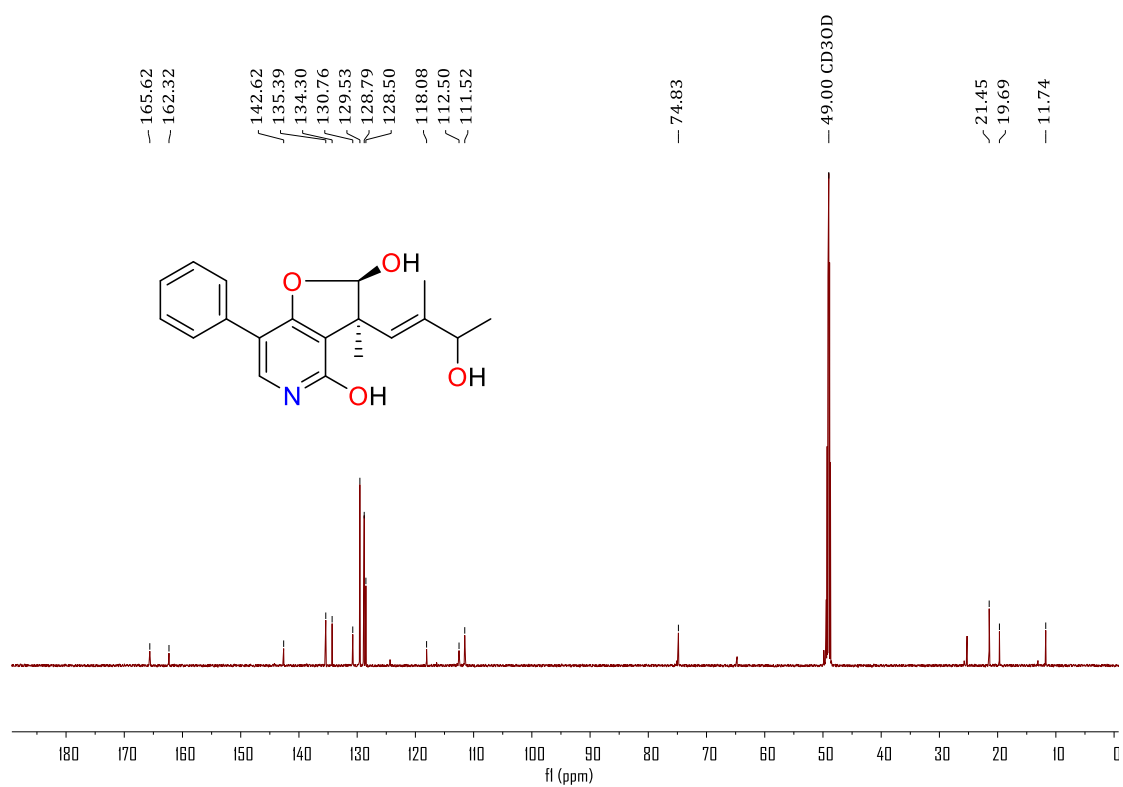


Figure S94. ¹³C NMR spectrum (150 MHz, CD₃OD) of **9**