

**New diterpenoid quinones derived from *Salvia miltiorrhiza* and
their cytotoxic and neuroprotective activities**

Zhao-Kun Yin, Zi-Ming Feng, Jian-Shuang Jiang, Xu Zhang, Pei-Cheng

Zhang*, and Ya-Nan Yang*

*State Key Laboratory of Bioactive Substance and Function of Natural Medicines,
Peking Union Medical College and Institute of Materia Medica, Chinese Academy of
Medical Sciences, Beijing 100050, China*

Corresponding author. Tel.: +86 10 63165231; fax: +86 10 63017757.

E-mail address: pczhang@imm.ac.cn (Pei-cheng Zhang) yyn@imm.ac.cn (Ya-nan Yang);

Supporting Information

Table of Contents

Table S1. The ^1H NMR spectroscopic data (δ) measured in $\text{DMSO-}d_6$ at 500 MHz for compounds 5–7	1
ECD calculation details	1
Figure S1. Most stable conformers of 1 (the relative proportions are in parentheses).....	1
Figure S2. Most stable conformers of 2 (the relative proportions are in parentheses).....	2
Figure S3. Most stable conformers of 3 (the relative proportions are in parentheses).....	3
Figure S4. Most stable conformers of 4A (the relative proportions are in parentheses).....	4
Figure S5. Most stable conformers of 5 (the relative proportions are in parentheses).....	4
Figure S6. Most stable conformers of 6 (the relative proportions are in parentheses).....	5
Figure S7. Most stable conformers of 7 (the relative proportions are in parentheses).....	6
Figure S8. Experimental and calculated ECD spectra of 2	7
Figure S9. Experimental and calculated ECD spectra of 3	7
Figure S10. Experimental and calculated ECD spectra of 4A/4B	8
Figure S11. Experimental and calculated ECD spectra of 5	8
Figure S12. Experimental and calculated ECD spectra of 6	9
Figure S13. Experimental and calculated ECD spectra of 7	9
Figure S14. ^1H NMR spectrum of compound 1 in $\text{DMSO-}d_6$ (500 MHz).....	10
Figure S15. ^{13}C NMR spectrum of compound 1 in $\text{DMSO-}d_6$ (125 MHz).....	10
Figure S16. HSQC spectrum of compound 1 in $\text{DMSO-}d_6$ (500 MHz).....	11
Figure S17. HMBC spectrum of compound 1 in $\text{DMSO-}d_6$ (500 MHz).....	11
Figure S18. ROESY spectrum of compound 1 in $\text{DMSO-}d_6$ (500 MHz).....	12
Figure S19. $^1\text{H-}^1\text{H}$ COSY spectrum of compound 1 in $\text{DMSO-}d_6$ (400 MHz).....	12
Figure S20. UV spectrum of compound 1	13
Figure S21. ECD spectrum of compound 1	13
Figure S22. IR spectrum of compound 1	14
Figure S23. HR-ESI-MS spectrum of compound 1	14

Figure S24. The crystal data and structure refinement of compound 2	15
Figure S25. ¹ H NMR spectrum of compound 2 in CDCl ₃ (500 MHz)	16
Figure S26. ¹³ C NMR spectrum of compound 2 in CDCl ₃ (125 MHz)	16
Figure S27. HSQC spectrum of compound 2 in CDCl ₃ (500 MHz)	17
Figure S28. HMBC spectrum of compound 2 in CDCl ₃ (500 MHz)	17
Figure S29. ¹ H- ¹ H COSY spectrum of compound 2 in CDCl ₃ (400 MHz)	18
Figure S30. ROESY spectrum of compound 2 in CDCl ₃ (400 MHz)	18
Figure S31. UV spectrum of compound 2	19
Figure S32. ECD spectrum of compound 2	19
Figure S33. IR spectrum of compound 2	20
Figure S34. HR-ESI-MS spectrum of compound 2	20
Figure S35. ¹ H NMR spectrum of compound 3 in CDCl ₃ (500 MHz)	21
Figure S36. ¹³ C NMR spectrum of compound 3 in CDCl ₃ (125 MHz)	21
Figure S37. HSQC spectrum of compound 3 in CDCl ₃ (500 MHz)	22
Figure S38. HMBC spectrum of compound 3 in CDCl ₃ (500 MHz)	22
Figure S39. ¹ H- ¹ H COSY spectrum of compound 3 in CDCl ₃ (400 MHz)	23
Figure S40. ROESY spectrum of compound 3 in CDCl ₃ (400 MHz)	23
Figure S41. UV spectrum of compound 3	24
Figure S42. ECD spectrum of compound 3	24
Figure S43. IR spectrum of compound 3	25
Figure S44. HR-ESI-MS spectrum of compound 3	25
Figure S45. ¹ H NMR spectrum of compound 4A/4B in CDCl ₃ (500 MHz)	26
Figure S46. ¹³ C NMR spectrum of compound 4A/4B in CDCl ₃ (125 MHz)	26
Figure S47. HSQC spectrum of compound 4A/4B in CDCl ₃ (500 MHz)	27
Figure S48. HMBC spectrum of compound 4A/4B in CDCl ₃ (500 MHz)	27
Figure S49. ¹ H- ¹ H COSY spectrum of compound 4A/4B in CDCl ₃ (400 MHz)	28
Figure S50. ROESY spectrum of compound 4A/4B in CDCl ₃ (400 MHz)	28
Figure S51. UV spectrum of compound 4A/4B	29
Figure S52. ECD spectrum of compound 4A	29
Figure S53. ECD spectrum of compound 4B	30
Figure S54. IR spectrum of compound 4A/4B	30
Figure S55. HR-ESI-MS spectrum of compound 4A/4B	31

Figure S56. The chiral HPLC chromatogram of 4A/4B	31
Figure S57. ^1H NMR spectrum of compound 5 in CDCl_3 (500 MHz).....	32
Figure S58. ^{13}C NMR spectrum of compound 5 in CDCl_3 (150 MHz).....	32
Figure S59. HSQC spectrum of compound 5 in CDCl_3 (500 MHz).....	33
Figure S60. HMBC spectrum of compound 5 in CDCl_3 (500 MHz).....	33
Figure S61. ^1H NMR spectrum of compound 5 in $\text{DMSO-}d_6$ (500 MHz)	34
Figure S62. ROESY spectrum of compound 5 in $\text{DMSO-}d_6$ (500 MHz).....	34
Figure S63. 1D NOESY spectrum of compound 5 in $\text{DMSO-}d_6$ (500 MHz).....	35
Figure S64. UV spectrum of compound 5	35
Figure S65. ECD spectrum of compound 5	36
Figure S66. IR spectrum of compound 5	36
Figure S67. HR-ESI-MS spectrum of compound 5	37
Figure S68. ^1H NMR spectrum of compound 6 in CDCl_3 (500 MHz).....	37
Figure S69. ^{13}C NMR spectrum of compound 6 in CDCl_3 (150 MHz).....	38
Figure S70. HSQC spectrum of compound 6 in CDCl_3 (500 MHz).....	38
Figure S71. HMBC spectrum of compound 6 in CDCl_3 (500 MHz).....	39
Figure S72. ^1H NMR spectrum of compound 6 in $\text{DMSO-}d_6$ (500 MHz)	39
Figure S73. ROESY spectrum of compound 6 in $\text{DMSO-}d_6$ (500 MHz).....	40
Figure S74. 1D NOESY spectrum of compound 6 in $\text{DMSO-}d_6$ (500 MHz).....	40
Figure S75. UV spectrum of compound 6	41
Figure S76. ECD spectrum of compound 6	41
Figure S77. IR spectrum of compound 6	42
Figure S78. HR-ESI-MS spectrum of compound 6	42
Figure S79. ^1H NMR spectrum of compound 7 in CDCl_3 (500 MHz).....	43
Figure S80. ^{13}C NMR spectrum of compound 7 in CDCl_3 (150 MHz).....	43
Figure S81. HSQC spectrum of compound 7 in CDCl_3 (500 MHz).....	44
Figure S82. HMBC spectrum of compound 7 in CDCl_3 (500 MHz).....	44
Figure S83. ^1H NMR spectrum of compound 7 in $\text{DMSO-}d_6$ (500 MHz)	45
Figure S84. ROESY spectrum of compound 7 in $\text{DMSO-}d_6$ (500 MHz).....	45
Figure S85. 1D NOESY spectrum of compound 7 in $\text{DMSO-}d_6$ (500 MHz).....	46
Figure S86. UV spectrum of compound 7	46
Figure S87. ECD spectrum of compound 7	47

Figure S88. IR spectrum of compound **7**47

Figure S89. HR-ESI-MS spectrum of compound **7**48

Table S1. The ^1H NMR spectroscopic data (δ) measured in $\text{DMSO-}d_6$ at 500 MHz for compounds **5–7**

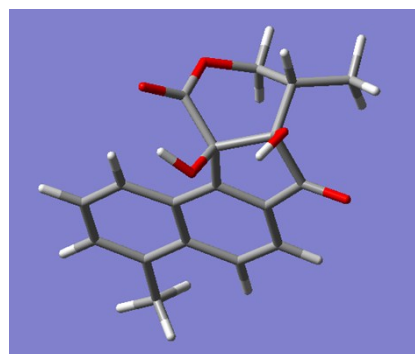
NO.	5	6	7
	δ_{H}	δ_{H}	δ_{H}
1	8.66, d (8.5)	8.69, d (8.5)	3.17, t (6.0)
2	7.96, dd (7.0, 8.5)	7.69, q (7.0, 8.5)	1.82, m
3	7.58, d (7.0)	7.57, d (7.0)	1.68, m
6	8.52, d (8.5)	8.48, d (8.5)	7.78, d (8.0)
7	7.69, d (8.5)	7.87, d (8.5)	7.47, d (8.0)
13	4.40, t (8.0)	4.42, t (6.5, 8.0)	4.31, t (7.5)
	3.85, t (8.0, 9.5)	3.95, dd (2.0, 8.0)	3.85, d (8.0)
14	2.95, m	2.94, m	2.87, m
15	3.59, d (11.0)	4.11, d (7.5)	3.89, d (8.5)
16	1.32, d (6.5)	1.34, d (7.0)	1.26, overlap
18	2.75, s	2.73, s	
19			1.28, overlap
-COOH	12.59, s	12.67, s	12.59, s

ECD calculation details

Conformation analysis of compounds **1–7** were completed with Spartan 10 software using the MMFF94 molecular mechanics force field. The optimized conformations, which the Boltzmann distributions over 1%, were further used for ECD calculation. The lowest-energy conformers with the Gaussian 5.0 program was optimized at the B3LYP/6-31+G (d, p) level in MeOH. The TDDFT methodology at the B3LYP/6-311+G (d, p) level was used for energy, oscillator strengths, and rotational strengths of the lowest-energy conformers calculation. ECD spectra of the conformers were simulated using the Gaussian function with a half-band width of 0.28 eV, and the final ECD spectrum of each compound was simulated based on Boltzmann weighting of each conformer. All quantum computations were performed on an IBM cluster machine located at the High Performance Computing Center of Peking Union Medical College.

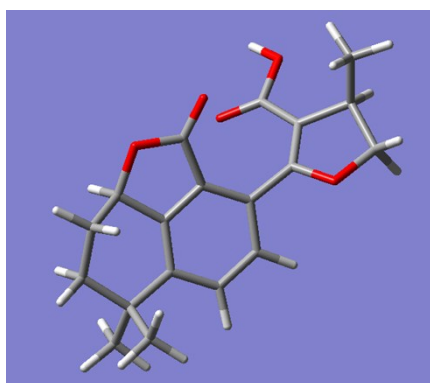


12R, 16S)-**1a-1** (64.1%)

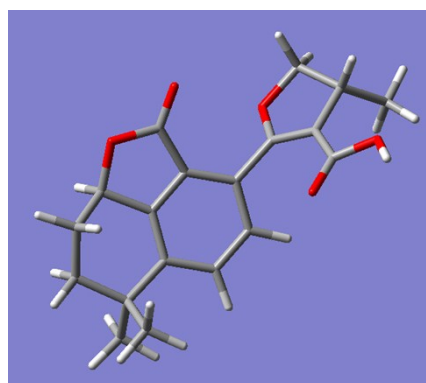


(*11R, 12R, 16S*)-**1a-2** (35.8%)

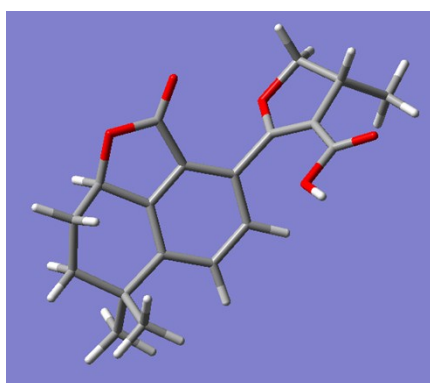
Figure S1. Most stable conformers of **1** (the relative proportions are in parentheses)



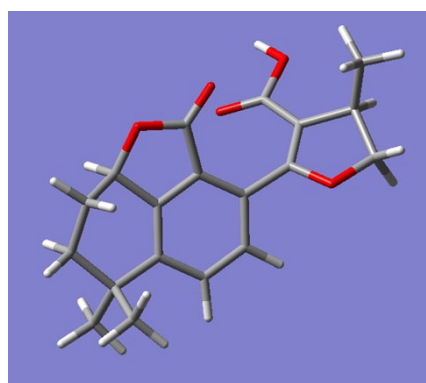
(1*R*, 16*R*)-2-1 (63.3%)



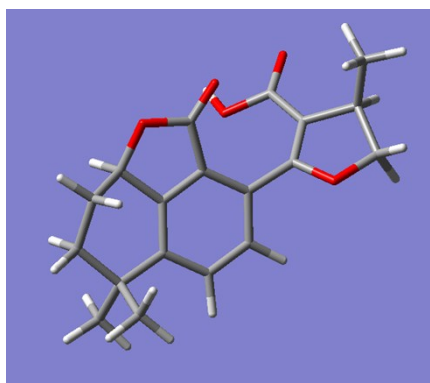
(1*R*, 16*R*)-2-2 (14.0%)



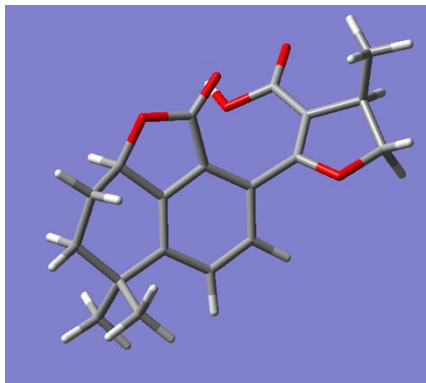
(1*R*, 16*R*)-2-3 (12.4%)



(1*R*, 16*R*)-2-4 (5.4%)

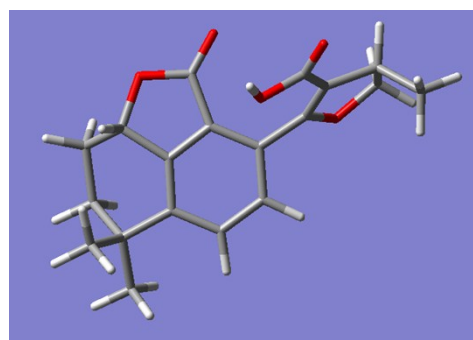
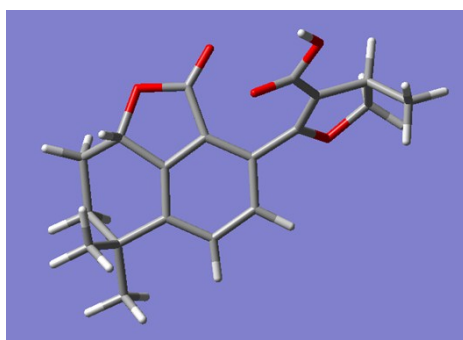


(1*R*, 16*R*)-2-5 (2.8%)

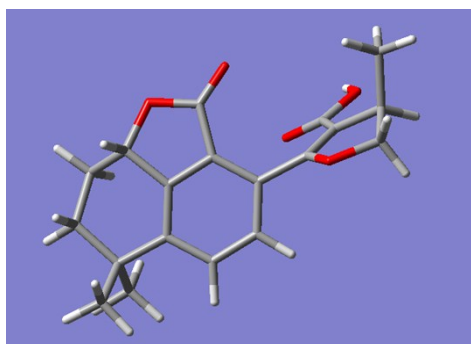


(1*R*, 16*R*)-2-6 (2.1%)

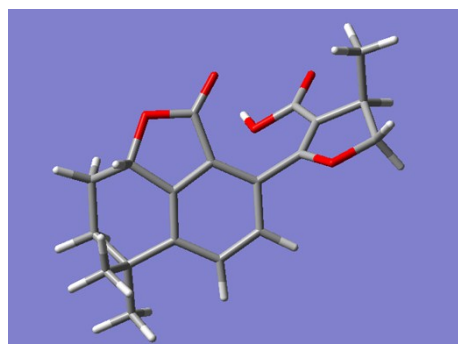
Figure S2. Most stable conformers of **2** (the relative proportions are in parentheses)



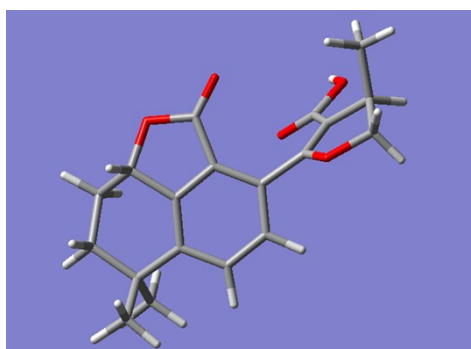
(1*S*, 16*R*)-**3a-1** (63.3%)



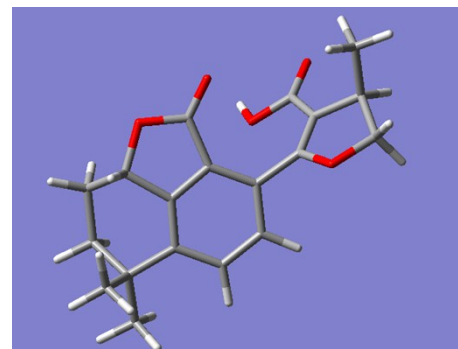
(1*S*, 16*R*)-**3a-2** (14.0%)



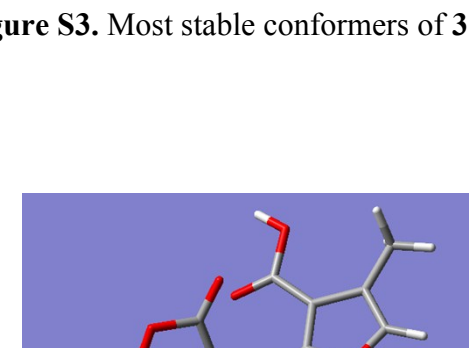
(1*S*, 16*R*)-**3a-3** (12.4%)



(1*S*, 16*R*)-**3a-4** (5.4%)



(1*S*, 16*R*)-**3a-5** (2.8%)



(1*S*, 16*R*)-**3a-6** (2.1%)

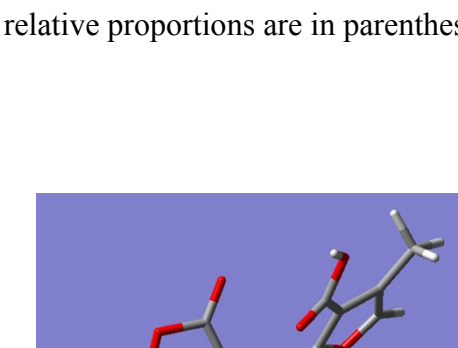
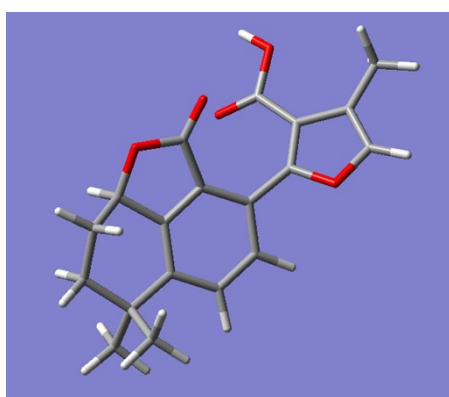
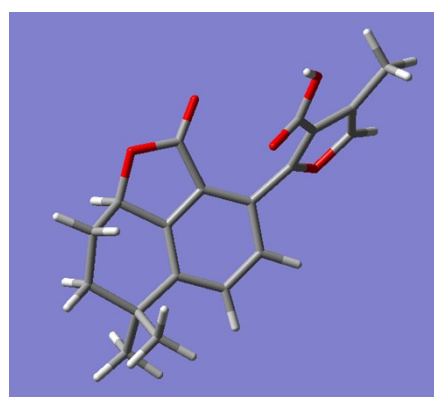


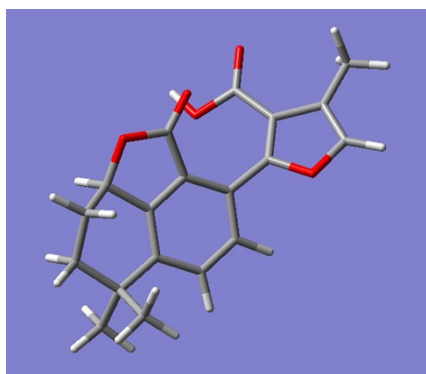
Figure S3. Most stable conformers of **3** (the relative proportions are in parentheses)



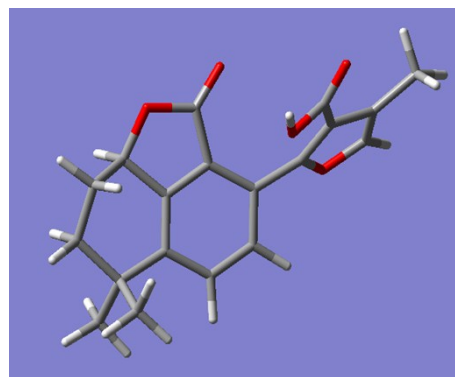
(1*S*)-**4A-1** (66.5%)



(1*S*)-**4A-2** (18.6%)

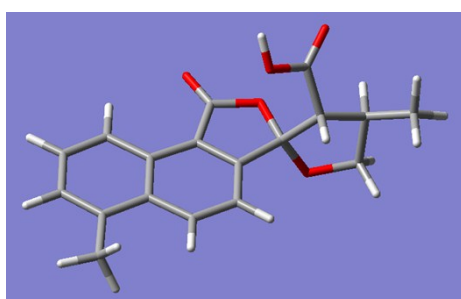


(1*S*)-4A-3 (9.1%)

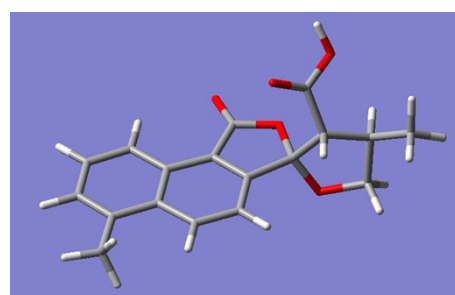


(1*S*)-4A-4 (5.8%)

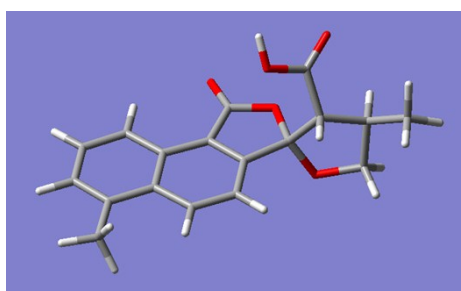
Figure S4. Most stable conformers of 4A (the relative proportions are in parentheses)



(12*S*, 14*R*, 16*R*)-5a-1 (62.6%)

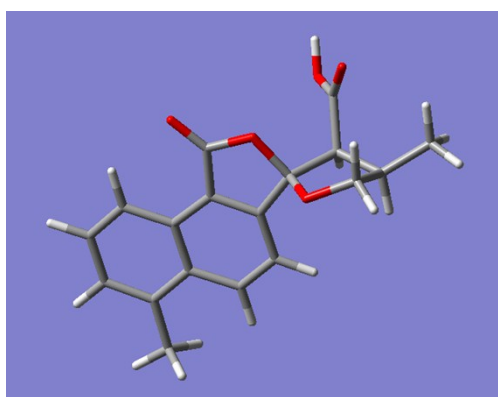


(12*S*, 14*R*, 16*R*)-5a-2 (34.3%)

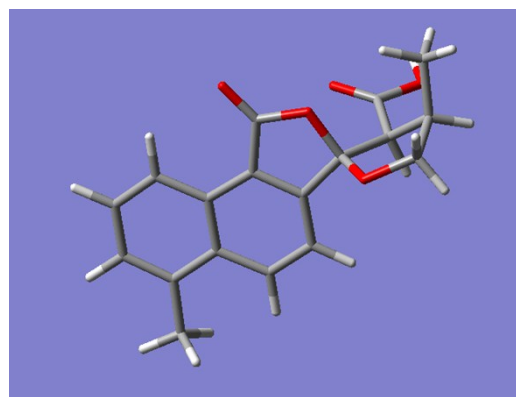


(12*S*, 14*R*, 16*R*)-5a-3 (2.9%)

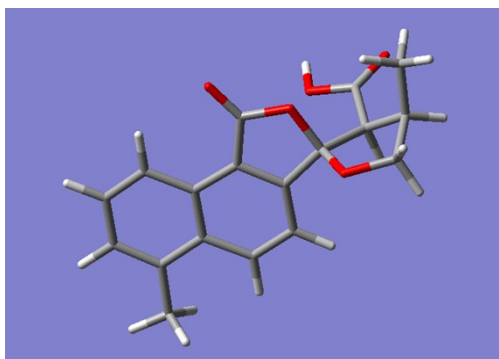
Figure S5. Most stable conformers of 5 (the relative proportions are in parentheses)



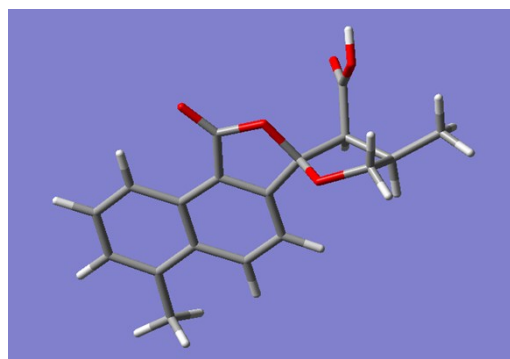
(12*R*, 14*R*, 15*S*)-6a-1 (69.0%)



(12*R*, 14*R*, 15*S*)-6a-2 (18.6%)

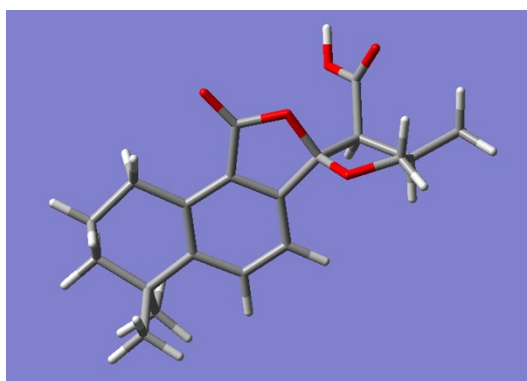


(12*R*, 14*R*, 15*S*)-**6a**-3 (9.0%)

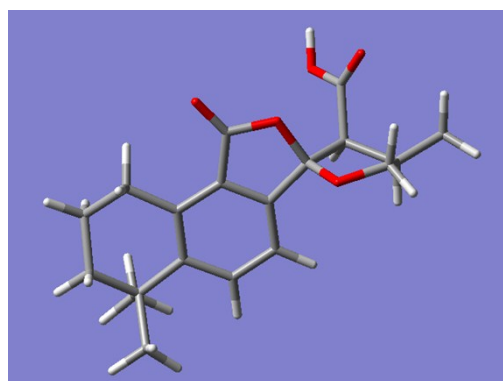


(12*R*, 14*R*, 15*S*)-**6a**-4 (3.4%)

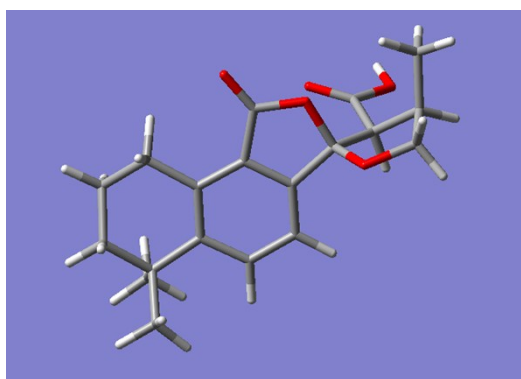
Figure S6. Most stable conformers of **6** (the relative proportions are in parentheses)



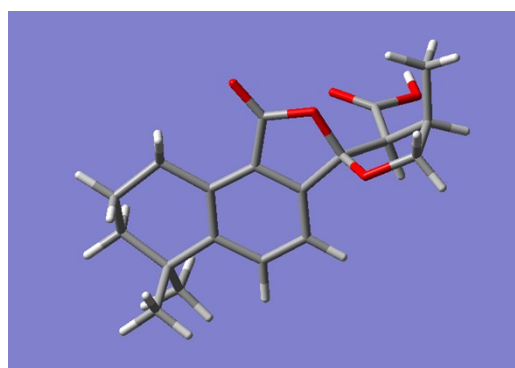
(12*R*, 14*R*, 16*S*)-**7a**-1 (36.9%)



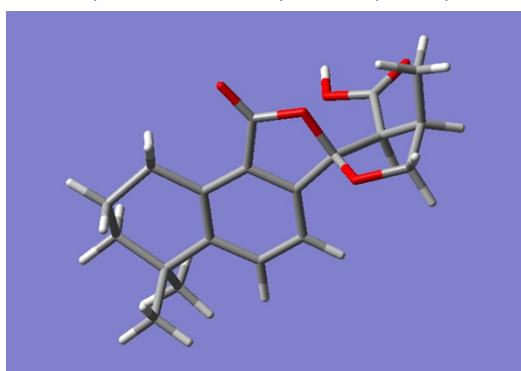
(12*R*, 14*R*, 16*S*)-**7a**-2 (34.1%)



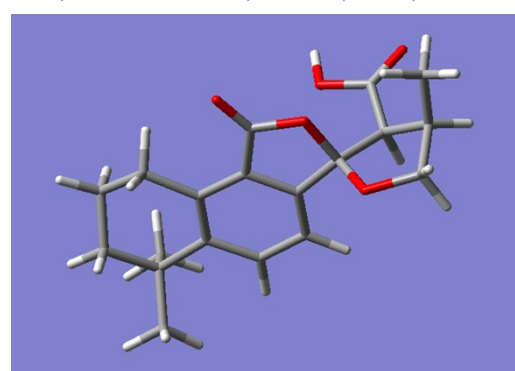
(12*R*, 14*R*, 16*S*)-**7a-3** (9.2%)



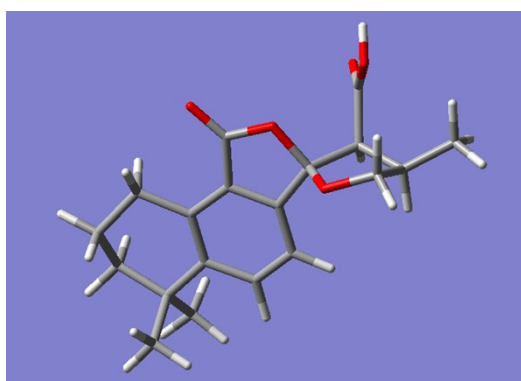
(12*R*, 14*R*, 16*S*)-**7a-4** (8.9%)



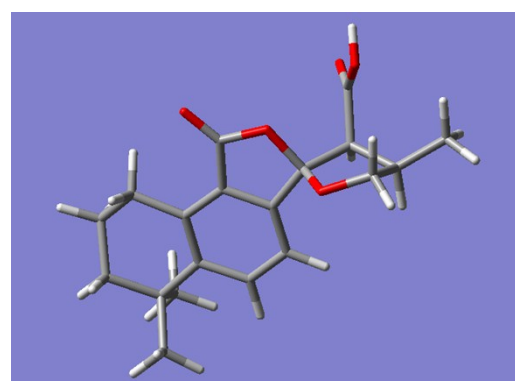
(12*R*, 14*R*, 16*S*)-**7a-5** (3.8%)



(12*R*, 14*R*, 16*S*)-**7a-6** (3.5%)



(12*R*, 14*R*, 16*S*)-**7a-7** (1.9%)



(12*R*, 14*R*, 16*S*)-**7a-8** (1.8%)

Figure S7. Most stable conformers of **7** (the relative proportions are in parentheses)

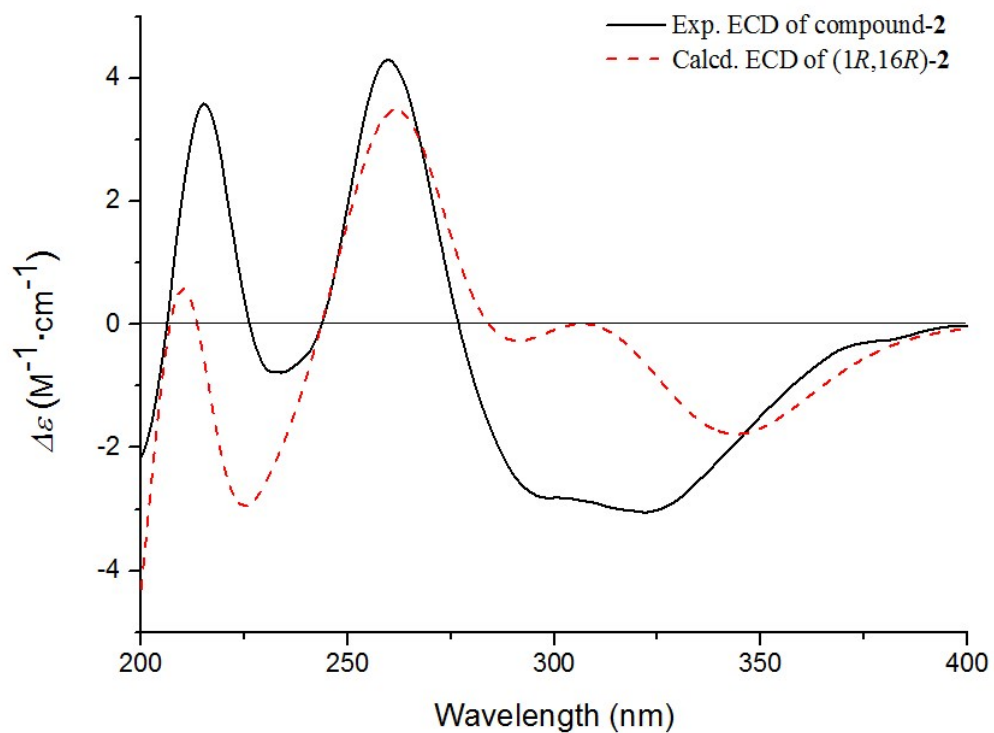


Figure S8. Experimental and calculated ECD spectra of 2.

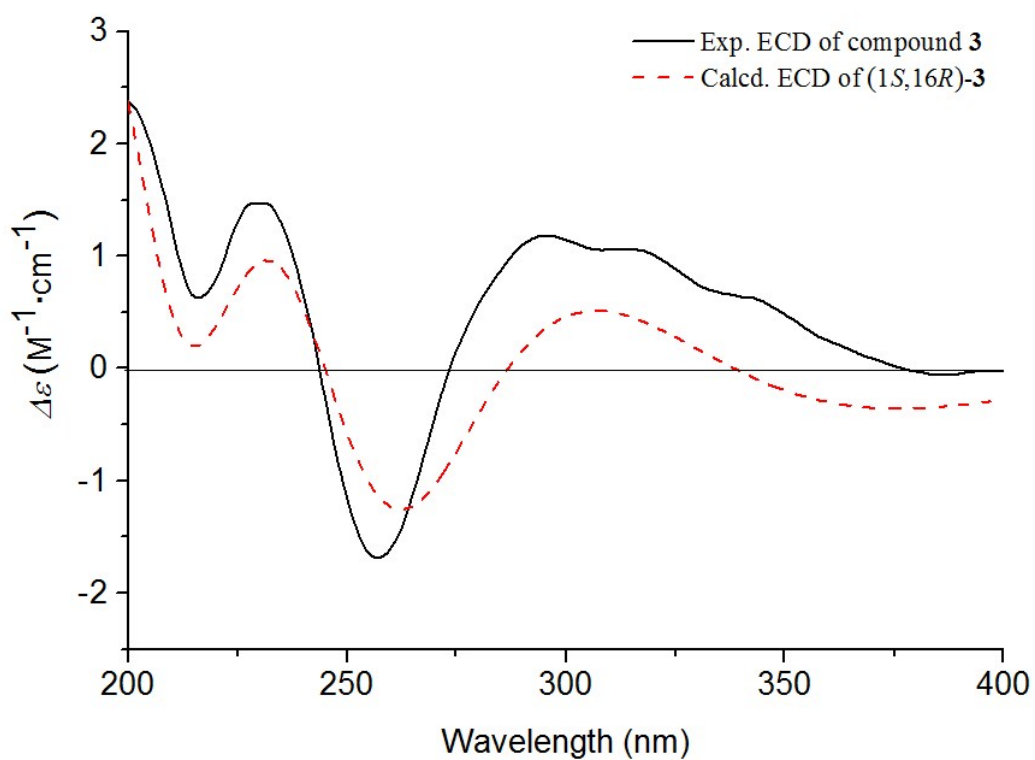


Figure S9. Experimental and calculated ECD spectra of 3.

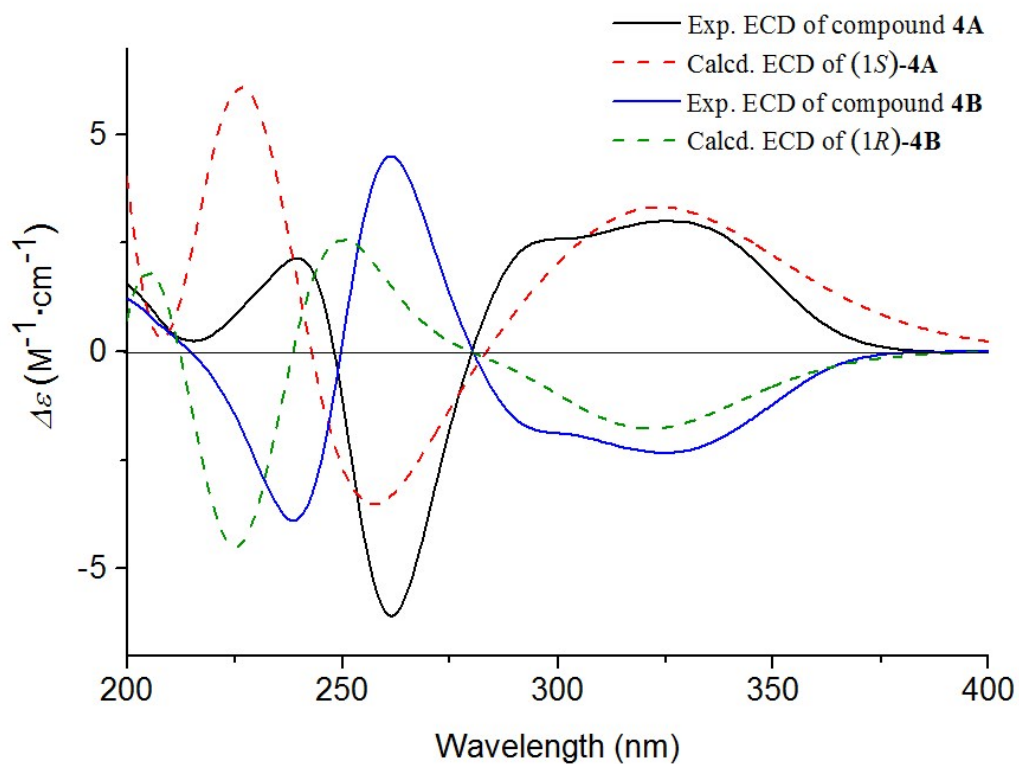


Figure S10. Experimental and calculated ECD spectra of 4A/4B.

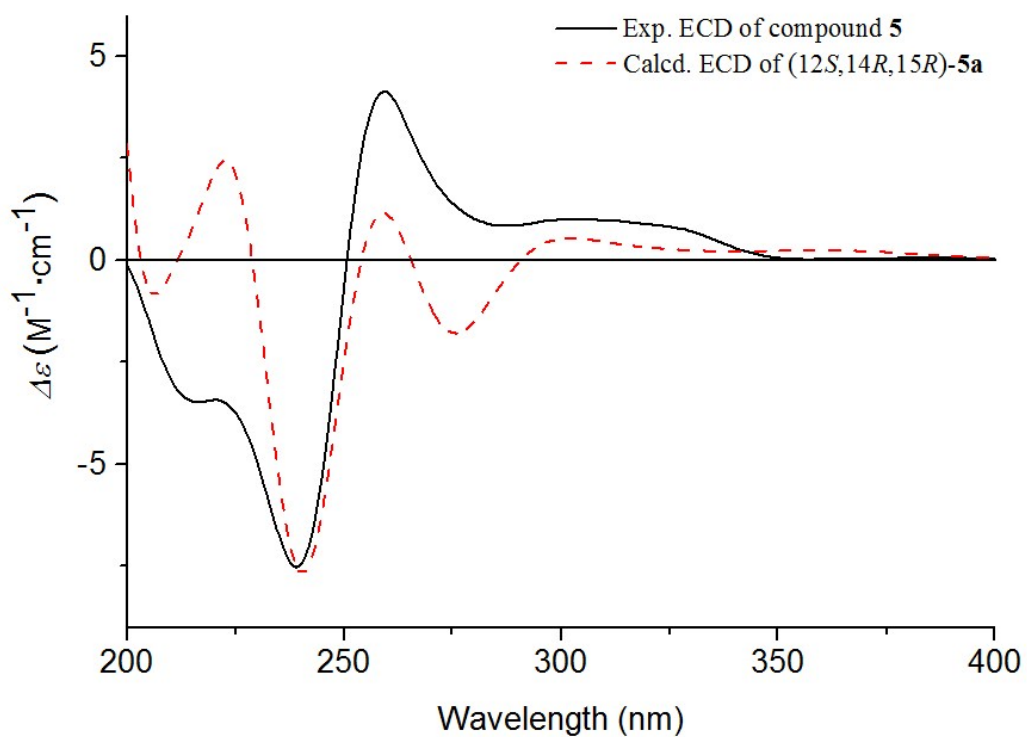


Figure S11. Experimental and calculated ECD spectra of 5.

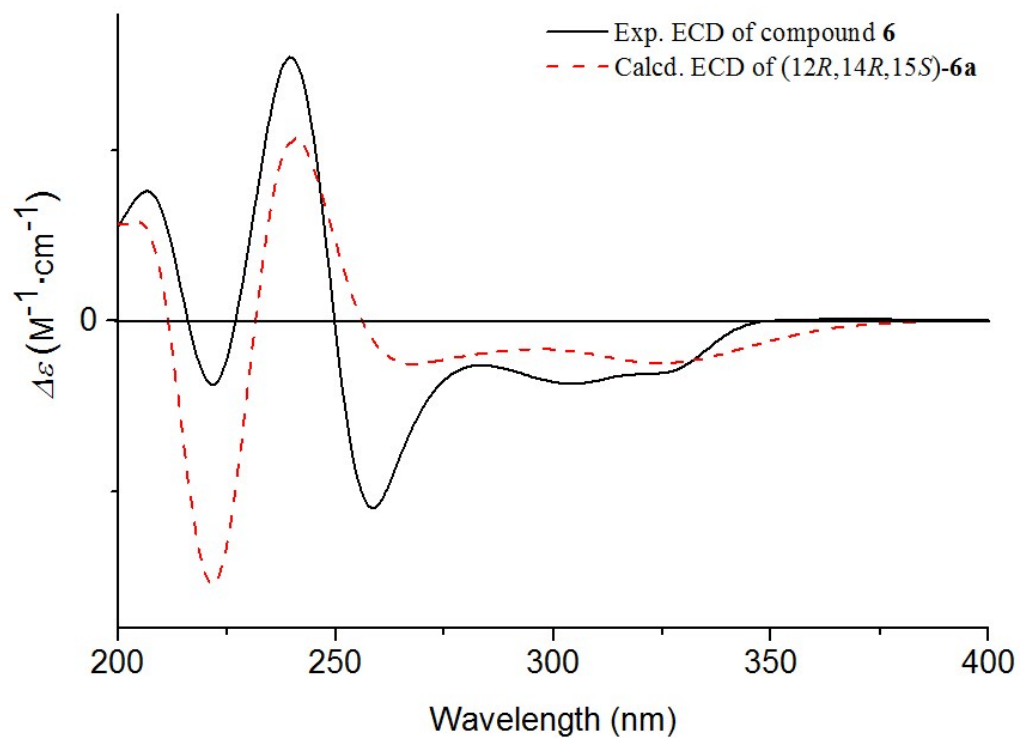


Figure S12. Experimental and calculated ECD spectra of 6.

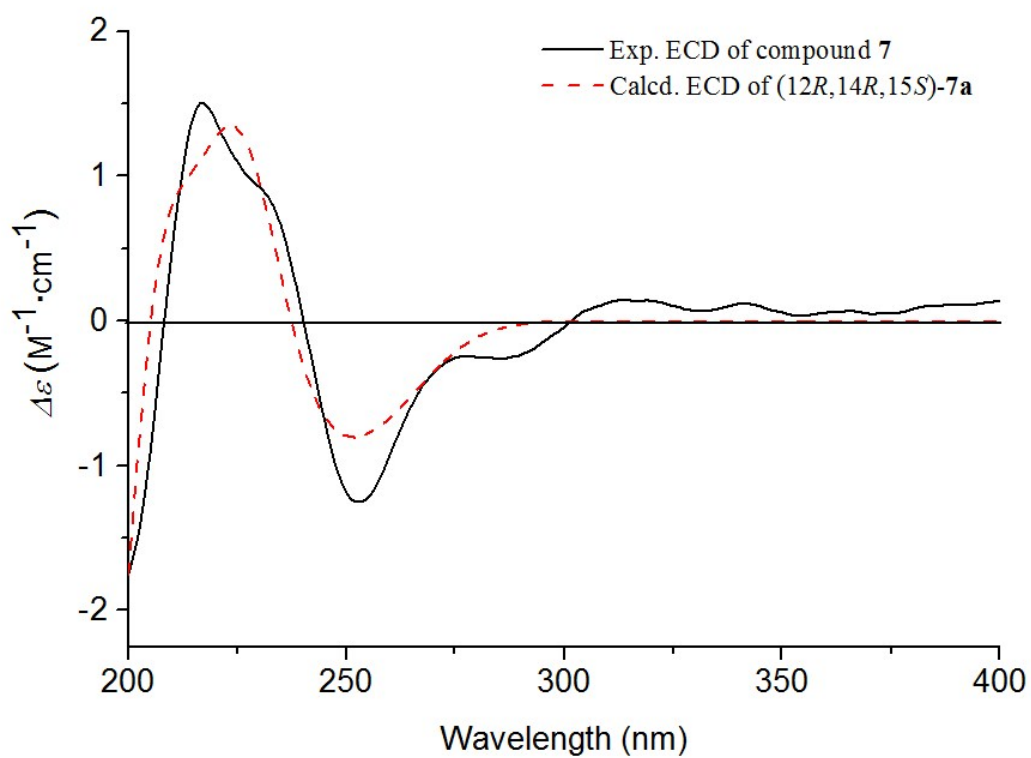


Figure S13. Experimental and calculated ECD spectra of 7.

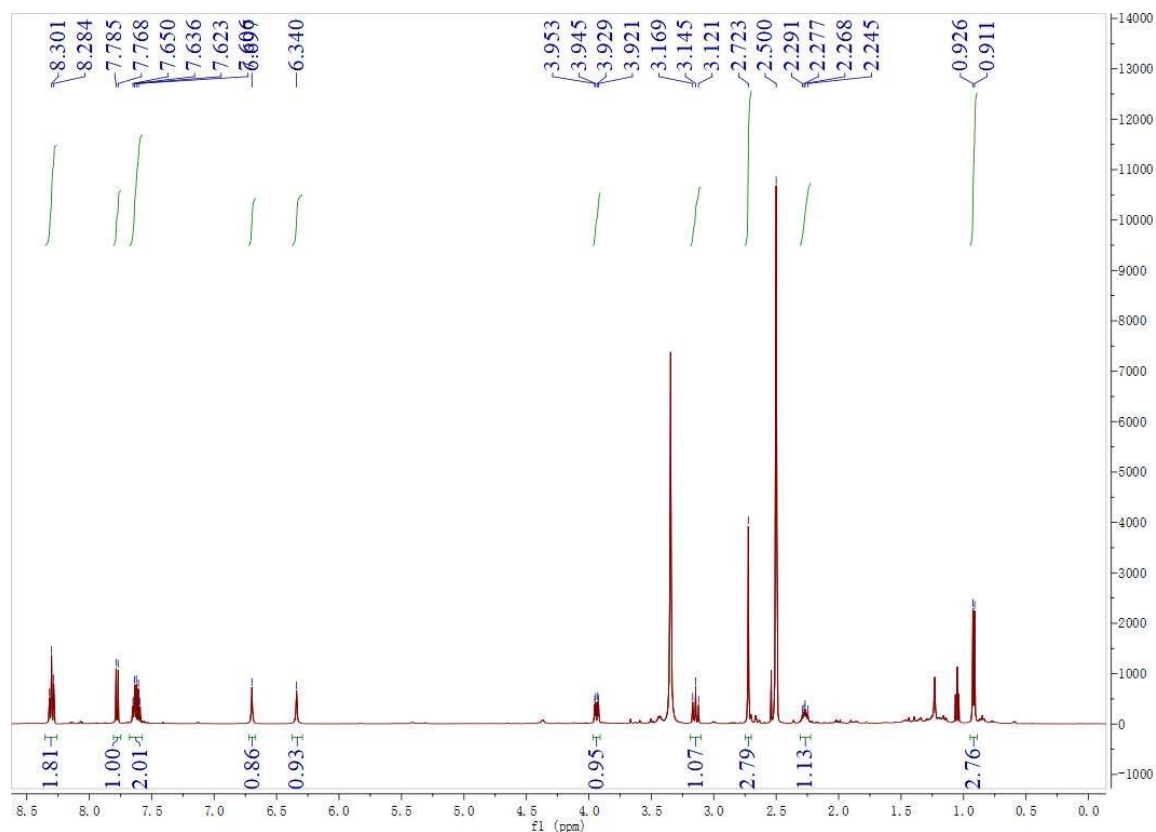


Figure S14. ^1H NMR spectrum of compound **1** in $\text{DMSO-}d_6$ (500 MHz)

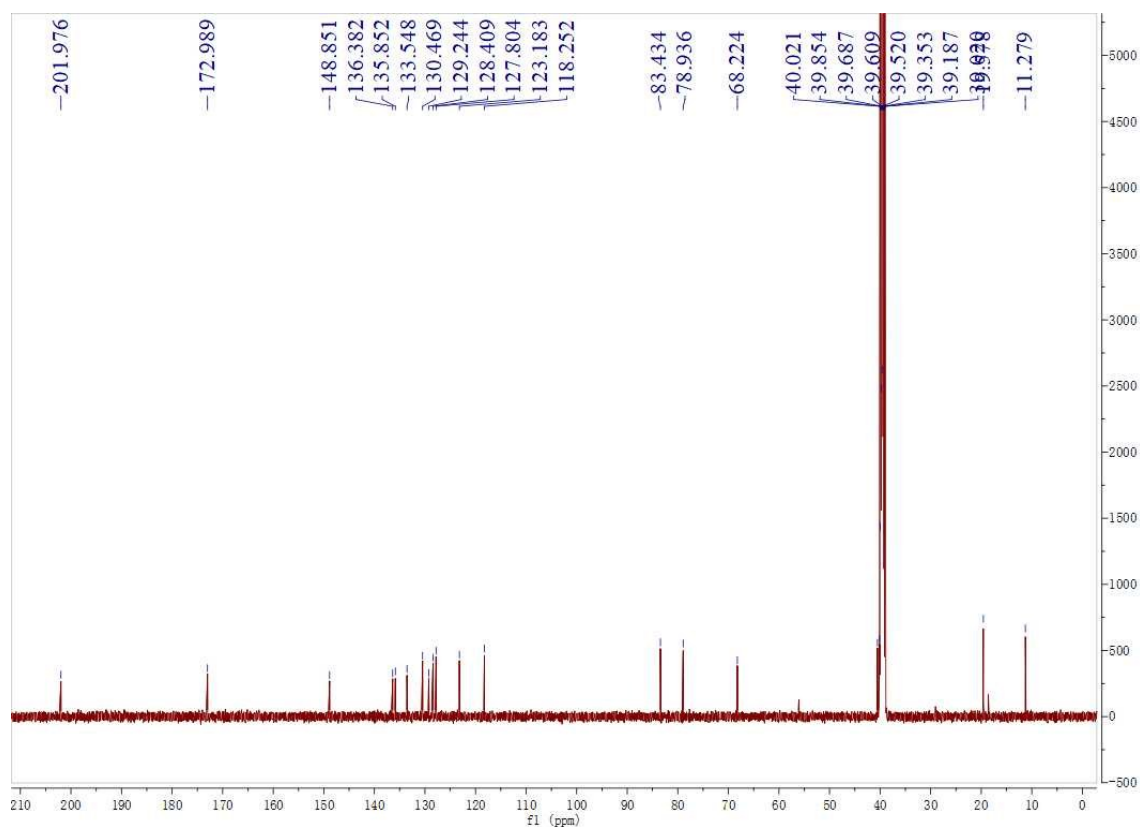


Figure S15. ^{13}C NMR spectrum of compound **1** in $\text{DMSO-}d_6$ (125 MHz)

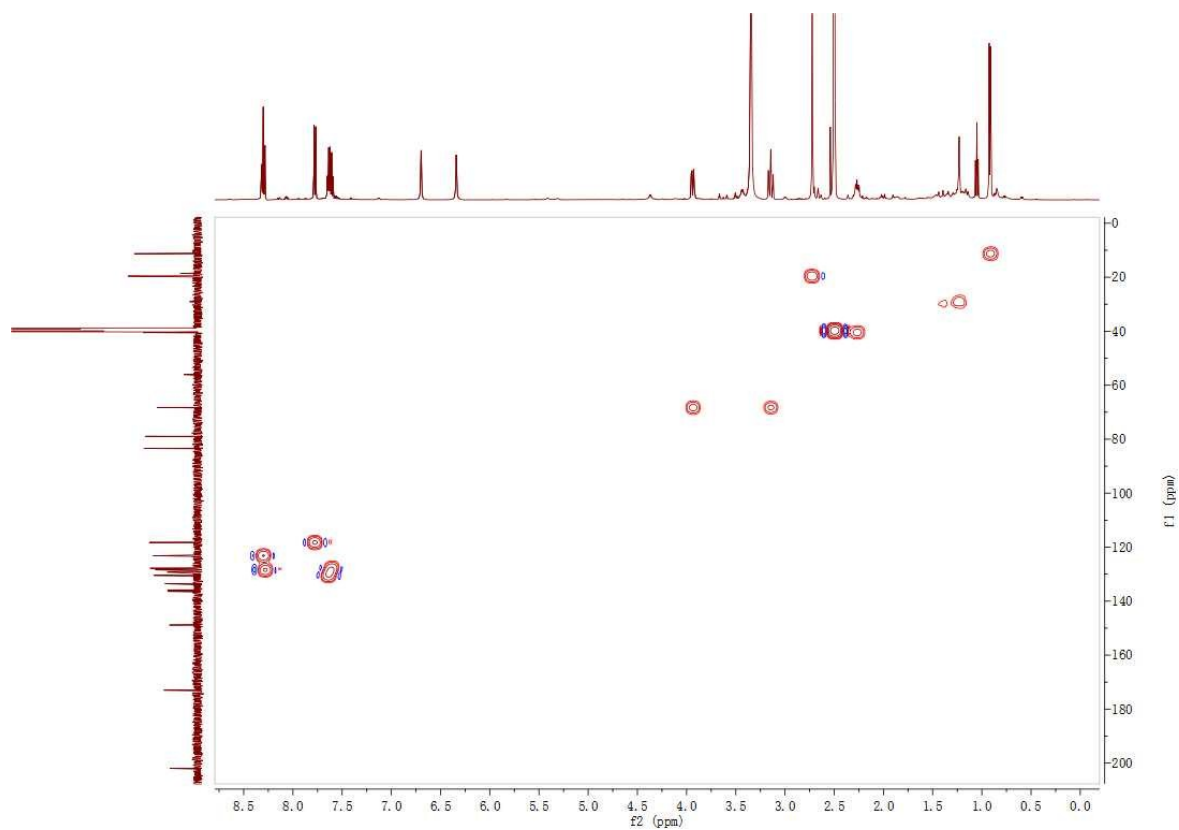


Figure S16. HSQC spectrum of compound 1 in DMSO- d_6 (500 MHz)

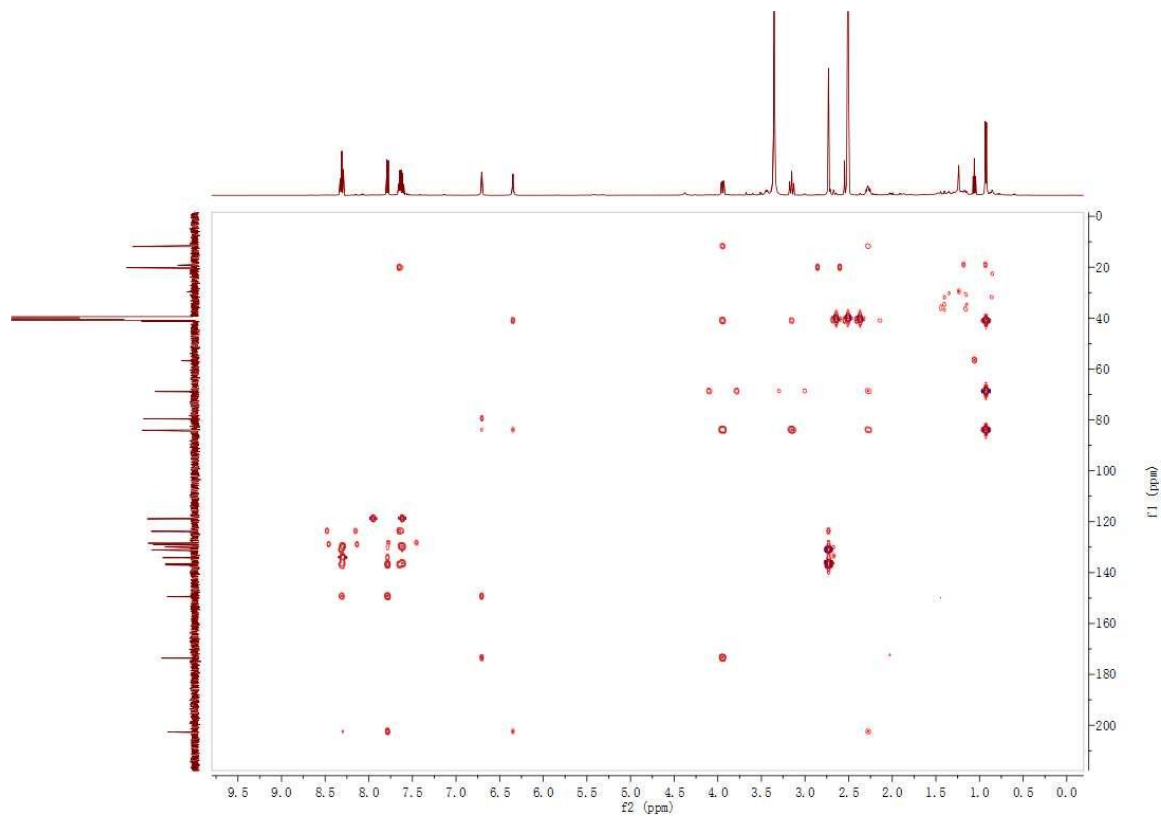


Figure S17. HMBC spectrum of compound 1 in DMSO- d_6 (500 MHz)

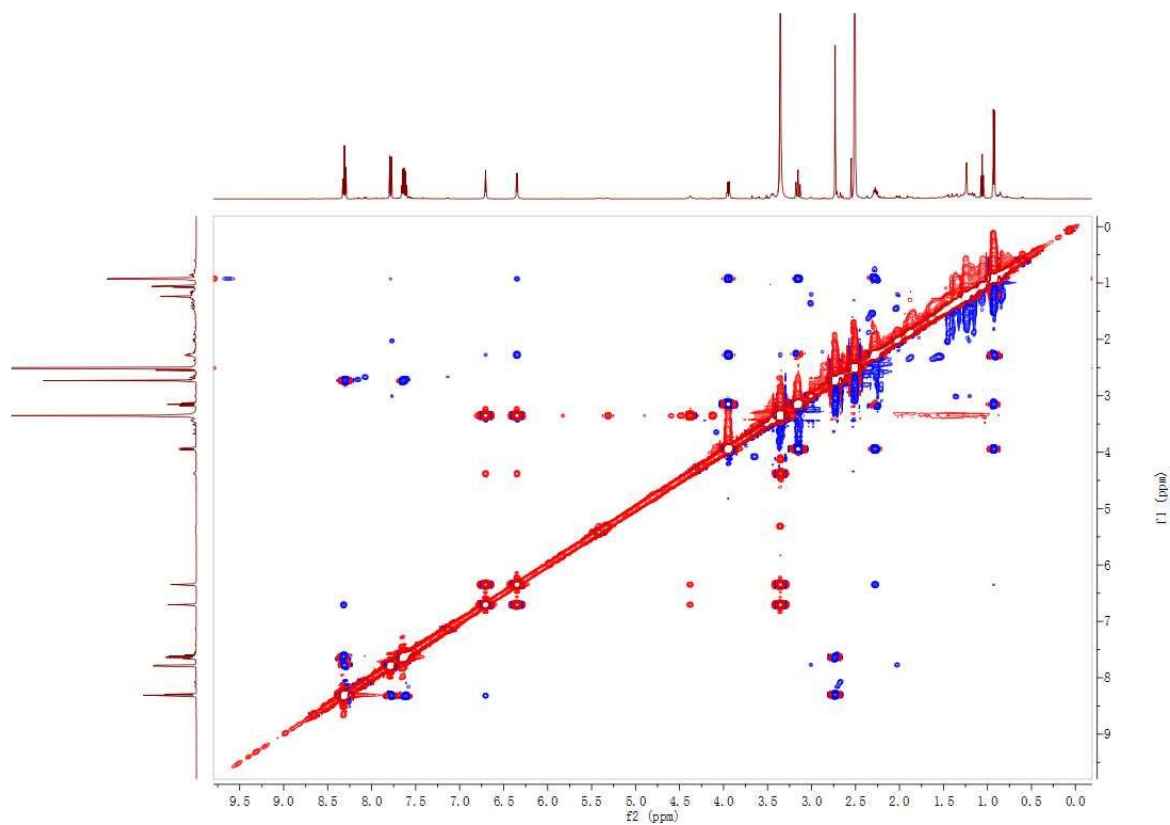


Figure S18. ROESY spectrum of compound **1** in DMSO- d_6 (500 MHz)

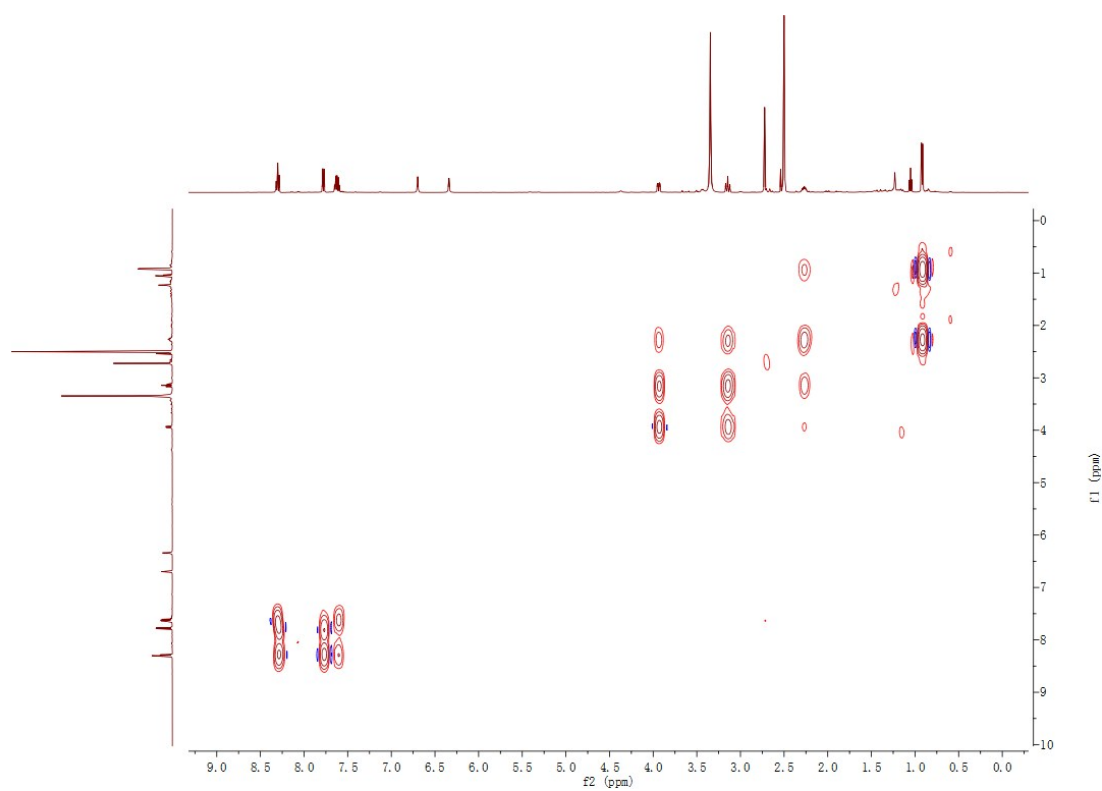


Figure S19. ^1H - ^1H COSY spectrum of compound **1** in DMSO- d_6 (400 MHz)

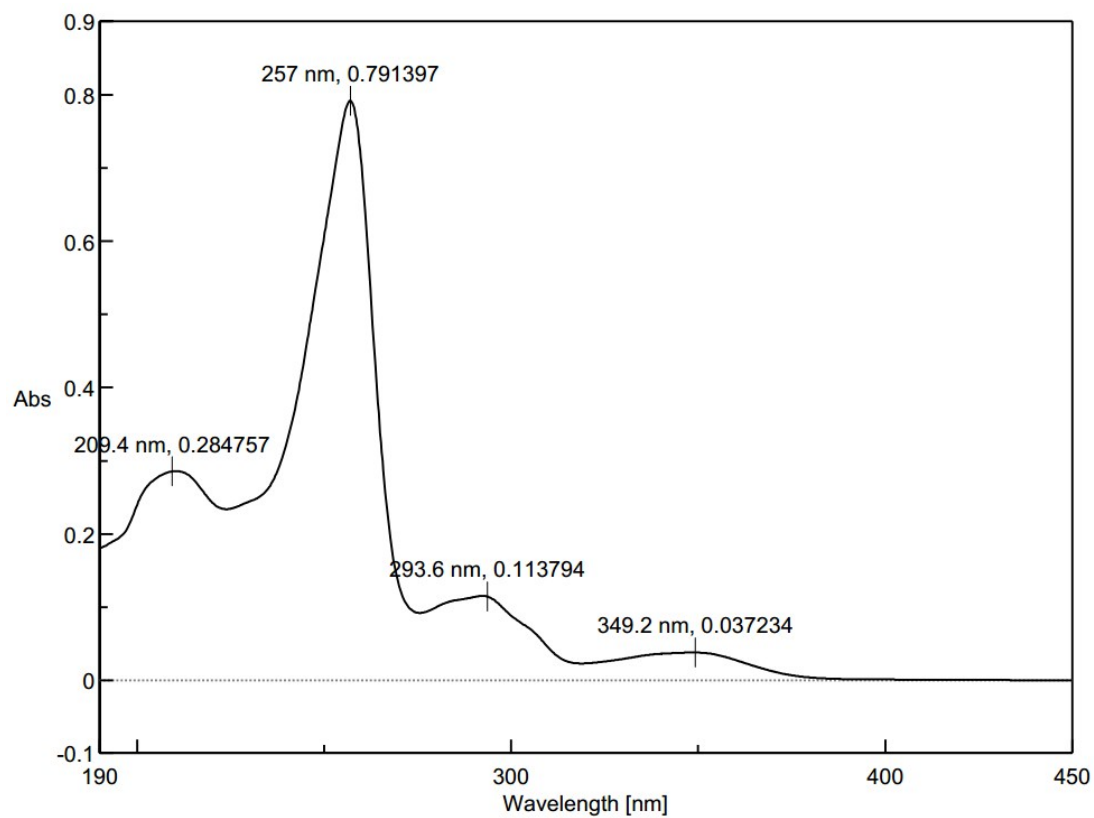


Figure S20. UV spectrum of compound **1**

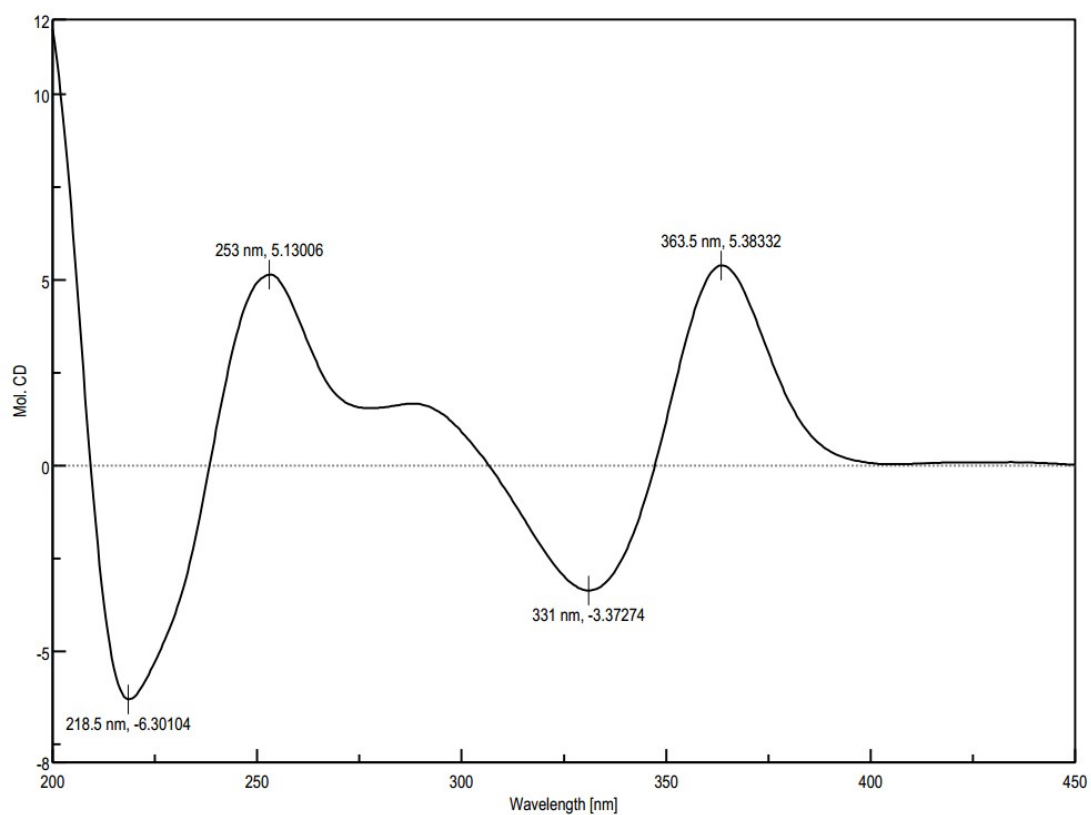


Figure S21. ECD spectrum of compound **1**

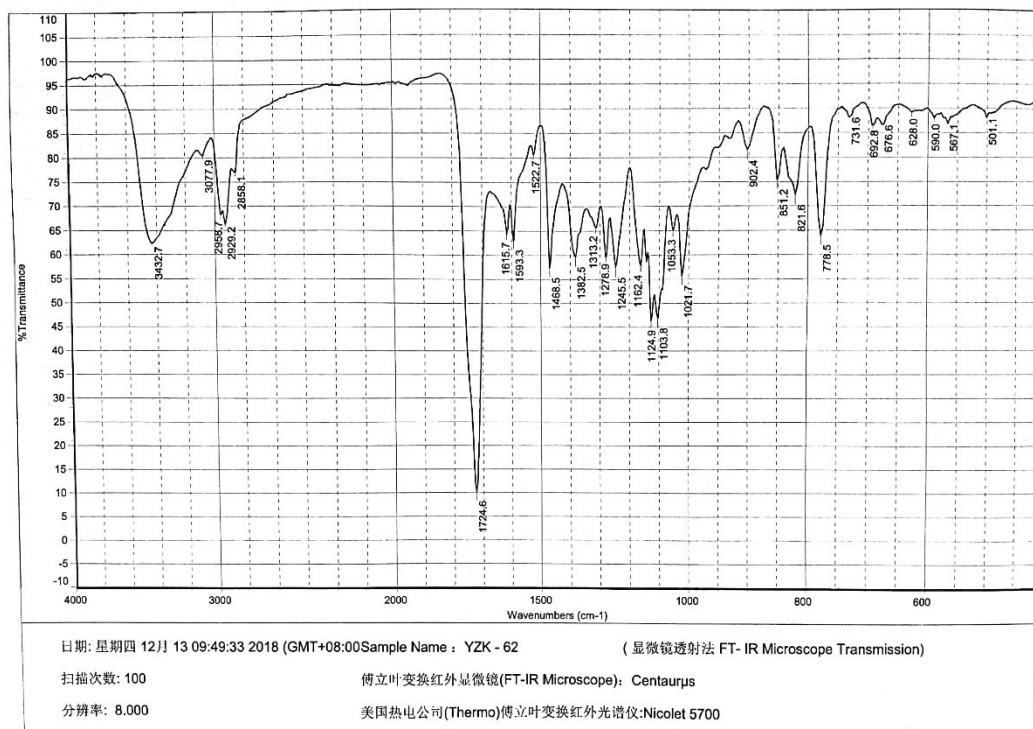
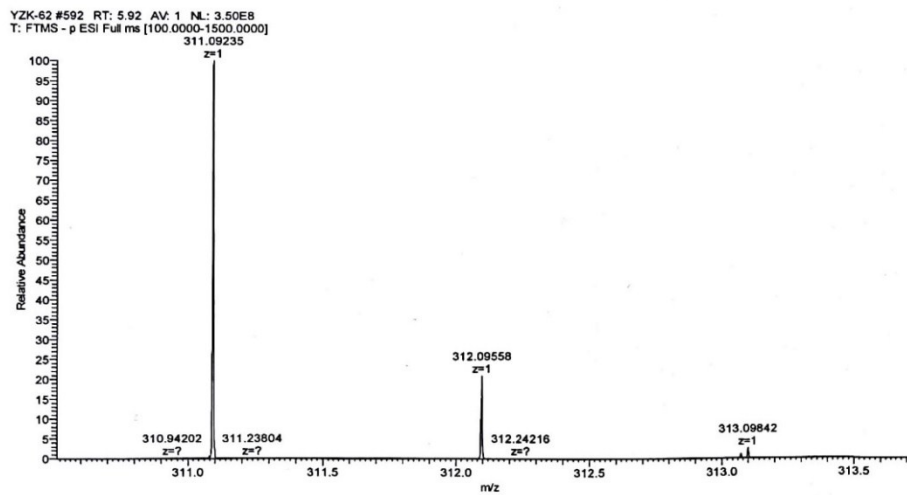


Figure S22. IR spectrum of compound 1



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
311.09235	311.09250	-0.47	11.5	C18 H15 O5	M-H

Figure S23. HR-ESI-MS spectrum of compound 1

Crystal Submitted by:
 Crystal Submitted on:
 Data Collected on:
 Structure Solved by:

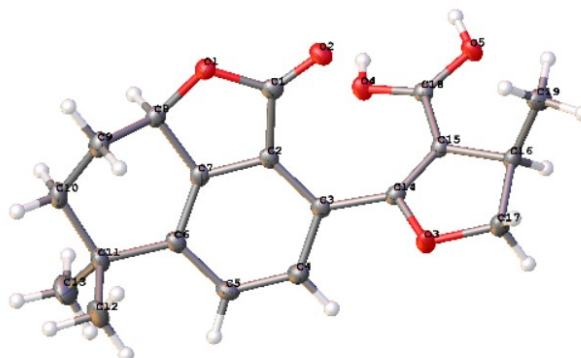


Table 1: Crystal data and structure refinement for exp_6141

Identification code	exp_6141
Empirical formula	C ₁₉ H ₂₀ O ₅
Formula weight	328.35
Temperature / K	109.90(10)
Crystal system	hexagonal
Space group	P6 ₄
a / Å, b / Å, c / Å	14.63788(16), 14.63788(16), 13.6616(2)
α/°, β/°, γ/°	90, 90, 120
Volume / Å ³	2535.06(7)
Z	6
ρ _{calc} / mg mm ⁻³	1.290
μ / mm ⁻¹	0.767
F(000)	1044
Crystal size / mm ³	0.400 × 0.350 × 0.300
2θ range for data collection	9.518 to 142.254°
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 16, -15 ≤ l ≤ 16
Reflections collected	14929
Independent reflections	3057[R(int) = 0.0262 (inf-0.9Å)]
Data/restraints/parameters	3057/1/222
Goodness-of-fit on F ²	1.082
Final R indexes [I > 2σ (I) i.e. F _o > 4σ (F _o)]	R ₁ = 0.0305, wR ₂ = 0.0769
Final R indexes [all data]	R ₁ = 0.0308, wR ₂ = 0.0771
Largest diff. peak/hole / e Å ⁻³	0.164/-0.265
Flack Parameters	0.09(6)
Completeness	0.9987

Experimental

Single crystals of C₁₉H₂₀O₅ [exp_6141] were recrystallised from [solvents] mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Crystal structure determination of [exp_6141]

Crystal Data. C₁₉H₂₀O₅, *M* = 328.35, hexagonal, *a* = 14.63788(16) Å, *c* = 13.6616(2) Å, *U* = 2535.06(7) Å³, *T* = 109.90(10), space group P6₄ (no. 172), *Z* = 6, μ(Cu Kα) = 0.767, 14929 reflections measured, 3057 unique (*R*_{int} = 0.0262) which were used in all calculations. The final *wR*(*F*₂) was 0.0771 (all data).

This report has been created with Olex2, compiled on 2011.02.15 svn.r1672. Please let us know if there are any errors or if you would like to have additional features.

Figure S24. The crystal data and structure refinement of compound 2

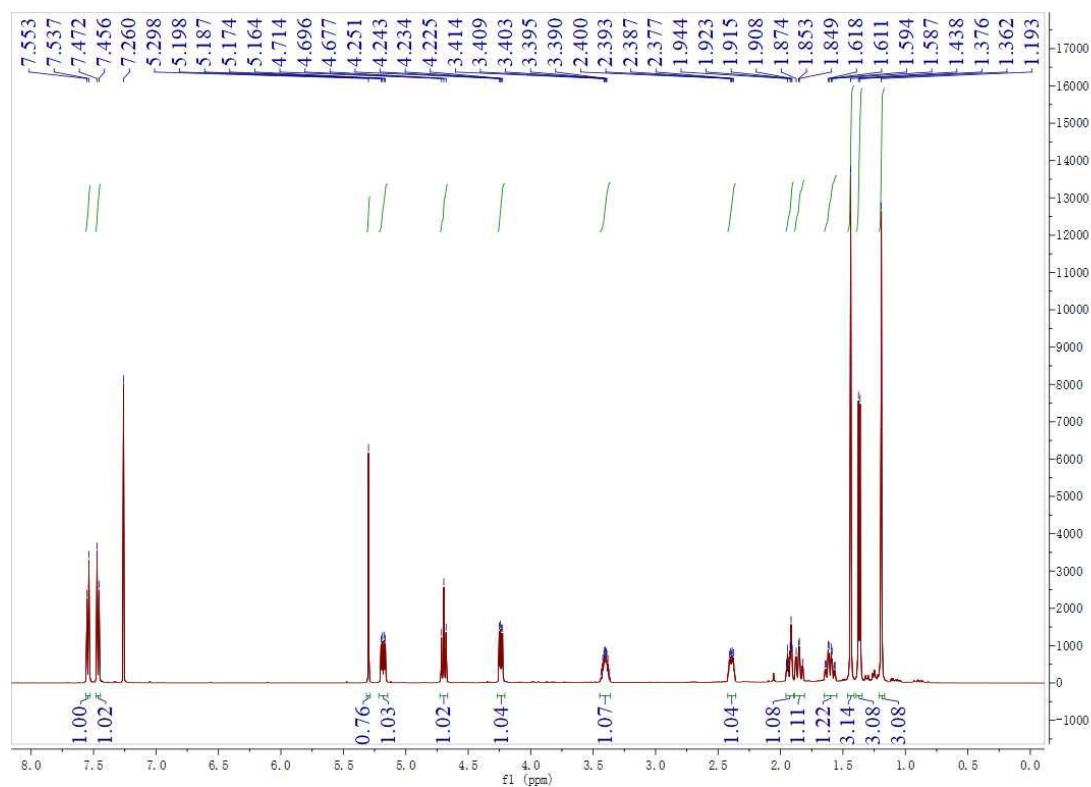


Figure S25. ^1H NMR spectrum of compound **2** in CDCl_3 (500 MHz)

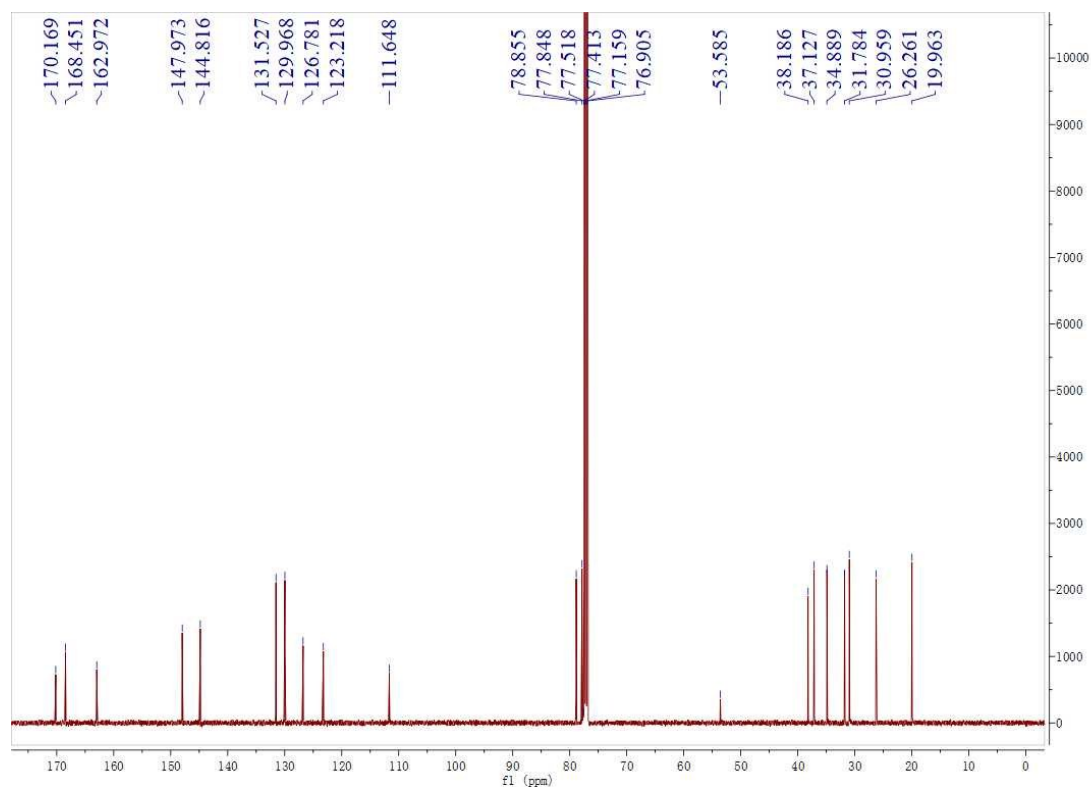


Figure S26. ^{13}C NMR spectrum of compound **2** in CDCl_3 (125 MHz)

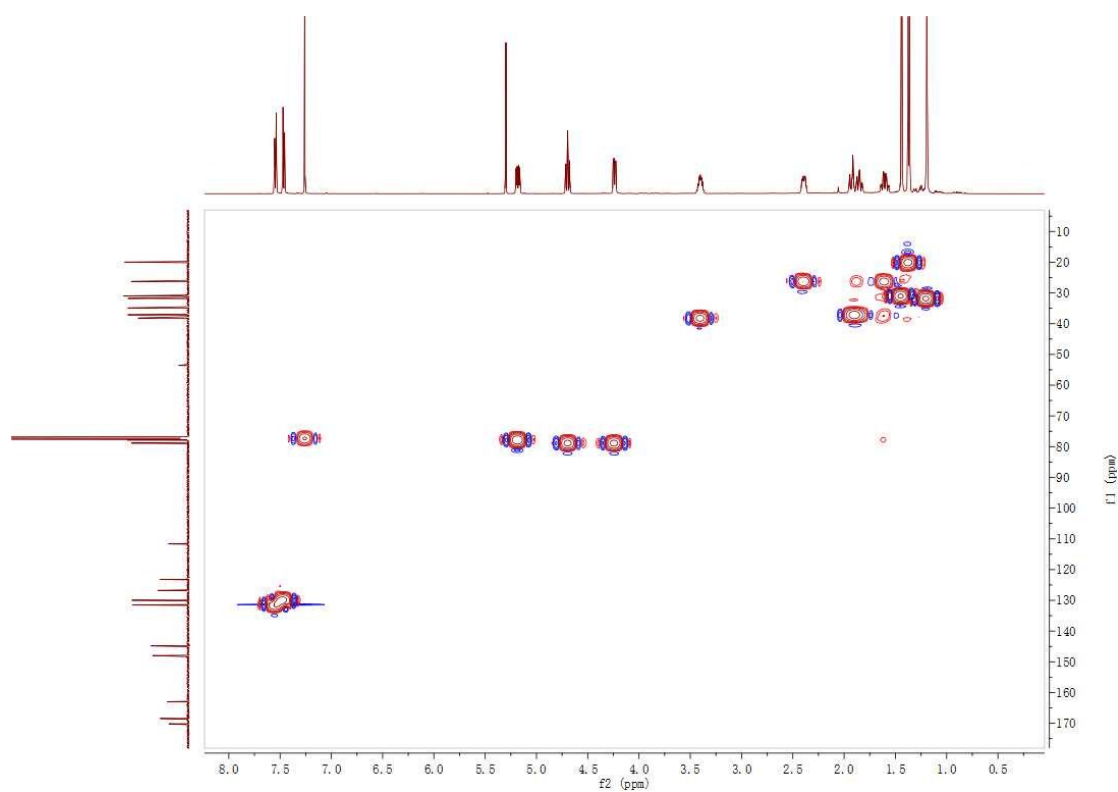


Figure S27. HSQC spectrum of compound **2** in CDCl_3 (500 MHz)

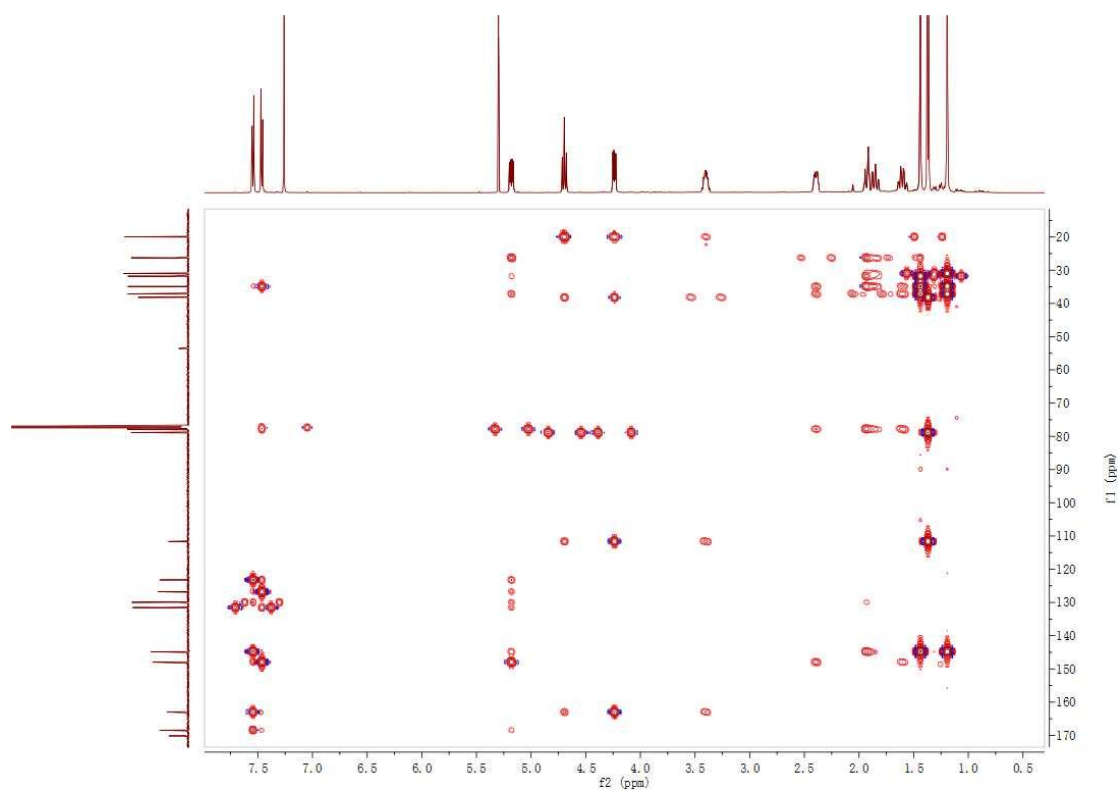


Figure S28. HMBC spectrum of compound **2** in CDCl_3 (500 MHz)

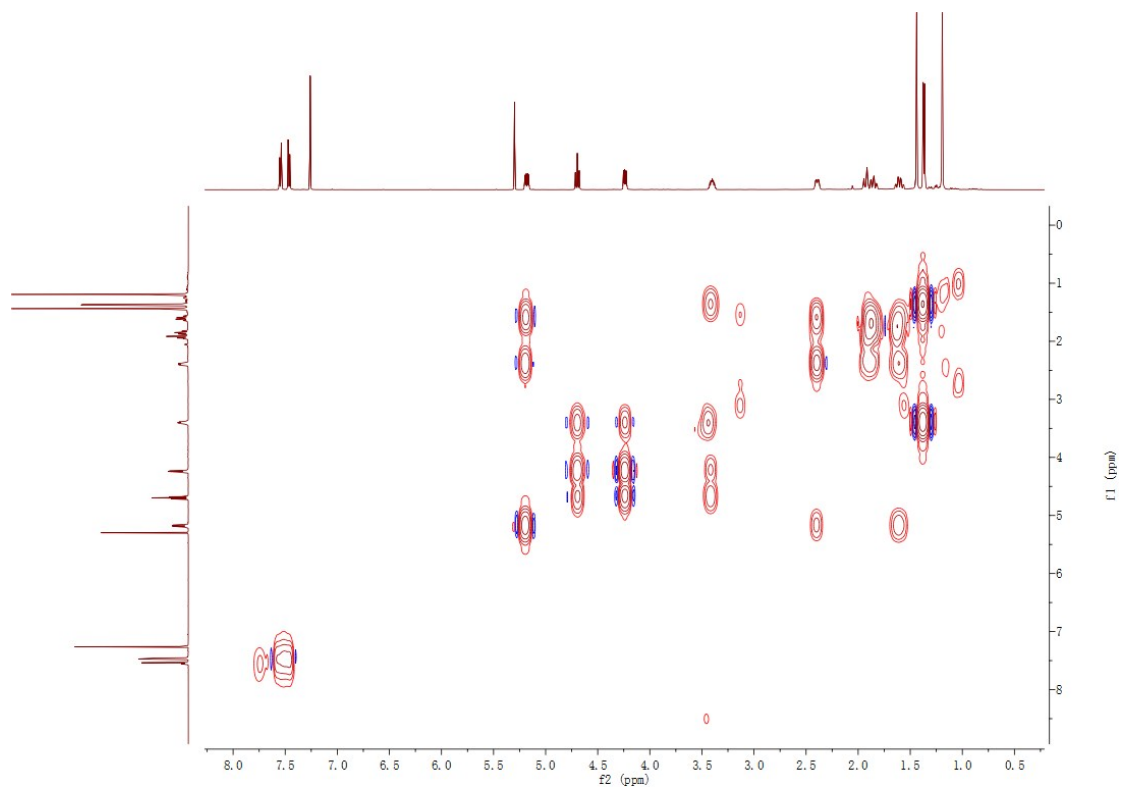


Figure S29. ^1H - ^1H COSY spectrum of compound **2** in CDCl_3 (400 MHz)

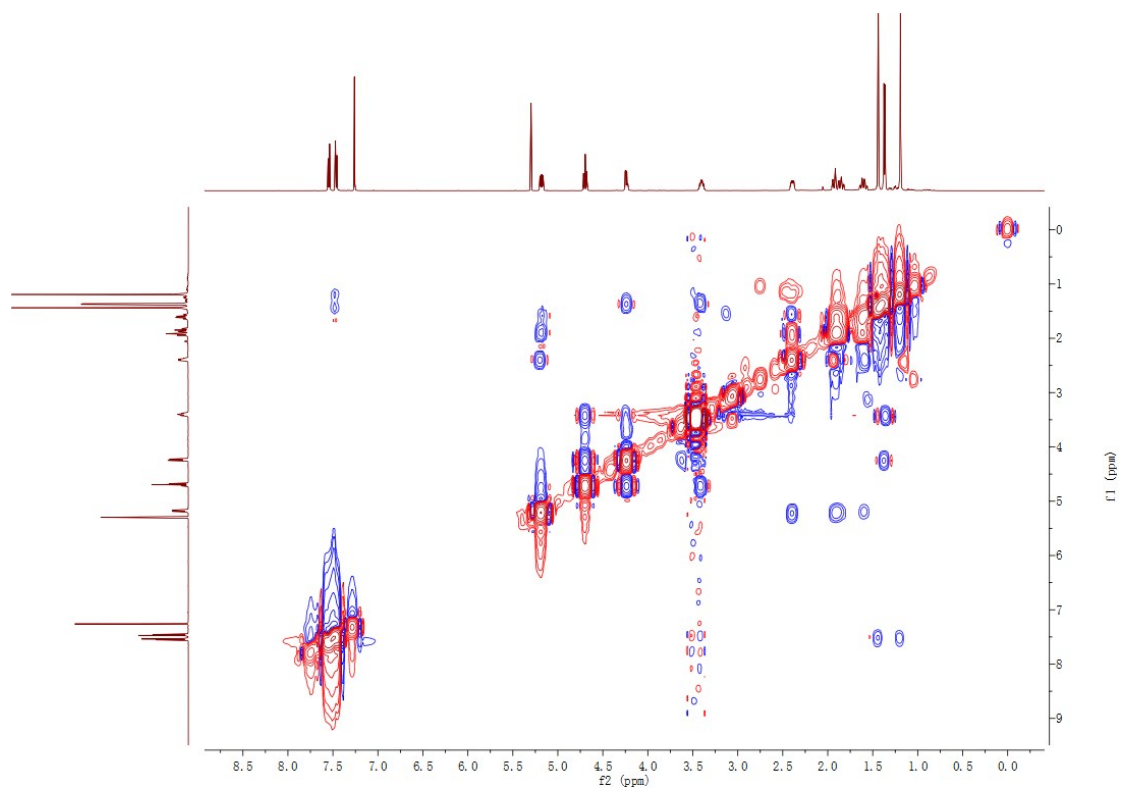


Figure S30. ROESY spectrum of compound **2** in CDCl_3 (400 MHz)

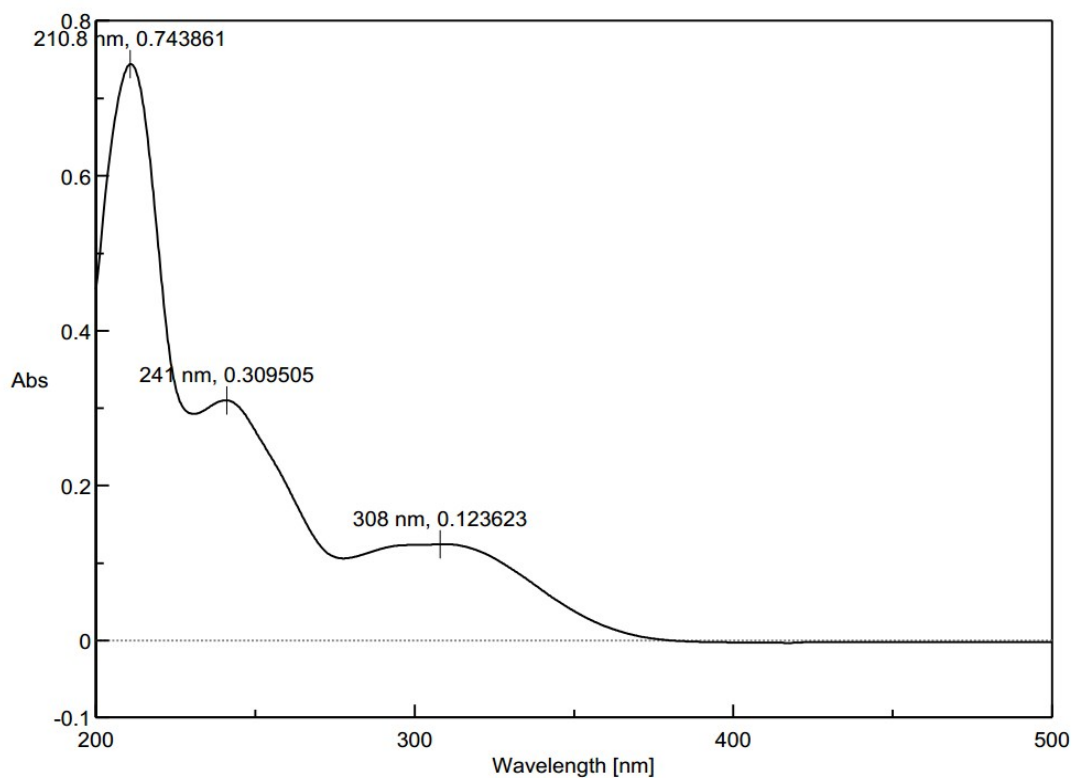


Figure S31. UV spectrum of compound 2

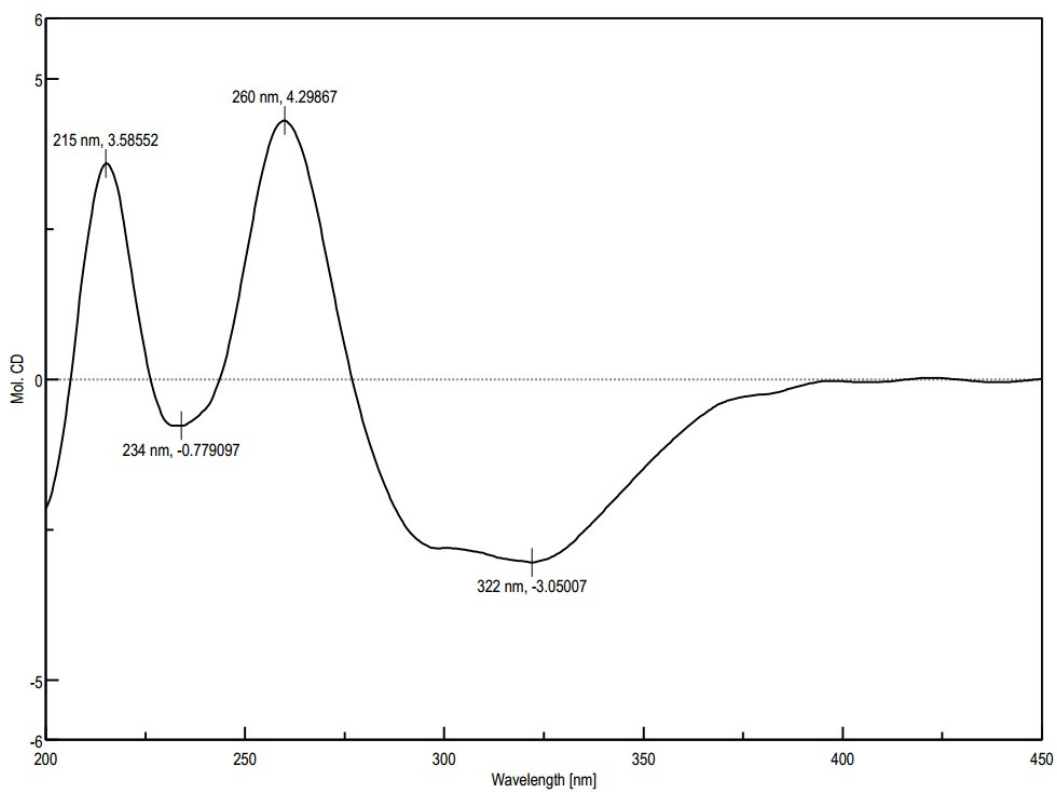


Figure S32. ECD spectrum of compound 2

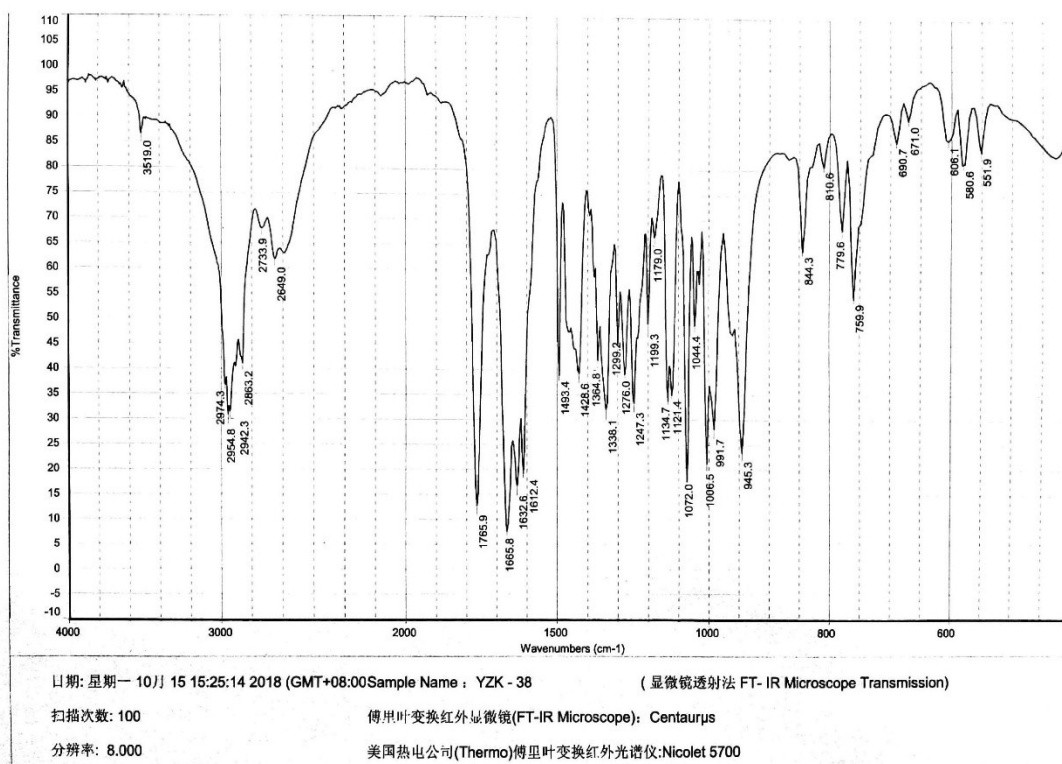
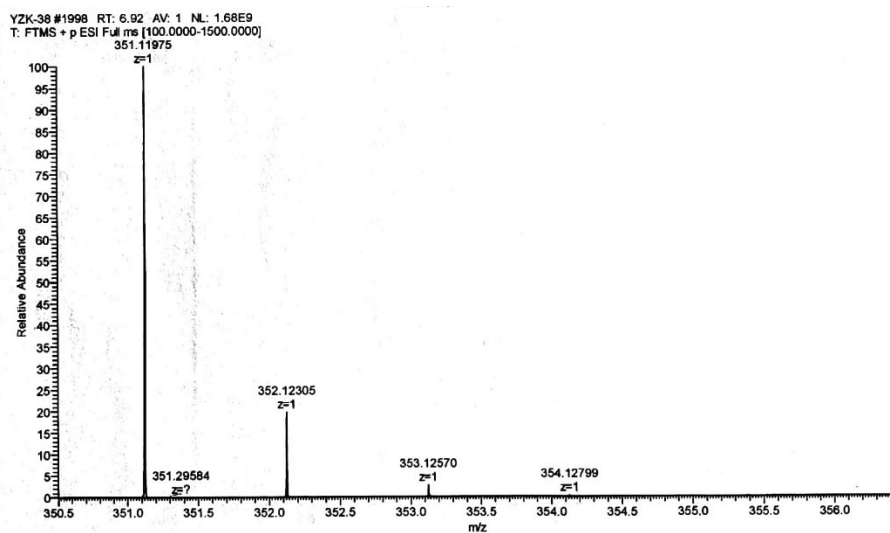


Figure S33. IR spectrum of compound 2



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
351.11975	351.12029	-1.55	9.5	C19 H20 O5 Na	M+Na

Figure S34. HR-ESI-MS spectrum of compound 2

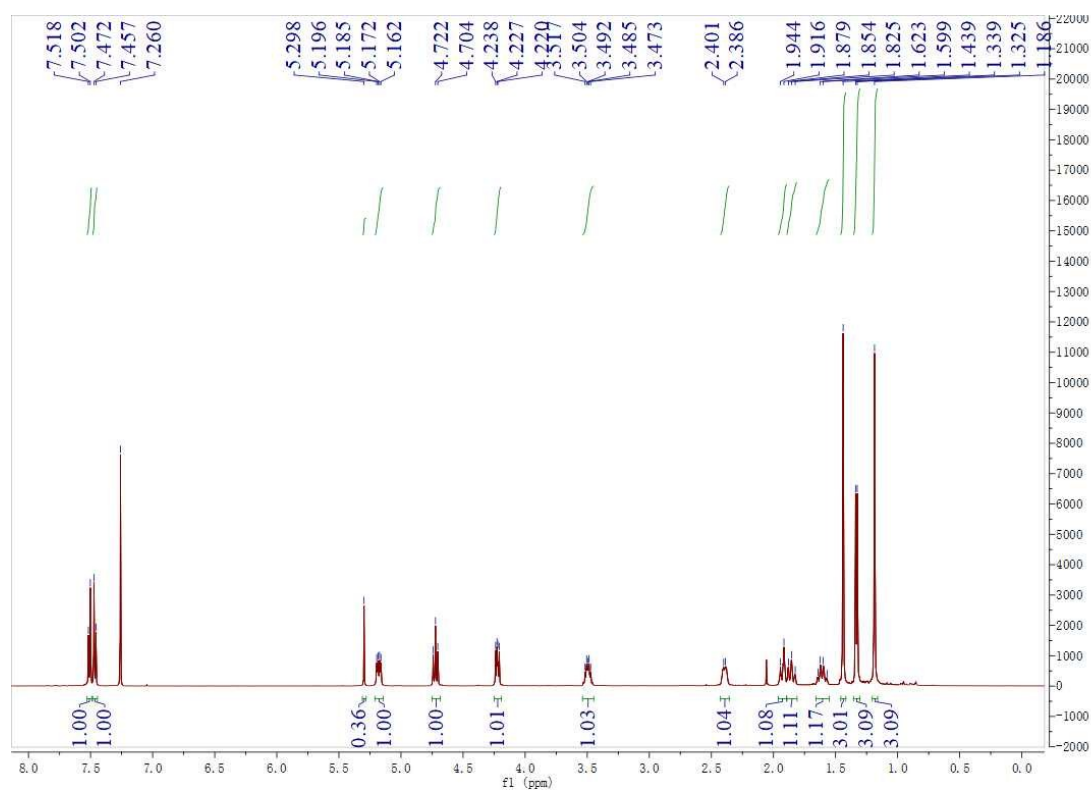


Figure S35. ^1H NMR spectrum of compound **3** in CDCl_3 (500 MHz)

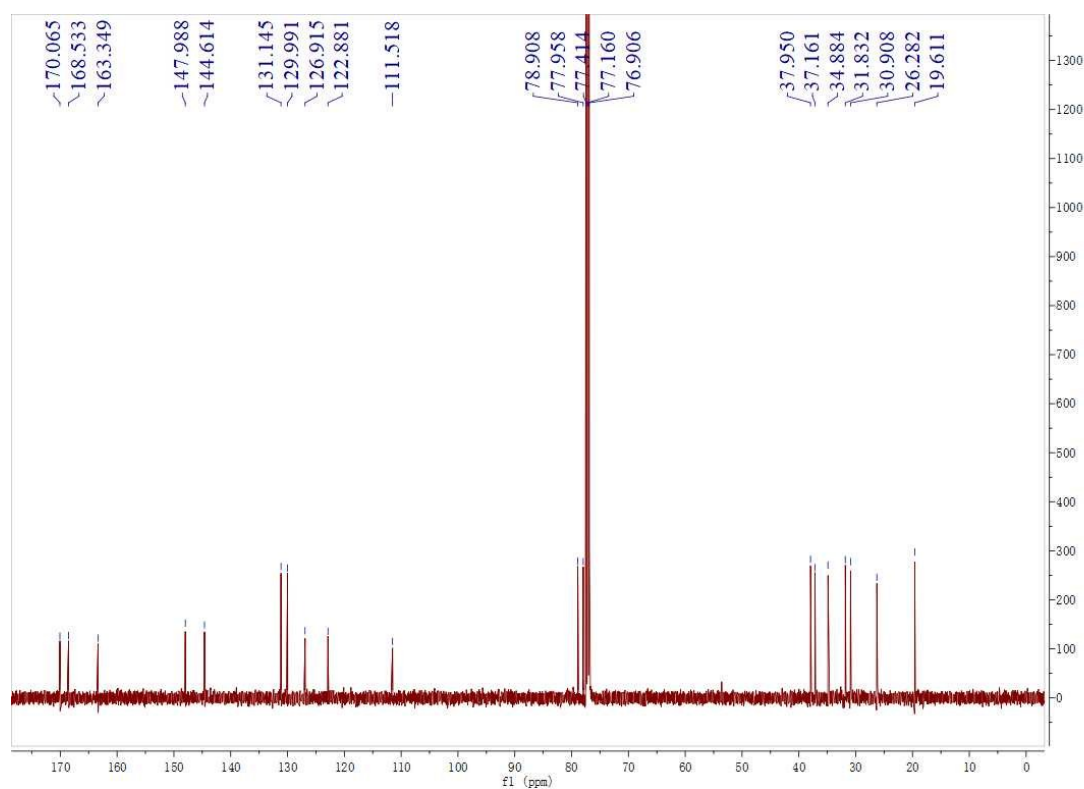


Figure S36. ^{13}C NMR spectrum of compound **3** in CDCl_3 (125 MHz)

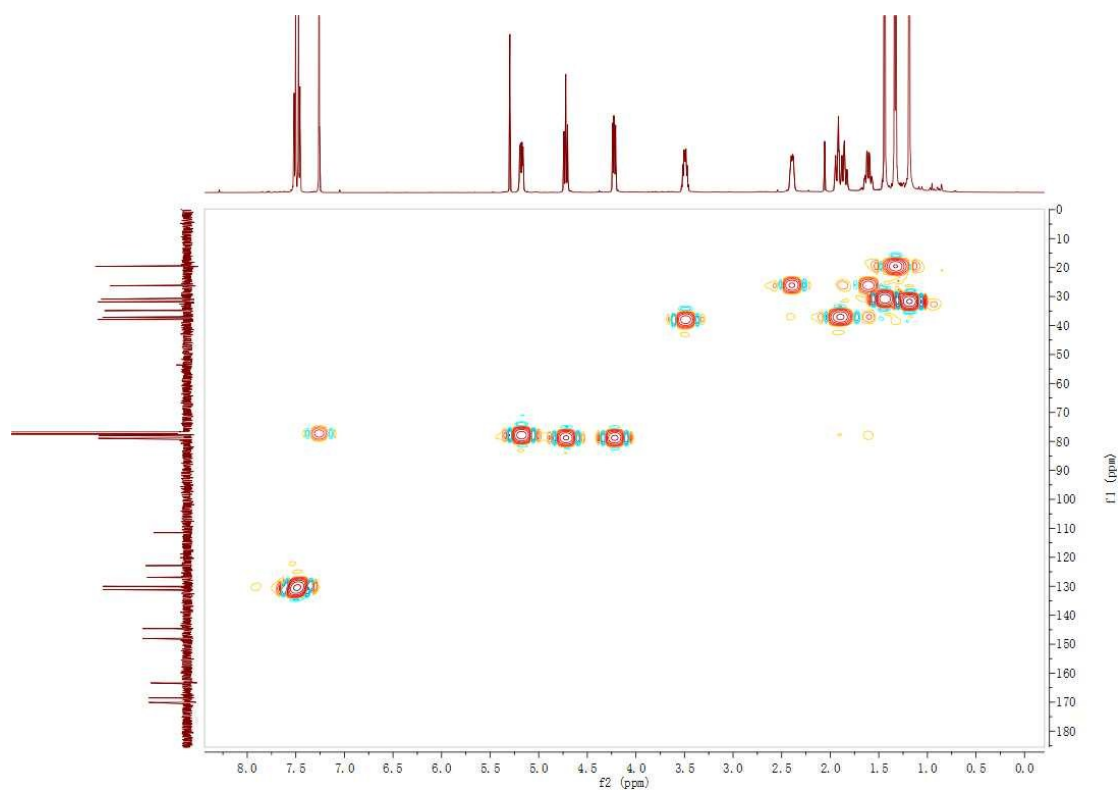


Figure S37. HSQC spectrum of compound **3** in CDCl_3 (500 MHz)

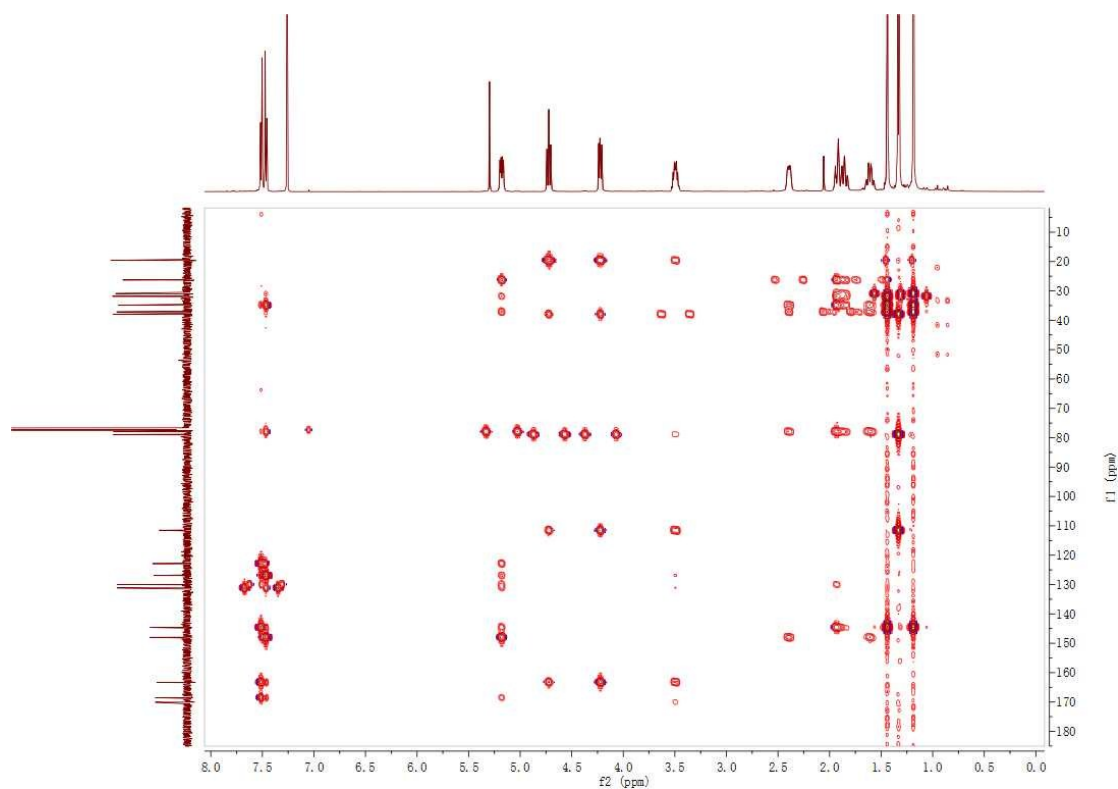


Figure S38. HMBC spectrum of compound **3** in CDCl_3 (500 MHz)

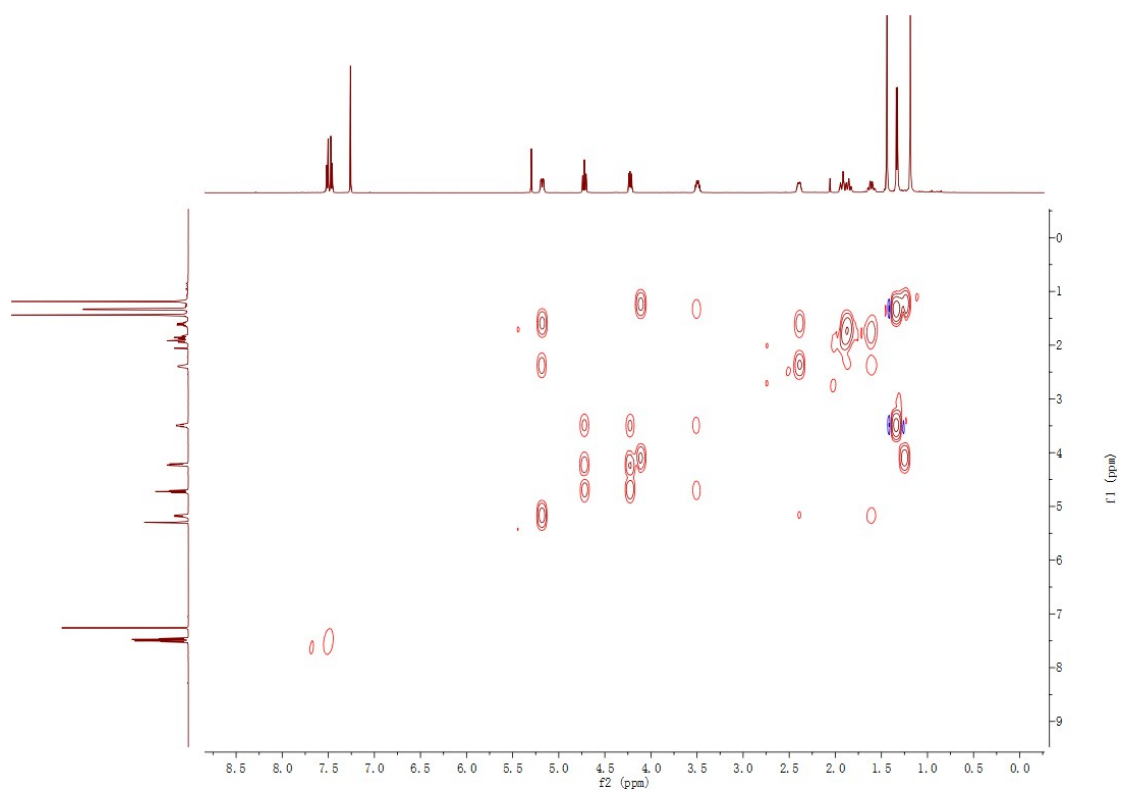


Figure S39. ^1H - ^1H COSY spectrum of compound **3** in CDCl_3 (400 MHz)

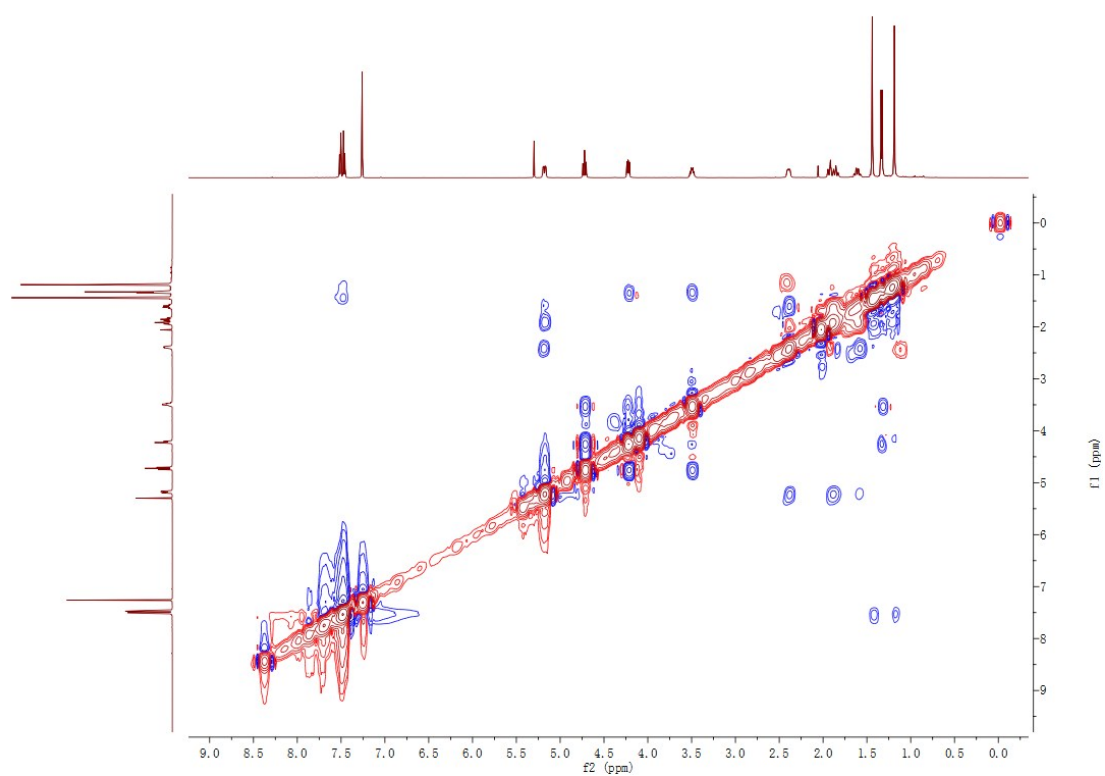


Figure S40. ROESY spectrum of compound **3** in CDCl_3 (400 MHz)

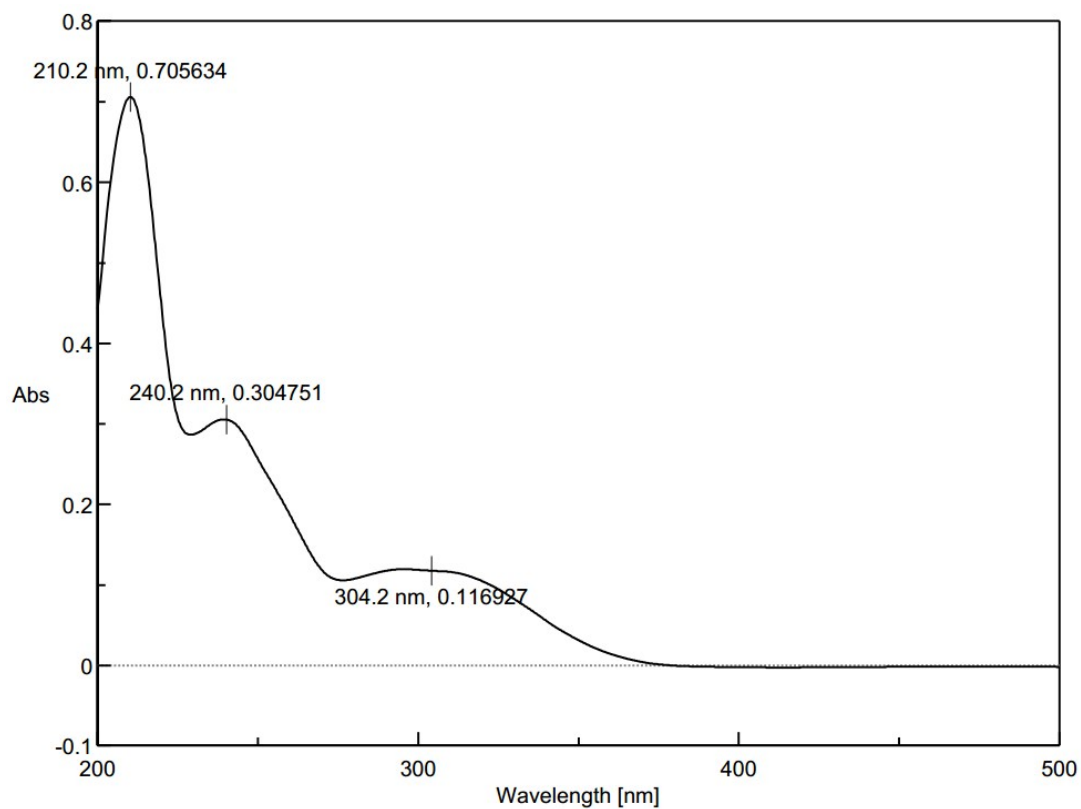


Figure S41. UV spectrum of compound **3**

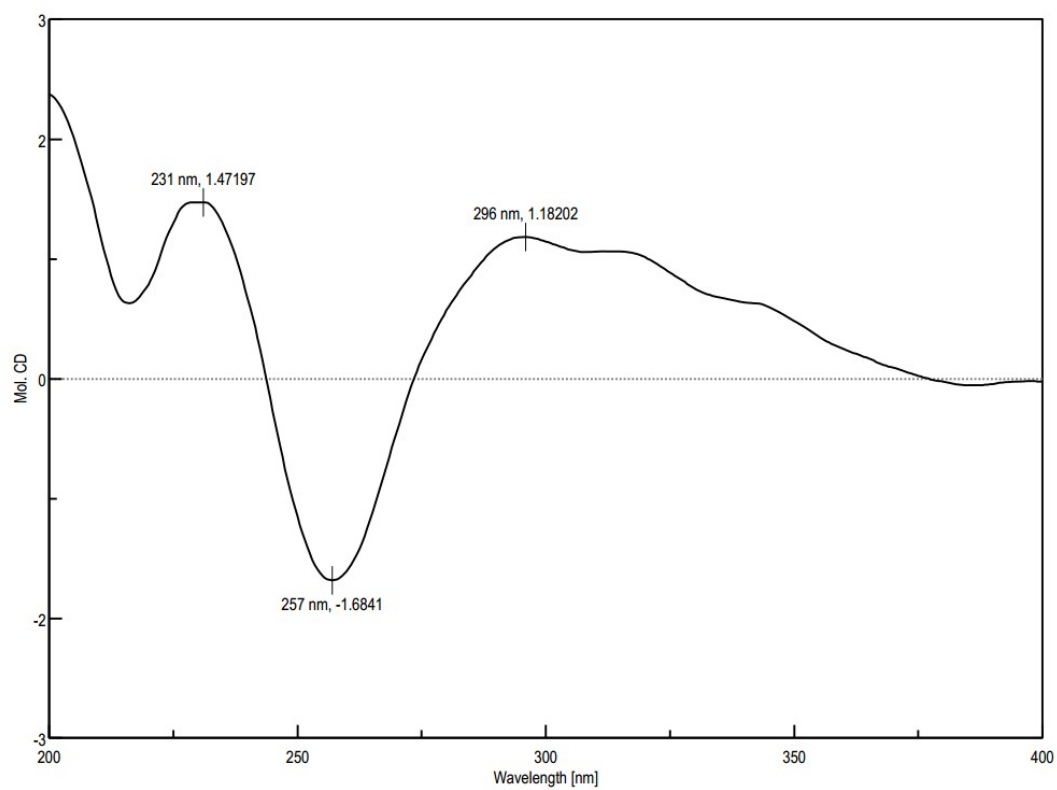


Figure S42. ECD spectrum of compound **3**

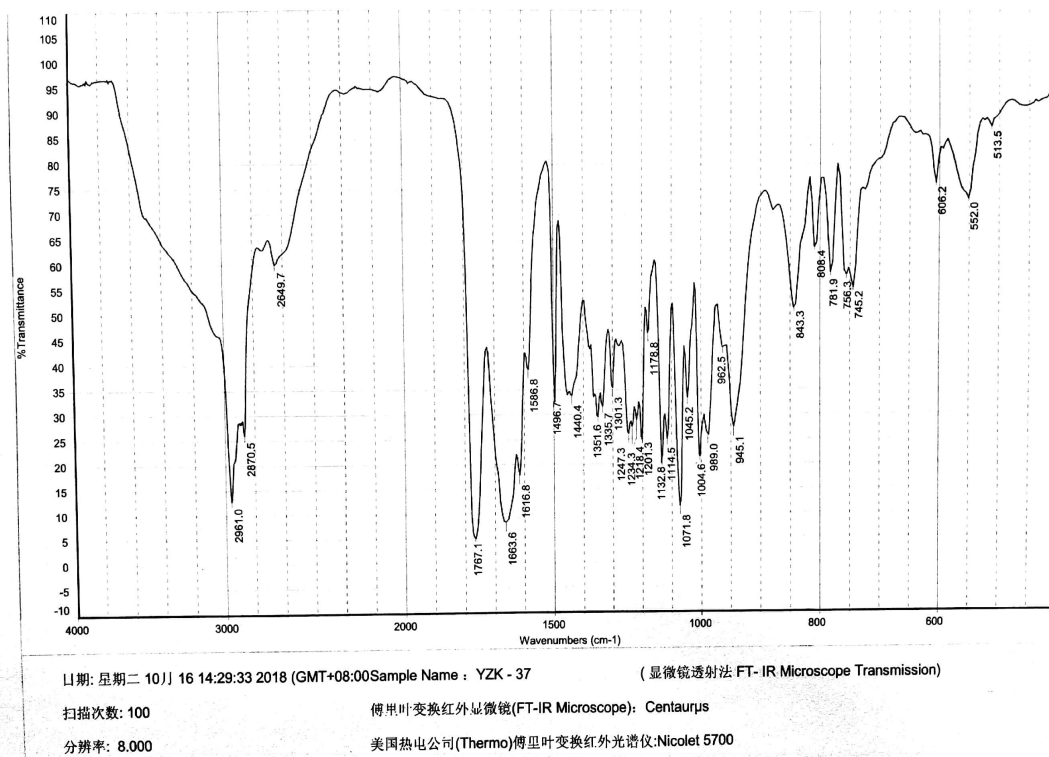
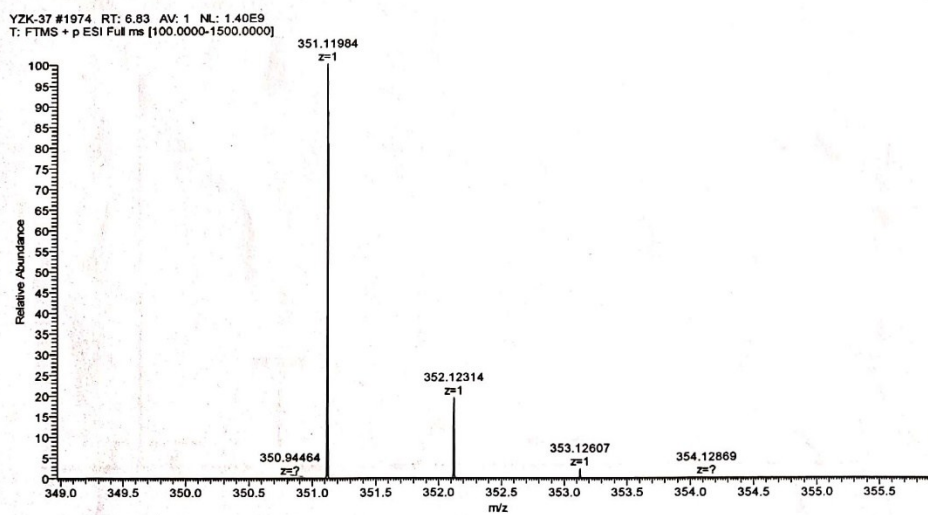


Figure S43. IR spectrum of compound 3



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
351.11984	351.12029	-1.3	9.5	C19 H20 O5 Na	M+Na

Figure S44. HR-ESI-MS spectrum of compound 3

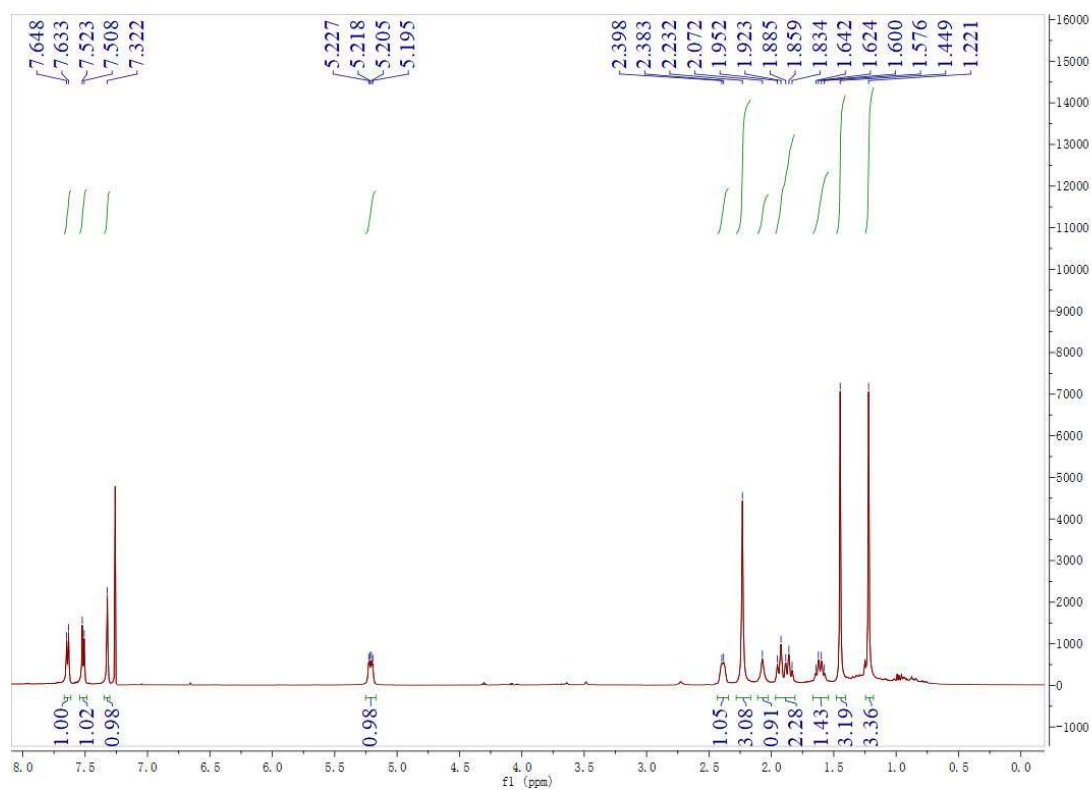


Figure S45. ^1H NMR spectrum of compound **4A/4B** in CDCl_3 (500 MHz)

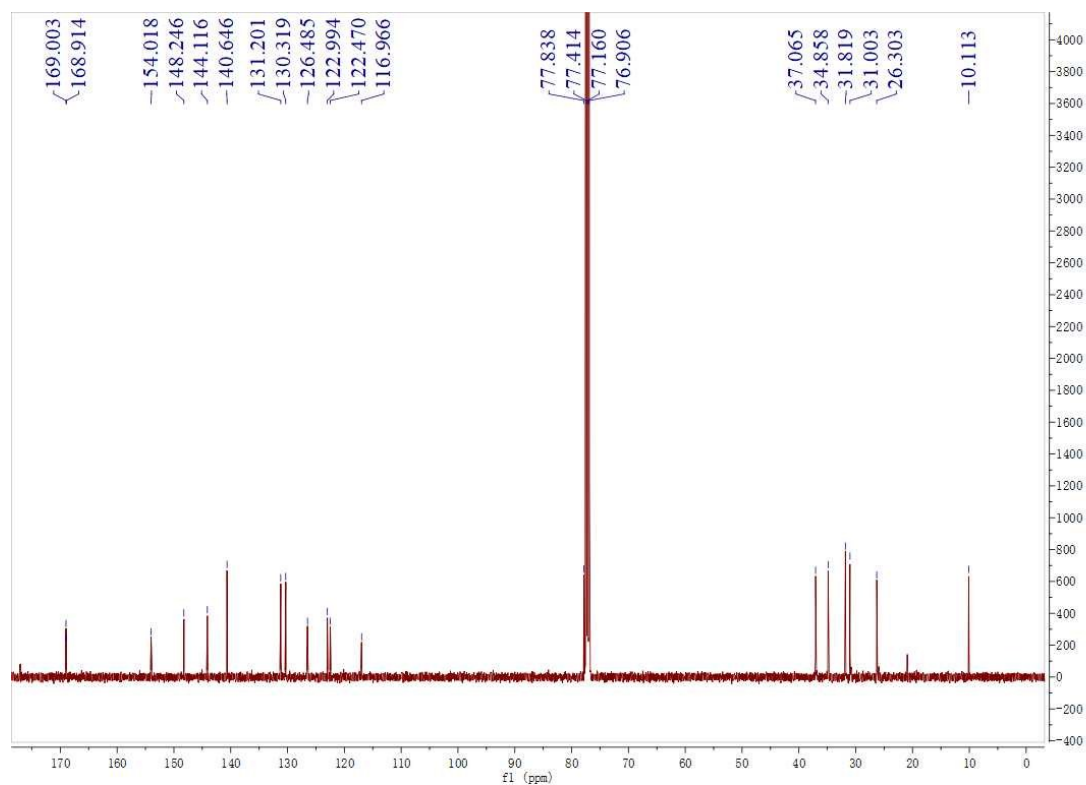


Figure S46. ^{13}C NMR spectrum of compound **4A/4B** in CDCl_3 (125 MHz)

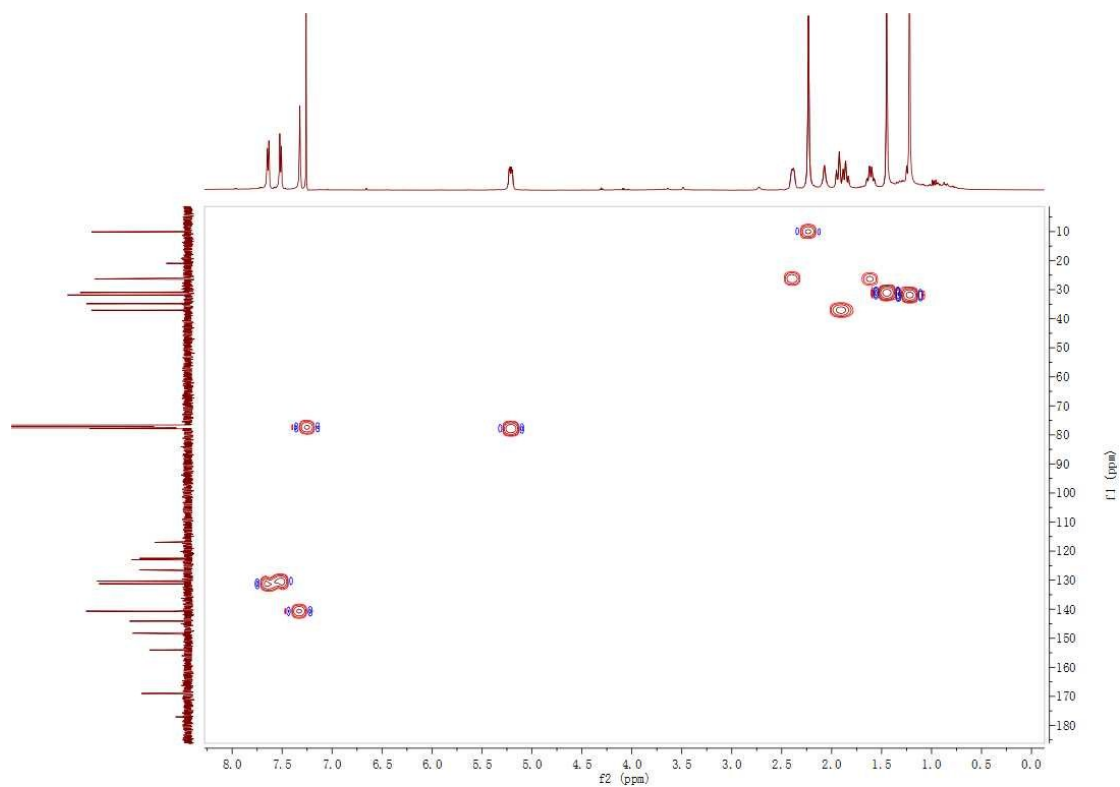


Figure S47. HSQC spectrum of compound **4A/4B** in CDCl_3 (500 MHz)

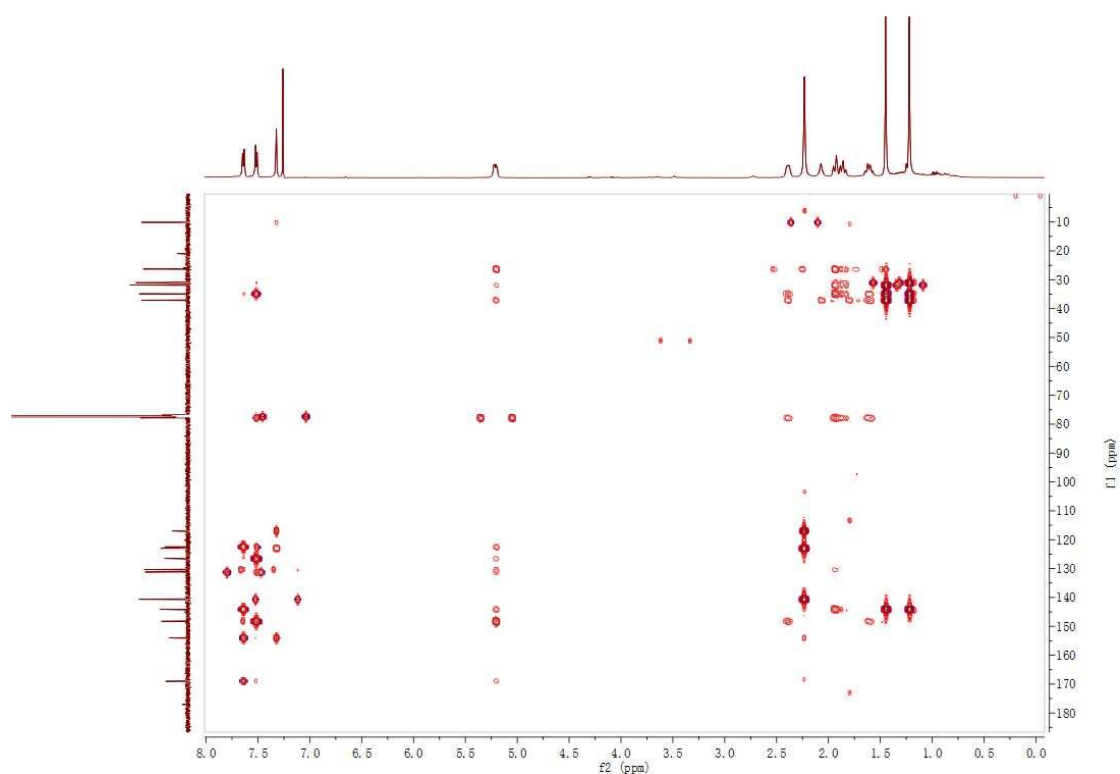


Figure S48. HMBC spectrum of compound **4A/4B** in CDCl_3 (500 MHz)

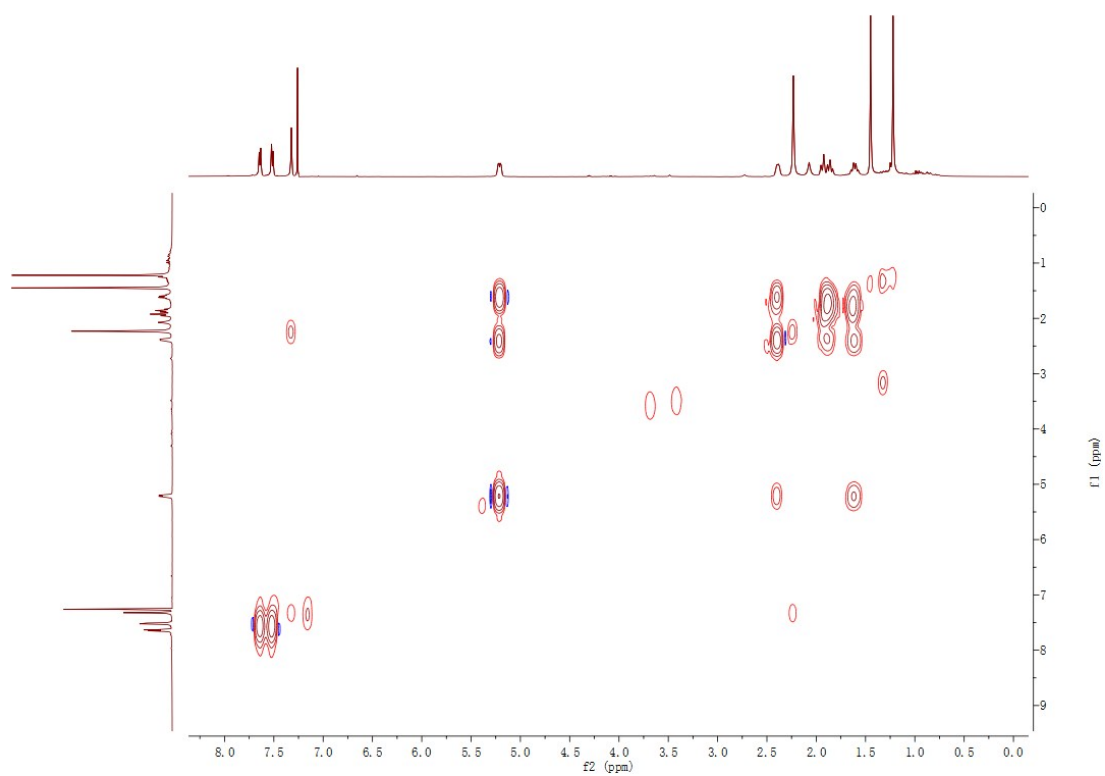


Figure S49. ¹H-¹H COSY spectrum of compound **4A/4B** in CDCl₃ (400 MHz)

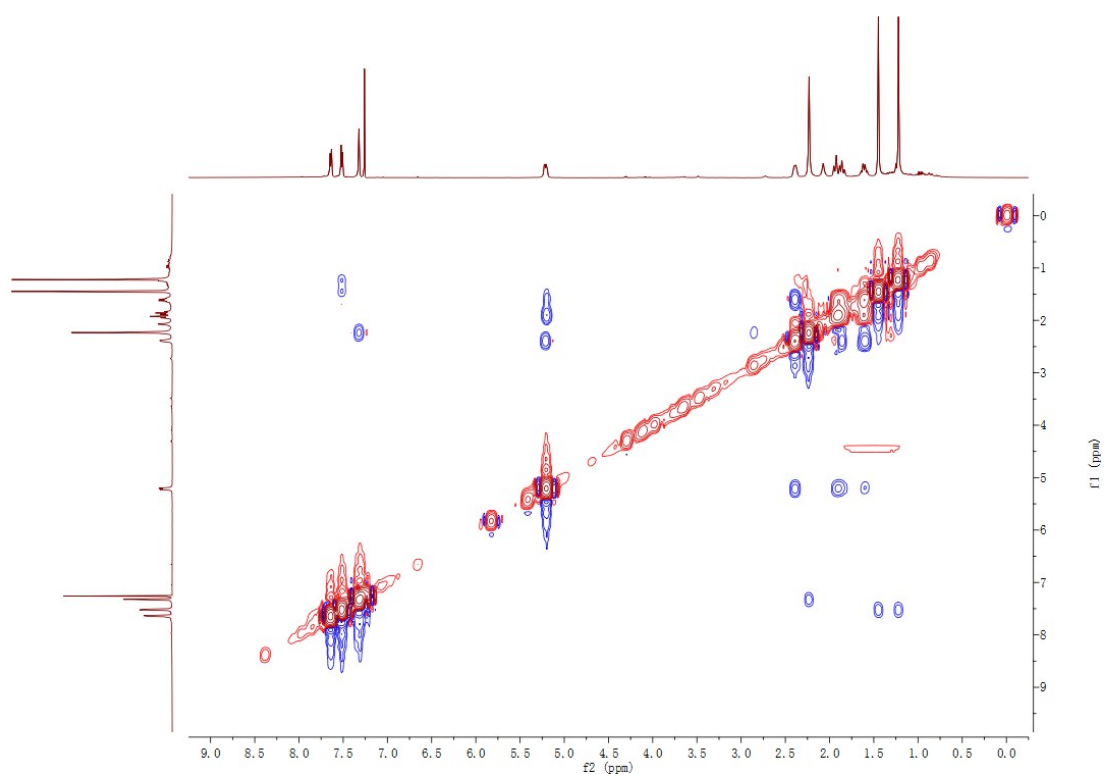


Figure S50. ROESY spectrum of compound **4A/4B** in CDCl₃ (400 MHz)

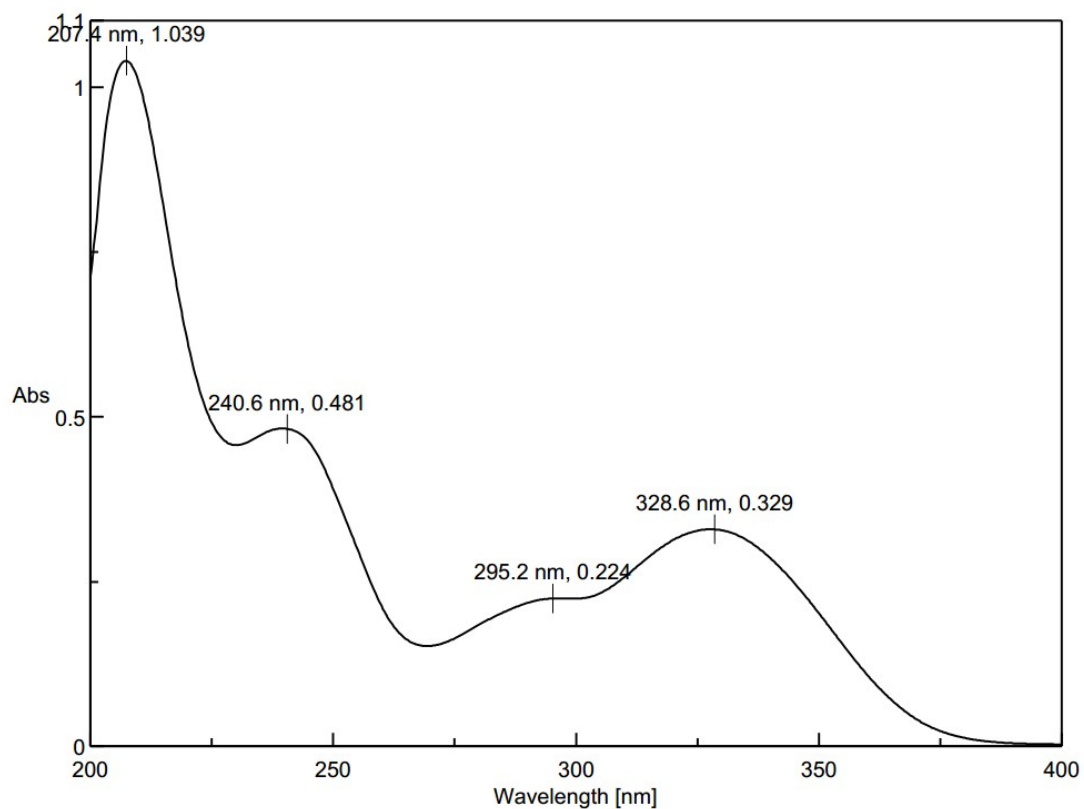


Figure S51. UV spectrum of compound 4A/4B

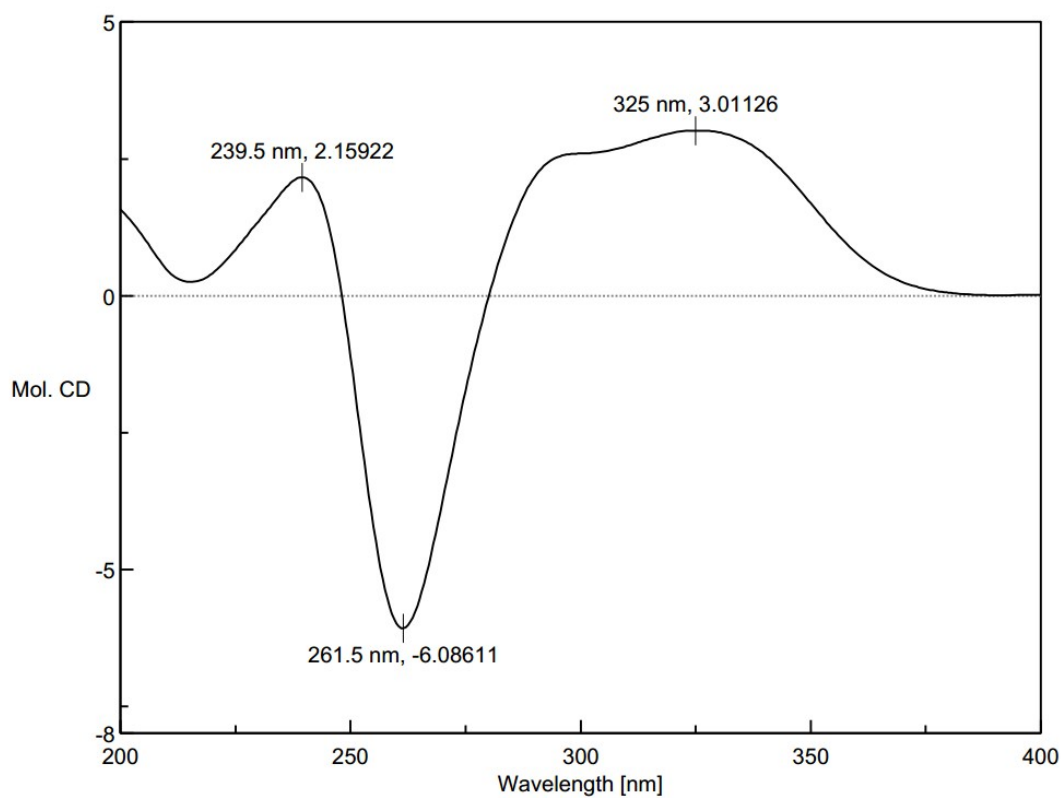


Figure S52. ECD spectrum of compound 4A

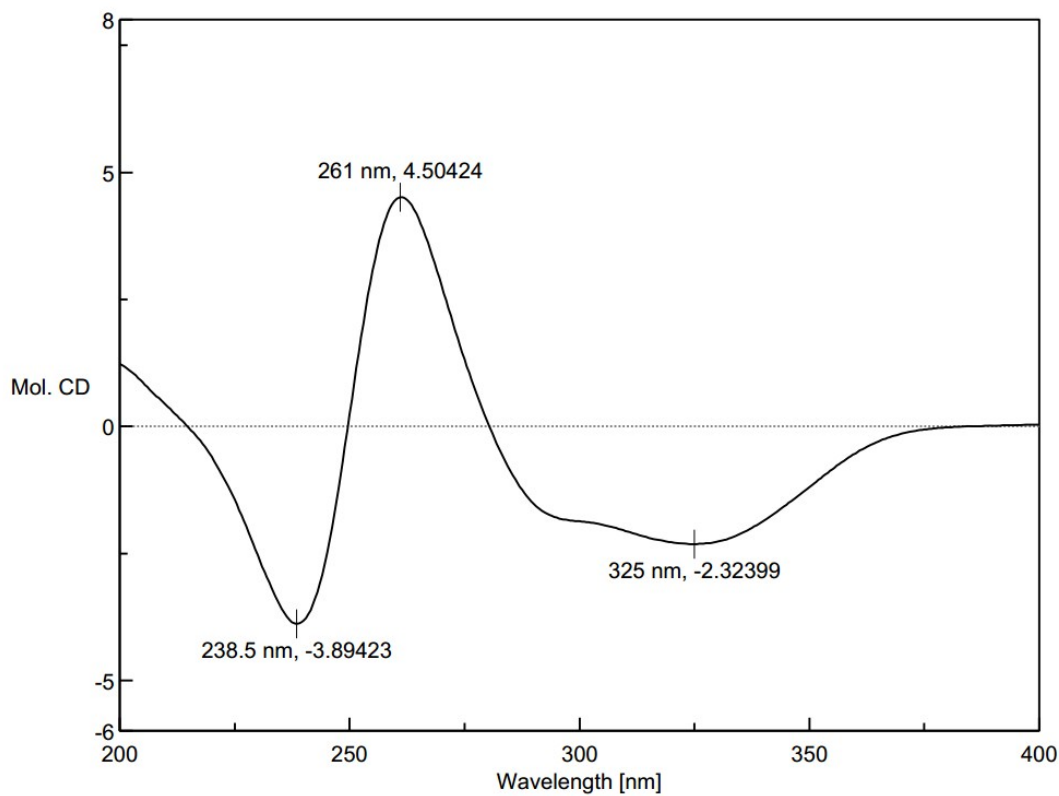


Figure S53. ECD spectrum of compound 4B

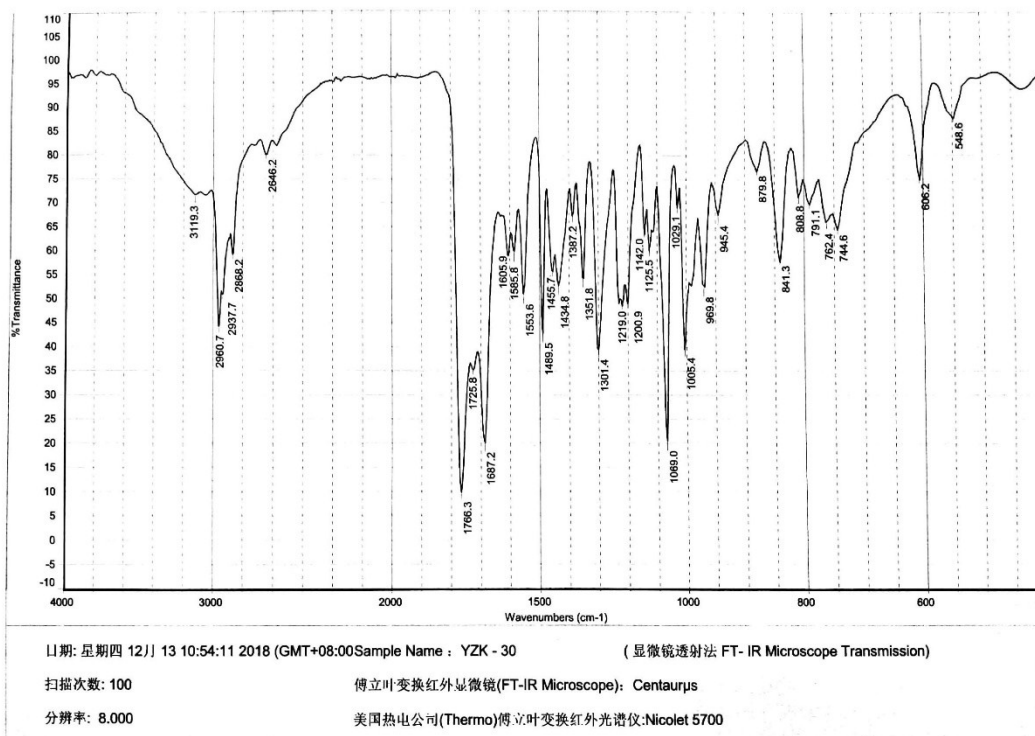
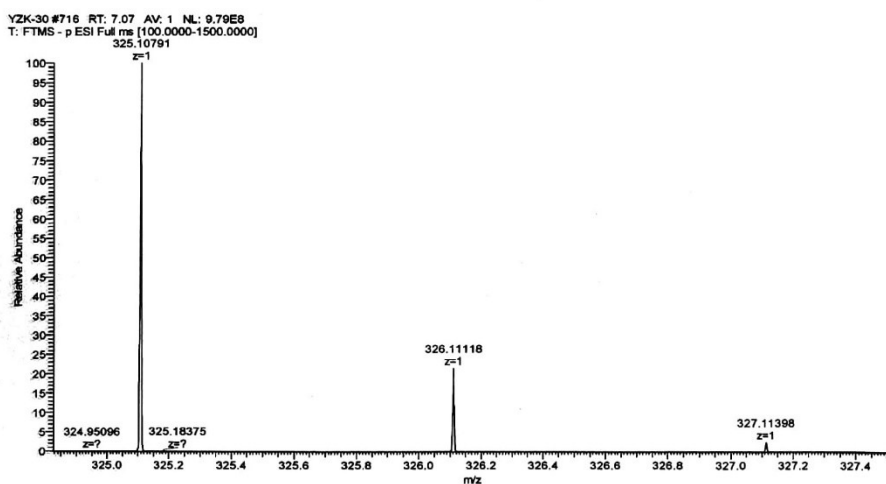


Figure S54. IR spectrum of compound 4A/4B



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
325.10791	325.10815	-0.73	11.5	C19 H17 O5	M-H

Figure S55. HR-ESI-MS spectrum of compound 4A/4B

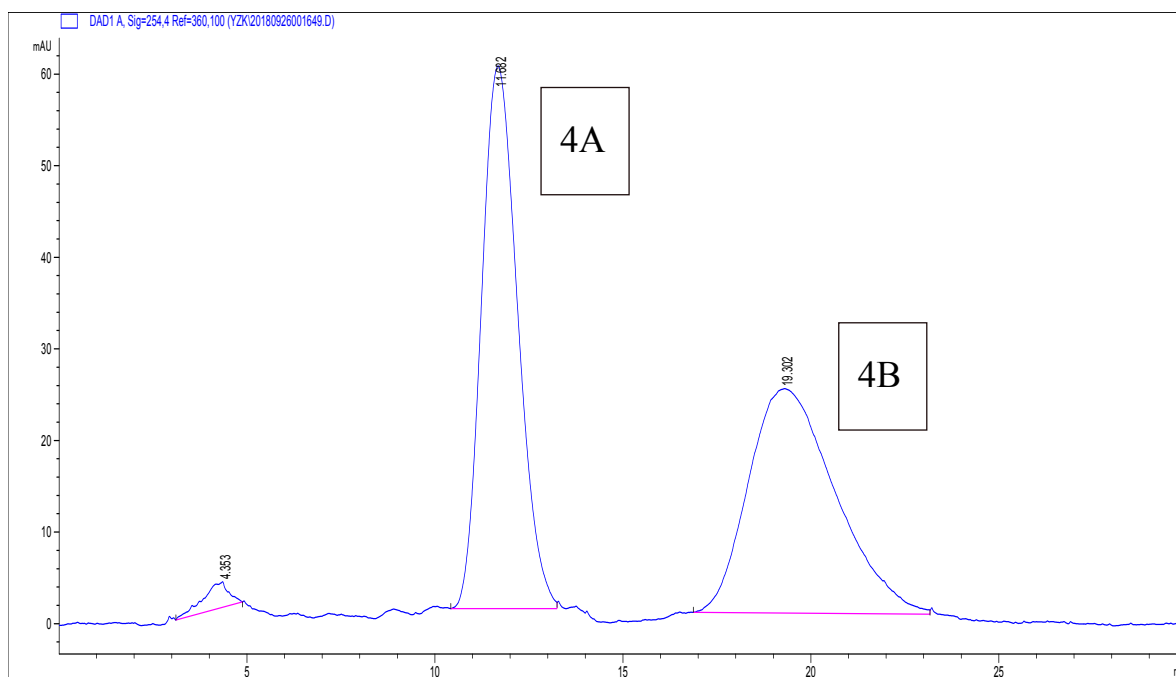


Figure S56. The chiral HPLC chromatogram of 4A/4B

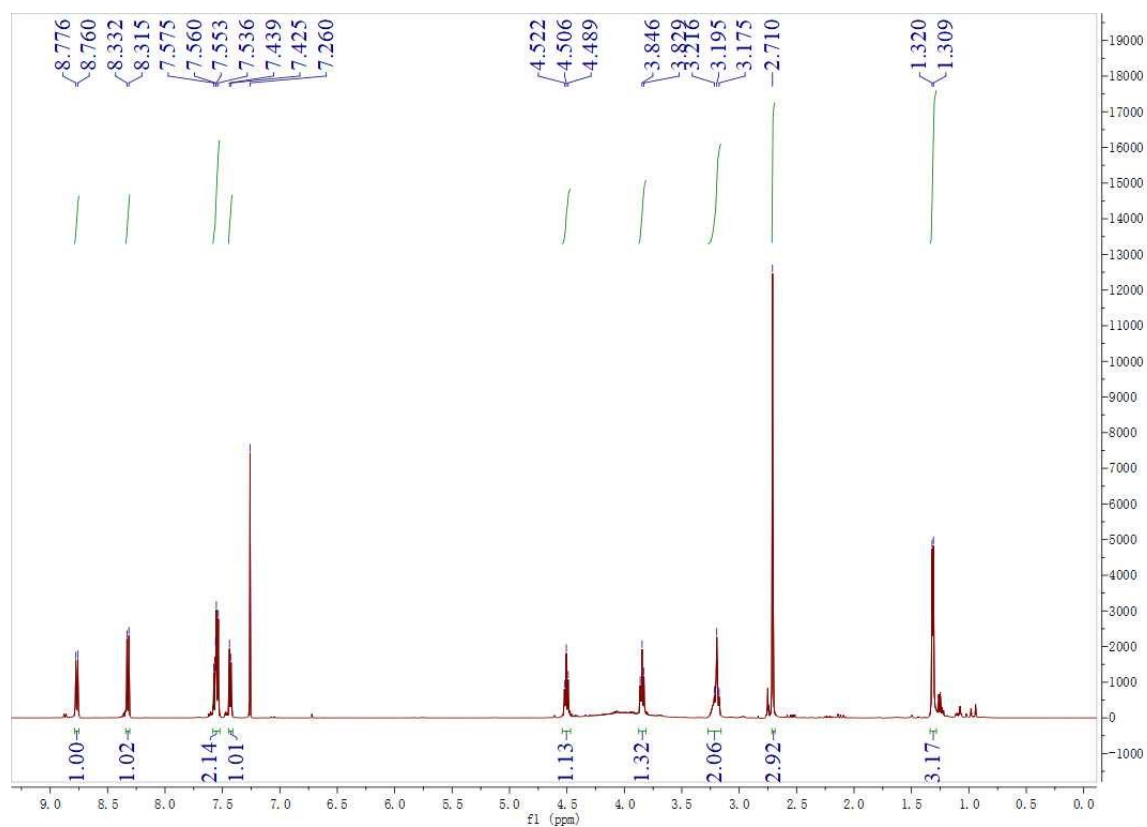


Figure S57. ^1H NMR spectrum of compound **5** in CDCl_3 (500 MHz)

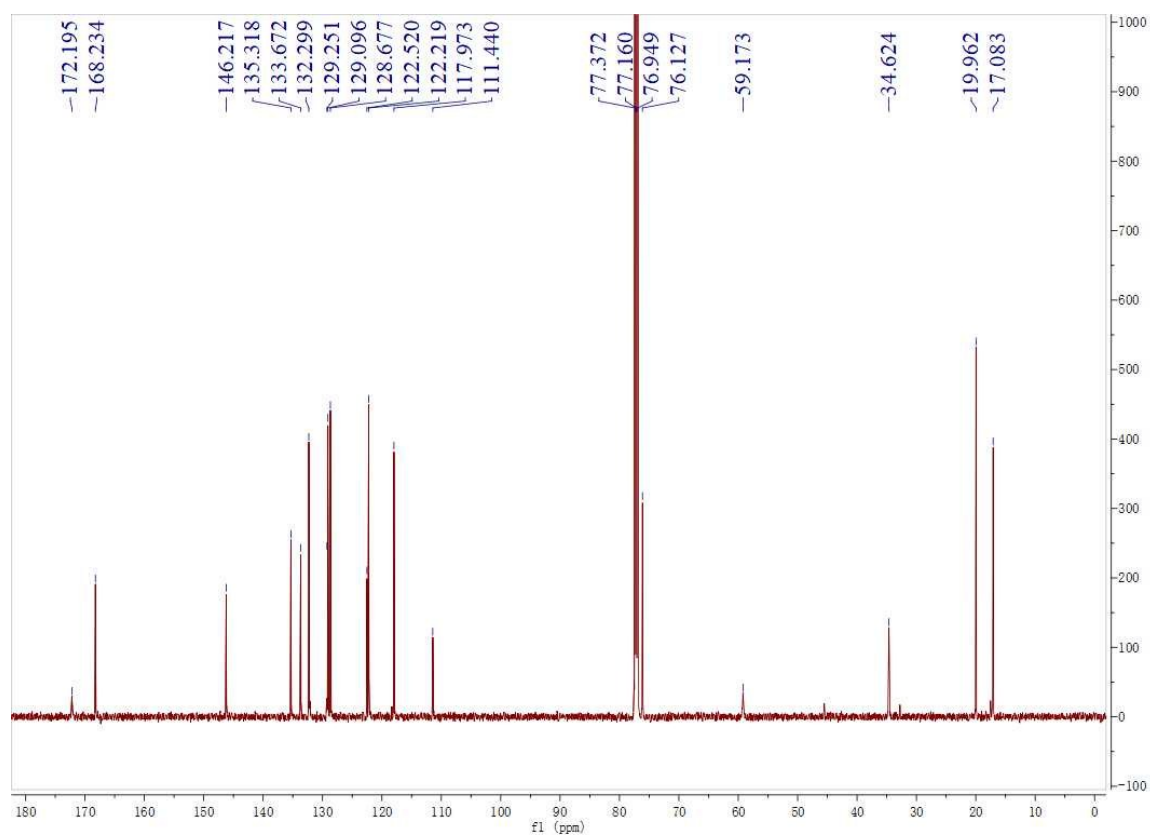


Figure S58. ^{13}C NMR spectrum of compound **5** in CDCl_3 (150 MHz)

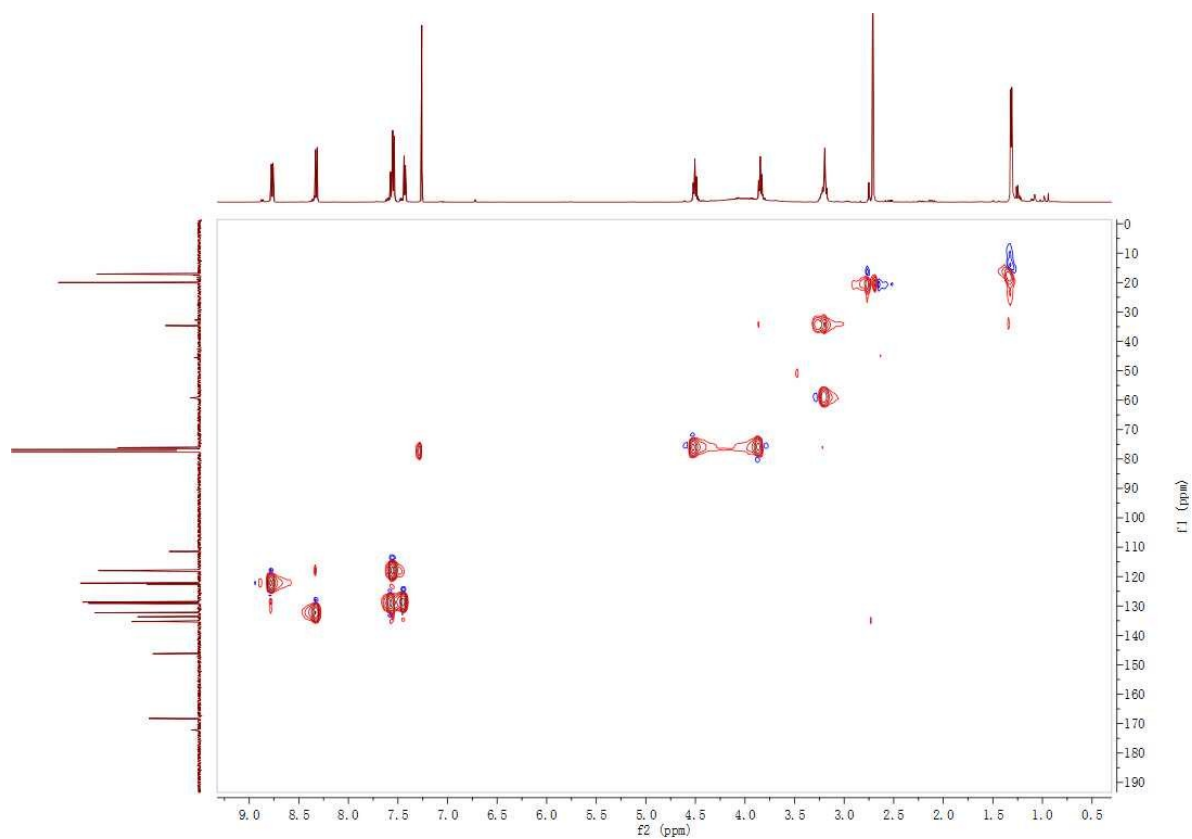


Figure S59. HSQC spectrum of compound **5** in CDCl₃ (500 MHz)

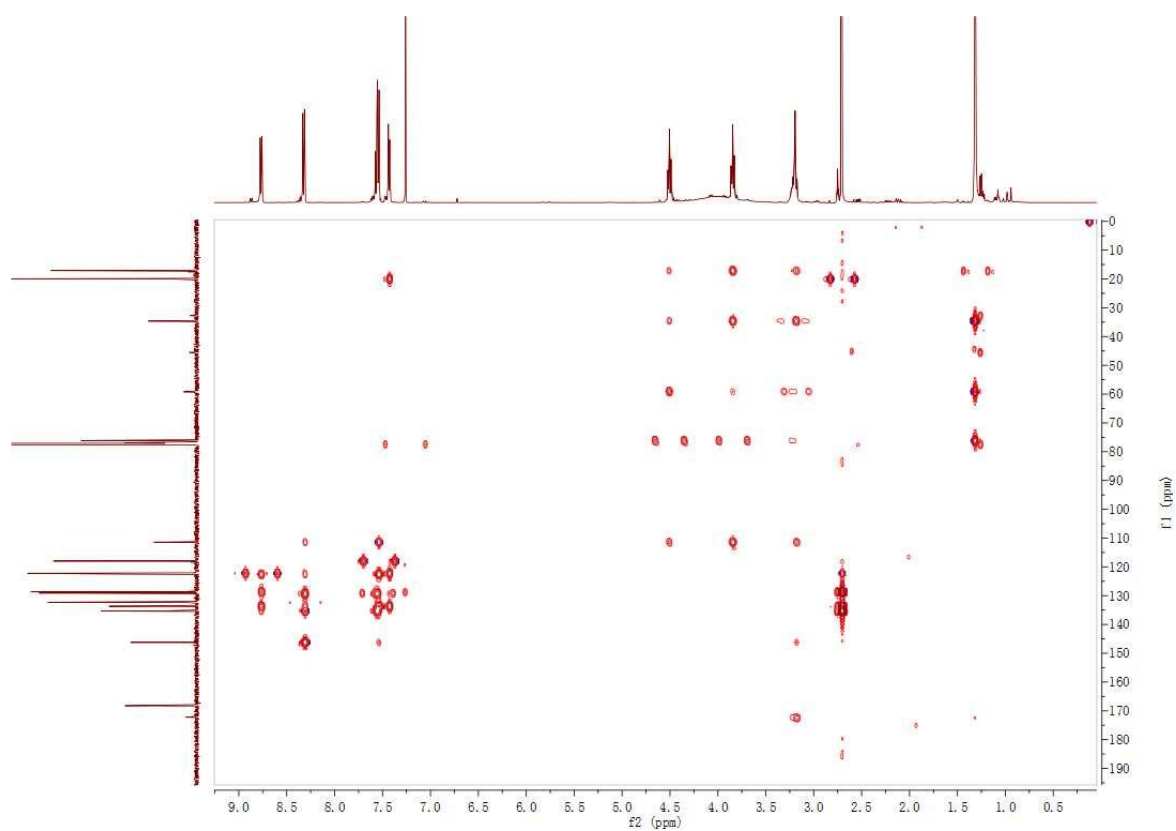


Figure S60. HMBC spectrum of compound **5** in CDCl₃ (500 MHz)

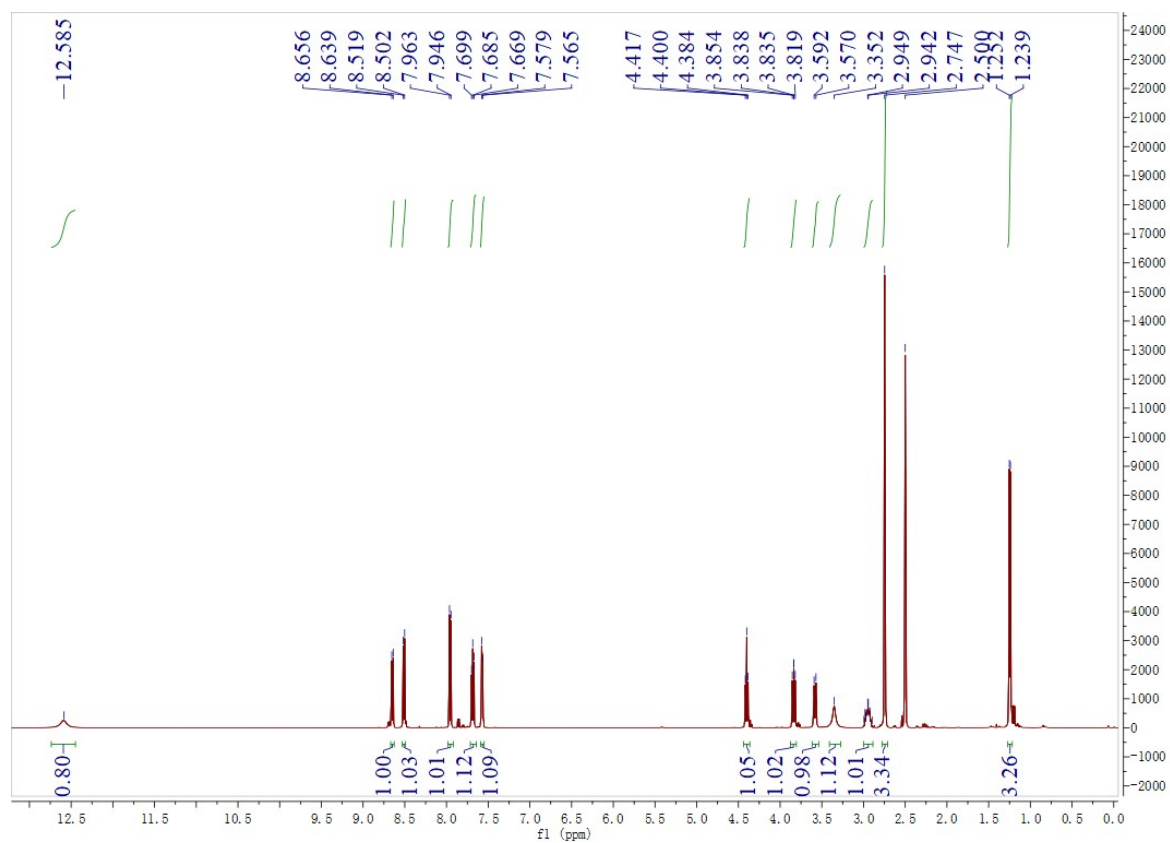


Figure S61. ^1H NMR spectrum of compound **5** in $\text{DMSO-}d_6$ (500 MHz)

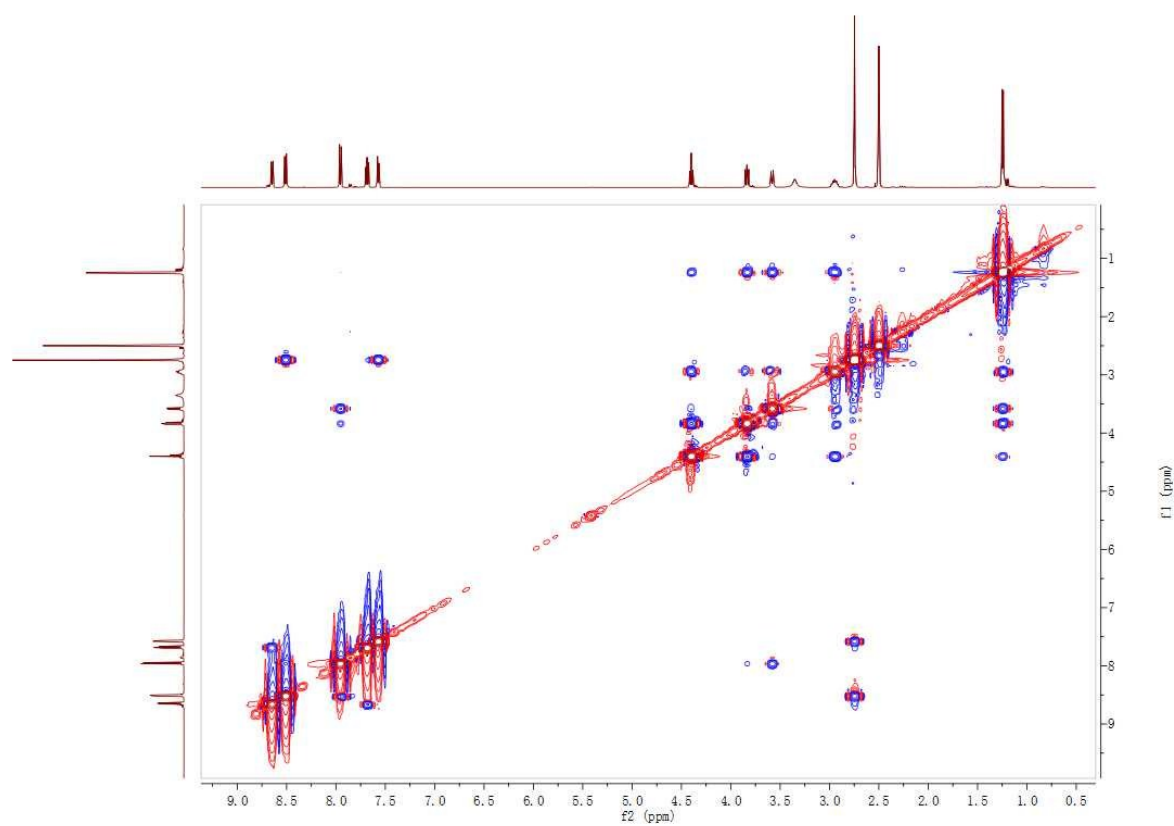


Figure S62. ROESY spectrum of compound **5** in $\text{DMSO-}d_6$ (500 MHz)

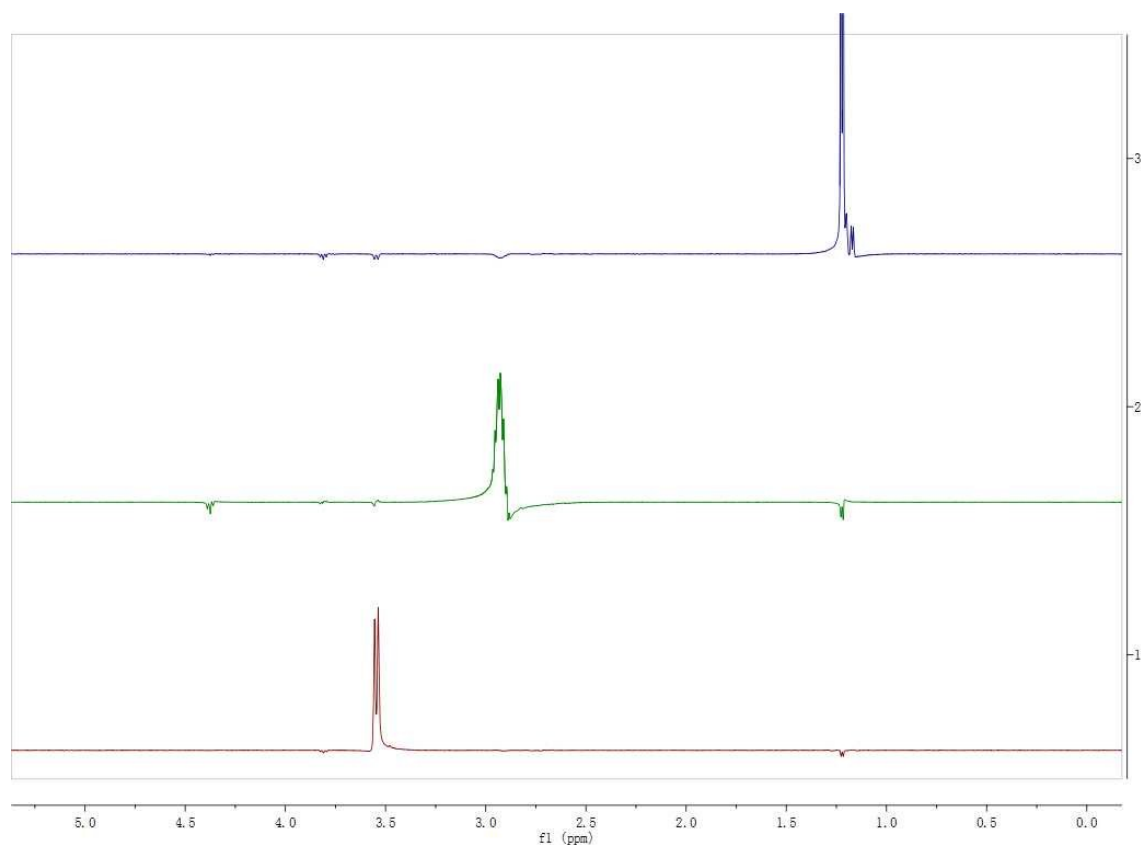


Figure S63. 1D NOESY spectrum of compound **5** in DMSO- d_6 (500 MHz)

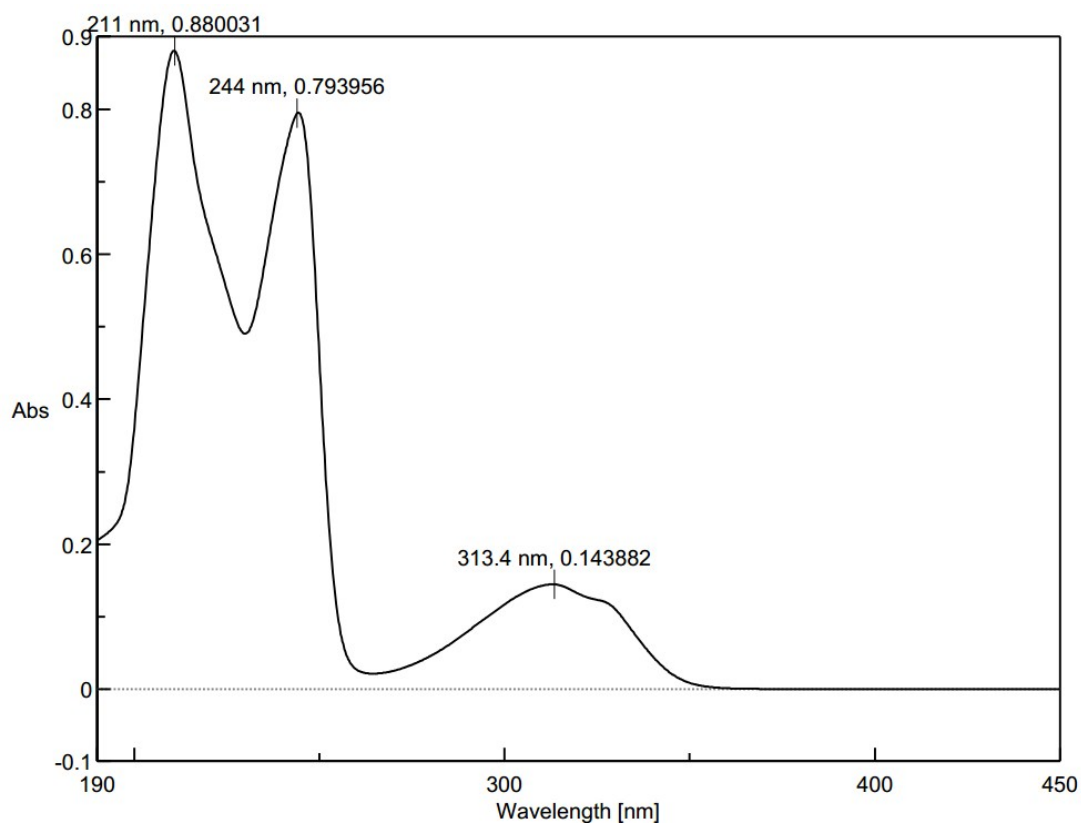


Figure S64. UV spectrum of compound **5**

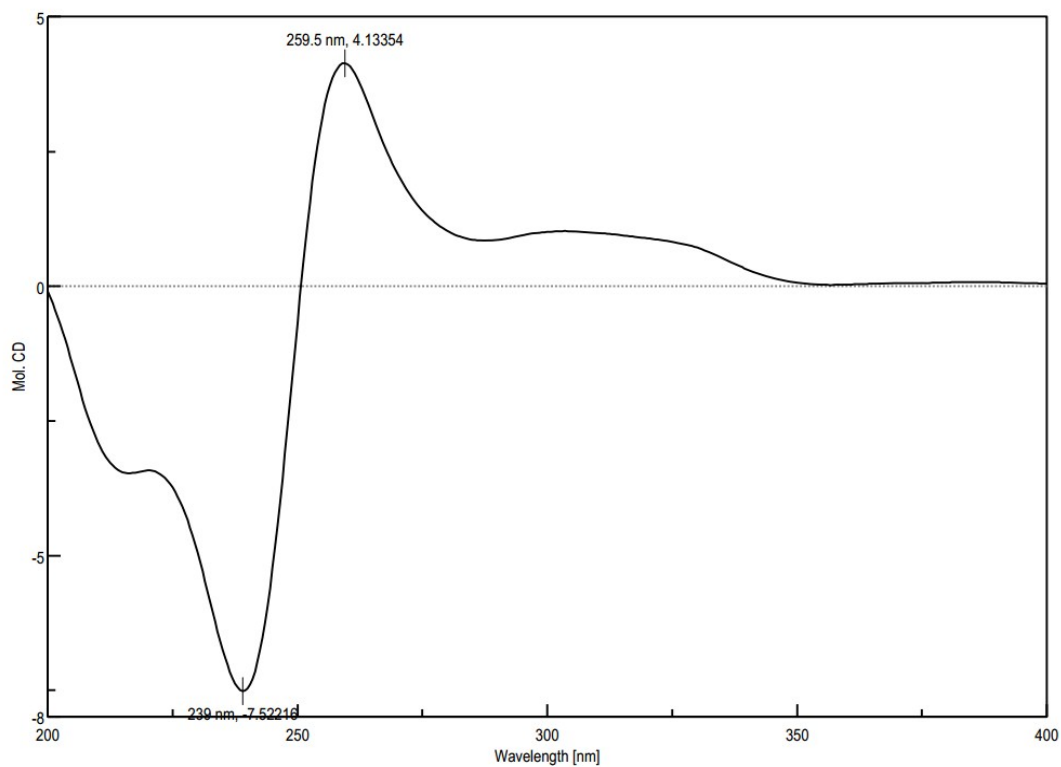


Figure S65. ECD spectrum of compound 5

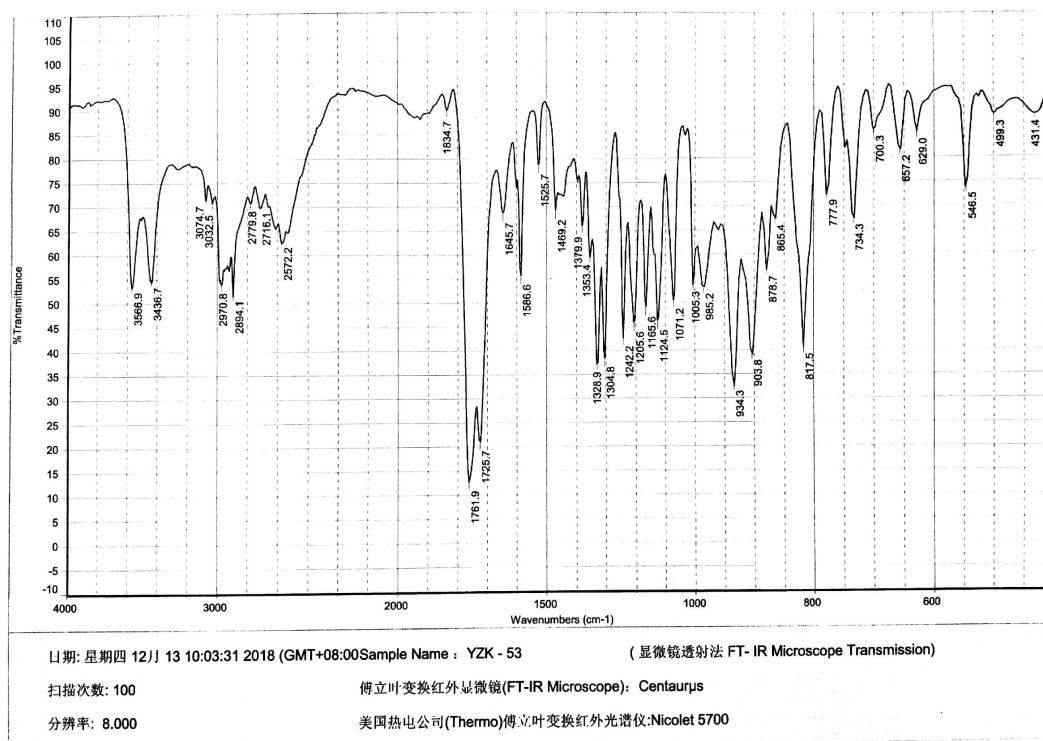
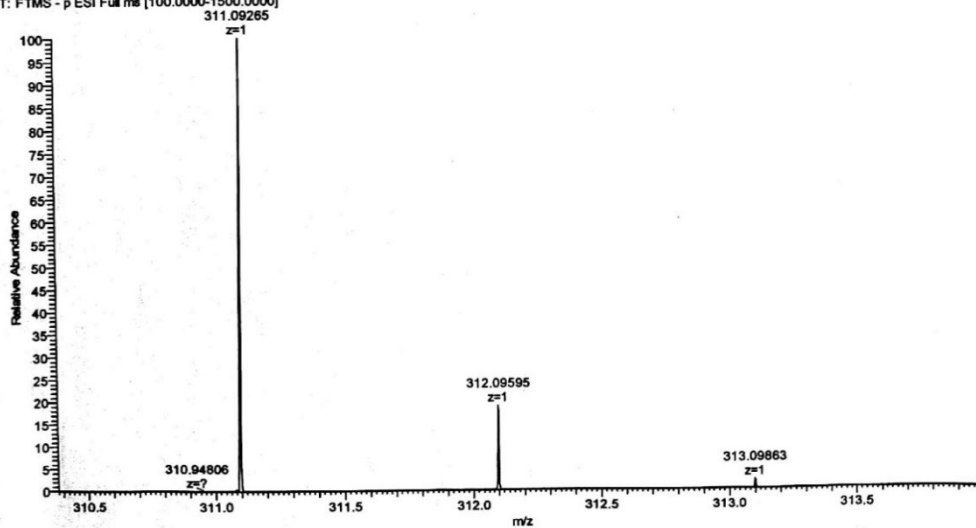


Figure S66. IR spectrum of compound 5

YZK-53 #672 RT: 6.72 AV: 1 NL: 8.67E8
 T: FTMS - p ESI Full ms [100.0000-1500.0000]



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
311.09265	311.09250	0.49	11.5	C18 H15 O5	M-H

Figure S67. HR-ESI-MS spectrum of compound 5

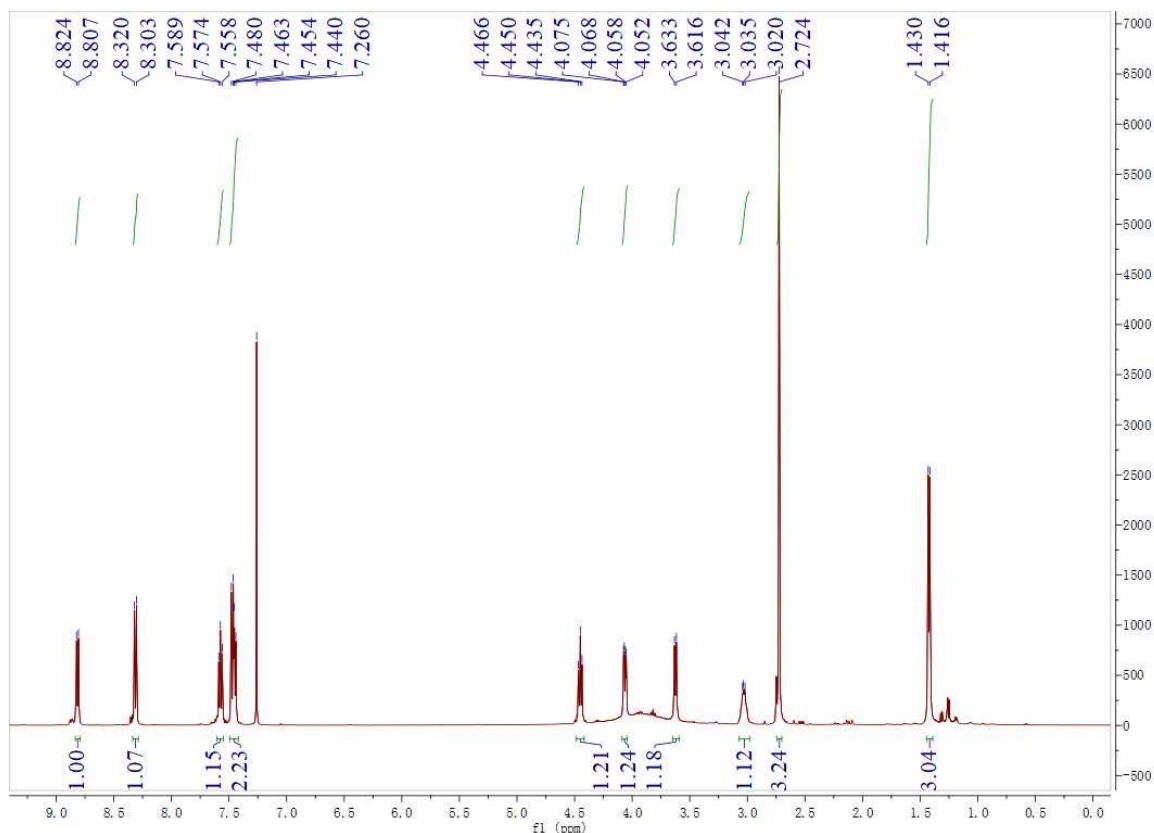


Figure S68. ¹H NMR spectrum of compound 6 in CDCl₃ (500 MHz)

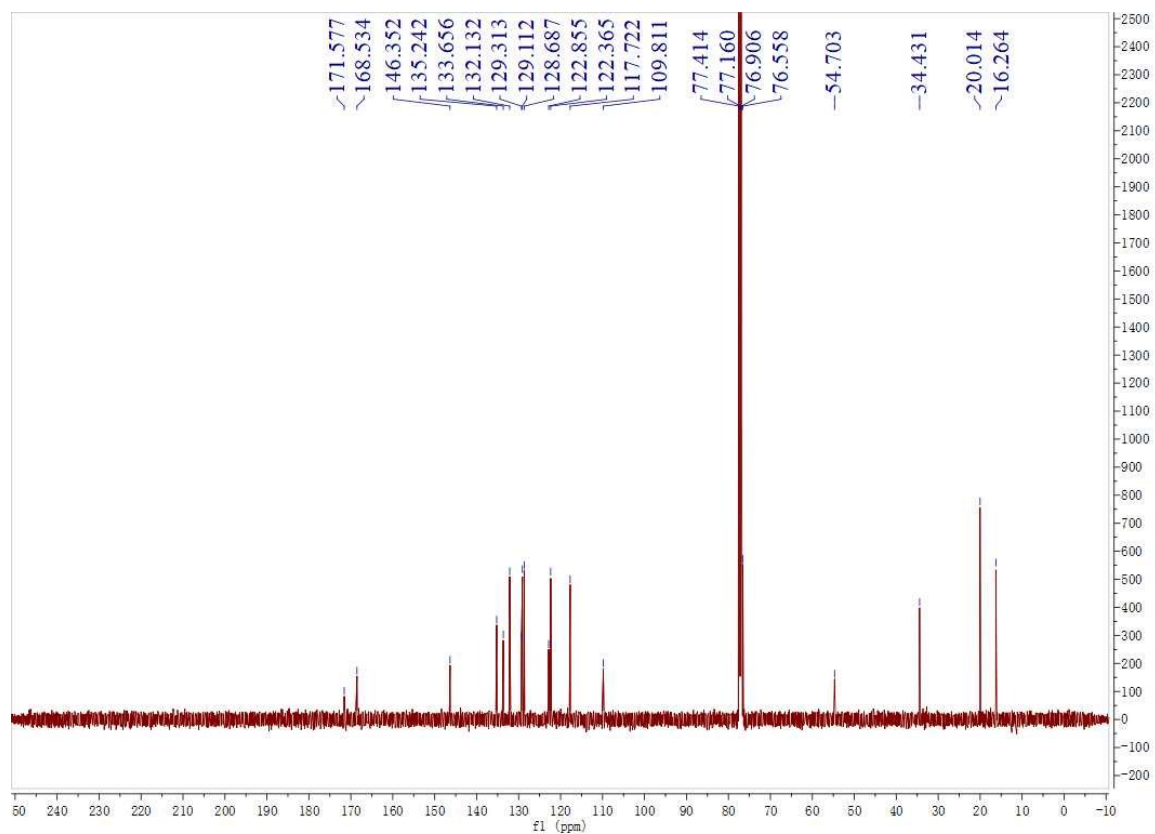


Figure S69. ^{13}C NMR spectrum of compound **6** in CDCl_3 (150 MHz)

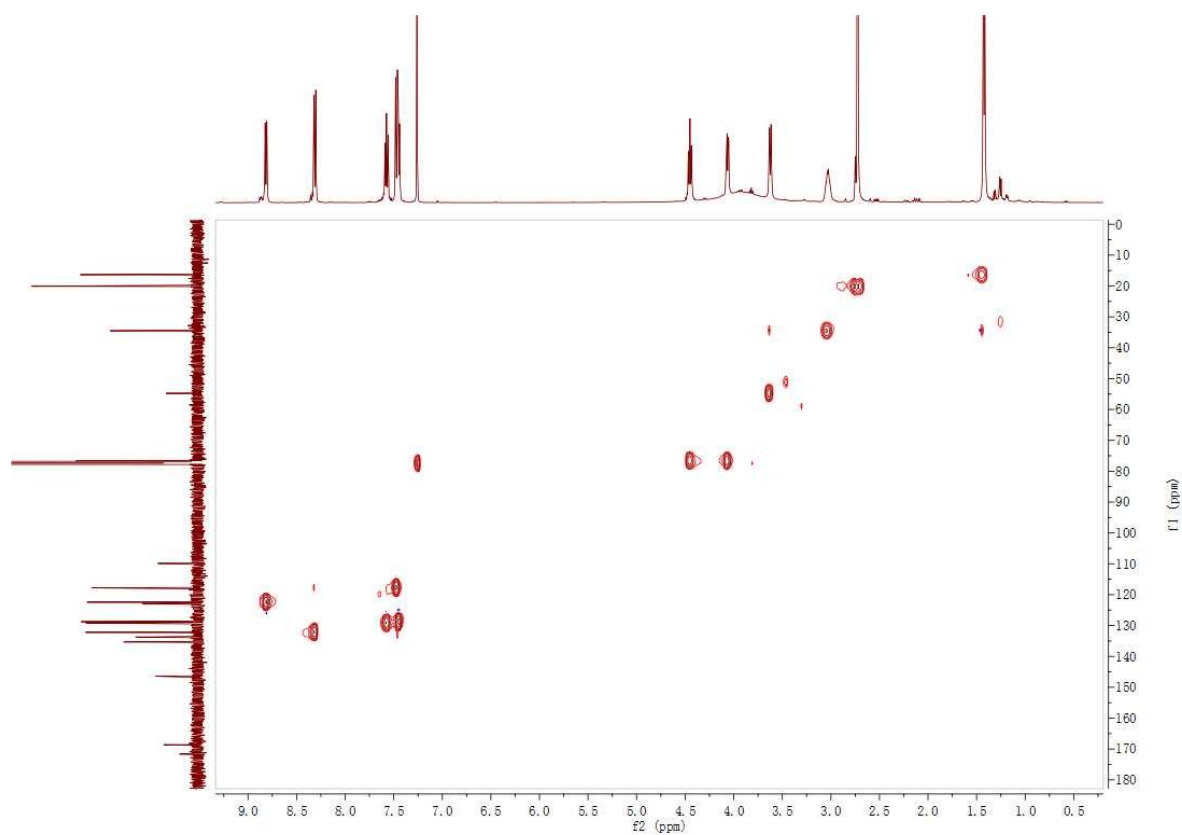


Figure S70. HSQC spectrum of compound **6** in CDCl_3 (500 MHz)

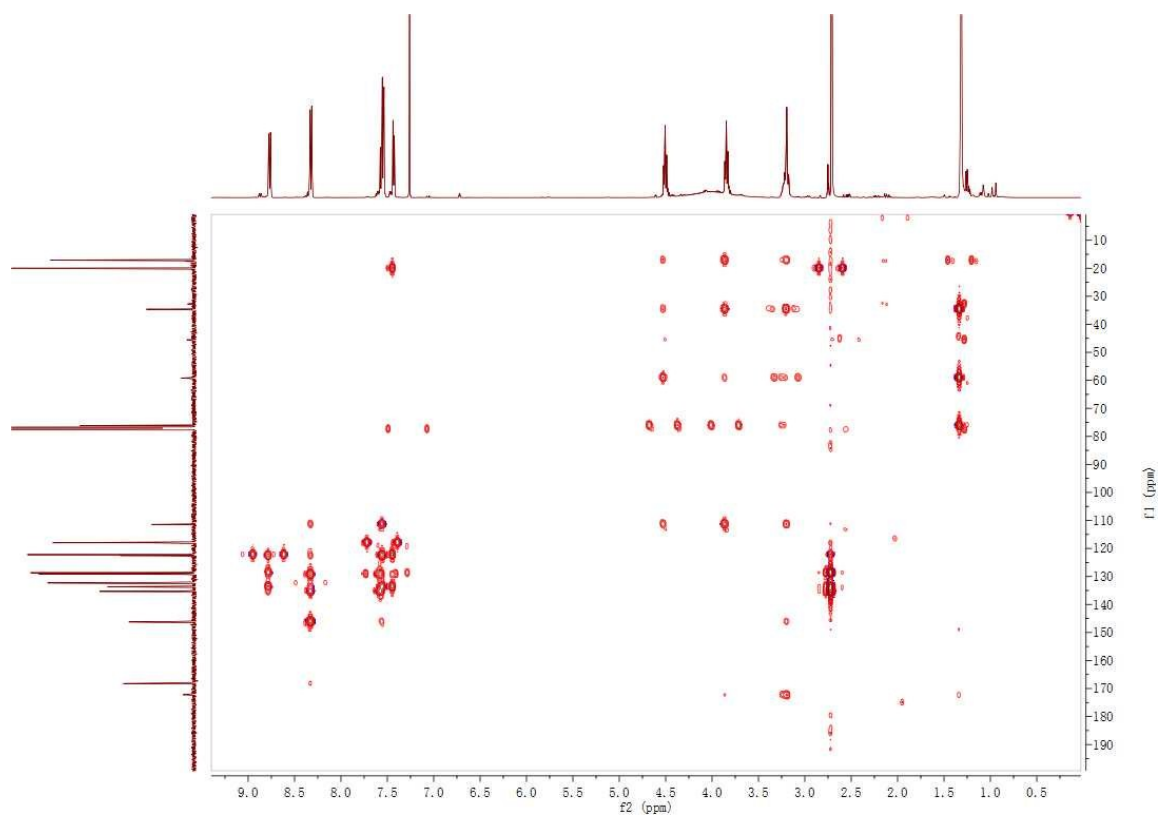


Figure S71. HMBC spectrum of compound **6** in CDCl₃ (500 MHz)

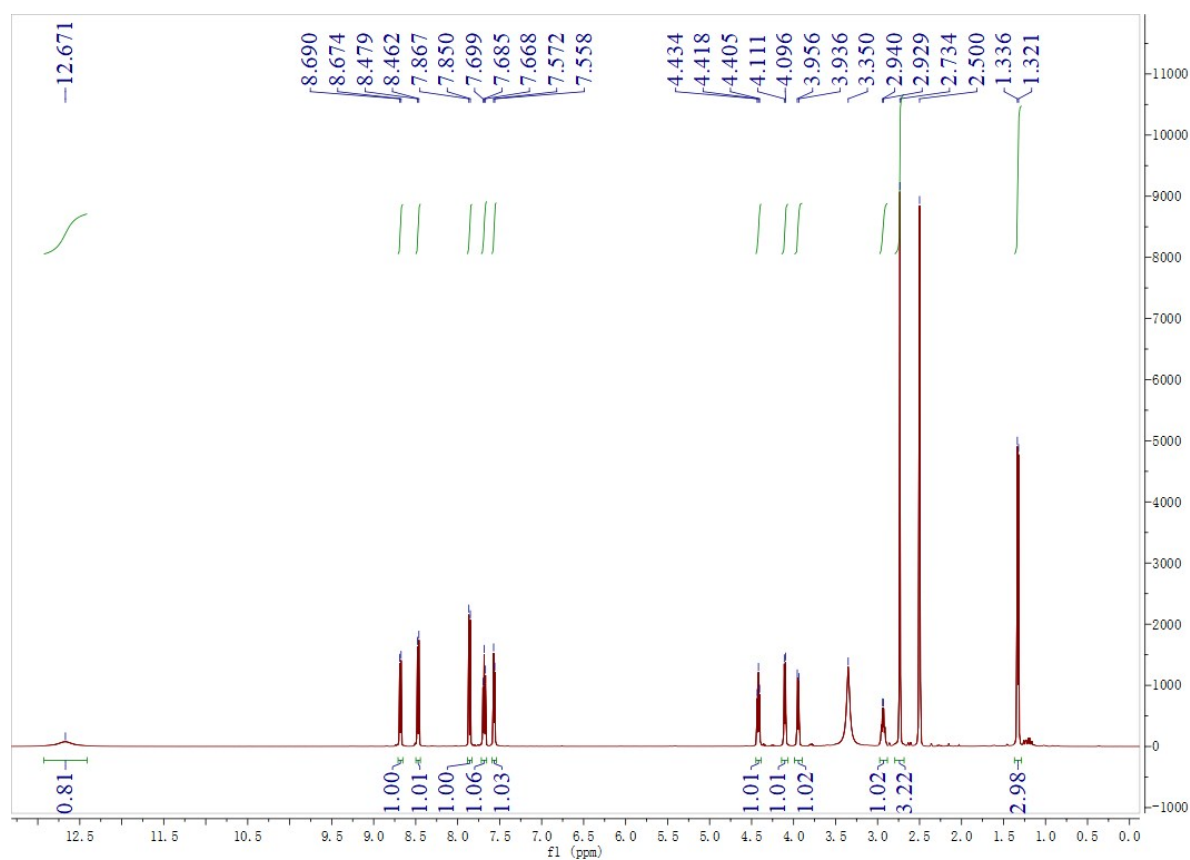


Figure S72. ¹H NMR spectrum of compound **6** in DMSO-*d*₆ (500 MHz)

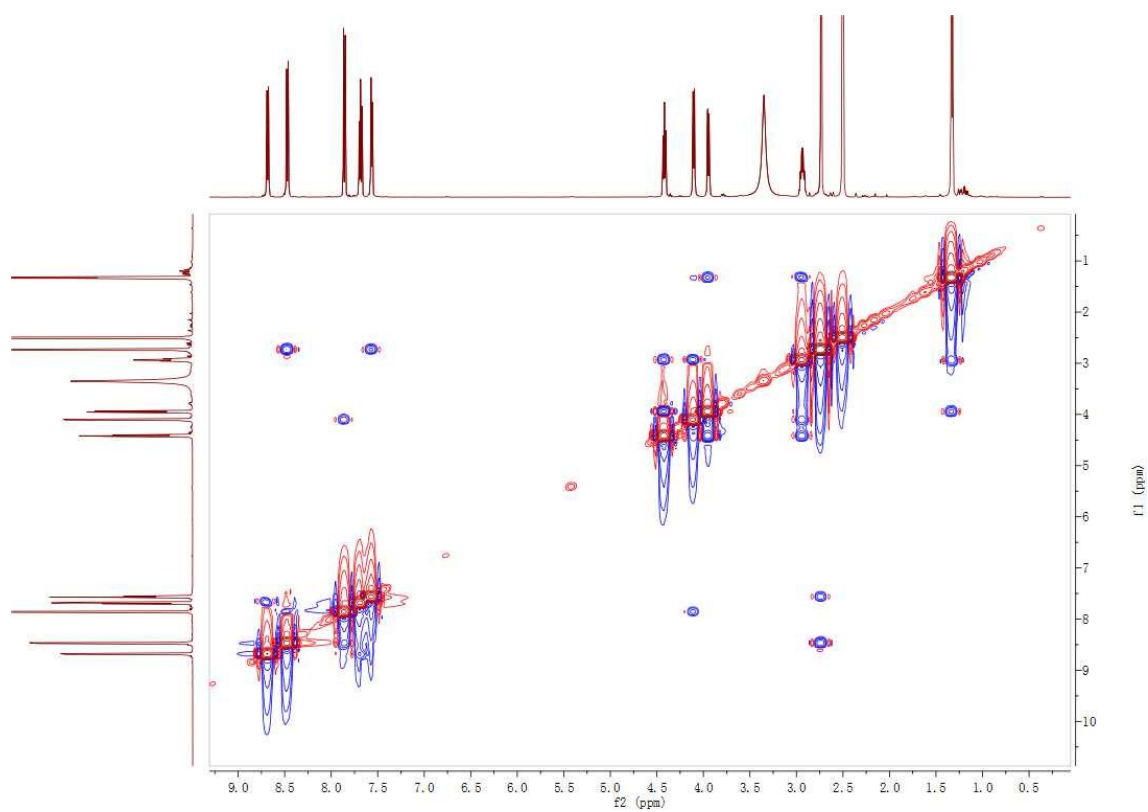


Figure S73. ROESY spectrum of compound **6** in DMSO- d_6 (500 MHz)

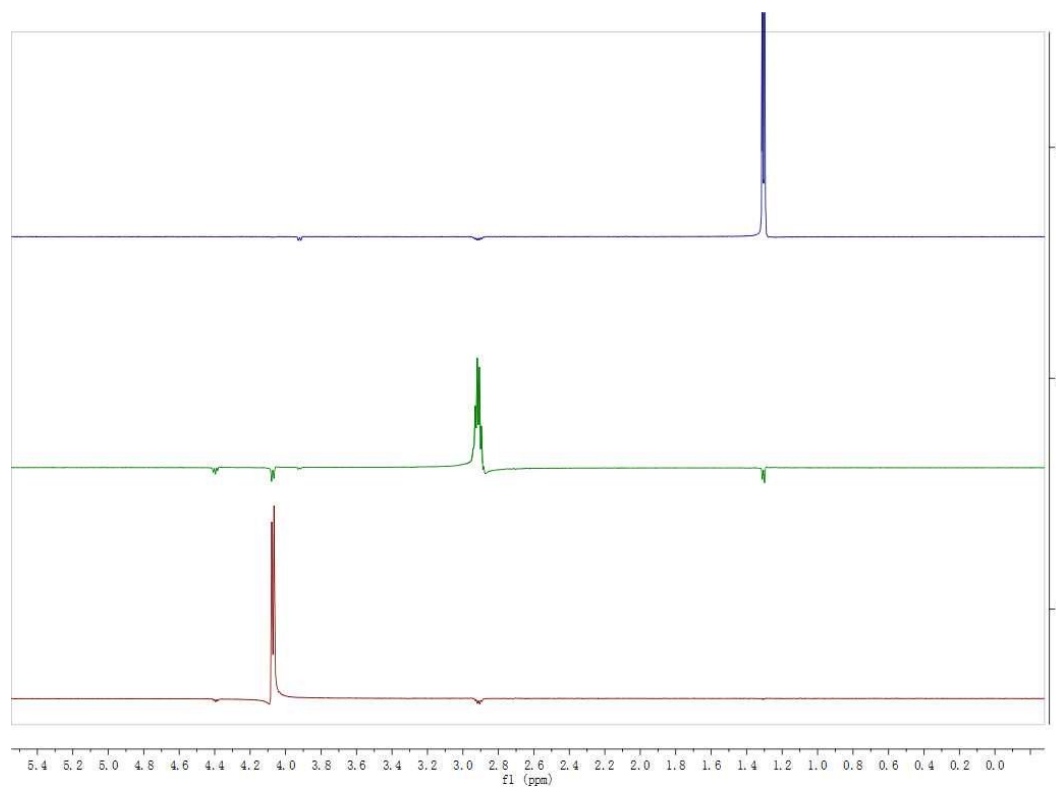


Figure S74. 1D NOESY spectrum of compound **6** in DMSO- d_6 (500 MHz)

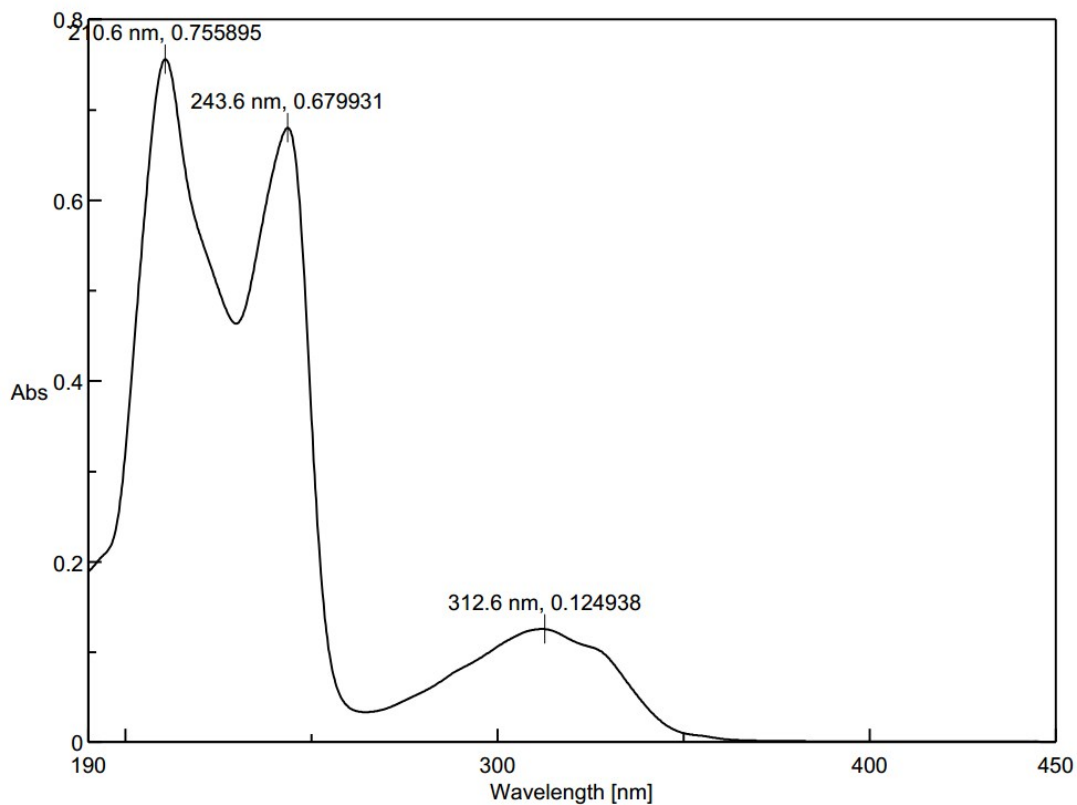


Figure S75. UV spectrum of compound 6

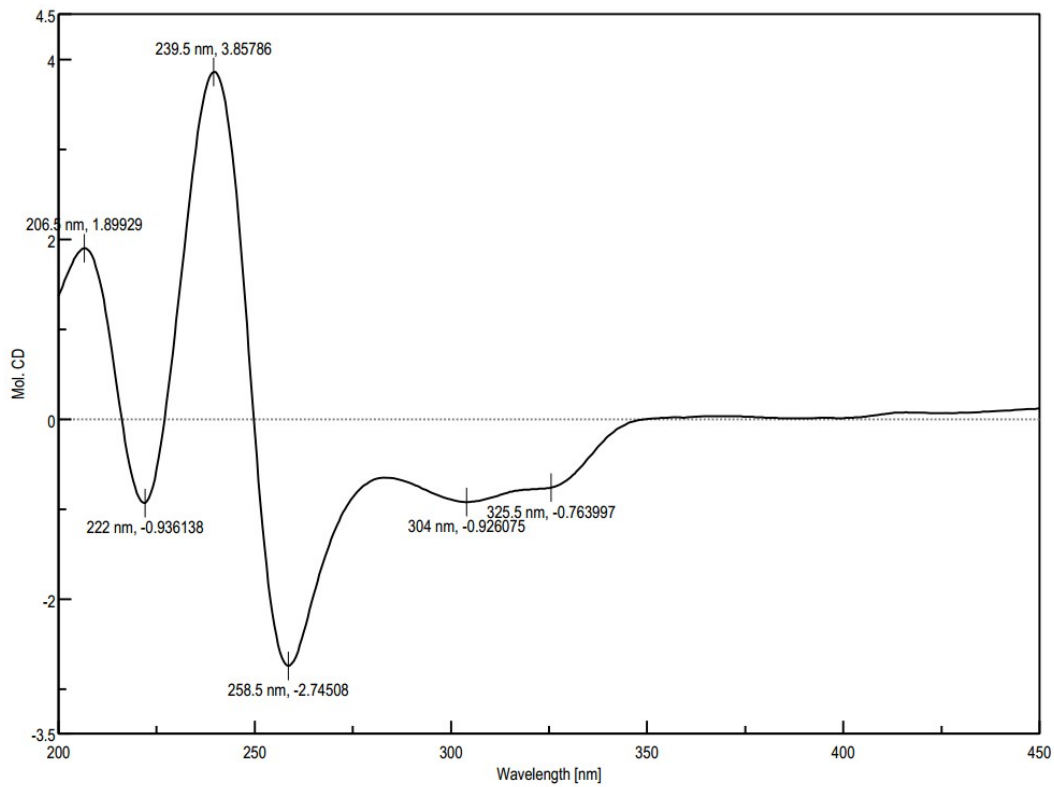


Figure S76. ECD spectrum of compound 6

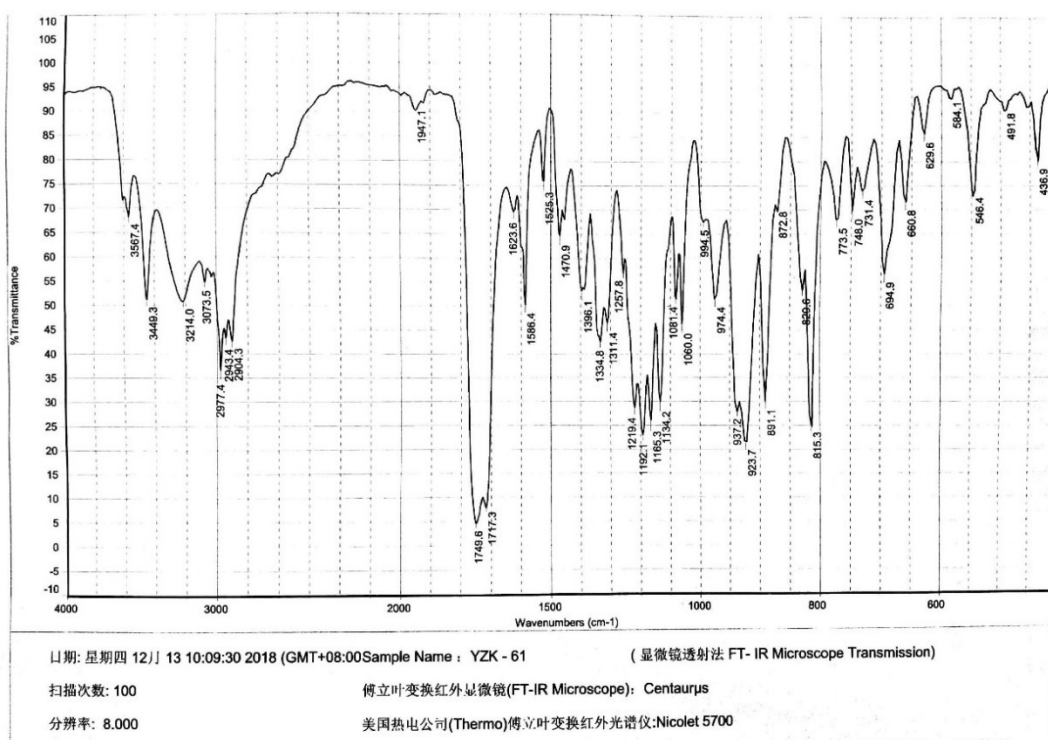
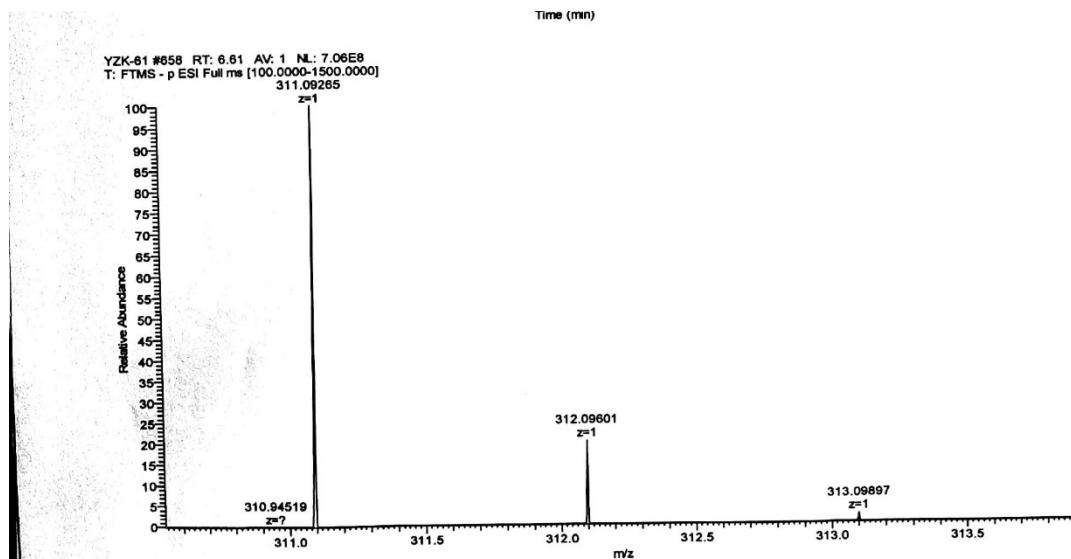


Figure S77. IR spectrum of compound 6



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
311.09265	311.09250	0.49	11.5	C18 H15 O5 M-H

Figure S78. HR-ESI-MS spectrum of compound 6

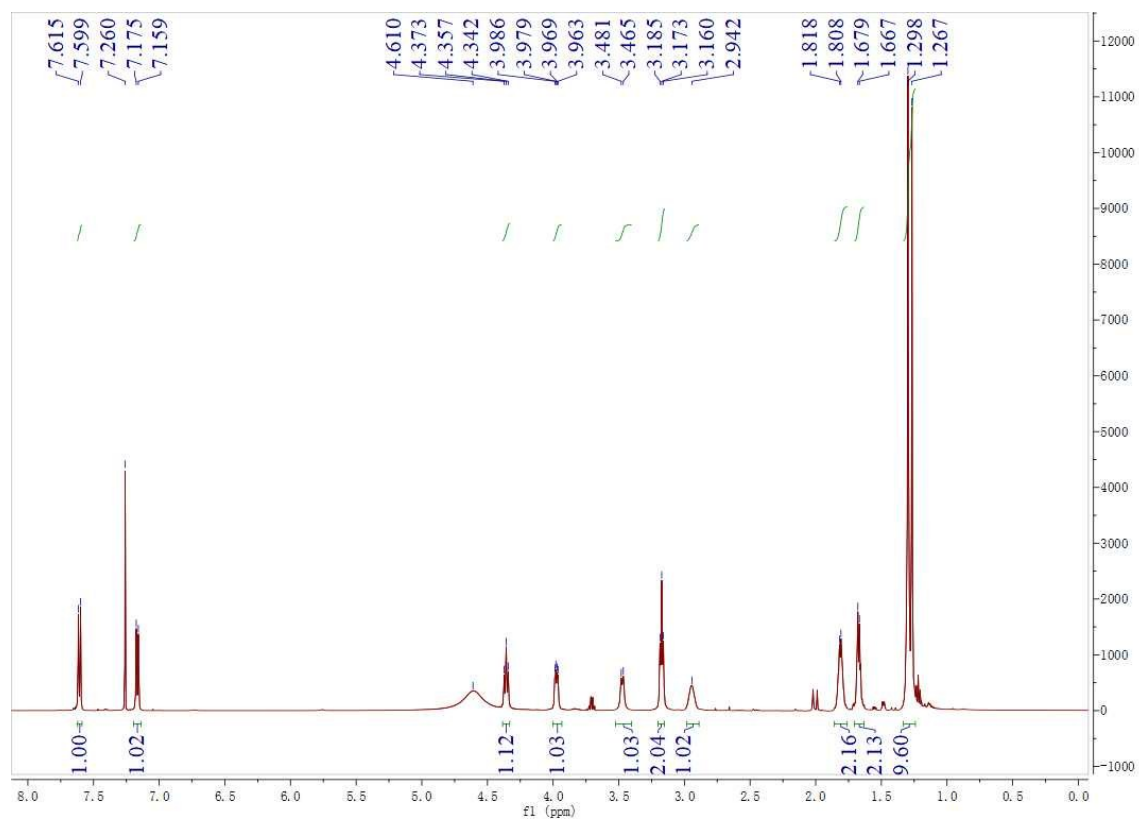


Figure S79. ^1H NMR spectrum of compound **7** in CDCl_3 (500 MHz)

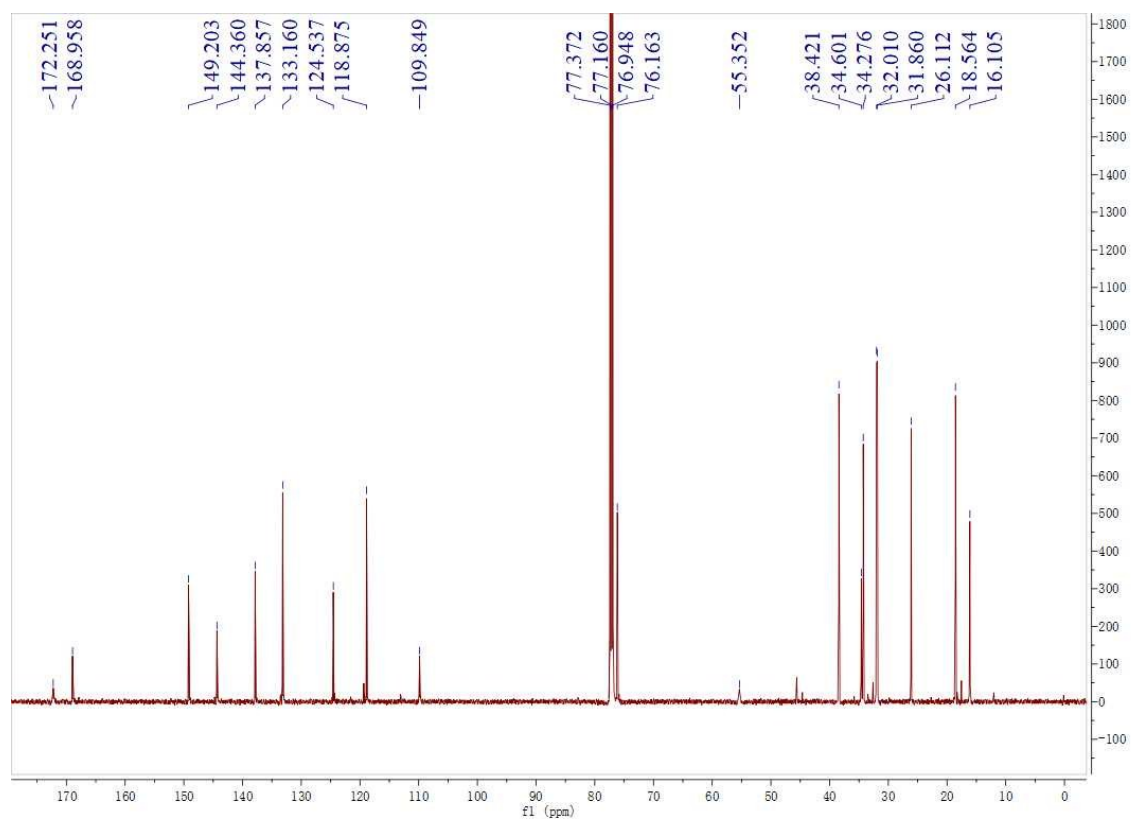


Figure S80. ^{13}C NMR spectrum of compound **7** in CDCl_3 (150 MHz)

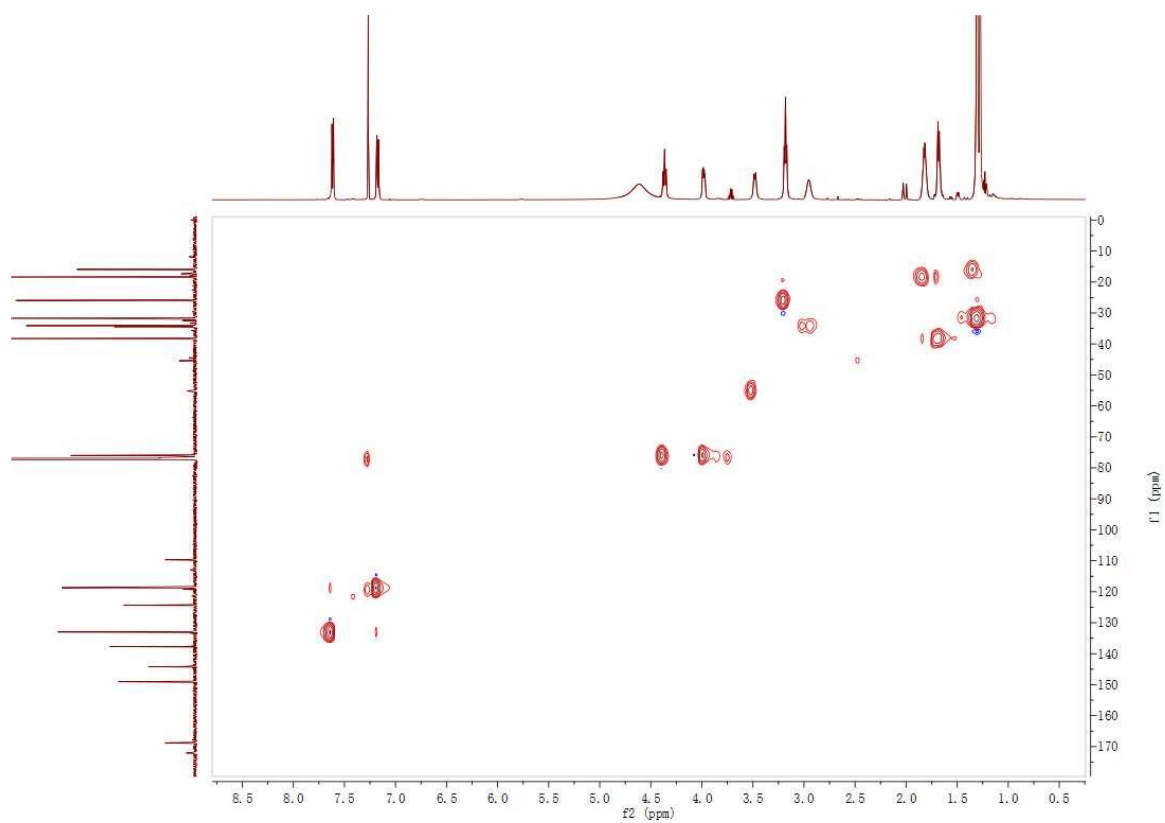


Figure S81. HSQC spectrum of compound **7** in CDCl₃ (500 MHz)

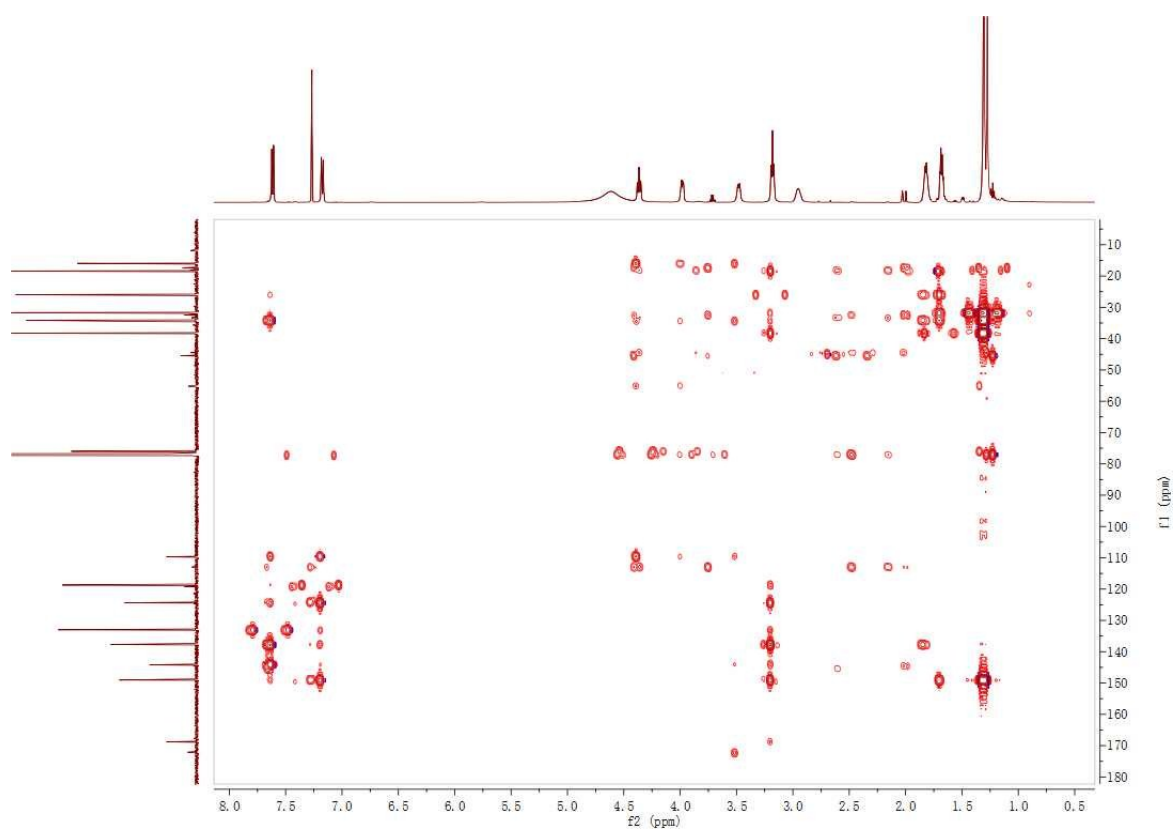


Figure S82. HMBC spectrum of compound **7** in CDCl₃ (500 MHz)

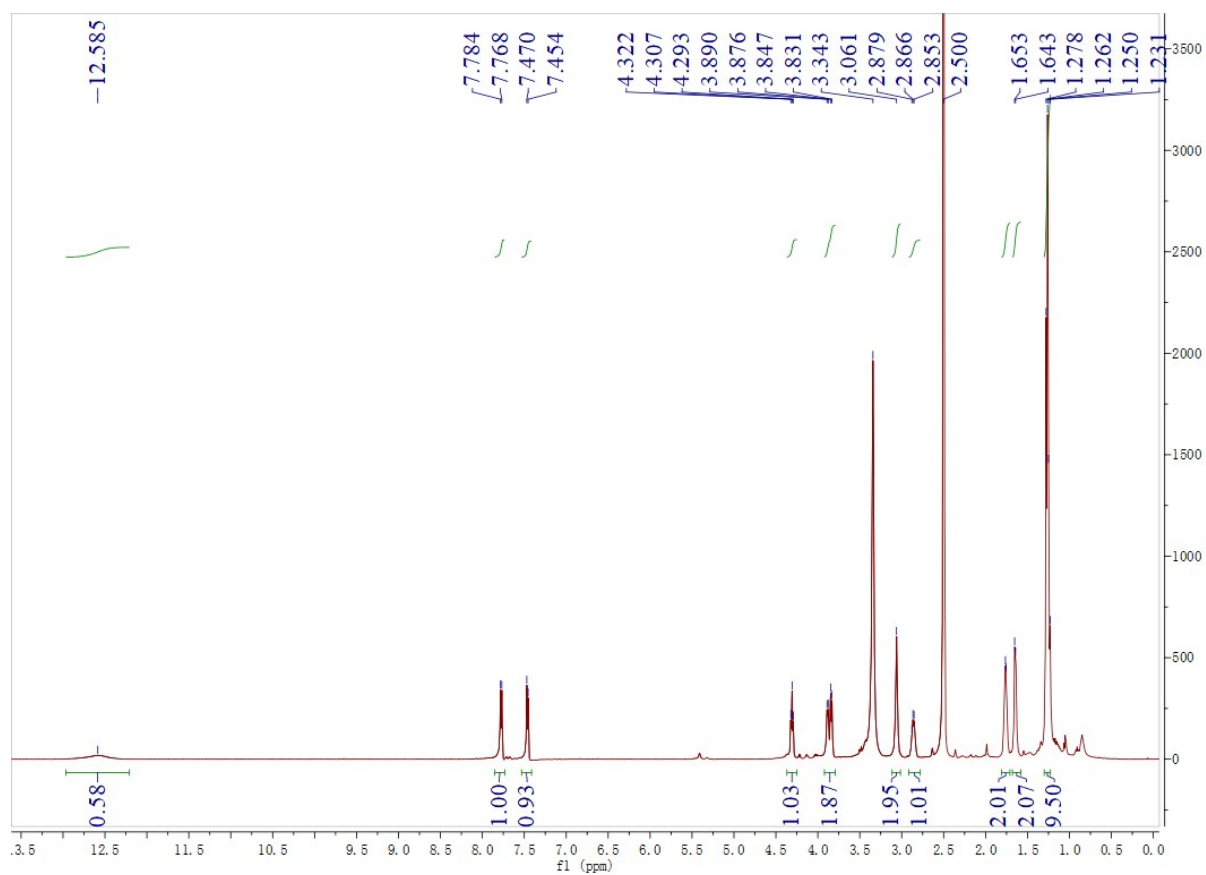


Figure S83. ^1H NMR spectrum of compound **7** in $\text{DMSO-}d_6$ (500 MHz)

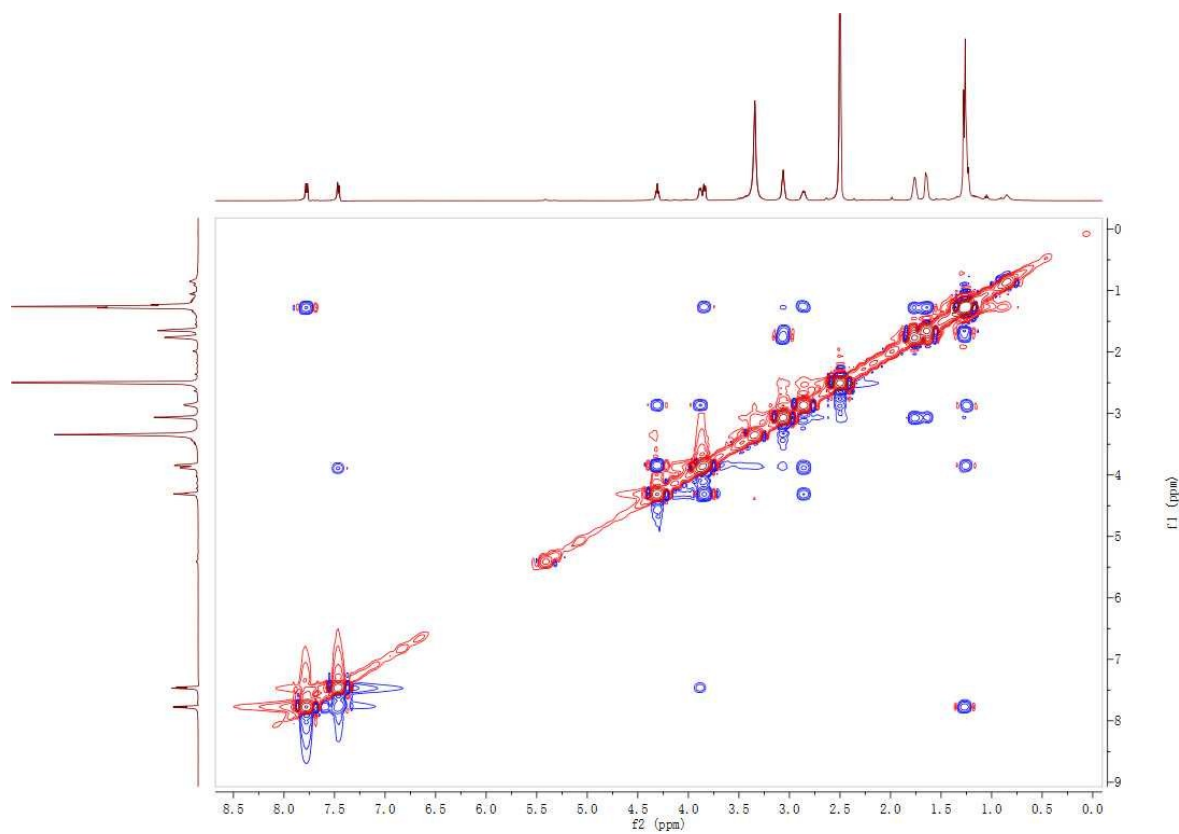


Figure S84. ROESY spectrum of compound **7** in $\text{DMSO-}d_6$ (500 MHz)

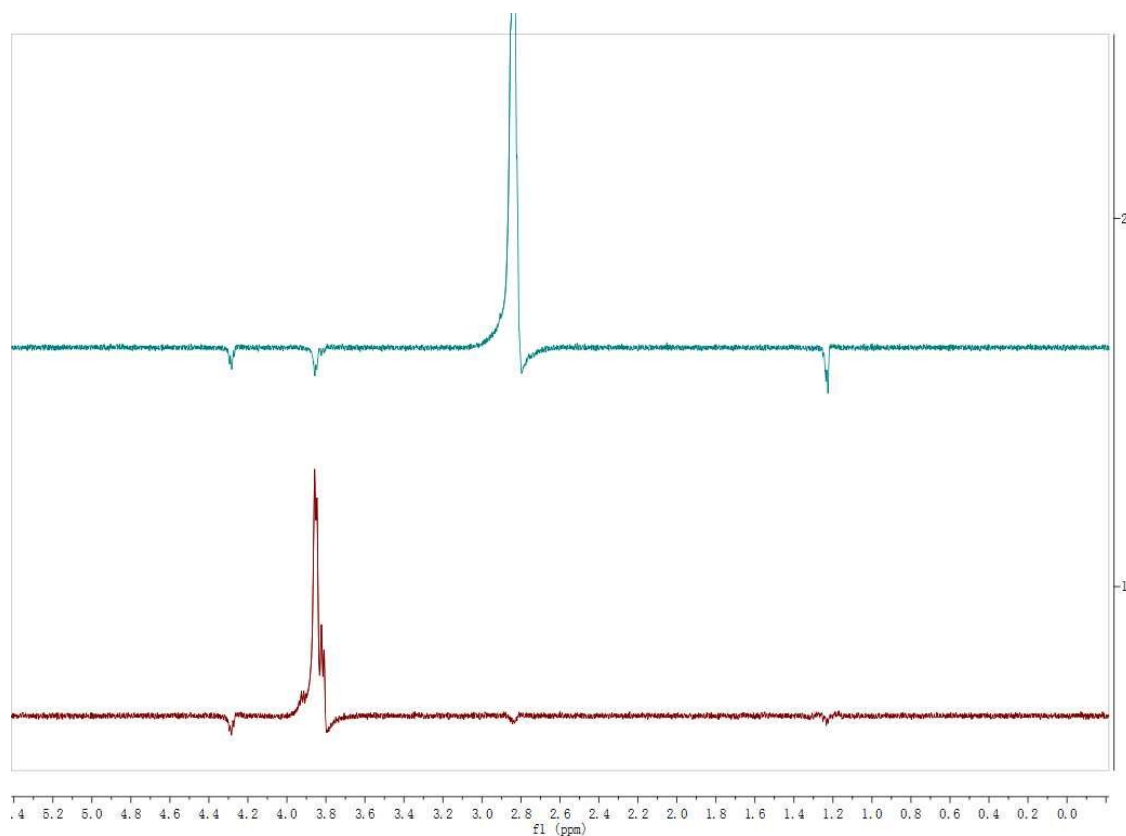


Figure S85. 1D NOESY spectrum of compound **7** in DMSO- d_6 (500 MHz)

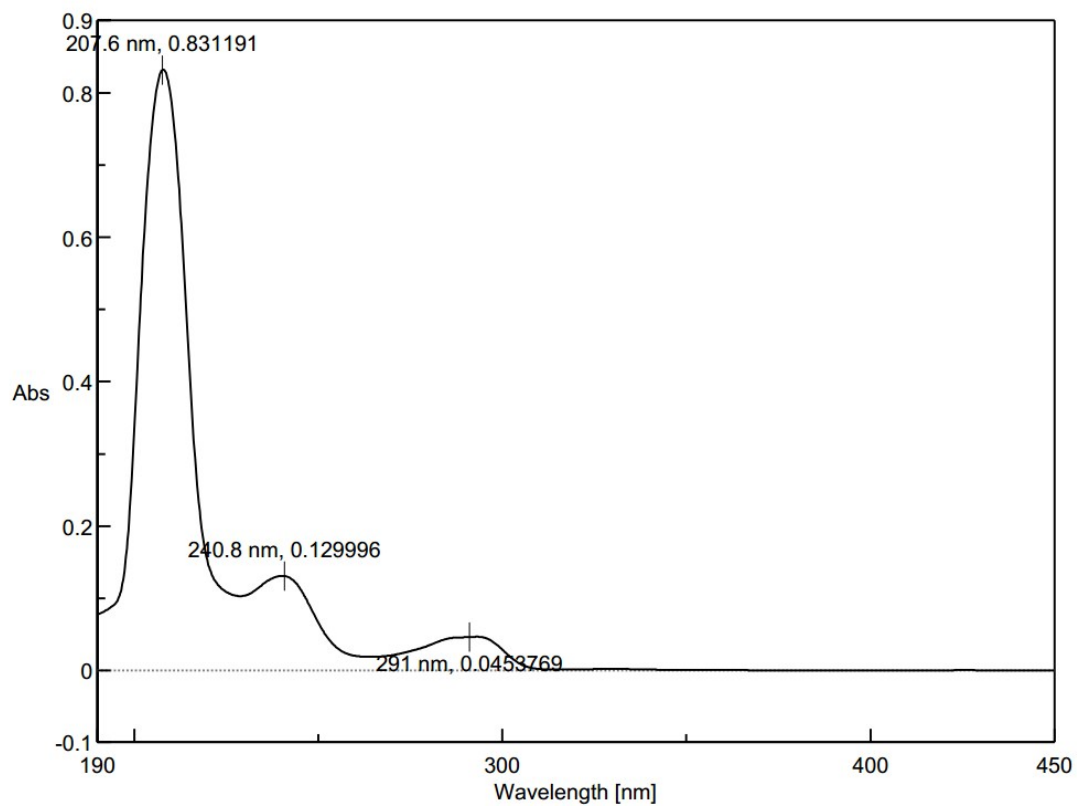


Figure S86. UV spectrum of compound **7**

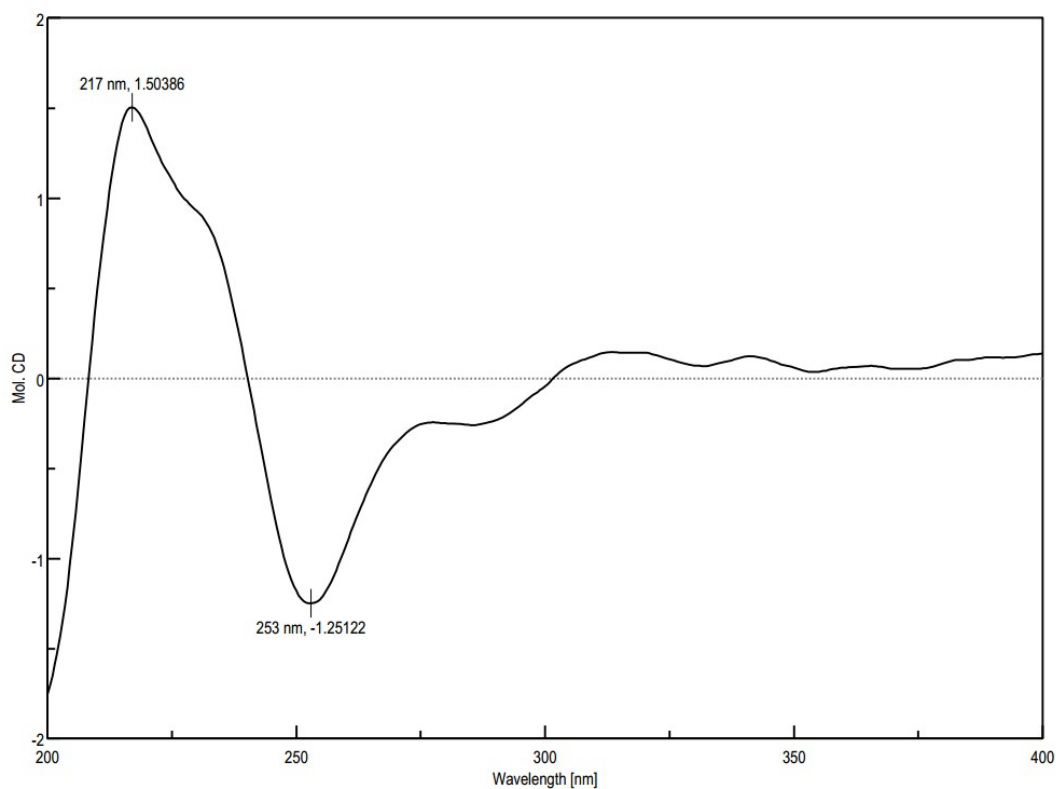


Figure S87. ECD spectrum of compound 7

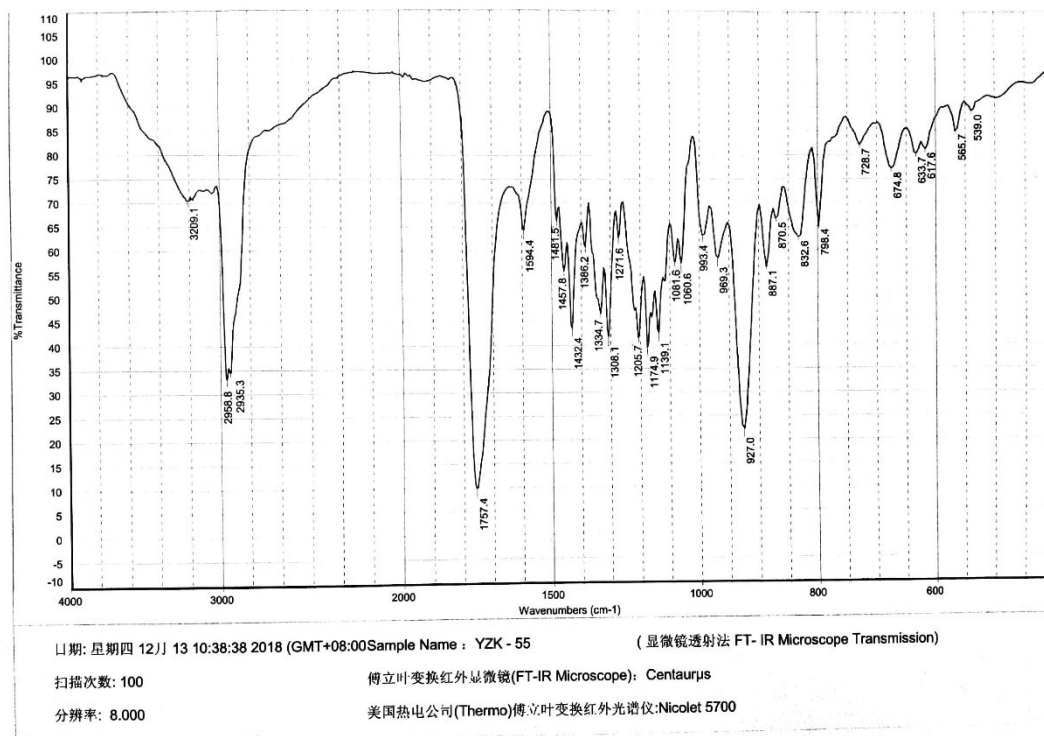
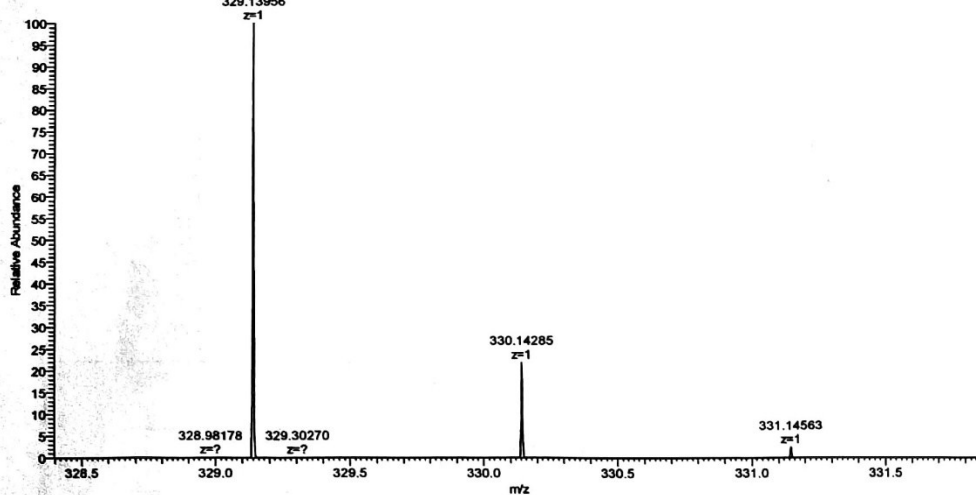


Figure S88. IR spectrum of compound 7

YZK-55 #718 RT: 7.19 AV: 1 NL: 1.40E9
T: FTMS - p ESI Full ms [100.0000-1500.0000]



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
329.13956	329.13945	0.34	9.5	C19 H21 O5	M-H

Figure S89. HR-ESI-MS spectrum of compound 7