

Gelserancines A-E, Monoterpenoid Indole Alkaloids with Unusual Skeletons from *Gelsemium elegans*

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Contents

1. Figure S1. Anti-inflammatory effects of compounds 1-5	6
2. Structural elucidation of 6-10	7
3. Dynamic HPLC analysis of 4 and 5 with different temperatures and irradiations	8
Figure S3. UV spectrum of 1 in MeOH	9
Figure S4. IR (KBr disc) spectrum of 1	9
Figure S5. HR-ESI-MS spectrum of 1	10
Figure S6. ¹ H NMR spectrum (400 MHz) of 1 in CDCl ₃	10
Figure S7. ¹ H NMR spectrum (500 MHz) of 1 in CDCl ₃	11
Figure S8. ¹³ C NMR spectrum of 1 in CDCl ₃	11
Figure S9. DEPT-135 spectrum of 1 in CDCl ₃	12
Figure S10. ¹ H- ¹ H COSY spectrum of 1 in CDCl ₃	12
Figure S11. HSQC NMR spectrum of 1 in CDCl ₃	13
Figure S12. HMBC spectrum of 1 in CDCl ₃	13
Figure S13. NOESY spectrum of 1 in CDCl ₃	14
Figure S14. UV spectrum of 2 in MeOH	14
Figure S15. IR (KBr disc) spectrum of 2	15
Figure S16. HR-ESI-MS spectrum of 2	15
Figure S17. ¹ H NMR spectrum of 2 in CDCl ₃	16
Figure S18. ¹³ C NMR spectrum of 2 in CDCl ₃	16
Figure S19. DEPT-135 spectrum of 2 in CDCl ₃	17
Figure S20. ¹ H- ¹ H COSY spectrum of 2 in CDCl ₃	17
Figure S21. HSQC spectrum of 2 in CDCl ₃	18
Figure S22. HMBC spectrum of 2 in CDCl ₃	18
Figure S23. NOESY spectrum of 2 in CDCl ₃	19
Figure S24. UV spectrum of 3 in MeOH	19
Figure S25. IR (KBr disc) spectrum of 3	20
Figure S26. HR-ESI-MS spectrum of 3	20

Figure S27. ^1H NMR spectrum of 3 in CDCl_3	21
Figure S28. ^{13}C NMR spectrum of 3 in CDCl_3	21
Figure S29. DEPT-135 spectrum of 3 in CDCl_3	22
Figure S30. ^1H - ^1H COSY spectrum of 3 in CDCl_3	22
Figure S31. HSQC spectrum of 3 in CDCl_3	23
Figure S32. HMBC spectrum of 3 in CDCl_3	23
Figure S33. NOESY spectrum of 3 in CDCl_3	24
Figure S34. UV spectrum of 4 in MeOH.....	24
Figure S35. IR (KBr disc) spectrum of 4	25
Figure S36. HR-ESI-MS spectrum of 4	25
Figure S37. ^1H NMR spectrum of 4 in CD_3OD	26
Figure S38. ^{13}C NMR spectrum of 4 in CD_3OD	26
Figure S39. DEPT-135 spectrum of 4 in CD_3OD	27
Figure S40. ^1H - ^1H COSY spectrum of 4 in CD_3OD	27
Figure S41. HSQC spectrum of 4 in CD_3OD	28
Figure S42. HMBC spectrum of 4 in CD_3OD	28
Figure S43. NOESY spectrum of 4 in CD_3OD	29
Figure S44. UV spectrum of 5 in MeOH.....	29
Figure S45. IR (KBr disc) spectrum of 5	30
Figure S46. HR-ESI-MS spectrum of 5	30
Figure S47. ^1H NMR spectrum of 5 in CD_3OD	31
Figure S48. ^{13}C NMR spectrum of 5 in CD_3OD	31
Figure S49. DEPT-135 spectrum of 5 in CD_3OD	32
Figure S50. ^1H - ^1H COSY spectrum of 5 in CD_3OD	32
Figure S51. HSQC spectrum of 5 in CD_3OD	33
Figure S52. HMBC spectrum of 5 in CD_3OD	33
Figure S53. NOESY spectrum of 5 in CD_3OD	34
Figure S54. UV spectrum of 6 in MeOH.....	34
Figure S55. IR (KBr disc) spectrum of 6	35
Figure S56. HR-ESI-MS spectrum of 6	35

Figure S57. ^1H NMR spectrum of 6 in CDCl_3	36
Figure S58. ^{13}C NMR spectrum of 6 in CDCl_3	36
Figure S59. DEPT-135 spectrum of 6 in CDCl_3	37
Figure S60. UV spectrum of 7 in MeOH.....	37
Figure S61. IR (KBr disc) spectrum of 7	38
Figure S62. HR-ESI-MS spectrum of 7	38
Figure S63. ^1H NMR spectrum of 7 in CDCl_3	39
Figure S64. ^{13}C NMR spectrum of 7 in CDCl_3	39
Figure S65. DEPT-135 spectrum of 7 in CDCl_3	40
Figure S66. UV spectrum of 8 in MeOH.....	40
Figure S67. IR (KBr disc) spectrum of 8	41
Figure S68. HR-ESI-MS spectrum of 8	41
Figure S69. ^1H NMR spectrum of 8 in CDCl_3	42
Figure S70. ^{13}C NMR spectrum of 8 in CDCl_3	42
Figure S71. DEPT-135 spectrum of 8 in CDCl_3	43
Figure S72. UV spectrum of 9 in MeOH.....	43
Figure S73. IR (KBr disc) spectrum of 9	44
Figure S74. HR-ESI-MS spectrum of 9	44
Figure S75. ^1H NMR spectrum of 9 in CDCl_3 (80%) + CD_3OD (20%).....	45
Figure S76. ^{13}C NMR spectrum of 9 in CDCl_3 (80%) + CD_3OD (20%).....	45
Figure S77. DEPT-135 spectrum of 9 in CDCl_3 (80%) + CD_3OD (20%).....	46
Figure S78. UV spectrum of 10 in MeOH.....	46
Figure S79. IR (KBr disc) spectrum of compound 10	47
Figure S80. HR-ESI-MS spectrum of 10	47
Figure S81. ^1H NMR spectrum of 10 in CDCl_3	48
Figure S82. ^{13}C NMR spectrum of 10 in CDCl_3	48
Figure S83. DEPT-135 spectrum of 10 in CDCl_3	49
Figure S84. Dynamic HPLC spectra of 4 with temperature increase.....	49
Figure S85. Dynamic HPLC spectra of 5 with temperature increase.....	50
Figure S86. Dynamic HPLC spectra of 4 with visible light irradiation.....	50

Figure S87. Dynamic HPLC spectra of 5 with visible light irradiation.....	51
Figure S88. Dynamic HPLC spectra of 4 with UV irradiation in 254 nm.....	51
Figure S89. Dynamic HPLC spectra of 5 with UV irradiation in 254 nm.....	52
Figure S90. Dynamic HPLC spectra of 4 with UV irradiation in 365 nm.....	52
Figure S91. Dynamic HPLC spectra of 5 with UV irradiation in 365 nm.....	53
Notes and references	54

1. The anti-inflammatory effects of compounds 1-5.

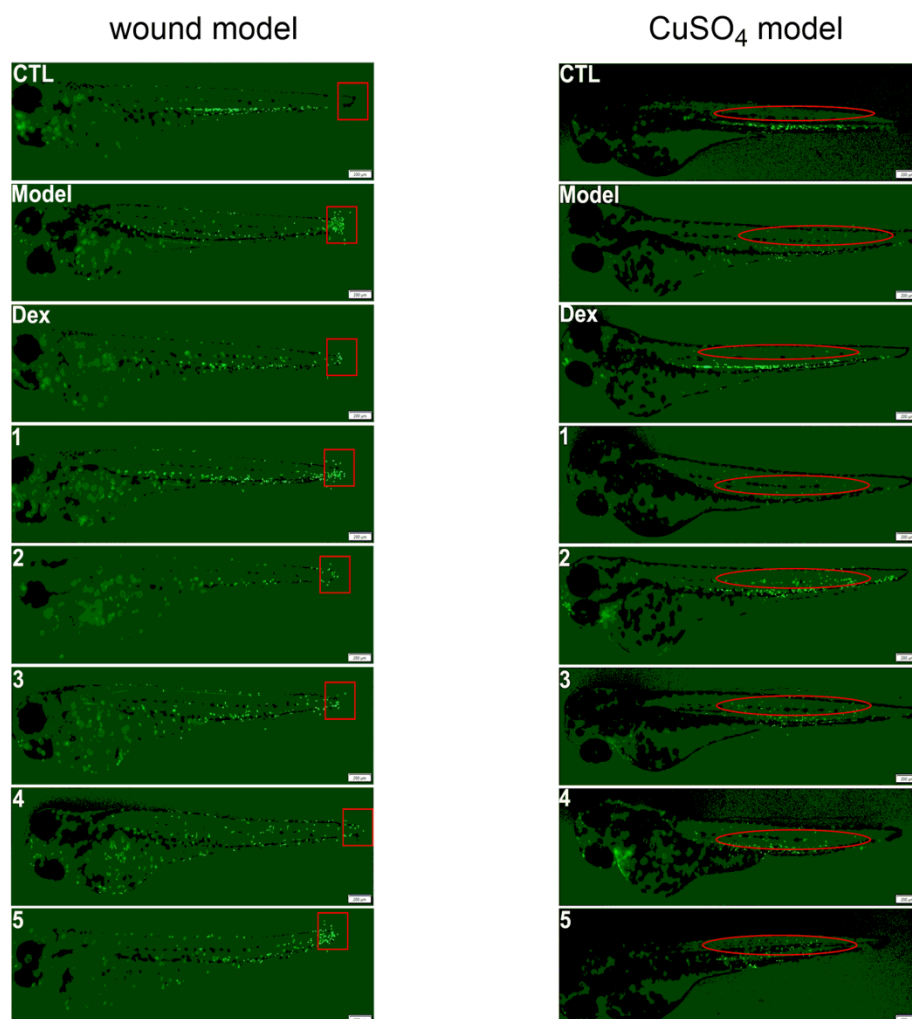


Figure S1. Anti-inflammatory effects of compounds **1-5**. The neutrophil number (green fluorescence) in inflammatory sites (red rectangle or ellipse marked) in wound (left panel) and CuSO₄ (right panel) models was observed by fluorescence microscopy (MVX10, Olympus, Japan).

2. Structural elucidation of 6-10.

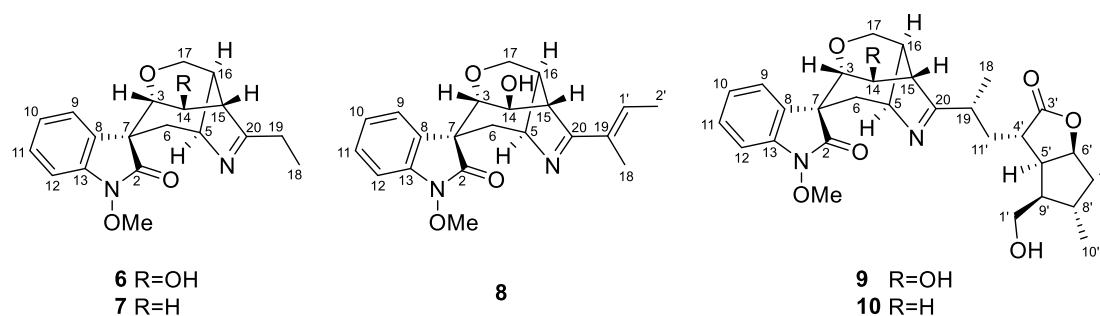


Figure S2. Chemical structures of **6-10**.

Compounds **6-10** were identified as 14-hydroxygelsenicine¹, gelsenicine², 14 β -hydroxygelsedethenine³, 14 α -hydroxygelsamydine⁴, and gelsamydine² by comparison their spectroscopic data with those of literatures, respectively.

Table S1. ¹H and ¹³C NMR data of compounds **6-10** (δ in ppm, *J* in Hz)

NO.	6^a		7^a		8^a		9^b		10^b	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
2		171.1		171.4		171.5		171.3		171.5
3	3.67 br s	79.5	3.69 dd (4.5, 1.9)	75.1	3.55 s	80.3	3.61 s	79.4	3.64 ^c	72.1
5	4.40 m	72.2	4.37 m	72.6	4.46 m	73.1	4.37 m	71.1	4.37 m	74.9
6	2.41 dd (15.6, 4.7)	37.8	2.36 ^c	37.8	2.38 dd (15.5, 4.7)	38.2	2.50 dd (16.0, 4.9)	36.7	2.38 ^c	37.2
	2.30 dd (15.6, 2.0)		2.25 dd (15.4, 2.2)		2.27 dd (15.5, 1.9)		2.27 ^c		2.38 ^c	
7		53.9		56.0		54.5		53.7		56.2
8		131.8		132.4		132.5		131.2		131.9
9	7.50 d (7.6)	124.8	7.50 d (7.6)	124.8	7.43 d (7.6)	125.5	7.53 d (7.6)	124.9	7.47 d (7.6)	125.2
10	7.07 dd (7.6, 7.6)	123.8	7.03 ddd (7.6, 7.6, 1.0)	123.5	7.00 dd (7.6, 7.6)	124.4	7.12 dd (7.6, 7.6)	123.7	7.07 dd (7.6, 7.6)	123.6
11	7.26 dd (7.6, 7.6)	128.6	7.22 ddd (7.6, 7.6, 1.0)	128.2	7.19 dd (7.6, 7.6)	129.1	7.30 dd (7.6, 7.6)	128.3	7.25 dd (7.6, 7.6)	128.4
12	6.87 d (7.6)	107.1	6.84 d (7.6)	106.7	6.79 d (7.6)	107.6	6.92 d (7.6)	106.8	6.87 d (7.6)	107.0
13		138.2		138.2		138.9		137.8		138.5
14	4.45 br s	66.8	2.35 ^c	25.8	4.35 d (2.0)	68.4	4.41 s	64.9	2.48 m	26.7
			2.10 m						2.12 ^c	
15	2.88 d (8.5)	52.5	2.83 t (9.3)	39.9	3.24 d (8.4)	54.5	3.10 d (8.1)	50.3	3.11 t (9.1)	39.5
16	2.59 td (8.2, 3.3)	38.5	2.53 br t (8.2)	42.6	2.55 td (8.1, 3.3)	38.9	2.57 m	37.8	2.50 m	40.3
17	4.43 dd (11.1, 3.7)	62.1	4.26 dd (11.0, 2.8)	62.3	4.40 dd (11.0, 3.6)	62.7	4.46 dd (11.0, 3.8)	61.0	4.27 ^c	62.0
	4.32 d (11.1)		4.23 dd (11.0, 1.7)		4.27 d (11.0)		4.33 d (11.0)		4.27 ^c	
18	1.29 t (7.3)	10.2	1.25 t (7.4)	10.2	2.00 s	13.7	1.29 d (7.3)	19.2	1.18 d (7.4)	20.4
19	2.76 dq (17.3, 7.3)	26.3	2.68 dq (17.0, 7.4)	27.2		133.9		33.0	3.53 ^c	35.9
	2.48 dq (17.3, 7.3)		2.37 ^c							
20		181.3		184.6		177.8		185.3		188.2
N-OMe	3.93 s	63.7	3.91 s	63.5	3.84 s	64.1	3.91 s	63.0	3.87 s	63.4
1'					6.27 q (6.8)	133.2	3.70 m	61.0	3.63 ^c	60.4
							3.54 d (11.1)		3.48 ^c	
2'					1.82 d (6.8)	15.5				
3'								182.0		182.2
4'							3.48 m	36.6	1.86 m	33.3
5'							2.91 m	47.9	2.83 m	48.8
6'							5.01 br t (6.0)	82.9	4.90 t (7.1)	82.1
7'							2.16 dd (13.5, 5.6)	41.9	2.10 ^c	42.6
							1.47 m		1.40 m	
8'							1.78 ^c	29.5	1.68 ^c	33.2
9'							1.88 m	51.7	1.72 ^c	52.7
10'							0.95 d (6.4)	17.0	0.87 d (6.3)	17.4
11'							2.27 ^c	36.8	2.29 ^c	37.7
							1.78 ^c		2.29 ^c	

^a Measured in CDCl₃. ^b Measured in CDCl₃ (80%) + CD₂O (20%) ^c Overlapped signals.

3. Dynamic HPLC analysis of 4 and 5 with different temperatures and irradiations.

Compounds **4** and **5** were solved in MeOH, then the HPLC spectra were recorded on an Agilent 1260 instrument equipped with DAD detector and a Waters Xbridge™ C₁₈ OBD reversed-phase column (4.6×250 mm, 5 μm, USA). The column temperature was controlled at 298 K by an Agilent 1260 TCCVL (USA). The mobile phase was MeCN-H₂O-Et₂NH (22:78:0.01 v/v/v), and the flow rate was 1 mL/min.

Elevated-temperature experiment: Compounds **4** and **5** was protected from light at different temperatures (298, 318, 338, 358 K) and analyzed by HPLC, respectively. Each temperature gradient was holding for 2 hours. (figure S84-85)

Visible/UV light irradiation experiment: Compounds **4** and **5** was exposed under an incandescent lamp (as a source of visible light) or UV light (254 or 365 nm) and analyzed by HPLC at different times (0, 1, 4, 24 h, at room temperature). (figure S86-91)

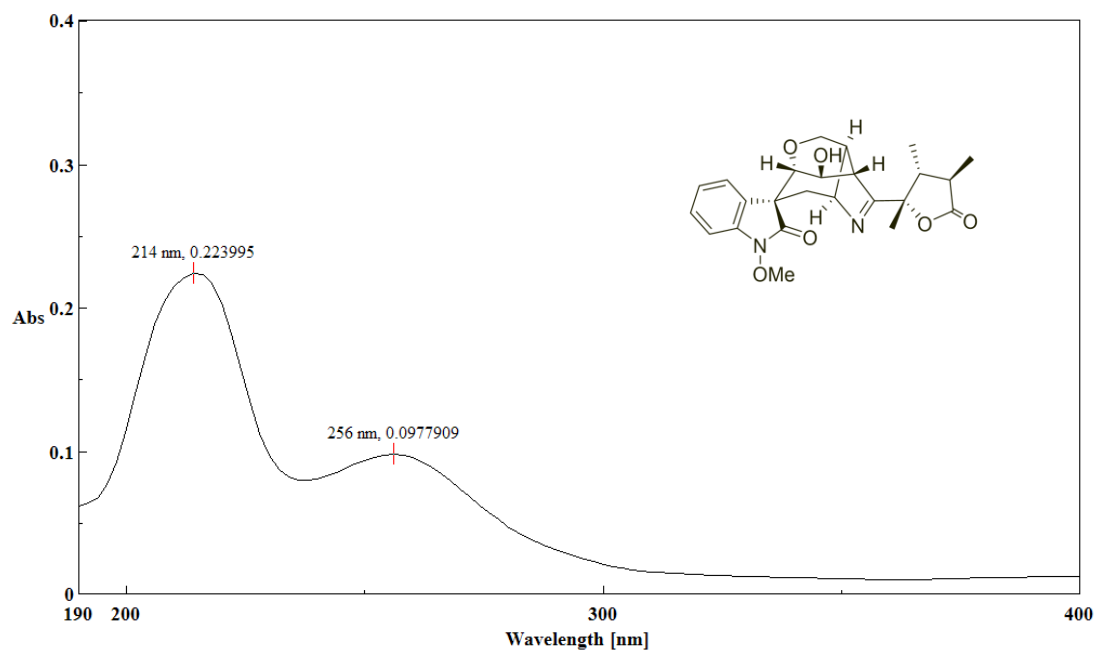


Figure S3. The UV of compound **1** in MeOH

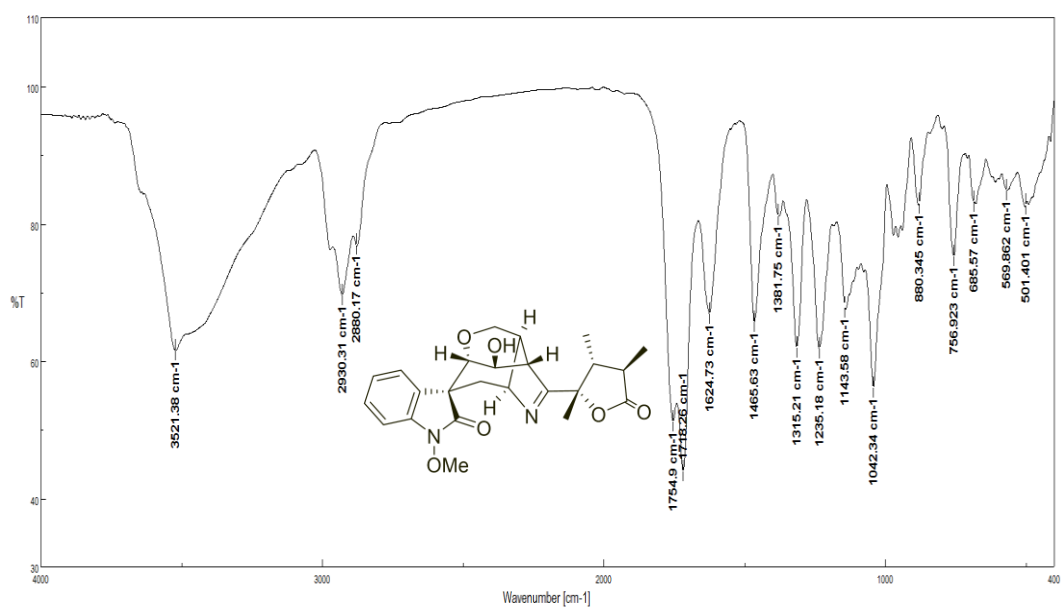


Figure S4. The IR (KBr disc) of compound **1**

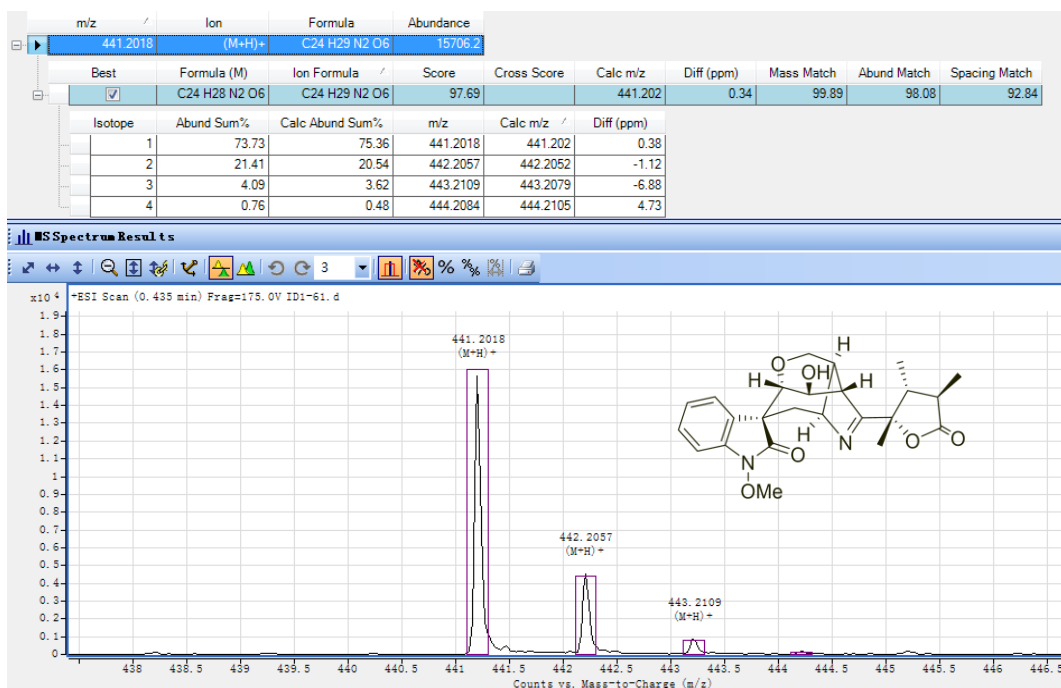


Figure S5 The HR-ESI-MS of compound **1**

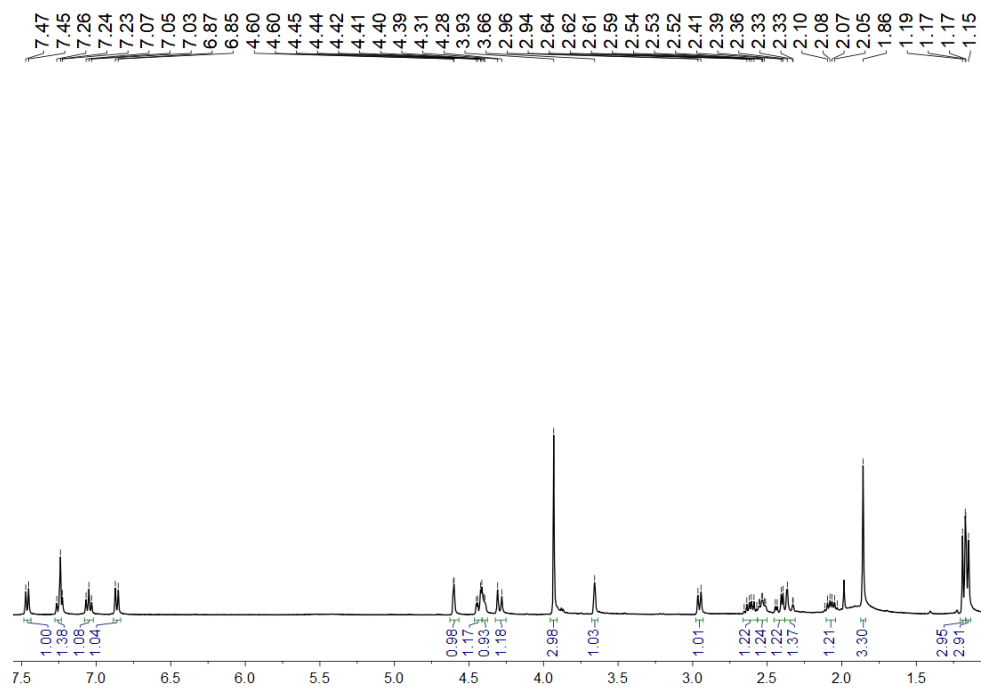


Figure S6. The ¹H NMR spectrum (400 MHz) of compound **1** in CDCl₃

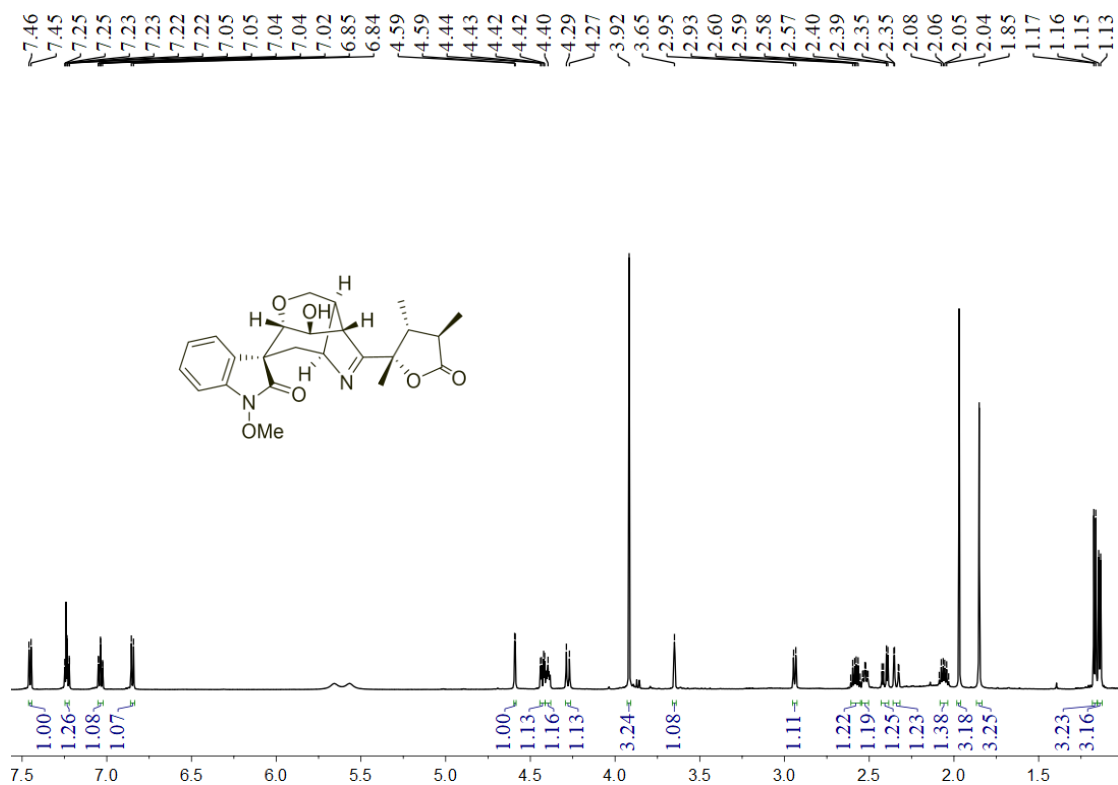


Figure S7. The ^1H NMR spectrum (500 MHz) of compound **1** in CDCl_3

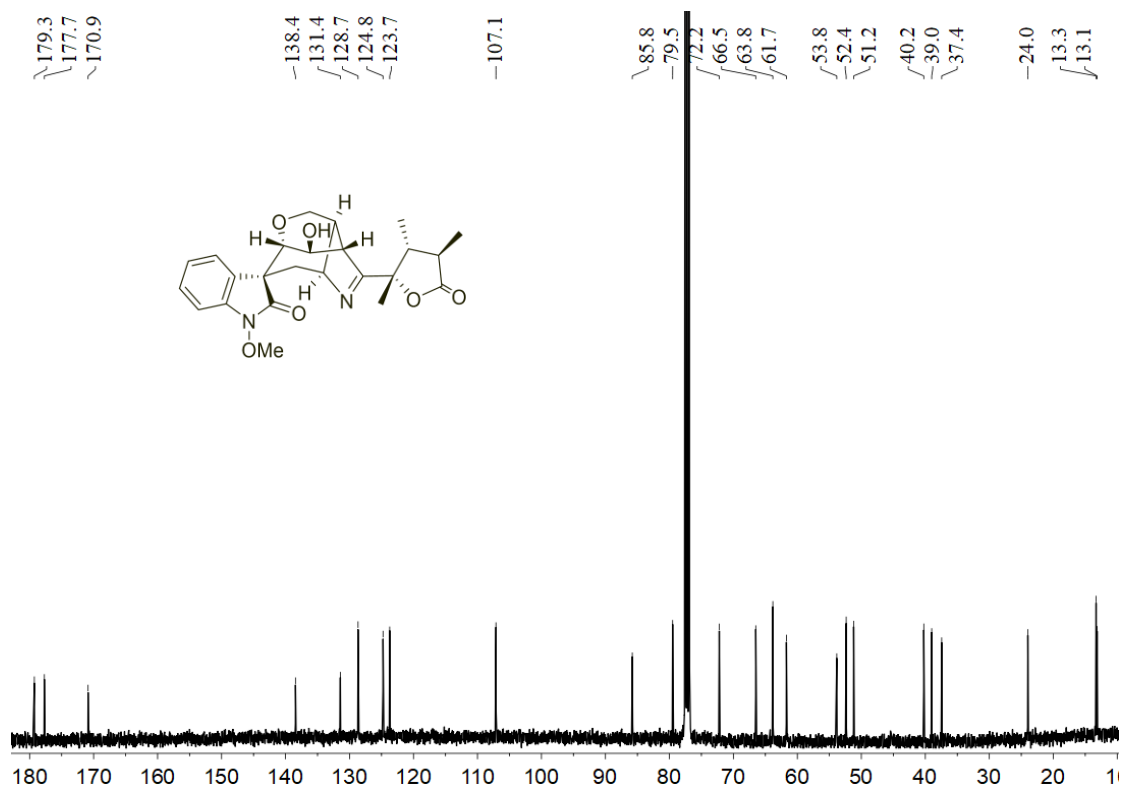


Figure S8. The ^{13}C NMR spectrum of compound **1** in CDCl_3

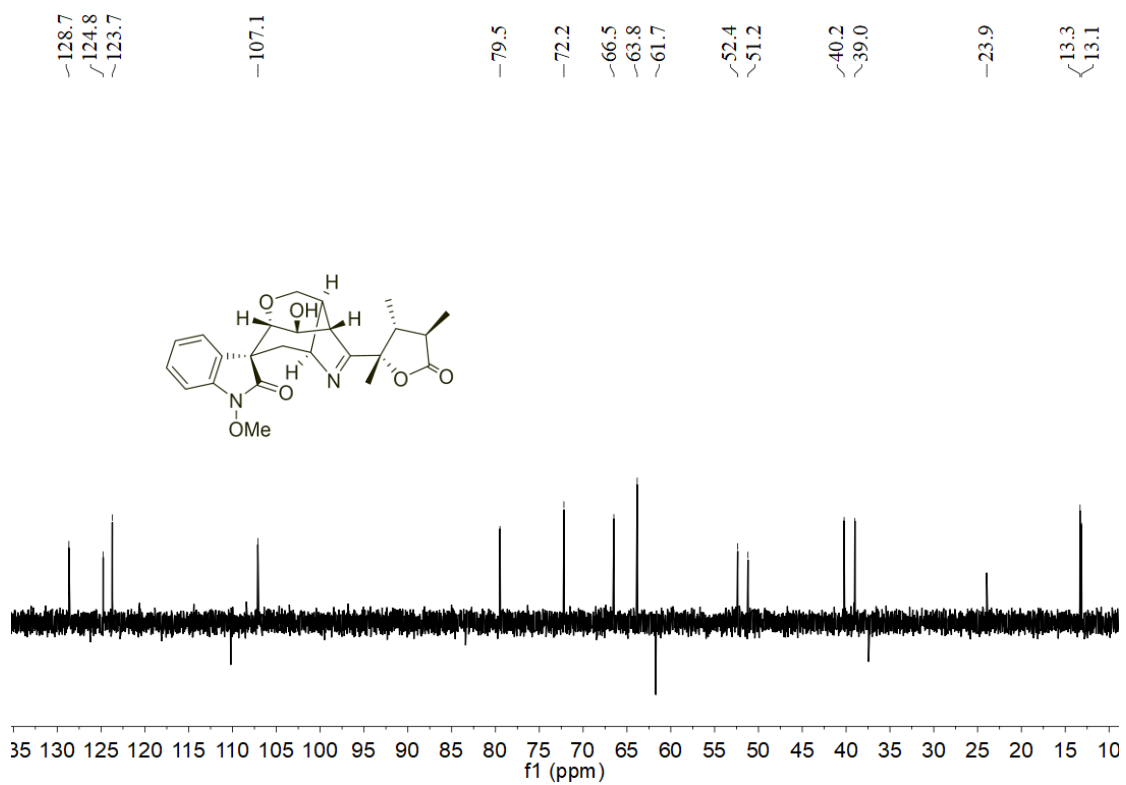


Figure S9. The DEPT-135 spectrum of compound **1** in CDCl₃

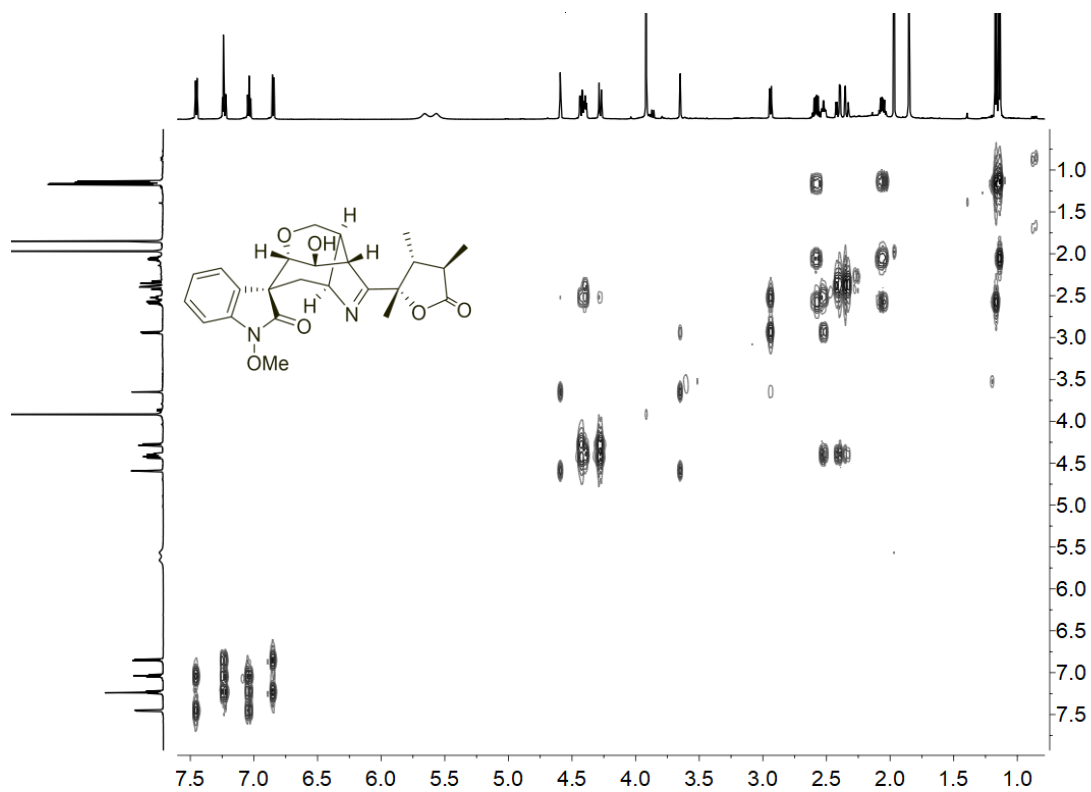


Figure S10. The ¹H-¹H COSY spectrum of compound **1** in CDCl₃

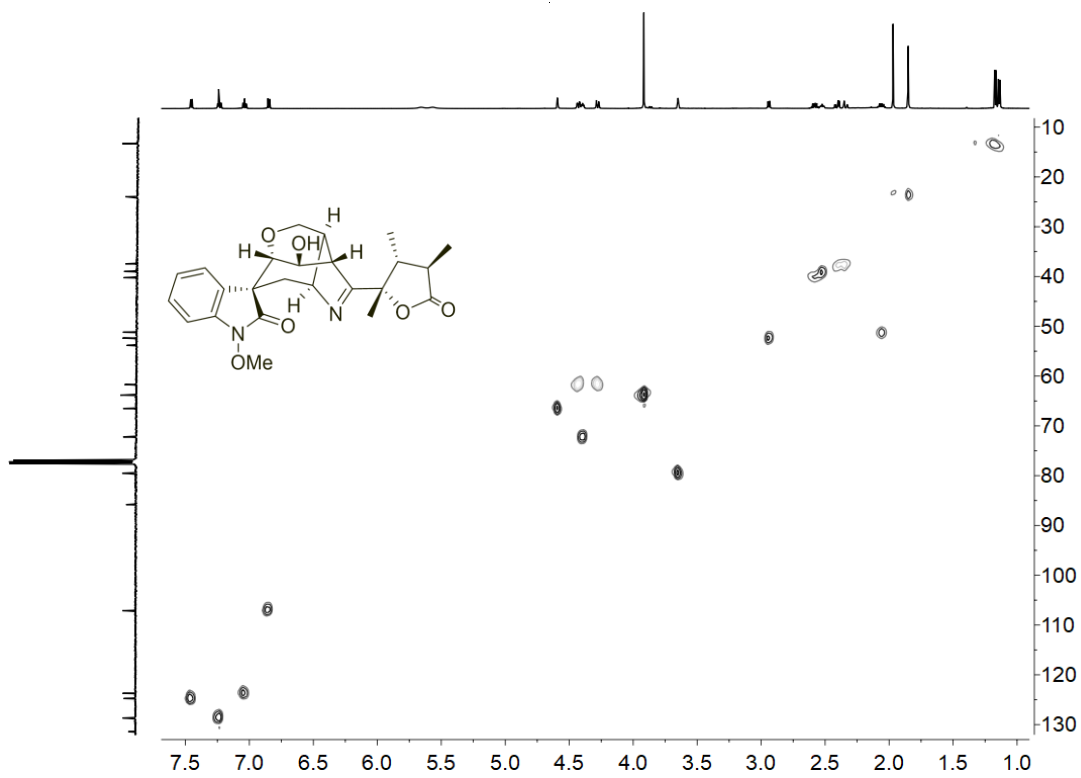


Figure S11. The HSQC spectrum of compound **1** in CDCl₃

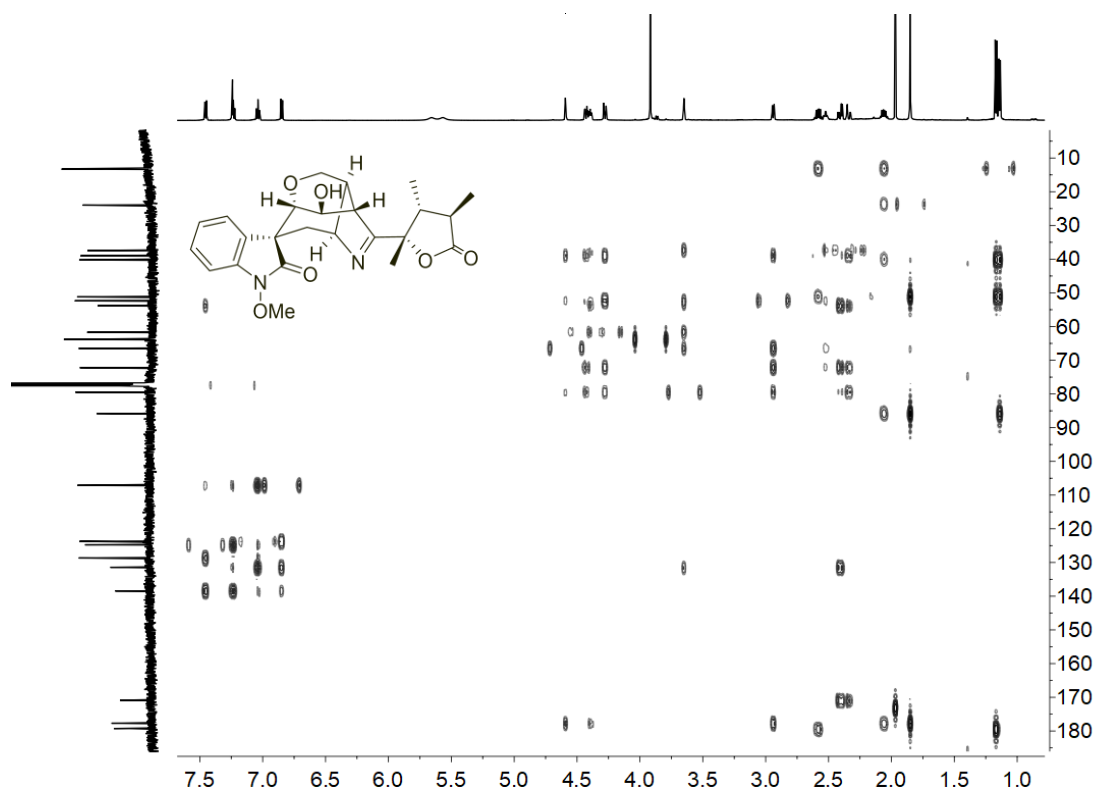


Figure S12. The HMBC spectrum of compound **1** in CDCl₃

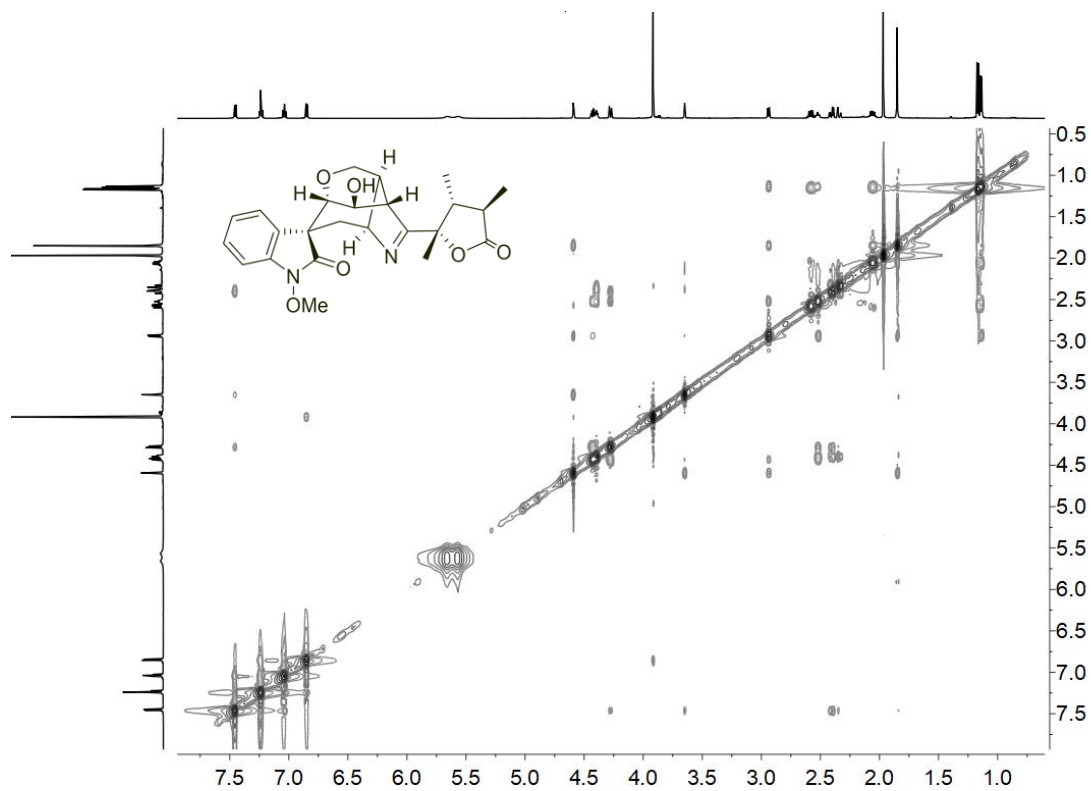


Figure S13. The NOESY spectrum of compound **1** in CDCl_3

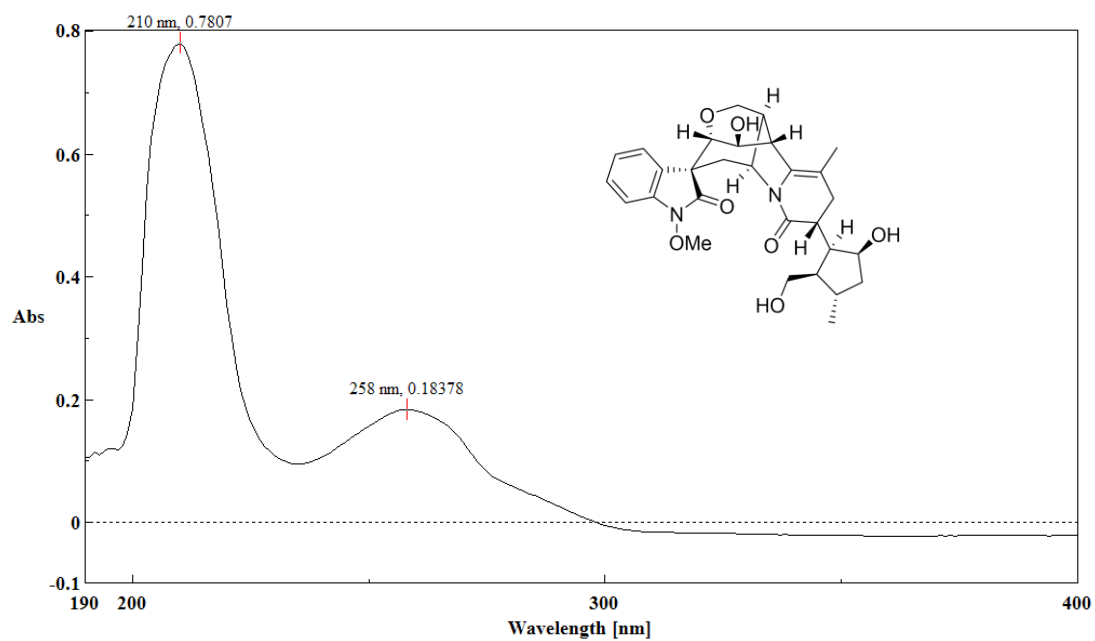


Figure S14. The UV of compound **2** in MeOH

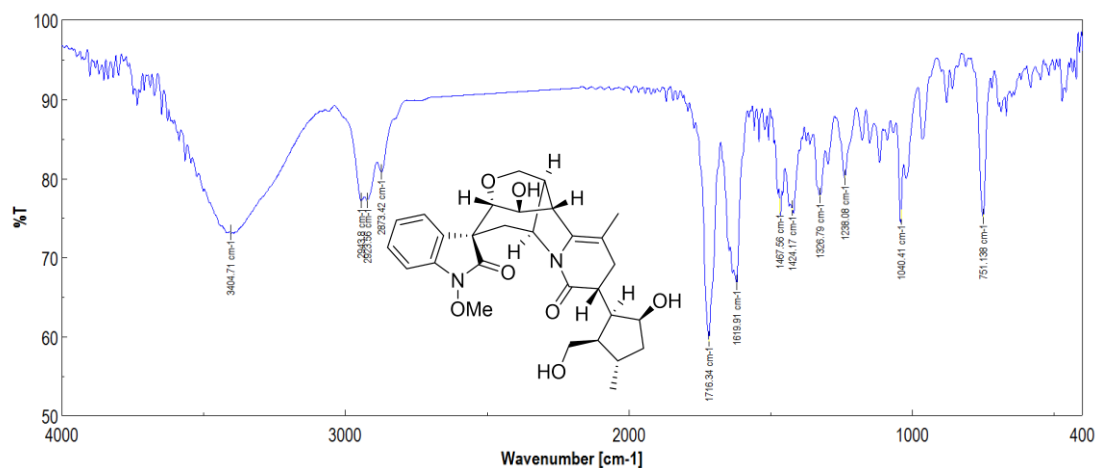


Figure S15. The IR (KBr disc) of compound 2

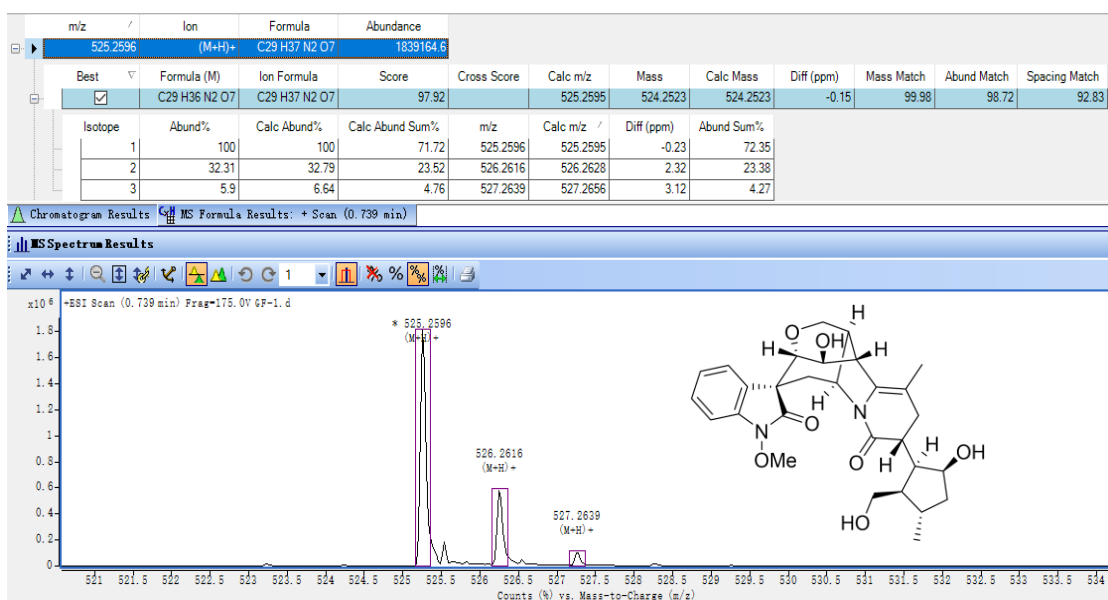
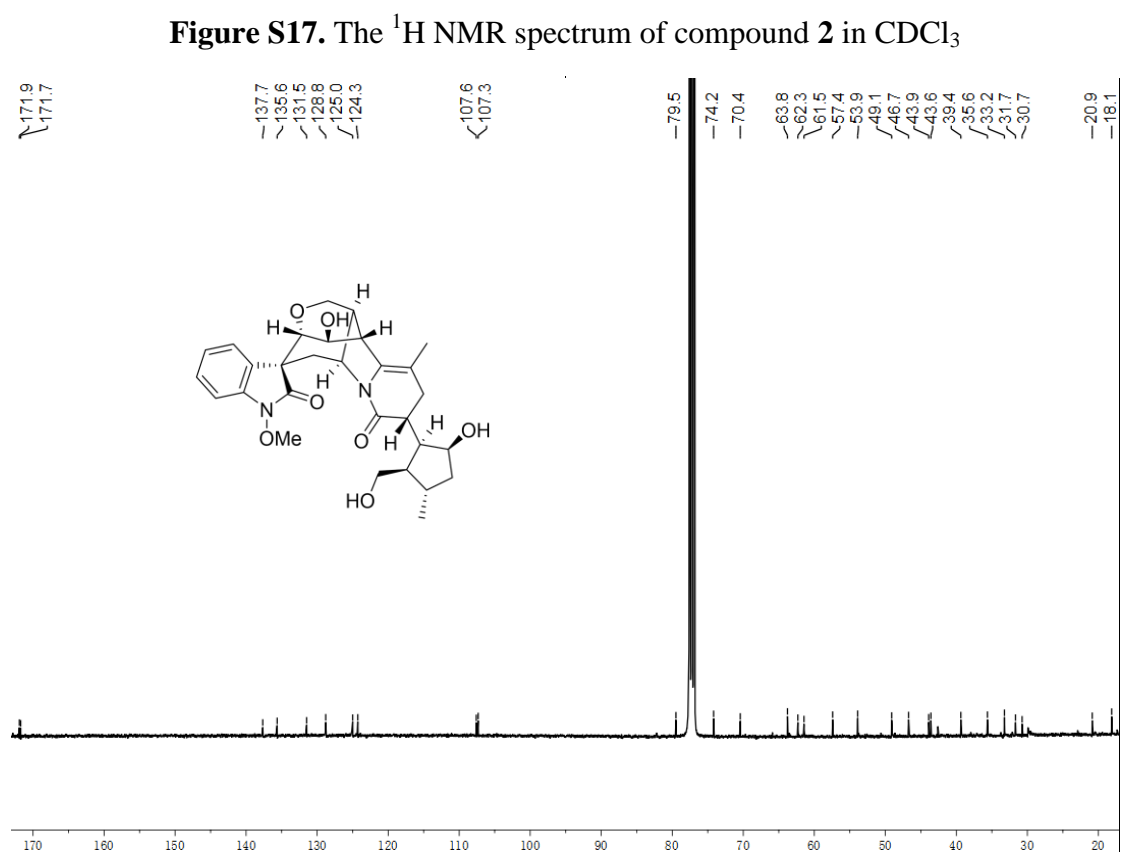
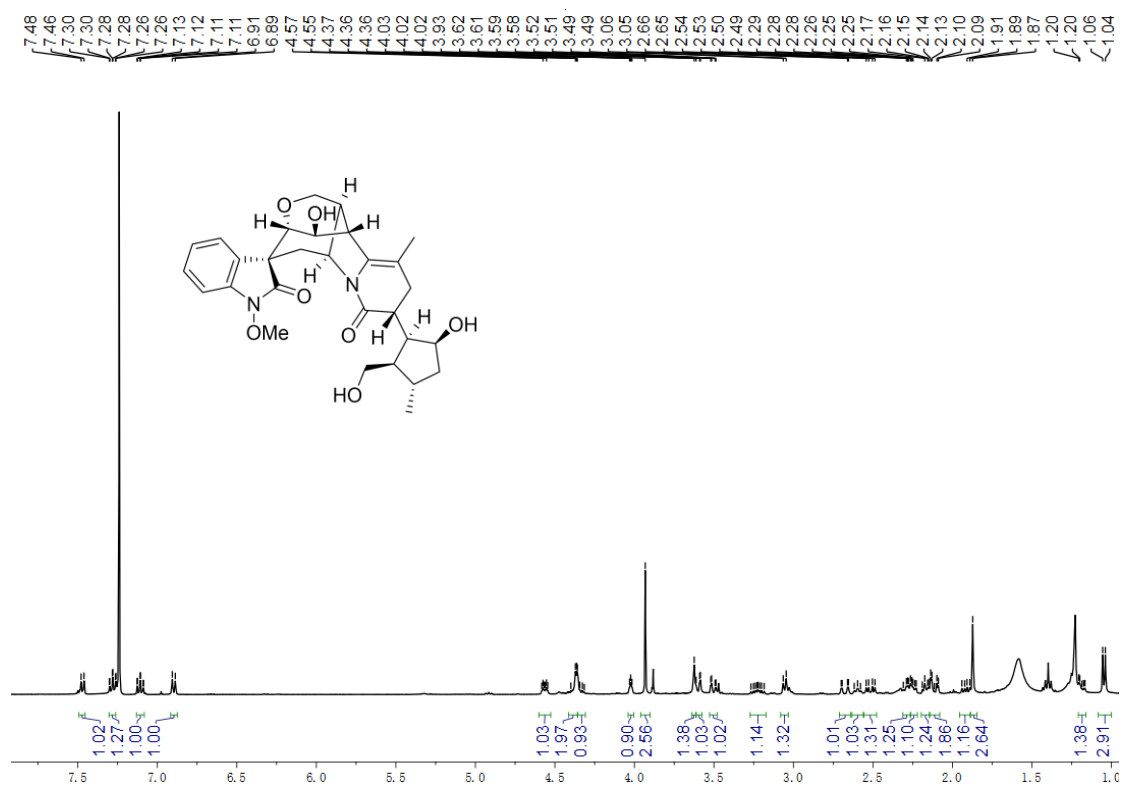


Figure S16. The HR-ESI-MS of compound 2



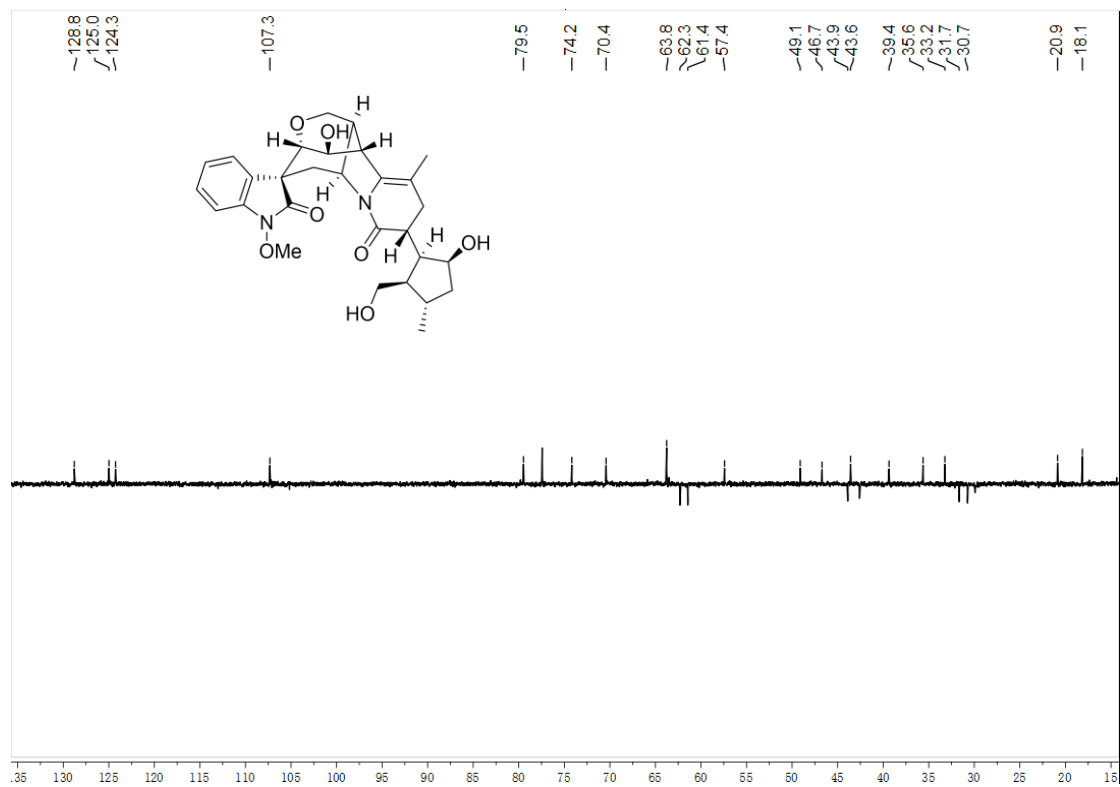


Figure S19. The DEPT-135 spectrum of compound **2** in CDCl_3

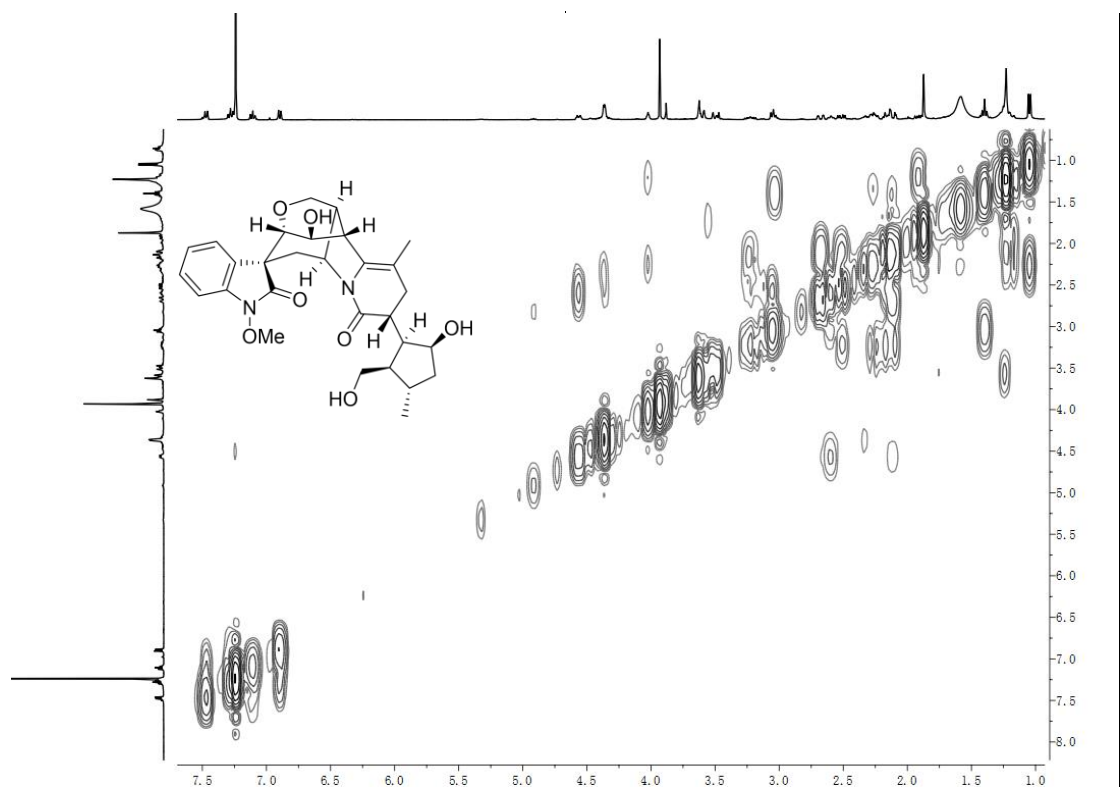


Figure S20. The ^1H - ^1H COSY spectrum of compound **2** in CDCl_3

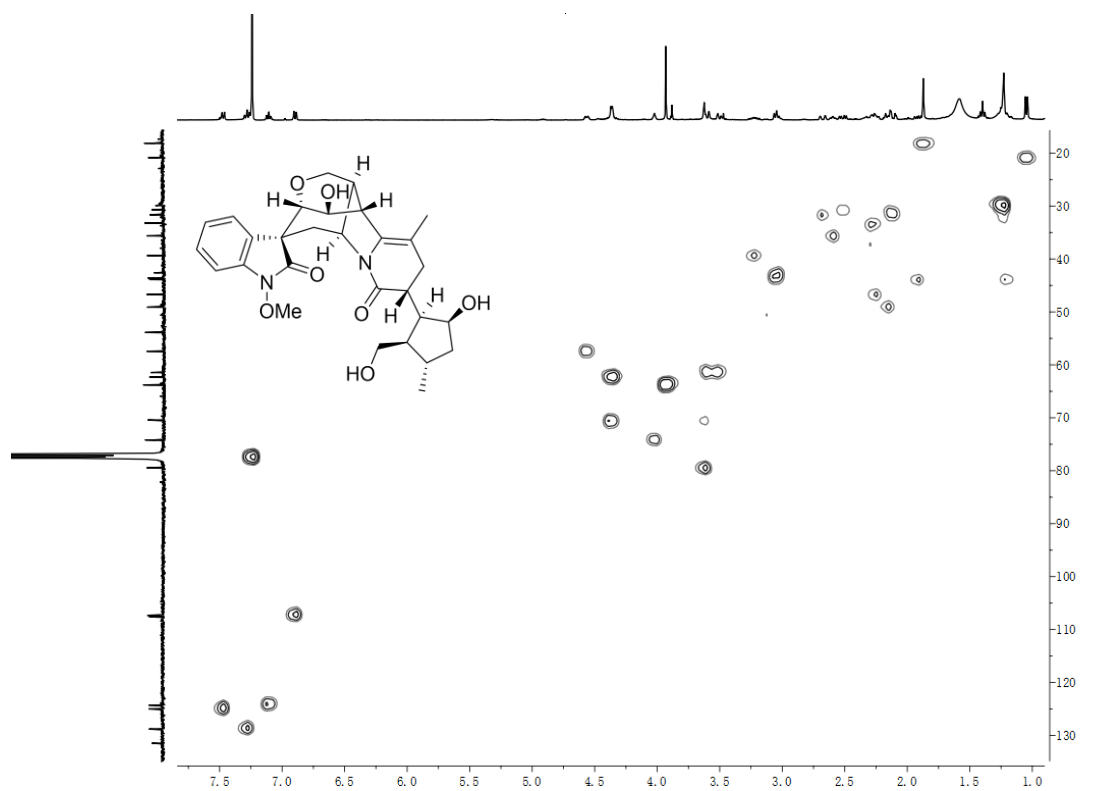


Figure S21. The HSQC spectrum of compound **2** in CDCl_3

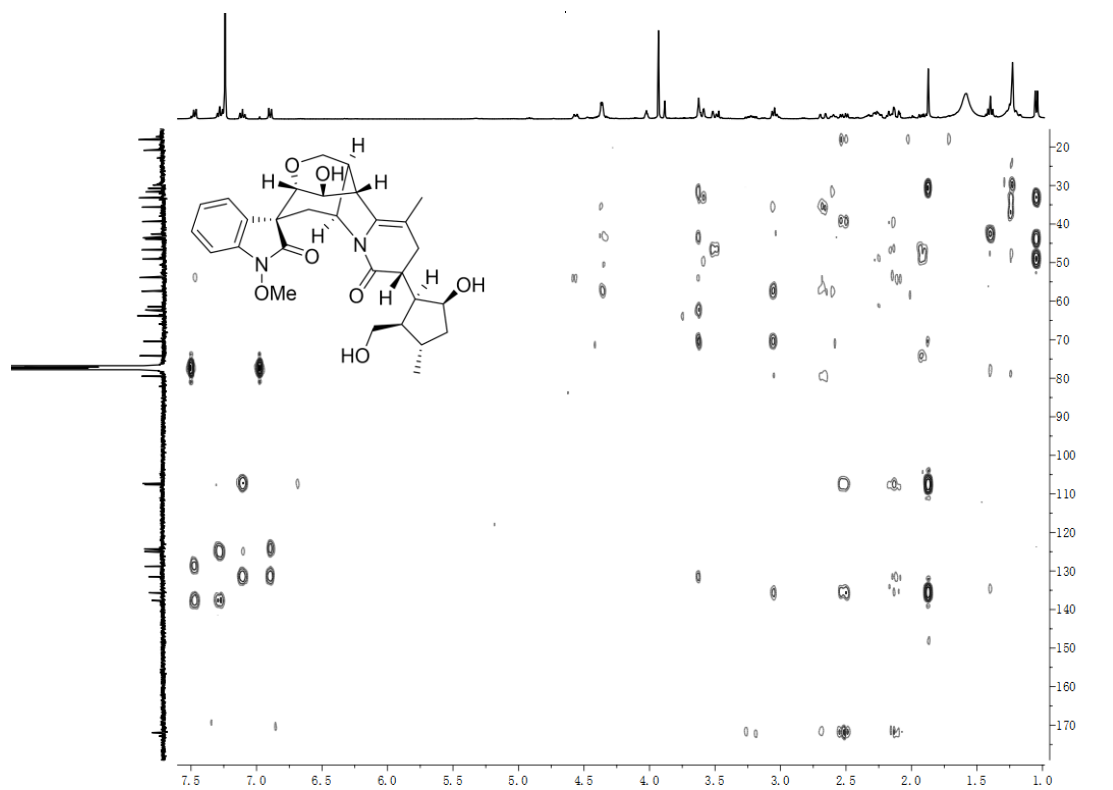


Figure S22. The HMBC spectrum of compound **2** in CDCl_3

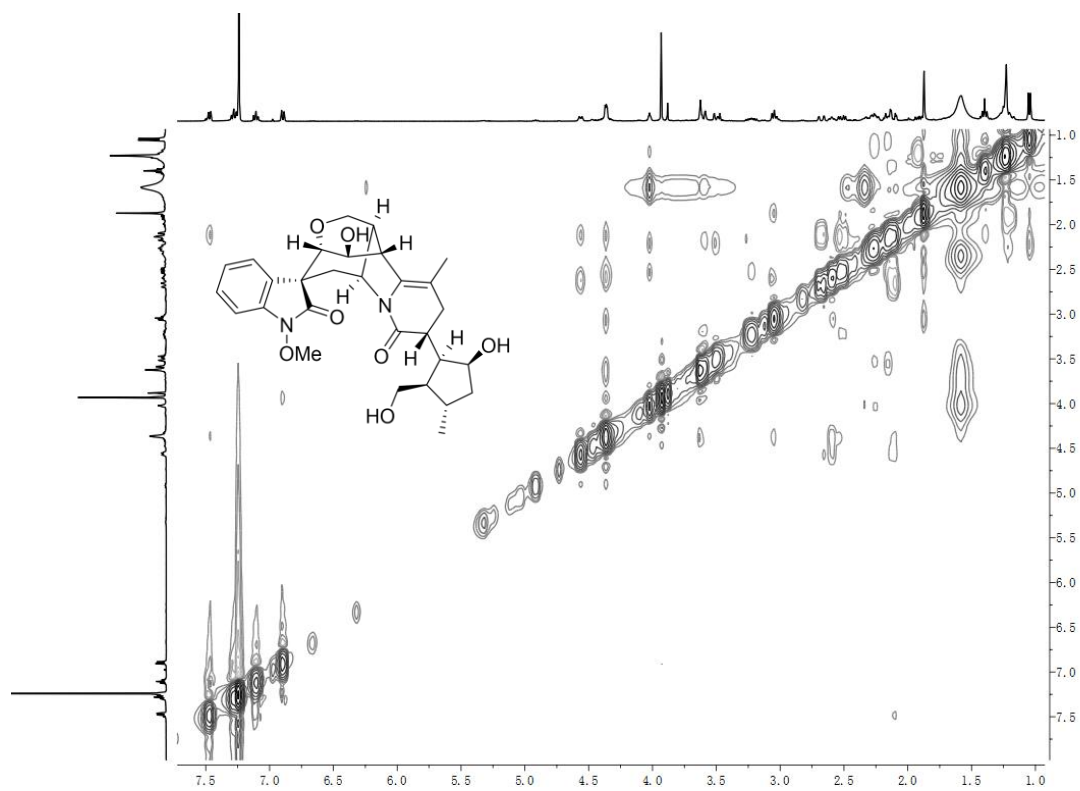


Figure S23. The NOESY spectrum of compound **2** in CDCl_3

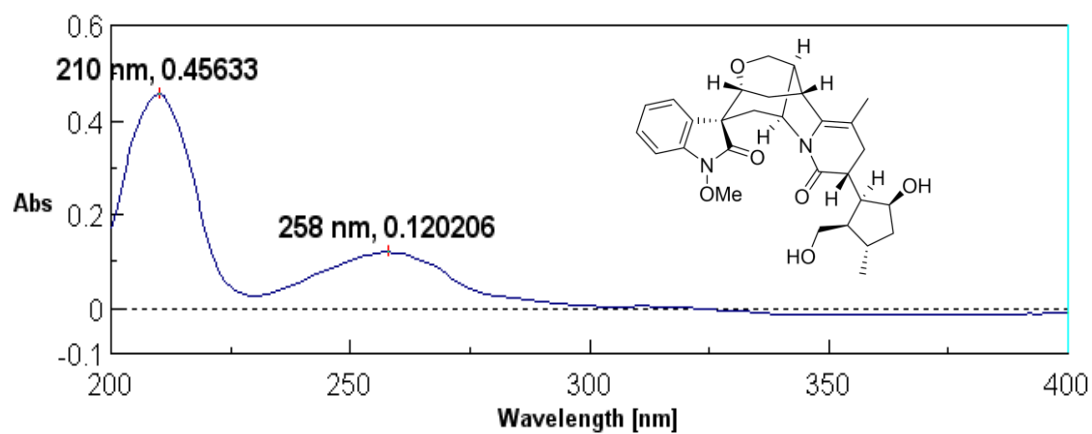


Figure S24. The UV of compound **3** in MeOH

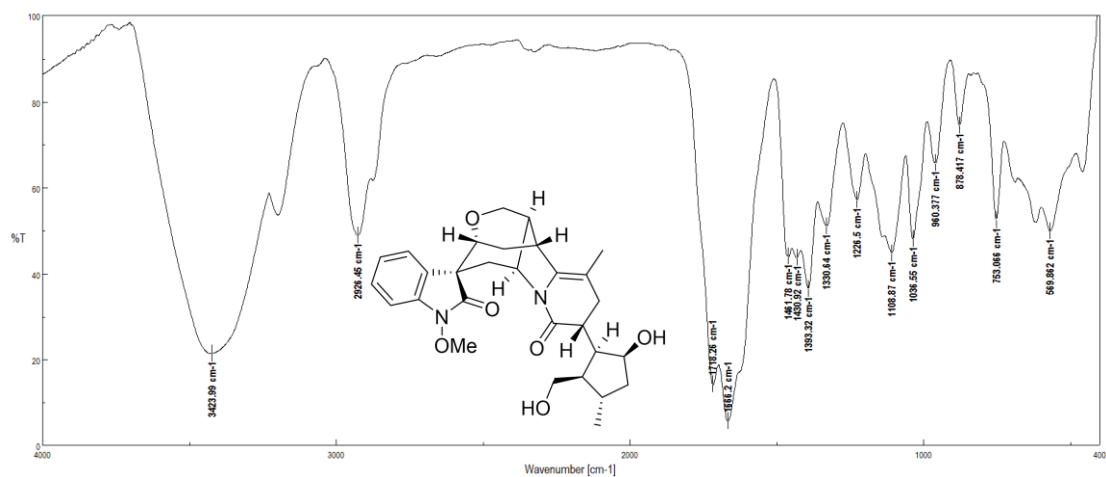


Figure S25. The IR (KBr disc) of compound **3**

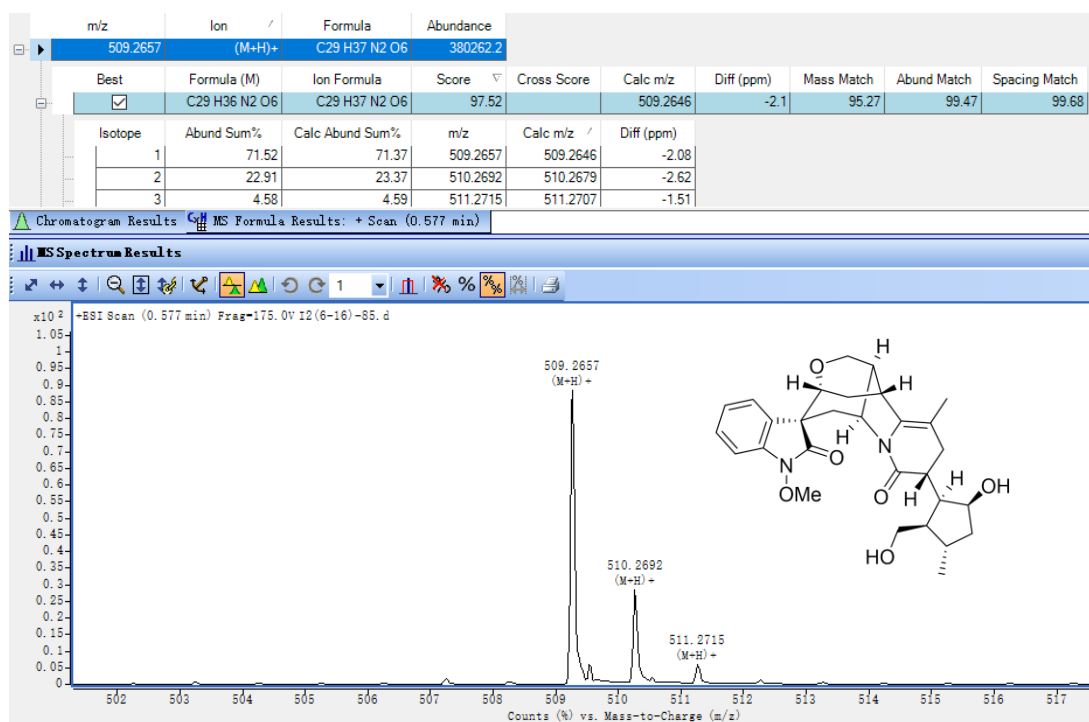


Figure S26. The HR-ESI-MS of compound **3**

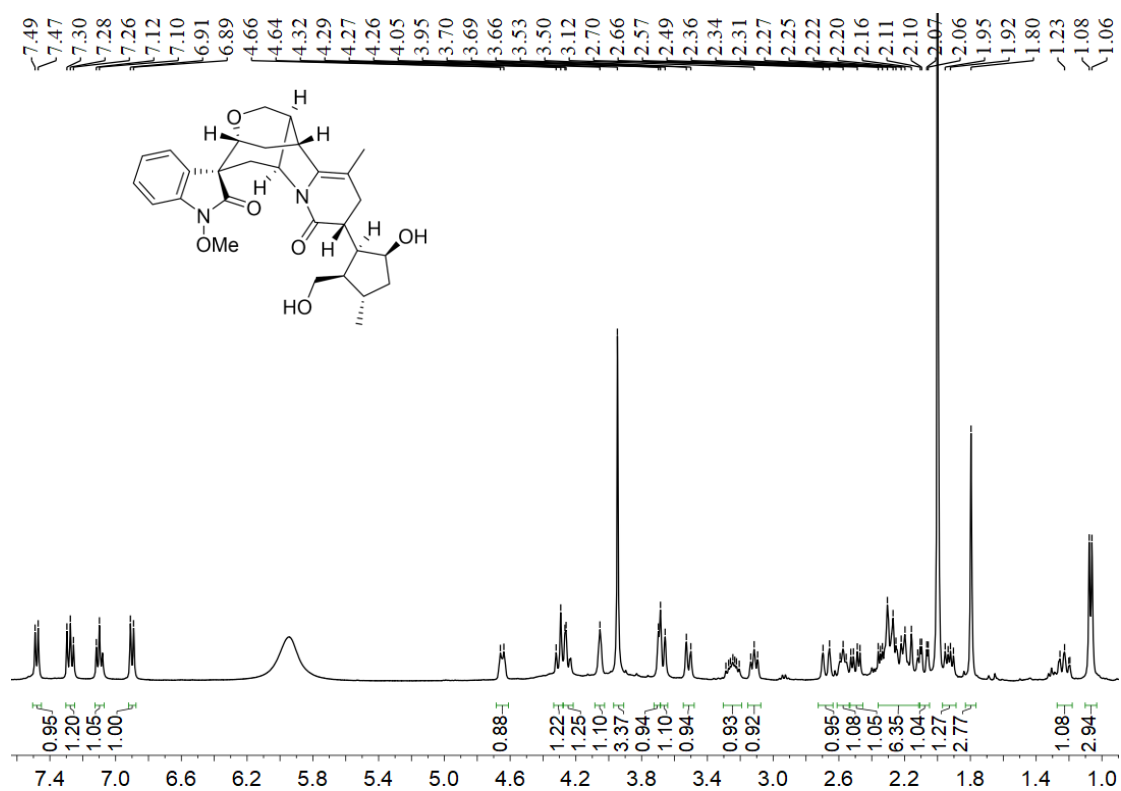


Figure S27. The ^1H NMR spectrum of compound **3** in CDCl_3

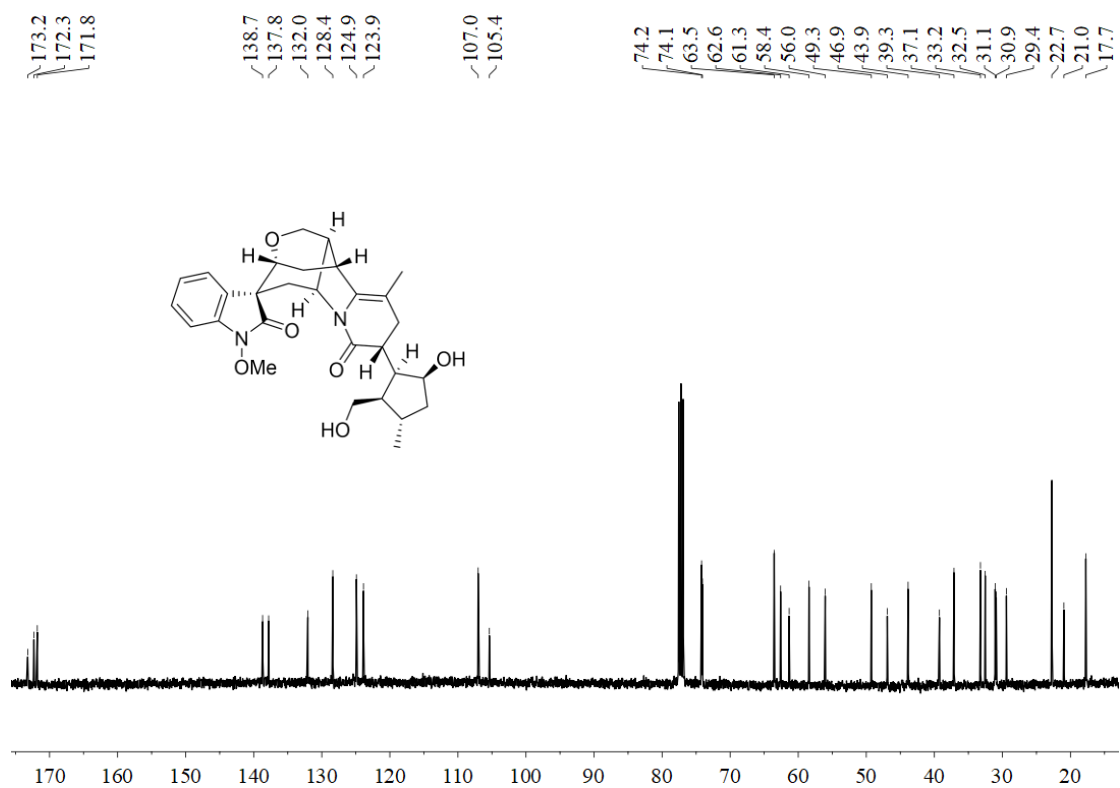


Figure S28. The ^{13}C NMR spectrum of compound **3** in CDCl_3

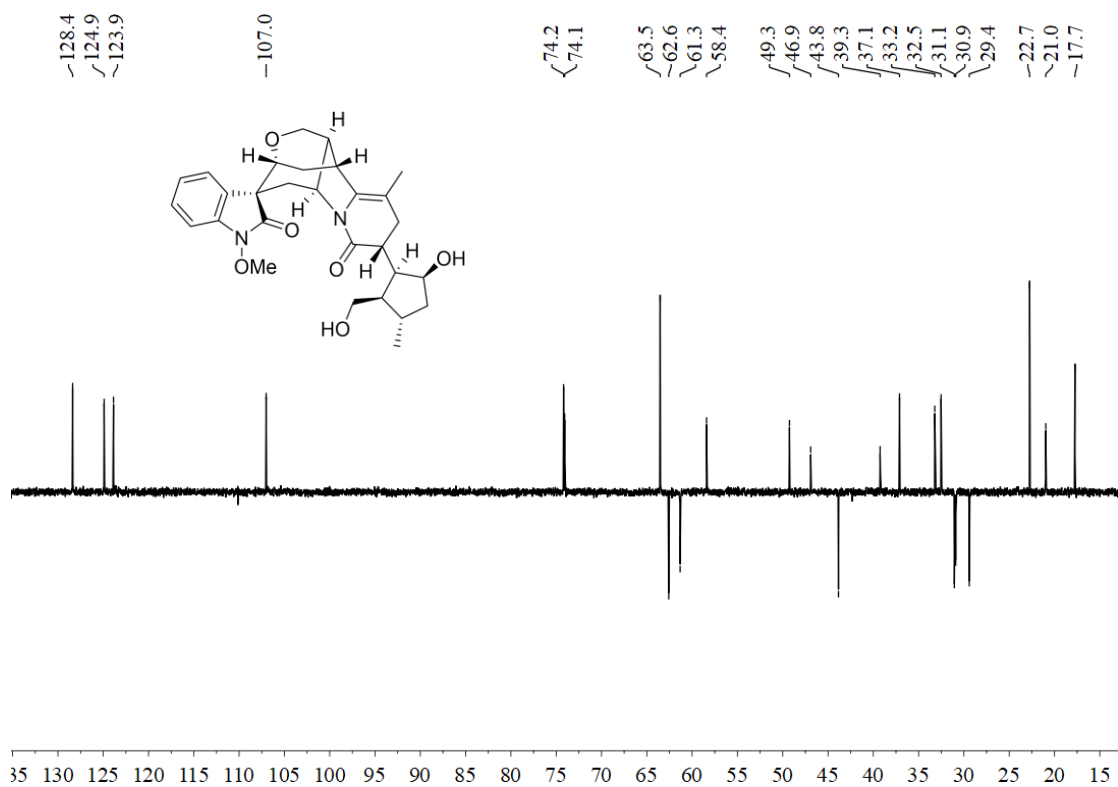


Figure S29. The DEPT-135 spectrum of compound **3** in CDCl_3

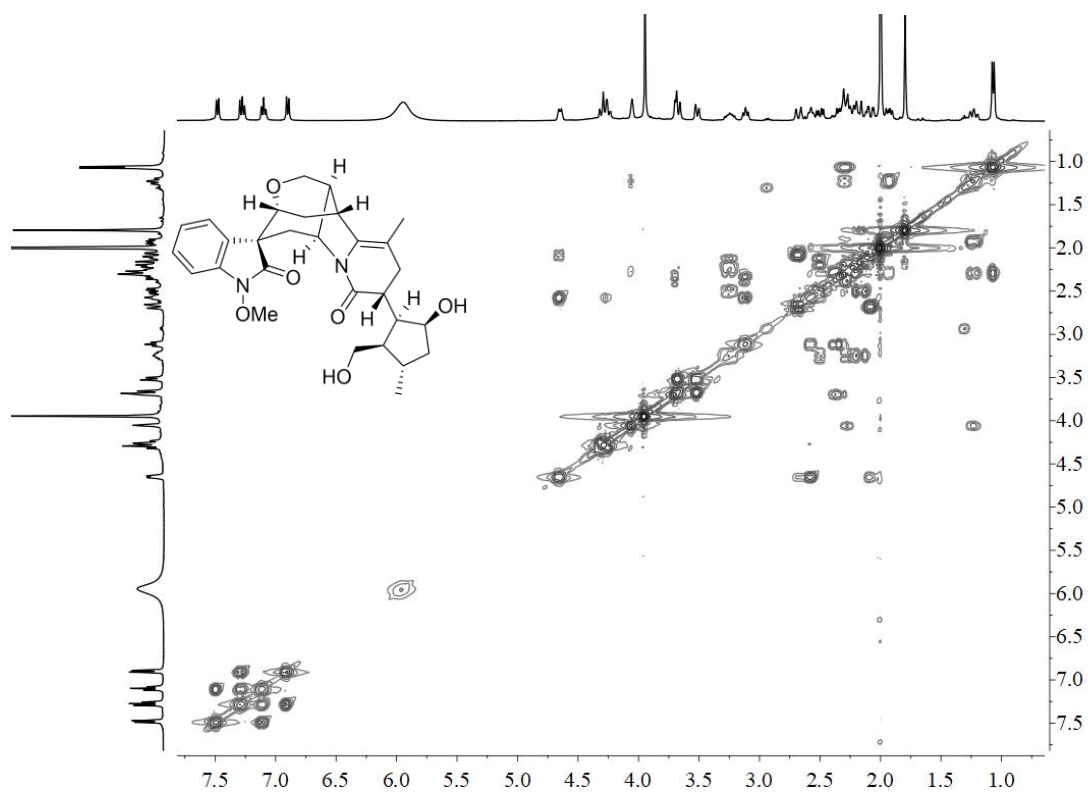


Figure S30. The ^1H - ^1H COSY spectrum of compound **3** in CDCl_3

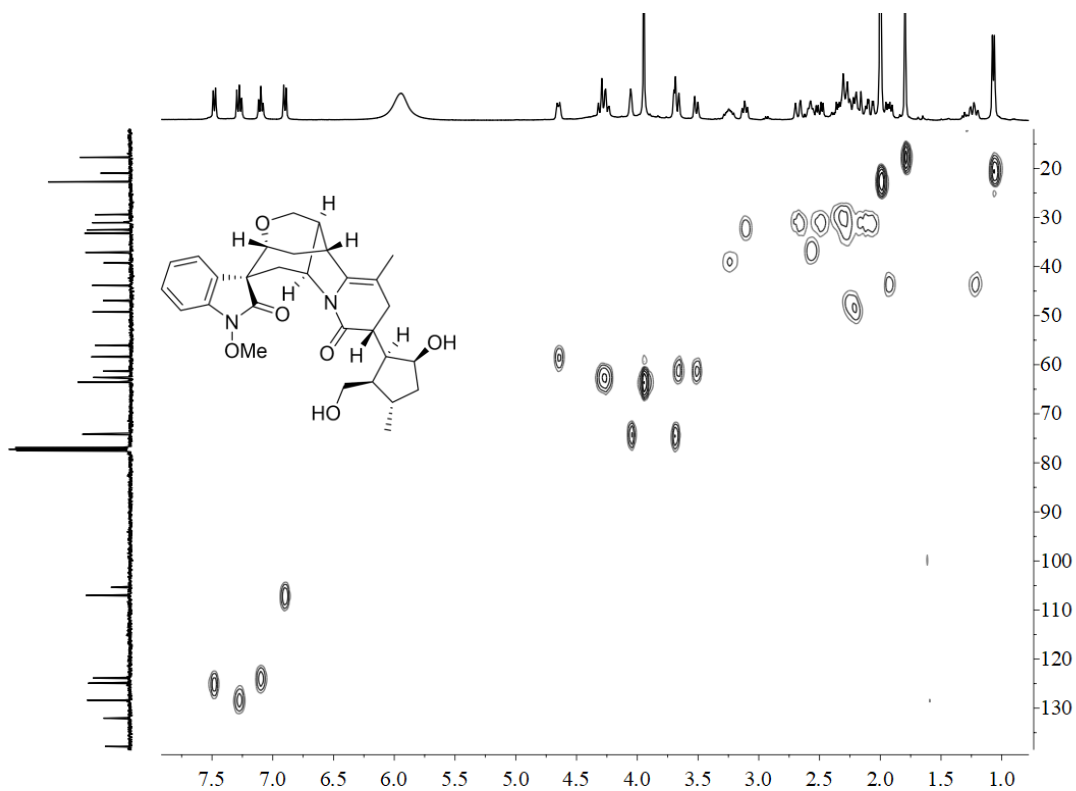


Figure S31. The HSQC spectrum of compound **3** in CDCl_3

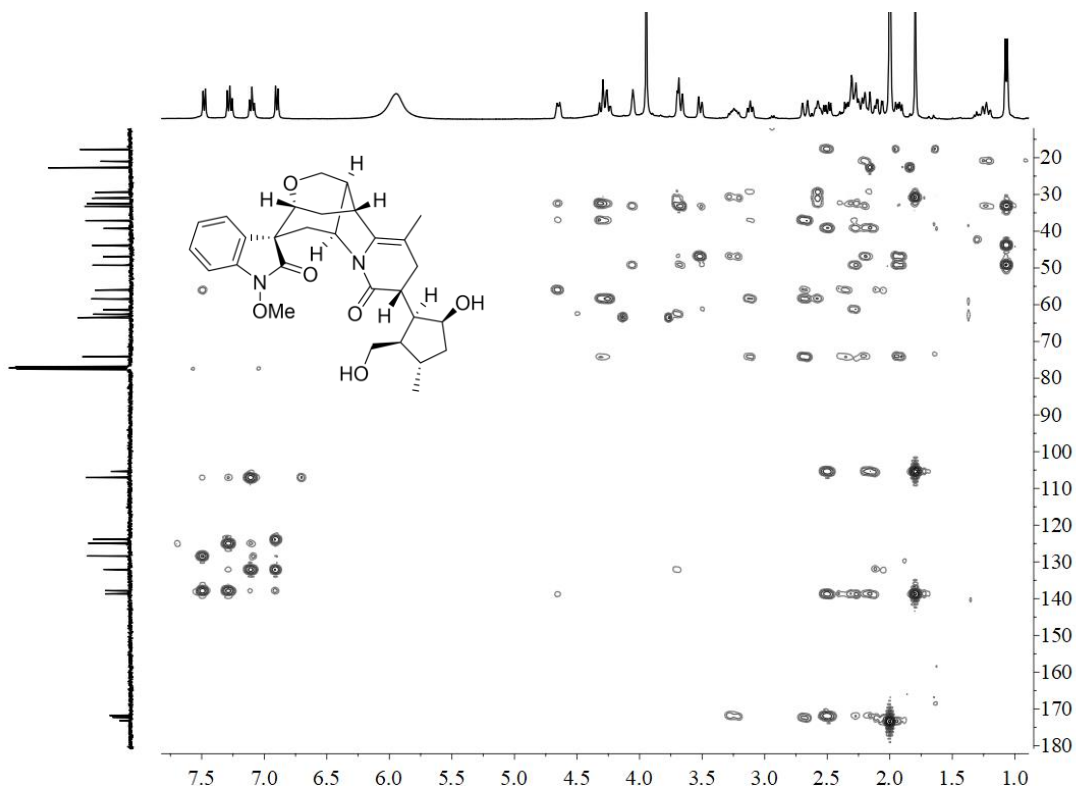


Figure S32. The HMBC spectrum of compound **3** in CDCl_3

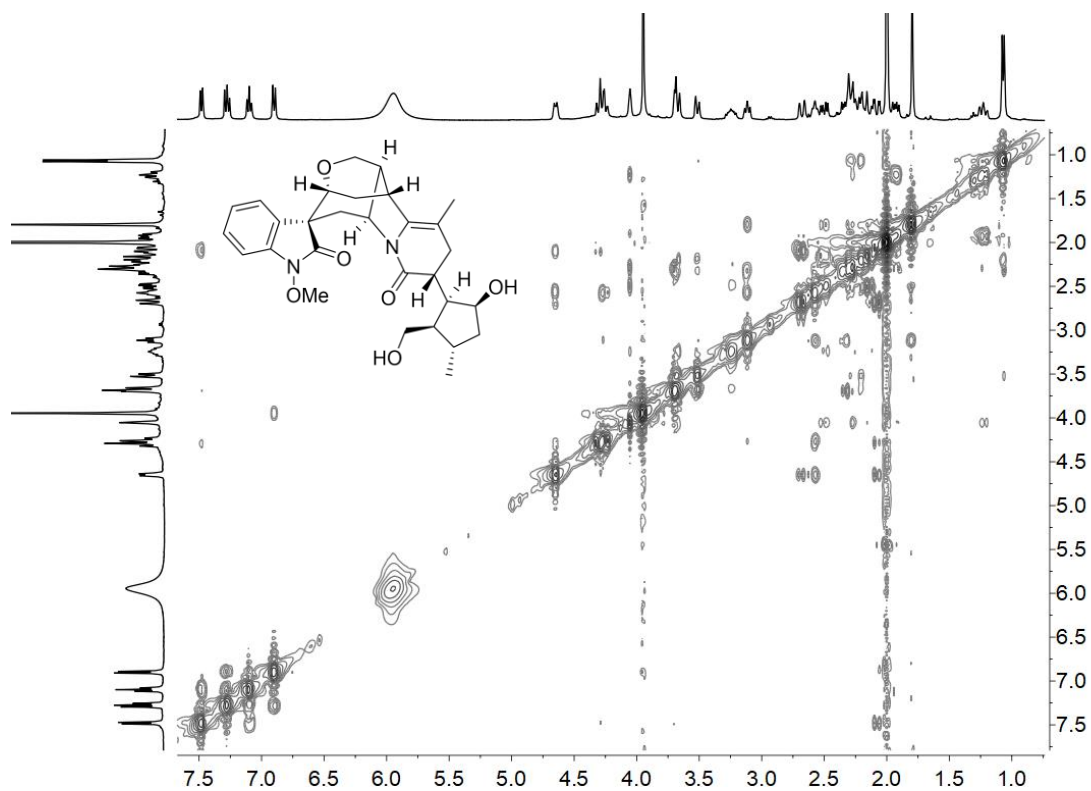


Figure S33. The NOESY spectrum of compound **3** in CDCl_3

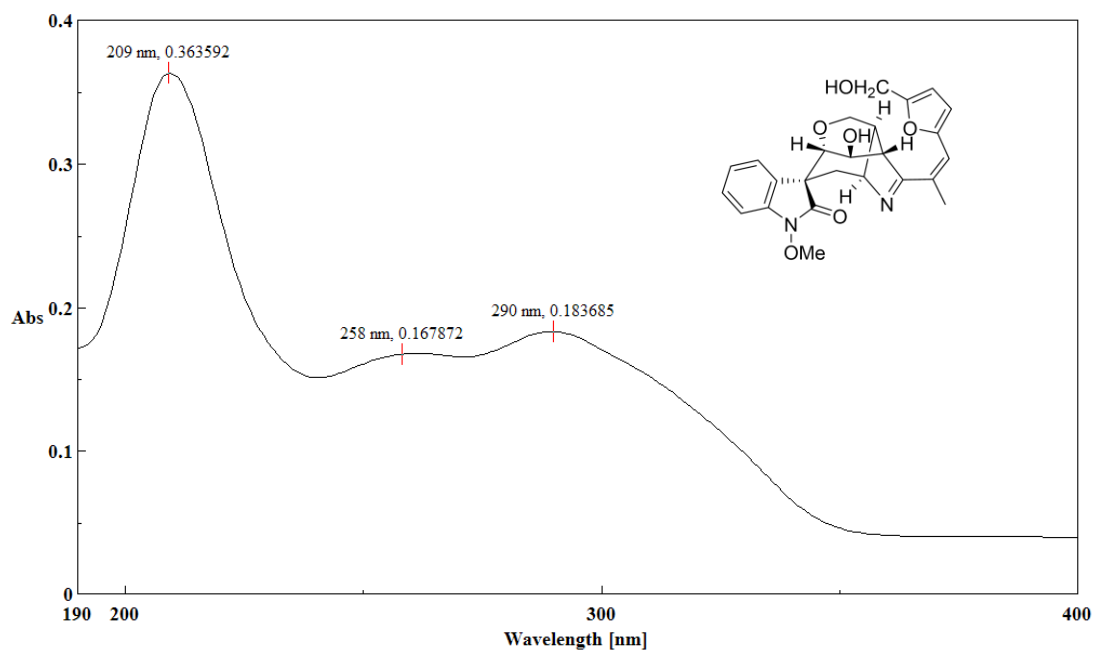


Figure S34. The UV of compound **4** in MeOH

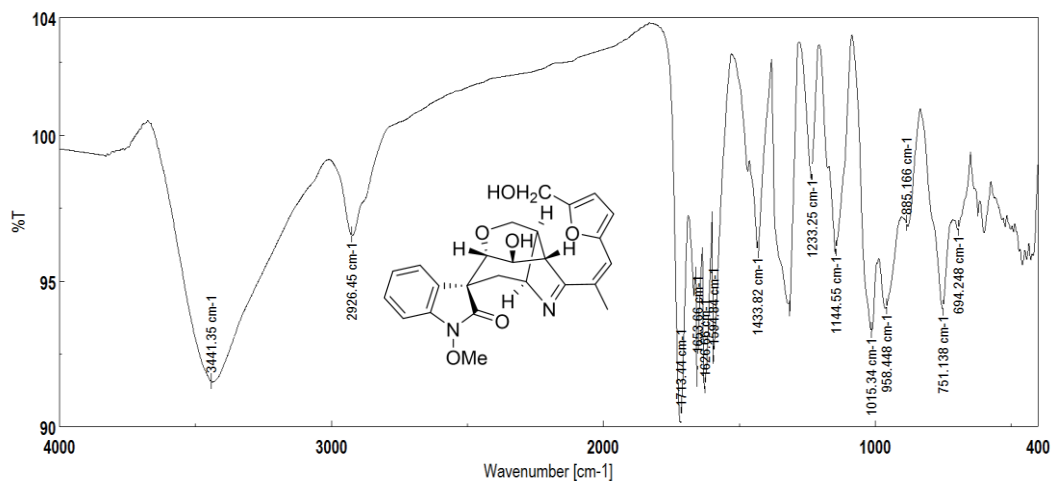


Figure S35. The IR (KBr disc) of compound 4

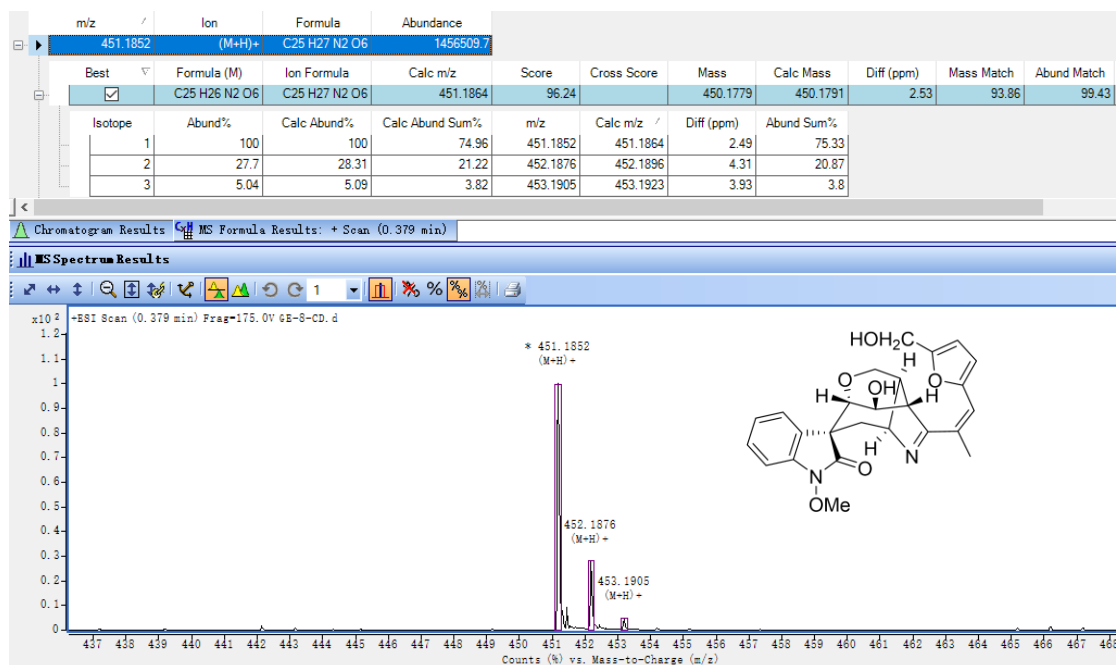


Figure S36. The HR-ESI-MS of compound 4

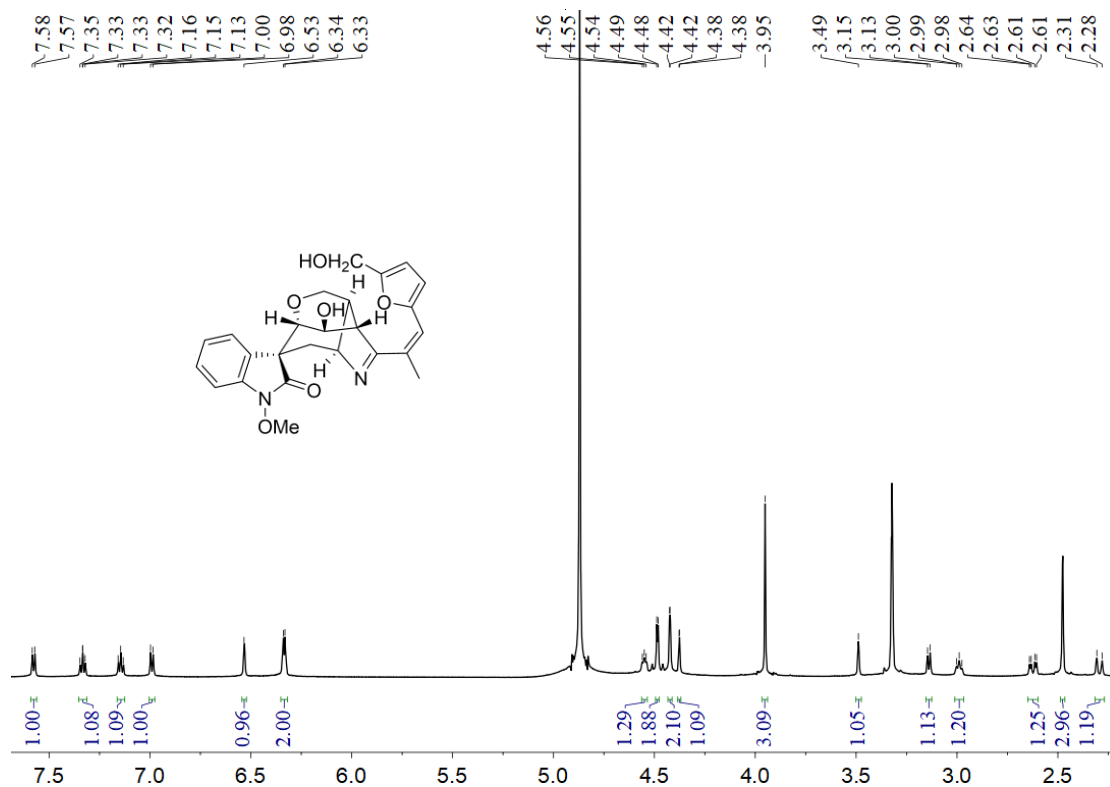


Figure S37. The ^1H NMR spectrum of compound **4** in CD_3OD

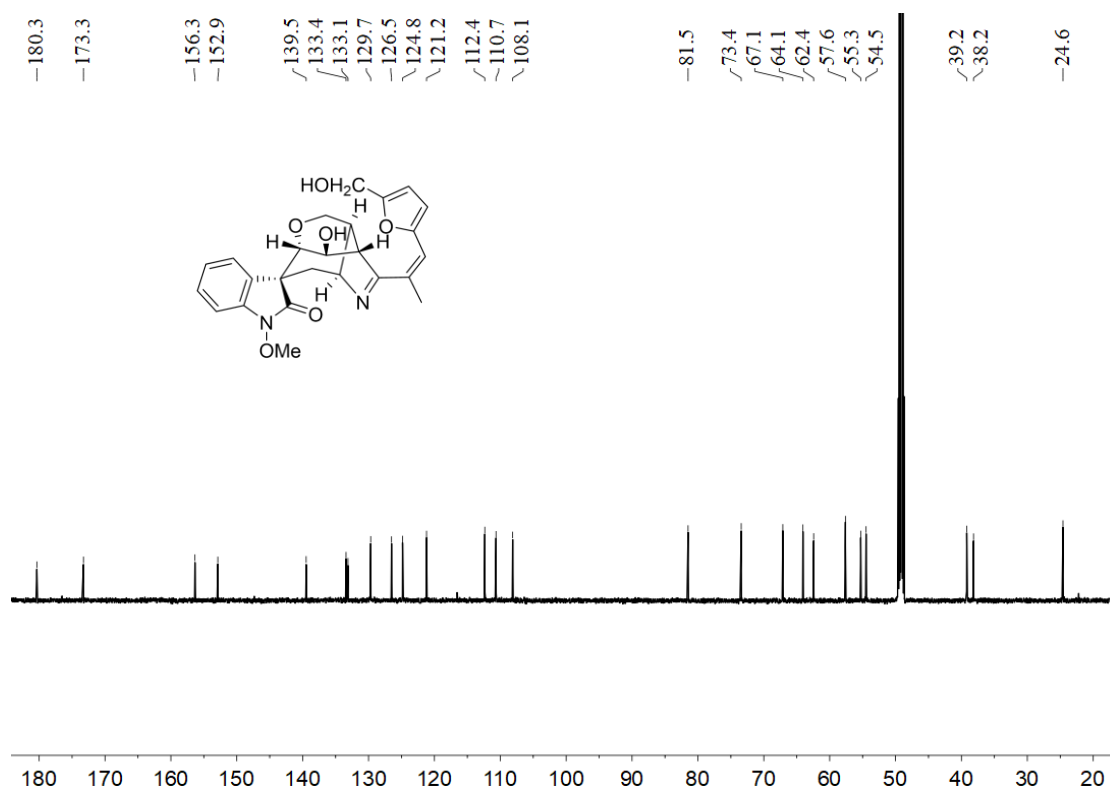
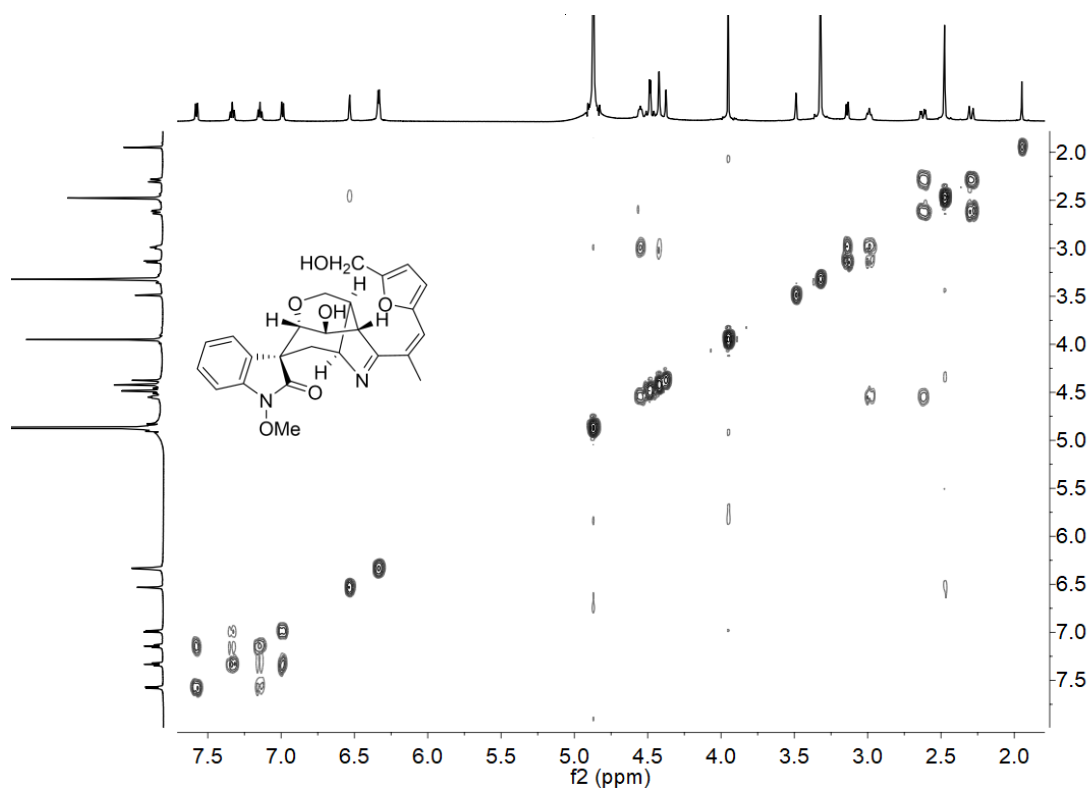
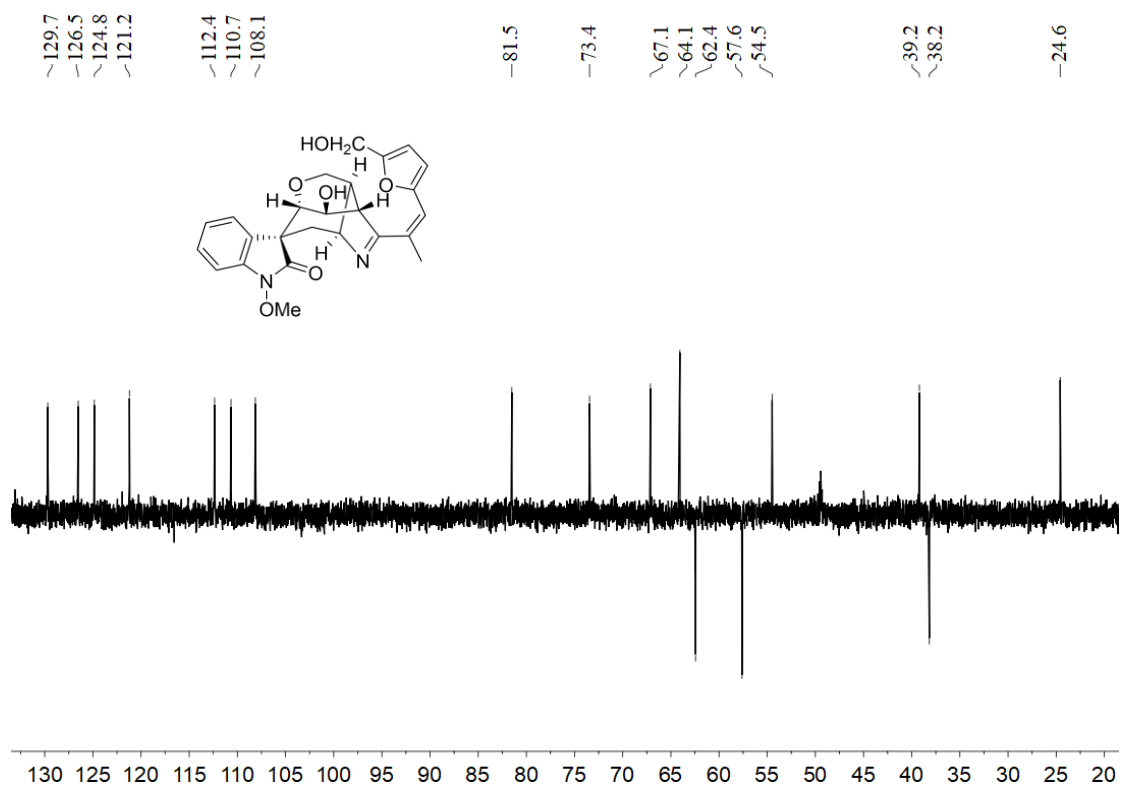


Figure S38. The ^{13}C NMR spectrum of compound **4** in CD_3OD



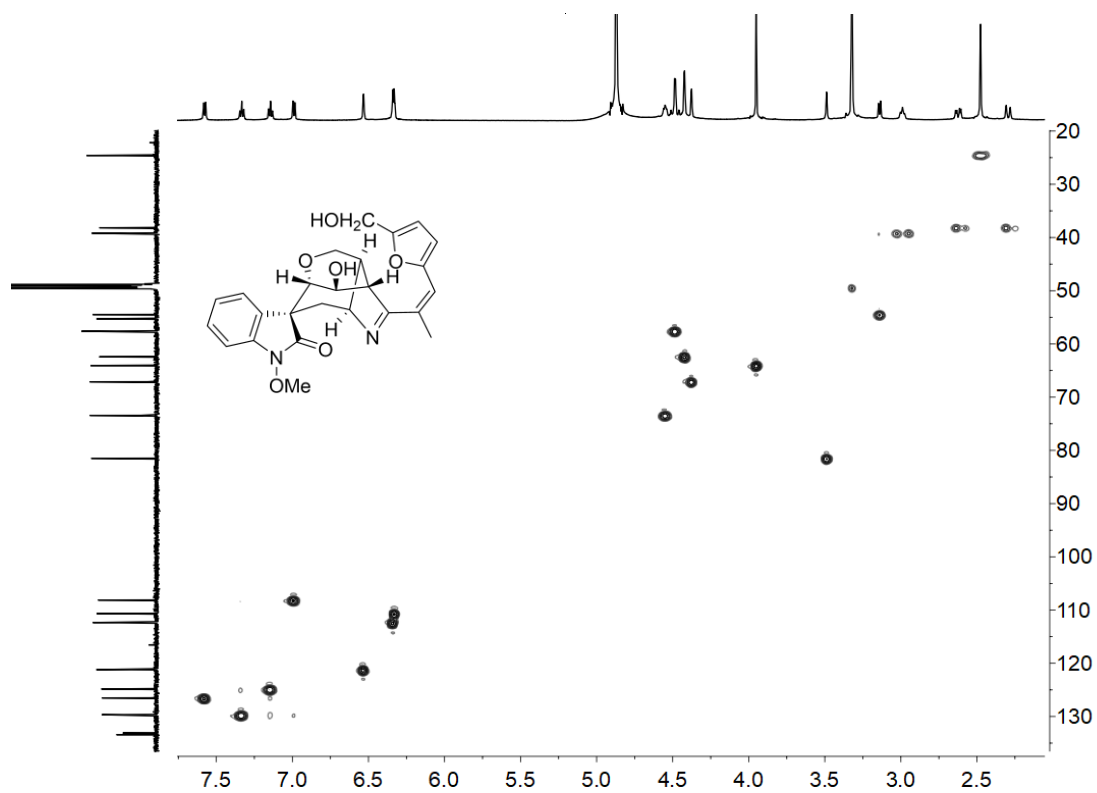


Figure S41. The HSQC spectrum of compound **4** in CD_3OD

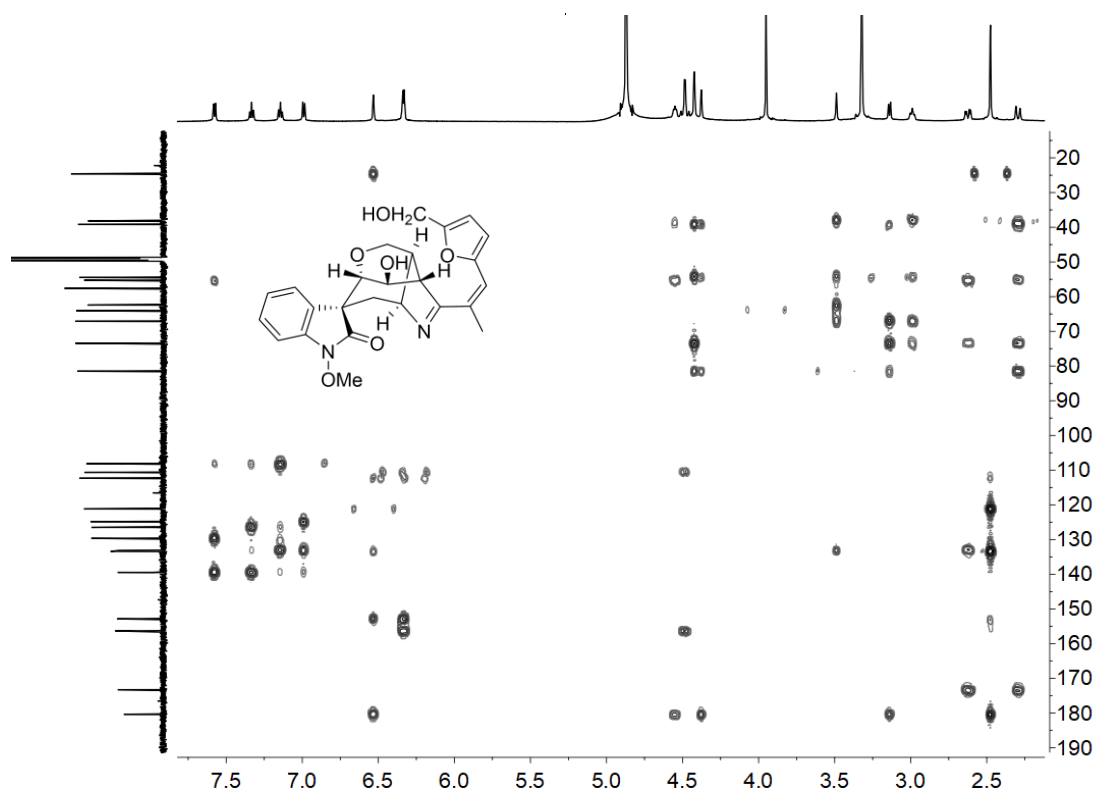


Figure S42. The HMBC spectrum of compound **4** in CD_3OD

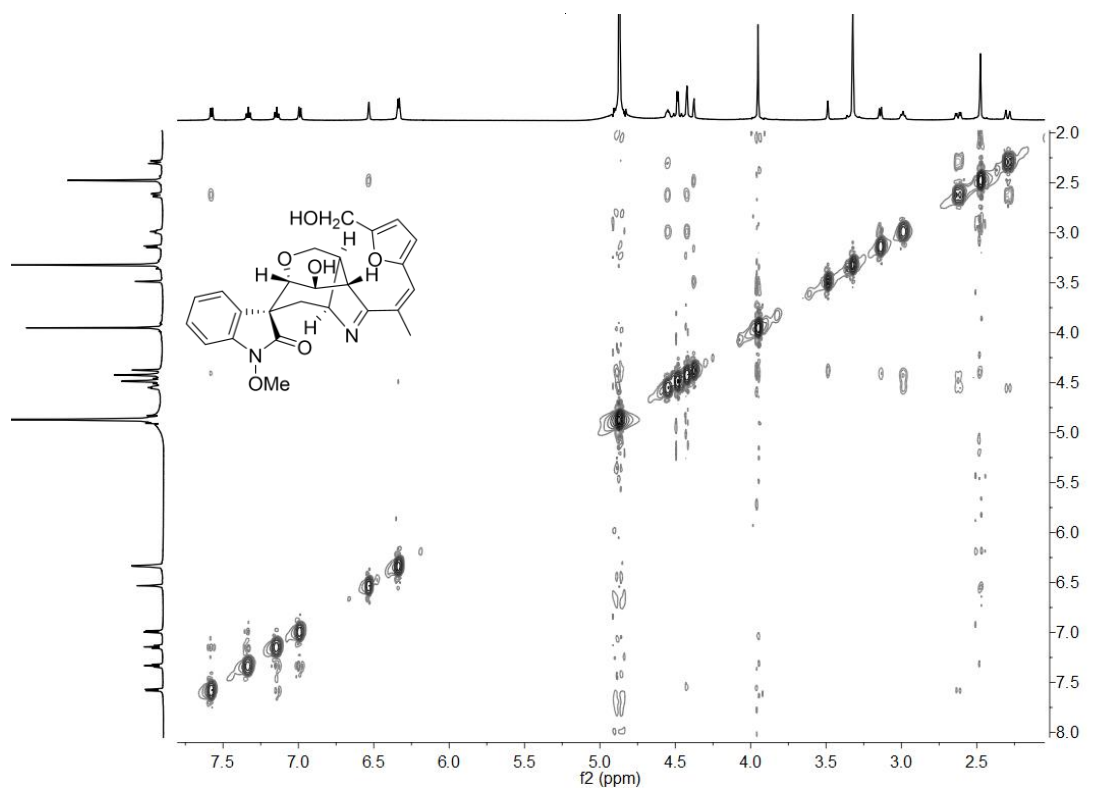


Figure S43. The NOESY spectrum of compound **4** in CD₃OD

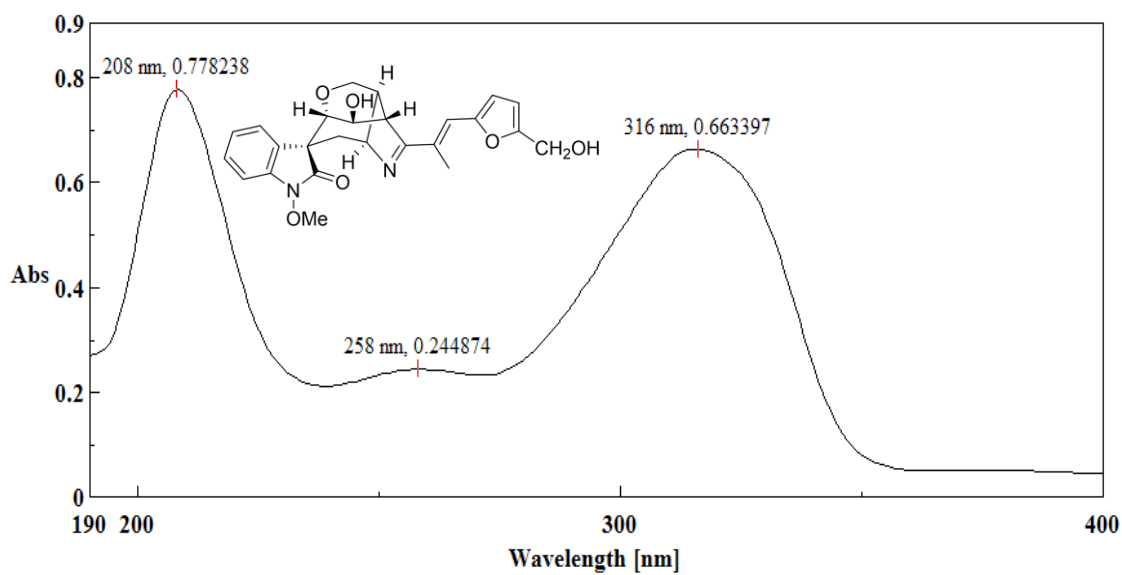


Figure S44. The UV of compound **5** in MeOH

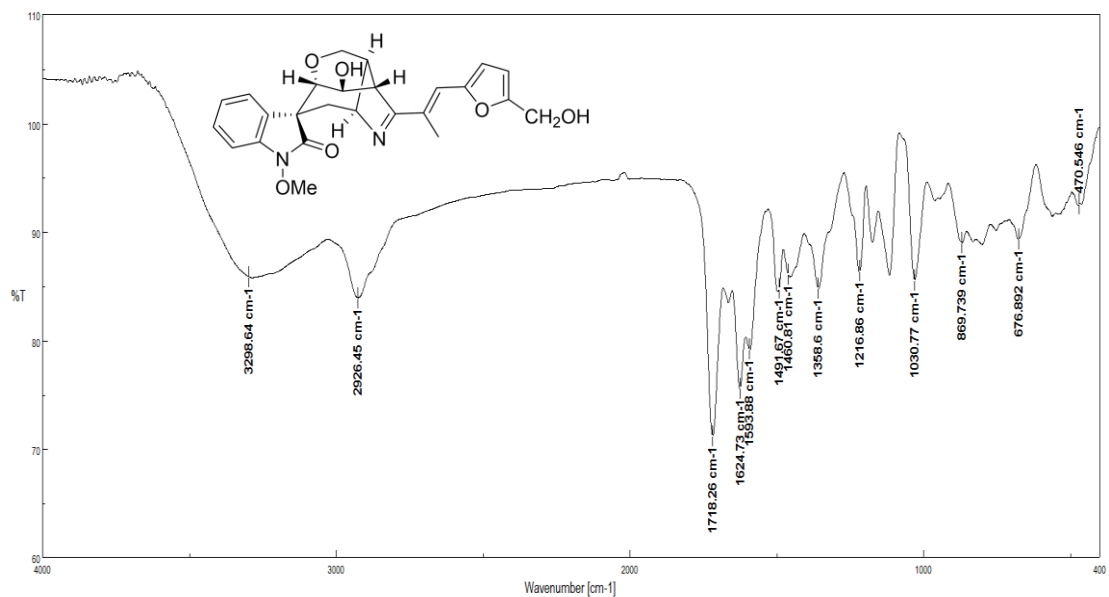


Figure S45. The IR (KBr disc) of compound 5

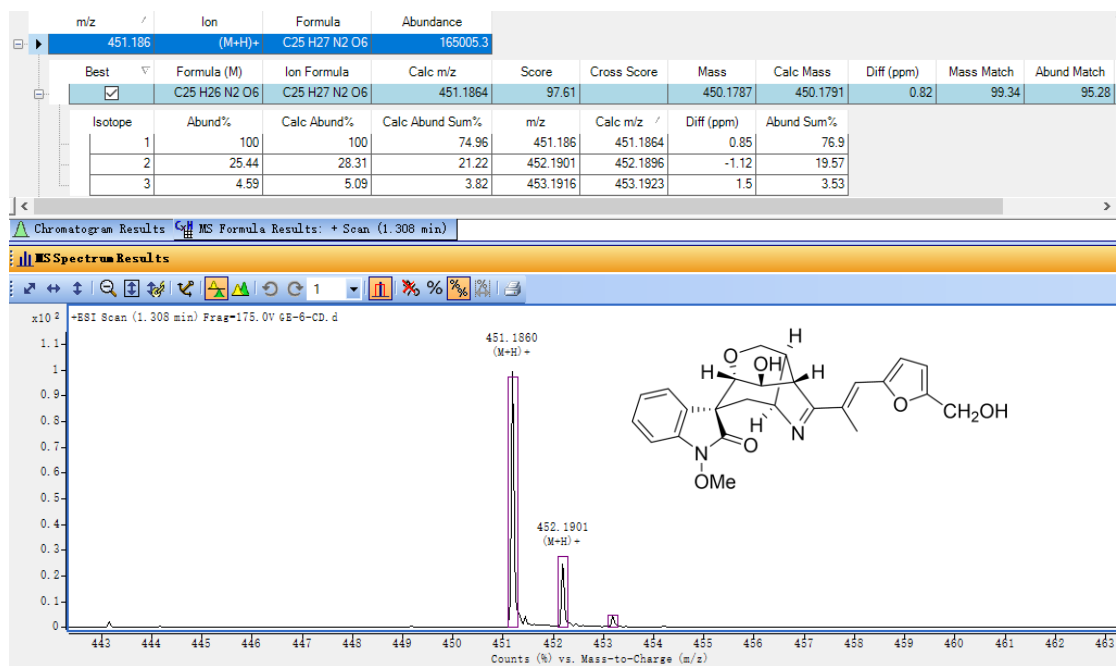


Figure S46. The HR-ESI-MS of compound 5

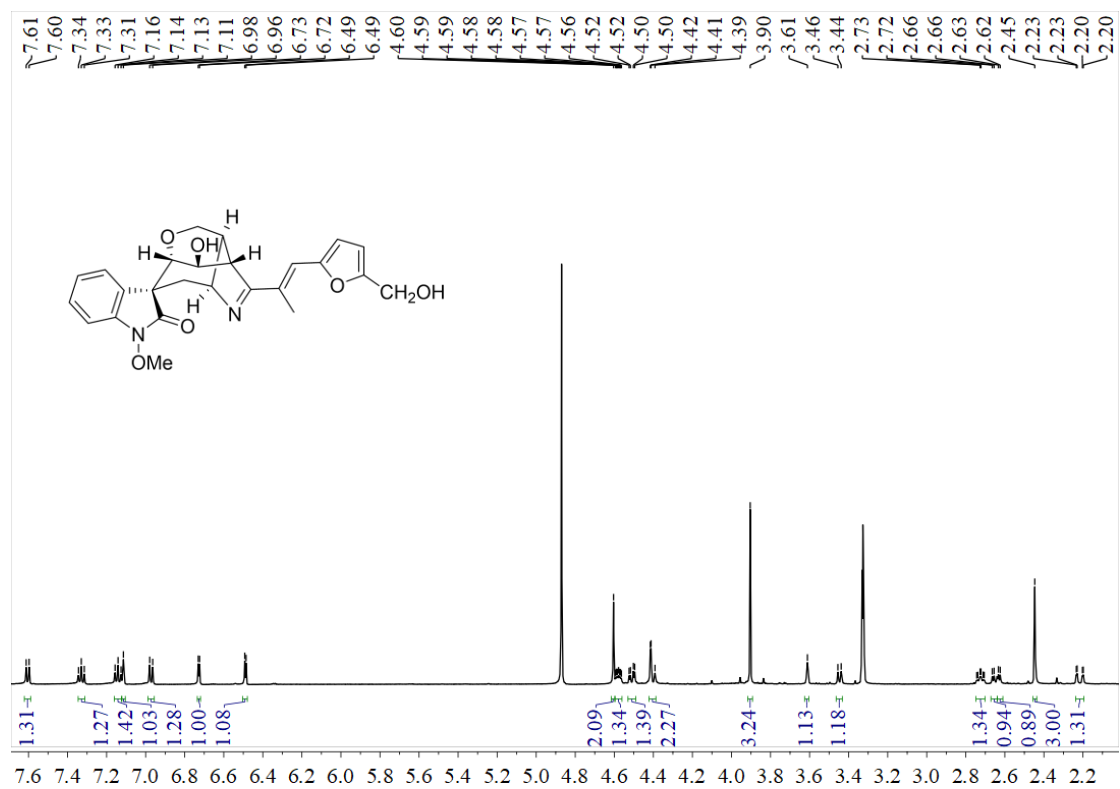


Figure S47. The ^1H NMR spectrum of compound **5** in CD_3OD

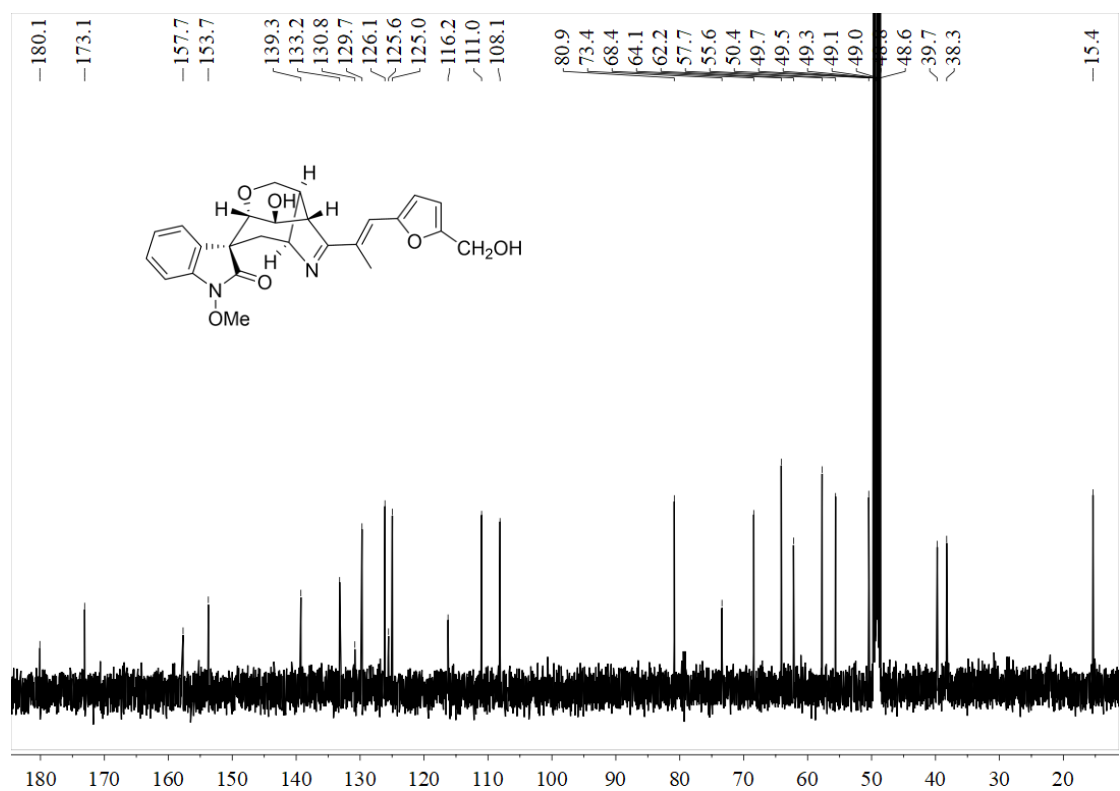


Figure S48. The ^{13}C NMR spectrum of compound **5** in CD_3OD

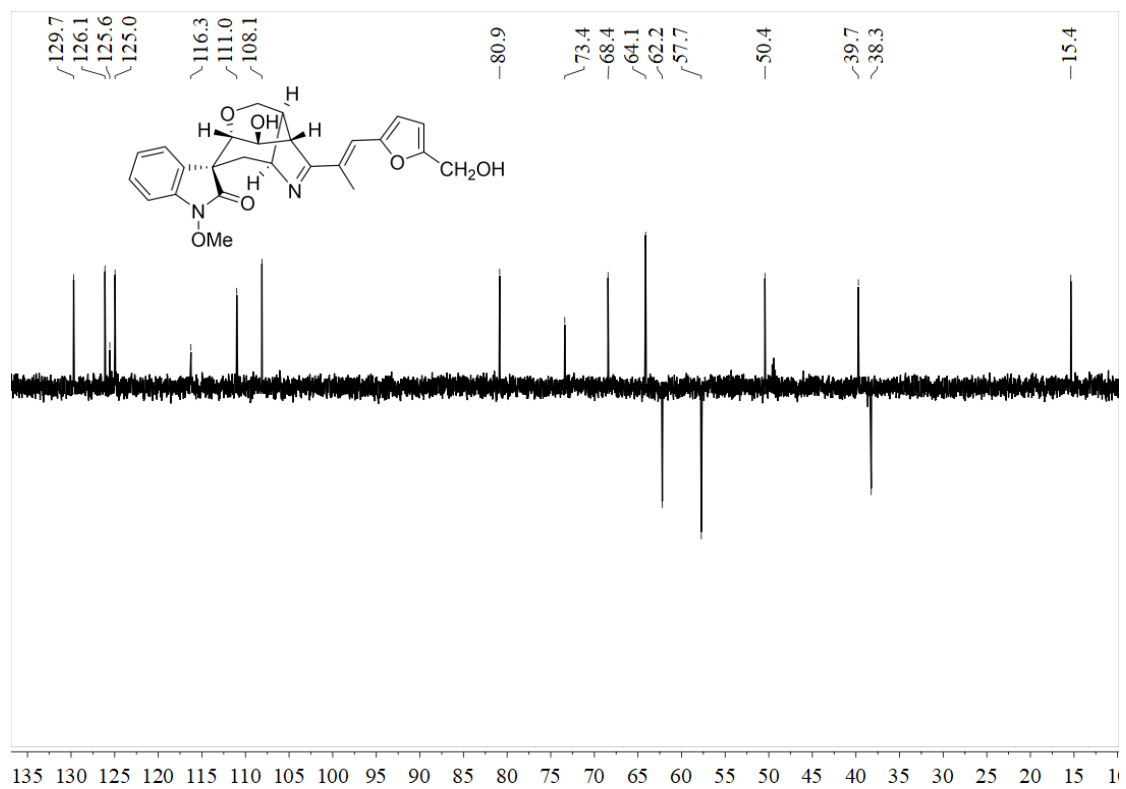


Figure S49. The DEPT-135 spectrum of compound **5** in CD₃OD

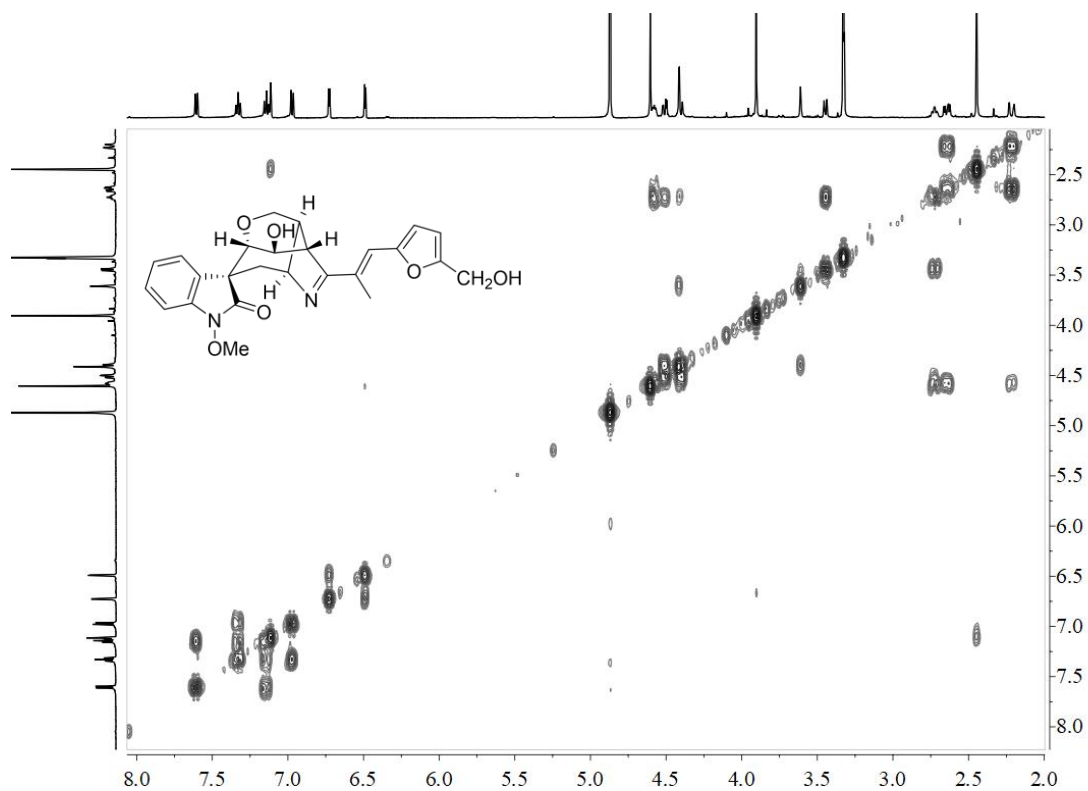


Figure S50. The ¹H-¹H COSY spectrum of compound **5** in CD₃OD

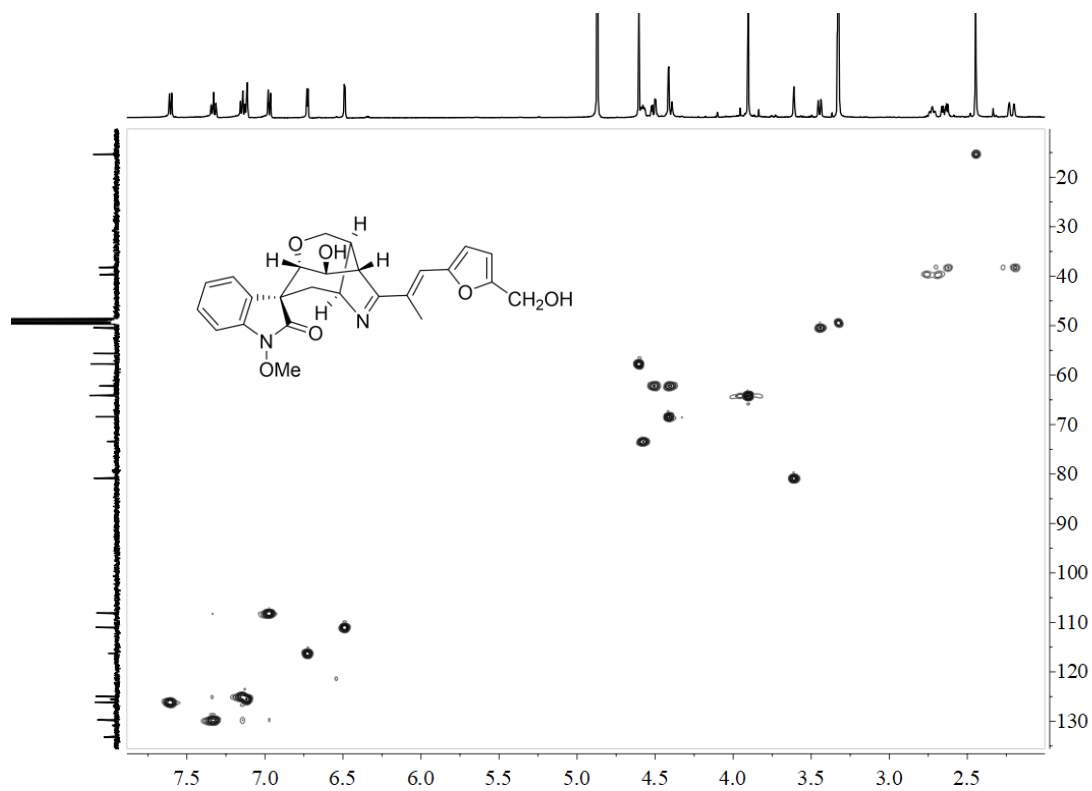


Figure S51. The HSQC spectrum of compound **5** in CD₃OD

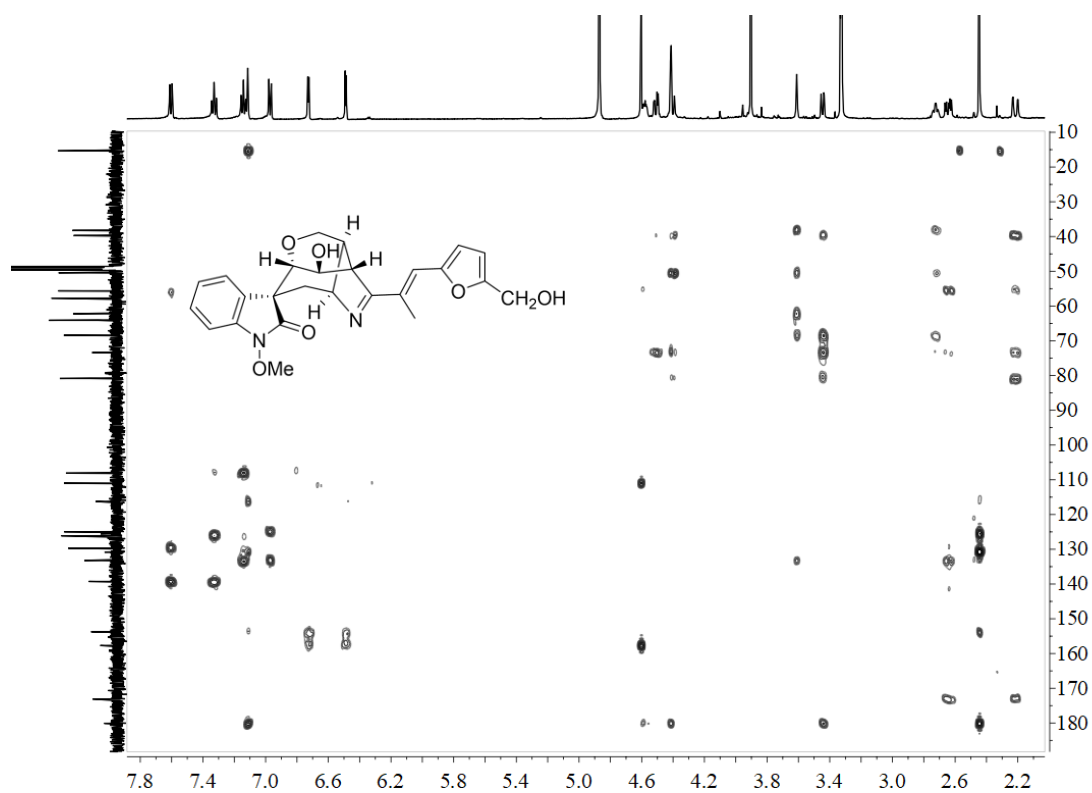


Figure S52. The HMBC spectrum of compound **5** in CD₃OD

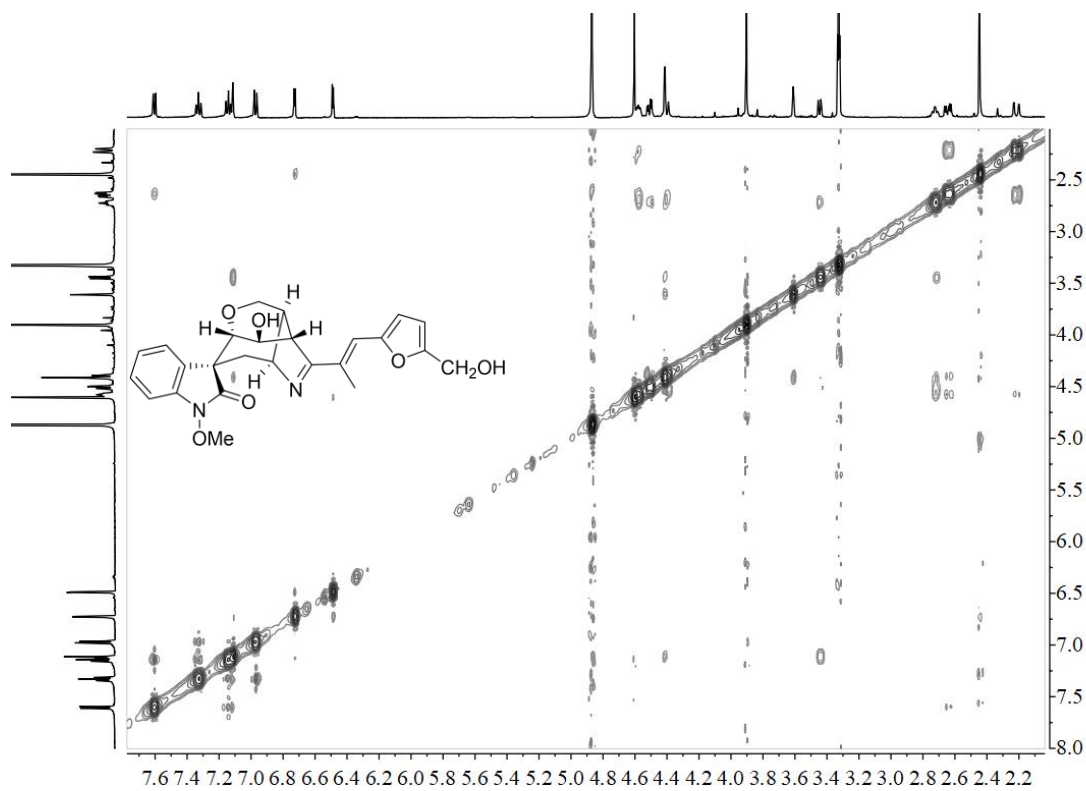


Figure S53. The NOESY spectrum of compound **5** in CD₃OD

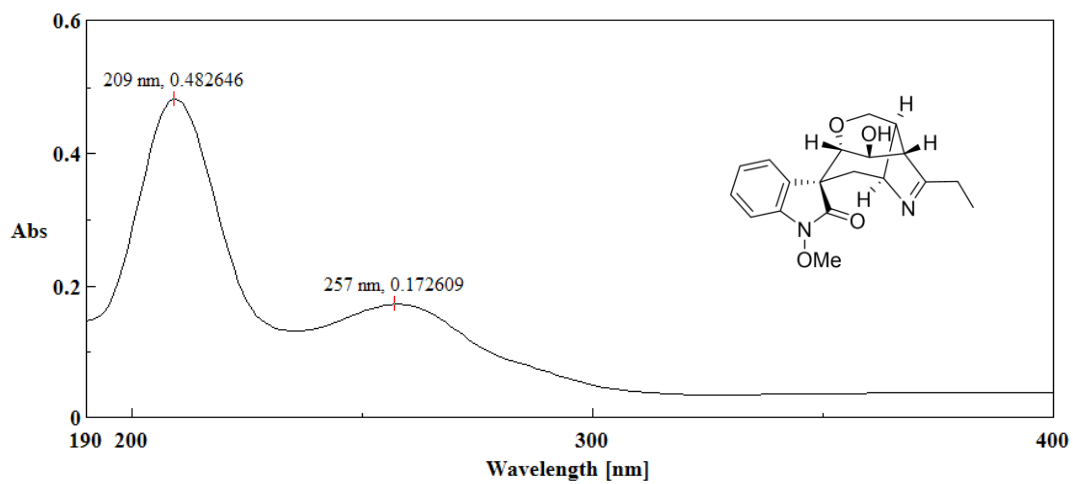


Figure S54. The UV of compound **6** in MeOH

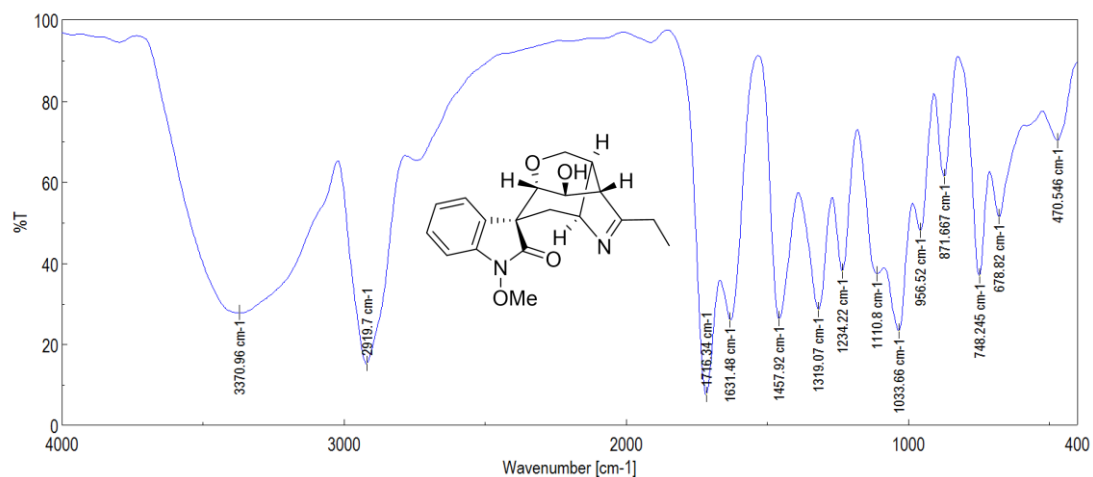


Figure S55. The IR (KBr disc) of compound 6

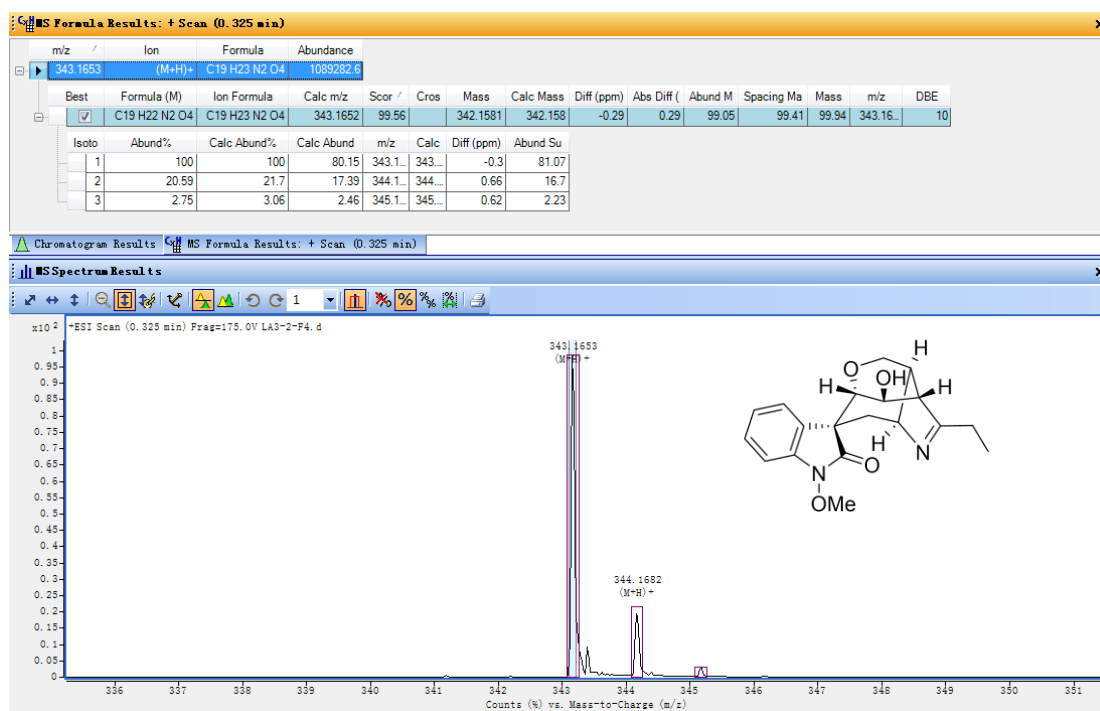


Figure S56. The HR-ESI-MS of compound 6

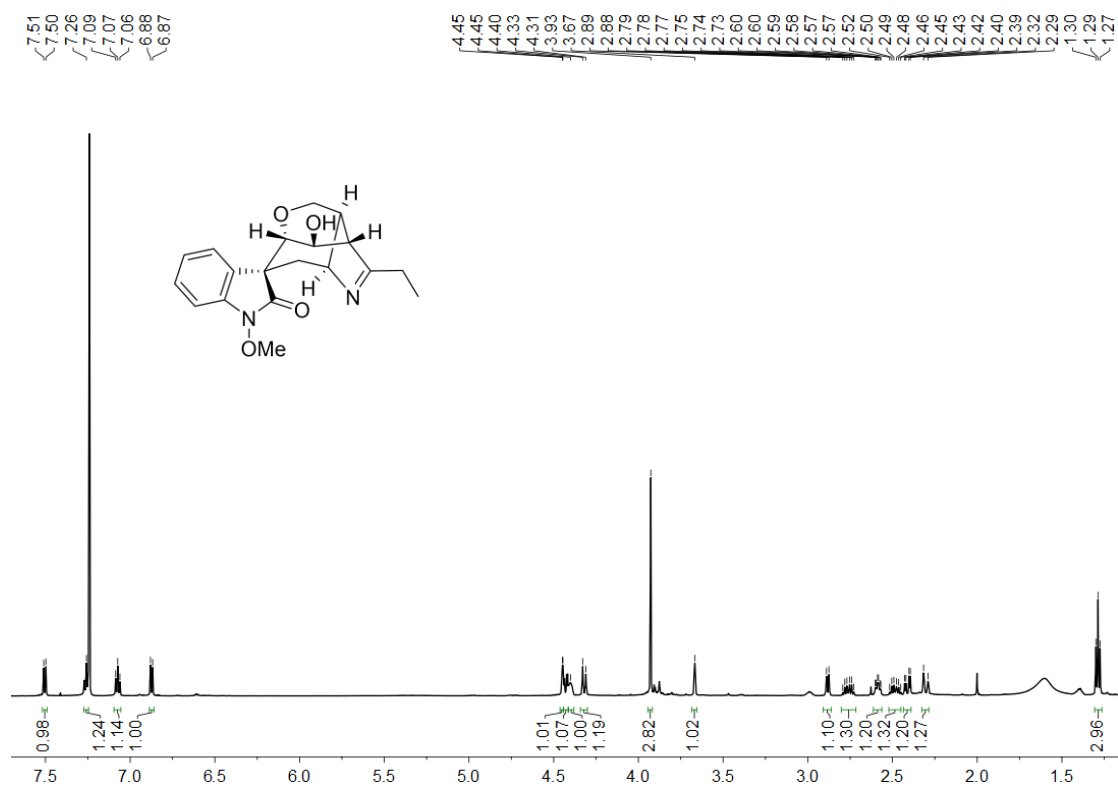


Figure S57. The ¹H NMR spectrum of compound 6 in CDCl₃

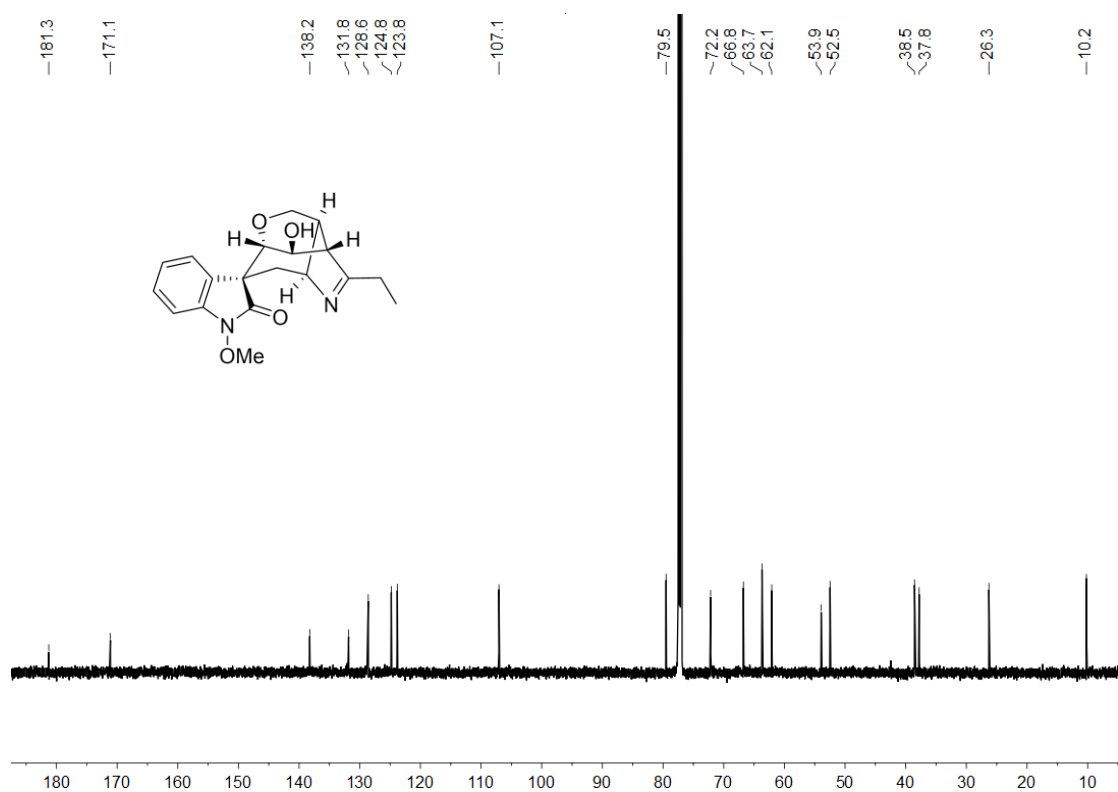


Figure S58. The ¹³C NMR spectrum of compound 6 in CDCl₃

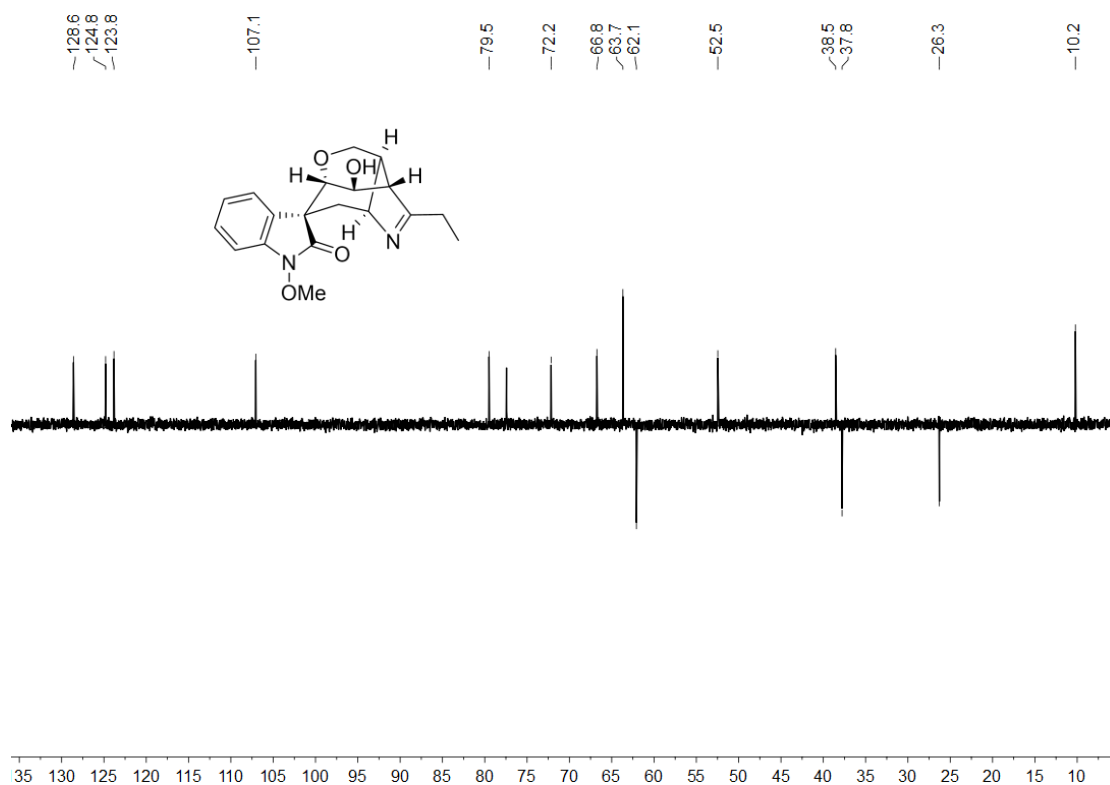


Figure S59. The DEPT-135 spectrum of compound **6** in CDCl₃

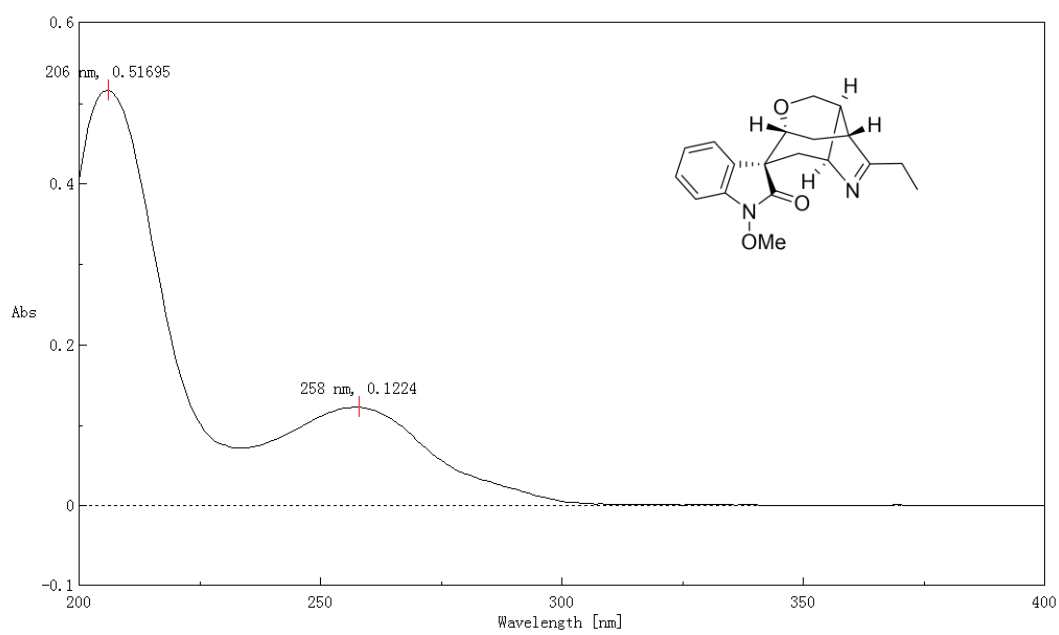


Figure S60. The UV of compound **7** in MeOH

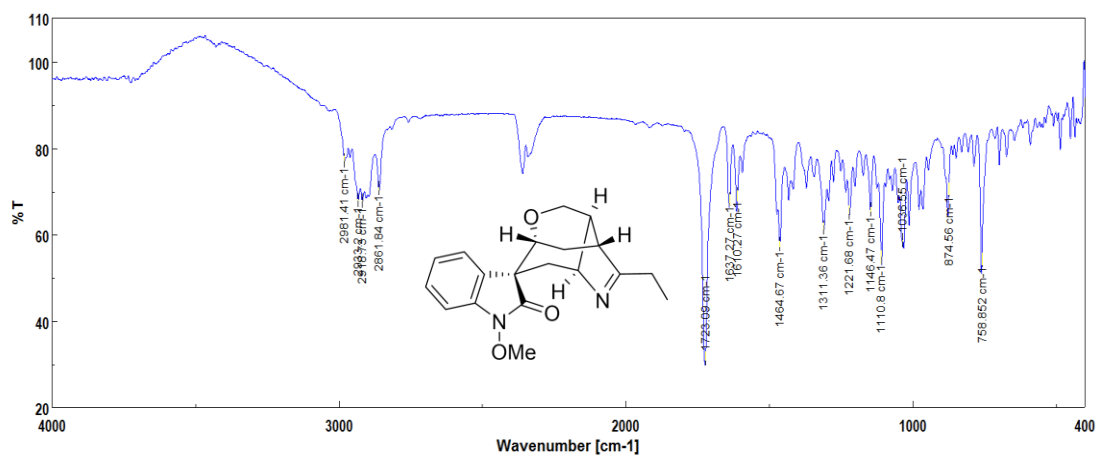


Figure S61. The IR (KBr disc) of compound 7

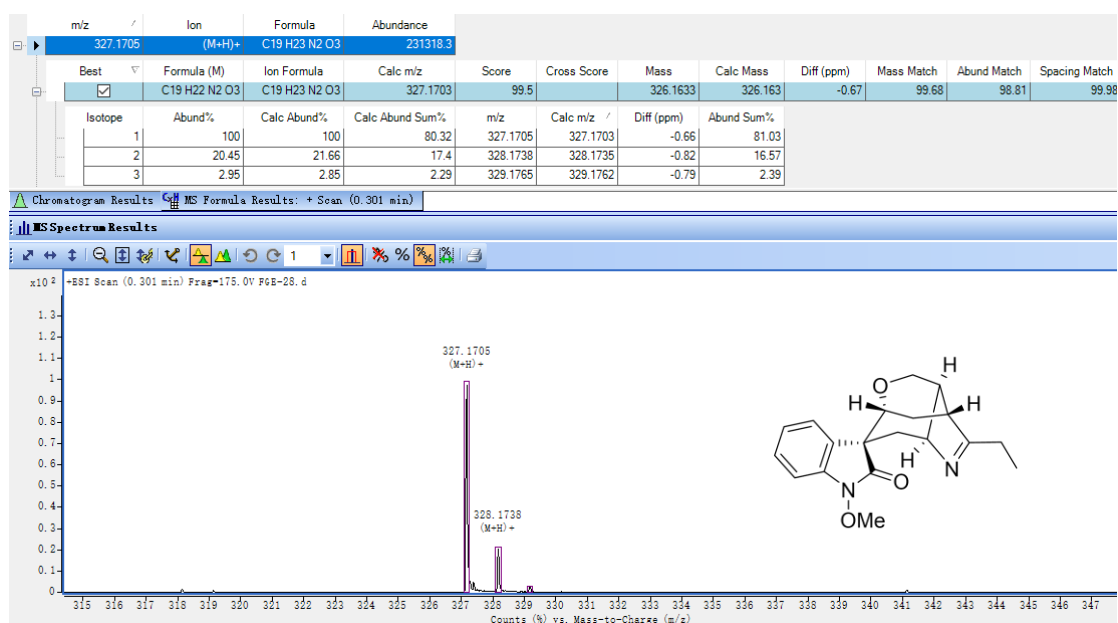


Figure S62. The ESI-MS of compound 7

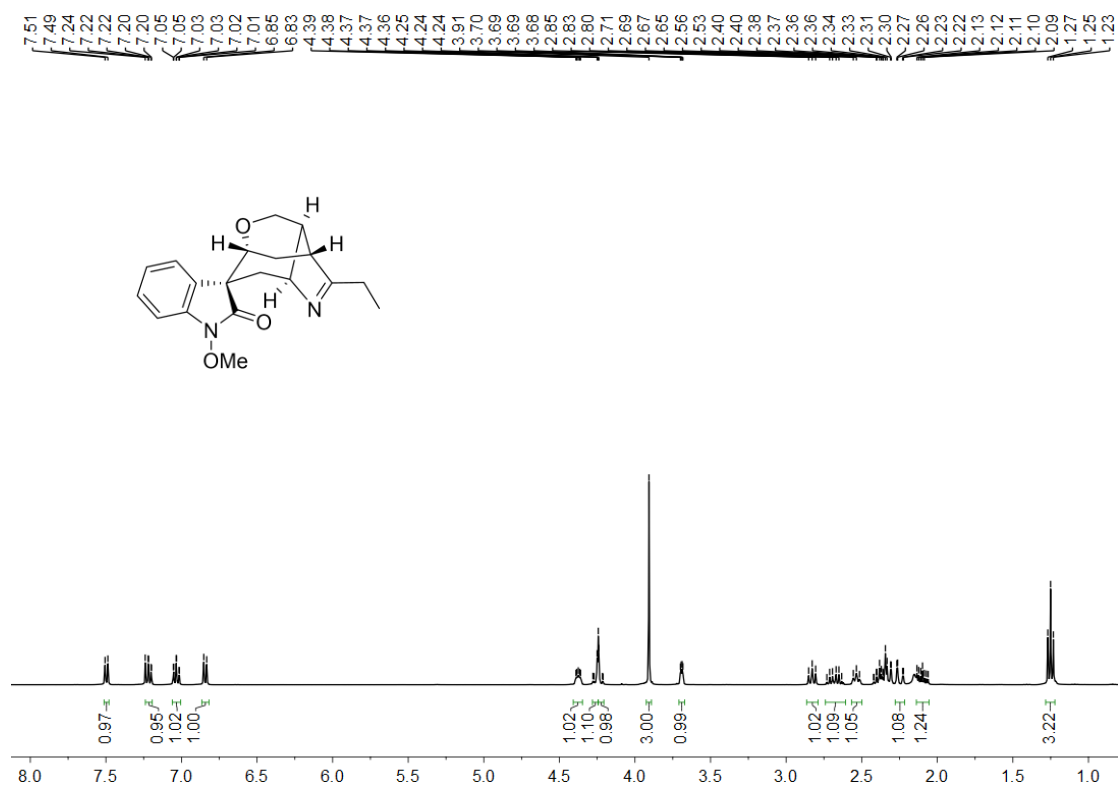


Figure S63. The ^1H NMR spectrum of compound **7** in CDCl_3

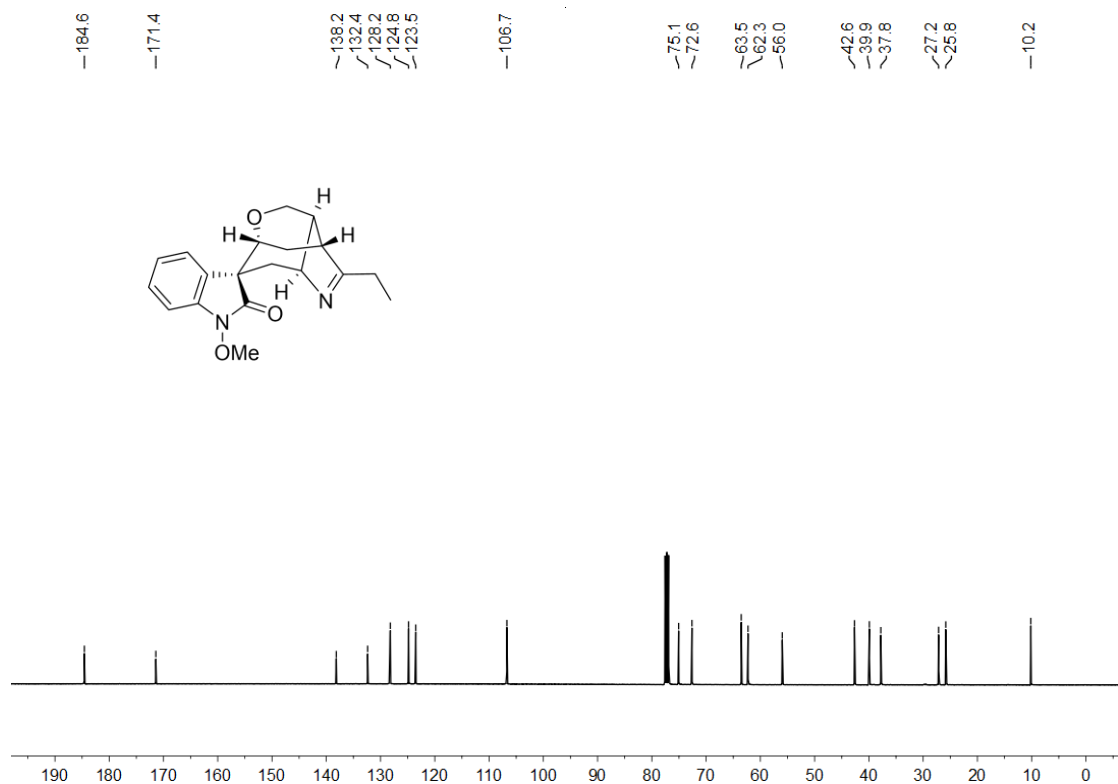


Figure S64. The ^{13}C NMR spectrum of compound **7** in CDCl_3

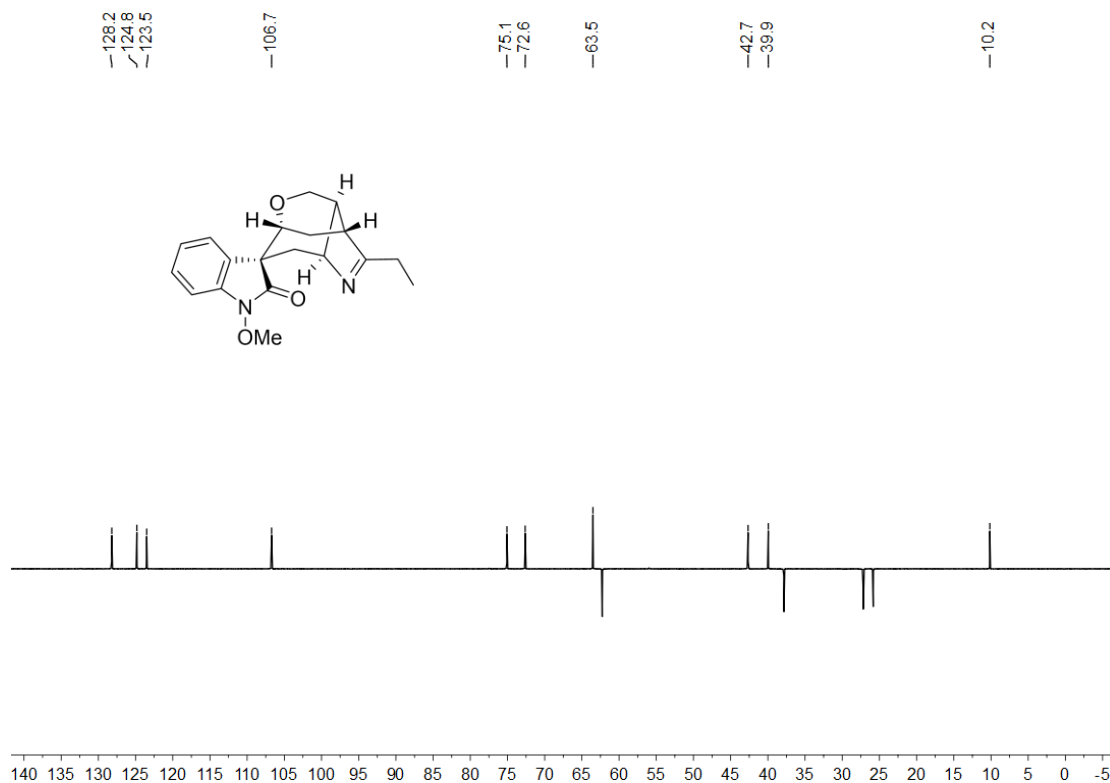


Figure S65. The DEPT-135 spectrum of compound **7** in CDCl₃

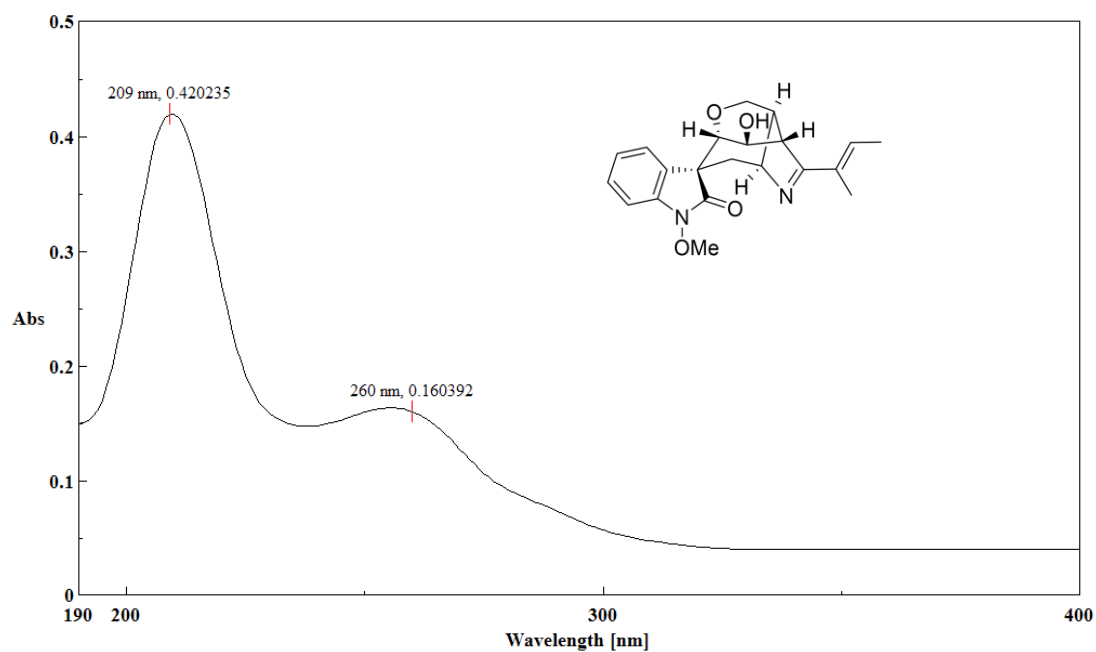


Figure S66. The UV of compound **8** in MeOH

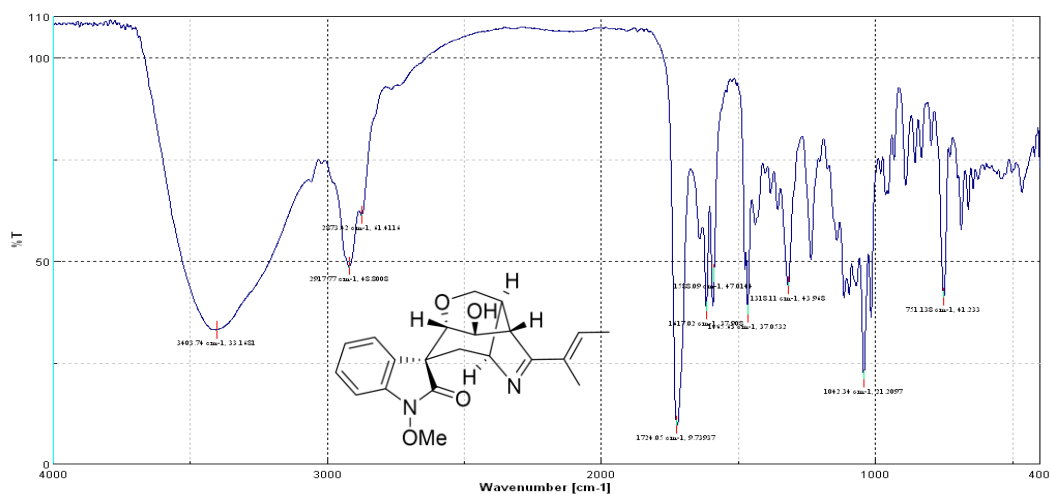


Figure S67. The IR (KBr disc) of compound **8**

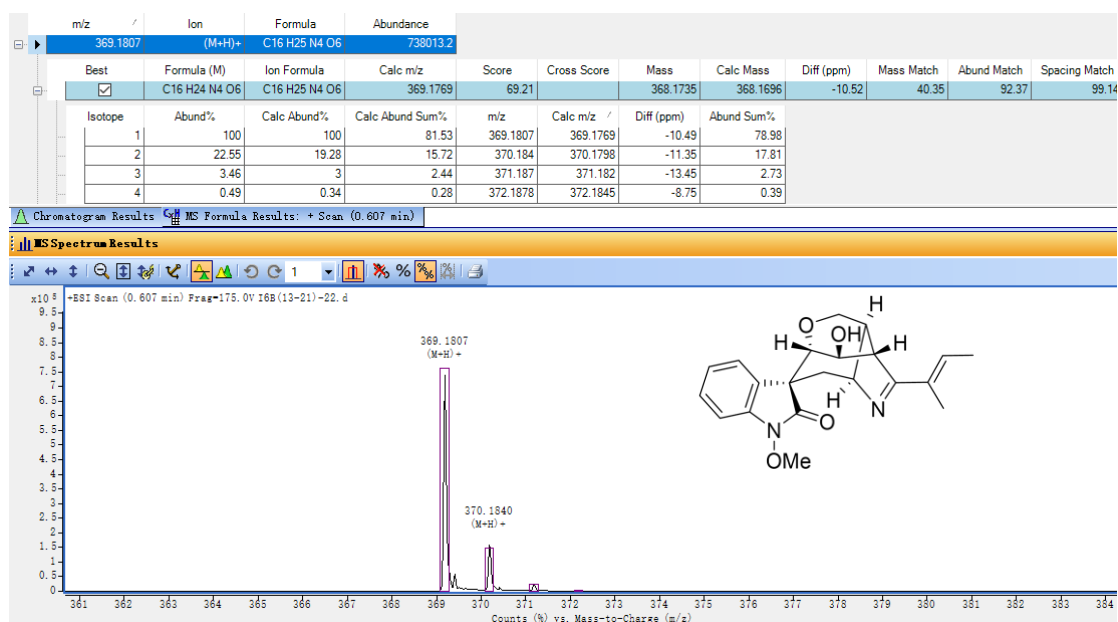


Figure S68. The HR-ESI-MS of compound **8**

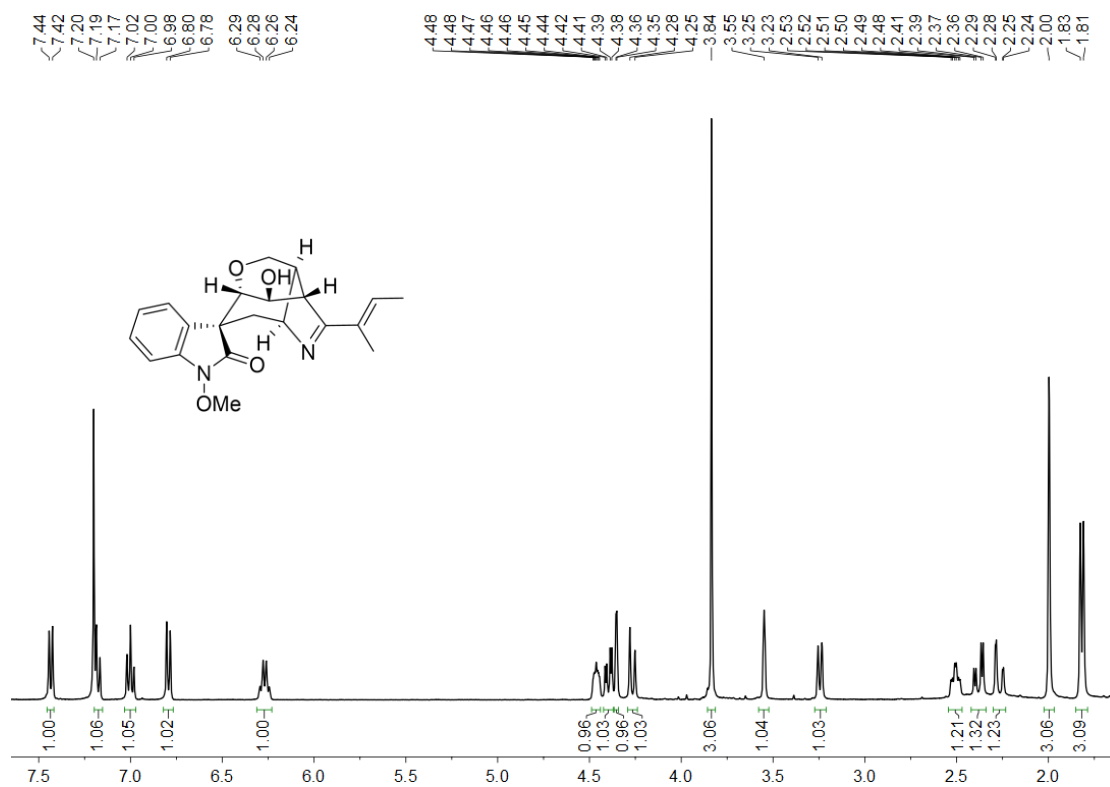


Figure S69. The ^1H NMR spectrum of compound **8** in CDCl_3

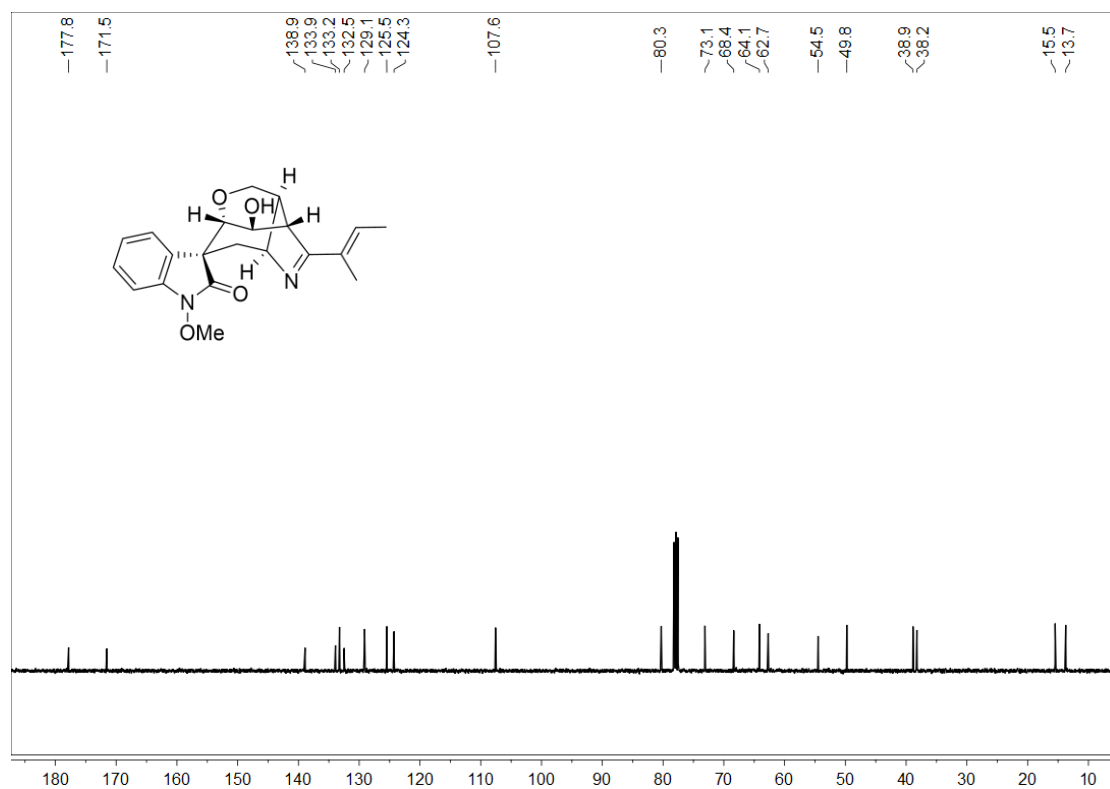


Figure S70. The ^{13}C NMR spectrum of compound **8** in CDCl_3

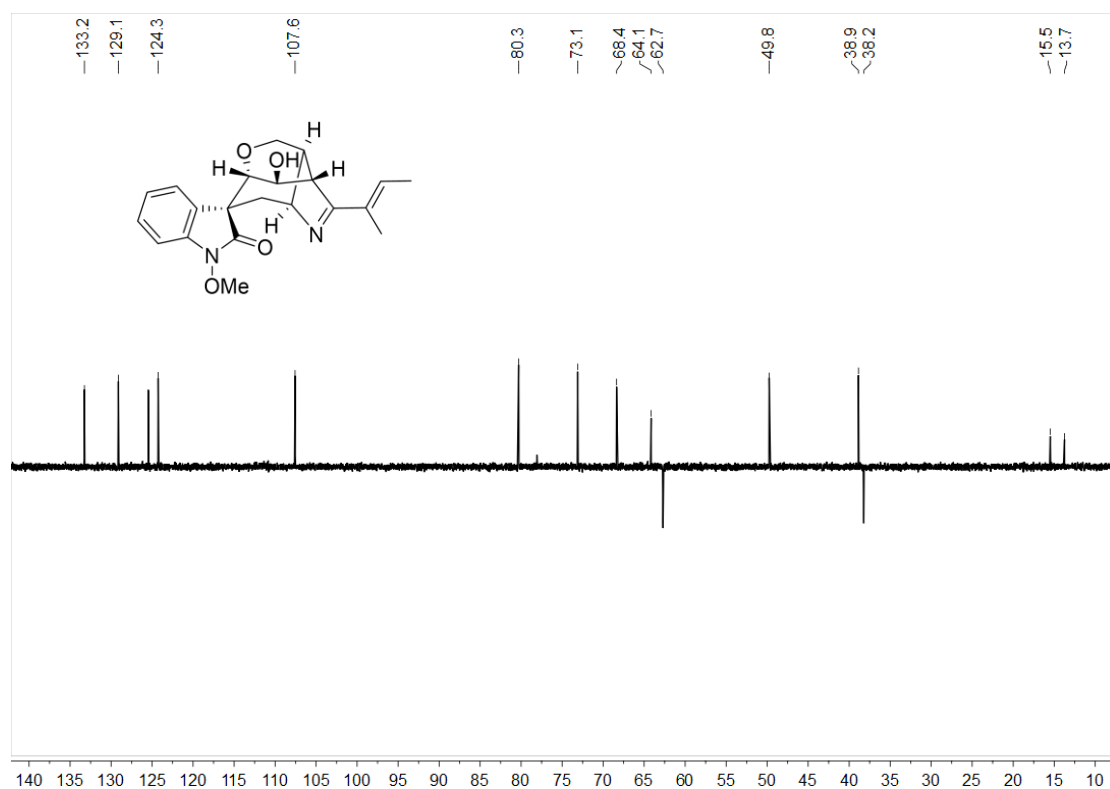


Figure S71. The DEPT-135 spectrum of compound **8** in CDCl_3

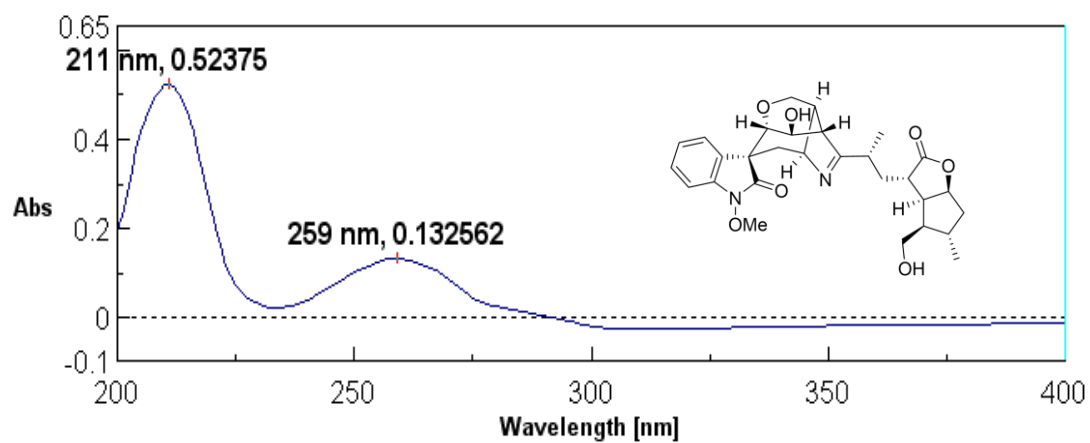


Figure S72. The UV of compound **9** in MeOH

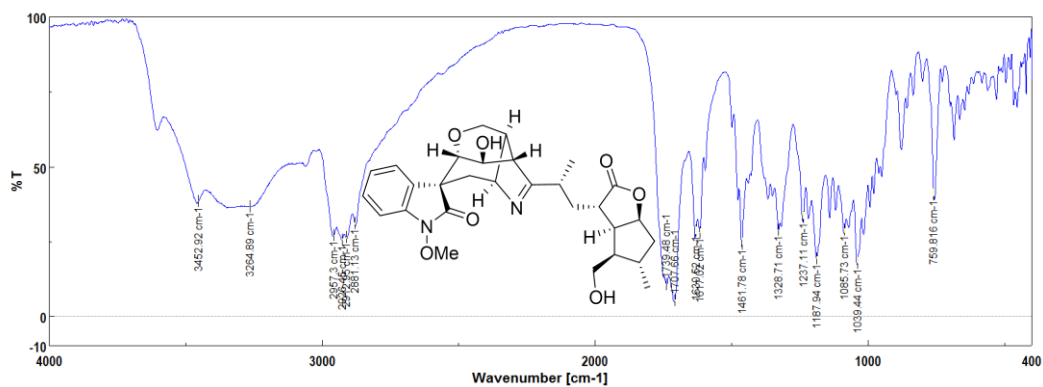


Figure S73. The IR (KBr disc) of compound **9**

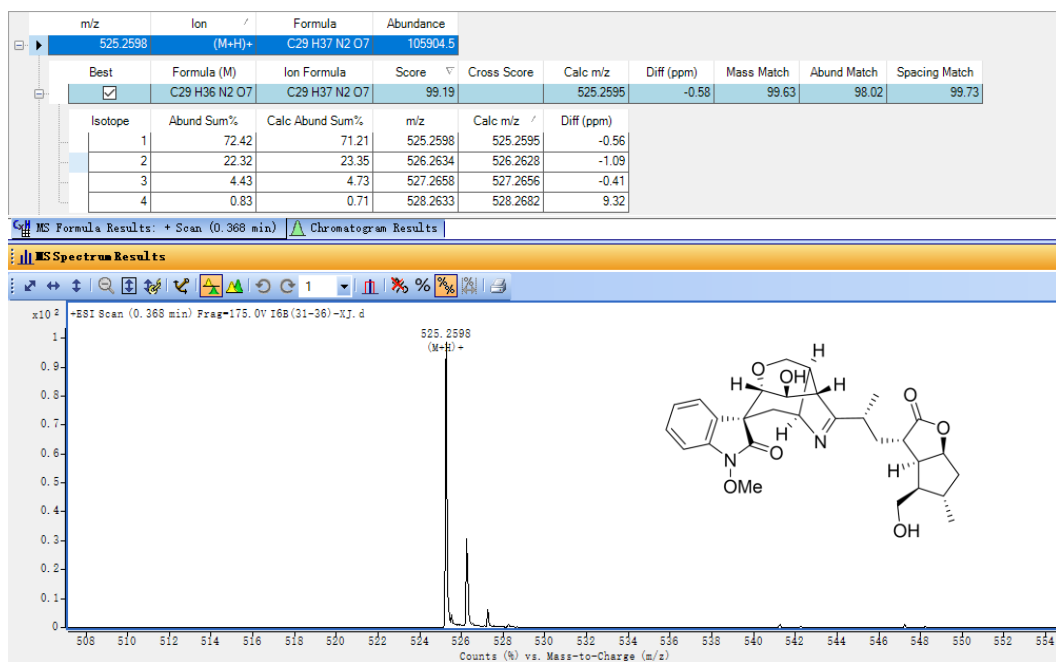


Figure S74. The HR-ESI-MS of compound **9**

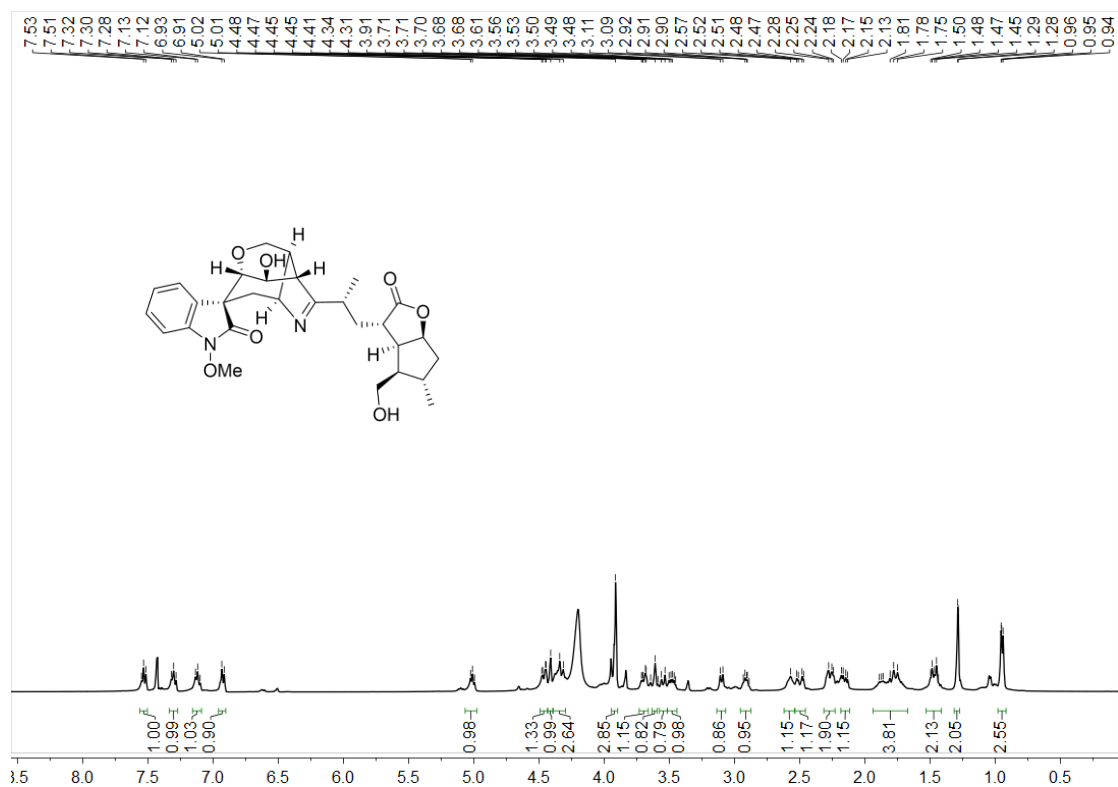


Figure S75. The ^1H NMR spectrum of compound **9** in CDCl_3 (80%) + CD_3OD (20%)

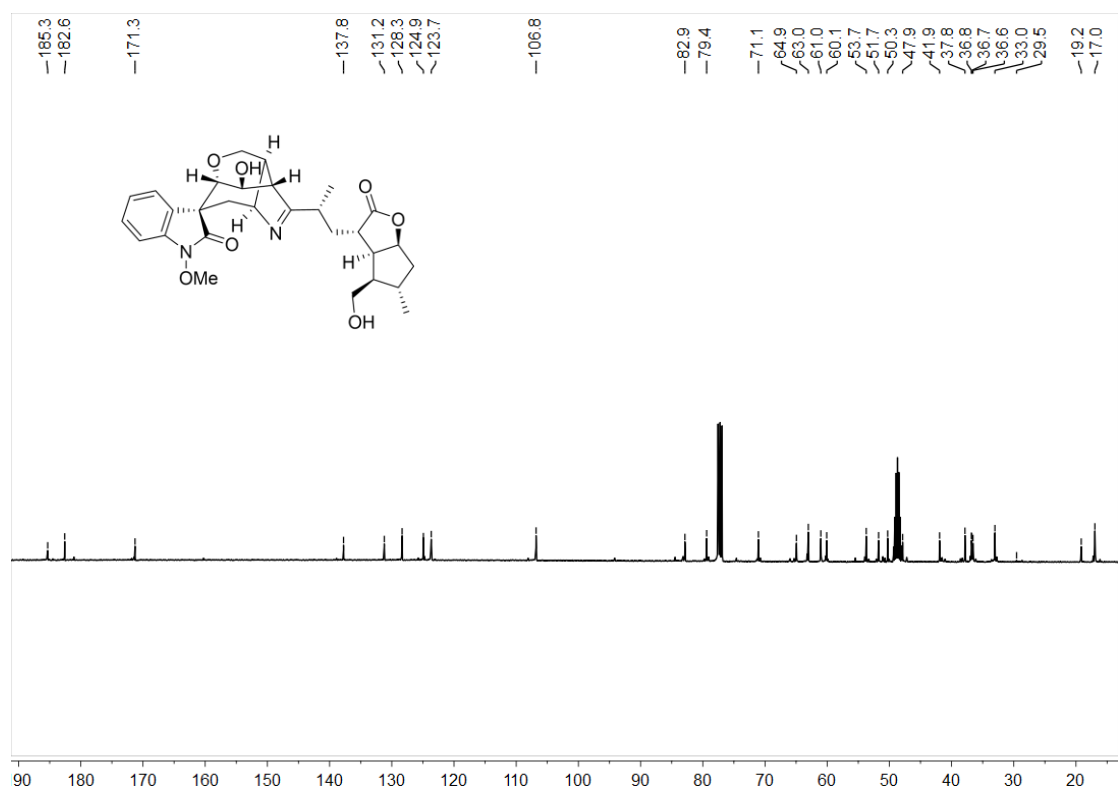


Figure S76. The ^{13}C NMR spectrum of **9** in CDCl_3 (80%) + CD_3OD (20%)

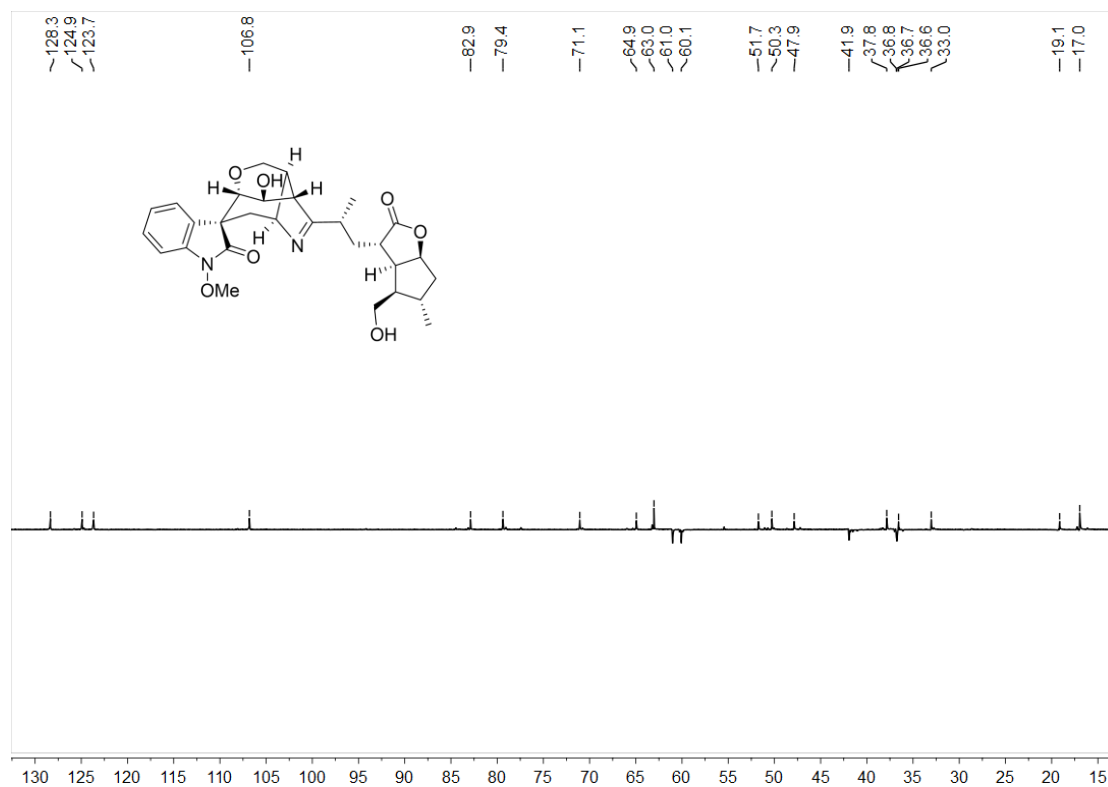


Figure S77. The DEPT-135 spectrum of **9** in CDCl_3 (80%) + CD_3OD (20%)

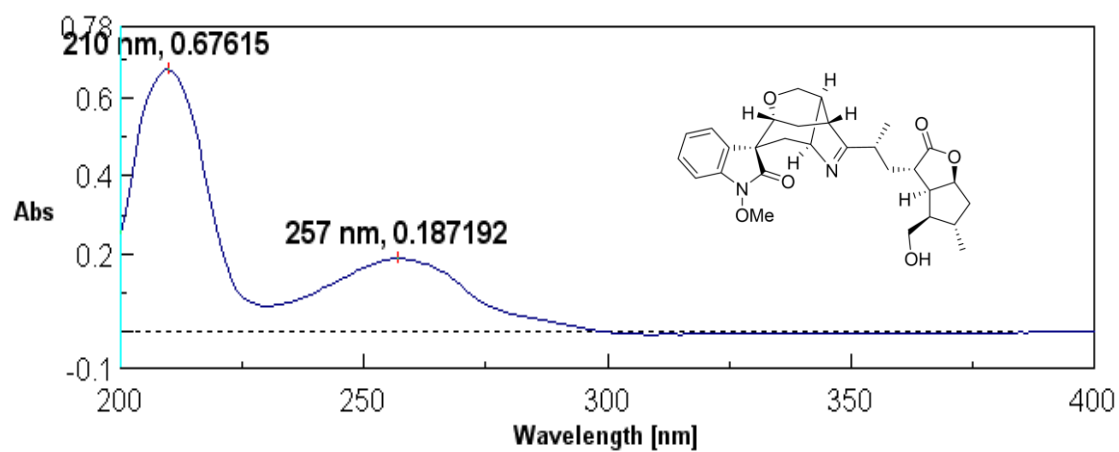


Figure S78. The UV of compound **10** in MeOH

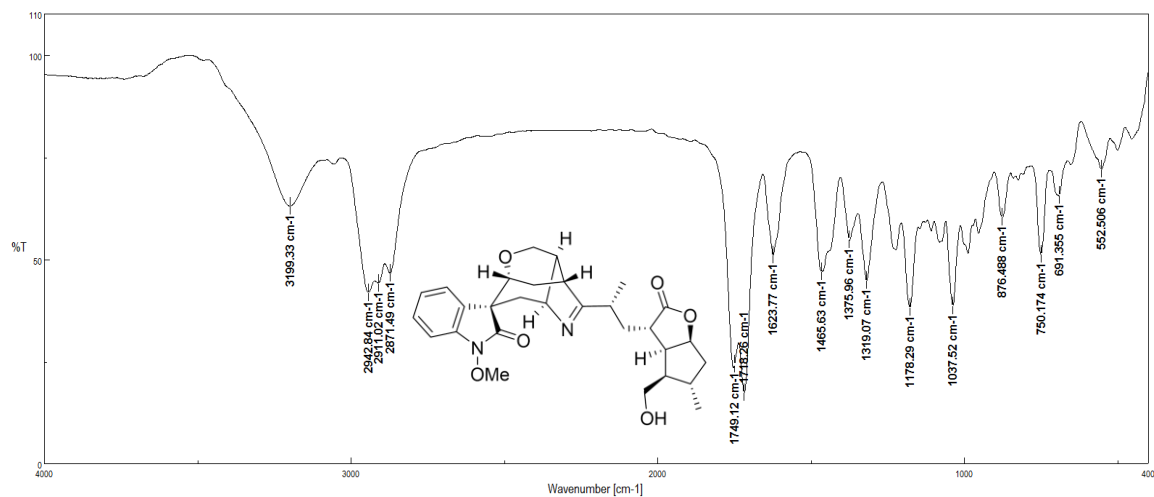


Figure S79. The IR (KBr disc) of compound **10**

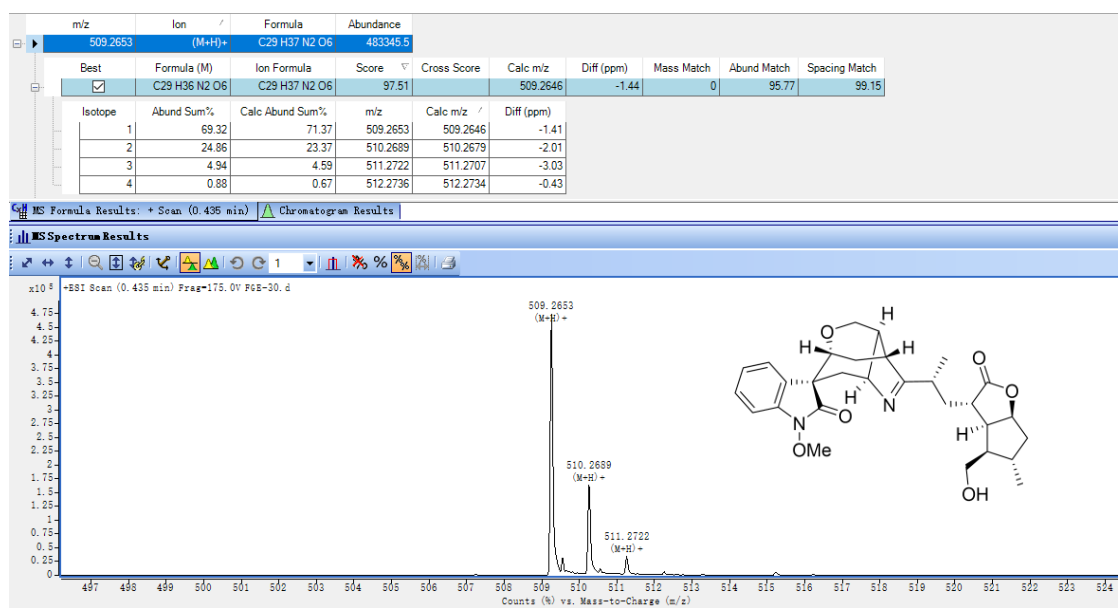


Figure S80. The HR-ESI-MS of compound **10**

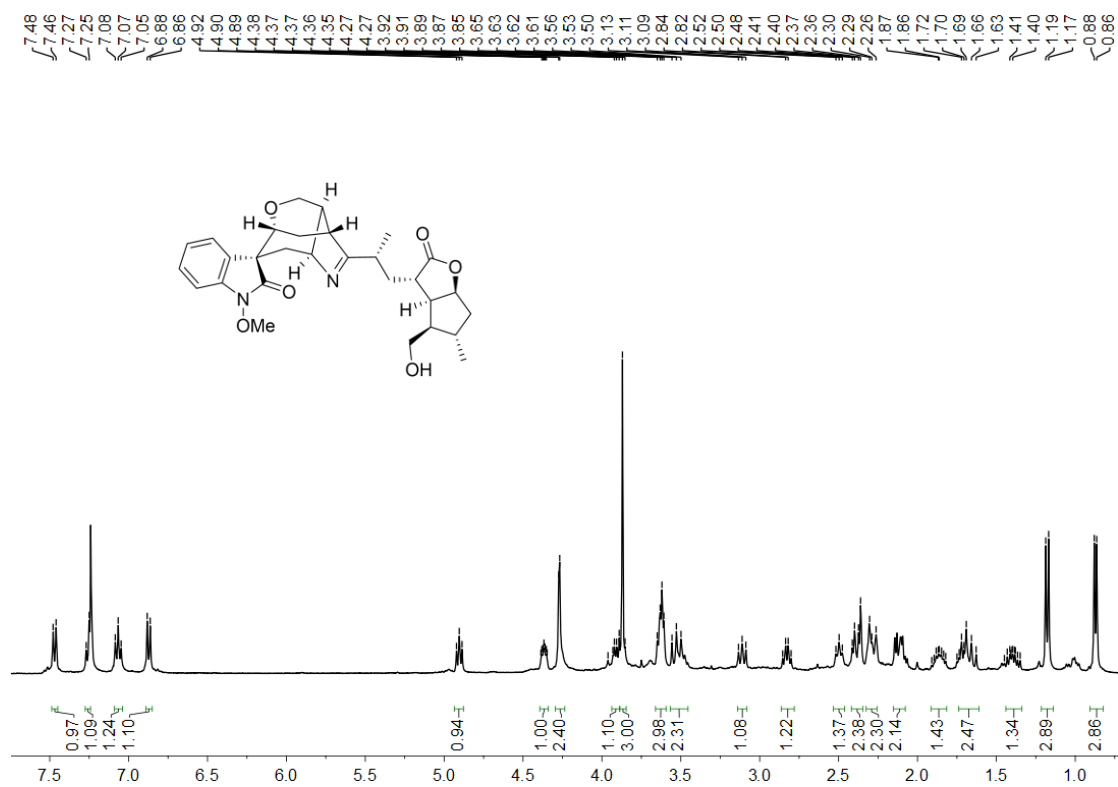


Figure S81. The ^1H NMR spectrum of compound **10** in CDCl_3

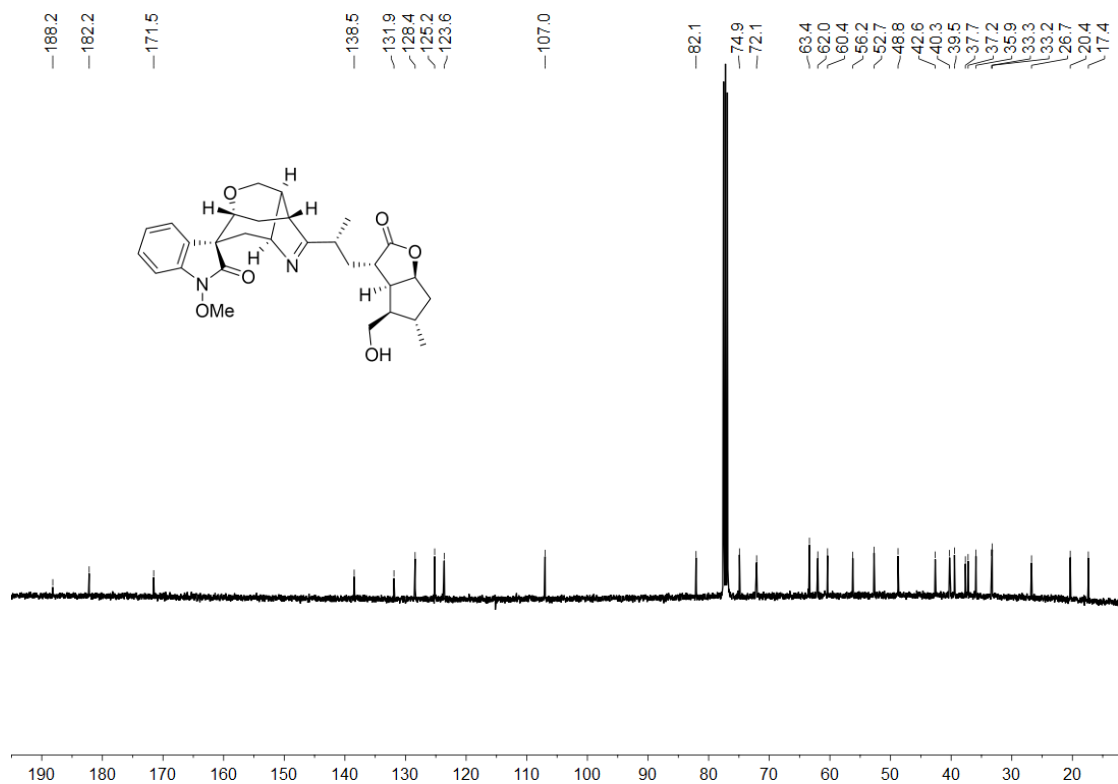


Figure S82. The ^{13}C NMR spectrum of **10** in CDCl_3

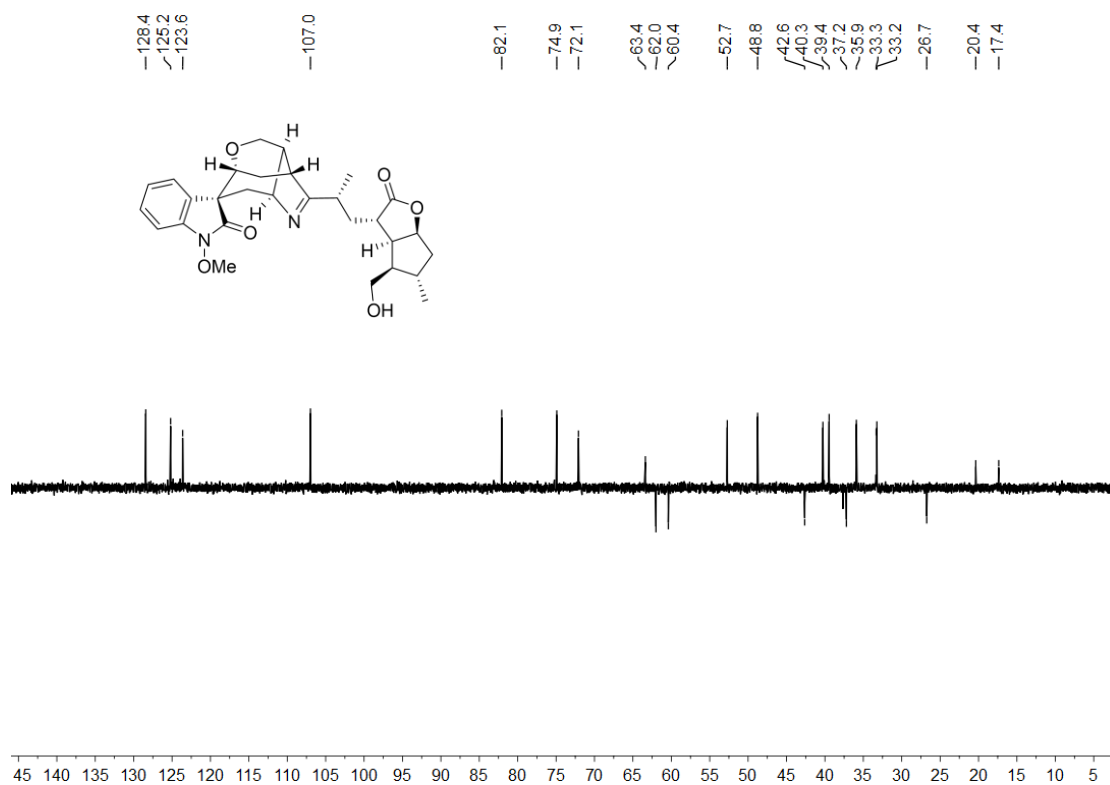


Figure S83. The DEPT-135 spectrum of **10** in CDCl₃

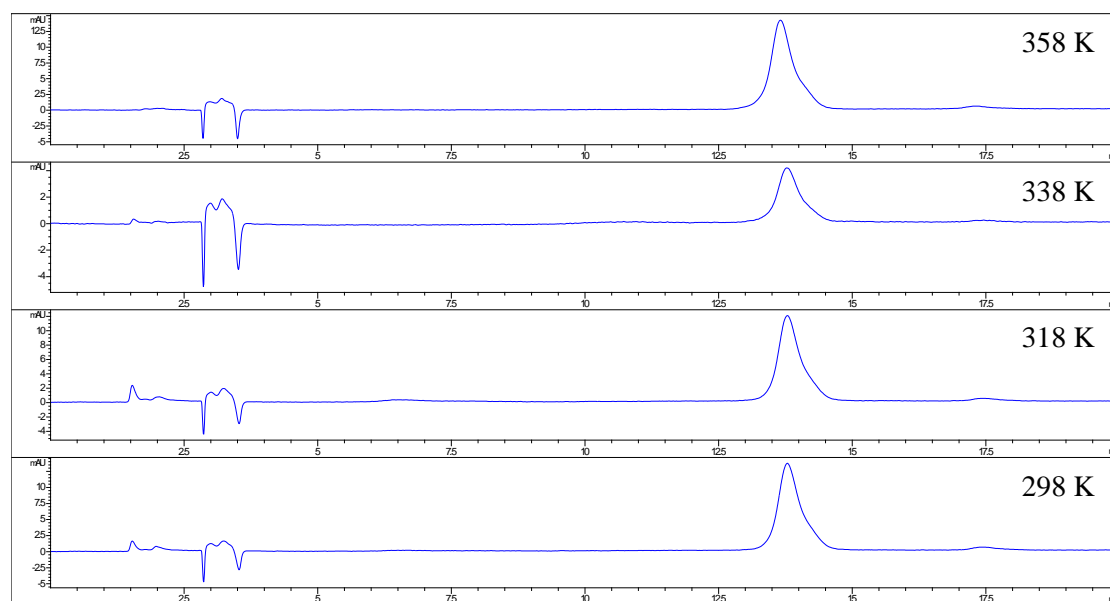


Figure S84. Dynamic HPLC spectra of **4** with temperature increase

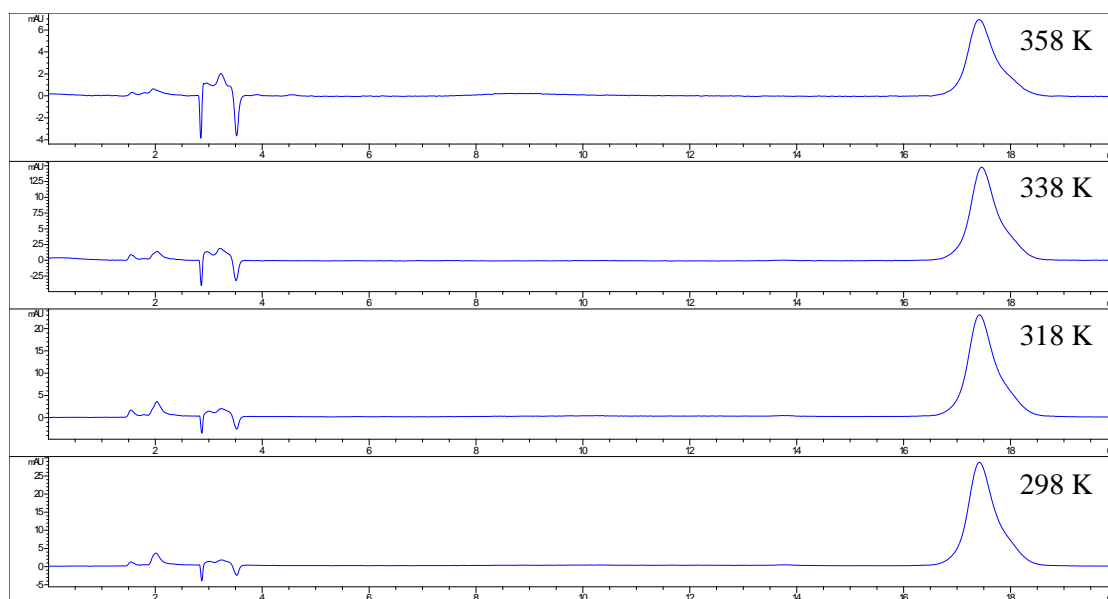


Figure S85. Dynamic HPLC spectra of **5** with temperature increase

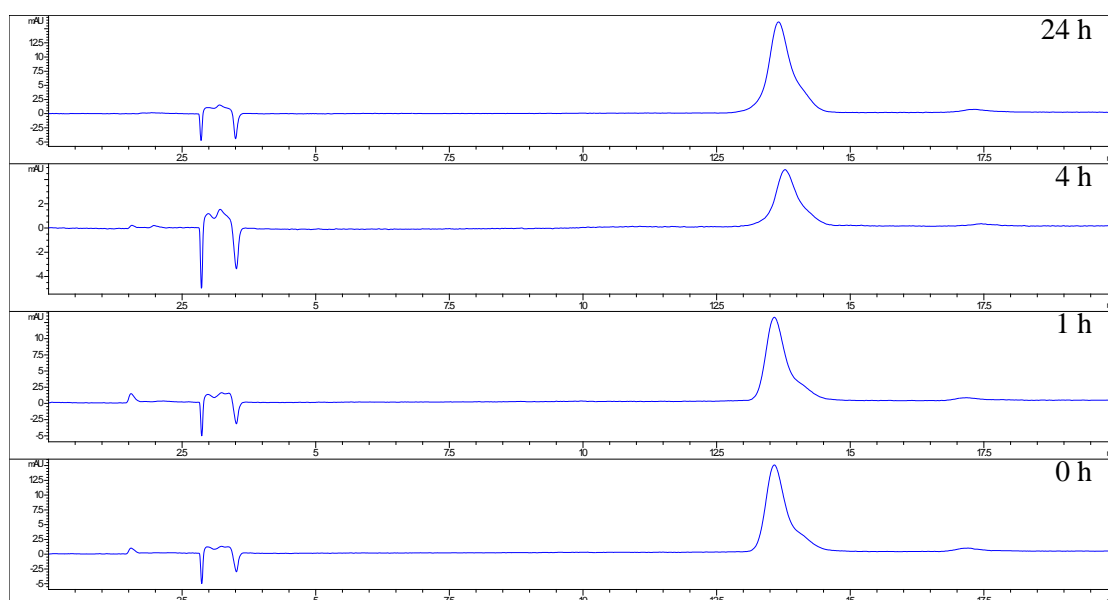


Figure S86. Dynamic HPLC spectra of **4** with visible light irradiation

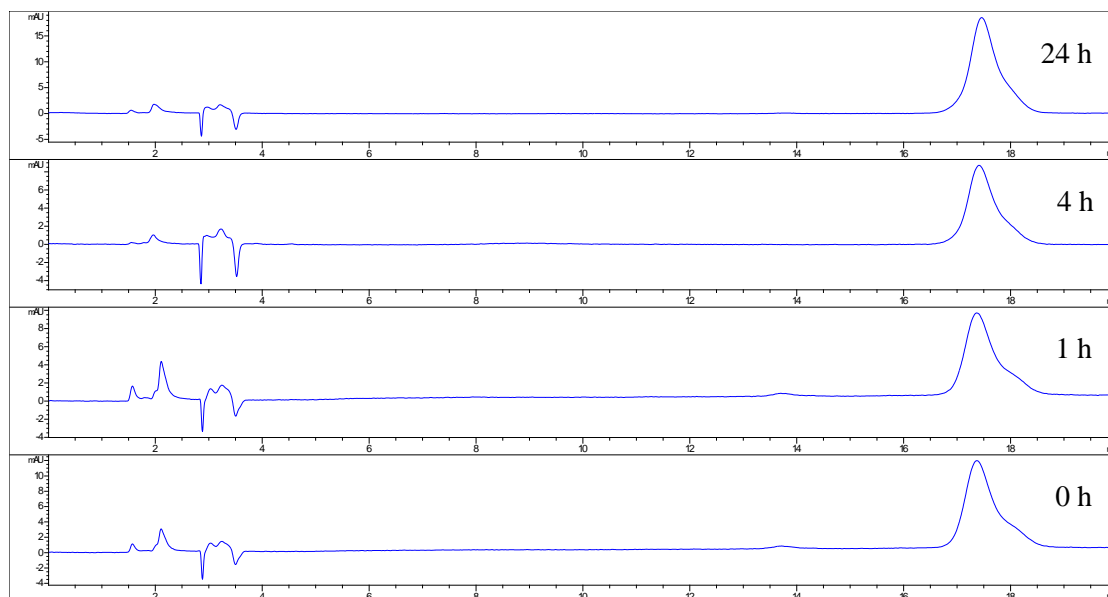


Figure S87. Dynamic HPLC spectra of **5** with visible light irradiation

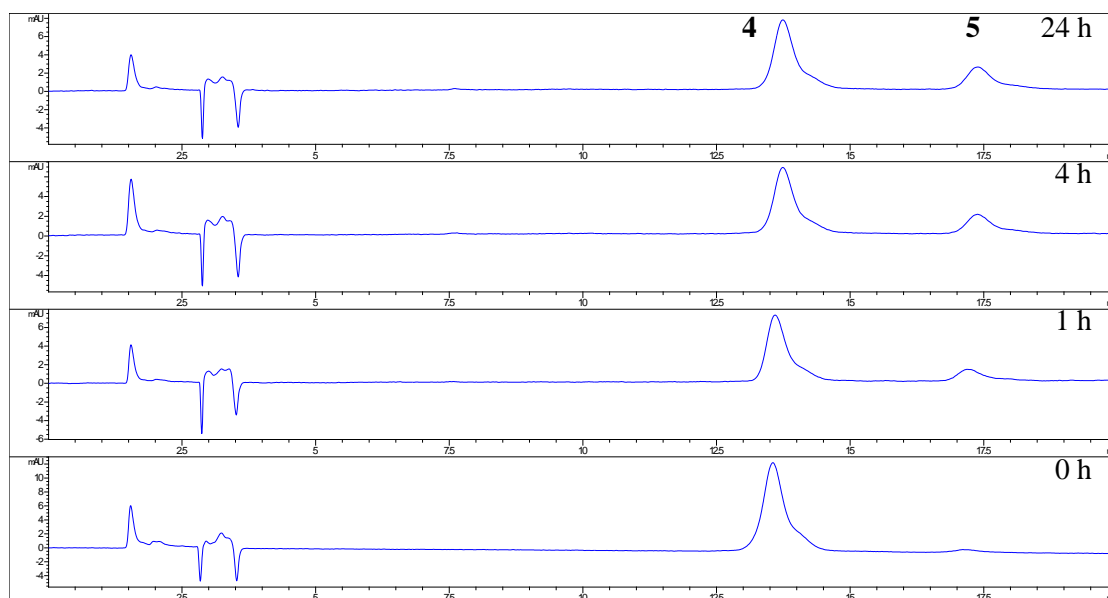


Figure S88. Dynamic HPLC spectra of **4** with UV irradiation in 254 nm

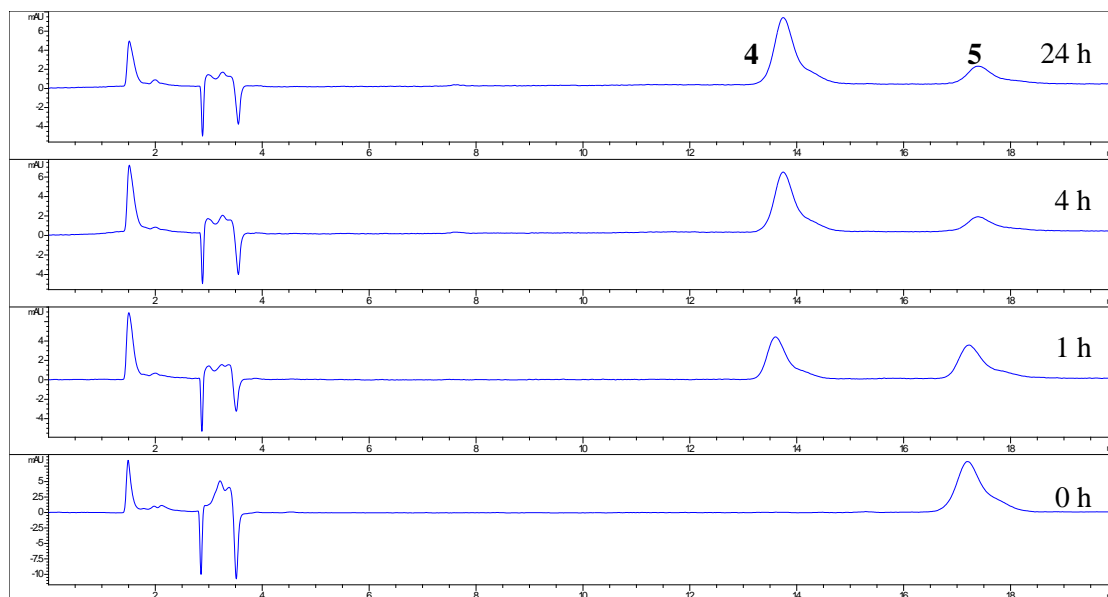


Figure S89. Dynamic HPLC spectra of **5** with UV irradiation in 254 nm

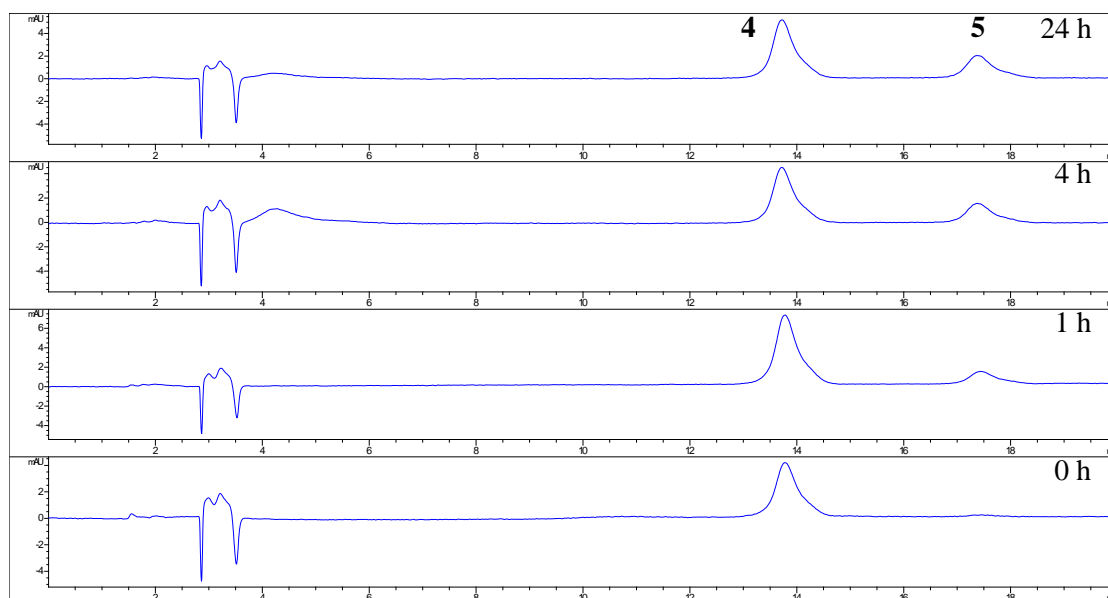


Figure S90. Dynamic HPLC spectra of **4** with UV irradiation in 365 nm

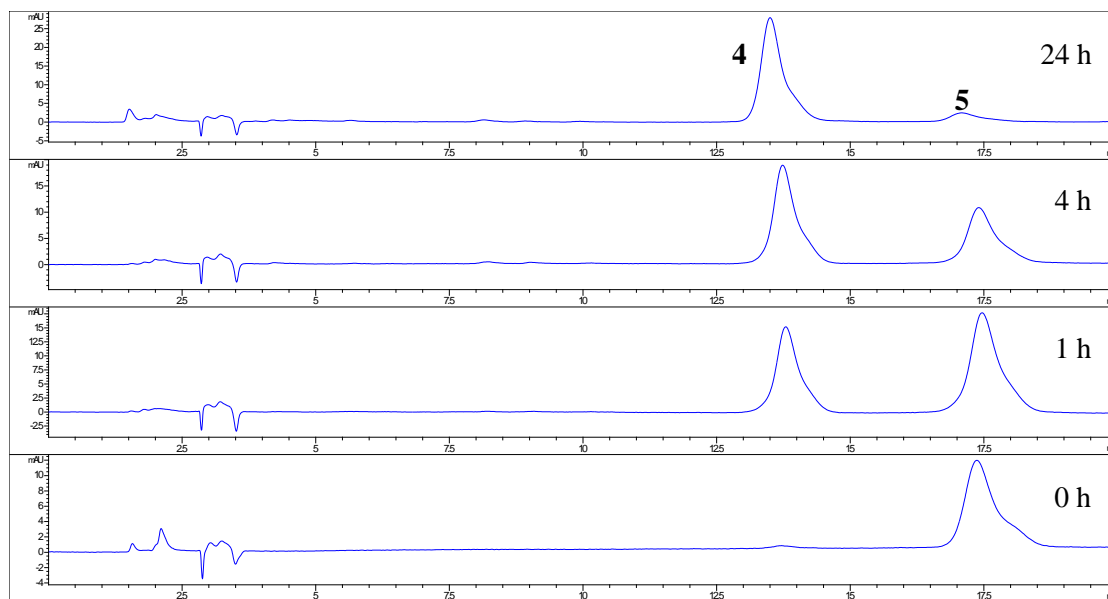


Figure S91. Dynamic HPLC spectra of **5** with UV irradiation in 365 nm

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- 2 L. Z. Lin, G. A. Cordel, Gelsamydine, an indole alkaloid from *Gelsemium elegans* with two monoterpene units, *J. Org. Chem.* 1989, **54**, 3199-3202.
- 3 Q. Xue, J. Hu, X. C. Liu, J. Gu, Cytotoxic gelsedine-type indole alkaloids from *Gelsemium elegans*, *J. Asian. Nat. Prod. Res.*, 2020, **22**, 1138-1144.
- 4 Y. K. Xu, S. P. Yang, S. G. Liao, H. Zhang, L. P. Lin, J. Ding, J. M. Yue, Alkaloids from *Gelsemium elegans*, *J. Nat. Prod.*, 2006, **69**, 1347-1350.