Supporting information

Phthalide Derivatives from *Ligusticum chuanxiong*

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Table of Contents

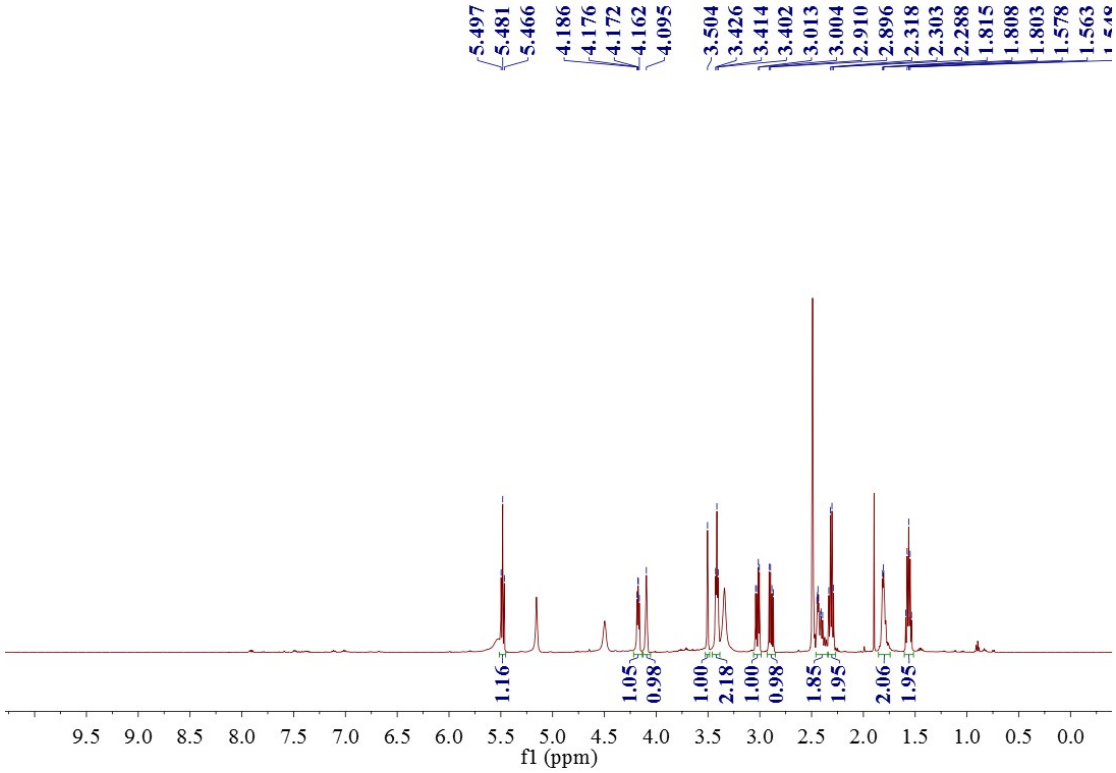


Figure S1. The ^{1}H NMR spectrum of compound **1** in DMSO-d_6

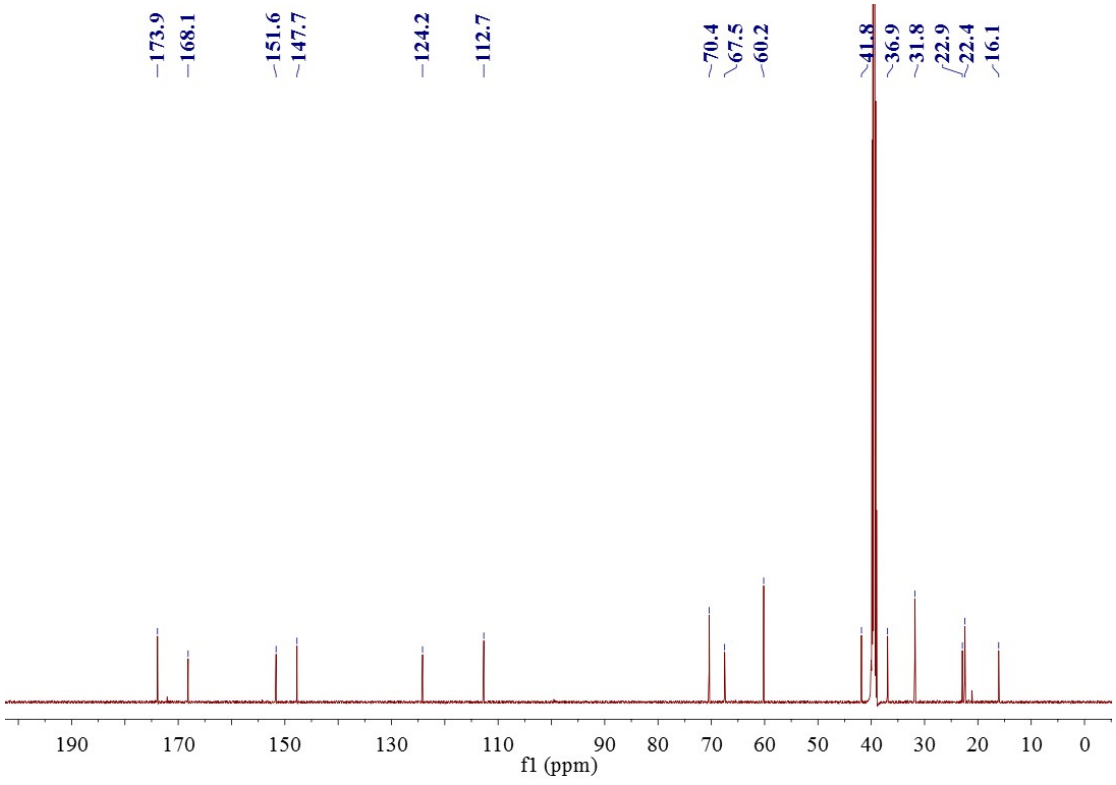


Figure S2. The ^{13}C NMR spectrum of compound **1** in DMSO-d_6

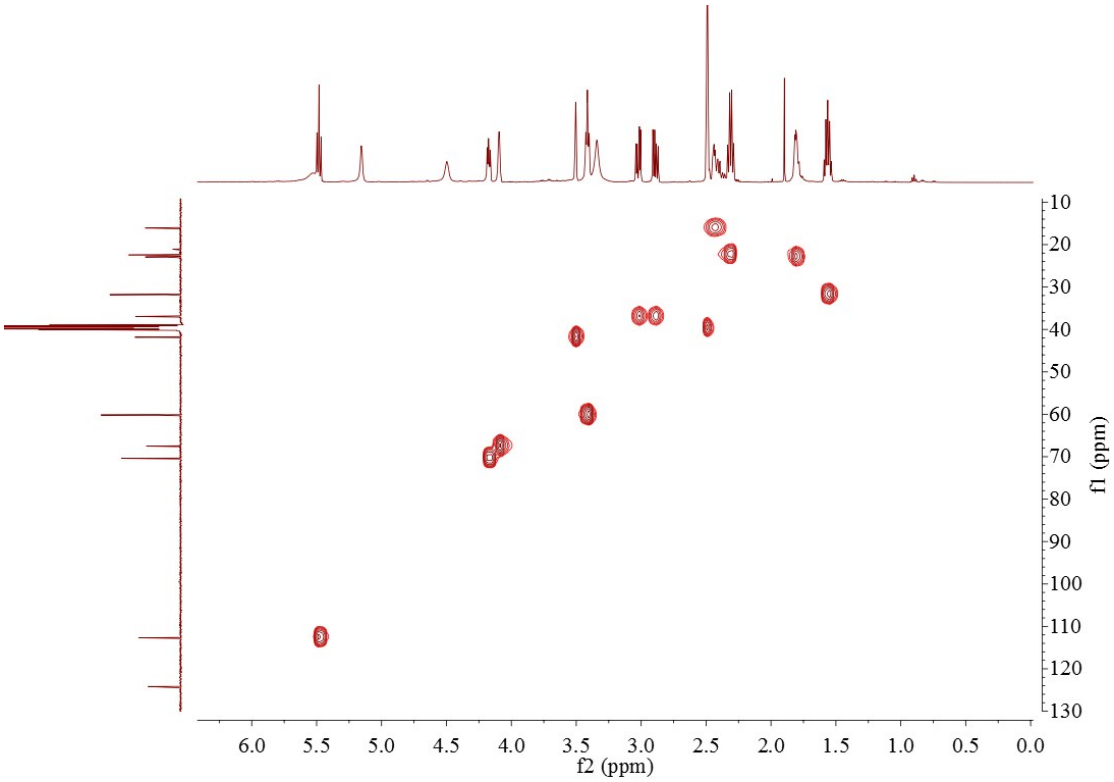


Figure S3. The HSQC spectrum of compound **1** in DMSO-d_6

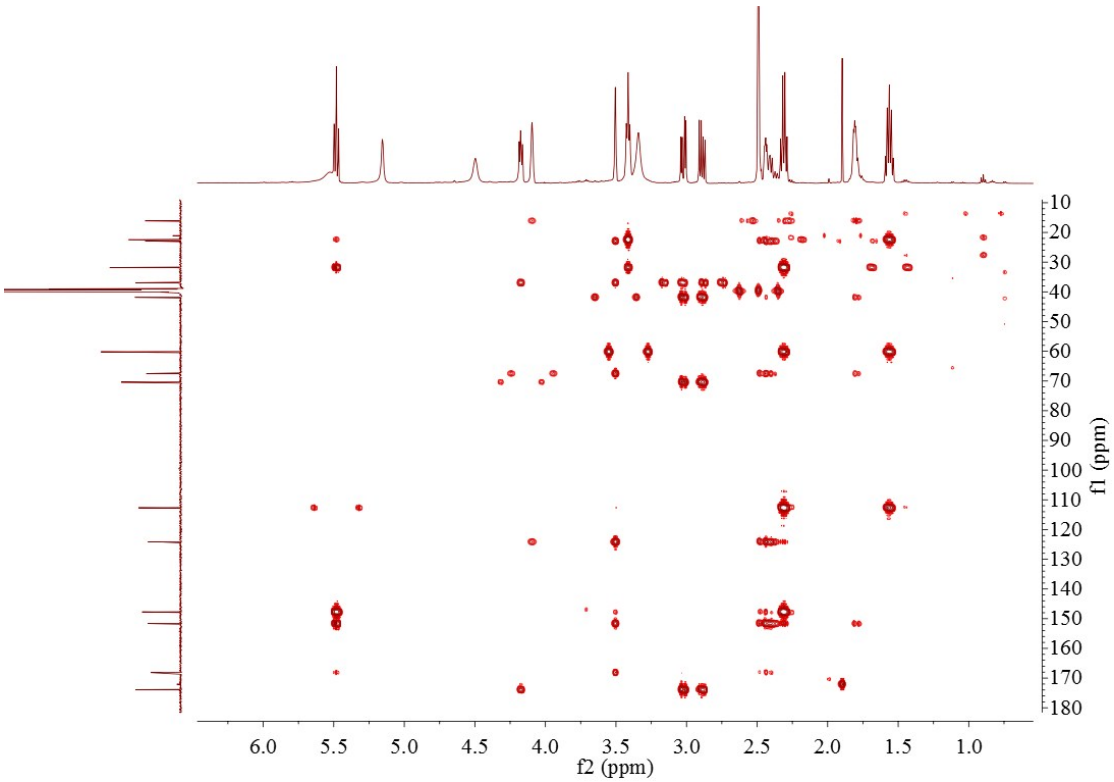


Figure S4. The HMBC spectrum of compound **1** in DMSO-d_6

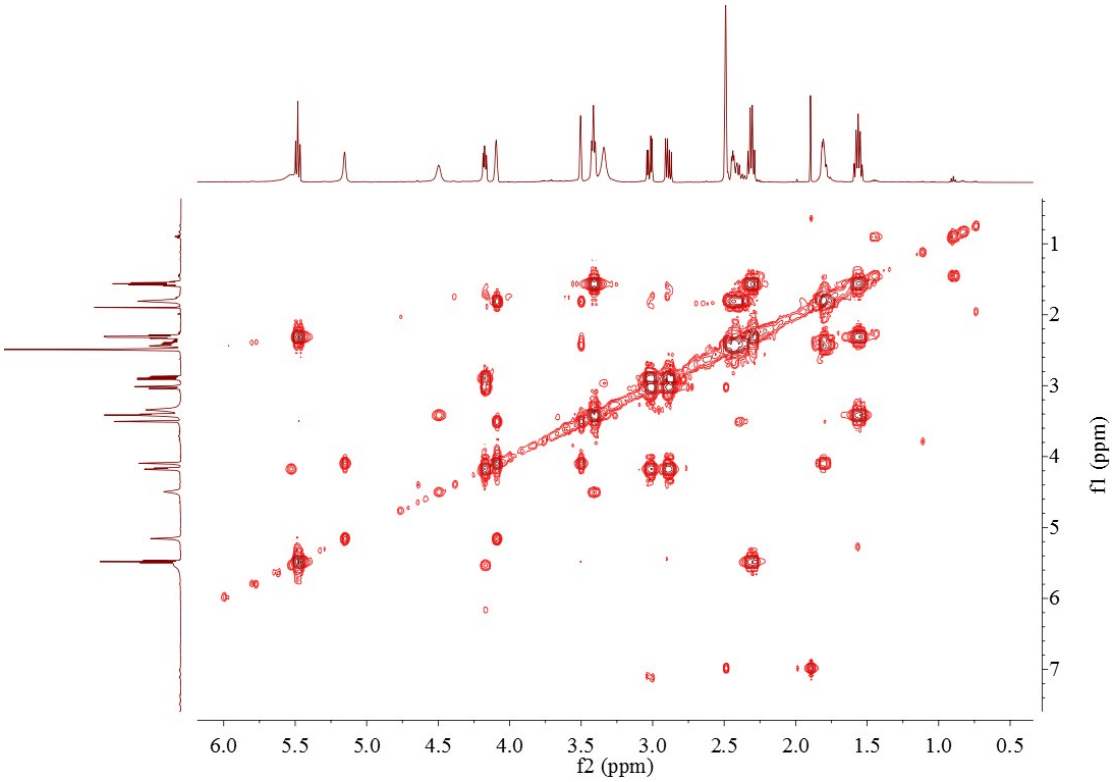


Figure S5. The ^{1}H-^{1}H COSY spectrum of compound **1** in DMSO-d_6

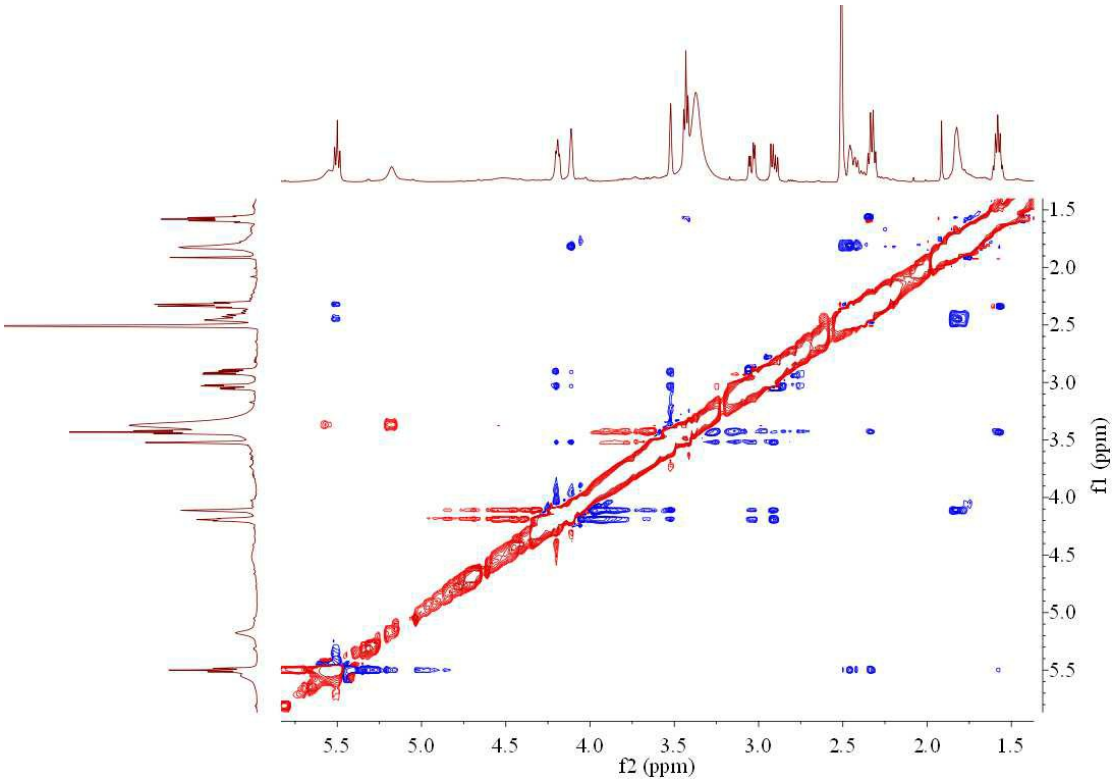


Figure S6. The ROESY spectrum of compound **1** in DMSO-d_6

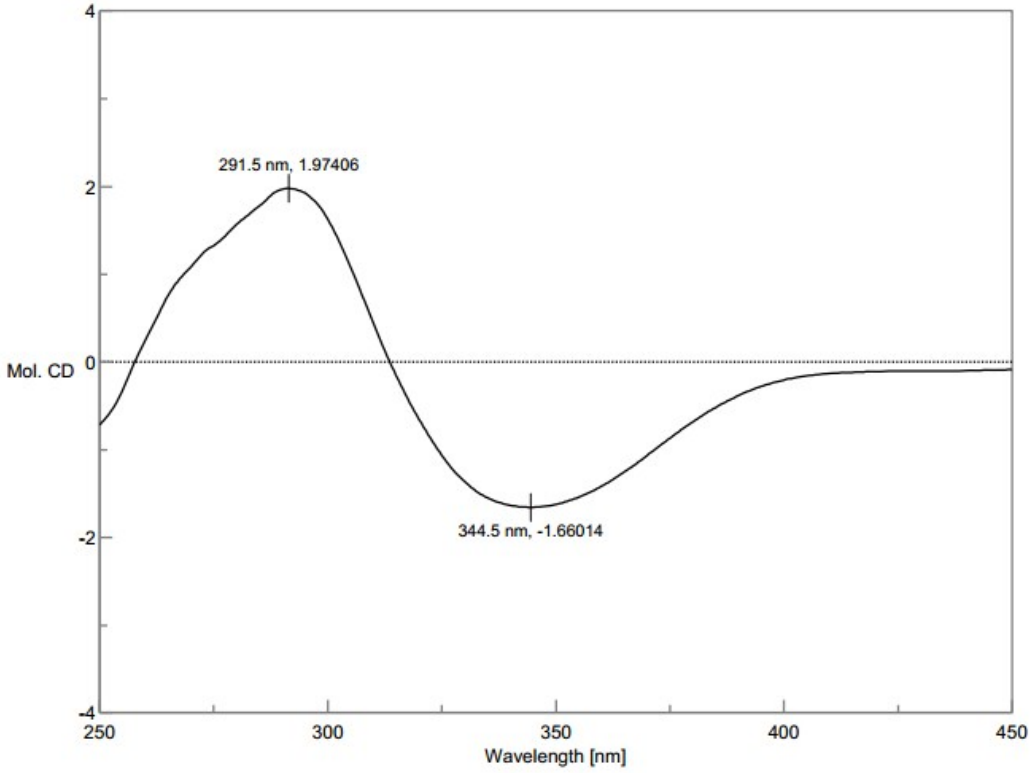


Figure S7. The $[Mo_2(AcO)_4]$ induced ECD spectrum of compound **1** in DMSO

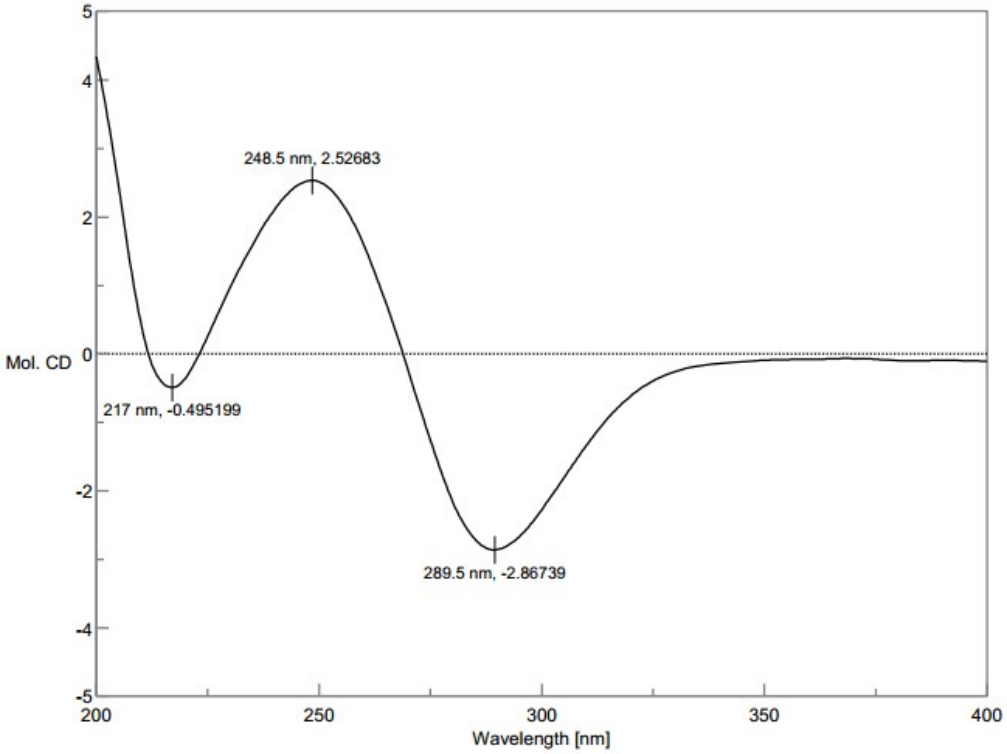


Figure S8. The ECD spectrum of compound **1** in MeOH

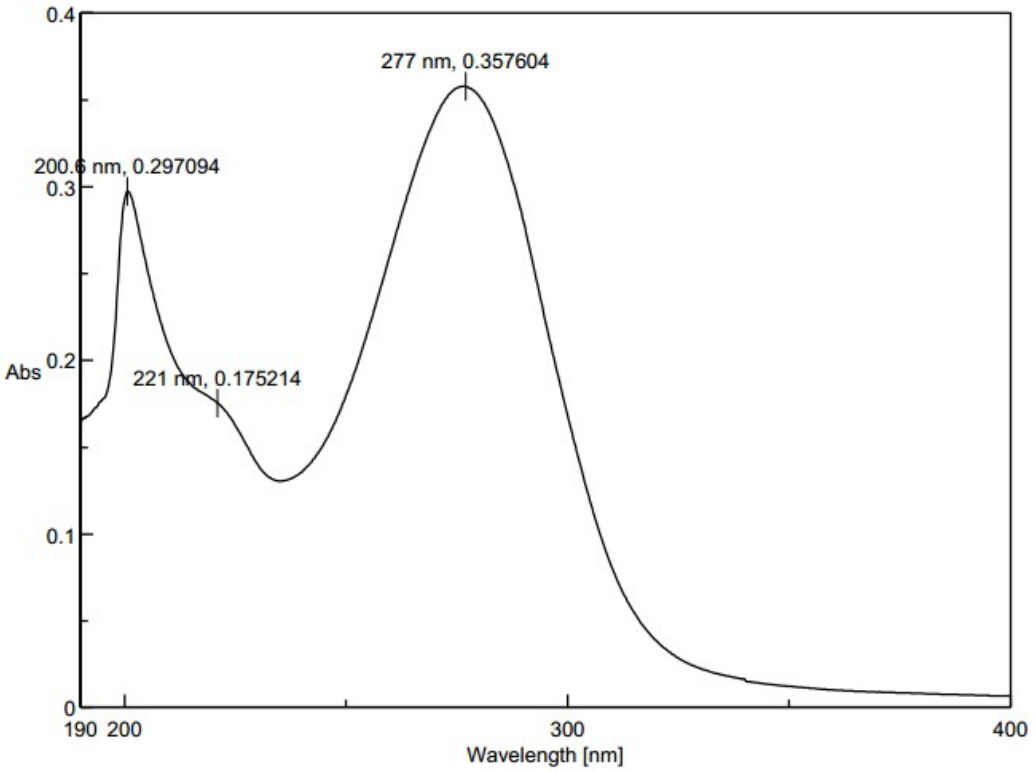


Figure S9. The UV spectrum of compound **1** in MeOH

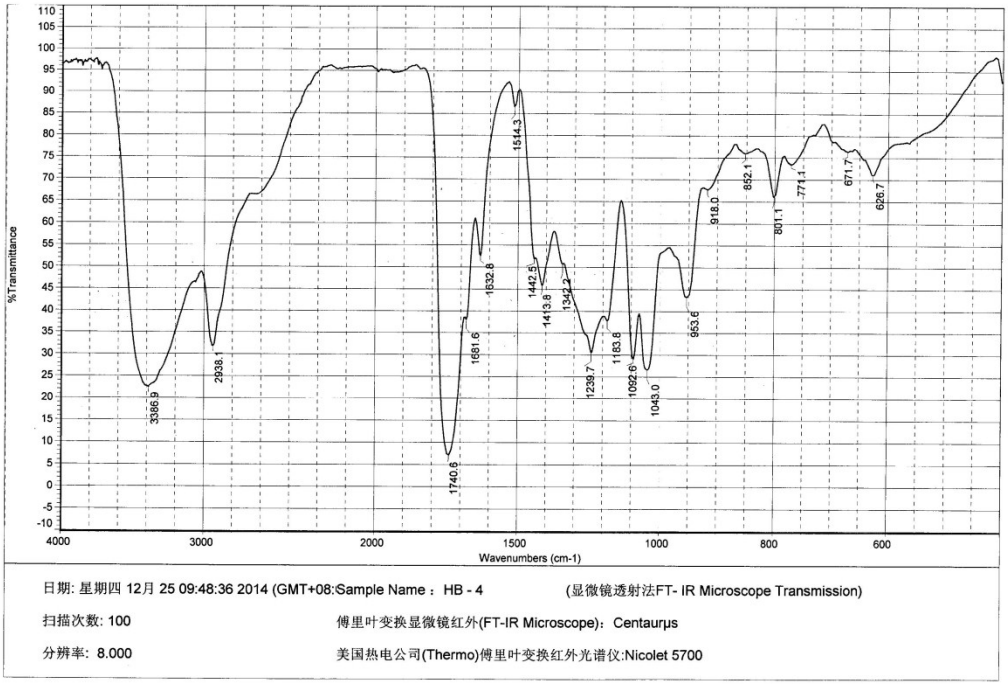
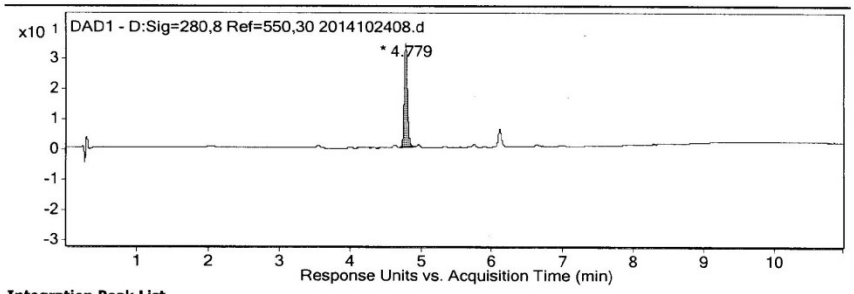


Figure S10. The IR spectrum (KBr) of compound **1**

Qualitative Analysis Report

Data Filename	2014102408.d	**Sample Name**	HB-4
Sample Type	Sample	**Position**	P1-C8
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST LCMS.m	**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
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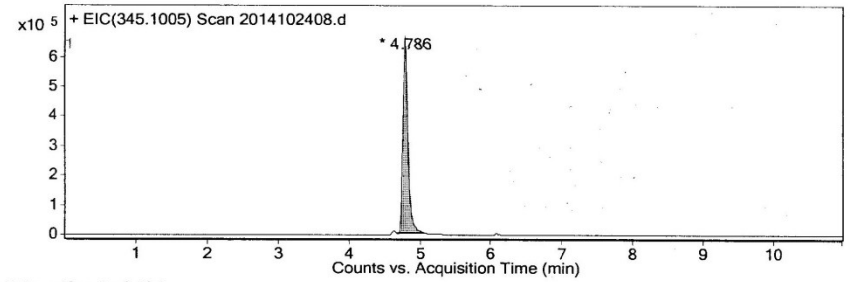
Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
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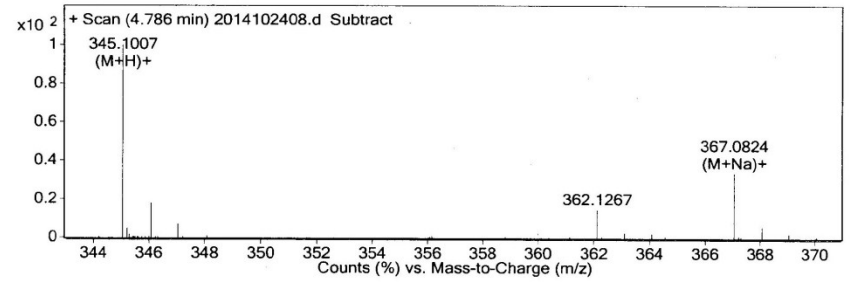
User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	Esi



Agilent Technologies Page 1 of 2 Printed at: 9:13 AM on: 10/31/2014

Figure S11. The HR-ESI-MS data of compound **1**

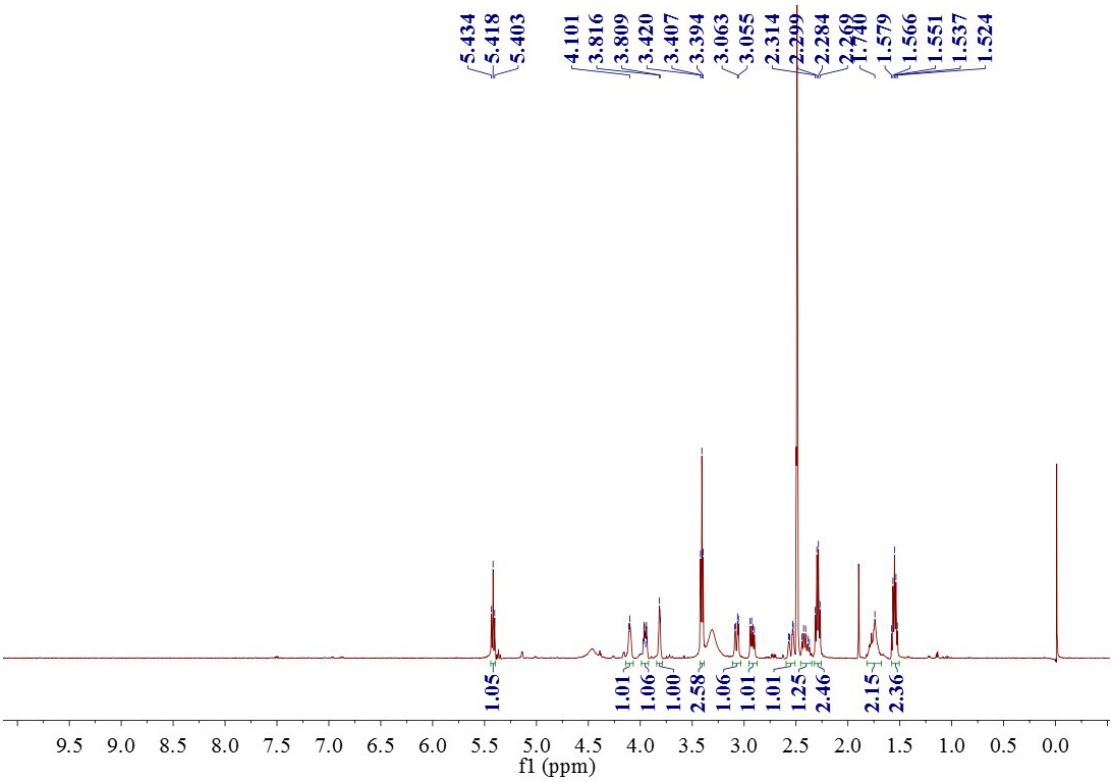


Figure S12. The ^{1}H NMR spectrum of compound **2** in DMSO-d_6

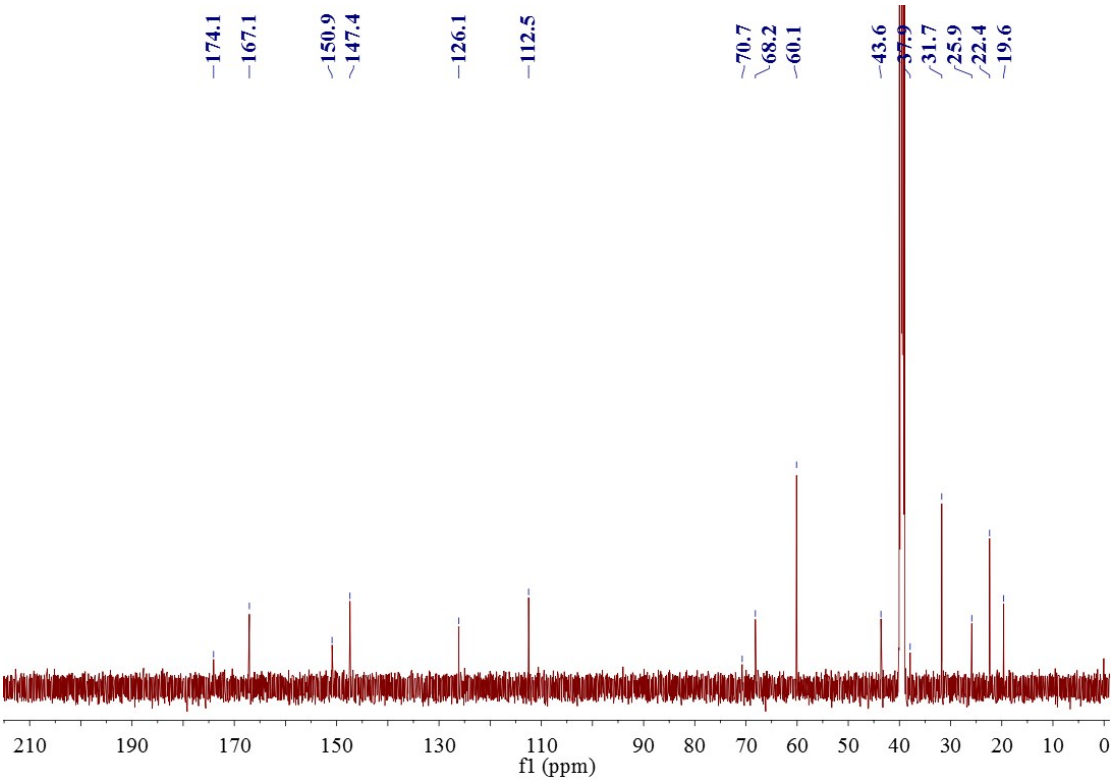


Figure S13. The ^{13}C NMR spectrum of compound **2** in DMSO-d_6

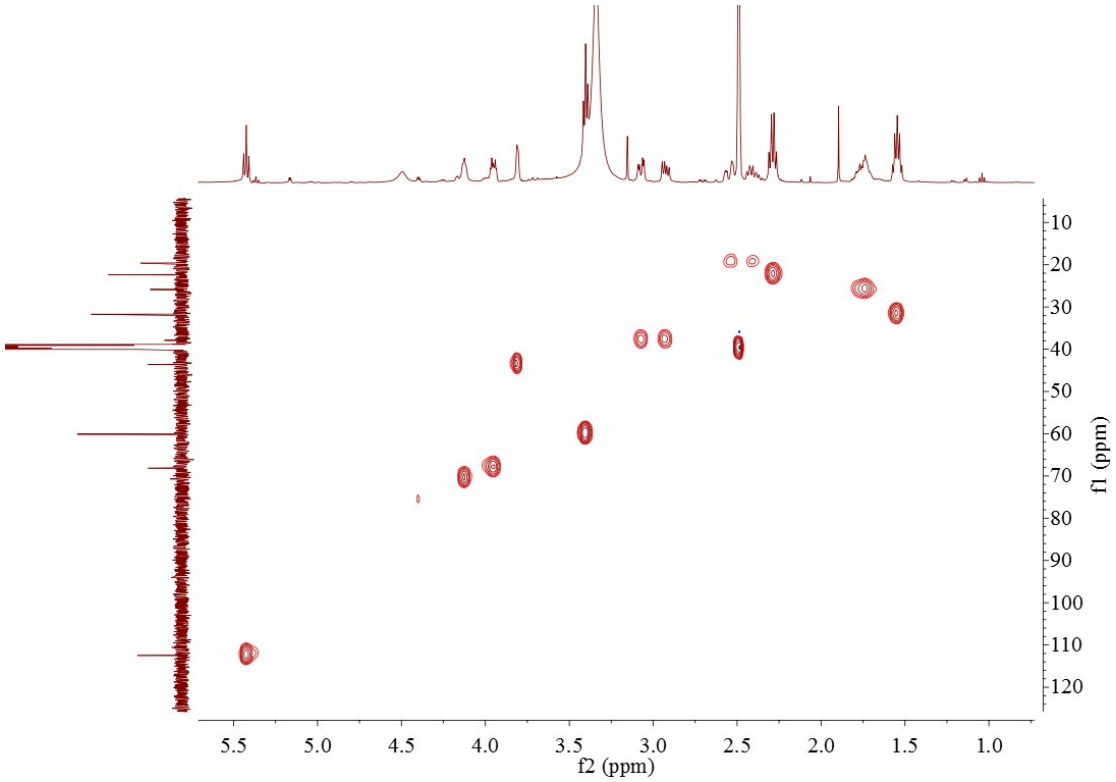


Figure S14. The HSQC spectrum of compound **2** in DMSO-d_6

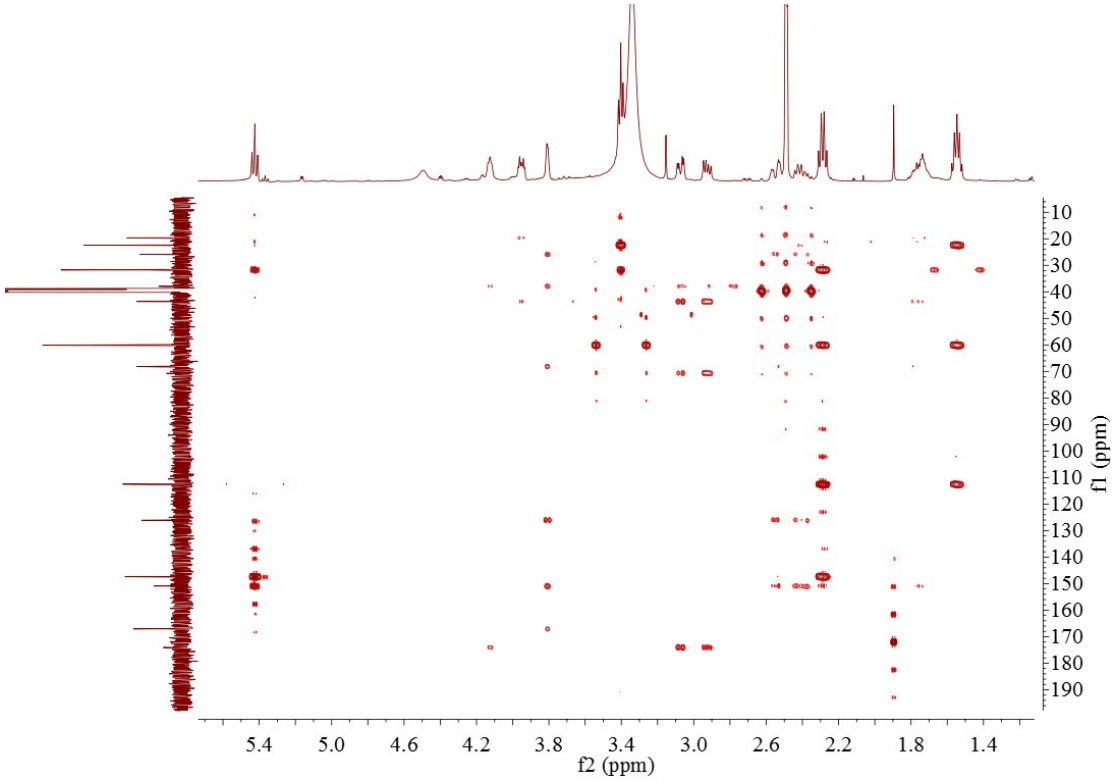


Figure S15. The HMBC spectrum of compound **2** in DMSO-d_6

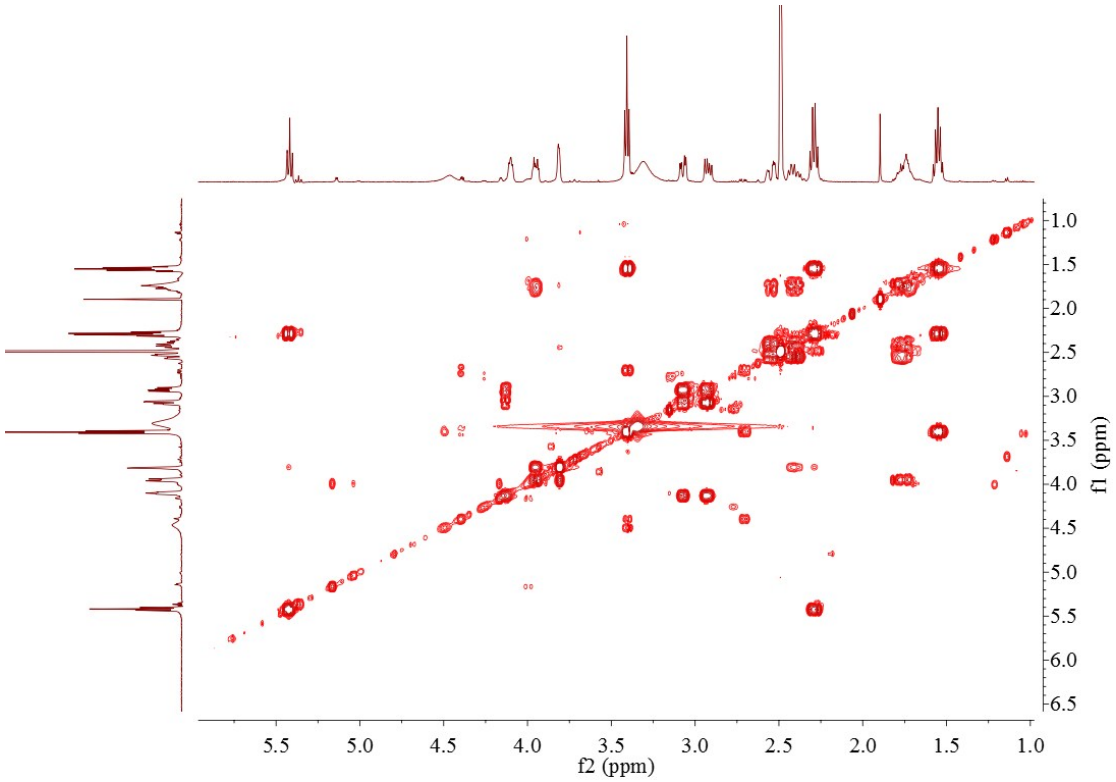


Figure S16. The ^{1}H-^{1}H COSY spectrum of compound **2** in DMSO-d_6

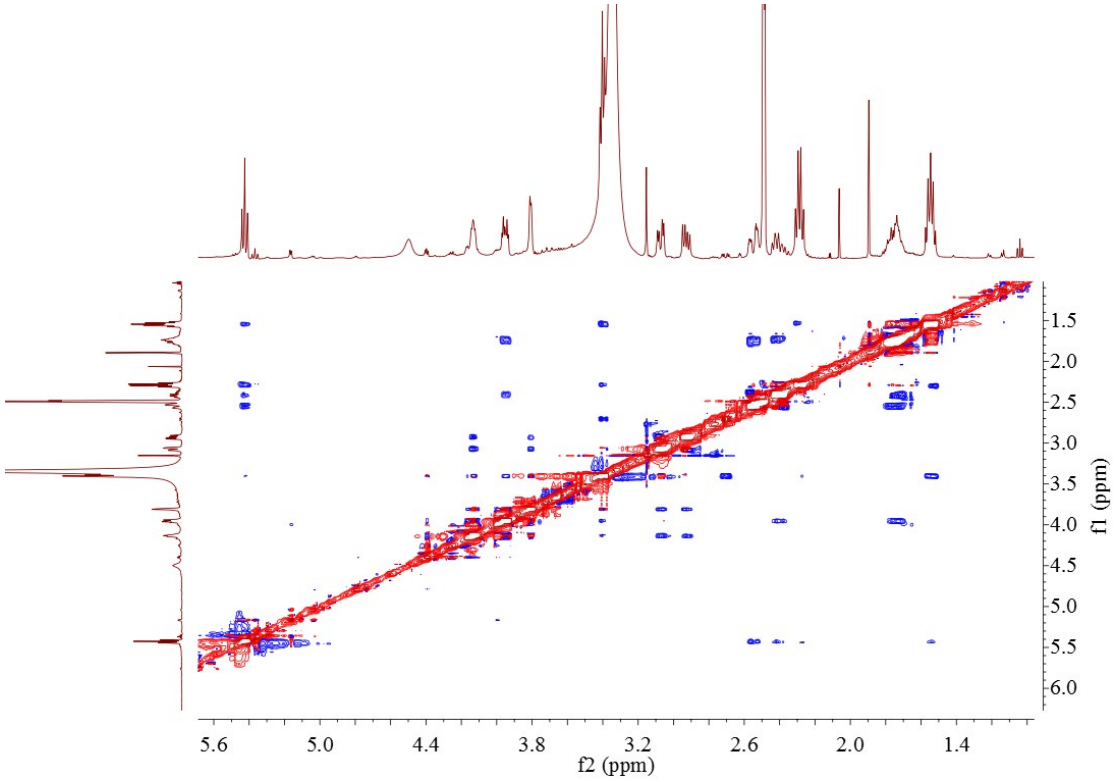


Figure S17. The ROESY spectrum of compound **2** in DMSO-d_6

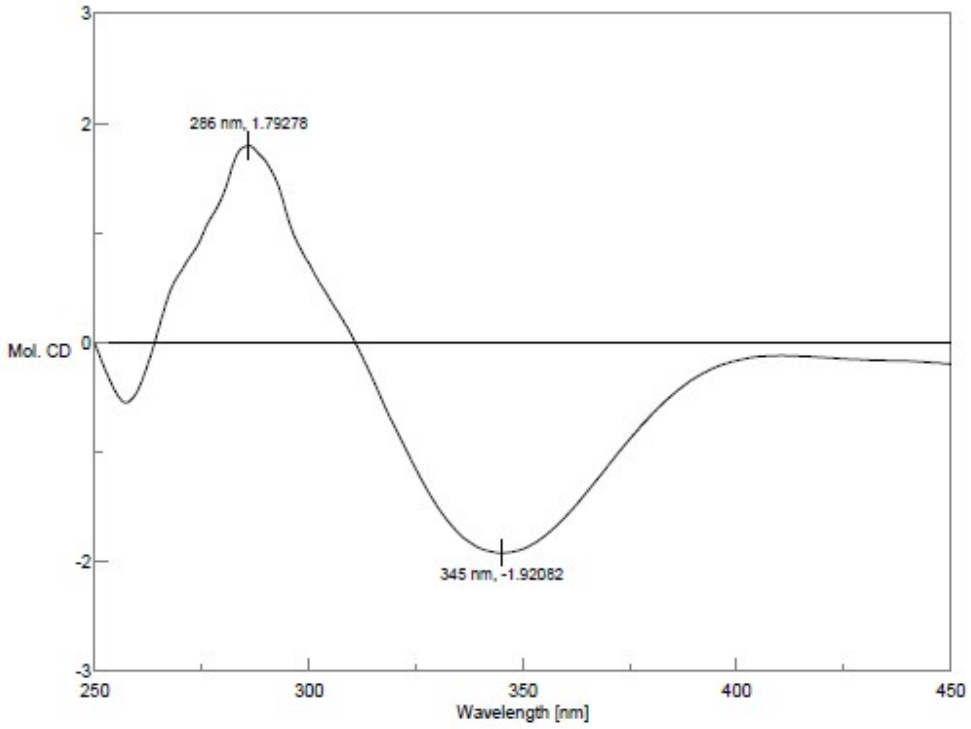


Figure S18. The $[Mo_2(AcO)_4]$ induced ECD spectrum of compound **2** in DMSO

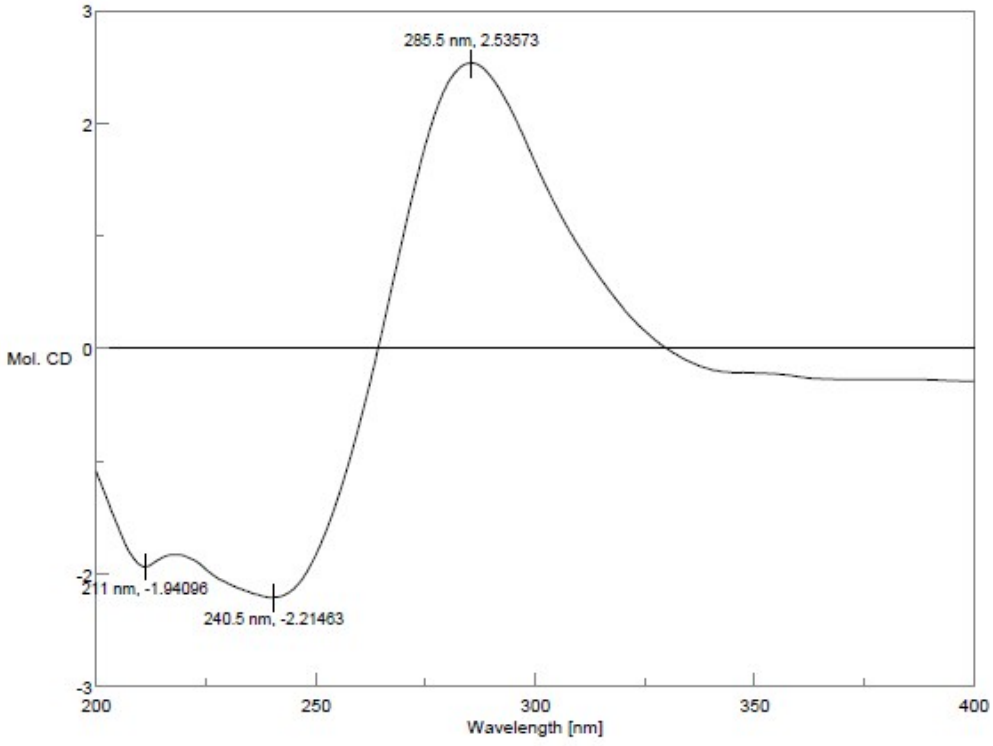


Figure S19. The ECD spectrum of compound **2** in MeOH

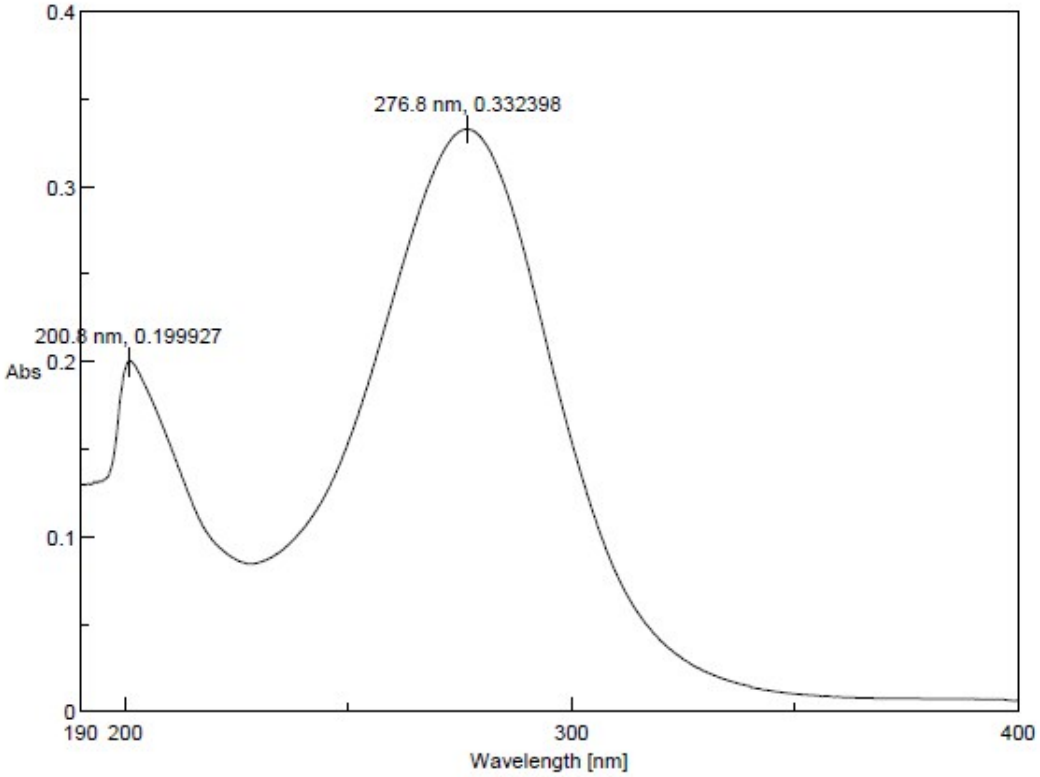


Figure S20. The UV spectrum of compound **2** in MeOH

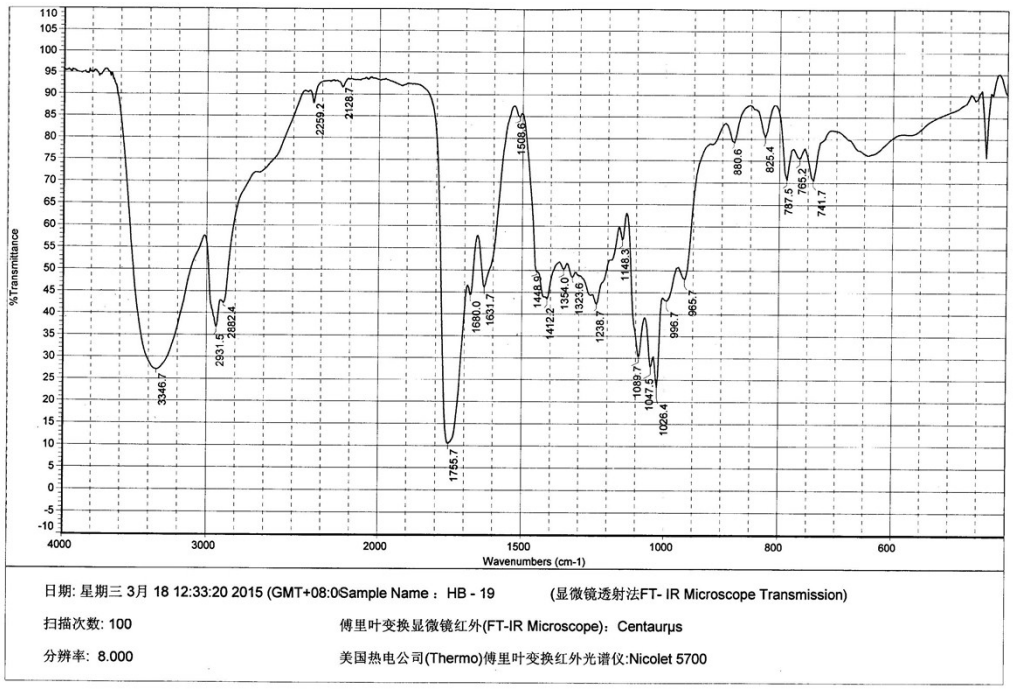
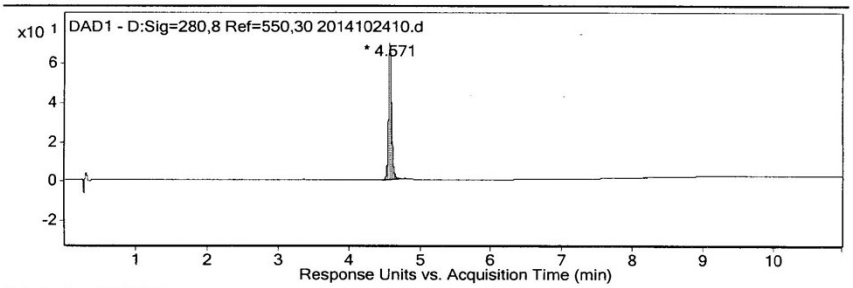


Figure S21. The IR spectrum (KBr) of compound **2**

Qualitative Analysis Report

Data Filename	2014102410.d	**Sample Name**	HB-19
Sample Type	Sample	**Position**	P1-D1
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST LCMS.m	**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
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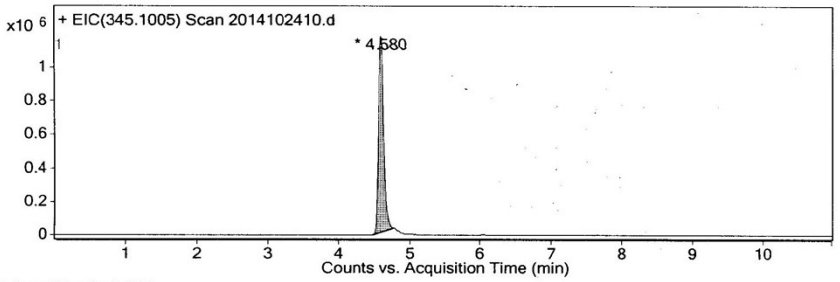
Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
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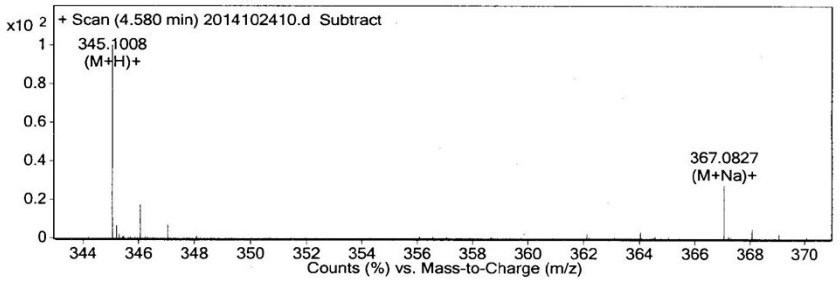
User Spectra

Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** Esi



Agilent Technologies Page 1 of 2 Printed at: 9:17 AM on: 10/31/2014

Figure S22. The HR-ESI-MS data of compound **2**

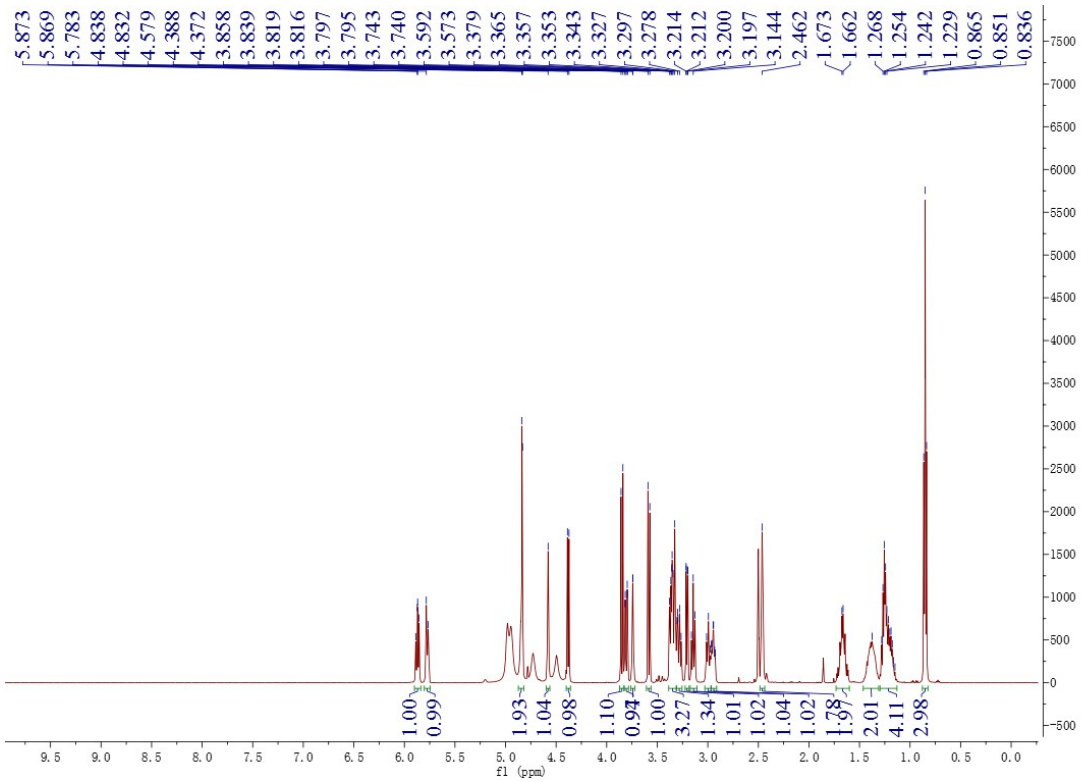


Figure S23. The ^{1}H NMR spectrum of compound **3** in DMSO-d_6

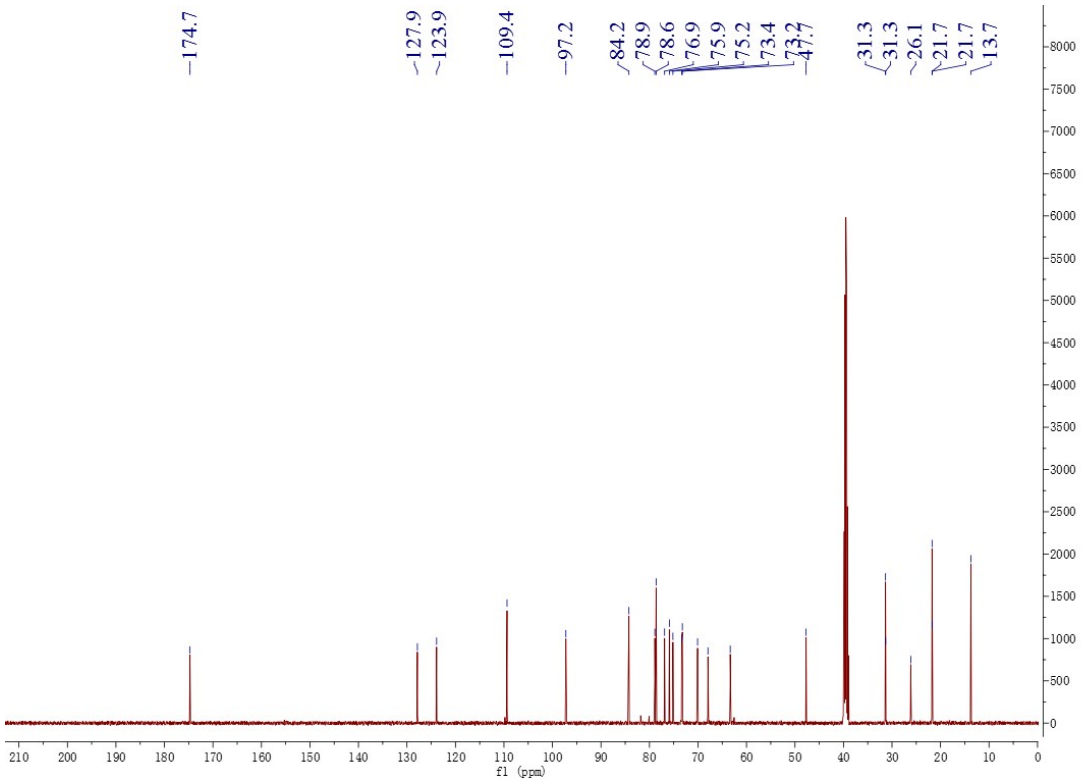


Figure S24. The ^{13}C NMR spectrum of compound **3** in DMSO-d_6

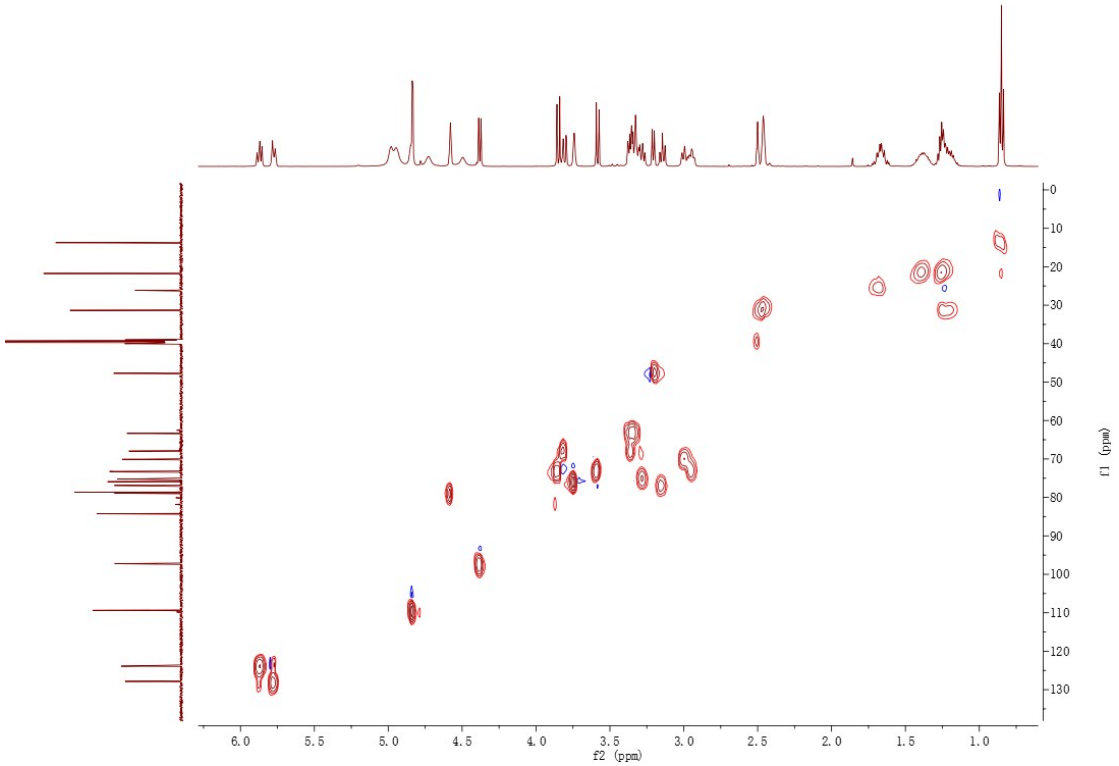


Figure S25. The HSQC spectrum of compound **3** in DMSO-d_6

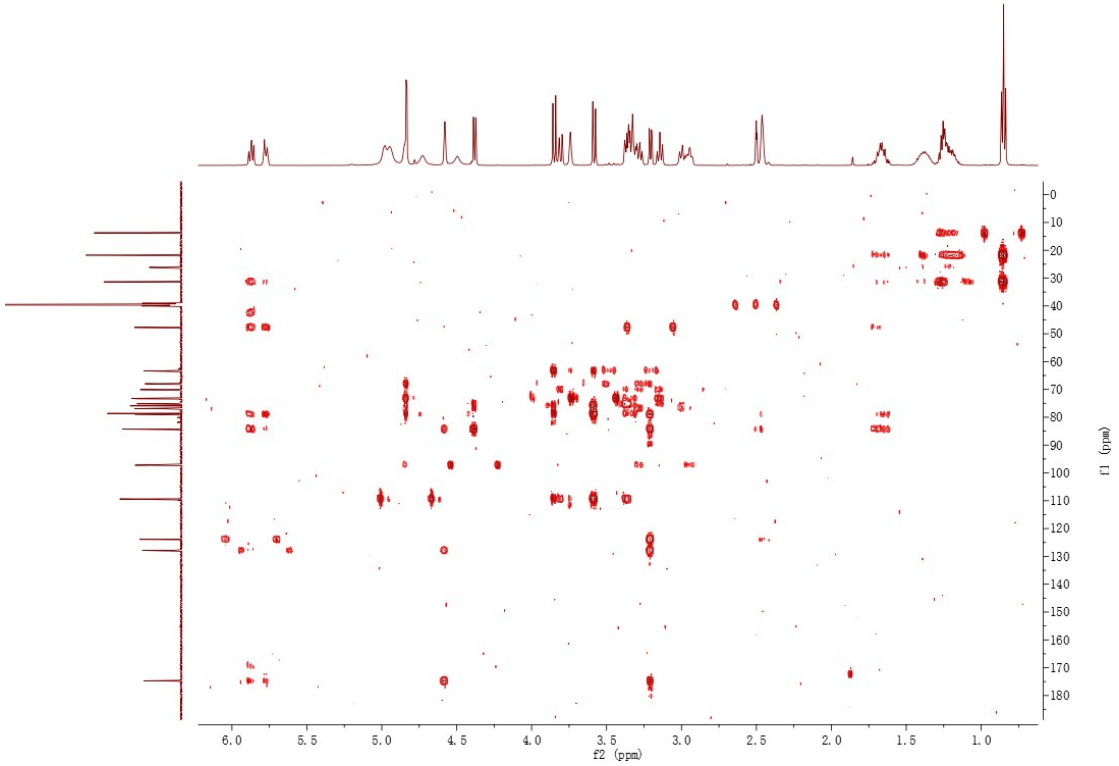


Figure S26. The HMBC spectrum of compound **3** in DMSO-d_6

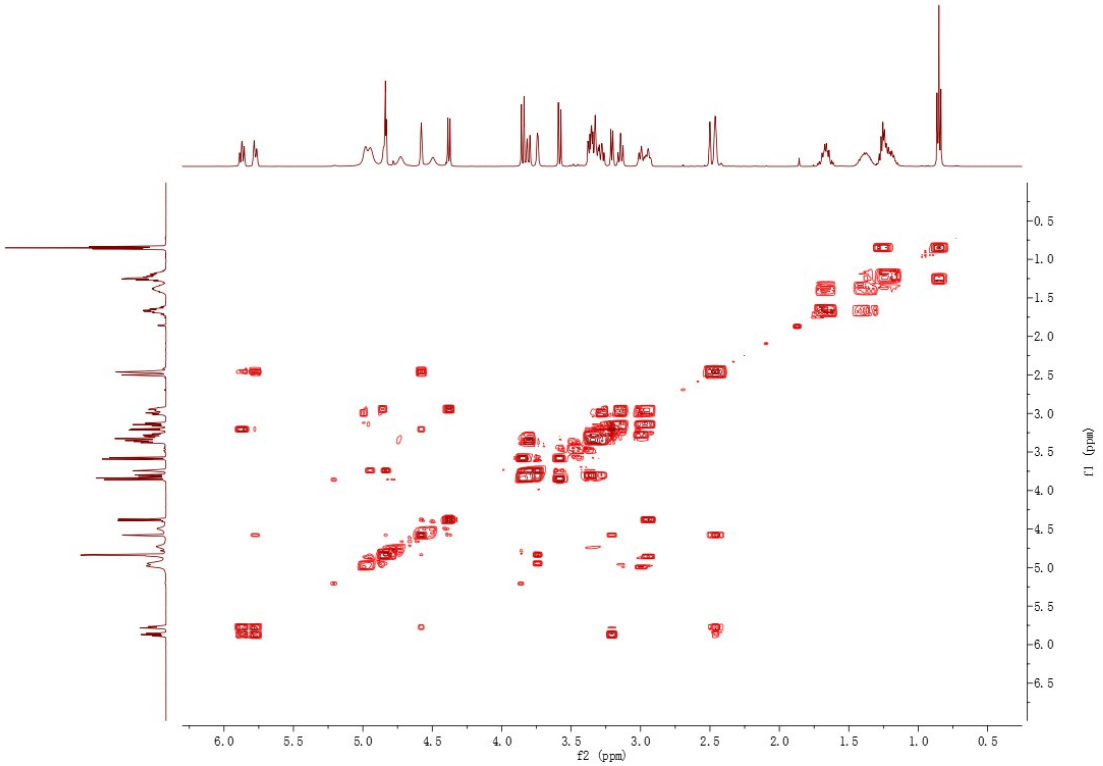


Figure S27. The ^{1}H-^{1}H COSY spectrum of compound **3** in DMSO-d_6

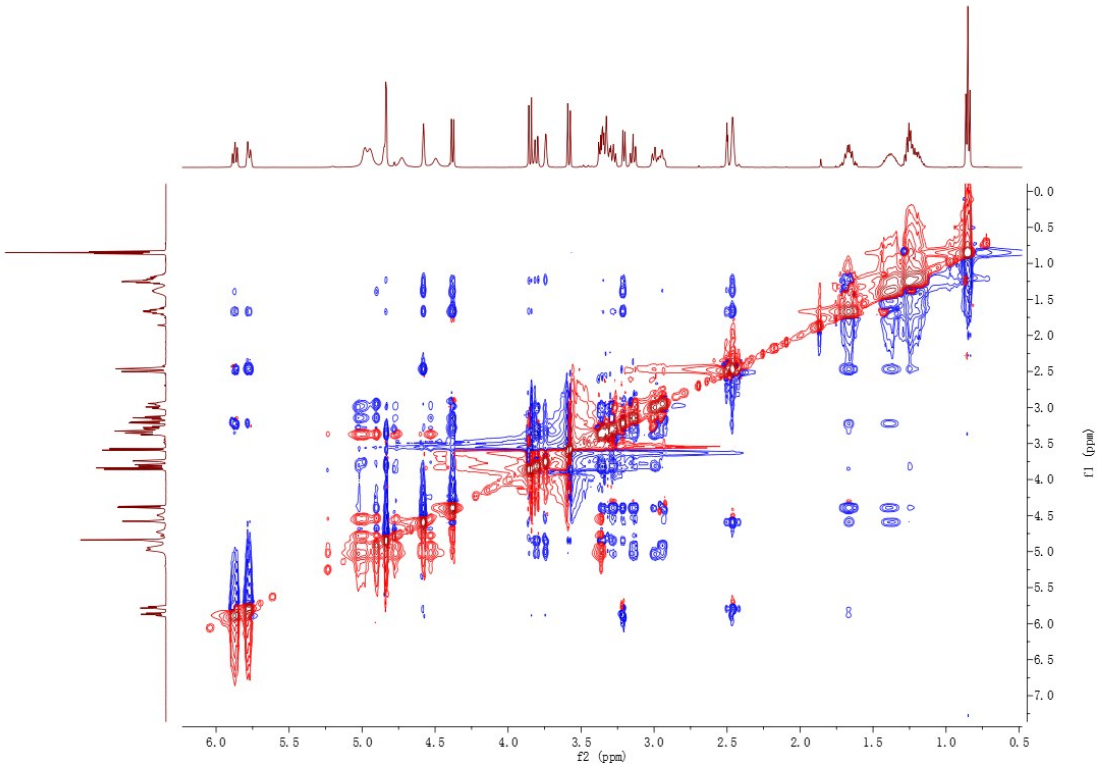


Figure S28. The ROESY spectrum of compound **3** in DMSO-d_6

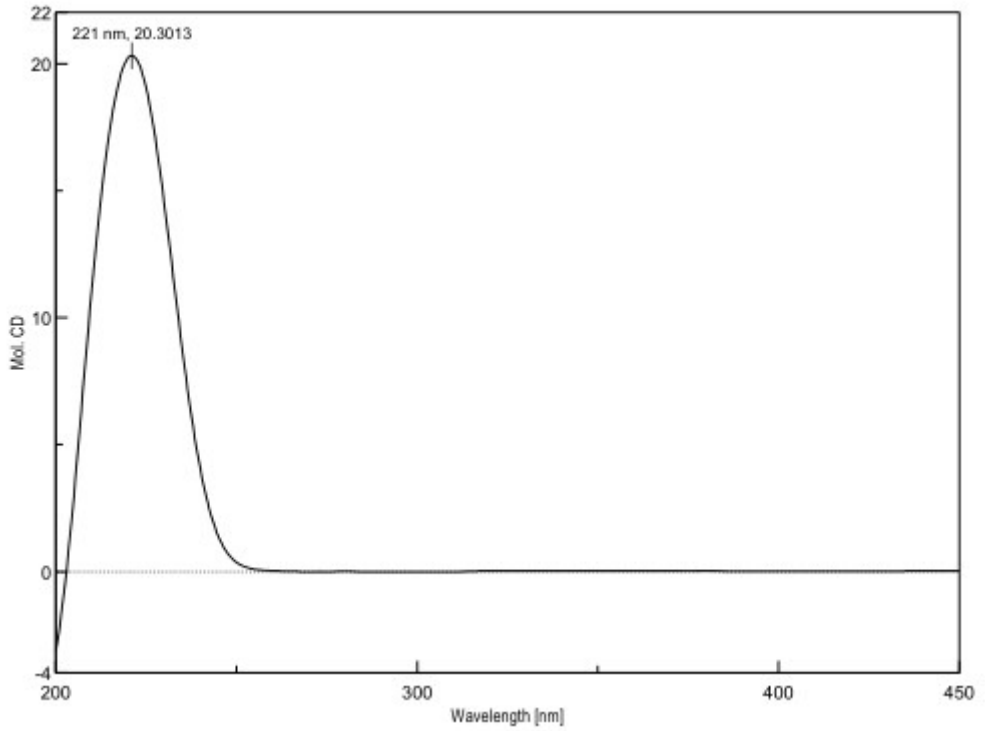


Figure S29. The ECD spectrum of compound **3a** in MeOH

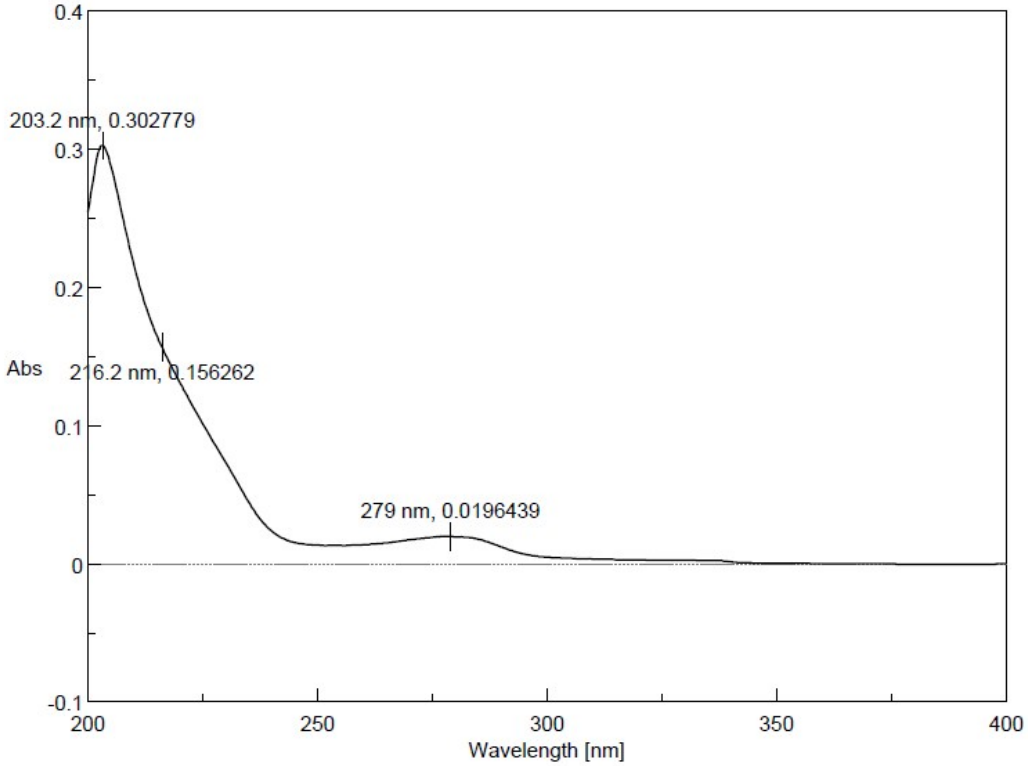


Figure S30. The UV spectrum of compound **3** in MeOH

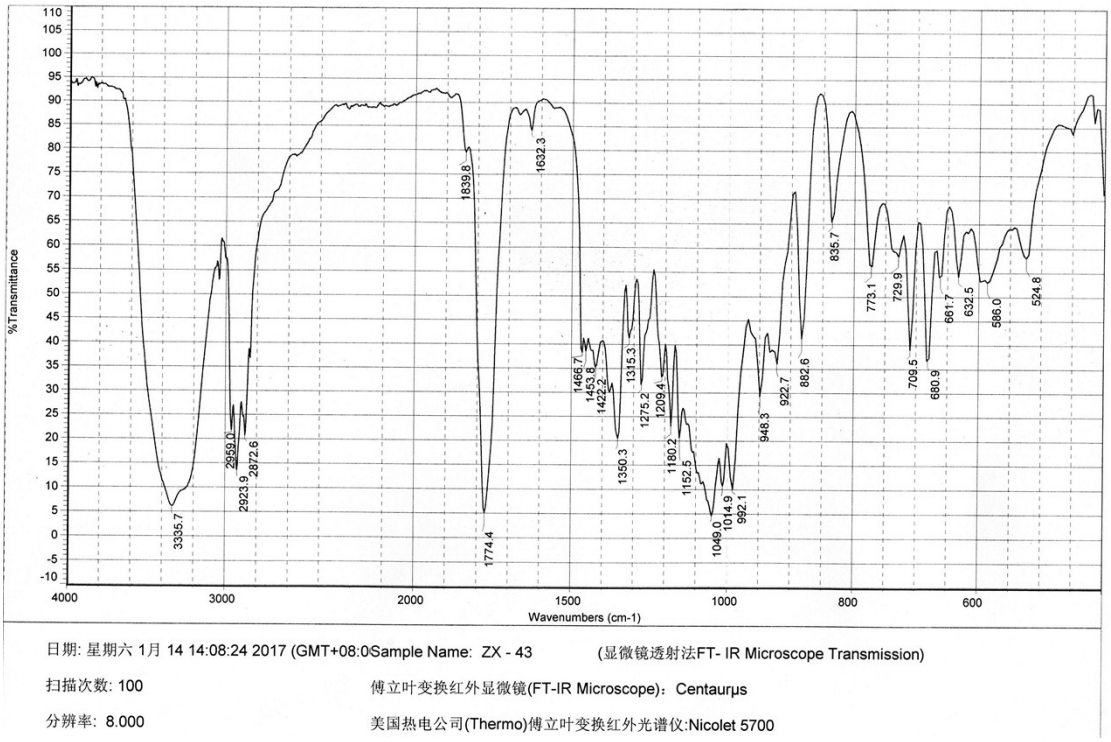
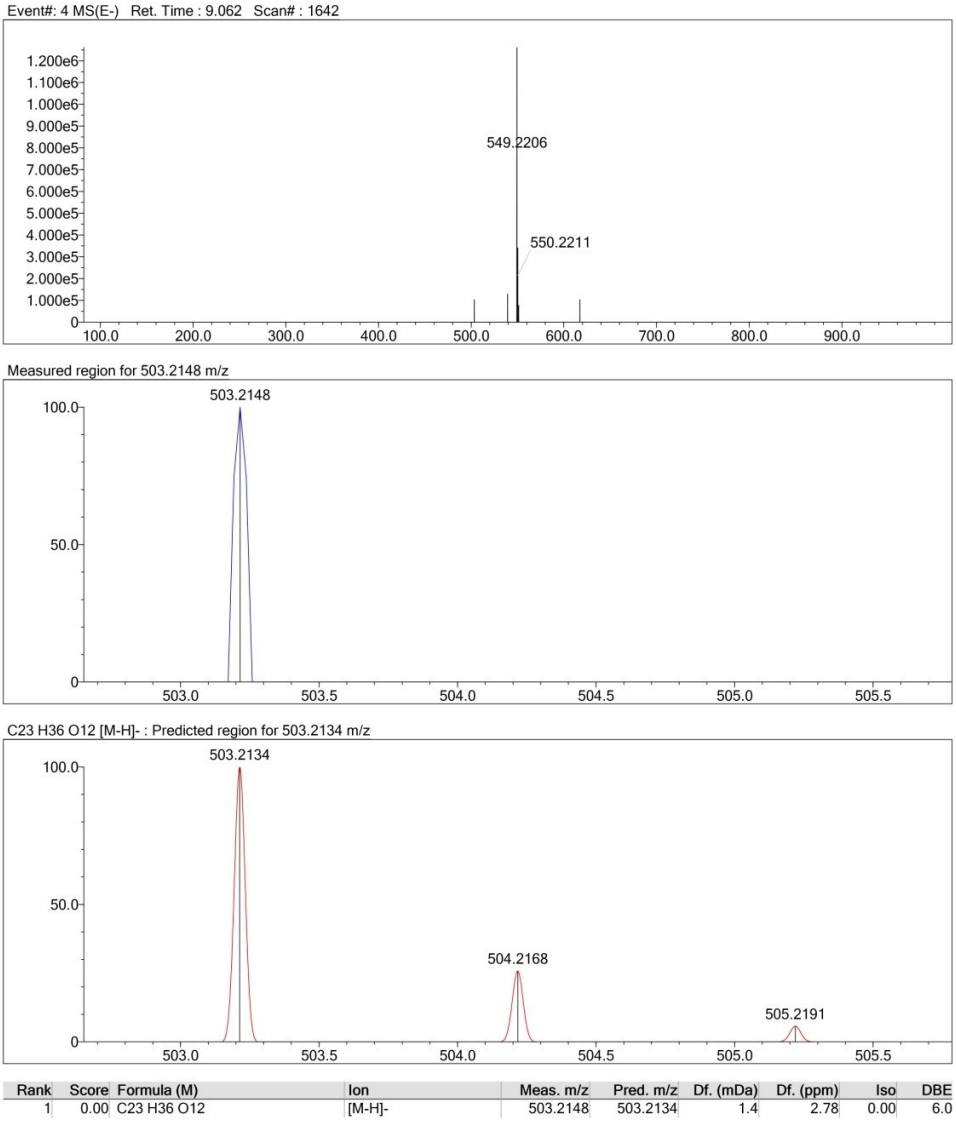


Figure S31. The IR spectrum (KBr) of compound **3**



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	0.00	C23 H36 O12	[M-H]-	503.2148	503.2134	1.4	2.78	0.00	6.0

Figure S32. The HR-ESI-MS data of compound **3**

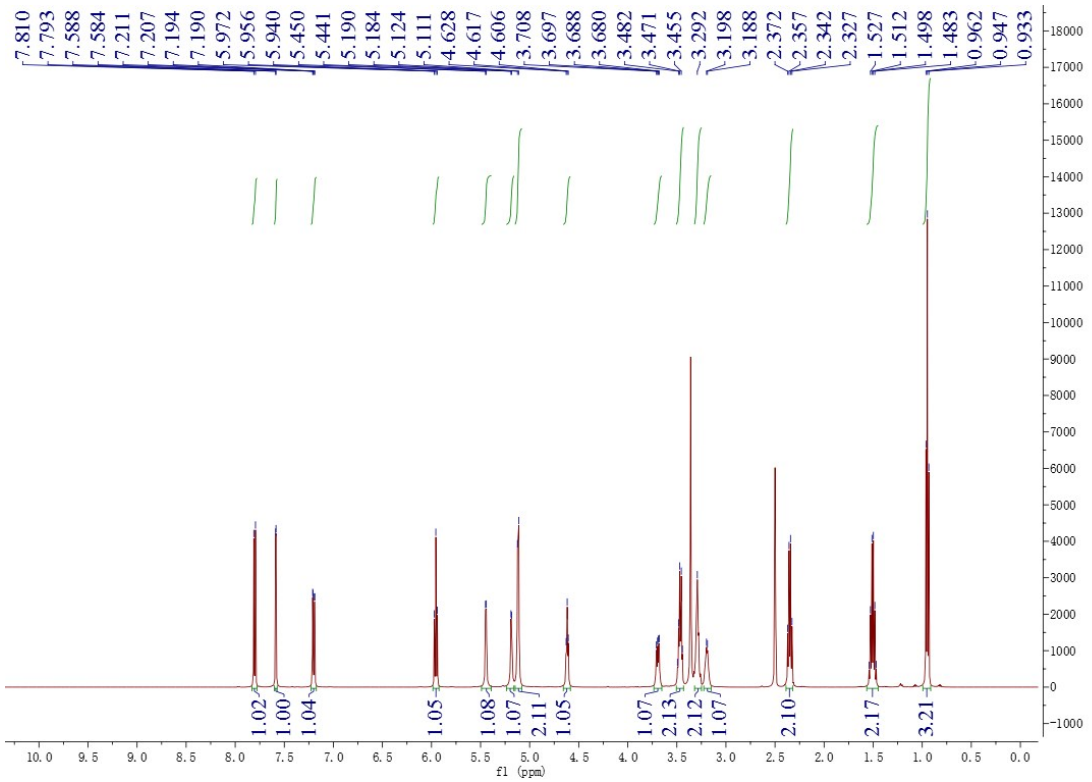


Figure S33. The ^{1}H NMR spectrum of compound **4** in DMSO-d_6

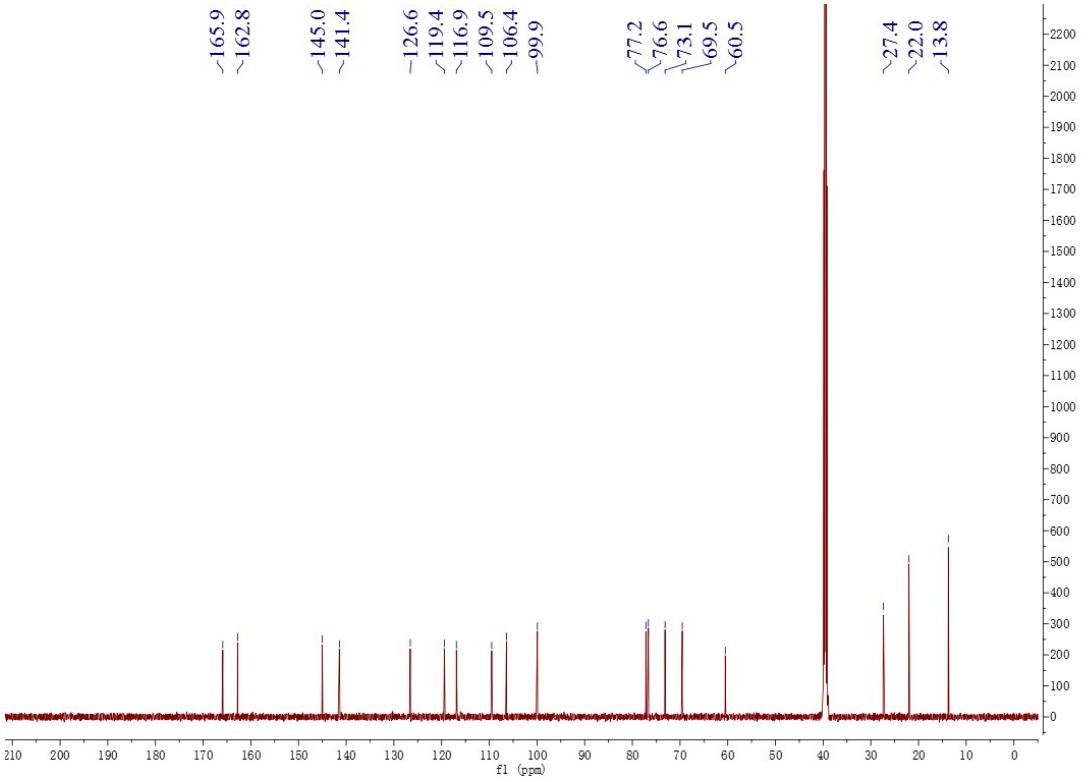


Figure S34. The ^{13}C NMR spectrum of compound **4** in DMSO-d_6

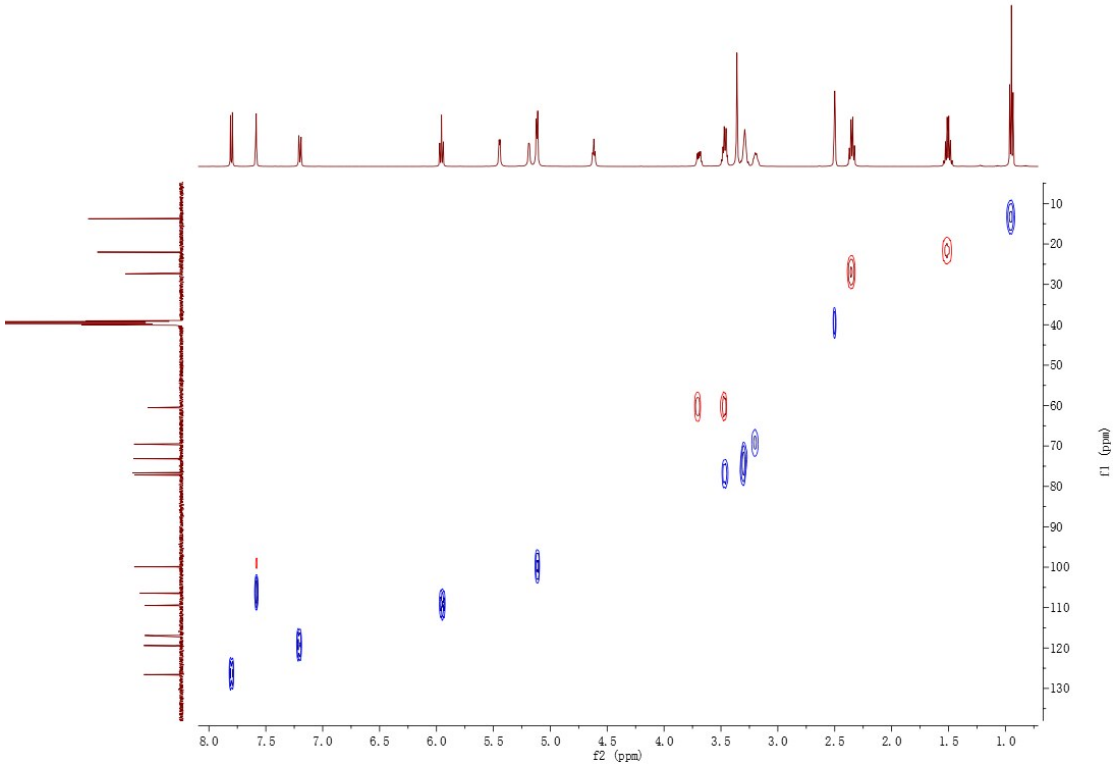


Figure S35. The HSQC spectrum of compound **4** in DMSO-d_6

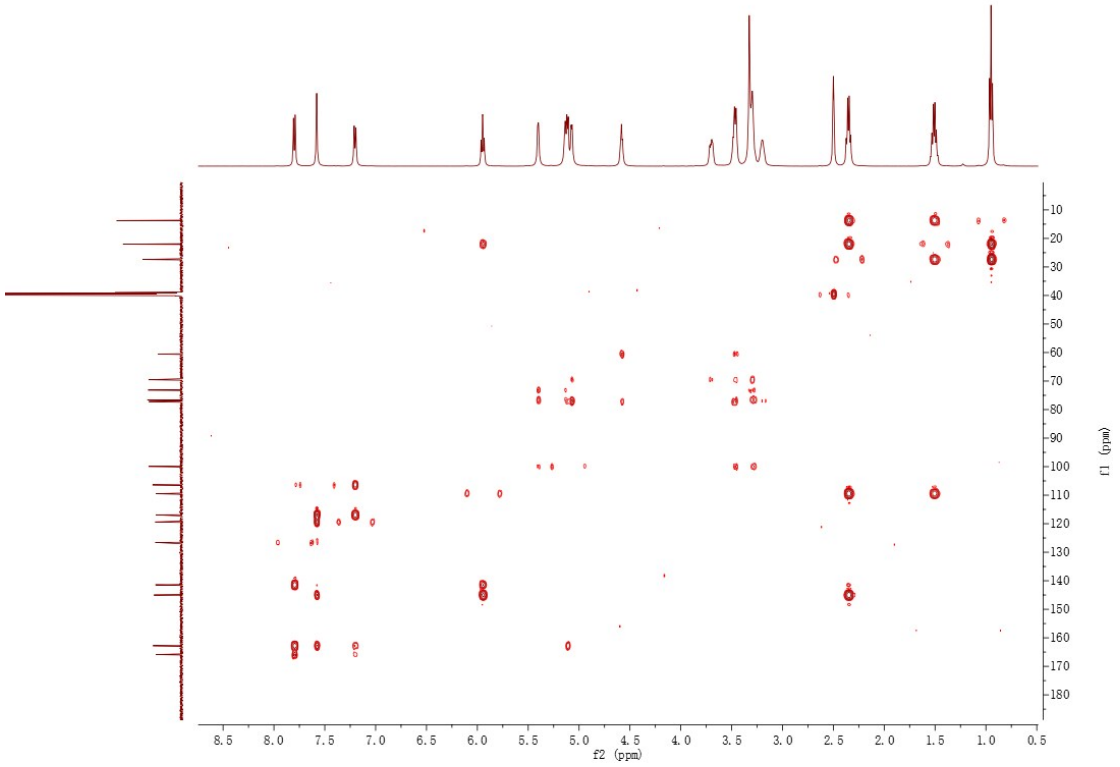


Figure S36. The HMBC spectrum of compound **4** in DMSO-d_6

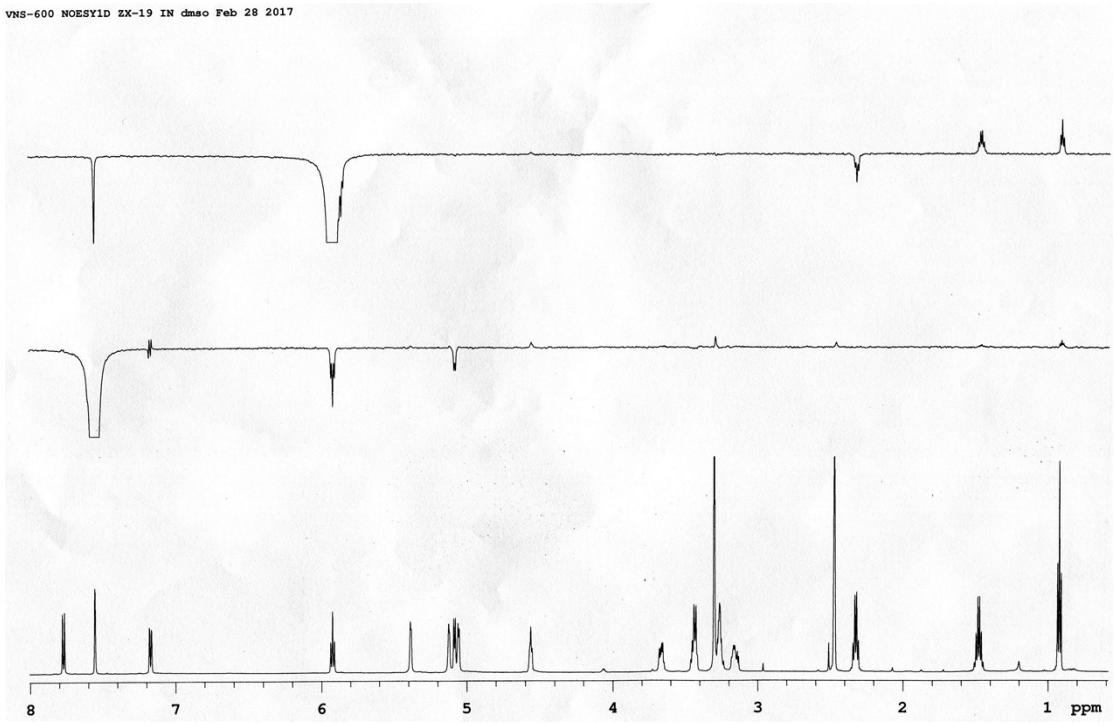


Figure S37. The NOE spectrum of compound **4** in DMSO-d_6

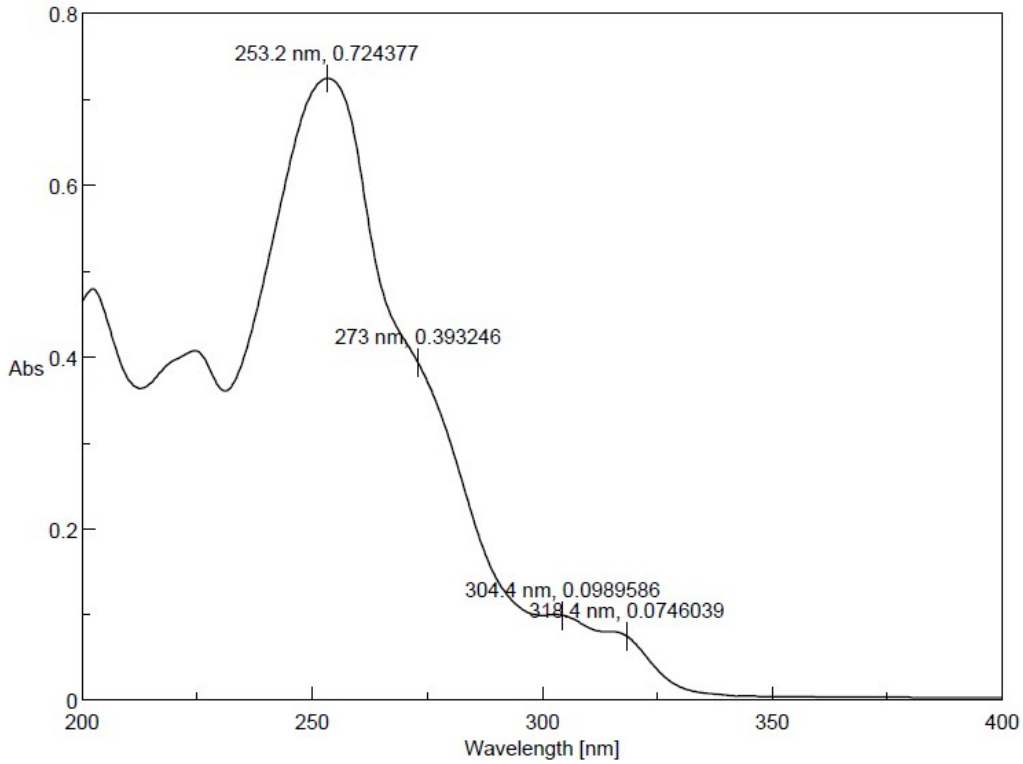


Figure S38. The UV spectrum of compound **4** in MeOH

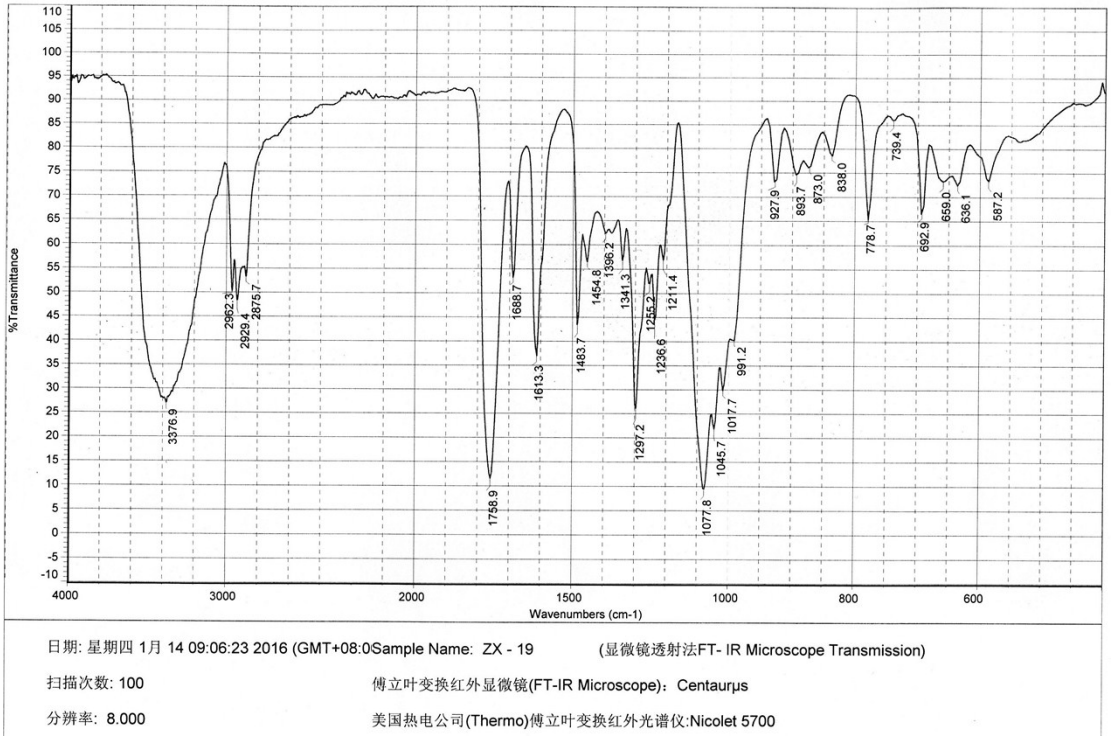
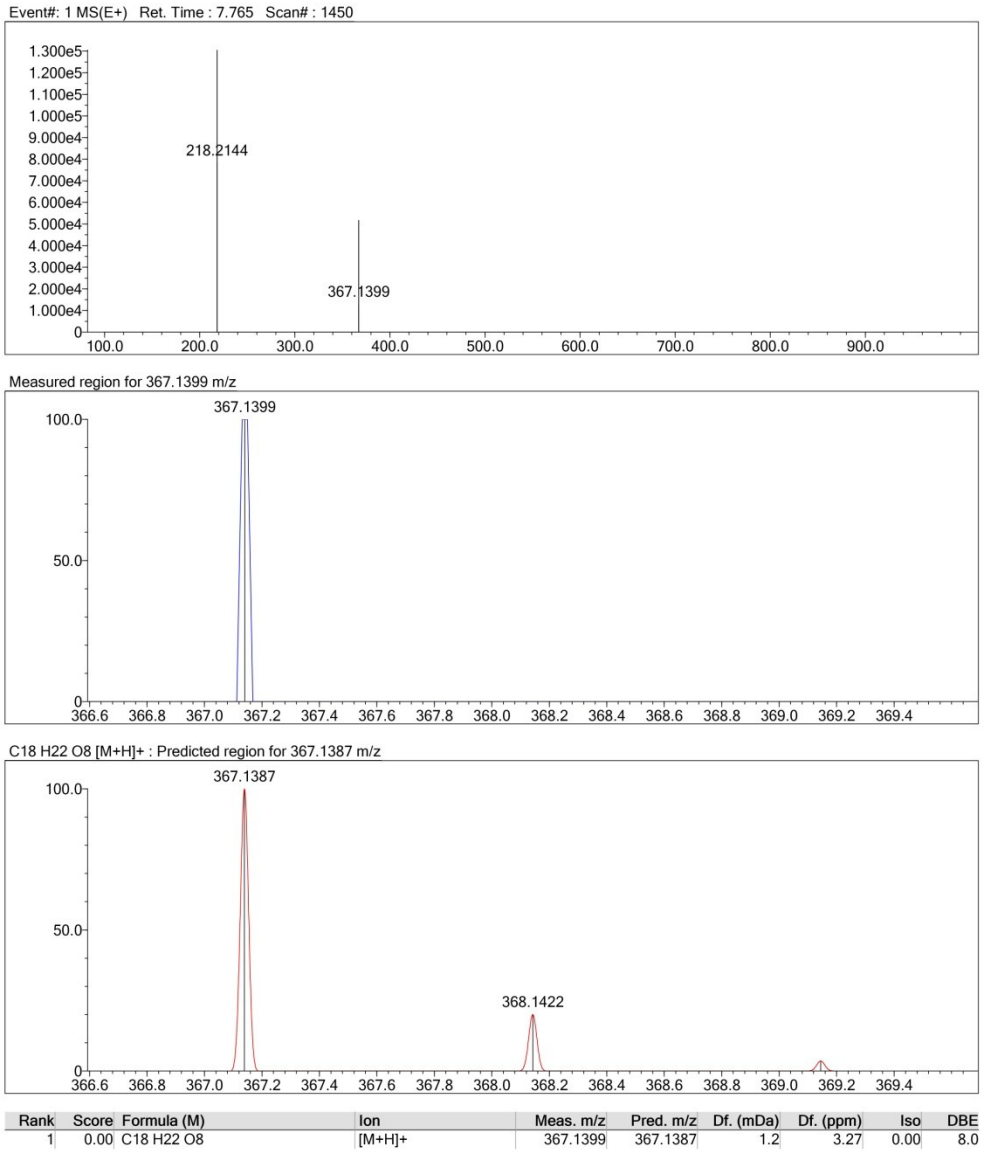


Figure S39. The IR spectrum (KBr) of compound **4**



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	0.00	C18 H22 O8	[M+H]+	367.1399	367.1387	1.2	3.27	0.00	8.0

Figure S40. The HR-ESI-MS data of compound **4**

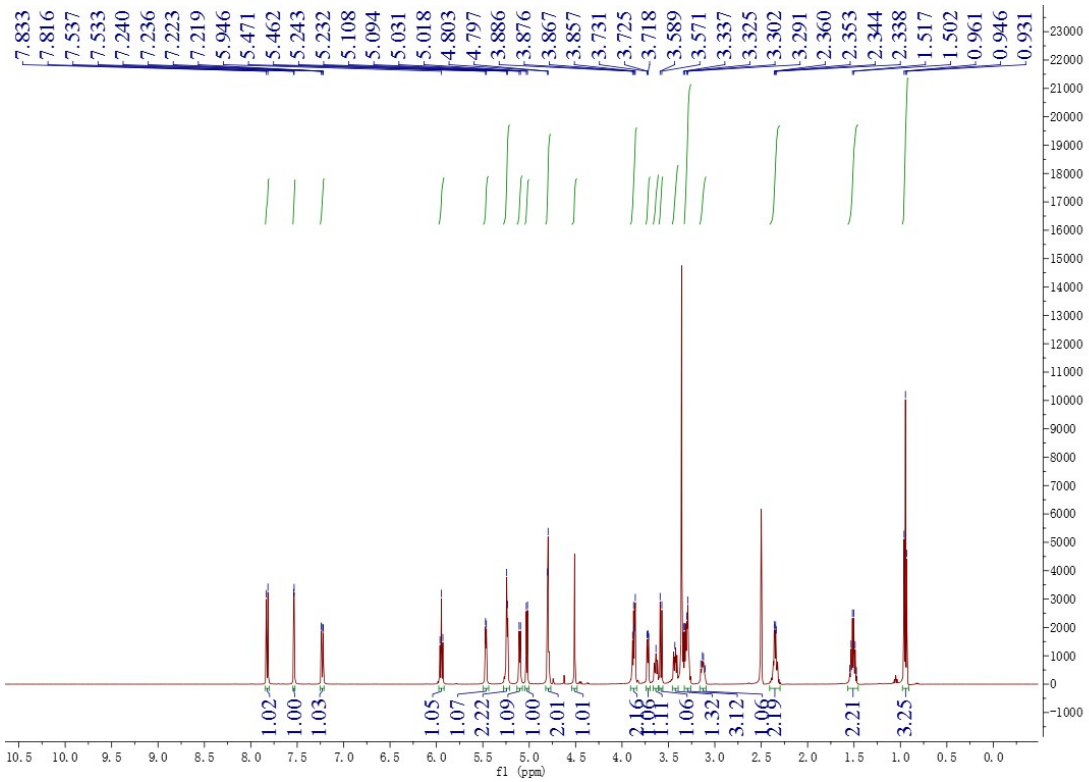


Figure S41. The ^{1}H NMR spectrum of compound **5** in DMSO-d_6

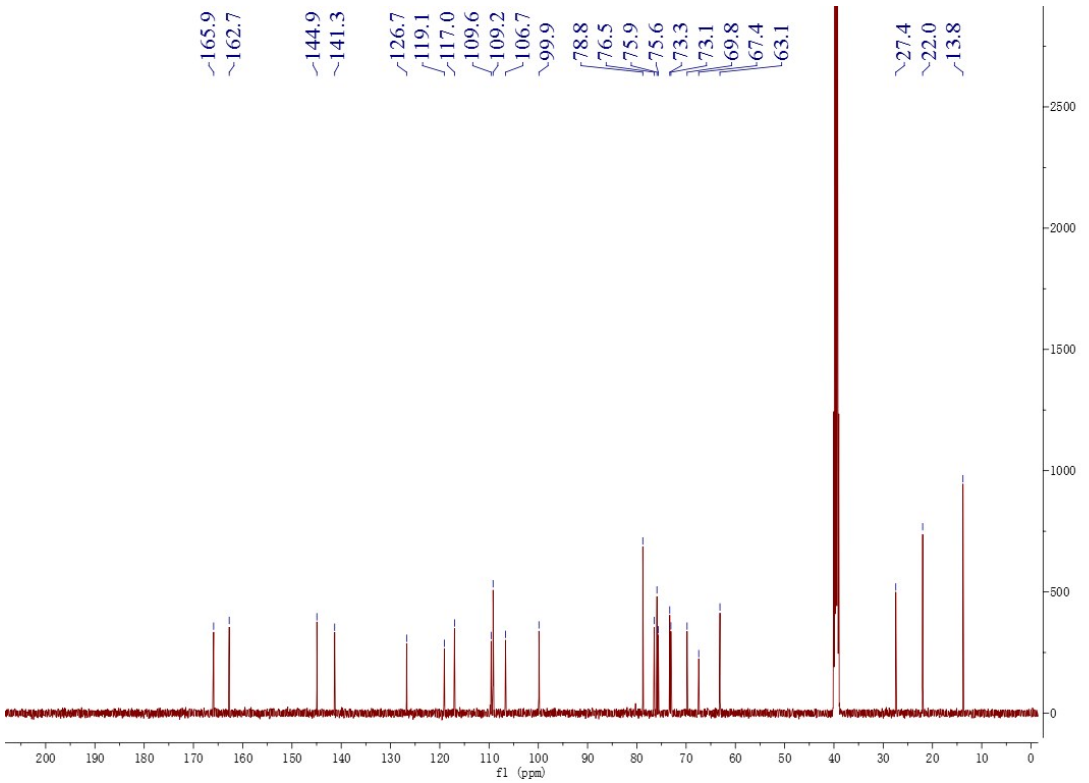


Figure S42. The ^{13}C NMR spectrum of compound **5** in DMSO-d_6

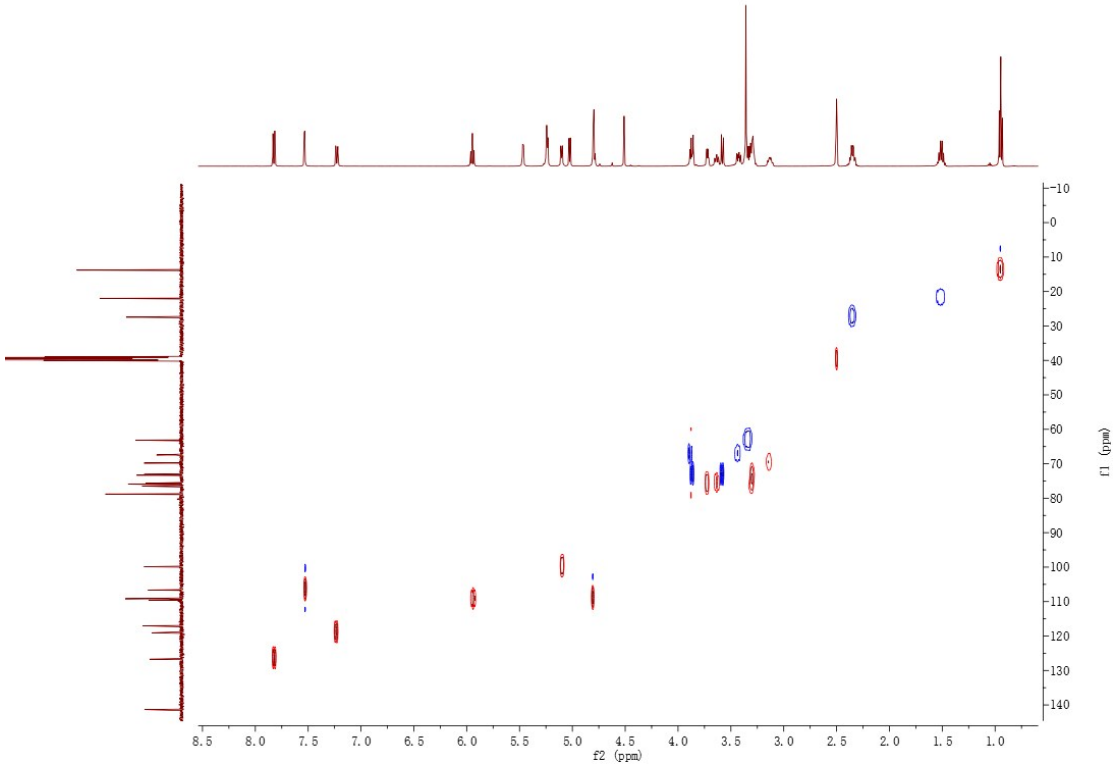


Figure S43. The HSQC spectrum of compound **5** in DMSO-d_6

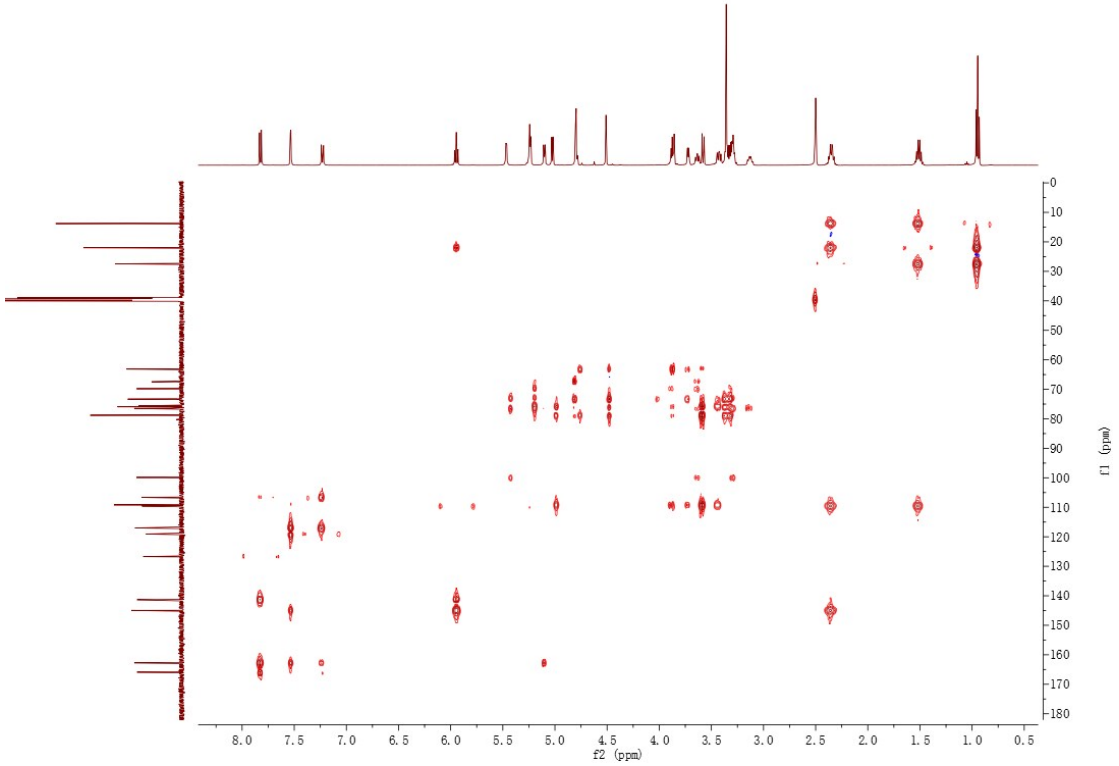


Figure S44. The HMBC spectrum of compound **5** in DMSO-d_6

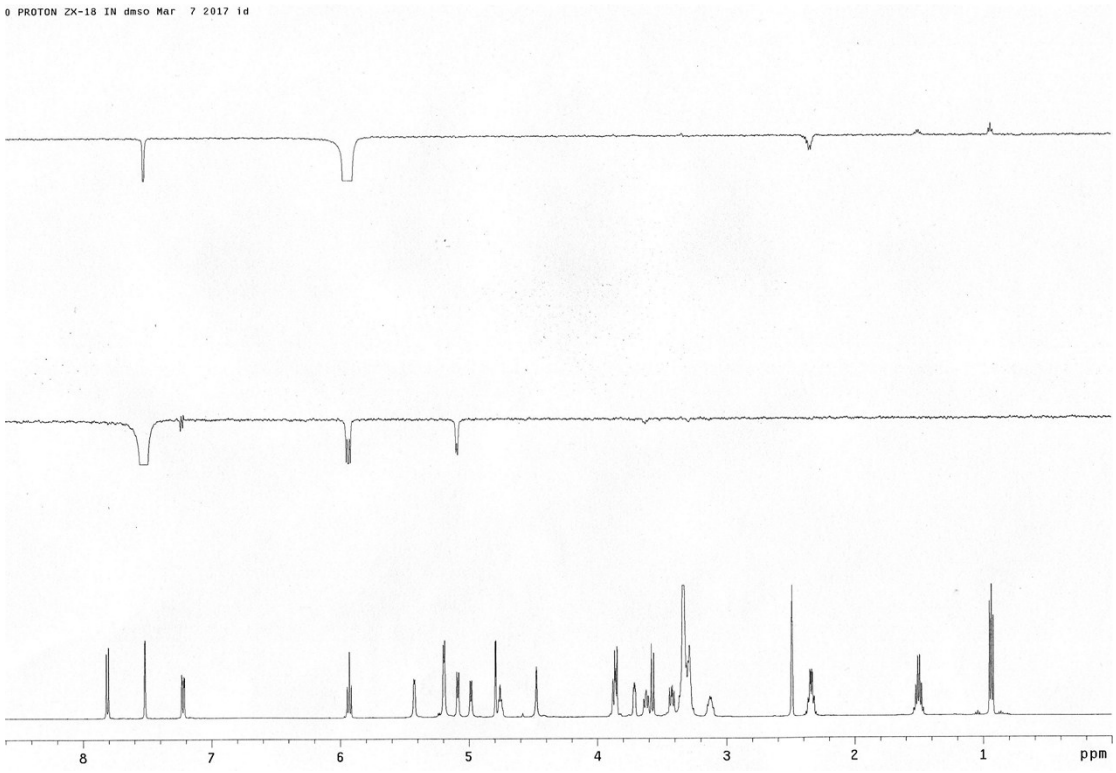


Figure S45. The NOE spectrum of compound **5** in DMSO-d_6

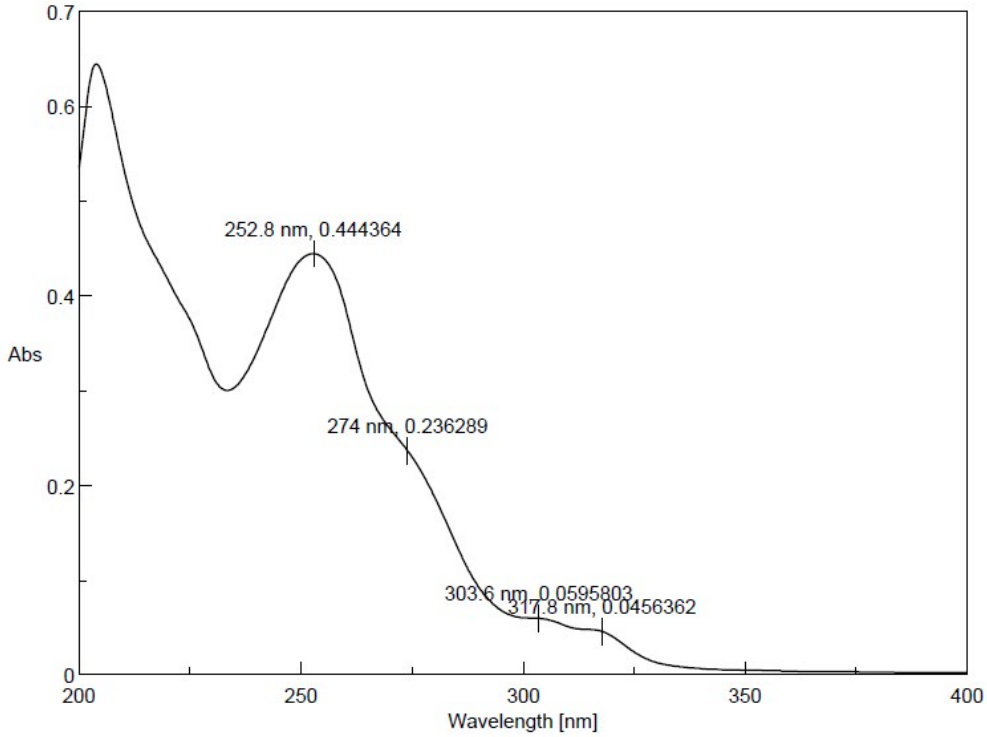


Figure S46. The UV spectrum of compound **5** in MeOH

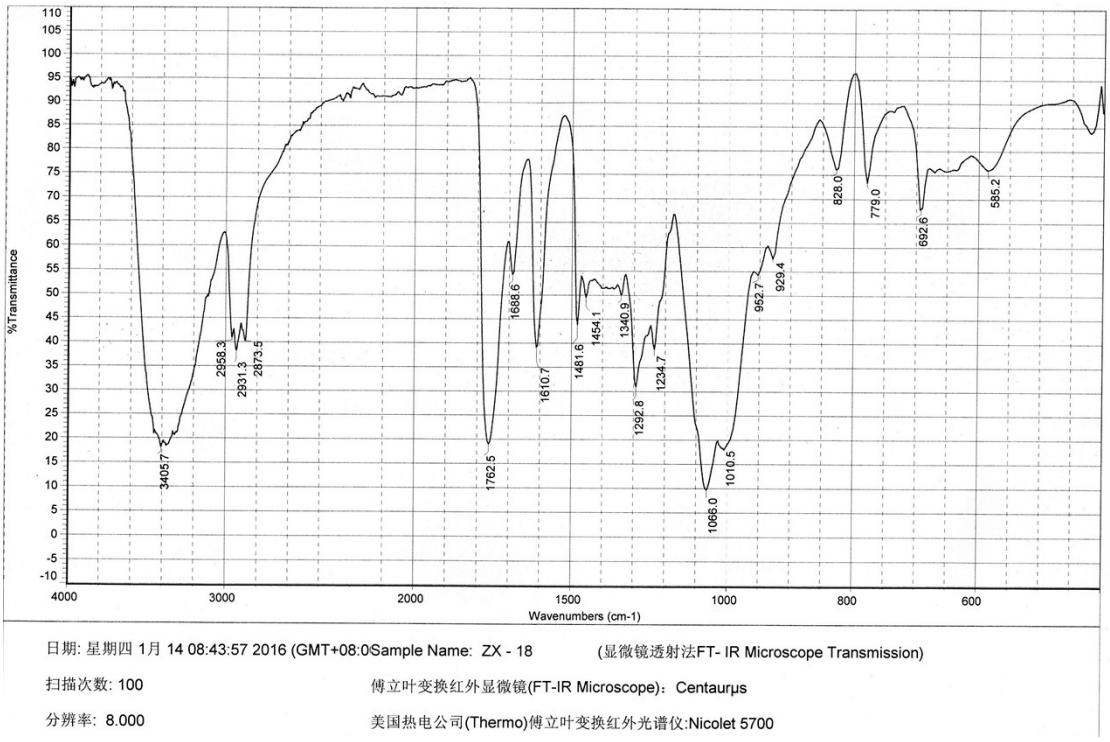
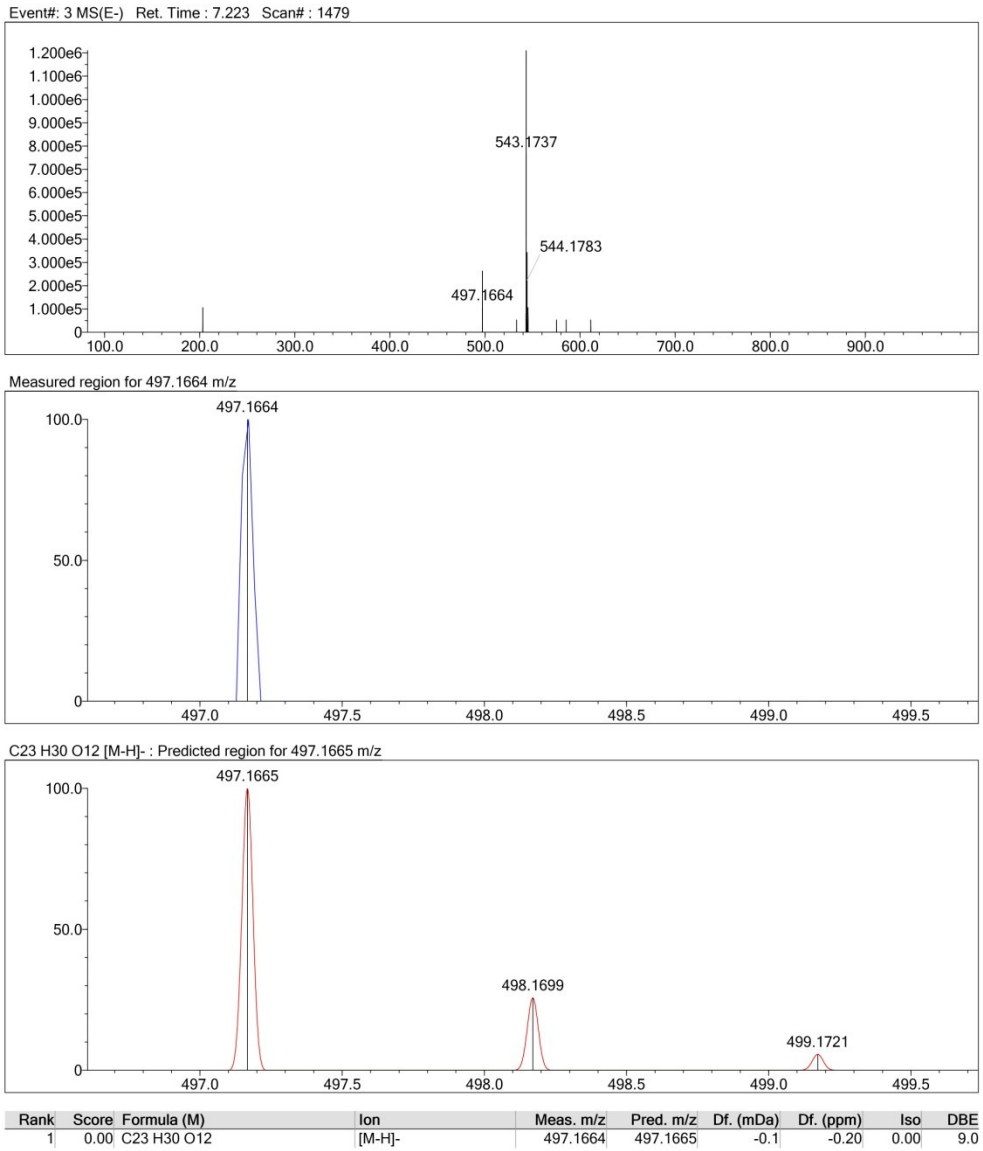


Figure S47. The IR spectrum (KBr) of compound **5**



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	0.00	C23 H30 O12	[M-H]-	497.1664	497.1665	-0.1	-0.20	0.00	9.0

Figure S48. The HR-ESI-MS data of compound **5**

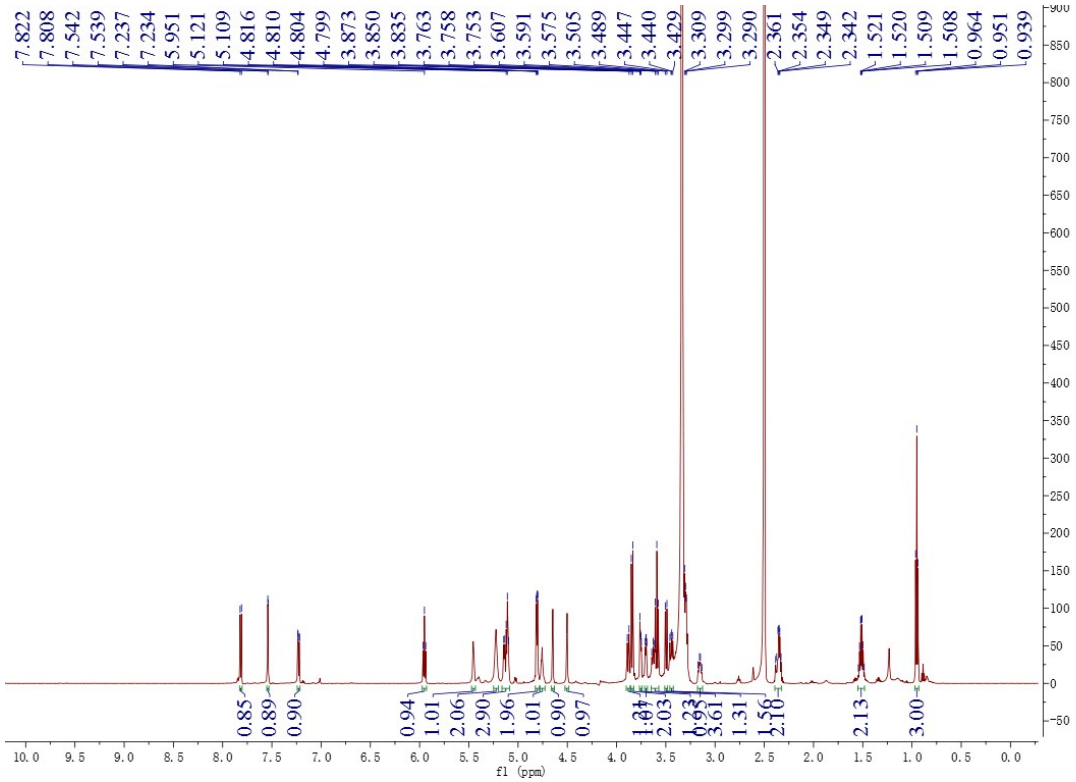


Figure S49. The ^{1}H NMR spectrum of compound **6** in DMSO-d_6

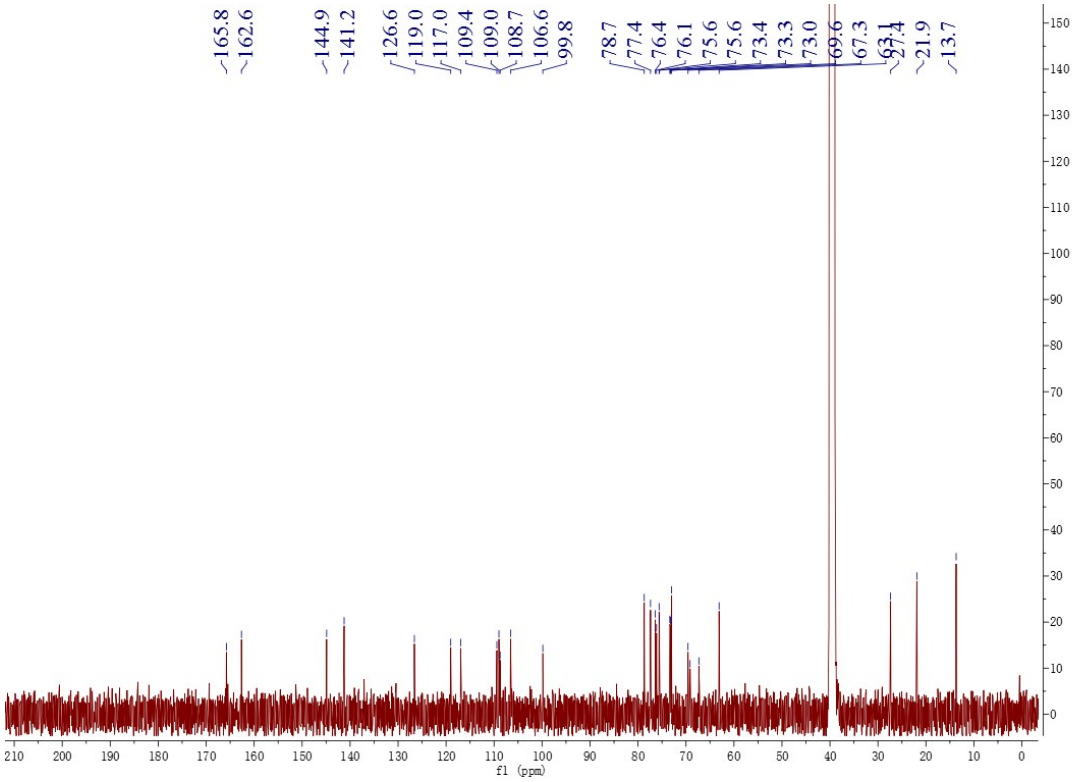


Figure S50. The ^{13}C NMR spectrum of compound **6** in DMSO-d_6

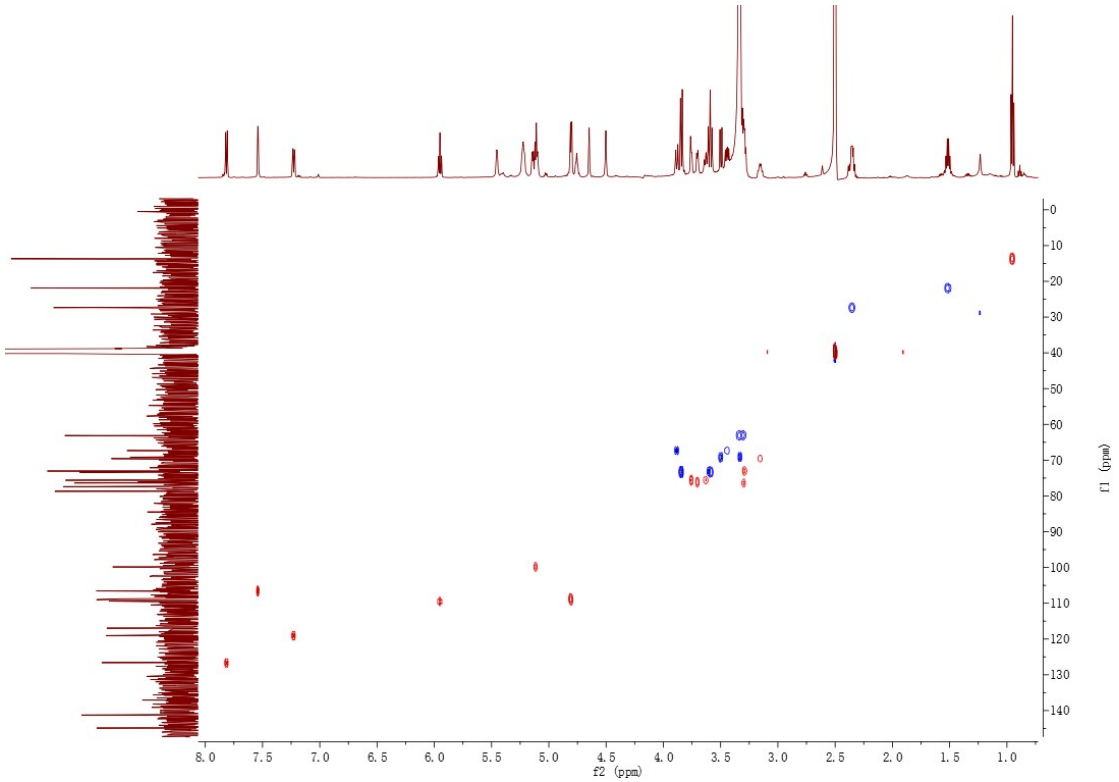


Figure S51. The HSQC spectrum of compound **6** in DMSO-d_6

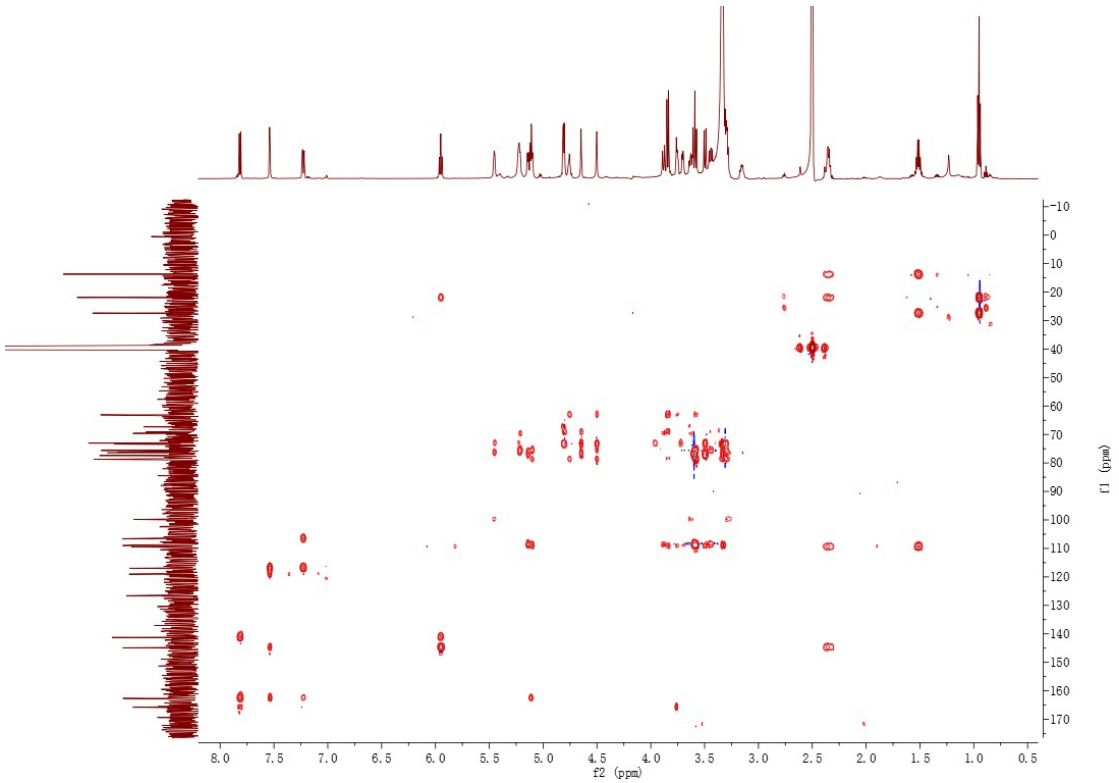


Figure S52. The HMBC spectrum of compound **6** in DMSO-d_6

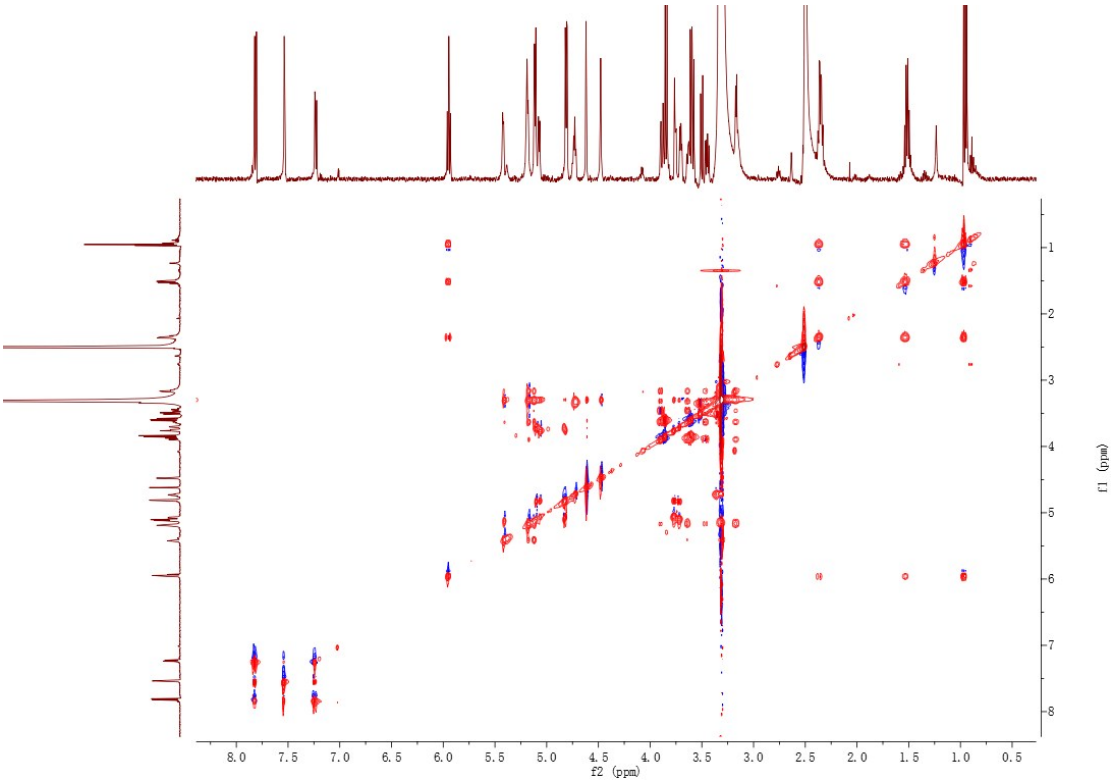


Figure S53. The TOCSY spectrum of compound **6** in DMSO-d_6

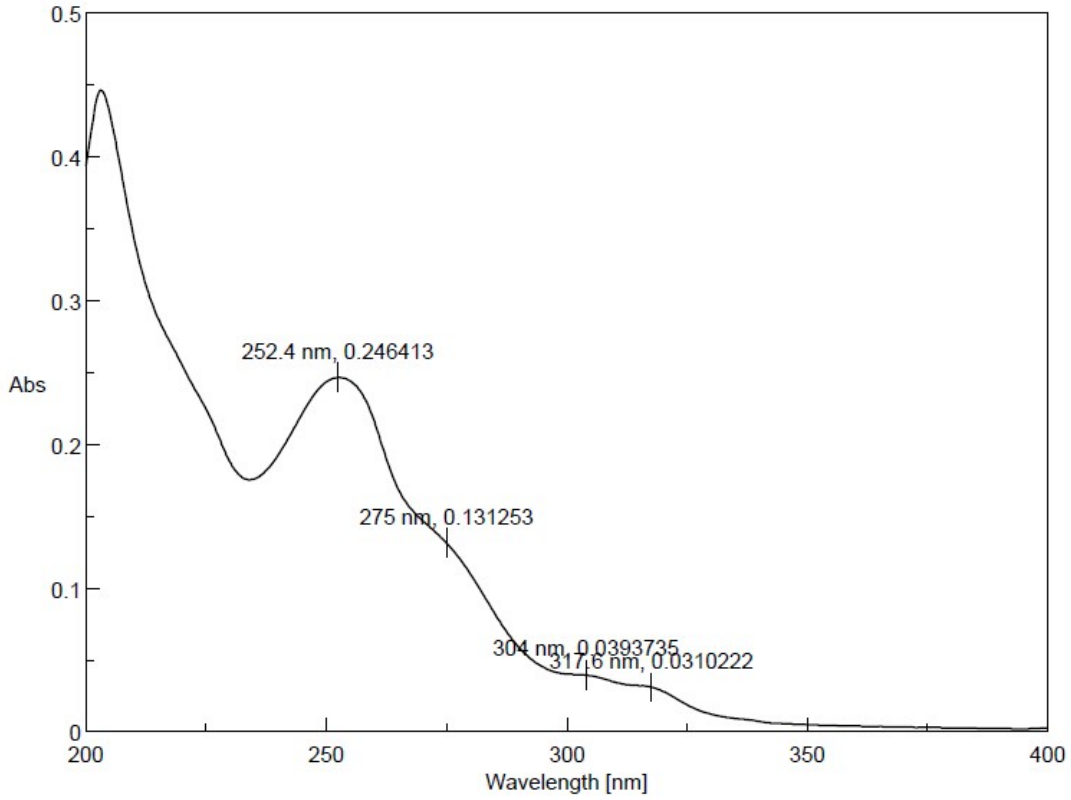


Figure S54. The UV spectrum of compound **6** in MeOH

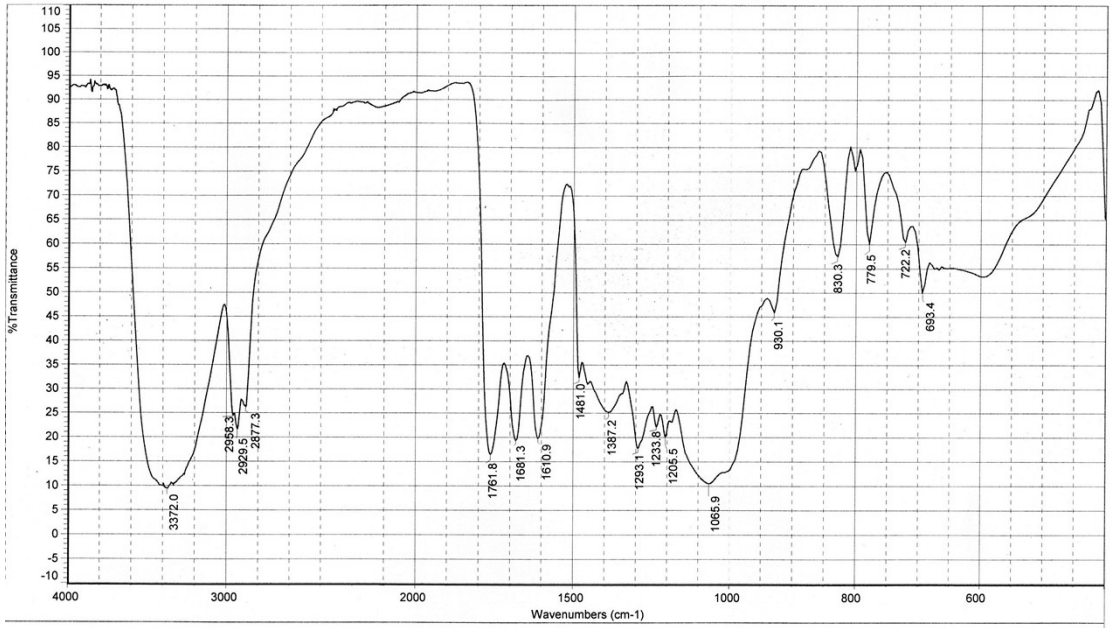


Figure S55. The IR spectrum (KBr) of compound **6**

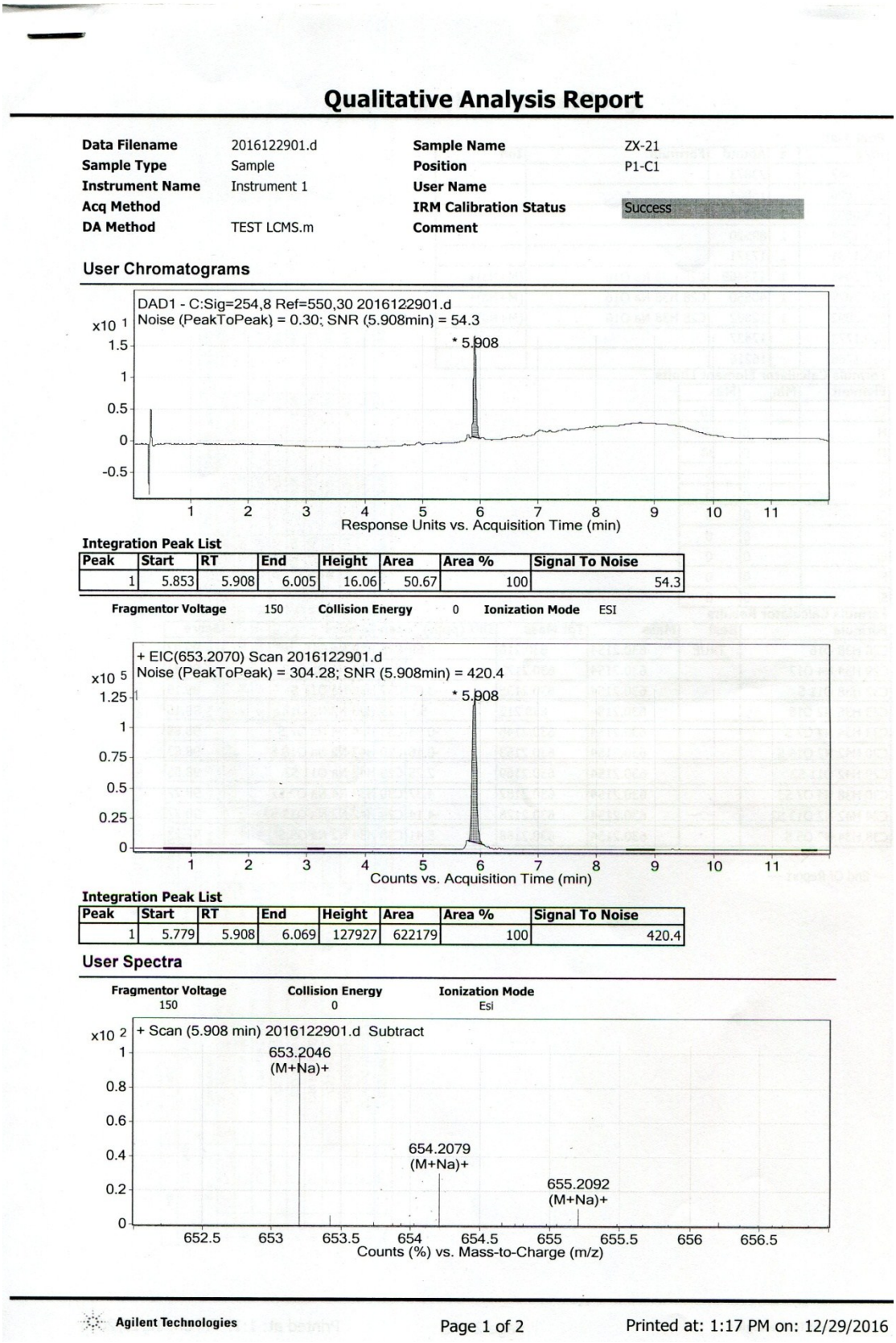


Figure S56. The HR-ESI-MS data of compound **6**

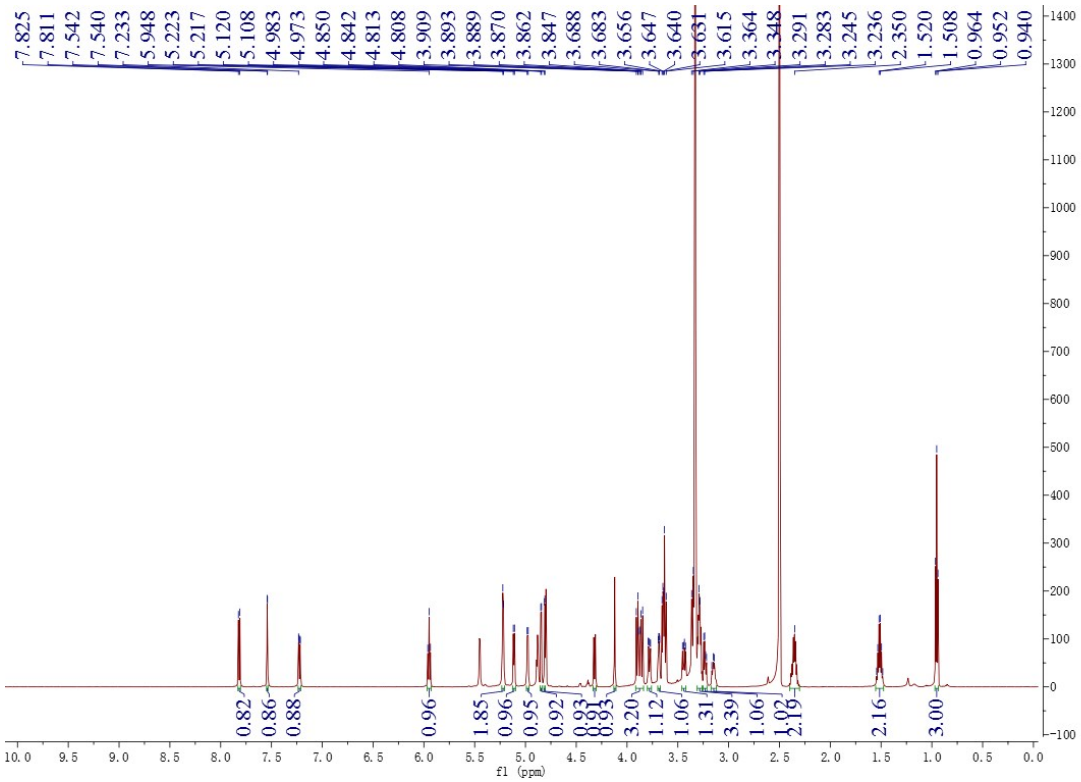


Figure S57. The ^{1}H NMR spectrum of compound **7** in DMSO-d_6

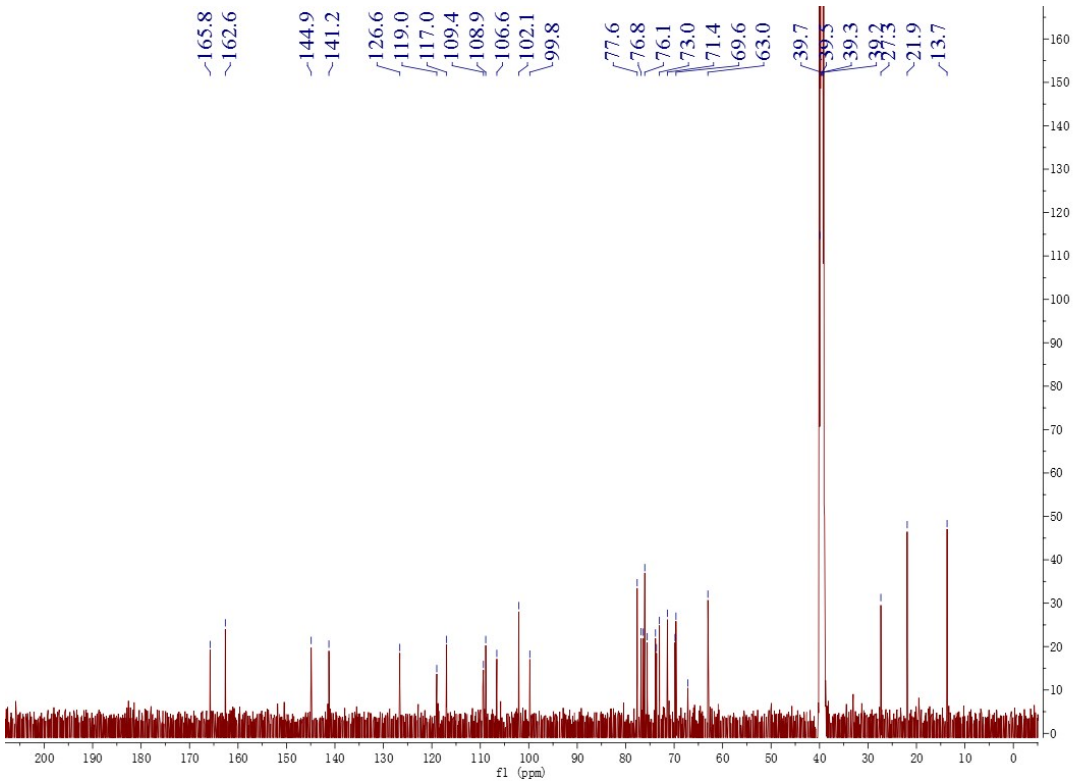


Figure S58. The ^{13}C NMR spectrum of compound **7** in DMSO-d_6

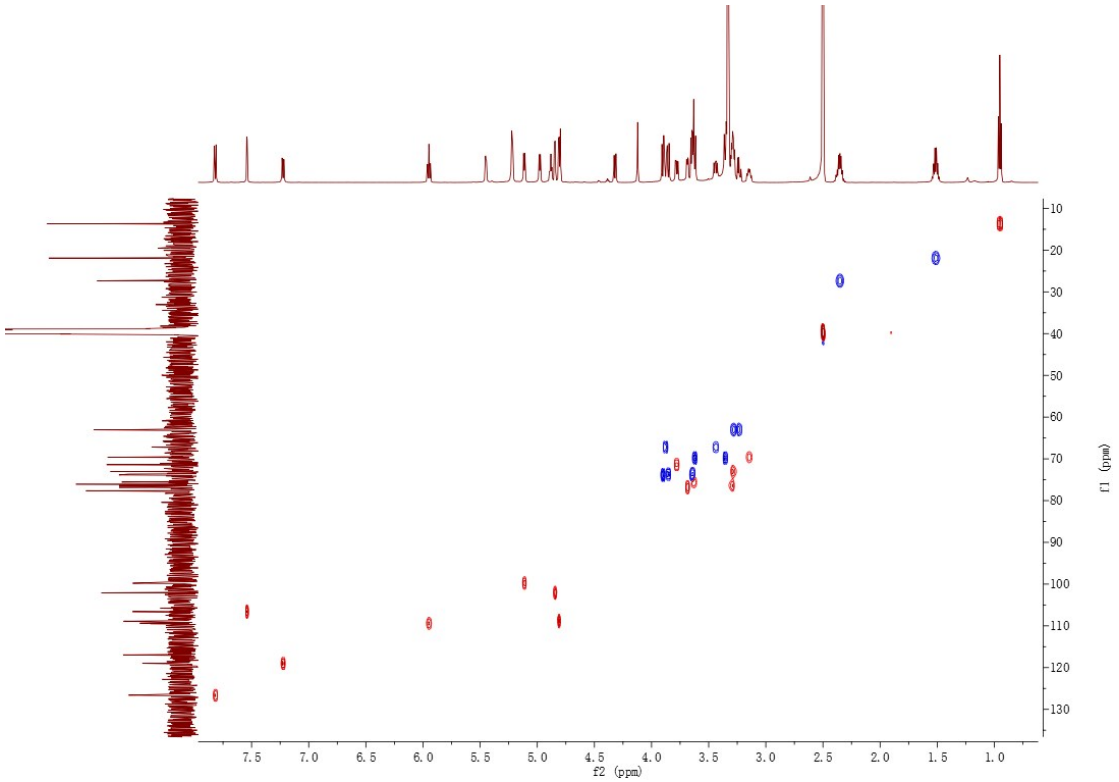


Figure S59. The HSQC spectrum of compound **7** in DMSO-d_6

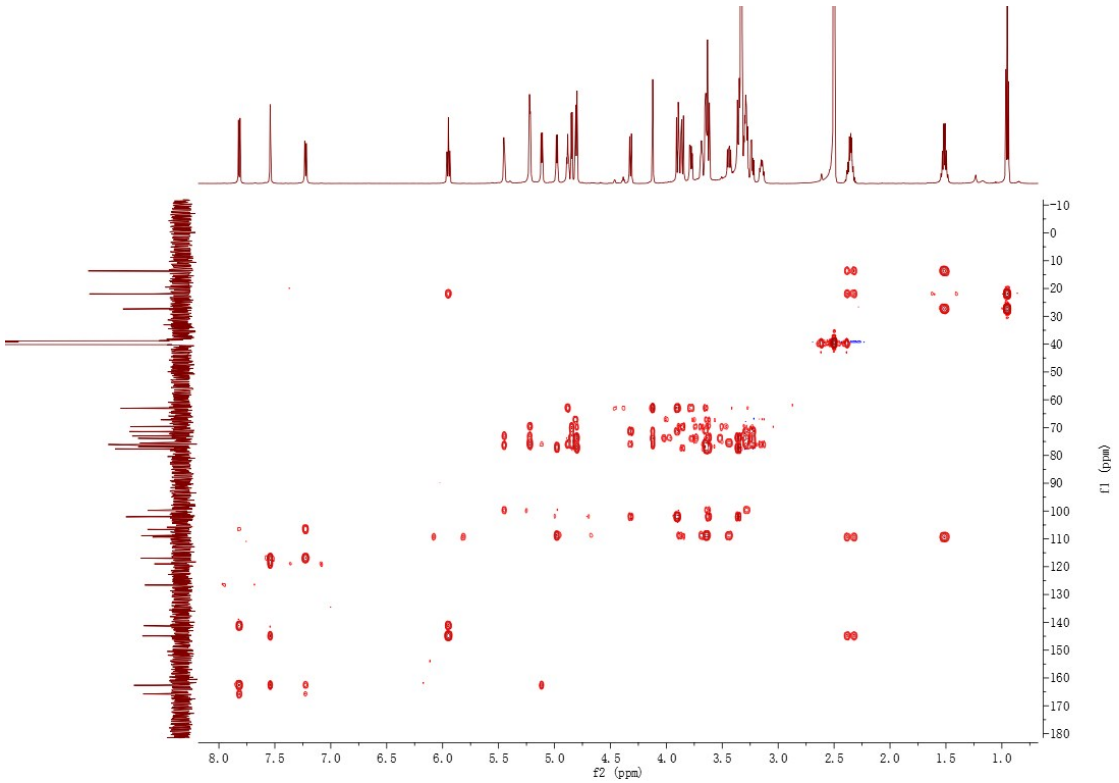


Figure S60. The HMBC spectrum of compound **7** in DMSO-d_6

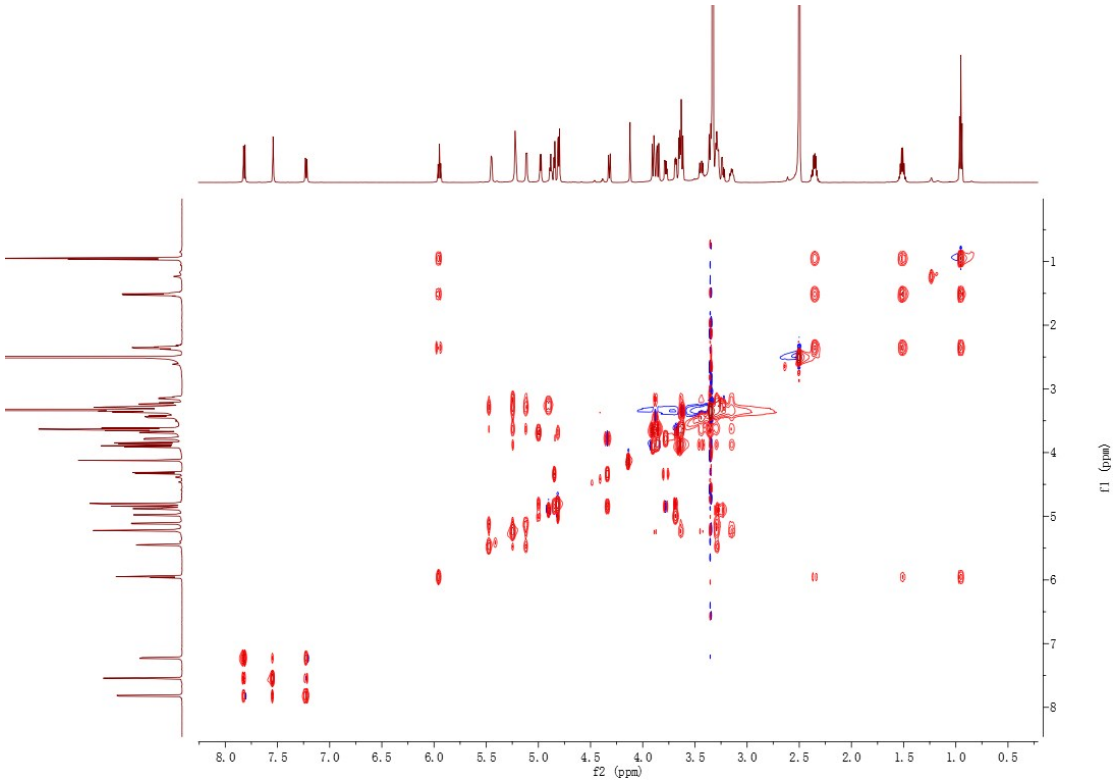


Figure S61. The TOCSY spectrum of compound **7** in DMSO-d_6

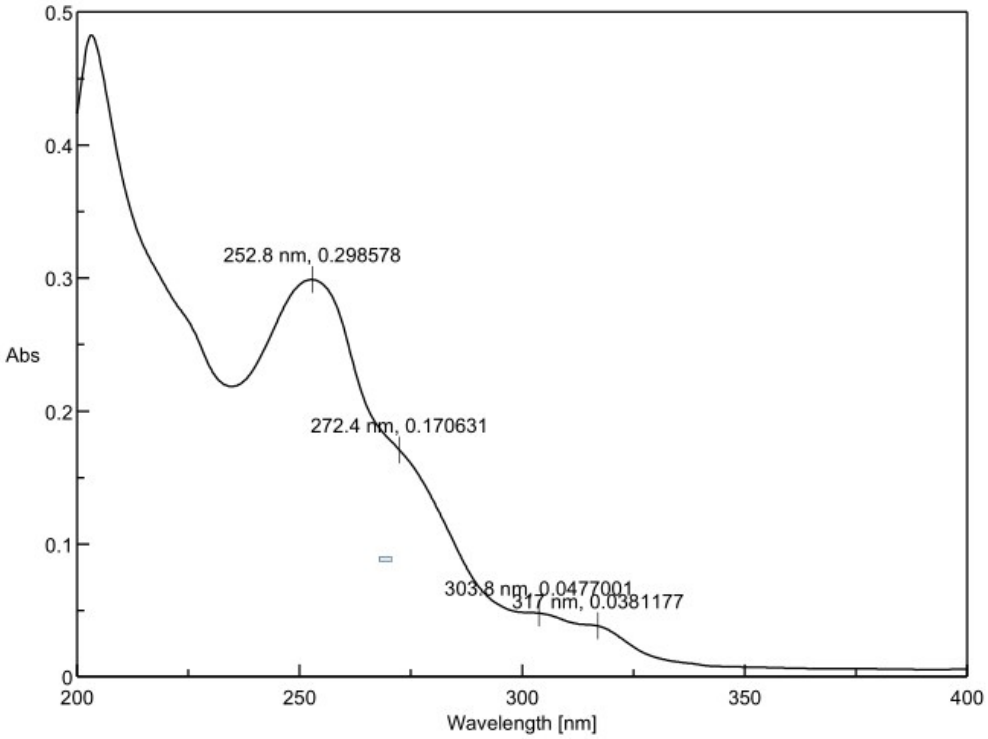


Figure S62. The UV spectrum of compound **7** in MeOH

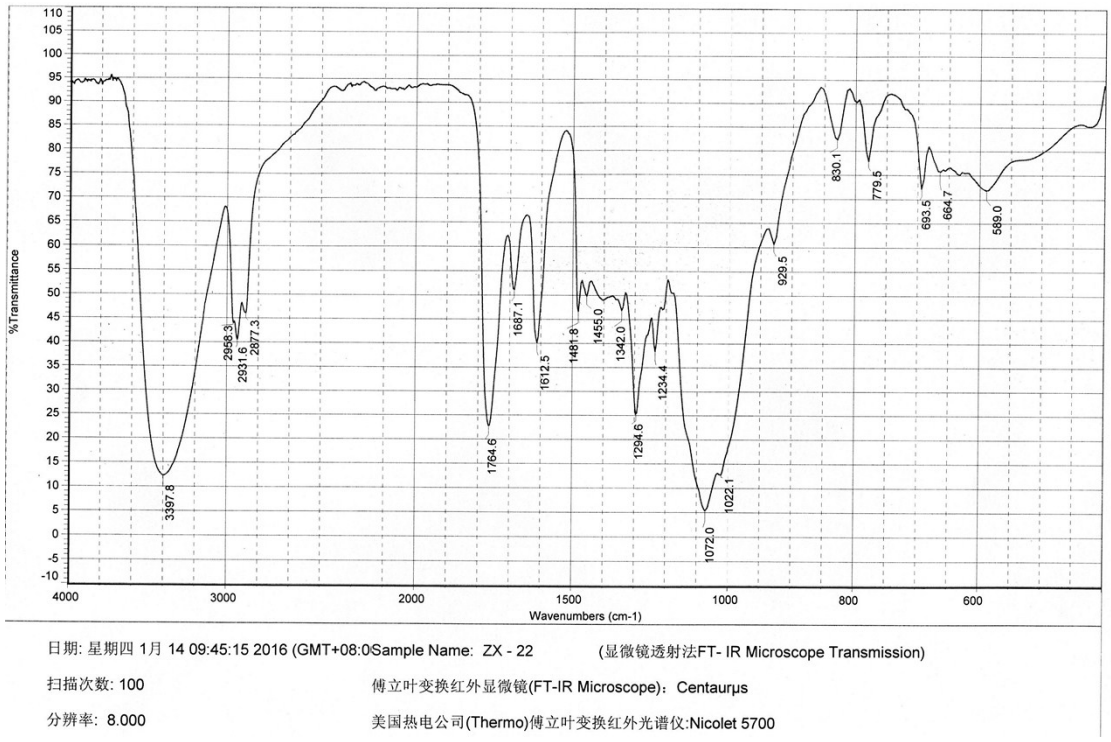


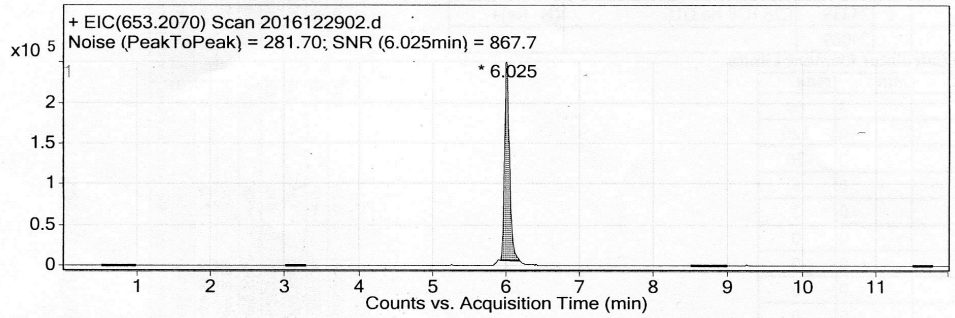
Figure S63. The IR spectrum (KBr) of compound **7**

Qualitative Analysis Report

Data Filename	2016122902.d	**Sample Name**	ZX-22
Sample Type	Sample	**Position**	P1-C2
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	Some Ions Missed
DA Method	TEST LCMS.m	**Comment**	

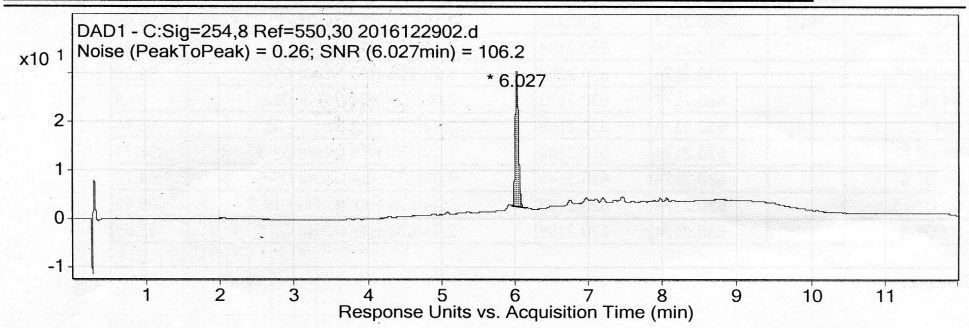
User Chromatograms

Fragmentor Voltage 150 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.928	6.025	6.186	244423	1274728	100	867.7



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.961	6.027	6.148	27.94	89.19	100	106.2

User Spectra

Fragmentor Voltage 150 **Collision Energy** 0 **Ionization Mode** Esi

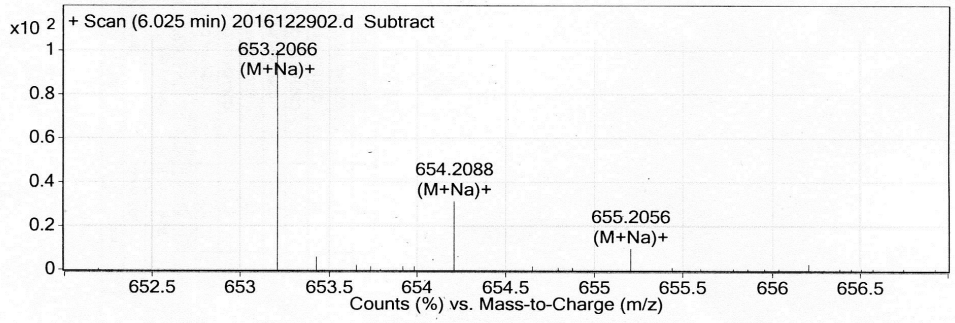


Figure S64. The HR-ESI-MS data of compound **7**

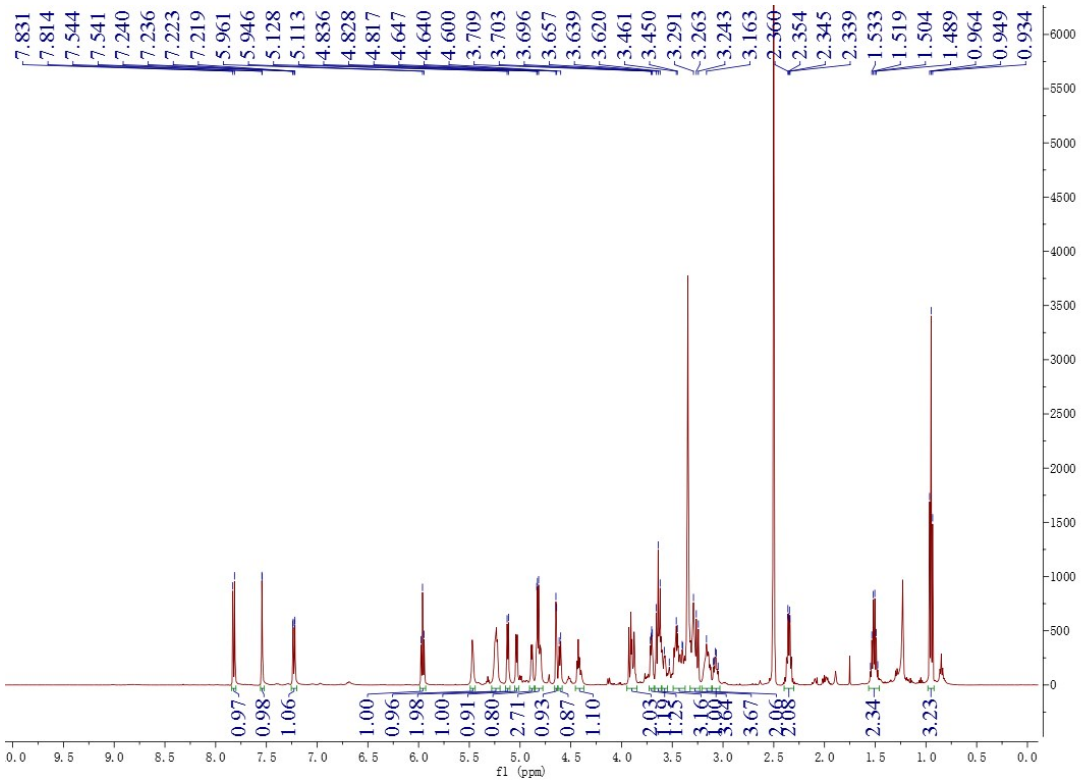


Figure S65. The ^{1}H NMR spectrum of compound **8** in DMSO-d_6

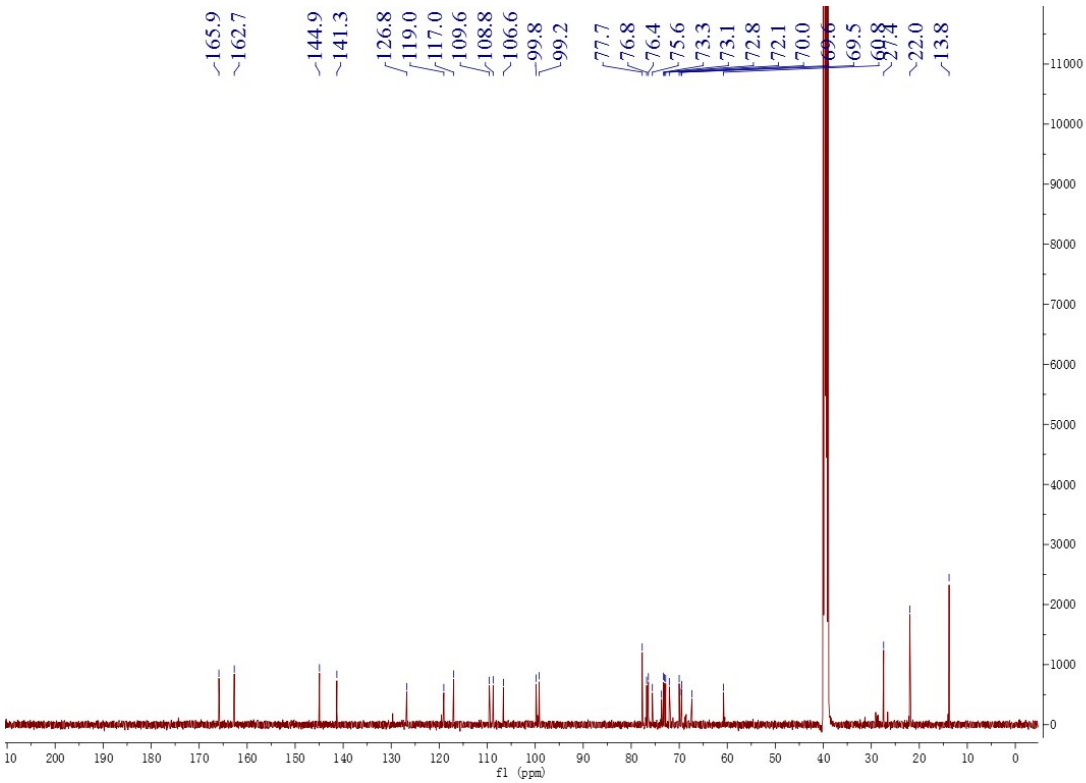


Figure S66. The ^{13}C NMR spectrum of compound **8** in DMSO-d_6

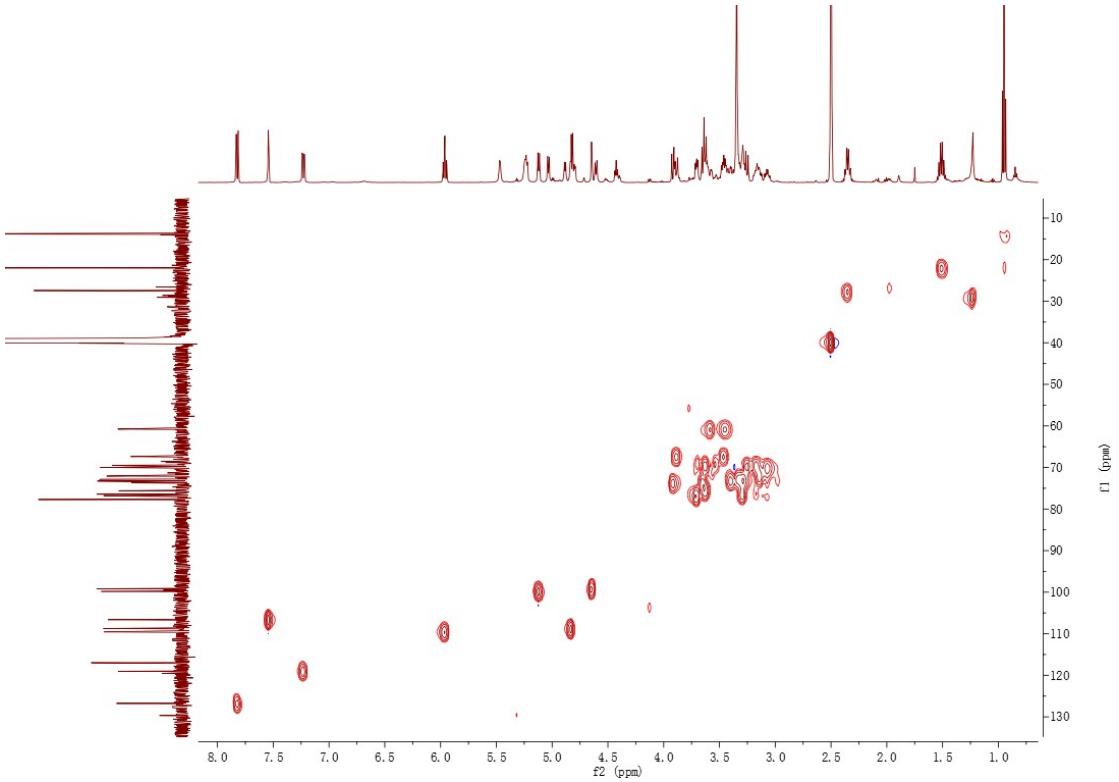


Figure S67. The HSQC spectrum of compound **8** in DMSO-d_6

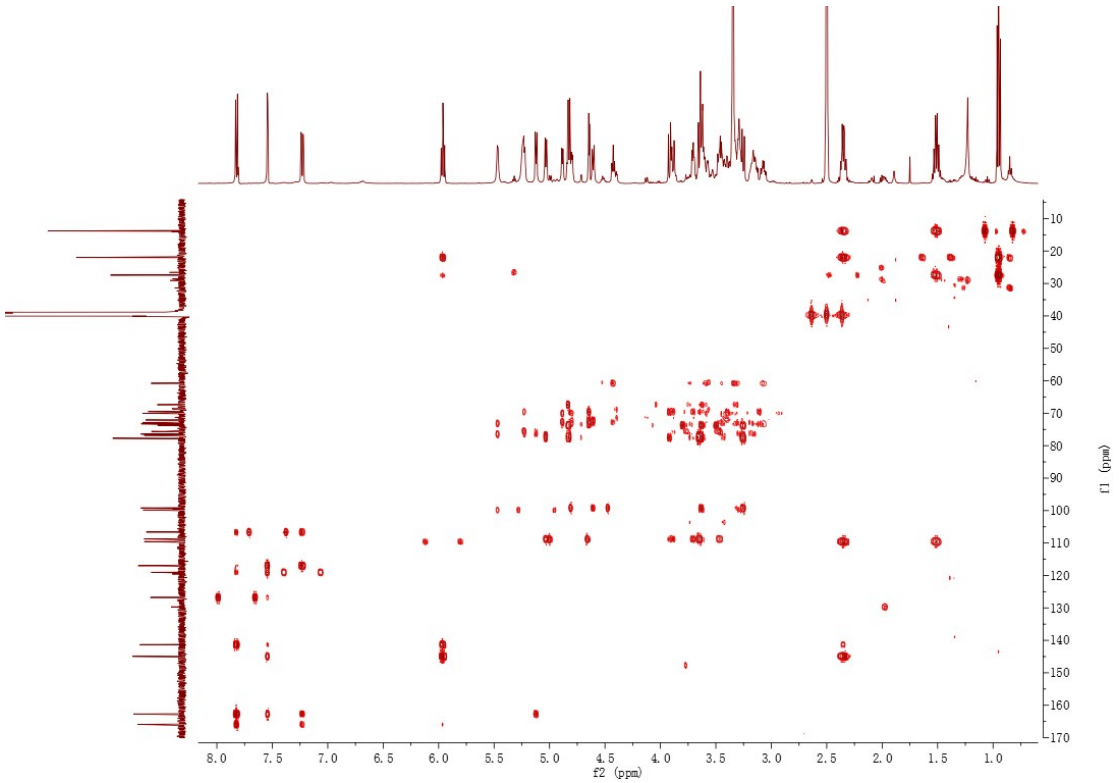


Figure S68. The HMBC spectrum of compound **8** in DMSO-d_6

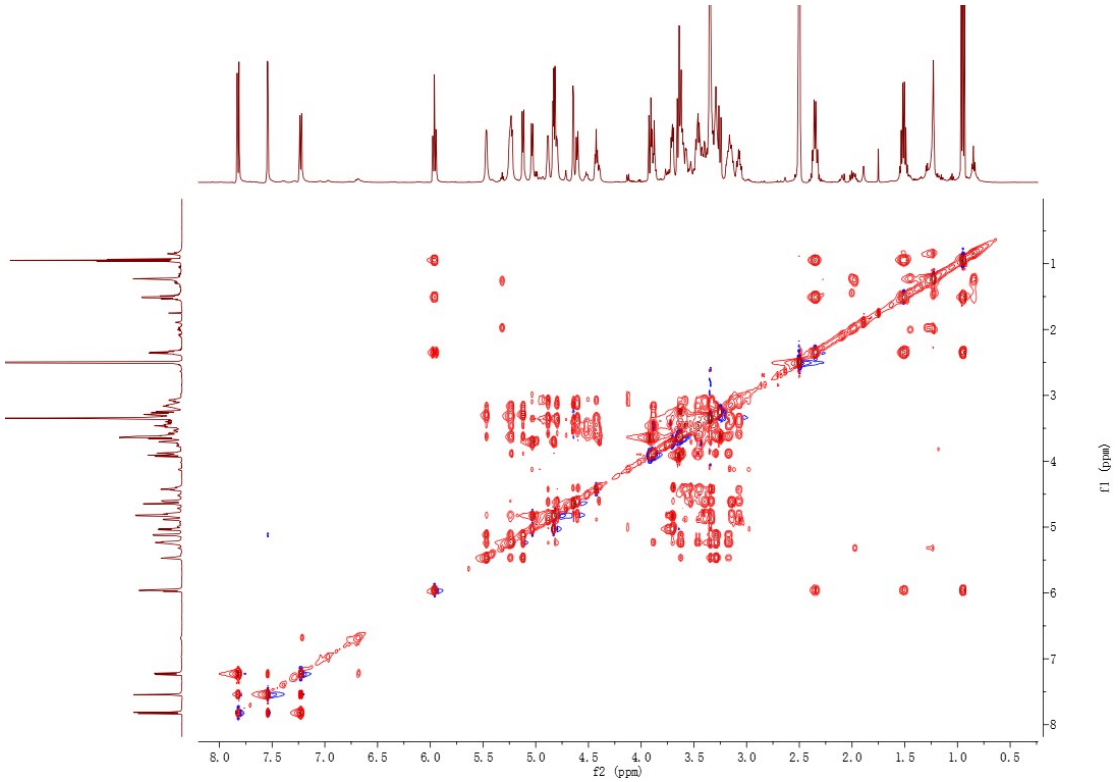


Figure S69. The TOCSY spectrum of compound **8** in DMSO-d_6

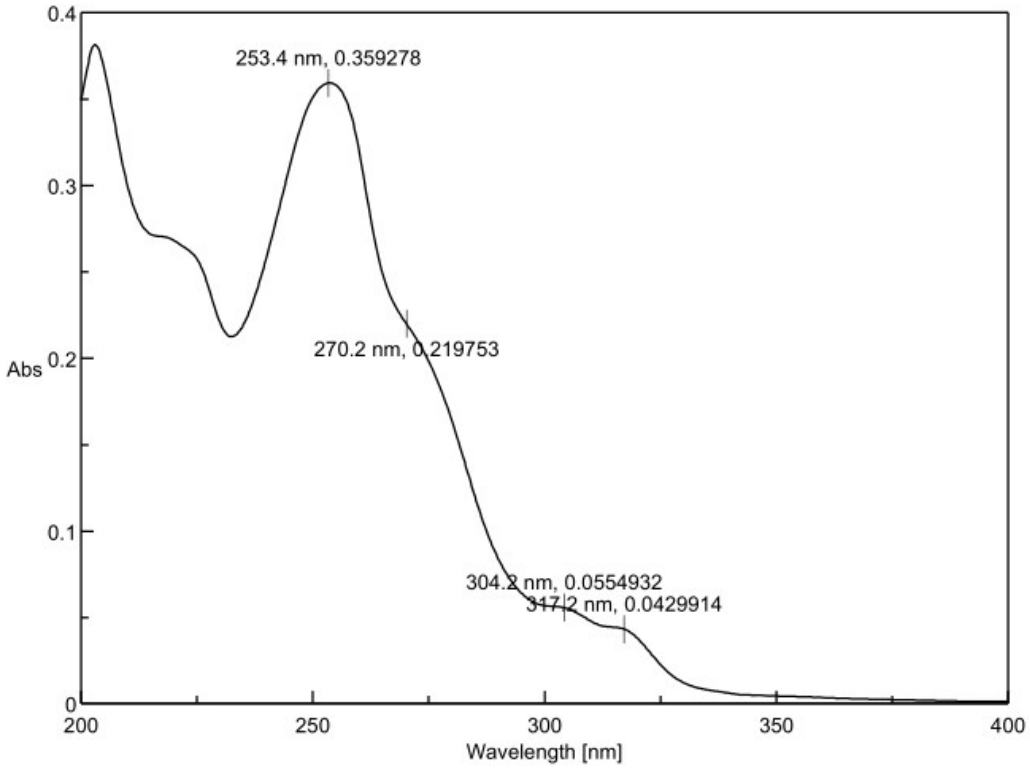


Figure S70. The UV spectrum of compound **8** in MeOH

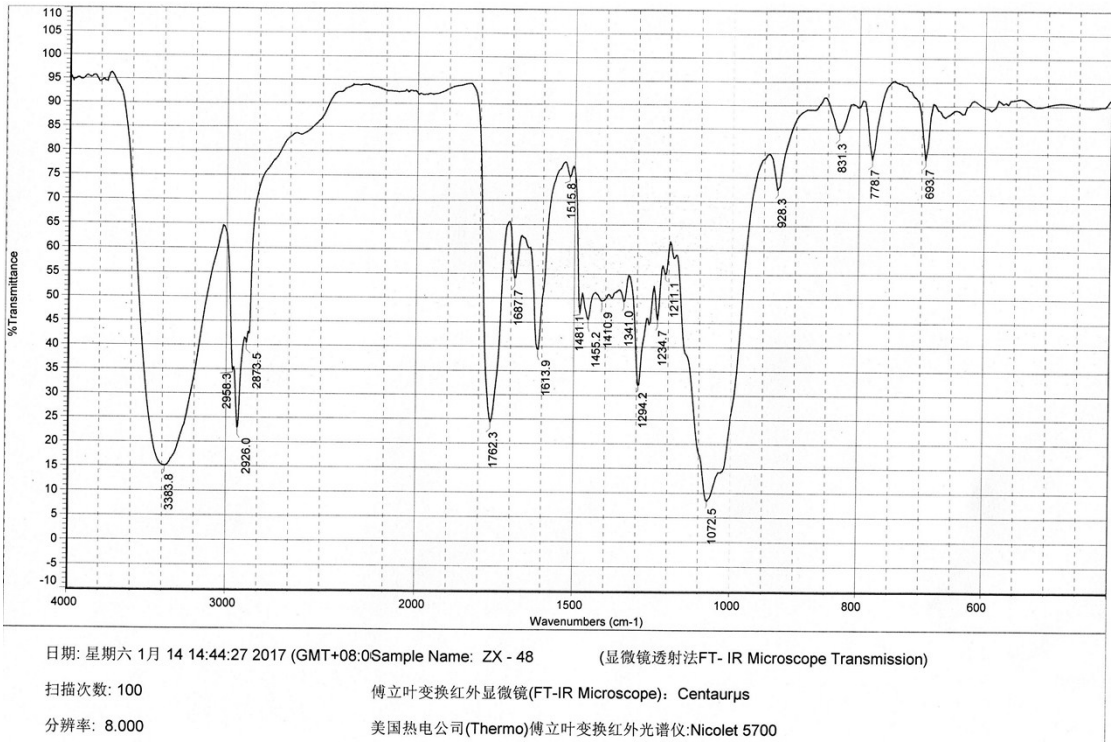


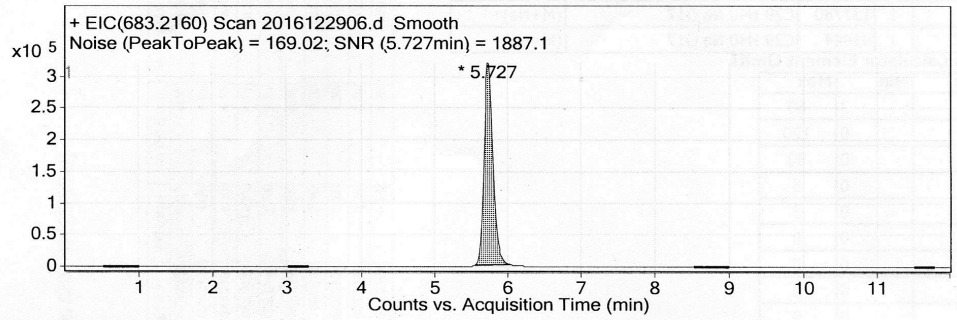
Figure S71. The IR spectrum (KBr) of compound **8**

Qualitative Analysis Report

Data Filename	2016122906.d	**Sample Name**	ZX-48
Sample Type	Sample	**Position**	P1-C6
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	Success
DA Method	TEST LCMS.m	**Comment**	

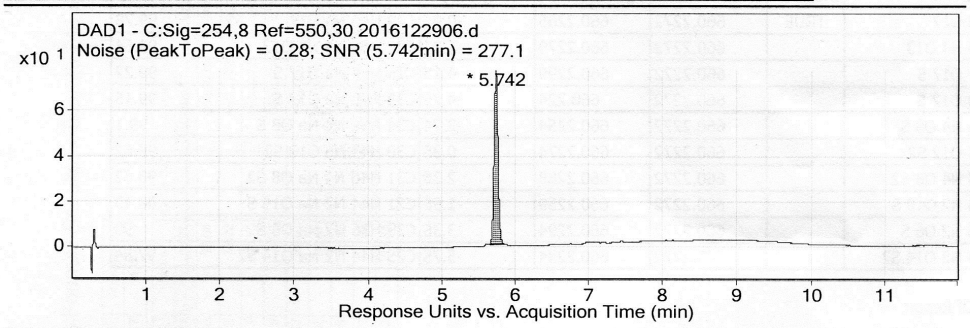
User Chromatograms

Fragmentor Voltage 150 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.55	5.727	6.033	318944	2749856	100	1887.1



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.653	5.742	5.851	76.51	277.61	100	277.1

User Spectra

Fragmentor Voltage 150 **Collision Energy** 0 **Ionization Mode** Esi

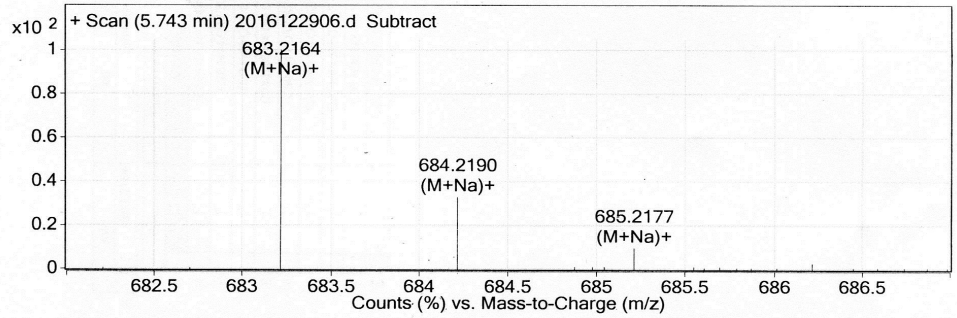


Figure S72. The HR-ESI-MS data of compound **8**

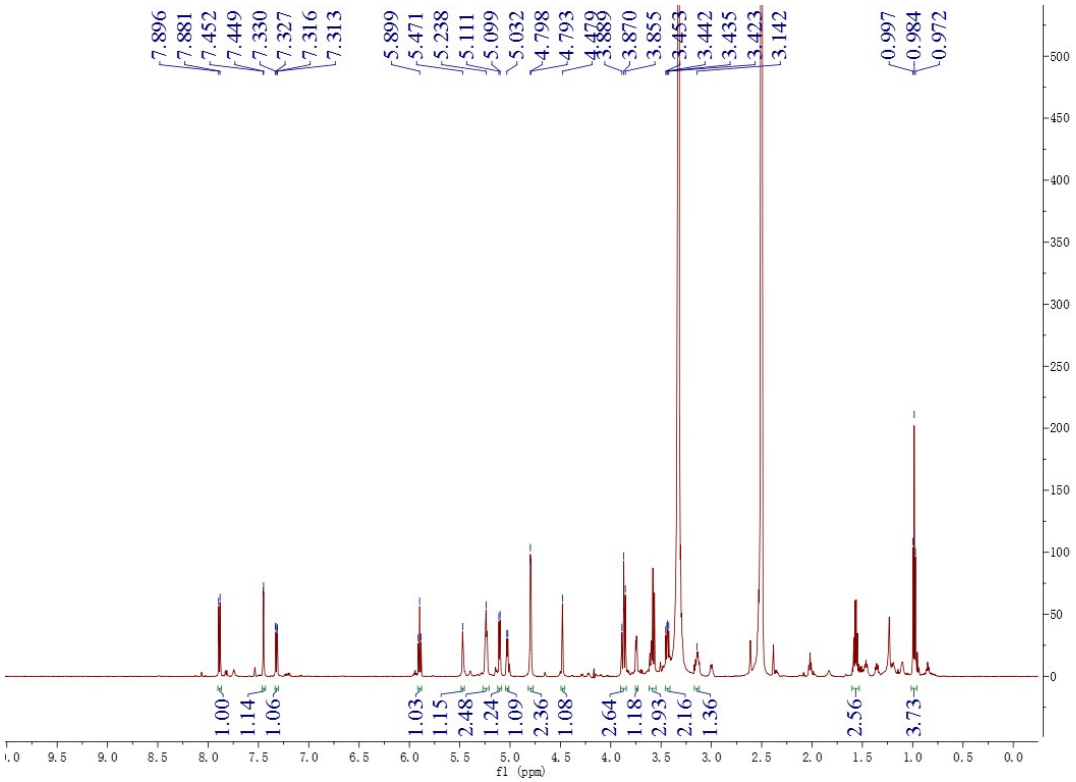


Figure S73. The ^{1}H NMR spectrum of compound **9** in DMSO-d_6

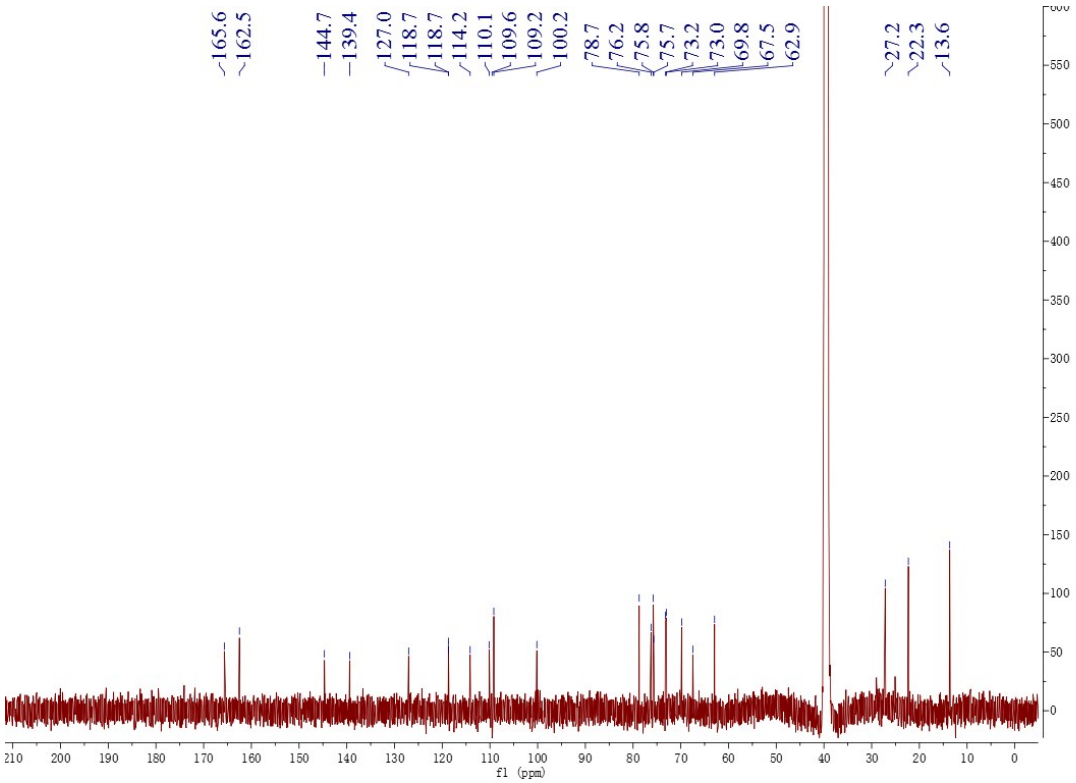


Figure S74. The ^{13}C NMR spectrum of compound **9** in DMSO-d_6

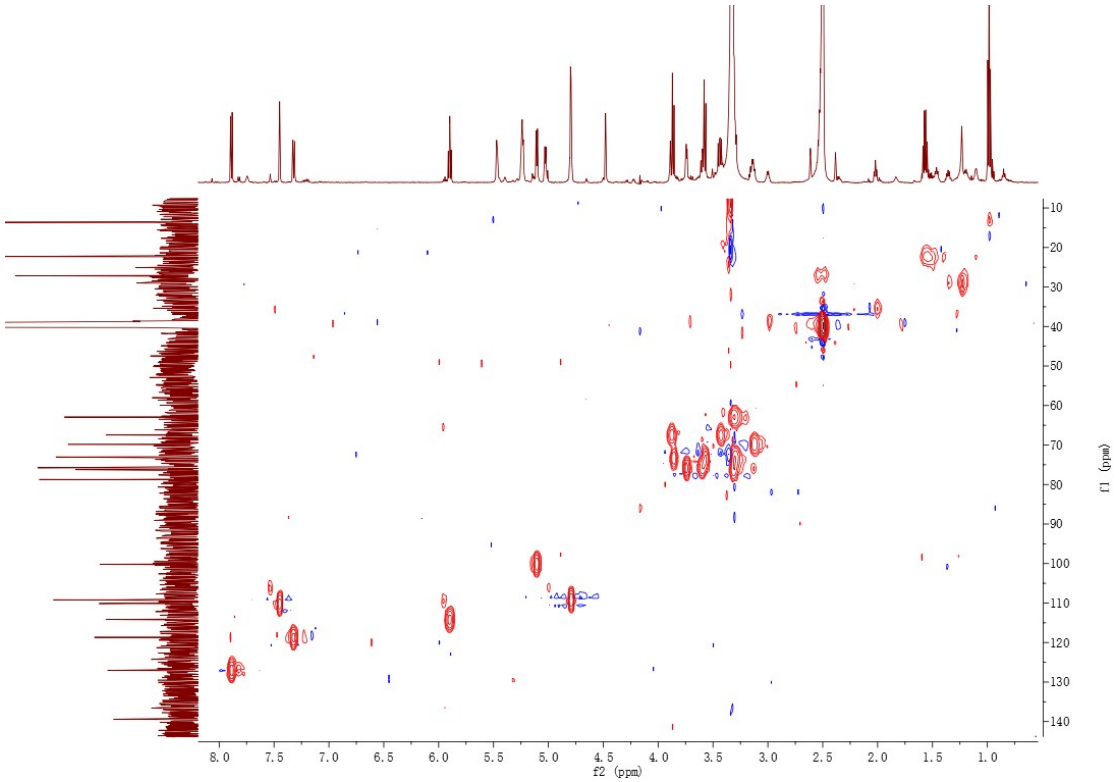


Figure S75. The HSQC spectrum of compound **9** in DMSO-d_6

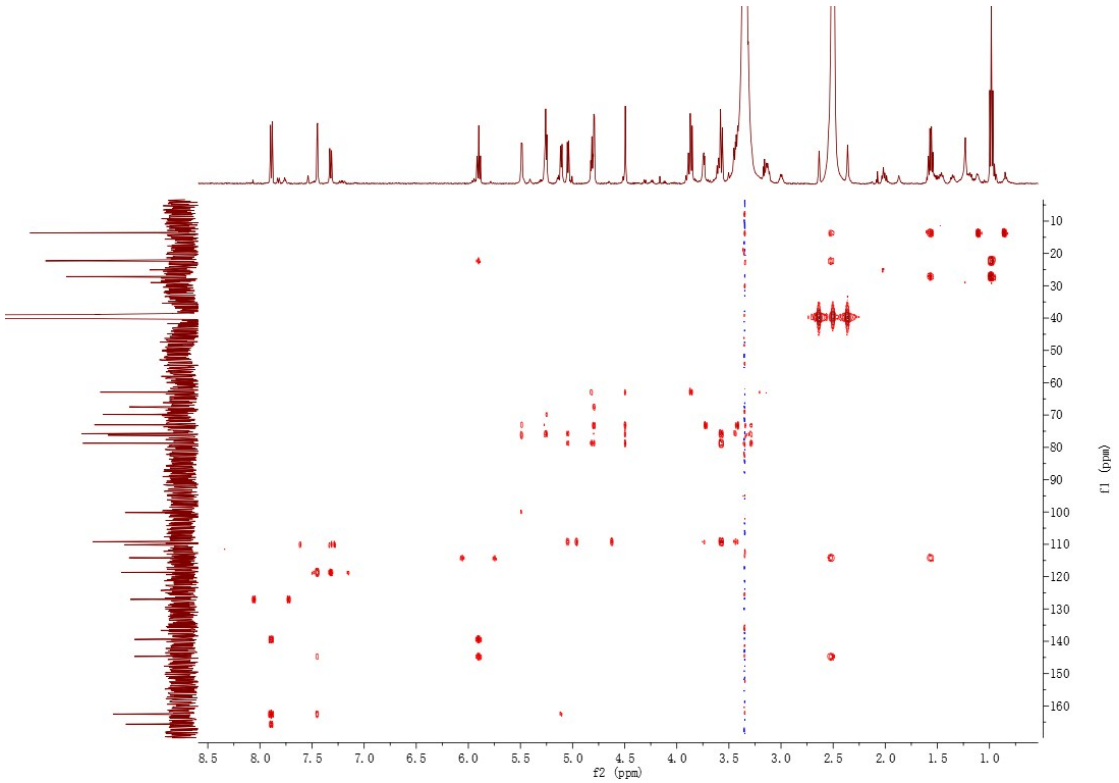


Figure S76. The HMBC spectrum of compound **9** in DMSO-d_6

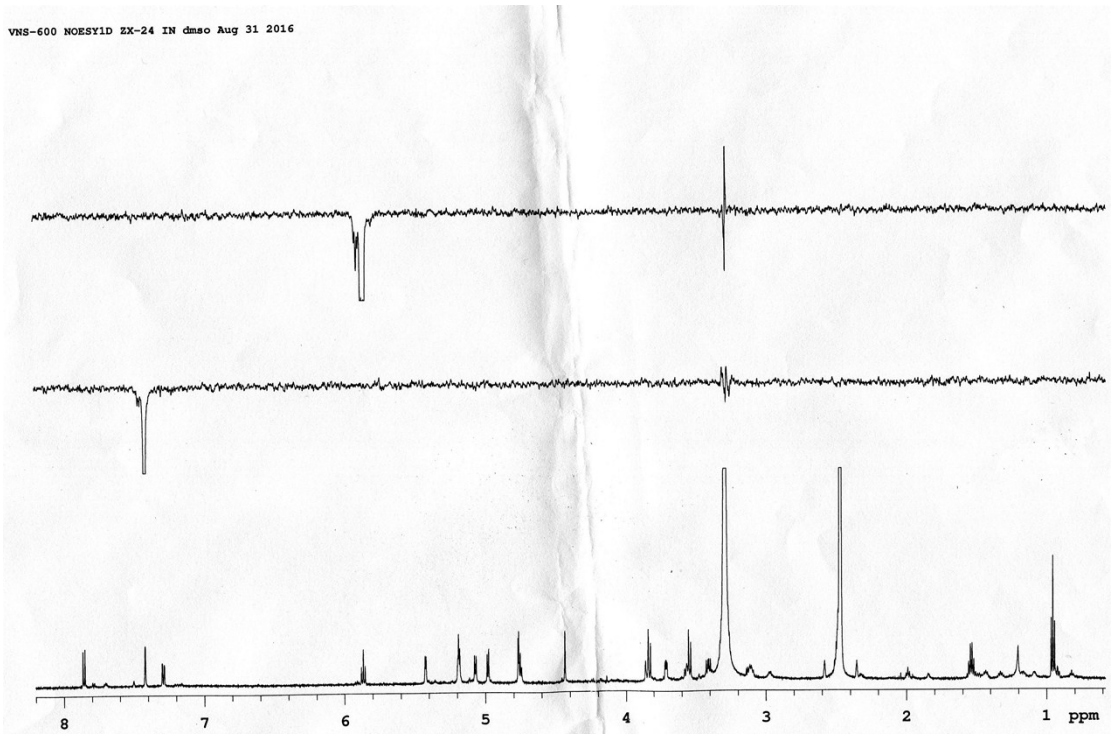


Figure S77. The NOE spectrum of compound **9** in DMSO-d_6

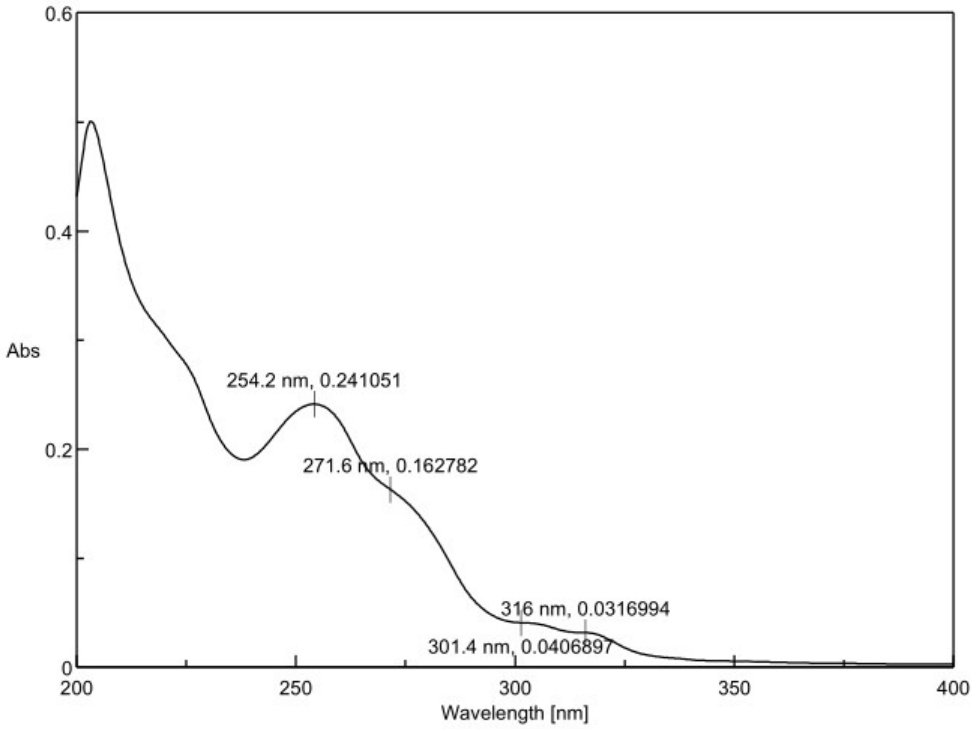


Figure S78. The UV spectrum of compound **9** in MeOH

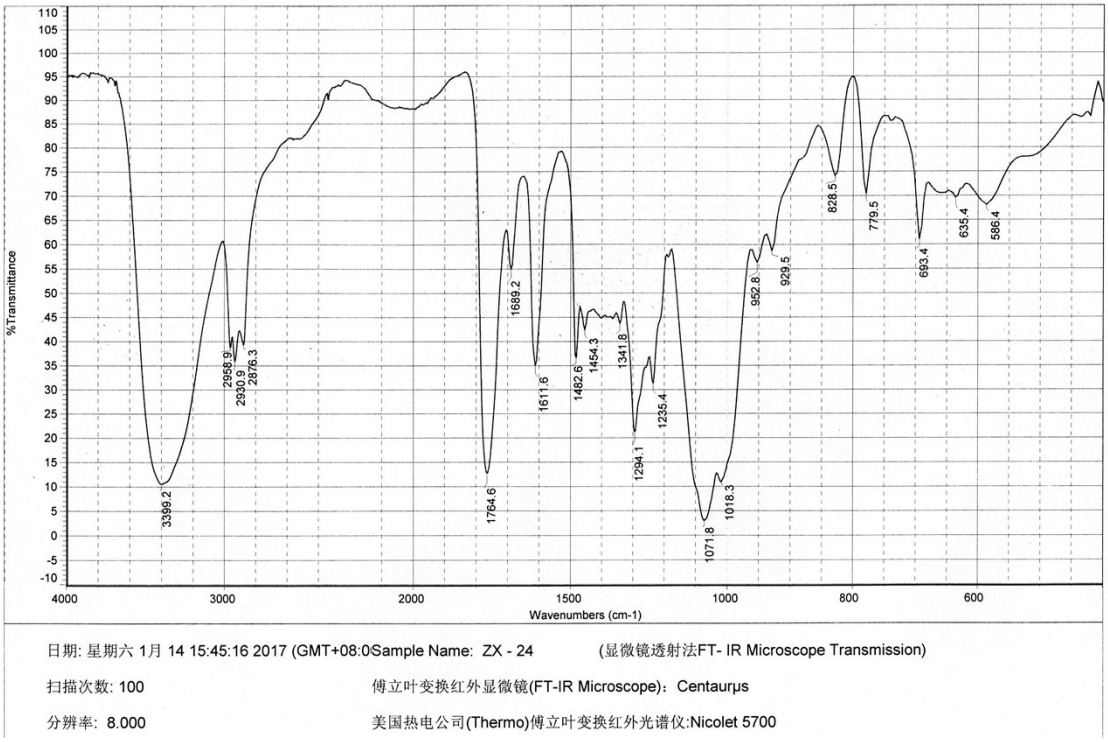
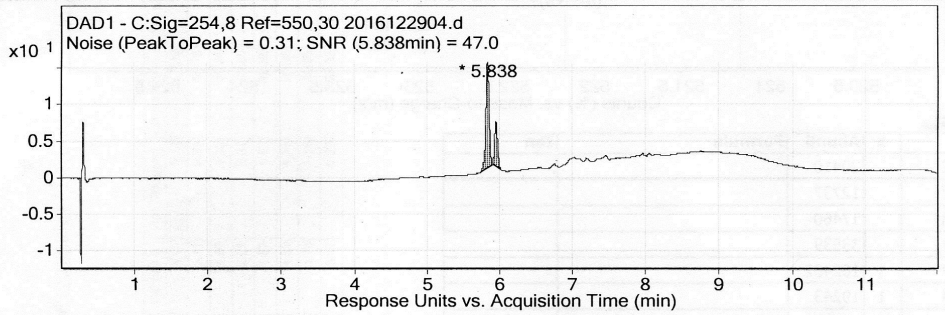


Figure S79. The IR spectrum (KBr) of compound **9**

Qualitative Analysis Report

Data Filename	2016122904.d	**Sample Name**	ZX-24
Sample Type	Sample	**Position**	P1-C4
Instrument Name	Instrument 1	**User Name**	
Acq Method		**IRM Calibration Status**	Success
DA Method	TEST LCMS.m	**Comment**	

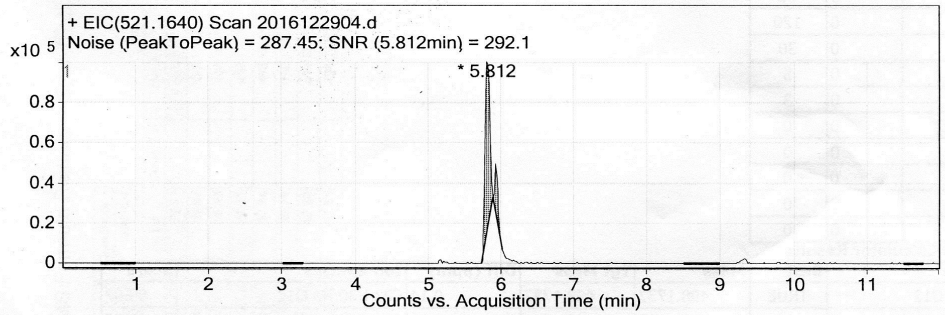
User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.748	5.838	5.901	14.43	46.33	100	47
2	5.913	5.955	6.018	6.06	17.44	37.65	19.7

Fragmentor Voltage 150 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.732	5.812	5.893	83969	373682	100	292.1
2	5.893	5.925	6.022	22748	67003	17.93	79.1

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
150	0	Esi

Figure S80. The HR-ESI-MS data of compound **9**

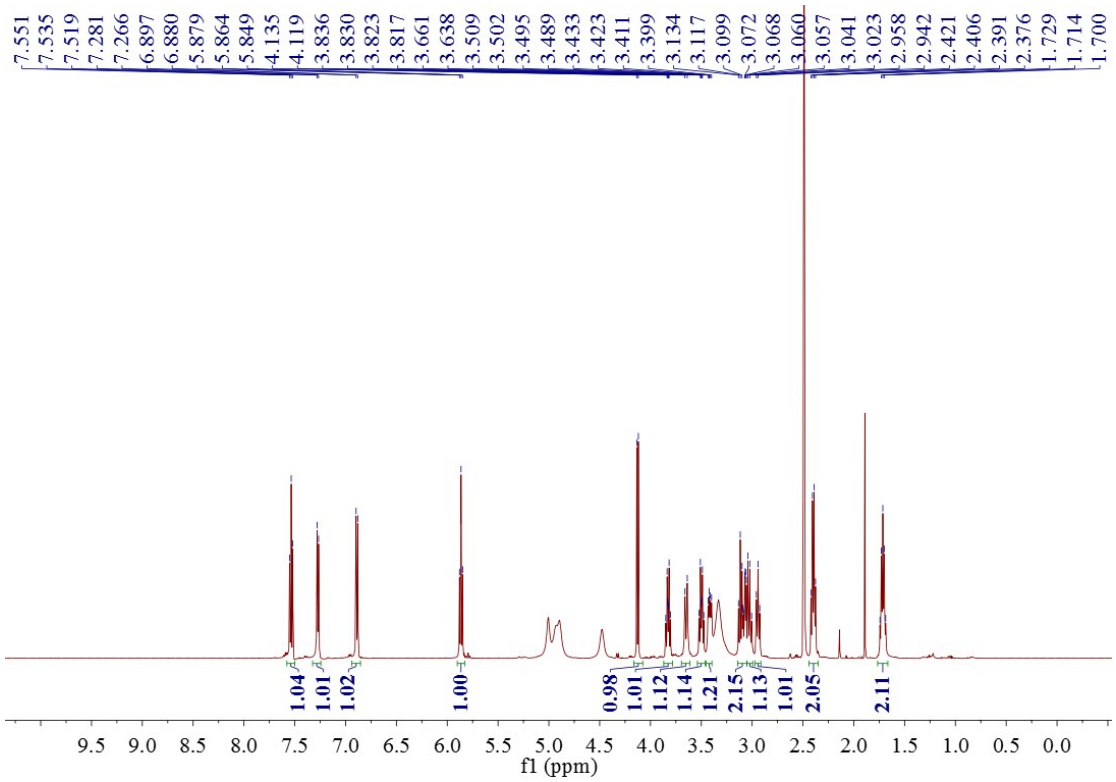


Figure S81. The ^{1}H NMR spectrum of compound **10** in DMSO-d_6

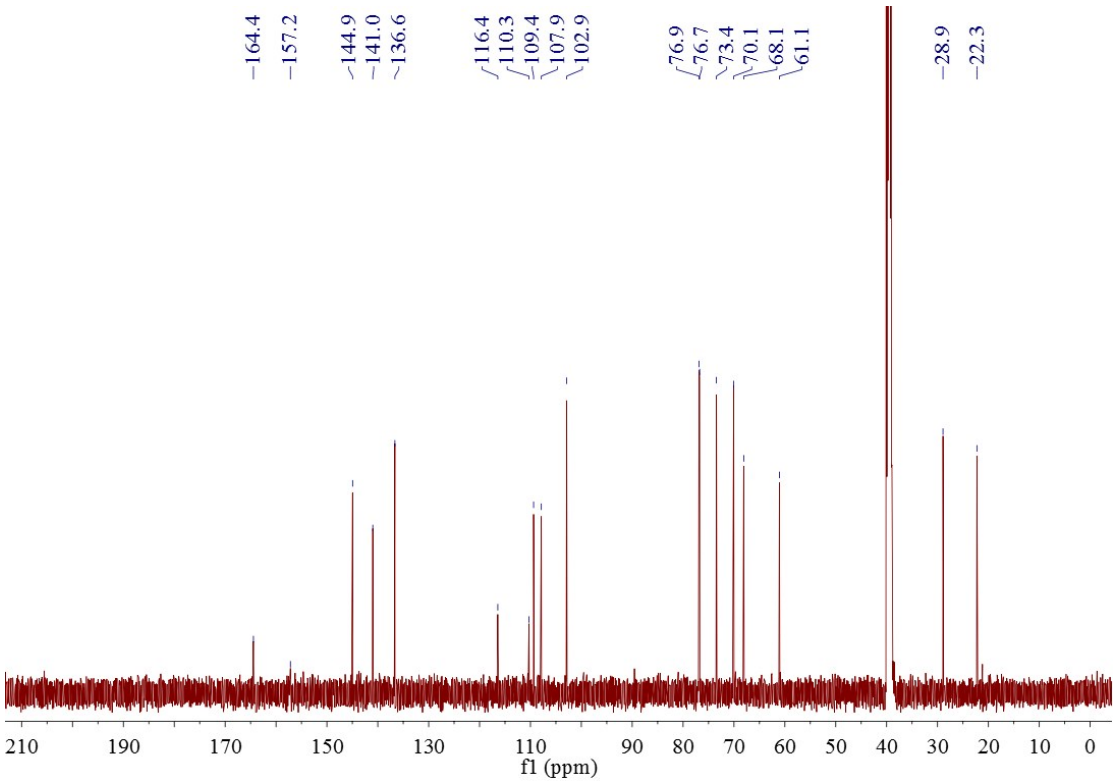


Figure S82. The ^{13}C NMR spectrum of compound **10** in DMSO-d_6

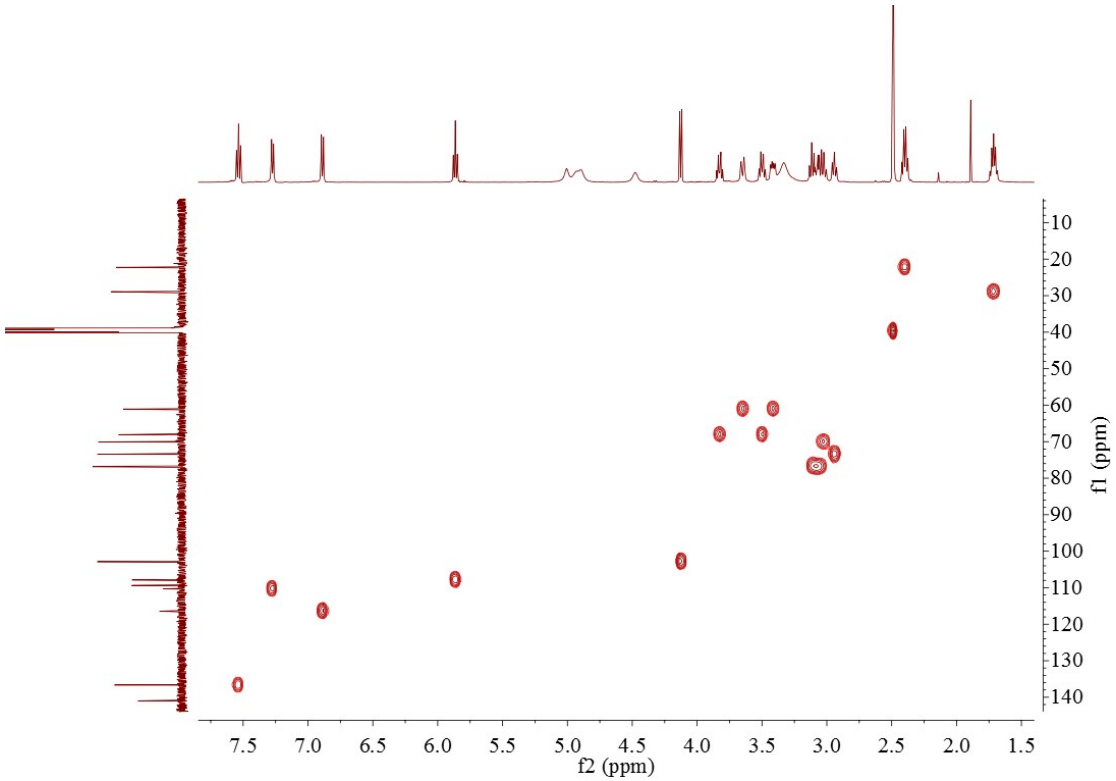


Figure S83. The HSQC spectrum of compound **10** in DMSO-d_6

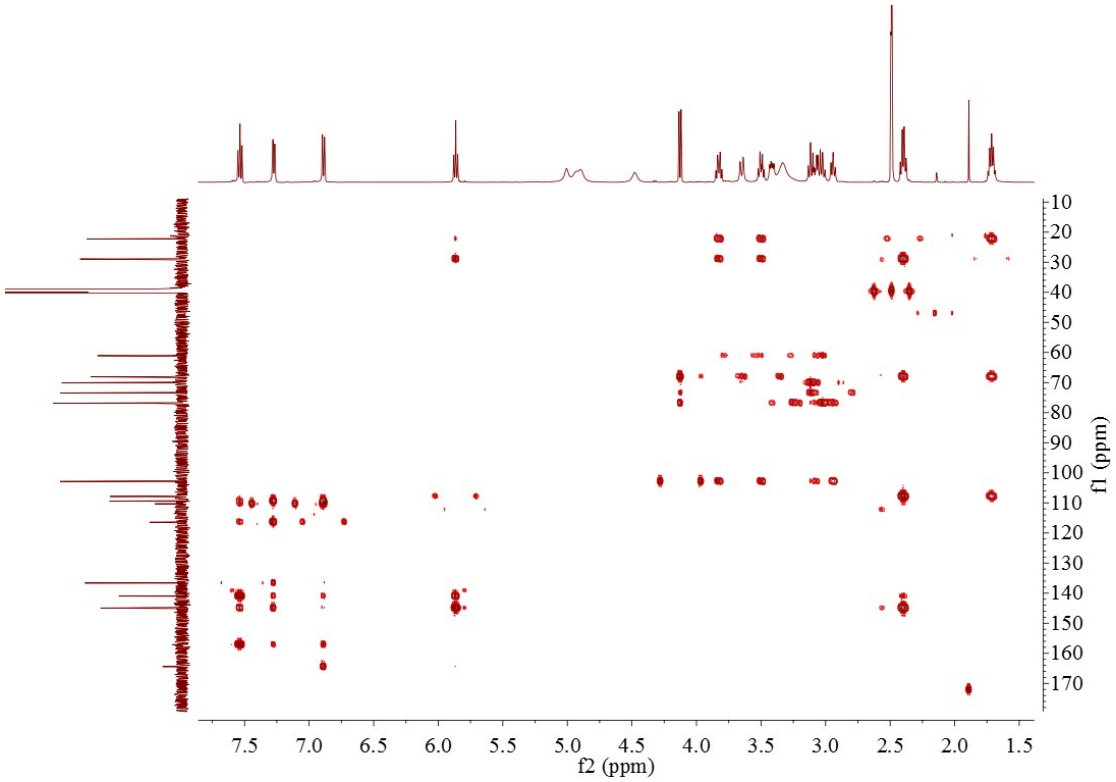


Figure S84. The HMBC spectrum of compound **10** in DMSO-d_6

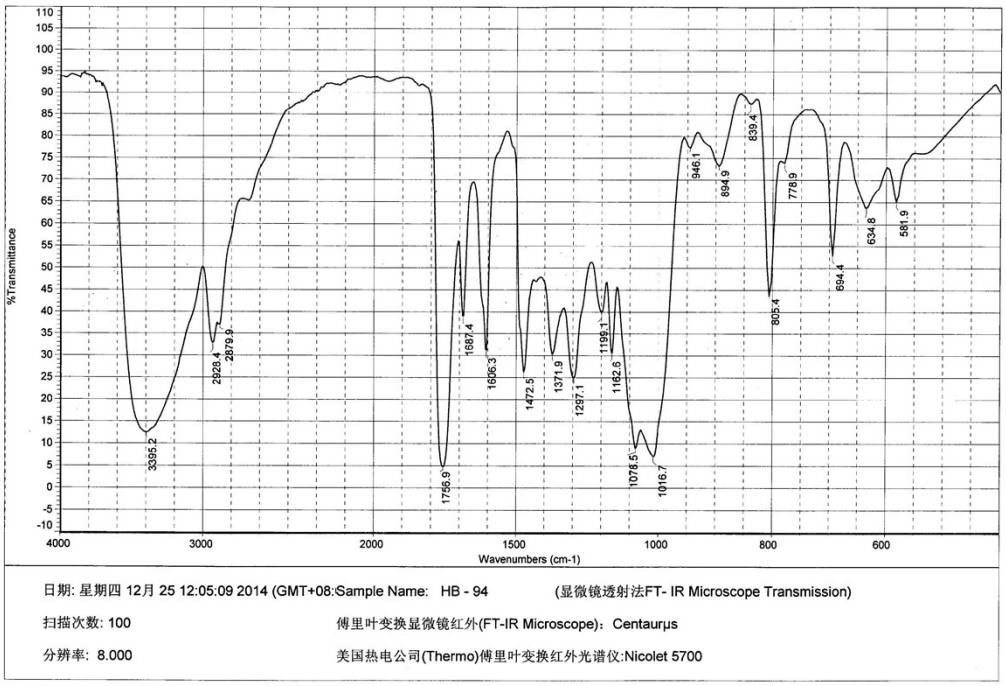


Figure S85. The IR spectrum (KBr) of compound **10**

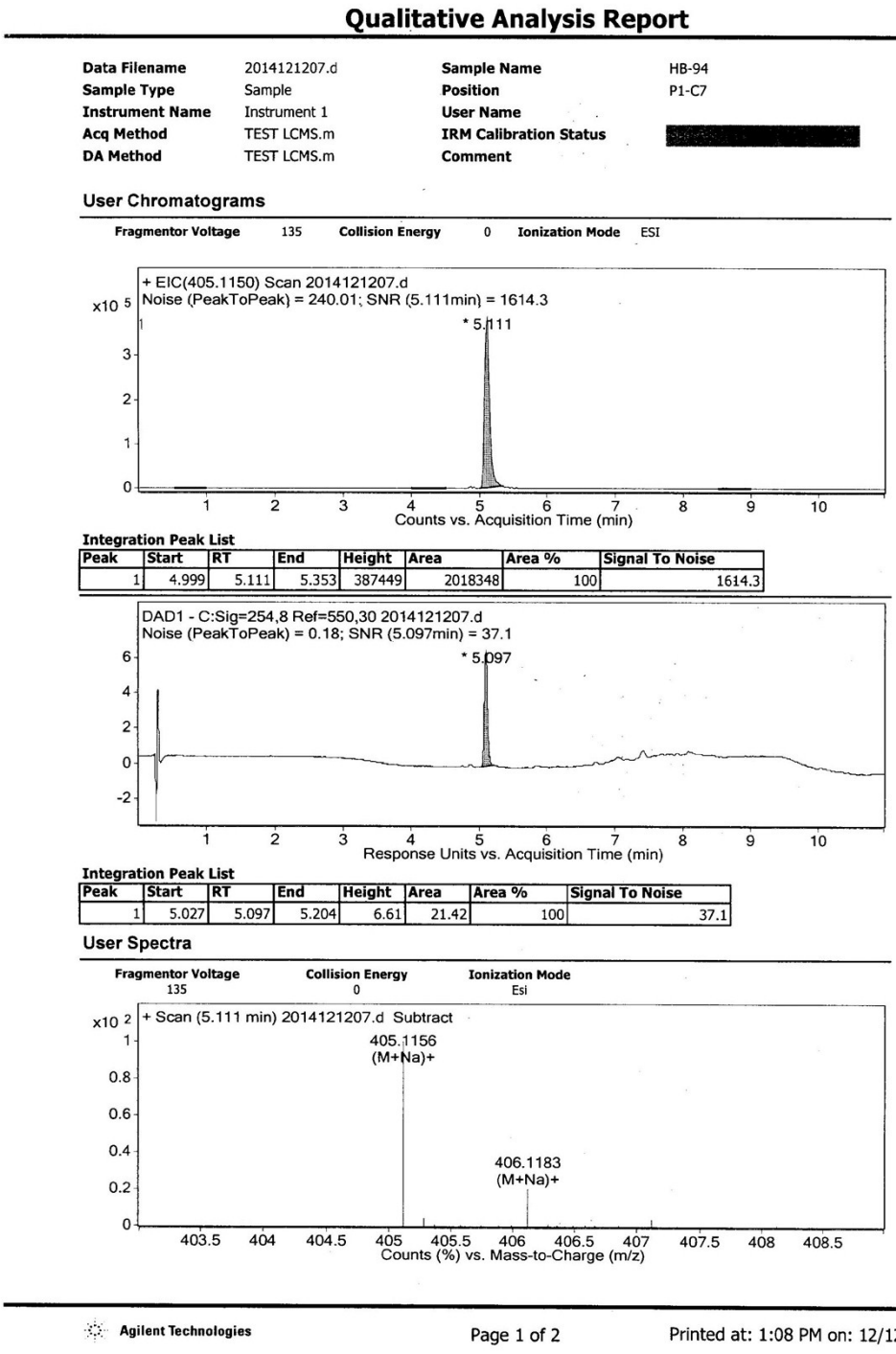


Figure S86. The HR-ESI-MS data of compound **10**

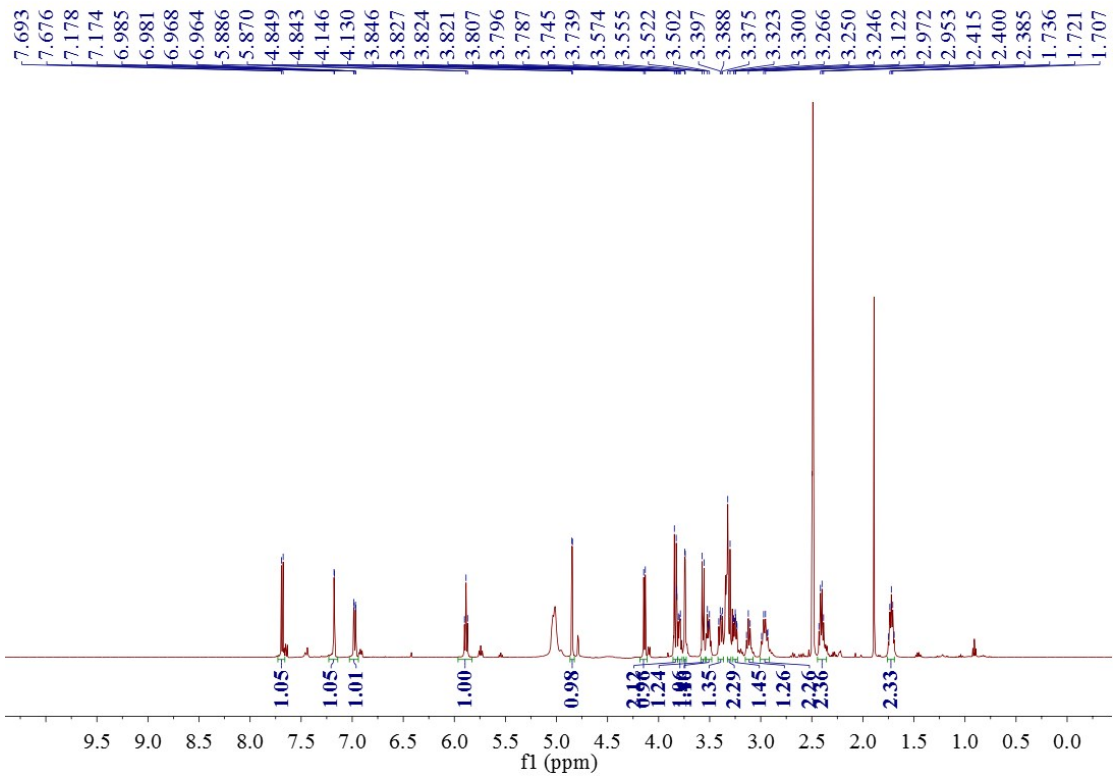


Figure S87. The ^{1}H NMR spectrum of compound **11** in DMSO-d_6

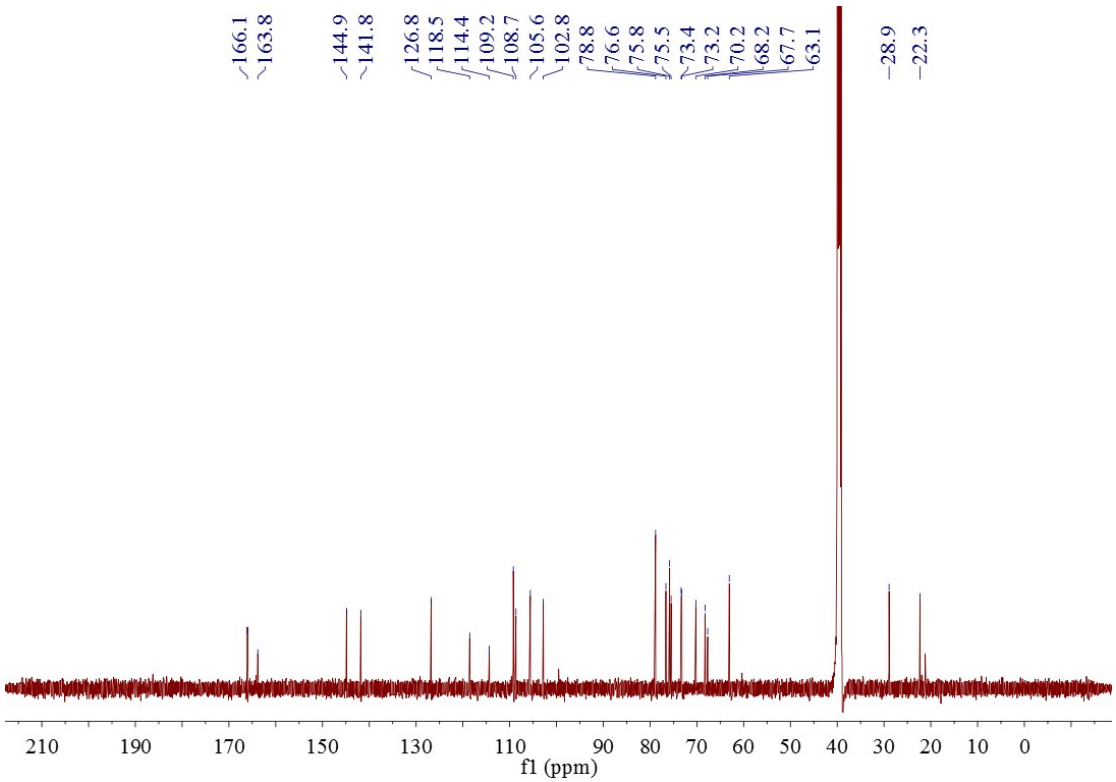


Figure S88. The ^{13}C NMR spectrum of compound **11** in DMSO-d_6

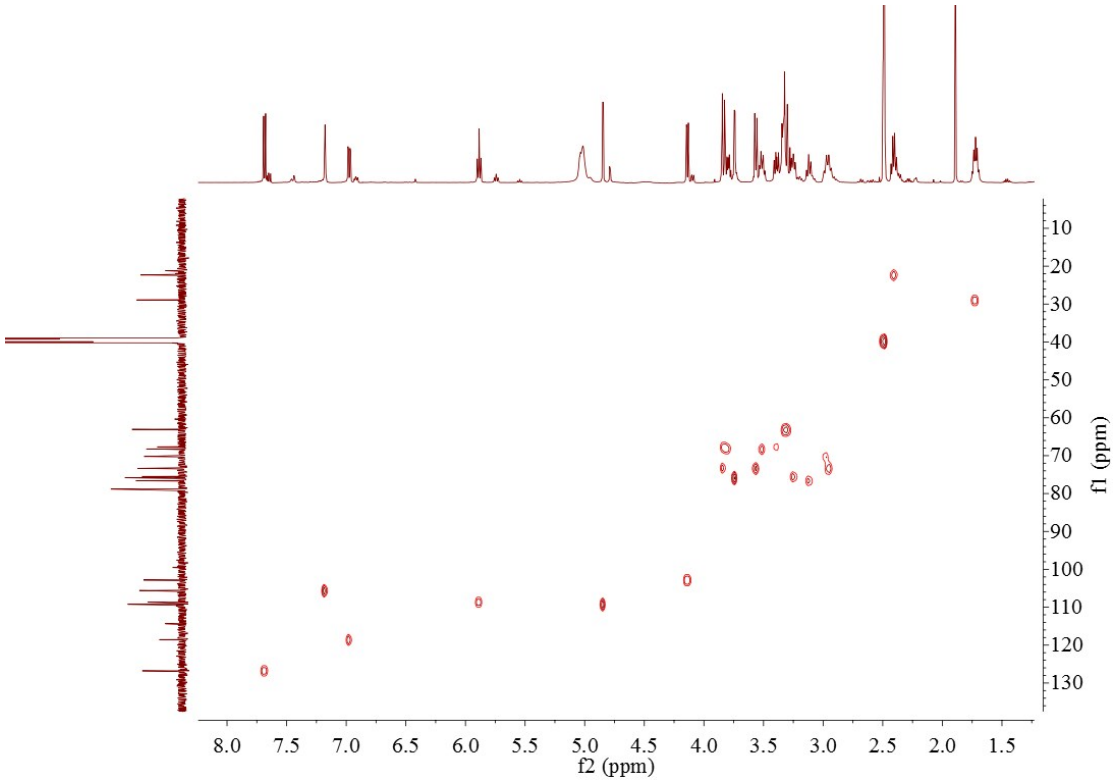


Figure S89. The HSQC spectrum of compound **11** in DMSO-d_6

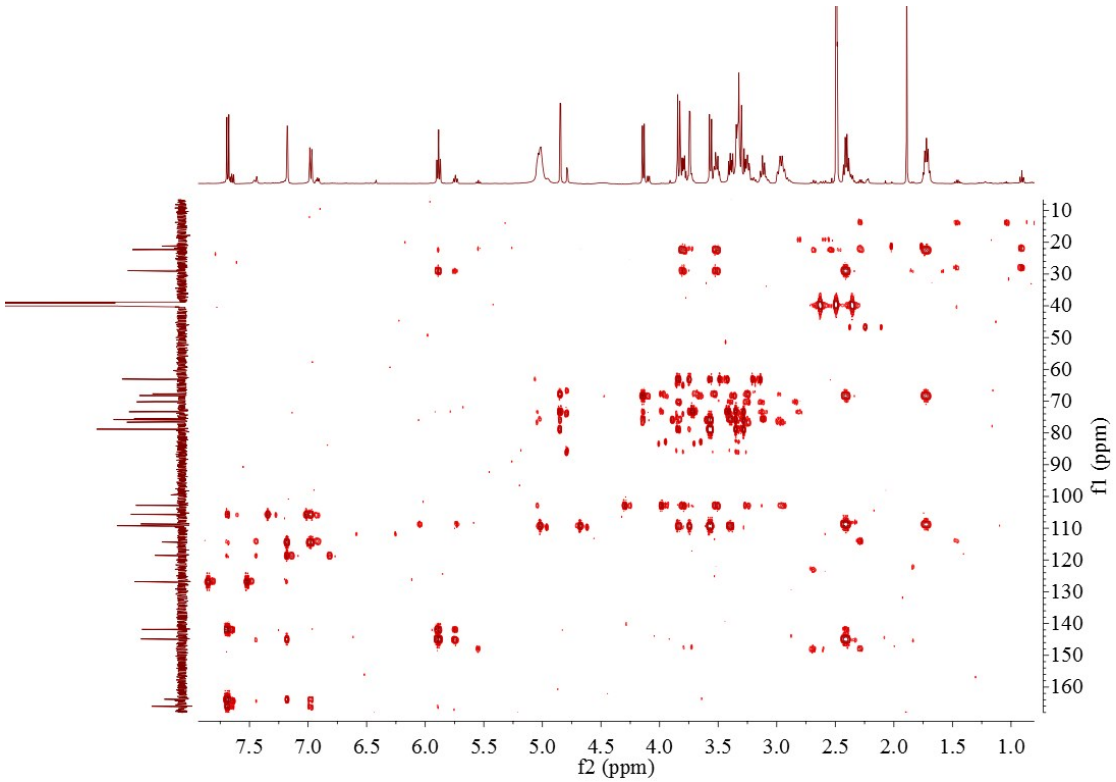


Figure S90. The HMBC spectrum of compound **11** in DMSO-d_6

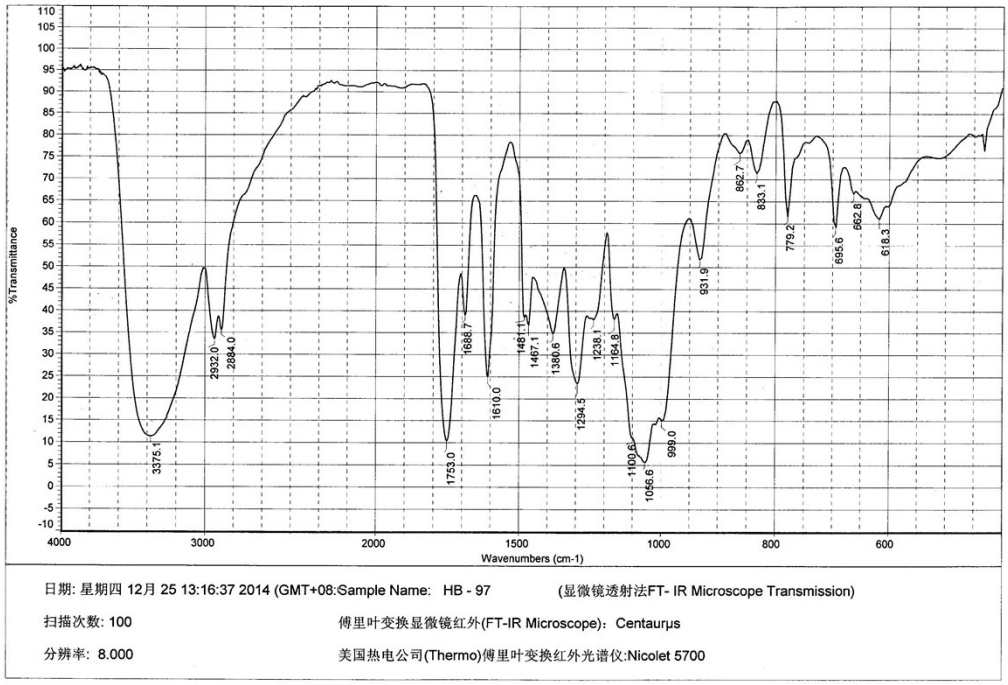
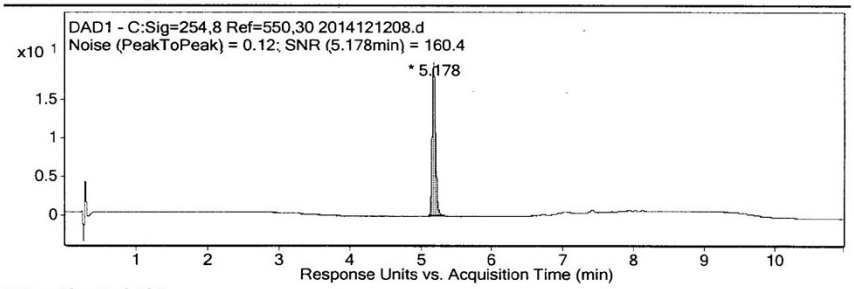


Figure S91. The IR spectrum (KBr) of compound **11**

Qualitative Analysis Report

Data Filename	2014121208.d	**Sample Name**	HB-97
Sample Type	Sample	**Position**	P1-C8
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST LCMS.m	**IRM Calibration Status**	[redacted]
DA Method	TEST LCMS.m	**Comment**	

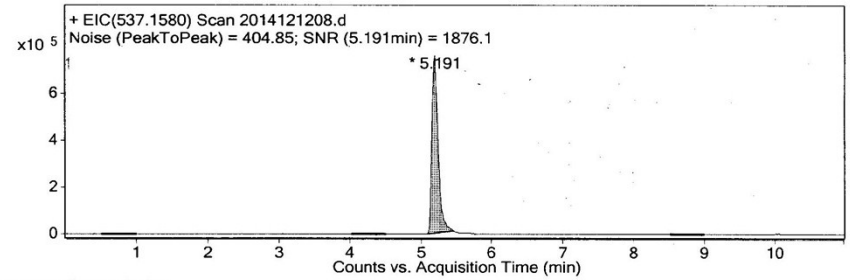
User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.098	5.178	5.334	19.97	66.73	100	160.4

Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.078	5.191	5.465	759520	4699563	100	1876.1

User Spectra

Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** Esi

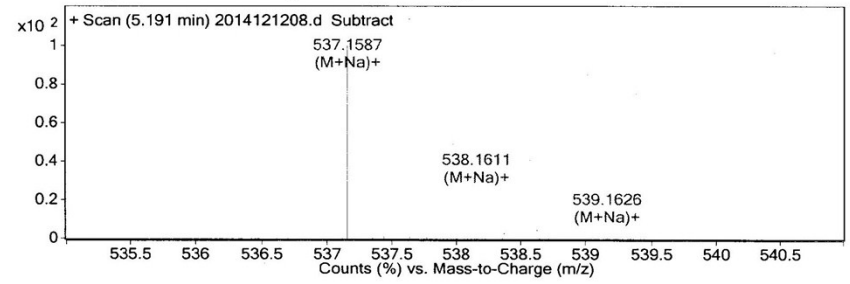


Figure S92. The HR-ESI-MS data of compound **11**

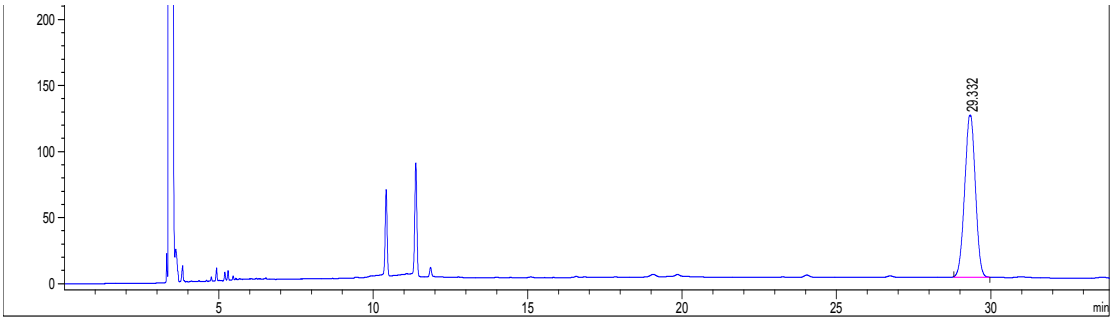


Figure S93. The Gas Chromatographic separation of D-Glc

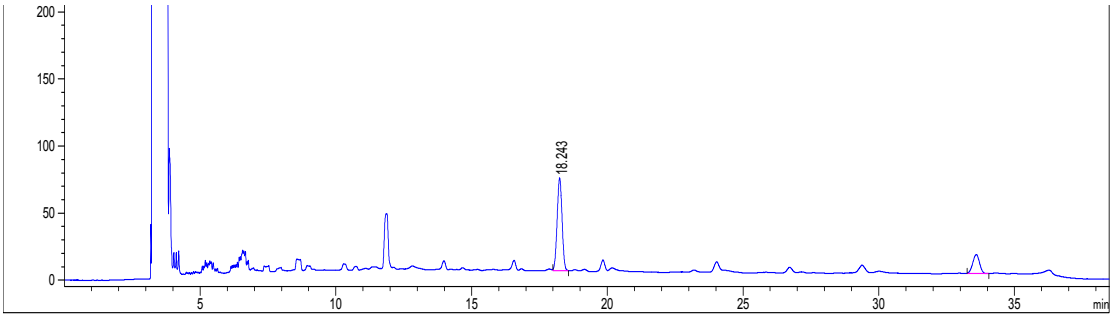


Figure S94. The Gas Chromatographic separation of D-Api

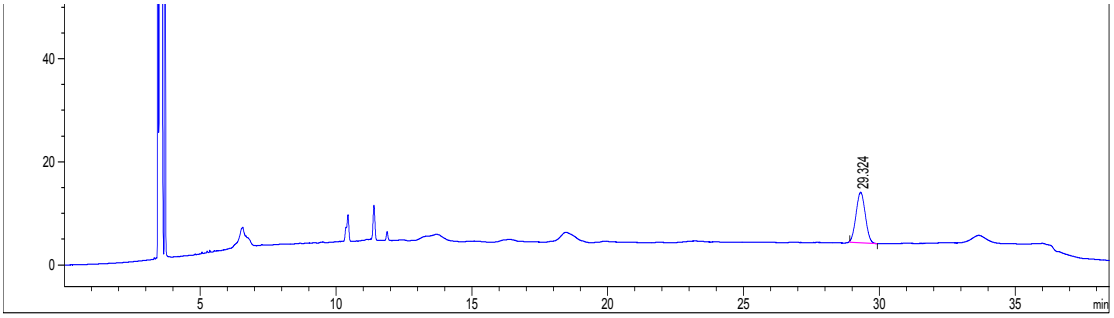


Figure S95. The Gas Chromatographic analyses of sugar moeities of compounds **4** and **10**

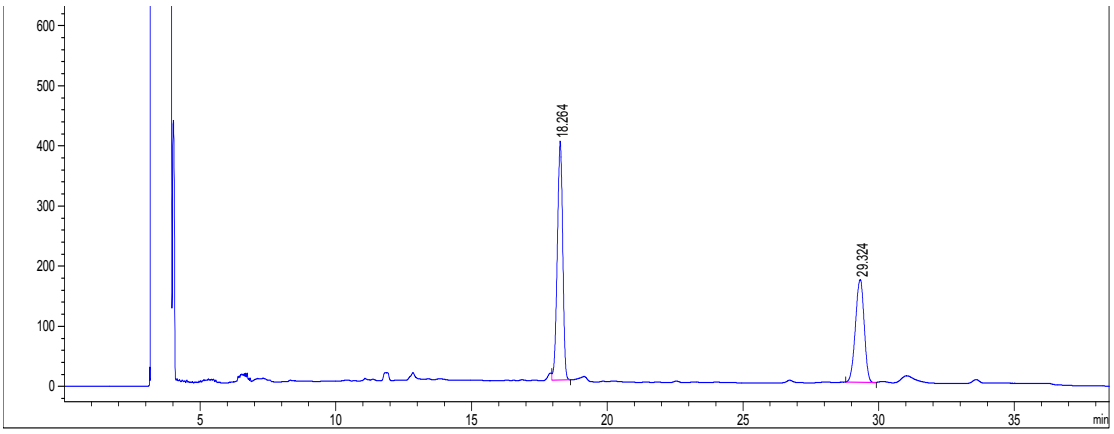


Figure S96. The Gas Chromatographic analyses of sugar moeities of compounds **3**, **5-9** and **11**

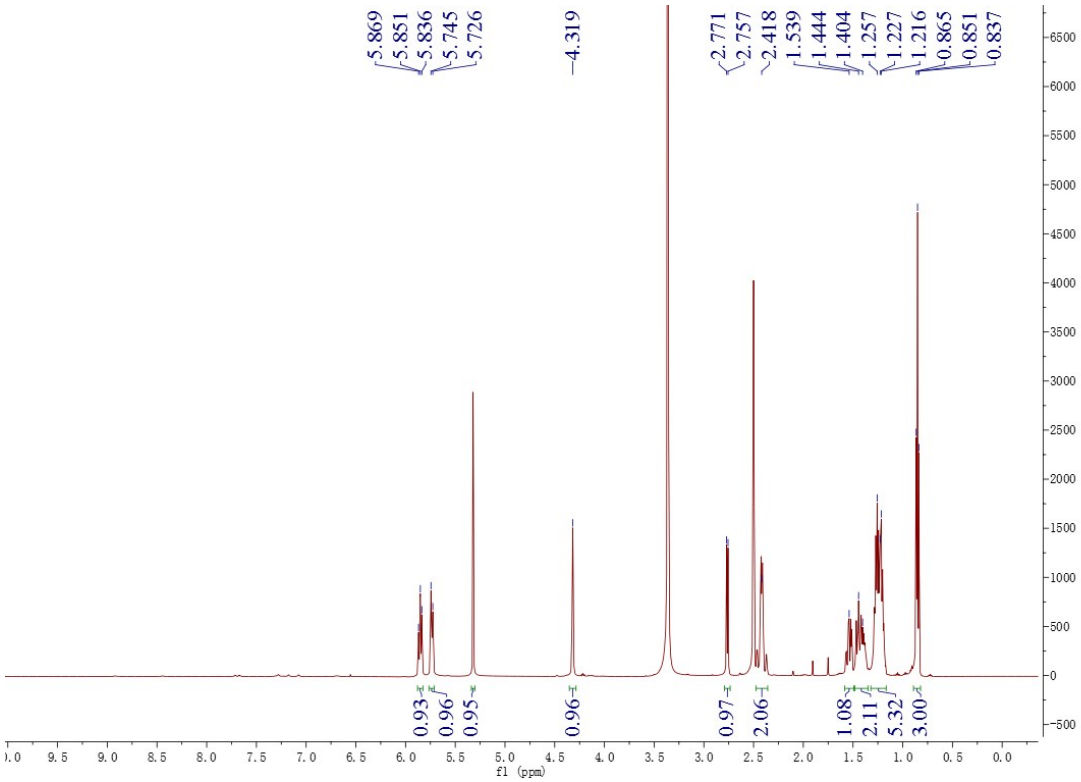


Figure S97. The ^{1}H NMR spectrum of compound **3a** in DMSO-d_6

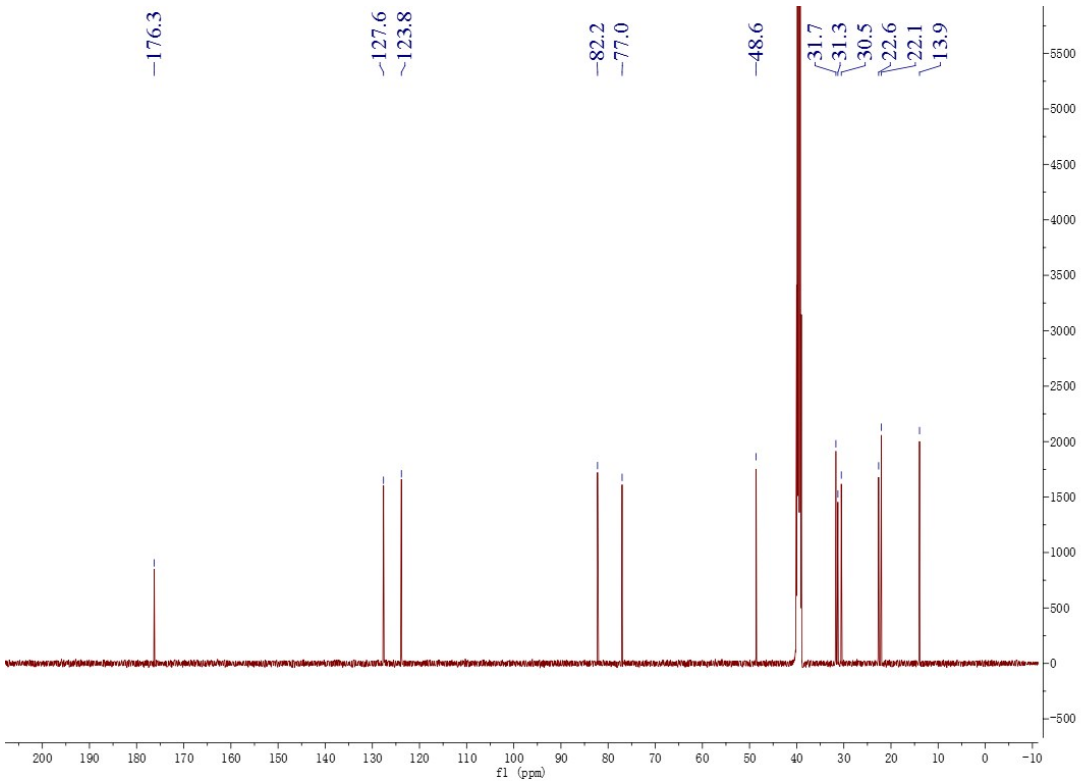


Figure S98. The ^{13}C NMR spectrum of compound **3a** in DMSO-d_6

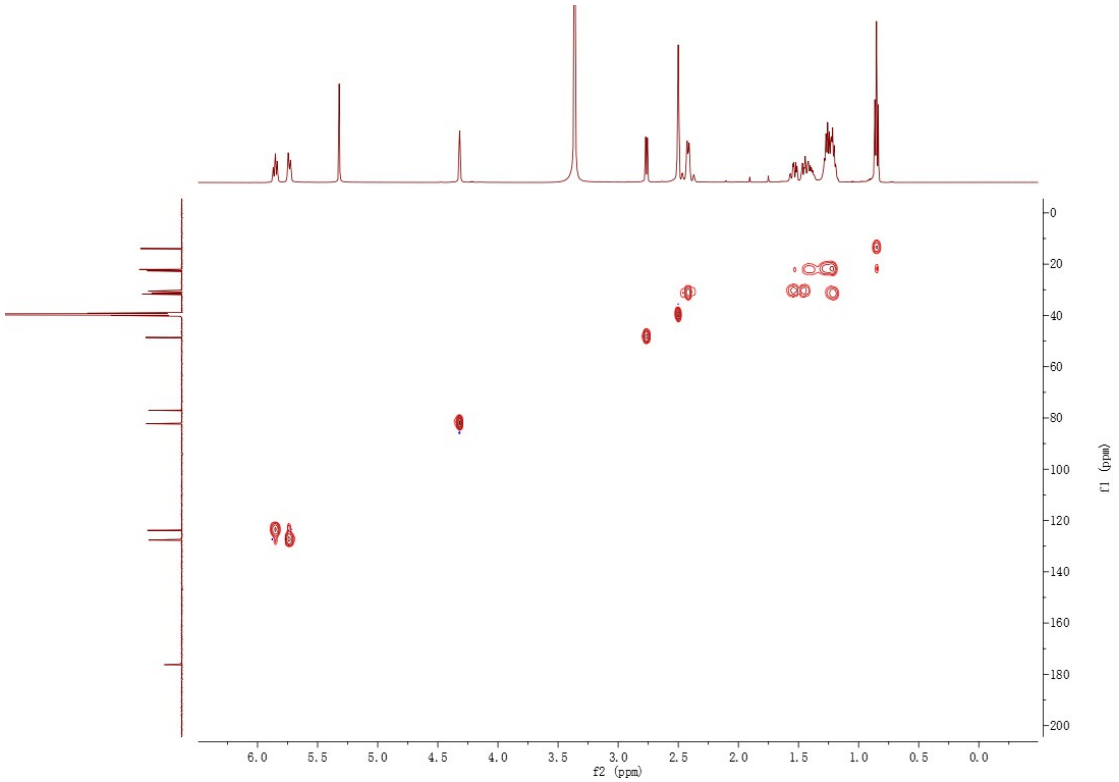


Figure S99. The HSQC spectrum of compound **3a** in DMSO-d_6

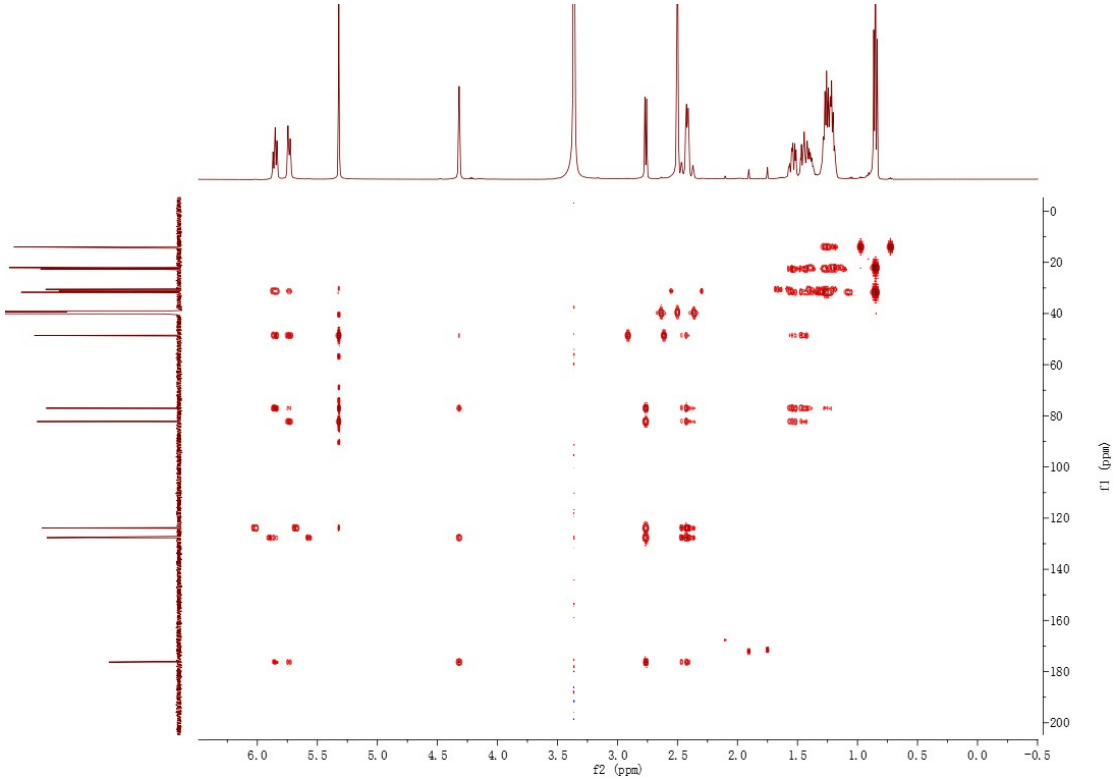


Figure S100. The HMBC spectrum of compound **3a** in DMSO-d_6

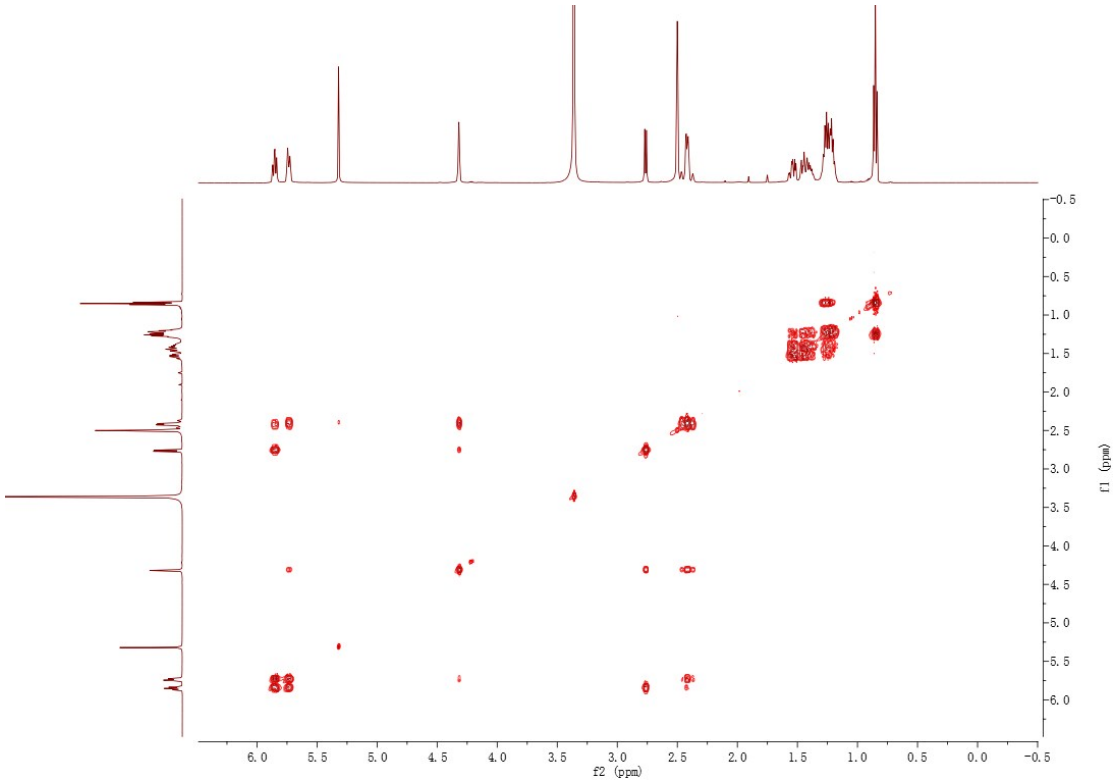


Figure S101. The ^{1}H-^{1}H COSY spectrum of compound **3a** in DMSO-d_6

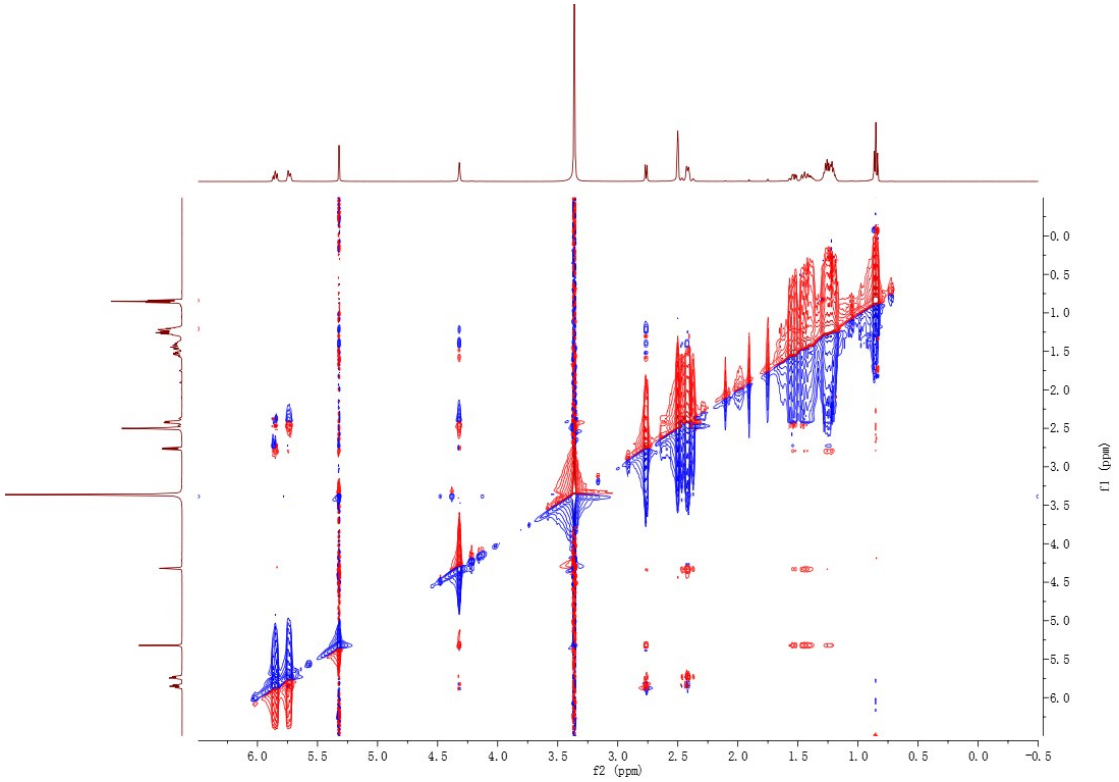


Figure S102. The ROESY spectrum of compound **3a** in DMSO-d_6