

Supplementary information

ORIGINAL ARTICLE

Bioactive thionic compounds and aromatic glycosides from *Ligusticum chuanxiong*

Xu Zhang[†], Bing Han[†], Ziming Feng, Jianshuang Jiang, Yanan Yang, Peicheng Zhang*

*State Key Laboratory of Bioactive Substance and Function of Natural Medicines,
Institute of Materia Medica, Peking Union Medical College and 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 (Peicheng Zhang).

†These authors made equal contributions to this work.

Table of Contents

No.	Contents	Compound	Page
1	The ¹ H NMR spectrum in DMSO- <i>d</i> ₆ (500 MHz)	1	S3
2	The ¹³ C NMR spectrum in DMSO- <i>d</i> ₆ (125 MHz)	1	S3
3	The HSQC spectrum in DMSO- <i>d</i> ₆ (500 MHz)	1	S4
4	The HMBC spectrum in DMSO- <i>d</i> ₆ (500 MHz)	1	S4
5	The UV spectrum in MeOH	1	S5
6	The IR spectrum	1	S5
7	The HR-ESI-MS data	1	S6
8	The [Mo ₂ (AcO) ₄] induced ECD spectrum in DMSO	1	S7
9	The ¹ H NMR spectrum in methanol- <i>d</i> ₄ (500 MHz)	2	S7
10	The ¹³ C NMR spectrum in methanol- <i>d</i> ₄ (125 MHz)	2	S8

11	The HSQC spectrum in methanol- <i>d</i> ₄ (500 MHz)	2	S8
12	The HMBC spectrum in methanol- <i>d</i> ₄ (500 MHz)	2	S9
13	The UV spectrum in MeOH	2	S9
14	The IR spectrum	2	S10
15	The HR-ESI-MS data	2	S11
16	The ¹ H NMR spectrum in DMSO- <i>d</i> ₆ (600 MHz)	3	S12
17	The ¹³ C NMR spectrum in DMSO- <i>d</i> ₆ (150 MHz)	3	S12
18	The HSQC spectrum in DMSO- <i>d</i> ₆ (600 MHz)	3	S13
19	The HMBC spectrum in DMSO- <i>d</i> ₆ (600 MHz)	3	S13
20	The UV spectrum in MeOH	3	S14
21	The IR spectrum	3	S14
22	The HR-ESI-MS data	3	S15
23	The [Mo ₂ (AcO) ₄] induced ECD spectrum in DMSO	3	S16
24	The ECD spectrum in MeOH	3	S16
25	The ¹ H NMR spectrum in DMSO- <i>d</i> ₆ (500 MHz)	4	S17
26	The ¹³ C NMR spectrum in DMSO- <i>d</i> ₆ (125 MHz)	4	S17
27	The HSQC spectrum in DMSO- <i>d</i> ₆ (500 MHz)	4	S18
28	The HMBC spectrum in DMSO- <i>d</i> ₆ (500 MHz)	4	S18
29	The UV spectrum in MeOH	4	S19
30	The IR spectrum	4	S19
31	The HR-ESI-MS data	4	S20
32	The ¹ H NMR spectrum in DMSO- <i>d</i> ₆ (500 MHz)	5	S21
33	The ¹³ C NMR spectrum in DMSO- <i>d</i> ₆ (125 MHz)	5	S21
34	The HSQC spectrum in DMSO- <i>d</i> ₆ (500 MHz)	5	S22
35	The HMBC spectrum in DMSO- <i>d</i> ₆ (500 MHz)	5	S22
36	The UV spectrum in MeOH	5	S23
37	The IR spectrum	5	S23
38	The HR-ESI-MS data	5	S24
39	The Gas Chromatographic separation of D-Glc		S25
40	The Gas Chromatographic separation of D-Api		S25
41	The Gas Chromatographic analyses of sugar moieties	4 and 5	S25
42	Sixteen optimized conformations of 3Jb		S26
43	The experimental UV spectrum of 3 and the calculated UV spectrum of 3Jb		S29
44	Experimental ECD and calculated ECD spectrum of 3 in MeOH	3	S30

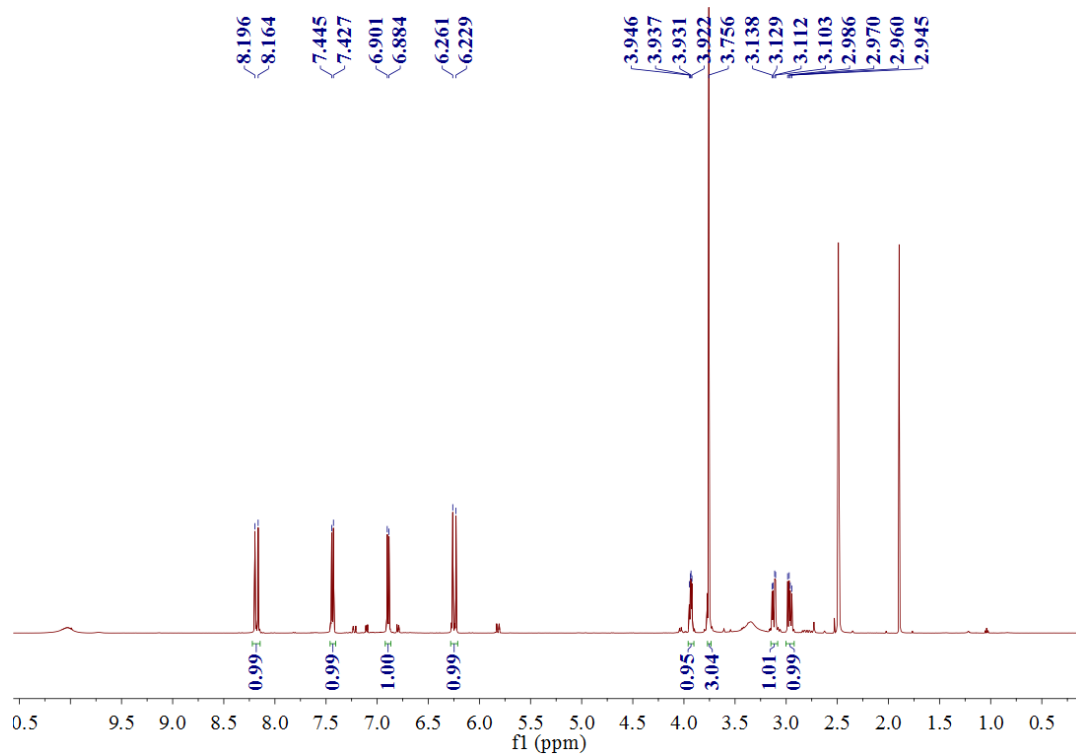


Fig. S1 The ^1H NMR spectrum of compound **1** in $\text{DMSO-}d_6$.

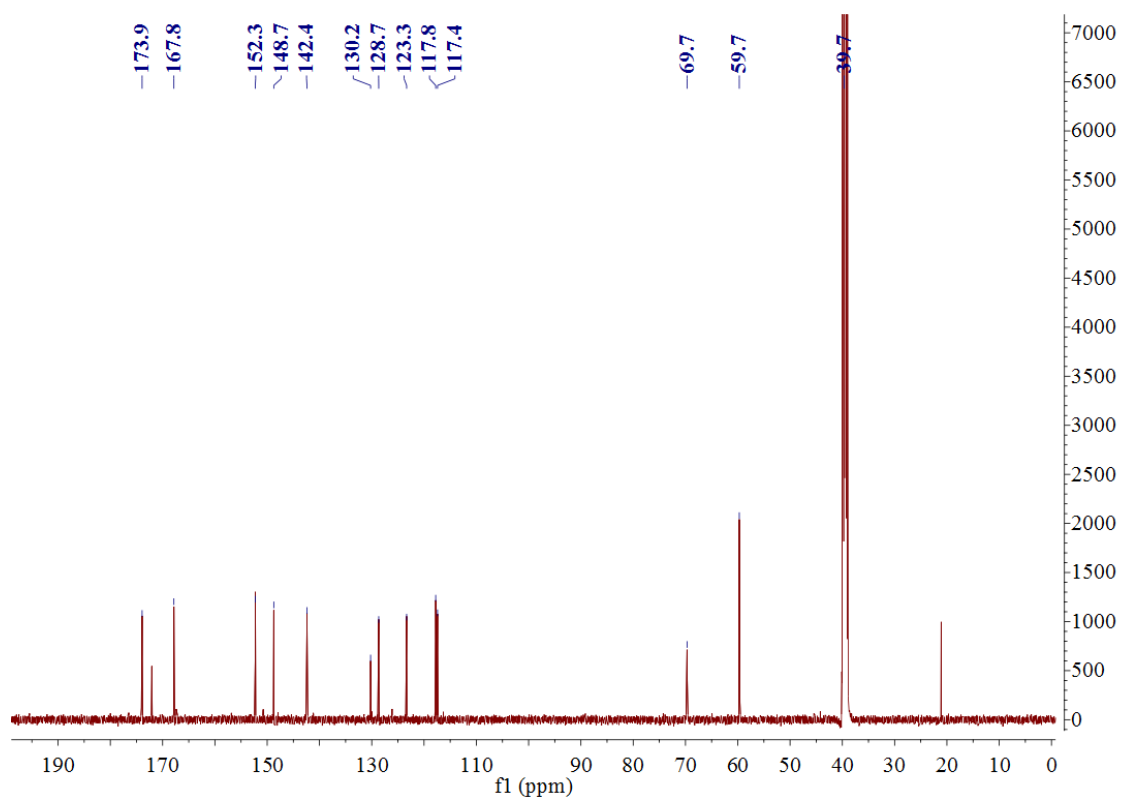


Fig. S2 The ^{13}C NMR spectrum of compound **1** in $\text{DMSO-}d_6$.

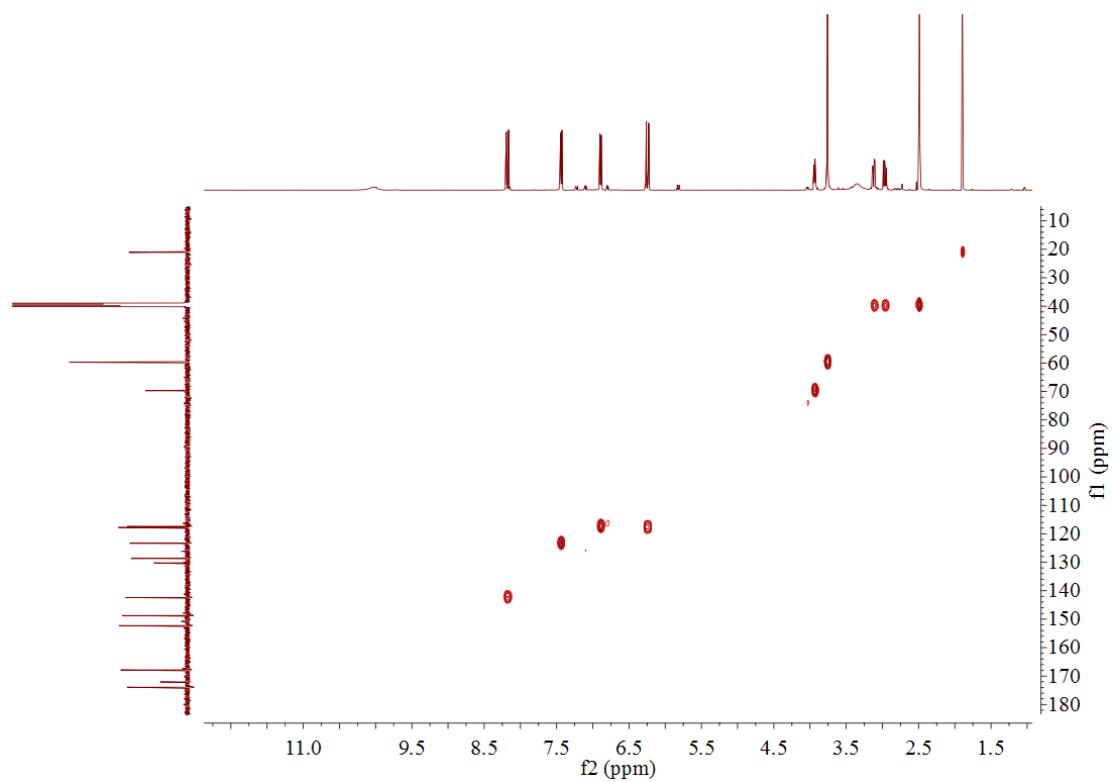


Fig. S3 The HSQC spectrum of compound **1** in DMSO- d_6 .

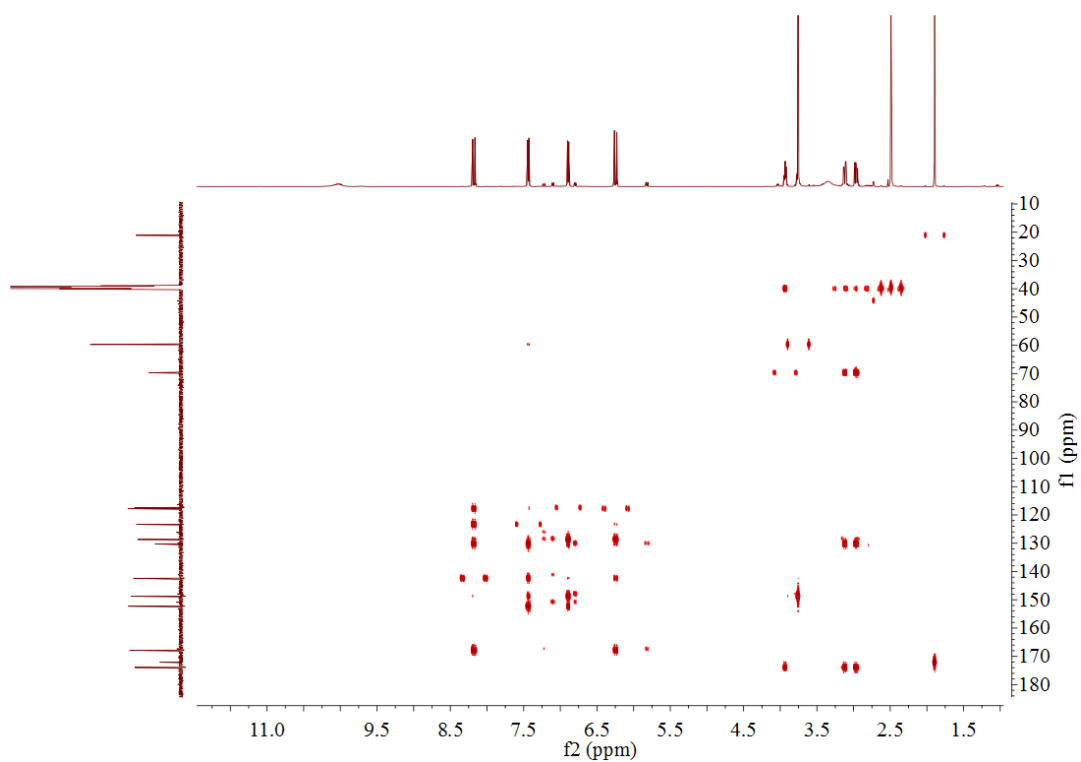


Fig. S4 The HMBC spectrum of compound **1** in DMSO- d_6 .

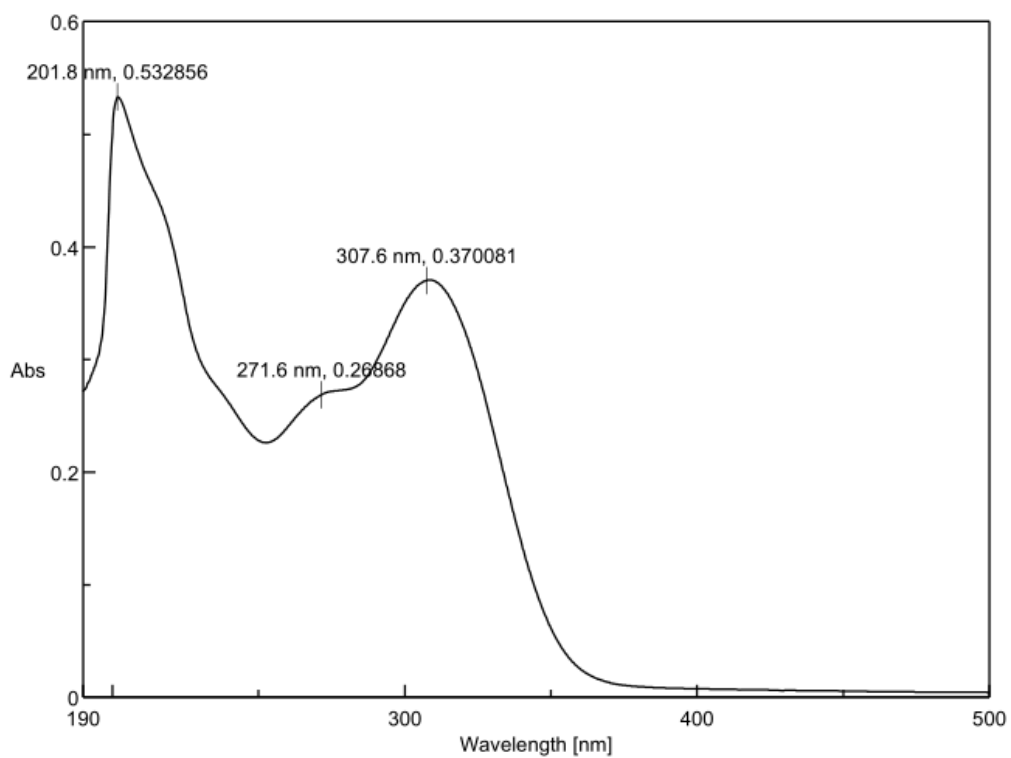


Fig. S5 The UV spectrum of compound **1** in MeOH.

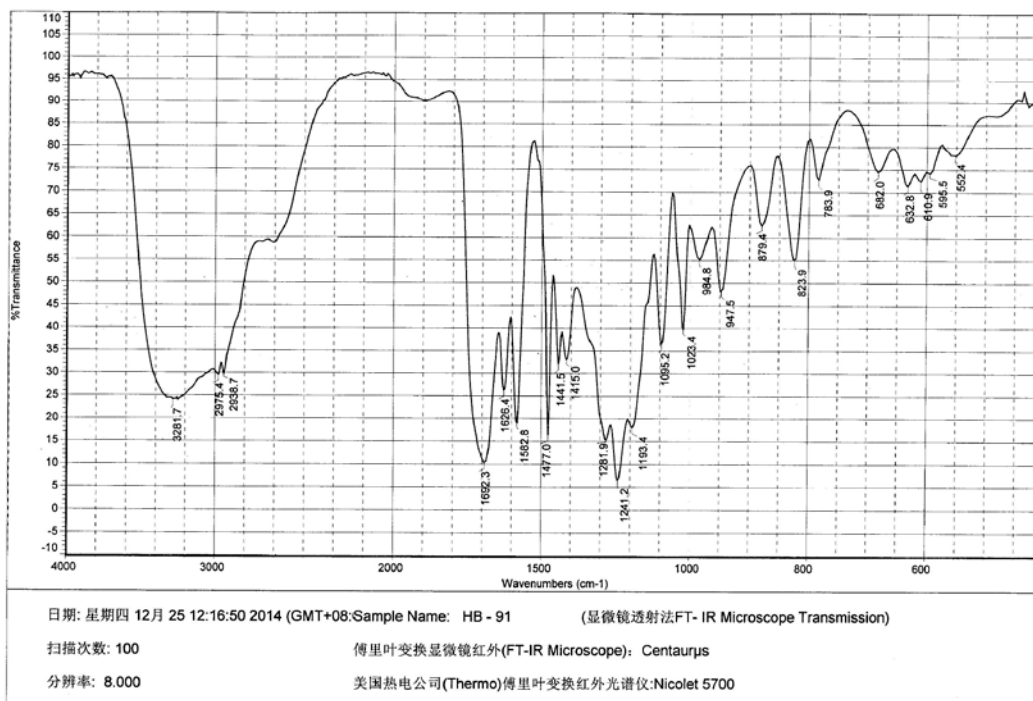


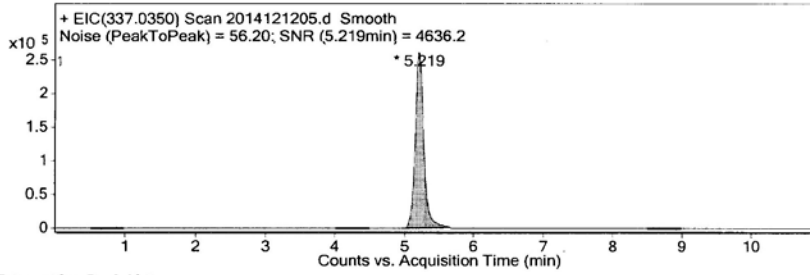
Fig. S6 The IR spectrum of compound **1**.

Qualitative Analysis Report

Data Filename	2014121205.d	Sample Name	HB-91
Sample Type	Sample	Position	P1-C5
Instrument Name	Instrument 1	User Name	
Acq Method	TEST LCMS.m	IRM Calibration Status	XXXXXXXXXX
DA Method	TEST LCMS.m	Comment	

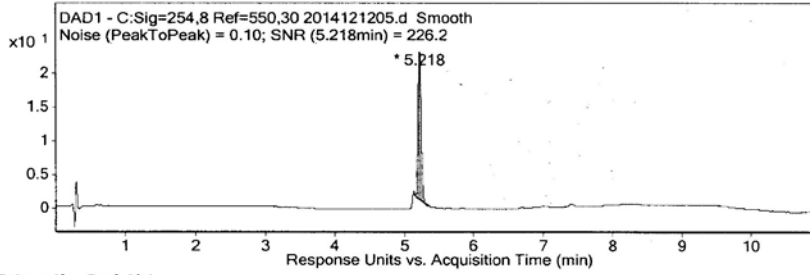
User Chromatograms

Fragmentor Voltage 135 Collision Energy 0 Ionization Mode ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	4.977	5.219	5.653	260570	2246187	100	4636.2



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	5.163	5.218	5.364	22.04	68.36	100	226.2

User Spectra

Fragmentor Voltage 135 Collision Energy 0 Ionization Mode ESI

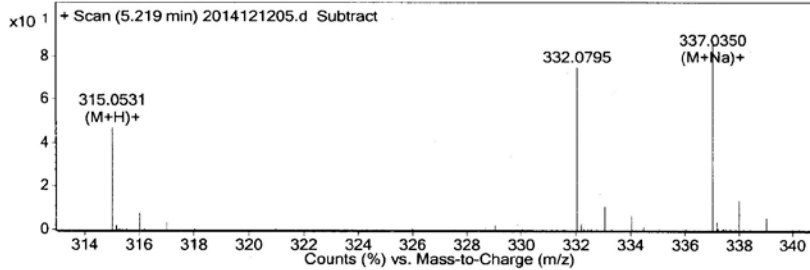


Fig. S7 The HR-ESI-MS data of compound 1.

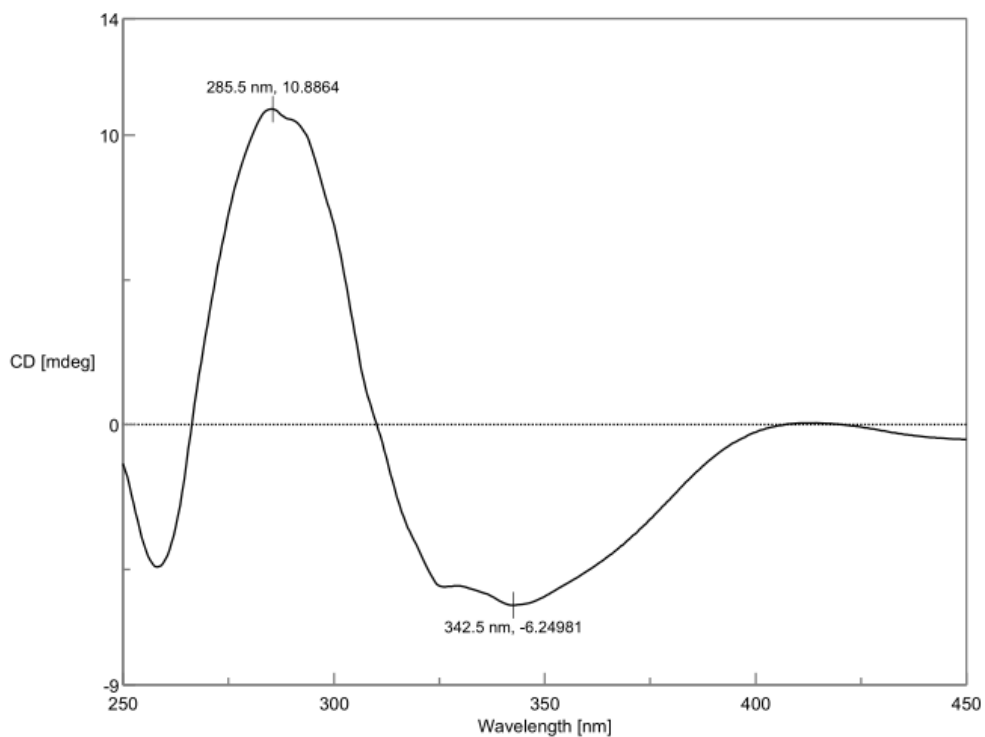


Fig. S8 The $[\text{Mo}_2(\text{AcO})_4]$ induced ECD spectrum of compound **1** in DMSO.

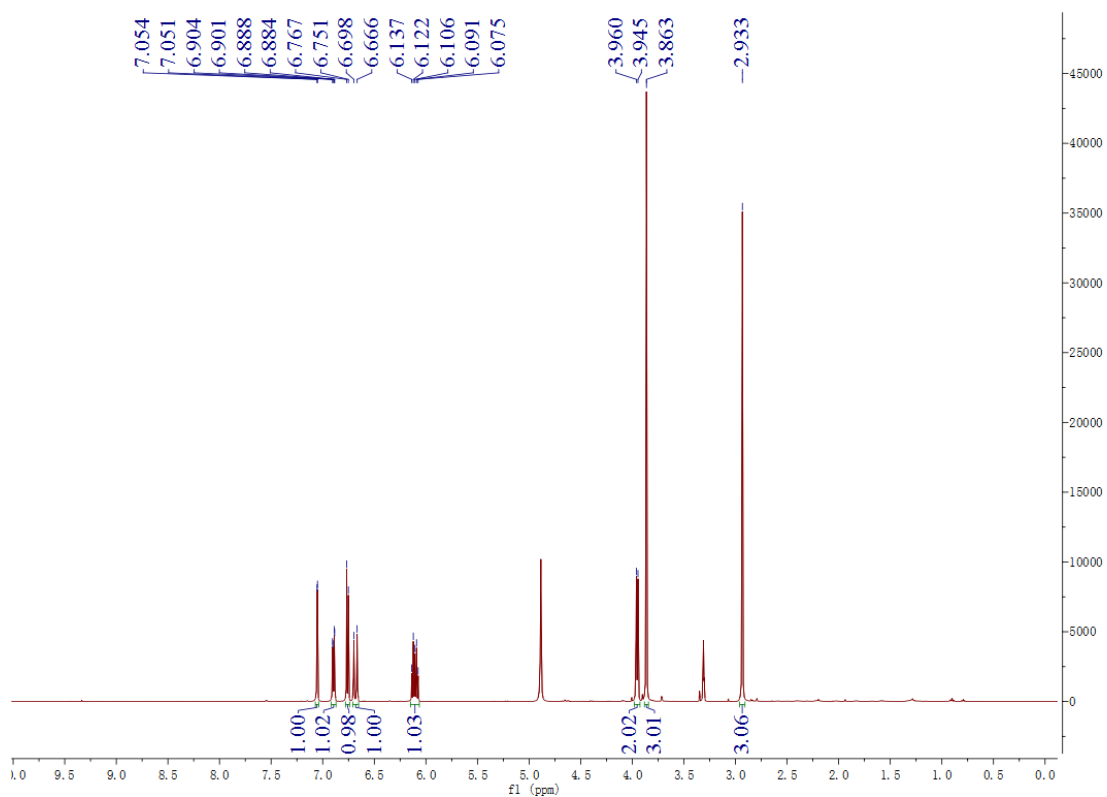


Fig. S9 The ^1H NMR spectrum of compound **2** in methanol- d_4 .

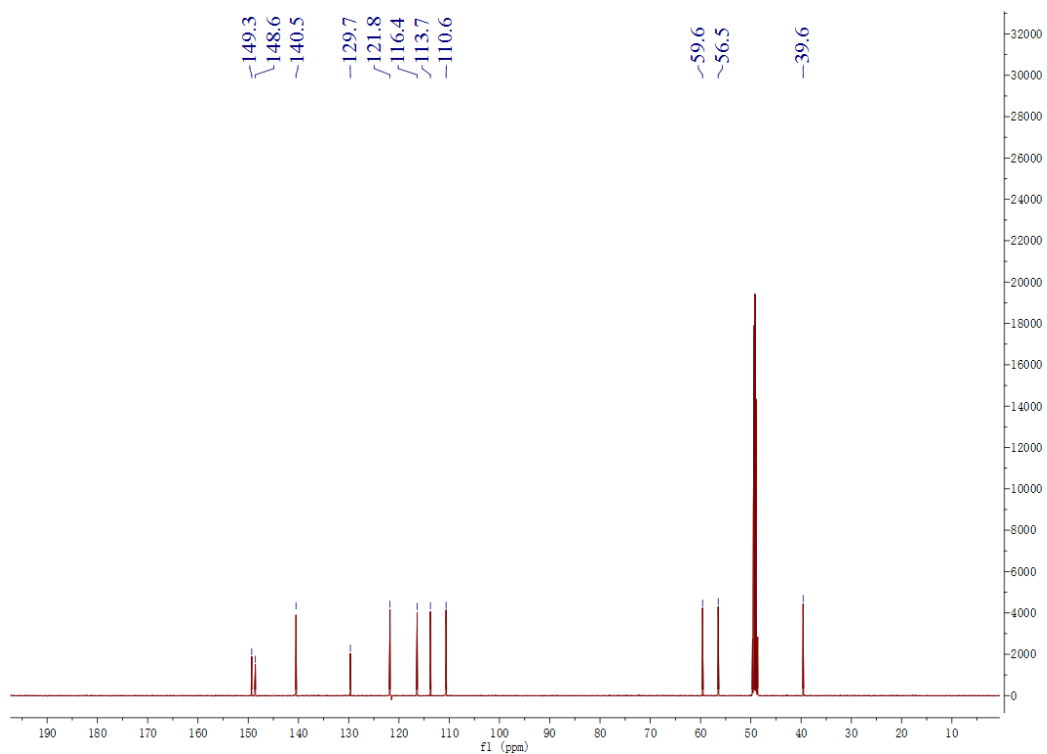


Fig. S10 The ^{13}C NMR spectrum of compound **2** in methanol- d_4 .

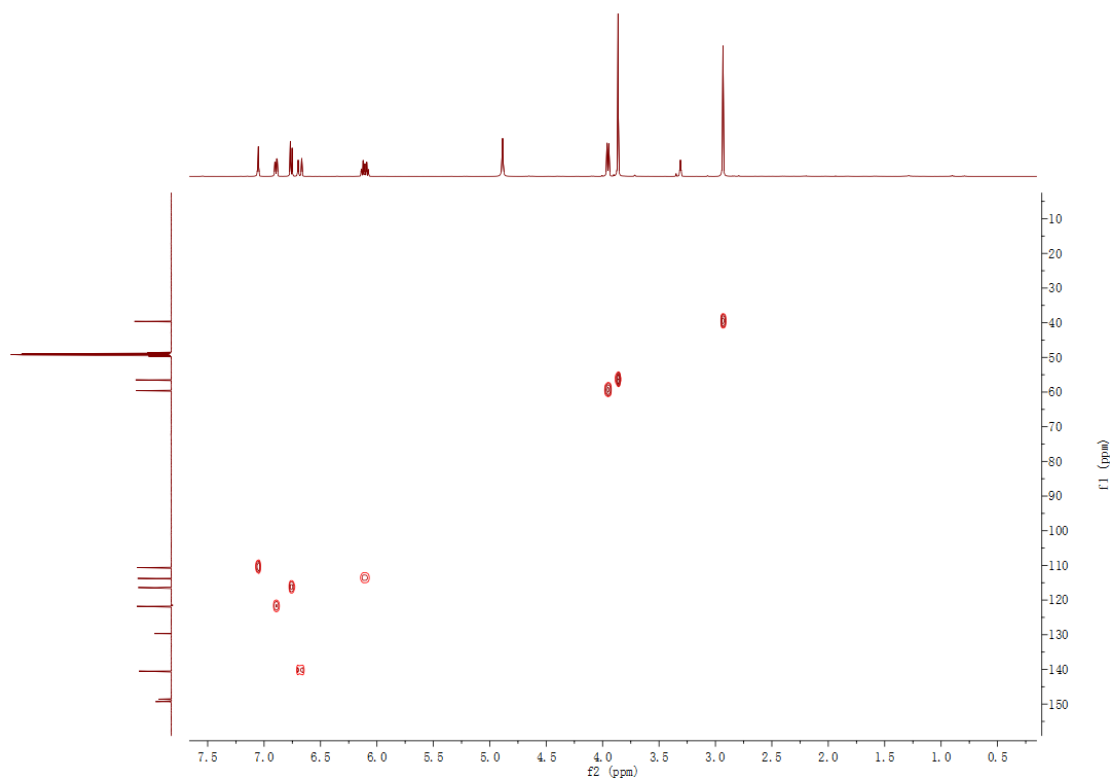


Fig. S11 The HSQC spectrum of compound **2** in methanol- d_4 .

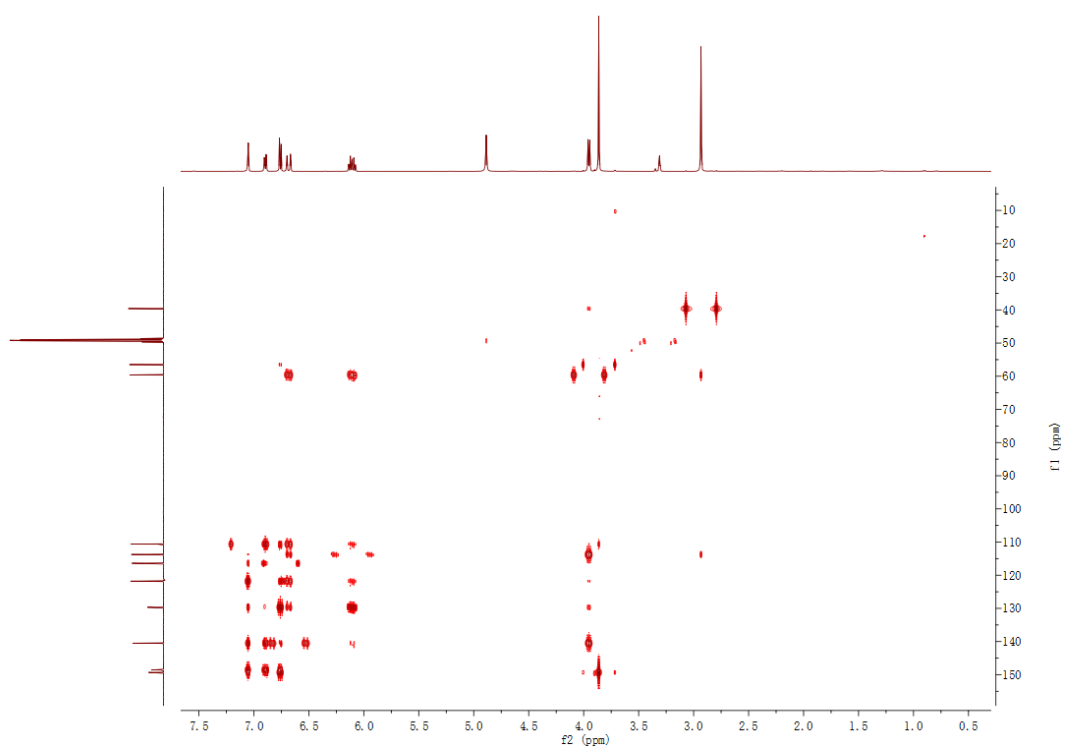


Fig. S12 The HMBC spectrum of compound **2** in methanol- d_4 .

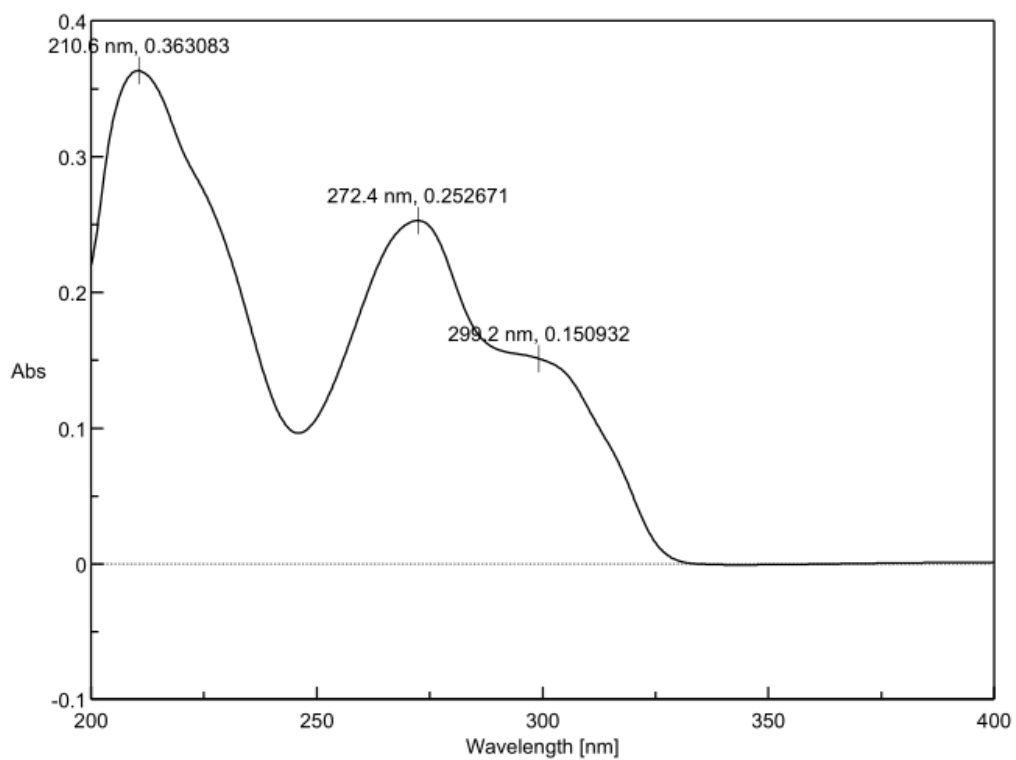


Fig. S13 The UV spectrum of compound **2** in MeOH.

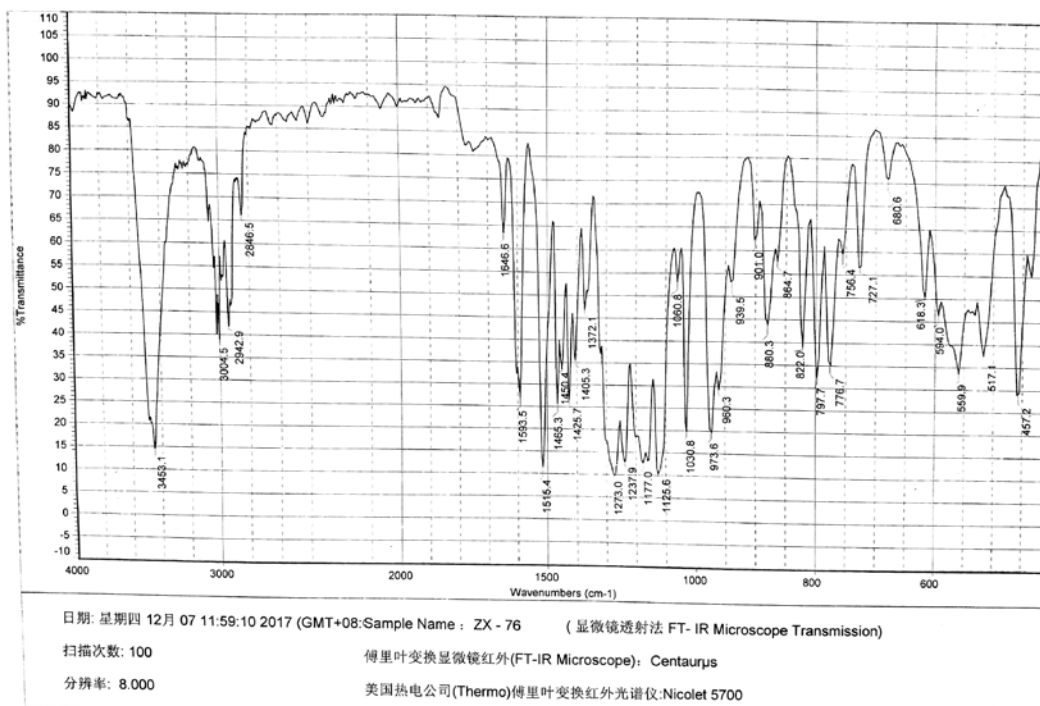
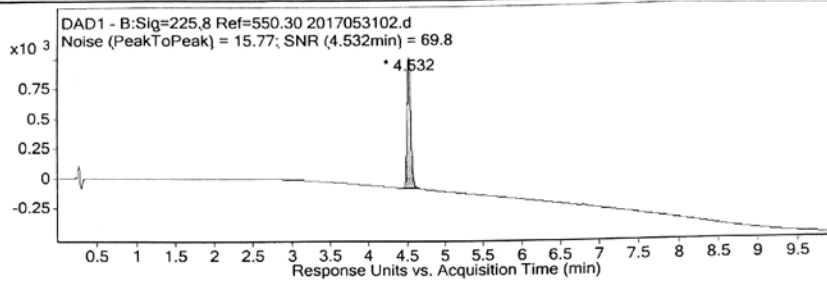


Fig. S14 The IR spectrum of compound **2**.

Qualitative Analysis Report

Data Filename	2017053102.d	Sample Name	ZX-76
Sample Type	Sample	Position	P1-C2
Instrument Name	Instrument 1	User Name	
Acq Method	TEST LCMS.m	IRM Calibration Status	Success
DA Method	TEST LCMS.m	Comment	

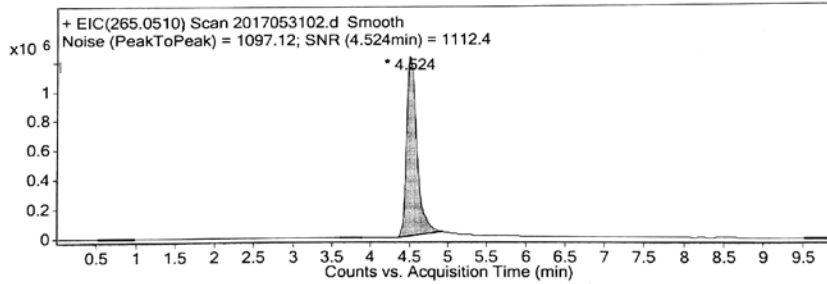
User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise	
1	4.44	4.532	4.663	4.663	1100.23	3765.91	100	69.8

Fragmentor Voltage 150 Collision Energy 0 Ionization Mode ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	4.347	4.524	4.927	1220411	11509860	100	1112.4

User Spectra

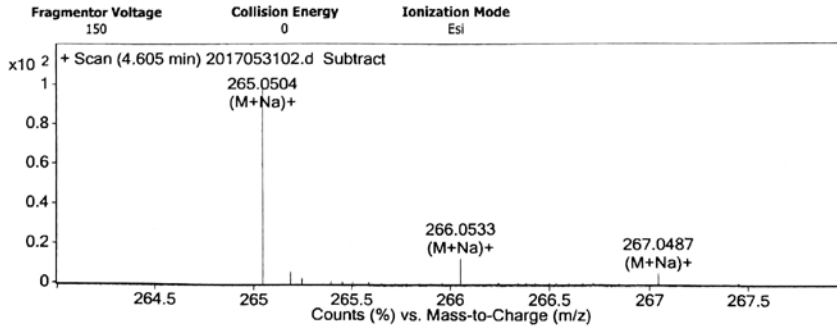


Fig. S15 The HR-ESI-MS data of compound 2.

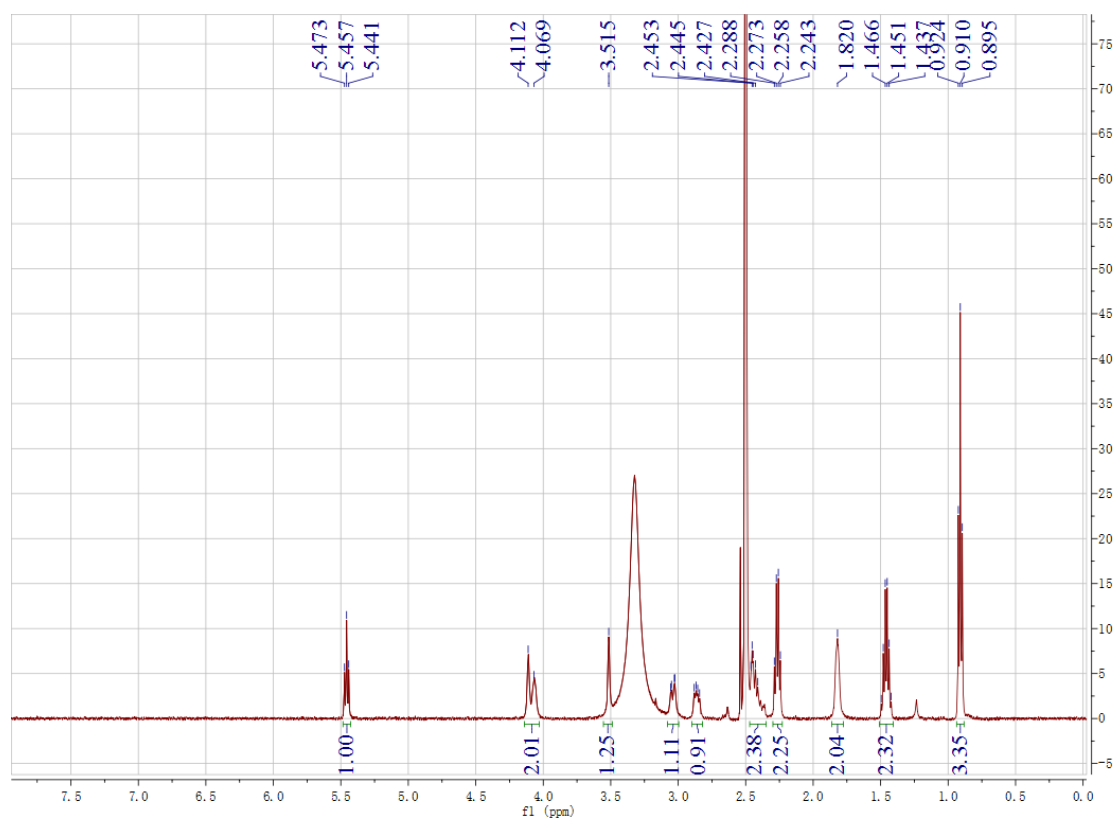


Fig. S16 The ^1H NMR spectrum of compound **3** in $\text{DMSO-}d_6$.

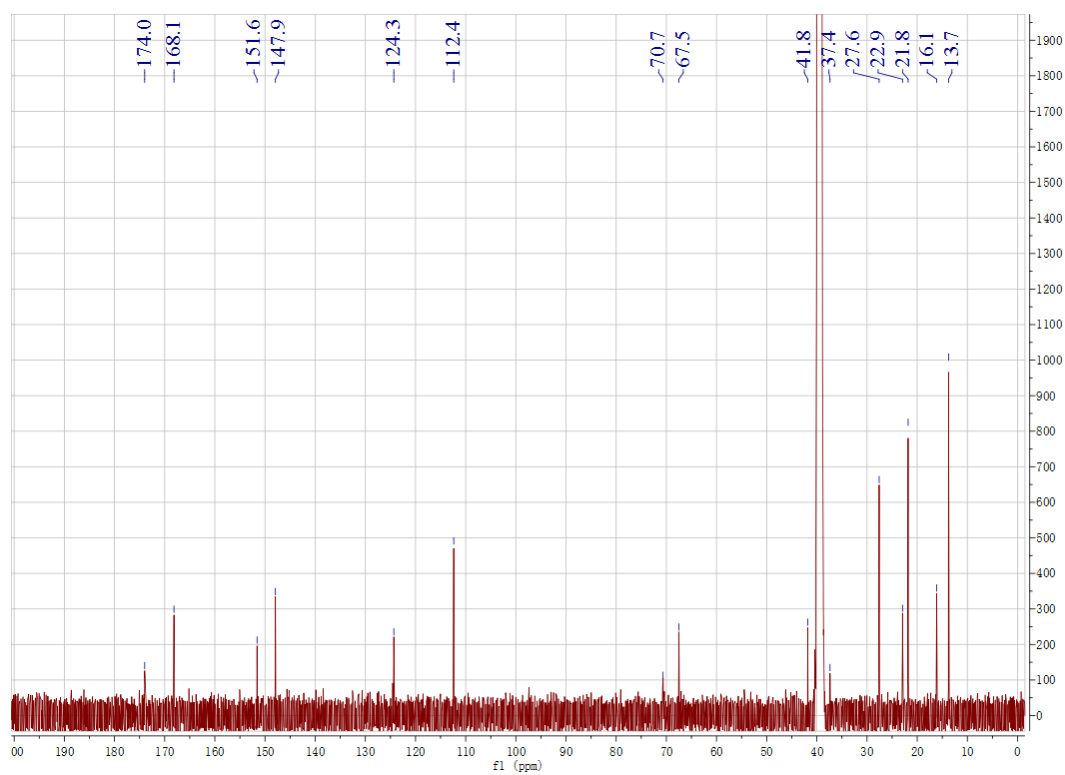


Fig. S17 The ^{13}C NMR spectrum of compound **3** in $\text{DMSO-}d_6$.

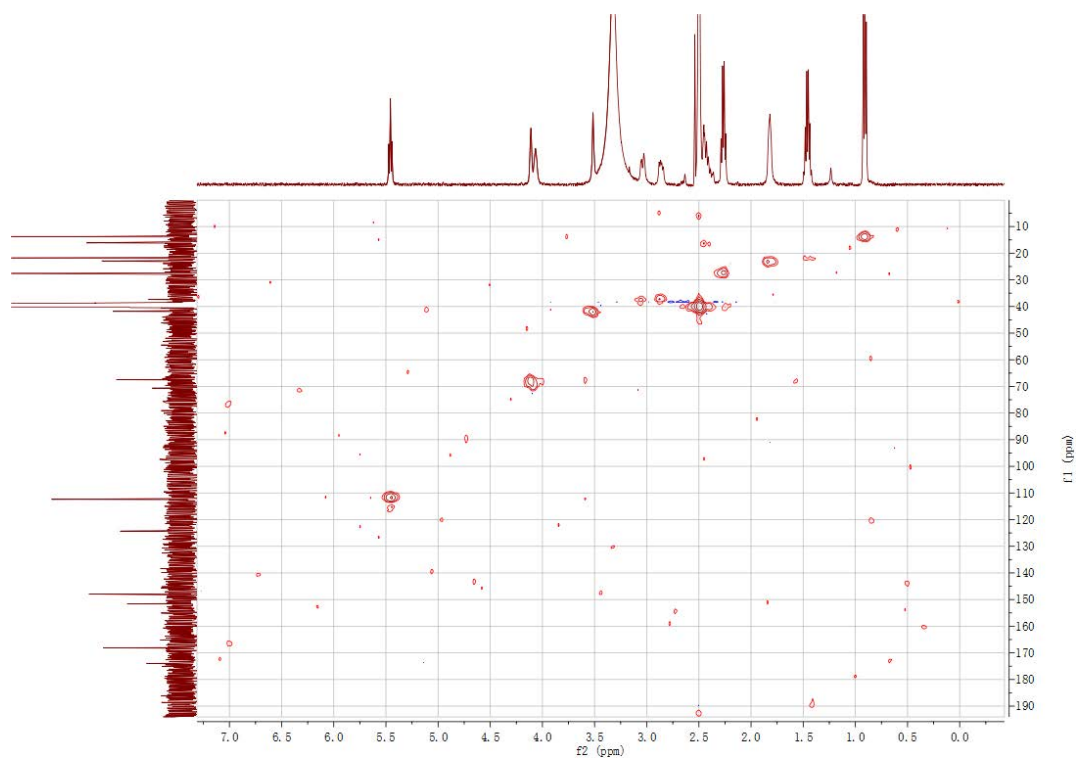


Fig. S18 The HSQC spectrum of compound **3** in DMSO- d_6 .

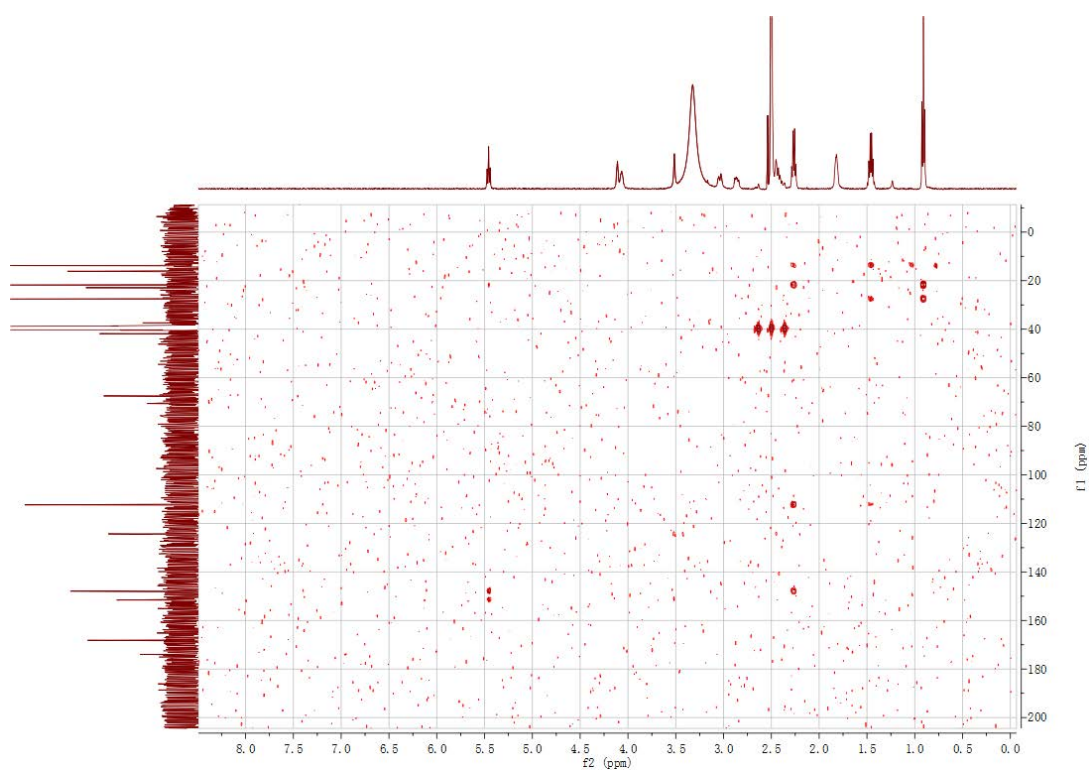


Fig. S19 The HMBC spectrum of compound **3** in DMSO- d_6 .

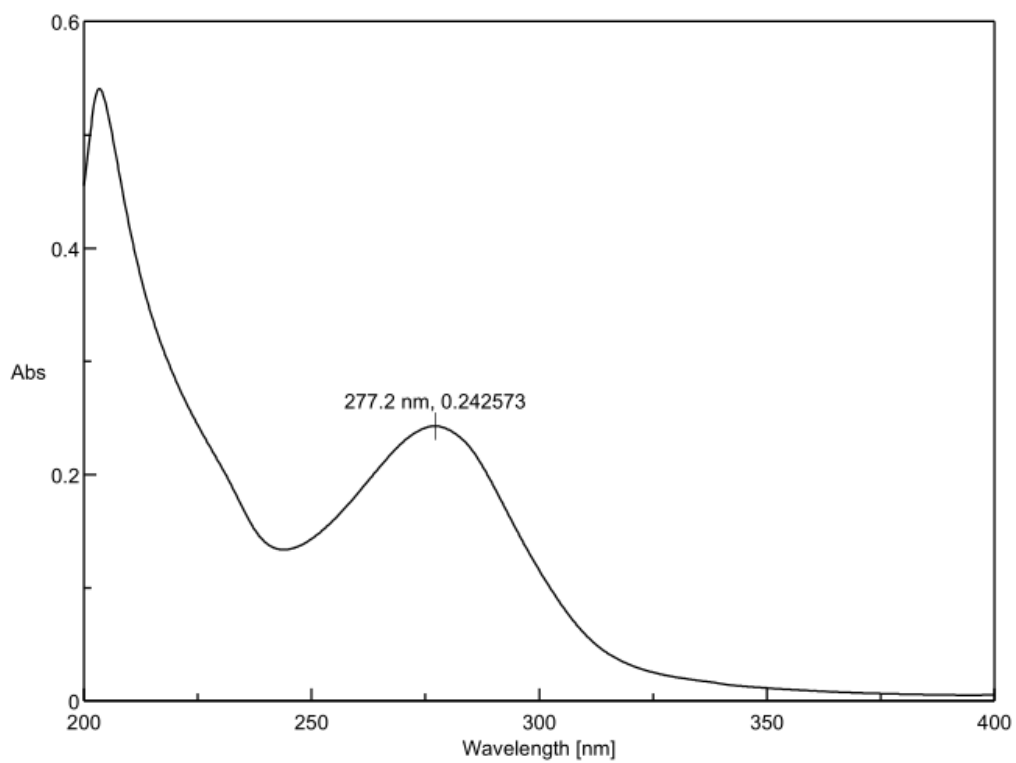


Fig. S20 The UV spectrum of compound **3** in MeOH.

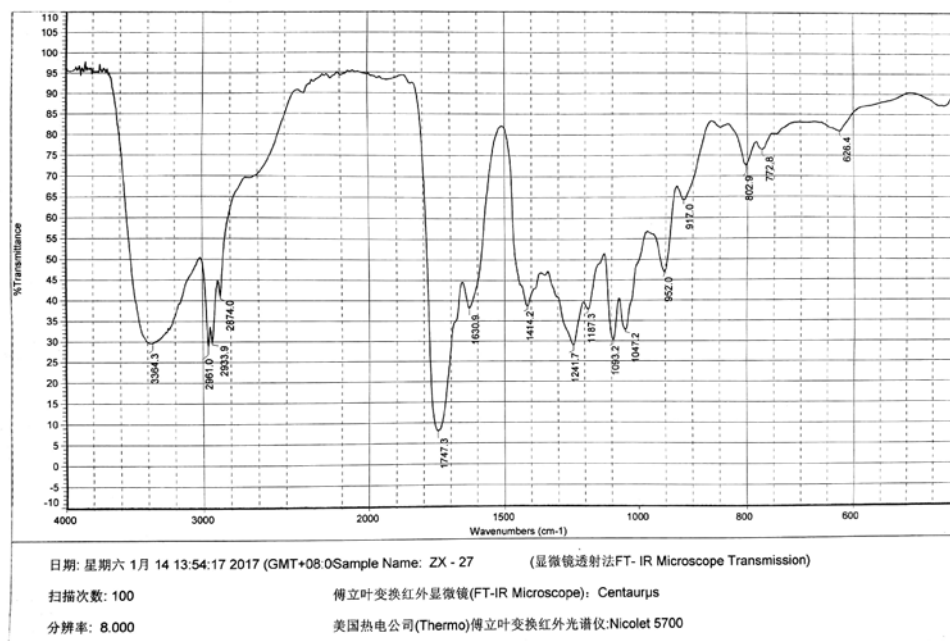
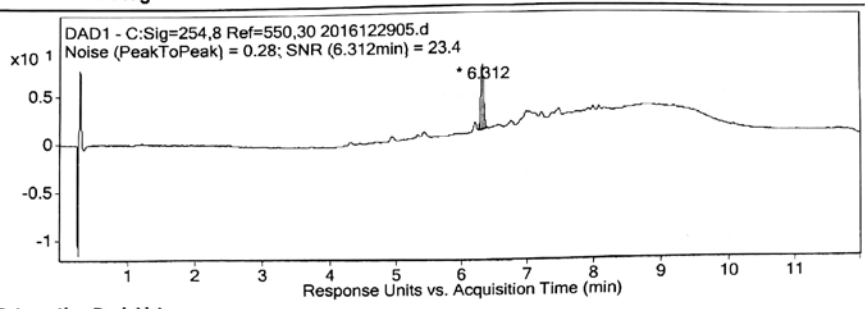


Fig. S21 The IR spectrum of compound **3**.

Qualitative Analysis Report

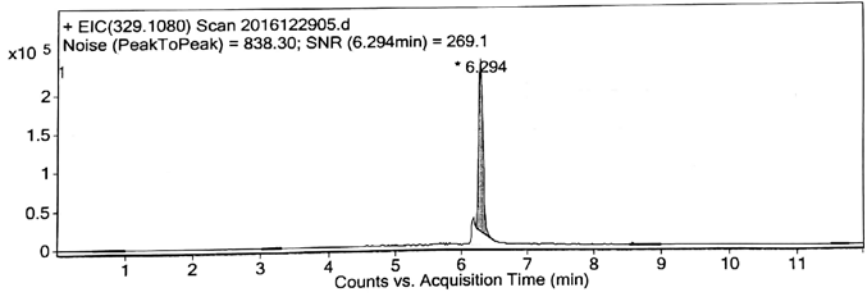
Data Filename	2016122905.d	Sample Name	ZX-27
Sample Type	Sample	Position	P1-C5
Instrument Name	Instrument 1	User Name	
Acq Method		IRM Calibration Status	Success
DA Method	TEST LCMS.m	Comment	

User Chromatograms



Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	6.25	6.312	6.403	6.6	20.29	100	23.4

Fragmentor Voltage 150 Collision Energy 0 Ionization Mode ESI



Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	6.23	6.294	6.536	225603	1003771	100	269.1

User Spectra

Fragmentor Voltage 150 Collision Energy 0 Ionization Mode ESI

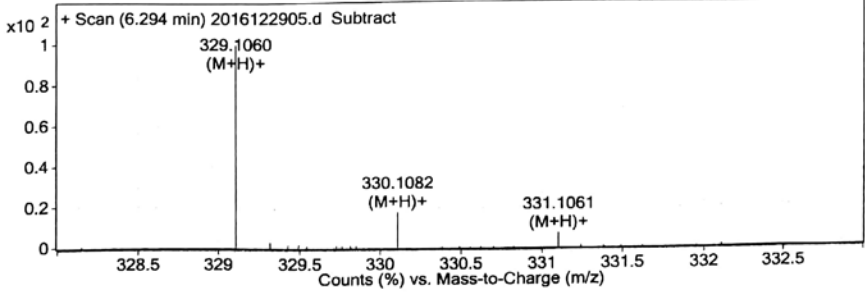


Fig. S22 The HR-ESI-MS data of compound 3.

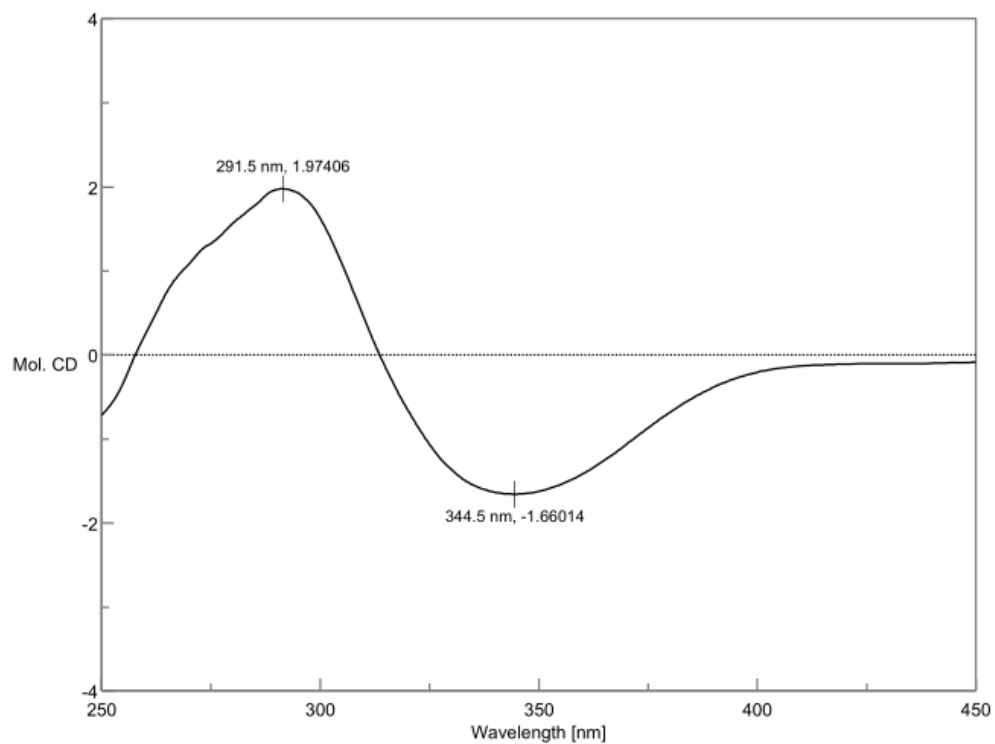


Fig. S23 The $[\text{Mo}_2(\text{AcO})_4]$ induced ECD spectrum of compound **3** in DMSO.

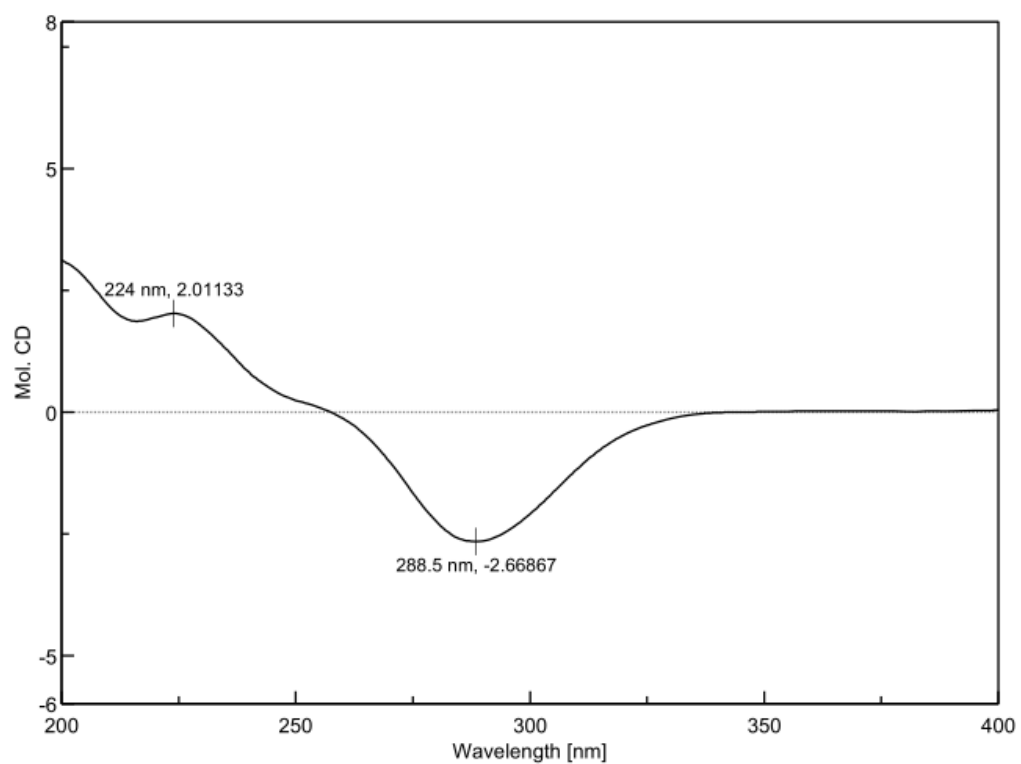


Fig. S24 The ECD spectrum of compound **3** in MeOH.

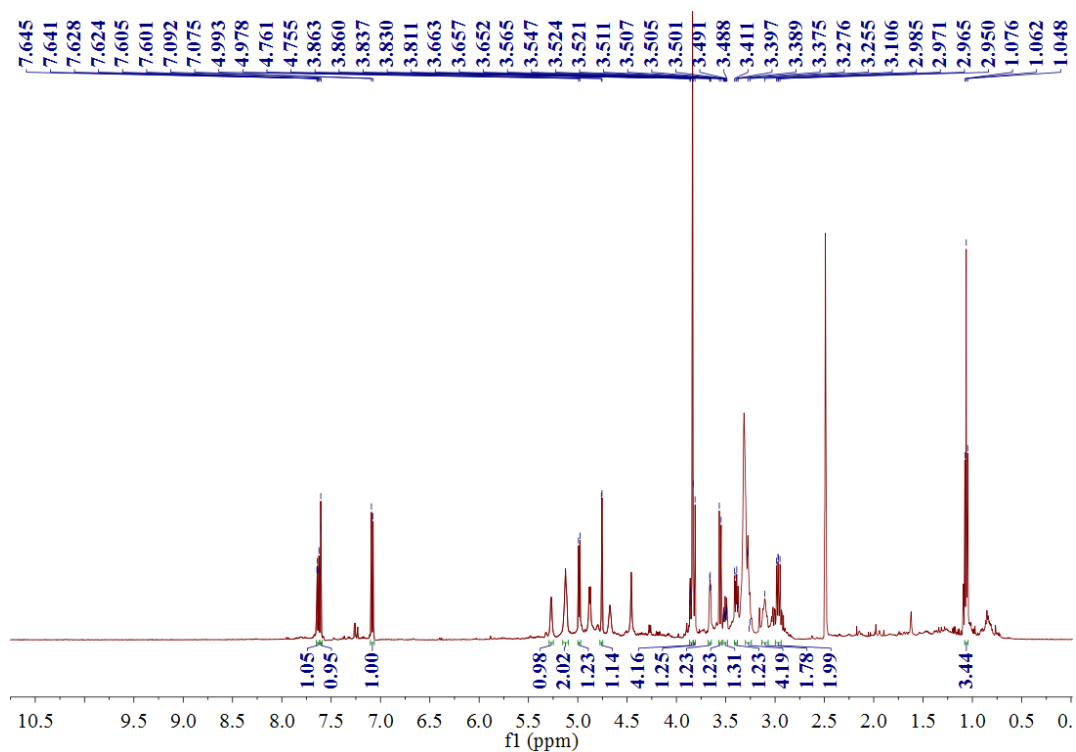


Fig. S25 The ^1H NMR spectrum of compound **4** in $\text{DMSO-}d_6$.

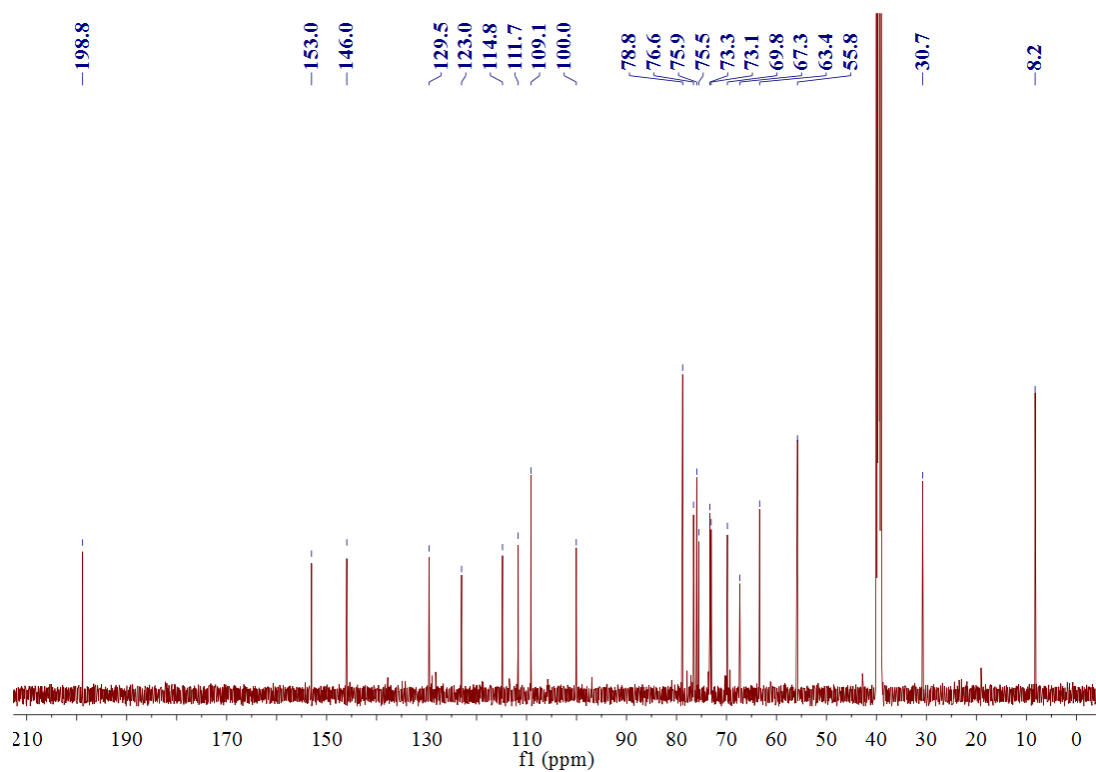


Fig. S26 The ^{13}C NMR spectrum of compound **4** in $\text{DMSO-}d_6$.

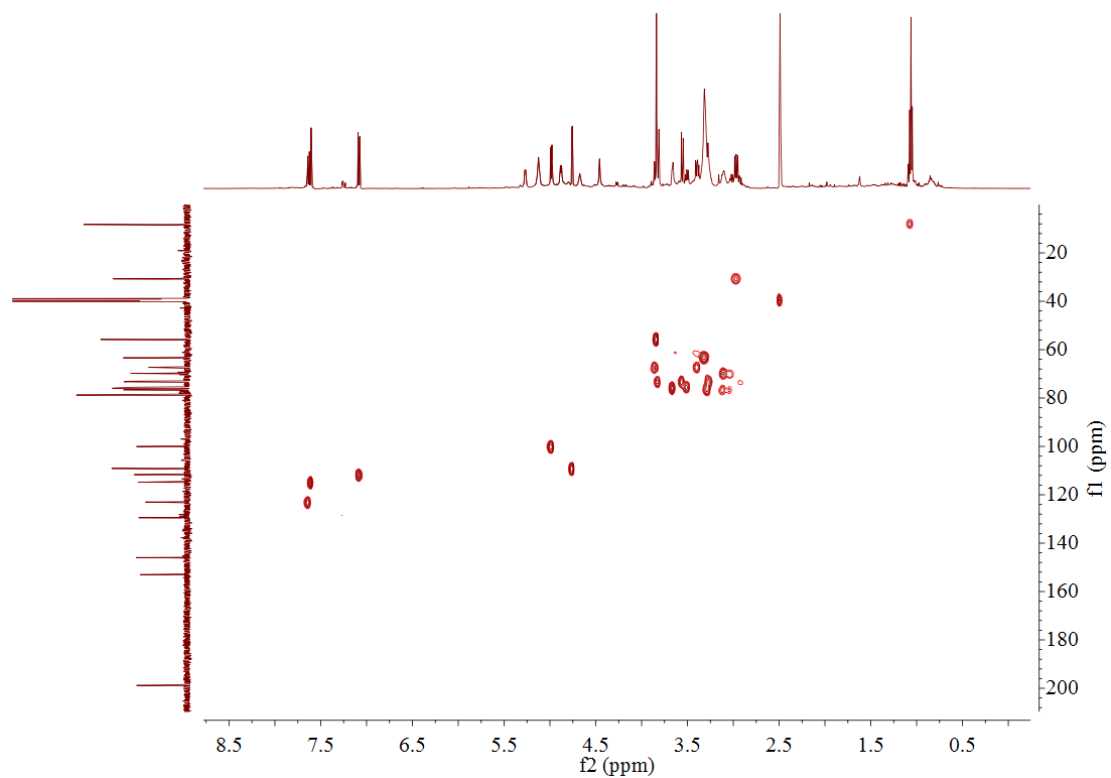


Fig. S27 The HSQC spectrum of compound **4** in DMSO-*d*₆.

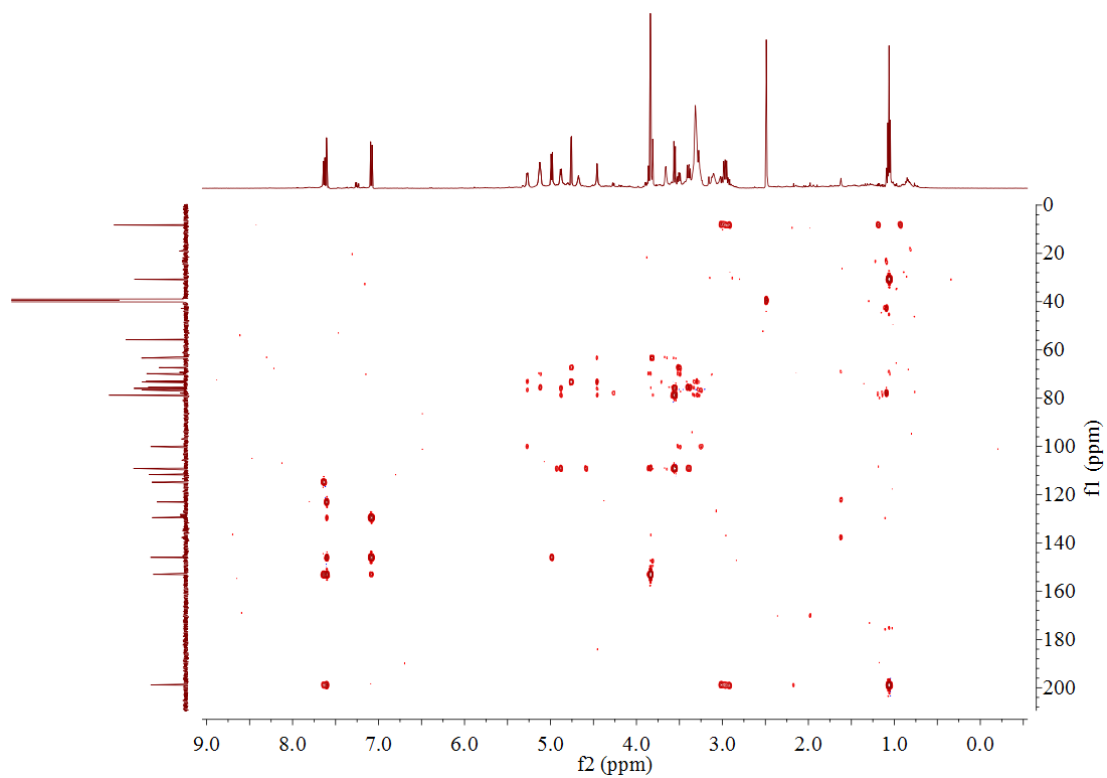


Fig. S28 The HMBC spectrum of compound **4** in DMSO-*d*₆.

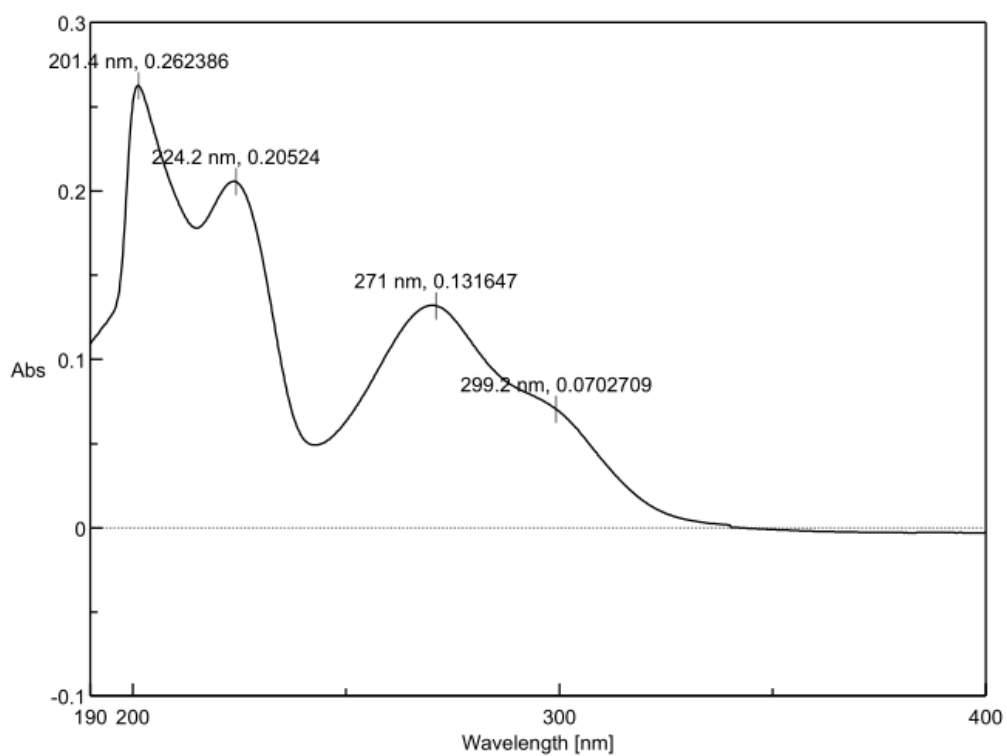


Fig. S29 The UV spectrum of compound 4 in MeOH.

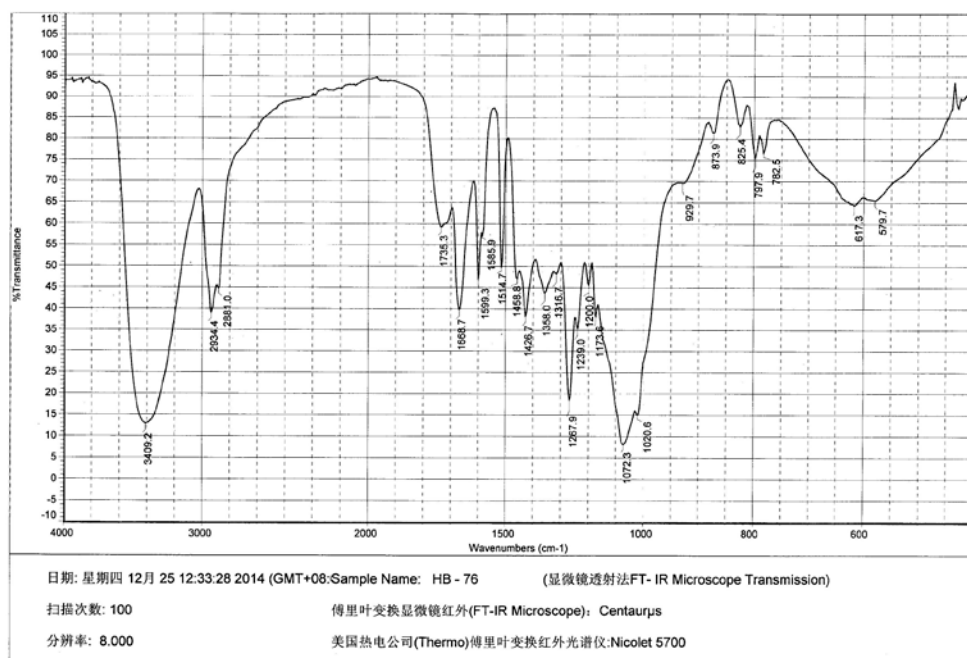


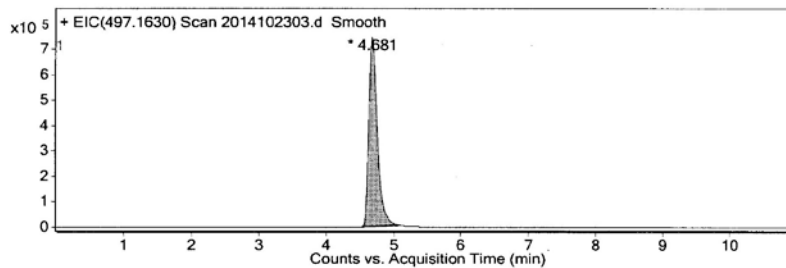
Fig. S30 The IR spectrum of compound 4.

Qualitative Analysis Report

Data Filename	2014102303.d	Sample Name	HB-76
Sample Type	Sample	Position	P1-C3
Instrument Name	Instrument 1	User Name	
Acq Method	TEST LCMS.m	IRM Calibration Status	██████████
DA Method	TEST LCMS.m	Comment	

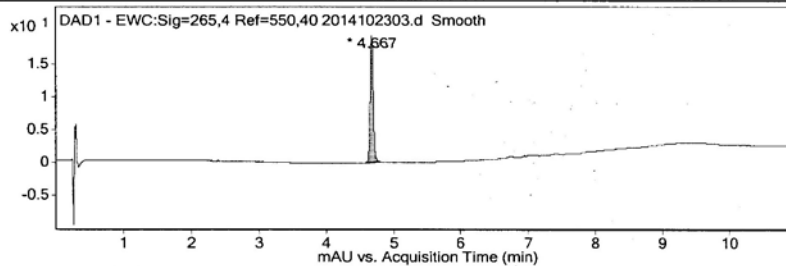
User Chromatograms

Fragmentor Voltage 135 Collision Energy 0 Ionization Mode ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	4.52	4.681	5.1	743357	6584825	100



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	4.58	4.667	4.793	19.43	62.639	100

User Spectra

Fragmentor Voltage 135 Collision Energy 0 Ionization Mode ESI

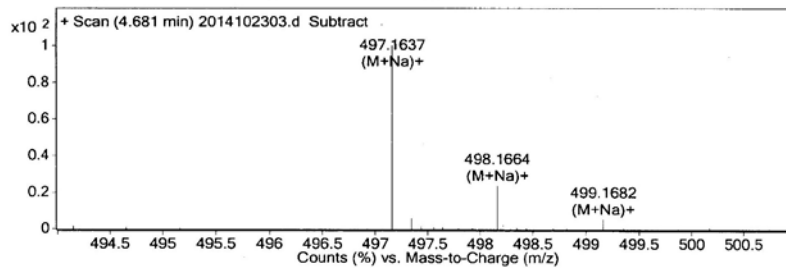


Fig. S31 The HR-ESI-MS data of compound 4.

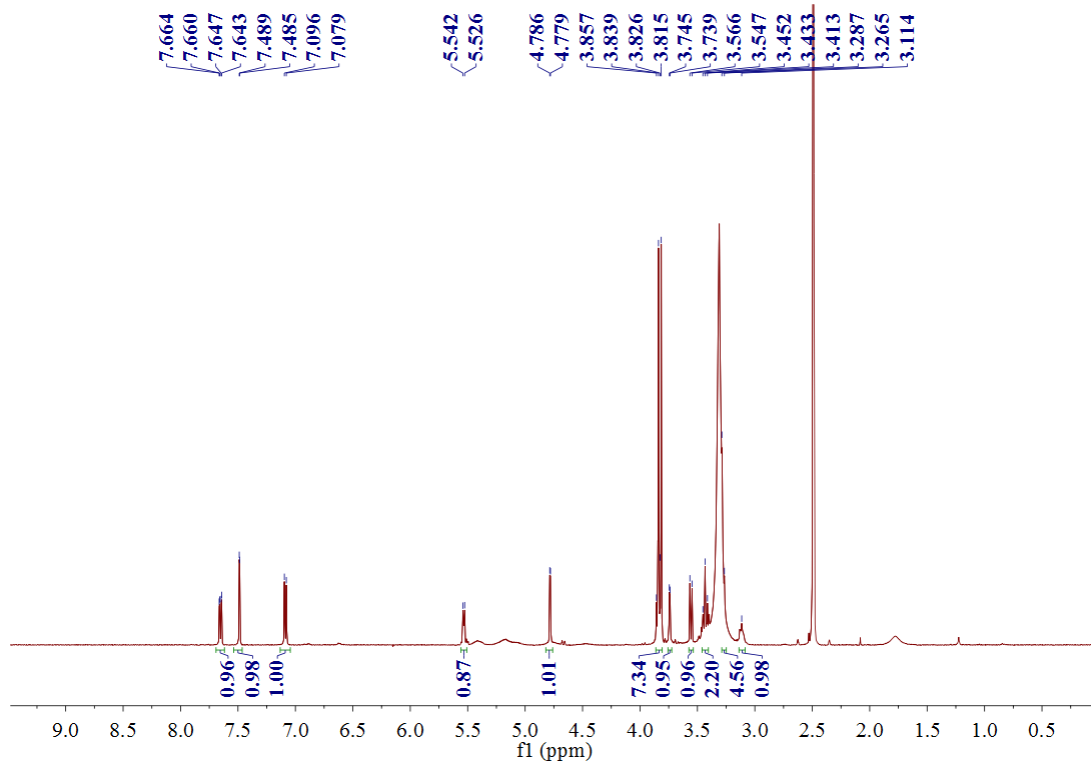


Fig. S32 The ^1H NMR spectrum of compound **5** in $\text{DMSO-}d_6$.

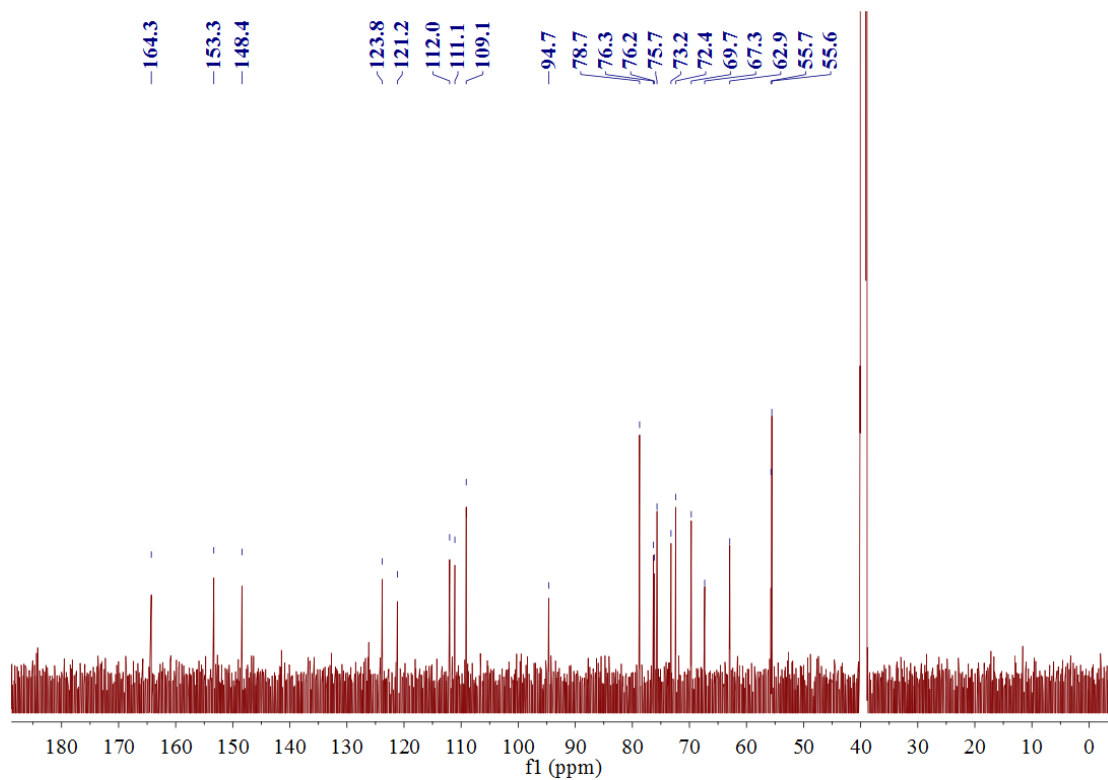


Fig. S33 The ^{13}C NMR spectrum of compound **5** in $\text{DMSO-}d_6$.

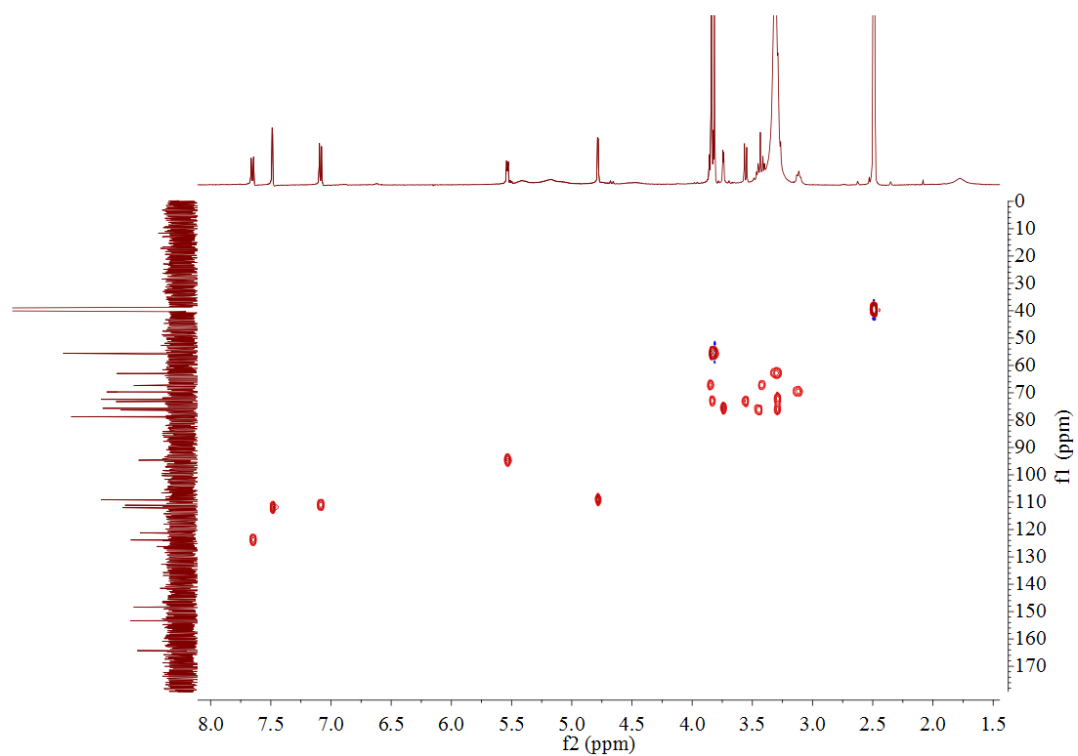


Fig. S34 The HSQC spectrum of compound **5** in DMSO- d_6 .

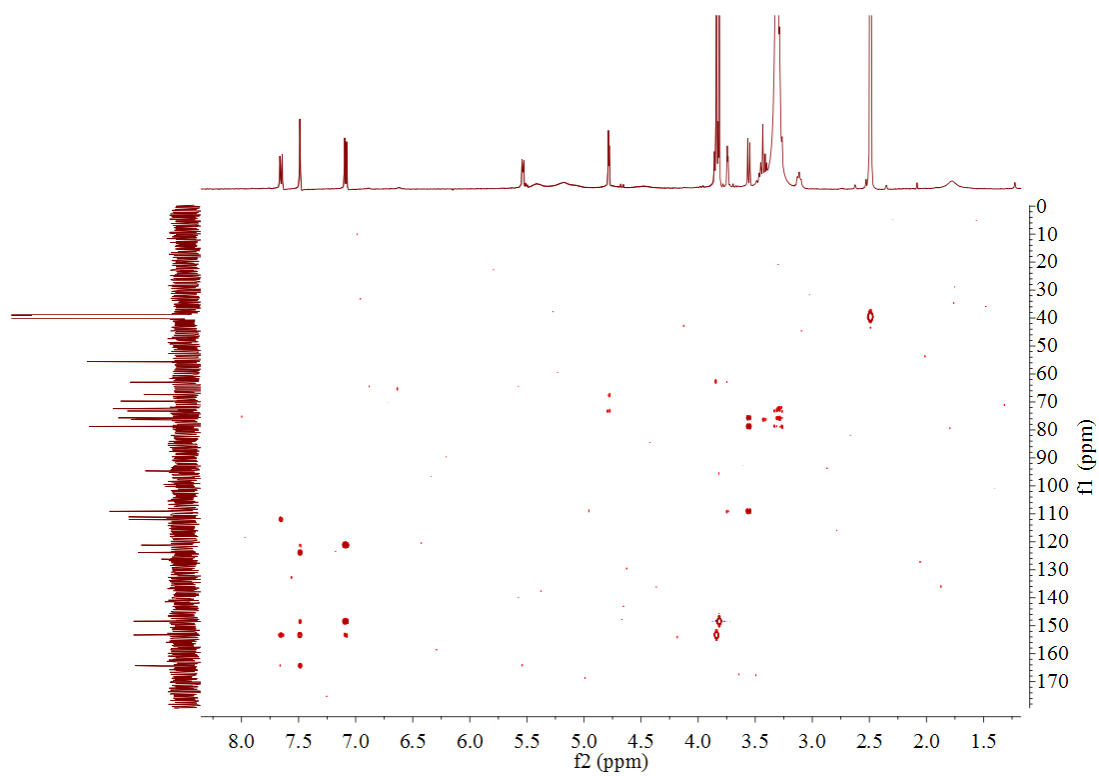


Fig. S35 The HMBC spectrum of compound **5** in DMSO- d_6 .

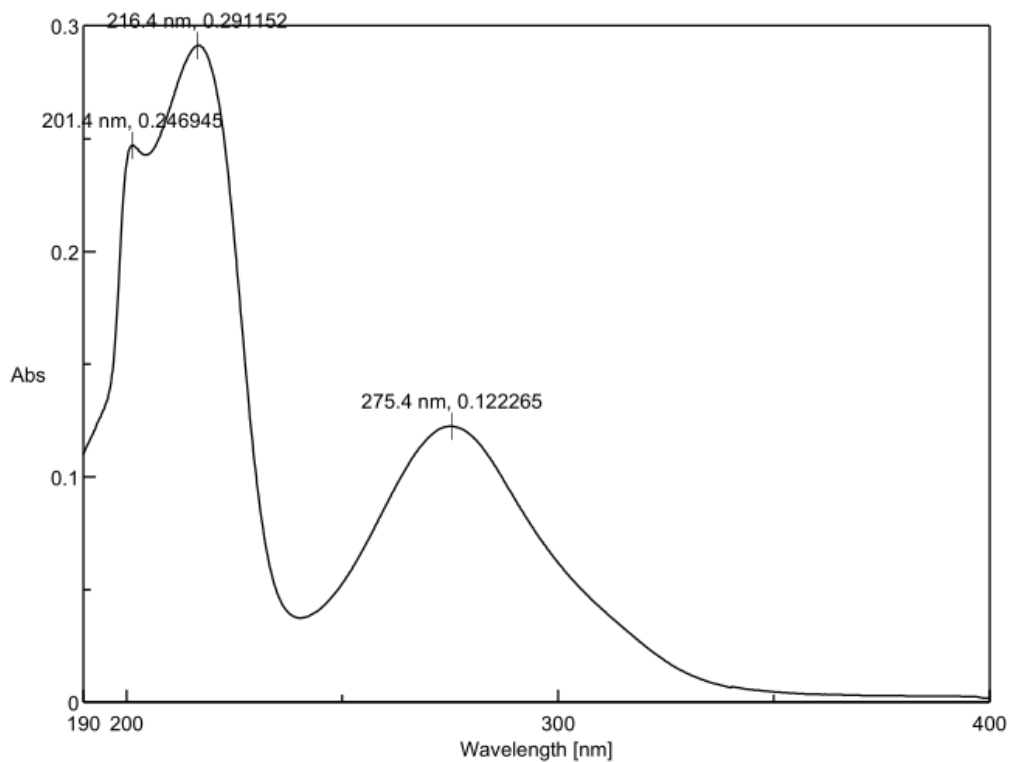


Fig. S36 The UV spectrum of compound **5** in MeOH.

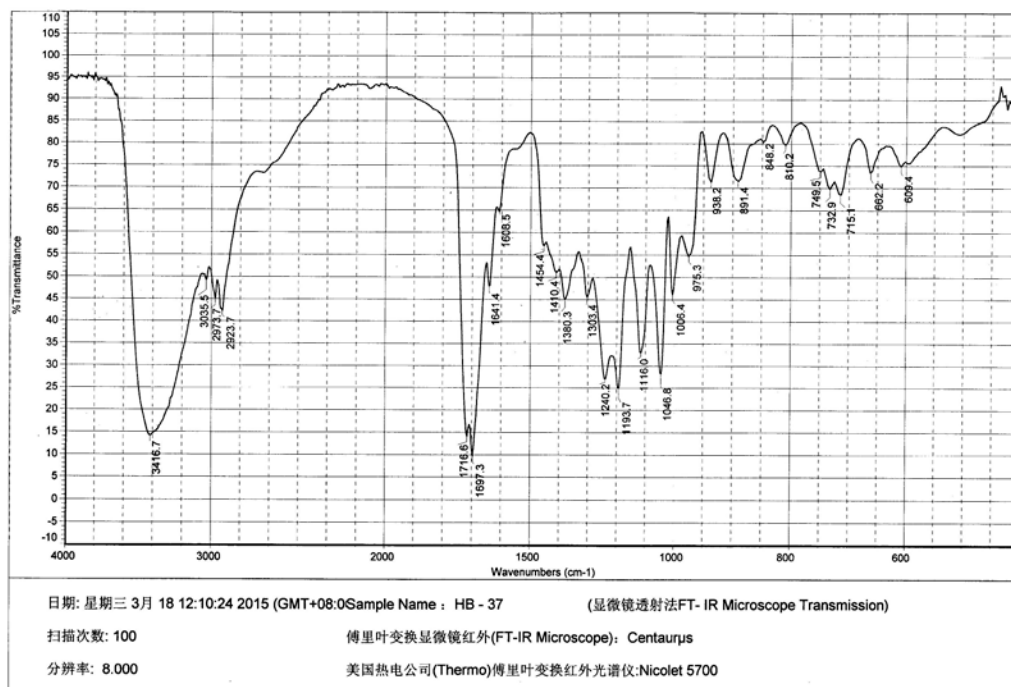


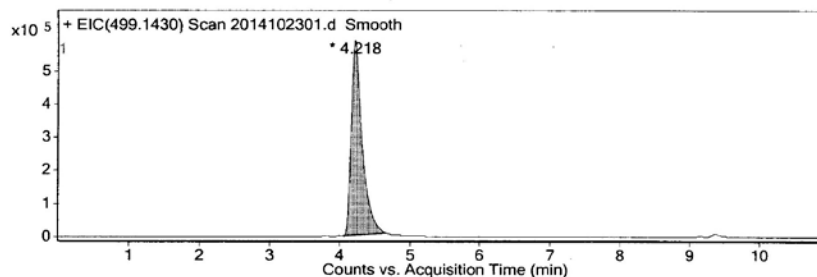
Fig. S37 The IR spectrum of compound **5**.

Qualitative Analysis Report

Data Filename	2014102301.d	Sample Name	HB-37
Sample Type	Sample	Position	P1-C1
Instrument Name	Instrument 1	User Name	
Acq Method	TEST LCMS.m	IRM Calibration Status	XXXXXXXXXX
DA Method	TEST LCMS.m	Comment	

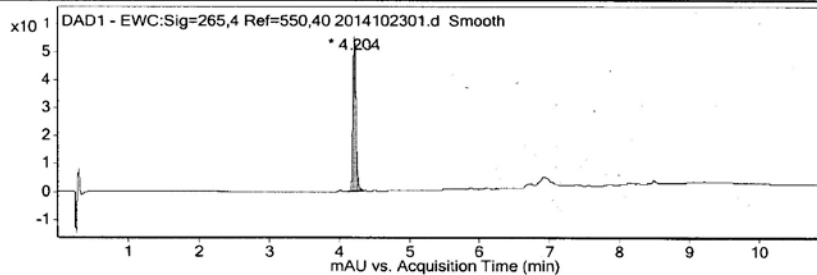
User Chromatograms

Fragmentor Voltage 135 Collision Energy 0 Ionization Mode ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	4.041	4.218	4.669	586539	6477393	100



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	4.109	4.204	4.358	55.12	175.529	100

User Spectra

Fragmentor Voltage 135 Collision Energy 0 Ionization Mode ESI

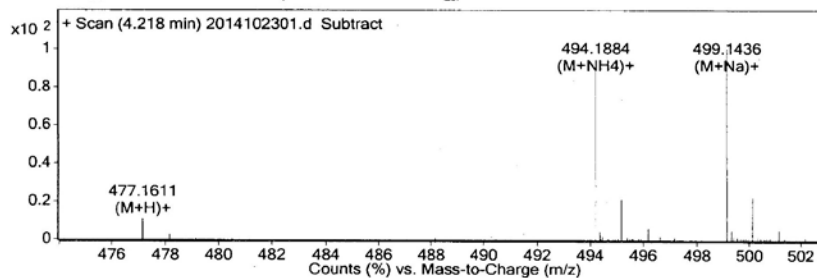


Fig. S38 The HR-ESI-MS data of compound 5.

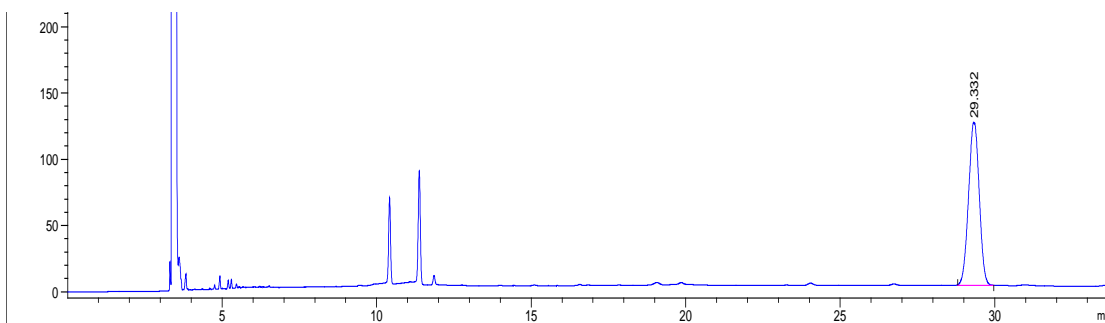


Fig. S39 The Gas Chromatographic separation of D-Glc.

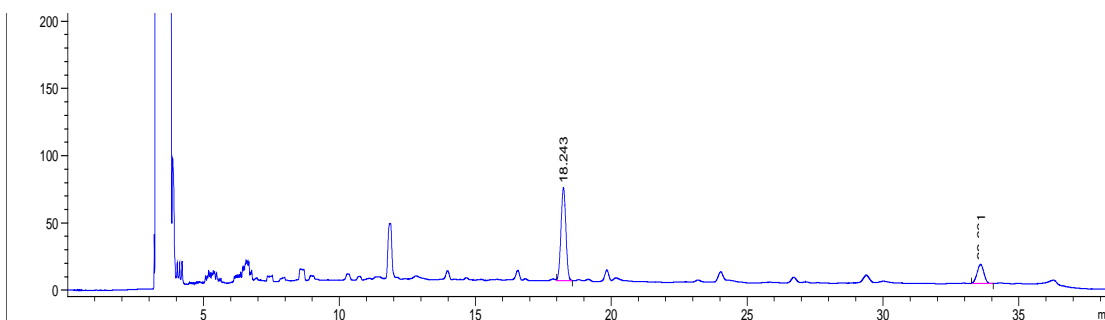


Fig. S40 The Gas Chromatographic separation of D-Api.

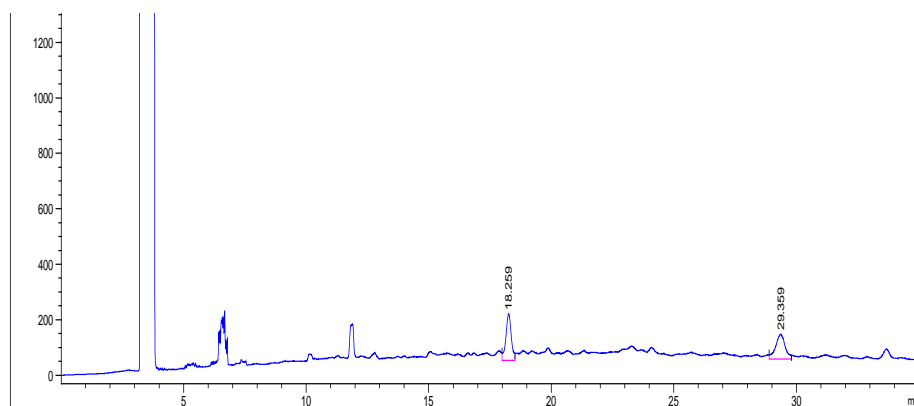
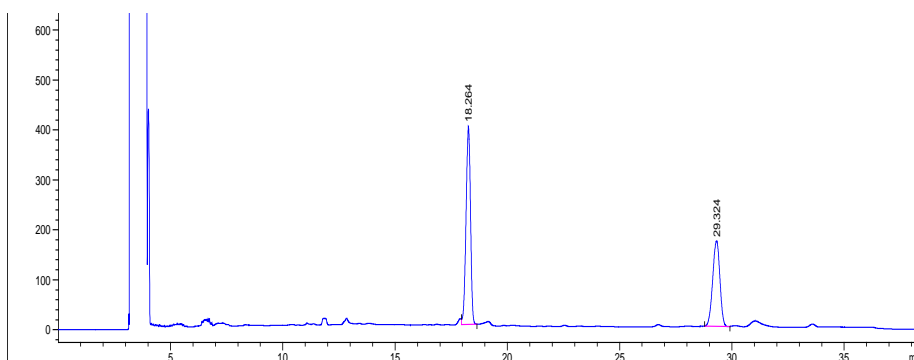
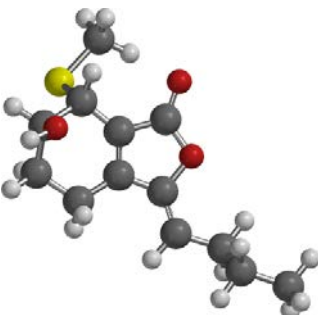
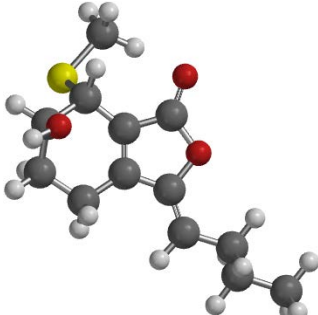
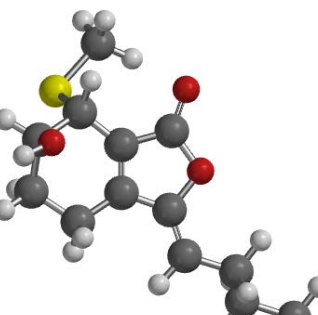
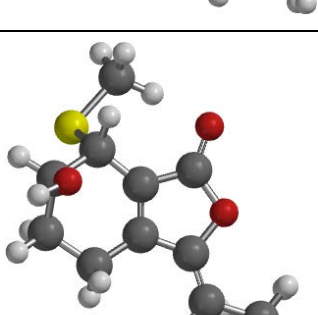
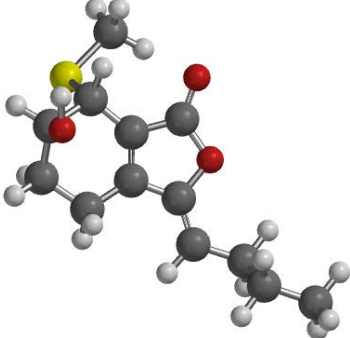
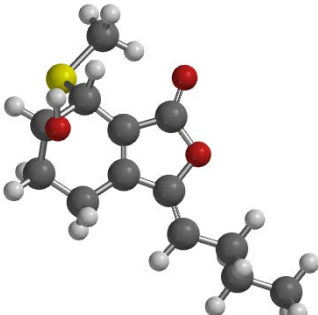
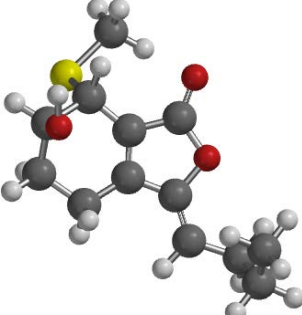
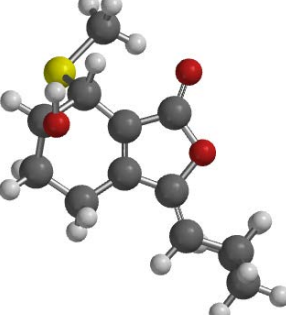
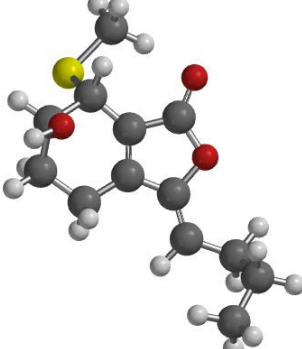
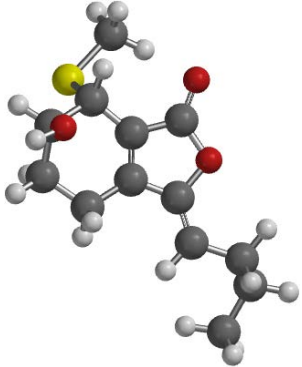
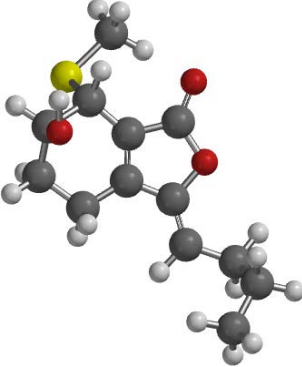
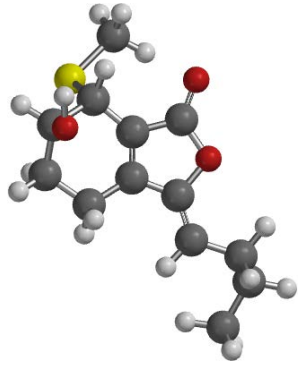
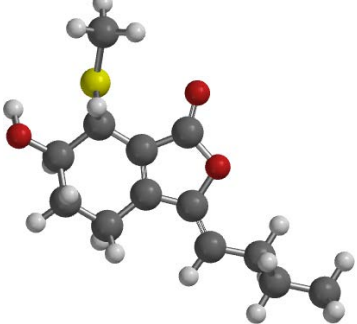
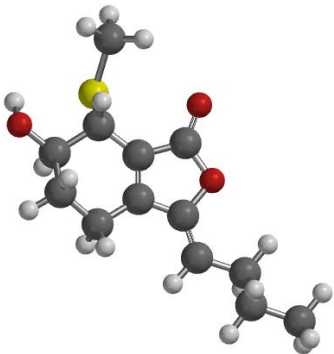


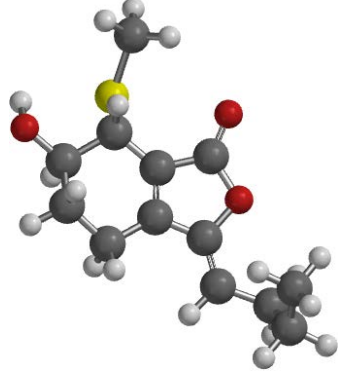
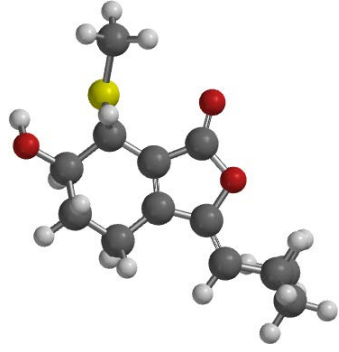
Fig. S41 The Gas Chromatographic analyses of sugar moieties of compounds **4** and **5**.

Table S42 Sixteen optimized conformations of **3Jb**.

no.	conformer	E (kJ/mol)	rel. E (kJ/mol)	Boltzmann Dist
1		55.98	0.00	0.107
2		56.00	0.02	0.107
3		56.06	0.08	0.104
4		56.09	0.12	0.102

5		57.16	1.18	0.067
6		57.18	1.20	0.066
7		57.23	1.26	0.065
8		57.28	1.30	0.064
9		57.94	1.96	0.049

10		57.97	2.00	0.048
11		59.11	3.14	0.030
12		59.15	3.18	0.030
13		60.78	4.80	0.015
14		60.81	4.83	0.015

15		60.88	4.90	0.015
16		60.92	4.94	0.015

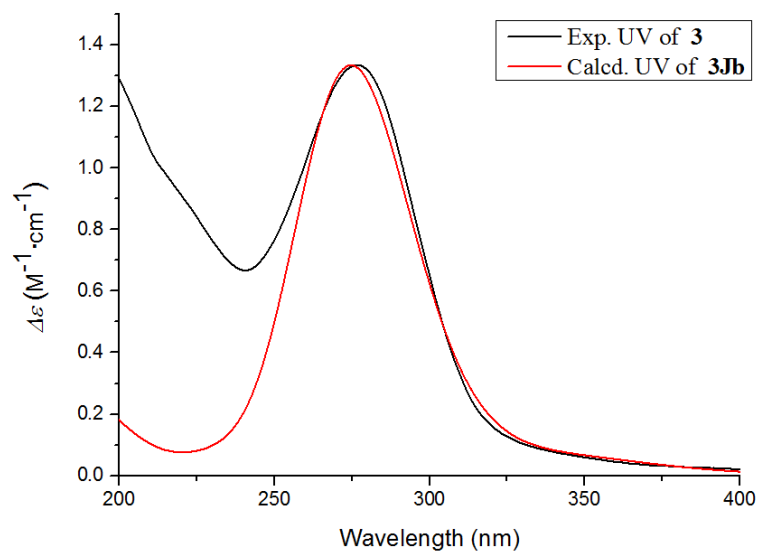


Fig. S43 The experimental UV spectrum of **3** and the calculated UV spectrum of **3Jb**.

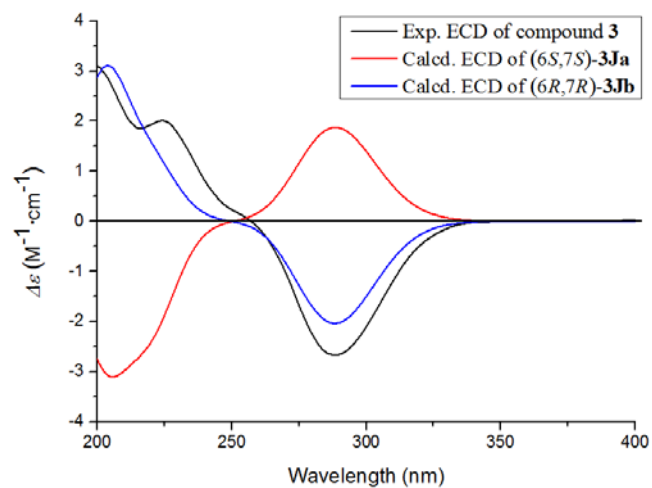


Fig. S44 Experimental ECD and calculated ECD spectrum of **3** in MeOH.