Supporting Information

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Sesquiterpenoids and Diterpenoids from the Flowers of *Nicotiana tabacum* L. and Their Antifungal Activity

Kuo Xu [1], Jiao Wang [1], Jing Liu [1], Lin Ni [3], Yong-Mei Du [1*] and Xiao-Yi Wei [2*]

[1] *Tobacco Research Institute of Chinese Academy of Agricultural Sciences, Qingdao 266101, China*

[2] *Key Laboratory of Plant Resources Conservation and Sustainable Utilization, South China Botanical Garden, Chinese Academy of Sciences, Guangzhou 510650, China*

[3] *Key Laboratory of Biopesticide and Chemical Biology, Ministry of Education, Fujian Agriculture and Forestry University, Fuzhou 350002, China*

Table of Contents	Pages
Figure S1: The ^{1}H NMR spectrum in DMSO-d_6 (600 MHz) of **1**	3
Figure S2: The ^{13}C NMR spectrum in DMSO-d_6 (150 MHz) of **1**	3
Figure S3: The ^{1}H-^{1}HCOSY spectrum in DMSO-d_6 (600 MHz) of **1**	4
Figure S4: The HSQC spectrum in DMSO-d_6 (600 MHz) of **1**	4
Figure S5: The HMBC spectrum in DMSO-d_6 (600 MHz) of **1**	5
Figure S6: The NOE spectrum in DMSO-d_6 (600 MHz) of **1**	5
Figure S7: The HR-ESI-MS data of **1**	6
Figure S8: The ^{1}H NMR spectrum in DMSO-d_6 (600 MHz) of **2**	6
Figure S9: The ^{13}C NMR spectrum in DMSO-d_6 (150 MHz) of **2**	7
Figure S10: The ^{1}H-^{1}HCOSY spectrum in DMSO-d_6 (600 MHz) of **2**	7
Figure S11: The HSQC spectrum in DMSO-d_6 (600 MHz) of **2**	8
Figure S12 : The HMBC spectrum in DMSO-d_6 (600 MHz) of **2**	8
Figure S13: The HR-ESI-MS data of **2**	9
Figure S14: The ^{1}H NMR spectrum in CD_3Cl (600 MHz) of **3**	9
Figure S15: The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **3**	10
Figure S16: The HR-ESI-MS data of **3**	10
Figure S17: The ^{1}H NMR spectrum in CD_3Cl (600 MHz) of **4**	11
Figure S18: The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **4**	11
Figure S19: The HR-ESI-MS data of **4**	12
Figure S20: The ^{1}H NMR spectrum in DMSO-d_6 (600 MHz) of **5**	12
Figure S21: The ^{13}C NMR spectrum in DMSO-d_6 (150 MHz) of **5**	13
Figure S22: The HR-ESI-MS data of **5**	**14**

Figure S23: The ^{1}H NMR spectrum in DMSO-d_6 (600 MHz) of **6**	**14**
Figure S24: The ^{13}C NMR spectrum in DMSO-d_6 (150 MHz) of **6**	**15**
Figure S25: The HR-ESI-MS data of **6**	**15**
Figure S26: The ^{1}H NMR spectrum in CD_3Cl (600 MHz) of **7**	**16**
Figure S27: The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **7**	**16**
Figure S28: The ^{1}H NMR spectrum in CD_3Cl (600 MHz) of **8**	**17**
Figure S29: The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **8**	**17**
Figure S30: The ^{1}H NMR spectrum in CD_3Cl (600 MHz) of **9**	**18**
Figure S31: The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **9**	**19**
S1. Antifungal activity assay	**20**
Table S1: ^{1}H and ^{13}C NMR spectroscopic data (400 MHz, ppm in CDCl) of three known structures similar to those of **1** and **2**	**21**
References	

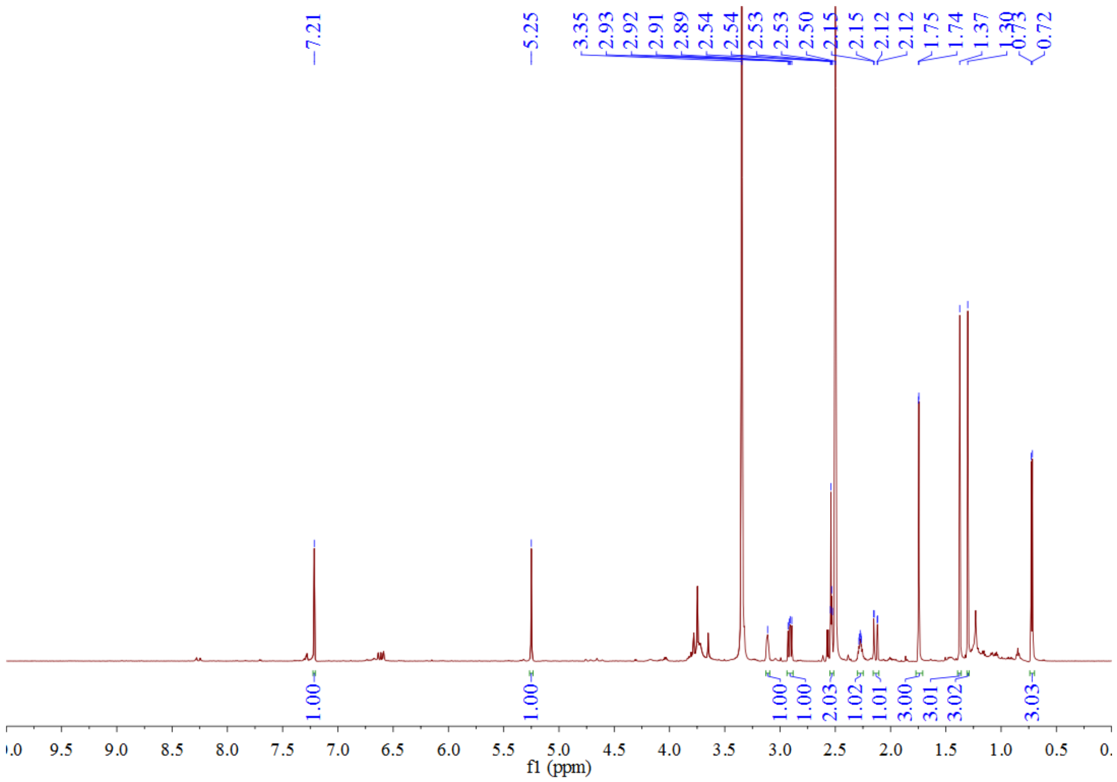


Figure S1: The [1]H NMR spectrum in DMSO-d_6 (600 MHz) of **1**

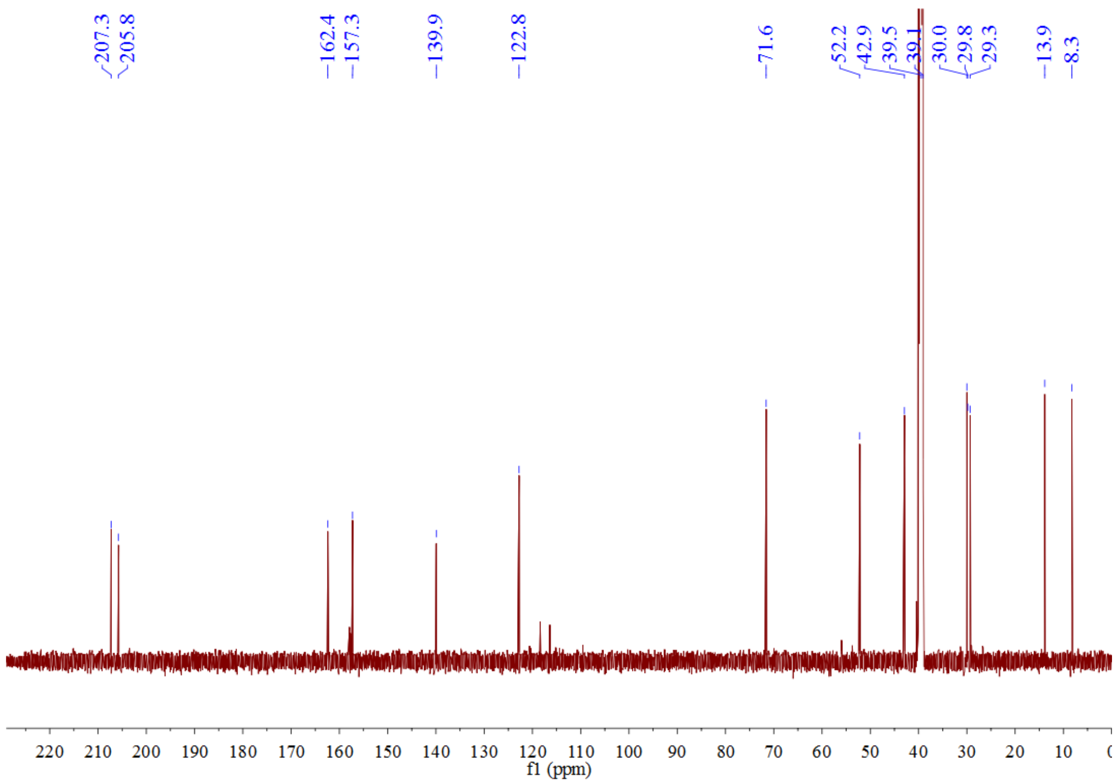


Figure S2: The [13]C NMR spectrum in DMSO-d_6 (150 MHz) of **1**

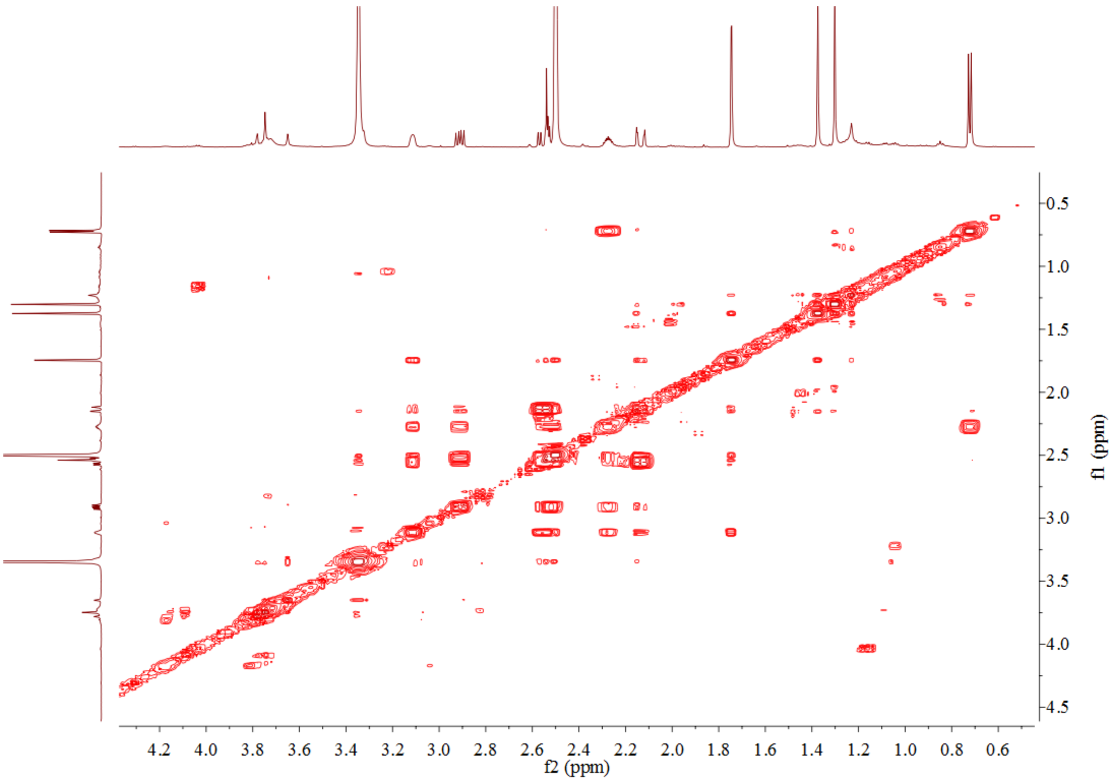


Figure S3: The [1]H-[1]HCOSY spectrum in DMSO-d_6 (600 MHz) of **1**

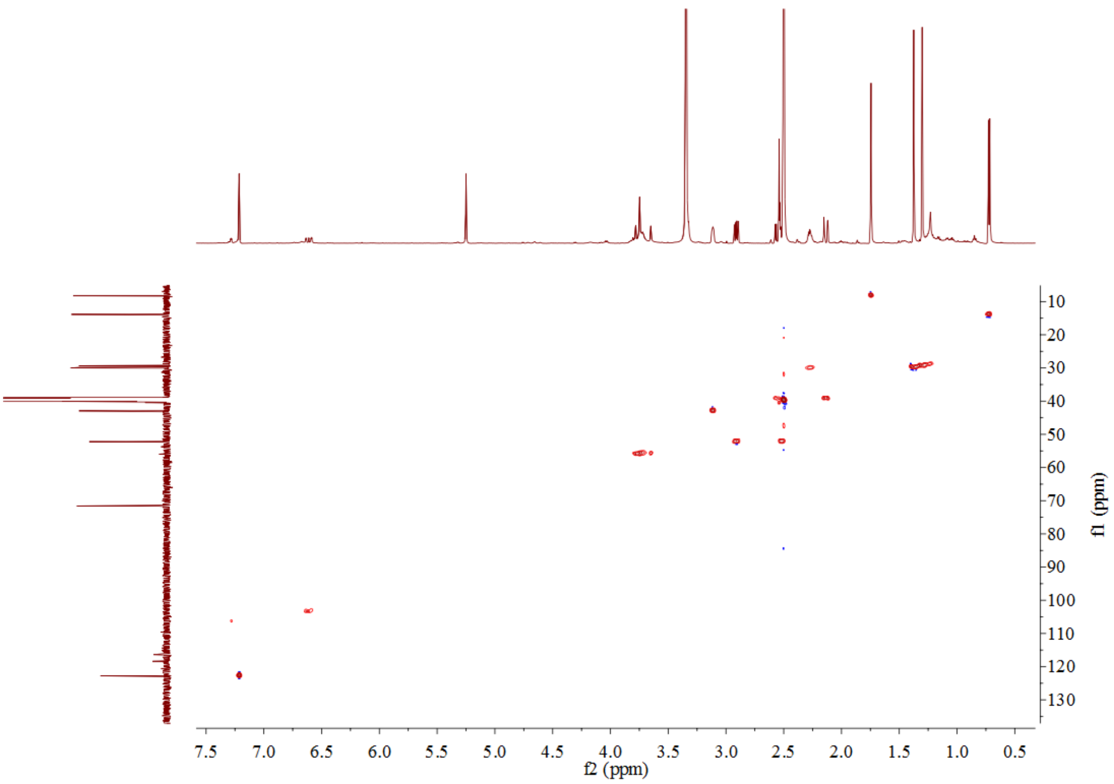


Figure S4: The HSQC spectrum in DMSO-d_6 (600 MHz) of **1**

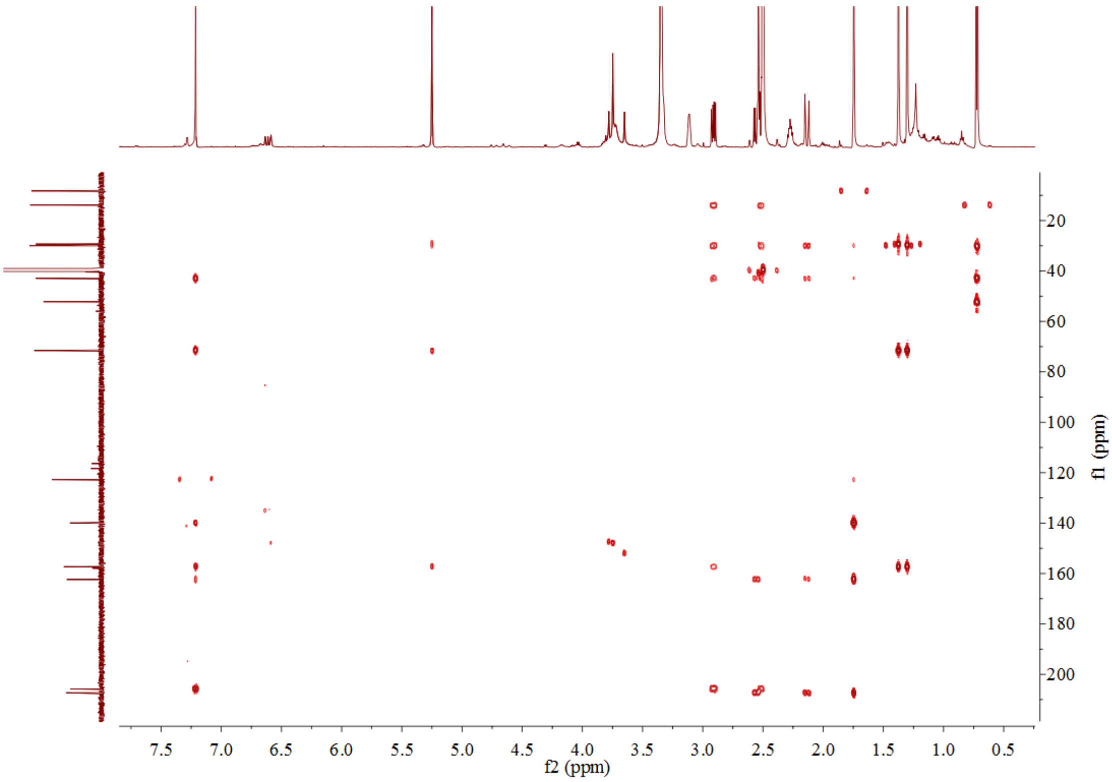


Figure S5: The HMBC spectrum in DMSO-d_6 (600 MHz) of **1**

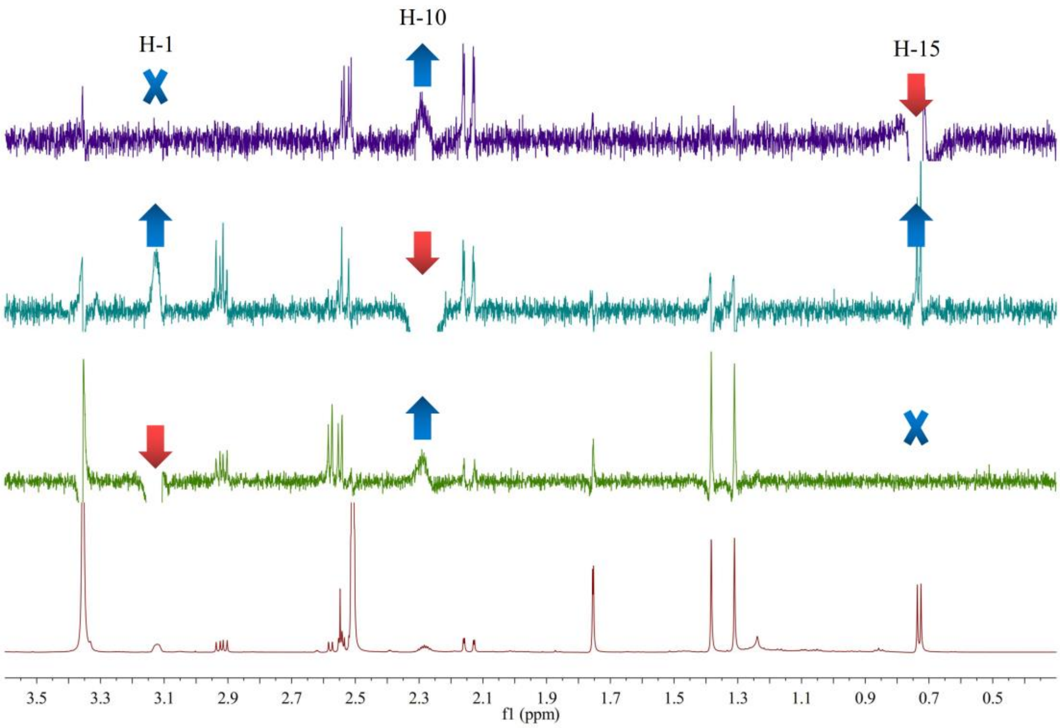


Figure S6: The NOE spectrum in DMSO-d_6 (600 MHz) of **1**

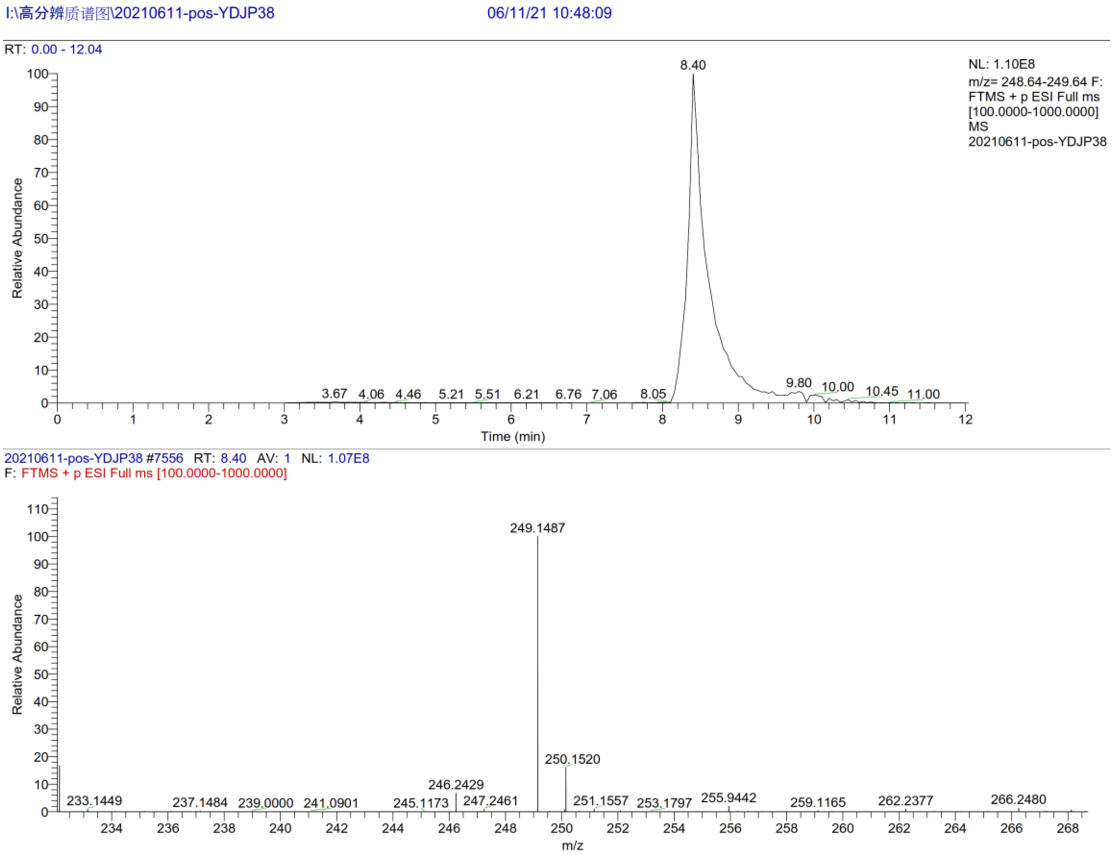


Figure S7: The HR-ESI-MS data of **1**

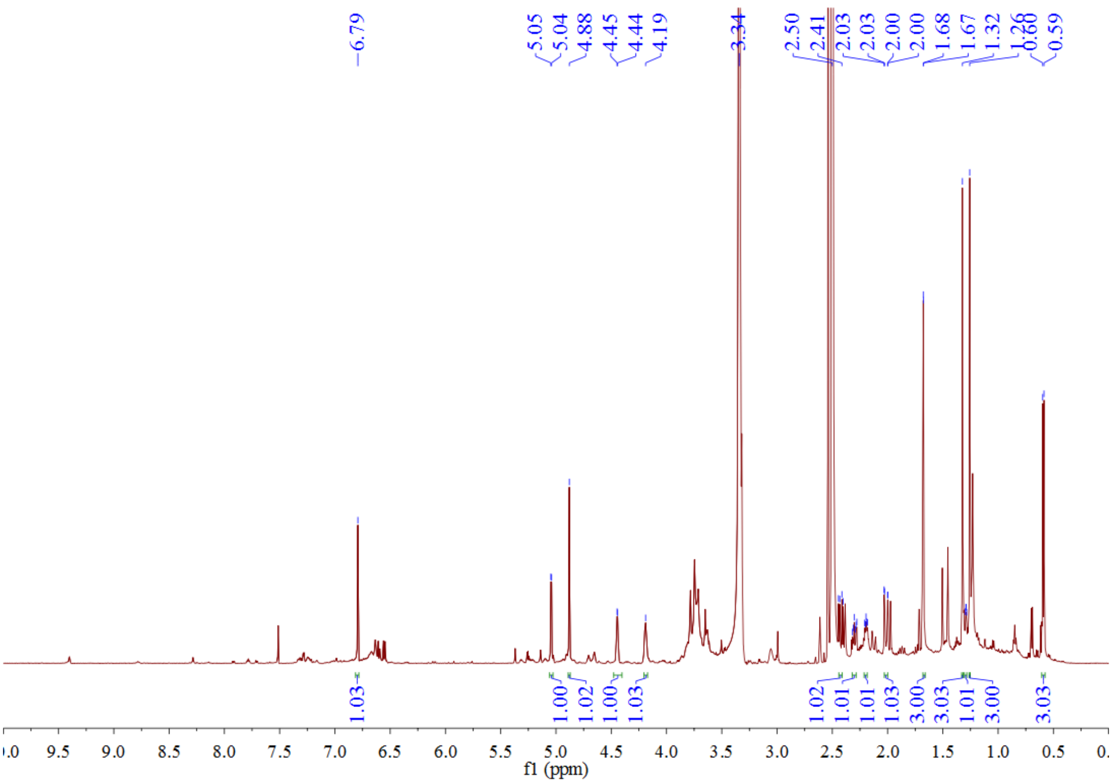


Figure S8: The [1]H NMR spectrum in DMSO-d_6 (600 MHz) of **2**

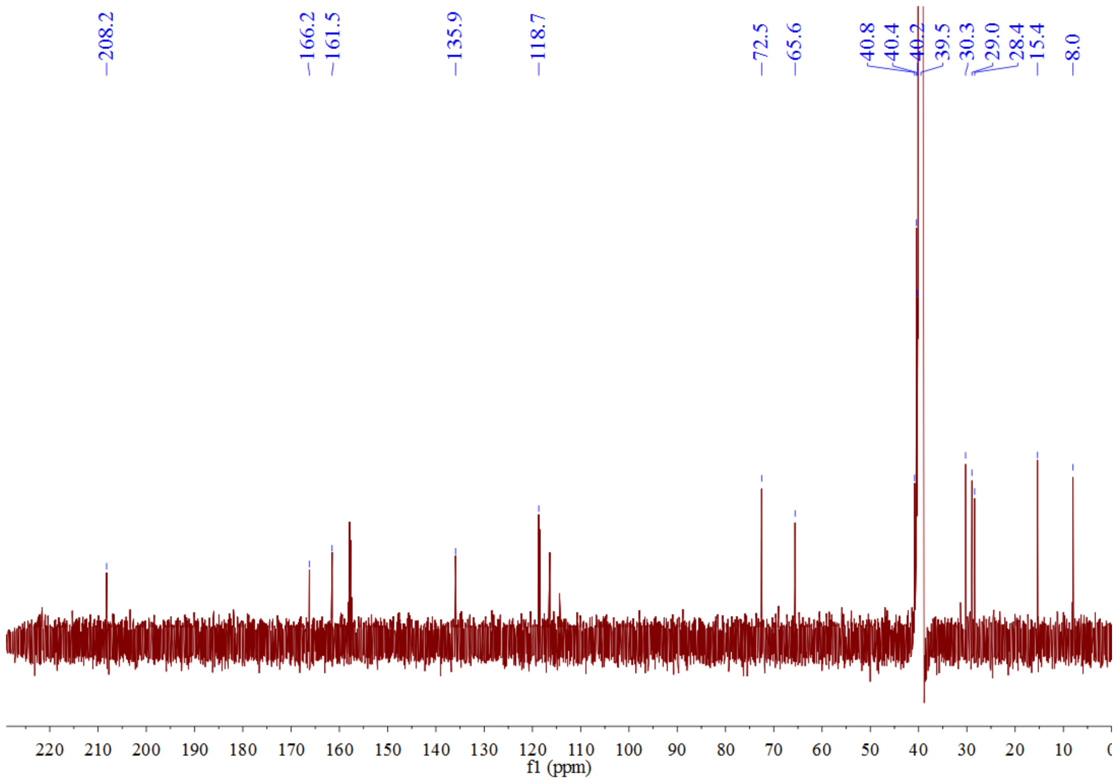


Figure S9: The ^{13}C NMR spectrum in DMSO-d_6 (150 MHz) of **2**

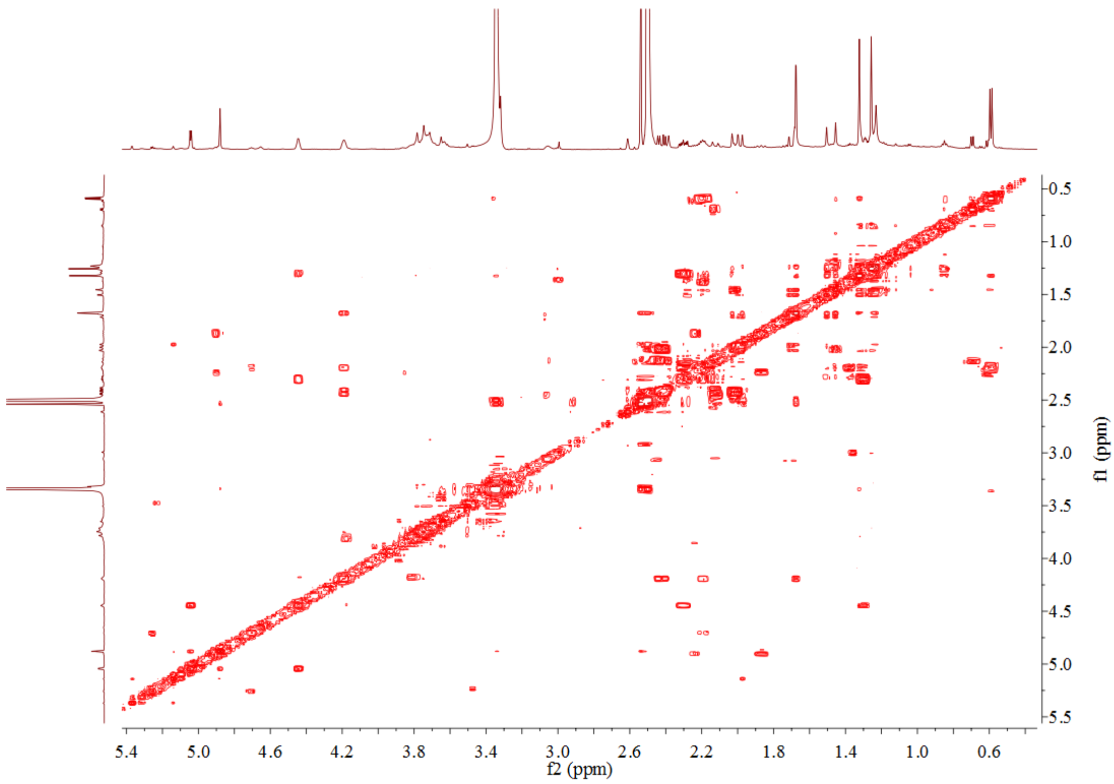


Figure S10: The ^{1}H-^{1}HCOSY spectrum in DMSO-d_6 (600 MHz) of **2**

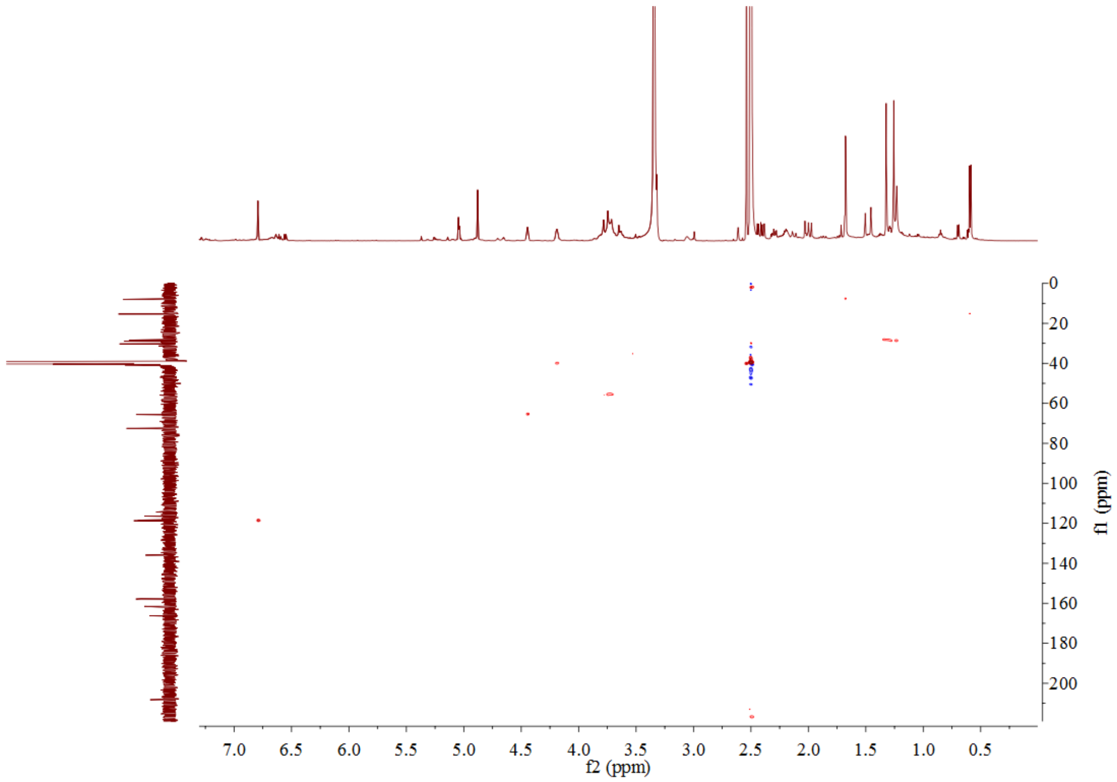


Figure S11: The HSQC spectrum in DMSO-d_6 (600 MHz) of **2**

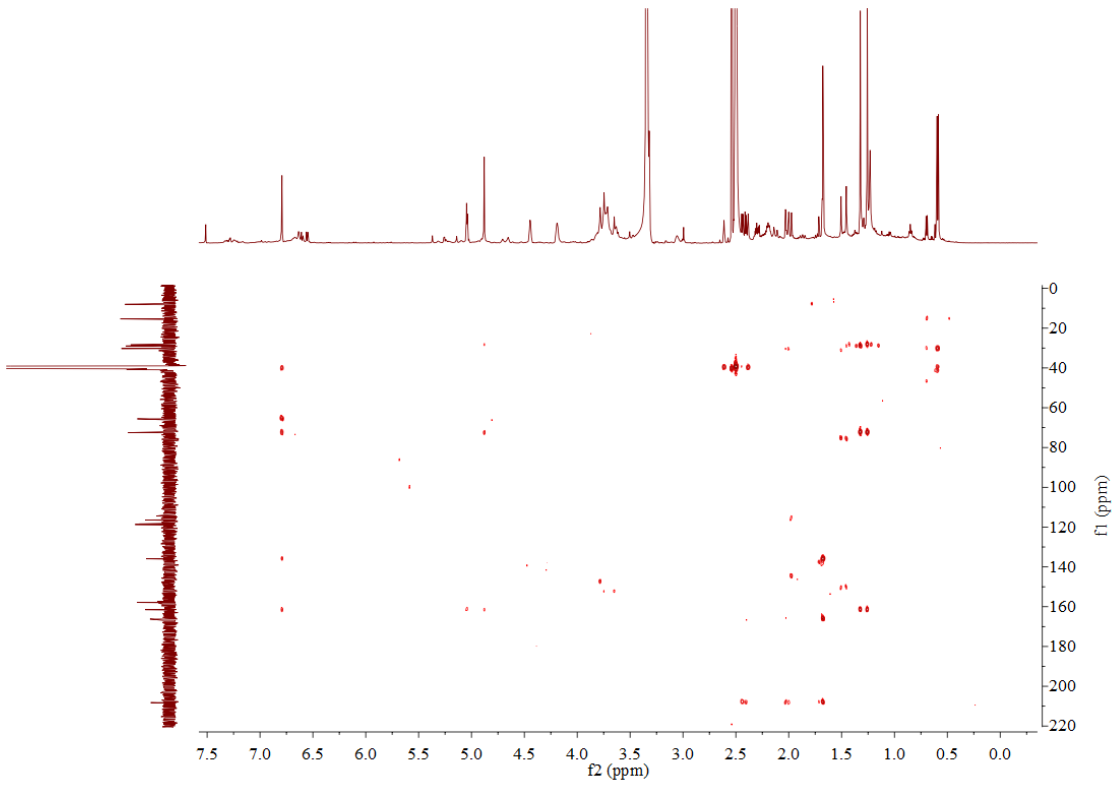


Figure S12: The HMBC spectrum in DMSO-d_6 (600 MHz) of **2**

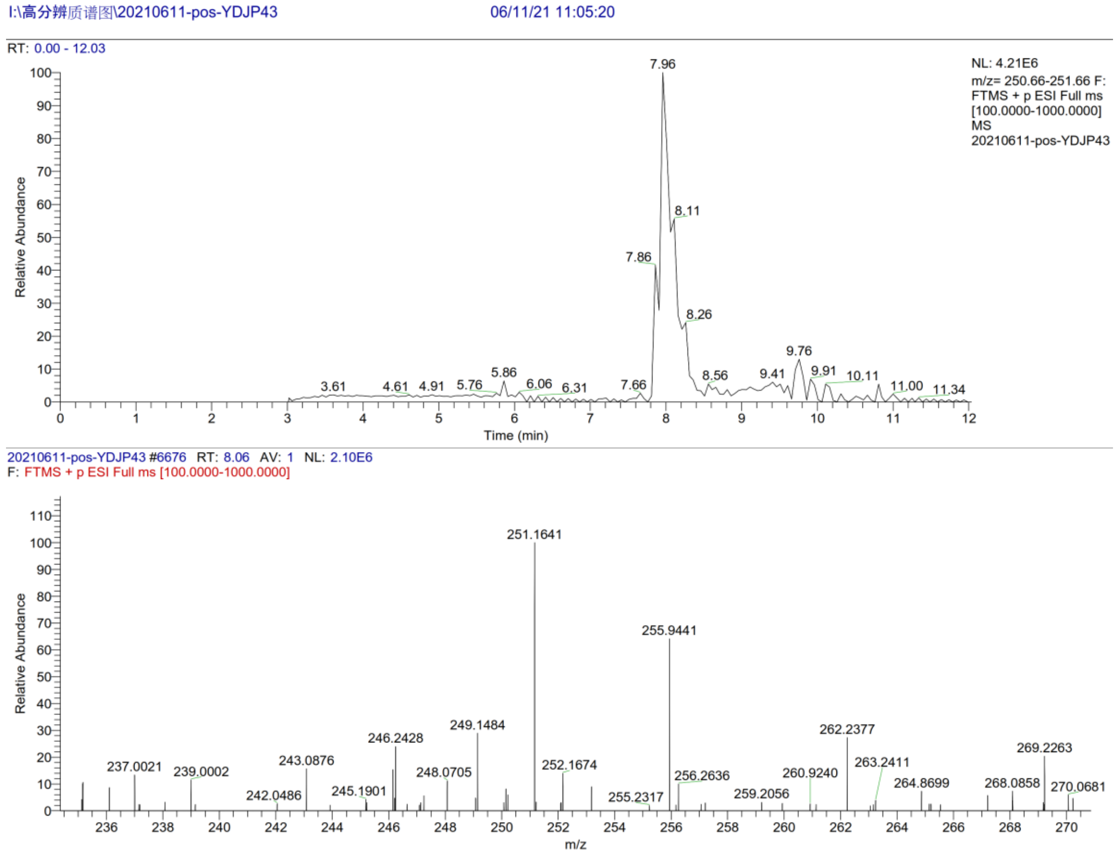


Figure S13: The HR-ESI-MS data of **2**

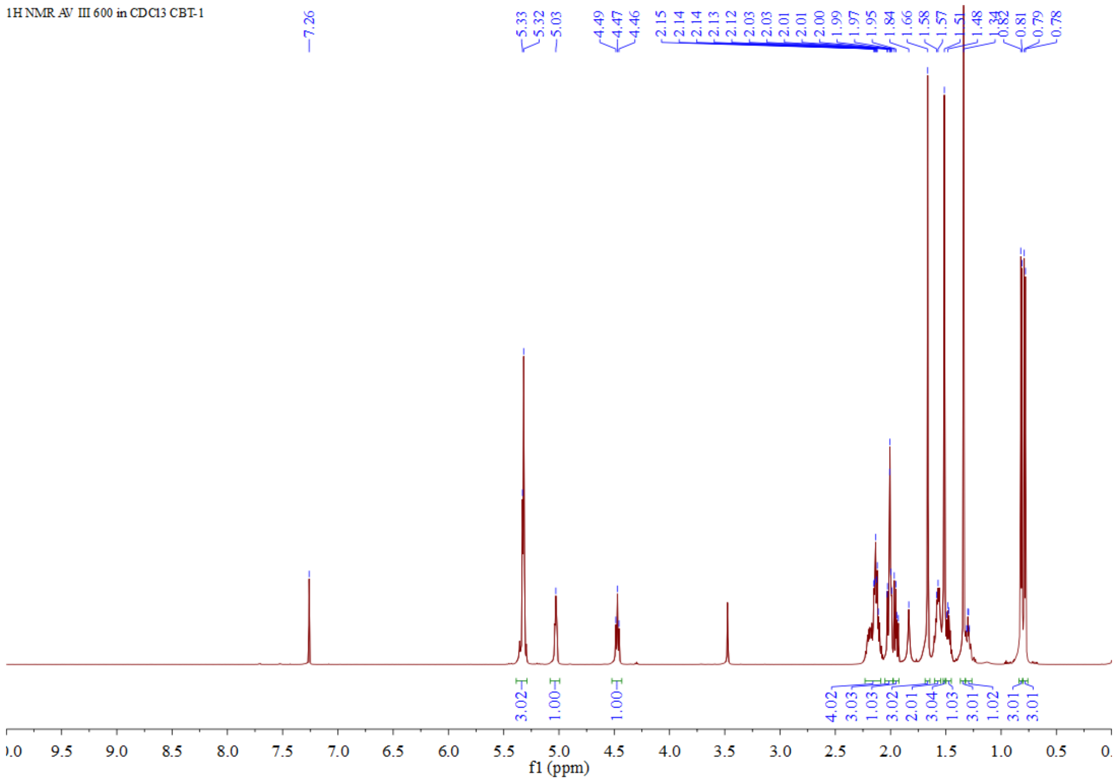


Figure S14: The ^{1}H NMR spectrum in CD_3Cl (600 MHz) of **3**

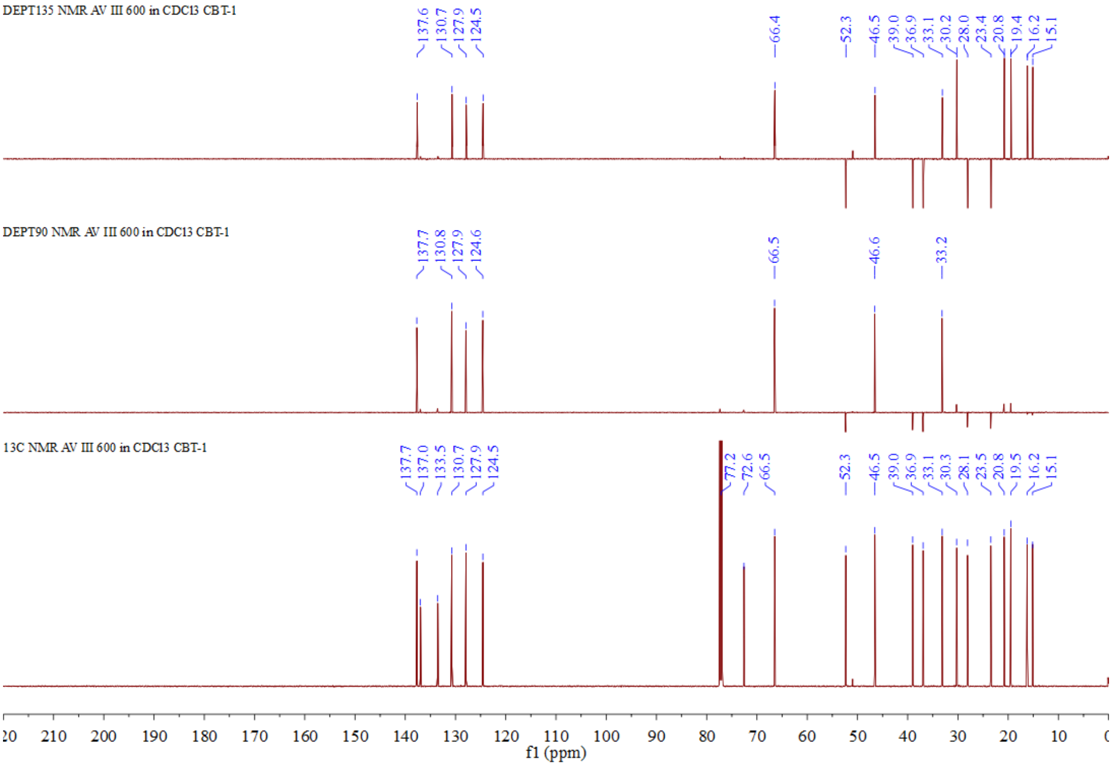
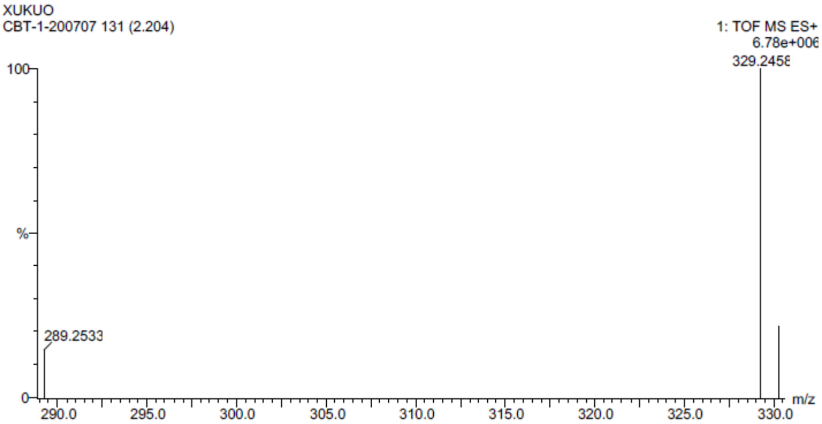


Figure S15: The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **3**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
82 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 O: 0-10 Na: 0-1
XUKUO
CBT-1-200707 131 (2.204)



Minimum: -1.5
Maximum: 1.0 1.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
329.2458	329.2456	0.2	0.6	3.5	44.5	n/a	n/a	C20 H34 O2 Na

Figure S16: The HR-ESI-MS data of **3**

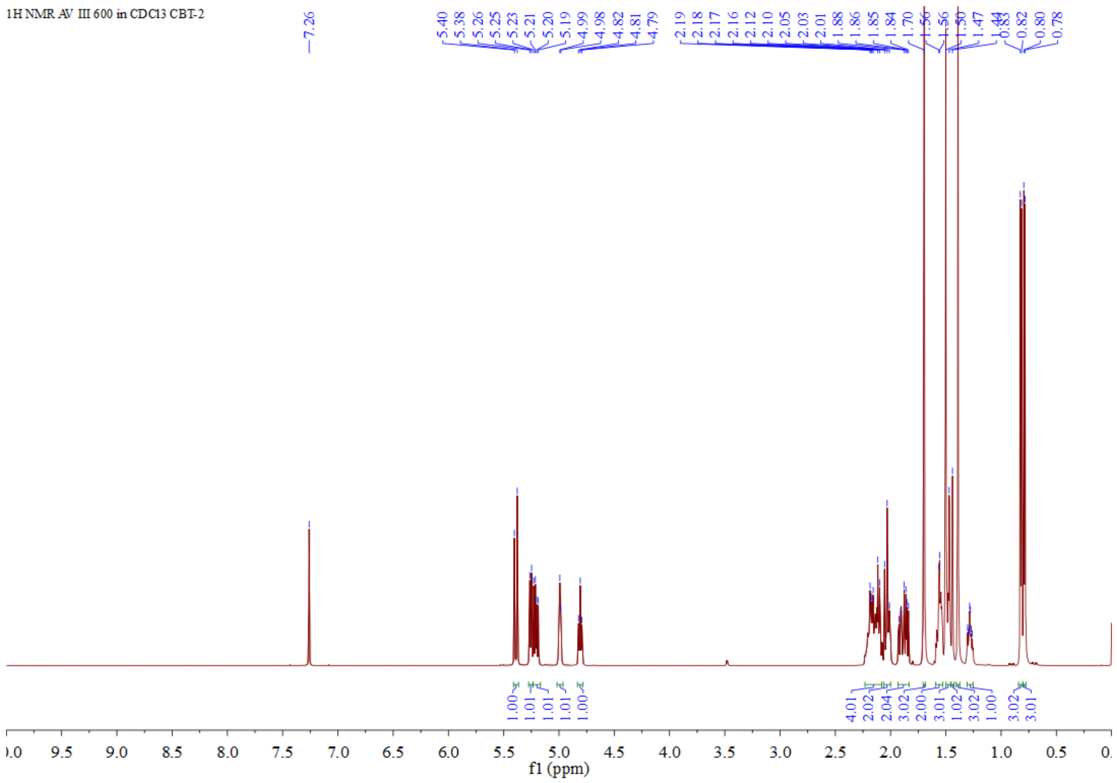


Figure S17: The ^{1}H NMR spectrum in CD_3Cl (600 MHz) of **4**

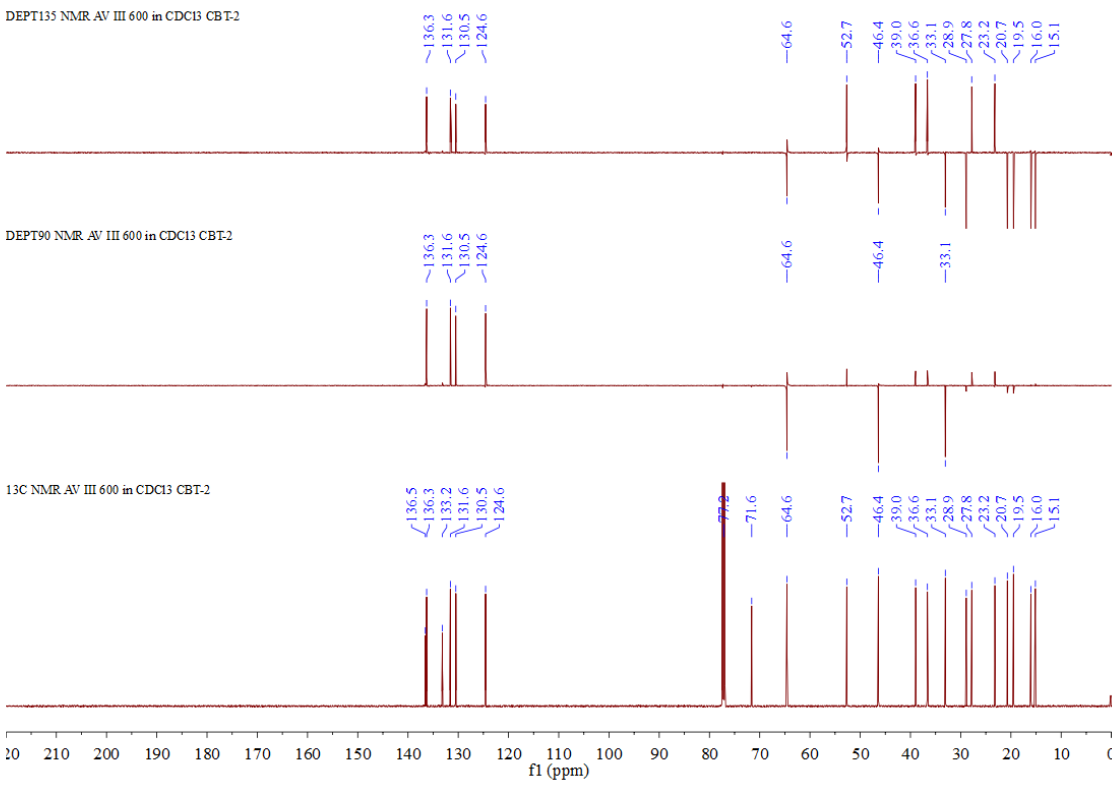
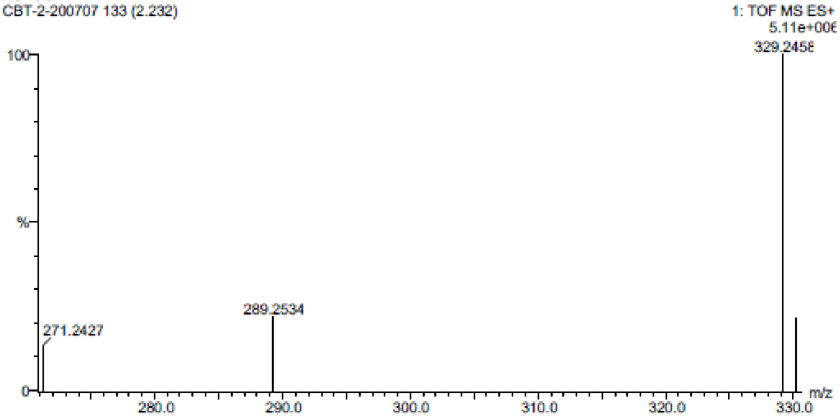


Figure S18: The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **4**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
82 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 O: 0-10 Na: 0-1
XUKUO
CBT-2-200707 133 (2.232)



Minimum: -1.5
Maximum: 1.0 1.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
329.2458	329.2456	0.2	0.6	3.5	43.7	n/a	n/a	C20 H34 O2 Na

Figure S19: The HR-ESI-MS data of **4**

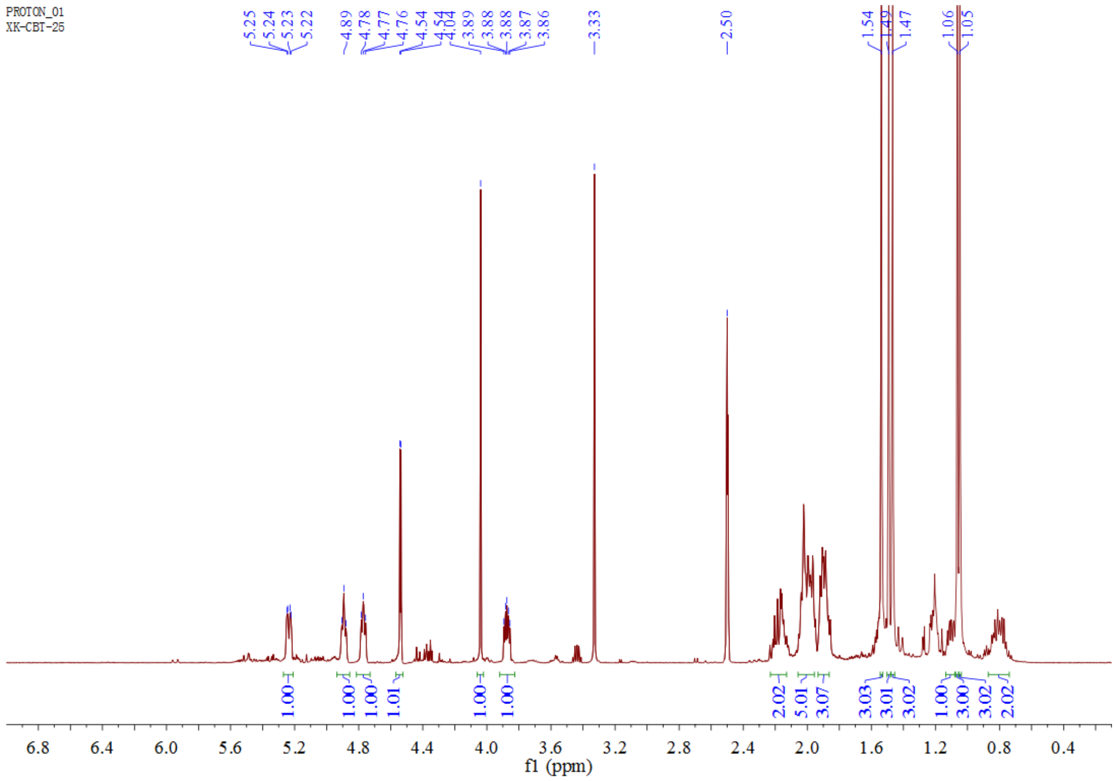


Figure S20: The ^{1}H NMR spectrum in DMSO-d_6 (600 MHz) of **5**

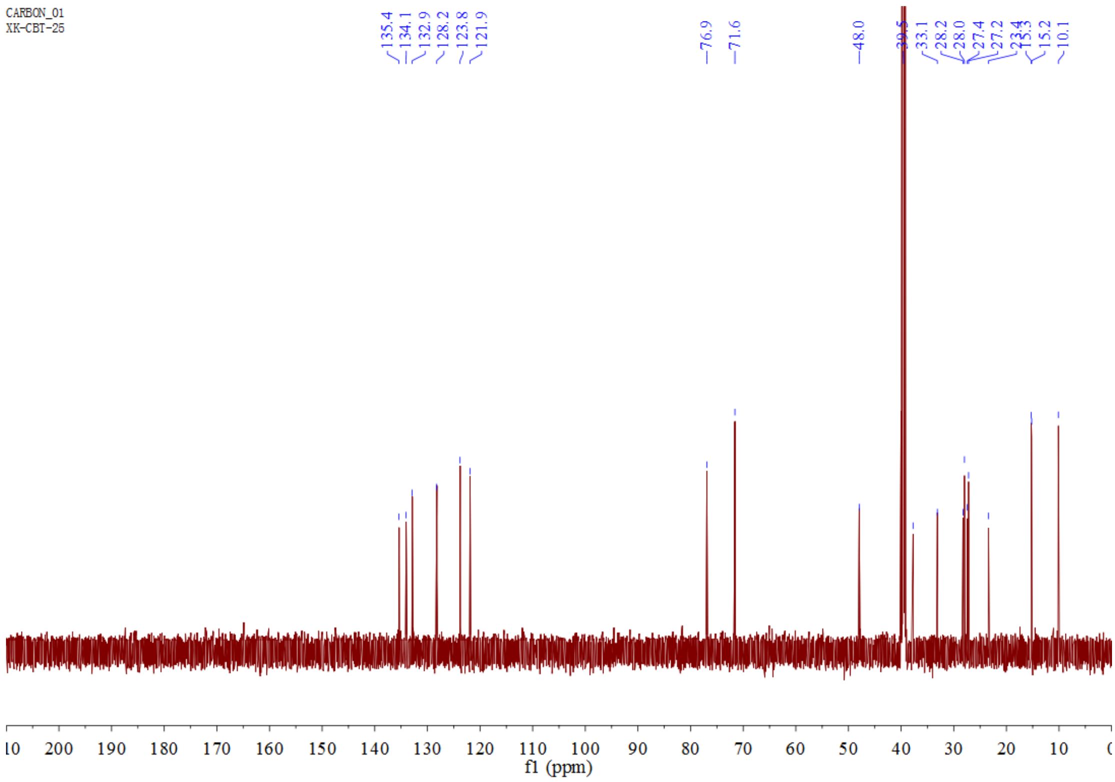


Figure S21: The ^{13}C NMR spectrum in DMSO-d_6 (150 MHz) of **5**

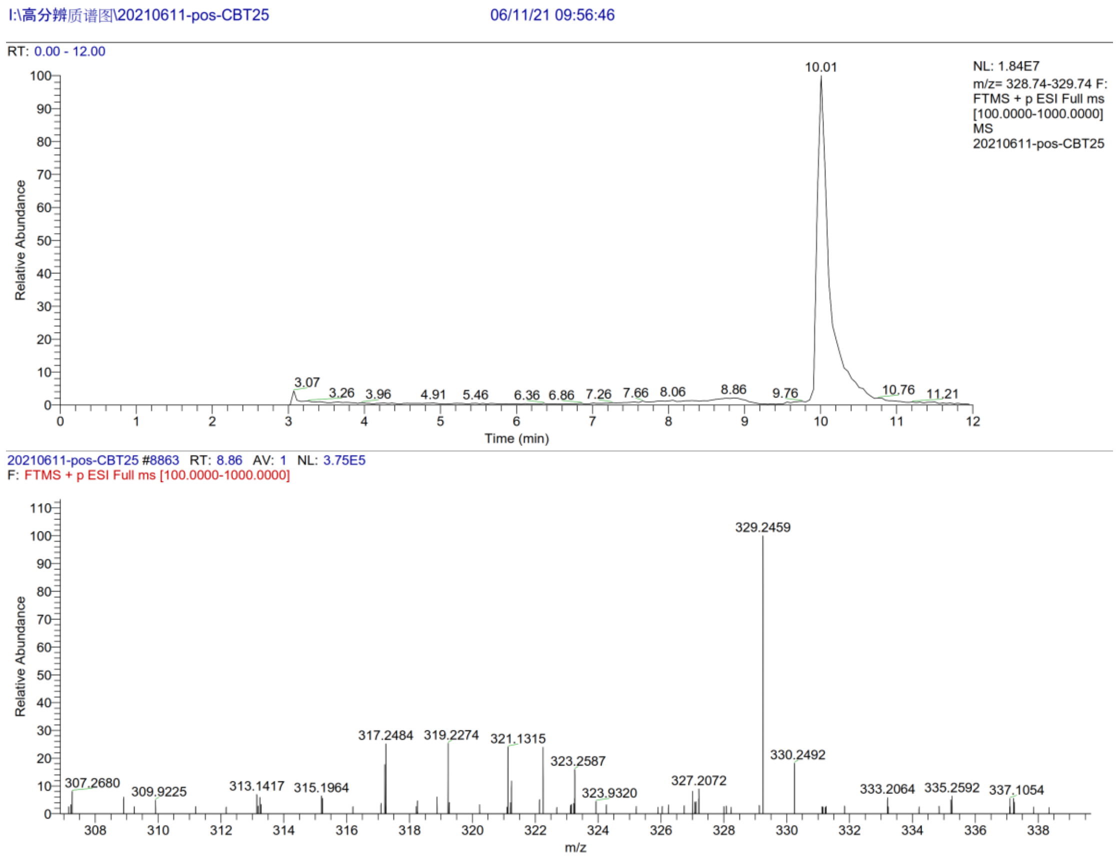


Figure S22: The HR-ESI-MS data of **5**

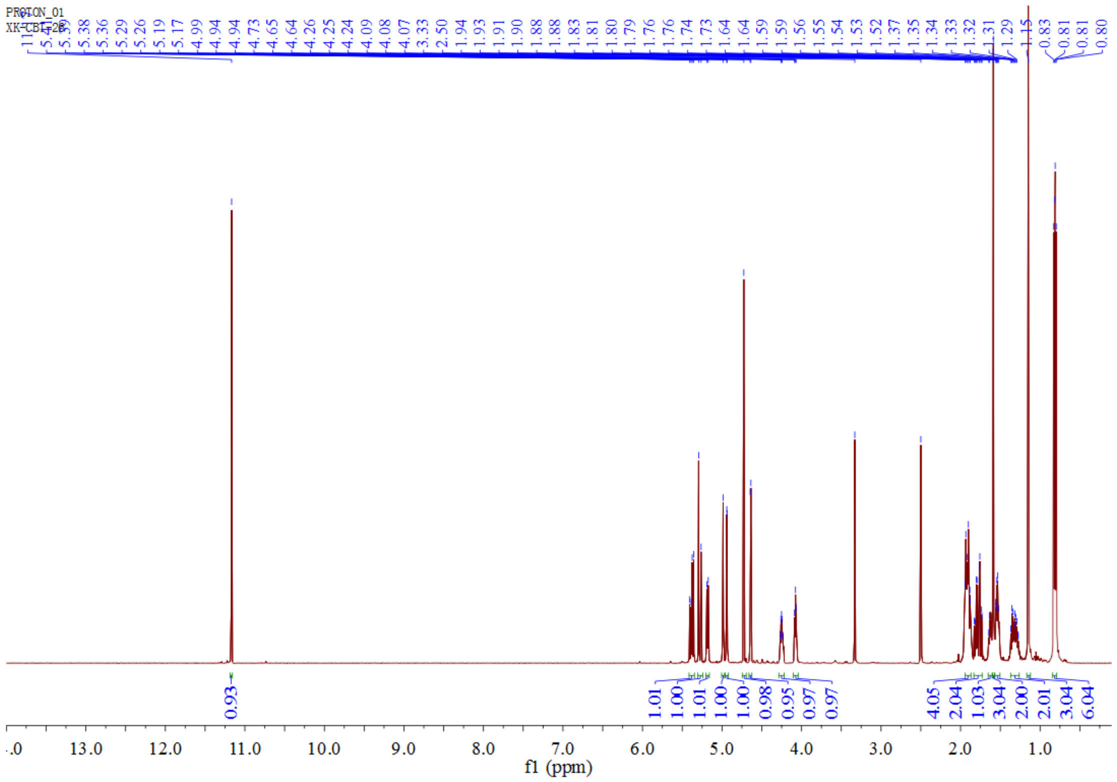


Figure S23: The [1]H NMR spectrum in DMSO-d_6 (600 MHz) of **6**

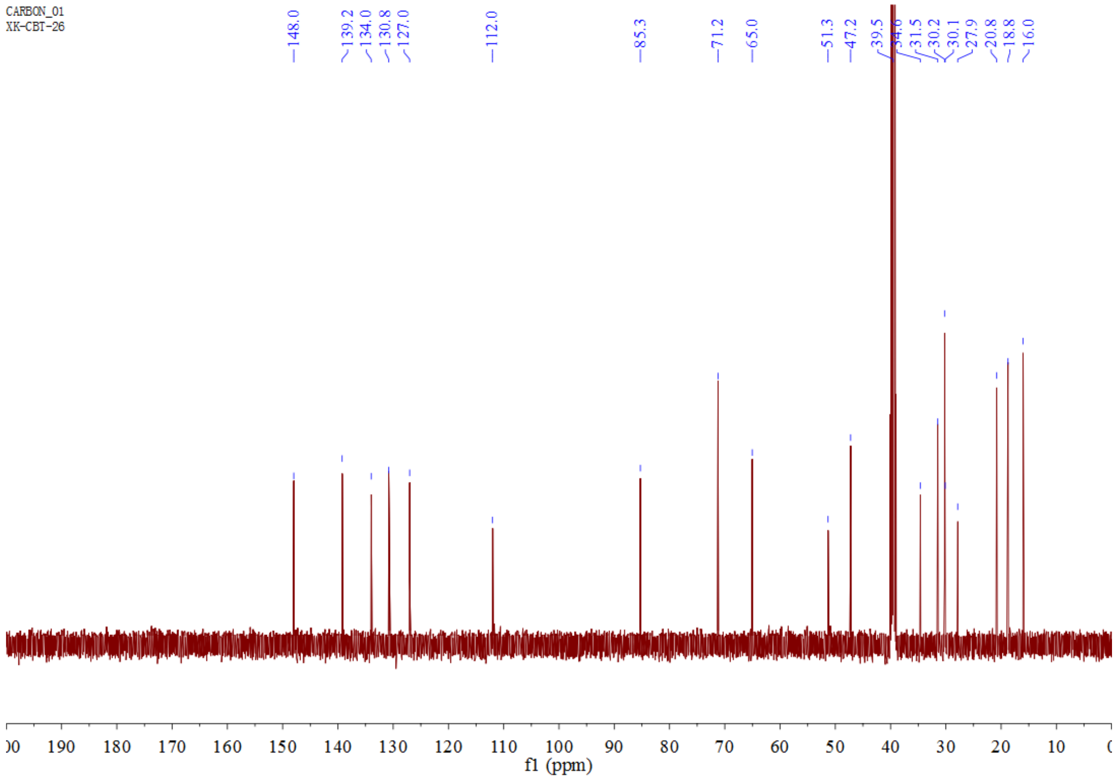


Figure S24: The ^{13}C NMR spectrum in DMSO-d_6 (150 MHz) of **6**

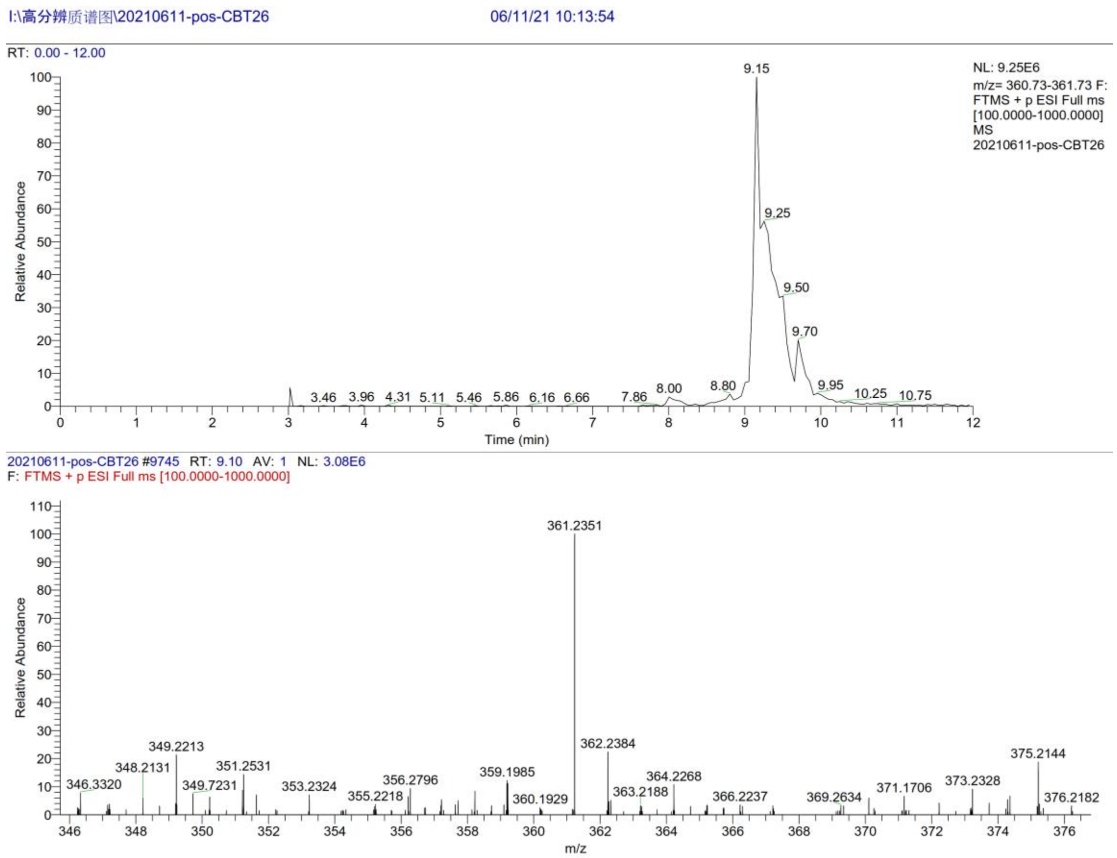


Figure S25: The HR-ESI-MS data of **6**

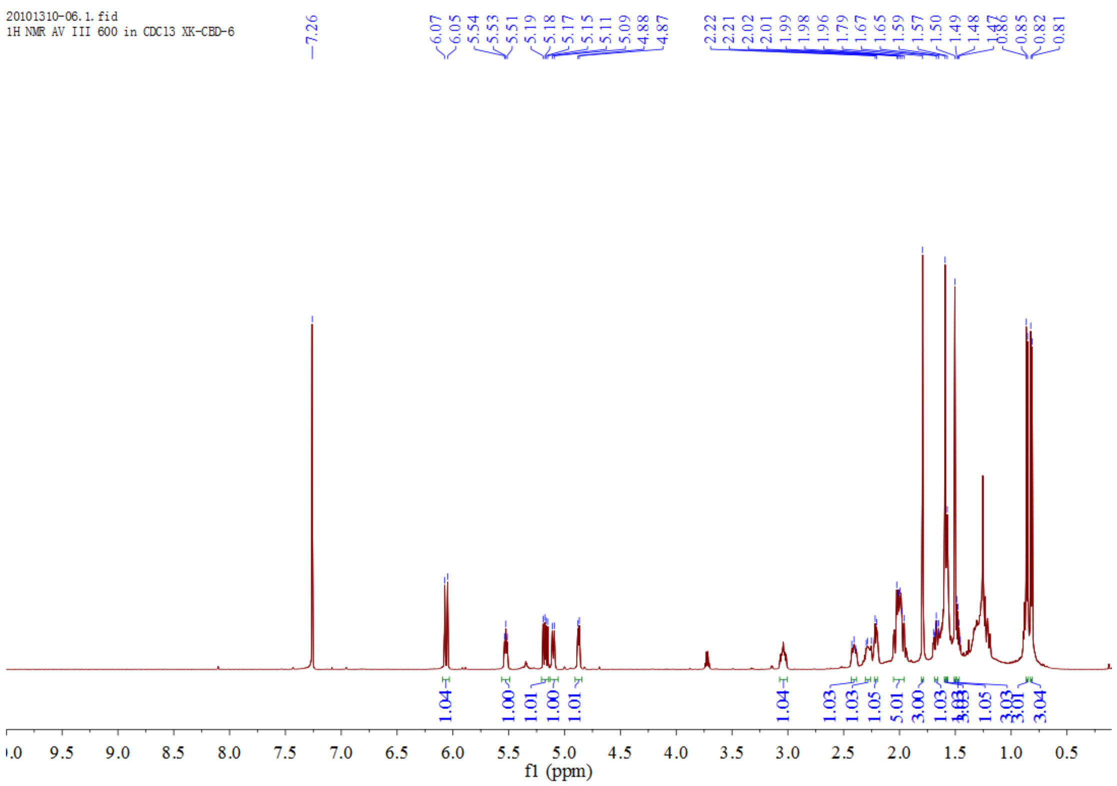


Figure S26: The [1]H NMR spectrum in CD_3Cl (600 MHz) of **7**

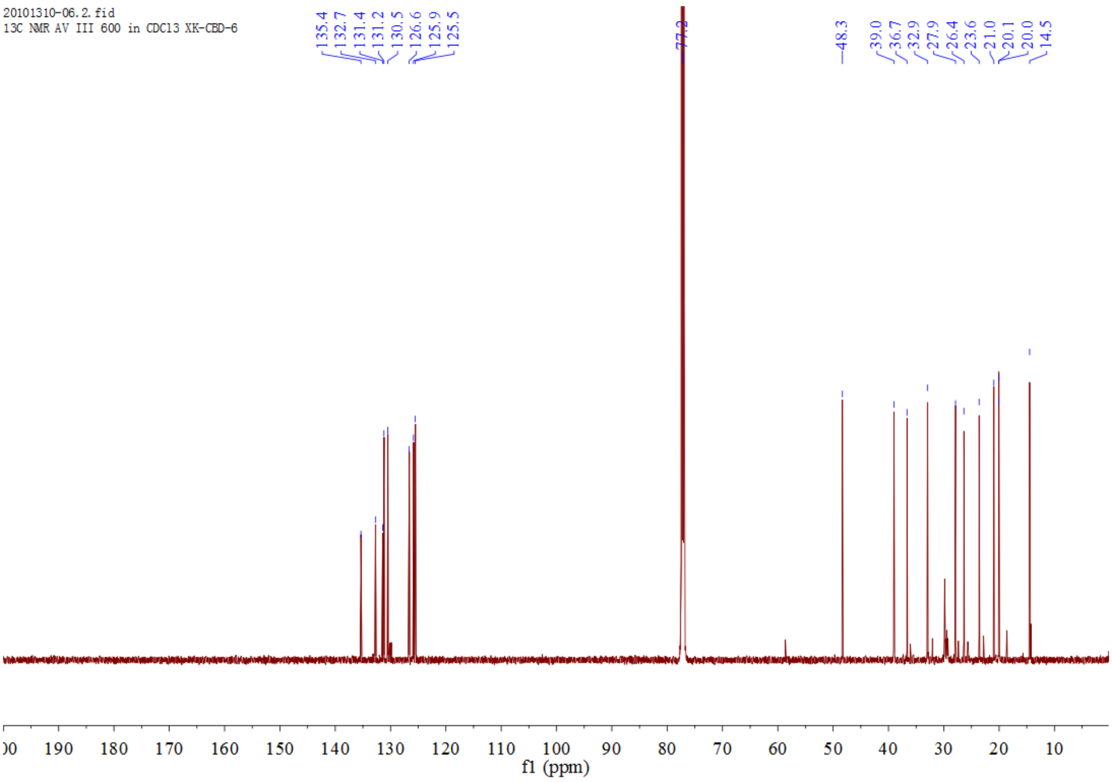


Figure S27: The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **7**

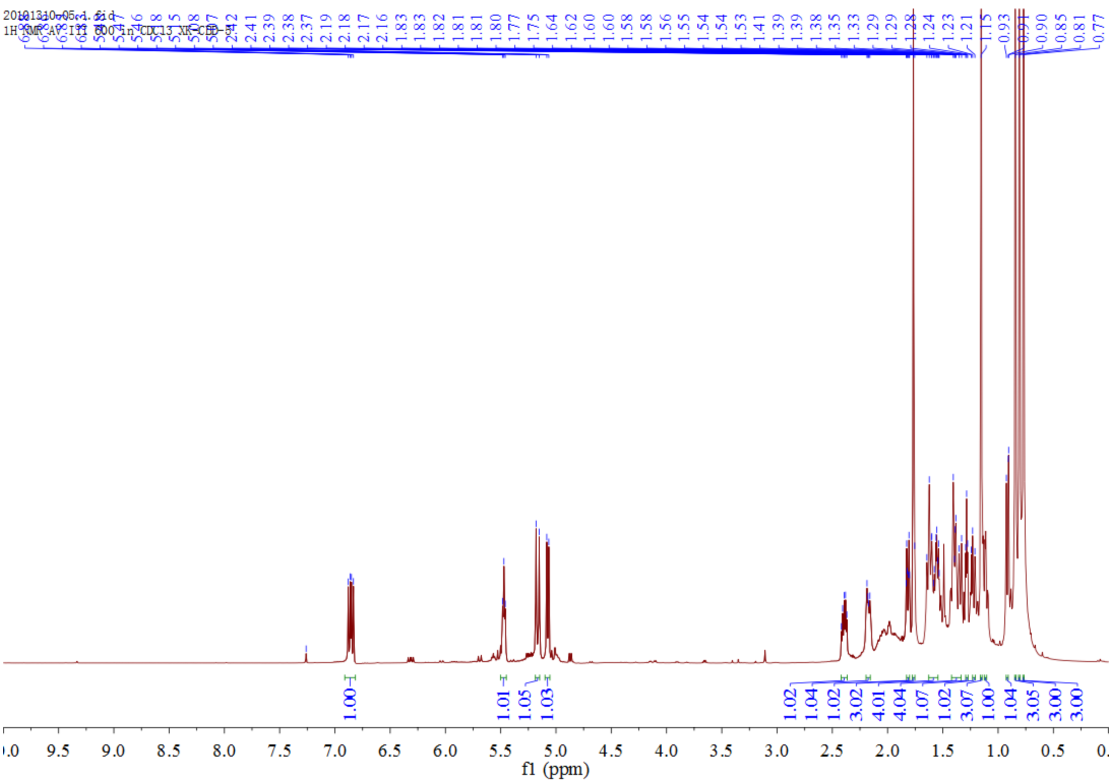


Figure S28: The ^{1}H NMR spectrum in CD_3Cl (600 MHz) of **8**

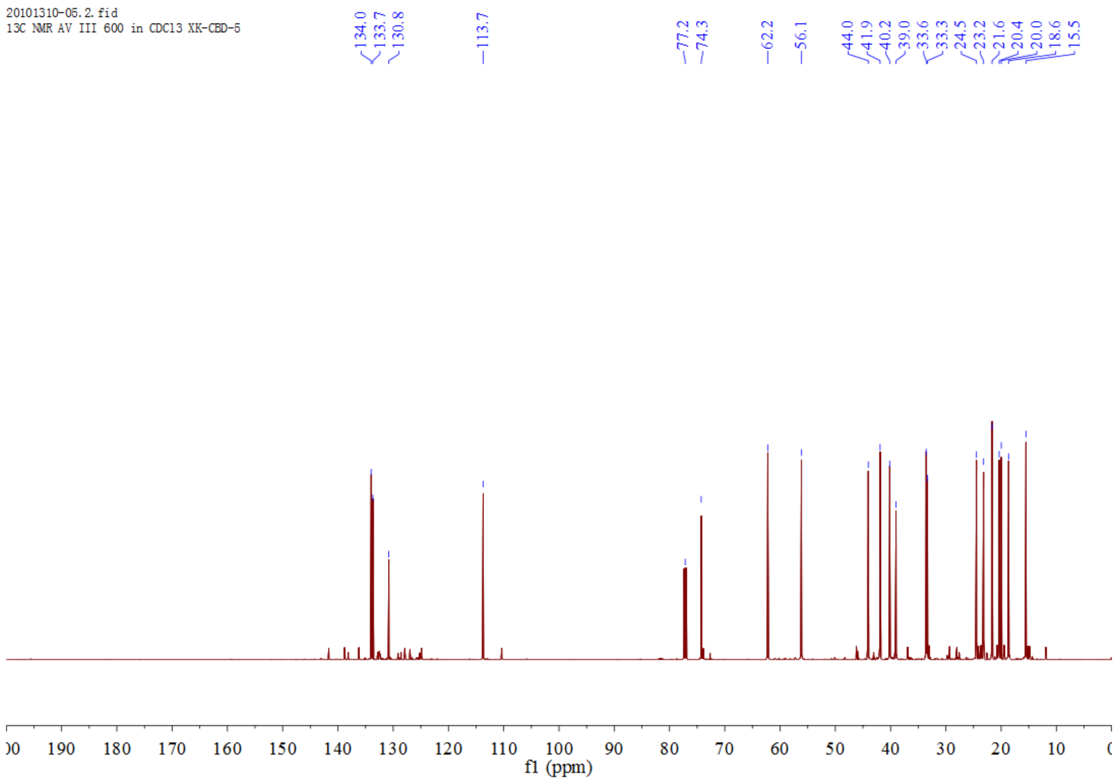


Figure S29:. The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **8**

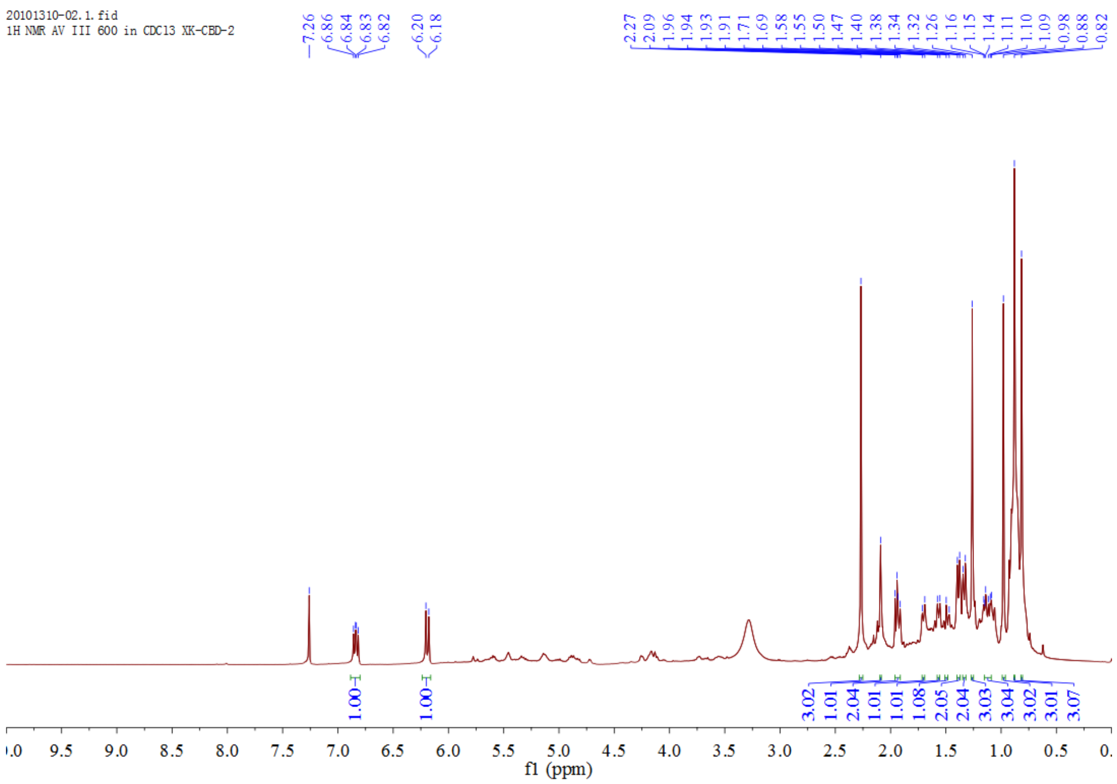


Figure S30: The ^{1}H NMR spectrum in CD_3Cl (600 MHz) of **9**

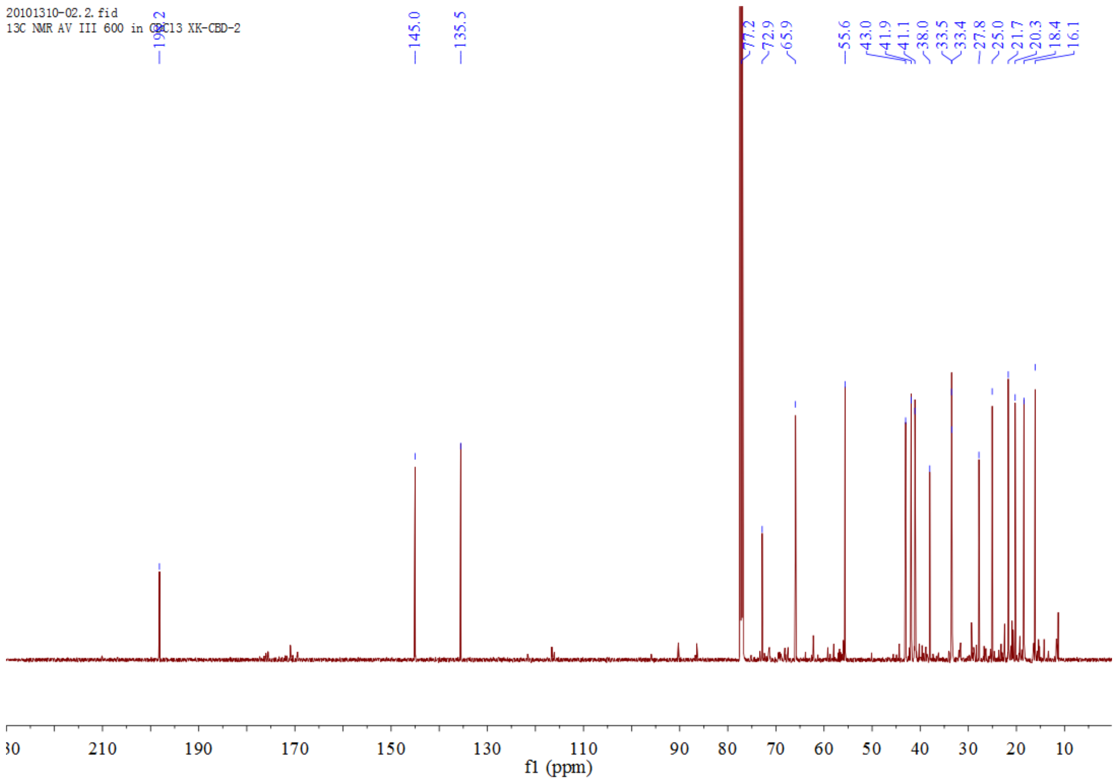
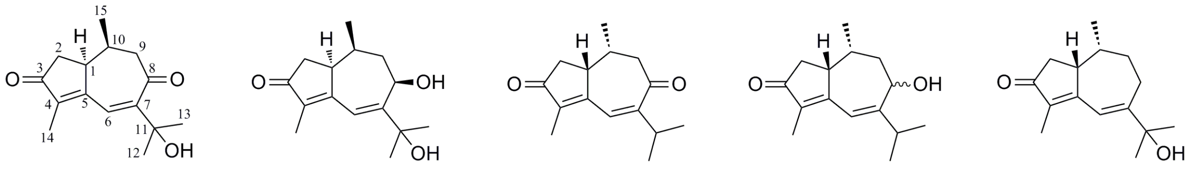


Figure S31: The ^{13}C NMR spectrum in CD_3Cl (150 MHz) of **9**

S1. Antifungal Activity Assay

The antifungal activity against three phytopathogenic fungi (*Valsa mali* var. *mali*, *Alternaria porri*, and *Botrytis cinerea*) were tested using a modified method previously described in the literature [1-2]. All plant pathogens were purchased from Qingdao Agricultural University (Qingdao, China). The isolated compounds were separately dissolved in 95% ethanol at a concentration of 1 mg/mL. After steam sterilization, culture dishes (90 mm) filled with liquid PDA (potato dextrose agar) medium were immediately added to 1 mL of the aforementioned solution and mixed thoroughly; these samples constituted the experimental group (EG). The final concentration of each compound was 10 μg/mL (the dilution ratio was 1:100). PDA medium containing 1 mL of 95% ethanol was used as the control group (CG). After the medium was naturally cooled and solidified, the fungal strains cultured in another PDA culture dish (φ = 9 mm) were inoculated into the center of each dish and repeated three times. The treated fungus was fermented under static conditions at 25 °C for 7 days. The final growth inhibition ratio of the samples was calculated by the cross patch method using the formula $[(\varphi CG–9\ mm) – (\varphi EG–9\ mm)]/(\varphi CG–9\ mm) \times 100\%$. α-CBT-diol, which is a characteristic antifungal constituent of tobacco, was used as the positive control [3].

Table S1: ^{1}H and ^{13}C NMR spectroscopic data (400 MHz, ppm in CDCl) of three known similar structures [4] to compounds **1** and **2**.



1 **2** **10** **11** **12**

Position	Compound **1**		Compound **2**		Compound **10**		Compound **11**		Compound **12**	
	δ_H (*J* in Hz)	δ_C (m)	δ_H (*J* in Hz)	δ_C (m)	δ_H (*J* in Hz)	δ_C (m)	δ_H (*J* in Hz)	δ_C (m)	δ_H (*J* in Hz)	δ_C (m)
1	3.11, brs	42.9, CH	4.19, brs	40.2, CH	2.57-2.63, m	47.3	2.50-2.60, m	49.0	2.58-2.72 (m)	47.0
2a	2.54, overlap	39.1, CH_2	2.42, dd (7.1, 18.6)	40.4, CH_2	2.68, dd (6.8, 18.0)	41.9	2.65, dd (6.0,18.4)	41.4	2.57 (dd, 6.5, 18.0)	42.5
2b	2.13, dd (2.1, 18.8)		2.01, dd (2.0, 18.6)		2.26, dd (2.0, 18.0)		2.19, dd (2.4, 18.4)		2.12 (dd, 1.4, 17.8)	
3		207.3, C		208.2, C		208.0		204.5		206.4
4		139.9, C		135.9, C		139.5		135.7		135.9
5		162.4, C		166.2, C		164.0		169.6		168.3
6	7.21, s	122.8, CH	6.79, s	118.7, CH	6.89, br.s	126.7	6.38, br.s	118.4	6.40 (br.s)	123.0
7		157.3, C		161.5, C		155.3		161.9		157.8
8a		205.8, C	4.44, d (3.0)	65.6, CH		204.3	4.50, dd (1.2, 7.6)	67.9	2.19 (dd, 8.5, 17.0)	26.5
8b									2.45 (dd, 7.4, 17.5)	
9a	2.91, dd (7.5, 13.1)	52.2, CH_2	2.30, m	40.8, CH_2	2.93, dd (4.8, 12.0)	51.6	2.10 (ddd, 4.0,7.6,14.0)	44.3	1.80-1.90 (m)	35.6
9b	2.54, overlap		1.29, overlap		2.44, dd (4.0, 12.0)		1.75 (ddd, 1.6,8.4,14.0)		1.50-1.70 (m)	
10	2.27, m	30.0, CH	2.19, m	30.3, CH	1.82-1.85, m	36.6	1.88-1.92 (m)	33.3	1.50-1.70 (m)	39.2
11		71.6, C		72.5, C	3.00, br.hept(6.9)	31.4	2.77 (br.hept, 6.8)	34.7	2.58-2.72 (m)	47.4
12	1.37, s	29.8, CH_3	1.26, s	29.0, CH_3	1.15, d (7.2)	21.3	1.16 (d, 6.8)	21.2	3.59-3.70 (m)	66.1
13	1.30, s	29.3, CH_3	1.32, s	28.4, CH_3	1.70, d (6.8)	21.5	1.19 (d, 6.8)	21.3	1.08 (d, 6.6)	16.0
14	1.75, d (1.7)	8.3, CH_3	1.68, d (1.6)	8.0, CH_3	1.88, d (1.6)	8.62	1.72 (d, 1.6)	6.7	1.77 (br.s)	8.6
15	0.72, d (7.0)	13.9, CH_3	0.59, d (7.0)	15.4, CH_3	1.19, d (6.4)	22.1	1.12 (d, 6.4)	20.9	1.04 (d, 6.5)	22.3
11-OH	5.25, s		4.88, s							
8-OH			5.04, d (4.2)							

References

[1] S. Duan, Y. Du, X. Hou, N.Yan, W.Dong, X.Mao and Z. Zhang (2016). Chemical basis of the fungicidal activity of tobacco extracts against *Valsa mali*, *Molecules* **21**,1743.

[2] S. Duan, Y. Du, X. Hou, S.Li, X.. Ren, W.Dong, W.Zhao, Z. Zhang (2015). Inhibitory effects of tobacco extracts on eleven phytopathogenic fungi, *Nat. Prod. Res. Dev*. **27** 470–474-480. (in Chinese)

[3] N. Yan, Y. Du, X. Liu, H. Zhang, Y. Liu, J. Shi, S.J. Xue and Z. Zhang (2017). Analyses of effects of a-cembratrien-diol on cell morphology and transcriptome of *Valsa mali* var. *mali*, *Food Chem*. 214, 110–118.

[4] S. Michalet, L. Payen-Fattaccioli, C. Beney, P. Cegiela, C. Bayet, G. Cartier, D. Noungoue-Tchamo, E. Tsamo, A.M. Mariotte and M. G. Dijoux-Franca (2008). New components including cyclopeptides from Barks of *Christiana africana* DC. (Tiliaceae).. *Helv. Chim Acta* **91**(**6**), 1106-1117.