Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Clerodane diterpenoid with anti-inflammatory and synergistic antibacterial activitives from *Tinospora crispa* †

Yang-Li Zhu,[a] Li Deng,[a] Jia-Qi Song,[a] Yan Zhu,[a] Rong-Wen Yuan,[a] Xian-Zhe Fan,[a] Hong Zhou,[b] Ya-si Huang,*[b] Li-Jun Zhang,*[a] Hai-Bing Liao*[a]

[a]*State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources/Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education of China), Collaborative Innovation Center for Guangxi Ethnic Medicine, School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, People's Republic of China. E-mail: lhbing188@163.com (H.-B. Liao); ajun840618@mailbox.gxnu.edu.cn (L.-J. Zhang)*

[b]*Key Laboratory of Basic Pharmacology of Ministry of Education and Joint International Research Laboratory of Ethnomedicine of Ministry of Education, Zunyi Medical University, Zunyi, Guizhou 563006, China. E-mail: uiuivtee@163.com (Y.-S. Huang)*

Contents of Supporting Information

Text S1. General experimental procedures

NMR spectra were acquired using a 400 or 600 MHz Bruker AVANCE apparatus ($CDCl_3$, δ_H 7.26 and δ_C77.2 ppm; CD_3OD, δ_H 3.31 and δ_C 49.0 ppm). HRESIMS data were measured on an Agilent 6545 Q-TOF LC-MS spectrometer. ECD spectra and UV spectra were measured on a JASCO J-1500 spectropolarimeter. IR spectra were measured on PerkinElmer Spectrum Two FT-IR using KBr pellets. Optical rotations were recorded on a JASCO P-2000 polarimeter. Semi-preparative HPLC was performed on a YMC-Pack ODS-A column (250 × 10 mm, S-5 μm, Japan) with an LC3050N instrument (Chuang Xin Tong Heng Science and Technology Co., Ltd., Beijing, China) equipped with a UV3050N detector (Chuang Xin Tong Heng Science and Technology Co., Ltd., Beijing, China). MTT (Mackin, C12029690) minocycline (The United States, APExBIO, B1791), fetal bovine serum (Australia, Gibco, 2233788CP) and LPS (The United States, Sigma, 028M4094V) were used in the bioactivity experiment. The other materials that were used to isolated and purified compounds were the same as in the published paper.[1,2]

References

1 X.-Z. Fan, Y.-L. Zhu, R.-W. Yuan, L. Deng, C. Hou, W. Li, T. Liu, X.-Q. Kong, L.-J. Zhang and H.-B, Liao, Terpenoids with α-glucosidase inhibitory activity from *Rhododendron minutiflorum* Hu, *Phytochemistry*, 2022, **196**, 113083.

2 F. Yang, B.-J. Su, Y.-J. Hu, J.-L. Liu, H. Li, Y.-Q. Wang, H.-B. Liao and D. Liang, Piperhancins A and B, two pairs of antineuroinflammatory cycloneolignane enantiomers from *Piper hancei*. *J. Org. Chem*., 2021, **86**, 5284–5291.

Figure S1. Key ^{1}H-^{1}H COSY and HMBC correlations of Compounds **1-14**

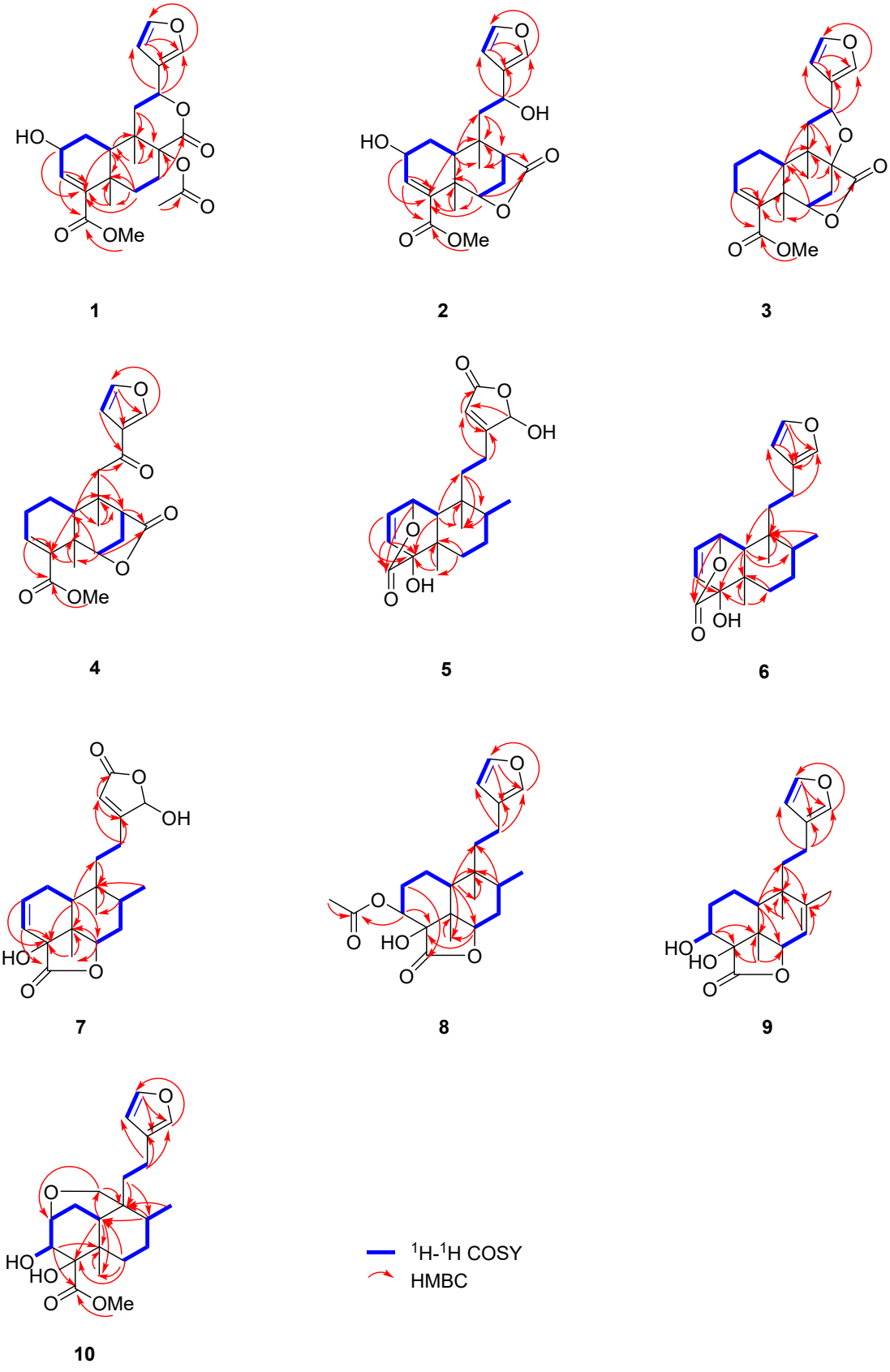


Figure S2. Key NOESY correlations of Compounds **1-10**

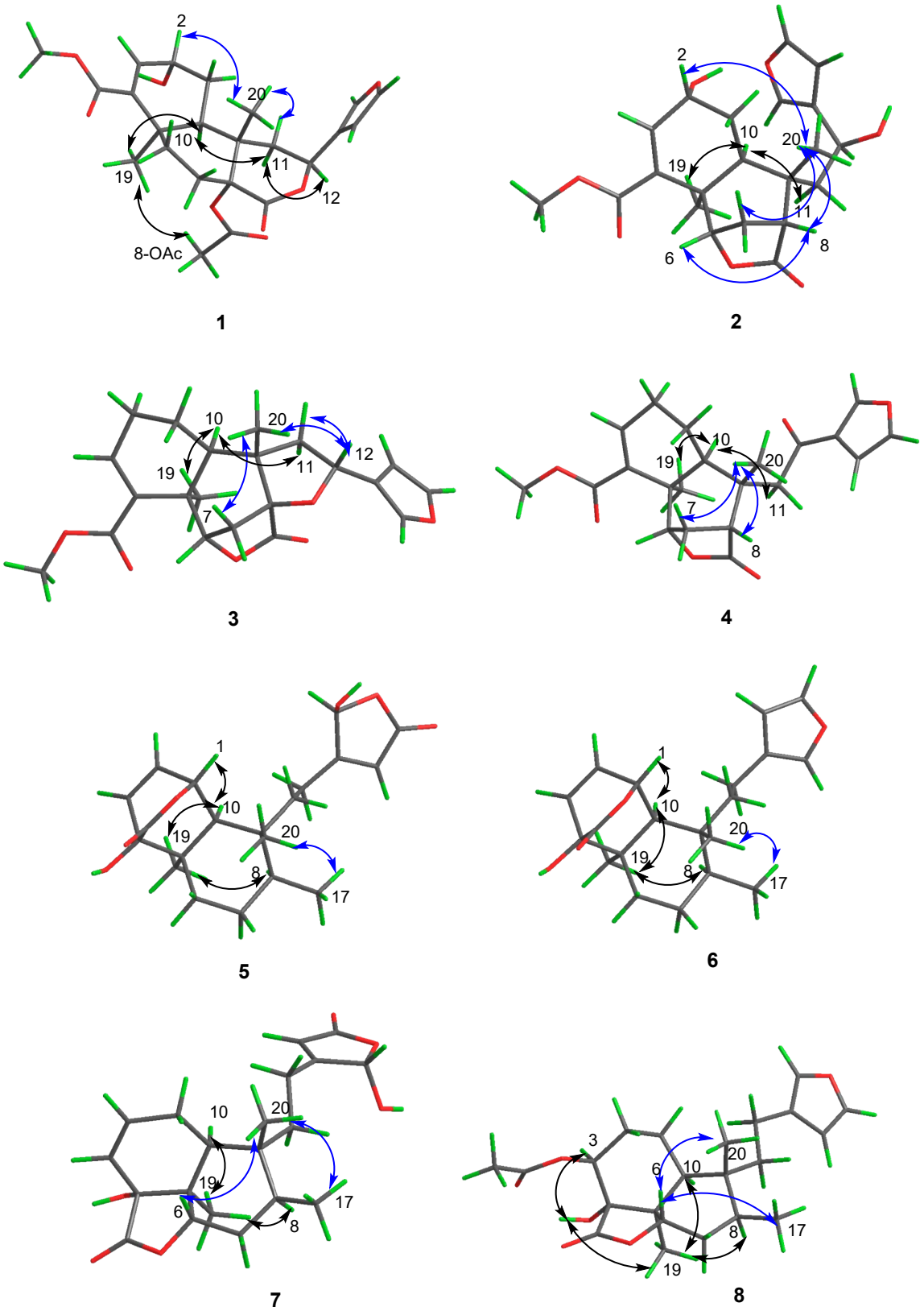
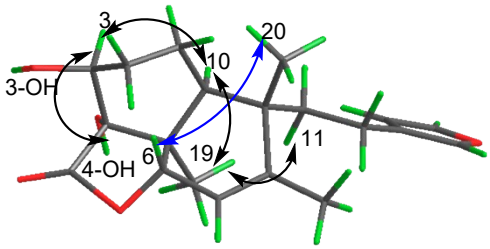
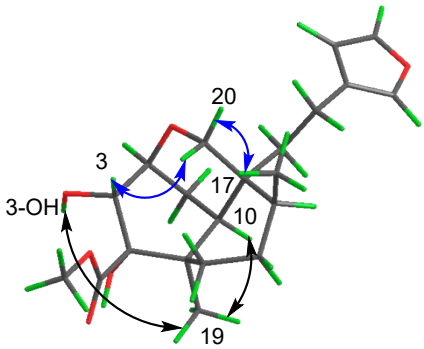


Figure S3. Key NOESY correlations of Compounds **9-10**



9



10

α-NOESY
β -NOESY

Scheme S1. Putative biosynthetic pathways of Compounds **3**, **7** and **10**

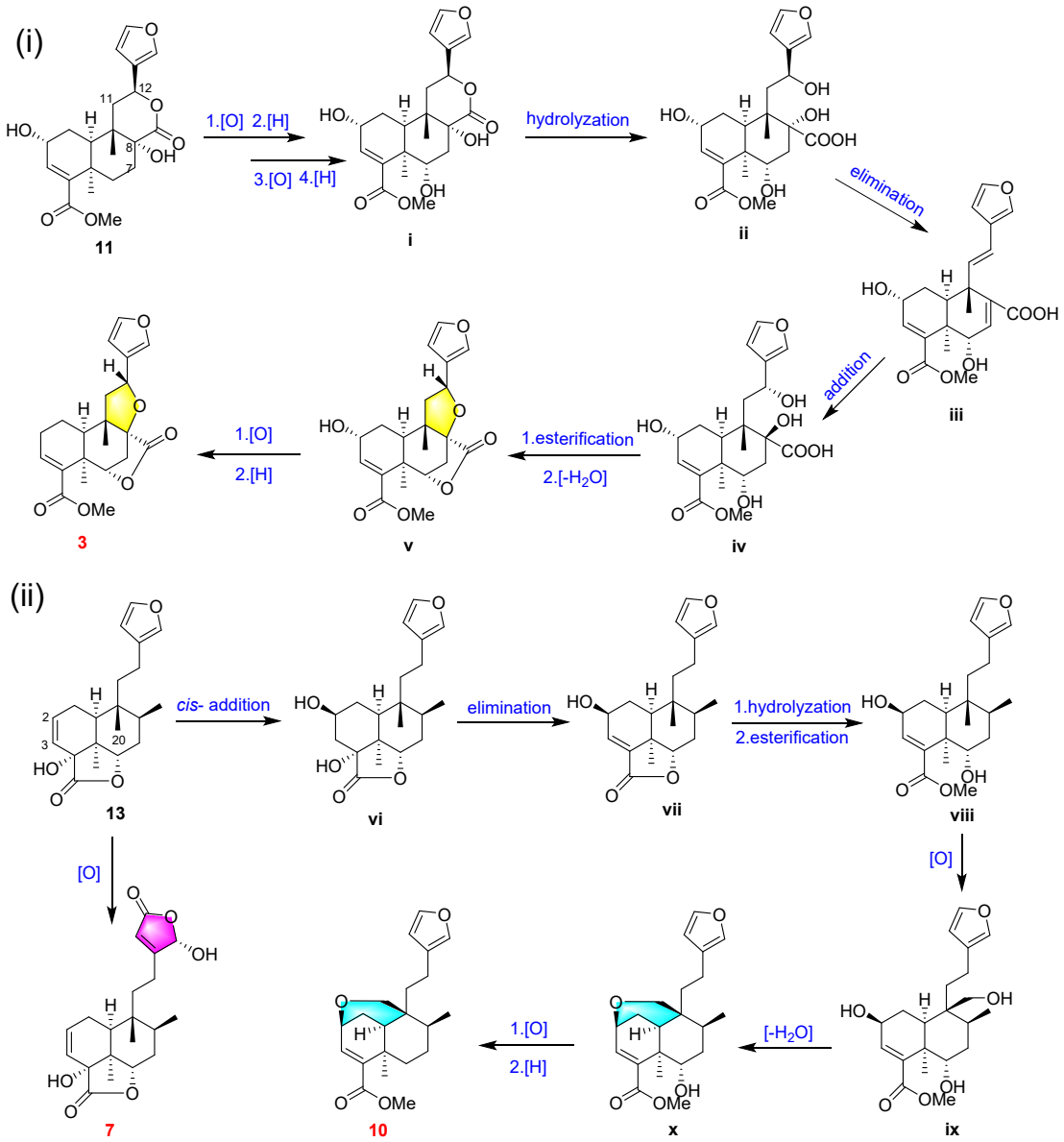


Table S1. ^{1}H NMR Data of Compounds **1-5**

No.	**1**[d]	**2**[c]	**3**[c]	**4**[d]	**5**[c]
1*α*	2.18, m[e]	1.86, ddd (14.8, 9.6, 6.4)	1.88, m	1.97, m	5.23, dd (5.2, 1.6)
1*β*	2.18, m[e]	2.36, dd (14.8, 8.0)	2.15, m[e]	1.97, m	
2*α*			2.46, m[e]	2.37, m	6.52, dd (8.0, 5.2)
2*β*	4.57, td (8.4, 4.0)	4.54, ddd (9.6, 8.0, 2.8)	2.46, m[e]	2.37, m	
3	6.42, d (4.0)	6.83, d (2.8)	7.07, t (4.0)	7.02, t (4.0)	6.21, dd (8.0, 1.6)
6*α*	1.37, td (15.2, 4.0)				1.73, m[e]
6*β*	2.49, dt (15.2, 4.0)	5.37, d (6.0)	5.54, d (6.0)	5.49, d (6.0)	1.32, m[e]
7*α*	2.31, dt (15.2, 3.6)	2.22, m	2.43, m[e]	2.15, m	1.86, m[e]
7*β*	1.73, td (15.2, 3.6)	1.99, d (12.4)	2.12, d (11.6)	1.96, d (12.4)	1.32, m[e]
8		2.64, d (5.6) (*β*)		2.93, d (5.6) (*β*)	1.74, m[e] (*α*)
10*α*	2.22, m	1.59, br d (6.4)	1.73, dd (6.4, 1.6)	1.54, dd (6.0, 2.0)	1.57, s
11*α*	2.16, m[e]	1.69, dd (14.8, 2.4)	1.96, d (10.8)	2.99, d (15.6)	1.74, m[e]
11*β*	1.94, dd (13.6, 8.8)	2.05, dd (14.8, 9.2)	2.16, m[e]	2.85, d (15.6)	1.65, m[e]
12*α*	5.51, t (8.8)	5.00, dd (9.2, 2.4)			2.33, m
12*β*			5.29, dd (10.8, 5.6)		2.33, m
14	6.39, dd (2.0, 0.8)	6.52, t (1.6)	6.86, dd (2.0, 0.8)	6.76, dd (1.6, 0.8)	6.00, s
15	7.42, t (2.0)	7.41, m[e]	7.43, t (2.0)	7.41, t (1.6)	
16	7.44, br s	7.41, m[e]	7.59, t (0.8)	8.30, t (1.6)	6.22, br s (*β*)
19	1.44, s	1.40, s	1.36, s	1.37, s	0.88, d (6.8)
20	1.06, s	1.25, s	1.33, s	1.26, s	1.13, s
OMe	3.74, s	3.76, s	3.74, s	3.73, s	0.90, s
8-OAc	2.19, s (*α*)				

[a] In MeOH-d_4, NMR at 600 MHz. [b] In $CDCl_3$, NMR at 600 MHz. [c] In MeOH-d_4, NMR at 400 MHz. [d] In $CDCl_3$, NMR at 400 MHz.

[e] Overlapped signals are reported without designating multiplicity

Table S2. ^{13}C NMR Spectroscopic Data of Compounds **1-10**.

No.	**1**[d]	**2**[c]	**3**[c]	**4**[d]	**5**[c]	**6**[c]	**7**[a]	**8**[d]	**9**[d]	**10**[d]
1	28.7	28.6	19.3	16.8	75.9	76.0	24.2	20.1	19.2	23.0
2	64.4	64.9	25.2	24.3	131.9	131.9	135.5	25.1	28.3	75.8
3	138.0	143.7	144.6	142.4	136.4	136.4	126.8	73.7	71.5	70.2
4	140.9	137.1	135.2	134.4	82.7	82.7	78.3	79.1	81.0	82.0
5	35.8	41.1	40.4	39.6	38.7	38.8	47.5	45.8	47.0	40.4
6	29.5	84.0	82.0	82.7	27.5	27.5	78.0	75.5	76.4	30.4
7	23.2	30.2	34.9	29.5	26.6	26.7	29.6	29.0	119.2	26.8
8	82.2	47.9	90.0	47.4	31.7	31.7	33.6	37.1	143.9	31.4
9	41.0	40.1	50.5	39.5	39.6	39.8	41.4	40.0	42.8	36.8
10	49.9	50.1	44.9	44.2	51.6	51.5	41.1	42.1	41.6	37.6
11	42.4	48.5	44.9	47.4	36.9	40.6	39.0	45.5	41.7	35.8
12	70.6	64.5	76.2	193.6	22.7	19.6	23.3	20.1	20.3	19.0
13	125.9	132.5	127.2	129.2	171.5[f]	126.6	171.4[f]	125.0	125.1	125.3
14	108.5	110.0	111.3	108.8	118.8[e]	111.9	118.6	111.0	111.0	111.1
15	144.1	144.2	144.0	144.2	173.6	144.1	173.6	143.0	143.0	142.9
16	139.5	139.8	142.5	148.5	----	139.9	----	138.7	138.7	138.7
17	168.9	179.8	179.8	178.5	15.6	15.7	17.5	18.8	19.5	15.8
18	168.1	168.3	168.1	166.8	177.7	177.8	180.7	178.9	181.5	175.6
19	34.2	27.6	27.6	27.4	25.9	25.9	18.3	17.9	18.3	25.3
20	23.8	23.1	18.2,	20.5	19.1	19.2	20.6	23.0	22.6	67.5
OMe	52.0	52.5	52.3	51.9						53.0
3-OAc								169.1 21.3		
8-OAc	168.9 21.1									

[a] In MeOH-d_4, NMR at 150 MHz. [b] In $CDCl_3$, NMR at 150 MHz. [c] In MeOH-d_4, NMR at 100 MHz. [d] In $CDCl_3$, NMR at 100 MHz. [e] The presence of this signal was inferred from the HSQC correlation. [f] The presence of this signal was inferred from the HMBC correlation. ---- No signal observed.

Table S3. ^{1}H NMR Data of Compounds **6-10**

No.	**6**[c]	**7**[a]	**8**[d]	**9**[d]	**10**[d]
1*α*	5.22, dd (5.2, 1.6)	2.37, m[e]	1.67, m	1.91, m[e]	2.19, m[e]
1*β*		2.23, m[e]	1.59, m	1.55, m	1.83, m[e]
2*α*	6.47, dd (8.0, 5.2)	6.26, ddd (9.6, 6.0, 2.4)	1.75, m	1.80, m[e]	3.91, t (3.2)
2*β*			1.99, ddd (14.8, 6.8, 3.6)	1.87, m[e]	
3	6.19, dd (8.0, 1.6)	5.77, dd (9.6, 3.0)	5.00, dd (3.6, 2.0) (*α*)	4.04, s (*α*)	4.62, br s (*β*)
6*α*	1.69, m[e]				0.91, ddd (13.6, 6.0, 3.2)
6*β*	1.30, m[e]	4.58, dd (11.4, 7.2)	4.87, dd (12.4, 5.6)	5.30, t (2.0)	1.89, td (12.8,3.2)
7*α*	1.85, m[e]	2.08, dd (12.0, 8.4)	2.20, dd (12.4, 7.2)	5.70, t (2.0)	1.70, m[e]
7*β*	1.30, m[e]	1.71, dt (13.2, 7.8)	1.82, m[e]		1.29, m
8	1.83, m[e] (*α*)	2.20, m[e] (*α*)	2.13, m (*α*)		1.77, m[e] (*α*)
10*α*	1.65, m[e]	2.05, m	1.86, m[e]	1.91, m[e]	1.40, t (3.6)
11*α*	1.73, m [e]	1.67, m	1.89, m [e]	1.64, td (12.8, 4.4)	2.29, m[e]
11*β*	1.62, m [e]	1.57, m	1.52, ddd (14.4, 12.4, 4.8)	1.79, m[e]	1.48, m
12*α*	2.35, m	2.37, m[e]	2.41, m	2.43, m	2.29, m[e]
12*β*	2.35, m	2.37, m[e]	2.41, m	2.43, m	2.29, m[e]
14	6.34, dd (2.0, 0.8)	5.96, s	6.25, dd (1.6, 0.8)	6.26, t (1.6)	6.28, br s
15	7.40, t (2.0)		7.35, t (1.6)	7.35, t (1.6)	7.35, t (1.6)
16	7.30, dd (2.0, 0.8)	6.21, br s (*β*)	7.21, dd (1.6, 0.8)	7.22, br s	7.22, br s
17	0.89, d (6.0)	1.02, d (6.6)	1.12, d (6.8)	1.79, m	0.83, d (7.2)
19	1.12, s	1.23, s	1.24, s	0.93, s	1.16 , s
20*α*	0.87, s	0.95, s	0.98, s	1.06, s	3.85, d (12.4)
20*β*					3.25, d (12.4)
OMe					3.83, s
3-OAc			2.07, s (*β*)		
3-OH				3.16, br s (*β*)	3.63, br s (*α*)
4-OH			2.90, br s (*α*)	3.42, br s (*α*)	

[a] In MeOH-d_4, NMR at 600 MHz. [b] In $CDCl_3$, NMR at 600 MHz. [c] In MeOH-d_4, NMR at 400 MHz. [d] In $CDCl_3$, NMR at 400 MHz.

[e] Overlapped signals are reported without designating multiplicity.

Table S4 X-ray Crystallographic Data for Compound **2**

Empirical formula	$C_{21}H_{26}O_7$
Formula weight	390.42
Temperature/K	293.00
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.1388(2)
b/Å	14.1451(4)
c/Å	8.5805(2)
α/°	90
β/°	94.182(2)
γ/°	90
Volume/Å^3	985.19(4)
Z	2
ρ_{calc}g/cm^3	1.316
μ/mm^{-1}	0.819
F(000)	416.0
Crystal size/mm^3	0.03 × 0.02 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.338 to 134.144
Index ranges	$-5 \le h \le 9$, $-16 \le k \le 16$, $-10 \le l \le 10$
Reflections collected	10439
Independent reflections	3455 [R_{int} = 0.0425, R_{sigma} = 0.0407]
Data/restraints/parameters	3455/183/324
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0531, wR_2 = 0.1508
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1564
Largest diff. peak/hole / e Å^{-3}	0.35/-0.47
Flack parameter	-0.02(11)

Table S5 X-ray Crystallographic Data for Compound **3**

Empirical formula	$C_{21}H_{24.5}O_{6.25}$
Formula weight	376.90
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	14.3159(3)
b/Å	10.5927(2)
c/Å	25.4095(6)
α/°	90
β/°	105.113(2)
γ/°	90
Volume/Å^3	3719.93(14)
Z	8
ρ_{calc}g/cm^3	1.346
μ/mm^{-1}	0.818
F(000)	1604.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.396 to 143.342
Index ranges	$-17 \le h \le 16$, $-12 \le k \le 12$, $-28 \le l \le 31$
Reflections collected	29302
Independent reflections	12802 [R_{int} = 0.0297, R_{sigma} = 0.0375]
Data/restraints/parameters	12802/1/997
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.1009
Final R indexes [all data]	R_1 = 0.0436, wR_2 = 0.1036
Largest diff. peak/hole / e Å^{-3}	0.43/-0.23
Flack/Hooft parameter	-0.02(7)/-0.02(5)

Table S6 X-ray Crystallographic Data for Compound **4**

Empirical formula	$C_{21}H_{24}O_6$
Formula weight	372.40
Temperature/K	298.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.6514(4)
b/Å	12.1518(5)
c/Å	18.3209(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1926.08(15)
Z	4
ρ_{calc}g/cm^3	1.284
μ/mm^{-1}	0.774
F(000)	792.0
Crystal size/mm^3	0.15 × 0.04 × 0.04
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	11.31 to 134.012
Index ranges	$-10 \le h \le 10$, $-13 \le k \le 14$, $-21 \le l \le 19$
Reflections collected	14025
Independent reflections	3402 [R_{int} = 0.0313, R_{sigma} = 0.0253]
Data/restraints/parameters	3402/0/247
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.1014
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.1029
Largest diff. peak/hole / e Å^{-3}	0.18/-0.18
Flack parameter	-0.01(6)

Table S7 X-ray Crystallographic Data for Compound **5**

Empirical formula	$C_{20}H_{26}O_6$
Formula weight	362.41
Temperature/K	293.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.3598(4)
b/Å	12.8810(5)
c/Å	13.9104(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1856.27(14)
Z	4
ρ_{calc}g/cm^3	1.297
μ/mm^{-1}	0.784
F(000)	776.0
Crystal size/mm^3	0.11 × 0.1 × 0. 08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.358 to 134.128
Index ranges	$-8 \le h \le 12$, $-15 \le k \le 14$, $-15 \le l \le 16$
Reflections collected	8990
Independent reflections	3282 [R_{int} = 0.0440, R_{sigma} = 0.0481]
Data/restraints/parameters	3282/142/306
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0829, wR_2 = 0.2489
Final R indexes [all data]	R_1 = 0.0968, wR_2 = 0.2635
Largest diff. peak/hole / e Å^{-3}	0.66/-0.35
Flack parameter	-0.5(3)

Table S8 X-ray Crystallographic Data for Compound **6**

Empirical formula	$C_{20}H_{26}O_4$
Formula weight	330.41
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P1
a/Å	6.55823(16)
b/Å	11.1807(3)
c/Å	12.2365(3)
α/°	86.0177(19)
β/°	75.071(2)
γ/°	83.9039(19)
Volume/Å^3	816.23(4)
Z	2
ρ_{calc}g/cm^3	1.274
μ/mm^{-1}	0.704
F(000)	356.0
Crystal size/mm^3	0.14 × 0.05 × 0. 04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.484 to 134.146
Index ranges	$-7 \le h \le 7$, $-13 \le k \le 13$, $-14 \le l \le 14$
Reflections collected	25530
Independent reflections	6009 [R_{int} = 0.0595, R_{sigma} = 0.0465]
Data/restraints/parameters	6009/3/441
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0345, wR_2 = 0.0878
Final R indexes [all data]	R_1 = 0.0360, wR_2 = 0.0891
Largest diff. peak/hole / e Å^{-3}	0.13/-0.17
Flack parameter	0.00(10)

Table S9 X-ray Crystallographic Data for Compound **7**

Empirical formula	$C_{20}H_{26}O_6$
Formula weight	362.41
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.49264(14)
b/Å	18.9905(4)
c/Å	7.55045(15)
α/°	90
β/°	100.551(2)
γ/°	90
Volume/Å^3	912.55(3)
Z	2
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	0.795
F(000)	388.0
Crystal size/mm^3	0.1 × 0.06 × 0. 2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.314 to 134.152
Index ranges	$-7 \le h \le 7$, $-22 \le k \le 22$, $-8 \le l \le 9$
Reflections collected	9095
Independent reflections	3223 [R_{int} = 0.0414, R_{sigma} = 0.0440]
Data/restraints/parameters	3223/1/240
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0930
Final R indexes [all data]	R_1 = 0.0392, wR_2 = 0.0948
Largest diff. peak/hole / e Å^{-3}	0.35/-0.15
Flack parameter	-0.06(12)

Table S10 X-ray Crystallographic Data for Compound **8**

Empirical formula	$C_{22}H_{30}O_6$
Formula weight	390.46
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.68330(10)
b/Å	10.38870(10)
c/Å	12.8658(2)
α/°	90
β/°	101.3330(10)
γ/°	90
Volume/Å^3	1006.92(2)
Z	2
ρ_{calc}g/cm^3	1.288
μ/mm^{-1}	0.759
F(000)	420.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.008 to 142.978
Index ranges	$-9 \le h \le 8$, $-12 \le k \le 9$, $-13 \le l \le 15$
Reflections collected	5765
Independent reflections	2966 [R_{int} = 0.0120, R_{sigma} = 0.0139]
Data/restraints/parameters	2966/16/269
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0263, wR_2 = 0.0688
Final R indexes [all data]	R_1 = 0.0265, wR_2 = 0.0689
Largest diff. peak/hole / e Å^{-3}	0.18/-0.14
Flack/Hooft parameter	-0.02(8)/-0.03(4)

Table S11 X-ray Crystallographic Data for Compound **9**

Empirical formula	$C_{20}H_{26}O_5$
Formula weight	346.41
Temperature/K	298.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.9441(7)
b/Å	10.7304 (7)
c/Å	17.5667(12)
α/°	90
β/°	97.762(3)
γ/°	90
Volume/Å^3	1857.3(2)
Z	4
ρ_{calc}g/cm^3	1.239
μ/mm^{-1}	0.718
F(000)	744.0
Crystal size/mm^3	0.13 × 0.08 × 0.05
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	8.974 to 134.126
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-20 \le l \le 20$
Reflections collected	24818
Independent reflections	6460 [R_{int} = 0.0457, R_{sigma} = 0.0377]
Data/restraints/parameters	6460/356/527
Goodness-of-fit on F^2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0628, wR_2 = 0.1831
Final R indexes [all data]	R_1 = 0.0679, wR_2 = 0.1901
Largest diff. peak/hole / e Å^{-3}	0.50/-0.44
Flack parameter	-0.01(7)

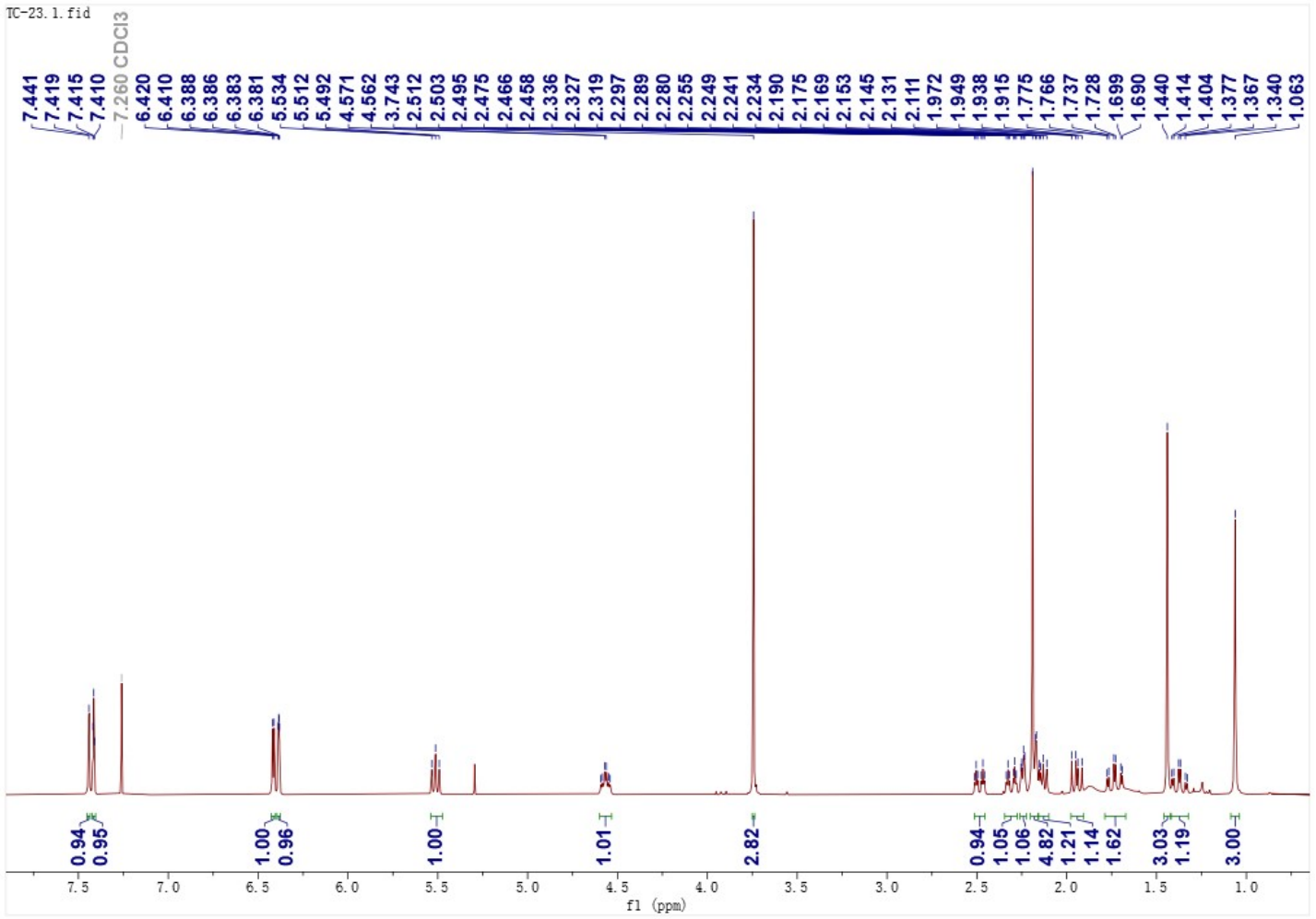
Table S12 X-ray Crystallographic Data for Compound **10**

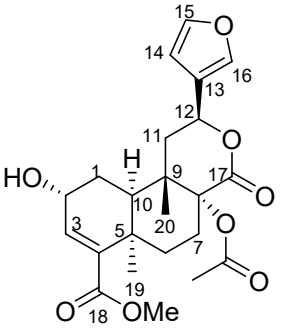
Empirical formula	$C_{21}H_{30}O_6$
Formula weight	378.45
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	C2
a/Å	22.8607(6)
b/Å	13.8482(3)
c/Å	12.0545(3)
α/°	90
β/°	92.794(2)
γ/°	90
Volume/Å^3	3811.67(16)
Z	8
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	0.783
F(000)	1632.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	7.342 to 143.944
Index ranges	-28 ≤ h ≤ 28, -17 ≤ k ≤ 17, -14 ≤ l ≤ 11
Reflections collected	18937
Independent reflections	6876 [R_{int} = 0.0366, R_{sigma} = 0.0287]
Data/restraints/parameters	6876/52/516
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.1025
Final R indexes [all data]	R_1 = 0.0384, wR_2 = 0.1029
Largest diff. peak/hole / e Å^{-3}	0.21/-0.20
Flack/Hooft parameter	0.14(6)/0.17(4)

Table S13 X-ray Crystallographic Data for Compound **11**

Empirical formula	$C_{21}H_{26}O_7$
Formula weight	390.42
Temperature/K	169.98(10)
Crystal system	monoclinic
Space group	C2
a/Å	17.1455(5)
b/Å	6.58147(20)
c/Å	17.5378(6)
α/°	90
β/°	106.154(3)
γ/°	90
Volume/Å^3	1900.88(11)
Z	4
ρ_{calc}g/cm^3	1.364
μ/mm^{-1}	0.849
F(000)	832.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.246 to 142.346
Index ranges	$-20 \leq h \leq 20$, $-6 \leq k \leq 7$, $-21 \leq l \leq 21$
Reflections collected	6338
Independent reflections	2962 [R_{int} = 0.0318, R_{sigma} = 0.0355]
Data/restraints/parameters	2962/1/264
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1108
Final R indexes [all data]	R_1 = 0.0434, wR_2 = 0.1115
Largest diff. peak/hole / e Å^{-3}	0.27/-0.24
Flack/Hooft parameter	0.03(14)/0.07(10)

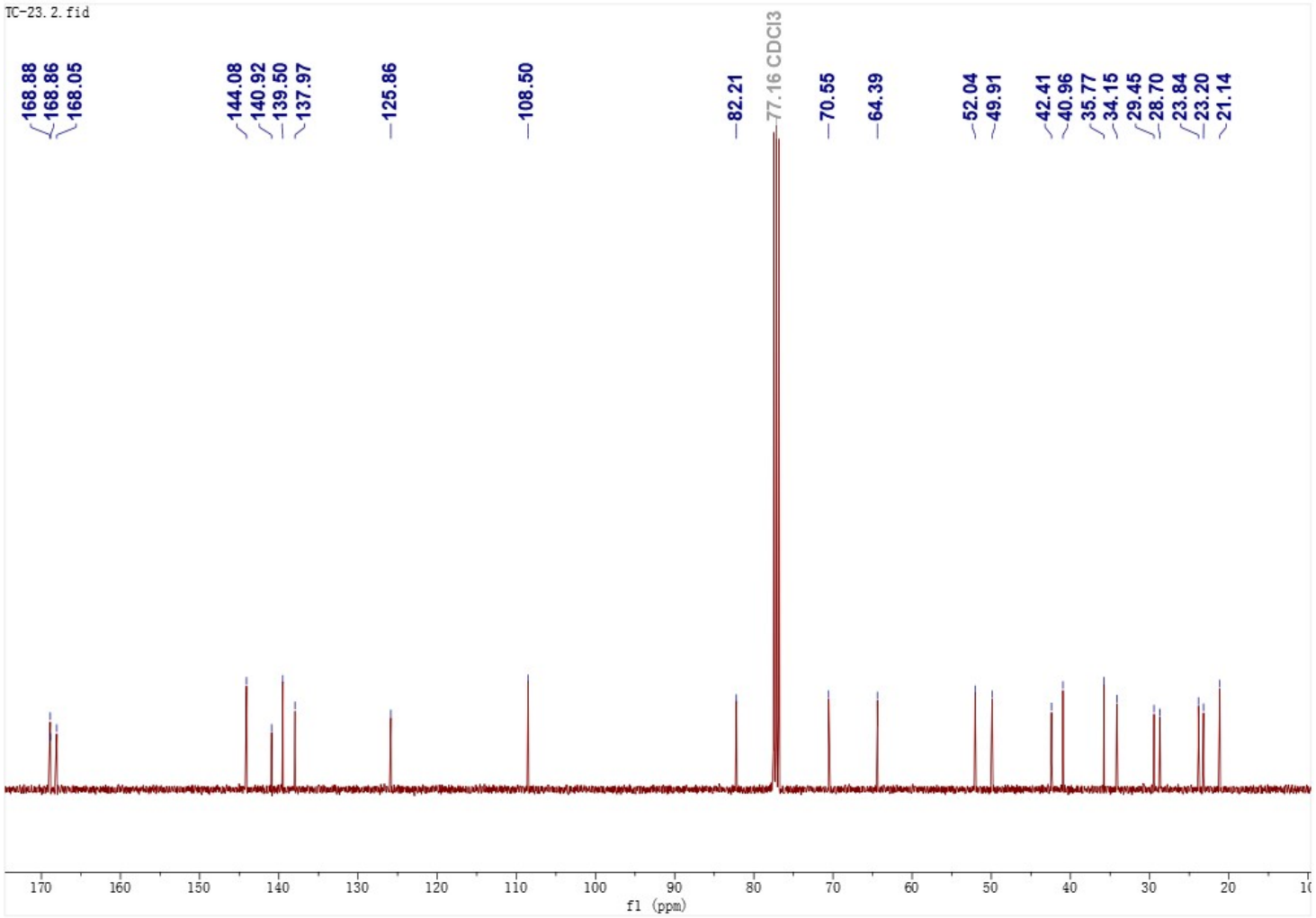
Figure S4. ^{1}H NMR Spectrum of Compound **1** in $CDCl_3$

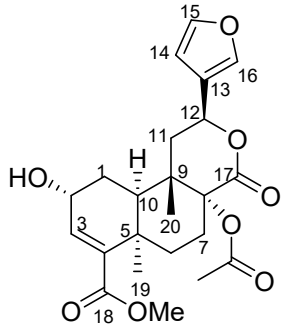




1

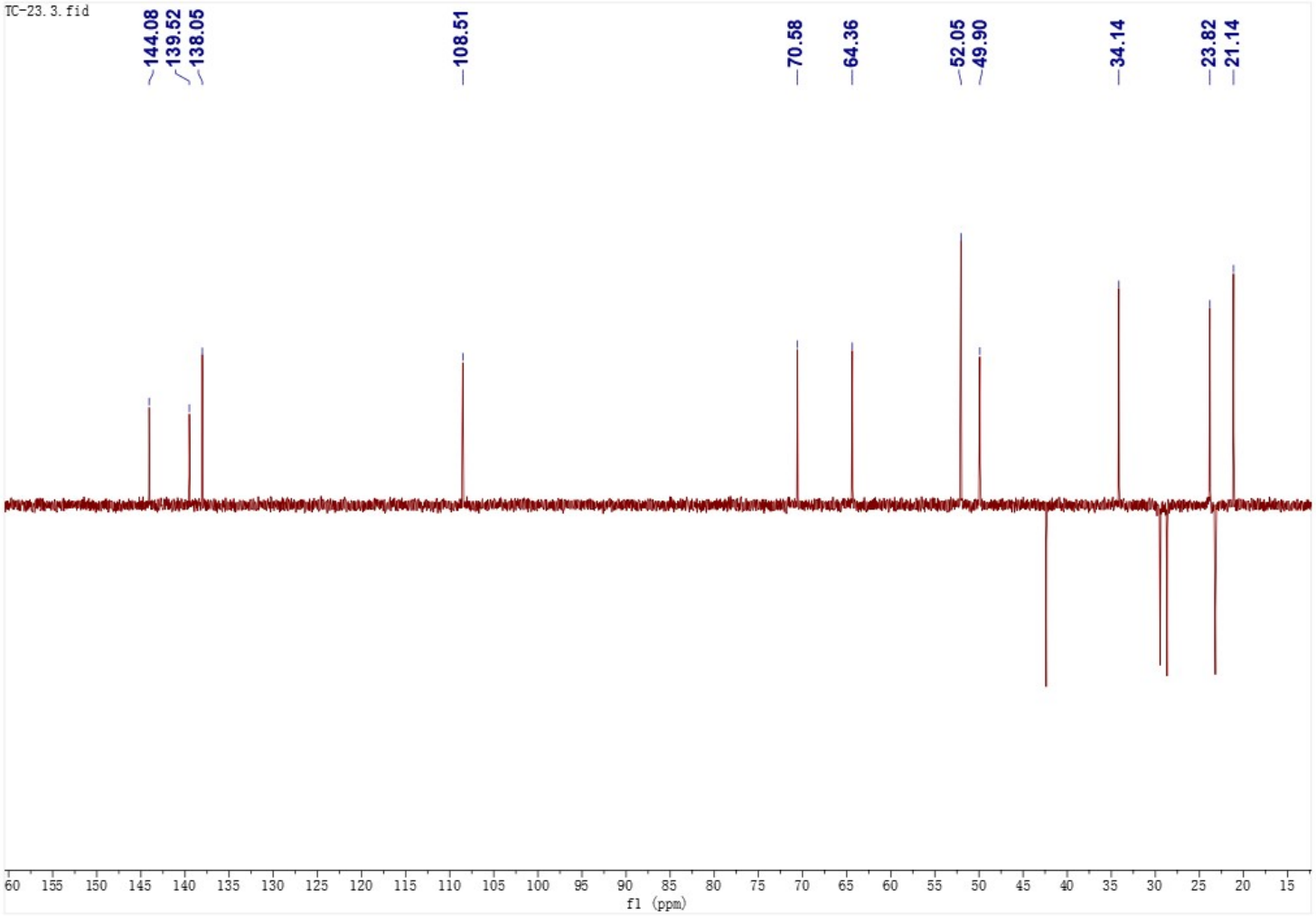
Figure S5. ^{13}C NMR Spectrum of Compound **1** in $CDCl_3$

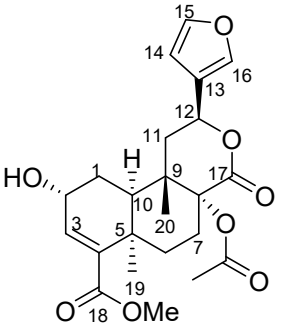




1

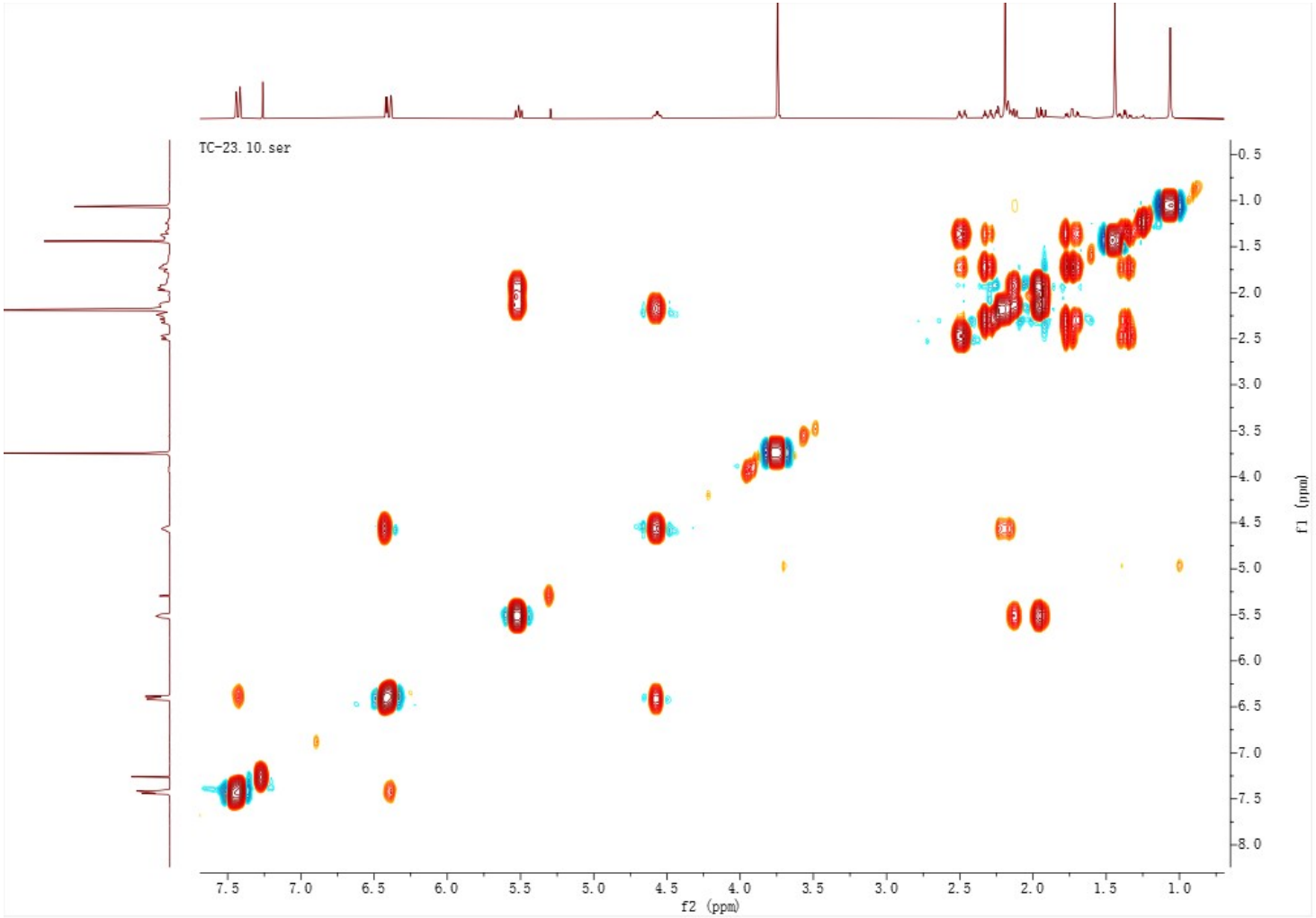
Figure S6. DEPT 135 Spectrum of Compound **1** in $CDCl_3$

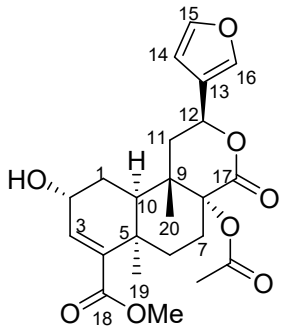




1

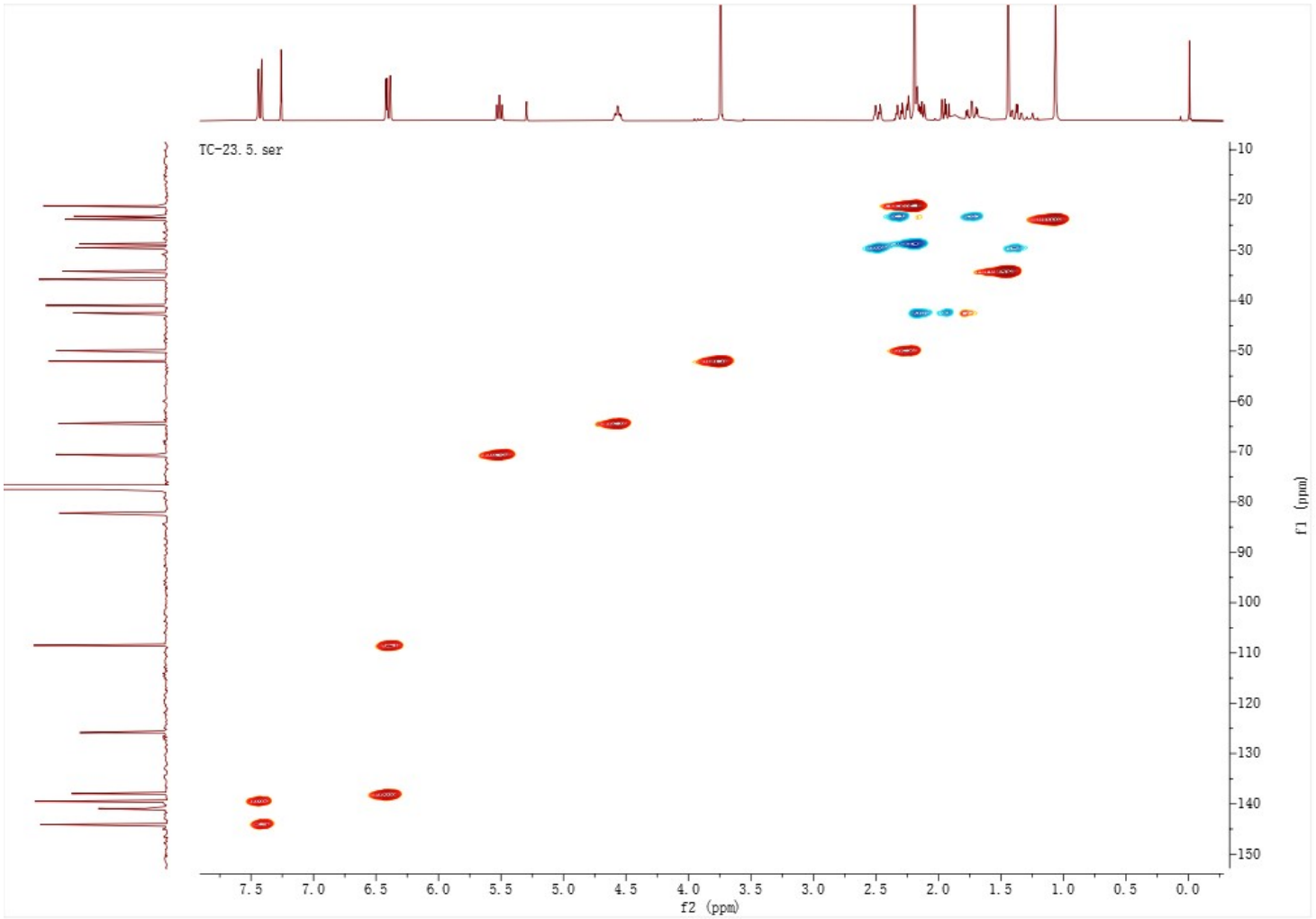
Figure S7. ^{1}H-^{1}H COSY Spectrum of Compound **1** in $CDCl_3$

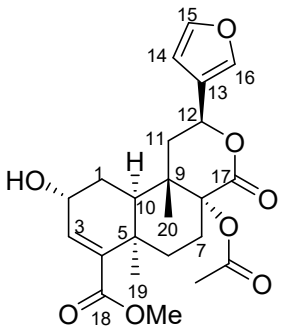




1

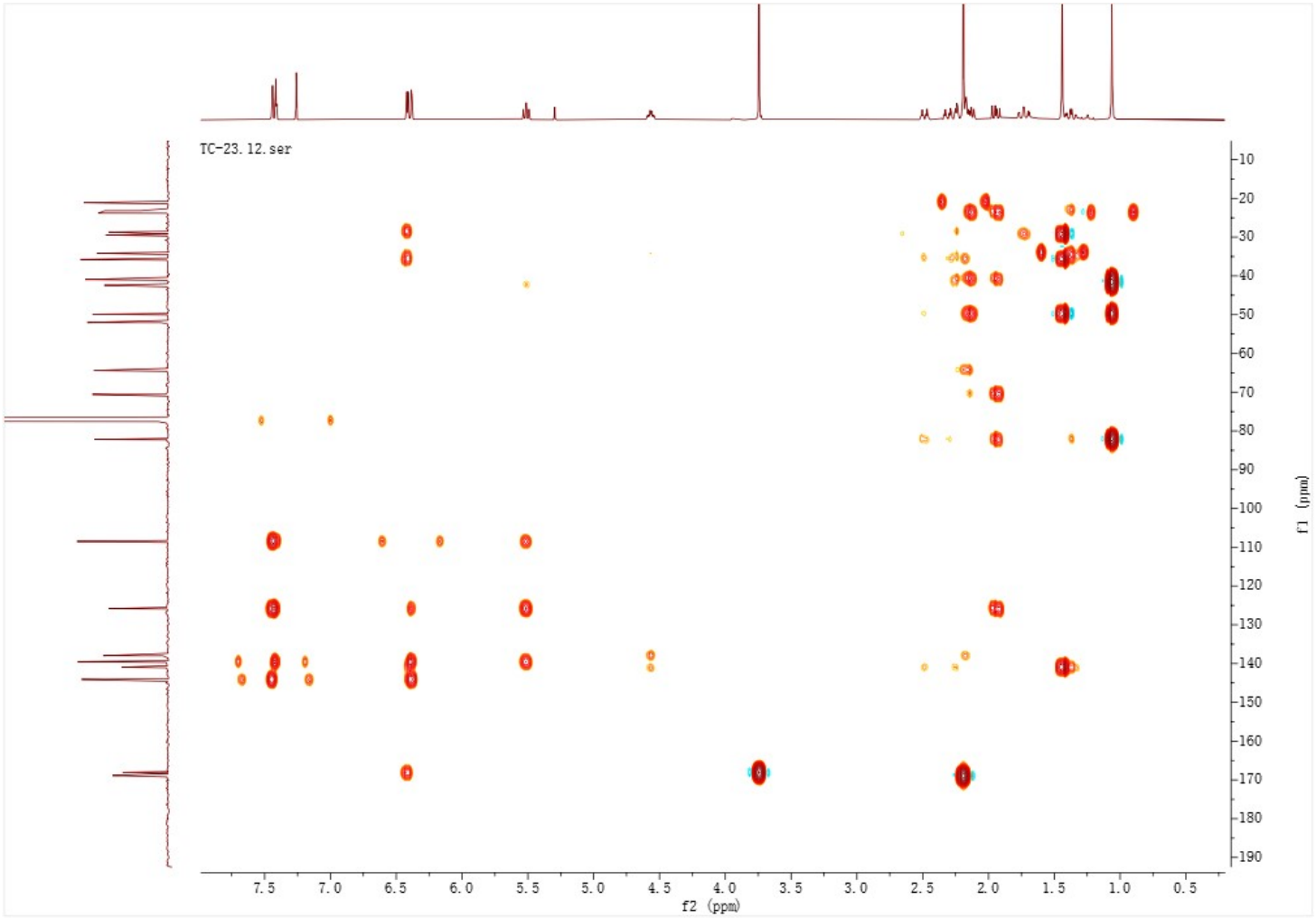
Figure S8. HSQC Spectrum of Compound **1** in $CDCl_3$

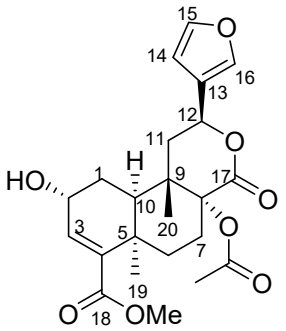




1

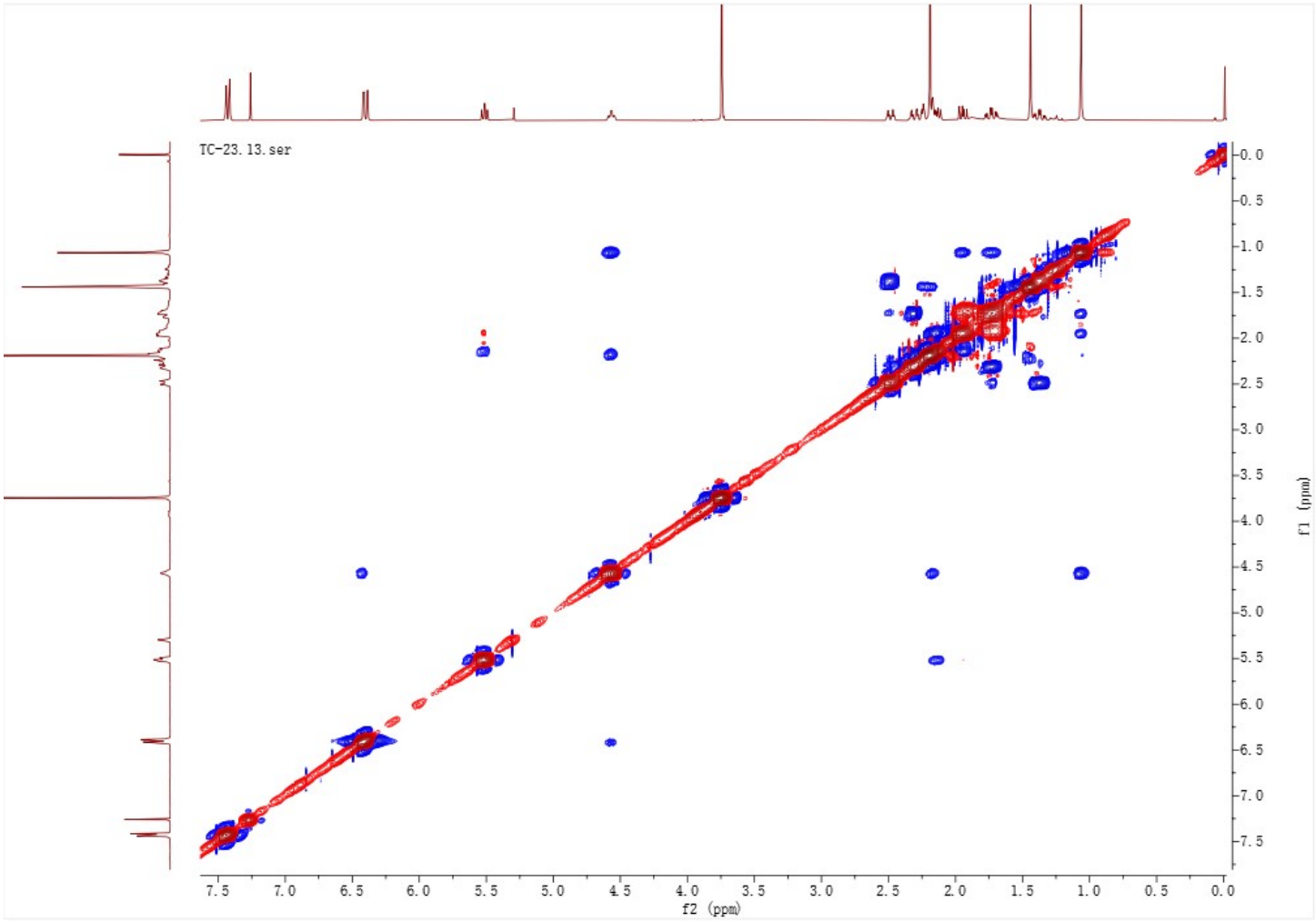
Figure S9. HMBC Spectrum of Compound **1** in $CDCl_3$

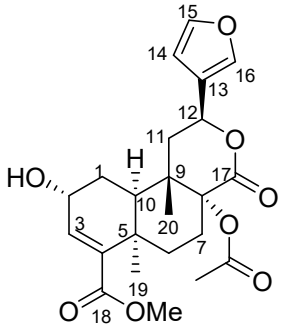




1

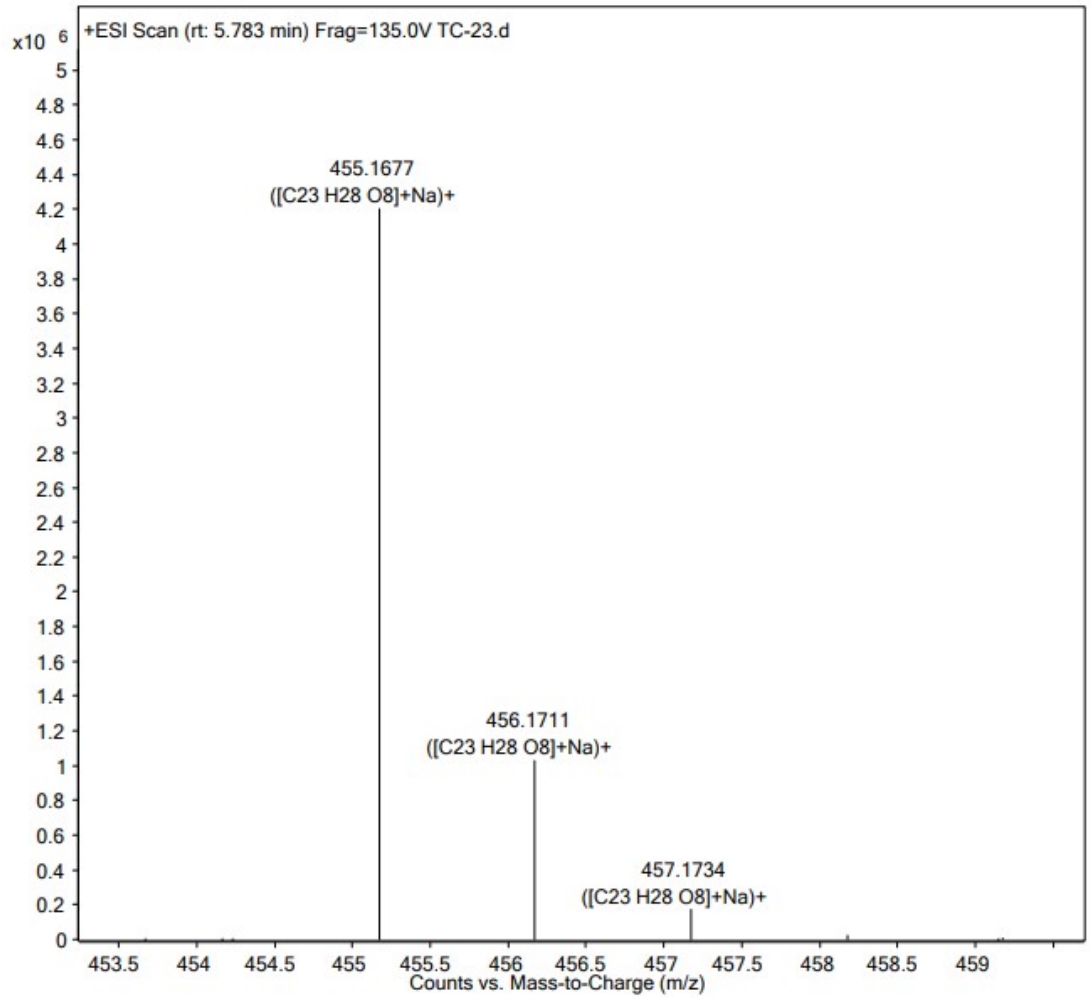
Figure S10. NOESY Spectrum of Compound **1** in $CDCl_3$

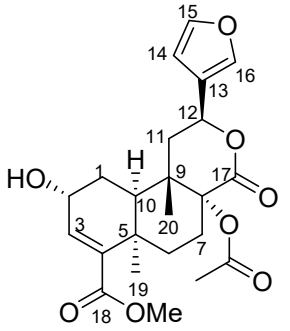




1

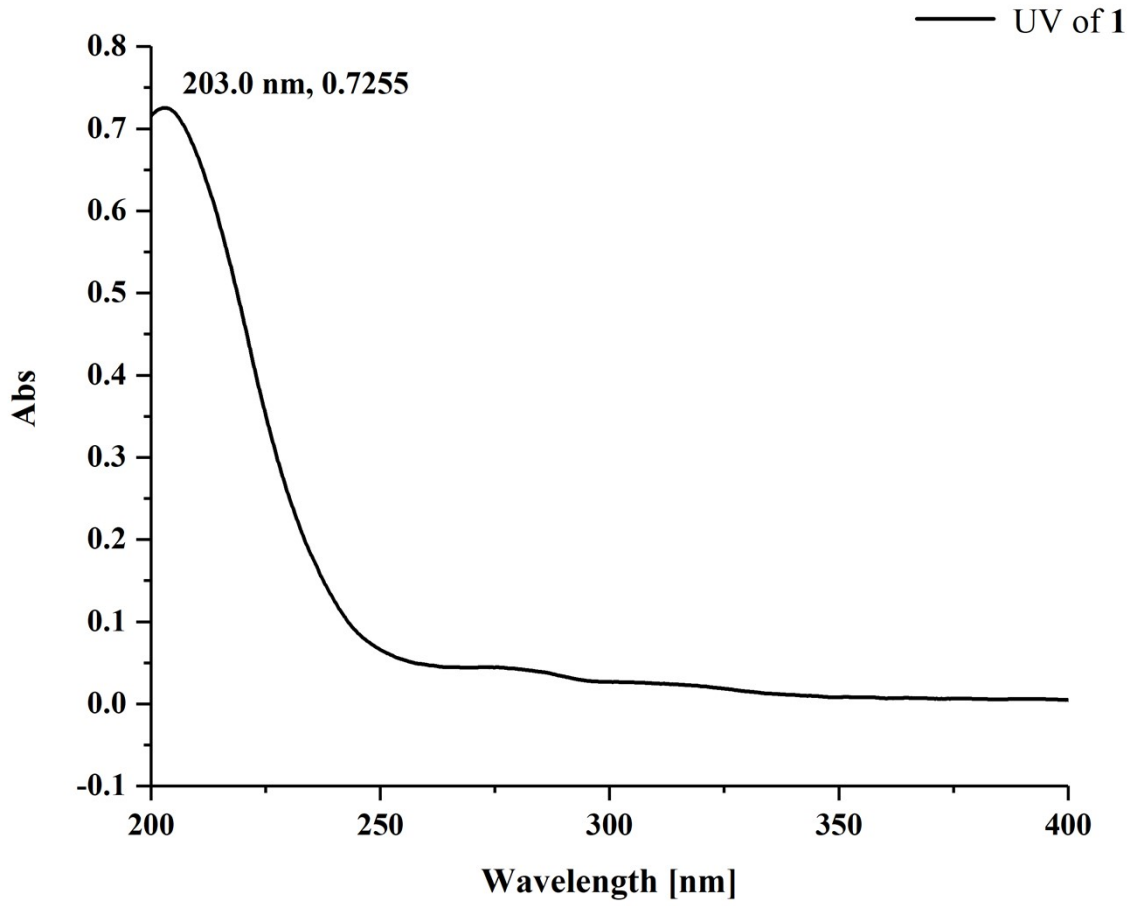
Figure S11. (+) HRESIMS Spectrum of Compound **1**

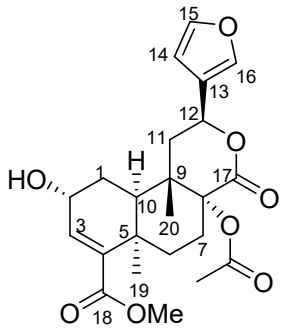




1

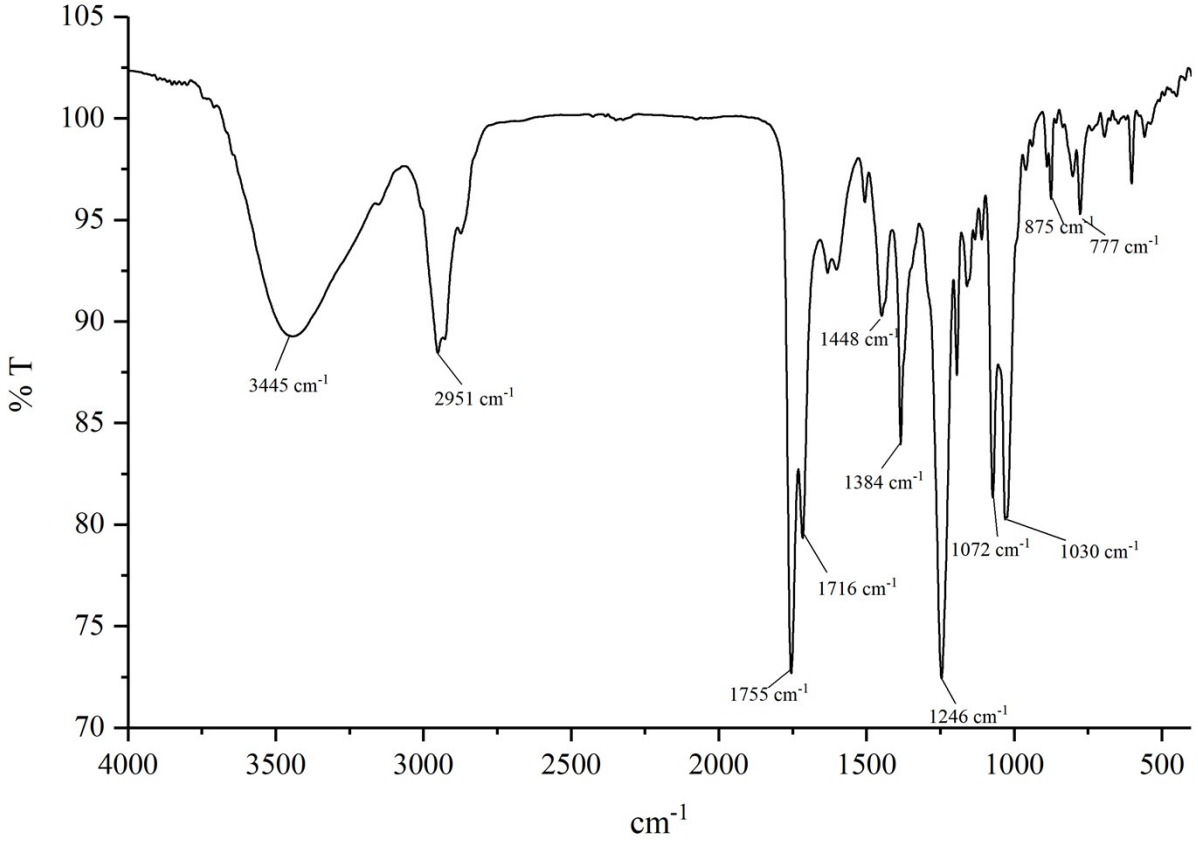
Figure S12. UV Spectrum of Compound **1**

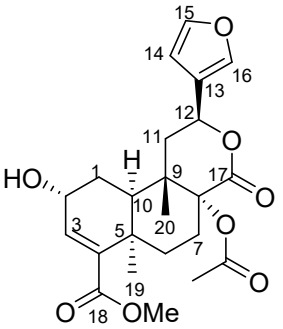




1

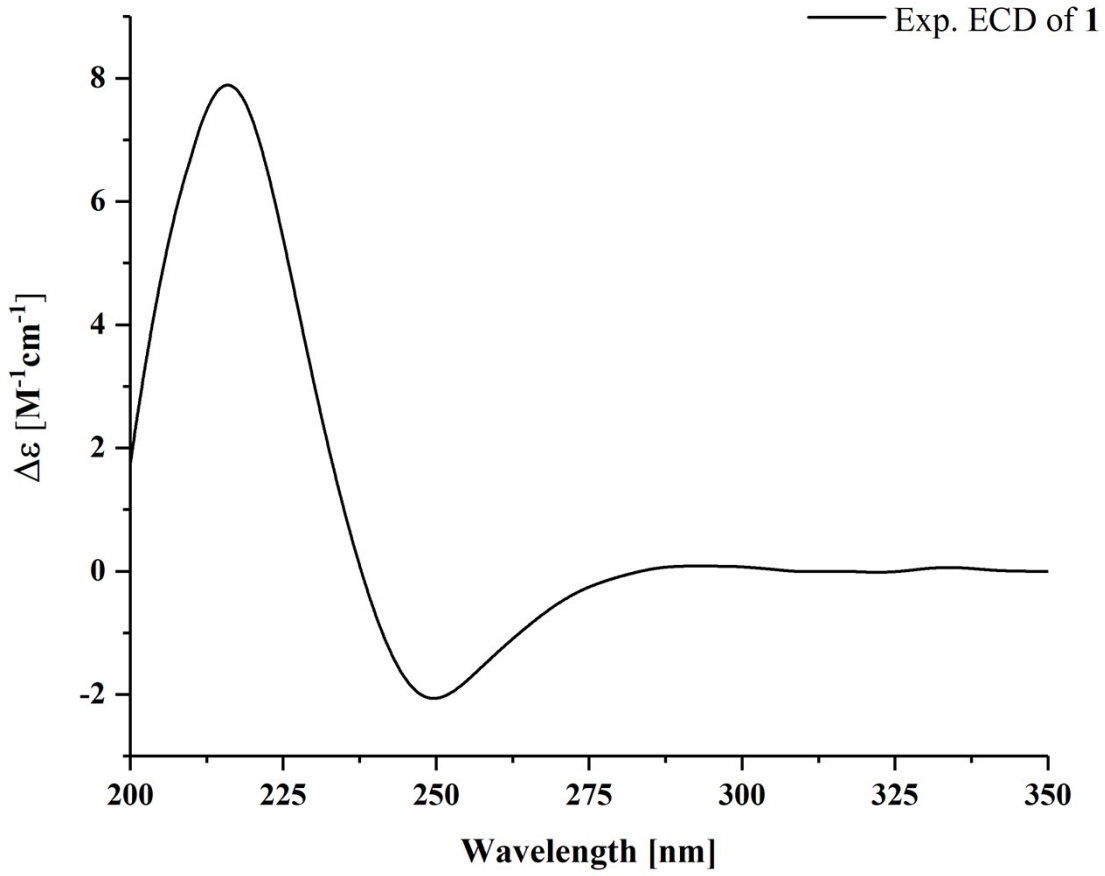
Figure S13. IR (KBr disc) Spectrum of Compound **1**

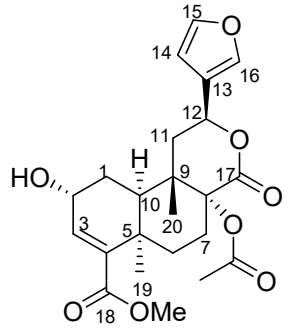




1

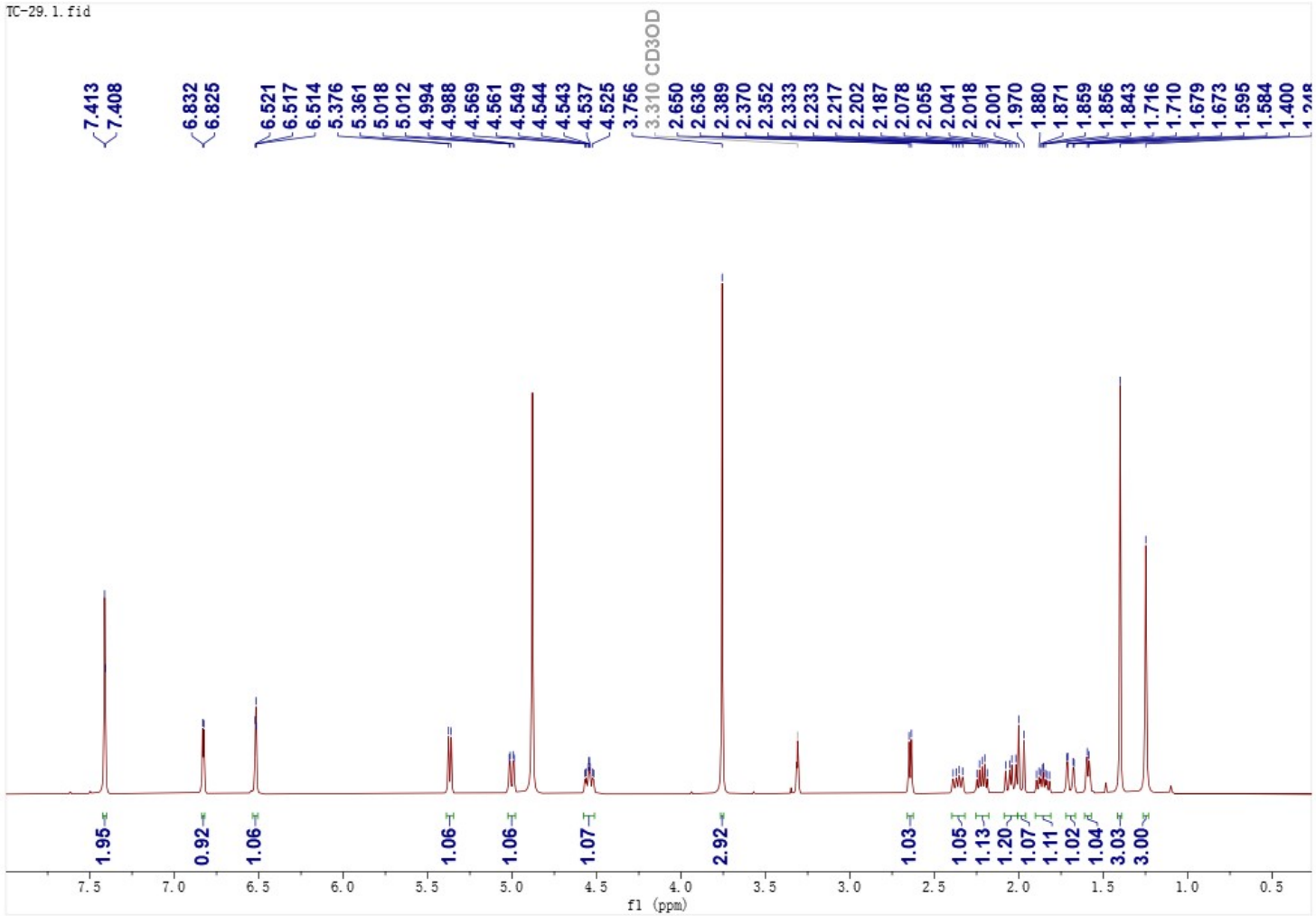
Figure S14. Experimental ECD spectra of Compound **1** in MeOH

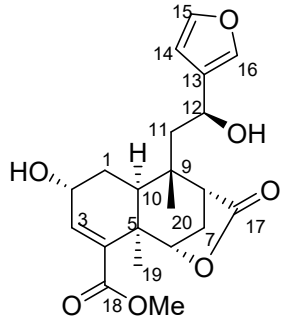




1

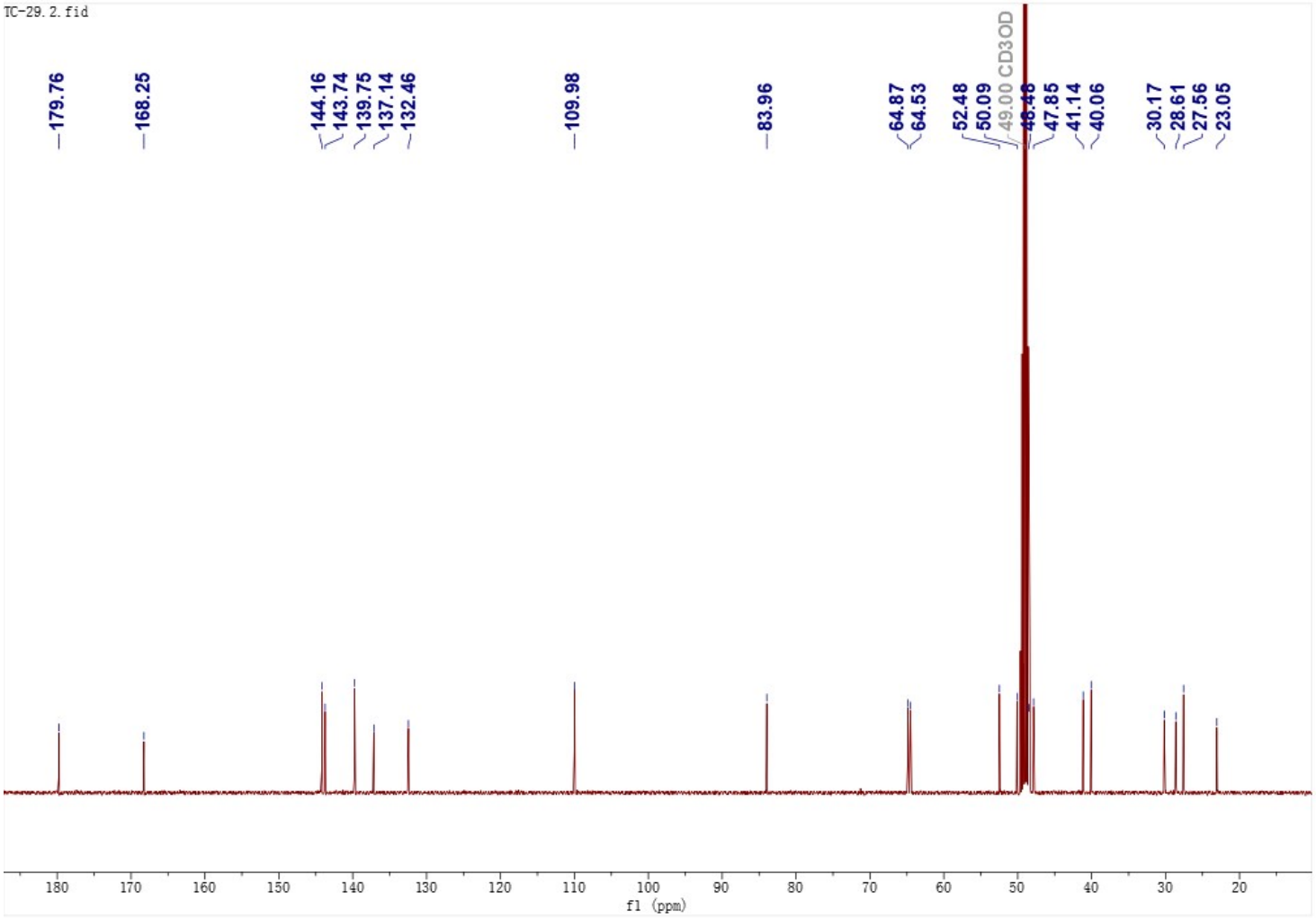
Figure S15. ^{1}H NMR Spectrum of Compound **2** in CD_3OD

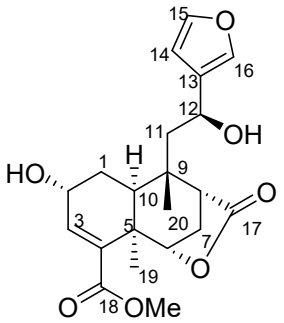




2

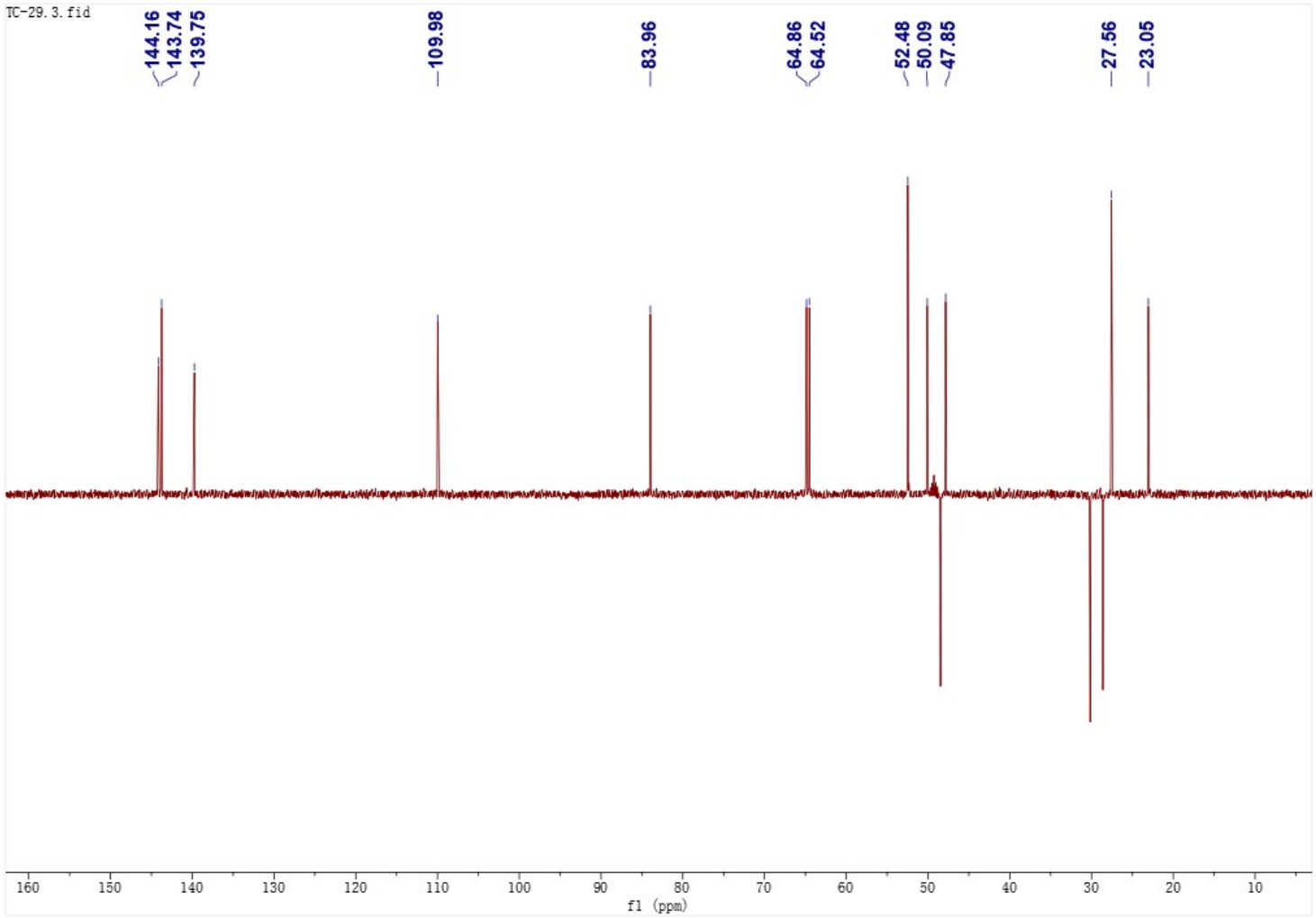
Figure S16. ^{13}C NMR Spectrum of Compound **2** in CD_3OD

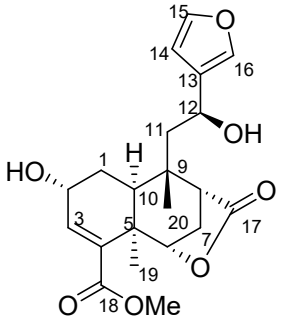




2

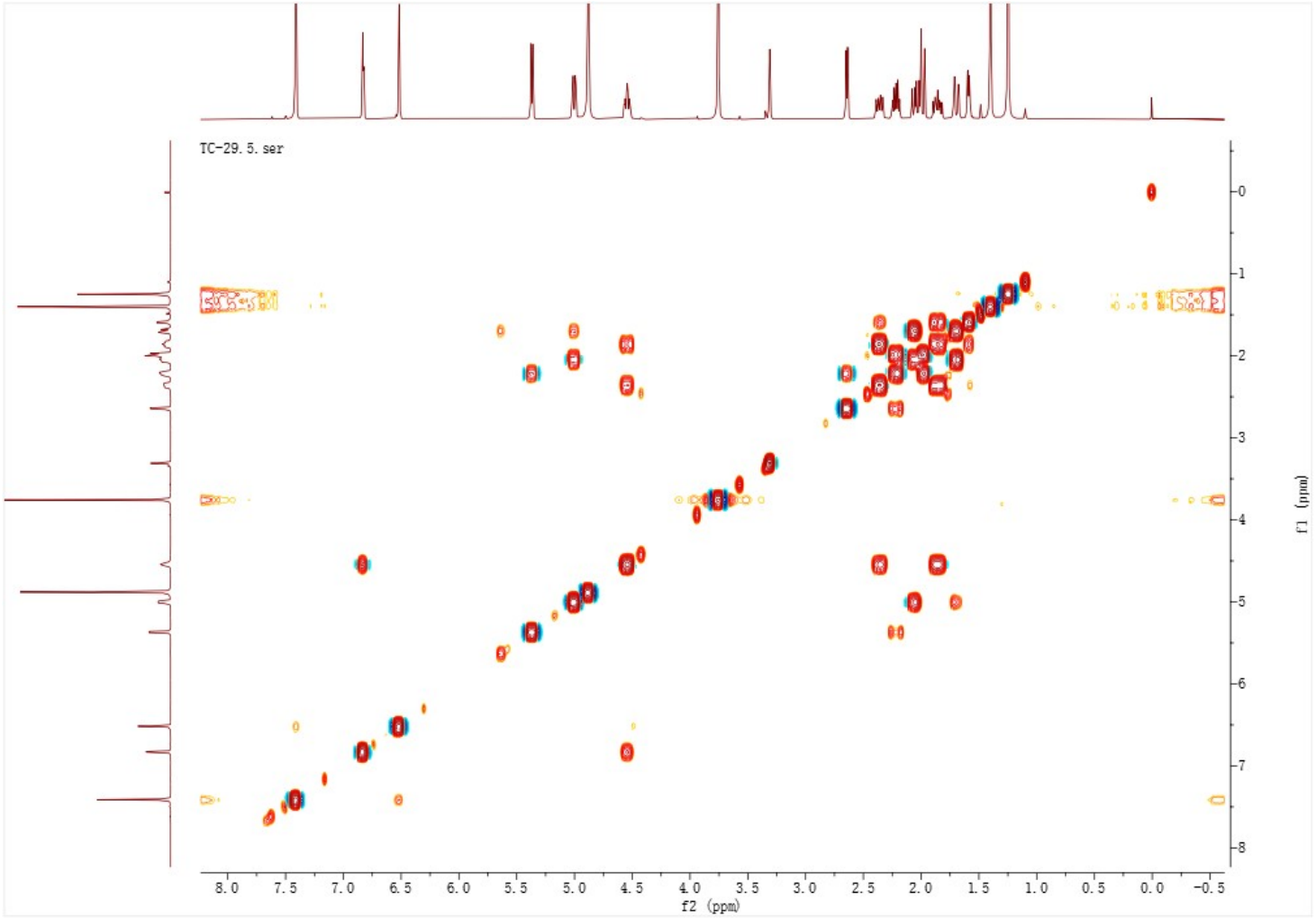
Figure S17. DEPT 135 Spectrum of Compound **2** in CD_3OD

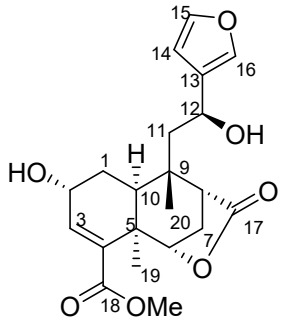




2

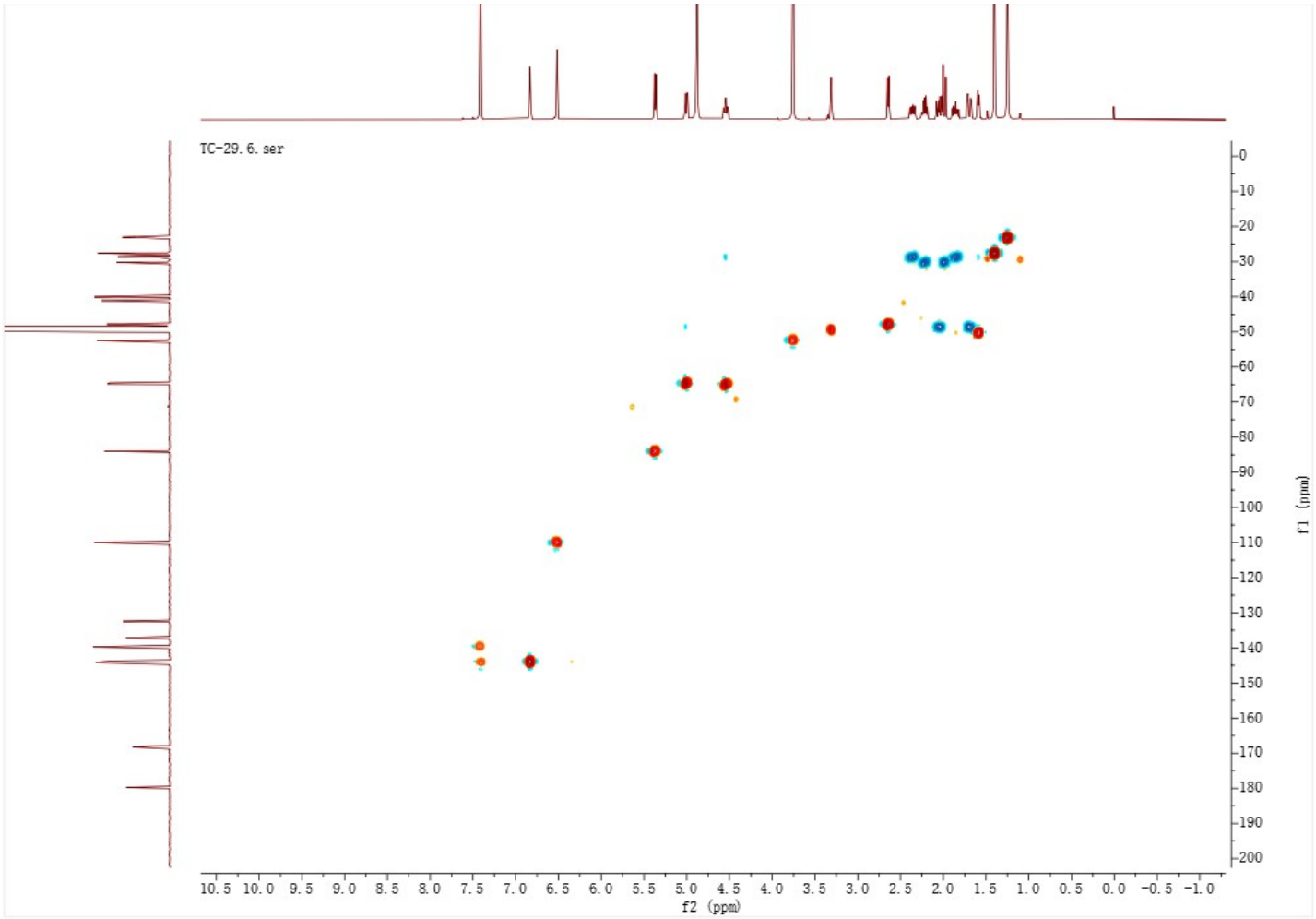
Figure S18. ^{1}H-^{1}H COSY Spectrum of Compound **2** in CD_3OD

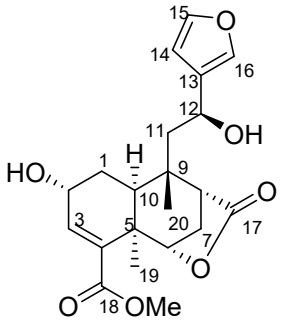




2

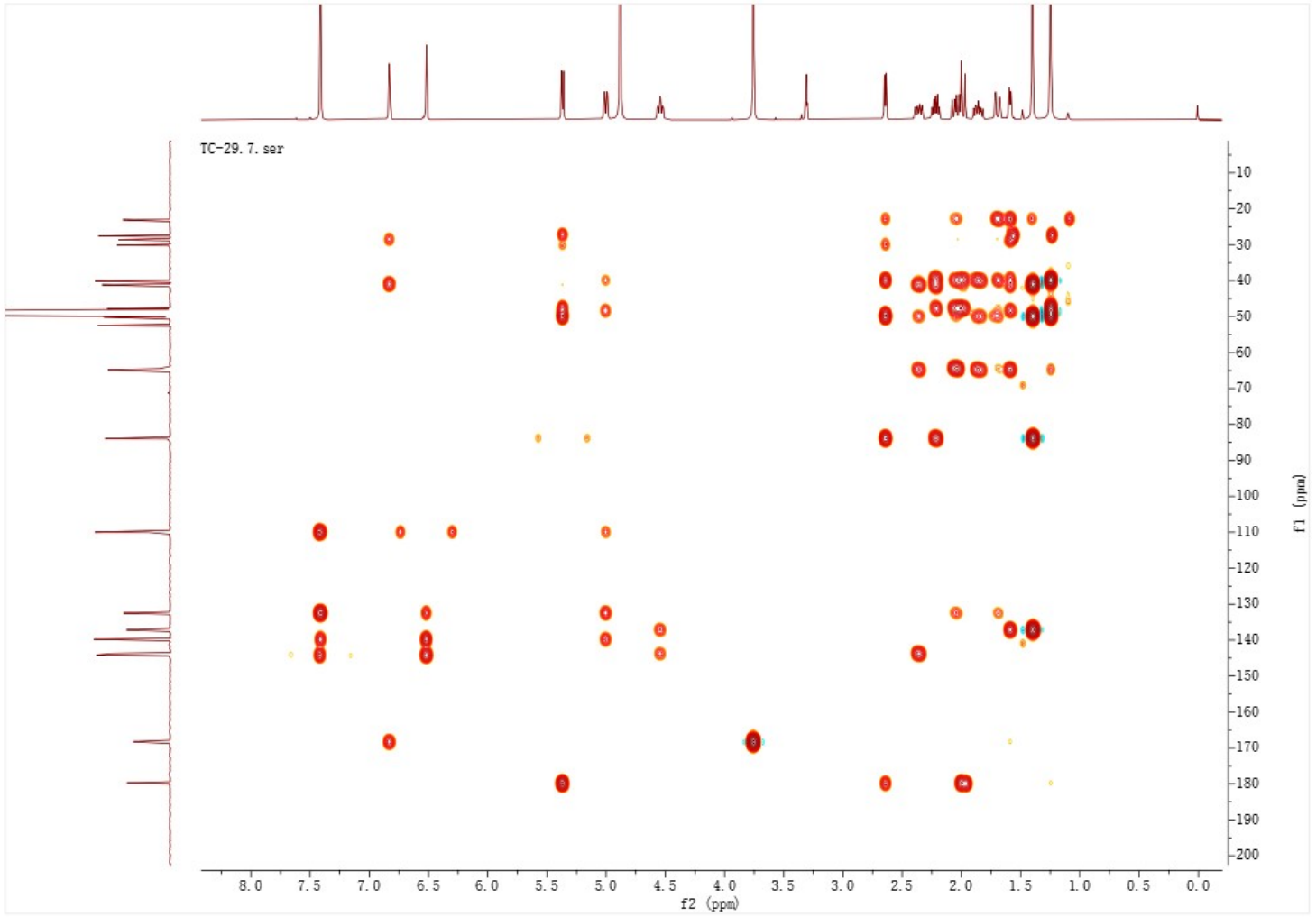
Figure S19. HSQC Spectrum of Compound **2** in CD_3OD

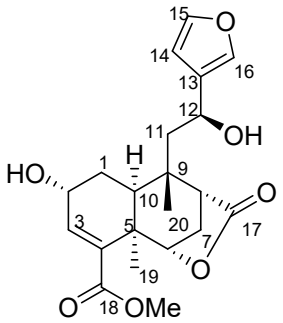




2

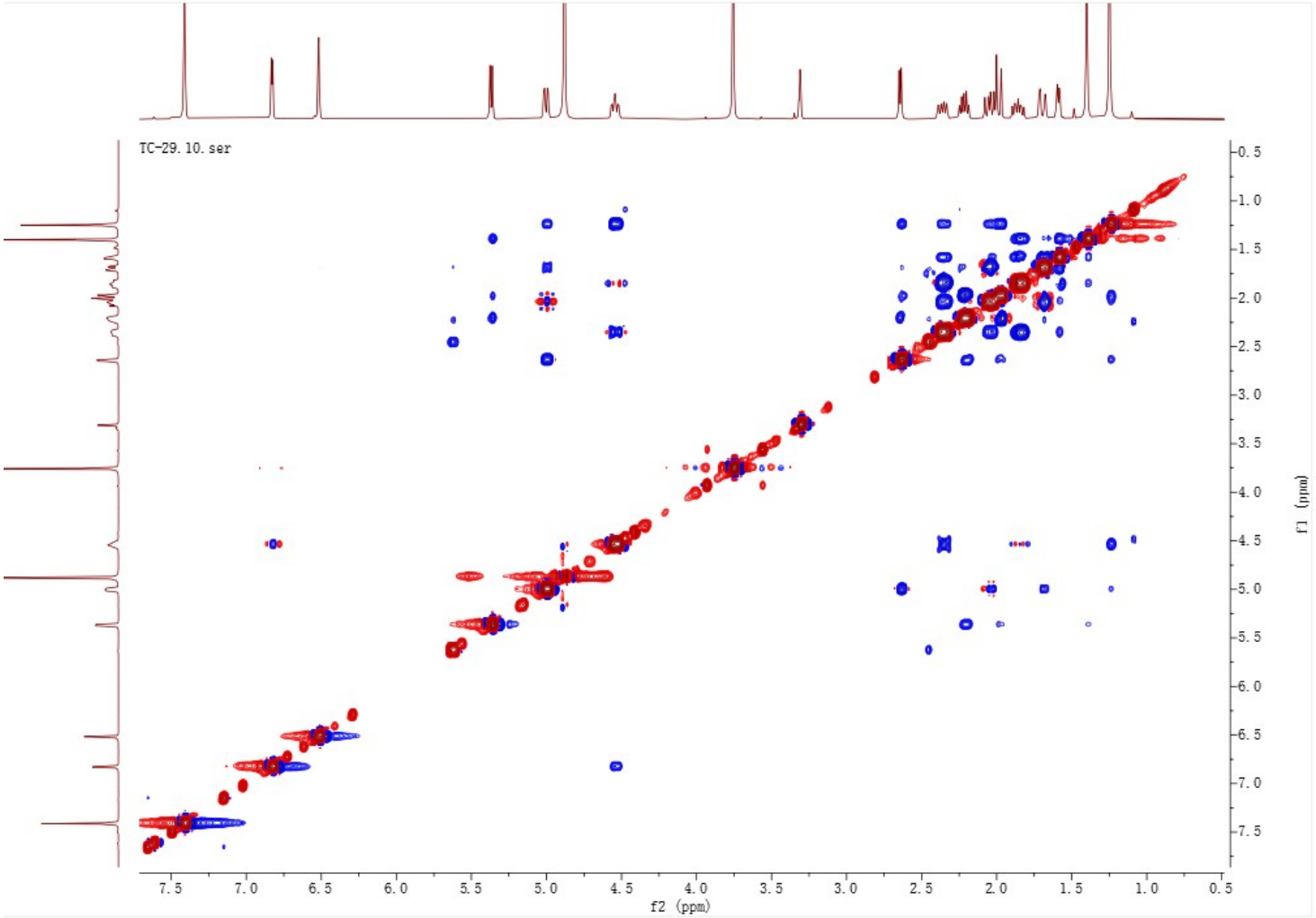
Figure S20. HMBC Spectrum of Compound **2** in CD_3OD

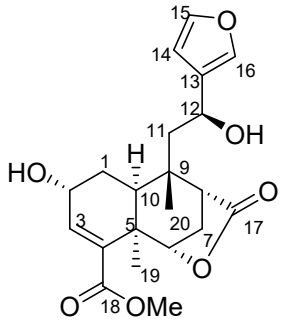




2

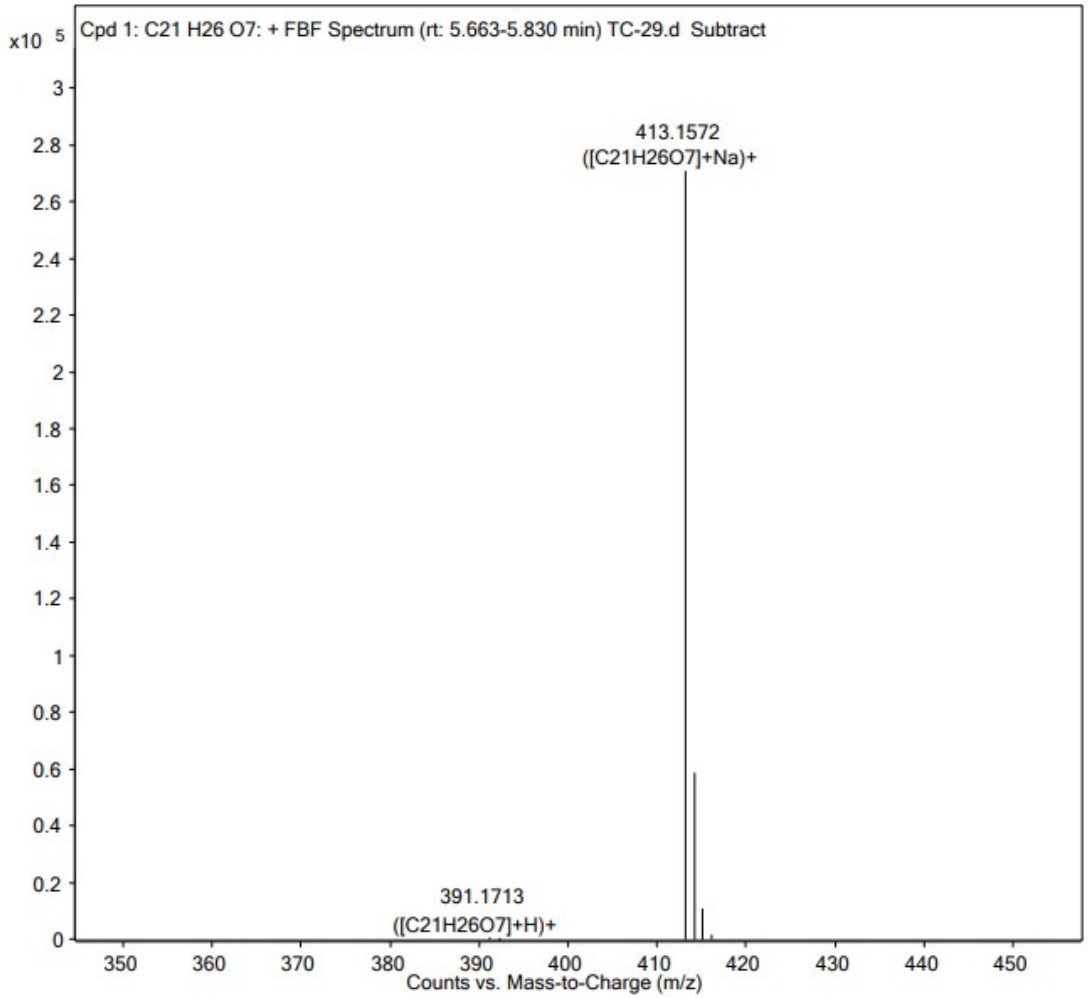
Figure S21. NOESY Spectrum of Compound **2** in CD_3OD

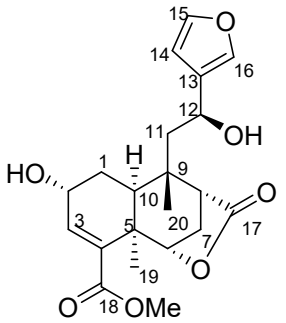




2

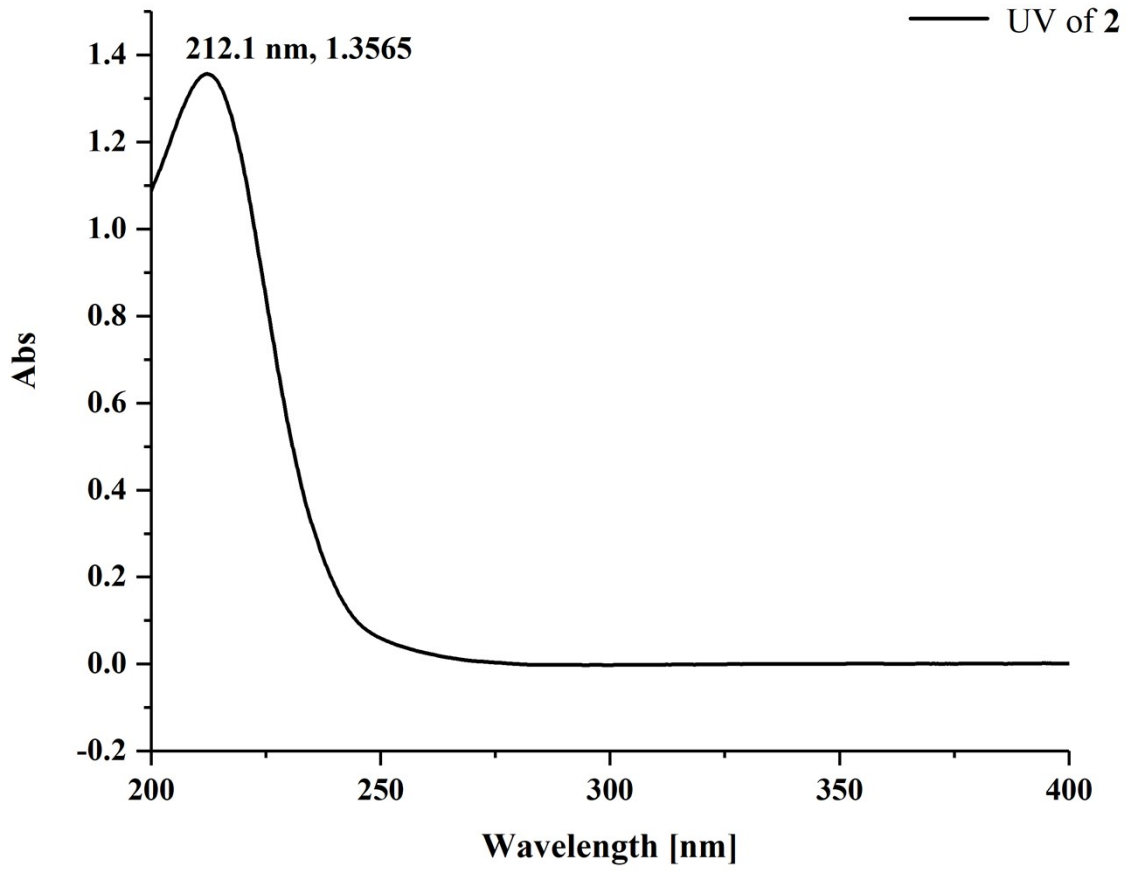
Figure S22. (+) HRESIMS Spectrum of Compound **2**

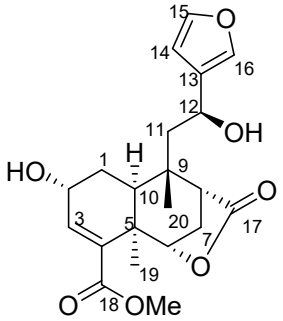




2

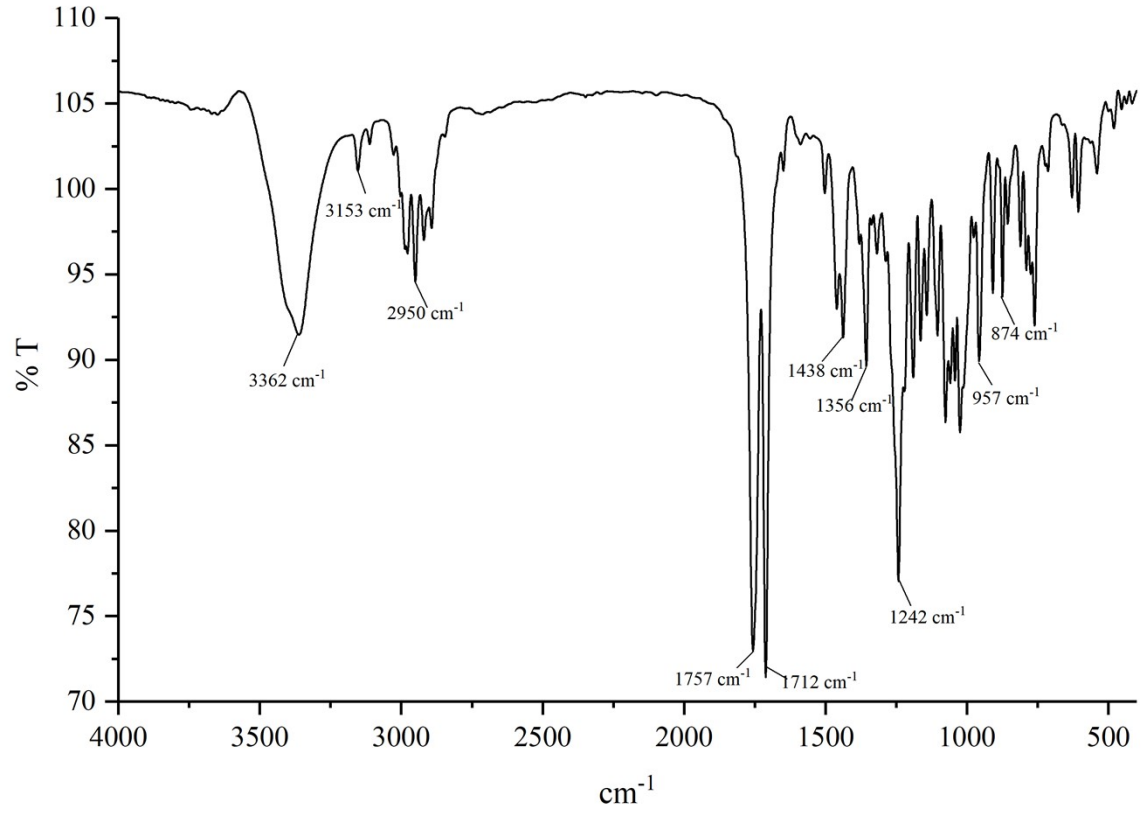
Figure S23. UV Spectrum of Compound **2**

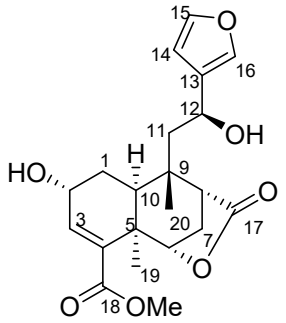




2

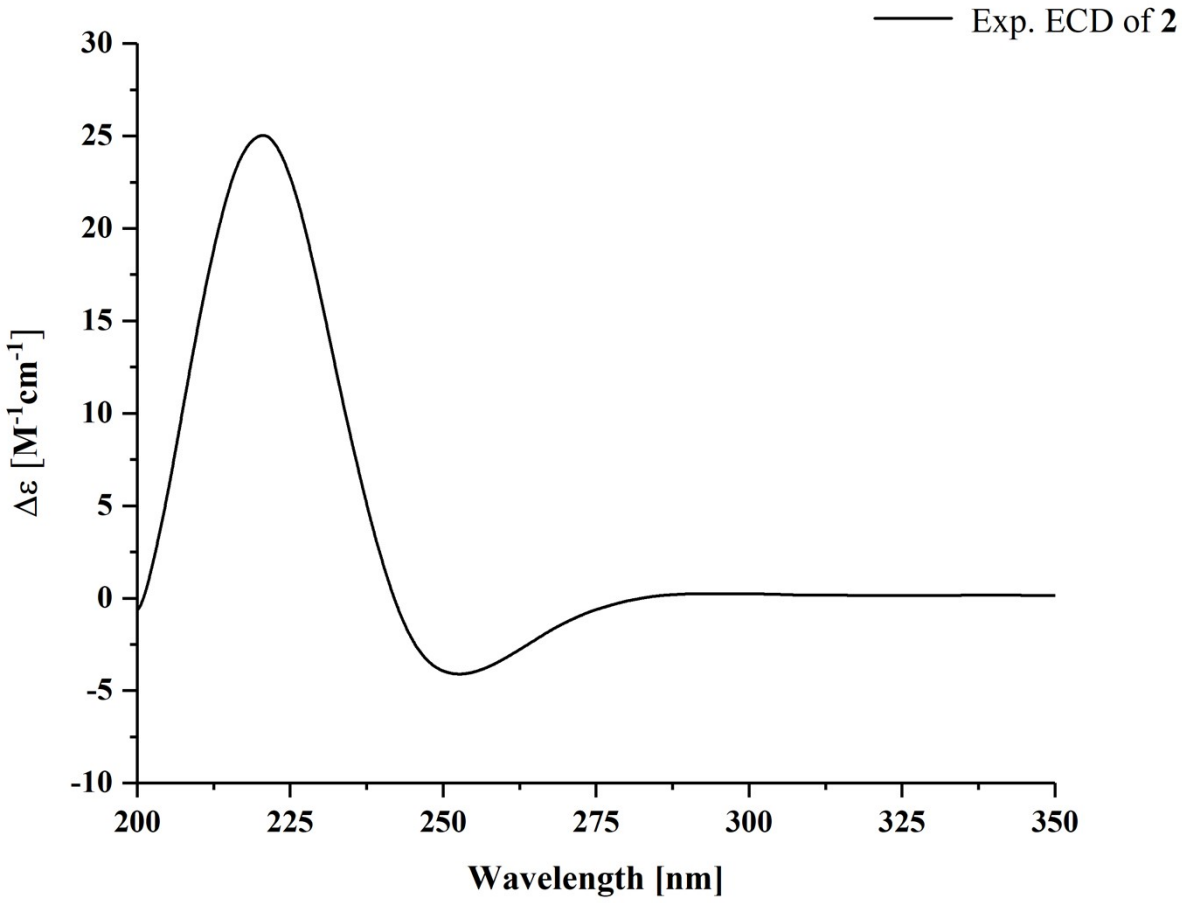
Figure S24. IR (KBr disc) Spectrum of Compound **2**

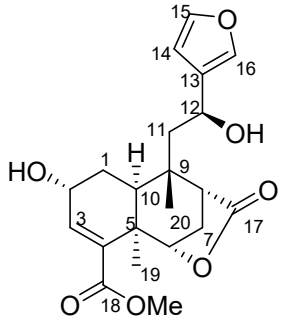




2

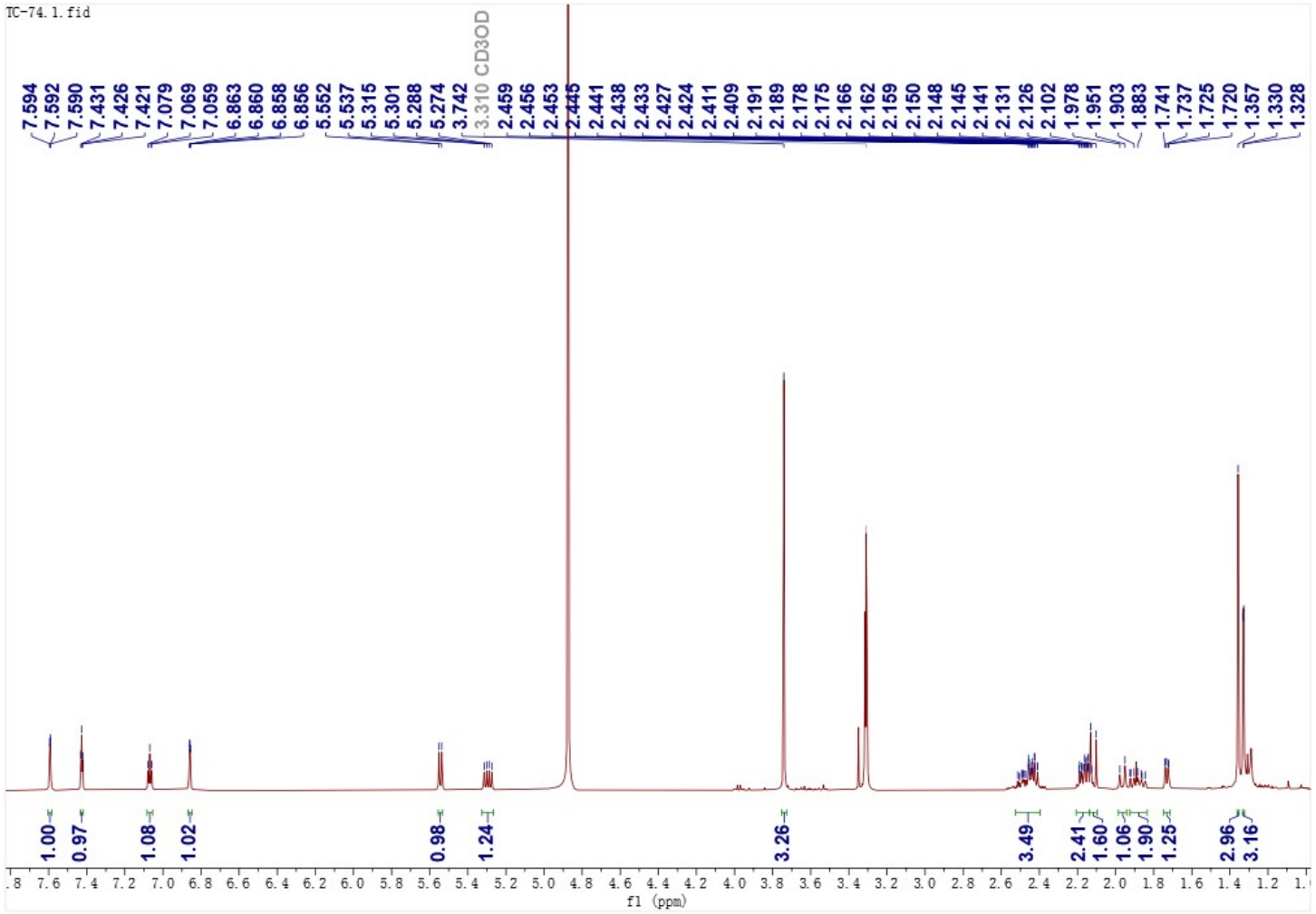
Figure S25. Experimental ECD spectra of Compound **2** in MeOH

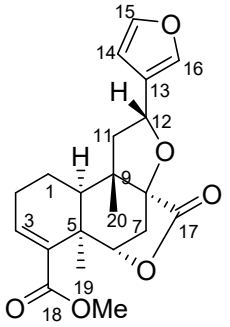




2

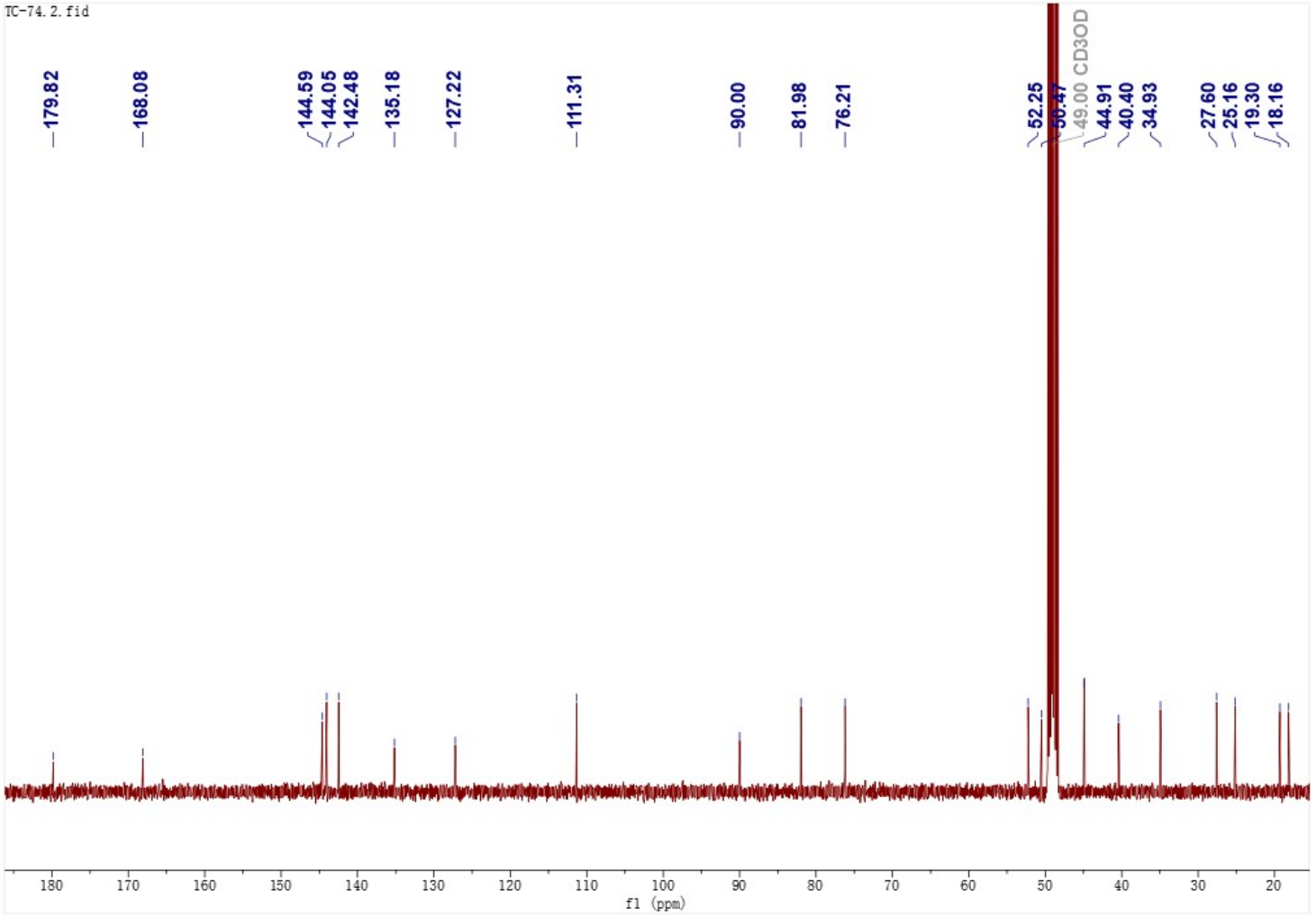
Figure S26. ^{1}H NMR Spectrum of Compound **3** in CD_3OD

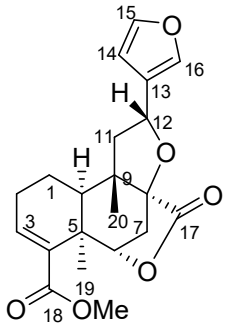




3

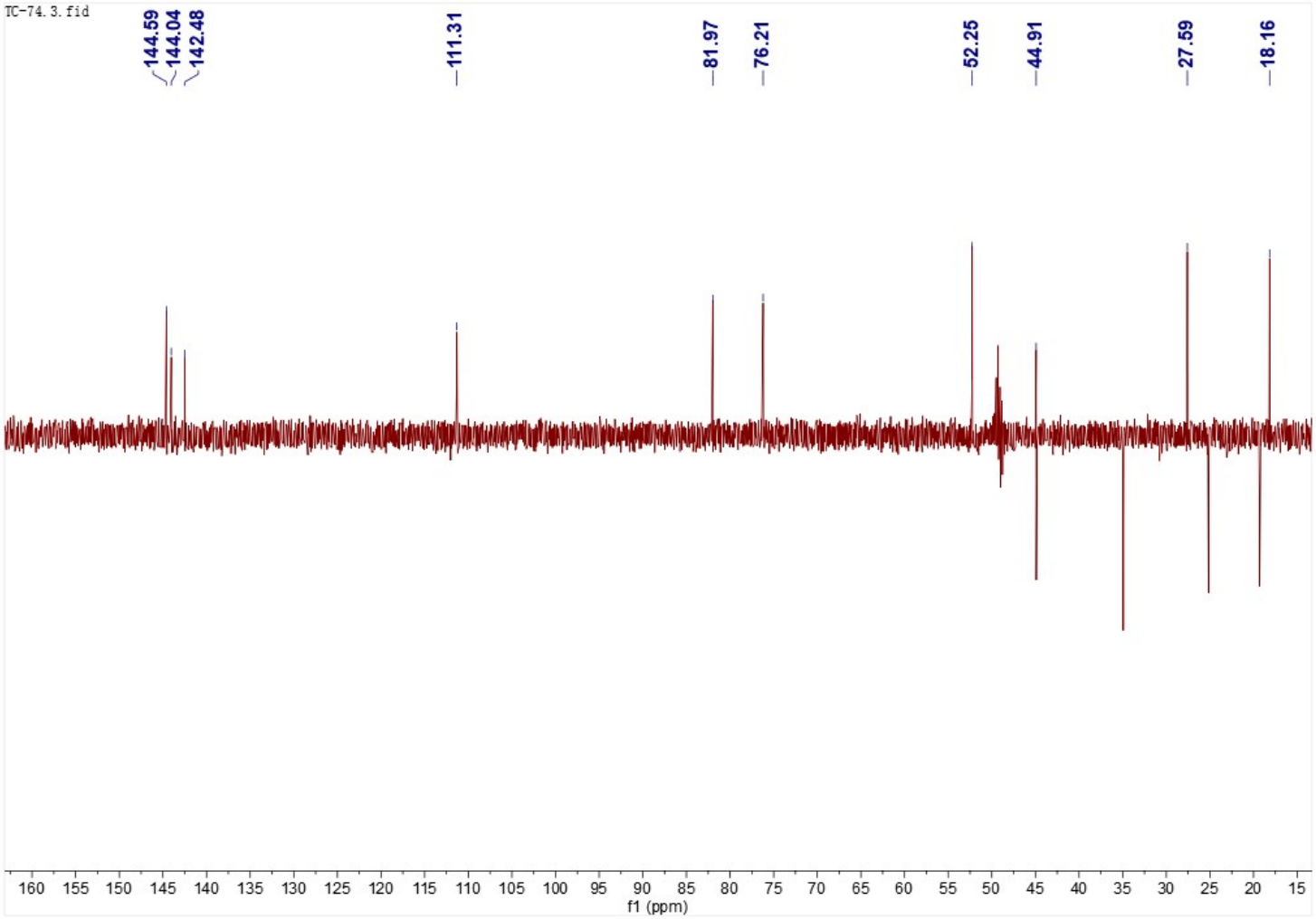
Figure S27. ^{13}C NMR Spectrum of Compound **3** in CD_3OD

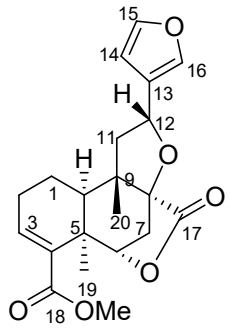




3

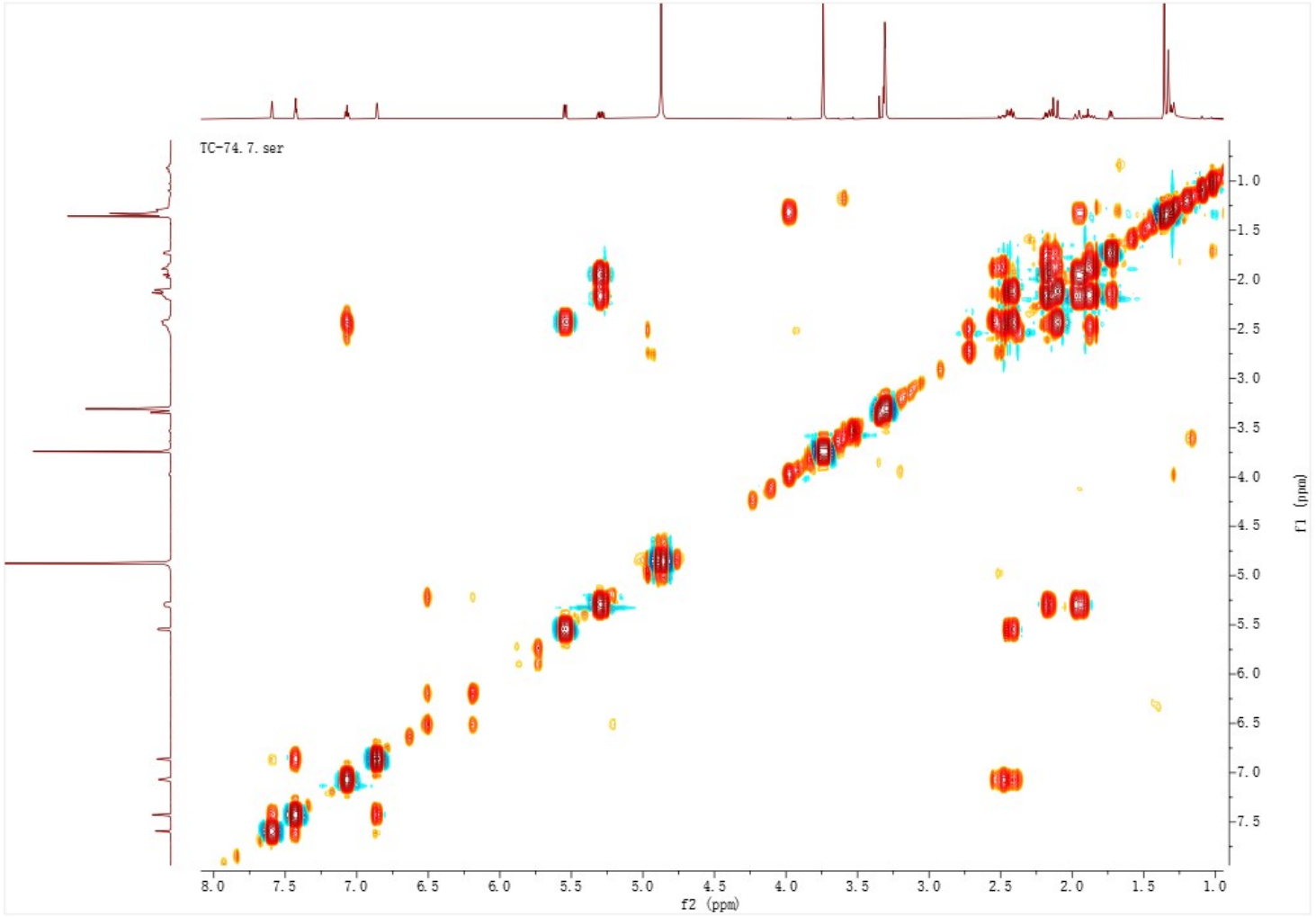
Figure S28. DEPT 135 Spectrum of Compound **3** in CD_3OD

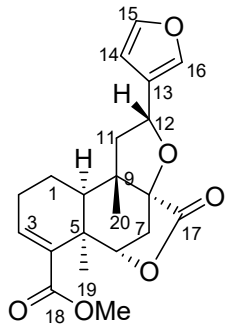




3

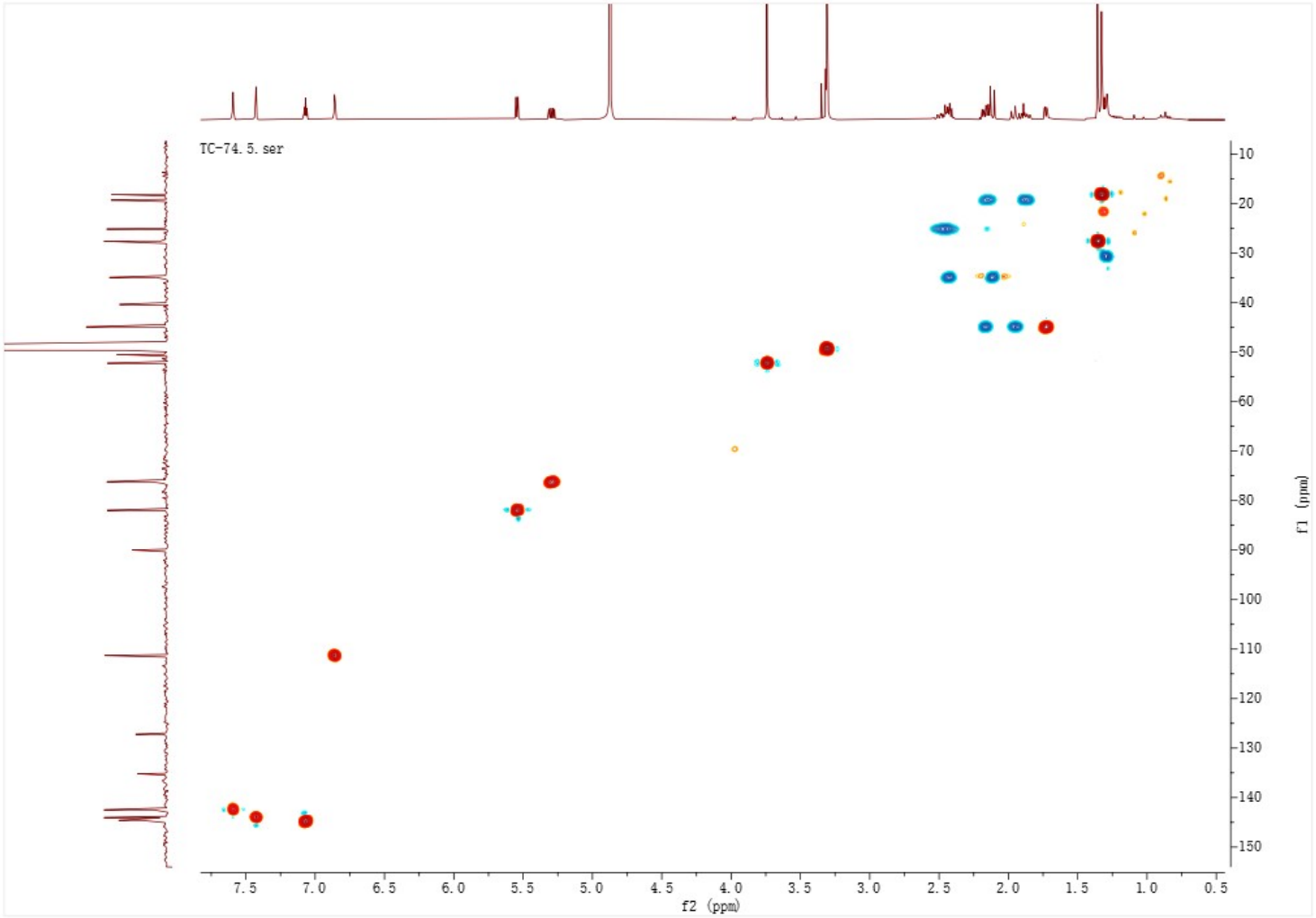
Figure S29. ^{1}H-^{1}H COSY Spectrum of Compound **3** in CD_3OD

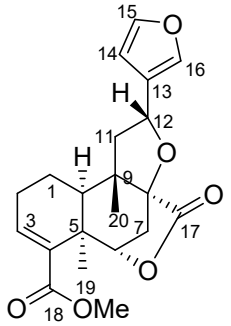




3

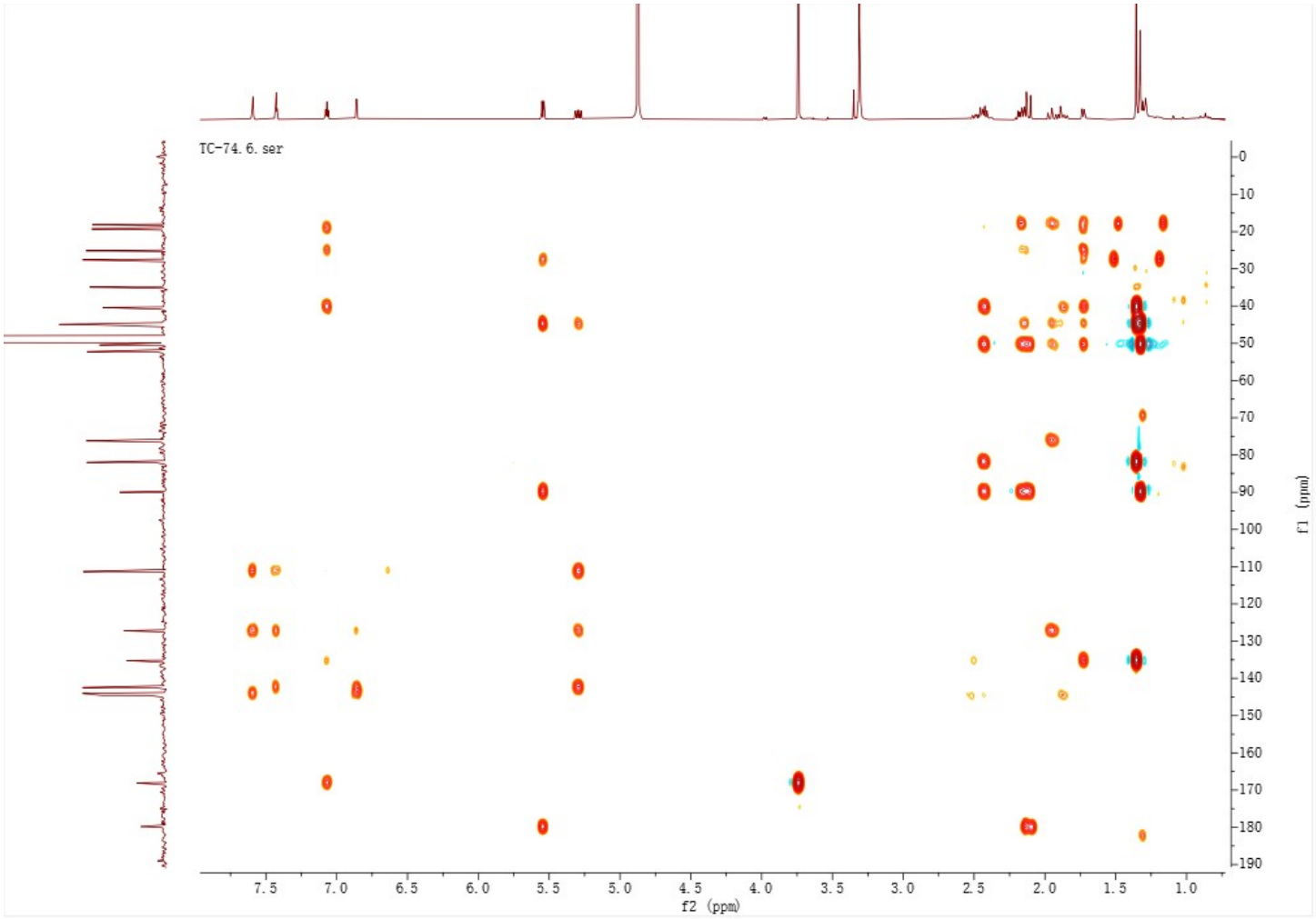
Figure S30. HSQC Spectrum of Compound **3** in CD_3OD

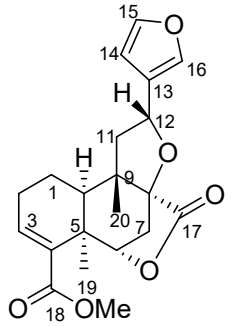




3

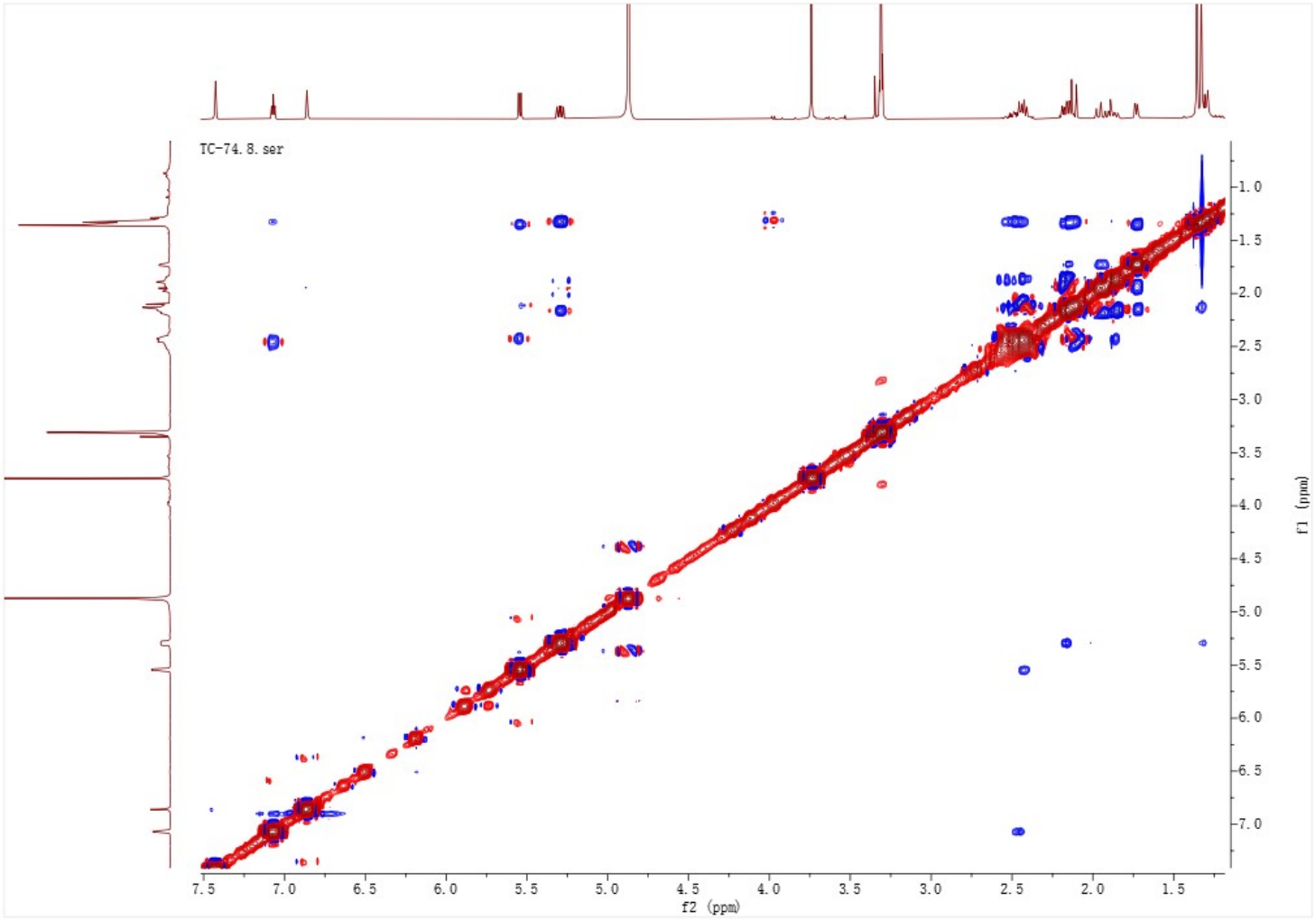
Figure S31. HMBC Spectrum of Compound **3** in CD_3OD

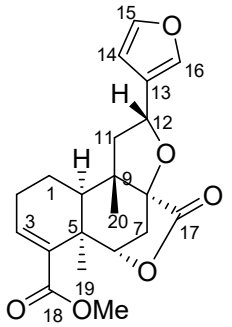




3

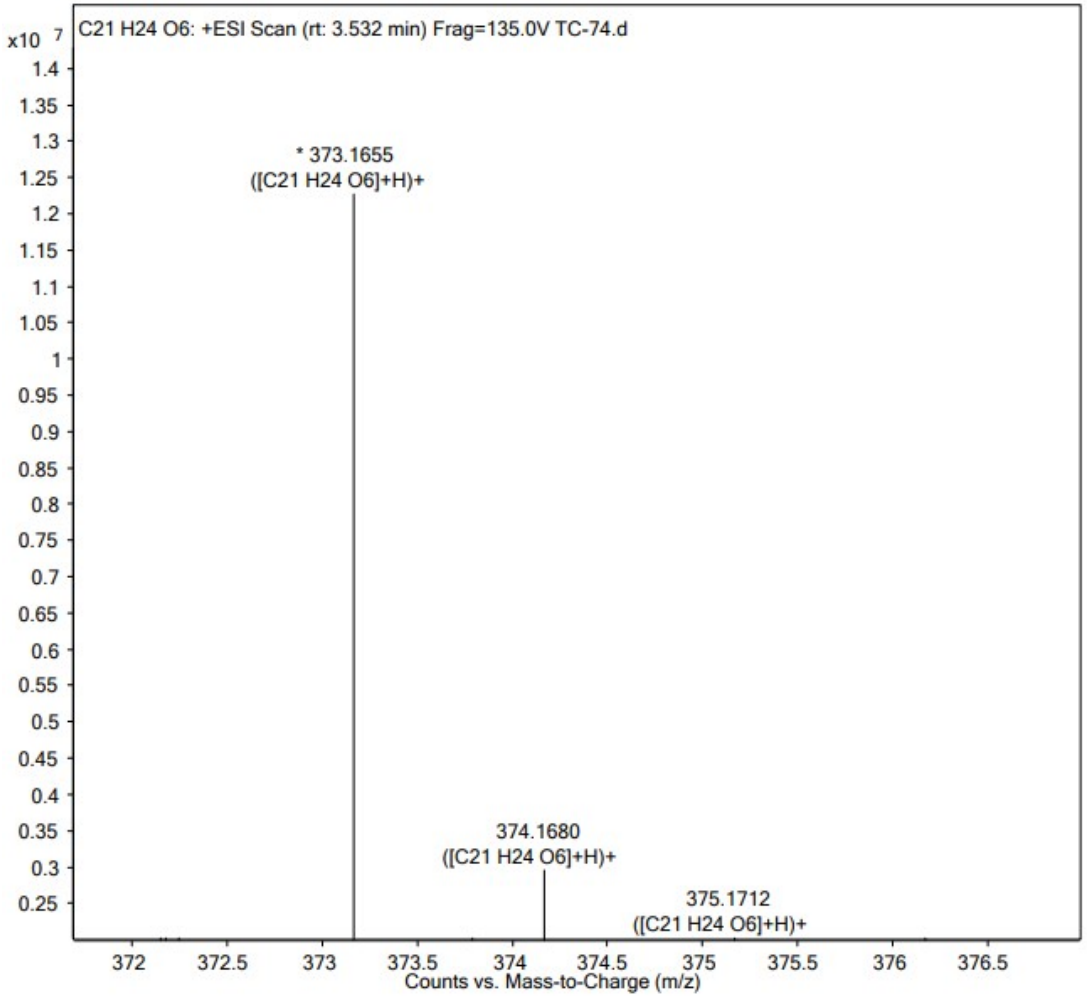
Figure S32. NOESY Spectrum of Compound **3** in CD_3OD

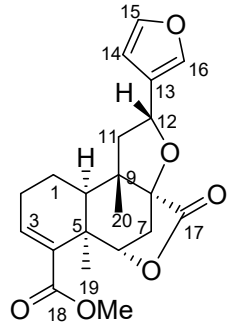




3

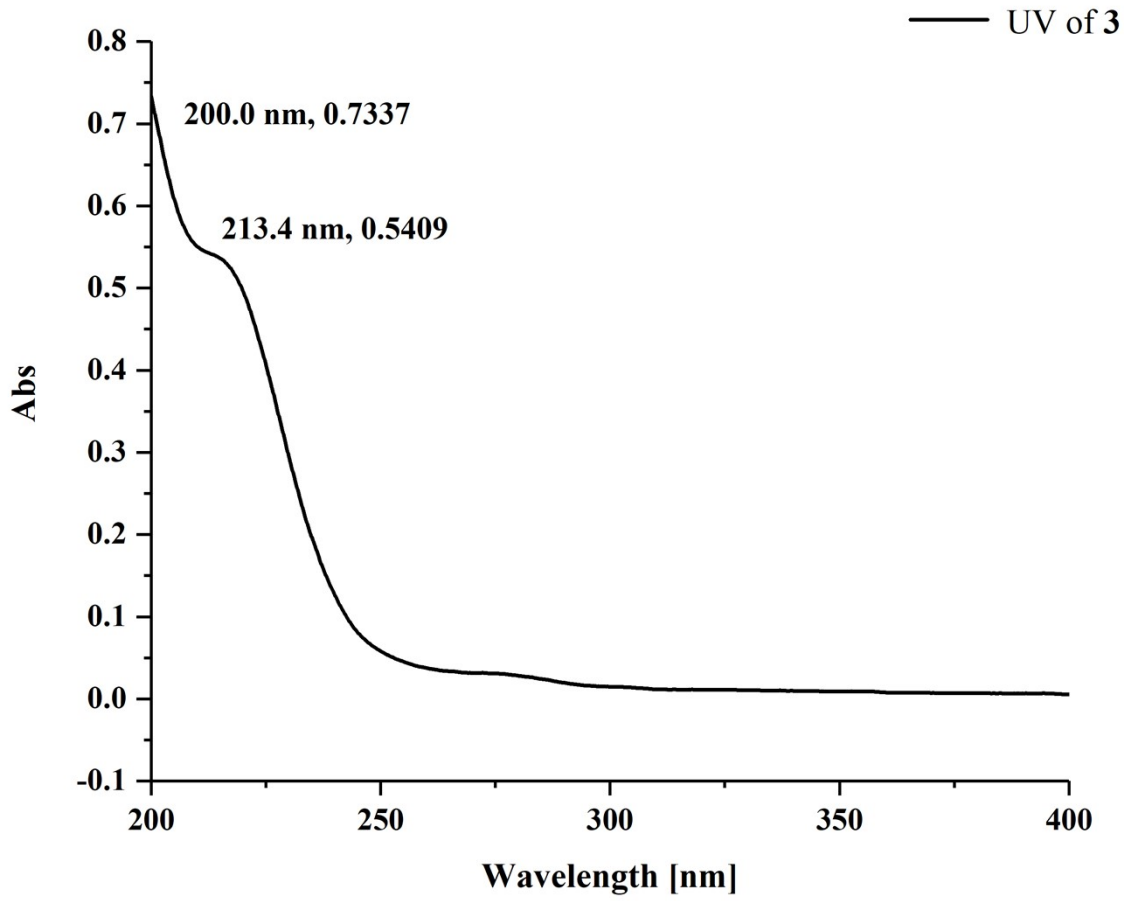
Figure S33. (+) HRESIMS Spectrum of Compound **3**

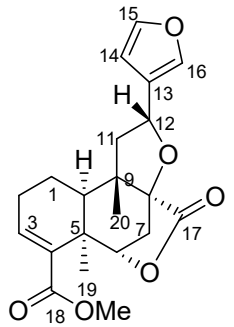




3

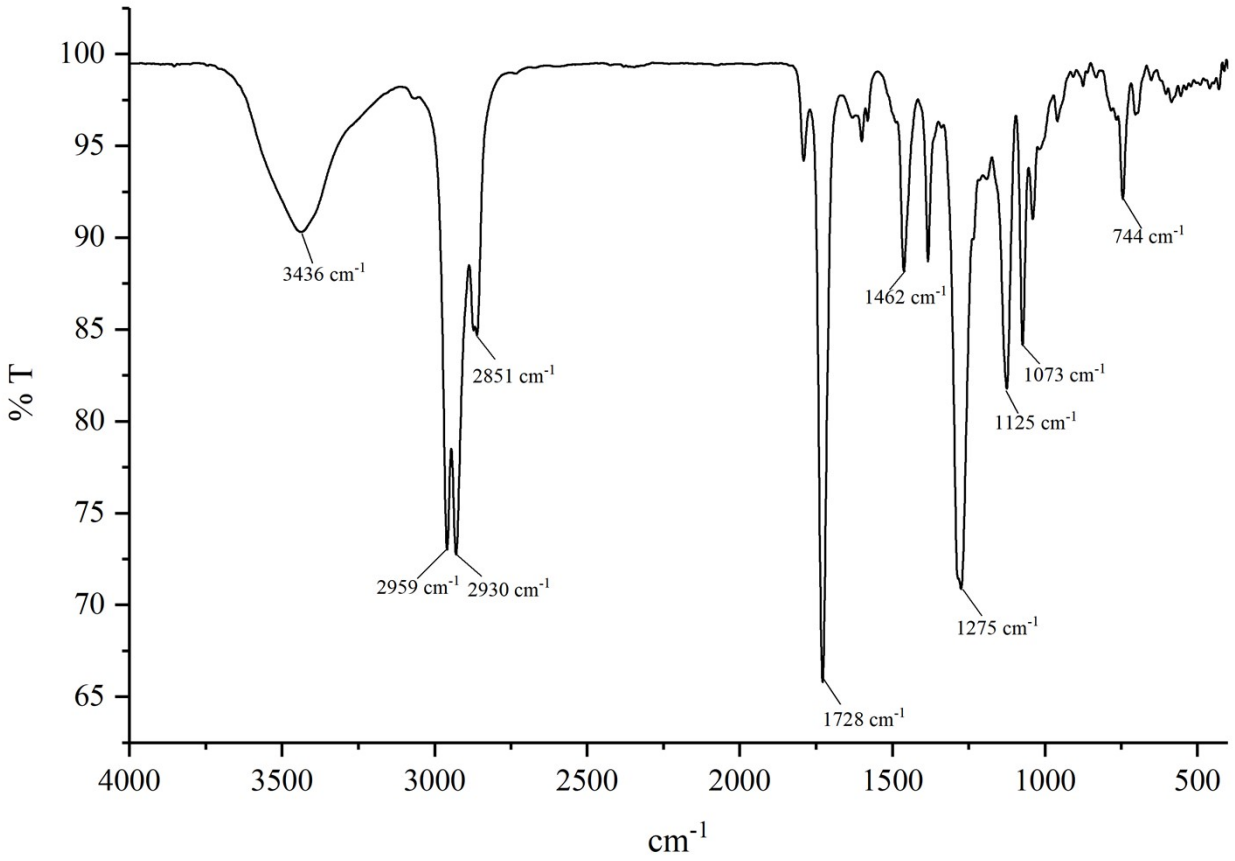
Figure S34. UV Spectrum of Compound **3**

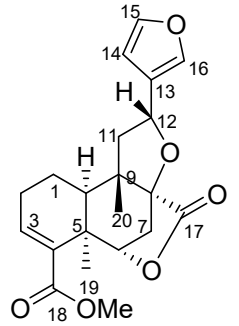




3

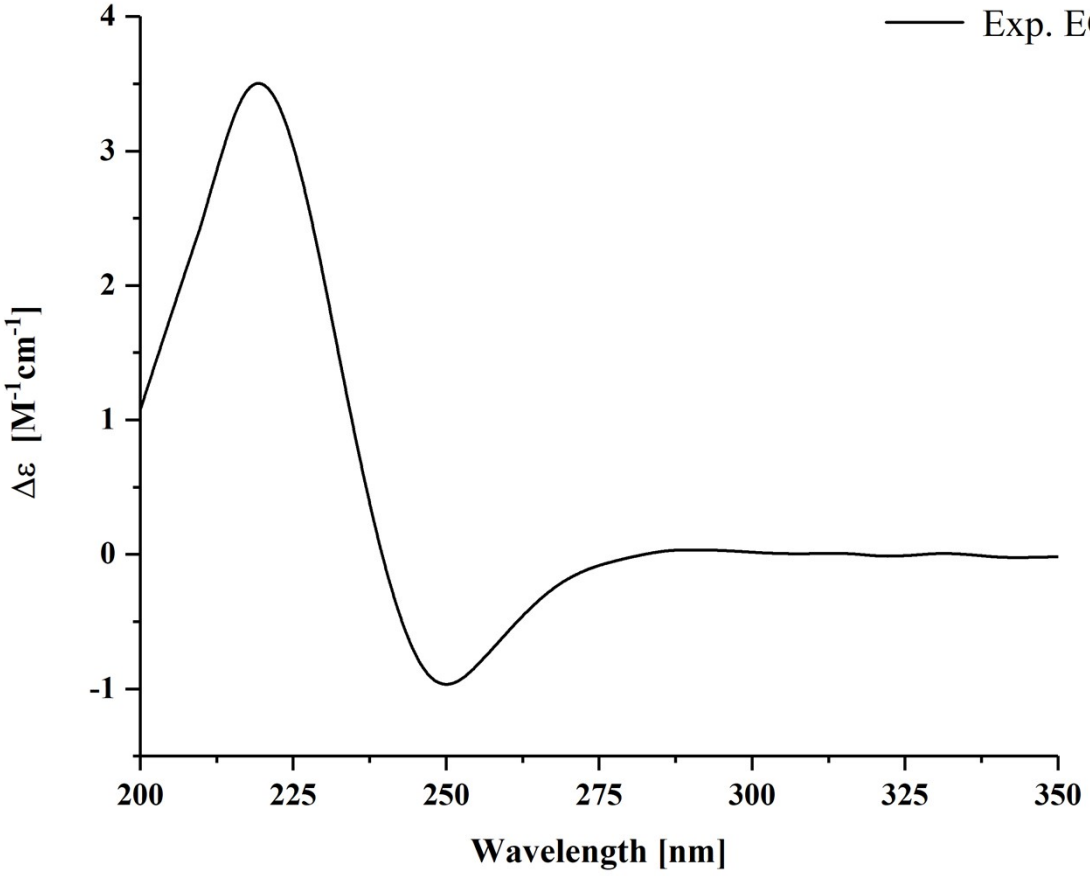
Figure S35. IR (KBr disc) Spectrum of Compound **3**

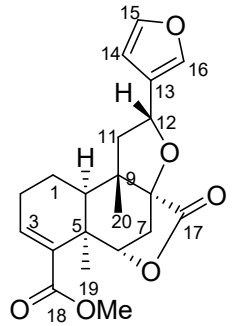




3

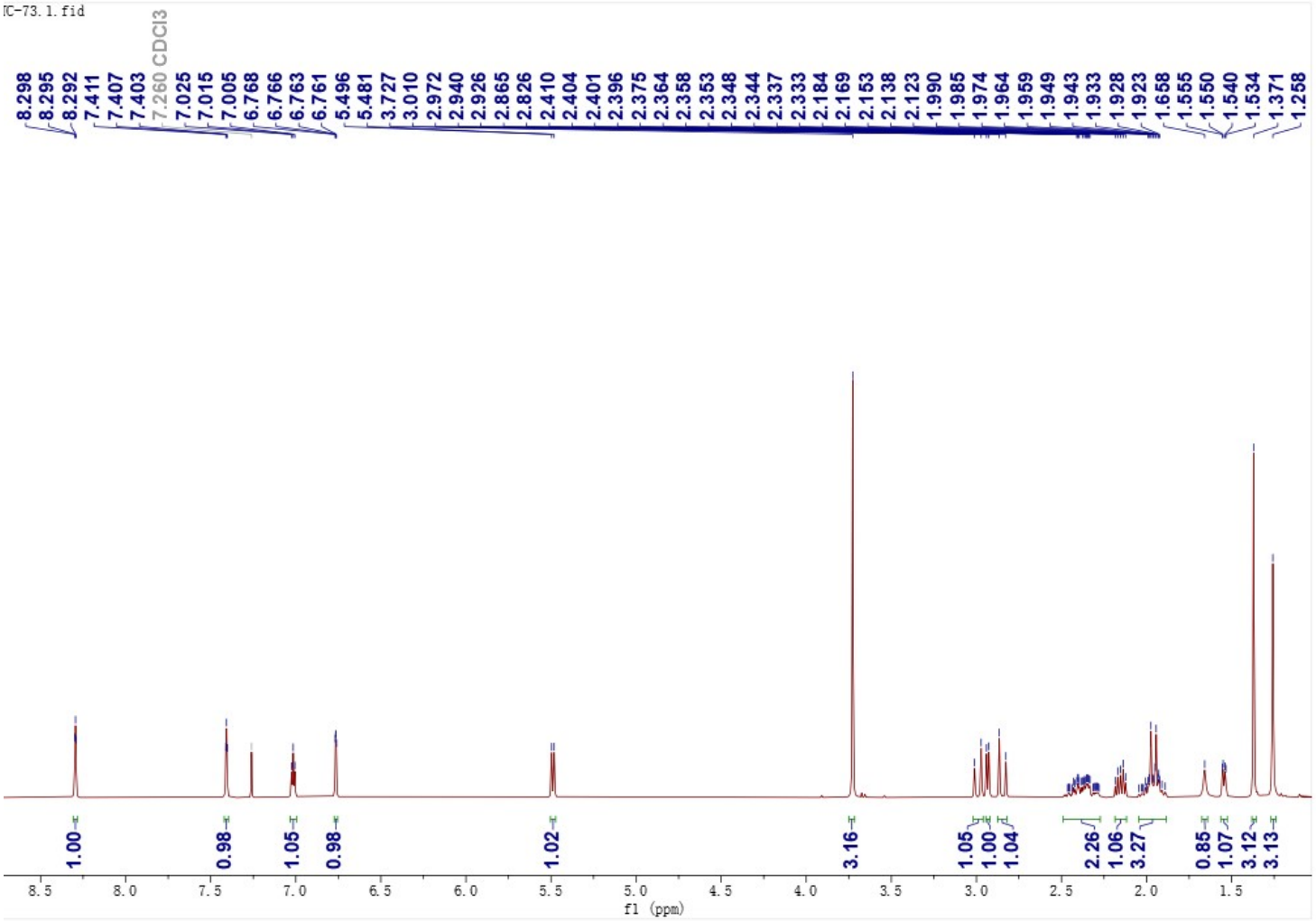
Figure S36. Experimental ECD spectra of Compound **3** in MeOH

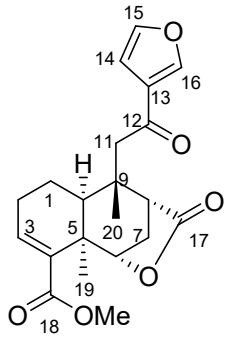




3

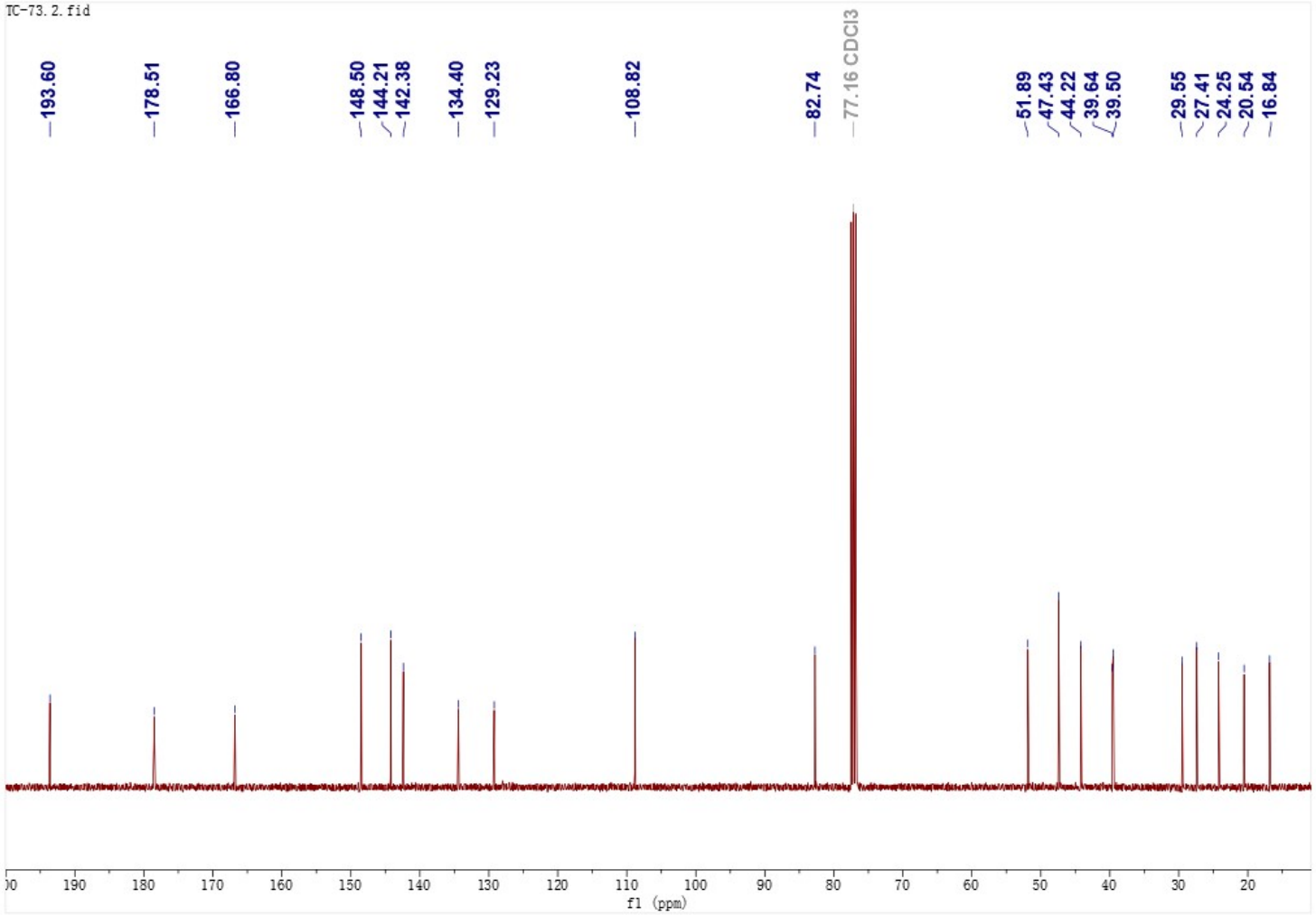
Figure S37. ^{1}H NMR Spectrum of Compound **4** in $CDCl_3$

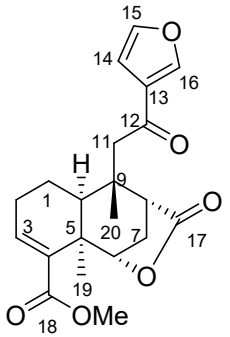




4

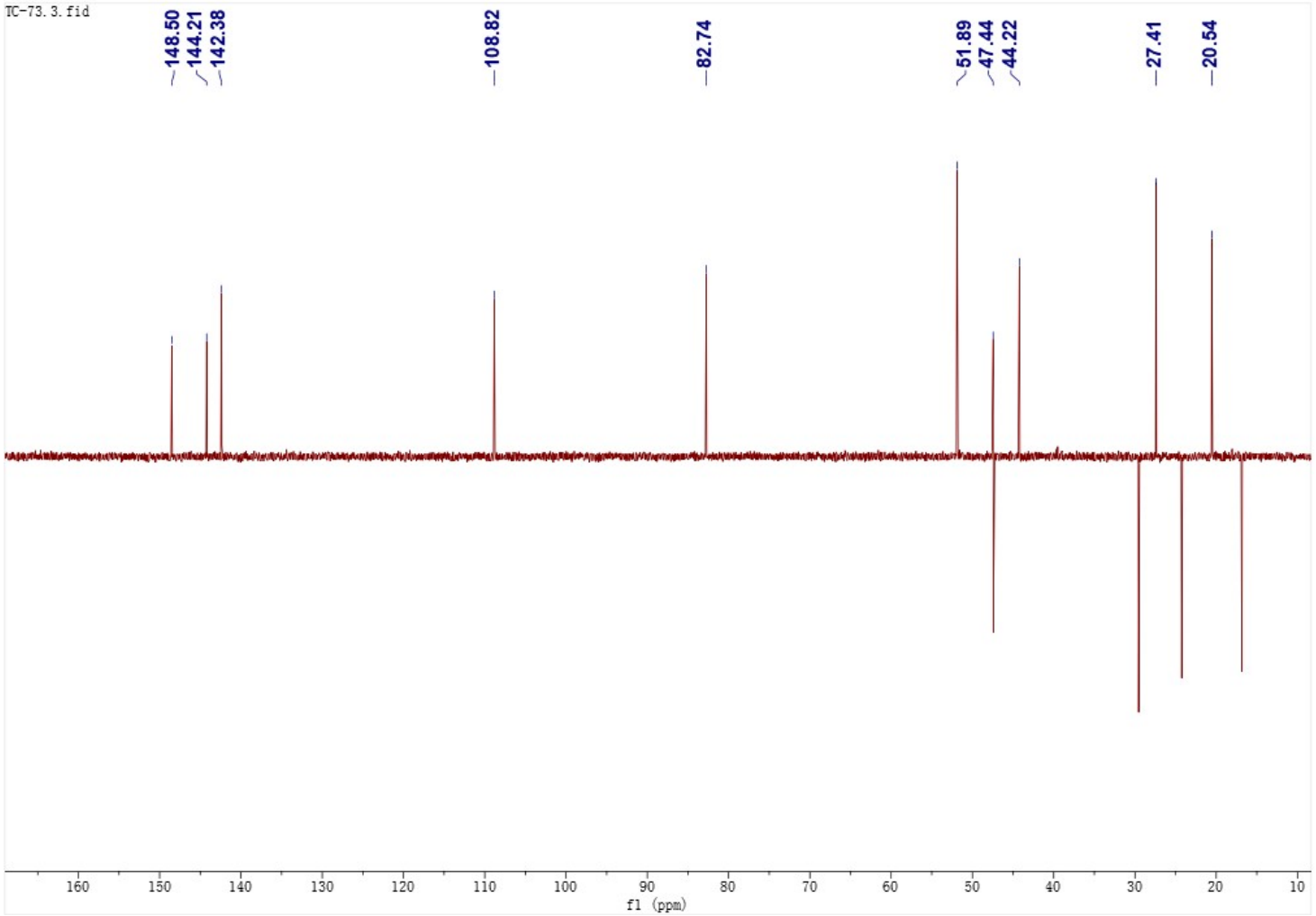
Figure S38. ^{13}C NMR Spectrum of Compound **4** in $CDCl_3$

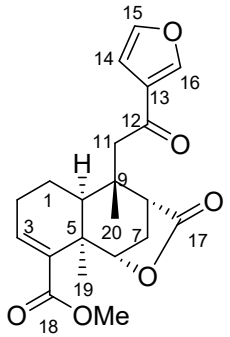




4

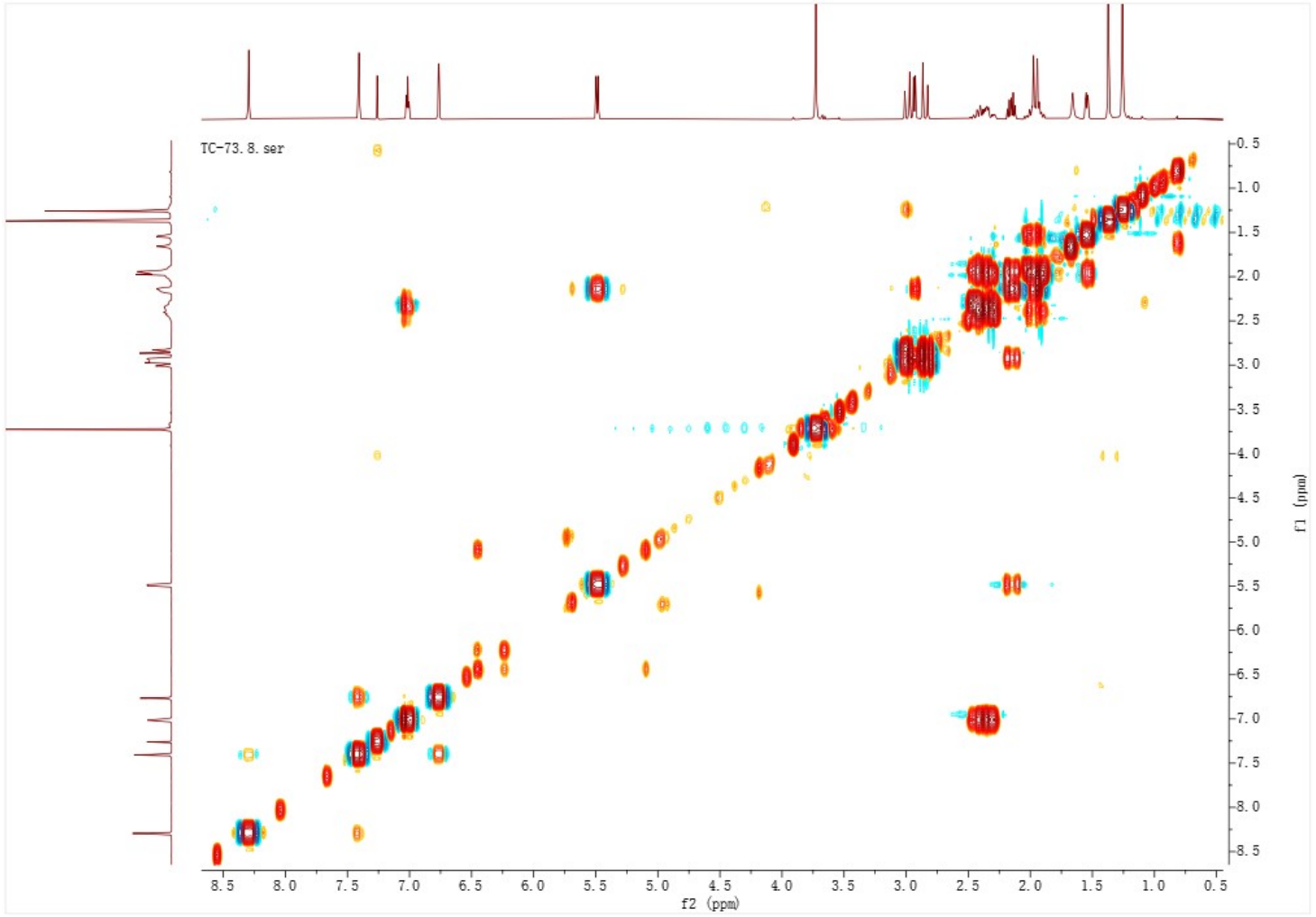
Figure S39. DEPT 135 Spectrum of Compound **4** in $CDCl_3$

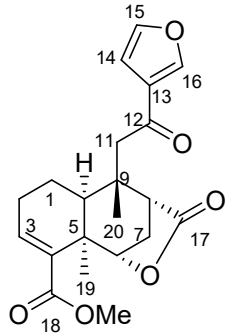




4

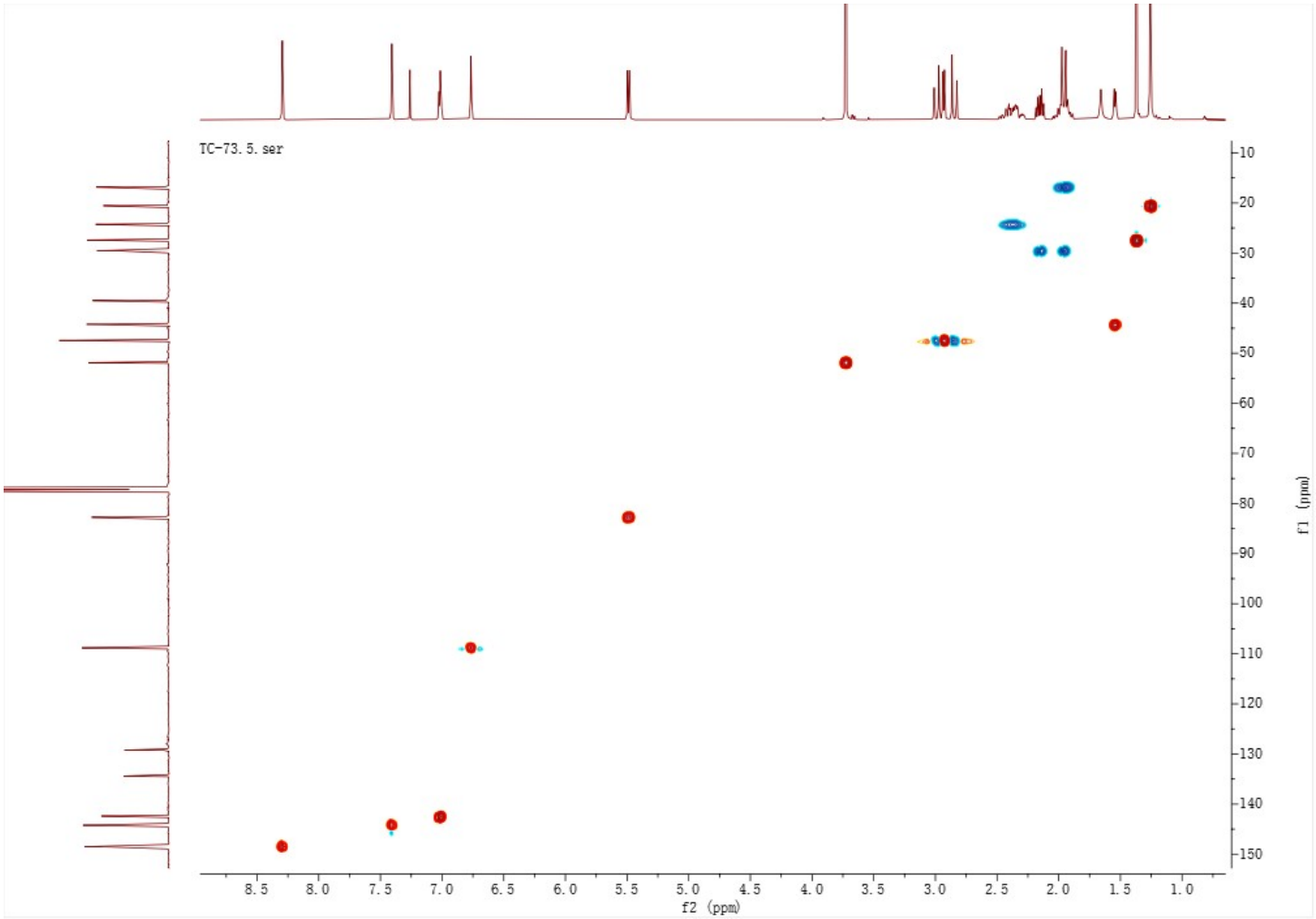
Figure S40. ^{1}H-^{1}H COSY Spectrum of Compound **4** in $CDCl_3$

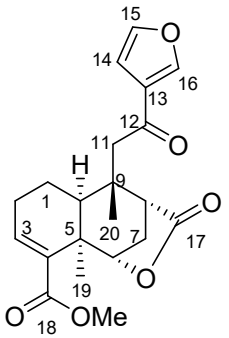




4

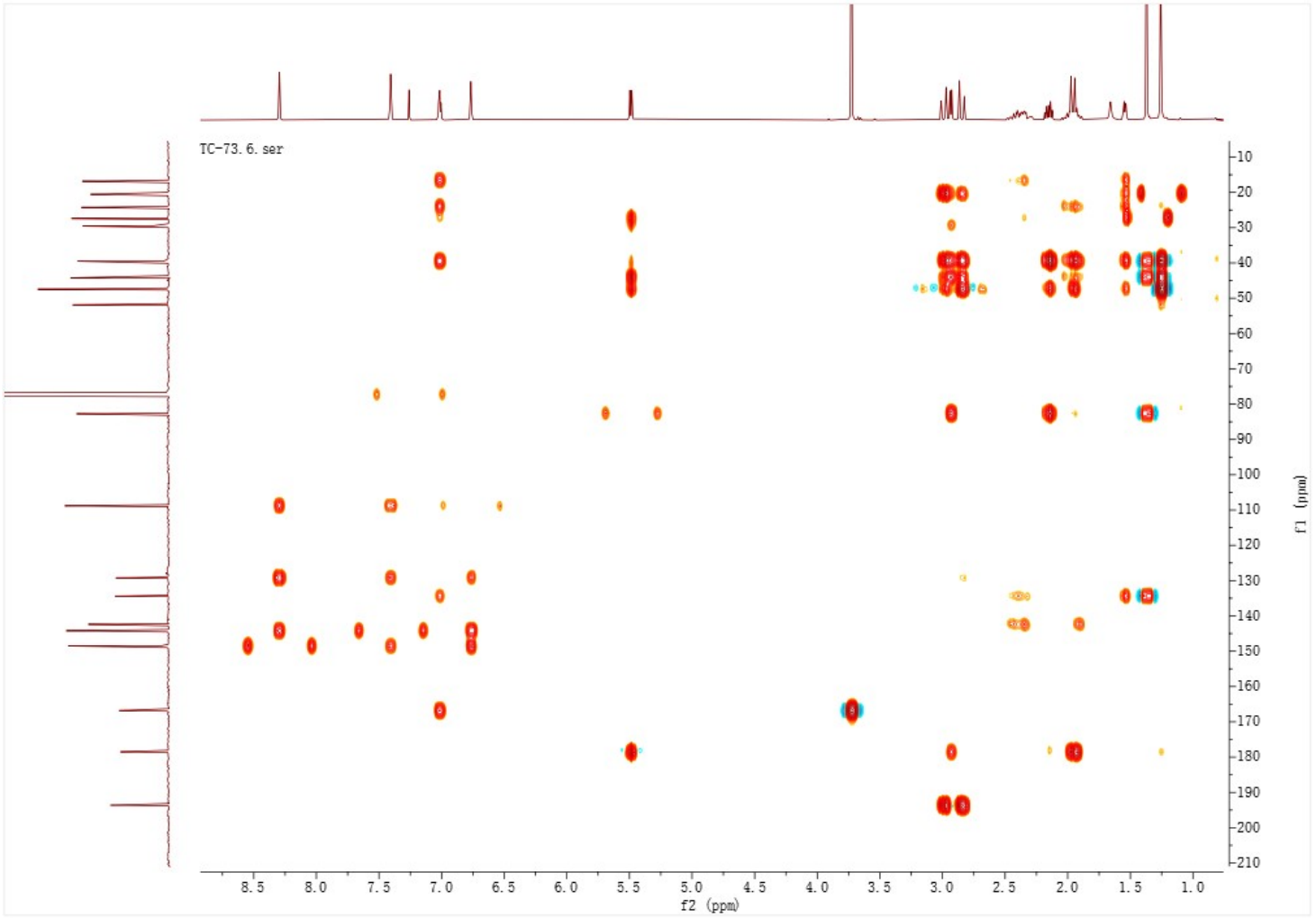
Figure S41. HSQC Spectrum of Compound **4** in $CDCl_3$

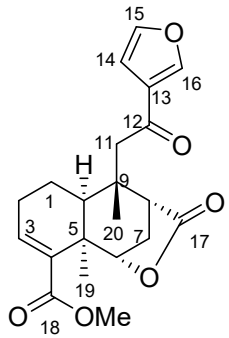




4

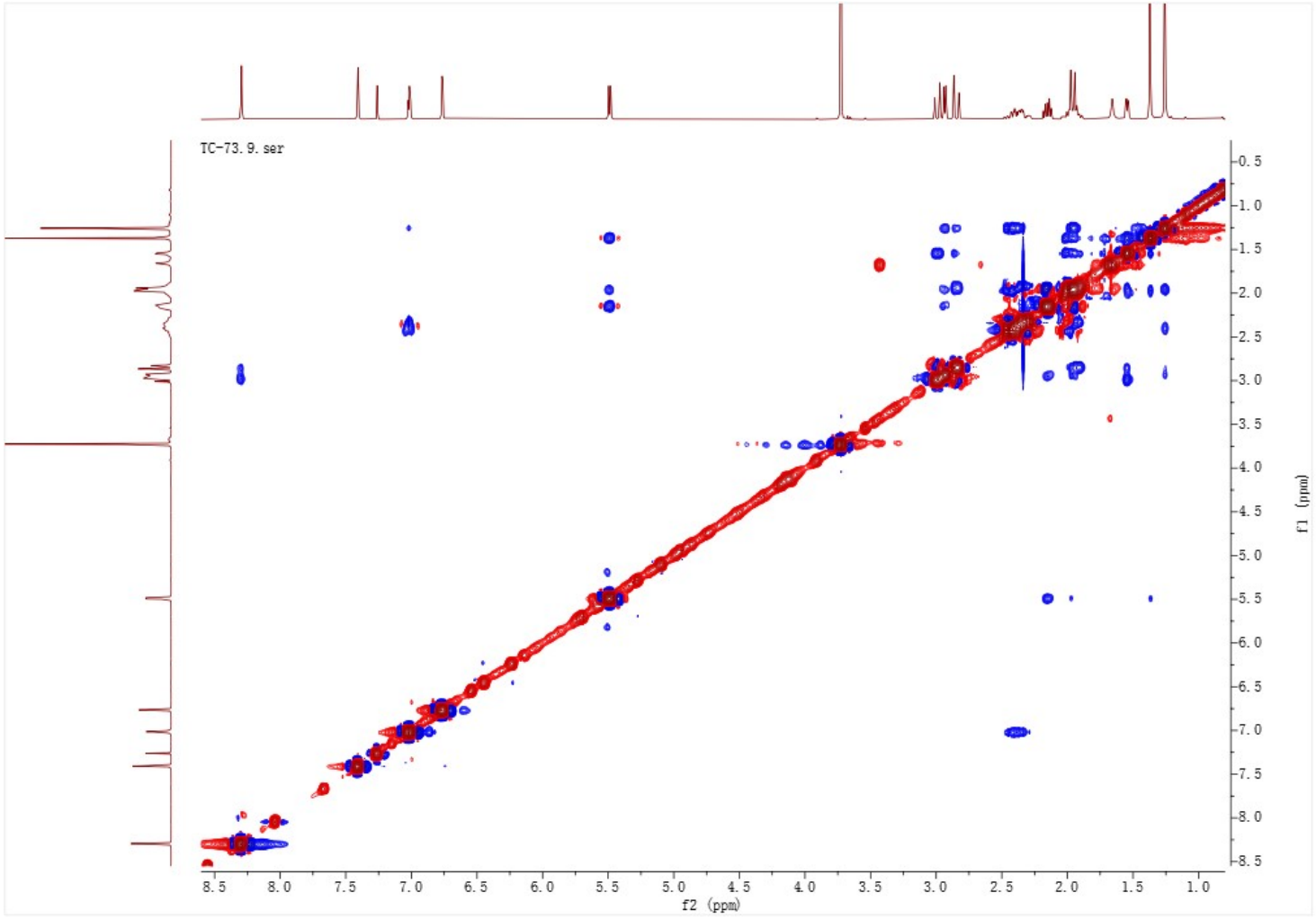
Figure S42. HMBC Spectrum of Compound **4** in $CDCl_3$

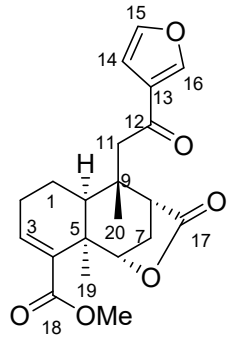




4

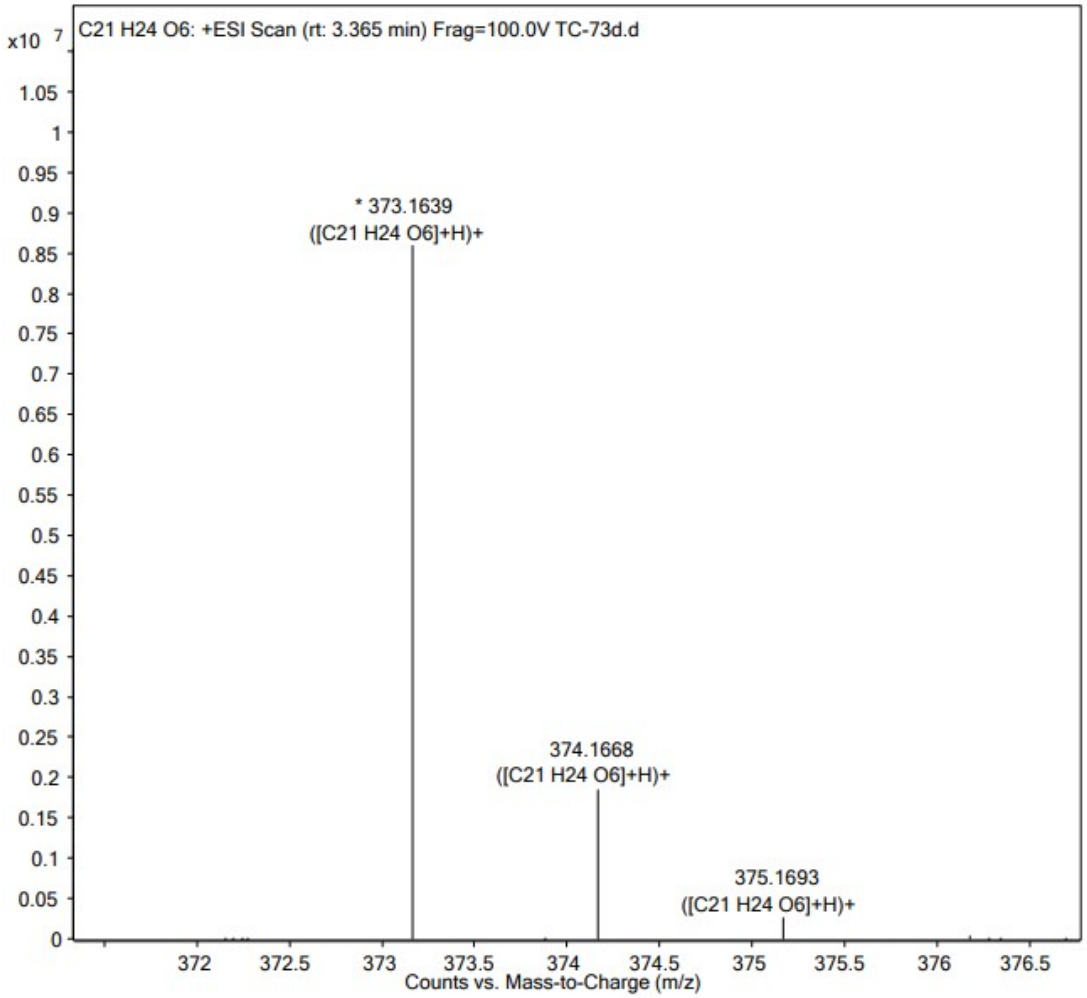
Figure S43. NOESY Spectrum of Compound **4** in $CDCl_3$

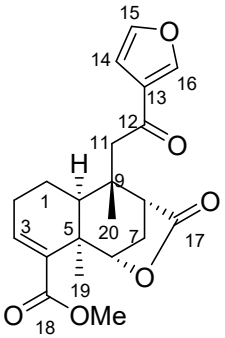




4

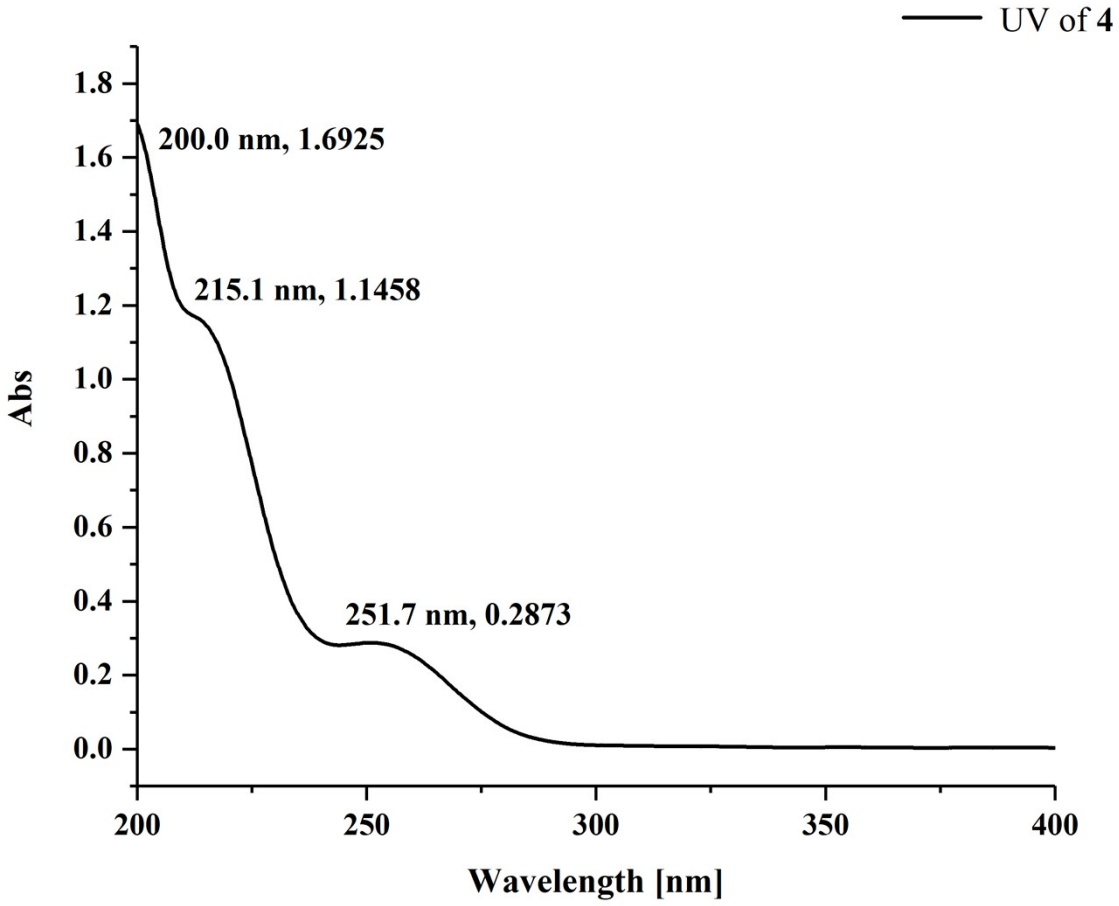
Figure S44. (+) HRESIMS Spectrum of Compound **4**

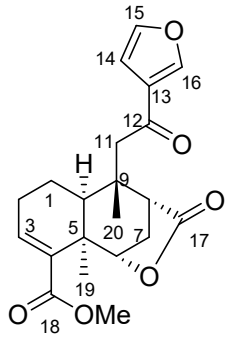




4

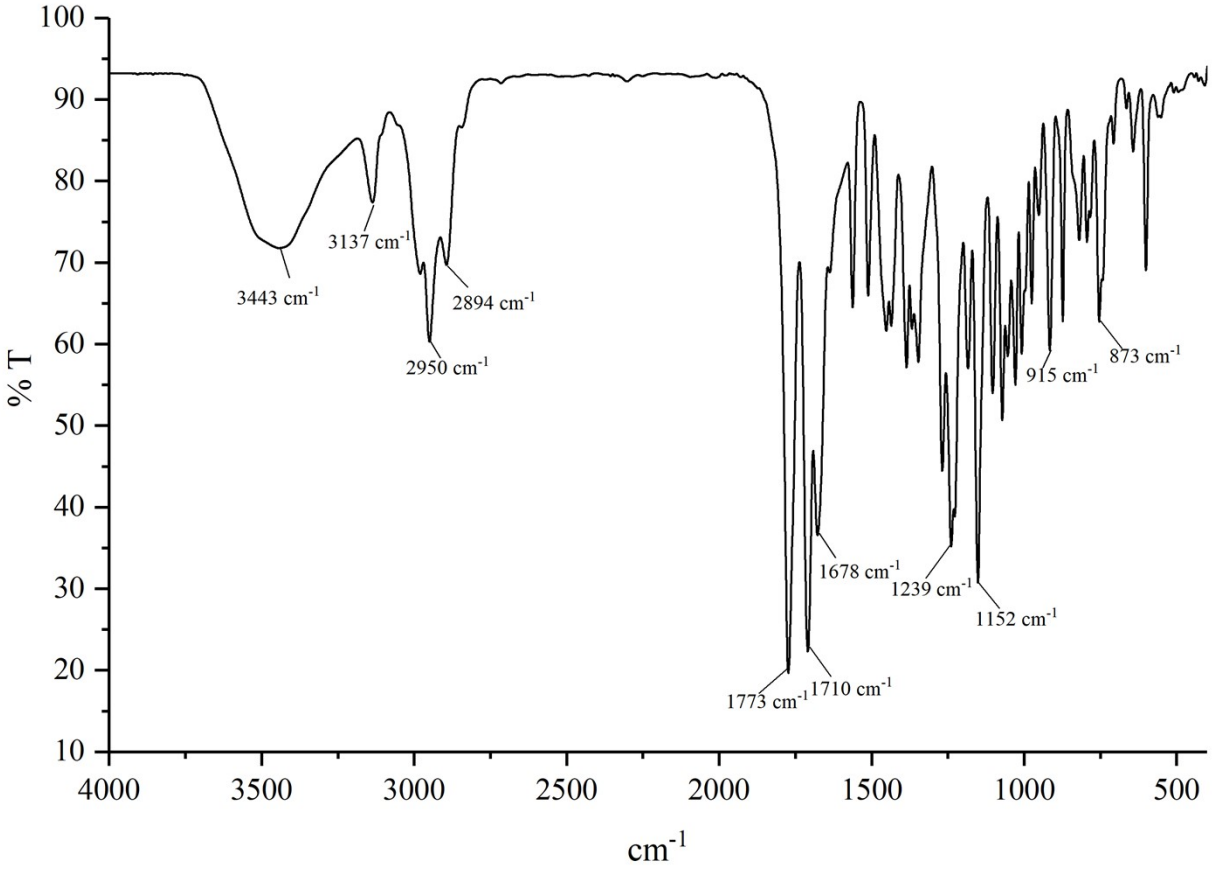
Figure S45. UV Spectrum of Compound **4**

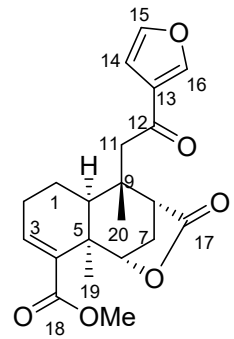




4

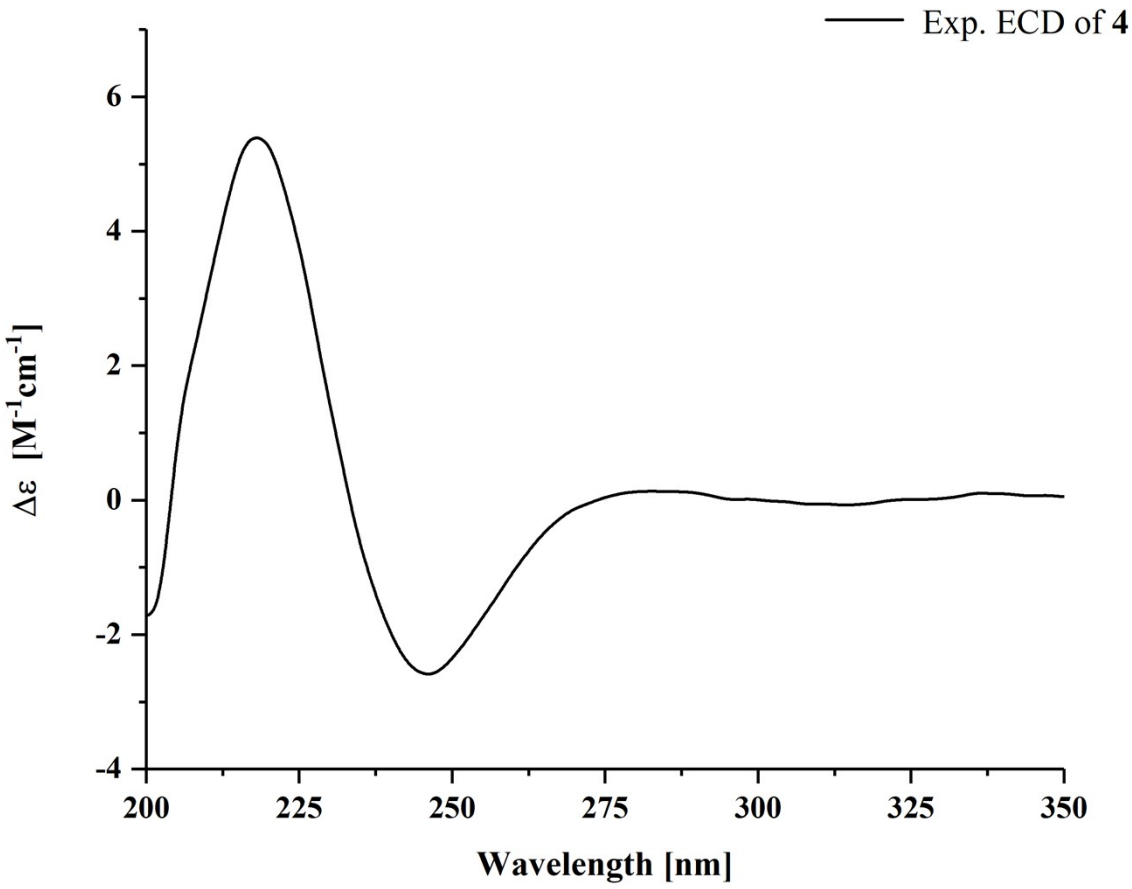
Figure S46. IR (KBr disc) Spectrum of Compound **4**

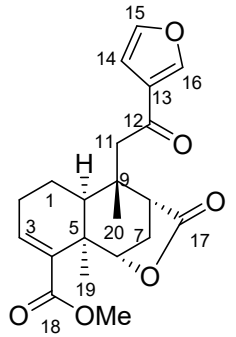




4

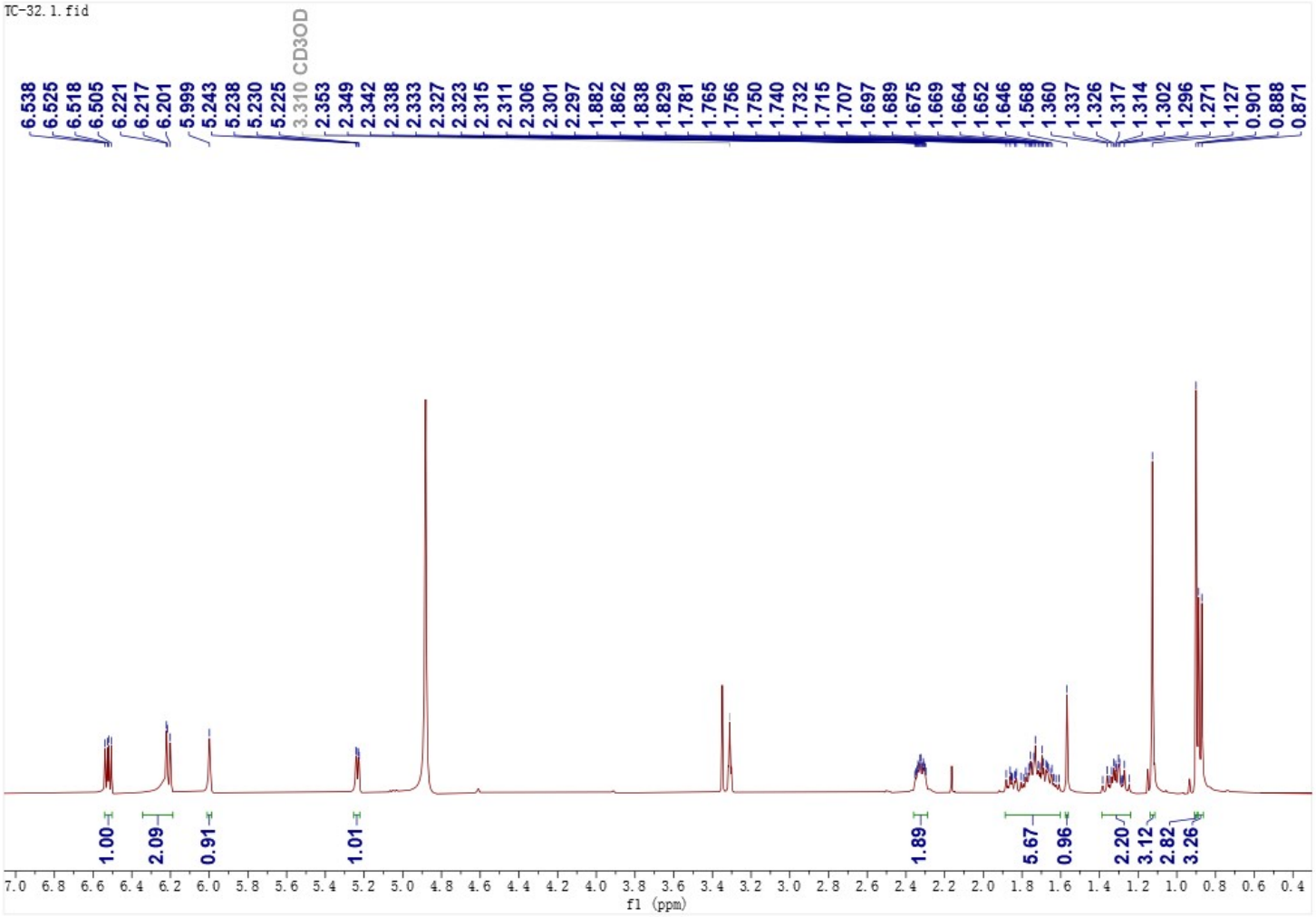
Figure S47. Experimental ECD spectra of Compound **4** in MeOH

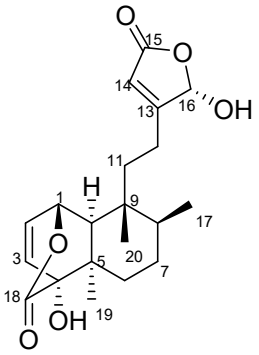




4

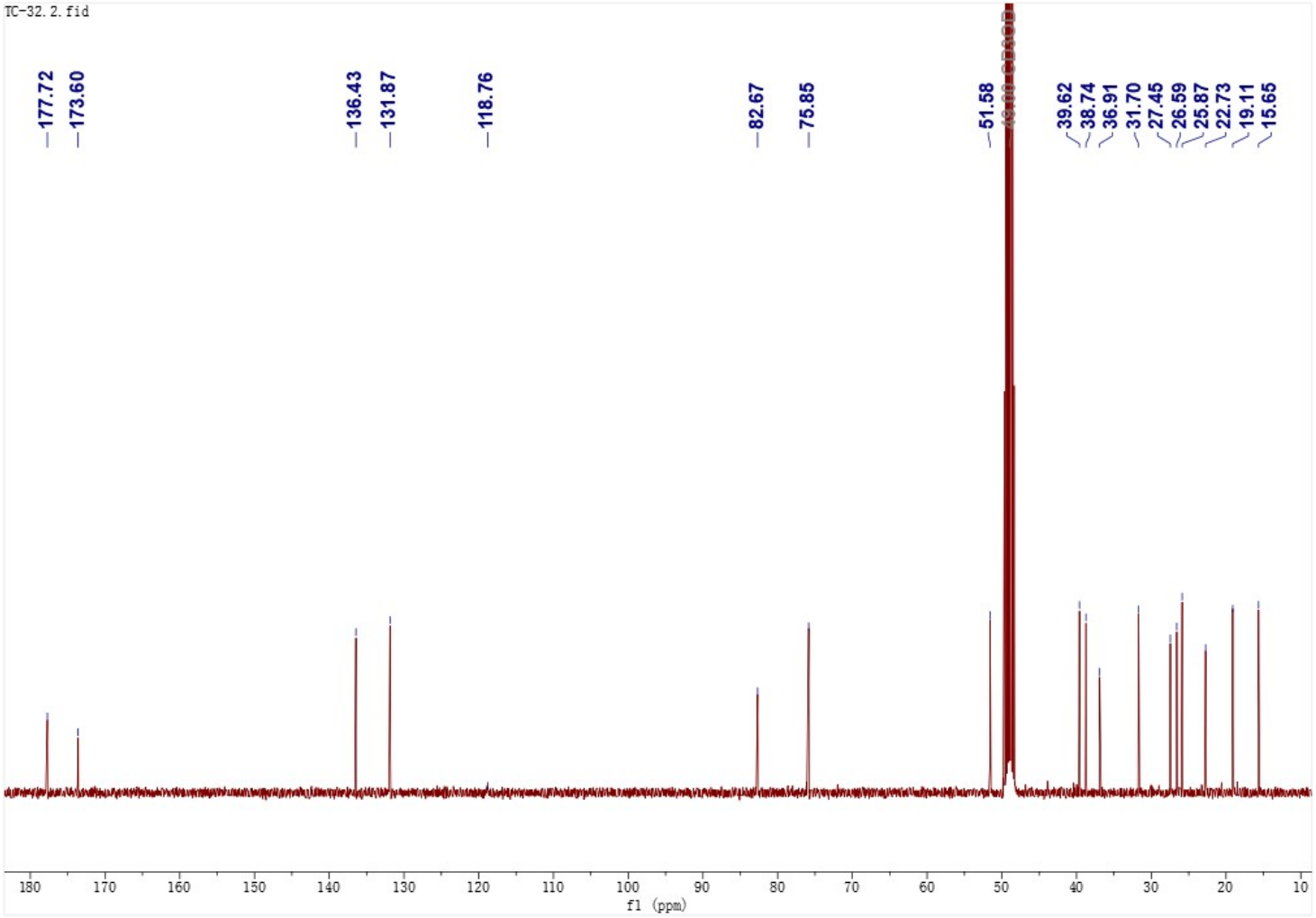
Figure S48. ^{1}H NMR Spectrum of Compound **5** in CD_3OD

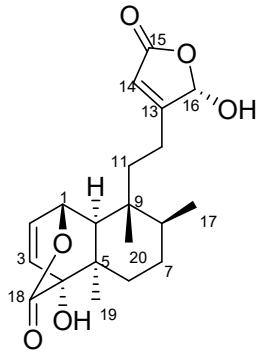




5

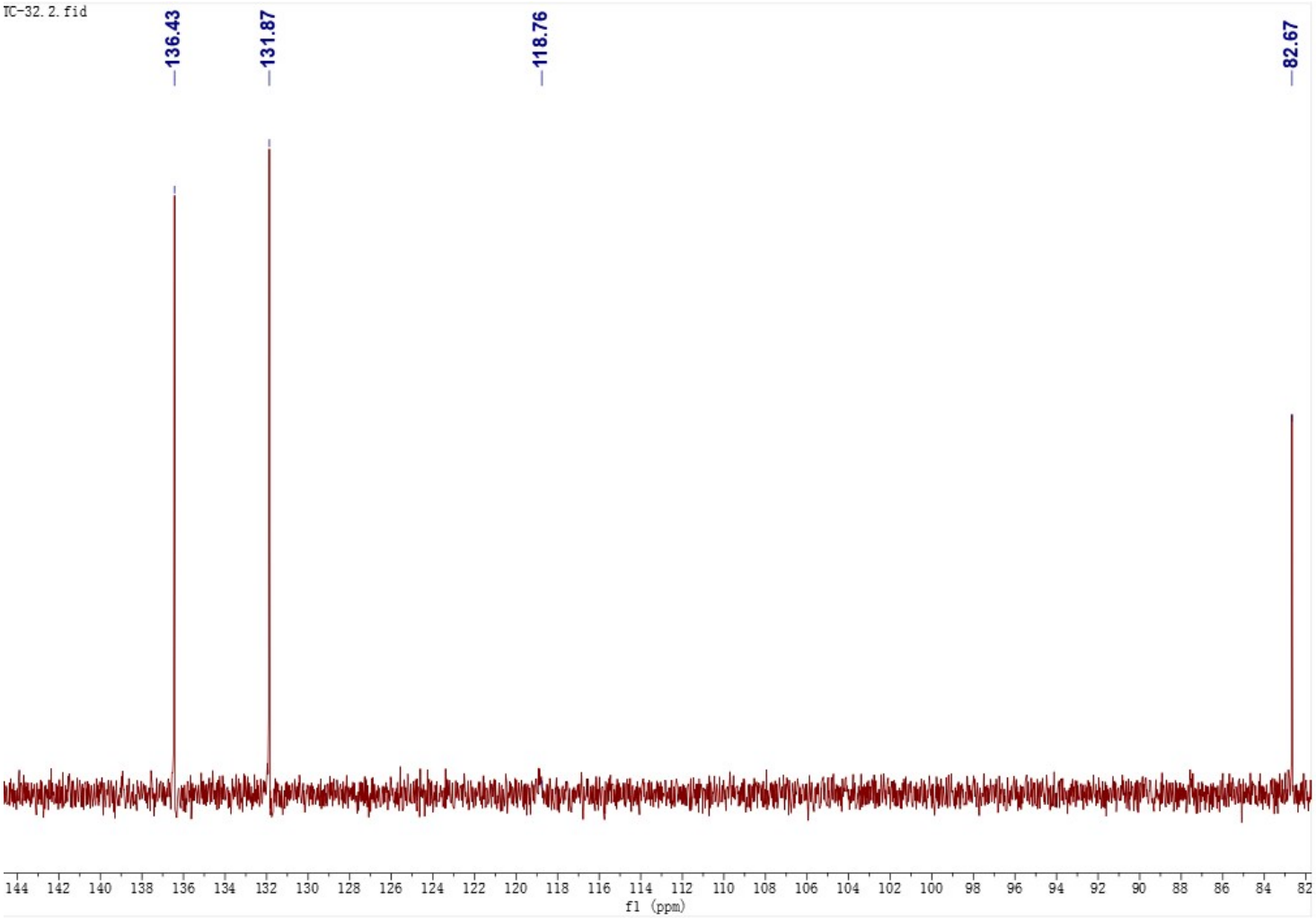
Figure S49. ^{13}C NMR Spectrum of Compound **5** in CD_3OD

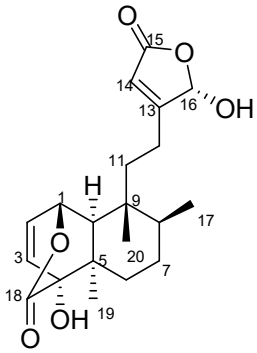




5

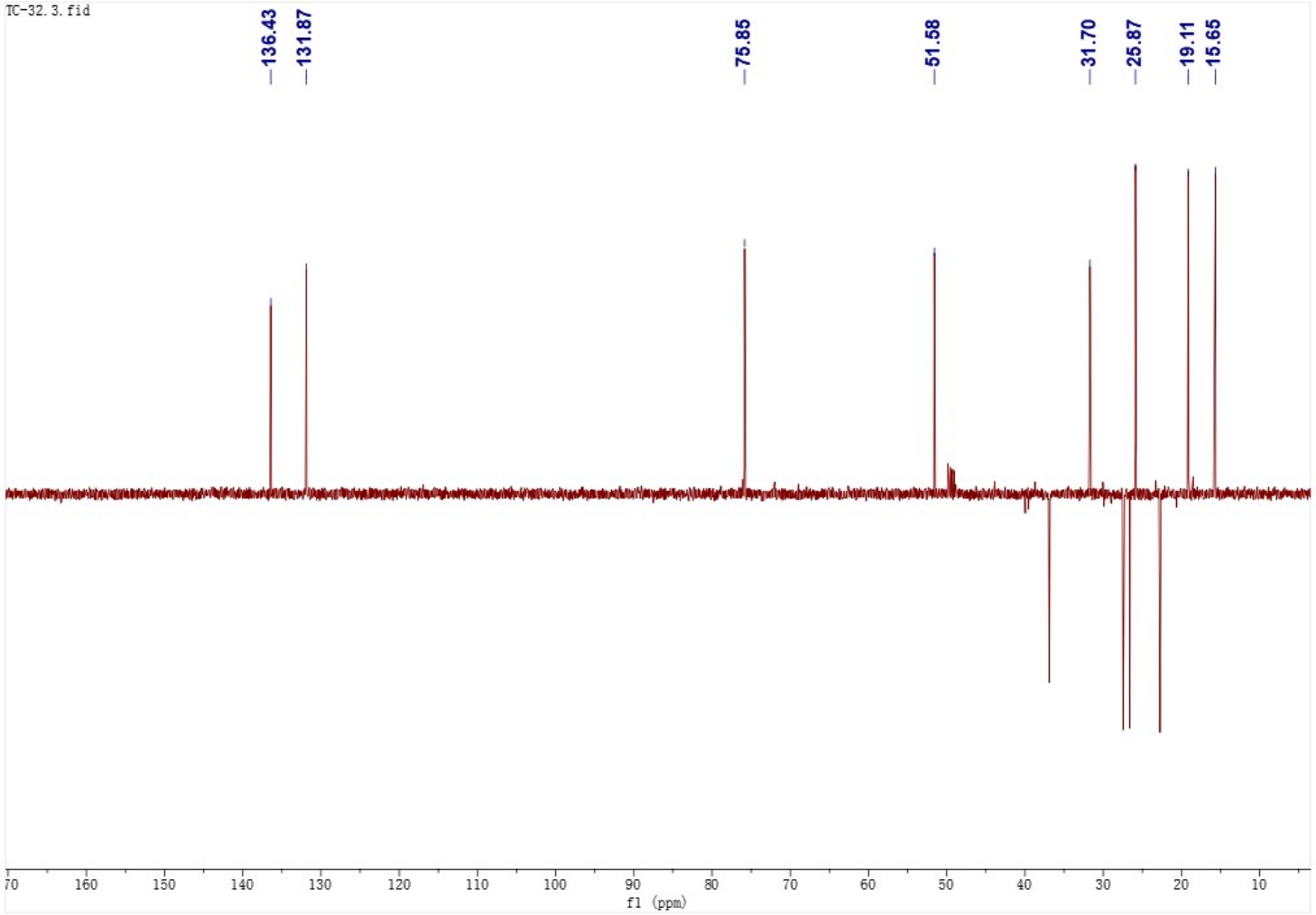
Figure S50. Partial ^{13}C NMR Spectrum of Compound **5** in CD_3OD

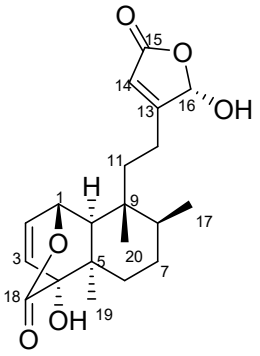




5

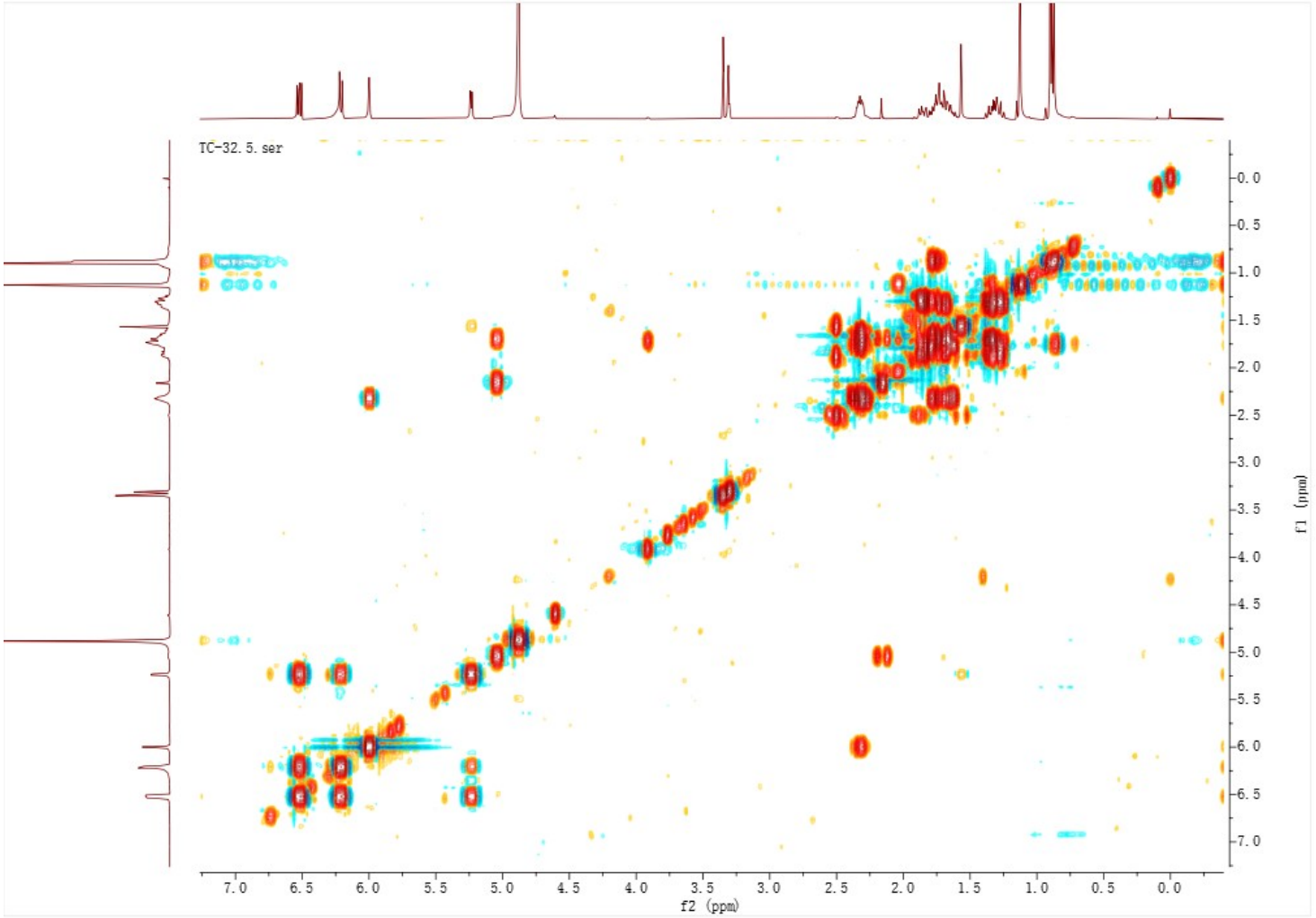
Figure S51. DEPT 135 Spectrum of Compound **5** in CD_3OD

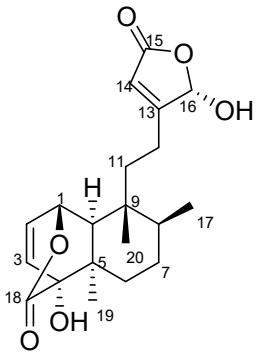




5

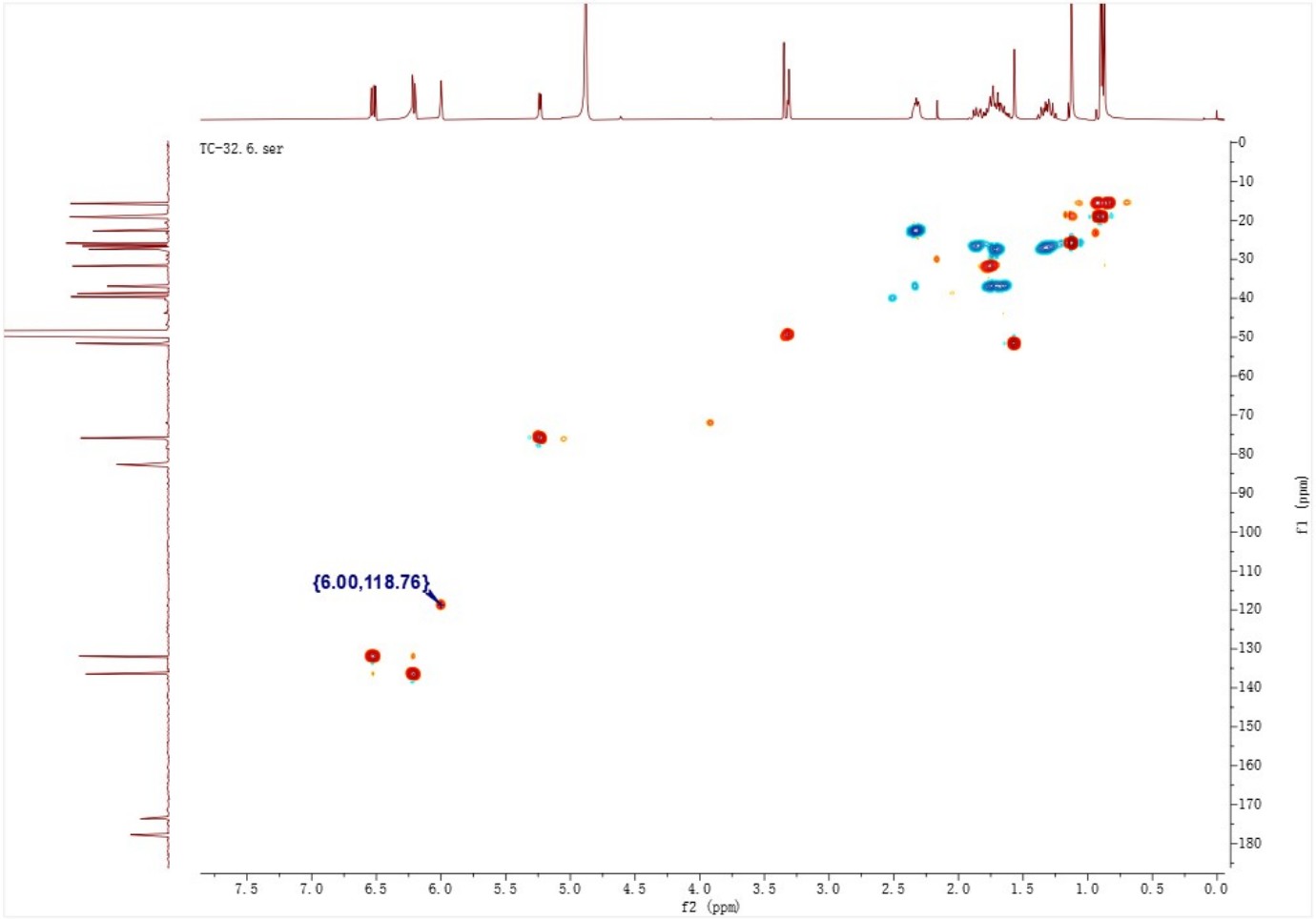
Figure S52. ^{1}H-^{1}H COSY Spectrum of Compound **5** in CD_3OD

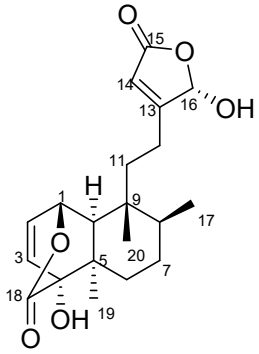




5

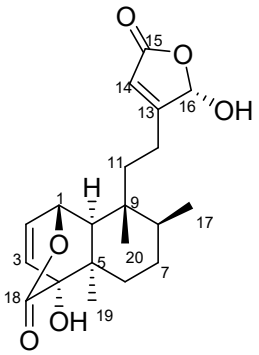
Figure S53. HSQC Spectrum of Compound **5** in CD_3OD





5

Figure S54. HMBC Spectrum of Compound **5** in CD_3OD



5

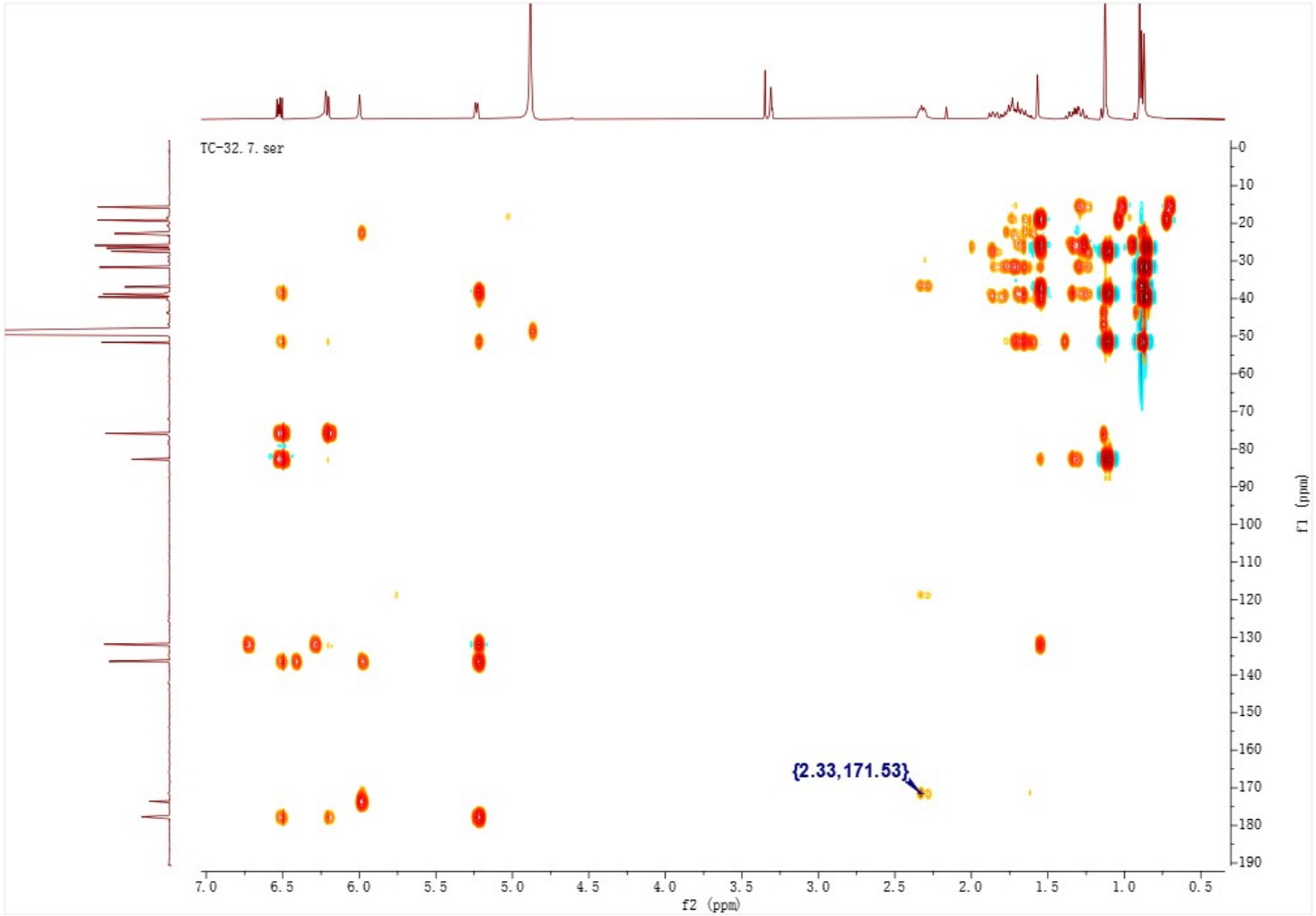
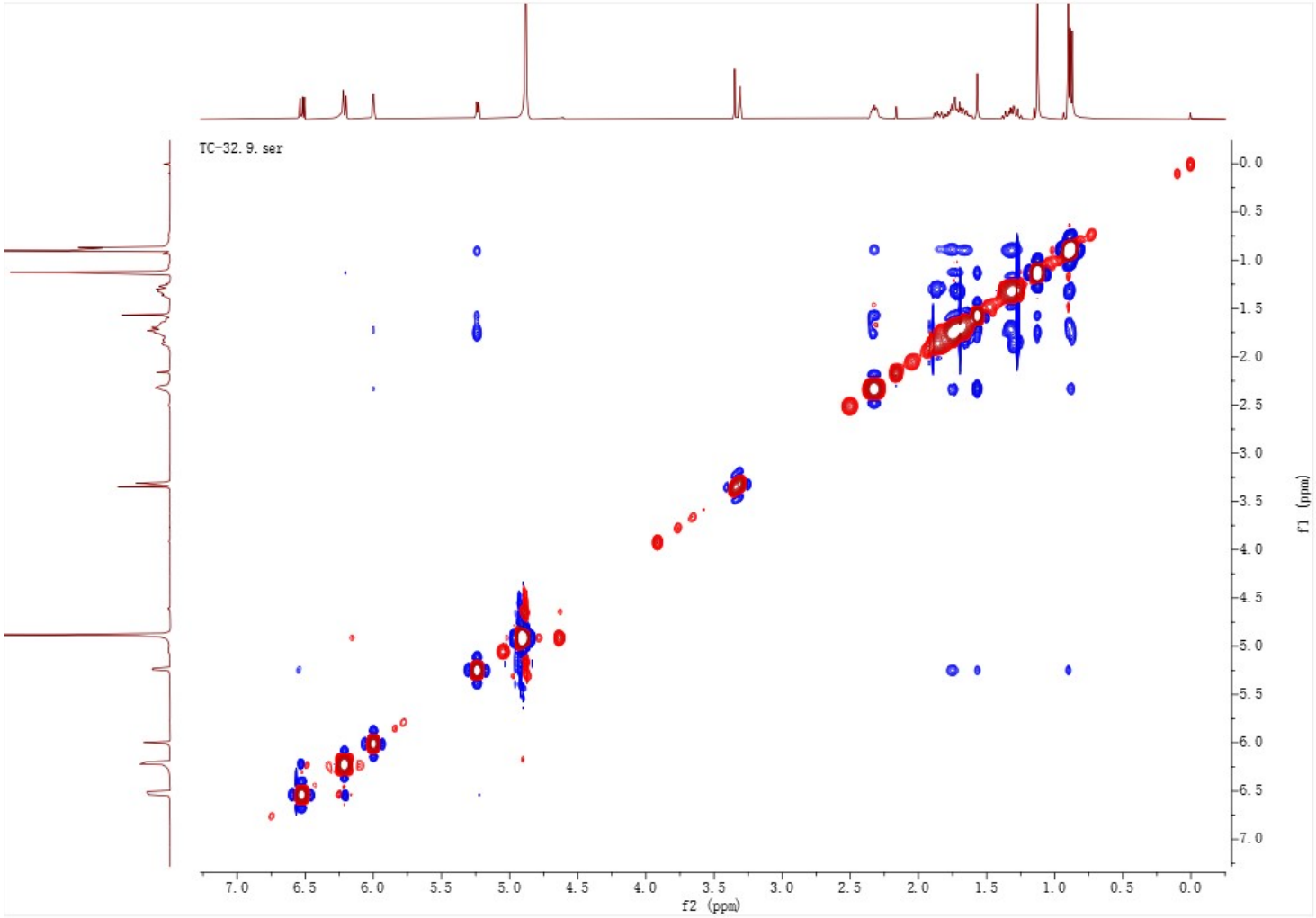
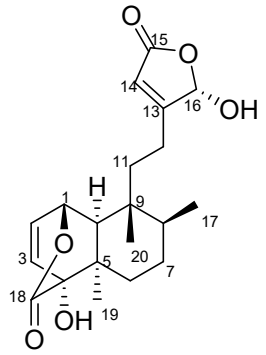


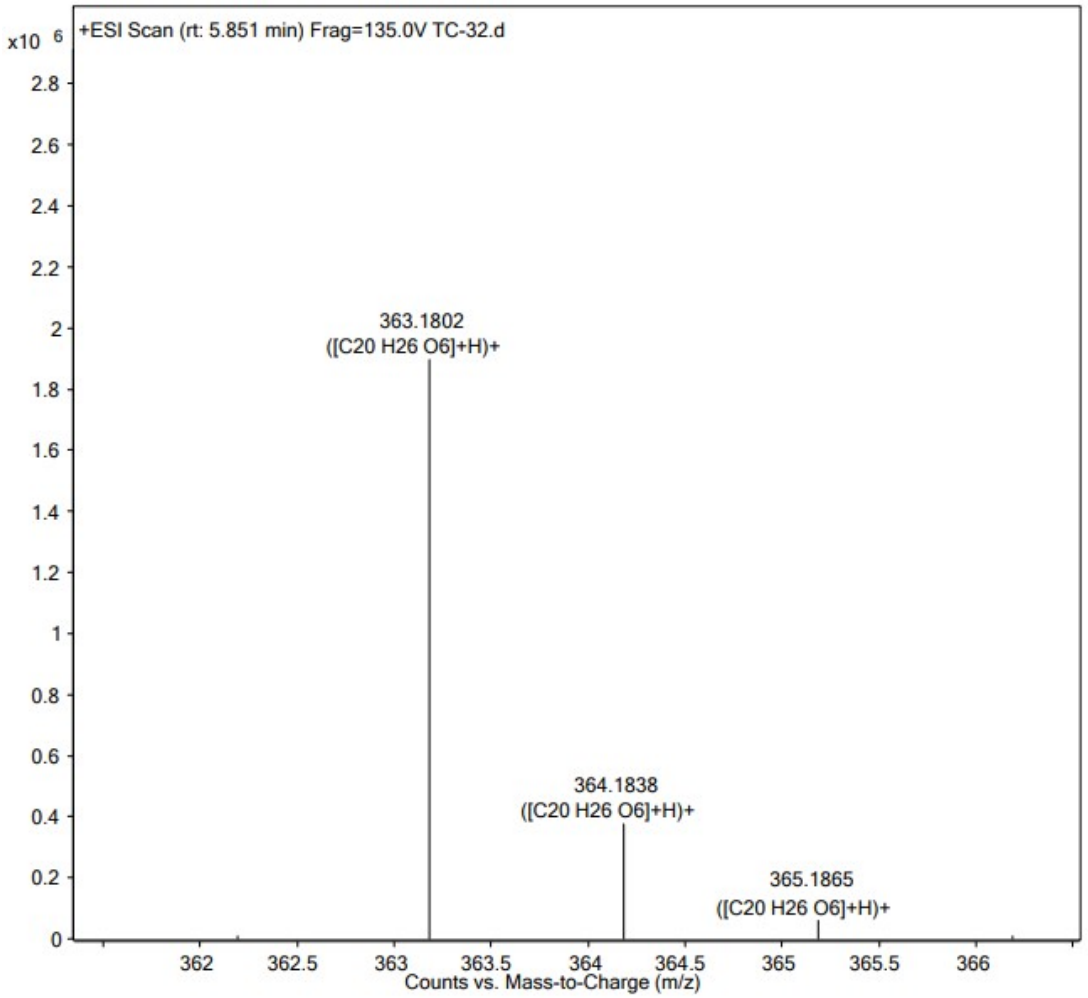
Figure S55. NOESY Spectrum of Compound **5** in CD_3OD

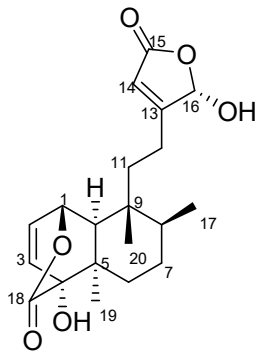




5

Figure S56. (+) HRESIMS Spectrum of Compound **5**





5

Figure S57. UV Spectrum of Compound **5**

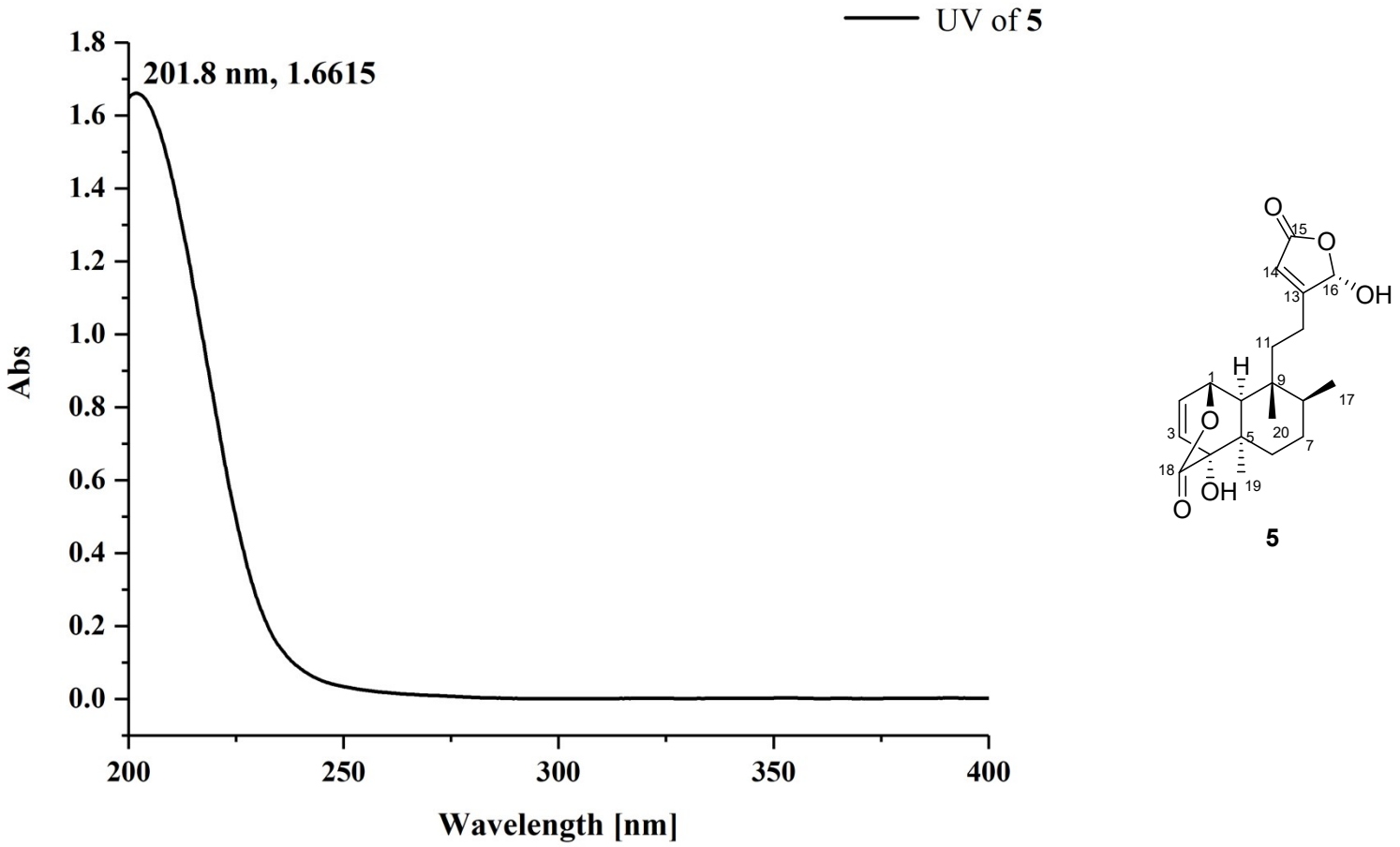
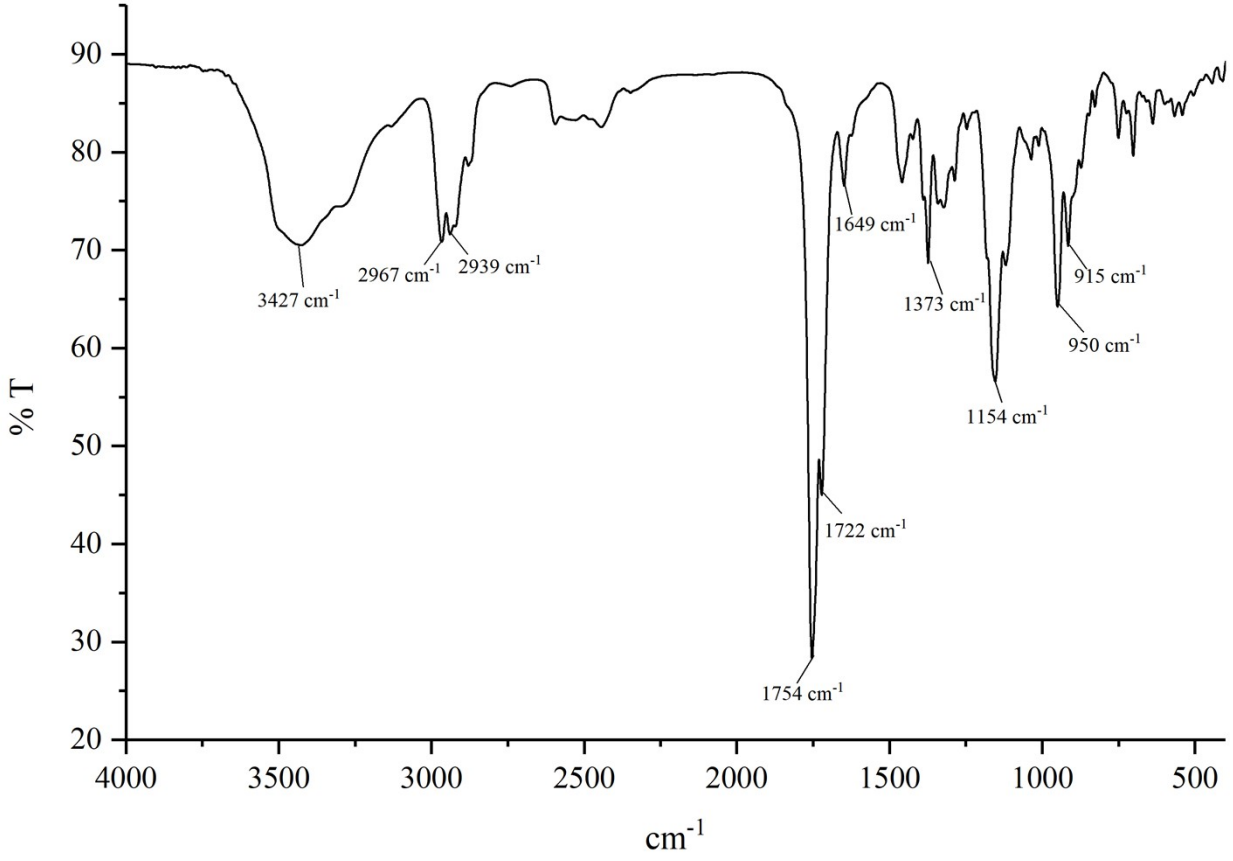
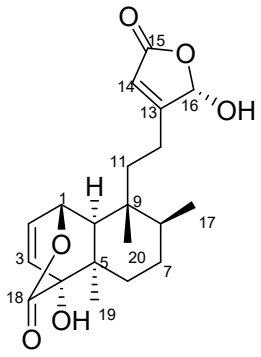


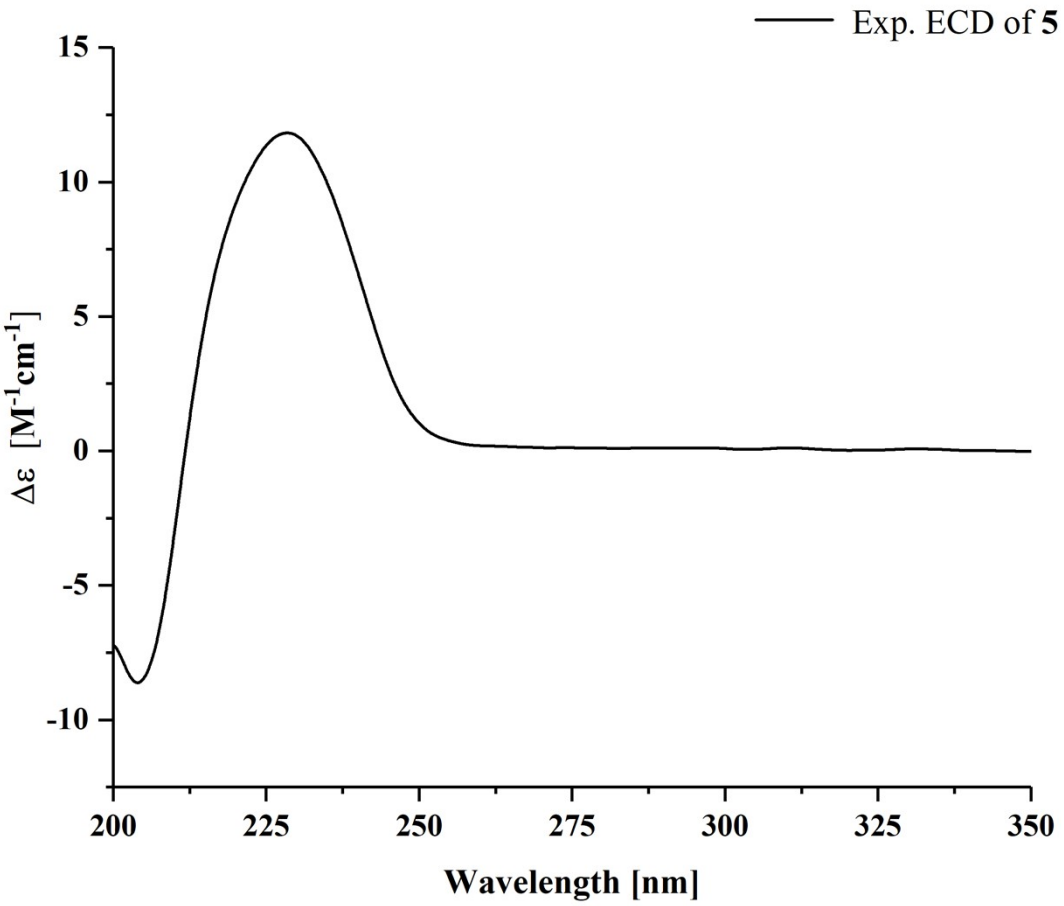
Figure S58. IR (KBr disc) Spectrum of Compound **5**

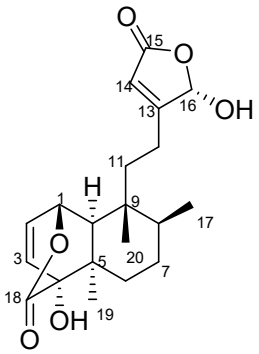




5

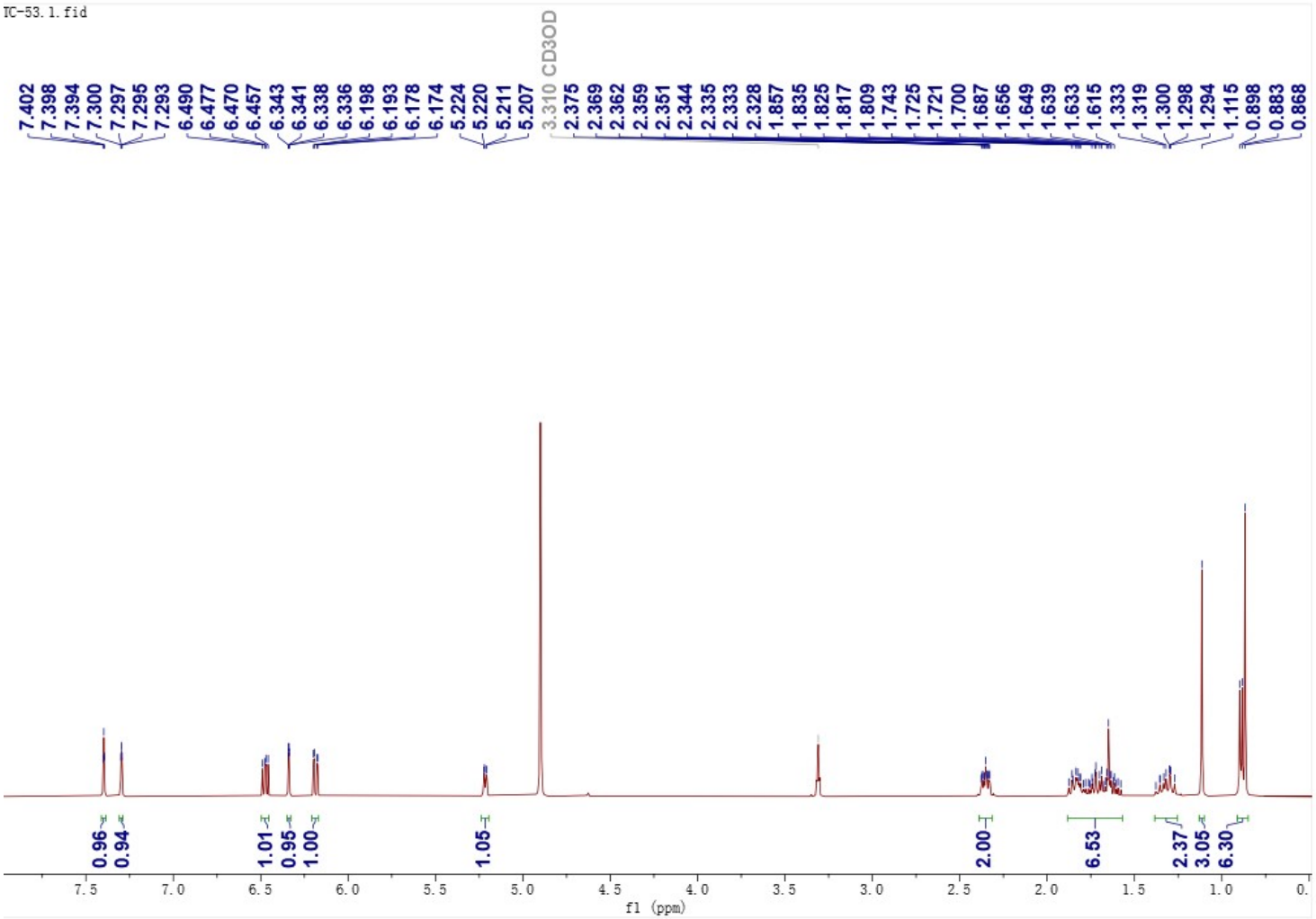
Figure S59. Experimental ECD spectra of Compound **5** in MeOH

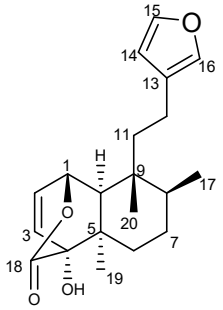




5

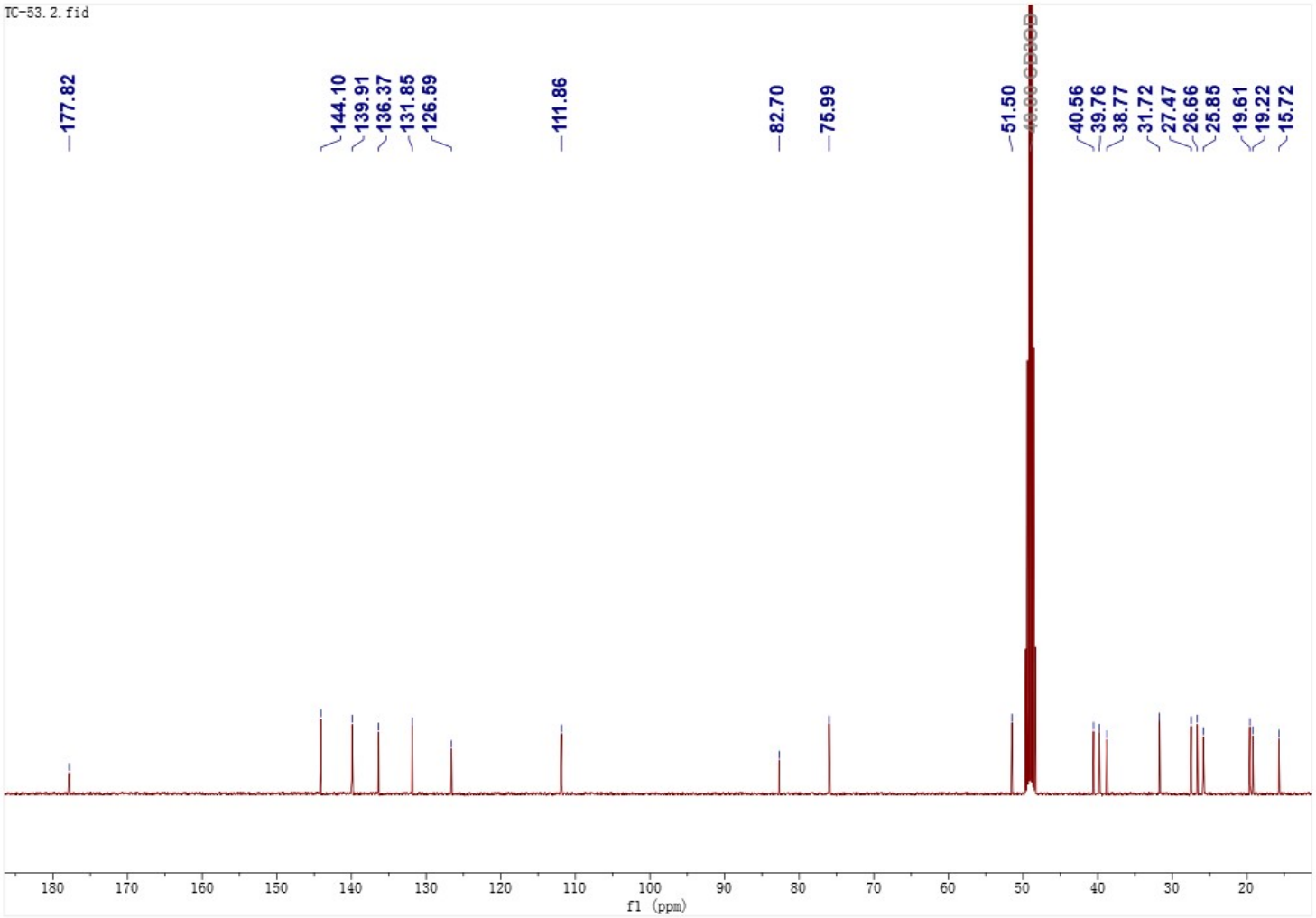
Figure S60. ^{1}H NMR Spectrum of Compound **6** in CD_3OD

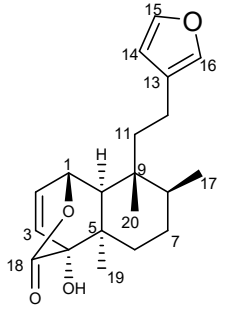




6

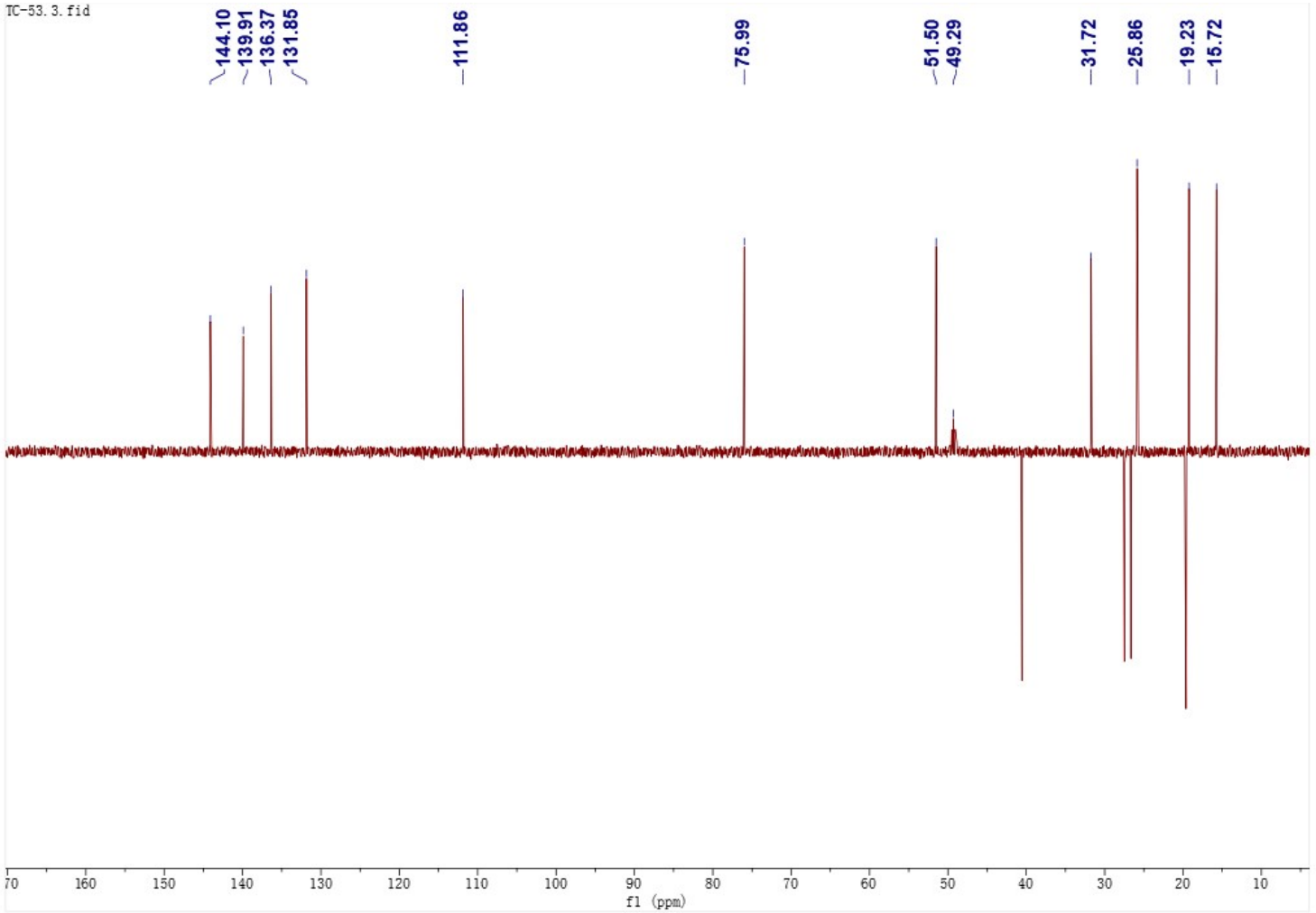
Figure S61. ^{13}C NMR Spectrum of Compound **6** in CD_3OD

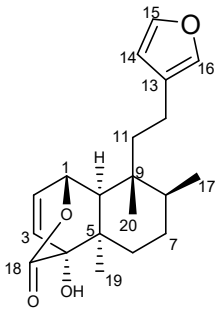




6

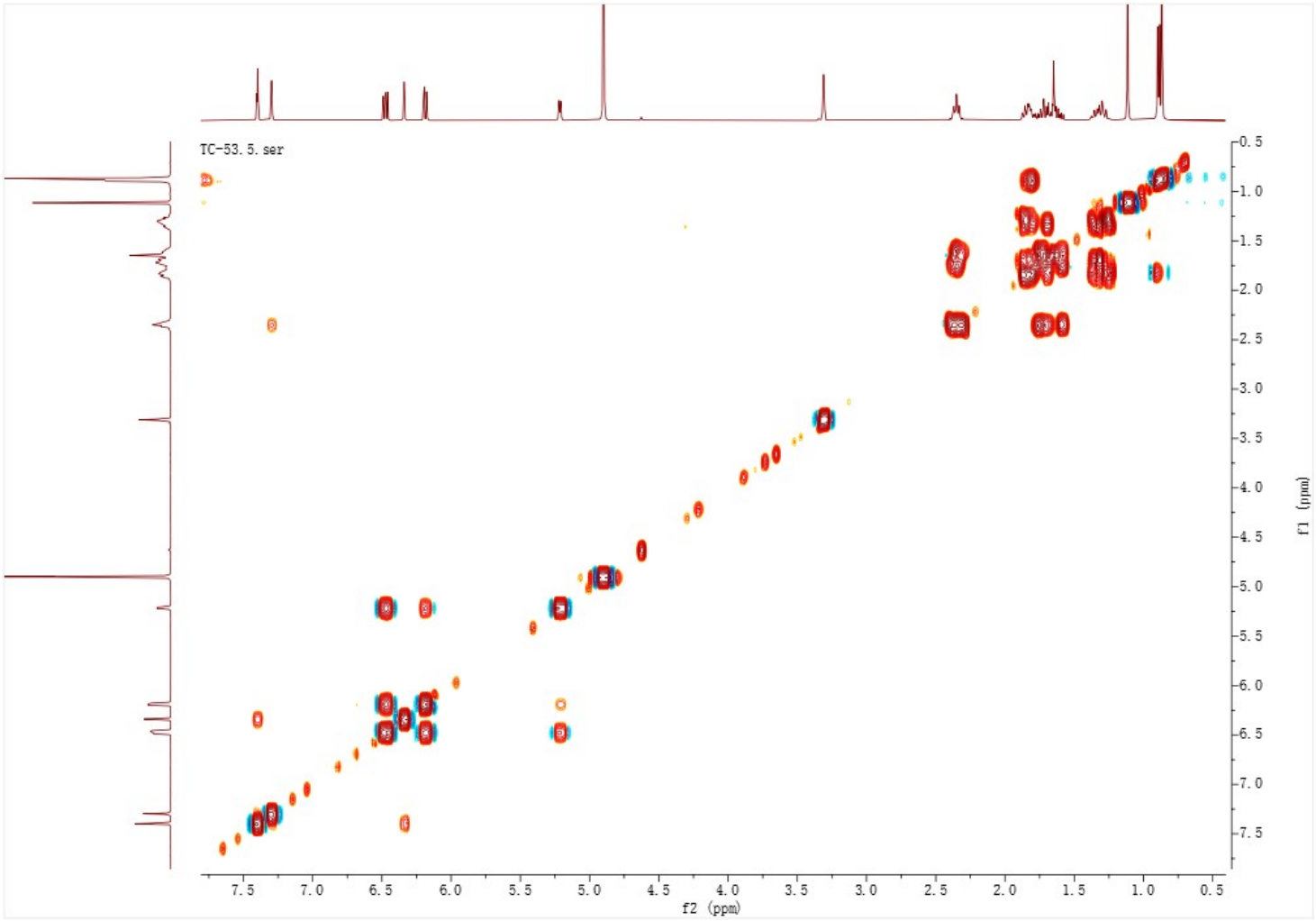
Figure S62. DEPT 135 Spectrum of Compound **6** in CD_3OD

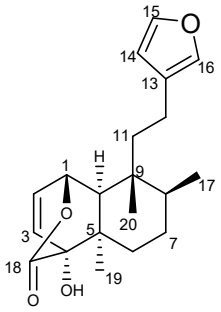




6

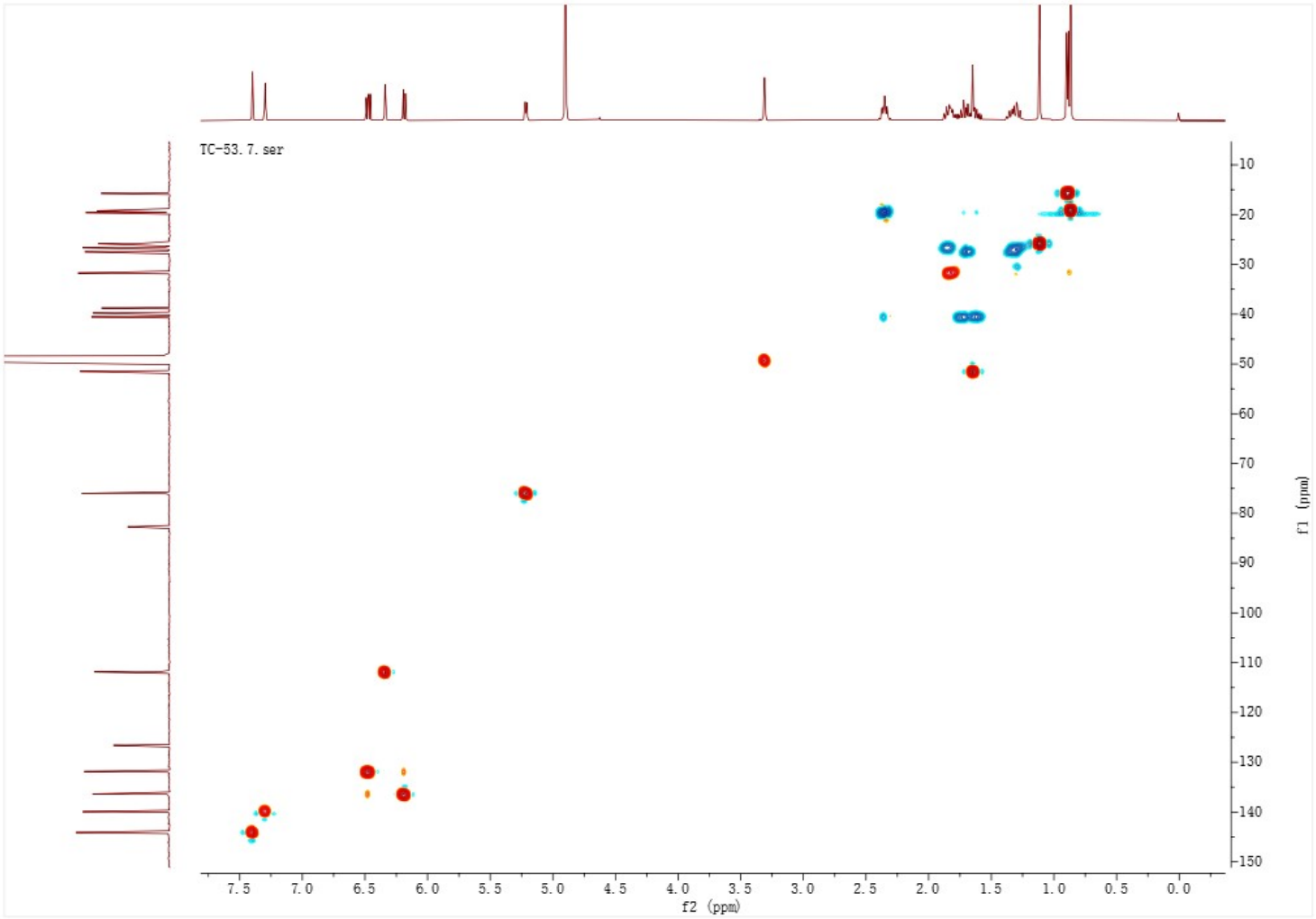
Figure S63. ^{1}H-^{1}H COSY Spectrum of Compound **6** in CD_3OD

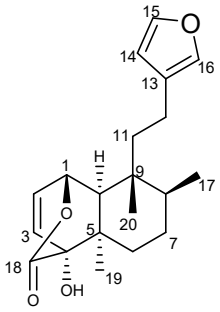




6

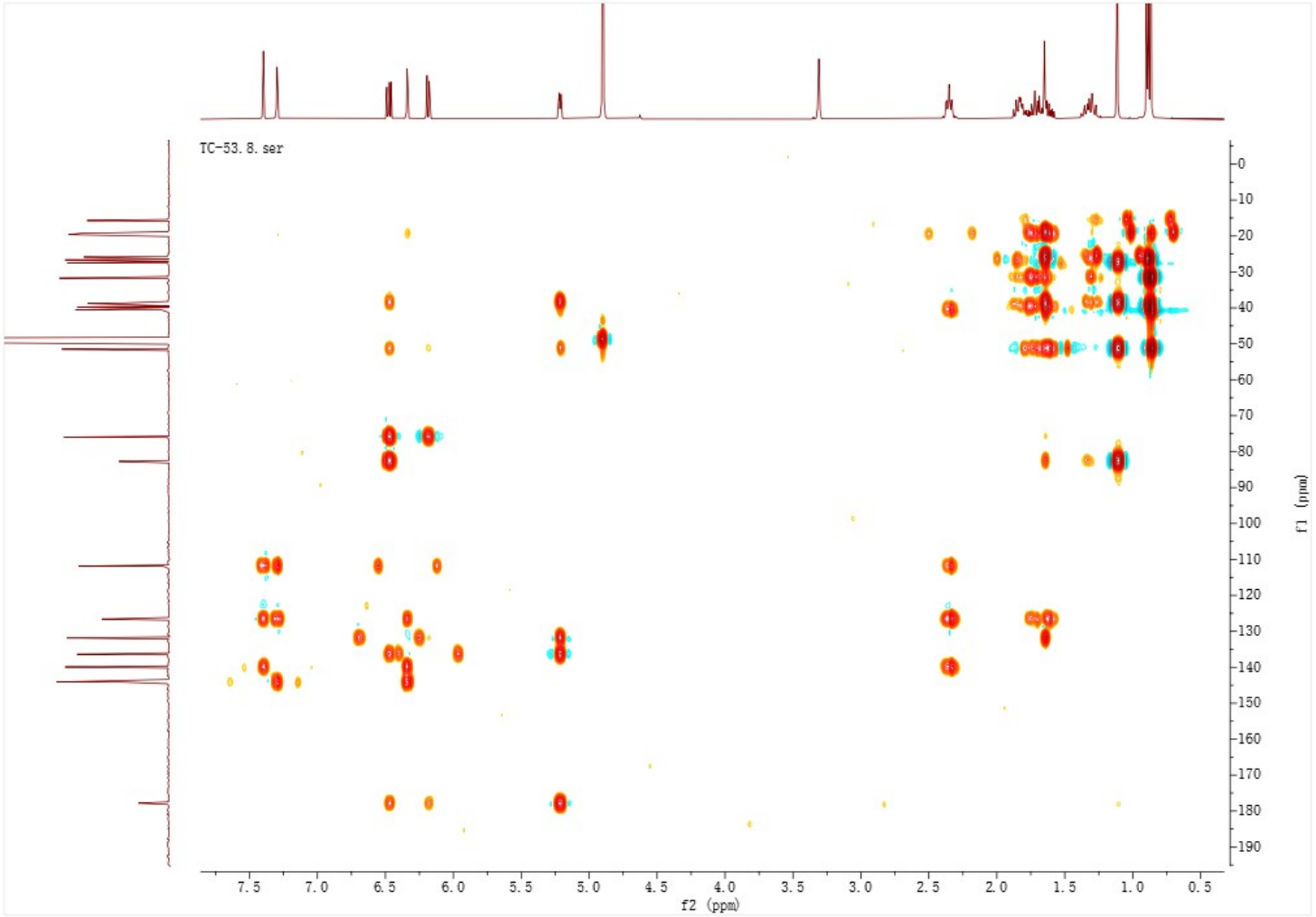
Figure S64. HSQC Spectrum of Compound **6** in CD_3OD

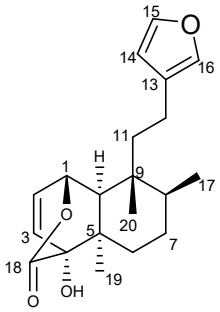




6

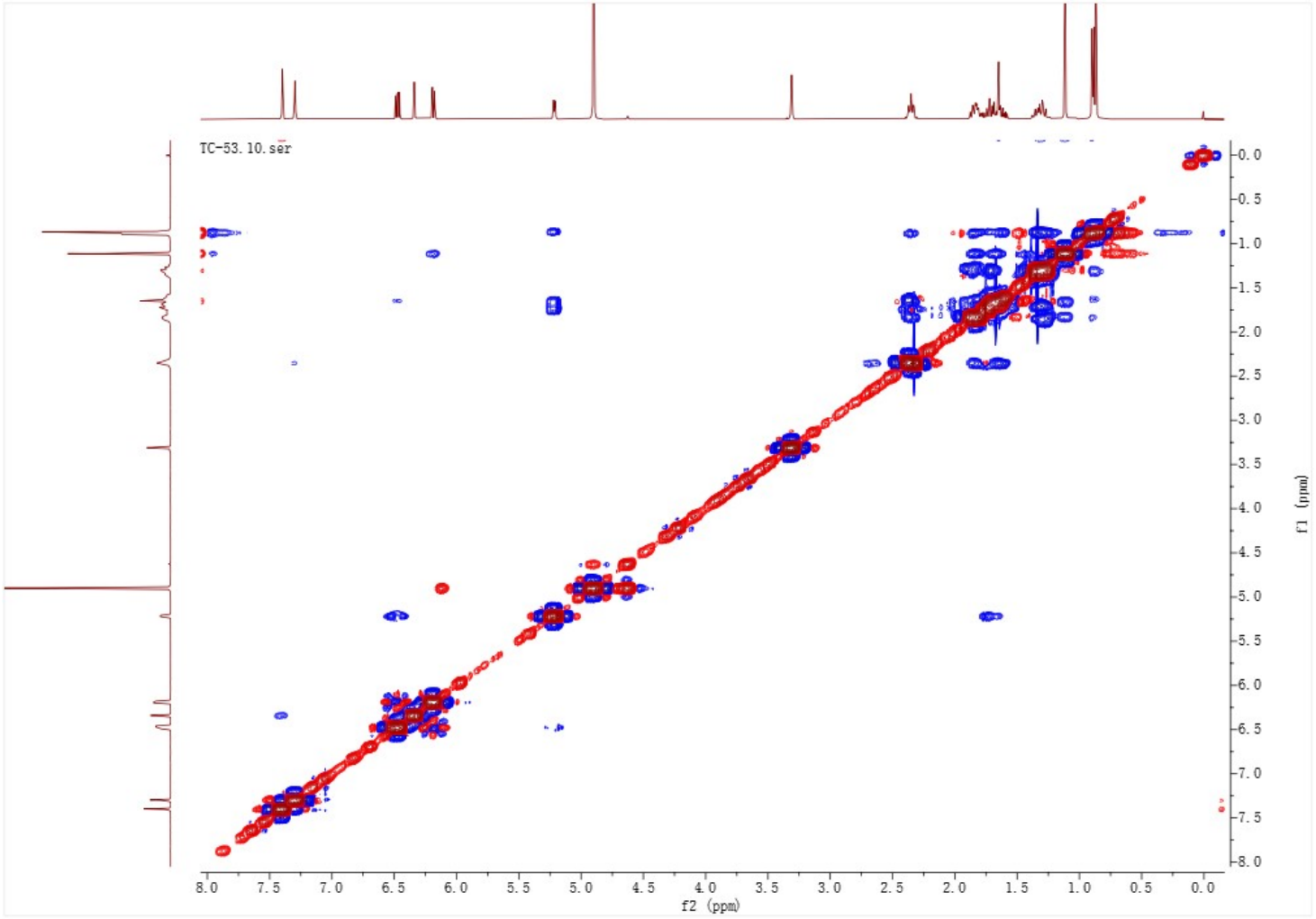
Figure S65. HMBC Spectrum of Compound **6** in CD_3OD

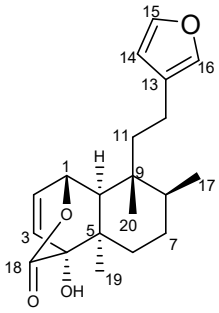




6

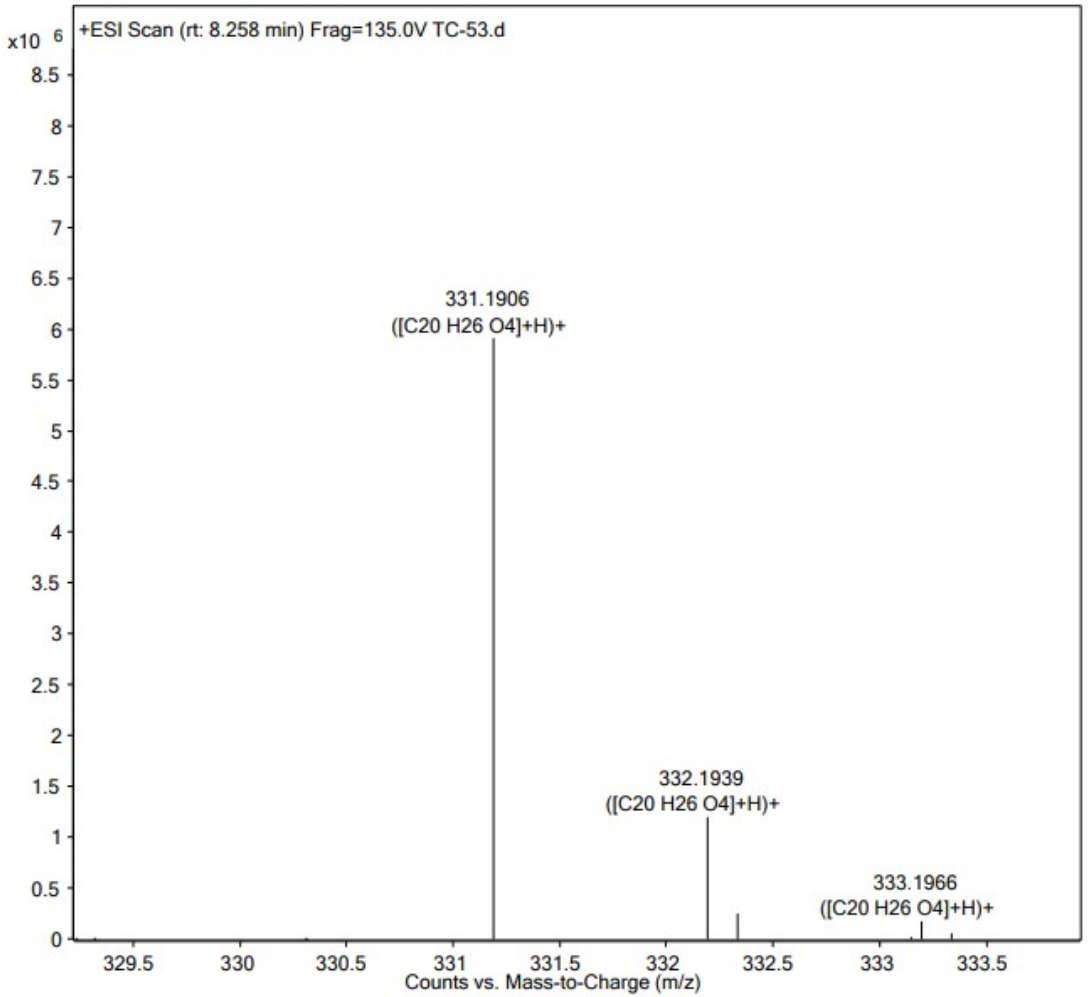
Figure S66. NOESY Spectrum of Compound **6** in CD_3OD

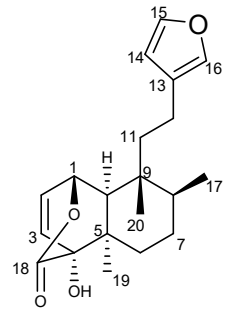




6

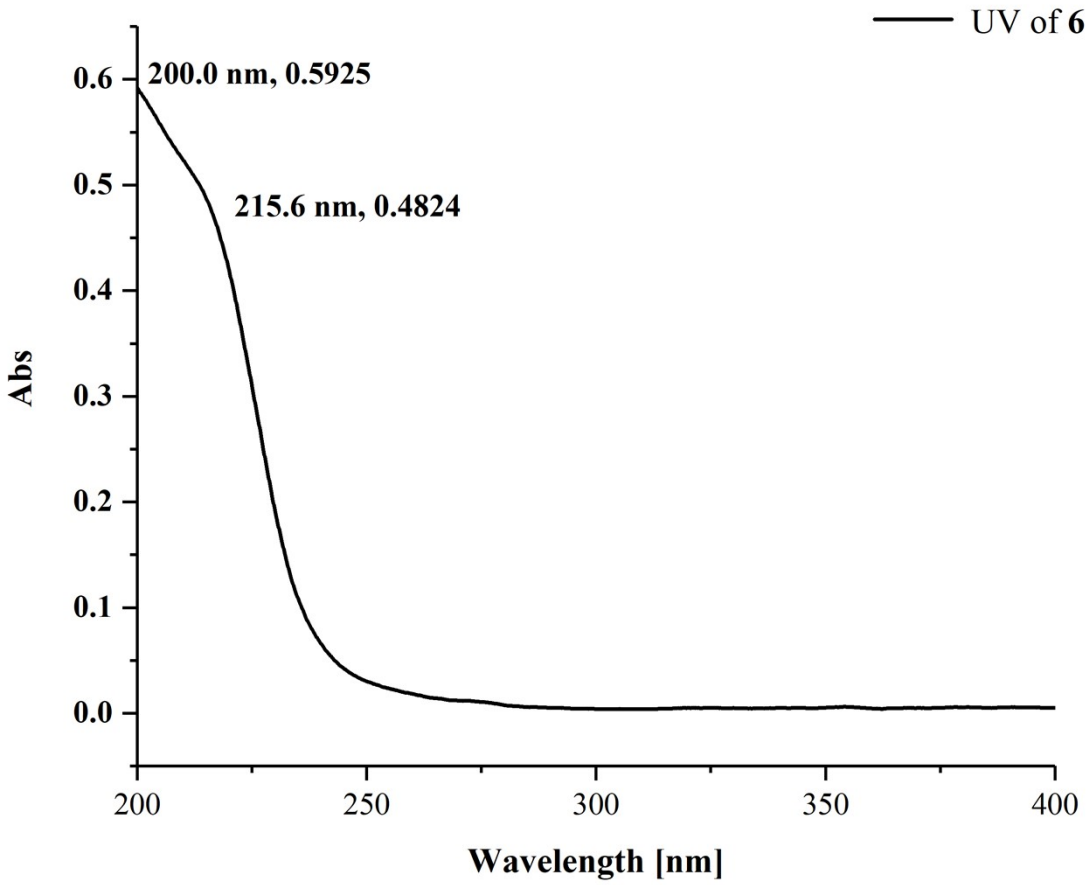
Figure S67. (+) HRESIMS Spectrum of Compound **6**

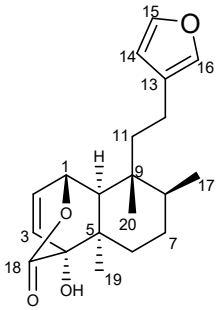




6

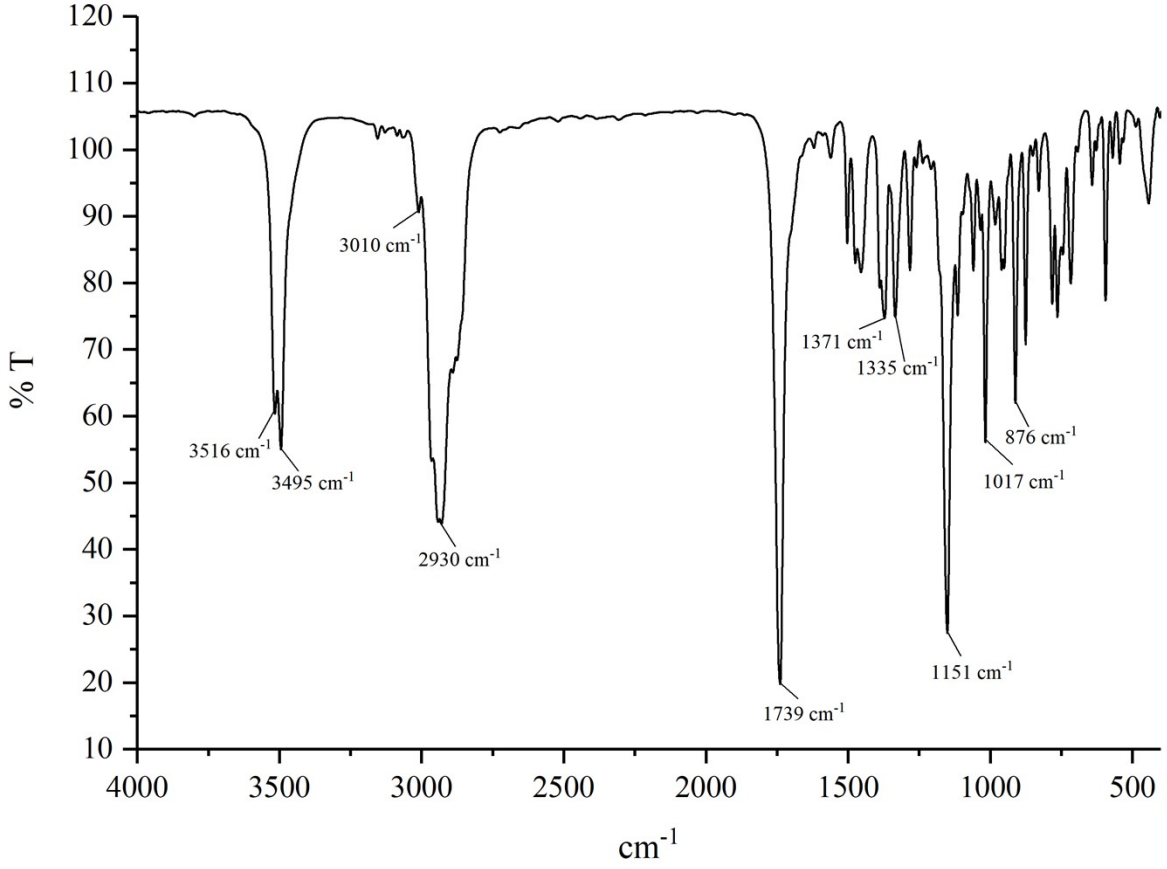
Figure S68. UV Spectrum of Compound **6**

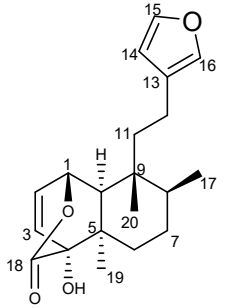




6

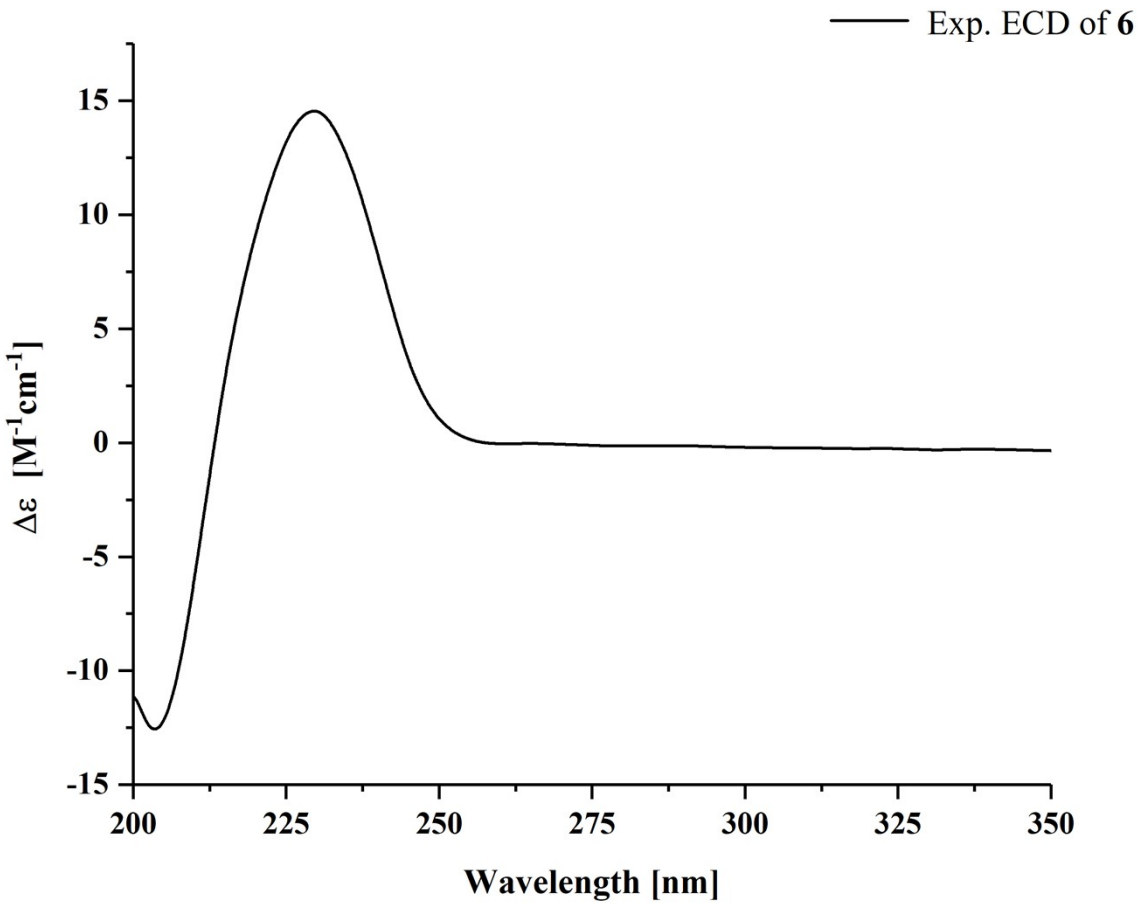
Figure S69. IR (KBr disc) Spectrum of Compound **6**

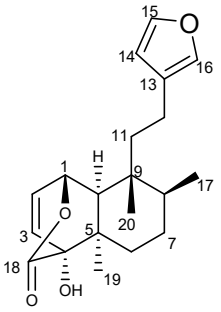




6

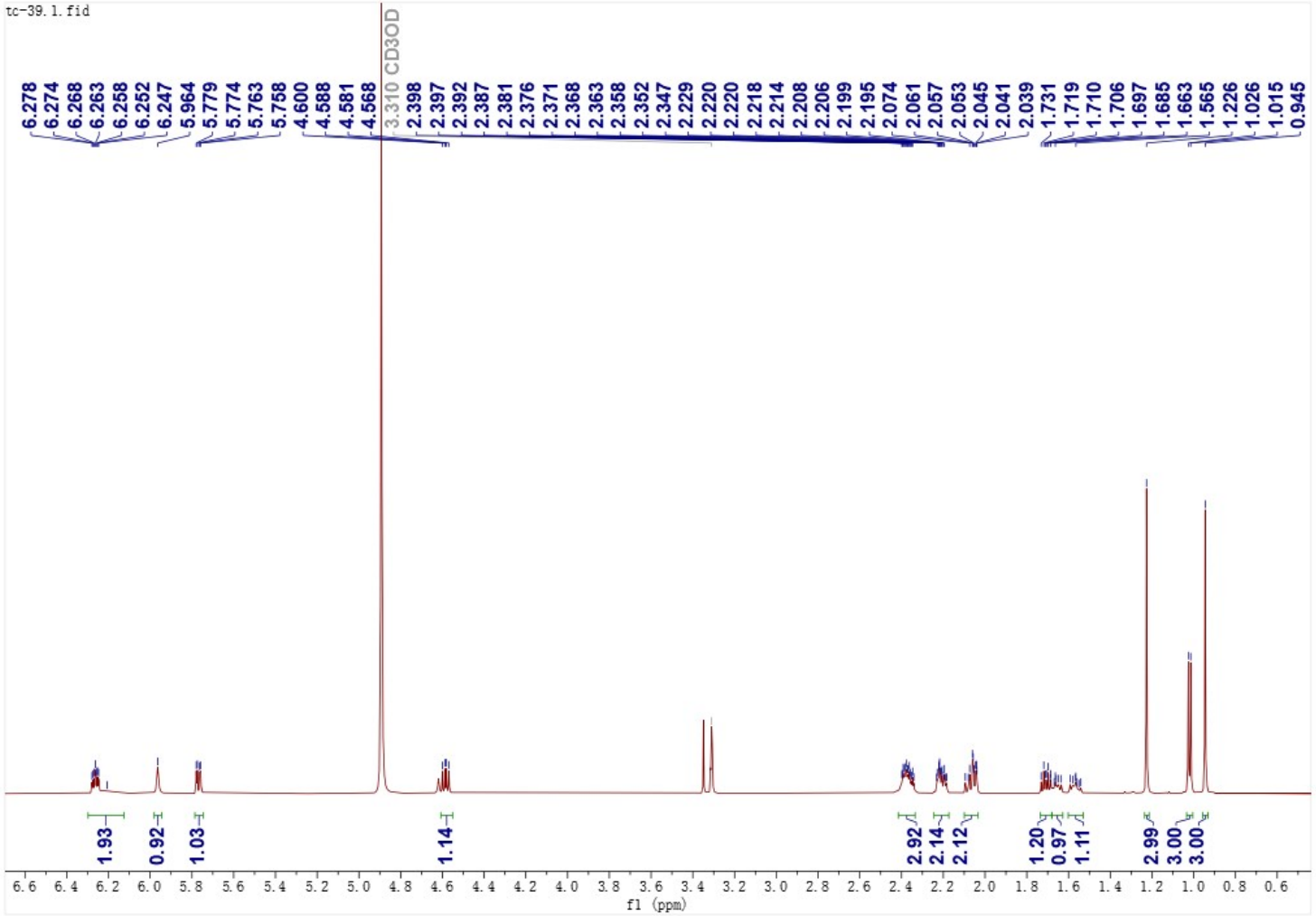
Figure S70. Experimental ECD spectra of Compound **6** in MeOH

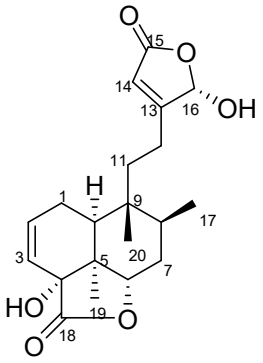




6

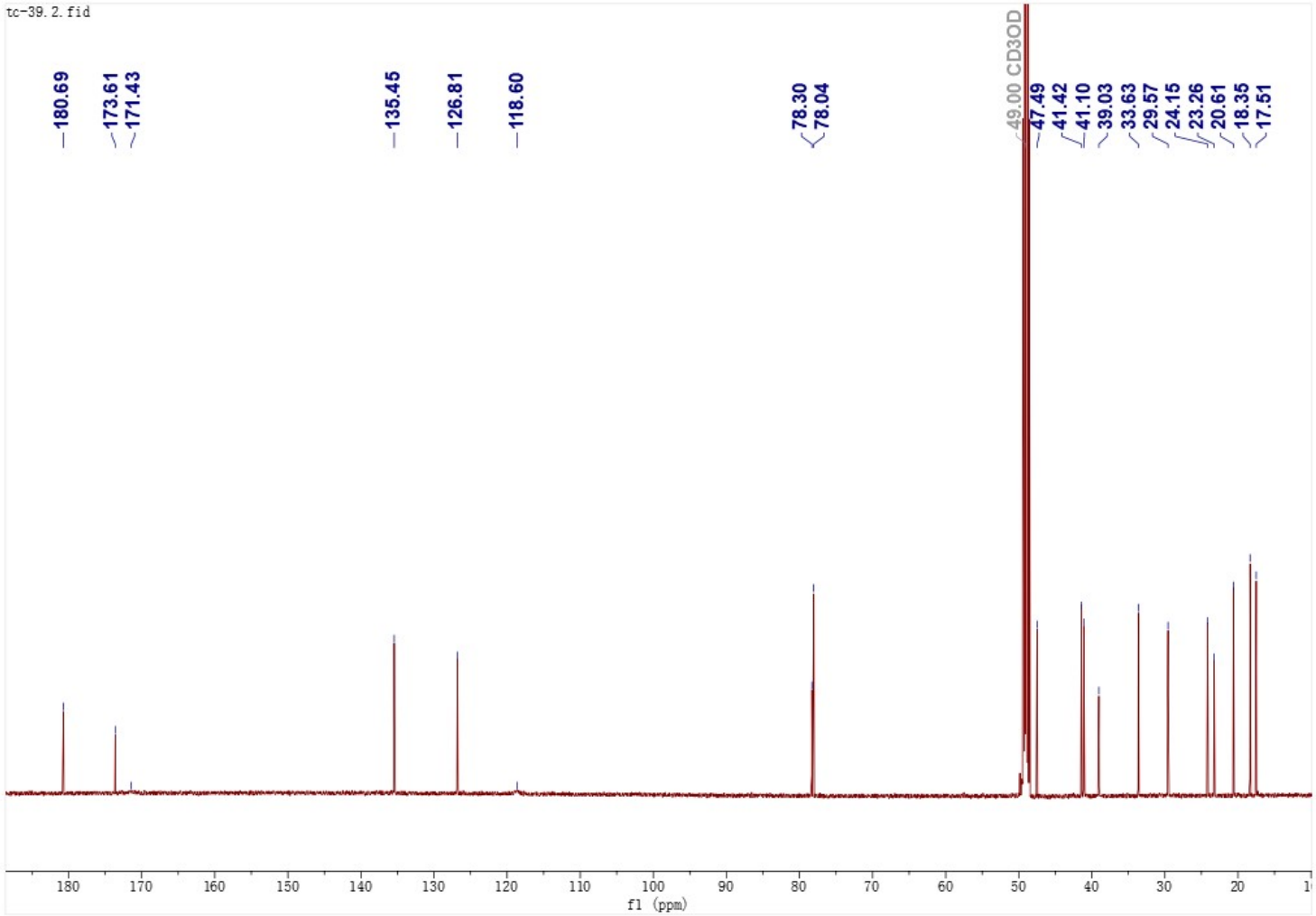
Figure S71. ^{1}H NMR Spectrum of Compound **7** in CD_3OD

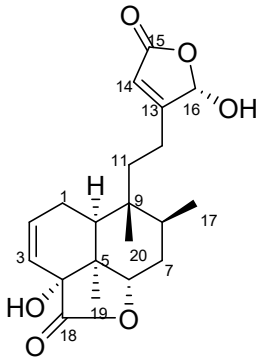




7

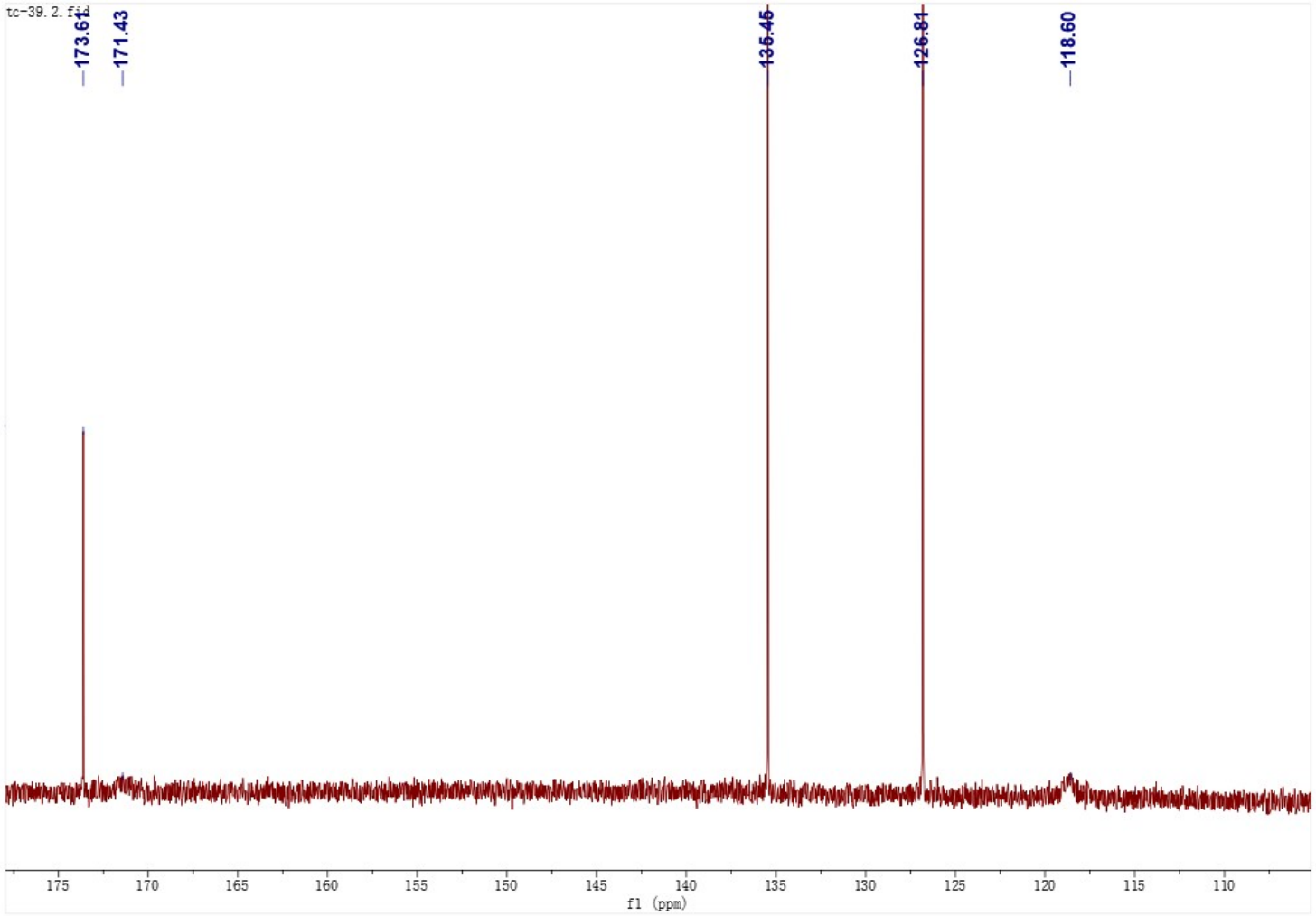
Figure S72. ^{13}C NMR Spectrum of Compound **7** in CD_3OD

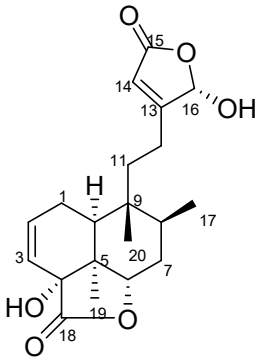




7

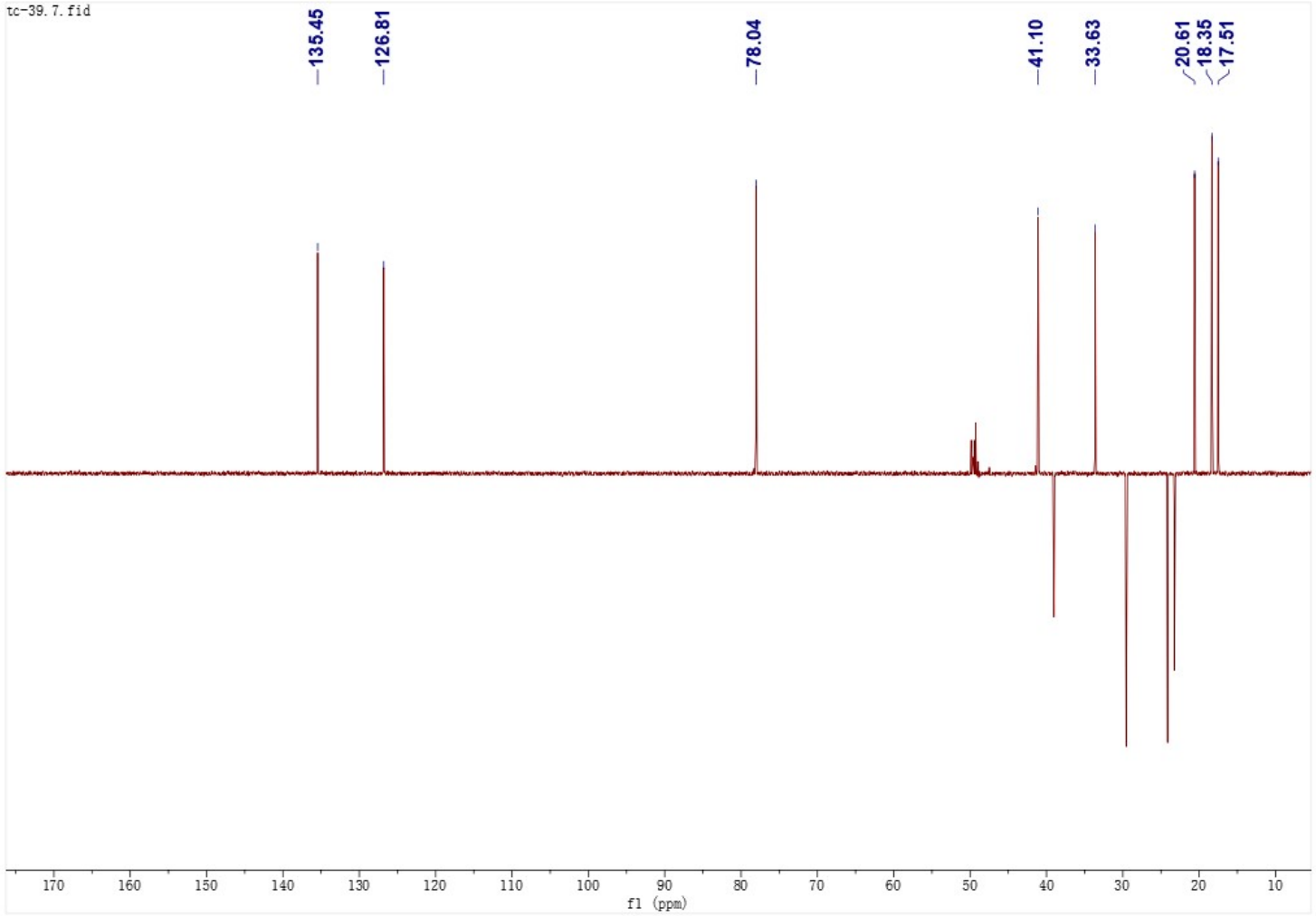
Figure S73. Partial ^{13}C NMR Spectrum of Compound **7** in CD_3OD

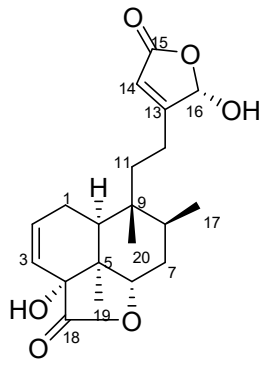




7

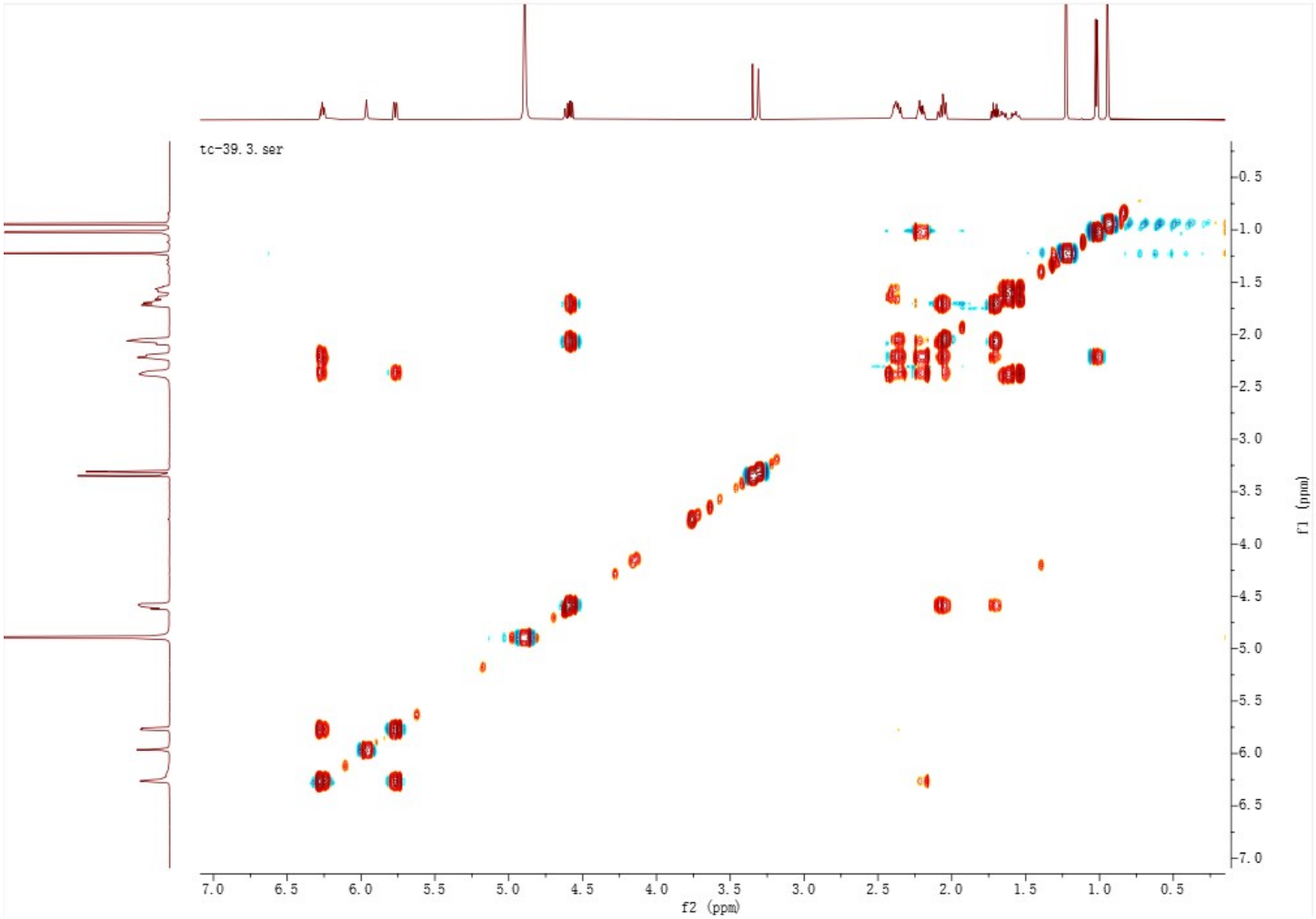
Figure S74. DEPT 135 Spectrum of Compound **7** in CD_3OD

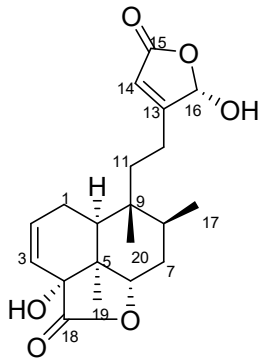




7

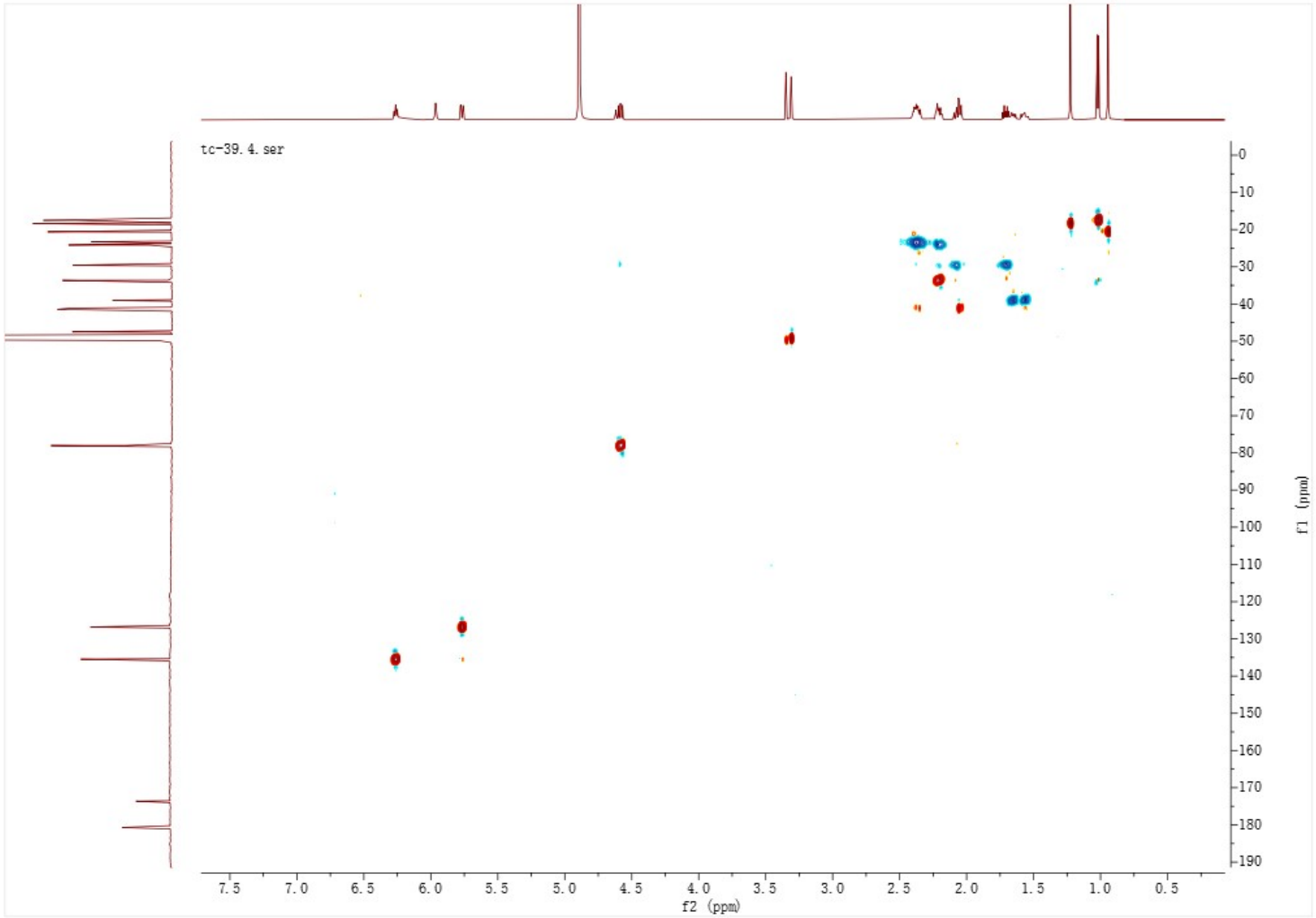
Figure S75. ^{1}H-^{1}H COSY Spectrum of Compound **7** in CD_3OD

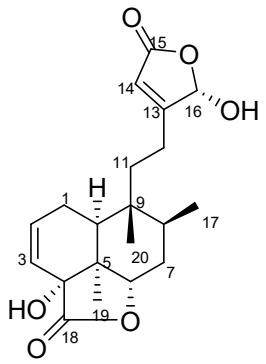




7

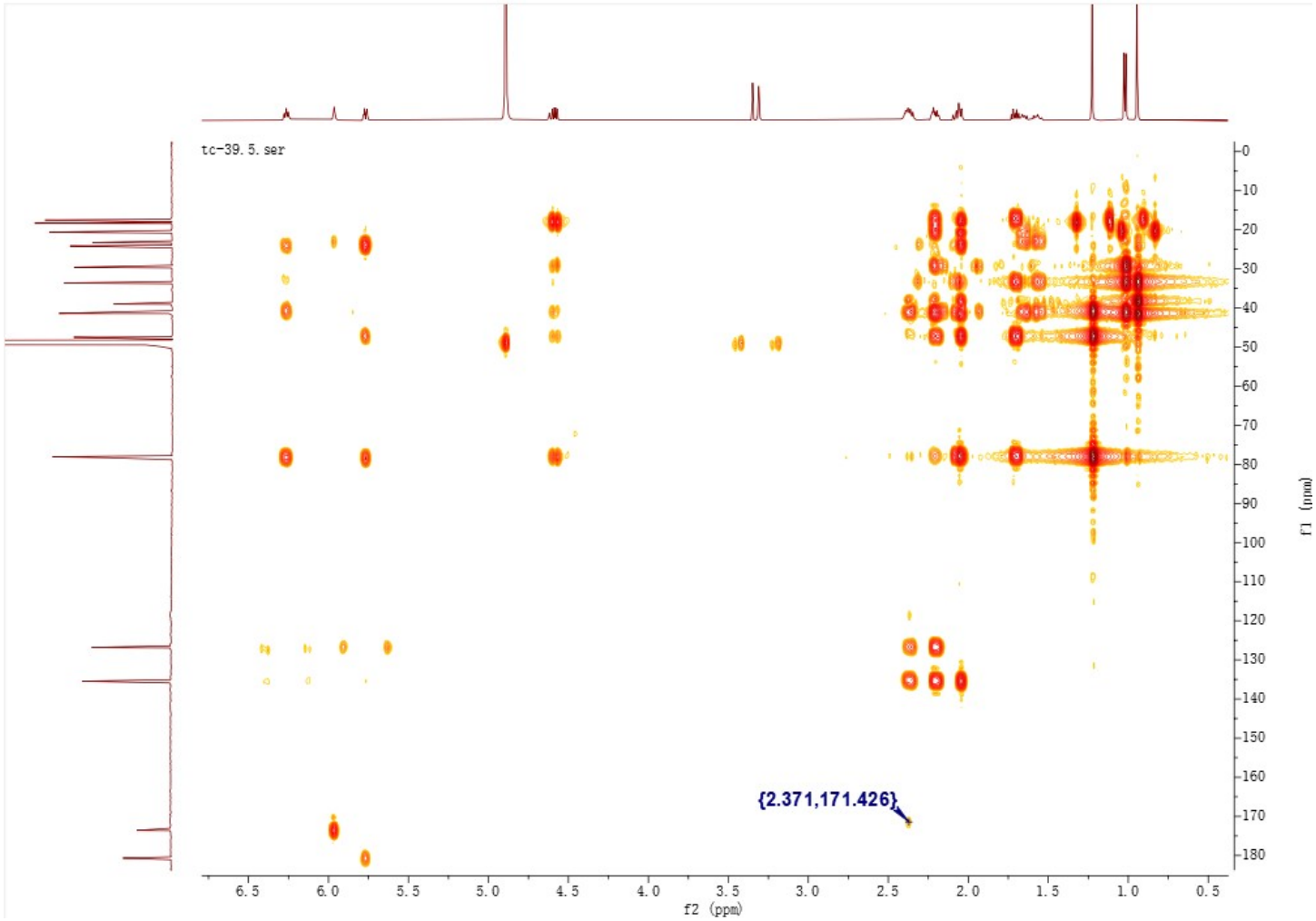
Figure S76. HSQC Spectrum of Compound **7** in CD_3OD

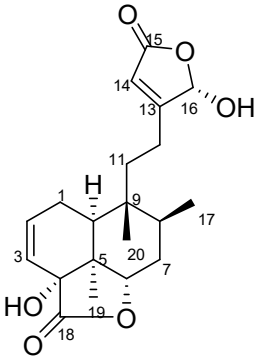




7

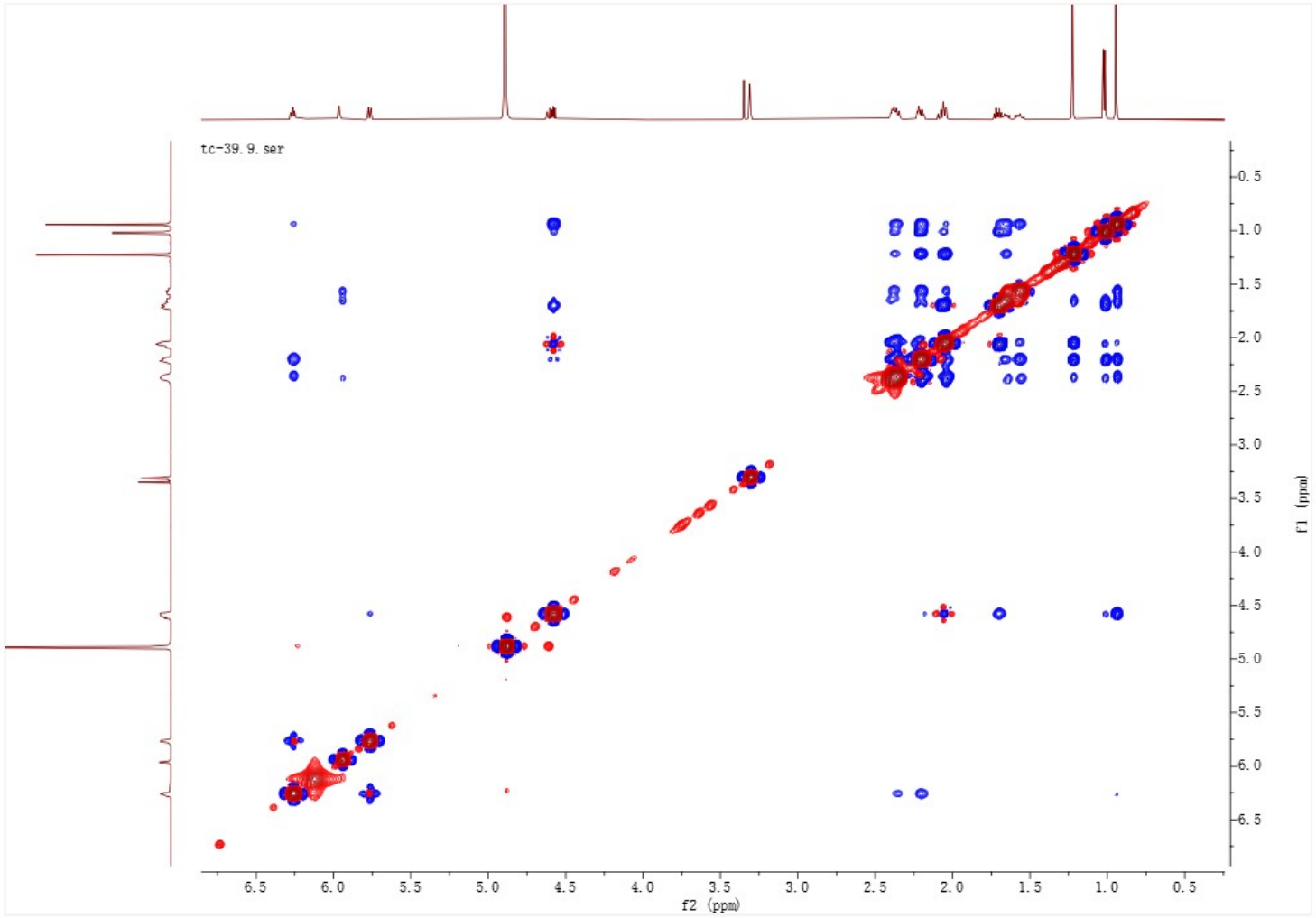
Figure S77. HMBC Spectrum of Compound **7** in CD_3OD

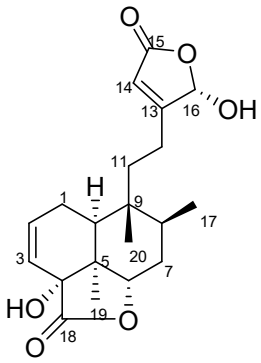




7

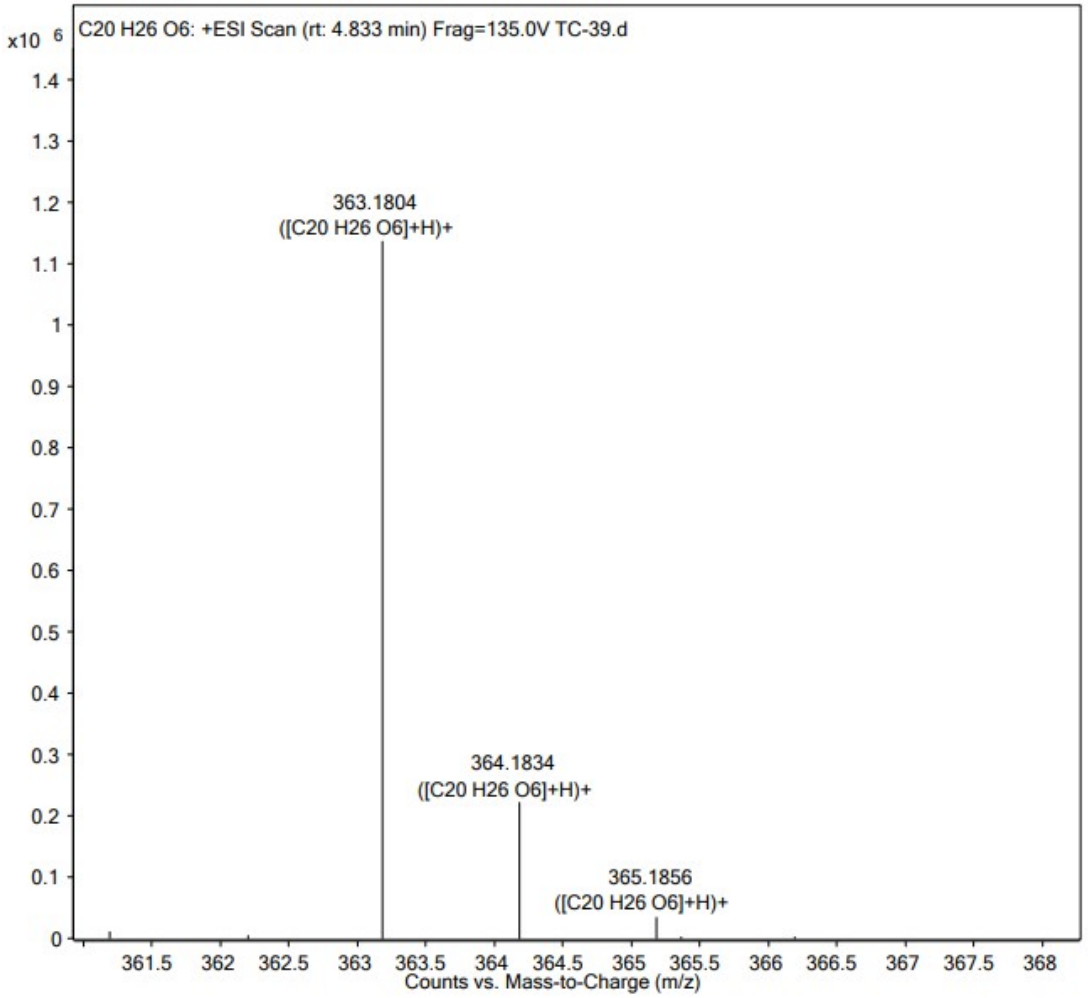
Figure S78. NOESY Spectrum of Compound **7** in CD_3OD

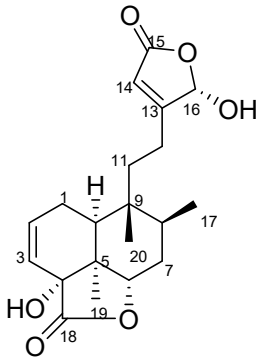




7

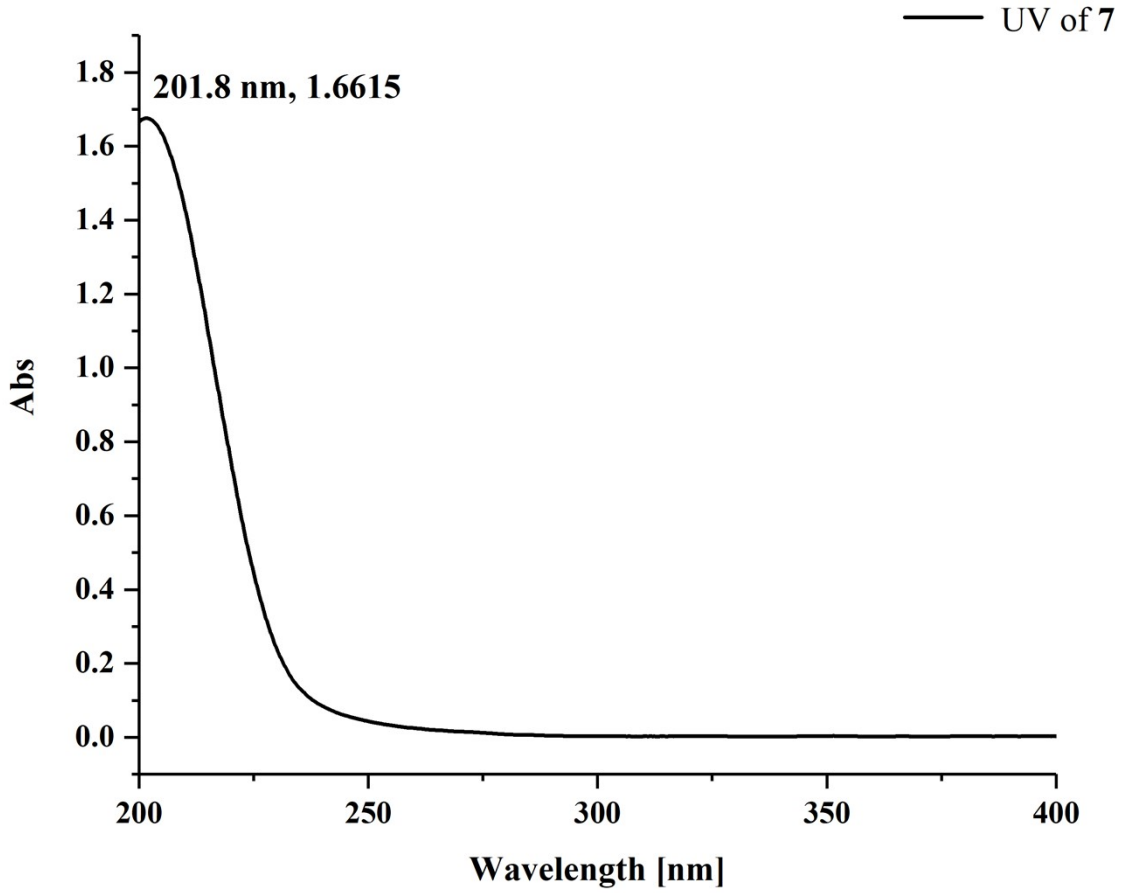
Figure S79. (+) HRESIMS Spectrum of Compound **7**

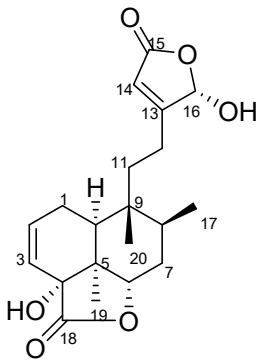




7

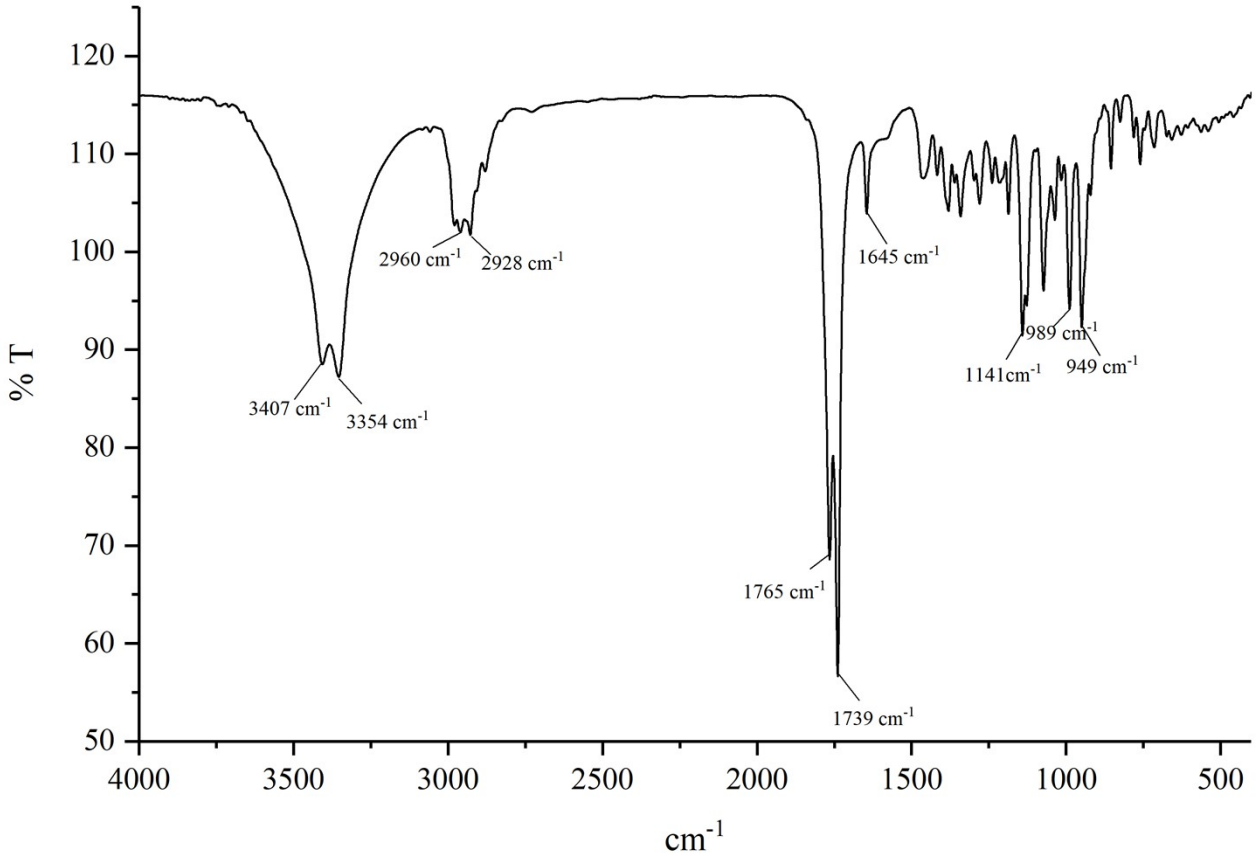
Figure S80. UV Spectrum of Compound **7**

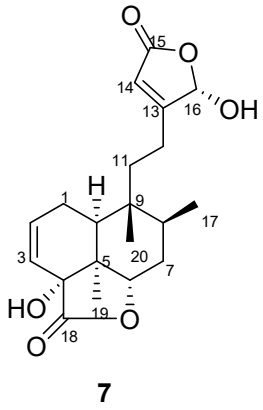




7

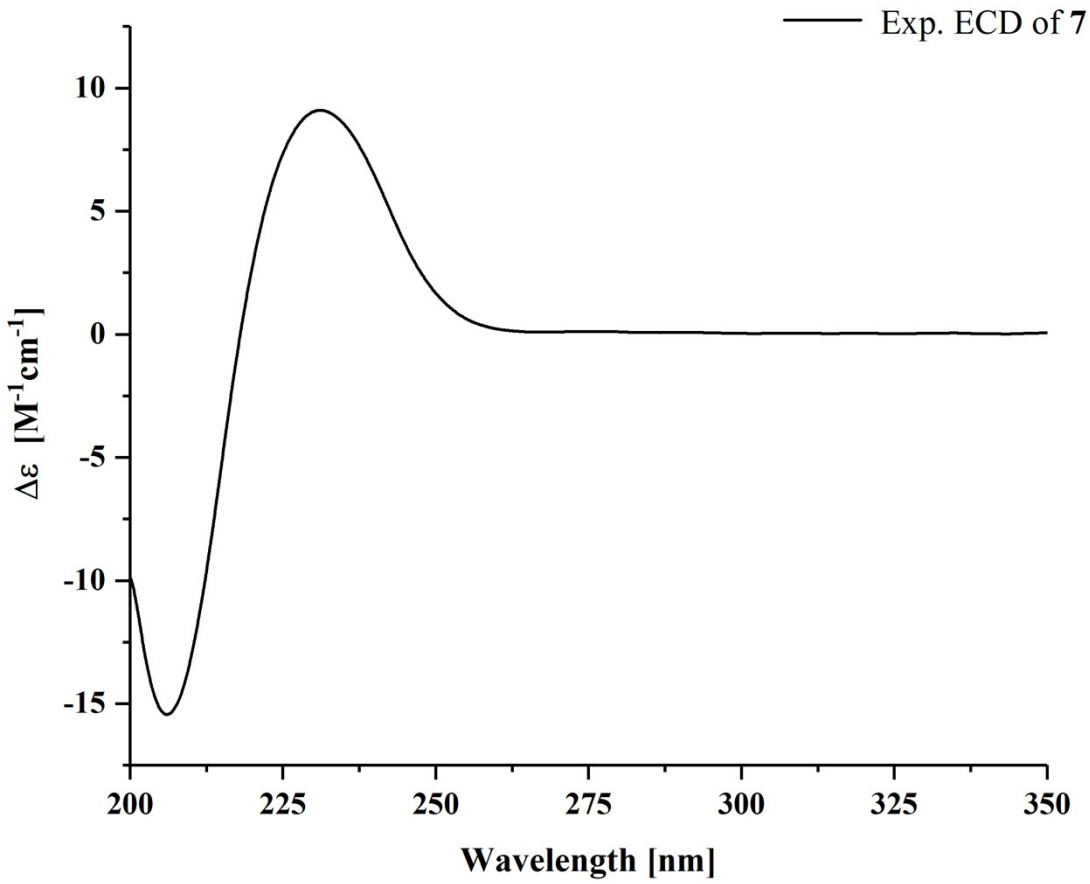
Figure S81. IR (KBr disc) Spectrum of Compound **7**

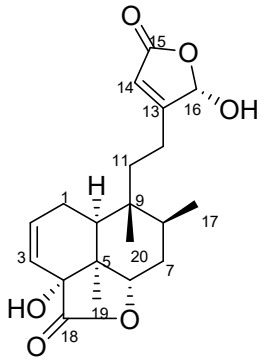




7

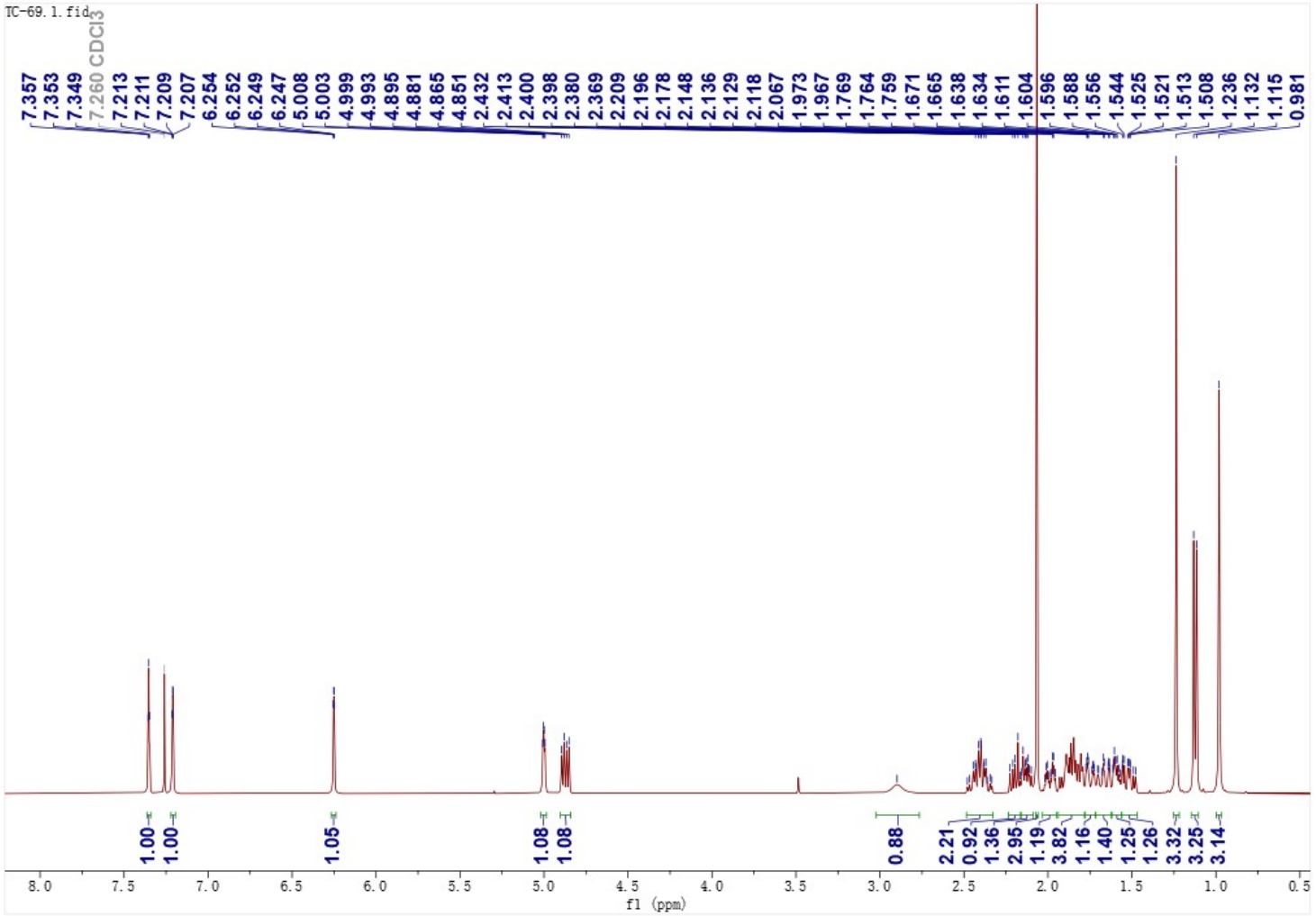
Figure S82. Experimental ECD spectra of Compound **7** in MeOH

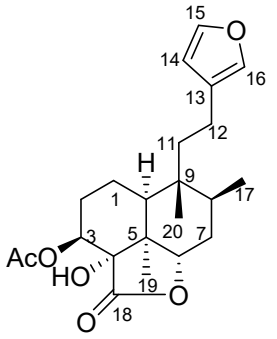




7

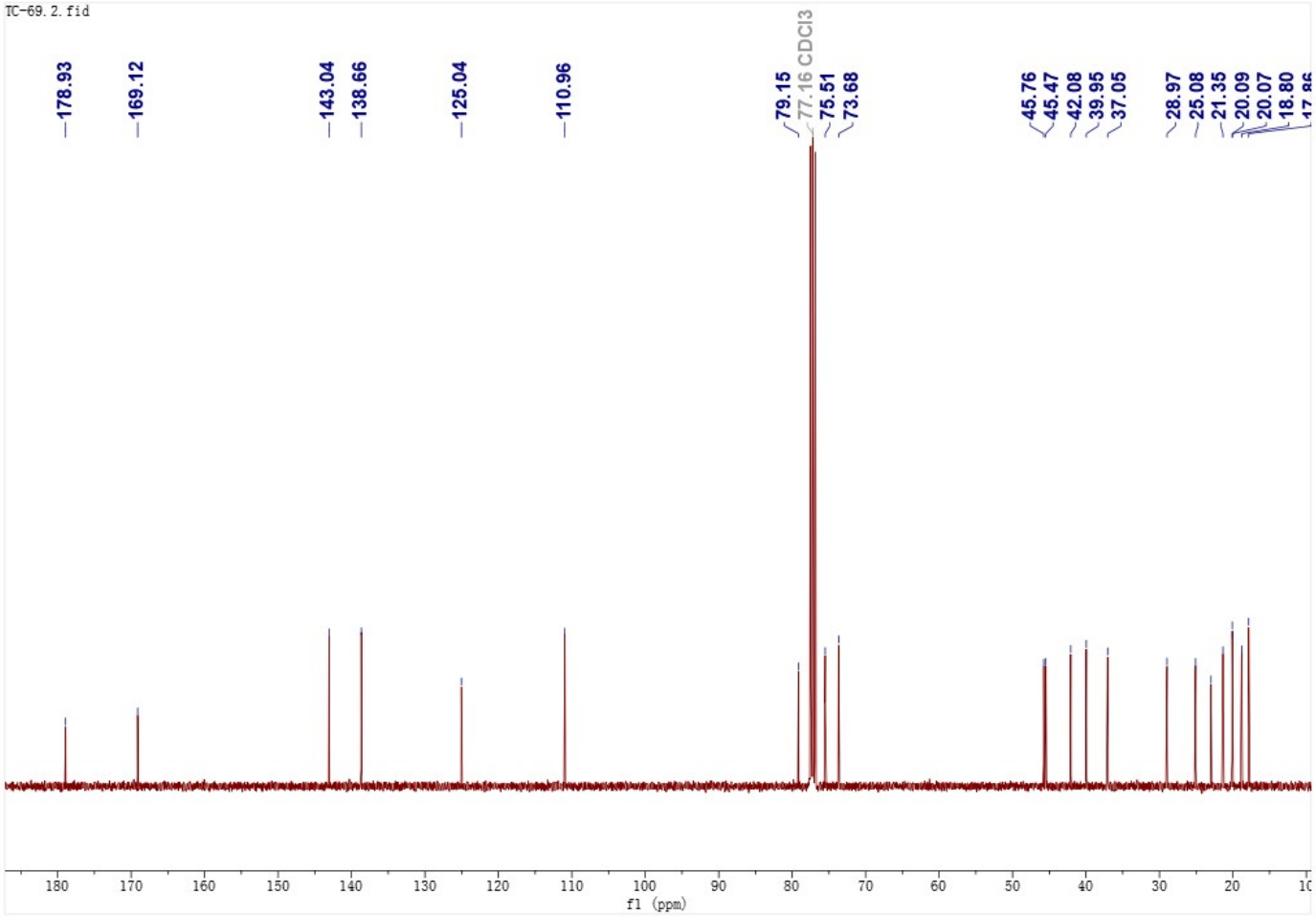
Figure S83. ^{1}H NMR Spectrum of Compound **8** in $CDCl_3$

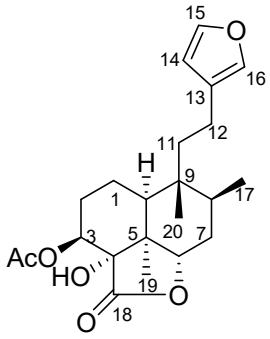




8

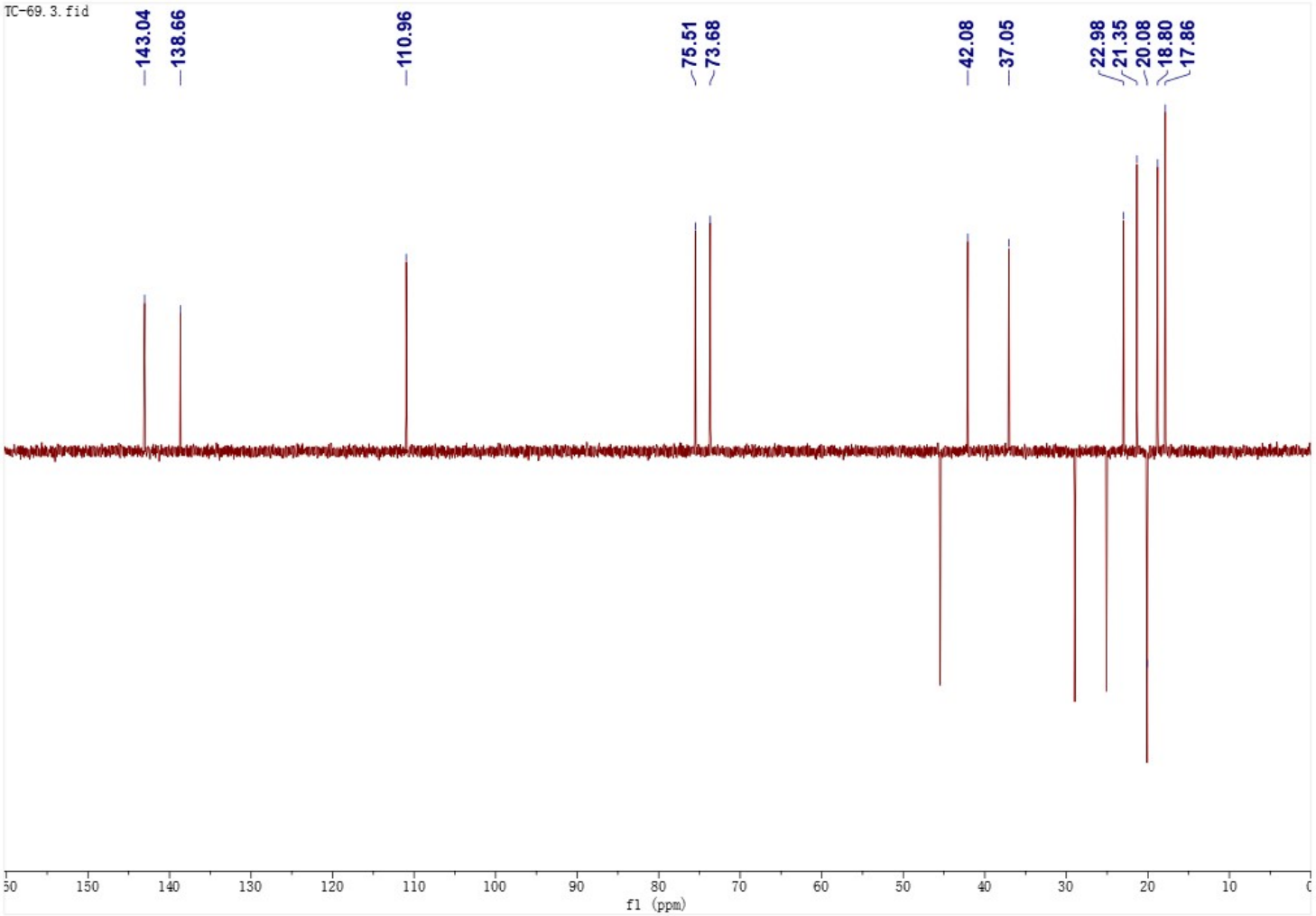
Figure S84. ^{13}C NMR Spectrum of Compound **8** in $CDCl_3$

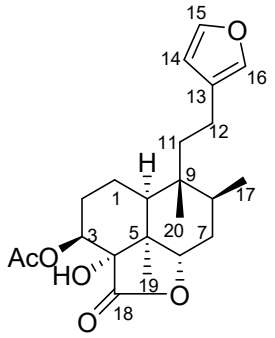




8

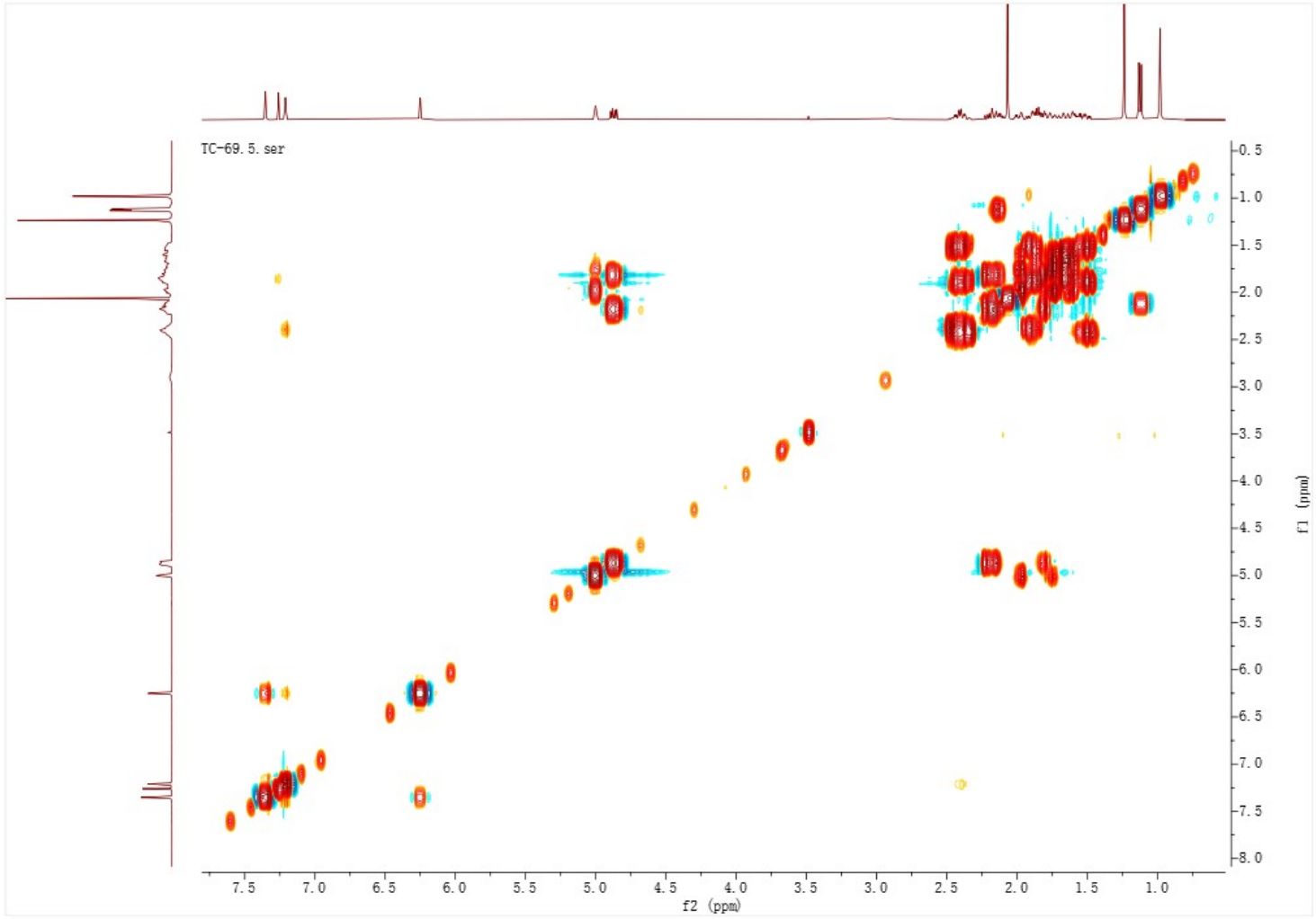
Figure S85. DEPT 135 Spectrum of Compound **8** in $CDCl_3$

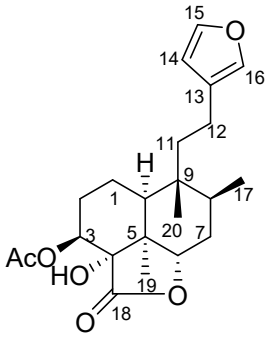




8

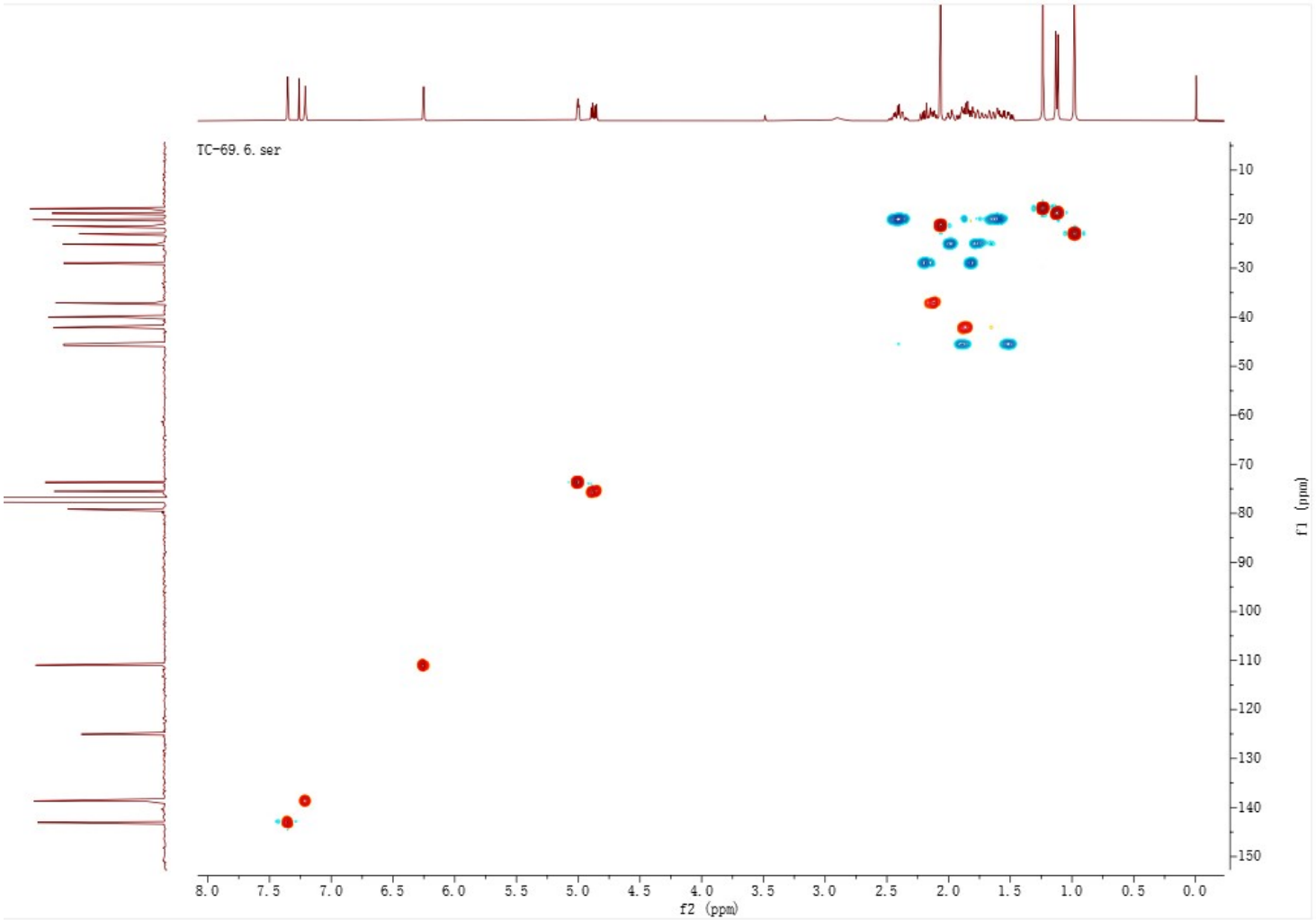
Figure S86. ^{1}H-^{1}H COSY Spectrum of Compound **8** in $CDCl_3$

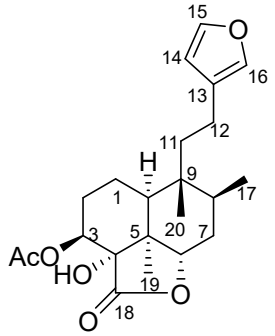




8

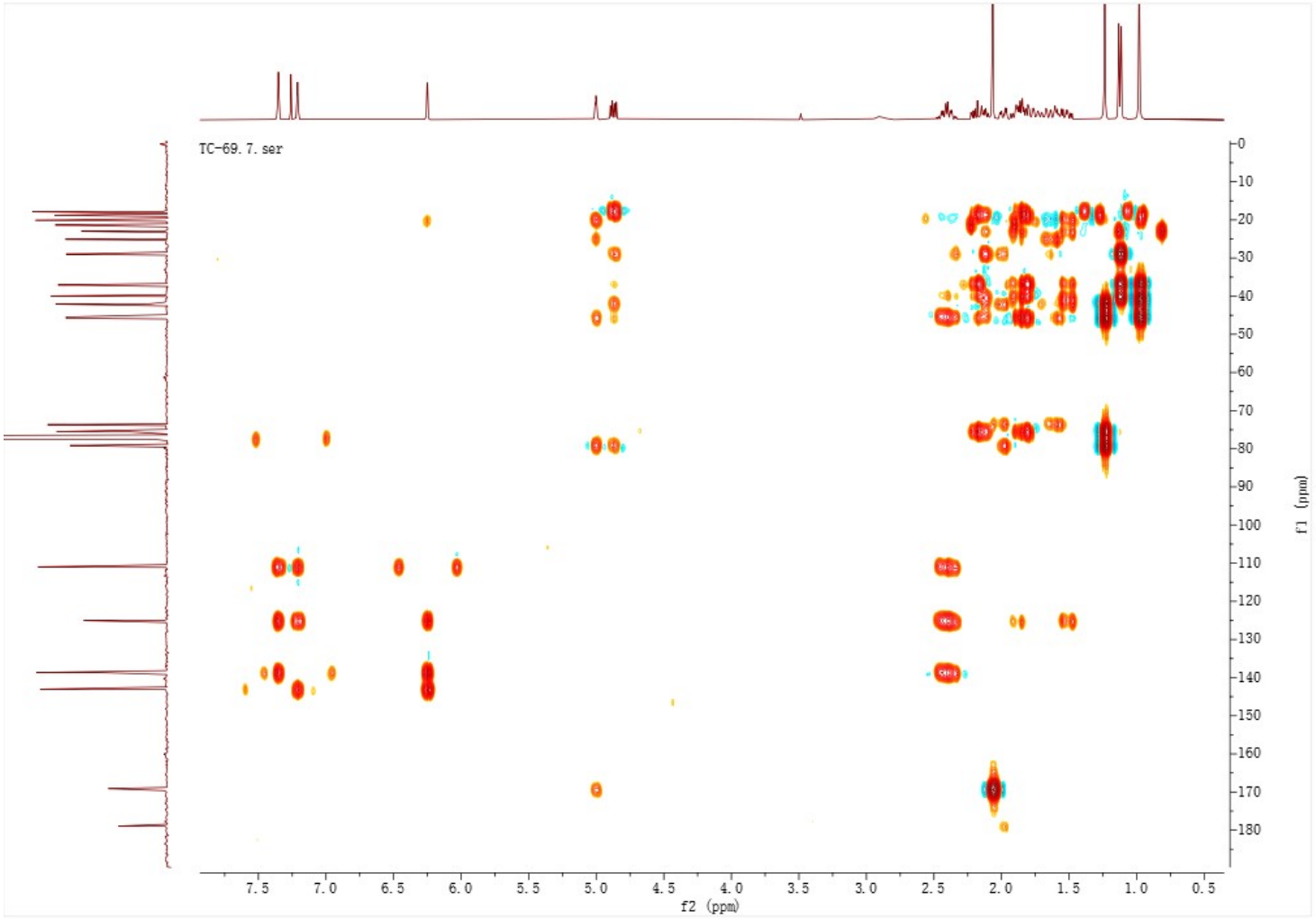
Figure S87. HSQC Spectrum of Compound **8** in $CDCl_3$

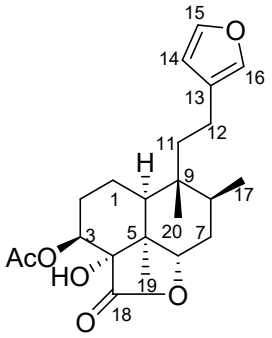




8

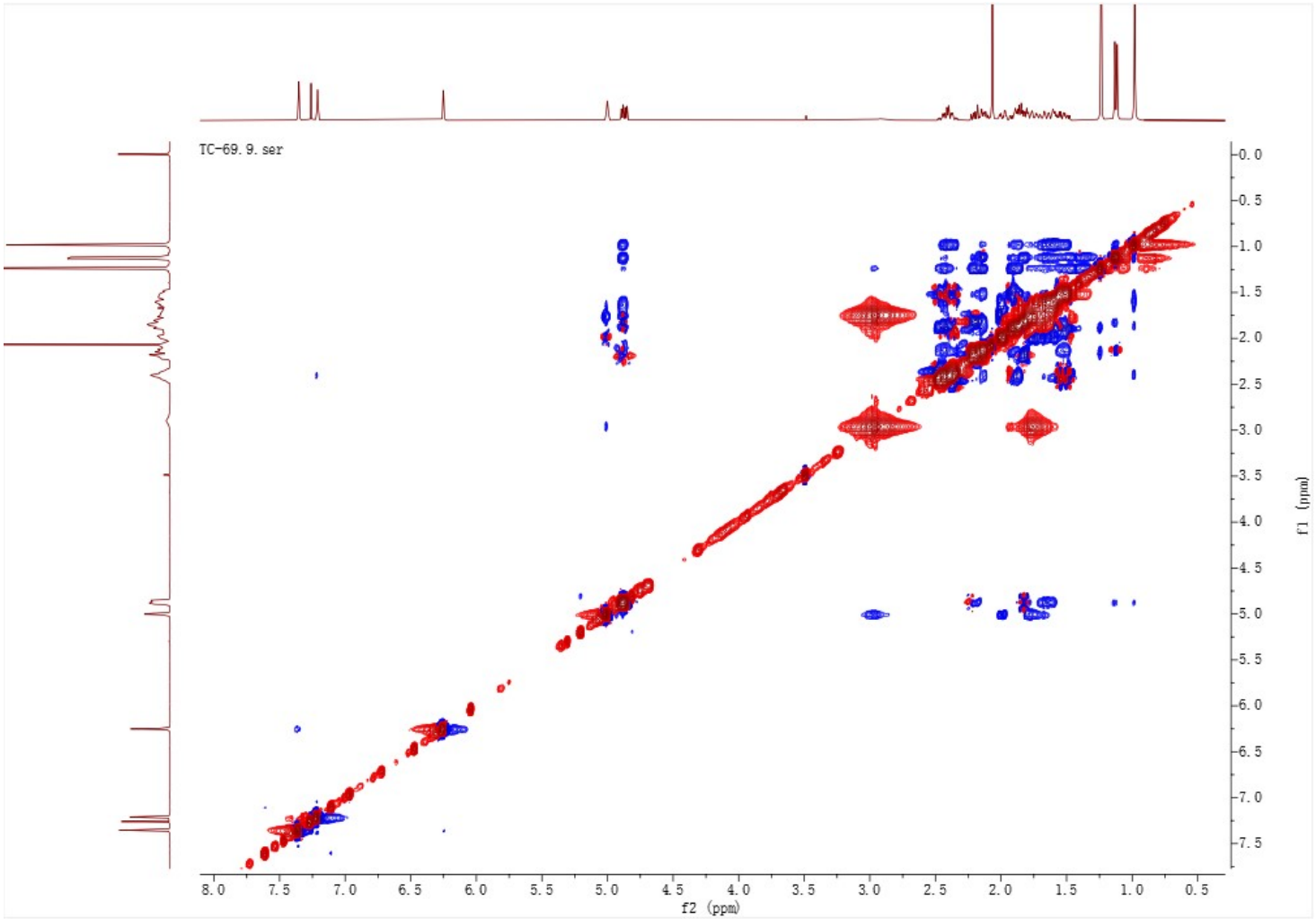
Figure S88. HMBC Spectrum of Compound **8** in $CDCl_3$

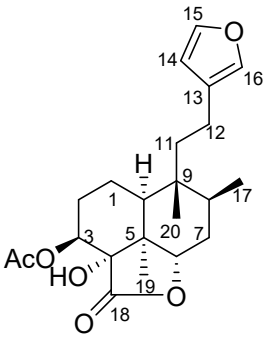




8

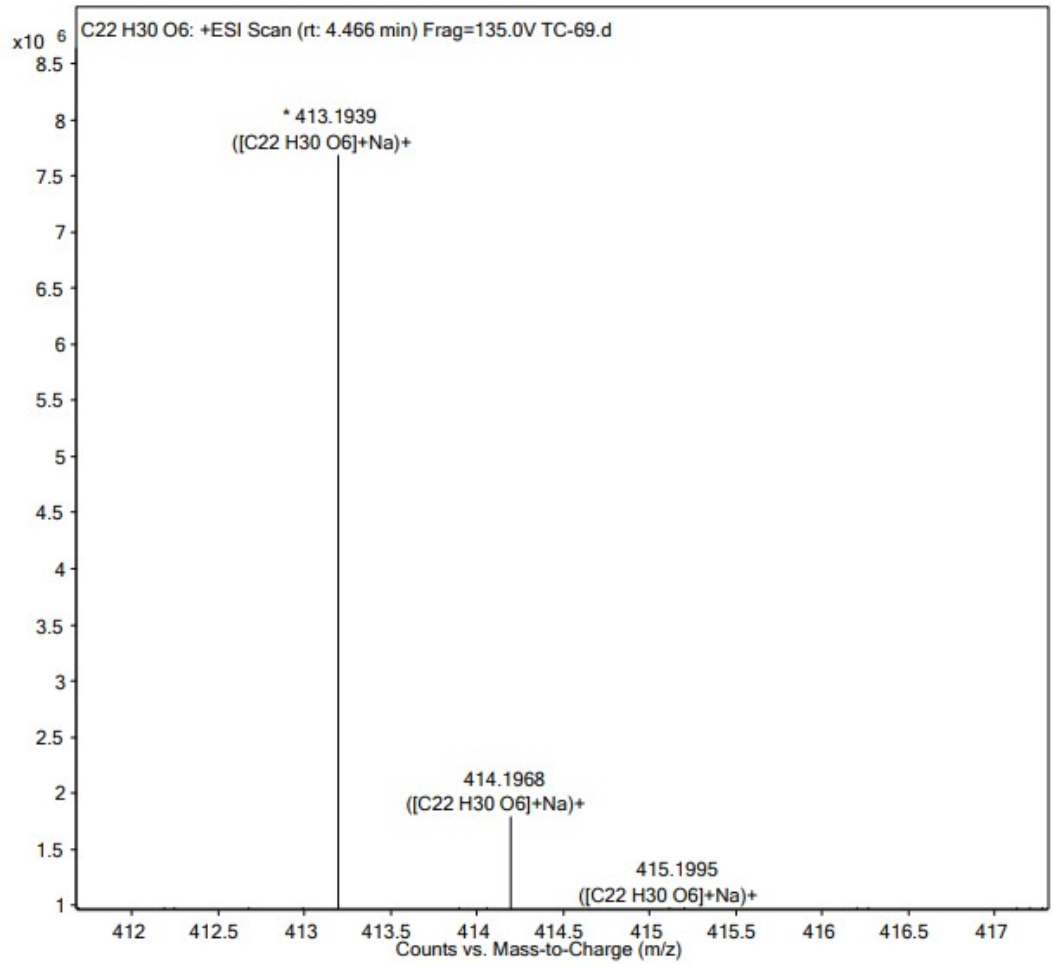
Figure S89. NOESY Spectrum of Compound **8** in $CDCl_3$

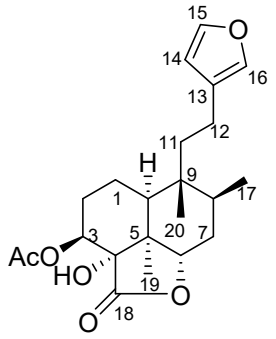




8

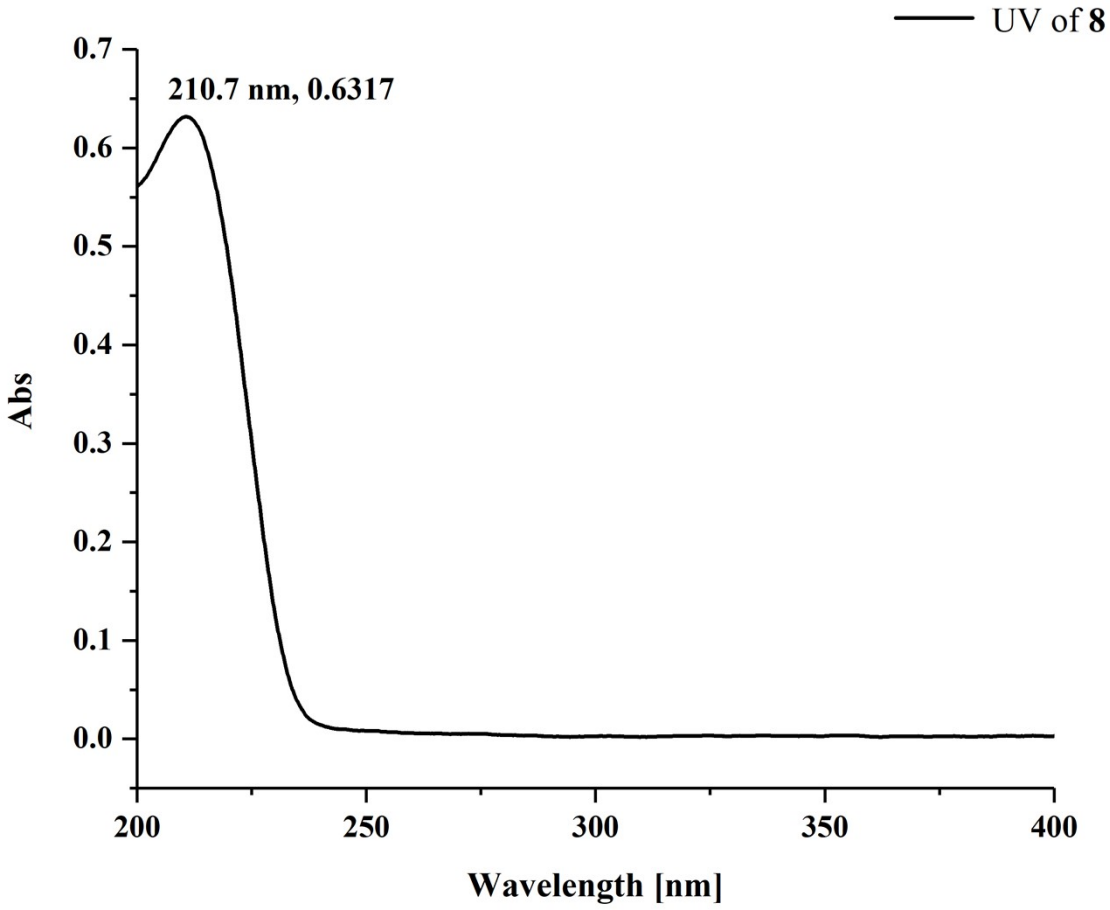
Figure S90. (+) HRESIMS Spectrum of Compound **8**

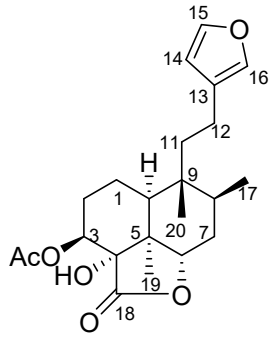




8

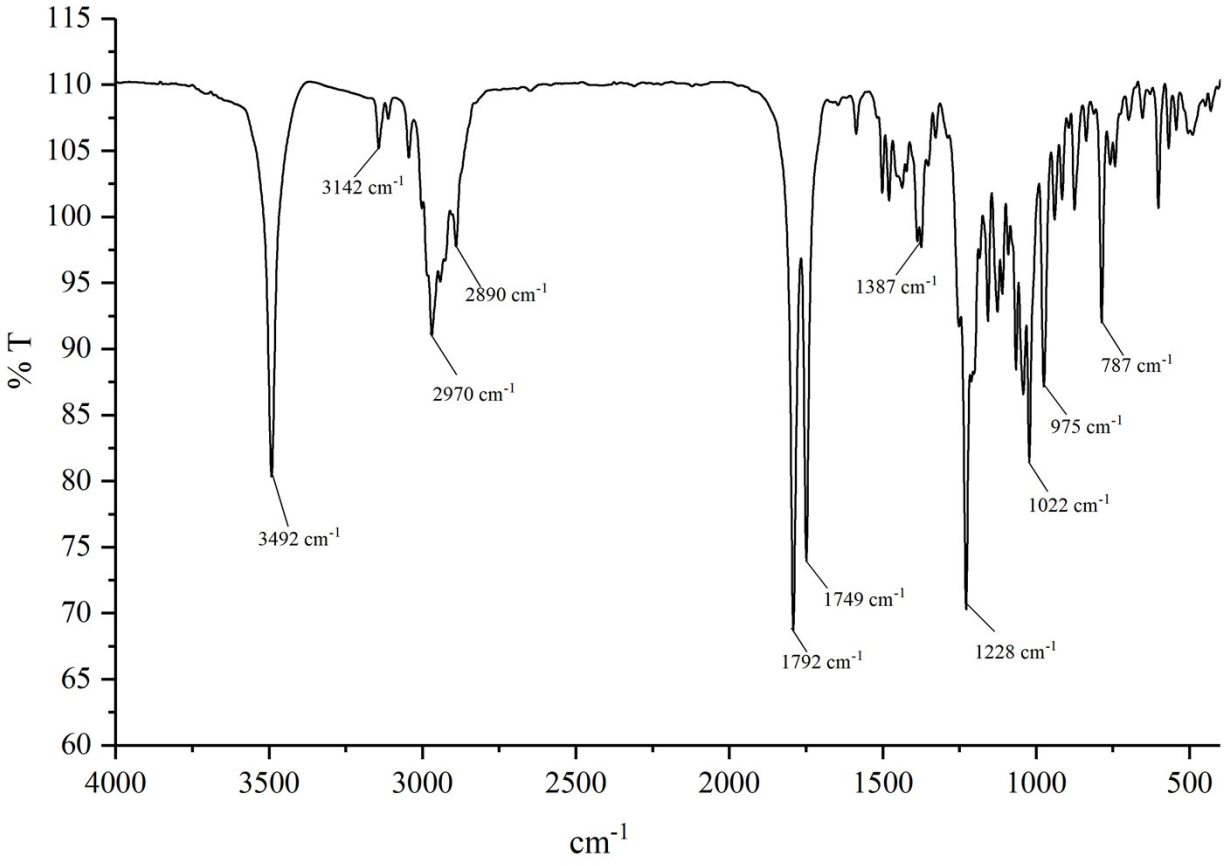
Figure S91. UV Spectrum of Compound **8**

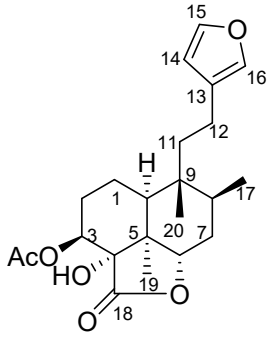




8

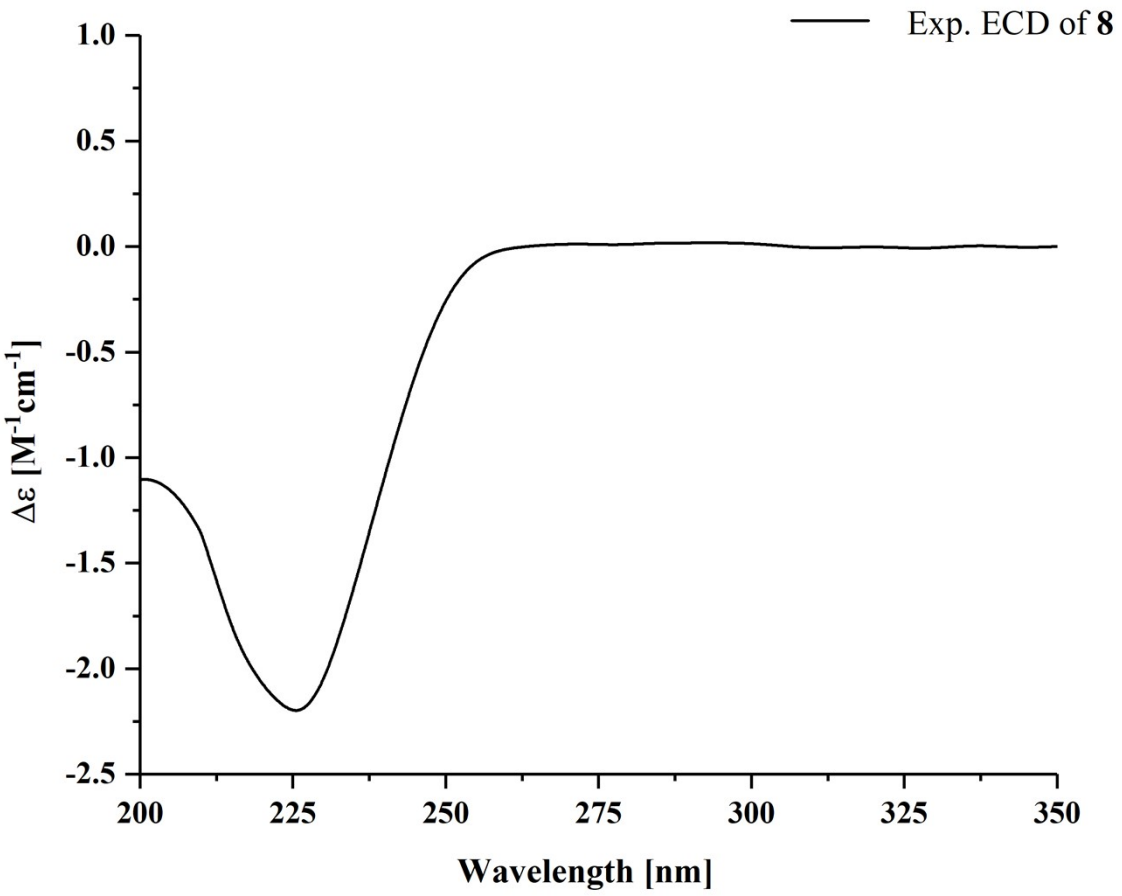
Figure S92. IR (KBr disc) Spectrum of Compound **8**

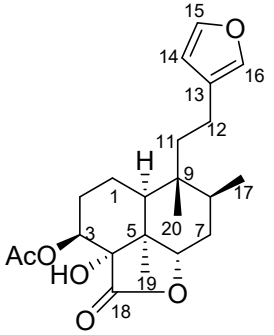




8

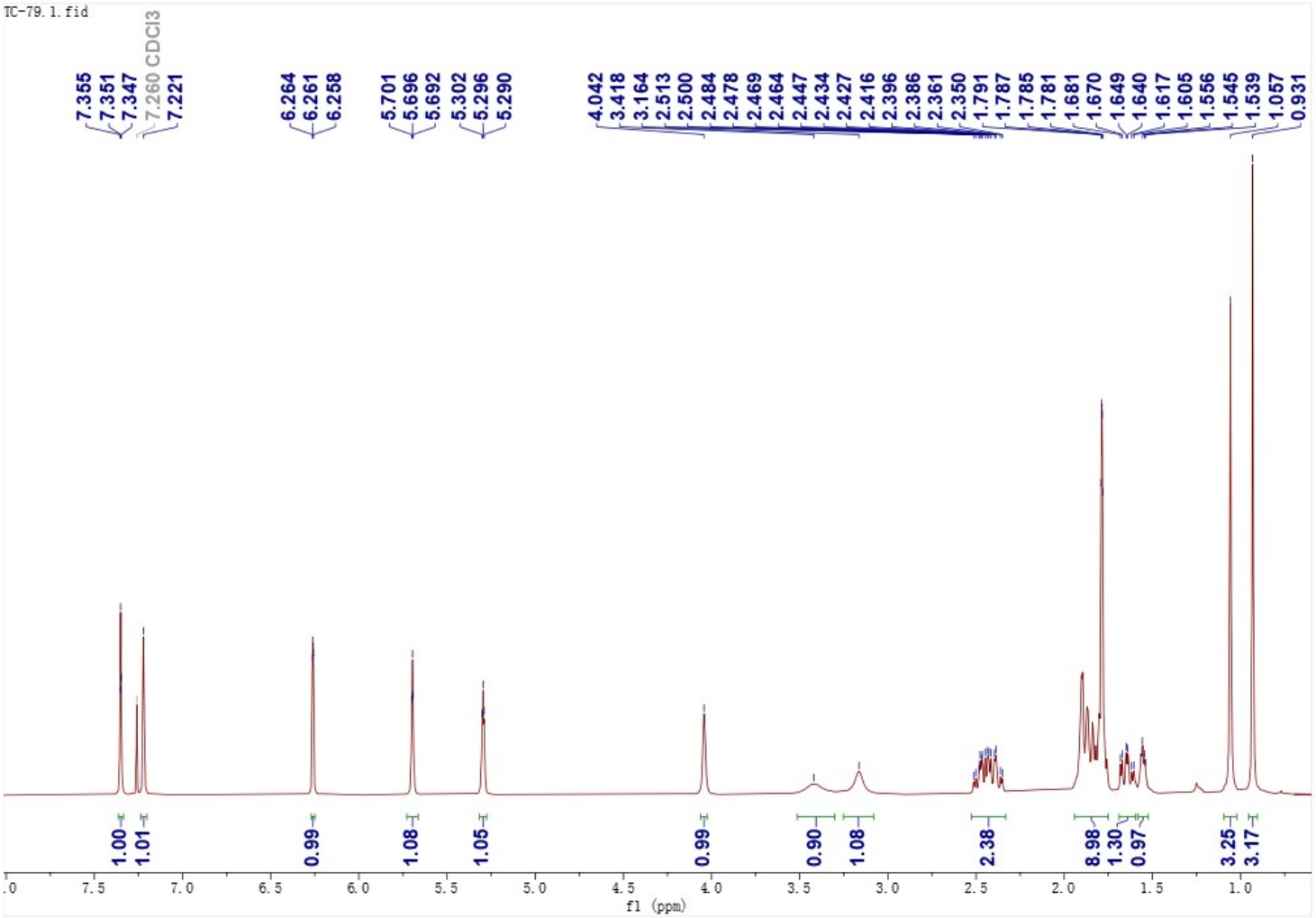
Figure S93. Experimental ECD spectra of Compound **8** in MeOH

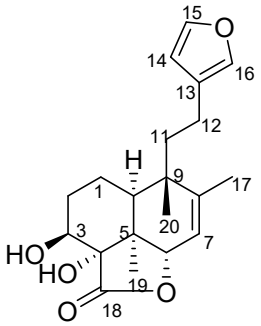




8

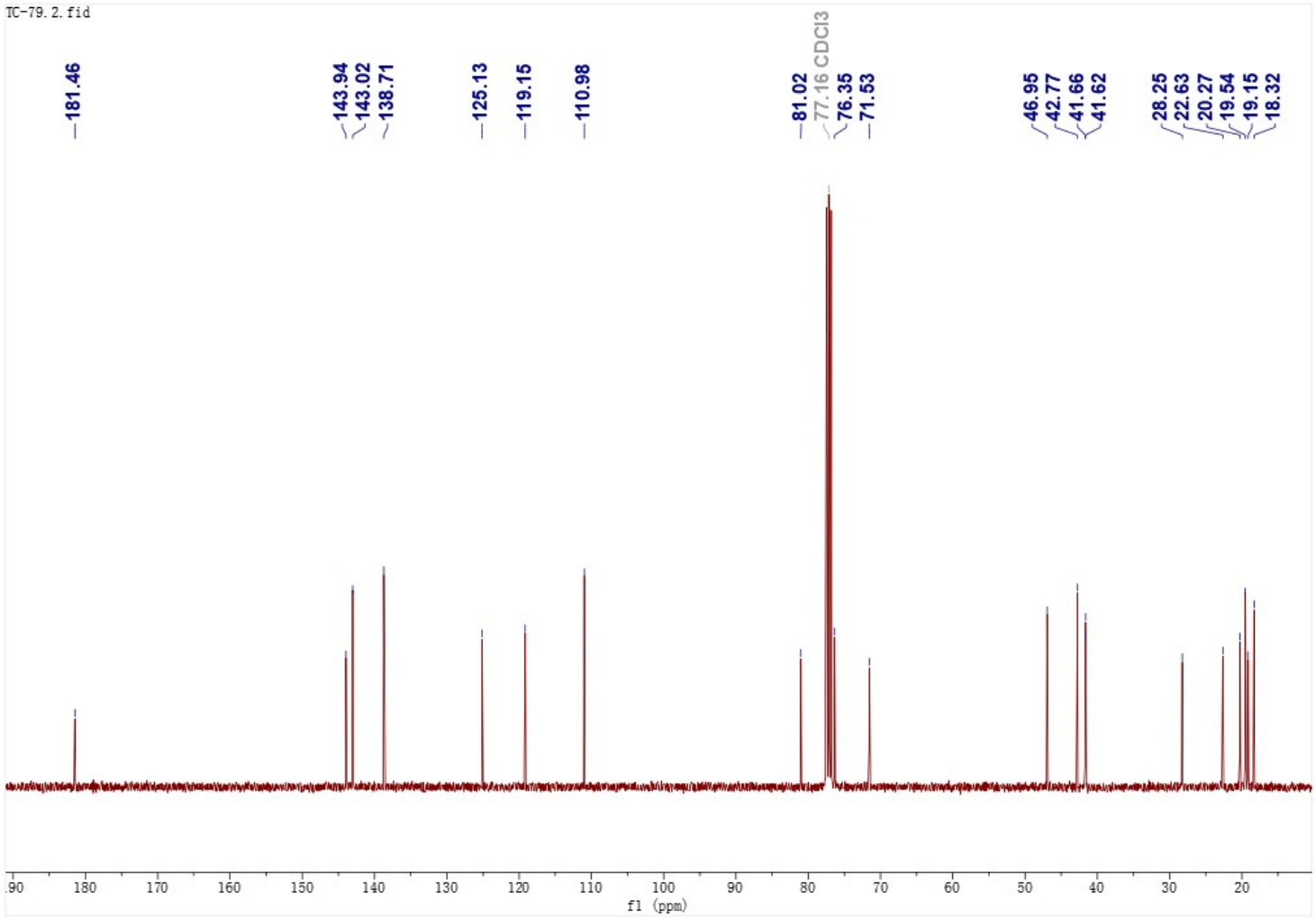
Figure S94. ^{1}H NMR Spectrum of Compound **9** in $CDCl_3$

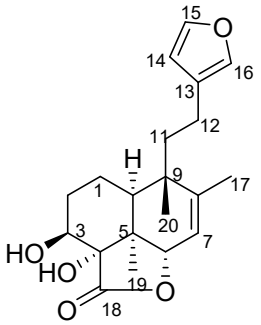




9

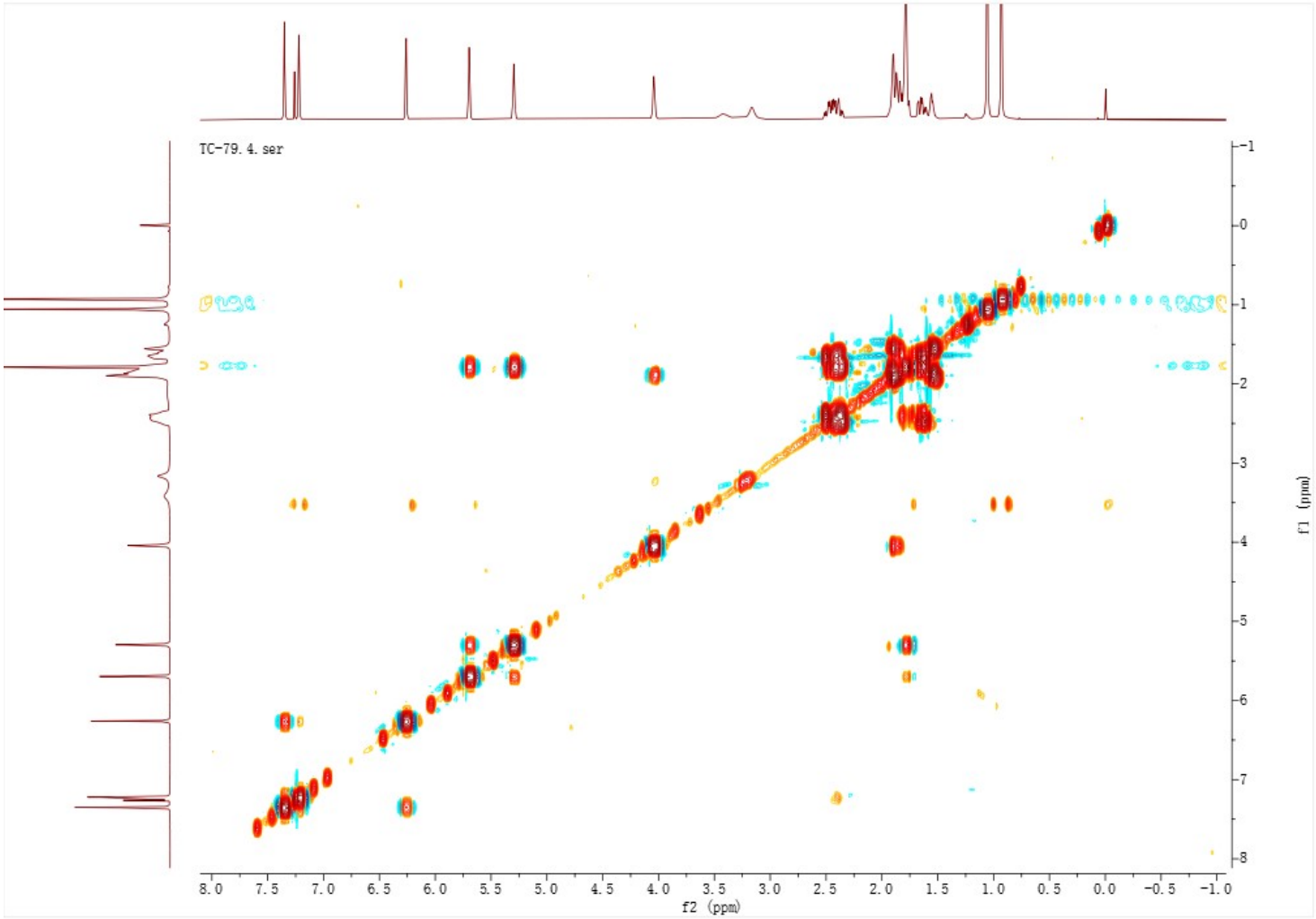
Figure S95. ^{13}C NMR Spectrum of Compound **9** in $CDCl_3$

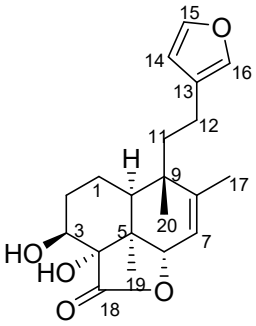




9

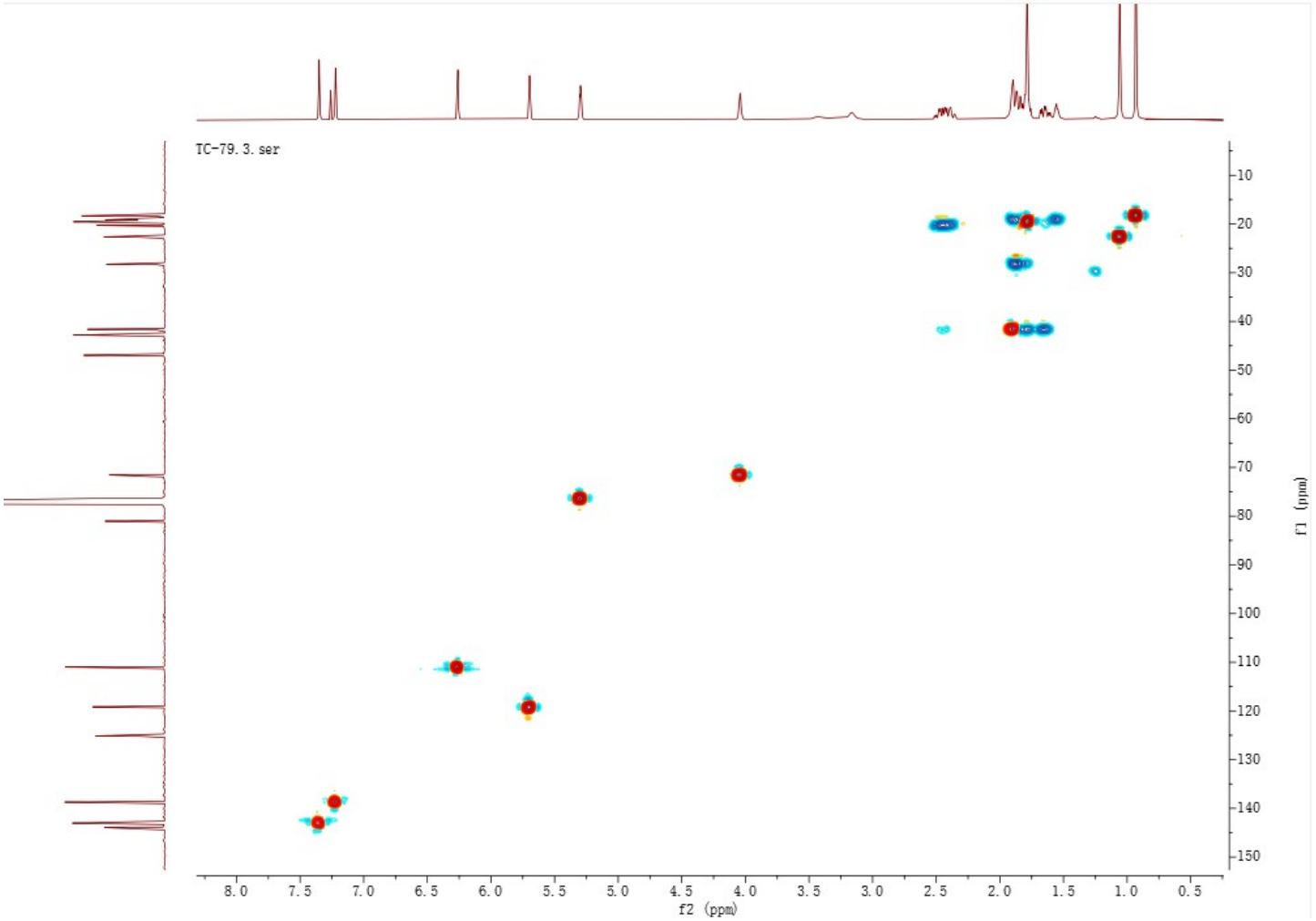
Figure S96. ^{1}H-^{1}H COSY Spectrum of Compound **9** in $CDCl_3$

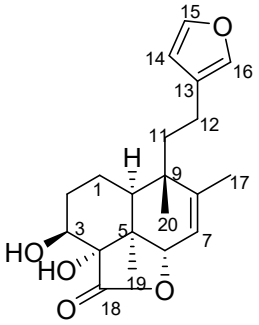




9

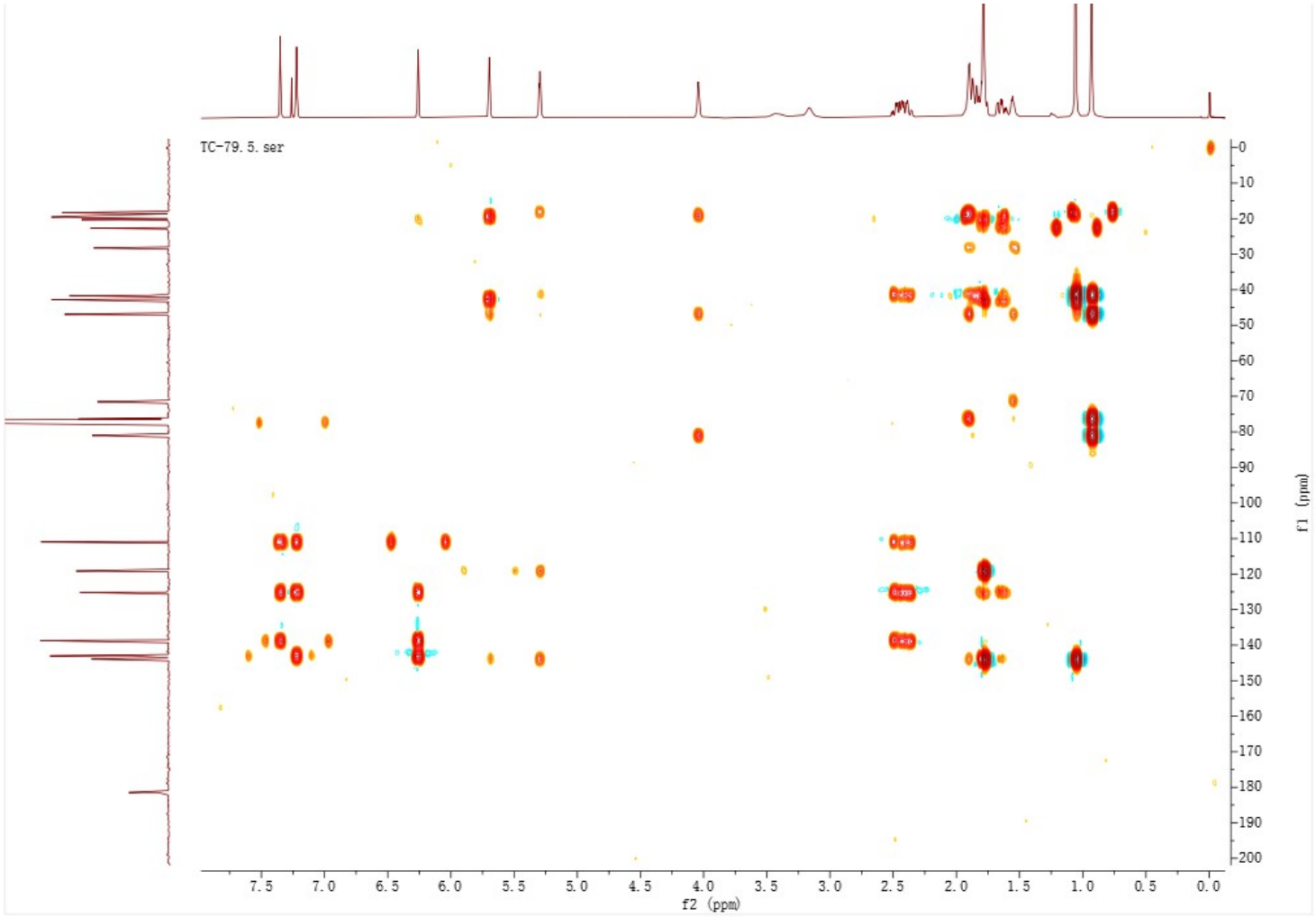
Figure S97. HSQC Spectrum of Compound **9** in $CDCl_3$

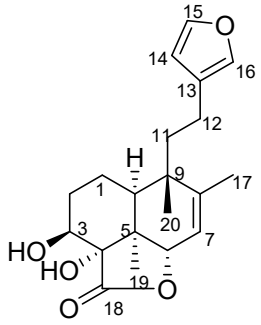




9

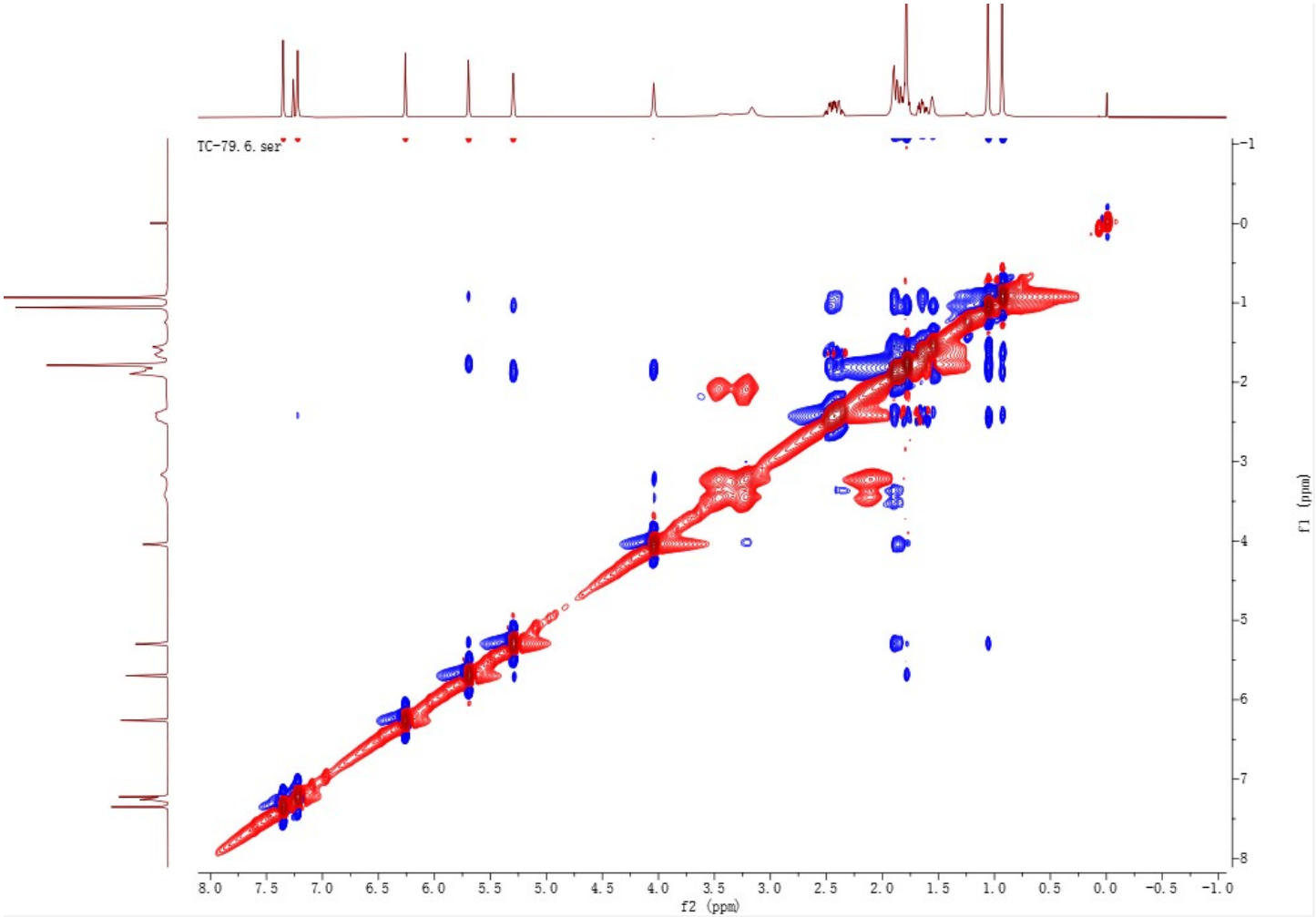
Figure S98. HMBC Spectrum of Compound **9** in $CDCl_3$

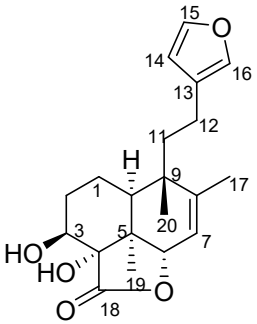




9

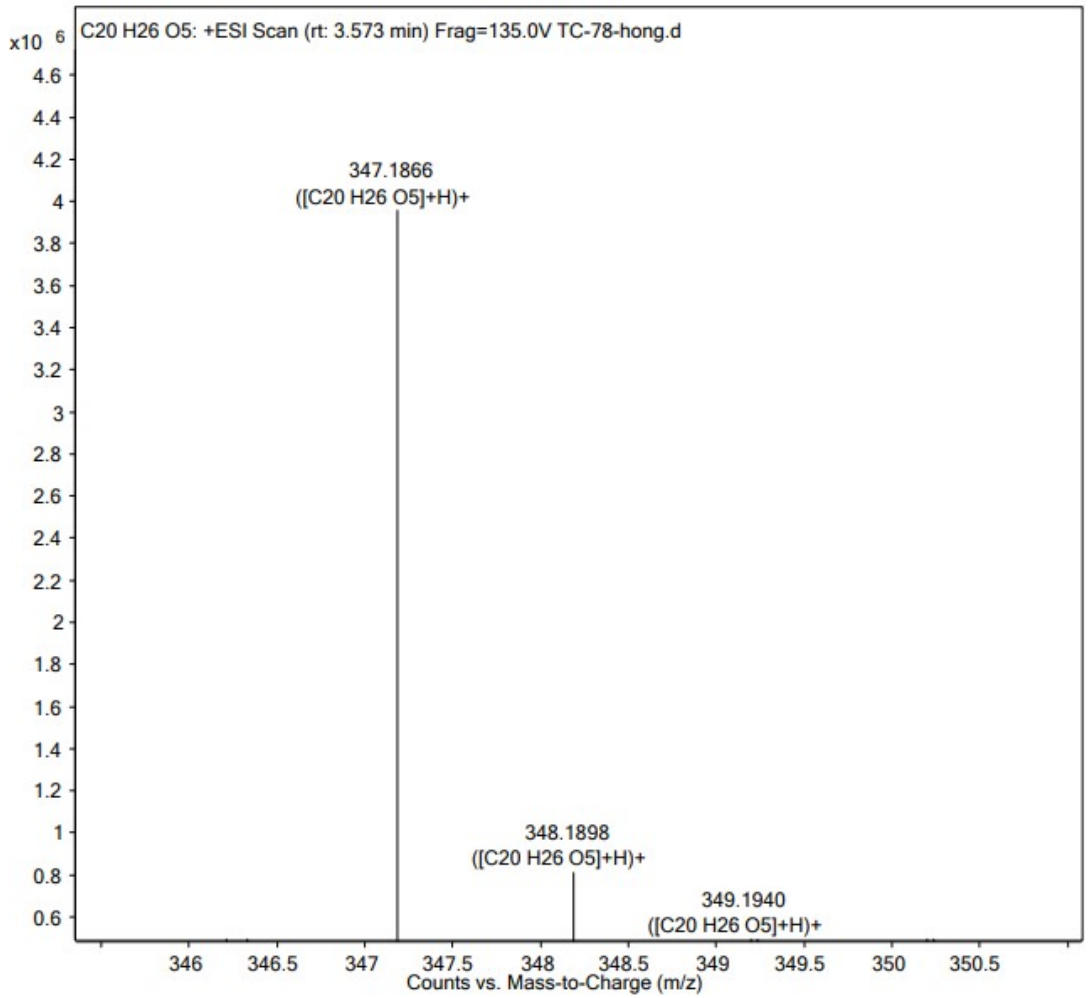
Figure S99. NOESY Spectrum of Compound **9** in $CDCl_3$

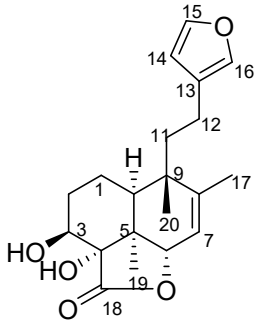




9

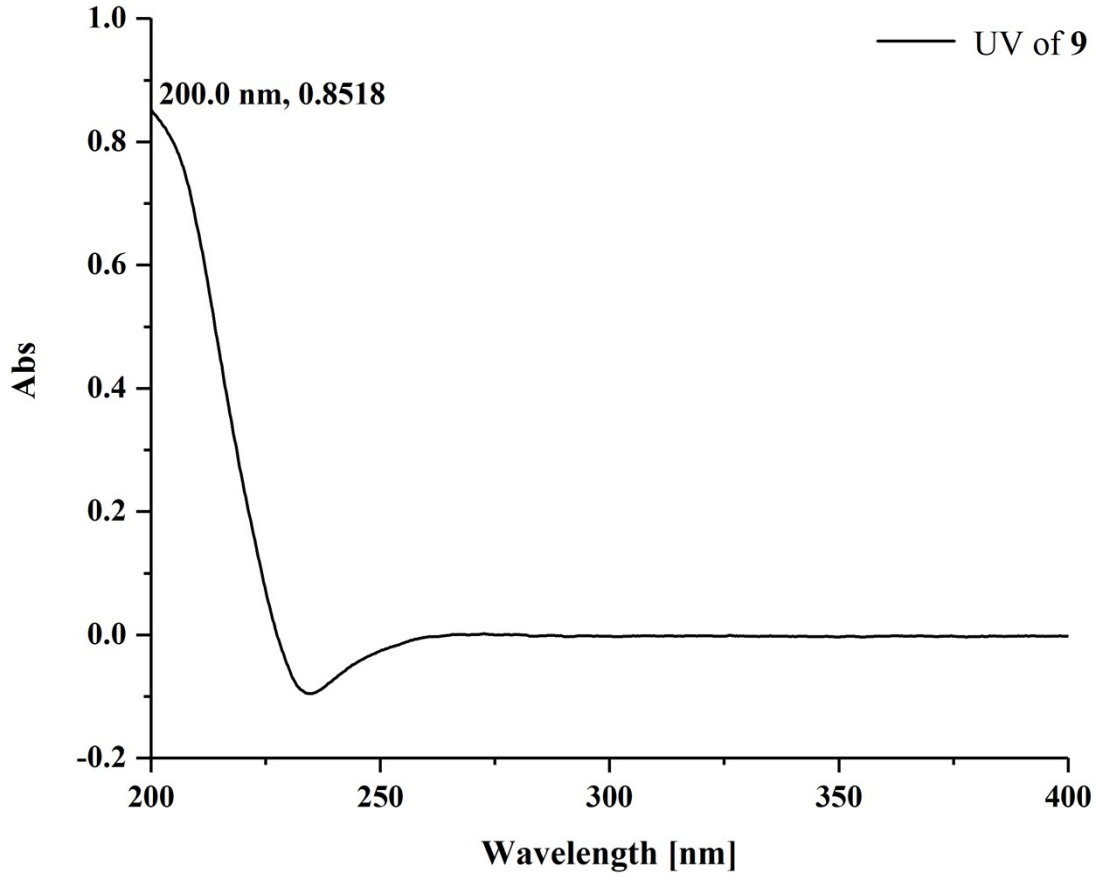
Figure S100. (+) HRESIMS Spectrum of Compound **9**

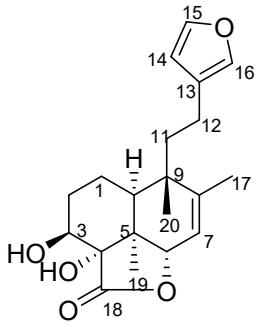




9

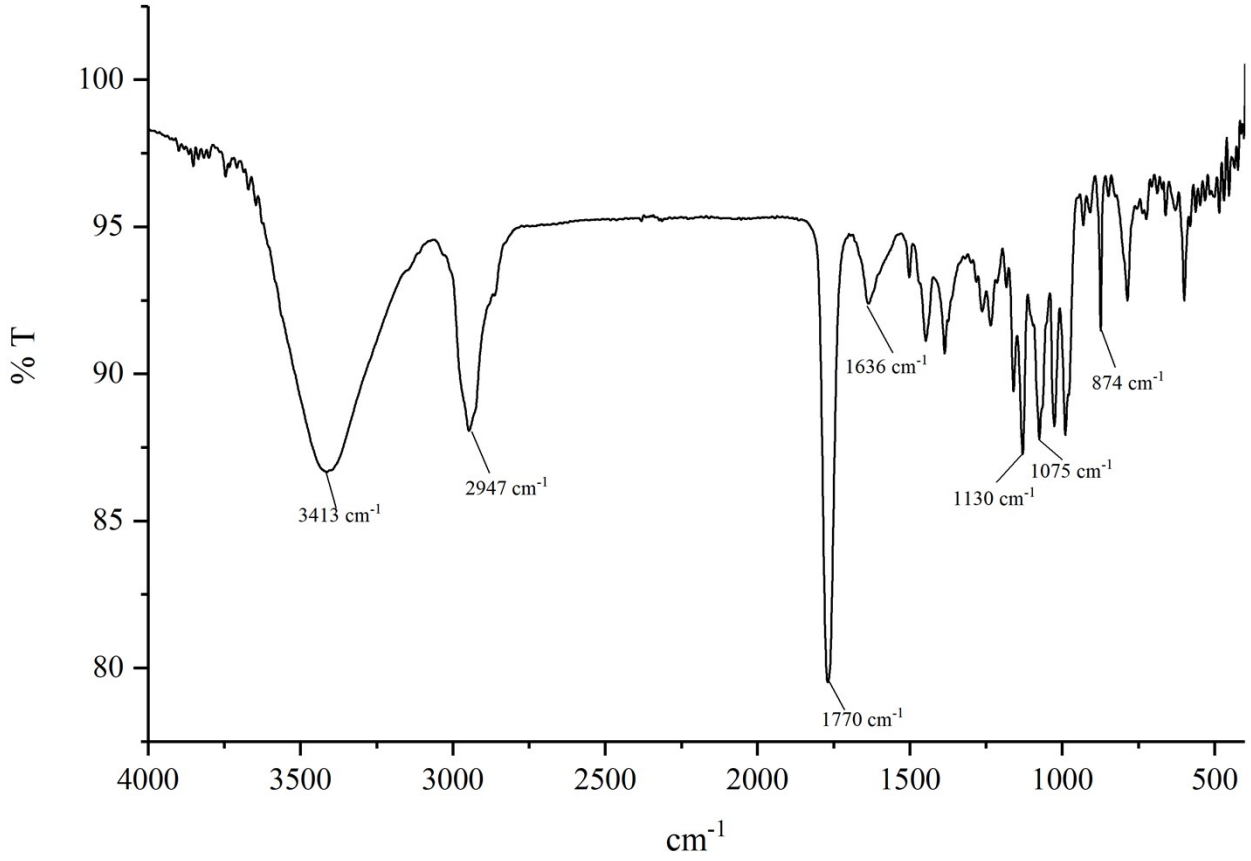
Figure S101. UV Spectrum of Compound **9**

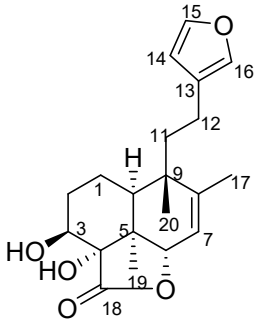




9

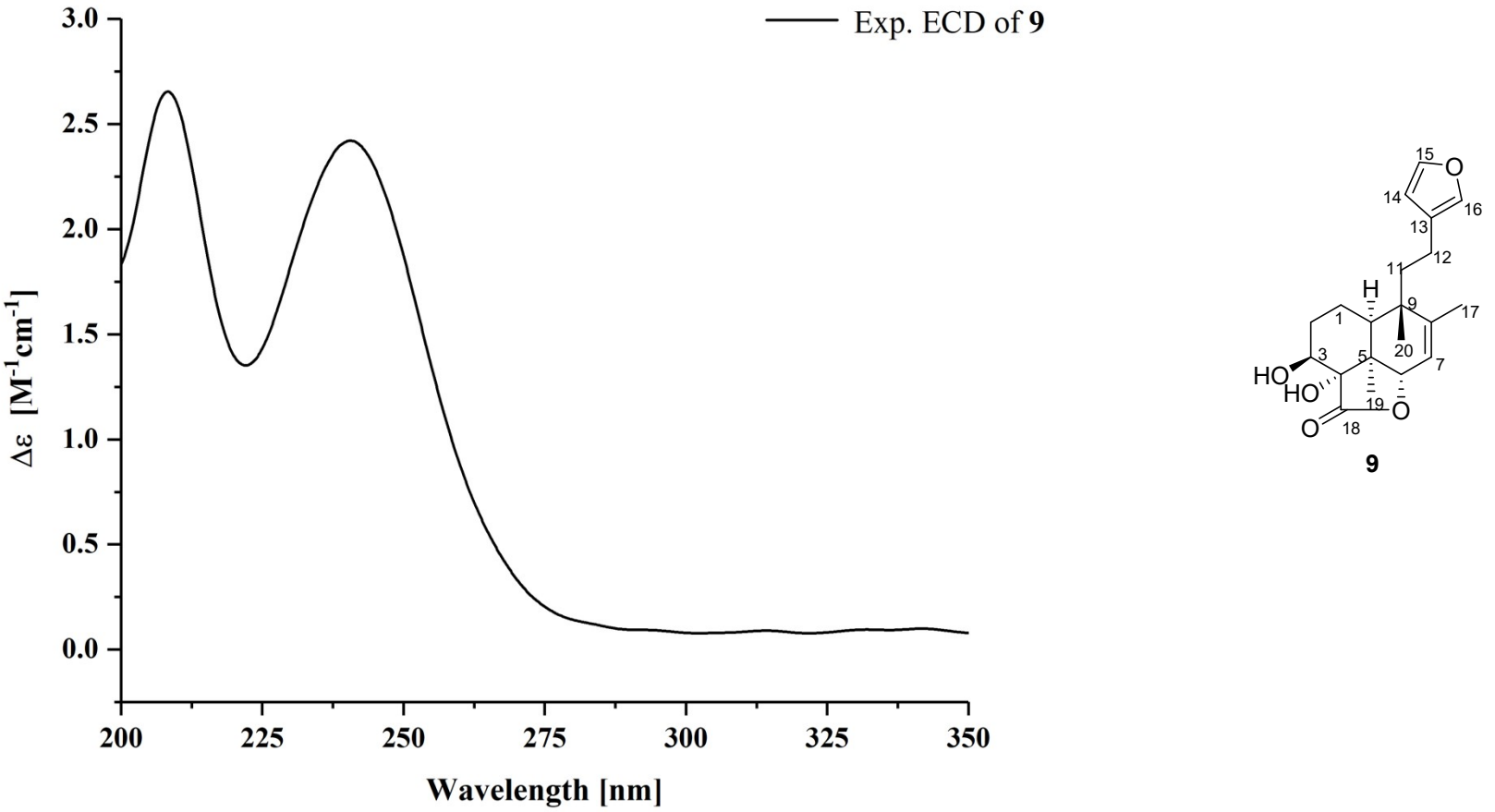
Figure S102. IR (KBr disc) Spectrum of Compound **9**





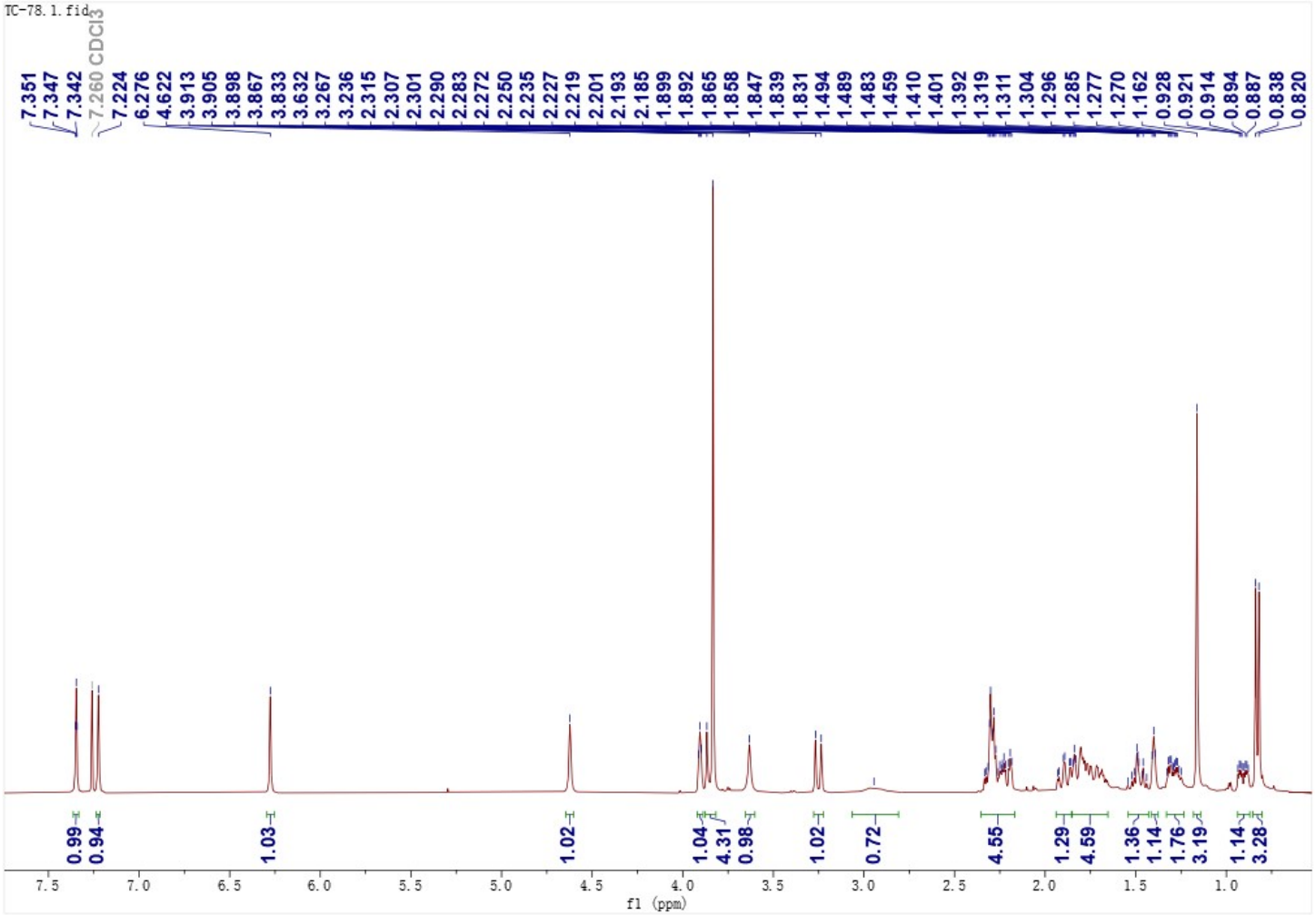
9

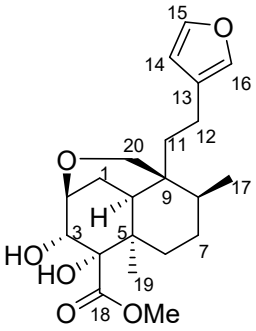
Figure S103. Experimental ECD spectra of Compound **9** in MeOH



9

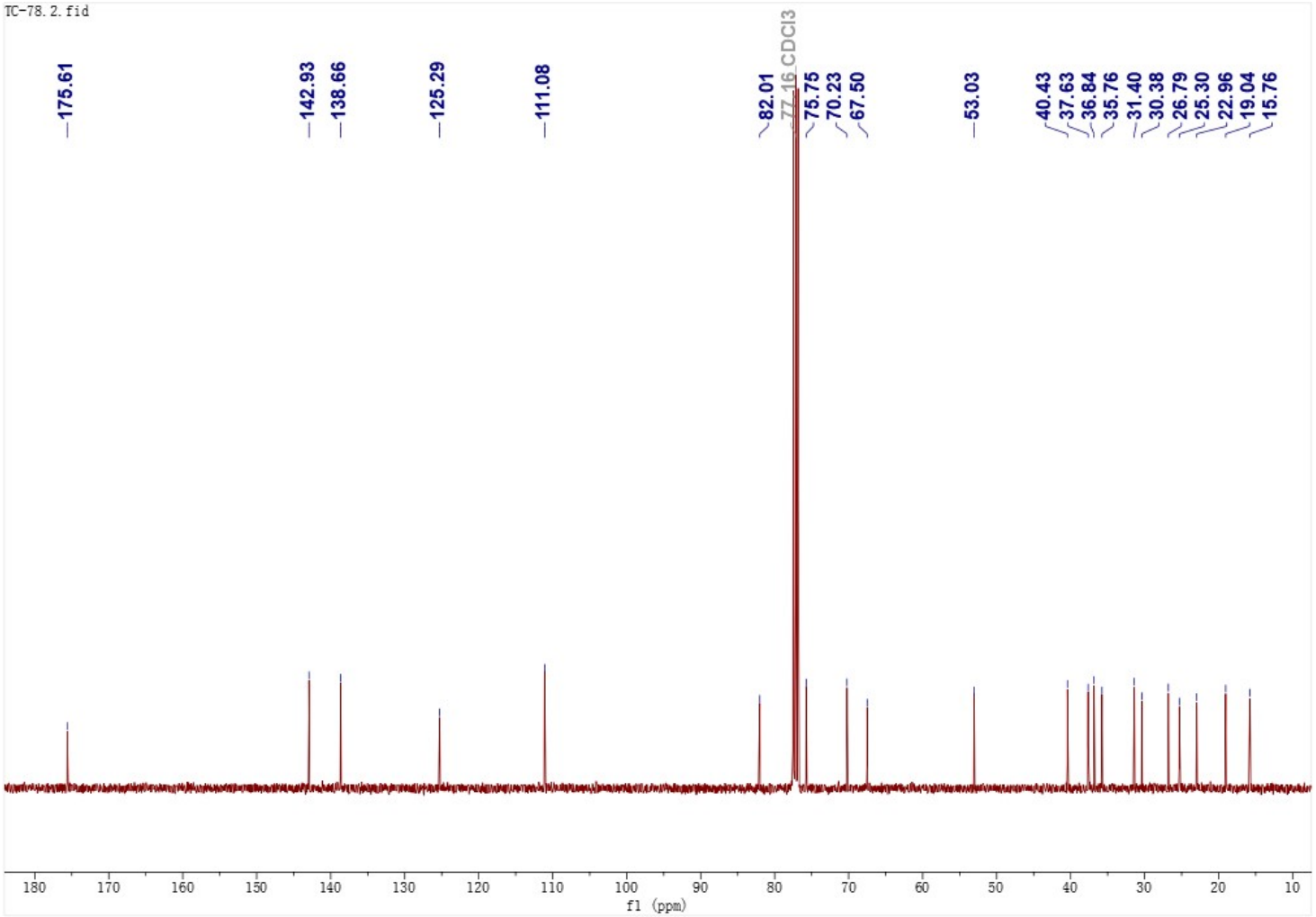
Figure S104. ^{1}H NMR Spectrum of Compound **10** in $CDCl_3$

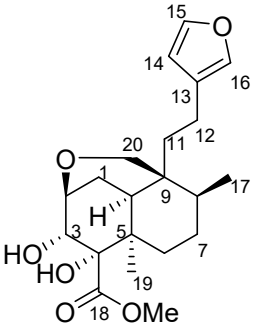




10

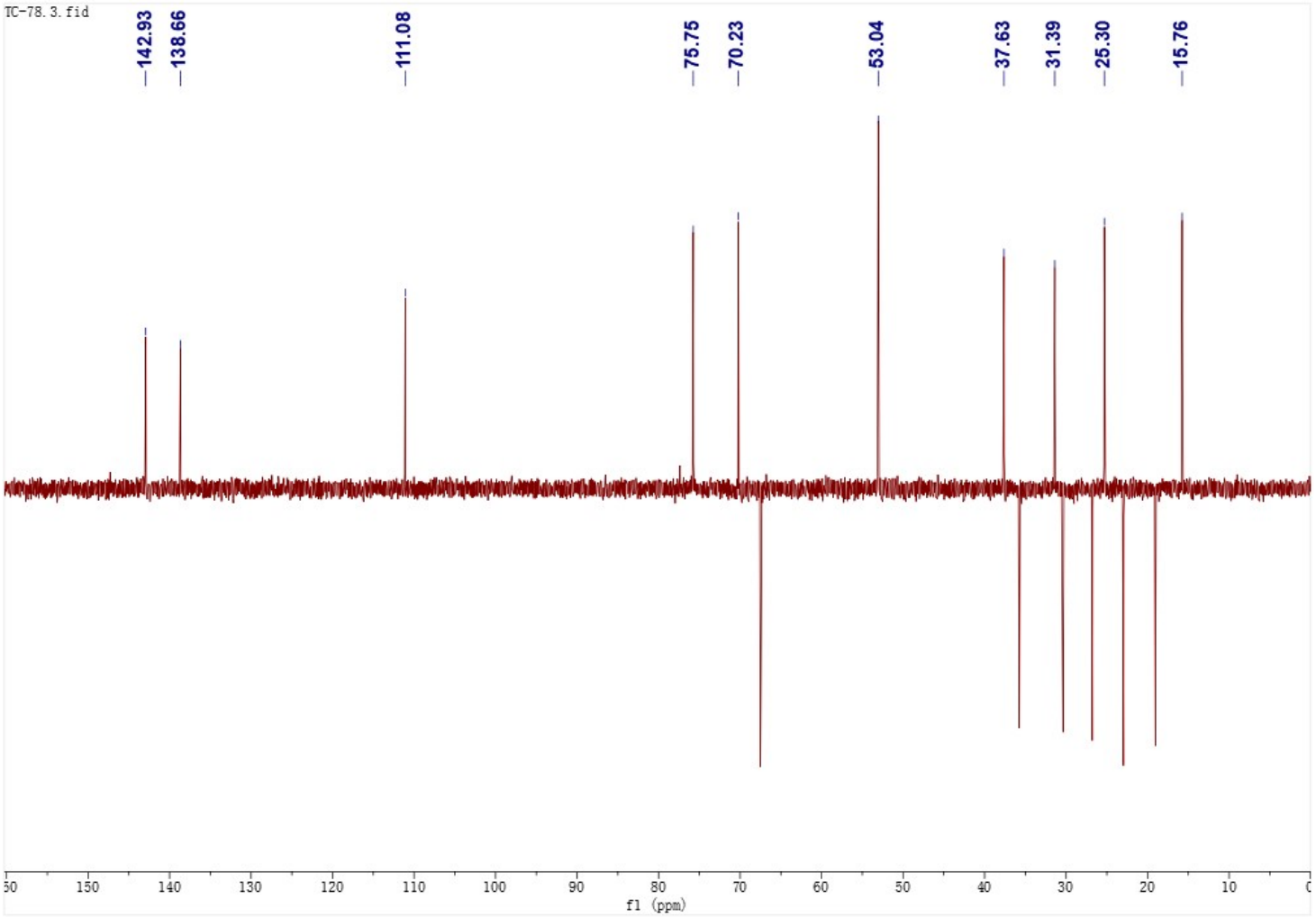
Figure S105. ^{13}C NMR Spectrum of Compound **10** in $CDCl_3$

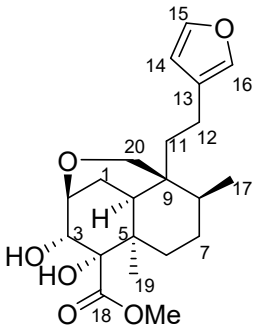




10

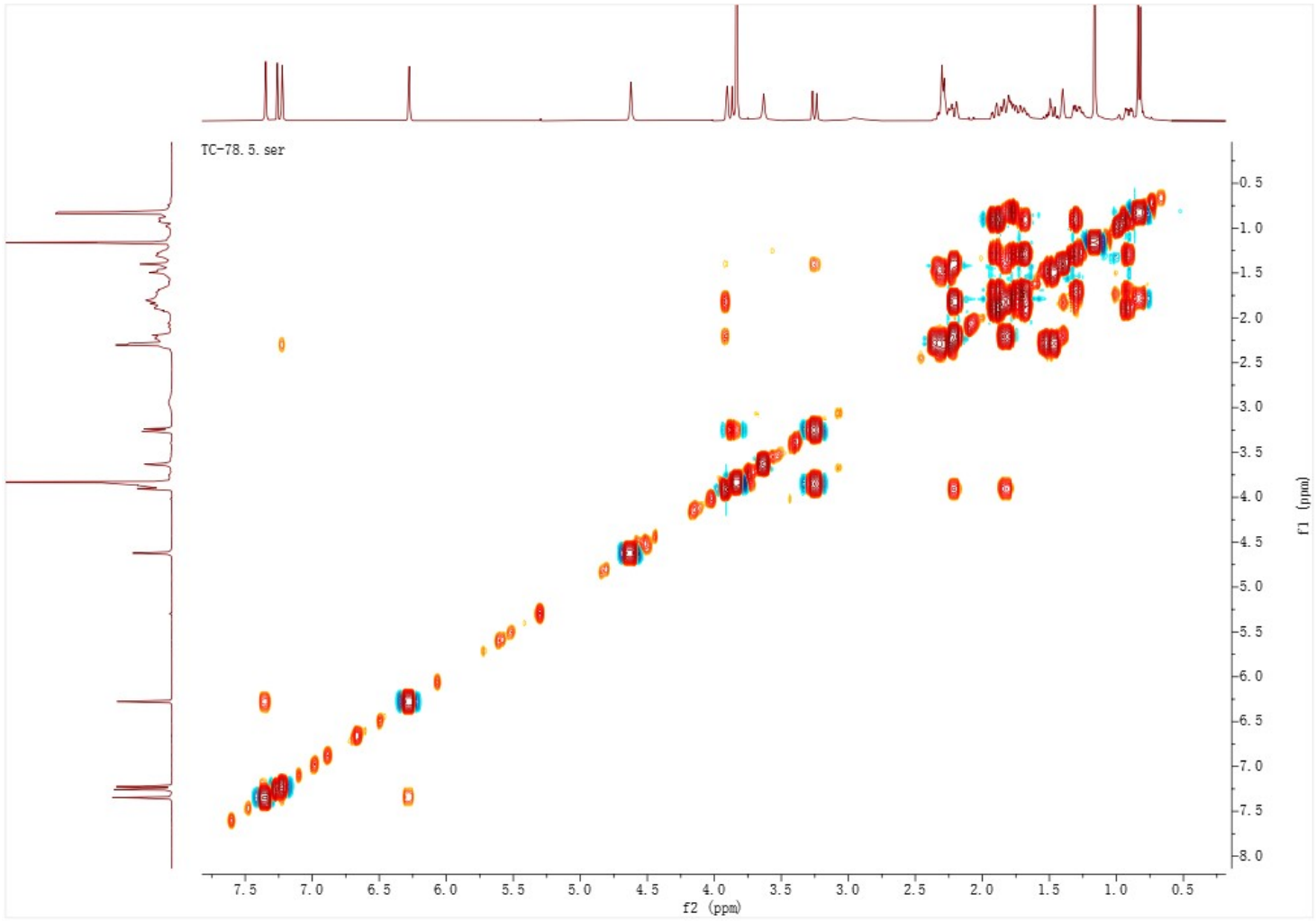
Figure S106. DEPT 135 Spectrum of Compound **10** in $CDCl_3$

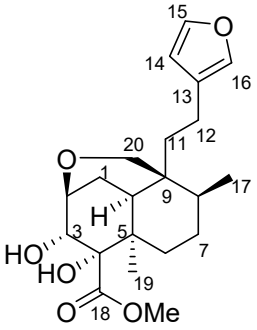




10

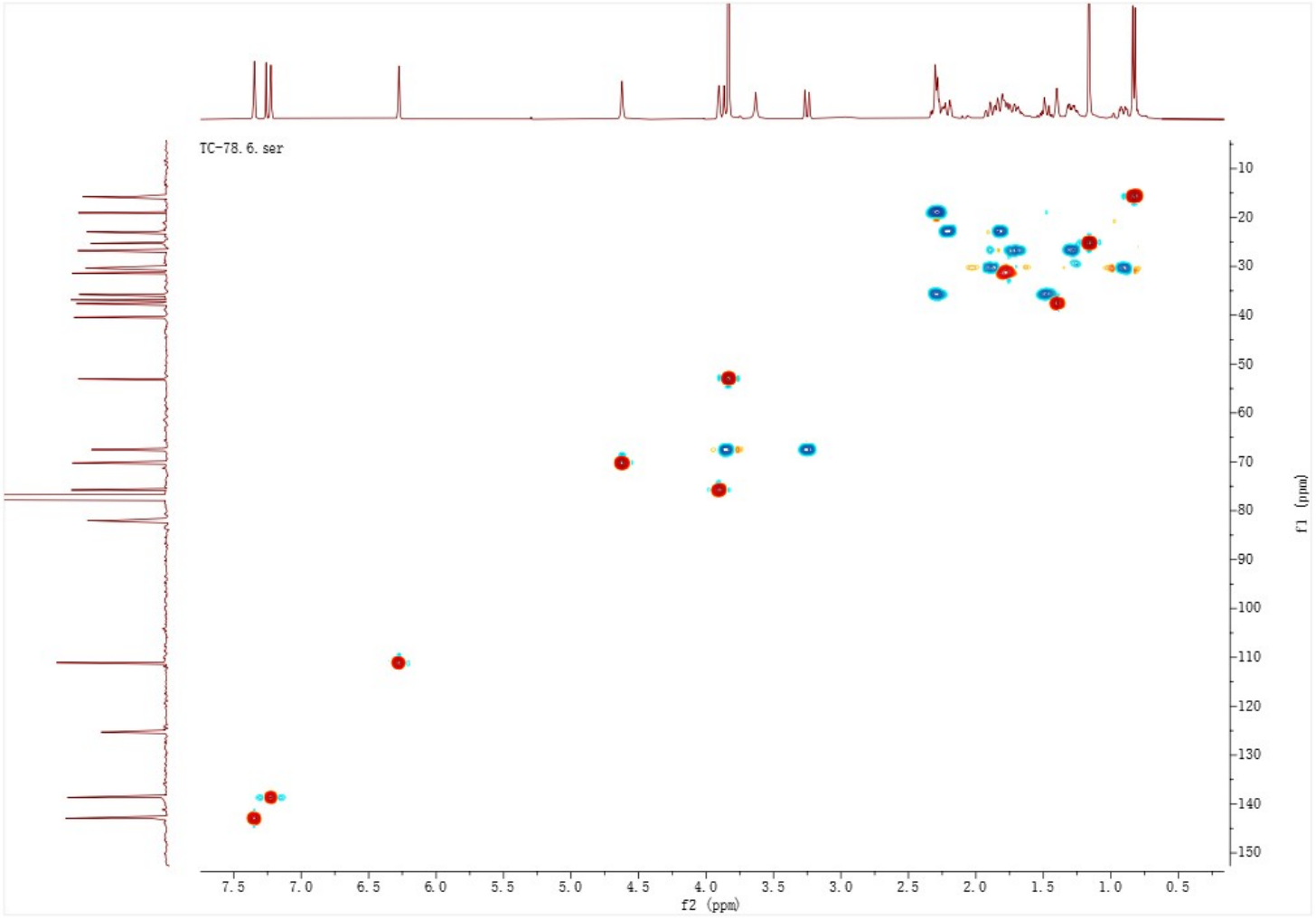
Figure S107. ^{1}H-^{1}H COSY Spectrum of Compound **10** in $CDCl_3$

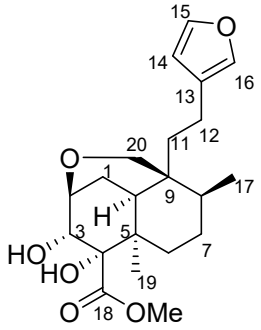




10

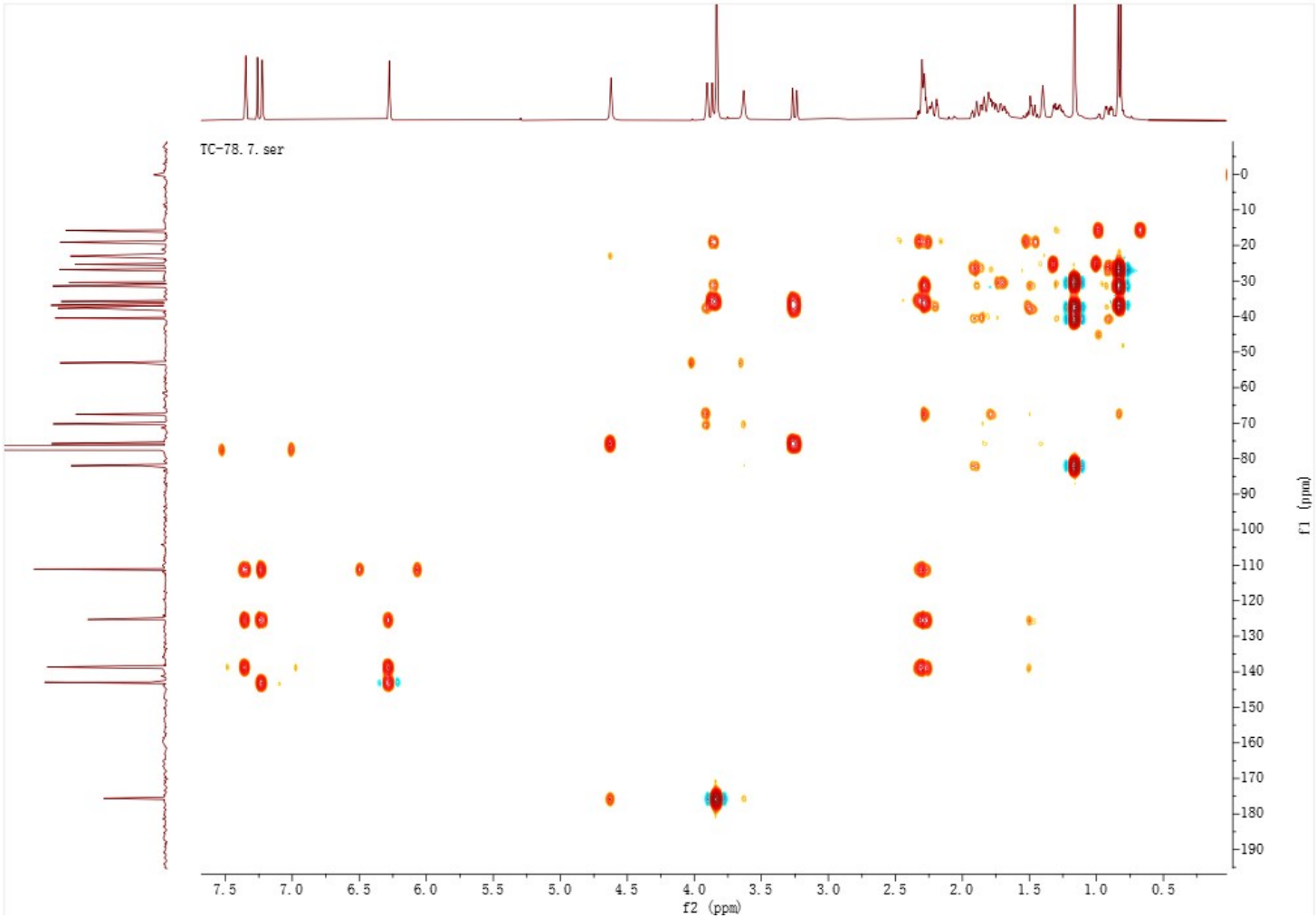
Figure S108. HSQC Spectrum of Compound 1**0** in $CDCl_3$

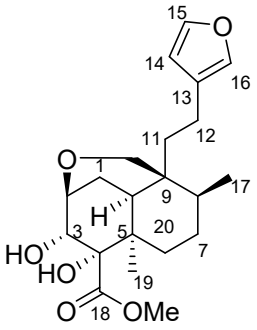




10

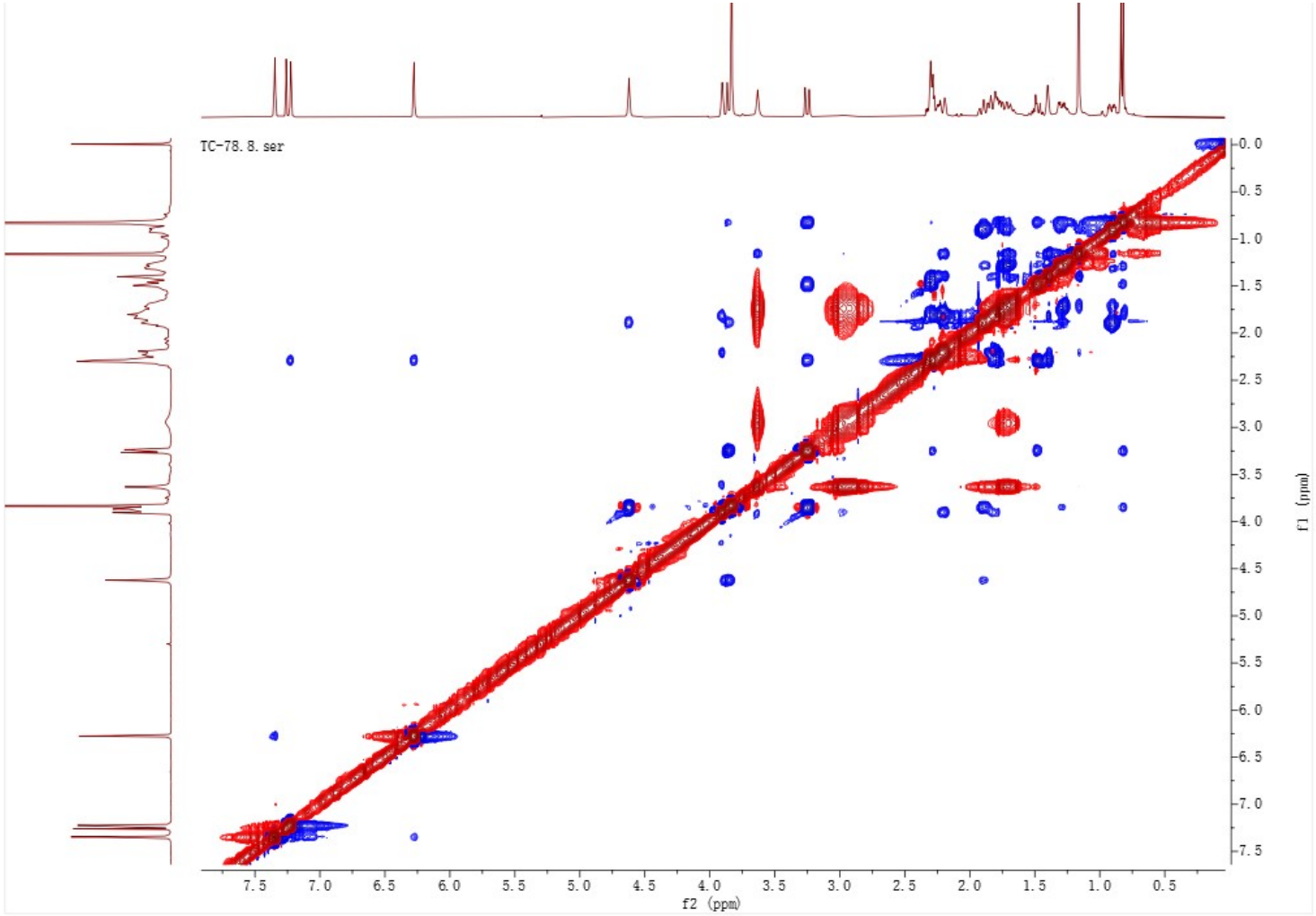
Figure S109. HMBC Spectrum of Compound **10** in $CDCl_3$

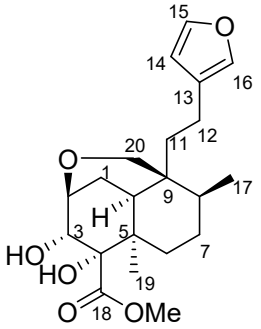




10

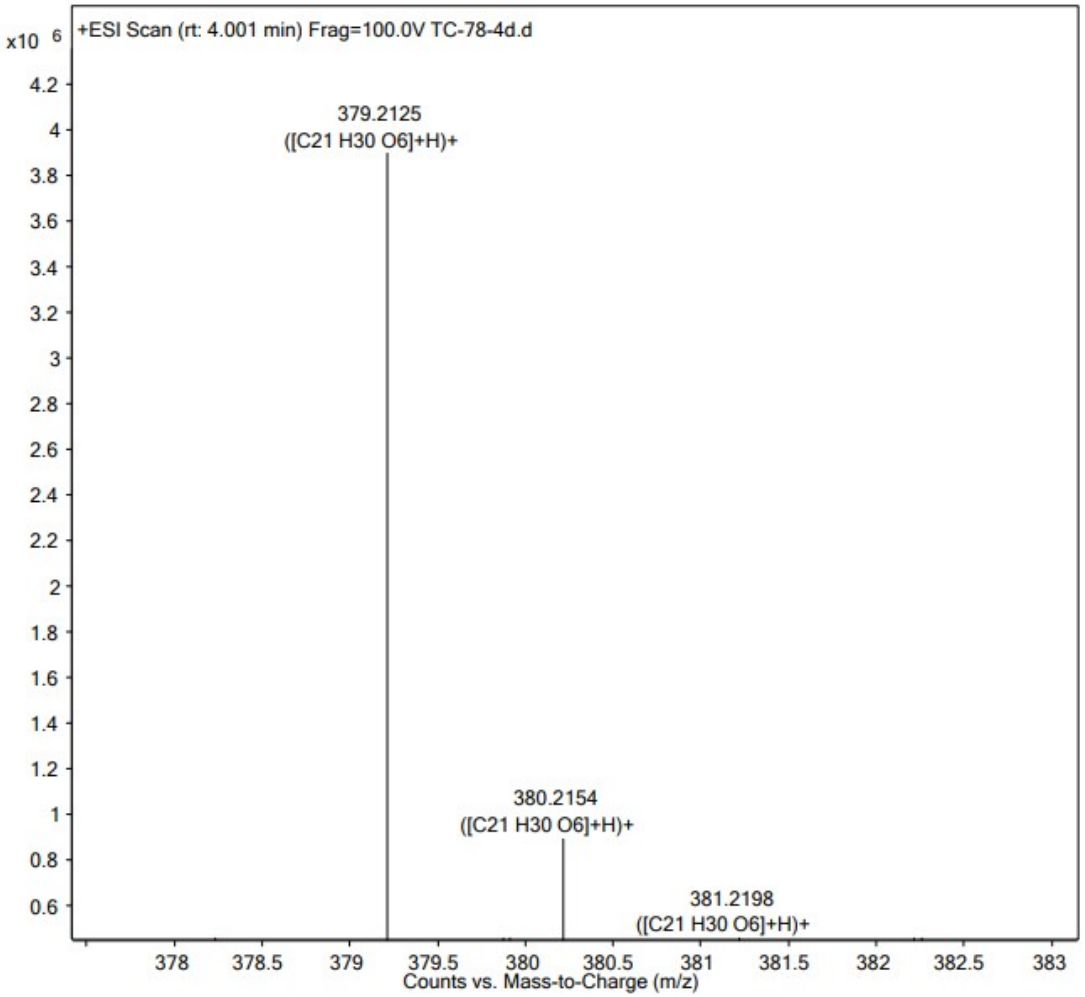
Figure S110. NOESY Spectrum of Compound **10** in $CDCl_3$

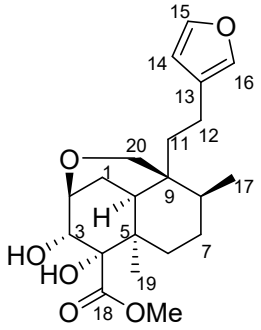




10

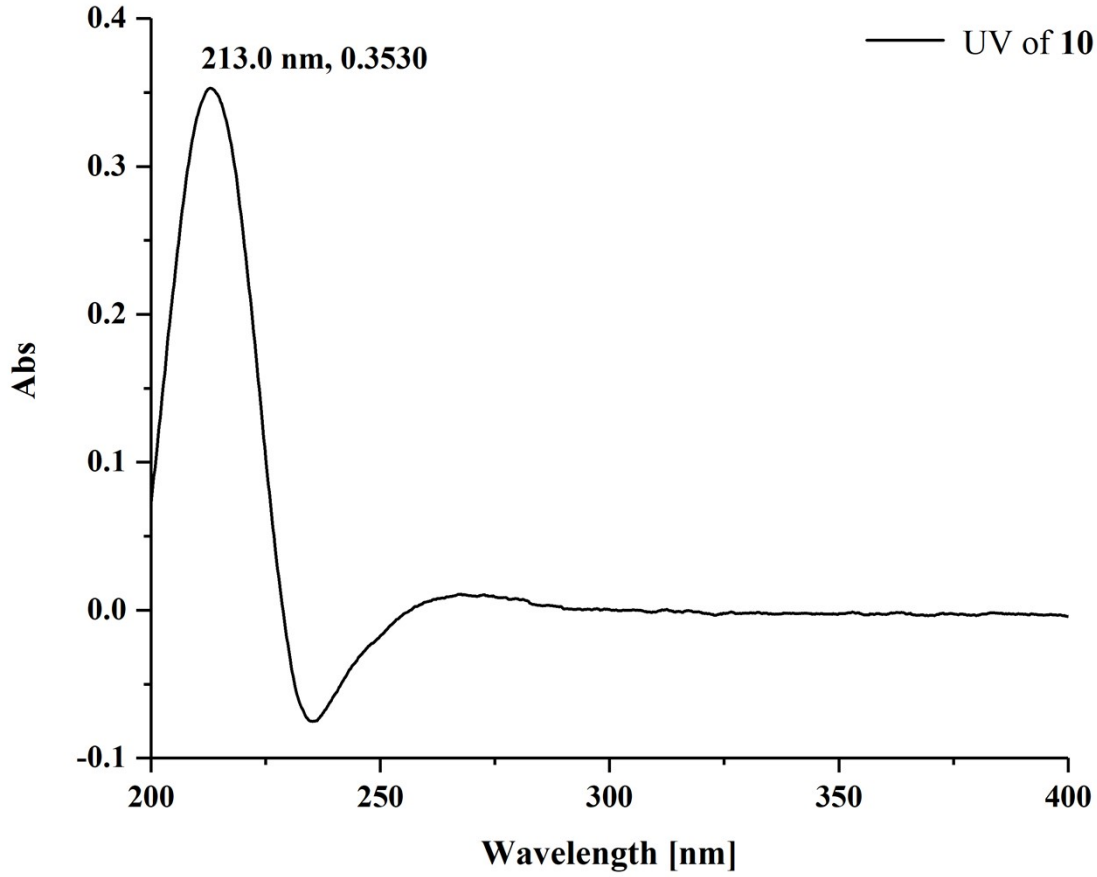
Figure S111. (+) HRESIMS Spectrum of Compound **10**

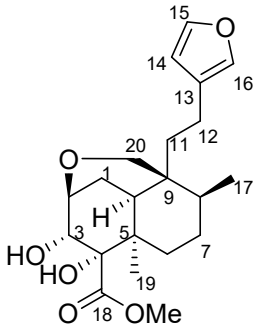




10

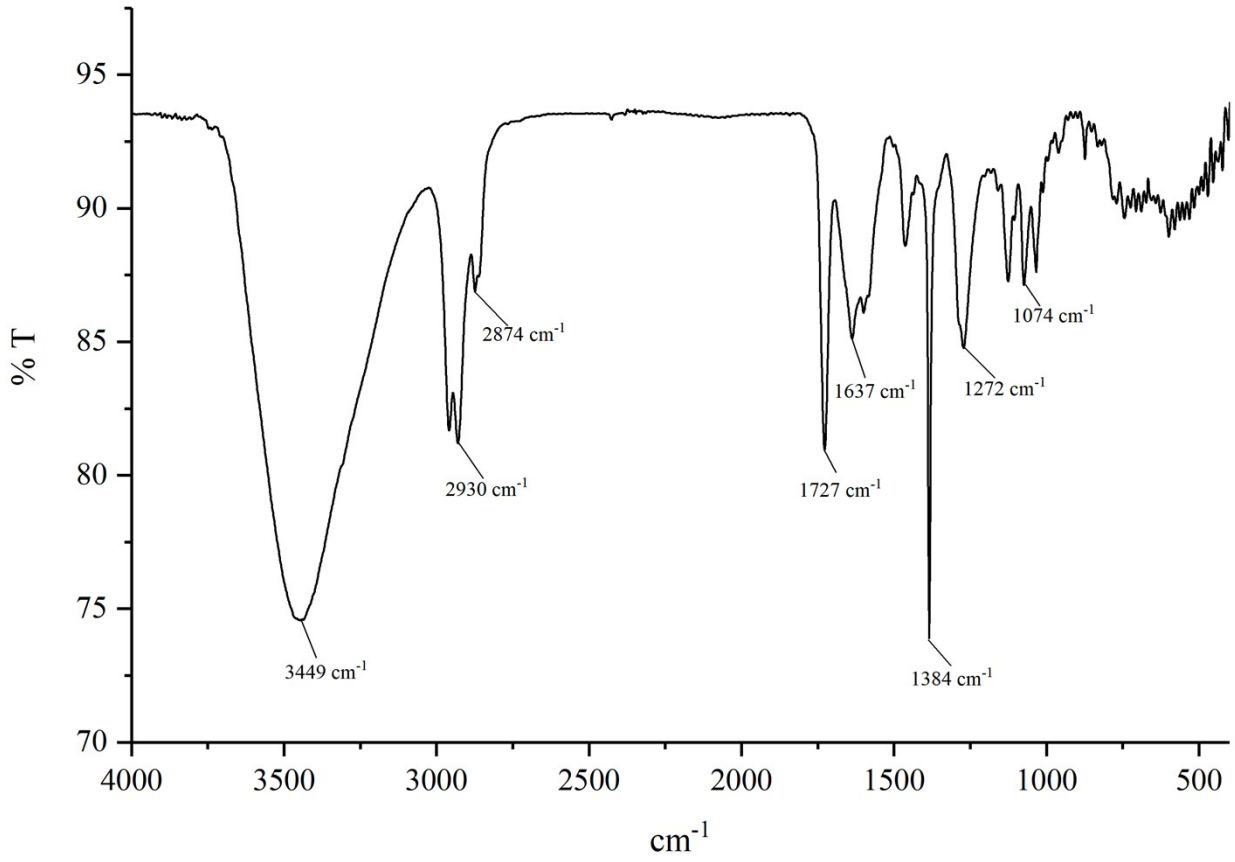
Figure S112. UV Spectrum of Compound **10**

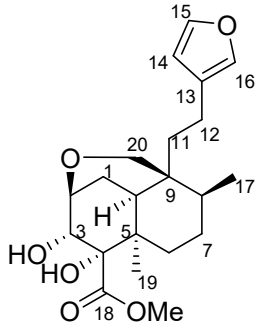




10

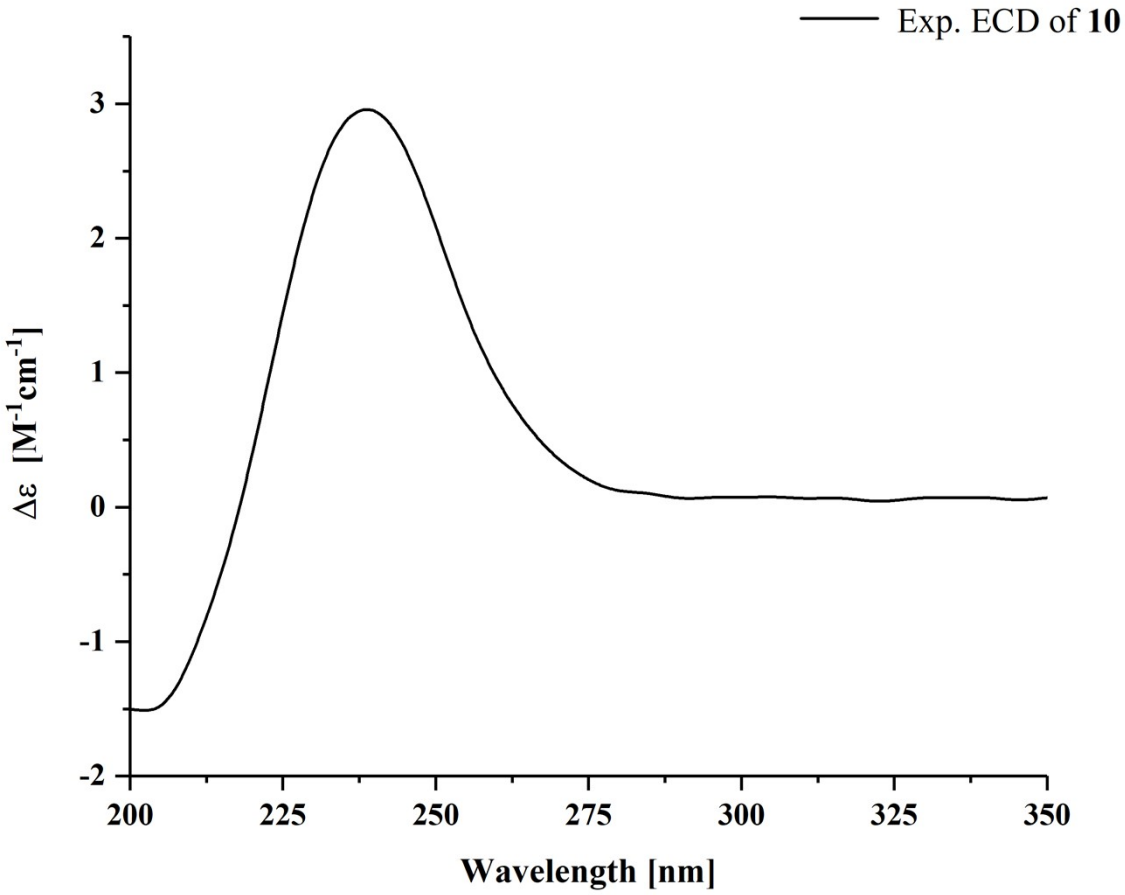
Figure S113. IR (KBr disc) Spectrum of Compound **10**

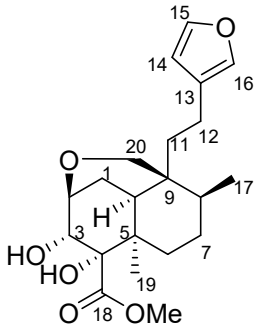




10

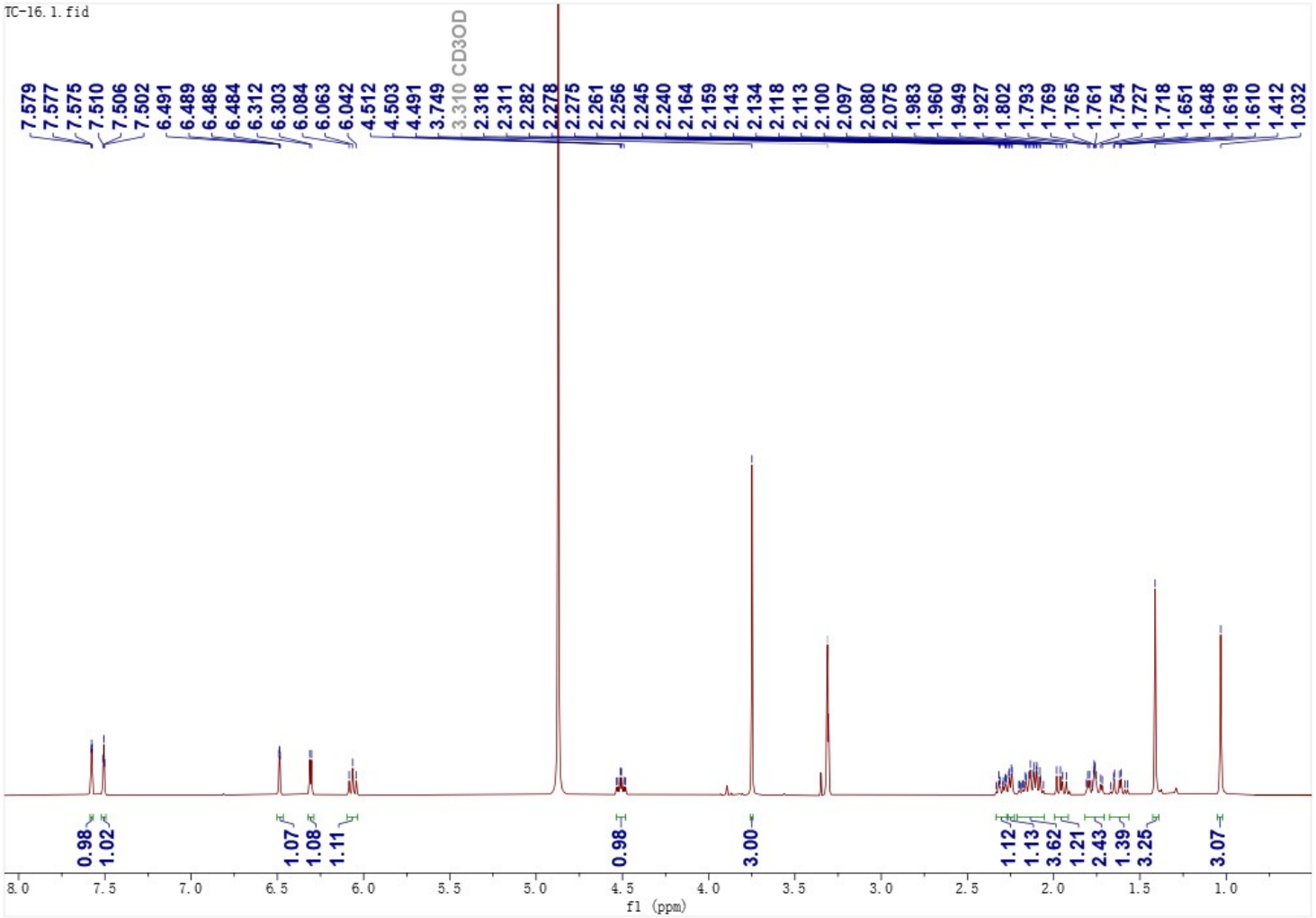
Figure S114. Experimental ECD spectra of Compound **10** in MeOH

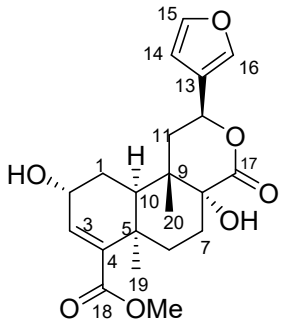




10

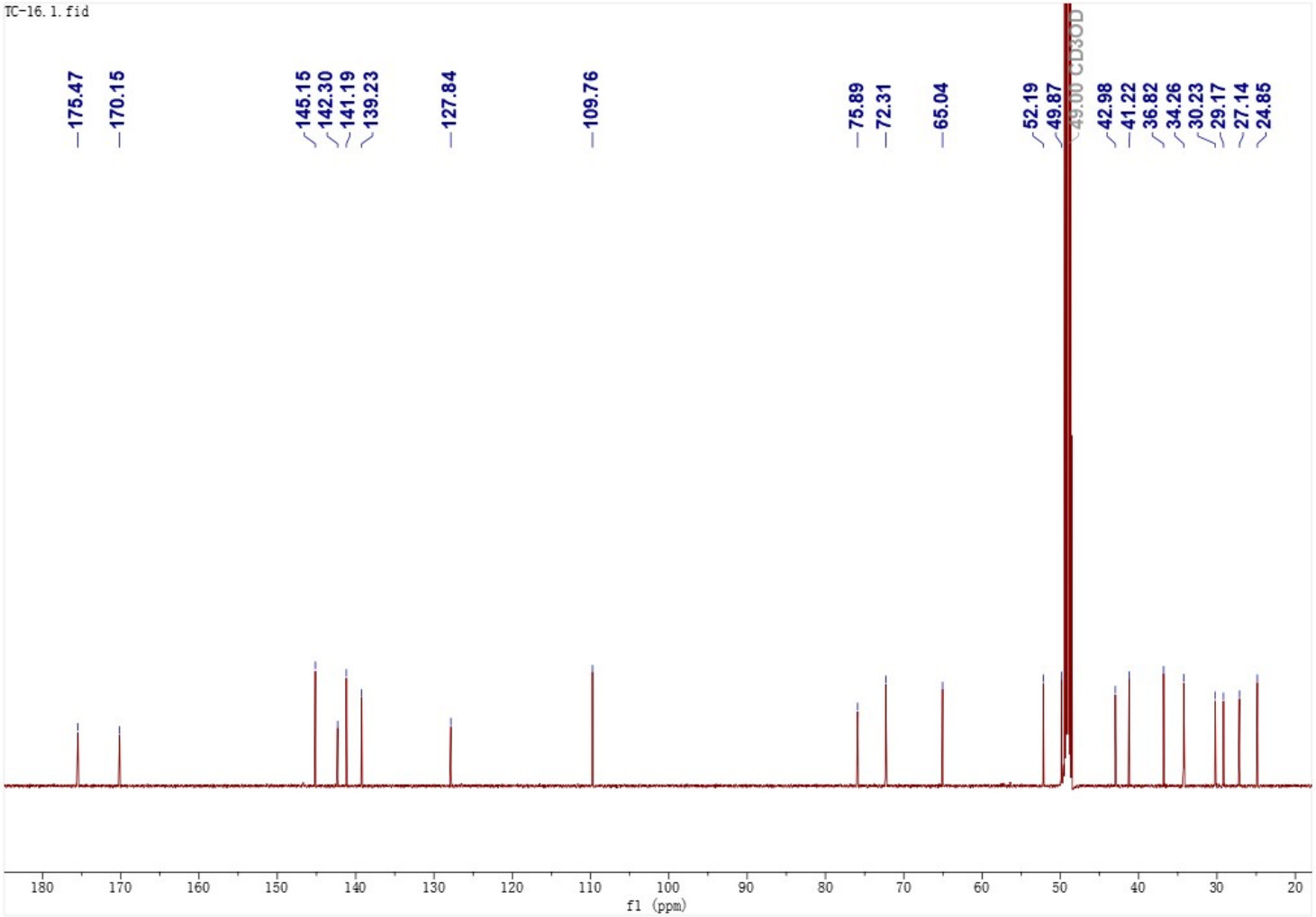
Figure S115. ^{1}H NMR Spectrum of Compound **11** in CD_3OD

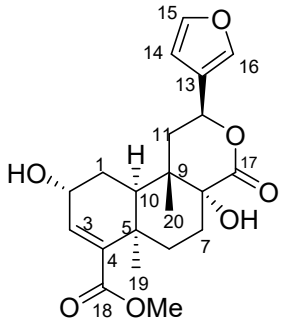




11

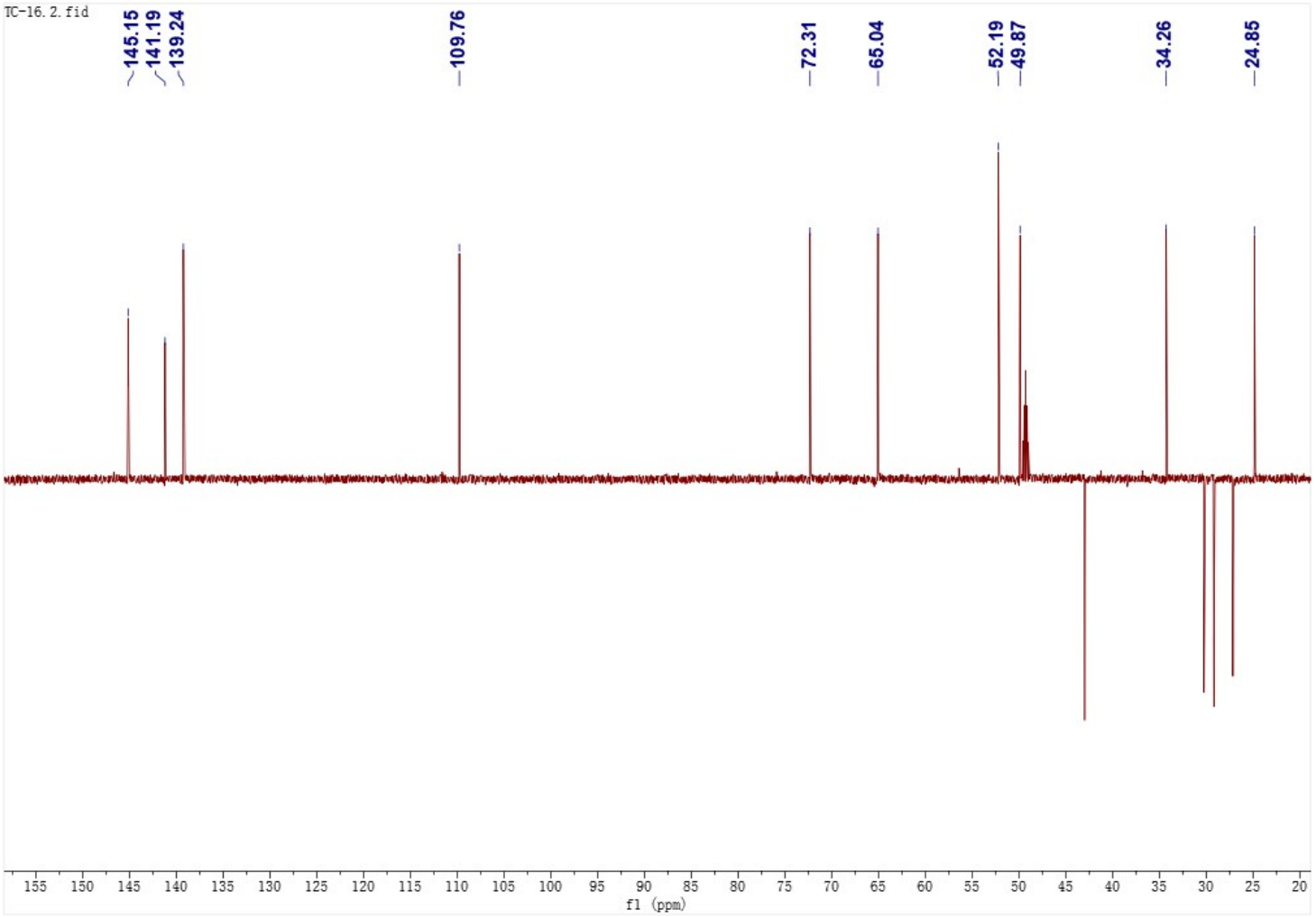
Figure S116. ^{13}C NMR Spectrum of Compound **11**in CD_3OD

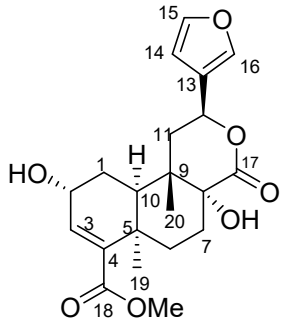




11

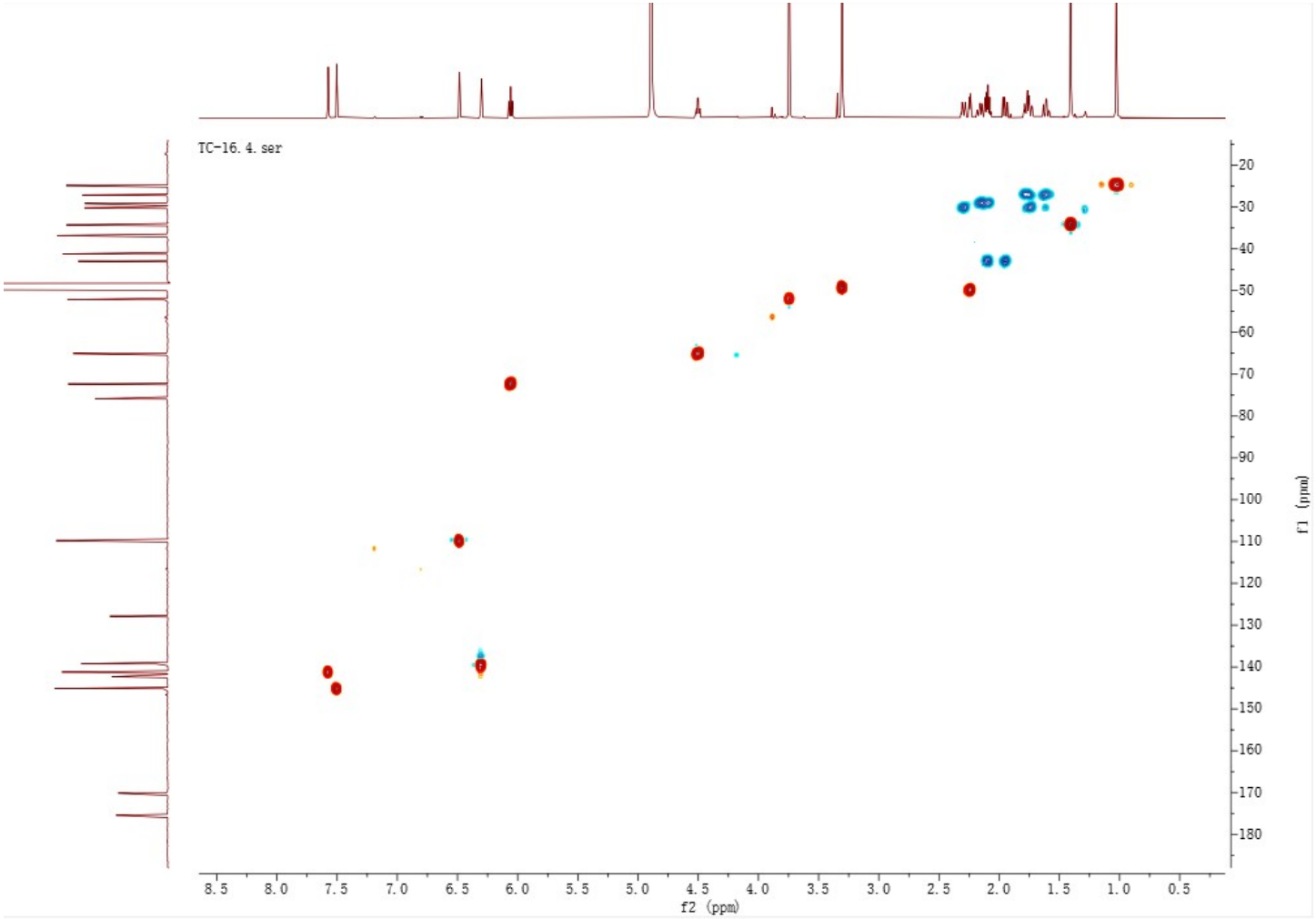
Figure S117. DEPT 135 Spectrum of Compound **11** in CD_3OD

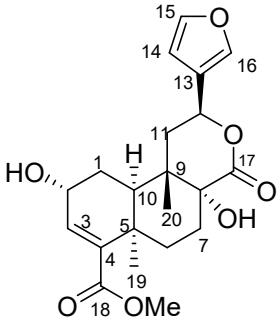




11

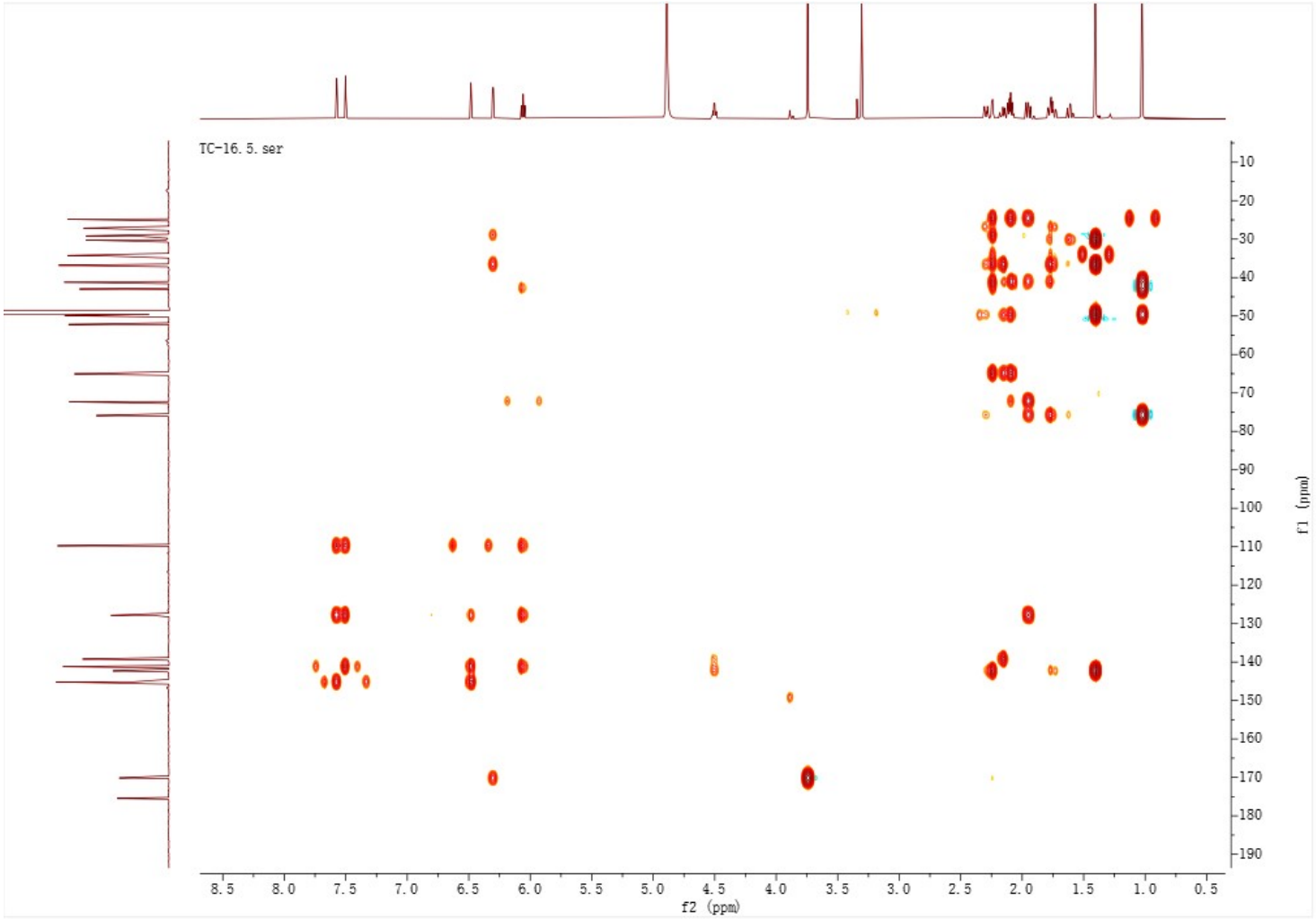
Figure S118. HSQC Spectrum of Compound **11**in CD_3OD

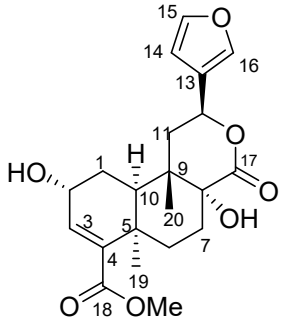




11

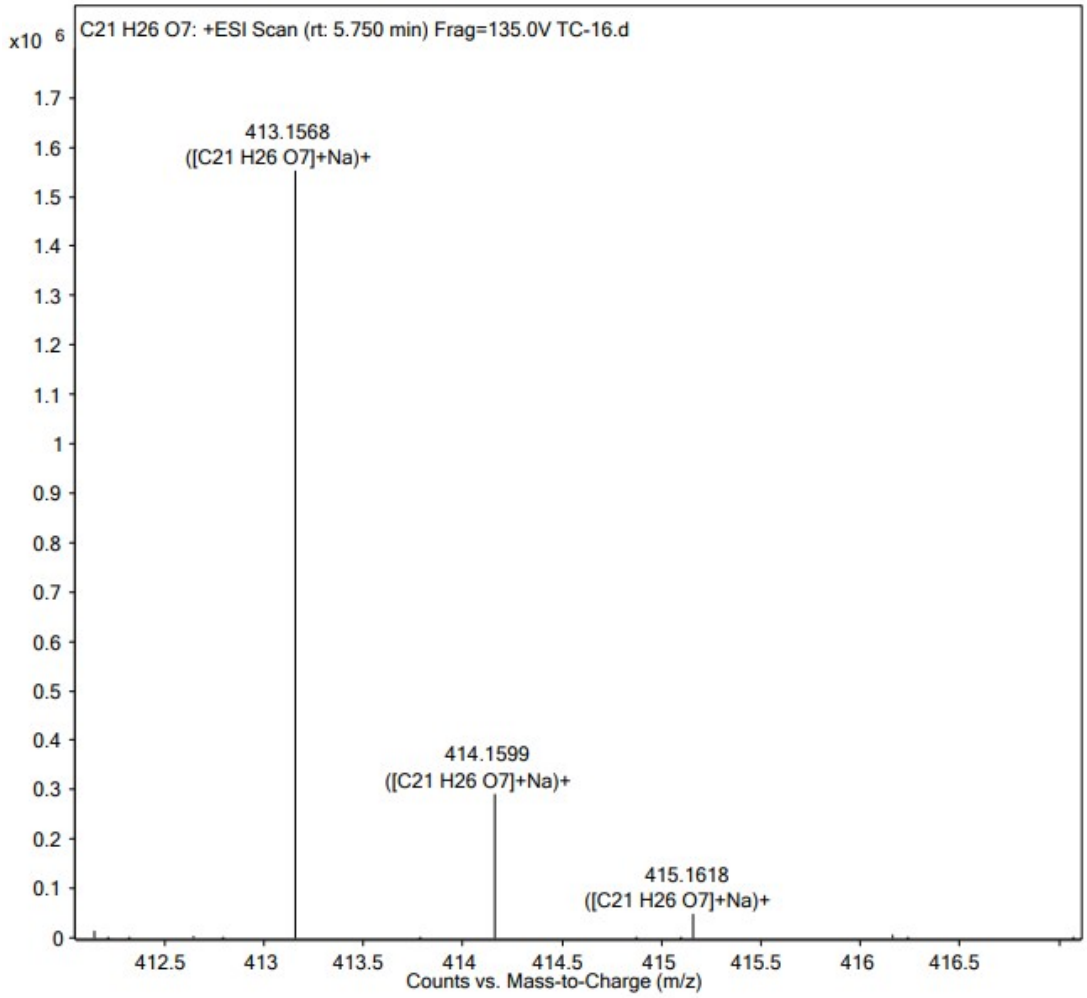
Figure S119. HMBC Spectrum of Compound **11** in CD_3OD

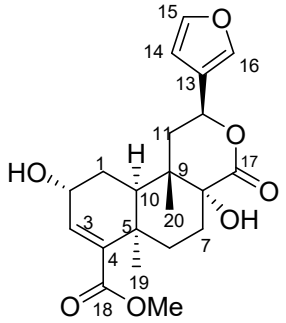




11

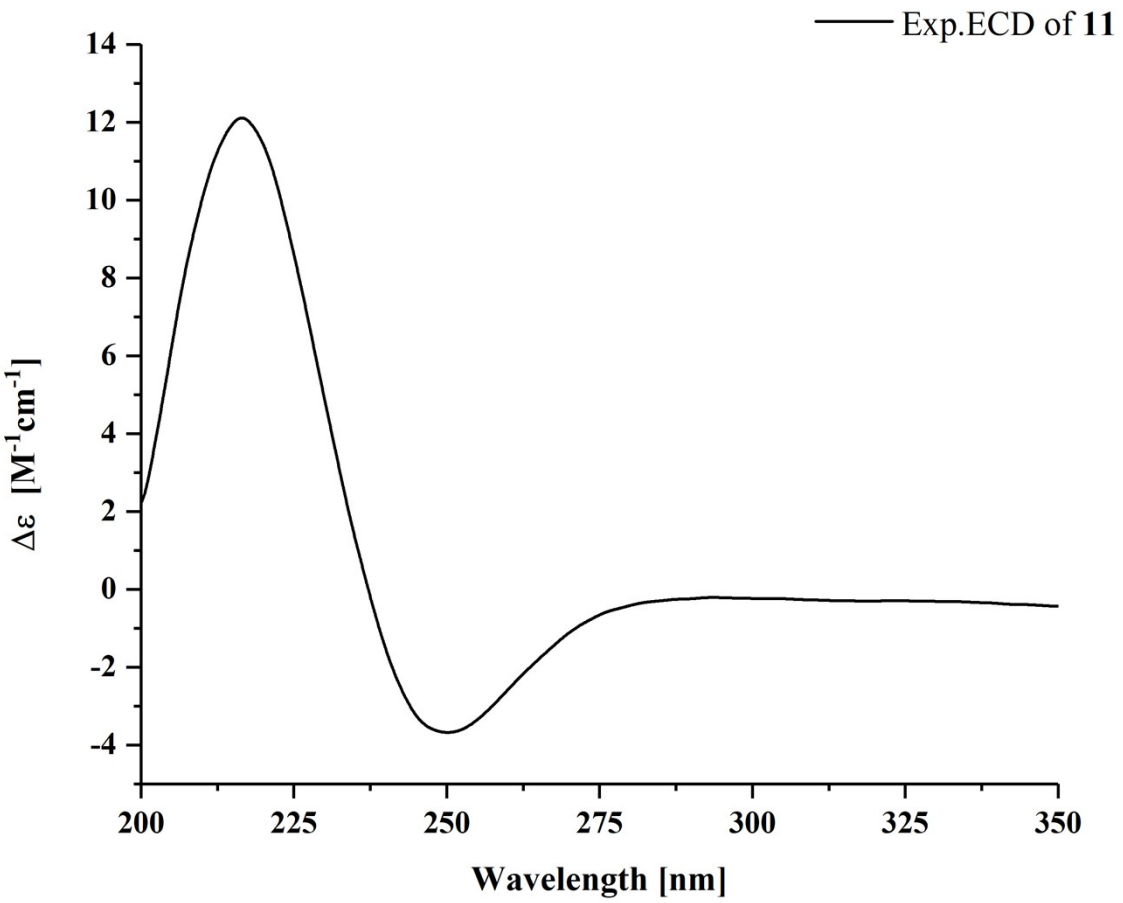
Figure S120. (+) HRESIMS Spectrum of Compound **11**

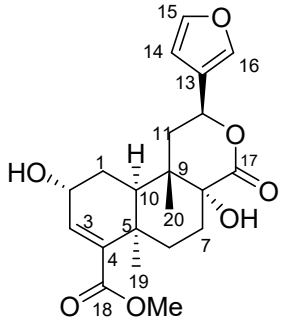




11

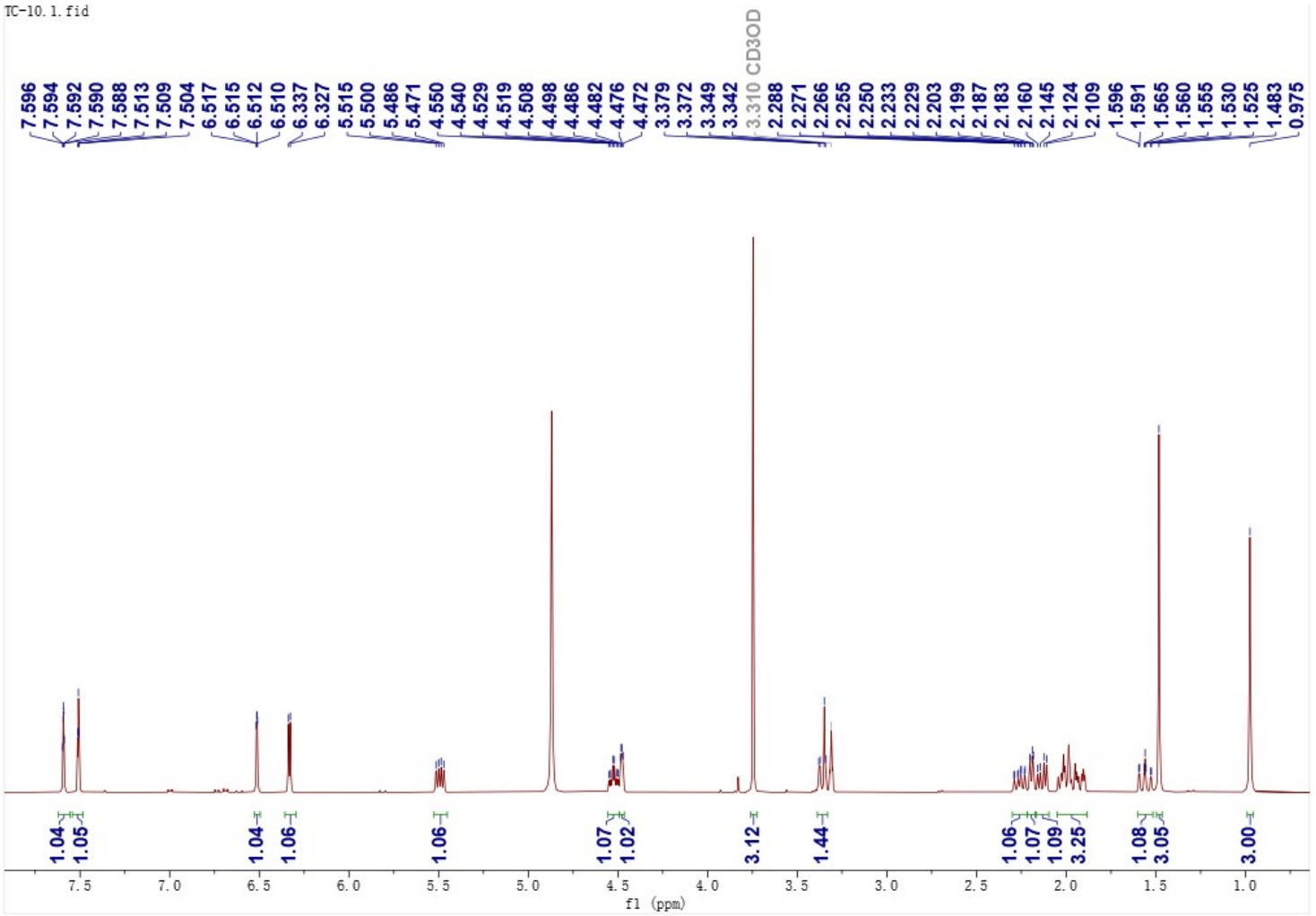
Figure S121 Experimental ECD spectra of Compound **11** in MeOH

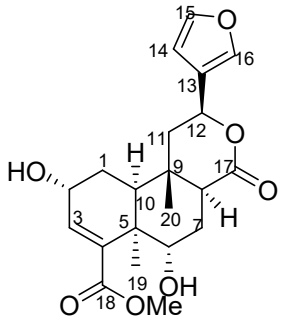




11

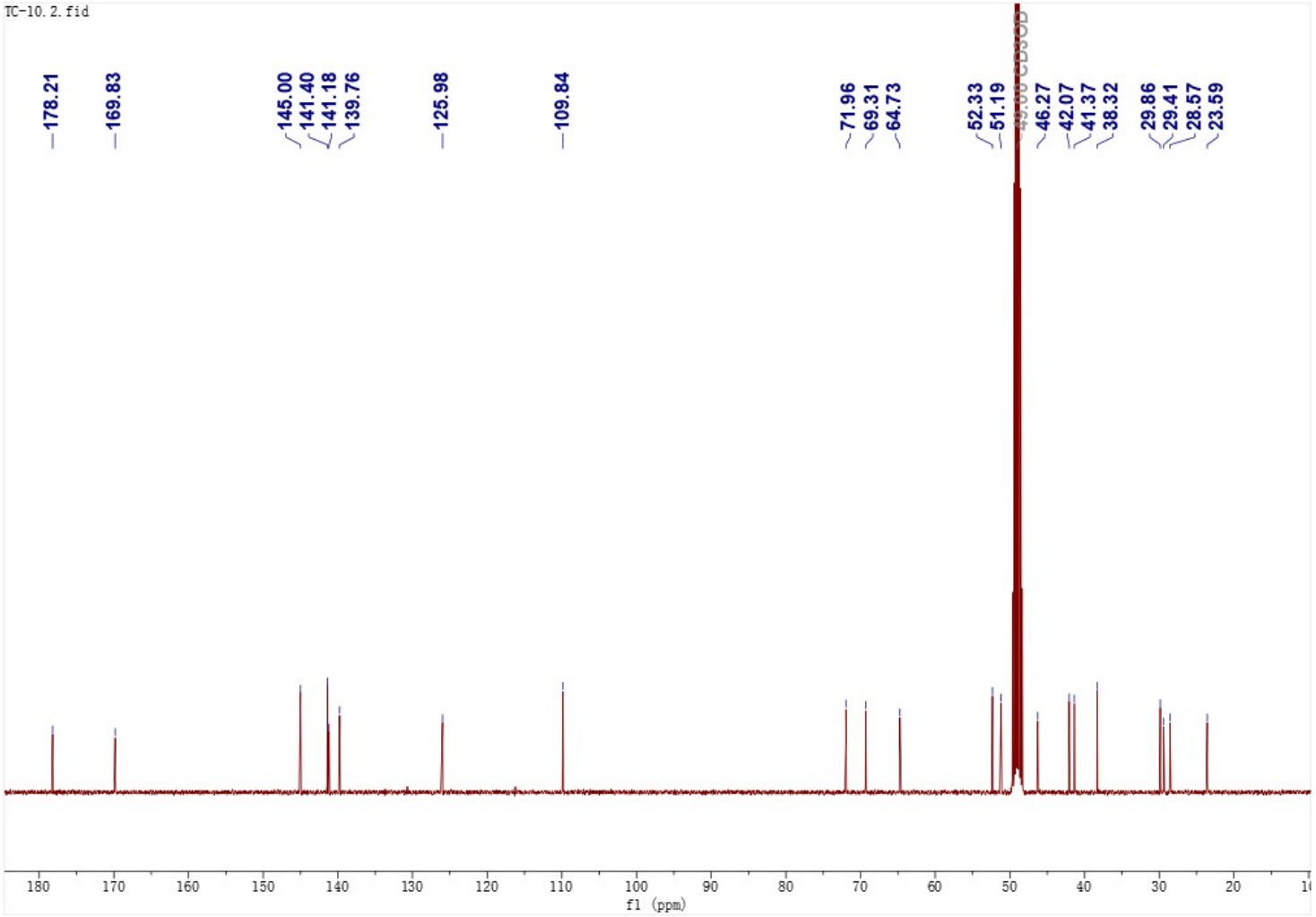
Figure S122. ^{1}H NMR Spectrum of Compound **12** in CD_3OD

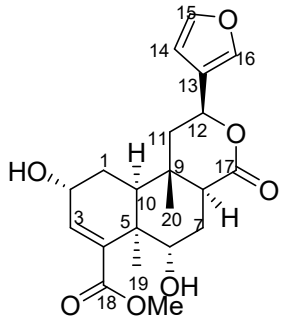




12

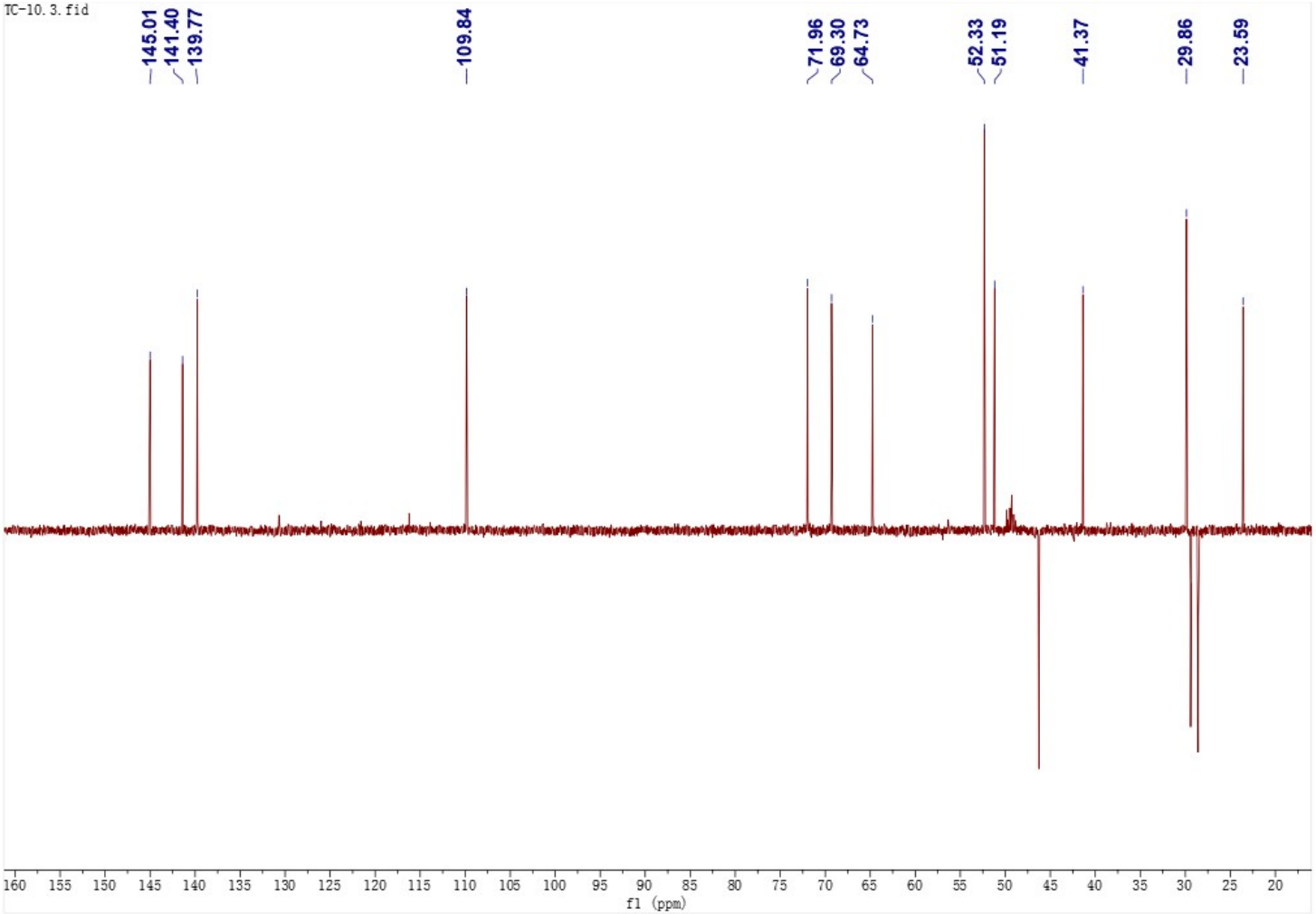
Figure S123. ^{13}C NMR Spectrum of Compound **12**in CD_3OD

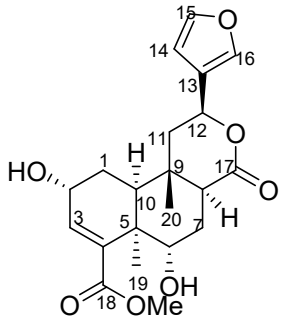




12

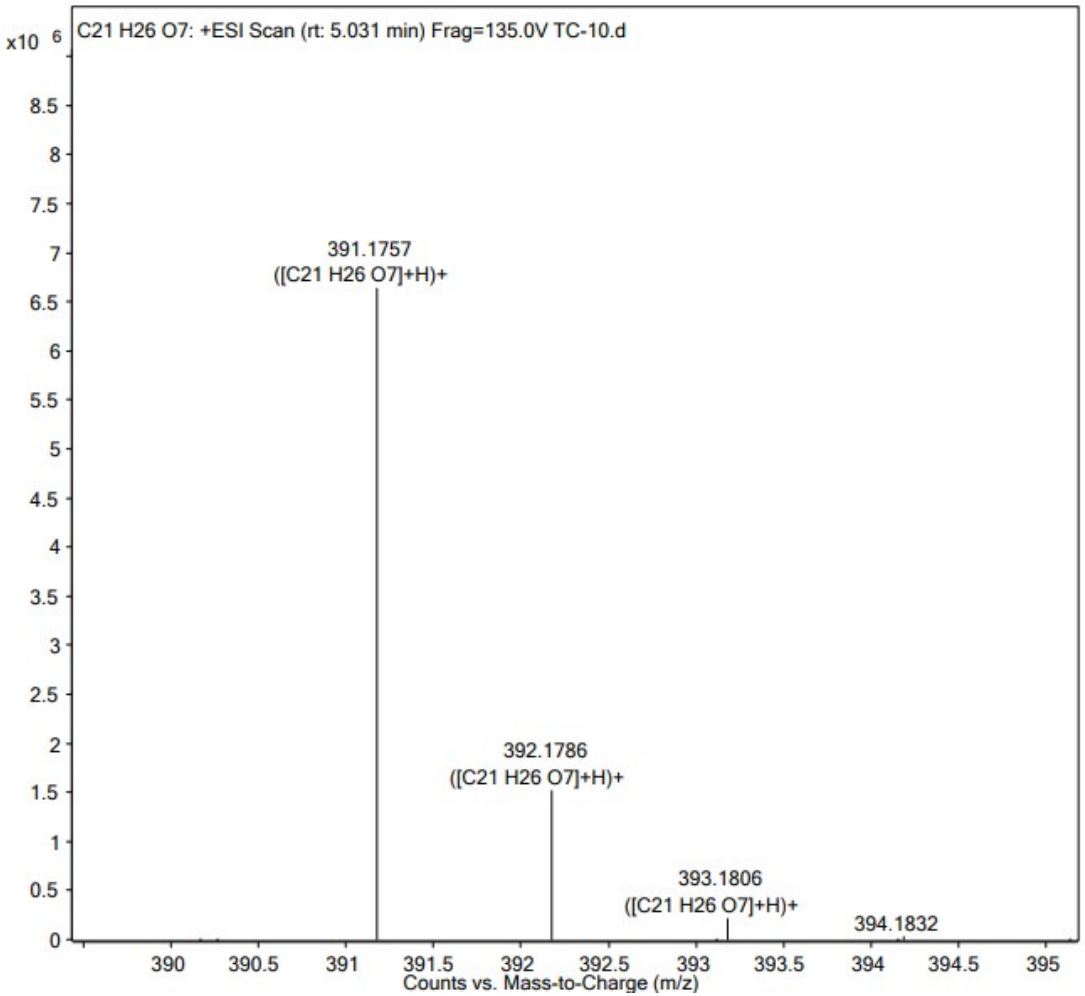
Figure S124. DEPT 135 Spectrum of Compound **12** in CD_3OD

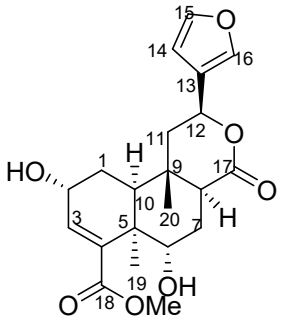




12

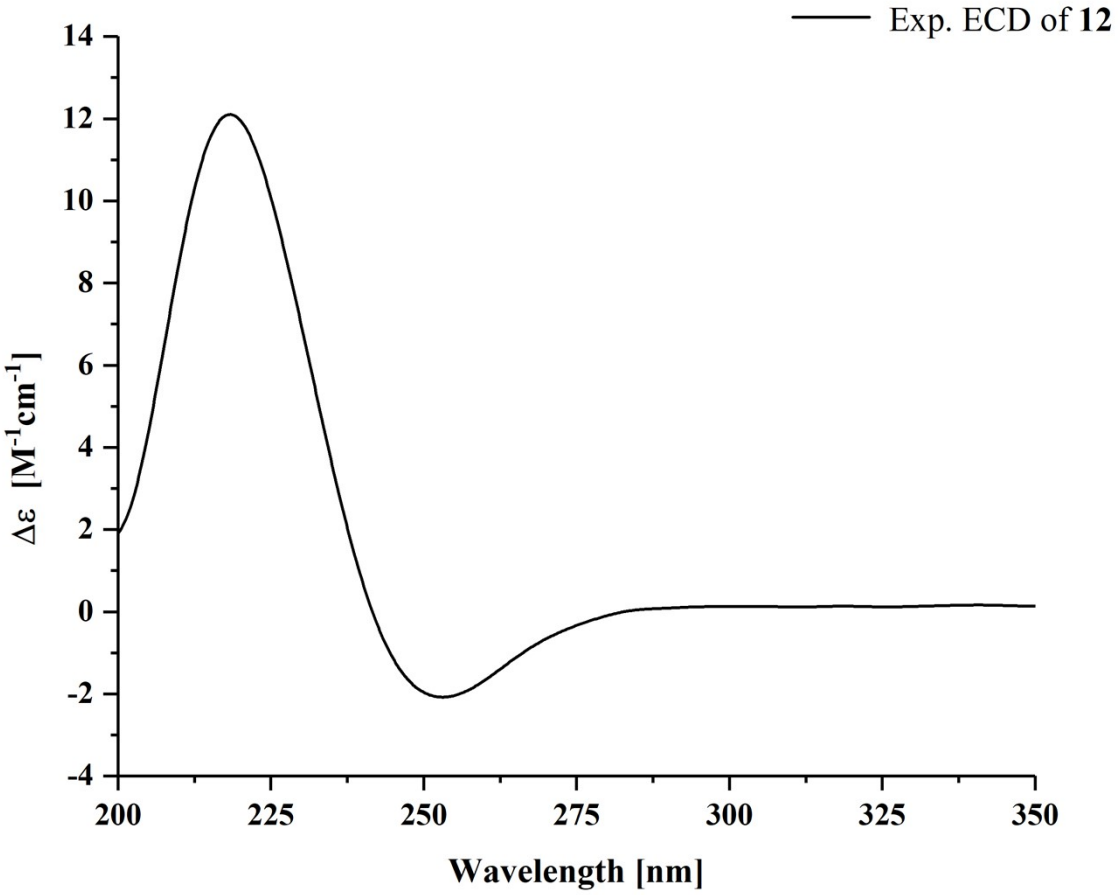
Figure S125. (+) HRESIMS Spectrum of Compound **12**

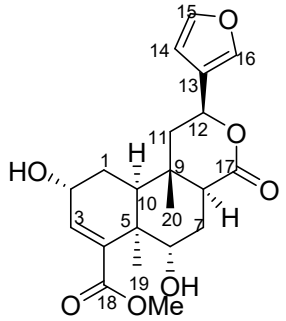




12

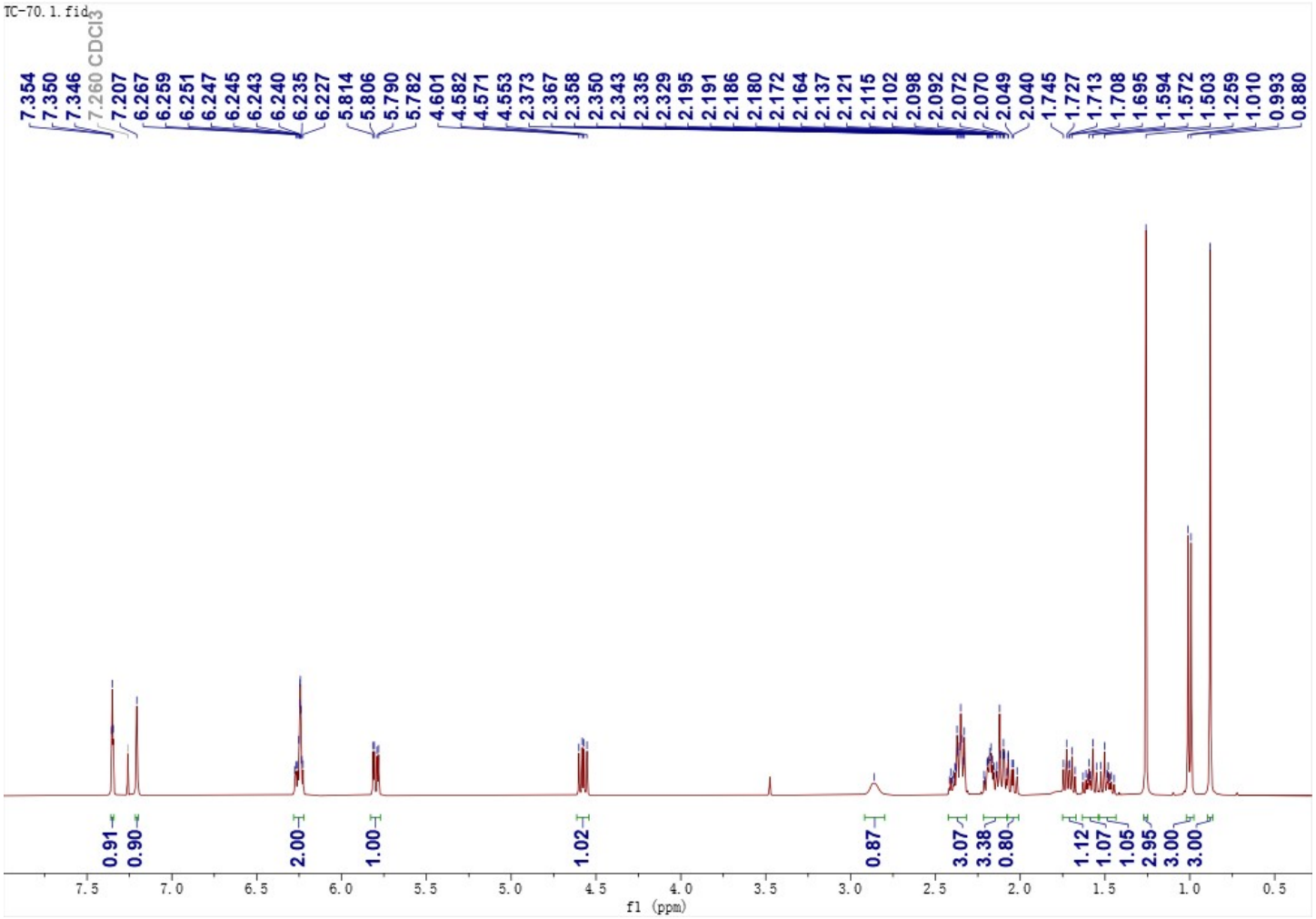
Figure S126. Experimental ECD spectra of Compound **12** in MeOH

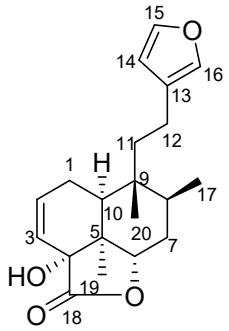




12

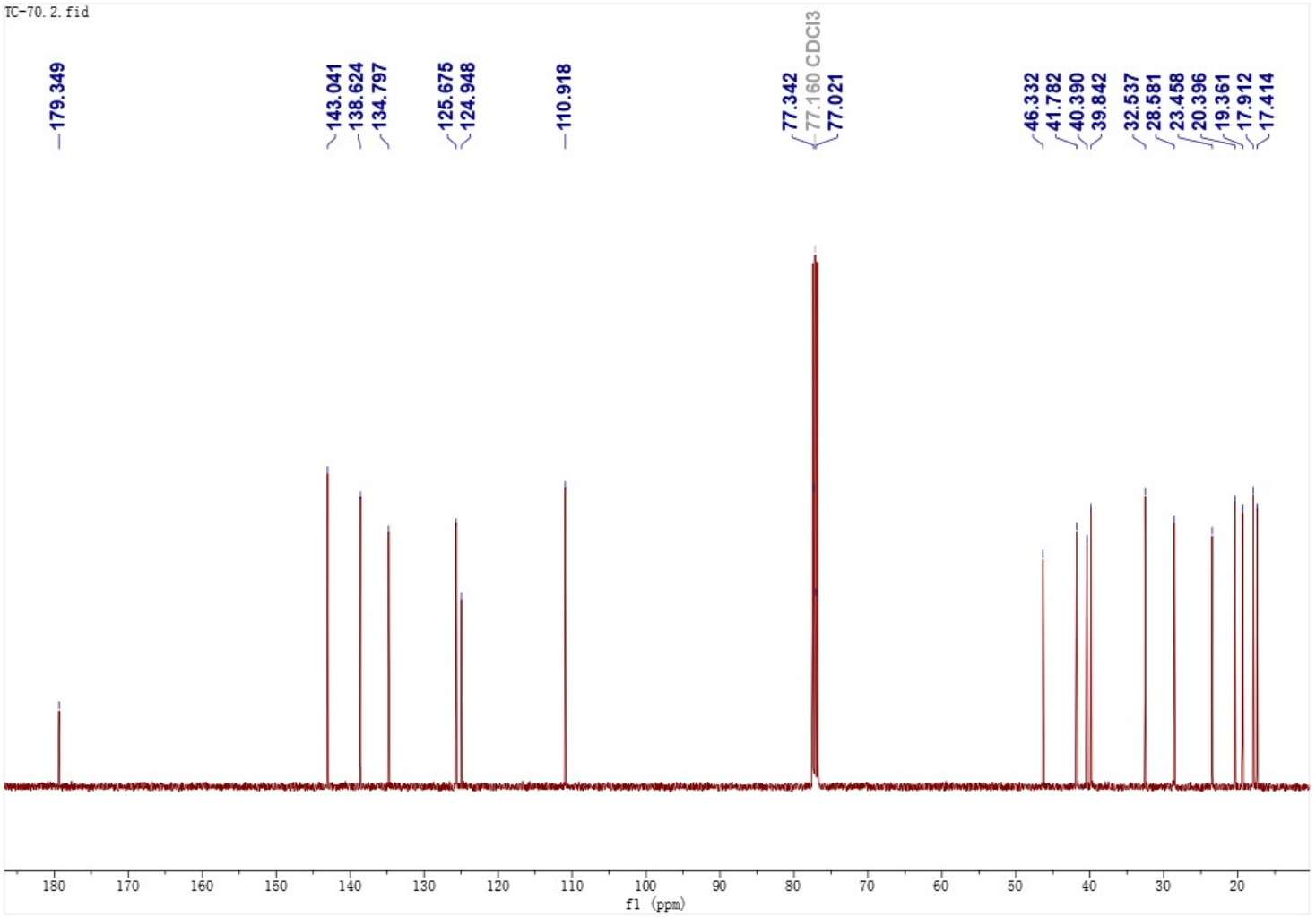
Figure S127. ^{1}H NMR Spectrum of Compound **13** in $CDCl_3$

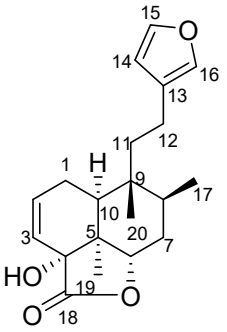




13

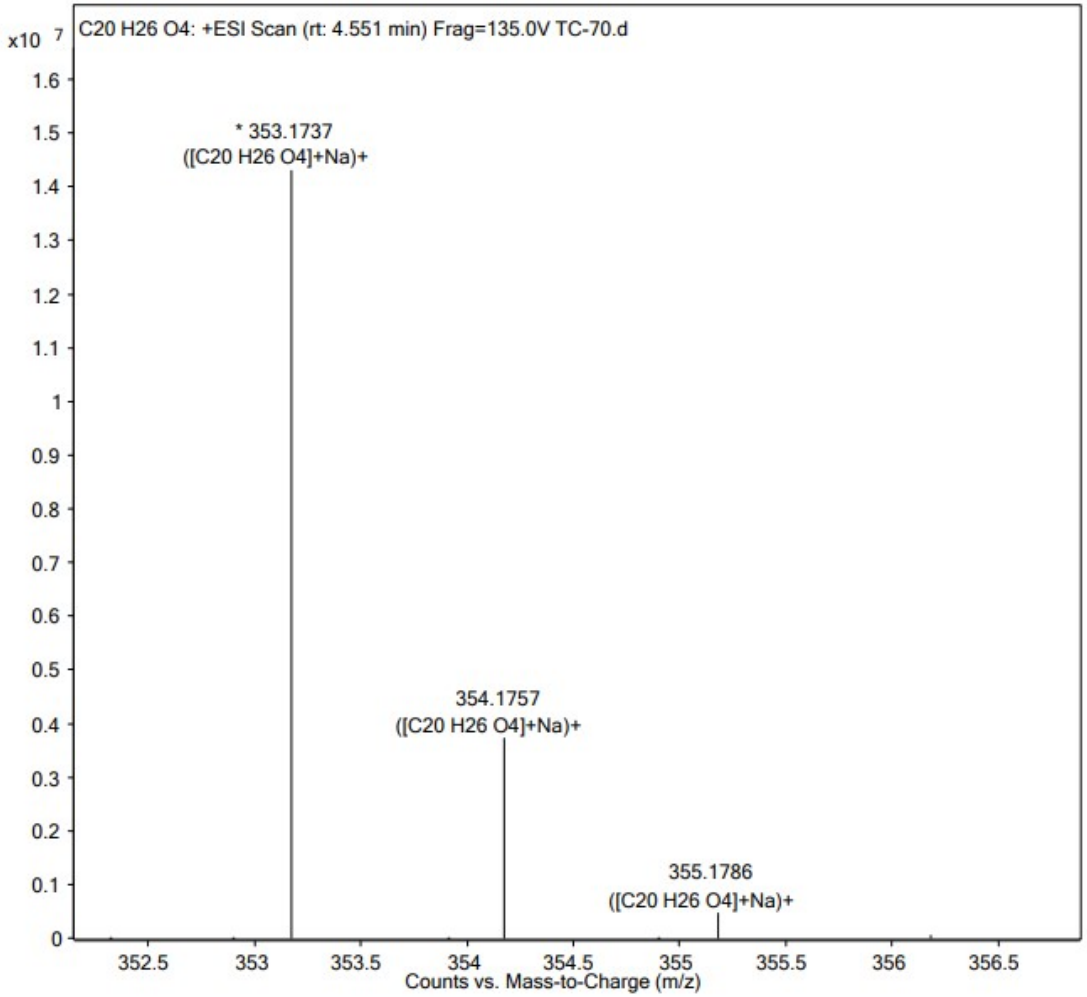
Figure S128. ^{13}C NMR Spectrum of Compound **13** in $CDCl_3$

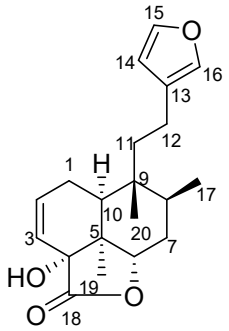




13

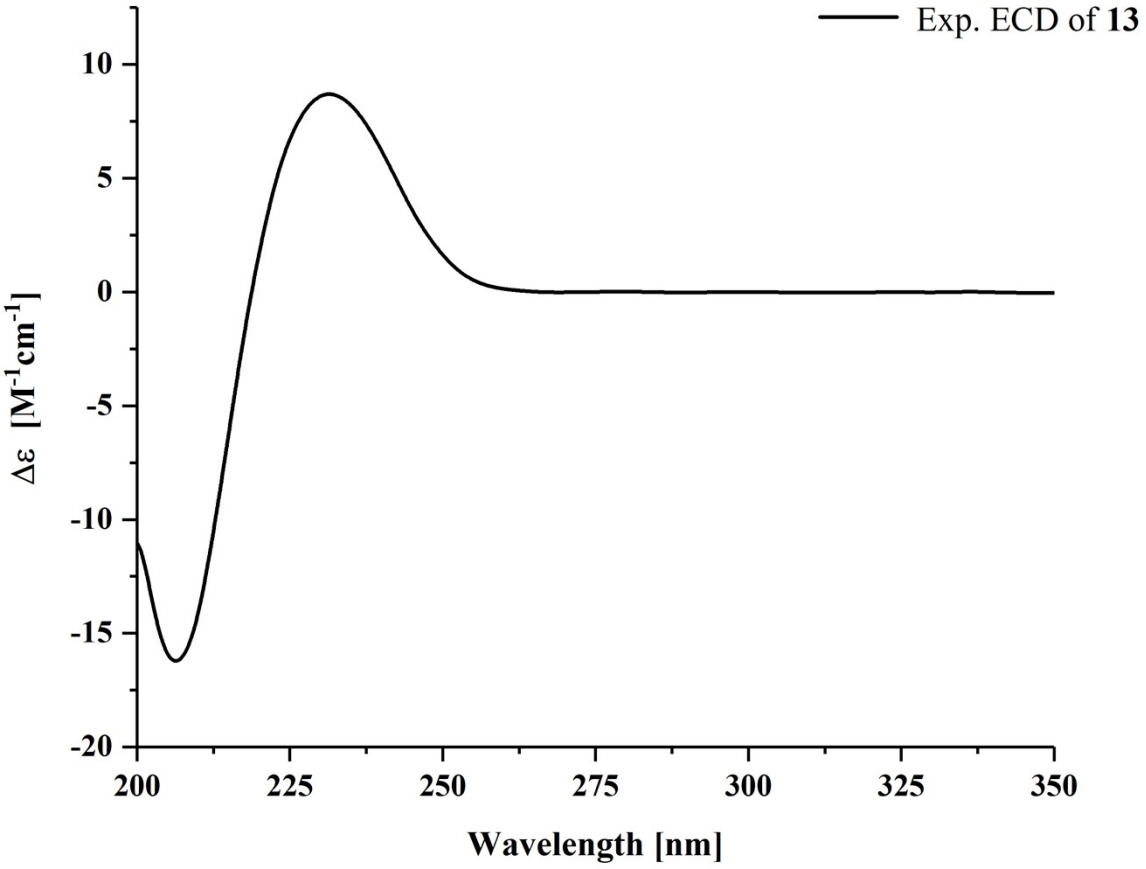
Figure S129. (+) HRESIMS Spectrum of Compound **13**

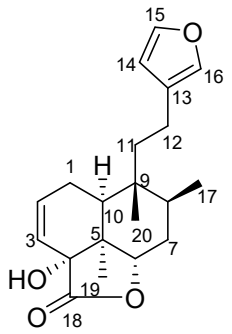




13

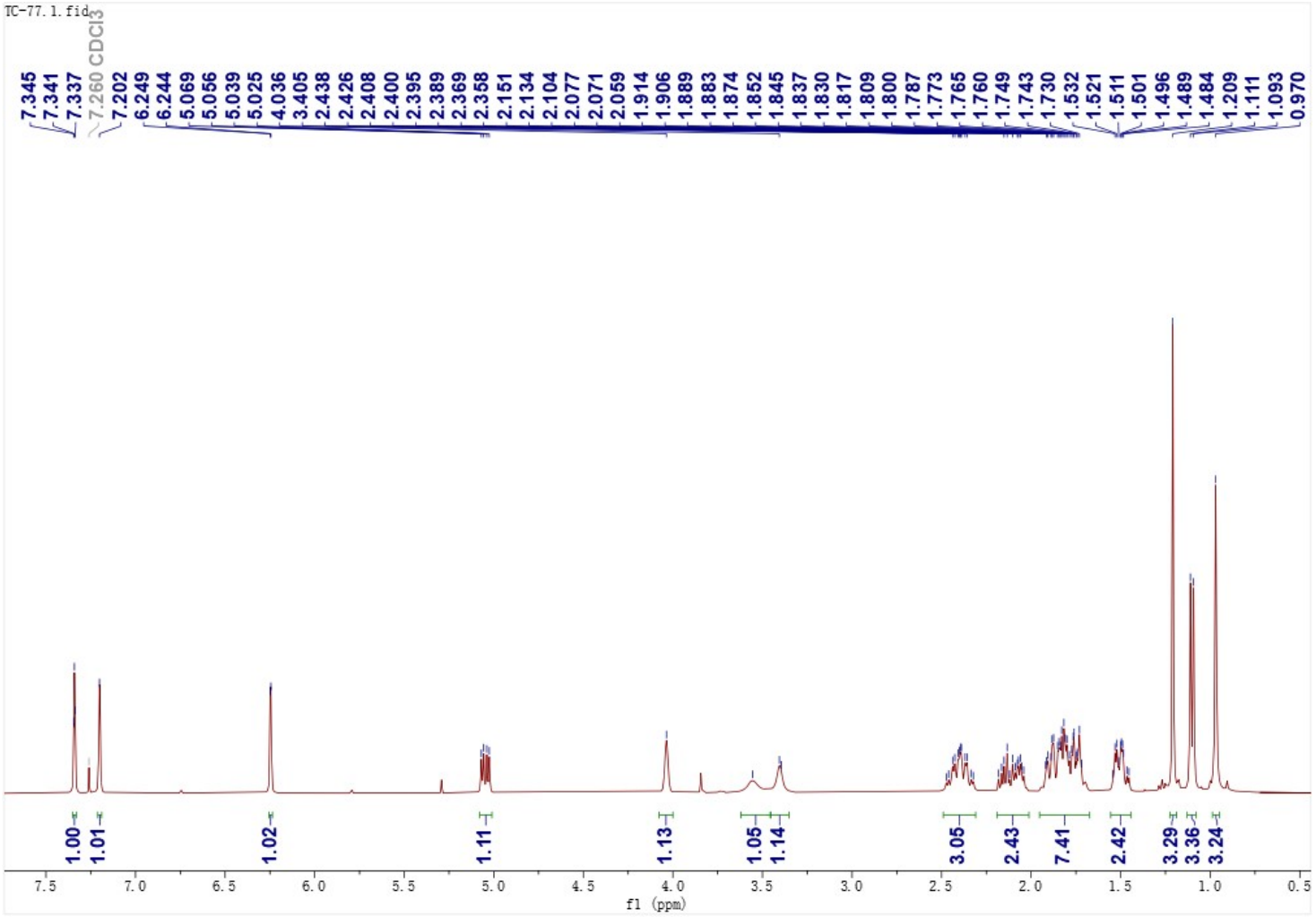
Figure S130. Experimental ECD spectra of Compound **13** in MeOH

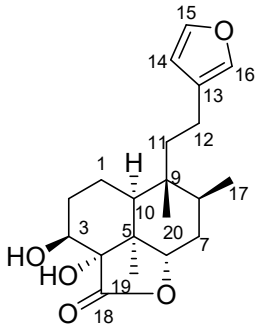




13

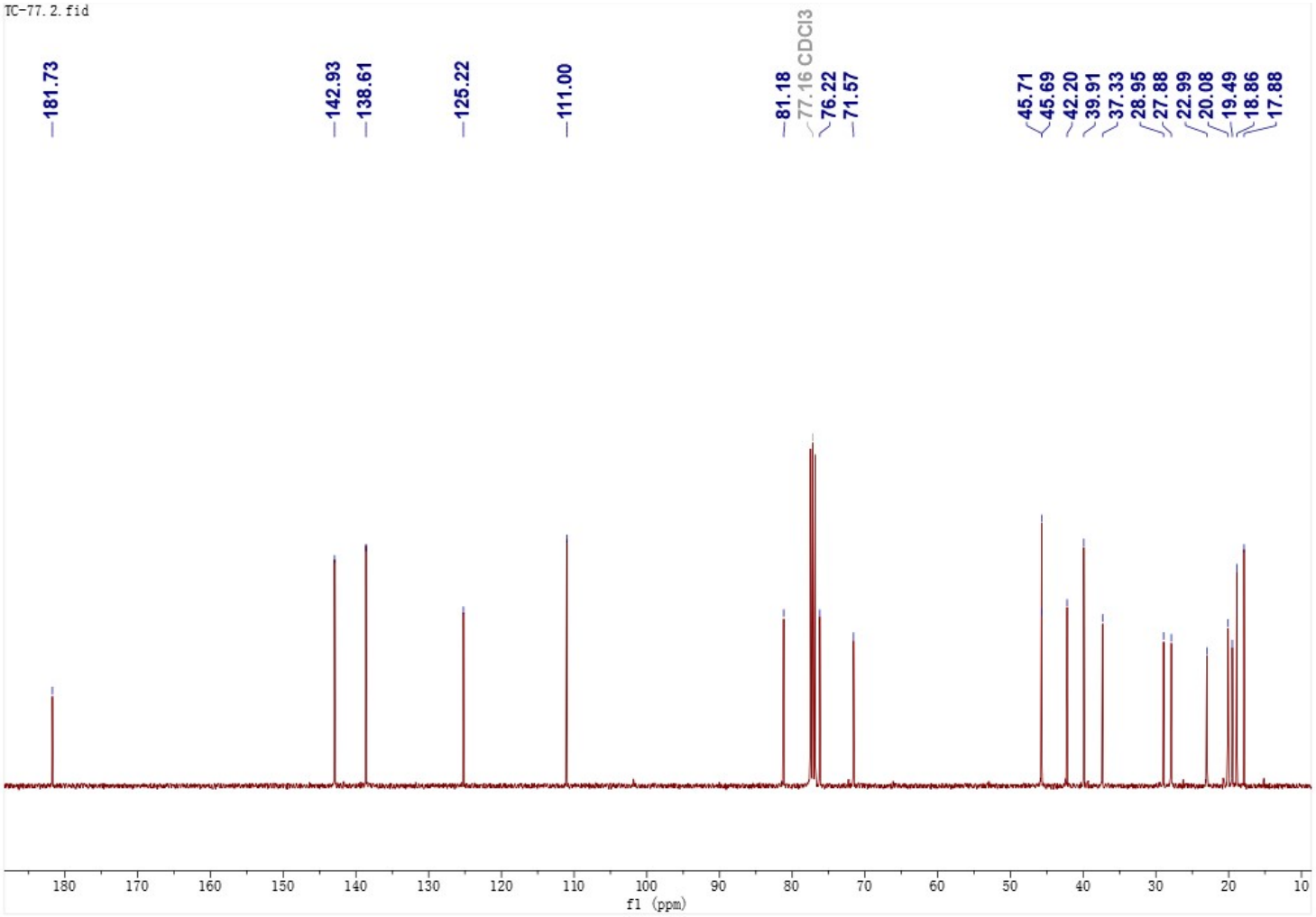
Figure S131. ^{1}H NMR Spectrum of Compound **14** in $CDCl_3$

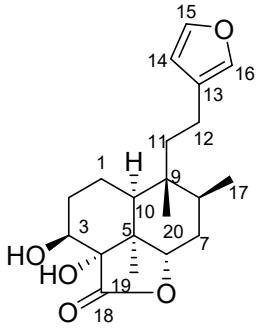




14

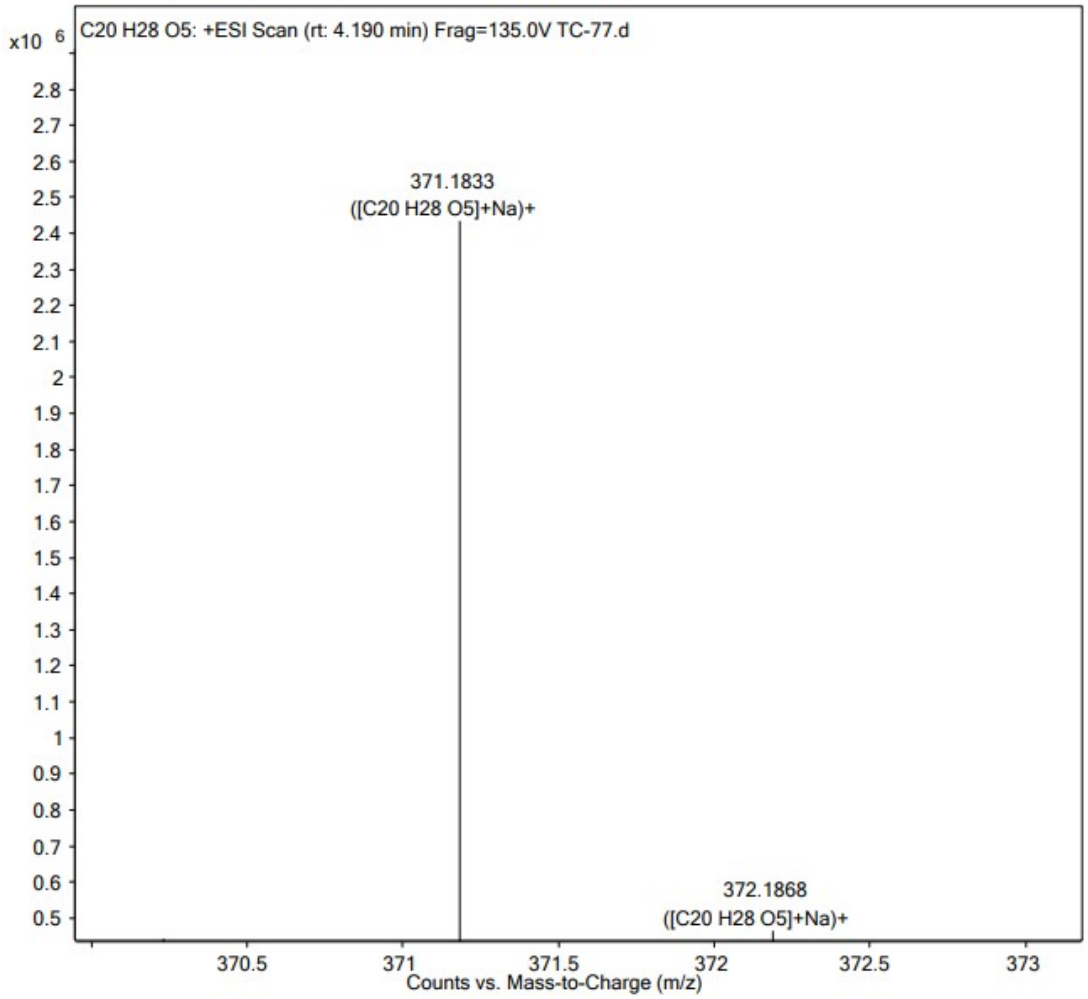
Figure S132. ^{13}C NMR Spectrum of Compound **14** in $CDCl_3$

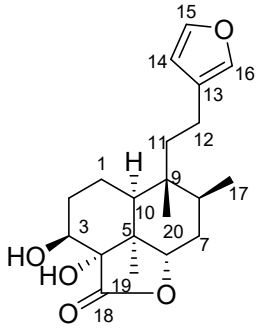




14

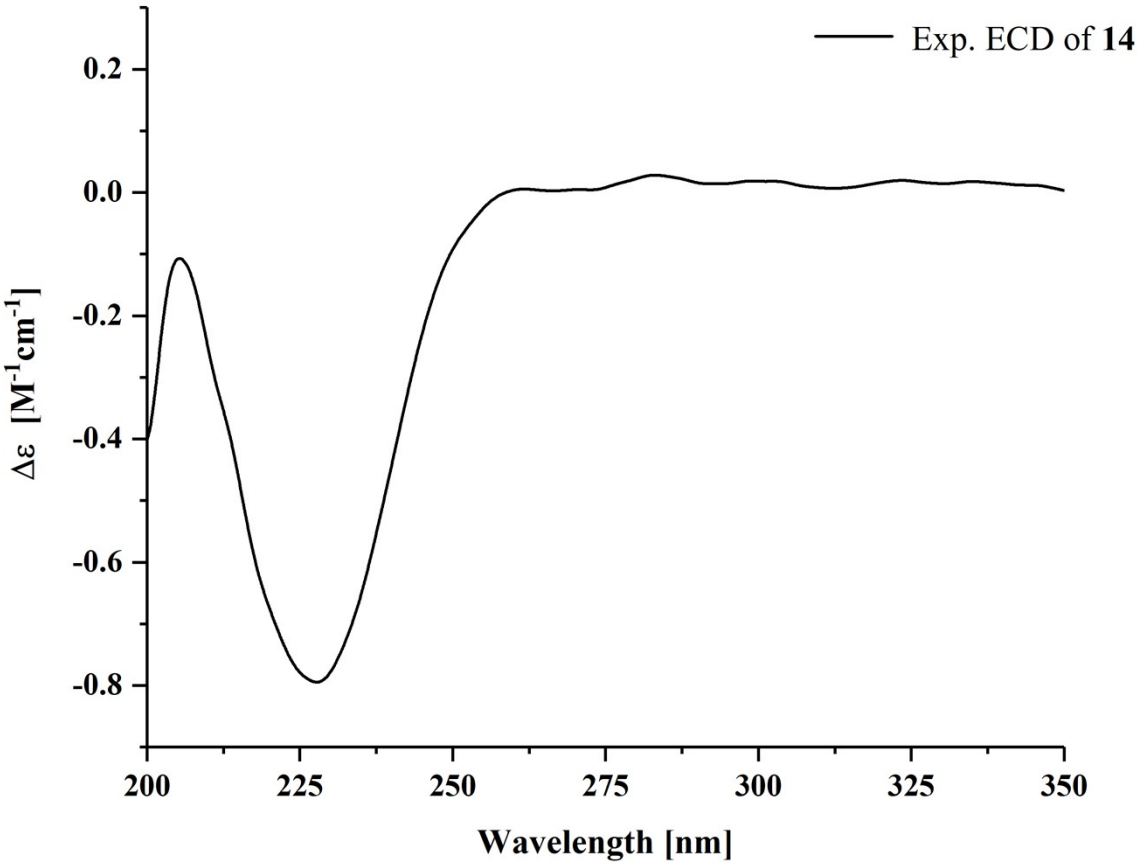
Figure S133. (+) HRESIMS Spectrum of Compound **14**

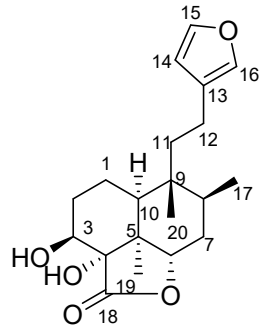




14

Figure S134. Experimental ECD spectra of Compound **14** in MeOH


Exp. ECD of 14
0.2
0.0
-0.2
-0.4
-0.6
-0.8
Δε [M-1cm-1]
200
225
250
275
300
325
350
Wavelength [nm]


15
O
14
16
13
12
11
1
H
9
17
10
3
5
20
7
HO
HO
19
O
O
18

14