Supplementary Materials

Preparative Separation and Purification of Trichothecene Mycotoxins from the Marine Fungus *Fusarium* sp. LS68 by High-Speed Counter-current Chromatography in Stepwise Elution Mode

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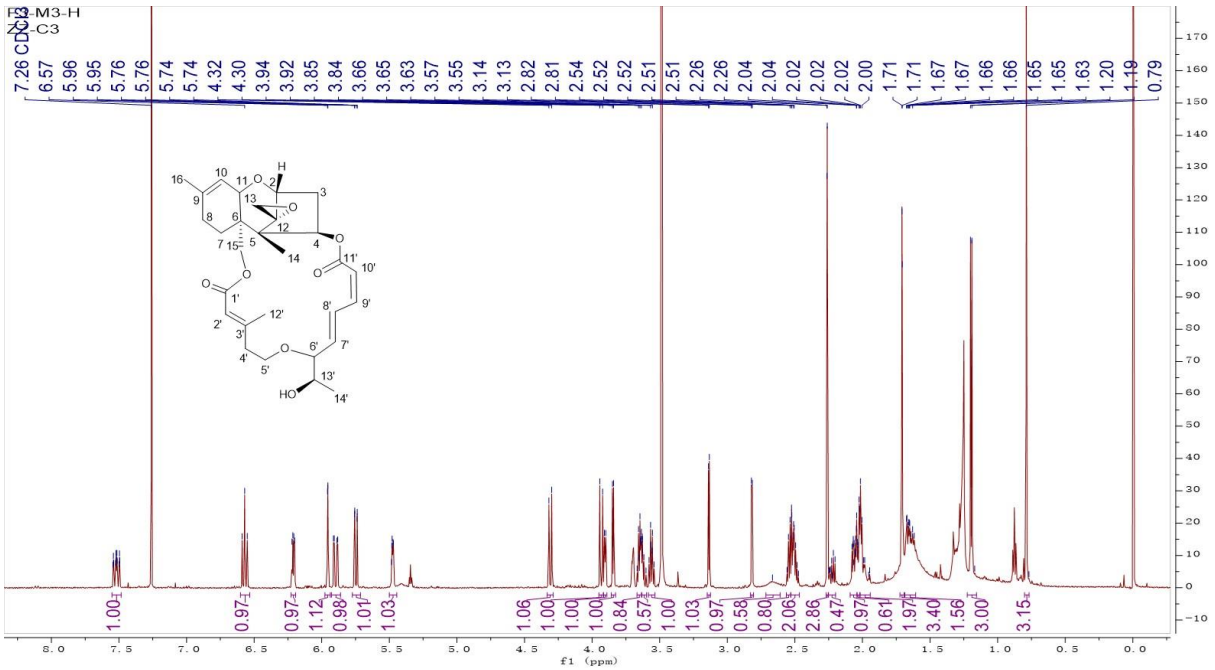


Figure S1a. ^{1}H NMR spectrum of compound **1** ($CDCl_3$, 600 MHz)

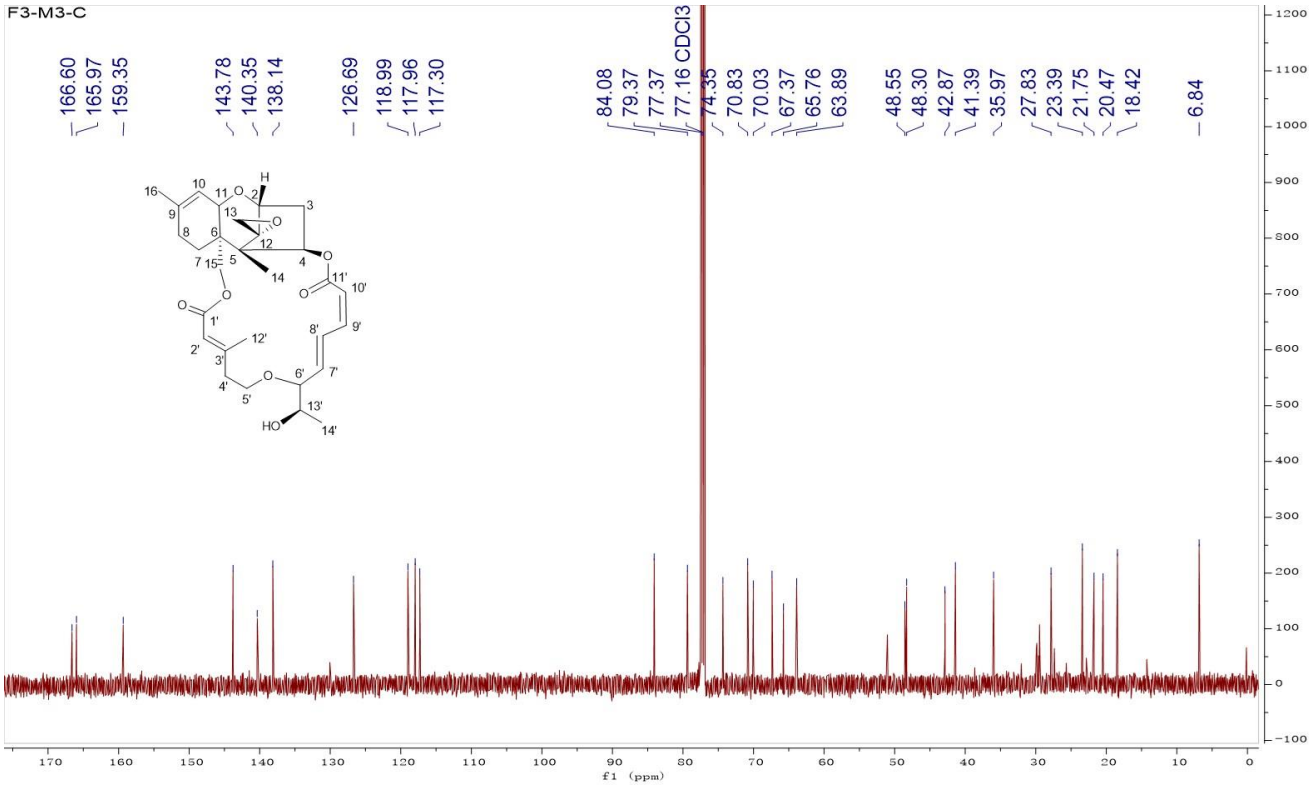


Figure S1b. ^{13}C NMR spectrum of compound **1** ($CDCl_3$, 150 MHz)

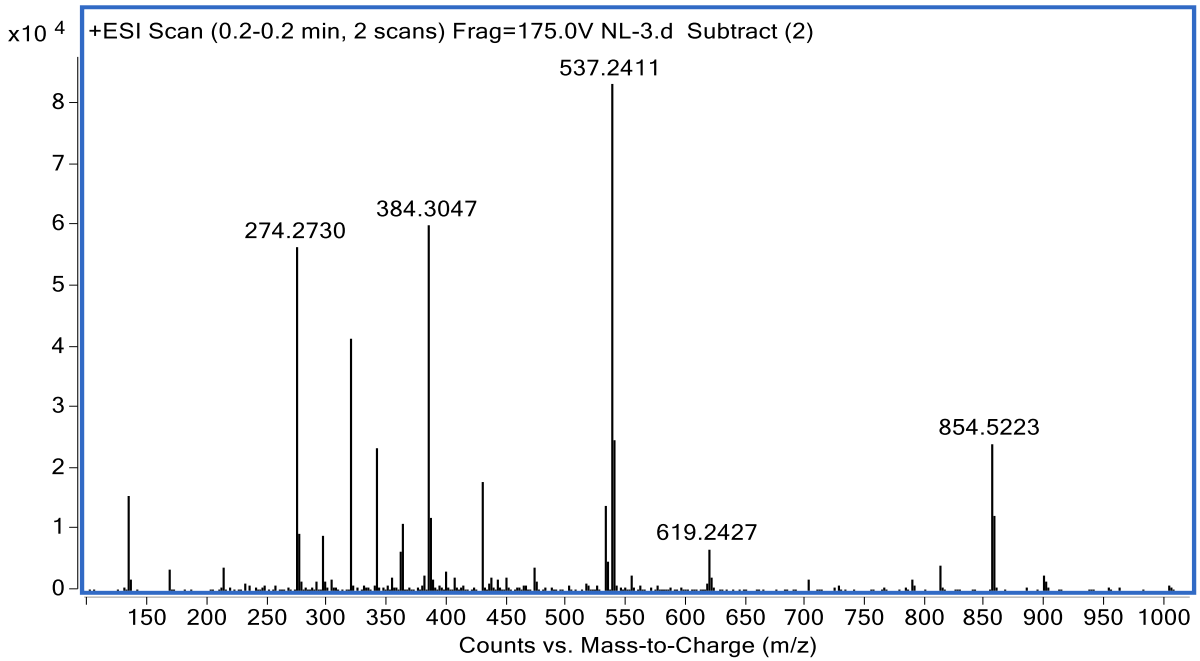


Figure S1c. HRESIMS spectrum of compound **1**

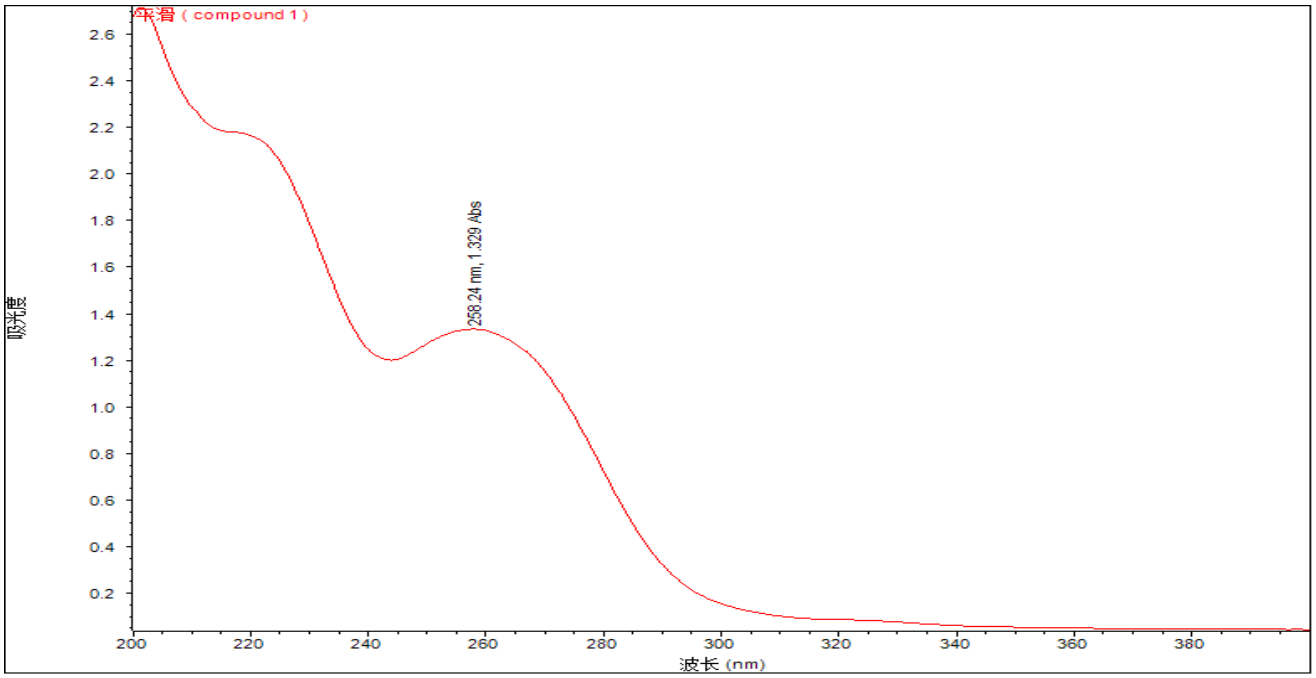


Figure S1d. UV spectrum of compound **1**

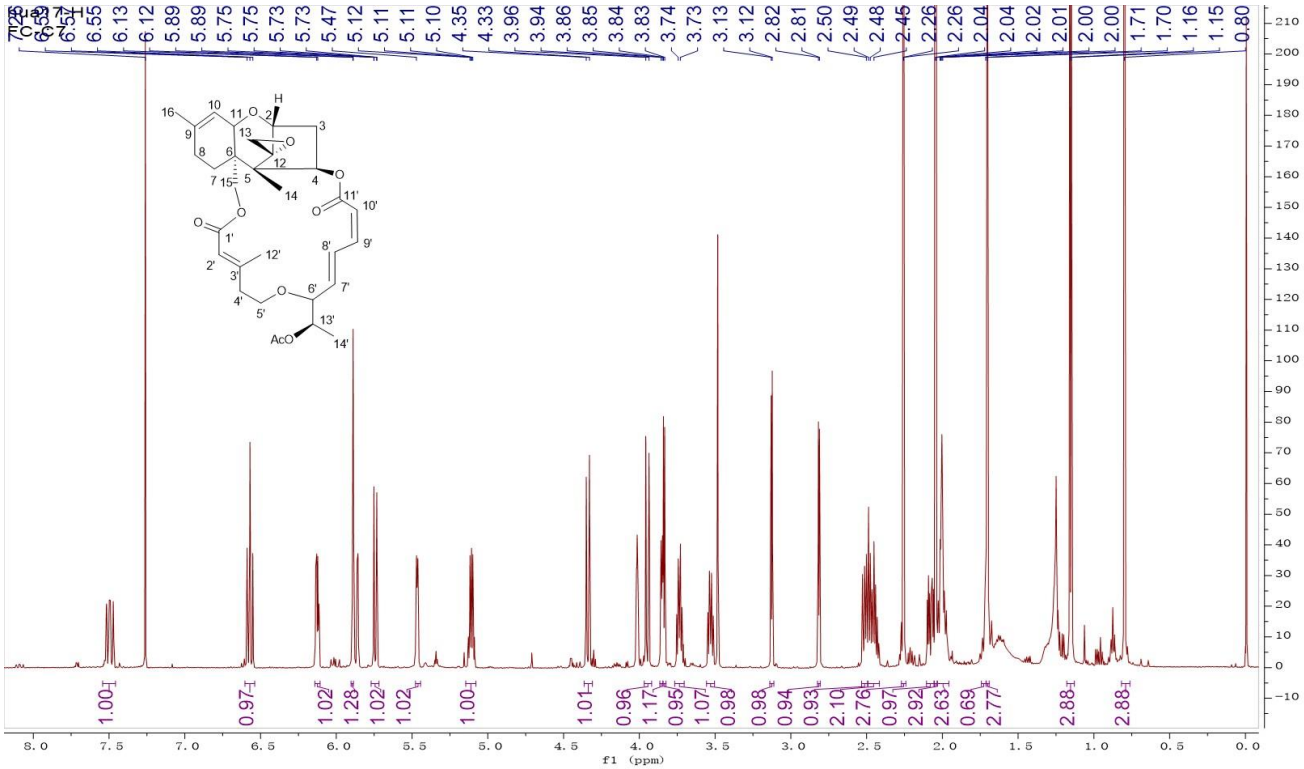


Figure S2a. ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 600 MHz)

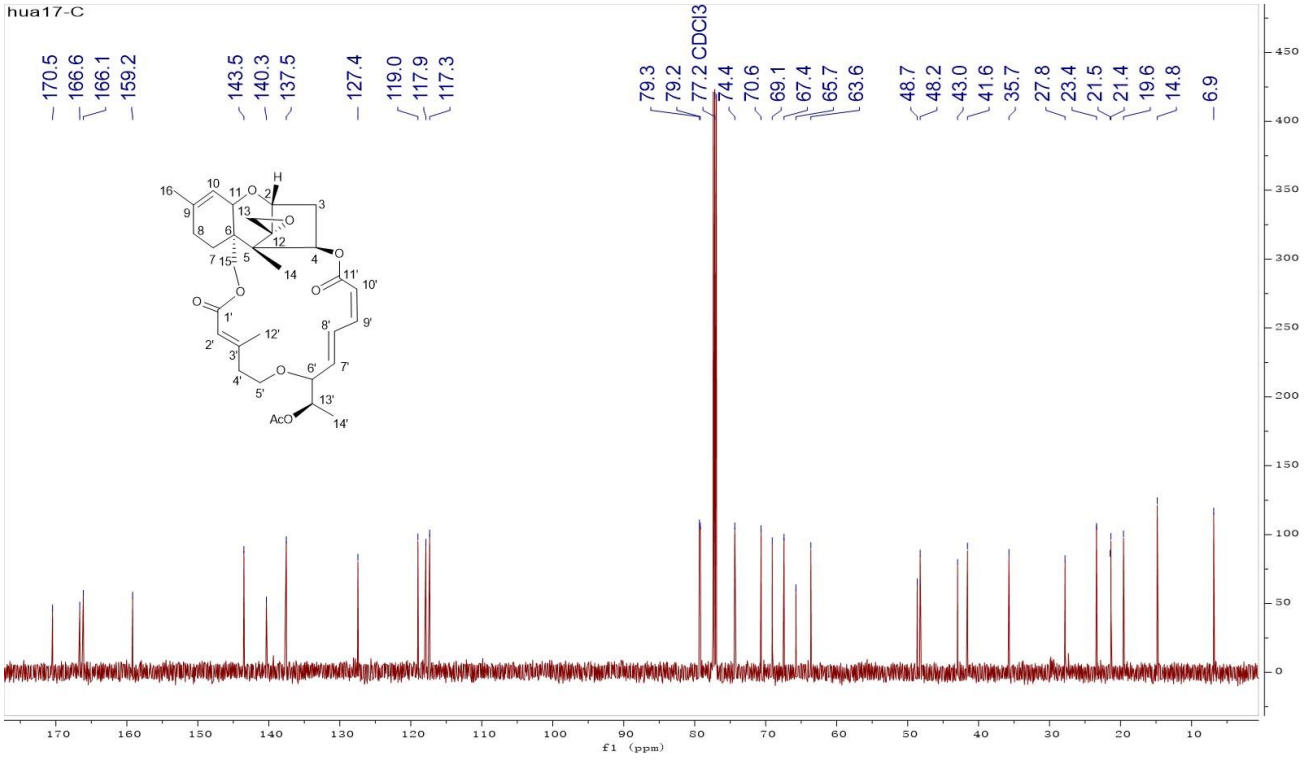


Figure S2b. ^{13}C NMR spectrum of compound **2** ($CDCl_3$, 150 MHz)

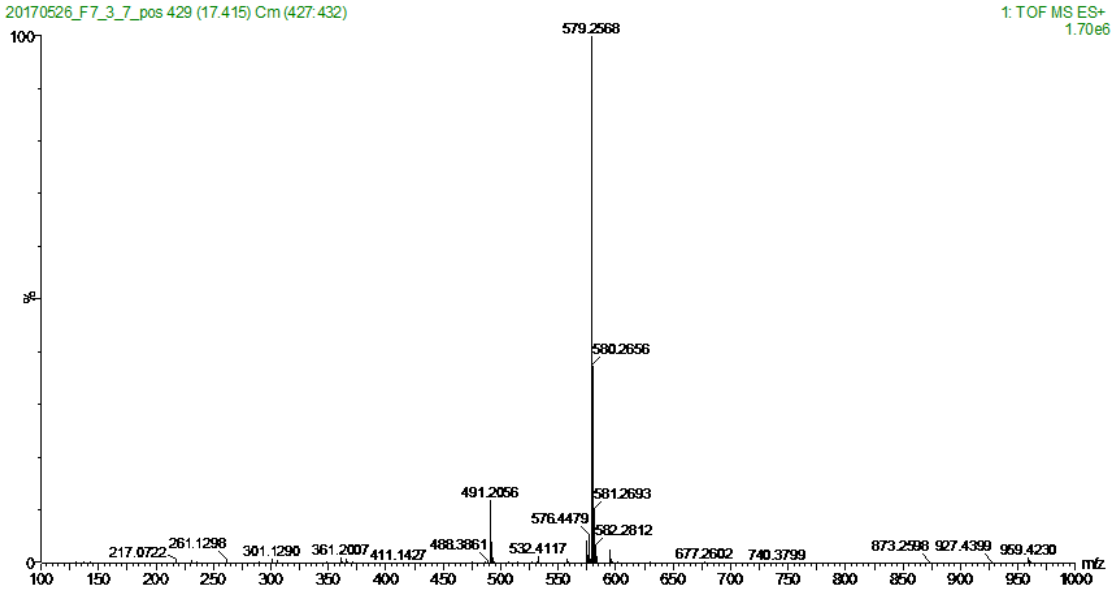
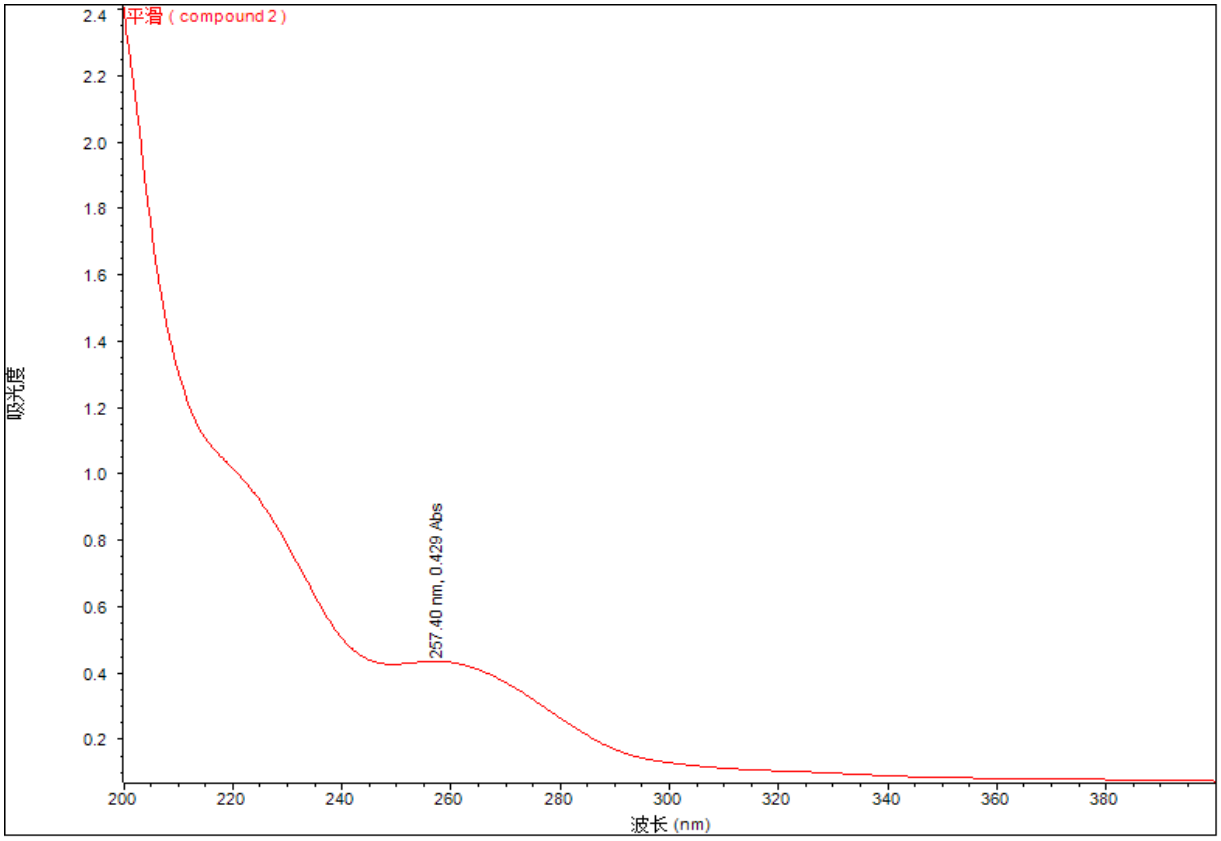


Figure S2c. HRESIMS spectrum of compound **2**



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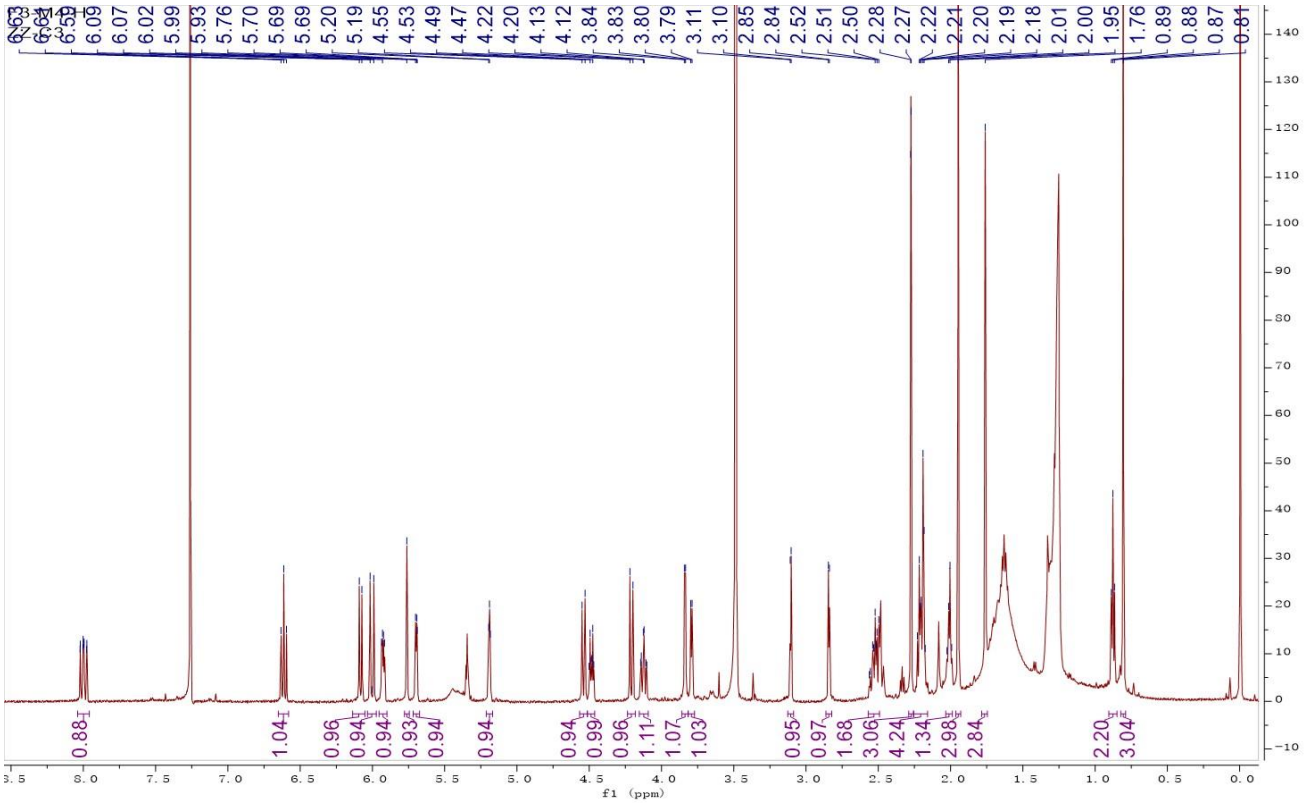

Figure S3a. ^{1}H NMR spectrum of compound **3** ($CDCl_3$, 600 MHz)

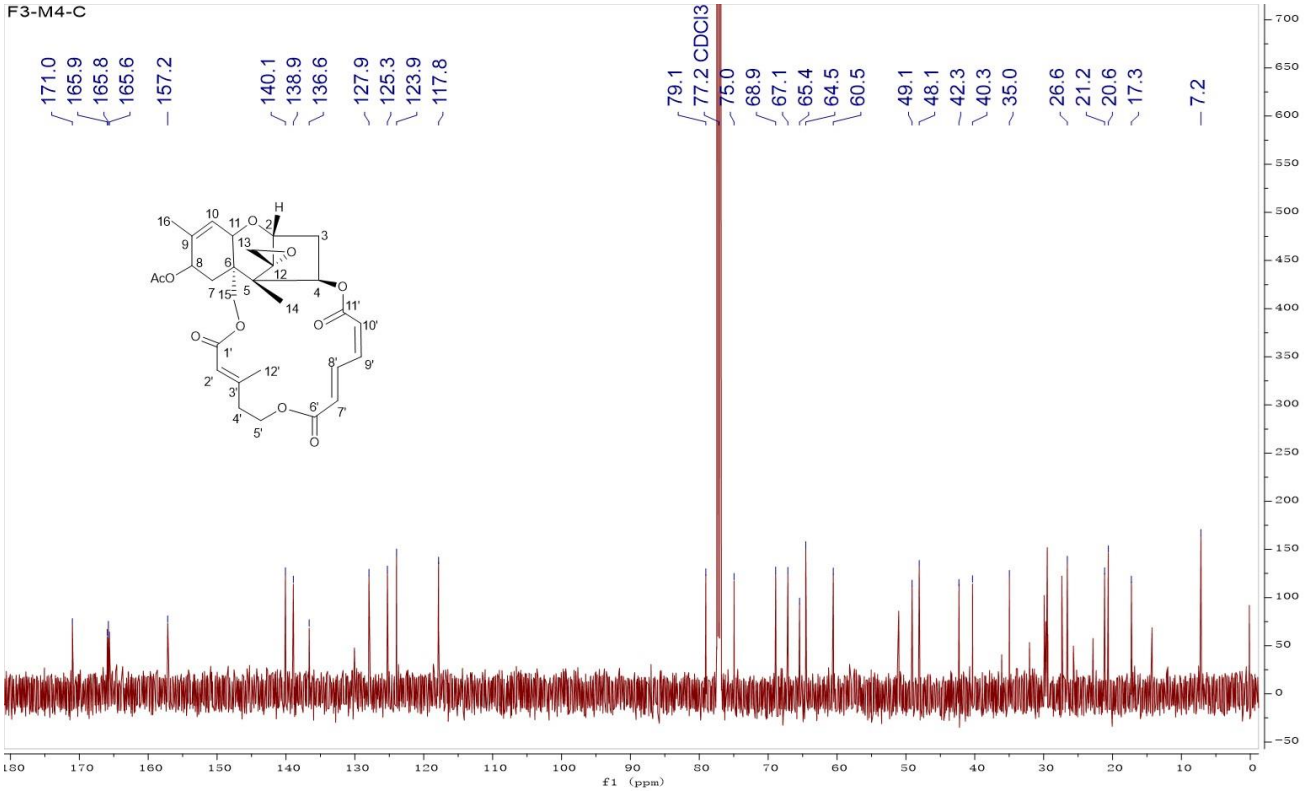

Figure S3b.^{13}CNMR spectrum of compound **3** ($CDCl_3$, 150 MHz)

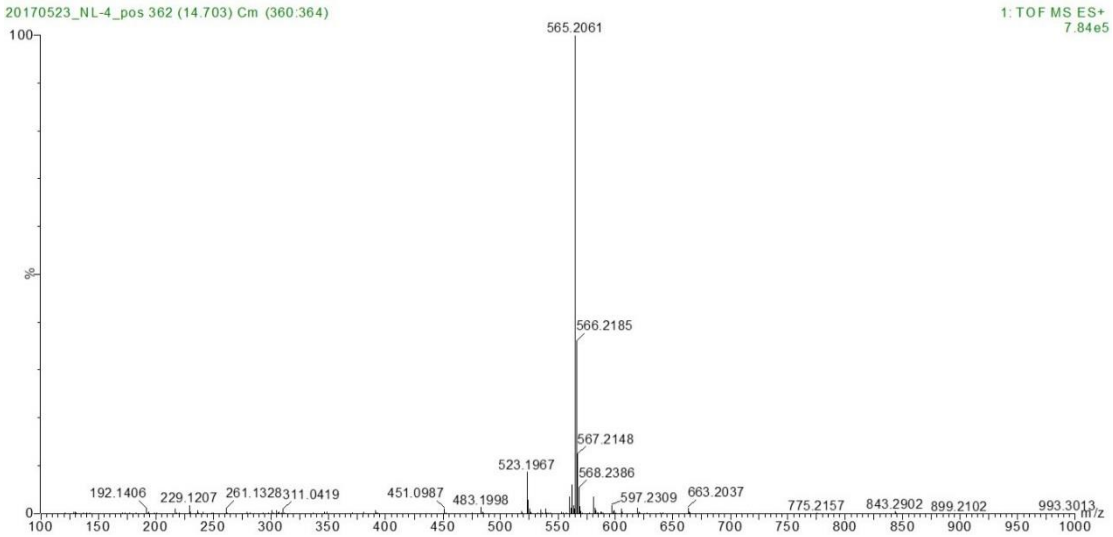

Figure S3c. HRESIMS spectrum of compound **3**

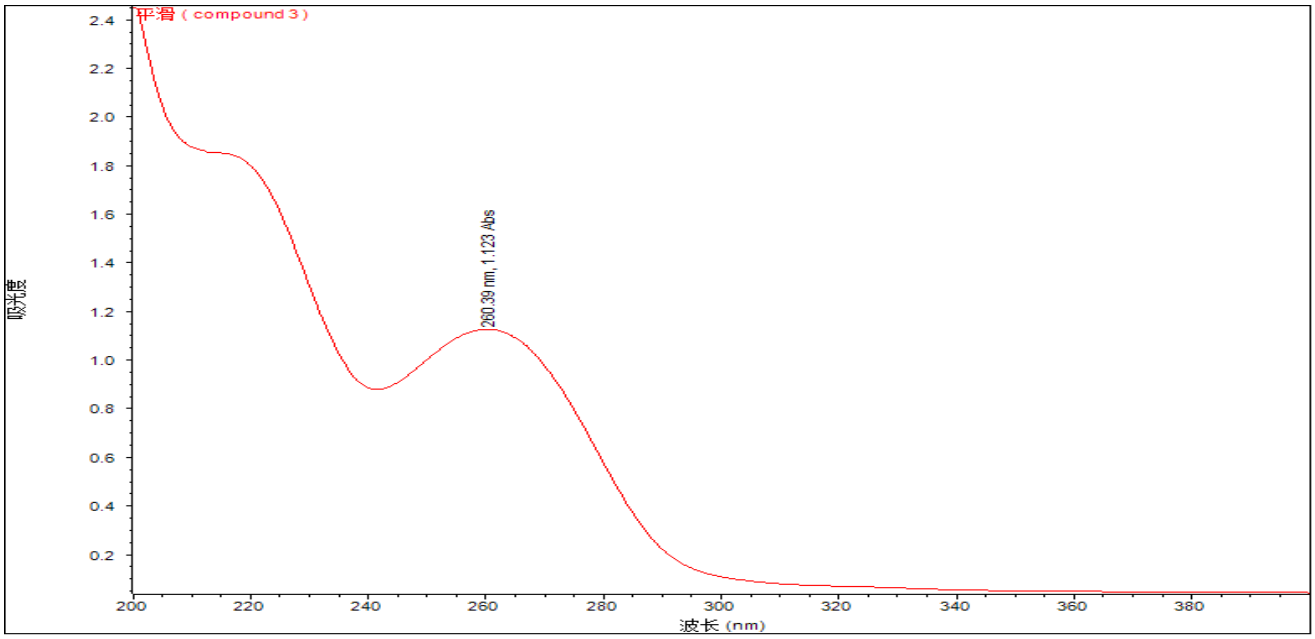

Figure S3d. UV spectrum of compound **3**

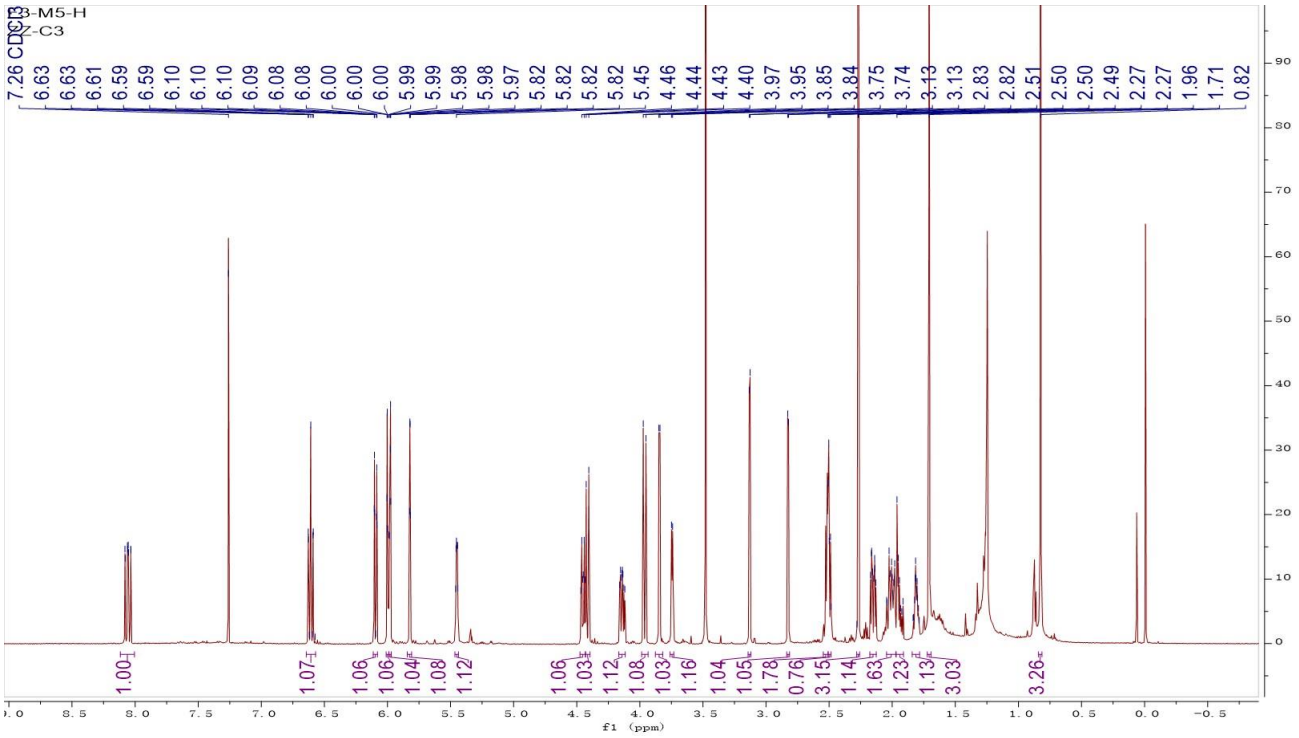

Figure S4a. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 600 MHz)

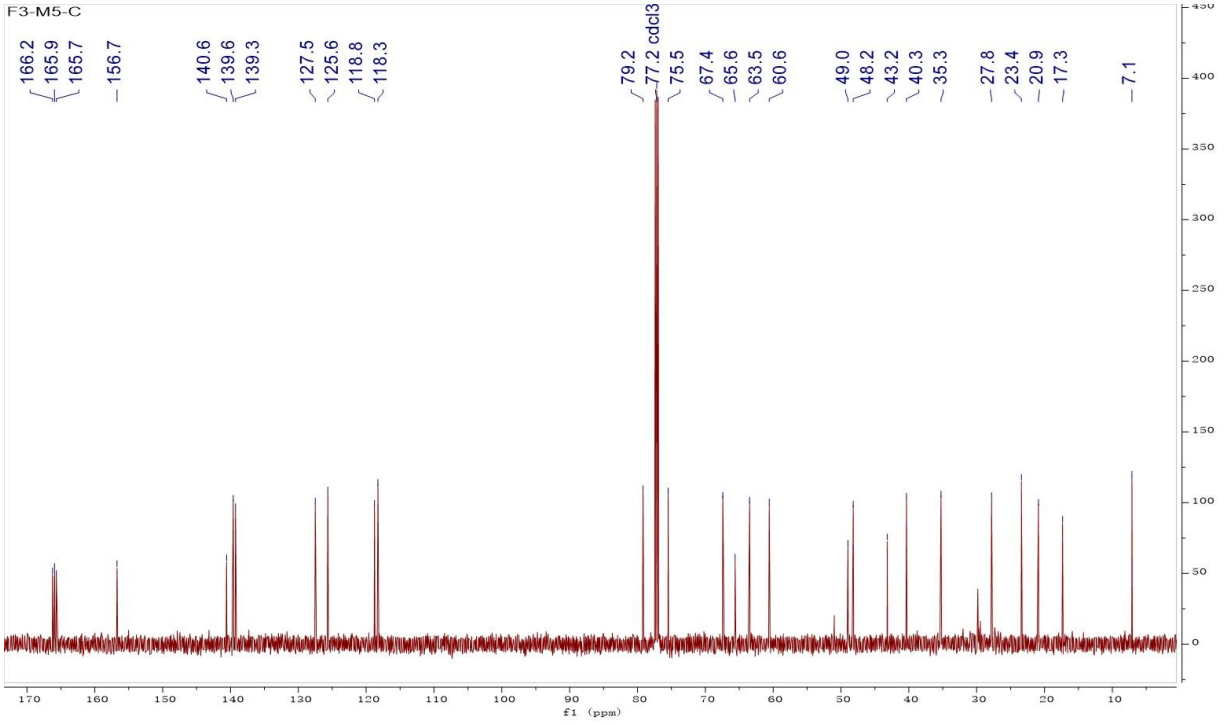

Figure S4b. ^{13}CNMR spectrum of compound **4** ($CDCl_3$, 150 MHz)

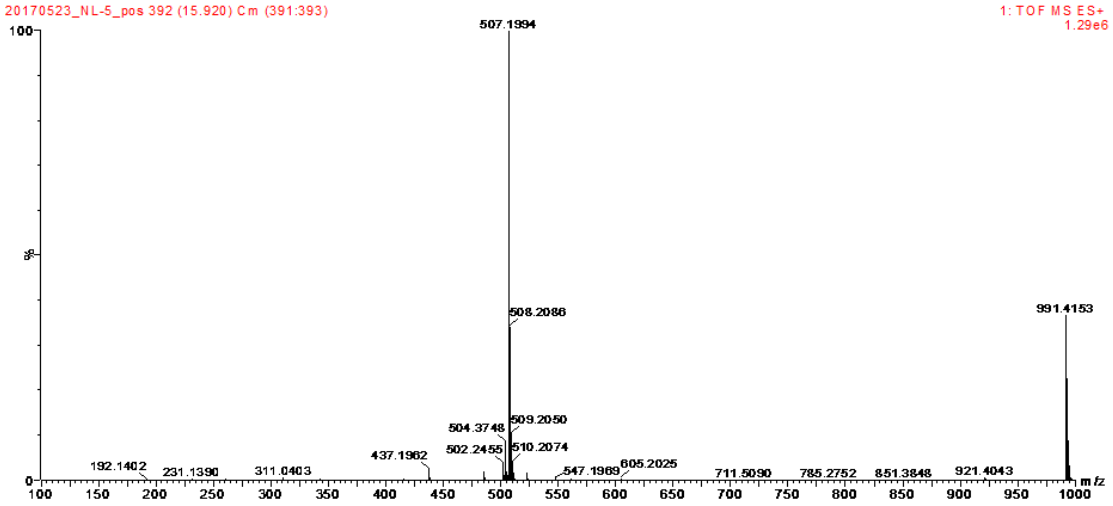

Figure S4c. HRESIMS spectrum of compound **4**

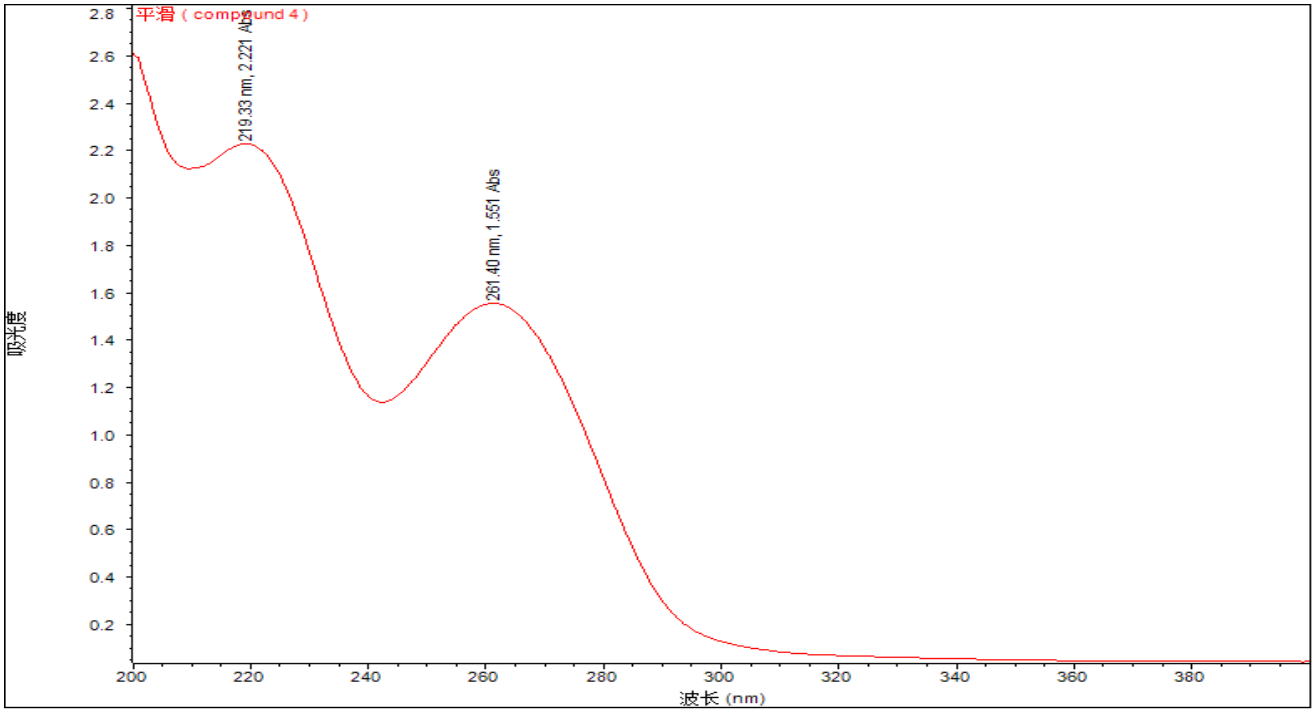

Figure S4d. UV spectrum of compound **4**

Table S1. NMR data of compound **1** in $CDCl_3$

Position	literature data (**^{1}H 600 MHz, ^{13}C 150 MHz**)[1]		experimental data(**^{1}H 600 MHz, ^{13}C 150 MHz**)	
	δ_H (mult, *J*)	δ_C	δ_H (mult, *J*)	δ_C
2	3.83 (1H, d, 5.0 Hz)	79.5	3.83 (1H, d, 5.1 Hz)	79.4
3	2.51 (1H, dd, 15.0, 8.0 Hz); 2.04 (1H, ddd, 15.0, 5.0, 4.0 Hz)	36.1	2.50 (1H,m); 2.05 (1H, m)	36.0
4	6.20 (1H, dd, 8.0, 4.0 Hz)	74.4	6.21 (1H, dd, 8.1, 3.9 Hz)	74.4
5		48.6		48.6
6		42.9		42.9
7	2.02 (1H, ddd, 12.6, 12.6, 5.5 Hz) 1.65 (1H, ddd, 12.6, 5.5, 1.4 Hz)	21.8	2.03 (1H, m)； 1.65 (1H, m)	21.8
8	2.01 (1H, ddd, 12.6, 12.6, 5.5 Hz)； 2.00 (1H, ddd, 12.6, 5.5, 1.4 Hz)	27.9	2.00 (2H, m)	27.8
9		140.4		140.4
10	5.46 (1H, brd)	119.1	5.48 (1H, m)	119.0
11	3.89 (1H, brd)	67.5	3.90 (1H, d, 5.7 Hz)	67.4
12		65.8		65.8
13	3.12 (1H, d, 4.1 Hz); 2.80 (1H, d, 4.1 Hz)	48.4	3.14 (1H, d, 4.1 Hz); 2.82 (1H, d, 4.0 Hz)	48.3
14	0.77 (3H, s)	6.9	0.79 (3H, s)	6.8
15	4.29 (1H, d, 12.5 Hz); 3.92 (1H, d, 12.5 Hz)	64.0	4.31 (1H, d, 12.5 Hz); 3.93 (1H, d, 12.5 Hz)	63.9
16	1.69 (3H, brs)	23.5	1.71 (3H, m)	23.4
1′		166.7		166.6
2′	5.94 (1H, brs)	117.4	5.90 (1H, dd, 15.7, 3.4 Hz)	117.3
3′		159.4		159.4
4′	2.51 (1H, dd, 13.0, 7.3, ~1.0 Hz)； 2.48 (1H, dd, 13.0, 6.8, <1.0 Hz)	41.5	2.51 (2H, m)	41.4
5′	3.62 (1H, ddd, 15.1, 6.8, ~1.0 Hz); 3.54 (1H, ddd, 15.1, 7.3, <1 Hz)	70.1	3.62 (1H, m); 3.56 (1H, dt, 8.4, 7.1 Hz)	70.0
6′	3.68 (1H, br,ddq, 6.7, 3.2, 1.0 Hz)	84.2		84.1
7′	5.88 (1H, dd, 15.7, 3.2 Hz)	138.2	5.96 (1H, d, 1.6 Hz)	138.1
8′	7.51 (1H, br.dd, 15.7, 11.3 Hz)	126.8	7.52 (1H, ddt, 15.8, 11.4, 1.5 Hz)	126.7
9′	6.55 (1H, t, 11.3 Hz)	143.9	6.57 (1H, t, 11.3 Hz)	143.8
10′	5.73 (1H, d, 11.3 Hz)	118.1	5.75 (1H, dd, 11.2, Hz)	118.0
11′		166.0		166.0
12′	2.24 (3H, d, 1.1 Hz)	20.6	2.26 (3H, d, 1.3 Hz)	20.5
13′	3.63 (1H, dq, 6.7, 6.2 Hz)	70.9	3.65 (1H, m)	70.8
14′	1.18 (3H, d, 6.2 Hz)	18.5	1.20 (3H, d, 6.3 Hz)	18.4
OH-13′	2.62		2.67	

Table S2. NMR data of compound **2** in $CDCl_3$

Position	literature data (**^{1}H 400 MHz**, **^{13}C 100 MHz**)[2]		experimental data (**^{1}H 600 MHz**, **^{13}C 150 MHz**)	
	δ_H (mult, *J*)	δ_C	δ_H (mult, *J*)	δ_C
2	3.86-3.84 (1H, m,)	79.3	3.84 (1H, d, 5.2 Hz)	79.3
3	2.53-2.45(1H, m); 2.09 (1H, m)	35.7	2.52 (1H, m)	35.7
4	6.13 (1H, dd, 8.1, 4.0 Hz)	74.3	6.13 (1H, dd, 8.2, 4.1 Hz)	74.4
5		48.6		48.7
6		42.9		43.0
7	2.05-1.98 (1H, m); 1.71 (1H, m)	21.4	2.03-1.98 (1H, m); 1.72 (1H, m)	21.4
8	2.05-1.98 (2H, m)	27.8	2.03-1.98 (3H, m)	27.8
9		140.3		140.3
10	5.47 (1H, d, 5.3 Hz)	119.0	5.47 (1H, dq, 5.6, 1.5 Hz)	119.0
11	3.86-3.84 (1H, m,)	67.4	3.85 (1H, d, 5.8 Hz)	67.4
12		65.7		65.7
13	3.13 (1H, d, 4.0 Hz); 2.82 (1H, d, 4.0 Hz)	48.2	3.13 (1H, d, 4.1 Hz); 2.81 (1H, d, 4.1 Hz)	48.2
14	0.80 (3H, s)	6.8	0.80 (3H, s)	6.9
15	4.35 (1H, d, 12.6 Hz); 3.95 (1H, d, 12.6 Hz)	63.6	4.34 (1H, d, 12.6 Hz); 3.95 (1H, d, 12.6 Hz)	63.6
16	1.68 (3H, brs)	23.3	1.70 (3H, s)	23.4
1′		166.1		166.1
2′	5.90 (1H, s)	117.3	5.89 (1H, d, 1.7 Hz)	117.3
3′		159.1		159.2
4′	2.53-2.45 (2H, m)	41.5	2.46 (2H, m)	41.6
5′	3.74 (1H, m); 3.53 (1H, m)	69.0	3.73 (1H, m); 3.53 (1H, ddd, 8.5, 5.9, 6.8 Hz)	69.1
6′		79.2		69.0
7′	5.88 (1H, m)	137.5	5.89 (1H, d, 1.7 Hz)	137.5
8′	7.50 (1H, m)	127.4	7.49 (1H, dddd, 15.7, 11.4, 2.0, 1.0 Hz)	127.4
9′	6.58 (1H, dd, 11.4, 11.3 Hz)	143.5	6.57 (1H, t, 11.3 Hz)	143.5
10′	5.75 (1H, d, 11.0 Hz)	117.9	5.74 (1H, dd, 11.2, 0.9 Hz)	117.9
11′		166.6		166.6
12′	2.26 (3H, s)	19.5	2.26 (3H, d, 1.3 Hz)	19.6
13′	5.12 (1H, qd, 6.3, 4.9 Hz)	70.6	5.11 (1H, qd, 6.4, 4.7 Hz)	70.6
14′	1.16 (3H, d, 6.5 Hz)	14.8	1.15 (3H, d, 6.4 Hz)	14.8
15′		170.4		170.5
16′	2.05 (3H, s)	21.3	2.04 (3H, s)	21.5

Table S3. NMR data of compound **3** in $CDCl_3$

Position	literature data (**^{1}H 400 MHz, ^{13}C 100 MHz**)[3]		experimental data (**^{1}H 600 MHz, ^{13}C 150 MHz**)	
	δ_H (mult, *J*)	δ_C	δ_H (mult, *J*)	δ_C
2	3.83 (1H, d, 5.0 Hz)	78.9	3.84 (1H, d, 5.1 Hz)	79.1
3	2.21 (1H, m); 2.49 (1H, m)	34.9	2,21 (1H, m); 2.48 (1H, m)	35.0
4	5.93 (1H, dd, 8.0, 4.0 Hz)	74.8	5.93 (1H, dd, 8.4, 4.3 Hz)	75.0
5		49.0		49.1
6		42.2		42.3
7	2.19 (2H, m)	26.5	2.19 (2H, d, 4.5 Hz)	26.6
8	5.19 (1H, m)	68.8	5.19 (1H, t, 3.2 Hz)	68.9
9		136.5		136.6
10	5.70 (1H, brd, 5.5 Hz)	123.8	5.70 (1H, d, 5.4 Hz)	123.9
11	3.80 (1H, d, 5.5 Hz)	67.0	3.84 (1H, d, 5.1 Hz)	67.1
12		65.3		65.4
13	2.84 (1H, d, 4.0 Hz); 3.11 (1H, d, 4.0 Hz)	47.9	2.84 (1H, d, 4.0 Hz); 3.11 (1H, d, 4.0 Hz)	48.1
14	0.81 (3H, s)	7.0	0.81 (3H, s)	7.2
15	4.21 (1H, d, 12.5 Hz); 4.54 (1H, d, 12.5 Hz)	64.4	4.21 (1H, d, 12.5 Hz); 4.54 (1H, d, 12.5 Hz)	64.5
16	1.76 (3H, s)	20.5	1.76 (3H, s)	20.6
17		170.9		171.0
18	1.95 (3H, s)	21.0	1.95 (3H, s)	21.2
1′		165.6		165.8
2′	5.77 (1H, brs)	117.7	5.76 (1H, s)	117.8
3′		157.0		157.2
4′	2.54 (2H, m)	40.2	2.52 (2H, m)	40.3
5′	4.13 (1H, ddd, 11.0, 11.0, 3.5 Hz) 4.49 (1H, ddd, 11.0, 4.0,4.0 Hz)	60.4	4.12 (1H, td, 11.2, 3.4 Hz) 4.48 (1H, dt, 11.4, 4.0,4.2 Hz)	60.5
6′		165.5		165.6
7′	6.01 (1H, d, 15.5 Hz)	127.8	6.00 (1H, d, 15.7 Hz)	127.9
8′	8.00 (1H, dd, 15.5, 11.5 Hz)	138.8	8.00 (1H, ddd, 15.5, 11.5, 1.1 Hz)	138.9
9′	6.62 (1H, dd, 11.5, 10.5 Hz)	139.9	6.61 (1H, t, 11.3 Hz)	140.1
10′	6.09 (1H, d, 10.5 Hz)	125.1	6.08 (1H, d, 11.1 Hz)	125.3
11′		165.8		165.9
12′	2.28 (3H, d, 1.0 Hz)	17.1	2.27 (3H, d, 1.2 Hz)	17.3

Table S4. NMR data of compound **4** in $CDCl_3$

Position	literature data (^{1}**H 400 MHz**, ^{13}**C 100 MHz)**[3]		experimental data (^{1}**H 600 MHz**, ^{13}**C 150 MHz)**	
	δ_H (mult, *J*)	δ_C	δ_H (mult, *J*)	δ_C
2	3.88 (1H, d, 5.0 Hz)	79.0	3.84 (1H, d, 5.1 Hz)	79.2
3	2.16 (1H, m); 2.45 (1H, m)	35.1	2.15 (1H, ddd, 15.3, 5.2, 4.2 Hz); 2.50 (1H, m)	35.3
4	6.00 (1H, m)	75.3	6.00 (1H, m)	75.5
5		48.8		49.0
6		43.0		43.2
7	1.84 (1H, m) 1.98 (1H, m)	20.8	1.81 (1H, m); 1.94 (1H, m)	20.9
8	2.00 (2H, m)	27.7	2.01 (2H, m)	27.8
9		140.4		140.6
10	5.28 (1H, brd, 5.0 Hz)	118.6	5.45 (1H, dq, 5.5, 3.3, 1.5 Hz)	118.3
11	3.68 (1H, d, 5.5 Hz)	67.3	3.74 (1H, d, 5.5 Hz)	67.4
12		65.5		65.6
13	2.83 (1H, d, 4.0 Hz); 3.12 (1H, d, 4.0 Hz)	48.1	2.82 (1H, d, 4.0 Hz); 3.13 (1H, d, 4.0 Hz)	48.2
14	0.83 (3H, s)	7.00	0.82 (3H, s)	7.1
15	3.98 (1H, d, 12.5 Hz); 4.42 (1H, d, 12.5 Hz)	63.3	3.96 (1H, d, 12.6 Hz); 4.41 (1H, d, 12.6 Hz)	63.5
16	1.72 (3H, s)	23.3	1.71 (3H, s)	23.4
1′		166.1		166.2
2′	5.83 (1H, s)	118.1	5.82 (1H, q, 1.2 Hz)	118.8
3′		156.6		156.7
4′	2.53 (2H, m)	40.2	2.51 (2H, m)	40.3
5′	4.15 (1H, m); 4.44 (1H, m)	60.4	4.14 (1H, ddd, 11.3, 9.0, 4.3 Hz); 4.45 (1H, dt, 11.3, 4.6 Hz)	60.6
6′		165.5		165.9
7′	6.02 (1H, d, 15.5 Hz)	127.4	6.09 (1H, dt, 11.1, 0.9 Hz)	127.5
8′	8.09 (1H, dd, 15.5, 11.2 Hz)	139.1	8.06 (1H, ddd, 15.7, 11.6, 1.1 Hz)	139.3
9′	6.62 (1H, dd, 11.2, 11.0 Hz)	139.5	6.60 (1H, m)	139.6
10′	6.10 (1H, d, 11.0 Hz)	125.5	6.09 (1H, dt, 11.1, 0.9 Hz)	125.6
11′		165.8		165.9.
12′	2.28 (3H, d, 1.5 Hz)	17.2	2.27 (3H, d, 1.3 Hz)	17.3

Table S5. Specific rotation values of compounds **1–4**.

compound	literature data	experimental data
1	$[\alpha]_D^{22.5}$ -22 (*c* 0.3, $CHCl_3$)[5]	$[\alpha]_D^{21}$ -25 (*c* 0.3, $CHCl_3$)
2	$[\alpha]_D^{23}$ +50 (*c* 0.85, $CHCl_3$)[2]	$[\alpha]_D^{21}$+52.5 (*c* 0.25, $CHCl_3$)
3	$[\alpha]_D^{27}$ +29.7 (*c* 0.52, $CHCl_3$)[4]	$[\alpha]_D^{22}$ +28 (*c* 0.3, $CHCl_3$)
4	$[\alpha]_D^{21}$ +8.1 (*c* 0.2, $CHCl_3$)[5]	$[\alpha]_D^{21}$ +6.7 (*c* 0.1, $CHCl_3$)

Table S6. UV values of compounds **1–4**.

compound	literature data (λ_{max} MeOH)	experimental data(λ_{max} MeOH)
1	263[5]	258
2	262[2]	257
3	262[3]	260
4	263[3]	261

References

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