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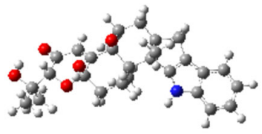
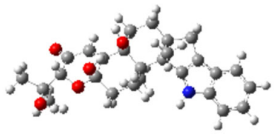
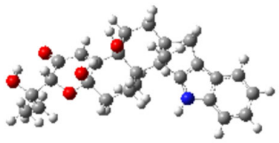
Table S1. The NMR data of **1** (DMSO-d_6, δ in ppm, J in Hz) and 7α-hydroxypaxilline ($CDCl_3$, δ in ppm, J in Hz).

No.	Compound **1**		7α-hydroxypaxilline [1]
	δ_C	δ_H	δ_H
1-NH		10.76 (1H, s)	7.68 (1H, s)
2	152.7, C		
3	50.4, C		
4	42.6, C		
5	25.3, CH_2	2.51 (1H, m) 1.83 (1H, m)	2.68 (1H, m) 1.43 (1H, m)
6	35.1, CH_2	2.18 (1H, m) 2.13 (1H, m)	2.07 (1H, m) 2.25 (1H, m)
7	93.8, C		
9	78.1, CH	4.16 (1H, s)	4.30 (1H, s)
10	198.3, C		
11	120.5, CH	5.76 (1H, s)	5.82 (1H, s)
12	161.4, C		
13	76.1, C		
14	32.6, CH_2	1.85 (1H, m) 1.70 (1H, m)	1.98 (1H, m) 1.67 (1H, m)
15	21.0, CH_2	1.94 (1H, m) 1.64 (1H, m)	2.02 (1H, m) 1.98 (1H, m)
16	49.4, CH	2.77 (1H, m)	2.78 (1H, m)
17	26.9, CH_2	2.62 (1H, m) 2.33 (1H, m)	2.68 (1H, m) 2.39 (1H, m)
18	115.0, C		
19	124.5, C		
20	117.7, CH	7.27 (1H, t, 7.0)	7.38 (1H, m)
21	118.5, CH	6.90 (1H, t, 7.4)	7.01 (1H, m)
22	119.3, CH	6.94 (1H, t, 7.6)	7.01 (1H, m)
23	111.8, CH	7.27 (1H, t, 7.0)	7.20 (1H, m)
24	139.8, C		
25	16.2, CH_3	1.18 (3H, s)	1.10 (3H, s)
26	19.0, CH_3	0.93 (3H, s)	1.02 (3H, s)
27	71.1, C		
28	26.2, CH_3	1.19 (3H, s)	1.19 (3H, s)
29	26.1, CH_3	1.26 (3H, s)	1.32 (3H, s)
7-OH			3.62 (1H, s)
13-OH		5.03 (1H, s)	3.92 (1H, s)
27-OH		4.32 (1H, s)	3.80 (1H, s)

Table S2. The NMR data of **2-4**, paspaline, paspalinine and 4a-demethylpaspaline-4a-carboxylic acid (DMSO-d_6, δ in ppm, J in Hz).

No.	2	Paspaline [2,3]	3	Paspalinine [4]	4	4a-Demethylpaspaline-4a-carboxylic acid [5]
	δ_C	δ_C	δ_C	δ_C	δ_C	δ_C
2	151.2, C	151.1, C	152.8, C	152.7, C	151.0, C	151.0, C
3	52.5, C	52.4, C	51.0, C	51.0, C	51.7, C	51.7, C
4	40.1, C	39.4, C	39.2, C	39.2, C	40.1, C	39.9, C
5	32.5, CH_2	32.4, CH_2	25.9, CH_2	26.1, CH_2	32.4, CH_2	32.4, CH_2
6	25.1, CH_2	25.0, CH_2	28.0, CH_2	28.0, CH_2	25.2, CH_2	25.2, CH_2
7	85.2, C	85.2, C	104.2, C	104.3, C	83.6, CH	83.7, CH
9	84.6, CH	84.5, CH	86.9, CH	87.1, CH	84.2, CH	84.3, CH
10	21.1, CH_2	21.0, CH_2	197.0, C	196.6, C	22.8, CH_2	22.8, CH_2
11	37.2, CH_2	37.2, CH_2	116.8, CH	116.8, CH	35.3, CH_2	35.3, CH_2
12	36.1, C	36.0, C	169.7, C	169.5, C	47.3, C	47.3, C
13	45.9, CH	45.9, CH	76.0, C	76.0, C	46.0, CH	46.1, CH
14	21.5, CH_2	21.5, CH_2	31.8, CH_2	32.0, CH_2	24.4, CH_2	21.6, CH_2
15	24.5, CH_2	24.5, CH_2	21.0, CH_2	21.0, CH_2	24.8, CH_2	24.8, CH_2
16	48.6, CH	48.5, CH	48.5, CH	48.5, CH	48.6, CH	48.7, CH
17	27.1, CH_2	27.0, CH_2	27.2, CH_2	27.3, CH_2	27.0, CH_2	27.0, CH_2
18	115.8, C	115.8, C	114.9, C	114.9, C	115.9, C	115.9, C
19	124.4, C	124.4, C	124.6, C	124.7, C	124.4, C	124.4, C
20	117.6, CH	117.5, CH	119.3, CH	119.1, CH	117.6, CH	117.7, CH
21	118.4, CH	118.3, CH	118.5, CH	118.4, CH	118.4, CH	118.5, CH
22	119.3, CH	119.3, CH	117.7, CH	117.6, CH	119.4, CH	119.4, CH
23	111.9, CH	111.8, CH	111.9, CH	111.8, CH	111.9, CH	111.9, CH
24	140.3, C	140.2, C	140.1, C	140.1, C	140.2, C	140.3, C
25	14.6, CH_3	14.5, CH_3	16.4, CH_3	16.3, CH_3	14.5, CH_3	14.5, CH_3
26	19.4, CH_3	19.4, CH_3	22.5, CH_3	22.5, CH_3	16.2, CH_3	16.2, CH_3
27	12.6, CH_3	12.6, CH_3	77.9, C	77.8, C	175.3, C	175.4, C
28	70.4, C	70.4, C	22.9, CH_3	22.8, CH_3	70.4, C	70.4, C
29	24.6, CH_3	24.6, CH_3	28.5, CH_3	28.6, CH_3	23.4, CH_3	24.5, CH_3
30	27.0, CH_3	26.8, CH_3			27.0, CH_3	27.0, CH_3

Table S3. Energies of the dominative conformers of compound **1**.

Compounds	No.	Structure	E (Hartree)	Population (%)
Compound 1	1		-1479.933308 12	86.17
	2		-1479.929718 53	0.57
	3		-1479.932361 16	13.26

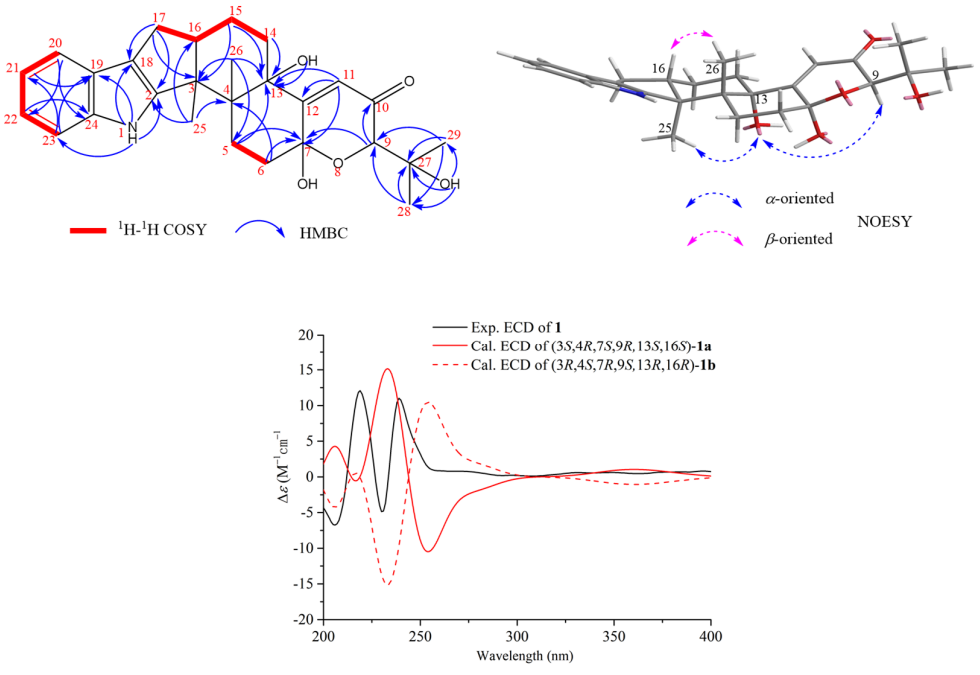


Figure S1. Key HMBC, ^{1}H−^{1}H COSY, NOESY correlations, and experimental and calculated ECD spectra of compound **1**.

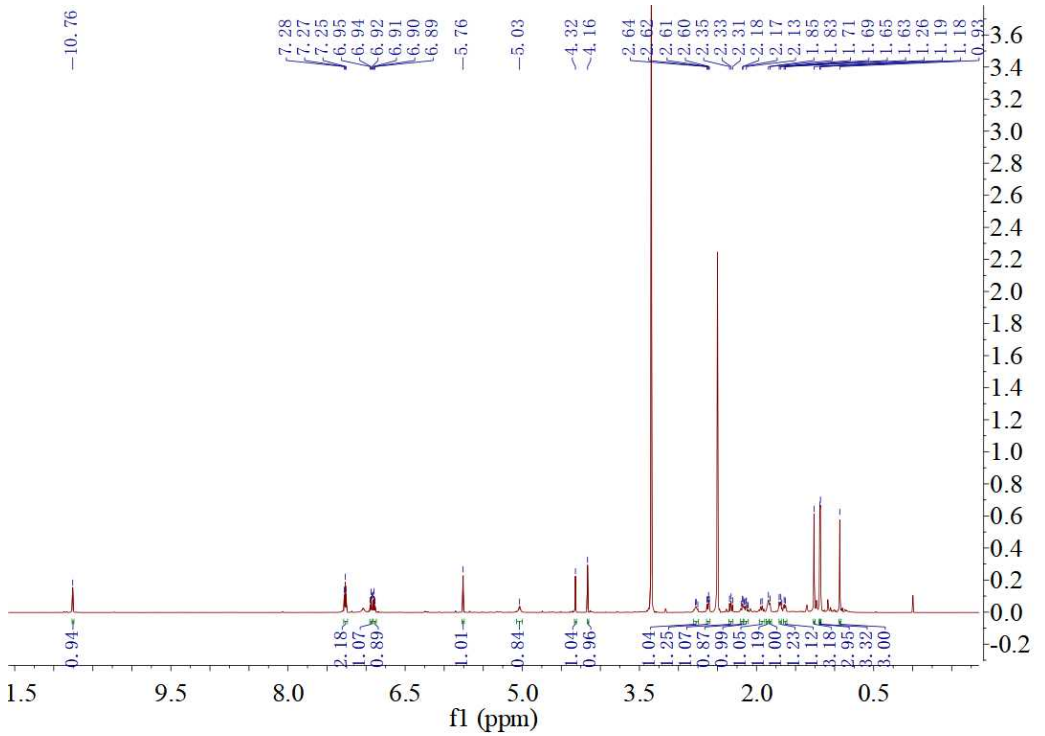


Figure S2. ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

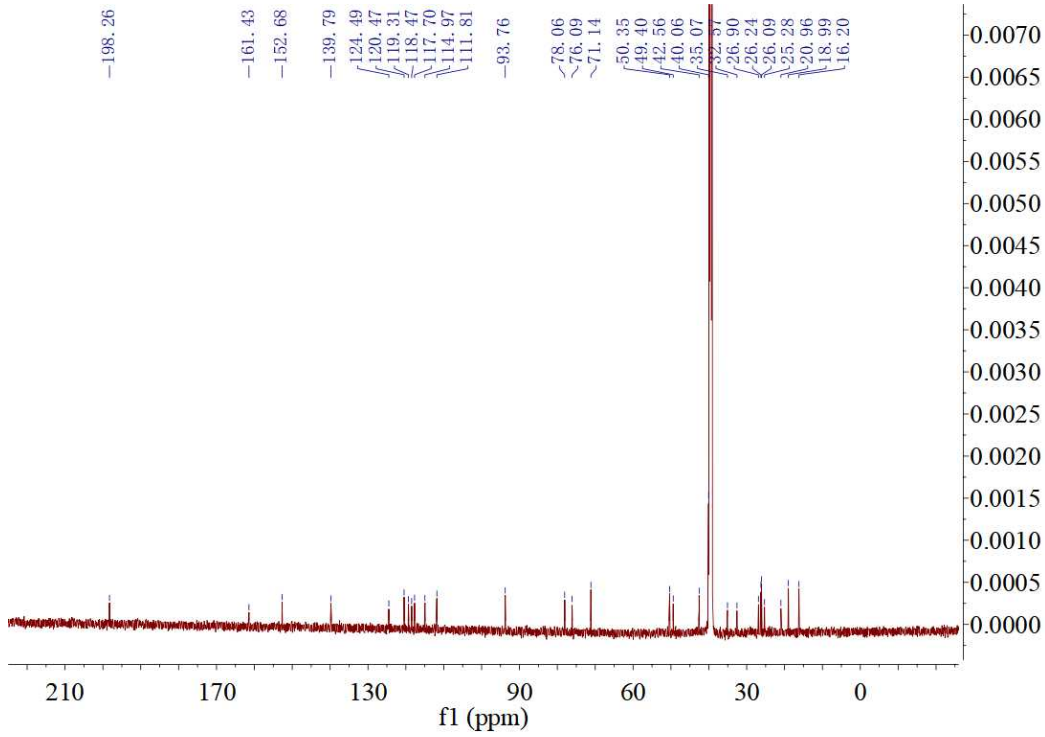


Figure S3. ^{13}C NMR spectrum of compound **1** in DMSO-d_6.

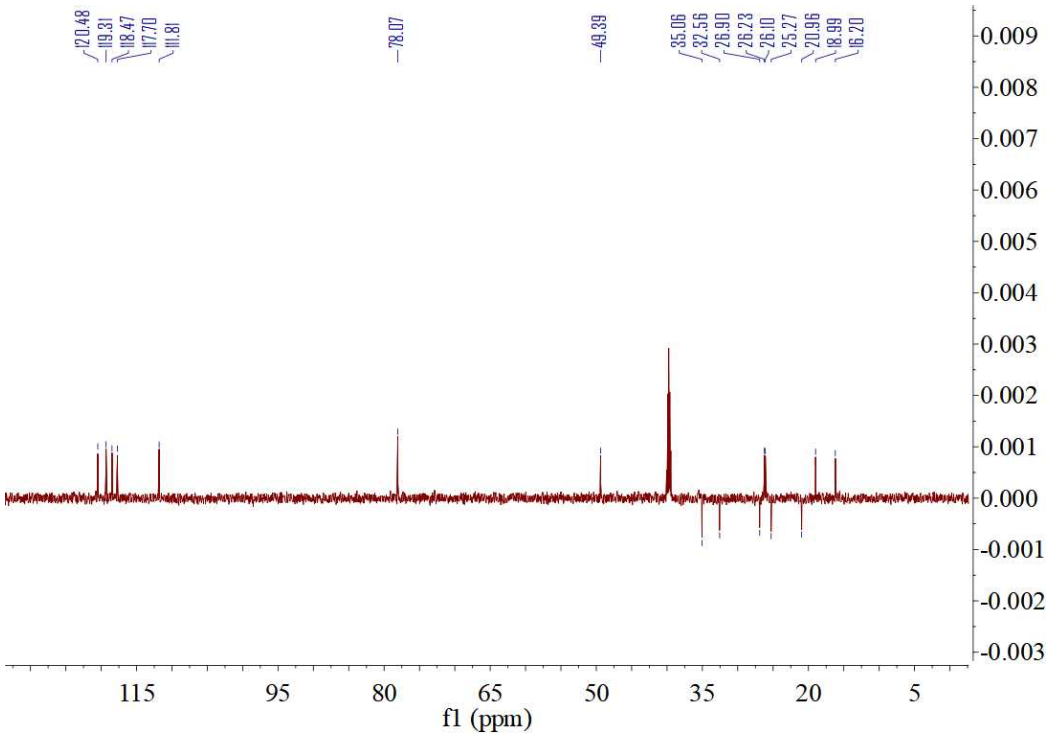


Figure S4. DEPT135 NMR spectra of compound **1** in DMSO-d_6.

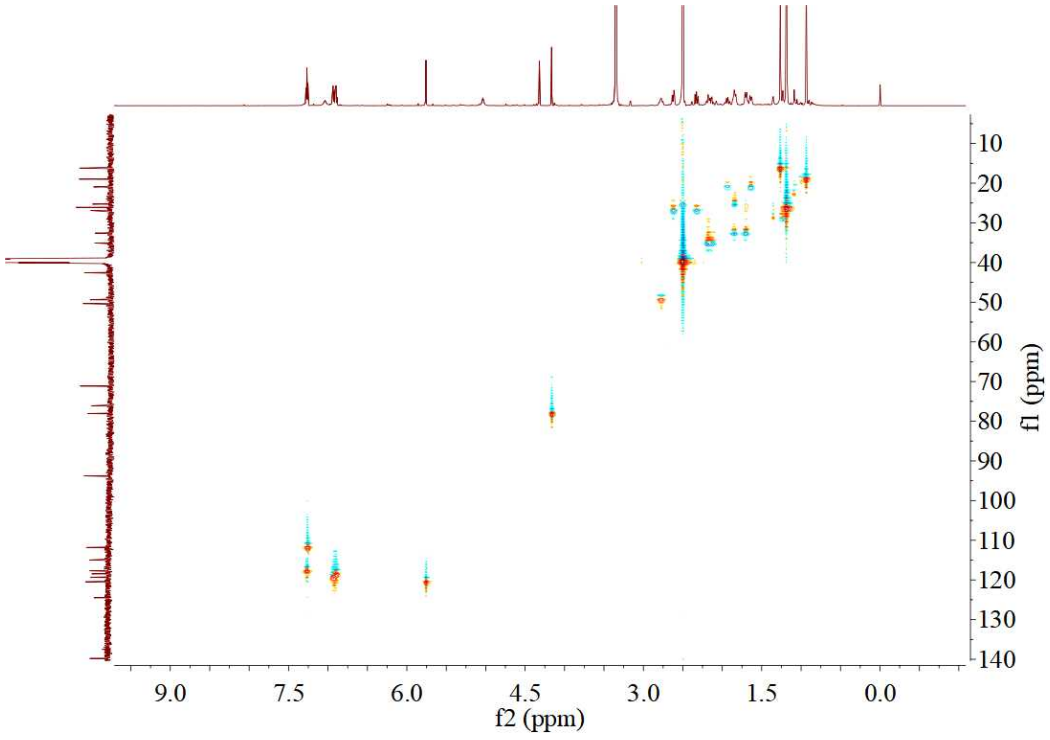


Figure S5. HSQC spectra of compound **1** in DMSO-d_6.

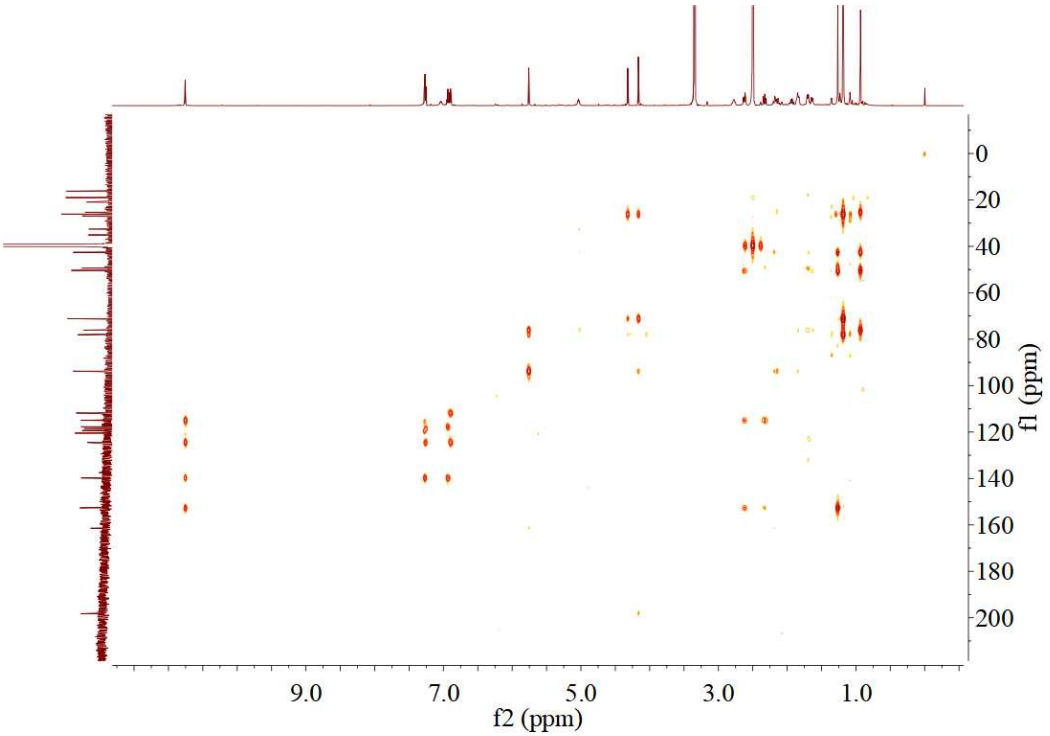


Figure S6. HMBC spectra of compound **1** in DMSO-d_6.

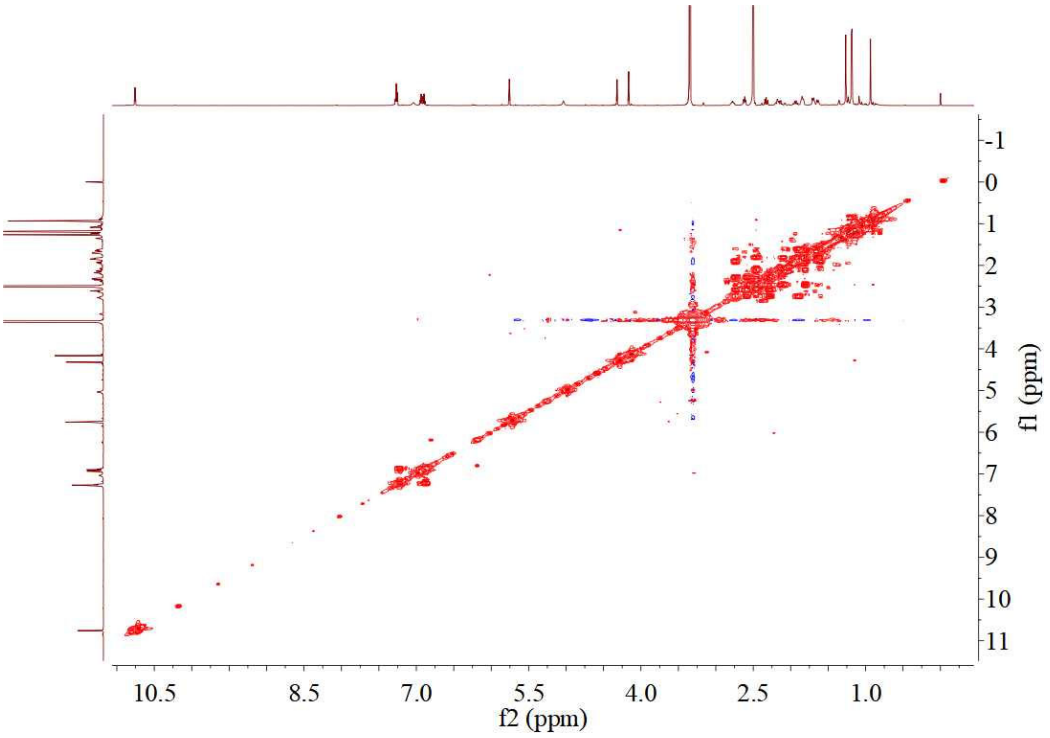


Figure S7. $^{1}H-^{1}H$ COSY spectra of compound **1** in DMSO-d_6.

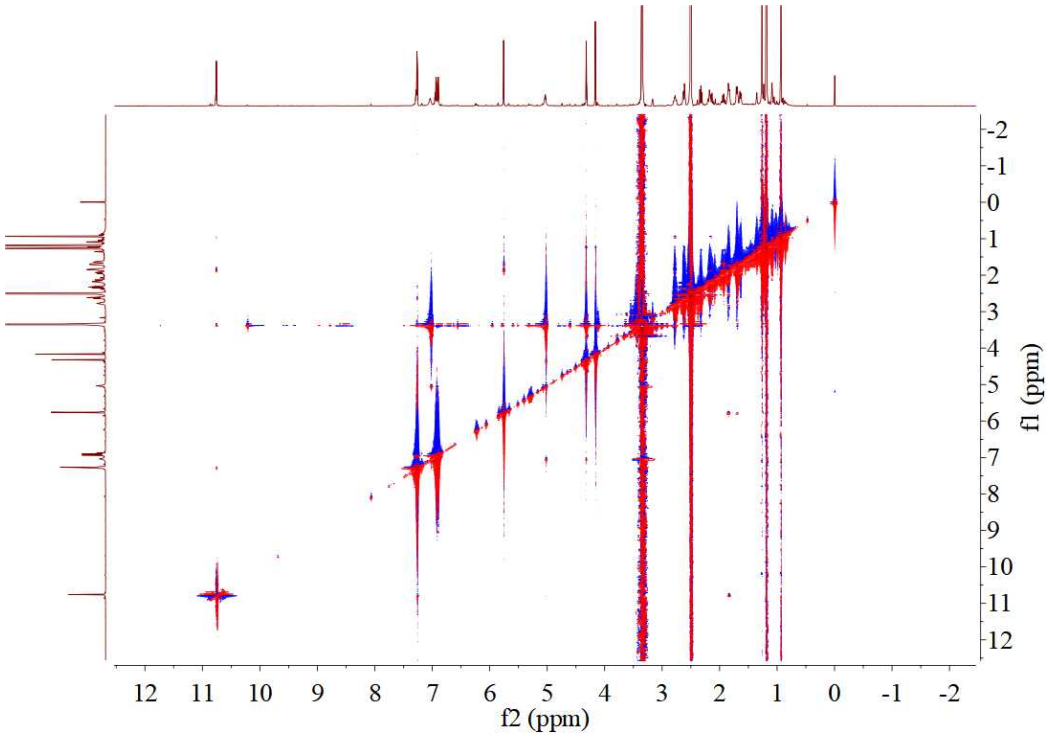


Figure S8. NOESY spectra of compound **1** in DMSO-d_6.

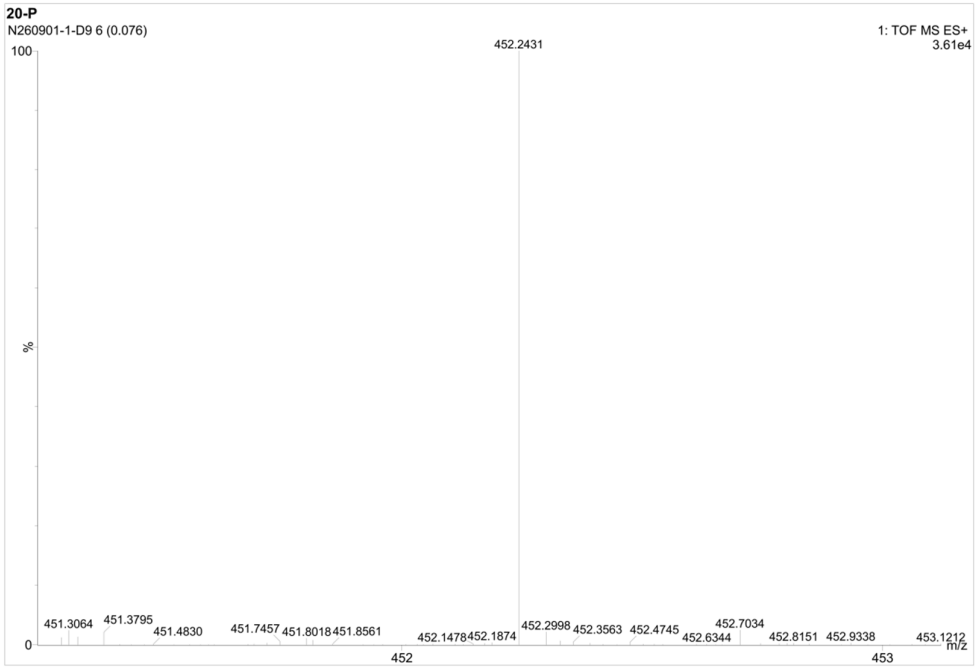


Figure S9. (+)-HRESIMS spectrum of compound **1.**

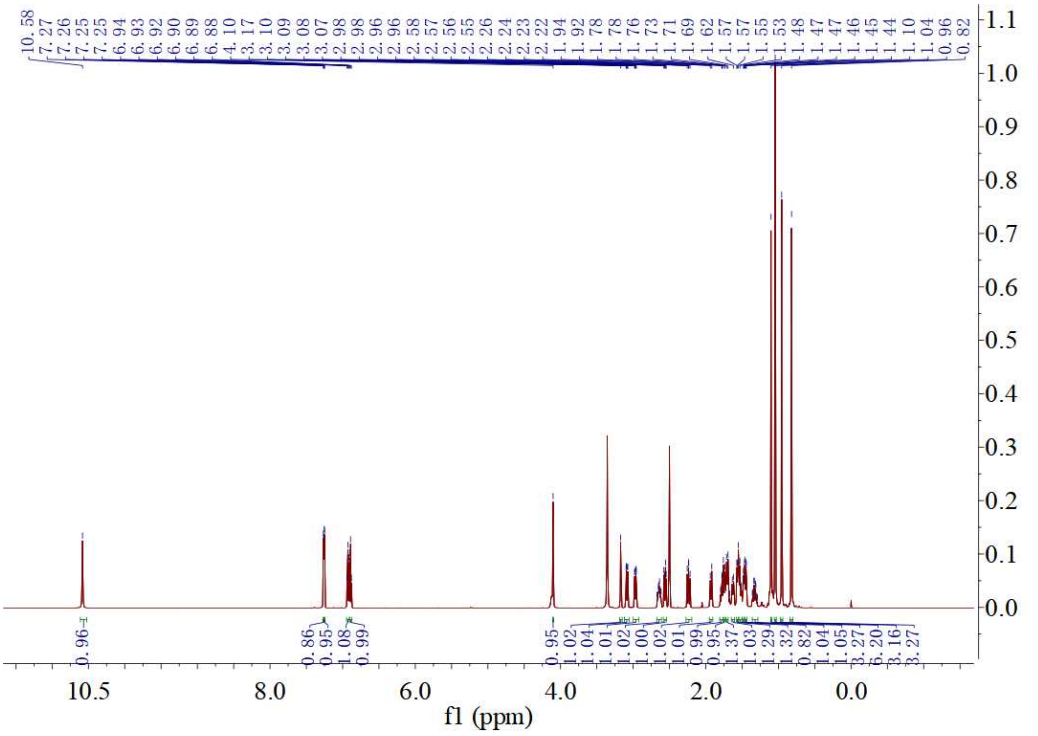


Figure S10. ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

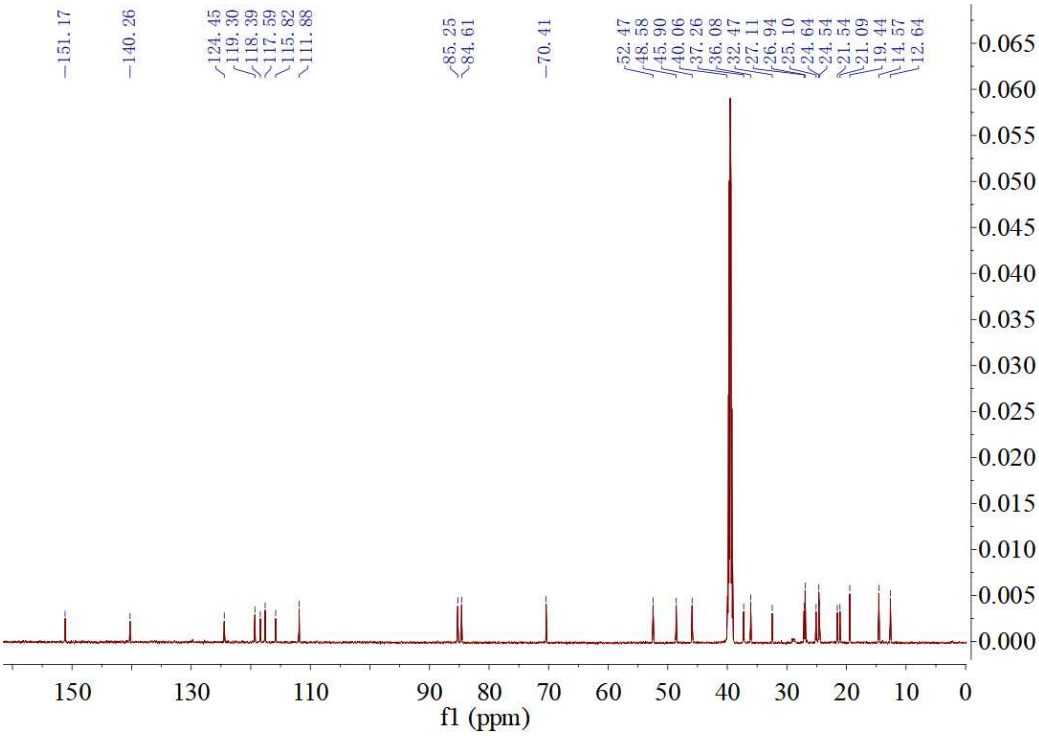


Figure S11. ^{13}C NMR spectrum of compound **2** in DMSO-d_6.

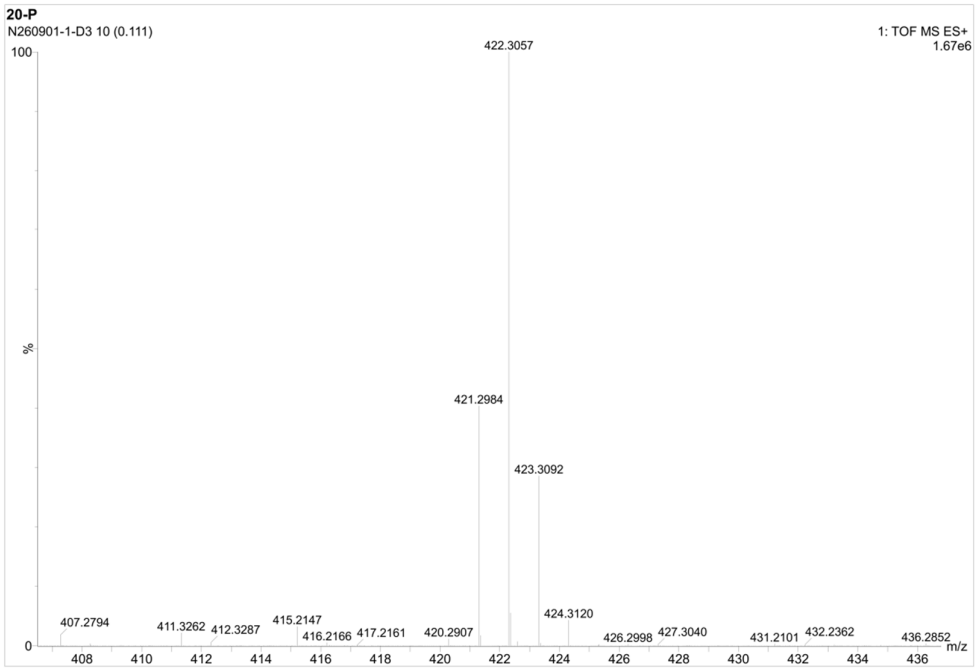


Figure S12. (+)-HRESIMS spectrum of compound **2.**

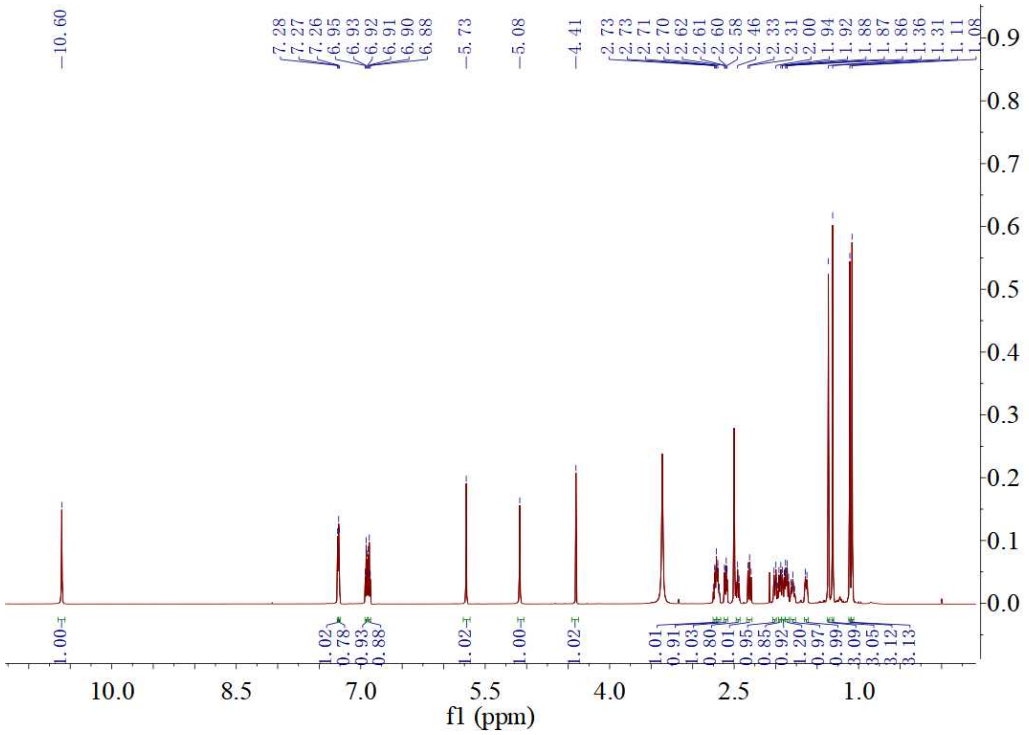


Figure S13. ^{1}H NMR spectrum of compound **3** in DMSO-d_6.

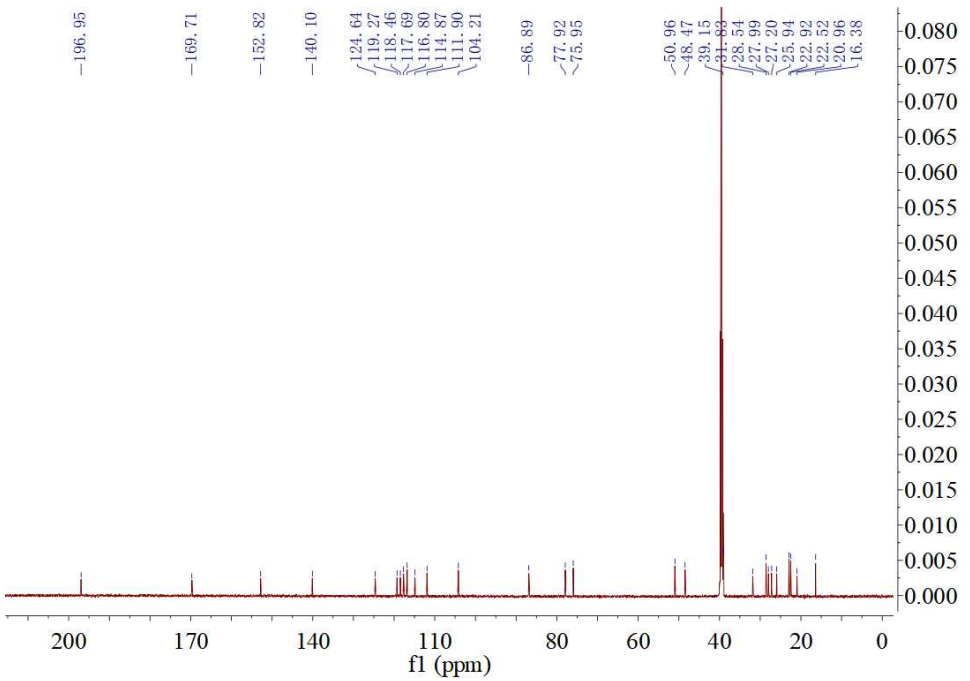


Figure S14. ^{13}C NMR spectrum of compound **3** in DMSO-d_6.

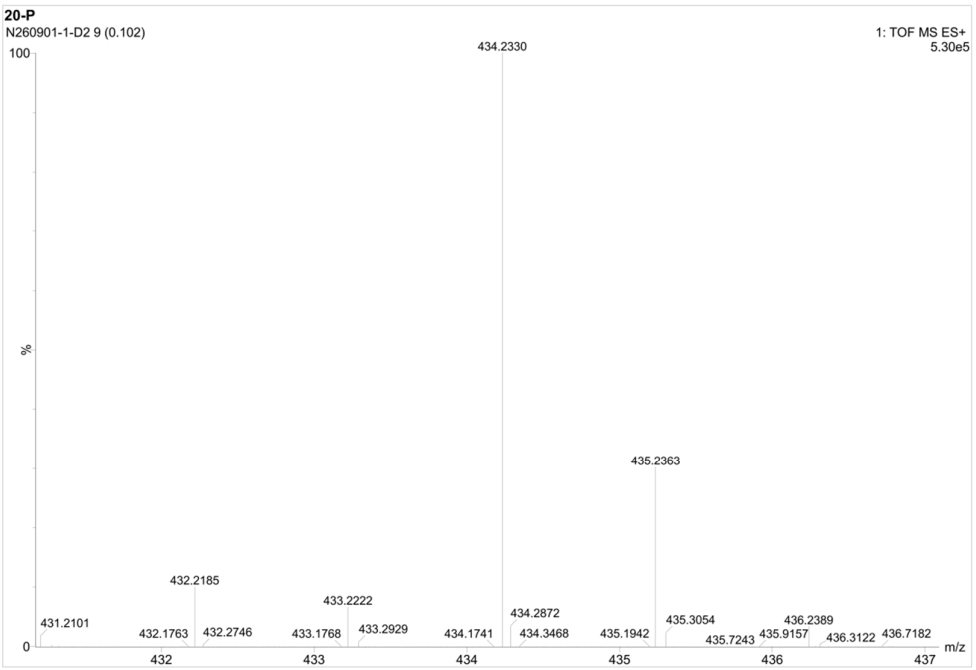


Figure S15. (+)-HRESIMS spectrum of compound **3.**

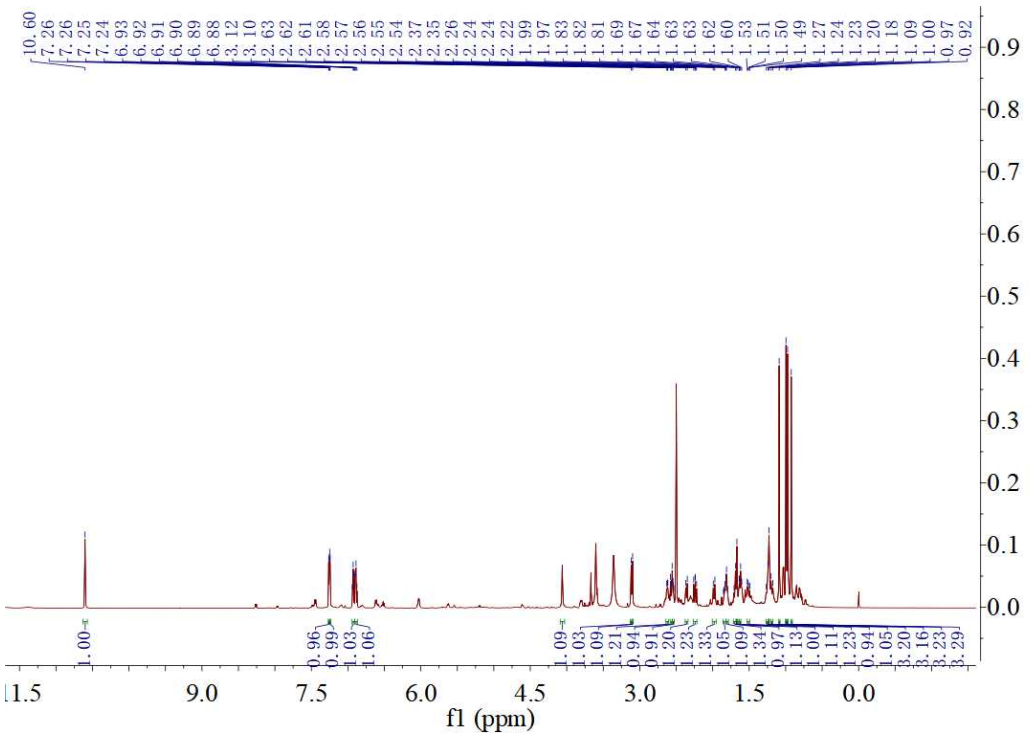


Figure S16. ^{1}H NMR spectrum of compound **4** in DMSO-d_6.

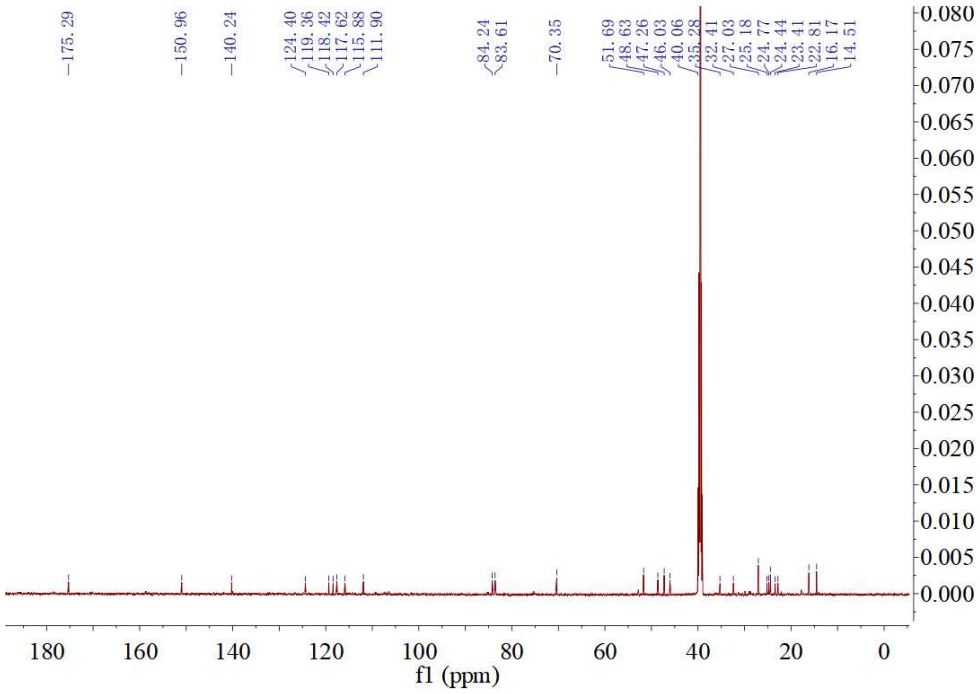


Figure S17. ^{13}C NMR spectrum of compound **4** in DMSO-d_6.

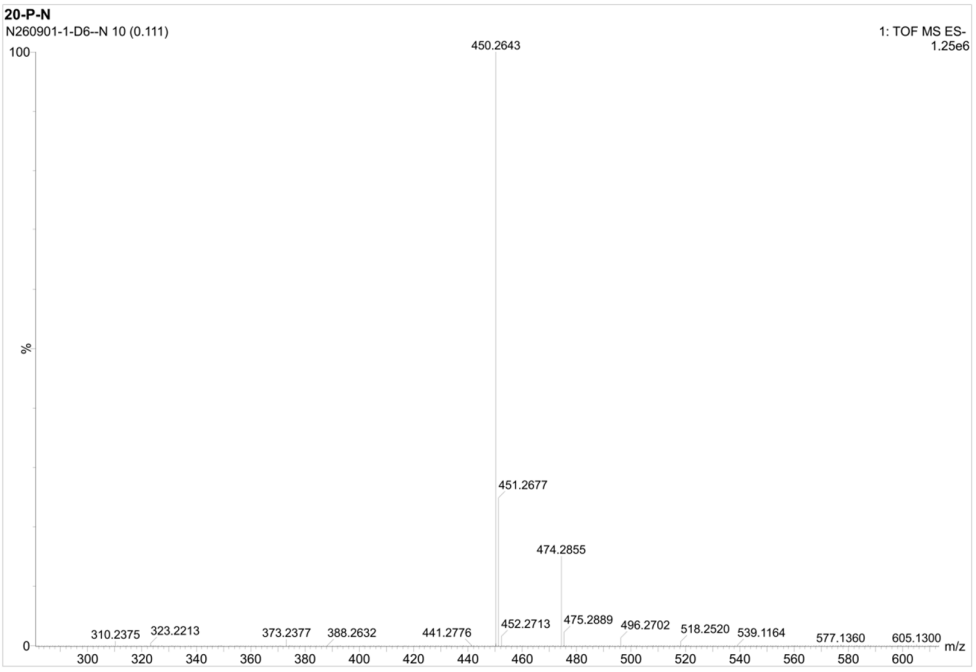


Figure S18. (–)-HRESIMS spectrum of compound **4.**

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