

## Supporting Information

### New steroidal saponins from the rhizomes of *Paris vietnamensis* and their cytotoxicity

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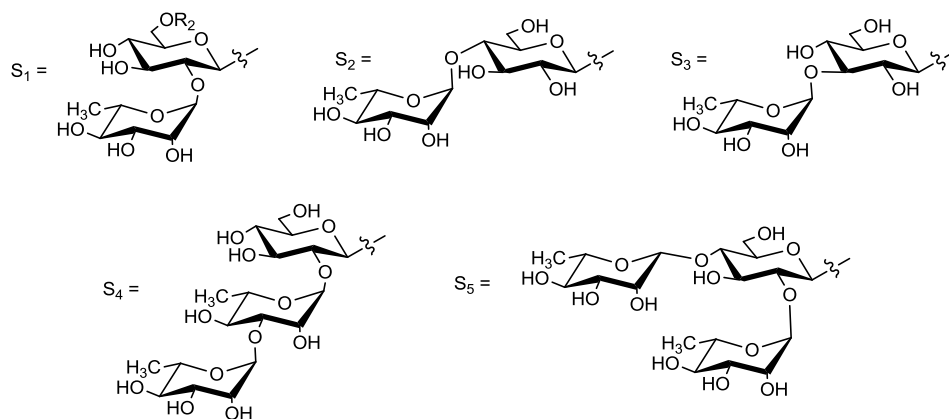
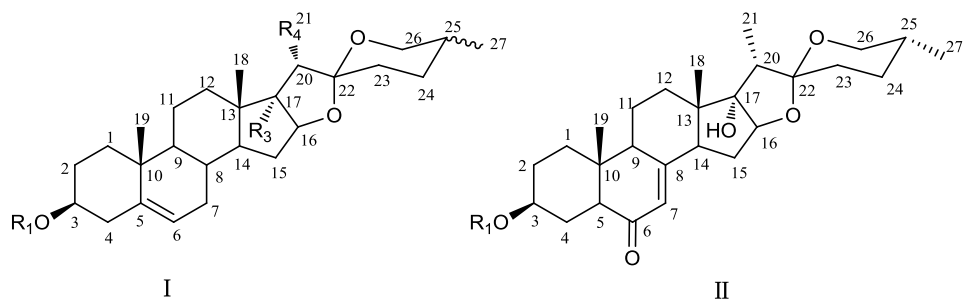
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	Aglycone	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Configuration of C-25
<b>1</b>	I	S <sub>1</sub>	COCH <sub>3</sub>	OH	CH <sub>3</sub>	25R
<b>2</b>	I	S <sub>1</sub>	H	OH	CH <sub>2</sub> OH	25R
<b>3</b>	II	S <sub>1</sub>	H	-	-	25R
<b>4</b>	II	S <sub>2</sub>	H	-	-	25R
<b>5</b>	I	S <sub>1</sub>	H	OH	CH <sub>3</sub>	25R
<b>6</b>	I	S <sub>1</sub>	H	OH	CH <sub>3</sub>	25S
<b>7</b>	I	S <sub>3</sub>	H	OH	CH <sub>3</sub>	25R
<b>8</b>	I	S <sub>4</sub>	H	H	CH <sub>3</sub>	25R
<b>9</b>	I	S <sub>5</sub>	H	OH	CH <sub>3</sub>	25R
<b>10</b>	I	S <sub>1</sub>	H	H	CH <sub>3</sub>	25R

**Figure S1** Structures of compounds **1–10** from *Paris vietnamensis*

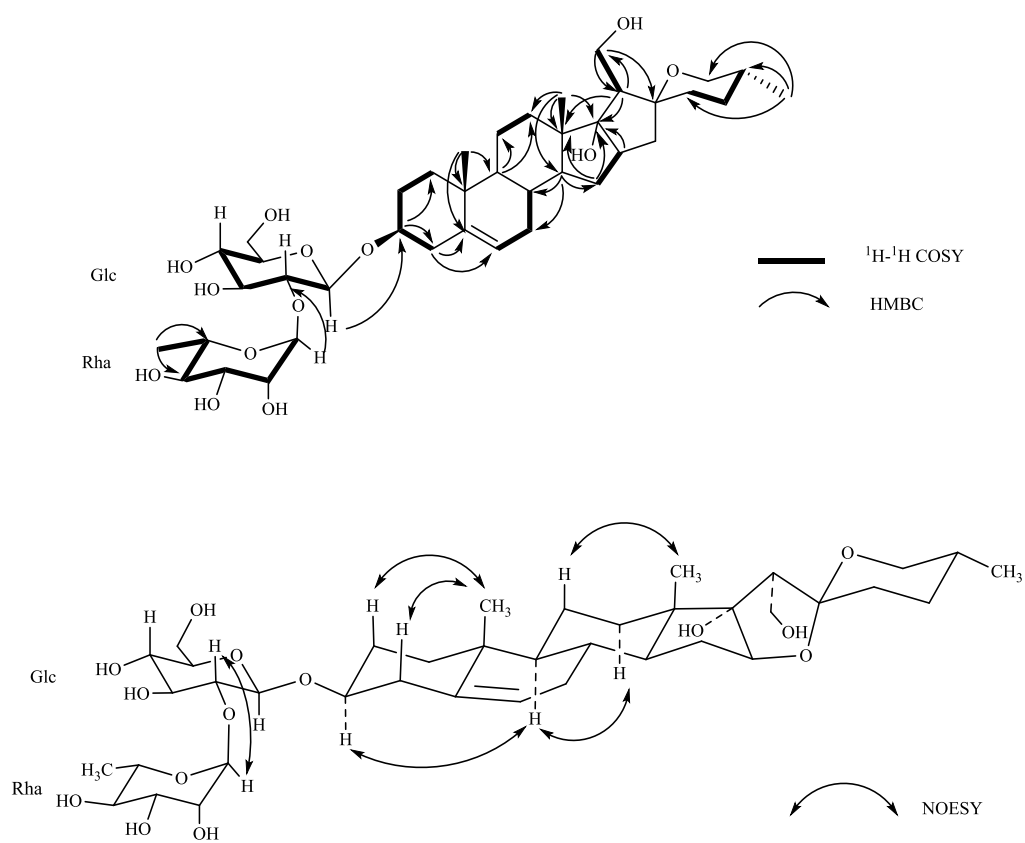


Figure S2 Key <sup>1</sup>H-<sup>1</sup>H COSY, HMBC and NOESY correlations of compound 2

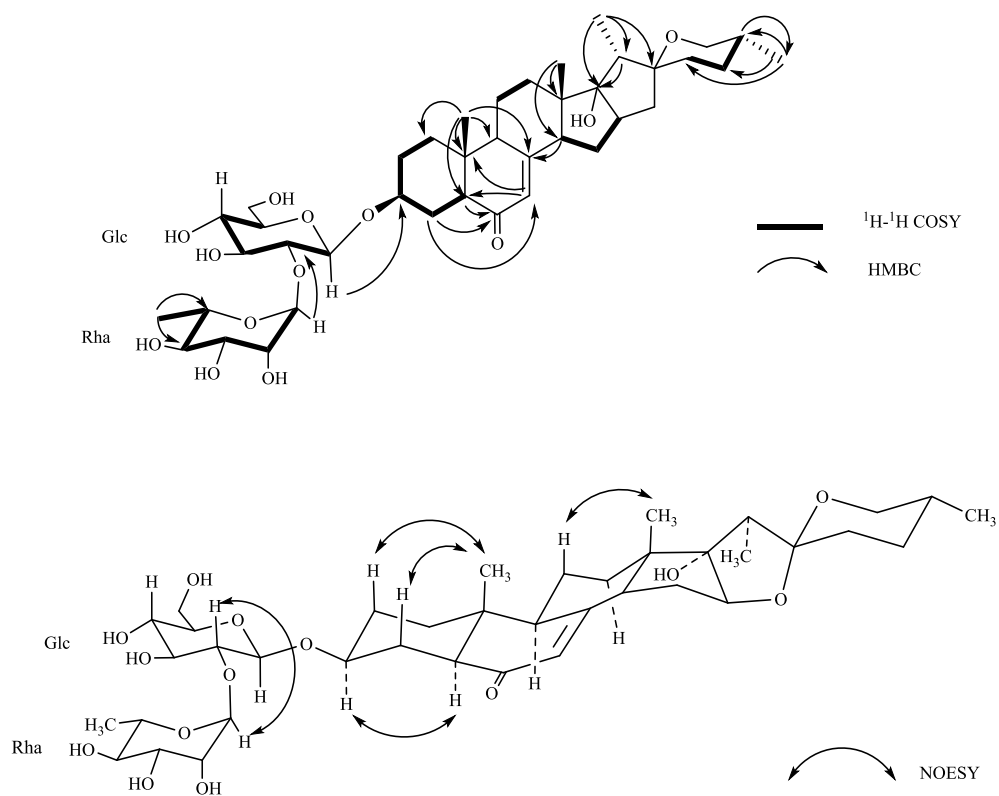


Figure S3 Key <sup>1</sup>H-<sup>1</sup>H COSY, HMBC and NOESY correlations of compound 3

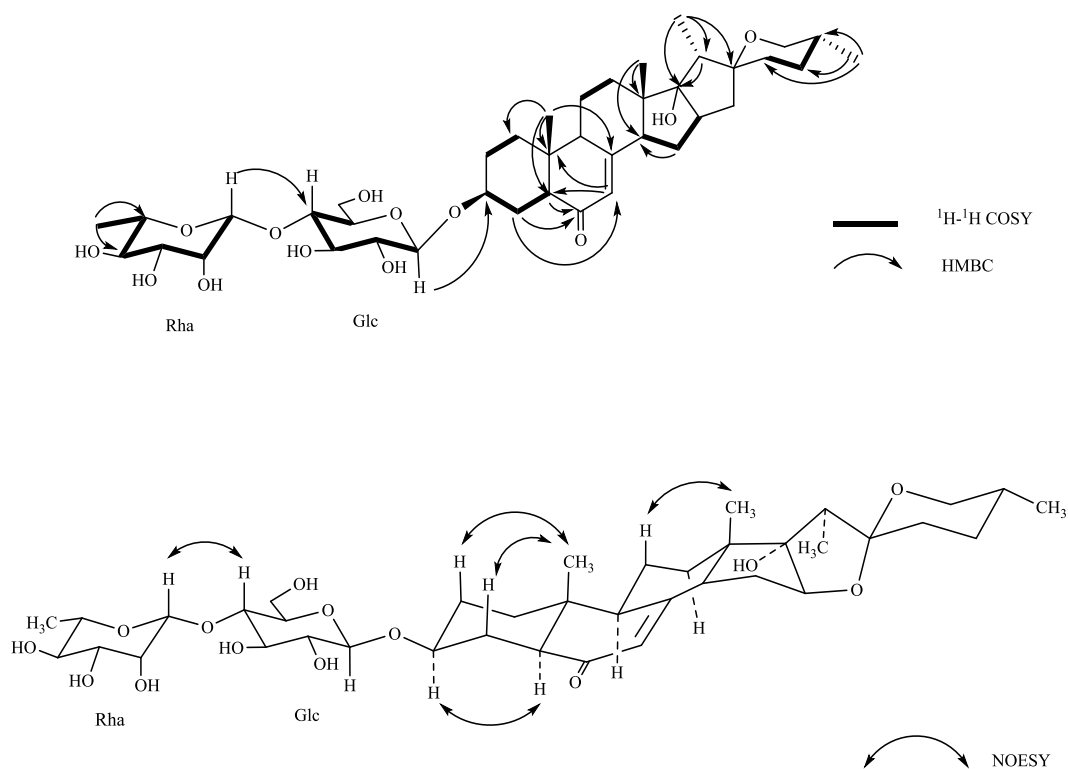


Figure S4 Key  $^1\text{H}$ - $^1\text{H}$  COSY, HMBC and NOESY correlations of compound 4

### Physical and spectroscopic data of compounds 5–10

**Compound 5:** White amorphous powder;  $^1\text{H}$ -NMR (500MHz,  $\text{CD}_3\text{OD}$ )  $\delta_{\text{H}}$ : 0.83 (3H, *s*, H-18), 1.05 (3H, *s*, H-19), 0.89 (3H, *d*,  $J = 6.4$  Hz, H-21), 0.80 (3H, *d*,  $J = 7.2$  Hz, H-27), 5.39 (1H, *br s*, H-6), 1.26 (3H, *d*,  $J = 6.24$  Hz, Me of Rha I), 4.48 (1H, *d*,  $J = 7.76$  Hz, Glc H-1), 5.20 (1H, *br s*, Rha H-1);  $^{13}\text{C}$ -NMR data, see **Table S1** and **Table S2**; ESI-MS (negative ion mode) 737  $[\text{M} - \text{H}]^-$ . Compared to the physical and spectroscopic data with literature values, compound 5 was identified as 25(*R*)-spirost-5-en-3 $\beta$ ,17 $\alpha$ -diol-3-*O*- $\alpha$ -L-rhamnopyranosyl-2- $\beta$ -D-glucopyranoside [1].

**Compound 6:** White amorphous powder;  $^1\text{H}$ -NMR (500MHz,  $\text{CD}_3\text{OD}$ )  $\delta_{\text{H}}$ : 0.89 (3H, *s*, H-18), 1.06 (3H, *s*, H-19), 0.93 (3H, *d*,  $J = 7.44$  Hz, H-21), 1.09 (3H, *d*,  $J = 7.12$  Hz, H-27), 5.39 (1H, *br s*, H-6), 1.24 (3H, *d*,  $J = 6.24$  Hz, Me of Rha I), 4.48 (1H, *d*,  $J = 7.76$  Hz, Glc

H-1), 5.19 (1H, *br s*, Rha H-1); <sup>13</sup>C-NMR data, see **Table S1** and **Table S2**; ESI-MS (negative ion mode) 737 [M – H]<sup>–</sup>. Compared to the physical and spectroscopic data with literature values, compound **6** was identified as 25(*S*)-spirost-5-en-3β,17α-diol-3-*O*-α-*L*-rhamnopyranosyl-(1 → 2)-β-*D*-glucopyranoside [2].

*Compound 7*: White amorphous powder; <sup>1</sup>H-NMR (500MHz, CD<sub>3</sub>OD) δ<sub>H</sub>: 0.83 (3H, *s*, H-18), 1.05 (3H, *s*, H-19), 0.89 (3H, *d*, *J* = 7.2 Hz, H-21), 0.80 (3H, *d*, *J* = 6.4 Hz, H-27), 5.39 (1H, *br s*, H-6), 1.24 (3H, *d*, *J* = 6.24 Hz, Me of Rha I), 4.48 (1H, *d*, *J* = 7.84 Hz, Glc H-1), 5.19 (1H, *br s*, Rha H-1); <sup>13</sup>C-NMR data, see **Table S1** and **Table S2**; ESI-MS (negative ion mode) 737 [M – H]<sup>–</sup>. Compared to the physical and spectroscopic data with literature values, compound **7** was identified as 25(*R*)-spirost-5-en-3β,17α-diol-3-*O*-α-*L*-rhamnopyranosyl-(1 → 3)-β-*D*-glucopyranoside [3].

*Compound 8*: White amorphous powder; <sup>1</sup>H-NMR (500MHz, CD<sub>3</sub>OD) δ<sub>H</sub>: 0.82 (3H, *s*, H-18), 1.07 (3H, *s*, H-19), 0.98 (3H, *d*, *J* = 7.0 Hz, H-21), 0.81 (3H, *d*, *J* = 6.4 Hz, H-27), 5.40 (1H, *br s*, H-6), 1.27 (3H, *d*, *J* = 6.25 Hz, Me of Rha I), 1.26 (3H, *d*, *J* = 6.25 Hz, Me of Rha II), 4.51 (1H, *d*, *J* = 7.8 Hz, Glc H-1), 5.22 (1H, *br s*, Rha I H-1), 4.85 (1H, *br s*, Rha II H-1); <sup>13</sup>C-NMR data, see **Table S1** and **Table S2**; ESI-MS (negative ion mode) 867 [M – H]<sup>–</sup>. Compared to the physical and spectroscopic data with literature values, compound **8** was identified as 25(*R*)-diosgenin-3-*O*-α-*L*-rhamnopyranosyl-(1 → 2)-α-*L*-rhamnopyranosyl-(1 → 3)-β-*D*-glucopyranoside [4].

*Compound 9*: White amorphous powder; <sup>1</sup>H-NMR (500MHz, CD<sub>3</sub>OD) δ<sub>H</sub>: 0.84 (3H, *s*,

H-18), 1.06 (3H, *s*, Me-19), 0.90 (3H, *d*,  $J = 7.25$  Hz, H-21), 0.80 (3H, *d*,  $J = 6.3$  Hz, H-27), 5.40 (1H, *br s*, H-6), 1.25 (3H, *d*,  $J = 6.25$  Hz, Me of Rha I), 1.27 (3H, *d*,  $J = 6.25$  Hz, Me of Rha II), 4.51 (1H, *d*,  $J = 7.85$  Hz, Glc H-1), 5.21 (1H, *br s*, Rha I H-1), 4.85 (1H, *br s*, Rha II H-1);  $^{13}\text{C}$ -NMR data, see **Table S1** and **Table S2**; ESI-MS (negative ion mode) 883  $[\text{M} - \text{H}]^-$ . Compared to the physical and spectroscopic data with literature values, compound **9** was identified as 25(*R*)-spirost-5-en-3 $\beta$ ,17 $\alpha$ -diol-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1  $\rightarrow$  4)-[ $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)]- $\beta$ -D-glucopyranoside [5].

*Compound 10*: White amorphous powder;  $^1\text{H}$ -NMR (500MHz,  $\text{CD}_3\text{OD}$ )  $\delta_{\text{H}}$ : 0.81 (3H, *s*, H-18), 1.05 (3H, *s*, Me-19), 0.96 (3H, *d*,  $J = 7.0$  Hz, H-21), 0.79 (3H, *d*,  $J = 6.4$  Hz, H-27), 5.38 (1H, *br s*, H-6), 1.24 (3H, *d*,  $J = 6.25$  Hz, Me of Rha), 4.48 (1H, *d*,  $J = 7.75$  Hz, Glc H-1), 5.19 (1H, *br s*, Rha H-1);  $^{13}\text{C}$ -NMR data, see **Table S1** and **Table S2**; ESI-MS (negative ion mode) 721  $[\text{M} - \text{H}]^-$ . Compared to the physical and spectroscopic data with literature values, compound **10** was identified as 25(*R*)-diosgenin-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\beta$ -D- glucopyranoside [6].

**Table S1**  $^{13}\text{C}$ -NMR data of the aglycone moieties of compounds 5-10

Position	Compounds					
	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
1	38.74	38.74	38.74	38.70	38.72	38.70
2	30.91	30.90	30.91	.0.89	30.87	30.89



3	79.32	79.33	79.32	79.43	79.39	79.35
4	39.66	39.66	39.66	39.65	39.63	39.66
5	142.05	142.06	142.05	142.04	141.99	142.07
6	122.75	122.72	122.75	122.78	122.78	122.74
7	32.66	33.36	32.66	32.88	32.64	32.89
8	33.44	33.38	33.44	32.93	33.41	32.93
9	51.64	51.62	51.63	51.84	51.59	51.85
10	38.15	38.15	38.15	38.19	38.12	38.19
11	21.84	21.91	21.84	22.12	21.84	22.13
12	33.01	33.38	33.00	41.08	32.98	41.08
13	46.00	46.49	46.00	41.57	45.97	41.56
14	54.08	53.36	54.07	57.95	54.05	57.95
15	32.25	32.94	32.25	33.32	32.24	33.35
16	90.69	89.78	90.69	82.35	90.68	82.36
17	91.45	90.06	91.45	63.89	91.43	63.88
18	17.67	18.01	17.67	16.69	17.69	16.92
19	19.99	19.98	19.99	19.99	19.99	19.99
20	45.68	46.75	45.68	43.06	45.66	43.05
21	9.25	10.06	9.25	15.01	9.27	15.03
22	111.10	112.31	111.10	110.73	111.09	110.73
23	33.37	22.49	33.37	32.57	33.36	32.57
24	29.59	25.33	29.59	30.03	29.57	30.03
25	31.44	28.58	31.44	31.58	31.42	31.59
26	67.86	69.56	67.86	68.00	67.84	68.00
27	17.64	16.67	17.64	17.64	17.65	17.64

**Table S2**  $^{13}\text{C}$ -NMR data of the sugar portion of compounds 5-10

Sugar portion	Compounds						
	5	6	7	8	9	10	
Glc	1	100.66	100.67	100.66	100.60	100.56	100.68

	2	79.18	79.18	79.54	79.45	79.46	79.18
	3	77.89	79.53	79.18	80.13	76.70	77.86
	4	79.54	77.88	77.89	76.72	80.06	79.52
	5	71.99	72.00	71.99	78.18	78.15	71.98
	6	62.91	62.91	62.91	62.09	62.07	62.91
Rha I	1	102.33	102.31	102.33	102.43	102.43	102.31
	2	72.38	72.37	72.38	72.33	72.30	72.36
	3	72.53	72.54	72.53	79.42	72.49	72.53
	4	74.09	74.10	74.09	73.87	74.04	74.07
	5	69.90	69.90	69.90	69.91	69.91	69.89
	6	18.11	18.11	18.11	18.13	18.02	18.11
Rha II	1				103.15	103.13	
	2				74.07	72.57	
	3				72.59	72.30	
	4				72.51	73.85	
	5				70.82	70.79	
	6				18.01	18.12	

## Reference

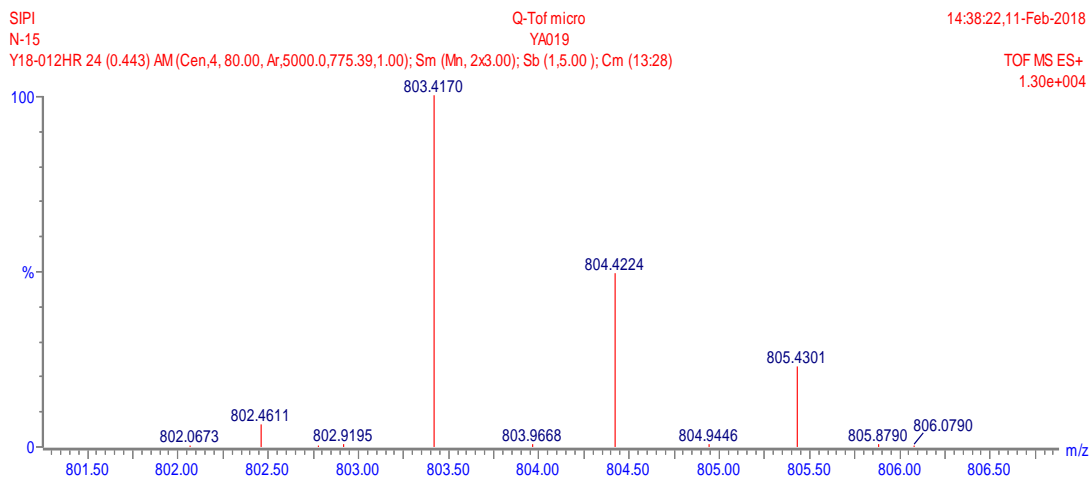
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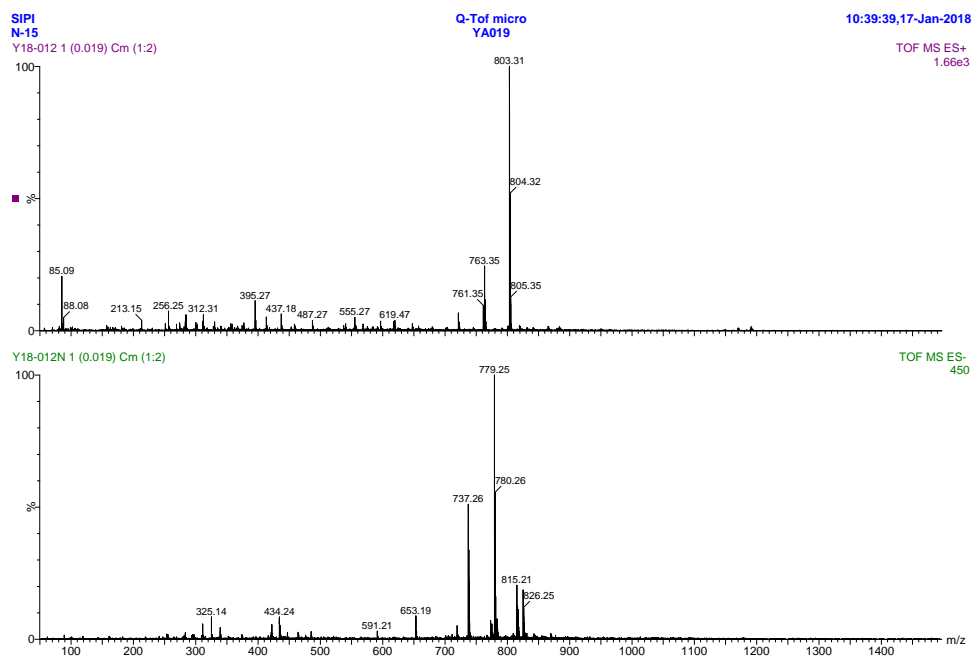
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#### S1. Positive HR-ESI-MS spectrum of compound **1**

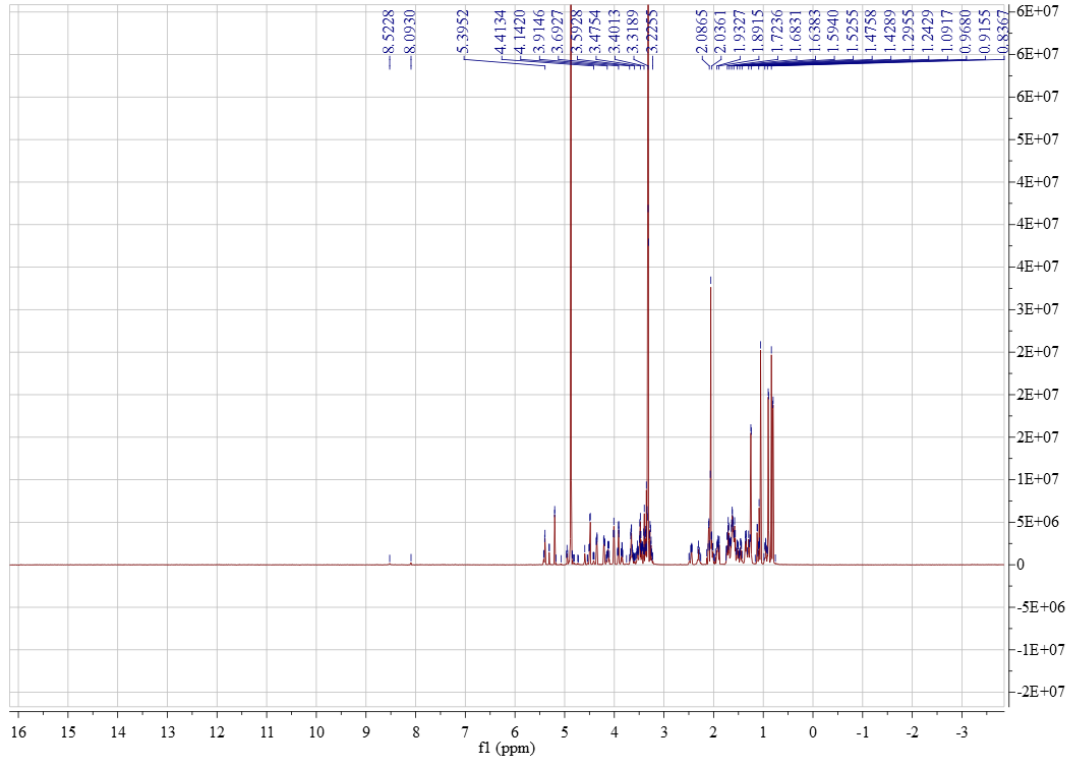
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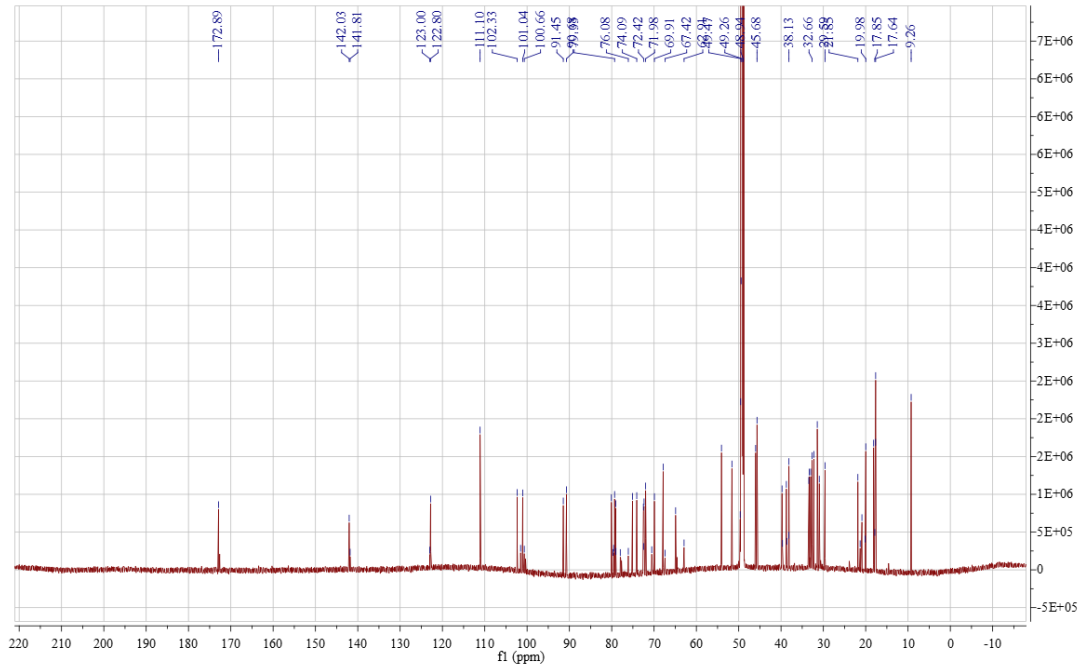
## S2. Positive and Negative ESI-MS spectrum of compound 1



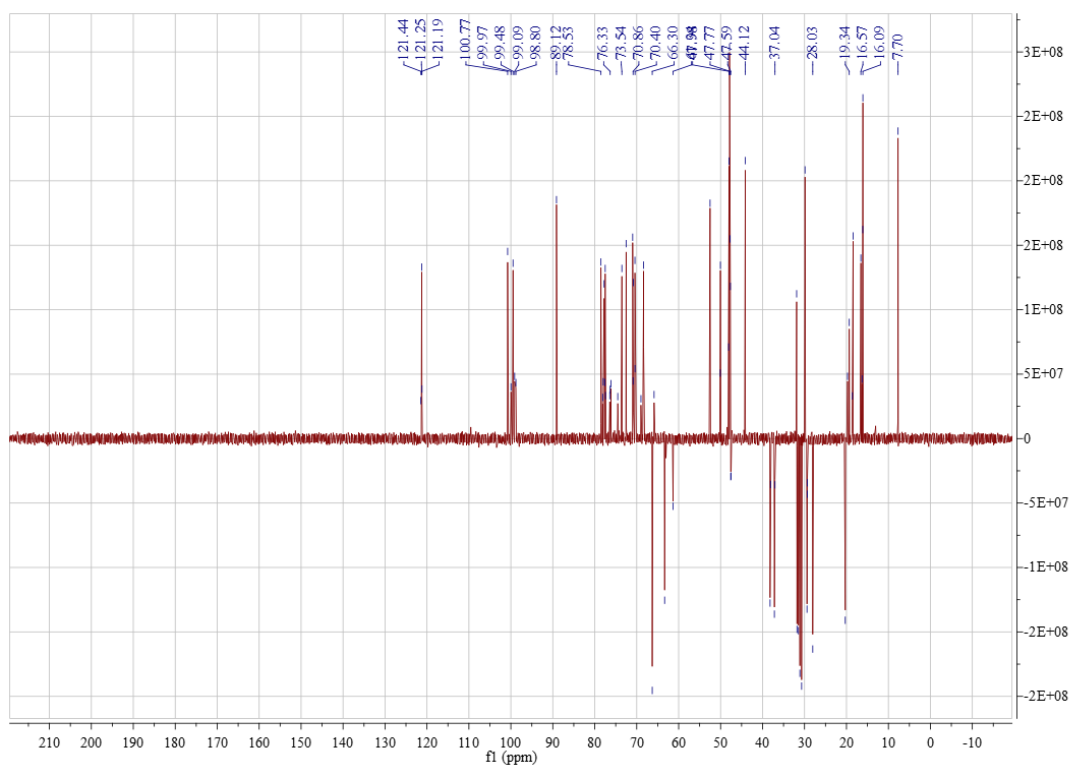
## S3. <sup>1</sup>H NMR (800 MHz, CD<sub>3</sub>OD) spectrum of compound 1



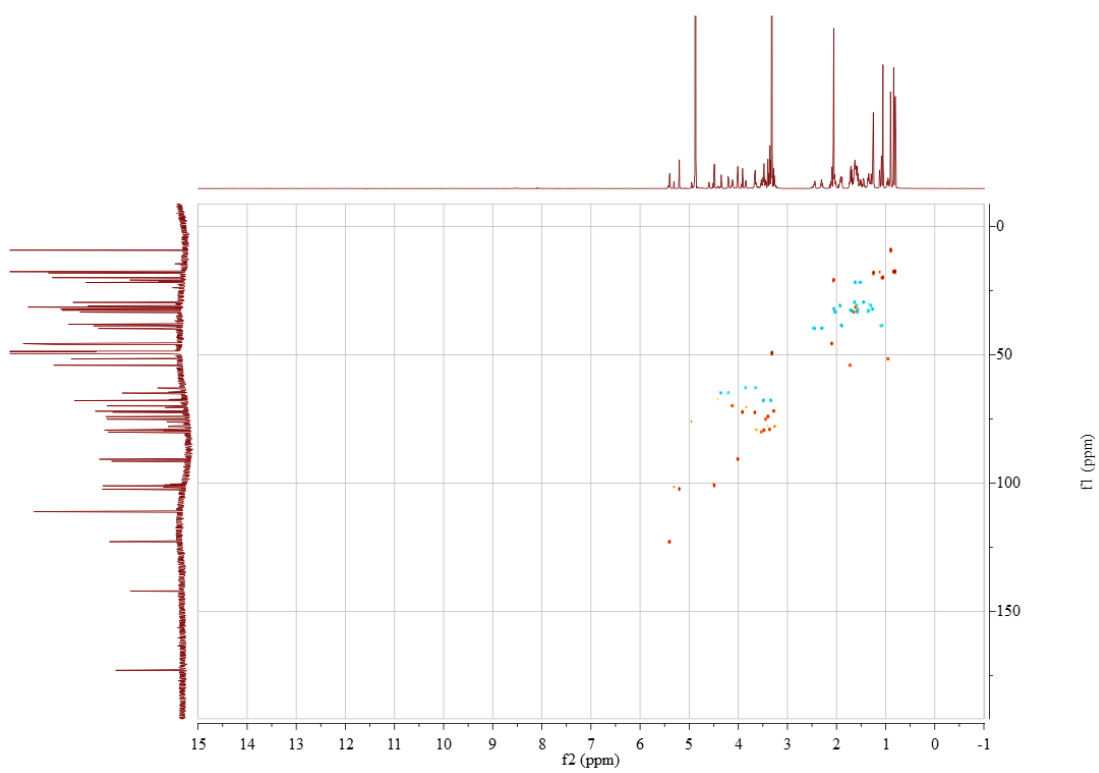
S4. <sup>13</sup>C NMR (201 MHz, CD<sub>3</sub>OD) spectrum of compound 1



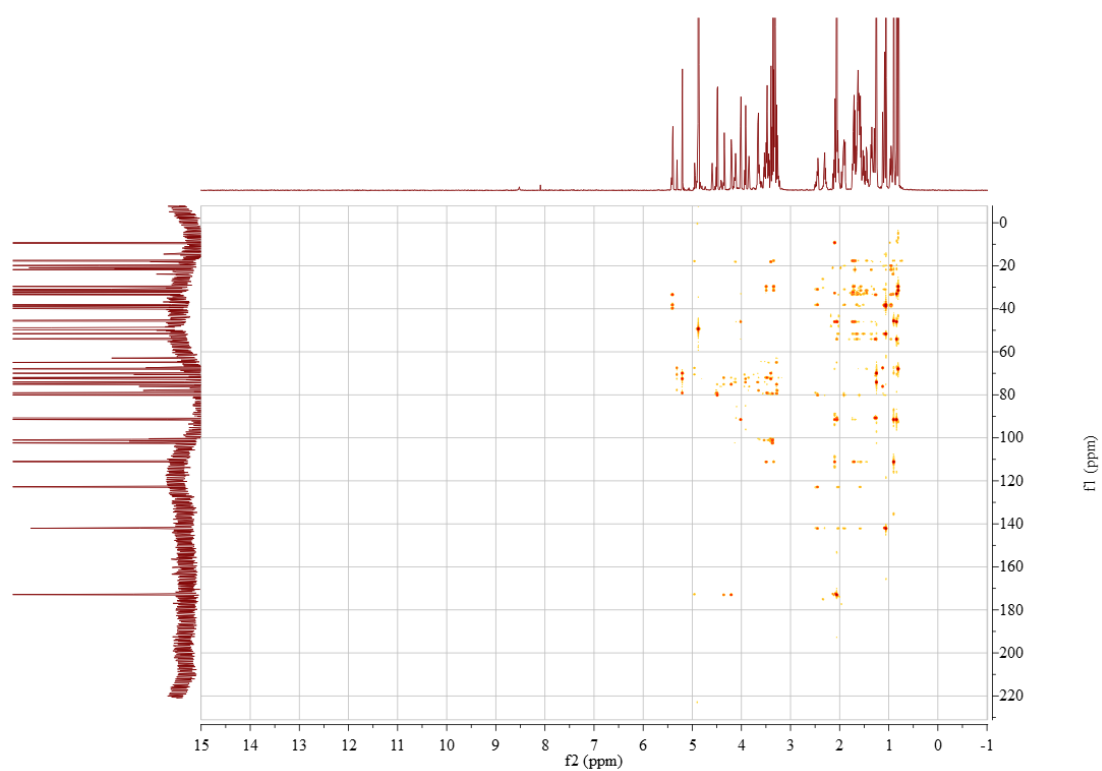
S5. DEPT 135 spectrum of compound 1



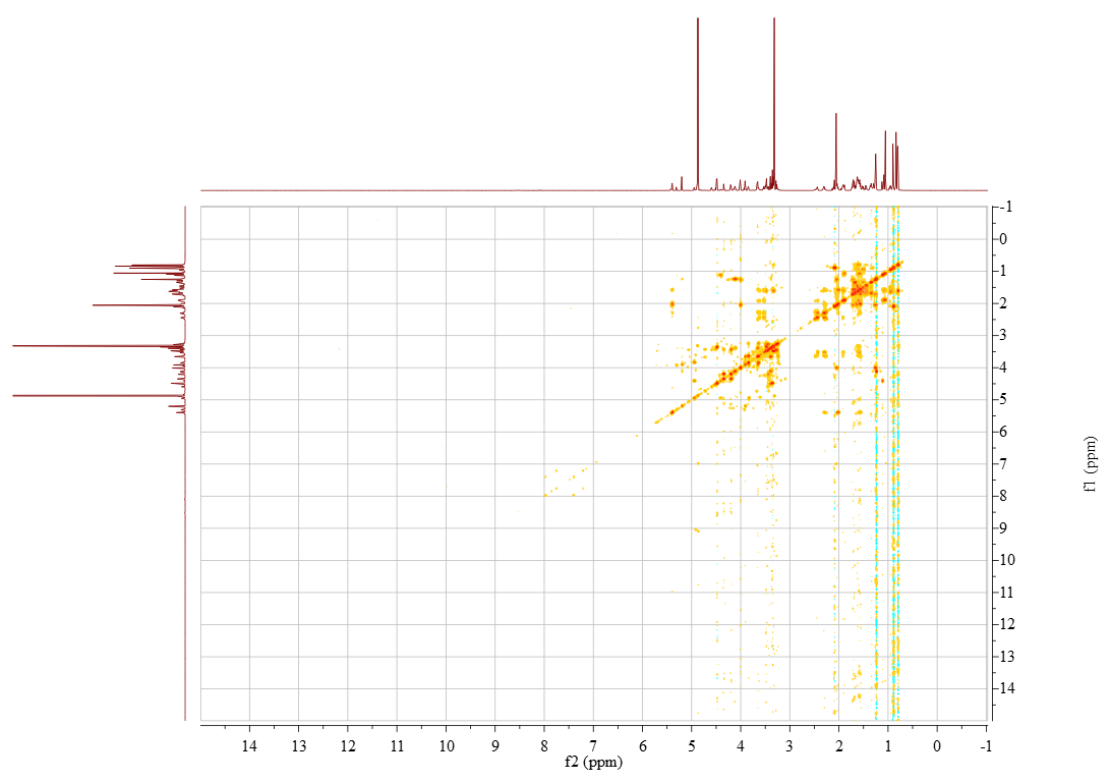
S6. HSQC spectrum of compound 1



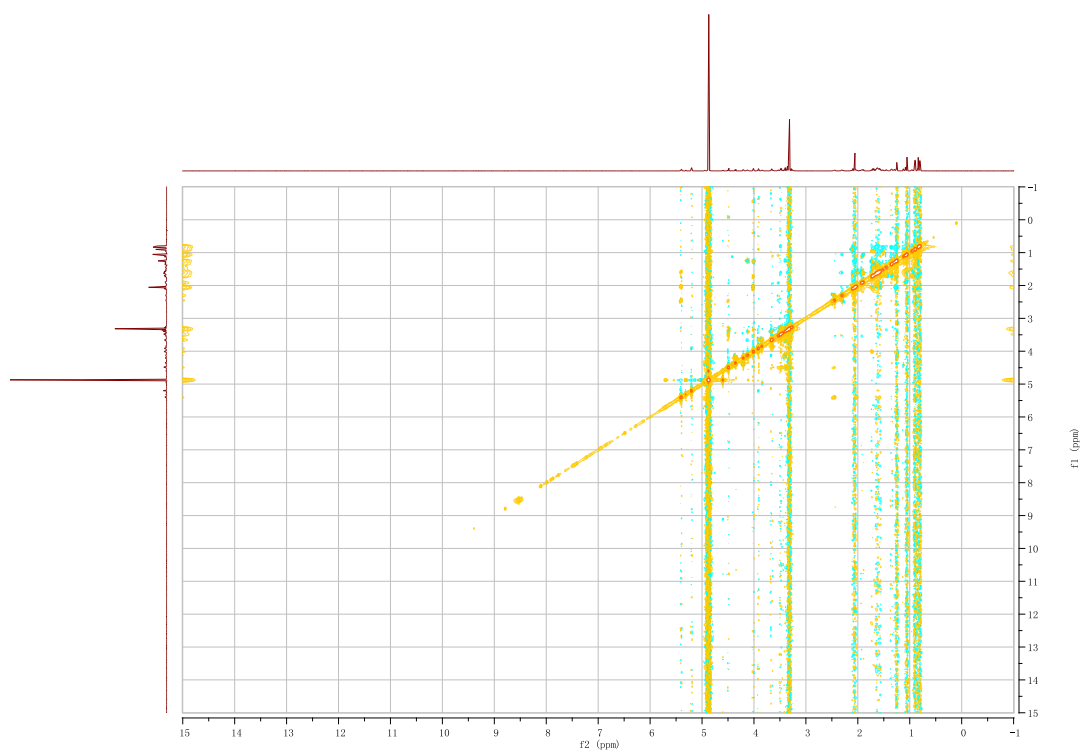
S7. HMBC spectrum of compound **1**



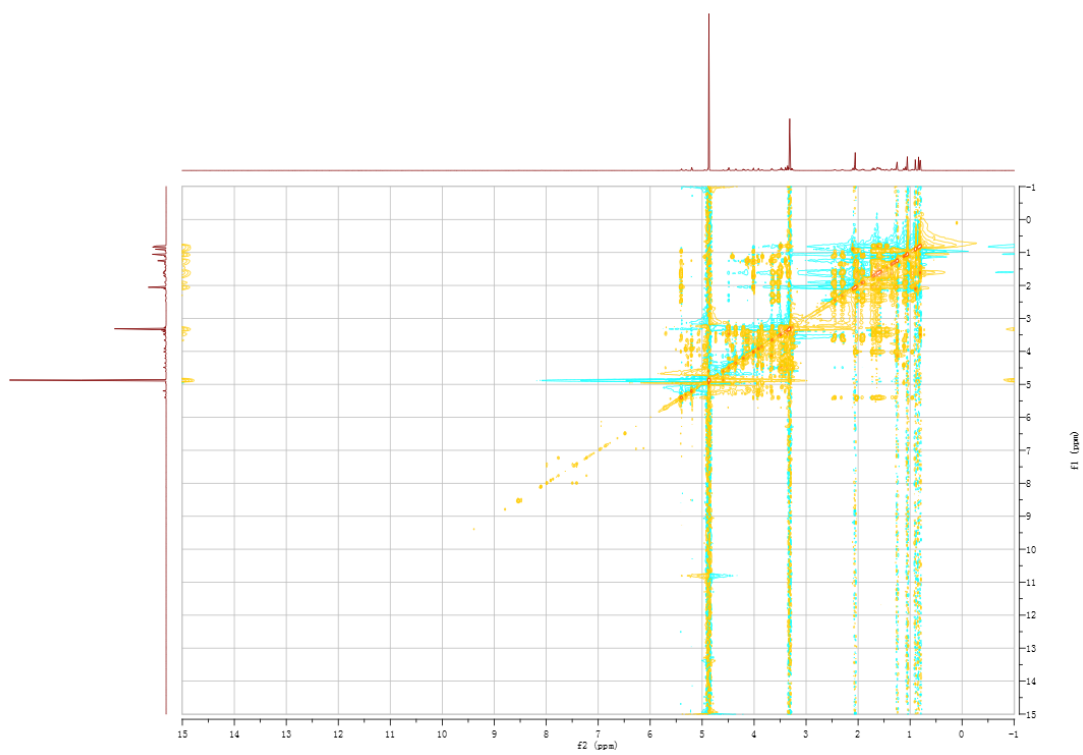
S8. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound **1**



S9. NOESY spectrum of compound **1**



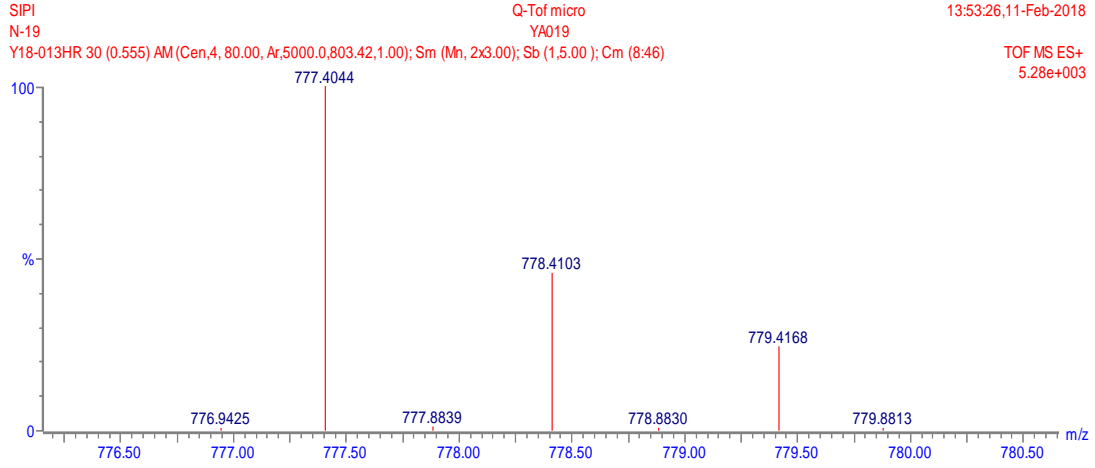
S10. TOCSY spectrum of compound **1**



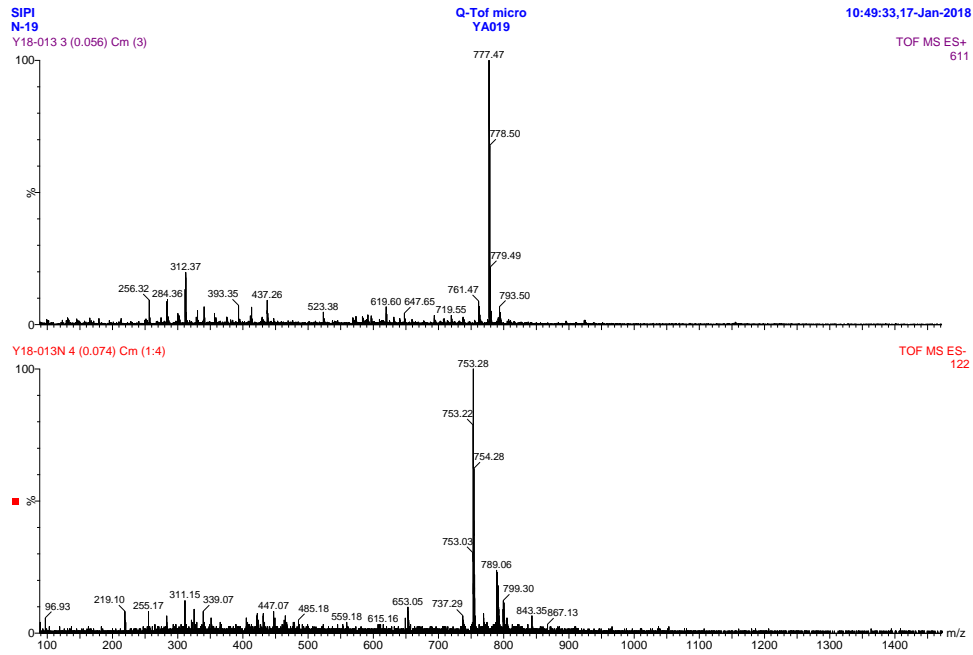


S11. Positive HR-ESI-MS spectrum of compound 2

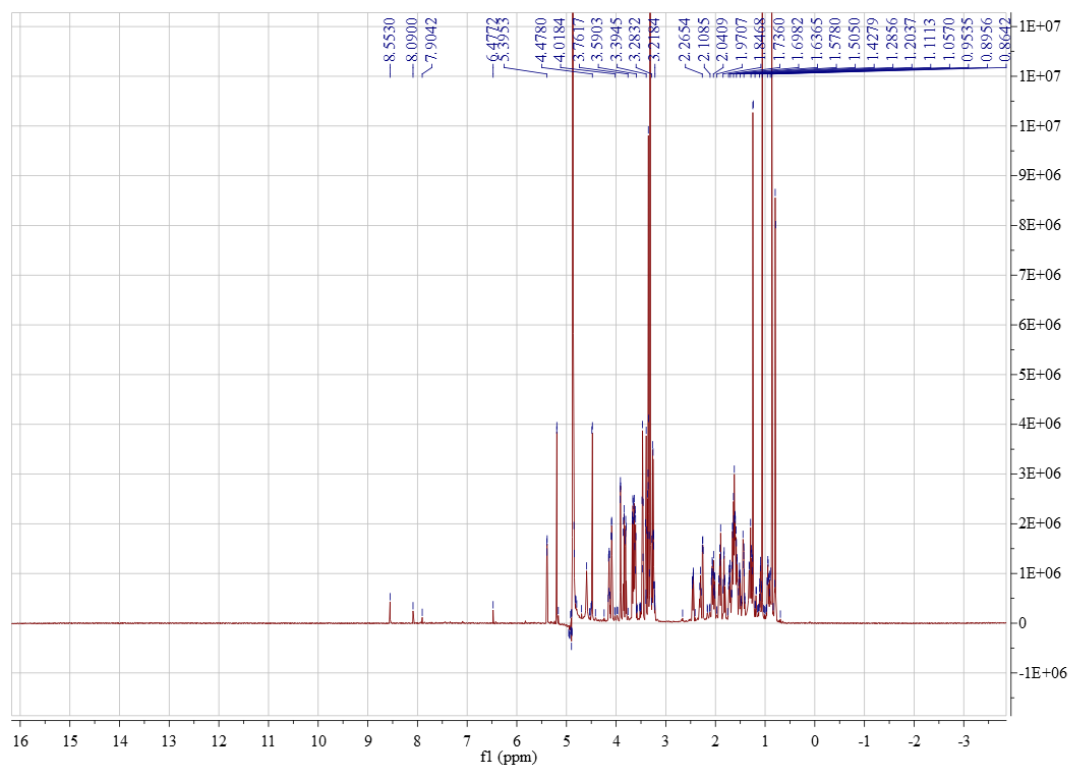
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT
777.4044	777.4037	0.7	0.9	8.5	C <sub>39</sub> H <sub>62</sub> O <sub>14</sub> Na



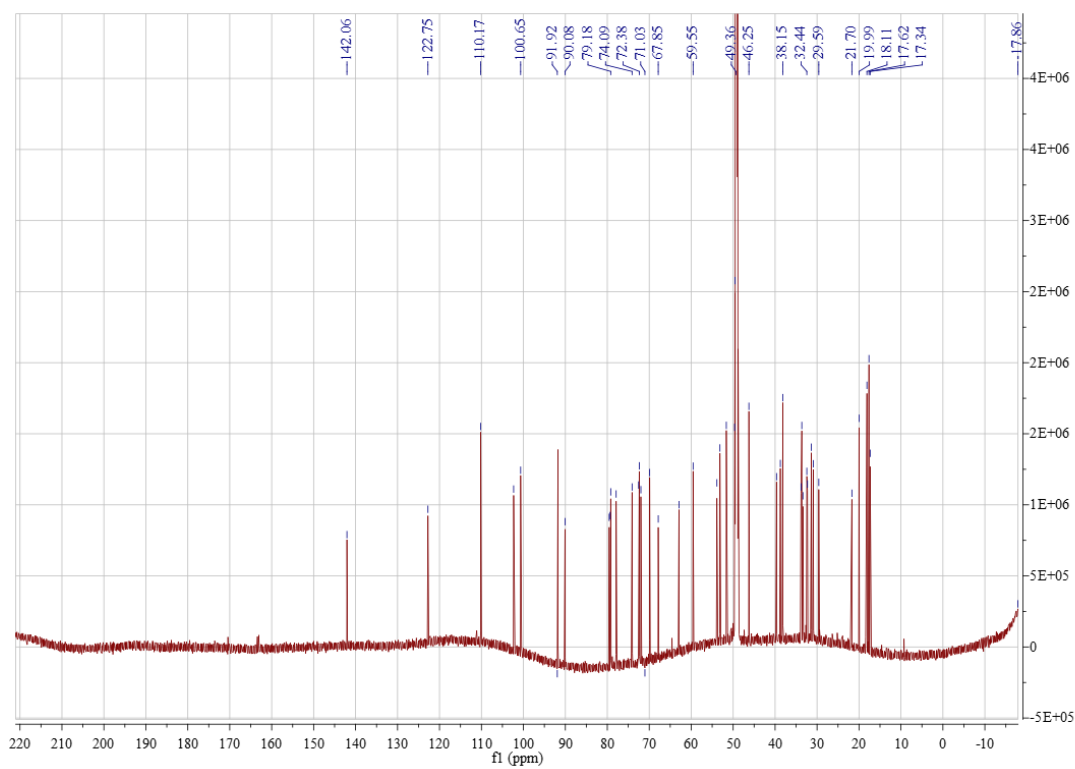
S12. Positive and Negative ESI-MS spectrum of compound 2



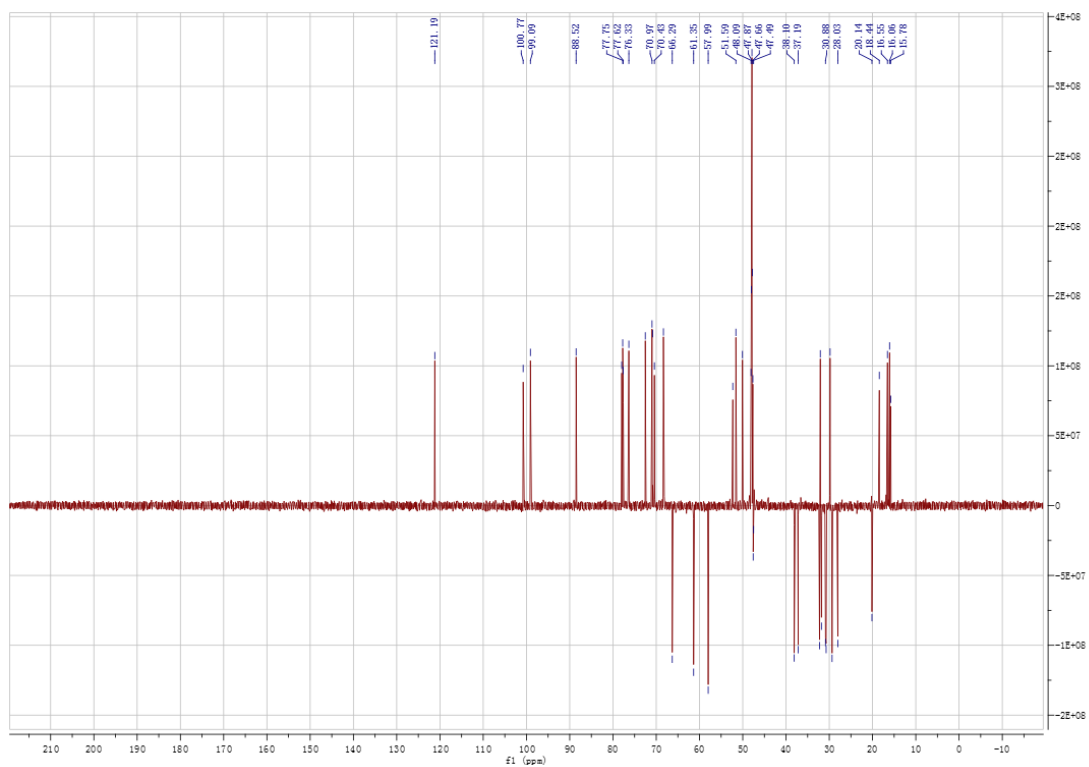
S13.  $^1\text{H}$  NMR (800 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound 2



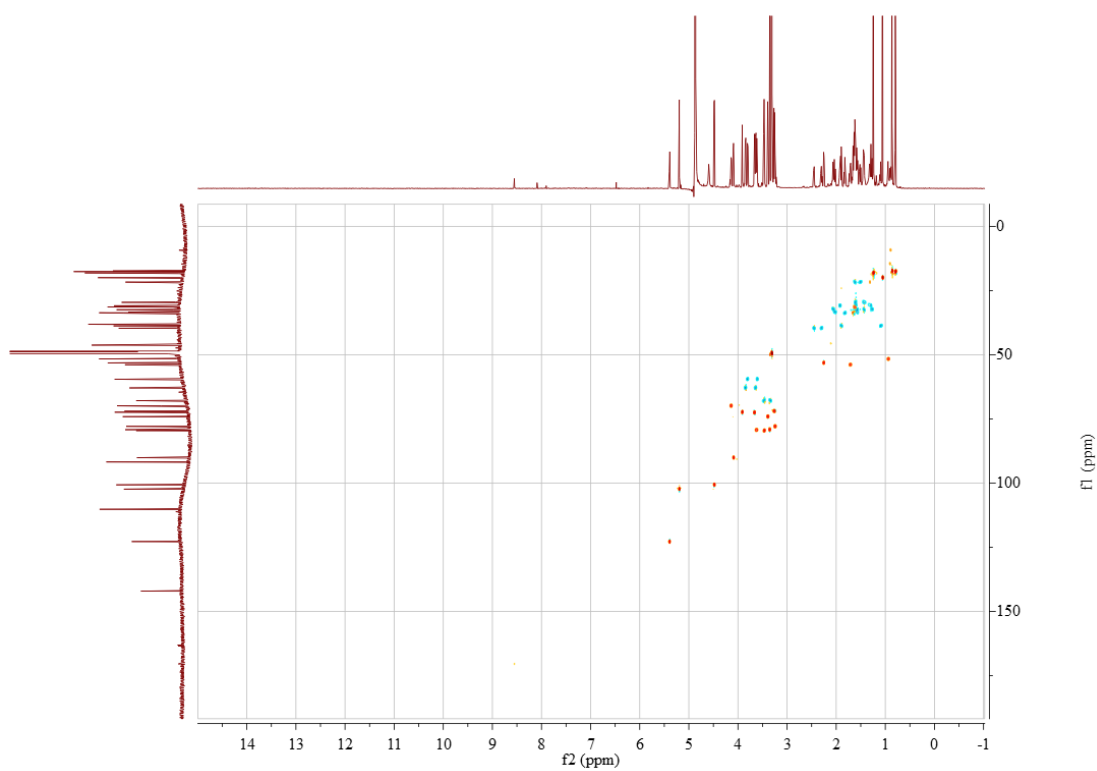
S14.  $^{13}\text{C}$  NMR (201 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound 2



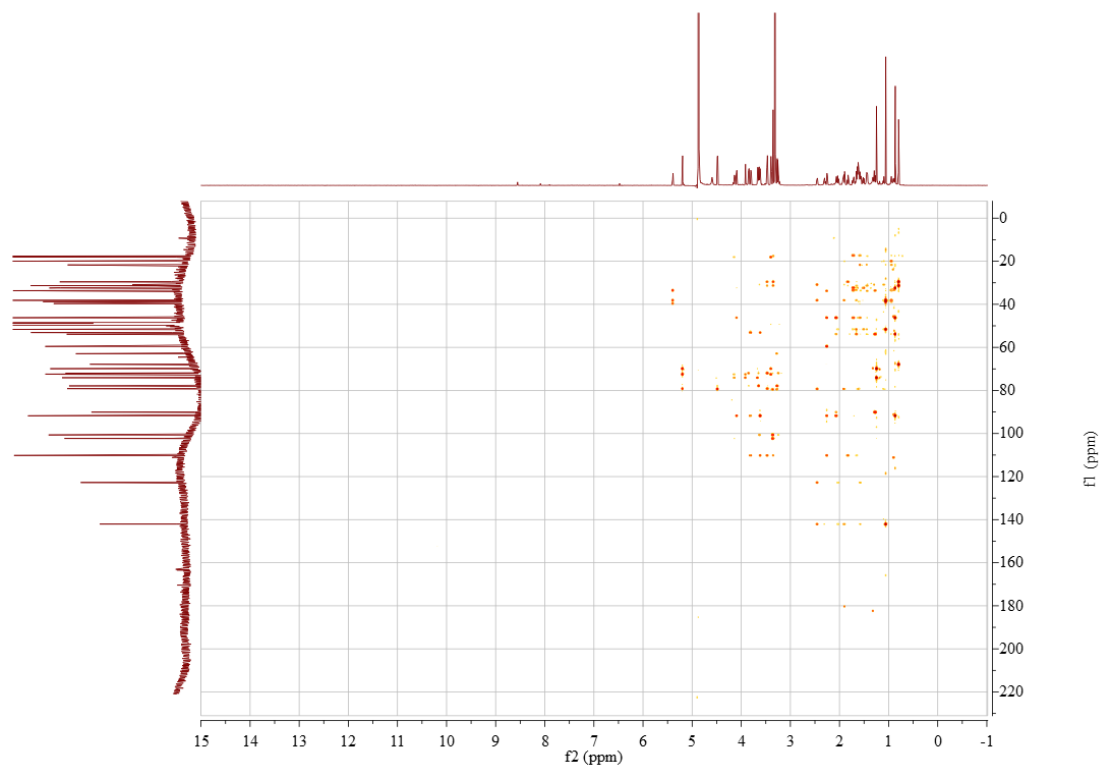
S15. DEPT 135 spectrum of compound 2



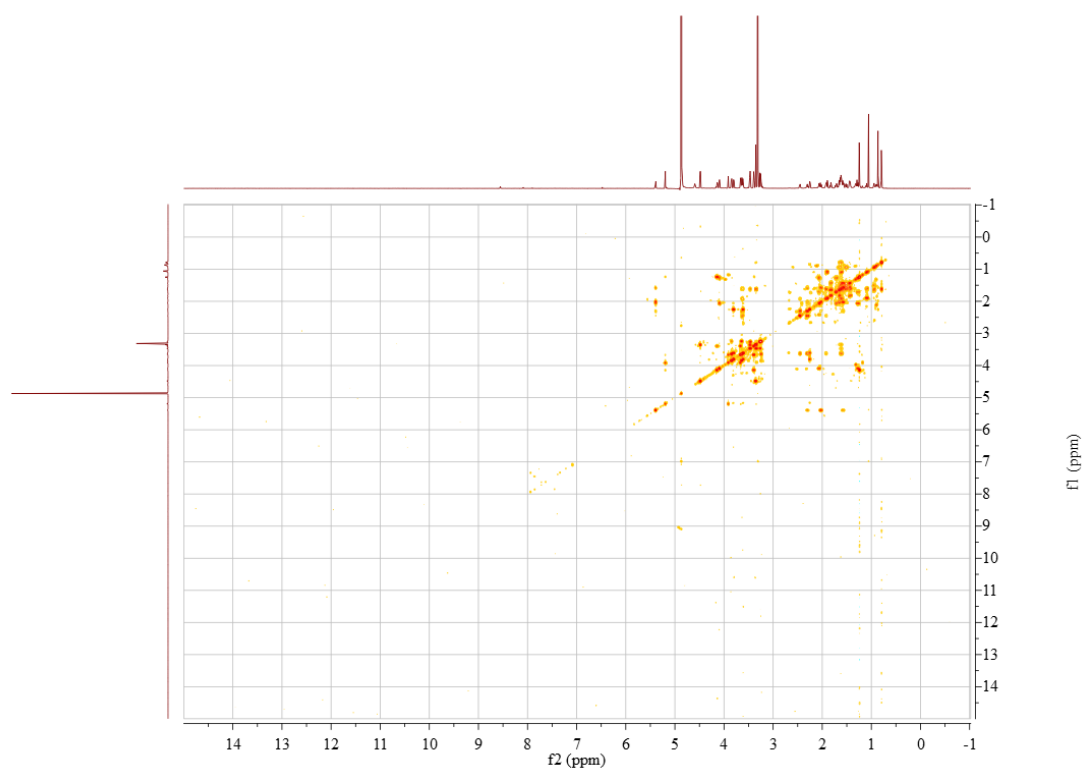
S16. HSQC spectrum of compound 2



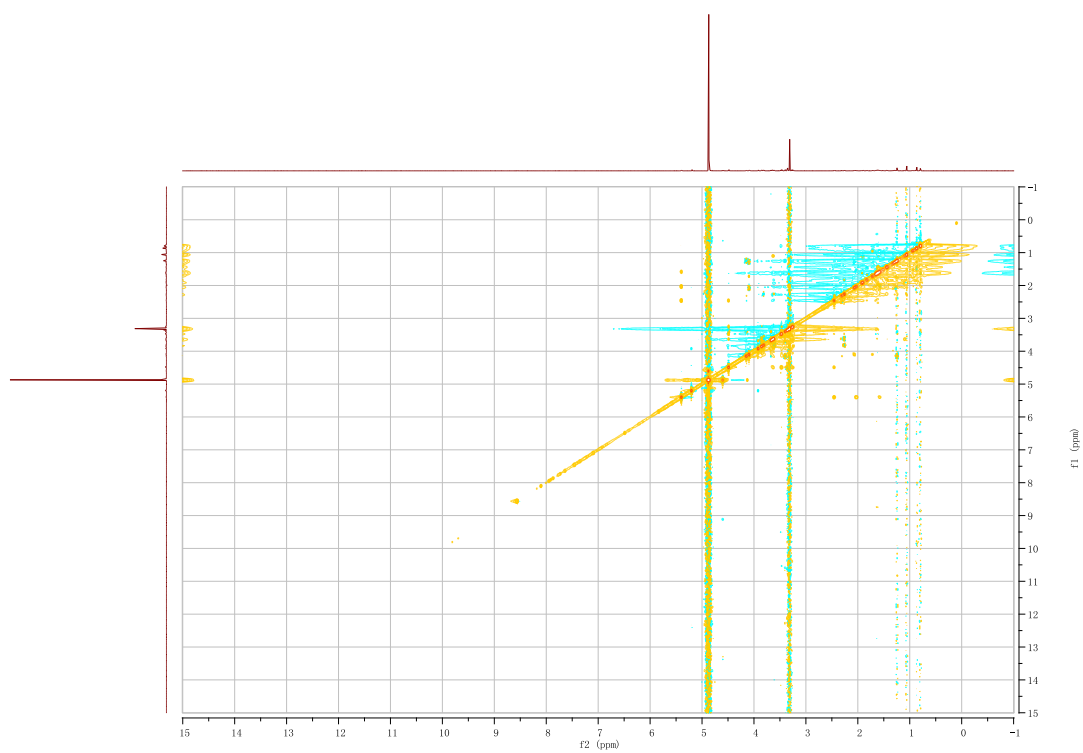
S17. HMBC spectrum of compound 2



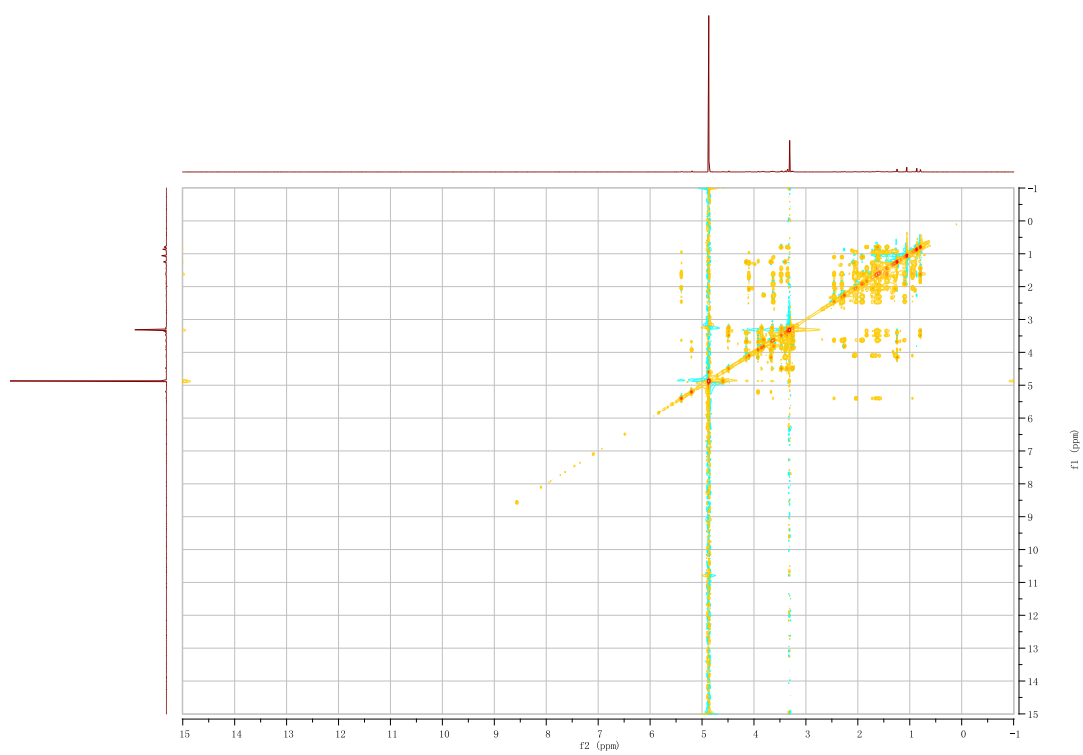
S18.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 2



S19. NOESY spectrum of compound 2

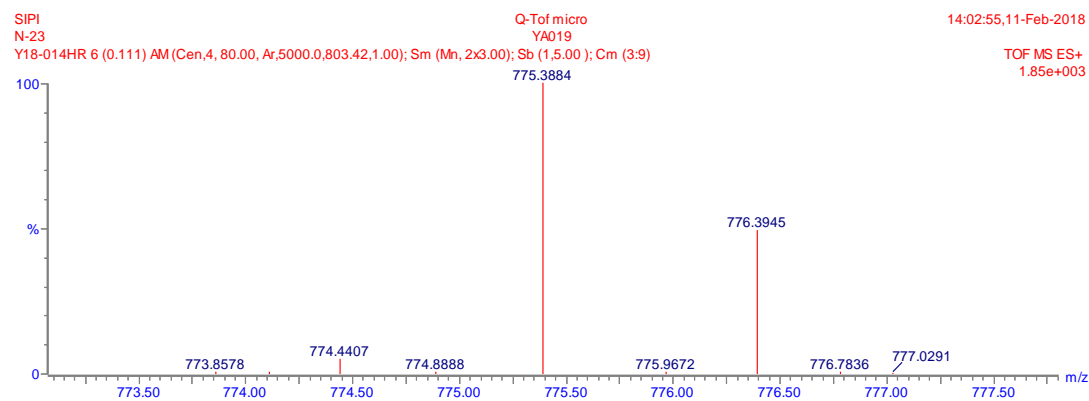


S20. TOCSY spectrum of compound 2

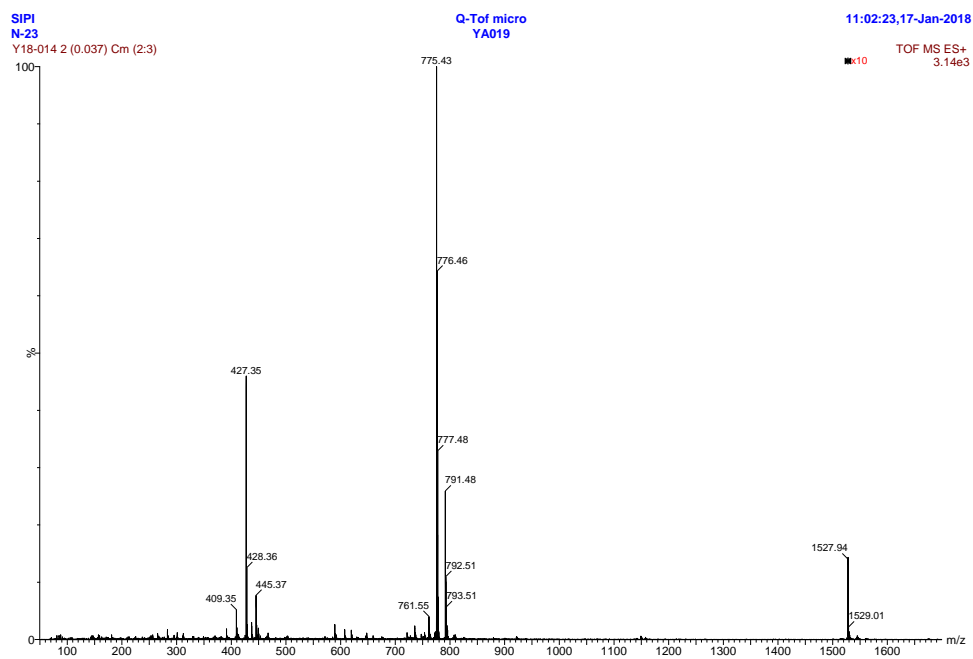


S21. Positive HR-ESI-MS spectrum of compound 3

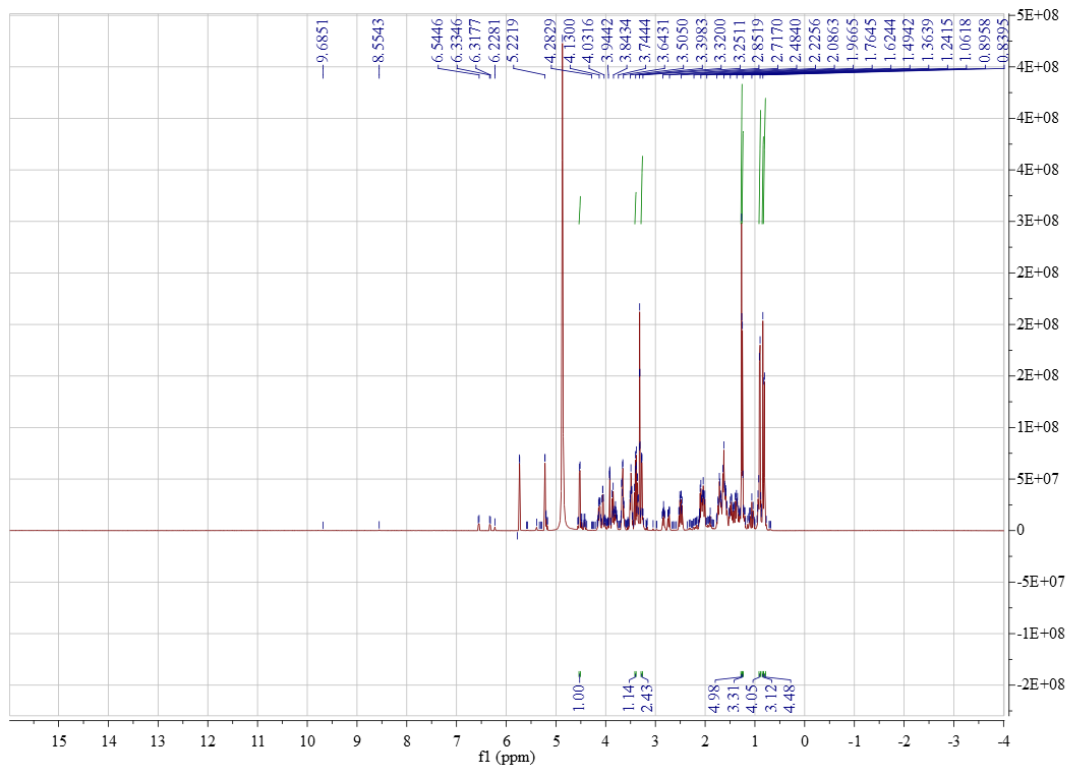
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
775.3884	775.3881	0.3	0.4	9.5	n/a	C <sub>39</sub> H <sub>60</sub> O <sub>14</sub> Na



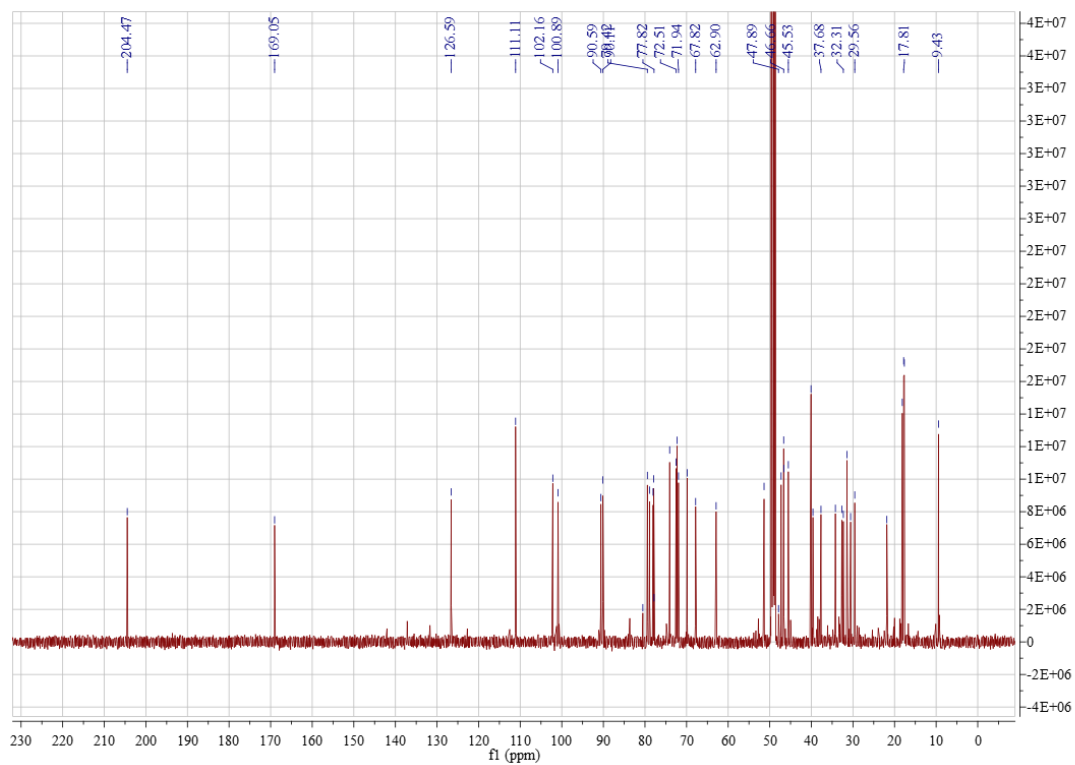
S22. Positive ESI-MS spectrum of compound 3



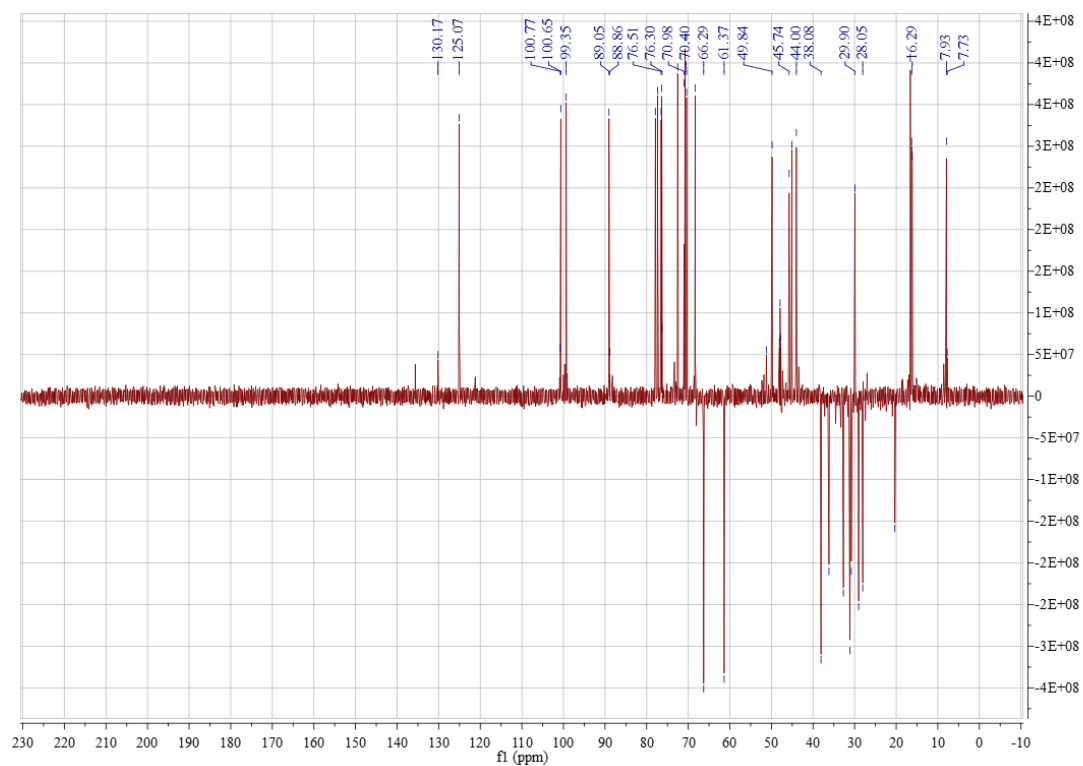
S23. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) spectrum of compound 3



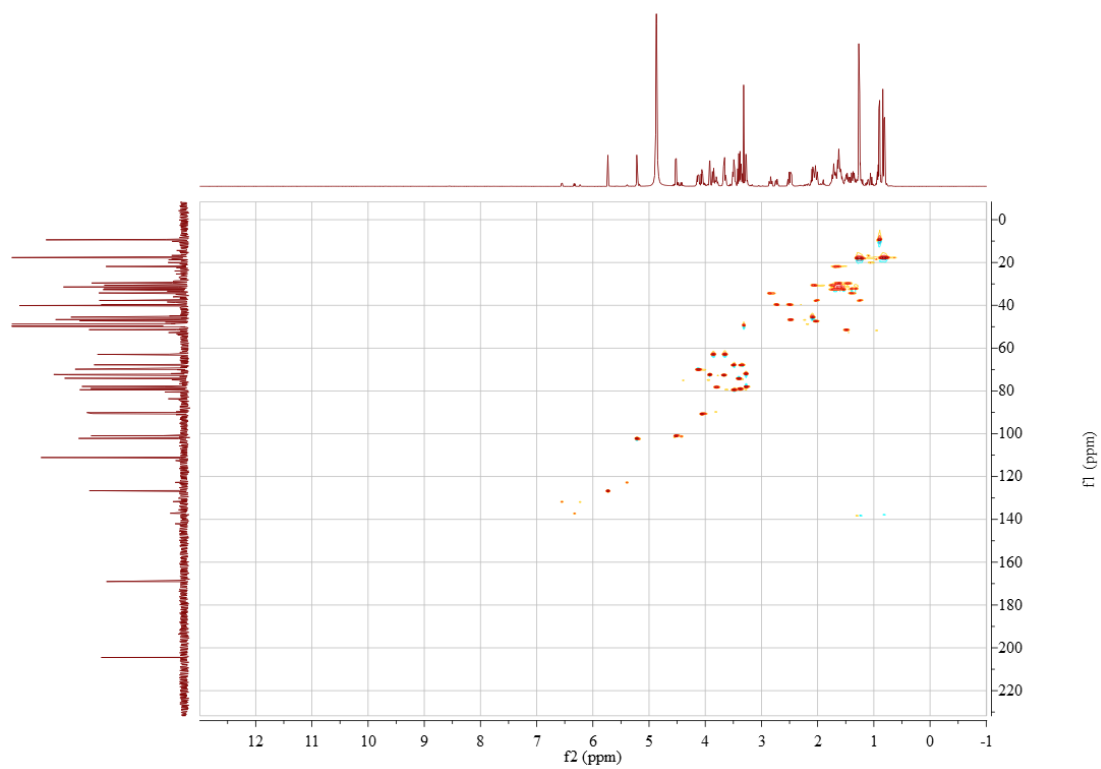
S24. <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD) spectrum of compound 3



S25. DEPT 135 spectrum of compound 3

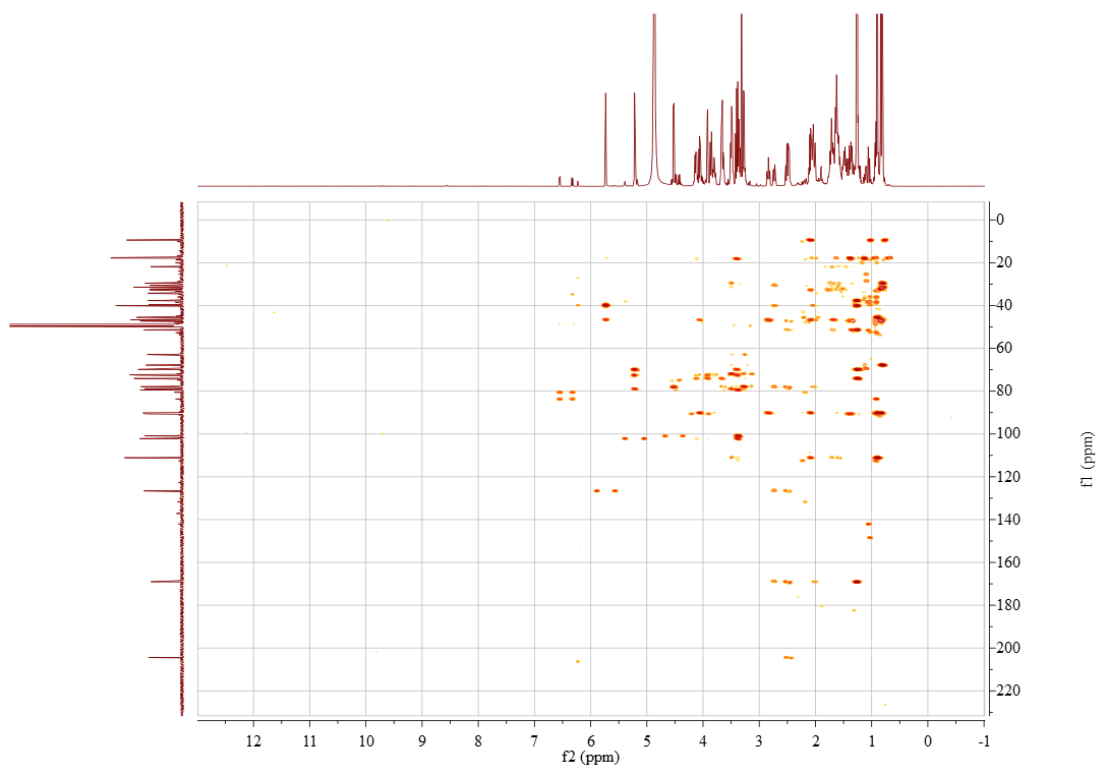


S26. HSQC spectrum of compound 3

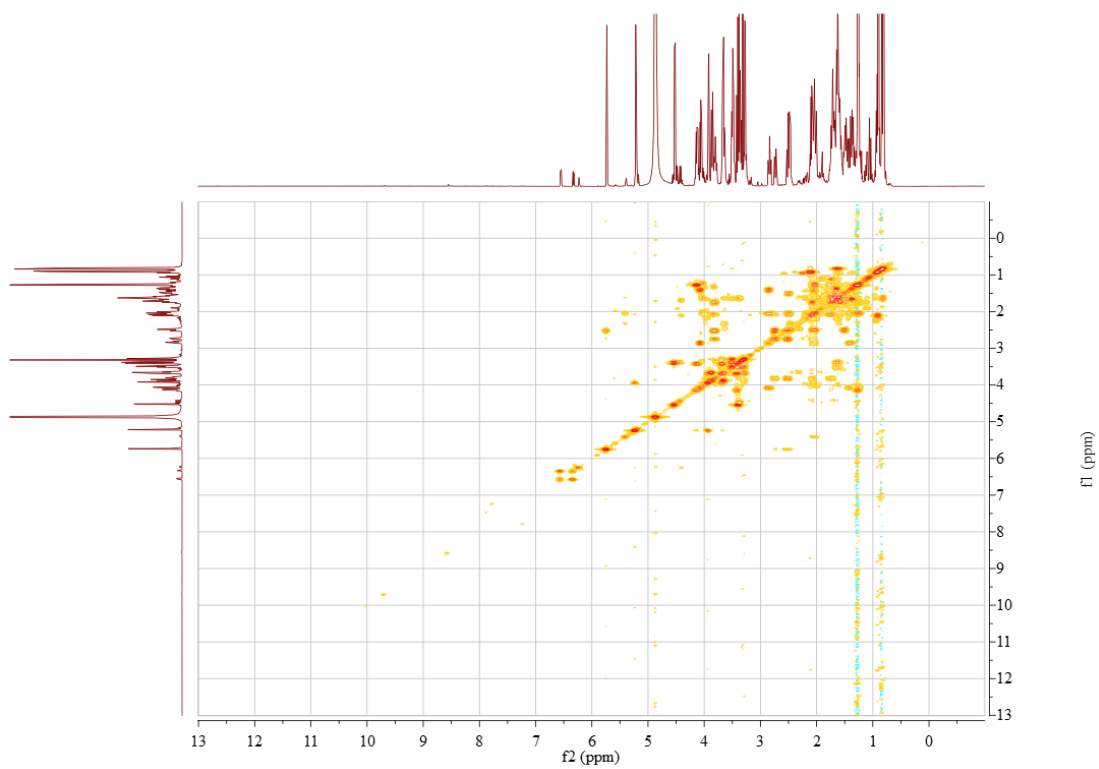


S27. HMBC spectrum of compound 3

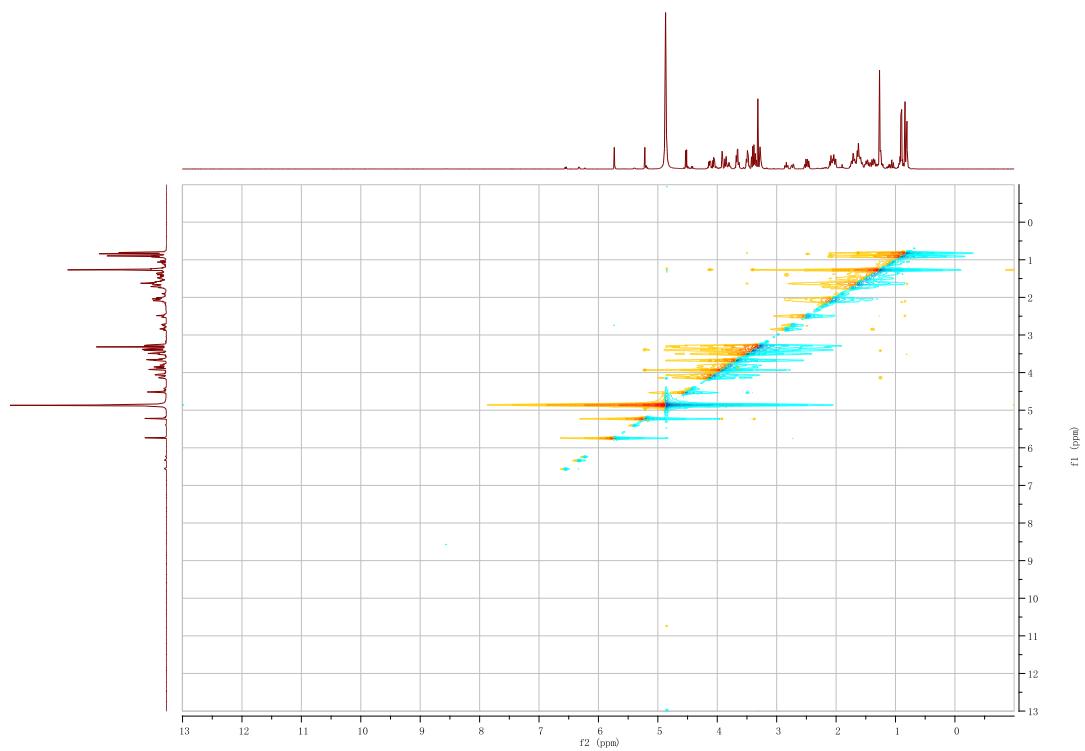




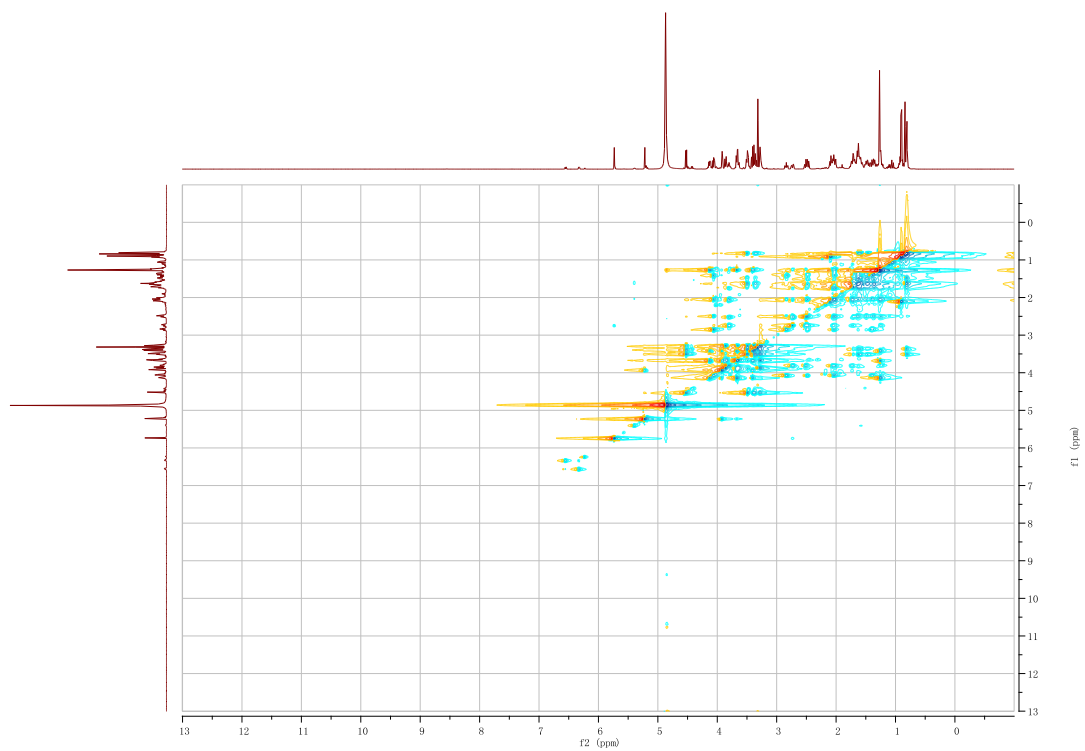
S28.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 3



S29. NOESY spectrum of compound 3

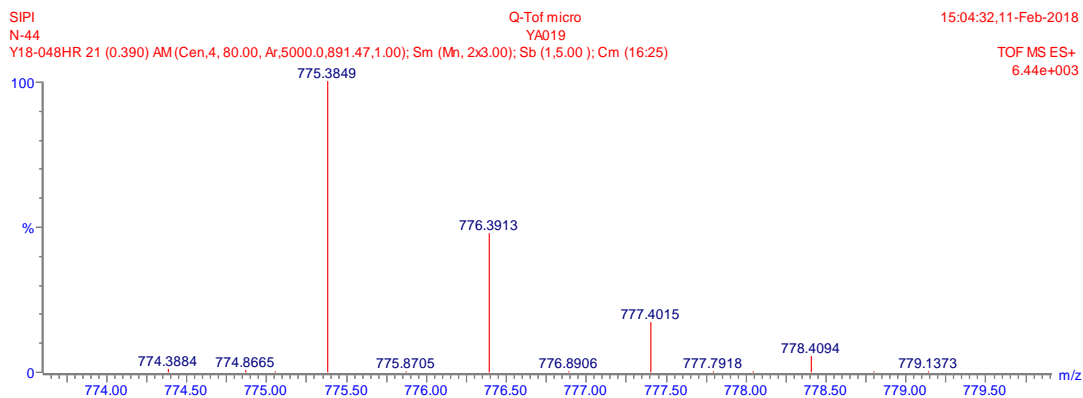


S30. TOCSY spectrum of compound 3

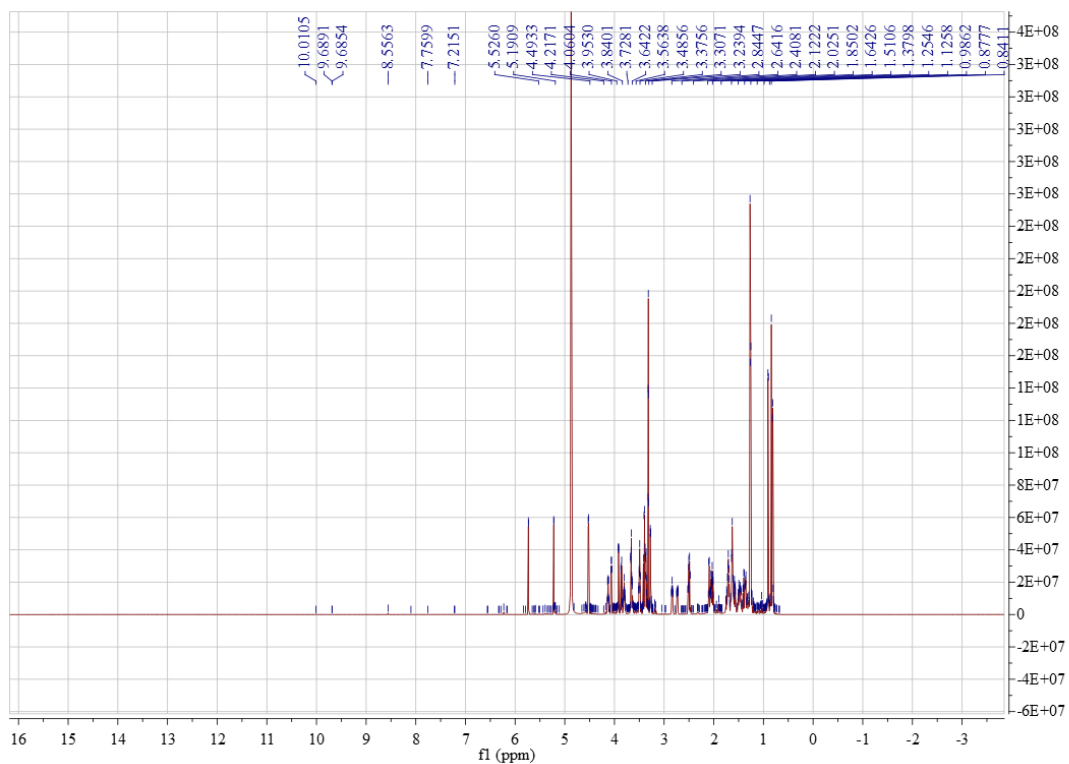


S31. Positive HR-ESI-MS spectrum of compound 4

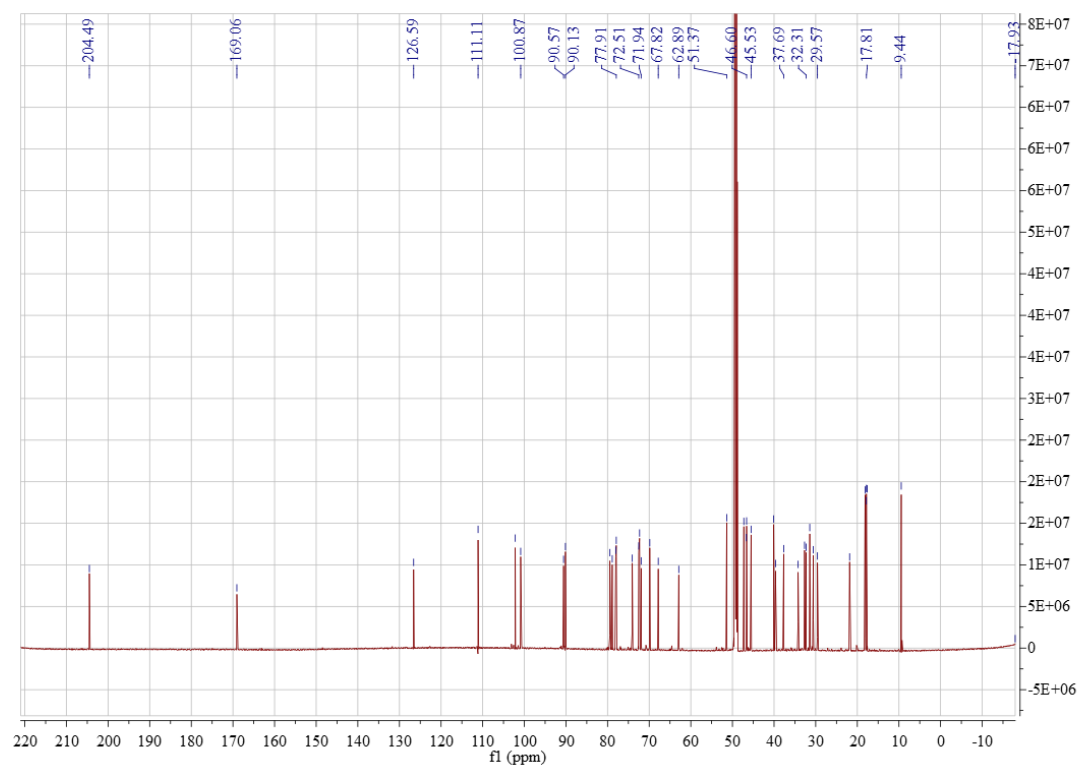
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
775.3849	775.3881	-3.2	-4.1	9.5	36.7	C <sub>39</sub> H <sub>60</sub> O <sub>14</sub> Na



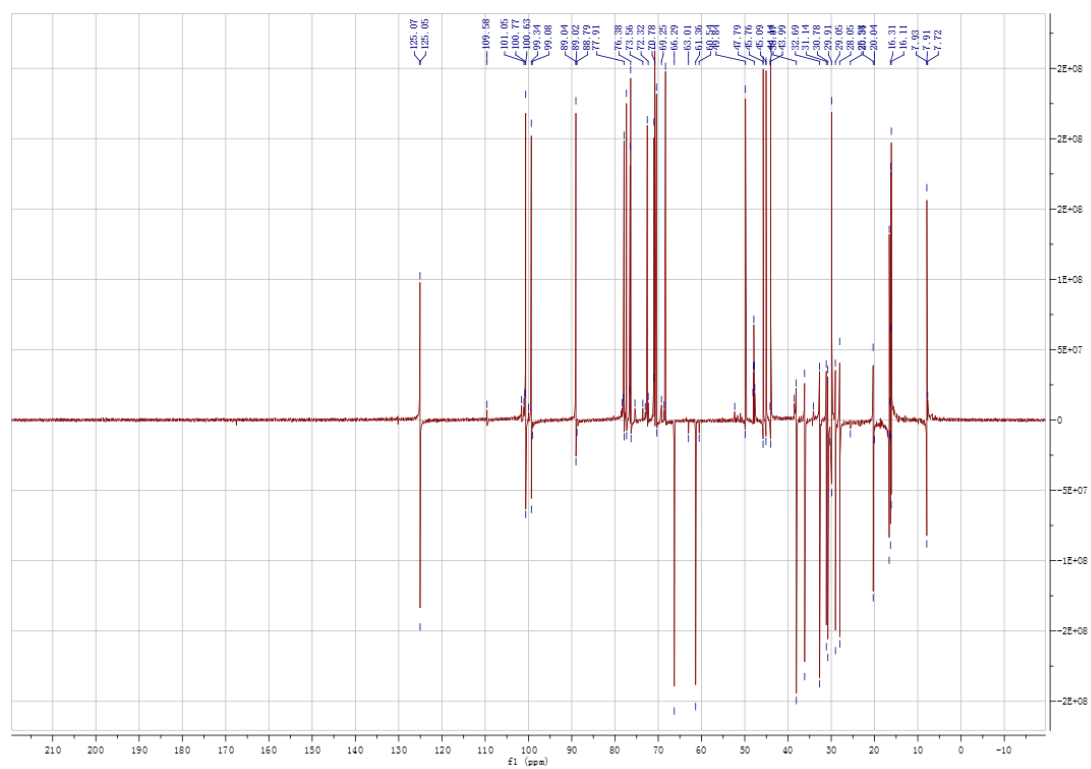
S32. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) spectrum of compound 4



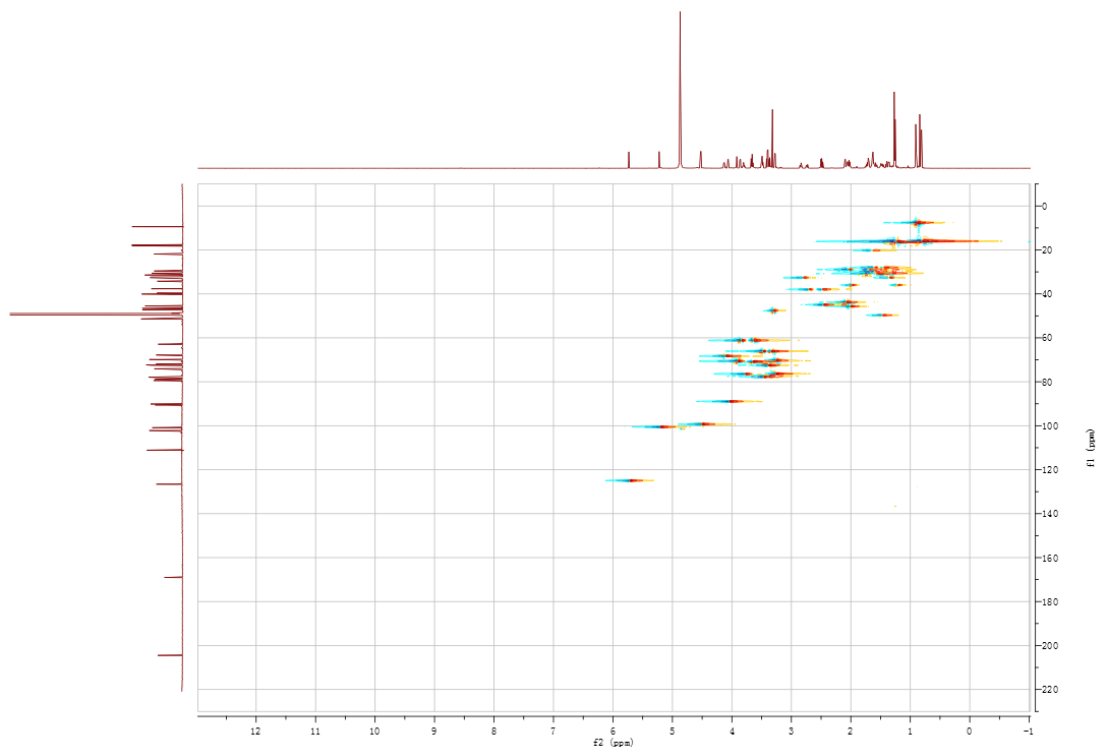
S33. <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD) spectrum of compound 4



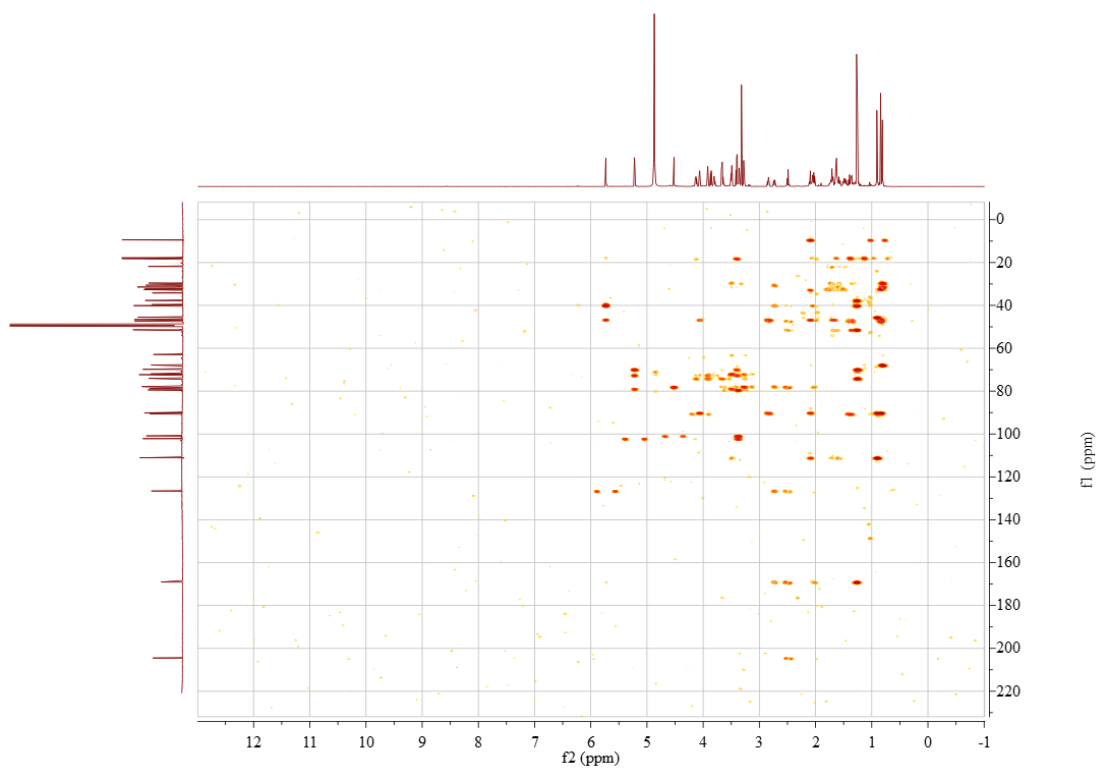
S34. DEPT 135 spectrum of compound 4



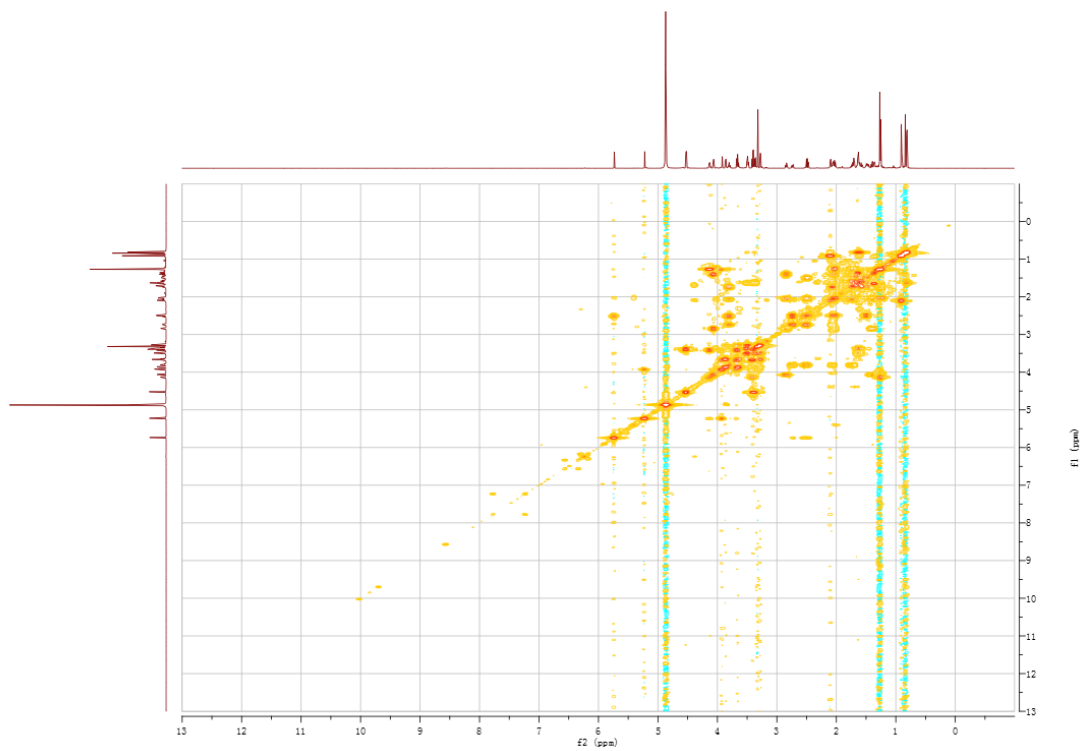
S35. HSQC spectrum of compound 4



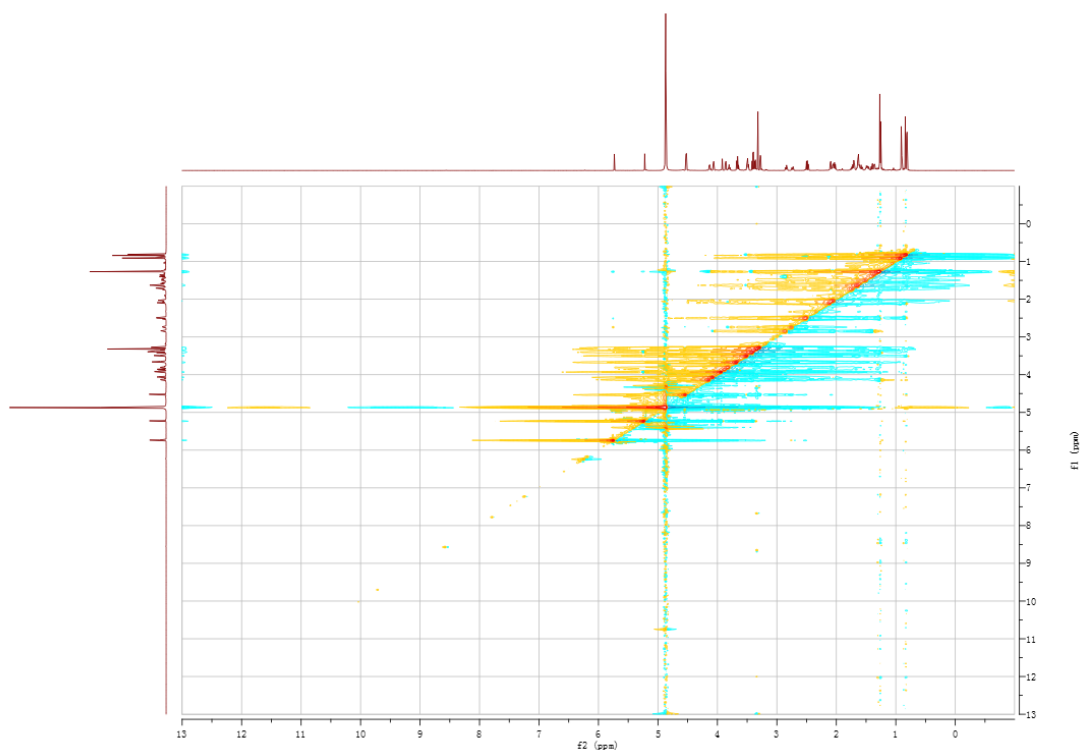
S36. HMBC spectrum of compound 4



S37. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 4



S38. NOESY spectrum of compound 4



S39. TOCSY spectrum of compound 4

