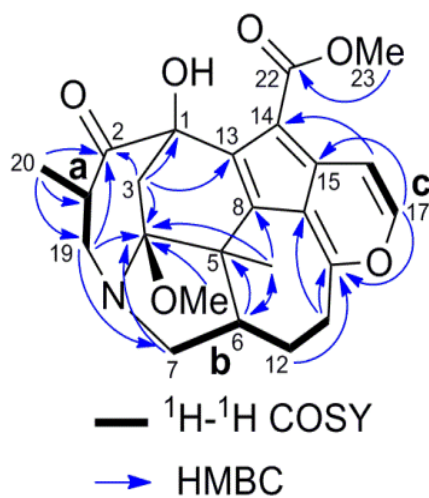
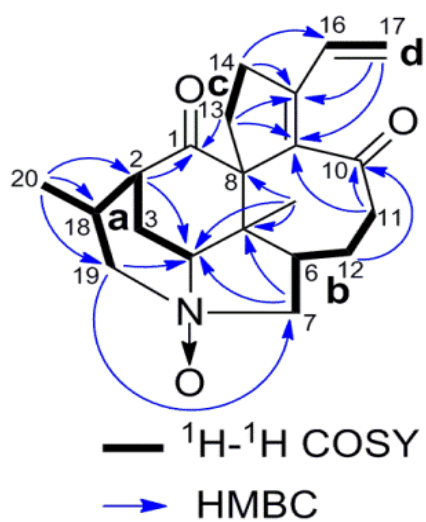


## Supporting Information

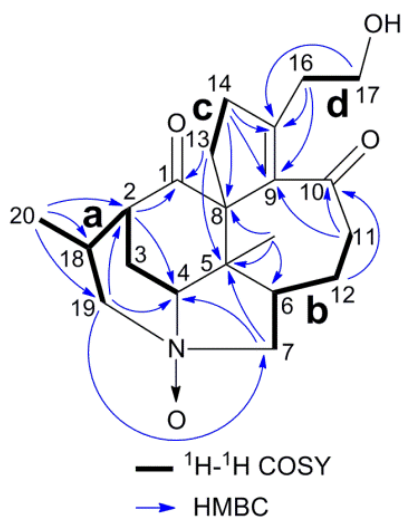
**Figure S1.** Selected 2D NMR correlations of daphnicyclidin N (**2**).

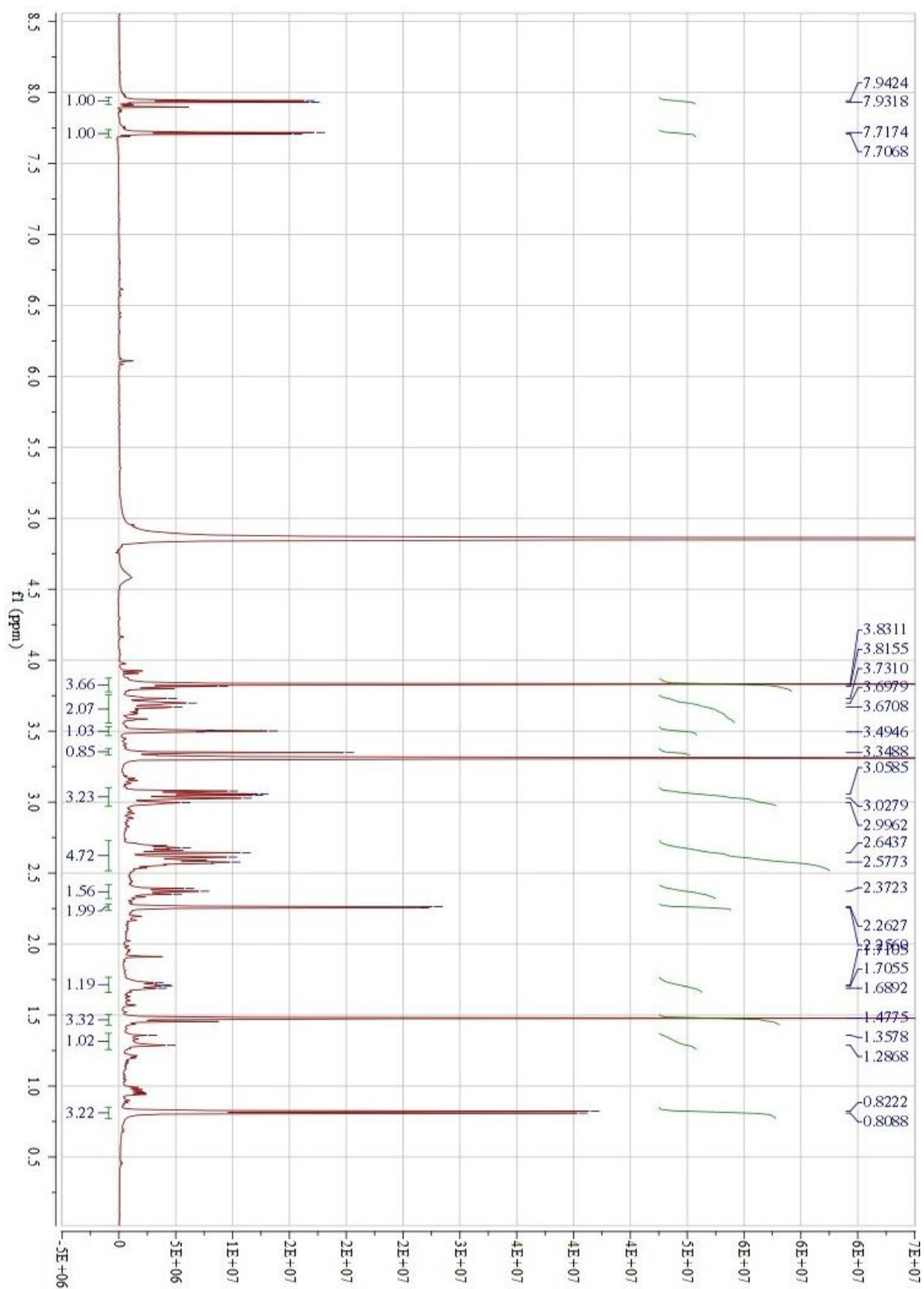


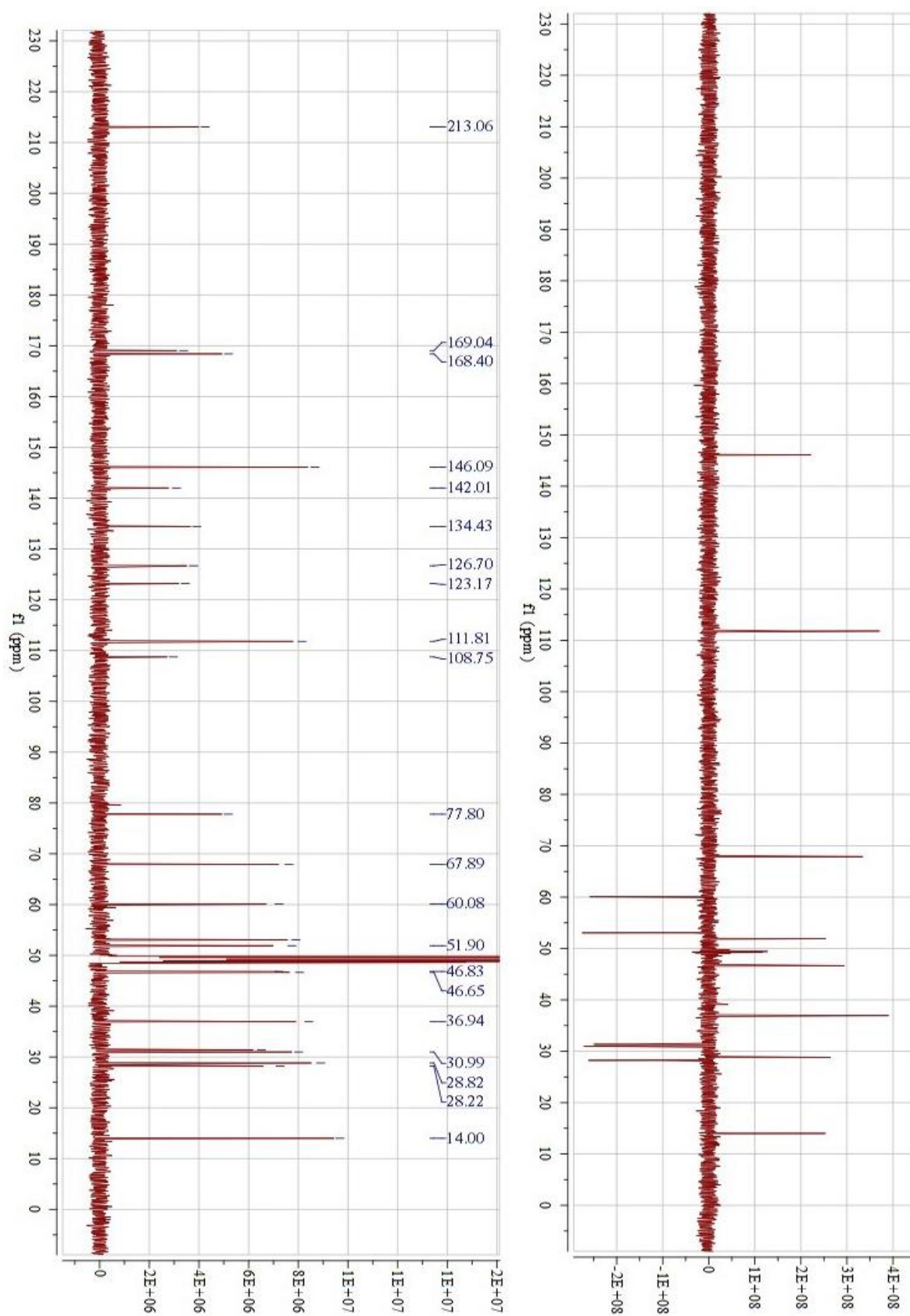
**Figure S2.** Selected 2D NMR correlations of calyciphylline R (**4**).

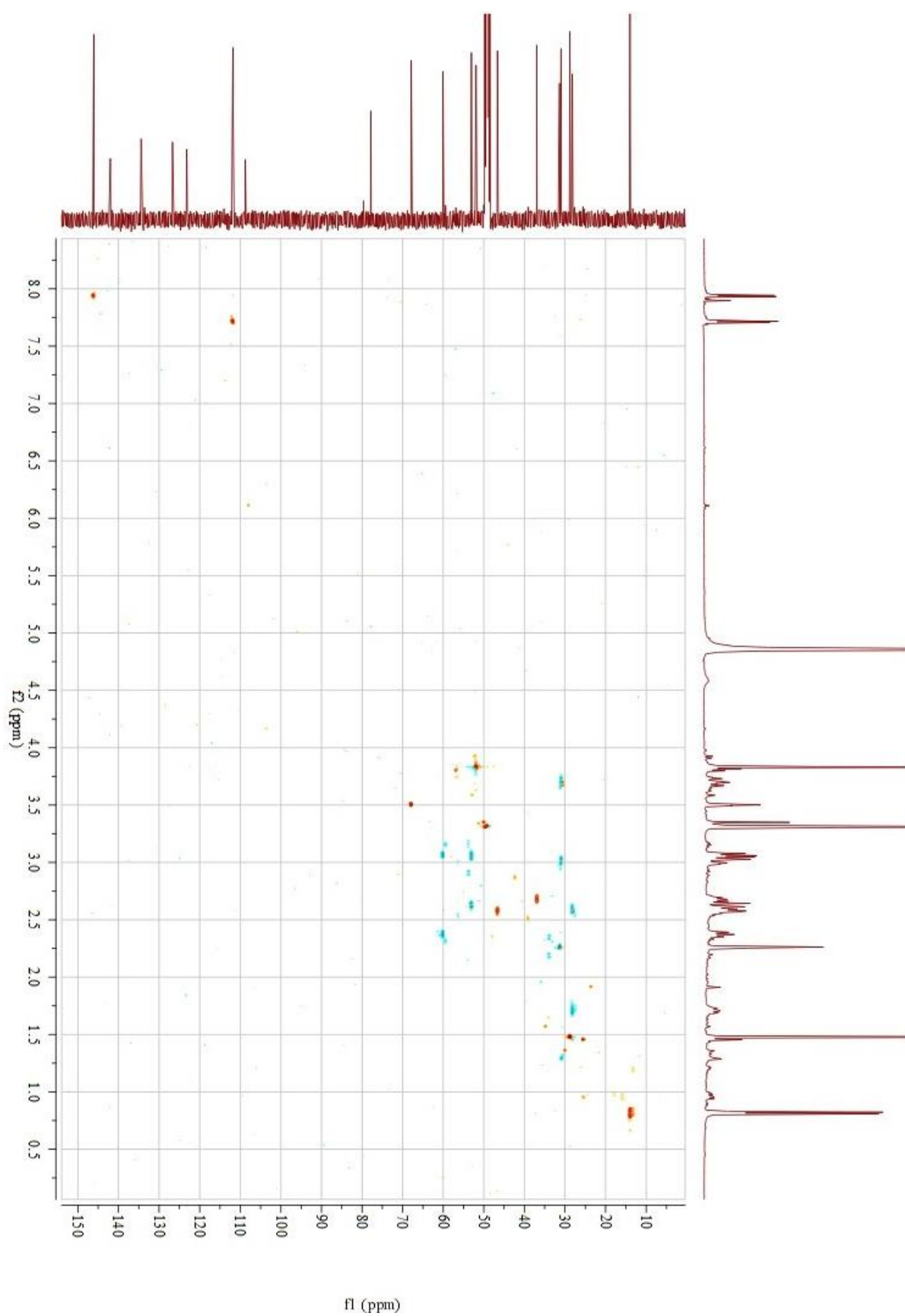


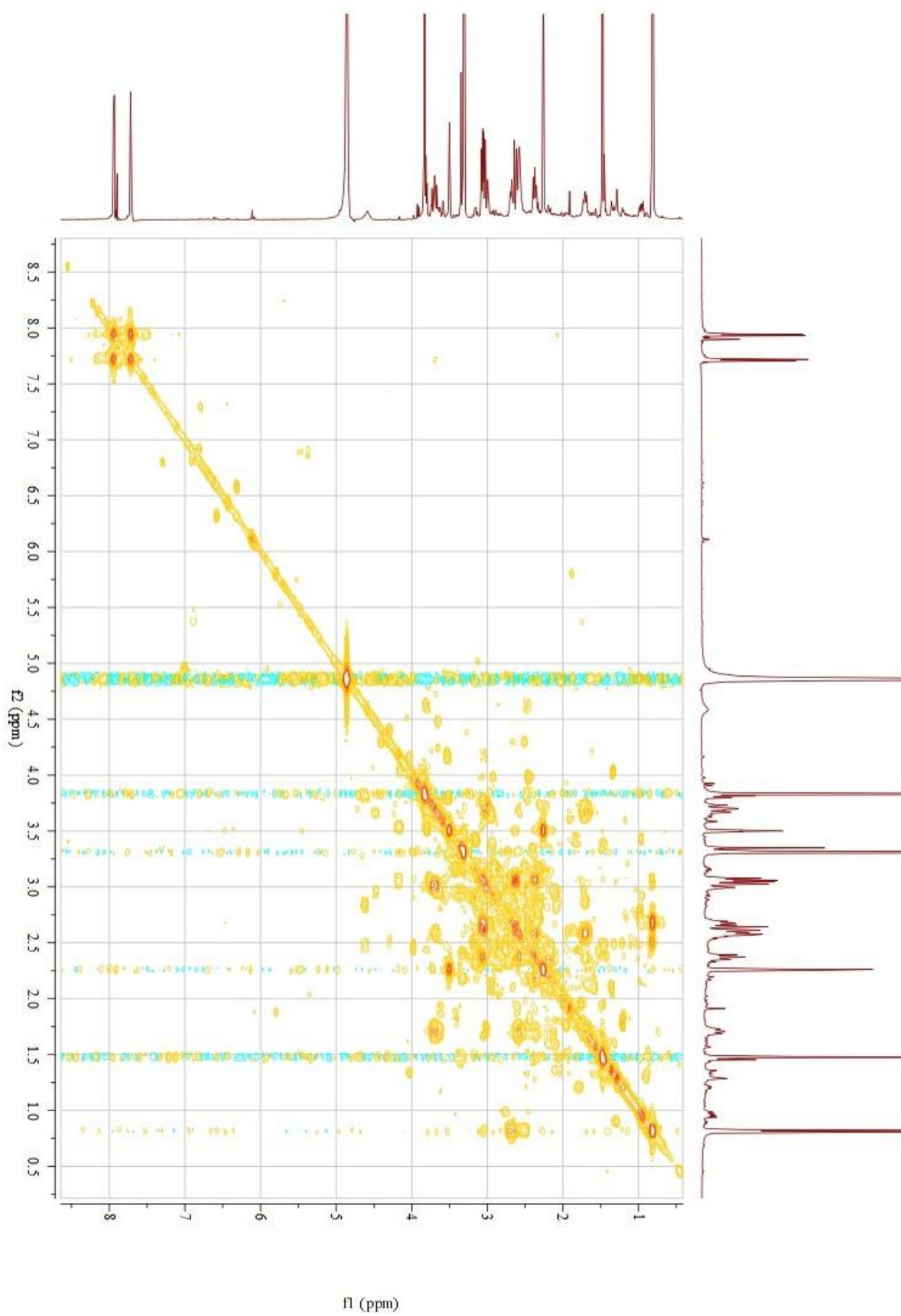
**Figure S3.** Selected 2D NMR correlations of calyciphylline S (**5**).

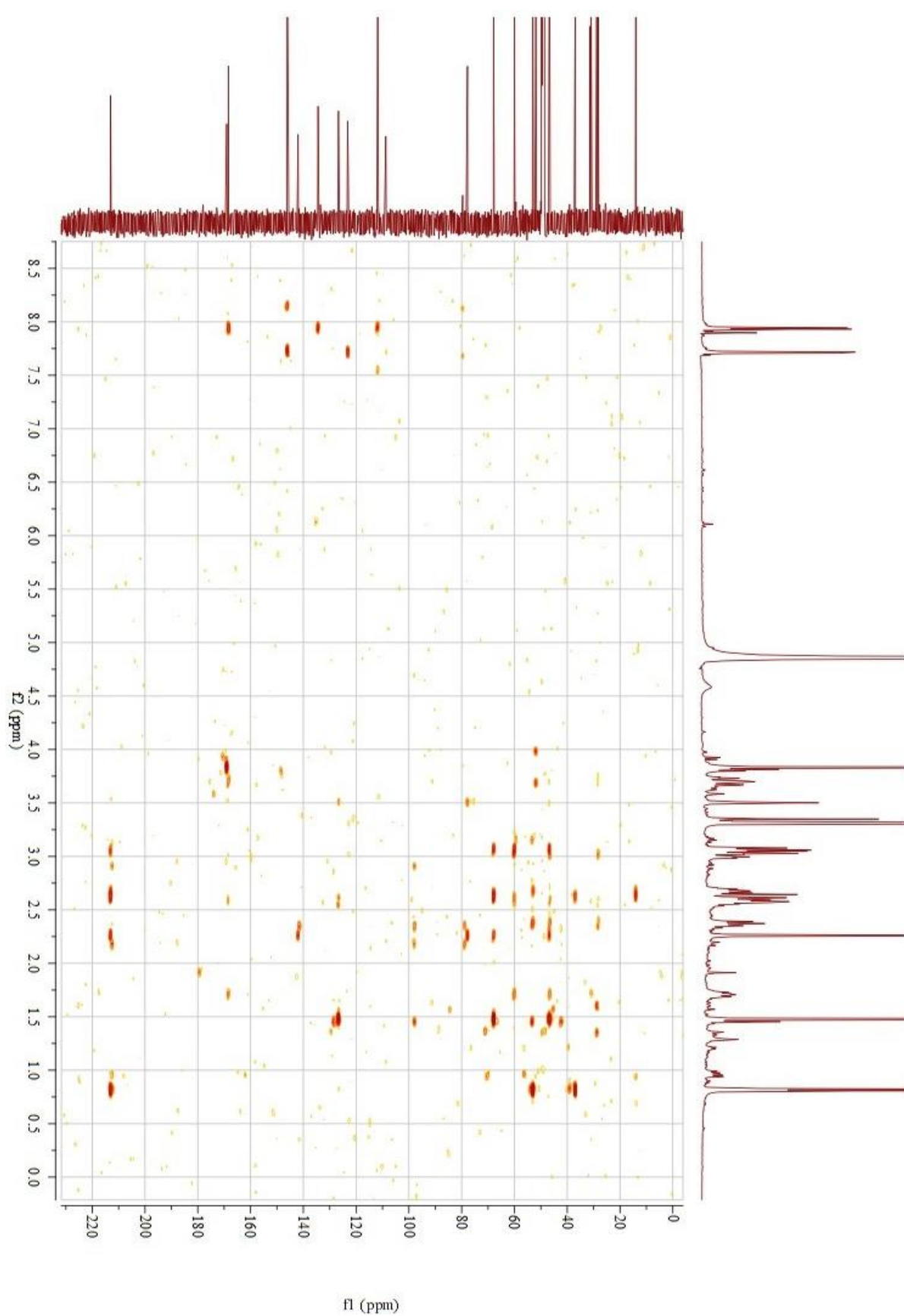


**Figure S4.**  $^1\text{H-NMR}$  (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of daphnicyclidin M (1).

**Figure S5.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of daphnicyclidin M (1).

**Figure S6.** HSQC spectrum of daphnicyclidin M (1) in CD<sub>3</sub>OD.

**Figure S7.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of daphnicyclidin M (**1**) in  $\text{CD}_3\text{OD}$ .

**Figure S8.** HMBC spectrum of daphnicyclidin M (1) in CD<sub>3</sub>OD.



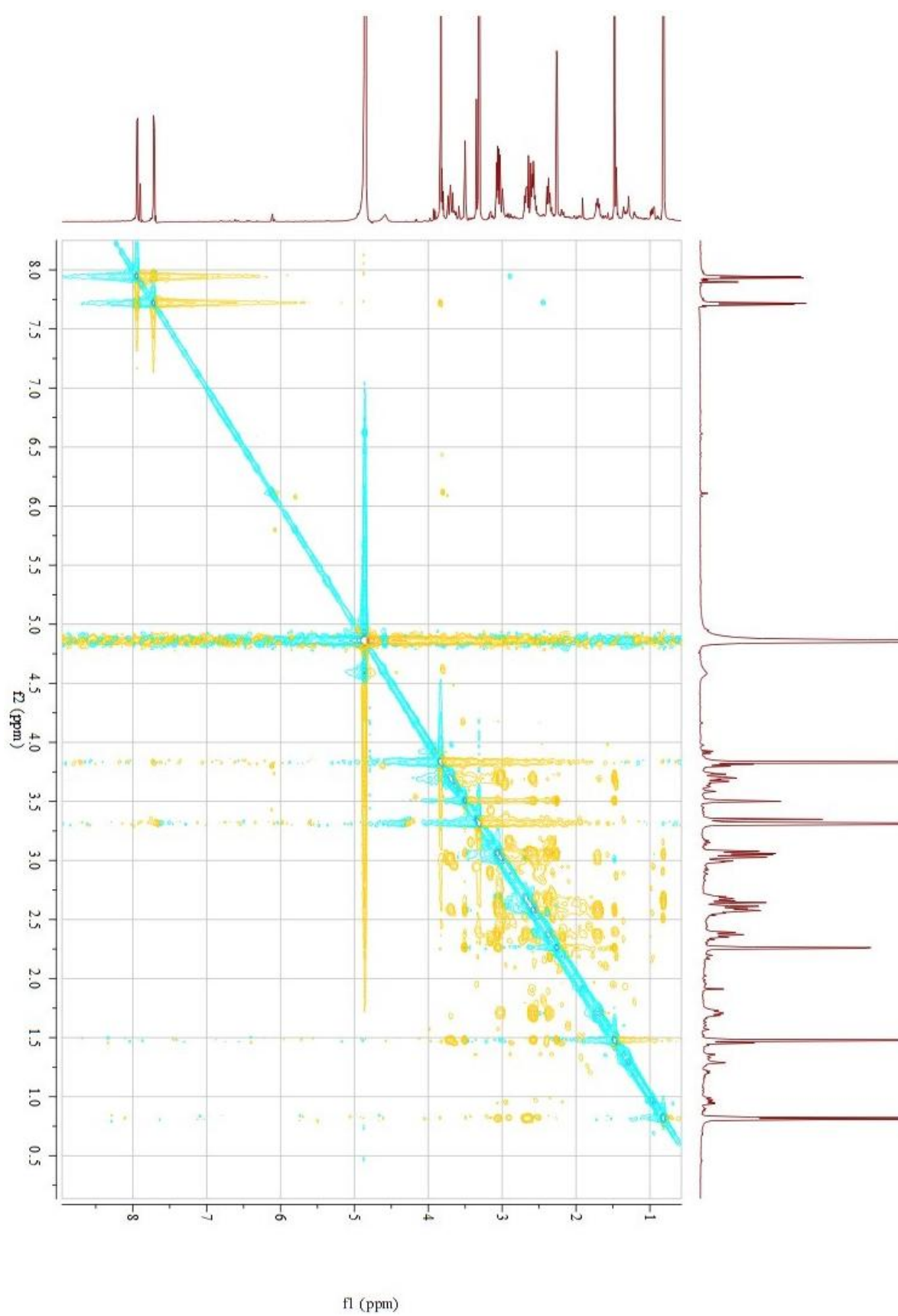
**Figure S9.** NOESY spectrum of daphnicyclidin M (1) in CD<sub>3</sub>OD.

Figure S10. ESIMS spectrum of daphnicyclidin M (1).

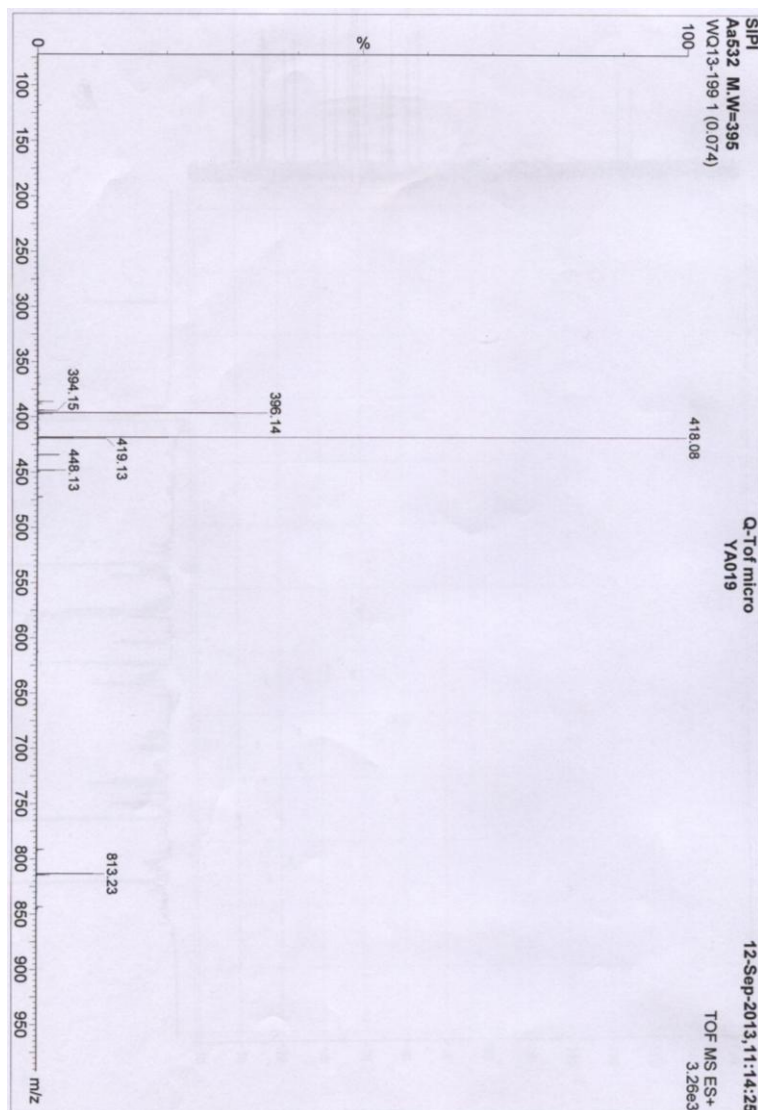
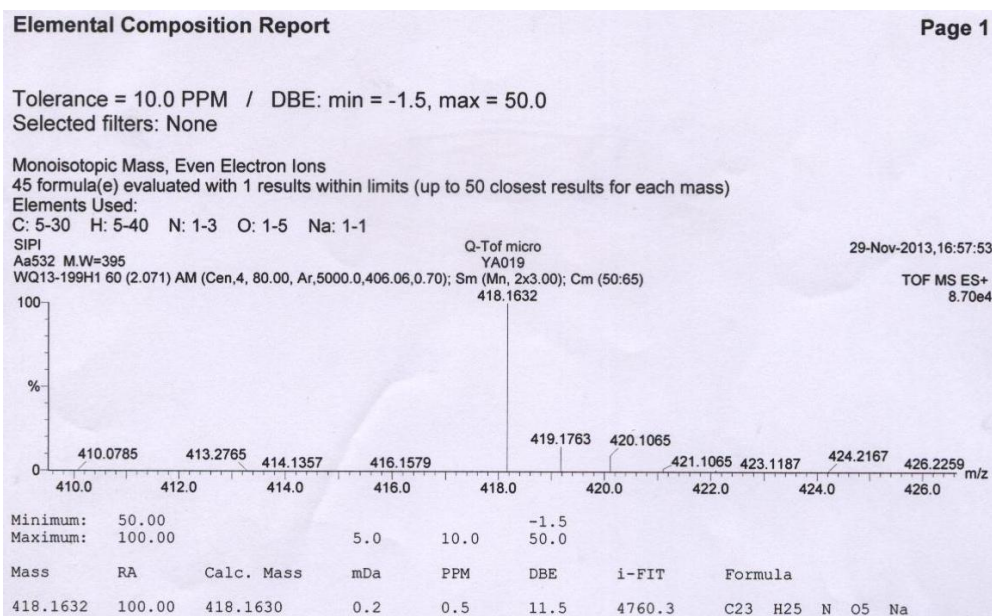
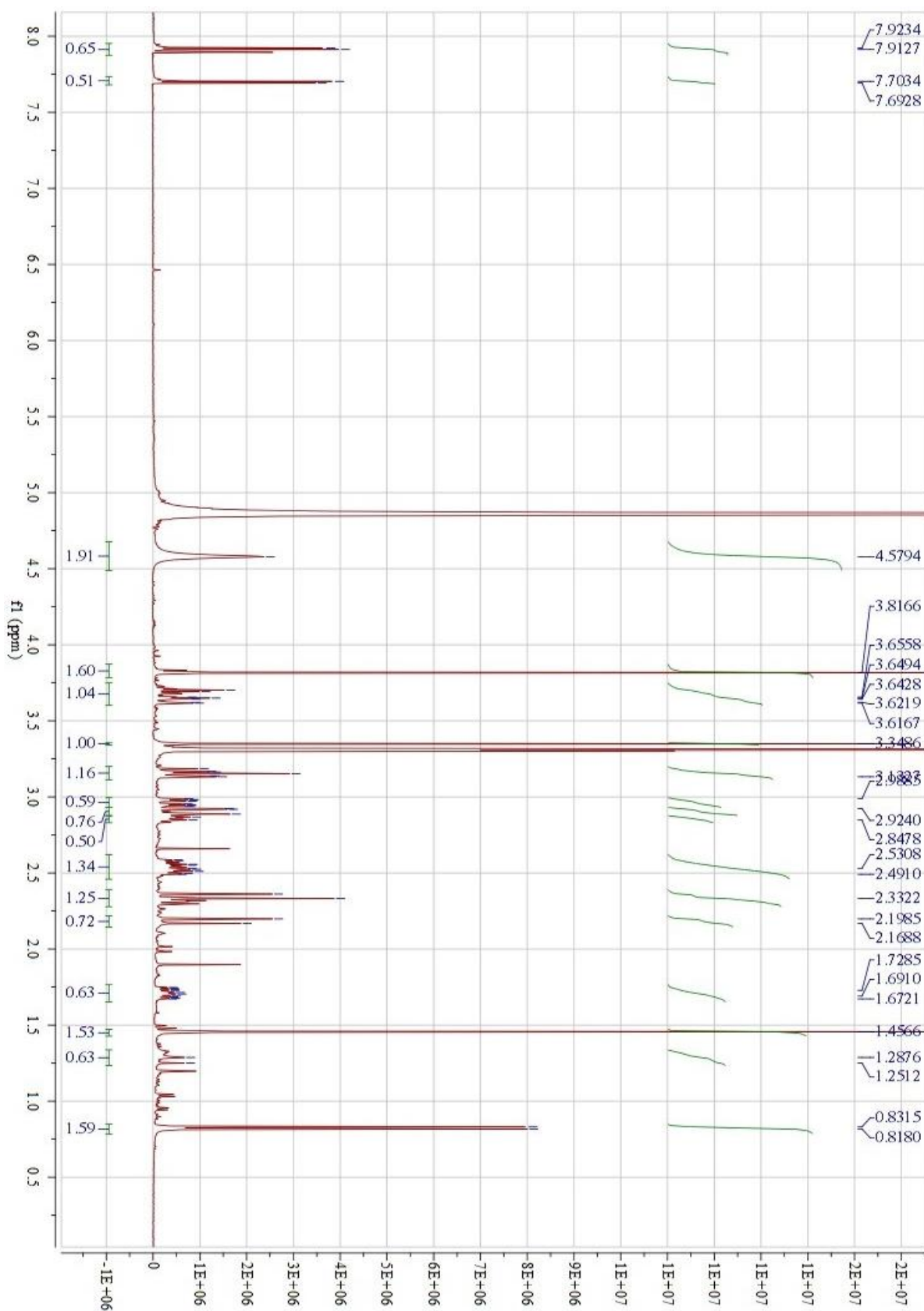
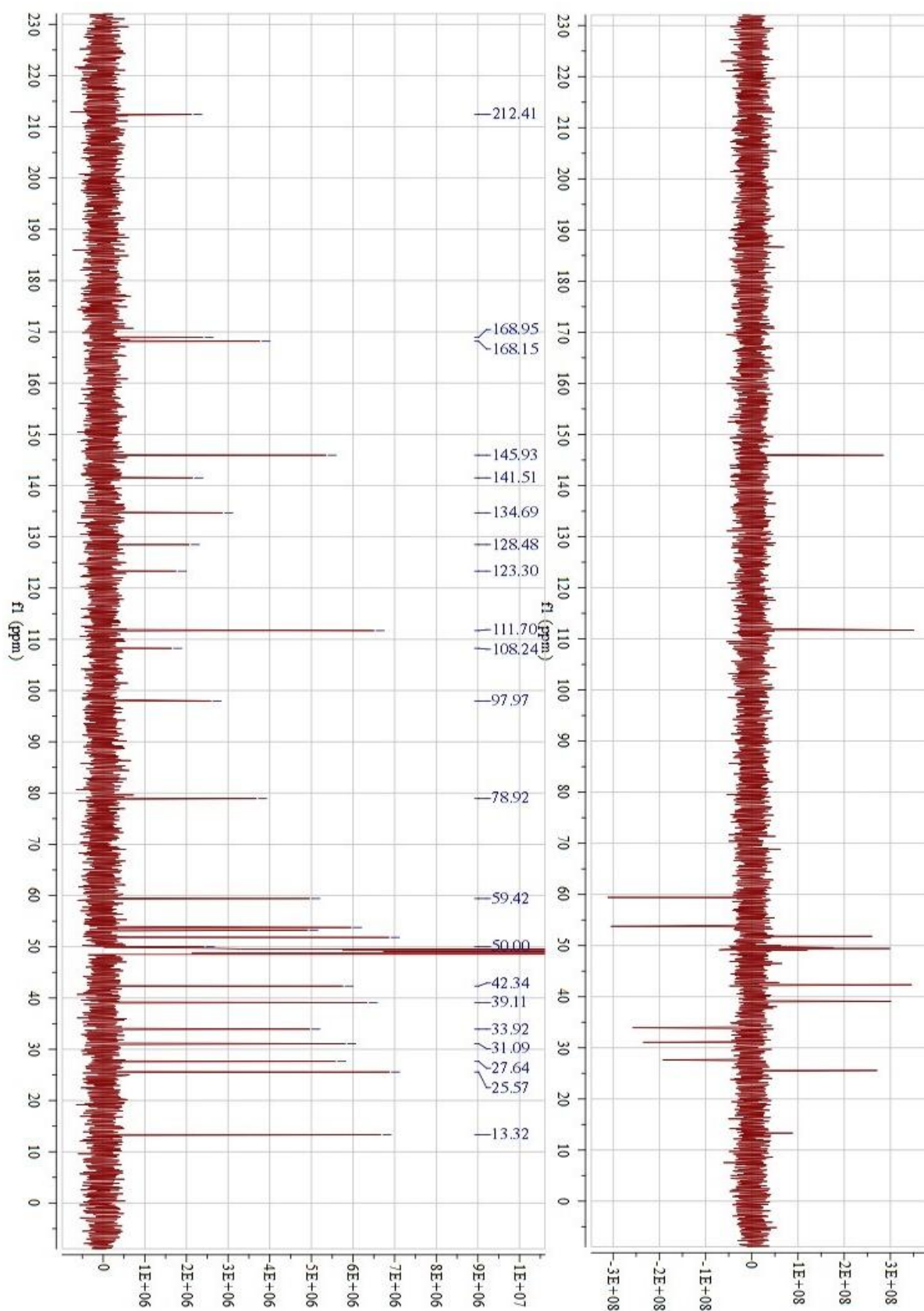


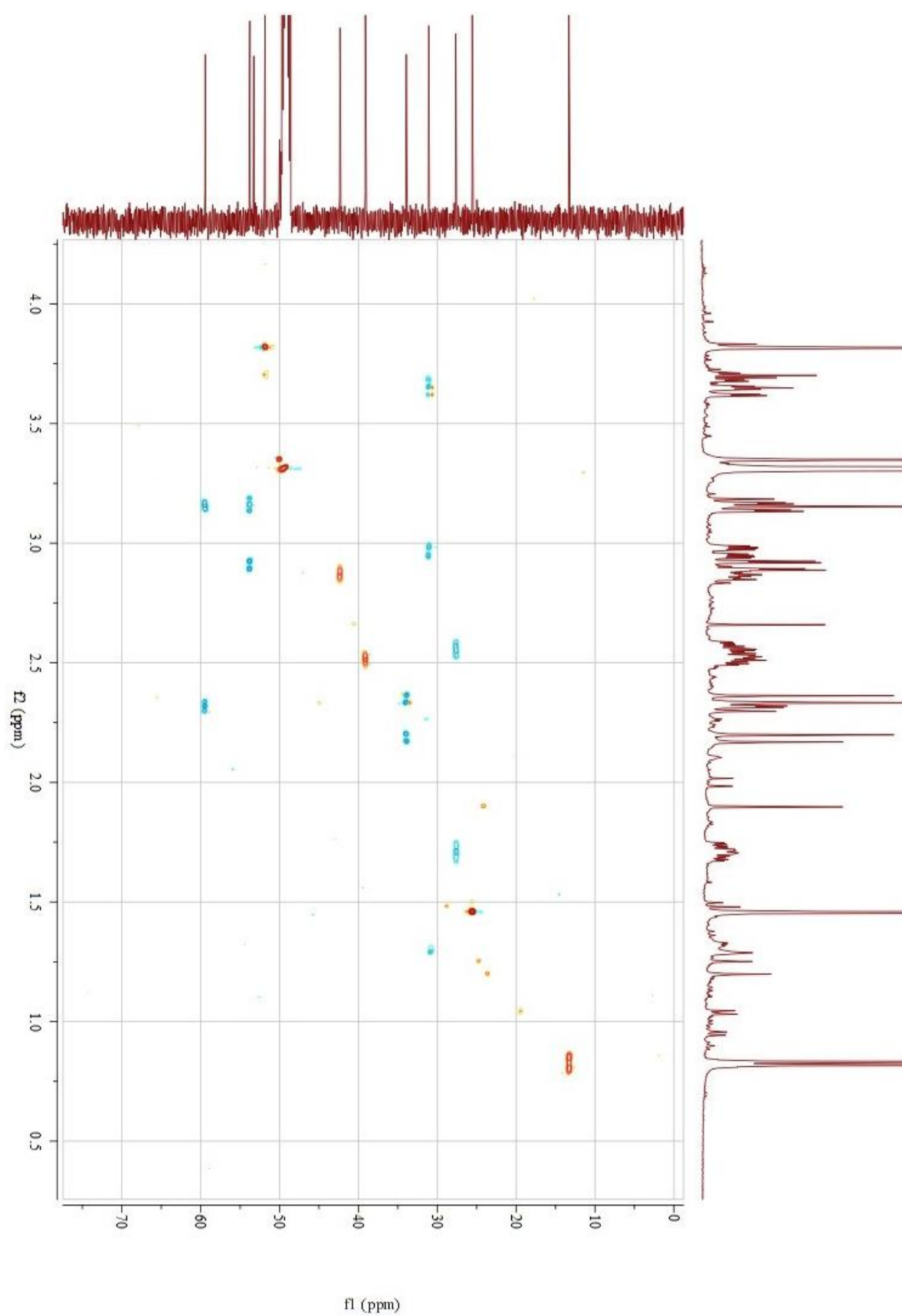
Figure S11. HRESIMS spectrum of daphnicyclidin M (1).

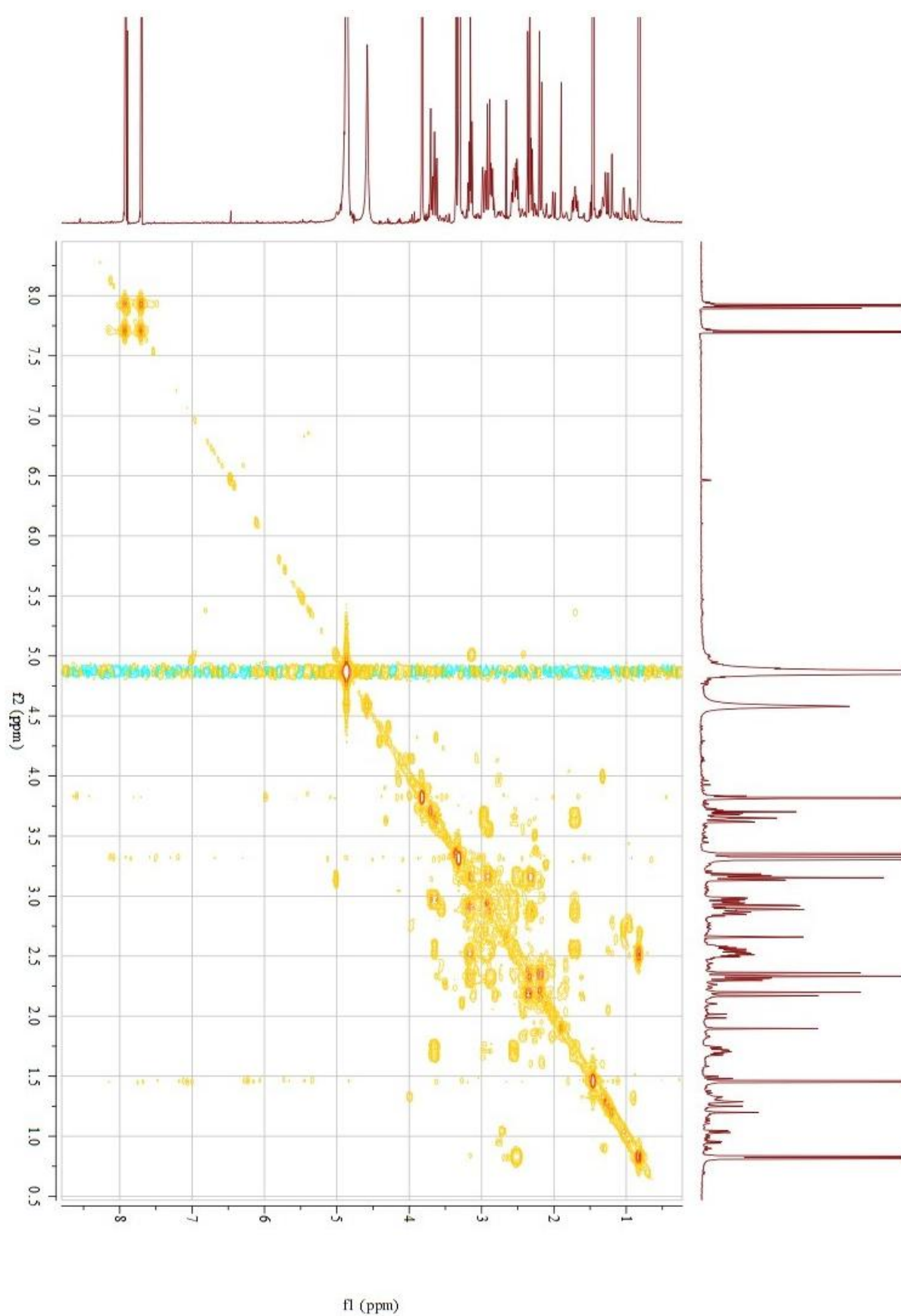


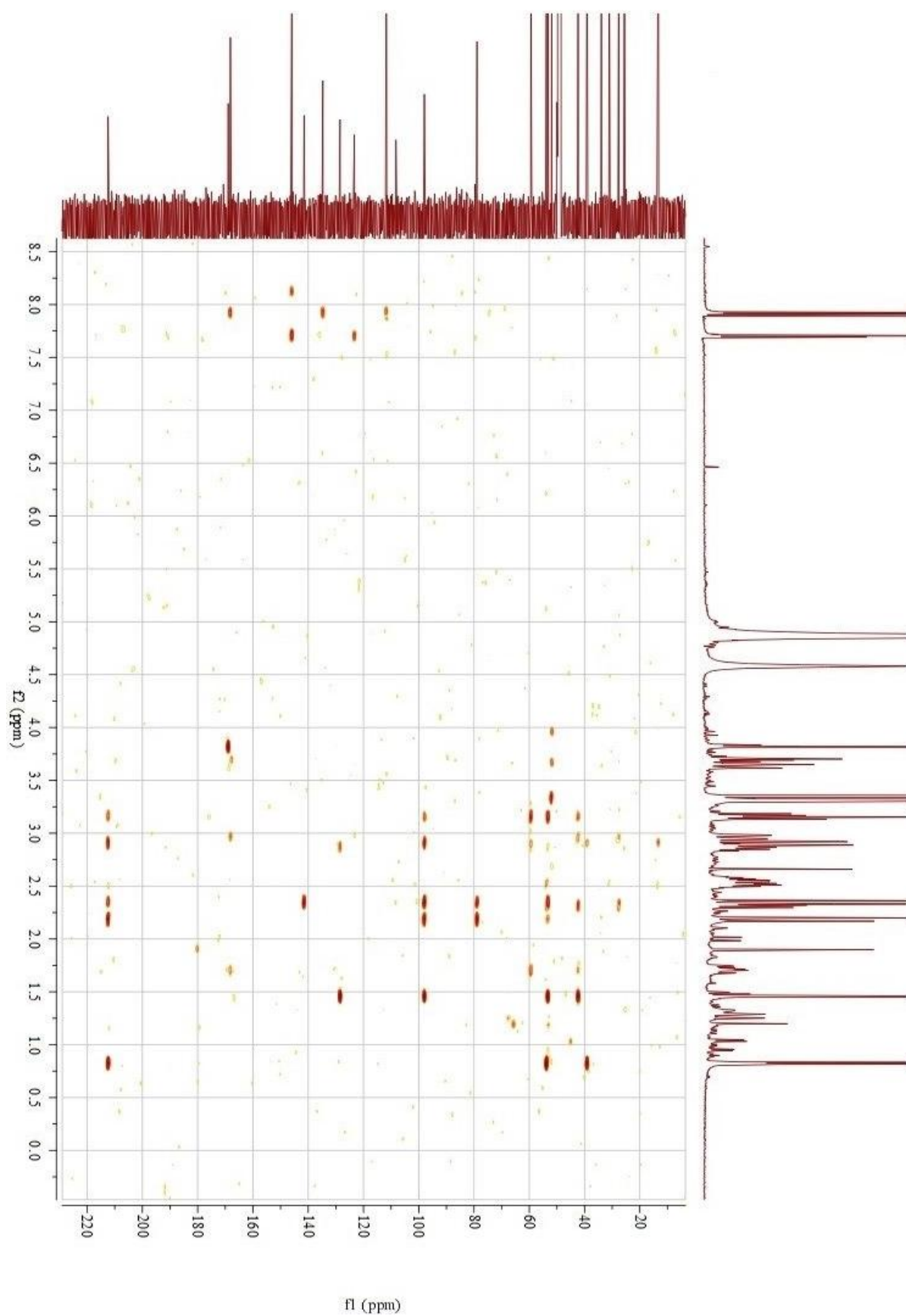


**Figure S12.**  $^1\text{H-NMR}$  (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of daphnicyclidin N (**2**).

**Figure S13.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of daphnicyclidin N (2).

**Figure S14.** HSQC spectrum of daphnicyclidin N (2) in CD<sub>3</sub>OD.

**Figure S15.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of daphnicyclidin N (2) in  $\text{CD}_3\text{OD}$ .

**Figure S16.** HMBC spectrum of daphnicyclidin N (2) in CD<sub>3</sub>OD.



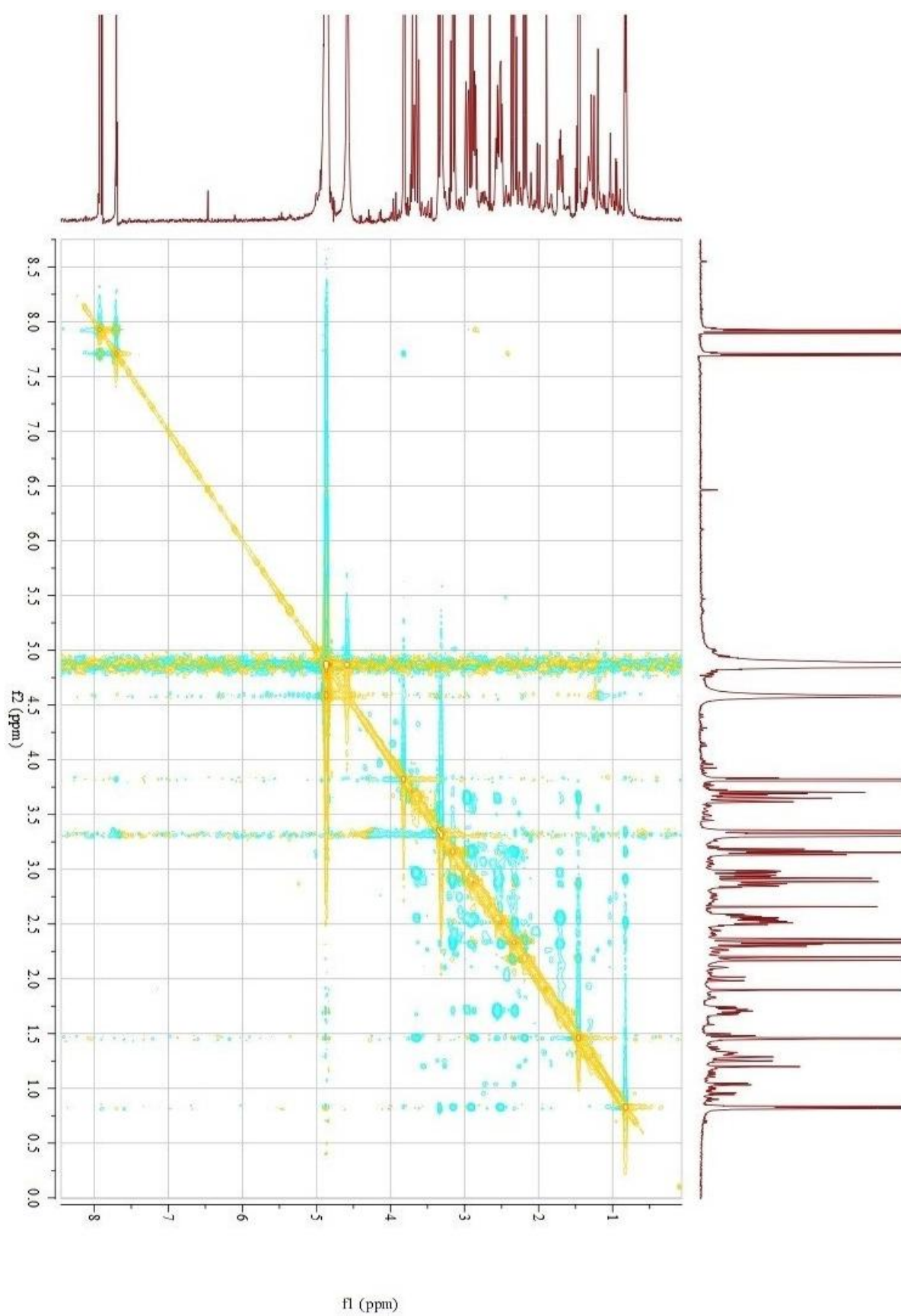
**Figure S17.** NOESY spectrum of daphnicyclidin N (2) in CD<sub>3</sub>OD.

Figure S18. ESIMS spectrum of daphnicyclidin N (2).

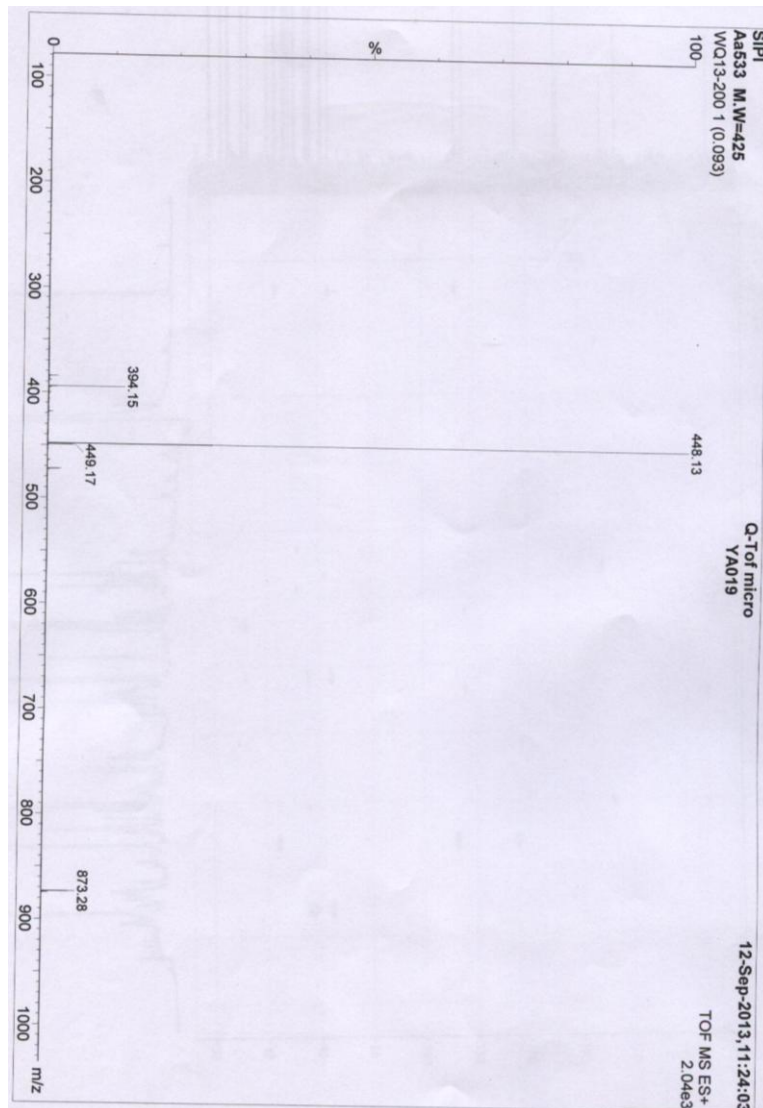


Figure S19. HRESIMS spectrum of daphnicyclidin N (2).

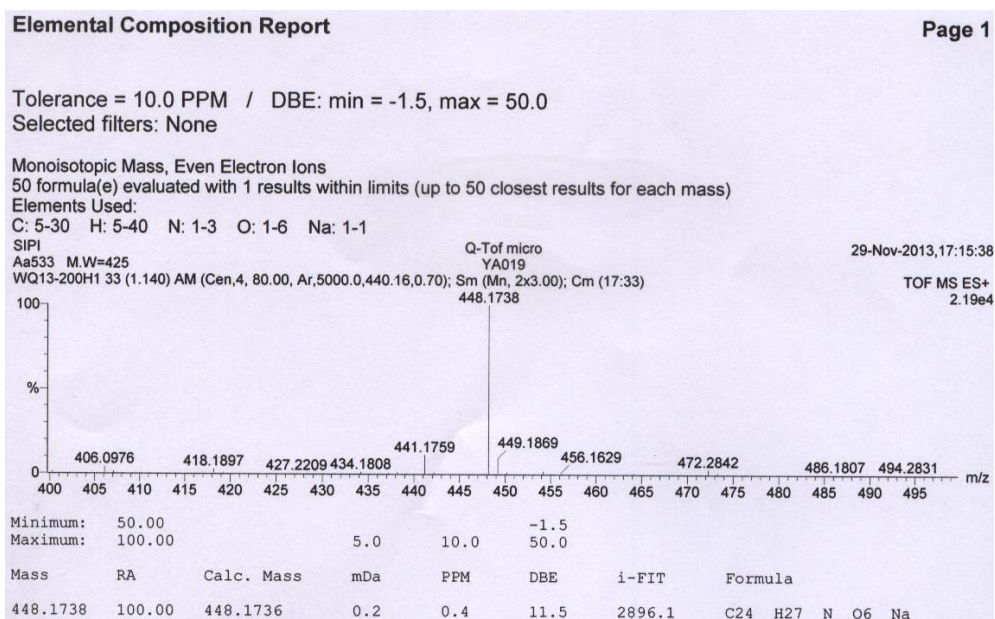
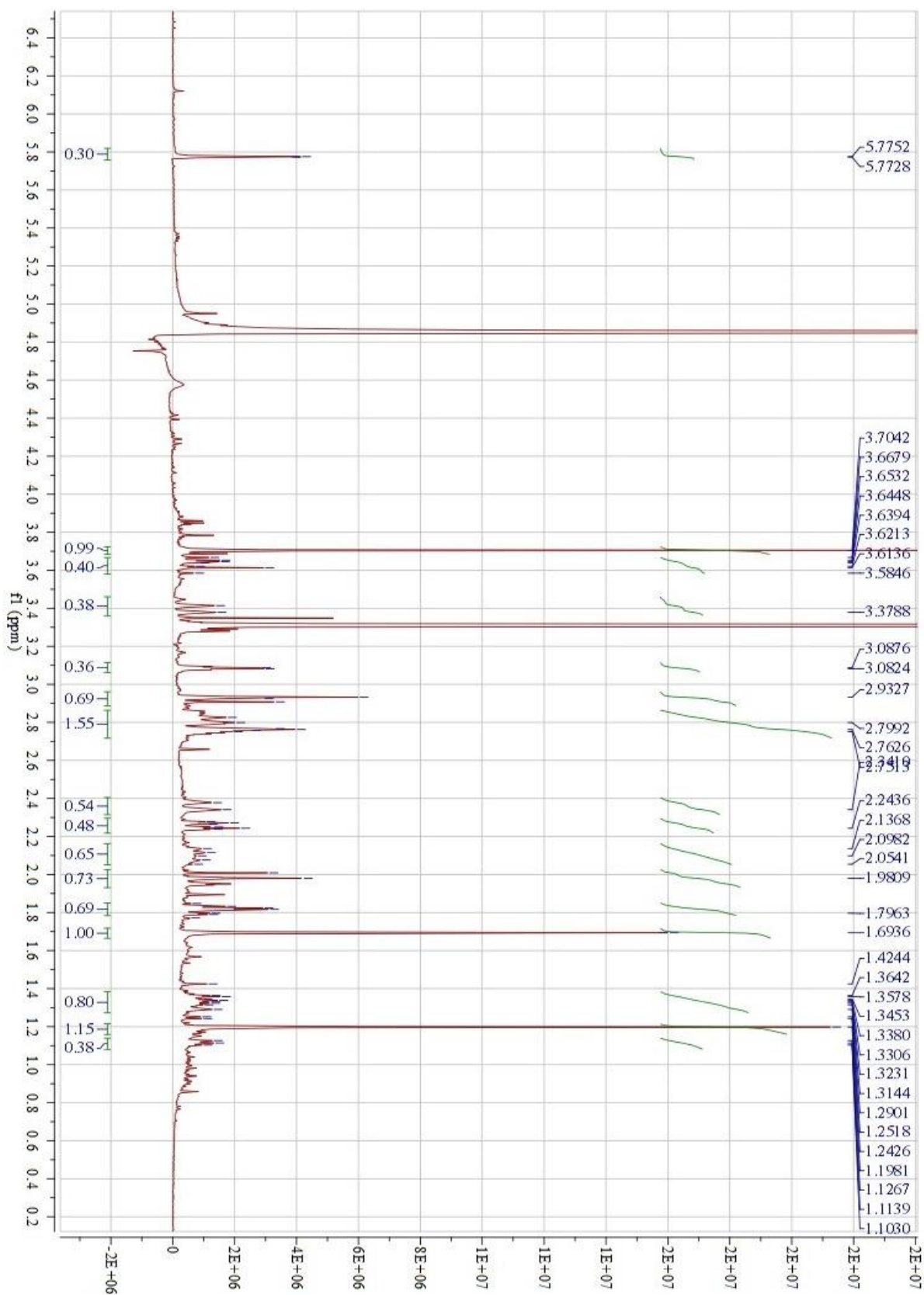


Figure S20.  $^1\text{H-NMR}$  (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of calyciphylline Q (3).

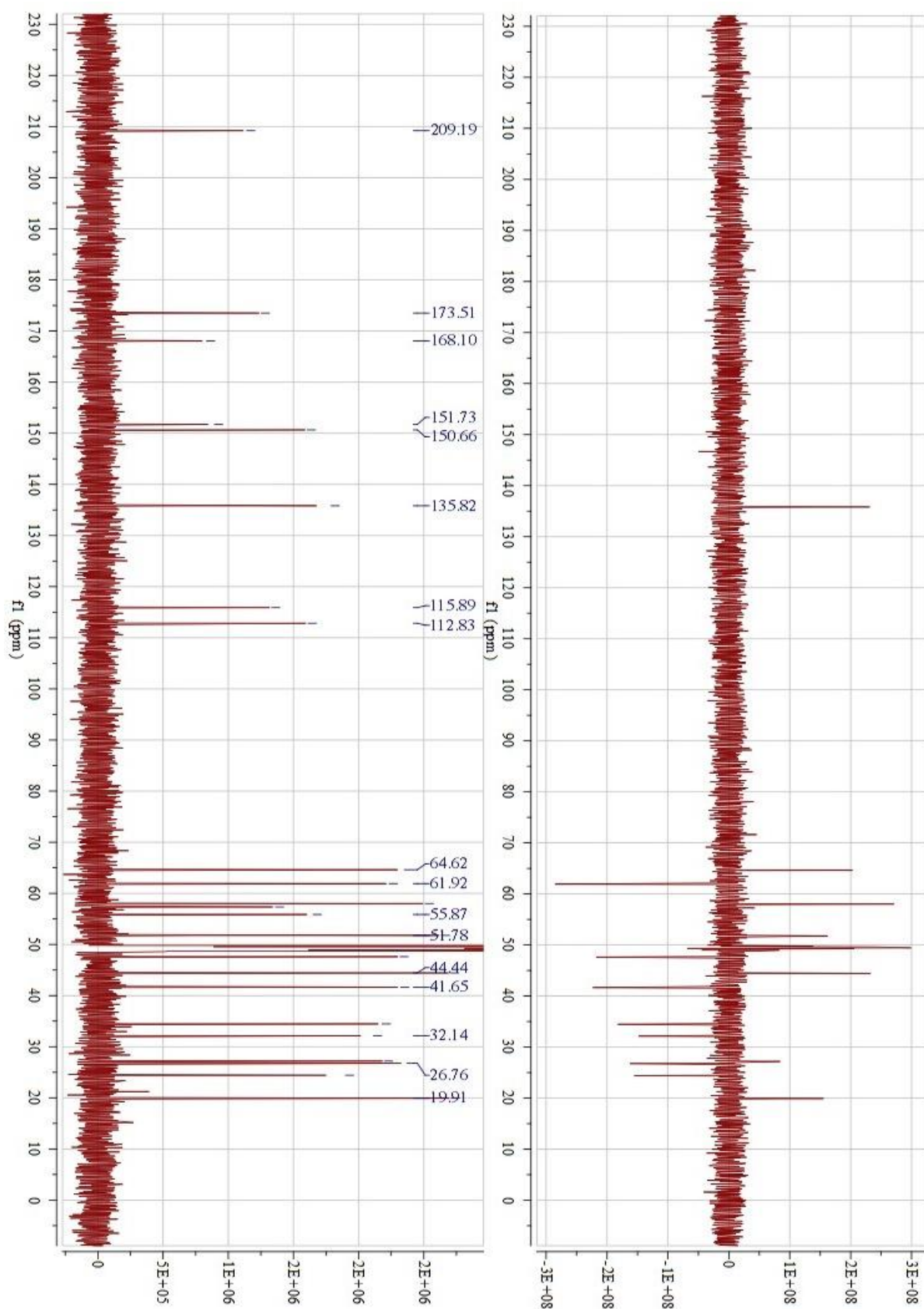
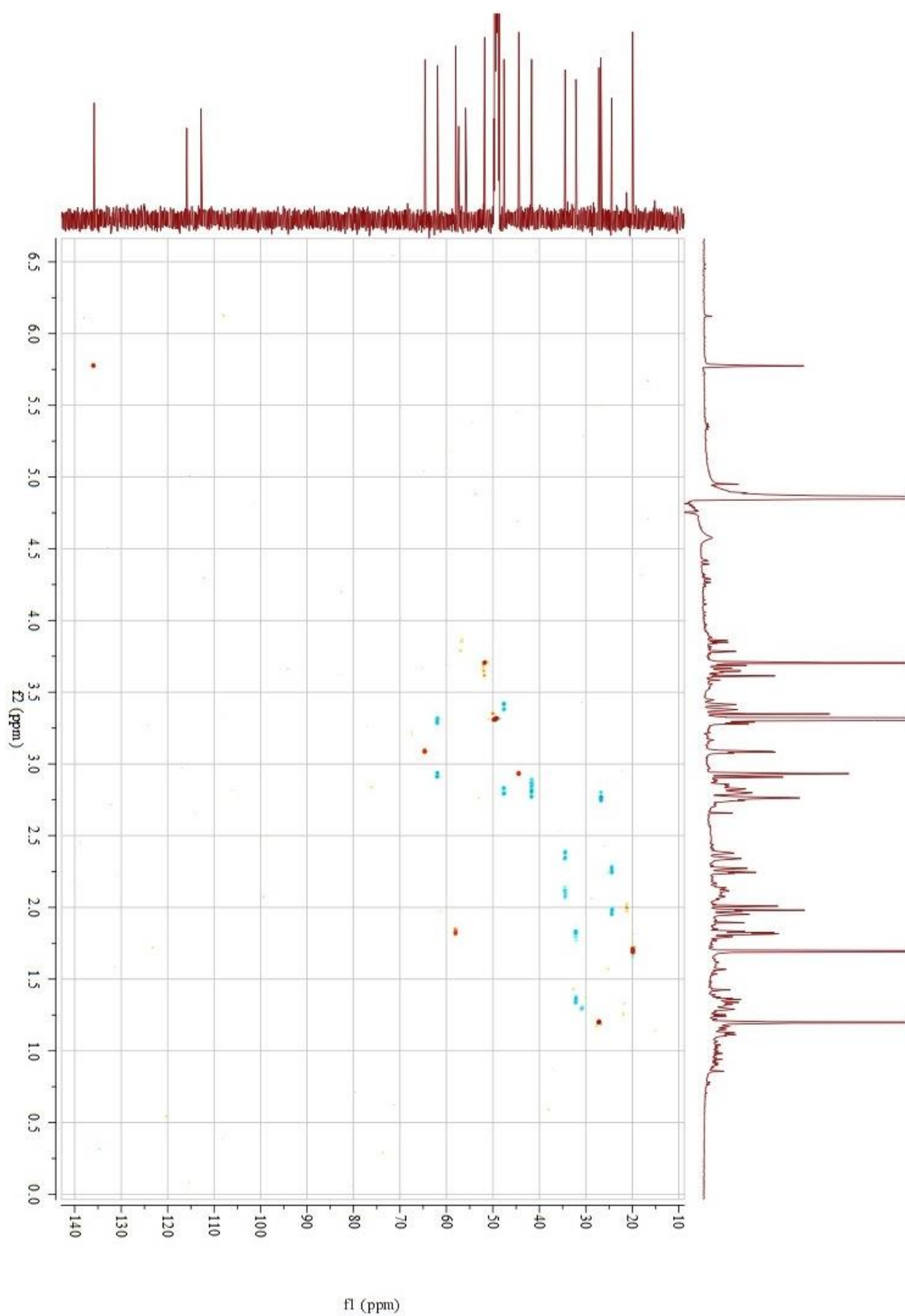
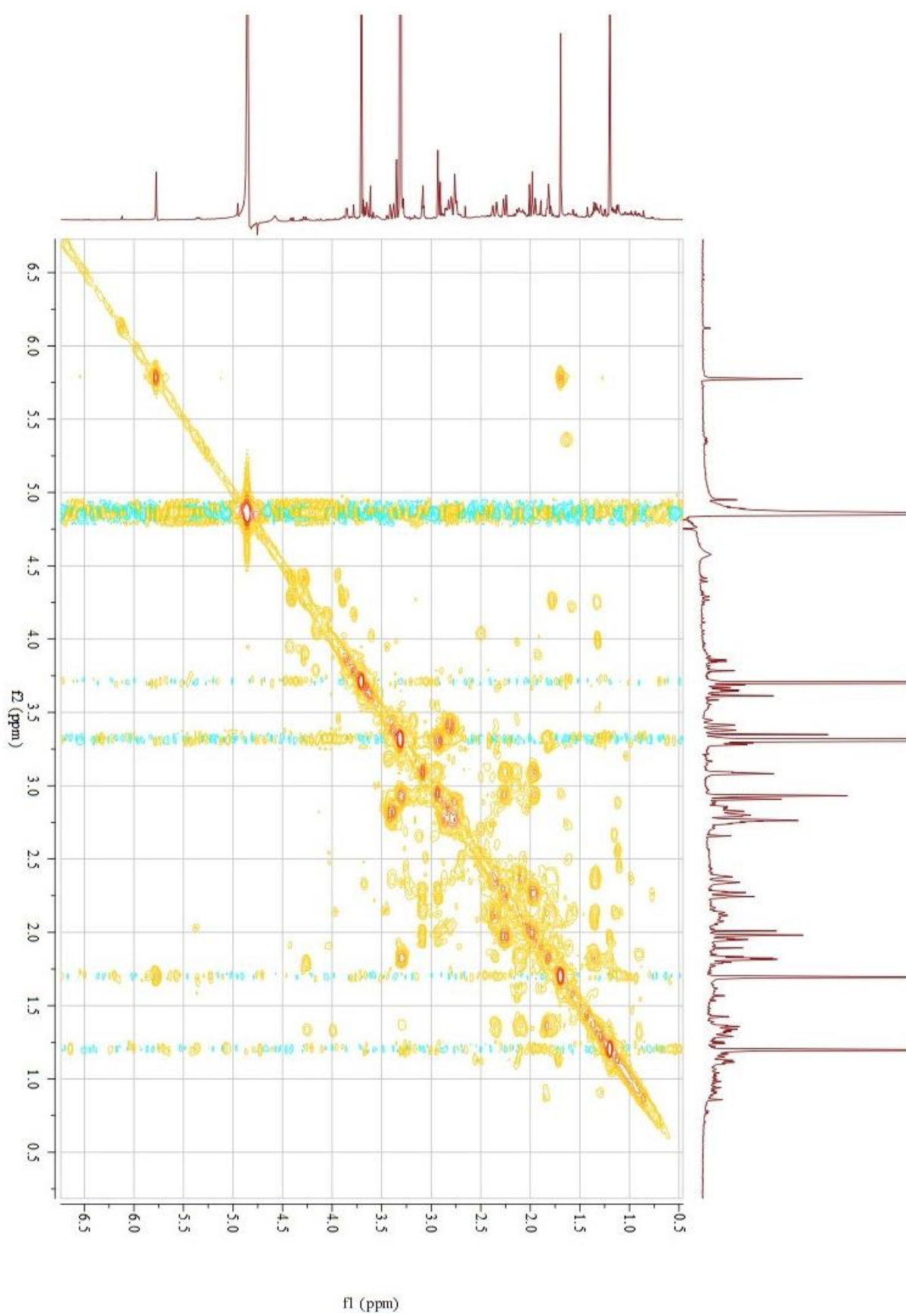
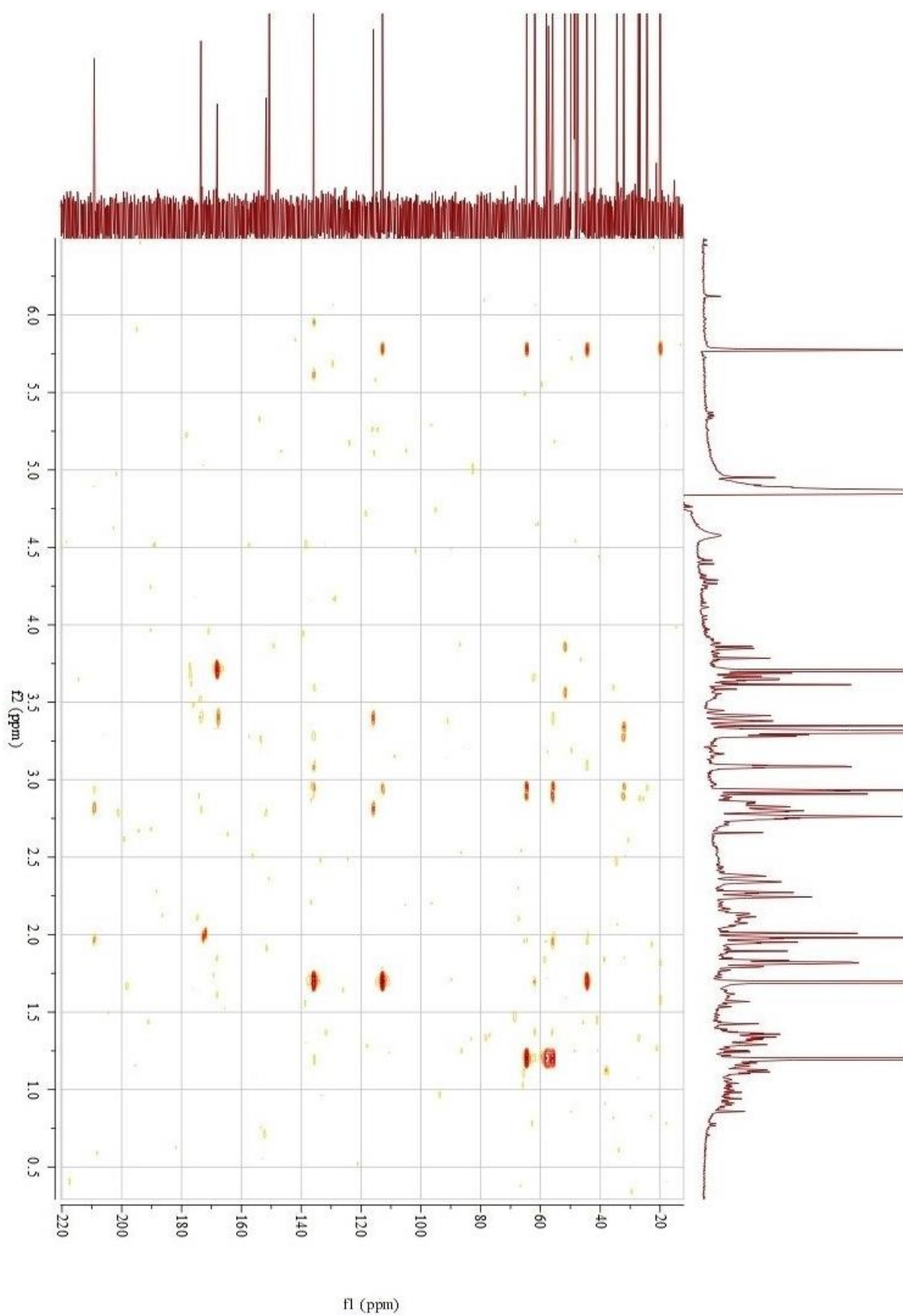
**Figure S21.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of calyciphylline Q (3).



Figure S22. HSQC spectrum of calyciphylline Q (3) in CD<sub>3</sub>OD.



**Figure S23.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of calyciphylline Q (**3**) in  $\text{CD}_3\text{OD}$ .

**Figure S24.** HMBC spectrum of calyciphylline Q (**3**) in CD<sub>3</sub>OD.

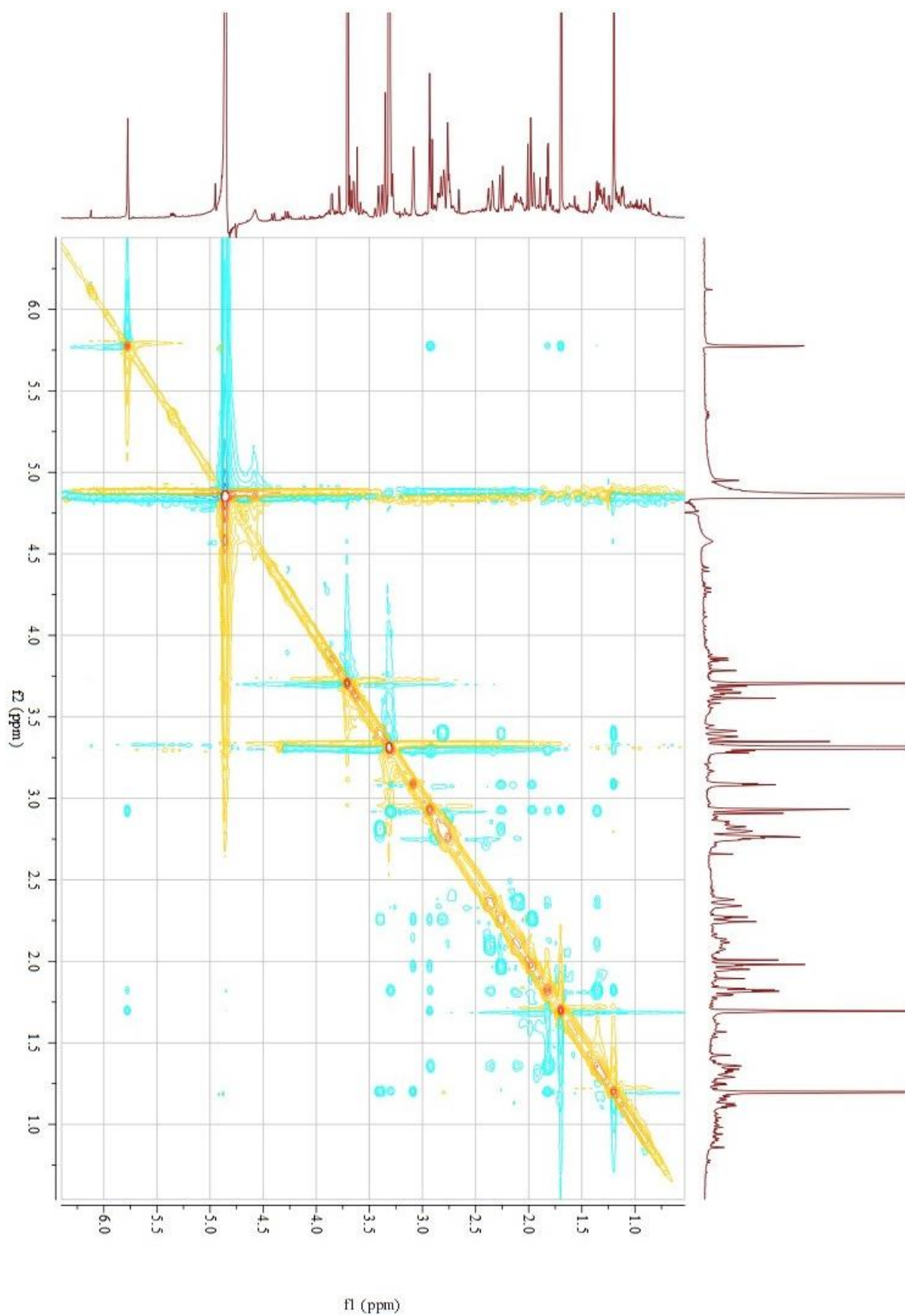
**Figure S25.** NOESY spectrum of calyciphylline Q (**3**) in CD<sub>3</sub>OD.

Figure S26. ESIMS spectrum of calyciphylline Q (3).

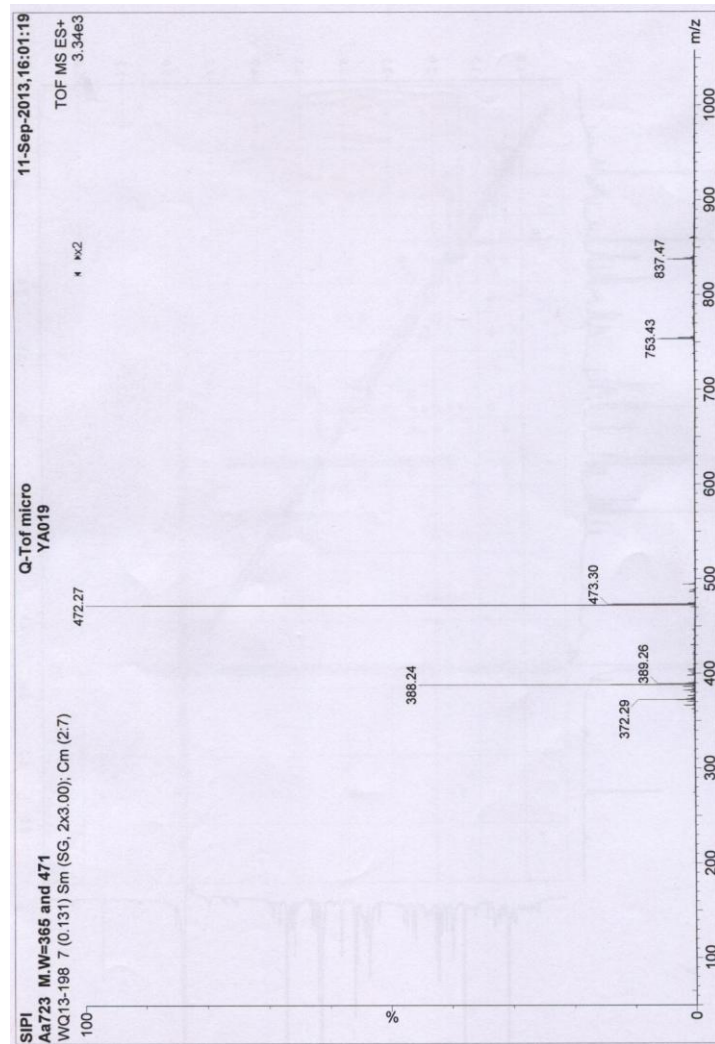


Figure S27. HRESIMS spectrum of calyciphylline Q (3).

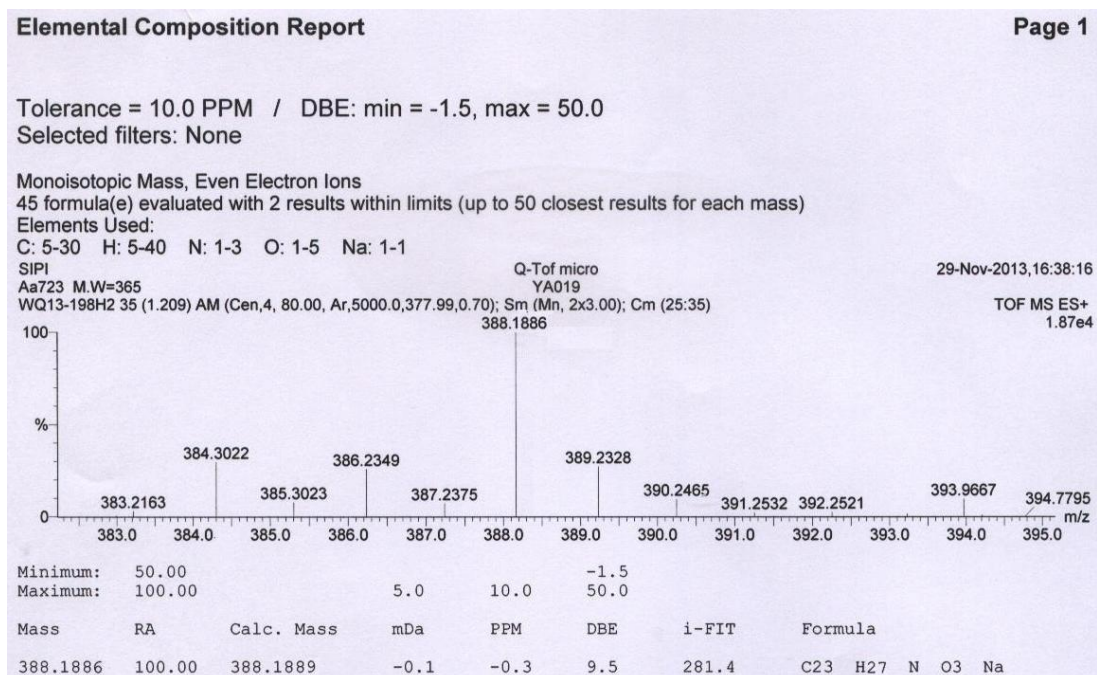
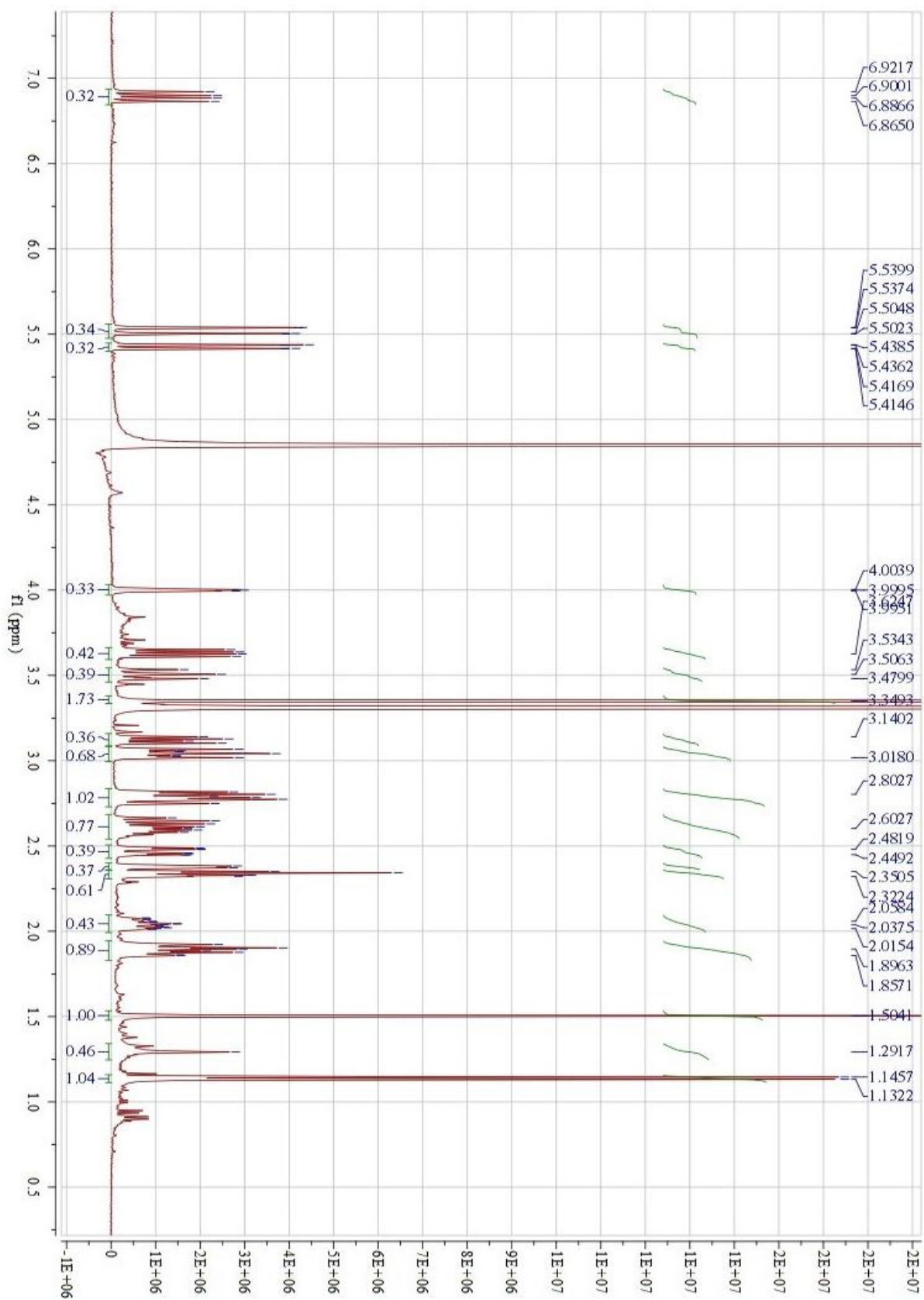




Figure S28.  $^1\text{H-NMR}$  (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of calyciphylline R (4).



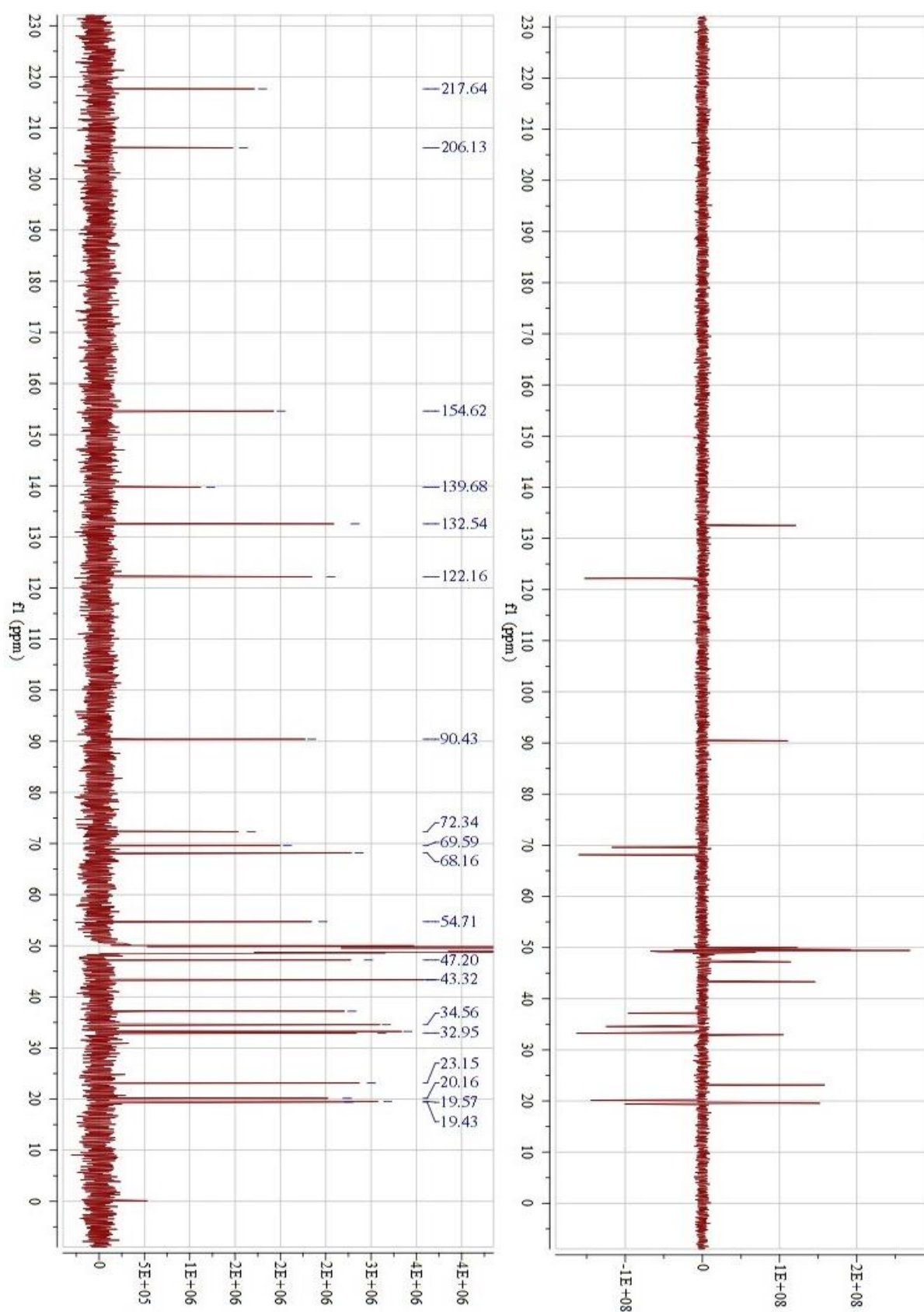
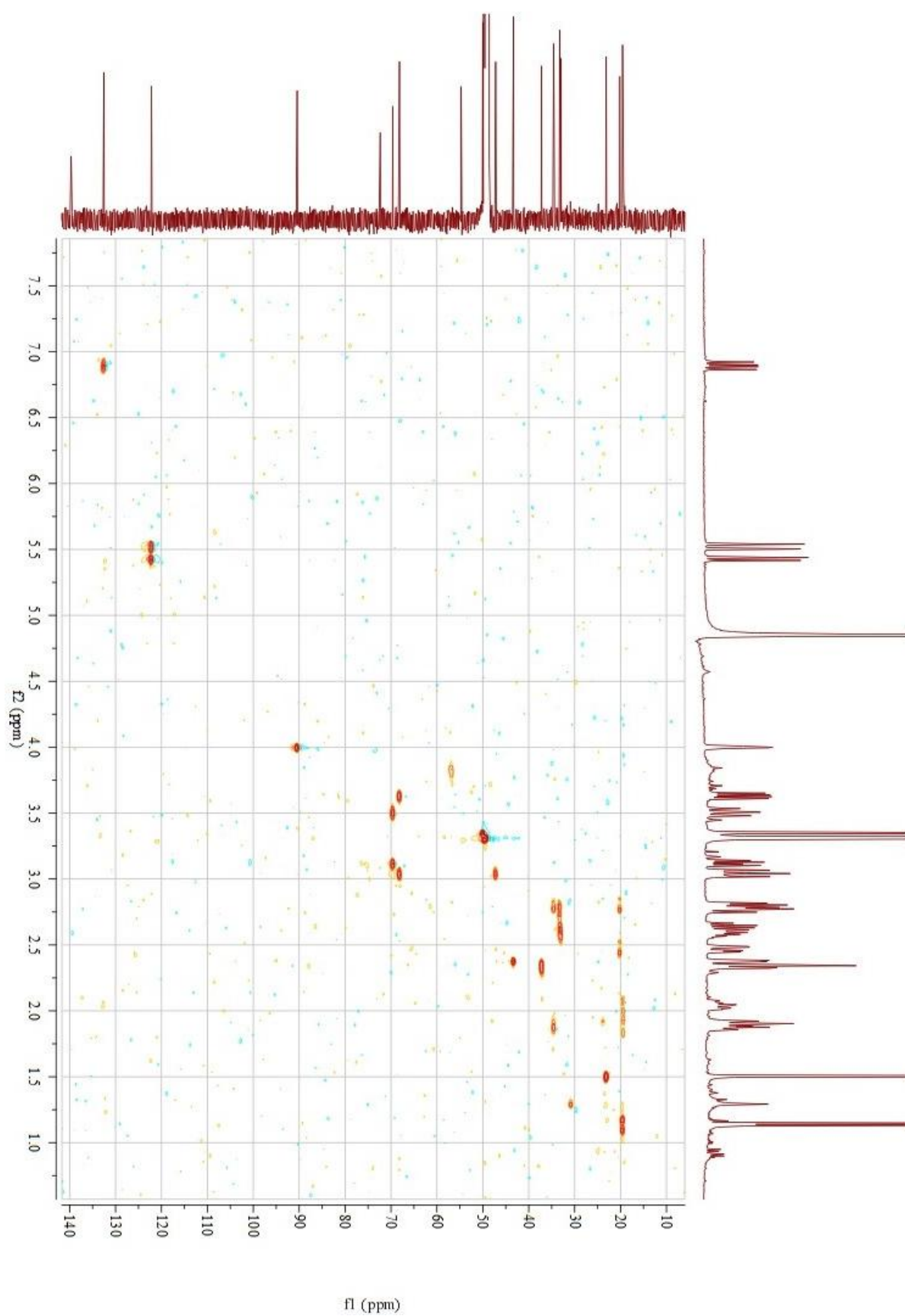
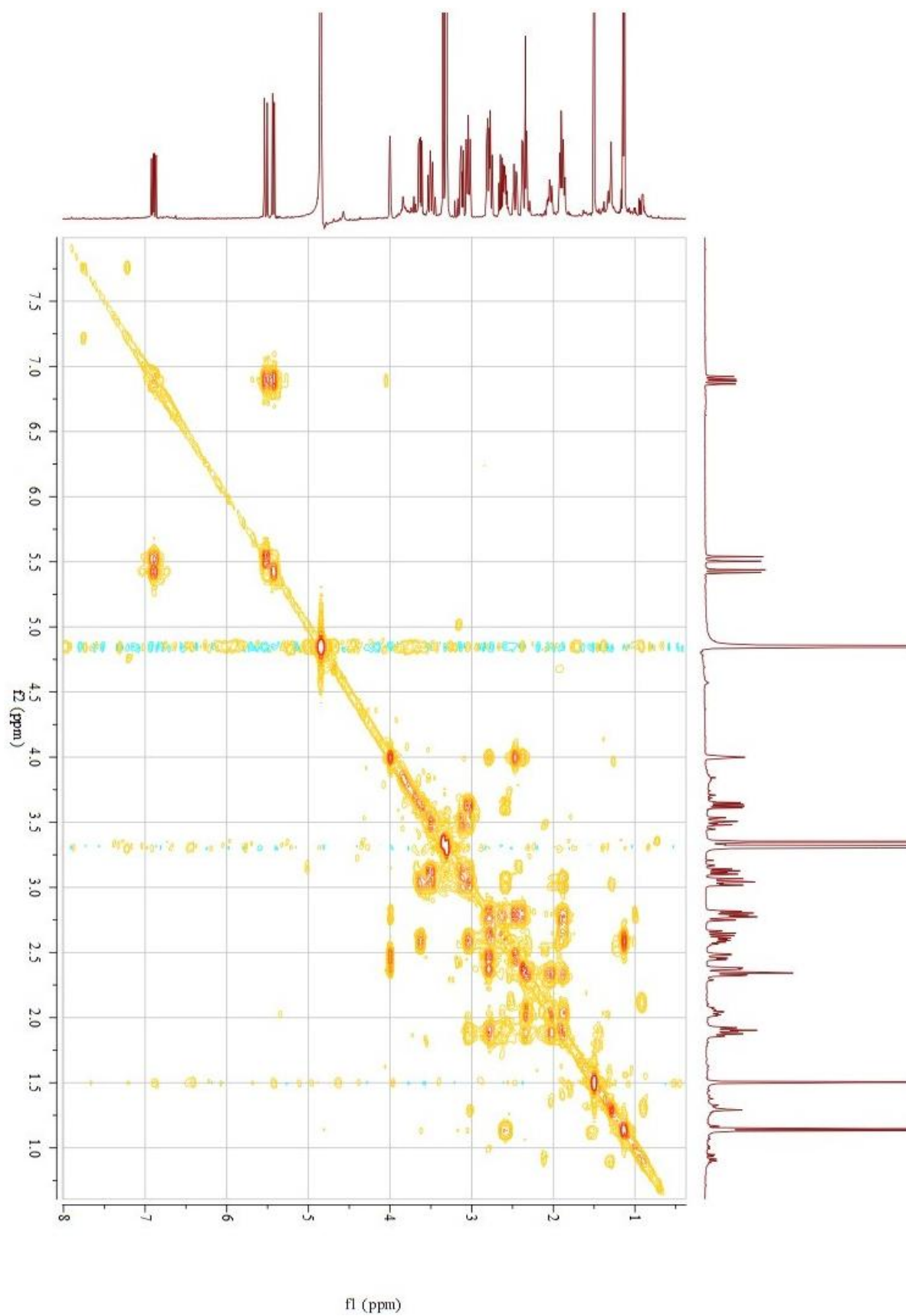
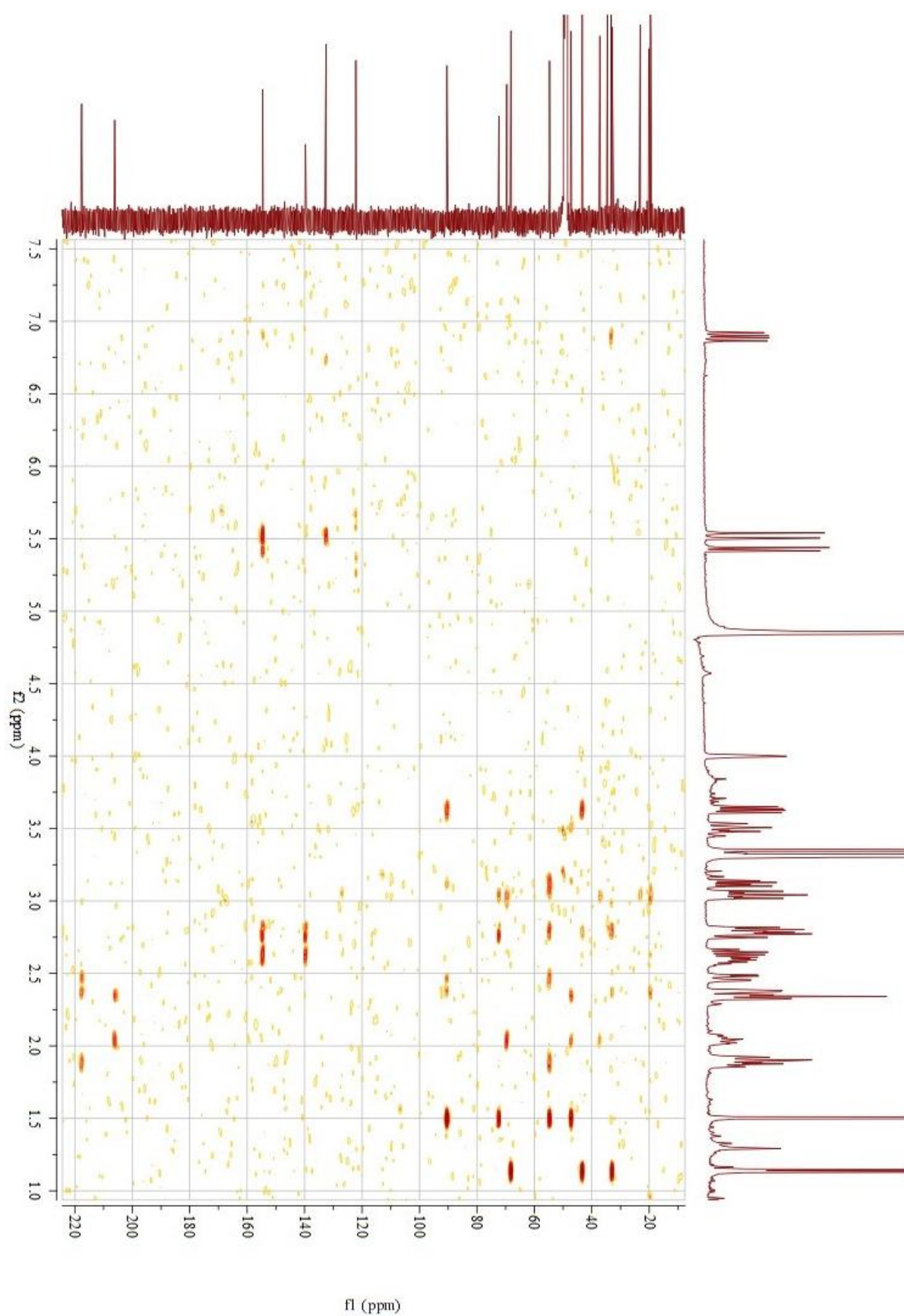
**Figure S29.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of calyciphylline R (4).

Figure S30. HSQC spectrum of calyciphylline R (4) in CD<sub>3</sub>OD.

**Figure S31.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of calyciphylline R (4) in  $\text{CD}_3\text{OD}$ .

**Figure S32.** HMBC spectrum of calyciphylline R (**4**) in CD<sub>3</sub>OD.

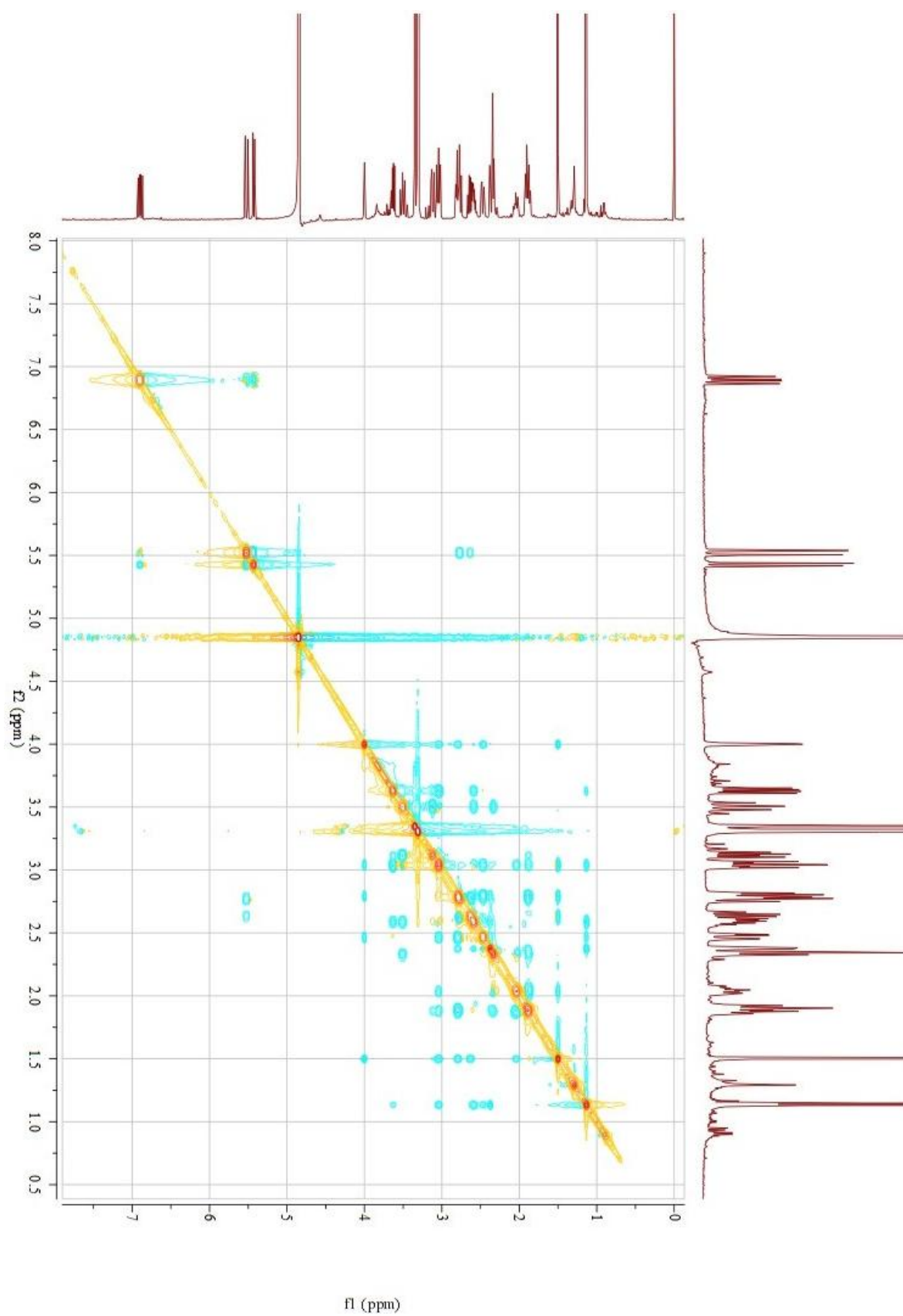
**Figure S33.** NOESY spectrum of calyciphylline R (4) in CD<sub>3</sub>OD.



Figure S34. ESIMS spectrum of calyciphylline R (4).

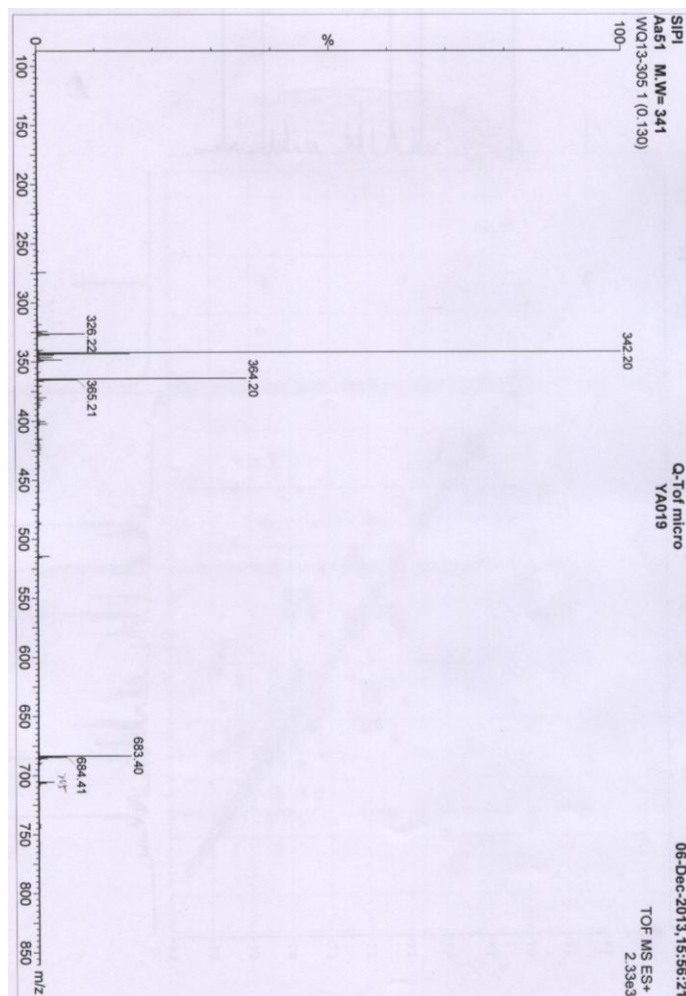
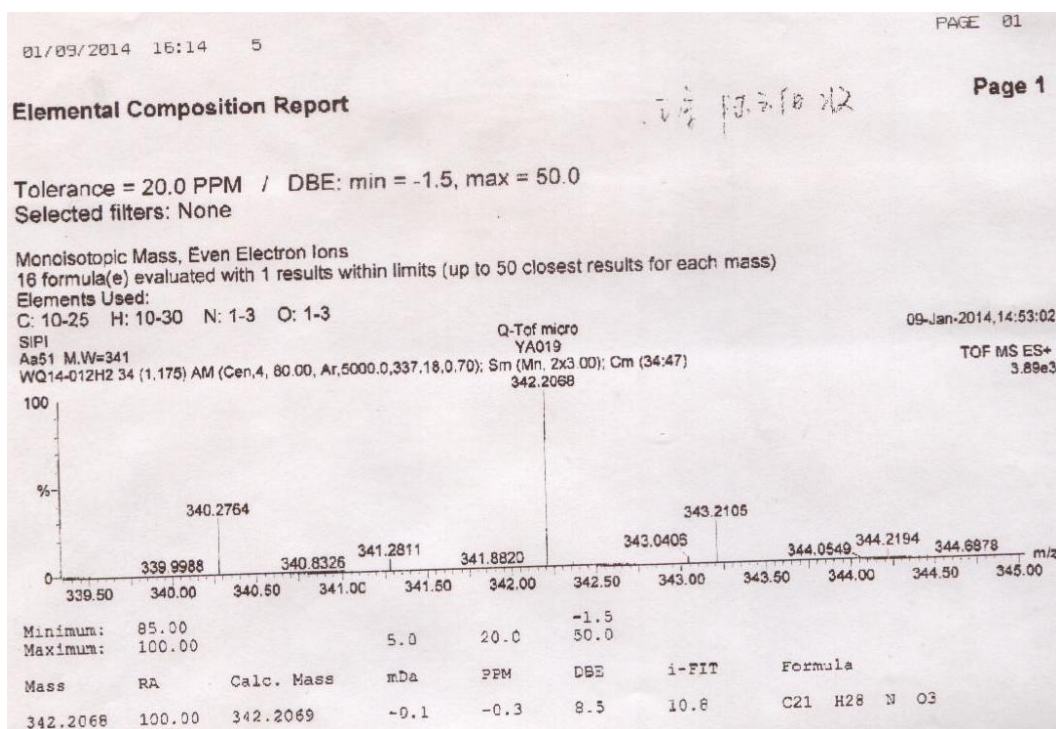
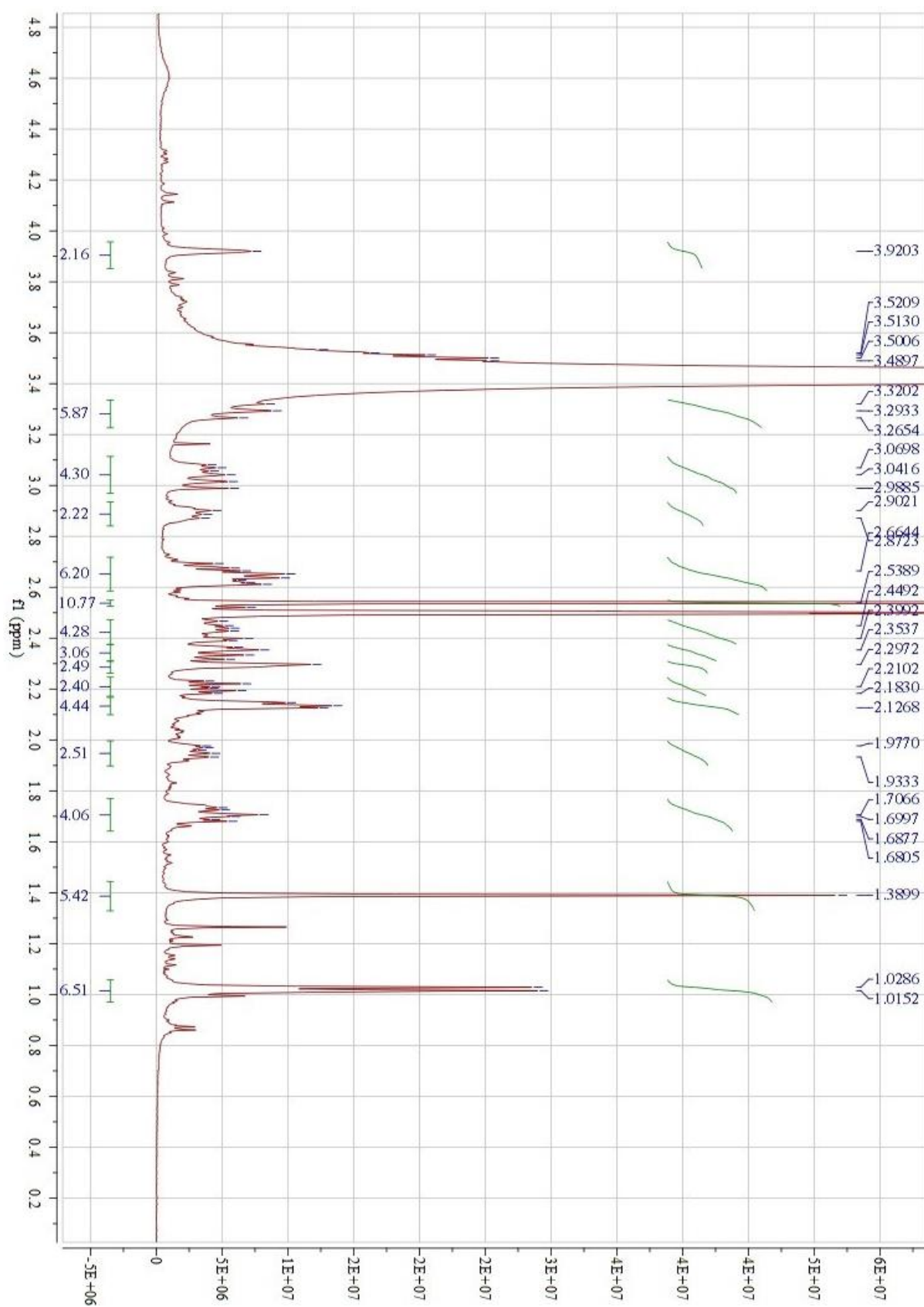
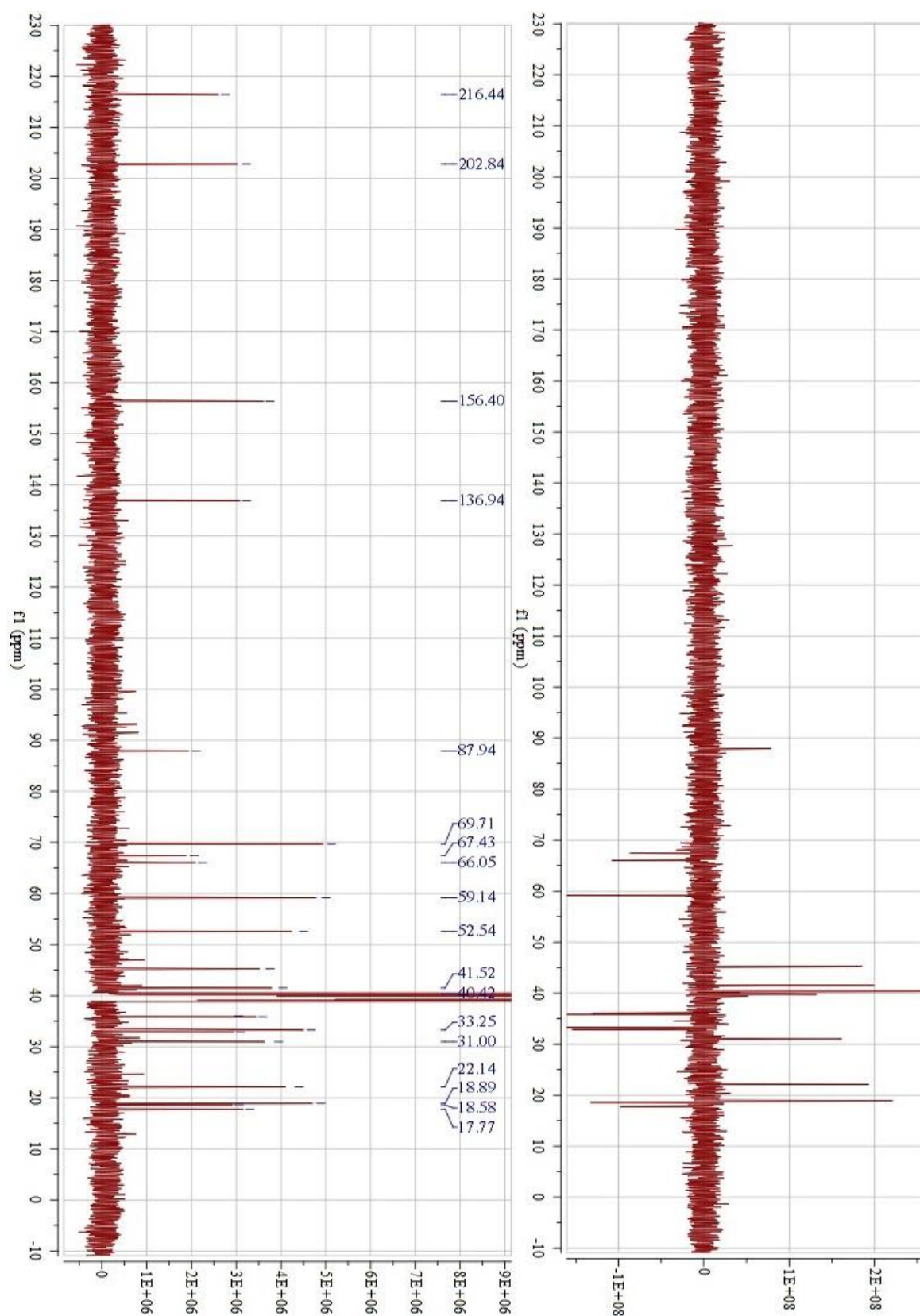
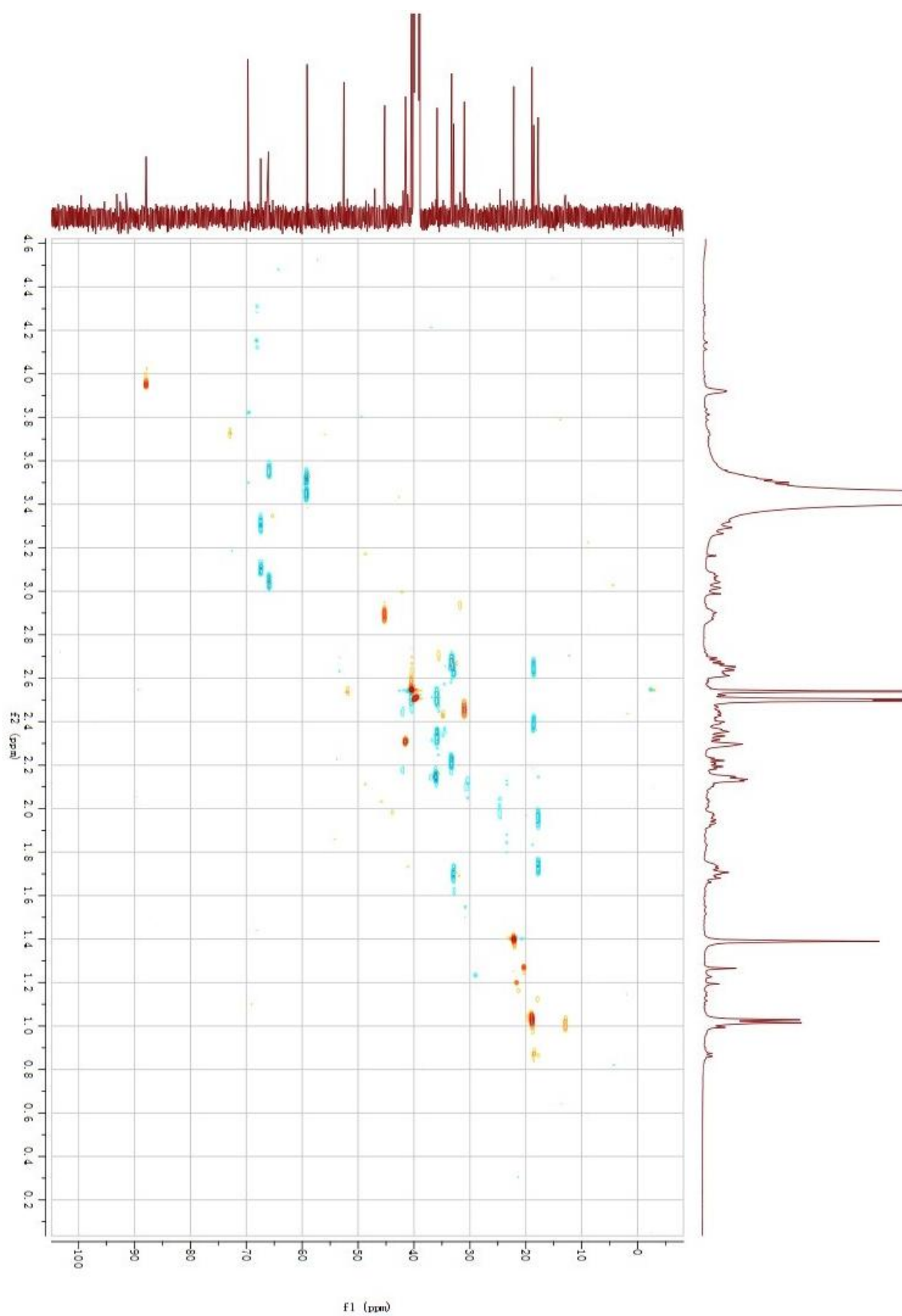


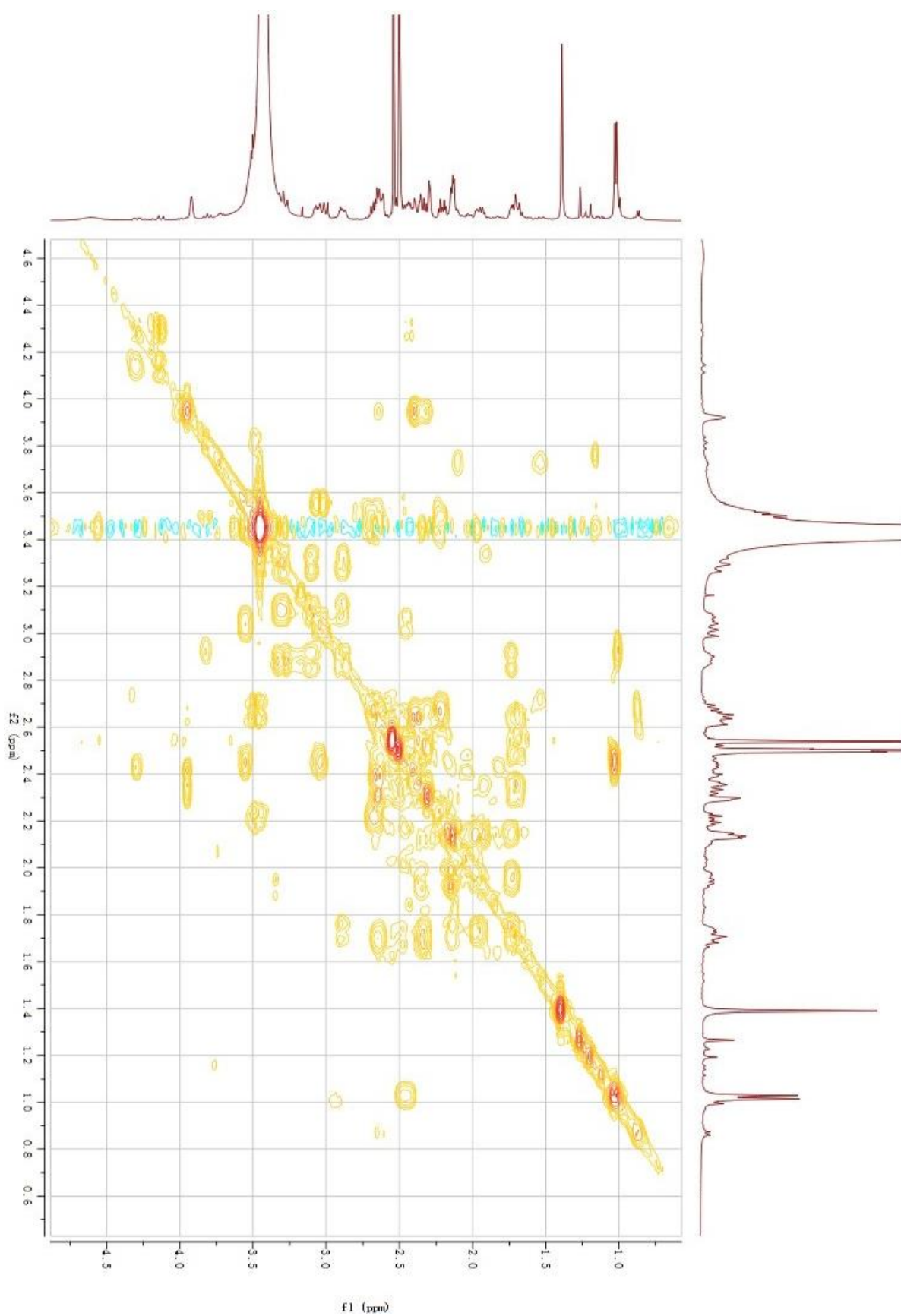
Figure S35. HRESIMS spectrum of calyciphylline R (4).



**Figure S36.**  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of calyciphylline S (5).

**Figure S37.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO-}d_6$ ) spectrum of calyciphylline S (5).

**Figure S38.** HSQC spectrum of calyciphylline S (5) in DMSO- $d_6$ .

**Figure S39.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of calyciphylline S (**5**) in  $\text{DMSO-}d_6$ .



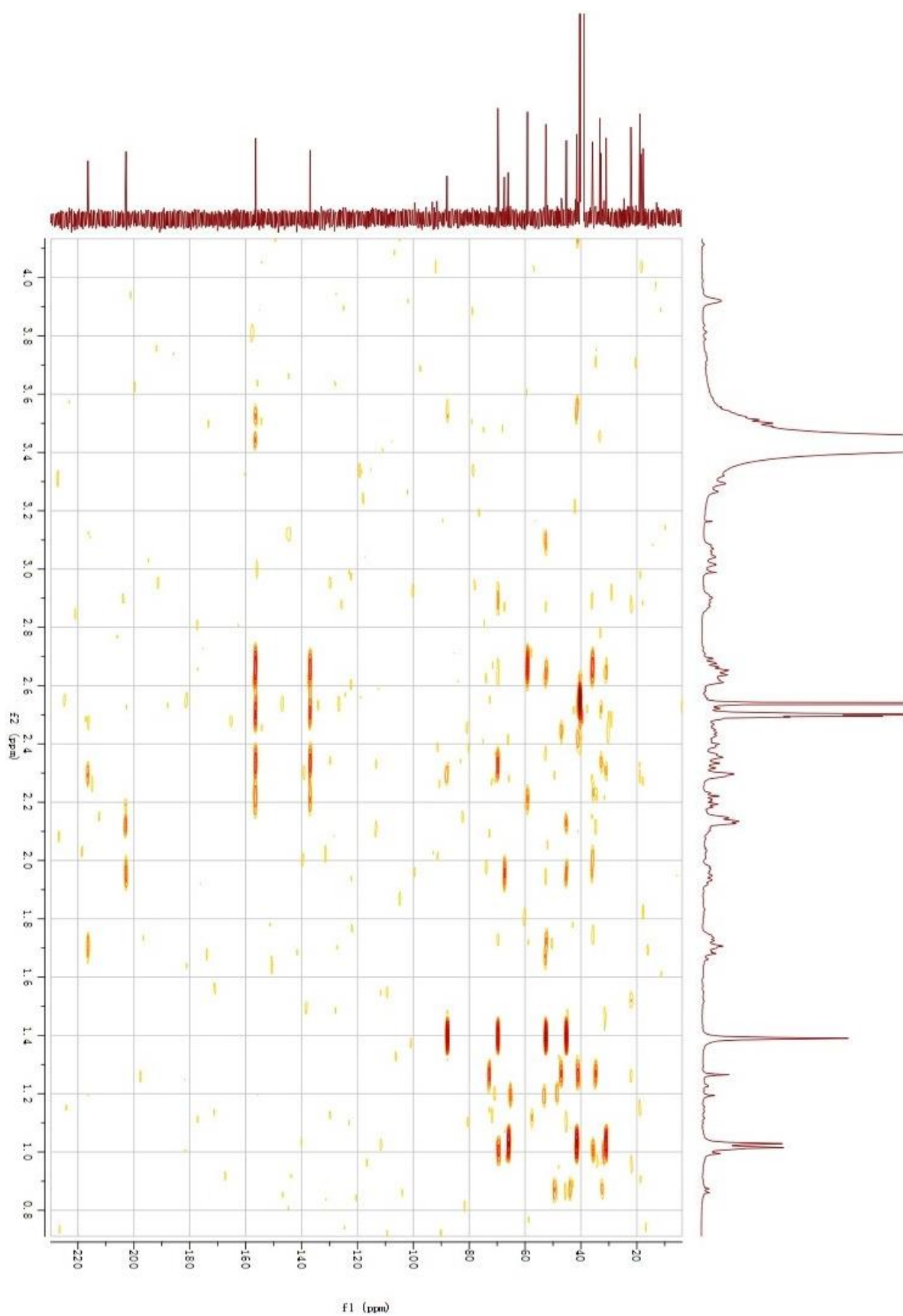
**Figure S40.** HMBC spectrum of calyciphylline S (**5**) in DMSO-*d*<sub>6</sub>.

Figure S41. ESIMS spectrum of calyciphylline S (5).

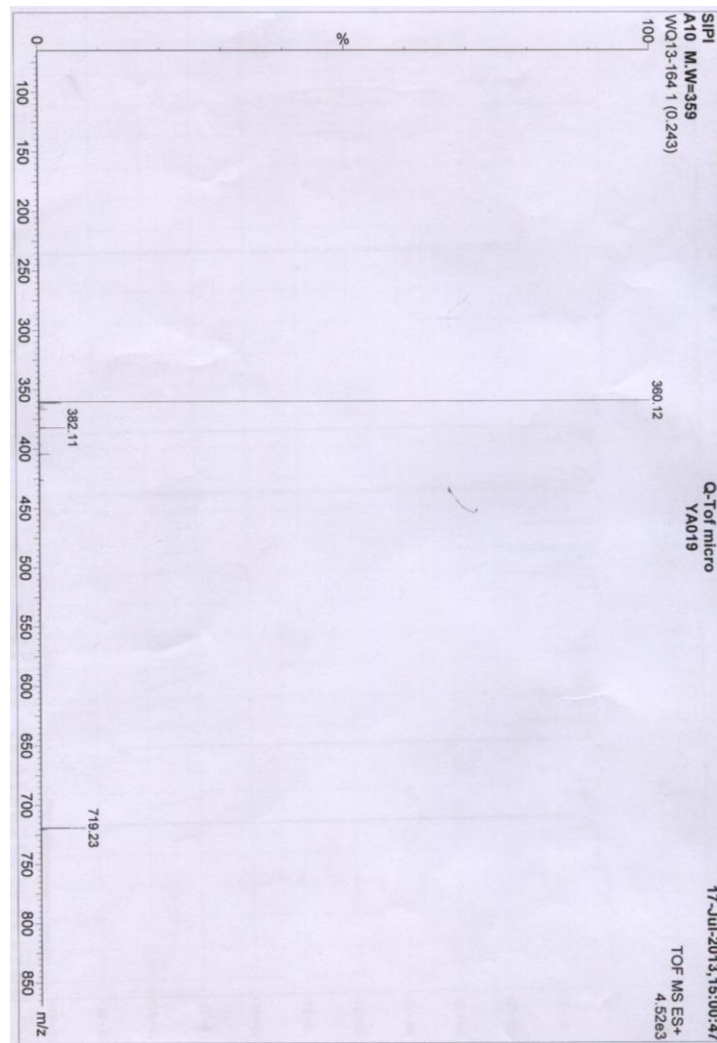
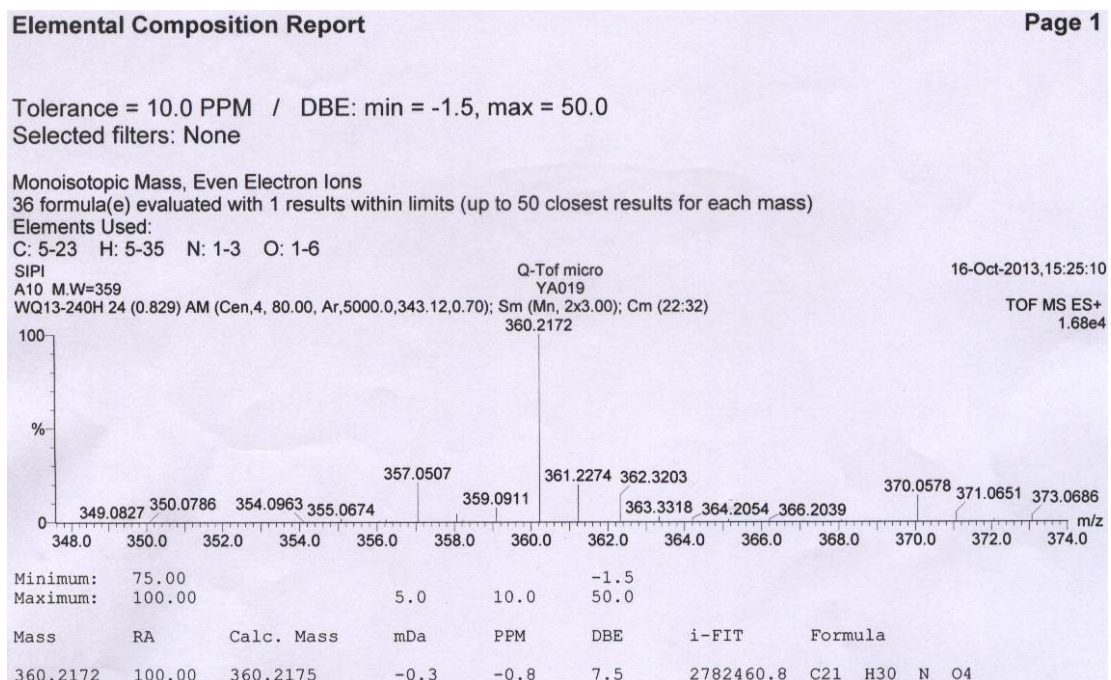
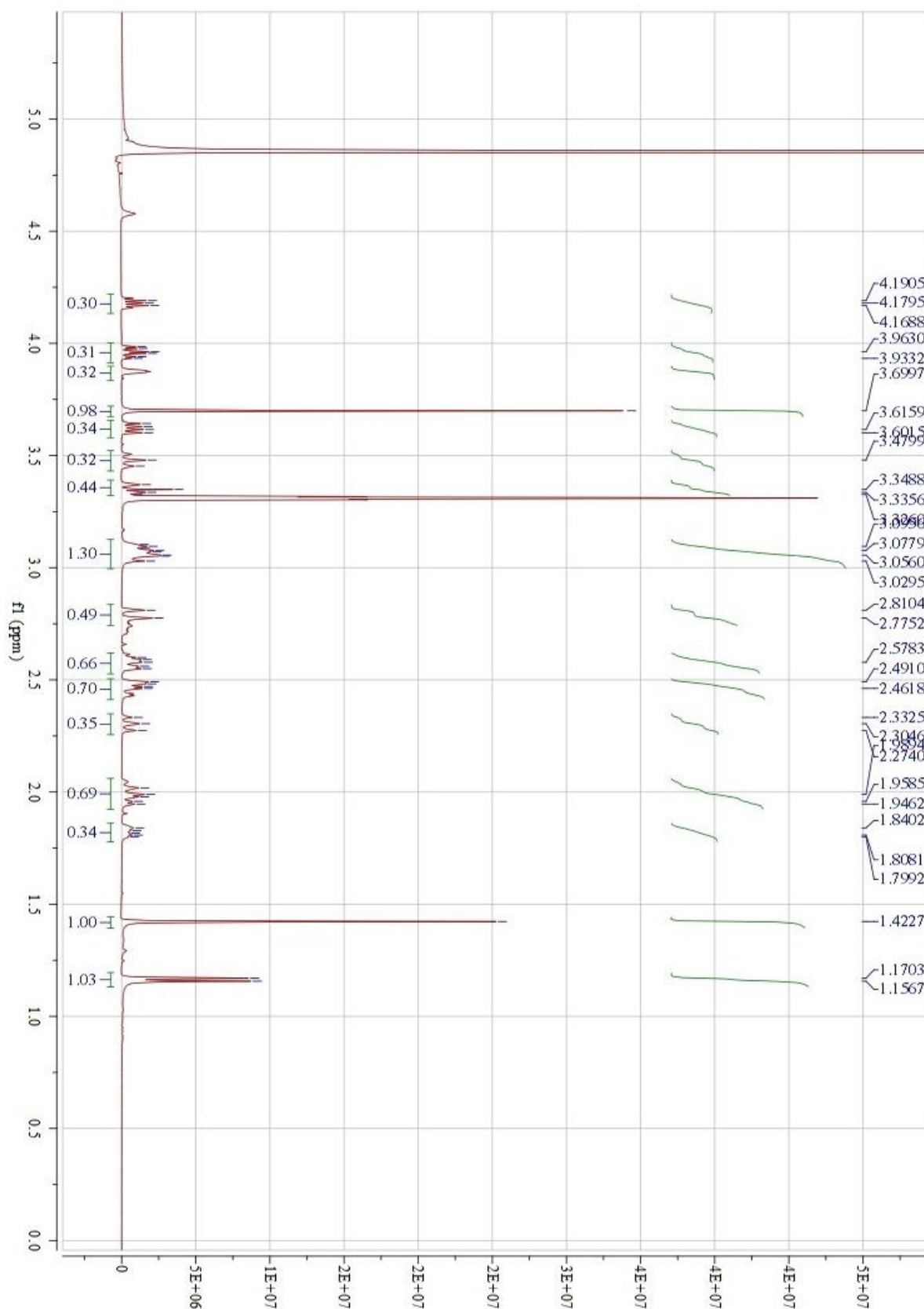
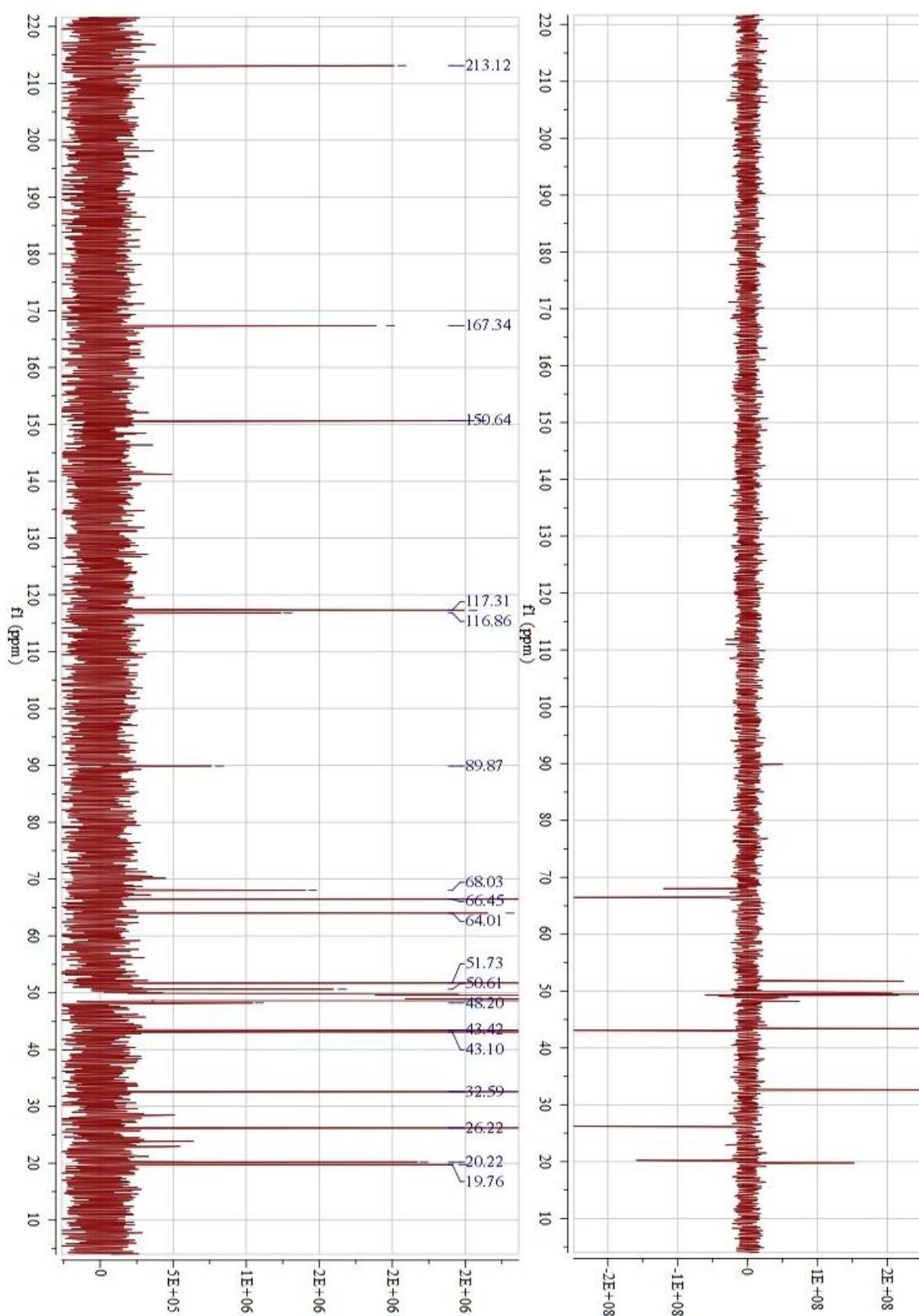


Figure S42. HRESIMS spectrum of calyciphylline S (5).



**Figure S43.**  $^1\text{H-NMR}$  (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of paxiphylline C (6).

**Figure S44.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of paxiphylline C (6).

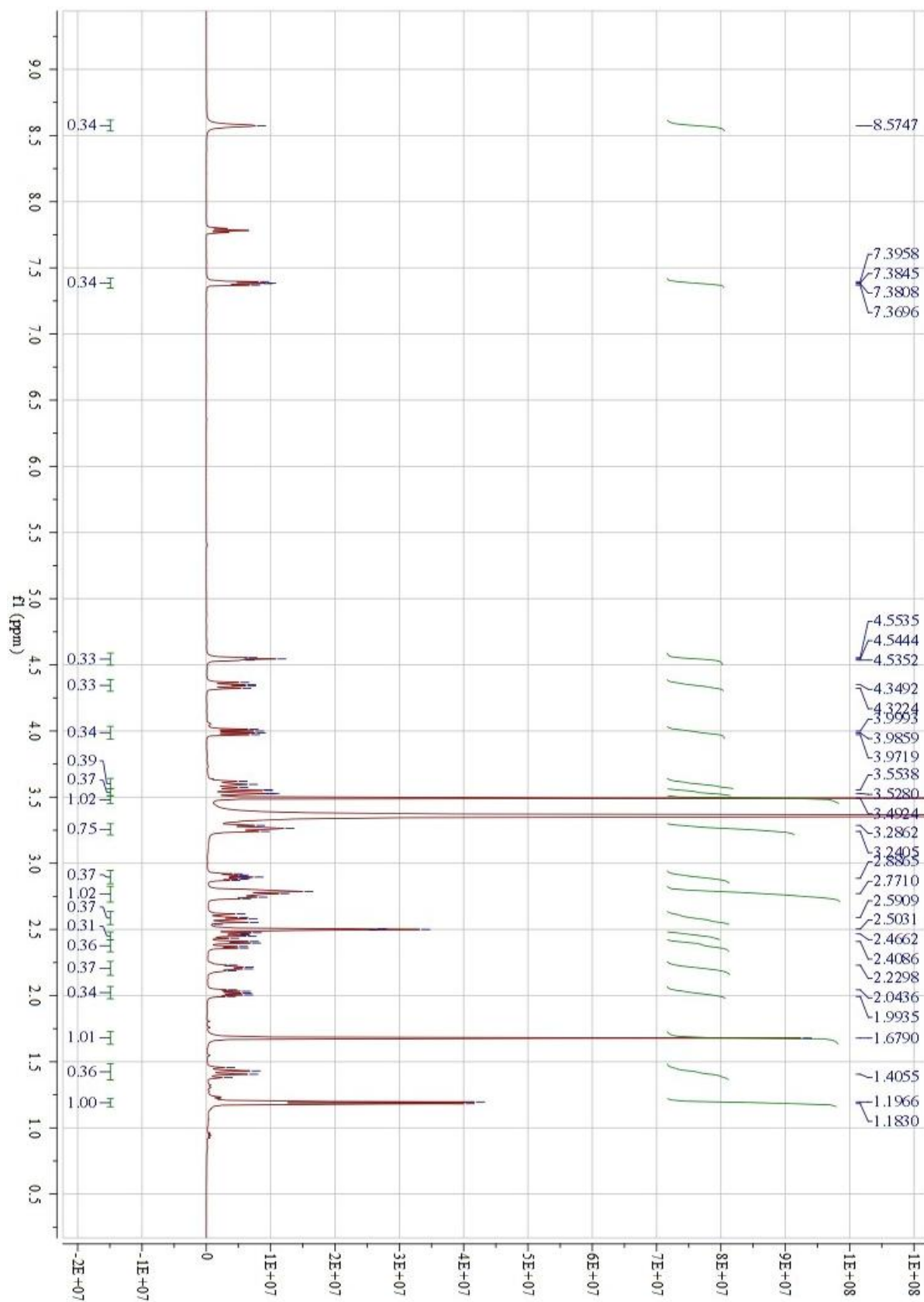
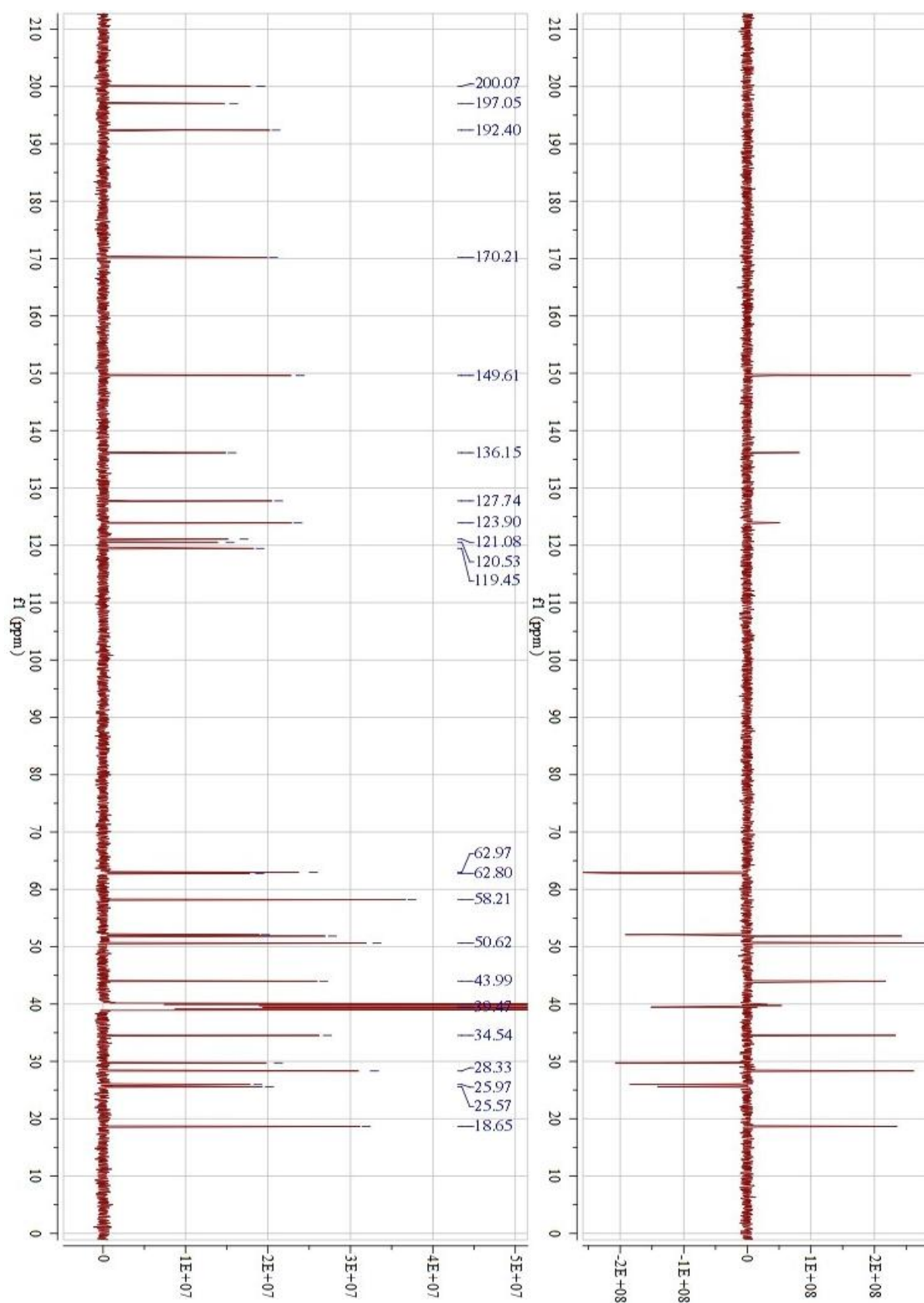
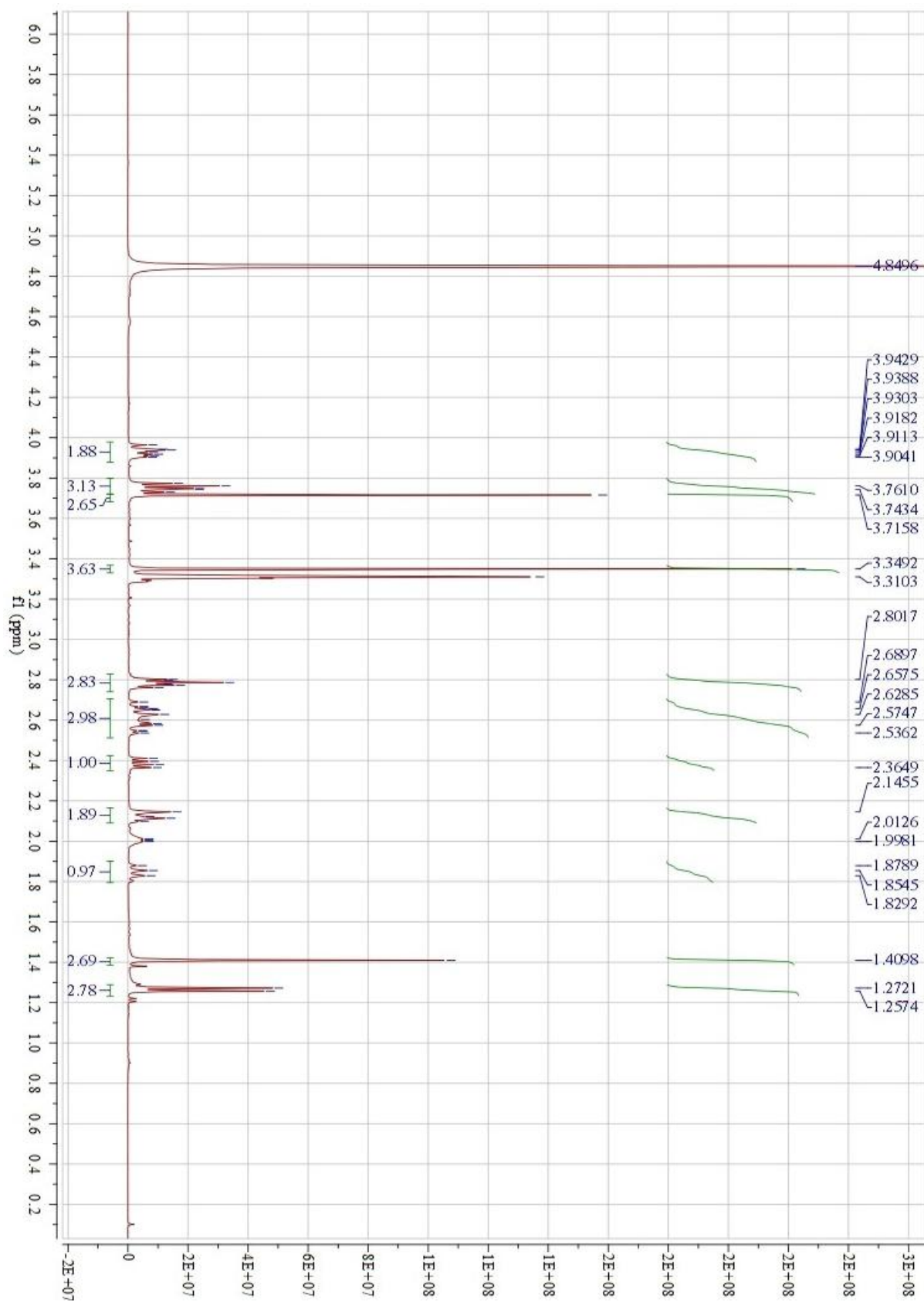
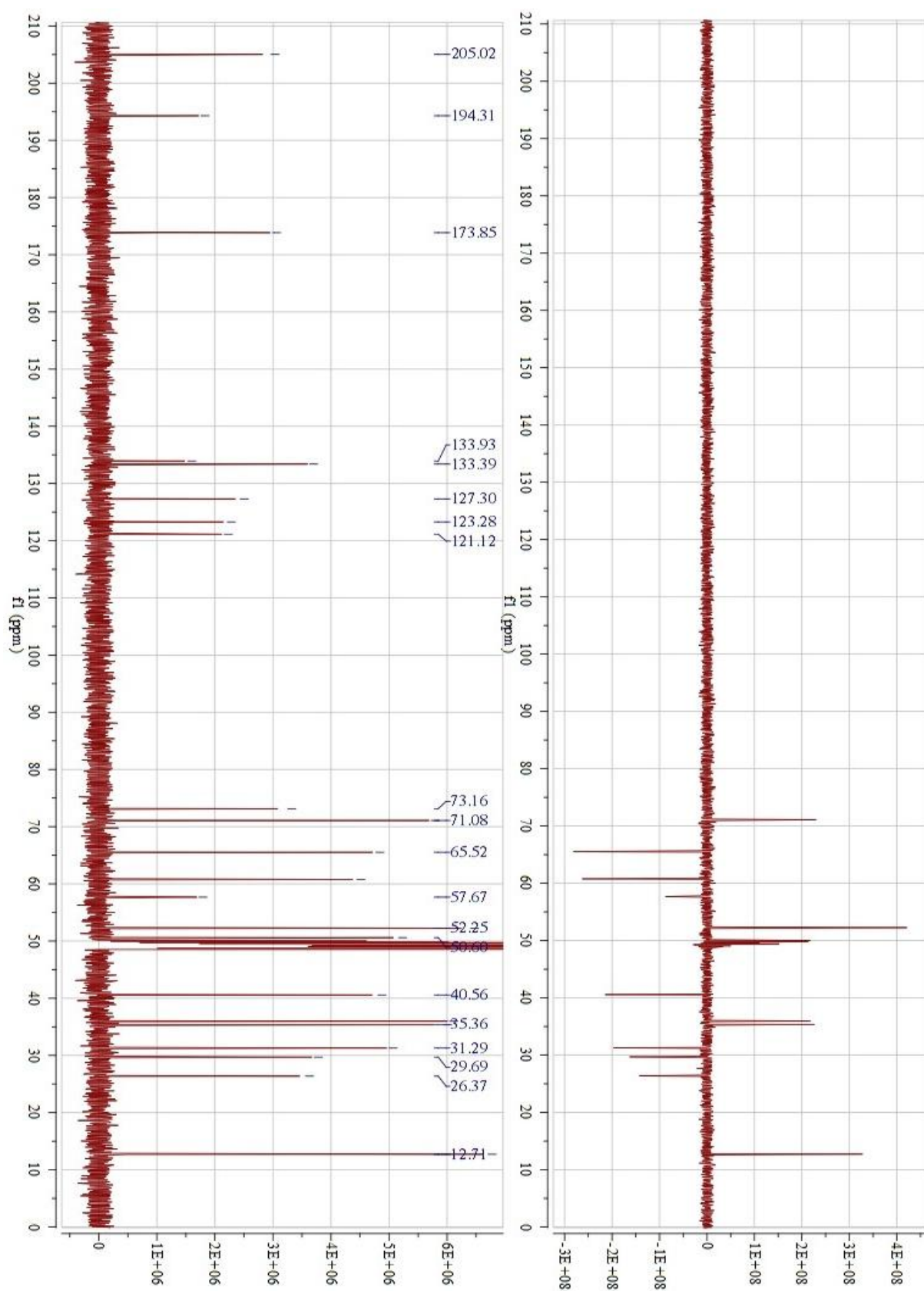
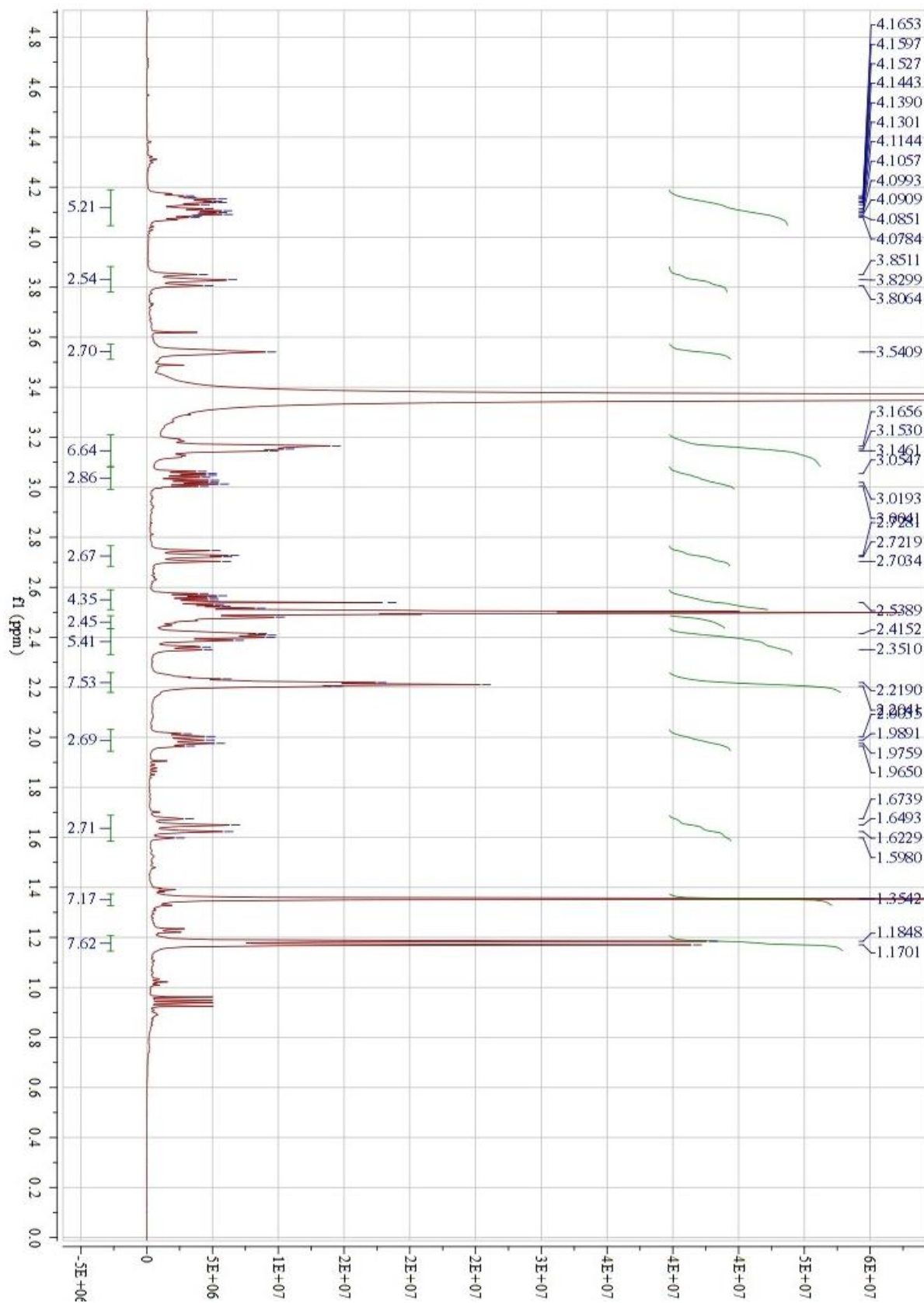
**Figure S45.**  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of macropodumine B (7).



Figure S46.  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO-}d_6$ ) spectrum of macropodumine B (7).

**Figure S47.**  $^1\text{H-NMR}$  (500 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of macropodumine C (**8**).

**Figure S48.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of macropodumine C (**8**).

**Figure S49.**  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of daphnicyclidin A (**9**).

**Figure S50.**  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO-}d_6$ ) spectrum of daphnicyclidin A (**9**).