

## *Electronic Supporting Information*

### **A water-soluble boronic acid sensor for caffeic acid based on double sites recognition**

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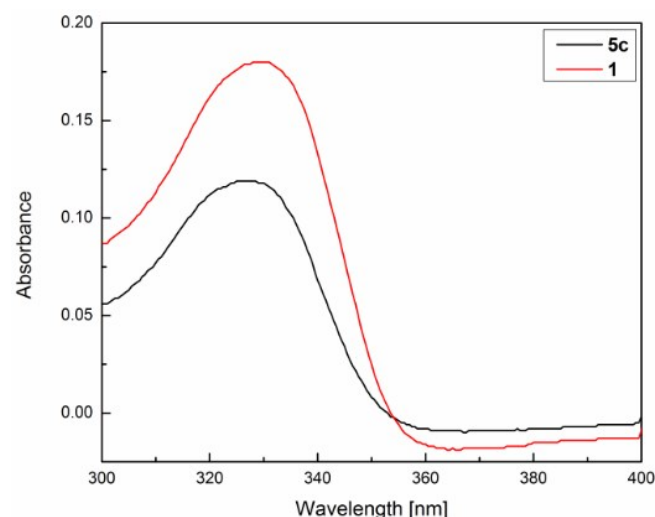
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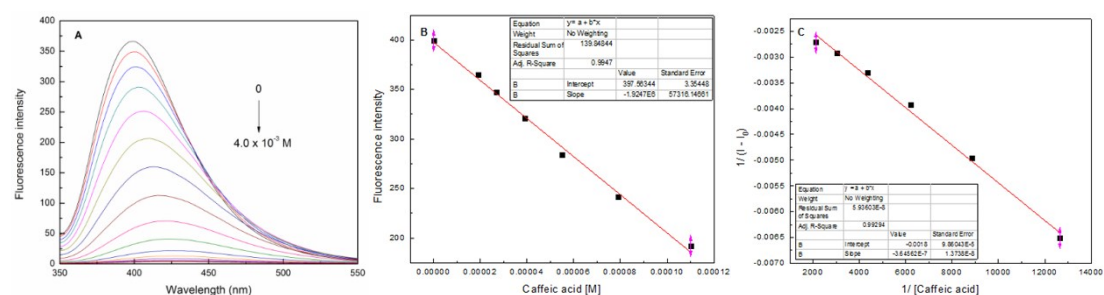
#### **1. UV-vis absorption spectra of sensor **1** and **5c****



**Fig. S1** UV-vis absorption spectra of sensor **1** in DMSO/PBS (pH 9, 0.1M) solution (1:99, v/v) and sensor **5c** in PBS solution, at room temperature.

#### **2. Fluorescence properties of sensors**

### (1) 5a



**Fig. S2** A) Fluorescence spectra of sensor **5a** ( $1 \times 10^{-5}$  M) in the presence of different concentrations of caffeic acid in PBS (pH 7.4) solution, at room temperature; B) The photograph of sensor **5a** linear range; C) Benesi-Hildebrand plot of sensor **5a**  $1/(I - I_0)$  versus  $1/[Caffeic\ acid]$ .

The calculation process of

LOD :

$$I = -1924700c + 397.56344$$

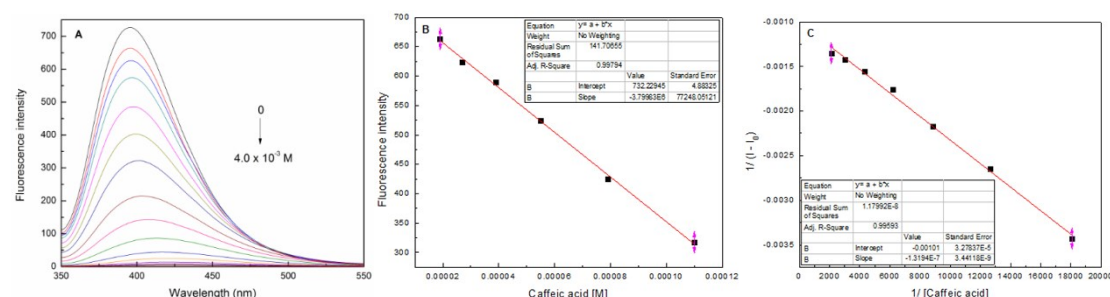
$$R^2 = 0.9947$$

$$S = -1924700$$

$$\delta = \sqrt{\frac{\Sigma(F_i - F_0)^2}{N - 1}} = 3.28 \quad (N=5) \quad K=3$$

$$LOD = K \times \delta/S = 5.11 \times 10^{-6} \text{ M}$$

### (2) 5b



**Fig. S3** A) Fluorescence spectra of sensor **5b** ( $1 \times 10^{-5}$  M) in the presence of different concentrations of caffeic acid in PBS (pH 7.4) solution, at room temperature; B) The photograph of sensor **5b** linear range; C) Benesi-Hildebrand plot of sensor **5b**  $1/(I - I_0)$  versus  $1/[Caffeic\ acid]$ .

The calculation process of LOD :

$$I = -3799830c + 732.22945$$

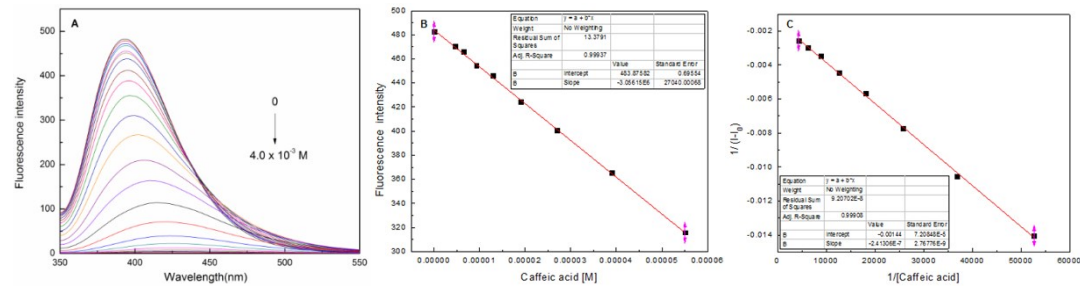
$$R^2 = 0.99794$$

$$S = -3799830$$

$$\delta = \sqrt{\frac{\sum(F_i - F_0)^2}{N - 1}} = 2.85 \text{ (N=5) } K=3$$

$$\text{LOD} = K \times \delta/S = 2.25 \times 10^{-6} \text{ M}$$

### (3) 5c



**Fig. S4** A) Fluorescence spectra of sensor **5c** ( $1 \times 10^{-5}$  M) in the presence of different concentrations of caffeic acid in PBS (pH 7.4) solution, at room temperature; B) The photograph of sensor **5c** linear range; C) Benesi-Hildebrand plot of sensor **5c**  $1/(I - I_0)$  versus  $1/[Caffeic\ acid]$ .

The calculation process of LOD :

$$I = -3056150c + 483.87582$$

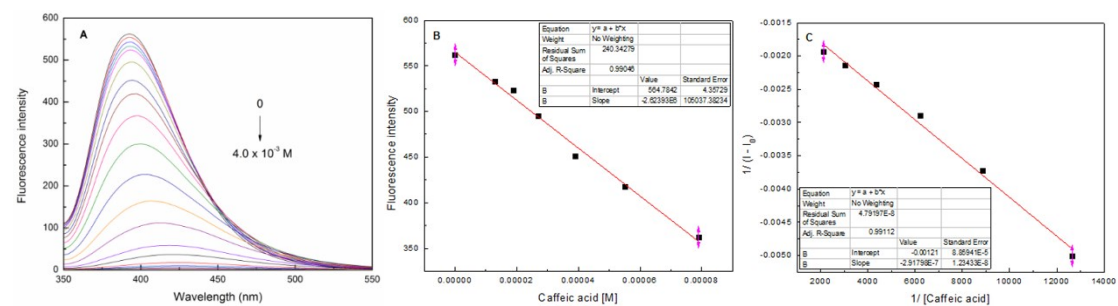
$$R^2 = 0.99937$$

$$S = -3056150$$

$$\delta = \sqrt{\frac{\sum(F_i - F_0)^2}{N - 1}} = 1.84 \text{ (N=5) } K=3$$

$$\text{LOD} = K \times \delta/S = 1.81 \times 10^{-6} \text{ M}$$

### (4) 5d



**Fig. S5** A) Fluorescence spectra of sensor **5d** ( $1 \times 10^{-5}$  M) in the presence of different concentrations of caffeic acid in PBS (pH 7.4) solution, at room temperature; B) The photograph of sensor **5d** linear range; C) Benesi-Hildebrand plot of sensor **5d**  $1/(I - I_0)$  versus  $1/[Caffeic\ acid]$ .

The calculation process of LOD :

$$I = -2623930c + 564.7842$$

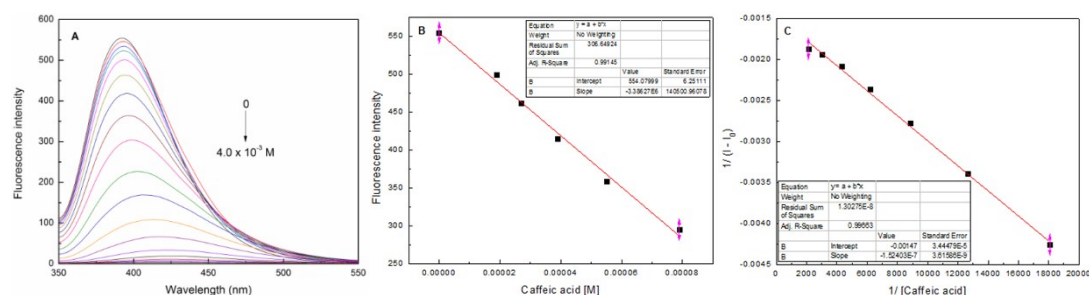
$$R^2 = 0.99046$$

$$S = -2623930$$

$$\delta = \sqrt{\frac{\sum(F_i - F_0)^2}{N - 1}} = 3.37 \text{ (N=5) } K=3$$

$$\text{LOD} = K \times \delta/S = 3.85 \times 10^{-6} \text{ M}$$

(5) 5e



**Fig. S6** A) Fluorescence spectra of sensor **5e** ( $1 \times 10^{-5}$  M) in the presence of different concentrations of caffeic acid in PBS (pH 7.4) solution, at room temperature; B) The photograph of sensor **5e** linear range; C) Benesi-Hildebrand plot of sensor **5e**  $1/(I - I_0)$  versus  $1/[\text{Caffeic acid}]$ .

The calculation process of LOD :

$$I = -3386270c + 554.07999$$

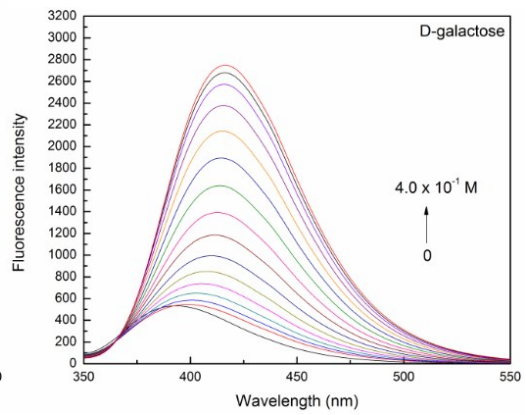
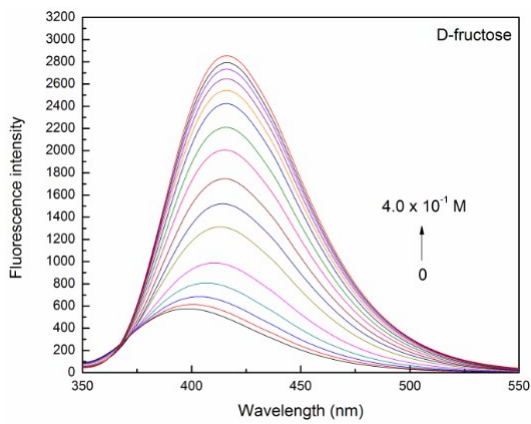
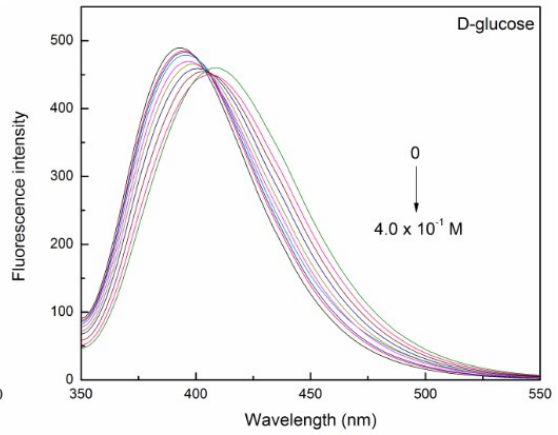
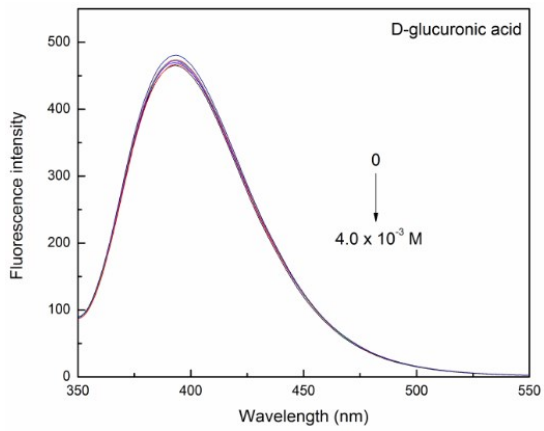
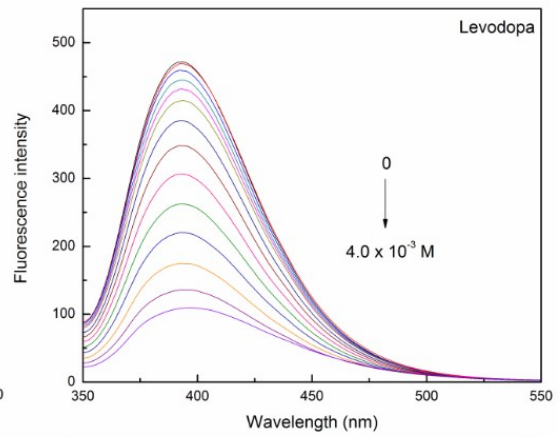
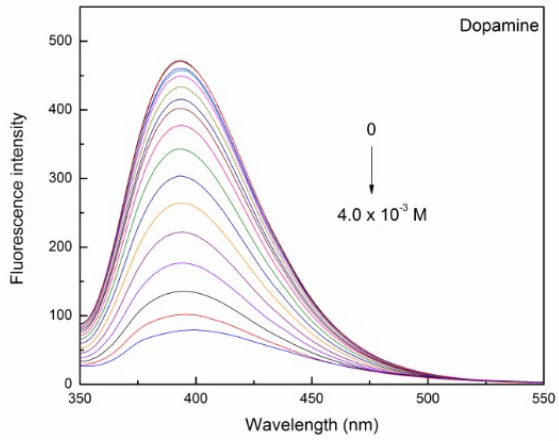
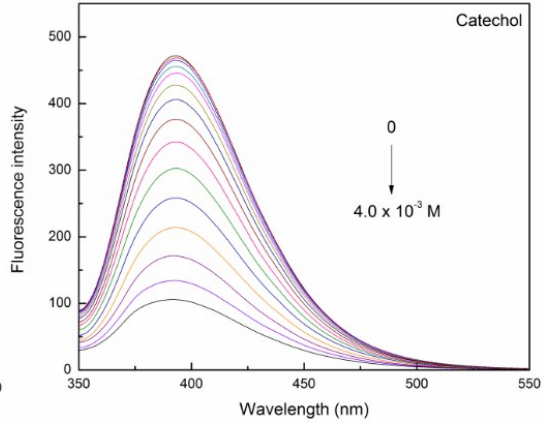
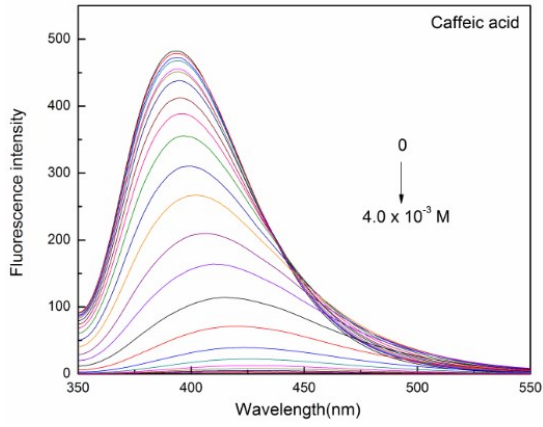
$$R^2 = 0.99145$$

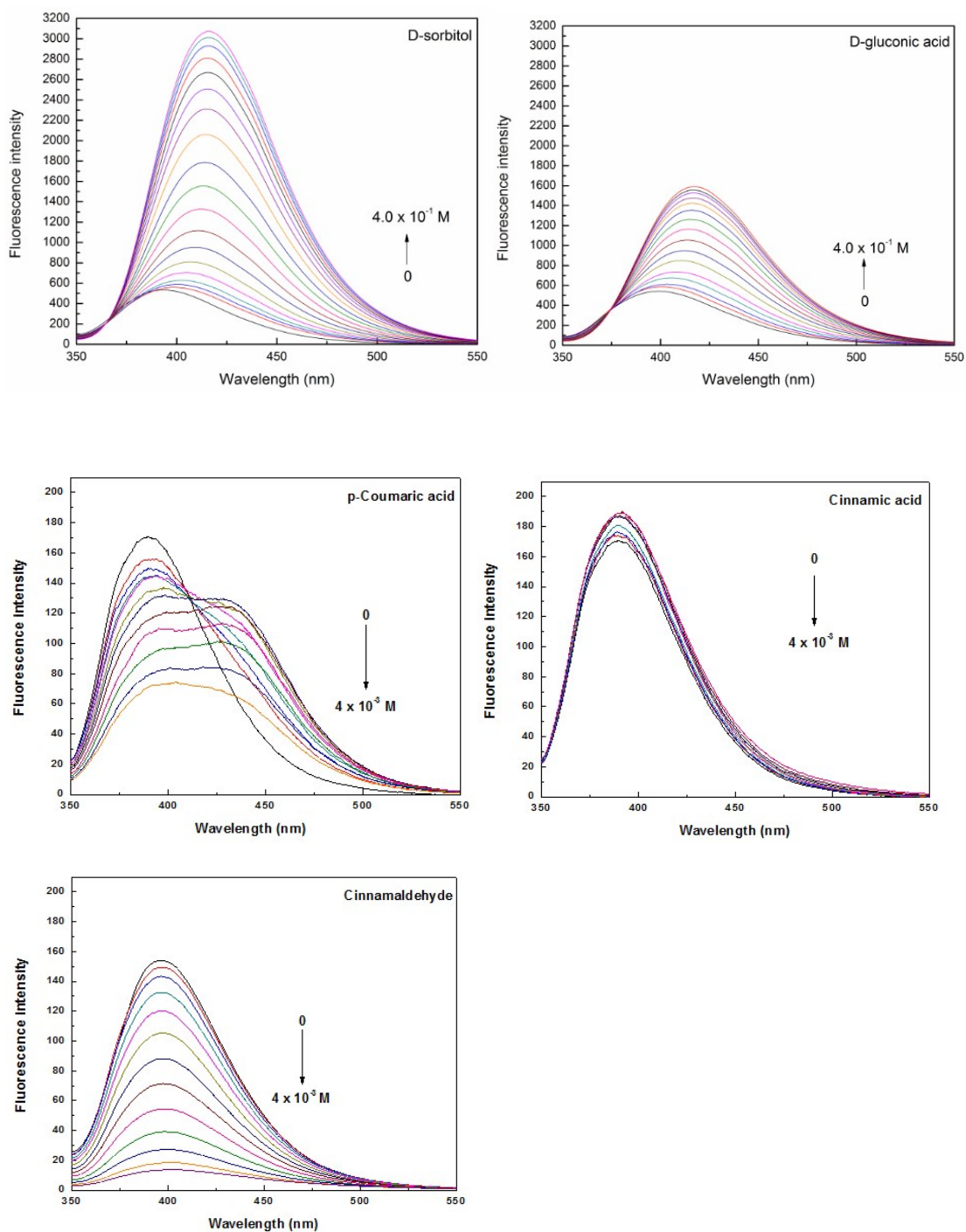
$$S = -3386270$$

$$\delta = \sqrt{\frac{\sum(F_i - F_0)^2}{N - 1}} = 6.24 \text{ (N=5) } K=3$$

$$\text{LOD} = K \times \delta/S = 5.53 \times 10^{-6} \text{ M}$$

**Different analytes fluorescence titrations**

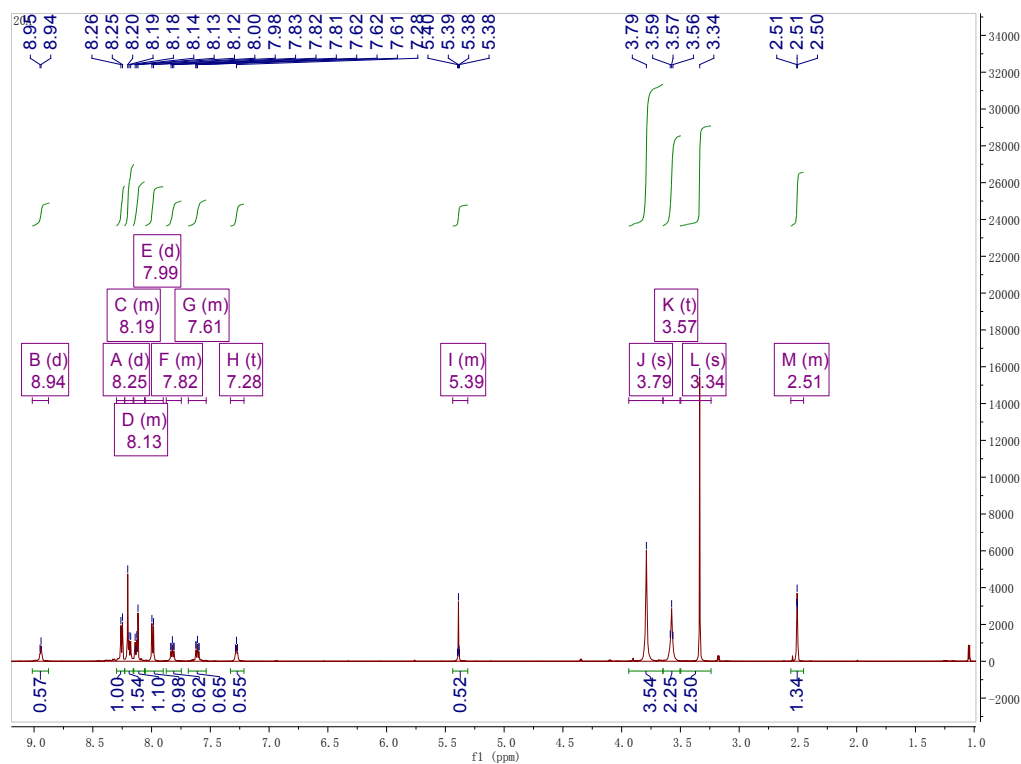




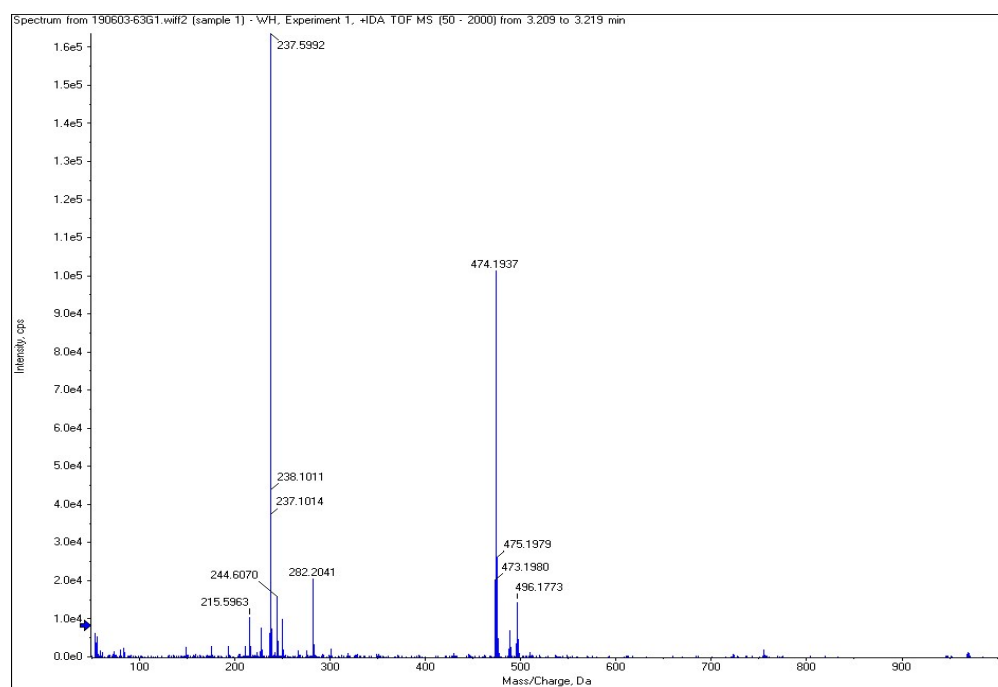
**Fig. S7** Fluorescence spectra of sensor **5c** ( $1 \times 10^{-5}$  M) in the presence of different analytes (from 0 to  $4.0 \times 10^{-3}$  M or  $4.0 \times 10^{-1}$  M) in PBS (pH 7.4) solution, at room temperature.

### 3. Copies of NMR ( $^1\text{H}$ and $^{13}\text{C}$ ) and HRMS spectra

(1)4a

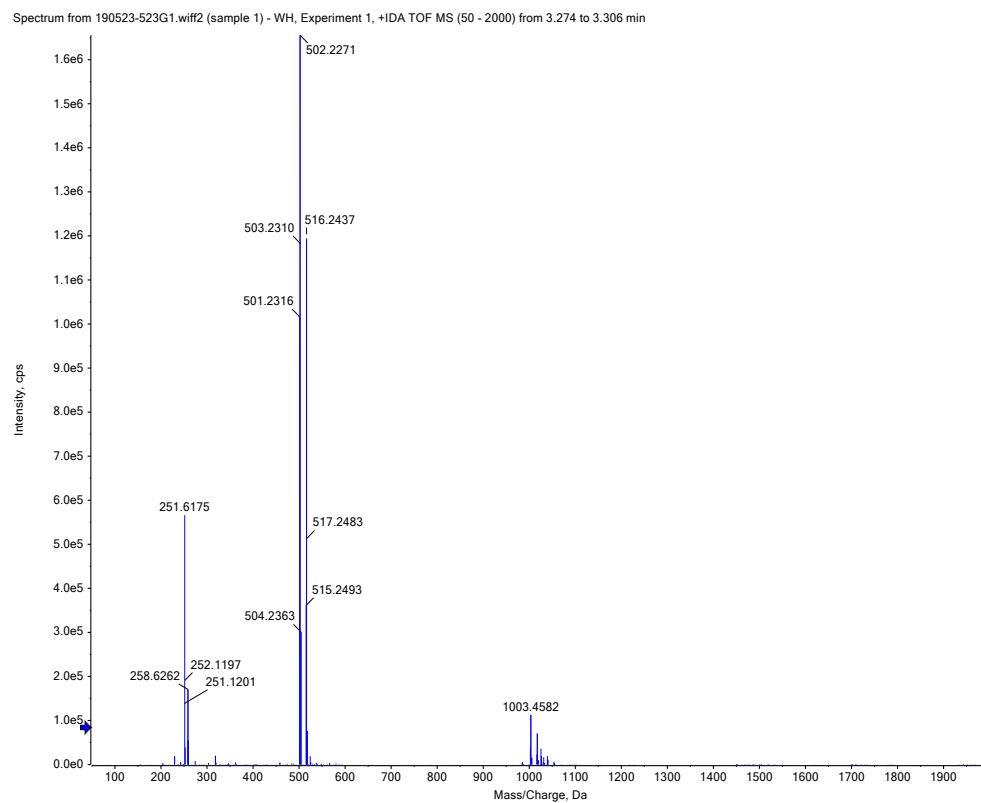


**Fig. S8**  $^1\text{H}$  NMR spectrum of **4a**



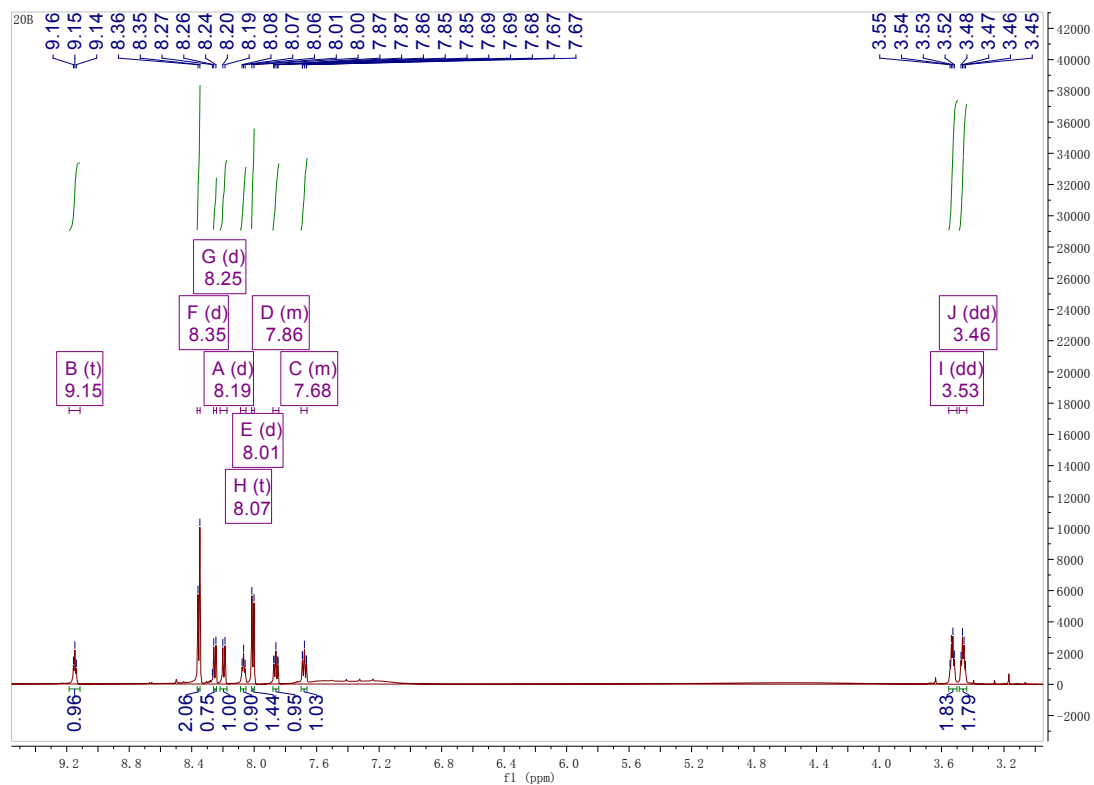
**Fig. S9** HRMS spectrum of compound **4a**

(2)**4c**



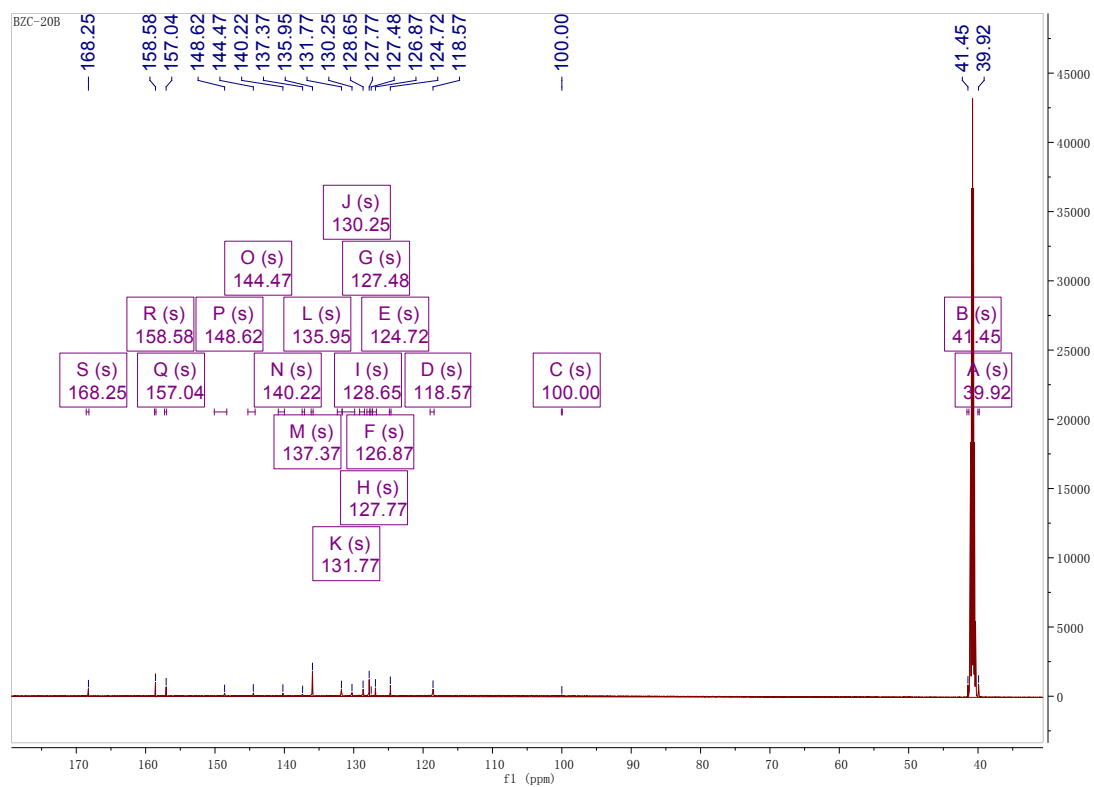
**Fig. S10** HRMS spectrum of compound **4c**

**(3)5a**

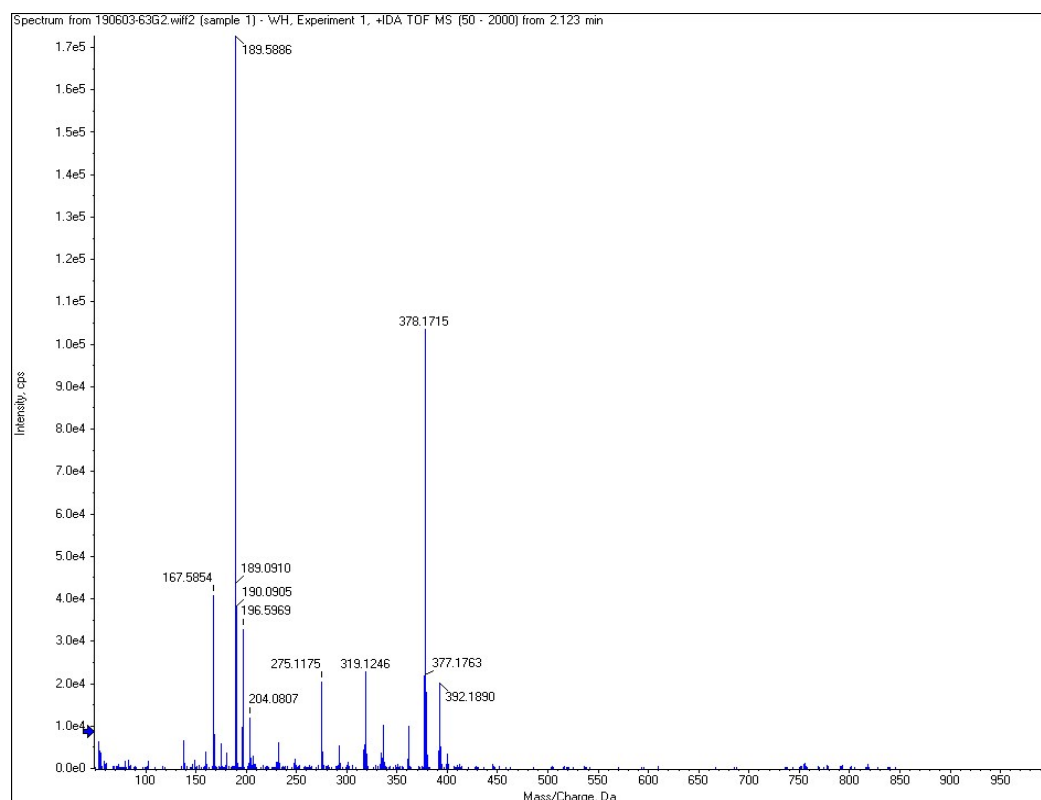


**Fig. S11** <sup>1</sup>H NMR spectrum of **5a**





**Fig. S12**  $^{13}\text{C}$  NMR spectrum of **5a**



**Fig. S13** HRMS spectrum of compound **5a**

#### (4) 5b

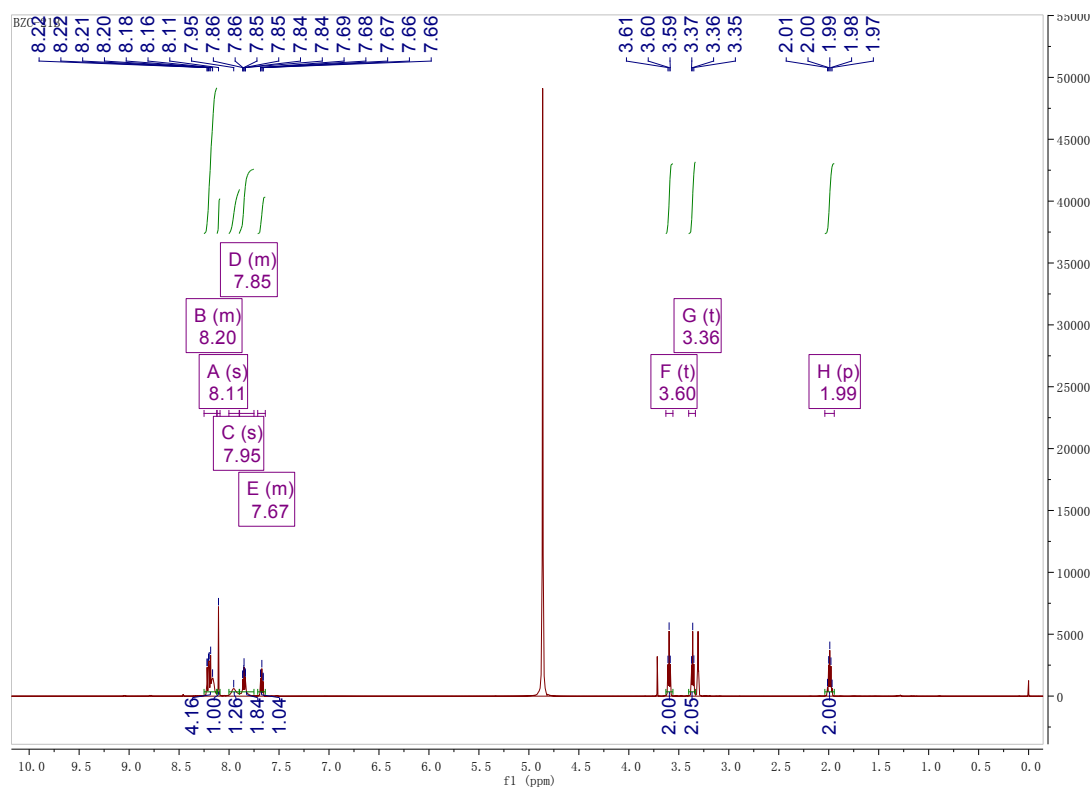


Fig. S14 <sup>1</sup>H NMR spectrum of 5b

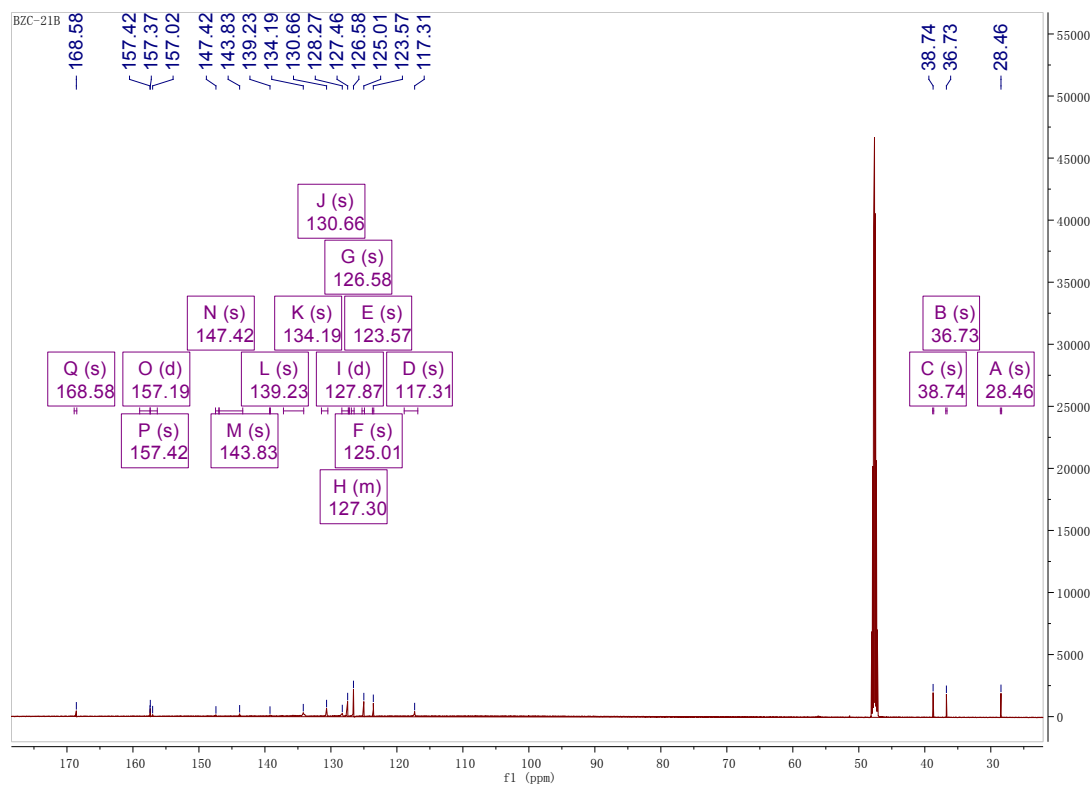


Fig. S15 <sup>13</sup>C NMR spectrum of 5b

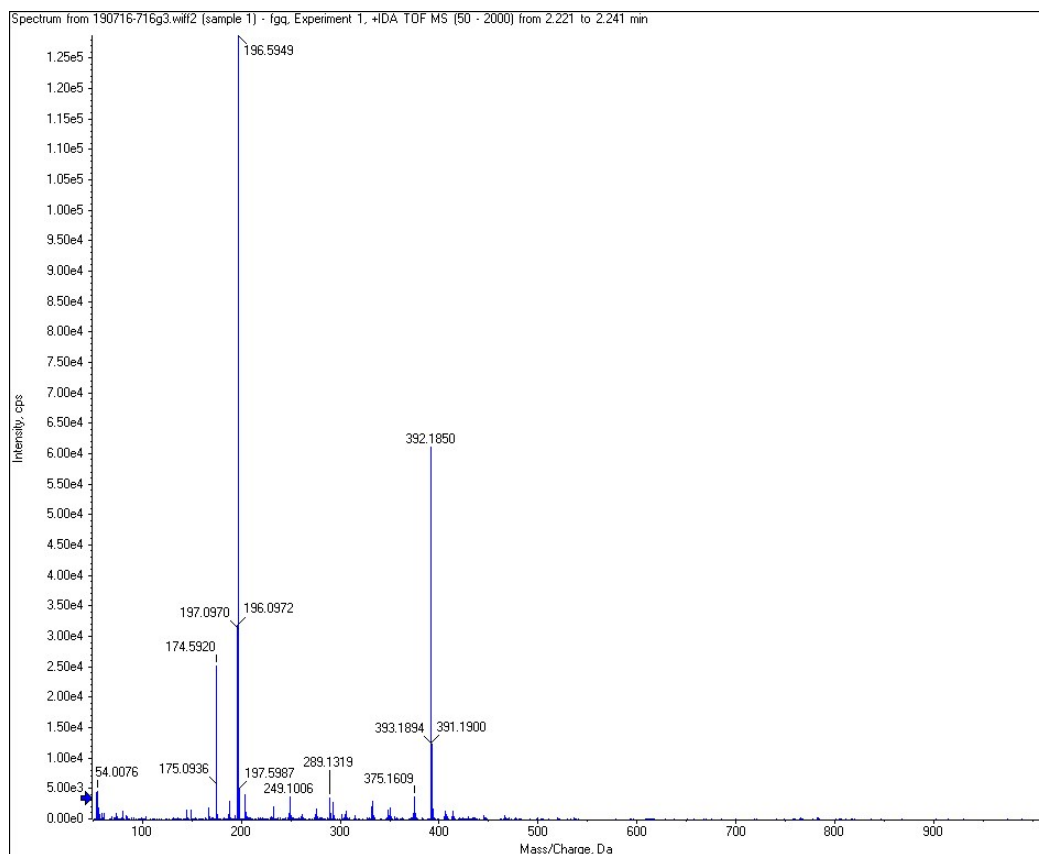


Fig. S16 HRMS spectrum of compound **5b**

(**5**) **5c**

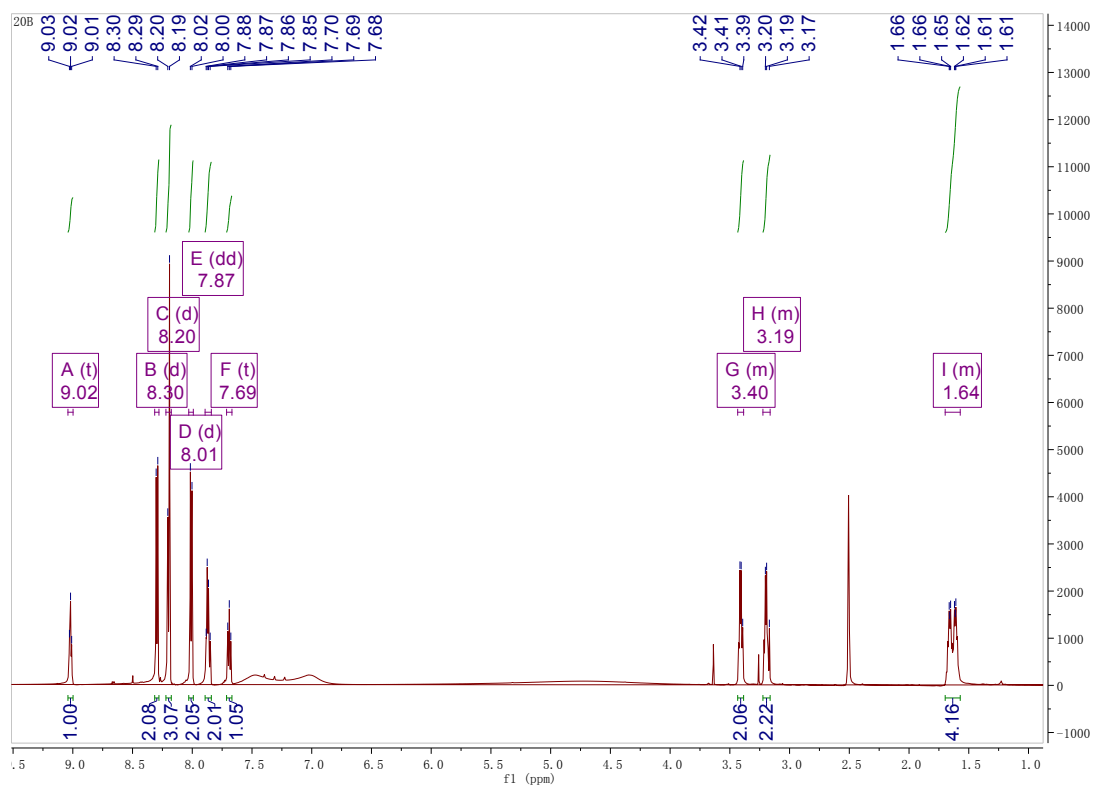
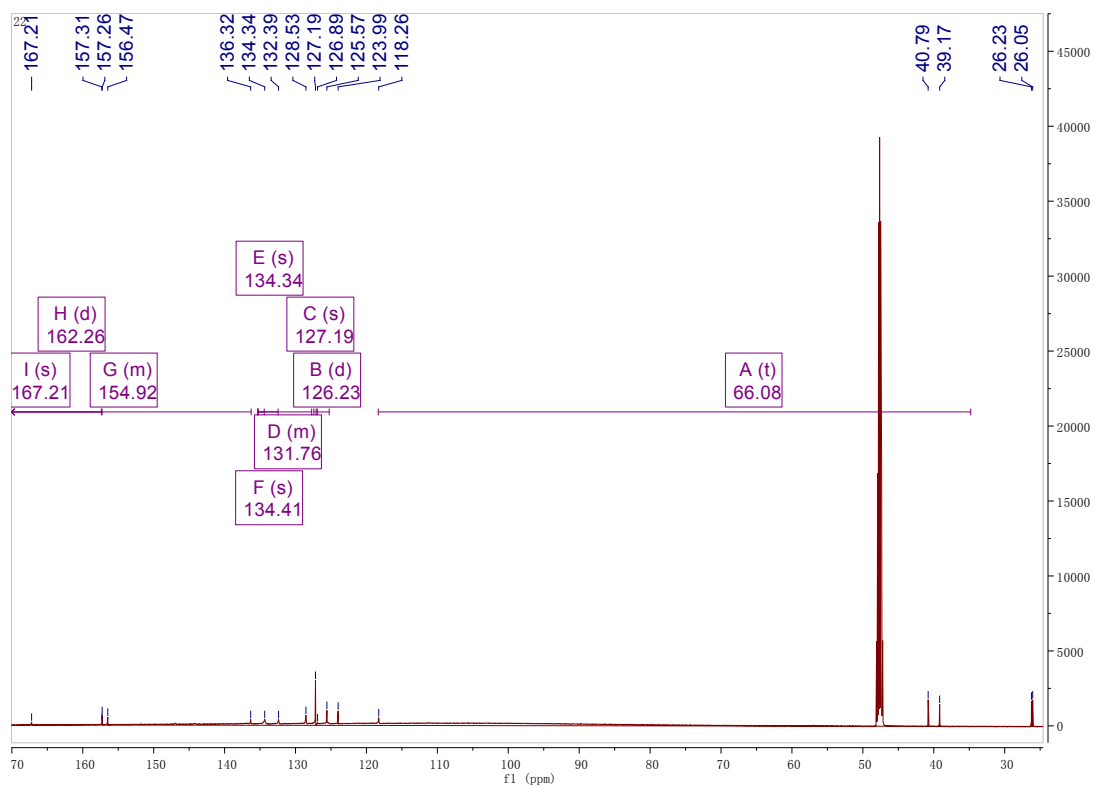
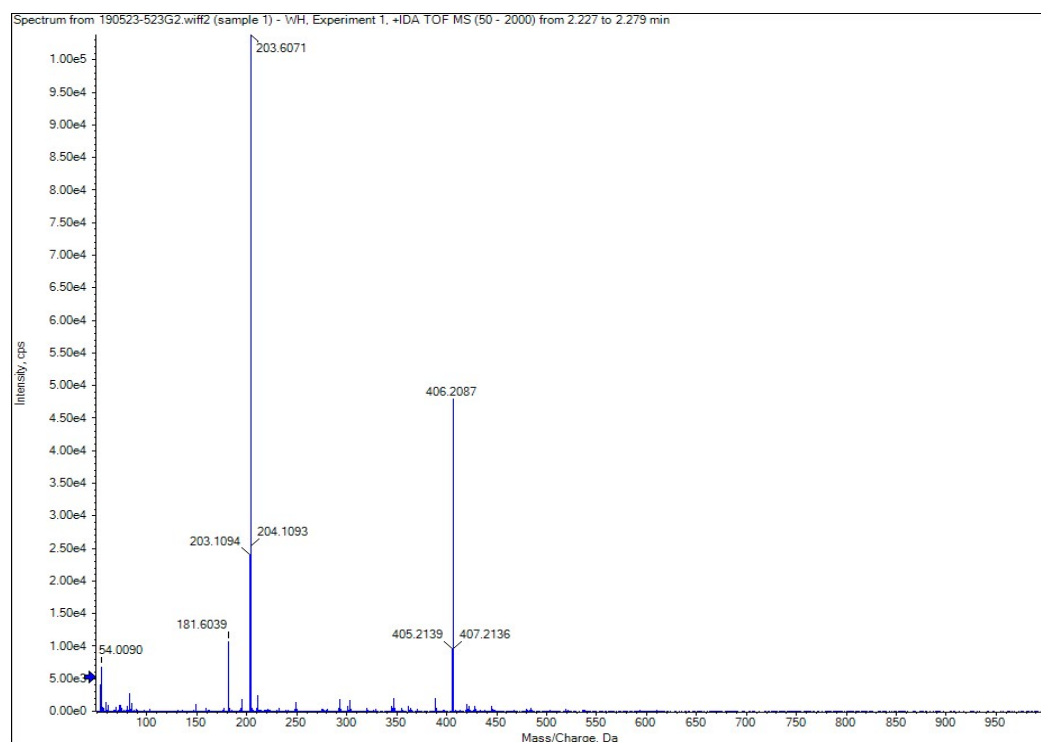


Fig. S17 <sup>1</sup>H NMR spectrum of **5c**

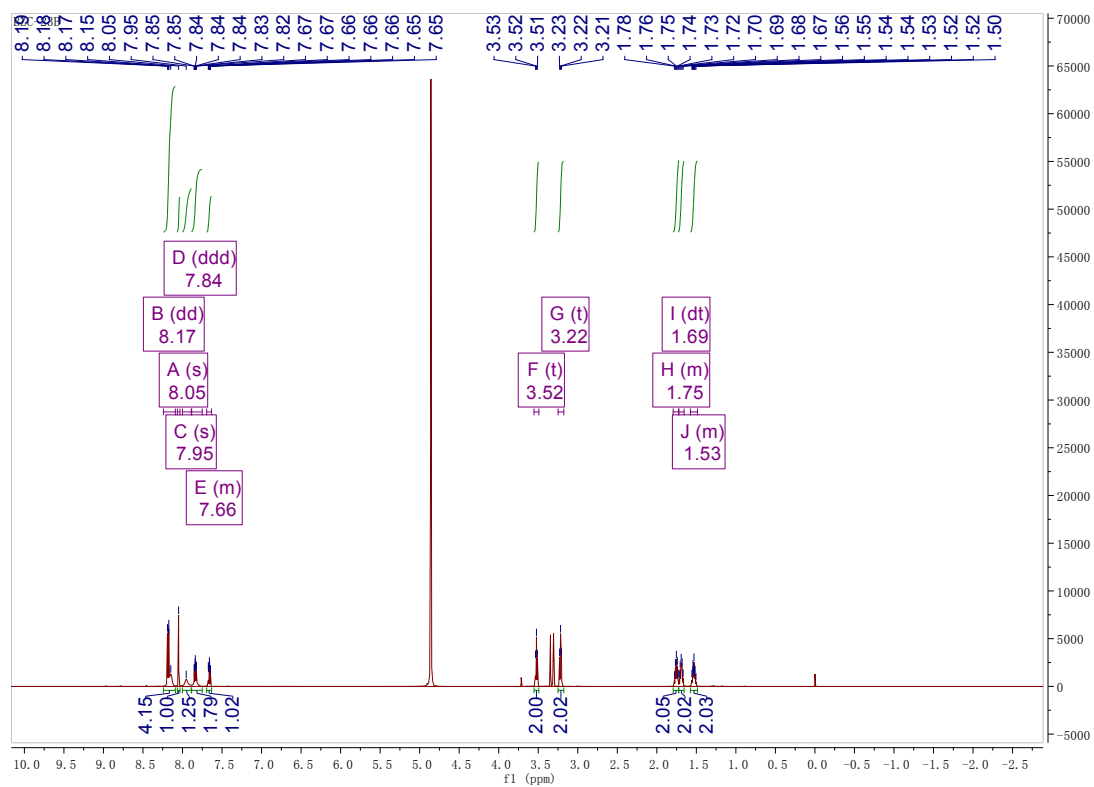


**Fig. S18** <sup>13</sup>C NMR spectrum of **5c**

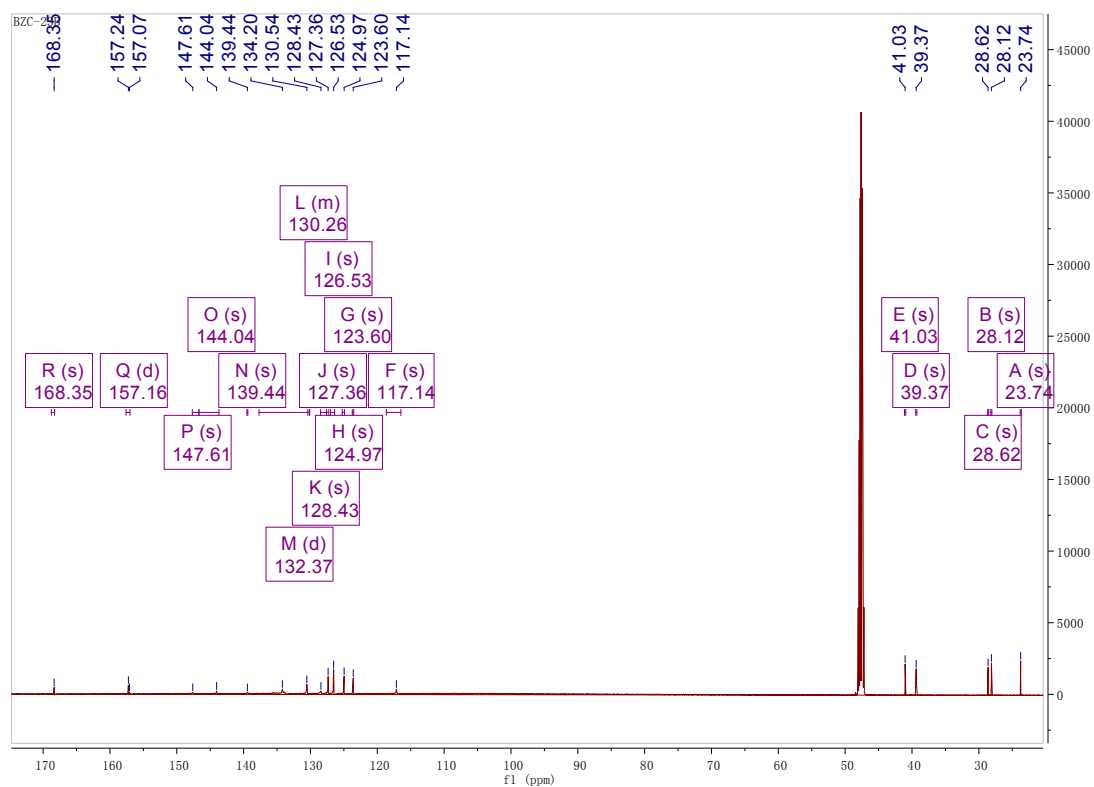


**Fig. S19** HRMS spectrum of compound **5c**

**(6) 5d**



**Fig. S20**  $^1\text{H}$  NMR spectrum of **5d**



**Fig. S21**  $^{13}\text{C}$  NMR spectrum of **5d**

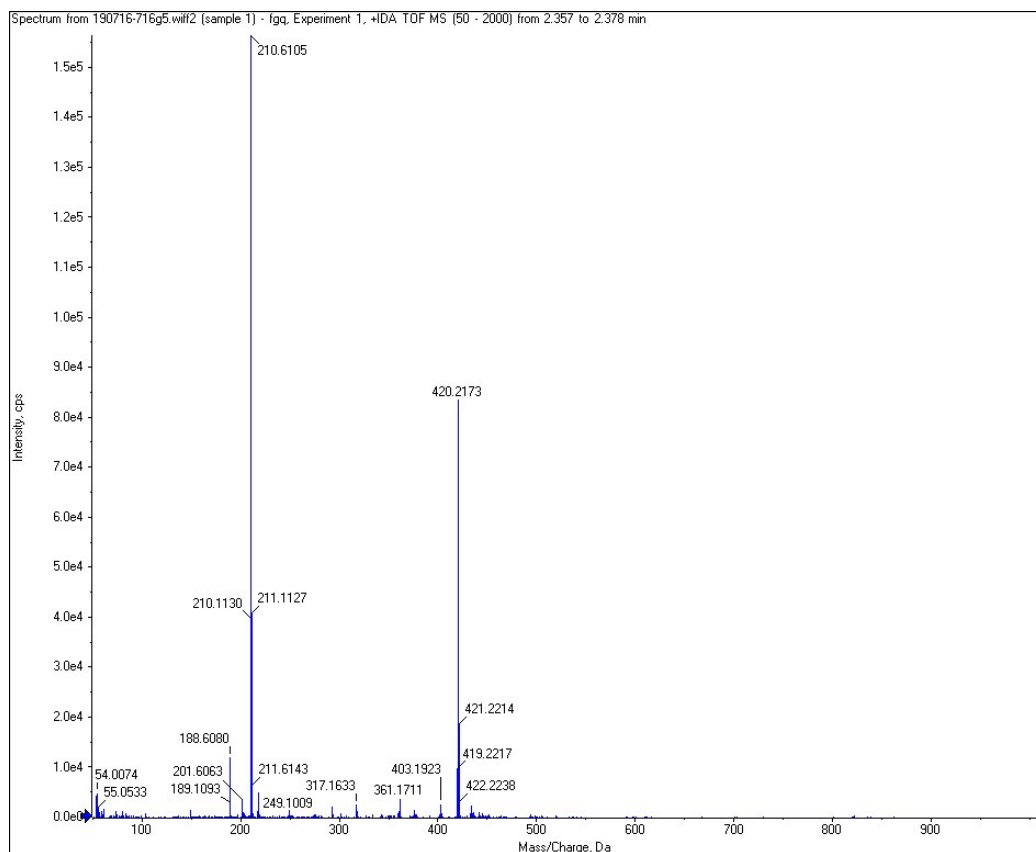


Fig. S22 HRMS spectrum of compound 5d

(7) 5e

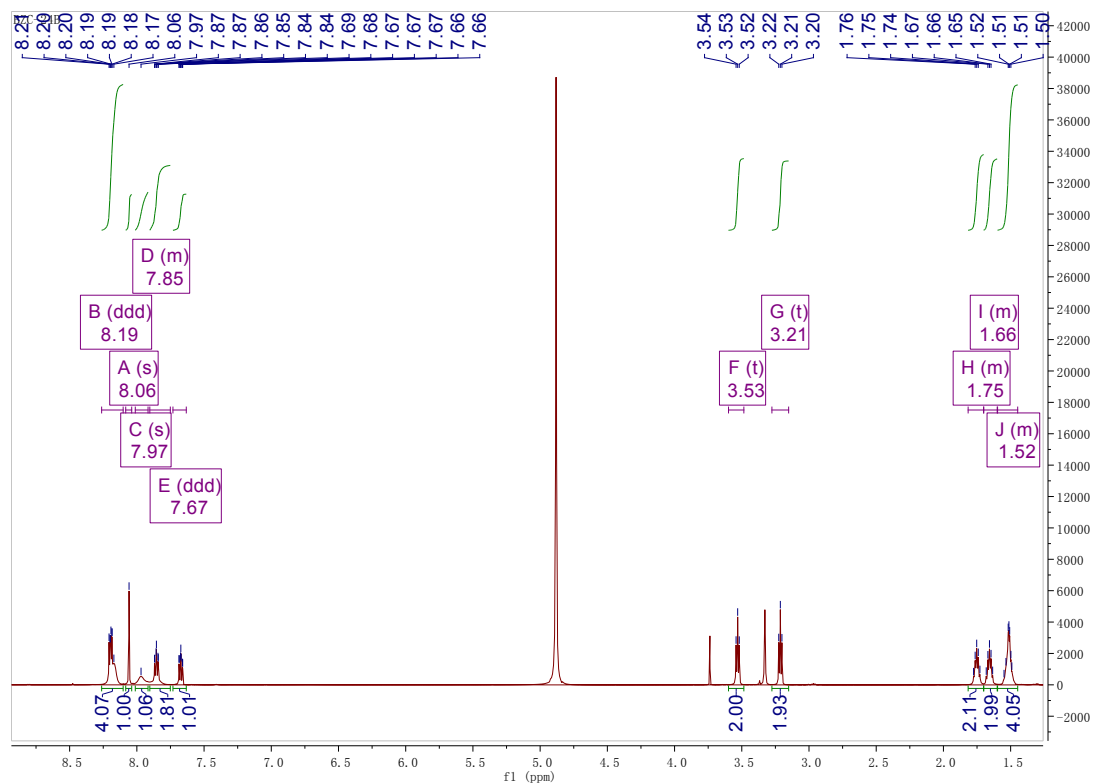
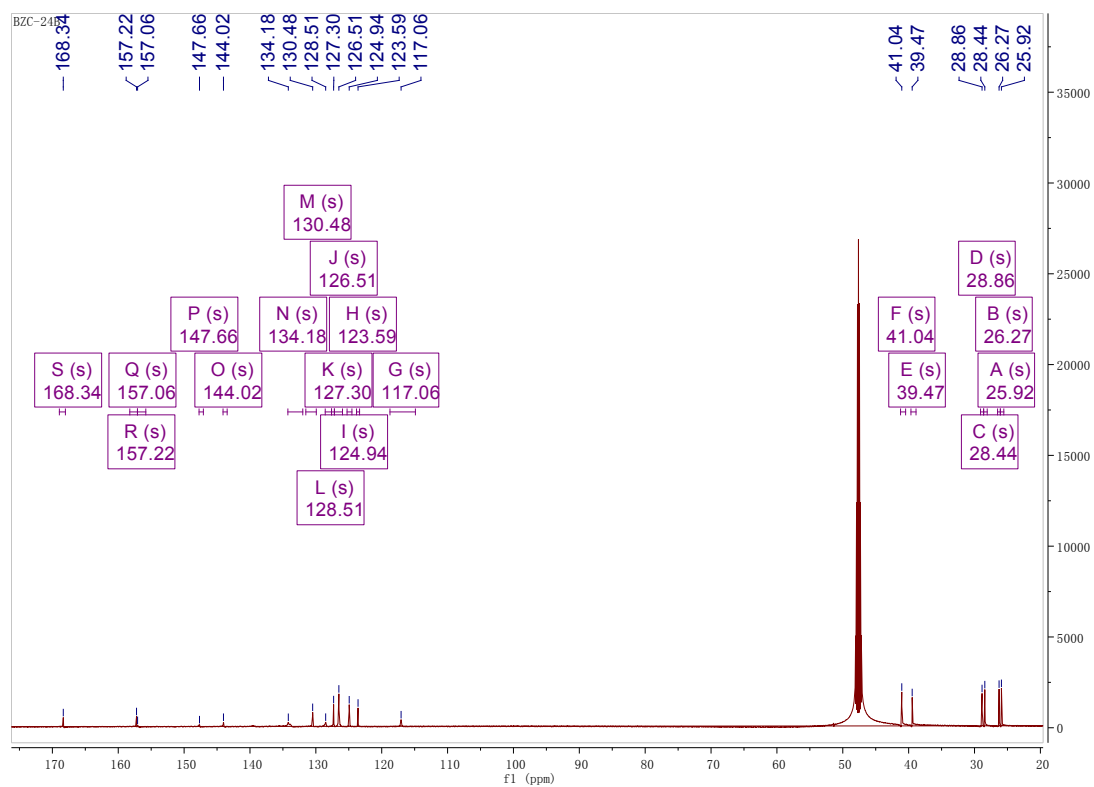
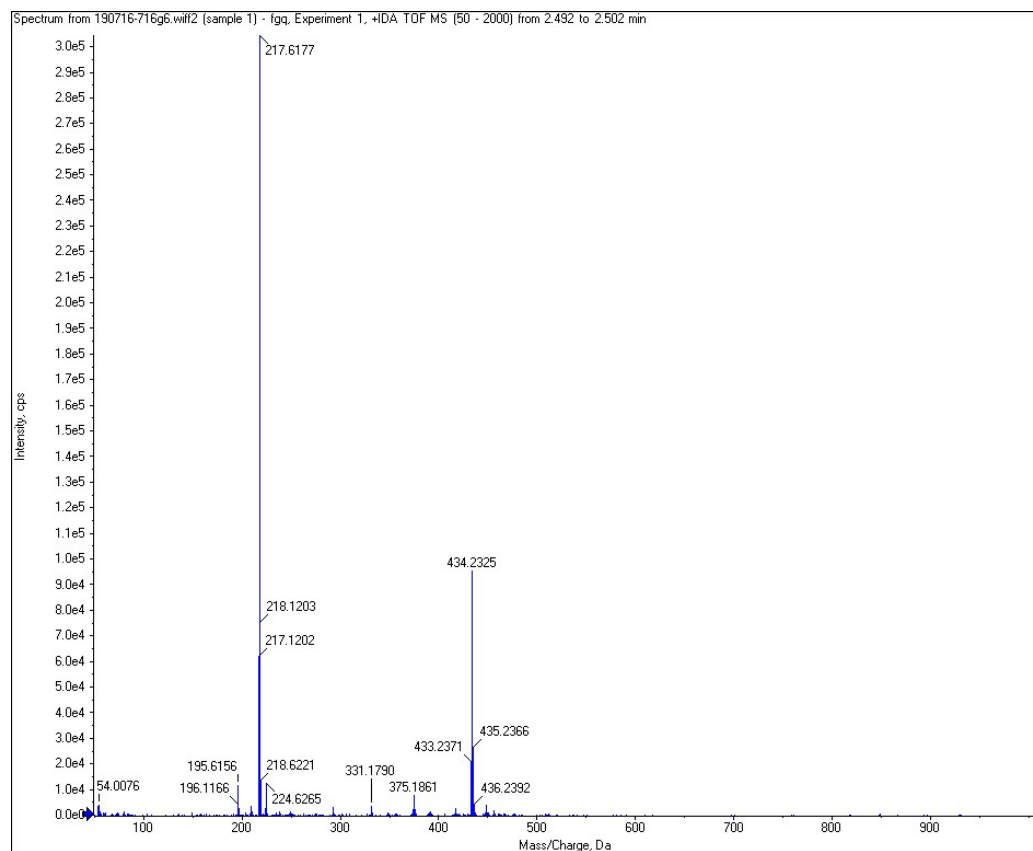


Fig. S23 <sup>1</sup>H NMR spectrum of 5e



**Fig. S24**  $^{13}\text{C}$  NMR spectrum of **5e**



**Fig. S25** HRMS spectrum of compound **5e**