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Supporting information

A novel AIE fluorescent probe based on myrtenal for Cu^{2+} in a near-perfect aqueous medium and bioimaging in vegetables and zebrafish

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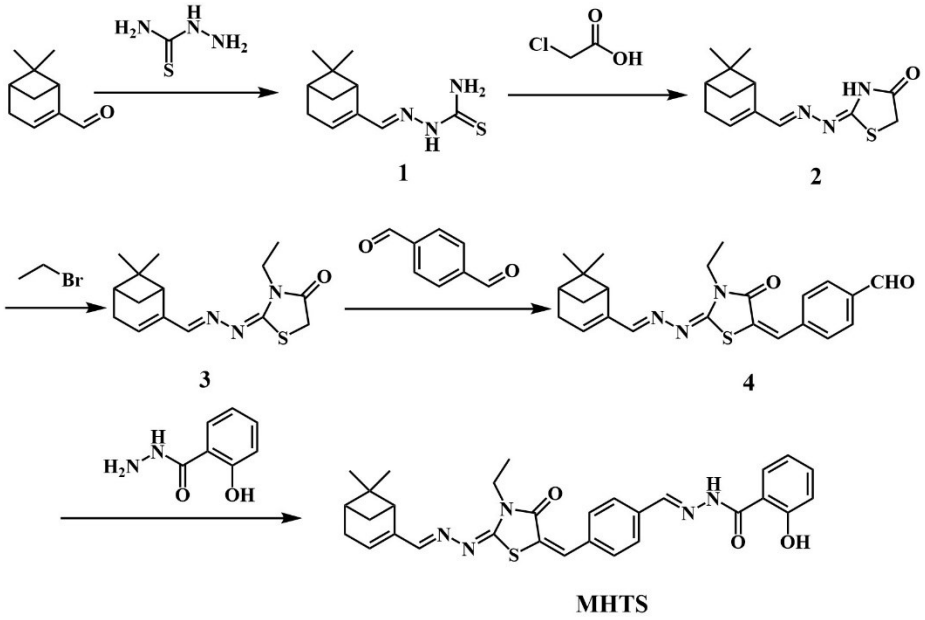
Table of Contents

Synthesis and characterization of compounds 1-4



Scheme. Synthetic route to **MHTS**.

Synthesis of compound 1

Thiosemicarbazide (1.8 g, 20 mmol) and 60 mL water were stirred and heated to 60 ℃, and the solution of myrtenal (3.0 g, 20 mmol) in 60 mL of ethanol was slowly added dropwise. The reaction was continued for another 1 h, and was cooled to room temperature. The precipitate was filtrated, washed with mixed solvent (deionized water : ethanol = 1:1, v/v) for 3 times, and recrystallized in ethanol to obtain white crystal compound **1** (3.8 g, yield 85%, mp: 160.9-161.4 ℃).^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.24 (s, 1H), 7.61 (s, 1H), 7.06 (s, 1H), 6.64 (s, 1H), 6.04 (s, 1H), 2.83 (t, J = 4.9 Hz, 1H), 2.47 – 2.42 (m, 2H), 2.40 (t, J = 3.1 Hz, 1H), 2.14 (s, 1H), 1.32 (s, 3H), 1.11 (d, J = 9.1 Hz, 1H), 0.76 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 177.75, 145.86, 144.74, 135.22, 40.78, 40.11, 37.80, 32.71, 31.16, 26.11, 20.99. HRMS (*m/z*) $[M + H]^+$: calculated for $C_{11}H_{17}N_3S + H^+$: 224.1221, found: 224.1224.

Synthesis of compound 2

Compound **1** (0.56 g, 2.5 mmol), sodium acetate (0.21 g, 2.5 mmol) and chloroacetic acid (0.24 g, 2.5 mmol) were dissolved in 50 mL of anhydrous ethanol and stirred at 80℃ for 10 h (monitored by TCL). The reacted mixture was cooled to room temperature, and the precipitate was filtrated, washed with cold ethanol for three times, and dried to obtain compound **2**, a white powder (0.59 g, yield 90%, mp: 235.1-236.3 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 12.12 (s, 1H), 8.35 (s, 1H), 6.19 (s, 1H), 3.75 (s, 2H), 2.98 (s, 1H), 2.48 (s, 3H), 2.16 (s, 1H), 1.36 (s, 3H), 1.17 (s, 1H), 0.81 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 174.90, 166.19, 159.06, 146.22, 136.25, 40.87, 40.13, 37.82, 33.75, 32.88, 31.33, 26.24, 21.09. HRMS (*m/z*) $[M+H]^+$: calculated for $C_{13}H_{17}N_3OS + H^+$: 264.1171, found: 264.1169.

Synthesis of compound 3

NaH (24 mg, 1 mmol) was slowly added to the solution of compound **2** (263 mg, 1 mmol) in 6 mL of DMF with stirring under ice bath for 0.5 h, and ethyl bromide (163 mg, 1.5 mmol) was then added dropwise. The ice-bath was removed after finishing dropping, and the reaction was continued at 20°C for another 9 h. The reaction was terminated by adding 30 mL water, and extracted with 80 mL of ethyl acetate for 3 times. The combined organic layer was washed with deionized water and saturated salt water (3 × 50 mL) until neutrality, and dried on anhydrous sodium sulfate. After distilling out of the solvent, the residue was purified by silica gel column chromatography (PE/EA = 10:1, v/v) to obtain product **3** (199.3 mg, yield 68.5%), a white solid, mp: 104.3-104.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.01 (s, 1H), 6.08 (s, 1H), 3.84 (q, J = 7.1 Hz, 2H), 3.71 (s, 2H), 3.01 (t, J = 5.7 Hz, 1H), 2.52 – 2.46 (m, 2H), 2.44 (t, J = 3.1 Hz, 1H), 2.16 (s, 1H), 1.35 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H), 1.16 (d, J = 9.0 Hz, 1H), 0.81 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 171.87, 162.11, 159.34, 146.30, 135.13, 40.76, 40.29, 38.49, 37.67, 32.74, 32.46, 31.21, 26.09, 20.94, 12.53. HRMS (m/z) $[M + H]^+$: calculated for $C_{15}H_{21}N_3OS + H^+$: 293.1484, found: 293.1483.

Synthesis of compound 4

Compounds **3** (291 mg, 1 mmol), terephthalaldehyde (134 mg, 1 mmol), and piperidine (26 mg, 0.3 mmol) were dissolved in anhydrous ethanol，and the mixture was reacted under refluxing at 80 ℃ for 6 h (monitored by TCL). After evaporating the solvent, the residue was dissolved in ethyl acetate, and washed with deionized water until neutrality. Undergoing drying, filtrating, and evaporating ethyl acetate, the crude product was purified by silica gel column chromatography (PE / EA = 10:1, v / v) to get yellow solid product **4** (311.4 mg, yield 76.4%, mp: 148.6-149.2 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.04 (s, 1H), 8.09 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.69 (s, 1H), 6.18 – 6.15 (m, 1H), 4.01 (q, J = 7.1 Hz, 2H), 3.08 (td, J = 5.6, 1.3 Hz, 1H), 2.54 (dt, J = 9.2, 5.8 Hz, 1H), 2.50 (dt, J = 16.7, 3.2 Hz, 2H), 2.22 – 2.17 (m, 1 H), 1.41 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.20 (d, J = 9.1 Hz, 1H), 0.83 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 191.31, 166.24, 160.48, 157.00, 146.21, 139.91, 136.55, 136.09, 130.35, 130.19, 130.13, 128.07, 126.25, 40.74, 40.28, 38.86, 37.76, 32.87, 31.26, 29.70, 26.13, 20.98, 12.82. HRMS (*m/z*) $[M + H]^+$: calculated for $C_{23}H_{25}N_3O_2S + H^+$: 408.1746, found: 408.1747.

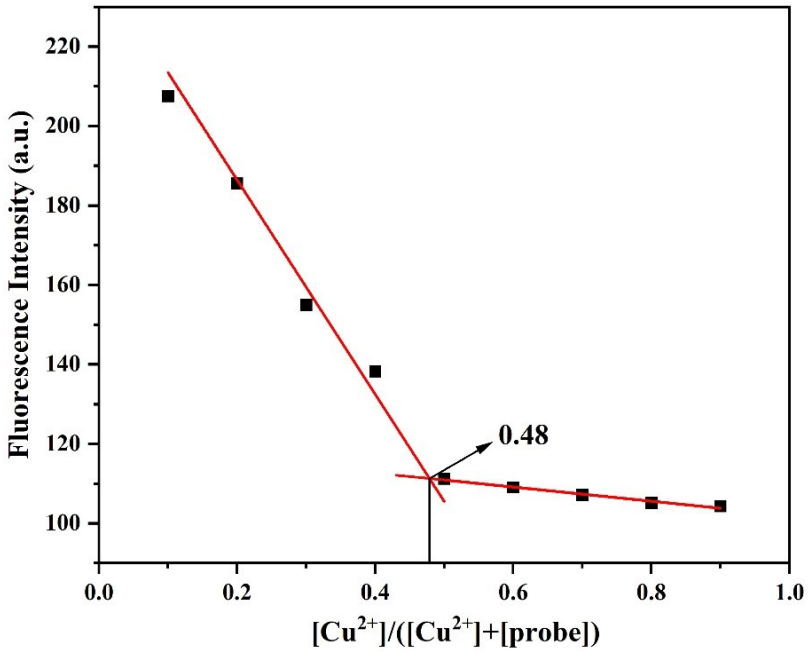


Fig. S1. Job's plot of fluorescence intensity for binding stoichiometry determination between **MHTS** and Cu^{2+} (the total concentration was 10 μM) in PBS buffer (pH = 7.4, 1% C_2H_5OH).

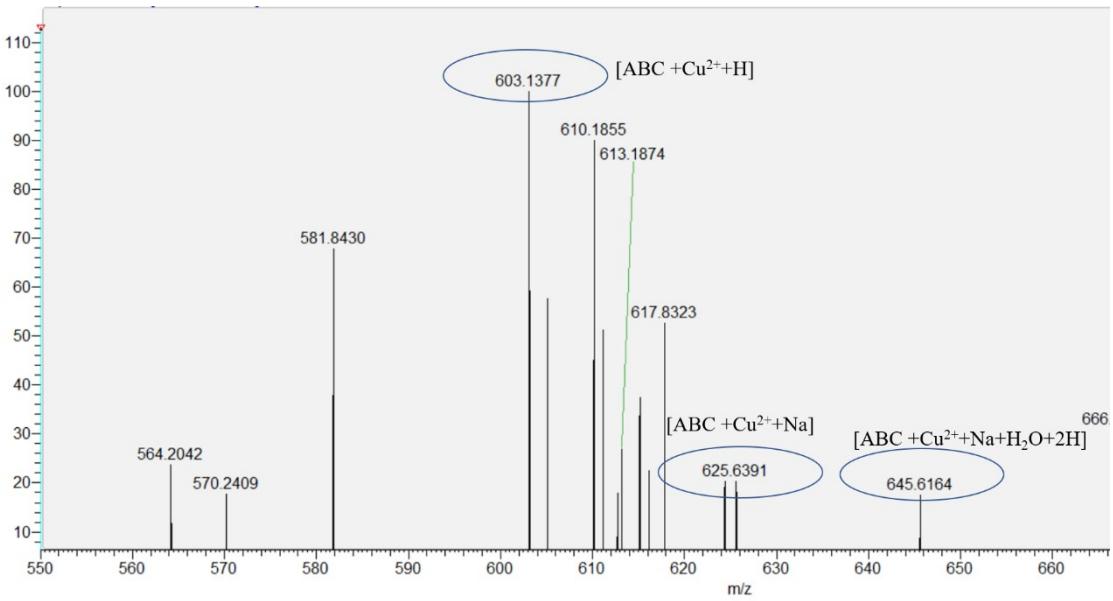


Fig. S2. The High-resolution mass spectra of probe **MHTS** towards Cu^{2+}.

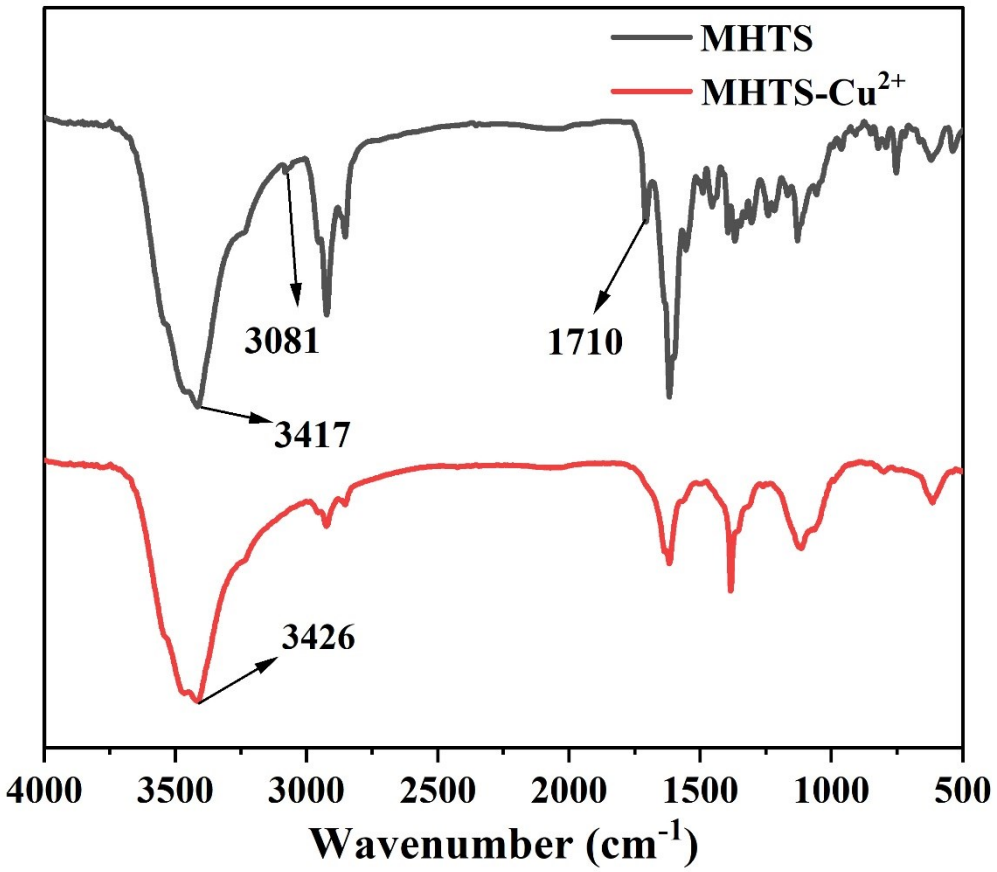


Fig. S3. FT-IR spectra of **MHTS** and **MHTS**-Cu^{2+} complexes.

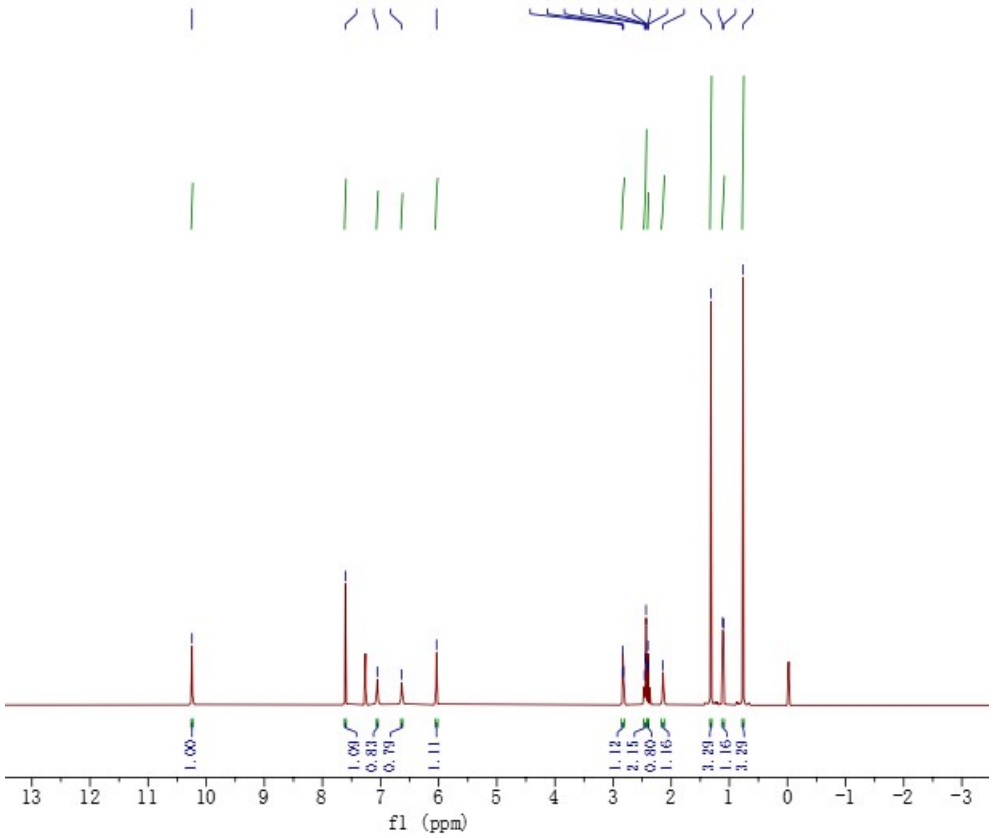


Fig. S4. ^{1}H NMR spectra of compound **1** in $CDCl_3$.

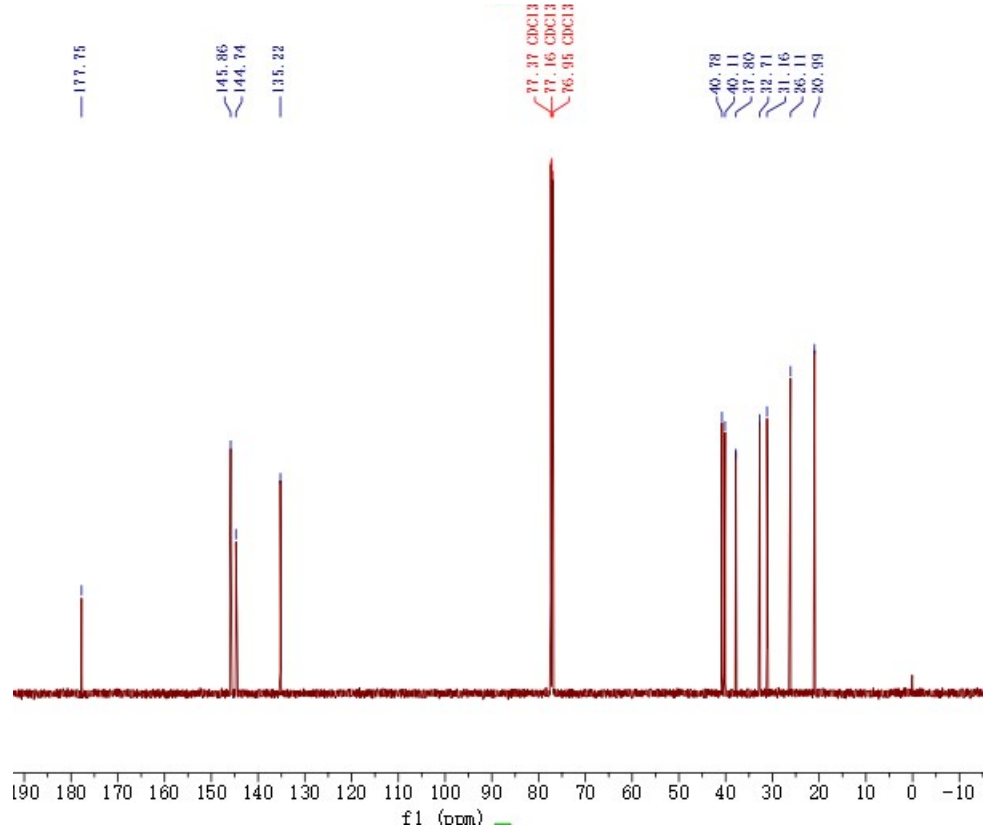


Fig. S5. ^{13}C NMR spectra of compound **1** in $CDCl_3$.

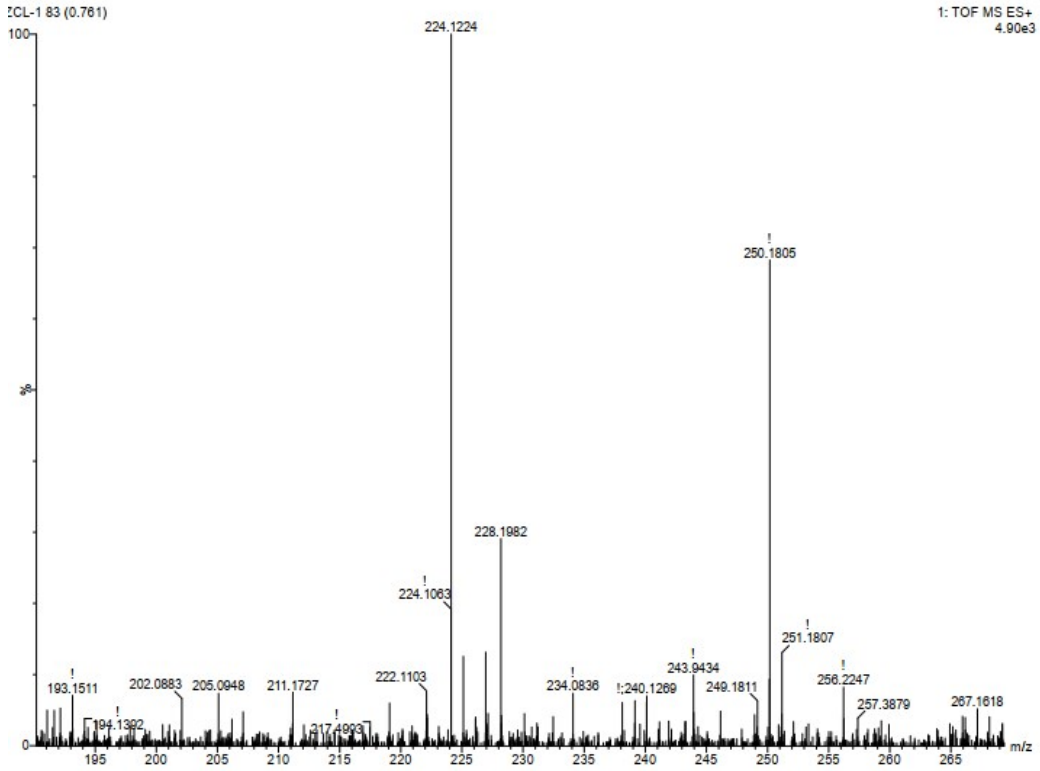


Fig. S6. HRMS of compound **1**.

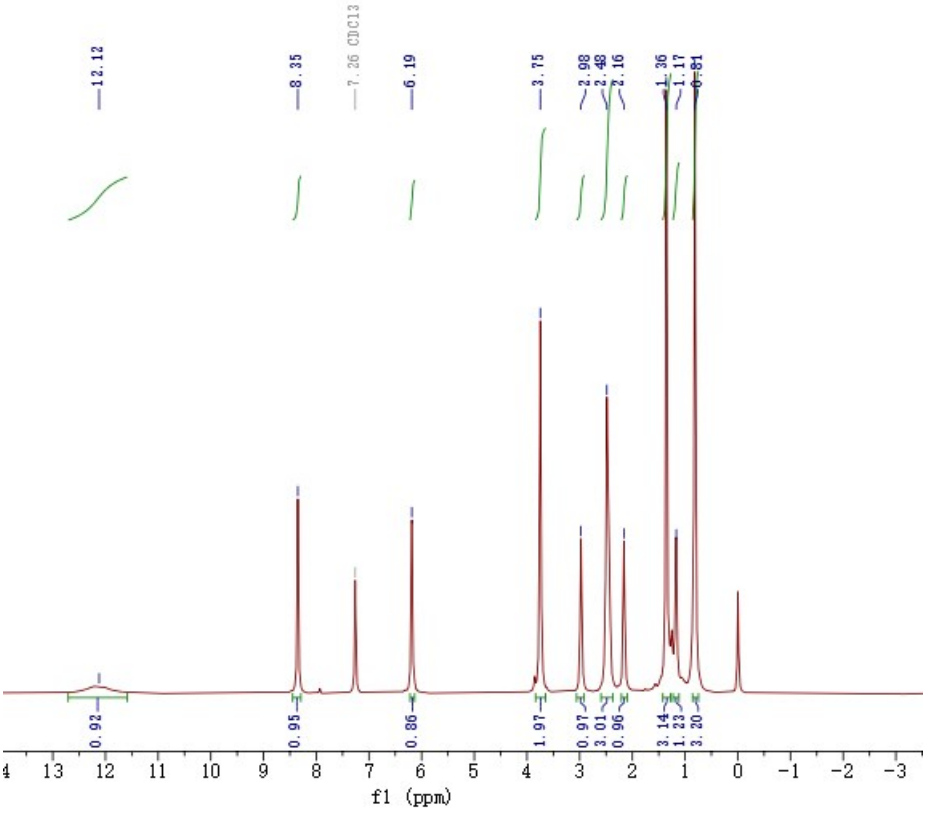


Fig. S7. ^{1}H NMR spectra of compound **2** in $CDCl_3$.

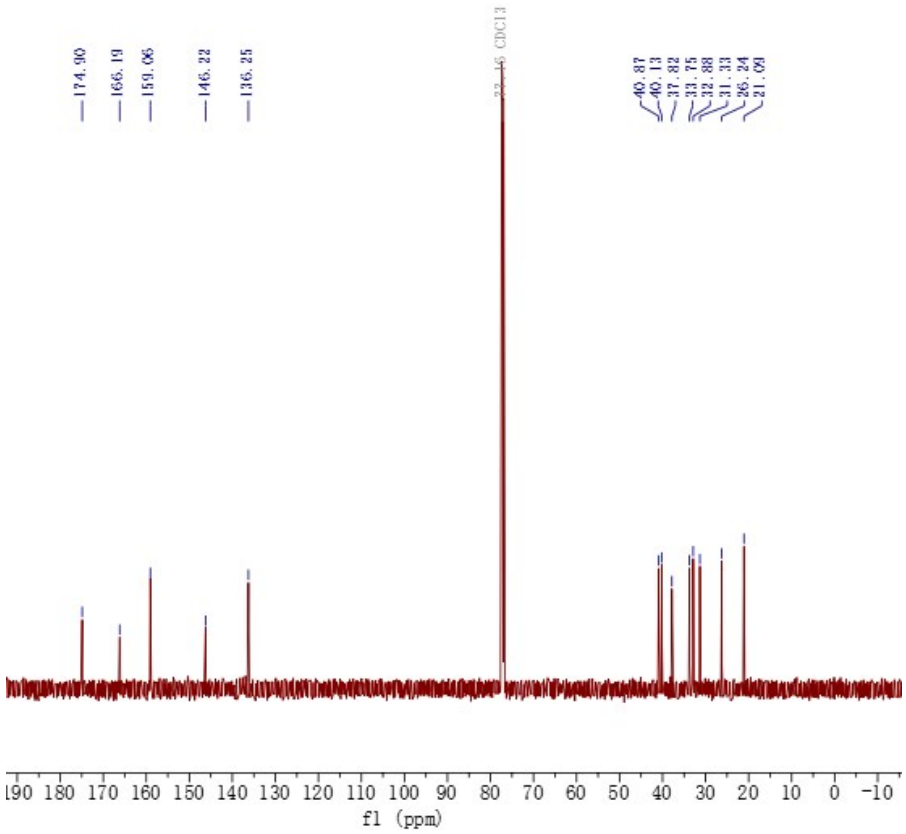


Fig. S8. ^{13}C NMR spectra of compound **2** in $CDCl_3$.

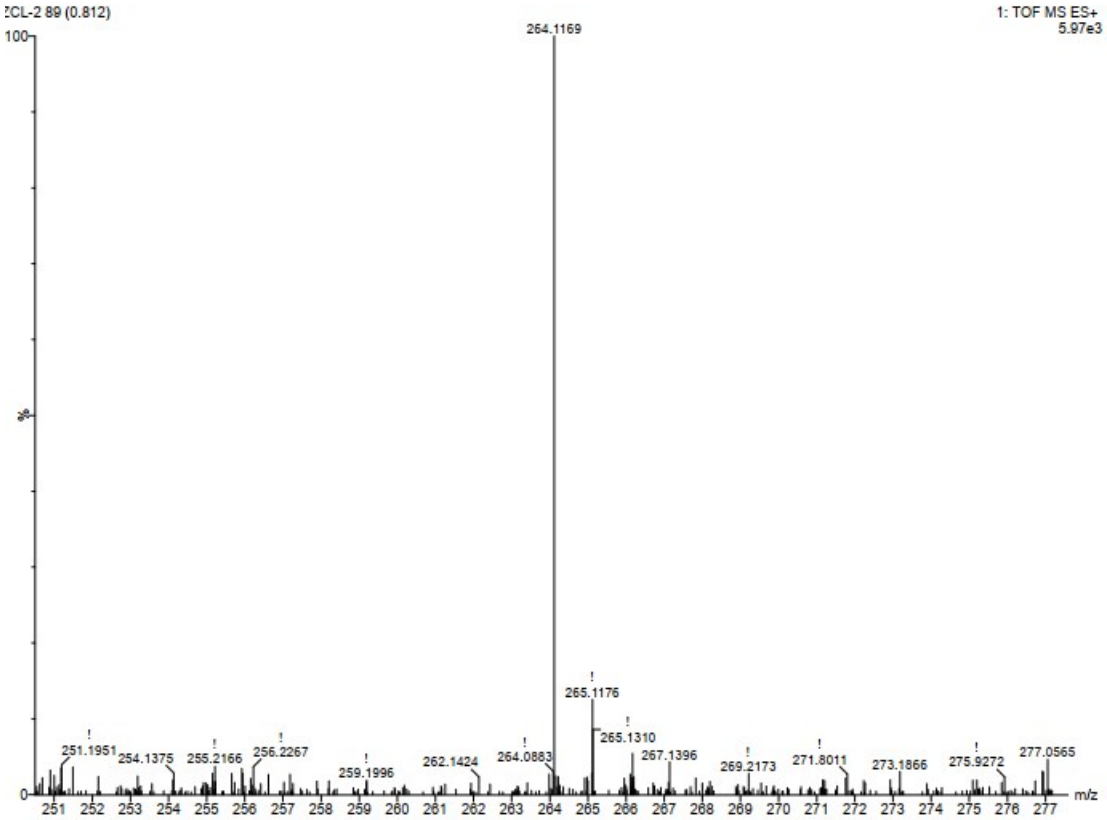


Fig. S9. HRMS of compound **2**.

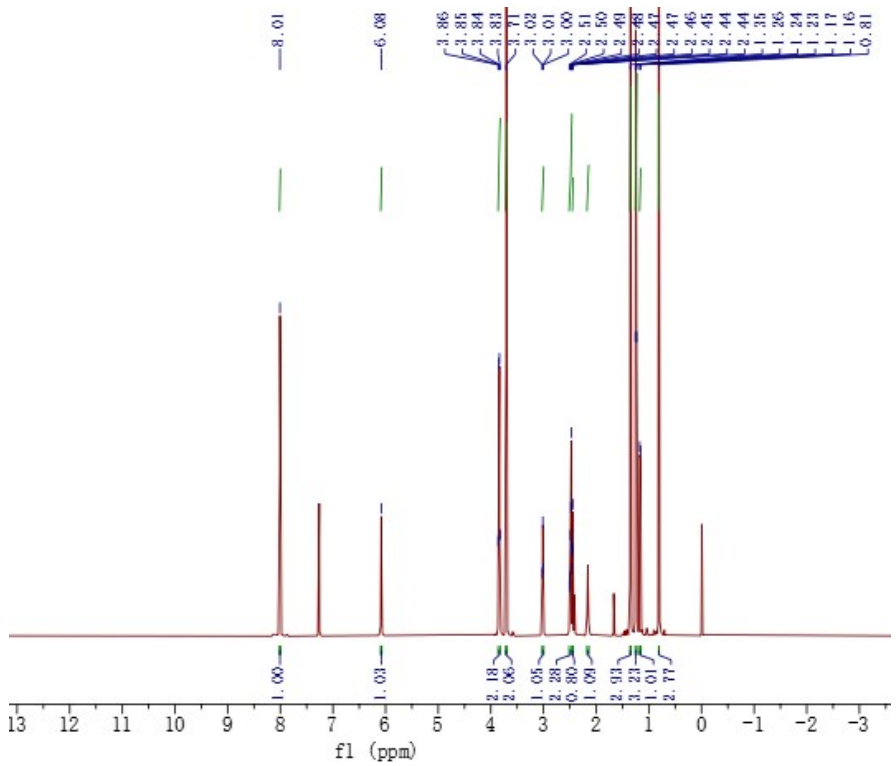


Fig. S10. ^{1}H NMR spectra of compound **3** in $CDCl_3$.

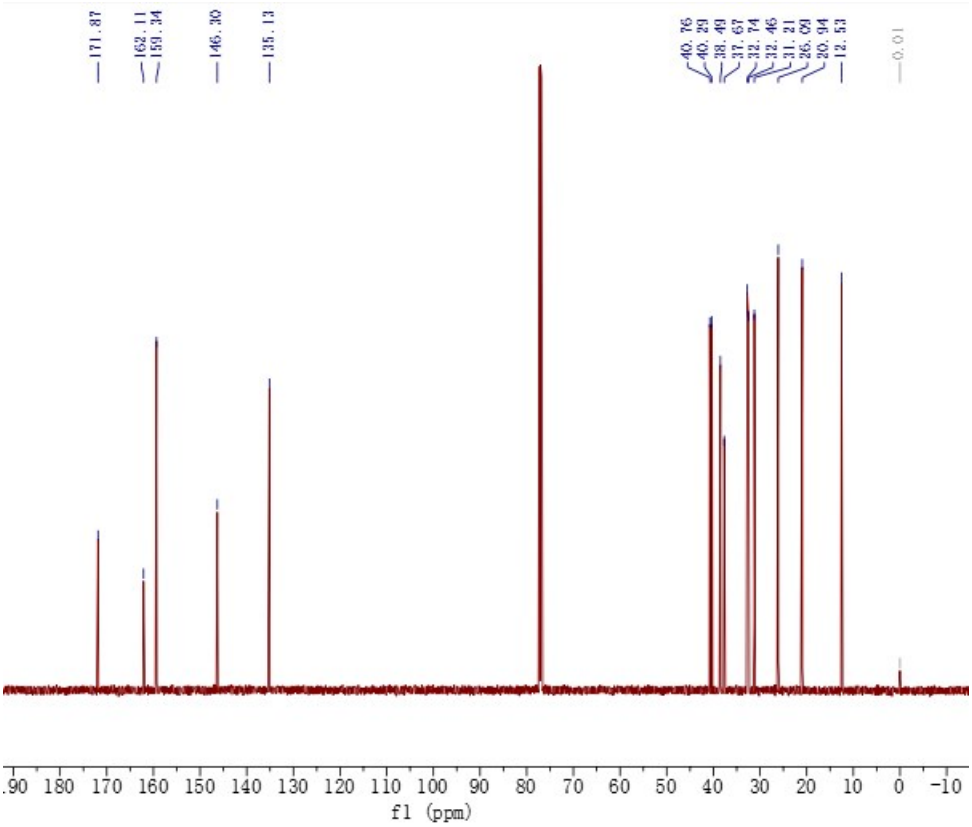


Fig. S11. ^{13}C NMR spectra of compound **3** in $CDCl_3$.

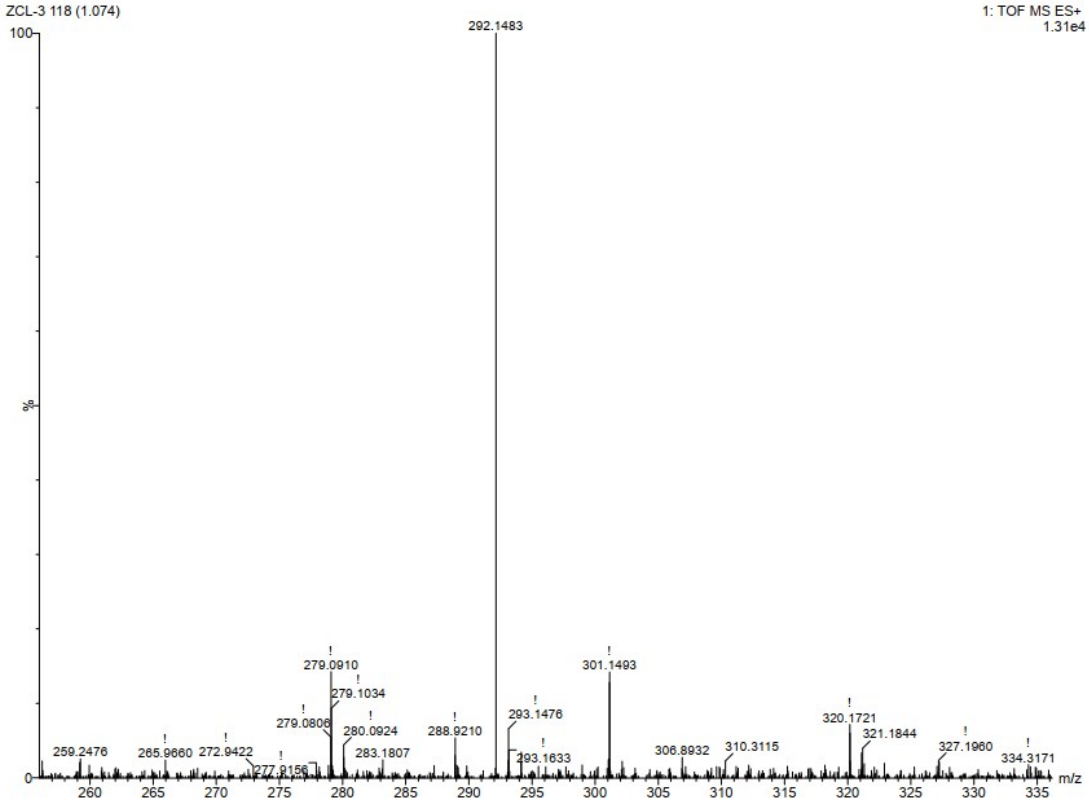


Fig. S12. HRMS of compound **3**.

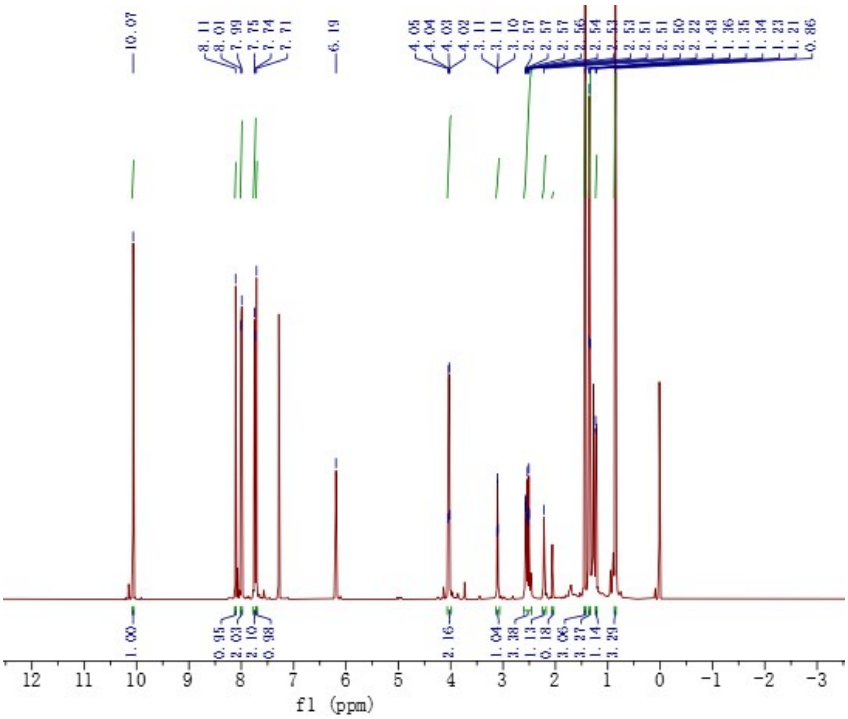


Fig. S13. ^{1}H NMR spectra of compound **4** in $CDCl_3$.

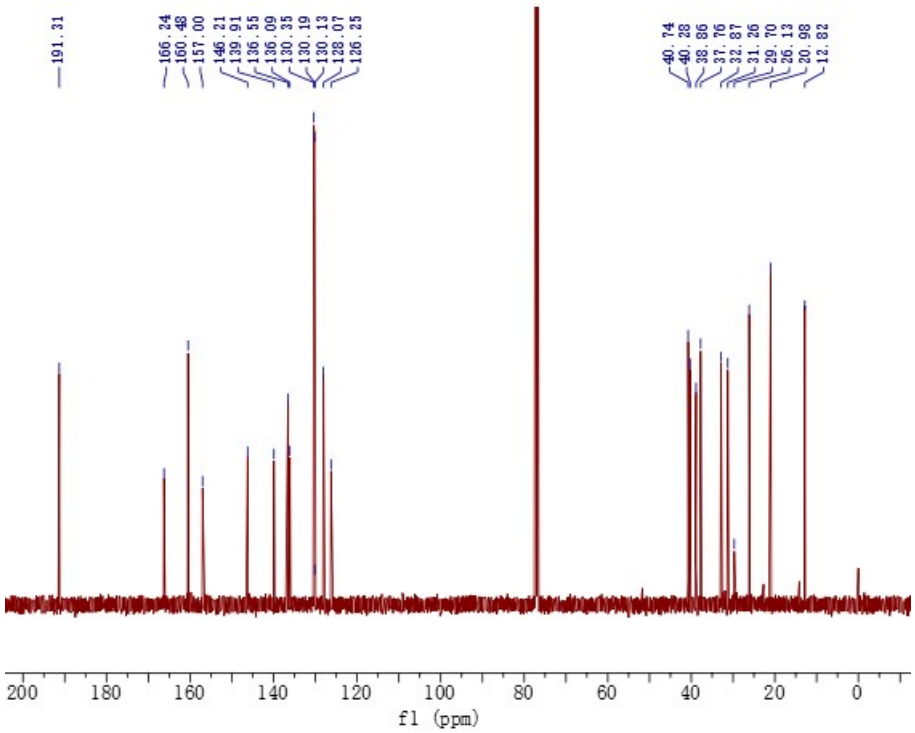


Fig. S14. ^{13}C NMR spectra of compound **4** in $CDCl_3$.

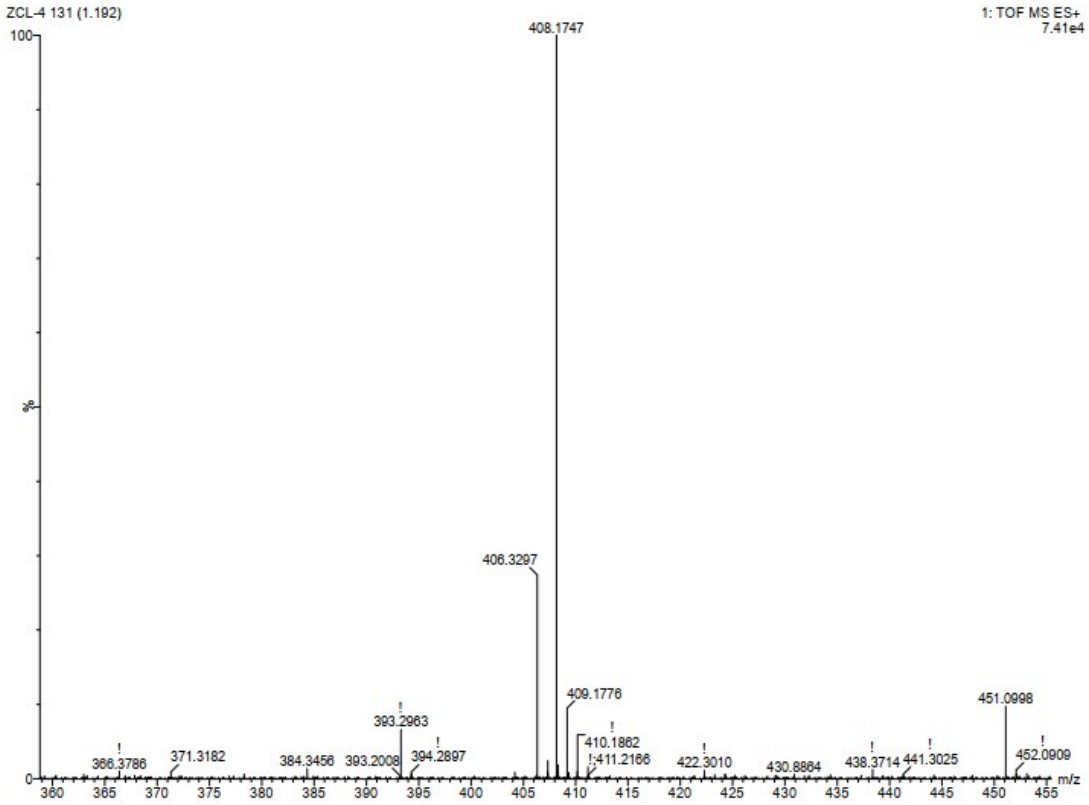


Fig. S15. HRMS of compound **4**.

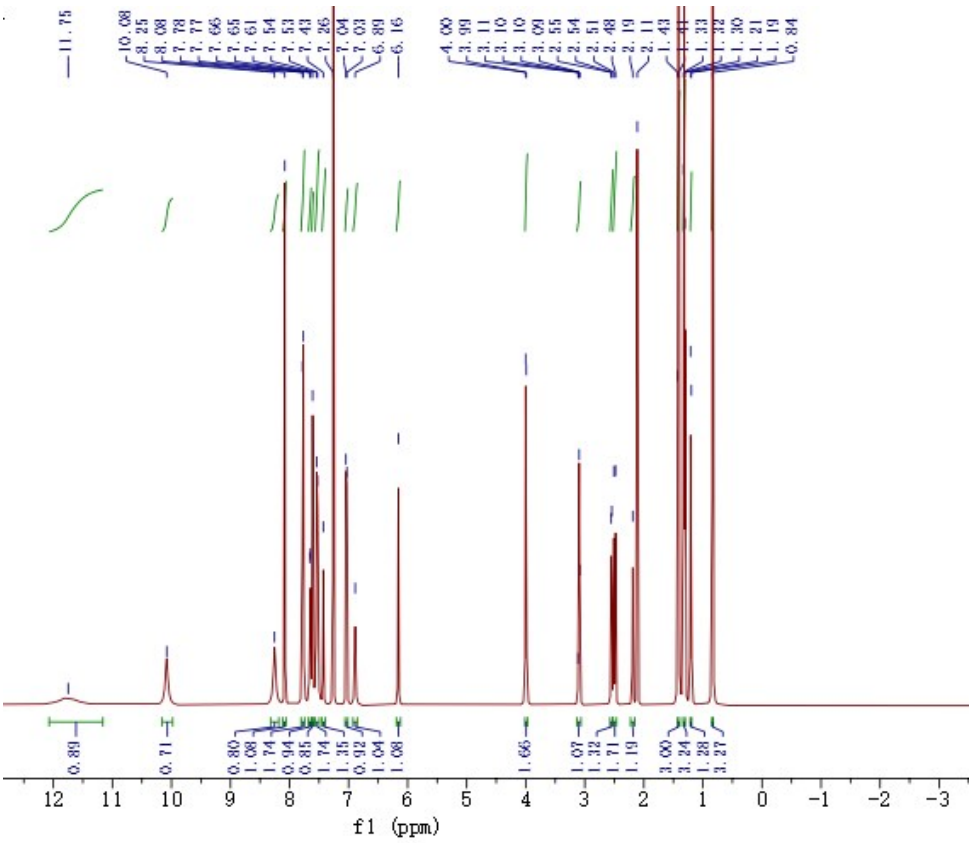


Fig. S16. ^{1}H NMR spectra of **MHTS** in $CDCl_3$.

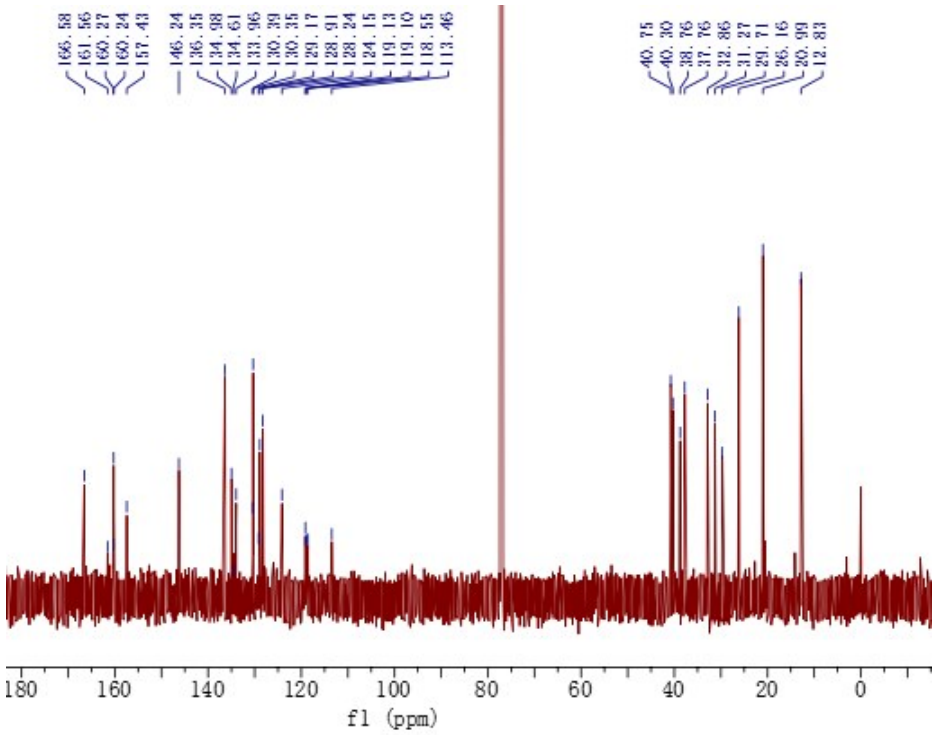


Fig. S17. ^{13}C NMR spectra of **MHTS** in $CDCl_3$.

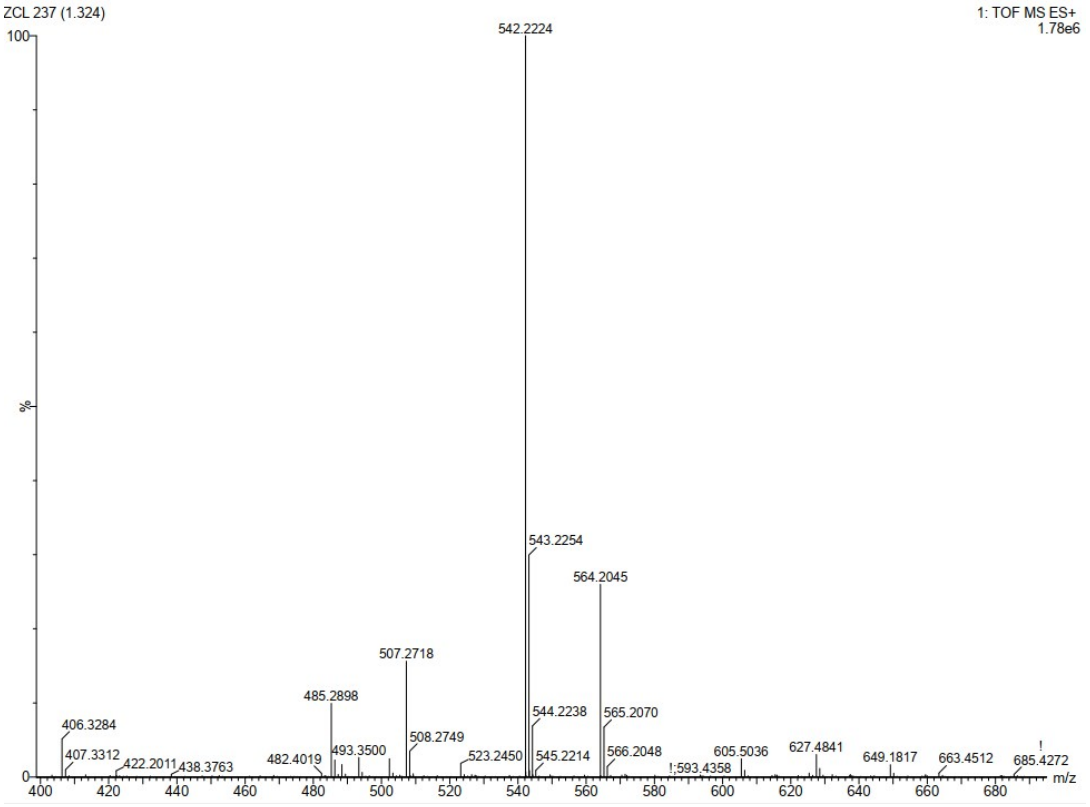
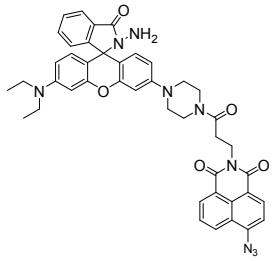
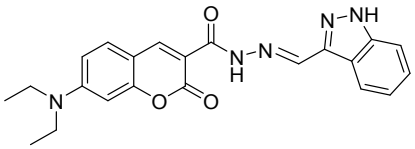
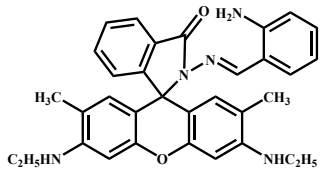
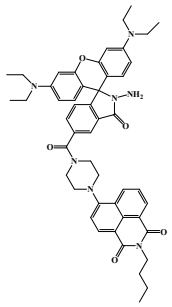
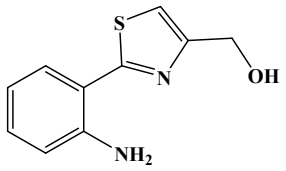
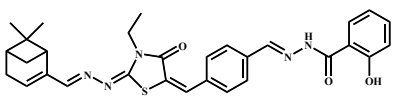


Fig. S18. HRMS of **MHTS**.

Table S1. Comparison with recent reported fluorescent probes in detecting Cu^{2+}

Probe	LOD (μM)	Detection System (v/v)	Linear range (μM)	Reference
	1.4	DMF/H_2O=3/7	0-30	1
	6	CH_3CN/HEPES = 3/2	0-30	2
	0.42	CH_3CN/ H_2O=1/1	0-10	3
	0.0423	C_2H_5OH/H_20=50/1	0-8	4
	1	C_2H_5OH	0-10	5
	0.125	C_2H_5OH/H_20=1/99	0-14	This work

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