Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting information

A very fast 3-hydroxy-coumarin-based fluorescent probe for highly selective and sensitive detection of thiophenols and its application in water samples

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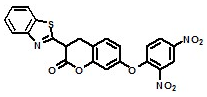
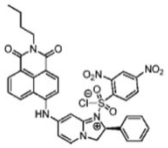
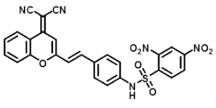
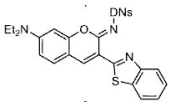
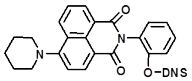
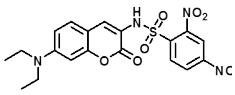
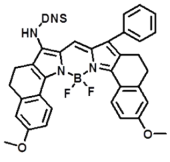
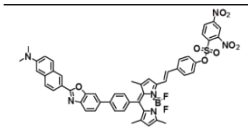
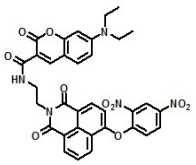
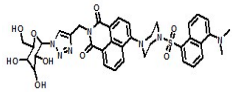
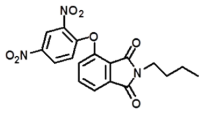
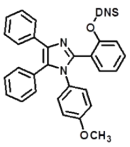
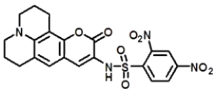
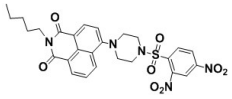
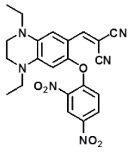
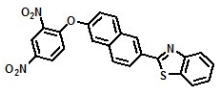
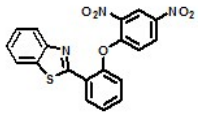
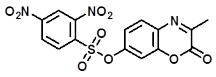
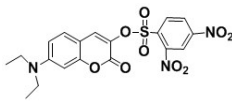
Table S1 Comparison of Fluorescent Probes for Thiophenols Detection

Probes	Time needed to reach FI plateau [a]	Detection time	Detection media	LOD [b]	Application in real water samples	ref
	40 min (5 equiv.)	30 min	Aqueous phosphate buffer (pH 7.0) containing 45% DMF	1.8 nM	Yes	1
	15 min (2 equiv.)	20 min	Aqueous phosphate buffer (pH 8.0)	20 nM	Yes	2
	6 min (10 equiv.)	10 min	Aqueous phosphate buffer (pH 7.4) containing 30% DMSO	70 nM	Yes	3
	1.5 min (10 equiv.)	5 min	Aqueous HEPES buffer (pH 7.4)	6.9 nM	No	4
	1 min (10 equiv.)	2 min	Aqueous HEPES buffer (pH 7.4)	224 nM	Yes	5
	30 min (4 equiv.)	60 min	Aqueous phosphate buffer (pH 7.4)	30 nM	Yes	6
	90 min (20 equiv.)	60 min	Aqueous phosphate buffer (pH 7.4) containing 50% CH_3CN	37 nM	No	7

	20 min (1 equiv.)	30 min	Aqueous phosphate buffer (pH 7.4) containing 50% EtOH	4.9 nM	Yes	8
	300 s (3 equiv.)	5 min	Aqueous phosphate buffer (pH 7.4) containing 40% DMF	120 nM	Yes	9
	Instant (50 equiv.)	Instant	Aqueous HCl-Tris buffer(pH 7.3)	3.8 nM	Yes	10
	60 min (5 equiv.)	60 min	Aqueous HEPES buffer (pH 7.4) containing 20% CH_3CN	3.5 nM	Yes	11
	150 s (0.5 equiv.)	2 min	Aqueous phosphate buffer (pH 7.4) containing 50% CH_3CN	189 nM	Yes	12
	40 min (4 equiv.)	>40min	Aqueous phosphate buffer (pH 7.4)	4.5 nM	Yes	13
	100 s (30 equiv.)	----- [c]	Aqueous HEPES buffer (pH 7.4) containing 50% DMSO	13 nM	No	14

	120 s (5 equiv.)	30 min	Aqueous HEPES buffer (pH 7.4)	8.2 nM	Yes	15
	----- [c]	15 min	Aqueous phosphate buffer (pH 7.4) containing 60% DMF	9.6 nM	Yes	16
	----- [c]	15 min	Aqueous phosphate buffer (pH 7.2) containing 45% DMF	30 nM	Yes	17
	Instant (any equiv.)	Instant	Aqueous HEPES buffer (pH 7.4) containing 50% THF	24 nM	Yes	18 (From our group)
	Instant (any equiv.)	Instant	Aqueous HEPES buffer (pH 7.4) containing 30% THF	7.3 nM	Yes	This work

[a] Values in the brackets are the amounts of PhSH relative to probe.

[b] Abbreviation of Limit of detection.

[c] Not mentioned.

Synthesis of Intermediates M1 and M2

7-Diethylamino-3-nitro-chromene-2-one (M1). 4-Diethylaminosalicylaldehyde (1.40 g, 7.21 mmol), ethyl nitroacetate (0.96 g, 7.21 mmol), 0.1 mL of piperidine, and 0.2 mL of glacial acetic acid were dissolved in 20 mL of anhydrous *n*-BuOH, and the reaction mixture was refluxed for 24 hours. Orange solids were formed during cooling. The crude product was recrystallized from 3 mL of DMF and an orange solid M1 (1.14 g) was obtained. Yield: 60.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 7.45 (d, *J* = 9.2 Hz, 1H), 6.72 (d, *J* = 9.2 Hz, 1H), 6.49 (s, 1H), 3.51(q, *J* = 6.8 Hz, 4H), 1.28 (t, *J* = 6.8 Hz, 6H).

3-Amino-7-diethylamino-chromene-2-one (M2). $SnCl_2{\cdot}2H_2O$ (1.55 g, 6.87 mmol) and 6 mL of 37% HCl were added into a 100 mL round-bottomed flask. Next, compound M1 (0.60 g, 2.29 mmol) was added

portion-wise, and the resultant solution was further stirred at room temperature for 4 hours. Then, a solution of 5 M NaOH was employed to neutralize the excessive acid, followed by extraction with ethyl acetate. The organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The product was obtained as a bright yellow solid (0.51 g). Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.4 Hz, 1H), 6.71 (s, 1H), 6.58 (d, *J* = 6.8 Hz, 1H), 6.54 (s, 1H), 3.88 (s, 2H), 3.37 (q, *J* = 7.2 Hz, 4H), 1.18 (t, *J* = 6.8 Hz, 6H).

Screening of Detection Media. To select the appropriate solvent system, we carried out the preliminary screening studies. The reaction between probe **1** and thiophenols can finish instantly in aqueous HEPES buffer (pH 7.4) containing 30% THF, which brings great convenience for the test. The reaction becomes slower when the proportion of the THF is less than 30%. The probe shows poor selectivity between thiophenols and biothiols when the proportion of the THF is higher than 30%. Thus we chose HEPES buffer (10 mM, pH 7.4) containing 30% THF as a co-solvent as the detection media.

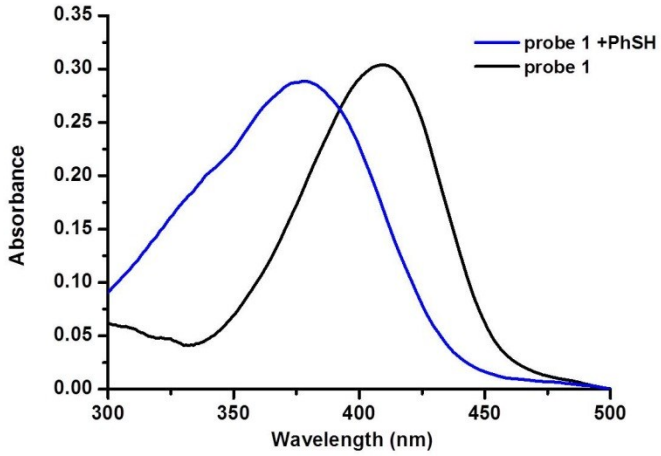


Figure S1 Absorption spectra of probe **1** before and after addition of PhSH in HEPES buffer (10 mM, pH 7.4) containing 30% THF as a co-solvent.

Determination of Quantum Yields. Quantum yields were determined using Quinine sulfate as a standard according to a published method. [18-19] The quantum yield was calculated according to the equation:

$$\Phi_{sample} = \Phi_{standard} * (F_{sample}/F_{standard}) * (A_{sample}/A_{standard})$$

Where Φ is the quantum yield, $\Phi_{standard}$ = 0.546 in 0.1 M H_2SO_4, F_{sample} and $F_{standard}$ are the integrated fluorescence intensities of the sample and the standard, A_{sample} and $A_{standard}$ are the optical densities, at the excitation wavelength, of the sample and the standard, respectively.

Quantum yield of Probe **1**: Φ = 0.0184.

Quantum yield of M3: Φ = 0.285.

Determination of the Detection Limits. The detection limit was determined from the fluorescence titration data based on a reported method. [20-23] According to the result of titrating experiment, the fluorescence intensity data at 493 nm were normalized between the minimum

intensity and the maximum intensity. As shown in Figure S2, a linear regression curve was then fitted to these normalized fluorescence intensity data, and the point at which this line crossed the abscissa axis was considered as the detection limit (7.3 nM).

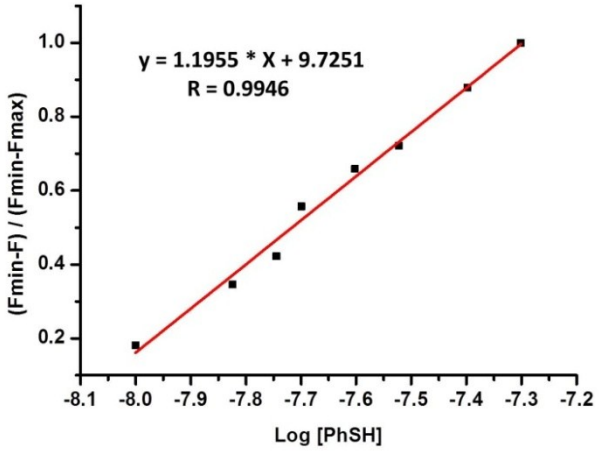


Figure S2 Normalized response of the fluorescence signal to changing PhSH concentrations (10, 15, 18, 20, 25, 30, 40, 50 nM)

Measurements of Thiophenols in Water Samples. The crude water samples from the Schoolyard River and Yuanboyuan Lake were passed through a microfiltration membrane before use. 10 mL aliquots of the water samples were then spiked with different concentrations of PhSH (0.5, 1, 5, 10, 30, 50, 100 μM) that had been accurately prepared. 1 mL sample was taken from each aliquot and further treated with probe **1** in THF-HEPES buffer (pH = 7.4, 10 mM, 3:6, v/v) to give the final mixtures (10 mL) containing probe **1** (final concentration = 10 μM) and PhSH (final concentration = 0.05, 0.1, 0.5, 1, 3, 5, 10 μM). The fluorescence at 493 nm of the mixed solutions was then measured at 1 min after the addition. The results were reported as the mean ± standard deviation of triplicate experiments.

Quantum chemical calculation. Quantum chemical calculations based on density functional theory (DFT) were carried out using a Gaussian 09 program. The optimized geometries and energy levels of frontier molecular orbitals were performed using the B3LYP functional and the 6-31 g (d, p) basis set.

Copies of NMR and Mass Spectra

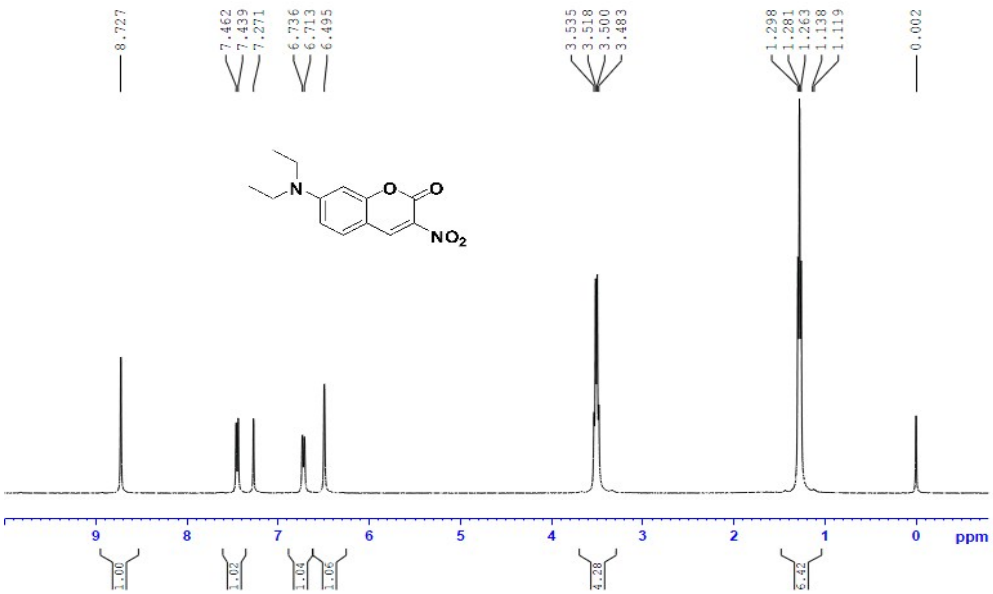


Figure S3 ^{1}H NMR spectrum of M1 in $CDCl_3$

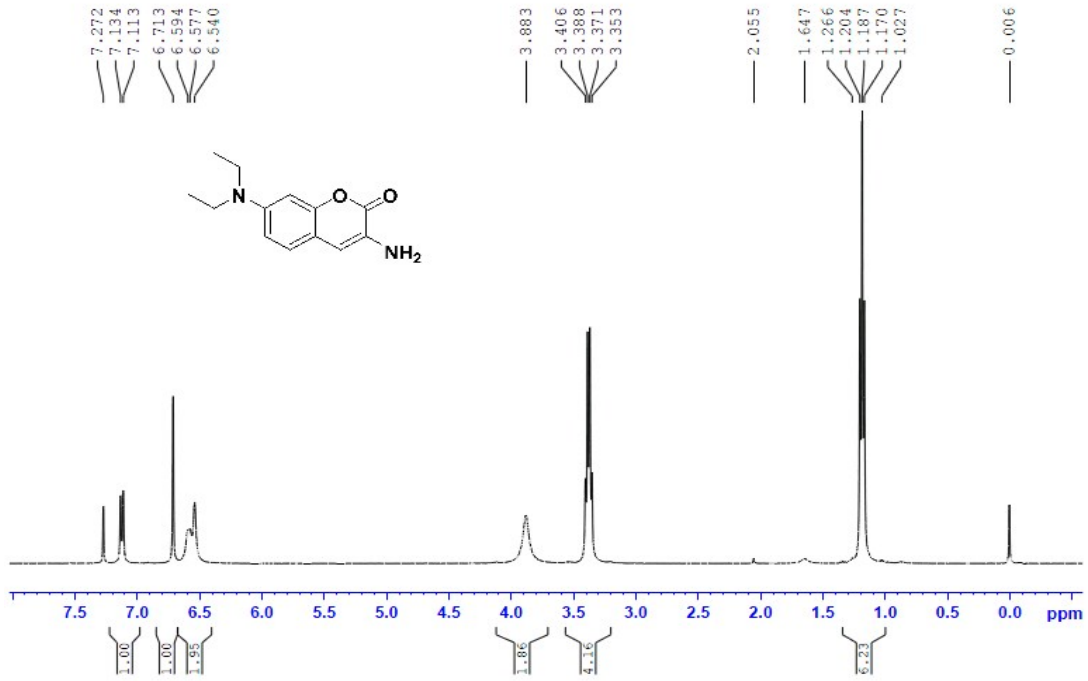


Figure S4 ^{1}H NMR spectrum of M2 in $CDCl_3$

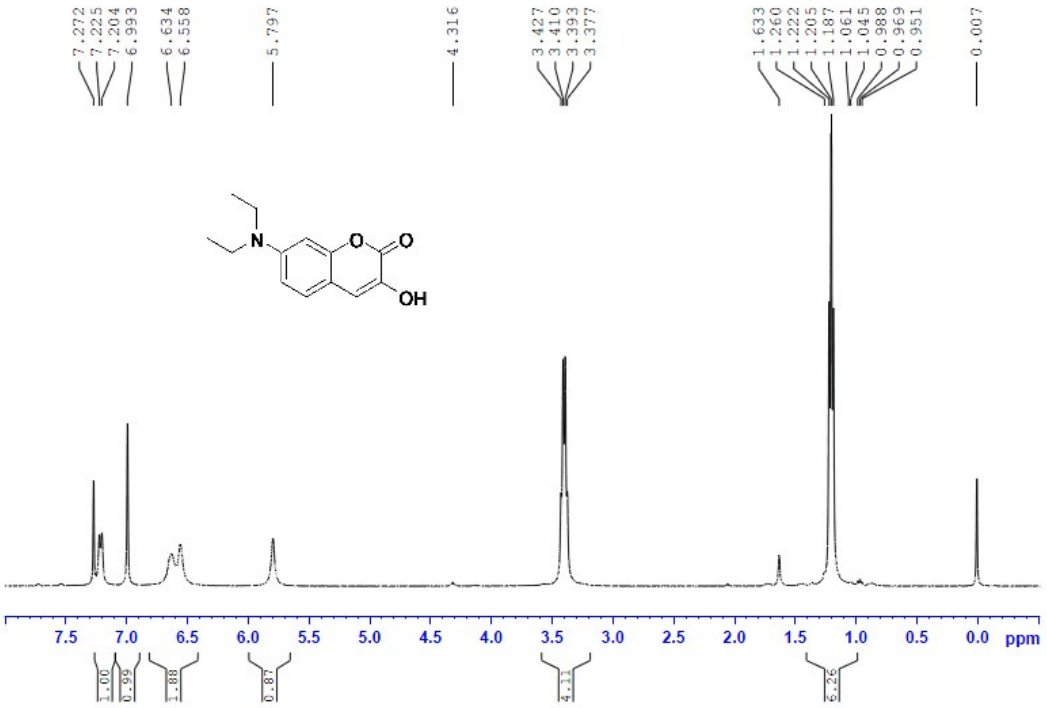


Figure S5 ^{1}H NMR spectrum of M3 in $CDCl_3$

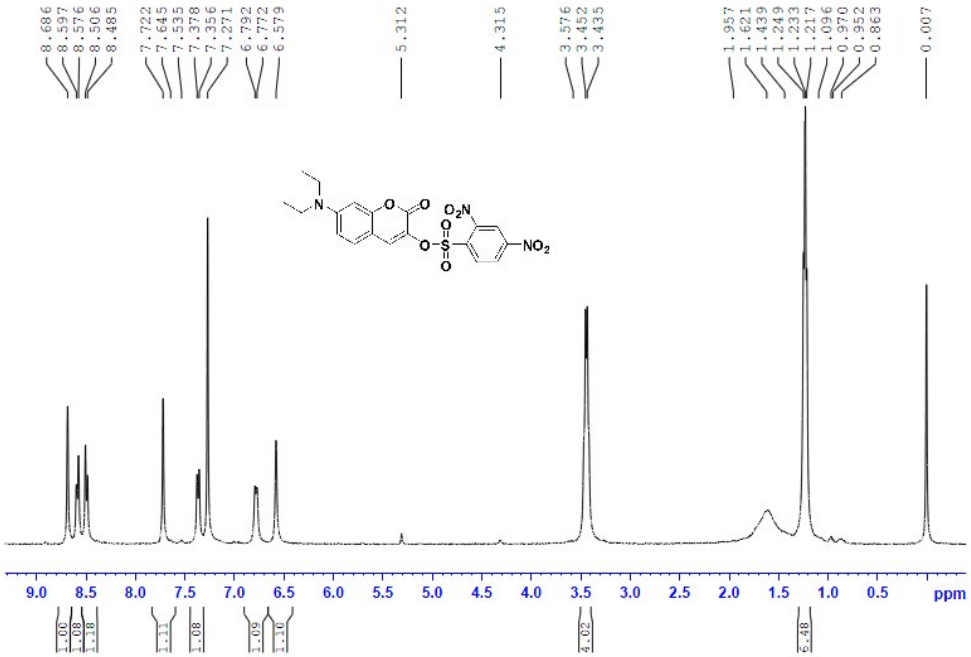


Figure S6 ^{1}H NMR spectrum of probe 1 in $CDCl_3$

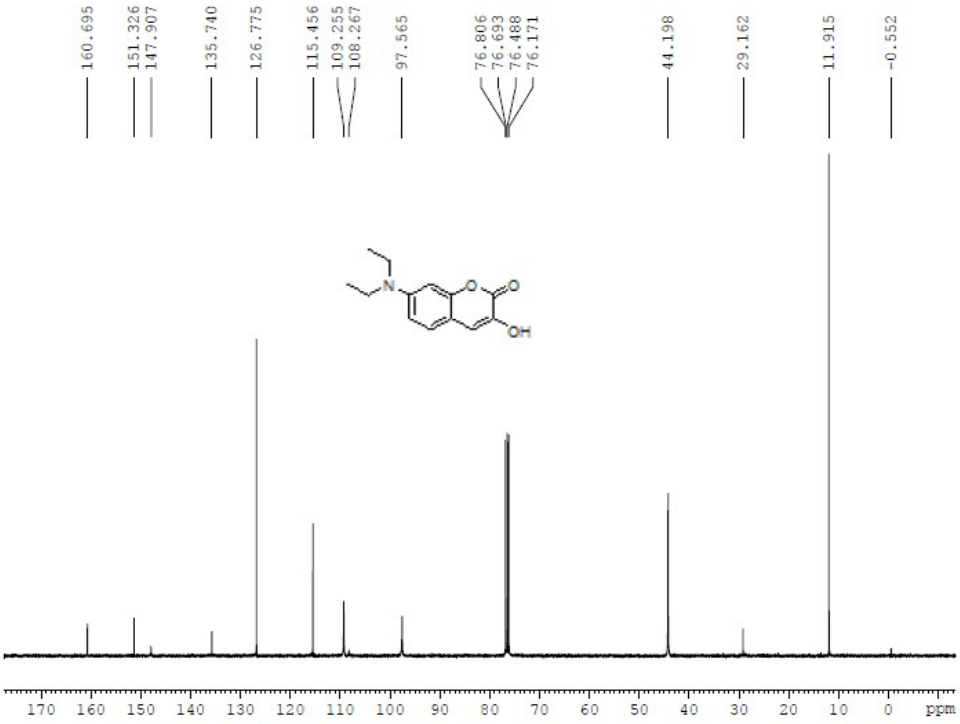


Figure S7 ^{13}C NMR spectrum of M3 in $CDCl_3$

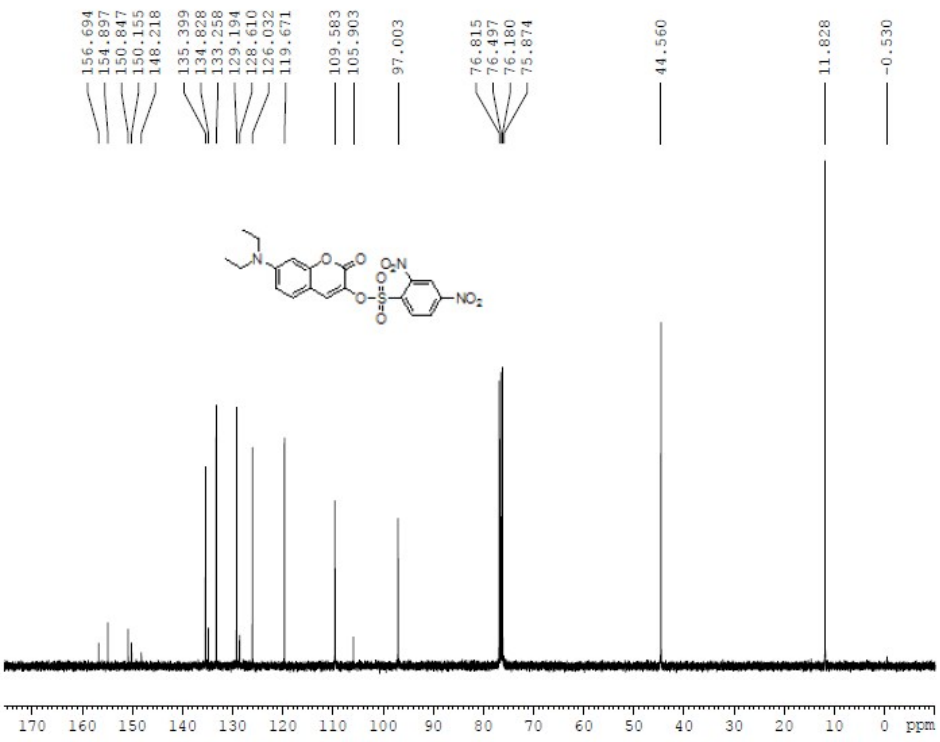


Figure S8 ^{13}C NMR spectrum of probe **1** in $CDCl_3$

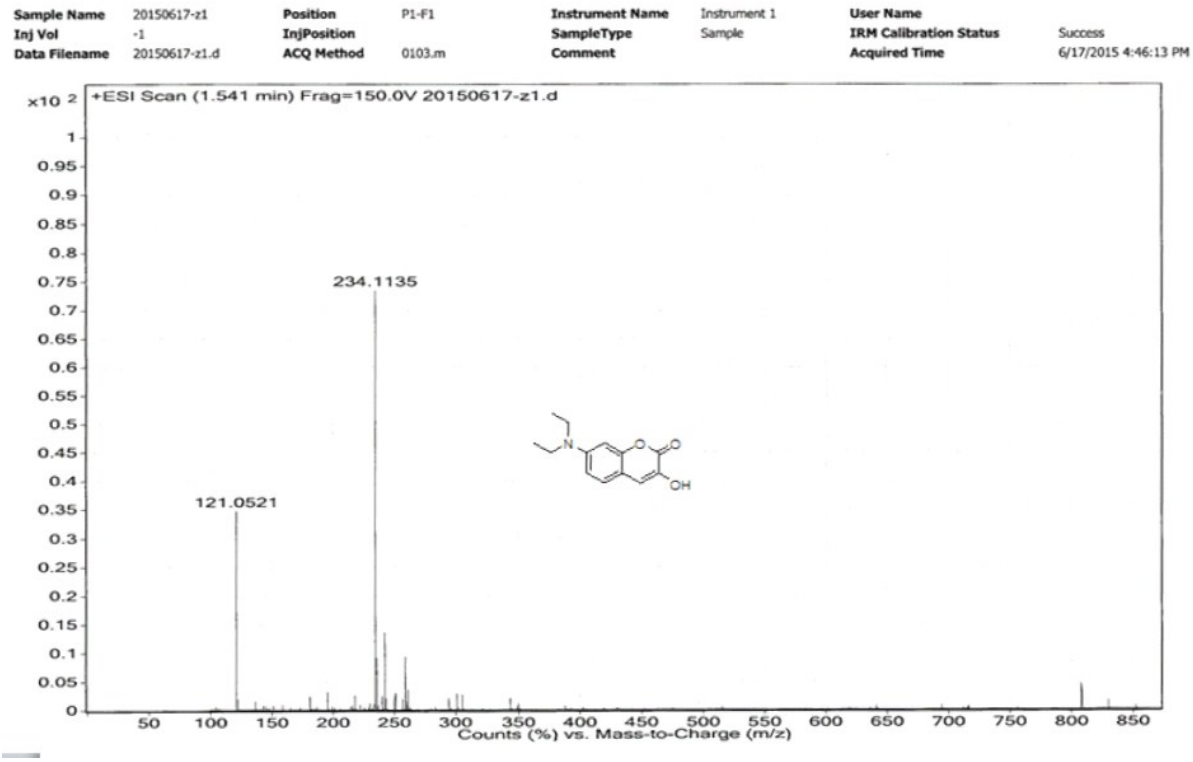


Figure S9 HRMS spectra of M3

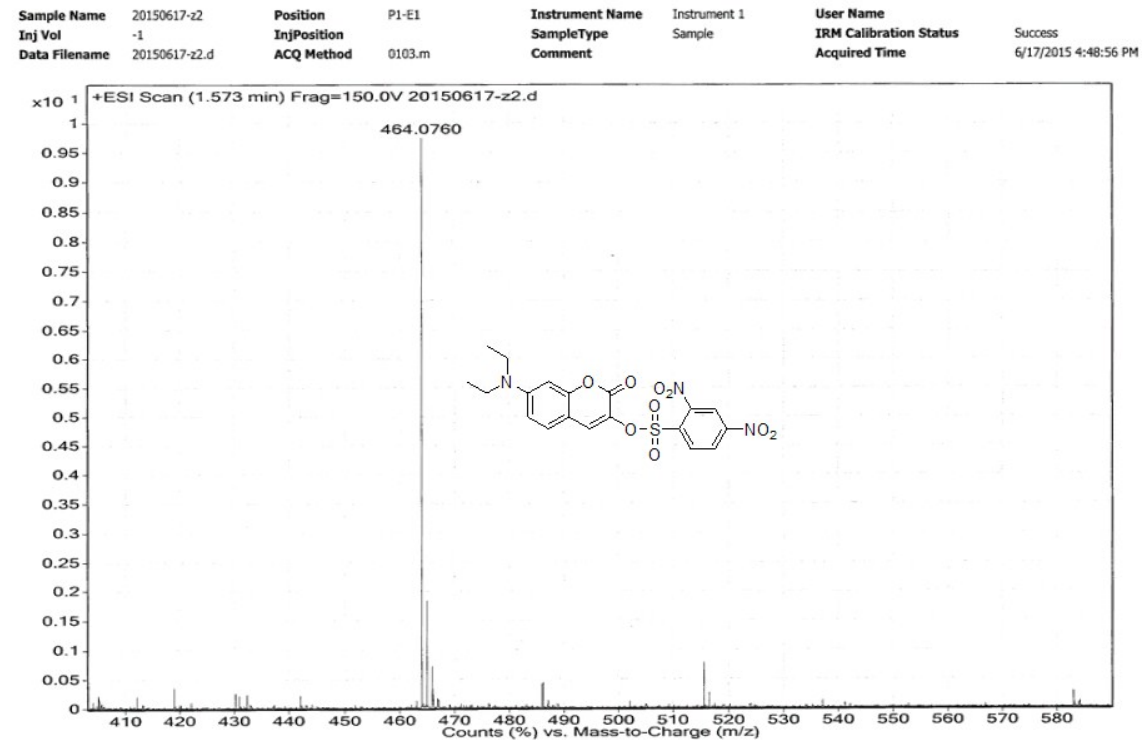


Figure S10 HRMS spectra of probe **1**

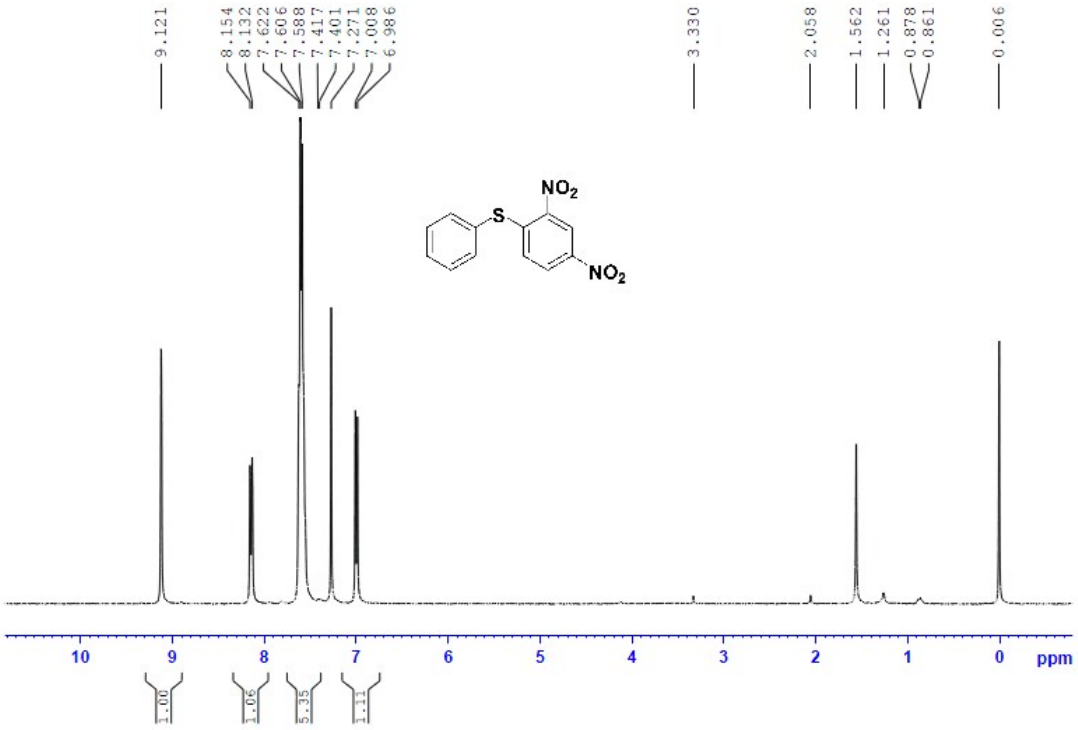


Figure S11 ^{1}H NMR spectrum of compound 2 in $CDCl_3$

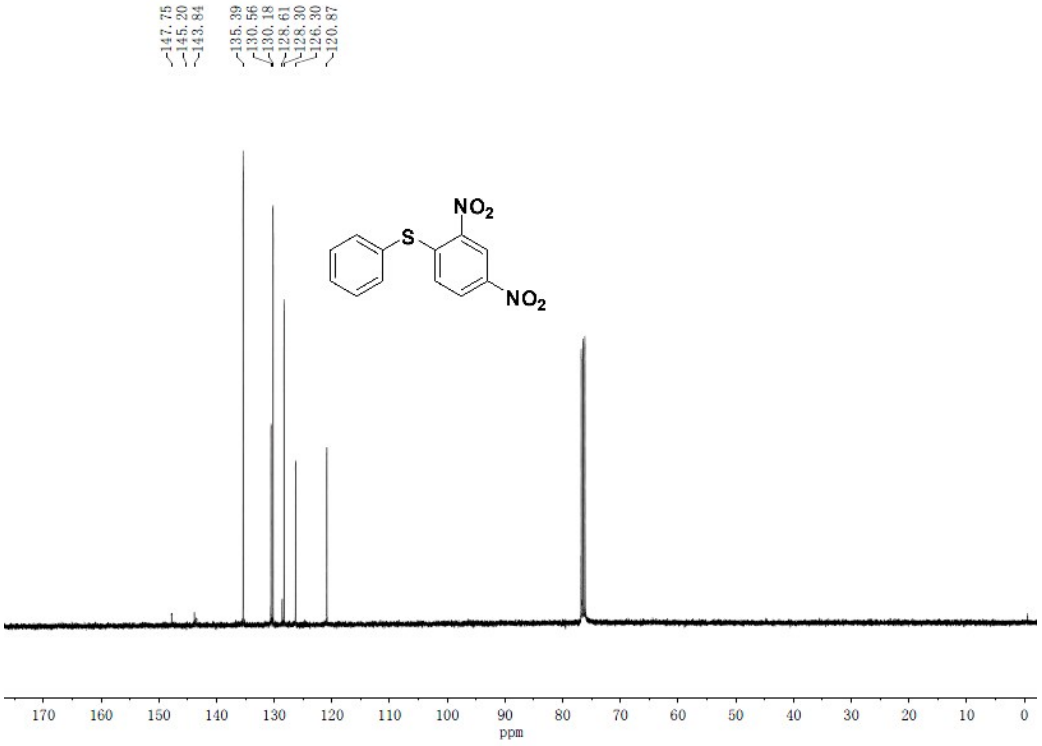


Figure S12 ^{13}C NMR spectrum of compound 2 in $CDCl_3$

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