A fluorescent probe based on benzothiazole and benzoindole for detecting hydrazine in various applications

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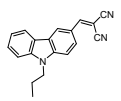
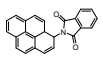
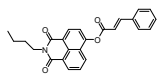
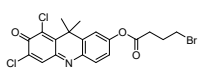
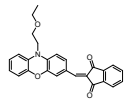
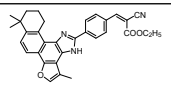
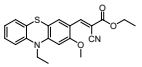
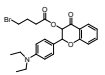
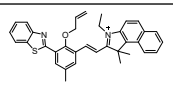
Table S1. Comparison of the detection performance of some recent fluorescent probes.

probe	solvent	λex	λem	LOD	smartphone app	application	Ref.
	DMSO/HEPES (1/99, v/v, pH 7.4)	420 nm	568 nm	6.3 nM	No	Soil, human serum, human urine plants foods, beverages, HeLa cells	19
	DMF/H_2O (1/1, v/v, pH 7.4)	383 nm	435 nm	1.85 μM	No	Soil, Water, gaseous hydrazine	46
	DMSO/PBS (9/1, v/v, pH 7.4)	342 nm	556 nm	0.29 μM	No	Soil, HepG-2 cells, zebrafish, water, test strips	47
	DMSO/PBS (1/99, v/v, pH 7.4)	405 nm	656 nm	0.18 μM	No	Soil, water, plants	48
	DMSO/PBS (1/3, v/v, pH 7.4)	445 nm	535 nm	0.85 nM	No	test strips, beverages, water, human urine	49
	THF/H_2O (4/6, v/v, pH 7.3)	365/430 nm	469/630 nm	58 nM	No	food, test strips, HeLa cells, zebrafish	50
	DMSO/PBS（1/1，v/v，pH 7.4）	365 nm	523 nm	0.15 μM	No	Soil, water, test strips, HeLa cells	15
	H_2O	334/345 nm	392/517 nm	0.1 mM	No	Soil, test strips	43
	DMSO/PBS (9/1, v/v, pH 7.4)	455 nm	501/561 nm	0.184 μM	No	HepG2 cells, soil, Zebrafish, water	51
	DMSO/PBS（4/1，v/v，pH 7.4）	375 nm	486 nm	0.025 μM	Yes	water, beverages, test strips, cotton swabs, hydrogel, soil, plant, food	This work

S1. Reagents and Instruments

Table S2. The instruments and their parameters.

Instrument Name	Model number	Source
NMR	Ascend TM NMR 500 MHz	Bruker (Beijing) Technology Co.
UV-Vis	Lambda 750	PerkinElmer
Fluorescence spectrophotometer	Cary Eclipse FL 1005	VARIAN USA
FTIR spectrometer	Nicolet Is5	Thermo Fisher Scientific
Electronic Analytical Balance	EL204	Mettler Toledo Instruments Ltd

Table S3. The reagents and their specifications

Reagent	Grade or purity	Source
5-Methylsalicylaldehyde	96%	Energy Chemmical
2-Aminothiophenol	96%	Aladdin
Hexamethylene tetramine	AR	Aladdin
Allyl bromide	98%	Aladdin
1,1,2-Trimethyl-11H-b3na[e]indole	98%	Energy Chemmical
Iodoethane	99%	RHAWN
Hydrazine hydrate	80%	XIHUA

S2. Fluorescence spectra test

All test samples of probe **1** (10 μM) were prepared in the mixture of DMSO/PBS (4:1, v/v, 10 mM, pH 7.4). The emission spectra were recorded at room temperature with the excitation wavelength of 375 nm and slit width of 10/10 nm.

S3. Water analysis

The detection data for N_2H_4 in actual water samples were obtained using the spiked recovery method. The water samples, including pond water and drinking water,

were collected from Guilin University of Technology, and were subjected to centrifugation and filtration. Then they were mixed with DMSO at 7:3 (v/v), and the pH was adjusted to 7.4.

S4. Preparation of test strips and swabs

The filter paper was cut into a circle of 1 cm × 1 cm and subsequently immersed in a dichloromethane solution containing the probe **1** (200 μM), and the probe-containing test paper was obtained after the solvent was completely evaporated.

For the detection of N_2H_4 in water samples, 15 μL of test solution containing different concentrations of N_2H_4 (0, 1%, 5%, 10%, 20%, 30%, 60%) was added dropwise onto the test paper, respectively. 1 min later, the color change of the test papers was observed under 365 nm UV light. 15 μL of Different beverages (milk, coconut milk, cola, orange juice, Sprite, white wine, pond water) without and with N_2H_4 (200 μM) were added dropwise onto the test papers to observe the fluorescence changes.

For N_2H_4 gas, the test papers loaded with probe **1** (200 μM) was placed at the mouth of the bottle of N_2H_4 solution at different concentrations (0, 1%, 5%, 10%, 20%, 30%, 40%) and waited for the volatilization of N_2H_4, and then the fluorescence change of the papers was detected by taking pictures with a smartphone under a hand-held UV lamp at 365 nm after 1 min.

The cotton swabs, soaked with probe **1** (200 μM), were directly placed into reagent bottles containing N_2H_4 at various concentrations (0, 20, 40, 60, 80, and 100 μM). Subsequently, the samples were heated to expedite the volatilization of N_2H_4. The images were taken using a smartphone under 365 nm UV light to monitor alterations in the fluorescence color.

S5. Soil analysis

The soil samples were collected form Guilin University of Technology campus, and treated with different concentrations of N_2H_4 from 0 to 200 μM for 6 h. Then 1g of each concentration of sample was added directly to 3 mL of the probe solution (20 μM) and reacted for about 20 min. Finally, the color values were extracted by capturing images for color identification using a smartphone application under 365

nm UV light.

S6. Plant analysis

The onions were grown in water for 7 days. The control group was treated with water for 8 h. The probe group underwent pre-treatment with the water containing probe **1** (10 μM) for 4 h. The N_2H_4 group was pretreated with N_2H_4 (50 μM) solution for 4 h and then transferred to water containing probe **1** (10 μM) for an additional 4 h. Then the onion root tips were washed three times with PBS buffer (pH 7.4).

S7. Food analysis

The food samples, comprising rice and mung beans, were procured from local supermarkets. The mung beans were germinated in a controlled humid environment for 48 h. Germinated mung bean sprouts and rice grains were subsequently soaked in the probe solution (20 μM) for 2 h and then divided into two groups. One group was soaked in distilled water; while the other was treated with N_2H_4 solution (200 μM) for 1h. Photographs of the samples were taken using a smartphone and analyzed with a color recognition application.

S8. Preparation of hydrogel-coated test paper and glove

The polyethylene glycol (2 g) and polyvinyl alcohol (2 g) were dissolved in 20 mL of a mixture of ethanol and water (v/v, 1:1), followed by stirring for 3 h. Subsequently, 5 mg of the probe was added to 5 mL of the aforementioned solution and stirred thoroughly to obtain an aqueous gel solution. Some circular filter papers with a diameter of 1 cm were immersed in the prepared aqueous gel solution and air-dried at room temperature to produce fluorescent hydrogel-coated test papers. Additionally, hydrogel-coated gloves were obtained by immersing laboratory latex gloves in the prepared hydrogel solution containing probe 1.

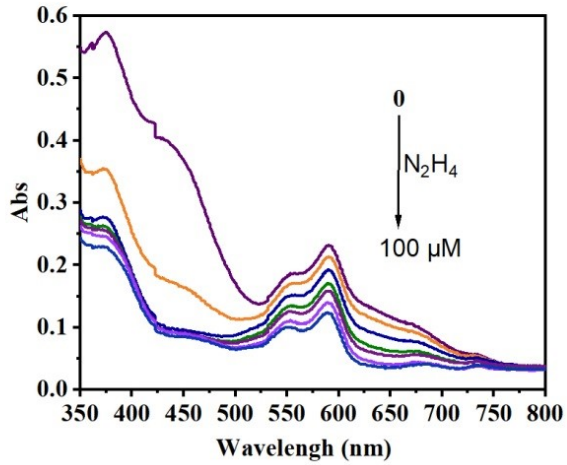


Fig. S1. Absorbance spectra of probe 1 (10 μM) with different concentrations of N_2H_4 (0–100 μM).

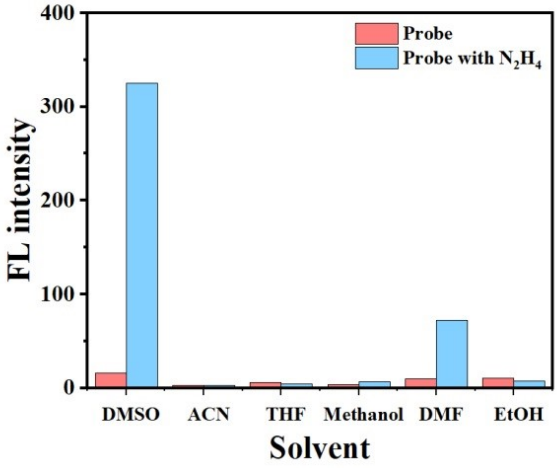


Fig. S2. Effect of different solvent on the fluorescence of probe 1.

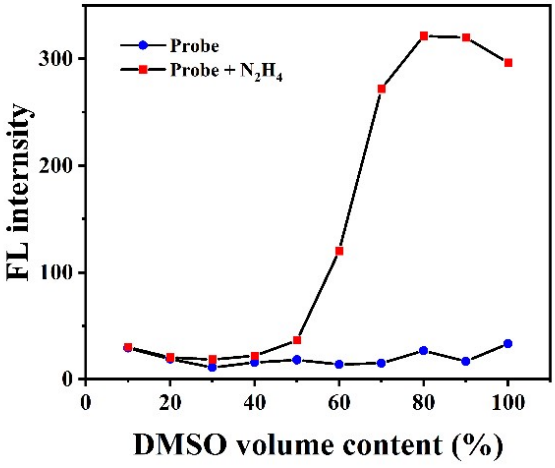


Fig. S3. Effect of solvent system (H_2O/DMSO) on the fluorescence of probe 1.

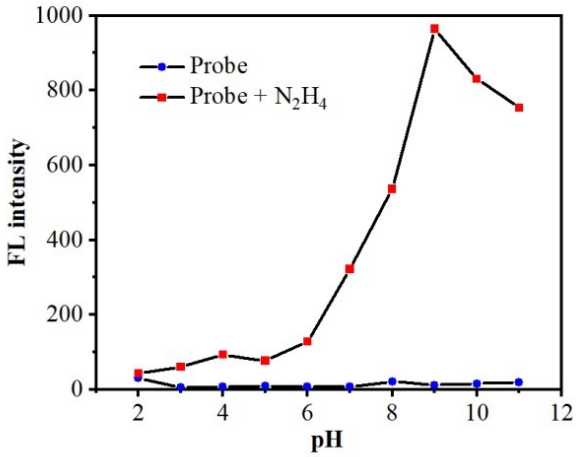


Fig. S4. The fluorescence intensity (I_{486}) of probe 1 (10 μM) changed with pH before and after adding N_2H_4 .

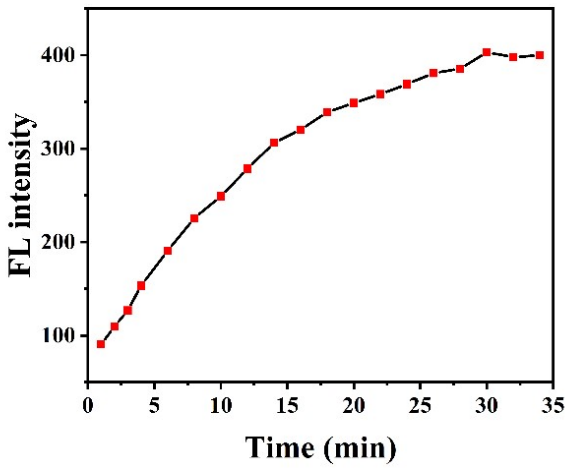


Fig. S5. Fluorescence intensity (I_{486}) of probe 1 (10 μM) changed with time before and after adding N_2H_4.

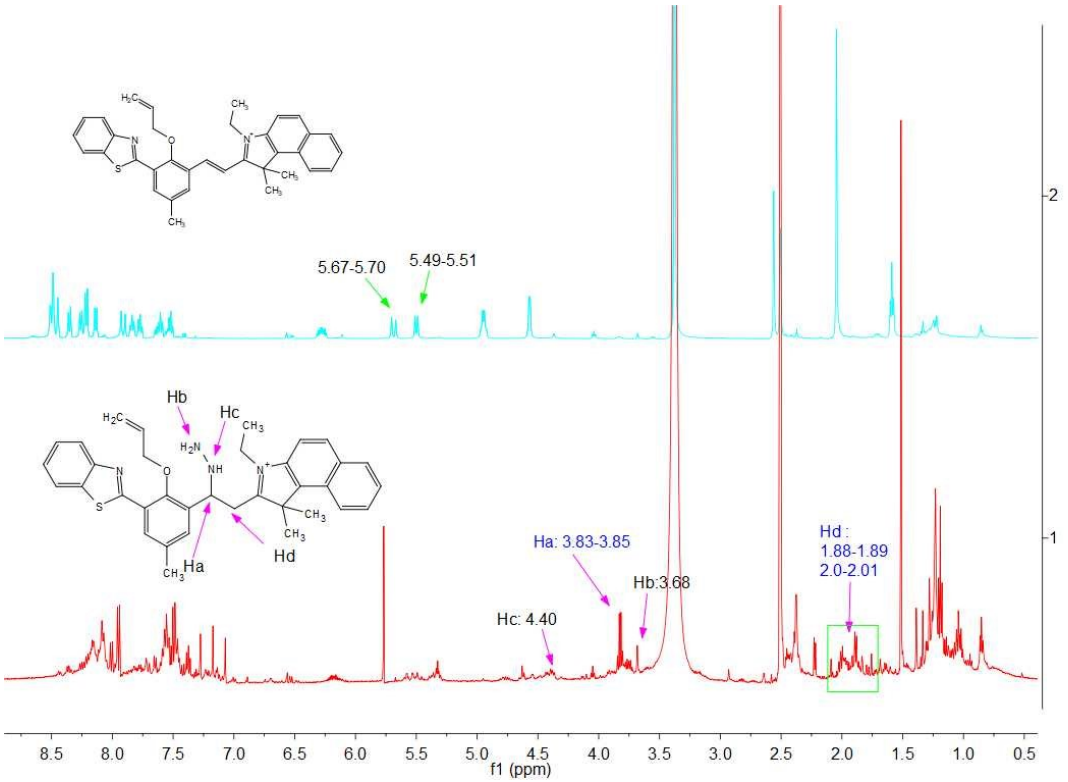


Fig. S6. ^{1}H NMR Spectra of probe 1 before and after reaction with N_2H_4.

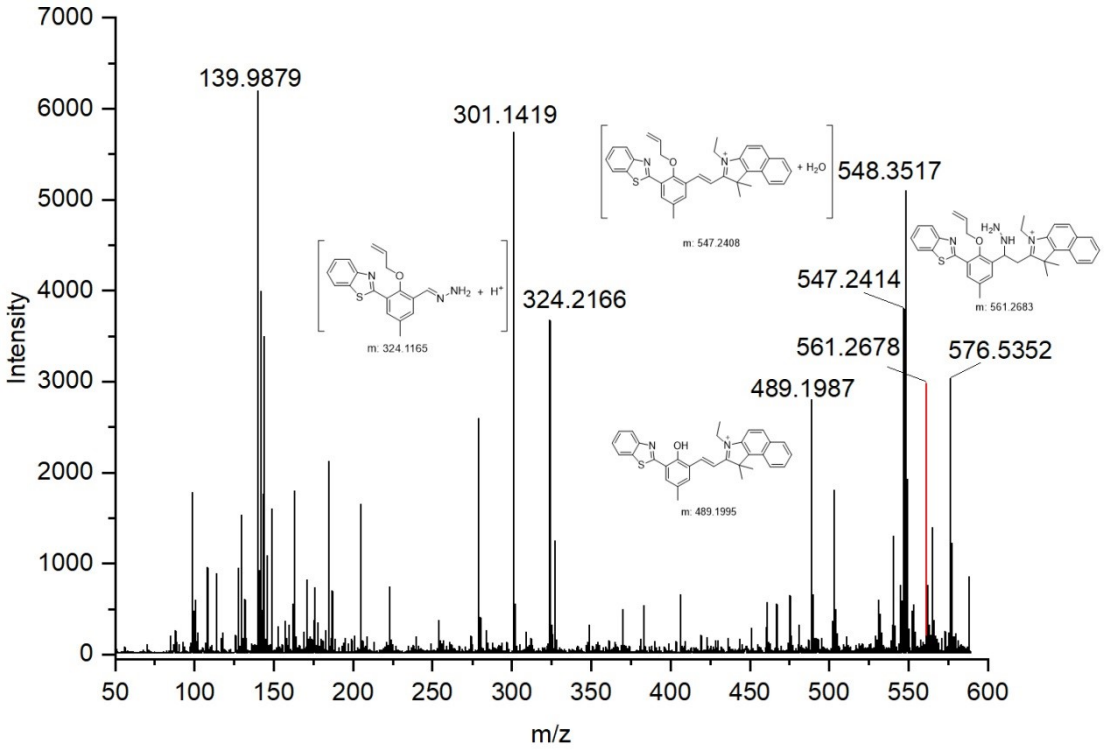


Fig. S7. HRMS of probe 1 treated with N_2H_4 in CH_3OH.

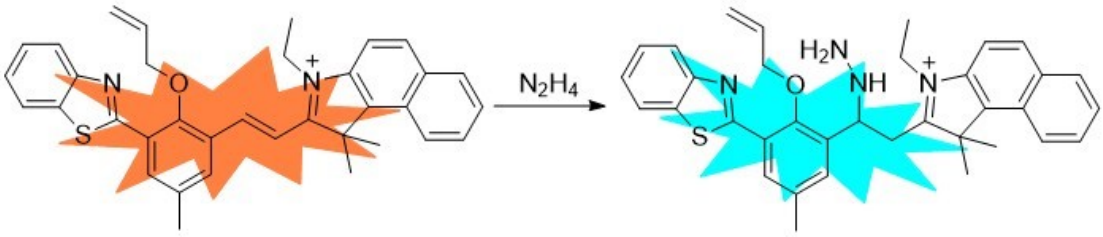


Fig. S8. A possible binding model of probe 1 to N_2H_4.

Table S4. Recovery of N_2H_4 in water samples achieved using probe 1.

Samples	Addition (μM)	Detection (μM)	Recovery (%)	RSD (%)
River water	2	2.01±0.08	100.50	4.00
	3	3.07±0.03	102.33	1.00
	10	9.87±0.24	98.70	2.40
Drinking water	2	1.96±0.1	98.00	5.00
	3	3.04±0.13	101.33	4.33
	10	10.46±0.63	104.60	6.30

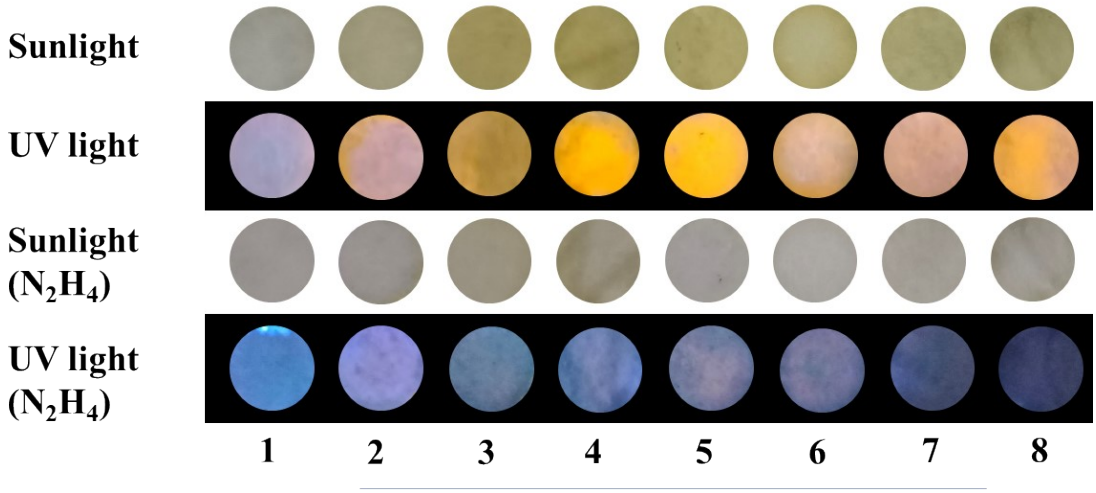


Fig. S9. Pictures of the test papers prepared with probe 1 after dropwise adding various beverages (200 μM). Analytes 1-8: Milk, coconut milk, Coca-Cola, Orange juice, Sprite, white wine, Chinese liquor and pond water.

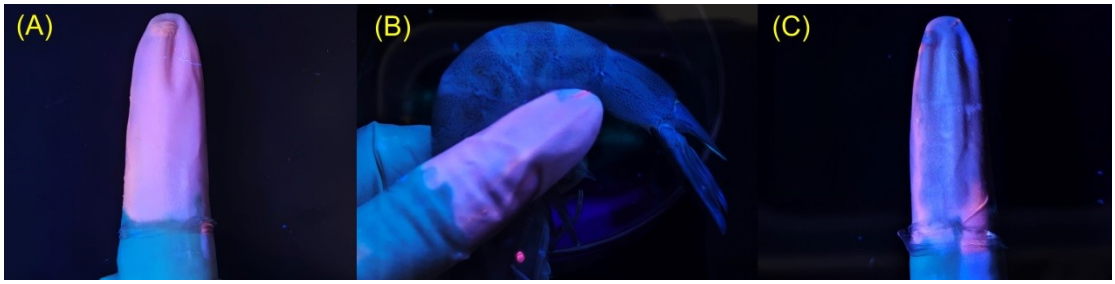


Fig. S10. The fluorescence color of the test glove loaded with hydrogel containing the probe changed before and after exposure to N_2H_4 contamination under 365 nm ultraviolet light.

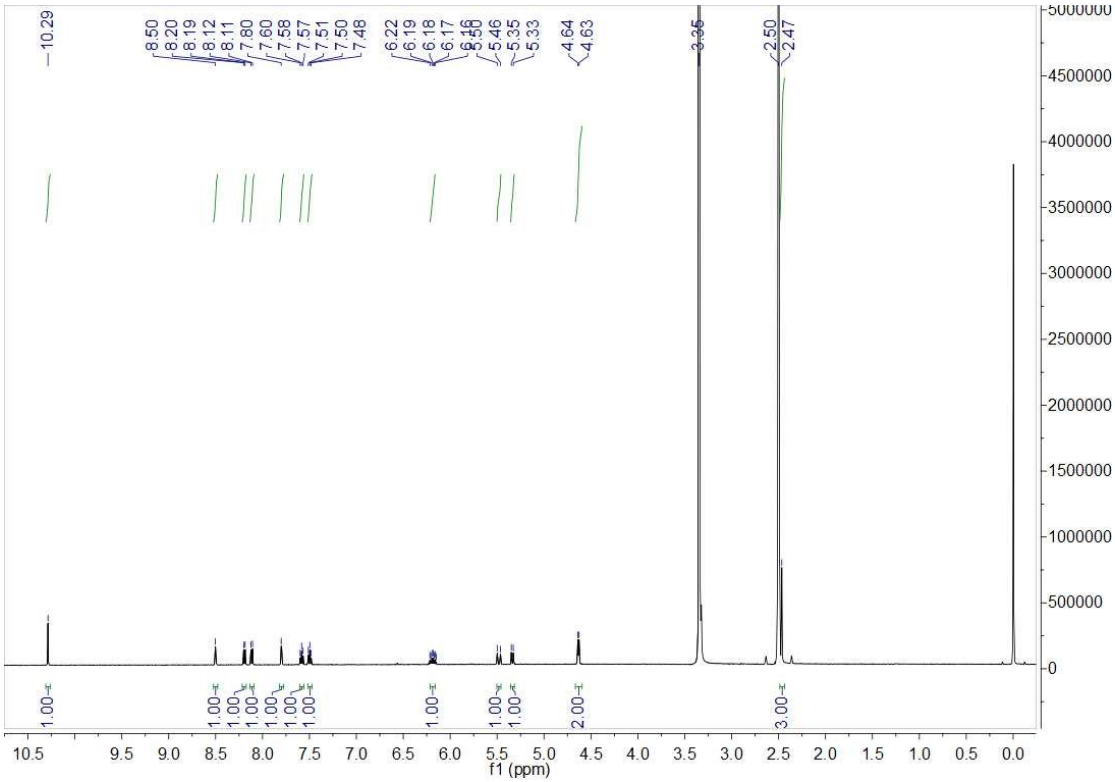


Figure S11. ^{1}H NMR of intermediate 3 in DMSO-d_6.

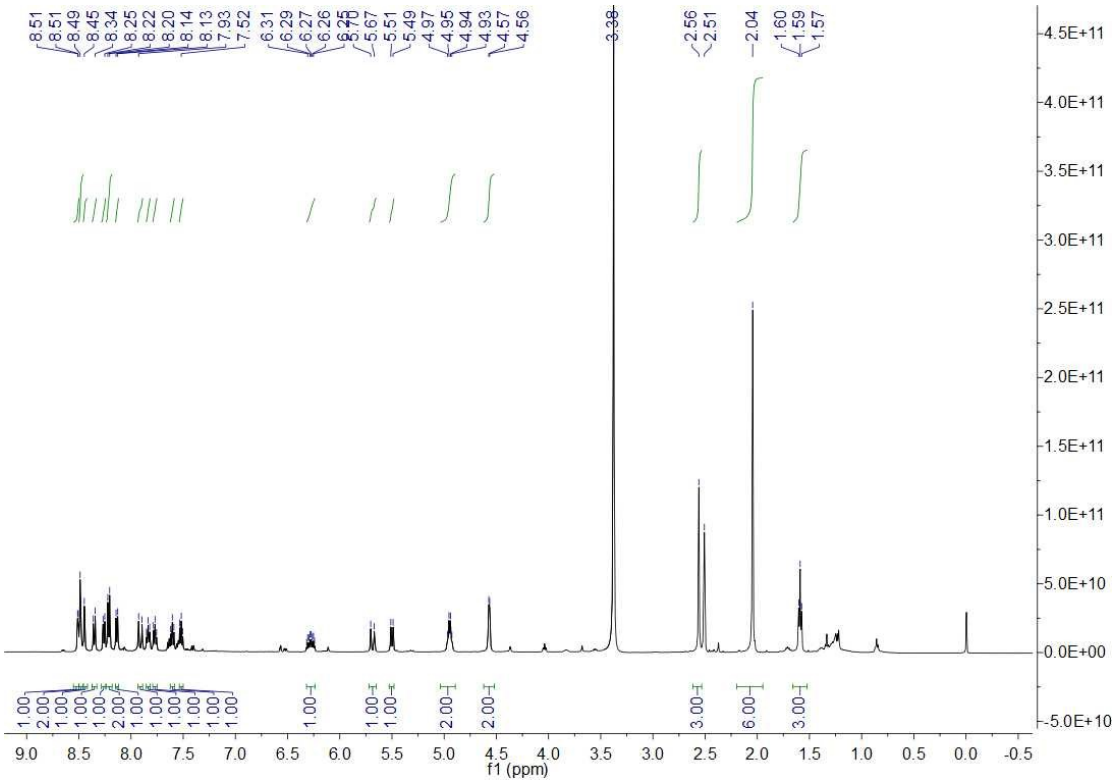


Figure S12. ^{1}H NMR of probe 1 in DMSO-d_6.

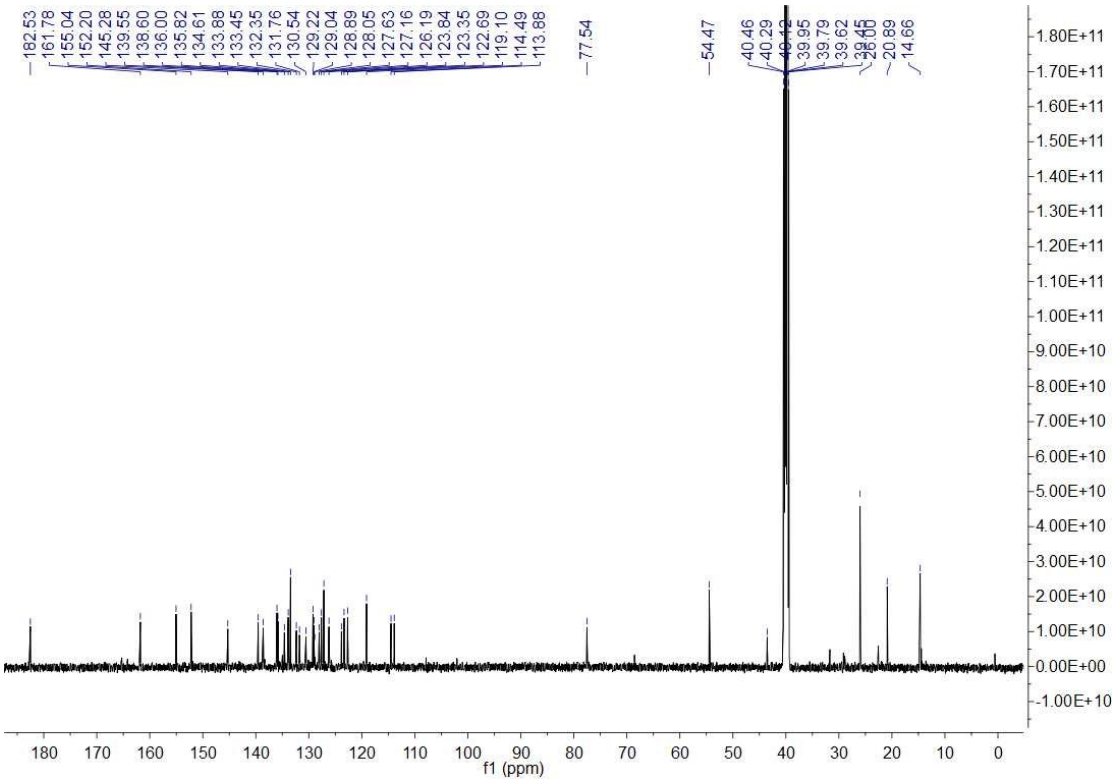


Figure S13. ^{13}C NMR of probe 1 in DMSO-d_6.

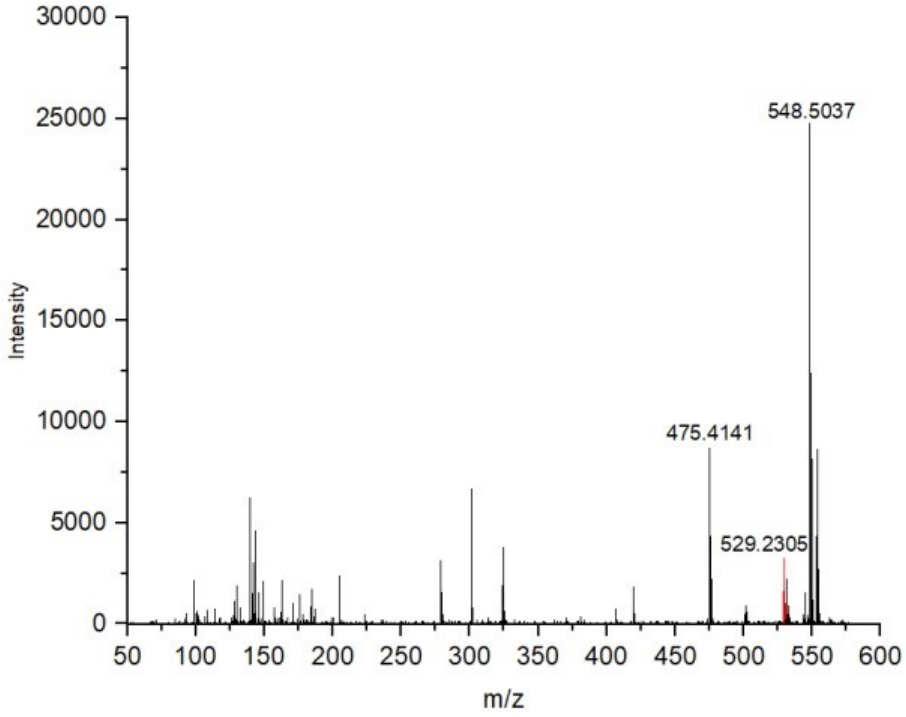


Figure S14. HRMS of probe 1 in CH_3OH.