Supporting information for

A coumarin-pyrazole-based probe for fluorescent detection of phosgene with high selectivity and sensitivity

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S1 Experimental section

S1.1. Materials and instrumentation

Solvents and starting materials for syntheses were purchased commercially and used as received. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. Fluorescence spectra were determined on a F97 fluorescence spectrophotometer made in Shanghai Lengguang Technology Co., Ltd. Time-resolved fluorescence was determined on a HORIBA Fluorolog-3 spectrophotometer. ESI-MS spectra were obtained on a Bruker Daltonics Esquire 6000 mass spectrometer. NMR spectra were recorded on a Bruker AV 400MHz spectrometer in MeCN-d_3 solution (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz). The X-ray diffraction measurement for **1** was performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo$K\alpha$ radiation (λ = 0.71073 Å) by using φ-ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program [1]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program [2].

*S1.2. Synthesis of Intermediates and probe **1***

The detailed synthesis of the probe **1** was given in Scheme 1. Compounds a and b were synthesized according to the literature [3,4]. To a solution of compound b (0.32 g, 1.3 mmol) in anhydrous ethanol (15 mL) was added hydrazine monohydrate (500 μL) [5]. The mixture was refluxed for 1h. After

cooling to room temperature, the reaction mixture was added to saturated brine and the precipitate was observed, which was then filtered, washed with water and dried to give compound as an off-white solid (probe **1**). Probe **1** was got by the recrystallization from the mixed solution of EtOH and H_2O. Yield: 258 mg (82%).^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.01 (dd, J = 7.8, 1.4 Hz, 1H), 7.59 – 7.49 (m, 1H), 7.34 – 7.23 (m, 2H), 6.75 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 153.50, 132.04, 125.03, 123.87, 116.60, 103.11. ESI-MS calculated for $C_{13}H_{10}N_2O_3$ $[M+H]^+$: 243.0725, found 243.0767. Crystal data for **1** ($C_{13}H_{10}N_2O_3$): crystal size: 0.18 × 0.16 × 0.15 mm, Monoclinic, space group C2/c. a = 34.36 (2) Å, b = 4.705 (3) Å, c = 14.141 (9) Å, α = 90°, β= 106.34(2)°, γ= 90°, Z = 8, T = 273 K, θ =2.47-24.60°, 14437 reflections measured, 1934 unique (Rint = 0.223). Final residual for 165 parameters and 1934 reflections with I>2σ(I): R_1 = 0.0769, wR_2 = 0.1730 and GOF = 0.978. (CCDC: 2181776).

S1.3. General UV-vis and fluorescence spectra measurements

The spectral analyses were performed in CH_3CN at room temperature. The concentration of the probe **1** for UV-vis and fluorescence measurement was 10 μM. Due to the high toxicity and volatility of phosgene, nonvolatile and less toxic triphosgene, a well-known precursor of phosgene, was employed to yield phosgene in situ in the presence of triethylamine (TEA) in solutions. All analytes were dissolved in CH_3CN. UV-vis and fluorescence spectrophotometric titrations were conducted directly in 2 mL cuvette by successive addition of corresponding chemical reagent using a microliter syringe. Upon addition of every aliquot, the solution was well mixed then the spectrum was measured.

S1.4. Phosgene sensing with filter paper

A piece of filter paper was cut to 1 × 3 cm and immersed in the **1** solution (1 mM in CH_3CN) for 3 seconds, then taken out and dried in air. In the test, the resultant paper strips embedded with the probe **1**

were deposited into 20 mL cylindrical vial. Different triphosgene concentrations (0-2 ppm) and other analyte (3 ppm) prepared according to literature procedures [6] were added to the vial followed by injection of two equivalents of TEA. After 2 minutes, the paper strips were taken out and photographed under a portable 365 nm UV light lamp.

[1] G. M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.

[2] G. M. Sheldrick, SHELX-97, Program for the Solution and the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[3] M. M. Abdou, 3-Acetyl-4-hydroxycoumarin: Synthesis, reactions and applications, Arabian J. Chem. 10 (2017) 3664-3675.

[4] A. Mustafa, O. H. Hsihmat, S. M. A. D. Zayed,A. A. Nawar, Experiments with substituted (3,2-c)-pyranyl-2,10-diones and benzopyranyl-(3,3-c)-pyran-2,8-diones, Tetrahedron.19 (1963) 1831-1839.

[5] D. Karia, A. Manvar, V. Trangadia, A. Shah, Synthesis and anti-HIV activity of some 3-acetyl/acetoacetyl- 4-hydroxy benzopyran-2-ones: An in vitro evalu. OCAIJ, 3 (2007) 170-175.

[6] T. Kim, D. Kim, J. Bouffard, Y. Kim, Rapid, specific, and ultrasensitive fluorogenic sensing of phosgene through an enhanced PET mechanism, Sens. Actuators, B, 283 (2019) 458-462.

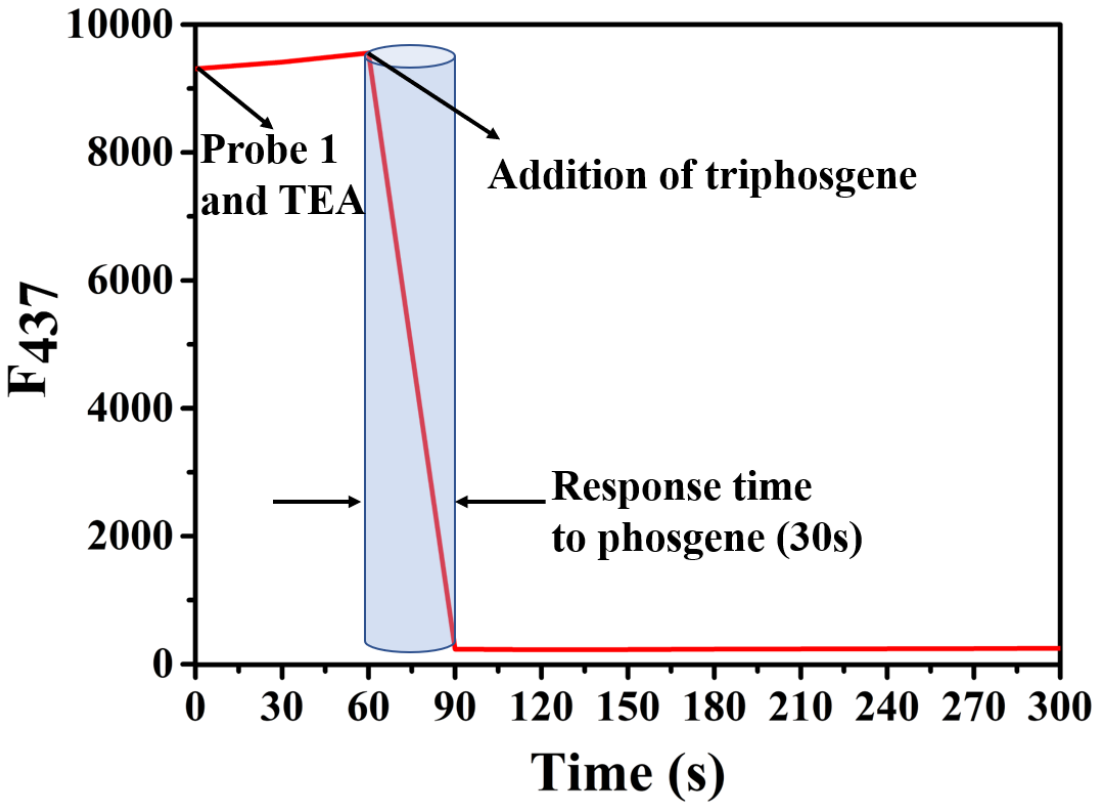


Fig. S1 Time course for the fluorescence response of 10 μM **1** upon the addition of 10 eq. phosgene in CH3CN (containing 0.5 mM TEA); (Eex= 350 nm).

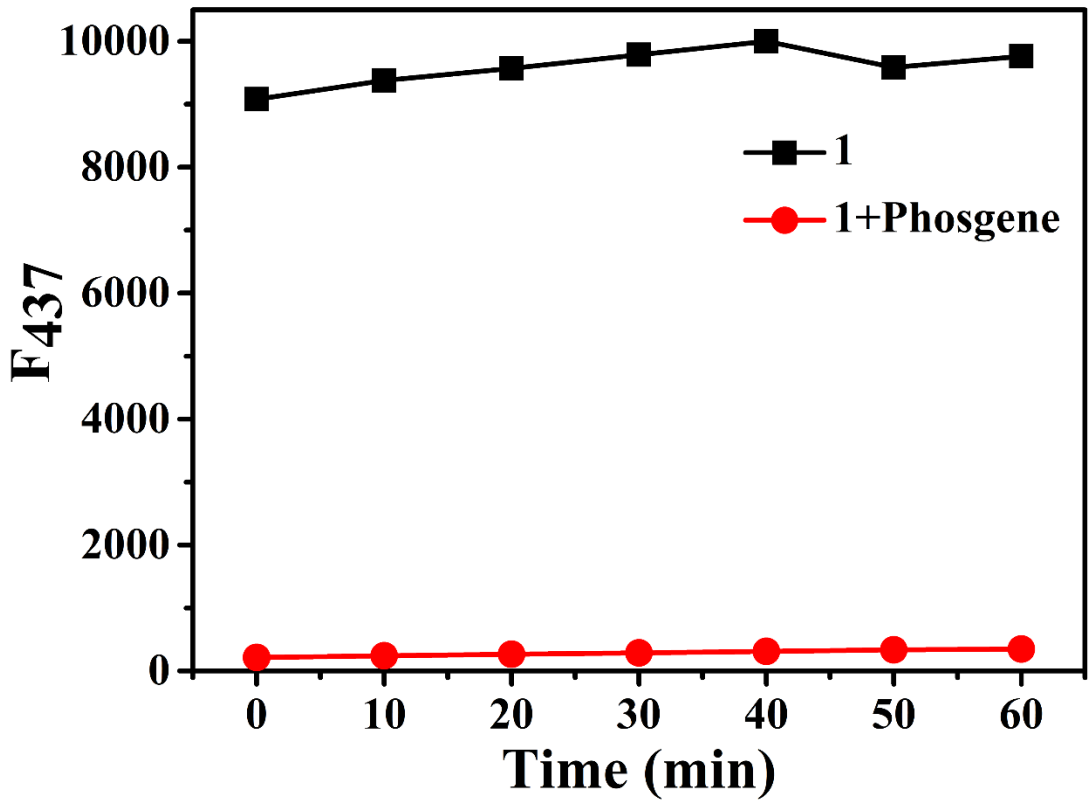


Fig. S2 Photostability of probe **1** (10 μM) with and without phosgene (100 μM) in CH_3CN; (Eex= 350 nm).

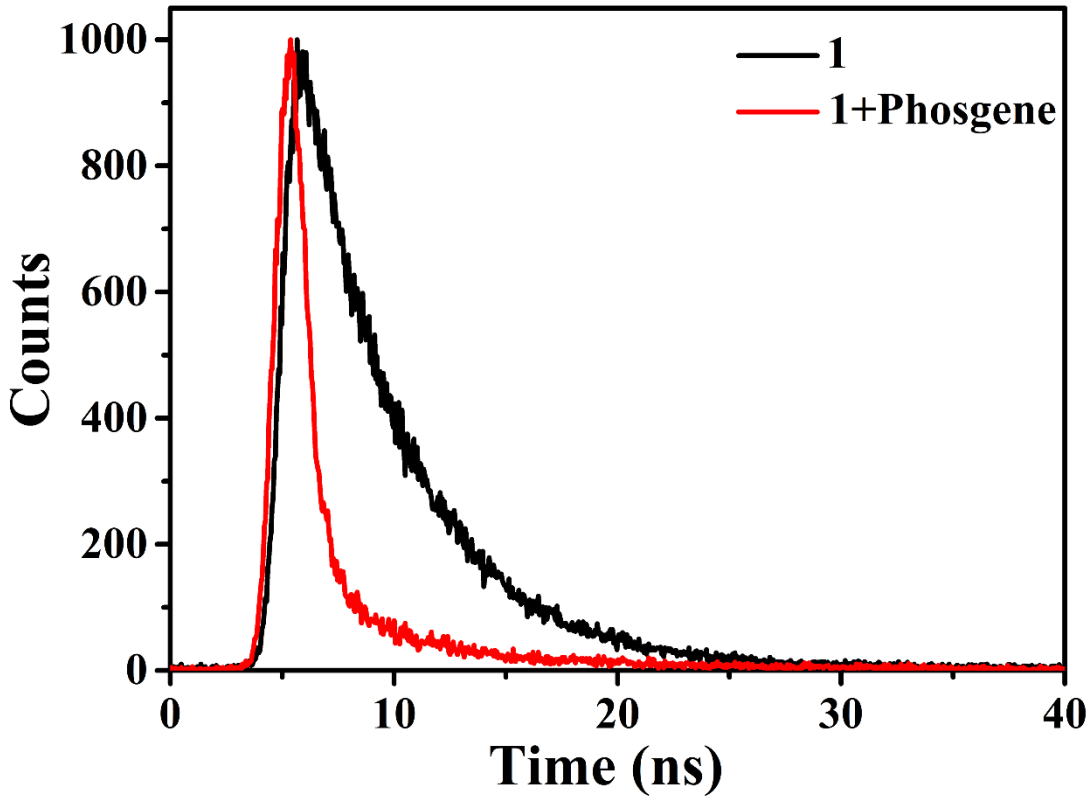


Fig. S3 Time resolved fluorescence spectra of **1** with and without phosgene in CH_3CN solution. Excitation wavelength was 350 nm.

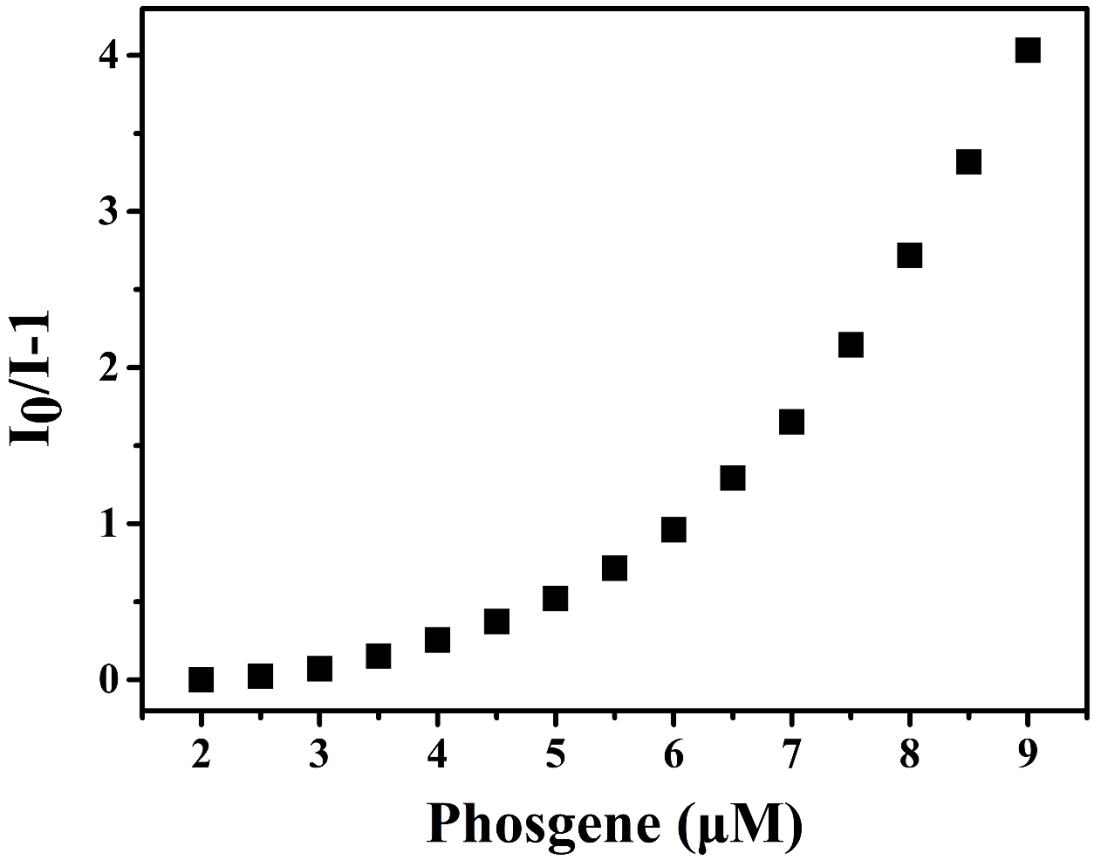


Fig. S4. Stern–Volmer plots for the quenching of 1 fluorescence by phosgene.

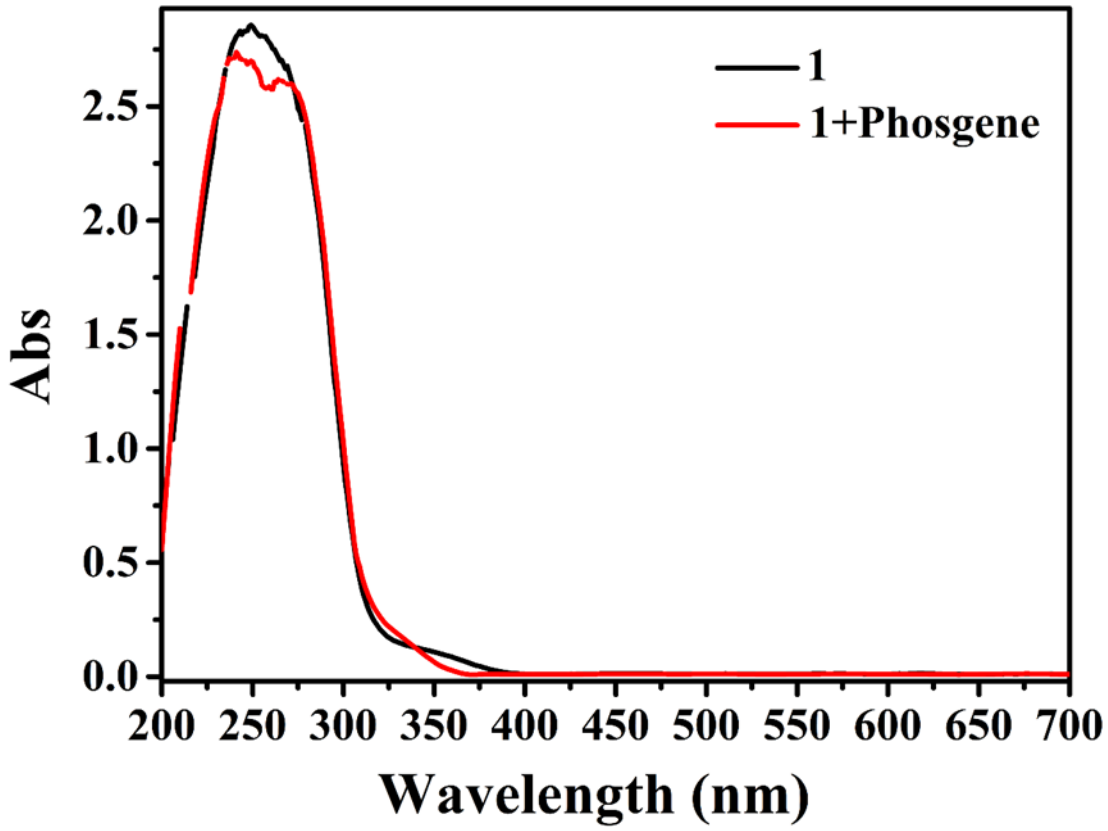


Fig. S5 Absorption spectra of **1** with and without phosgene in CH_3CN.

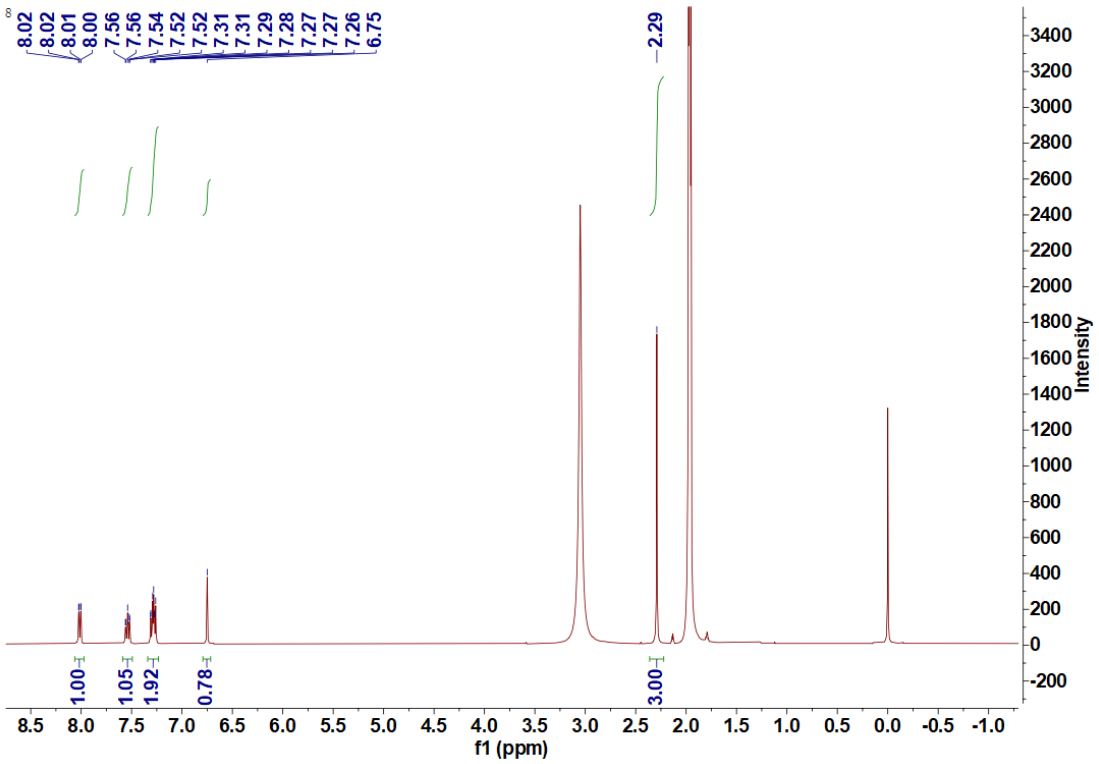


Fig. S6 ^{1}H NMR spectrum of **1** in MeCN-d_3.

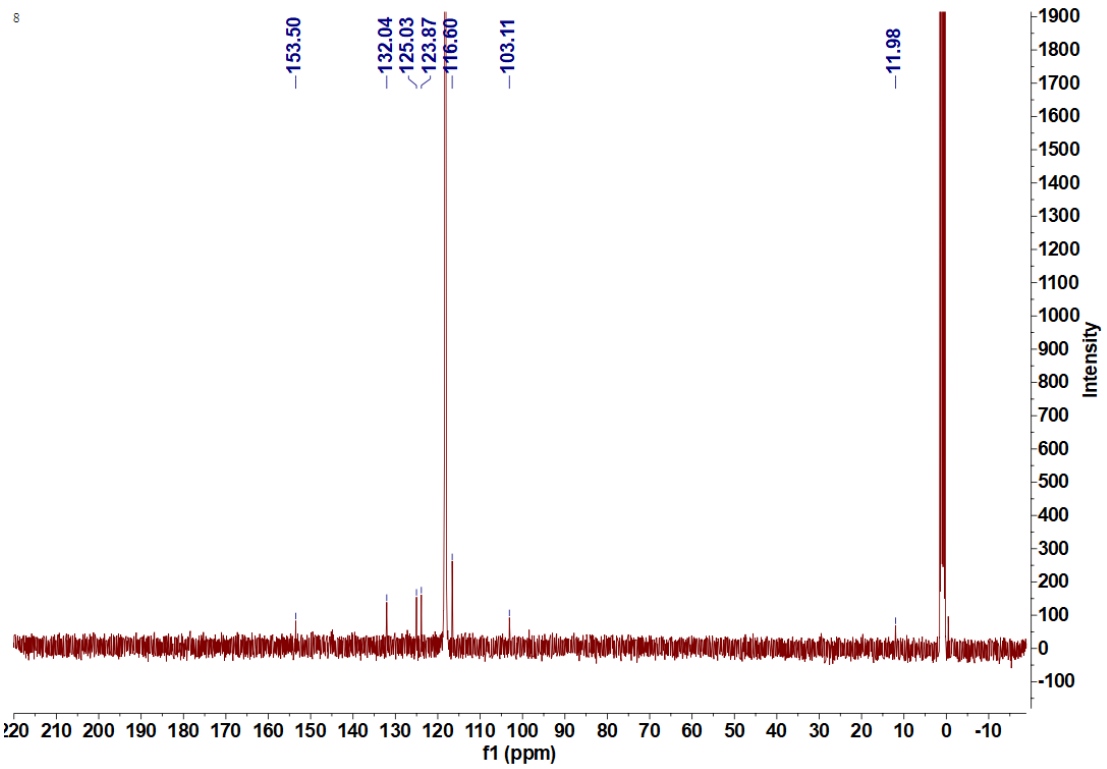


Fig. S7 ^{13}C NMR spectrum of **1** in MeCN-d_3.

Table S1 Comparasion of some reported fluorescent probes for phosgene.

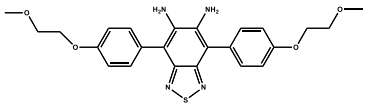
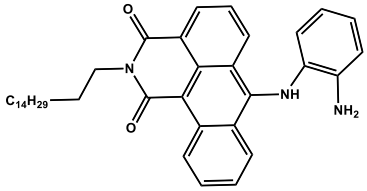
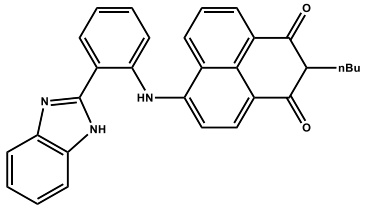
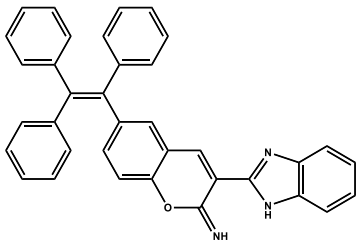
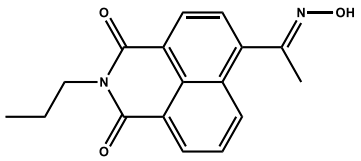
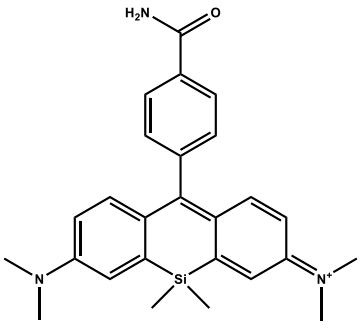
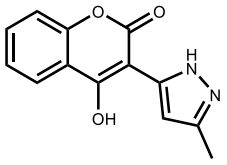
Ref	Structure	LOD (solution/gas)	Response time (solution/gas)	Stokes shift
19		20 nM/10 ppm	20 min/5 min	128 nm
20		72 nM/1 ppm	2 min/2 min	60 nm
21		6.7 nM/135.87 ppm	3.33 min /1 min	65 nm
22		360 nM/0.27 ppm	0.1 min/2 min	130 nm
23		6.3 nM/1 ppm	15 min/-	81 nm
24		8.9 nM/135.87 ppm	4 min/5 min	26 nm
This work		4.78 nM/0.014 ppm	0.5 min /2 min	87 nm

Table S2. Lifetimes (T1, T2) and relative amplitudes (B1, B2) of **1** (10 μM) with and without phosgene in CH_3CN solution.

Entry	T1(ns)	B1(Rel.Amp.%)	T2(ns)	B2(Rel.Amp.%)	T(ns)
1	4.63	100.00	/	/	4.63
1+phosgene	0.96	93.03	8.01	6.97	3.67