

## Supporting Information

*for*

### **Seven-membered Heterocycle Containing Coumarin- Based Probe for Selective Detection of Chemical Warfare Agent Phosgene in Solution and Gas Phase**

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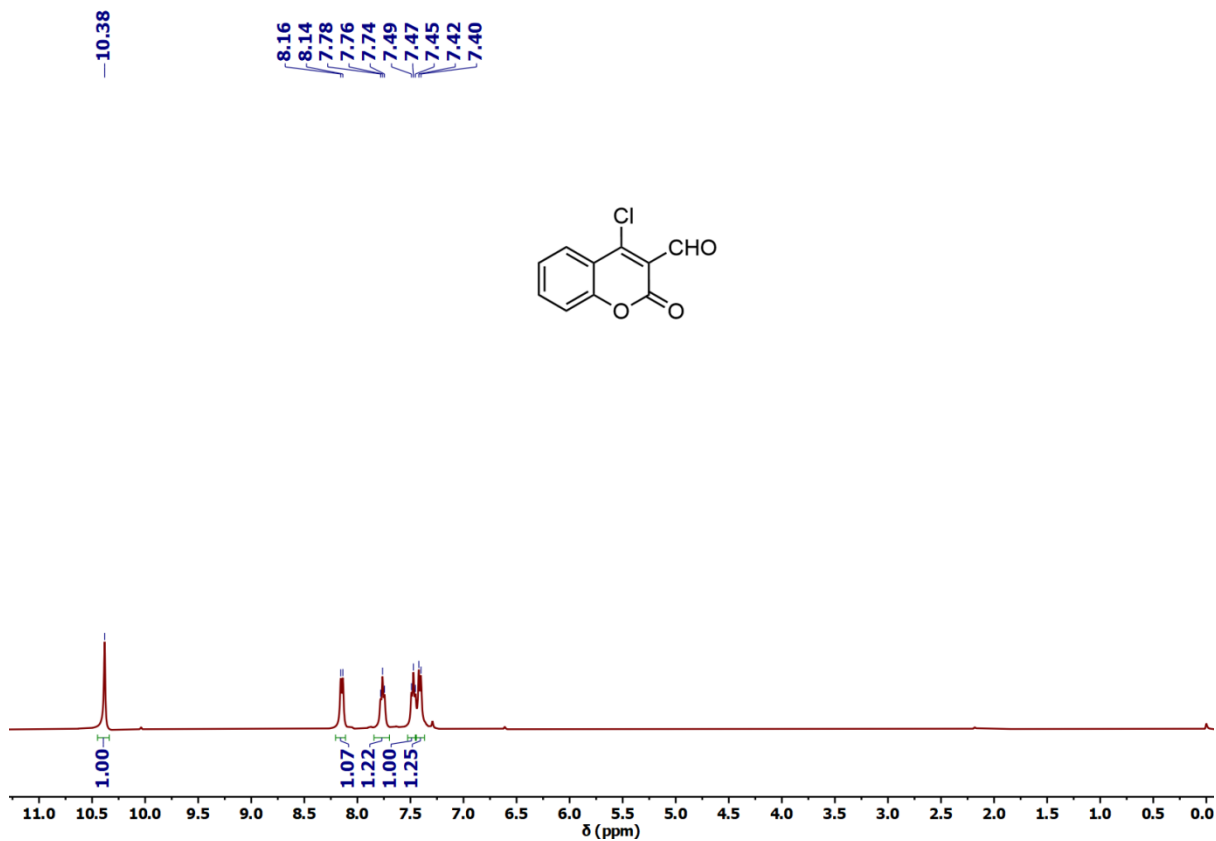


Figure S1:  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$ .

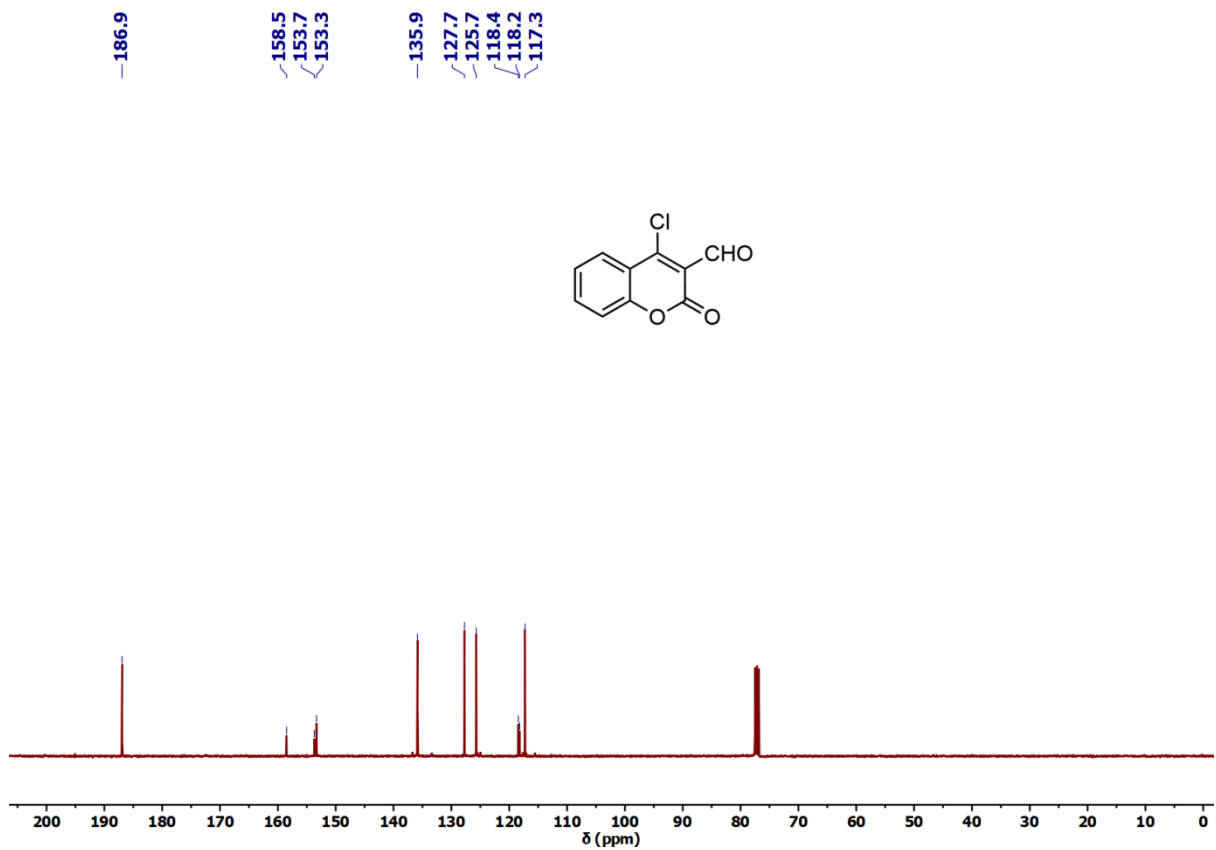


Figure S2:  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{CDCl}_3$ .

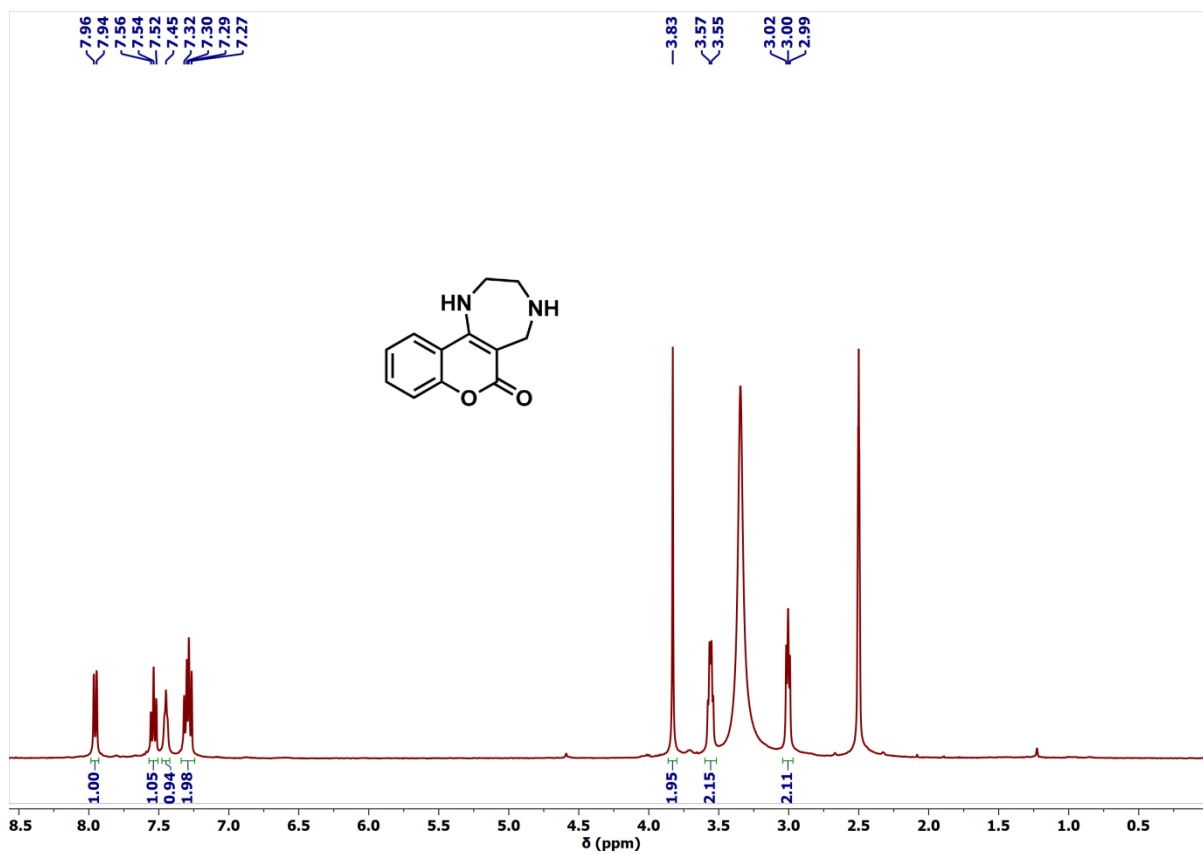


Figure S3:  $^1\text{H}$  NMR spectrum of **2** in  $\text{DMSO-}d_6$ .

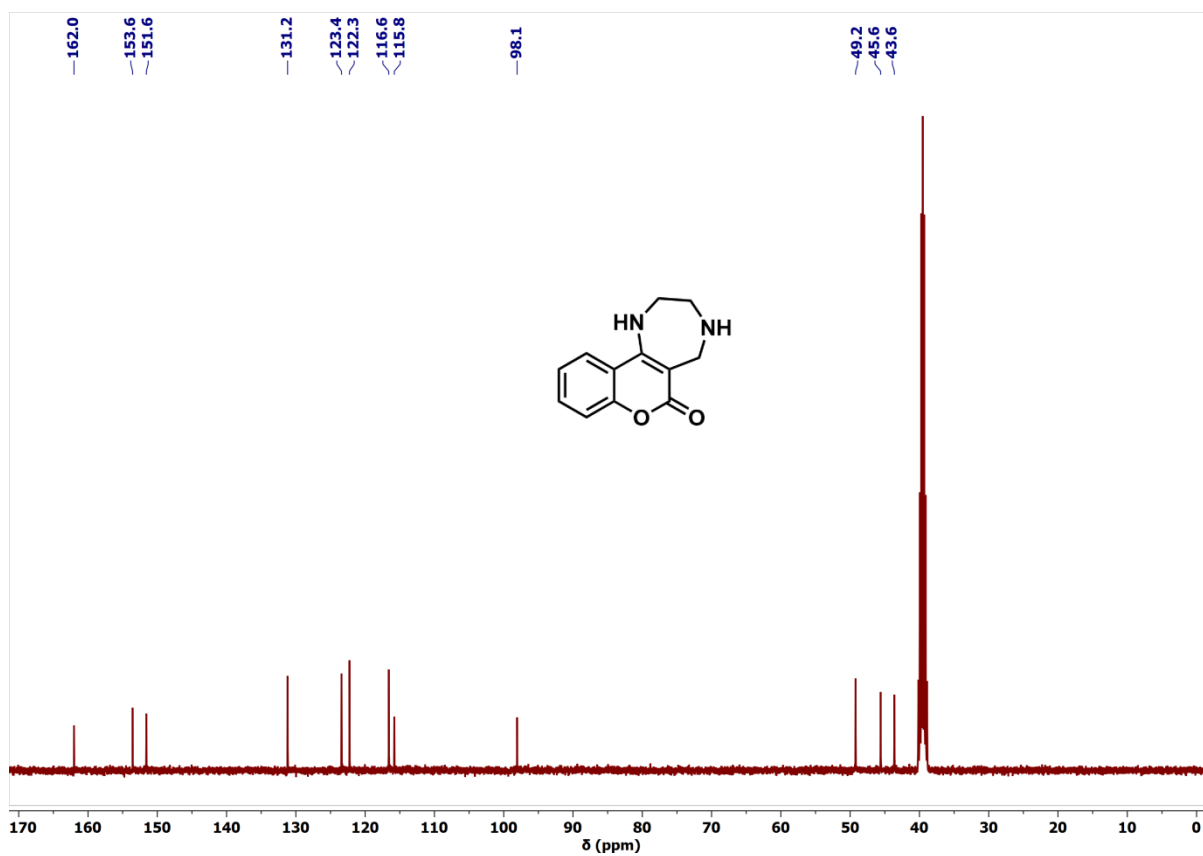


Figure S4:  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{DMSO-}d_6$ .

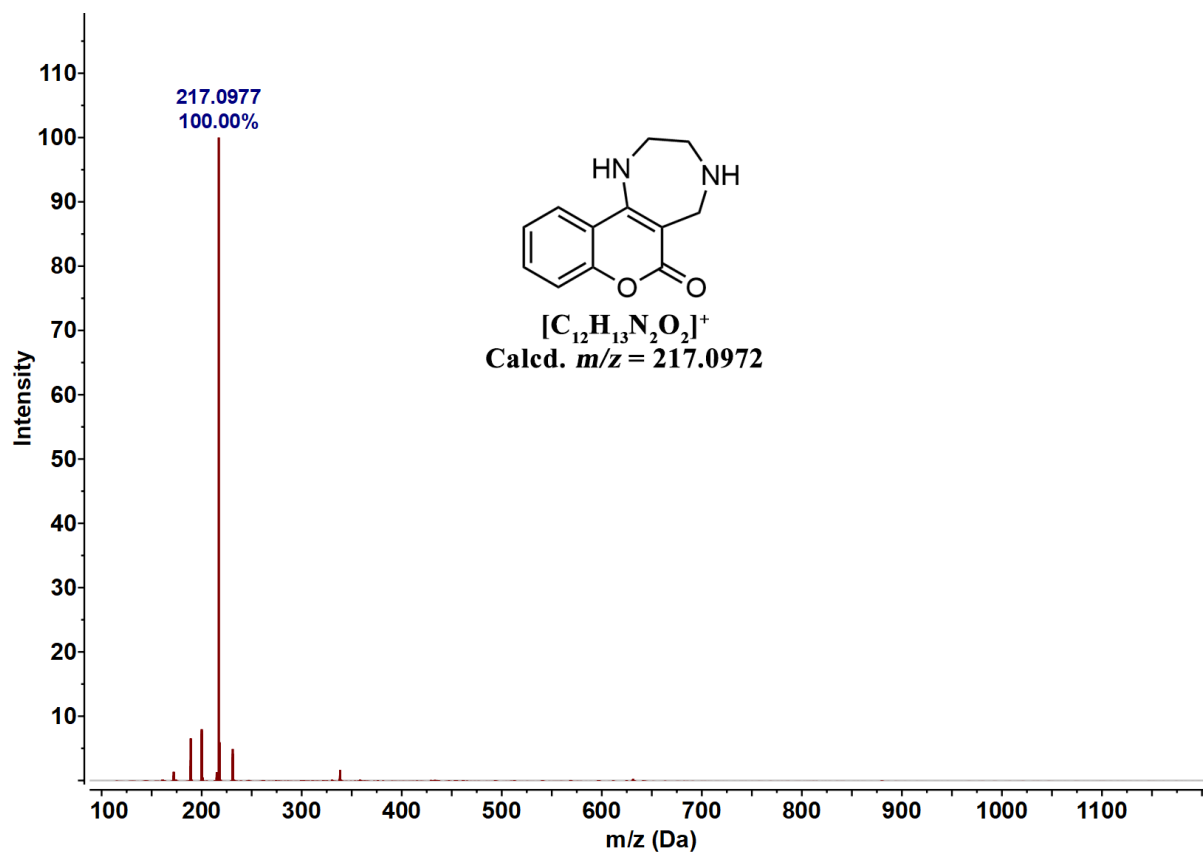


Figure S5: ESI-HRMS spectrum of **2** in CH<sub>3</sub>CN.

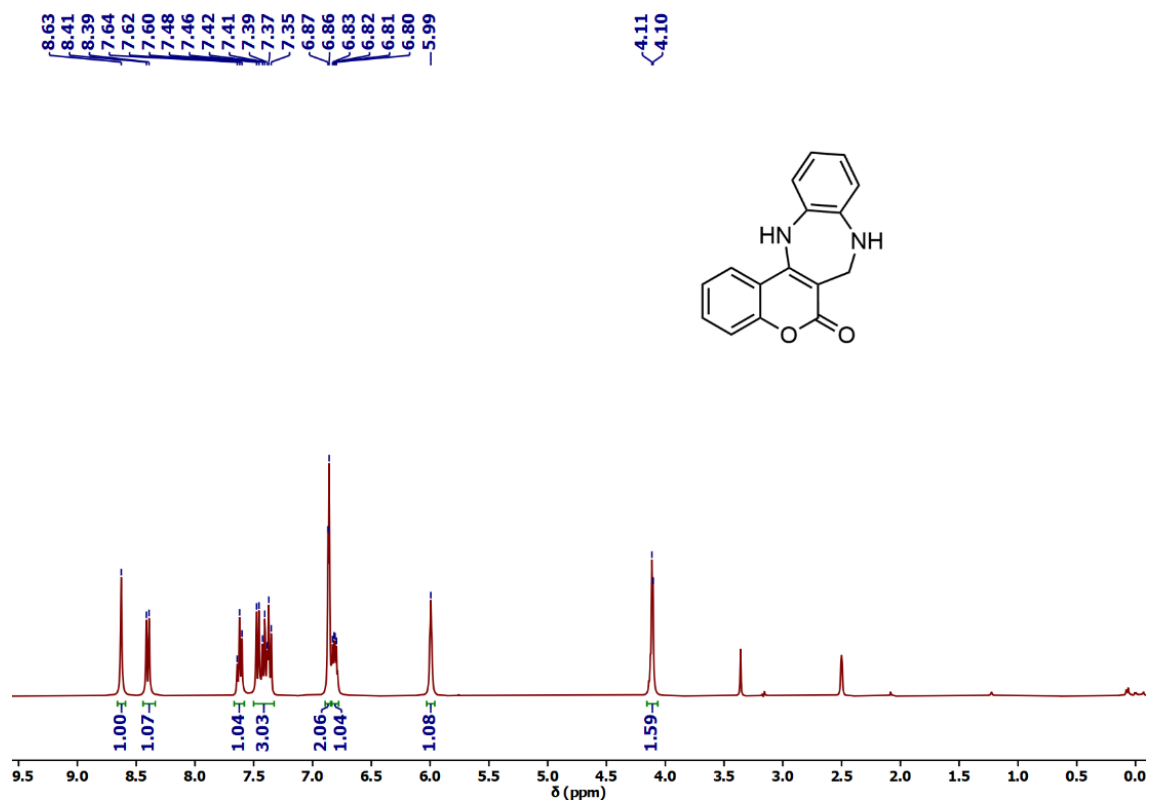
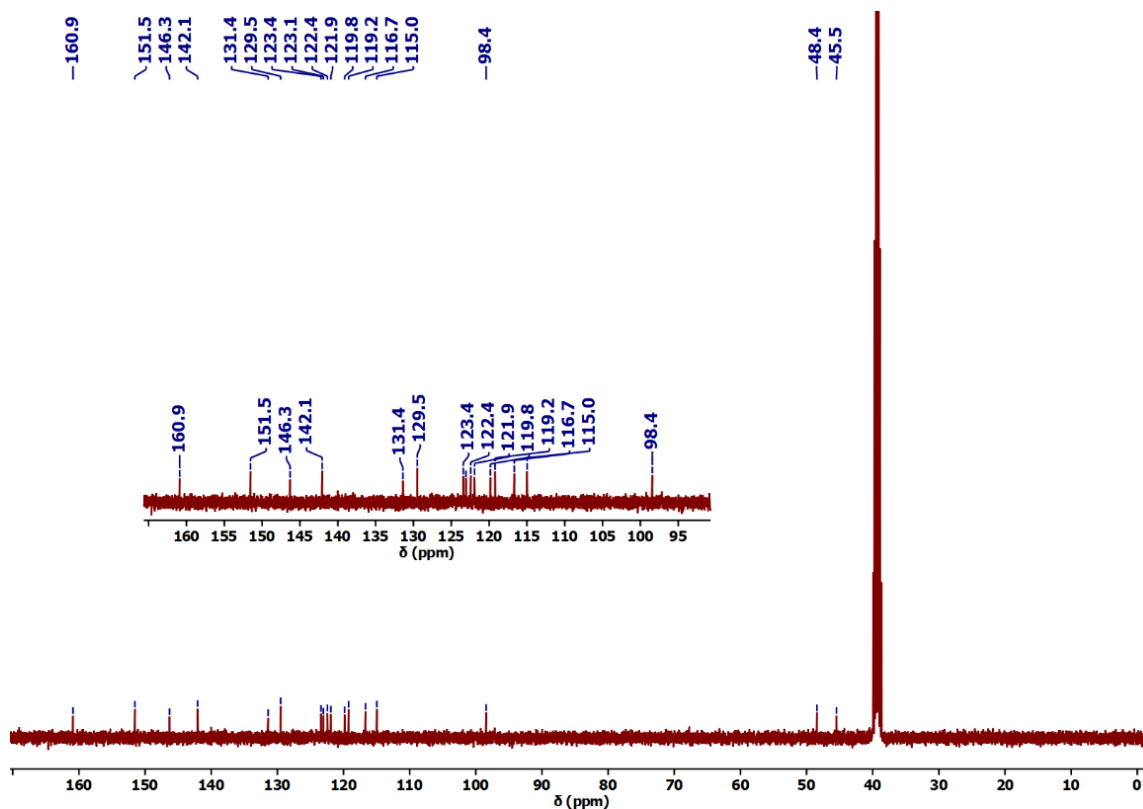
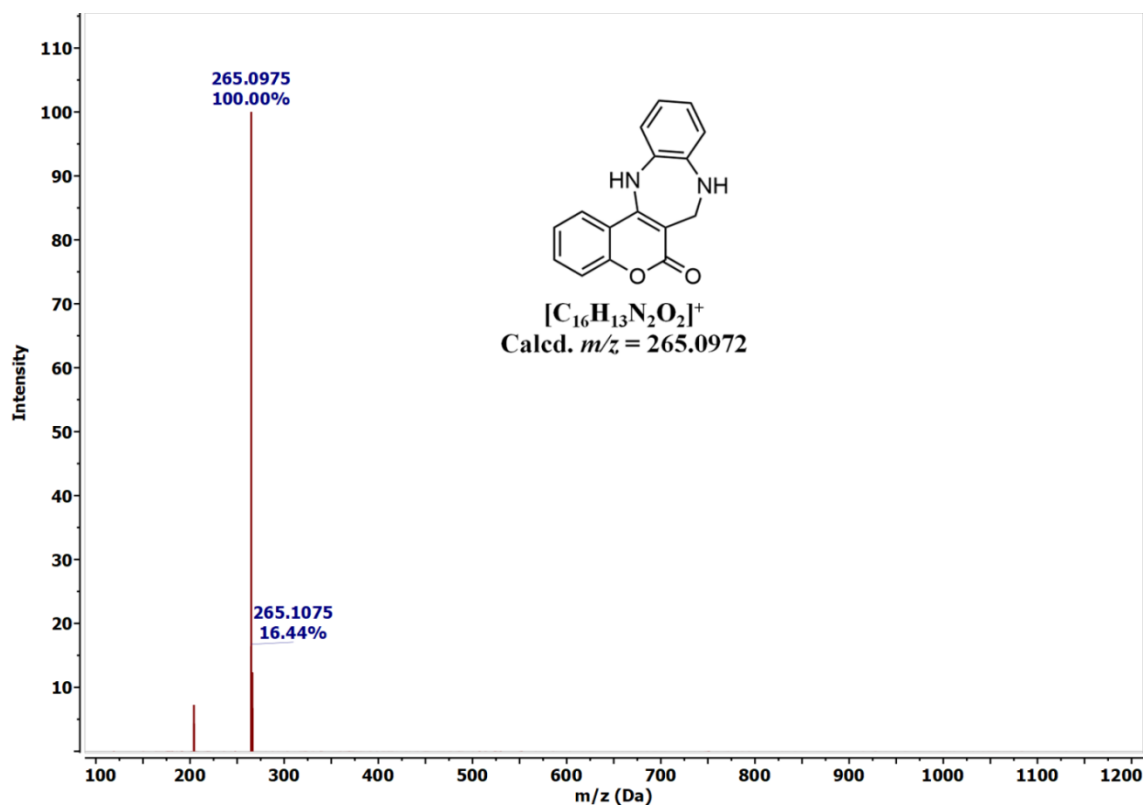


Figure S6: <sup>1</sup>H NMR spectrum of **3** in CDCl<sub>3</sub>.



FigureS7:  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .



FigureS8: ESI-HRMS spectrum of **3** in  $\text{CH}_3\text{CN}$ .

**Table S1:** Crystal data and structure refinement for **3**.

CCDC No.	2434999	
Empirical formula	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	
Formula weight	296.32	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 7.5973(6) Å	<i>α</i> = 71.346(8)°.
	<i>b</i> = 8.5961(8) Å	<i>β</i> = 88.560(7)°.
	<i>c</i> = 11.7834(11) Å	<i>γ</i> = 83.085(7)°.
Volume	723.74(12) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.360 Mg/m <sup>3</sup>	
Absorption coefficient	0.095 mm <sup>-1</sup>	
F(000)	312	
Crystal size	0.230 x 0.120 x 0.070 mm <sup>3</sup>	
Theta range for data collection	3.238 to 26.371°.	
Index ranges	-9 ≤ <i>h</i> ≤ 9, -10 ≤ <i>k</i> ≤ 7, -14 ≤ <i>l</i> ≤ 14	
Reflections collected	4588	
Independent reflections	2951 [ <i>R</i> ( <i>int</i> ) = 0.0190]	
Completeness to theta = 26.000°	99.3 %	
Data / restraints / parameters	2951 / 0 / 212	
Goodness-of-fit on F <sup>2</sup>	1.026	
Final R indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0490, <i>wR</i> 2 = 0.1130	
R indices (all data) <sup>a</sup>	<i>R</i> 1 = 0.0693, <i>wR</i> 2 = 0.1238	

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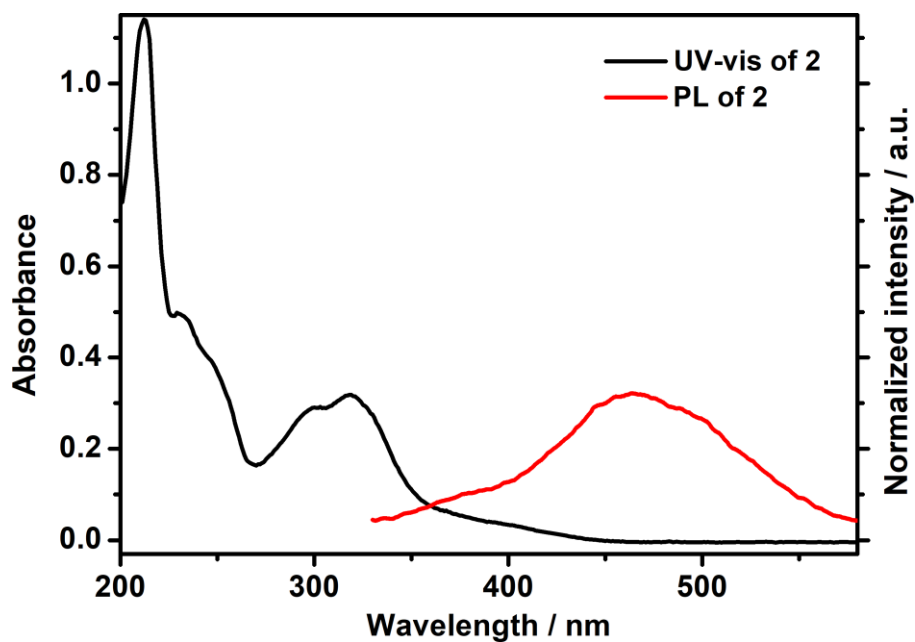
<sup>a</sup> $R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ;  $wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right\}^{1/2}$ .

**Table S2:** Selected bond lengths [Å] and angles [°] for **3**.

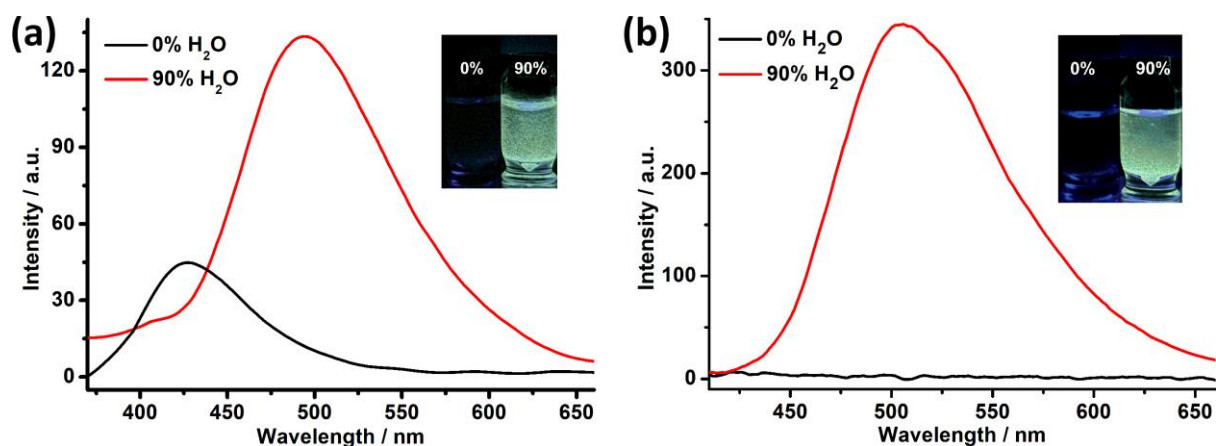
<b>Bond Length (Å)</b>			
C(1)-O(1)	1.2203(19)	C(1)-O(2)	1.363(2)
C(1)-C(9)	1.427(2)	C(2)-O(2)	1.373(2)
C(2)-C(3)	1.385(2)	C(2)-C(7)	1.394(2)
C(3)-C(4)	1.372(3)	C(3)-H(3)	0.9300
C(4)-C(5)	1.387(3)	C(4)-H(4)	0.9300
C(5)-C(6)	1.375(2)	C(5)-H(5)	0.9300
C(6)-C(7)	1.400(2)	C(6)-H(6)	0.9300
C(7)-C(8)	1.464(2)	C(8)-N(2)	1.3636(19)
C(8)-C(9)	1.375(2)	C(9)-C(10)	1.498(2)
C(10)-N(1)	1.472(2)	C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700	C(11)-C(16)	1.391(2)
C(11)-C(12)	1.394(2)	C(11)-N(2)	1.415(2)
C(12)-C(13)	1.372(2)	C(12)-H(12)	0.9300
C(13)-C(14)	1.378(3)	C(13)-H(13)	0.9300
C(14)-C(15)	1.376(3)	C(14)-H(14)	0.9300
C(15)-C(16)	1.392(2)	C(15)-H(15)	0.9300
C(16)-N(1)	1.412(2)	C(17)-O(3)	1.384(3)
C(17)-H(17A)	0.9600	C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600	N(1)-H(1N)	0.89(2)
N(2)-H(2N)	0.902(19)	O(3)-H(3O)	1.01(3)

<b>Bond Angles (°)</b>			
O(1)-C(1)-O(2)	115.45(15)	O(1)-C(1)-C(9)	124.62(17)
O(2)-C(1)-C(9)	119.92(14)	O(2)-C(2)-C(3)	115.93(14)
O(2)-C(2)-C(7)	121.58(15)	C(3)-C(2)-C(7)	122.49(16)
C(4)-C(3)-C(2)	119.05(16)	C(3)-C(4)-C(5)	120.11(17)
C(6)-C(5)-C(4)	120.34(17)	C(5)-C(6)-C(7)	121.16(16)
C(2)-C(7)-C(6)	116.78(15)	C(2)-C(7)-C(8)	118.27(14)
C(6)-C(7)-C(8)	124.93(14)	N(2)-C(8)-C(9)	125.68(15)
N(2)-C(8)-C(7)	116.00(13)	C(9)-C(8)-C(7)	118.32(14)
C(8)-C(9)-C(1)	120.64(15)	C(8)-C(9)-C(10)	124.94(14)

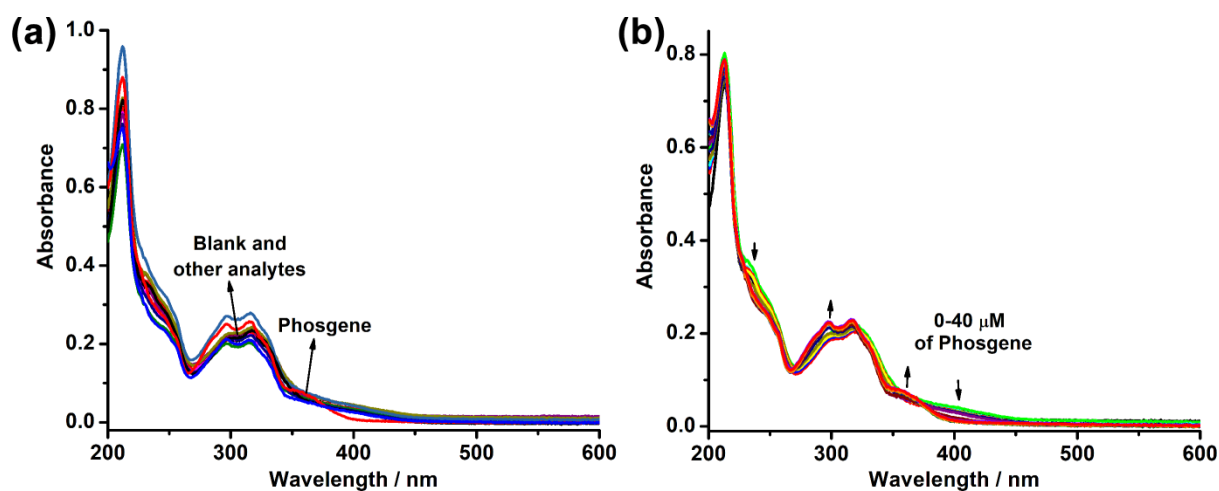
C(1)-C(9)-C(10)	114.42(14)	N(1)-C(10)-C(9)	112.66(14)
C(16)-C(11)-C(12)	119.32(15)	C(16)-C(11)-N(2)	123.49(14)
C(12)-C(11)-N(2)	117.05(14)	C(13)-C(12)-C(11)	120.62(17)
C(12)-C(13)-C(14)	120.24(17)	C(15)-C(14)-C(13)	119.80(17)
C(14)-C(15)-C(16)	120.84(17)	C(11)-C(16)-C(15)	119.18(15)
C(11)-C(16)-N(1)	120.23(14)	C(15)-C(16)-N(1)	120.56(15)
C(16)-N(1)-C(10)	114.09(14)	C(16)-N(1)-H(1N)	109.4(12)
C(10)-N(1)-H(1N)	108.5(12)	C(8)-N(2)-C(11)	131.71(13)
C(8)-N(2)-H(2N)	116.2(12)	C(11)-N(2)-H(2N)	111.9(12)
C(1)-O(2)-C(2)	120.83(12)	C(17)-O(3)-H(3O)	108.1(17)



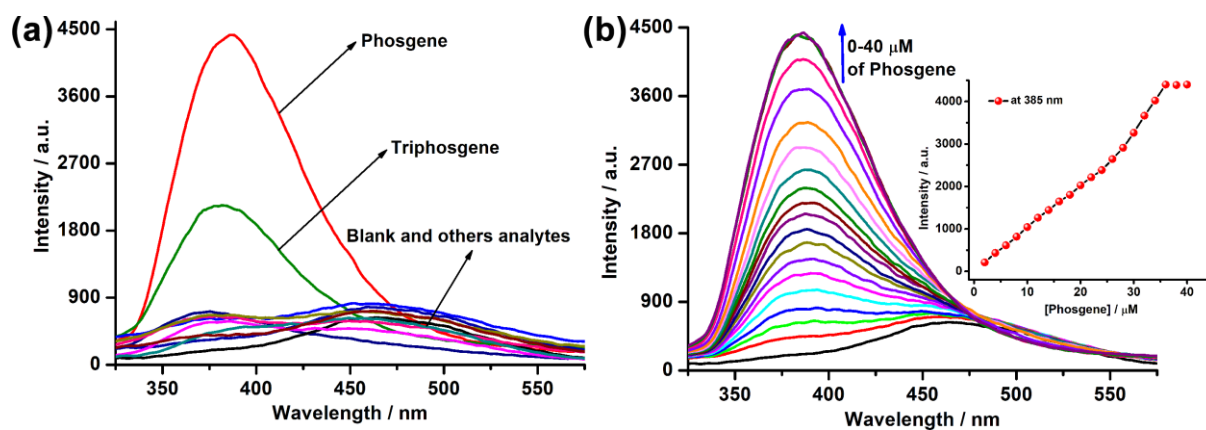
**Figure S9:** Normalized UV-vis and PL spectra of **2** in CH<sub>3</sub>CN (20 μM) ( $\lambda_{\text{ex}} = 300$  nm,  $\lambda_{\text{em}} = 465$  nm).



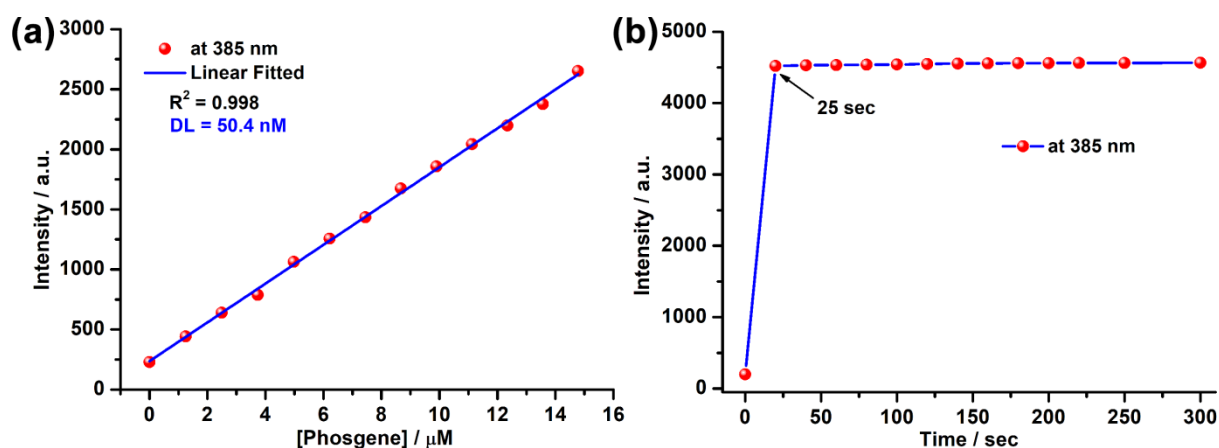
**Figure S10:** PL spectra of **3** in (a) THF-water mixture 0% and 90% H<sub>2</sub>O, (b) methanol-water mixture (0% and 90% H<sub>2</sub>O) ( $\lambda_{\text{ex}} = 350$  nm).



**Figure S11:** (a) UV-vis selectivity of **2** (20  $\mu\text{M}$ ) with phosgene (40  $\mu\text{M}$ ) and other analytes in dry CH<sub>3</sub>CN. (b) UV-vis titration of **2** (20  $\mu\text{M}$ ) with phosgene (0-40  $\mu\text{M}$ ) in dry CH<sub>3</sub>CN.



**Figure S12:** (a) PL selectivity of **2** (20 μM,  $\lambda_{\text{ex}} = 300$  nm) with phosgene (40 μM) and other analytes in dry CH<sub>3</sub>CN. (b) PL titration of **2** (20 μM,  $\lambda_{\text{ex}} = 300$  nm) with phosgene (0-40 μM) in dry CH<sub>3</sub>CN ( $\lambda_{\text{ex}} = 300$  nm) (*inset*: plot of intensity vs phosgene concentration).



**Figure S13:** (a) Calibration plot of PL intensity ( $\lambda_{\text{ex}} = 300$  nm) vs concentration of phosgene for the calculation of LOD. (b) PL response of probe **2** (20 μM) to phosgene (40 μM) in dry CH<sub>3</sub>CN monitored at 385 nm.

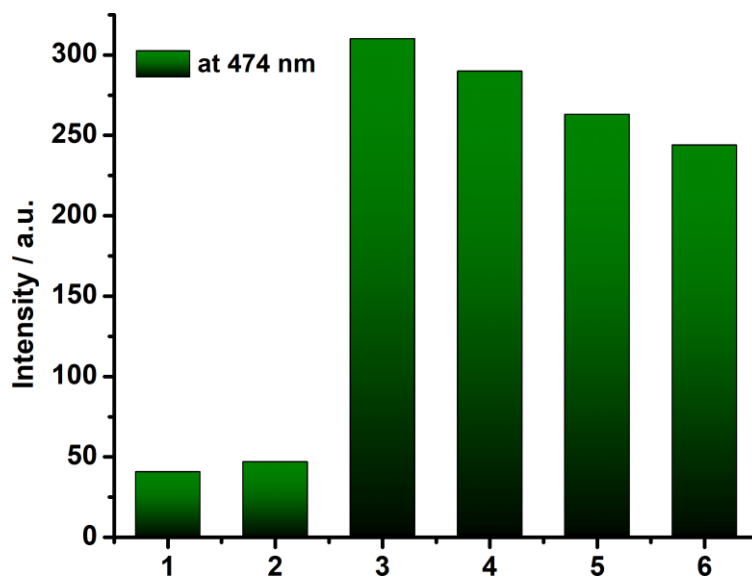
## Time-resolved Emission Lifetime Measurements:

Emission lifetime measurements were performed at 25°C using a QuantaMaster (QM-40) TCSPC module supplied by Photon Technology International (PTI). An 374 nm laser diode was used as excitation source. All the emission decays were monitored at the corresponding emission maxima as observed in the PL spectra. The emission decay traces were fitted (double exponential) by non-linear least square analysis based on the Levenberg-Marquardt algorithm with reference to the instrument response function (IRF), collected at the excitation wavelength using a scattering solution. The average lifetimes ( $\tau_{av}$ ) were calculated using the following equation:

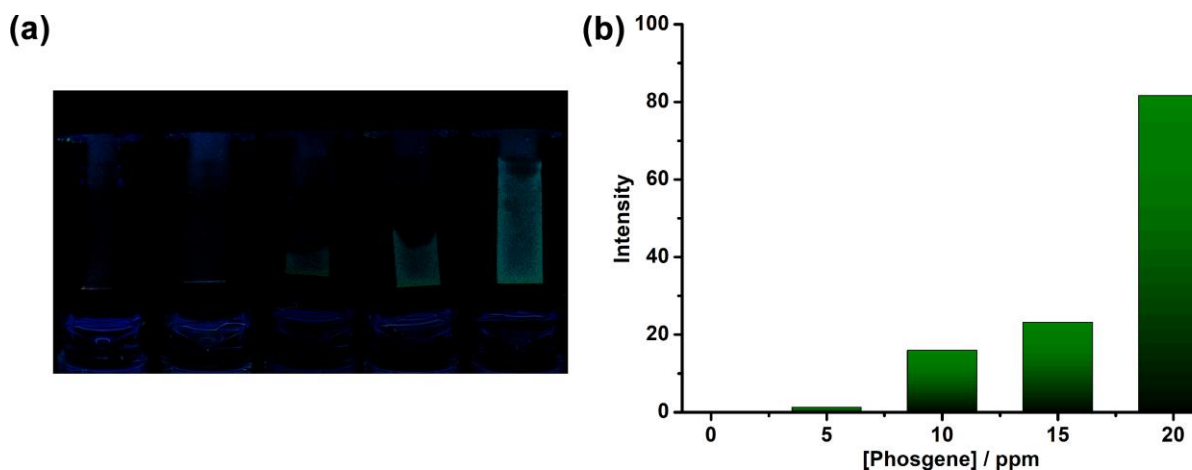
$$\langle \tau_{av} \rangle = \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i}$$

**Table S3:** TCSPC data for emission lifetime for phosgene sensing.

Condition	$\alpha_1$	$\tau_1$ (ns)	$\alpha_2$	$\tau_2$ (ns)	$\alpha_3$	$\tau_3$ (ns)	$\tau_{av}$	$\chi^2$
<b>3</b>	1.44	7.58	98.56	1.00	-	-	1.65	1.71
<b>3-Phos</b>	90.96	0.24	1.65	8.59	7.39	1.62	3.05	1.39



**Figure S14:** Bar diagram of intensity against different conditions for probe **3** (20  $\mu\text{M}$ ) (Conditions: (1) **3** (20  $\mu\text{M}$ ); (2) **3** (20  $\mu\text{M}$ ) + 2 equiv. Triphosgene; (3) **3** (20  $\mu\text{M}$ ) + 1 equiv.  $\text{Et}_3\text{N}$  + 2 equiv. Triphosgene; (4) **3** (20  $\mu\text{M}$ ) + 5 equiv.  $\text{Et}_3\text{N}$  + 2 equiv. Triphosgene; (5) **3** (20  $\mu\text{M}$ ) + 10 equiv.  $\text{Et}_3\text{N}$  + 2 equiv. Triphosgene; (6) **3** (20  $\mu\text{M}$ ) + 20 equiv.  $\text{Et}_3\text{N}$  + 2 equiv. Triphosgene).



**Figure S15:** (a) Paper strips of probe **3** exposed to variable concentration of phosgene (0-20 ppm). (b) Bar diagram of intensity against different amount of  $\text{Et}_3\text{N}$  for probe **3**.

**Table S4:** The x,y,z Cartesian coordinates of the probe **3** calculated using Gaussian 09 at [B3LYP/6-31G+ (d)] level.

	X	Y	Z		X	Y	Z
C	-3.218462	-2.608070	-0.254920	C	-4.331485	-1.764173	-0.154793
C	-4.153581	-0.395213	-0.014257	C	-2.860010	0.132854	0.039532
C	-1.723619	-0.692980	-0.026232	C	-1.937863	-2.075376	-0.196446
O	-2.766410	1.483216	0.149647	C	-1.534298	2.137671	0.165300
C	-0.337415	1.321815	0.126183	C	-0.405699	-0.050267	0.068840
O	-1.564813	3.349814	0.239457	C	0.952278	2.092491	0.202981
N	2.000276	1.593517	-0.701096	C	2.723476	0.461677	-0.318187
C	2.070830	-0.721735	0.094998	N	0.671284	-0.901305	0.105006
C	4.127241	0.459005	-0.372523	C	4.878328	-0.665643	-0.049167
C	4.229987	-1.825576	0.376702	C	2.842020	-1.839695	0.450714
H	-3.351825	-3.676483	-0.388829	H	-5.334891	-2.175815	-0.199235
H	-4.991266	0.290370	0.049031	H	-1.099529	-2.754278	-0.320120
H	1.314444	2.112711	1.243779	H	0.725590	3.123471	-0.071845
H	2.621500	2.344071	-0.977724	H	0.420445	-1.863884	0.265495
H	4.627523	1.372907	-0.684476	H	5.961091	-0.629393	-0.114674
H	4.794841	-2.710968	0.649078	H	2.330584	-2.743147	0.776966

**Table S5:** The x,y,z Cartesian coordinates of the probe **3-Phos** calculated using Gaussian 09 at [B3LYP/6-31G+ (d)] level.

	X	Y	Z		X	Y	Z
C	3.272051	-2.255865	0.610542	C	4.208670	-1.549793	-0.159793
C	3.894044	-0.307805	-0.700308	C	2.626124	0.228209	-0.471708
C	1.667911	-0.470610	0.287465	C	2.012661	-1.719501	0.835370
O	2.358938	1.455853	-1.009232	C	1.139138	2.100825	-0.841746
C	0.121770	1.392658	-0.071751	C	0.385089	0.162291	0.459242
O	0.989866	3.188929	-1.350201	C	-1.221499	2.089878	0.106671
N	-2.213913	1.182595	0.787733	C	-2.538153	0.050115	-0.042618
C	-1.640628	-0.996013	0.207125	N	-0.669505	-0.544223	1.193501
C	-3.579567	-0.099218	-0.943729	C	-3.688471	-1.330358	-1.606923
C	-2.790811	-2.370811	-1.354385	C	-1.746233	-2.219269	-0.430222
C	-1.403894	0.569801	1.826592	O	-1.258313	0.951129	2.946558
H	3.535660	-3.218195	1.036792	H	5.194202	-1.970915	-0.332649
H	4.605065	0.258785	-1.290995	H	1.277898	-2.234413	1.444028
H	-1.628332	2.408076	-0.856371	H	-1.106044	2.985777	0.724789
H	-4.283544	0.706180	-1.124211	H	-4.492199	-1.479826	-2.321052
H	-2.906077	-3.315913	-1.875607	H	-1.045845	-3.022630	-0.229317