Supporting Information

to accompany

Phosgene invites selective switch-on fluorescence at ppm concentrations in a Betti base by hindering 2-way PET

Ankita Gangopadhyay,[†] Ajit Kumar Mahapatra*[,†]

† Department of Chemistry, Indian Institute of Engineering Science and Technology (formerly Bengal Engineering and Science University) Shibpur, Howrah, West Bengal 711103, India.

*Corresponding author. Fax: +91 33 26684564; Tel: +91 33 2668 4561;

E-mail: mahapatra574@gmail.com (A. K. Mahapatra)

Contents

1. Calculation of Limit of Detection (LOD)

The calibration curve was derived from a plot of fluorescence intensity at 430 nm as a function of phosgene concentration. The regression equation was obtained for the part corresponding to lower phosgene concentrations (1.0 – 5.0 μM).

$$LOD = {}^{3\sigma}/_{k}$$

where k is the slope of the curve and σ stands for the standard deviation of the fluorescence intensity of **BB** in presence of phosgene.

$F_{430} = 1.92859E + 6x - 277260.46119$ ($R^2 = 0.99208$)

$LOD = (3 \times 256568.86844) \div (1.92859E + 6) = 0.40\ \mu M$

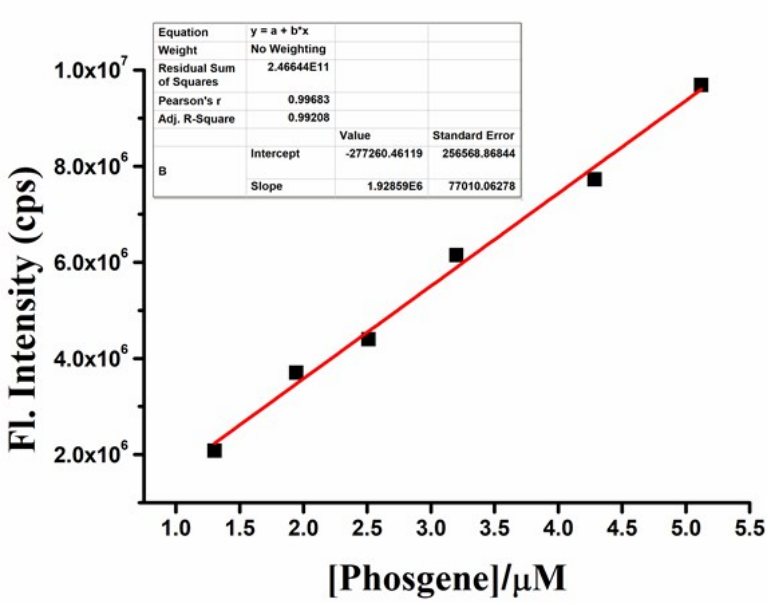


Figure S1. Calibration curve of fluorescence intensity (at 430 nm) of 10.0 μMof **BB** as a function of phosgeneconcentration. (λ_{ex}= 350 nm, λ_{em}= 430nm).

2. Calculation of pseudo first order rate constant: k'

Measurement of the fluorescence enhancement of BB (10.0μM) at 430 nm in presence of an excess of triphosgene (150.0 μM) containing added TEA led to the determination of the pseudo first order rate constant from the following equation:

$ln[(F_{max} - F_t)/F_{max}] = -k't$

where F_t and F_{max} the maximum value obtained upon com seudo-first order rate constant which has

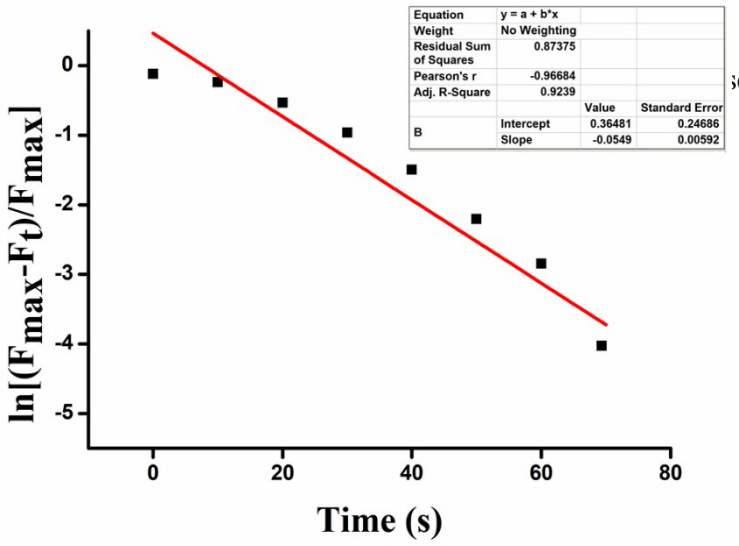


Figure S2. Pseudo first order kinetic plot of **BB** (10.0 μM) in the presence of triphosgene/TEA (150 μM). (λ_{ex}= 350 nm).

3. Determination of fluorescence quantum yields

The fluorescence quantum yields of **BB**and **BBC**were determined in 0.05M $H_2SO_4$with quinine sulfate (φ = 0.52) as the fluorescence standard. The quantum yields were calculated using the following equation:

$$\varphi_S = \varphi_A \times \frac{F_S}{F_A} \times \frac{A_A}{A_S} \times \frac{\eta_S^2}{\eta_A^2}$$

where $A_A$and $A_S$are the absorbances of quinine sulfate and sample solutions at the same excitation wavelength; $F_A$and $F_S$are the corresponding integrated fluorescence intensities of quinine sulfate and sample solutions; $\eta_A$and $\eta_S$are the refractive indices of the respective solvents employed which in this case is 0.05M $H_2SO_4$for both measurements.

4. Fluorescence Lifetime Data

Radiative (k_r) and non-radiative (k_{nr}) rate constants of **BB** and **BBC** were evaluated using the following equations:

$$\tau^{-1} = k_r + k_{nr}$$

$$k_r = \varphi / \tau$$

where τ, k_r, $k_{nr}$and φ are the mean fluorescence lifetime, radiative rate constant, non-radiative rate constant and fluorescence quantum yield, respectively.All photo-physical parameters are given below.

Species	φ	τ	$k_r(ns^{-1})$	$k_{nr}(ns^{-1})$
BB	0.049	0.917	0.053	1.037
BBC	0.706	1.025	0.688	0.286

Table S1: Fluorescence life time data

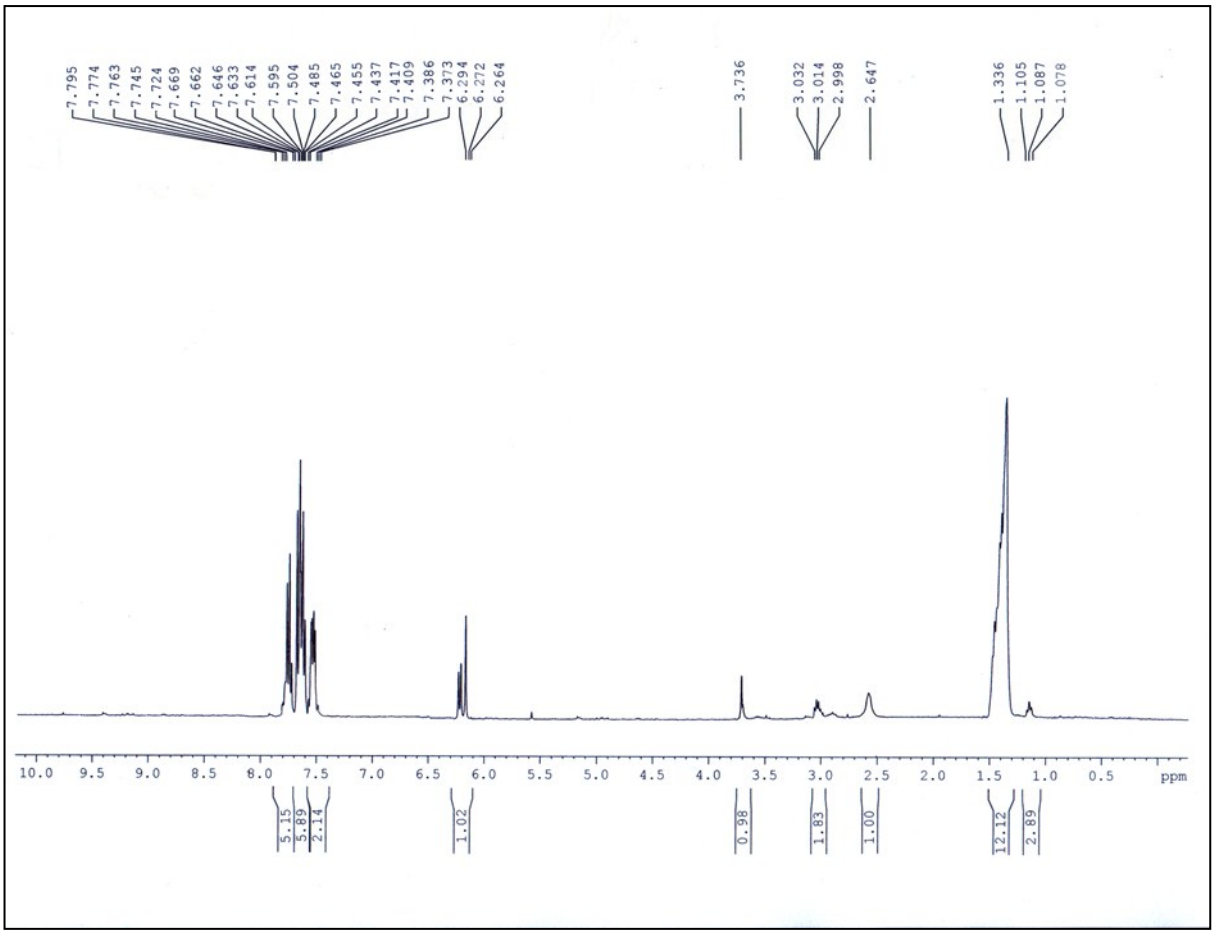


Figure S3: ^{1}H NMR of**BB**in $CDCl_3$

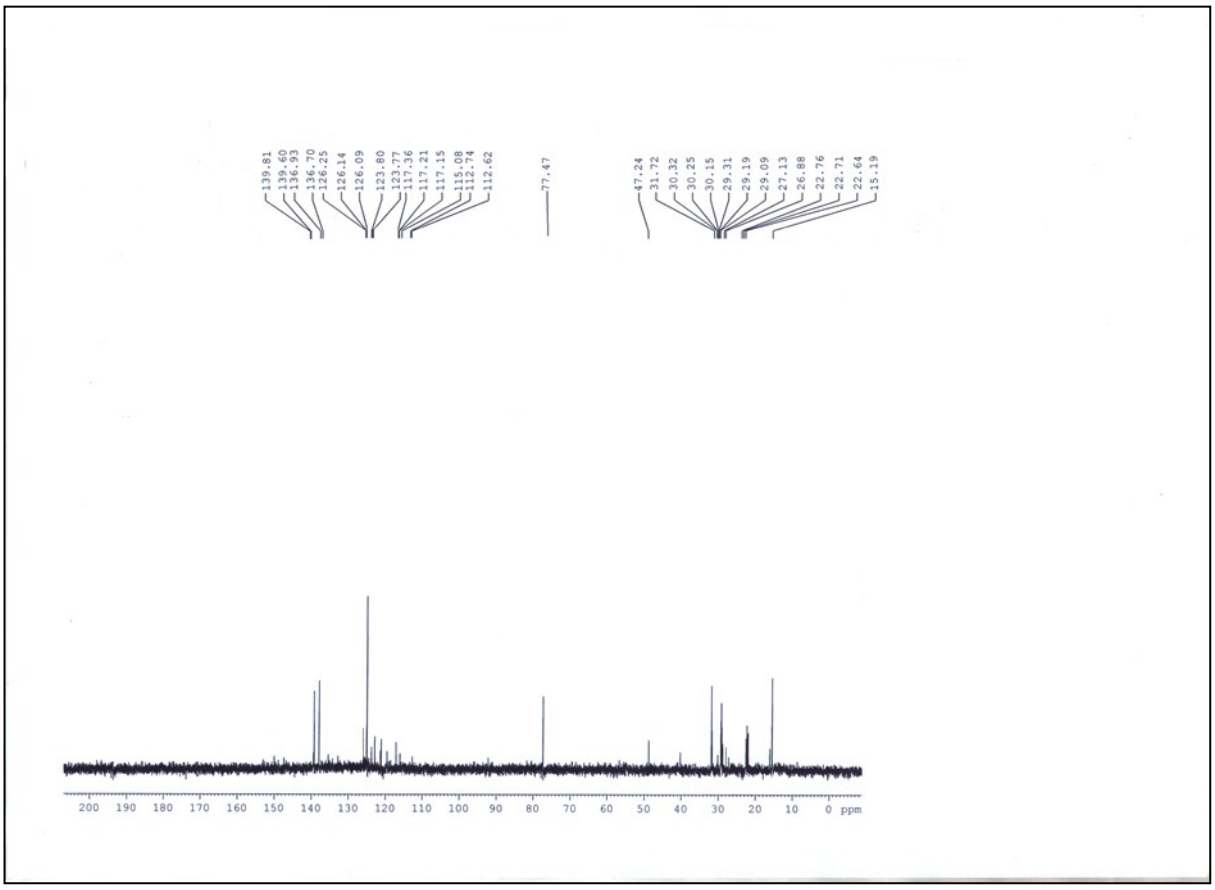


Figure S4: ^{13}C NMR of**BB**in $CDCl_3$

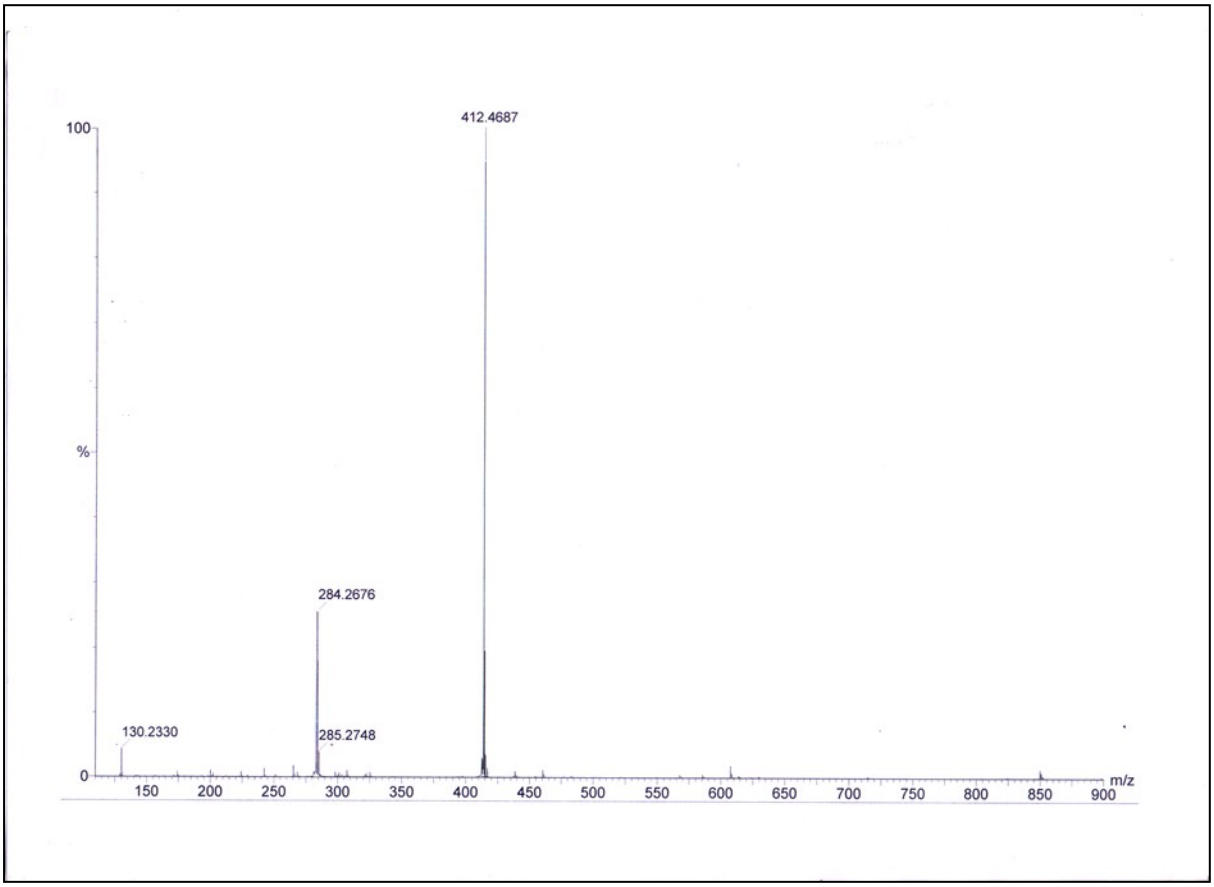


Figure S5: ESI-MS of **BB**

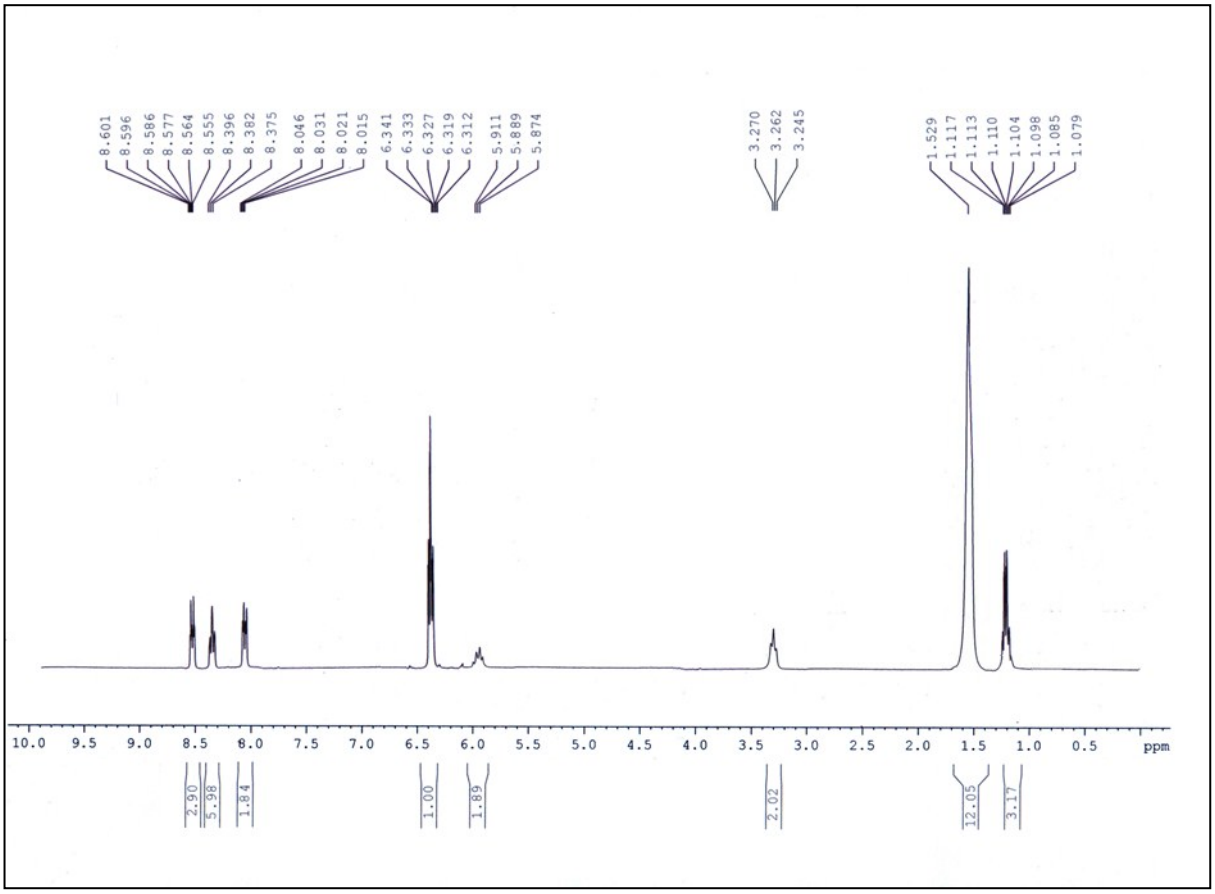


Figure S6: ^{1}H NMR of **BBC**in $CDCl_3$

^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 1.10 (m, 3H), 1.52 (s, 12H), 3.25 (t, J=10.0Hz,2H), 5.89 (t, J = 14.8Hz, 2H), 6.32 (m, 1H), 8.02 (q, J=12.4 Hz, 2H), 8.38 (t, J=8.4 Hz,6H), 8.56 (m, 3H).

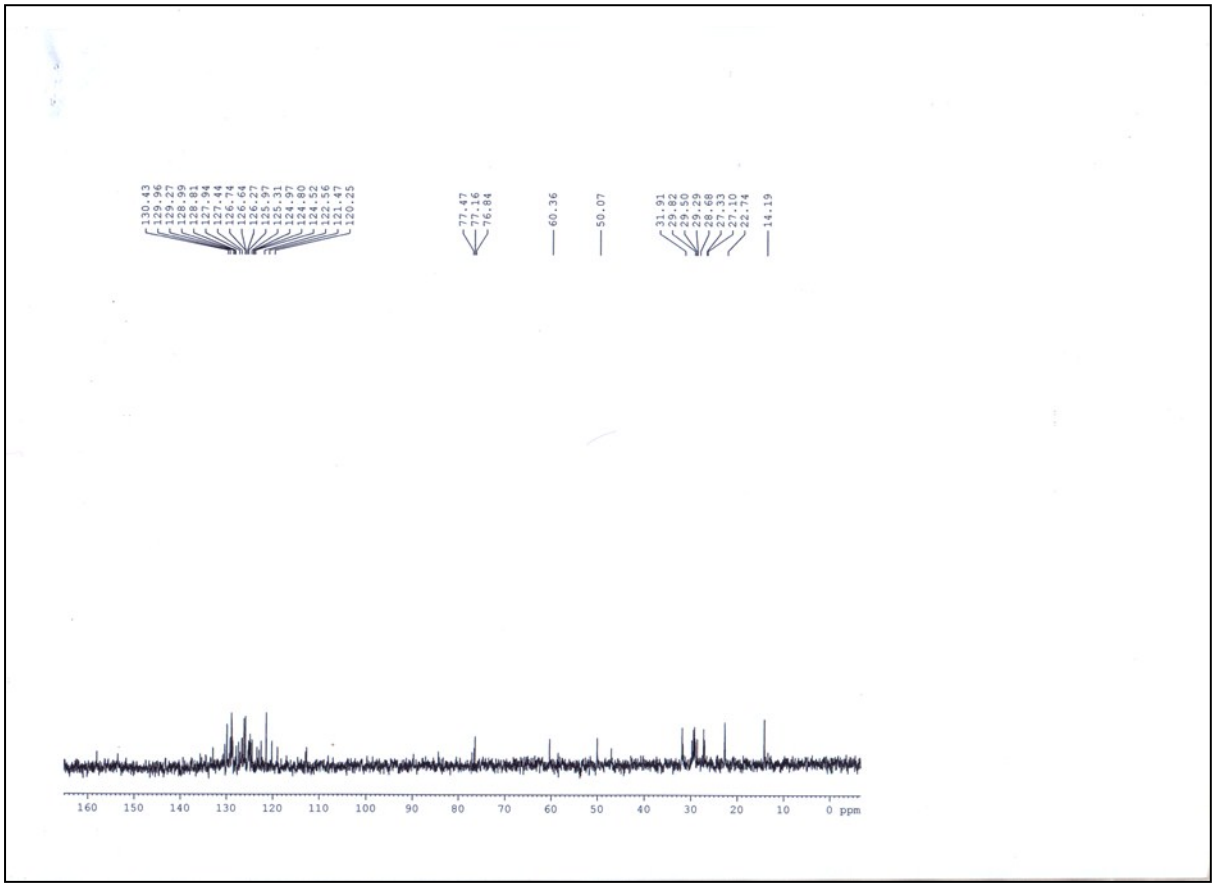


Figure S7: ^{13}C NMR of **BBC** in $CDCl_3$

^{13}C NMR (400 MHz, $CDCl_3$) δ (TMS, ppm): 14.19 (1C), 22.74 (1C), 27.21 (1C), 28.68 (1C), 29.53 (3C), 31.91 (1C), 50.07 (1C), 60.36 (1C), 77.15 (2C), 120.25 (1C), 121.47 (3C), 122.56 (2C), 124.90 (3C), 126.40 (2C), 127.44 (2C), 127.94 (2C), 128.90 (2C), 130.19 (1C).

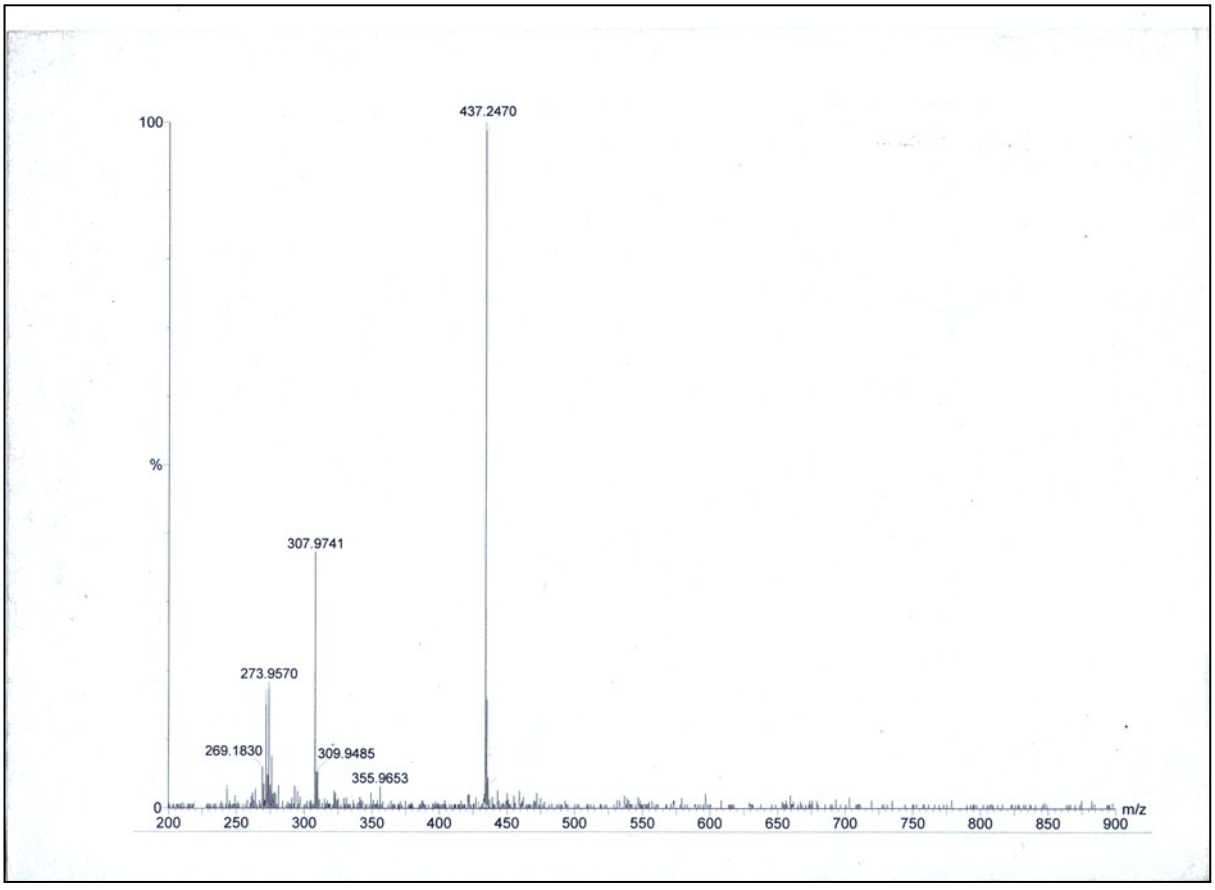


Figure S8: ESI-MSof **BBC**

(ESI (+)-HRMS (m/z): **[M]**$^{+}$calculated for $\mathbf{C_{30}H_{31}NO_2}$:**437.2355**, found:**437.2470**)

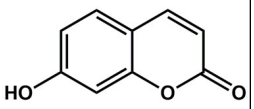
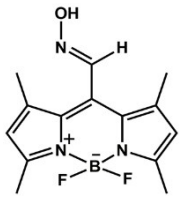
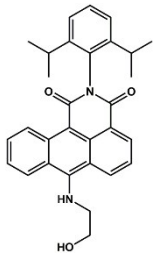
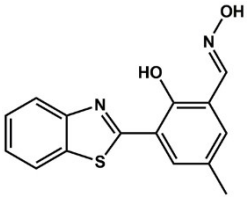
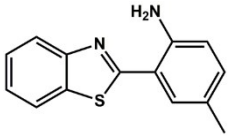
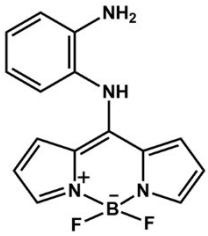
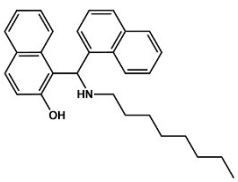
Compound	Response Time	Detection Limit	Application	Reference
	--------	1 nM	Not reported	Hwang et al. *Anal. Chem.***2012**, 84, 10, 4594-4597
	< 10s	0.09 ppb	TLC stick based test kit	Kim et al. *Anal. Chem.***2017**, 89, 23, 12837-12842
	< 5 min	2.3 nM	Polystyrene membrane-based test strips	Sheng et al. *Anal. Chem.***2018**, 90, 14, 8686-8691
	--------	0.48 nM	Probe embedded TLC sticks as test strips	Feng et al. *Dyes and Pigments.* **2019**, 163, 483-488
	--------	0.14 ppm	Filter paper-based test strips	Yoon et al. *Anal. Chem.***2017**, 89, 22, 12596-12601
	~15 s	2.7 nM	TLC plate-based test kit	Song et al. *Anal. Chem.* **2017**, 89, 7, 4192-4197
	< 20 s	0.40µM	TLC plate-based test strip	This work.

Table S2: Comparison table indicating several notable phosgene sensors and this work