

## **Supporting Information**

### **A highly selective visual detection of tabun mimic diethyl cyanophosphate (DCNP): effective discrimination of DCNP from other nerve agent mimics**

D. Raghavender Goud, Deepak Pardasani, Vijay Tak and Devendra Kumar Dubey\*

Vertex Laboratory, Defence Research and Development Establishment  
Jhansi Road, Gwalior, M.P. 474002 (India), Fax: (+) 0751-2341148, E-mail:dkdubey@rediffmail.com

### **Contents**

<b>1. General details</b>	<b>P2</b>
<b>2. Procedure for synthesis of chemodosimeter (I)</b>	<b>P3</b>
<b>3. Selected copies of <sup>1</sup>H, <sup>13</sup>C NMR and Mass spectra</b>	<b>P4-P8</b>
<b>4. Procedure for chromogenic detection of DCP and DCNP with (I)</b>	<b>P9</b>
<b>5. Calibration curves and detection limit determination</b>	<b>P9-P10</b>
<b>6. References</b>	<b>P11</b>

## 1. General details

Reagents were obtained from commercial supplier, and used without further purification. DCNP was synthesised using a reported procedure<sup>1</sup>. Solvents used were purified by standard methods prior to use. Mass analysis was performed using an LCQ Advantage ion trap mass spectrometer from Thermo Finnigan. NMR spectra were recorded on a Bruker 600 MHz. Chemical shifts were expressed in parts per millions ( $\delta$ ) downfield from the internal standard tetramethylsilane and were reported as s (singlet), d (doublet), bs (broad singlet), t (triplet) and m (multiplet). Absorbance spectra were recorded at room temperature with Perkin-Elmer UV-Visible spectrophotometer. IR spectrum was recorded with Thermo Nicolet 6700 FT-IR instrument. TLC analysis was performed on silica gel 60 F<sub>254</sub> plates and column chromatography was conducted over silica gel (mesh 100-200).

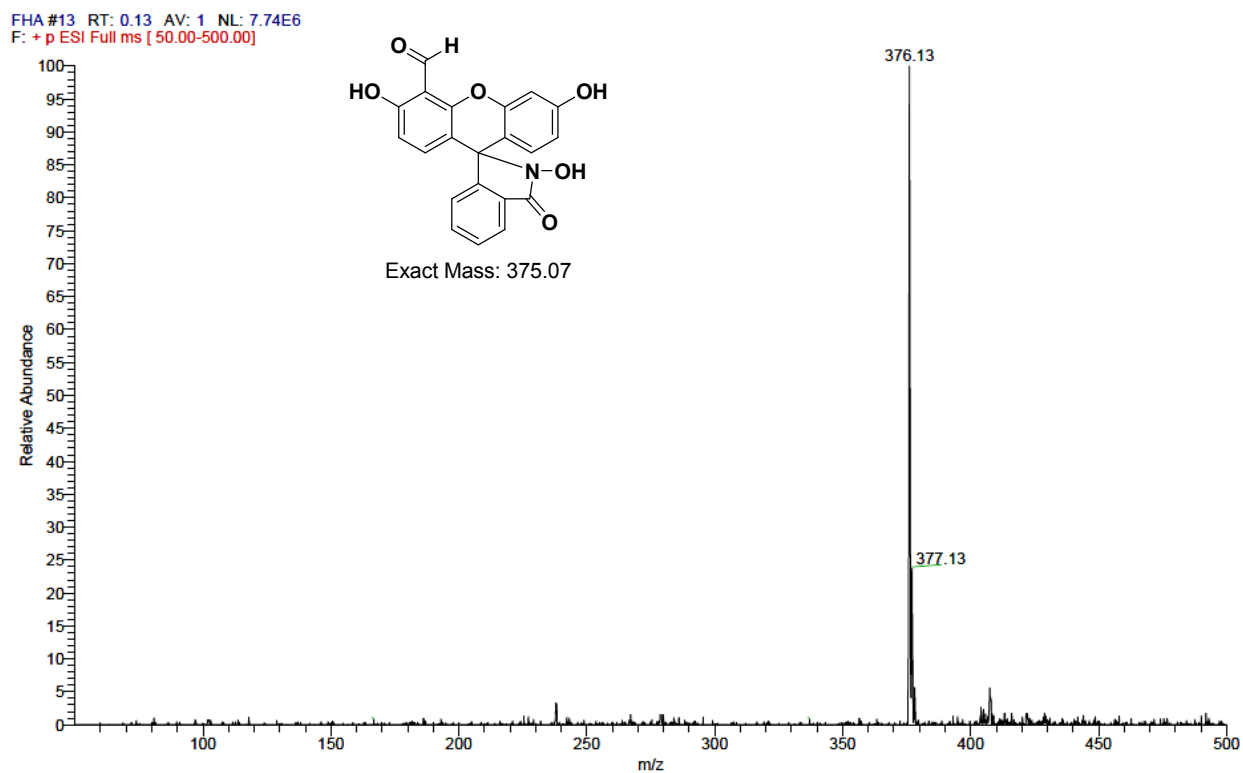
## 2. Procedure for synthesis of chemodosimeter (I)

Compounds (B) and (C) were synthesized using reported procedures<sup>2,3</sup>.

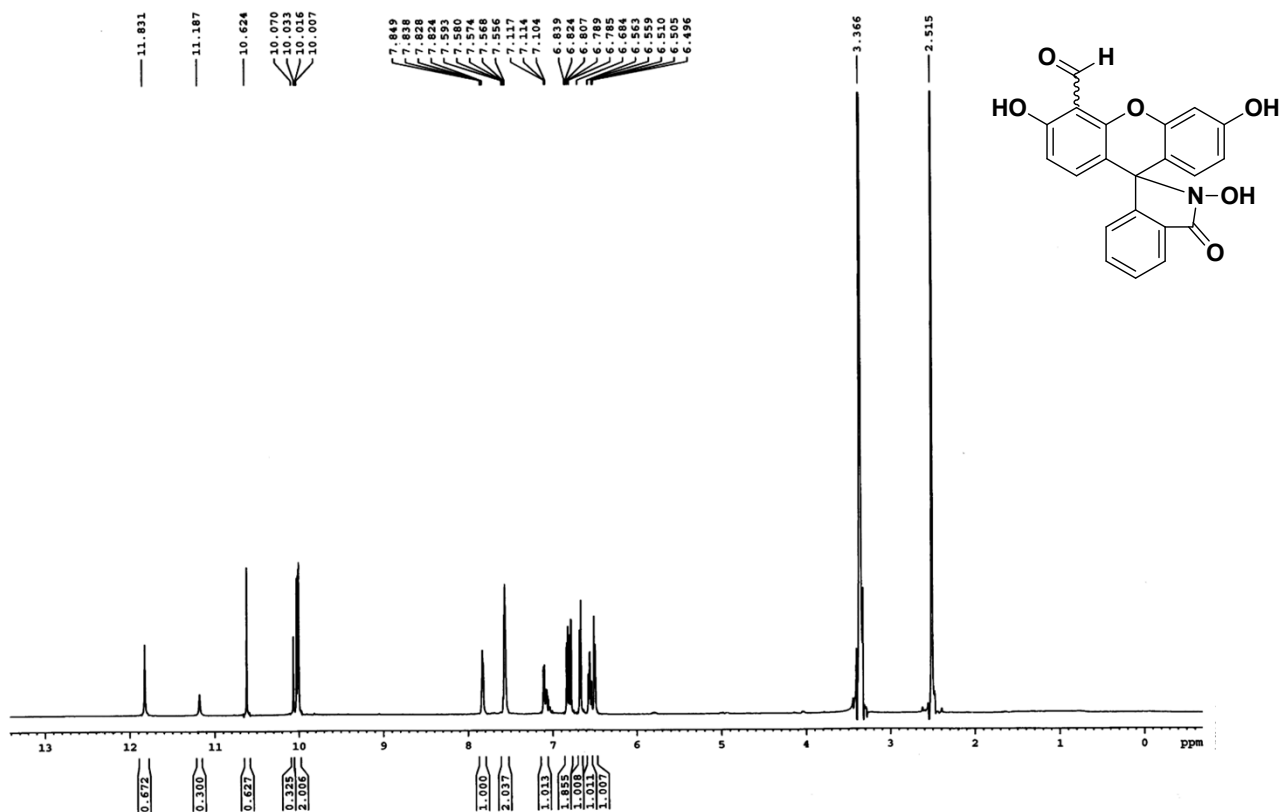
**Synthesis of Compound (I):** To a solution of NaOH (0.24 g, 6.1 mmol) in 5 ml 1:4 ethanol/water, compound (C) (0.3 g, 0.87 mmol) was added and heated to 60°C. Chloroform (0.25 ml, 3.0 mmol) was added in five portions for 30 minutes and the heating was continued for additional 1.5 hr. Progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled and neutralised with dil.HCl. A yellow solid was separated out. The solid was filter and washed with 10 ml of water. The solid was dried and the crude product was purified by silica gel coloumn chromatography (5% methanol in Dichloromethane) to afford 0.19 g (0.51 mmol, 58%) of compound (I) as a light yellow solid.

<sup>1</sup>H NMR (600MHz, DMSO-d<sub>6</sub>): δ = 11.83&11.19 (s, 1H), 10.62 & 10.07 (s, 1H), 10.03-10.01 (m, 2H), 7.85-7.83 (m, 1H), 7.59-7.55 (m, 2H), 7.12-7.10 (m, 1H), 6.84-6.79 (m, 2H), 6.68 (m, 1H), 6.56 (m, 1H), 6.51(m, 1H). MS (ESI): m/z = 376.13 [M+H]<sup>+</sup>.<sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>): δ = 193.70, 189.72, 162.78, 162.74, 159.19, 157.50, 153.80, 152.39, 149.77, 136.94, 133.50, 129.53, 128.86, 124.01, 123.06, 120.21, 113.51, 111.86, 109.64, 109.44, 109.34, 103.99, 103.20. ESI-MS: m/z 376.13 [M+H]<sup>+</sup>.

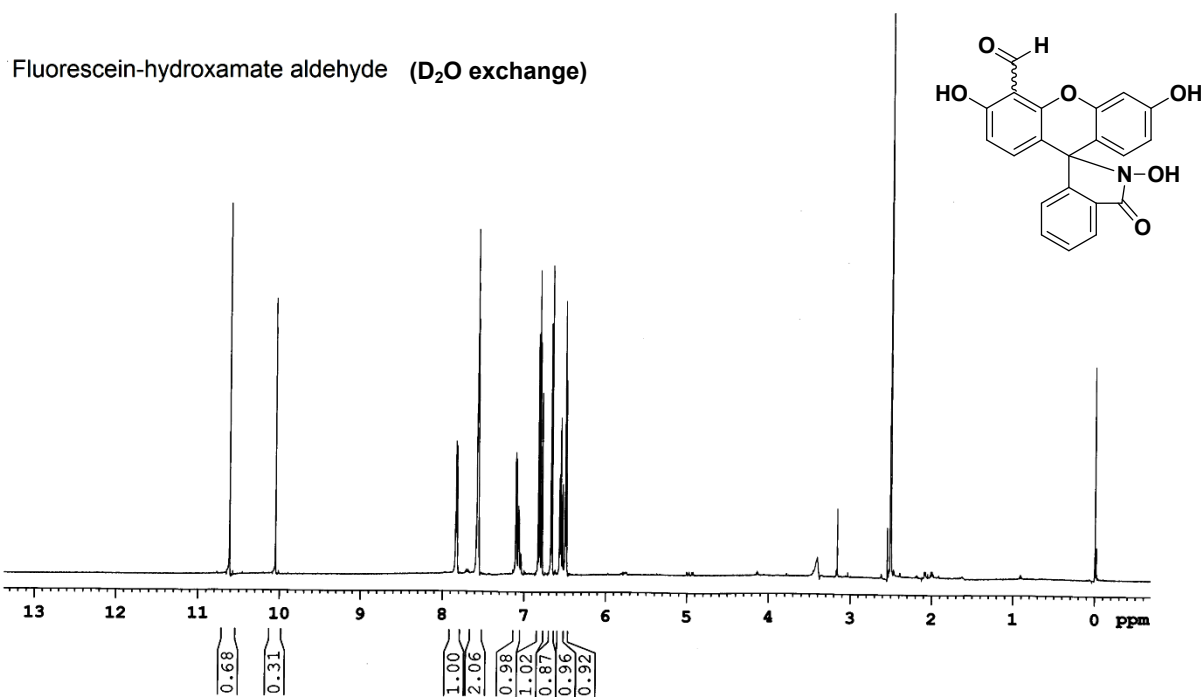
### 3. Selected copies of $^1\text{H}$ , $^{13}\text{C}$ NMR and Mass spectra



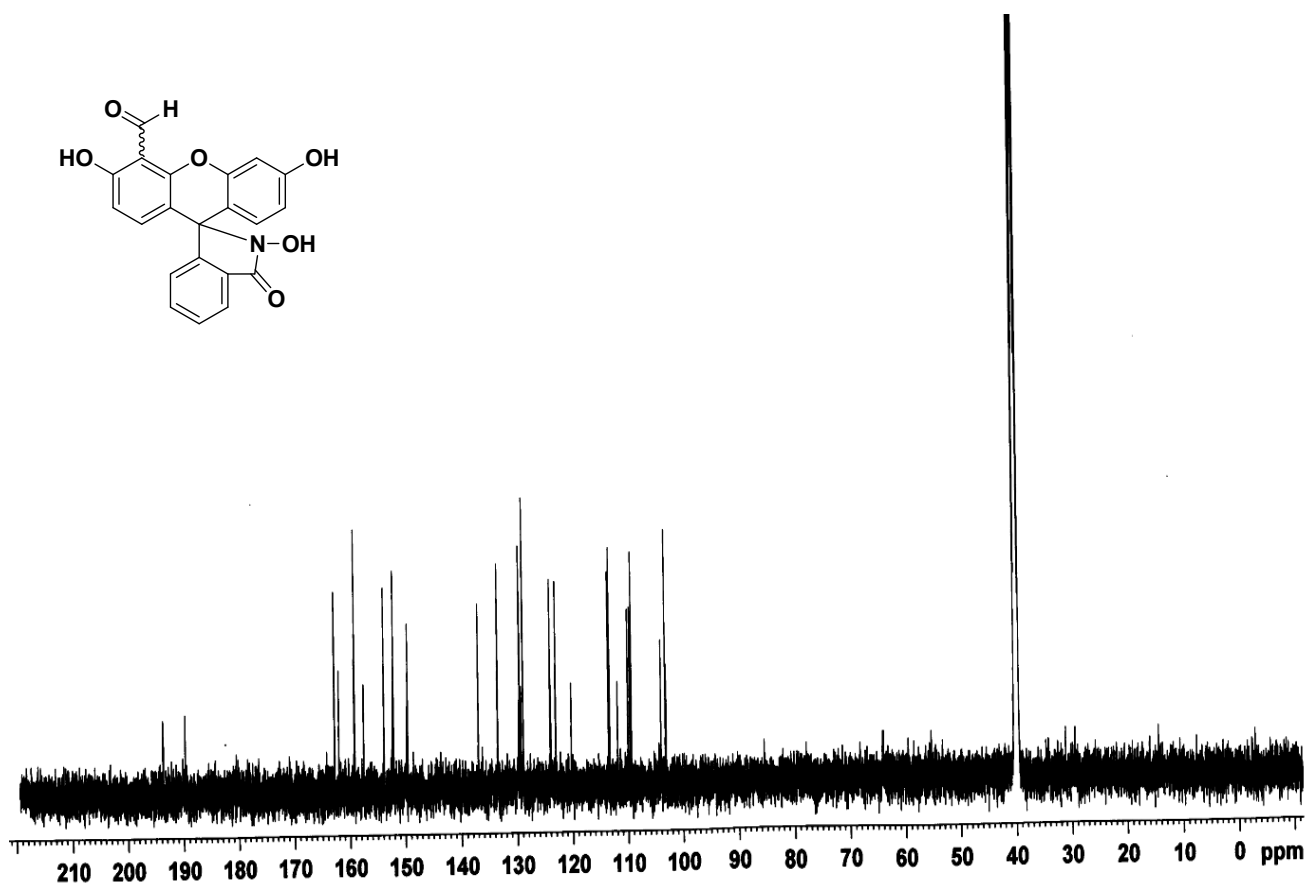
**Fig. S1:** Mass Spectrum of Compound (I)



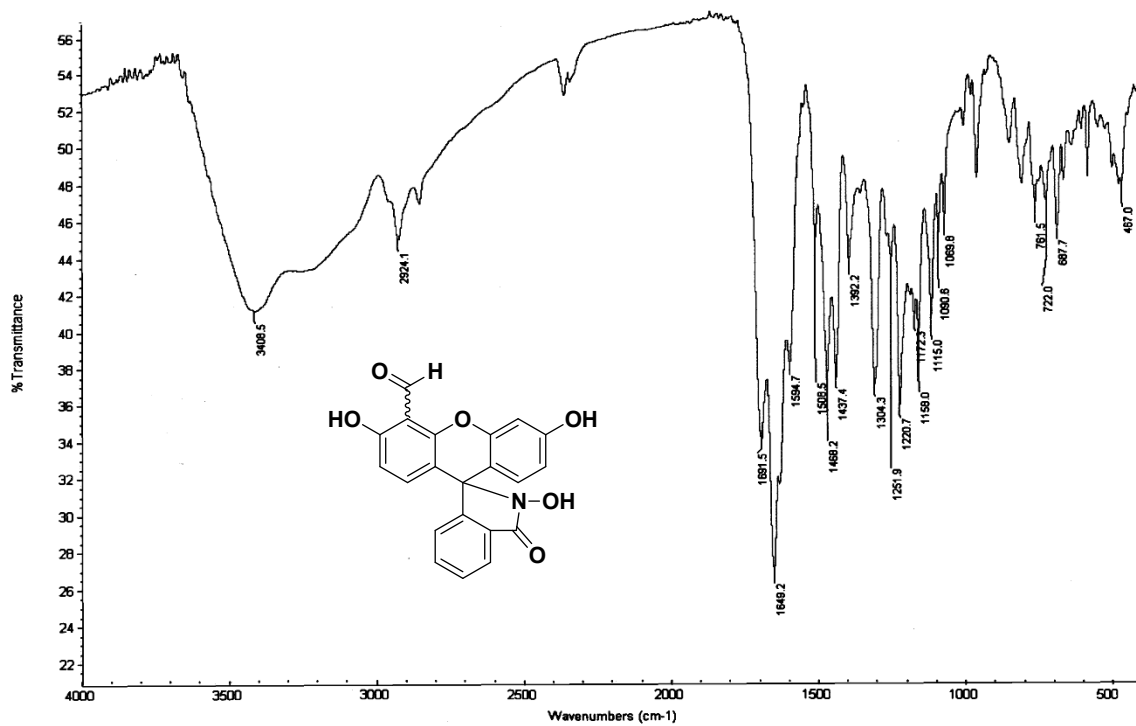
**Fig. S2:**  $^1\text{H}$  NMR Spectrum of Compound (I)



**Fig. S3:** D<sub>2</sub>O Exchange - <sup>1</sup>H NMR Spectrum of Compound (I)

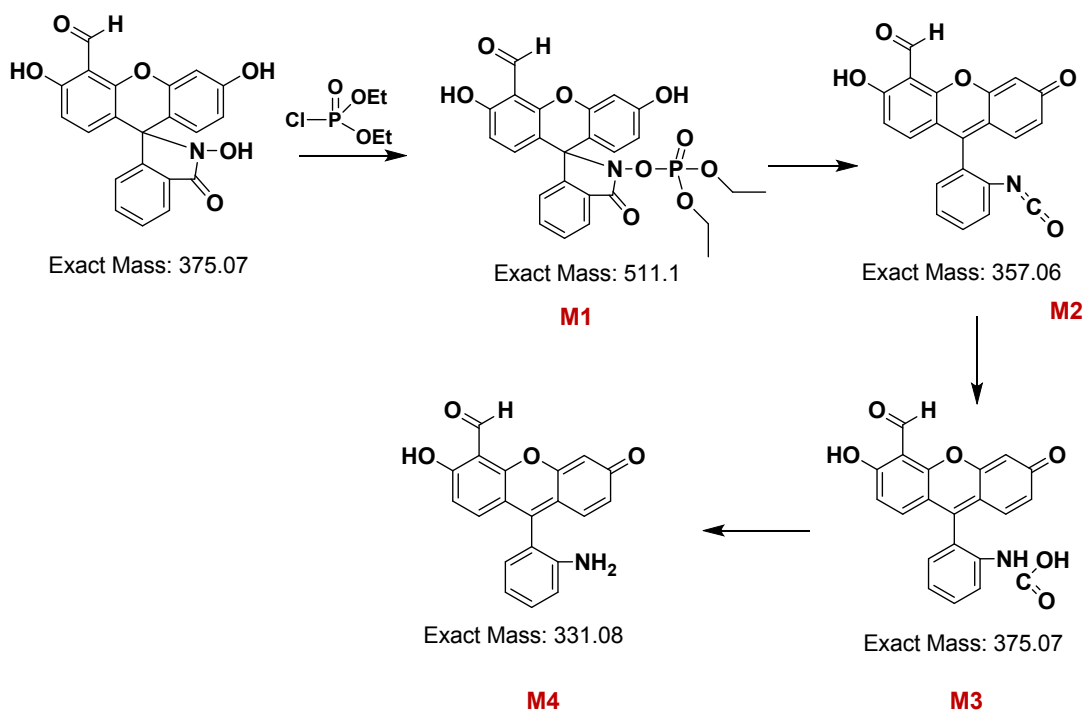


**Fig. S4:** <sup>13</sup>C NMR Spectrum of Compound (I)

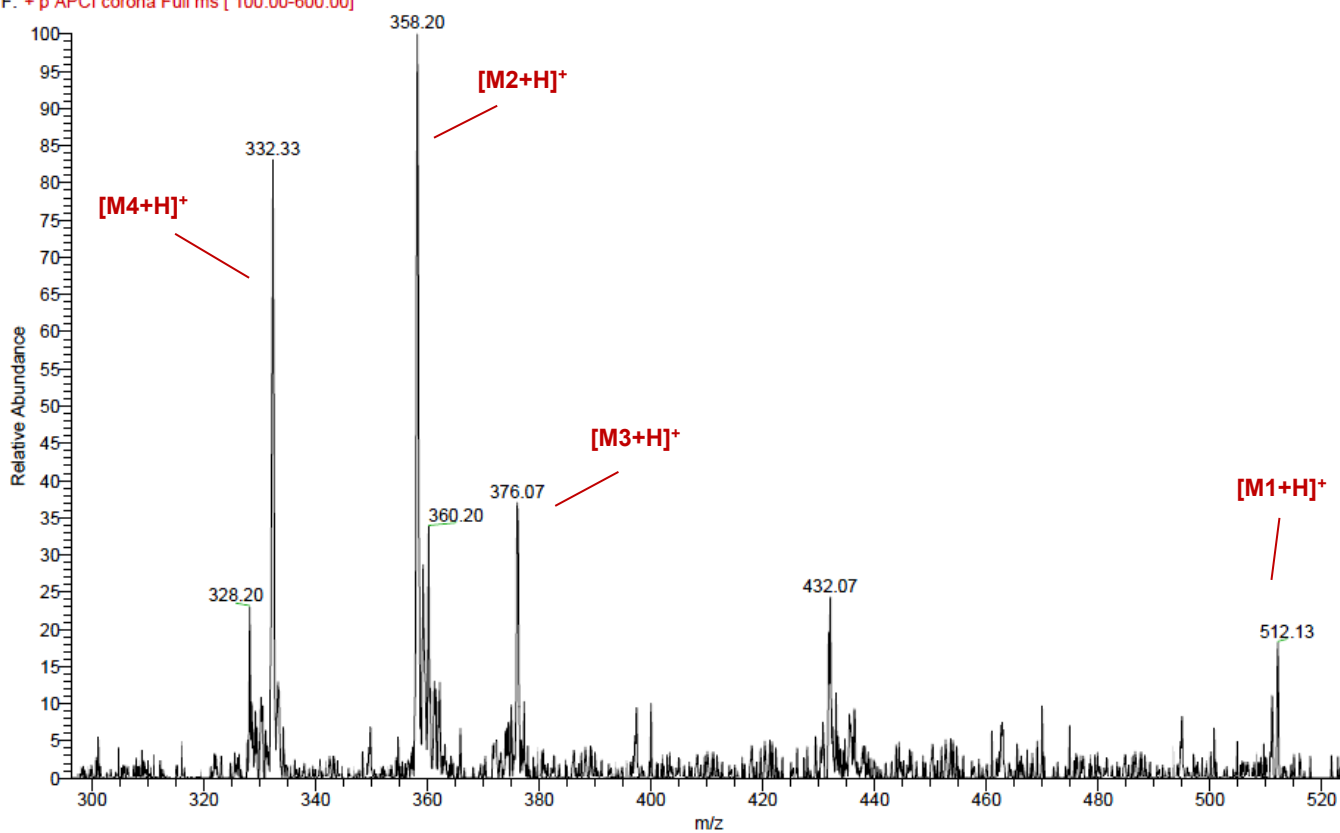


**Fig. S5:** IR Spectrum of Compound (I)

### Reaction of (I) with DCP

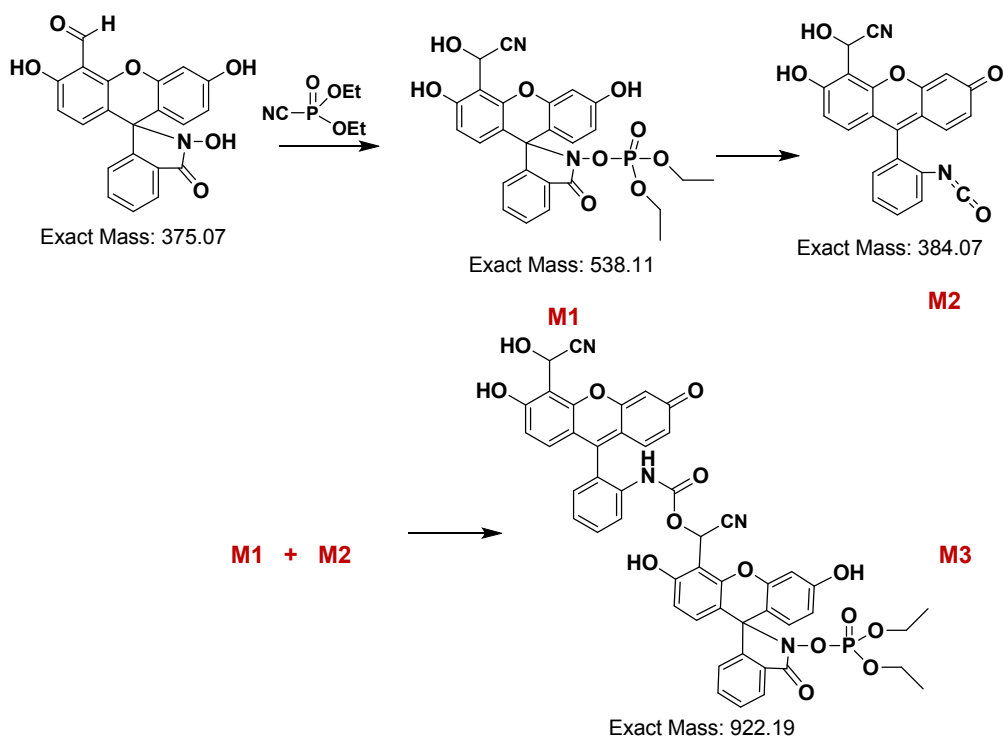


FHA+DCP02 #8 RT: 0.09 AV: 1 NL: 3.83E6  
F: + p APCI corona Full ms [ 100.00-600.00]

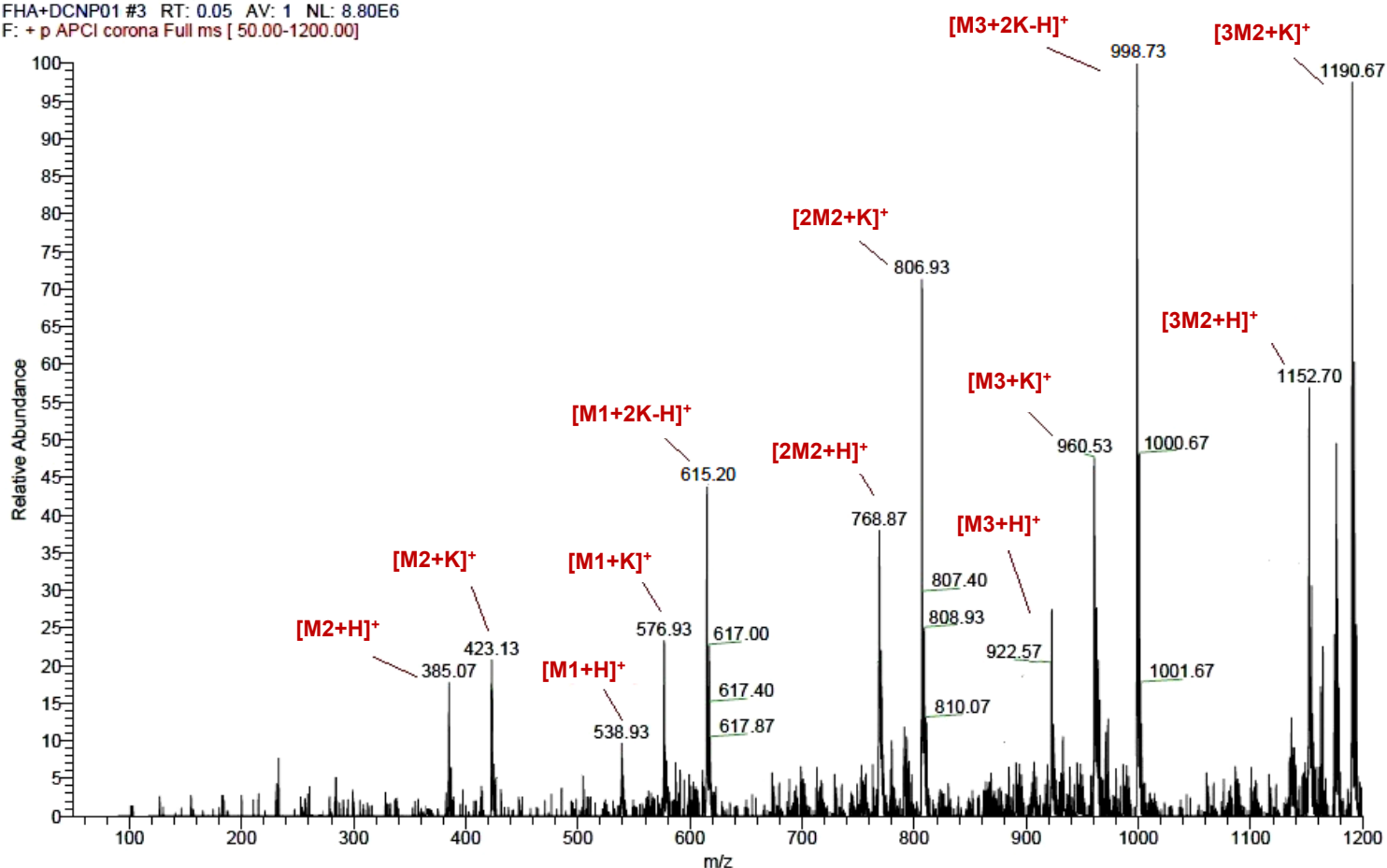


**Fig. S6:** Mass Spectrum of reaction of (I) with DCP

### Reaction of (I) with DCNP



FHA+DCNP01 #3 RT: 0.05 AV: 1 NL: 8.80E6  
F: + p APCI corona Full ms [ 50.00-1200.00]



**Fig. S7:** Mass Spectrum of reaction of (I) with DCNP

Note: Potassium adduct ion of potassium salt  $[M+2K-H]^+$  is also formed<sup>4,5</sup>



#### **4. Procedure for chromogenic detection of DCP and DCNP with (I):**

##### **Procedure for chromogenic detection of DCP using (I):**

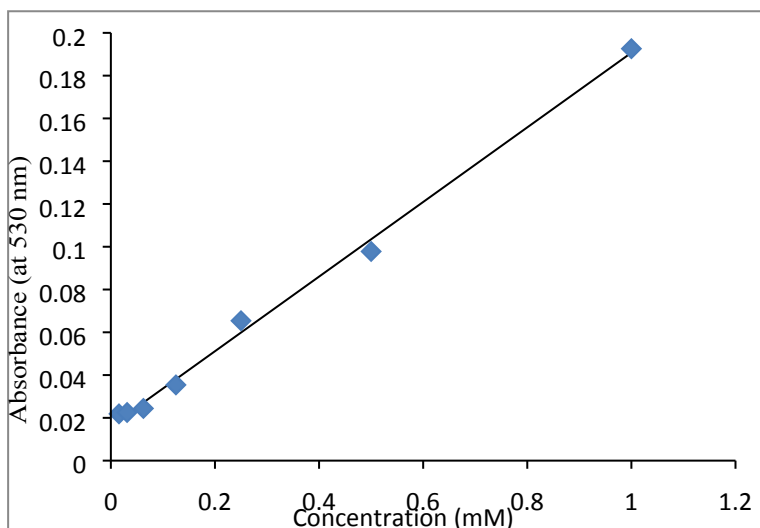
To the reagent solution containing the Probe molecule (I) (1 mg, 2.8 mM) in DMF (1 ml) and 3% (v/v) triethylamine, solution of DCP (4.8 mg, 28mM) was added. Instantaneous colour change to red was observed and the colour intensified up to 15 min. The similar protocol was applied for other analytes like  $\text{SOCl}_2$ ,  $\text{POCl}_3$ , p-Toluenesulphonyl chloride, acetyl chloride and anions like cyanide, iodide, bromide and fluoride. These vials were photographed.

##### **Procedure for chromogenic detection of DCNP using (I):**

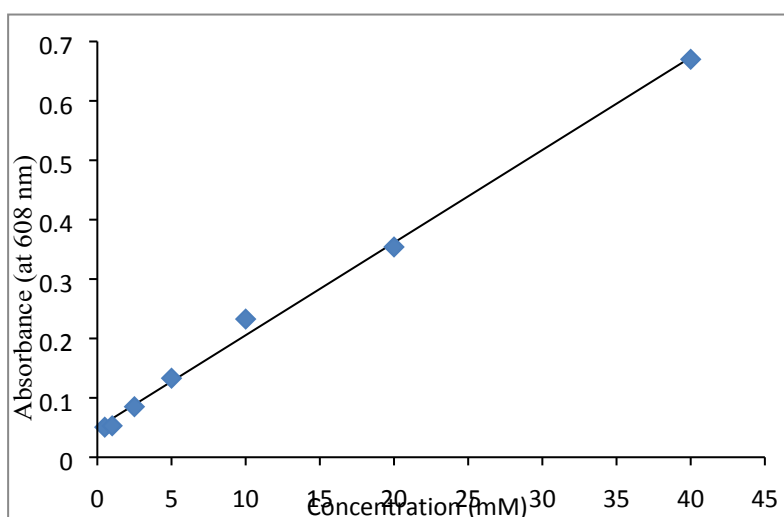
To the reagent solution containing the Probe molecule (I) (1 mg, 2.8 mM) in DMSO (1 ml), 3% (v/v) triethylamine and 5 mg KI, solution of DCNP (4.5 mg, 28mM) was added. Slow colour change to blue was observed and the colour intensified up to 1 hr. This vial was photographed. At concentration 3mM of DCNP the chromogenic response was too slow, but maximum absorbance was achieved by heating the solution at 60°C for 15 min.

**5. Calibration curves and Detection limits determination:** Increasing amounts of a solution of the corresponding simulant in their respective solvents were added to the solutions of Chemodosimeter (I) (1mM). After each addition following the above experimental procedure the maximum absorbance was recorded. The experiments were repeated three times each (differences were lower than 5%). Calibration curves were plotted using the maximum absorbance

of compound (I) in the presence of the analyte (DCP or DCNP). The limit of detection was calculated when  $\Delta A_{bst} \geq K \times S_{b1}/S$  where  $\Delta A_{bst}$  is the difference of absorbance from the blank at a given time,  $K=3$ ,  $S_{b1}$  is the standard deviation of the blank solution and  $S$  is the slope of the calibration curve.



**Fig. S8:** Plot of Absorbance (at 530 nm) versus the concentrations of DCP in the range of 0.0156 - 1 mM [slope (S) = 0.152,  $S_{b1} = 0.00753$ , Detection limit = 0.15mM].



**Fig. S9:** Plot of Absorbance (at 608 nm) versus the concentrations of DCNP in the range of 0.25 - 40 mM [slope(S) = 0.0131,  $S_{b1} = 0.0129$ , Detection limit = 3mM].

**References:**

1. E. Shi and C. Pei, *Syn. Comm.*, 2005, **35**, 669.
2. W. Feuerstein and M. Dutoit, *Ber. Dtsch. Chem. Ges.* 1901, **34**, 2637.
3. M. Adamczyk and J. Grote, *Tetrahedron Lett.*, 2000, **41**, 807.
4. MS Solutions #4: Dealing with metal adduct ions in electrospray: Part-2. [www.sepscience.com/Techniques/MS/Articles//234-/MS-Solutions-4-Dealing-with-Metal-Adduct-Ions-in-Electrospray-Partt-2](http://www.sepscience.com/Techniques/MS/Articles//234-/MS-Solutions-4-Dealing-with-Metal-Adduct-Ions-in-Electrospray-Partt-2)
5. N. Huang, M. M. Siegel, G. H. Kruppa, F. H. Laukien, *J. Am. Soc. Mass Spectrom.* 1999, 1166