Relay recognition of F^- and a Nerve-agent Mimic diethyl cyanophosphonate in mixed aqueous media: Discrimination of diethyl cyanophosphonate and diethyl chlorophosphate by cyclization induced fluorescence enhancement

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Calculation of the detection limit:

The detection limit (DL) of **BSNA** towards F^- and **BBCI** towards DCNP in emission spectra was determined from the following equation[1]:

$DL = K^* Sb_1/S$

Where K = 2 or 3 (we take 2 in this case); Sb_1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph Fig.S1(a), we get slope = 7404.61, and Sb_1 value is 10523.06.

Thus using the formula we have detected the green fluorescence of **BSNA** using mininum 2.84 μM TBAF.

From the graph Fig.S1(b), we get slope = 117056.89, and Sb1 value is 154622.2.

Thus using the formula we have detected the green fluorescence of **BBCI** using mininum 3.09 μM DCNP.

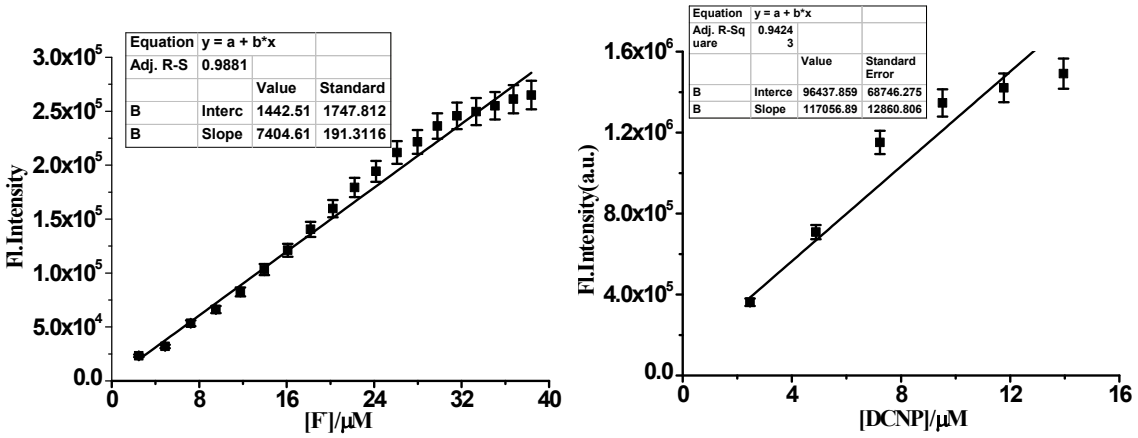


Figure S1: (a) Changes of emission intensity of **BSNA** (c = 2 x10^{-5}M) as a function of [TBAF] (c = 2x10^{-4}M) at 486 nm. **(b)** Changes of emission intensity of **BBCI** (c = 2 x10^{-5}M) as a function of [DCNP] (c = 2x10^{-4}M) at 480 nm.

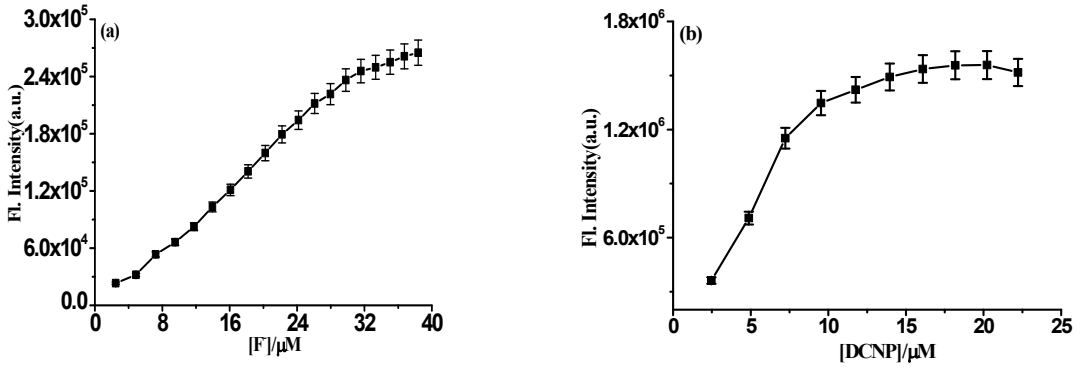


Figure S2: (a) Fluorescence changes of **BSNA** on addition of TBAF**. (b)** Concentration vs. intensity plot of the fluorescence spectra of isolated de-silylation product of **BSNA** with TBAF (**BBCI**) with DCNP in CH_3CN/H_2O (5/5, v/v, 25°C) at pH 7.4 by using 10 mM HEPES buffer solution.

Kinetic behavior:

Fig S3(a) represents the changes of emission at different time interval by addition of F^{-}.

From the time vs. emission intensity plot (Fig.S3(a)) and linear detection range at fixed wavelength at 486 nm by using pseudo first order rate equation we get the rate constant K=slope x 2.303= 0.00873 × 2.303= 2.01×10^{-2} Sec^{-1}.

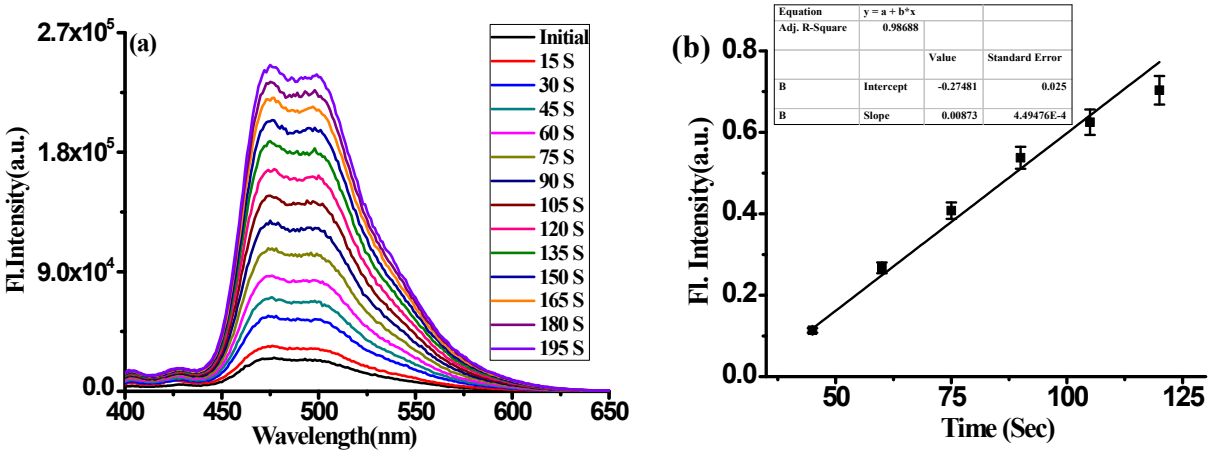


Figure S3: (a) The changes of emission spectra at different time intervals of **BSNA** in presence of F^{-} in CH_3CN: HEPES buffer solution (v:v, 5:5) at pH 7.4. **Inset:** Different time intervals are shown in the rectangle ('S' denotes Second). (b) The first order rate equation by using Time vs. fluorescent intensity plot at 486 nm.

Fig S4 (a) represents the changes of emission at different time interval by addition of DCNP to the **BBCI** solution.

From the time vs. emission intensity plot (Fig.S4 (b)) and liner detection range at fixed wavelength at 480 nm by using pseudo first order rate equation we get the rate constant K= slope x 2.303= 0.00595×2.303=1.4×10^{-2} Sec^{-1}.

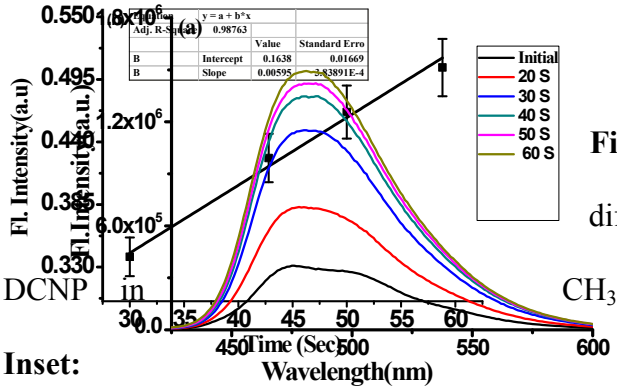
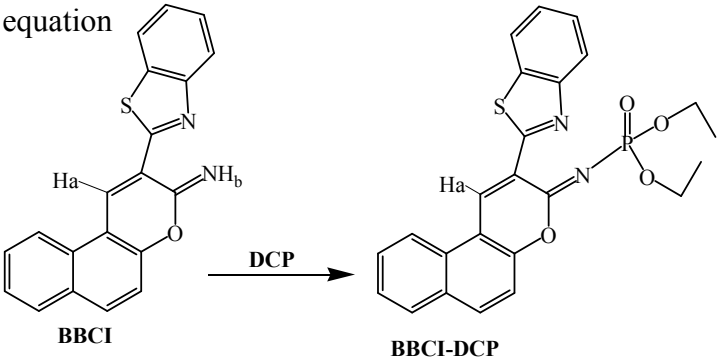


Figure S4: (a) The changes of emission spectra at different time intervals of **BBCI** in presence of DCNP in CH_3CN: HEPES buffer solution (v:v, 5:5) at pH 7.4. **Inset:** Different time intervals are shown in the rectangle ('S' denotes Second). (b) The first order rate equation by using Time vs. fluorescent intensity plot at 480 nm.



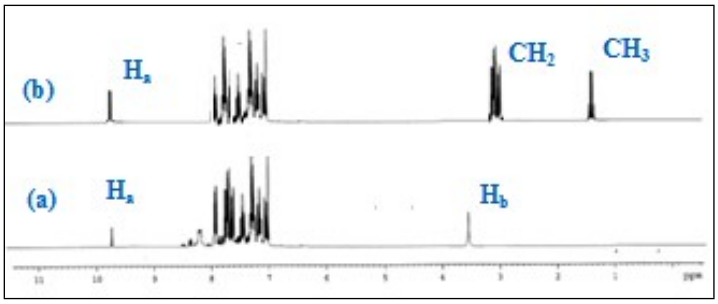
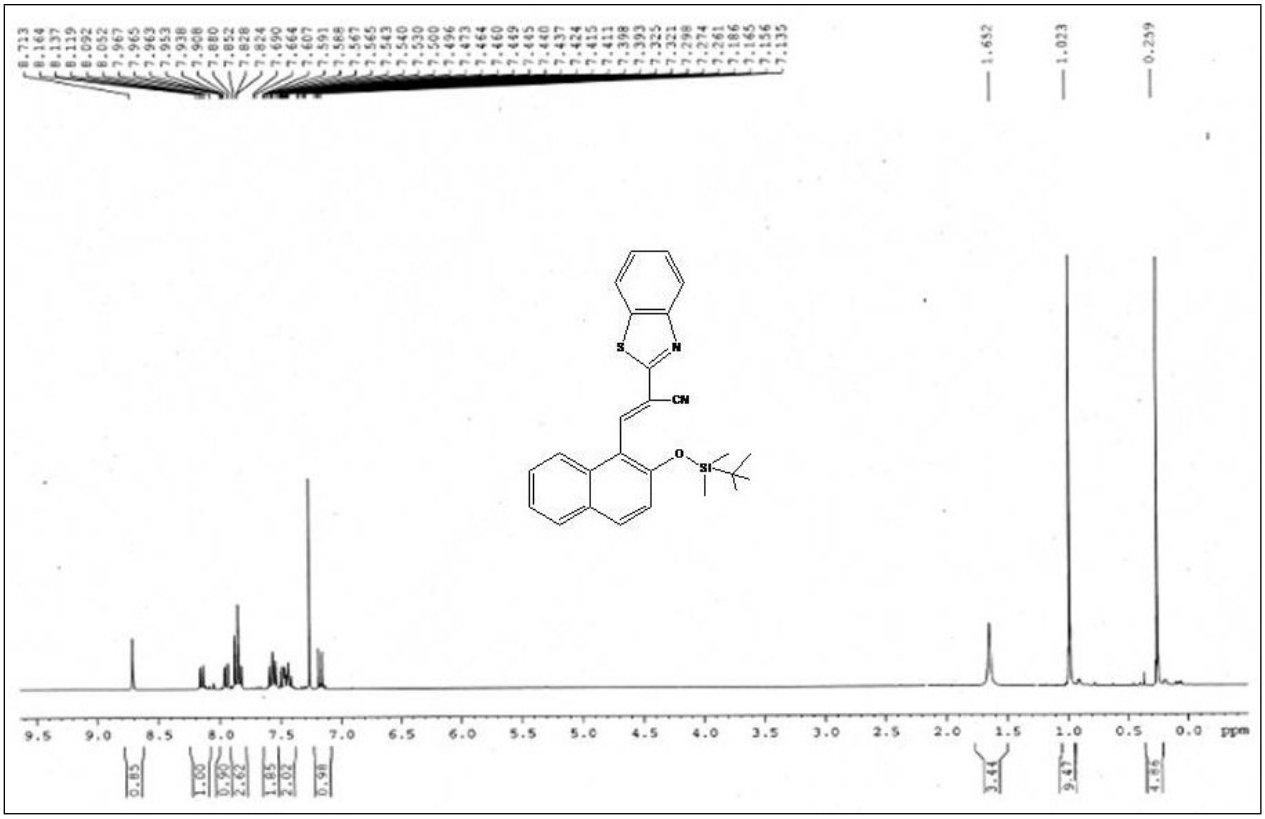
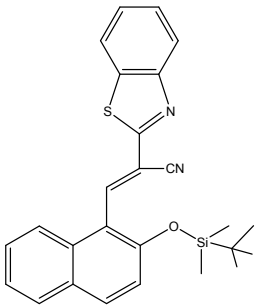


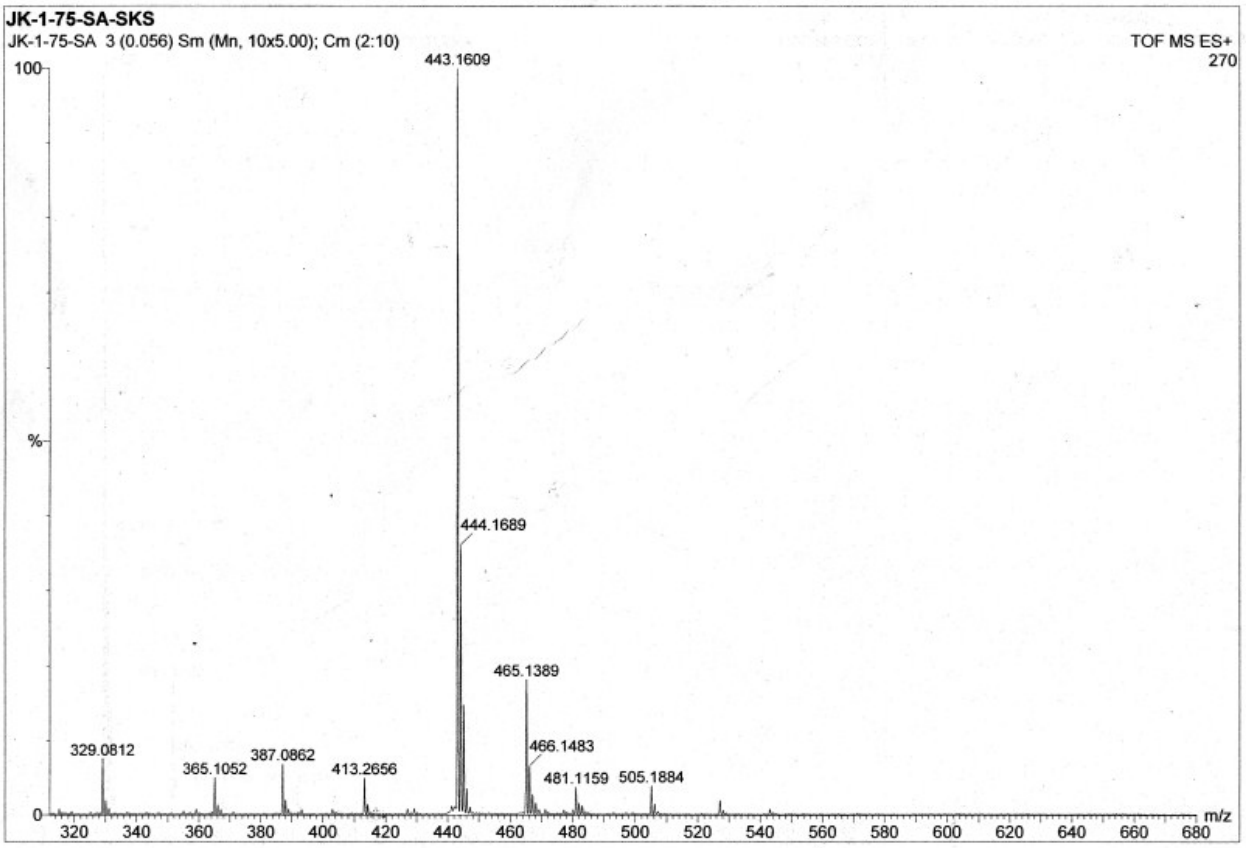
Figure S5: Comparison of partial ^{1}H-NMR spectra of (a) **BBCI**; (c) **BBCI**+DCP in $CDCl_3$.

^{1}H NMR spectra (S6) of BSNA:

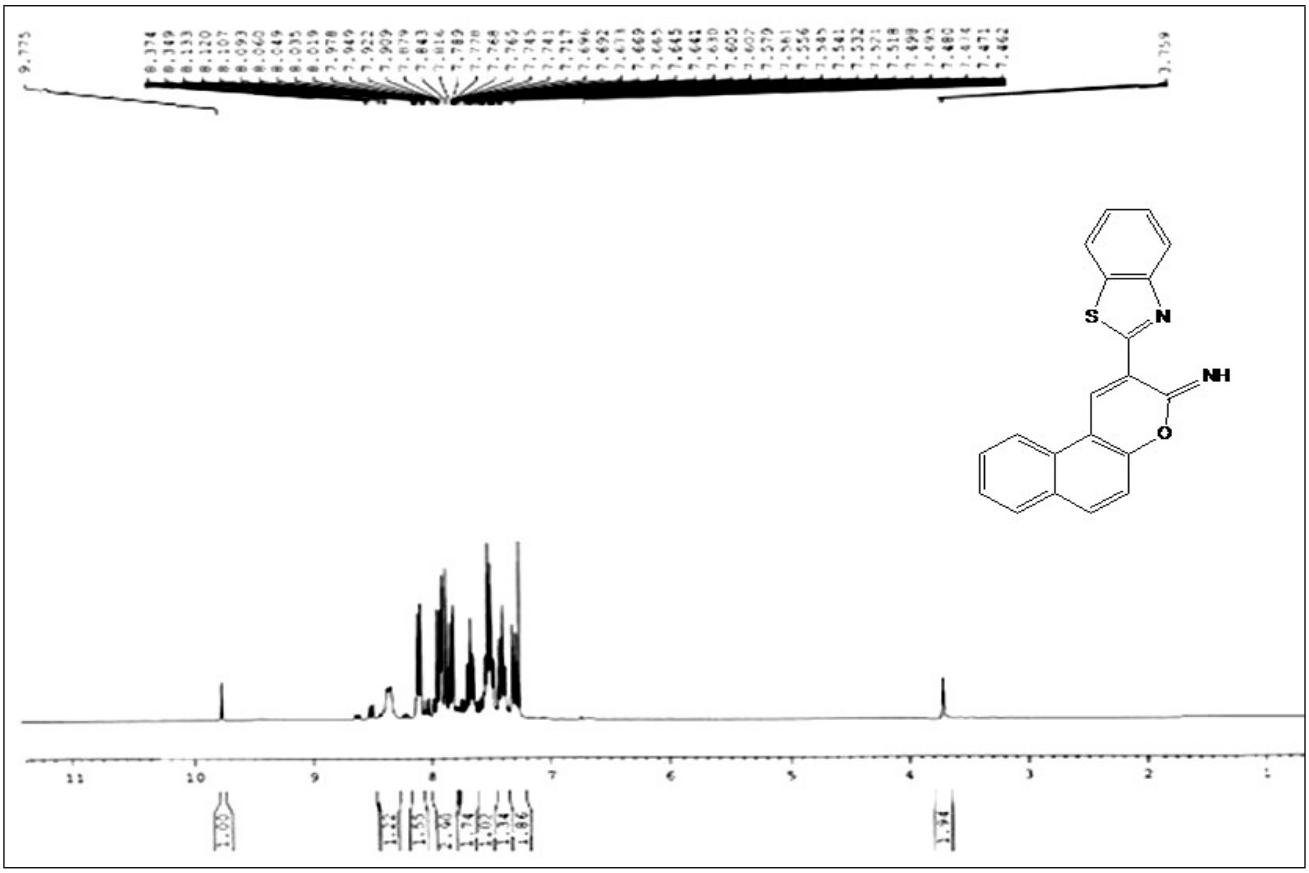


Mass spectra (S7) of BSNA:

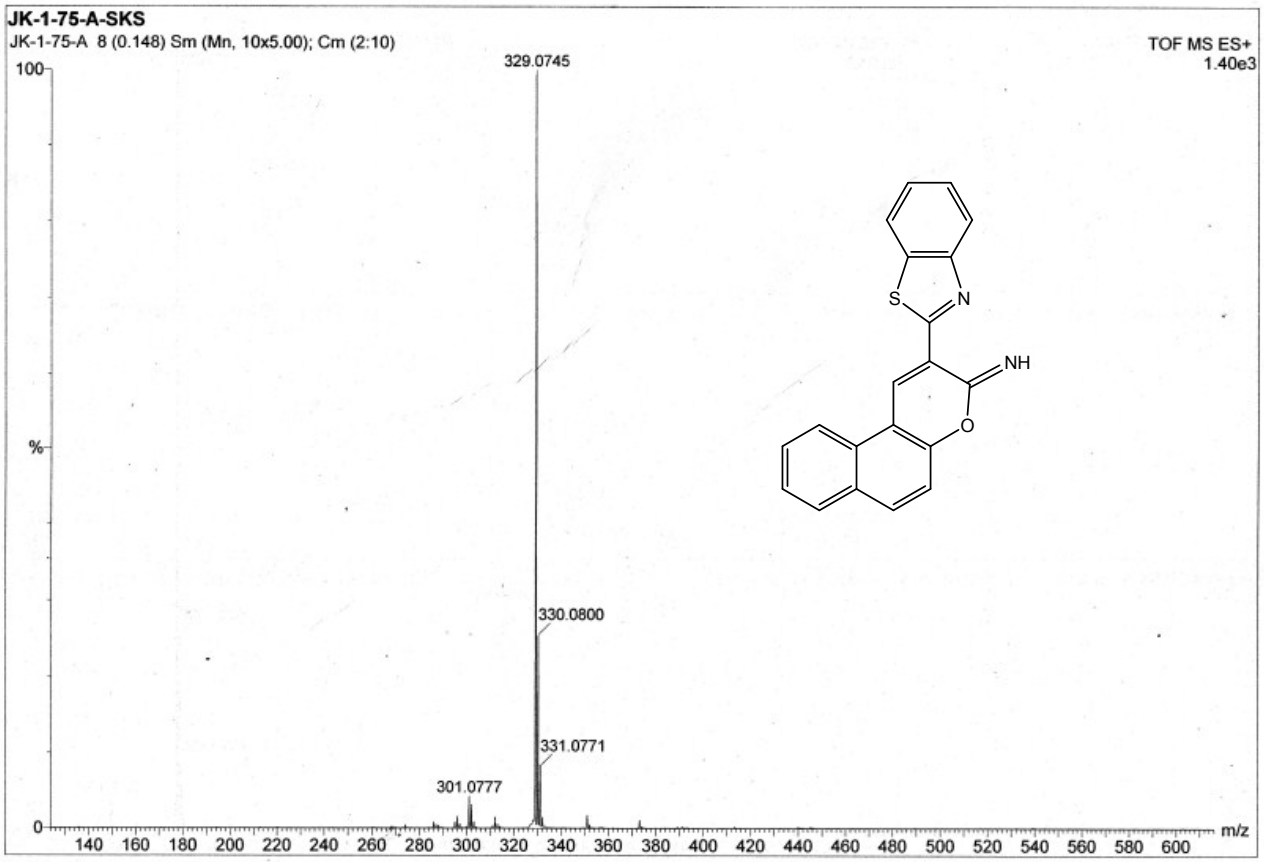



JK-1-75-SA-SKS
JK-1-75-SA 3 (0.056) Sm (Mn, 10x5.00); Cm (2:10)
TOF MS ES+
270
100
%
0
443.1609
444.1689
465.1389
466.1483
329.0812
365.1052
387.0862
413.2656
481.1159
505.1884
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
m/z

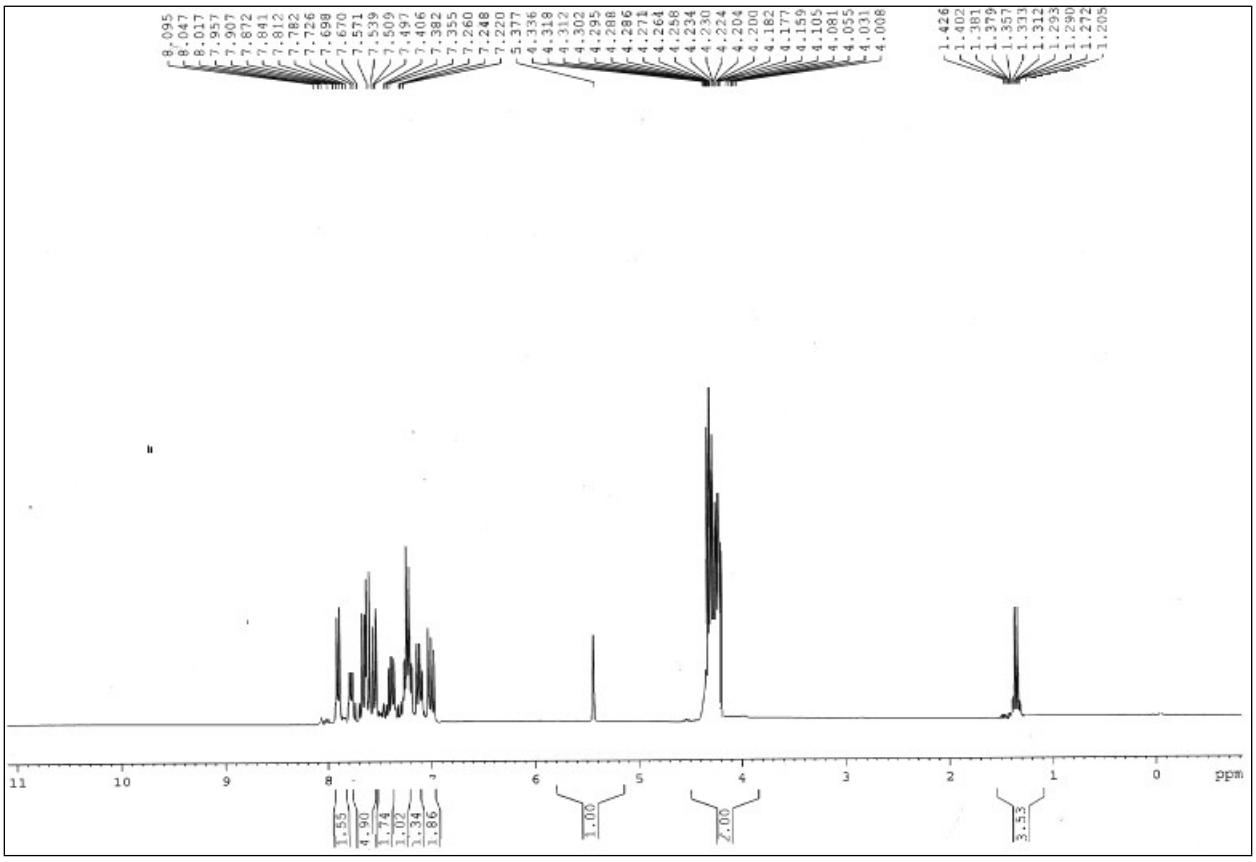
^{1}H NMR spectra (S8) of BBCI:



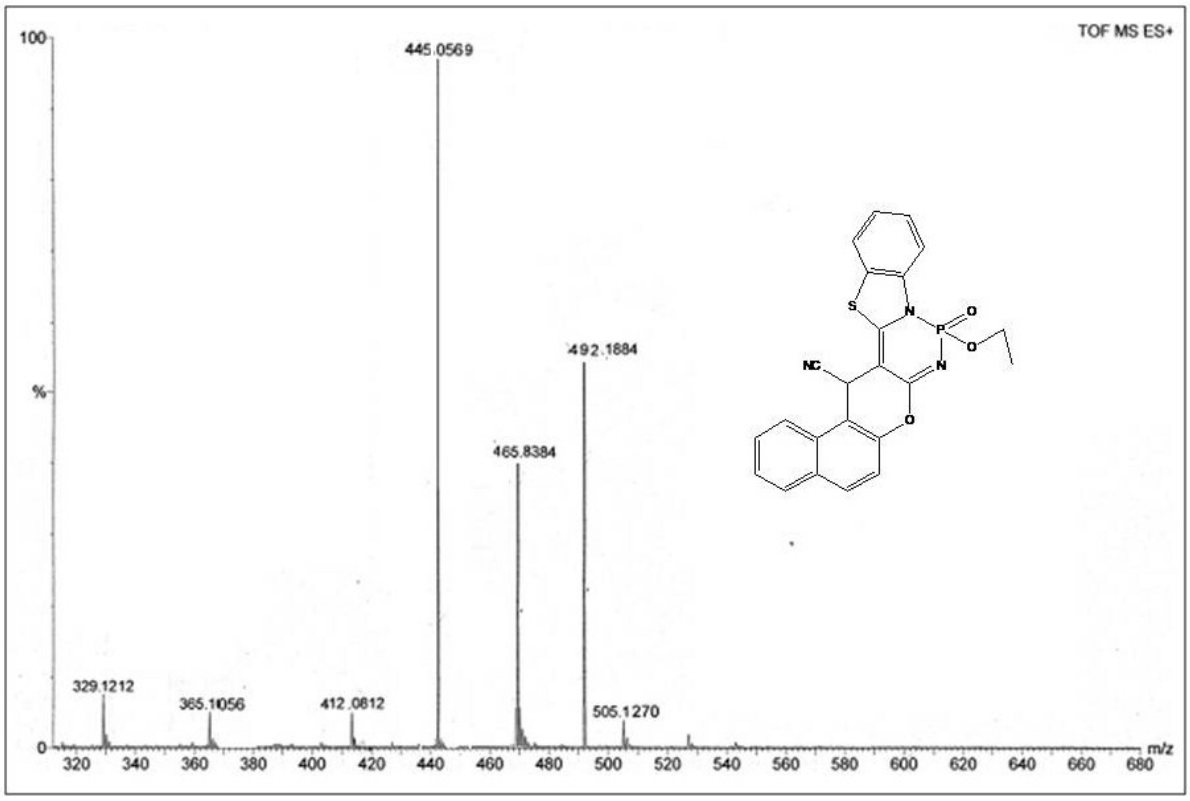
Mass spectra (S9) of BBCI:



^{1}H NMR spectra (S10) of BBCI+DCNP adduct:



Mass spectra (S11) of the resulting product BBCI+DCNP:



X-ray Crystallography:

Crystal structure of the **BBCI** was determined by single crystal X-ray diffraction from data collected at room temperature. A single crystal of 0.54 × 0.14 × 0.09 mm^3 in size was mounted on a glass fibre with epoxy cement for X-ray crystallographic study. The data were collected using a Bruker APEX II DUO CCD diffractometer with the graphite monochromated MoKα radiation at a detector distance of 5 cm and with APEX II software. The collected data were reduced using SAINT program and the empirical absorption corrections were performed using the SADABS program. The structure was solved by direct methods and refined by least-squares using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were refined isotropically. The position of the N-bound H atom was located in a difference Fourier map and refined as a riding atom: N—H = 0.8602 Å with $U_{iso}(H)$ = 1.5 $U_{eq}(N)$. The C-bound H atoms were positioned geometrically and refined using a riding model: C—H = 0.93 Å with $U_{iso}(H)$ = 1.2 $U_{eq}(C)$. Two outlier reflections, 2 1 1 and 3 5 6, were omitted from the refinement. Crystallographic data for FS397 are presented in Table X1 and has been deposited with the Cambridge Crystallographic Data Center No. CCDC 1415425.

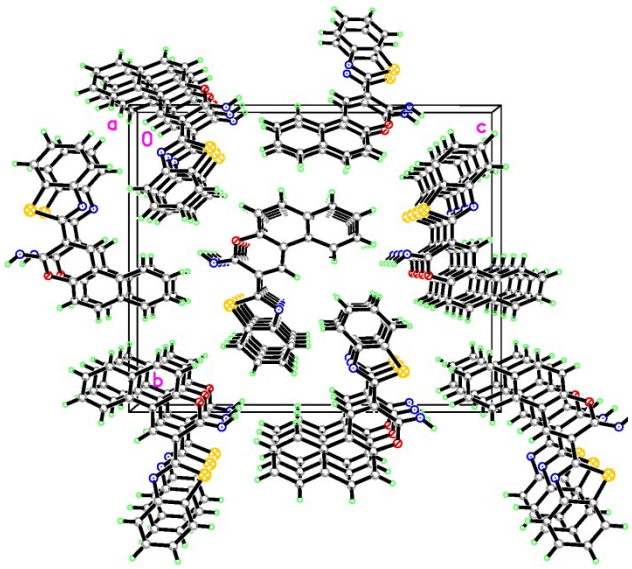


Figure S12: The crystal packing, viewed along the *a* axis, showing the molecules are stacked along the [100].

Table S1: Experimental details

Crystal data (CCDC 1415425)	
Chemical formula	$C_{20}H_{12}N_2OS$
M_r	328.38
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	294
a, *b*, *c* (Å)	4.6985 (4), 16.2304 (13), 19.7042 (15)
V (Å^3)	1502.6 (2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.22
Crystal size (mm)	0.54 × 0.14 × 0.09

Data collection	
Diffractometer	Bruker *SMART APEX* II DUO CCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.886, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14735, 3684, 3232
R_{int}	0.033
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.665
Refinement	
$R[F^2 > 2\sigma(F^2)]$,$wR(F^2)$, S	0.034, 0.084, 1.03
No. of reflections	3684
No. of parameters	217
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.14
Absolute structure	Flack x determined using 1226 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	−0.07 (3)

References:

1. (a) Reddi, A. R.; Guzman, T. R.; Breece, R. M.; Tiemey, D. L.; Gibney, B. R.; *J. Am. Chem. Soc.*, **2007**, *129*, 12815–12827. (b) Lohani, C. R.; Kim, J-M.; Chung, S-Y.; Yoon, J.; Lee, K-H.; *Analyst*, **2010**, *135*, 2079-2084.