Supporting Information

An ESIPT Fluorescence Probe and a Nanofiber Platform for Selective and Sensitive Detection of a Nerve Gas Mimic

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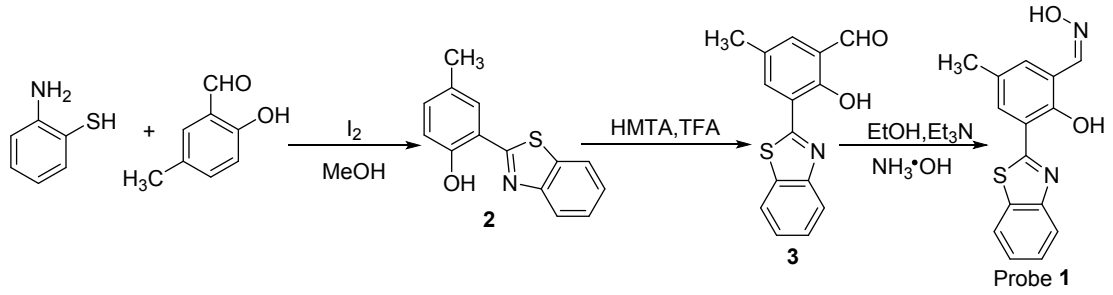
Table of Contents

1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded at 75 MHz with complete proton decoupling. Fluorescence emission spectra were obtained using a RF-5301/PC spectrofluorophotometer (Shimadzu). UV absorption spectroscopy measurements were carried out on Scinco S-3100 using a 1 cm optical path length cell at room temperature. The high resolution mass spectra (HRMS) were measured on a Bruker Ultraflex Xtreme MALDI-TOF/TOF mass spectrometer by ESI.

2. Synthetic pathway of probe 1.



Scheme S1. Synthetic pathway of probe **1**.

Synthesis of compounds 2:[1]

2-hydroxy-5-methylbenzaldehyde (680 mg, 5.0 mmol) and 2-aminobenzenethiol (550 mg, 5.0 mmol) were dissolved in anhydrous MeOH (40 mL). I_2 (630 mg, 2.5 mmol) was then added to the mixture and stirred at room temperature over night until large amounts of yellow solid was precipitated gradually. The solid was filtered and washed with cold MeOH. This yellow solid was used for the next step directly.

Synthesis of compounds 3:[1]

Compound **2** (720 mg, 3 mmol) and hexamethylenetetramine (HMTA, 630 mg, 4.5 mmol) were dissolved in 20 mL anhydrous trifluoroacetic acid (TFA). The mixture was heated to reflux and stirred over night until compound **2** was totally consumed monitored by TLC. The mixture was poured into 30 mL HCl solution (6 N) and then extracted with DCM. The combined organic solutions were removed and purified by column chromatography to afford the compound **3**. δ ^{1}H NMR (300 MHz, $CDCl_3$): 12.94 (s, 1H), 10.42 (s, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.77 (s, 1H), 7.62 (s, 1H), 7.55-7.45 (m 1H), 7.45-7.31 (m, 1H), 2.33 (s, 3H); δ ^{13}C NMR (75 MHz, $CDCl_3$): 190.61, 166.82, 158.38, 151.37, 134.92, 132.98, 132.30, 128.74, 126.72, 125.70, 123.61, 122.24, 121.46, 118.48, 20.21.

Synthesis of probe 1:[2]

Compound **3** (135 mg, 0.5 mmol) and $NH_2OH{\cdot}HCl$ (42 mg, 0.6 mmol) were dissolved in 30 mL of anhydrous EtOH. Et_3N (335 μL, 0.6 mmol) was then added to this mixture. The mixture was heated to reflux and stirred over night until most products were precipitated from the viscous solution. The solid was filtered and washed by cold MeOH.

Probe **1**: δ ^{1}H NMR (300 MHz, DMSO): 12.14 (s, 1H), 11.65 (s, 1H), 8.41 (s, 1H), 8.21 – 8.10 (m, 1H), 8.10 – 7.98 (m, 1H), 8.00-7.90 (m, 1H), 7.60 – 7.35 (m, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, DMSO): 165.78, 153.54, 151.92, 147.69, 134.68, 132.00, 130.25, 129.47, 127.38, 126.12, 122.88, 122.82, 120.42, 119.15, 20.67. HRMS (ESI) m/z = 285.0716, calcd for $[M+H]^+$ $C_{15}H_{11}N_2O_2S$ = 285.0698.

3. UV-vis spectrum of probe 1 towards DECP

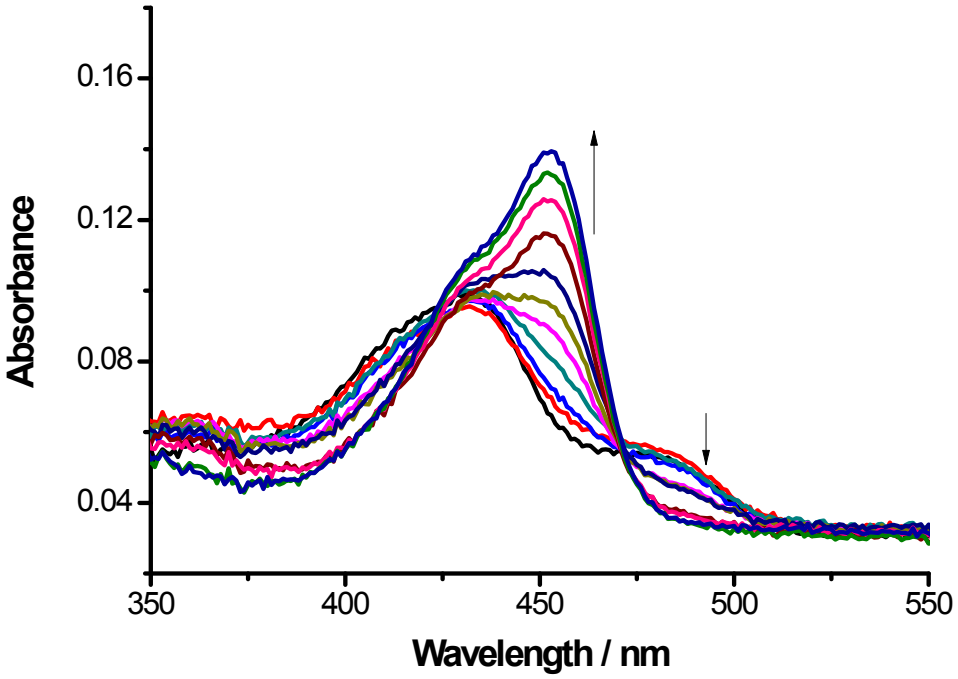
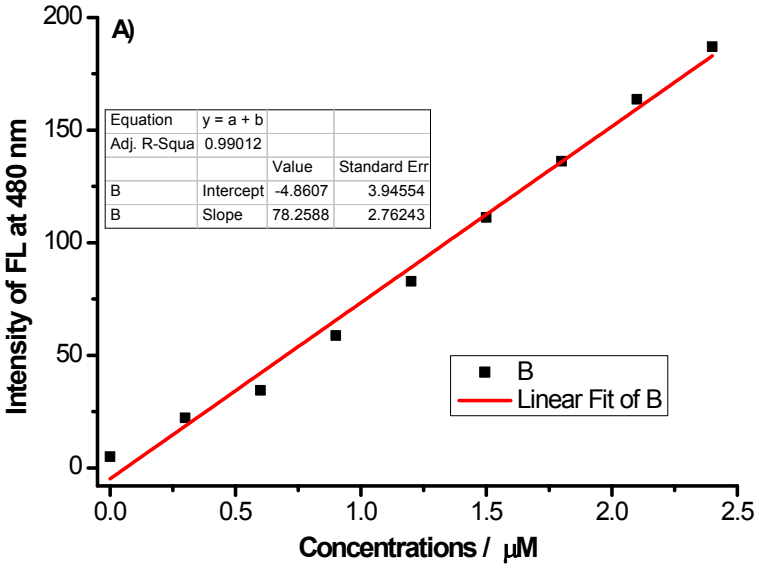
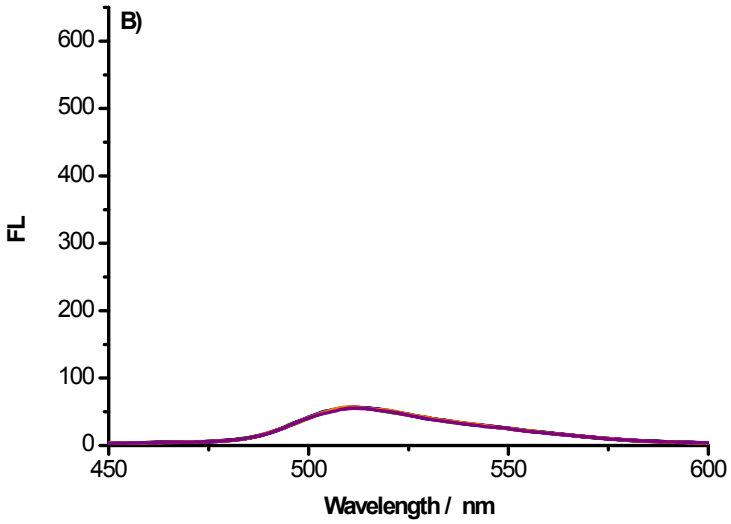


Figure S1. UV-vis spectra of probe **1** (10 μM) was obtained upon additions of DECP (0-15 μM) in DMF.

4. Detection Limit of probe 1

The detection limit was calculated on the basis of fluorescence titration results. The fluorescence emission spectra of **1** were measured, and the standard deviation of blank measurements was determined. The value for the slope was obtained by plotting the values of fluorescence intensity at 480 nm against DECP concentration. The detection limit was calculated from the equation : Detection Limit = $3\delta/k$, in which δ is the standard deviation of ten blank measurements, and k is the absolute value of the slope of fluorescence intensity at 480 nm versus DECP concentration. More details are listed following：





C)	I_{480}
7.222	
7.254	
7.226	
7.214	
7.208	
7.315	
7.237	
7.198	
7.231	
7.219	
δ	0.0329

Figure S2. Detection limit of probe **1** response to DECP: A) Linearship of fluorescence intensity at 480 nm of **1** (10 μM) to DECP concentration (0-2.5 μM); B) Fluorescence spectra of 10 μM probe **1** in DMF, λ_{ex} = 420 nm; C) Standard deviation (δ) of blank measurement from figure S2B.

5. Reaction rate of probe 1 toward DECP

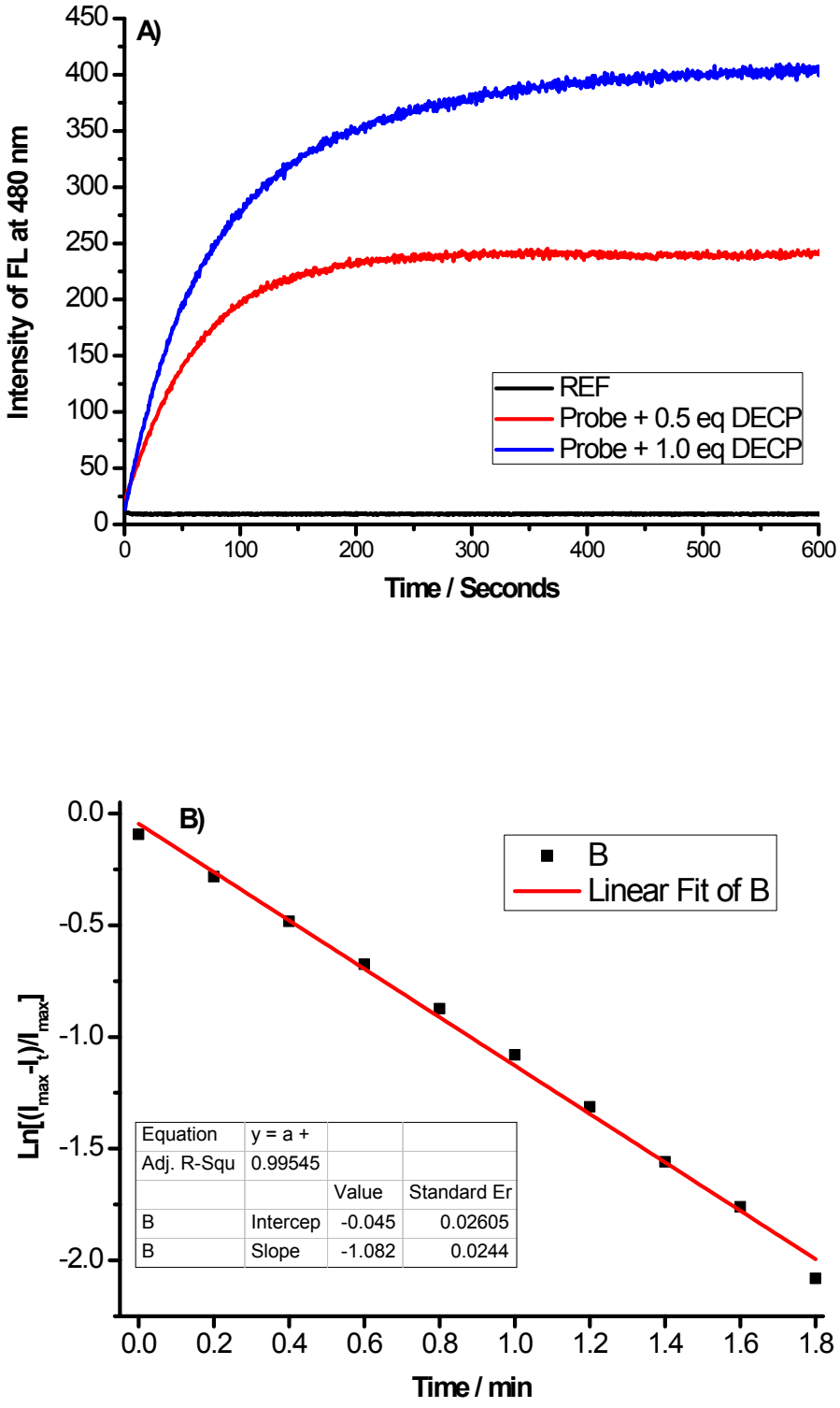


Figure S3. A) Time-dependence of the intensity of fluorescence at 480 nm for DMF solution of probe **1** (10 μM) following addition of DECP (5 μM and 10 μM); B) Pseudo first-order kinetic plot of probe **1** (10 μM) with the addition of DECP (5 μM) in DMF.

6. Sensing DECP in aqueous media

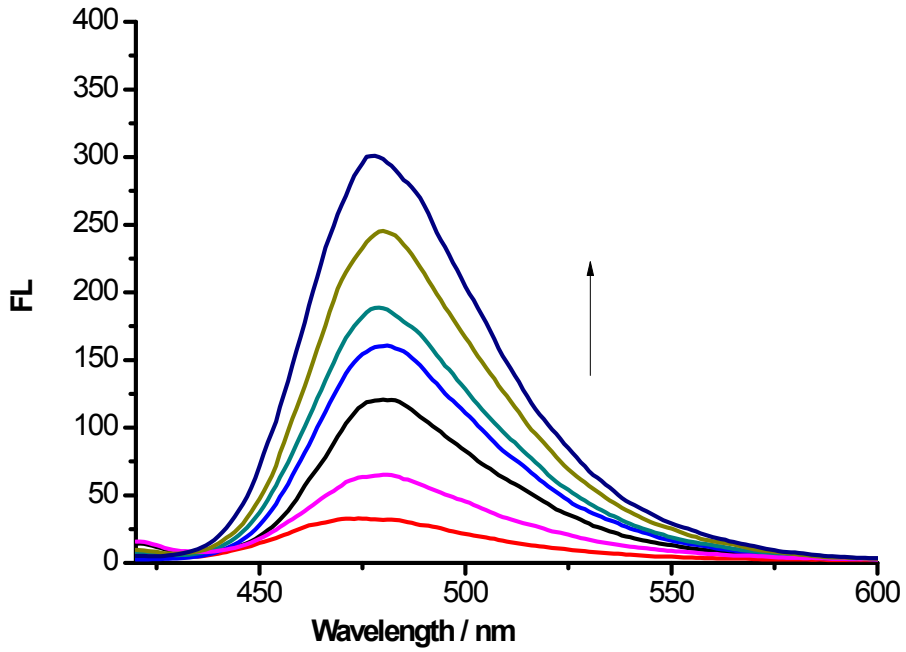
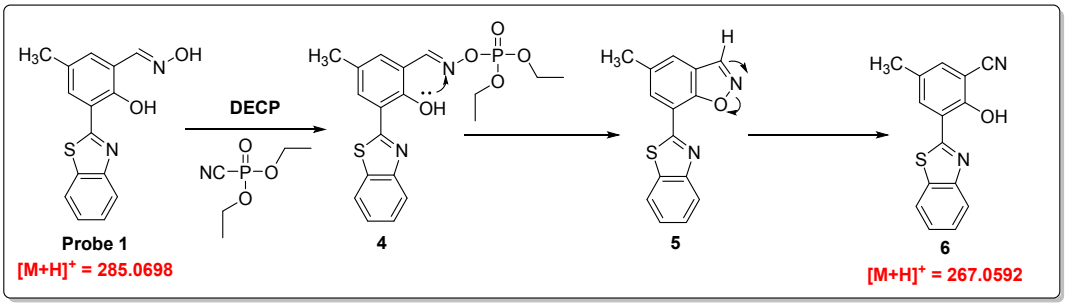


Figure S4. Fluorescence spectra of **1** (10 μM) was obtained upon additions of DECP (0-500 μM) in PBS solutions (1.0 mM; pH = 7.4); λ_{ex} = 410 nm.

7. Reaction mechanism of probe reacted with DECP



Scheme S2. Sensing mechanism of probe **1** and DECP.

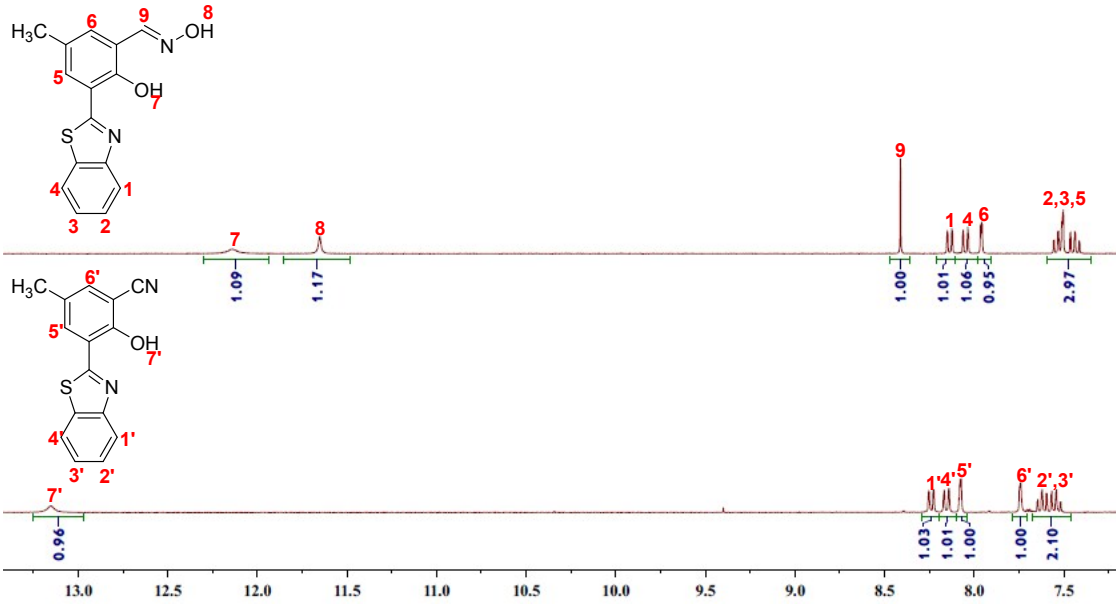
Procedure:

Probe **1** (15 mg, 0.05 mmol, 1.0 equiv.) and DECP (14.5 μL, 17 mg, 0.1 mmol, 2.0 eq.) were totally dissolved in DMF (10 mL). The reaction was stirred over night at room temperature. 20 mL H_2O was added to the mixture and extracted with dichloromethane (3*20 mL). The combined organic solvents were dried and purified by column chromatography to give the puried product **6** 10.4 mg (78 % yield).

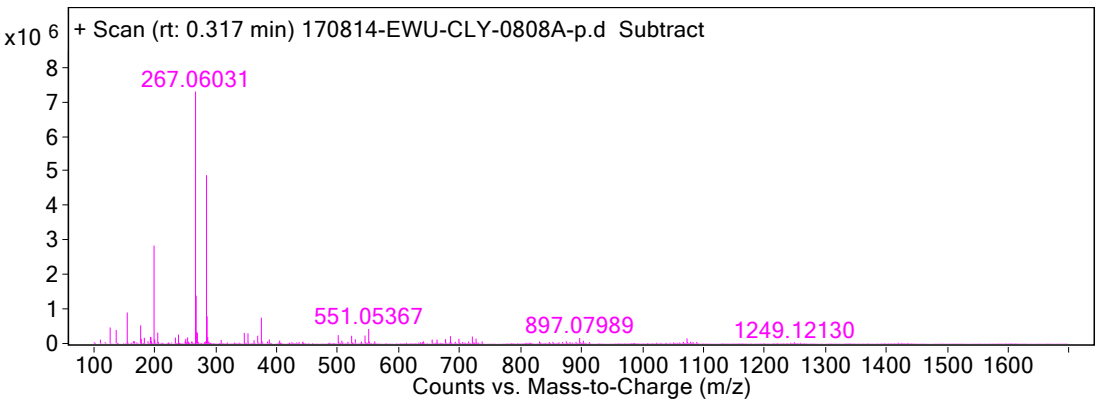
δ ^{1}H NMR (300 MHz, DMSO): 13.15 (s, 1H), 8.30-8.20 (m, 1H), 8.15 (d, J = 7.9 Hz, 1H), 8.10-8.02 (m, 1H), 7.74 (d, *J* = 1.4 Hz, 1H), 7.68 – 7.46 (m, 2H), 2.36 (s, 3H); δ ^{13}C NMR (75 MHz, DMSO): 167.17,

157.21, 151.15, 136.88, 134.05, 133.23, 130.33, 127.67, 126.72, 122.93, 122.72, 118.22, 116.49, 101.39, 19.94. HRMS (ESI) m/z = 267.0603, calcd for $[M+H]^+$ $C_{15}H_{11}N_2OS$ = 267.0592.

A)



B)



Peak List

m/z	z	Abund
127.01558		464302.63
155.04688	1	898464.31
177.02878		526028.56
199.01125	1	2837217.25
267.06031	1	7299256
268.06214	1	1387490.13
285.07008	1	4877827
286.07269	1	788559.44
375.03212	1	747342.63
551.05367	1	419661.69

Figure S5. Reaction mechanism of probe **1** and DECP: A) Partial ^{1}H NMR spectra of **1** and **6** (DMSO-d_6, 300 MHz); B) HRMS spectrum of product **6**.

8. Preparation of different concentration of DECP vapor

The sensing experiment was carried out by suspending the paper filters/spin coaters/nanofibers in the middle of a 250 mL glass flask. The flask was sealed and then heated to 150 ^{o}C. The inner atmosphere was contaminated with DECP by adding different amounts via syringe to the bottom of the flask. The concentrations of gaseous DECP were estimated to 3 ppm (0.75 μL DECP in 250 mL flask); 5 ppm (1.25 μL DECP in 250 mL flask); 10 ppm (2. 5 μL DECP in 250 mL flask) according to the reference 3. Within 5 min, it was cooled down and the photographs were taken.

9. Fluorescence response on filter papers

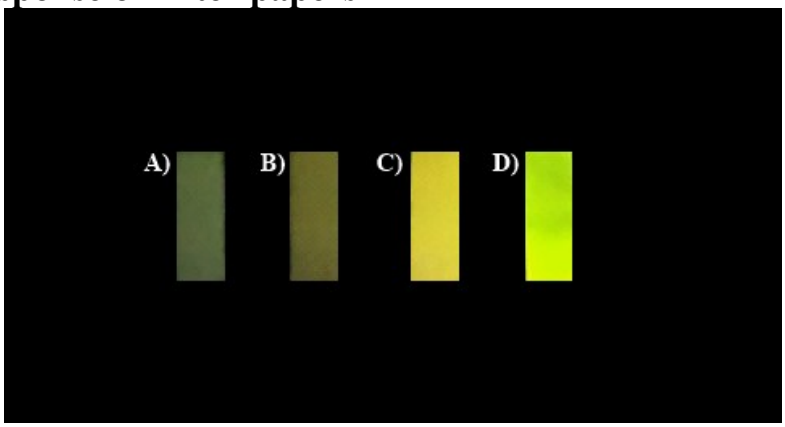


Figure S6. A) Probe **1** based filter paper under 365 nm UV lamp light; B) Fluorescent responses of probe **1** containing filter paper upon exposure to 3 ppm DECP gas under 365 nm UV lamp light; C) Fluorescent responses of probe **1** containing filter paper upon exposure to 5 ppm DECP gas under 365 nm UV lamp light; D) Fluorescent responses of probe **1** containing filter paper upon exposure to 10 ppm DECP gas under 365 nm UV lamp light.

10. Fluorescence response on spin coaters

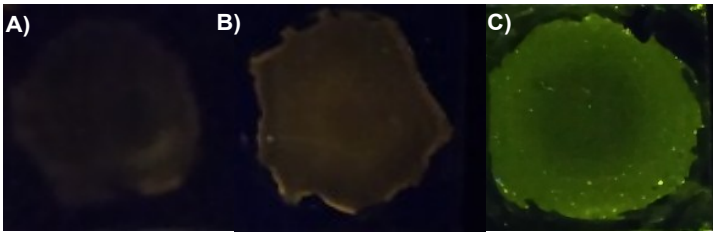


Figure S7. A) Probe **1** based filter paper under 365 nm UV lamp light; B) Fluorescent responses of probe **1** containing filter paper upon exposure to 5 ppm DECP gas under 365 nm UV lamp light; C) Fluorescent responses of probe **1** containing filter paper upon exposure to 10 ppm DECP gas under 365 nm UV lamp light.

11. Preparation of electrospun fibers

A solution of 2.0 mg of probe 1 and 440 mg of polyvinylpyrrolidone (PVP Mw ~1,300,000) in the 2.0 mL of dimethylformamide (DMF) was stirred overnight and then loaded into a syringe connected to a 21 gauge needle. The precursor solution was ejected from the syringe at a flow rate of 11-12 μL/min while applying a 12-13 kV. To fabricate uniform nanofibers, the distance between the collector, aluminum foil, and the end of the needle was 20 cm. After collecting on the substrate, the electrospun nanofibers were dried in a 40 ℃ vacuum oven for 1 h. The morphology of the nanofibers before and after exposure to DECP was determined using scanning electron microscopy (FE-SEM, JEOL JSM-7610F).

12. Preparation for the composite nanofibers

The backbone of the solid phase is the matrix polymer of PVP containing very small amounts of the probe molecules which might be randomly distributed into the entire PVP polymer at the initial stage of the electrospinning process. On the other hand, it is expected that the probe molecular phase wound be moved into the surface of PVP matrix polymer during thermal evaporation process and then when they are exposed under chemical nerve agent simulant, they could quickly response in the heterogeneous regime between the solid surface and the gas. The following figure has shown the general scheme of the preparation for the composite nanofibers:

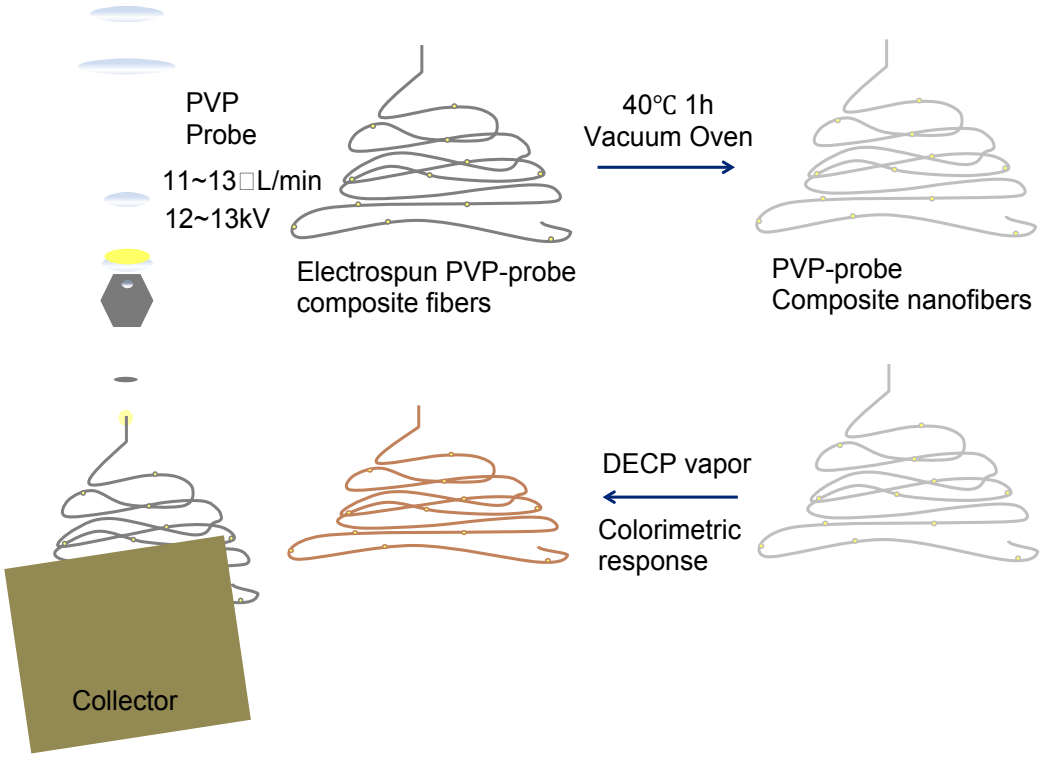
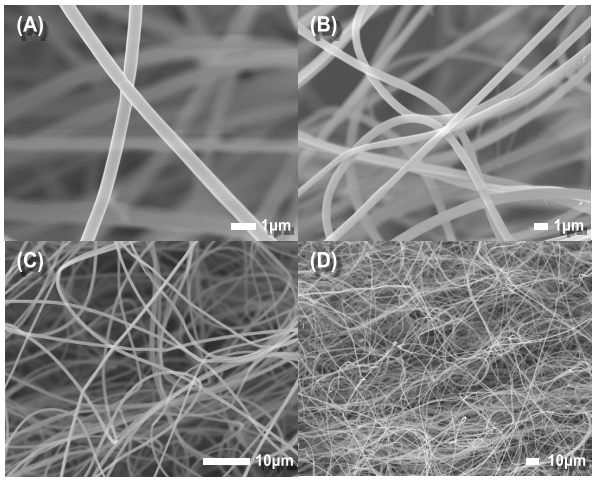


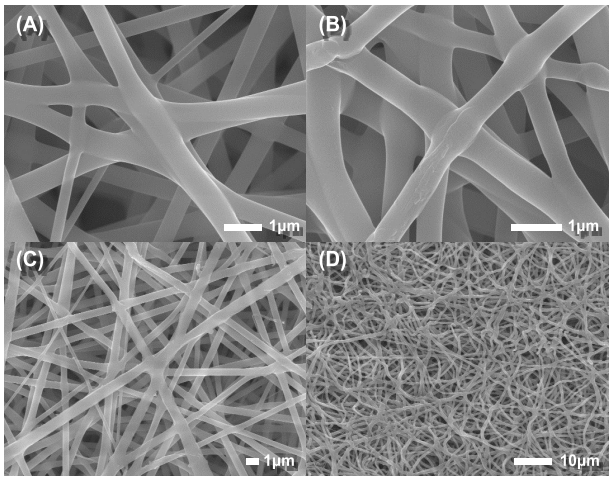
Figure S8. General scheme of the preparation for the composite nanofibers.

13. SEM images of nanofibers

(I) Before DECP exposure:



(II) After exposure to DECP for 5 min:



(III) After exposure to DECP for 10 min:

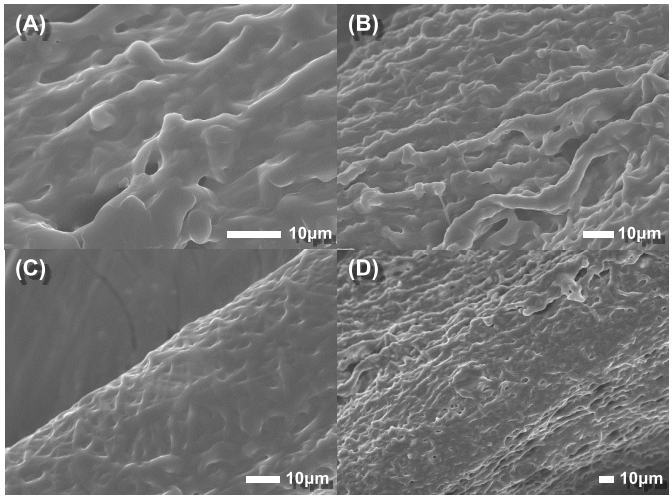
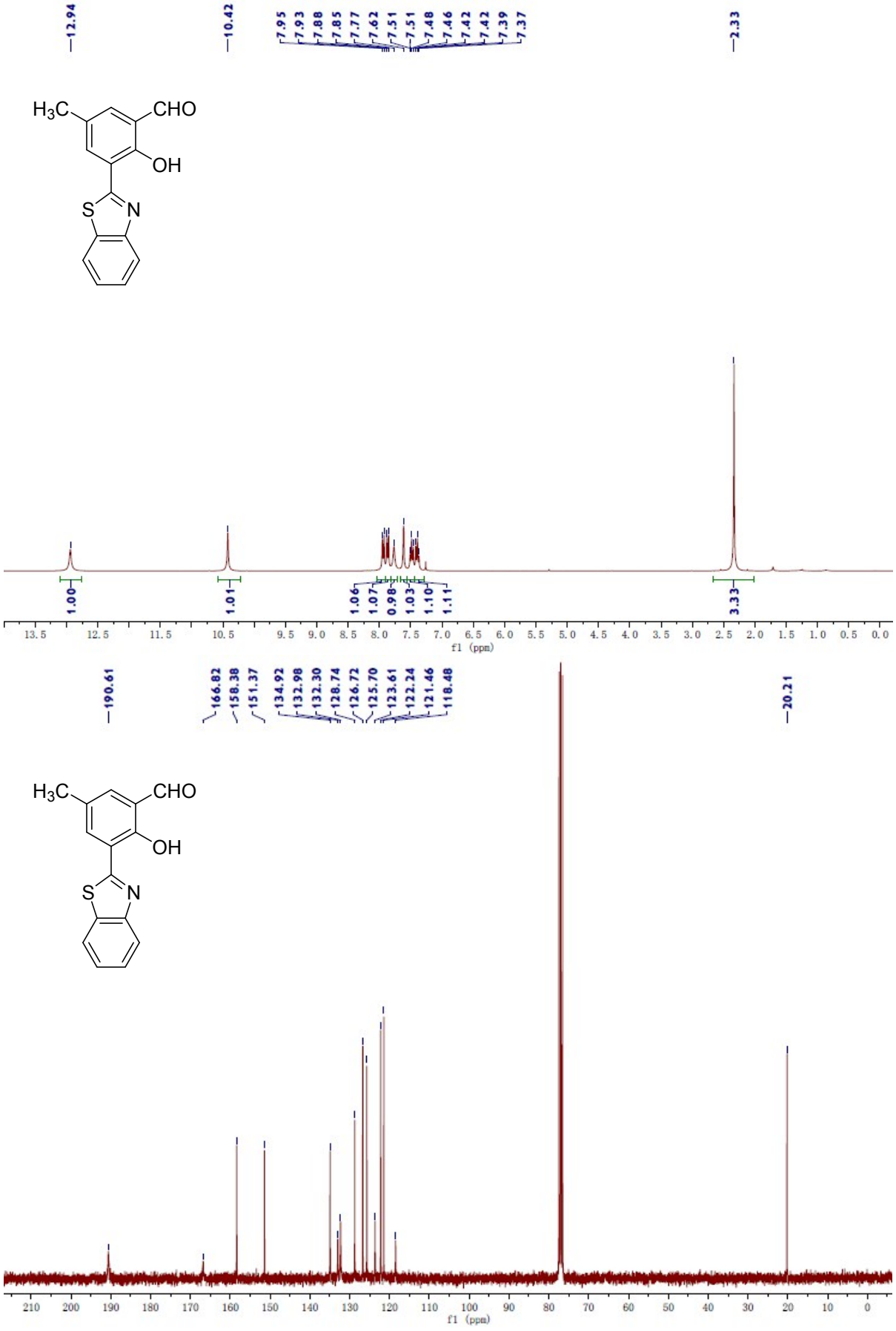
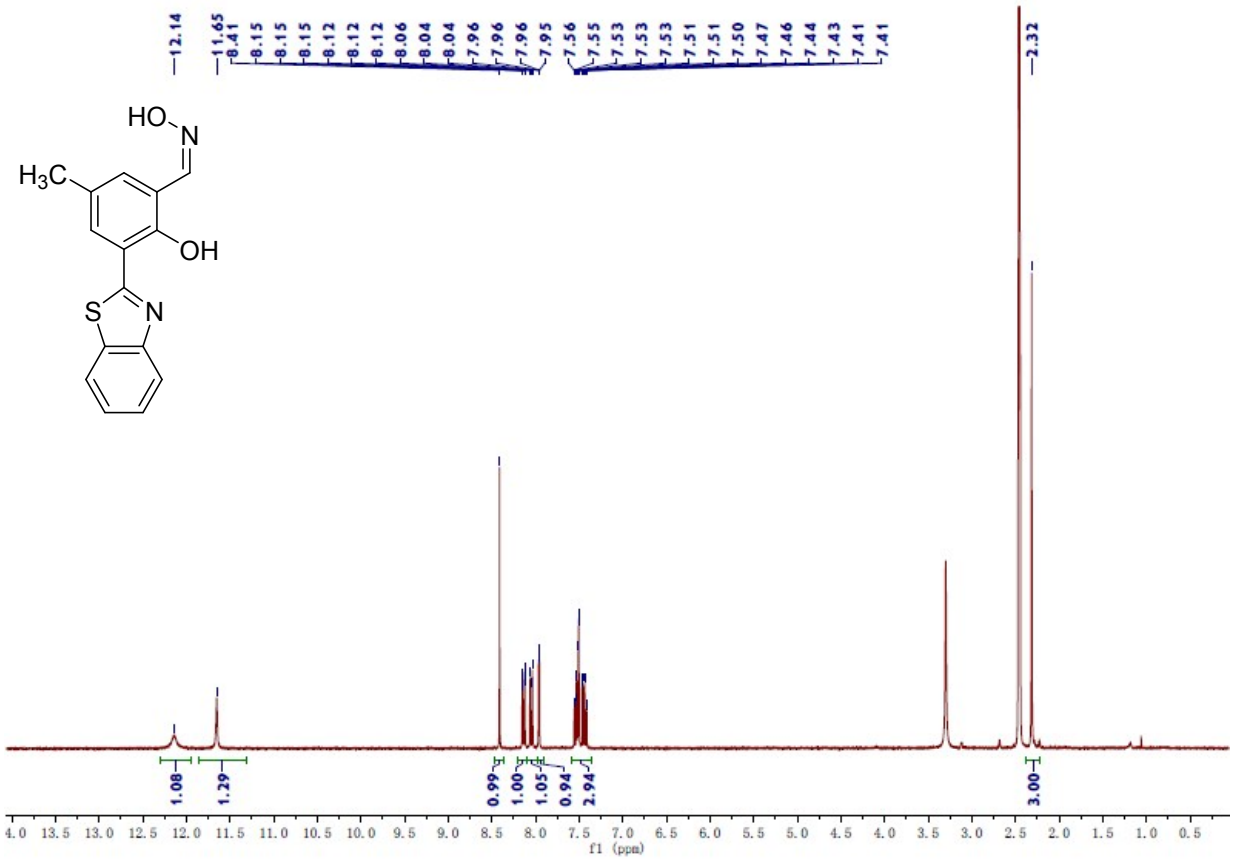


Figure S9. Scanning electron microscope images of probe **1** PVP nanofibers after exposure to 20 ppm DECP gas for 0 min (I), 5 min (II) and 10 min (III).

14. Copies of ^{1}H NMR, ^{13}C NMR and Mass Spectra

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11.65
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8.15
8.15
8.15
8.12
8.12
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7.96
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7.46
7.44
7.43
7.41
7.41
2.32
HO
N
H3C
OH
S
N
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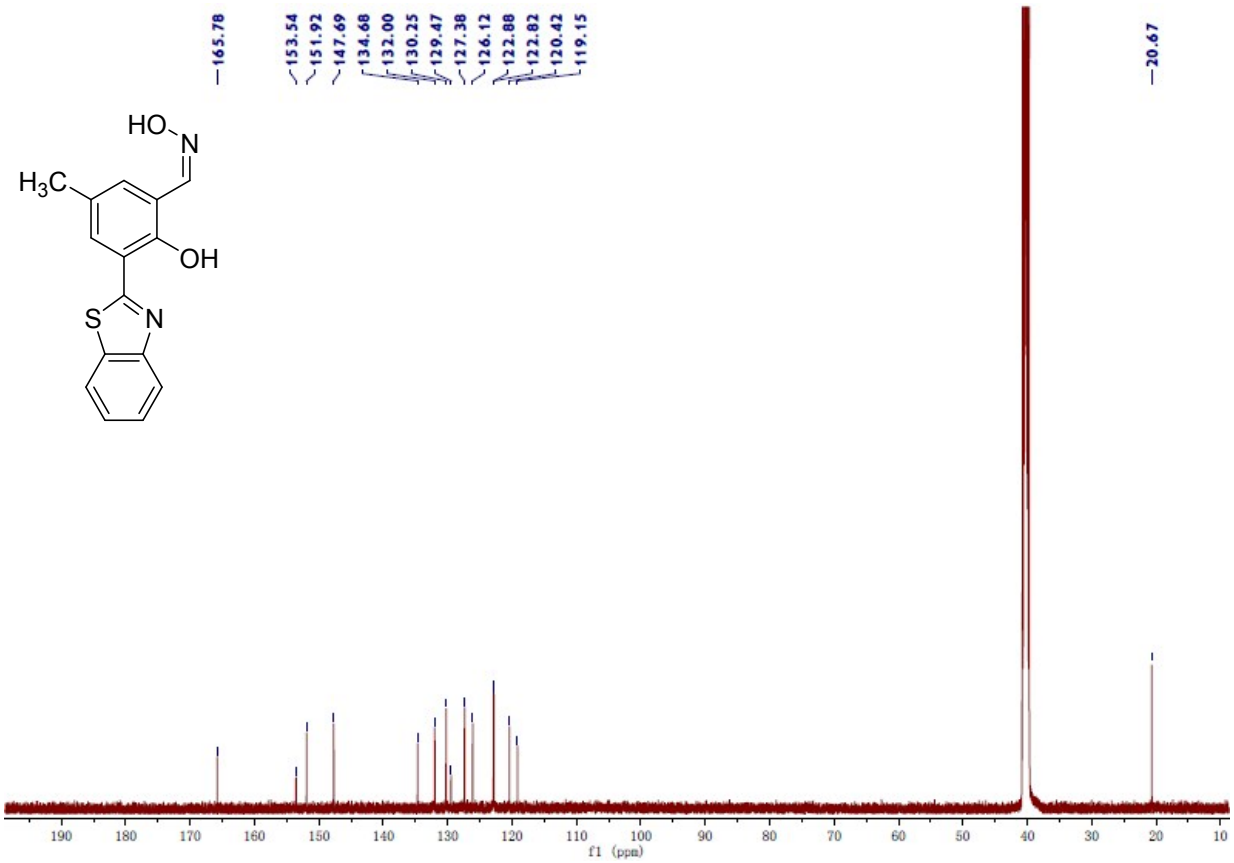
1.00
1.05
0.94
2.94
3.00
f1 (ppm)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127.38
126.12
122.88
122.82
120.42
119.15
20.67
HO
N
H3C
OH
S
N
f1 (ppm)

Fragmentor Voltage	Collision Energy	Ionization Mode
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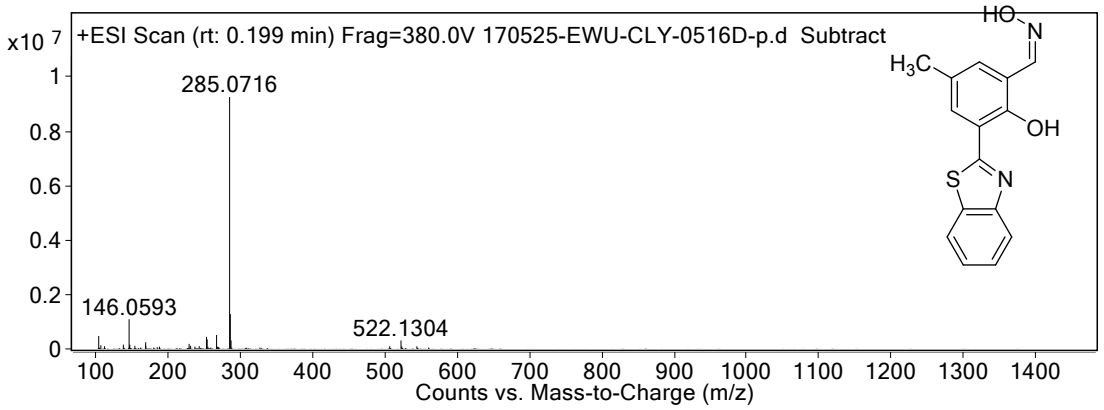

Peak List

m/z	z	Abund
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254.0644	1	352614.63
267.0595	1	511720.94
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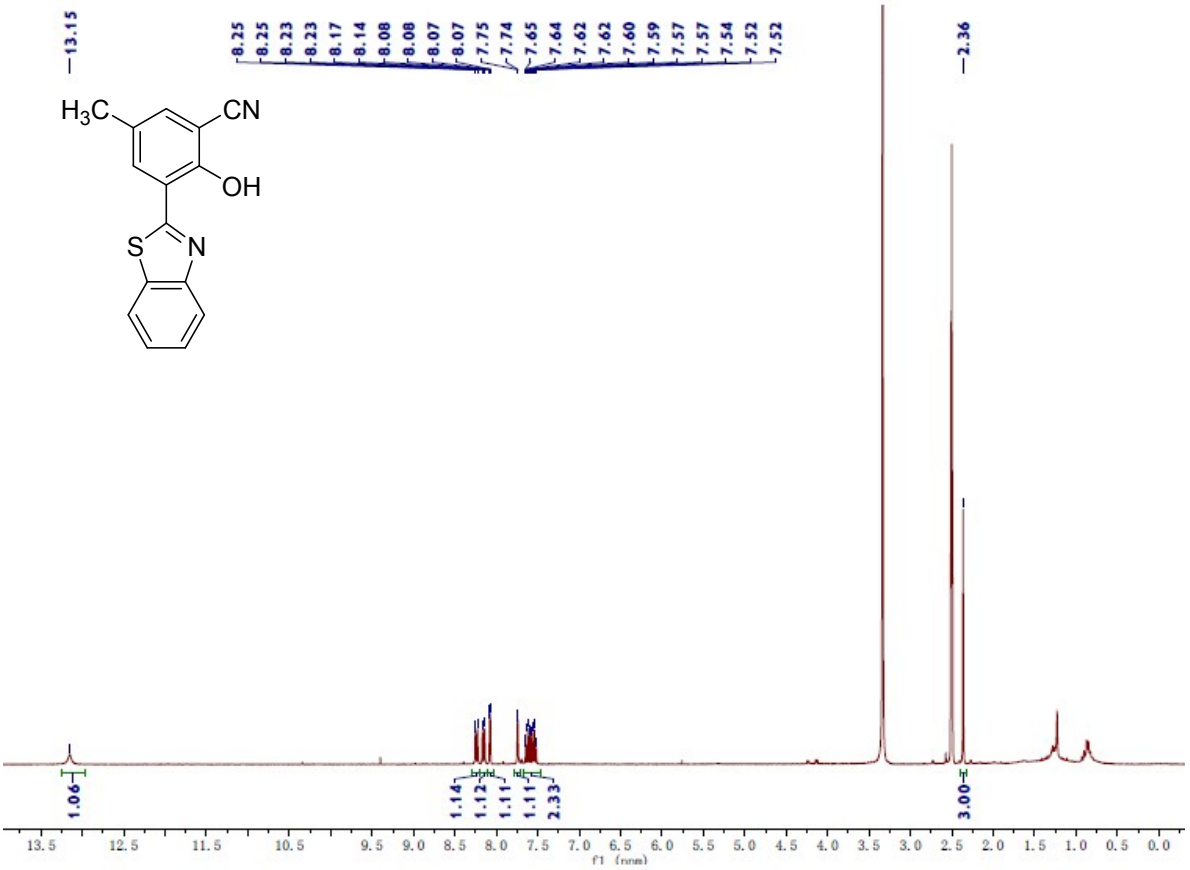
522.1304	1	312364.19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8.08
8.08
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7.65
7.64
7.62
7.62
7.60
7.59
7.57
7.57
7.54
7.52
7.52
2.36
H3C
CN
OH
S
N
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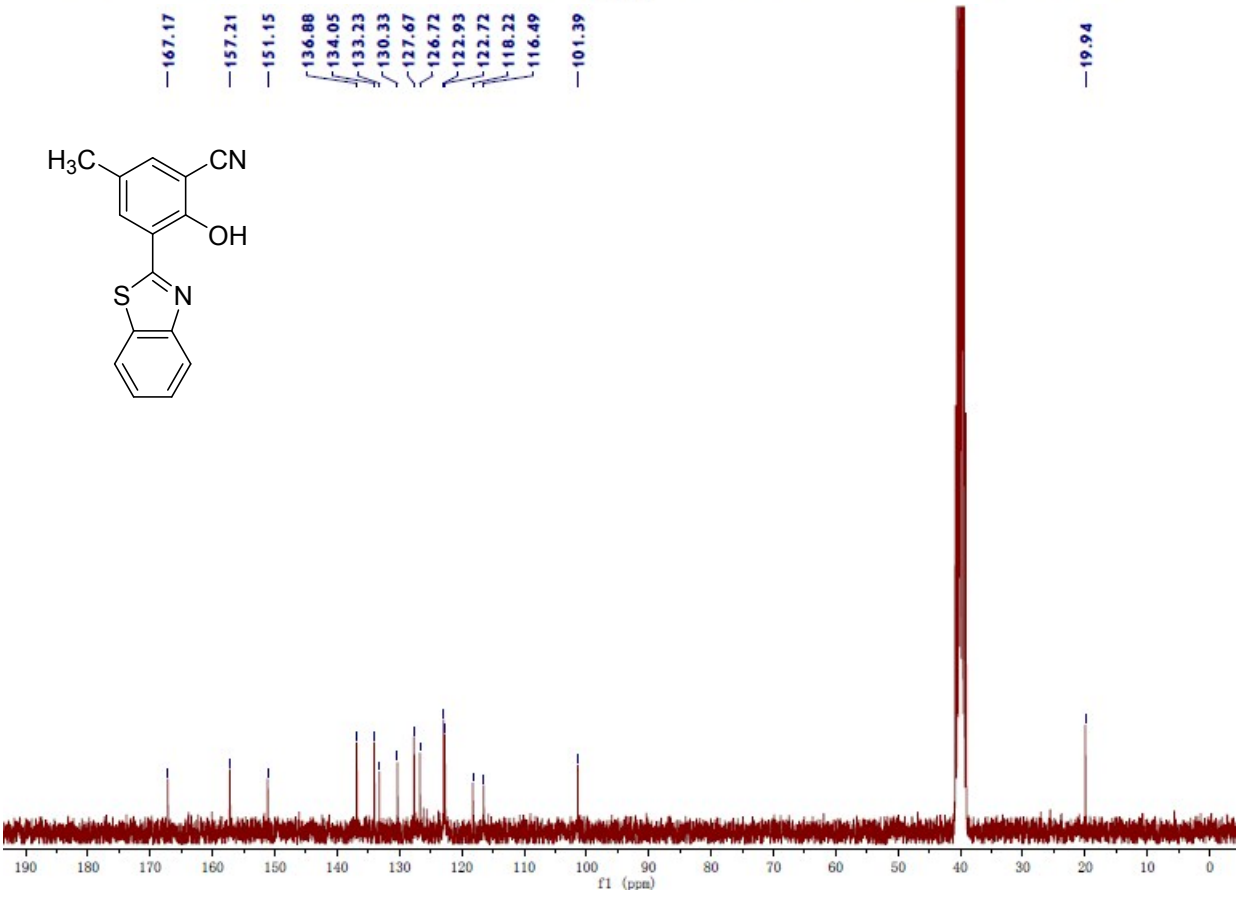
1.14
1.12
1.11
1.11
2.33
3.00
f1 (ppm)


167.17
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127.67
126.72
122.93
122.72
118.22
116.49
101.39
19.94
H3C
CN
OH
S
N
f1 (ppm)

15. References

(1) Huang, Z.; Ding, S.; Yu, D.; Huang, F.; Feng, G. Aldehyde group assisted thiolysis of dinitrophenyl ether: a new promising approach for efficient hydrogen sulfide probes. *Chem. Commun.* **2014**, *50*, 9185-9187.

(2) Yang, Y. J.; Tsay, O. G.; Murale, D. P.; Jeong, J. A.; Segev, A.; Churchill, D. G. Novel and selective detection of Tabun mimics. *Chem. Commun.* **2014**, *50*, 7531—7534.

(3) Gotor, R.; Costero, A. M.; Gaviña, P.; G. Salvador; Ratiometric Double Channel Borondipyrromethene Based Chemodosimeter for the Selective Detection of Nerve Agent Mimics. Dyes. Pigm. **2014**, *108*, 76-83.