

## SUPPORTING INFORMATION

### Novel and selective detection of Tabun mimics

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## Experimental Section

All reagents used herein were used as received from the suppliers (Aldrich, Acros, and Junsei companies). Synthetic details for the preparation of the dipyrromethanes and for the BODIPY systems follow literature methods.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were acquired using a Bruker Avance 400 MHz spectrometer. TMS was used for  $^1\text{H}$  NMR and phosphoric acid was used for  $^{31}\text{P}$  NMR spectra as internal standards. ESI-mass spectrometry was performed on a VG AUTOSPEC ULTIMA by the research support staff at KAIST. This instrument possesses a trisector double focusing magnetic sector analyzer and was operated at a resolution of 80,000. Absorption spectra were measured using a JASCO V-530 UV/Vis spectrophotometer. Fluorescence measurements were carried out with a Shimadzu RF-5301pc spectrofluorophotometer (slit width Ex, Em = 1.5).

## General Remarks.

### Synthesis

**Compound 1** 5-bromo-2-hydroxybenzaldehyde (2.0 g, 10 mmol) and 20 mL of THF was added into a round bottle flask and then 200 mg of NaBH<sub>4</sub> was added in 3 portions. This mixture was stirred for 30 min at 0°C and during the reaction, the color of the mixture changed from white to yellow and then to white again. Then, this mixture was washed by water and diethyl ether. Diethyl ether phase was collected and dried. White solid was obtained. Yield (1.84 g, 9.06 mmol, and 92 %).

**Compound 2, 3, 4 and 5** These species were synthesized by previous methods (Fig. S1)<sup>1</sup>.

### Compound 6

Probe **6** was prepared by a multistep reaction starting from 5-bromo-2-hydroxybenzaldehyde. Synthetic procedure of intermediate **5** has been previously reported.

Compound **5** (27 mg, 0.073 mmol), NH<sub>2</sub>OH·HCl (5.0 mg, 0.072 mmol) and Et<sub>3</sub>N (40 μL, 0.072 mmol) were added into round bottom flask followed by 20 mL of DCM. Then, this mixture was refluxed for 6 h at 40 °C. This mixture was cooled down to room temperature and DCM was removed by rotary evaporation. 1 mL of THF and DCM was added and the mixture was allowed to stand overnight. Red crystals were thus obtained. Yield (52.3 mg, 55.04 %).

$^1\text{H}$  NMR (300 MHz, THF: 3.58 and 1.73 ppm)  $\delta$ , 10.75 (s, 1H, OH), 10.33 (s, 1H, OH), 7.29 (s, 1H, CH), 7.21 (d,  $^3J_{\text{H-H}} = 8.64$  Hz, 1H), 7.07 (d,  $^3J_{\text{H-H}} = 8.37$  Hz, 1H), 6.01 (s, 2H), 2.48 (s, 6H, 2CH<sub>3</sub>), 1.48 (s, 6H, 2CH<sub>3</sub>). HMS (ESI) calculated for C<sub>20</sub>H<sub>20</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Na<sup>+</sup>: 406.1509, m/z value found 406.1509 (M + Na)<sup>+</sup>, 789.3153 (2M + Na)<sup>+</sup>.

### Compound 12

Na<sub>2</sub>CO<sub>3</sub> (2.39 g, 22.6 mmol) and NH<sub>2</sub>OH·HCl (1.57 g, 22.6 mmol) were added into a round bottom flask and dissolved in 20 mL of water and 5 mL of ethanol at room temperature over the course of 5 min. Then, benzaldehyde (1.92 mL, 18.8 mmol) was added to the mixture and was stirred for another 15 min. This reaction was monitored by TLC; then the mixture was extracted with ethyl acetate and washed with water 3 times. The extracted part was dried using anhydrous Na<sub>2</sub>SO<sub>4</sub>; ethyl acetate was removed under vacuum. A transparent liquid was obtained.<sup>2</sup> Yield (1.87 g, 82.3 %).

$^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>) :  $\delta$  7.36 (s,  $^1\text{H}$ ), 7.39–7.47 (m, 3H), 7.91–7.97 (m, 2H), 8.35 (s, OH, D<sub>2</sub>O exchangeable);  $^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  128.4, 130.1, 130.3, 130.8, 147.0; HMS(EI): m/z calcd for C<sub>7</sub>H<sub>7</sub>NO: 121.0528; found: 121.0529.

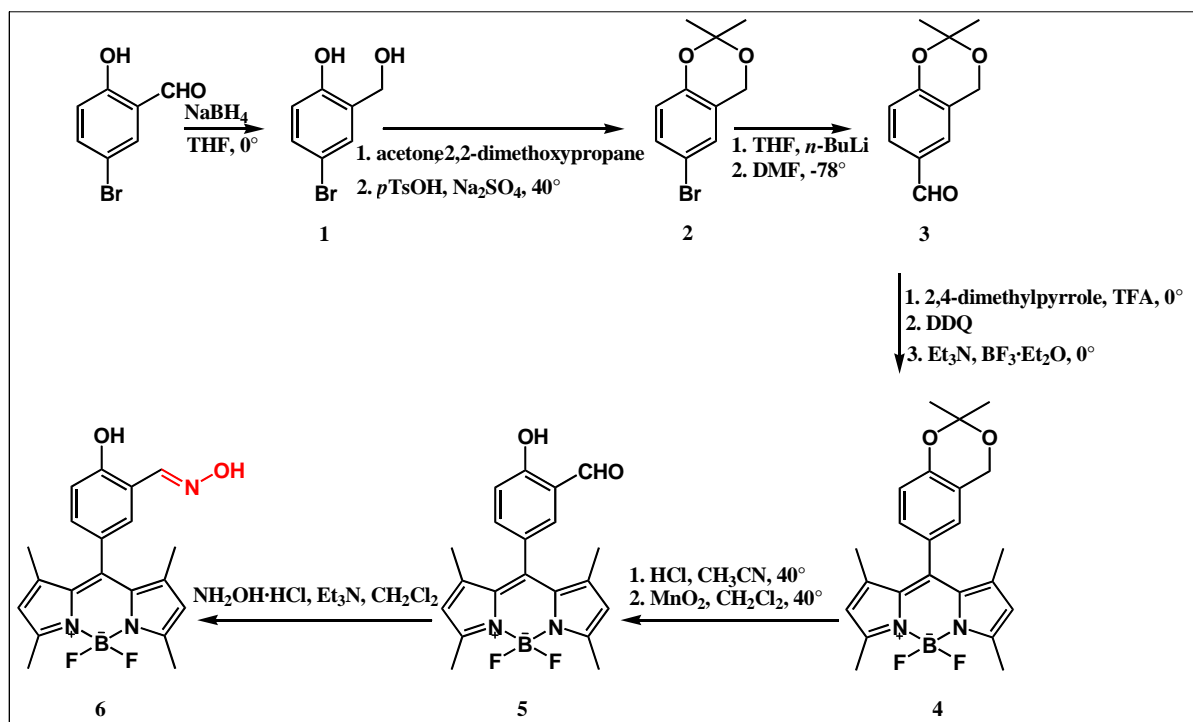
### Compound 13

NH<sub>2</sub>OH·HCl (521 mg, 7.50 mmol) and NaOH (300.0 mg, 7.50 mmol) was dissolved in 20 mL of deionized water. Salicylaldehyde (610.6 mg, 5.00 mmol) was added; the mixture was stirred at 80 °C for 4 h. The organic phase was extracted with ethyl acetate and dried with

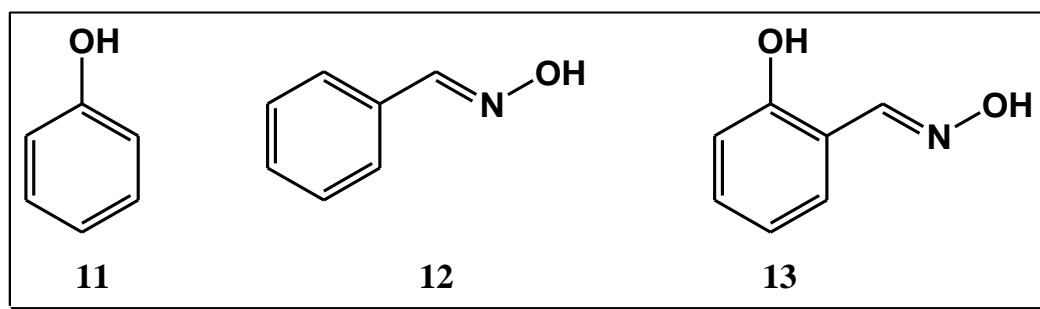
Na<sub>2</sub>SO<sub>4</sub> anhydrous; ethyl acetate was evaporated under vacuum. A light brown solid was obtained.<sup>3</sup> Yield (657.0 mg, 95.8 %).

### **General procedure for synthesis of model molecules**

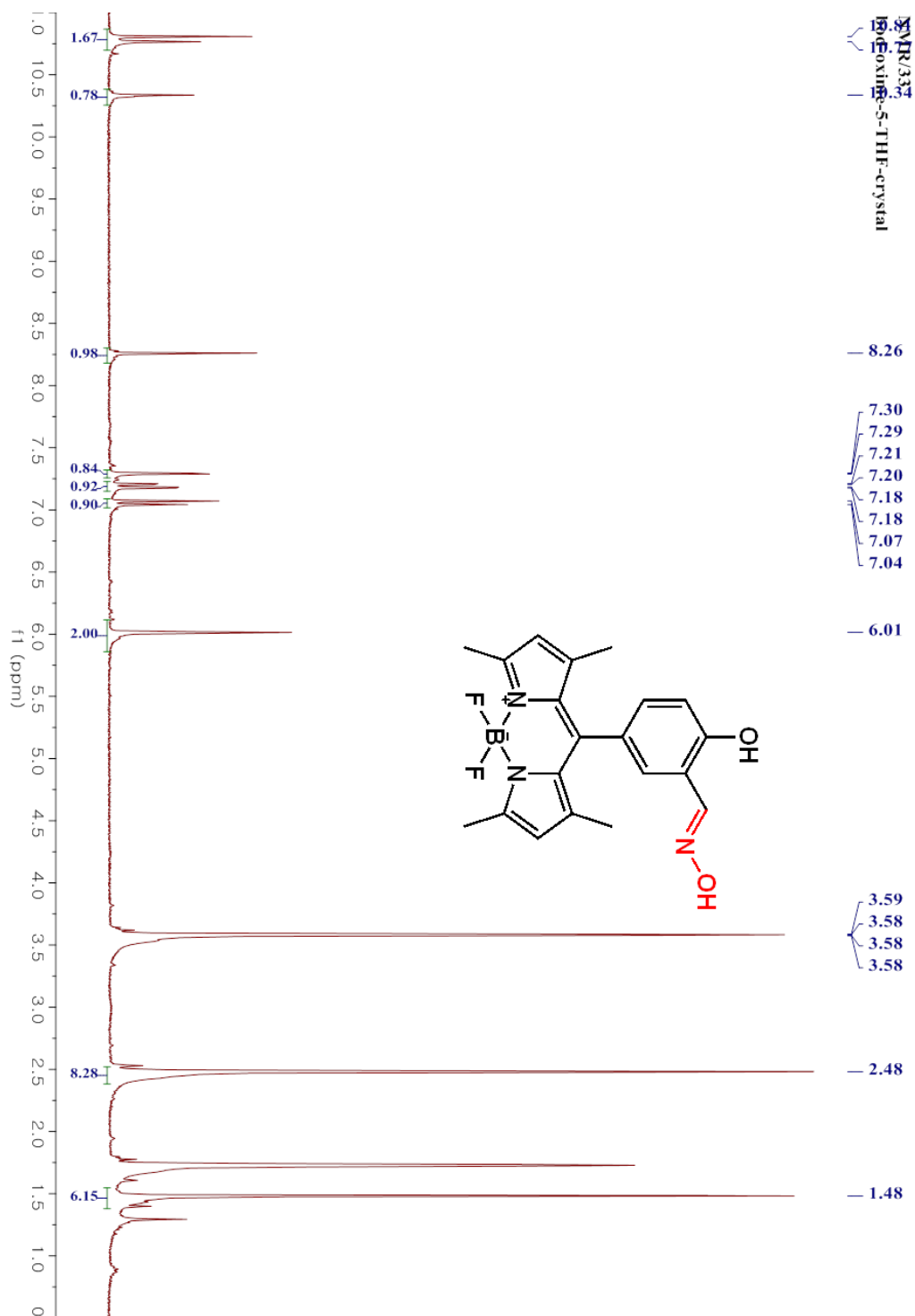
50 mg of phenol and oxime (compounds **12** and **13**) was dissolved in 4 mL of acetonitrile and 1 equiv triethylamine; diethyl chlorophosphate or diethyl cyanophosphonate was then added, respectively. These mixtures were stirred at room temperature overnight (12 h). These reactions were monitored by TLC. Acetonitrile was removed by rotary evaporator and the major compound was purified using a small silica gel chromatographic column (hexane and dichloromethane).



**Figure S1.** Synthesis of compound **6**.

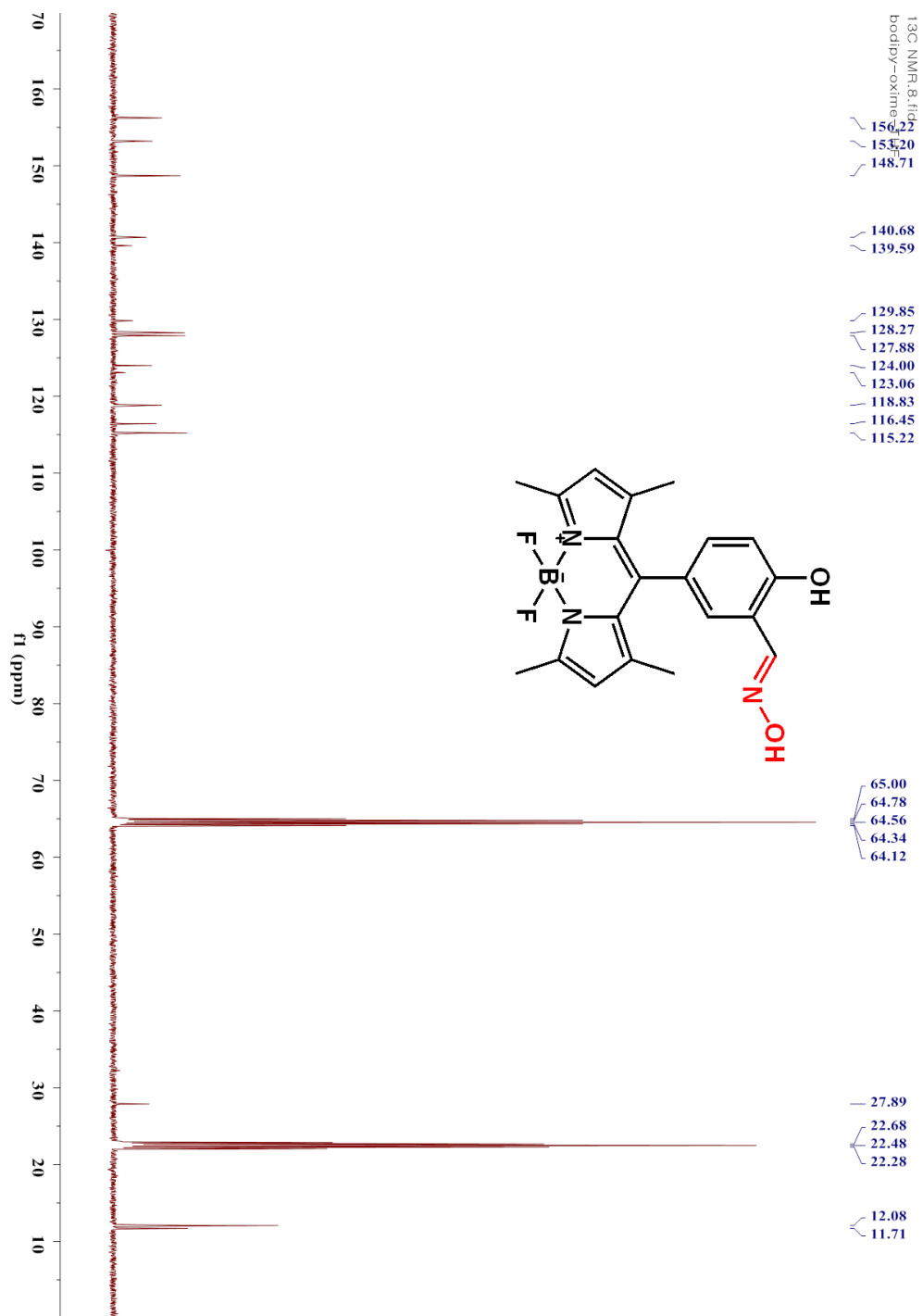


**Figure S2.** Chemical structures for the model study: phenol (compound **11**), benzaldehyde oxime (compound **12**), and salicylaldehyde oxime (compound **13**).



**Figure S3.** <sup>1</sup>H NMR spectrum of compound **6** in THF-d<sub>8</sub>.





**Figure S4.** <sup>13</sup>C NMR spectrum of compound **6** in THF-d<sub>8</sub>.

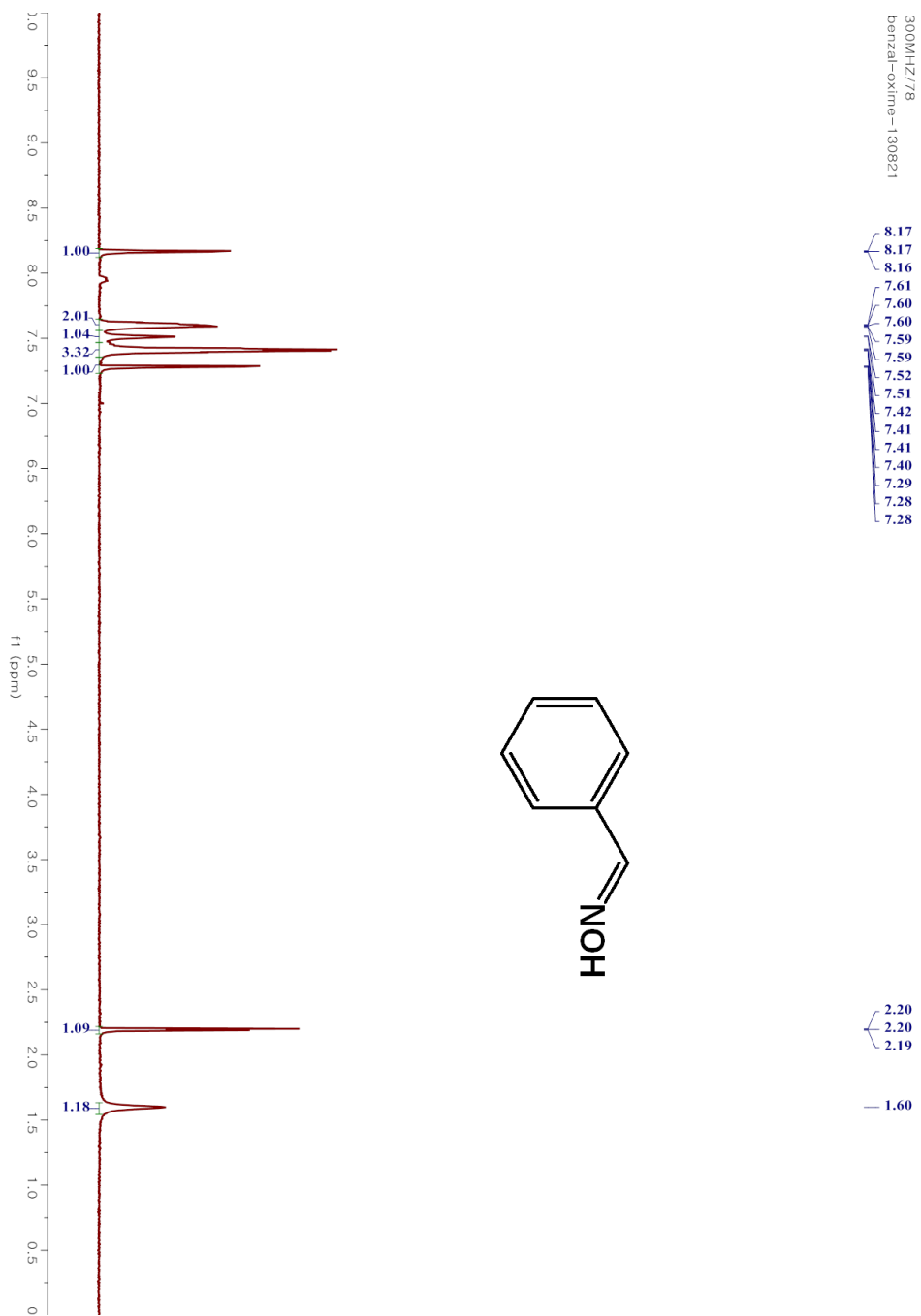
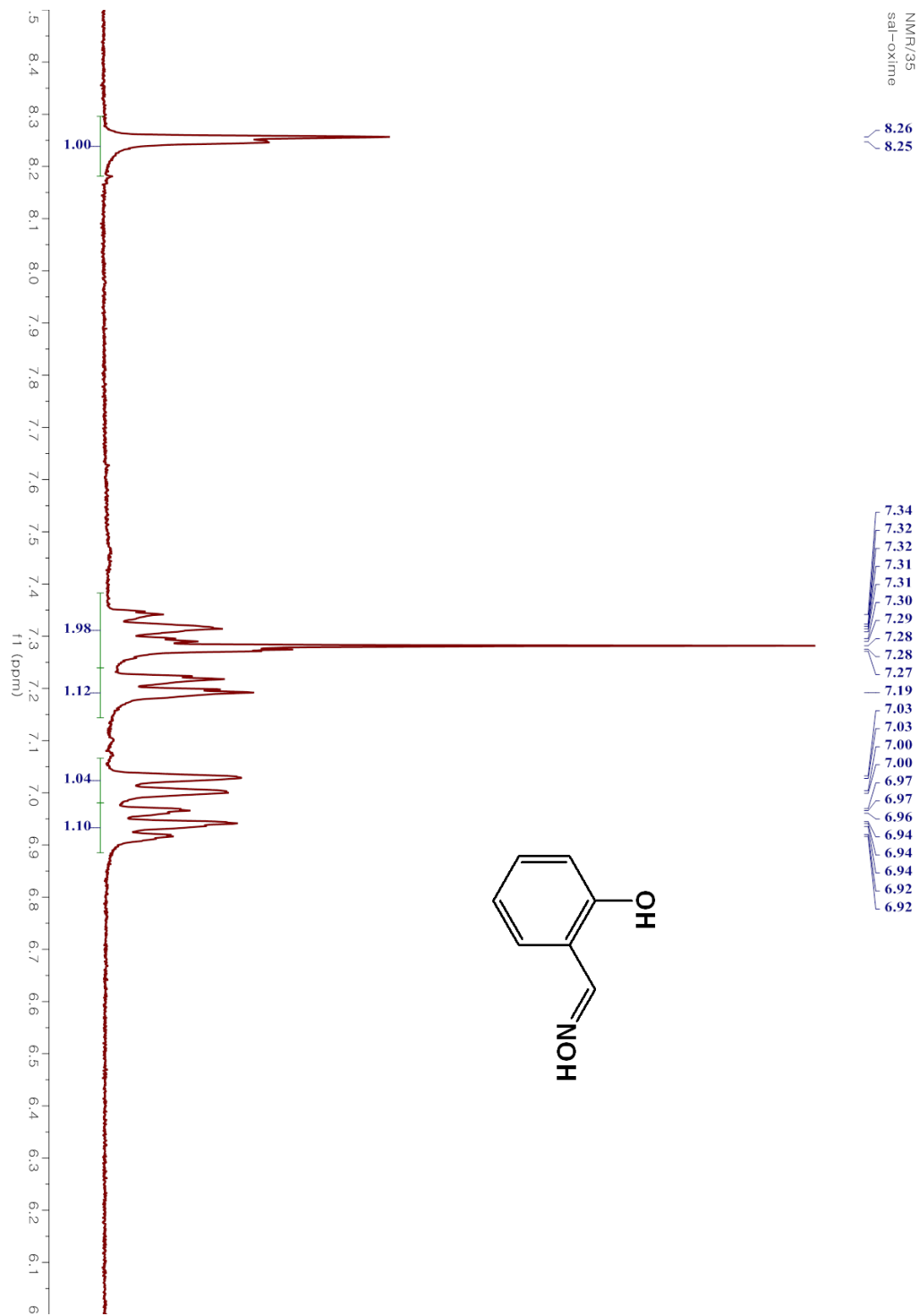
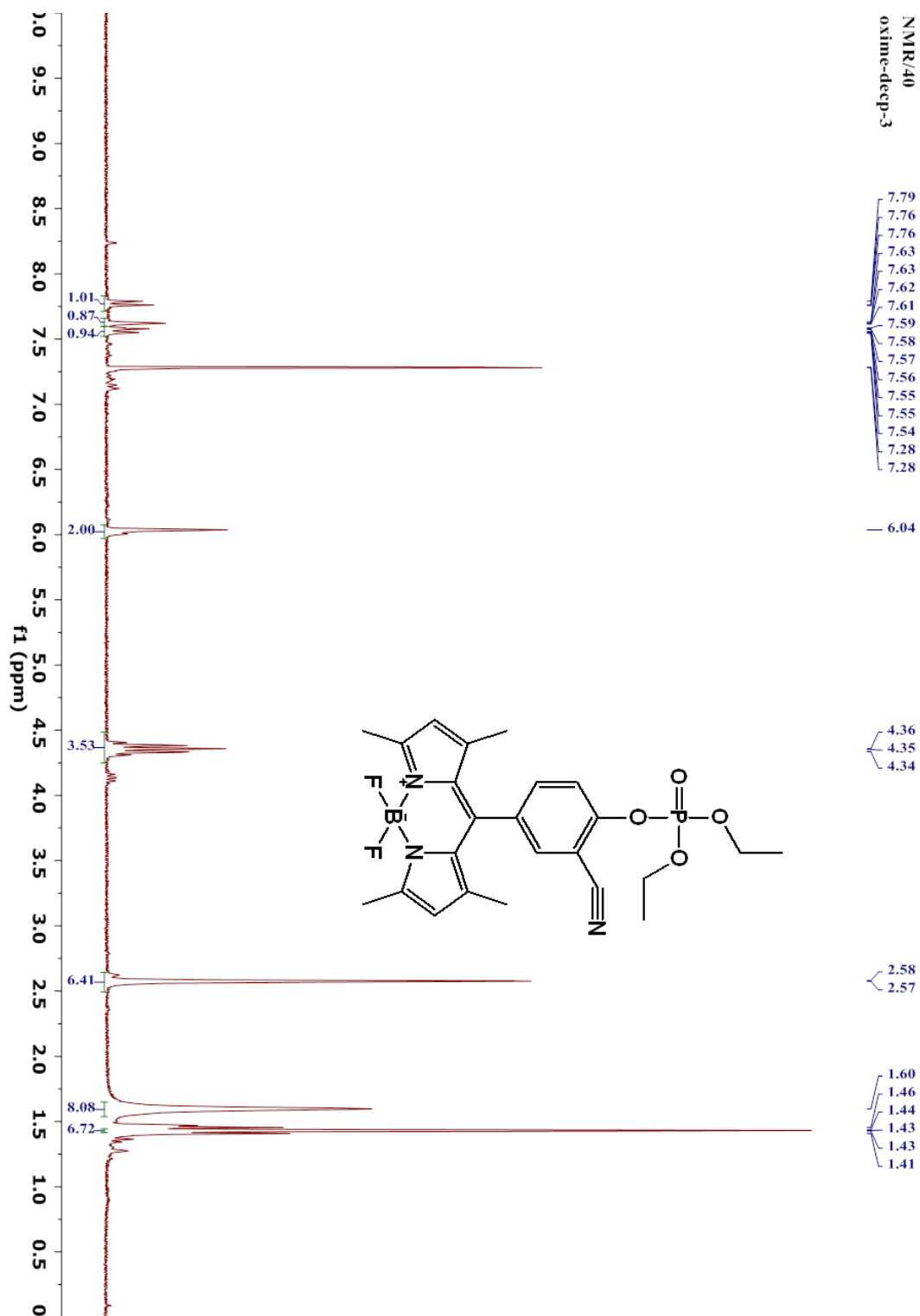


Figure S5.  $^1\text{H}$  NMR spectrum of compound 12.



**Figure S6.**  $^1\text{H}$  NMR spectrum of compound **13**.

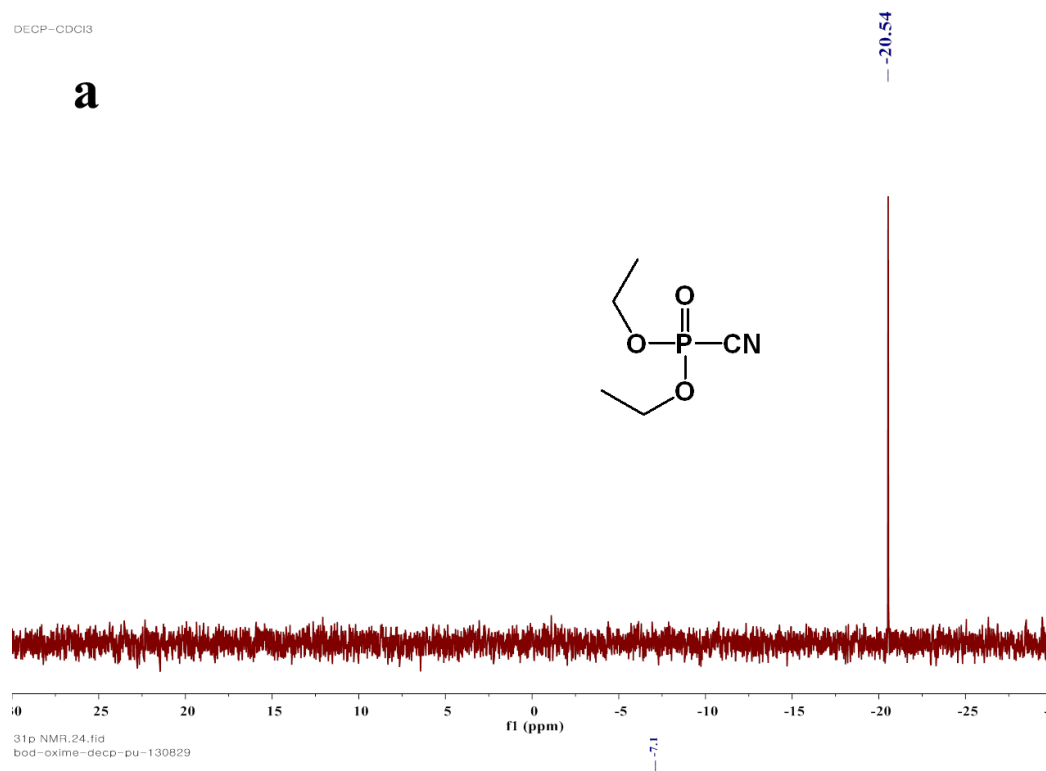




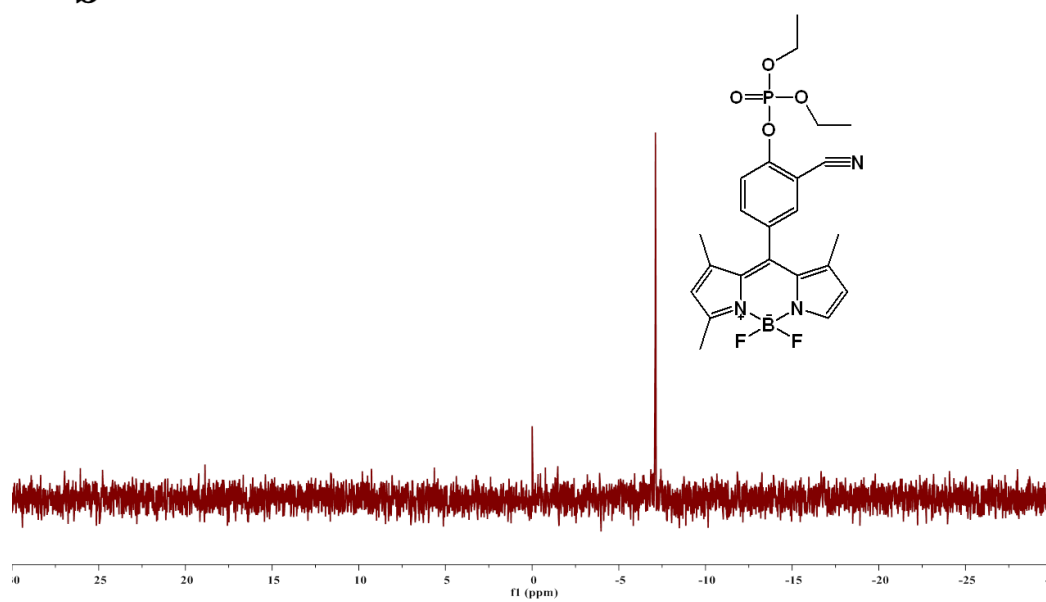
**Figure S8.** <sup>1</sup>H NMR spectrum of compound **6** with DECP in CDCl<sub>3</sub>.

DECP-CDCl<sub>3</sub>

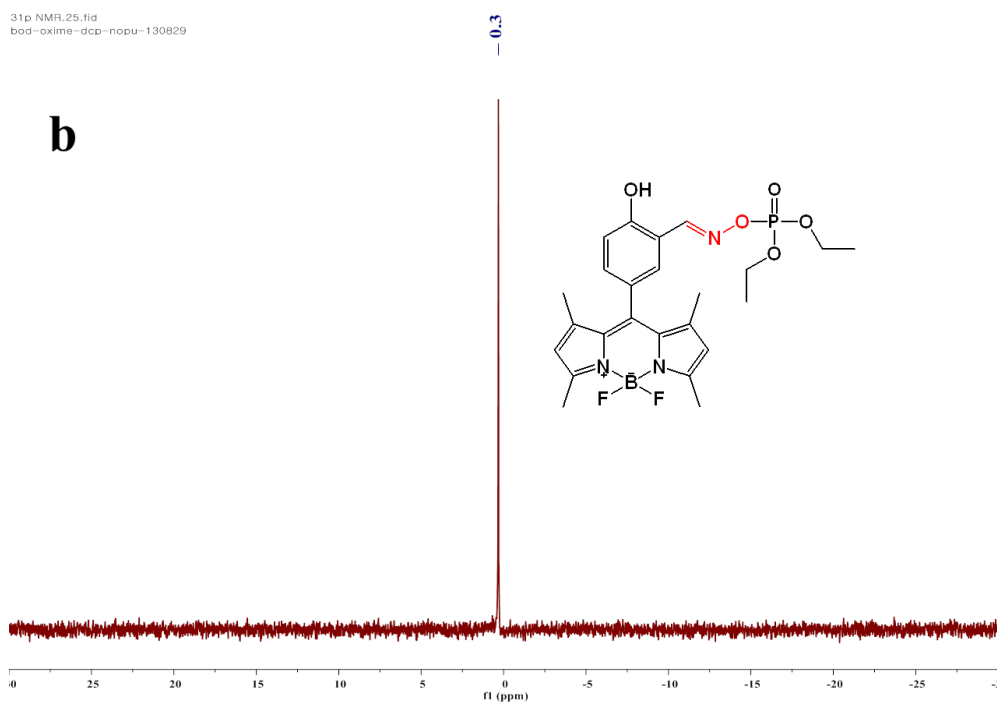
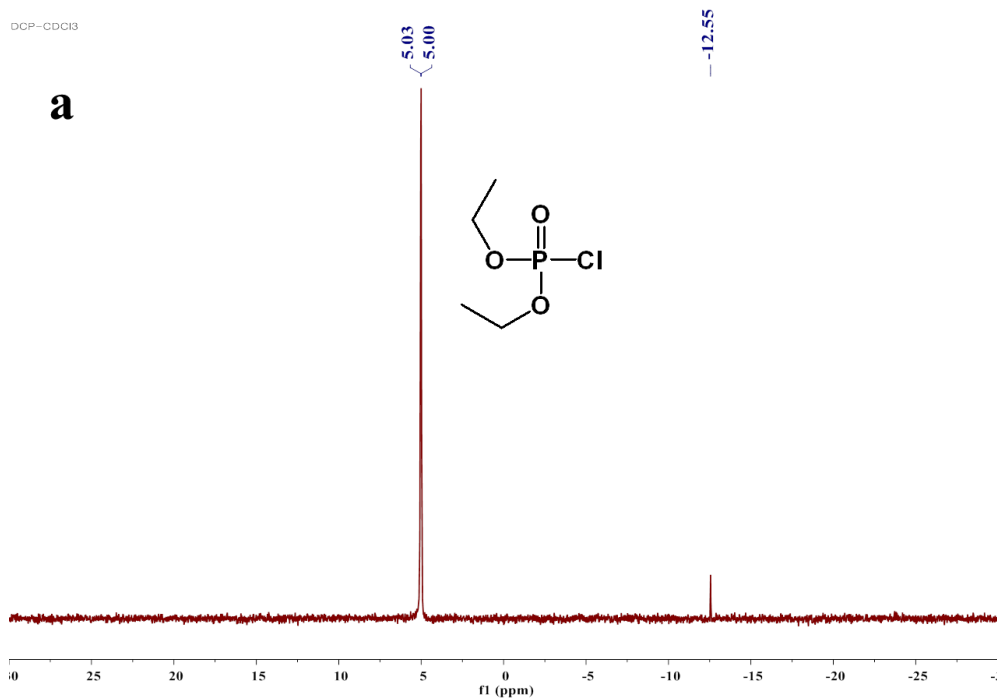
**a**



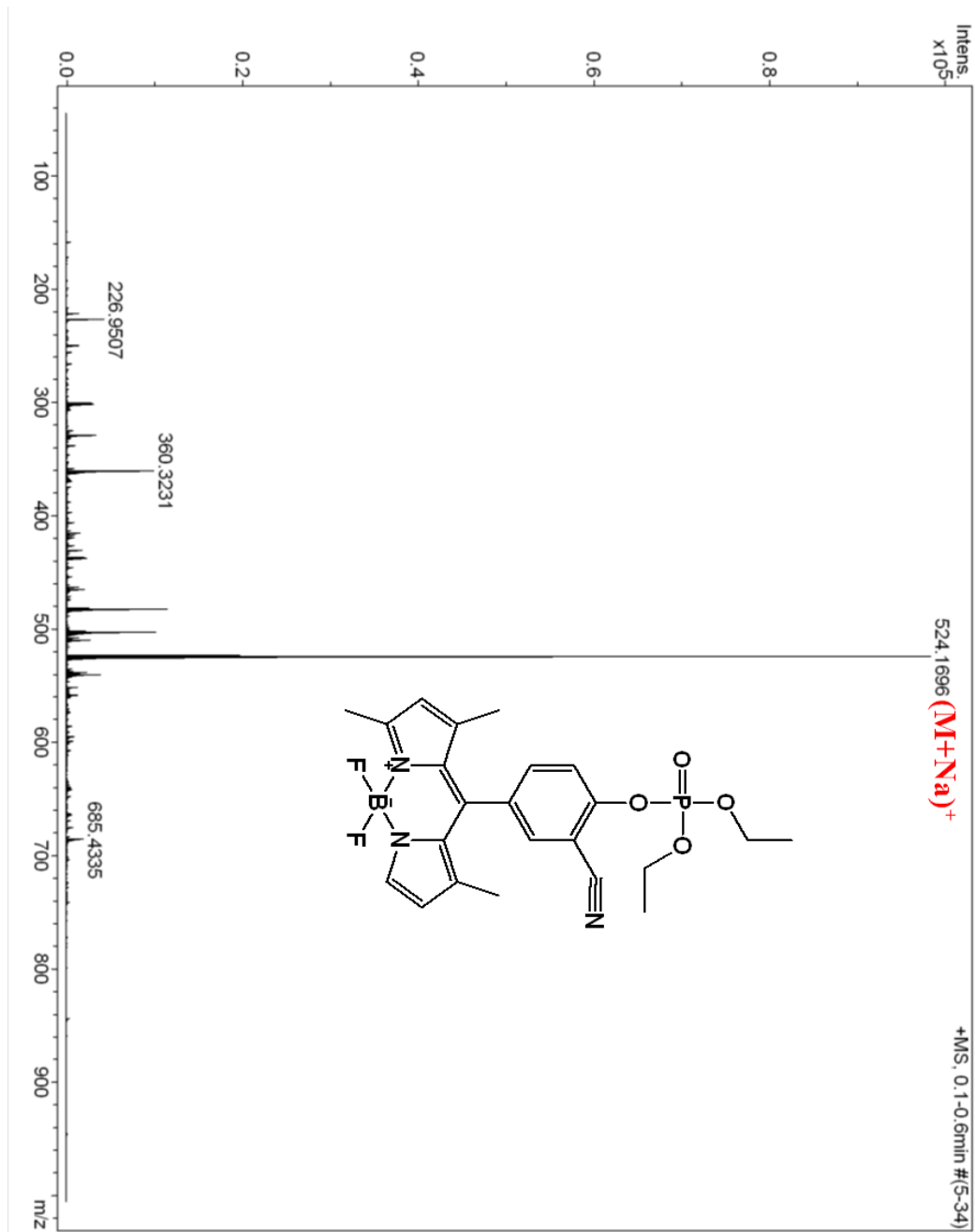
**b**



**Figure S9.** <sup>31</sup>P NMR spectra of DECP (*a*) and B-SAL-OXIME with DECP (*b*) in CDCl<sub>3</sub>.



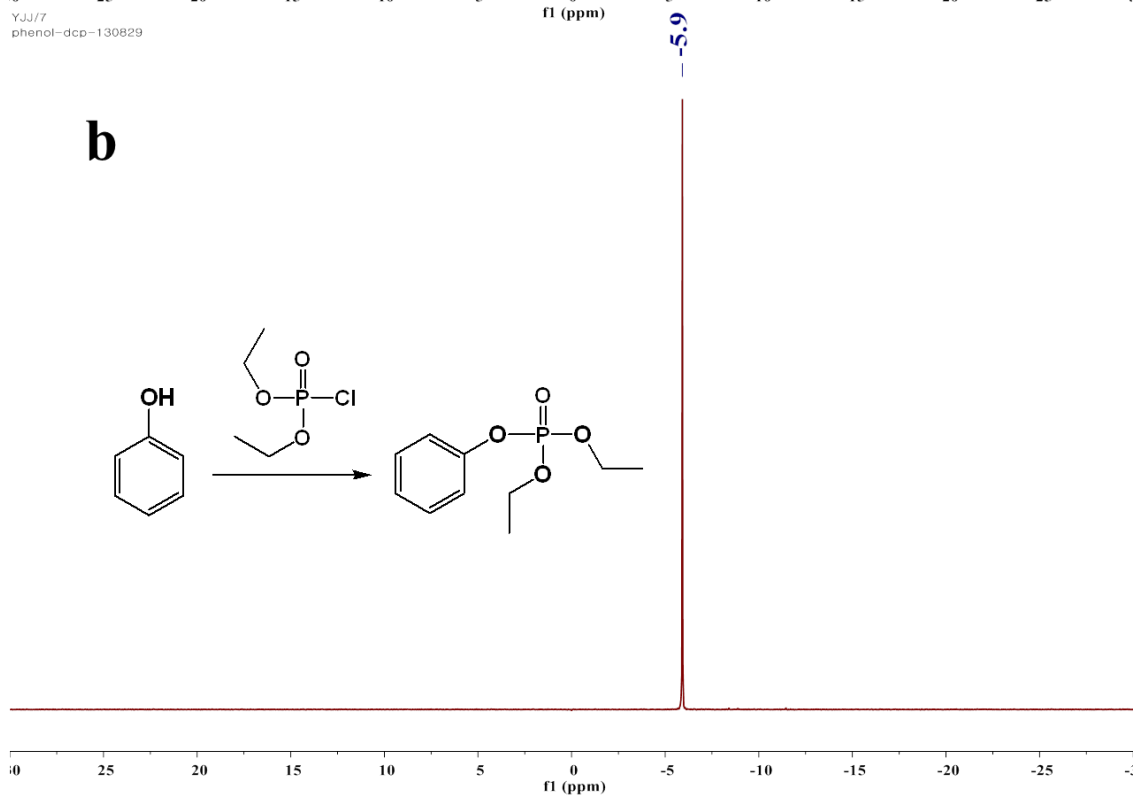
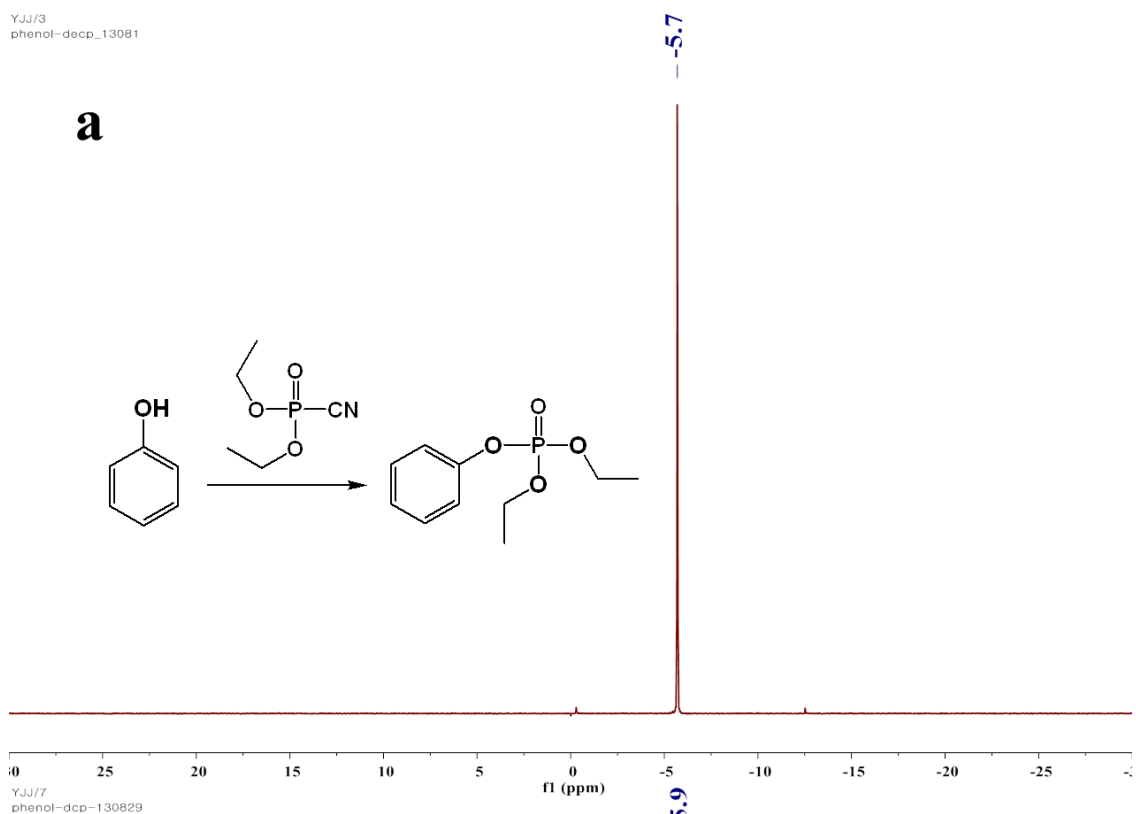
**Figure S10.** <sup>31</sup>P NMR spectra of DCP (*a*) and B-SAL-OXIME with DCP (*b*) in CDCl<sub>3</sub>.



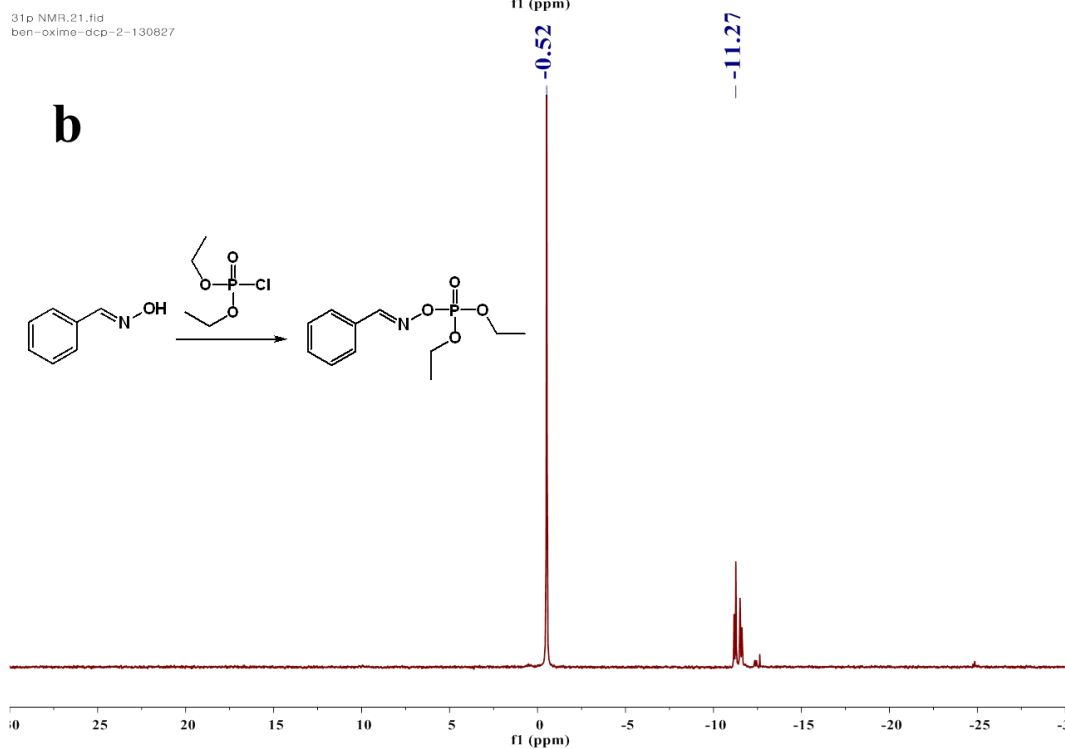
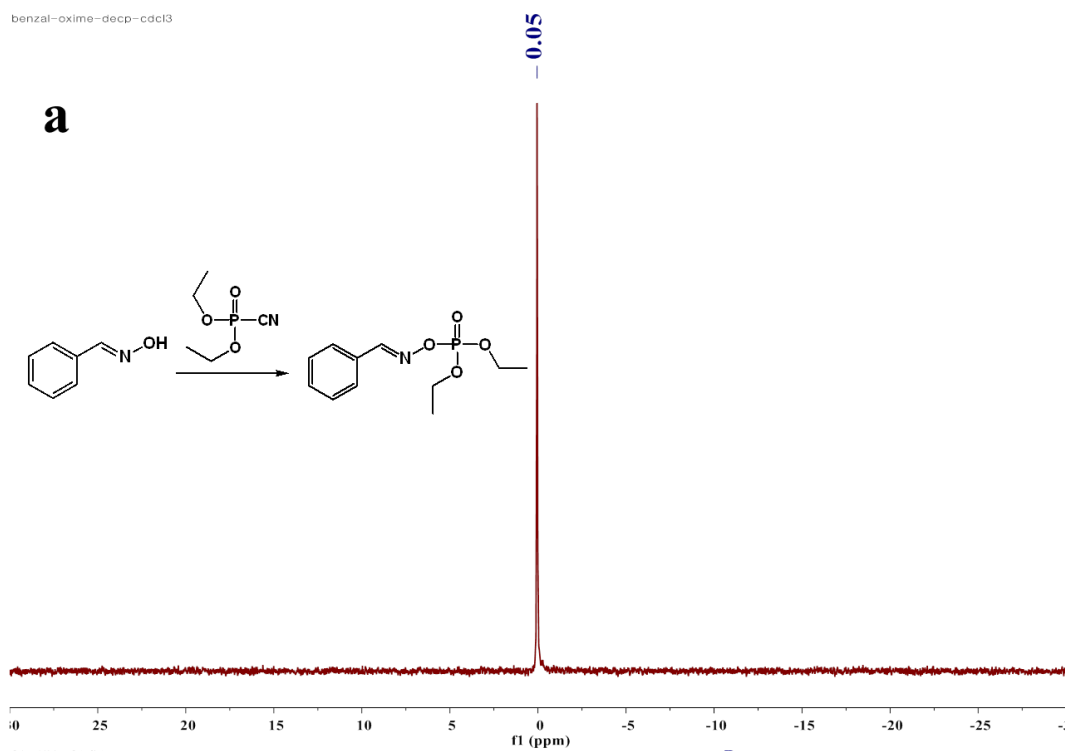
**Figure S11.** HMS (ESI) spectrum of compound **6** with DECP which is observed at 524.1696 and calculated for  $C_{24}H_{27}BF_2N_3O_4PNa^+$  is 524.1693.



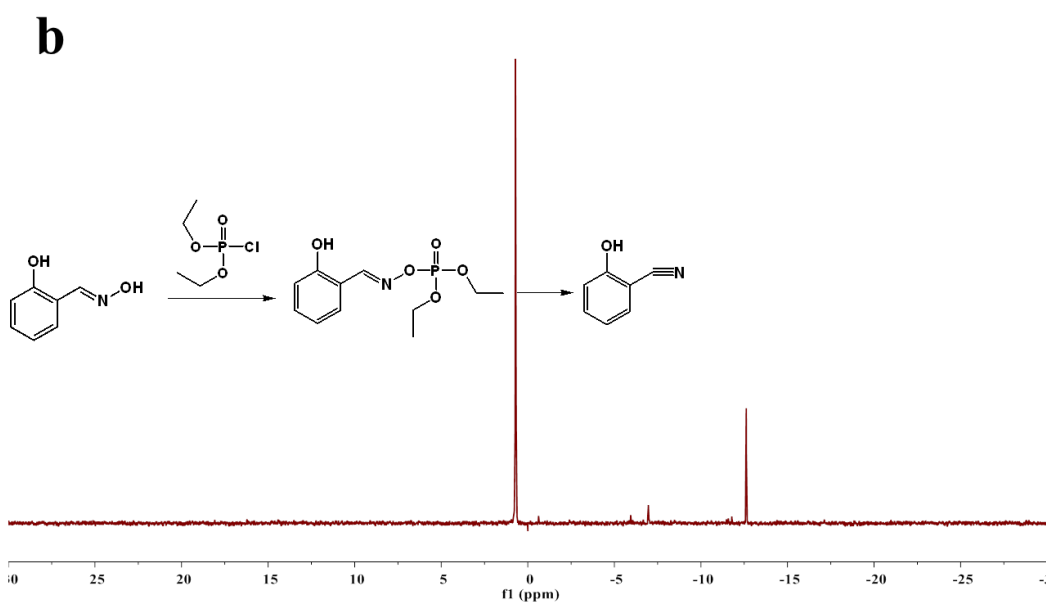
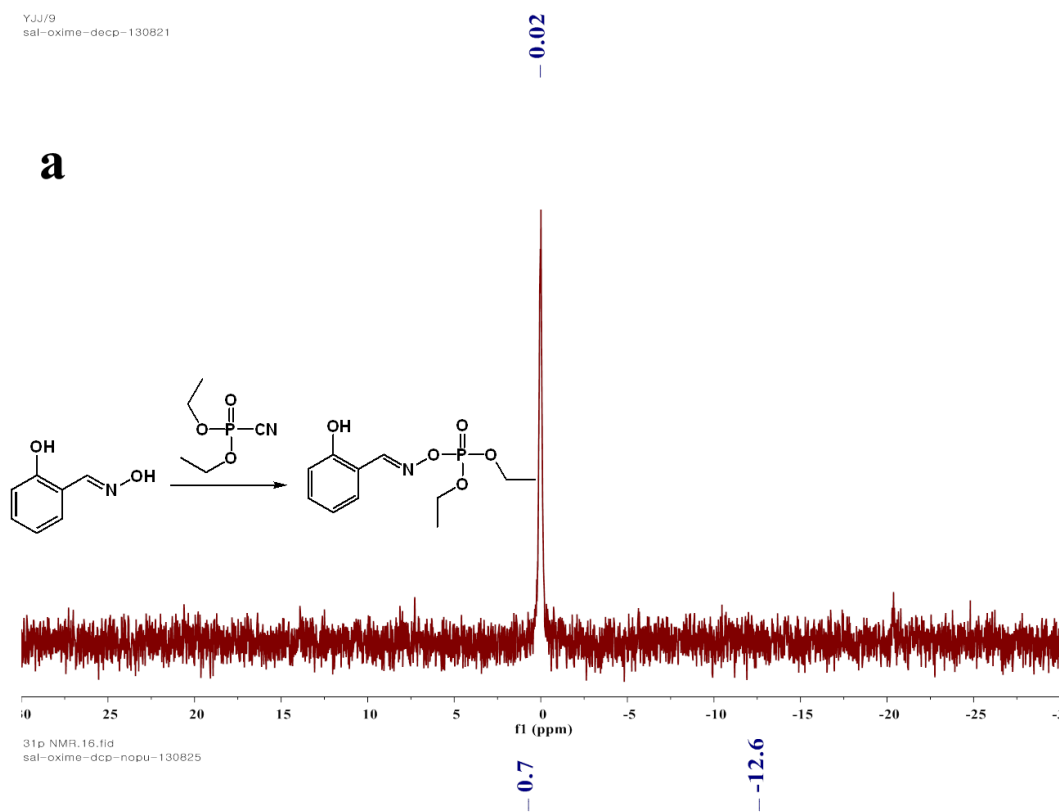
YJJ/3  
phenol-decp\_13081



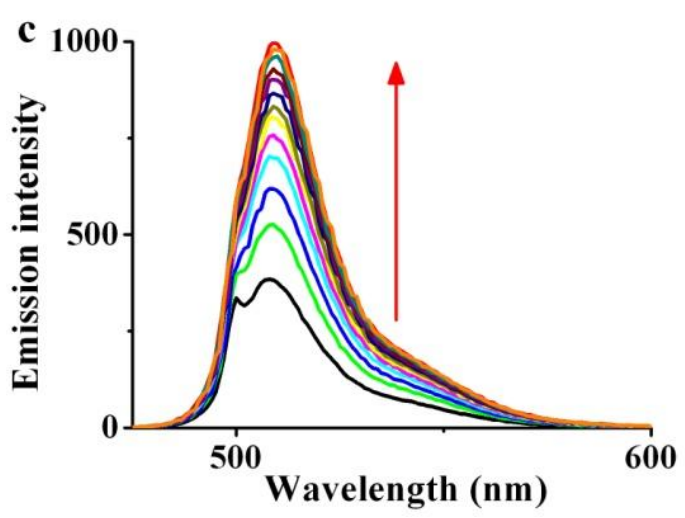
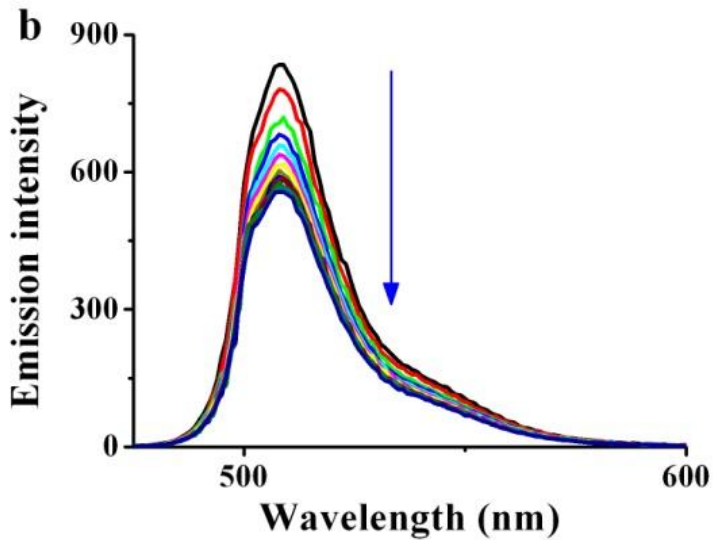
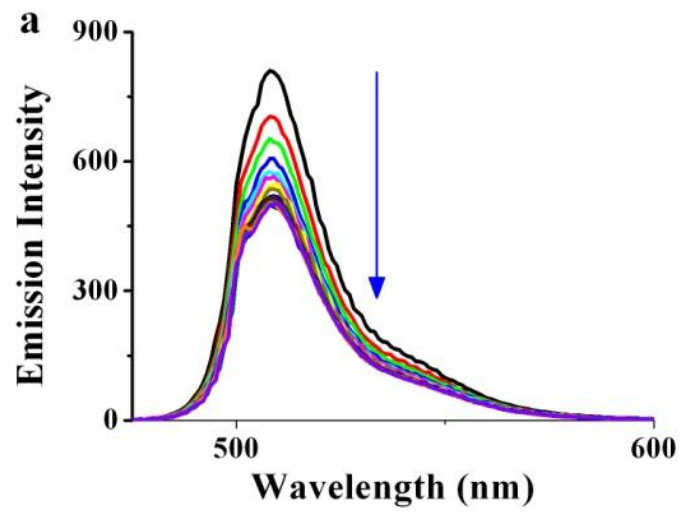
**Figure S12.**  $^{31}\text{P}$  NMR spectra of phenol with DECP (A) and DCP (B) in  $\text{CDCl}_3$ .



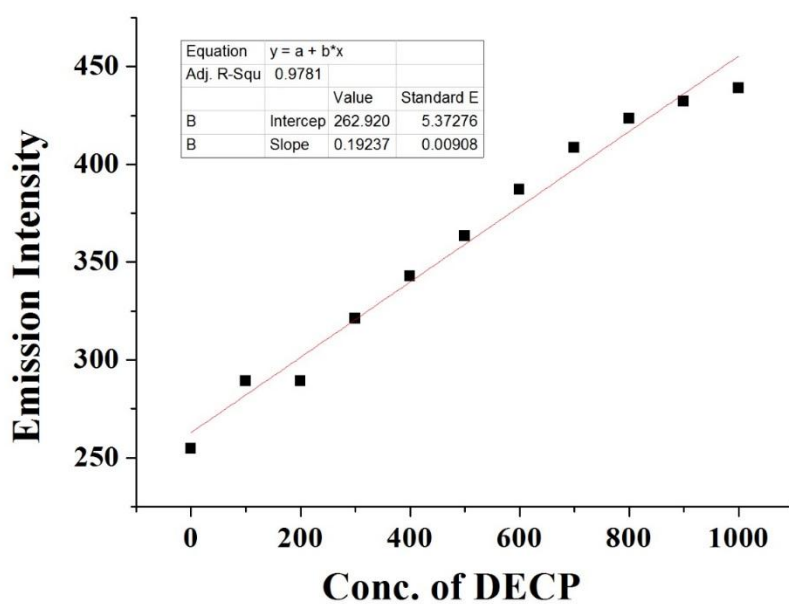
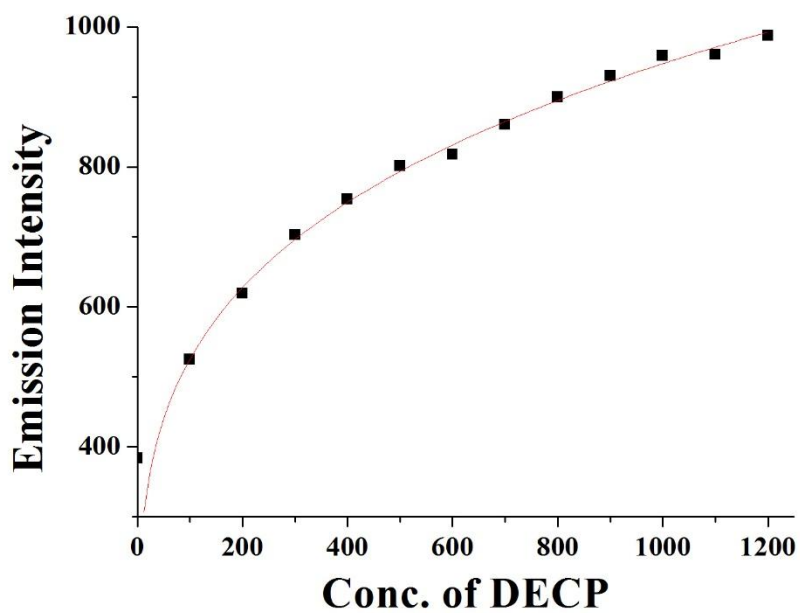
**Figure S13.**  $^{31}\text{P}$  NMR spectra of benzaldehyde oxime with DECP (*a*) and DCP (*b*) in  $\text{CDCl}_3$ .



**Figure S14.**  $^{31}\text{P}$  NMR spectra of salicylaldehyde oxime with DECP (a) and DCP (b) in  $\text{CDCl}_3$ .



**Figure S15.** Fluorescent titrations of B-SAL-OXIME ( $1 \times 10^{-6}$  M in 0.1 mM, pH 7.4 HEPES buffer from 100 to 1500  $\mu$ M of DCP (a), B-SAL-OXIME ( $1 \times 10^{-6}$  M) from 100 to 1500  $\mu$ M of DEMP (b), and B-SAL-OXIME ( $2 \times 10^{-7}$  M) from 100 to 1200  $\mu$ M of DECP (c) in acetonitrile at  $\lambda_{\text{exc}} = 499$  nm,  $\lambda_{\text{emis}} = 508$  nm.

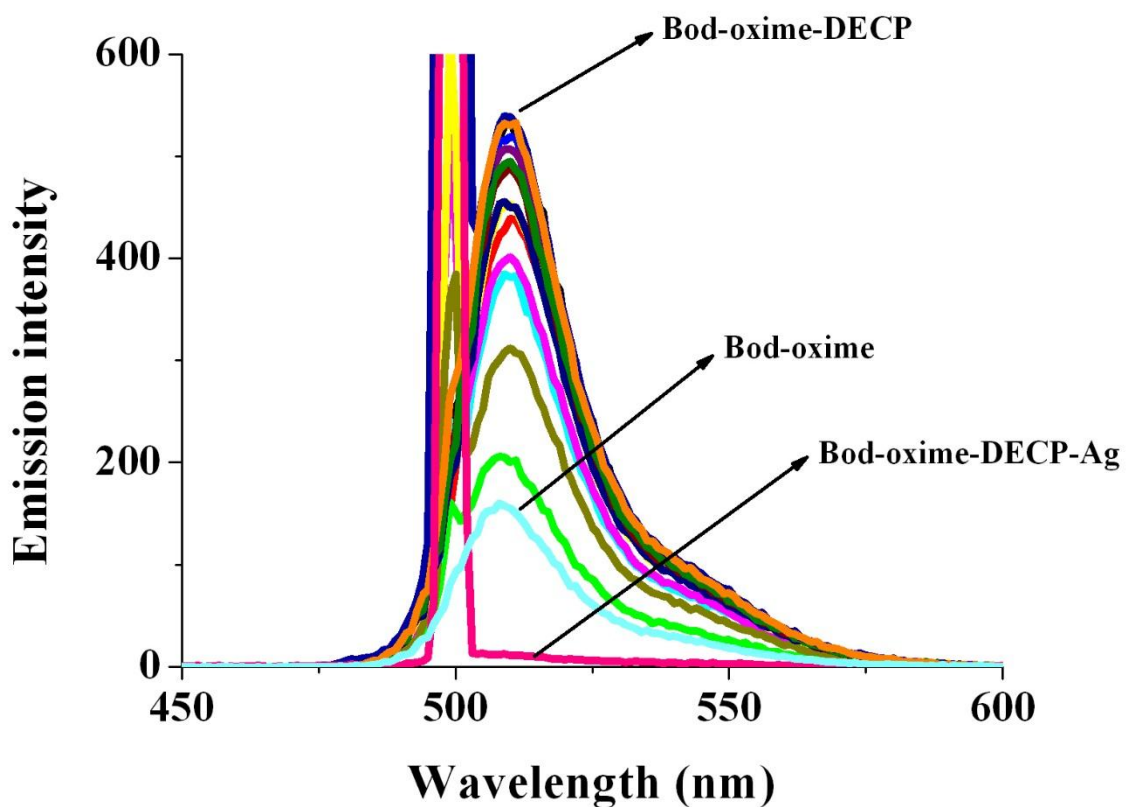


**Figure S16.** LOD for B–SAL–OXIME with DECP in acetonitrile at  $\lambda_{exc} = 499$  nm,  $\lambda_{emis} = 508$  nm. (*upper*) LOD is 977 nM (data fit to the nonlinear equation:

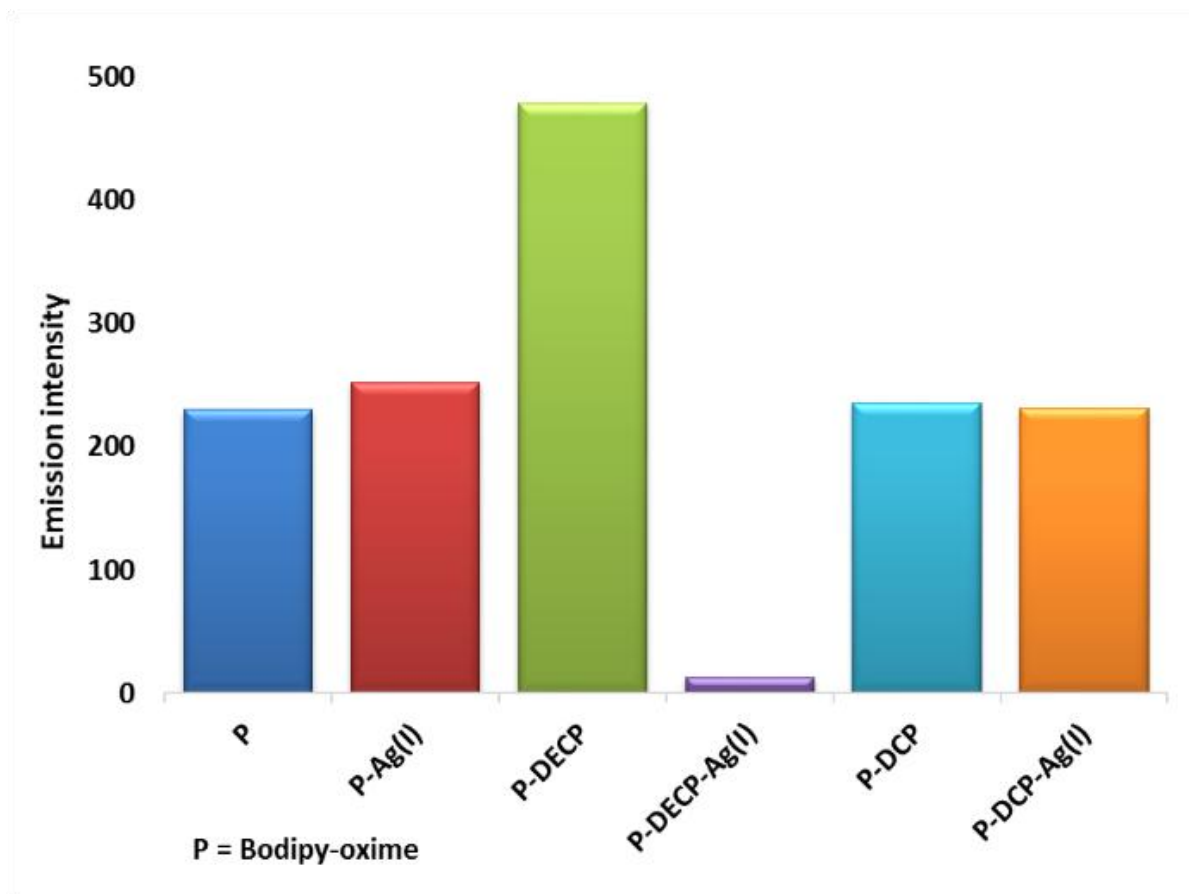
$$y = 18.11 \times \text{sqrt}(x) + 383.85, \quad R^2 = 0.99$$

and (*lower*) LOD is 92.2  $\mu\text{M}$  (data fit to the linear equation:

$$y = 0.192 \times x + 262.92, \quad R^2 = 0.98.^4$$

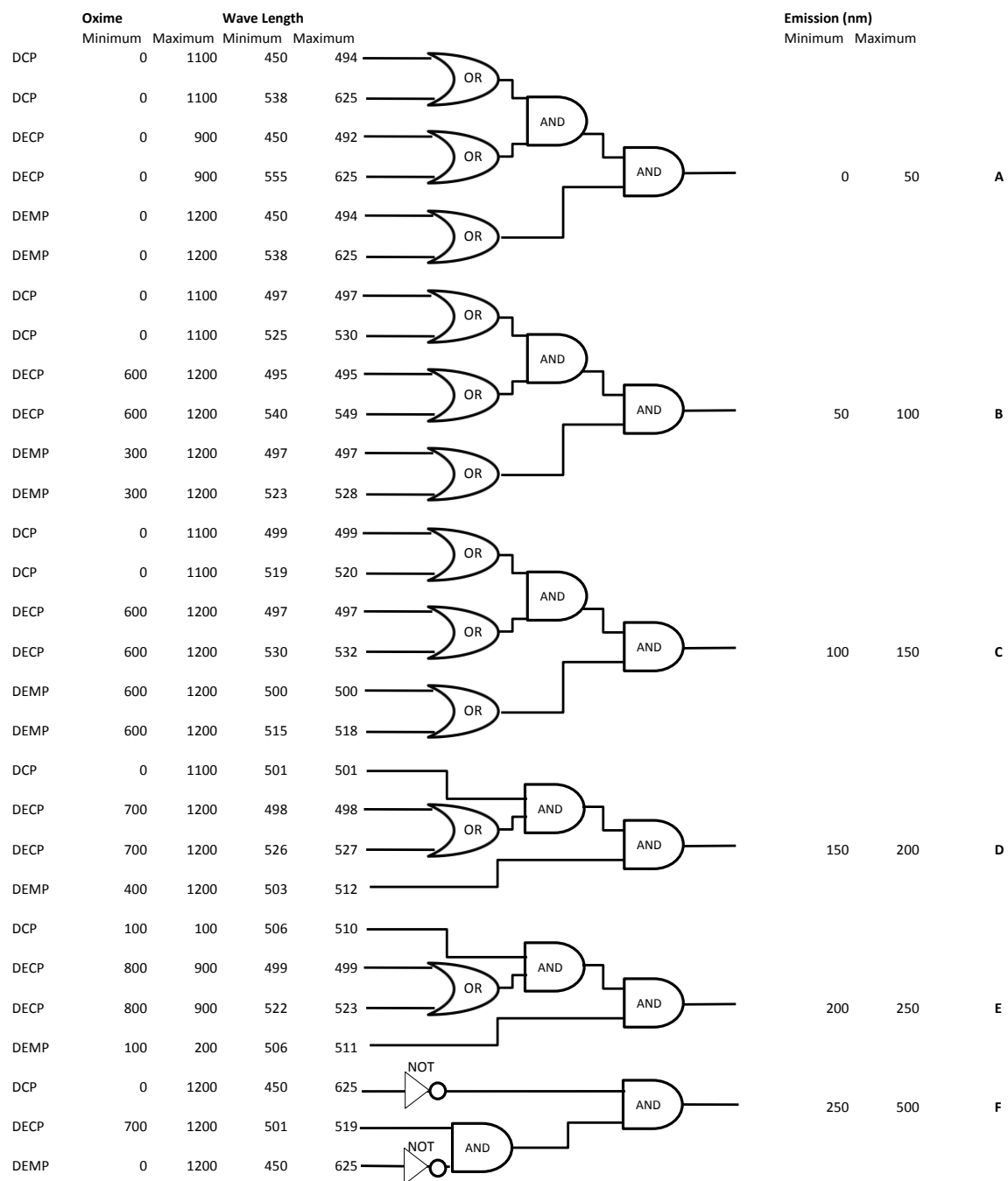


**Figure S17.** Fluorescence intensity of compound **8** ( $1 \times 10^{-6}$  M in 0.1 mM, pH 7.4 HEPES buffer) with 1200  $\mu$ M of metal ions ( $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{K}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ) in acetonitrile at  $\lambda_{\text{exc}} = 499$  nm,  $\lambda_{\text{emis}} = 508$  nm

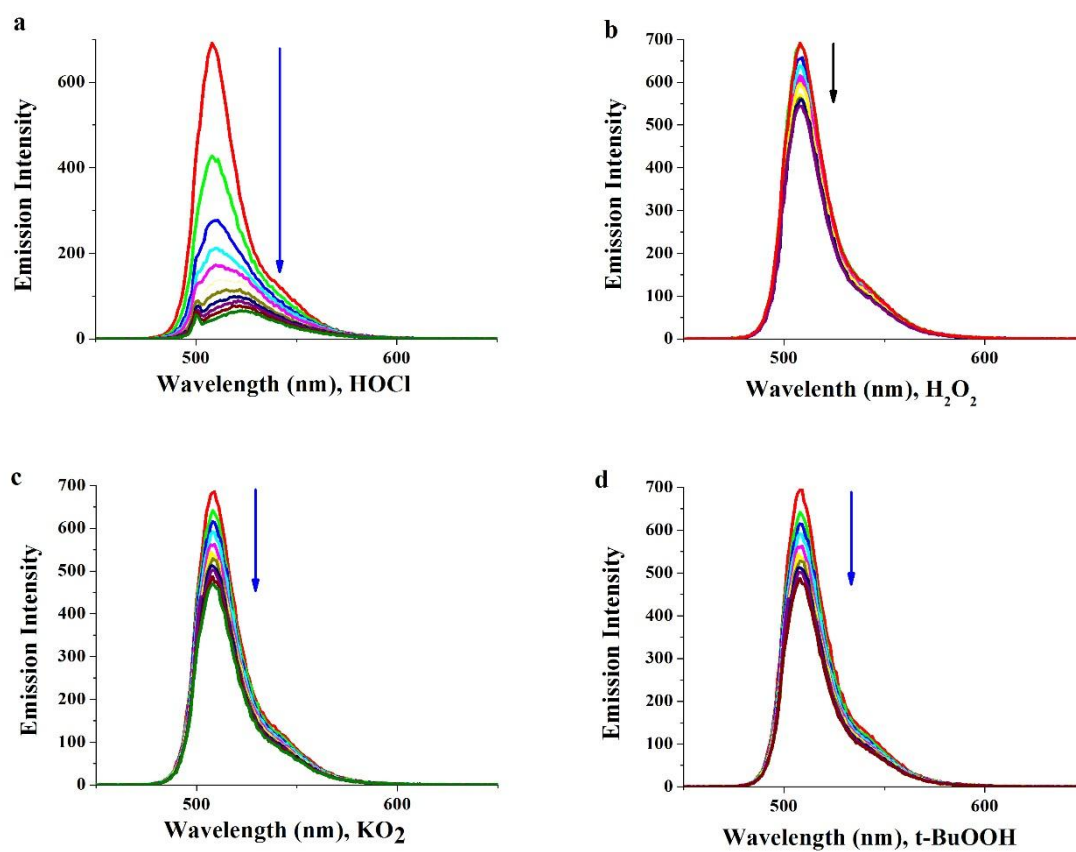


**Figure S18.** Fluorescence intensity comparing bar graph among compounds **6**, **7** and **9** ( $1 \times 10^{-6}$  M in 0.1 mM, pH 7.4 HEPES buffer) with  $1200 \mu\text{M}$   $\text{Ag}^+$  in acetonitrile at  $\lambda_{exc} = 498$  nm,  $\lambda_{emis} = 508$  nm.





**Figure S19.** Detailed Logic gate construct for B-SAL-OXIME with DCP, DEMP and DECP according to fluorescence intensity.



**Figure S20.** Fluorescent titrations of B-SAL-OXIME ( $1 \times 10^{-6}$  M in 0.1 mM, pH 7.4 HEPES buffer from 100 to 1000  $\mu$ M of (a) NaOCl, (b)  $\text{H}_2\text{O}_2$ , (c)  $\text{KO}_2$  and (d)  $t\text{-BuOOH}$  at  $\lambda_{\text{exc}} = 499$  nm,  $\lambda_{\text{emis}} = 508$  nm.

<b>Nerve agent</b>	<b>LC<sub>50</sub> Inhalation mg·min/m<sup>3</sup></b>	<b>LD<sub>50</sub> Skin mg/individual</b>
<b>GA</b>	<b>200</b>	<b>4000</b>
<b>GB</b>	<b>100</b>	<b>1700</b>
<b>GD</b>	<b>100</b>	<b>30</b>
<b>VX</b>	<b>50</b>	<b>10</b>

**Table. S1** Lethal concentration & time and lethal dose of GA, GB, GD and VX.<sup>5</sup>

## References

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