

Supplementary Information

A highly sensitive fluorescence probe for on-site detection of nerve agent mimic diethylchlorophosphonate DCP

Changzhou Chen,^a Wei Zhang,^a Yingjun Ke,^a Lirong Jiang,^{b*} and Xichao Hu^{c*}

^a School of Light Industry and Food Engineering, Guangxi University, Nanning, 530004, China.

^b School of Chemistry and Chemical Engineering, Guangxi Minzu University, Nanning, 530006, China. *E-mail: jianglirong_2000@163.com (L. Jiang)*

^c School of Food and Drug, Luoyang Normal University, Henan Luoyang, 471934, China. *E-mail: hxc30@163.com (X. Hu)*

Table of Contents

1. Experimental details

Fig. S1. Synthetic route of NZNN, NZOH, NZN

Fig. S2. UV spectral changes of NZOH and NZN

Fig. S3. UV spectral changes of of probe NZNN

Fig. S4. Plot of fluorescence intensity of NZNN versus concentrations of phosgene

Fig. S5-S6. ¹H NMR, ¹³C NMR of compound 1b in DMSO-*d*₆

Fig. S7-S8. ¹H NMR, ¹³C NMR of NZNN in DMSO-*d*₆

Fig. S9-S10. ¹H NMR, ¹³C NMR of compound 2 in DMSO-*d*₆

Fig. S11-S12. ¹H NMR, ¹³C NMR of NZOH in DMSO-*d*₆

Fig. S13-S14. ¹H NMR, ¹³C NMR of compound 3 in DMSO-*d*₆

Fig. S15-S16. ¹H NMR, ¹³C NMR of NZN in DMSO-*d*₆

Fig. S17. HR-MS spectra of NZNN

Fig. S18. HR-MS spectra of NZOH

Fig. S19. HR-MS spectra of NZN

Fig. S20. Chemical structures of fluorescence probes for the determination of DCP

Table S1. Comparison of data from this study with other studies

1. Experimental details

1.1. Synthesis of compound 1a

4-Bromo-1,8-naphthalic anhydride (554 mg, 2 mmol) and 2-nitrobenzene-1,4-diamine (306 mg, 2 mmol) were placed in a 50 ml round bottom flask. The reaction was heated to 80 °C under nitrogen atmosphere for 6 h. After completion of the reaction, the reaction mixture was cooled to room temperature and a yellow solid was gradually deposited within the solution, filtered in vacuum and washed 2-3 times with anhydrous ethanol. After drying, compound 1a was obtained (774 mg, 91% yield).

1.2. Synthesis of NZOH

4-bromo-1, 8-naphthalenedicarboxylic anhydride (1 g, 4 mmol) and 2-aminophenol (0.4 g, 4 mmol) were dissolved in 20 mL of ethanol under a nitrogen atmosphere. After heating at reflux for 8h at 80°C and cooling, a white solid precipitate was gradually formed in the reaction system. The precipitate was finally filtered out, washed three times with anhydrous ethanol and dried to obtain the compound 2 (1.1 g, 75%).

¹H NMR (500 MHz, DMSO-*d*₆) δ 9.68 (s, 1H), 8.59 (ddd, J = 18.9, 7.8, 1.1 Hz, 2H), 8.41 (d, J = 7.9 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.34 – 7.28 (m, 1H), 6.88 (ddd, J = 8.3, 2.3, 1.1 Hz, 1H), 6.80 (dt, J = 6.3, 1.9 Hz, 2H).

The compound 2 (400 mg, 1.13 mmol) and n-butylamine (1 mL, 5 mmol) were added into 10 mL 2-methoxyethanol under a nitrogen atmosphere, and the mixture was magnetic stirred and refluxed at 130°C for 8 h. After the reaction, the resulting mixture was subjected to chloroform extraction, leading to gradual formation of an orange solid precipitate within the reaction system. Finally, the precipitate was

filtered out, washed three times with anhydrous ethanol and dried to obtain the orange NZOH powder (268 mg, 70%).

^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.6 (s, 1H), 8.7 (dd, $J = 8.6, 1.2$ Hz, 1H), 8.4 (dd, $J = 7.3, 1.0$ Hz, 1H), 8.3 (d, $J = 8.6$ Hz, 1H), 7.8 (t, $J = 5.5$ Hz, 1H), 7.7 (dd, $J = 8.4, 7.3$ Hz, 1H), 7.3 (t, $J = 8.0$ Hz, 1H), 6.9 – 6.8 (m, 2H), 6.7 – 6.7 (m, 2H), 3.4 (d, $J = 7.1$ Hz, 2H), 1.8 – 1.7 (m, 2H), 1.5 (dt, $J = 14.8, 7.4$ Hz, 2H), 1.0 (t, $J = 7.4$ Hz, 3H).

HR-MS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_3$: 361.1507; found: 361.1542.

1.3. Synthesis of NZN

4-Bromo-1, 8-naphthalic anhydride (1 g, 4 mmol) and isophthalamide (0.4 g, 4 mmol) were dissolved in 20 mL ethanol under a nitrogen atmosphere. Subsequently, the mixture was magnetic stirred and refluxed at 80°C for 6 h. After cooling, a dark yellow solid precipitate appeared in the reaction system. The precipitate was obtained through filtration and dried by rotary evaporation to remove the residual solvent. The crude product was purified by column chromatography (eluent: dichloromethane/methanol = 10/1) to obtain compound 3 (548 mg, 61%).

^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 8.61 (dd, $J = 8.4, 1.2$ Hz, 1H), 8.57 (dd, $J = 7.3, 1.2$ Hz, 1H), 8.42 (d, $J = 7.9$ Hz, 1H), 8.08 – 7.99 (m, 2H), 7.14 (t, $J = 7.9$ Hz, 1H), 6.65 (ddd, $J = 8.1, 2.3, 1.0$ Hz, 1H), 6.54 – 6.47 (m, 2H), 5.22 (s, 2H).

The compound 3 (500 mg, 1.13 mmol) and n-butylamine (1 mL, 1 mmol) were added into 10 mL 2-methoxyethanol under a nitrogen atmosphere nitrogen. The mixture was magnetic stirred and refluxed at 130°C for 8 h. After the reaction, the resulting mixture was extracted with chloroform and then subjected to rotary

evaporation to give the crude product of NZN. Finally, the crude product was purified by column chromatography (eluent: dichloromethane/methanol = 10/1) yielding pure dark orange NZN powder (300 mg, 70%).

¹H NMR (500 MHz, DMSO-*d*₆) δ 8.79 (dd, J = 8.4, 1.2 Hz, 1H), 8.56 (dd, J = 7.3, 1.2 Hz, 1H), 8.40 (d, J = 8.3 Hz, 1H), 7.91 (dd, J = 8.4, 7.3 Hz, 1H), 7.08 (ddd, J = 8.4, 7.3, 1.4 Hz, 1H), 7.03 (dd, J = 8.0, 1.4 Hz, 1H), 6.92 (dd, J = 8.1, 1.6 Hz, 1H), 6.81 (d, J = 8.3 Hz, 1H), 6.66 (td, J = 7.6, 1.6 Hz, 1H), 5.15 (s, 2H), 4.04 – 3.98 (m, 2H), 1.71 – 1.60 (m, 2H), 1.50 - 1.38 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H).

HR-MS (ESI, m/z): [M+H]⁺ calcd for C₂₂H₂₁N₃O₂: 360.1667; found: 361.1702.

1.4 Determination of the detection limit for NZNN test strip

The calibration curve was obtained by plotting the G values of the NZNN strips as a function of DCP level, and a regression curve equation was obtained.

$$\text{Detection limit (LOD)} = 3 \times \sigma/k$$

where k is the slope of the curve equation, and σ represents the standard deviation for the G values of the NZNN strips in the absence of DCP.

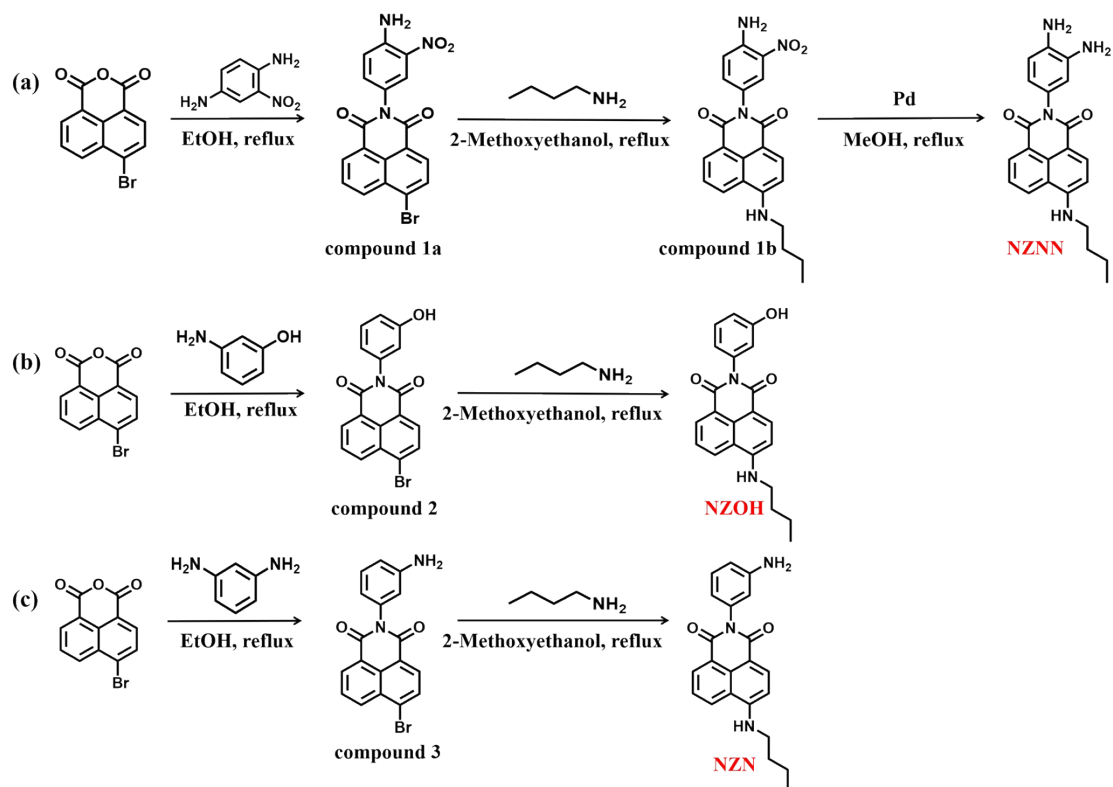


Figure S1. (a) Synthetic route of NZNN. (b) Synthetic route of NZOH. (c) Synthetic route of NZN.

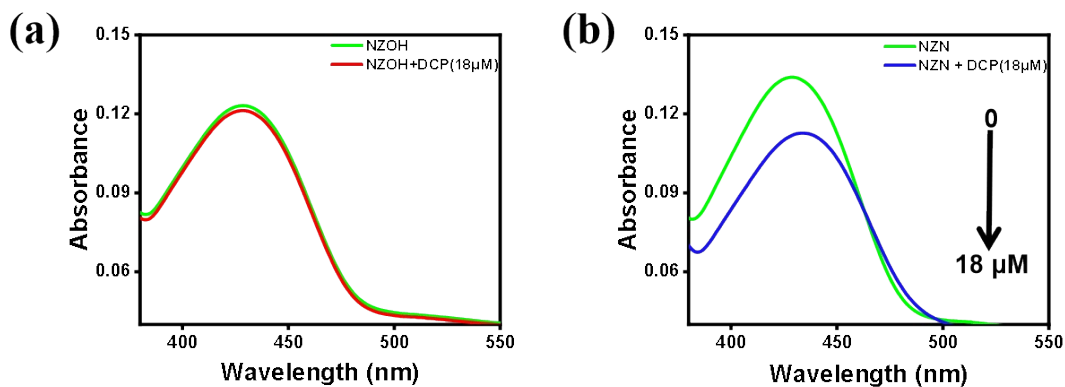


Figure S2. (a) UV spectral changes of NZOH (10 μM) in chloroform. (b) UV spectral changes of NZN (10 μM) in chloroform.

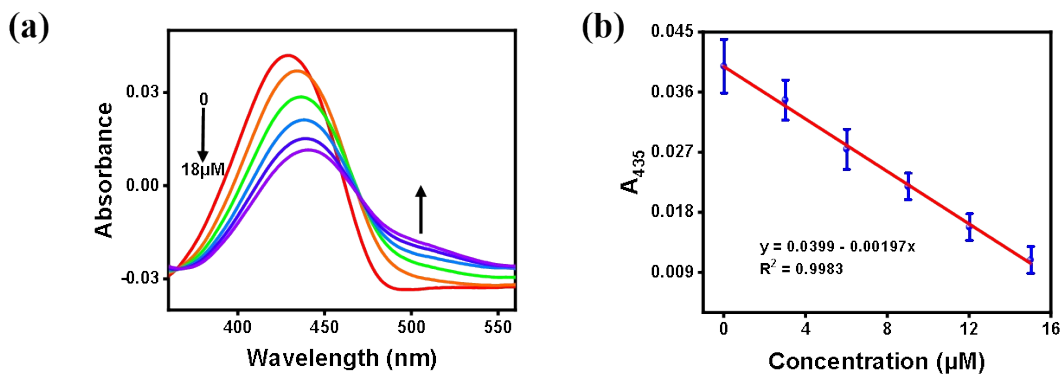


Figure S3. (a) UV-visible spectral response of probe NZNN (10 μM) in chloroform with gradual addition of DCP in the concentration range of 0-18 μM . (b) The UV absorption intensity of NZNN was linearly correlated with the concentration of DCP at an absorption wavelength of 435 nm.

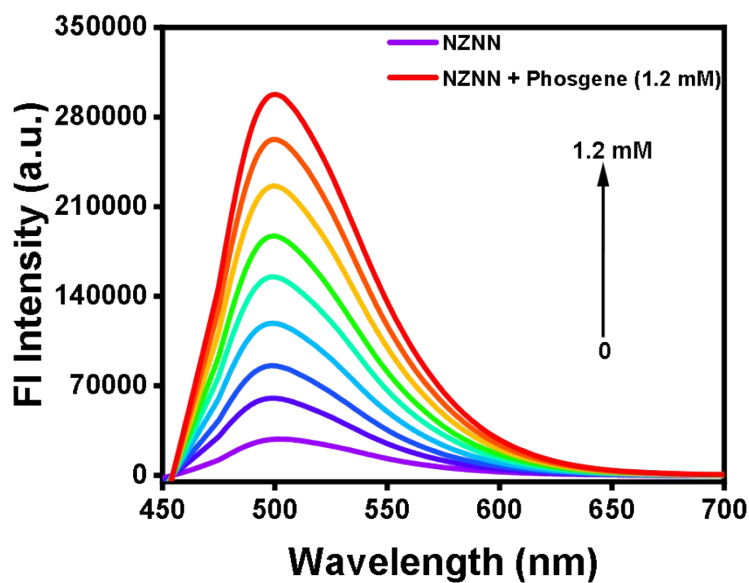


Figure S4. Fluorescence spectra changes of NZNN (10 μM) in the presence of Phosgene (1.2 mM) in chloroform. $\lambda_{\text{ex}} = 360 \text{ nm}$, slits: 2/2 nm.

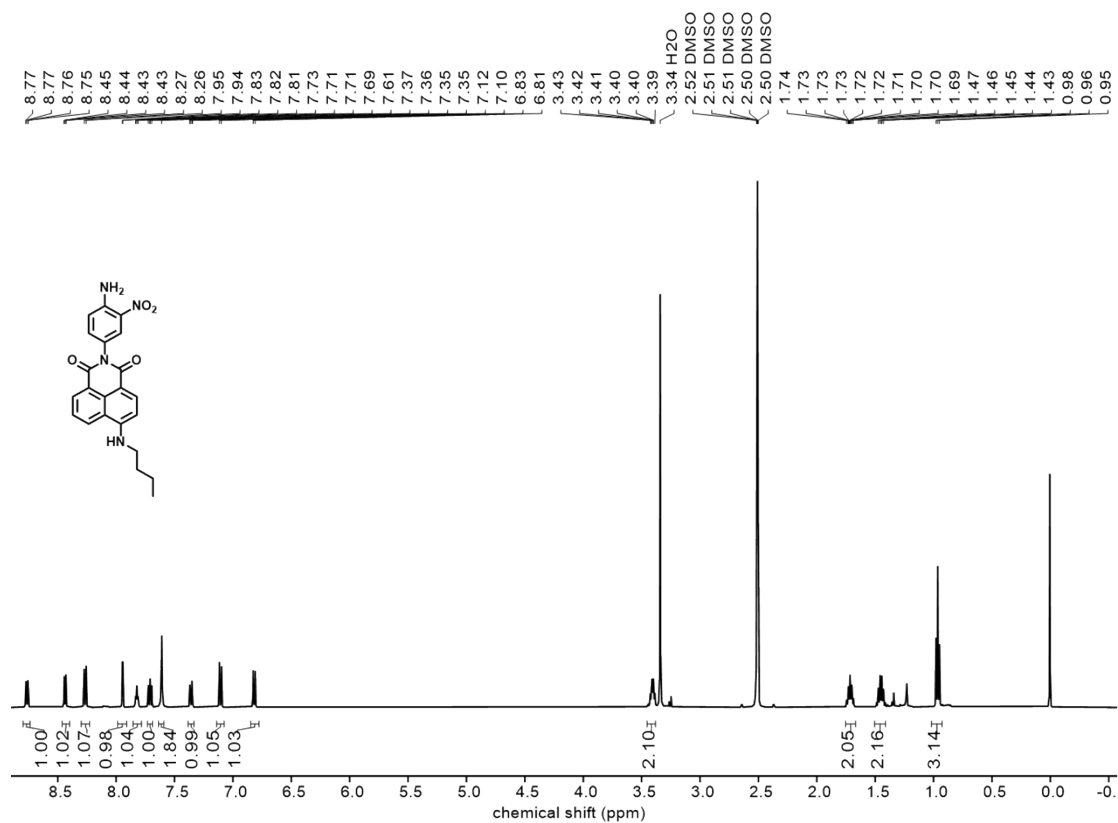


Figure S5. ¹H NMR spectrum of compound 1b in DMSO-*d*₆ (500 MHz).

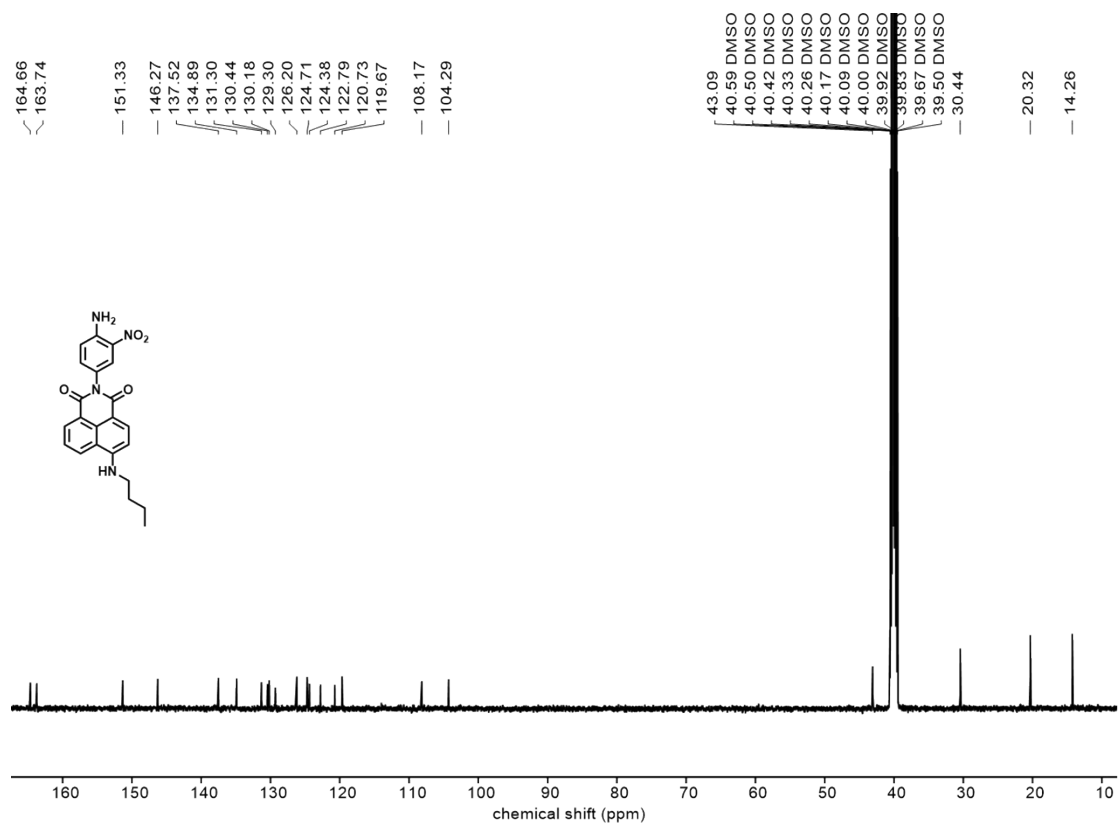


Figure S6. ¹³C NMR spectrum of compound 1b in DMSO-*d*₆ (500 MHz).

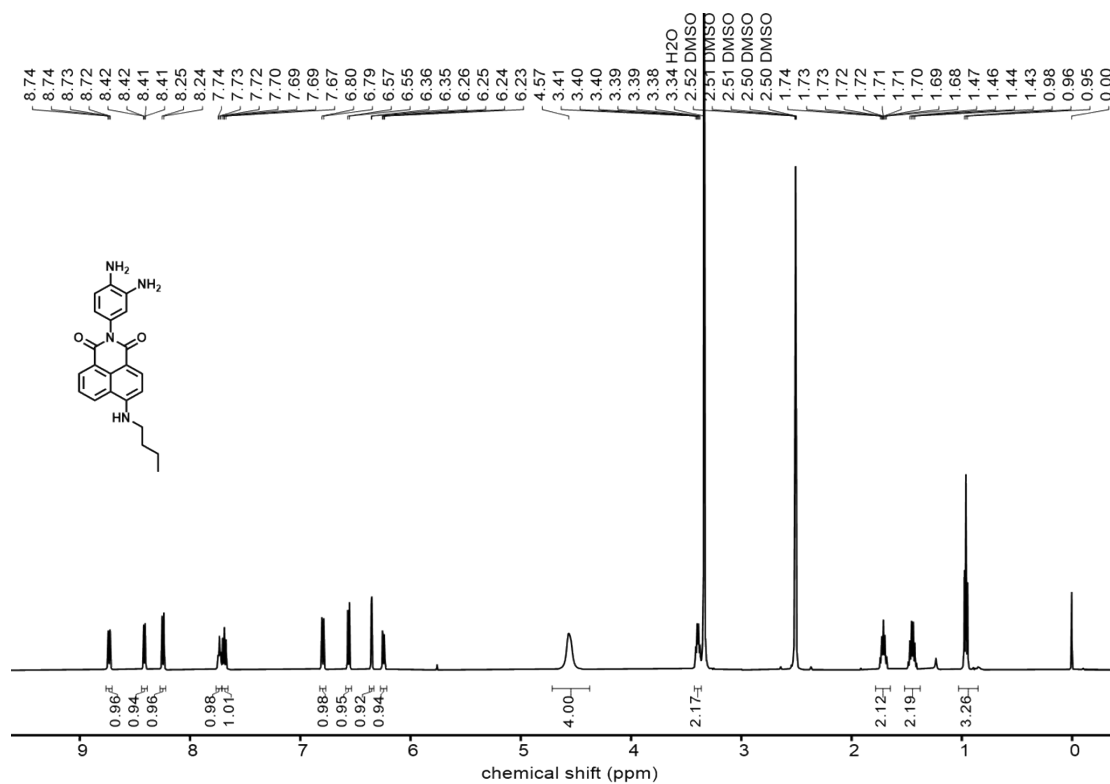


Figure S7. ¹H NMR spectrum of NZNN in DMSO-*d*₆ (500 MHz).

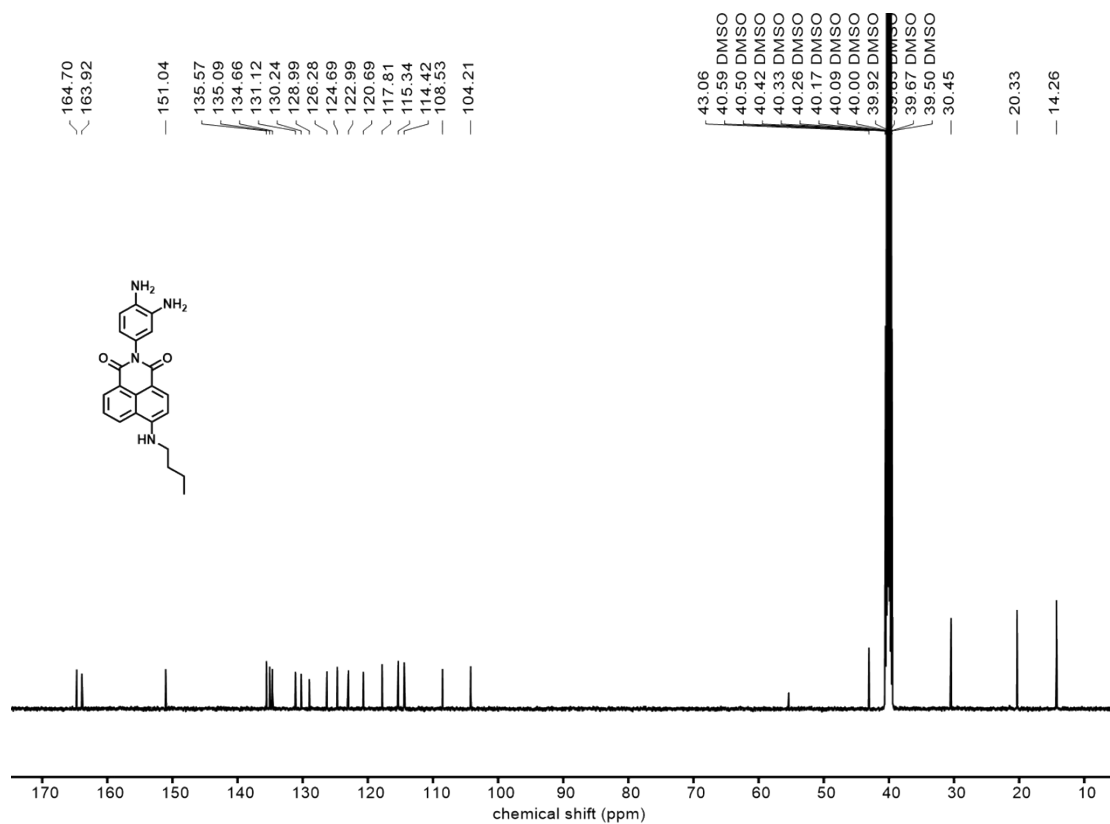


Figure S8. ¹³C NMR spectrum of NZNN in DMSO-*d*₆ (500 MHz).

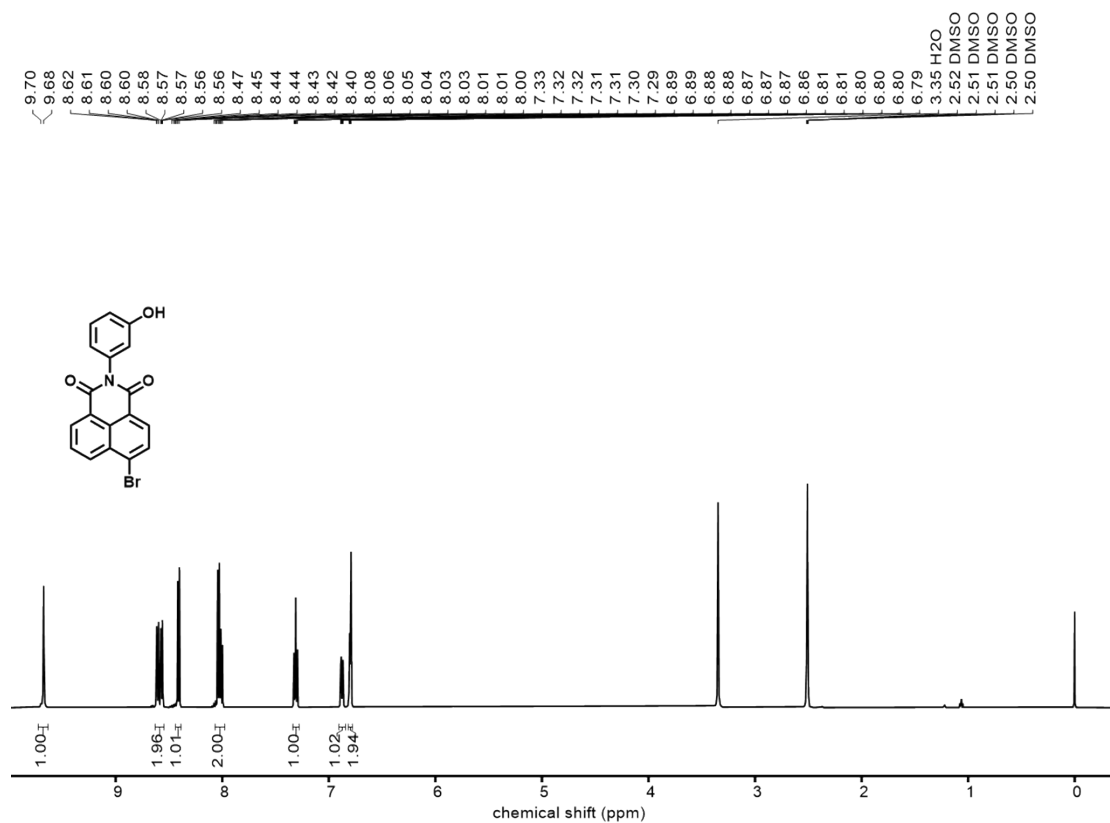


Figure S9. ¹H NMR spectrum of compound 2 in DMSO-*d*₆ (500 MHz).

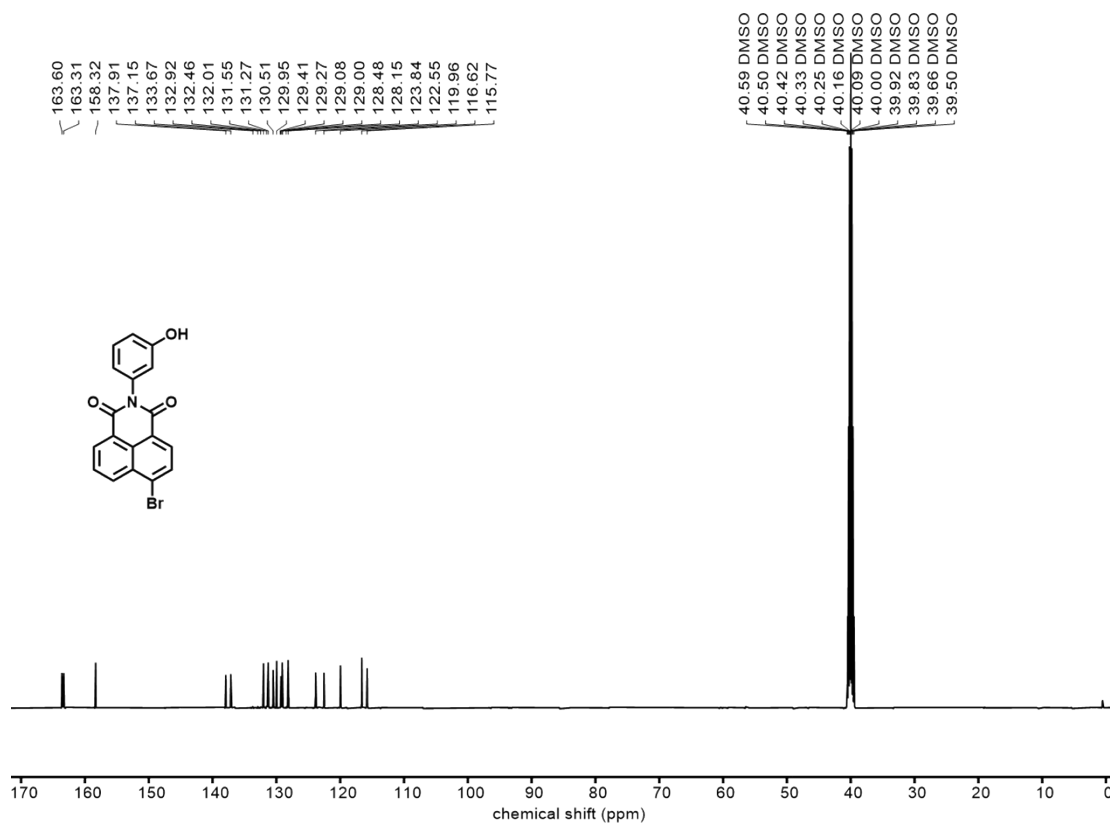


Figure S10. ¹³C NMR spectrum of compound 2 in DMSO-*d*₆ (500 MHz).

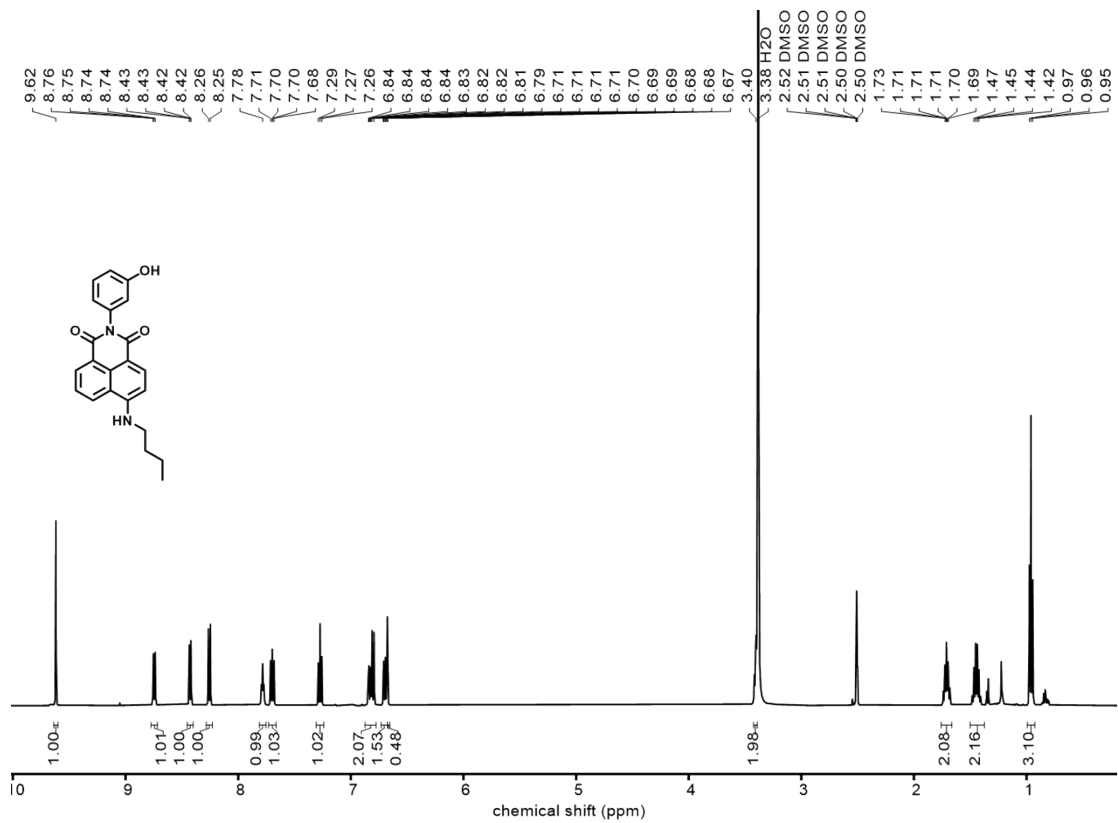


Figure S11. ¹H NMR spectrum of NZOH in DMSO-*d*₆ (500 MHz).

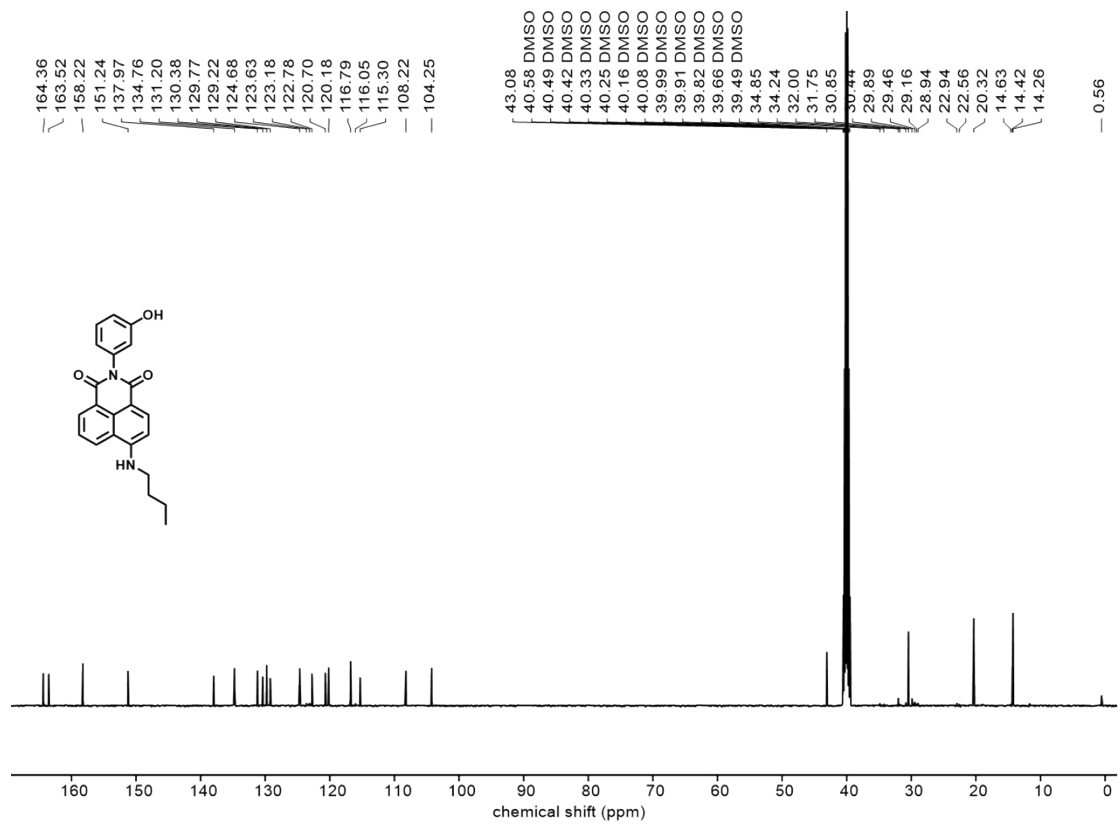


Figure S12. ¹³C NMR spectrum of NZOH in DMSO-*d*₆ (500 MHz).

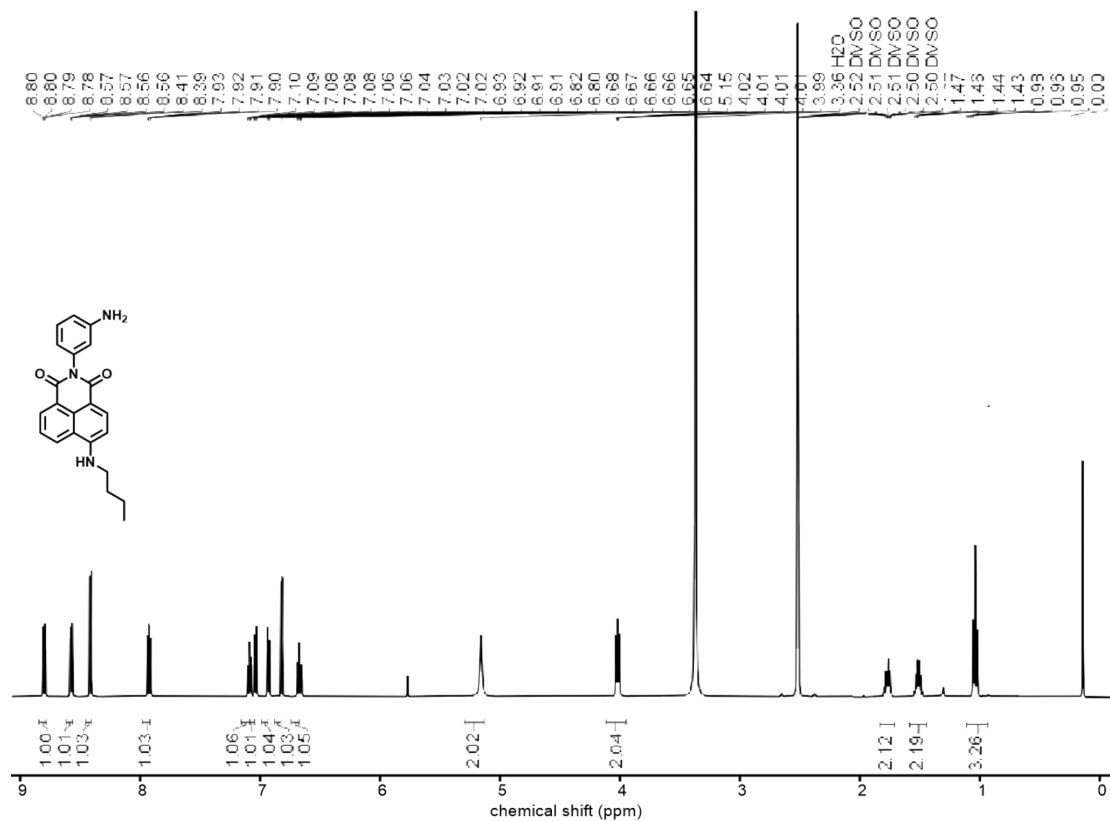


Figure S15. ¹H NMR spectrum of NZN in DMSO-*d*₆ (500 MHz).

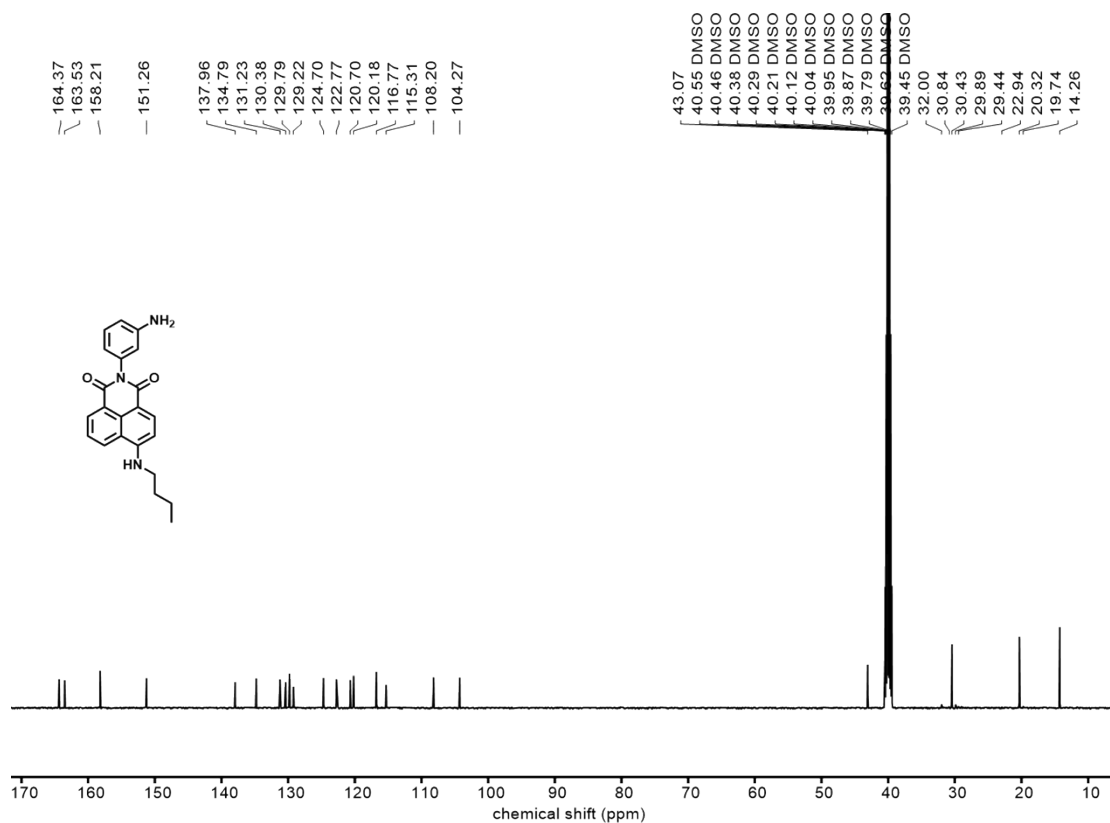


Figure S16. ¹³C NMR spectrum of NZN in DMSO-*d*₆ (500 MHz).

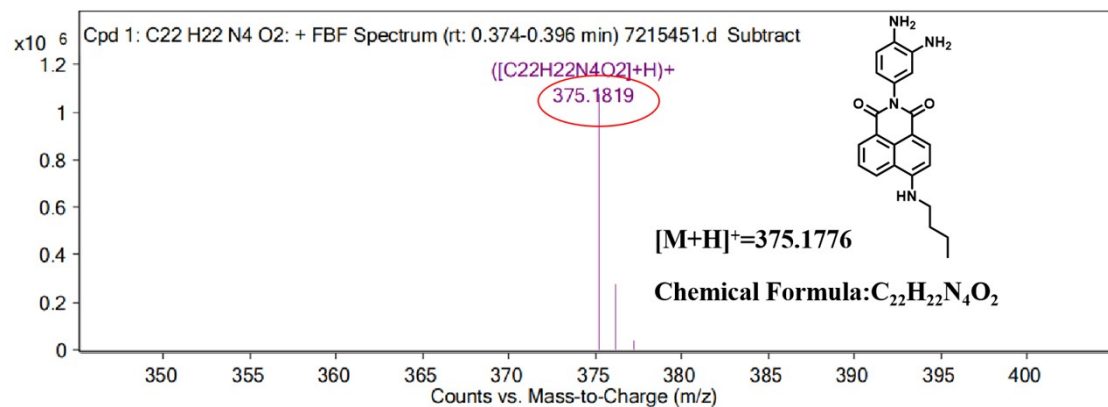


Figure S17. HR-MS (ESI) spectrum of NZNN.

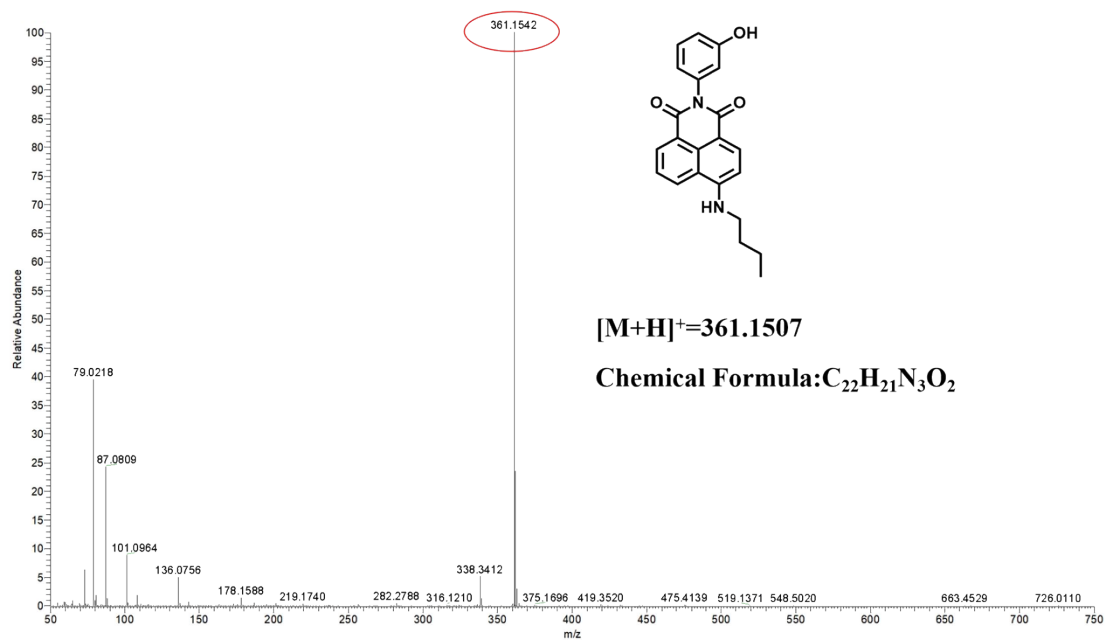


Figure S18. HR-MS (ESI) spectrum of NZOH.

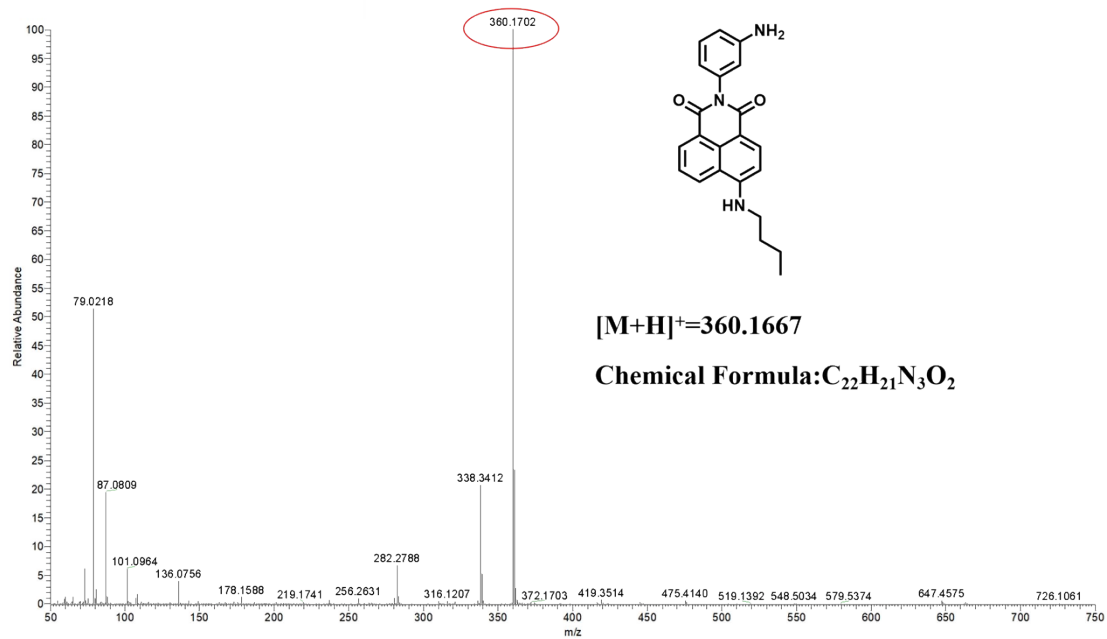


Figure S19. HR-MS (ESI) spectrum of NZN.

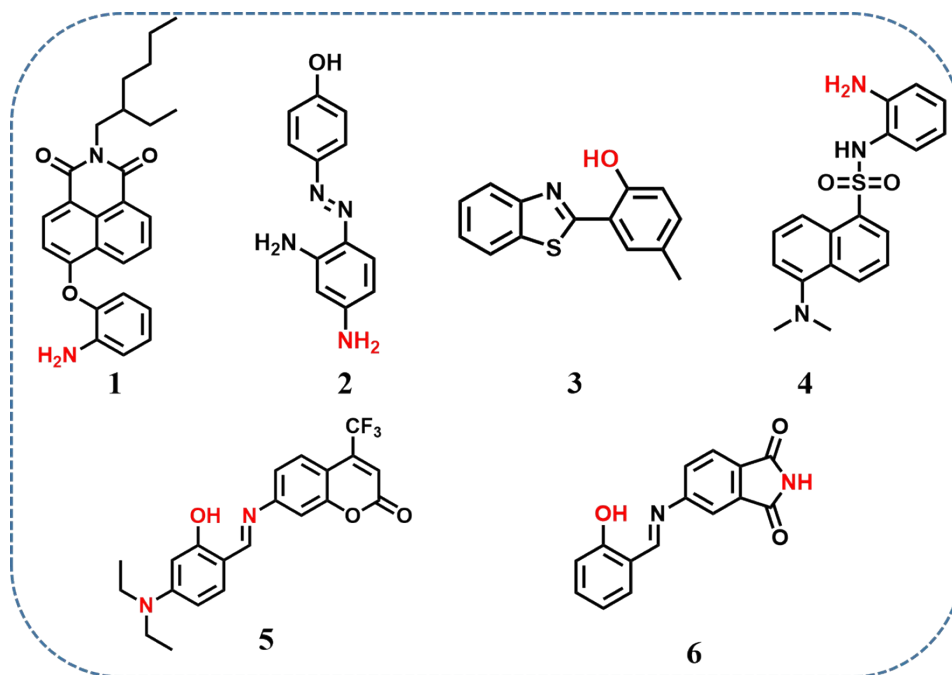


Fig S20. Some fluorescent probes used to detect DCP.

Table S1. Comparison of data from this study with other studies

Probe	Emission	Fluorescence response	Response time (s)	Selectivity	LOD	Paper strip	Application	Devitrization	Reference
1	414	Turn on	60	Good	13.6 μM	No	No	No	[1]
2	455	Turn on	60	Bad	200 μM	No	No	No	[2]
3	453	Turn on	6	Good	0.186 μM	Yes	No	No	[3]
4	515	Turn on	120	Good	10 μM	Yes	No	No	[4]
5	480	Turn on	No	Bad	8.7 nM	Yes	Yes	No	[5]
6	475	Turn on	No	Bad	0.1 μM	Yes	Yes	No	[6]
NZNN	500	Turn on	< 6	Good	30.1 nM	Yes	Yes	Yes	This work

References

1. M. Burnworth, S. J. Rowan and C. Weder, *Chemistry*, 2007, **13**, 7828-7836.
2. J. Yao, Y. Fu, W. Xu, T. Fan, Y. Gao, Q. He, D. Zhu, H. Cao and J. Cheng, *Anal Chem*, 2016, **88**, 2497-2501.
3. Y. Kim, Y. J. Jang, D. Lee, B.-S. Kim and D. G. Churchill, *Sensors Actuat B-chem*, 2017, **238**, 145-149.
4. M. Gupta and P. H.-i. Lee, *Sensors and Actuators B: Chemical*, 2017, **242**, 977-982.
5. B. Du, F.-H. Zhang, W. Cao, P.-H. Wang, Z.-J. Li and Z.-J. Ding, *ChemistrySelect*, 2018, **3**, 13470-13473.

6. X. Hu, H. Zeng, T. Chen, H.-Q. Yuan, L. Zeng and G.-M. Bao, *Sensors Actuat B-chem*, 2020, **319**, 128282.