Supplementary Information for

Supramolecular modulation of π-extended pyridinium photosensitizers for enhanced dual reactive oxygen species photocatalysis

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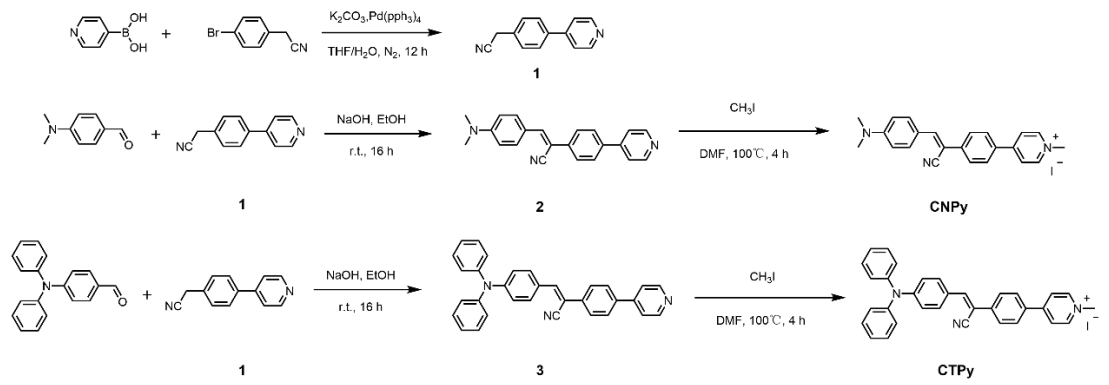
Materials and instruments.

Unless otherwise stated, all chemicals were purchased from commercial suppliers (Bide Pharmatech Ltd., Sigma Aldrich, TCI, Heowns Biochem) and used without further purification. ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) at 298 K, and the chemical shifts (δ) were expressed in ppm, and J values were given in Hz. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR). Multiplicities were presented as: s (singlet); d (doublet); t (triplet); and m (multiplet). UV-vis absorption spectra were characterized by a Shimadzu UV-2450 spectrophotometer. Fluorescence emission spectra were obtained by fluorescence spectrophotometer F-380A. Zeta potential tests was constructed on Malvern Zeta sizer Nano ZS90. The time-resolved fluorescence decay curve was obtained by the FLS 920 Steady-State/Transient Fluorescence Spectrometer. The photocatalytic reaction was performed on WATTCAS Parallel Photocatalytic Reactor (WP-TEC-HSL) with 10W LED.

Synthesis of CNPy and CTPy



Scheme S1. Synthetic route of CNPy and CTPy.

Synthetic of intermediate 1: Under a nitrogen atmosphere, a round-bottom flask equipped with a condenser was charged successively with 4-pyridineboronic acid (30.0 mmol), 3-bromophenylacetonitrile (30.0 mmol), potassium carbonate (60.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.5 mmol). A mixture of tetrahydrofuran (72 mL) and water (8 mL) was then added. The reaction mixture was stirred and refluxed at 80 °C for 12 hours. After completion of the reaction, the mixture was cooled to room temperature and extracted with dichloromethane (10 mL × 3). The combined organic layers were washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford compound 1 (5.42 g, 93% yield) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.66 (m, 2H), 7.67 (d, J = 8.2 Hz, 3H), 7.53 – 7.50 (m, 2H), 7.47 (d, J = 8.1 Hz, 2H), 3.83 (s, 2H).

Synthetic of intermediate 2 and 3: In a dried 50 mL round-bottom flask, a mixture of 4-(dimethylamino)benzaldehyde (4.0 mmol) and compound 1 (4.6 mmol) was dissolved in anhydrous ethanol (20 mL). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 0.5 hours. Subsequently, a solution of sodium hydroxide (4.6 mmol) in anhydrous ethanol (4 mL) was added dropwise to the system. After complete addition, the mixture was continued to stir under nitrogen at room temperature for 16 hours. Upon completion, the reaction mixture was filtered

under vacuum to afford an orange solid, which was washed with petroleum ether. The crude product was purified by silica gel column chromatography using dichloromethane as the eluent, yielding compound 3 (1.19 g, 92%) as an orange solid powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.66 (m, 2H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.78 – 7.73 (m, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.52 (m, 2H), 7.48 (s, 1H), 6.73 (d, *J* = 9.0 Hz, 2H), 3.08 (s, 6H). Similarly, target compound **3** was obtained as an orange-red solid powder (1.78 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.67 (m, 2H), 7.79 (dd, *J* = 13.3, 8.5 Hz, 4H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.50 (s, 1H), 7.33 (t, *J* = 7.7 Hz, 4H), 7.17 (d, *J* = 8.3 Hz, 4H), 7.14 – 7.09 (m, 2H), 7.06 (d, *J* = 8.6 Hz, 2H).

Synthetic of intermediate CNPy and CTPy: Compound 2 (1 mmol, 0.325 g) was added to 25 mL N,N-dimethylformamide (DMF) and dissolved with stirring. The mixture was heated to 100 °C in an oil bath for 4 hours, during which a gradual darkening of the solution color was observed. After the reaction completed, the mixture was cooled to room temperature, washed with ethyl acetate, and filtered under reduced pressure. The resulting orange-red solid powder was the target product CNPy, with a mass of 0.406 g and a yield of 87%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (d, *J* = 6.4 Hz, 2H), 8.56 (d, *J* = 6.4 Hz, 2H), 8.21 (d, *J* = 8.4 Hz, 2H), 8.07 (s, 1H), 7.95 (dd, *J* = 8.7, 6.8 Hz, 4H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.33 (s, 3H), 3.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.57, 152.60, 146.02, 145.09, 139.03, 132.67, 132.23, 129.22, 126.26, 124.15, 120.97, 119.52, 112.11, 100.98, 47.49. Similarly, the target compound CTPy was obtained as a red solid powder (0.491 g, 83% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (d, *J* = 6.7 Hz, 2H), 8.57 (d, *J* = 6.7 Hz, 2H), 8.22 (d, *J* = 8.6 Hz, 2H), 8.15 (s, 1H), 8.00 – 7.90 (m, 4H), 7.42 (t, *J* = 7.8 Hz, 4H), 7.20 (dd, *J* = 18.4, 7.6 Hz, 6H), 6.97 (d, *J* = 8.9 Hz, 2H), 4.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.49, 150.48, 146.29, 146.11, 144.37, 138.23, 133.52, 131.75, 130.42, 129.28, 126.77, 126.30, 126.10, 125.45, 124.34, 120.00, 118.72, 105.09.

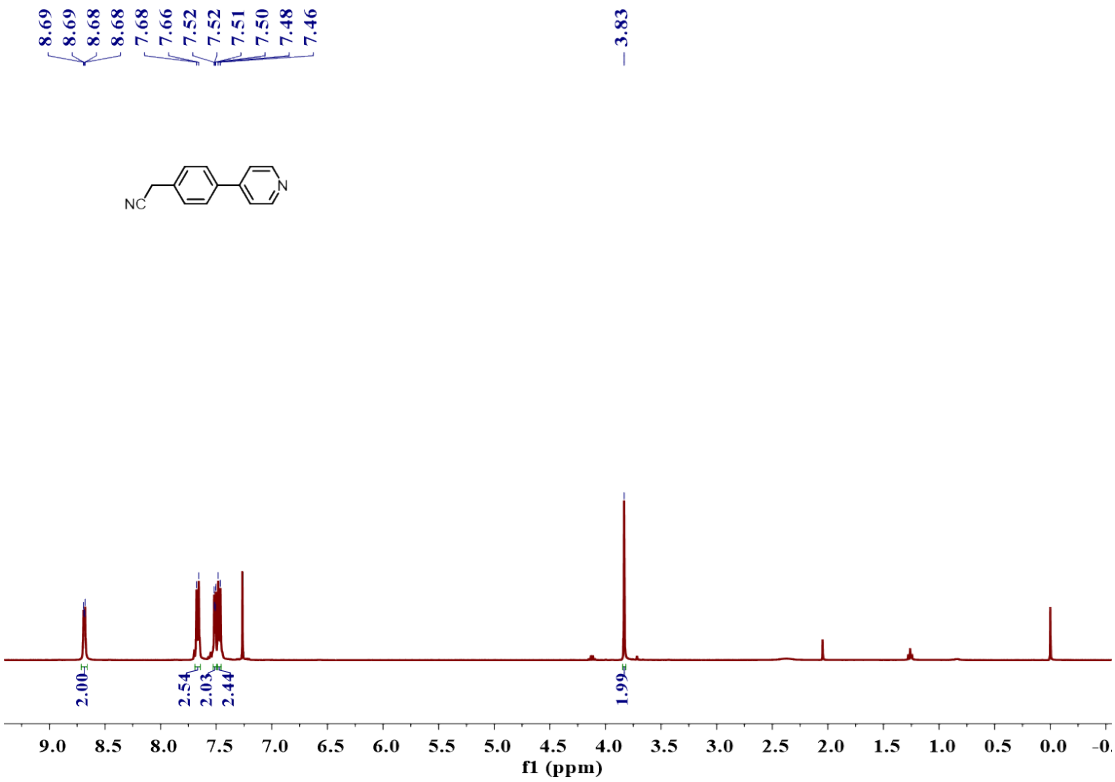


Fig. S1. ^{1}H NMR spectra of **1** in $CDCl_3$.

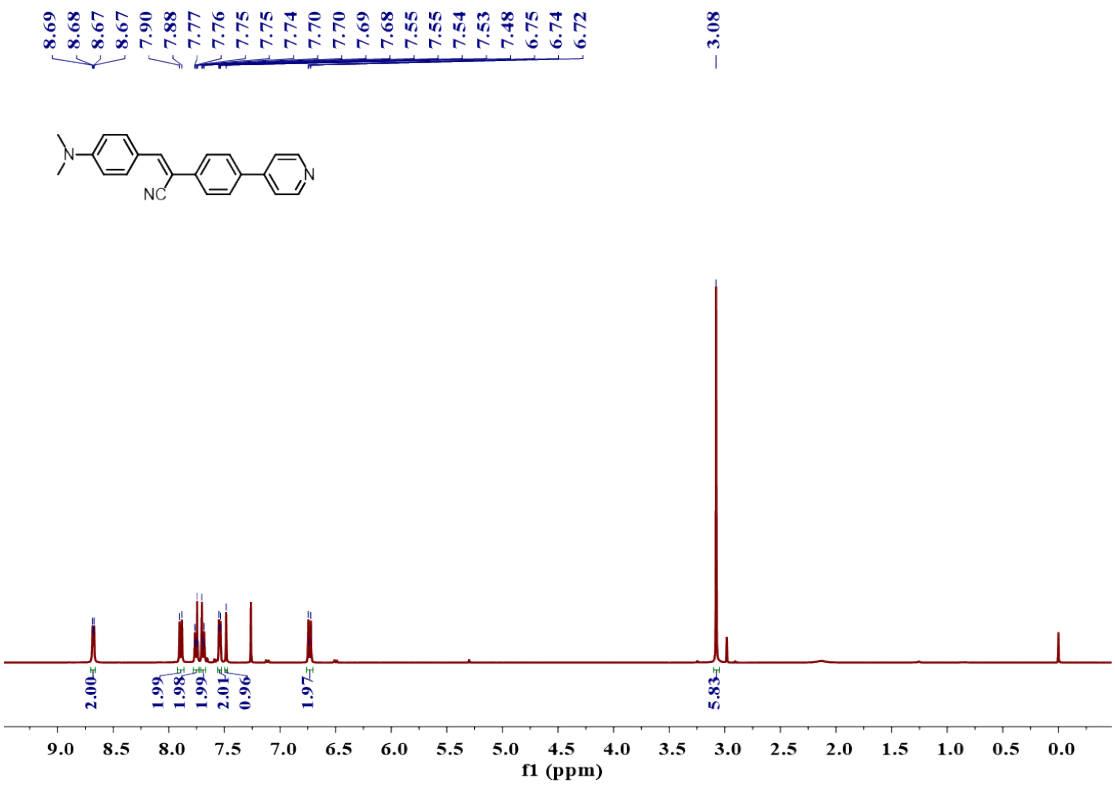


Fig. S2. ^{1}H NMR of **2** in $CDCl_3$

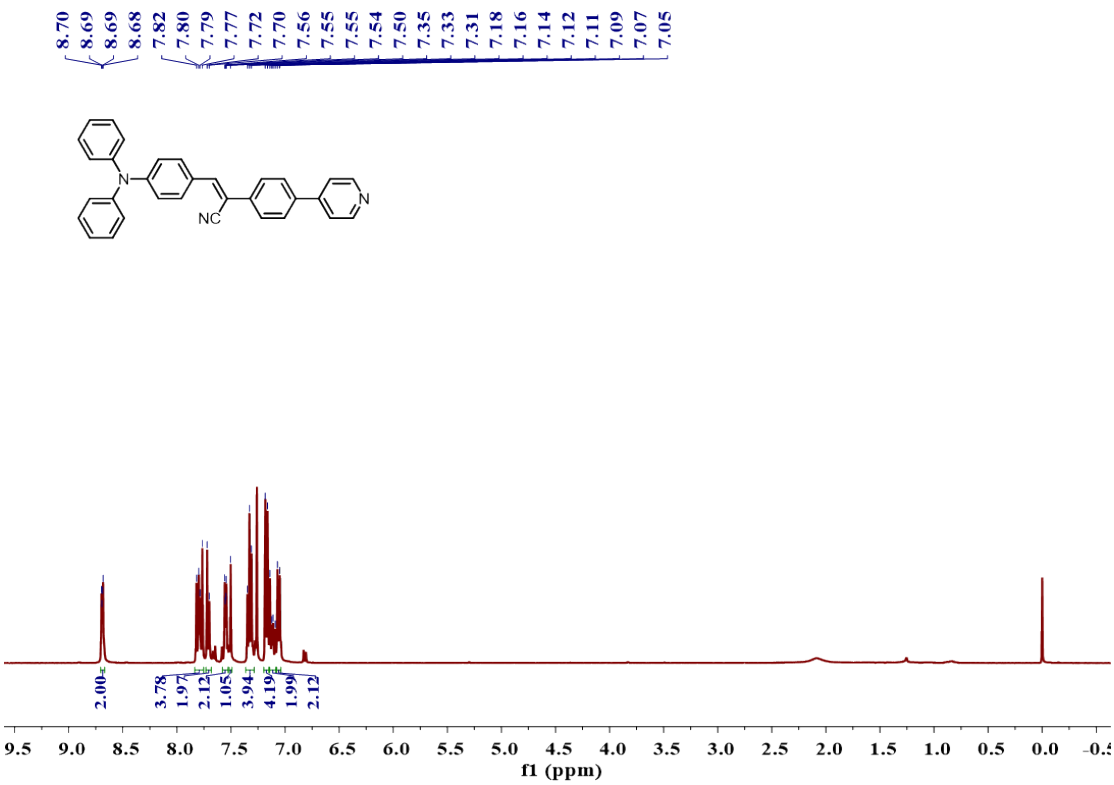


Fig. S3. ^{1}H NMR of **3** in $CDCl_3$

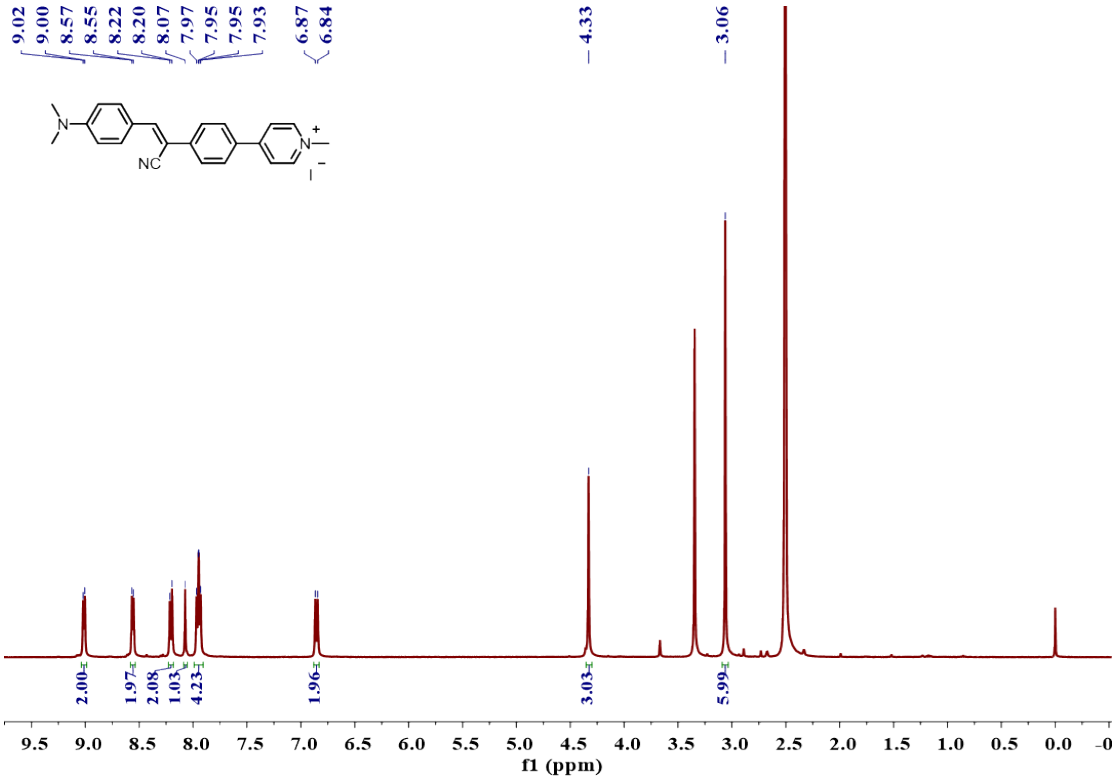


Fig. S4. [1]H NMR of **CNPy** in DMSO-d_6.

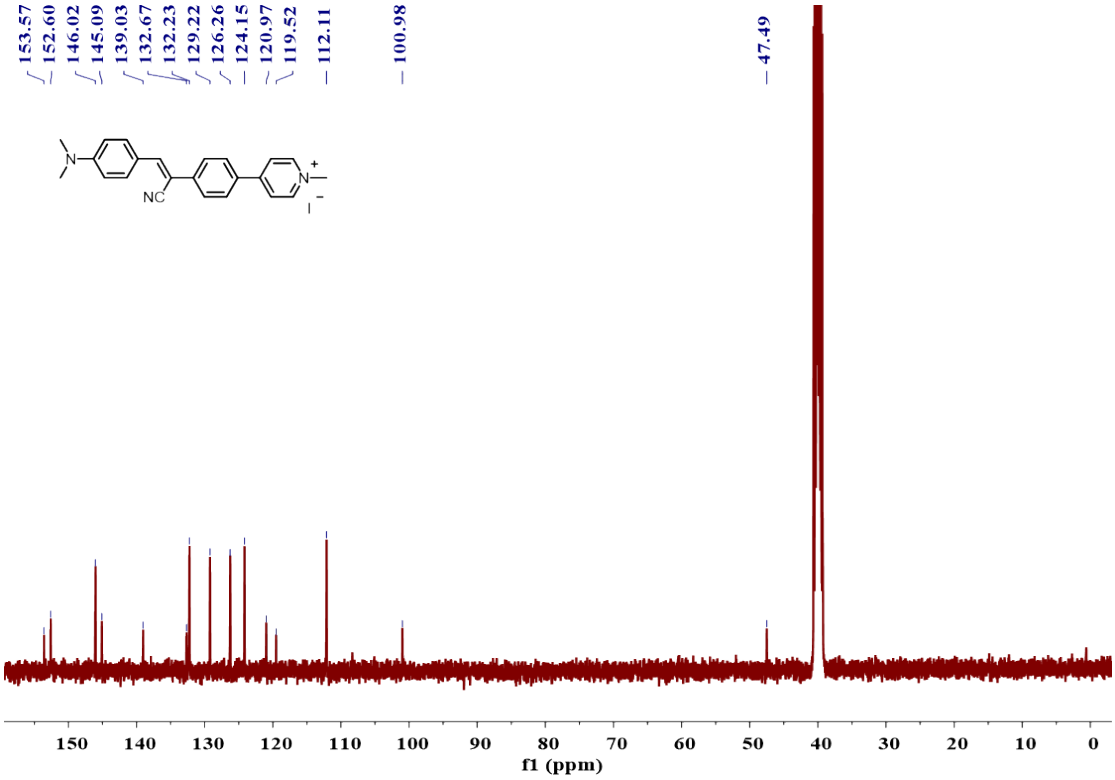


Fig. S5. [13]C NMR of **CNPy** in DMSO-d_6.

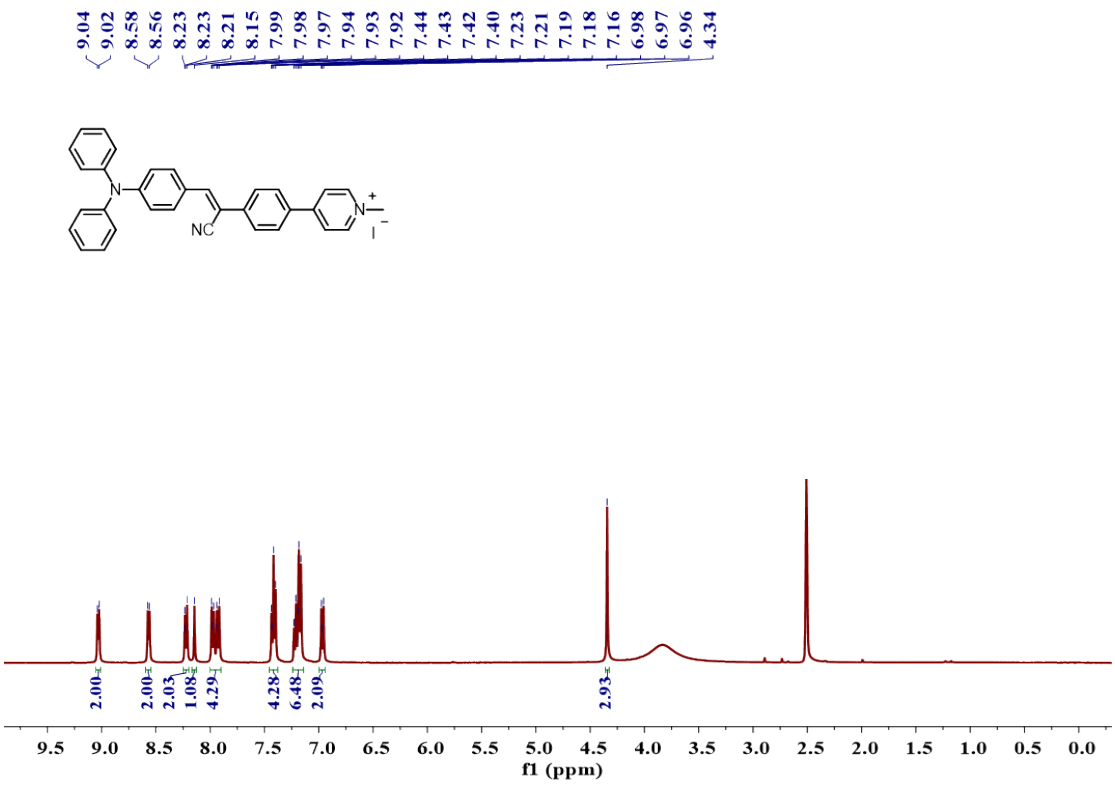


Fig. S6. ^{1}H NMR of **CTPy** in DMSO-d_6.

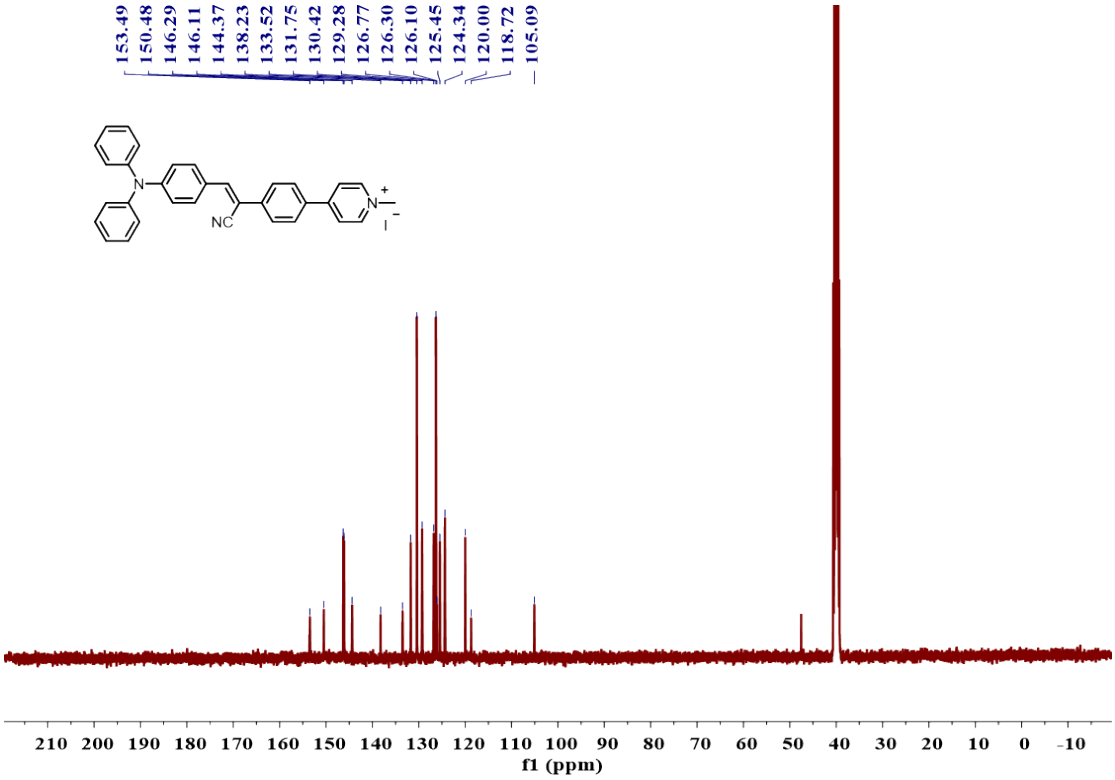


Fig. S7. ^{13}C NMR of **CTPy** in DMSO-d_6.

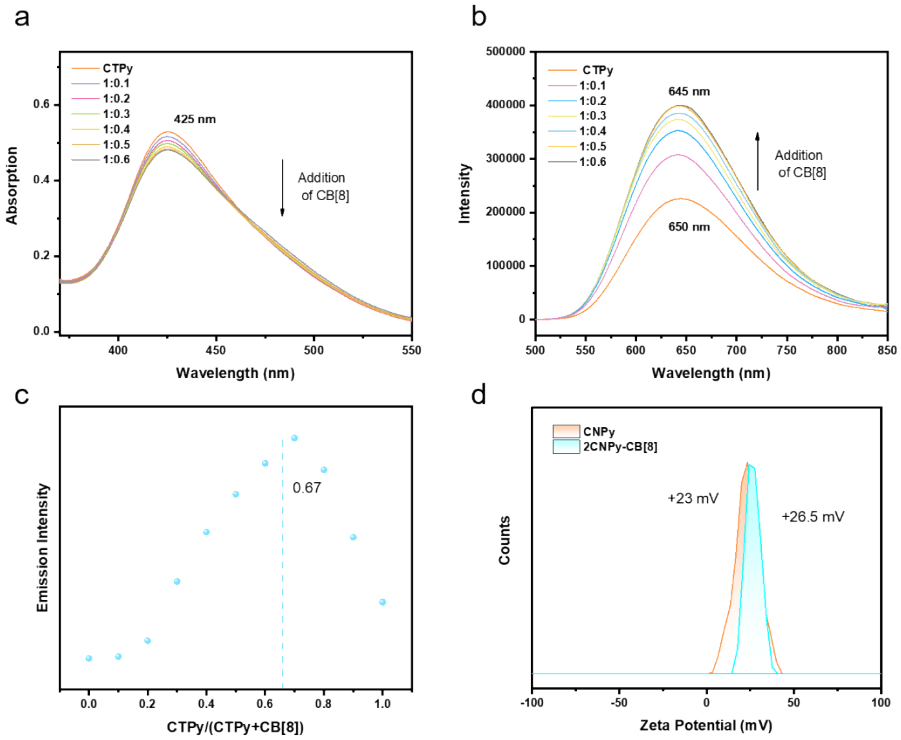


Fig. S8. (a) UV-vis absorption spectra of CTPy upon successive addition of CB[8] in aqueous solution; (b) fluorescence emission spectra of CTPy upon successive addition of CB[8] in aqueous solution (λ_{ex} = 425 nm); (c) Job's plot for the complexation between CTPy and CB[8] with the total concentration of CTPy and CB[8] fixed at 2.0 × 10^{-5} M; (d) zeta potentials of CTPy and 2CTPy-CB[8].

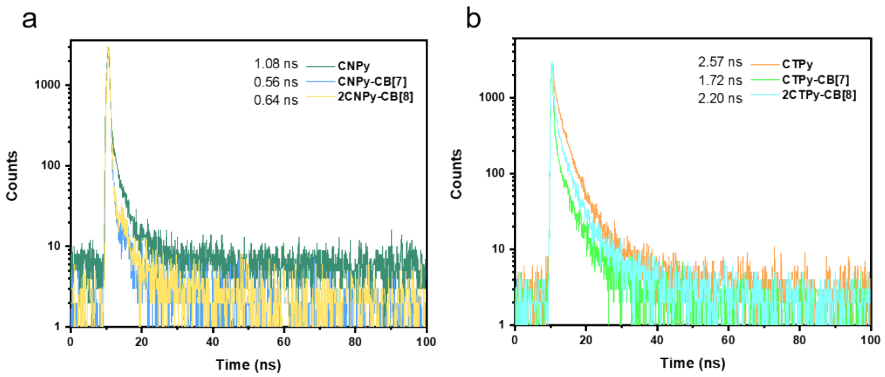


Fig. S9. Time-resolved fluorescence decay curves of (a) CNPy and (b) CTPy systems.

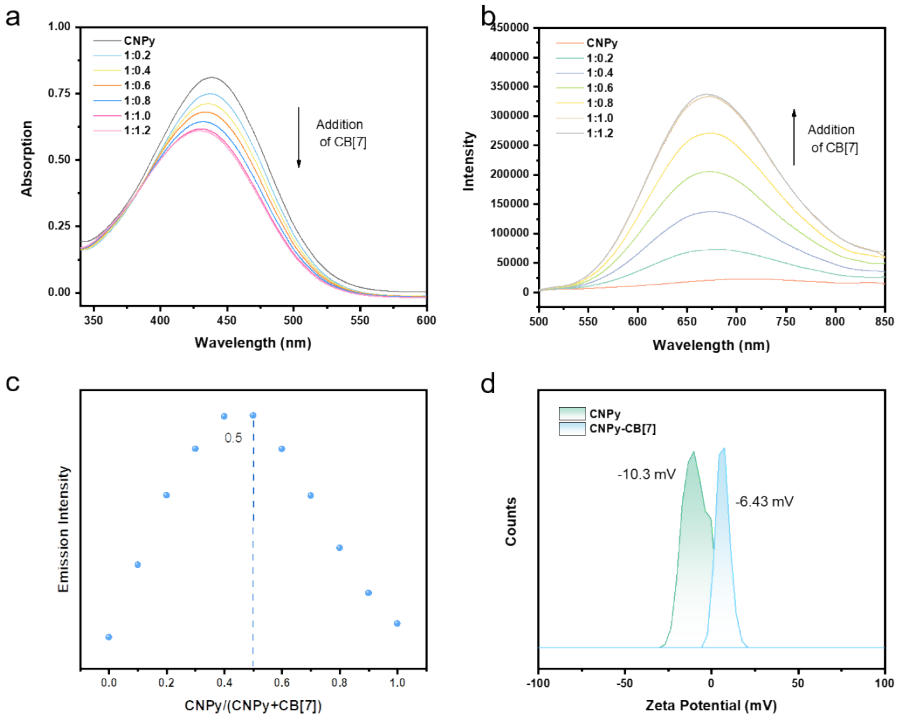


Fig. S10. (a) UV-vis absorption spectra of CNPy upon successive addition of CB[7] in aqueous solution; (b) fluorescence emission spectra of CNPy upon successive addition of CB[7] in aqueous solution (λ_{ex} = 425 nm); (c) Job's plot for the complexation between CNPy and CB[7] with the total concentration of CNPy and CB[7] fixed at 2.0 × 10^{-5} M; (d) zeta potentials of CNPy and CNPy-CB[7].

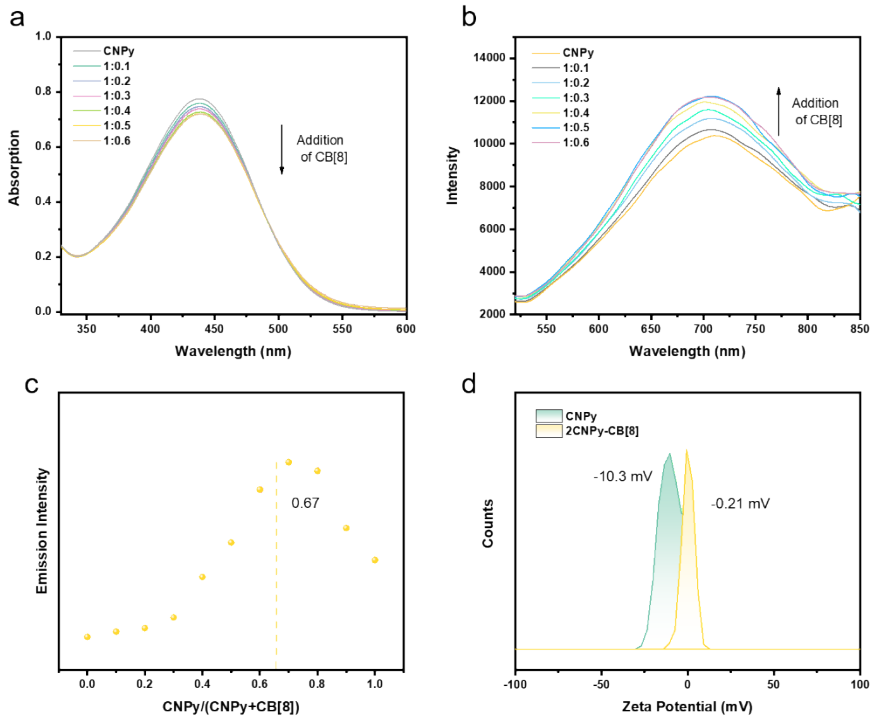
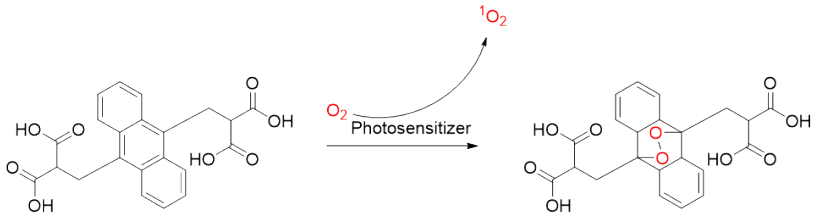


Fig. S11. (a) UV-vis absorption spectra of CNPy upon successive addition of CB[8] in aqueous solution; (b) fluorescence emission spectra of CNPy upon successive addition of CB[8] in aqueous solution (λ_{ex} = 425 nm); (c) Job's plot for the complexation between CNPy and CB[8] with the total concentration of CNPy and CB[8] fixed at 2.0 × 10^{-5} M; (d) zeta potentials of CNPy and 2CNPy-CB[8].

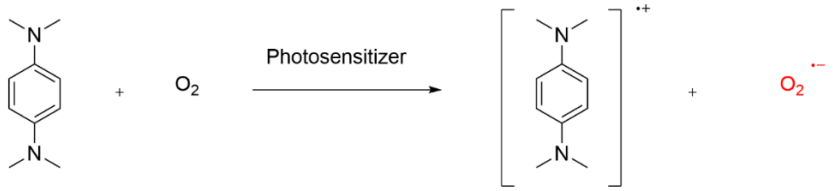
The generation of $^1O_2$ detected by 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA).

Compound 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA) was used as an indicator for detection of $^1O_2$ in solution. $^1O_2$ selectively reacted with ABDA and resulting in a corresponding decrease in its absorbance.50 μM of photocatalyst was dissolved in 3.0 mL solution containing 250 μM of ABDA. The mixture was then placed in a cuvette and irradiated with a blue light (455 nm). The absorption change of the sample at 378 nm was recorded by the UV-vis absorption spectrophotometer.



The generation of $O_2^{\bullet-}$ detected by N, N, N', N'-tetramethyl-phenylenediamine (TMPD)

N, N, N′, N′-tetramethyl-phenylenediamine (TMPD) was used as the scavenger monitors $O_2^{\bullet-}$. The 5 mM TMPD solution in DMSO was added to the aqueous solution to form a 0.25 mM solution. 50 μM photocatalyst were added into TMPD solution respectively for $O_2^{\bullet-}$ generation measurement. The mixture was then placed in a cuvette and irradiated with a blue light (455 nm). The generation of $O_2^{\bullet-}$ was detected by monitoring the absorption at 612 nm through UV-vis absorption spectra.



Procedure for $^1O_2$ Quantum Yield Measurement.

The $^1O_2$ quantum yield was measured using Rose Bengal (RB) as the reference photosensitizer and calculated using the following Equation 1:

$$\Phi_{probe}=\Phi_{RB}\times(K_{probe}A_{RB}/\ K_{RB}A_{probe}) \text{ (Equation 1)}$$

where K_{probe} and K_{RB} are the decomposition rate constants of ABDA in the presence of the probe and RB, respectively. Φ_{RB} is the $^1O_2$ quantum yield of RB (Φ_{RB} = 0.75 in water). A_{probe} and A_{RB} represent the integration area of absorption bands ranging from 450 to 455 nm of the probe and RB, respectively. The ABDA (1.5×10^{-7} mol) in 3 mL of the probe solution was exposed to Blue light irradiation (455 nm) with a power density of 10W. The natural logarithm of the absorbance ratio (A_0/A) of ABDA at 378 nm was plotted against irradiation time and the slope is regarded as the decomposition rate.

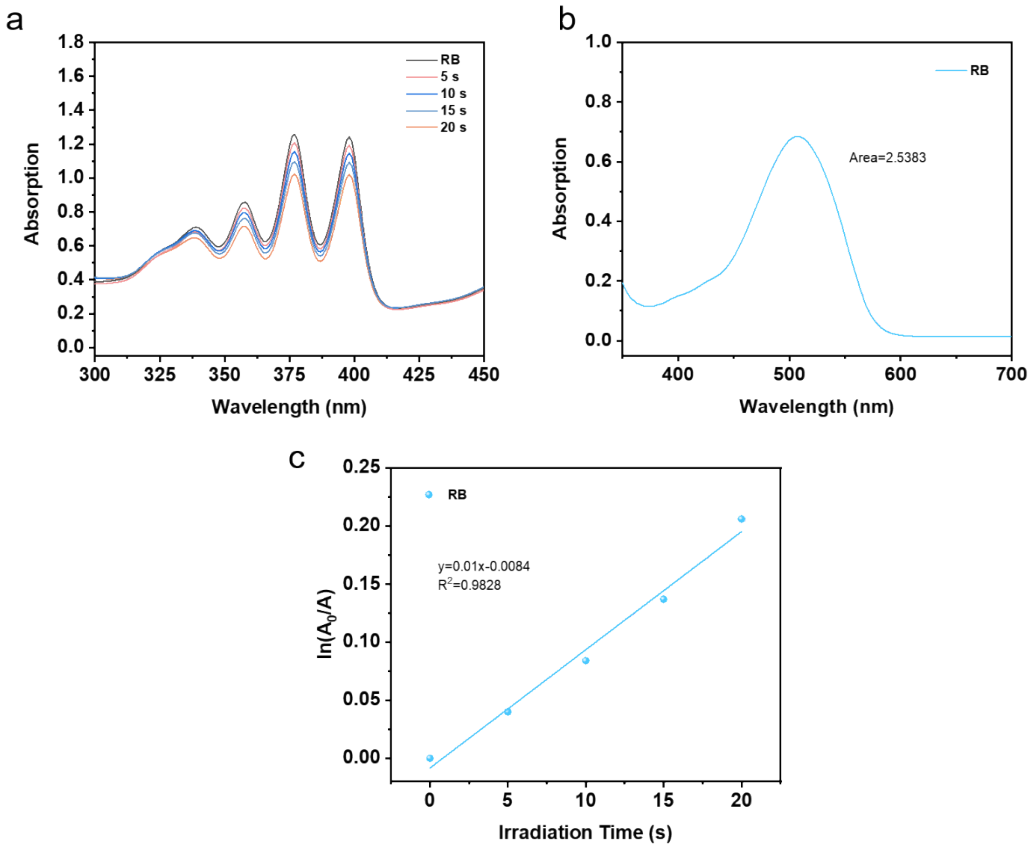


Fig. S12. (a) UV-vis absorption spectra of ABDA after irradiation (455 nm, 10 W) for different time in the presence of RB; (b) UV-vis absorption spectra of RB in the aqueous solution; (c) the decomposition rates of ABDA in the presence of RB.

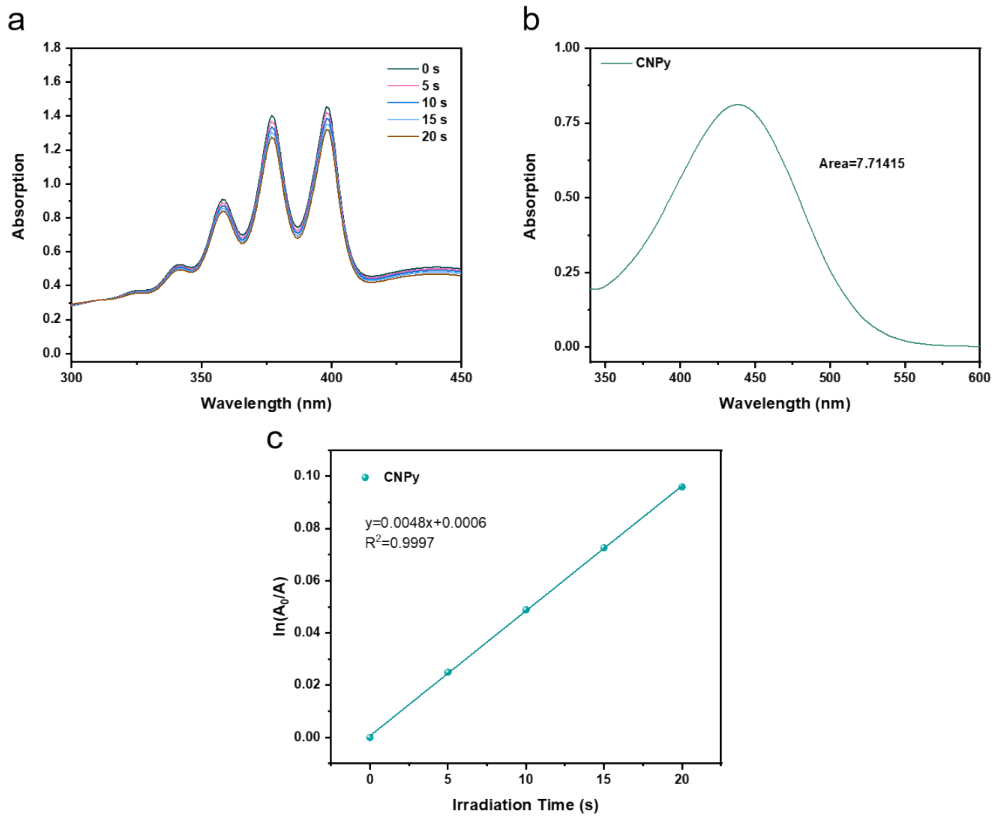


Fig. S13. (a) UV-vis absorption spectra of ABDA after irradiation (455 nm, 10 W) for different time in the presence of CNPy; (b) UV-vis absorption spectra of CNPy in the aqueous solution; (c) the decomposition rates of ABDA in the presence of CNPy. [CNPy] = 2.0×10^{-5} M.

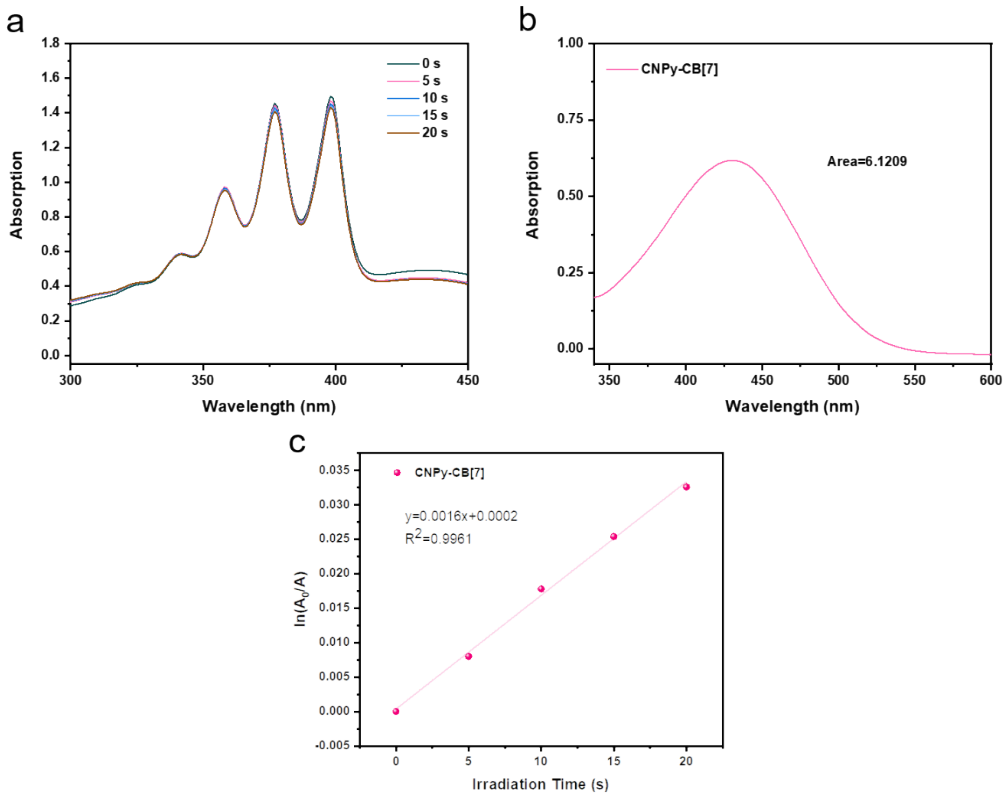


Fig. S14. (a) UV-vis absorption spectra of ABDA after irradiation (455 nm, 10 W) for different time in the presence of CNPy-CB[7]; (b) UV-vis absorption spectra of CNPy-CB[7] in the aqueous solution; (c) the decomposition rates of ABDA in the presence of CNPy-CB[7]. [CNPy-CB[7]] = 2.0×10^{-5} M.

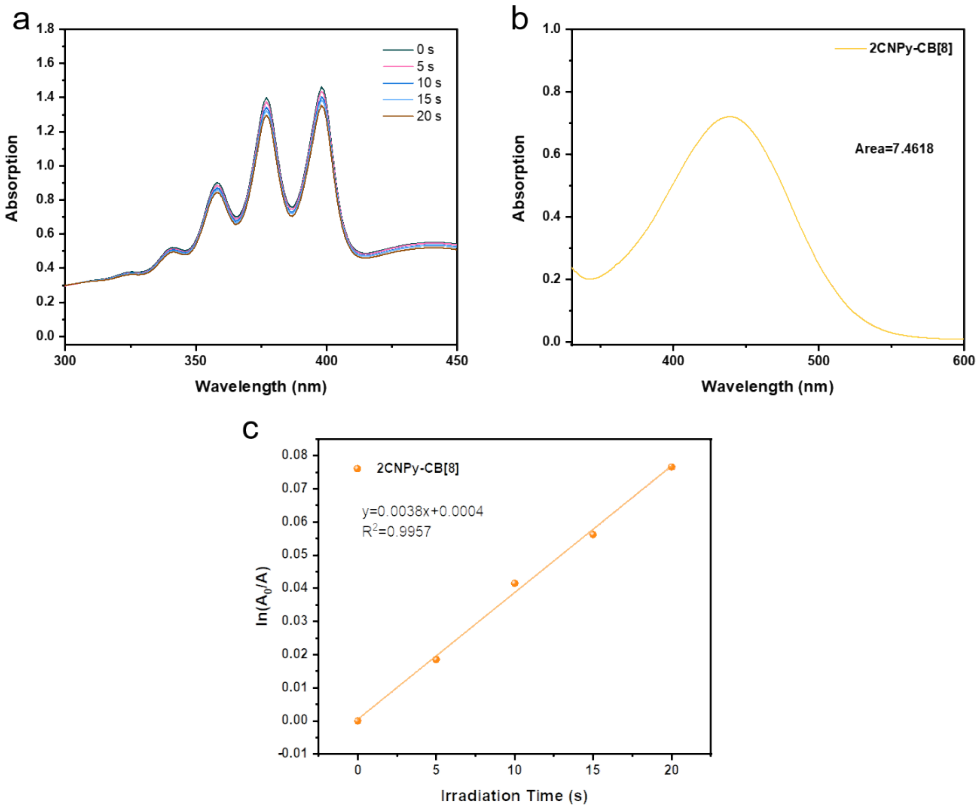


Fig. S15. (a) UV-vis absorption spectra of ABDA after irradiation (455 nm, 10 W) for different time in the presence of 2CNPy-CB[8]; (b) UV-vis absorption spectra of 2CNPy-CB[8] in the aqueous solution; (c) the decomposition rates of ABDA in the presence of 2CNPy-CB[8]. [2CNPy-CB[8]] = 2.0×10^{-5} M.

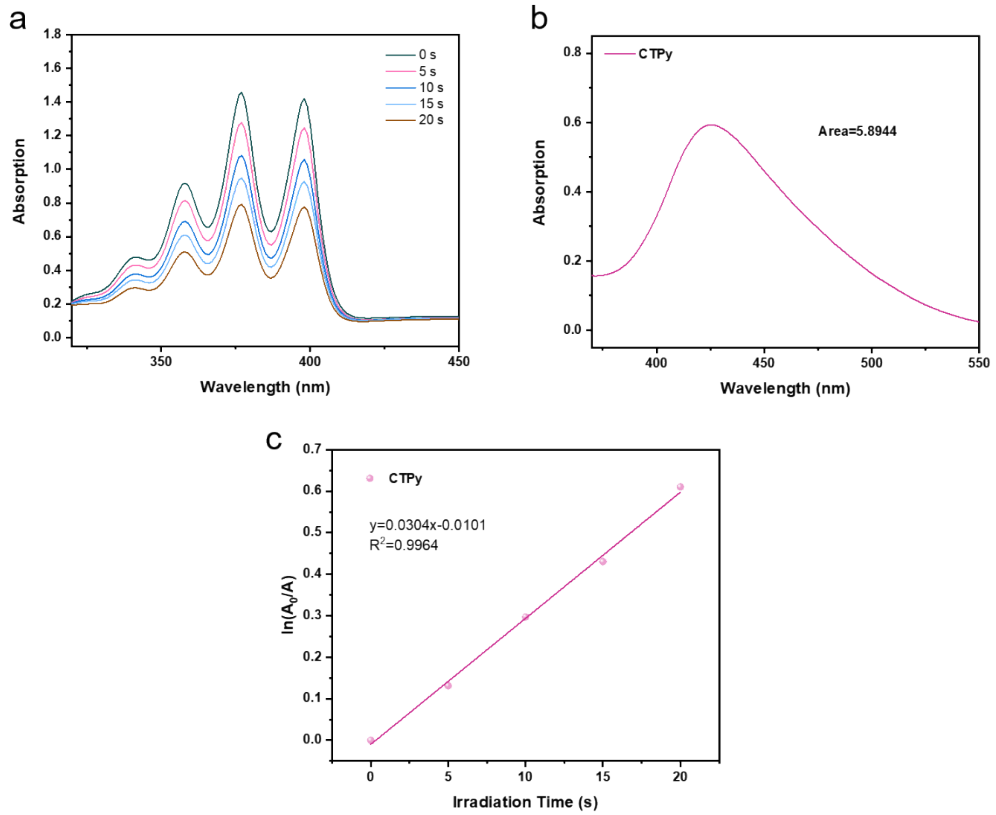


Fig. S16. (a) UV-vis absorption spectra of ABDA after irradiation (455 nm, 10 W) for different time in the presence of CTPy; (b) UV-vis absorption spectra of CTPy in the aqueous solution; (c) the decomposition rates of ABDA in the presence of CTPy CTPy. [CTPy] = 2.0×10^{-5} M.

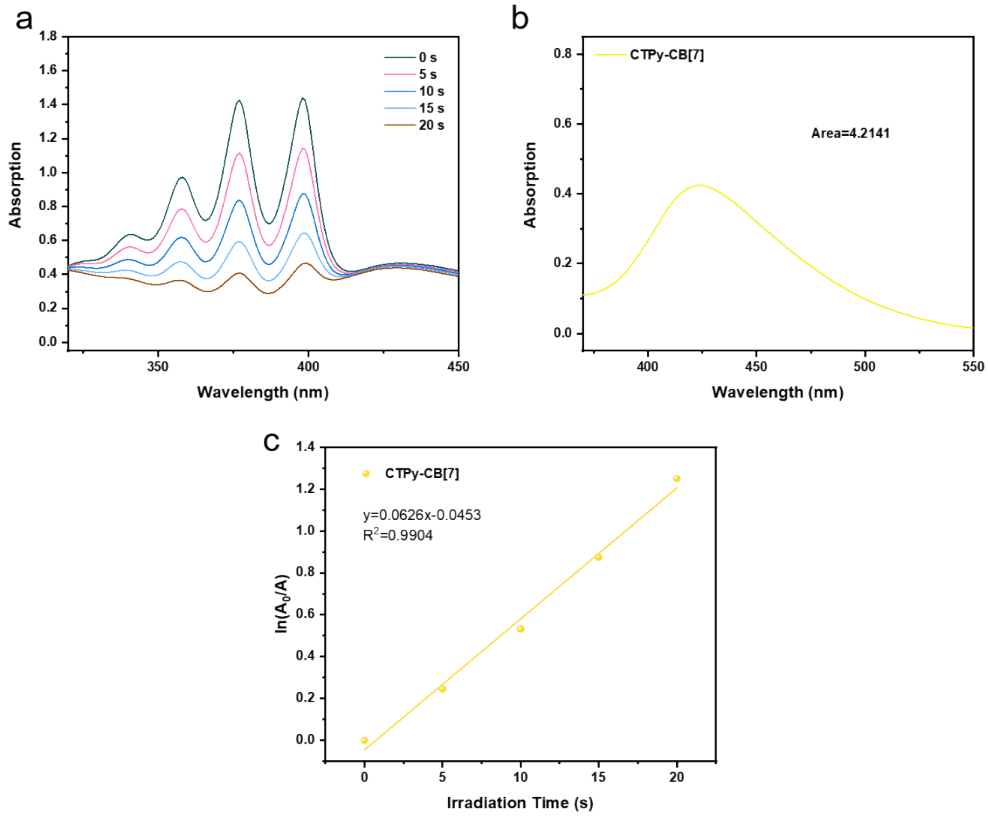


Fig. S17. (a) UV-vis absorption spectra of ABDA after irradiation (455 nm, 10 W) for different time in the presence of CTPy-CB[7]; (b) UV-vis absorption spectra of CTPy-CB[7] in the aqueous solution; (c) the decomposition rates of ABDA in the presence of CTPy-CB[7]. [CTPy-CB[7]] = 2.0×10^{-5} M.

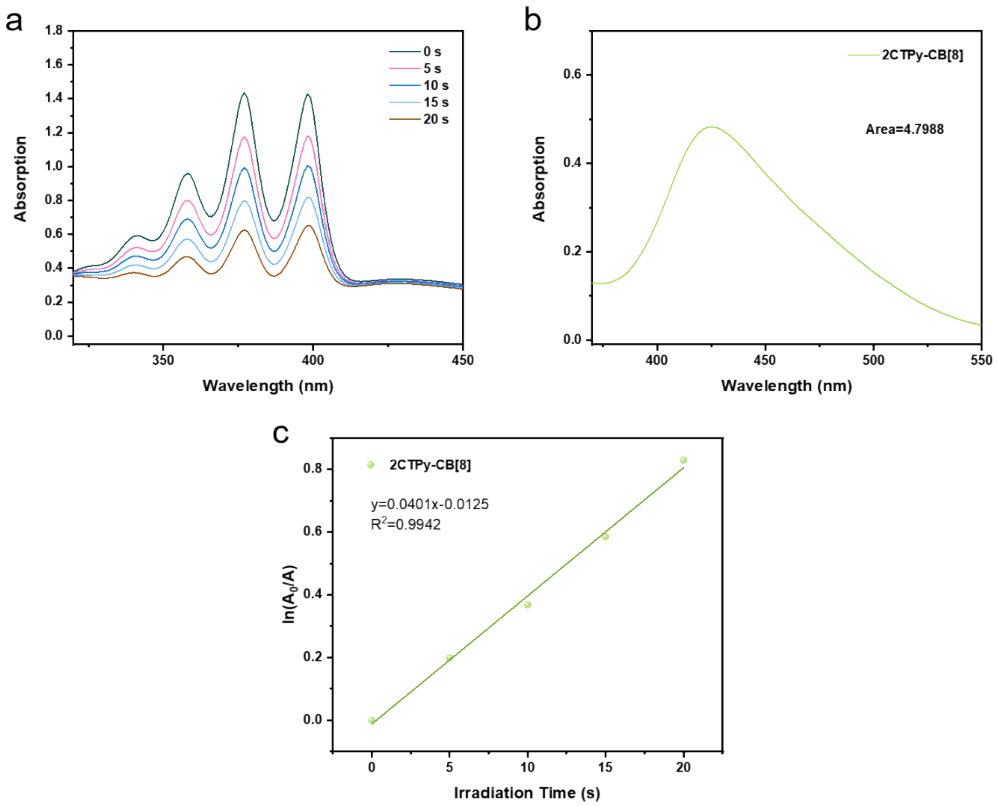


Fig. S18. (a) UV-vis absorption spectra of ABDA after irradiation (455 nm, 10 W) for different time in the presence of 2CTPy-CB[8]; (b) UV-vis absorption spectra of 2CTPy-CB[8] in the aqueous solution; (c) the decomposition rates of ABDA in the presence of 2CTPy-CB[8]. [2CTPy-CB[8]] = 2.0×10^{-5} M.

Procedure for $O_2^{\bullet-}$ Generation Efficiency Measurement.

The amounts of $O_2^{\bullet-}$ was quantitatively detected by nitroblue tetrazolium (NBT) conversion detection. NBT, which can react with $O_2^{\bullet-}$ and displays a maximum absorbance at 260 nm, was selected to determine the amounts of $O_2^{\bullet-}$ generated over the photocatalysts. By recording the concentration of NBT on a UV-vis spectrophotometer, the production of $O_2^{\bullet-}$ was quantitatively analyzed. 40 μM of photocatalyst was dissolved in 3 mL solution containing 13.3 μM of NBT. The mixture was then placed in a cuvette and irradiated with a blue light (455 nm). At appropriate intervals, record the change in absorbance of NBT at 260 nm by UV-vis spectrophotometer, the production of $O_2^{\bullet-}$ was quantitatively analyzed.

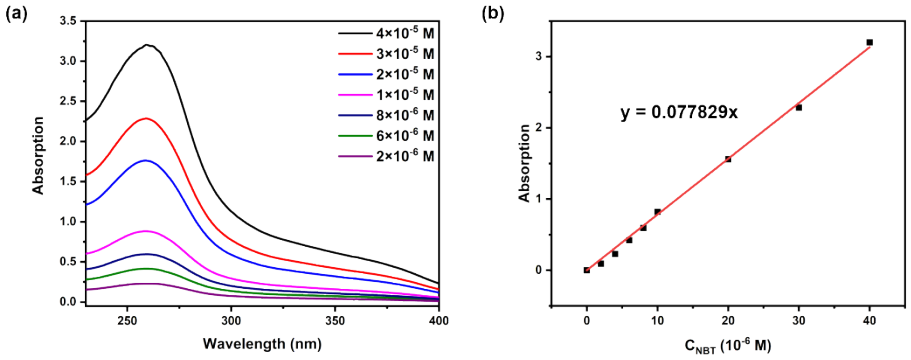


Fig. S19. (a) UV-vis absorption spectra of different concentrations of NBT in the aqueous solution; (b) the relation curve of UV-vis absorption intensity of NBT at 260 nm and NBT concentration in aqueous solutions.

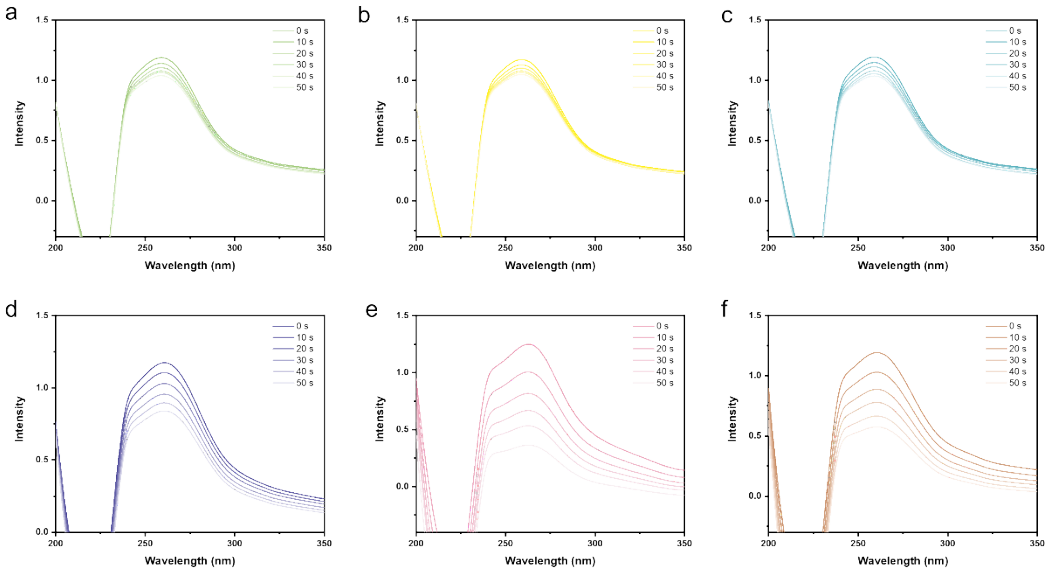
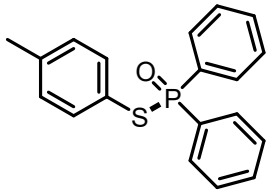


Fig. S20 UV-vis absorption spectra of NBT after irradiation (455 nm, 10 W) for different time in the presence of (a) CNPy; (b) CNPy-CB[7]; (c) 2CNPy-CB[8]; (d) CTPy; (e) CTPy-CB[7] and (f) 2CTPy-CB[8].

^{1}H NMR data of 3a-3w

3a. S-(p-tolyl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3a as a colorless oil. (60.9mg, 94% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 4H), 7.54 – 7.47 (m, 2H), 7.43 (tdd, *J* = 6.7, 3.5, 1.5 Hz, 4H), 7.32 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 2.24 (d, *J* = 1.5 Hz, 3H).[1]

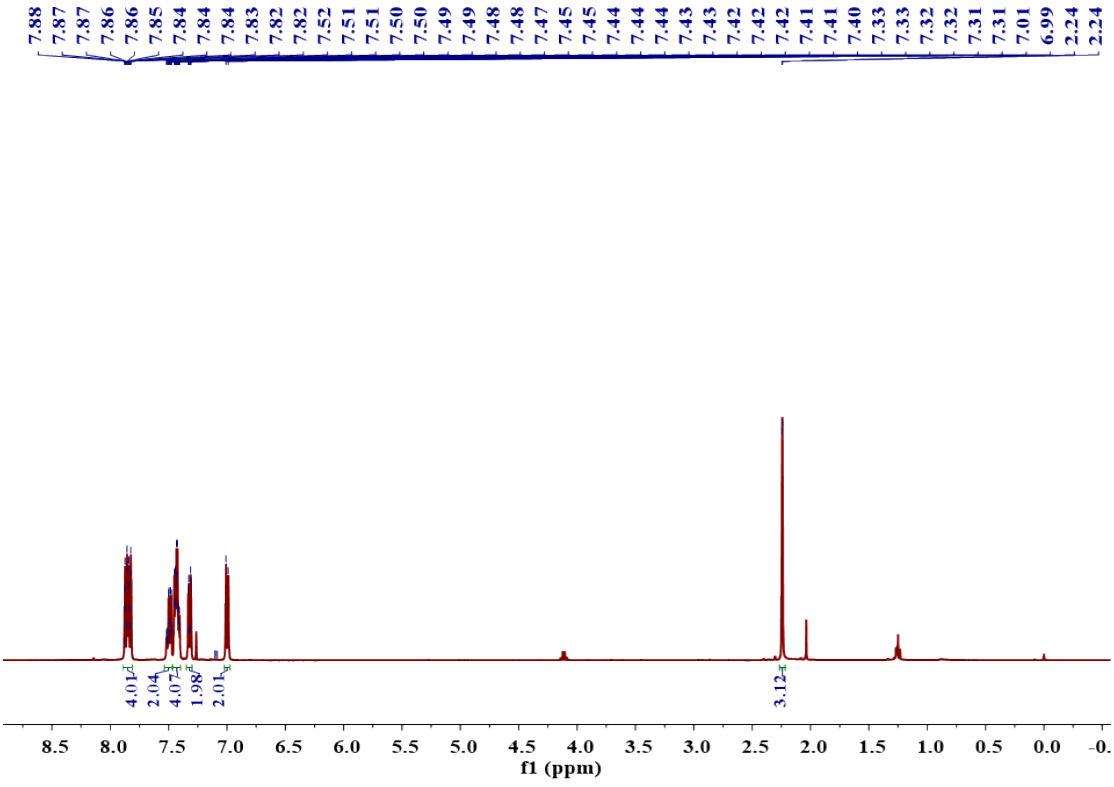
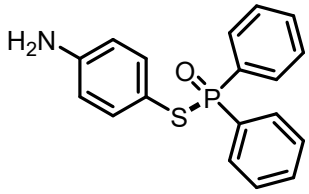


Fig. S21. ^{1}H NMR spectra of **3a** in $CDCl_3$.

3b. S-(4-aminophenyl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=4:1) to give 3b as orange clear liquid. (62.4 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.88 – 7.79 (m, 4H), 7.54 – 7.40 (m, 6H), 7.16 (dt, *J* = 8.4, 1.6 Hz, 2H), 6.46 (d, *J* = 8.6 Hz, 2H).[1]

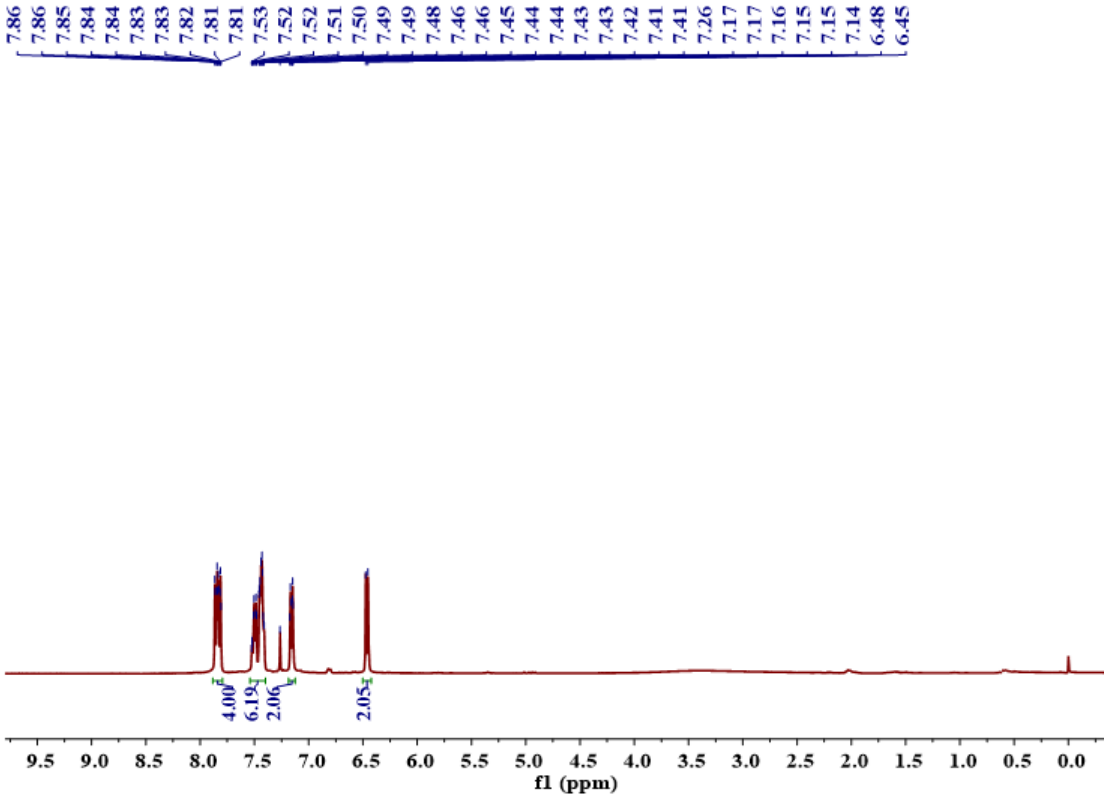
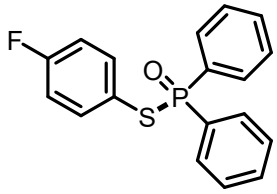


Fig. S22. ^{1}H NMR spectra of **3b** in $CDCl_3$.

3c. S-(4-fluorophenyl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3c as a colorless oil. (47.2 mg, 72% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (ddd, *J* = 12.9, 8.3, 1.4 Hz, 4H), 7.56 – 7.50 (m, 2H), 7.48 – 7.38 (m, 6H), 6.90 (s, 2H).[1]

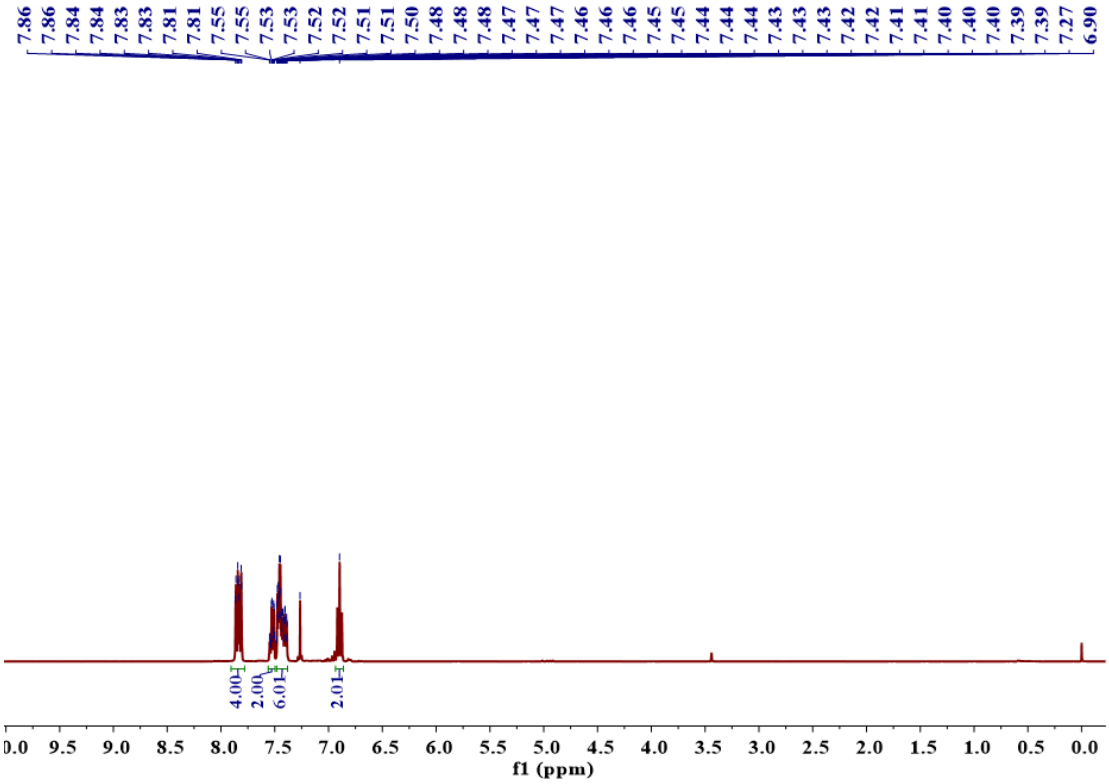
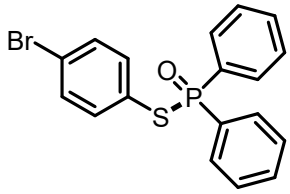


Fig. S23. ^{1}H NMR spectra of **3c** in $CDCl_3$.

3d. S-(4-bromophenyl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3d as a colorless oil. (52.8 mg, 68% yield).[1]H NMR (400 MHz, $CDCl_3$) δ 7.84 (ddd, J = 13.0, 8.2, 1.4 Hz, 4H), 7.54 (ddd, J = 7.2, 5.2, 1.6 Hz, 2H), 7.46 (td, J = 7.4, 3.6 Hz, 4H), 7.35 – 7.29 (m, 4H).[2]

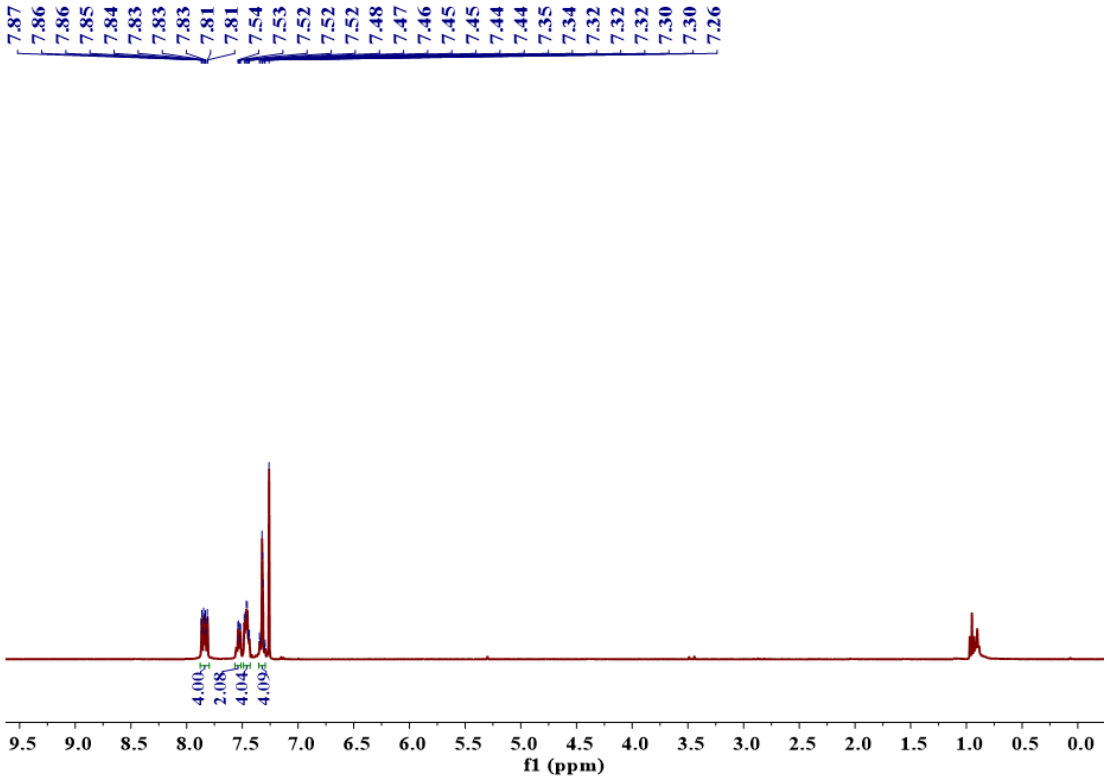
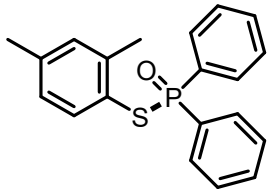


Fig. S24. [1]H NMR spectra of **3d** in $CDCl_3$.

3e. S-(2,4-dimethylphenyl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=4:1) to give 3e as a colorless oil. (48.6 mg, 72% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 4H), 7.54 – 7.48 (m, 2H), 7.46 – 7.40 (m, 4H), 7.30 (dd, J = 7.9, 1.7 Hz, 1H), 6.98 – 6.94 (m, 1H), 6.82 (dd, J = 8.0, 2.0 Hz, 1H), 2.31 (s, 3H), 2.23 (d, J = 1.5 Hz, 3H).[3]

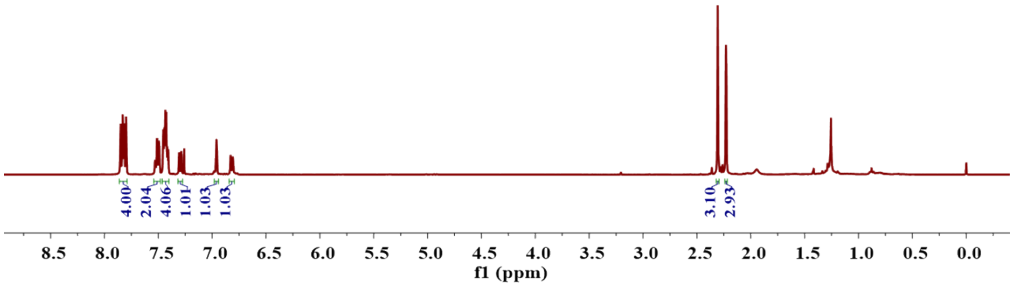
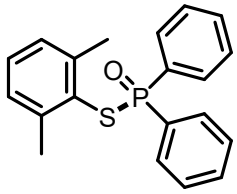


Fig. S25. ^{1}H NMR spectra of **3e** in $CDCl_3$.

3f. S-(2,6-dimethylphenyl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=4:1) to give 3f as a colorless oil. (42.6 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 4H), 7.57 – 7.51 (m, 2H), 7.43 (tdd, J = 6.5, 3.7, 1.3 Hz, 4H), 7.12 (ddd, J = 8.3, 6.8, 1.6 Hz, 2H), 6.78 – 6.73 (m, 1H), 2.29 (d, J = 0.9 Hz, 6H).[3]

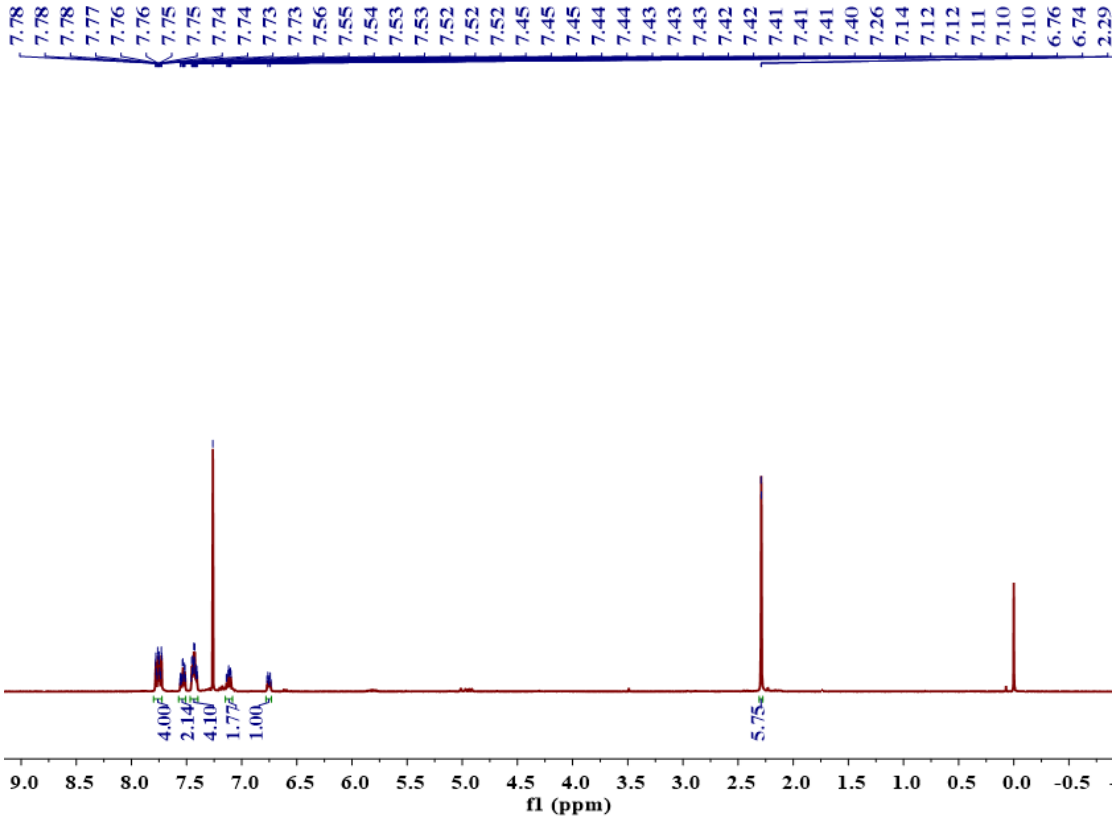
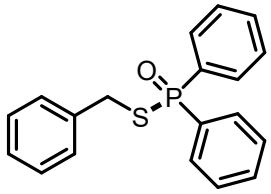


Fig. S26. ^{1}H NMR spectra of **3f** in $CDCl_3$.

3g. S-benzyl diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=4:1) to give 3g as a colorless oil. (53.7 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 4H), 7.53 (dd, J = 7.4, 1.8 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.23 – 7.17 (m, 5H), 4.02 (d, J = 9.2 Hz, 2H).[2]

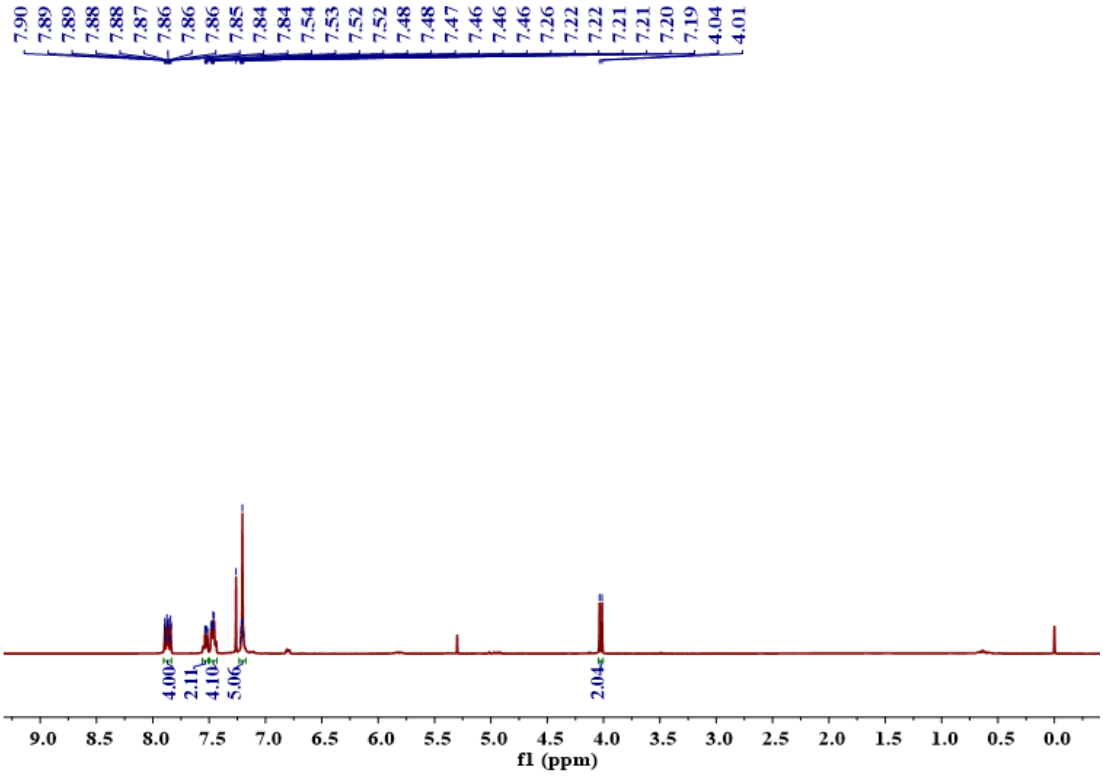
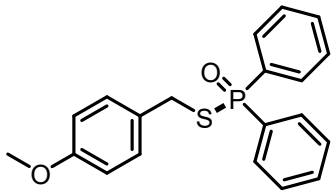


Fig. S27. ^{1}H NMR spectra of **3g** in $CDCl_3$.

3h. S-(4-methoxybenzyl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=4:1) to give 3h as a colorless oil. (67.2 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 4H), 7.56 – 7.51 (m, 2H), 7.49 – 7.43 (m, 4H), 7.13 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 3.99 (d, J = 9.0 Hz, 2H), 3.76 (s, 3H).[2]

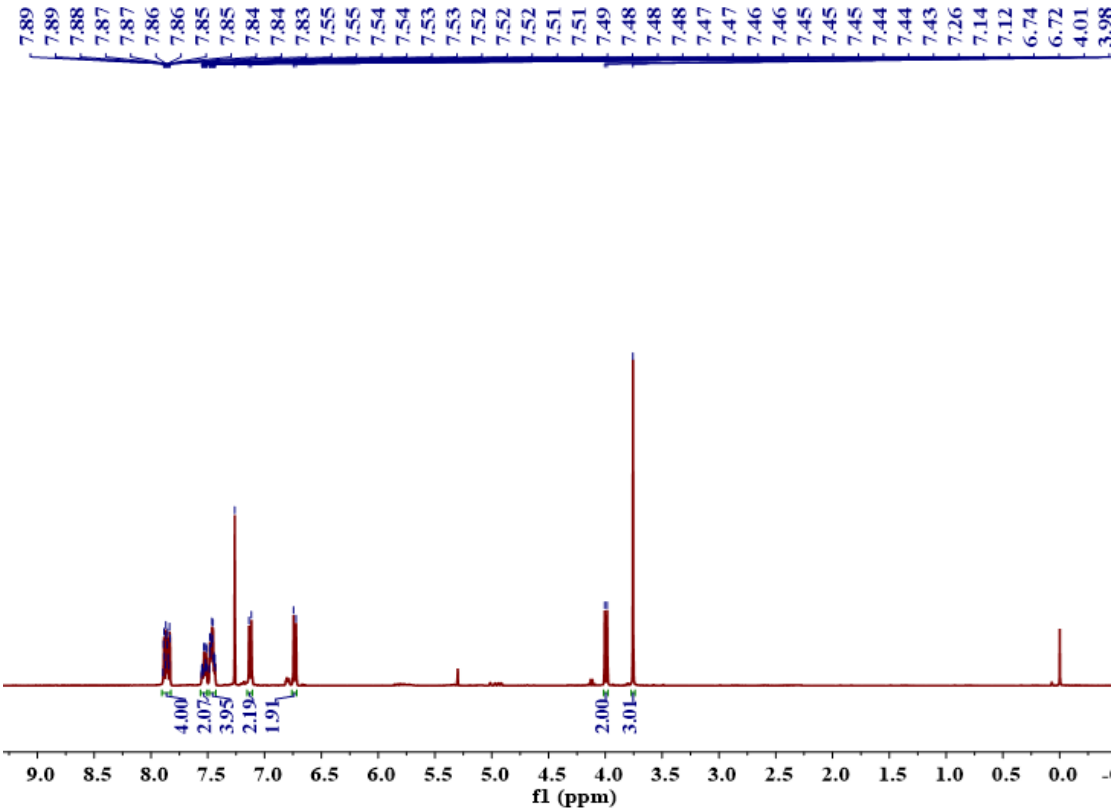
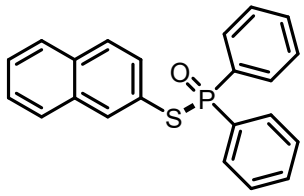


Fig. S28. ^{1}H NMR spectra of **3h** in $CDCl_3$.

3i. S-(naphthalen-2-yl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=4:1) to give 3i as a colorless oil. (54 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 1.9 Hz, 2H), 7.82 – 7.76 (m, 4H), 7.76 – 7.71 (m, 3H), 7.65 – 7.60 (m, 2H), 7.52 – 7.41 (m, 6H).[1]

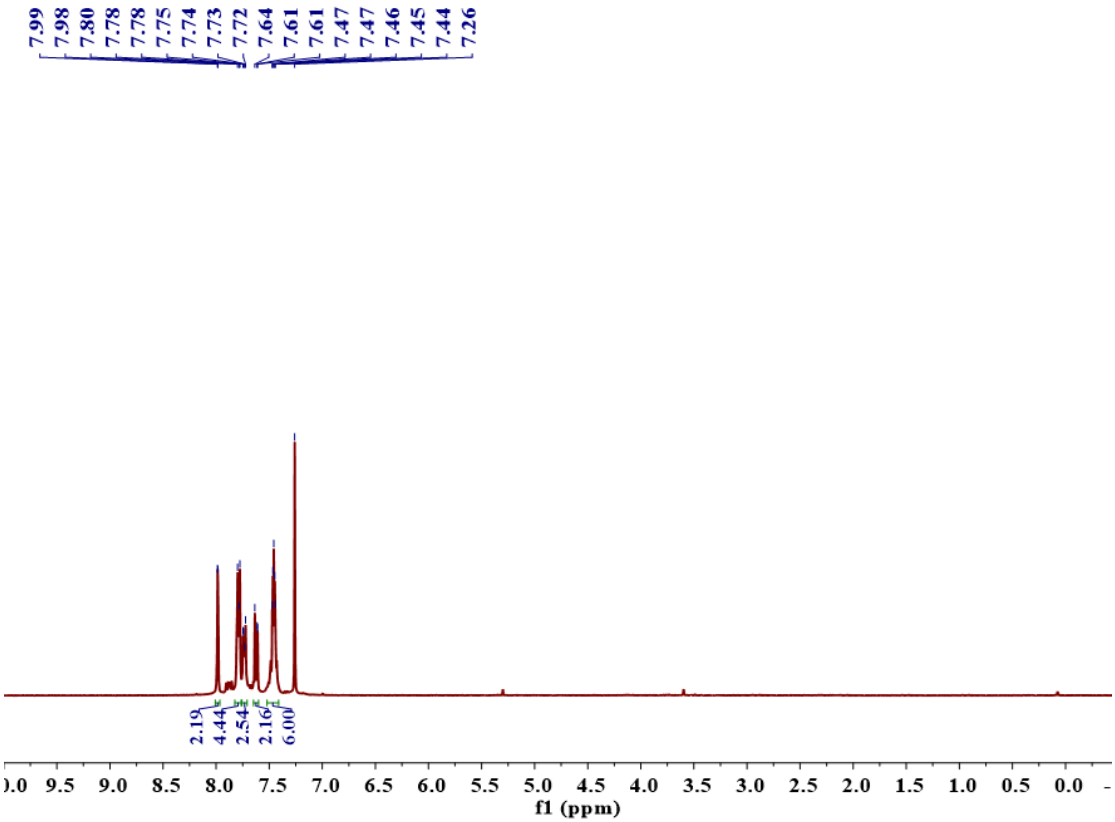
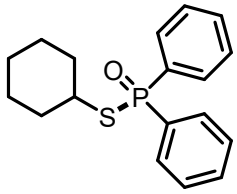


Fig. S29. ^{1}H NMR spectra of **3i** in $CDCl_3$.

3j. S-cyclohexyl diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=8:1) to give 3j as a colorless oil. (48.1 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 4H), 7.56 – 7.50 (m, 2H), 7.47 (ddd, *J* = 8.5, 6.4, 3.5 Hz, 4H), 3.34 – 3.25 (m, 1H), 1.99 – 1.87 (m, 3H), 1.71 – 1.62 (m, 2H), 1.51 (tt, *J* = 10.0, 3.3 Hz, 3H), 1.35 – 1.26 (m, 2H).[1]

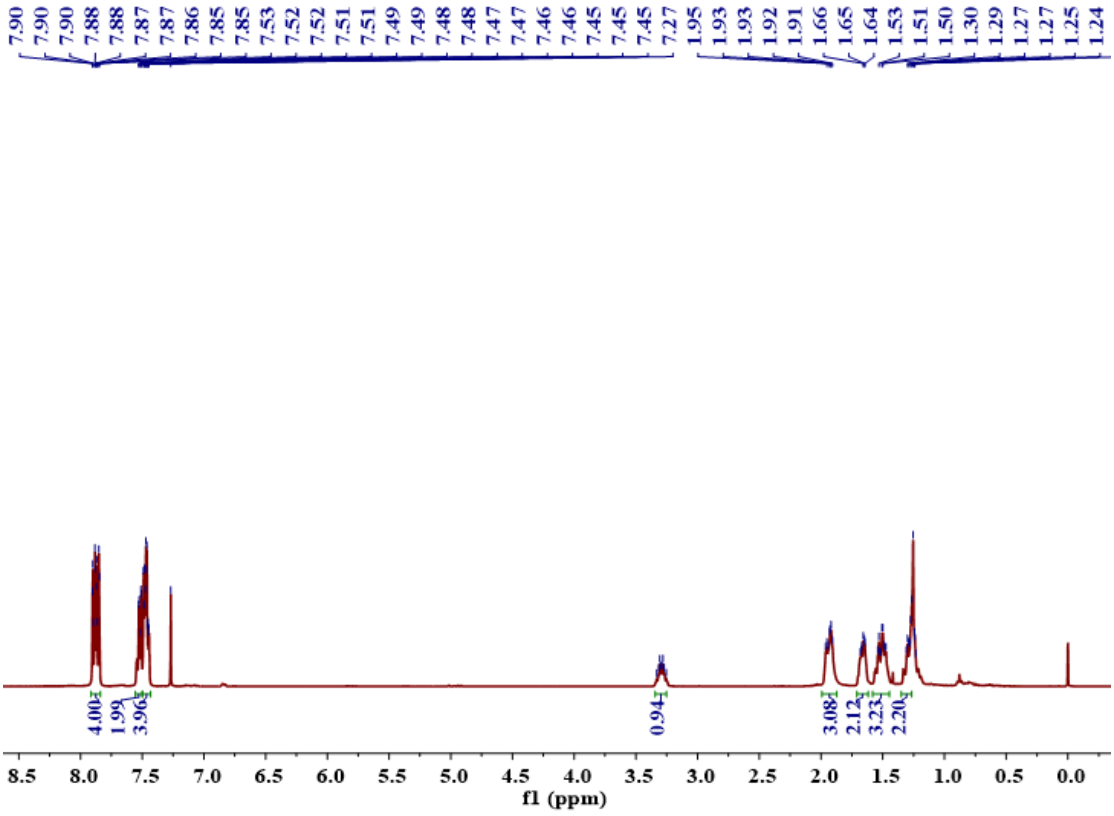
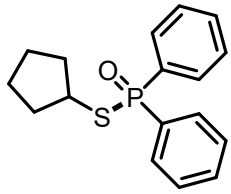


Fig. S30. ^{1}H NMR spectra of **3j** in $CDCl_3$.

3k. S-cyclopentyl diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=8:1) to give 3k as a colorless oil. (42.2 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 4H), 7.49 (dtd, J = 14.5, 7.0, 2.6 Hz, 6H), 3.45 (h, J = 7.2 Hz, 1H), 1.95 (t, J = 9.8 Hz, 2H), 1.76 – 1.60 (m, 4H), 1.54 – 1.46 (m, 2H).[2]

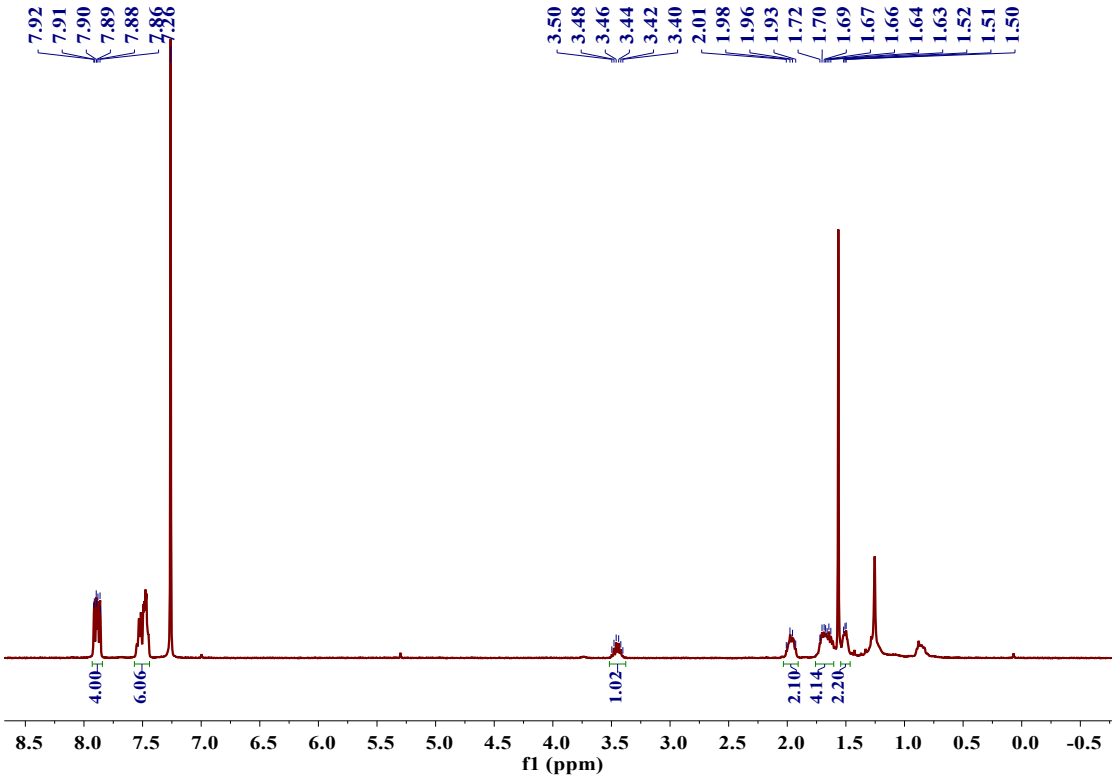
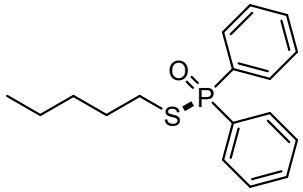


Fig. S31. ^{1}H NMR spectra of **3k** in $CDCl_3$.

3l S-pentyl diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=8:1) to give 3l as a colorless oil. (44.9 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 4H), 7.56 – 7.44 (m, 6H), 2.79 (dt, J = 10.2, 7.3 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.31 (dd, J = 6.6, 2.6 Hz, 2H), 1.22 (ddd, J = 9.0, 6.1, 1.5 Hz, 2H), 0.83 (t, J = 7.1 Hz, 3H).

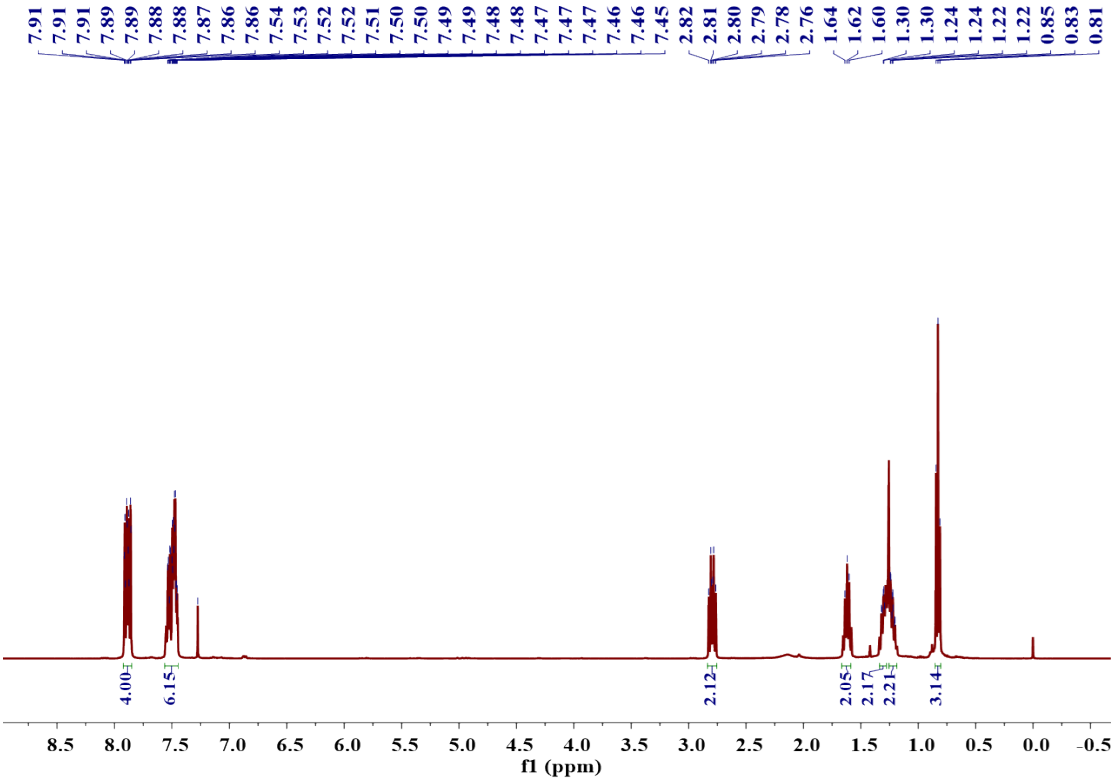
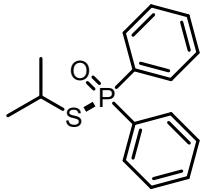


Fig. S32. ^{1}H NMR spectra of **3l** in $CDCl_3$.

3m S-isopropyl diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3m as a colorless oil. (40.6 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 4H), 7.56 – 7.43 (m, 6H), 1.36 (s, 3H), 1.34 (s, 3H).[1]

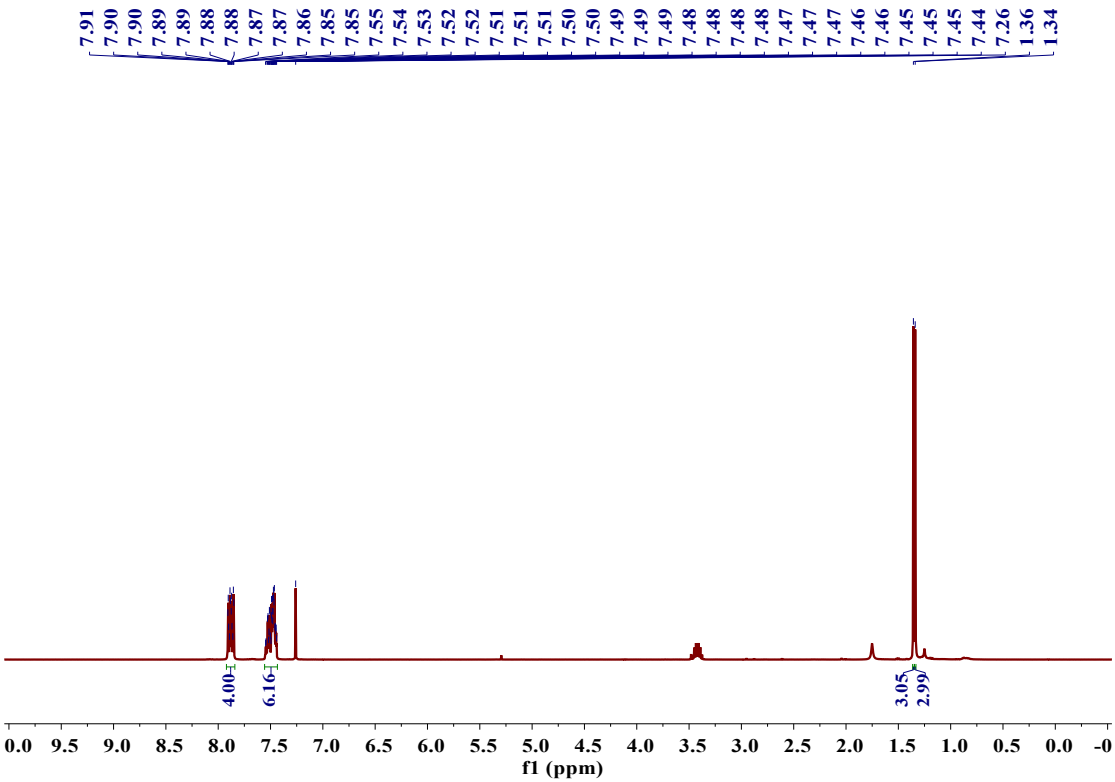
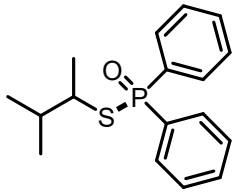


Fig. S33. ^{1}H NMR spectra of **3m** in $CDCl_3$.

3n S-(3-methylbutan-2-yl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3n as a colorless oil. (40.7 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (ddt, J = 12.9, 8.5, 1.7 Hz, 4H), 7.57 – 7.43 (m, 6H), 3.26 (dqd, J = 11.2, 7.0, 4.1 Hz, 1H), 1.89 (pd, J = 6.8, 4.1 Hz, 1H), 1.30 (d, J = 7.0 Hz, 3H), 0.91 (dd, J = 8.7, 6.8 Hz, 6H).[1]

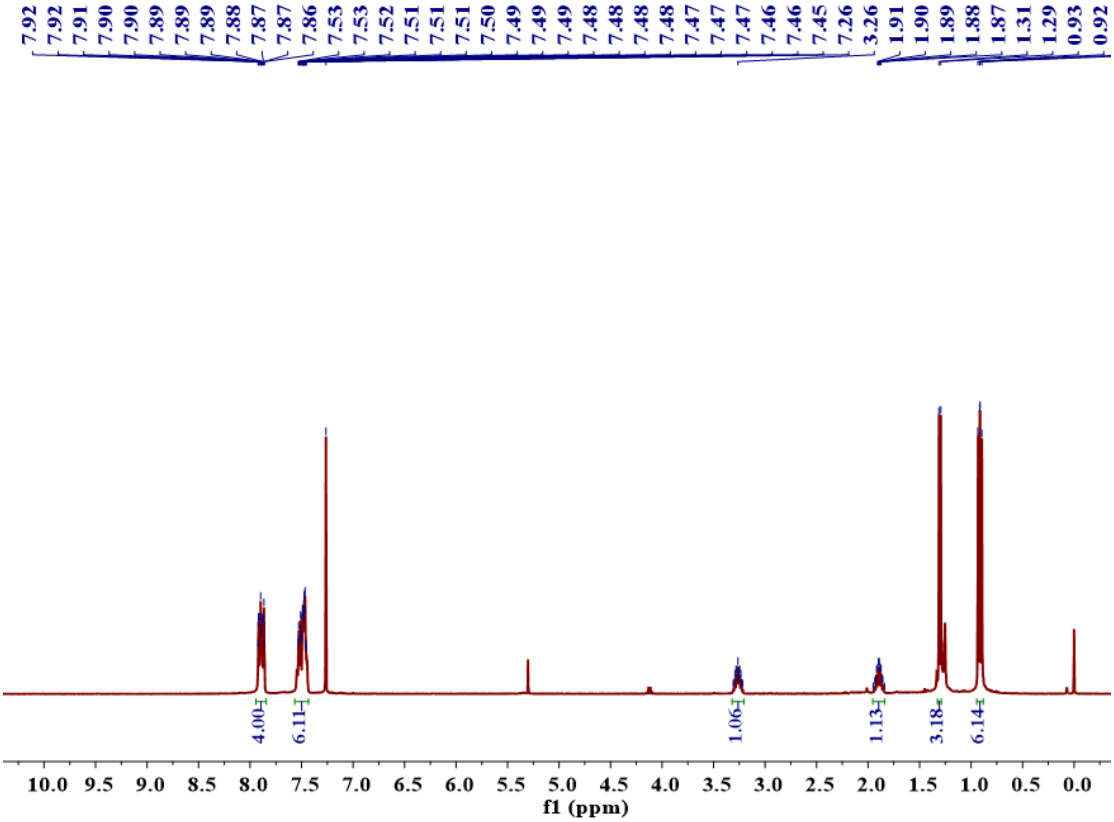
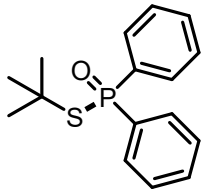


Fig. S34. ^{1}H NMR spectra of **3n** in $CDCl_3$.

3o S-(tert-butyl) diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3o as a colorless oil. (31.3 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 4H), 7.53 – 7.42 (m, 6H), 1.48 (d, J = 1.0 Hz, 9H).[1]

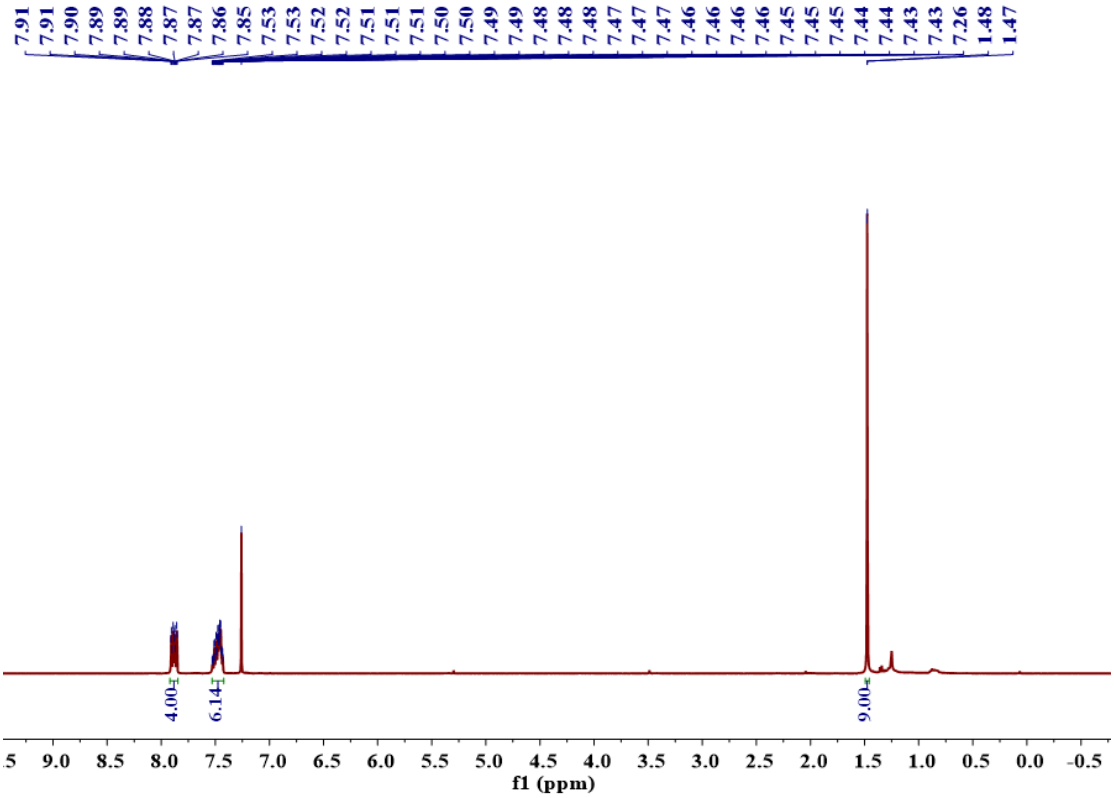
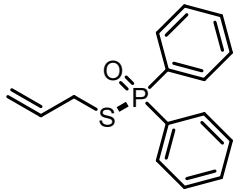


Fig. S35. ^{1}H NMR spectra of **3o** in $CDCl_3$.

3p S-allyl diphenylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3p as a colorless oil. (33.9 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 4H), 7.55 (td, J = 7.1, 1.7 Hz, 2H), 7.48 (ddd, J = 7.0, 5.7, 2.7 Hz, 4H), 5.86 – 5.66 (m, 1H), 5.17 – 5.11 (m, 1H), 5.09 – 5.00 (m, 1H), 3.46 (dd, J = 10.4, 7.1 Hz, 2H).[2]

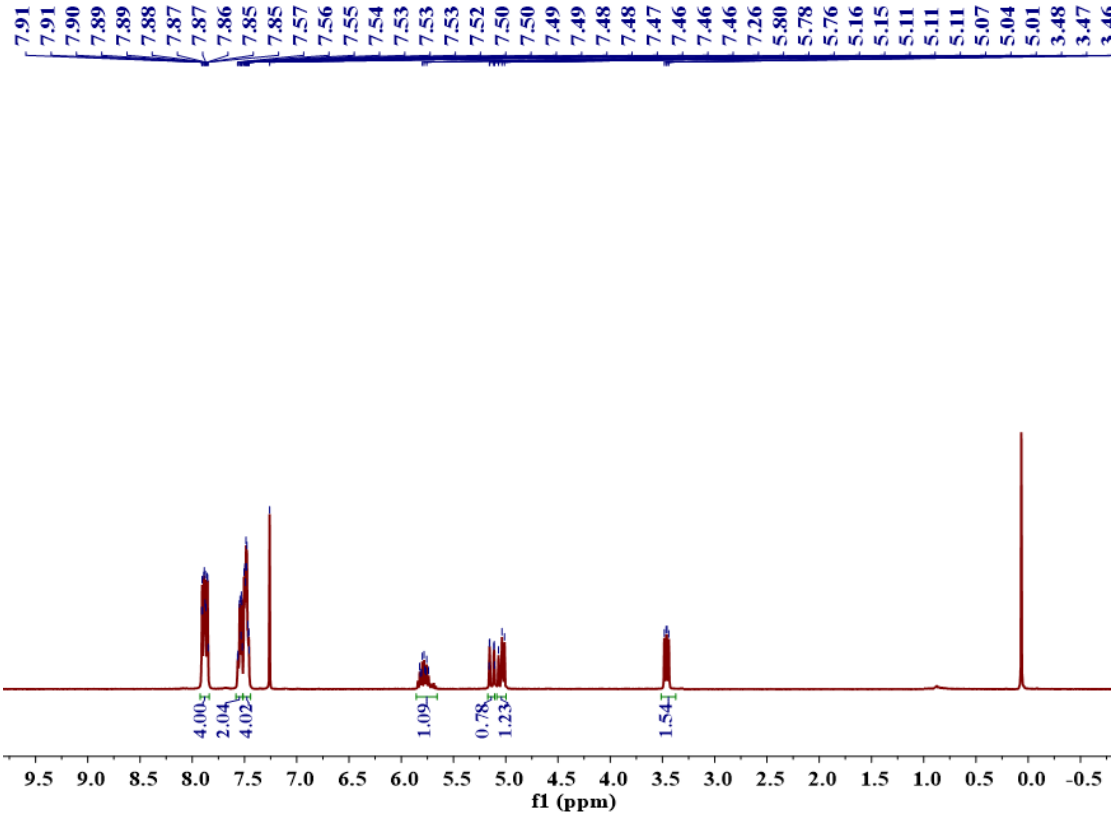
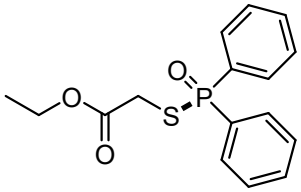


Fig. S36. ^{1}H NMR spectra of **3p** in $CDCl_3$.

3q ethyl 2-((diphenylphosphoryl)thio)acetate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=4:1) to give 3q as a colorless oil. (58.2 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (ddd, *J* = 13.2, 8.3, 1.4 Hz, 4H), 7.60 – 7.54 (m, 2H), 7.54 – 7.47 (m, 4H), 4.02 (d, *J* = 7.1 Hz, 2H), 3.61 (d, *J* = 10.5 Hz, 2H), 1.15 (s, 3H).

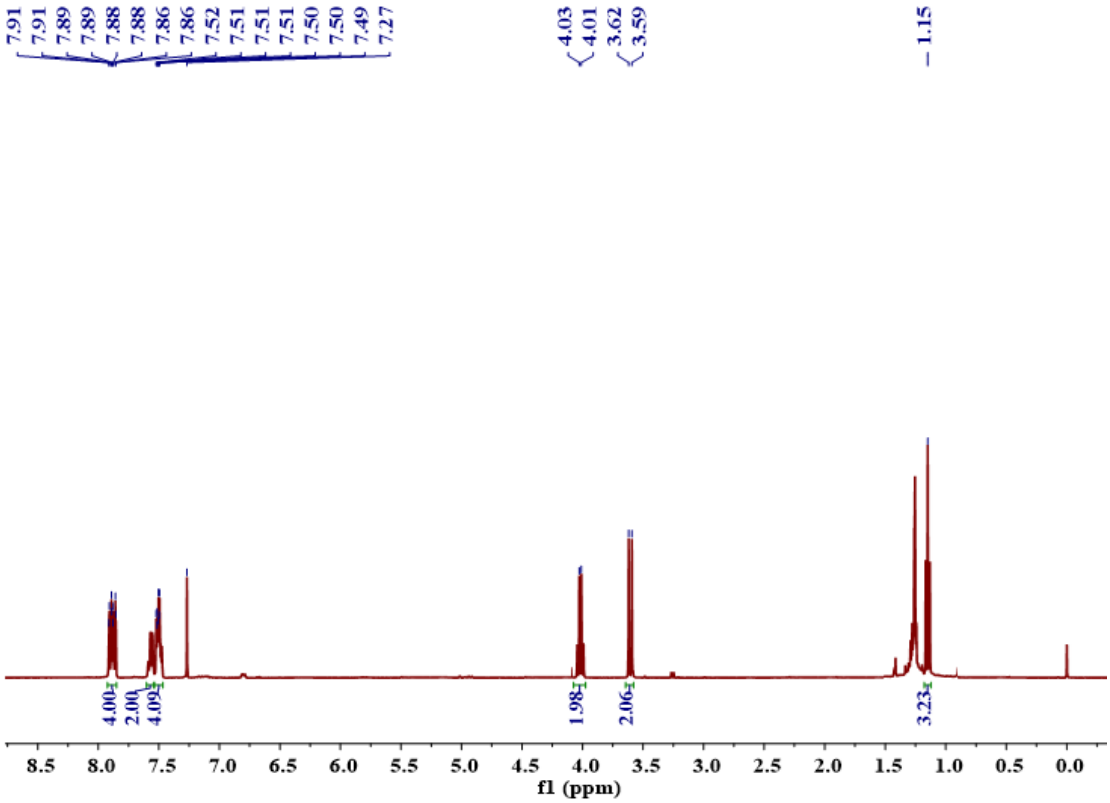
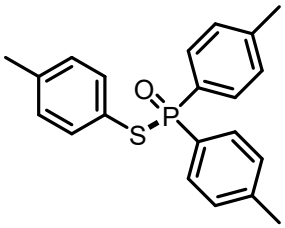


Fig. S37. ^{1}H NMR spectra of 3q in $CDCl_3$.

3r. S-(p-tolyl) di-p-tolylphosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=5:1) to give 3r as a colorless oil. (65.5 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 4H), 7.32 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.23 (dd, *J* = 8.1, 3.4 Hz, 4H), 7.00 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 6H), 2.25 (d, *J* = 1.4 Hz, 3H).[1]

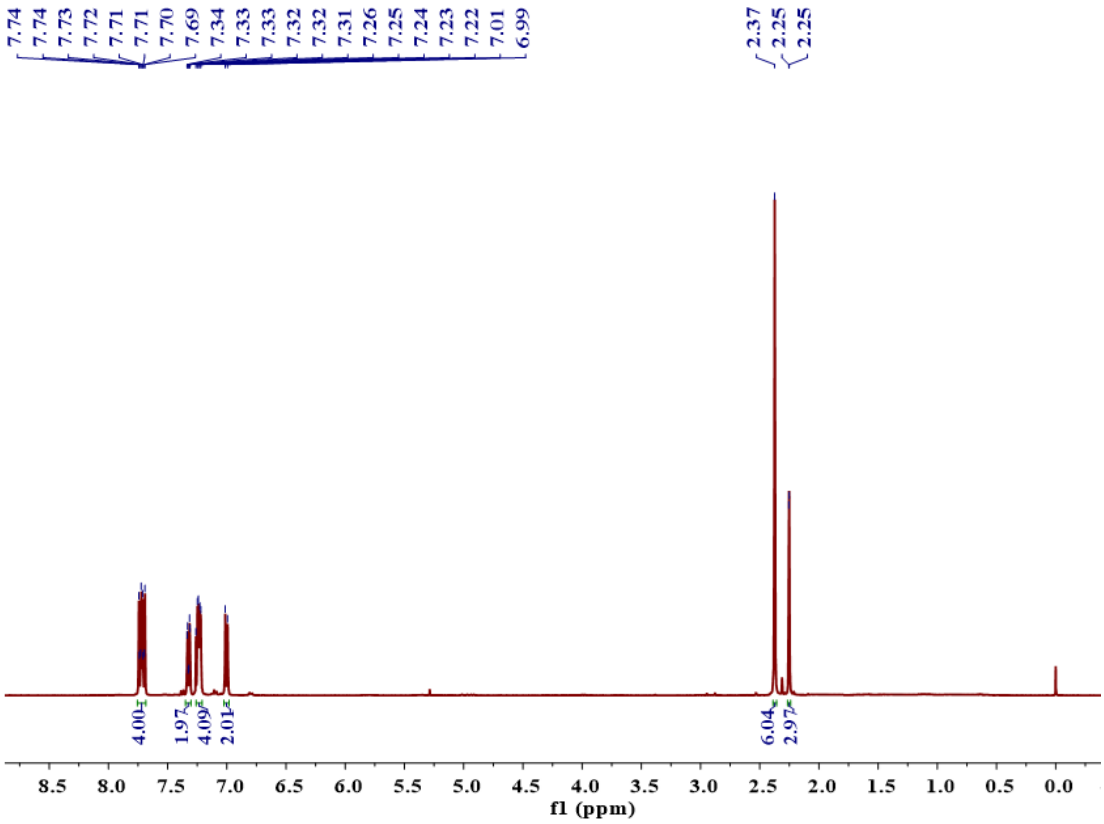
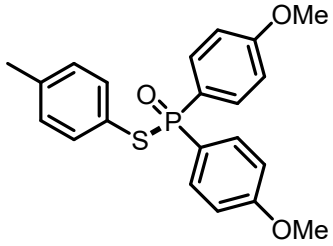


Fig. S38. ^{1}H NMR spectra of **3r** in $CDCl_3$.

3s. S-(p-tolyl) bis(4-methoxyphenyl)phosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=5:1) to give 3s as a colorless oil. (64.5 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 12.2, 8.5 Hz, 4H), 7.32 (dd, J = 8.1, 1.6 Hz, 2H), 7.01 (d, J = 7.8 Hz, 2H), 6.93 (dd, J = 8.8, 2.8 Hz, 4H), 3.83 (s, 6H), 2.25 (s, 3H).[1]

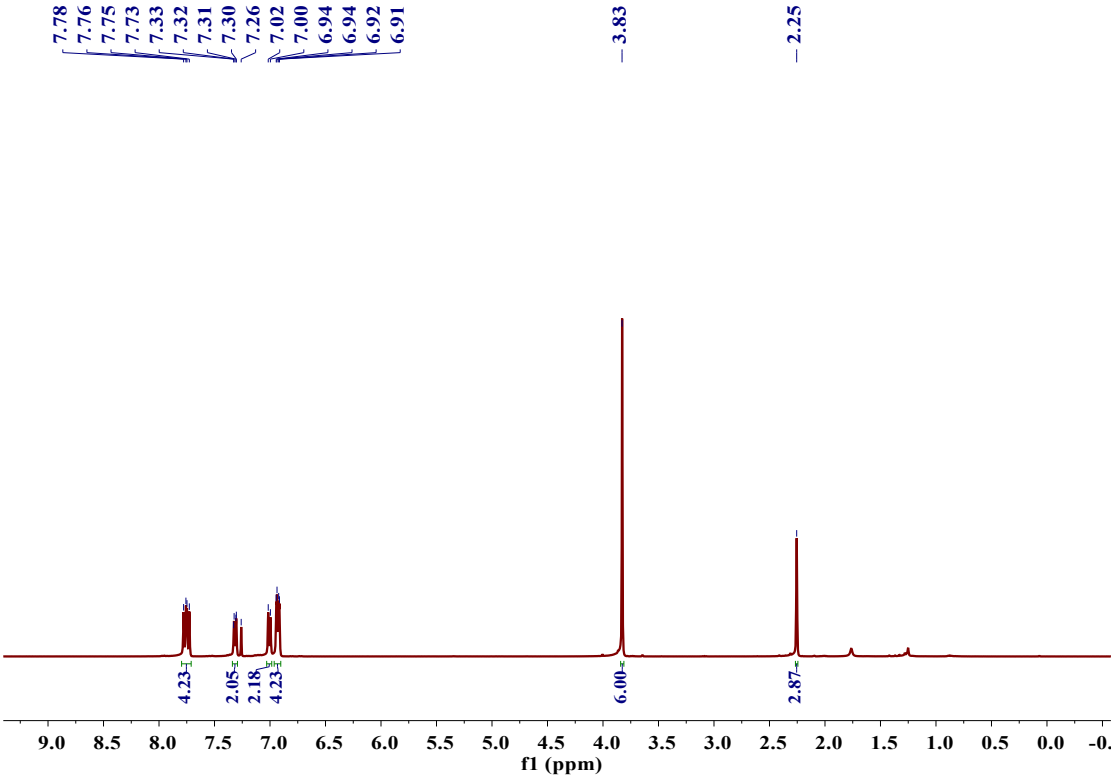
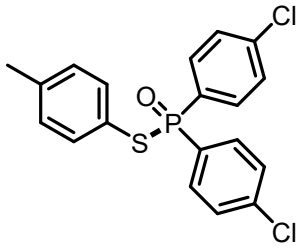


Fig. S39. ^{1}H NMR spectra of **3s** in $CDCl_3$.

3t. S-(p-tolyl) bis(4-chlorophenyl)phosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=5:1) to give 3t as a colorless oil. (58.2 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 12.4, 8.5 Hz, 4H), 7.43 (dd, J = 8.4, 2.8 Hz, 4H), 7.30 (s, 2H), 7.04 (d, J = 7.9 Hz, 2H), 2.28 (d, J = 1.5 Hz, 3H).[1]

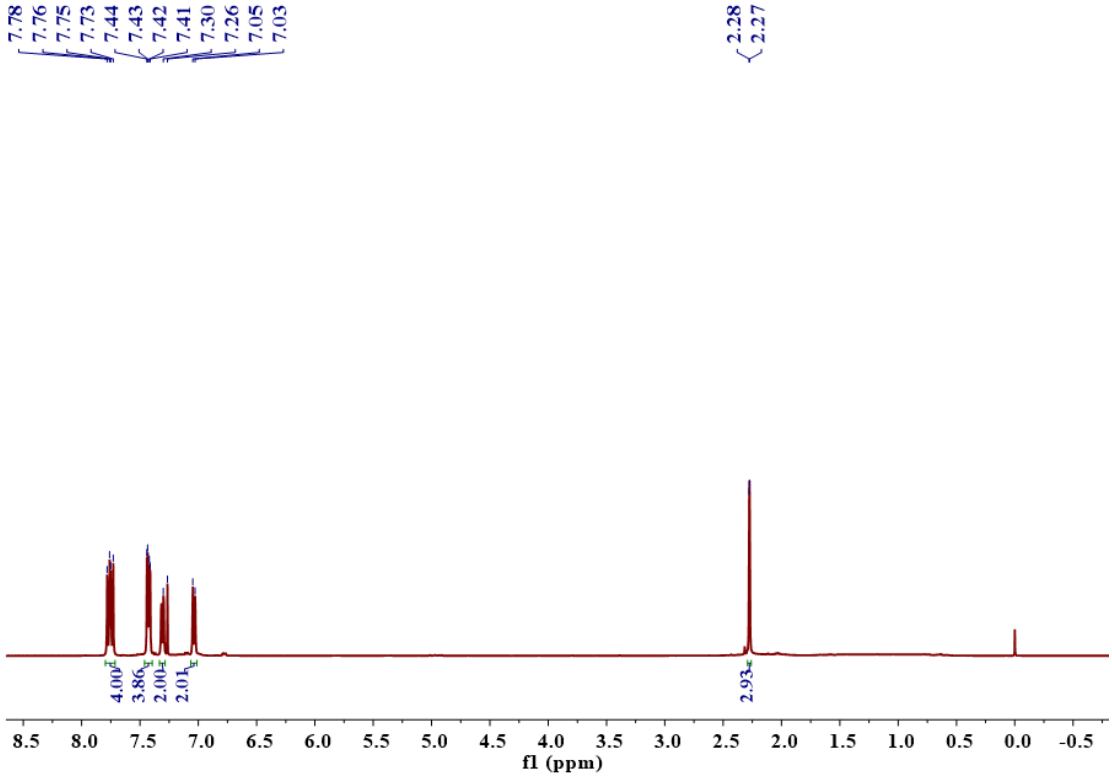
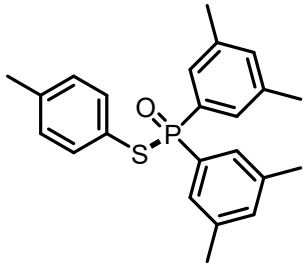


Fig. 40. ^{1}H NMR spectra of **3t** in $CDCl_3$.

3u. S-(p-tolyl) bis(3,5-dimethylphenyl)phosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=5:1) to give 3u as a colorless oil. (54.7 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 4H), 7.32 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.23 (dd, *J* = 8.1, 3.4 Hz, 4H), 7.00 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 6H), 2.25 (d, *J* = 1.4 Hz, 3H).

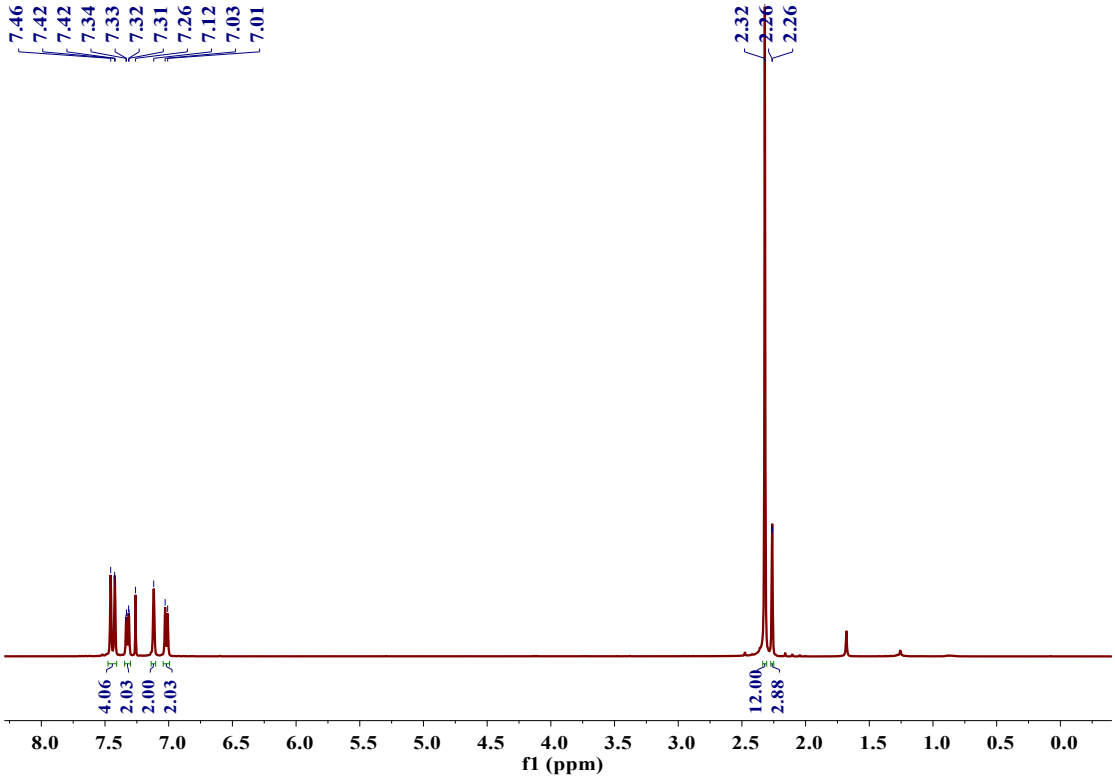
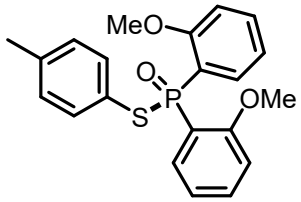


Fig. S41. ^{1}H NMR spectra of **3u** in $CDCl_3$.

3v. S-(p-tolyl) bis(2-methoxyphenyl)phosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=5:1) to give 3v as a colorless oil. (49.8 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (ddd, J = 15.2, 7.6, 1.7 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.33 (dd, J = 8.1, 1.8 Hz, 2H), 6.99 (dtd, J = 6.5, 3.3, 2.7, 1.4 Hz, 4H), 6.84 (dd, J = 8.3, 6.3 Hz, 2H), 3.65 (s, 6H), 2.25 (d, J = 1.6 Hz, 3H).[1]

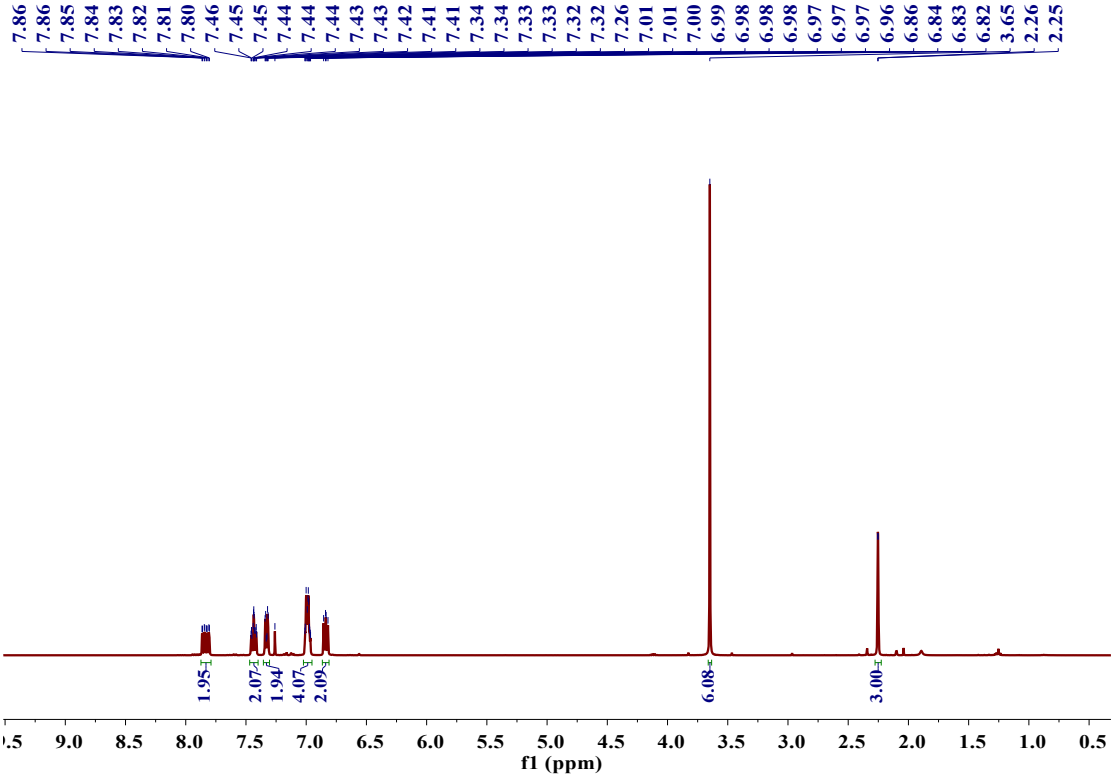
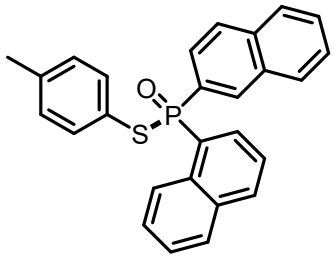


Fig. S42. ^{1}H NMR spectra of **3v** in $CDCl_3$.

3w. S-(p-tolyl) naphthalen-1-yl(naphthalen-2-yl)phosphinothioate



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=4:1) to give 3w as a colorless oil. (55.9 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 14.7 Hz, 2H), 7.94 – 7.85 (m, 8H), 7.63 – 7.52 (m, 4H), 7.10 (d, J = 7.9 Hz, 4H), 2.21 (s, 3H).[1]

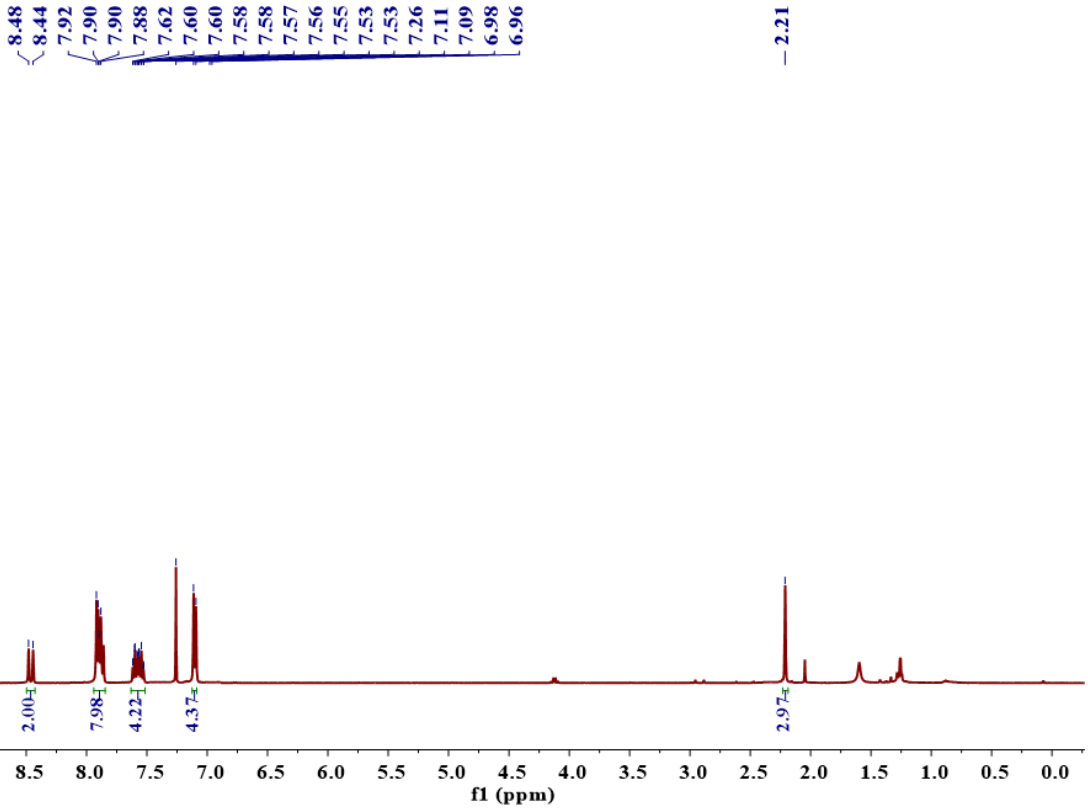


Fig. S43. ^{1}H NMR spectra of **3w** in $CDCl_3$.

Radical adduct 4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H), 1.76 – 1.41 (m, 15H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.13, 139.46, 129.29, 125.96, 61.21, 58.74, 43.54, 41.44, 35.39, 32.63, 28.77, 27.99, 21.27, 17.34.

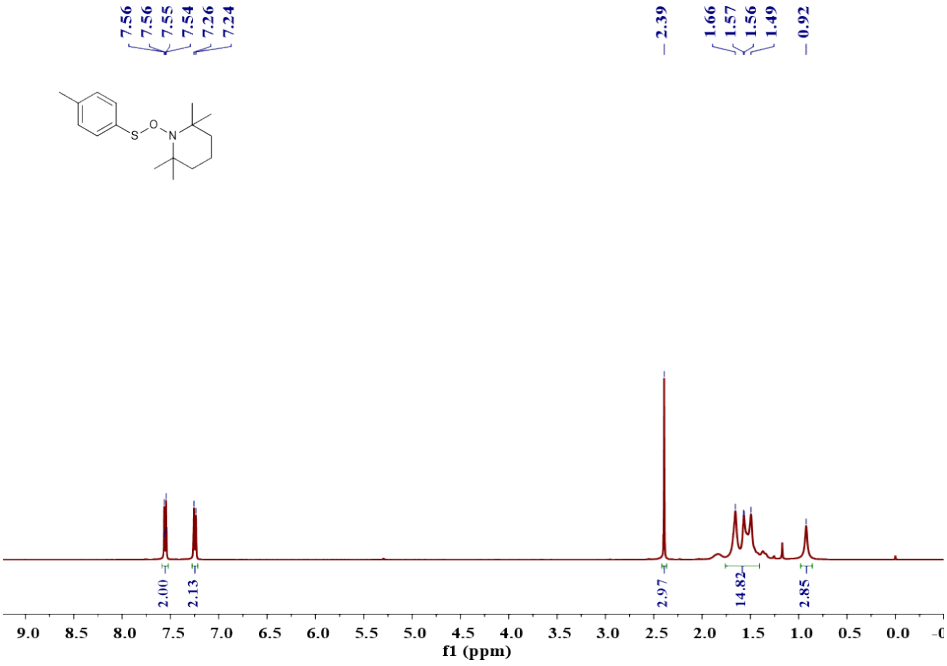


Fig. S44. ^{1}H NMR spectra of **4** in $CDCl_3$.

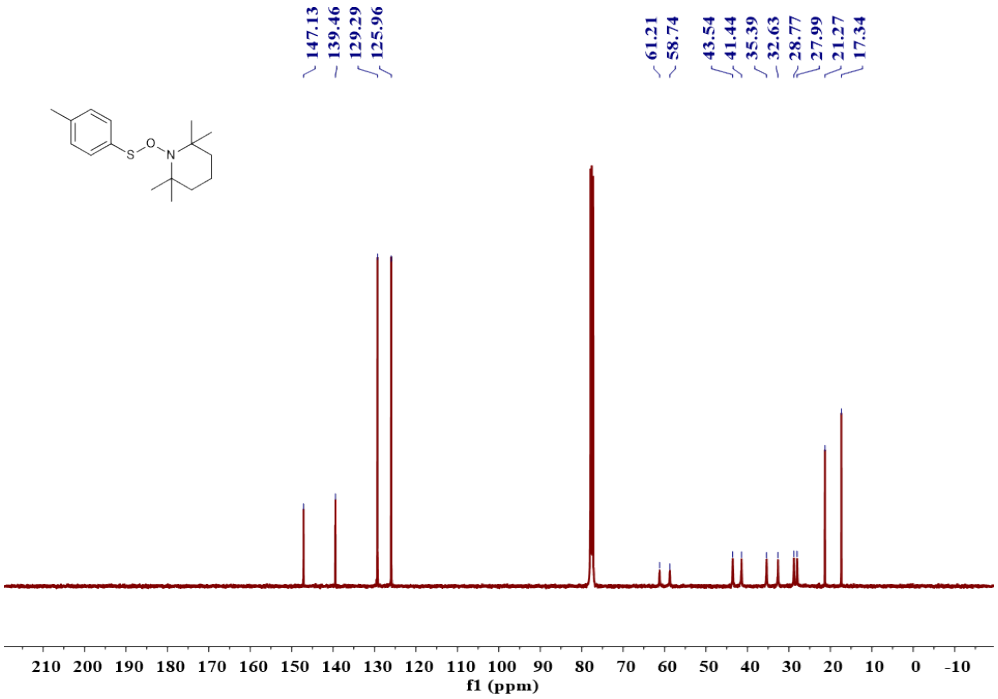


Fig. S45. ^{13}C NMR spectra of **4** in $CDCl_3$.

Radical adduct 5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H), 1.76 – 1.41 (m, 15H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.13, 139.46, 129.29, 125.96, 61.21, 58.74, 43.54, 41.44, 35.39, 32.63, 28.77, 27.99, 21.27, 17.34.

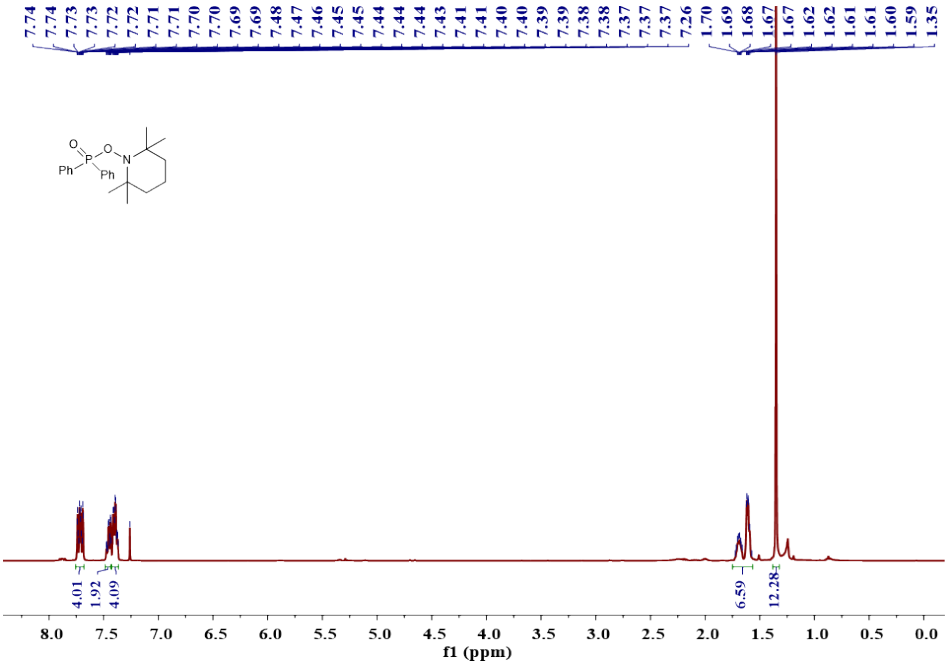


Fig. S46. ^{1}H NMR spectra of **5** in $CDCl_3$.

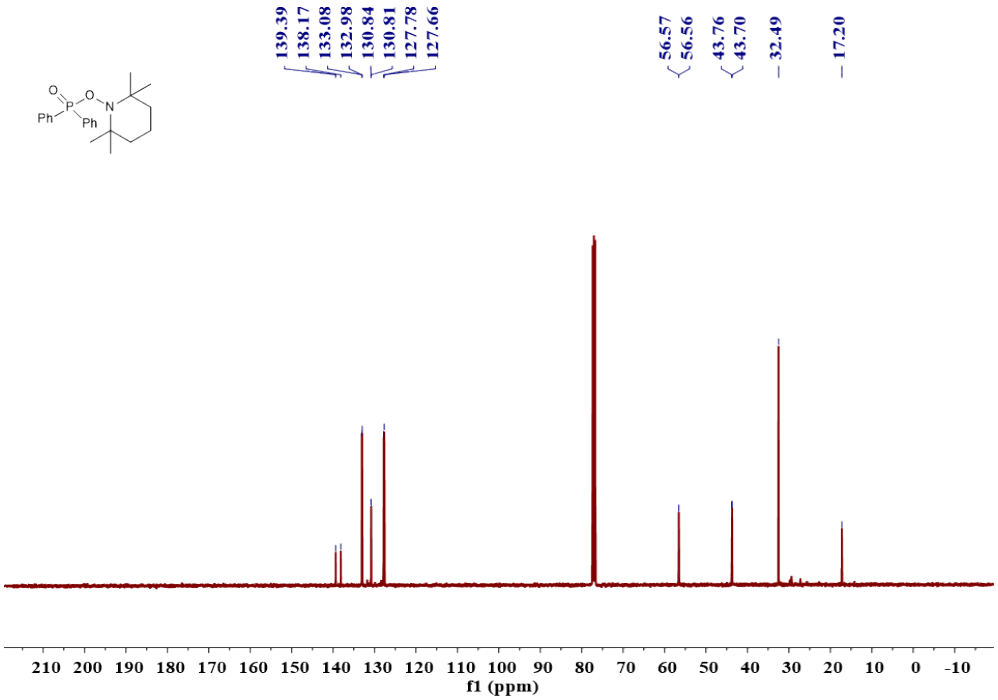


Fig. S47. ^{13}C NMR spectra of **5** in $CDCl_3$.

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[2] L. Huang, F. Meng, W. Guo, X. Dai, Z. Lv, P. Tang, Y. Guo, C. Cheng and Z. Gao, Electrochemical Cross-Coupling of P(O)-H with Thioesters: Green Synthesis of Phosphorothioates, *Org. Lett.*, 2025, **27**, 12729-12734.

[3] W. Zhang, Z. Deng, J. Deng, C.-T. Au, Y. Liao, H. Yang and Q. Liu, Regulating the exciton binding energy of covalent triazine frameworks for enhancing photocatalysis, *J Mater. Chem. A*, 2022, **10**, 22419-22427.