Electronic Supplementary Information

Phenazine-based photosensitizers for singlet oxygen generation

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Materials

All solvents and reagents were used as received, unless otherwise noted. Rose bengal (RB) was purchased from Sigma Aldrich and recrystallized from MeOH twice. 1,3-Diphenylisobenzofuran (DPBF) was purchased from Tokyo Chemical Industry and recrystallized from a mixture of CH_2Cl_2 and MeOH. 2,2,6,6-Tetramethyl-4-piperidone (4-oxo-TEMP) was purchased from FUJIFILM Wako Pure Chemical and purified by sublimation twice.

General

^{1}H NMR and ^{13}C NMR spectra were recorded using Varian-400 (400 MHz) and Varian-500 (500 MHz) FT NMR spectrometers. FT-IR spectra were recorded on a Perkin Elmer Spectrum One NTS using the ATR method. High-resolution mass spectral data were acquired using a Thermo Fisher Scientific LTQ Orbitrap XL. Photoabsorption spectra were recorded using Shimadzu UV-3150 and UV-3600-plus spectrophotometers. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields (Φ_{fl}s) were determined with a Hamamatsu C9920-01 instrument equipped with CCD by use of a calibrated integrating sphere system. Irradiance of monochromatic and continuous lights for photosensitizing reactions was adjusted using a Newport 1918-C optical power meter.

Synthesis

Phenazine derivatives with formyl, *n*-hexyl, and nitro groups (**KI-1**, **KI-2**, **KI-3**, **KI-4**, and **KI-5**) were synthesized by the palladium-catalyzed coupling reaction between dibromo-substituted precursor phenazines and corresponding tributylstannyl thiophenes followed by deprotection of hydroxyl and formyl groups, as shown in Scheme 1. Phenazine **KI-6** was obtained by reduction of **KI-2** using $NaBH_4$ as shown in Fig. 6a.

Compound 1. A solution of bromanilic acid (1.49 g, 5.00 mmol) and *o*-phenylenediamine (0.541 g, 5.00 mmol) in 2-methoxyethyl acetate (50 mL) was prepared and stirred at 120 °C. After disappearance of the reactants, the reaction mixture was cooled to room temperature and concentrated

to give crude product of compound **1** as brown solid (1.84 g). HRMS (APCI): 368.88727 $[M+H]^+$, calculated for $C_{12}H_7Br_2N_2O_2$ $[M+H]^+$: 368.88688.

Compound 2. A solution of bromanilic acid (1.49 g, 5.00 mmol) and 4-nitro-1,2-phenylenediamine (0.765 g, 5.00 mmol) in 2-methoxyethyl acetate (50 mL) was prepared and stirred at 120 °C. After disappearance of the reactants, the reaction mixture was cooled to room temperature and concentrated to give crude product of compound **2** as dark red solid (2.10 g). HRMS (ESI): 411.85803 $[M-H]^-$, calculated for $C_{12}H_4Br_2N_3O_4$ $[M-H]^-$: 411.85740.

Compound 3. A solution of crude product **1** (1.84 g) in tetrahydrofuran (THF, 100 mL) was stirred in ice bath for 15 min. Diisopropylamine (2.90 mL, 20.6 mmol) was added to the solution, and the mixture was stirred in ice bath for 1 h. Then, chloromethyl methyl acetate (1.50 mL, 20.0 mmol) was added to the solution, and the mixture was stirred in ice bath for 1 h and at room temperature overnight. Ethyl acetate was added to the solution, and the mixture was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, concentrated, and purified by column chromatography (silica, ethyl acetate/hexane = 1/2) to give compound **3** as yellow solid (0.555 g, 24% yield in two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.37 (dd, J = 6.8 and 3.3 Hz, 2H, aromatic), 7.90 (dd, J = 7.0 and 3.5 Hz, 2H, aromatic), 5.43 (s, 4H, CH_2), 3.76 (s, 6H, CH_3). HRMS (APCI): 456.93954 $[M+H]^+$, calculated for $C_{16}H_{15}Br_2N_2O_4$ $[M+H]^+$: 456.93931.

Compound 4. A solution of crude product **2** (2.10 g) in THF (50 mL) was stirred in ice bath for 15 min. Diisopropylamine (2.90 mL, 20.6 mmol) was added to the solution, and the mixture was stirred in ice bath for 1 h. Then, chloromethyl methyl acetate (1.50 mL, 20.0 mmol) was added to the solution, and the mixture was stirred in ice bath for 1 h and at room temperature overnight. Ethyl acetate was added to the solution, and the mixture was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, concentrated, and purified by column chromatography (silica, ethyl acetate/hexane = 1/4) to give compound **4** as yellow solid (0.368 g, 15% yield in two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.33 (d, J = 2.0 Hz, 1H, aromatic), 8.63 (dd, J = 9.5 and 2.5 Hz, 1H, aromatic), 8.52 (d, J = 9.5 Hz, 1H, aromatic), 5.48 (s, 2H, CH_2), 5.47 (s, 2H, CH_2), 3.76 (s, 3H, CH_3), 3.76 (s, 3H, CH_3). HRMS (APCI): 501.92429 $[M+H]^+$, calculated for $C_{16}H_{14}Br_2N_3O_6$ $[M]^+$: 501.92439.

Compound 5. A solution of 2-thiophenecarboxaldehyde (2.25 mL, 24.5 mmol) and ethylene glycol (6.00 mL, 108 mmol) in toluene (100 mL) was prepared under N_2 atmosphere, and the mixture was stirred at room temperature for 10 min. *p*-Toluenesulfonic acid monohydrate (68 mg, 0.357 mmol) was added to the solution, and the mixture was stirred at 140 °C for 43 h with a Dean-Stark trap to remove water. After cooling to room temperature, ethyl acetate was added to the mixture, and the mixture was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, and concentrated to give compound **5** as brown liquid (3.41 g, 89% yield). ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) = 7.47 (dd, J = 5.0 and 1.0 Hz, 1H, aromatic), 7.19 (ddd, J = 3.8, 1.3, and 0.5 Hz, 1H, aromatic), 7.01 (dd, J = 5.0 and 3.5 Hz, 1H, aromatic), 6.05 (s, 1H, CH), 3.93–4.11 (m, 4H, CH_2).

Compound 6. A solution of compound **5** (3.00 g, 19.3 mmol) in THF (60 mL) was prepared under N_2 atmosphere and stirred at -78 °C for 30 min. 1.6 M *n*-BuLi in hexane (13.1 mL, 21.0 mmol) was slowly dropped into the solution, and the mixture was stirred at -78 °C for 1 h. Then, tributylthin (Ⅳ) chloride (5.80 mL, 21.5 mmol) was added to the solution, and the mixture was stirred at room temperature overnight. Water was added to the solution to stop the reaction. Ethyl acetate was added to the mixture, and the extracted organic layer was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, and concentrated to give compound **6** as brown liquid (7.75 g, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.28 (d, J = 2.8 Hz, 1H, aromatic), 7.05 (d, J = 3.0 Hz, 1H, aromatic), 6.15 (s, 1H, CH), 3.98–4.20 (m, 4H, CH_2), 1.39–1.66 (m, 6H, CH_2), 1.22–1.39 (m, 6H, CH_2), 1.00–1.20 (m, 6H, CH_2), 0.89 (t, J = 7.5, 9H, CH_3).

Compound 7. A solution of 2-hexylthiophene (1.68 g, 9.98 mmol) in THF (50 mL) was prepared under N_2 atmosphere and stirred at -78 °C for 30 min. 1.6 M *n*-BuLi in hexane (7.5 mL, 12.0 mmol) was slowly dropped into the solution, and the mixture was stirred at -78 °C for 1 h. Then, tributylthin (Ⅳ) chloride (3.23 mL, 11.9 mmol) was added to the solution, and the mixture was stirred at room temperature overnight. Water was added to the solution to stop the reaction. Ethyl acetate was added to the mixture, and the extracted organic layer was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, and concentrated to give compound **7** as yellow liquid

(3.44 g, 75% yield). ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) = 7.01 (d, J = 3.0 Hz, 1H, aromatic), 6.93 (d, J = 3.0 Hz, 1H, aromatic), 0.80–1.70 (m, 40H, CH_2 and CH_3).

Compound 8. A solution of compound **3** (0.244 g, 0.533 mmol) and 2-(tributylstannyl)thiophene (0.400 g, 1.07 mmol) in toluene (30 mL) was prepared under N_2 atmosphere and bubbled with N_2 for 15 min. $Pd(PPh_3)_4$ (35 mg, 30.3 μmol) was added to the solution, and the mixture was stirred at 70 °C overnight with light blocking by aluminum foil cover. Water was added to the solution to stop the reaction. Ethyl acetate was added to the mixture, and the extracted organic layer was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, concentrated, purified by column chromatography (silica, ethyl acetate/hexane = 1/2), and washed with hexane to give compound **8** as yellow solid (75 mg, 30% yield). ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) = 8.23 (dd, J = 6.8 and 3.3 Hz, 2H, aromatic), 7.91–7.96 (m, 4H, aromatic), 7.77 (dd, J = 5.0 and 1.0 Hz, 2H, aromatic), 7.29 (dd, J = 5.0 and 3.5 Hz, 2H, aromatic), 5.26 (s, 4H, CH_2), 3.27 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 150.73, 141.92, 140.31, 133.53, 131.40, 130.20, 129.74, 128.29, 126.37, 124.93, 99.69, 57.91. HRMS (APCI): 465.09357 $[M+H]^+$, calculated for $C_{24}H_{21}S_2N_2O_4$ $[M]^+$: 465.09373.

Compound 9. A solution of compound **3** (0.443 g, 0.967 mmol) and **6** (1.02 g, 2.29 mmol) in toluene (70 mL) was prepared under N_2 atmosphere and bubbled with N_2 for 15 min. $Pd(PPh_3)_4$ (58 mg, 50.2 μmol) was added to the solution, and the mixture was stirred at 70 °C overnight with light blocking by aluminum foil cover. Water was added to the solution to stop the reaction. Ethyl acetate was added to the mixture, and the extracted organic layer was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, concentrated, purified by column chromatography (silica, ethyl acetate/hexane = 1/1), and washed with hexane to give compound **9** as yellow solid (0.220 g, 37% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.25 (dd, J = 8.3 and 4.3 Hz, 2H, aromatic), 7.74–7.82 (m, 4H, aromatic), 7.29 (dd, J = 4.5 and 1.0 Hz, 2H, aromatic), 6.26 (s, 2H, CH), 5.20 (s, 4H, CH_2), 4.04–4.27 (m, 8H, CH_2), 3.30 (s, 6H, CH_3). HRMS (ESI): 609.13617 $[M+H]^+$, calculated for $C_{30}H_{29}O_8N_2S_2$ $[M+H]^+$: 608.13598.

Compound 10. A solution of compound **4** (0.337 g, 0.670 mmol) and **6** (0.758 g, 1.70 mmol) in toluene (50 mL) was prepared under N_2 atmosphere and bubbled with N_2 for 15 min. $Pd(PPh_3)_4$ (45

mg, 38.9 μmol) was added to the solution, and the mixture was stirred at 70 °C overnight with light blocking by aluminum foil cover. Water was added to the solution to stop the reaction. Ethyl acetate was added to the mixture, and the extracted organic layer was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, concentrated, purified by column chromatography (silica, ethyl acetate/hexane = 1/1), and washed with hexane to give compound **10** as red solid (0.108 g, 25% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.20 (d, J = 3.0 Hz, 1H, aromatic), 8.52 (dd, J = 9.5 and 2.5 Hz, 1H, aromatic), 8.39 (d, J = 9.5 Hz, 1H, aromatic), 7.73 (dd, J = 8.8 and 3.8 Hz, 2H, aromatic), 7.30–7.33 (m, 2H, aromatic), 6.25 (s, 1H, CH), 6.25 (s, 1H, CH), 5.23 (s, 2H, CH_2), 5.21 (s, 2H, CH_2), 4.06–4.29 (m, 8H, CH_2), 3.31 (s, 3H, CH_3), 3.30 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 153.04, 152.20, 148.03, 144.80, 144.60, 143.20, 141.87, 141.71, 139.94, 133.82, 133.78, 133.70, 131.57, 131.49, 131.42, 126.67, 125.71, 125.06, 124.87, 123.09, 100.72, 100.67, 99.94, 99.89, 65.48, 58.09. HRMS (ESI): 654.12140 $[M+H]^+$, calculated for $C_{30}H_{28}O_{10}N_3S_2$ $[M+H]^+$: 654.12106.

Compound 11. A solution of compound **3** (0.225 g, 0.491 mmol) and **7** (0.565 g, 1.24 mmol) in toluene (40 mL) was prepared under N_2 atmosphere and bubbled with N_2 for 15 min. $Pd(PPh_3)_4$ (57 mg, 49.3 μmol) was added to the solution, and the mixture was stirred at 70 °C overnight with light blocking by aluminum foil cover. Water was added to the solution to stop the reaction. Ethyl acetate was added to the mixture, and the extracted organic layer was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, concentrated, purified by column chromatography (silica, ethyl acetate/hexane = 1/4), and washed with hexane to give compound **11** as yellow solid (0.185 g, 60% yield). ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) = 8.22 (dd, J = 6.8 and 3.3 Hz, 2H, aromatic), 7.91 (dd, J = 6.5 and 3.5 Hz, 2H, aromatic), 7.75 (d, J = 3.5 Hz, 2H, aromatic), 6.98 (d, J = 4.0 Hz, 2H, aromatic), 5.25 (s, 4H, CH_2), 3.31 (s, 6H, CH_3), 2.97 (t, J = 7.8 Hz, 4H, CH_2), 1.27–1.84 (m, 16H, CH_2), 0.85–0.96 (m, 6H, CH_3). ^{13}C NMR (125 MHz, acetone-d_6): δ (ppm) = 151.74, 149.31, 142.29, 140.90, 132.17, 132.13, 131.82, 131.27, 130.16, 130.04, 125.26, 124.49, 124.31, 100.33, 100.15, 57.98, 57.93, 32.63, 32.36, 30.64, 27.44, 23.32, 14.36, 13.90. HRMS (ESI): 633.28174 $[M+H]^+$, calculated for $C_{36}H_{45}O_4N_2S_2$ $[M+H]^+$: 633.28153.

Compound 12. A solution of compound **4** (0.827 g, 1.64 mmol) and **7** (1.10 g, 2.41 mmol) in toluene (30 mL) was prepared under N_2 atmosphere and bubbled with N_2 for 15 min. $Pd(PPh_3)_4$ (30 mg, 26.0 μmol) was added to the solution, and the mixture was stirred at 70 °C overnight with light blocking by aluminum foil cover. Water was added to the solution to stop the reaction. Ethyl acetate was added to the mixture, and the extracted organic layer was washed twice with each of water and saturated saline, dried over anhydrous $MgSO_4$, filtered, concentrated, purified by column chromatography (silica, ethyl acetate/hexane = 1/4), and washed with hexane to give compound **12** as brown solid (0.310 g, 28% yield). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) = 9.01 (d, J = 1.6 Hz, 1H, aromatic), 8.55 (dd, J = 7.6 and 2.0 Hz, 1H, aromatic), 8.37 (d, J = 7.6 Hz, 1H, aromatic), 7.77 (d, J = 3.2 Hz, 1H, aromatic), 7.74 (d, J = 2.8 Hz, 1H, aromatic), 6.96–7.02 (m, 2H, aromatic), 5.29 (s, 2H, CH_2), 5.28 (s, 2H, CH_2), 3.33 (s, 3H, CH_3), 3.32 (s, 3H, CH_3), 2.94–3.01 (m, 4H, CH_2), 1.75–1.84 (m, 4H, CH_2), 1.23–1.52 (m, 12H, CH_2), 0.84–0.96 (m, 6H, CH_3). HRMS (ESI): 678.26740 $[M+H]^+$, calculated for $C_{36}H_{44}O_6N_3S_2$ $[M+H]^+$: 678.26660.

Phenazine KI-1. A solution of compound **8** (44 mg, 94.7 μmol) in THF (20 mL) that was bubbled with N_2 for 15 min in advance was prepared and stirred at room temperature for 15 min. Concentrated HCl solution (1 mL) was added to the solution, and the mixture was stirred at room temperature with light blocking by aluminum foil cover. After disappearance of the reactant and stirring for additional 2 h, saturated $NaHCO_3$ solution was added to the mixture for neutralization. Then, Ethyl acetate was added to the mixture, and the extracted organic layer was washed with water once and saturated saline twice, dried over anhydrous Na_2SO_4, filtered, concentrated, and washed with hexane and water. The crude product was dissolved in THF and precipitated in hexane to give phenazine **KI-1** as red solid (17 mg, 48% yield). ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) = 8.40 (br, 2H, OH), 8.04–8.13 (m, 2H, aromatic), 7.60 (dd, J = 6.3 and 3.3 Hz, 2H, aromatic), 7.44 (d, J = 4.0 Hz, 2H, aromatic), 7.16 (dd, J = 5.0 and 4.0 Hz, 2H, aromatic). ^{13}C NMR spectrum could not be obtained because of the low solubility in any solvents. HRMS (ESI): 375.02631 $[M-H]^-$, calculated for $C_{20}H_{11}O_2N_2S_2$ $[M-H]^-$: 375.02674.

Phenazine KI-2. A solution of compound **9** (0.228 g, 0.375 mmol) in THF (40 mL) that was bubbled with N_2 for 15 min in advance was prepared and stirred at room temperature for 15 min.

Concentrated HCl solution (6 mL) was added to the solution, and the mixture was stirred at room temperature with light blocking by aluminum foil cover. After disappearance of the reactant and stirring for additional 2 h, saturated $NaHCO_3$ solution was added to the mixture for neutralization. Then, Ethyl acetate was added to the mixture, and the extracted organic layer was washed with water once and saturated saline twice, dried over anhydrous Na_2SO_4, filtered, concentrated, and washed with hexane and water. The crude product was dissolved in THF and precipitated in hexane to give phenazine **KI-2** as red solid (0.145 g, 89% yield). ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) = 9.98 (s, 2H, CHO), 9.04 (d, J = 4.0 Hz, 2H, aromatic), 8.22 (dd, J = 6.5 and 3.3 Hz, 2H, aromatic), 7.90 (d, J = 4.0 Hz, 2H, aromatic), 7.66 (dd, J = 6.5 and 3.5 Hz, 2H, aromatic). ^{13}C NMR spectrum could not be obtained because of the low solubility in any solvents. HRMS (ESI): 431.01642 $[M-H]^-$, calculated for $C_{22}H_{11}O_4N_2S_2$ $[M-H]^-$: 431.01657.

Phenazine KI-3. A solution of compound **10** (0.160 g, 0.245 mmol) in THF (30 mL) that was bubbled with N_2 for 15 min in advance was prepared and stirred at room temperature for 15 min. Concentrated HCl solution (5 mL) was added to the solution, and the mixture was stirred at room temperature with light blocking by aluminum foil cover. After disappearance of the reactant and stirring for additional 2 h, saturated $NaHCO_3$ solution was added to the mixture for neutralization. Then, Ethyl acetate was added to the mixture, and the extracted organic layer was washed with water once and saturated saline twice, dried over anhydrous Na_2SO_4, filtered, concentrated, and washed with hexane and water. The crude product was dissolved in THF and precipitated in hexane to give phenazine **KI-3** as black solid (80 mg, 68% yield). ^{1}H NMR (500 MHz, dimethyl sulfoxide (DMSO)-d_6): δ (ppm) = 9.98 (s, 1H, CHO), 9.93 (s, 1H, CHO), 9.04 (d, J = 4.0 Hz, 1H, aromatic), 8.88 (d, J = 2.5 Hz, 1H, aromatic), 8.75 (d, J = 4.0 Hz, 1H, aromatic), 8.41 (dd, J = 9.5 and 2.5 Hz, 1H, aromatic), 8.24 (d, J = 9.5 Hz, 1H, aromatic), 8.04 (d, J = 4.0 Hz, 1H, aromatic), 8.00 (d, J = 4.0 Hz, 1H, aromatic). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 184.23, 183.80, 163.72, 158.39, 148.31, 146.33, 144.30, 142.16, 141.44, 141.22, 140.84, 139.13, 137.24, 136.94, 135.11, 128.59, 128.35, 127.03, 123.45, 120.80, 105.40, 105.26. HRMS (ESI): 476.00101 $[M-H]^-$, calculated for $C_{22}H_{10}O_6N_3S_2$ $[M-H]^-$: 476.00165.

Phenazine KI-4. A solution of compound **11** (0.171 g, 0.270 mmol) in THF (20 mL) that was bubbled with N_2 for 15 min in advance was prepared and stirred at room temperature for 15 min.

Concentrated HCl solution (3.5 mL) was added to the solution, and the mixture was stirred at room temperature with light blocking by aluminum foil cover. After disappearance of the reactant and stirring for additional 2 h, saturated $NaHCO_3$ solution was added to the mixture for neutralization. Then, Ethyl acetate was added to the mixture, and the extracted organic layer was washed with water once and saturated saline twice, dried over anhydrous Na_2SO_4, filtered, concentrated, and washed with hexane and water. The crude product was dissolved in THF and precipitated in hexane to give phenazine **KI-4** as brown solid (66 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 10.02 (s, 2H, OH), 8.25 (d, J = 8.0 Hz, 1H, aromatic), 8.08 (d, J = 4.0 Hz, 1H, aromatic), 7.63 (t, J = 7.3 Hz, 1H, aromatic), 7.53 (t, J = 7.8 Hz, 1H, aromatic), 7.40 (d, J = 8.0 Hz, 1H, aromatic), 7.13 (d, J = 3.5 Hz, 1H, aromatic), 6.93 (d, J = 3.0 Hz, 1H, aromatic), 6.91 (d, J = 3.5 Hz, 1H, aromatic), 2.87–2.95 (m, 4H, CH_2), 1.72–1.82 (m, 4H, CH_2), 1.31–1.49 (m, 12H, CH_2), 0.91 (t, J = 7.0 Hz, 6H, CH_3). ^{13}C NMR spectrum could not be obtained because of the low solubility in any solvents. HRMS (ESI): 543.21454 $[M-H]^-$, calculated for $C_{32}H_{35}O_2N_2S_2$ $[M-H]^-$: 543.21454.

Phenazine KI-5. A solution of compound **12** (0.140 g, 0.207 mmol) in THF (10 mL) that was bubbled with N_2 for 15 min in advance was prepared and stirred at room temperature for 15 min. Concentrated HCl solution (2.5 mL) was added to the solution, and the mixture was stirred at room temperature with light blocking by aluminum foil cover. After disappearance of the reactant and stirring for additional 2 h, saturated $NaHCO_3$ solution was added to the mixture for neutralization. Then, Ethyl acetate was added to the mixture, and the extracted organic layer was washed with water once and saturated saline twice, dried over anhydrous Na_2SO_4, filtered, concentrated, and washed with hexane and water. The crude product was dissolved in THF and precipitated in hexane to give phenazine **KI-5** as black solid (0.100 g, 82% yield). ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) = 8.95 (d, J = 2.5 Hz, 1H, aromatic), 8.69 (d, J = 3.0 Hz, 1H, aromatic), 8.37 (d, J = 3.0 Hz, 1H, aromatic), 8.33 (dd, J = 9.0 and 2.5 Hz, 1H, aromatic), 8.16 (d, J = 9.0 Hz, 1H, aromatic), 6.85 (d, J = 3.5 Hz, 1H, aromatic), 6.80 (d, J = 3.5 Hz, 1H, aromatic), 2.85–2.94 (m, 4H, CH_2), 1.72–1.82 (m, 4H, CH_2), 1.31–1.52 (m, 12H, CH_2), 0.86–0.95 (m, 6H, CH_3). HRMS (ESI): 588.19849 $[M-H]^-$, calculated for $C_{32}H_{34}O_4N_3S_2$ $[M-H]^-$: 588.19962.

Phenazine KI-6. A solution of phenazine **KI-2** (50 mg, 0.116 mmol) and $NaBH_4$ (18 mg, 0.476 mmol) in THF (120 mL) that was bubbled with N_2 in advance was prepared and stirred at 50 °C for 18 h. After cooling to room temperature, ethyl acetate was added to the solution, and the mixture was washed with saturated saline four times, dried over anhydrous Na_2SO_4, filtered, concentrated, and washed with hexane. Then, the crude product was dissolved in an ethyl acetate/acetone mixture, washed with saturated saline, dried over anhydrous Na_2SO_4, filtered, concentrated, dissolved in THF, and precipitated in hexane to give phenazine **KI-6** as black solid (12 mg, 24% yield). ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) = 8.65 (d, J = 3.5 Hz, 2H, aromatic), 8.12 (dd, J = 6.5 and 3.5 Hz, 2H, aromatic), 7.53 (dd, J = 6.8 and 3.3 Hz, 2H, aromatic), 6.97 (d, J = 4.0 Hz, 2H, aromatic), 4.81 (s, 4H, CH_2). HRMS (ESI): 435.04736 $[M-H]^-$, calculated for $C_{22}H_{15}O_4N_2S_2$ $[M-H]^-$: 435.04787.

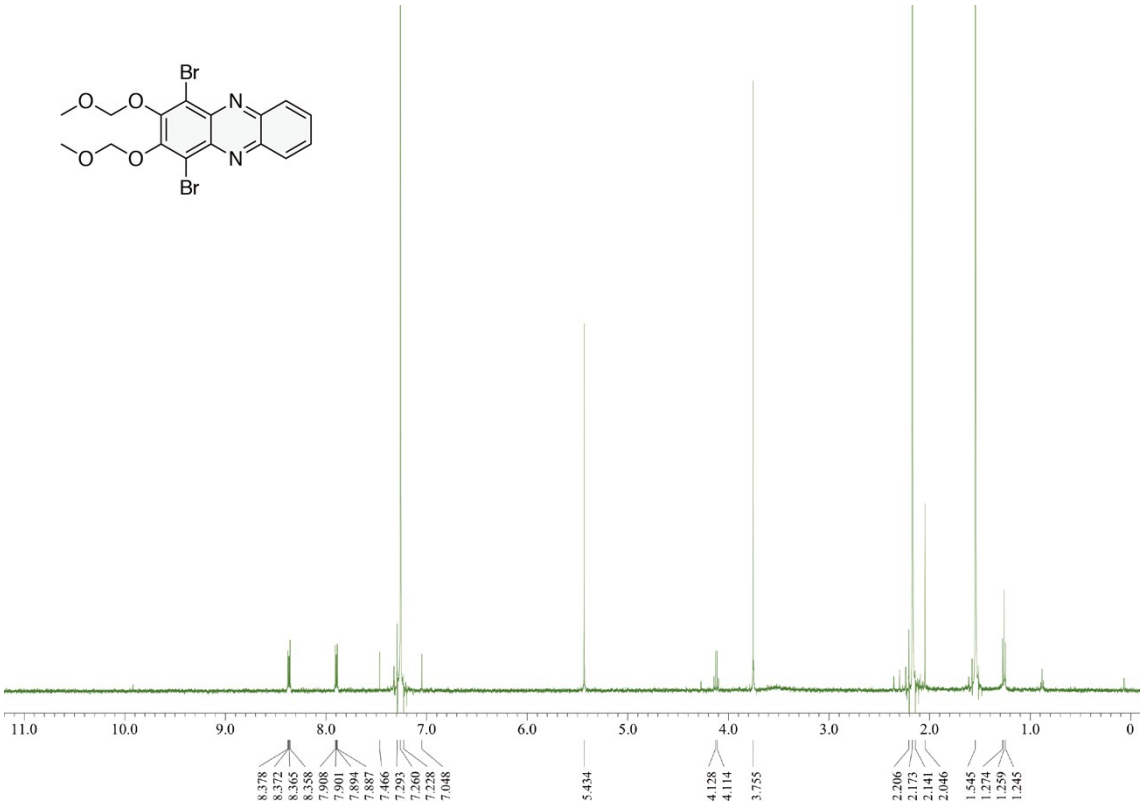

Fig. S1 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

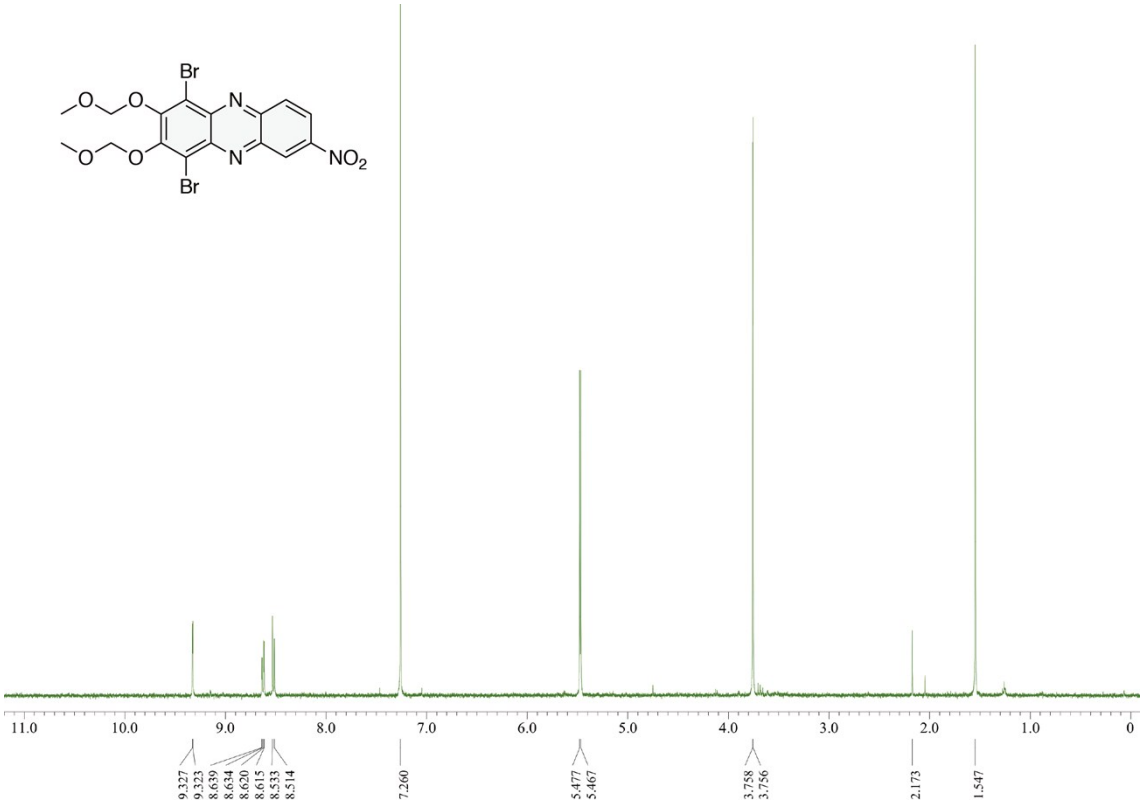

Fig. S2 ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

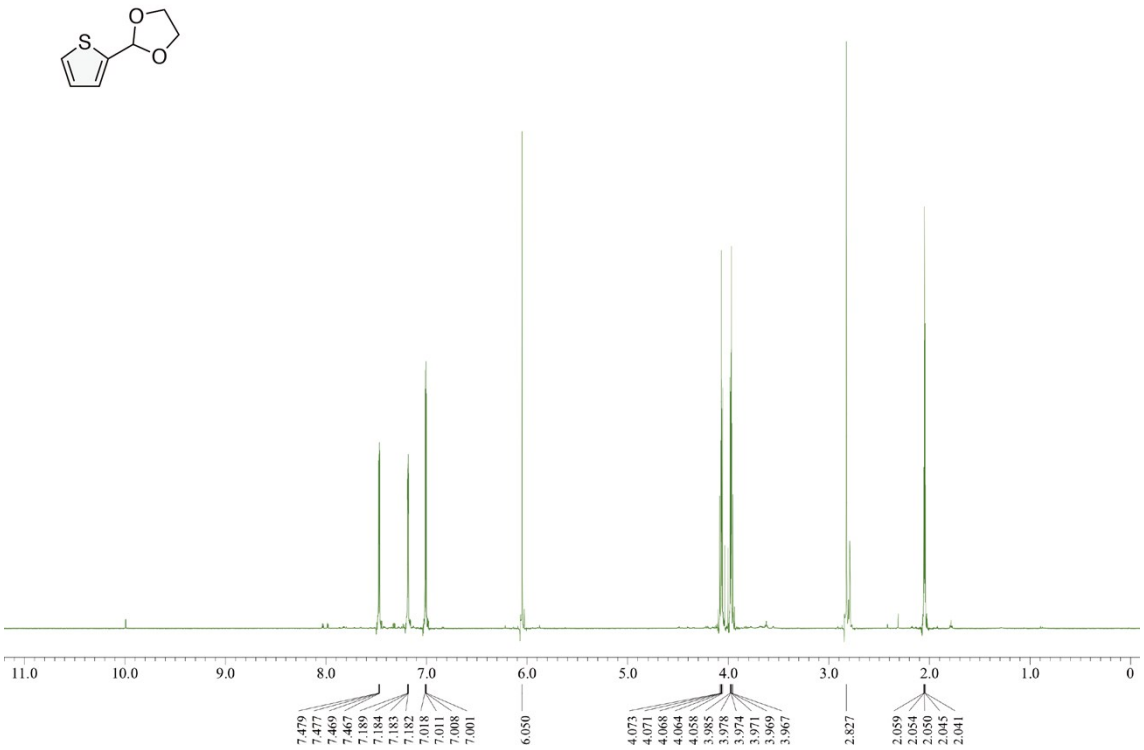

Fig. S3 ^{1}H NMR spectrum of compound **5** in acetone-d_6.

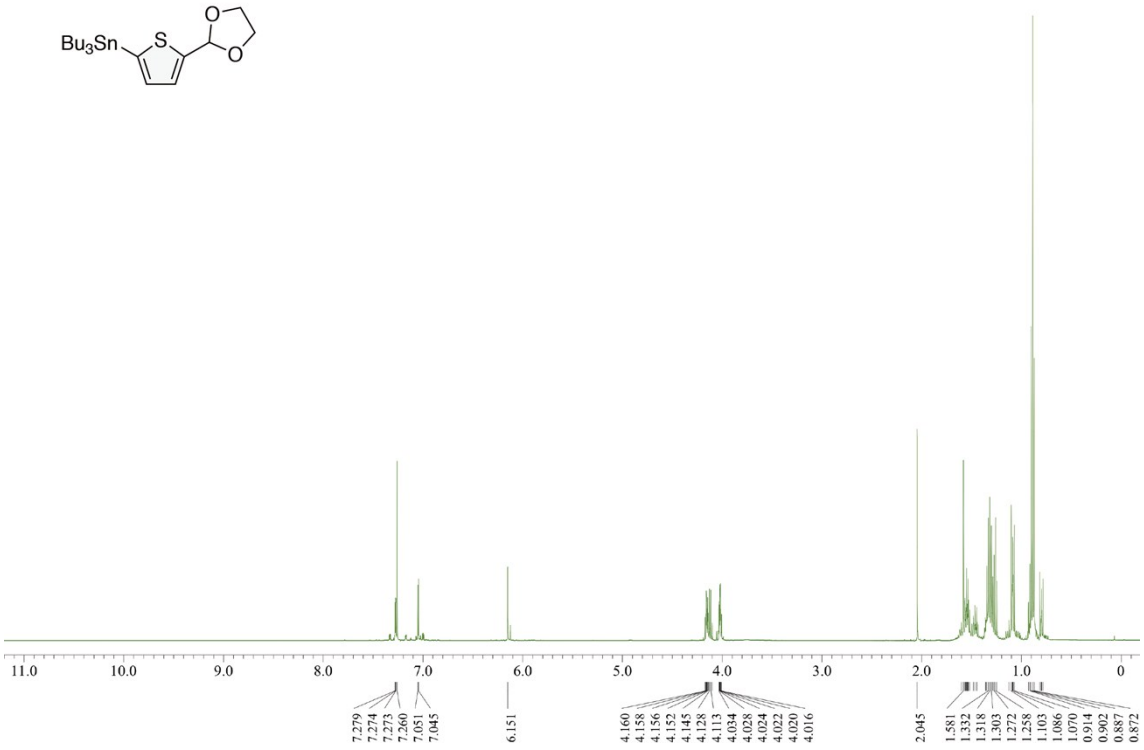

Fig. S4 ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

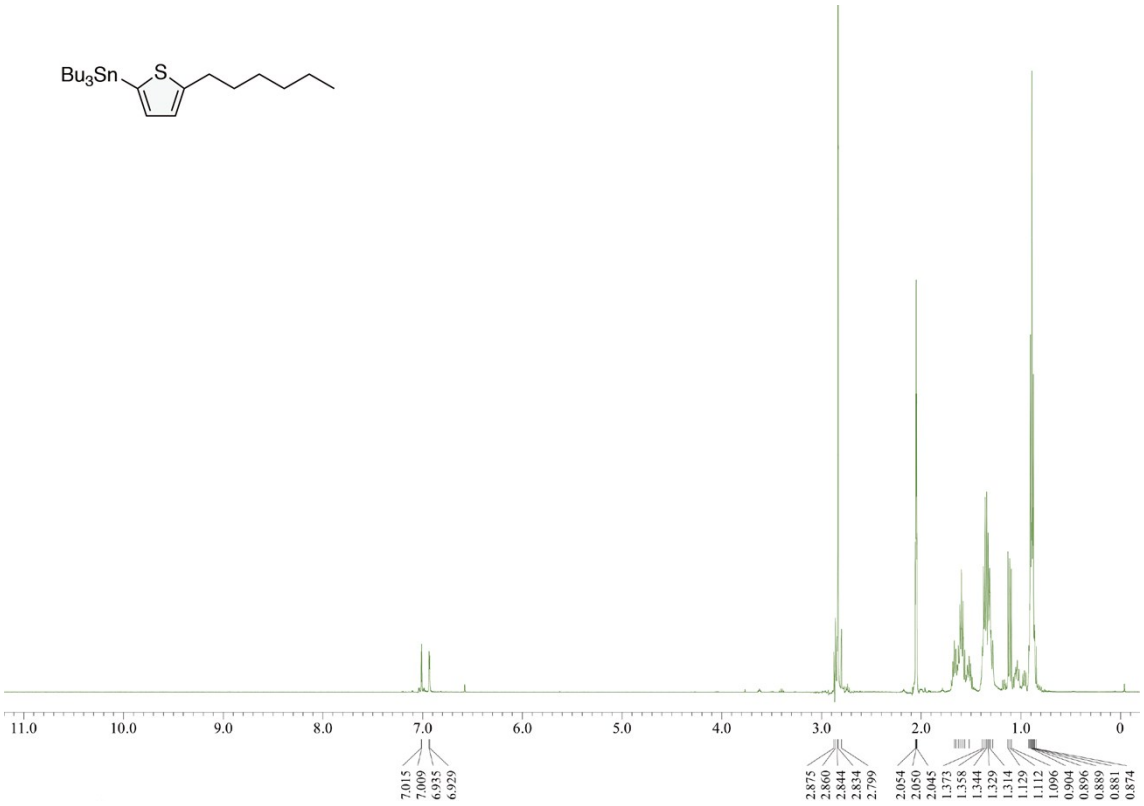

Fig. S5 ^{1}H NMR spectrum of compound **7** in acetone-d_6.

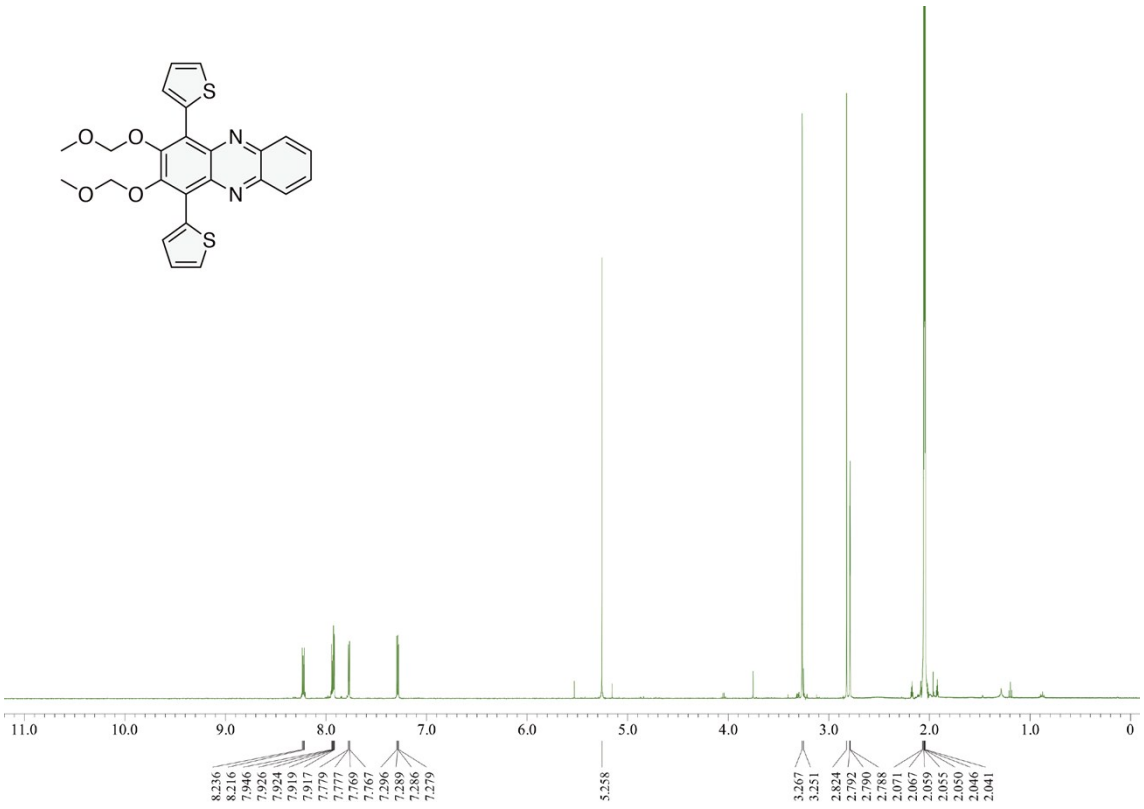

Fig. S6 ^{1}H NMR spectrum of compound **8** in acetone-d_6.

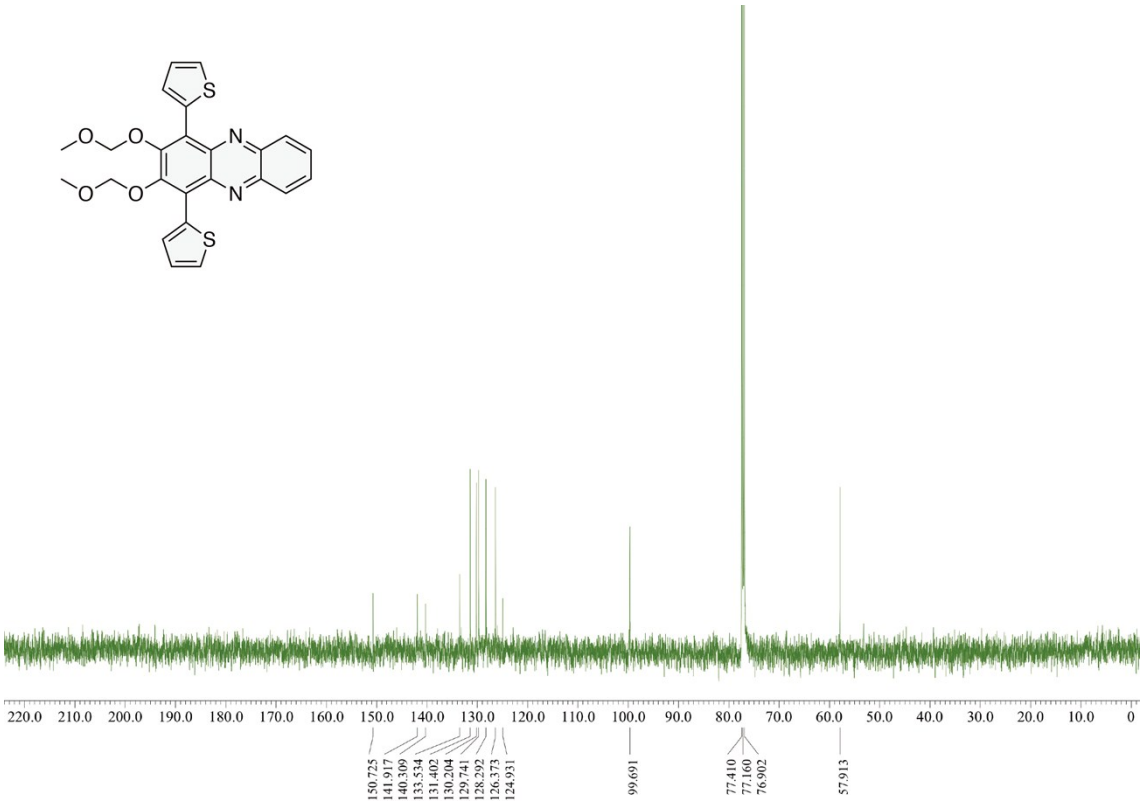

Fig. S7 ^{1}H NMR spectrum of compound **8** in $CDCl_3$.

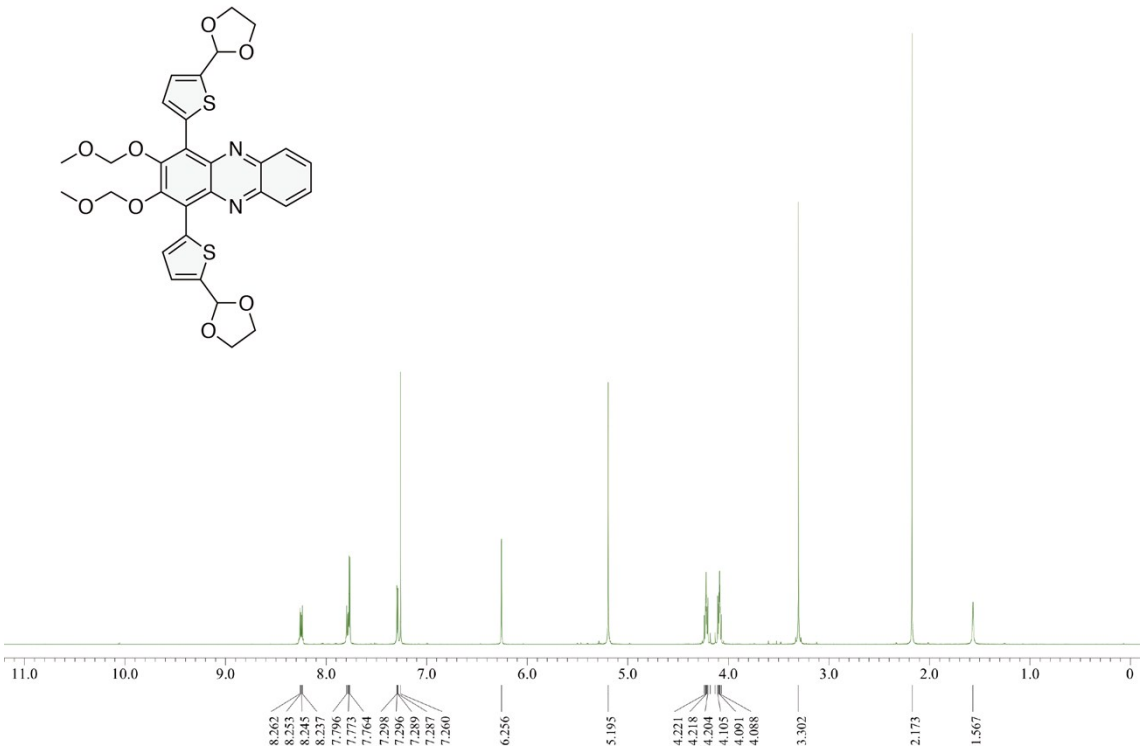

Fig. S8 ^{1}H NMR spectrum of compound **9** in $CDCl_3$.

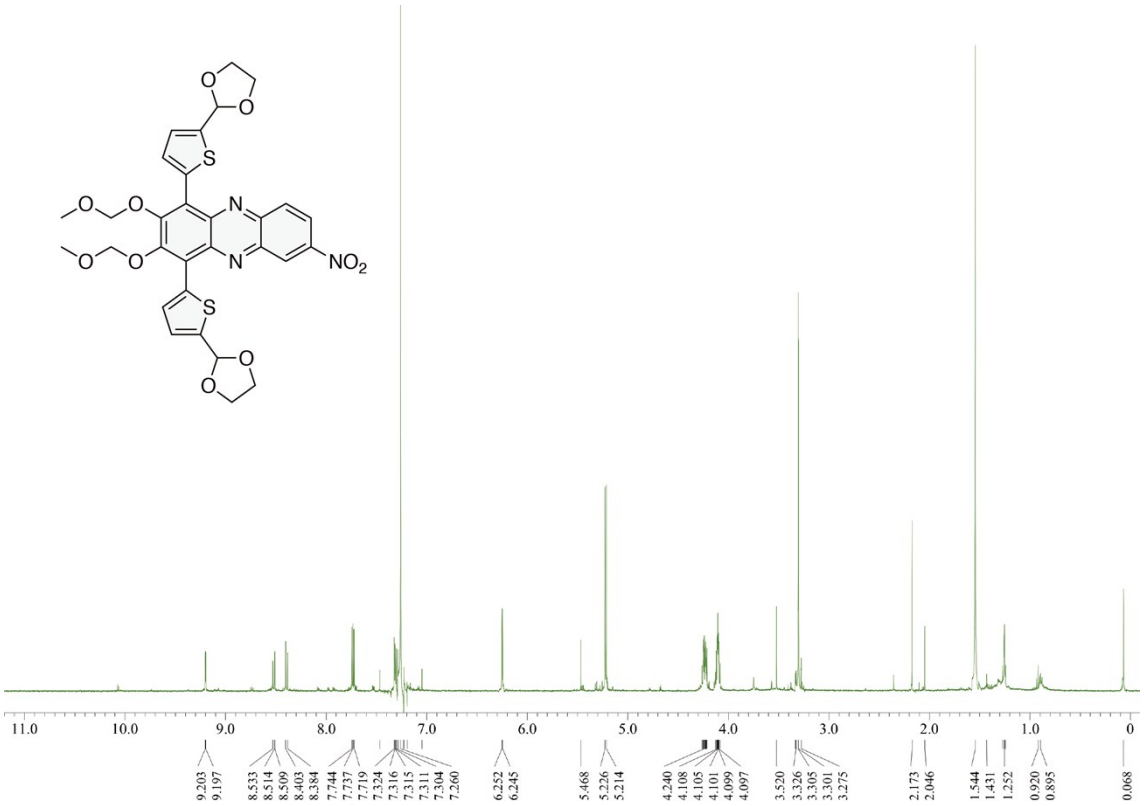

Fig. S9 ^{1}H NMR spectrum of compound **10** in $CDCl_3$.

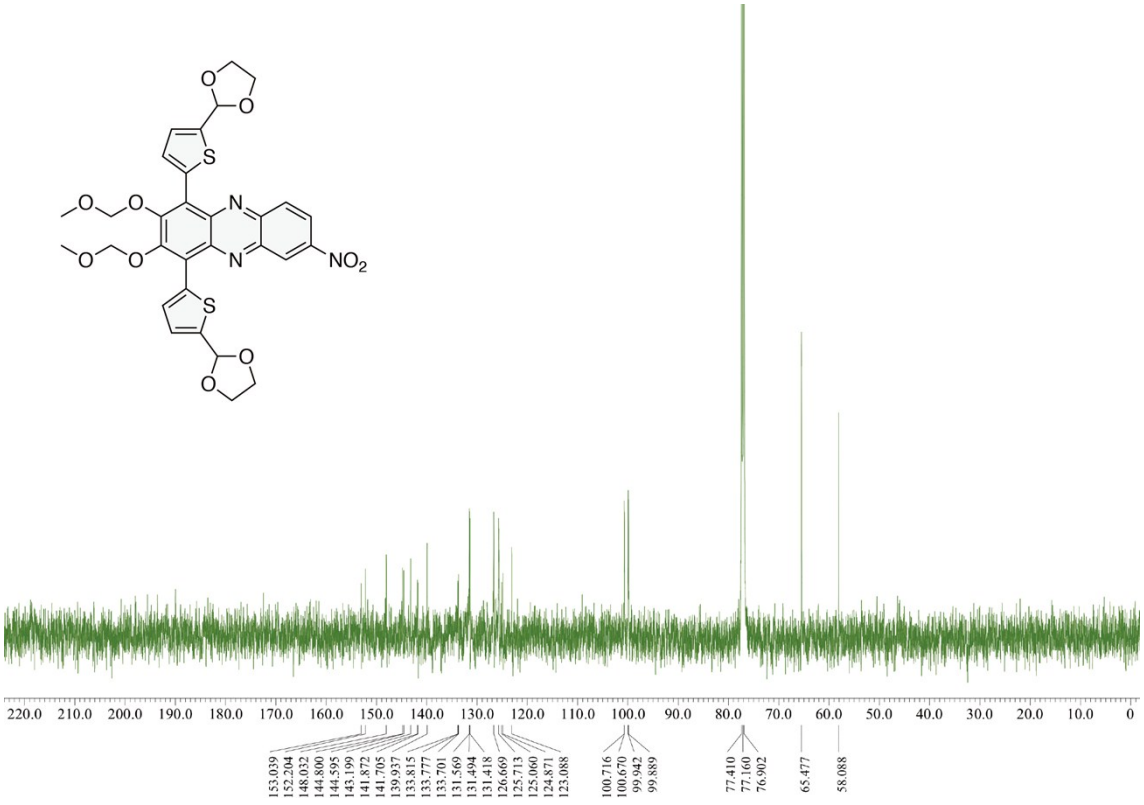

Fig. S10 ^{13}C NMR spectrum of compound **10** in $CDCl_3$.

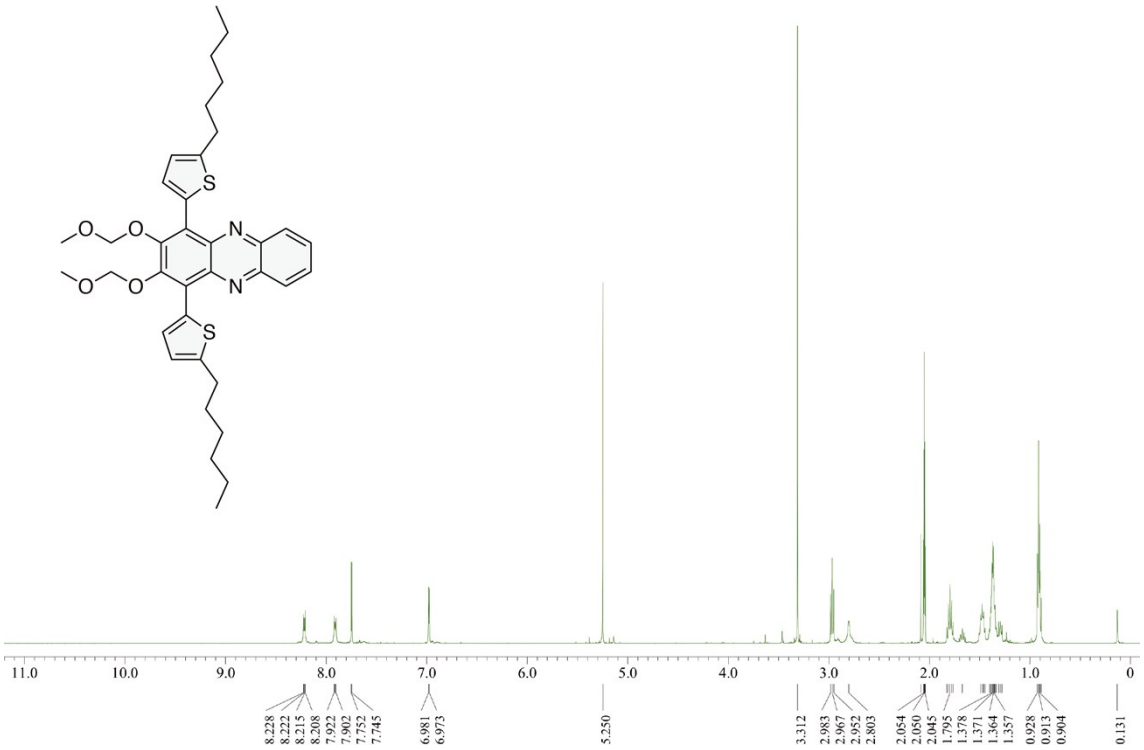

Fig. S11 [1]H NMR spectrum of compound **11** in acetone-d_6.

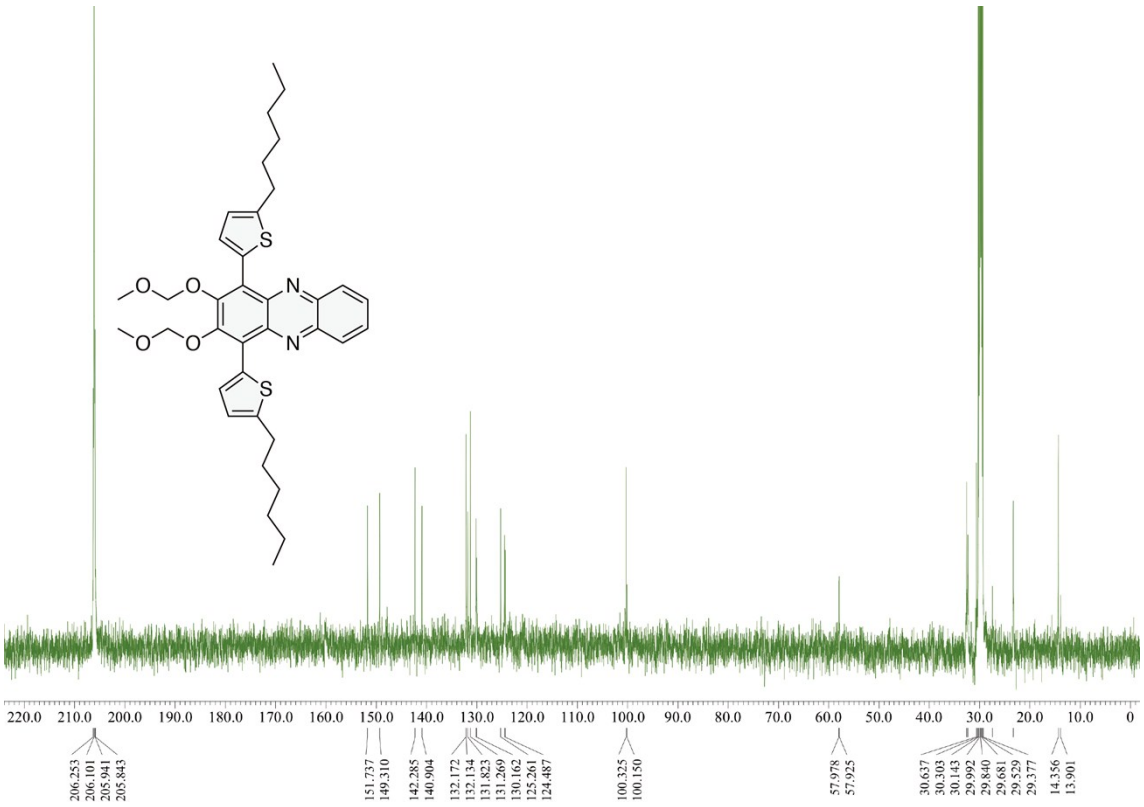

Fig. S12 [13]C NMR spectrum of compound **11** in acetone-d_6.

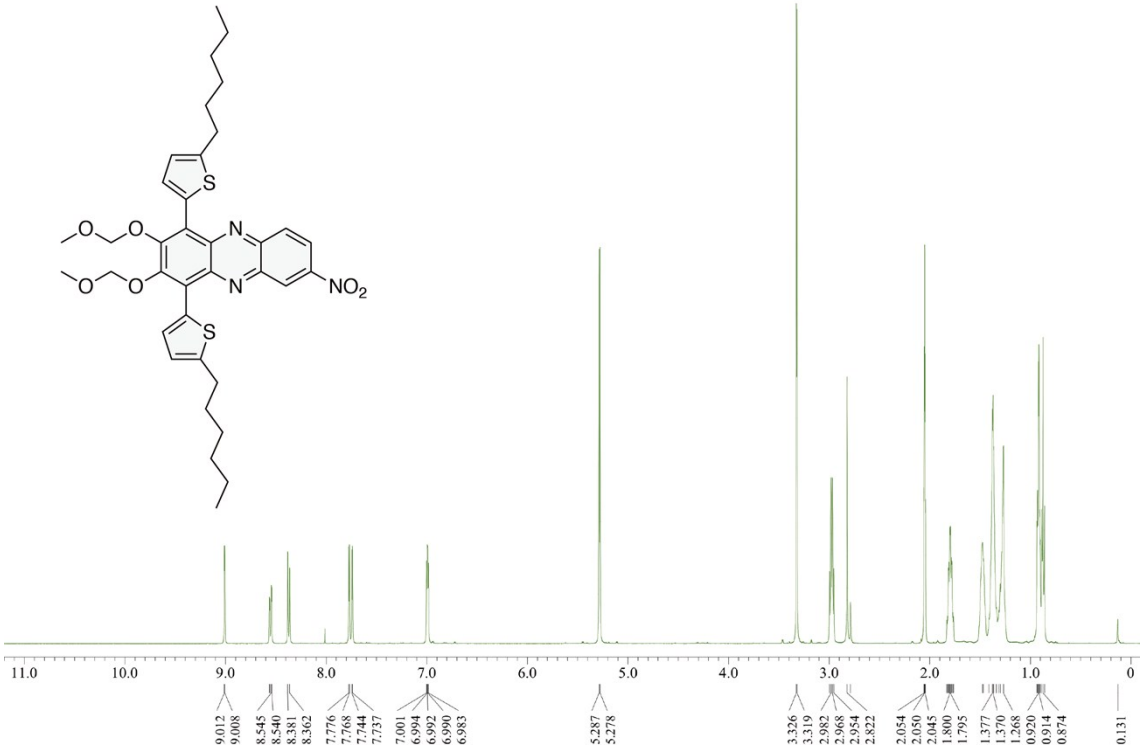

Fig. S13 [1]H NMR spectrum of compound **12** in acetone-d_6.

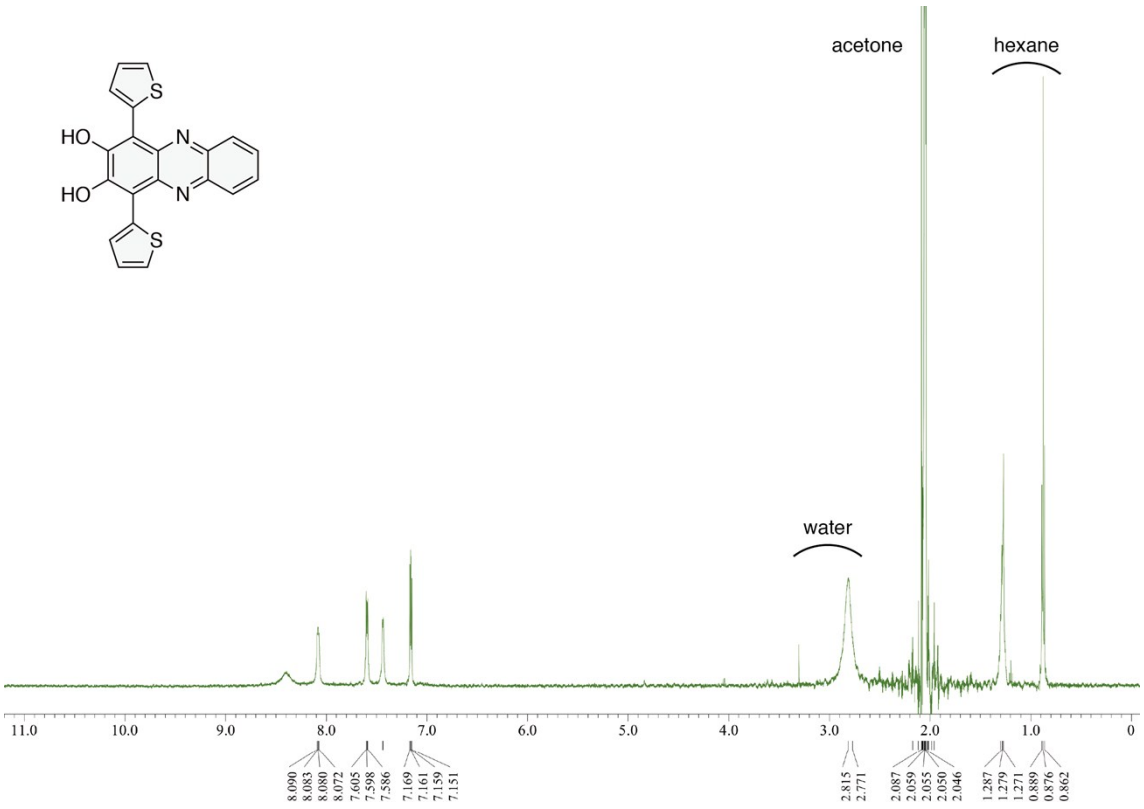

Fig. S14 [1]H NMR spectrum of phenazine derivative **KI-1** in acetone-d_6.

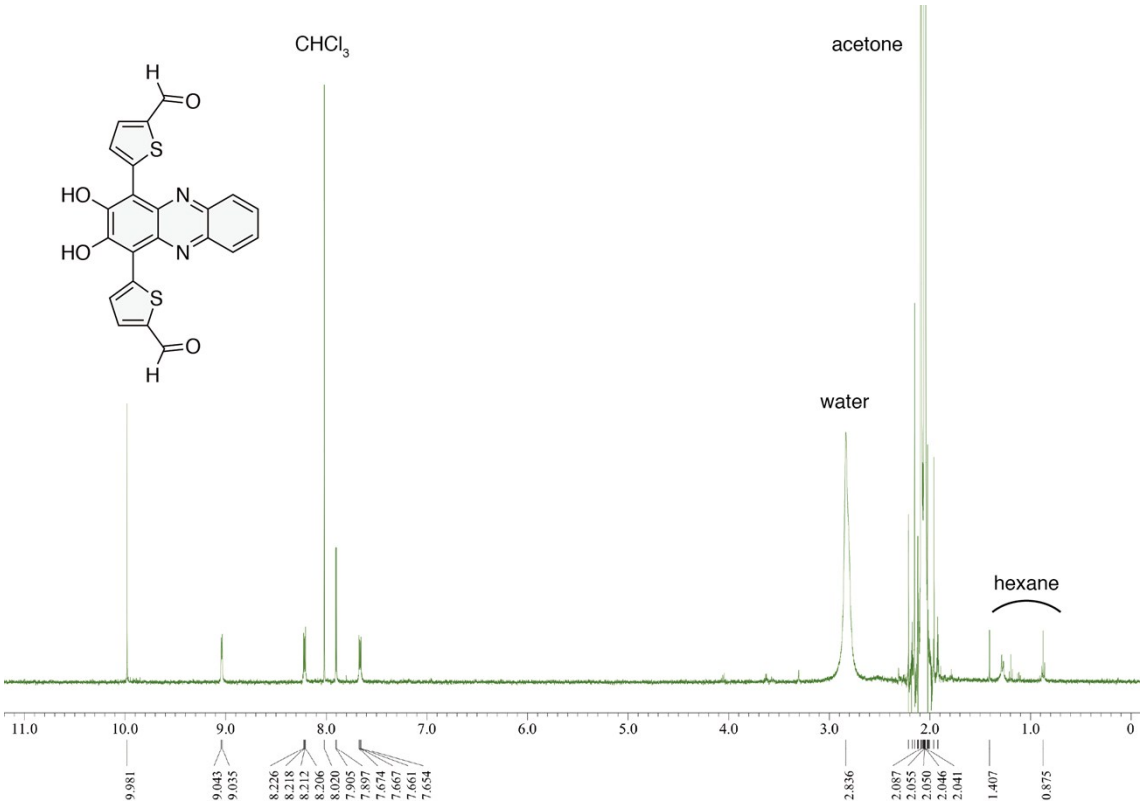

Fig. S15 [1]H NMR spectrum of phenazine derivative **KI-2** in acetone-d_6.

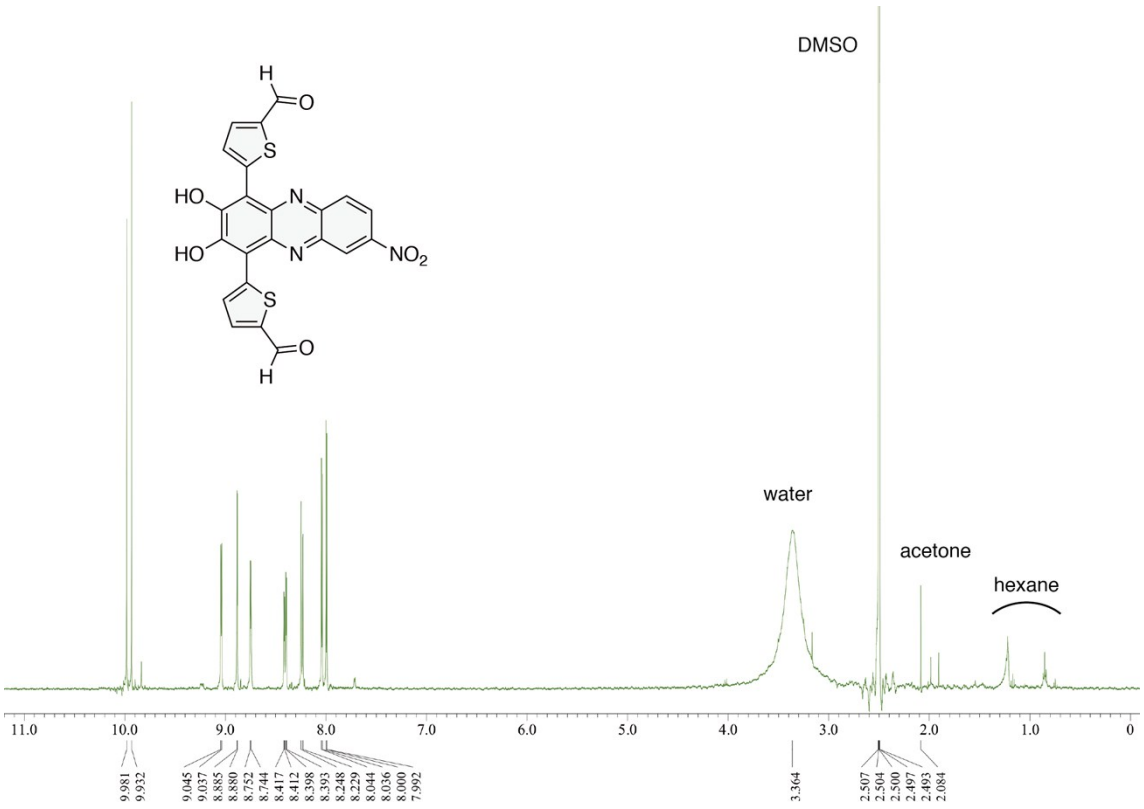

Fig. S16 [1]H NMR spectrum of phenazine derivative **KI-3** in DMSO-d_6.

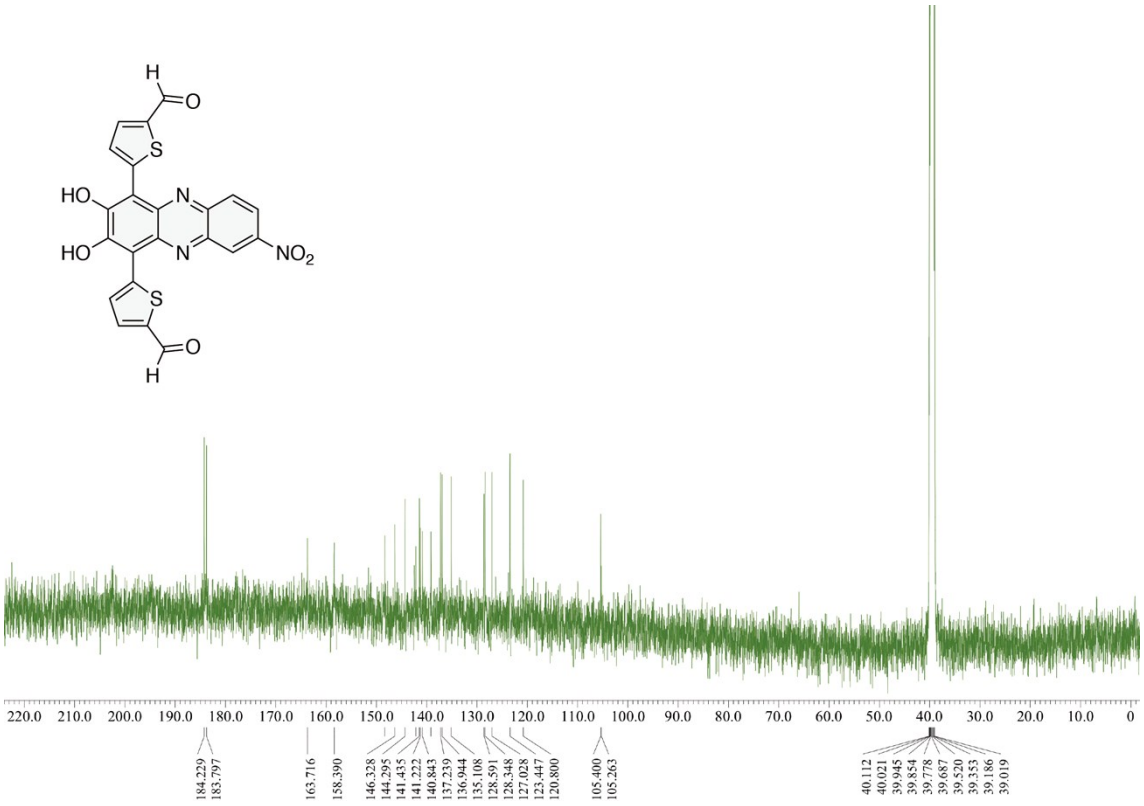

Fig. S17 ^{13}C NMR spectrum of phenazine derivative **KI-3** in DMSO-d_6.

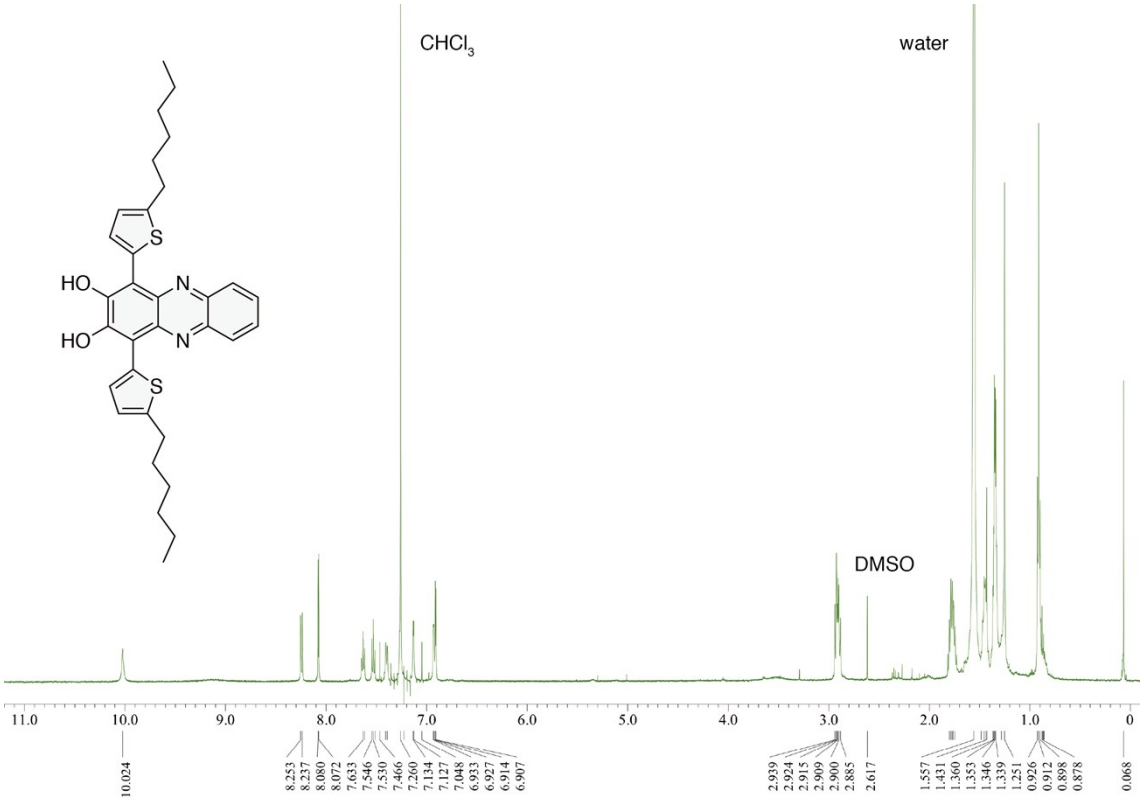

Fig. S18 ^{1}H NMR spectrum of phenazine derivative **KI-4** in $CDCl_3$.

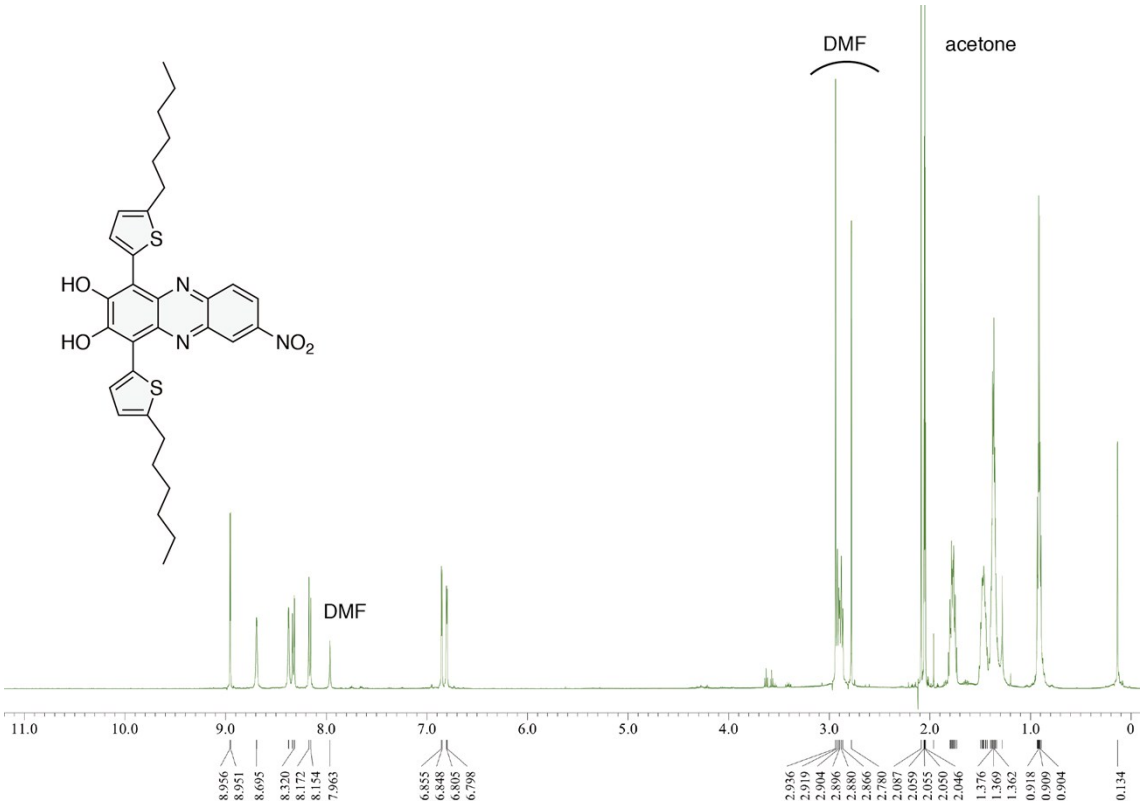

Fig. S19 [1]H NMR spectrum of phenazine derivative **KI-5** in acetone-d_6.

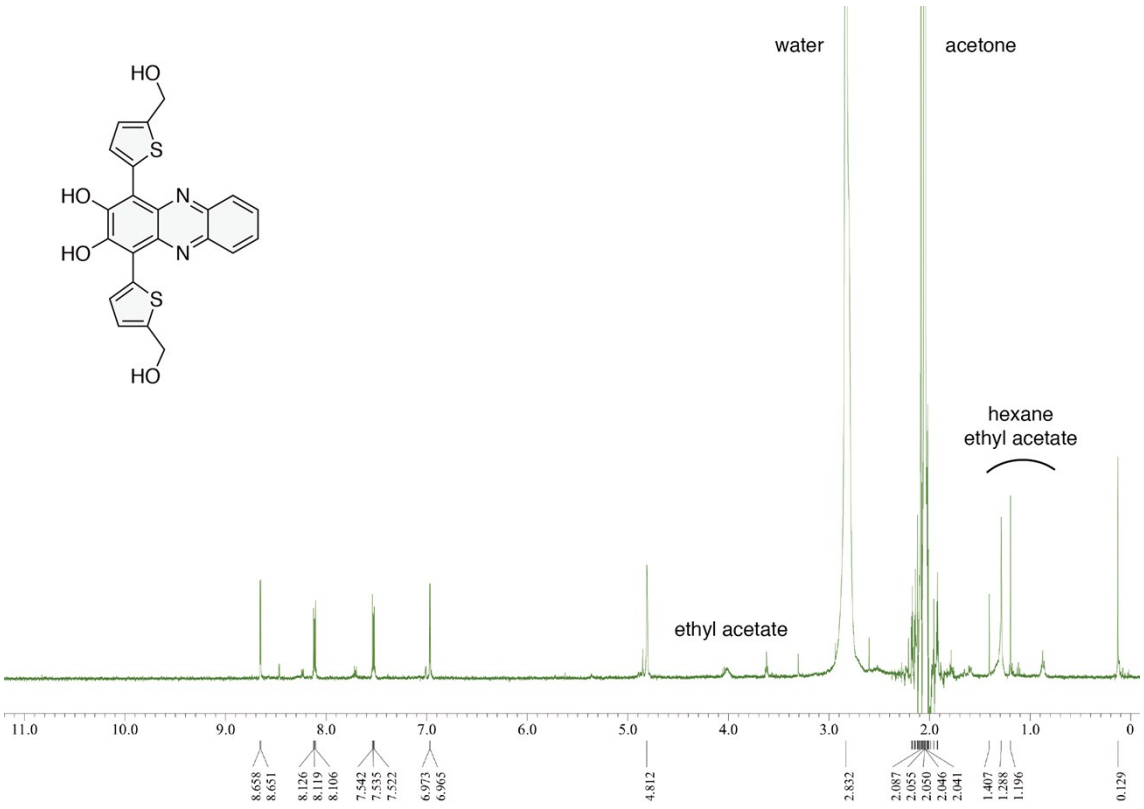

Fig. S20 [1]H NMR spectrum of phenazine derivative **KI-6** in acetone-d_6.

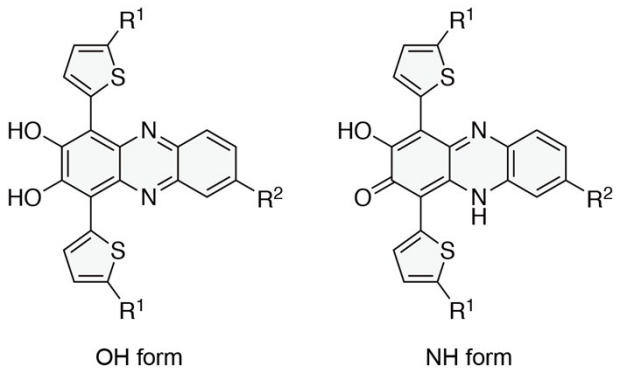

Fig. S21 Chemical structures of OH form (left) and NH form (right) for phenazine derivatives.

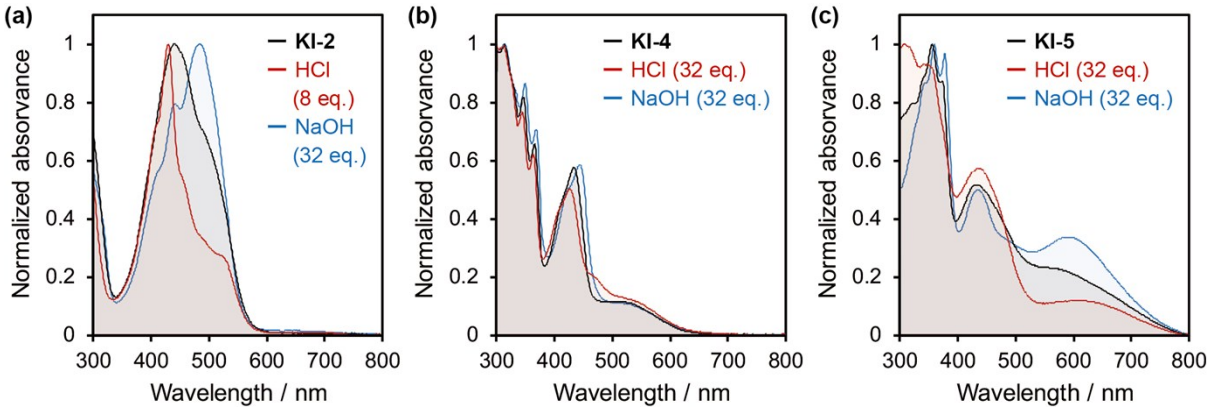

Fig. S22 Effect of HCl and NaOH addition on photoabsorption spectra of phenazine derivatives. Normalized photoabsorption spectra of (a) **KI-2**, (b) **KI-4**, and (c) **KI-5** in DMSO before and after addition of HCl or NaOH.

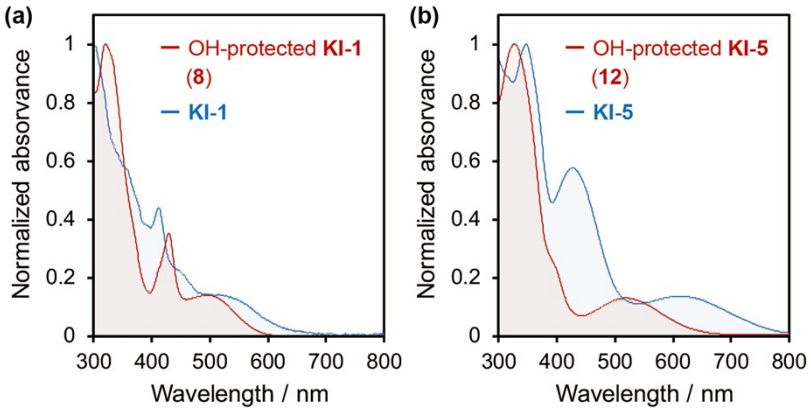

Fig. S23 Effect of protection and deprotection of hydroxyl groups on photoabsorption spectra of phenazine derivatives. Normalized photoabsorption spectra of (a) **KI-1** and (b) **KI-5** in THF with and without protection of hydroxyl groups.

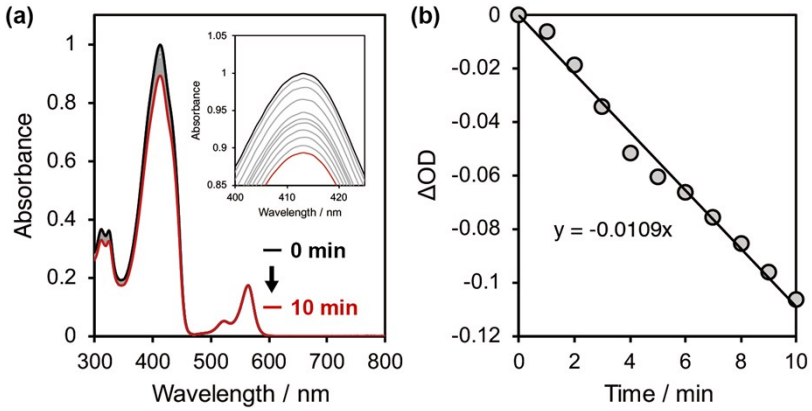

Fig. S24 (a) Photoabsorption spectra of DPBF (Abs. @413 nm = ca. 1) in the presence of RB (Abs. @509 nm = ca. 0.03) upon irradiation with a monochromatic light (509 nm, 300 μW cm^{-2}) in THF. Inset is magnification of peak tops in the spectra around 410 nm. (b) Plot of changes in optical density (ΔOD) of DPBF at 413 nm against photoirradiation time (509 nm, 300 μW cm^{-2}) in the presence of RB in THF.

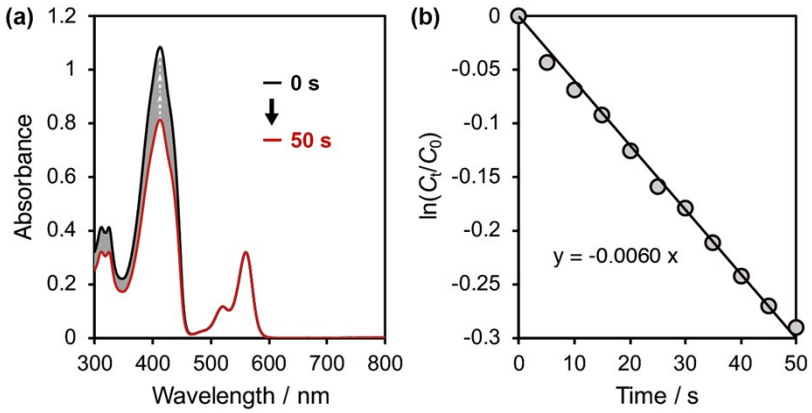

Fig. S25 (a) Photoabsorption spectra of DPBF (50 μM) in the presence of RB (5 μM) upon irradiation with a continuous light (>510 nm, 30 mW cm^{-2}) in THF. (b) Plot of $\ln(C_t/C_0)$ of DPBF against photoirradiation time (>510 nm, 30 mW cm^{-2}) in the presence of RB in THF.

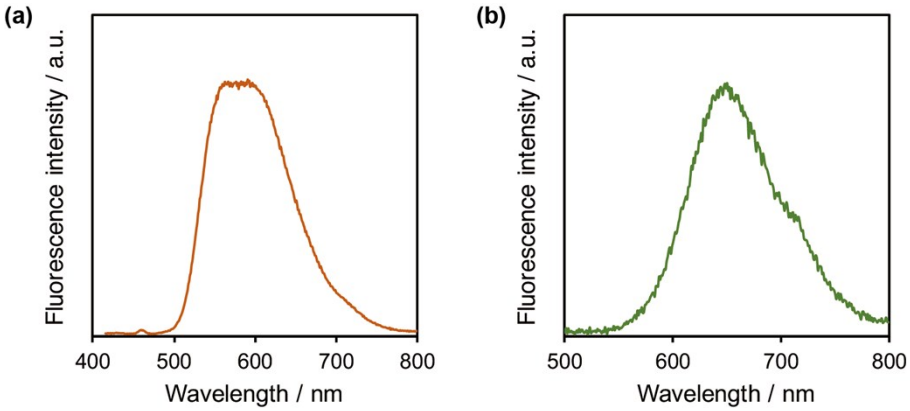

Fig. S26 Fluorescence spectra of (a) **KI-2** (λ_{ex} = 407 nm) and (b) **KI-4** (λ_{ex} = 430 nm) in THF (1.0×10^{-5} M). The Φ_{fl} values of **KI-2** and **KI-4** are 0.04 (λ_{ex} = 400 nm) and 0.09 (λ_{ex} = 310 nm), respectively. In contrast, **KI-3** and **KI-5** show a feeble fluorescence (Φ_{fl} < 0.02).

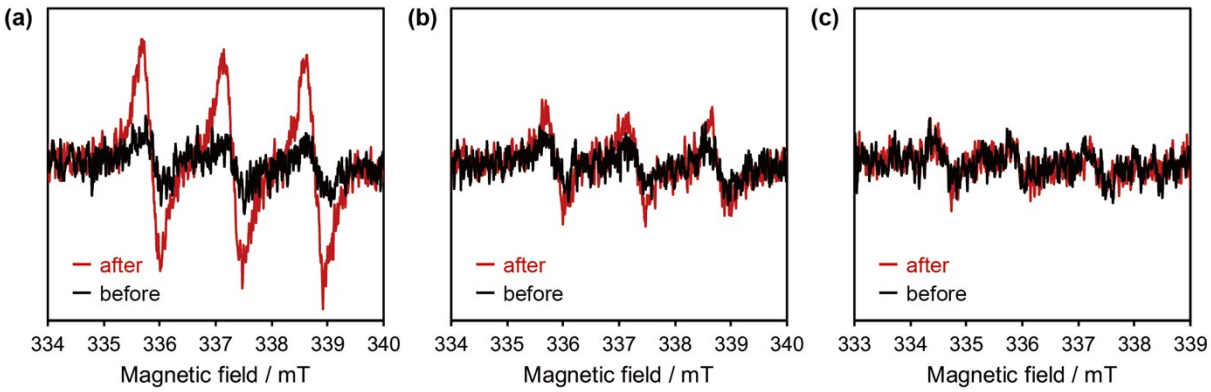

Fig. S27 Electron paramagnetic resonance (EPR) spectra of air-saturated THF solutions containing 4-oxo-TEMP and (a) RB, (b) **KI-2**, or (c) **KI-3** before and after exposure to a continuous visible light (>510 nm, 30 mW cm^{-2}) for 60 min. The characteristic 1:1:1 triplet signal originates from a stable nitroxide radical (4-oxo-TEMPO) formed by the reaction of 4-oxo-TEMP with $^1O_2$.

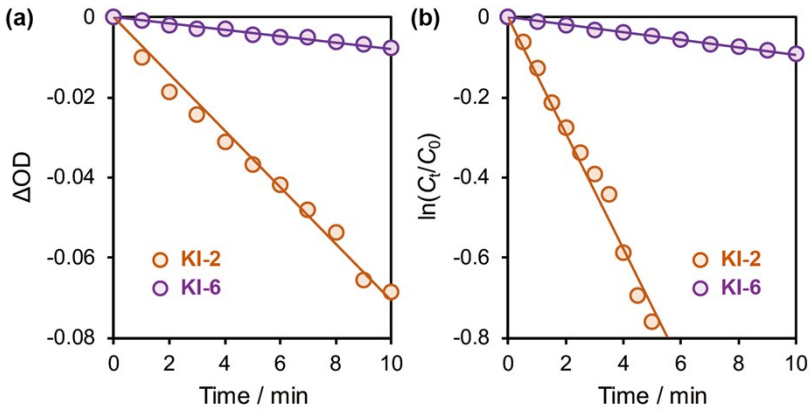

Fig. S28 (a) Plots of ΔOD of DPBF at 413 nm against photoirradiation time (509 nm, 300 μW cm^{-2}) in the presence of **KI-2** or **KI-6** in THF. (b) Plots of $\ln(C_t/C_0)$ of DPBF against photoirradiation time (>510 nm, 30 mW cm^{-2}) in the presence of **KI-2** or **KI-6** in THF.