Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information

Development of phenazine-2,3-diol-based photosensitizers: effect of formyl groups on singlet oxygen generation

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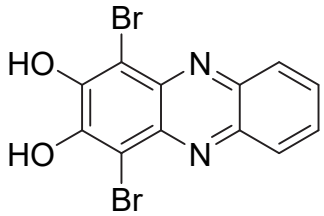
Materials

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

General

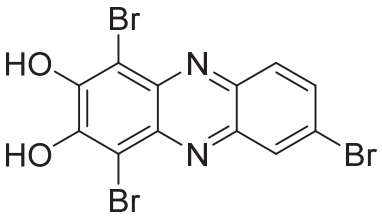
^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian-500 (500 MHz) FT NMR spectrometer. FT-IR spectra were recorded using a Shimadzu IRTracer-100. High-resolution mass spectral data were acquired using a Thermo Fisher Scientific LTQ Orbitrap XL. Photoabsorption spectra were recorded using Shimadzu UV-3150 and UV-3600-plus spectrophotometers. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields (Φ_{fl}) 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

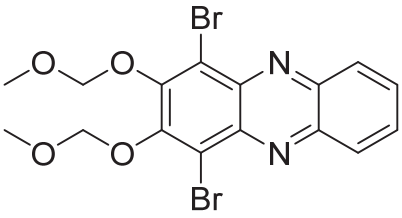


Compound 1. A solution of bromanilic acid (0.296 g, 1.00 mmol) and 1,2-phenylenediamine (0.109 g, 0.988 mmol) in ethanol (35 mL) was stirred at 80 °C. After disappearance of the reactants, the reaction mixture was cooled to room temperature, and the precipitate was filtered and washed with a small amount of ethanol to give compound **1** as red solid (308 mg, 85% yield); m.p. over 300 °C; IR (ATR):

$\tilde{\nu}$ = 3231, 2900, 1603, 1574, 1551, 1516 cm^{-1}; ^1H NMR (500 MHz, dimethyl sulfoxide (DMSO)-d_6): δ = 12.6 (br, OH), 8.16 (br, 2H, aromatic), 7.73 (br, 2H, aromatic) ppm; ^{13}C NMR spectrum could not be obtained because of the low solubility in any solvents; HRMS (APCI): *m/z* found 366.87265 $[M-H]^-$, calculated for $C_{12}H_5Br_2N_2O_2$ $[M-H]^-$: 366.87233.

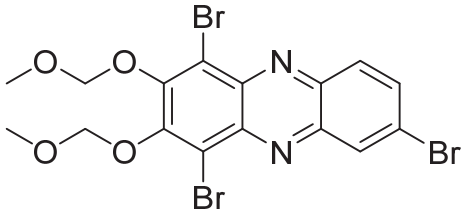


Compound 2. A solution of bromanilic acid (0.296 g, 1.00 mmol) and 4-bromo-1,2-benzenediamine (0.187 g, 1.00 mmol) in ethanol (30 mL) was stirred at 80 °C. After disappearance of the reactants, the reaction mixture was cooled to room temperature, and the precipitate was filtered and washed with a small amount of ethanol to give compound **2** as red solid (287 mg, 64% yield); m.p. over 300 °C; IR (ATR): $\tilde{\nu}$ = 3260, 3060, 2920, 1624, 1568, 1512 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 8.37 (br, 1H, aromatic), 8.07 (d, J = 8.7 Hz, 2H, aromatic), 7.82 (d, J = 8.2 Hz, 2H, aromatic) ppm; ^{13}C NMR spectrum could not be obtained because of the low solubility in any solvents; HRMS (APCI): *m/z* found 446.79834 $[M+H]^+$, calculated for $C_{12}H_6Br_3N_2O_2$ $[M+H]^+$: 446.79739.

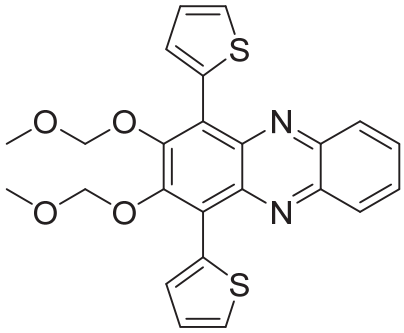


Compound 3. A solution of sodium hydride abt. 60 % oil suspension (0.0803 g) and compound **1** (0.0370 g, 0.101 mmol) in THF (25 mL) was stirred at 0 °C for 30 min. Then, chloromethyl methyl ether (152 μL, 2.00 mmol) was added to the solution, and the mixture was stirred at 0 °C overnight. After concentrating under reduced pressure, the residue was chromatographed on silica gel (ethyl acetate/hexane = 1/4 as eluent) to give compound **3** as a yellow solid (0.0363 g, 80% yield); m.p. 155–157 °C; IR (ATR): $\tilde{\nu}$ = 3057, 2994, 2899, 1539, 1454, 1423 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.39–8.34 (m, 2H, aromatic), 7.92–7.87 (m, 2H, aromatic), 5.43 (s, 4H, CH_2), 3.75 (s, 6H, CH_3) ppm;

^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.165, 143.241, 139.545, 131.420, 129.624, 116.987, 100.327, 58.892 ppm; HRMS (APCI): *m/z* found 456.93978 $[M+H]^+$, calculated for $C_{16}H_{15}Br_2N_2O_4$ $[M+H]^+$: 456.93931.

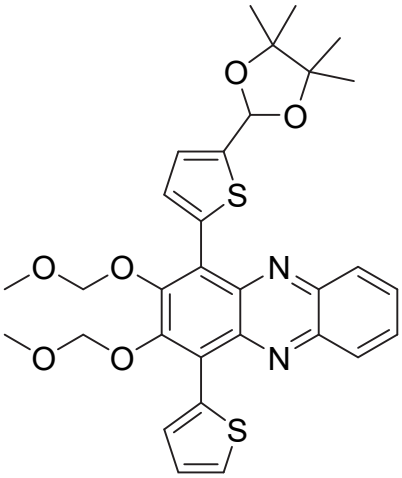


Compound 4. A solution of sodium hydride abt. 60 % oil suspension (0.0803 g) and compound **2** (0.0452 g, 0.100 mmol) in THF (25 mL) was stirred at 0 °C for 30 min. Then, bromomethyl methyl ether (162 μL, 2.00 mmol) was added to the solution, and the mixture was stirred at 0 °C overnight. After concentrating under reduced pressure, the residue was chromatographed on silica gel (ethyl acetate/hexane = 1/4 as eluent) to give compound **4** as yellow solid (0.0252 g, 47% yield); m.p. 159–160 °C; IR (ATR): $\tilde{\nu}$ = 2961, 2918, 2830, 1611, 1584, 1530 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 2.1 Hz, 1H, aromatic), 8.23 (d, J = 9.2 Hz, 1H, aromatic), 7.94 (dd, J = 9.2 and 2.1 Hz, 1H, aromatic), 5.43 (s, 2H, CH_2), 5.43 (s, 2H, CH_2), 3.75 (s, 6H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.819, 152.506, 143.288, 141.756, 139.897, 139.596, 135.131, 131.579, 130.756, 126.064, 117.015, 116.882, 100.369, 100.333, 58.909 ppm; HRMS (APCI): *m/z* found 534.84991 $[M+H]^+$, calculated for $C_{16}H_{14}Br_3N_2O_4$ $[M+H]^+$: 534.84982.

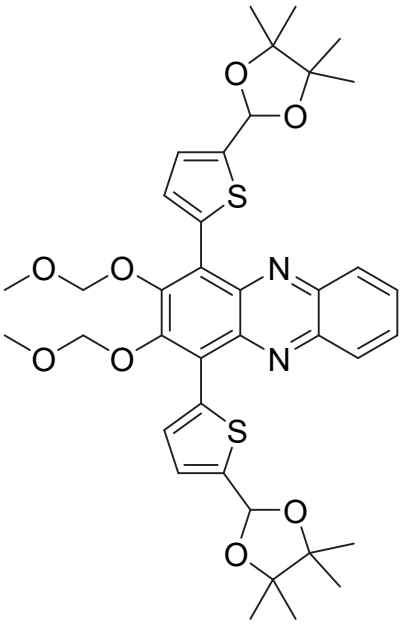


Compound 5. A solution of compound **2** (0.363 g, 0.795 mmol), **S1** (760 μL, 2.40 mmol), and $Pd(PPh_3)_4$ (0.184 g, 0.159 mmol) in toluene (40 mL) was stirred at 110 °C overnight. After concentrating under reduced pressure, the residue was chromatographed on silica gel (ethyl acetate/hexane = 1/4 as eluent).

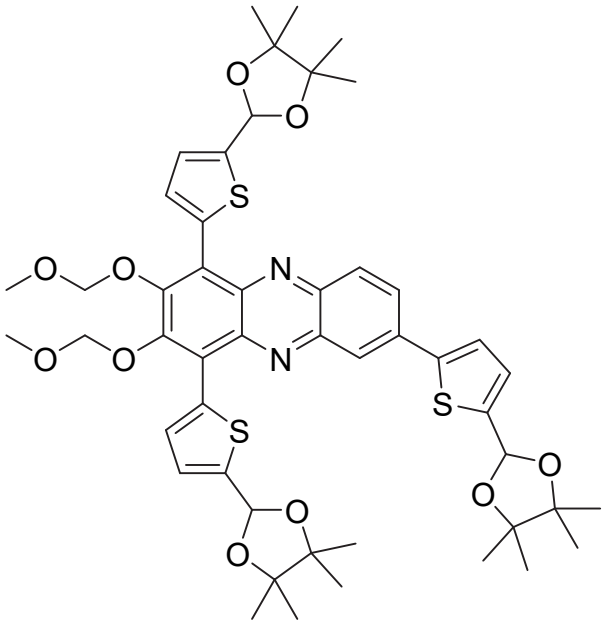
The crude was dissolved in toluene, and gel permeation chromatography (GPC) was performed to give compound **5** as yellow solid (0.215 g, 66% yield); m.p. 161–164 °C; IR (ATR): $\tilde{\nu}$ = 3098, 3057, 2986, 2955, 2928, 2828, 1713, 1549 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6): δ = 8.19–8.24 (m, 2H, aromatic), 7.89–7.94 (m, 4H, aromatic), 7.77 (dd, J = 5.2 and 1.2 Hz, 2H, aromatic), 7.28 (dd, J = 5.4 and 3.7 Hz, 2H, aromatic), 5.26 (s, 4H, CH_2), 3.27 (s, 6H, CH_3) ppm; ^{13}C NMR (125 MHz, acetone-d_6): δ = 152.03, 142.38, 140.87, 134.24, 132.13, 131.42, 130.10, 129.13, 126.92, 125.37, 100.41, 57.87 ppm; HRMS (APCI): *m/z* found 465.09406 $[M+H]^+$, calculated for $C_{24}H_{21}S_2N_2O_4$ $[M+H]^+$: 465.09373.



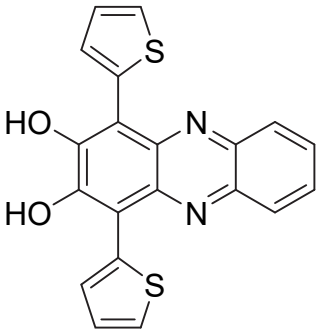
Compound 6. A solution of compound **3** (0.351 g, 0.769 mmol), **S1** (0.430 g, 1.15 mmol), **S3** (0.576 g, 1.15 mmol), and $Pd(PPh_3)_4$ (0.183 g, 0.158 mmol) in toluene (40 mL) was stirred at 110 °C overnight. After concentrating under reduced pressure, the residue was chromatographed on silica gel (ethyl acetate/hexane = 1/4 as eluent). The crude was dissolved in toluene, and GPC was performed to give compound **6** as yellow solid (0.033 g, 7% yield); m.p. 149–150 °C; IR (ATR): $\tilde{\nu}$ = 3094, 3069, 2982, 2907, 2828, 1713, 1618, 1582, 1541 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6): δ = 8.19–8.26 (m, 2H, aromatic), 7.90–7.96 (m, 3H, aromatic), 7.76–7.79 (m, 2H, aromatic), 7.27–7.31 (m, 2H, aromatic), 6.30 (s, 1H, CH), 5.28 (s, 2H, CH_2), 5.25 (s, 2H, CH_2), 3.30 (s, 3H, CH_3), 3.27 (s, 3H, CH_3), 1.36 (s, 6H, CH_3), 1.32 (s, 6H, CH_3) ppm; ^{13}C NMR (125 MHz, acetone-d_6): δ = 152.11, 151.98, 147.74, 142.38, 142,36, 140.84, 140.82, 134.82, 134.21, 132.15, 131.64, 131.46, 131.43, 130.10, 130.08, 129.16, 126.92, 125.84, 125.45, 125.33, 100.45, 100.42, 97.78, 83.57, 57.98, 57.88, 24.61, 22.39 ppm; HRMS (APCI): *m/z* found 593.17725 $[M+H]^+$, calculated for $C_{31}H_{33}S_2N_2O_6$ $[M+H]^+$: 593.17745.



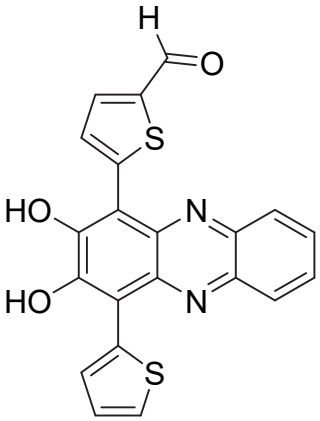
Compound 7. A solution of compound **3** (0.283 g, 0.618 mmol), **S3** (0.930 g, 1.85 mmol), and $Pd(PPh_3)_4$ (0.0715 g, 0.0619 mmol) in toluene (30 mL) was stirred at 110 °C overnight. After concentrating under reduced pressure, the residue was chromatographed on silica gel (ethyl acetate/hexane = 1/4 as eluent). The crude was dissolved in toluene, and GPC was performed to give compound **7** as yellow solid (0.246 g, 34% yield); m.p. 162–164 °C; IR (ATR): $\tilde{\nu}$ = 3071, 2986, 2972, 2911, 2826, 1618, 1584, 1537, 1514 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6): δ = 8.20–8.24 (m, 2H, aromatic), 7.91–7.97 (m, 2H, aromatic), 7.78 (d, J = 3.7 Hz, 2H, aromatic), 7.30 (dd, J = 3.7 and 0.6 Hz, 2H, aromatic), 6.30 (s, 2H, CH), 5.27 (s, 4H, CH_2), 3.30 (s, 6H, CH_3), 1.36 (s, 12H, CH_3), 1.32 (s, 12H, CH_3) ppm. ^{13}C NMR (125 MHz, acetone-d_6): δ = 152.09, 147.80, 142.40, 140.82, 134.80, 131.67, 131.50, 130.11, 125.84, 125.43, 100.48, 97.78, 83.58, 57.99, 24.62, 22.40 ppm. HRMS (APCI): *m/z* found 721.26141 $[M+H]^+$, calculated for $C_{38}H_{45}S_2N_2O_8$ $[M+H]^+$: 721.26118.



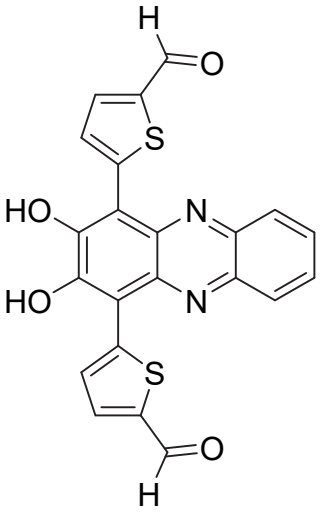
Compound 8. A solution of compound **4** (0.743 g, 1.38 mmol), **S3** (2.78 g, 5.53 mmol), and $Pd(PPh_3)_4$ (175 mg, 0.151 mmol) in toluene (80 mL) was stirred at 110 °C for 6 h. After concentrating under reduced pressure, the residue was chromatographed on silica gel (ethyl acetate/hexane = 1/4 as eluent) to give compound **8** as red solid (857 mg, 67% yield); m.p. 80–81 °C; IR (ATR): $\tilde{\nu}$ = 2976, 2930, 2868, 1618, 1545, 1420 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6): δ = 8.38 (d, J = 2.0 Hz, 1H, aromatic), 8.32 (dd, J = 9.1 and 2.1 Hz, 1H, aromatic), 8.23 (d, J = 9.1 Hz, 1H, aromatic), 7.81 (d, J = 3.7 Hz, 1H, aromatic), 7.77 (d, J = 3.7 Hz, 1H, aromatic), 7.73 (d, J = 3.7 Hz, 1H, aromatic), 7.26–7.33 (m, 3H, aromatic), 6.31 (s, 1H, CH), 6.30 (s, 1H, CH), 6.21 (s, 1H, CH), 5.29 (s, 2H, CH_2), 5.27 (s, 2H, CH_2), 3.31 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 1.26–1.38 (m, 36H, CH_3) ppm; ^{13}C NMR (125 MHz, acetone-d_6): δ = 152.07, 151.85, 147.75, 147.66, 147.08, 143.67, 142.48, 141.89, 141.17, 140.42, 136.81, 134.79, 134.69, 131.69, 131.59, 130.68, 129.62, 128.51, 126.07, 125.89, 125.81, 125.45, 125.22, 124.08, 100.44, 100.43, 97.82, 97.75, 97.25, 83.69, 83.53, 83.52, 58.01, 57.98, 24.66, 24.65, 24.61, 22.42, 22.40, 22.36 ppm; HRMS (ESI): *m/z* found 931.33263 $[M+H]^+$, calculated for $C_{49}H_{59}O_{10}N_2S_3$ $[M+H]^+$: 931.33263.



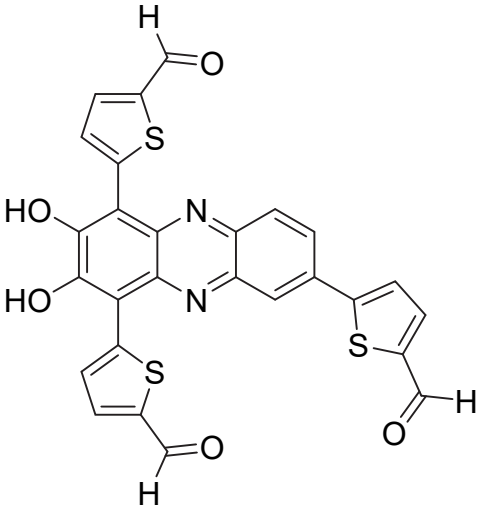
Phenazine KO-0. KO-0 was synthesized by the method reported in our previous study[24]; m.p. over 300 °C; IR (ATR): $\tilde{\nu}$ = 3065 (br), 1614, 1549, 1510, 1483 cm^{-1}.



Phenazine KO-1. A solution of compound **6** (0.015 g, 0.0253 mmol) and 1N HCl aq. (2 mL) in the mixture of THF (10 mL) and water (10 mL) was stirred at 70 °C. After disappearance of the reactants, 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 saturated saline once, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was dissolved in THF and precipitated in hexane to give phenazine **KO-1** as brown solid (0.010 g, 98% yield); m.p. over 300 °C; IR (ATR): $\tilde{\nu}$ = 3316 (br), 2924, 2851, 1597, 1551 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.86 (s, 1H, CHO), 9.27 (d, J = 4.3 Hz, 1H, aromatic), 8.34 (d, J = 3.8 Hz, 1H, aromatic), 8.05–8.18 (m, 2H, aromatic), 7.92 (d, J = 4.3 Hz, 1H, aromatic), 7.65–7.75 (m, 1H, aromatic), 7.57–7.65 (m, 2H, aromatic), 7.20 (dd, J = 5.3 and 3.8 Hz, 1H, aromatic) ppm; ^{13}C NMR spectrum could not be obtained because of the low solubility in any solvents; HRMS (APCI): *m/z* found 403.02133 $[M\text{-}H]^-$, calculated for $C_{21}H_{11}O_3N_2S_2$ $[M\text{-}H]^-$: 403.02166.

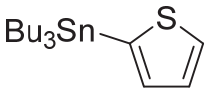


Phenazine KO-2. A solution of compound **7** (0.0506 g, 0.0702 mmol) and 1N HCl aq. (4 mL) in the mixture of THF (25 mL) and water (25 mL) was stirred at 70 °C until insoluble components precipitated. The precipitate was filtered and washed with hexane to give phenazine **KO-2** as black solid (0.0264 g, 87% yield); m.p. over 300 °C; IR (ATR): $\tilde{\nu}$ = 3177 (br), 1647, 1636, 1616, 1541 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.97 (s, 2H, CHO), 8.56 (br, 2H, aromatic), 8.08–8.17 (m, 2H, aromatic), 8.05 (d, J = 4.1 Hz, 1H, aromatic), 7.68–7.77 (m, 2H, aromatic) ppm; ^{13}C NMR spectrum could not be obtained because of the low solubility in any solvents; HRMS (APCI): *m/z* found 431.01569 $[M-H]^-$, calculated for $C_{22}H_{11}O_4N_2S_2$ $[M-H]^-$: 431.01657.

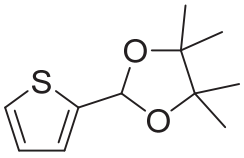


Phenazine KO-3. A solution of compound **8** (51.3 mg, 55.0 μmol) and 1N HCl aq. (4 mL) in the mixture of THF (25 mL) and water (25 mL) was stirred at 70 °C for 24 h. The precipitate was filtered and washed with water and hexane to give phenazine **KO-3** as black solid (26.8 mg, 90% yield); m.p. over 300 °C;

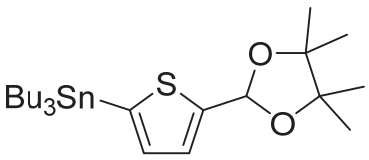
IR (ATR): $\tilde{\nu}$ = 3146 (br), 3092, 2924, 2847, 2124, 1896, 1653, 1616, 1545, 1516 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 9.97 (s, 2H, CHO), 9.96 (s, 1H, CHO), 8.58–8.99 (br, 2H, aromatic), 8.46 (d, J = 2.1 Hz, 1H, aromatic), 8.19 (d, J = 8.7 Hz, 1H, aromatic), 8.10–8.16 (2H, aromatic), 7.99–8.07 (m, 3H, aromatic) ppm; ^{13}C NMR spectrum could not be obtained because of the low solubility in any solvents; HRMS (APCI): *m/z* found 540.99799 $[M-H]^-$, calculated for $C_{27}H_{13}O_5N_2S_3$ $[M-H]^-$: 540.99921.



S1. A solution of thiophene (1.99 g, 23.7 mmol) in THF (25 mL) was stirred at -78 °C for 30 min under N_2 atmosphere. 1.6 M *n*-BuLi in hexane (15.0 mL, 24.0 mmol) was slowly dropped into the solution, and the mixture was stirred at -78 °C for 2 h. Then, tributyltin (IV) chloride (9.29 g, 28.5 mmol) was added to the solution, and the mixture was stirred at room temperature overnight. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed twice with each of water and saturated saline. The organic extract was dried over anhydrous $MgSO_4$, filtered, concentrated, and chromatographed on alumina (hexane as eluent) to give **S1** as colorless liquid (2.65 g, 30% yield); ^1H NMR (500 MHz, acetone-d_6): δ = 7.75 (dd, J = 4.6 and 0.8 Hz, 1H, aromatic), 7.27 (dd, J = 4.6 and 3.2 Hz, 1H, aromatic), 7.24 (dd, J = 3.2 and 0.8 Hz, 1H, aromatic), 1.46–1.73 (m, 6H, CH_2), 1.25–1.46 (m, 6H, CH_2), 1.06–1.25 (m, 6H, CH_2), 0.82–0.97 (m, 9H, CH_3) ppm; HRMS (APCI): *m/z* found 503.19891 $[M+H]^+$, calculated for $C_{23}H_{43}O_2SSn$ $[M+H]^+$: 503.20002.



S2. S2 was synthesized by the method reported in our previous study[25]; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, J = 5.0 Hz, 1H, aromatic), 7.16 (d, J = 3.5 Hz, 1H, aromatic), 6.97 (dd, J = 5.0 and 3.5 Hz, 1H, aromatic), 6.21 (s, 1H, CH), 1.29–1.35 (m, 12H, CH_3) ppm.



S3. A solution of **S2** (10.6 g, 50.0 mmol) in THF (200 mL) was prepared under N_2 atmosphere and stirred at -78 °C for 30 min. 2.6 M *n*-BuLi in hexane (20.0 mL, 52.0 mmol) was slowly dropped into the solution, and the mixture was stirred at -78 °C for 2 h. Then, tributyltin (IV) chloride (16.3 g, 50.1 mmol) was added to the solution, and the mixture was stirred at -78 °C overnight. After concentrating under reduced pressure, the resulting residue was dissolved in ethyl acetate, and washed twice with each of water and saturated saline. The organic extract was dried over anhydrous $MgSO_4$, filtered, concentrated, and chromatographed on alumina (hexane as eluent) to give **S3** as colorless liquid (20.1 g, 80% yield); ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.26 (d, J = 3.3 Hz, 1H, aromatic), 7.03 (d, J = 3.2 Hz, 1H, aromatic), 6.14 (s, 1H, CH), 1.41–1.61 (m, 6H, CH_2), 1.23–1.35 (m, 6H, CH_2), 1.17–1.23 (m, 12H, CH_3), 0.98–1.17 (m, 6H, CH_2), 0.82–0.91 (m, 9H, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 149.16, 136.99, 134.95, 127.70, 95.67, 82.34, 28.44, 26.56, 24.00, 21.81, 13.52, 10.48 ppm; HRMS (APCI): *m/z* found 503.19891 $[M+H]^+$, calculated for $C_{23}H_{43}O_2SSn$ $[M+H]^+$: 503.20002.

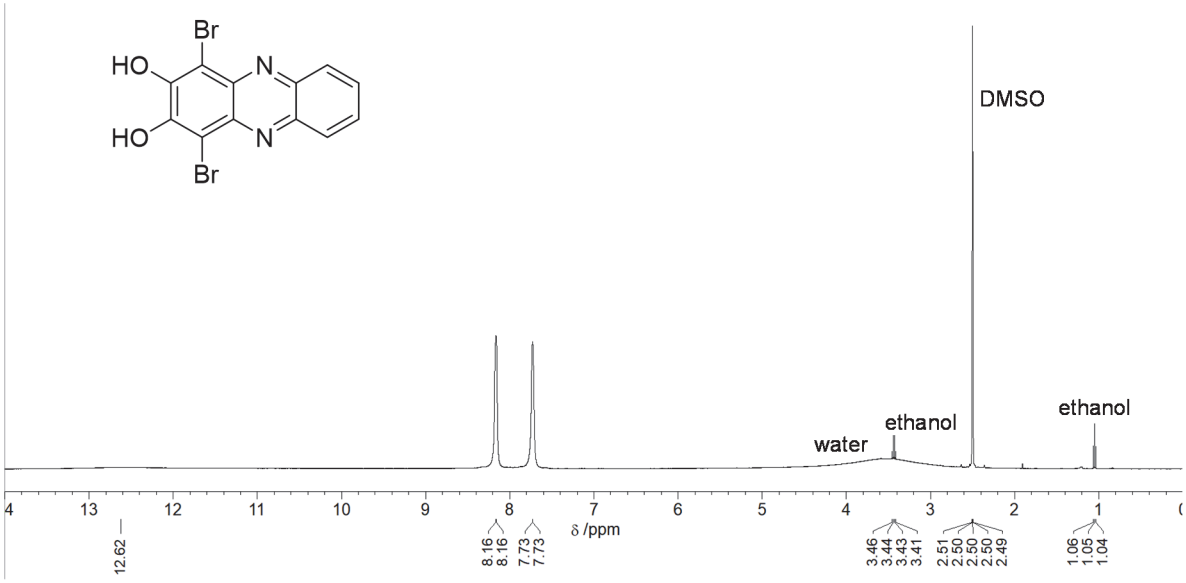


Fig. S1 ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

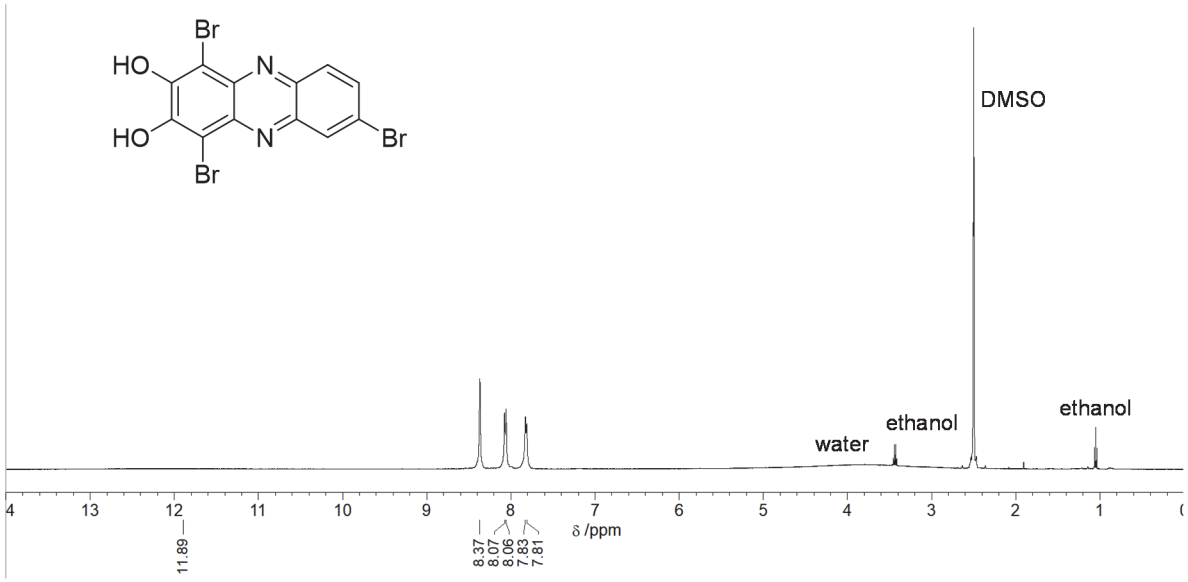


Fig. S2 ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

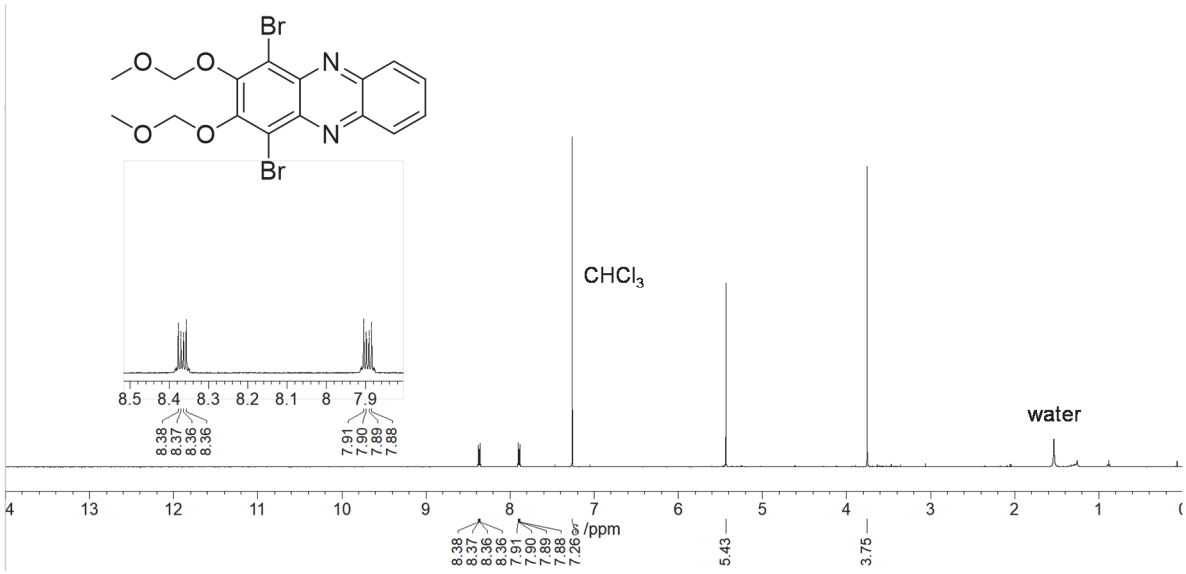


Fig. S3 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

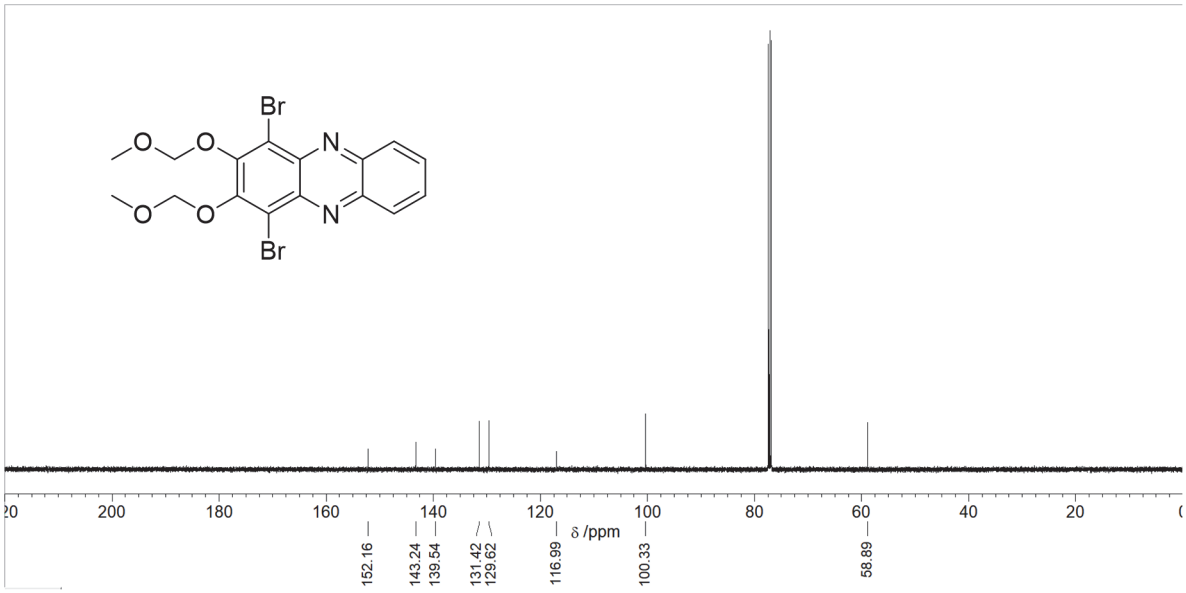


Fig. S4 ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

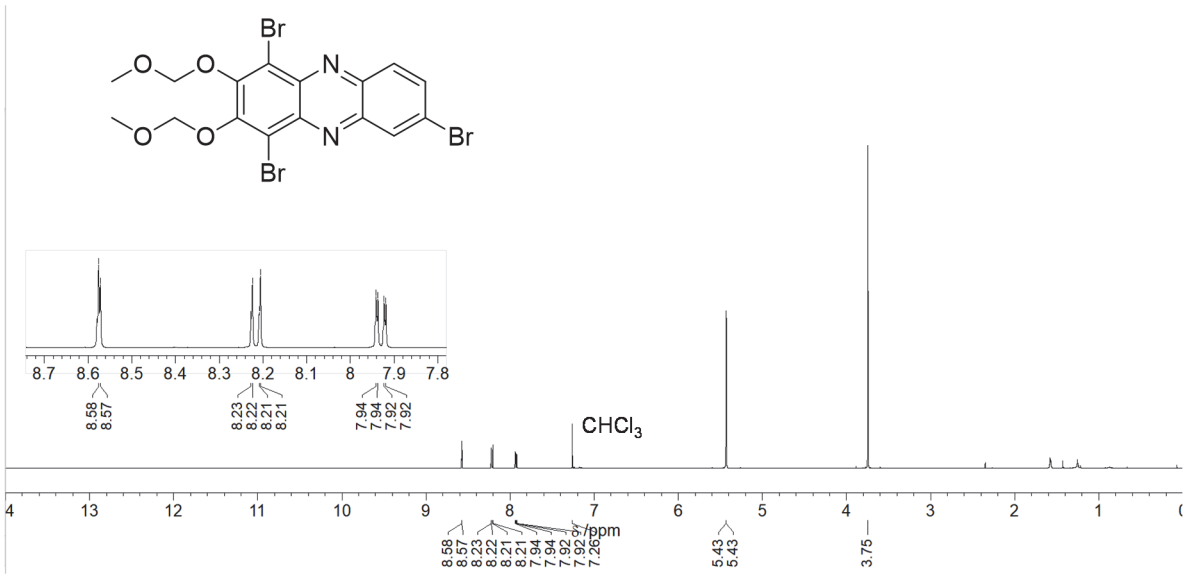


Fig. S5 ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

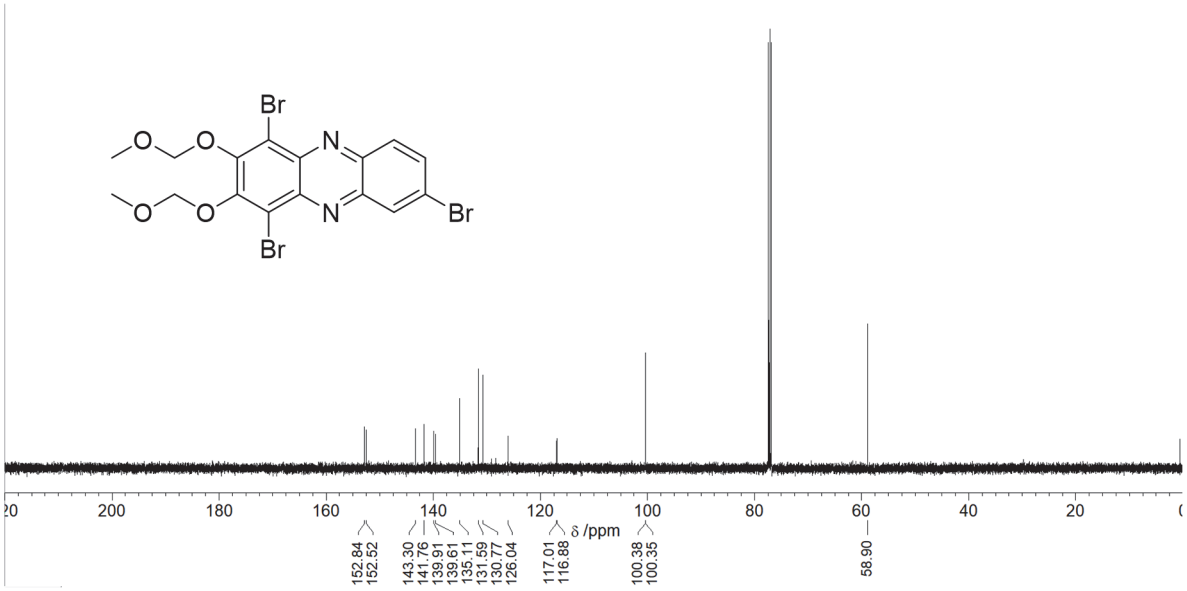


Fig. S6 ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

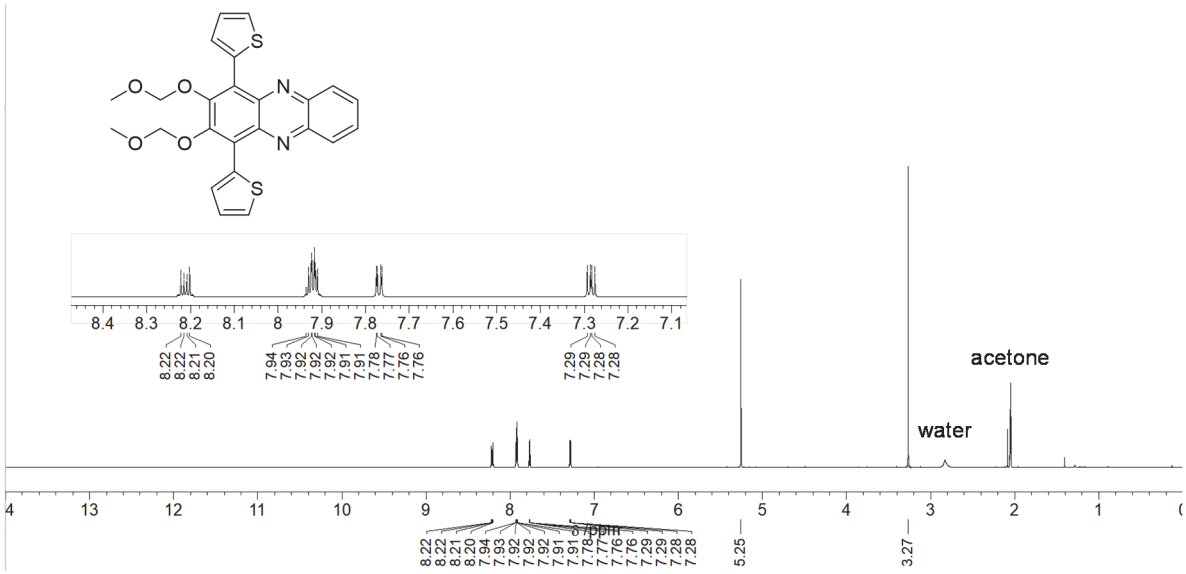


Fig. S7 ^{1}H NMR spectrum of compound **5** in acetone-d_6.

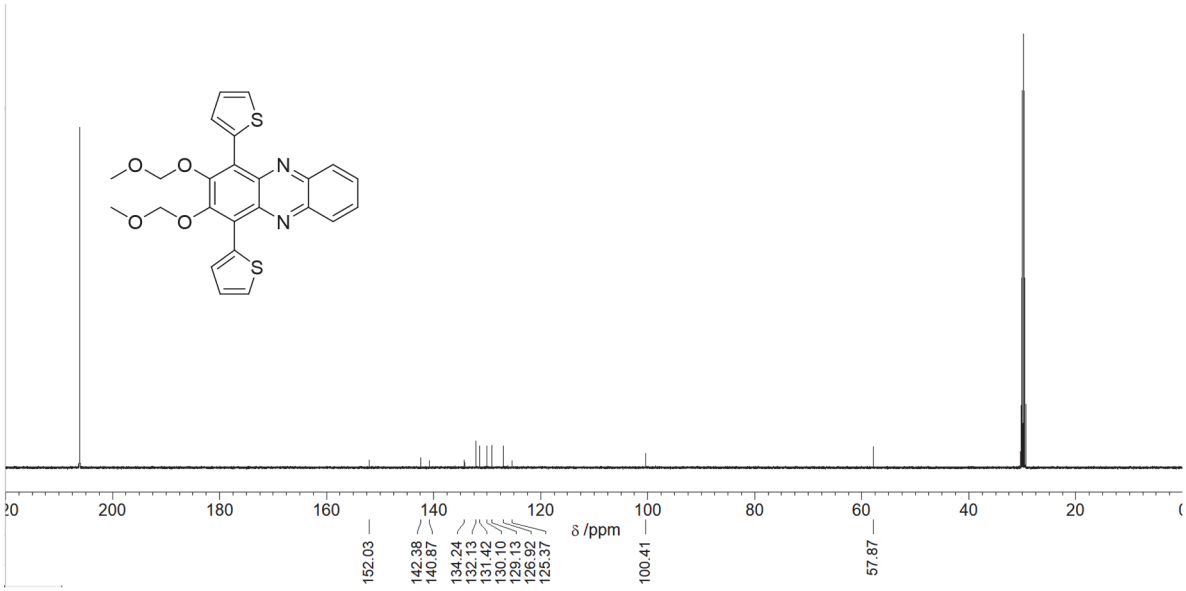


Fig. S8 ^{13}C NMR spectrum of compound **5** in acetone-d_6.

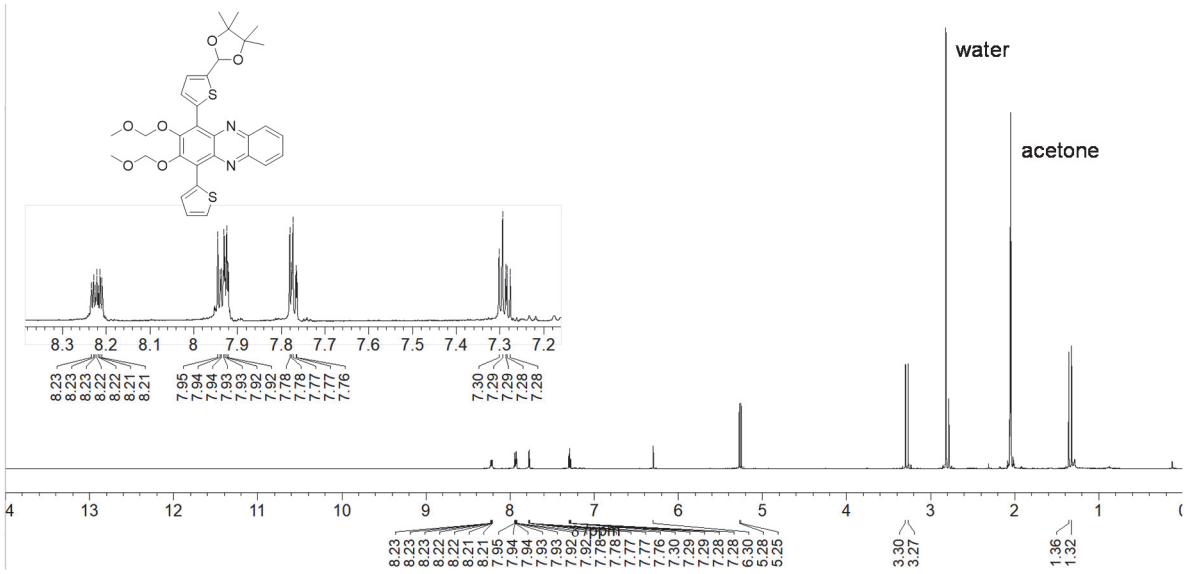


Fig. S9 ^{1}H NMR spectrum of compound **6** in acetone-d_6.

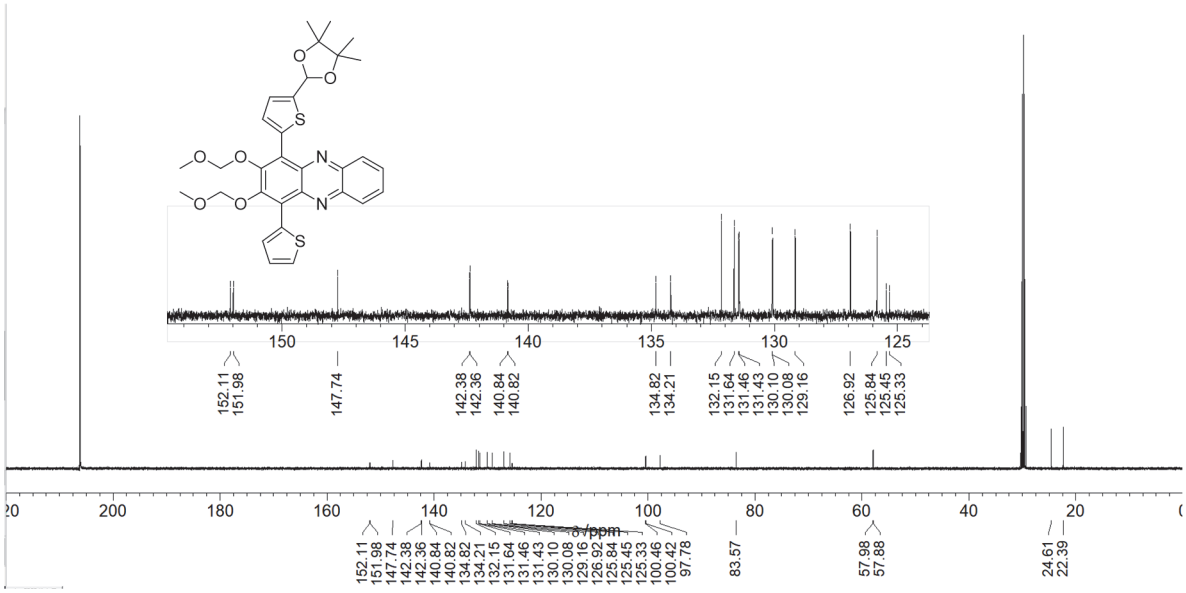


Fig. S10 ^{13}C NMR spectrum of compound **6** in acetone-d_6.

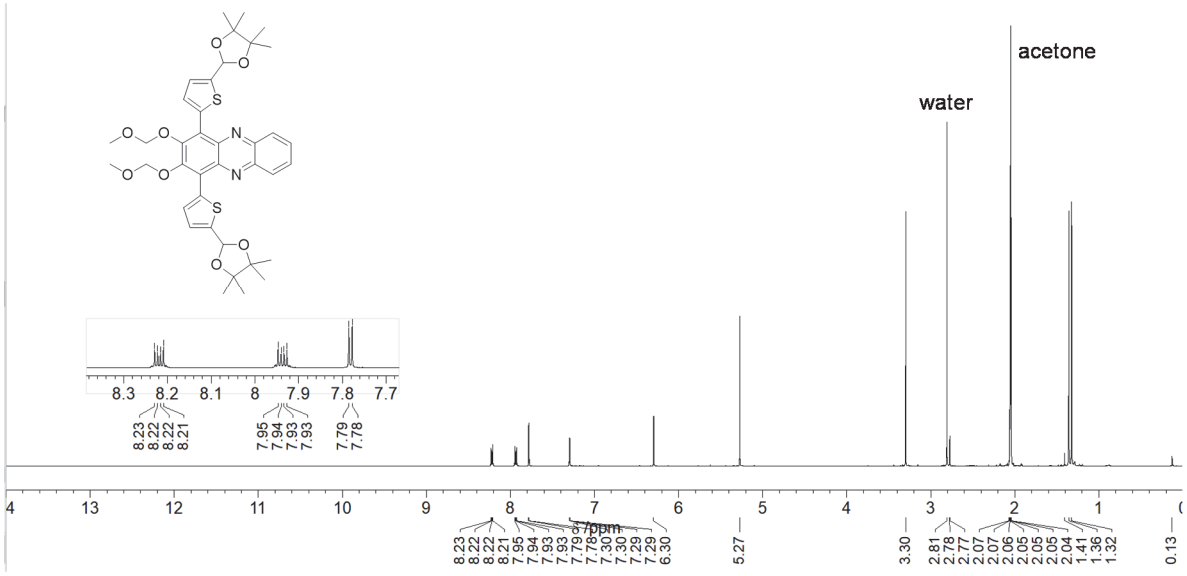


Fig. S11 ^{1}H NMR spectrum of compound **7** in acetone-d_6.

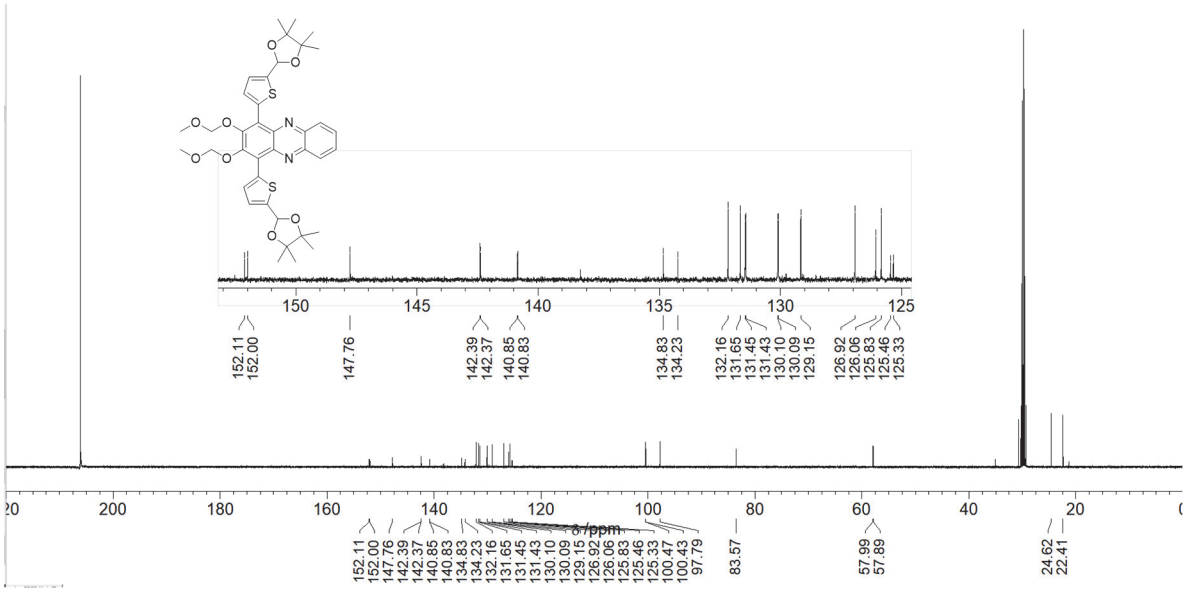


Fig. S12 ^{13}C NMR spectrum of compound **7** in acetone-d_6.

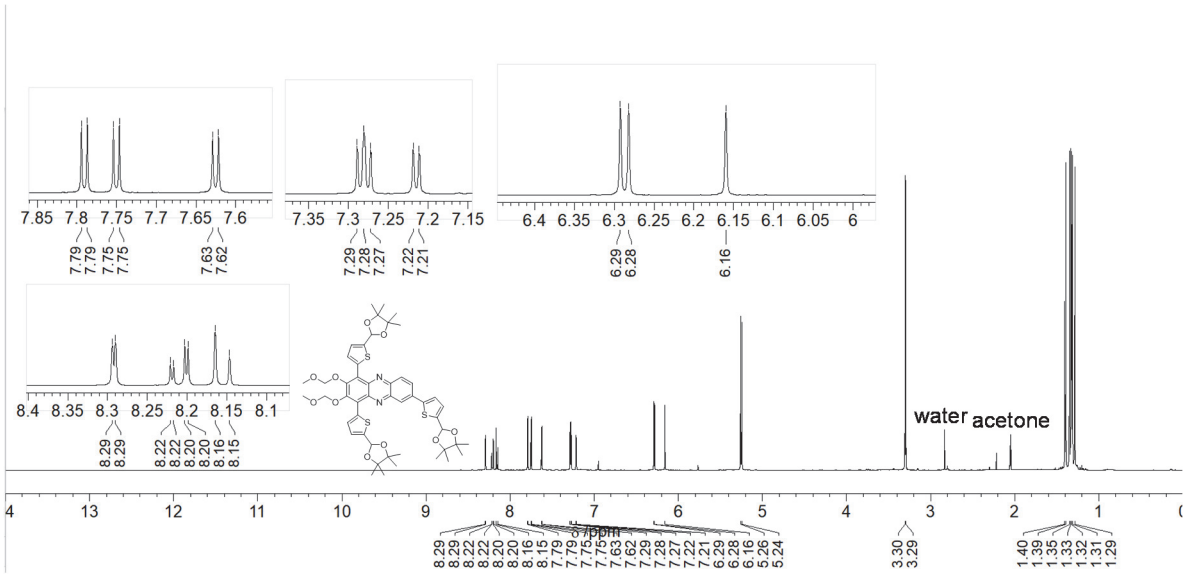


Fig. S13 ^{1}H NMR spectrum of compound **8** in acetone-d_6.

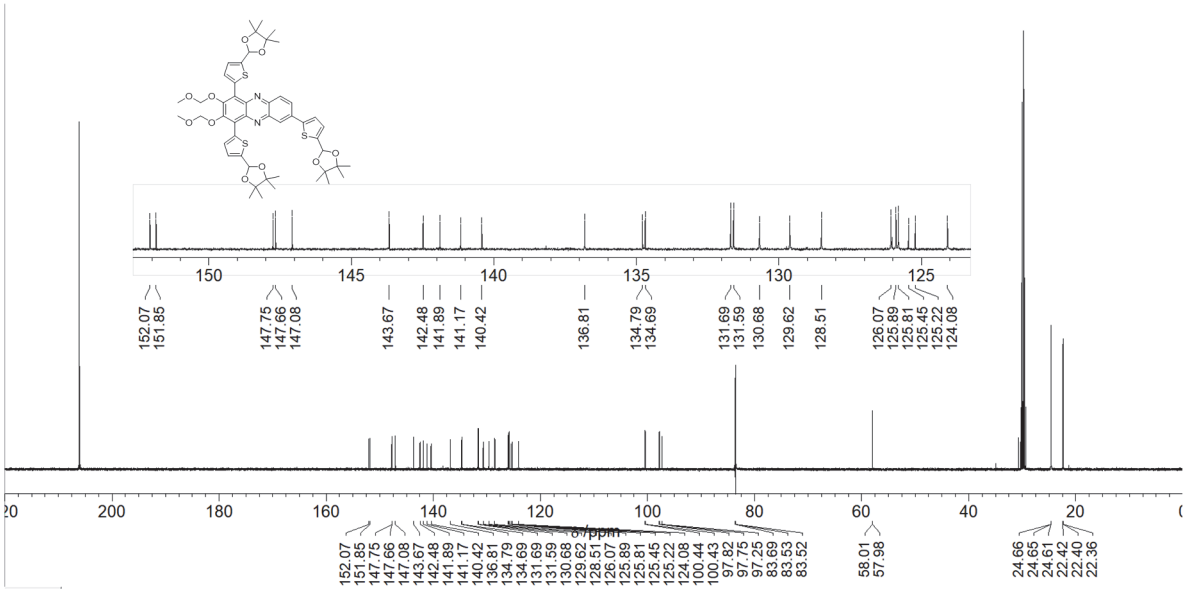


Fig. S14 ^{13}C NMR spectrum of compound **8** in acetone-d_6.

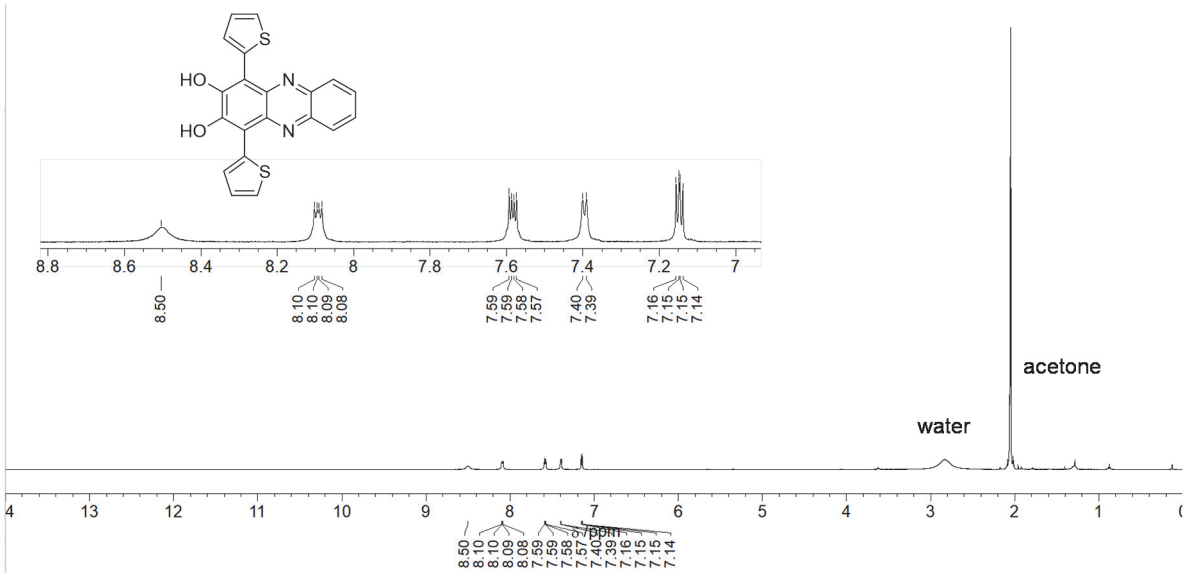


Fig. S15 ^{1}H NMR spectrum of **KO-0** in acetone-d_6.

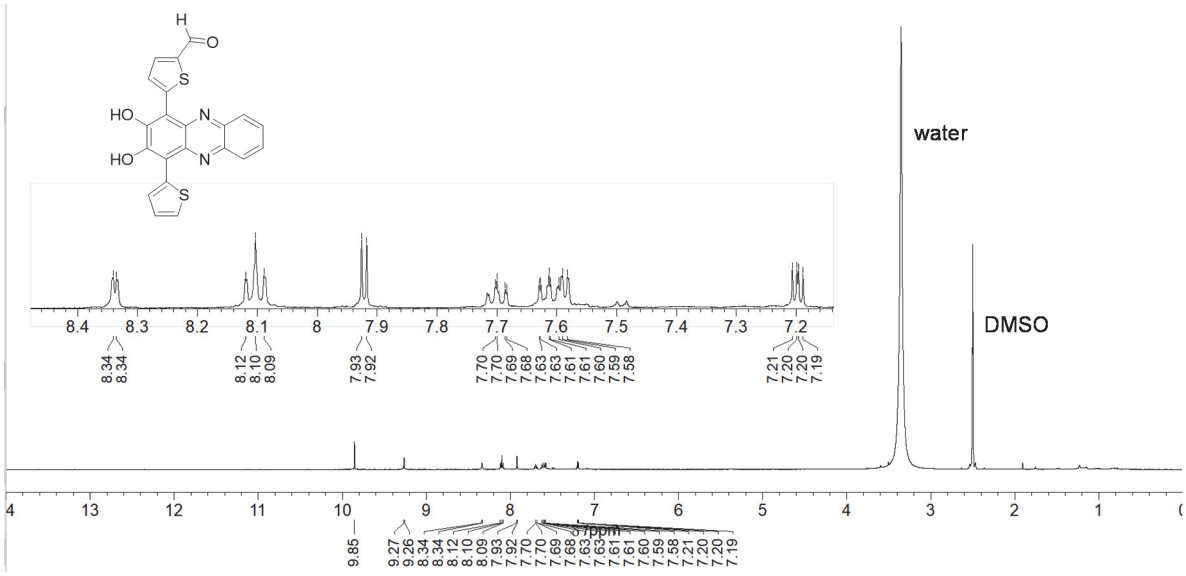


Fig. S16 ^{1}H NMR spectrum of **KO-1** in DMSO-d_6.

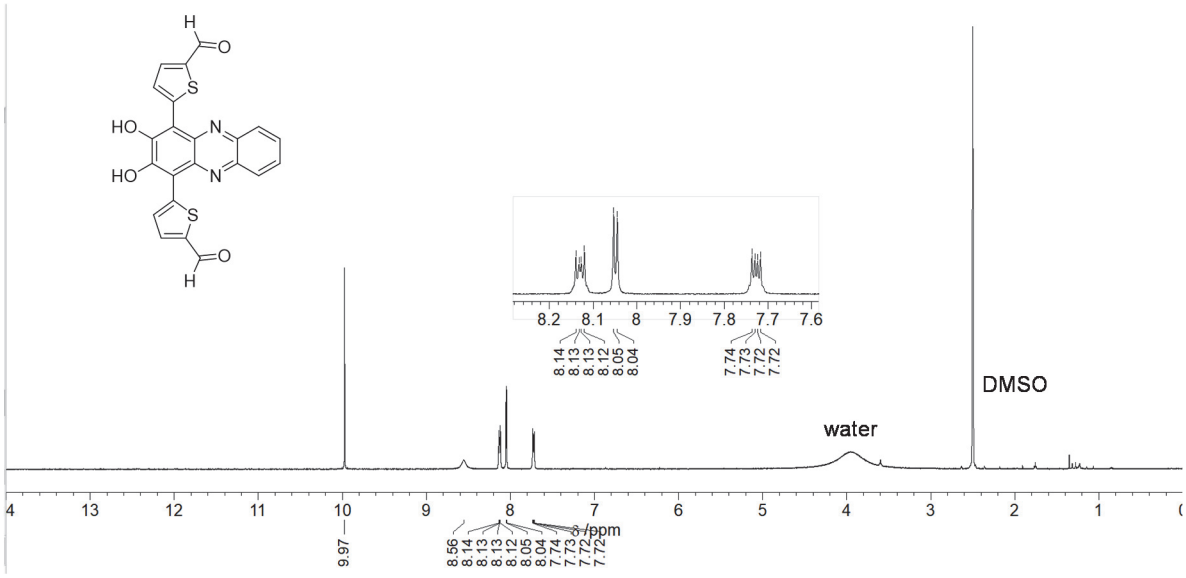


Fig. S17 ^{1}H NMR spectrum of **KO-2** in DMSO-d_6.

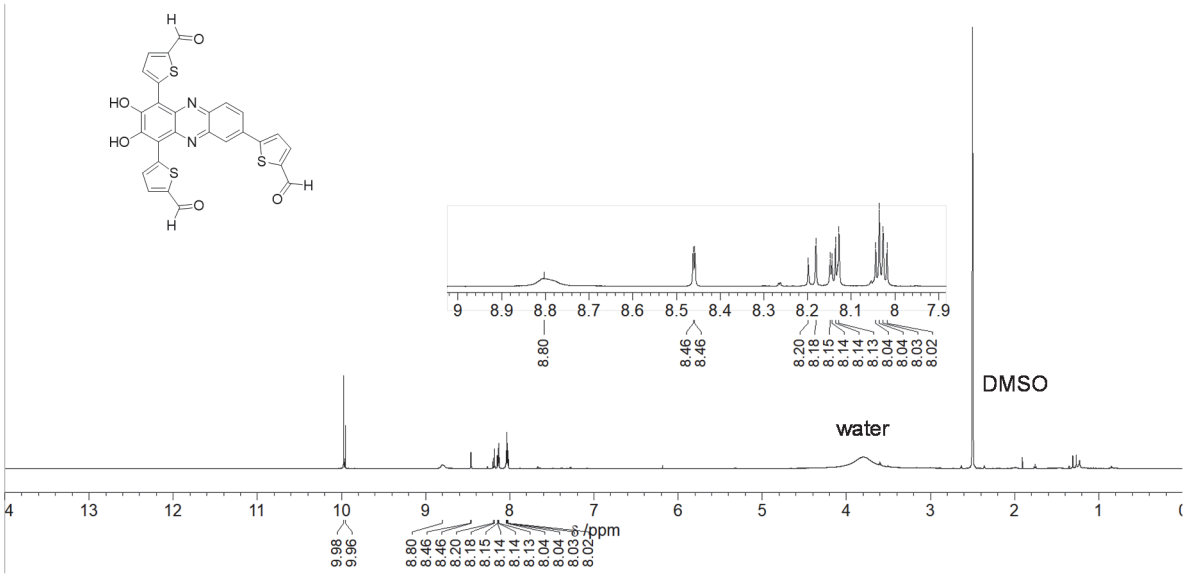


Fig. S18 ^{1}H NMR spectrum of **KO-3** in DMSO-d_6.

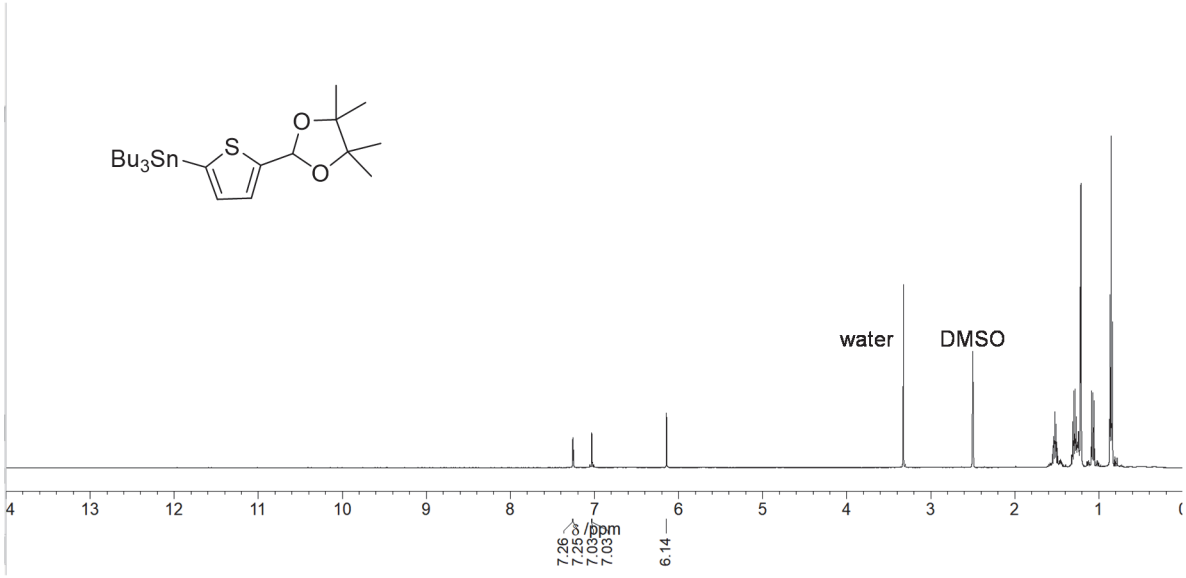


Fig. S19 ^{1}H NMR spectrum of **S3** in DMSO-d_6.

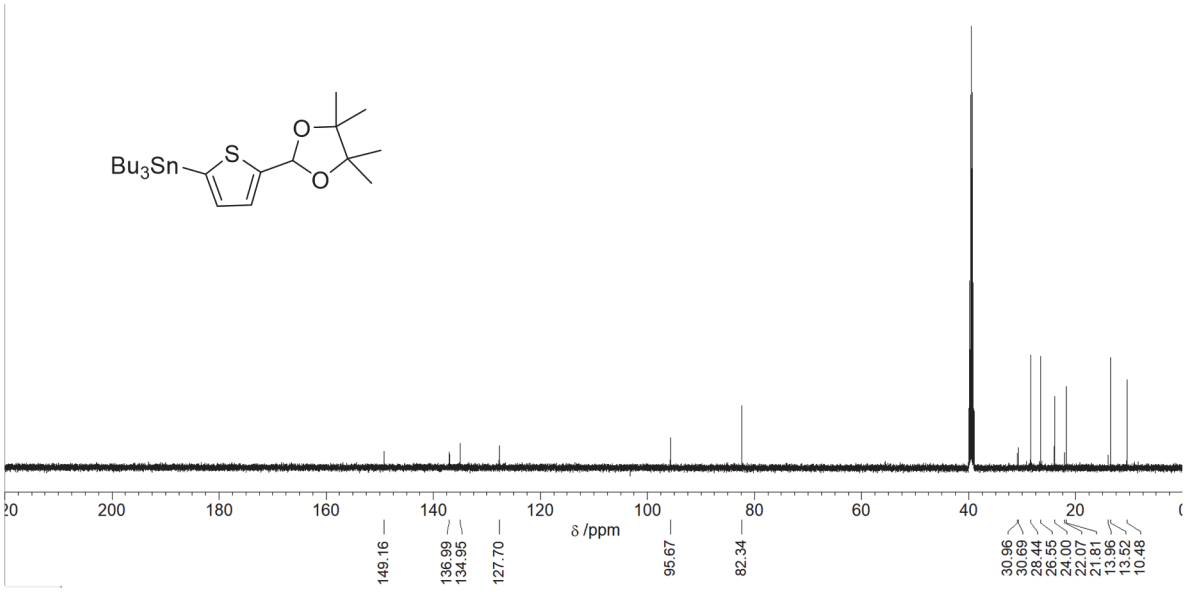


Fig. S20 ^{13}C NMR spectrum of **S3** in DMSO-d_6.

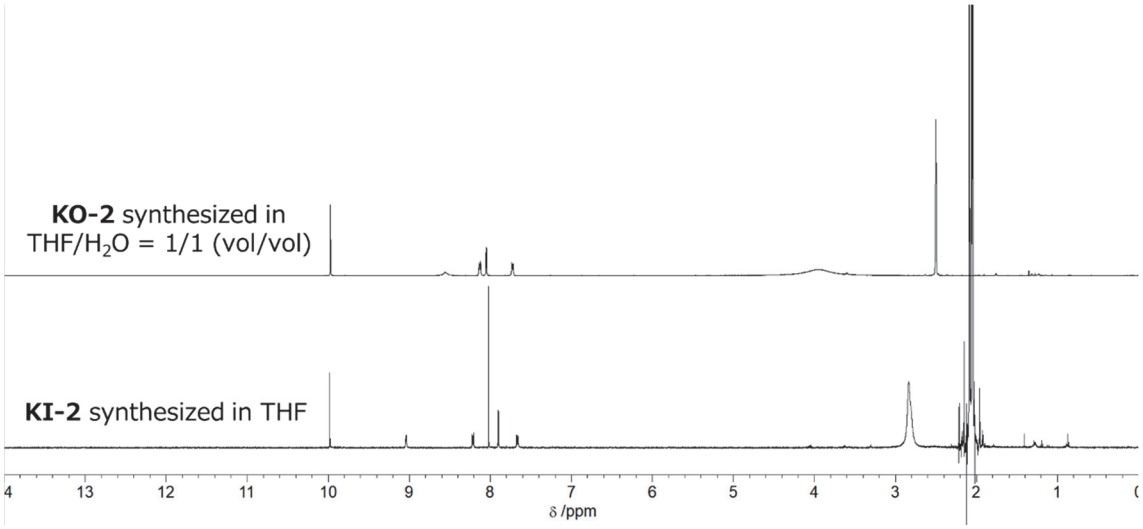


Fig. S21 ^{1}H NMR spectrum of **KO-2** and **KI-2** in acetone-d_6.

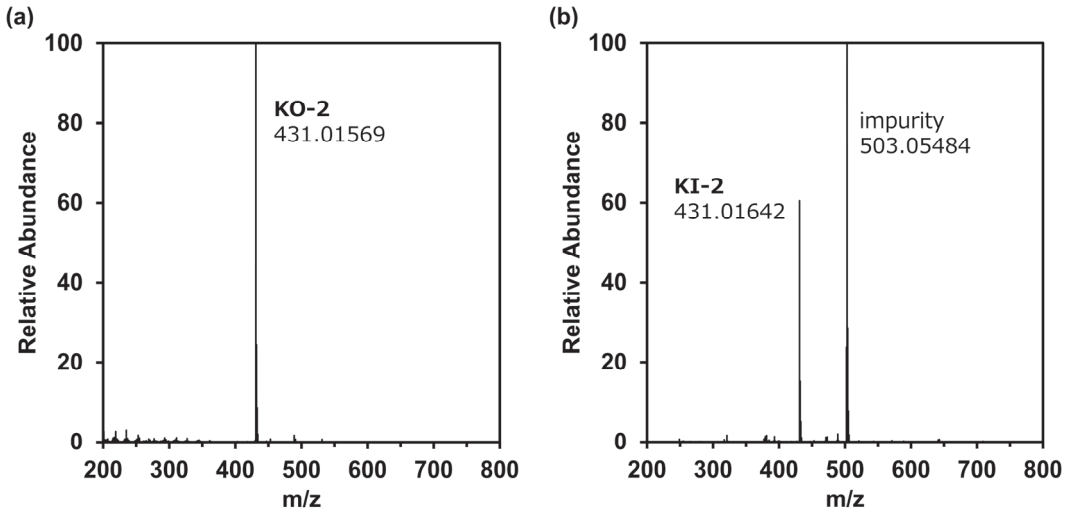


Fig. S22 MS spectra of (a) **KO-2** and (b) **KI-2**.

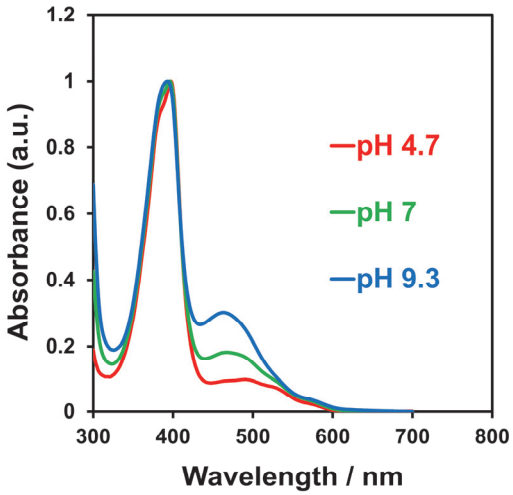


Fig. S23 pH dependence of photoabsorption spectra of phenazine-2,3-diol in the mixtures of DMSO (80 vol%) and HCl aq. (pH 4.7), neutral H_2O (pH 7), or NaOH aq. (pH 9.3) (20 vol%). The pH values are calculated under the assumption that HCl and NaOH are completely ionized in the mixture solutions.

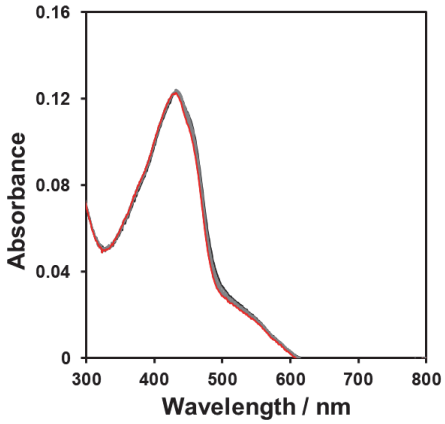


Fig. S24 Photoabsorption spectra of **KO-3** (Abs. @509 nm = *ca*. 0.03) upon irradiation with a monochromatic light (509 nm, 300 μW cm^{-2}) in THF. Photoirradiation for 1 min was promptly repeated until the total time reached 10 min.