Electronic Supplementary Information

Cyano Positional Isomerism Strategy for Constructing Mitochondria-Targeted AIEgens with Type I Reactive Oxygen Species Generation Capability

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1. Experimental procedures

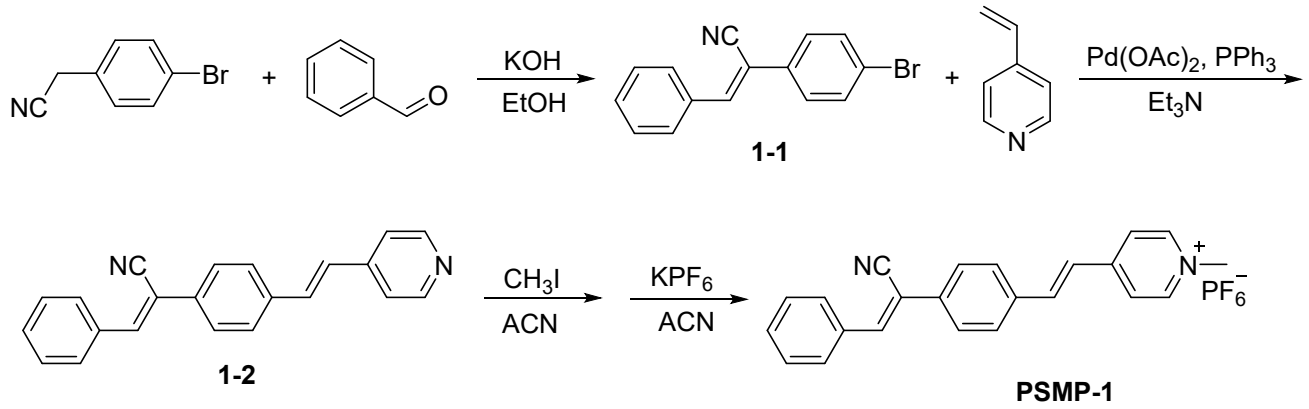
1.1 Chemicals and materials

9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA), carbonyl cyanide 3-chlorophenylhydrazone (CCCP), and 2',7'-dichlorodihydrofluorescein diacetate (DCFH-DA) were obtained from Sigma-Aldrich (USA). Singlet oxygen sensor green (SOSG), HCS LipidTOX™ Deep Red Neutral Lipid (HCSLT), Lyso Tracker Deep Red (LTDR) and fetal bovine serum (FBS) were obtained from Thermo Fisher Scientific (USA). Rhodamine 123 and dihydroethidium (DHE) was obtained from Macklin (Shanghai, China). Dihydrorhodamine 123 (DHR 123) was obtained from TargetMol (USA). Hydroxyphenyl fluorescein (HPF) was obtained from Maokang Biotechnology (Shanghai, China). Annexin V-FITC/PI and Mito-Sox red were obtained from Yeasen (Shanghai, China). Phosphate buffered saline (PBS) and Dulbecco's Modified Eagle Medium (DMEM) were obtained from Corning (China). Hoechst 33342, ER-Tracker Red (ETR), Mito-Tracker Deep Red FM (MTDR) 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) kit, calcein AM cell viability assay kit and Mitochondrial membrane potential assay kit with JC-1 was obtained from Beyotime Biotech (Shanghai, China). Petroleum ether and ethyl acetate for chromatography were distilled before used. All other reagents and solvents were used directly from the corresponding supplier without further purification. All starting 0materials were purchased from Sigma-Aldrich, Bidepharm, Energy, Tansoole and use directly.

1.2 Instrument

Nuclear magnetic resonance spectra (^{1}H, ^{13}C NMR) were recorded on a JNM-ECZ40S/L (^{1}H at 400 MHz, ^{13}C at 100 MHz) or a Bruker Ascend 600 (^{1}H at 600 MHz, ^{13}C at 150 MHz). The chemical shifts are reported as ppm and solvent residual peaks were shown as following: $CDCl_3$ δ H (7.26 ppm) and δ C (77.16 ppm); DMSO-d_6 δ H (2.50 ppm) and δ C (39.52 ppm). UV-visible absorption spectra were measured on Purkinje TU-1950 spectrometer (Persee, China). Fluorescence spectra were measured on Hitachi F-7000 spectrometer. Fluorescence quantum yields were measured using Hamamatsu C9920-02G. Lifetime (τ) was measured on Horiba Quanta Master 8000 spectrometer. Single crystal was collected on Bruker D8 Venture detector. The fluorescence images in vitro were collected on Olympus FV1200. The Flow cytometry was measured on FACS Calibur (Bio-Rad, USA). Dynamic light scattering (DLS) was carried out on NanoBrook 90PlusPALS. High-resolution mass spectrometry (HRMS) was obtained on a Bruker Maxis and Microflex and reported as m/z (relative intensity). Accurate masses are presented as molecular ion $[M–PF_6]^+$.

1.3 Synthetic procedure



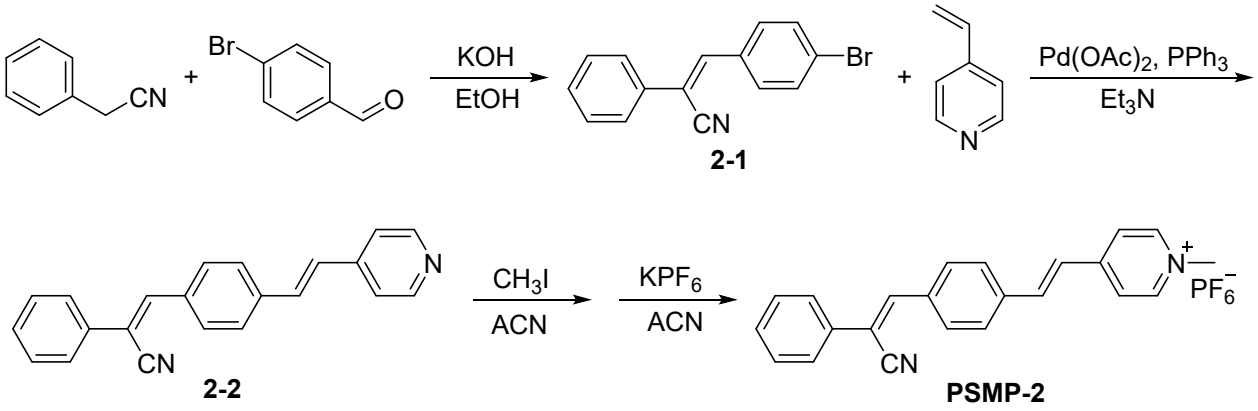
Scheme **S1**. The structure and synthetic route of **PSMP-1**.

Synthesis of 1-1: Firstly, p-bromophenylacetonitrile (980 mg, 5.00 mmol) was dissolved in ethanol (10 mL), followed by benzaldehyde (0.51 mL, 5.00 mmol). Then, KOH (50 μL, 40%) was slowly added with stirring and allowed to react at room temperature for 1 hour. After the reaction was complete, the precipitate generated in the solution was filtered, washed with ethanol, and vacuum dried to obtain white solid powder compound 1-1. (65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.89 (d, J = 6.3 Hz, 2H), 7.58-7.52 (m, 5H), 7.49-7.44 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.71, 133.56, 132.35, 130.94, 129.45, 129.15, 127.60, 123.55, 117.70, 110.72.

Synthesis of 1-2: Under the protection of N_2, compound 1-1 (710 mg, 2.50 mmol), palladium acetate (28 mg, 0.13 mmol), and triphenylphosphine (79 mg, 0.30 mmol) were first added to freshly evaporated Et_3N (15 mL). 4-vinylpyridine (0.27 mL, 2.50 mmol) was then added to the mixture using a syringe. The reaction mixture was refluxed at 100 °C for 1.5 days. When the reaction was completed, the mixture was cooled to room temperature and extracted with dichloromethane and water. After three extractions, the organic phases were combined, dried over anhydrous sodium sulfate, and concentrated. The target product 1-2 was purified by column chromatography. (56% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.61 (d, J = 4.8 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.60 (t, J = 8.4 Hz, 3H), 7.51-7.45 (m, 3H), 7.39 (q, J = 6.0 Hz, 2H), 7.33 (d, J = 16.3 Hz, 1H), 7.10 (d, J = 16.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.45, 144.38, 142.28, 137.23, 134.74, 133.79, 132.12, 130.87, 129.51, 129.17, 127.76, 127.40, 126.55, 121.06, 117.93, 111.29.

Synthesis of PSMP-1: Dissolve the five synthesized compounds 1-2 in acetonitrile solution and stir them with heating and ultrasonic waves to dissolve them. Then, place them in an ice bath and add iodomethane dropwise under dark conditions. Continue stirring the reaction solution in the ice bath for 4 hours. Monitor the completion of the reaction using thin-layer chromatography. After the reaction is complete, evaporate the solvent in the solution by rotation, dissolve the crude product in acetonitrile, and add potassium hexafluorophosphate solid. Stir and replace at room temperature for 2 hours.

Monitor the reaction using thin-layer chromatography. When the reaction is complete, evaporate acetonitrile by rotation and purify it using column chromatography to obtain PSMP-1. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.88 (d, J = 6.7 Hz, 2H), 8.24 (d, J = 6.6 Hz, 2H), 8.18 (s, 1H), 8.06 (d, J = 16.4 Hz, 1H), 7.98 (d, J = 6.9 Hz, 2H), 7.92-7.87 (m, 4H), 7.62-7.52 (m, 4H), 4.26 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 152.17, 145.15, 143.56, 139.35, 135.89, 135.24, 133.61, 130.89, 129.27, 129.00, 128.77, 126.38, 124.29, 123.67, 117.63, 109.68, 46.96. HRMS (ESI-TOF) m/z: $[M\text{-}FP_6]^+$ calcd for $C_{23}H_{19}N_2^+$ 323.1543, found 323.1535.

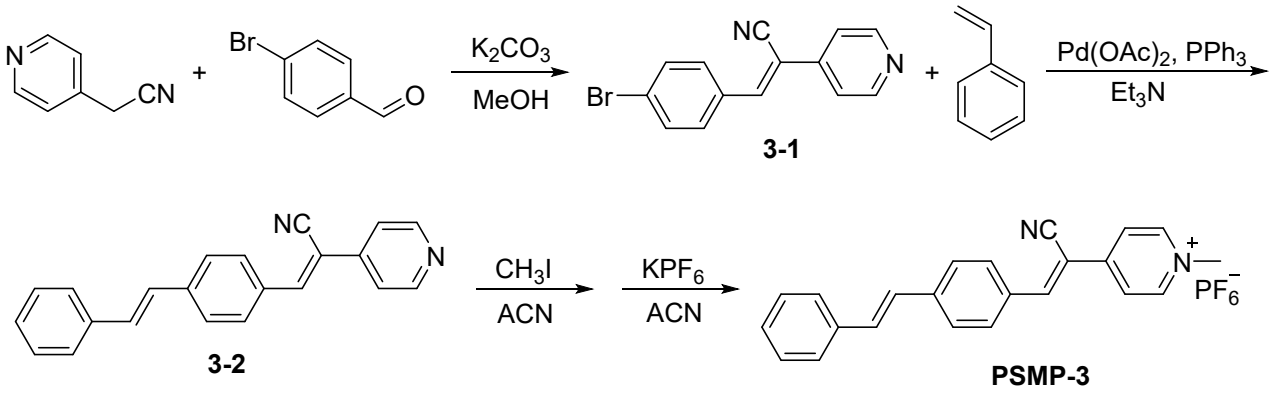


Scheme **S2**. The structure and synthetic route of **PSMP-2**.

Synthesis of 2-1: Firstly, dissolve p-bromobenzaldehyde (925 mg, 5.00 mmol) in ethanol (10 mL), then add phenylacetonitrile (0.56 mL, 5.00 mmol), and dropwise add KOH (2 d, 40%) under stirring conditions. Stir the reaction at room temperature for 1 hour. After the reaction is complete, filter and wash with ethanol to obtain white solid compound 2-1. (71% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.76 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 7.4 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.46-7.40 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.80, 134.27, 132.72, 132.34, 130.75, 129.58, 129.26, 126.13, 124.97, 117.83, 112.58.

Synthesis of 2-2: Under the protection of N_2, compound 2-1 (710 mg, 2.50 mmol), palladium acetate (28 mg, 0.13 mmol), and triphenylphosphine (79 mg, 0.30 mmol) were added to freshly evaporated Et_3N (15 mL), followed by 4-vinylpyridine (0.27 mL, 2.50 mmol). The mixture was heated to 100 °C and refluxed for 1.5 days. Thin layer chromatography was used to detect the completion of the reaction. When the reaction was complete, the solution was cooled to room temperature, and appropriate amounts of dichloromethane and water were added for extraction. The organic phases were combined, dried over anhydrous sodium sulfate, concentrated, and subjected to column chromatography to obtain the desired product 2-2. (58% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.60 (d, J = 6.0 Hz, 2H), 7.92 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 7.3 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.51 (s, 1H), 7.45 (t, J = 7.1 Hz, 2H), 7.41-7.36 (m, 3H), 7.31 (d, J = 16.4 Hz, 1H), 7.10 (d, J = 16.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.42, 144.24, 141.32, 138.35, 134.52, 134.03, 132.15, 129.95, 129.44, 129.23, 127.90, 127.57, 126.12, 121.07, 118.13, 111.85.

Synthesis of PSMP-2: Dissolve the five synthesized compounds 2-2 in acetonitrile solution and stir them with heating and ultrasonic waves to dissolve them. Then, place them in an ice bath and add iodomethane dropwise under dark conditions. Continue stirring the reaction solution in the ice bath for 4 hours. Monitor the completion of the reaction using thin-layer chromatography. After the reaction is complete, evaporate the solvent in the solution by rotation, dissolve the crude product in acetonitrile, and add potassium hexafluorophosphate solid. Stir and replace at room temperature for 2 hours. Monitor the reaction using thin-layer chromatography. When the reaction is complete, evaporate acetonitrile by rotation and purify it using column chromatography to obtain PSMP-2. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 8.89 (d, J = 6.6 Hz, 2H), 8.25 (d, J = 6.7 Hz, 2H), 8.11-8.03 (m, 4H), 7.92 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 16.3 Hz, 1H), 7.56-7.47 (m, 3H), 4.27 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 152.04, 145.16, 141.77, 139.31, 137.03, 135.22, 133.62, 129.78, 129.48, 129.22, 128.46, 125.85, 124.85, 123.77, 117.81, 110.99, 46.98. HRMS (ESI-TOF) m/z: $[M\text{-}FP_6]^+$ calcd for $C_{23}H_{19}N_2^+$ 323.1543, found 323.1541.



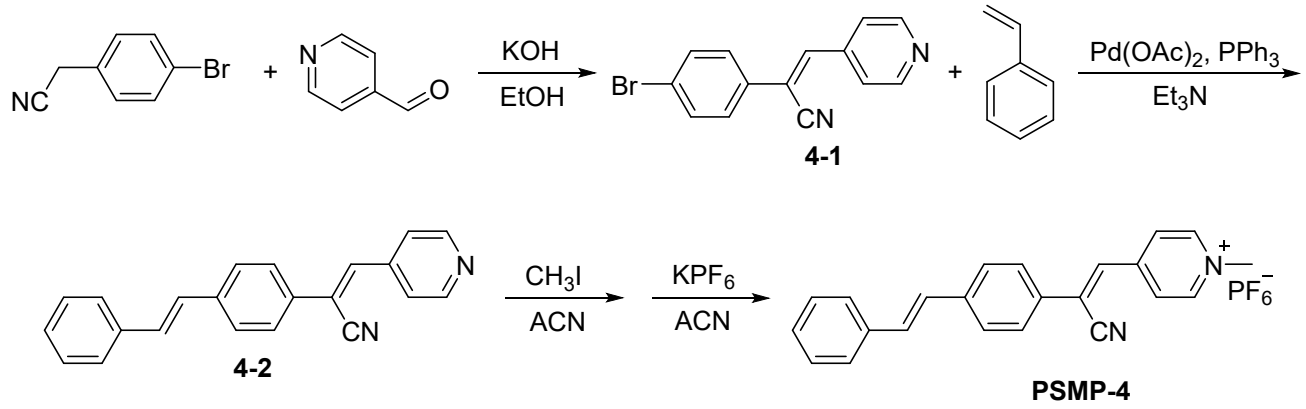
Scheme **S3**. The structure and synthetic route of **PSMP-3**.

Synthesis of 3-1: Dissolve 4-pyridineacetonitrile (155 mg, 1.00 mmol), p-bromobenzaldehyde (185 mg, 1 mmol), and K_2CO_3 (152 mg, 1.00 mmol) in dry methanol (3 mL), stir the reaction at 65 °C for 2 hours. After the reaction is complete, evaporate the solvent by rotary evaporation, purify the crude product by column chromatography, and obtain white product 3-1. (46% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.71-8.70 (m, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.56 (dd, J = 4.6, 1.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.54, 143.42, 141.16, 132.28, 131.51, 130.92, 126.05, 119.71, 116.51, 109.69.

Synthesis of 3-2: Under the protection of N_2, compound 3-1 (285 mg, 1.00 mmol), palladium acetate (12 mg, 0.05 mmol), and triphenylphosphine (32 mg, 0.12 mmol) were dissolved in freshly evaporated Et_3N (5 mL). Styrene (0.12 mL, 1.00 mmol) was also added using a syringe. The reaction mixture was heated to 100 °C and refluxed for 1.5 days. The reaction was detected by thin-layer chromatography (TLC). When complete, the mixed solution was cooled to room temperature, and appropriate amounts of dichloromethane and water were added for extraction. After three extractions, the organic phases

were combined and dried over anhydrous sodium sulfate before concentration. The target product 3-2 was purified by column chromatography. (42% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 8.71-8.70 (m, 3H), 8.33 (d, J = 3.1 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.82-7.79 (m, 3H), 7.75-7.73 (m, 3H), 7.66 (d, J = 7.1 Hz, 1H), 7.47-7.40 (m, 1H), 7.36-7.30 (m, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 150.54, 150.49, 145.51, 144.97, 140.84, 132.17, 131.38, 130.20, 128.78, 126.99, 126.81, 125.02, 119.89, 119.76, 116.78, 108.84.

Synthesis of PSMP-3: Dissolve the five synthesized compounds 3-2 in acetonitrile solution and stir them with heating and ultrasonic waves to dissolve them. Then, place them in an ice bath and add iodomethane dropwise under dark conditions. Continue stirring the reaction solution in the ice bath for 4 hours. Monitor the completion of the reaction using thin-layer chromatography. After the reaction is complete, evaporate the solvent in the solution by rotation, dissolve the crude product in acetonitrile, and add potassium hexafluorophosphate solid. Stir and replace at room temperature for 2 hours. Monitor the reaction using thin-layer chromatography. When the reaction is complete, evaporate acetonitrile by rotation and purify it using column chromatography to obtain PSMP-3. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.02 (d, J = 6.3 Hz, 2H), 8.67 (s, 1H), 8.40 (d, J = 6.3 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 7.4 Hz, 2H), 7.53-7.31 (m, 5H), 4.32 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 150.84, 149.03, 145.72, 142.03, 136.46, 132.14, 131.34, 131.23, 128.82, 128.49, 127.23, 127.20, 126.96, 122.97, 116.39, 104.27, 47.30. HRMS (ESI-TOF) m/z: $[M\text{-}FP_6]^+$ calcd for $C_{23}H_{19}N_2^+$ 323.1543, found 323.1537.



Scheme **S4**. The structure and synthetic route of **PSMP-4**.

Synthesis of 4-1: Dissolve p-bromophenylacetonitrile (1.07 g, 10.00 mmol) in ethanol (20 mL), then add 4-formylpyridine (0.95 mL, 10.00 mmol), slowly add KOH (2 d, 40%) under stirring conditions, and react at room temperature for 1 hour. After the reaction is complete, filter the precipitate generated in the solution under reduced pressure, wash the precipitate with ethanol, vacuum dry it, and obtain white solid powder compound 4-1. (68% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.73 (d, J = 4.8 Hz, 2H), 7.67 (d, J = 5.0 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.44 (s, 1H). ^{13}C

NMR (150 MHz, $CDCl_3$) δ 150.86, 140.40, 139.26, 132.56, 132.42, 127.81, 124.75, 122.67, 116.58, 115.50.

Synthesis of 4-2: Under the protection of N_2, compound 4-1 (0.57 g, 2.00 mmol), palladium acetate (23 mg, 0.10 mmol), and triphenylphosphine (63 mg, 0.24 mmol) were first added to freshly evaporated Et_3N (15 mL). Then, styrene (0.23 mL, 2.00 mmol) was added to the mixture using a syringe. The reaction mixture was refluxed at 100 °C for 1.5 days. When the reaction was detected to be complete by thin-layer chromatography, the mixture was cooled to room temperature, and dichloromethane and water were added for extraction. After three extractions, the organic phases were combined, dried over anhydrous sodium sulfate, concentrated, and purified by column chromatography to obtain the target product 4-2. (43% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.75 (d, J = 5.5 Hz, 2H), 7.71 (t, J = 4.3 Hz, 4H), 7.62-7.60 (m, 2H), 7.57-7.53 (m, 2H), 7.48 (d, J = 13.0 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.22 (d, J = 16.3 Hz, 1H), 7.14 (d, J = 16.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.87, 150.78, 140.81, 139.51, 139.27, 137.98, 136.85, 132.59, 130.81, 128.91, 128.34, 127.84, 127.33, 126.85, 126.70, 122.75.

Synthesis of PSMP-4: Dissolve the five synthesized compounds 4-2 in acetonitrile solution and stir them with heating and ultrasonic waves to dissolve them. Then, place them in an ice bath and add iodomethane dropwise under dark conditions. Continue stirring the reaction solution in the ice bath for 4 hours. Monitor the completion of the reaction using thin-layer chromatography. After the reaction is complete, evaporate the solvent in the solution by rotation, dissolve the crude product in acetonitrile, and add potassium hexafluorophosphate solid. Stir and replace at room temperature for 2 hours. Monitor the reaction using thin-layer chromatography. When the reaction is complete, evaporate acetonitrile by rotation and purify it using column chromatography to obtain PSMP-4. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.07 (d, J = 6.7 Hz, 2H), 8.44 (d, J = 6.7 Hz, 2H), 8.34 (s, 1H), 7.91 (q, J = 8.5 Hz, 4H), 7.67 (d, J = 7.4 Hz, 2H), 7.44-7.32 (m, 5H), 4.36 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.12, 146.38, 140.55, 137.09, 135.85, 131.56, 131.48, 129.29, 128.74, 127.86, 127.60, 127.29, 126.76, 119.62, 116.60, 48.28. HRMS (ESI-TOF) m/z: $[M\text{-}FP_6]^+$ calcd for $C_{23}H_{19}N_2^+$ 323.1543, found 323.1555.

1.4 UV-visible absorption spectra

5 mM stock solution of desired PSMP (PSMP-1, PSMP-2, PSMP-3, PSMP-4) in DMSO was firstly prepared. Then aliquots of above stock solution were transferred into 5 mL volumetric flasks and appropriate amounts of DMSO were added to obtain 50 μM solution. After that, the UV-visible absorption spectra measurements of the resulting solutions were performed immediately.

1.5 AIE effect

5 mM stock solution of desired PSMP (PSMP-1, PSMP-2, PSMP-3, PSMP-4) in DMSO was firstly prepared. Then aliquots of above stock solution were transferred into 5 mL volumetric flasks and

appropriate amounts of water were added to obtain 50 μM solutions with different volume fractions of water (0%, 10%, 30%, 50%, 70%, 80%, 90%, 95%, 99%). After that, the PL, UV-vis, DLS, Lifetime (τ), Fluorescence quantum yields measurements of the resulting solutions were performed immediately.

1.6 Stability experiments of PSMP-4

5 mM stock solution of PSMP-4 in DMSO was firstly prepared. Then the above stock solution was transferred into 15 mL centrifuge tubes, PBS solution with 10% FBS were added to obtain 50 μM solution with the water volume fractions of 99%. After that, the PL spectra measurements of the resulting solutions were performed in different time.

1.7 Photodynamic properties

Extracellular ROS detection: The ROS generation was measured by using 2',7'-dichlorodihydrofluorescein diacetate (DCFH-DA) as an indicator since the emission of DCFH-DA increases once reacting with ROS. To convert DCFH-DA into dichlorofluorescein, 0.1 mL of 1 mM DCFH-DA in DMSO was added into 1 mL NaOH (0.01M) and resulted solution was stirred for half an hour at room temperature. The hydrolysis product was neutralized with 19 mL PBS (pH 7.4) and stored on ice until further use. For ROS detection, the DCFH-DA (5 μM) was mixed with 50 μM of desired PSMP in DMSO/PBS (1:99, v/v) and exposed to white light (25 mW cm^{-2}). The oxidized DCF was monitored by recording the emission increment at 525 nm with the excitation of 488 nm.

Extracellular ·OH detection: The ·OH generation was measured by using hydroxyphenyl fluorescein (HPF) as an indicator since the emission of HPF increases once reacting with ·OH. 1 mM stock solution of HPF and desired PSMP in DMF were firstly prepared. Then, 1 μL of HPF stock solution and 10 μL of PSMP stock solution (or 10 μL DMF for control group) were added into 989 μL of PBS to give the solutions with final concentrations of HPF and PSMP of 1 μM and 50 μM, respectively. Above solution was exposed to white light (25 mW cm^{-2}) and the emission increment of HPF at 515 nm with the excitation of 490 nm.

Extracellular $O^{\bullet-}_2$ detection: The $O^{\bullet-}_2$ generation was measured by using dihydrorhodamine 123 (DHR123) as an indicator since the emission of DHR123 increases once reacting with $O^{\bullet-}_2$. 1 mM stock solution of DHR123 and 10 mM stock solution of desired PSMP in DMSO were firstly prepared. Then, 15 μL of DHR123 stock solution and 15 μL of PSMP stock solution (or 15 μL DMSO for control group) were added into 2970 μL of H_2O to give the solutions with final concentrations of DHR123 and PSMP of 5 μM and 50 μM, respectively. Above solution was exposed to white light (25 mW cm^{-2}) and the emission increment of DHR123 at 529 nm with the excitation of 495 nm.

Extracellular $^1O_2$ detection: The $^1O_2$ generation was measured by using 9,10-anthracenediyl-bis (methylene)dimalonic acid (ABDA) as indicator since the absorbance of ABDA decreases once reacting with $^1O_2$. 50 μM of desired PSMP in DMSO/H_2O (1:99, v/v) was mixed with ABDA (100 μM) and

exposed to white light (25 mW cm^{-2}). The decomposition of ABDA was monitored by recording the absorbance decrease at 378 nm.

1.8 Compression-chromic:

The PSMP (PSMP-1, PSMP-2, PSMP-3, PSMP-4) compound powder was attached to the quartz sheet, the fluorescence emission spectrum was measured, and the emission displacement was recorded, and then the powder was ground until the emission displacement no longer changed, the fluorescence emission spectrum was recorded, and then the ground powder was fumigated with acetone (heated to 30 ^{o}C) steam, and after 45 min, the fluorescence spectrum or XRD pattern were determined.

1.9 Cell culture

The adherent HeLa cells were cultured in DMEM medium containing 10% FBS. The cells were incubated at 37°C in a 5% CO_2 atmosphere. Corresponding cells were seeded onto 35 mm glass-bottom dishes and allowed to grow until the confluence reached to 60-80%.

1.10 Cell imaging

Stainging experiments: After the cell confluence reached to ca. 60%, the HeLa or CHO cells were washed with PBS to remove the remnant DMEM medium. Then, 1 mM stock solution of PSMP-1 (PSMP-2, PSMP-3 or PSMP-4) was added into DMEM medium to give the staining solution with the final concentration of 10 μM. The cells were incubated with above staining solution for 30 min at 37°C, followed by PBS washing for two times and used for bio-imaging subsequently. Under CLSM, the PSMP-1 (or PSMP-2) was excited at 405 nm and the emission was collected at 450-550 nm, the PSMP-3 (or PSMP-4) was excited at 405 nm and the emission was collected at 500-600 nm. No background fluorescence of cells was detected under the setting condition.

Co-stainging experiments using different PSMP: After the cell confluence reached to ca. 60%, the HeLa or CHO cells were washed with PBS to remove the remnant DMEM. Then, 1 mM stock solution of PSMP-1 (PSMP-2, PSMP-3 or PSMP-4) and 0.5 mM solution of MTDR were added into DMEM to give the staining solution with the final concentration of 10 μM for PSMP-1 (PSMP-2, PSMP-3 or PSMP-4) and 500 nM for MTDR. The cells were incubated with above staining solution for 30 min or 60 min at 37°C, followed by PBS washing for two times and used for bio-imaging subsequently. Under CLSM, the PSMP-1 (or PSMP-2) was excited at 405 nm and the emission was collected at 450-550 nm, the PSMP-3 (or PSMP-4) was excited at 405 nm and the emission was collected at 500-600 nm. MTDR was excited at 635 nm and the emission was collected at 655-755 nm. No background fluorescence of cells was detected under the setting condition.

Co-stainging experiments using different commerical organelle probes: After the cell confluence reached to ca. 60%, the HeLa cells were washed with PBS to remove the remnant DMEM. Then, solution of PSMP-4 and ETR (or LTDR, HCSLT, Hoechst 33342) were added into DMEM to give the staining solution, respectively. The cells were incubated with above staining solution for 30 min at

37°C, followed by PBS washing for two times and used for bio-imaging subsequently. Under CLSM, the PSMP-4 was excited at 405 nm and the emission was collected at 500-600 nm. ETR was excited at 559 nm and the emission was collected at 600-650 nm. HCSLT or LTDR was excited at 635 nm and the emission was collected at 655-755 nm. Hoechst 33342 was excited at 405 nm and the emission was collected at 430–480 nm. No background fluorescence of cells was detected under the setting condition.

Time-dependment stainging experiments: After the cell confluence reached to ca. 60%, the HeLa cells were washed with PBS to remove the remnant DMEM medium. Then, 1 mM stock solution of PSMP-4 was added into DMEM medium to give the staining solution with the final concentration of 10 μM. The cells were incubated with above staining solution for different times (0, 5, 10, 30, and 60 min) at 37°C, followed by PBS washing for two times and used for bio-imaging subsequently. Under CLSM, the PSMP-4 was excited at 405 nm and the emission was collected at 500-600 nm. No background fluorescence of cells was detected under the setting condition.

Mitochondrial membrane potential indicating: After the cell confluence reached to 60–80%, the HeLa cells were washed with PBS to remove the remnant DMEM medium. The resulted HeLa cells were pretreated with different concentrations of CCCP solutions (0, 10, 20, 50, 70, 100 μM) for 30 min at 37 ^{o}C. The medium was then removed and the cells were washed with PBS. After that, the PSMP-4 stock solution (0.5 mM) was added into the cell plates to give the final concentration of 5 μM., and the cells were incubated for another 30 min at 37^{o}C. The resulted cells were washed twice with PBS and used for bio-imaging subsequently. Under CLSM, the PSMP-4 was excited at 405 nm and the emission was collected at 500-600 nm. No background fluorescence of cells was detected under the setting condition. The fluorescence intensity of cells was acquired using imageJ software. Data were expressed as mean ± standard deviation (n = 3).

Intracellular photostabilities: After the cell confluence reached to 60–80%, the HeLa cells were washed with PBS to remove the remnant DMEM medium. Then, 1 mM stock solution of PSMP-4 or 0.5 mM solution of MTDR were added into DMEM to give the staining solution with the final concentration of 10 μM for PSMP-4 or 500 nM for MTDR. The cells were incubated with above staining solution for 30 min at 37°C, followed by PBS washing for two times. The CLSM images of pre-stained cells were collected by continuous laser excitation. Under CLSM, the PSMP-4 was excited at 405 nm and the emission was collected at 500-600 nm. No background fluorescence of cells was detected under the setting condition. The fluorescence intensity of cells was acquired using imageJ software. Data were expressed as mean ± standard deviation (n = 3).

1.11 ROS detection

Set up the intracellular hypoxic microenvironment: The intracellular hypoxic microenvironment was set up according to previous literature[1], the specific experimental protocol is as follows. After the cell confluence reached to ca. 80%, HeLa cells were transfered into an incubator under humidified hypoxic

atmosphere (< 2% O_2) and cultured in DMEM or PBS (pre-bubbled for 5 minutes by N_2) for additional 3 h. The oxygen detector (BH-90A) was simultaneously used to 10 monitor the oxygen content in the chamber.

Intracellular ROS detection: After the cell confluence reached to 60-80%, the HeLa cells were washed with PBS to remove the remnant DMEM medium. The cells were stained with 10 μM PSMP-4 for 30 min. The medium was discarded and the cells were further stained by DCFH-DA (200 μM) in fresh medium for another 30 min. The cells were then exposed to white light (25 mW cm^{-2}) for different times and collected the CLSM images subsequently. DCFH-DA was excited at 488 nm and the emission was collected at 500–550 nm. No background fluorescence of cells was detected under the setting condition. Flow cytometry was exerted by digestion of HeLa cells from the 6 well plate and treated following aforementioned manipulation.

Intracellular ROS imaging: DHE, HPF and SOSG was used as intracellular O•− 2, ·OH and $^1O_2$ indicator, respectively. After the cell confluence reached to 60–80%, the HeLa cells were stained with 10 μM PSMP-4 (or w/o PSMP-4) for 30 min. The medium was discarded and the cells were further stained by 10 μM DHE (10 μM HPF or 1 μM SOSG) in fresh medium for another 30 min (for HPF, the staining time prolonged to 60 min). The cells were then exposed (or not) to white light (25 mW cm^{-2}) for 3 min and collected the CLSM images subsequently. For hypoxic conditions, when the cell confluence reached ca. 80% at normoxic conditions, HeLa cells were transferred to a hypoxic (< 2% O_2) atmosphere in the hypoxic chamber and cultured for an additional 3 h. Then, the HeLa cells were treated based on the above protocol. DHE was excited at 488 nm and the emission was collected at 570–630 nm. HPF was excited at 488 nm and the emission was collected at 500–550 nm. SOSG was excited at 488 nm and the emission was collected at 500–550 nm. The fluorescence intensity of cells was acquired using ImageJ software. Data were expressed as mean ± standard deviation (n = 3).

Intracellular mitochondrial ROS detection: After the cell confluence reached to 60-80%, the HeLa cells were washed with PBS to remove the remnant DMEM medium. The cells were stained with 10 μM PSMP-4 (or w/o PSMP-4) for 30 min. The medium was discarded and the cells were further stained by 5 μM Mito-SOX red in fresh medium for another 30 min. The cells were then exposed (or not) to white light (25 mW cm^{-2}) for 3 min and collected the CLSM images subsequently. Mito-SOX red was excited at 405 nm and the emission was collected at 600–700 nm. No background fluorescence of cells was detected under the setting condition. The fluorescence intensity of cells was acquired using ImageJ software. Data were expressed as mean ± standard deviation (n = 3).

1.12 Mitochondrial dysfunction detection

After the cell confluence reached to 60-80%, the HeLa cells were washed with PBS to remove the remnant DMEM medium. The cells were treated with PSMP-4 (10 μM) in DMEM for 60 min. Then, the medium was replaced by fresh DMEM and selected wells were exposed to white light (25 mW

cm^{-2}, 30 min). For control group, similar procedure was performed except white light. The resulted cells were stained with Rhodamine 123 and collected the CLSM images. Rhodamine 123 was excited at 488 nm and the emission was collected at 500-550 nm, No background fluorescence of cells was detected under the setting condition. The fluorescence intensity of cells was acquired using ImageJ software. Data were expressed as mean ± standard deviation (n = 3).

1.13 Mitochondrial membrane potential (MMP) assay

JC-1 was used to determin the change of mitochondrial membrane potential. For normoxic condition, when the cell confluence reached to ca. 50% The resulting cells were treated under the following conditions: blank w/o light group (without any treatment), blank w light group (treated with DMEM for 60 min and exposed to 25 mW cm^{-2} white light for 30 min), PSMP-4 w/o light group (treated with 10 μM PSMP-4 in DMEM for 60 min), PSMP-4 w light group (treated with 10 μM PSMP-4 in DMEM for 60 min and exposed to 25 mW cm^{-2} white light for 30 min). After that, the cells were stained by JC-1 following the manufacture's protocol and collected the CLSM images subsequently. Under CLSM, JC-1 was excited at 488 nm and the emission of green channel was collected at 500–550 nm, while the emission of red channel was collected at 580–630 nm.

1.13 Dead/live cell staining

After the cell confluence reached to 60-80%, the HeLa cells were washed with PBS to remove the remnant DMEM medium. The resulting cells were treated under the following conditions: blank w/o light group (without any treatment), PSMP-4 w/o light group (treated with 10 μM PSMP-4 in DMEM for 60 min), PSMP-4 w light group (treated with 10 μM PSMP-4 in DMEM for 60 min and exposed to 25 mW cm^{-2} white light for 30 min), PSMP-4 w light (2 h) group (treated with 10 μM PSMP-4 in DMEM for 60 min and exposed to 25 mW cm^{-2} white light for 30 min; the resulting cells were allowed to stand for 2 h in the dark). Then, co-staining of calcein AM and PI (2 μg/mL) was performed and the CLSM images were collected subsequently. Calcein AM was excited at 488 nm and the emission was collected at 500-550 nm, PI was excited at 559 nm and the emission was collected at 580–630 nm. No background fluorescence of cells was detected under the setting condition. Flow cytometry was exerted by digestion of HeLa cells from the 6 well plate and treated following aforementioned manipulation.

1.14 Cell apoptosis detection

After the cell confluence reached to 60-80%, the HeLa cells were washed with PBS to remove the remnant DMEM medium. The resulting cells were treated with PSMP-4 (10 μM) in DMEM for 60 min. Then, the medium was replaced by fresh DMEM and selected wells were exposed to white light (25 mW cm^{-2}, 30 min). After that, the cells were allowed to grow for different times in the dark. For control group, similar procedure was performed except white light irradiation. The resulted cells were stained with both Annexin V-FITC and PI by following the protocols from the manufacturer and collected the CLSM images with the elapse of time. Annexin V-FITC was excited at 488 nm and the emission was

collected at 500-550 nm, PI was excited at 559 nm and the emission was collected at 580–630 nm. No background fluorescence of cells was detected under the setting condition.

1.15 Cytotoxicity assays

Cytotoxicity under normoxic condition: The MTT assay was used to evaluate the cytotoxicity of PSMP-4 with (or without) white light, the HeLa cells (or CHO cells) were seeded at a density of 10000 cells/well in 96 well plate and incubated for 24 h. The cells were treated with different concentrations of PSMP-4 in DMEM for 60 min and exposed to white light (25 mW cm^{-2}, 30 min). After that, the cells were cultured for 2 h under dark (for control group, the cells were treated by fresh DMEM for 2.5 h under dark), followed by incubating with MTT for additional 4 h. The resulted formazan crystals were solubilized in 100 μL of lysate buffer. The absorbance at 570 nm of each wells was measured and the data was recorded using Softmax Pro 6.4 software. Data were expressed as mean ± standard deviation (n = 5).

Cytotoxicity under hypoxic condition: The MTT assay was used to evaluate the cytotoxicity of PSMP-4 with (or without) white light, the HeLa cells were seeded at a density of 10000 cells/well in 96 well plate and incubated for 24 h. After that, the cells were cultured for another 3 h with the O_2 content < 2%. The cells were treated with different concentrations of PSMP-4 in DMEM for 60 min with the O_2 content < 2%, and exposed to white light (25 mW cm^{-2}, 30 min, < 2% O_2). After that, the cells were cultured for 2 h under dark with O_2 content < 2% (for control group, the cells were treated by fresh DMEM for 2.5 h under darkwith O_2 content < 2%), followed by incubating with MTT for additional 4 h. The resulted formazan crystals were solubilized in 100 μL of lysate buffer. The absorbance at 570 nm of each wells was measured and the data was recorded using Softmax Pro 6.4 software. Data were expressed as mean ± standard deviation (n = 5).

1.16 MCTSs model of HeLa cells

MCTSs from HeLa cells were obtained using hanging drop technique. 10 μL HeLa cell suspension was seeded on the slide treated with paraffin, and then inverted onto the dish and cultured for 4 d to aggregate into tumor spheroids.

1.17 PDT treatment for MCTSs

MCTSs were treated with PSMP-4 (50 μM) in DMEM for 30 min and exposed with (or w/o) white light (25 mW cm^{-2}) for 30 min each day. PDT experiments for MCTSs were performed for 2 days. The control group was not stained with PSMP-4 and treated with the aforementioned therapeutic protocol. Then, co-staining of calcein AM and PI (2 μg/mL) was performed and the CLSM images were collected subsequently. Calcein AM was excited at 488 nm and the emission was collected at 500-550 nm, PI was excited at 559 nm and the emission was collected at 580–630 nm. No background fluorescence of cells was detected under the setting condition.

2. Supplementary figures

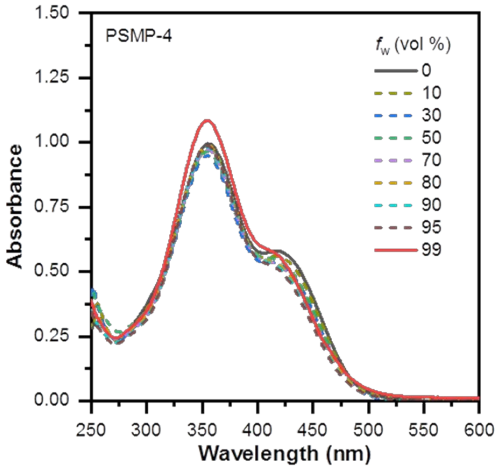


Fig. S1 Absorption spectra of PSMP-4 (50 μM) in DMSO/water binary mixtures with different f_w.

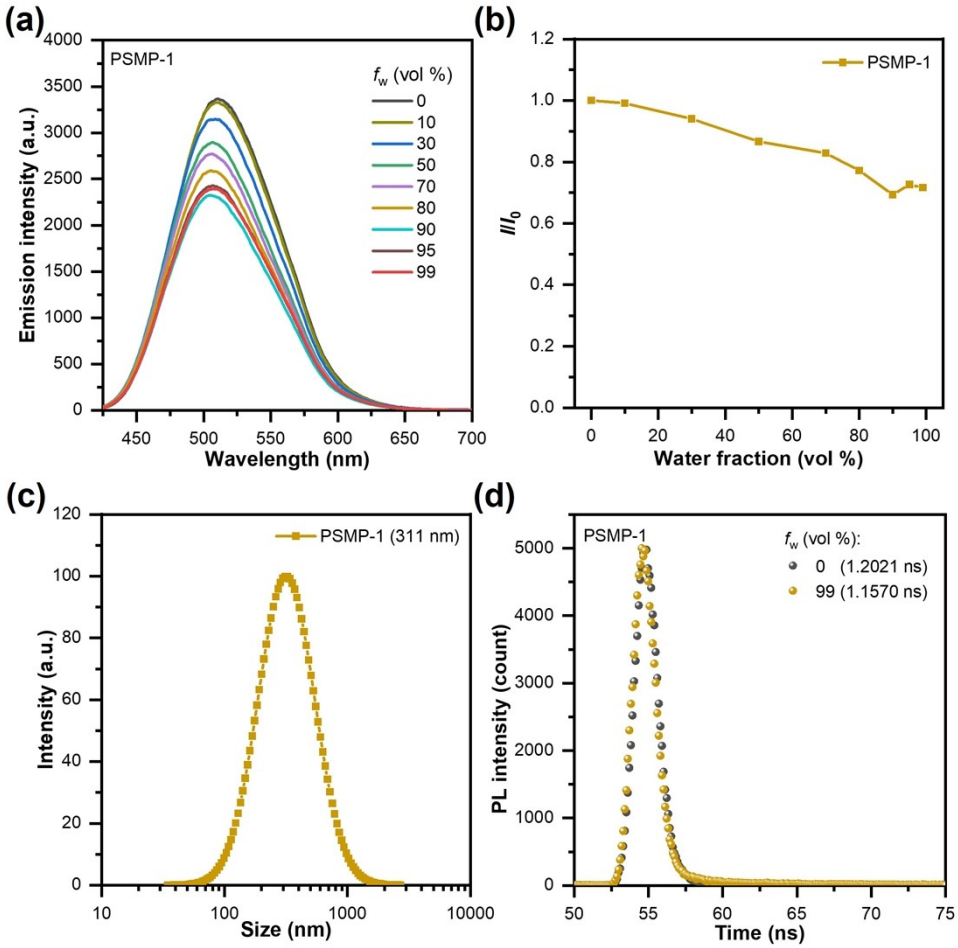


Fig. S2 (a) Fluorescence spectra of PSMP-1 (50 μM) in DMSO/water binary mixtures with different f_w. (b) Plots of I/I_0 versus different fw for PSMP-1. I_0 and I represent the fluorescence intensity before and after addition of water in DMSO. (c) The particle size distribution of the PSMP-1 (50 μM) in aqueous medium with f_w of 99%. (d) The fluorescence lifetime of the PSMP-1 (50 μM) in aqueous medium with f_w of 0% and 99%.

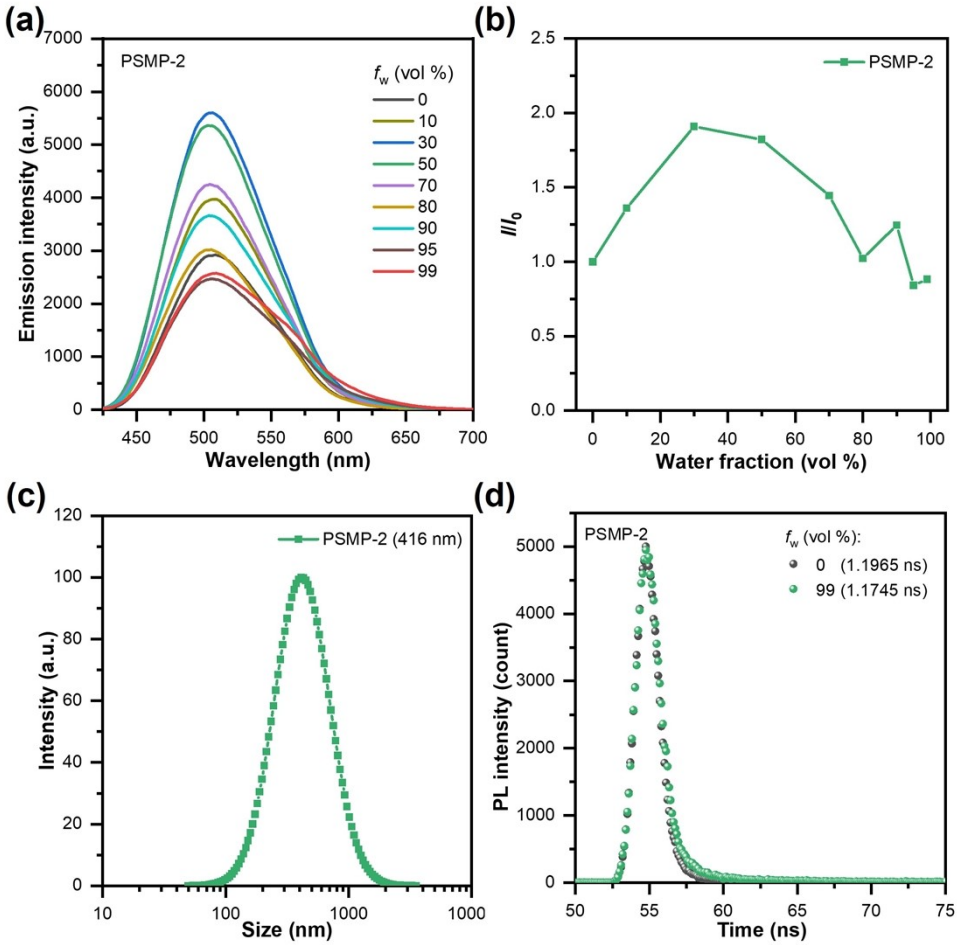


Fig. S3 (a) Fluorescence spectra of PSMP-2 (50 μM) in DMSO/water binary mixtures with different f_w. (b) Plots of I/I_0 versus different fw for PSMP-2. I_0 and I represent the fluorescence intensity before and after addition of water in DMSO. (c) The particle size distribution of the PSMP-2 (50 μM) in aqueous medium with f_w of 99%. (d) The fluorescence lifetime of the PSMP-2 (50 μM) in aqueous medium with f_w of 0% and 99%.

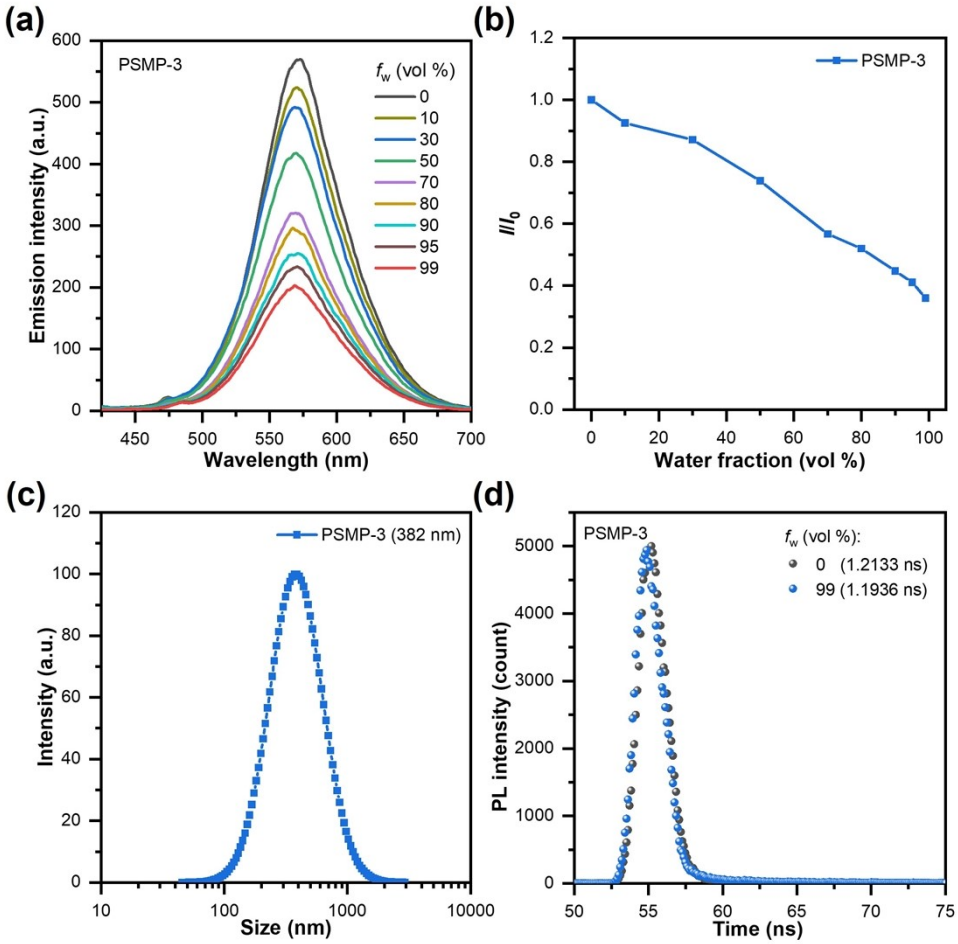


Fig. S4 (a) Fluorescence spectra of PSMP-3 (50 μM) in DMSO/water binary mixtures with different f_w. (b) Plots of I/I_0 versus different fw for PSMP-3. I_0 and I represent the fluorescence intensity before and after addition of water in DMSO. (c) The particle size distribution of the PSMP-3 (50 μM) in aqueous medium with f_w of 99%. (d) The fluorescence lifetime of the PSMP-3 (50 μM) in aqueous medium with f_w of 0% and 99%.

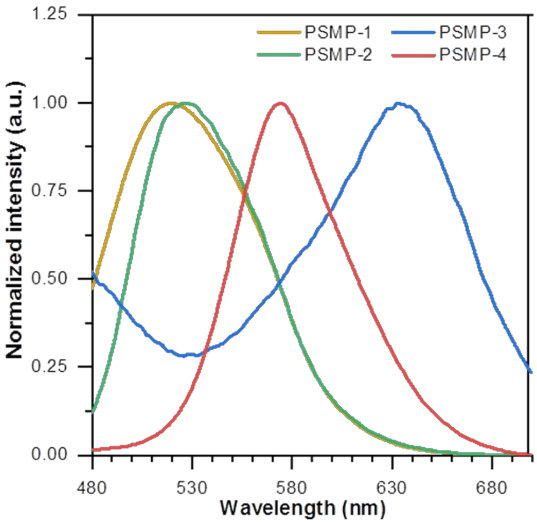


Fig. S5 The emission spectra of four isomers in solid state.

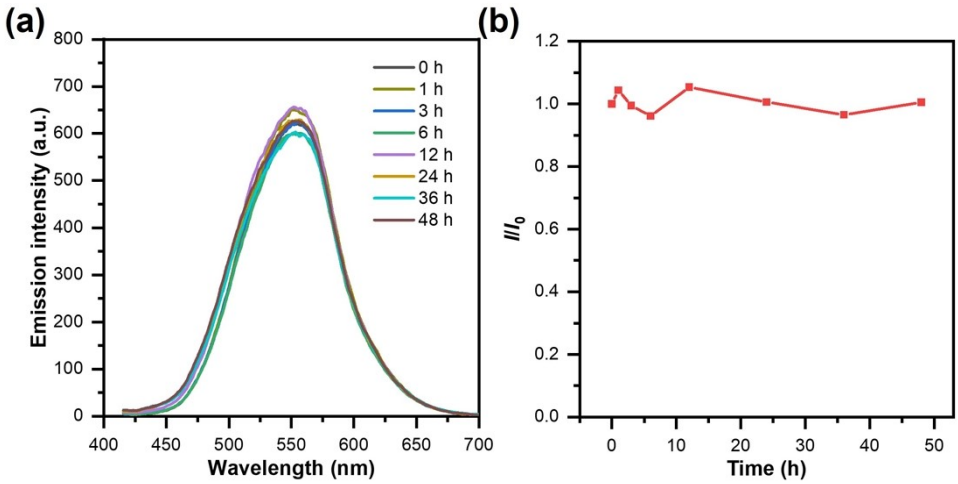


Fig. S6 (a) Change of emission spectra of PSMP-4 (50 μM) in DMSO/PBS mixtures with f_{PBS} of 99% with 10% FBS. (b) I/I_0 of PSMP-4 (50 μM) at f_{PBS} of 99% with 10% FBS.

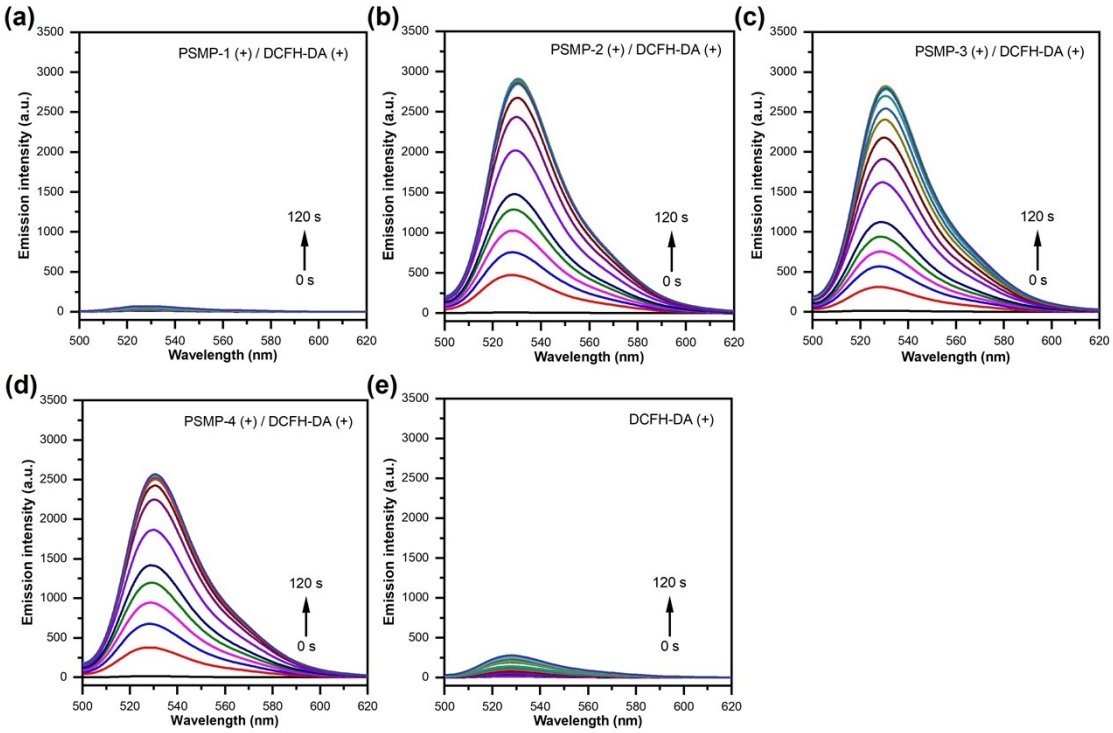


Fig. S7 Emission spectra change of DCFH-DA (5 μM) in the presence of (a) PSMP-1 (50 μM), (b) PSMP-2 (50 μM), (c) PSMP-3 (50 μM), (d) PSMP-4 (50 μM) and (e) DCFH-DA alone in DMSO/PBS mixtures with f_{PBS} of 99% after different durations under white light (25 mW cm^{-2}).

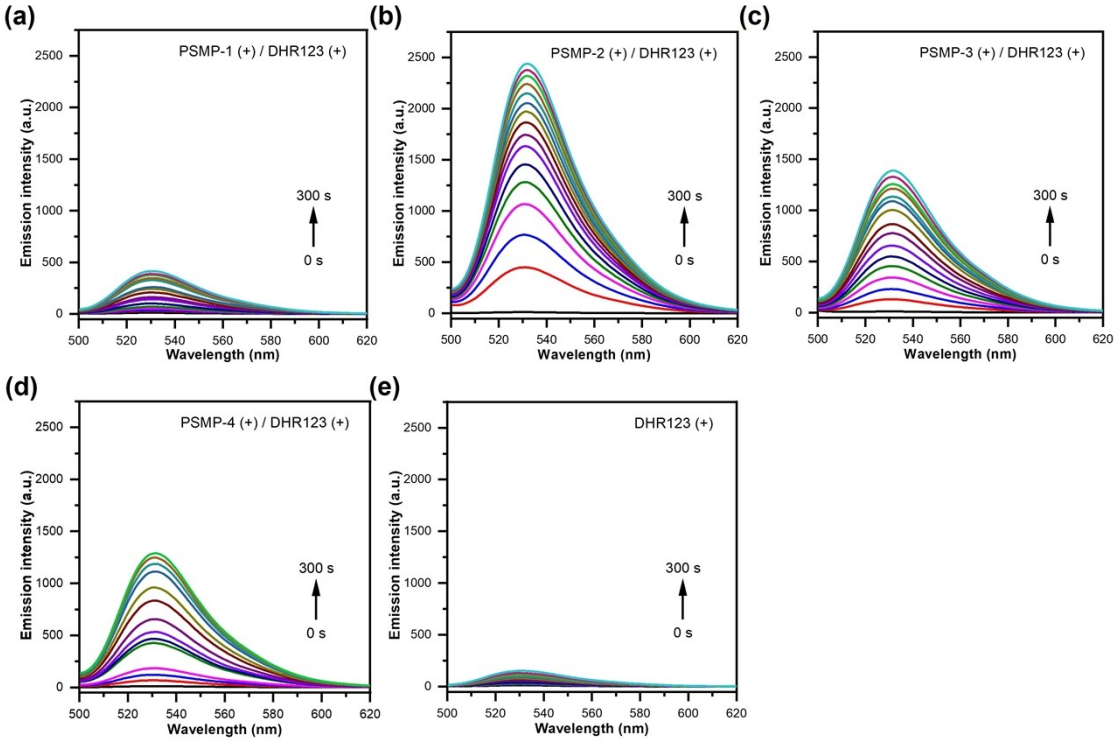


Fig. S8 Emission spectra change of DHR123 (10 μM) in the presence of (a) PSMP-1 (50 μM), (b) PSMP-2 (50 μM), (c) PSMP-3 (50 μM), (d) PSMP-4 (50 μM) and (e) DHR123 alone in DMSO/water mixtures with f_w of 99% after different durations under white light (25 mW cm^{-2}).

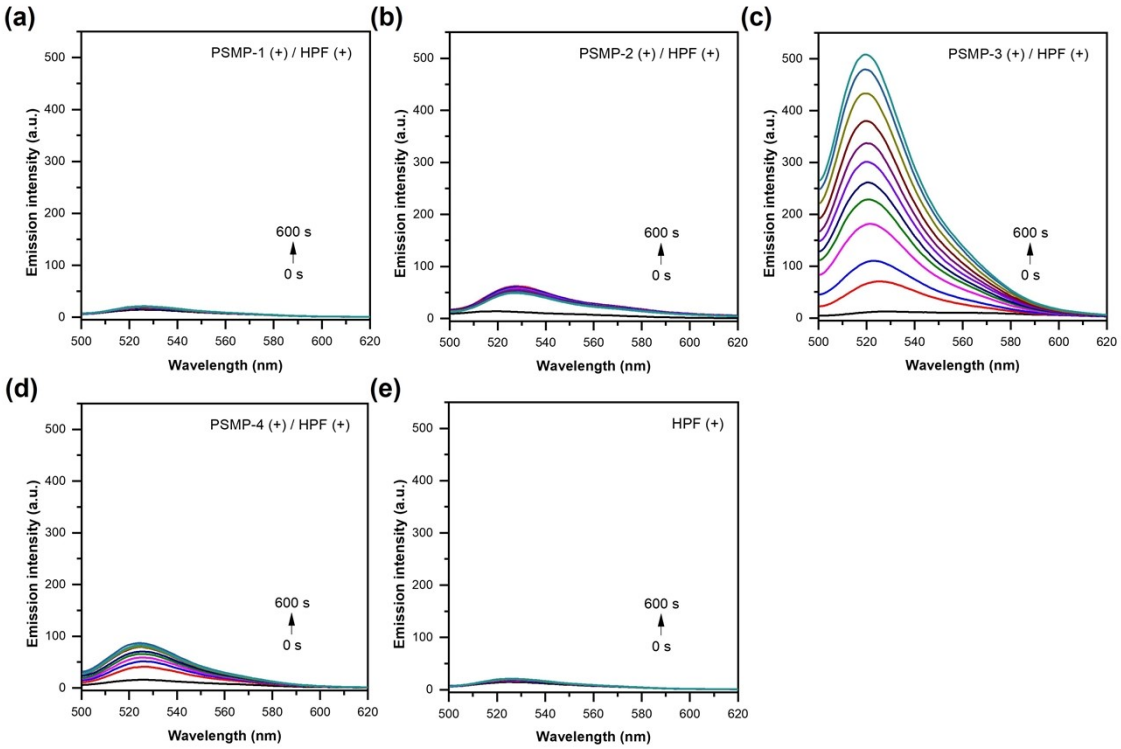


Fig. S9 Emission spectra change of HPF (5 μM) in the presence of (a) PSMP-1 (50 μM), (b) PSMP-2 (50 μM), (c) PSMP-3 (50 μM), (d) PSMP-4 (50 μM) and (e) HPF alone in DMF/PBS mixtures with f_{PBS} of 99% after different durations under white light (25 mW cm^{-2}).

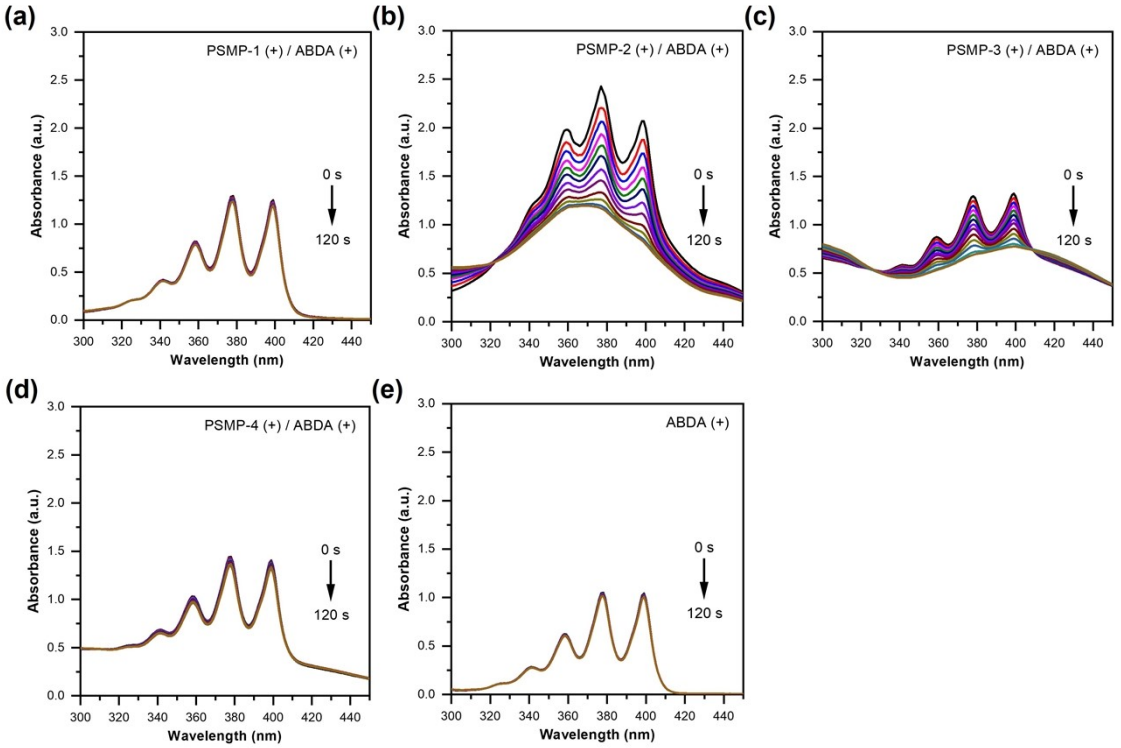


Fig. S10 Absorption spectra change of ABDA (100 μM) in the presence of (a) PSMP-1 (50 μM), (b) PSMP-2 (50 μM), (c) PSMP-3 (50 μM), (d) PSMP-4 (50 μM) and (e) ABDA alone in DMSO/water mixtures with f_w of 99% after different durations under white light (25 mW cm^{-2}).

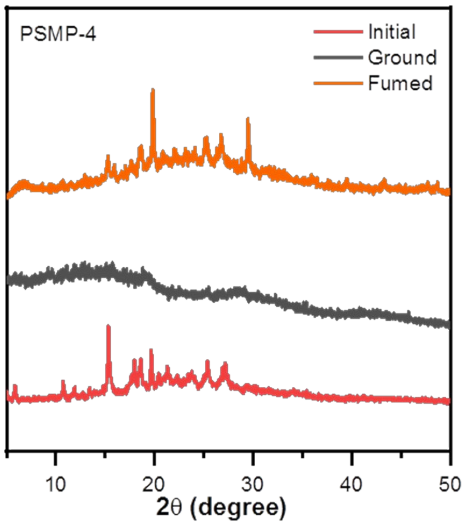


Fig. S11 The XRD pattern of PSMP-4 after different treatment.

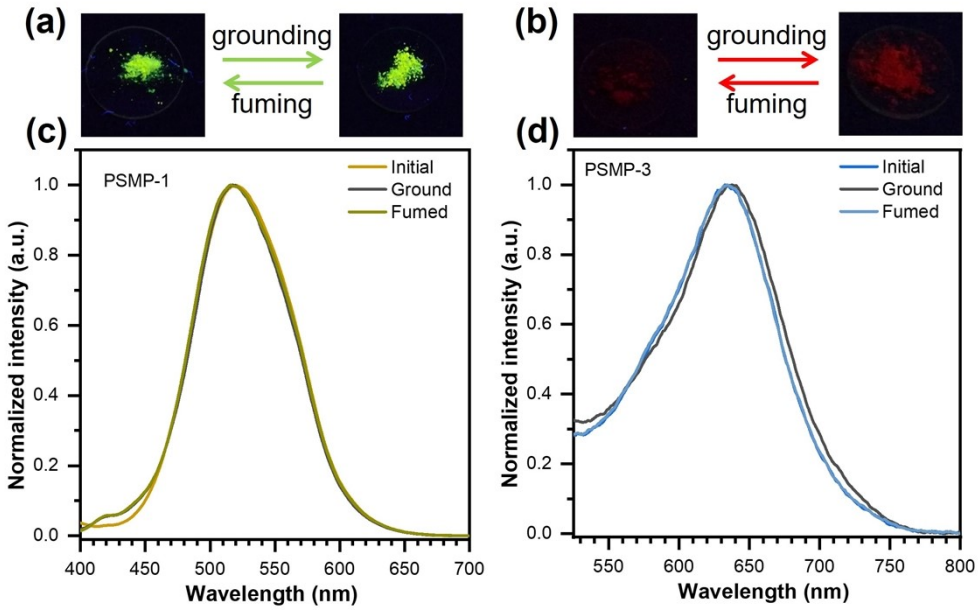


Fig. S12 (a) Fluorescence images of PSMP-1 and (b) PSMP-3 solids after grinding and fumigation (acetone) under 365 nm excitation. (c) Fluorescence spectra of PSMP-1 and (d) PSMP-3 solids after grinding and fumigation (acetone).

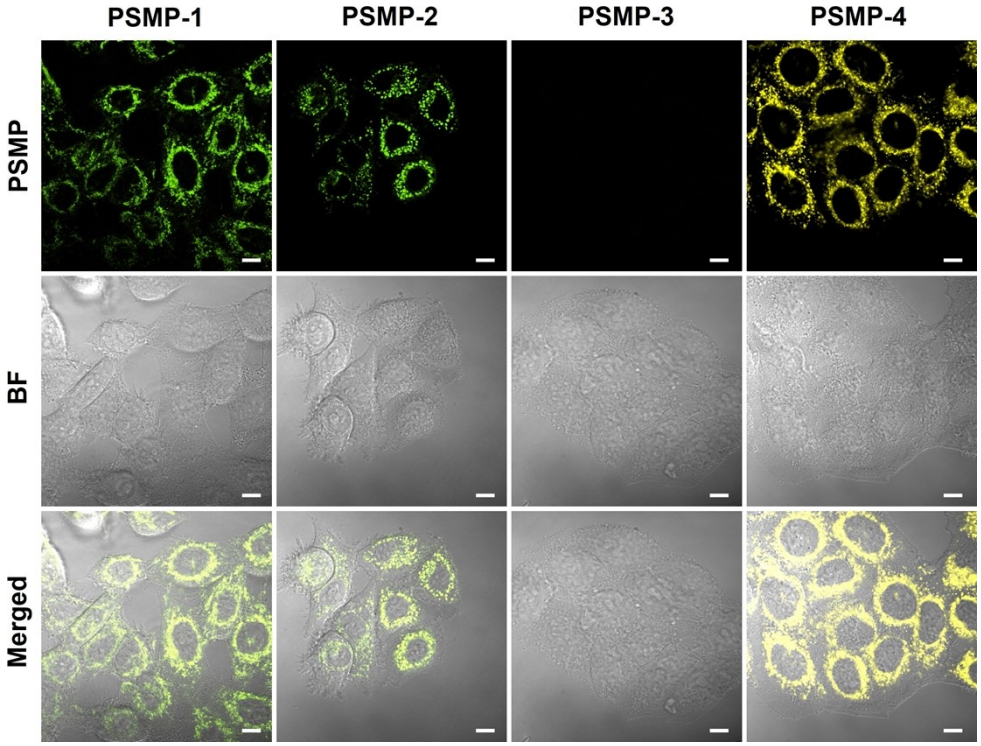


Fig. S13 CLSM images of HeLa cells stained with PSMP (10 μM). Scale bar: 10 μm.

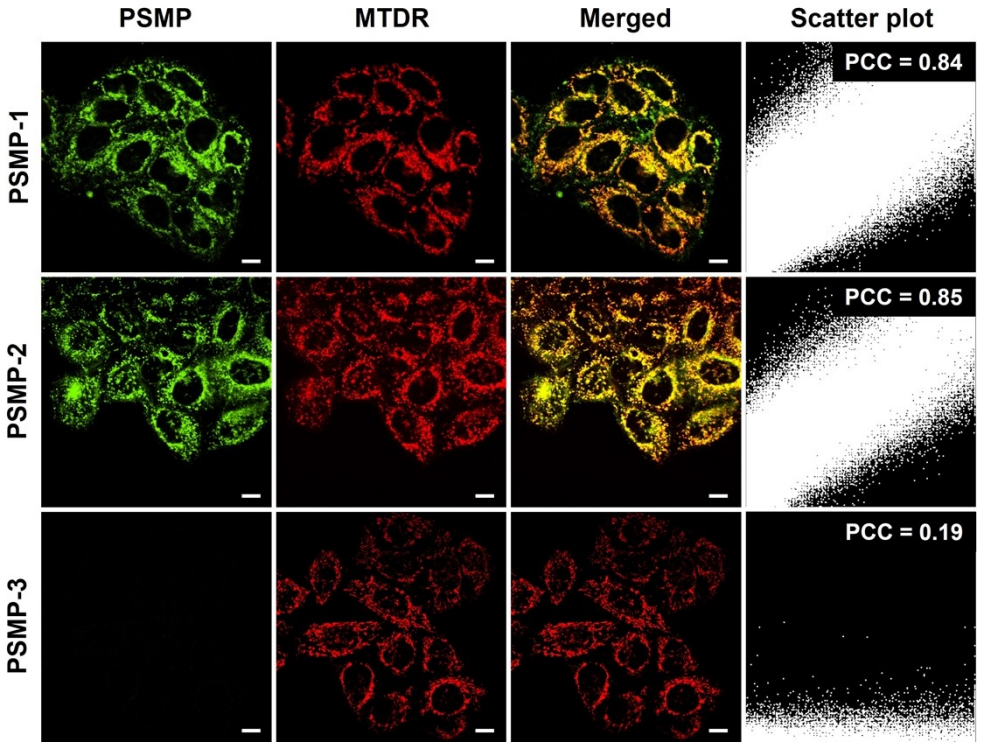


Fig. S14 Colocalization CLSM images of HeLa cells stained by 10 μM PSMP-1(PSMP-2 or PSMP-3) and MTDR. Scale bar: 10 μm.

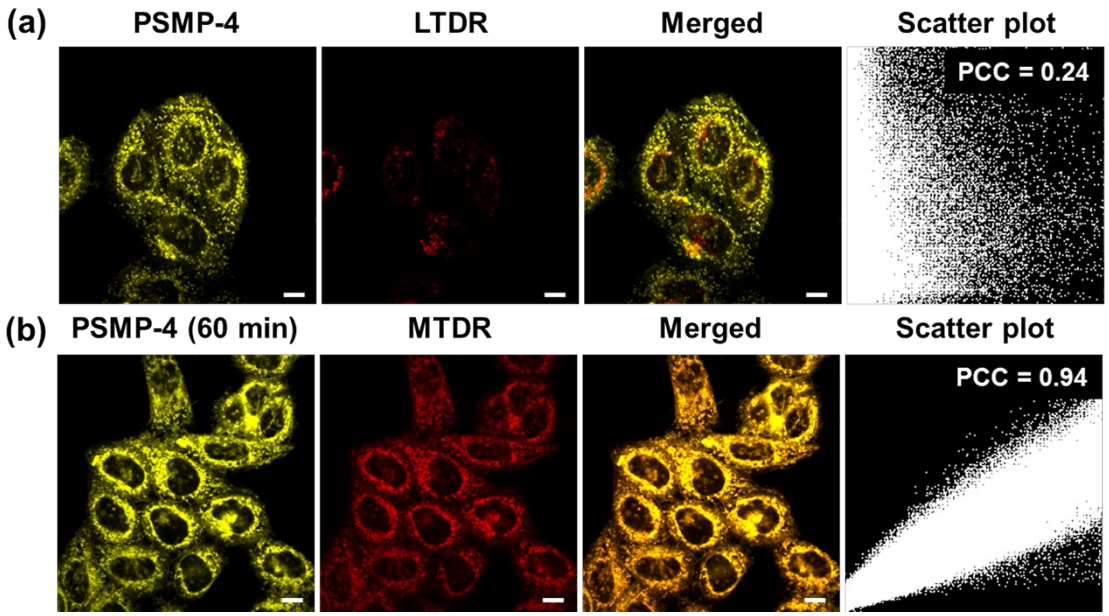


Fig. S15 Colocalization CLSM images of HeLa cells stained by (a) PSMP-4 and LDTR and (b) PSMP-4 for 60 min and MTDR. Scale bar: 10 μm.

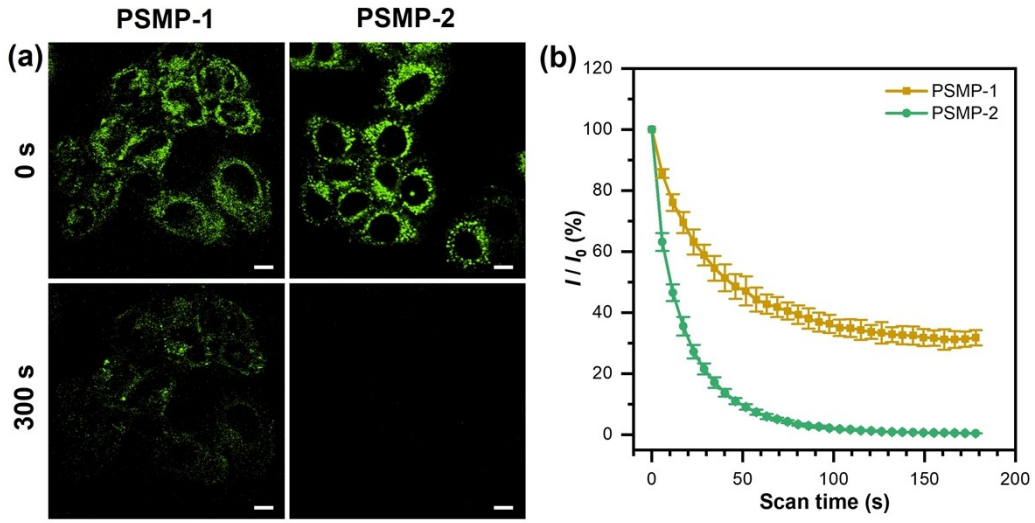


Fig. S16 (a) CLSM images of 10 μM PSMP-1 (or PSMP-2) pre-stained HeLa cells at 0 and 180 s under continuous laser scan. (b) The loss of fluorescence signals versus the time of laser scans for PSMP-1 and PSMP-2. Scale bar: 10 μm.

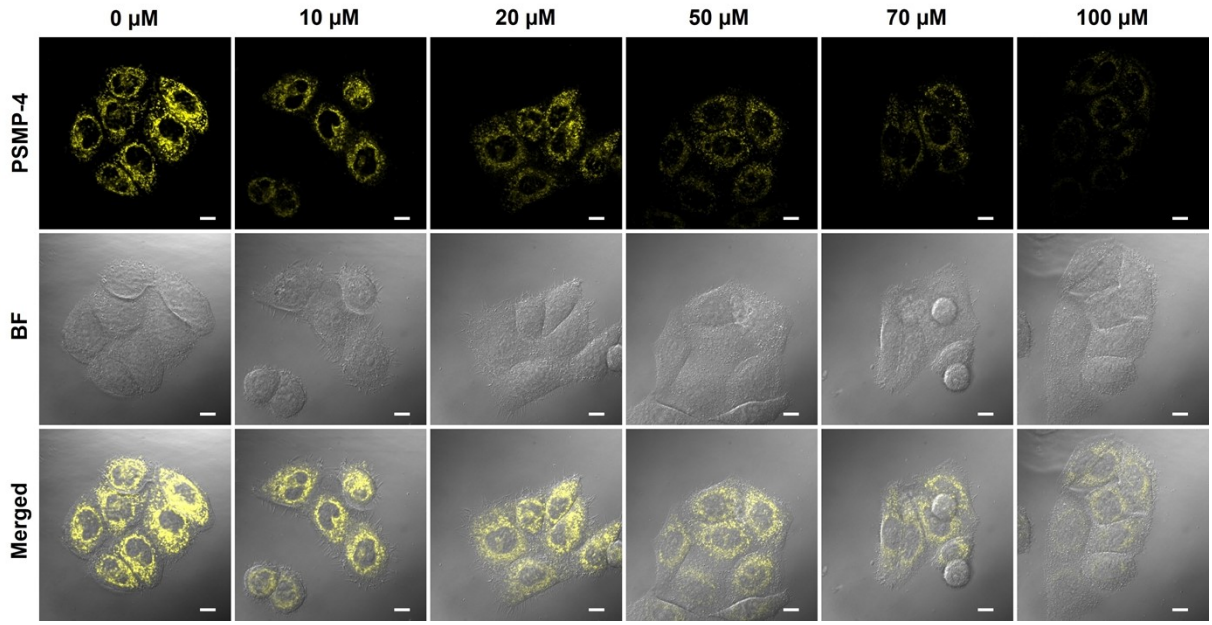


Fig. S17 CLSM images of MMP changes when HeLa cells were treated with PSMP-4 (5 μM) and different concentrations of CCCP. Scale bar: 10 μm.

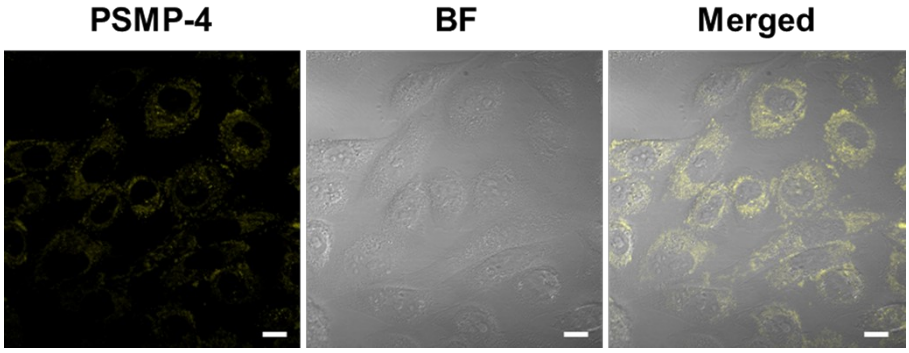


Fig. S18 CLSM images of CHO cells were treated with PSMP-4 (10 μM). Scale bar: 10 μm.

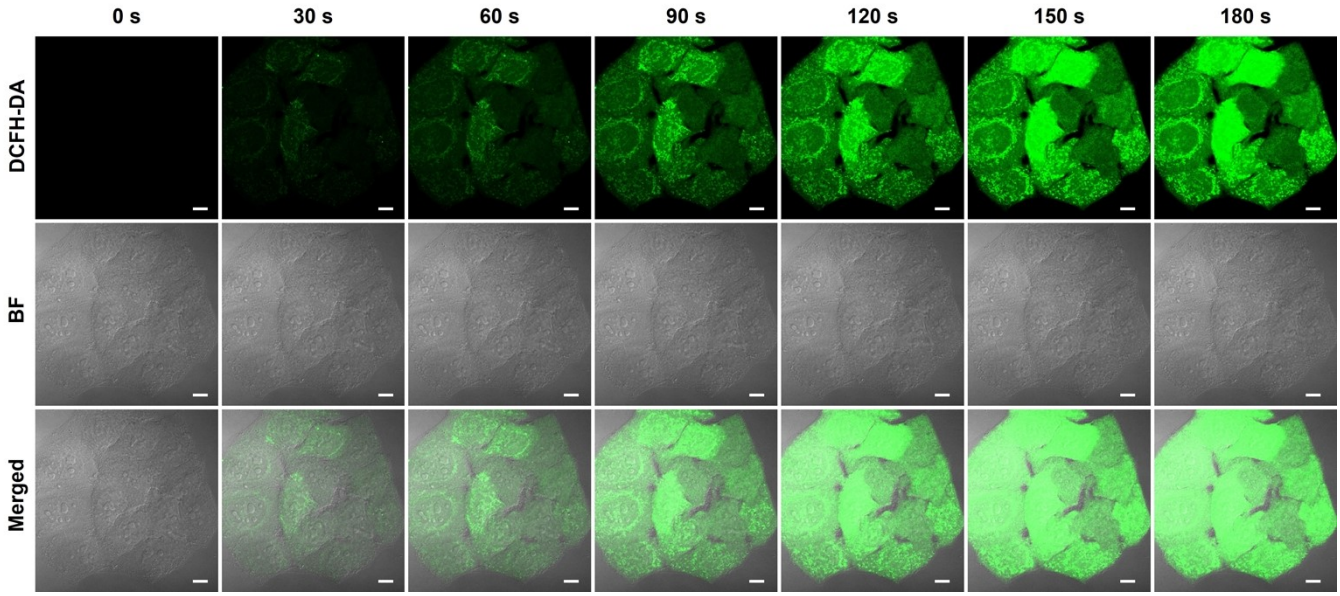


Fig. S19 Time-dependent CLSM image of DCFH-DA staining of HeLa cells after incubation with PSMP-4 (10 μM) and white light (25 mW cm^{-2}). Scale bar: 10 μm.

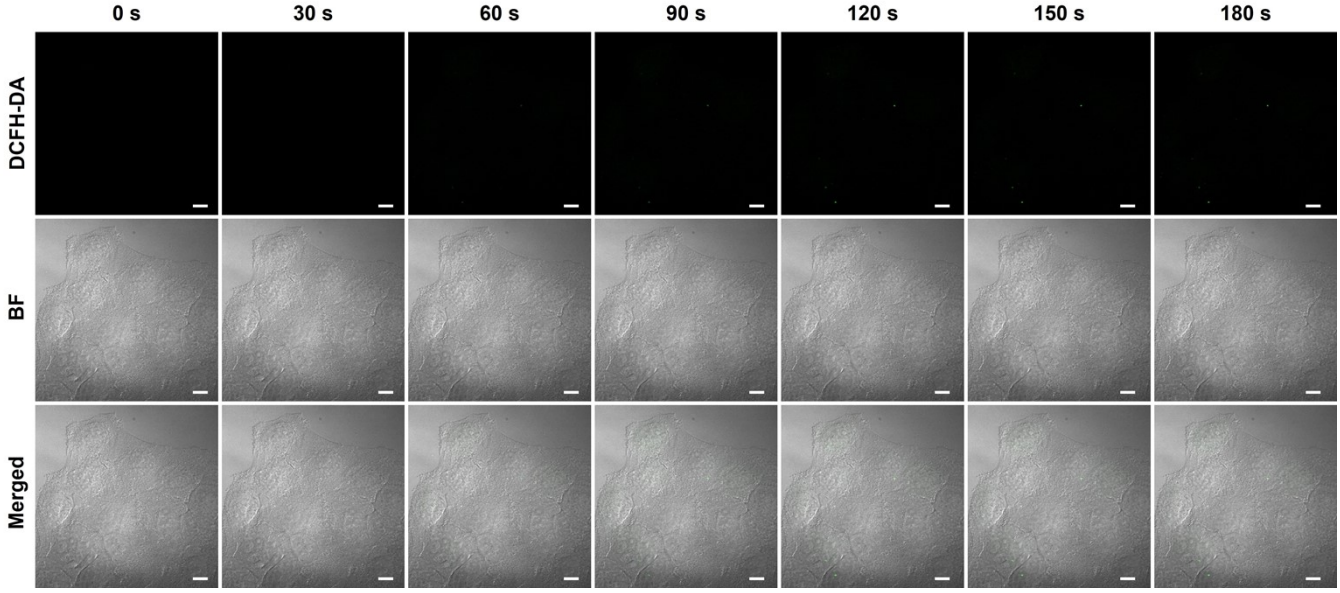


Fig. S20 Time-dependent CLSM image of DCFH-DA staining of HeLa cells after white light (25 mW cm^{-2}). Scale bar: 10 μm.

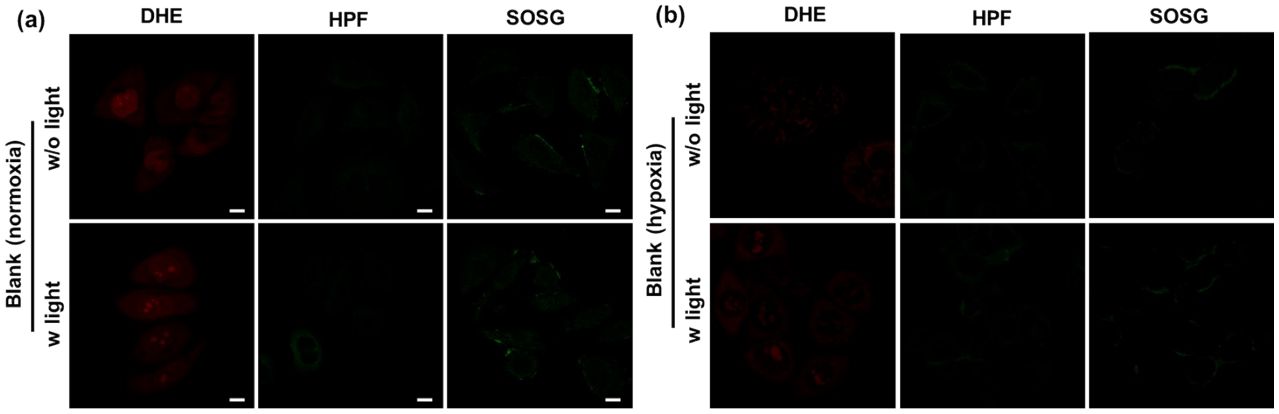


Fig. S21 CLSM images of DHE, HPF and SOSG staining of HeLa cells after white light (25 mW cm^{-2}, 3 min). Scale bar: 10 μm.

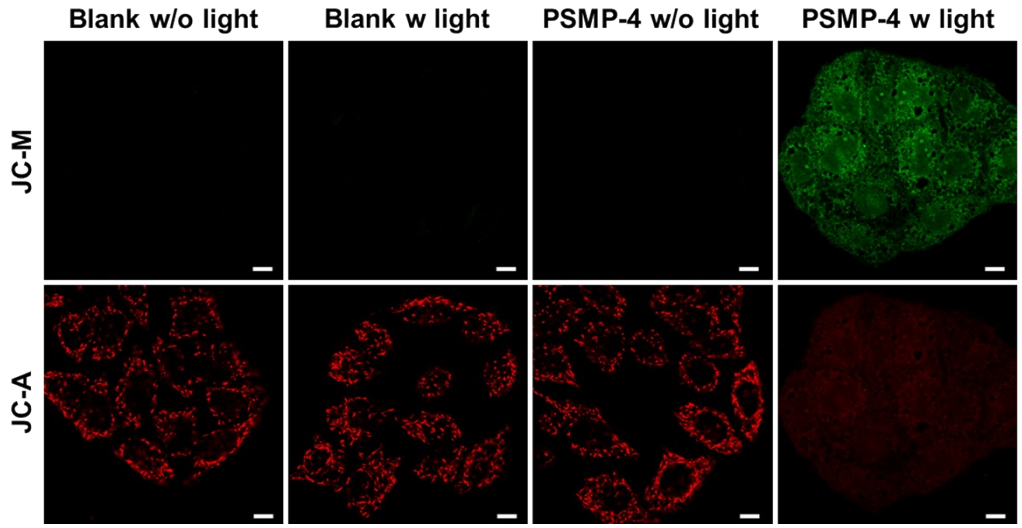


Fig. S22 CLSM images of JC-1 under different treatment. Scale bar: 10 μm.

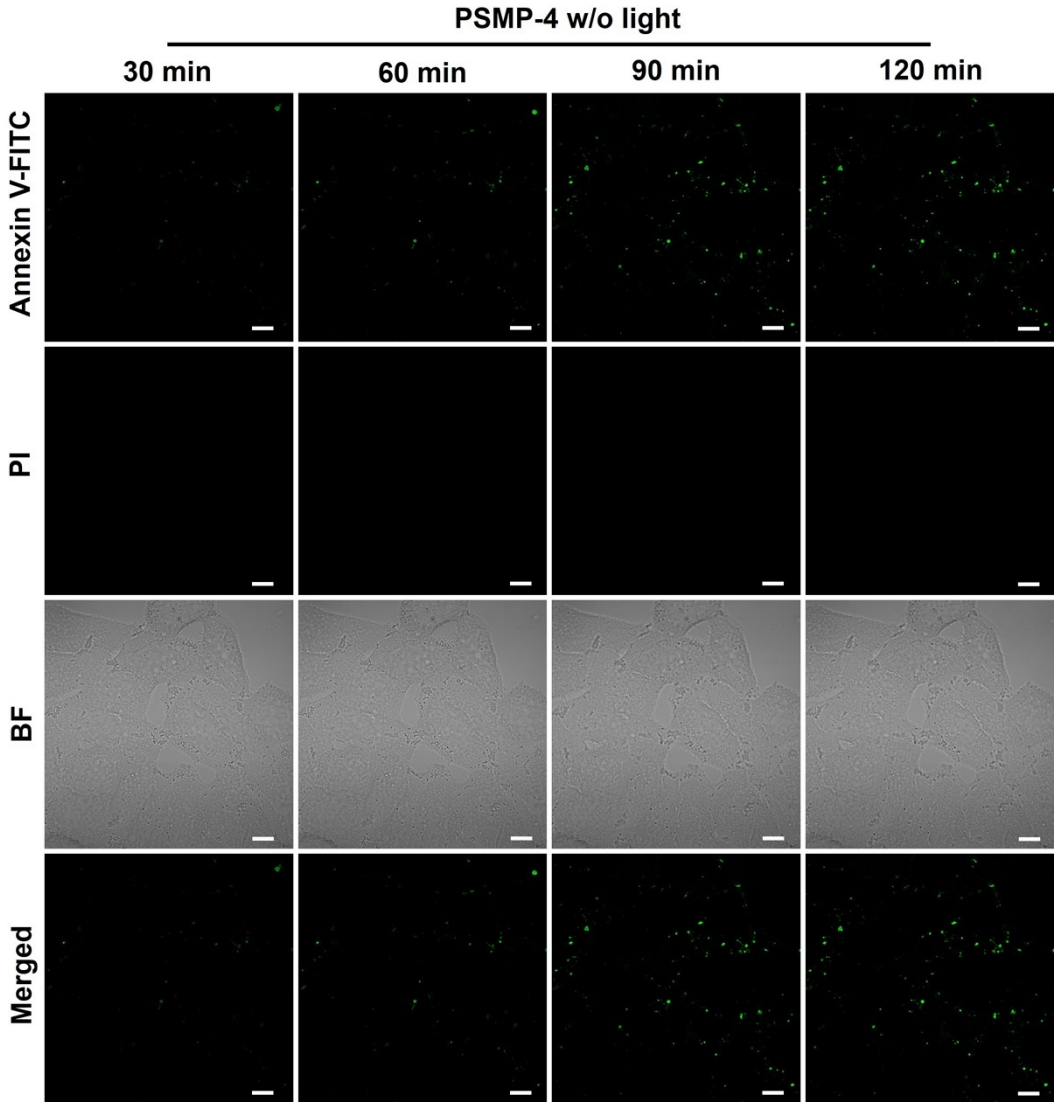


Fig. S23 Time-dependent CLSM images of Annexin V-FITC/PI staining of HeLa cells after treating with PSMP-4 (10 μM). Scale bar: 10 μm.

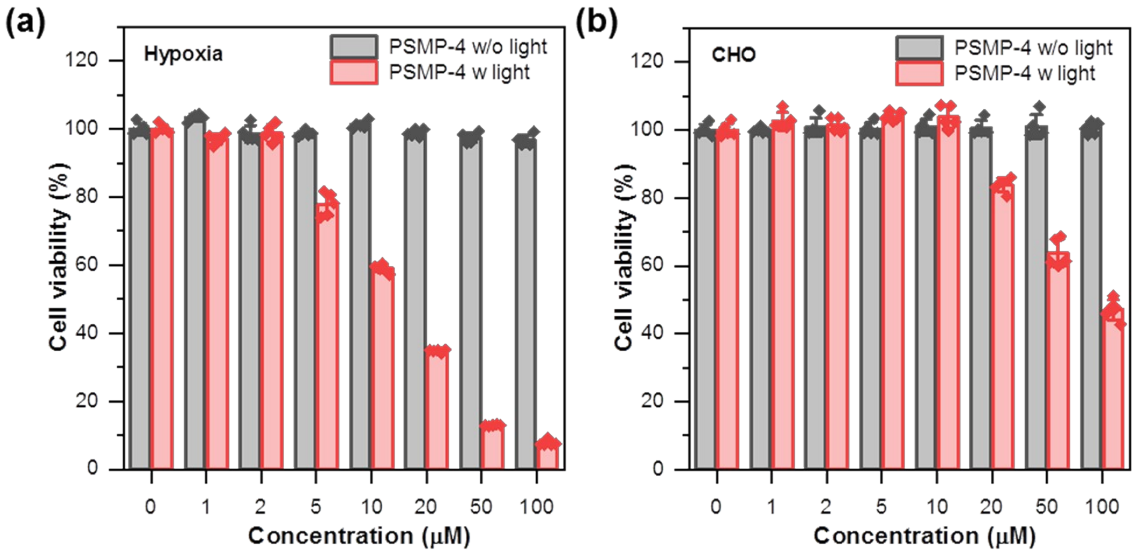


Fig. S24 (a) Cell viability assays of HeLa cells subjected to different concentration of PSMP-4 with or without white light (25 mW cm^{-2}, 30 min) in hypoxia. (b) Cell viability assays of CHO cells subjected to different concentration of PSMP-4 with or without white light (25 mW cm^{-2}, 30 min).

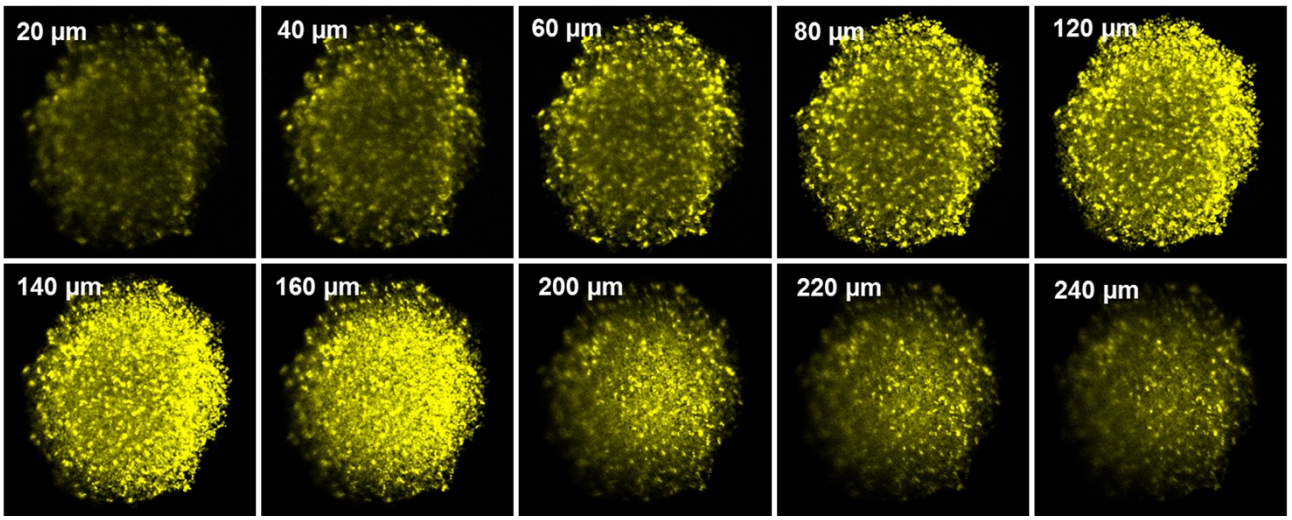


Fig. S25 Z-stack images after incubation of PSMP-4 (50 μM) in HeLa cells MCTS, respectively. Z-axis images scanning from the top to the bottom of an intact spheroid every 20 μm. Scale bars : 200 μm

3. Supplementary table

Table S1. Optical Properties of PSMP isomers.

Compd.	Solution[a]				Aggregation[b]		
	λ_{abs} [nm]	λ_{em} [nm]	Φ_f[c] [%]	τ[d] (ns)	λ_{em} [nm]	Φ_f[c] [%]	τ[d] (ns)
PSMP-1	381	510	13	1.2021	507	4.6	1.1570
PSMP-2	388	507	26	1.1965	509	21	1.1745
PSMP-3	409	572	3.1	1.2133	569	1.2	1.1936
PSMP-4	418	603	2.8	3.0095	547	9.9	13.4722

[a]In DMSO solution. [b]In DMSO/water mixtures with f_w of 99%. [c]Determined by using a calibrated integrating sphere. [d]Mean fluorescence lifetime (τ_{avg}).

4. ^{1}H, ^{13}C NMR, and HR-MS spectra

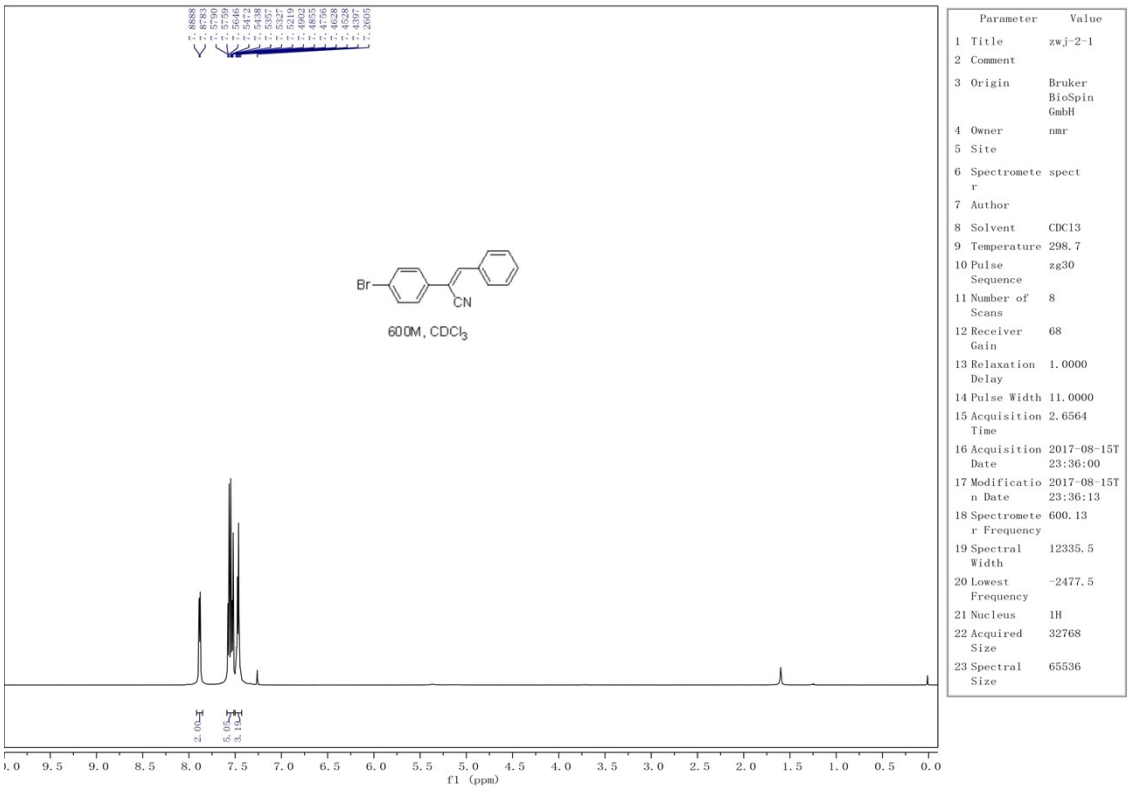


Fig. S26 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1-1.

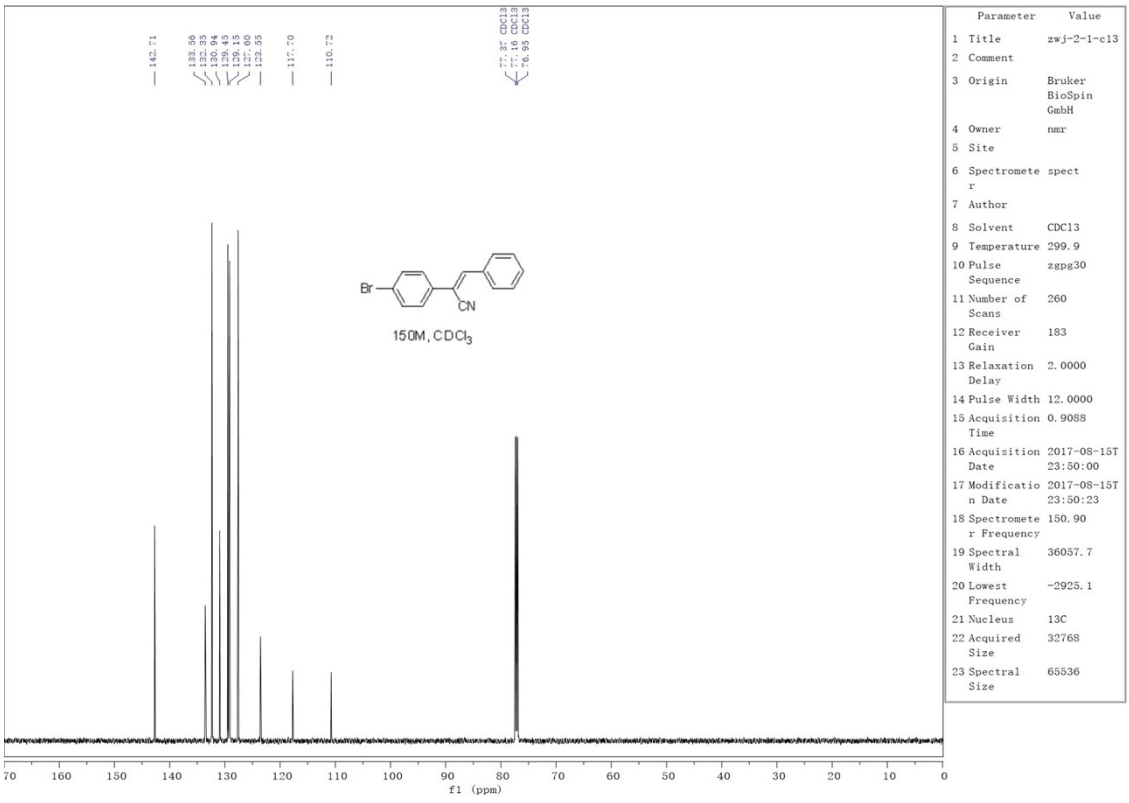
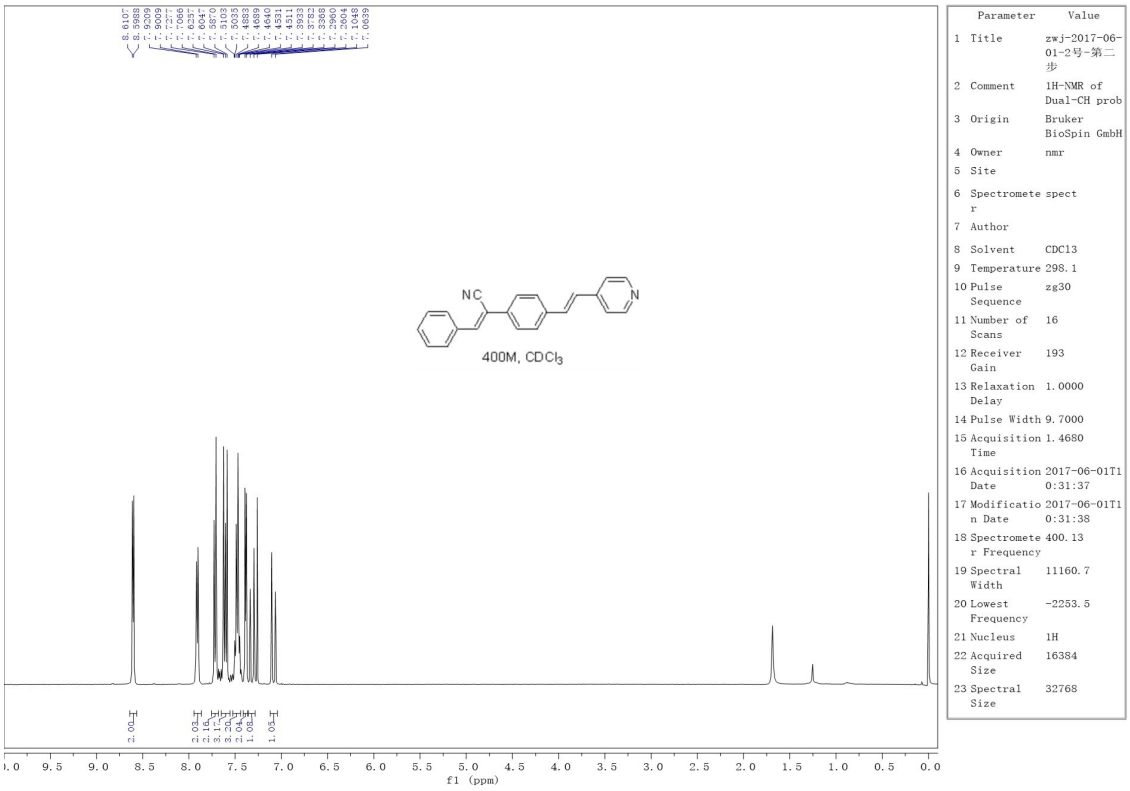


Fig. S27 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1-1.



	Parameter	Value
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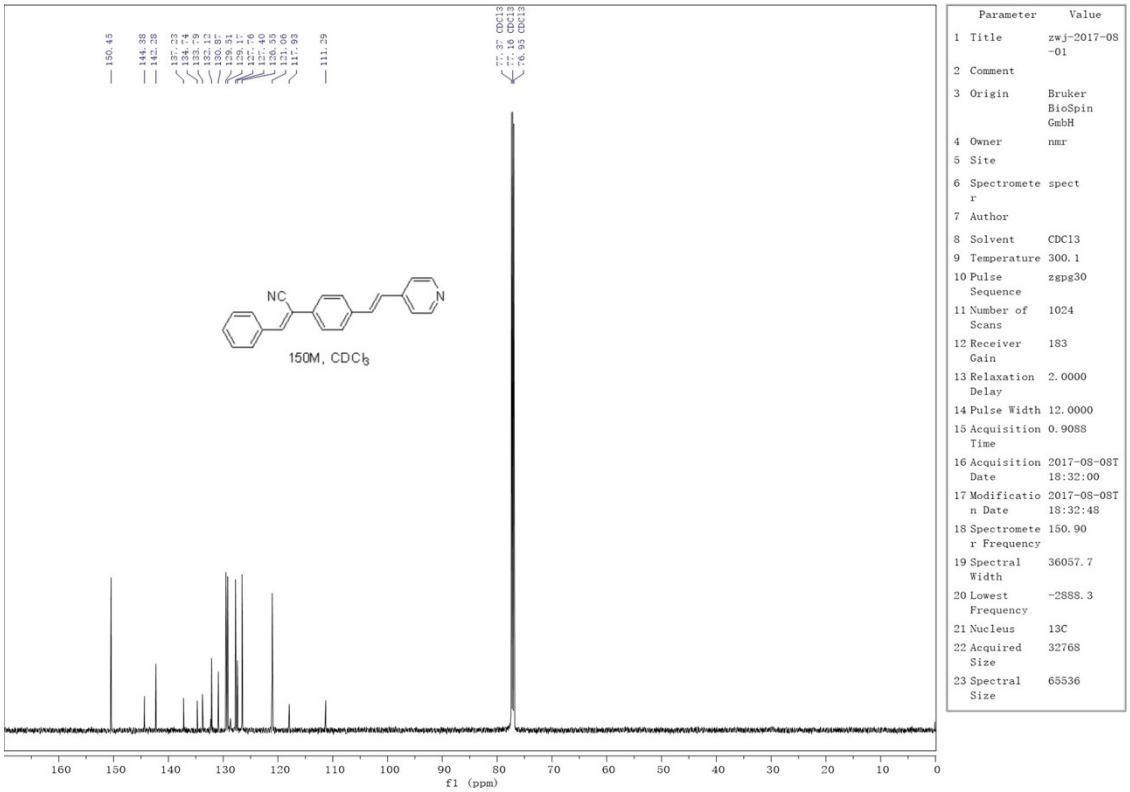
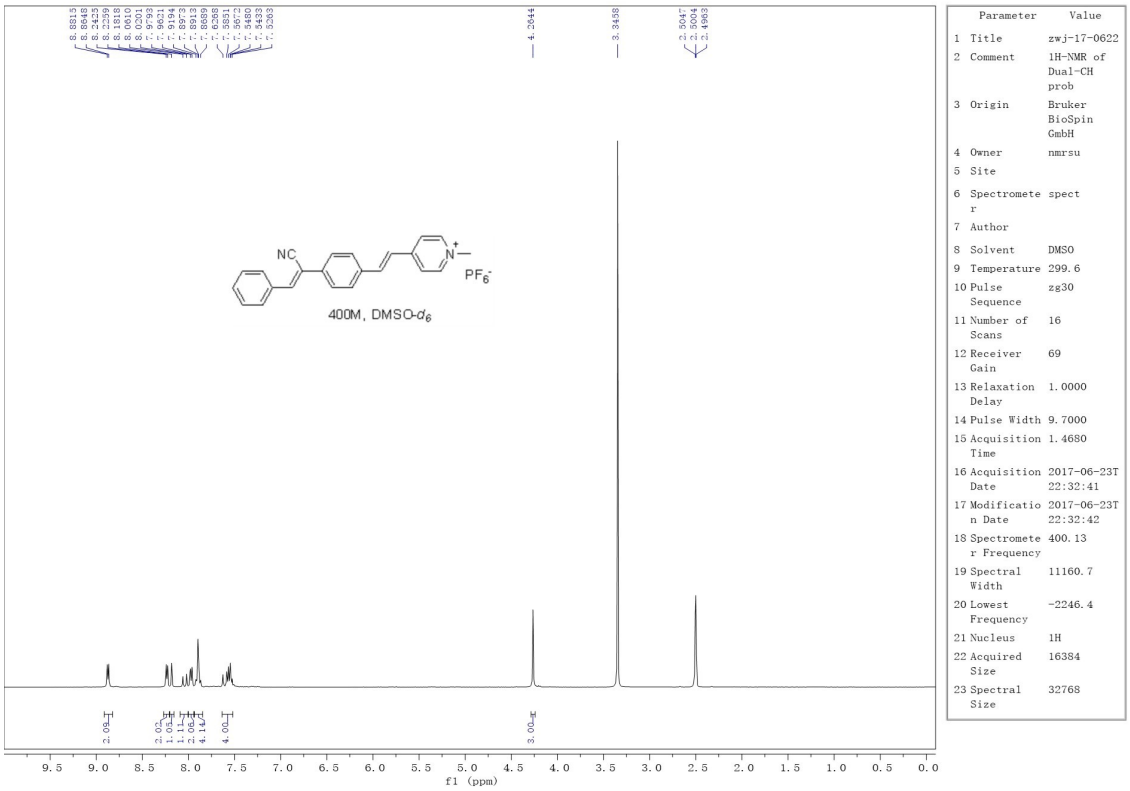
2	Comment	1H-NMR of Dual-CH prob
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect r
7	Author	
8	Solvent	CDCl3
9	Temperature	298.1
10	Pulse Sequence	zg30
11	Number of Scans	16
12	Receiver Gain	193
13	Relaxation Delay	1.0000
14	Pulse Width	9.7000
15	Acquisition Time	1.4680
16	Acquisition Date	2017-06-01T10:31:37
17	Modification Date	2017-06-01T10:31:38
18	Spectrometer Frequency	400.13
19	Spectral Width	11160.7
20	Lowest Frequency	-2253.5
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	32768

Fig. S28 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-2.



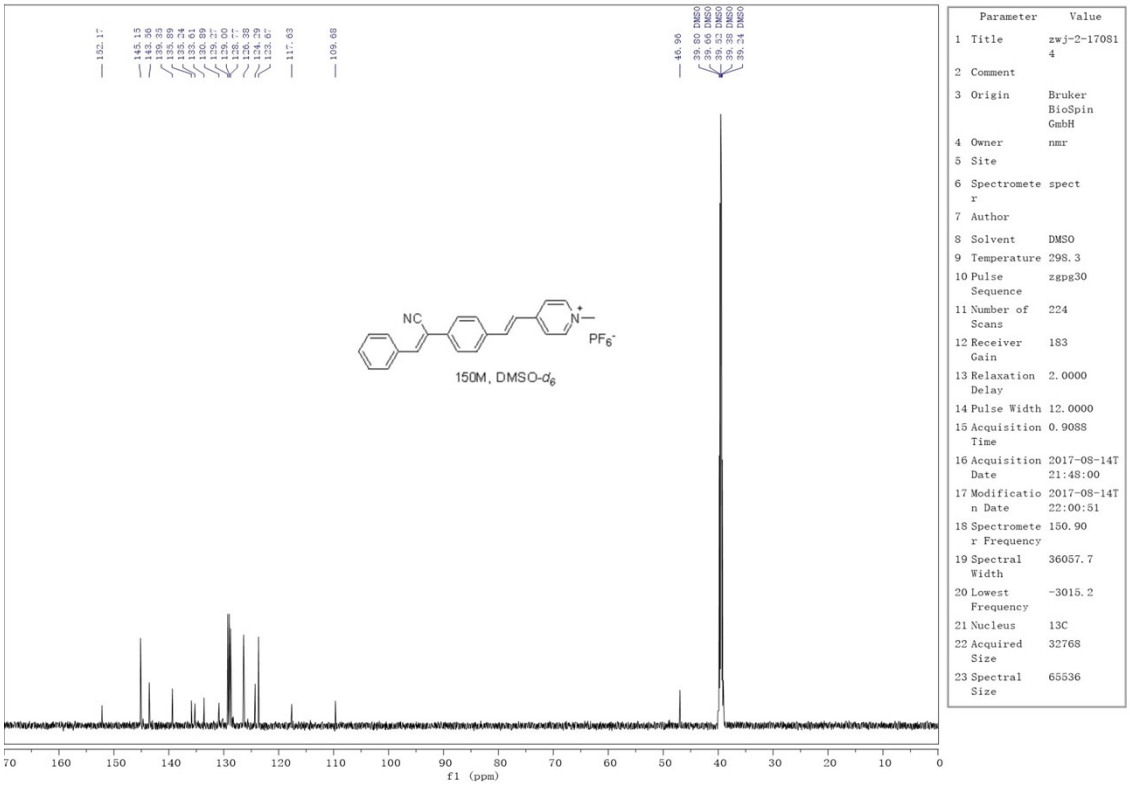
	Parameter	Value
1	Title	zwj-2017-08-01
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect r
7	Author	
8	Solvent	CDCl3
9	Temperature	300.1
10	Pulse Sequence	zgpg30
11	Number of Scans	1024
12	Receiver Gain	183
13	Relaxation Delay	2.0000
14	Pulse Width	12.0000
15	Acquisition Time	0.9088
16	Acquisition Date	2017-08-08T18:32:00
17	Modification Date	2017-08-08T18:32:48
18	Spectrometer Frequency	150.90
19	Spectral Width	36057.7
20	Lowest Frequency	-2888.3
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536

Fig. S29 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1-2.



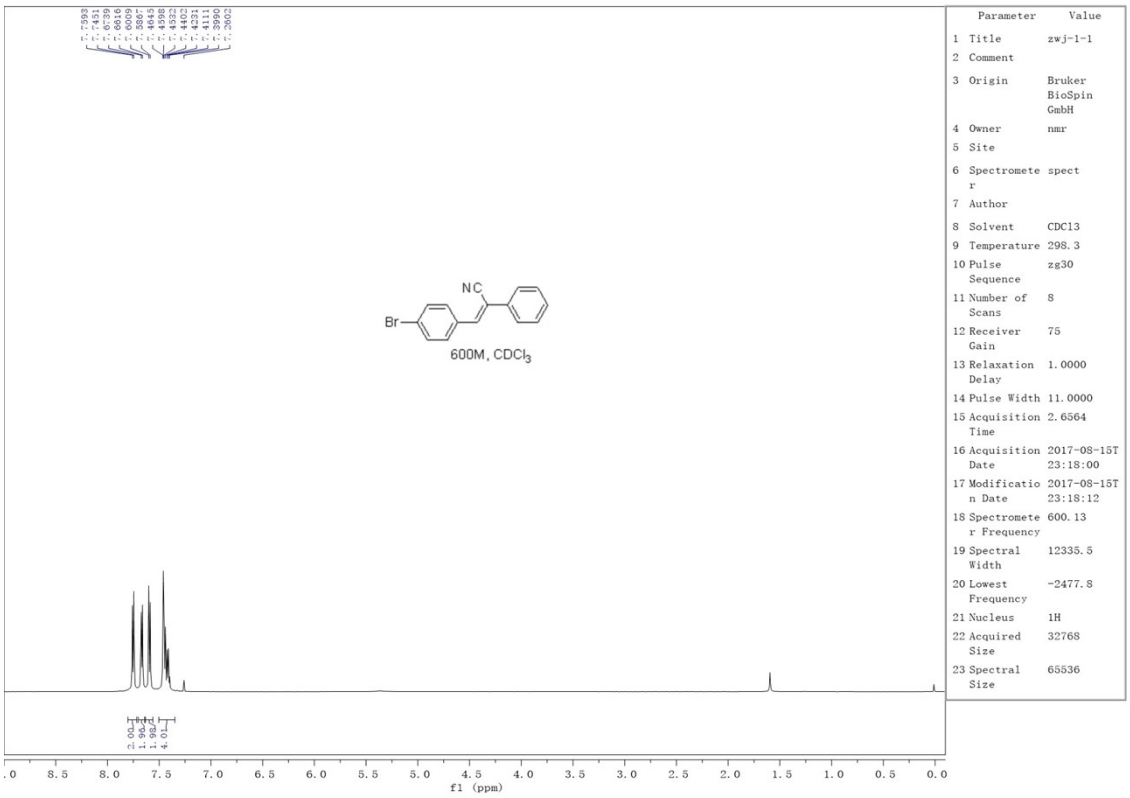
Parameter	Value
1 Title	zwj-17-0622
2 Comment	1H-NMR of Dual-CH prob
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	DMSO
9 Temperature	299.6
10 Pulse Sequence	zg30
11 Number of Scans	16
12 Receiver Gain	69
13 Relaxation Delay	1.0000
14 Pulse Width	9.7000
15 Acquisition Time	1.4680
16 Acquisition Date	2017-06-23T 22:32:41
17 Modification Date	2017-06-23T 22:32:42
18 Spectrometer Frequency	400.13
19 Spectral Width	11160.7
20 Lowest Frequency	-2246.4
21 Nucleus	1H
22 Acquired Size	16384
23 Spectral Size	32768

Fig. S30 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of PSMP-1.



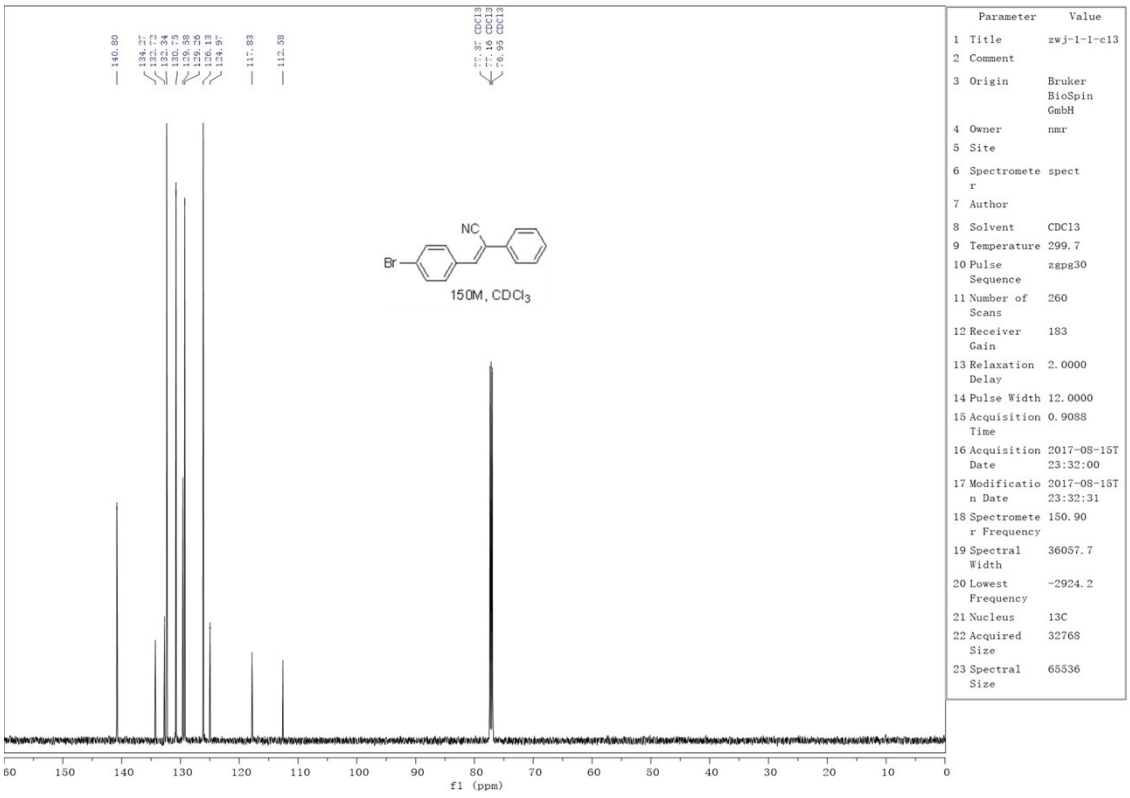
Parameter	Value
1 Title	zwj-2-170814
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	DMSO
9 Temperature	298.3
10 Pulse Sequence	zgpg30
11 Number of Scans	224
12 Receiver Gain	183
13 Relaxation Delay	2.0000
14 Pulse Width	12.0000
15 Acquisition Time	0.9088
16 Acquisition Date	2017-08-14T 21:48:00
17 Modification Date	2017-08-14T 22:00:51
18 Spectrometer Frequency	150.90
19 Spectral Width	36057.7
20 Lowest Frequency	-3015.2
21 Nucleus	13C
22 Acquired Size	32768
23 Spectral Size	65536

Fig. S31 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of PSMP-1.



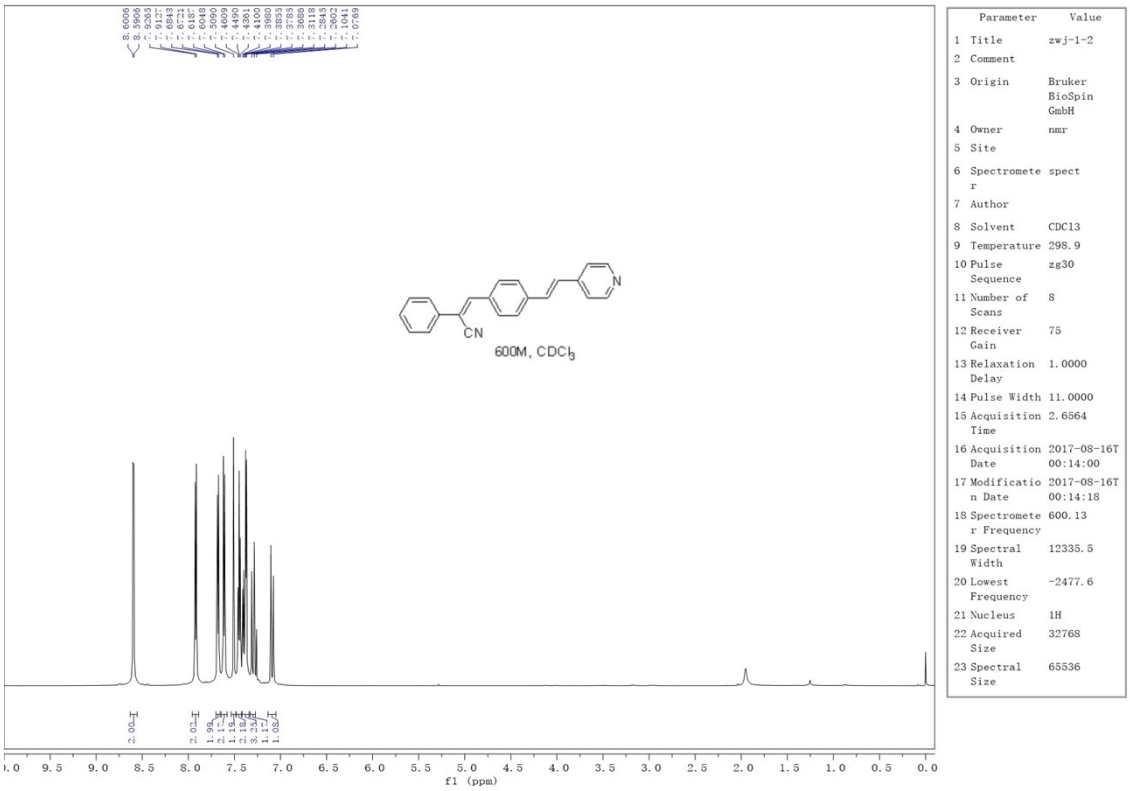
	Parameter	Value
1	Title	zwj-1-1
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect r
7	Author	
8	Solvent	CDCl3
9	Temperature	298.3
10	Pulse Sequence	zg30
11	Number of Scans	8
12	Receiver Gain	75
13	Relaxation Delay	1.0000
14	Pulse Width	11.0000
15	Acquisition Time	2.6564
16	Acquisition Date	2017-08-15T 23:18:00
17	Modification Date	2017-08-15T 23:18:12
18	Spectrometer Frequency	600.13
19	Spectral Width	12335.5
20	Lowest Frequency	-2477.8
21	Nucleus	1H
22	Acquired Size	32768
23	Spectral Size	65536

Fig. S32 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 2-1.



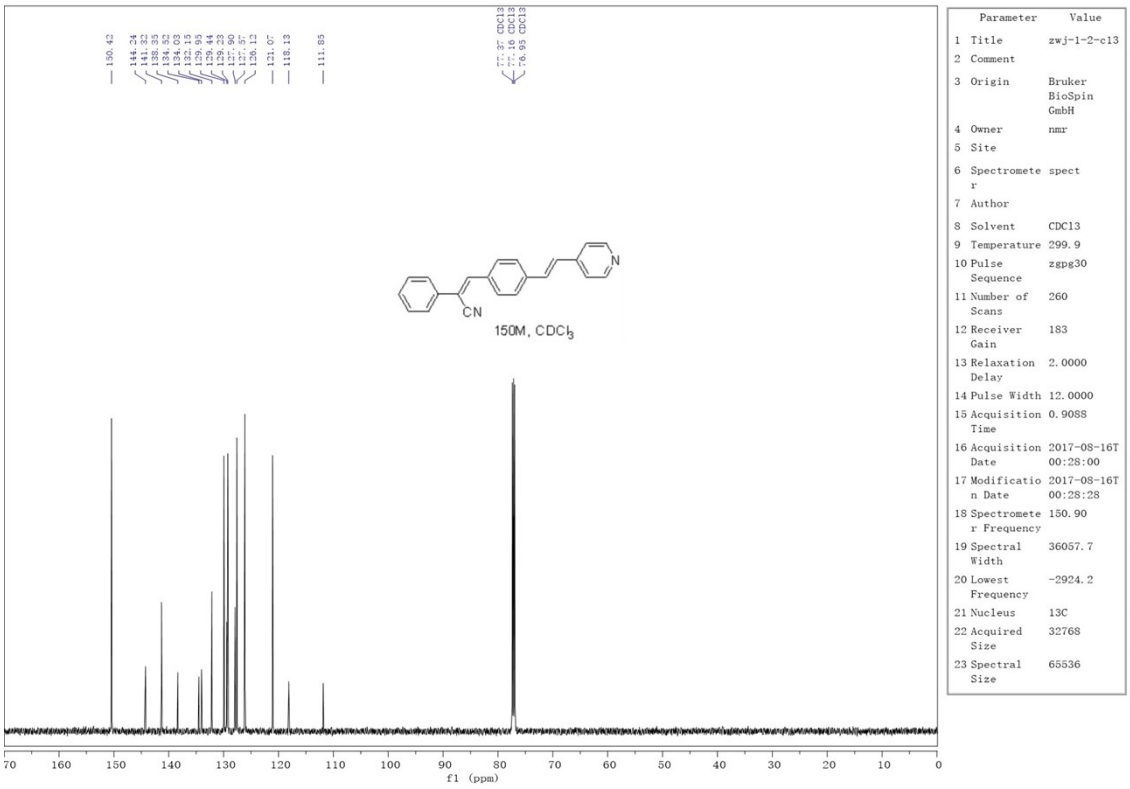
	Parameter	Value
1	Title	zwj-1-1-c13
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect r
7	Author	
8	Solvent	CDCl3
9	Temperature	299.7
10	Pulse Sequence	zgpg30
11	Number of Scans	260
12	Receiver Gain	183
13	Relaxation Delay	2.0000
14	Pulse Width	12.0000
15	Acquisition Time	0.9088
16	Acquisition Date	2017-08-15T 23:32:00
17	Modification Date	2017-08-15T 23:32:31
18	Spectrometer Frequency	150.90
19	Spectral Width	36057.7
20	Lowest Frequency	-2924.2
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536

Fig. S33 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 2-1.



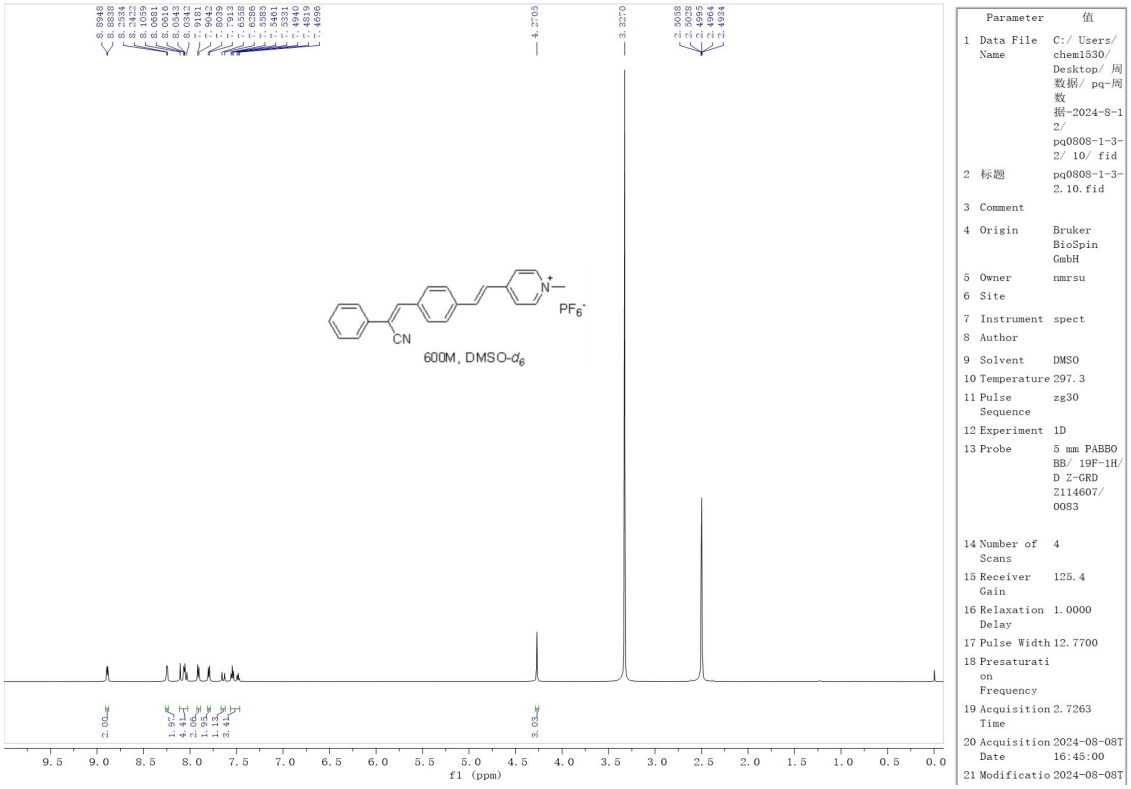
Parameter	Value
1 Title	zwj-1-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	CDCl3
9 Temperature	298.9
10 Pulse Sequence	zg30
11 Number of Scans	8
12 Receiver Gain	75
13 Relaxation Delay	1.0000
14 Pulse Width	11.0000
15 Acquisition Time	2.6564
16 Acquisition Date	2017-08-16T 00:14:00
17 Modification Date	2017-08-16T 00:14:18
18 Spectrometer Frequency	600.13
19 Spectral Width	12335.5
20 Lowest Frequency	-2477.6
21 Nucleus	1H
22 Acquired Size	32768
23 Spectral Size	65536

Fig. S34 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 2-2.



Parameter	Value
1 Title	zwj-1-2-c13
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	CDCl3
9 Temperature	299.9
10 Pulse Sequence	zgpg30
11 Number of Scans	260
12 Receiver Gain	183
13 Relaxation Delay	2.0000
14 Pulse Width	12.0000
15 Acquisition Time	0.9088
16 Acquisition Date	2017-08-16T 00:28:00
17 Modification Date	2017-08-16T 00:28:28
18 Spectrometer Frequency	150.90
19 Spectral Width	36057.7
20 Lowest Frequency	-2924.2
21 Nucleus	13C
22 Acquired Size	32768
23 Spectral Size	65536

Fig. S35 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 2-2.



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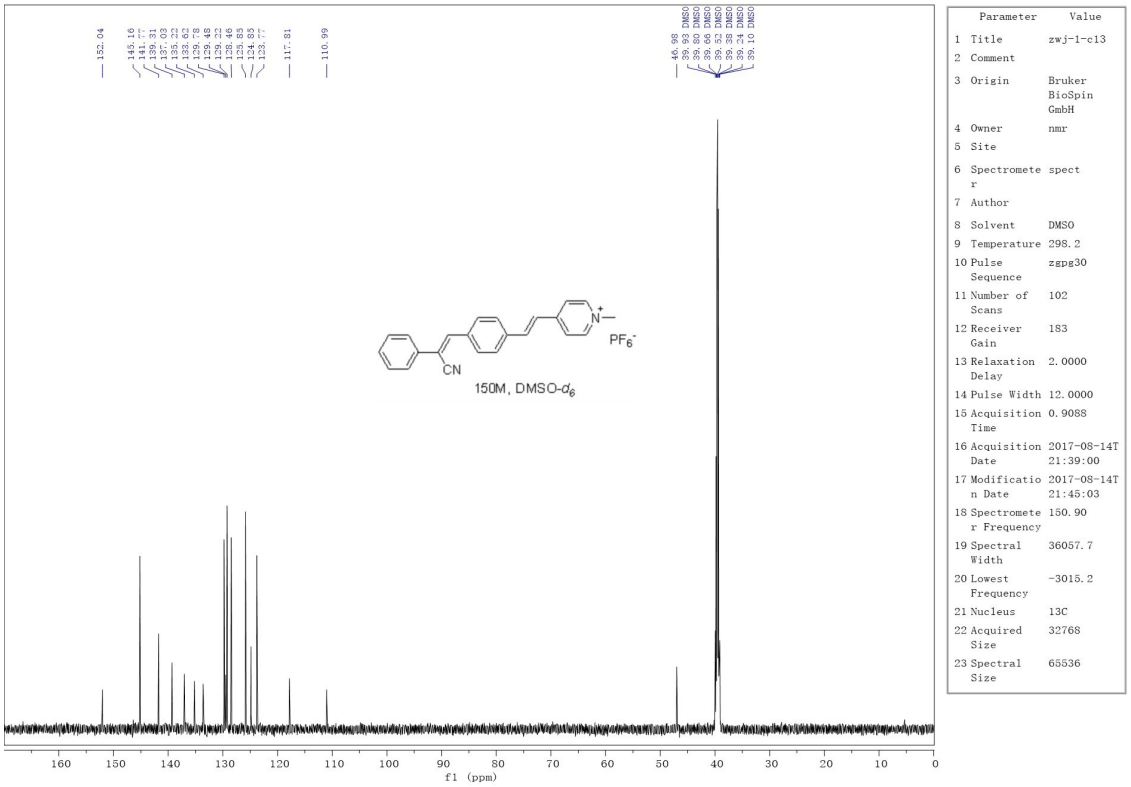
1 Data File Name	C:/ Users/ chem1530/ Desktop/ 周数据/ pq-周数据-2024-8-12/ pq0808-1-3-2/ 10/ fid
2 标题	pq0808-1-3-2.10.fid
3 Comment	
4 Origin	Bruker BioSpin GmbH
5 Owner	nmrsu
6 Site	
7 Instrument	spect
8 Author	
9 Solvent	DMSO
10 Temperature	297.3
11 Pulse Sequence	zg30
12 Experiment	1D
13 Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0083
14 Number of Scans	4
15 Receiver Gain	125.4
16 Relaxation Delay	1.0000
17 Pulse Width	12.7700
18 Presaturation Frequency	
19 Acquisition Time	2.7263
20 Acquisition Date	2024-08-08T 16:45:00
21 Modificatio	2024-08-08T

Fig. S36 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of compound PSMP-2.



Parameter	Value
1 Title	zwj-1-c13
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	DMSO
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Number of Scans	102
12 Receiver Gain	183
13 Relaxation Delay	2.0000
14 Pulse Width	12.0000
15 Acquisition Time	0.9088
16 Acquisition Date	2017-08-14T 21:39:00
17 Modification Date	2017-08-14T 21:45:03
18 Spectrometer Frequency	150.90
19 Spectral Width	36057.7
20 Lowest Frequency	-3015.2
21 Nucleus	13C
22 Acquired Size	32768
23 Spectral Size	65536

Fig. S37 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of compound PSMP-2.

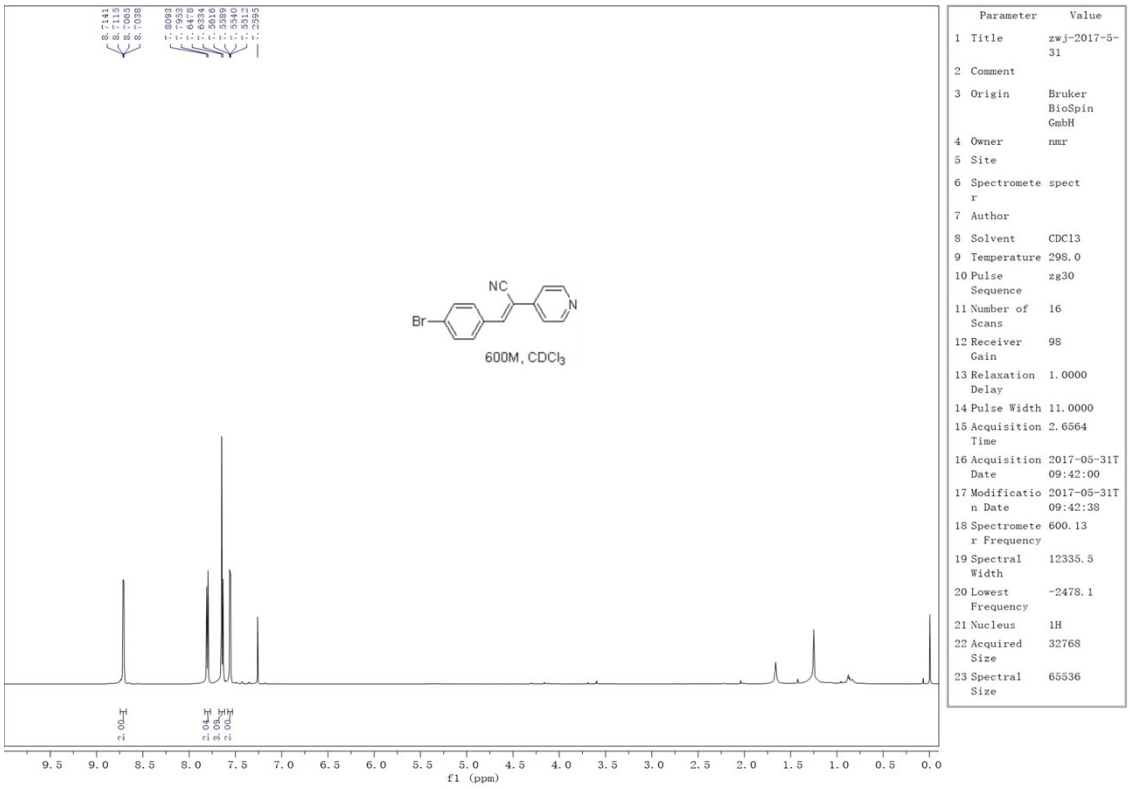


Fig. S38 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3-1.

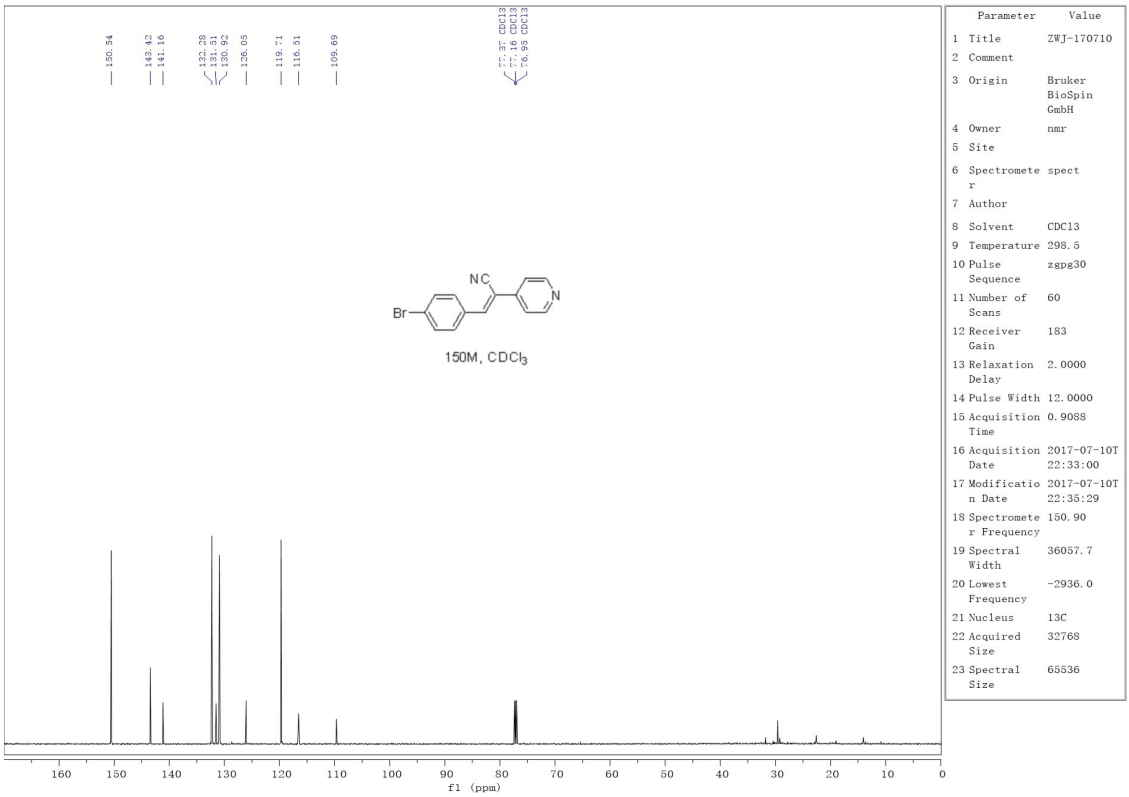


Fig. S39 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 3-1.

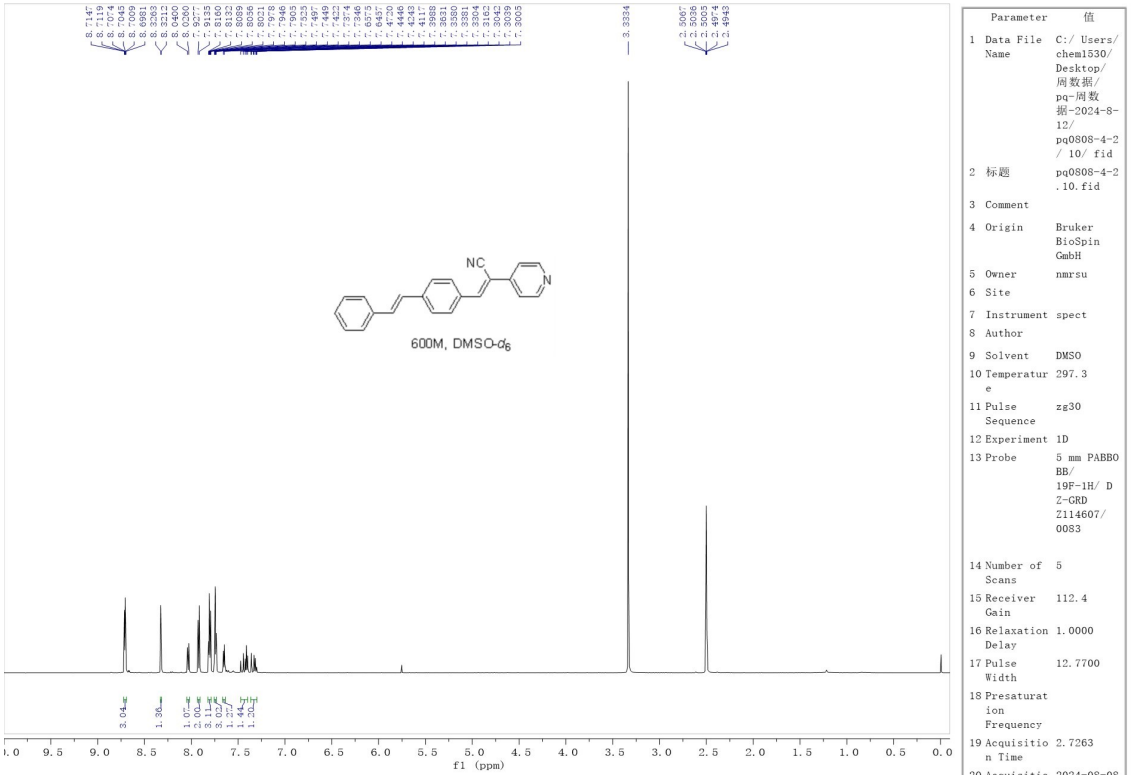


Fig. S40 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of compound 3-2.

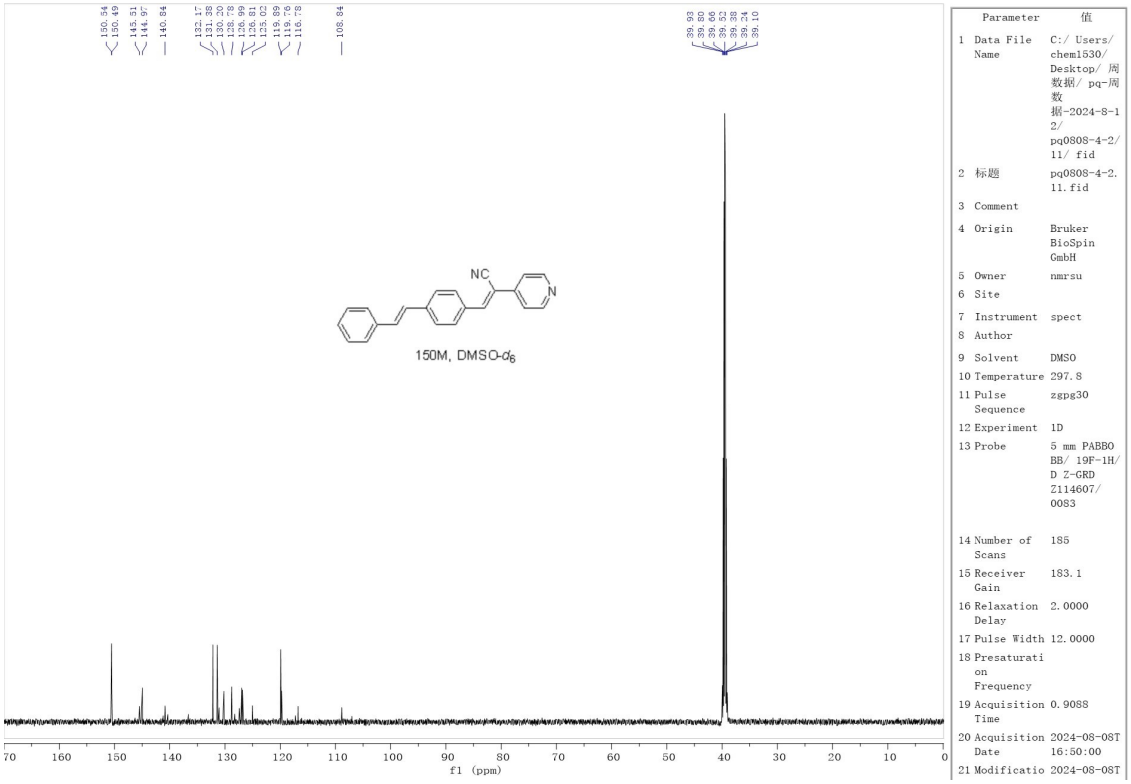
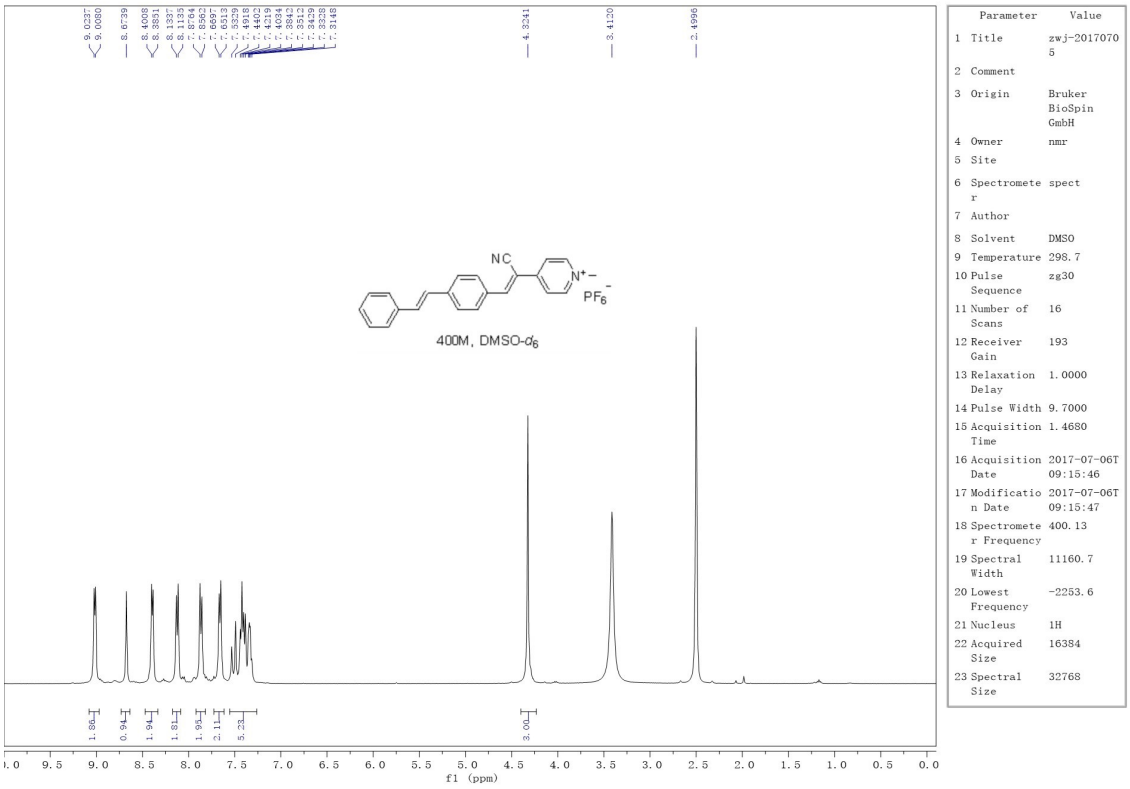
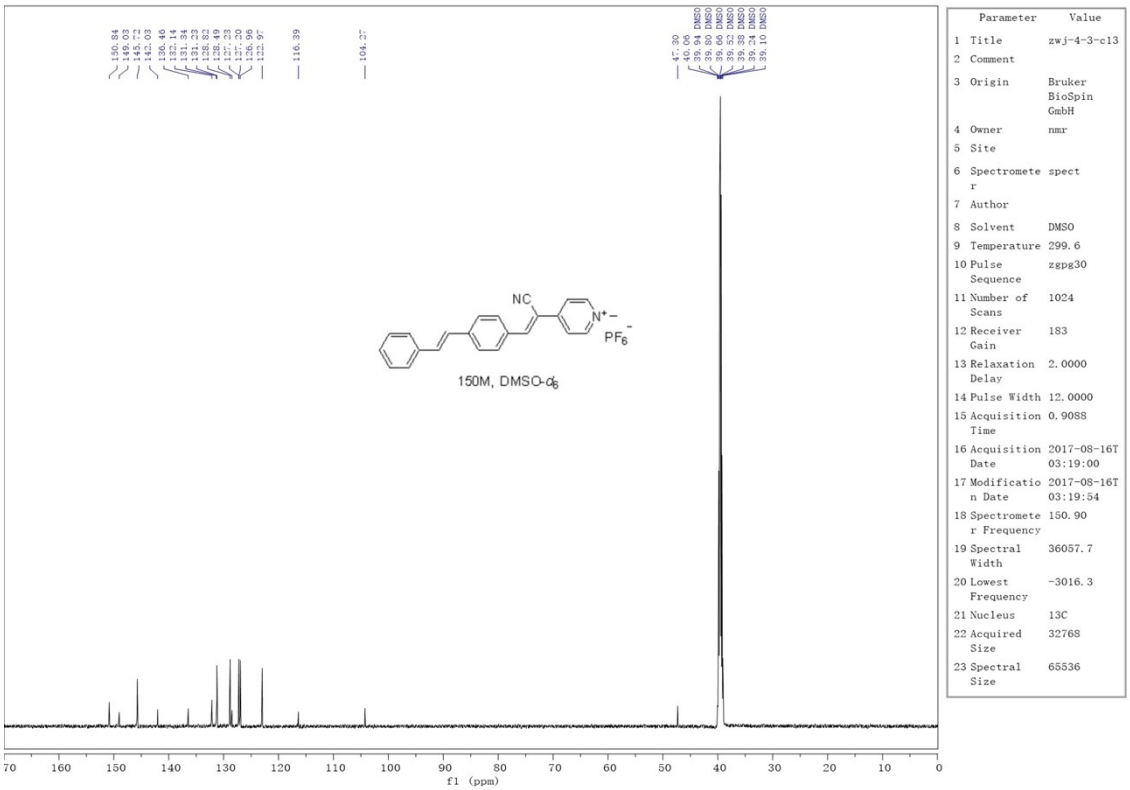


Fig. S41 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of compound 3-2.



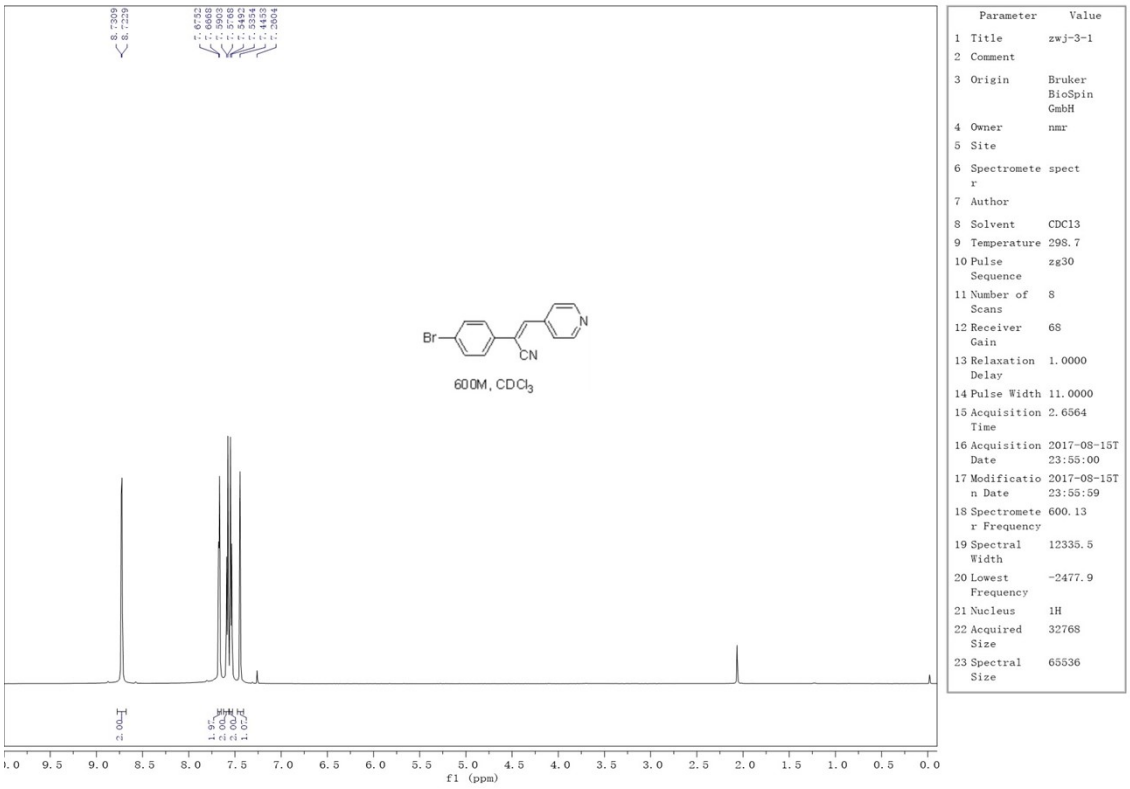
Parameter	Value
1 Title	zwj-20170705
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	DMSO
9 Temperature	298.7
10 Pulse Sequence	zg30
11 Number of Scans	16
12 Receiver Gain	193
13 Relaxation Delay	1.0000
14 Pulse Width	9.7000
15 Acquisition Time	1.4680
16 Acquisition Date	2017-07-06T 09:15:46
17 Modification Date	2017-07-06T 09:15:47
18 Spectrometer Frequency	400.13
19 Spectral Width	11160.7
20 Lowest Frequency	-2253.6
21 Nucleus	1H
22 Acquired Size	16384
23 Spectral Size	32768

Fig. S42 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound PSMP-3.



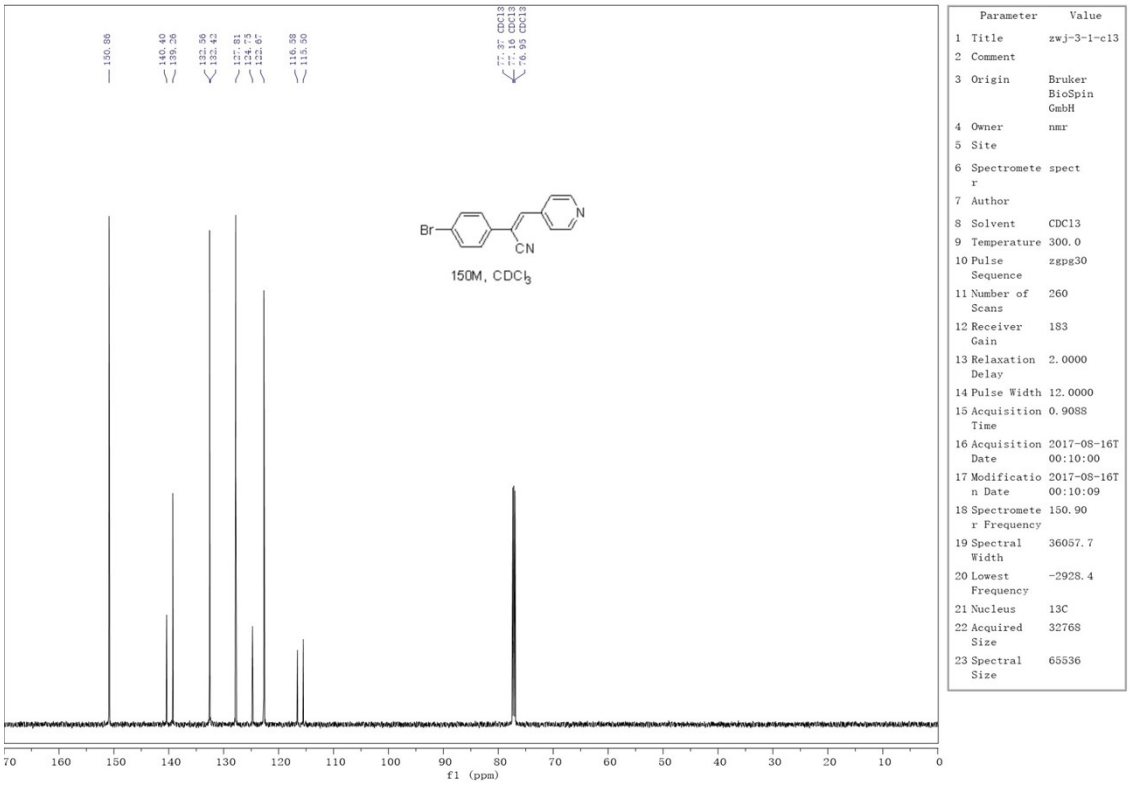
Parameter	Value
1 Title	zwj-4-3-c13
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	DMSO
9 Temperature	299.6
10 Pulse Sequence	zgpg30
11 Number of Scans	1024
12 Receiver Gain	183
13 Relaxation Delay	2.0000
14 Pulse Width	12.0000
15 Acquisition Time	0.9088
16 Acquisition Date	2017-08-16T 03:19:00
17 Modification Date	2017-08-16T 03:19:54
18 Spectrometer Frequency	150.90
19 Spectral Width	36057.7
20 Lowest Frequency	-3016.3
21 Nucleus	13C
22 Acquired Size	32768
23 Spectral Size	65536

Fig. S43 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of compound PSMP-3.



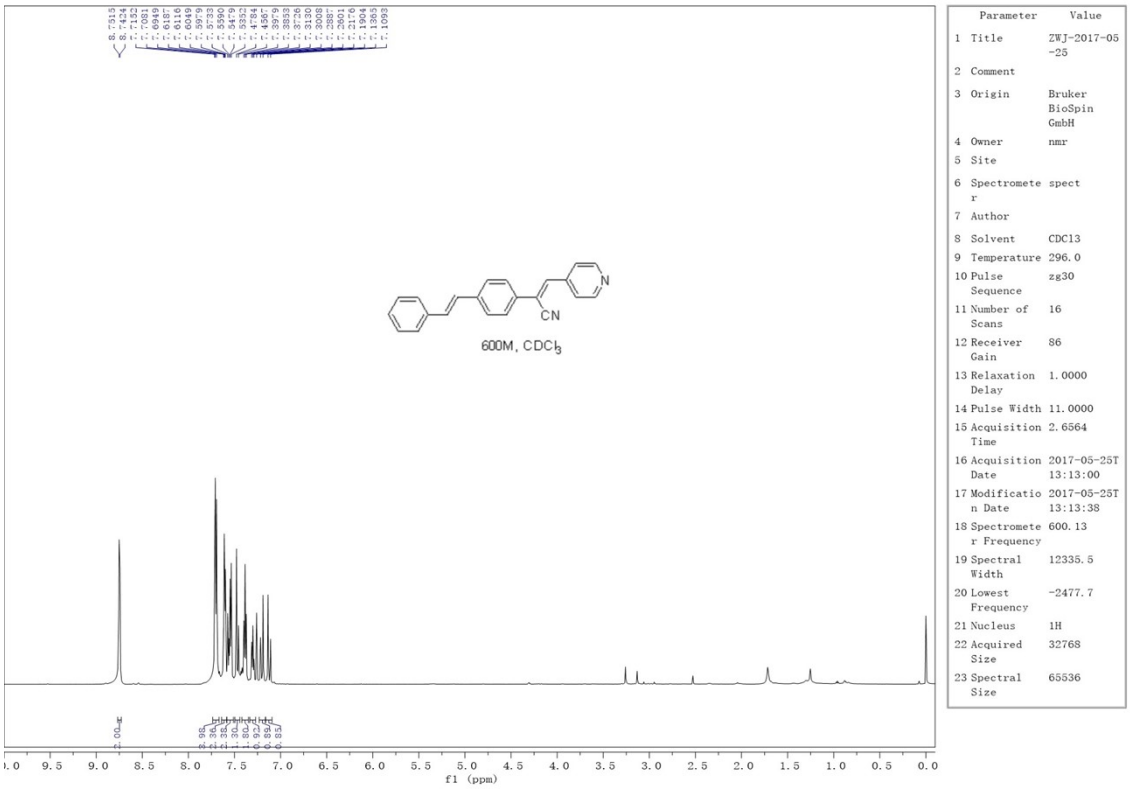
	Parameter	Value
1	Title	zwj-3-1
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect
7	Author	
8	Solvent	CDCl3
9	Temperature	298.7
10	Pulse Sequence	zg30
11	Number of Scans	8
12	Receiver Gain	68
13	Relaxation Delay	1.0000
14	Pulse Width	11.0000
15	Acquisition Time	2.6564
16	Acquisition Date	2017-08-15T 23:55:00
17	Modification Date	2017-08-15T 23:55:59
18	Spectrometer Frequency	600.13
19	Spectral Width	12335.5
20	Lowest Frequency	-2477.9
21	Nucleus	1H
22	Acquired Size	32768
23	Spectral Size	65536

Fig. S44 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4-1.



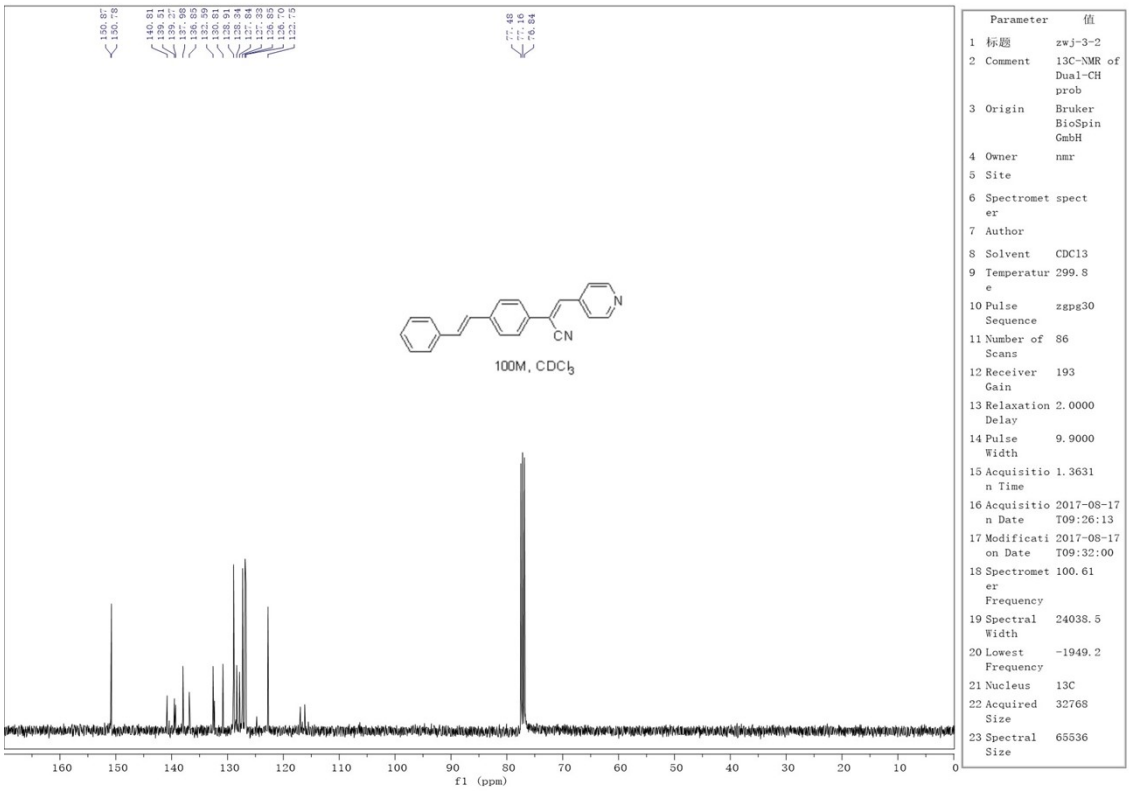
	Parameter	Value
1	Title	zwj-3-1-c13
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect
7	Author	
8	Solvent	CDCl3
9	Temperature	300.0
10	Pulse Sequence	zgpg30
11	Number of Scans	260
12	Receiver Gain	183
13	Relaxation Delay	2.0000
14	Pulse Width	12.0000
15	Acquisition Time	0.9088
16	Acquisition Date	2017-08-16T 00:10:00
17	Modification Date	2017-08-16T 00:10:09
18	Spectrometer Frequency	150.90
19	Spectral Width	36057.7
20	Lowest Frequency	-2928.4
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536

Fig. S45 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 4-1.



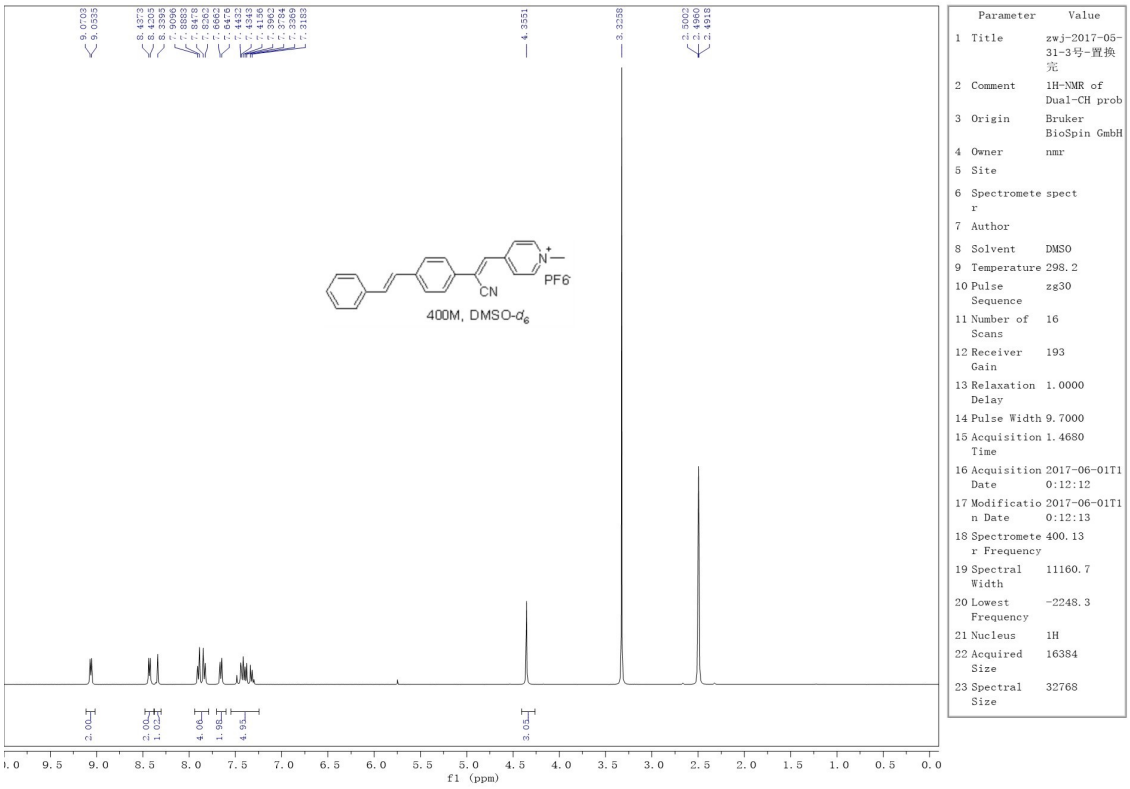
	Parameter	Value
1	Title	ZWJ-2017-05-25
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect
7	Author	
8	Solvent	CDCl3
9	Temperature	296.0
10	Pulse Sequence	zg30
11	Number of Scans	16
12	Receiver Gain	86
13	Relaxation Delay	1.0000
14	Pulse Width	11.0000
15	Acquisition Time	2.6564
16	Acquisition Date	2017-05-25T13:13:00
17	Modification Date	2017-05-25T13:13:38
18	Spectrometer Frequency	600.13
19	Spectral Width	12335.5
20	Lowest Frequency	-2477.7
21	Nucleus	1H
22	Acquired Size	32768
23	Spectral Size	65536

Fig. S46 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4-2.



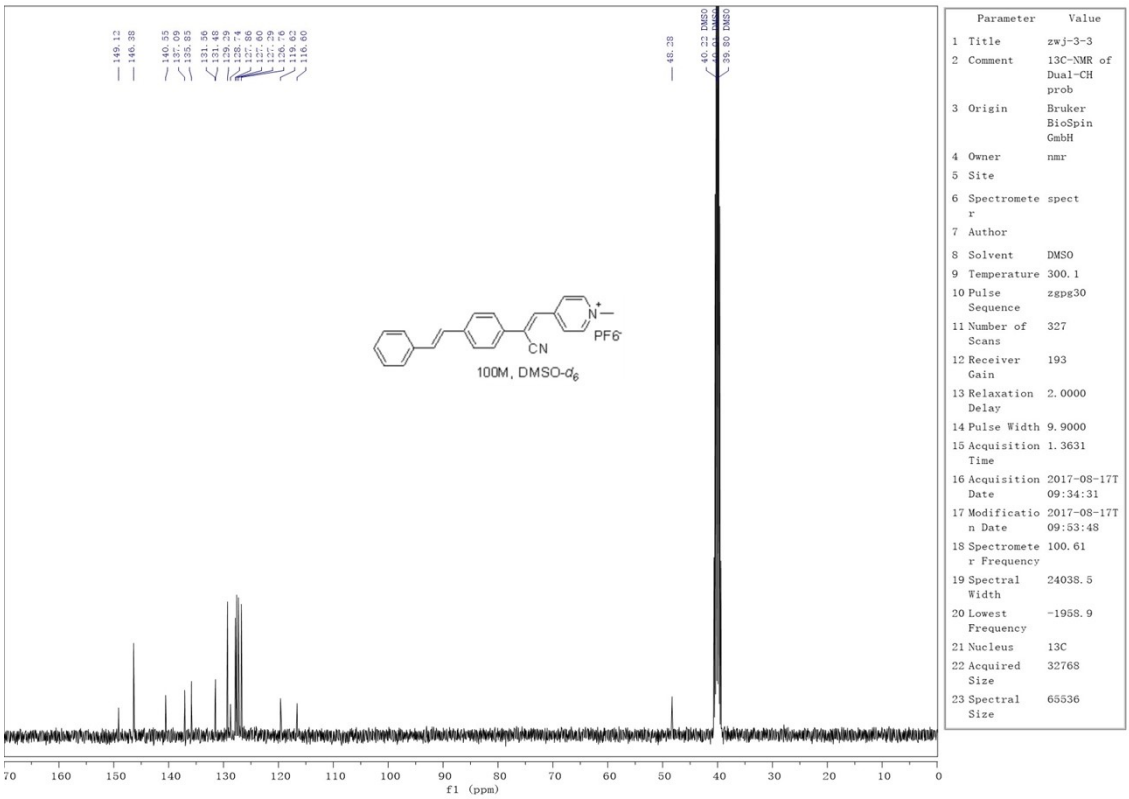
	Parameter	值
1	标题	zwj-3-2
2	Comment	13C-NMR of Dual-CH prob
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect
7	Author	
8	Solvent	CDCl3
9	Temperature	299.8
10	Pulse Sequence	zgpg30
11	Number of Scans	86
12	Receiver Gain	193
13	Relaxation Delay	2.0000
14	Pulse Width	9.9000
15	Acquisition Time	1.3631
16	Acquisition Date	2017-08-17T09:26:13
17	Modification Date	2017-08-17T09:32:00
18	Spectrometer Frequency	100.61
19	Spectral Width	24038.5
20	Lowest Frequency	-1949.2
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536

Fig. S47 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 4-2.



Parameter	Value
1 Title	zwj-2017-05-31-3号-置换完
2 Comment	1H-NMR of Dual-CH prob
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect r
7 Author	
8 Solvent	DMSO
9 Temperature	298.2
10 Pulse Sequence	zg30
11 Number of Scans	16
12 Receiver Gain	193
13 Relaxation Delay	1.0000
14 Pulse Width	9.7000
15 Acquisition Time	1.4680
16 Acquisition Date	2017-06-01T10:12:12
17 Modification Date	2017-06-01T10:12:13
18 Spectrometer Frequency	400.13
19 Spectral Width	11160.7
20 Lowest Frequency	-2248.3
21 Nucleus	1H
22 Acquired Size	16384
23 Spectral Size	32768

Fig. S48 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound PSMP-4.



Parameter	Value
1 Title	zwj-3-3
2 Comment	13C-NMR of Dual-CH prob
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect r
7 Author	
8 Solvent	DMSO
9 Temperature	300.1
10 Pulse Sequence	zgpg30
11 Number of Scans	327
12 Receiver Gain	193
13 Relaxation Delay	2.0000
14 Pulse Width	9.9000
15 Acquisition Time	1.3631
16 Acquisition Date	2017-08-17T09:34:31
17 Modification Date	2017-08-17T09:53:48
18 Spectrometer Frequency	100.61
19 Spectral Width	24038.5
20 Lowest Frequency	-1958.9
21 Nucleus	13C
22 Acquired Size	32768
23 Spectral Size	65536

Fig. S49 ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound PSMP-4.

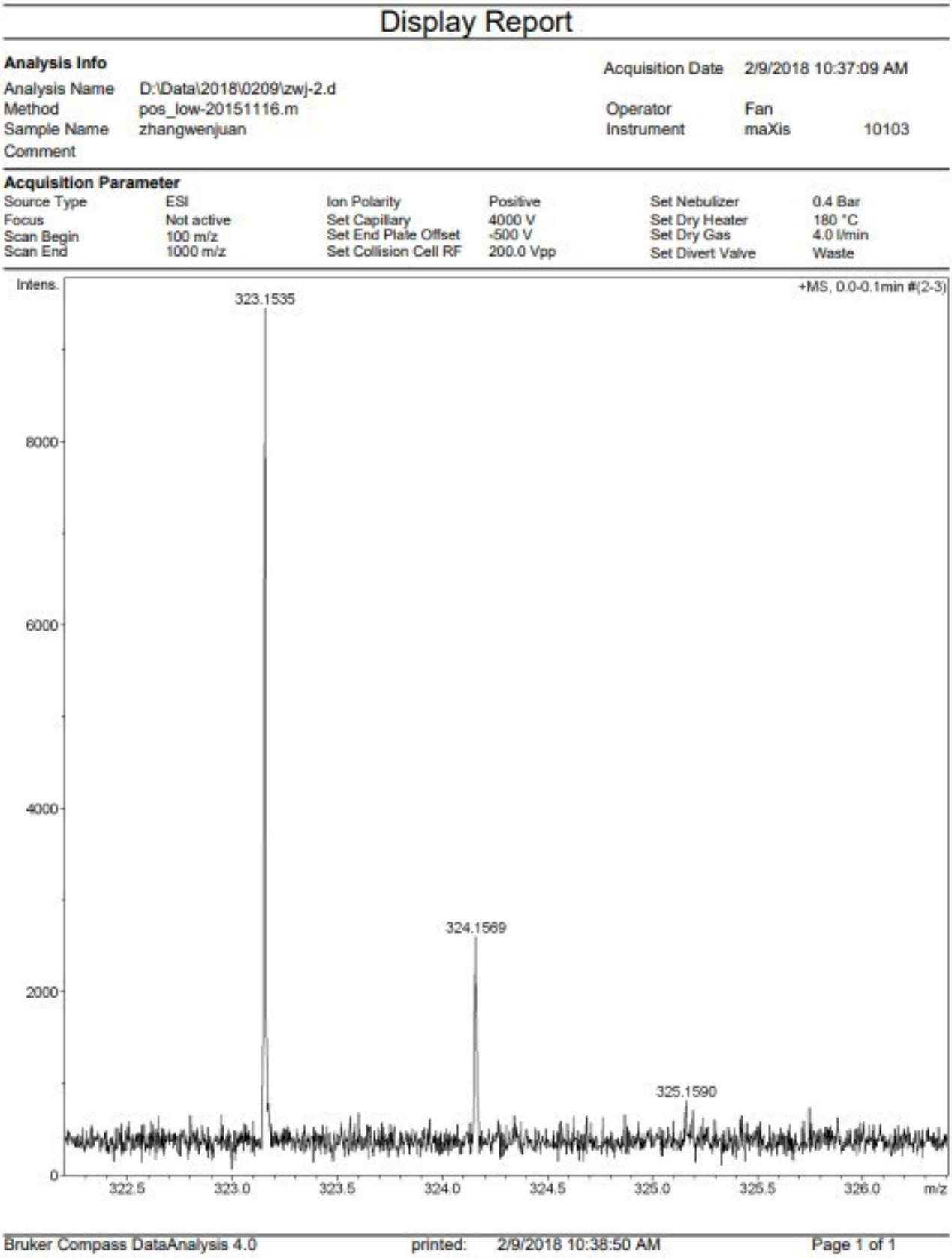


Fig. S50 High-resolution mass spectrum of PSMP-1.

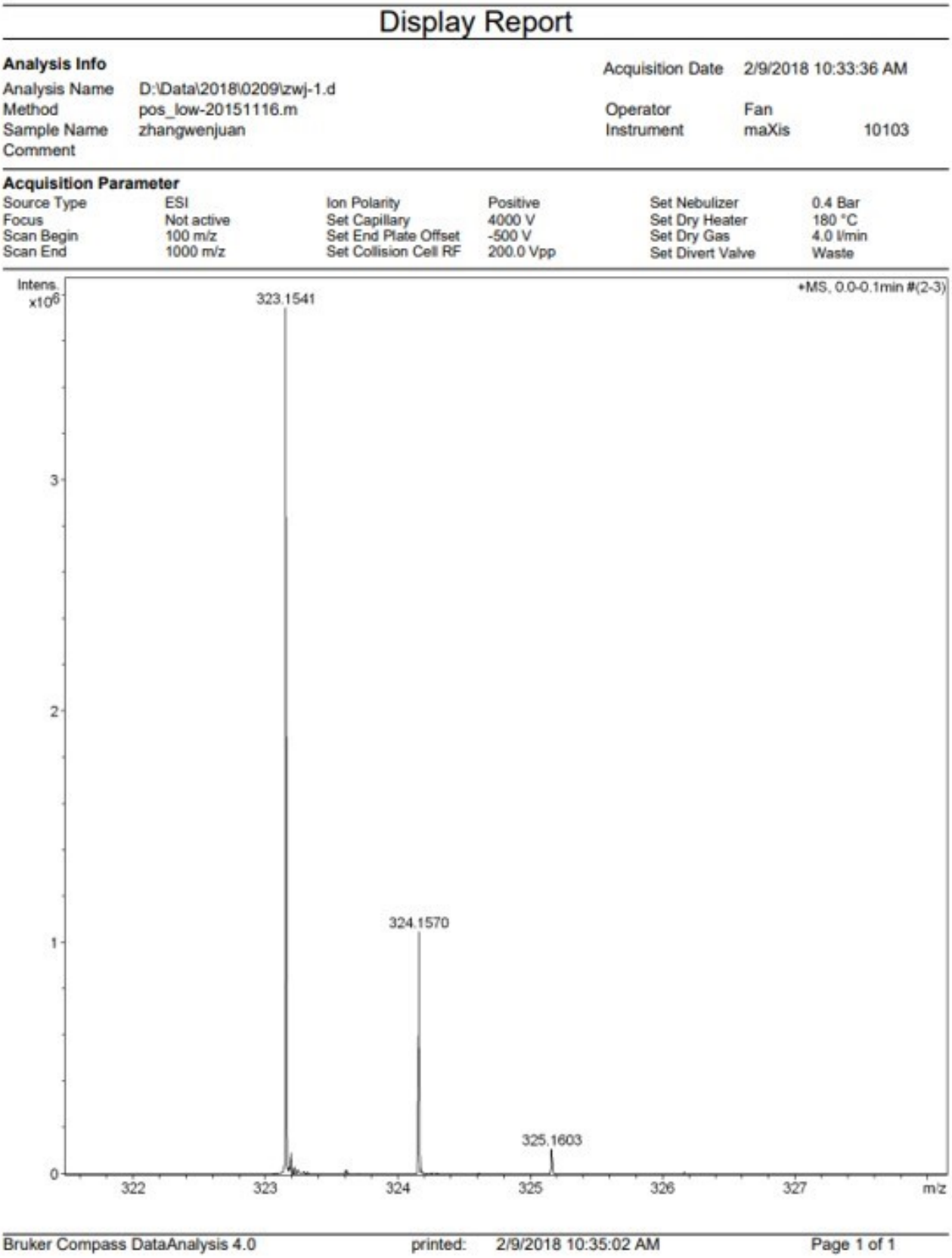


Fig. S51 High-resolution mass spectrum of PSMP-2.

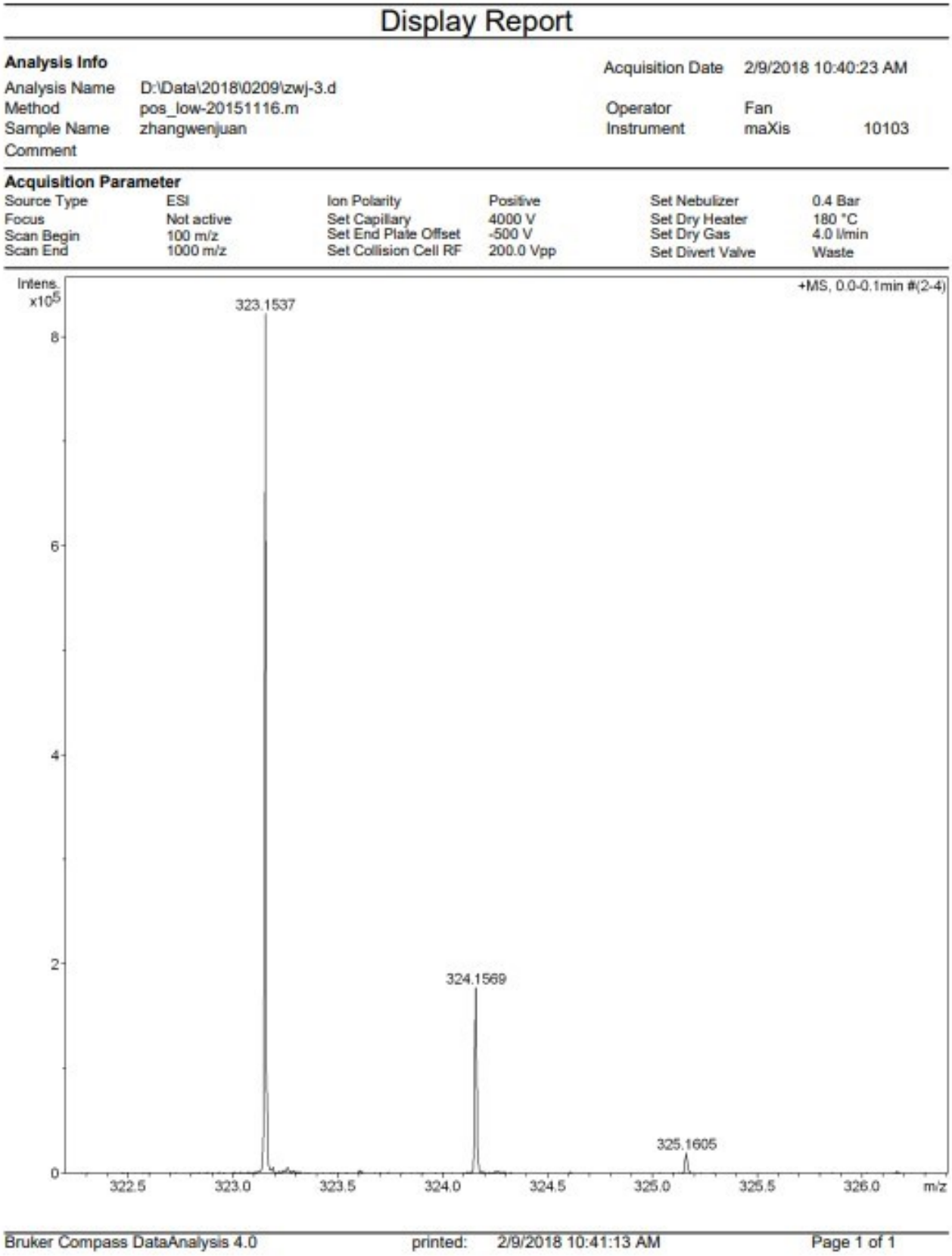


Fig. S52 High-resolution mass spectrum of PSMP-3.

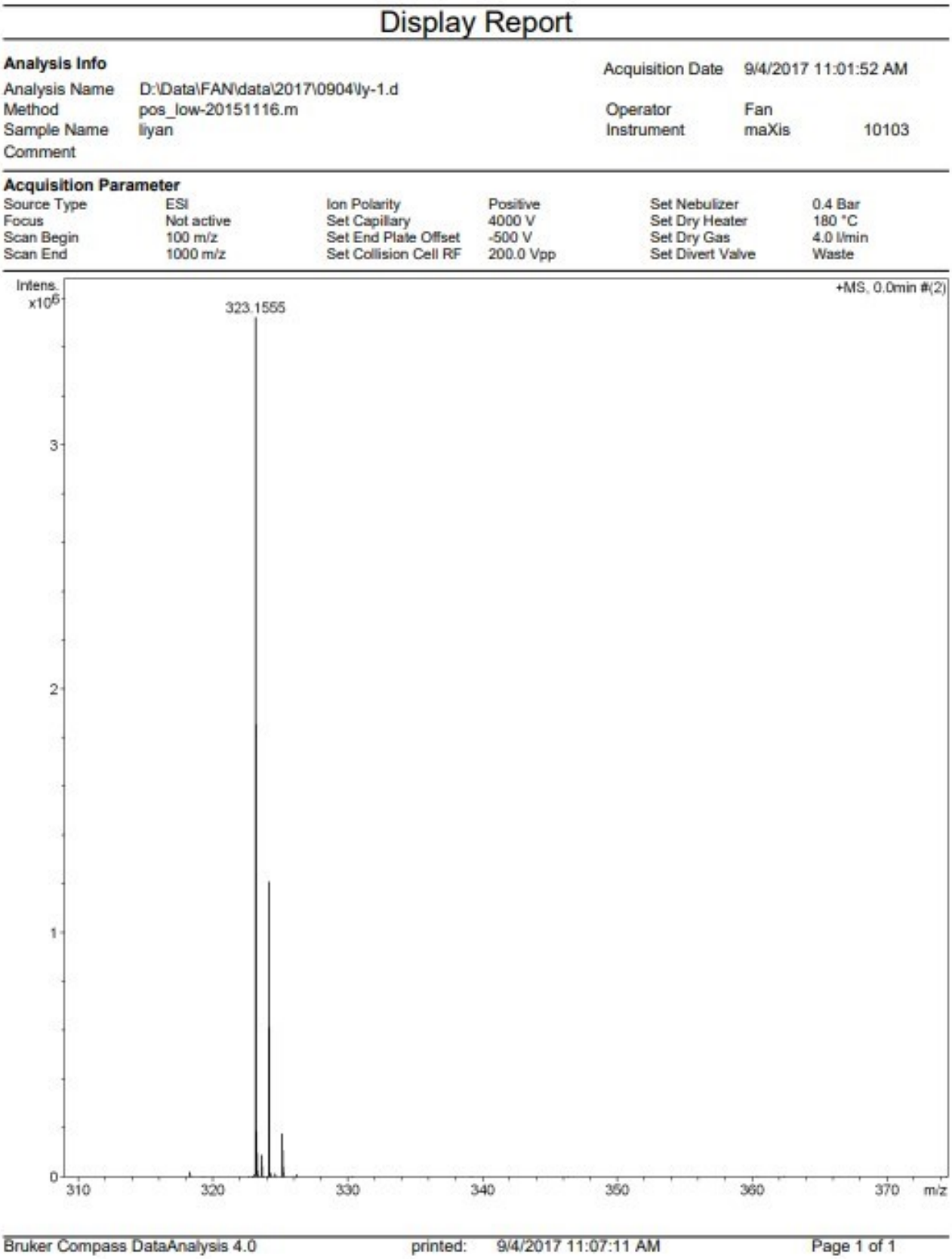


Fig. S53 High-resolution mass spectrum of PSMP-4.

References

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