

Supporting Information

A Nano Cocktail of NIR-II Emissive Fluorophore and Organoplatinum(II) Metallacycle for Efficient Cancer Imaging and Therapy

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1. Supplementary figures

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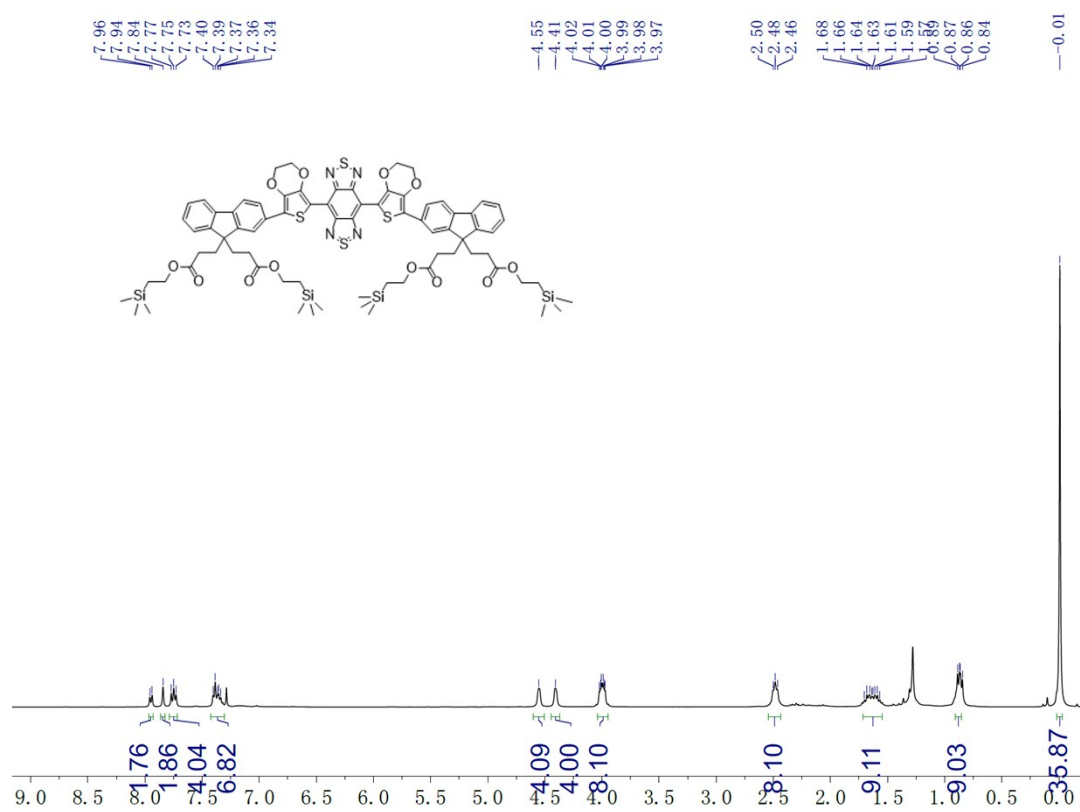


Figure S1. $^1\text{H-NMR}$ spectrum of SY1030.

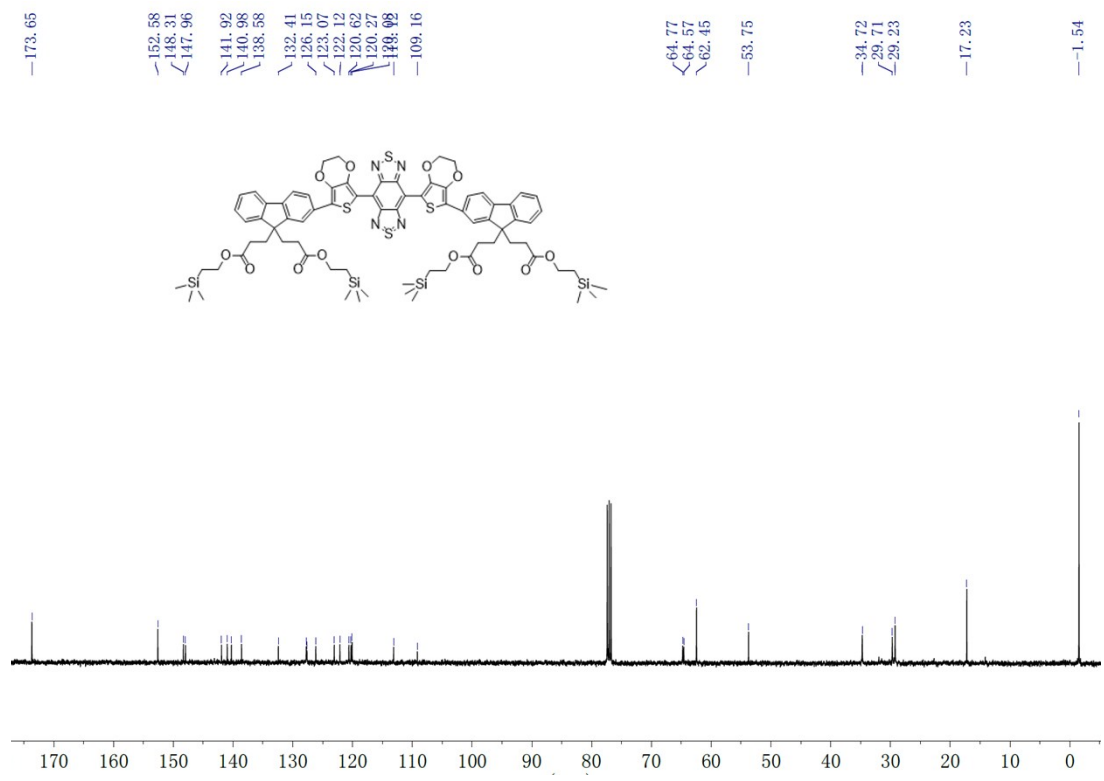


Figure S2. ¹³C-NMR spectrum of SY1030.

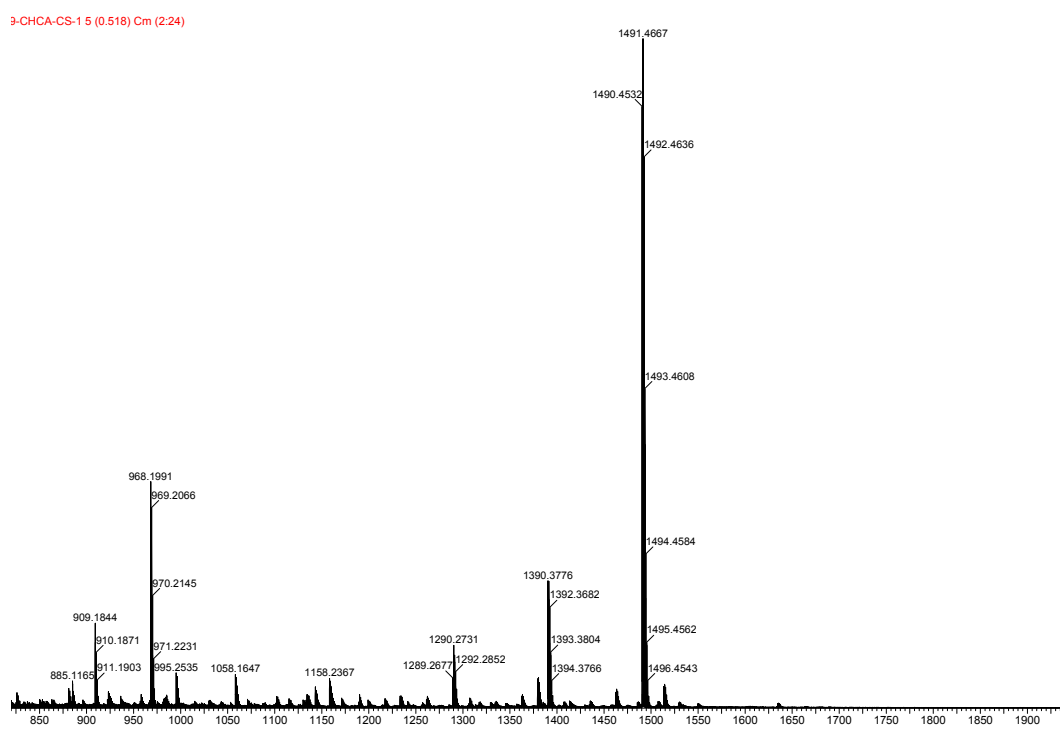


Figure S3. MALDI-TOF-MS of SY1030.

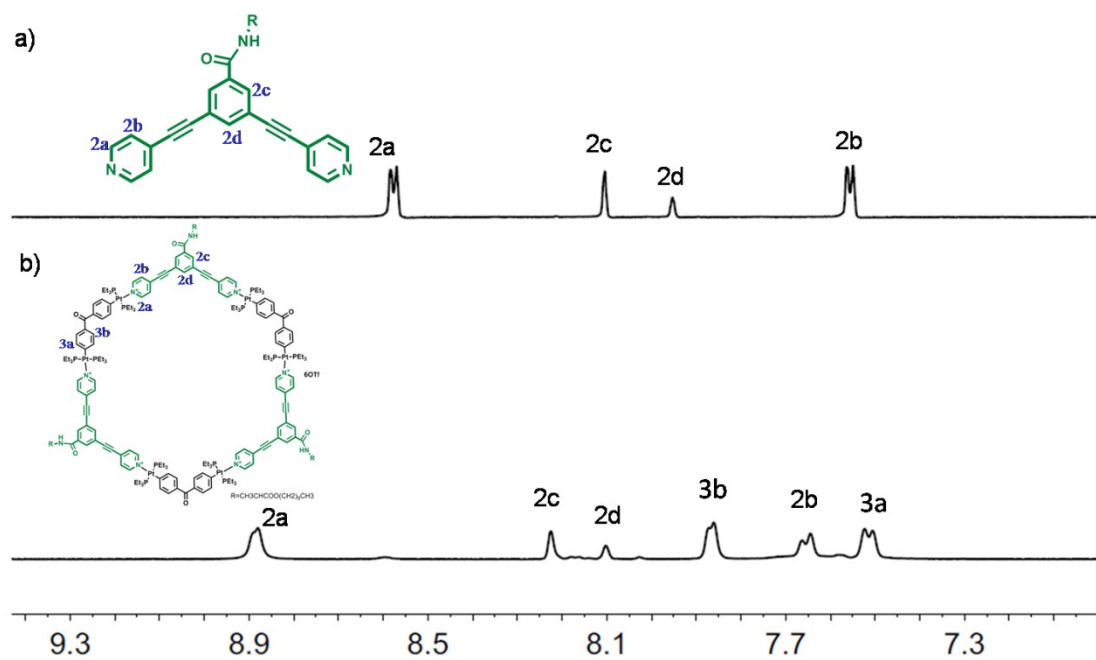


Figure S4. The comparison of downfield shifts of the ^1H protons on the a) ligand, b) **P1**.

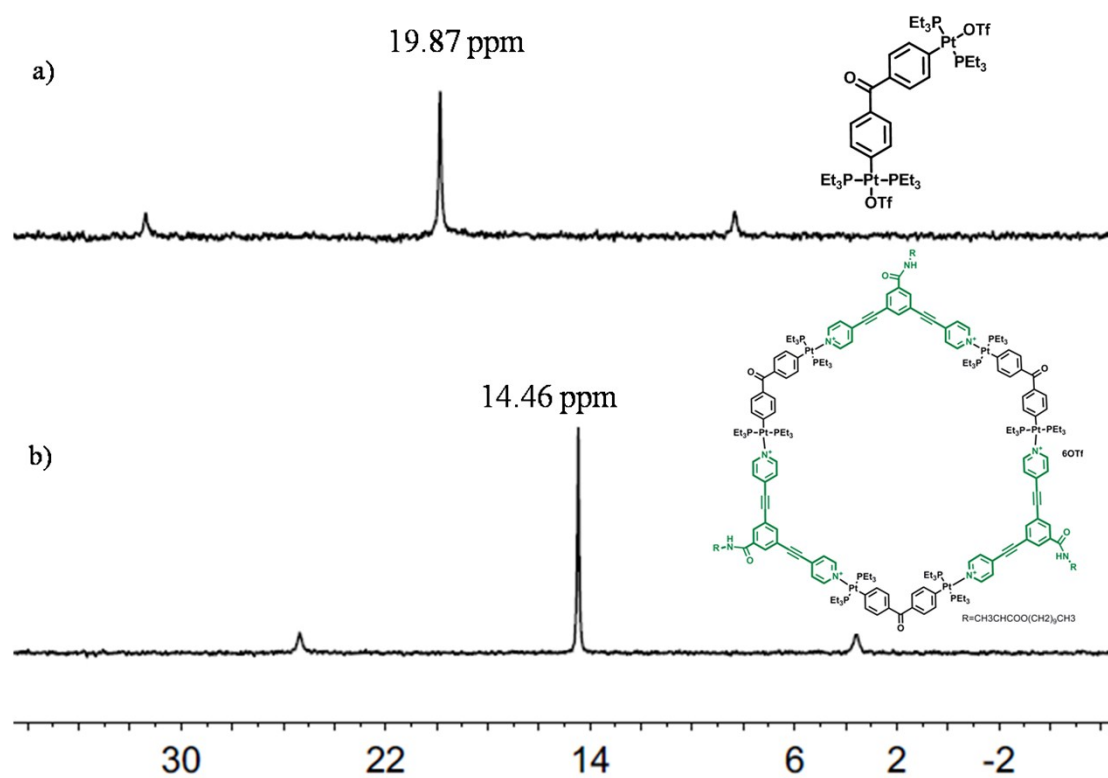


Figure S5. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of a) Pt(II) precursor and b) P1.

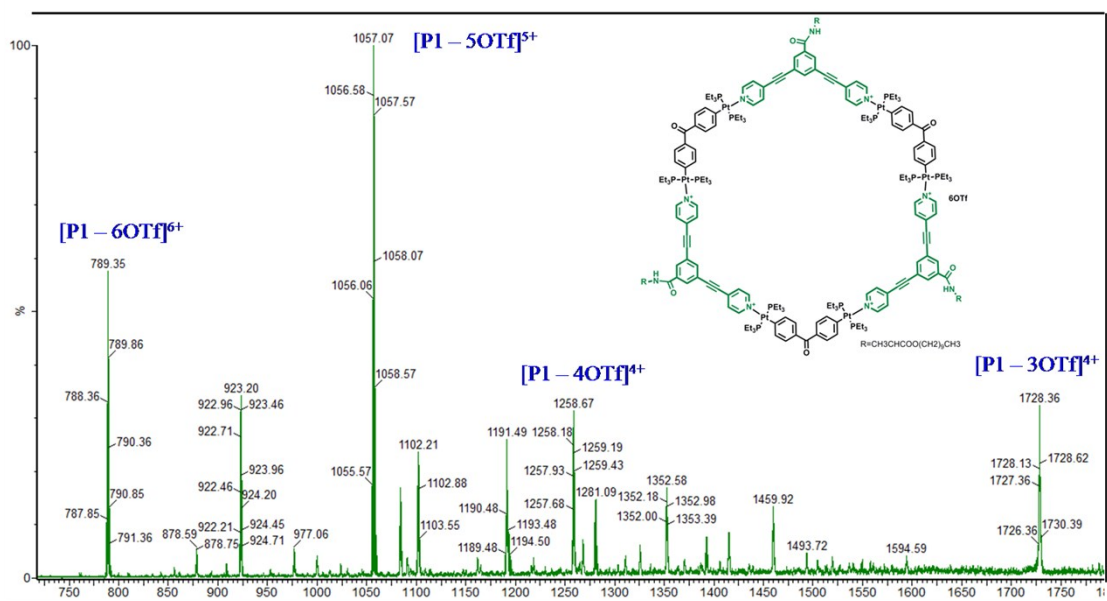


Figure S6. ESI-TOF-MS of P1.

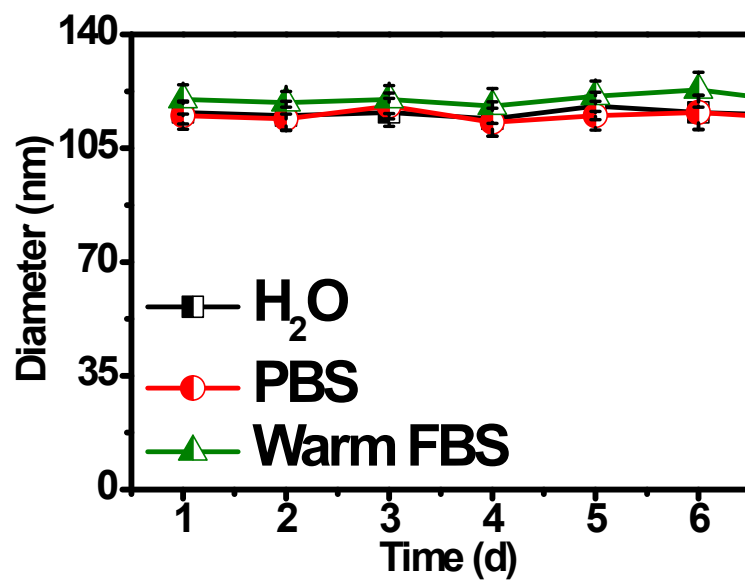


Figure S7. Long-term stability of PSY in 37 °C warm FBS, PBS and water solution reflected by the hydrodynamic size.

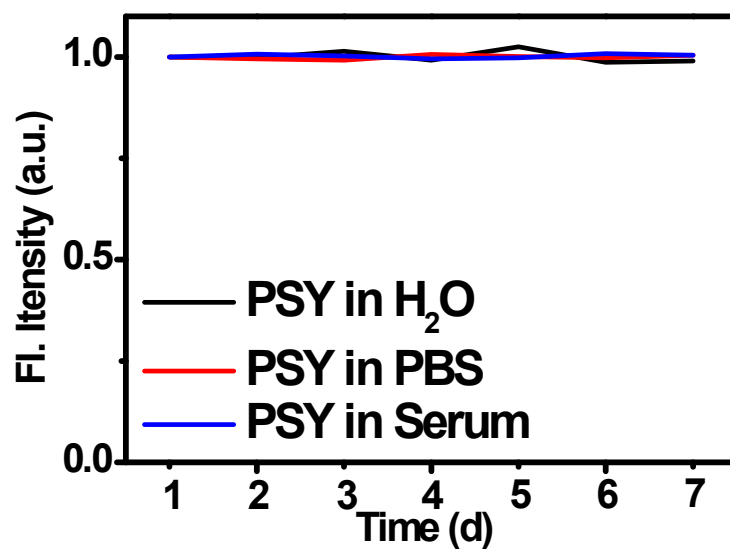


Figure S8. Fluorescence intensity of PSY in 37 °C warm FBS, PBS and water solution recorded at every day for 7 days.

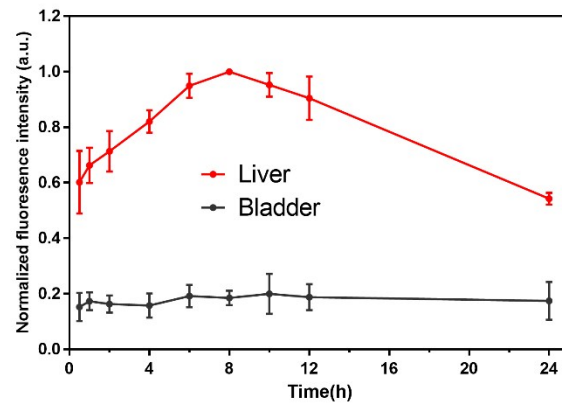
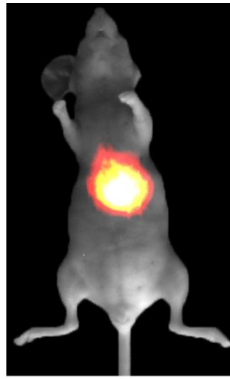


Figure S9. NIR-II imaging of the excretion routes of **PSY** *in vivo* for 0-24 h (82 mW/cm², 75 ms, 1000 LP).

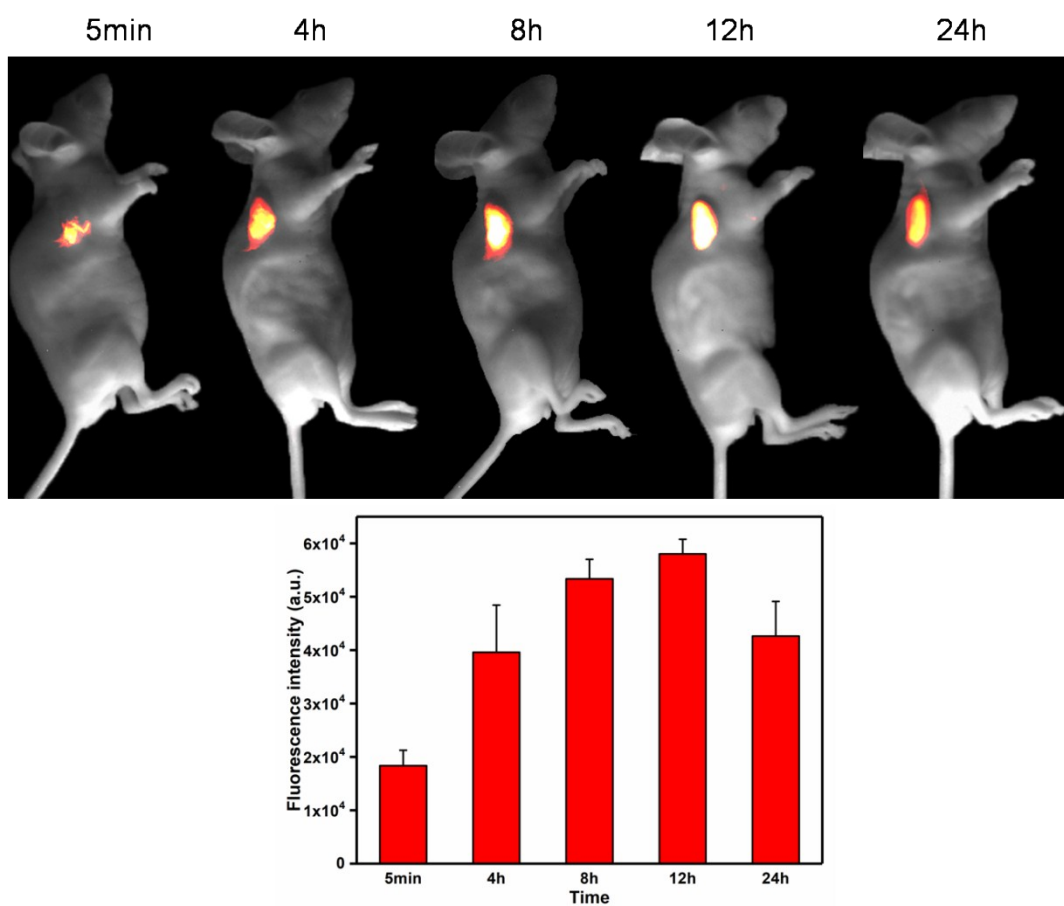


Figure S10. NIR-II images of U87MG tumor bearing mice ($n = 3$) at 5 min, 4 h, 8 h, 12 h and 24 h after vein injection of PSY under 808 nm laser illumination (82 mW/cm^2 , 90 ms, 1000 LP).

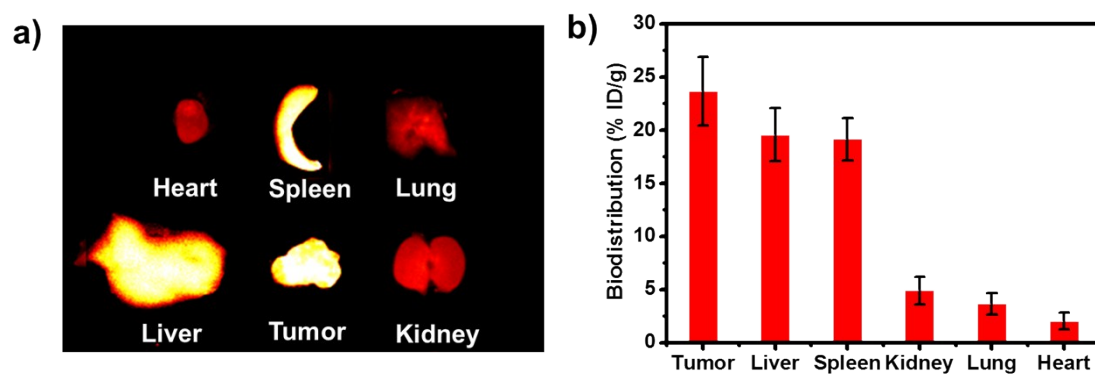


Figure S11. *Ex-vivo* biodistribution of PSY in tumor and organs after injecting PSY to U87MG tumor-bearing mice at 24 h under 808 nm laser illumination (82 mW/cm², 40 ms, 1000 LP).

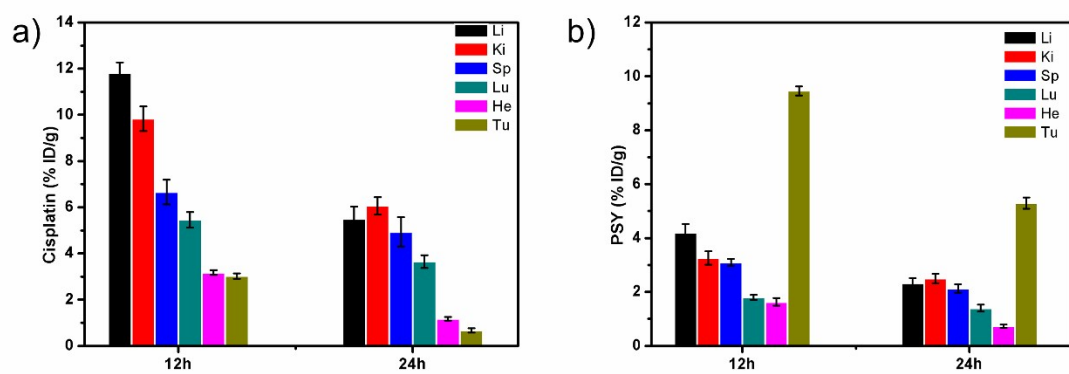


Figure S12. Tissue distribution of the Pt(II) in the main organs after injection with **PSY** and cisplatin for 12 h and 24 h.

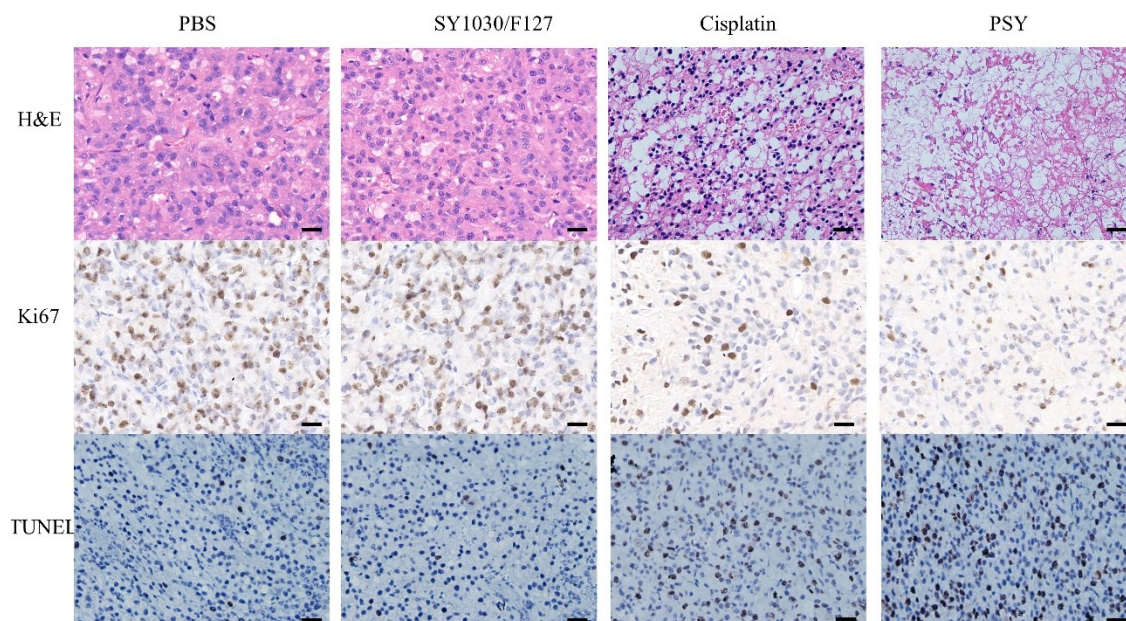


Figure S13. H&E, Ki67, and TUNEL analyses of tumor tissues after treatment with PBS, SY1030/F127, cisplatin or **PSY**. Ki67-positive or TUNEL positive tumor cells were stained brown. Scale bar: 20 μ m

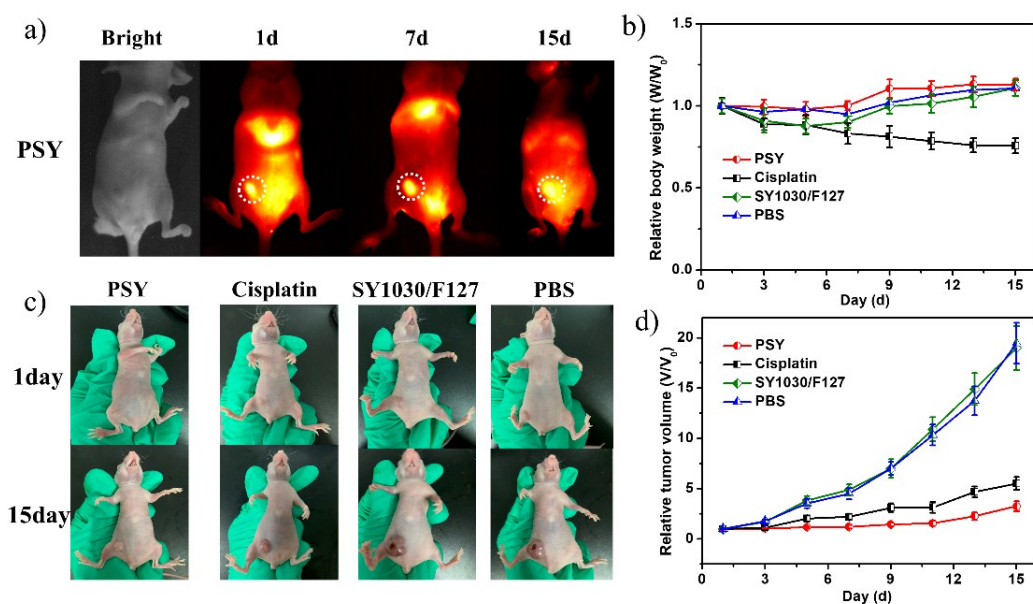


Figure S14. *In vivo* therapeutic efficacy of **PSY** on mice with orthotopic breast cancer. a) NIR-II images of monitoring the **PSY** therapeutic response ($82\text{mW}/\text{cm}^2$, 100ms , LP1000); b) Relative body weights of mice treated with different formulations; c) Bright images of mice treated with different formulations at 1 day and 15 days; d) Relative tumor size of mice treated with different formulations.

U87MG			
cytoplasm	nucleus	cytoplasm	nucleus
1.84 ± 0.158	103 ± 13.4	98.2%	1.8%

Table S1. Pt(II) content per milligram of protein in the nucleus and cytoplasm (ng Pt/mg protein) of U87MG cell line after treatment for 12 h with **PSY** (the concentration of Pt was ~ 10.0 μM) following an previous reported procedure.^[1]

General methods

All chemicals were purchased from commercial sources (such as Aldrich and conjugate-probe). The ^1H and ^{13}C NMR spectra were acquired on a Bruker 400 MHz magnetic resonance spectrometer. $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 . Data for ^1H NMR spectra are reported as follows: chemical shifts are reported as δ in units of parts per million (ppm) relative to chloroform-d (δ 7.26, s); multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), or br (broadened); coupling constants are reported as a J value in Hertz (Hz); the number of protons (n) for a given resonance is indicated nH, and based on the spectral integration values. MALDI-MS spectrometric analyses were performed on an Applied Biosystems 4700 MALDI TOF mass spectrometer. UV-Vis absorbance of the probe was recorded on a PekingElmer Lambda 25 UV-Vis spectrophotometer. The NIR-II system was purchased from Suzhou NIR-Optics Technologies Co., Ltd. NIR-II fluorescence spectrum was recorded on an Applied NanoFluorescence spectrometer at room temperature with an excitation laser source of 785 nm. NIR-II cell images were taken with exposure time of 300 ms using an NIR-II fluorescence Microscope (Suzhou NIR-Optics Co., Ltd, China): 808 nm laser diode excitation. Hydrodynamic diameter was measured using a Malvern Zetasizer Nano ZS. HPLC was performed on a Dionex HPLC System (Dionex Corporation) and a reversed-phase C18 column was used for analysis (Phenomenax, 5 μm , 4.6 mm \times 250 mm) and semi-preparation (Agilent, 5 μm , 10 mm \times 250 mm). Transmission electron microscopy (TEM) images were recorded on a Hitachi TEM system. TEM samples were prepared by dropping **PSY** probe solution onto carbon-coated copper grids and dried at room temperature overnight without staining before measurement, the measurements were conducted with transmission electron microscopy operated at 200 kV.

General procedure for the synthesis of PSY. The nanoprobe **PSY** containing the P1 and SY1030 was prepared *via* matrix-encapsulation method.⁴⁹ Briefly, a mixture of SY1030 (1 mg), P1 (2 mg) and F127 (7 mg) were dissolved in CHCl₃ (1.5 mL). The mixture was stirred at room temperature for 2h and dried over under vacuum to remove CHCl₃. Then, 1.5 mL of PBS was added in to the obtained lipidic film, and the solution was stirred in the dark for overnight. After passing through a 0.2 μm syringe filter, the **PSY** suspension was obtained and stored at 4 °C for further use. 29 nm.

Synthesis of SY1030/F127.The nanoprobe SY1030/F127(as a control probe for *in vivo*) was prepared via matrix-encapsulation method. Briefly, a mixture of SY1030 (1 mg) and F127 (9 mg) were dissolved in CHCl₃ (1.5 mL). The mixture was stirred at room temperature for 2h and dried over under vacuum to remove CHCl₃. Then, 1.5 mL of PBS was added in to the obtained lipidic film, and the solution was stirred in the dark for overnight. After passing through a 0.2 μm syringe filter, the SY1030/F127 suspension was obtained and stored at 4 °C for further use.

Absorption spectrum, PL excitation spectra and fluorescence quantum yield. UV-Vis-NIR absorbance of the **PSY** was recorded on a PerkinElmer Lambda 25 UV-Vis spectrophotometer. PLE spectrum of the **PSY** solutions were taken using an Applied NanoFluorescence spectrometer. The fluorescence quantum yield of **PSY** in water solution was calculated following a previous literature with the dye IR-26 as reference (quantum yield has been reported as 0.05% in 1,2-dichloroethane (DCE)). Briefly, a serial dilution with OD < 0.1 of **PSY** were performed with absorbance values to be ~ 0.10, ~ 0.08, ~ 0.06, ~0.04 and ~0.02. Absorption and fluorescence spectra of IR26 were measured using the instruments described previously. Same solution preparation, absorption and fluorescence spectra measurements were performed for **PSY**. The integrated fluorescence was plotted against absorbance for both IR26 and **PSY** and fitted into a linear function. Comparison of the slopes led to the determination of the quantum yield of **PSY**. In this paper, the quantum yield of IR-26 was determined to be 0.05%.

In Vitro Photostability Test. **PSY** and ICG aqueous solution were continuously irradiated under 808 nm laser at 1 W/cm² for 60 min. NIR-II fluorescent images (LP 1000, 10 ms) were collected at every 5 min on an NIR-II imaging system (Series III 900/1700 equipment, NIR-Optics Technologies Co., Ltd., Suzhou). Then the fluorescence intensity of images at various time points was calculated

by ImageJ. Besides, fluorescent images of **1** in H₂O, PBS and PBS containing 50% FBS solution were continuously irradiated under 808 nm laser at 1W/cm² for 1 h or irradiated every day for 7 days. NIR-II fluorescent images (LP 1000, 10 ms) were collected at various time points on an NIR-II imaging system (Series III 900/1700 equipment, NIR-Optics Technologies Co., Ltd., Suzhou). Then the fluorescence intensity of images at various time points was calculated by ImageJ.

In vitro drug release test. **PSY** was suspended in 5 mL of PBS buffer (50 mM, pH 7.4) and then transferred into a dialysis tube (MWCO, 5 k Da). The dialysis tube was placed into the same buffered solution, and then the release study was performed at 37°C in an incubator shaker. At certain time intervals, solution outside the dialysis tube was removed for quantitative analysis and replaced with fresh buffer.

Quantitative measurement of SY1030 encapsulated in PSY. The amount of SY1030 encapsulated in the **PSY** was measured by NIR absorbance spectrophotometer at 750 nm. The calibration curve was linear in the range of 5-50 µg/mL with a correlation coefficient of R²=0.995. The encapsulated efficiency was defined as the ratio between the amount of SY1030 encapsulated in the F127 and that added in the **PSY** preparation process. The SY1030 encapsulation efficiency of **PSY** was 87.4 ± 1.7 % (n=3).

Cell line and animal model. The U87MG cells were cultured in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% (v/v) fetal bovine serum and 1% (v/v) penicillin at 37°C and 5% CO₂. The U87MG glioblastoma tumor models were established by subcutaneous injection of U87MG cells (1 × 10⁶ in 100 µL of PBS) the right-hand sides of female athymic nude mice (Suzhou Belda Bio-Pharmaceutical Co.). The mice were subjected to imaging studies when the tumor volume reached about 100 mm³ (about 2 weeks after inoculation). The orthotopic breast tumor models were purchased from ServiceBio, The mice were subjected to imaging studies when the tumor volume reached about 100 mm³.

Cell viability studies. *In vitro* cytotoxicity of **PSY**, **P1** and **SY1030** were determined in U87MG cells by the MTT assay. U87MG cells were incubated on 96-well plate in DMEM medium containing 10% FBS and 1% penicillin/streptomycin at 37 °C in 5% CO₂ humidified atmosphere for 24 h and 0.5×10⁴ cells were seeded per well. Cells were then cultured in the medium

supplemented with **PSY**, **P1** and **SY1030** at various concentrations for 24 h. Addition of 10 μL of MTT (0.5 mg/mL) solution to each well and incubation for 3 h at 37 °C was followed to produce formazan crystals. Then, the supernatant was removed and the products were lysed with 200 μL of DMSO. The absorbance value was recorded at 590 nm using a microplate reader. The absorbance of the untreated cells was used as a control and its absorbance was as the reference value for calculating 100% cellular viability.

Cellular Uptake of the Platinum Contents by ICP-MS. U87MG cells were seeded at a density of 3×10^5 cells in 12-well cell culture plates. The cells were left to grow for 24 h in DMEM medium containing 10% FBS and 1% penicillin/streptomycin at 37 °C in 5% CO_2 humidified atmosphere. After 24 h, **PSY** (the concentration of Pt was at $\sim 10 \mu\text{M}$) were added into the wells and the cells were incubated for 1 h, 2 h, 3 h, and 4 h, respectively. Following incubation, the cells were washed, digested and collected, and the Pt content in cells was determined by ICP-MS. All experiments were carried out with three replicates.

Analysis of pKs and the Platinum Contents on Tissue Distribution. Mice received cisplatin or **PSY** at a dose of 2 mg of Pt per kg body weight by tail vein injection. Animals were killed at different time points. Blood was collected by cardiac puncture and kept in heparinized tubes. The amount of platinum in the plasma was determined by ICP-MS. The liver, kidney, spleen, tumor and heart were excised after injection of **PSY** or cisplatin for 12h and 24 h and kept in dry ice before analysis. Organs were digested in concentrated nitric acid for at least 24 h and the amount of platinum was analyzed by ICP-MS.

In vivo NIR-II fluorescence imaging. For lymphatic system imaging, **PSY** PBS solution (50 μL , 50 μg) was injected into the hindfoot pad of C57BL/6 mice ($n = 3$) intradermally. After injection, the lymphatic system was visualized at different time points by the NIR-II imaging apparatus. For brain vessel imaging, **PSY** PBS solution (200 μL , 100 μg) was injected into the vein of C57BL/6 mice ($n = 3$) tail. After injection, the brain vessel system was visualized by the NIR-II imaging apparatus. For tumor imaging, U87MG tumor-bearing animals and mice with orthotopic breast tumor were mounted on the imaging stage beneath the laser. NIR-II fluorescence images were collected using a NIR-II imaging system which was purchased from Suzhou NIR-Optics

Technologies CO., Ltd. The excitation light was provided by an 808-nm diode laser. The laser power density was 82mW/cm² during imaging.

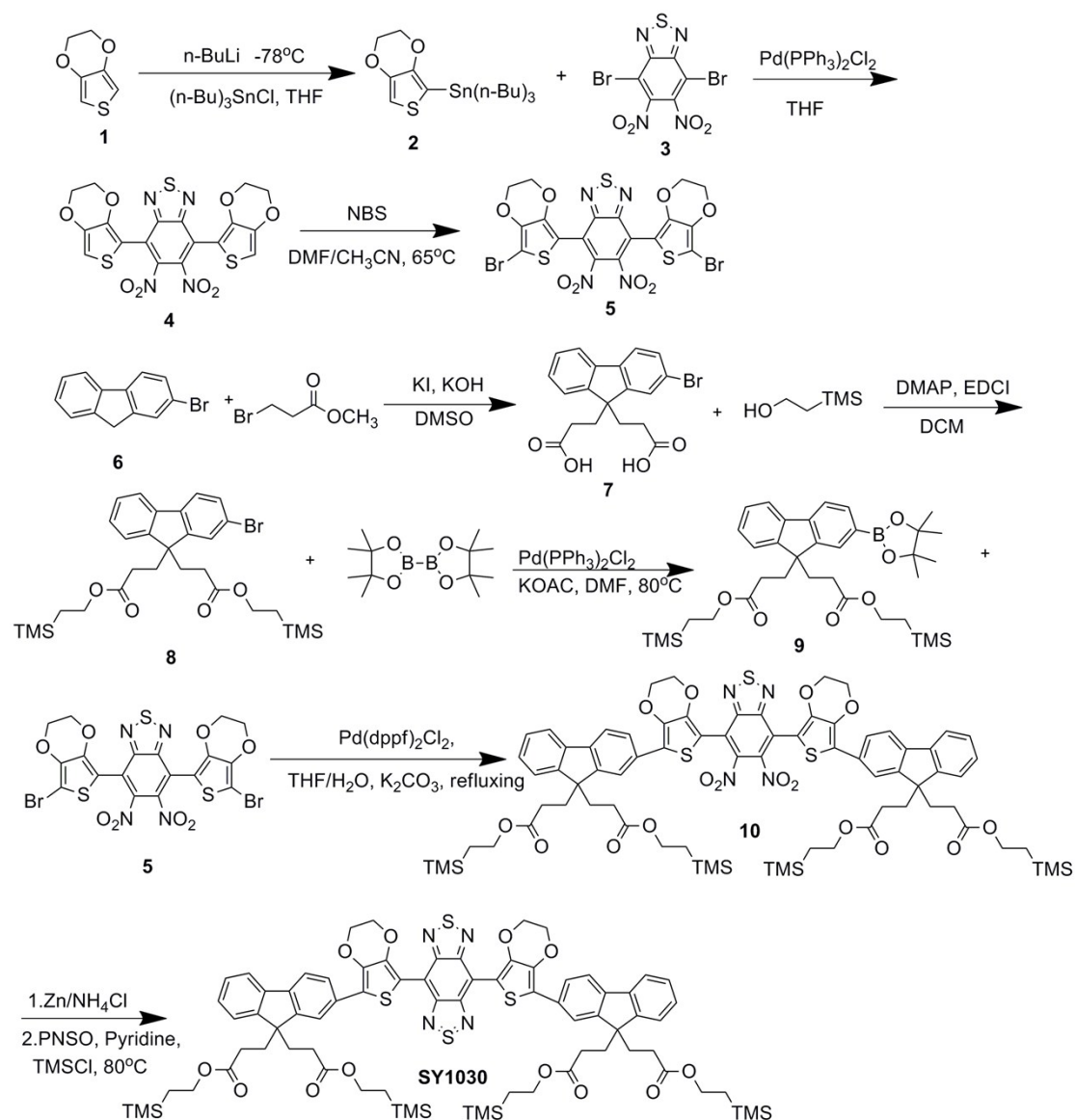
Biodistribution analysis. Ex vivo fluorescence imaging of tumor and major organs were performed with a home-built NIR-II fluorescence imaging system with an InGaAs camera under illumination of an 808 nm laser diode at a power density of 82 mW/cm². U87MG glioblastoma tumor models (n=3) were sacrificed at 24 h after injection of **PSY**, the tumor and major organs were collected. The NIR-II fluorescence image was then obtained by the NIR-II imaging system. The tumor and organs homogenate solution were obtained by completed ultrasonication of tissues in saline. Subsequently, all samples were placed to facilitate the residue sedimentation, then after twice centrifugation, the biodistribution of **PSY** in tumor and organs was quantified by the fluorescence signal in organ homogenate.

In vivo antitumor Activity. Tumor volume and body weights were measured for individual animals in all experiments. Tumor volume was determined by measuring the tumor in two dimensions with calipers and calculated using the formula tumor volume = (length × width²)/2. The mice were divided into four treatment groups randomly (n = 10), when the mean tumor volume reached about 100 mm³ and this day was set as day 0. Mice were administrated intravenously with PBS, cisplatin, **SY1030** or **PSY** at dose of 2 mg Pt per kg body weight every 3 days. Tumor volume and body weight were measured every 3 days for U87MG tumor-bearing mice and every 2 days for orthotopic breast tumor models. The tumor inhibition study was stopped on the 22th day for U87MG tumor-bearing mice and 15th for orthotopic breast tumor models.

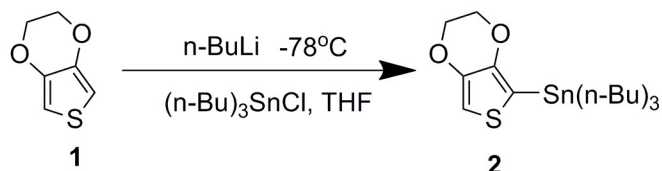
Statistical Analysis. The measurement was performed to quantities NIR-II signal intensity through the software Image J. Data are given as mean ± standard deviation. The differences between two groups were analyzed by Student's t-test, over two experimental groups were analyzed by analysis of variance (ANOVA). P <0.05 (*) was considered as statistically significant difference, and P <0.01 (**) was considered as extremely significant difference. All statistical analyses were performed by SPSS.

Chemical synthesis and characterization

General procedure for the synthesis of SY1030

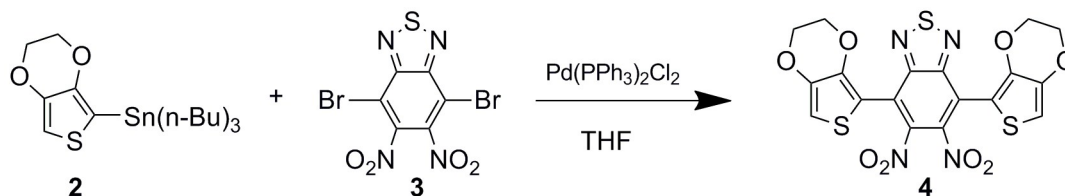


The scheme for the total synthesis of SY1030

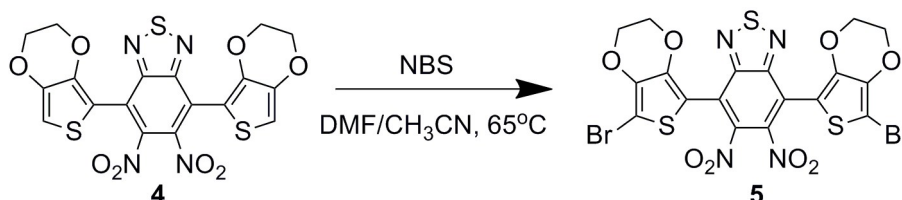


Synthesis of 2: Compound **1** (665.5 mg, 4.68 mmol) was cooled at -78°C under N_2 , adding n -butyllithium (2.43 mL) into the solution and the temperature was slowly recovered to room temperature during 2h. The reaction mixture was cooled at -78°C when slowly added tributyltin chloride (1.98 g, 6.08 mmol) and then stirred overnight at room temperature. After TLC monitored

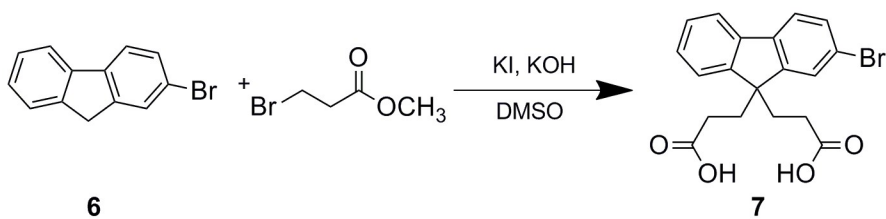
the completion of the reaction, the reaction mixture was extracted and dried over anhydrous sodium sulfate. The crude product **2** was obtained as yellow oil liquid and was used directly for the next step without purification (1.52g, 85% yield).



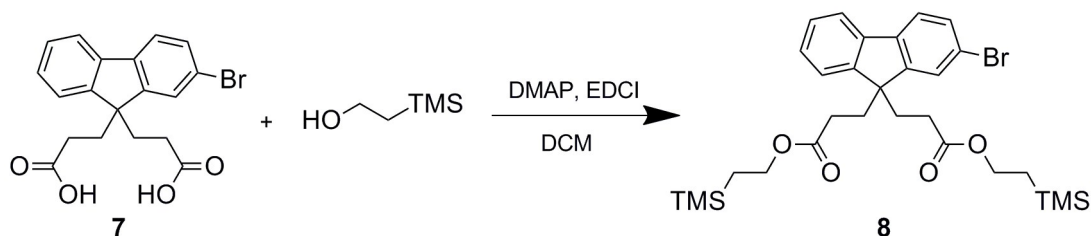
Synthesis of 4: The mixture of compound **2** (200 mg, 0.523 mmol) and compound **3** (476 mg, 1.10 mmol) in anhydrous THF under N_2 . Then $Pd(PPh_3)_4$ (30.0 mg, 0.026 mmol) was added to the above reaction mixture under N_2 . The reaction mixture was heated and reflux overnight. The reaction mixture was filtered through Celite pad and washed with DCM. The organic layer was washed with saturated NaCl, dried over $MgSO_4$ and then concentration under reduced pressure. The residue was purified by silica gel chromatography to obtain the desired product **4** as a red powder (237.63 mg, 89% yield). 1H NMR (400 MHz, $CDCl_3$): δ = 6.79 (s, 2H), 4.26 (d, J = 4.0 Hz, 2H), 4.22 (d, J = 4.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.61, 142.52, 141.21, 120.27, 105.50, 104.60, 64.69, 64.37, 26.80, 13.61.



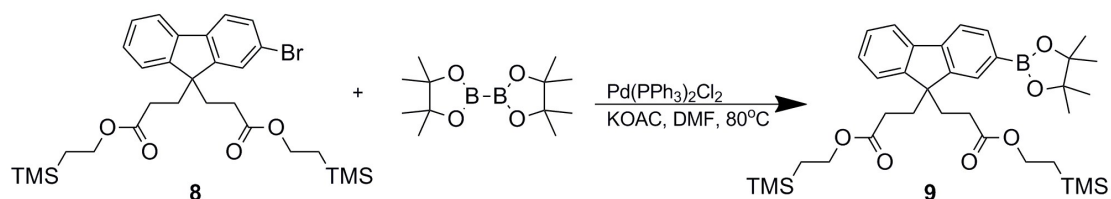
Synthesis of 5: Compound **4** (384.5 mg, 0.753 mmol) was dissolved in a mixture of DMF (10 mL) and MeCN (5 mL). The reaction mixture was heated to 65°C, adding *N*-bromosuccinimide (312.7 mg, 1.76 mmol) in one portion and then the reaction was stirred for 6 h under the dark. After cooling, the reaction mixture was acidified with hydrochloric acid (180 mL, 2 M) and the precipitate was collected by filtration and washed with water and methanol to give the desired compound **5** as a red powder (463.27 mg, 92%). 1H NMR (300 MHz, $CDCl_3$): δ 3.26 (d, J = 8.0 Hz, 4H), 3.21 (d, J = 4.0 Hz, 4H); ^{13}C NMR (101 MHz, C_6D_6) δ 151.64, 141.83, 139.82, 118.95, 108.17, 107.35, 106.43, 105.71, 105.56, 94.71, 77.40, 77.09, 76.76, 63.91, 63.84.



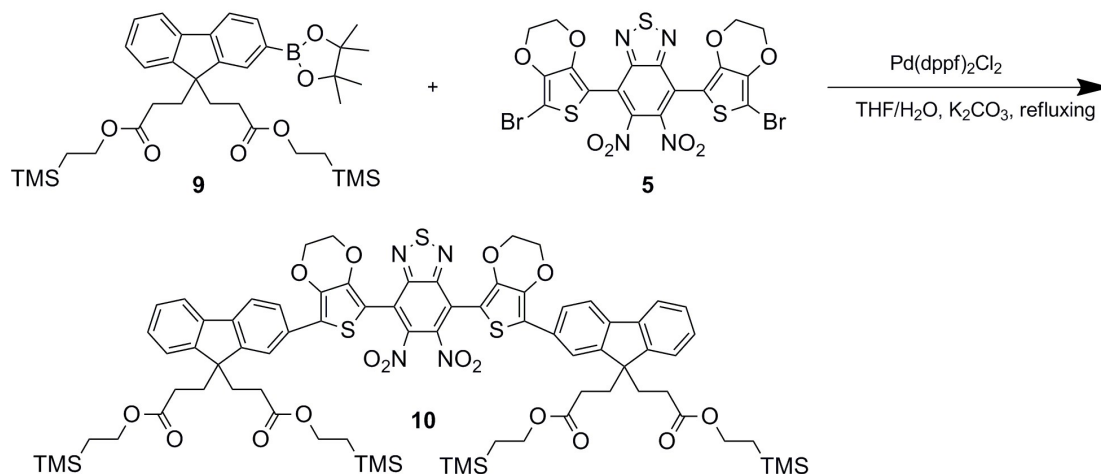
Synthesis of 7: The mixture of compound 6 (3.00 g, 12.24 mmol) and KI (406 mg, 2.45 mmol) were dissolved in DMSO (40 mL) under N₂, following added Methyl 3-bromopropionate (26.93 mmol, 4.50 g) and KOH (3.4 g, 61.2 mmol, 10 portions). The reaction mixture was stirred at room temperature for 24 h and quenched with water. The mixture was acidified to pH 5 with 2 M aq. HCl solution, then extracted with EtOAc (3×150 mL). The combined organic layers were dried with MgSO₄, filtered and concentrated. The desired crude product 7 was obtained as a white solid and was used in the next step without further purification (2.9 g, 60.6%). ¹H NMR (400 MHz, DMSO) δ 11.95 (br, 2H), 7.88-7.79 (m, 3H), 7.58-7.51 (m, 2H), 7.40-7.38 (m, 2H), 2.38-2.34 (m, 4H), 1.37-1.33 (m, 4H); ¹³C NMR (101 MHz, DMSO) δ 174.25, 173.09, 151.05, 148.20, 140.34, 139.97, 131.01, 128.60, 128.19, 126.87, 123.66, 122.40, 121.30, 120.85, 54.27, 54.21, 51.59, 34.12, 29.25, 29.09.



Synthesis of 8: To a solution of compound 7 (2.70 g, 6.94 mmol) and 2-trimethylsilylethanol (37.48 mmol, 4.43 g) in CH₂Cl₂ (24 mL) was cooled at 0 °C under N₂. Then EDCI (6.65 g, 34.7 mmol) and DMAP (170 mg, 1.38 mmol) were added in a single portion and the reaction mixture was stirred at room temperature for 12 h. After diluted with CH₂Cl₂, the organic layer was washed with saturated NH₄Cl solution, water, saturated NaCl (100 mL), dried over MgSO₄, filtered and concentrated to dryness. The residue was crystallized by *n*-hexane/EtOAc to yield compound 8 (3.4 g, 78.2%). ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.68 (m, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.35 (s, 3H), 4.00-3.95 (m, 4H), 2.43-2.38 (m, 4H), 1.57-1.53 (t, J = 12.0 Hz, 4H), 0.87-0.82 (m, 4H), 0.01 (s, 18H); ¹³C NMR (101 MHz, CDCl₃) δ 173.26, 149.87, 147.30, 140.29, 140.19, 130.89, 128.07, 127.89, 126.43, 123.08, 121.48, 121.40, 120.15, 62.53, 53.96, 34.60, 29.16, 17.21, -1.54.

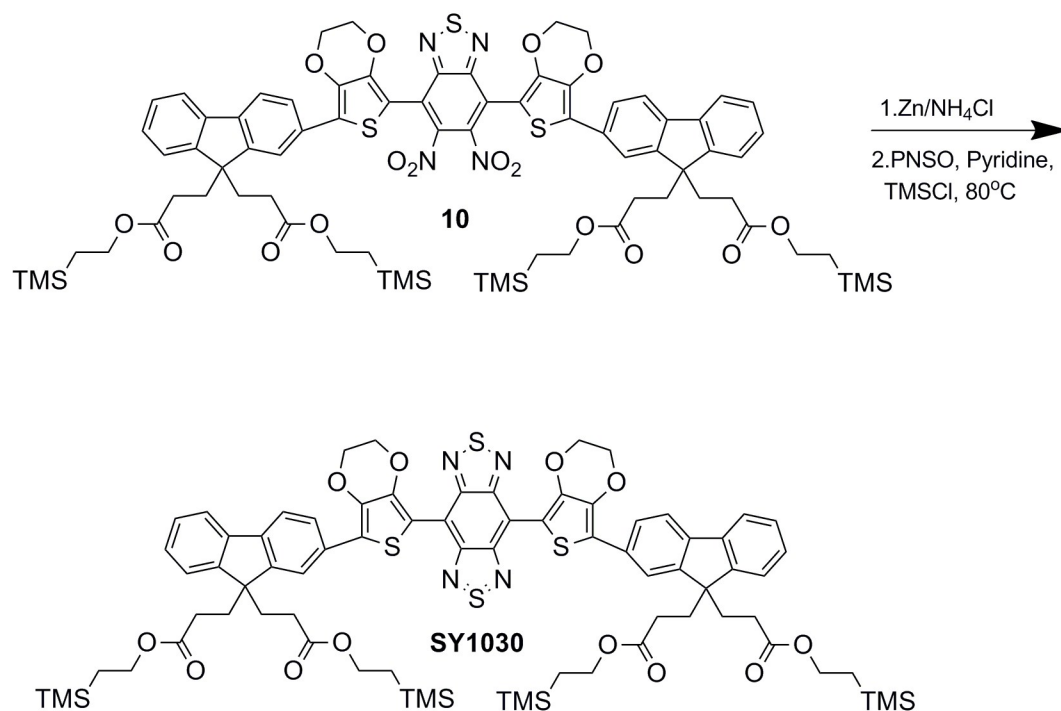


Synthesis of 9: To a solution of compound **8** (2.92 g, 4.96 mmol), bis(pinacolate)diboron (2.54 g, 8.93 mmol) and KOAc (1.168 g, 11.90 mmol) in DMF (60 mL). Then the solution was added Pd(PPh₃)₂Cl₂ (384.15 mg, 0.496 mmol) under N₂. The reaction mixture was heated in an oil bath at 80 °C for 12 h. The reaction mixture was cooled, dilute with H₂O and extracted with EA. The combined organic layer was and then warmed to room temperature for overnight. The reaction mixture was purified by silica gel chromatography to obtain the desired product **9** as white solid (2.89 g, 89.9 %). ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.78 (m, 2H), 7.69-7.67 (m, 2H), 7.38-7.28 (m, 3H), 3.95 (t, J = 8.0 Hz, 4H), 2.48-2.36 (m, 4H), 1.54-1.45 (m, 4H), 1.41 (s, 12H), 0.81 (t, J = 12.0 Hz, 4H), 0.07 (s, 18H); ¹³C NMR (101 MHz, CDCl₃) δ 173.4, 148.19, 146.85, 144.07, 141.00, 134.54, 128.92, 128.07, 127.63, 123.06, 120.44, 119.30, 83.74, 62.21, 53.54, 34.63, 29.16, 24.93, 17.15, -1.54.



Synthesis of 10: Compound **9** (200 mg, 0.25 mmol), compound **5** (74.7 mg, 0.11 mmol), Pd(dppf)₂Cl₂ (20.5 mg, 0.025 mmol) and K₂CO₃ (41.3 mg, 0.31 mmol) were dissolved in the mixture of THF/H₂O under Ar. The reaction mixture was heated in an oil bath at 75 °C for 14 h. The reaction mixture was cooled and purified by silica gel chromatography to obtain the desired product **10** as a dark purple solid (143.3 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.89-7.73 (m, 8H), 7.40-7.33 (m,

6H), 4.44 (s, 4H), 4.32 (s, 4H), 4.01-3.97 (m, 8H), 2.49 (t, $J = 12$ Hz, 8H), 1.67-1.56 (m, 9H), 0.88-0.83 (m, 9H), -0.01 (s, 36H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.57, 152.61, 148.40, 148.01, 143.16, 142.91, 140.90, 140.76, 137.71, 131.57, 127.80, 126.25, 124.32, 123.09, 120.74, 120.33, 120.21, 119.59, 102.86, 64.61, 64.49, 62.46, 53.79, 34.69, 29.69, 29.20, 17.23, -1.55.



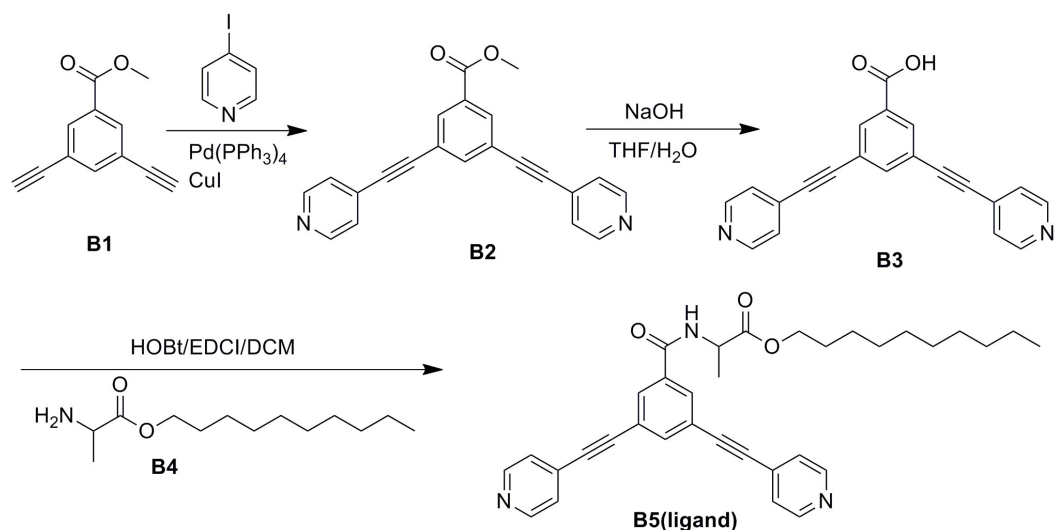
Synthesis of SY1030: Zinc dust (447 mg, 6.8 mmol) and NH_4Cl (109.56 mg, 2.0 mmol) were added to a solution of compound **10** (78 mg, 0.057 mmol) in DCM/MeOH under an argon atmosphere. The reaction mixture was stirred at roomtemperature for 4 h and then filtered through Celite pad. The obtained organic layer was diluted with DCM, and washed with water, saturated NaHCO_3 , and saturated NaCl. The organic phase was dried over anhydrous MgSO_4 and concentrated under vacuum to afford a yellow solid as crude product, which was utilized for the nextstep without further purification.

N-thionylaniline (2.07 mmol, 284.05 mg), chlorotrimethylsilane (4.0 mmol, 427 mg) and above crude product were added into a anhydrous pyridine solution. The reaction mixture was heated in an oil bath at 80°C for 20 h. The reaction mixture was cool to room temperature and then poured into ice water, which was extracted with DCM. The combined organic layer was washed with water, saturated NaCl, and then dried over anhydrous MgSO_4 . The crude product was purified by flash

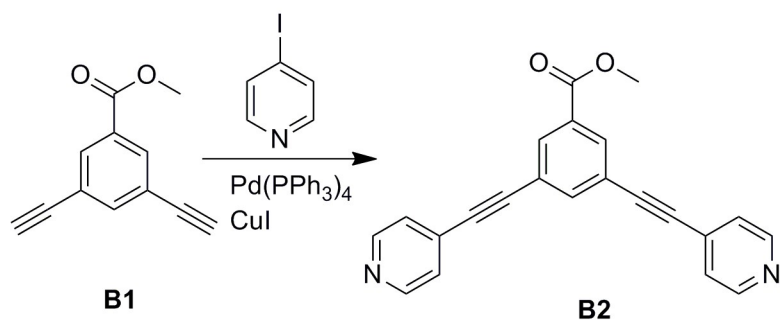
column chromatography on silica gel to obtain the desired product **SY1030** as a green solid (45 mg, two step 52.9 % yield). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.0 Hz), 7.84 (s, 2H), 7.77-7.73 (m, 4H), 7.40-7.34 (m, 7H), 4.55 (s, 4H), 4.41 (s, 4H), 4.02-3.97 (m, 8H), 2.50 (t, *J* = 12 Hz, 8H), 1.68-1.57 (m, 9H), 0.89-0.84 (m, 9H), -0.01 (s, 36H); ¹³C NMR (101 MHz, CDCl₃) δ 173.65, 152.58, 148.31, 147.96, 141.92, 140.98, 138.58, 132.41, 126.15, 123.07, 122.12, 120.62, 120.27, 120.08, 113.12, 109.16, 64.77, 64.57, 62.45, 53.75, 34.72, 29.71, 29.23, 17.23, -1.54; MS ([M+H]⁺): Calcd. for: C₇₆H₉₁N₄O₁₂S₄Si₄⁺ ([M+H]⁺): 1491.4588, found: 1491.4667.

General procedure for the synthesis of P1

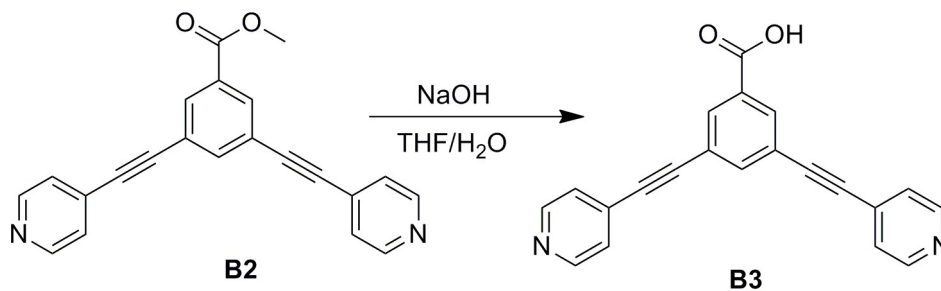
1) The synthesis of Ligand (B5)



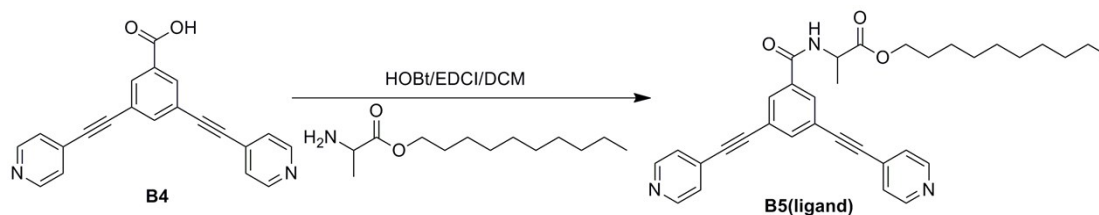
The scheme for the total synthesis of ligand (B5)



Synthesis of compound B2: Compound B1 (552.1 mg, 3.0 mmol) and 4-Iodopyridine (1.3 g, 6 mmol) were dissolved in dry mix solvents (Et₃N/THF, v:v = 1:3). Then tetrakis(triphenylphosphine)palladium (173.0 mg, 0.15 mmol) and cuprous iodide (28.5 mg, 0.15 mmol) were added in the N₂ atmosphere and the reaction mixture was stirred at 60°C for 72 h. The reaction mixture restores up to room temperature and finally concentrated. The pure product B2 is obtained by flash chromatography on silica gel (CH₂Cl₂/CH₃OH = 50 : 1) (660.3 mg, yield: 65 %). ¹H NMR (400 MHz, CDCl₃): 8.63 (d, J = 4.0 Hz, 4H), 8.20 (s, 2H), 7.89 (s, 1H), 7.39 (d, J = 8.0 Hz, 4H), 3.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 165.21, 149.86, 138.47, 133.11, 131.11, 130.51, 125.45, 123.17, 91.44, 88.20, 52.55. LRESI-MS: calcd. for [M + H]⁺, 339.1. Found :339.1.

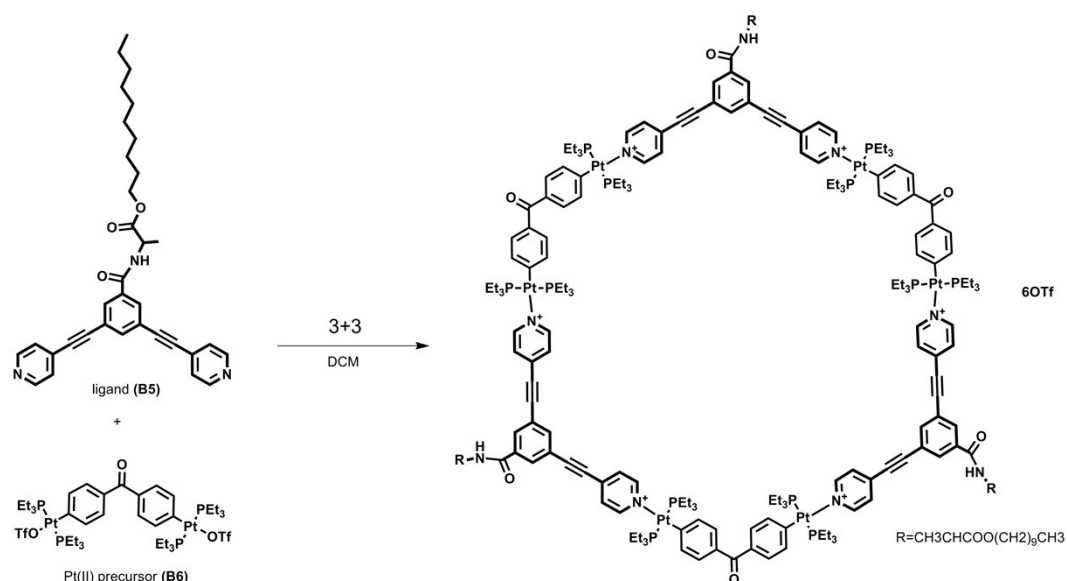


Synthesis of compound B3: Compound B2 (338.4 mg, 1.0 mmol) and NaOH (80.0 mg, 2 mmol) were dissolved in mix solvents (H₂O/THF, v:v = 1:5). Then the reaction mixture was stirred at 60 °C for 24 h. The reaction mixture restores upto room temperature and added the HCl (1 M) to the solution until acidic. The pure product B3 is obtained by flash chromatography on silica gel (CH₂Cl₂/CH₃OH = 10 : 1)(285.1 mg, yield: 88 %). ¹H NMR (400 MHz, DMSO-d₆): 8.64 (d, J = 4.0 Hz, 4H), 8.12 (s, 2H), 8.05(s, 1H), 7.56 (d, J = 4.0 Hz, 4H). ¹³C NMR (100 MHz, DMSO-d₆): 165.99, 150.45, 138.43, 133.66, 133.33, 133.01, 132.65, 132.45, 132.43, 131.95, 131.85, 129.99, 129.22, 129.11, 125.90, 123.02, 91.65, 88.67. LRESI-MS: calcd. for [M + H]⁺, 324.9; Found :324.9.



Synthesis of compound B5: Compound B3 (324.3 mg, 1.0 mmol) and B4 (229.4 mg, 1 mmol) were dissolved in dry DCM (30 mL). Then EDCI (383.4 mg, 2.0 mmol) and HOBt (270.2 mg, 2.0 mmol) were added and the reaction mixture was stirred at room temperature for 72 h under nitrogen atmosphere. Then the organic layer is washed with H₂O (3 x10 mL) and finally concentrated. The pure product B5 is obtained by flash chromatography on silica gel (CH₂Cl₂/CH₃OH = 20 : 1) (257.2 mg, yield: 48 %). ¹H NMR (400 MHz, CD₂Cl₂): 8.63 (d, J = 8.0 Hz, 4H), 8.00(d, J = 4.0 Hz, 2H), 7.99(t, 1H), 7.43 (t, J = 4.0 Hz, 4H), 6.80(d, J = 4.0 Hz, 1H), 4.75 (t, J = 4.0 Hz, 1H), 4.20 (m, 2H), 1.69 (t, J = 8.0 Hz, 2H), 1.27 (m, 14H), 0.89 (t, J = 8.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 173.15, 164.80, 149.87, 137.34, 134.99, 130.80, 130.56, 125.50, 123.31, 91.52, 88.30, 65.97, 48.75, 31.83, 29.46, 29.45, 29.24, 29.15, 28.49, 25.77, 22.63, 18.62, 14.06. LRESI-MS: calcd. for [M + H]⁺, 536.28. Found : 536.30.

2) The synthesis of P1



Synthesis of P1. Pt(II) precursor (**B6**) (13.4 mg, 0.01 mmol) and ligand (**B5**) (5.36 mg, 0.01 mmol) were added in DCM and reacted at room temperature for 10 h. The resulting homogeneous solution was added diethyl ether to precipitate the product, which was isolated, dried under reduced pressure (17.8 mg, 95%). ¹H NMR (400 MHz, MeOD): δ 8.88 (s, 12H), 8.22 (s, 6H), 8.10 (s, 3H), 7.86 (s, 12H), 7.66 (d, J = 8.0 Hz, 12H), 7.52 (d, J = 4.0 Hz, 12H), 4.61 (d, J = 4.0 Hz, 12H), 4.17 (d, J = 8.0 Hz, 6H), 1.67 (m, 7H), 1.54 (d, J = 8.0 Hz, 12H), 1.43 (s, 86H), 1.25 (m, 176H), 0.88 (m, 10H). ³¹P{¹H} NMR (MeOD, 121.4 MHz) δ (ppm): 14.46ppm. ESI-TOF-MS: m/z = 789.35 for [M – 6OTf]⁶⁺; m/z = 1057.07 for [M – 5OTf]⁵⁺; m/z = 1258.67 for [M – 4OTf]⁴⁺; m/z = 1728.36 for [M – 3OTf]³⁺.

Reference:

1. A. Naik, R. Rubbiani, G. Gasser and B. Spingler, *Angew. Chem. Int. Ed. Engl.*, 2014, **53**, 6938-6941.
2. O. E. Semonin, J. C. Johnson, J. M. Luther, A. G. Midgett, A. J. Nozik and M. C. Beard, *J. Phys. Chem. Lett.*, 2010, **1**, 2445-2450.

NMR Spectra

Figure S15. ^1H NMR and ^{13}C NMR for **4**.

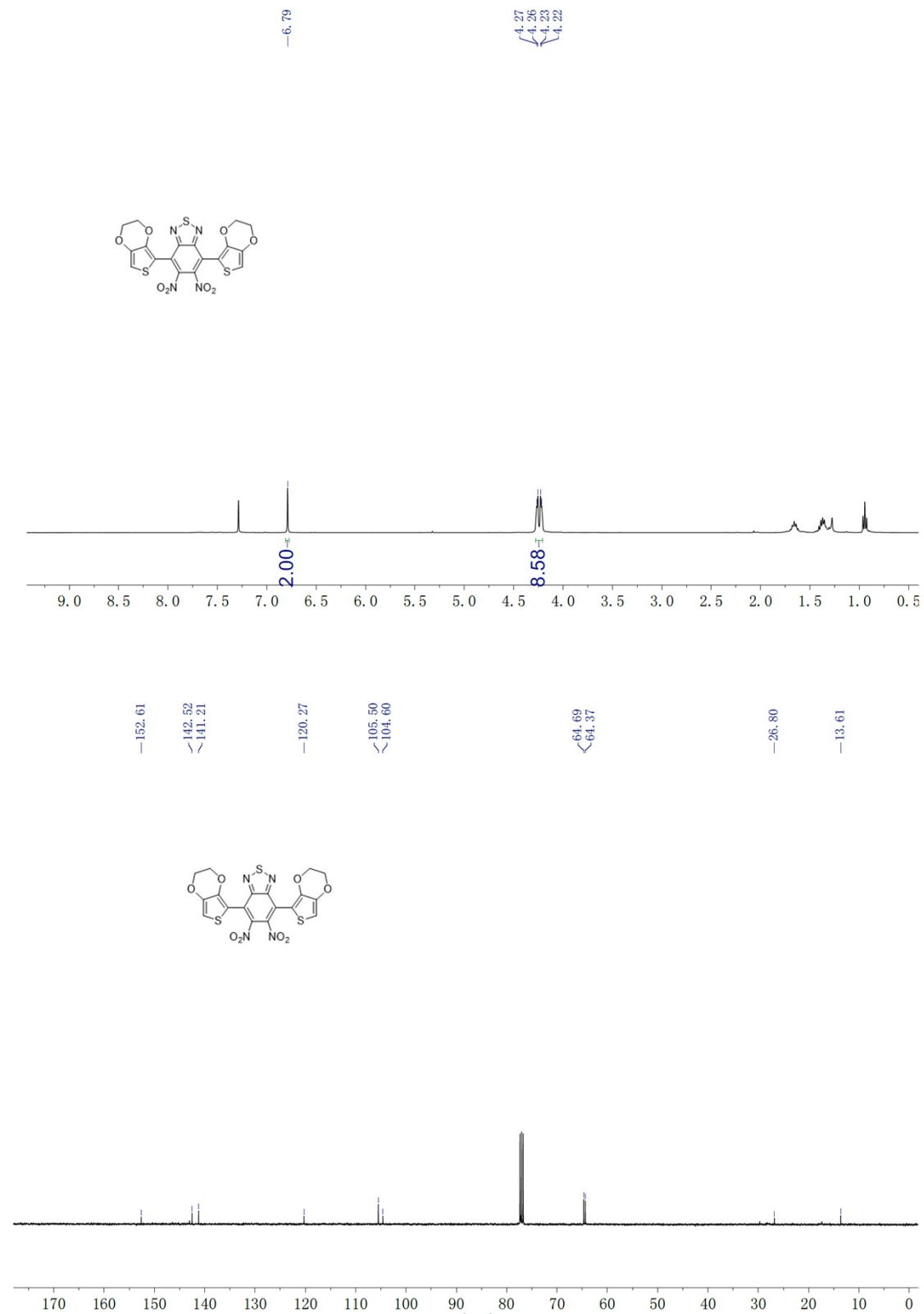


Figure S16. ¹H NMR and ¹³C NMR for **5**.

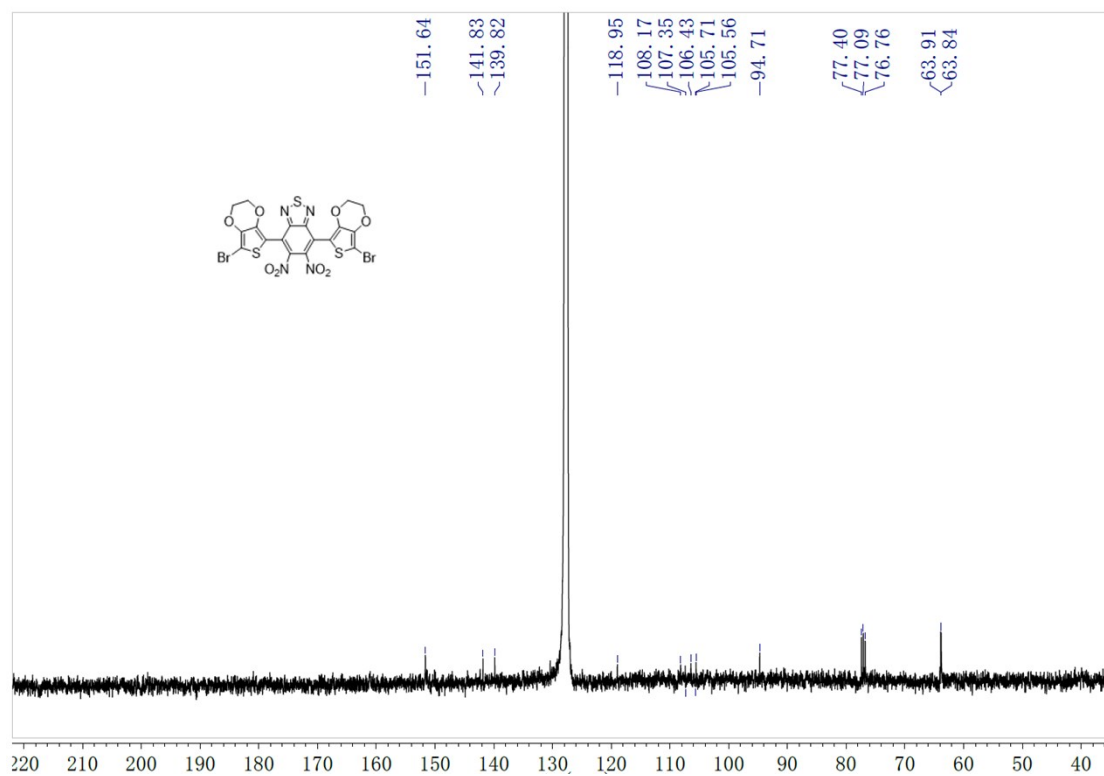
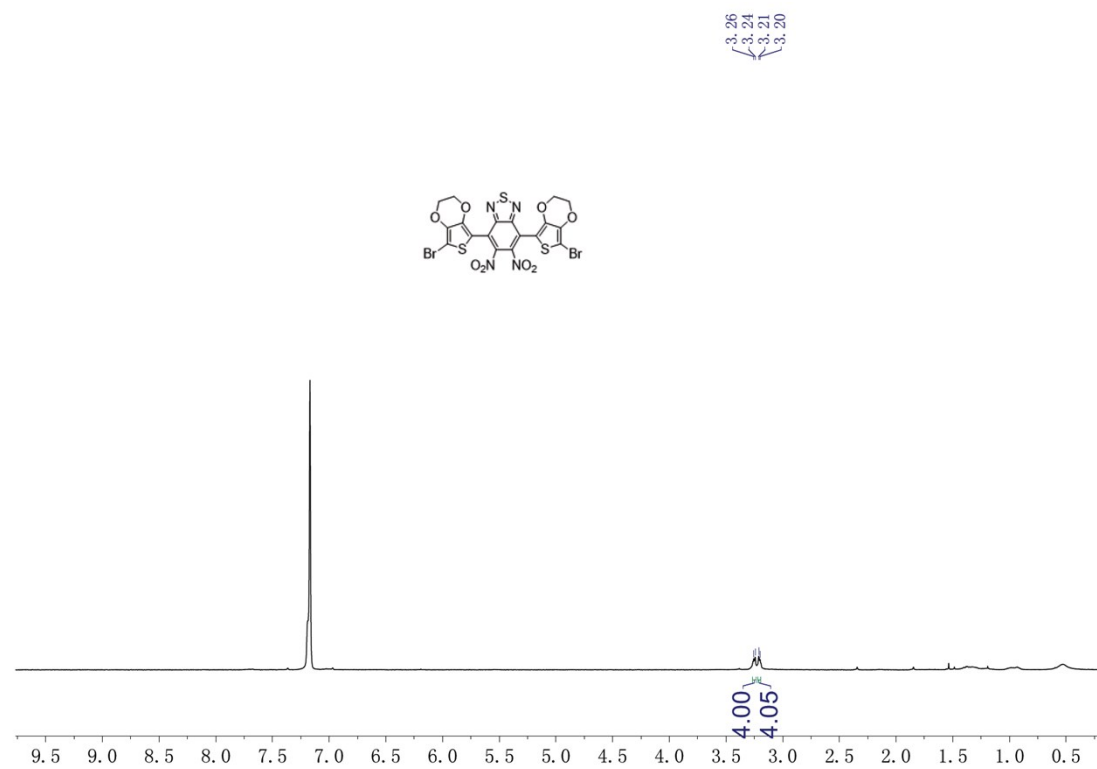


Figure S17. ^1H NMR and ^{13}C NMR for 7.

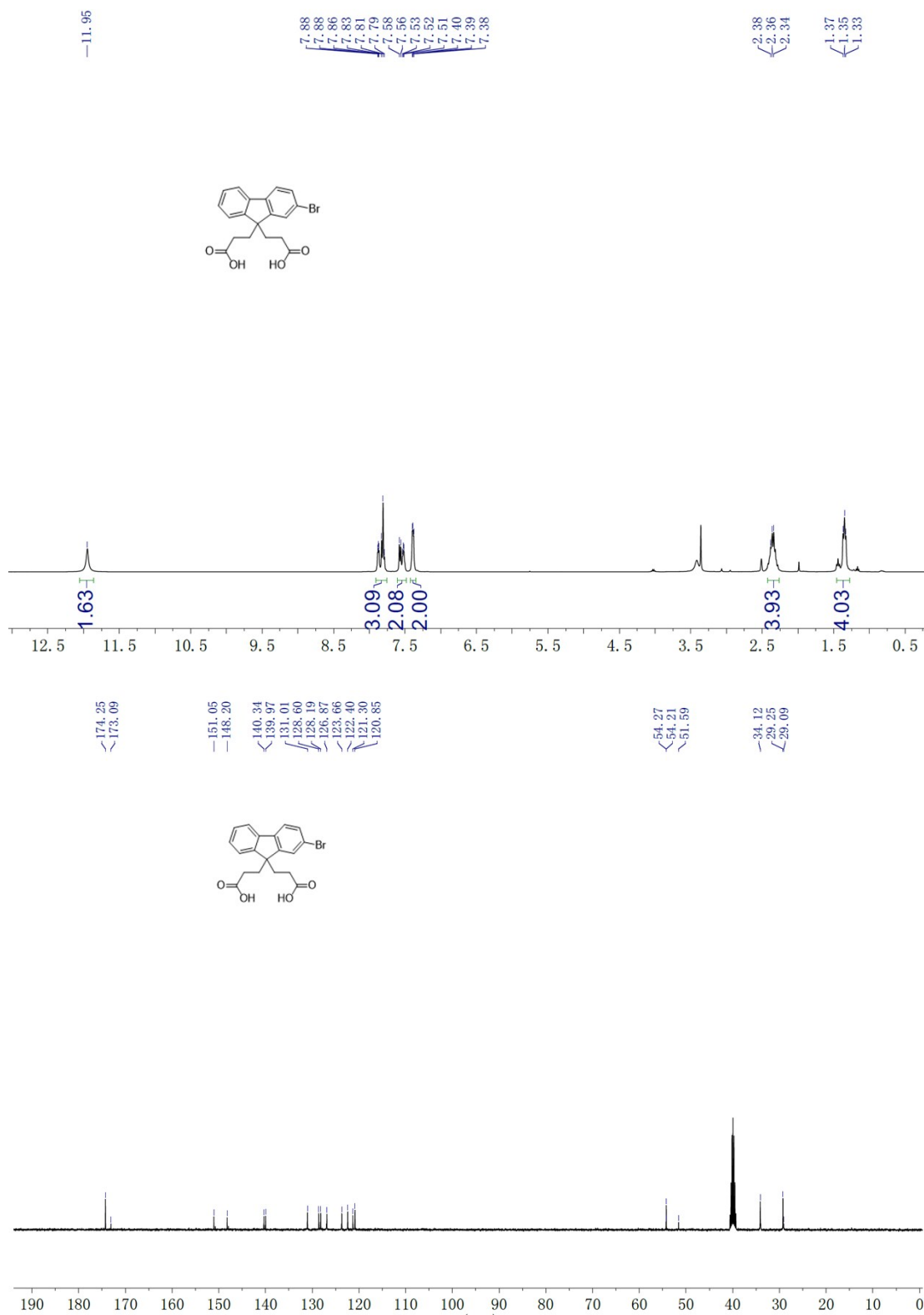


Figure S18. ^1H NMR and ^{13}C NMR for **8**.

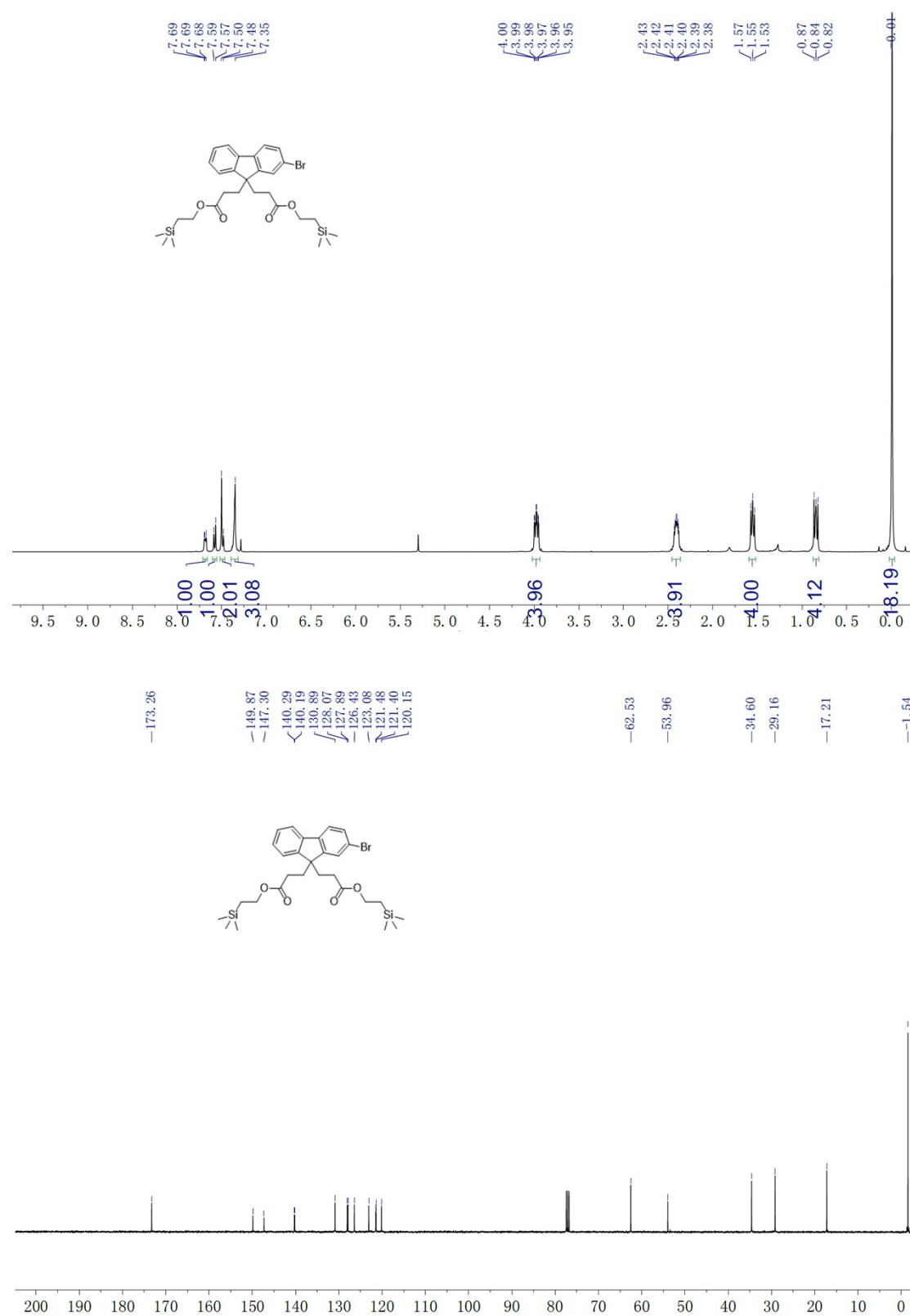


Figure S19. ^1H NMR and ^{13}C NMR for **9**.

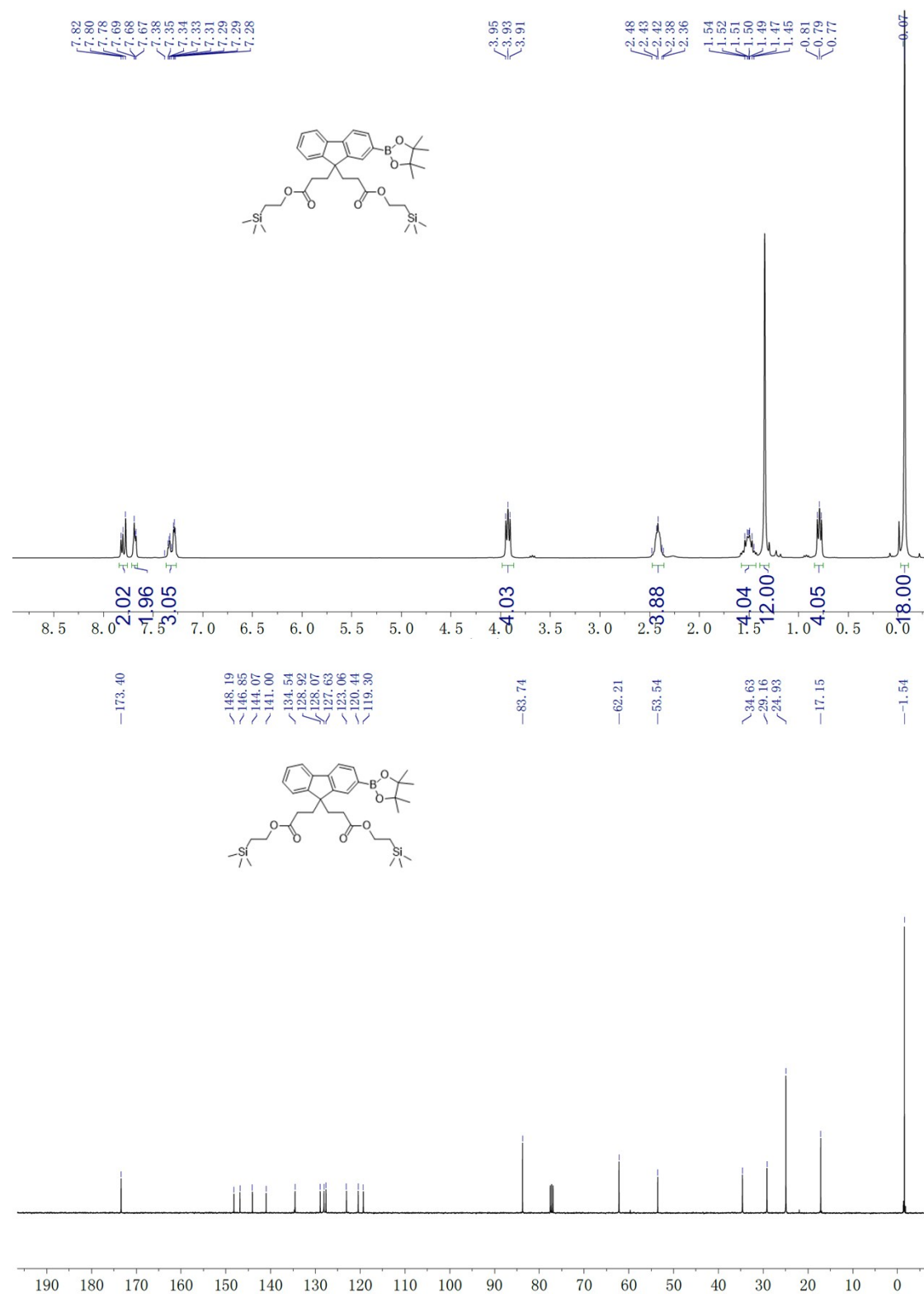


Figure S20. ^1H NMR and ^{13}C NMR for **10**.

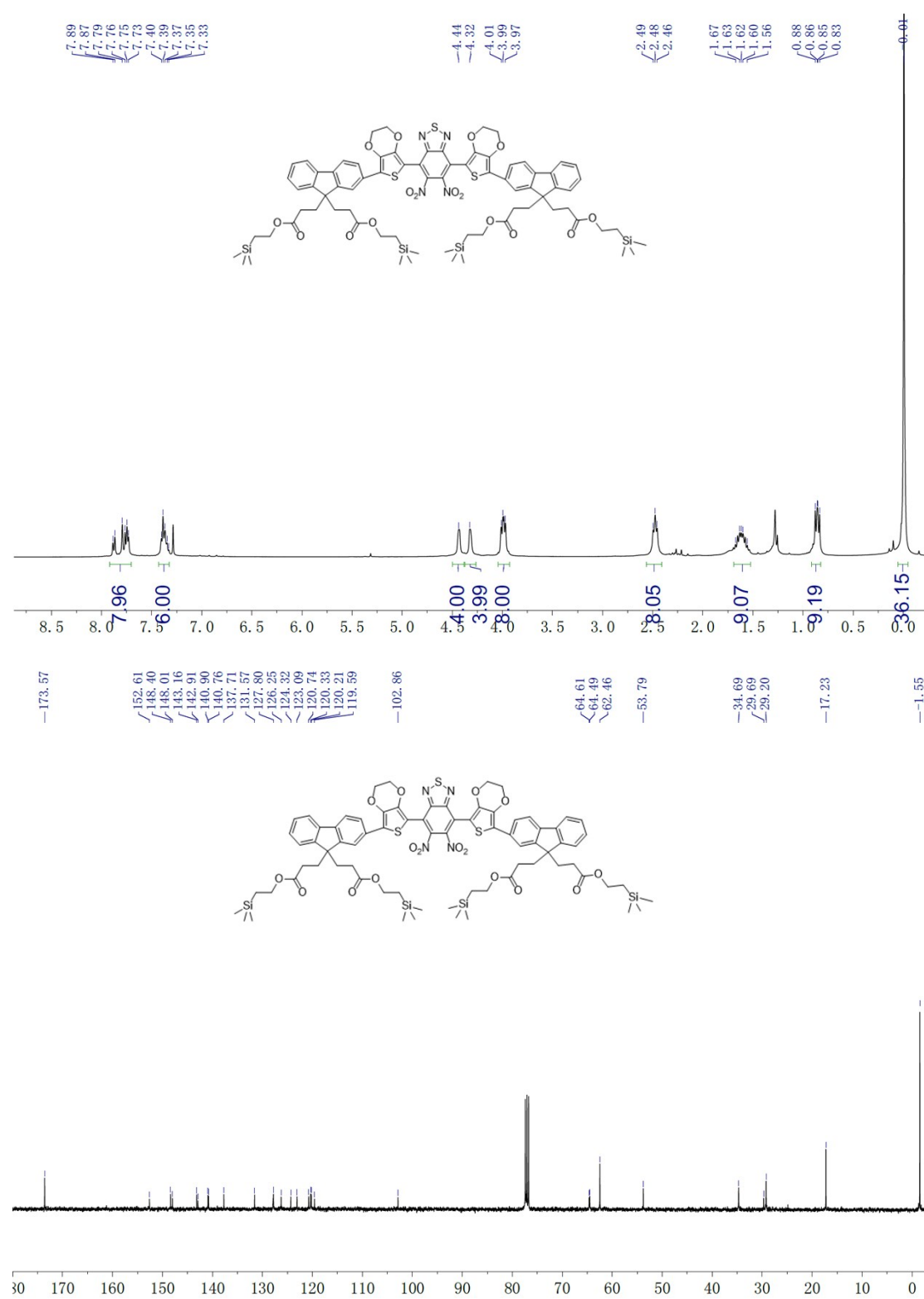


Figure S21. ¹H NMR and ¹³C NMR for B2.

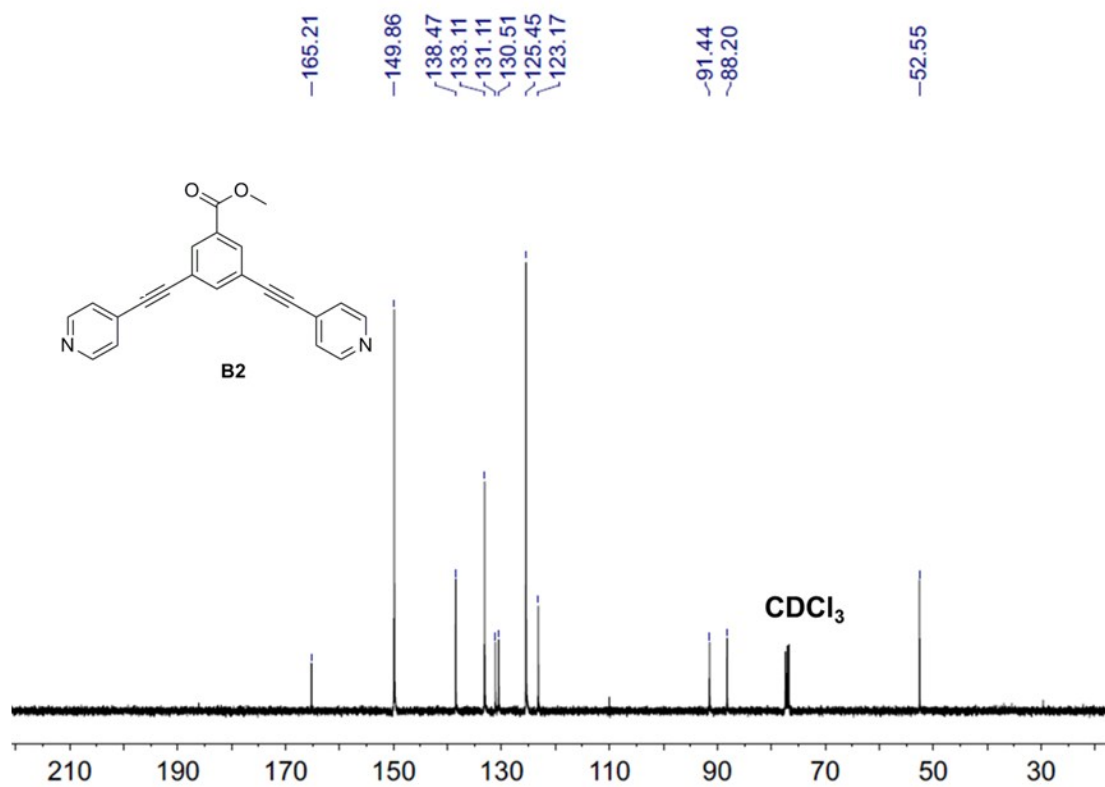
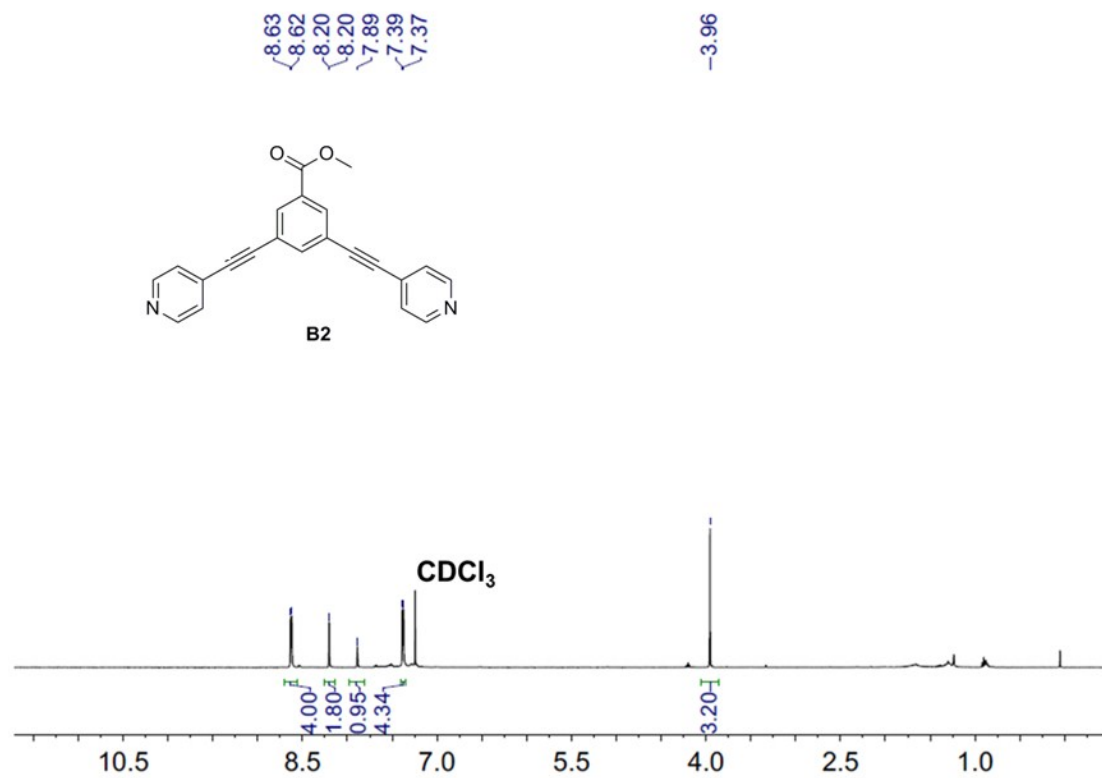


Figure S22. ^1H NMR and ^{13}C NMR for **B3**.

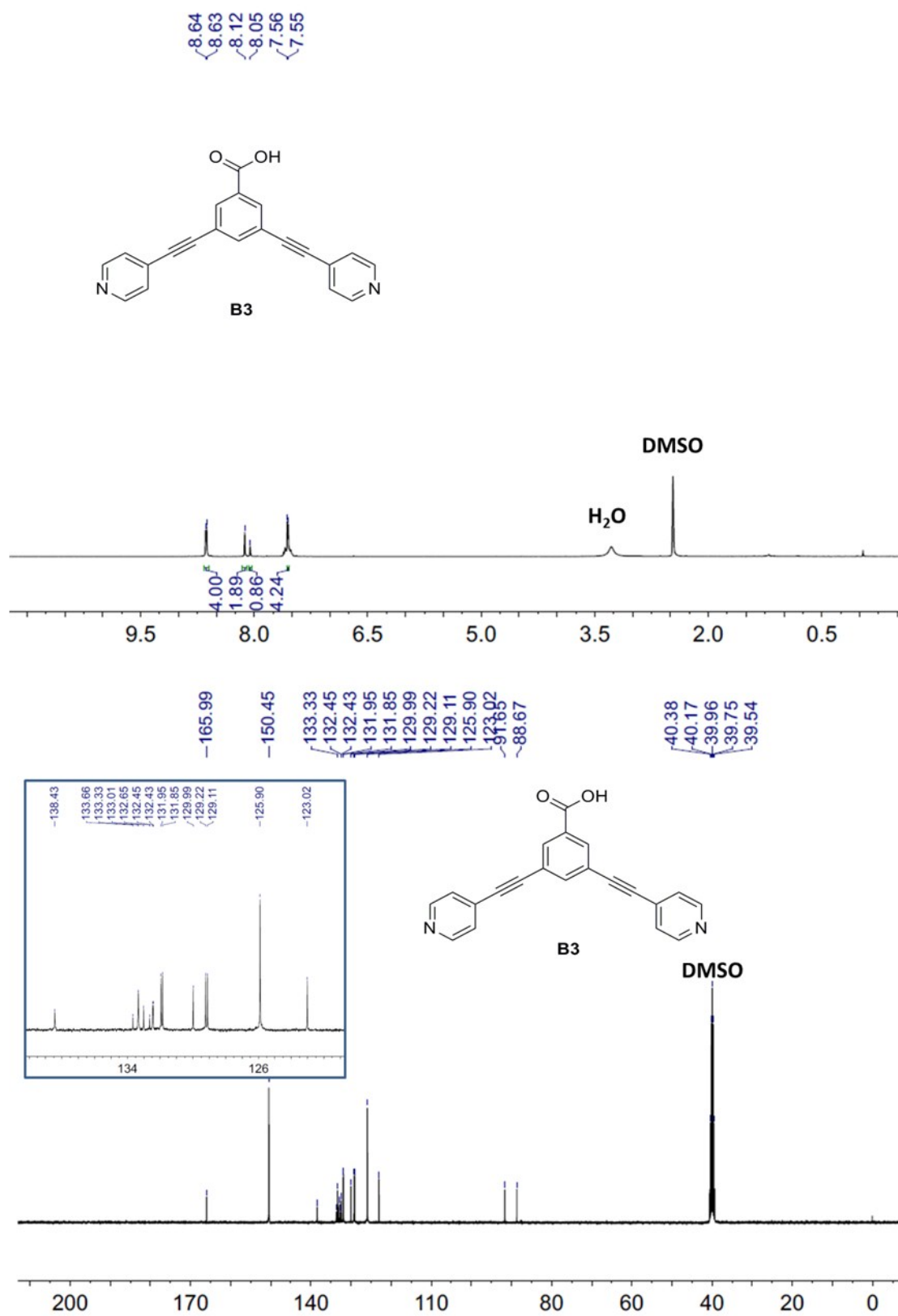


Figure S23. ^1H NMR and ^{13}C NMR for **B5**.

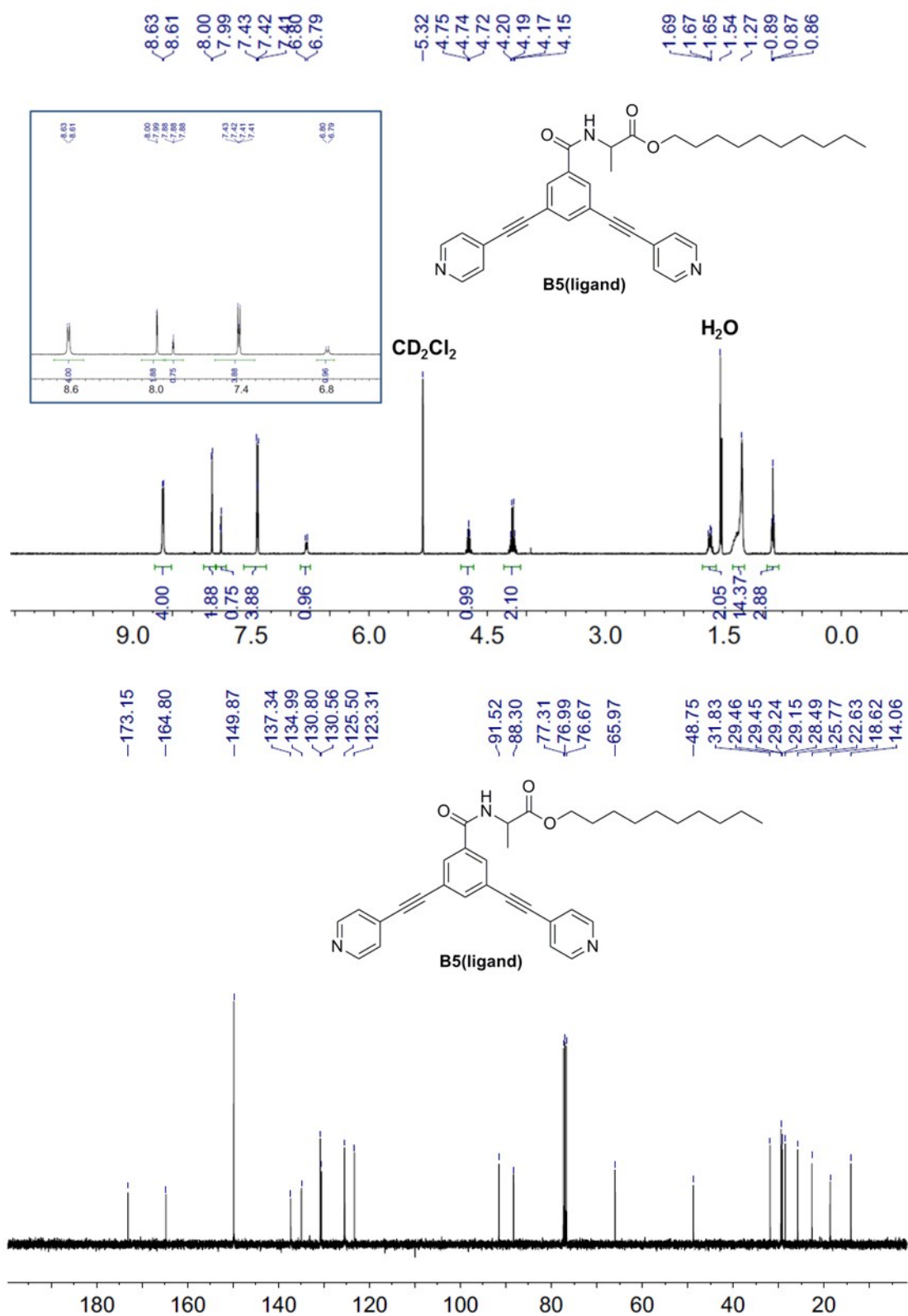


Figure S24. ¹H NMR for P1.

