Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information for

# A photoluminescence and electrochemiluminescence probe based on iridium(III) complex with a boronic acid-functionalised ancillary ligand for the selective detection of mercury(II) ion

Kyoung-Rok Kim, Jinrok Oh, and Jong-In Hong*

*Department of Chemistry, Seoul National University, Seoul 08826, Korea*

*E-mail: jihong@snu.ac.kr*

## Contents

## 1. Materials and instruments

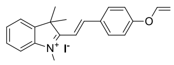
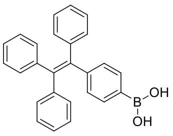
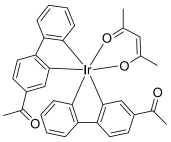
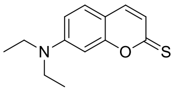
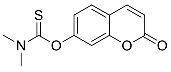
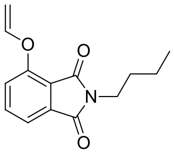
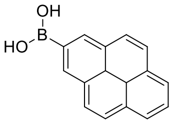
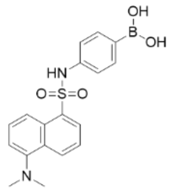
Commercially available reagents were purchased from TCI (Tokyo Chemical Industry, Tokyo, Japan), Alfa (Alfa Aesar, MA, USA), Sigma-Aldrich (Sigma-Aldrich Corp., MO, USA) and were used as received without further purification. Analytical thin-layer chromatography (TLC) was performed using aluminium sheets coated with Merck silica gel 60 F254. Crude compounds were purified by flash column chromatography using silica gel 60 (230-400 mesh) from SILICYCLE as the stationary phase. Deuterated solvents for nuclear magnetic resonance (NMR) spectra were purchased from Cambridge Isotopic Laboratories (Cambridge, MA, USA) and the chemical shifts of the NMR spectra were calibrated using the deuterated solvent signals as an internal reference. $^{1}$H and $^{13}$C NMR spectra were obtained using Bruker Avance DPX-300 (300 MHz), Agilent DD2MR400 NMR system (400 MHz), and Varian NMR system (500 MHz). High-resolution fast atom bombardment mass spectrometry (HR-FAB-MS) data (JEOL, JMS-700) with positive mode were received directly from the National Center for Inter-University Research Facilities (NCIRF). Mass analyses of compounds were conducted using Thermo Scientific Vanquish Core high-performance liquid chromatography coupled with Thermo Scientific linear ion trap-orbitrap mass spectrometry (HPLC-LTQ-orbitrap). UV-vis absorption spectra were recorded on a JASCO V-730 spectrometer. The PL spectra were obtained with a JASCO FP-8300 spectrophotometer and a SpectraMax M2 multi-mode microplate reader. Bandwidths for both excitation and emission were 5 nm, except for the data recorded using the SpectraMax M2 multi-mode microplate reader (sensitivity: high, 30). Fluorescence lifetime measurements were performed using a time-correlated single-photon counting (TCSPC) technique (FluoTime 250, PicoQuant, Berlin, Germany). A pulsed laser of 377 nm was used as the excitation source for the TCSPC method. All samples for the measurements were prepared freshly before experiments from corresponding stock solutions (2 mM probe in dimethyl sulfoxide and 2 mM metal ions in water). All metal ion sources were nitrate salts.

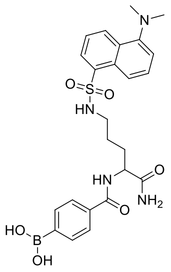
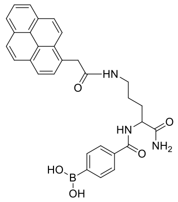
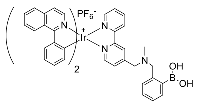
## 2. Electrochemical and electrochemiluminescent measurements

Differential pulse voltammetry (DPV) with a CH Instruments 650 B electrochemical analyzer (CH Instruments, Inc., TX, USA) was performed on each sample to investigate electrochemical properties. All redox potential values were calibrated using ferrocene as an internal reference. ECL measurements were performed with a low-voltage photomultiplier tube module (H-6780, Hamamatsu photonics K.K., Tokyo, Japan) on which a home-made ECL flow cell was directly mounted in a 9:1 (v/v) mixture of HEPES-buffered solution (0.1 M, pH 7.4) and $CH_3CN$ (ACROS) containing 100 mM 2-(dibutylamino)ethanol (DBAE) (Sigma-Aldrich), 0.1 % polidocanol (Sigma-Aldrich), and 0.1 M tetrabutylammonium perchlorate (TBAP) (TCI) as the co-reactant, surfactant, and the supporting electrolyte, respectively. All ECL experiments were simultaneously performed with cyclic voltammetry (CV) by a CH Instruments 650 B electrochemical analyzer (CH Instruments, Inc., TX, USA) using a three-electrode setup. The three-electrode system consists of a 2 mm diameter glassy carbon (GC) working electrode, platinum as a counter electrode, and a silver wire as a quasi reference electrode. The GC working electrode was polished on a polishing pad with 0.05 μm alumina (Buehler, IL, USA) and sonicated in a 1:1 (v/v) mixture of distilled water and absolute ethanol (Samchun Chemical) for 5 min. And then the electrode was fully dried using ultra-pure $N_2$ gas. All samples for electrochemical and ECL measurments were freshly prepared before experiments. All ECL data were the average of the maximum ECL intensity values from three repeated experiments.

# 3. Additional figures and tables

**Table S1.** Comparison of probe **1** with previously reported PL/ECL probes for the detection of $Hg^{2+}$ ion.

| Probe | Interference/ detection range | Detection medium | Response type/Response time | Detection limit | ref |
|---|---|---|---|---|---|
|  | -/0–30 μM | Aqueous PBS buffer (pH 7.4, 10 mM PBS) | Turn-on (PL)/60 s | $25 \times 10^{-6}$ M | 1 |
|  | -/0–10 μM | $H_2O$/THF (9:1 v/v) | Turn-on (PL)/10 min | $0.6 \times 10^{-6}$ M | 2 |
|  | -/9–30 μM (PL),<br>0–100 μM (ECL) | $H_2O/CH_3CN$ (1:9 v/v) for PL analysis, $H_2O/CH_3CN$ (1 : 9 v/v) (30 mM TPA, and 0.1 M TBAP) for ECL analysis | Turn-on (PL), Turn-off (ECL) /- | $73 \times 10^{-9}$ M (PL),<br>$1.9 \times 10^{-9}$ M (ECL) | 3 |
|  | $Ag^+$/0–15 μM | Aqueous PBS buffer (pH 7.4, 10 mM PBS) | Ratiometric (PL)/ 5 min | $9.23 \times 10^{-9}$ M | 4 |
|  | -/0–10 μM | Aqueous HEPES buffer (pH 7.4, 5 mM HEPES) | Turn-on (PL)/ 10 min | $0.3 \times 10^{-9}$ M | 5 |
|  | -/0–16 μM | Aqueous PBS buffer (pH 7.4, 10 mM PBS) | Turn-on (PL)/ 10 min | $9.47 \times 10^{-9}$ M | 6 |
|  | -/0–3 μM | $H_2O$ | Turn-off (PL)/ 10 min | $6.6 \times 10^{-9}$ M | 7 |
|  | -/0–7 μM | Aqueous HEPES buffer (pH 7.4, 20 mM HEPES) | Turn-on (PL)/ <2 min | $4.02 \times 10^{-9}$ M | 8 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
|  | -/0–8 μM | Aqueous HEPES buffer (pH 7.4, 10 mM HEPES) | Ratiometric (PL)/ 60 min | 7.0 × $10^{-9}$ M | 9 |
|  | -/0–22 μM | Aqueous HEPES buffer (pH 7.4, 10 mM HEPES) | Ratiometric (PL)/ 10 min | 15.2 × $10^{-9}$ M | 10 |
|  | -/0–9 μM (PL),<br>0–10 μM (ECL) | HEPES buffer /$CH_3CN$ (9 : 1 v/v, pH 7.4 10 mM HEPES) for PL analysis, HEPES buffer /$CH_3CN$ (9 : 1 v/v, pH 7.4, 100 mM DBAE, 0.1 M HEPES, 0.1% polidocanol and 0.1 M TBAP) for ECL analysis | Turn-off (PL), Turn-off (ECL)/ <2 min | 0.72 × $10^{-6}$ M (PL),<br>8.03 × $10^{-9}$ M (ECL) | This work (Probe **1**) |

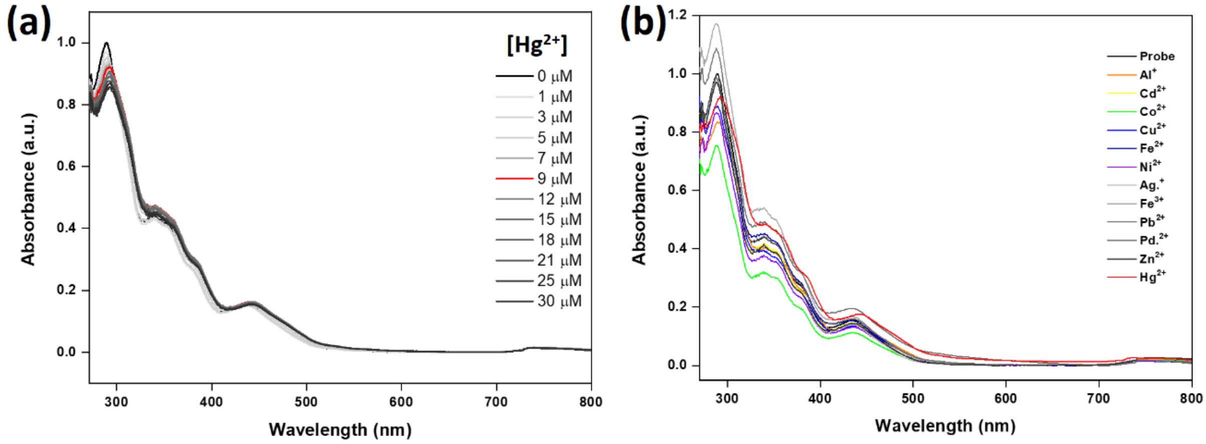


**Figure S1.** (a) UV-vis absorption spectra of probe **1** in the presence of an increasing amount of $Hg^{2+}$. (b) UV-vis absorption spectra of probe **1** in the presence of various metal ions (40 μM each; 20 μM for $Hg^{2+}$). Media: $CH_3CN/H_2O$, 1:9 v/v, pH 7.4, 10 mM HEPES.

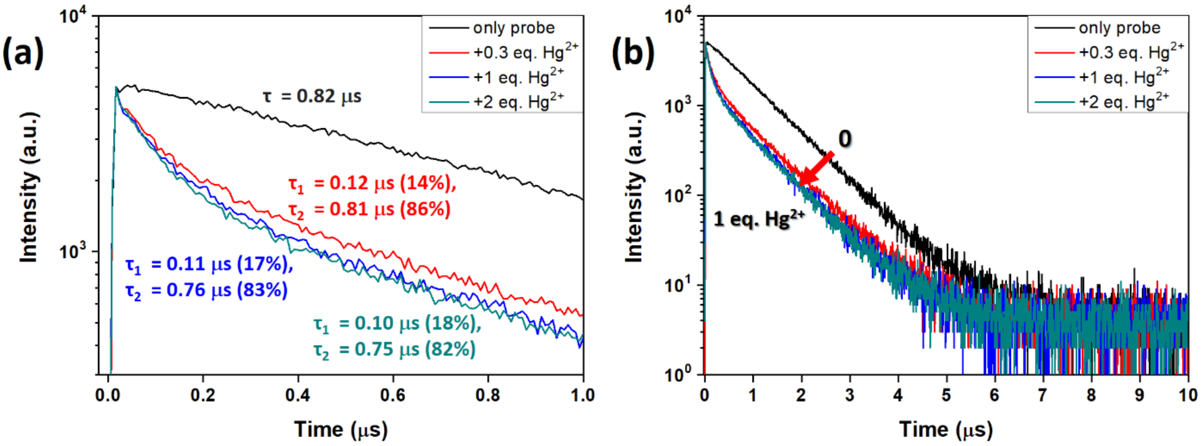


**Figure S2.** Photoluminescence decay profiles of probe **1** (10 μM) recorded in the presence of different concentrations of $Hg^{2+}$ (0, 3, 10 and 20 μM) in the range of (a) 0–1 μs and (b) 0–10 μs. Media: $CH_3CN/H_2O$, 1:9 v/v, pH 7.4, 10 mM HEPES.

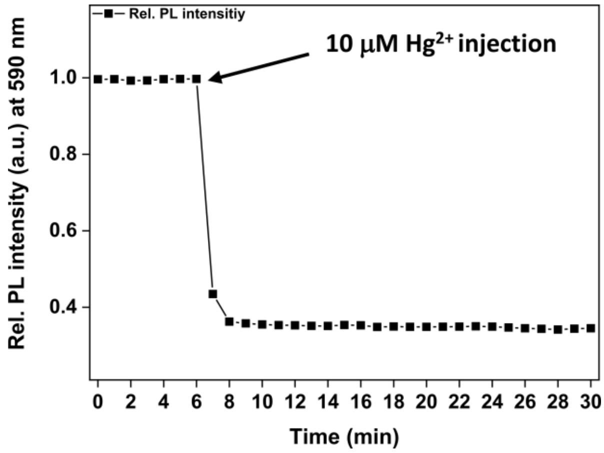


**Figure S3.** Time-dependent changes of the PL intensity at 590 nm for probe **1** (10 μM) after the addition of 10 μM $Hg^{2+}$ ions. Media: $CH_3CN/H_2O$ (1:9 v/v), pH 7.4, 10 mM HEPES.

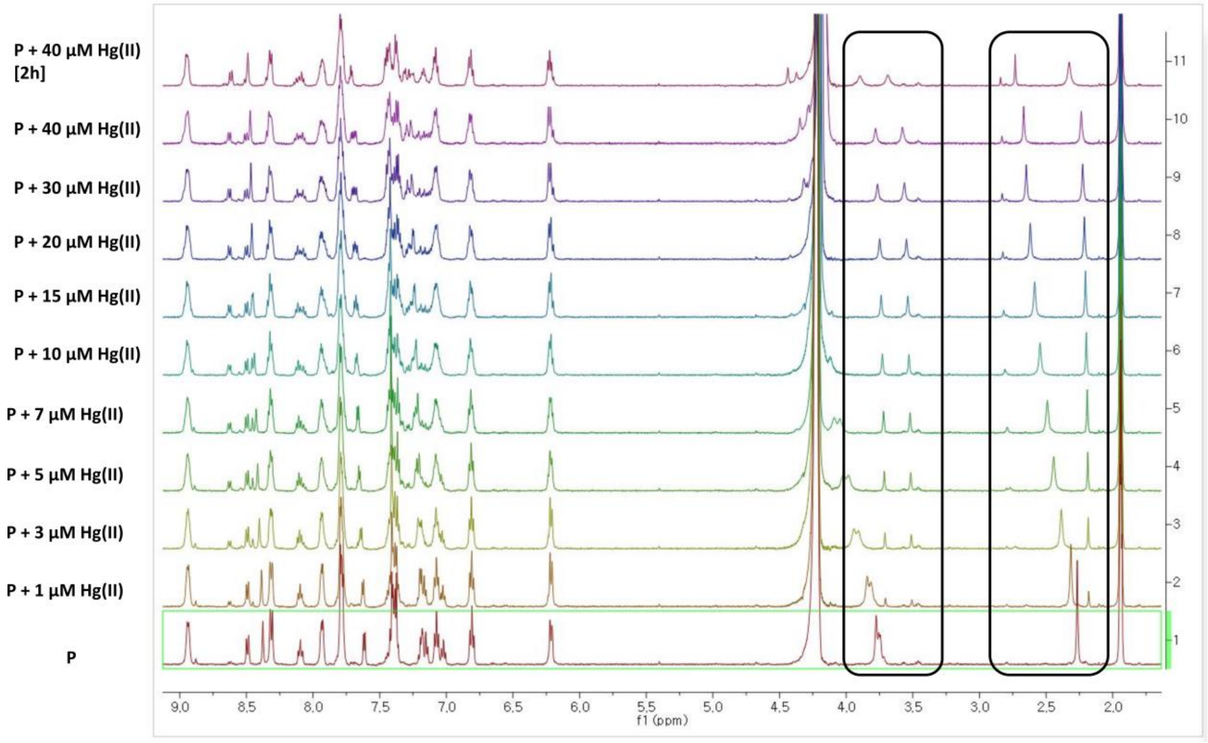


**Figure S4.** Partial $^1$H NMR spectra of probe **1** upon the addition of an increasing amount of $Hg^{2+}$ ion in $CD_3CN/D_2O$ 1:1 mixture.

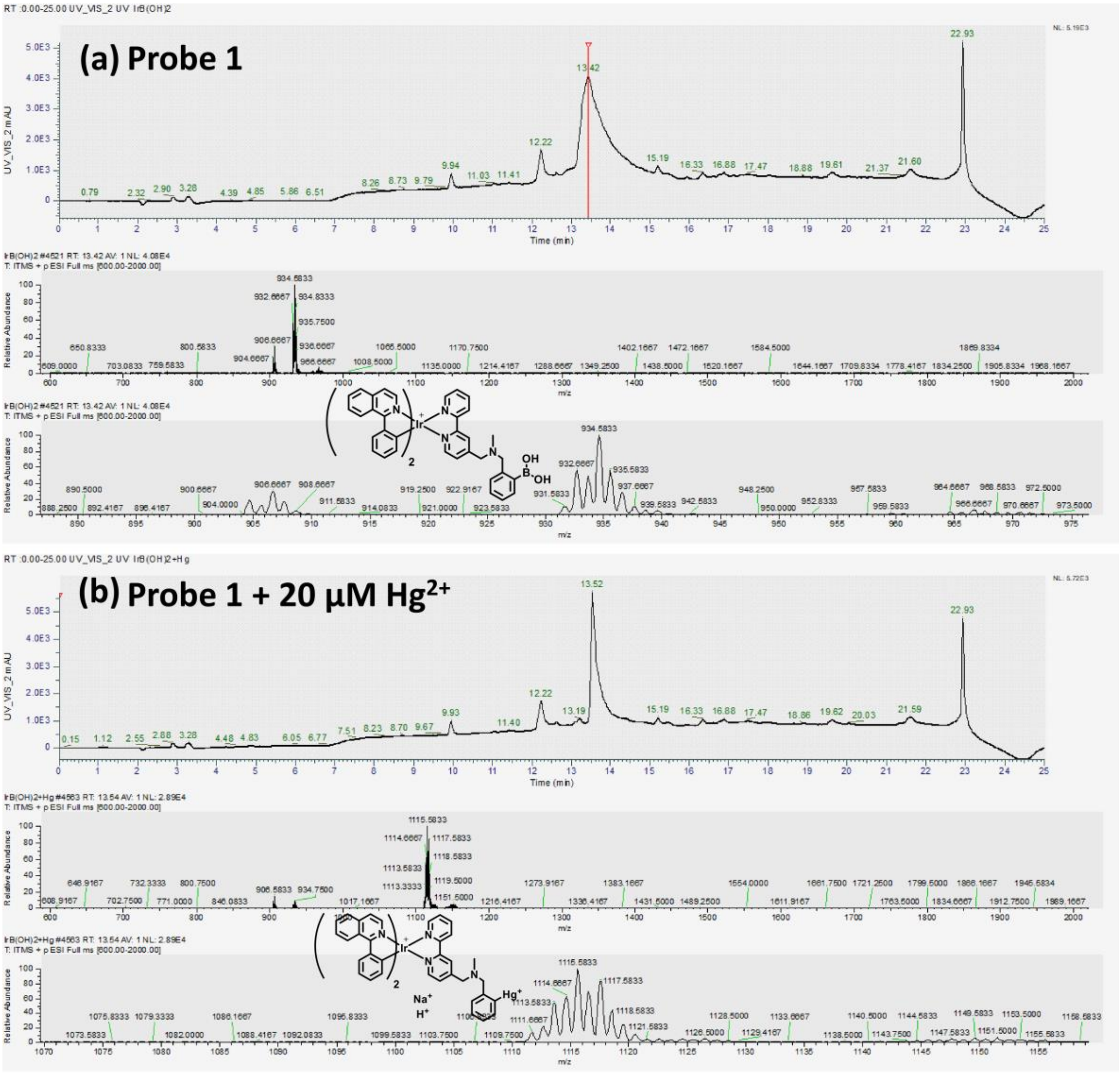


**Figure S5.** HPLC-LTQ-orbitrap analysis of 10 µM probe **1** (a) before and (b) after the addition of 20 µM $Hg^{2+}$ ions.

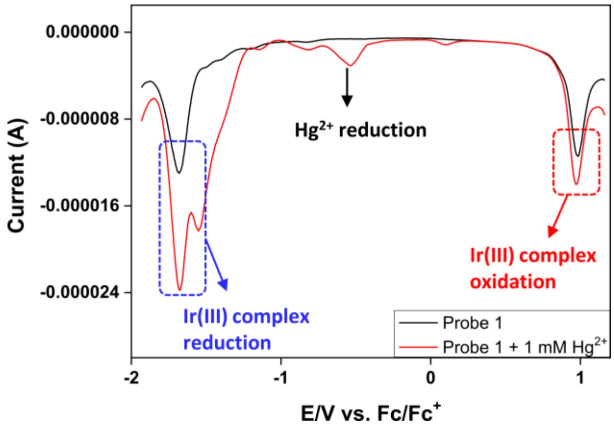


**Figure S6.** Differential pulse voltammetry (DPV) signals of 1 mM probe **1** before (black line) and after (red line) the addition of 1 mM $Hg^{2+}$ ion in acetonitrile containing 0.1 M $TBAPF_6$ as the supporting electrolyte (scan rate: 0.1 V/s, working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: $Ag/AgNO_3$).

**Table S2.** Electrochemical properties of probe **1**, probe **1** with 10 µM $Hg^{2+}$, and DBAE.[a]

| | $E_{ox}$ (V *vs.* Fc/$Fc^+$) | HOMO (eV) | $E_{red}$ (V *vs.* Fc/$Fc^+$) | LUMO (eV) | $E_g$ (eV) |
|---|---|---|---|---|---|
| Probe **1** | 0.98 | −5.78 | −1.68 | −3.12 | 2.66 |
| Probe **1** + 10 µM $Hg^{2+}$ | 0.97 | −5.77 | −0.54<br>($Hg^+$ species)<br>−1.55<br>(Ir(III) complex) | −4.26<br>($Hg^+$ species)<br>−3.25<br>(Ir(III) complex) | 2.52<br>(Ir(III) complex) |
| DBAE | 0.46 | −5.26 | - | - | - |

[a] Cyclic voltammetric measurements of each compound (1 mM) were performed in acetonitrile solution with 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte at the scan rate of 0.1 V/s. The values were calibrated against the oxidation of 1 mM ferrocene (Fc/$Fc^+$) as a standard. The corresponding HOMO/LUMO energy levels of each compound were calculated using the equation: $E_{HOMO/LUMO}$ (eV) = − ($E_{ox/red}$ − $E_{Fc/Fc^+}$) − 4.80 eV.[11]

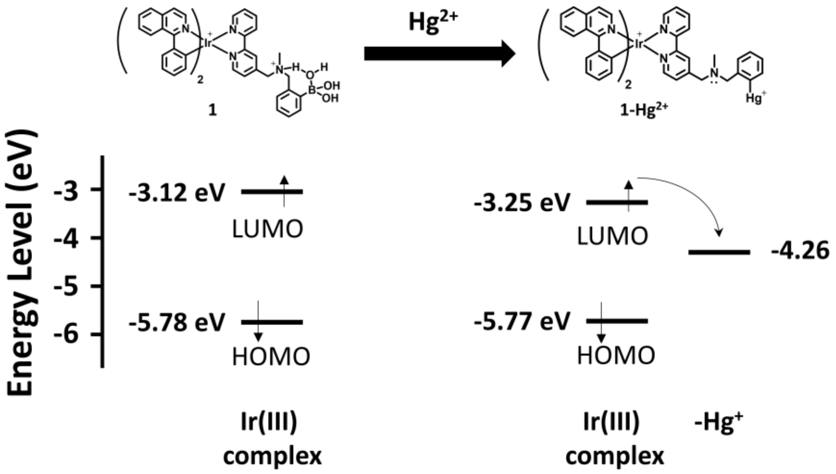


**Figure S7.** The HOMO/LUMO energy levels of probe **1** and **1**-$Hg^{2+}$ calculated from the CV to explain the PeT quenching process.

# 4. Synthesis and Characterization

**Synthesis of 3**

A mixture of 2-acetylpyridine (3.70 mL, 33.02 mmol) and iodine (9.22 g, 36.32 mmol) was dissolved in 40 mL of pyridine and stirred at 140 °C for 3 h. After cooling down to room temperature, the precipitate formed was collected by filtration, washed with cold pyridine. The crude product was recrystallised from methanol to afford 3 (6.71 g, 62%). Compound 3 was used for the next step without further purification. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 9.00 (d, $J$ = 5.6 Hz, 2H), 8.87 (d, $J$ = 4.6 Hz, 1H), 8.72 (t, $J$ = 7.8 Hz, 1H), 8.36 – 8.21 (m, 2H), 8.11 (ddd, $J$ = 17.0, 11.6, 4.6 Hz, 2H), 7.93 – 7.77 (m, 1H), 6.50 (s, 2H).

**Synthesis of 4**

A solution of 3 (4.19 g, 12.68 mmol), crotonaldehyde (2.58 mL, 29.92 mmol), and $NH_4OAc$ (4.72 g, 63.37 mmol) in methanol (50 mL) was refluxed for 24 h. After cooling down to room temperature, the solvent was removed under reduced pressure and the residue was extracted with dichloromethane ($CH_2Cl_2$). The combined organic layer was washed with brine and dried over anhydrous sodium sulphate, and evaporated. The residue was purified by alumina column chromatography ($CH_2Cl_2$/MeOH = 50:1) to give 4 (706 mg, 33%). $^1$H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, $J$ = 4.4 Hz, 1H), 8.55 (d, $J$ = 4.9 Hz, 1H), 8.40 (d, $J$ = 8.0 Hz, 1H), 8.24 (s, 1H), 7.82 (td, $J$ = 7.8, 1.7 Hz, 1H), 7.39 – 7.25 (m, 1H), 7.15 (d, $J$ = 4.5 Hz, 1H), 2.45 (s, 3H).

**Synthesis of 5**

A mixture of 4 (706 mg, 4.15 mmol) and selenium dioxide (690 mg, 6.22 mmol) in dioxane (47 mL) was refluxed for 24 h. The hot solution of the mixture was filtered, and the filtrate was evaporated under reduced pressure. The resulting residue was purified by alumina column chromatography ($CH_2Cl_2$/MeOH = 50:1) to afford 5 (408 mg, 53%). $^1$H NMR (300 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.92 (d, $J$ = 4.9 Hz, 1H), 8.88 (s, 1H), 8.75 (d, $J$ = 4.6 Hz, 1H), 8.47 (d, $J$ = 8.0 Hz, 1H), 7.90 (td, $J$ = 7.8, 1.6 Hz, 1H), 7.75 (dd, $J$ = 4.9, 1.3 Hz, 1H), 7.40 (dd, $J$ = 6.9, 5.4 Hz, 1H).

**Synthesis of 7**

A mixture of 5 (222 mg, 1.21 mmol) and 2 M methylamine solution in THF (0.66 mL, 1.32 mmol) was dissolved in 10 mL of toluene and refluxed with a Dean-Stark trap for 24 h. After cooling down to room temperature, the organic solvent was evaporated under reduced pressure. The residue was re-dissolved in methanol (10 mL) and stirred at room temperature for 24 h with sodium borohydride (228 mg, 6.05 mmol). Then, 1 mL of 1 M HCl solution was added to the mixture to destroy excessive hydride. The reaction mixture was neutralised to pH 7 by the addition of a saturated aqueous sodium bicarbonate solution and extracted with $CH_2Cl_2$ three times. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate, and evaporated under reduced pressure to afford a crude compound 6. Compound 6 was used for the next step without further purification.-Compound 6 was re-dissolved in 10 mL of $CH_2Cl_2$ and stirred at room temperature for 12 h with di-tert-butyl dicarbonate (396 mg, 1.82 mmol). The solution was diluted with water and extracted with dichloromethane three times. The combined organic layer was dried over anhydrous sodium sulphate, filtered, and concentrated under reduced pressure. The residue was purified by alumina column chromatography ($CH_2Cl_2$/MeOH = 50:1) to give 7 (203 mg, 56%). $^1$H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, $J$ = 4.2 Hz, 1H), 8.64 (d, $J$ = 5.0 Hz, 1H), 8.43 (d, $J$ = 7.9 Hz, 1H), 8.29 (s, 1H), 7.84 (td, $J$ = 7.8, 1.5 Hz, 1H), 7.33 (dd, $J$ = 6.9, 5.2 Hz, 1H), 7.18 (s, 1H), 4.51 (s, 2H), 2.91 (d, $J$ = 16.4 Hz, 3H), 1.48 (d, $J$ = 17.2 Hz, 9H).

**Synthesis of 8**

A solution of *o*-tolylboronic acid (1.99 g, 14.52 mmol) and 2,2-dimethyl-1,3-propanediol (2.65 g, 18.88 mmol) in 50 mL of toluene was refluxed with a Dean-Stark trap for 24 h. After cooling down to room temperature, the solution was diluted with dichloromethane and filtered through a thin pad of silica gel. The combined solution was evaporated under reduced pressure. The residue was re-dissolved in 45 mL of 1,2-dichloroethane and stirred at reflux for 12 h with N-bromosuccinimide (2.58 g, 14.47 mmol) and AIBN (32 mg, 0. 19 mmol). The solution was cooled down to room temperature and then filtered. The filtrate was evaporated under reduced pressure to afford 8 (3.50 g, 90%). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 4.1 Hz, 2H), 7.28 (dd, *J* = 4.6, 2.8 Hz, 1H), 4.92 (s, 2H), 3.81 (s, 4H), 1.06 (s, 6H).

**Synthesis of 9**

1-Phenylisoquinoline (700 mg, 3.41 mmol) and iridium chloride hydrate (485 mg, 1.62 mmol) were dissolved in a mixture of 2-ethoxyethanol (21 mL) and water (7 mL). The reaction mixture was stirred at 110°C for 18 h. After cooling down to room temperature, water was poured into the reaction mixture. Then, the dark red precipitate was filtered, washed with $H_2O$ and hexane, and dried in vacuo to afford a crude chloro-bridged cyclometalated Ir(III) complex dimer 9 (600 mg, 58%). Compound 9 was used for the next step without further purification.

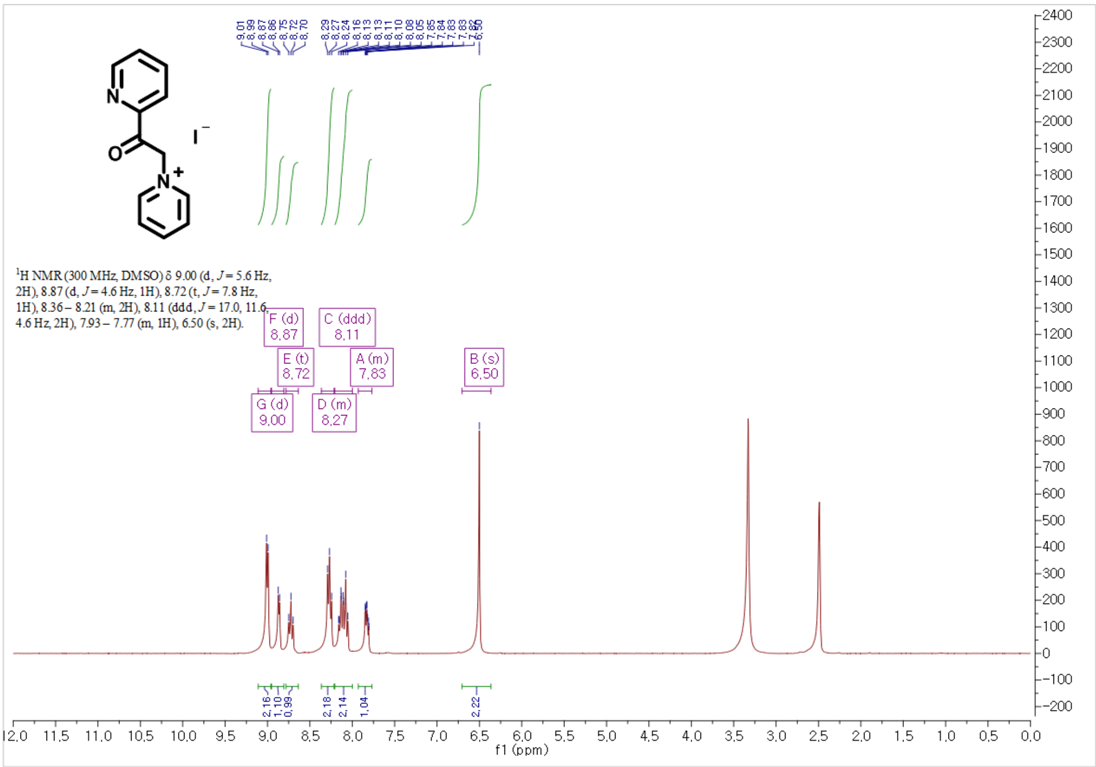
**Synthesis of 10**

A mixture of compound 9 (85 mg, 67 μmol), compound 7 (40 mg, 0.134 mmol) in dichloromethane/methanol (1:1, 2 mL) was reluxed for 12 h. After cooling down to room temperature, the solution was filtered and evaporated, and the residue was purified by silica gel column chromatography ($CH_2Cl_2$/MeOH = 50:1) to afford 10 (56 mg, 45% yield). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 3.7 Hz, 2H), 8.75 – 8.59 (m, 1H), 8.48 (d, *J* = 25.9 Hz, 1H), 8.26 (d, *J* = 7.9 Hz, 2H), 8.10 (t, *J* = 7.4 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.76 (ddt, *J* = 14.4, 9.7, 5.0 Hz, 5H), 7.69 – 7.62 (m, 1H), 7.44 (d, *J* = 6.4 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.21 (d, *J* = 5.5 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.88 (t, *J* = 6.0 Hz, 2H), 6.28 (d, *J* = 7.5 Hz, 2H), 4.68 (s, 2H), 2.94 (d, *J* = 19.7 Hz, 3H), 1.45 (s, 6H), 1.25 (s, 3H). $^{13}$C NMR (125 MHz, acetone-$d_6$) δ 168.76, 168.71, 155.89, 155.84, 154.02, 153.99, 153.82, 153.80, 150.58, 150.54, 150.43, 150.39, 145.61, 145.58, 140.75, 140.73, 139.68, 139.65, 137.19, 137.14, 132.14, 132.11, 132.01, 131.97, 130.77, 130.75, 130.54, 130.52, 129.15, 129.12, 128.60, 128.56, 127.77, 127.72, 126.71, 126.67, 126.45, 126.40, 126.24, 126.22, 124.84, 124.82, 123.27, 123.24, 123.10, 123.04, 122.28, 122.23, 122.08, 122.00, 79.50, 78.32, 51.86, 51.02, 34.82, 34.47, 27.55, 27.53. MS (MALDI-TOF) **m/z**: $[M]^+$ calc. for $C_{47}H_{41}IrN_5O_2$ 900.289, found 899.874.

**Synthesis of 11**

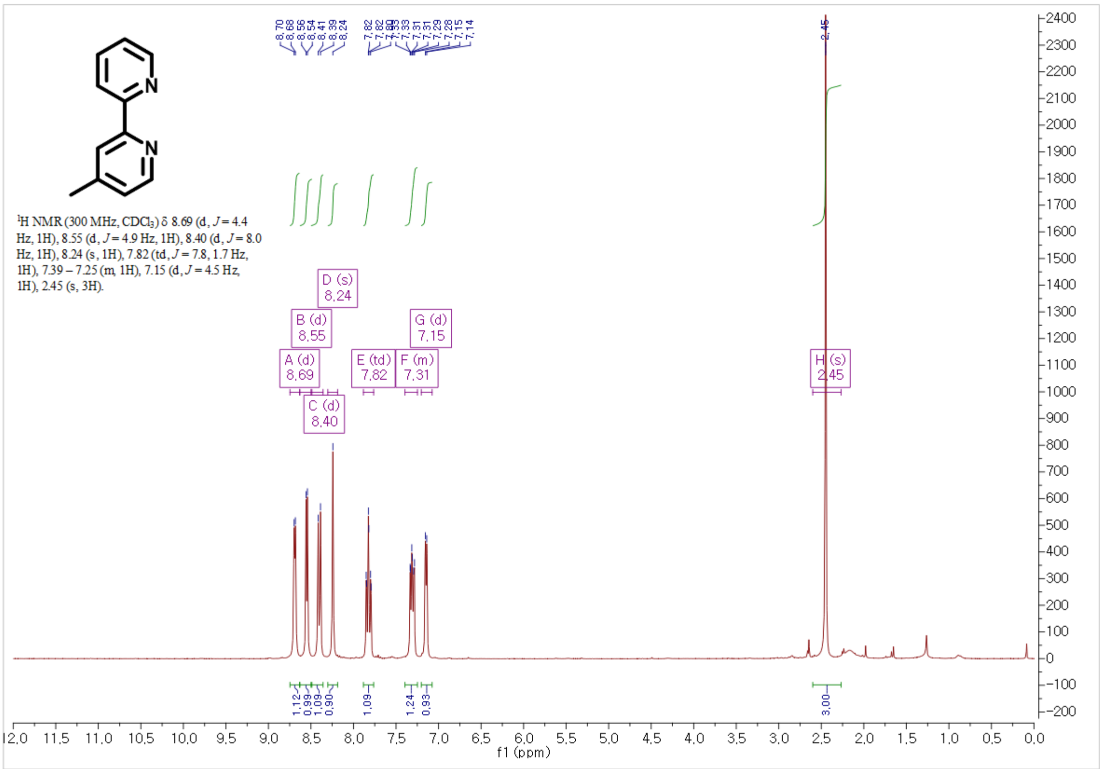
The compound 10 (56 mg, 53 μmol) in 1 mL of dichloromethane was treated with 0.25 mL of trifluoroacetic acid. The reaction mixture was stirred at room temperature for 4 h and neutralised to pH 7 by the addition of saturated aqueous sodium bicarbonate solution and extracted with dichloromethane three times and washed the dichloromethane solution with brine. The combined organic layer was dried over anhydrous sodium sulphate, filtered, and concentrated under reduced pressure to give a crude compound 11 (42 mg, 95%). Compound 11 was used for the next step without further purification.

# 5. Copies of NMR spectra



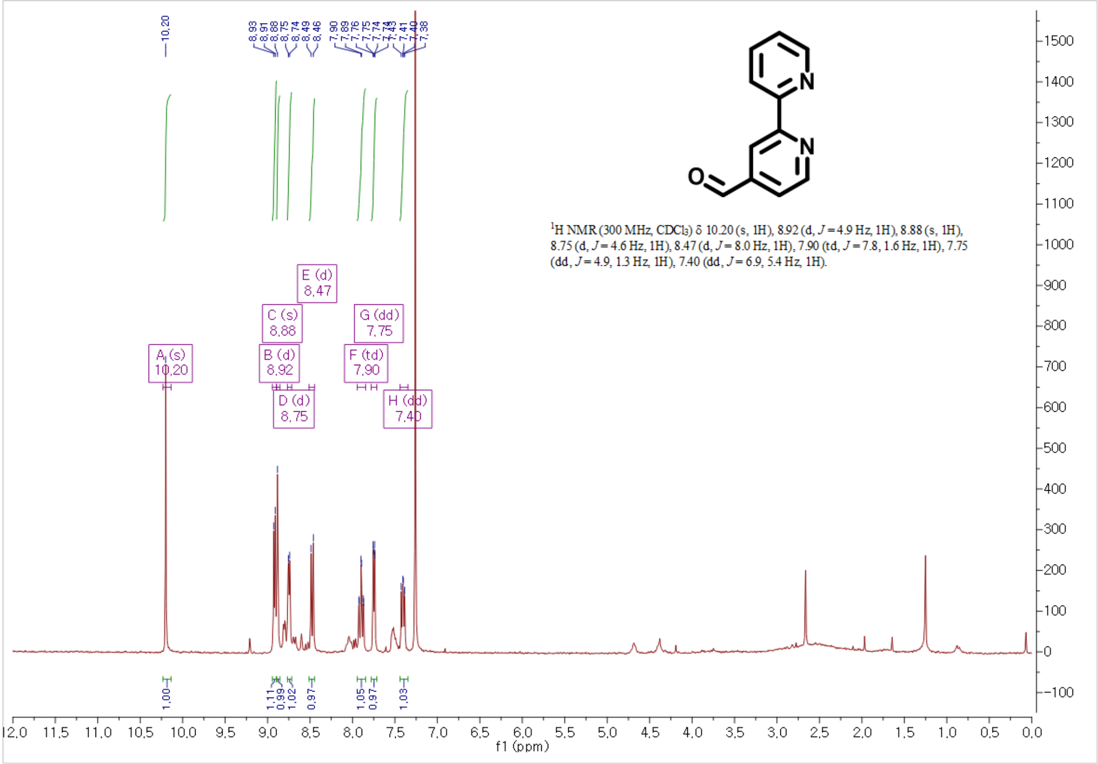
$^1$H NMR (300 MHz, DMSO) δ 9.00 (d, *J* = 5.6 Hz, 2H), 8.87 (d, *J* = 4.6 Hz, 1H), 8.72 (t, *J* = 7.8 Hz, 1H), 8.36 – 8.21 (m, 2H), 8.11 (ddd, *J* = 17.0, 11.6, 4.6 Hz, 2H), 7.93 – 7.77 (m, 1H), 6.50 (s, 2H).

**Figure S8.** $^1$H NMR spectrum of compound **3** (300 MHz, DMSO-*d*$_6$).



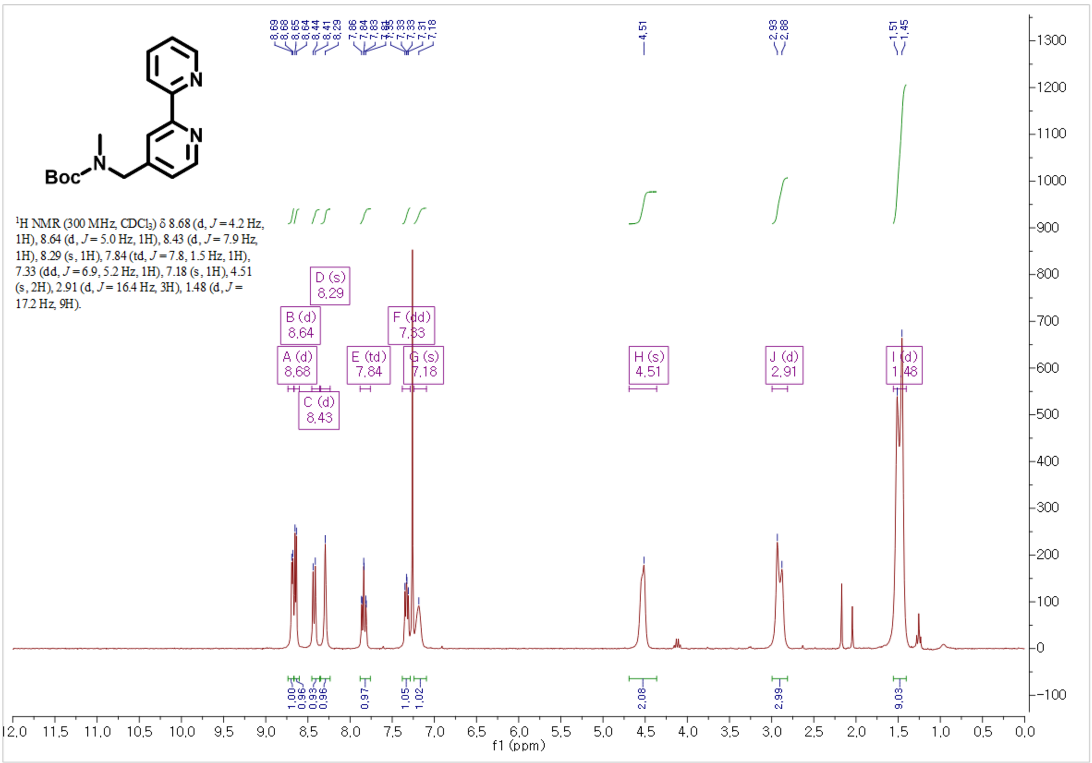
$^1$H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.4 Hz, 1H), 8.55 (d, *J* = 4.9 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 1H), 7.82 (td, *J* = 7.8, 1.7 Hz, 1H), 7.39 – 7.25 (m, 1H), 7.15 (d, *J* = 4.5 Hz, 1H), 2.45 (s, 3H).

**Figure S9.** $^1$H NMR spectrum of compound **4** (300 MHz, $CDCl_3$).



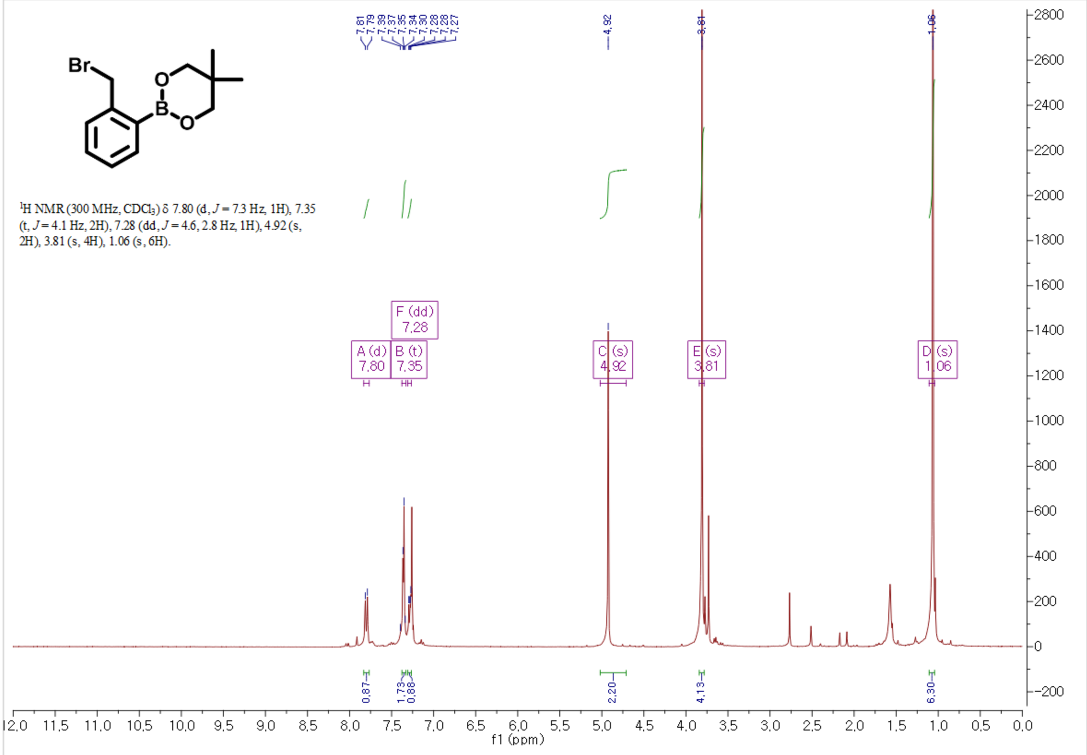
$^1$H NMR (300 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.92 (d, *J* = 4.9 Hz, 1H), 8.88 (s, 1H), 8.75 (d, *J* = 4.6 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 7.90 (td, *J* = 7.8, 1.6 Hz, 1H), 7.75 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.40 (dd, *J* = 6.9, 5.4 Hz, 1H).

**Figure S10.** $^1$H NMR spectrum of compound **5** (300 MHz, $CDCl_3$).



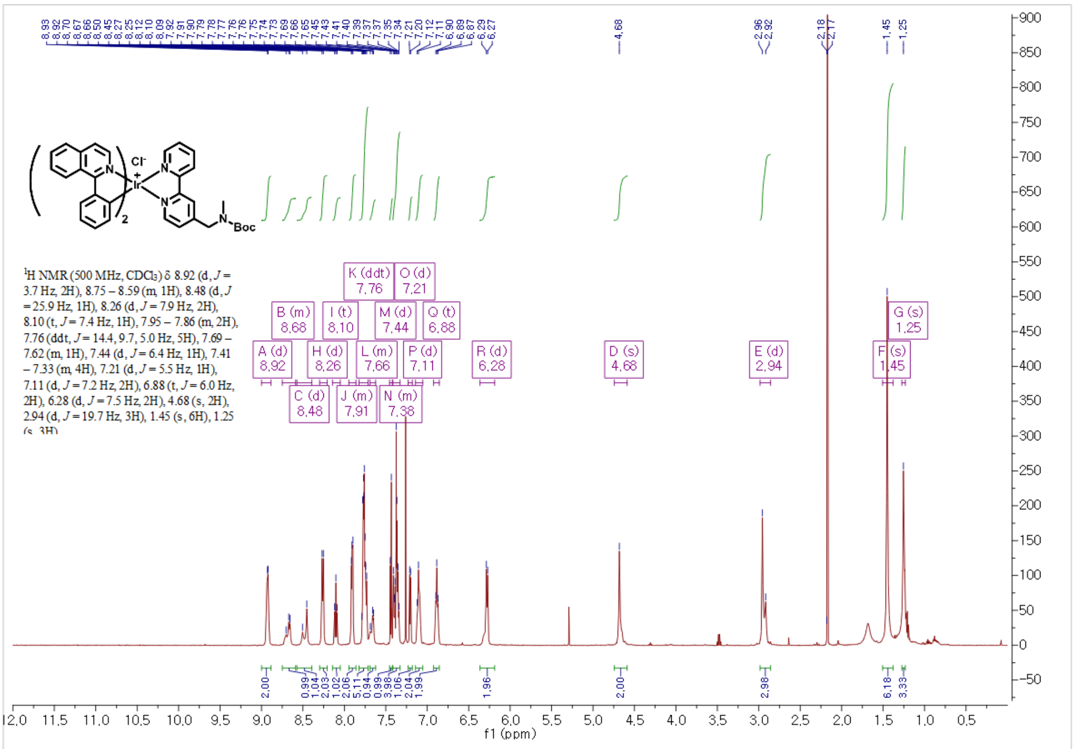
$^1$H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.2 Hz, 1H), 8.64 (d, *J* = 5.0 Hz, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 8.29 (s, 1H), 7.84 (td, *J* = 7.8, 1.5 Hz, 1H), 7.33 (dd, *J* = 6.9, 5.2 Hz, 1H), 7.18 (s, 1H), 4.51 (s, 2H), 2.91 (d, *J* = 16.4 Hz, 3H), 1.48 (d, *J* = 17.2 Hz, 9H).

**Figure S11.** $^1$H NMR spectrum of compound **6** (300 MHz, $CDCl_3$).



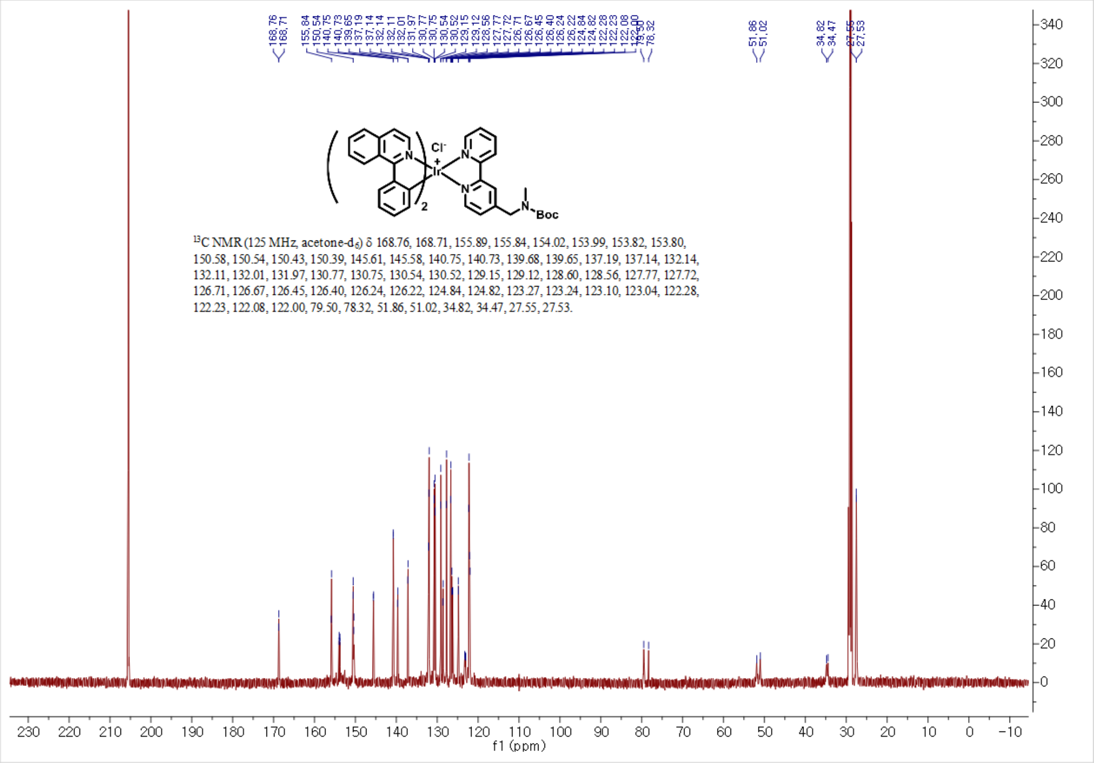
$^1$H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 4.1 Hz, 2H), 7.28 (dd, *J* = 4.6, 2.8 Hz, 1H), 4.92 (s, 2H), 3.81 (s, 4H), 1.06 (s, 6H).

**Figure S12.** $^1$H NMR spectrum of compound **7** (300 MHz, $CDCl_3$).



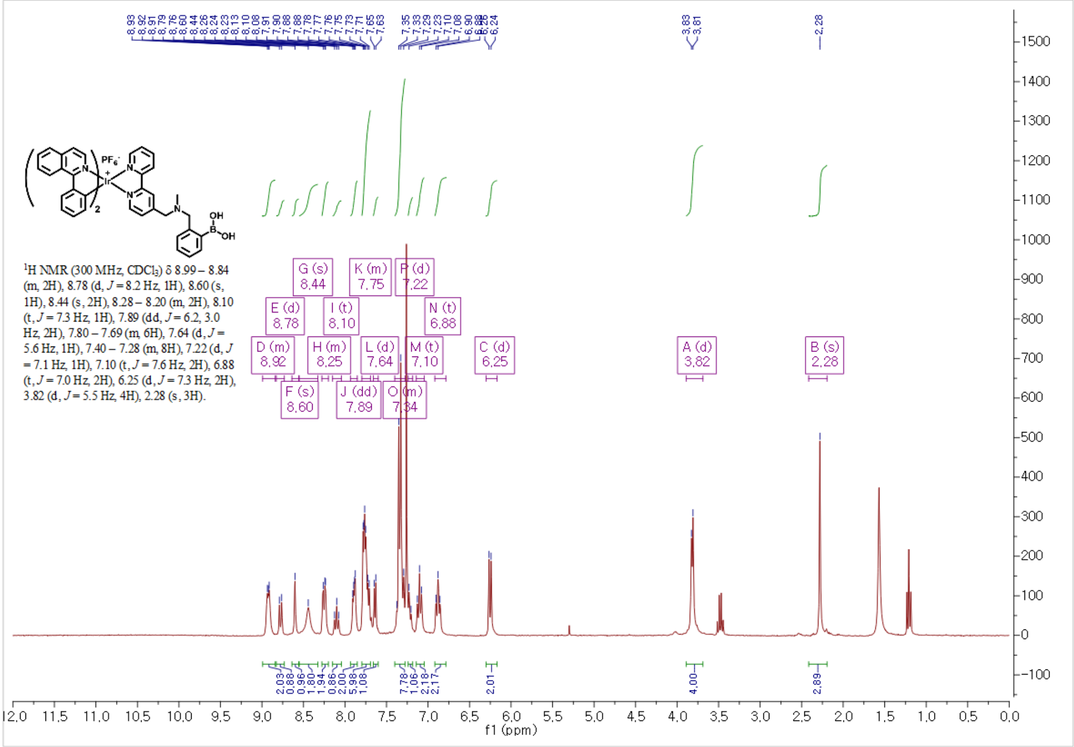
$^1$H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 3.7 Hz, 2H), 8.75 – 8.59 (m, 1H), 8.48 (d, *J* = 25.9 Hz, 1H), 8.26 (d, *J* = 7.9 Hz, 2H), 8.10 (t, *J* = 7.4 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.76 (ddt, *J* = 14.4, 9.7, 5.0 Hz, 5H), 7.69 – 7.62 (m, 1H), 7.44 (d, *J* = 6.4 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.21 (d, *J* = 5.5 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.88 (t, *J* = 6.0 Hz, 2H), 6.28 (d, *J* = 7.5 Hz, 2H), 4.68 (s, 2H), 2.94 (d, *J* = 19.7 Hz, 3H), 1.45 (s, 6H), 1.25 (s, 3H)

**Figure S13.** $^1$H NMR spectrum of compound **8** (500 MHz, $CDCl_3$).



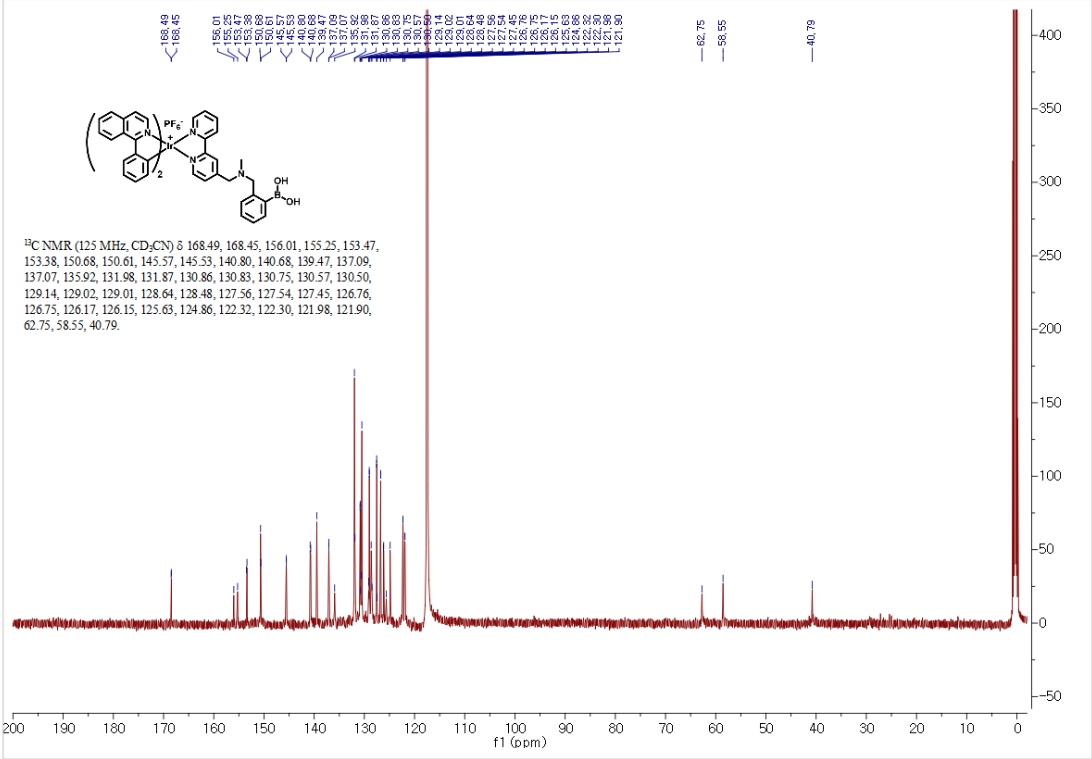
$^{13}$C NMR (125 MHz, acetone-d$_6$) δ 168.76, 168.71, 155.89, 155.84, 154.02, 153.99, 153.82, 153.80, 150.58, 150.54, 150.43, 150.39, 145.61, 145.58, 140.75, 140.73, 139.68, 139.65, 137.19, 137.14, 132.14, 132.11, 132.01, 131.97, 130.77, 130.75, 130.54, 130.52, 129.15, 129.12, 128.60, 128.56, 127.77, 127.72, 126.71, 126.67, 126.45, 126.40, 126.24, 126.22, 124.84, 124.82, 123.27, 123.24, 123.10, 123.04, 122.28, 122.23, 122.08, 122.00, 79.50, 78.32, 51.86, 51.02, 34.82, 34.47, 27.55, 27.53.

**Figure S14.** $^{13}$C NMR spectrum of compound **8** (125 MHz, acetone-$d_6$).



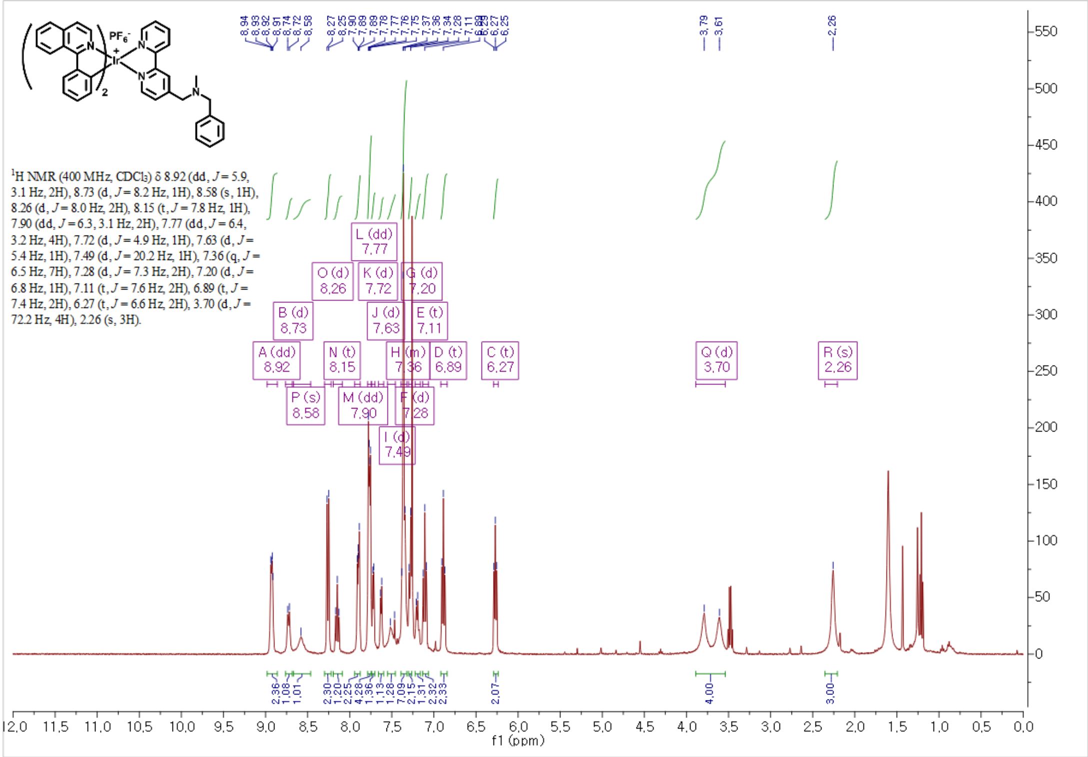
$^1$H NMR (300 MHz, CDCl$_3$) δ 8.99 – 8.84 (m, 2H), 8.78 (d, $J$ = 8.2 Hz, 1H), 8.60 (s, 1H), 8.44 (s, 2H), 8.28 – 8.20 (m, 2H), 8.10 (t, $J$ = 7.3 Hz, 1H), 7.89 (dd, $J$ = 6.2, 3.0 Hz, 2H), 7.80 – 7.69 (m, 6H), 7.64 (d, $J$ = 5.6 Hz, 1H), 7.40 – 7.28 (m, 8H), 7.22 (d, $J$ = 7.1 Hz, 1H), 7.10 (t, $J$ = 7.6 Hz, 2H), 6.88 (t, $J$ = 7.0 Hz, 2H), 6.25 (d, $J$ = 7.3 Hz, 2H), 3.82 (d, $J$ = 5.5 Hz, 4H), 2.28 (s, 3H).

**Figure S15.** $^1$H NMR spectrum of probe **1** (300 MHz, CDCl$_3$).



$^{13}$C NMR (125 MHz, CD$_3$CN) δ 168.49, 168.45, 156.01, 155.25, 153.47, 153.38, 150.68, 150.61, 145.57, 145.53, 140.80, 140.68, 139.47, 137.09, 137.07, 135.92, 131.98, 131.87, 130.86, 130.83, 130.75, 130.57, 130.50, 129.14, 129.02, 129.01, 128.64, 128.48, 127.56, 127.54, 127.45, 126.76, 126.75, 126.17, 126.15, 125.63, 124.86, 122.32, 122.30, 121.98, 121.90, 62.75, 58.55, 40.79.

**Figure S16.** $^{13}$C NMR spectrum of probe **1** (125 MHz, CD$_3$CN).



$^1$H NMR (400 MHz, CDCl$_3$) δ 8.92 (dd, $J$ = 5.9, 3.1 Hz, 2H), 8.73 (d, $J$ = 8.2 Hz, 1H), 8.58 (s, 1H), 8.26 (d, $J$ = 8.0 Hz, 2H), 8.15 (t, $J$ = 7.8 Hz, 1H), 7.90 (dd, $J$ = 6.3, 3.1 Hz, 2H), 7.77 (dd, $J$ = 6.4, 3.2 Hz, 4H), 7.72 (d, $J$ = 4.9 Hz, 1H), 7.63 (d, $J$ = 5.4 Hz, 1H), 7.49 (d, $J$ = 20.2 Hz, 1H), 7.36 (q, $J$ = 6.5 Hz, 7H), 7.28 (d, $J$ = 7.3 Hz, 2H), 7.20 (d, $J$ = 6.8 Hz, 1H), 7.11 (t, $J$ = 7.6 Hz, 2H), 6.89 (t, $J$ = 7.4 Hz, 2H), 6.27 (t, $J$ = 6.6 Hz, 2H), 3.70 (d, $J$ = 72.2 Hz, 4H), 2.26 (s, 3H).

**Figure S17.** $^1$H NMR spectrum of probe **2** (400 MHz, CDCl$_3$).

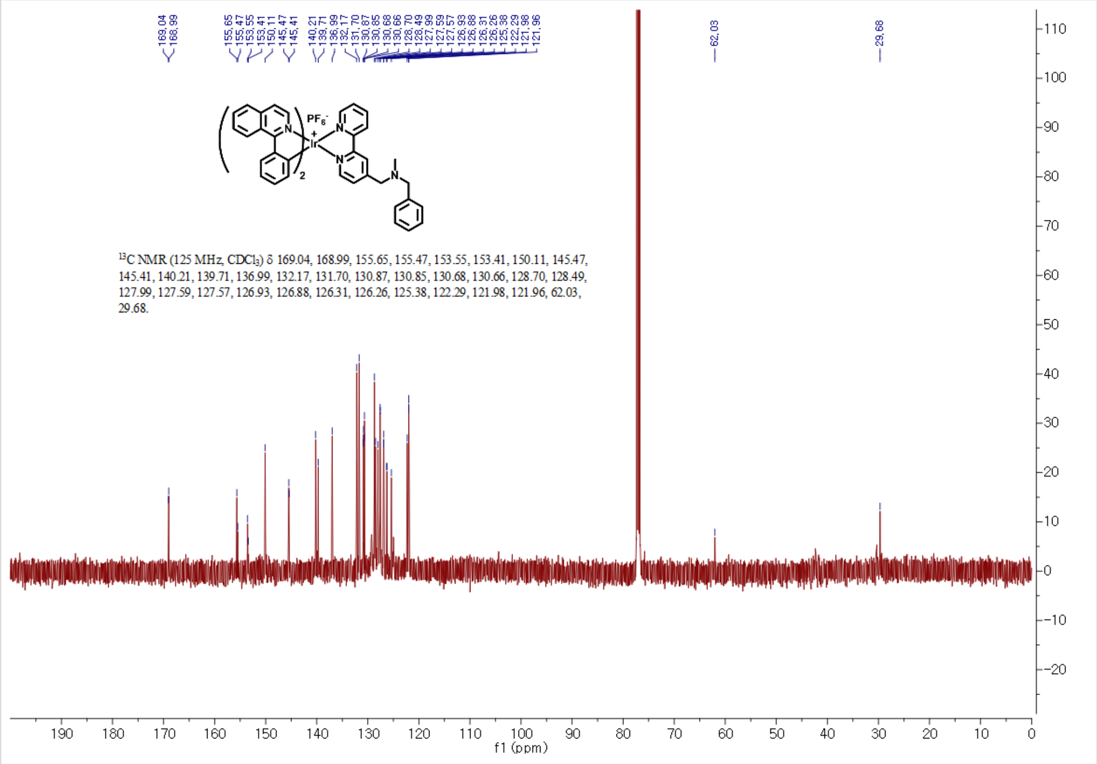

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 169.04, 168.99, 155.65, 155.47, 153.55, 153.41, 150.11, 145.47, 145.41, 140.21, 139.71, 136.99, 132.17, 131.70, 130.87, 130.85, 130.68, 130.66, 128.70, 128.49, 127.99, 127.59, 127.57, 126.93, 126.88, 126.31, 126.26, 125.38, 122.29, 121.98, 121.96, 62.03, 29.68.

**Figure S18.** $^{13}$C NMR spectrum of probe **2** (125 MHz, CDCl$_3$).

## 6. References

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