

Supporting Information

Rational design of boron-dipyrromethene-based fluorescent probe for detecting Pd²⁺ sensitively and selectively in aqueous medium

*Yannan Li, Li Yang * , Mengqi Du, Guanjun Chang **

State Key Laboratory of Environment Friendly Energy Materials, School of Material Science and Engineering, and National Engineering Technology Center for Insulation Materials, Southwest University of Science and Technology, Mianyang, 621010, P. R. China

Corresponding Authors. E-mails: yanglichem628@126.com or gjchang@mail.ustc.edu.cn

Table of contents

| | |
|---|-----|
| 1. General remarks of optical spectroscopic studies..... | S3 |
| 2. General UV–vis and fluorescence spectra measurements..... | S4 |
| 3. Synthetic procedures of compounds 2-5..... | S5 |
| 4. Optical spectroscopic studies of compound 1 | S7 |
| 5. Binding studies of compounds 1 with Pd ²⁺ cations..... | S8 |
| 6. Copies of ¹ H and ¹³ C NMR spectra compound 1 | S14 |
| 7. Copies of ¹ H NMR spectra of compounds 2-5..... | S15 |

1. General remarks of optical spectroscopic studies

The optical properties of compounds **1** were performed in N,N-Dimethylformamide (DMF). In addition, the studies on the binding properties of **1** were carried out in DMF/H₂O system (95:5, v/v, 10 mM potassium phosphate buffer, pH 5.5). A variety of metal salts were also dissolved in DMF. DMF was either HPLC or spectroscopic grade and water was distilled for twice. All solutions were prepared using volumetric syringes, pipettes, and volumetric flasks. The stock solutions of fluorophores and analytes were freshly prepared and used for each measurement. Each time a 3 mL of receptor was filled in a quartz cell of 1 cm of optical path length, and the stock solution of cation was added into a quartz cell dropwise using a micro-syringe. The volume of analyte stock solution added was less than 100 μ L to remain the concentration of receptor unchanged. The pH of the solution was fixed with Model PHS-25 pH Meter, calibrated with buffer solution of pH 4.00 and 9.00 before each measurement. The pH of test solution was adjusted with *ca.* 10^{-3} M HCl and NaOH solution in water. The Absorption spectra were detected on a SHIMADZU UV-3150 uv-vis-NIR spectrophotometer. Fluorescent emission spectra were collected on a PerkinElmer LS-55 fluorescence spectrometer.

2. General UV–vis and fluorescence spectra measurements

The stock solutions of **1** (1×10^{-4} M) were prepared by directly dissolving in N,N-Dimethylformamide (DMF). For the spectroscopic determination, the stock solution were diluted with 10 mM potassium phosphate buffer (pH 5.5) to the desired concentration (1 μ M). The final experimental buffer condition is set to DMF:H₂O = 95:5 (v/v) and pH = 5.5. A variety of stock solutions (0.1 M) of metal salts including Cu²⁺, Cd²⁺, Pd²⁺, Ni²⁺, Hg²⁺, Pb²⁺, Zn²⁺, Cr³⁺, Sr²⁺, Ag⁺ and Mn²⁺ were also dissolved in DMF and diluted to the desired concentrations (1×10^{-2} M). For titration of metallic ions, aliquots of 0.3 μ L aqueous metallic ion solutions (1×10^{-2} M) were added to 3 mL diluted **1** (1 μ M) solution (DMF:H₂O = 95:5, v/v, pH = 5.5). The measurements were performed after 1 min of response time. All experiments were carried out at 298 K. To make sure the reproducibility and stability of experimental data, all experiments weretested at least three times.

3. Synthetic procedures of compound 2-5

Synthesis of compound 2

p-Iodobenzoic acid (4.96 g, 20 mmol) was added to SOCl_2 (10 mL) and refluxed for 5h. SOCl_2 was removed in vacuo to afford a white solid. The compound was dissolved in dichloromethane (50 mL) and 2, 4-dimethylpyrrole (4.12 mL) under nitrogen and the mixture was subsequently stirred at room temperature until the compound was completely dissolved. Then Et_3N (8 mL) was added followed by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (8 mL). The reaction was stopped after stirring at room temperature for 24 h. The resulting solution was washed three times with water and the aqueous phase was extracted with dichloromethane. The organic phases were combined, dried over anhydrous sodium sulfate, filtered, and the filtrate was evaporated in vacuo. The residue was then loaded onto a column of silica gel (petroleum ether/dichloromethane = 3: 1) to afford 1.97 g of the compound 2 as a red solid in 22% yield. ^1H NMR (400 MHz, CDCl_3), δ : 7.84 (d, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 8.0$ Hz, 2H), 5.99 (s, 2H), 2.55 (s, 6H), 1.42 (s, 6H). Anal. Calc. (%) for $\text{C}_{19}\text{H}_{18}\text{BF}_2\text{IN}_2$: C, 50.70; H, 4.03; N, 6.22. Found: C, 50.79; H, 3.88; and N, 6.32.

Synthesis of compound 3

Compound 2 (1.35 g, 3 mmol), CuI (0.018 g, 0.18 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.13 g, 18 mmol), $^i\text{Pr}_2\text{NH}$ (15 mL), THF (60 mL) and TMSA (1 mL, 7.08 mmol) were mixed under a nitrogen atmosphere, then the mixture was sonicated for 10 min,

followed by stirring at room temperature for 2d. Afterwards, the resulting solution was filtered, washed with dichloromethane several times, dried under reduced vacuum, and then purified by column chromatography to afford compound 3 (0.96g, 70%). ^1H NMR (400 MHz, CDCl_3), δ : 7.59 (d, $J = 8.4$ Hz, 2 H), 7.23 (d, $J = 8.4$ Hz, 2 H), 5.98 (s, 2H), 2.55 (s, 6H), 1.39 (s, 6H), 0.28 (s, 9H). Anal. Calc. (%) for $\text{C}_{24}\text{H}_{27}\text{BF}_2\text{N}_2\text{Si}$: C, 68.57; H, 6.47; N, 6.66. Found: C, 68.43; H, 6.32; and N, 6.93.

Synthesis of compound 4

Compound 3 (0.54 g, 1.3 mmol), $\text{KF}\cdot 2\text{H}_2\text{O}$ (3.35 g, 35.6 mmol) in 10% MeOH/ CH_2Cl_2 (9 mL / 9 mL) were mixed under a nitrogen and stirred at room temperature for 48 h and the solvent was removed in vacuo. The reaction mixture was purified by column chromatography (petroleum ether / dichloromethane = 3: 1) to give product 4 as a red solid in 60% yield, ^1H NMR (400 MHz, $\text{DMSO}-d_6$), δ : 7.65 (d, $J = 7.6$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 6.19 (s, 2H), 4.36 (s, 1H), 2.45 (s, 6H), 1.36 (s, 6H). Anal. Calc. (%) for $\text{C}_{21}\text{H}_{19}\text{BF}_2\text{N}_2$: C, 72.44; H, 5.50; N, 8.05. Found: C, 72.26; H, 5.64; and N, 8.16.

Synthesis of compound 5

To a two-neck flask (100 mL) equipped with sym-bromobenzene (6.30 g, 20 mmol), imidazole (3.00 g, 44 mmol), CuI (1.52 g, 8 mmol) and K_2CO_3 (11.06 g, 80 mmol).

Then DMF (60 mL) was added and the mixture was heated up to 130 °C for 48 h under nitrogen. Cooled to room temperature, after vacuum filtration the solvent was removed by vacuum distillation, and then purified by column chromatography (dichloromethane/methanol=15:1) to afford compound 4, (1.56 g, 27%). ¹H NMR (400 MHz, DMSO-*d*₆), δ: 8.50 (s, 2H), 7.97 ~ 8.07(m, 5H),7.17 (s, 2H). Anal. Calc. (%) for C₁₂H₉BrN₄: C, 49.85; H, 3.14; N, 19.38. Found: C, 49.98; H, 3.06; and N, 19.26.

4. Optical spectroscopic studies of compounds 1

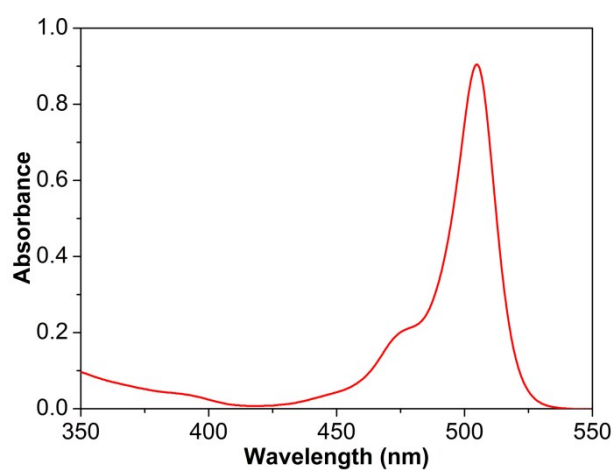


Fig. S1 UV spectra of **1** in DMF (1.0×10^{-5} M).

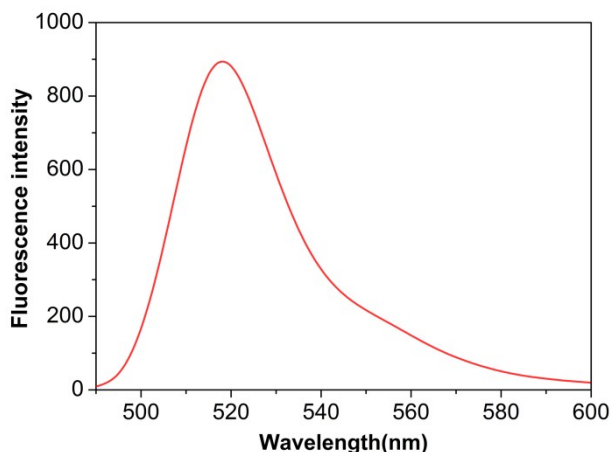


Fig.S2 Fluorescence spectra of **1** (1.0×10^{-6} M) in DMF. Solution concentration: 1.0×10^{-6} M; excitation wavelength: 500 nm; excitation and emission slits (nm): 10 nm and 2.5 nm, respectively.

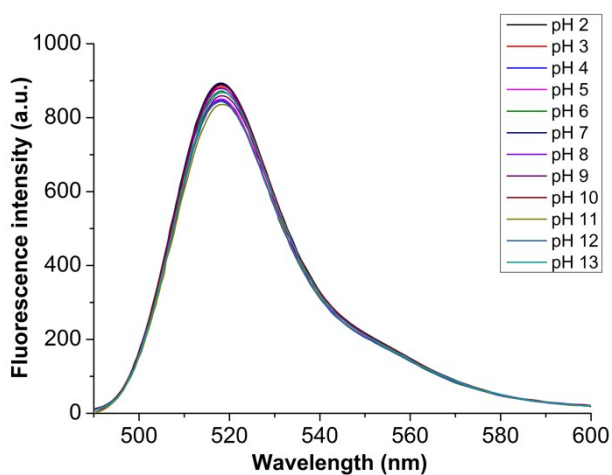


Fig. S3 Fluorescence spectra of **1** (1.0×10^{-6} M) in DMF-water (95:5, v/v) solution with different pH values at 25 °C, pH is adjusted by using aqueous solutions of 1.0×10^{-3} M HCl or 1.0×10^{-3} M NaOH. (excitation wavelength: 500 nm; excitation and emission slits (nm): 10.0 nm and 2.5 nm, respectively.)

5. Binding studies of compound **1** with Pd²⁺ cations

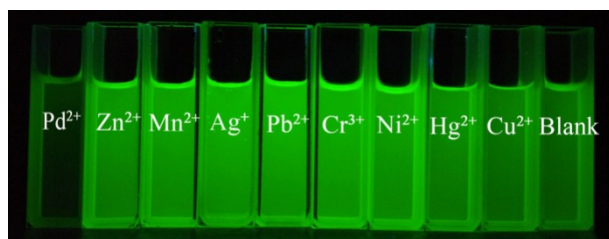


Fig. S4 The emission image observed for **1** (1 μ M) upon addition of various cations (50 equiv.) in DMF:H₂O (95:5, v/v) solution with a potassium phosphate buffer (10 mM, pH 5.5).

Calculation of the detection limit

The typical limit of detection (LOD) is obtained by using the equation followed:

$$LOD = \frac{3\sigma}{S}$$

Where σ is the standard deviation of the background (blank **1**) and S is the sensitivity.

S can be obtained from the slope of the linear fit (using data available from fluorescence titration).

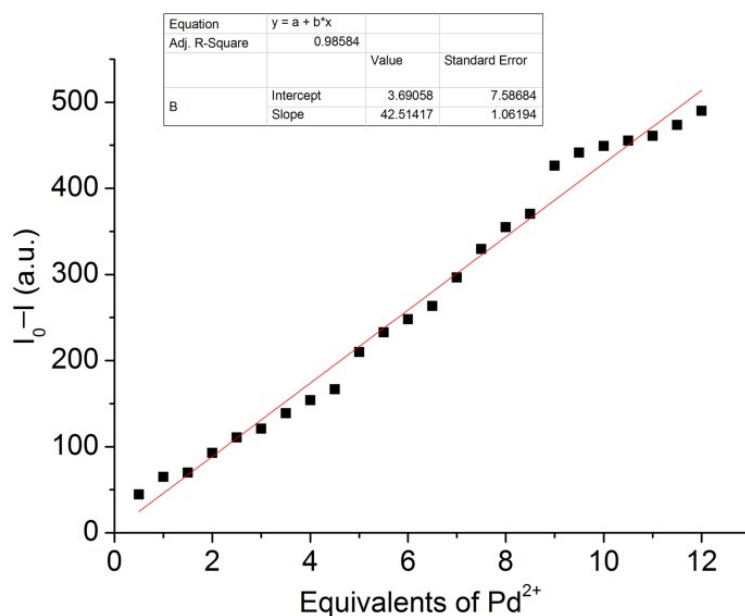


Fig. S5 Representative plot of (I_0-I) vs. $[Pd^{2+}]$ from fluorescence titration. (The concentration of **1** was 1.0×10^{-6} M)

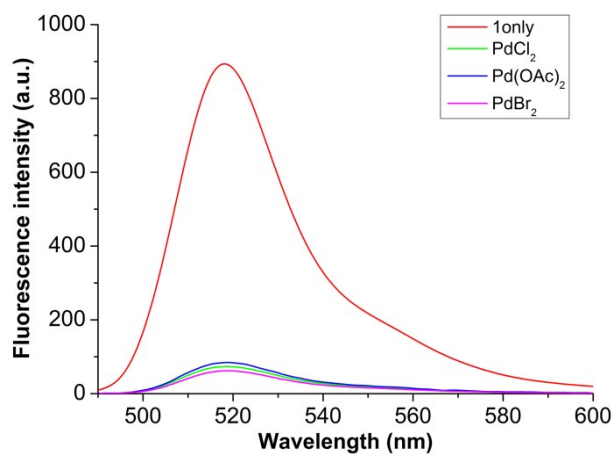


Fig. S6 Fluorescence spectra of **1** ($1 \mu\text{M}$) upon addition of $100 \mu\text{M}$ of $\text{Pd}(\text{OAc})_2$, PdCl_2 and PdBr_2 , respectively, in $\text{DMF}:\text{H}_2\text{O}$ (95:5, v/v) solution with a potassium

phosphate buffer (10 mM, pH 5.5), excited at 500 nm.

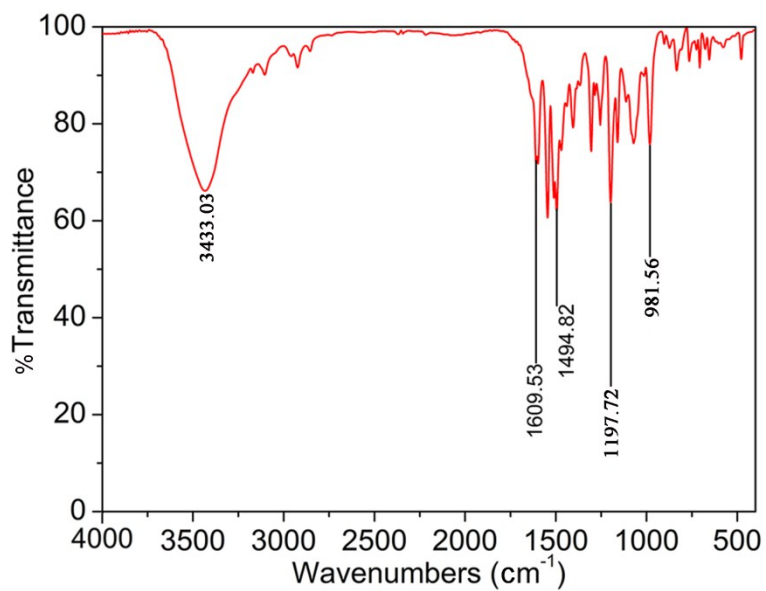


Fig. S7 FT-IR spectrum of compound **1**.

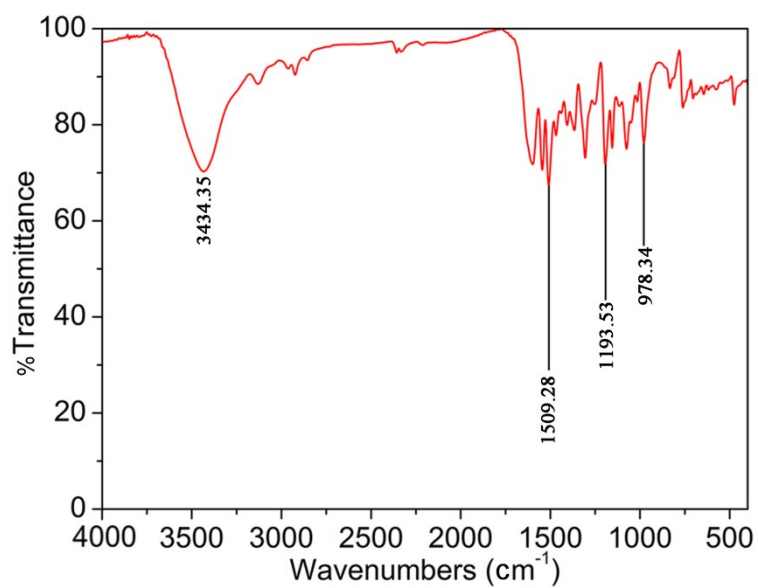


Fig. S8 FT-IR spectrum of compound **1** coordinated with Pd²⁺ in 1:2 stoichiometry.

Proof-of-concept experiments

First, tap water were collected and filtered. Second, 1 mL of stock solution of Pd(OAc)₂ (0.001 M) standard solutions were prepared. Then, three samples of **1** (3 ml each, 1 × 10⁻⁶ M) were taken and spiked with 18, 36, and 54 μL of stock solution of Pd(OAc)₂ (0.001 M) to obtain 6 μM, 12 μM, and 18 μM Pd²⁺ (known) concentrations, respectively. The fluorescence emission spectra of all the samples were recorded. The calculated Pd²⁺ concentrations were deduced from the linear fit equation: $Y = 0.02362X + 0.0737$. The error (%) was calculated using the formula: $([\text{Pd}^{2+}]_{\text{added}} - [\text{Pd}^{2+}]_{\text{calculated}}) / [\text{Pd}^{2+}]_{\text{added}} \times 100$.

Table S1 Estimation of Pd²⁺ in the samples with its known concentrations.

| Sample | Pd ²⁺ added (μM) | Pd ²⁺ calculated (μM) | Error (100%) |
|--------|-----------------------------|----------------------------------|--------------|
| 1 | 6 | 6.41 | -6.83 |
| 2 | 12 | 12.59 | -4.92 |
| 3 | 18 | 18.87 | -4.83 |

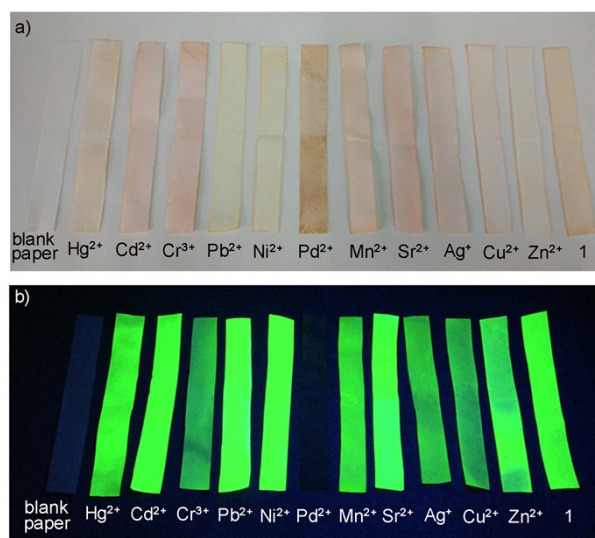


Fig. S9 Photographs of the test kits with **1** for detecting Pd²⁺ were taken under (a) normal room lighting (RL) and (b) UV illumination (365 nm).

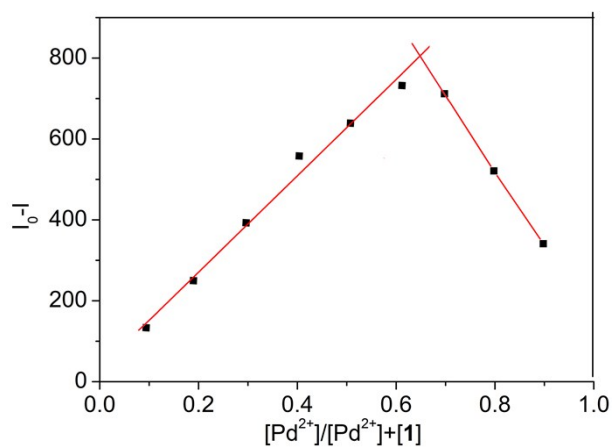


Fig. S10. Job's plot of **1** with Pd²⁺ in DMF/H₂O = 95:5. The total concentration of [1] + [Pd²⁺] was kept constant at 1 μM.

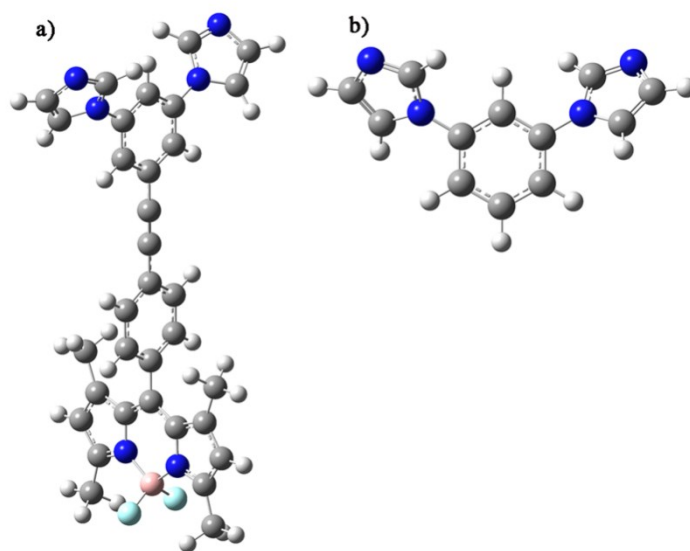


Fig.S11 Optimized ground-state geometries of a) probe **1** and b) m-bisimidazolylbenzene. Color code: C (dark gray), N (blue), O (red), H (white), Pd (cyan), and B (pink), F (Light blue).

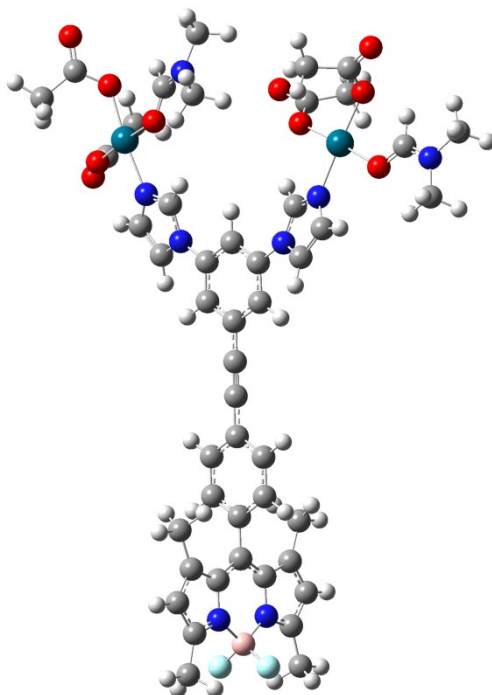
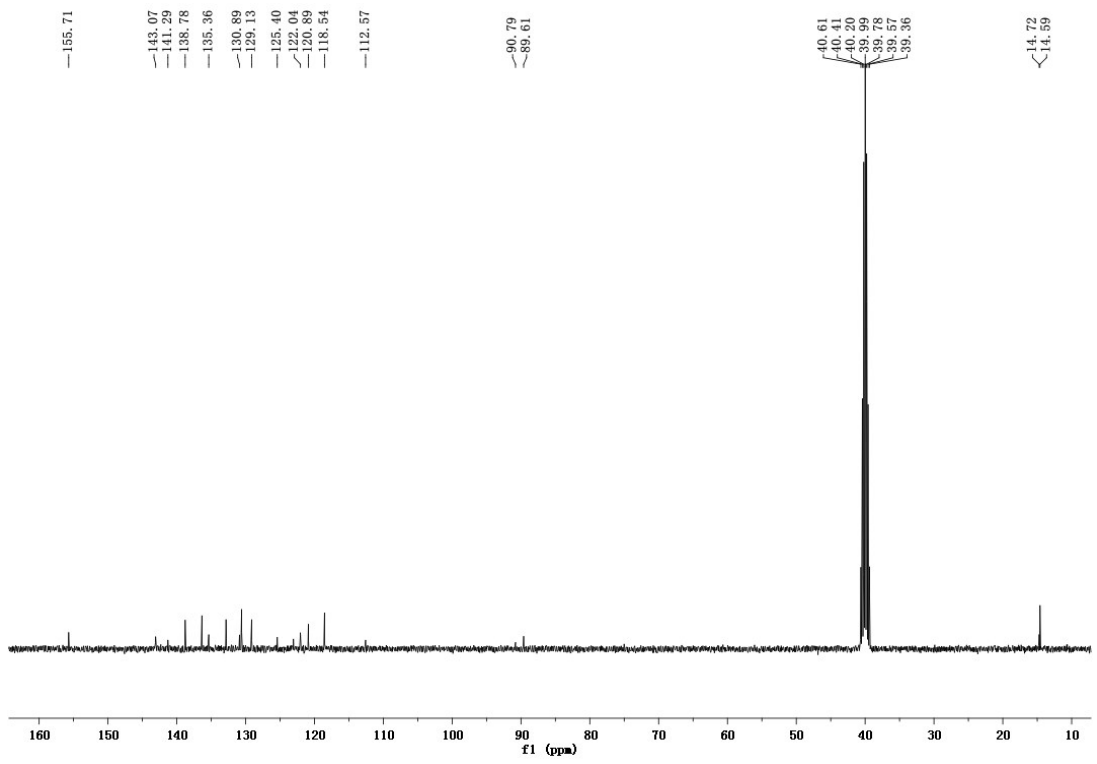
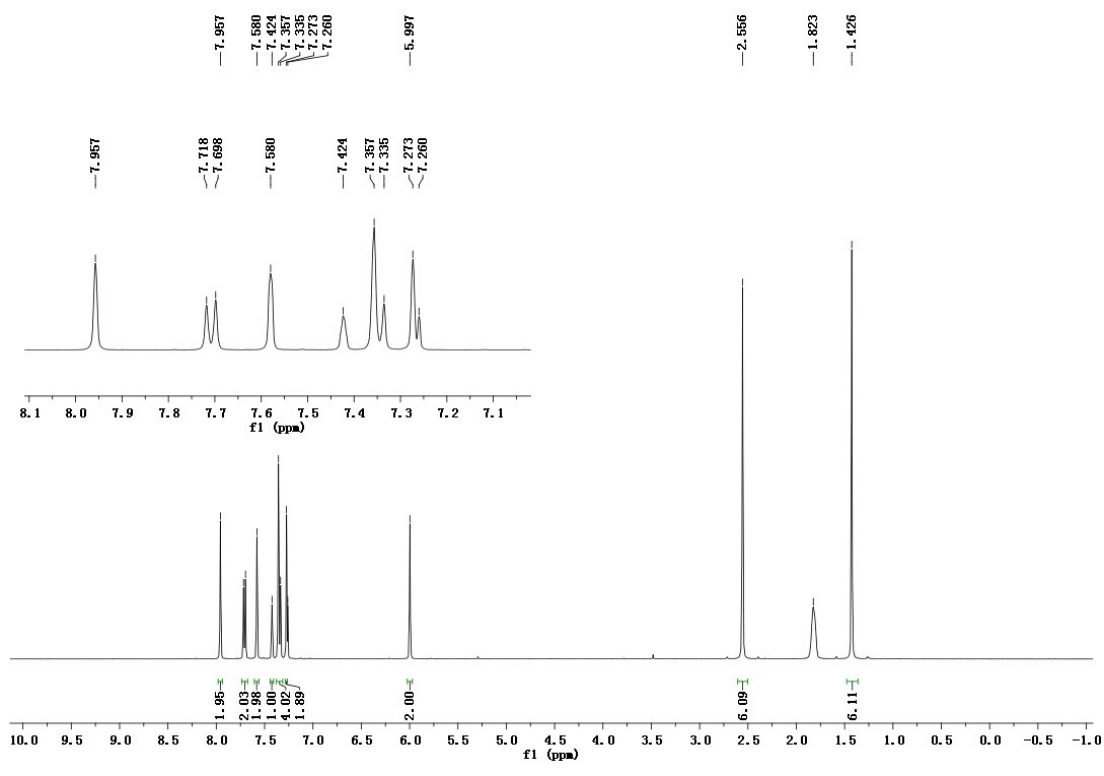


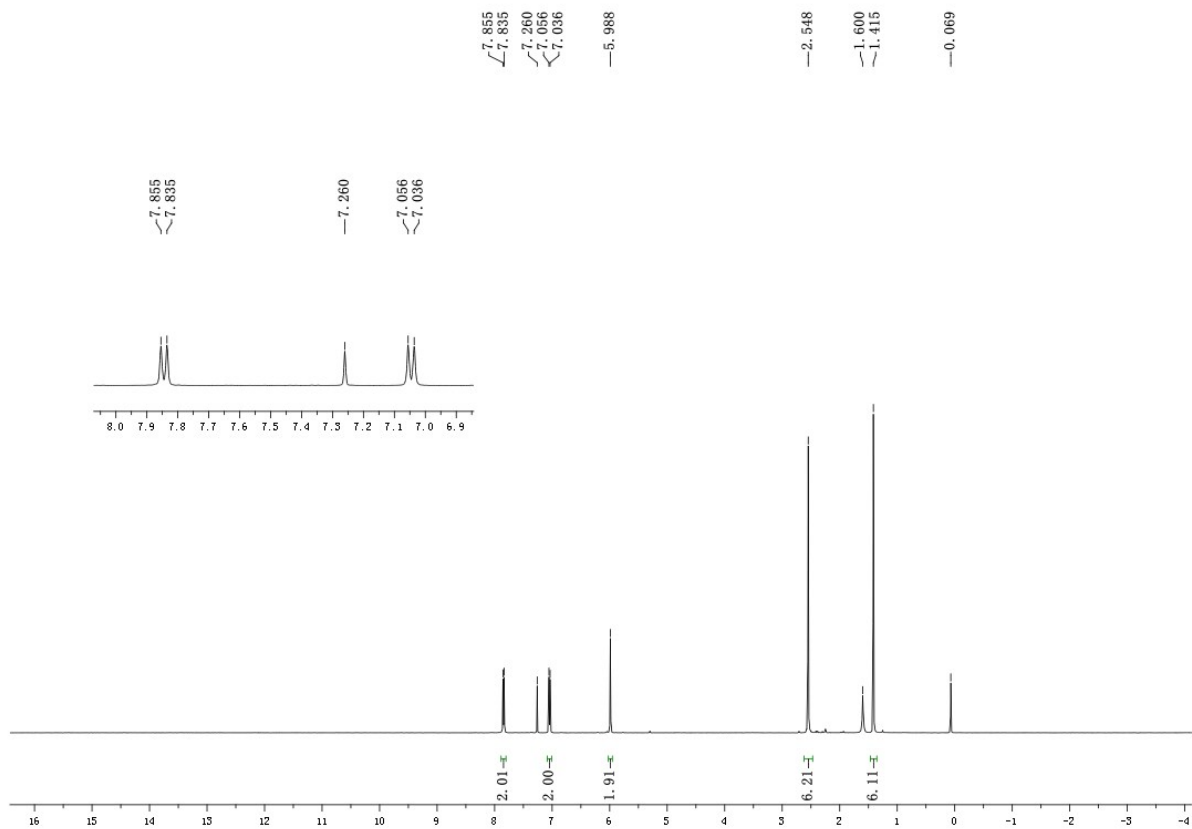
Fig. S12 Optimized ground-state geometry of the complex of **1** with Pd²⁺. Color code: C (dark gray), N (blue), O (red), H (white), Pd (cyan), and B (pink), F (Light blue).

6. Copies of ¹H and ¹³C NMR spectra of compound **1**

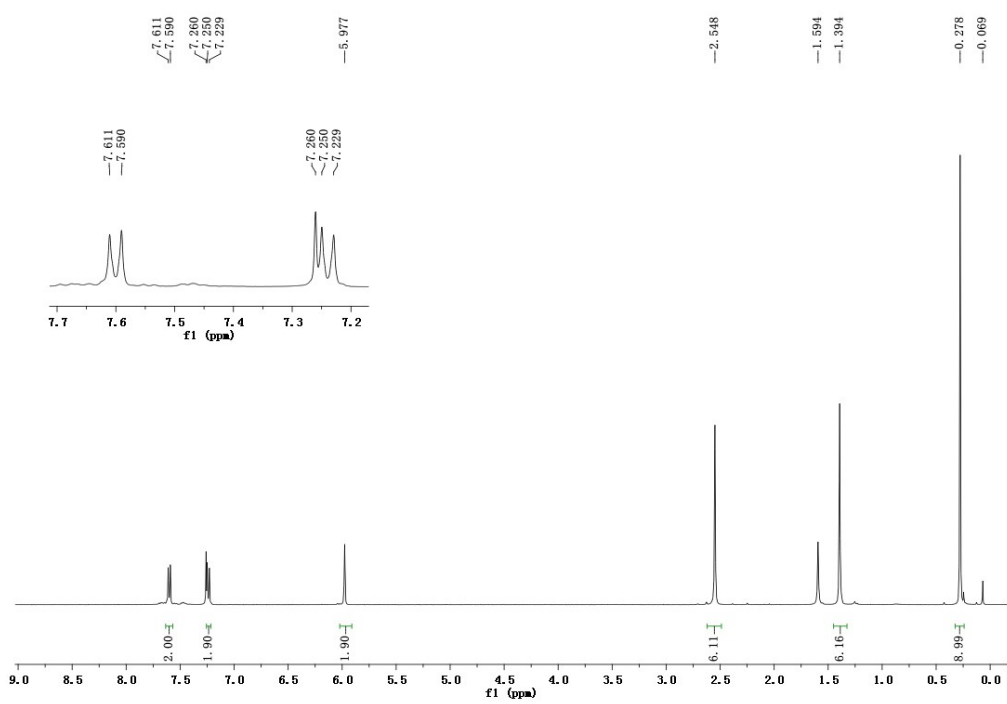


7. Copies of ^1H NMR spectra of compounds 2-5

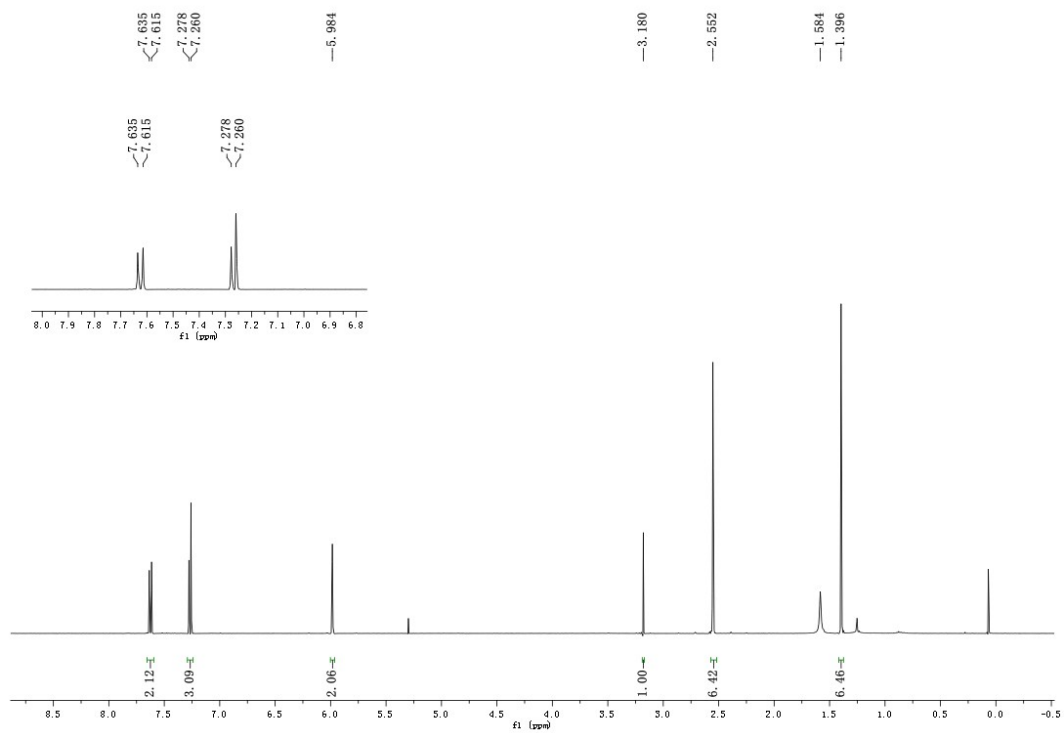
^1H NMR spectra of compound 2



^1H NMR spectra of compound 3



¹H NMR spectra of compound 4



^1H NMR spectra of compound 5

