Supporting information

A fluorescent probe for the discrimination of different oxidation states of palladium

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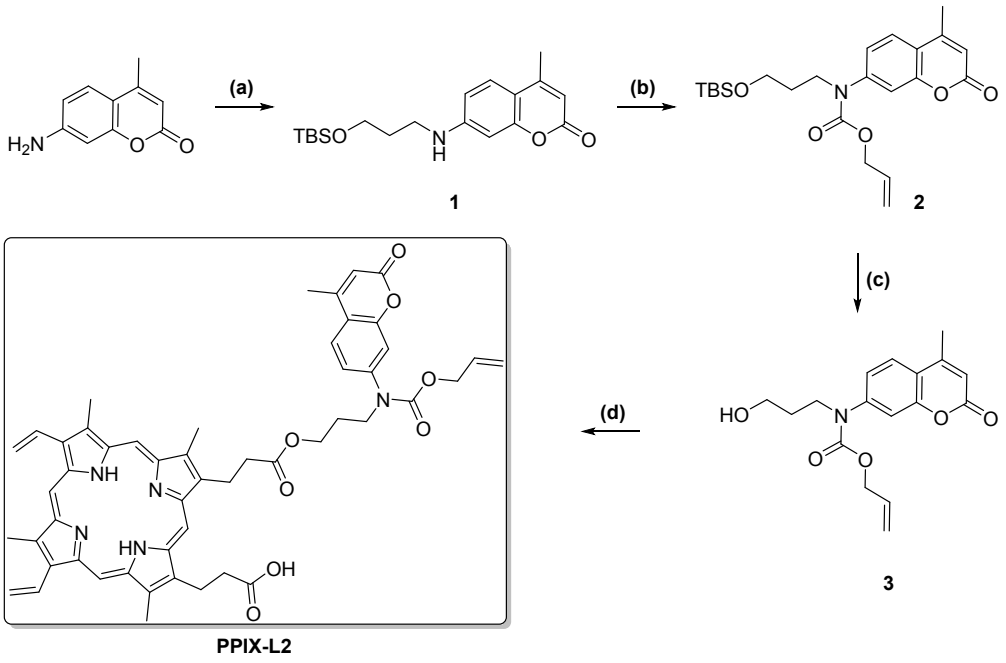
General considerations

All moisture-sensitive reactions were conducted under a nitrogen atmosphere. Anhydrous solvents were obtained from departmental solvent towers and stored over 3 Å molecular sieves. Deuterated solvents were purchased from Goss Scientific. All other solvents and reagents were of reagent grade and purchased from either Sigma-Aldrich Chemical Co. or VWR International Co. and used without further purification. ^{1}H NMR were recorded on Bruker AV-400 spectrometers at 298 K. Chemical shifts δ were reported in parts per million (ppm) using tetramethylsilane (TMS) or the residue proton impurities in the solvent for ^{1}H NMR spectroscopy, TMS or the residue carbon impurities in the solvent for ^{13}C NMR spectroscopy. Coupling constants *J* were reported in Hertz (Hz) and multiplicities were abbreviated as: s = singlet, d = doublet, t = triplet, dd = doublets of doublet, td = triplets of doublet and m = multiplet. High-resolution mass spectra, reported as *m/z*, were conducted by the Mass Spectrometry Service, Imperial College London. Thin-layer chromatography (TLC) was performed using pre-coated silica gel 60, F254 plates with a thickness of 0.2 mm. Column chromatography was conducted using silica gel and laboratory grade solvents either manually or on a Biotage flash purification system Isolera™ Prime. Fluorescent spectra were recorded on either Horiba FluoroMax 4 Spectrofluorometer or Agilent Cary Eclipse Fluorescence Spectrophotometer in a quartz cuvette.

Synthesis of PPIX-L2

Synthesis of (3-bromopropoxy)-*tert*-butyldimethylsilane. (3-Bromopropoxy)-*tert*-butyldimethylsilane was synthesized according to a previous report.[1] A solution of *tert*-butyldimethylsilyl chloride (TBSCl) (3.78 mmol) in dichloromethane (DCM) (2 mL) was added dropwise over 1 minute to a stirred solution of 3-bromo-1-propanol (3.60 mmol) and imidazole (7.20 mmol) in DCM (2 mL) at room temperature. The resulting mixture was stirred at room temperature for 1 hour. Water (5 mL) was added when the reaction was complete (monitored by TLC), the aqueous phase was extracted with DCM (3 × 5 mL). The organic phase was combined and dried using anhydrous magnesium sulfate ($MgSO_4$), and then filtered. The filtrate was concentrated *in vacuo* to give (3-bromopropoxy)-*tert*-butyldimethylsilane as a pale-yellow oil (Yield: 90%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H (ppm): 3.74 (2H, t, J = 5.8 Hz), 3.52 (2H, t, J = 6.6 Hz), 2.03 (2H, m), 0.81 (9H, s), 0.07 (6H, s). ^{13}C-NMR (101 MHz, $CDCl_3$) δ: 60.52, 35.67, 30.71, 26.01, 18.40, -5.27.



Synthesis of compounds 1 and 2. Compound **1** was synthesized according to a previous report.[2] To a stirred solution of 7-amino-4-methylcoumarin (0.57 mmol) in dimethyl formamide (DMF) (3 mL) at room temperature were added (3-bromopropoxy)-tert-butyldimethylsilane (1.14 mmol) and K_2CO_3 (2.85 mmol). The resulting mixture was refluxed for 2 hours. The progress of the reaction was checked by TLC. When the reaction was complete, the mixture was allowed to cool to room

temperature. The reaction mixture was evaporated to dryness under reduced pressure, and the residue was chromatographed on silica gel using hexane (HEX) and ethyl acetate (EA) as the eluent to afford compound **1** as white or pale-yellow solid (Yield: 31%). Compound **2** was subsequently synthesized according to a previous report.[3] Allyl chloroformate (1.42 mmol) was added to a stirred solution of compound **1** (0.14 mmol) and *N,N*-diisopropylethylamine (DIPEA) (0.71 mmol) in anhydrous DCM (10 mL) under a nitrogen atmosphere. The reaction mixture was stirred under room temperature for 12 hours. When the reaction was complete (monitored by TLC), the mixture was filtered, and the filtrate was washed with water (3 × 5 mL). The organic phase was dried using anhydrous $MgSO_4$, and then filtered. The filtrate was evaporated to dryness under reduced pressure, and the residue was chromatographed on silica gel using HEX and EA as the eluent to give compound **2** as the white or pale-yellow oil (Yield: 80%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H (ppm): 7.56 (1H, dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz), 7.27 - 7.24 (2H, m), 6.26 (1H, d, J = 1.2 Hz), 5.96 – 5.86 (1H, m), 5.28 – 5.19 (2H, m), 4.64 (2H, td, J_1 = 5.6 Hz, J_2 = 1.2 Hz), 3.86 (2H, t, J = 7.2 Hz), 3.63 (2H, t, J = 6.0 Hz), 2.43 (3H, d, J = 1.2 Hz), 1.83 (2H, m), 0.84 (9H, s), 0.00 (6H, s). ^{13}C-NMR (101 MHz, $CDCl_3$) δ: 160.73, 154.63, 153.78, 152.03, 145.43, 132.30, 124.77, 122.33, 117.95, 117.73, 114.46, 66.59, 60.22, 47.54, 31.60, 25.82, 18.59, 18.17, -5.46. HRMS (TOF ES$^+$): *m/z* calcd. for $C_{23}H_{34}NO_5Si$ $[M+H]^+$ 432.2206, found 432.2221.

Synthesis of compound 3. Tetra-*n*-butylammonium fluoride (TBAF) (0.12 mmol) was added to a solution of compound **2** (0.11 mmol) in tetrahydrofuran (THF) (5 mL). The resulting mixture was stirred at room temperature for 1 hour. When the reaction was complete (checked by TLC), the mixture was concentrated *in vacuo*. The resulting solid was dissolved in DCM (10 mL), and the resulting solution was washed with H_2O (3 × 5 mL). The organic phase was dried using anhydrous $MgSO_4$, and then filtered. The filtrate was evaporated to dryness under reduced pressure, and the resulting crude was chromatographed on Biotage using HEX and EA as the eluent to give compound **3** as the white or pale-yellow solid (Yield: 78%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H (ppm): 7.59 (1H, d, J = 8.4 Hz), 7.26 (1H), 7.21 (1H, t, J = 2.0 Hz), 6.29 (1H, d, J = 1.2 Hz), 5.92 – 5.83 (1H, m), 5.25 – 5.18 (2H, m), 4.63 (2H, td, J_1 = 5.6 Hz, J_2 = 1.6 Hz), 3.91 (2H, t, J = 6.4 Hz), 3.69 (2H, t, J = 6.0 Hz), 2.44 (3H, d, J = 1.2 Hz), 1.76 (2H, m). ^{13}C-NMR (101 MHz, $CDCl_3$) δ: 160.60, 155.29, 153.72, 152.06, 144.71, 132.07, 125.02, 122.72, 118.12, 118.05, 114.77, 114.60, 66.75, 58.95, 46.99, 30.94, 18.56. HRMS (TOF ES$^+$): *m/z* calcd. for $C_{17}H_{20}NO_5$ $[M+H]^+$ 318.1341, found 318.1329.

Synthesis of PPIX-L2. Anhydrous DMF (2 mL) was added to a Schlenk flask charged with protoporphyrin IX (PPIX) (0.0467 mmol), N,N'-dicyclohexylcarbodiimide (DCC) (0.0467 mmol) and 4-dimethylaminopyridine (DMAP) (0.0187 mmol) and the resulting

mixture was stirred at 0 °C using an ice bath with a constant flow of nitrogen. After 15 minutes, compound **3** (0.561 mmol) was added and the solution was allowed to stir in the dark at room temperature for 36 hours. The progress of the reaction was checked by TLC. When the reaction was complete, the reaction mixture was evaporated to dryness under reduced pressure, and the residue was chromatographed on silica gel using MeOH-DCM mixtures as the eluent to give **PPIX-L2** as a deeply coloured pigment (Yield: 51%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.18 – 9.90 (m, 6H), 8.39 – 8.10 (m, 3H), 6.37 (dd, *J* = 17.9, 6.8 Hz, 3H), 6.20 (dt, *J* = 11.6, 4.5 Hz, 3H), 5.95 (s, 2H), 5.77 – 5.60 (m, 1H), 5.13 – 4.95 (m, 2H), 4.35 (d, *J* = 7.9 Hz, 6H), 3.99 (t, *J* = 5.7 Hz, 2H), 3.70 – 3.64 (m, 7H), 3.61 – 3.54 (m, 7H), 3.51 (s, 1H), 3.46 (d, J = 4.0 Hz, 1H), 3.29 (t, J = 7.4 Hz, 4H), -4.07 (s, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ: 176.23, 173.81, 160.57, 153.94, 153.72, 152.80, 151.57, 151.55, 143.46, 143.42, 137.79, 136.03, 132.00, 131.98, 130.12, 130.03, 129.94, 123.67, 120.12, 120.01, 117.80, 117.79, 113.79, 97.01, 96.52, 96.28, 95.71, 77.48, 77.36, 77.16, 76.84, 66.49, 66.46, 62.02, 46.35, 37.07, 36.81, 26.76, 17.75, 17.71, 12.49, 12.40, 11.48, 11.39. HRMS (TOF ES^{+}): *m/z* calcd. for $C_{51}H_{52}N_5O_8$ $[M+H]^+$ 862.3816, found 862.3801.

Photophysical measurements

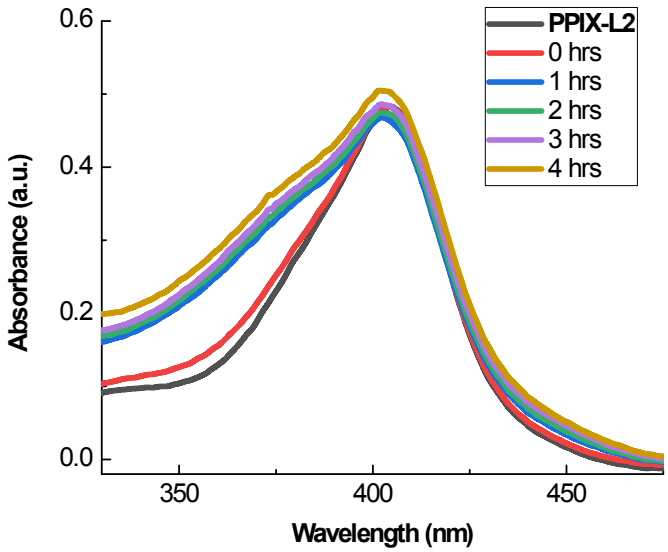


Fig. S1 UV-visible spectra of 5 µM **PPIX-L2** in MeOH. Time points represent 0, 1, 2, 3 and 4 hours after the addition of 5 equivalent of Pd^0 to **PPIX-L2**.

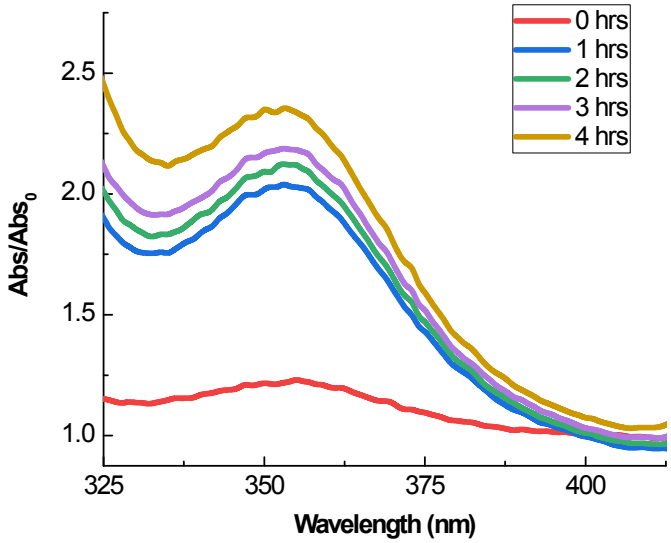


Fig. S2 Abs/Abs_0 *vs* wavelength spectra of 5µM **PPIX-L2**. Time points represent 0, 1, 2, 3 and 4 hours after the addition of 5 equivalent of Pd^0 to **PPIX-L2**.

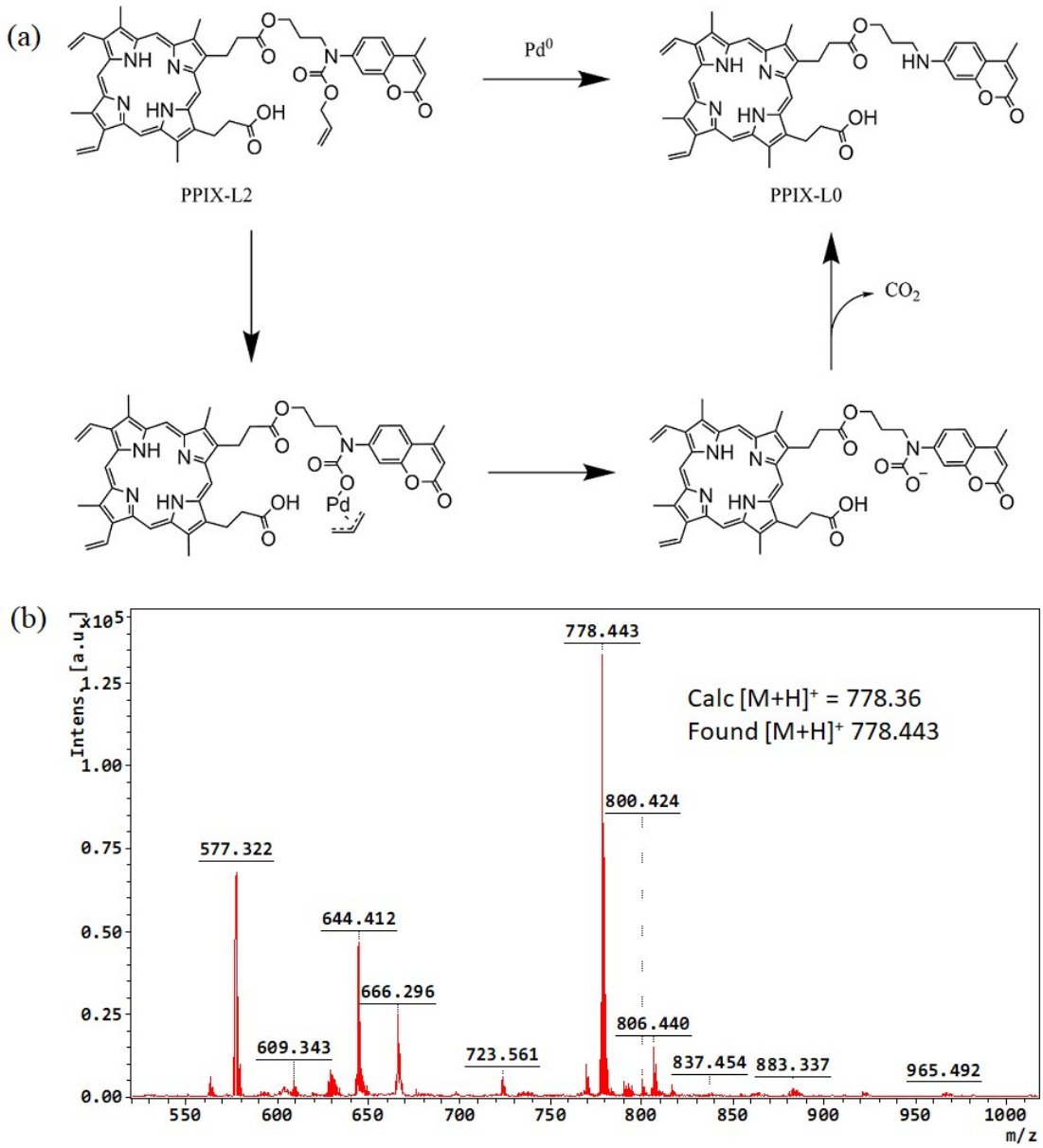


Fig. S3 (a) A detailed Tsuji-Trost reaction mechanism for Pd^0 sensing by **PPIX-L2**. (b) MALDI-TOF mass spectrum of the reaction between **PPIX-L2** with 5 equivalents of Pd^0 to form **PPIX-L0**.

Table S1 Quantification of Pd^0 and Pd^{2+} by **PPIX-L2** in a sample mixture. The measurements were performed three times and the mean values were taken for calculation.

	Intensity measured (a.u.)	**Calculated concentration (μM)**	**Actual concentration (μM)**	**% Error**
Pd^0	73617.16	0.23	0.25	-8.58
Pd^{2+}	735794.35	2.17	2	8.36

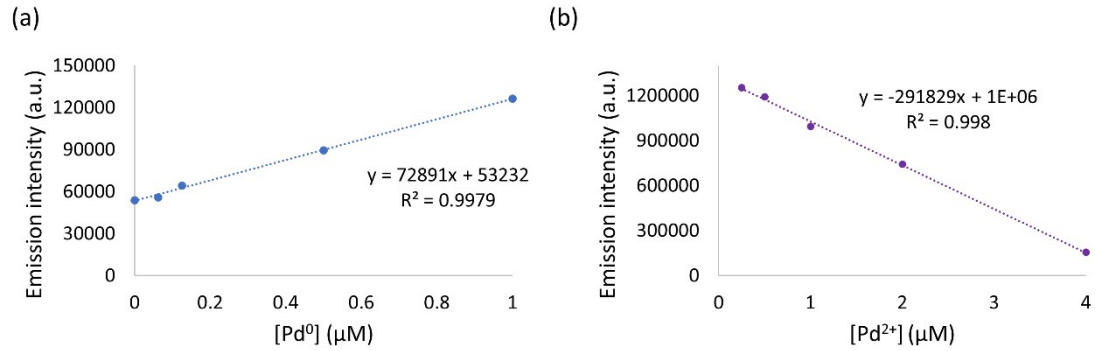


Fig. S4 Fluorescence analysis of **PPIX-L2** against various concentrations of Pd^0 and Pd^{2+} in MeOH for the determination of detection limit in the mixed sample solution. (a) Linear correlation between coumarin fluorescence intensity of 5 μM **PPIX-L2** at 440 nm and [Pd^0]. Fluorescence intensity was recorded at 2 hours after the addition of various concentrations of Pd^0 and 0.5 μM Pd^{2+} (λ_{ex} = 361 nm). (b) Linear correlation between porphyrin fluorescence intensity of 2 μM **PPIX-L2** at 631 nm and [Pd^{2+}]. Fluorescence intensity was recorded at 1 hour after the addition of various concentrations of Pd^{2+} and 0.25 μM Pd^0 (λ_{ex} = 400 nm).

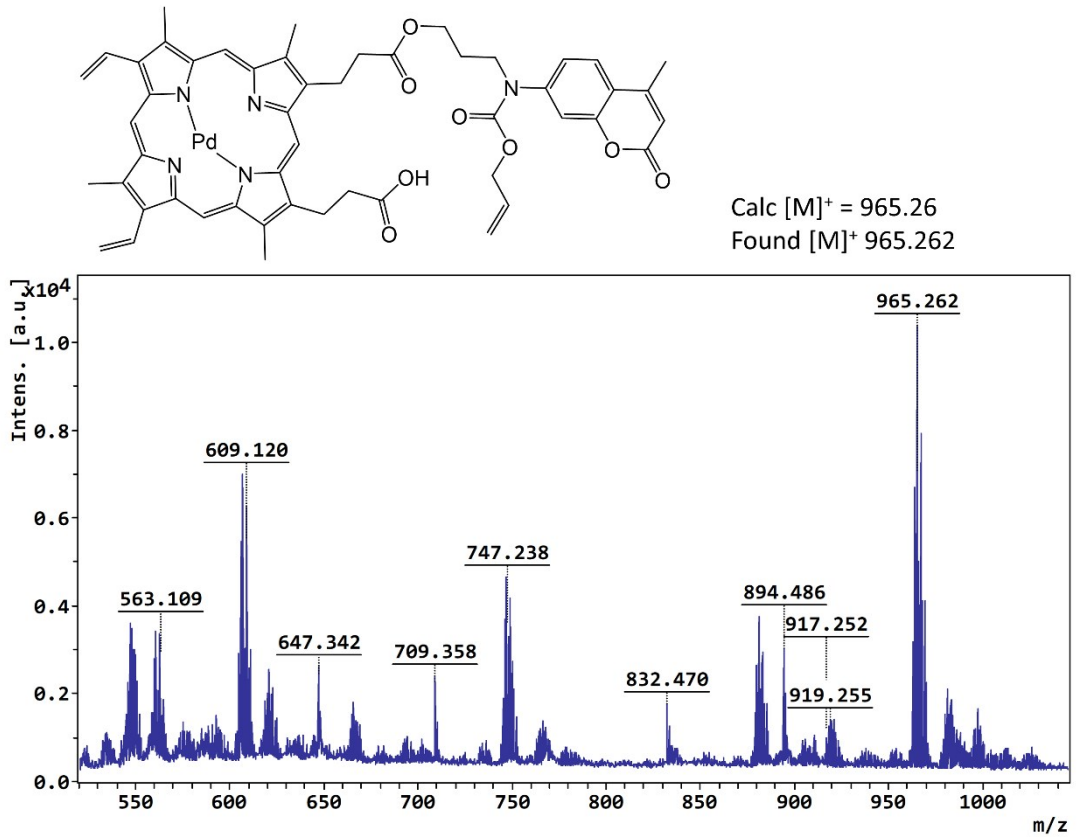


Fig. S5 MALDI-TOF mass spectrum of the reaction between **PPIX-L2** with 5 equivalents of Pd^{2+} to form Pd-PPIX-L2.

Characterization

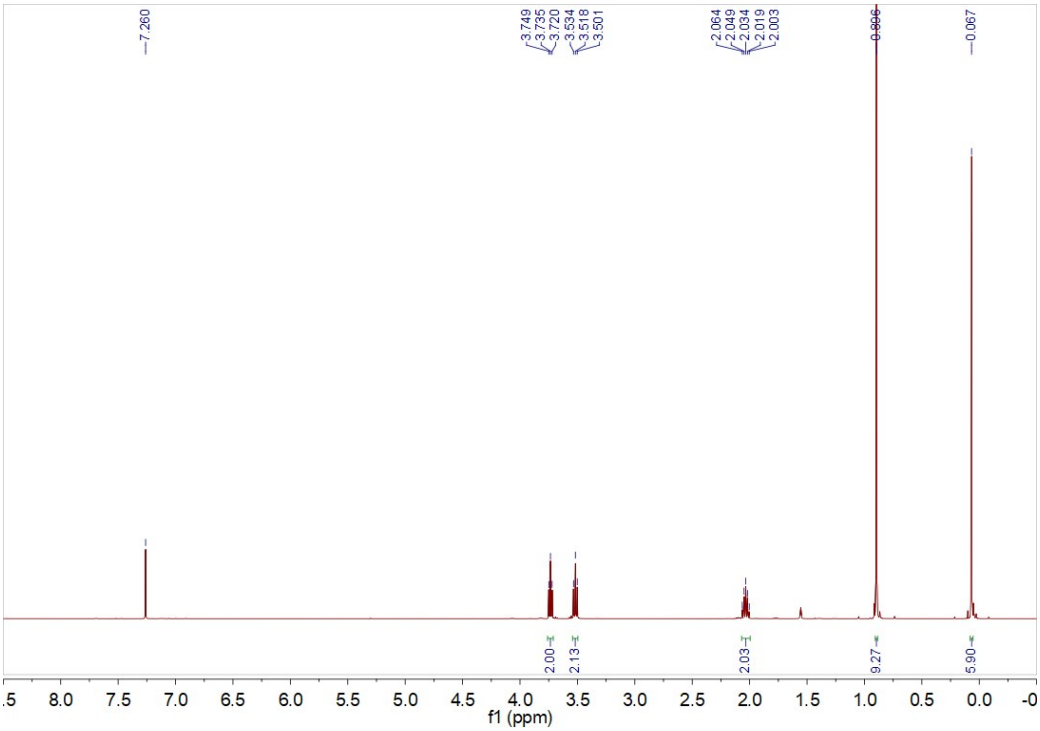


Fig. S6 ^{1}H NMR spectrum of (3-bromopropoxy)-*tert*-butyldimethylsilane (400 MHz, $CDCl_3$).

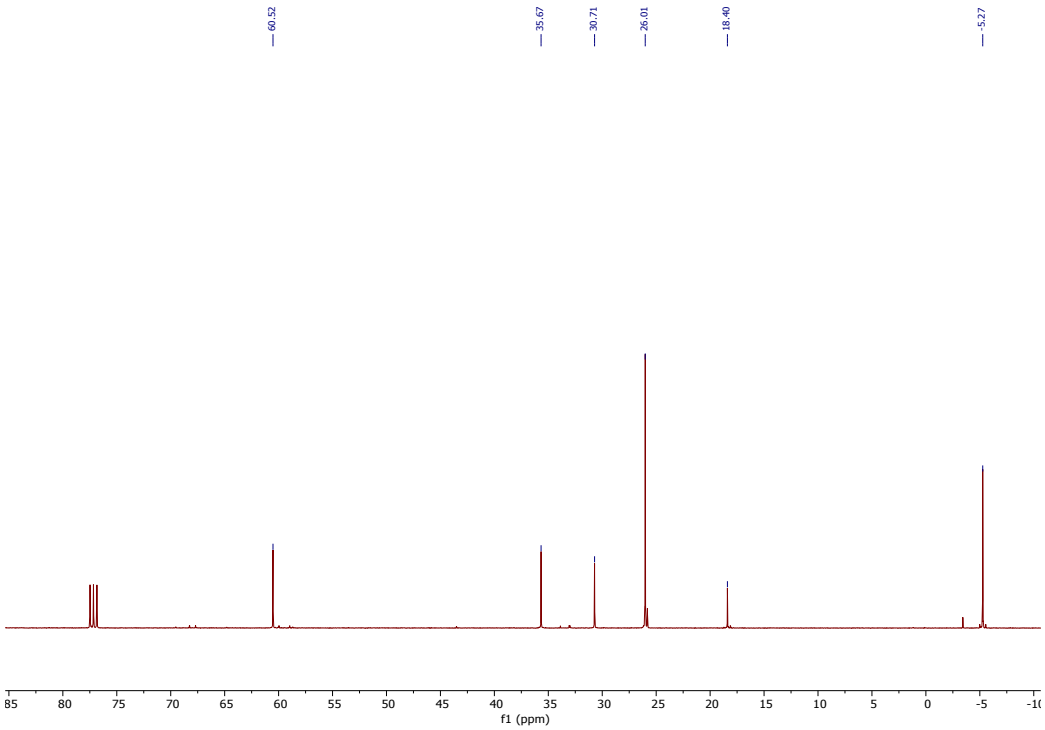


Fig. S7 ^{13}C NMR spectrum of (3-bromopropoxy)-tert-butyldimethylsilane (101 MHz, $CDCl_3$).

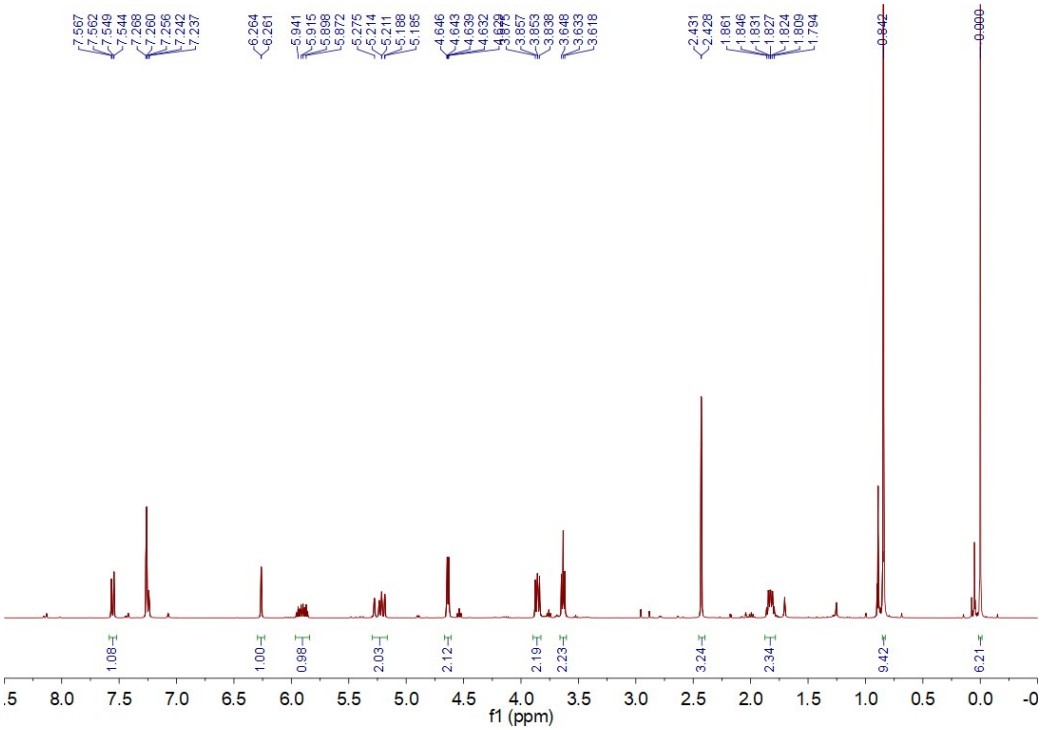


Fig. S8 ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$).

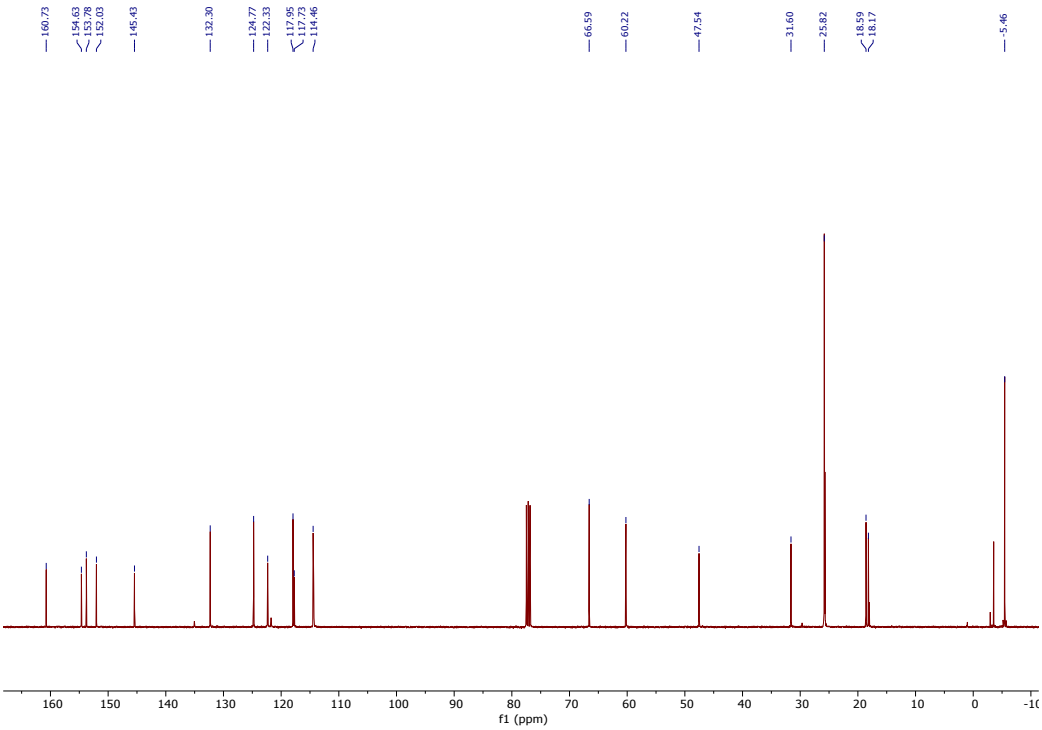


Fig. S9 ^{13}C NMR spectrum of compound **2** (101 MHz, $CDCl_3$).

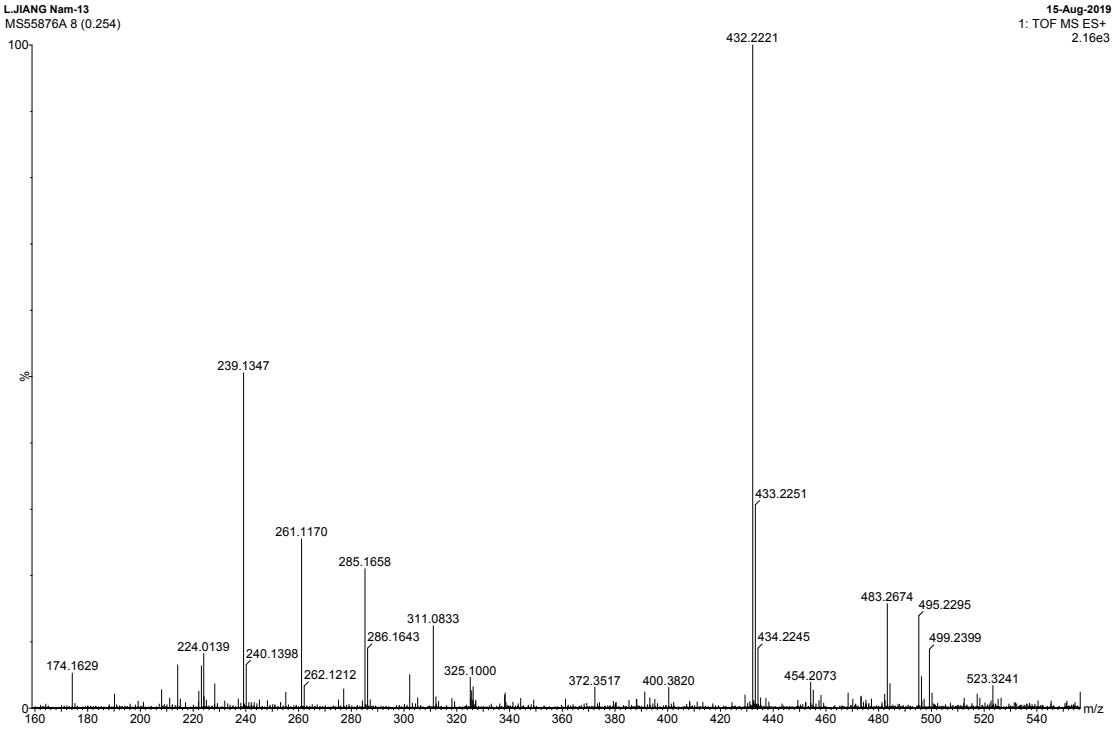


Fig. S10 High-resolution mass spectrum of compound **2**.

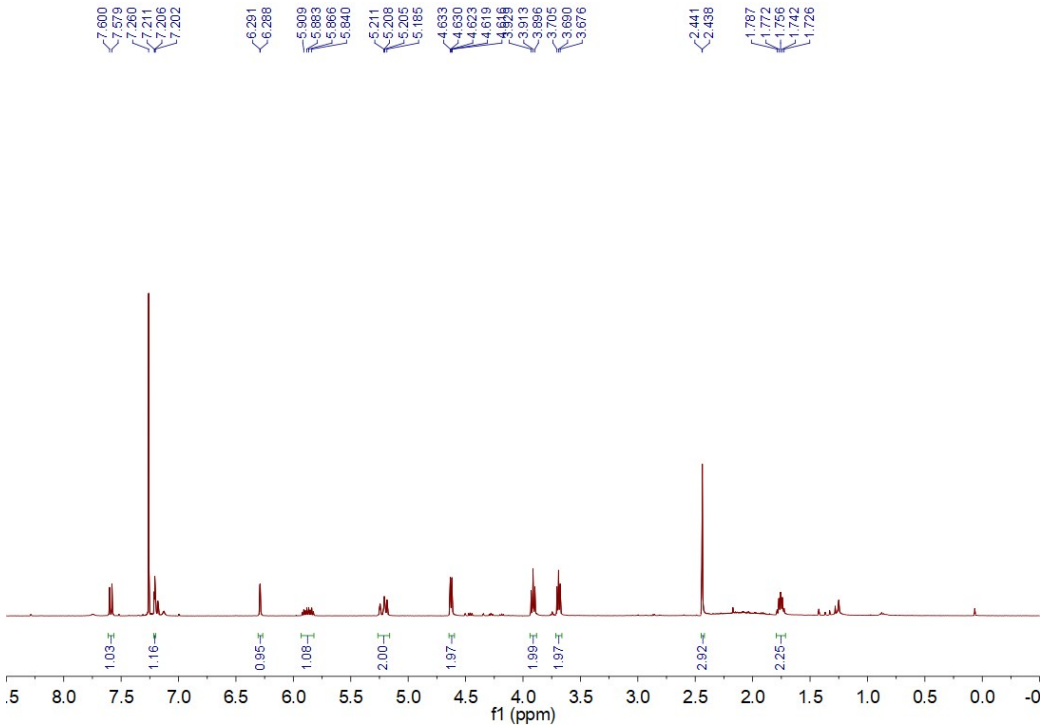


Fig. S11 ^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$).

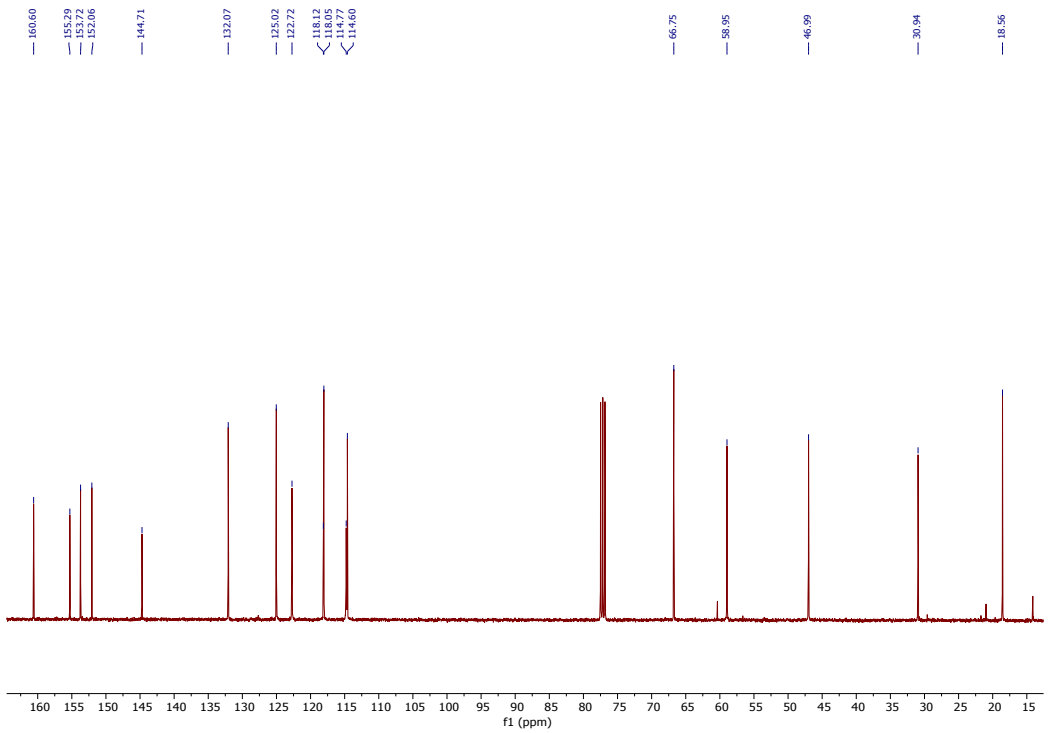


Fig. S12 ^{13}C NMR spectrum of compound **3** (101 MHz, $CDCl_3$).

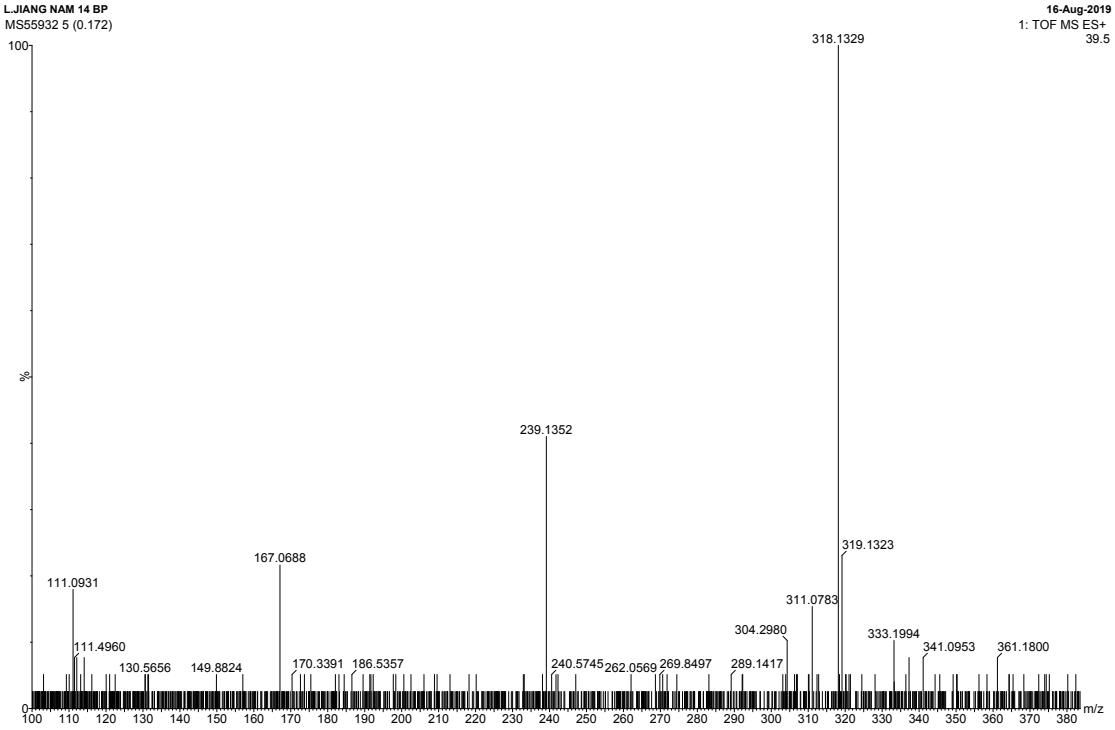


Fig. S13 High-resolution mass spectrum of compound **3**.

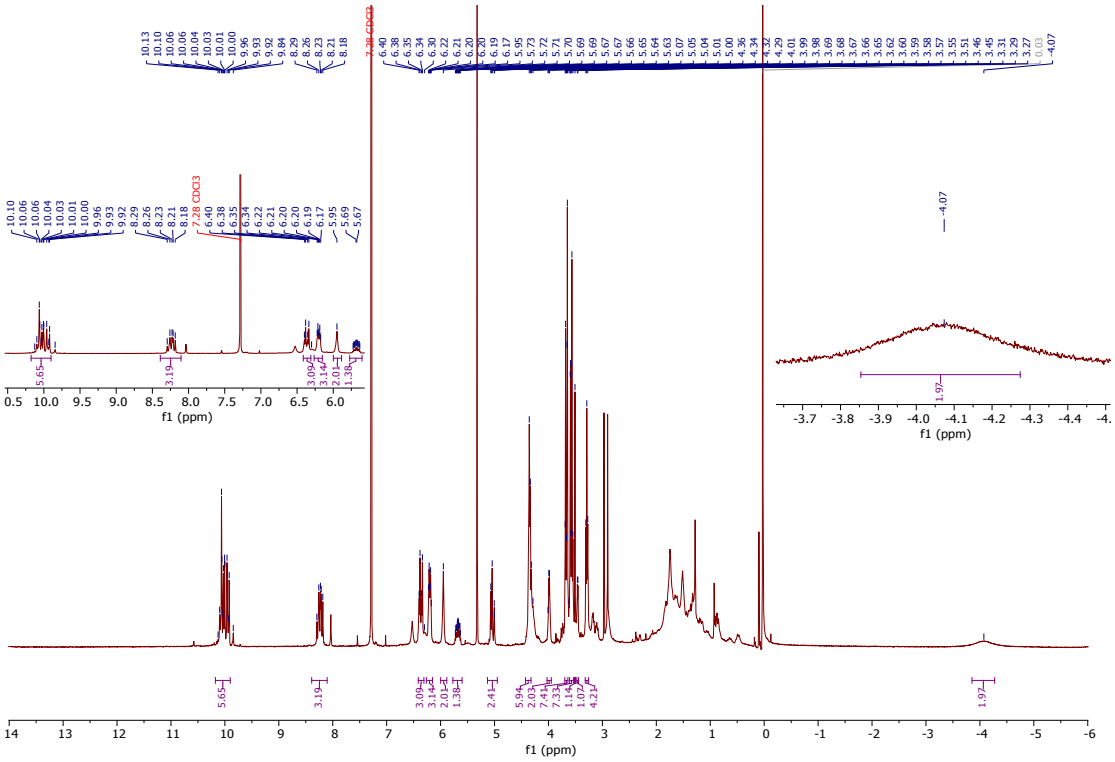


Fig. S14 ^{1}H NMR spectrum of **PPIX-L2** (400 MHz, $CDCl_3$).

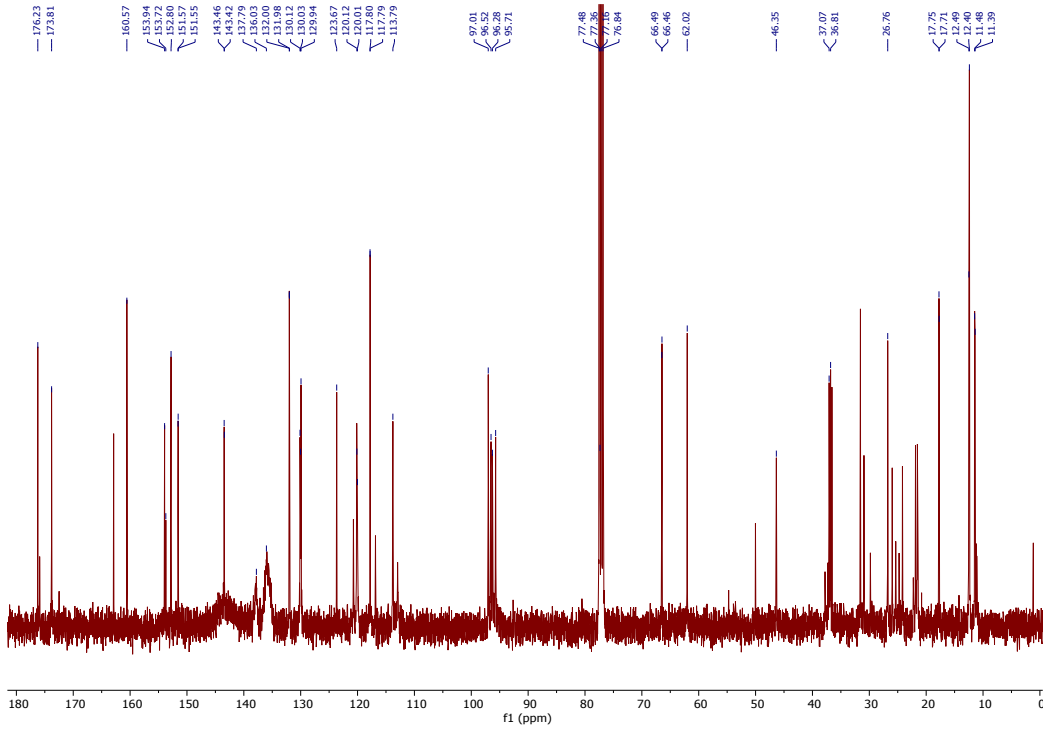


Fig. S15 ^{13}C NMR spectrum of **PPIX-L2** (101 MHz, $CDCl_3$).

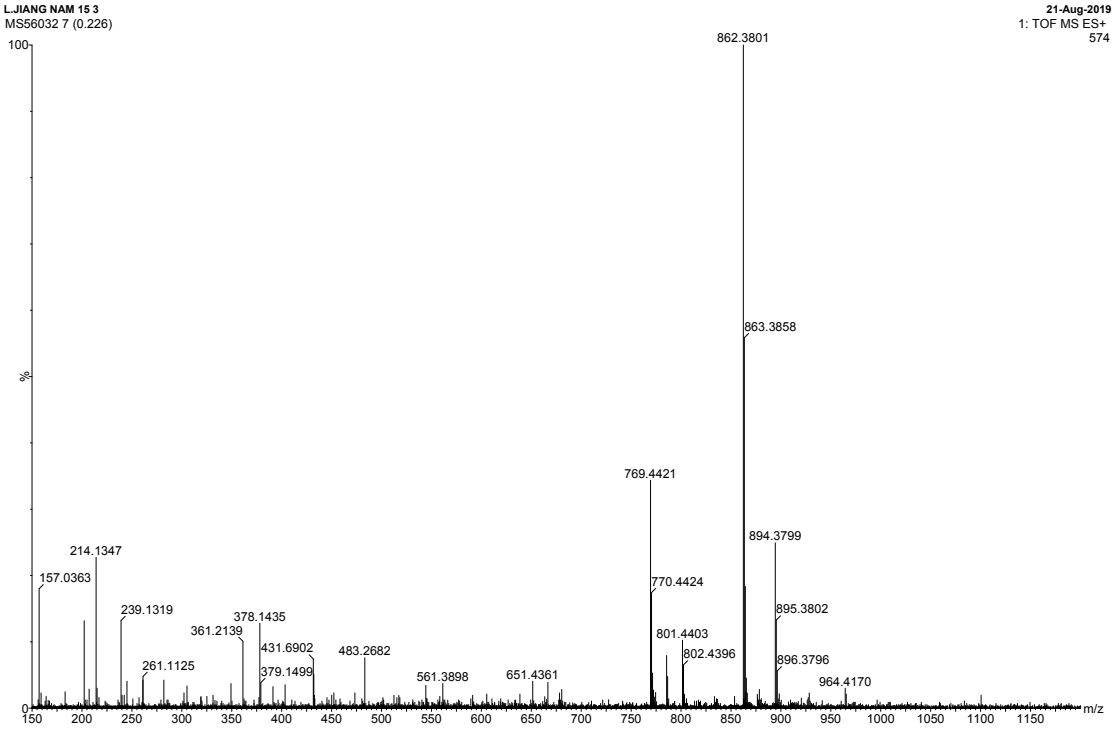


Fig. S16 High-resolution mass spectrum of **PPIX-L2**.

References

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