Supporting Information

Building Metal-Induced Inherent Chirality: Chiral Stability/Phosphorescence Enhancement via Ring Expansion Strategy of Pt(II) Complexes

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Section S1. Experimental Section

S1.1 Materials and Instruments

The detailed information of the materials and the instrumental information used for characterizations was given.

The information of the purchased materials used in this work.

Name	CAS No.	Specification	Supplier
o-Phenylenediamine	95-54-5	99%	Energy Chemical, Shanghai, China
2-Nitroaniline	88-74-4	98%	Energy Chemical, Shanghai, China
2-Diphenylphosphinobenzaldehyde	50777-69-0	95%	Energy Chemical, Shanghai, China
Sodium thiosulfate	7772-98-7	99%	Energy Chemical, Shanghai, China
Sodium metabisulfitenol	7681-57-4	96%	Giant, Chengdu, China
Trichlorosilane	10025-78-2	99.9%	Giant, Chengdu, China
Potassium tetrachloroplatinate(II)	10025-99-7	99%	Giant, Chengdu, China
Ethylene glycol monoethyl ether	110-80-5	99%	Giant, Chengdu, China

2-(2,4-Difluorophenyl)pyridine	391604-55-0	98%	Energy Chemical, Shanghai, China
Sodium carbonate	497-19-8	99.8%	Adamas-beta®, Shanghai, China
Methanol	67-56-1	AR	KESHI,Chengdu, China
Sodium hydride	7646-69-7	60% dispersion in mineral oil	Energy Chemical, Shanghai, China
Toluene	108-88-3	AR	CHRON Chemical, Chengdu, China
Sodium hydroxide	1310-58-3	99%	Energy Chemical, Shanghai, China
Dichloromethane	75-09-2	AR	CHRON Chemical, Chengdu, China
1,2-Dichloroethane	107-06-2	99%	J&K Scientific, Shanghai, China
Ethanol	64-17-5	AR	CHRON Chemical, Chengdu, China
2-Fluorobenzaldehyde	446-52-6	98%	J&K Scientific, Shanghai, China
N,N-Dimethylformamide	68-12-2	99.8%	Adamas-beta®, Shanghai, China

The instrumental information used for characterizations in this work.

Characterization items	Type	Manufacturer
UV/Vis absorption spectra	Lambda-950	Perkin Elmer, USA
Fluorescence/Phosphorescence	FluoroMax-4 spectrofluorometer	Horiba Scientific, USA/Hitachi,Japan
Fluorescence/Phosphorescence	Edinburgh FLS1000	Edinburgh, US

quantum yield	Spectrofuorophotometer with an integrating sphere (142 mm in diameter)	
Fluorescence/Phosphorescence lifetime	Fluolog-3 spectrofluorometer	Horiba Jobin Yvon, USA
High resolution mass spectra (HR-MS)	Shimadzu LCMS-IT-TOF (ESI)	Shimadzu mass spectrometer, Japan
^{1}H NMR and ^{13}C NMR AVANCE NEO 400M and AVANCE NEO 600M	Nuclear Magnetic Resonance Spectrometer (400 MHz, AVANCE III HD and 600 MHz, AVANCE III HD)	Bruker, Germany
CD spectra	J-1500-50	JASCO, Japan
Circulariy Polarized Luminescence	CPL-300	JASCO, Japan
CCD X-ray single crystal diffractometer	Bruker D8 VENTURE	Bruker, Germany

S1.2 General experimental details

S1.2.1 Measurement of luminescence Quantum Yield (Φ)

Absolute quantum yields in powder and films were determined by direct method in a integrating sphere (142 mm in diameter) using Edinburgh FLS1000 Spectrofuorophotometer.

S1.3 Theoretical calculation method:

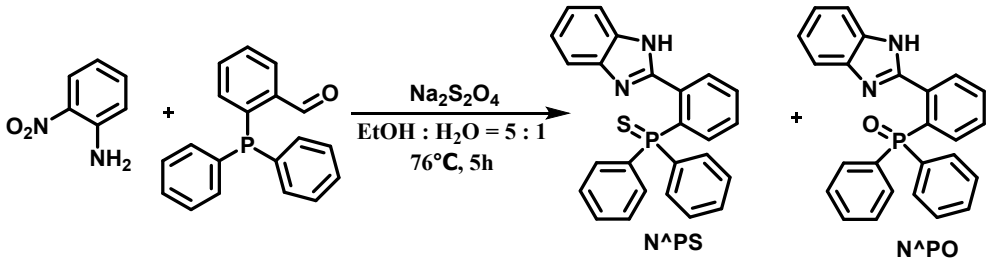
DFT and TD-DFT calculations (PBE0/SDD/6-31G) were done by Gaussian 09 software. The ground-state geometry was optimized by DFT based on the X-ray single-crystal structure of these Pt(II) complexes. After that, the optimized structure was used to calculate the UV/vis absorption and CD spectra by TD-DFT (CH_2Cl_2 as the solvent, pcm method, 80 singlet−singlet transitions).

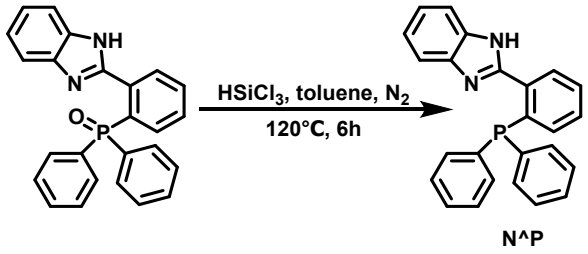
S1.4 Chirality High-Performance Liquid Chromatography. Conditions:

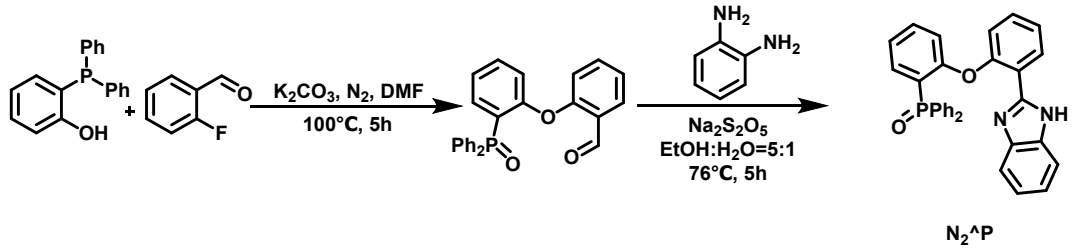
Column: DAICEL Chiralpak IC; mobile phase: eluent: isopropanol:hexane:triethylamine 40:60:0.001; flow rate = 1.0 mL/min; temperature: 25 °C

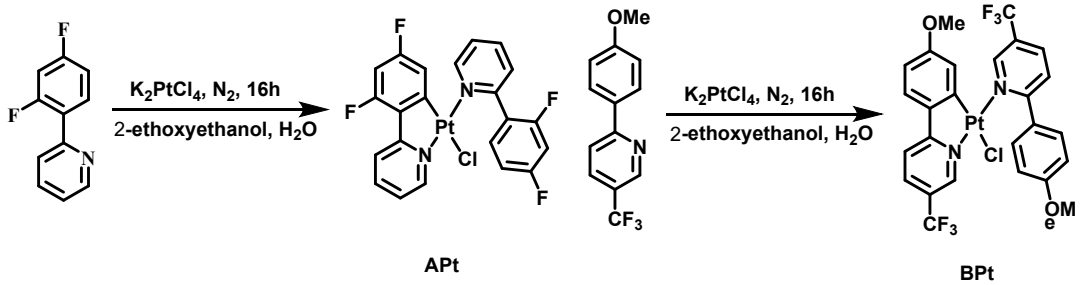
Section S2. Synthesis

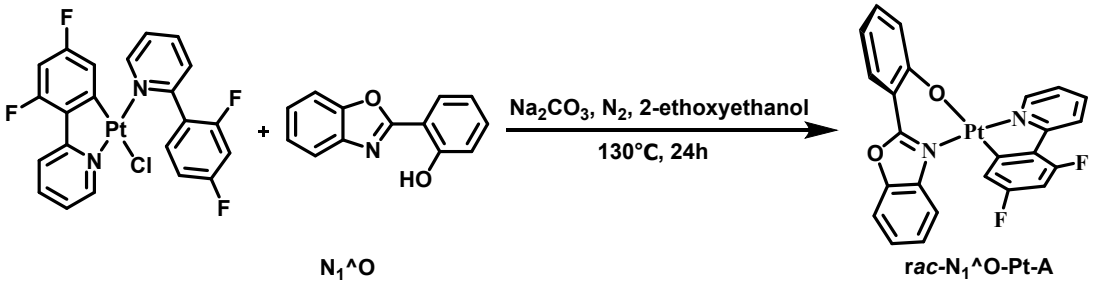
S2.1 Synthetic routes for the compounds used in this work.





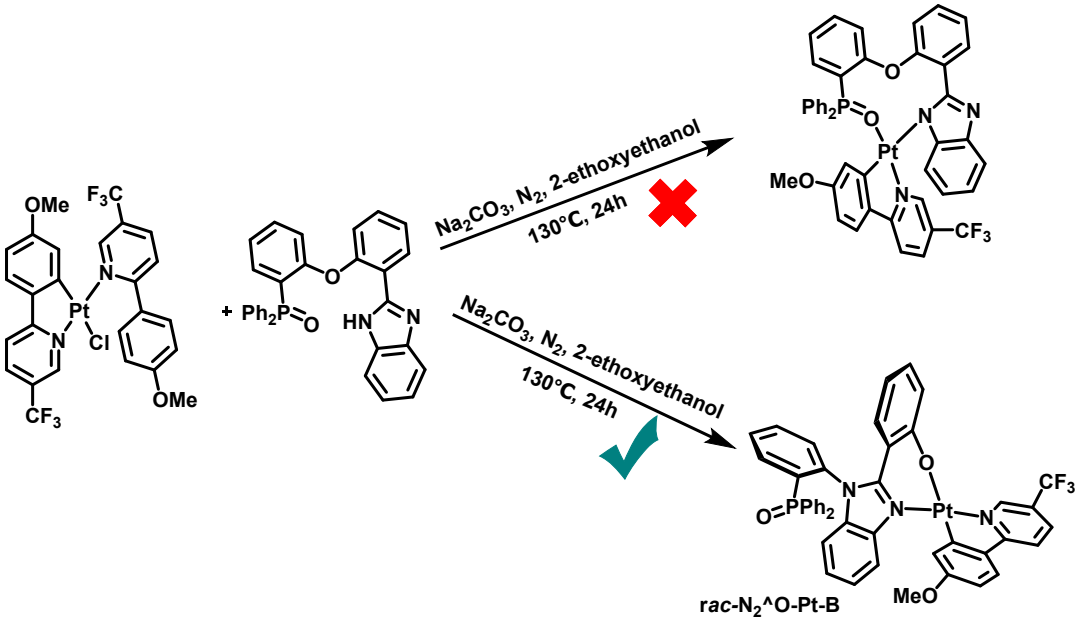




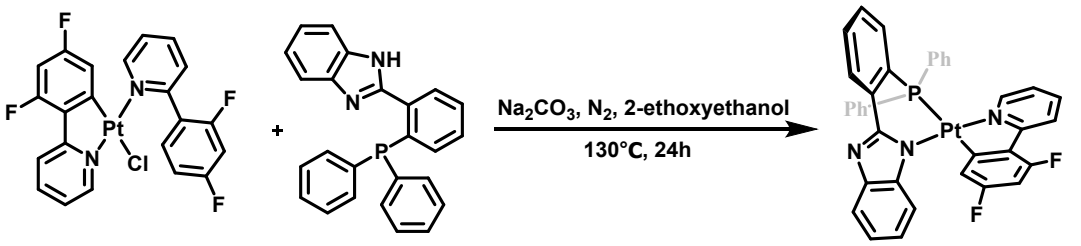


N_1^O

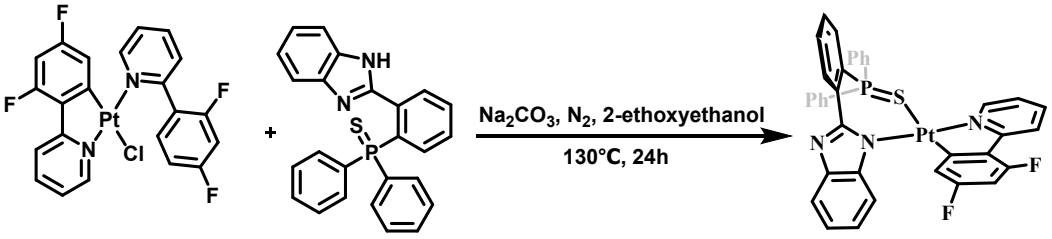
rac-N_1^O-Pt-A



rac-N_2^O-Pt-B



rac-N^P-Pt-A



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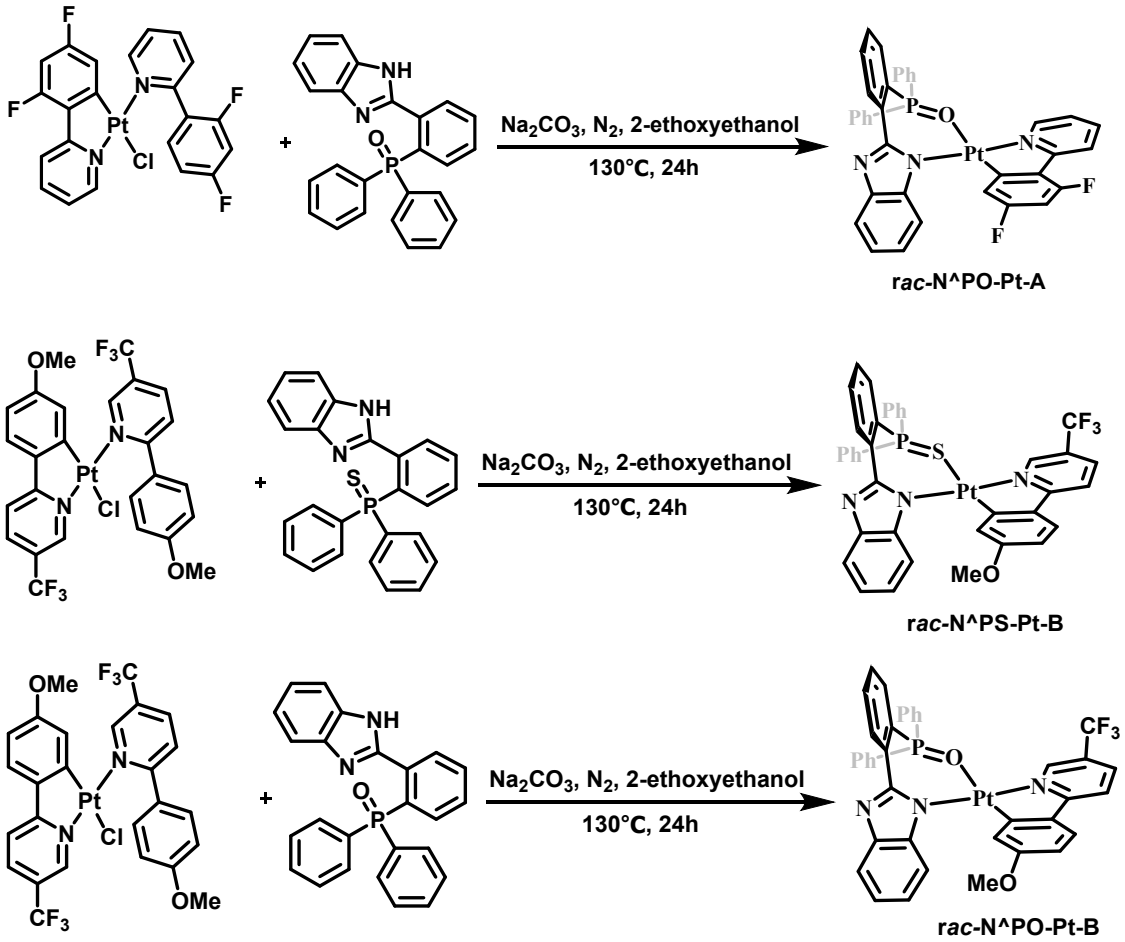


Section S3 General Experimental Details.

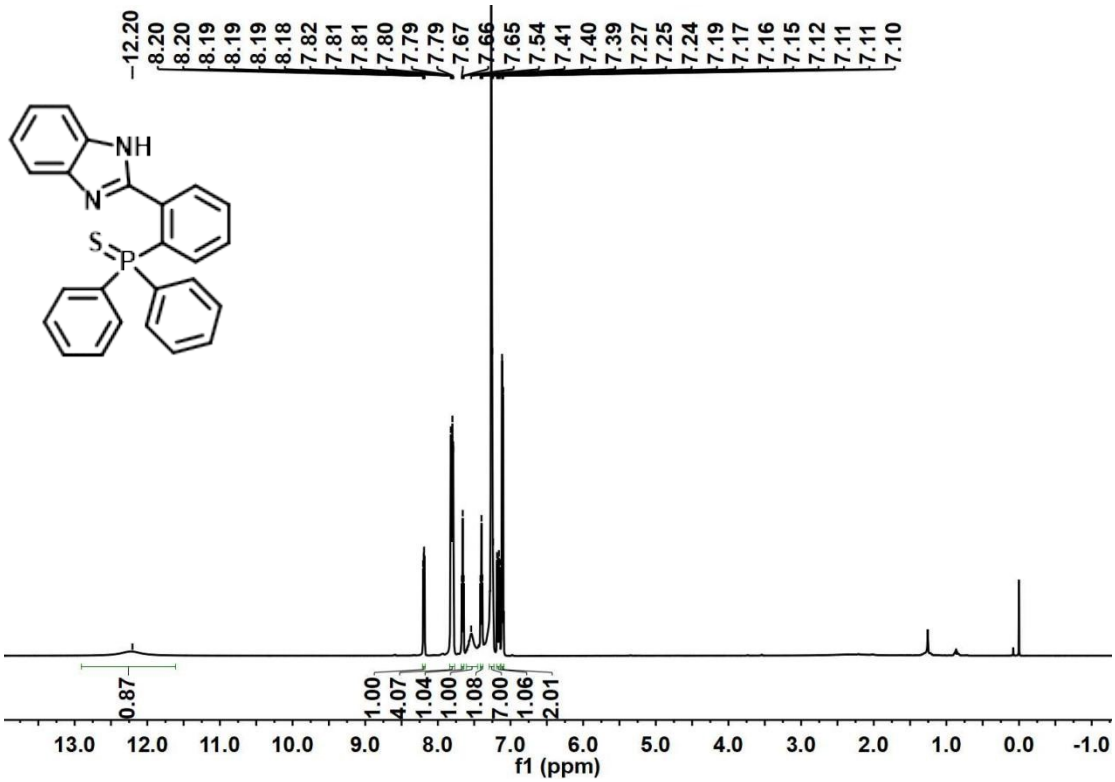
General procedure for the preparation of N^PS and N^PO.

A mixture of 2-nitroaniline (5.0 mmol) and 2-(diphenylphosphino)benzaldehyde (1.74 g, 6.0 mmol) in a 5:1 ratio of ethanol to water was treated with sodium sulfite (3.48 g, 20.0 mmol). The reaction was maintained at 76°C for 5 hours and then cooled to room temperature. The mixture was concentrated using a rotary evaporator and extracted with ethyl acetate. The resulting residue was purified by silica gel column chromatography with ethyl acetate/hexane as the eluent, yielding a pure white solid.

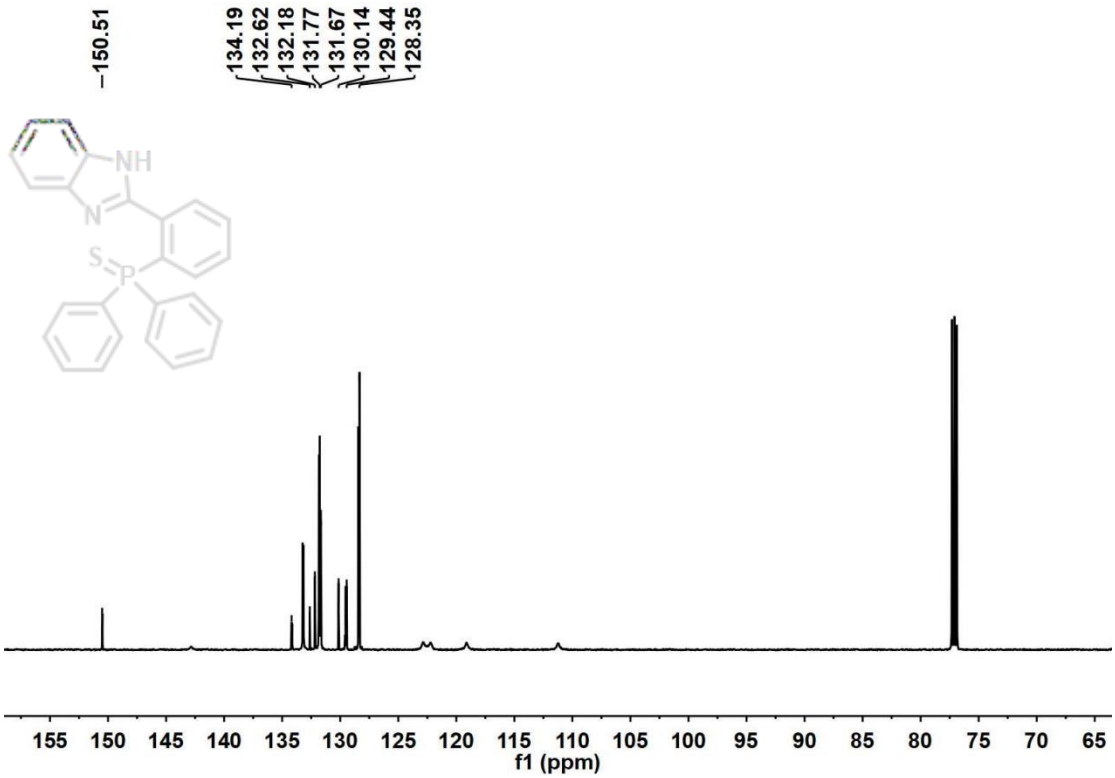
N^PS: Yield: 31%, **HRMS (ESI$^+$)**: calcd for ([M+H]$^+$) 411.1007, found 411.1067.

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.20 (s, 1H), 8.21 – 8.17 (m, 1H), 7.84 – 7.77 (m, 4H), 7.65-7.67 (t, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.39-7.41 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 9.0 Hz, 7H), 7.17 (dd, *J* = 15.3, 7.2 Hz, 1H), 7.11 (dd, *J* = 6.0, 3.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.51, 134.19, 132.62, 132.18, 131.77, 130.14, 129.44, 128.35.



^{1}H NMR of **N^PS** in $CDCl_3$-d

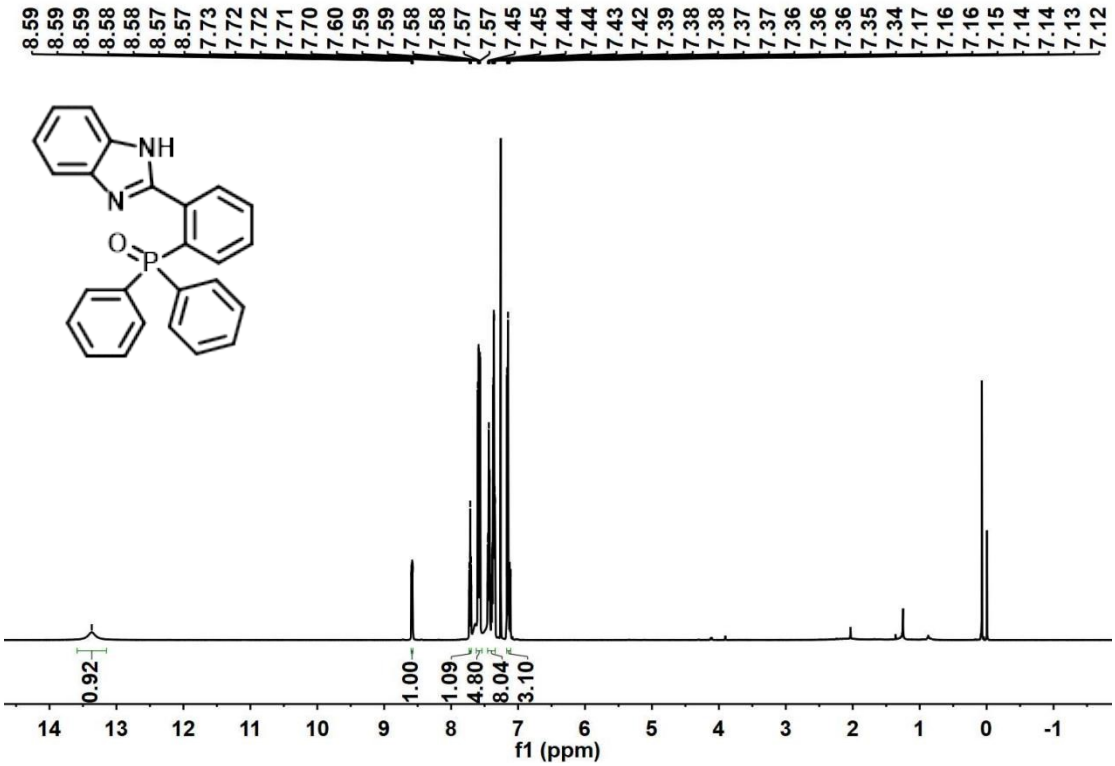


^{13}C NMR of **N^PS** in $CDCl_3$-d

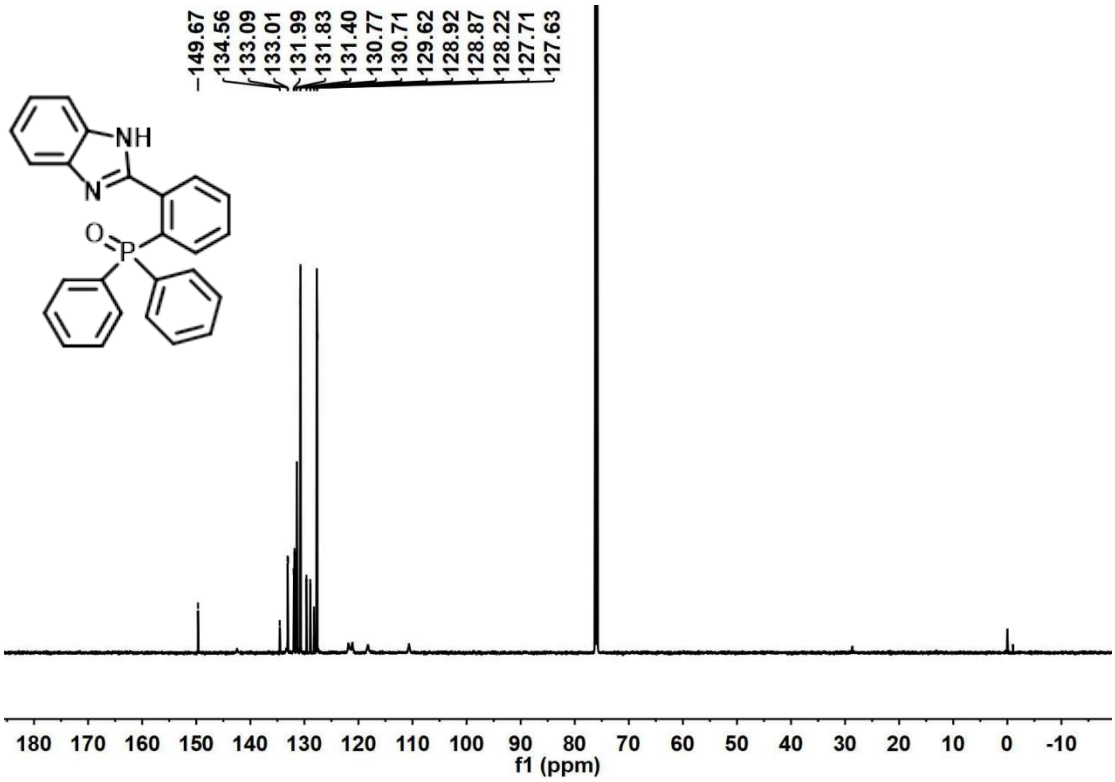
N^PO: Yield: 42%, **HRMS (ESI$^+$)**: calcd for ([M+H]$^+$) 395.1235, found 395.1296.

^{1}H NMR (600 MHz, $CDCl_3$) δ 13.37 (s, 1H), 8.57-8.60 (m, 8H), 7.70-7.73 (m, 9H), 7.62 – 7.54 (m, 5H), 7.45 – 7.34 (m, 8H), 7.17 – 7.11 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.67, 133.09, 133.01, 131.99, 131.83, 131.40, 130.77, 130.71, 129.62, 128.92, 128.87, 128.22, 127.71, 127.63.



^{1}H NMR of **N^PO** in $CDCl_3$-d



^{13}C NMR of **N^PO** in $CDCl_3$-d

General procedure for the preparation of N^P.

PO (1.30 mmol) was added to anhydrous toluene, and trichlorosilane (1.0 g, 8.1 mmol) was added dropwise to the mixture, which was then heated at 120°C for 6 hours under a nitrogen atmosphere. After natural cooling to room temperature, the product did not require purification and proceeded directly to the next step.

N^P: Yield: 87% **HRMS (ESI+):** calcd for ($[M+H]^+$) 379.1286, found 379.1359.

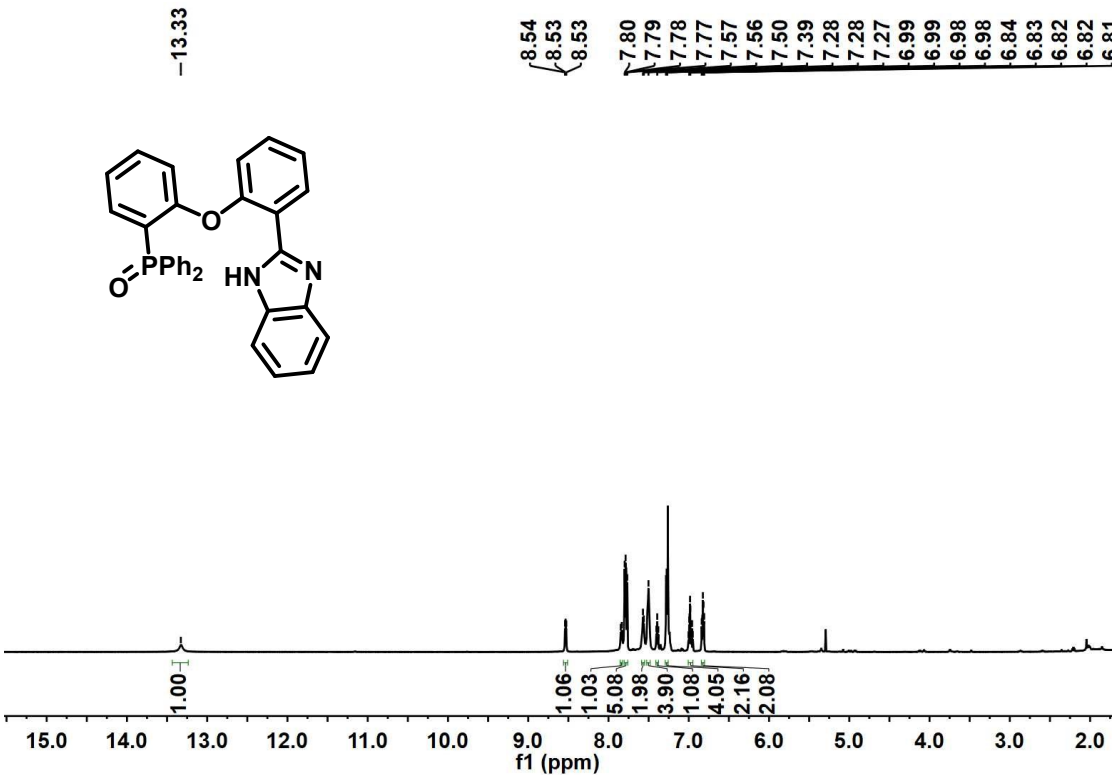
General procedure for the preparation of N_2^O.

A mixture of 2-(2-(diphenylphosphino)benzaldehyde (1.00 g, 3.60 mmol), 2-fluorobenzaldehyde (0.45 g, 3.60 mmol), and potassium carbonate (0.75 g, 5.40 mmol) was added to dry dimethylformamide (DMF, 10 mL) and stirred under a nitrogen atmosphere for 3 hours at 100°C to obtain the crude product, which did not require further purification. Subsequently, 1.0 mmol of the corresponding o-phenylenediamine and 0.48 g (1.25 mmol) of the crude product were mixed in ethanol and water (5:1) and reacted with sodium metabisulfite (0.8 g, 4.17 mmol) for 5 hours at 76°C. After cooling to room temperature, the mixture was concentrated using a rotary evaporator and extracted with ethyl acetate. Finally, the crude product was chromatographed on a silica column to yield a pure white solid.

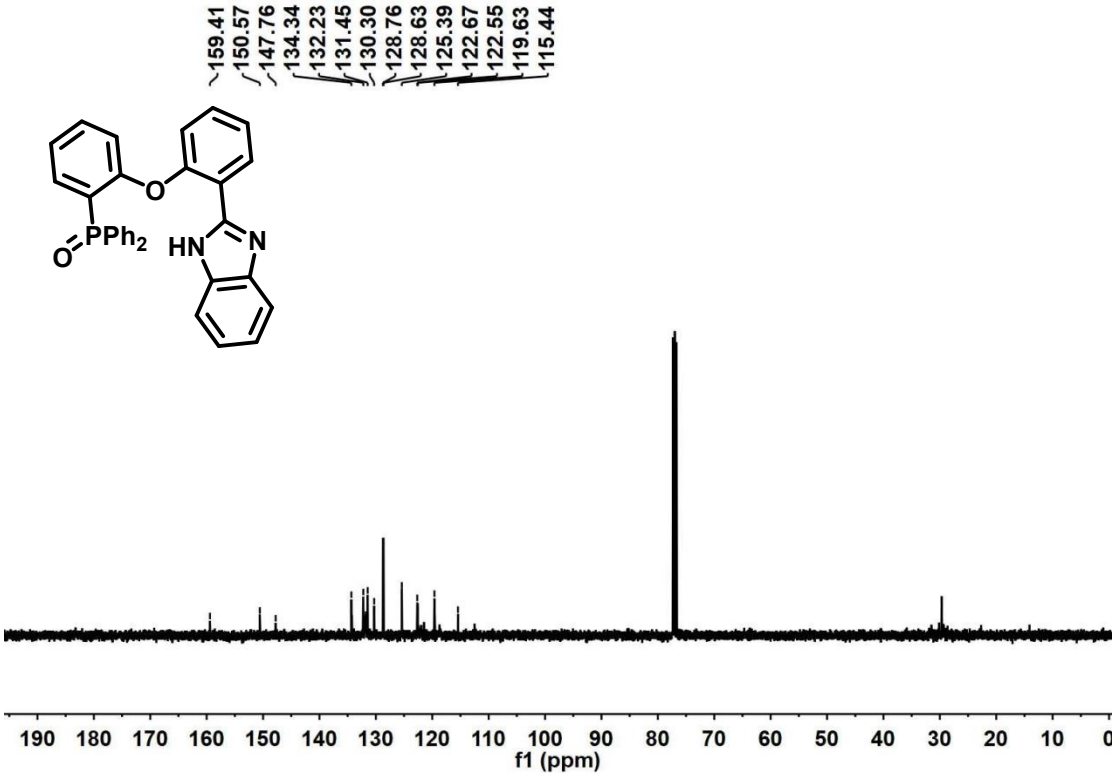
N_2^O: Yield: 42%, **HRMS (ESI^+)**: calcd for ($[M+H]^+$) 487.1497, found 487.1529.

^{1}H NMR (600 MHz, $CDCl_3$) δ 13.33 (s, 1H), 8.56 – 8.51 (m, 3H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.78 (m, 5H), 7.57 (d, *J* = 6.8 Hz, 2H), 7.50 (s, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.26 (m, 4H), 7.01 – 6.95 (m, 8H), 6.82 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.41, 150.57, 147.76, 134.34, 132.23, 131.45, 130.30, 128.76, 128.63, 125.39, 122.67, 122.55, 119.63, 115.44.



^{1}H NMR of **N_2^O** in $CDCl_3$-d



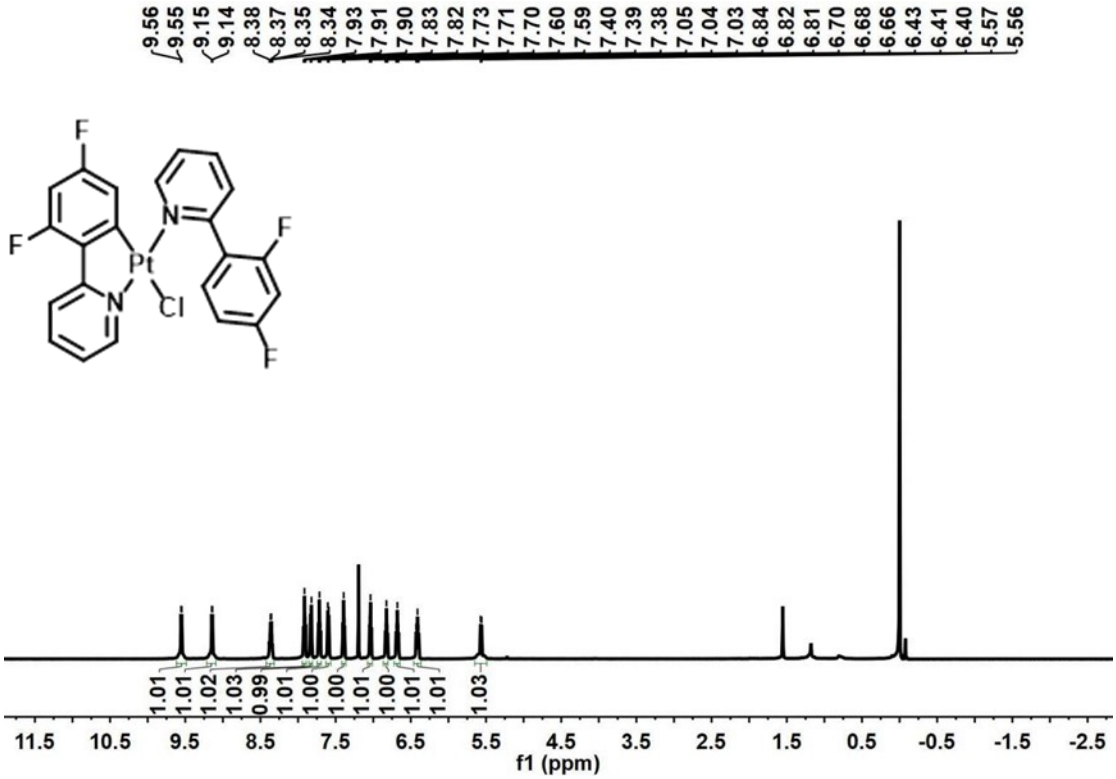
^{13}C NMR of **N_2^O** in $CDCl_3$-d

General procedure for the preparation of APt and BPt.

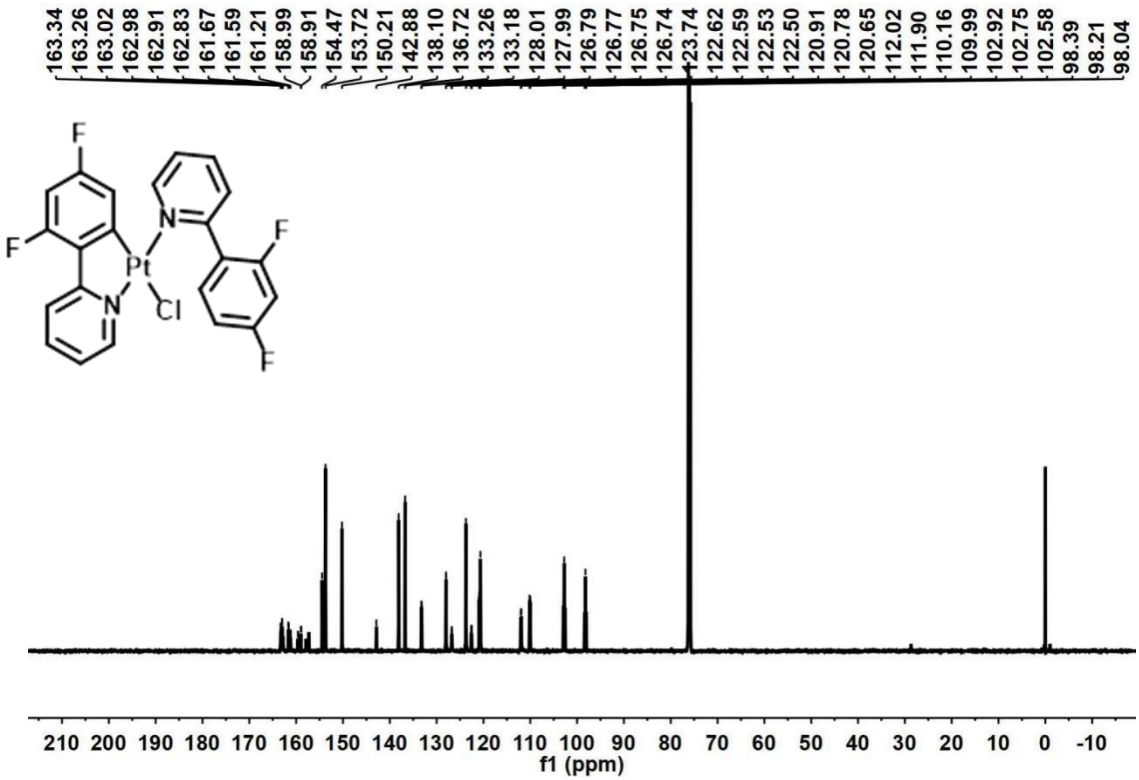
A 100-mL round-bottom flask was charged with 2-(2,4-difluorophenyl)pyridine (1 mL, 3.9 mmol) and K_2PtCl_4 (0.78 g, 1.88 mmol) in a solvent mixture of 2-ethoxyethanol (24 mL) and water (8 mL) under an argon atmosphere. The reaction was maintained at 85°C for 16 hours. After the reaction, water was added to the mixture, causing the precipitation of a solid, which was then washed with ice-cold methanol and dried under vacuum to yield a chlorine-bridged dimer as a yellow-green solid.

APt：^{1}H NMR (600 MHz, $CDCl_3$) δ 9.55 (d, *J* = 5.7 Hz, 1H), 9.14 (d, *J* = 5.7 Hz, 1H), 8.34-8.33 (m, 1H), 7.90-7.33 (t, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.70-7.73 (t, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.38-7.40 (t, *J* = 6.7 Hz, 1H), 7.03-7.05 (t, *J* = 6.6 Hz, 1H), 6.81-6.84 (t, *J* = 8.2 Hz, 1H), 6.66-6.70 (t, *J* = 9.4 Hz, 1H), 6.40-6.43 (t, *J* = 10.6 Hz, 1H), 5.57 (d, *J* = 8.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.36, 163.28, 163.04, 162.99, 161.68, 161.60, 159.01, 158.93, 157.92, 157.83, 157.34, 157.26, 153.74, 150.22, 142.89, 138.12, 136.73, 133.28, 133.21, 128.02, 128.00, 123.75, 120.92, 120.80, 120.66, 112.04, 111.91, 110.17, 110.00, 102.93, 102.76, 102.59, 98.40, 98.22, 98.05.



^{1}H NMR of **APt** in $CDCl_3$-d



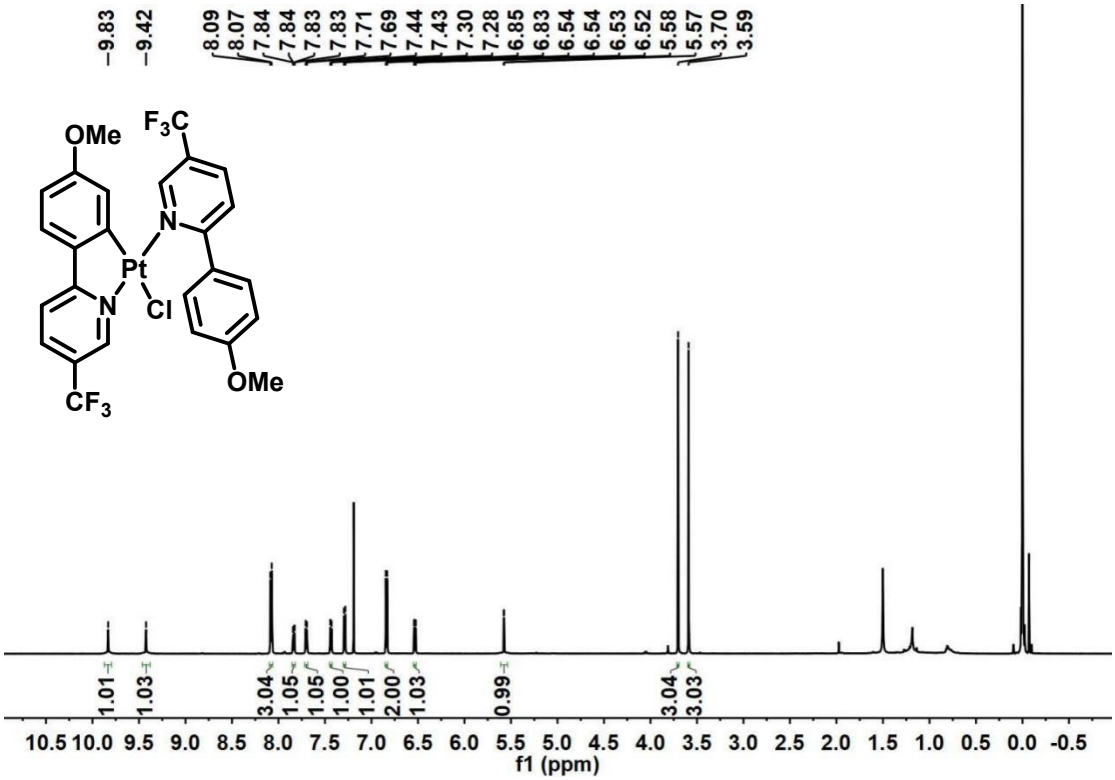
^{13}C NMR of **APt** in $CDCl_3$-d

General procedure for the preparation of BPt.

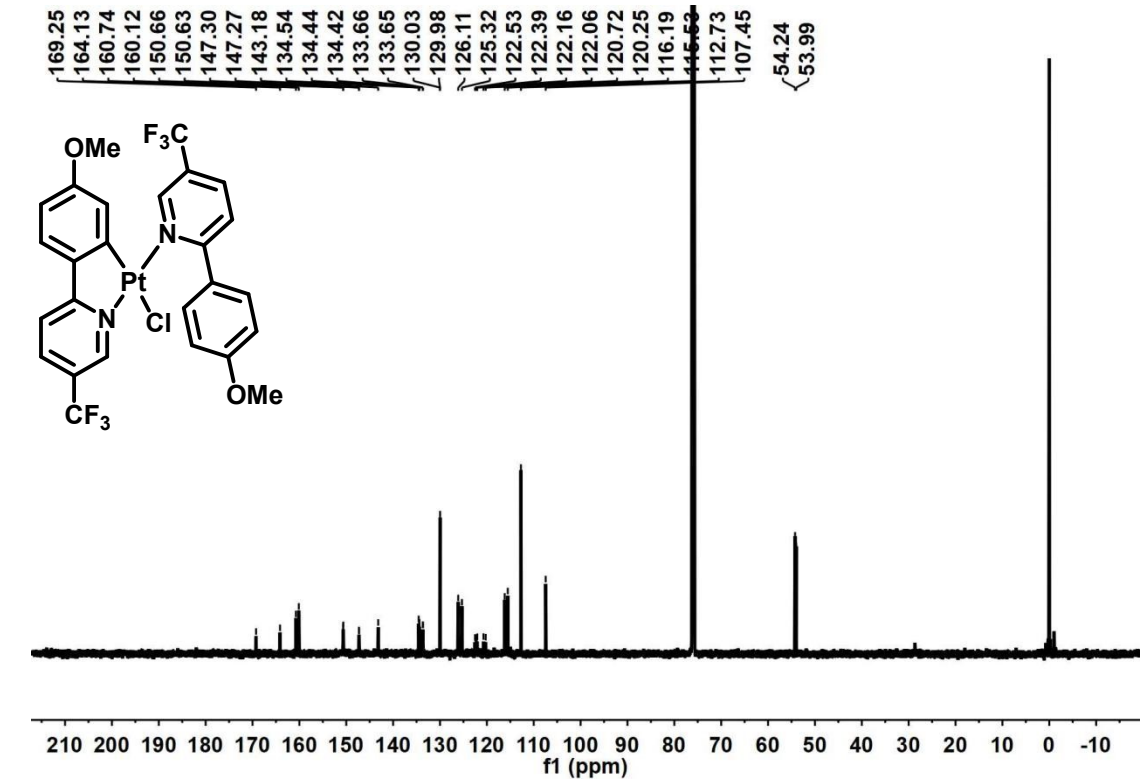
A 100-mL round-bottomed flask was charged with 2-(4-methoxyphenyl)-5-(trifluoromethyl)pyridine (4 mL, 16.1 mmol) and K_2PtCl_4 (3.3 g, 8.0 mmol) in a solvent mixture of 2-ethoxyethanol (100 mL) and water (35 mL) under an argon atmosphere for a controlled reaction at 85°C for 16 h. Water was added to the reaction mixture, and the precipitate. The precipitate was then washed with ice methanol and dried under vacuum to allow the chlorine-bridged dimer to form a yellow-green solid.

BPt：^{1}H NMR (600 MHz, $CDCl_3$) δ 9.83 (s, 1H), 9.42 (s, 1H), 8.08 (d, *J* = 8.8 Hz, 3H), 7.84 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.53 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.58 (d, *J* = 2.4 Hz, 1H), 3.70 (s, 3H), 3.59 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.25, 164.13, 160.74, 160.12, 150.66, 150.63, 147.30, 147.27, 143.18, 134.54, 134.44, 134.42, 133.66, 133.65, 130.03, 129.98, 126.11, 125.32, 122.53, 122.16, 122.06, 120.72, 120.25, 116.19, 115.53, 112.73, 107.45, 54.24, 53.99.



^{1}H NMR of **B** in $CDCl_3$-d



^{13}C NMR of **BPt** in $CDCl_3$-d

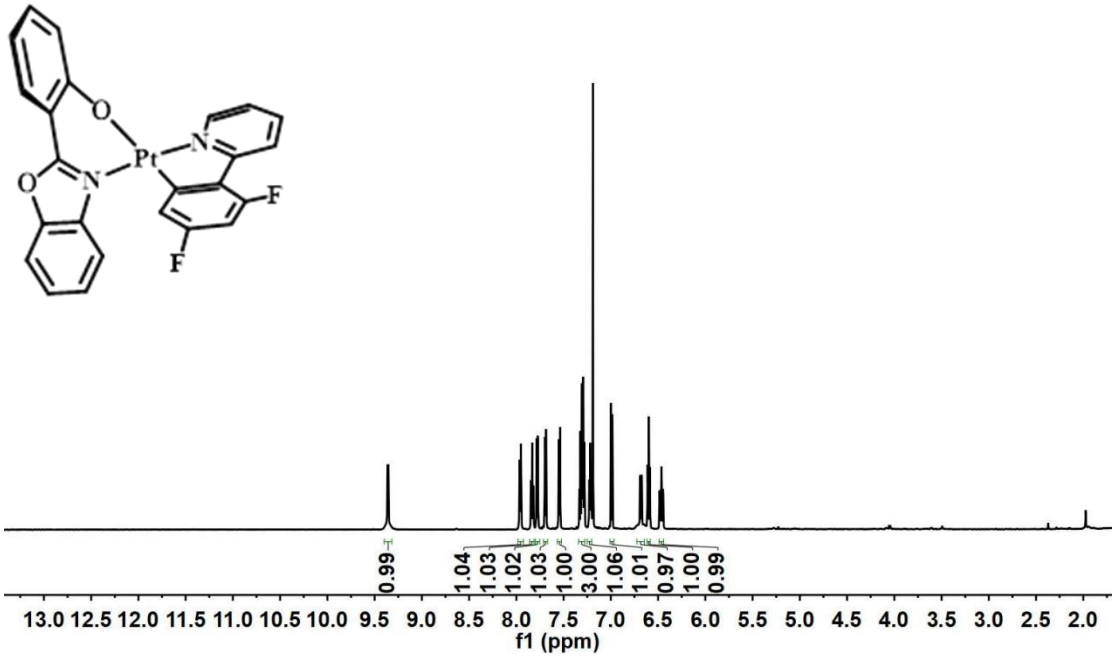
General procedure for the preparation of N_1^O-Pt-A.

Compound **A** (0.43 g, 0.71 mmol) and 2-(benzo[d]oxazol-2-yl)phenol (0.47 mmol) were added to 15 mL of 2-ethoxyethanol in the presence of sodium carbonate (0.15 g, 1.41 mmol) in a 250-mL two-neck flask. The mixture was heated under a nitrogen atmosphere at 130°C for 24 hours. After cooling to room temperature, deionized water was added, and the residue was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Further purification by column chromatography using ethyl acetate/dichloromethane as the eluent yielded pure **N_1^O-Pt-A**.

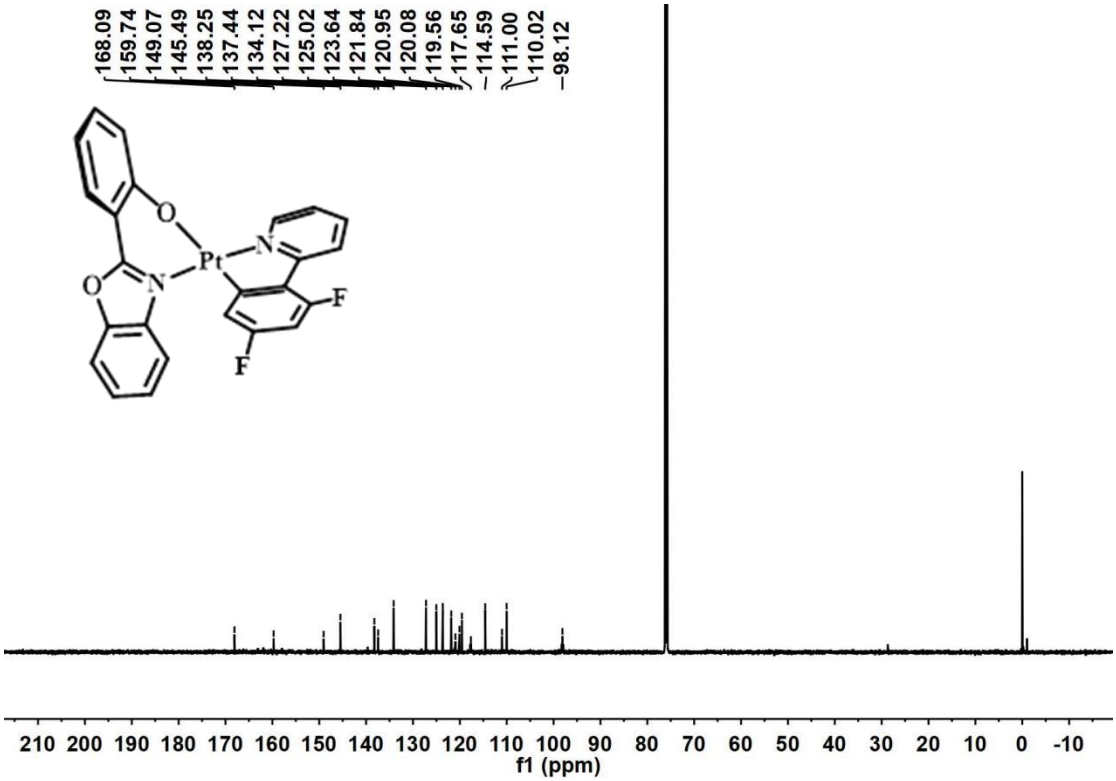
N_1^O-Pt-A：Yield: 54% **HRMS (ESI^+)**: calcd for ($[M+H]^+$) 595.0671, found 596.0748.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.36 (d, *J* = 5.2 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.78 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.25 – 7.20 (m, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.68 (dd, *J* = 9.3, 2.2 Hz, 1H), 6.59-6.61 (t, *J* = 7.4 Hz, 1H), 6.46 (dd, *J* = 11.6, 9.0, 2.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.09, 159.74, 149.07, 145.49, 138.25, 137.44, 134.12, 127.22, 125.02, 123.64, 121.84, 120.95, 120.08, 119.56, 117.65, 114.59, 111.00, 110.02, 98.12.



^{1}H NMR of **N_1^O-Pt-A** in $CDCl_3$-d



^{13}C NMR of **N_1^O-Pt-A** in $CDCl_3$-d

General procedure for the preparation of N_2^O-Pt-B.

Compound **B** (0.58 g, 0.8 mmol) and the corresponding imine (0.8 mmol) were added to 30 mL of 2-ethoxyethanol in the presence of sodium carbonate (0.84 g, 8.0 mmol) in a 250-mL two-neck flask. The mixture was heated under a nitrogen atmosphere at 130°C for 24 hours. After cooling to room temperature, deionized water was added, and the residue was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Further purification by column chromatography using ethyl acetate/dichloromethane as the eluent yielded trace amounts of **N_2^O-Pt-A**. The structure of this complex was characterized using single-crystal data and **HRMS (ESI+)** (calcd for ($[M+H]^+$) 933.1703, found 933.1721)

General procedure for the preparation of *rac*-N^P-Pt-A.

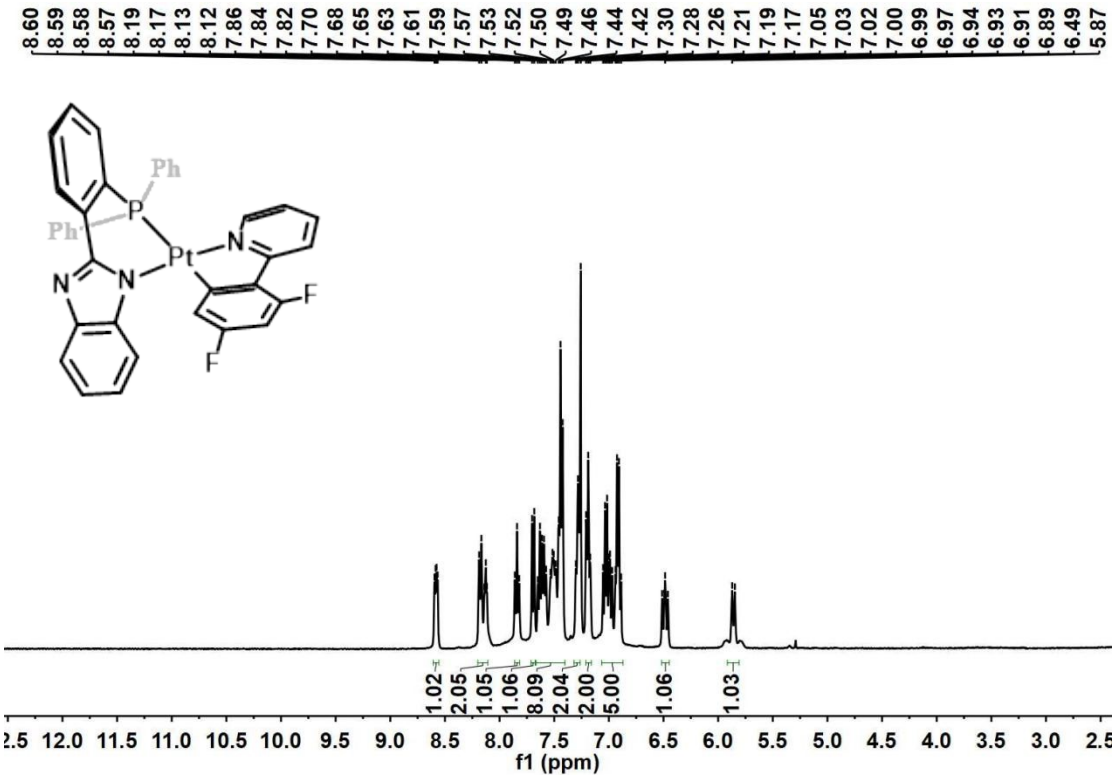
Compound **A** (0.32 g, 0.55 mmol) and the corresponding reagent **N^P** (0.55 mmol) were added to 30 mL of 2-ethoxyethanol in the presence of sodium carbonate (0.58 g, 5.55 mmol) in a 250-mL two-neck flask. The mixture was heated under a nitrogen atmosphere at 130°C for 24 hours. After cooling to room temperature, deionized water was added, and the residue was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified using silica gel column chromatography with DCM/CH_3OH as the eluent to obtain pure ***rac*-N^P-Pt-A**.

***rac*-N^P-Pt-A**：Yield: 39% **HRMS (ESI+):** calcd for ($[M+H]^+$) 763.1324, found 763.1396

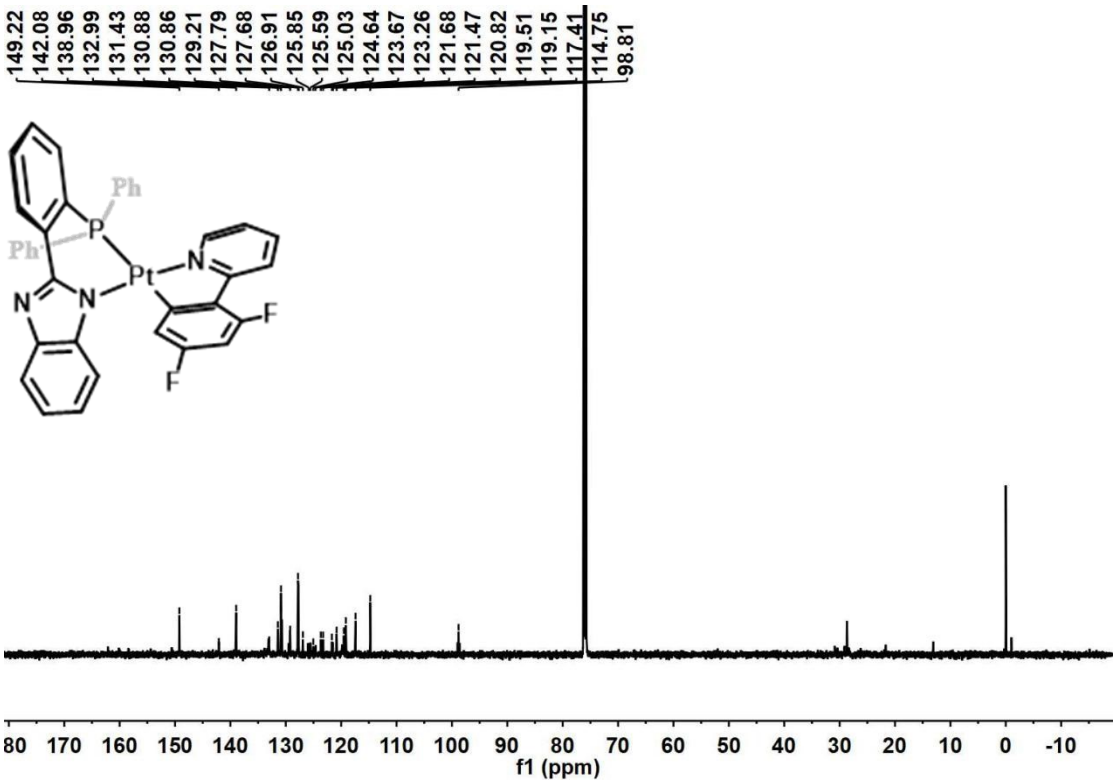
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 7.6, 4.1 Hz, 1H), 8.20 – 8.11 (m, 2H), 7.82-7.86 (t, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.40 (m, 8H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.17-7.21 (t, *J* = 7.5 Hz, 2H), 7.07 – 6.87 (m, 5H), 6.52 – 6.45 (m, 1H), 5.86 (d, *J* = 9.7 Hz,

1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.22, 142.08, 138.96, 132.99, 131.43, 130.88, 130.86, 129.21, 127.79, 127.68, 126.91, 123.67, 123.26, 121.68, 120.82, 119.51, 119.15, 117.41, 114.75, 98.81



^{1}H NMR of ***rac*-N^P-Pt-A** in $CDCl_3$-d



^{13}C NMR of ***rac*-N^P-Pt-A** in $CDCl_3$-d

General procedure for the preparation of *rac*-N^PS-Pt-A.

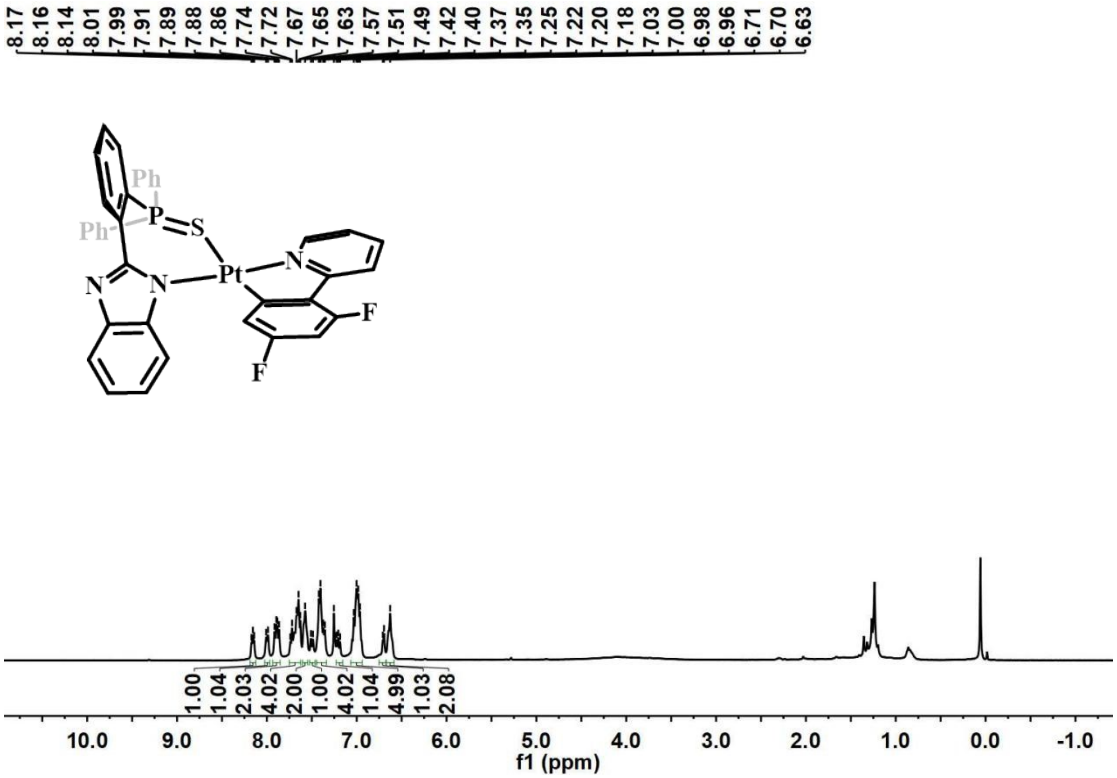
Compound **A** (0.73 g, 1.2 mmol) and the corresponding reagent **N^PS** (1.2 mmol) were added to 50 mL of 2-ethoxyethanol, along with sodium carbonate (1.2 g, 12.0 mmol) in a 250-mL two-neck flask. The mixture was heated under a nitrogen atmosphere at 130°C for 24 hours. After cooling to room temperature, deionized water was added, and the residue was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified using silica gel column chromatography with DCM/CH_3OH as the eluent to obtain pure ***rac*-N^PS-Pt-A**.

***rac*-N^PS-Pt-A**：Yield: 25% **HRMS (ESI+):** calcd for ($[M+H]^+$) 795.1044, found 795.1052

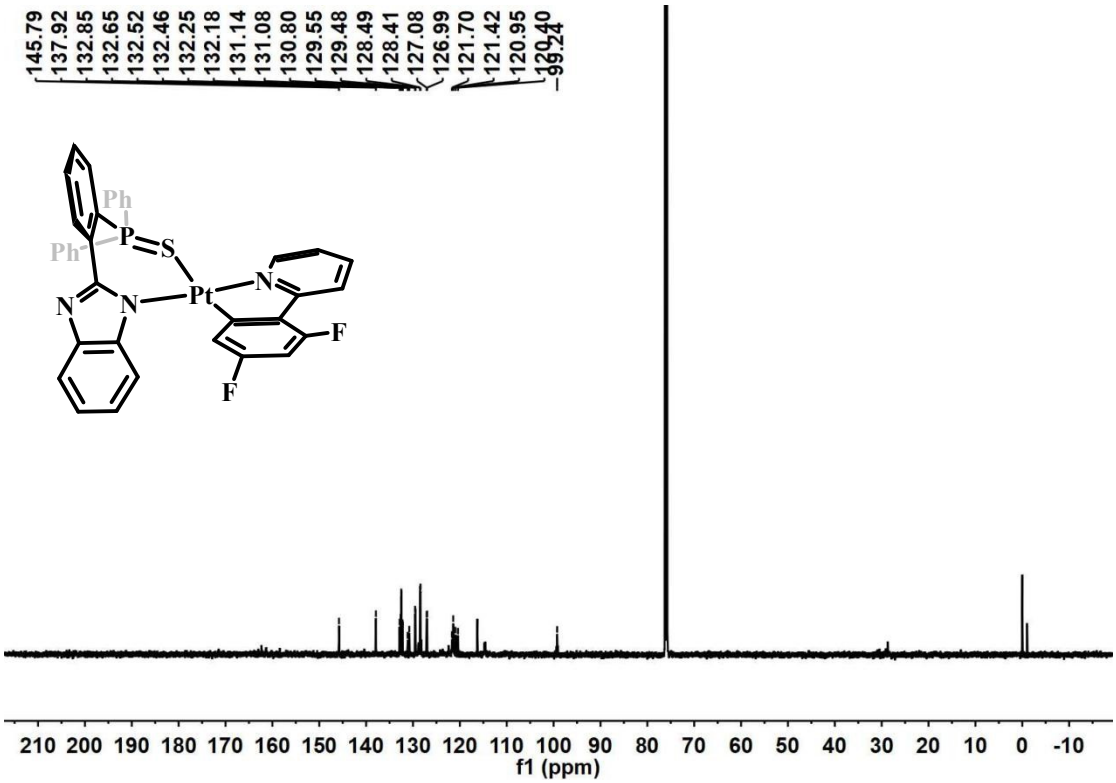
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.12 (m, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 12.0, 7.9 Hz, 2H), 7.75 – 7.62 (m, 4H), 7.57 (s, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.39 (dd, *J* =

19.3, 7.3 Hz, 4H), 7.23 – 7.16 (m, 1H), 6.95-7.05 (m, 5H), 6.70 (d, *J* = 5.4 Hz, 1H), 6.64 (d, *J* = 6.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.79, 137.92, 132.85, 132.65, 132.52, 132.46, 132.25, 132.18, 131.14, 131.08, 130.80, 129.55, 129.48, 128.49, 128.41, 127.08, 126.99, 121.70, 121.56, 121.42, 120.95, 120.40, 99.24.



^{1}H NMR of ***rac*-N^PS-Pt-A** in $CDCl_3$-d



^{13}C NMR of ***rac*-N^PS-Pt-A** in $CDCl_3$-d

General procedure for the preparation of *rac*-N^PO-Pt-A.

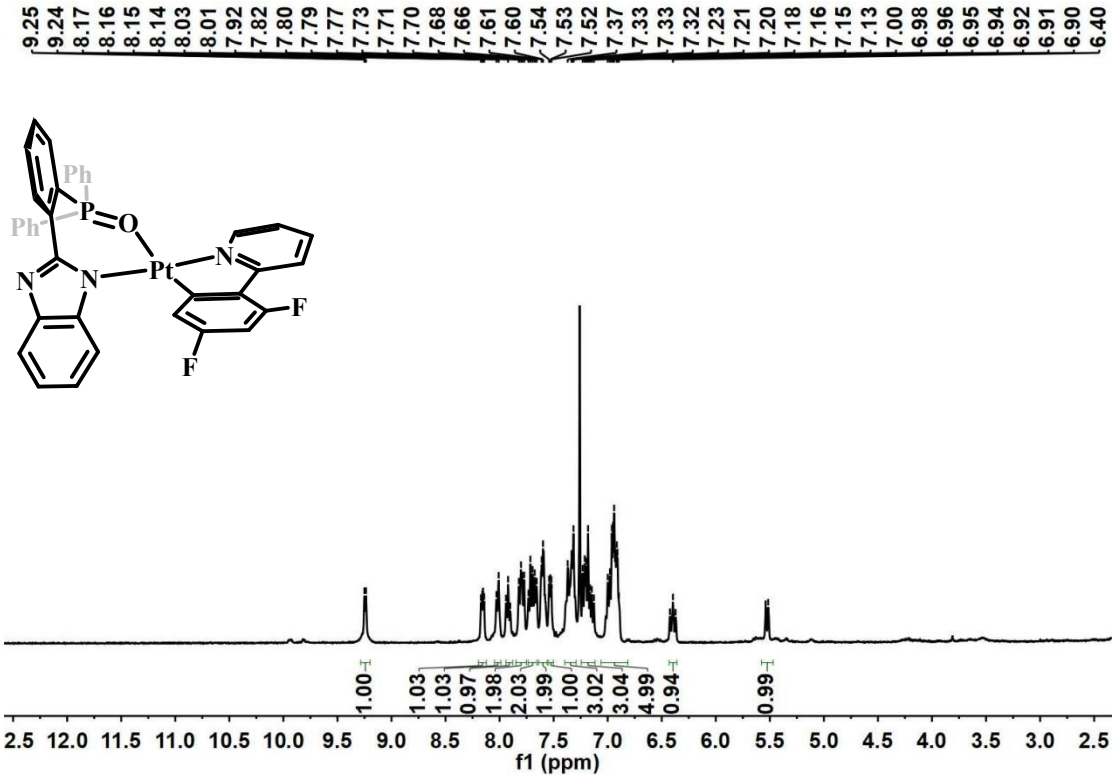
Compound **A** (0.136 g, 0.24 mmol) and the corresponding reagent **N^PO** (0.24 mmol) were added to 15 mL of 2-ethoxyethanol, along with sodium carbonate (0.25 g, 2.4 mmol), in a 250-mL two-neck flask. The mixture was heated under a nitrogen atmosphere at 130°C for 24 hours. After cooling to room temperature, deionized water was added, and the residue was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified using silica gel column chromatography with DCM/CH_3OH as the eluent to obtain pure ***rac*-N^PO-Pt-A**.

***rac*-N^PO-Pt-A:** Yield: 55% **HRMS (ESI+):** calcd for ($[M+H]^+$) 779.1273, found 779.1304

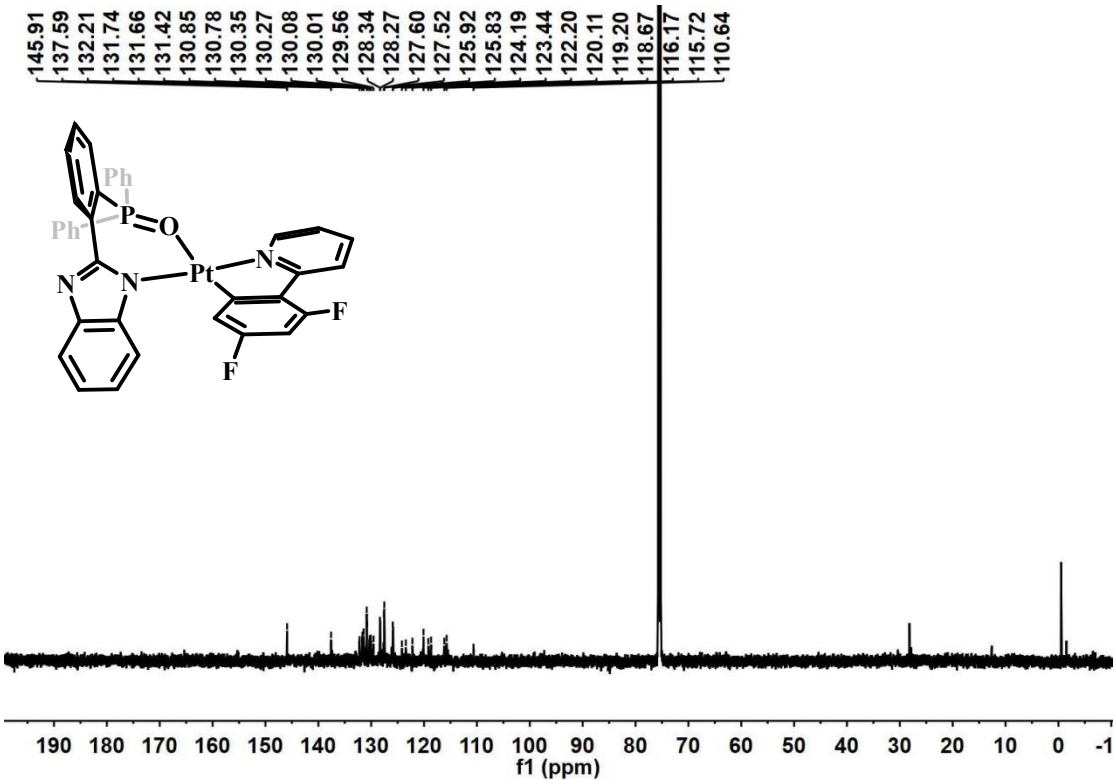
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.16 (dd, *J* = 7.4, 4.2 Hz, 3H), 8.02 (d, *J* = 8.2

Hz, 2H), 7.97 – 7.88 (m, 2H), 7.85 – 7.77 (m, 3H), 7.80 – 7.65 (m, 5H), 7.68 – 7.57 (m, 7H), 7.57 – 7.50 (m, 4H), 7.39 – 7.29 (m, 4H), 7.13-7.23 (m, 13.1, 7.2 Hz, 8H), 7.13 (s, 1H), 7.04 – 6.88 (m, 12H), 6.38 (d, *J* = 9.8 Hz, 1H), 5.53 (d, *J* = 8.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.92, 132.24, 131.67, 131.43, 130.86, 130.79, 128.36, 128.28, 127.61, 127.53, 125.93, 125.84, 118.68, 115.73.



^{1}H NMR of ***rac*-N^PO-Pt-A** in $CDCl_3$-d



^{13}C NMR of ***rac*-N^PO-Pt-A** in $CDCl_3$-d

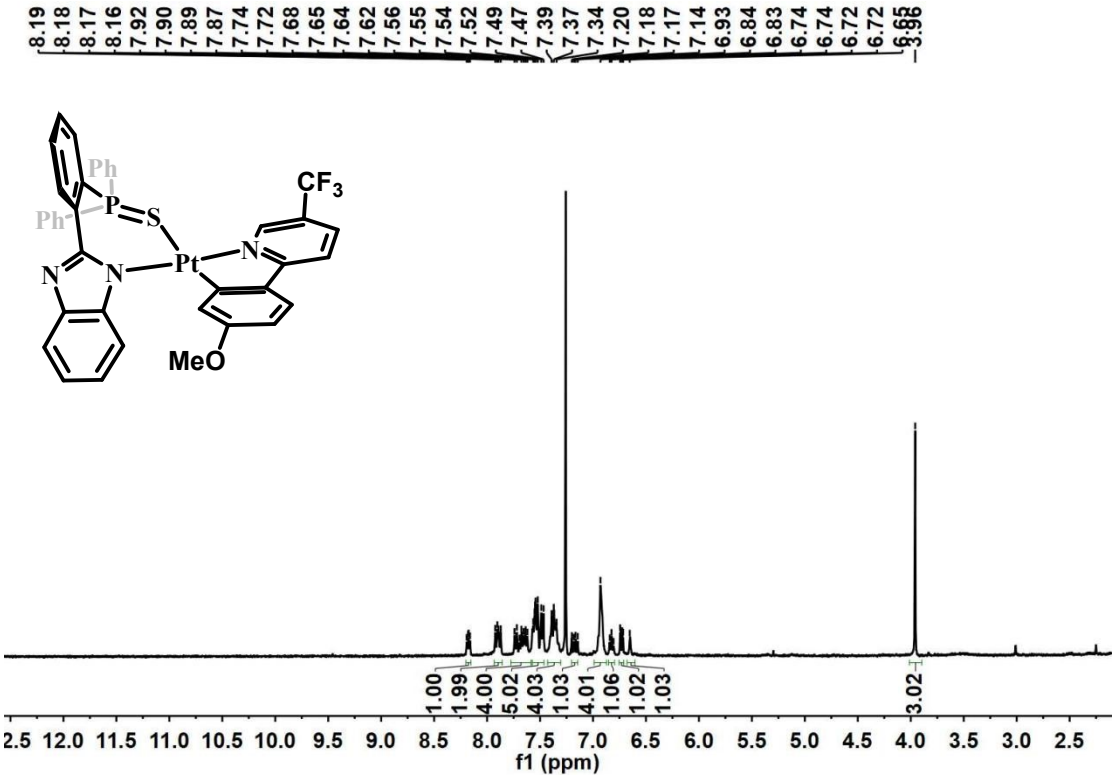
General procedure for the preparation of *rac*-N^PS-Pt-B.

Compound **A** (0.58 g, 0.8 mmol) and the corresponding reagent **N^PS** (0.8 mmol) were added to 30 mL of 2-ethoxyethanol, along with sodium carbonate (0.84 g, 8.0 mmol), in a 250-mL two-neck flask. The mixture was heated under a nitrogen atmosphere at 130°C for 24 hours. After cooling to room temperature, deionized water was added, and the residue was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified using silica gel column chromatography with DCM/CH_3OH as the eluent to obtain pure ***rac*-N^PS-Pt-B**.

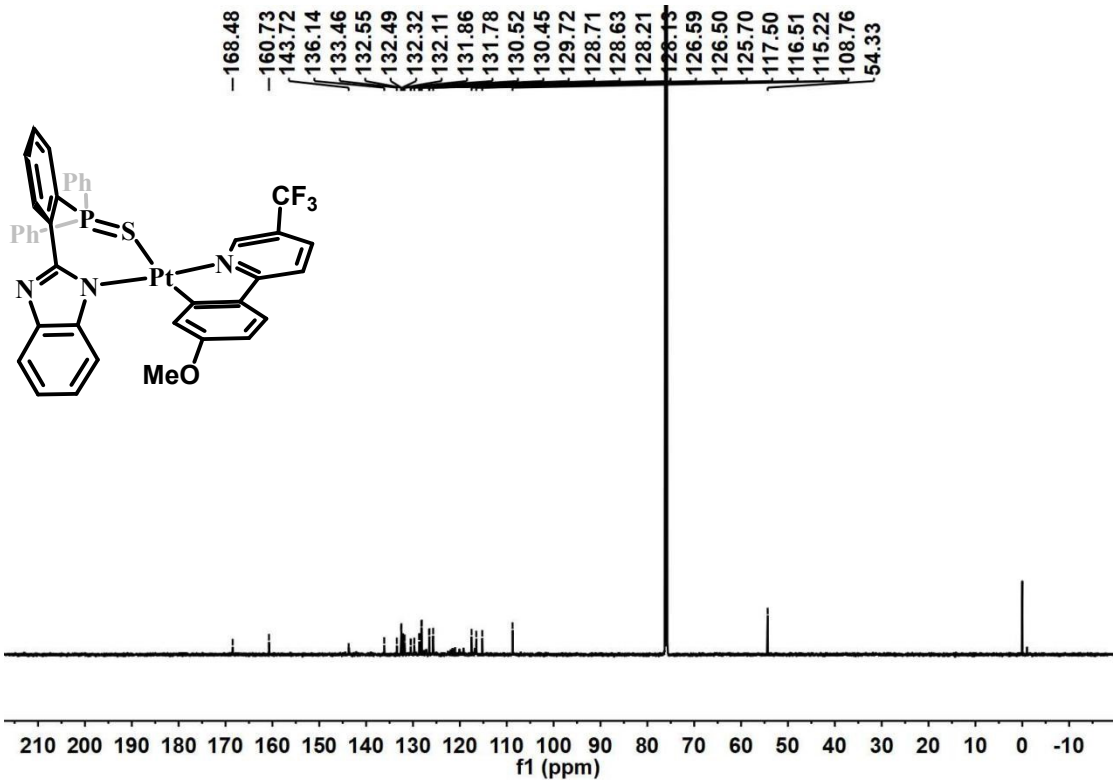
***rac*-N^PS-Pt-B:** Yield: 32% **HRMS (ESI+):** calcd for ($[M+H]^+$) 857.1212, found 857.1227

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.3, 5.1 Hz, 1H), 7.90 (dd, *J* = 12.6, 8.2 Hz, 2H), 7.77 – 7.59 (m, 4H), 7.57 – 7.46 (m, 5H), 7.43 – 7.31 (m, 4H), 7.20 – 7.15 (m, 1H), 6.93 (s, 4H), 6.85 – 6.80 (m, 1H), 6.73 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.65 (s, 1H), 3.96 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.48, 160.73, 136.14, 133.46, 132.55, 132.49, 132.32, 132.11, 131.86, 131.78, 130.52, 130.45, 129.72, 128.63, 128.21, 128.13, 126.59, 126.50, 125.70, 117.50, 116.51, 115.22, 108.76, 54.33.



^1H NMR of ***rac*-N^PS-Pt-B** in $CDCl_3$-d



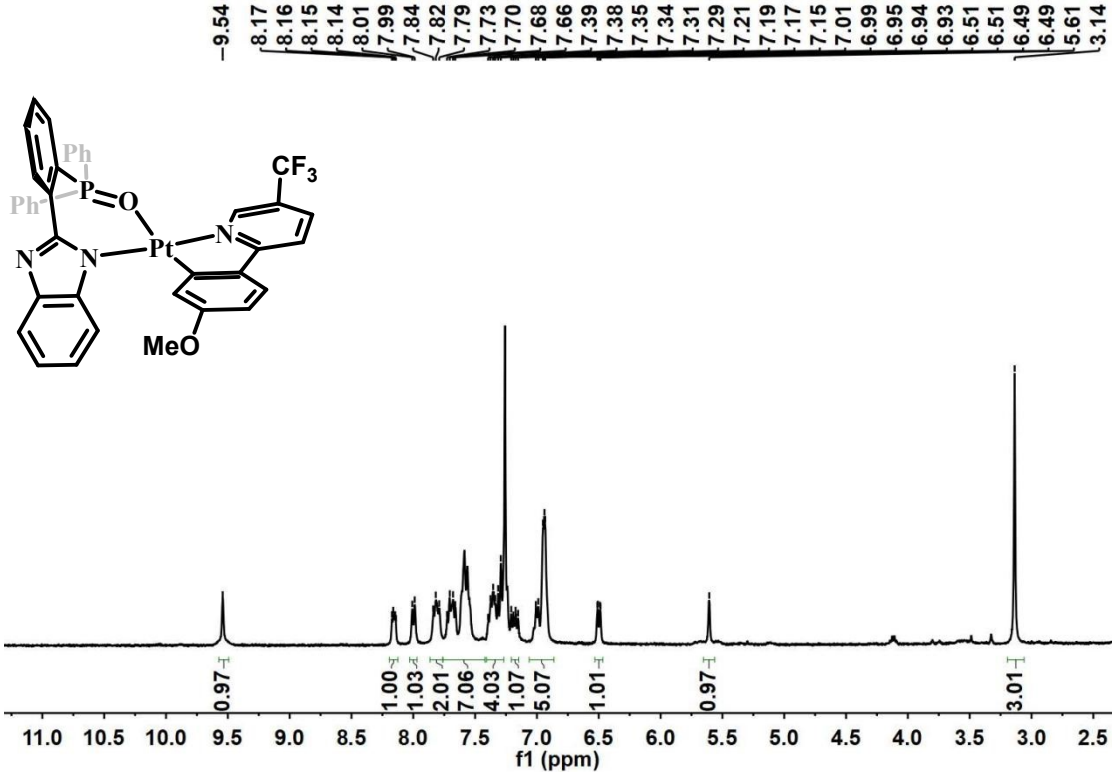
^{13}C NMR of ***rac*-N^PS-Pt-B** in $CDCl_3$-d

General procedure for the preparation of *rac*-N^PO-Pt-B.

B (0.38 g, 0.53 mmol) and the corresponding reagent **N^PO** (0.53 mmol) were added to 25 mL of 2-ethoxyethanol, along with sodium carbonate (0.56 g, 5.3 mmol), in a 250-mL two-neck flask. The mixture was heated under a nitrogen atmosphere at 130°C for 24 hours. After cooling to room temperature, deionized water was added, and the residue was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified using silica gel column chromatography with DCM/CH_3OH as the eluent to obtain pure ***rac*-N^PO-Pt-B**.

***rac*-N^PO-Pt-B:** Yield: 41% **HRMS (ESI+):** calcd for ([M+H]+) 841.1441, found 841.1476. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.19 – 8.13 (m, 1H), 8.00 (d, *J* = 8.7 Hz, 1H),

7.86 – 7.77 (m, 2H), 7.75 – 7.47 (m, 7H), 7.41 – 7.27 (m, 4H), 7.20 – 7.15 (m, 1H), 7.04 – 6.89 (m, 5H), 6.50 (d, *J* = 9.9 Hz, 1H), 5.61 (s, 1H), 3.14 (s, 3H).



^{1}H NMR of ***rac*-N^PO-Pt-B** in $CDCl_3$-d

Section S4 Experimental determination of rotational barrier

Following the procedure outlined by Curran, the Pt(II) complexes were dissolved in toluene to prepare a 2 mg/mL solution in sealed tubes. The tubes containing ***cS*-N^P-Pt-A**, ***cS*-N^PO-Pt-A**, and ***cS*-N^PS-Pt-A** were maintained in a pre-equilibrated oil bath at temperatures of 50 °C, 120 °C, and 80 °C, respectively. At 10-60 minute intervals, each sealed tube was briefly removed from the oil bath (for 1-2 minutes), and a 20 µL aliquot was drawn via syringe and injected onto the analytical HPLC column to determine the enantiomeric excess (ee). The ee values were plotted against time, and the barrier to rotation was calculated from this plot. In the y-axis of the graph, “m”

represents the percentage of the minor enantiomer, while “M” denotes the percentage of the major enantiomer.

k_B = Boltzmann’s constant [1.381×10^{-23} J·K^{-1}],

T = temperature in K,

h = Planck’s constant [6.626×10^{-34} J·s],

R = gas constant [8.3145 J·mol^{-1}].

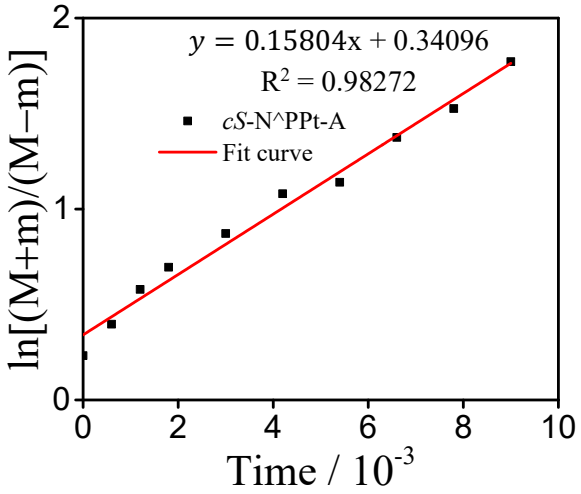
Then the simplified equation for racemization is:

$$\ln [(M + m) / (M - m)] = k_{rac}t + c = 2k_{rot}t + c$$

$$k_{rot} = (\text{slope}/2)$$

Table S1. The experimental data of ***cS*-N^P-Pt-A** is shown below: 50 °C

Time (min)	% of major enantiomer (M)	% of minor enantiomer (m)	M + m	M - m	(M+m)/ (M-m)	ln(M+m) /(M-m)
0	98.204	1.796	100	96.408	1.261	0.232
10	95.995	4.005	100	91.990	1.488	0.397
20	93.713	6.287	100	87.426	1.785	0.579
30	89.645	10.355	100	79.290	2.004	0.695
50	83.602	16.398	100	67.204	2.391	0.872
70	78.017	21.983	100	56.034	2.944	1.080
90	75.444	25.556	100	49.888	3.126	1.140
110	70.908	29.092	100	41.816	3.954	1.375
130	66.981	33.019	100	33.962	4.599	1.526
150	65.994	34.006	100	31.988	5.884	1.772



k_{rot} = (slope/2) = 7.902×10^{-5} s^{-1}

$K_{rot}‡ = [(k_{rot}\times h)/k_BT] = 1.1733\times10^{-17}$

$\Delta G_{rot}‡ = -RTln (K_{rot}‡) = 104.7439$ kJ/mol = 25.02 Kcal/mol

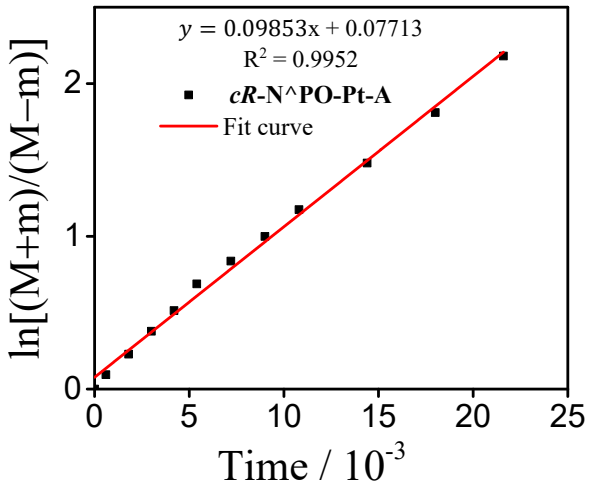
$t_{1/2}$ = 0.0041 years (25 ℃)

Racemization data and calculation of the barrier to racemization

Table S2. The experimental data of ***cS*-N^PO-Pt-A** is shown below:120 ℃

Time (min)	% of major enantiomer (M)	% of minor enantiomer (m)	M + m	M - m	(M+m)/ (M-m)	ln (M+m) /(M-m)
0	100	0	100	100	1	0
10	95.519	4.481	100	91.038	1.098442	0.093893
30	89.779	10.221	100	79.558	1.256945	0.228684
50	84.242	15.758	100	68.484	1.460195	0.378570
70	79.912	20.088	100	59.824	1.67157	0.513763
90	75.117	24.883	100	50.234	1.990684	0.688478
120	71.631	28.369	100	43.262	2.311497	0.837895
150	68.410	31.590	100	36.82	2.715915	0.999129

180	65.444	34.556	100	30.888	3.237503	1.174802
240	61.389	38.611	100	22.778	4.390201	1.479375
300	58.184	41.816	100	16.368	6.109482	1.809842
360	55.650	44.350	100	11.3	8.849558	2.180368



k_{rot} = (slope/2) = 9.853×10^{-5} s^{-1}/2 = 4.9265×10^{-5} s^{-1}

$K_{rot}‡$ = [(k_{rot}×h)/k_BT] = 6.0123×10^{-18}

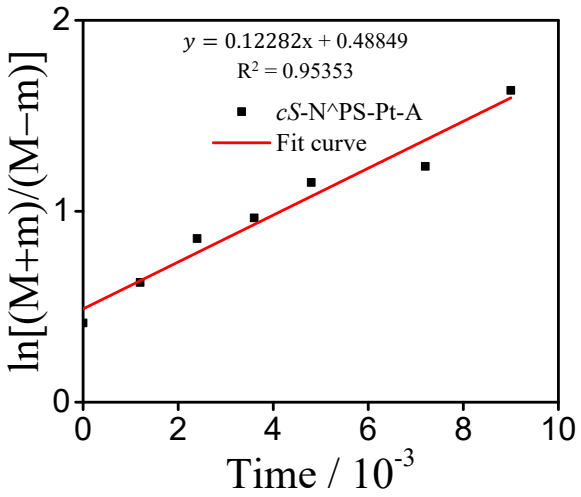
$\Delta G_{rot}‡$ = -RTln ($K_{rot}‡$) = 129.6187 kJ/mol = 30.97 Kcal/mol

$t_{1/2}$ = 94 years (25 ℃)

Table S3. The experimental data of ***cS*-N^PS-Pt-A** is shown below: 80 ℃

Time (min)	% of major enantiomer (M)	% of minor enantiomer (m)	M + m	M - m	(M+m)/ (M-m)	Ln (M+m) /(M-m)
0	83.028	16.972	100	66.056	1.514	0.415
20	76.715	23.285	100	53.430	1.872	0.627
40	71.225	28.775	100	42.450	2.356	0.857
60	69.057	30.943	100	38.114	2.624	0.965
80	65.812	34.188	100	31.624	3.162	1.151
120	64.535	35.465	100	29.070	3.440	1.235

150	59.763	40.237	100	19.526	5.121	1.633



k_{rot} = (slope/2) = 6.141×10^{-5} s^{-1}

$K_{rot}^{‡}$ = [(k_{rot}×h)/k_BT] = 8.3433×10^{-18}

$\Delta G_{rot}^{‡}$ = -RTln ($K_{rot}^{‡}$) = 115.4689 kJ/mol = 27.59 Kcal/mol

$t_{1/2}$ = 0.31 years (25 ℃)

Section S5. Photophysical properties

Table S1. Room-temperature photophysical properties of Pt(II) complexes.

Compounds	medium	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-3})	λ_{em}/nm	Φ_{PL}
***rac*-N$_1$^O-Pt-A**	CH_2Cl_2	260 (1.73×10^4), 296 (7.46×10^3), 319 (4.49×10^3),402 (3.69×10^3)	517/556	0.42%
	Powder	/	519/560	3.76%
***rac*-N$_2$^O-Pt-B**	CH_2Cl_2	258 (3.05×10^4), 290 (1.63×10^4), 351 (4.47×10^3), 426 (2.27×10^3)	535/574	0.36
	Powder	/	544/572	4.40%

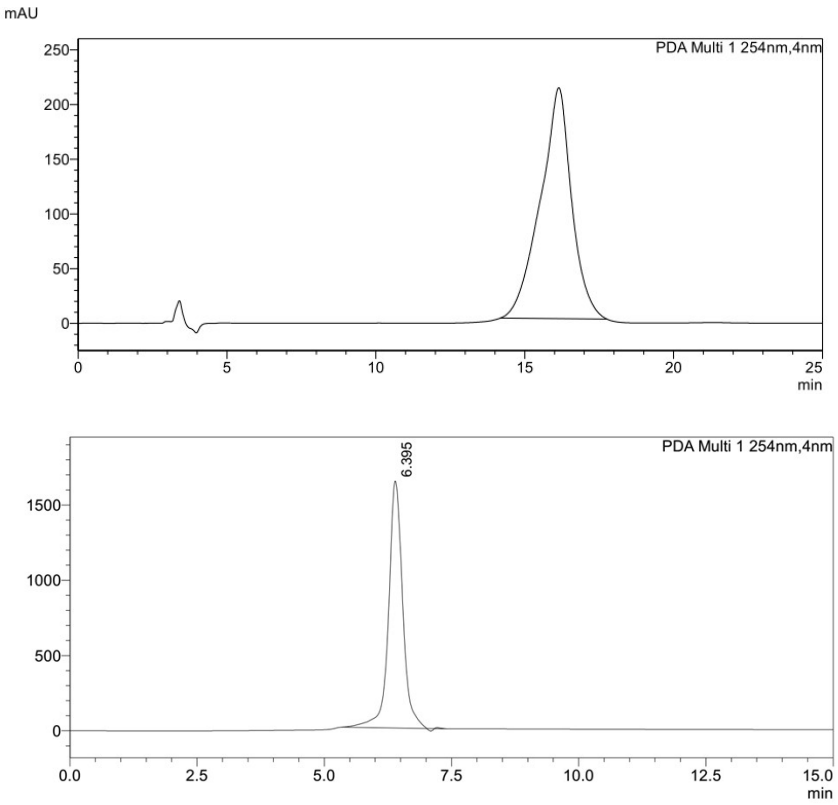


Fig. S1. HPLC traces of **N_1^O-Pt-A** (top), and **N_2^O-Pt-B** (bottom).

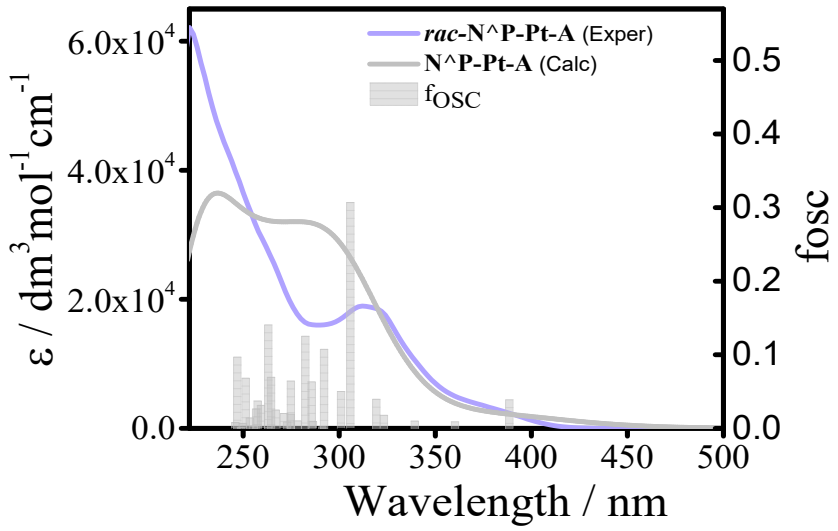


Fig. S2. The absorption spectra of ***rac*-N^P-Pt-A** in DCM solution (5.0×10^{-5} mol dm^{-3}).

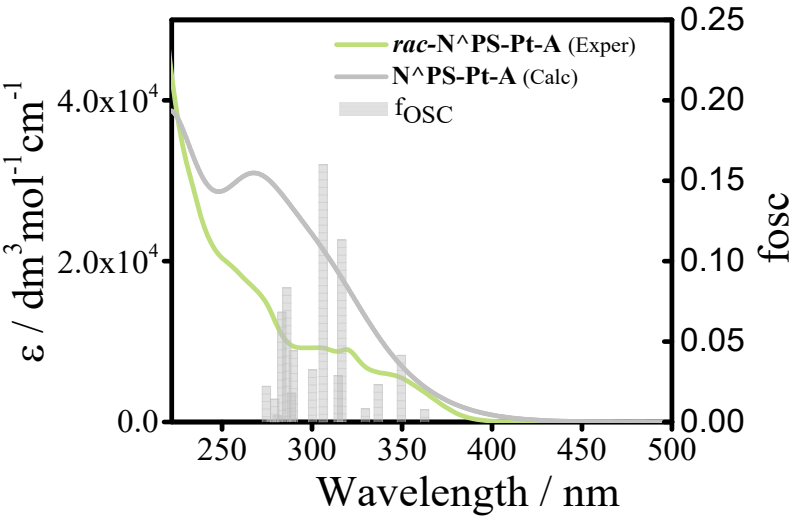


Fig. S3. The absorption spectra of ***rac*-N^PS-Pt-A** in DCM solution (5.0×10^{-5} mol dm^{-3}).

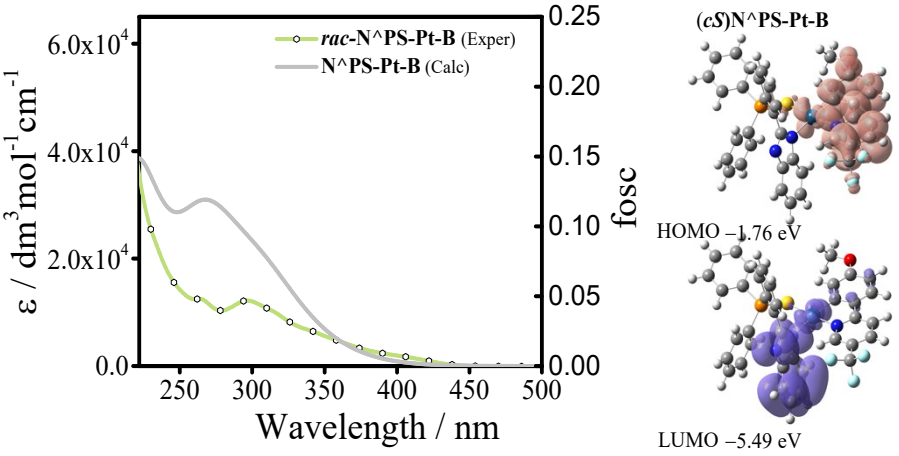


Fig. S4. The absorption spectra of ***rac*-N^PS-Pt-B** in DCM solution (5.0×10^{-5} mol dm^{-3}).

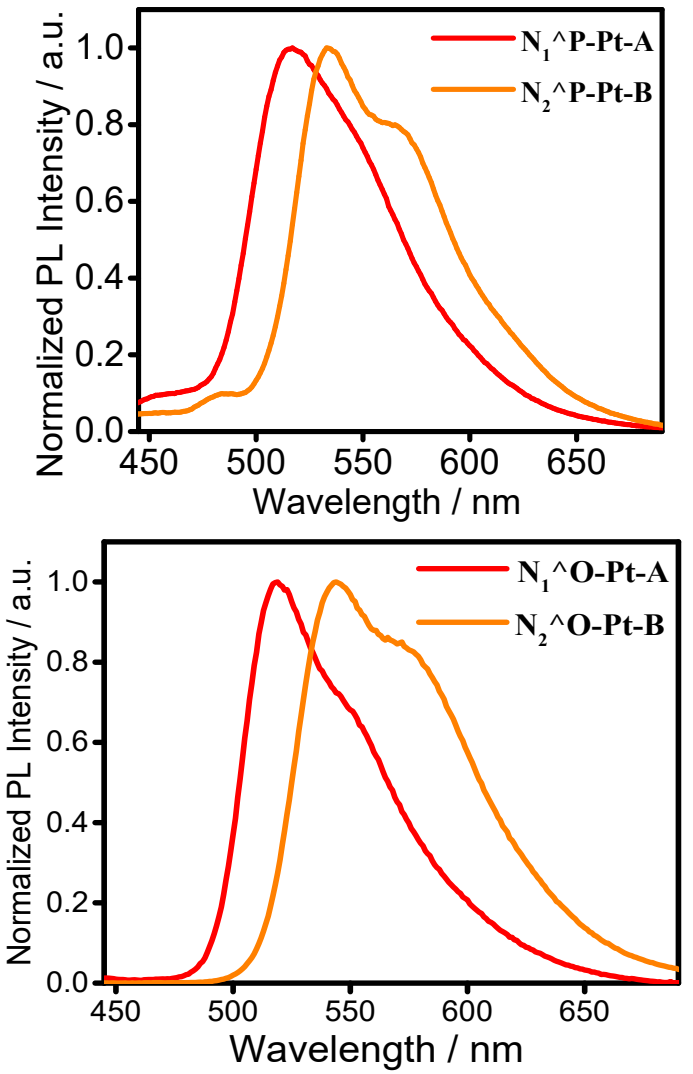


Fig. S5. PL spectra of **N_1^O-Pt-A**, and **N_2^O-Pt-B** in CH_2Cl_2 solution (top) and powder (bottom).

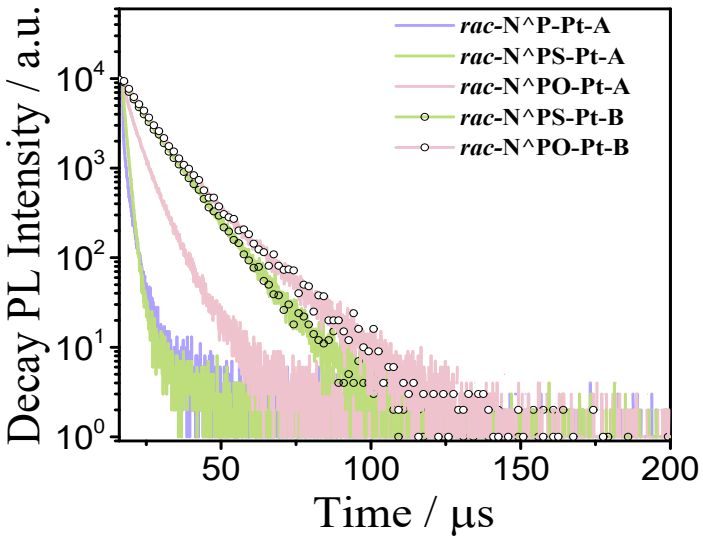


Fig. S6. The PL decay spectra of ***rac*-N^P-Pt-A**, ***rac*-N^PS-Pt-A**, ***rac*-N^PO-Pt-A**, ***rac*-**

N^PS-Pt-B, and ***rac*-N^PO-Pt-B** in powder.

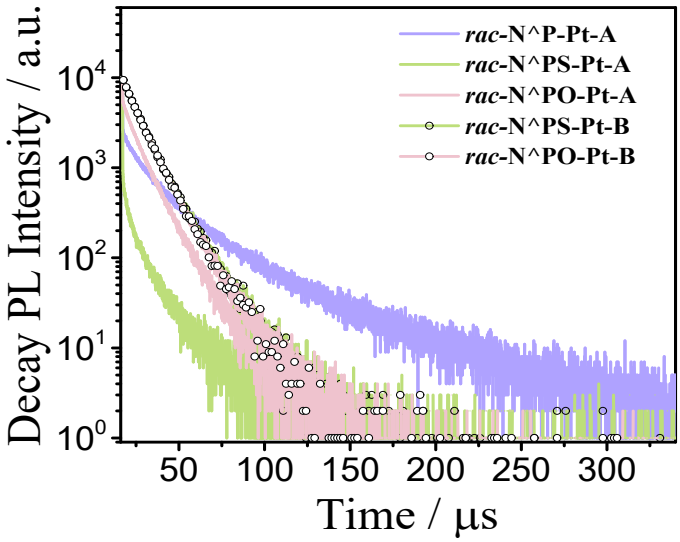


Fig. S7. The PL decay spectra of ***rac*-N^P-Pt-A**, ***rac*-N^PS-Pt-A**, ***rac*-N^PO-Pt-A**, ***rac*-N^PS-Pt-B**, and ***rac*-N^PO-Pt-B** in 5%-doped in PMMA film.

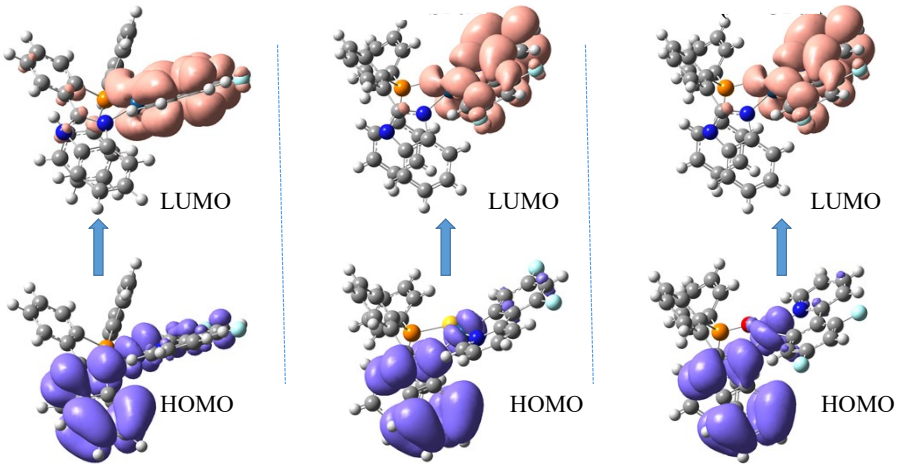


Fig. S8. Triplet frontier molecular orbitals of ***cS*-N^P-Pt-A** (left), ***cS*-N^PS-Pt-A** (middle), and ***cS*-N^PO-Pt-A** (right) in CH_2Cl_2 solution.

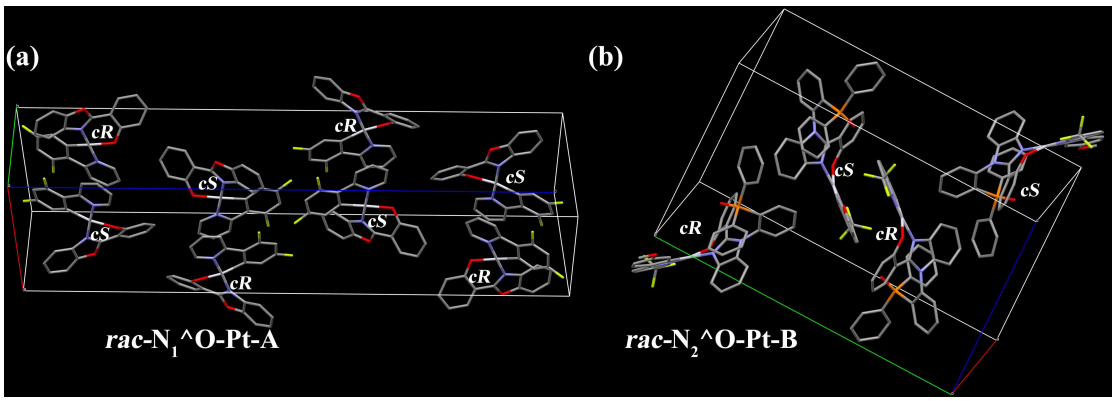


Fig. S9. X-ray single-crystal structures of ***rac*-N$_1$^O-Pt-A**, and ***rac*-N$_2$^O-Pt-B**: (a) one crystal cell of ***rac*-N$_1$^O-Pt-A**; (b) one crystal cell of ***rac*-N$_2$^O-Pt-B** (H atoms are omitted).

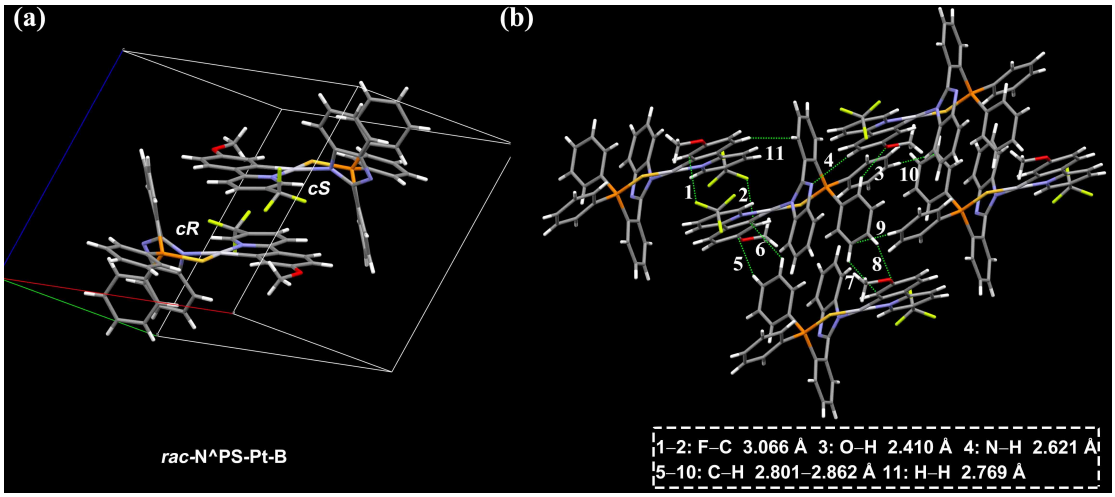


Fig. S10. X-ray single-crystal structures of ***rac*-N^PS-Pt-B**: (a) one crystal cell; (b) intermolecular non-covalent bonding interactions.

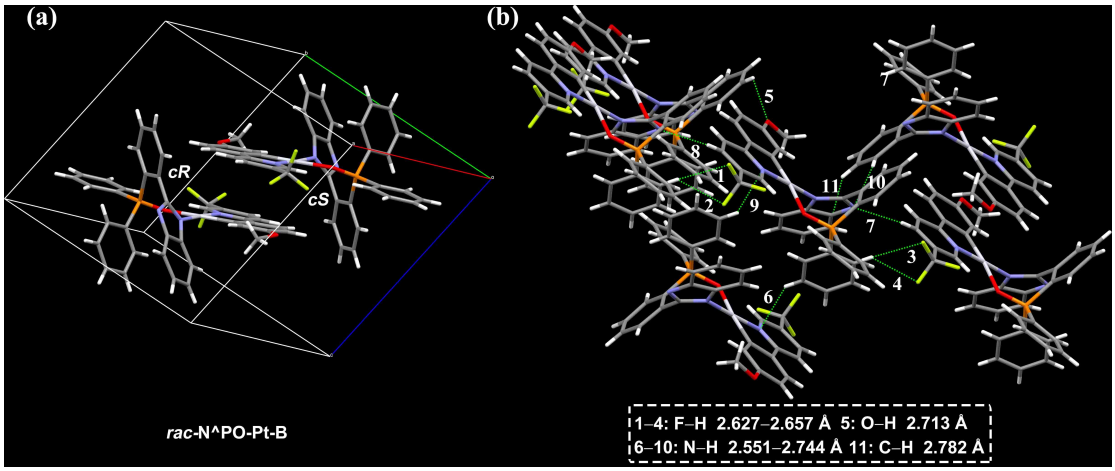


Fig. S11. X-ray single-crystal structures of ***rac*-N^PO-Pt-B**: (a) one crystal cell; (b) intermolecular non-covalent bonding interactions.

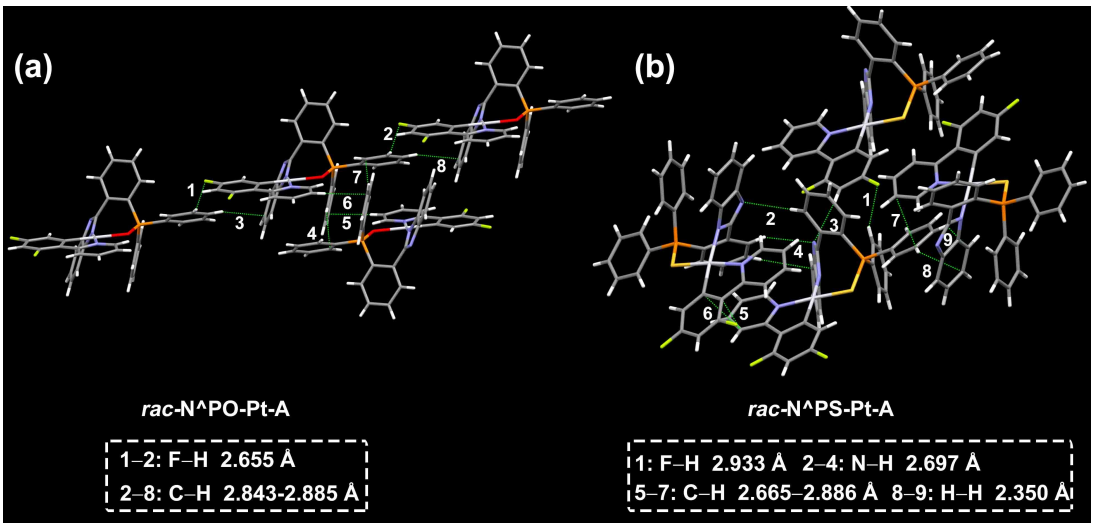


Fig. S12. intermolecular non-covalent bonding interactions of X-ray single-crystal structures of ***rac*-N^PO-Pt-A**, and ***rac*-N^PS-Pt-A**.