Synthesis of P-stereogenic cyclicphosphinic amide via electrochemical enabled cobalt-catalyzed enantioselective C–H annulation

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Supporting Information

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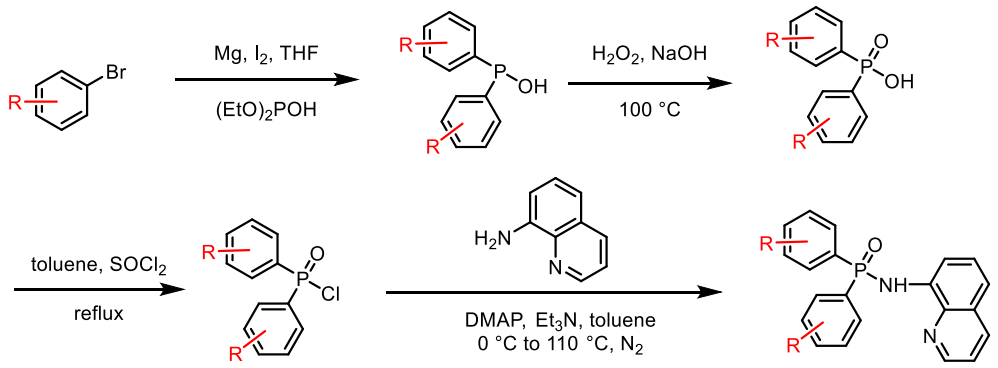
General Information

Commercial reagents were purchased from Adamas-beta, Aladdin, Bidepharm, Energy Chemical and TCI. All air-sensitive manipulations were carried out with standard Schlenk techniques under argon. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254 nm and 365 nm). Melting points were determined using a Büchi B-540 capillary melting point apparatus. Optical rotations were determined using a Rudolph AUTOPOL® V polarimeter. HPLC analyses were performed on Agilent 1100 and Waters e2695 with Daicel chiral columns. NMR spectra were recorded on Bruker Ascend TM (400 MHz for ^{1}H, 100 MHz for ^{13}C, 375 MHz for ^{19}F, 162 MHz for ^{31}P) or Oxford Varian Me (400 MHz for ^{1}H, 100 MHz for ^{13}C, 375 MHz for ^{19}F, 162 MHz for 31P). Chemical shifts were reported in δ (ppm) referenced to the residual solvent peak of $CDCl_3$ (δ 7.26), DMSO-d_6 (δ 2.50) for ^{1}H NMR and $CDCl_3$ (δ 77.1), DMSO-d_6 (δ 39.5) for ^{13}C NMR. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets), dd (double of doublet). Coupling constants were reported in Hertz (Hz). HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer. Cyclic voltammetry experiments were carried out in an equipment of CHI600E. CV curves were recorded using a three-electrode scheme. The working electrode was a glassy carbon electrode, a platinum electrode served as counter electrode. Ag/AgCl (KCl sat'd) was used as the reference electrode. The working electrode was polished before recording each CV curve.

General Procedure for the Synthesis of Substrates and Ligands

Synthesis of Substituted Aryl Phosphinamides 1a-1k

1a-1k were synthesized according to previously published works.[1] The procedure was showed as following:

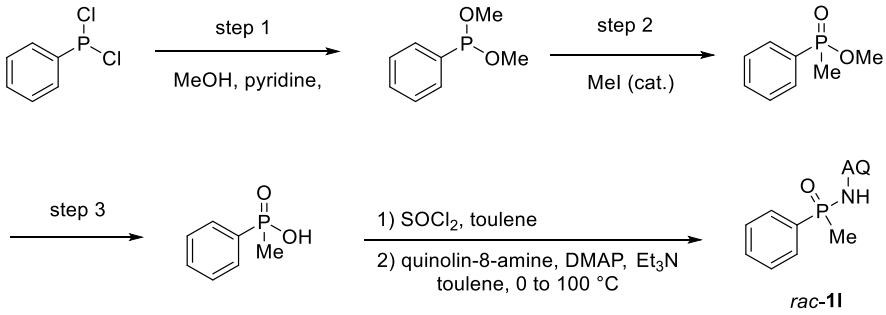


Step 1: I_2 (0.05 g, 0.2 mmol) was added to a stirred extra dry THF (20 mL) solution containing magnesium turnings (0.50 g, 20 mmol) under nitrogen protection. Then, a fraction of aryl bromide (10.0 mmol) in THF (extra dry, 5 mL) was added slowly to the mixture and heated to initiate the reaction. When the color of I_2 faded, the remainder of aryl bromide (10 mmol) was added dropwise over the course of 20 min at room temperature. After 4 h, diethyl phosphate (0.8 ml, 6 mmol) in THF (2 mL) was added slowly into the reaction mixture at 0 °C, then stirred at 80 °C for 4 h. After the reaction was completed, the reaction mixture was cooled to 0°C, acidifying the reaction mixture to pH = 1 by diluted HCl (4 N). The solution was evaporated under reduced pressure and the residue was extracted with 20 mL EtOAc three times. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give crude product.

Step 2: Hydrogen peroxide (30%, 5.0 mL) was added dropwise to a suspension of crude product in aqueous NaOH (5 N, 4 mL) at 0 ℃, and the mixture was stirred for 3 h at 100 ℃. After the solution was cooled to room temperature, 20 mL water was added to the mixture and extracted with 20 mL EtOAc. The aqueous phase was separated and hydrochloric acid (4 N) was added dropwise to aqueous phase at 0 ℃ until no white solid was precipitated out. The white solid was filtered out and dry in the oven as crude phosphonic.

Step 3: A suspension of phosphonic acid and thionyl chloride in toluene (10 mL) was stirred at 80 °C for 3 h. After removal of thionyl chloride and toluene under reduced pressure, the residue was re-dissolved in toluene (5 mL), which was added to a mixture of 8-aminoquinoline (5 mmol), *N,N*-dimethyl-4-aminopyridine (0.2 mmol), and triethylamine (6 mmol) in toluene (5 mL) at 0 ℃ under N_2. Then, the solution was stirred at 110 ℃ for 24 h. After removal of the volatiles under reduced pressure, the residue was dissolved in DCM (20 mL) and washed with saturated ammonium chloride (25 mL × 2). Combined organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the desired product.

Synthesis of Rac-1l[2]



rac-**1l**

Step 1: Under an atmosphere of nitrogen dichlorophenylphosphine (5.9 g, 33 mmol, 1.0 eq.) was added to a solution of anhydrous pyridine (5.5 g, 69.5 mmol, 2.1 eq.) in hexane (30 mL). The white suspension was cooled in an ice bath. A solution of anhydrous methanol (2.1 g, 66.0 mmol, 2.0 equiv.) in hexane (10 mL) was added drop-wise over 2 h, the ice bath was maintained at 0 ˚C throughout. After complete addition the white suspension was removed from the ice bath and allowed to warm to room temperature. Stirring was continued for a further hour. The suspension was then filtered through a sintered glass funnel under a stream of nitrogen to remove the pyridine hydrochloride salt precipitate. The filtrate was concentrated on the rotary evaporator to yield the title compound as a grainy yellow liquid that was not further purified (4.0 g, 70%)。

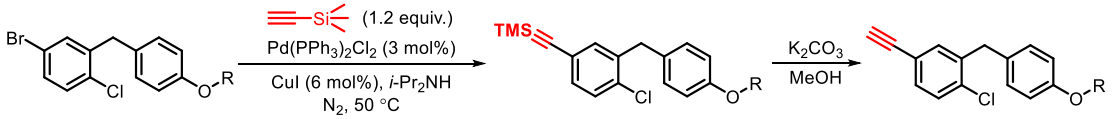
Step 2:A small amount of the crude phosphonite (2.0 g) was charged into a 15 mL pressure tube and mixed with a few drops of methyl iodide. The reaction mixture was carefully warmed under a nitrogen blanket until a vigorous exothermic reaction began (caution: danger of dramatic pressure increase). The resulting orange solution was then stirred 3h at 70 ℃. Purification by column chromatography on silica gel afforded the corresponding product (±)-methyl methylphenylphosphinate as a clear yellow oil (1.6 g, 80%).

Step 3: (±)-Methyl methylphenylphosphinate was charged into a 25 mL 2-necked round bottom flask. A solution of NaOH (4 N) in MeOH was added under ice bath then stirred 2h and maintained at 0 ˚C. Methanol removed in vacuo, hydrochloric acid (conc.) was added dropwise until no white solid was precipitated out. Filter the white solid obtained corresponding product

methylphenylphosphinic acid (1.4 g, 90%).

Rac-1l was synthesized from methylphenylphosphinic acid according to the step 3 of **1a-1k**.

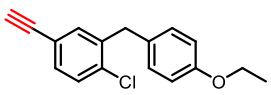
Synthesis of Terminal Alkynes containing Drug Fragments (2aq, 2ar)



Step 1: Charging 2 mmol of bromobenzene, 0.06 mmol of $Pd(PPh_3)_2Cl_2$ (42 mg, 0.03 eq.), 0.12 mmol of CuI (23 mg, 0.06 eq.), 2.4 mmol of trimethylsilylacetylene (236 mg, 1.2 eq.) and 10 mL of diisopropyamine as solvent into a 100 mL flask with three necks equipped with a stir bar under argon atmosphere. Placing the reaction mixture into a pre heated to 50 °C oil bath for 12 h and then monitoring the reaction by (TLC). Evaporating solvent under decompression at the end of the reaction. Diluting the reaction mixture with 30 mL of EtOAc. Filtering the reaction mixture through thin pad of Celite and then washing the filtrate with water (3×5 mL) and concentrate to obtain crude products.

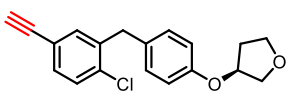
Step 2: Adding 4.0 mmol (552 mg, 2.0 eq.) of anhydrous K_2CO_3 to a solution of 2.0 mmol of 1-aryl-2-trimethylsilylacetylene in 5 mL of dry MeOH. Stir the reaction mixture for 12 h at room temperature. Removing the solvent under reduced pressure. Purifying the residue by column chromatography on silica gel (eluent HE to HE/EtOAc = 60:1 v/v) to afford **2aq, 2ar**.

1-Chloro-2-(4-ethoxybenzyl)-4-ethynylbenzene (2aq)



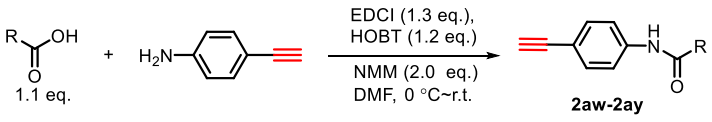
The title compound was purified by column chromatography on silica gel (eluent HE) as yellow oil liquid (181.6 mg, 67% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.32 (m, 1H), 7.30 – 7.28 (m, 2H), 7.11 (dt, *J* = 8.4, 2.4 Hz, 2H), 6.86 (dt, *J* = 8.4, 2.4 Hz, 2H), 4.05 – 4.00 (m, 4H), 3.08 (s, 1H), 1.42 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.6, 139.6, 135.0, 134.4, 131.2, 130.7, 130.0, 129.6, 120.9, 114.6, 82.8, 78.0, 63.4, 38.2, 14.9. **HRMS (ESI)** calculated for $C_{17}H_{16}ClO$ $[M + H]^+$: 271.0884, found: 271.0876.

(*S*)-3-(4-(2-Chloro-5-ethynylbenzyl)phenoxy)tetrahydrofuran (2ar)



The title compound was purified by column chromatography on silica gel (eluent HE) as yellow oil liquid (237.2 mg, 76% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.33 (m, 1H), 7.31 – 7.28 (m, 2H), 7.12 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.82 (d, *J* = 8.8, 2.4 Hz, 2H), 4.93 – 4.90 (m, 1H), 4.04 – 4.01 (m, 3H), 4.00 – 3.97 (m, 2H), 3.94 – 3.89 (m, 1H), 3.10 (s, 1H), 2.23 – 2.16 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.1, 139.4, 134.9, 134.4, 131.2, 130.1, 129.6, 120.9, 115.5, 115.5, 82.7, 78.0, 77.3, 73.2, 67.2, 38.1, 33.0. **HRMS (ESI)** calculated for $C_{19}H_{18}ClO_2$ $[M + H]^+$: 313.0990, found: 313.0986.

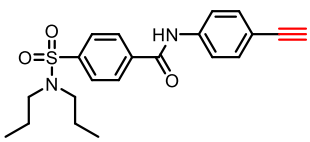
Synthesis of Terminal Alkyne Derived from Drugs containing Carboxylic Acid (2au, 2aw-2ay)



To a solution of carboxylic acid (2.2 mmol, 1.1 eq.), 4-ethynylaniline (2.0 mmol, 234 mg, 1.0

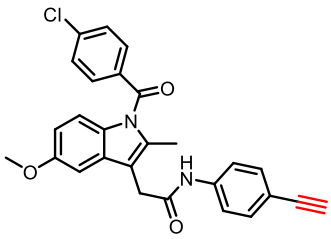
eq.), 1-hydroxybenzotriazole (HOBT, 2.4 mmol, 324 mg, 1.2 eq.) and 4-methylmorpholine (NMM, 4.0 mmol, 404 mg, 2.0 eq.), 5 mL DMF were added. The reaction mixture was stirred at 0 ºC for 5 minutes under N_2 atmosphere before EDCI (2.6 mmol, 498 mg, 1.3 eq.) was added. Then, the reaction mixture was stirred at 0 ºC for 30 minutes until the system turned into orange clarification state. The reaction mixture was stirred at room temperature for 6 h. The reaction progress was monitored by TLC. After the starting material carboxylic acid was consumed, the reaction mixture was quenched with saturated $NaHCO_3$ solution (30 mL) and extracted with EtOAc for 2–3 times. The combined organic phases were washed with dilute HCl (2 N, 10 mL × 3) and brine (10 mL × 3), respectively. And then, the organic phase was dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography (HE/EtOAc = 10:1 to 2:1 v/v) to afford **2au, 2aw-2ay**.

4-(*N*,*N*-dipropylsulfamoyl)-*N*-(4-ethynylphenyl)benzamide (2au)



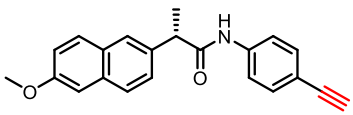
The title compound was purified by column chromatography on silica gel (HE/EtOAc = 2:1 v/v) as a light-yellow solid (637.7 mg, 83% yield). M.p.: 120 - 121 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.98 (s, 1H), 7.89 – 7.85 (m, 2H), 7.72 – 7.68 (m, 2H), 7.62 (q, *J* = 7.6 Hz, 2H), 7.48 – 7.41 (m, 2H), 3.07 – 3.00 (m, 5H), 1.54 – 1.46 (m, 4H), 0.87 – 0.80 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.0, 142.5, 138.7, 138.5, 132.9, 128.2, 127.1, 120.0, 118.2, 83.4, 77.1, 50.0, 21.9, 11.1. **HRMS (ESI)** calculated for $C_{21}H_{25}N_2O_3S$ $[M+H]^+$: 385.1580, found: 385.1567.

1-(4-Chlorobenzoyl)-*N*-(4-ethynylphenyl)-5-methoxy-2-methyl-1*H*-indole-3-carboxamide (2aw)



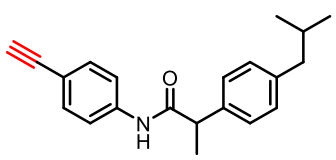
The title compound was purified by column chromatography on silica gel (HE/EtOAc = 3:1 v/v) as a light-yellow solid (709.1 mg, 81% yield). M.p.: 181 - 182 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (dt, *J* = 8.8 Hz, 2.4 Hz, 2H), 7.48 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.41 – 7.35 (m, 5H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.87 (d, *J* = 9.2Hz, 1H), 6.71 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.80 (d, *J* = 2.0 Hz, 5H), 3.03 (s, 1H), 2.44 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.4, 168.3, 156.5, 139.8, 137.9, 136.8, 133.5, 132.9, 131.3, 131.0, 130.1, 129.3, 119.6, 118.1, 115.3, 112.5, 112.1, 100.8, 83.2, 77.0, 55.8, 33.4, 13.3. **HRMS (ESI)** calculated for $C_{27}H_{22}ClN_2O_3$ $[M+H]^+$: 457.1313, found: 457.1309.

(S)-*N*-(4-Ethynylphenyl)-2-(6-methoxynaphthalen-2-yl)propenamide (2ax)



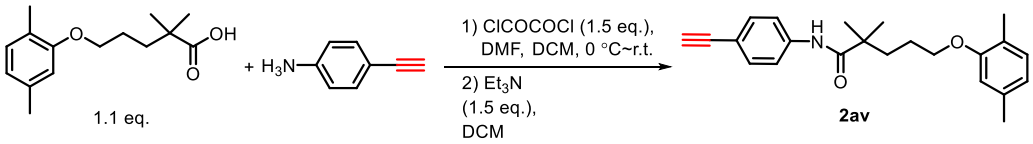
The title compound was purified by column chromatography on silica gel (HE/EtOAc = 4:1 v/v) as a light-yellow solid (493.7 mg, 83% yield). M.p.: 169 - 170 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (dd, *J* = 15.2, 8.4 Hz, 3H), 7.42 – 7.35 (m, 6H), 7.18 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.13 (d, *J* = 2.8 Hz, 1H), 3.92 (s, 3H), 3.83 (q, *J* = 7.2 Hz, 1H), 3.02 (s, 1H), 1.65 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.6, 158.0, 138.4, 135.7, 134.0, 132.8, 129.3, 129.1, 127.9, 126.4, 126.0, 119.4, 119.3, 117.6, 105.8, 83.4, 76.8, 55.4, 48.1, 18.5. **HRMS (ESI)** calculated for $[C_{22}H_{20}NO_2]^+$: 330.1489, found: 330.1478.

***N*-(4-ethynylphenyl)-2-(4-*iso*butylphenyl)propenamide (2ay)**



The title compound was purified by column chromatography on silica gel (He/EtOAc = 5:1 v/v) as yellow liquid (470.0 mg, 77% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.39 (m, 5H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 3.72 (q, *J* = 7.2 Hz, 1H), 3.05 (s, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.94 – 1.84 (m, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 141.2, 138.4, 137.8, 132.8, 129.9, 127.4, 119.3, 117.6, 83.4, 76.8, 47.7, 45.0, 30.2, 22.4, 18.5. **HRMS (ESI)** calculated for $C_{21}H_{24}NO$ $[M + H]^+$: 306.1852, found: 306.1847.

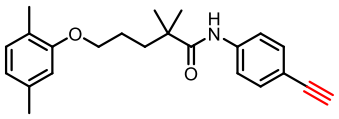
Synthesis of Terminal Alkyne 2av



Step 1: Adding oxalyl chloride (0.254 mL, 3.0 mmol, 1.5 eq.) and a portion of DMF to a solution of gemfibrozil (550 mg, 2.2 mmol, 1.1 eq.) in DCM (5 mL) was stirred at 0 ºC for 1 h. Next, the stirring system was continued to react at room temperature for 3 h. After the starting material carboxylic acid was consumed, the leftover oxalyl chloride and solvent were removed in vacuo.

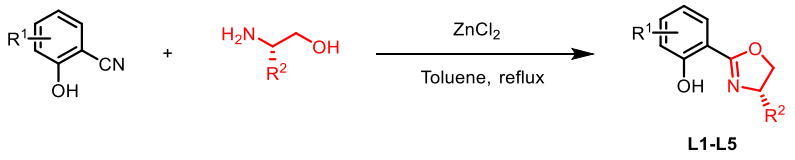
Step 2: A solution of acyl chloride in DCM (5 mL) was injected into a solution of 4-ethynylaniline (2.0 mmol, 234 mg, 1.0 eq.) in DCM (5 mL) at room temperature for 14 h. The reaction progress was monitored by TLC. After the starting material 4-ethynylaniline was consumed, the reaction mixture was quenched with saturated $NaHCO_3$ solution (10 ml) and extracted with EtOAc for 2–3 times. The combined organic phases were washed with brine (10 ml×3). Then, the organic phase was dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography (HE/EtOAc = 6:1 v/v) to afford **2av** as a light-yellow solid.

5-(2,5-dimethylphenoxy)-*N*-(4-ethynylphenyl)-2,2-dimethylpentanamide (2av)



The title compound was purified by column chromatography on silica gel (HE/EtOAc = 10:1 v/v) as a light-yellow solid (460.9 mg, 66% yield). m.p.: 135 - 136 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 8.6 Hz, 3H), 7.44 (d, *J* = 8.6 Hz, 3H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.62 (s, 1H), 3.95 (t, *J* = 3.0 Hz, 2H), 3.06 (s, 1H), 2.31 (s, 3H), 2.19 (s, 3H), 1.82 (t, *J* = 2.8 Hz, 4H), 1.34 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.8, 156.9, 138.4, 136.6, 132.9, 130.4, 123.5, 121.0, 119.8, 117.7, 112.3, 83.4, 76.8, 67.9, 43.0, 37.7, 25.6, 25.2, 21.4, 15.8. **HRMS (ESI)** calculated for $C_{23}H_{28}NO_2$ $[M +H]^+$: 350.2115, found: 350.2111.

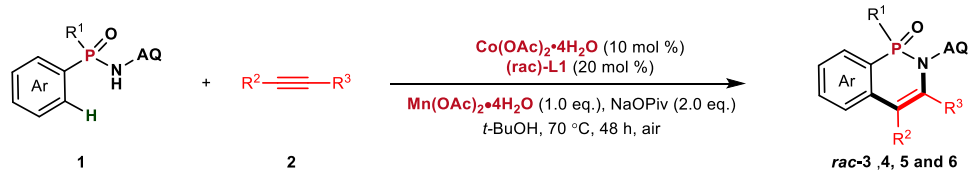
Synthesis of L1-L5[1d]



Ligands **L1-L5** were synthesized according reference 1d: $ZnCl_2$ (1.14 g, 8.5 mmol, 0.1 eq) was

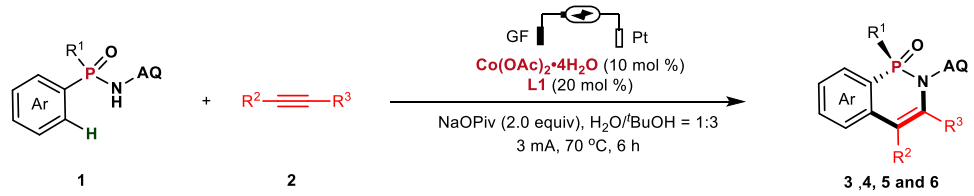
added to a 250 mL round-bottomed flask, toluene (150 mL) was added to the flask under N_2. L-amino alcohol (126 mmol, 1.5 eq) was added, followed by 2-hydroxybenzonitrile (84.0 mmol, 1.0 eq). The solution was heated at reflux (oil bath 130 ℃) under N_2 and maintained at this temperature for 10 h. The reaction progress was monitored by TLC. After the starting material 2-hydroxybenzonitrile was consumed, toluene was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (HE/EtOAc/DCM = 15:1:1 v/v/v) to afford the chiral ligand.

General Procedure for the Racemic C-H Annulation[1d]



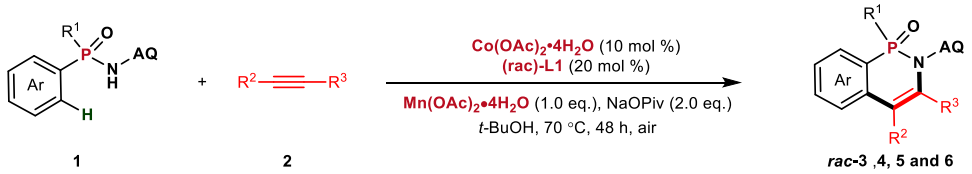
Phosphinic amide **1a** (0.1 mmol), alkyne **2a** (0.15 mmol), $Co(OAc)_2 \cdot 4H_2O$ (10 mol%), (*rac*)-**L1** (20 mol%), $Mn(OAc)_2 \cdot 4H_2O$ (0.1 mmol), NaOPiv (0.2 mmol) and *t*-BuOH (4 mL) were added to an oven dried vial equipped with stirring bars. Then, the vial was instantly placed in a heating block set at 50 ℃ under air for 48 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the desired product.

General Procedure for the Electrochemically Enantioselective C-H Annulation



The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1** (0.2 mmol, 1.0 eq.), alkyne **2** or **4** (0.30 mmol, 1.5 eq.), $Co(OAc)_2 \bullet 4H_2O$ (10 mol%), (*S*)-**L1** (20 mol%), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the desired product **3, 4, 5 and 6**.

The racemic product was synthesized according to the following procedure:[1d]

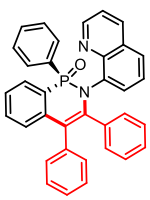


Phosphinic amide **1a** (0.1 mmol), alkyne **2a** (0.15 mmol), $Co(OAc)_2 \cdot 4H_2O$ (10 mol%), (*rac*)-**L1** (20 mol%), $Mn(OAc)_2 \cdot 4H_2O$ (0.1 mmol), NaOPiv (0.2 mmol) and *t*-BuOH (4 mL) were added to an oven dried vial equipped with stirring bars. Then, the vial was instantly placed in a heating block set at 70 ℃ under air for 48 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the racemic product.

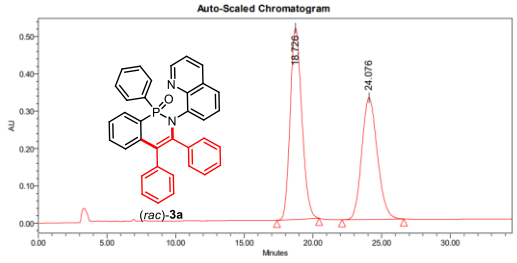
Synthetic Procedure and Characterization of 3a

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2a** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product **3a** (93.6 mg) in 90% yield as a light-yellow foam with >99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1,3,4-Triphenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine1-oxide (3a)

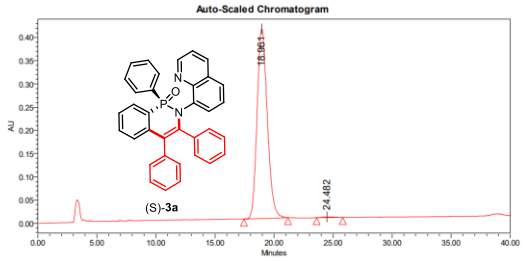


M.p.: 135 -136 °C, $[\alpha]_D^{20}$ = +305.4 (c = 1.0, $CHCl_3$), >99% ee, lit[1d]: $[\alpha]_D^{20}$ = +269.2 [c = 1.0, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 18.961 min, t (minor) = 24.482 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.82 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.48 (dd, *J* = 14.0, 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.14 (m, 9H), 7.12 – 7.01 (m, 2H), 6.99 – 6.95 (m, 4H), 6.56 – 6.53 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.3, 144.5 (d, J_{CP} = 3.5 Hz), 142.6, 139.3 (d, J_{CP} = 3.6 Hz), 138.8 (d, J_{CP} = 0.9 Hz), 137.7 (d, J_{CP} = 2.4 Hz), 136.7 (d, J_{CP} = 3.9 Hz), 135.5, 133.5 (d, J_{CP} = 10.4 Hz), 132.5, 131.7 (d, J_{CP} = 2.9 Hz), 131.5 (d, J_{CP} = 3.4 Hz), 131.4 (d, J_{CP} = 2.9 Hz), 131.0, 131.0, 130.7 (d, J_{CP} = 98.9 Hz), 128.2, 127.7, 127.4, 127.1, 127.0, 126.4, 126.3, 125.8, 125.7 (d, J_{CP} = 14.5 Hz), 125.4, 123.9 (d, J_{CP} = 128.1 Hz), 121.0, 117.9 (d, J_{CP} = 7.4 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.23; **HRMS (ESI)** calculated for $C_{35}H_{26}N_2OP$ $[M+H]^+$: 521.1777, found: 521.1776.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	18.726	30165289	53.96	511946
2	W2489 ChB 210nm	24.076	25742423	46.04	325475



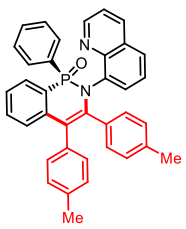
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	18.961	24508000	99.61	407943
2	W2489 ChB 210nm	24.482	97034	0.39	1400

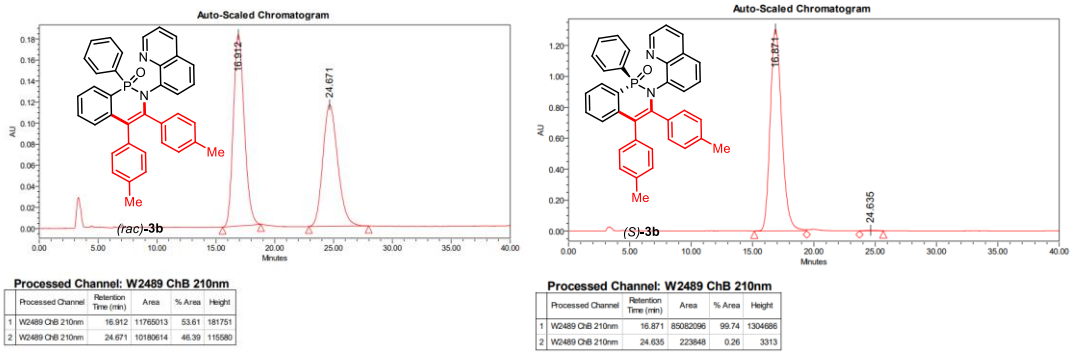
Synthetic Procedure and Characterization of 3b

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2b** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product **3b** (94.3 mg) in 86% yield as a light-yellow foam with >99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1-Phenyl-2-(quinolin-8-yl)-3,4-di-*p*-tolyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3b)



M.p.: 134 -135 °C, $[\alpha]_D^{20}$ = +285.8 (c = 1.0, $CHCl_3$), >99% ee, lit[1d]: $[\alpha]_D^{20}$ = +243.9 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 16.912 min, t (minor) = 24.671 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.80 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.81 – 7.66 (m, 3H), 7.49 – 7.43 (m, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.04 (m, 8H), 7.02 – 6.92 (m, 4H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 8.0 Hz, 2H), 2.23 (s, 3H), 1.81 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.3, 144.4 (d, J_{CP} = 3.6 Hz), 142.6, 139.3 (d, J_{CP} = 3.6 Hz), 138.7 (d, J_{CP} = 1.4 Hz), 137.6 (d, J_{CP} = 2.3 Hz), 136.6 (d, J_{CP} = 3.9 Hz), 135.5, 133.4 (d, J_{CP} = 10.5 Hz), 132.4, 131.6 (d, J_{CP} = 2.9 Hz), 131.4 (d, J_{CP} = 2.9 Hz), 131.4 (d, J_{CP} = 1.6 Hz), 131.0, 131.0, 130.2 (d, J_{CP} = 124.8 Hz), 128.2, 127.7, 127.4, 127.0 (d, J_{CP} = 13.6 Hz), 126.5, 126.4, 126.3, 125.8, 125.7 (d, J_{CP} = 14.6 Hz), 125.4, 123.7 (d, J_{CP} = 129.3 Hz), 121.0, 117.7 (d, J_{CP} = 7.3 Hz), 21.2, 20.9; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.37; **HRMS (ESI)** calculated for $C_{37}H_{30}N_2OP$ $[M + H]^+$: 549.2090, found: 549.2091.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	16.912	11765013	53.61	181751
2	W2489 ChB 210nm	24.671	10180614	46.39	115580

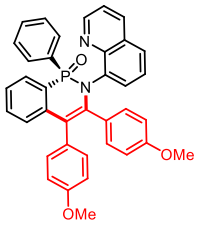
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	16.871	85082096	99.74	1304686
2	W2489 ChB 210nm	24.635	223848	0.26	3313

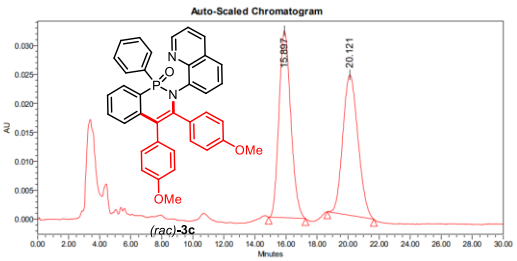
Synthetic Procedure and Characterization of 3c

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2c** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3c** (91.7 mg) in 79% yield as a light-yellow foam with >99% ee. Product exists as a 14:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Bis(4-methoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphos-phinine 1-oxide (3c)

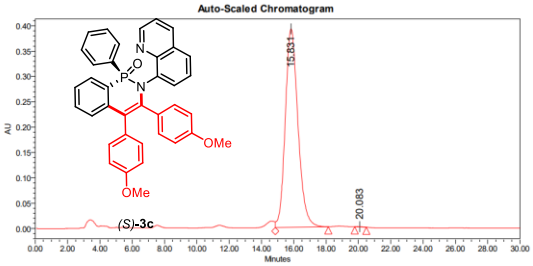


M.p.: 135 -136 °C, $[\alpha]_D^{20}$ = +287.0 (c = 1.0, $CHCl_3$), >99% ee, lit[1d]: $[\alpha]_D^{20}$ = +229.9 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (major) = 15.897 min, t (minor) = 24.121 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.80 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.69 (m, 3H), 7.52 – 7.36 (m, 2H), 7.25 (s, 1H), 7.22 – 7.13 (m, 6H), 7.11 – 7.04 (m, 1H), 6.99 – 6.93 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.09 (d, *J* = 8.4 Hz,2H), 3.70 (s, 3H), 3.37 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.9, 157.6, 149.2, 144.5 (d, *J* = 3.5 Hz), 142.6, 139.8 (d, *J* = 4.5 Hz), 137.9 (d, *J* = 2.4 Hz), 135.5, 133.4, 133.3, 133.2 (d, *J* = 127.2 Hz), 132.2, 131.4 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 2.2 Hz), 131.2 (d, *J* = 1.3 Hz), 130.8 (d, *J* = 12.6 Hz), 129.5 (d, *J* = 4.0 Hz), 128.2, 127.3, 127.0, 126.9, 126.4 (d, *J* = 9.0 Hz), 125.4, 123.8 (d, *J* = 128.9 Hz), 121.0, 117.5 (d, *J* = 7.2 Hz), 113.3, 111.4, 55.1, 54.6; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.54; **HRMS (ESI)** calculated for $C_{37}H_{30}N_2O_3P$ $[M + H]^+$: 581.1989, found: 581.1988.



Processed Channel: W2489 ChB 220nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	15.897	1705643	50.92	32240
2	W2489 ChB 220nm	20.121	1643940	49.08	24233



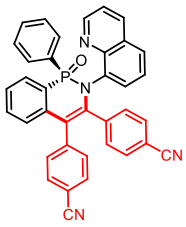
Processed Channel: W2489 ChB 220nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	15.831	21365486	99.95	391604
2	W2489 ChB 220nm	20.083	11406	0.05	421

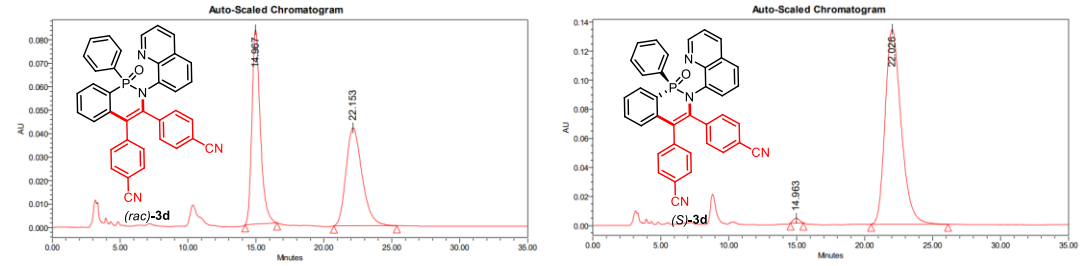
Synthetic Procedure and Characterization of 3d

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2d** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3d** (98.06 mg) in 86% yield as a light-yellow foam with 98% ee. Product exists as a 22:1 mixture of atropisomers due to the hindered rotation about the N-quinoline bond and the structure of major isomer was shown.

(*S*)-4,4'-(1-oxido-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine-3,4-diyl)dibenzonitrile (3d)



M.p.: 130 - 132 ℃, $[\alpha]_D^{20}$ = +369.2 (c = 1.0, $CHCl_3$), 98% ee, lit[1d]: $[\alpha]_D^{20}$ = +343.9 [c = 0.5, $CHCl_3$, 98% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (minor) =14.967 min, t (major) = 22.153 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.82 (d, *J* = 4.4 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.70 (dd, *J* = 12.8, 7.2 Hz, 2H), 7.58 – 7.42 (m, 4H), 7.38 – 7.30 (m, 3H), 7.26 – 7.17 (m, 2H), 7.15 – 7.05 (m, 4H), 7.03 – 6.97 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.7, 143.9 (d, J_{CP} = 2.9 Hz), 143.4, 141.1, 140.8 (d, J_{CP}= 3.0 Hz), 137.6 (d, J_{CP} = 4.0 Hz), 136.7(d, J_{CP} = 2.9 Hz), 135.9, 133.5, 133.4, 133.2, 132.1, 132.0, 131.5, 131.4, 131.3, 130.1, 128.4, 128.2, 127.3 (d, J_{CP} = 13.2 Hz), 126.8 (d, J_{CP} = 14.3 Hz), 126.0 (d, J_{CP} = 8.8 Hz), 125.6, 121.5, 118.6, 118.2, 116.8 (d, J_{CP} = 6.9 Hz), 111.0, 110.8; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.45; **HRMS (ESI)** calculated for $C_{37}H_{24}N_4OP$ $[M + H]^+$: 571.1982, found: 571.1984.



Processed Channel: W2489 ChB 220nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	14.967	3537256	50.78	82761
2	W2489 ChB 220nm	22.153	3428893	49.22	41736

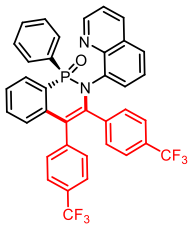
Processed Channel: W2489 ChB 220nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	14.963	102103	0.92	3249
2	W2489 ChB 220nm	22.026	10943739	99.08	134052

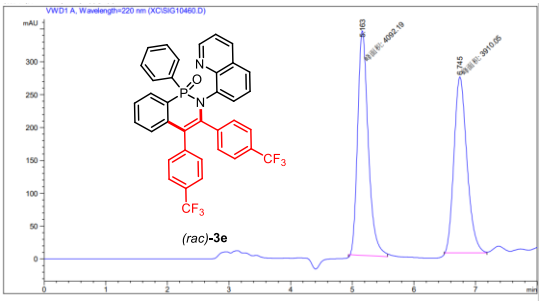
Synthetic Procedure and Characterization of 3e

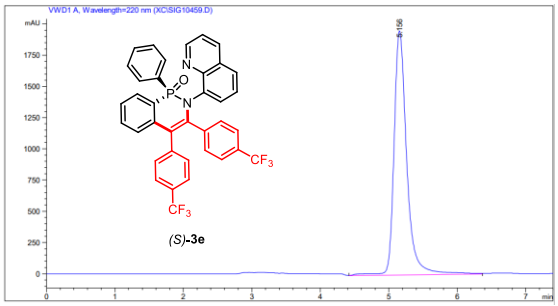
The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2e** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3e** (108.9 mg) in 83% yield as a yellow oil with >99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1-Phenyl-2-(quinolin-8-yl)-3,4-bis(4-(trifluoromethyl)phenyl)-2*H*-benzo[*c*][1,2] azaphosphinine 1-oxide (3e)



$[\alpha]_D^{20}$ = +79.9 (c = 1.0, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (major) = 5.163 min, t (minor) = 6.745 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.86 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.31 (d, *J* = 7.6 Hz, 1H), 8.03 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.91 – 7.81 (m, 2H), 7.76 (d, *J* = 7.6 Hz, 4H), 7.69 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.49 – 7.45 (m, 4H), 7.30 (dd, *J* = 8.0, 4.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 3H), 7.13 – 7.03 (m, 3H), 6.17 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.1, 145.2 (d, *J* = 3.7 Hz), 142.8, 137.6 (d, *J* = 1.6 Hz), 137.5 (d, *J* = 4.2 Hz), 135.8, 133.7, 133.6, 132.5, 132.0 (d, *J* = 2.8 Hz), 131.7 (d, *J* = 2.6 Hz), 131.3 (d, *J* = 12.4 Hz), 131.0 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 185.6 Hz), 130.8, 130.1 (d, *J* = 4.7 Hz), 129.8 (d, *J* = 4.3 Hz), 128.6, 128.1, 127.5, 127.3, 127.0 (d, *J* = 14.5 Hz), 126.4 (d, *J* = 8.9 Hz), 126.1, 125.8 (d, *J* = 14.7 Hz), 125.5, 125.4 – 125.1 (m), 125.0 – 124.8 (m), 124.6 (d, *J* = 157.2 Hz), 123.2 – 123.1 (m), 121.4.**^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.45, -63.09; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.50; **HRMS (ESI)** calculated for $C_{37}H_{24}F_6N_2OP$ $[M + H]^+$: 657.1530, found: 657.1533.





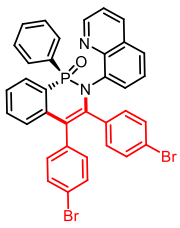
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.163	MM	0.1998	4092.18774	341.42752	51.1380
2	6.745	MM	0.2435	3910.05347	267.64615	48.8620

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.156	BV	0.1969	2.54011e4	1953.19031	100.0000

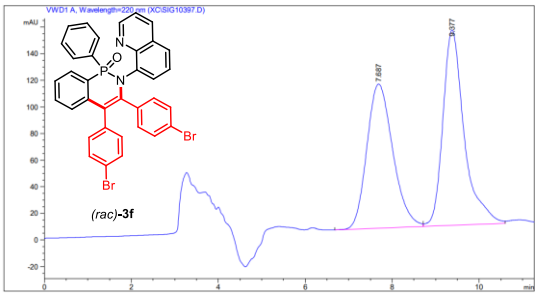
Synthetic Procedure and Characterization of 3f

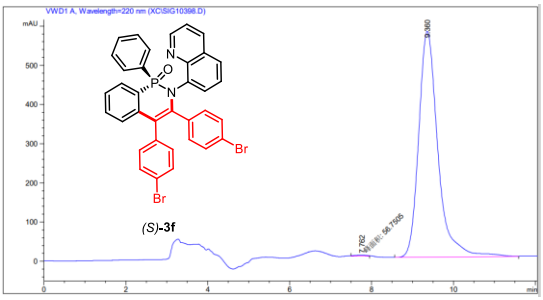
The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2f** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3f** (97.3 mg) in 72% yield as a light-yellow foam with 99% ee. Product exists as a 17:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Bis(4-bromophenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphos-phinine 1-oxide (3f)



M.p.: 165 - 171 °C, $[\alpha]_D^{20}$ = +264.3 (c = 1.0, $CHCl_3$), 99% ee, lit[1d]: $[\alpha]_D^{20}$ = +258.7 [c = 1.0, $CHCl_3$, 98% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (minor) = 7.687 min, t (major) = 9.377 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.80 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.85 – 7.65 (m, 3H), 7.53 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 7.28 – 7.22 (m, 2H), 7.20 – 7.07 (m, 6H), 6.95 (td, *J* = 7.6, 3.6 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.4, 144.2 (d, J_{CP} = 3.4 Hz), 141.5, 138.6 (d, J_{CP} = 4.4 Hz), 137.4, 137.2 (d, J_{CP} = 2.4 Hz), 135.7, 135.4 (d, J_{CP} = 3.9 Hz), 134.0, 133.3 (d, J_{CP} = 10.6 Hz), 132.4, 131.6 (d, J_{CP} = 2.9 Hz), 131.5 (d, J_{CP} = 2.5 Hz), 131.3 (d, J_{CP} = 2.8 Hz), 131.2, 131.0 (d, J_{CP} = 12.7 Hz), 130.3(d, J_{CP} = 136.8 Hz), 129.3, 128.2, 127.8, 127.0 (d, J_{CP} = 13.6 Hz), 126.3 (d, J_{CP} = 26.4 Hz), 126.2 (d, J_{CP} = 3.2 Hz), 125.5, 123.9 (d, J_{CP} = 128.7 Hz), 121.2, 121.0, 120.8, 116.8 (d, J_{CP} = 7.3 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.39; **HRMS (ESI)** calculated for$C_{35}H_{24}Br_2N_2OP$ $[M + H]^+$: 676.9988, found:676. 9992.





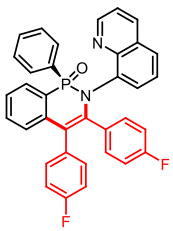
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.687	BV	0.6411	4494.16699	108.35613	47.3371
2	9.377	VV	0.5125	4999.79053	146.74965	52.6629

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.762	MM	0.3600	56.75049	2.62759	0.3013
2	9.360	BV	0.4952	1.87768e4	576.18195	99.6987

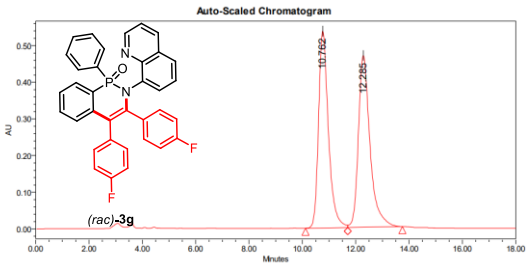
Synthetic Procedure and Characterization of 3g

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2g** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product **3g** (95.6 mg) in 85% yield as a light-yellow foam with >99% ee. Product exists as a 14:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Bis(4-fluorophenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphos-phinine 1-oxide (3g)

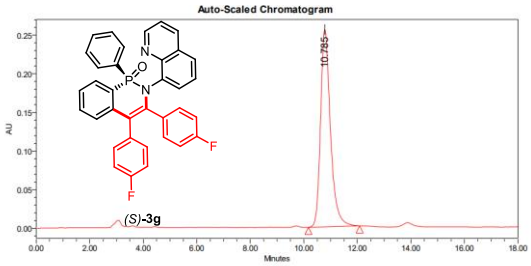


M.p.: 125 - 126 °C, $[\alpha]_D^{20}$ = +90.33 (c = 1.2, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 10.762 min, t (minor) = 12.285 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.84 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.30 (d, *J* = 7.2 Hz, 1H), 7.99 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.84 (dd, *J* = 12.8, 7.6 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.27 (m, 4H), 7.33 – 7.22 (m, 2H), 7.18 – 7.13 (m, 4H), 7.06 – 7.03 (m, 2H), 6.62 (t, *J* = 8.8 Hz, 2H), 6.15 – 6.11 (m, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.5 (d, *J* = 1.8 Hz), 161.1 (d, *J* = 5.8 Hz), 150.0, 145.2, 138.2 (d, *J* = 2.3 Hz), 137.8, 135.6, 134.7 (d, *J* = 3.3 Hz), 133.6 (d, *J* = 9.9 Hz), 132.5, 132.4, 132.2 (d, *J* = 27.8 Hz), 131.8, 131.4, 131.07 (d, *J* = 12.1 Hz), 130.9, 130.6 (d, *J* = 139.1 Hz), 128.5, 127.9, 127.3 (d, *J* = 13.5 Hz), 126.7 (d, *J* = 32.3 Hz), 126.4 (d, *J* = 8.6 Hz), 126.0, 125.6 (d, *J* = 128.5 Hz), 122.4 (d, *J* = 6.0 Hz), 121.2, 118.0 (d, *J* = 3.5 Hz), 115.14 (dd, *J* = 22.2, 7.9 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ 110.23, 114.70; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.42; **HRMS (ESI)** calculated for$C_{35}H_{24}F_2N_2OP$ $[M + H]^+$: 557.1594, found: 521.1595.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	10.762	13778770	49.33	537398
2	W2489 ChB 210nm	12.285	14154069	50.67	468560



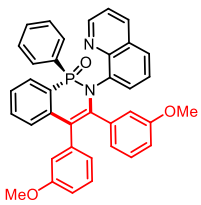
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	10.785	6545307	100.00	255439

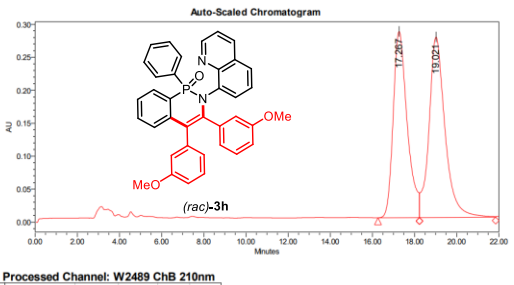
Synthetic Procedure and Characterization of 3h

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2h** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3h** (100.9 mg) in 87% yield as a light-yellow foam with >99% ee. Product exists as a 14:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Bis(3-methoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphos-phinine 1-oxide (3h)

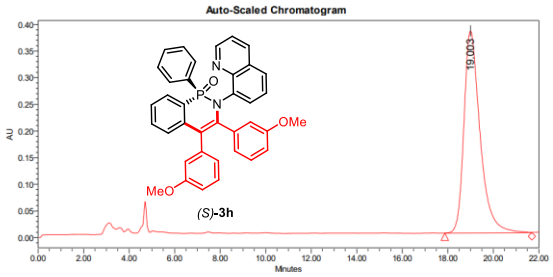


M.p.: 93 - 95 °C, $[\alpha]_D^{20}$ = +178.8 (c = 1.0, $CHCl_3$), >99% ee, lit[1d]: $[\alpha]_D^{20}$ = +189.8 [c = 0.5, $CHCl_3$, 98% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (minor) = 17.267 min, t (major) = 19.021 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 7.98 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.86 (dd, *J* = 13.2, 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.34 (m, 5H), 7.27 – 7.22 (m, 3H), 7.19 – 7.12 (m, 2H), 7.04 (td, *J* = 7.6, 3.2 Hz, 2H), 6.95 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.57 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.80 (d, *J* = 7.6 Hz, 1H), 5.64 (s, 1H), 3.80 (s, 3H), 3.54 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.6, 158.8, 145.0, 145.3 (d, J_{CP} = 3.6 Hz), 140.1, 138.18 (d, J_{CP} = 4.2 Hz), 137.9, 135.6, 133.7 (d, J_{CP} = 10.6 Hz), 131.7 (d, J_{CP} = 2.8 Hz), 131.4 (d, J_{CP} = 2.4 Hz), 131.1 (d, J_{CP} = 5.3 Hz), 130.9, 130.1 (d, J_{CP} = 139.8 Hz), 129.1, 128.9, 128.5, 127.8, 127.3, 127.2, 126.9, 126.7 (d, J_{CP} = 8.2 Hz), 126.4 (d, J_{CP} = 14.5 Hz), 126.0, 125.6 (d, J_{CP} = 127.5 Hz), 123.6 (d, J_{CP} = 6.9 Hz), 123.1 (d, J_{CP} = 2.4 Hz), 121.3, 121.0, 115.9, 115.3, 115.0, 113.7, 55.4, 55.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.48; **HRMS (ESI)** calculated for$C_{37}H_{30}N_2O_3P$ $[M + H]^+$: 581.1989, found: 581.1985.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	17.267	13009611	47.44	282430
2	W2489 ChB 210nm	19.021	14414124	52.56	273660



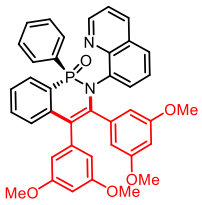
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	19.003	18575538	100.00	378974

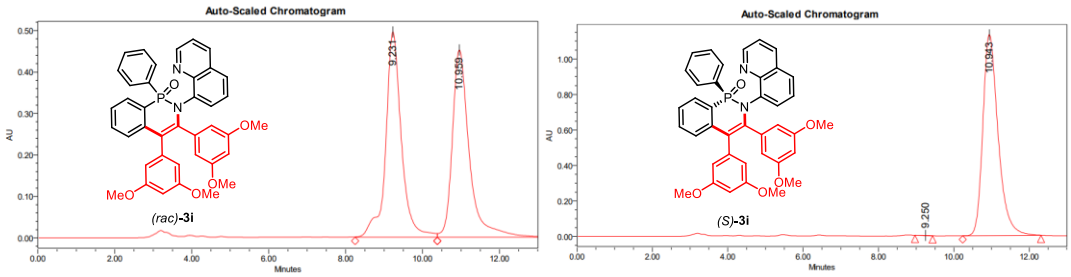
Synthetic Procedure and Characterization of 3i

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2i** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3i** (115.2 mg) in 90% yield as a light-yellow foam with >99% ee. Product exists as a 17:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Bis(3,5-dimethoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2] azaphosphinine 1-oxide (3i)



M.p.: 65 - 71 °C, $[\alpha]_D^{20}$ = +50.0 (c = 1.1, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (major) = 9.231 min, t (minor) = 10.959 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.82 (d, *J* = 4.4 Hz, 1H), 8.31 (d, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.85 (dd, *J* = 13.2, 6.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.39 (m, 4H), 7.30 (dd, *J* = 8.0, 4.5 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.19 – 7.11 (m, 1H), 7.09 – 6.99 (m, 2H), 6.52 (t, *J* = 2.4 Hz, 1H), 6.15 (s, 1H), 5.35 (d, *J* = 2.4 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.53 (s, 3H), 3.52 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.6, 160.0, 150.0, 145.3 (d, J_{CP} = 3.5 Hz), 140.7, 138.0 (d, J_{CP} = 4.4 Hz), 137.8 (d, J_{CP} = 1.8 Hz), 135.5, 133.7, 133.6, 131.7 (d, J_{CP} = 2.8 Hz), 131.4 (d, J_{CP} = 2.5 Hz), 131.1 (d, J_{CP} = 2.9 Hz), 130.9 (d, J_{CP} = 12.7 Hz), 123.0 (d, J_{CP} = 139.5 Hz) , 128.5, 127.8, 127.3, 127.2, 126.7 (d, J_{CP} = 9.0 Hz), 126.5, 126.3, 126.0, 124.8 (d, J_{CP} = 128.3 Hz), 123.6 (d, J_{CP} = 7.0 Hz), 108.3, 101.8, 100.3, 97.6, 55.4, 55.1; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.53; **HRMS (ESI)** calculated for $C_{39}H_{34}N_2O_5P$ $[M + H]^+$: 641.2205, found: 641.2202.



Processed Channel: W2489 ChB 220nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	9.231	14068494	50.45	495418
2	W2489 ChB 220nm	10.959	13818016	49.55	451665

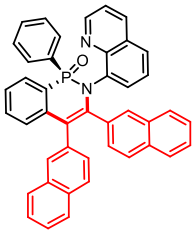
Processed Channel: W2489 ChB 220nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	9.250	10660	0.03	739
2	W2489 ChB 220nm	10.943	31818349	99.97	1133009

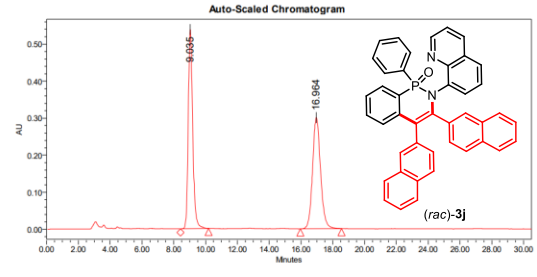
Synthetic Procedure and Characterization of 3j

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2j** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3j** (84.4 mg) in 68% yield as a light-yellow foam with >99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Di(naphthalen-2-yl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphos-phinine 1-oxide (3j)

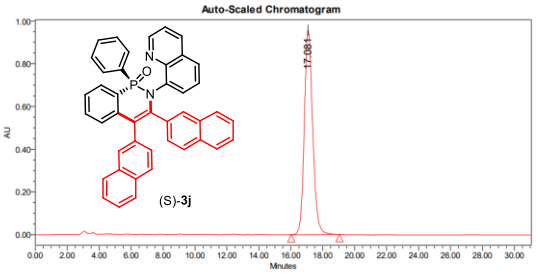


M.p.: 114 - 115 °C, $[\alpha]_D^{20}$ = +168.6 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (minor) = 9.035 min, t (major) = 16.964 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.90 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.36 (d, *J* = 7.2 Hz, 1H), 8.03 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.99 – 7.94 (m, 3H), 7.95 – 7.84 (m, 4H), 7.71 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.54 – 7.49 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.28 – 7.26 (m, 2H), 7.23 (s, 1H), 7.21 – 7.13 (m, 2H), 7.08 (dd, *J* = 7.8, 3.5 Hz, 2H), 6.40 (s, 1H), 6.00 (dd, *J* = 8.4, 1.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.1, 138.0, 136.4, 135.7, 133.8, 133.7, 133.7, 132.9, 132.4, 132.3, 132.2, 132.0, 131.9, 131.7,131.7, 131.4, 131.4, 131.2, 131.1, 131.0, 130.9, 129.8 (d, J_{CP} = 167.2 Hz), 128.9 (d, J_{CP} = 3.1 Hz), 128.2, 127.9, 127.7, 127.5, 127.4, 127.3, 127.3, 127.2, 127.0, 126.8 (d, J_{CP} = 9.0 Hz), 126.5, 126.2, 126.0 (d, J_{CP} = 2.0 Hz), 121.3, 119.3; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.58; **HRMS (ESI)** calculated for $C_{43}H_{30}N_2OP$ $[M + H]^+$: 621.2096, found: 621.2091.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	9.035	10435745	49.79	538207
2	W2489 ChB 210nm	16.964	10523502	50.21	300302



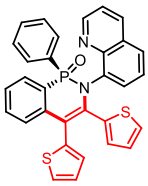
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	17.081	34777738	100.00	956763

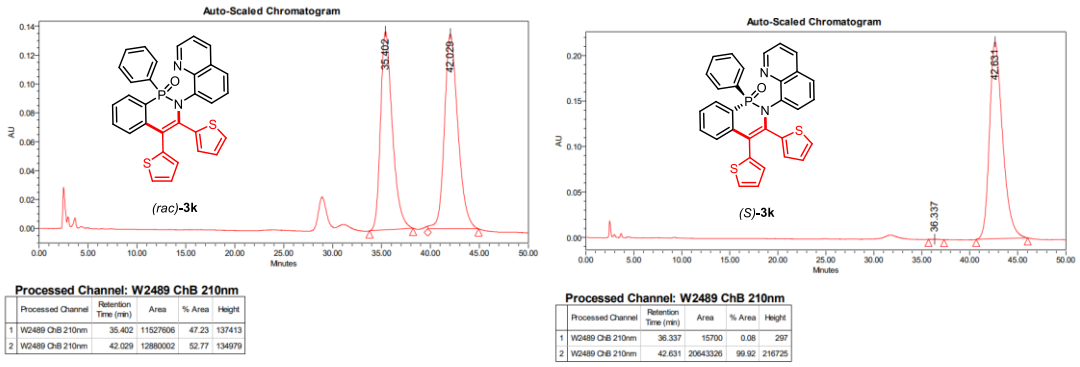
Synthetic Procedure and Characterization of 3k

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2k** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3k** (104.1 mg) in 84% yield as a light-yellow foam with >99% ee. Product exists as a 11:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1-Phenyl-2-(quinolin-8-yl)-3,4-di(thiophen-2-yl)-2*H*-benzo[*c*][1,2]azaphos-phinine 1-oxide (3k)



M.p.: 129 - 133 °C, $[\alpha]_D^{20}$ = +168.6 (c = 1.0, $CHCl_3$), >99% ee, lit[1d]: $[\alpha]_D^{20}$ = +238.5 [c = 1.0, $CHCl_3$, 98% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 210 nm, t (minor) = 35.402 min, t (major) = 42.029 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.82 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 13.2, 8.0 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.41 – 7.37 (m, 2H), 7.29 (dd, *J* = 7.6, 2.8 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.13 – 7.08 (m, 1H), 7.03 – 6.95 (m, 3H), 6.92 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.71 (d, *J* = 4.8 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 6.23 (dd, *J* = 4.8, 3.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.5, 144.8(d, J_{CP} = 2.5 Hz), 139.8, 139.3 (d, J_{CP} = 4.8 Hz), 138.4, 137.5 (d, J_{CP} = 4.5 Hz), 137.3 (d, J_{CP} = 1.8 Hz), 135.5, 133.3, 133.2, 131.7 (d, J_{CP} = 4.2 Hz), 131.6 (d, J_{CP} = 4.2 Hz), 131.5 (d, J_{CP} = 3.0 Hz), 131.0, 130.8 (d, J_{CP} = 12.1 Hz), 130.3, 129.7, 128.3, 127.6, 127.1, 126.9, 126.8 (d, J_{CP} = 9.0 Hz), 126.5(d, J_{CP} = 7.3 Hz), 126.3(d, J_{CP} = 7.0 Hz), 125.5, 124.4, 123.1, 121.2, 112.9 (d, J_{CP} = 7.2 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.96; **HRMS (ESI)** calculated for $C_{31}H_{22}N_2OPS_2$ $[M + H]^+$: 533.0906, found: 533.0903.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	35.402	11527606	47.23	137413
2	W2489 ChB 210nm	42.029	12880002	52.77	134979

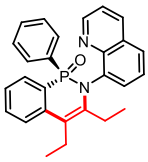
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	36.337	15700	0.08	297
2	W2489 ChB 210nm	42.631	20643326	99.92	216725

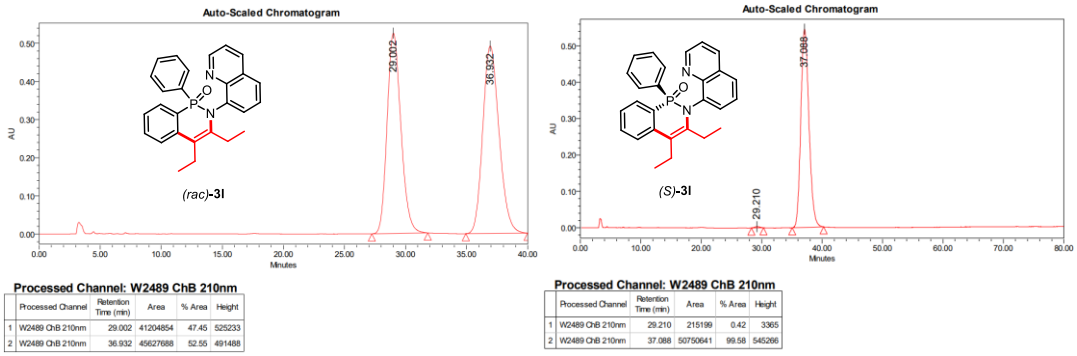
Synthetic Procedure and Characterization of 3l

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2l** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3l** (71.2 mg) in 84% yield as a light-yellow foam with 99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Diethyl-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3l)



M.p.: 197 - 201 °C, $[\alpha]_D^{20}$ = +399.9 (c = 1.0, $CHCl_3$), 99% ee, lit[1d]: $[\alpha]_D^{20}$ = +625.0 [c = 0.5, $CHCl_3$, 99% ee (*S*)]. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 29.002 min, t (minor) = 36.932 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.63 – 7.50 (m, 4H), 7.35 – 7.27 (m, 3H), 7.17 (td, *J* = 7.6, 2.8 Hz, 1H), 7.09 – 7.05 (m, 1H), 6.92 (td, *J* = 7.6, 3.2 Hz, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 2.53– 2.43 (m, 1H), 1.85 – 1.76 (m, 1H), 1.33 (t, *J* = 7.6 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.1, 145.3 (d, J_{CP} = 3.7 Hz), 142.2, 139.0 (d, J_{CP} = 4.2 Hz), 137.4 (d, J_{CP} = 2.6 Hz), 135.8, 133.2 (d, J_{CP} = 10.2 Hz), 131.4 (d, J_{CP} = 2.4 Hz), 131.2 (d, J_{CP} = 2.8 Hz), 130.7 (d, J_{CP} = 12.8 Hz), 130.7 (d, J_{CP} = 135.3 Hz), 130.6 (d, J_{CP} = 3.4 Hz), 128.5, 127.4, 126.9 (d, J_{CP} = 13.3 Hz), 125.8, 124.9 (d, J_{CP} = 129.7 Hz), 124.8 (d, J_{CP} = 14.7 Hz), 123.5 (d, J_{CP} = 9.4 Hz), 121.2, 114.2 (d, J_{CP} = 8.3 Hz), 24.8 (d, J_{CP} = 2.6 Hz), 22.39, 14.93, 13.29; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.098; **HRMS (ESI)** calculated for $C_{27}H_{26}N_2OP$ $[M + H]^+$: 425.1777, found: 425.1776.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	29.002	41204854	47.45	525233
2	W2489 ChB 210nm	36.932	45627688	52.55	491488

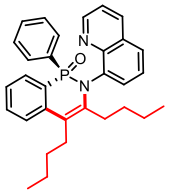
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	29.210	215199	0.42	3365
2	W2489 ChB 210nm	37.088	50750641	99.58	545266

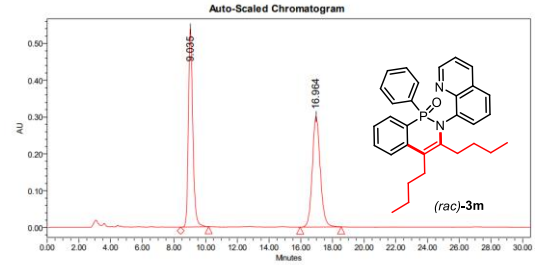
Synthetic Procedure and Characterization of 3m

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2m** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3m** (83.5 mg) in 87% yield as a yellow oil with >99% ee. Product exists as a 11:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Dibutyl-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3m)

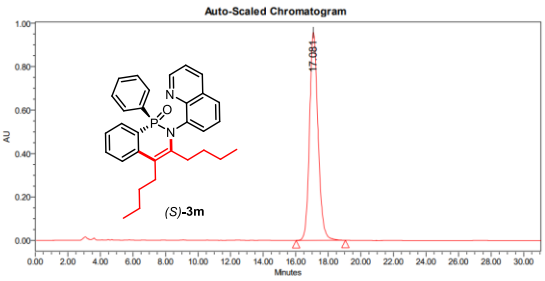


$[\alpha]_D^{20}$ = +399.9 (c = 1.0, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (minor) = 9.035 min, t (major) = 16.964 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.94 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.69 – 7.47 (m, 6H), 7.36 – 7.22 (m, 3H), 7.14 (td, *J* = 7.2, 2.8 Hz, 1H), 7.06 (td, *J* = 7.6, 1.6 Hz, 1H), 6.91 (td, *J* = 7.6, 3.2 Hz, 2H), 2.79 – 2.64 (m, 2H), 2.48 – 2.38 (m, 1H), 1.86 – 1.62 (m, 3H), 1.58 – 1.47 (m, 3H), 1.46 – 1.35 (m, 1H), 1.08 – 0.93 (m, 5H), 0.57 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.0, 145.3 (d, J_{CP} = 3.7 Hz), 141.3, 139.2 (d, J_{CP} = 4.2 Hz), 137.5 (d, J_{CP} = 2.6 Hz), 135.7, 133.2 (, J_{CP} = 10.1 Hz), 131.4 (d, J_{CP} = 135.1 Hz), 131.2 (d, J_{CP} = 2.4 Hz), 131.1 (d, J_{CP} = 2.7 Hz), 130.6 (d, J_{CP} = 12.7 Hz), 130.4 (d, J_{CP} = 3.2 Hz), 128.4, 127.3, 126.9, 126.7, 125.6, 125.5 (d, J_{CP} = 129.8 Hz), 124.7 (d, J_{CP} = 14.8 Hz), 123.5 (d, J_{CP} = 9.5 Hz), 121.2, 113.3 (d, J_{CP} = 8.4 Hz), 32.6, 31.4 (d, J_{CP} = 2.4 Hz), 30.8, 29.3, 23.1, 22.4, 14.0, 13.5; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.098; **HRMS (ESI)** calculated for $C_{31}H_{34}N_2OP$ $[M + H]^+$: 481.2403, found: 481.2401.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	9.035	10435745	49.79	538207
2	W2489 ChB 210nm	16.964	10523502	50.21	300302



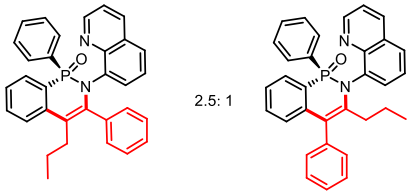
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	17.081	34777738	100.00	956763

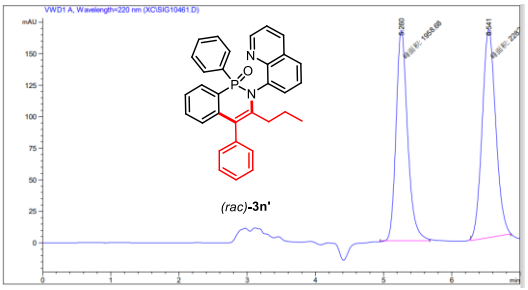
Synthetic Procedure and Characterization of 3an and 3n'

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2n** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give mixture **3n** and **3n'** (2.5:1, 70.0 mg) in 72% yield as a yellow oil with all >99% ees. Major product exists as a 12:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

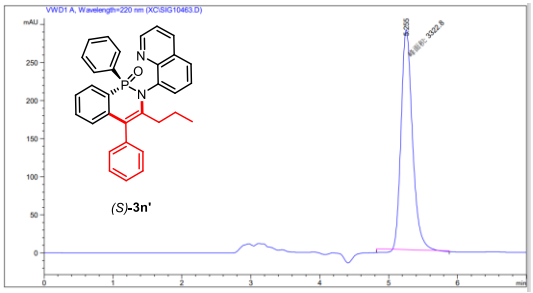
Compounds 3n and 3n'



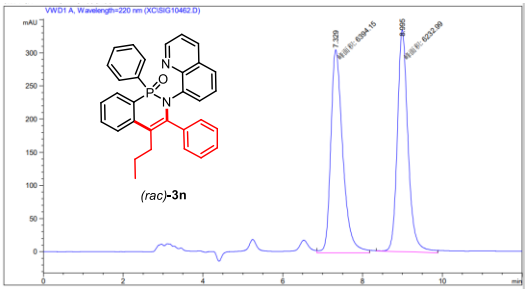
$[\alpha]_D^{20}$ = +294.6 (c = 1.0, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t_1 (major) = 5.260 min, t_1 (minor) = 6.541 min, t_2 (major) = 7.329 min, t_2 (minor) = 8.995 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.90 – 8.74 (m, 1H), 8.29 – 6.73 (m, 20H), 3.13 – 2.35 (m, 2H), 1.76 – 1.44 (m, 2H), 0.85 – 0.32 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.1 (d, J_{CP} = 26.1 Hz), 149.7, 149.3, 145.5 (d, J_{CP} = 3.7 Hz), 144.7 (d, J_{CP} = 3.8 Hz), 141.1, 138.45 (d, J_{CP} = 4.5 Hz), 138.0 (d, J_{CP} = 2.6 Hz), 137.1 (d, J_{CP} = 3.6 Hz), 135.5 (d, J_{CP} = 6.6 Hz), 133.6, 133.4 (d, J_{CP} = 10.4 Hz), 132.5 (d, J_{CP} = 10.1 Hz), 131.5 (d, J_{CP} = 2.3 Hz), 131.4 (d, J_{CP} = 3.0 Hz), 131.2 (d, J_{CP} = 12.6 Hz), 131.0 (d, J_{CP} = 7.1 Hz), 130.9 (d, J_{CP} = 3.6 Hz), 130.5, 129.1 (d, J_{CP} = 116.3 Hz), 128.2, 127.3 (d, J_{CP} = 33.8 Hz), 127.0 (d, J_{CP} = 6.8 Hz), 126.6, 125.7 (d, J_{CP} = 14.7 Hz), 125.4, 124.5 (d, J = 9.5 Hz), 124.1 (d, J_{CP} = 9.6 Hz), 121.0 119.7 (d, J_{CP} = 6.8 Hz), 114.9 (d, J_{CP} = 7.5 Hz), 98.6, 31.9, 23.1, 21.4, 21.0, 14.0, 13.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.79, 15.33; **HRMS (ESI)** calculated for $C_{32}H_{28}N_2OP$ $[M + H]^+$: 487.1939, found: 487.1942.



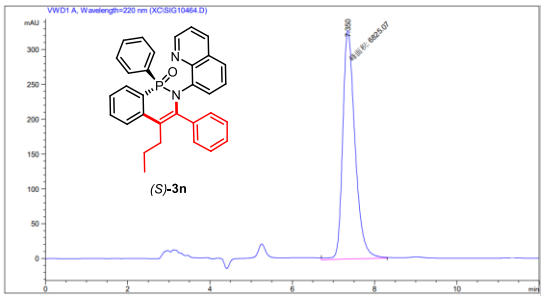
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.260	MM	0.1956	1958.68433	166.89757	46.1850
2	6.541	MM	0.2304	2282.26807	165.08578	53.8150



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.255	MM	0.1920	3322.79712	288.50125	100.0000



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.329	MM	0.3482	6394.15283	306.07852	50.6381
2	8.995	MM	0.3108	6232.99414	334.24207	49.3619

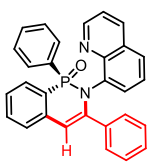


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.350	MM	0.3470	6825.07275	327.85458	100.0000

Synthetic Procedure and Characterization of 3o

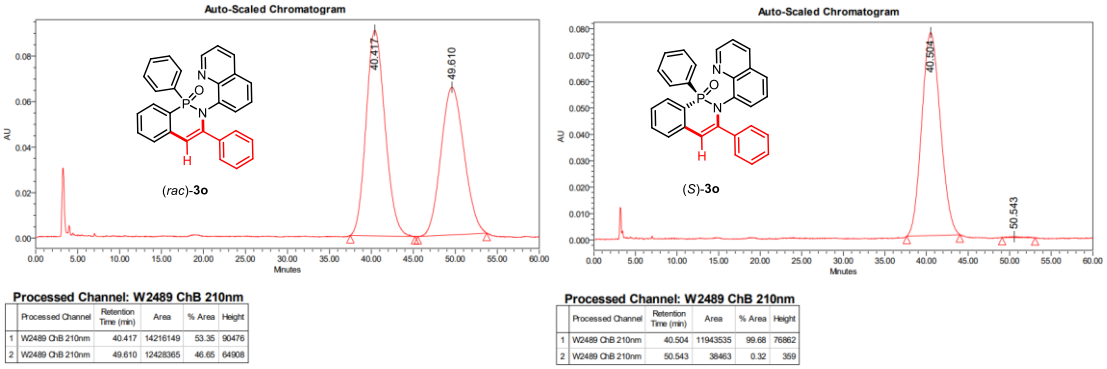
The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2o** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 °C with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3o** (80.8 mg) in 91% yield as a light-yellow foam with >99% ee. Product exists as a 8:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1,3-Diphenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3o)



M.p.: 136 - 137 °C, $[\alpha]_D^{20}$ = +363.6 (c = 1.0, $CHCl_3$), >99% ee, lit[1d]: $[\alpha]_D^{20}$ = +472.7 [c = 0.5, $CHCl_3$, 98% ee (*S*)]. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 40.417 min, t (minor) = 49.610 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.12 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.76 – 7.64 (m, 3H), 7.59 – 7.49 (m, 1H), 7.50 – 7.40 (m, 2H), 7.38 – 7.32 (m, 3H), 7.29 – 7.19 (m, 2H), 7.16 – 7.05 (m, 2H), 6.97 (td, *J* = 7.7, 3.4 Hz, 2H), 6.89 (dd, *J* = 5.0, 2.0 Hz, 3H), 6.33 (d, *J* = 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.3, 145.3, 144.1 (d, J_{CP} = 3.3 Hz), 138.4 (d, J_{CP} = 4.3 Hz), 138.1 (d, J_{CP} = 5.0 Hz), 137.8 (d, J_{CP} = 2.4 Hz),

135.4, 133.1, 133.0, 131.8(d, J_{CP} = 2.5 Hz), 131.4 (d, J_{CP} = 2.9 Hz), 131.0 (d, J_{CP} = 12.3 Hz), 130.4 (d, J_{CP} = 2.9 Hz), 129.0, 128.4, 127.4, 127.3, 127.2, 127.0, 126.9, 126.7 (d, J_{CP} = 9.3 Hz), 125.9 (d, J_{CP} = 12.4 Hz), 125.5, 124.1 (d, J_{CP} = 126.9 Hz), 121.0, 107.7; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.77; **HRMS (ESI)** calculated for $C_{29}H_{22}N_2OP$ $[M + H]^+$: 445.1464, found: 445.1466.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	40.417	14216149	53.35	90476
2	W2489 ChB 210nm	49.610	12428365	46.65	64908

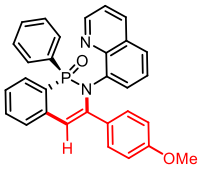
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	40.504	1193535	99.68	76862
2	W2489 ChB 210nm	50.543	38463	0.32	359

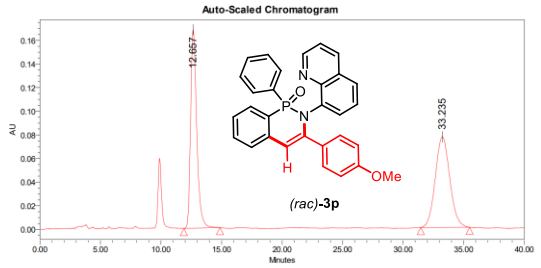
Synthetic Procedure and Characterization of 3p

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2p** (0.30 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3p** (67.4 mg) in 71% yield as a light-yellow foam with 98% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(4-Methoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphini-ne 1-oxide (3p)

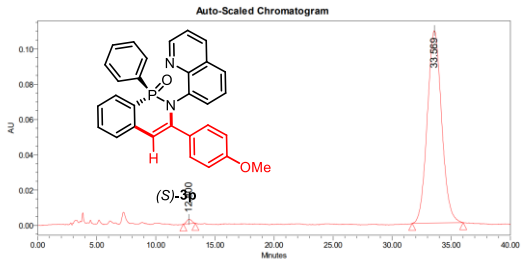


M.p.: 120 - 122 °C; $[\alpha]_D^{20}$ = +272.5 (c = 0.4, $CHCl_3$), 98% ee. lit[1d]: $[\alpha]_D^{20}$ = +381.5 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 12.800 min, t (major) = 24.482 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72-8.75 (m, 1H), 8.10 (d, *J* = 6.4, 1H), 7.77-7.73 (m, 1H), 7.72-7.65 (m, 2H), 7.56-7.51 (m, 1H), 7.49-7.43 (m, 2H), 7.38-7.34 (m, 1H), 7.31 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.25-7.20 (m, 2H), 7.16-7.09 (m, 2H), 7.01-6.96 (m, 2H), 6.45 (dd, *J* = 8.8, 3.2 Hz, 2H), 6.31 (s, 1H), 3.57 (s, 1H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 158.8, 149.2, 144.9, 144.1 (d, *J* = 3.2 Hz), 138.2 (d, *J* = 5.0 Hz), 137.8 (d, J_{CP} = 2.4 Hz), 135.4, 132.9(d, J_{CP} = 10.6 Hz), 131.7 (d, J_{CP} = 2.3 Hz), 131.4 (d, J_{CP} = 2.8 Hz), 131.0 (d, J_{CP} = 4.5 Hz), 130.9 (d, J_{CP} = 141.5 Hz),130.7 (d, J_{CP} = 12.2 Hz), 130.3 (d, J_{CP} = 2.8 Hz), 130.2, 128.4, 127.2 (d, J_{CP} = 9.5 Hz), 127.0, 126.5 (d, J_{CP} = 9.3 Hz), 125.7 (d, J_{CP} = 14.3 Hz), 125.4, 123.3 (d, J_{CP} = 127.6 Hz), 121.0, 112.5, 107.2 (d, J_{CP} = 7.6 Hz), 55.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 19.11; **HRMS (ESI)** calculated for $C_{30}H_{24}N_2O_2P$ $[M + H]^+$: 475.1570, found: 475.1568.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	12.657	5878948	47.94	168051
2	W2489 ChA 254nm	33.235	6383054	52.06	76805



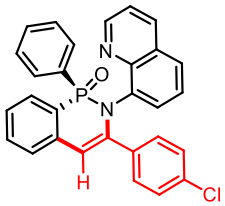
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	12.800	76663	0.83	2489
2	W2489 ChA 254nm	33.569	9199315	99.17	109030

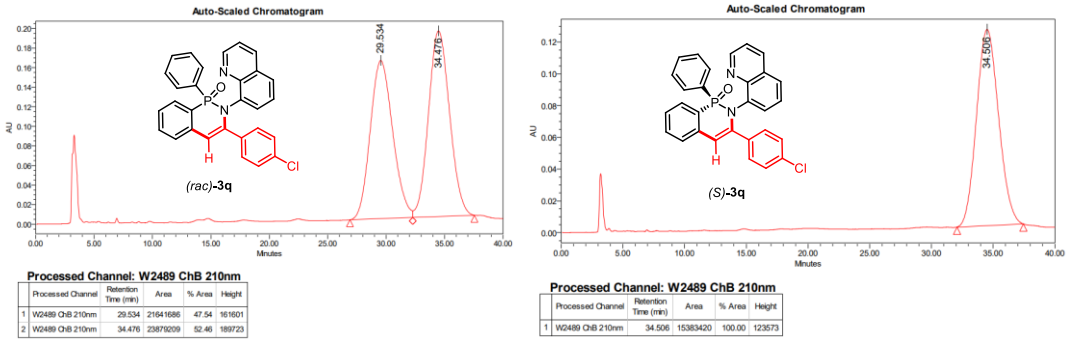
Synthetic Procedure and Characterization of 3q

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2q** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3q** (78.3 mg) in 82% yield as a light-yellow foam with >99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(4-Chlorophenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3q)



M.p.: 126 - 127 °C, $[\alpha]_D^{20}$ = +381.4 (c = 1.0, $CHCl_3$), >99% ee, lit[1d]: $[\alpha]_D^{20}$ = +327.2 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (minor) = 29.534 min, t (major) = 34.476 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.58 – 7.51 (m, 1H), 7.49 – 7.35 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.25 (s, 1H), 7.15 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.96 (td, *J* = 8.0, 3.6 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.30 (d, *J* = 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.4, 144.1, 143.9 (d, J_{CP} = 3.2 Hz), 137.8 (d, J_{CP} = 5.0 Hz), 137.5 (d, J_{CP} = 2.5 Hz), 1367.0 (d, J_{CP} = 4.4 Hz), 135.6, 133.3, 133.0, 132.9, 131.8 (d, J_{CP} = 2.4 Hz), 131.5 (d, J_{CP} = 2.9 Hz), 131.4 (d, J_{CP} = 197.0 Hz), 130.9 (d, J_{CP} = 12.4 Hz), 130.2 (d, J_{CP} = 2.9 Hz), 130.2, 128.5, 127.5, 127.3, 127.2 (d, J_{CP} =3.6 Hz), 126.7 (d, J_{CP} = 9.3 Hz), 126.1 (d, J_{CP} = 14.4 Hz), 125.5, 123.6 (d, J_{CP} = 127.8 Hz), 121.2, 107.8 (d, J_{CP} = 7.8 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.83; **HRMS (ESI)** calculated for $C_{29}H_{21}ClN_2OP$ $[M + H]^+$: 479.1075, found: 479.1076.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	29.534	21641686	47.54	161601
2	W2489 ChB 210nm	34.476	23879209	52.46	189723

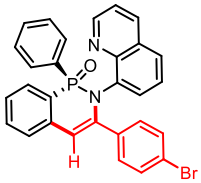
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	34.506	15383420	100.00	123573

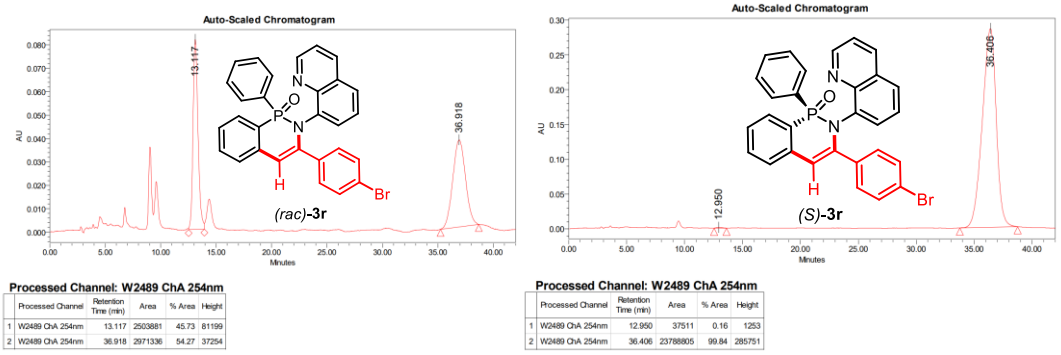
Synthetic Procedure and Characterization of 3r

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2r** (0.30 mmol, 1.5 eq.), $Co(OAc)_2 \cdot 4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product **3r** (98.4 mg) in 94% yield as a light-yellow foam with >99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(4-Methoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphini-ne 1-oxide (3r)



M.p.: 122 - 124 °C; $[\alpha]_D^{20}$ = +336.6 (c = 0.4, $CHCl_3$), >99% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 12.950 min, t (major) = 36.406 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (d, *J* = 4.0 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.47-7.39 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.27-7.20 (m, 4H), 7.16-7.11 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.99-6.91 (m, 2H), 6.29 (s, 1H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 149.4, 144.0, 143.8 (d, J_{CP} = 3.0 Hz), 137.7 (d, J_{CP} = 5.0 Hz), 137.5 (d, J_{CP} = 4.0 Hz), 137.4, 135.6, 133.0 (d, J_{CP} = 11.0 Hz), 131.9 (d, J_{CP} = 3.0 Hz), 131.6 (d, J_{CP} = 3.0 Hz), 130.9, 130.8 (d, J_{CP} = 117.5 Hz), 130.5, 130.2, 130.1 (d, J_{CP} = 2.0 Hz), 128.4, 127.5, 127.2 (d, J_{CP} = 13.0 Hz), 126.8 (d, J_{CP} = 11.0 Hz), 126.2 (d, J_{CP} = 14.0 Hz), 125.5, 124.2 (d, J_{CP} = 126.0 Hz), 121.6, 121.2, 107.9 (d, J_{CP} = 8.0Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.85; **HRMS (ESI)** calculated for $C_{29}H_{21}BrN_2OP$ $[M+H]^+$: 523.0569, found: 523.0569.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	13.117	2503881	45.73	81199
2	W2489 ChA 254nm	36.918	2971336	54.27	37254

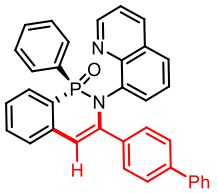
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	12.950	37511	0.16	1253
2	W2489 ChA 254nm	36.406	23788805	99.84	285751

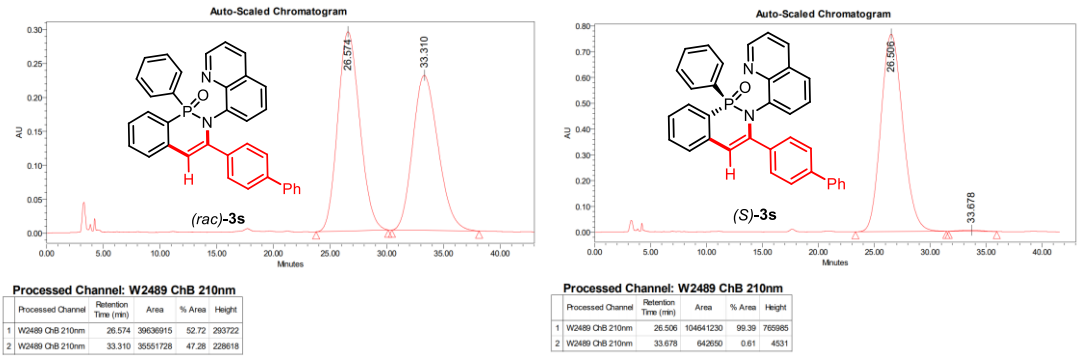
Synthetic Procedure and Characterization of 3s

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2s** (0.30 mmol, 1.5 eq.), $Co(OAc)_2 \cdot 4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product **3s** (85.8 mg) in 82% yield as a light-yellow foam with 99% ee. Product exists as a 11:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-([1,1'-Biphenyl]-4-yl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphi-nine 1-oxide (3s)



M.p.: 132 - 135 °C; $[\alpha]_D^{20}$ = +255.2 (c = 1.2, $CHCl_3$), 99% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 26.506 min, t (minor) = 33.678 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, *J* = 4.4 Hz, 1H), 8.13 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 6.0 Hz, 2H), 7.55-7.7.47 (m, 2H), 7.45-7.40 (m, 4H), 7.33-7.26 (m, 3H), 7.24-7.16 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 4.0 Hz, 1H), 7.08-7.03 (m, 2H), 6.96 (td, *J* = 7.6, 3.2 Hz, 2H), 6.38 (s, 1H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 149.3, 144.9, 144.1 (d, J_{CP} = 3.3 Hz), 140.2, 139.9, 138.0 (d, J_{CP} = 5.0 Hz), 137.8 (d, J_{CP} = 2.4 Hz), 137.5 (d, J_{CP} = 4.3 Hz), 135.5, 133.0 (d, J_{CP} = 10.5 Hz), 131.8 (d, J_{CP} = 2.5 Hz), 131.7 (d, J_{CP} = 135.2 Hz), 131.5 (d, J_{CP} = 2.8 Hz), 130.9 (d, J_{CP} = 12.1 Hz), 130.3 (d, J_{CP} = 2.8 Hz), 129.3, 128.6, 128.5, 127.4, 127.3, 127.2, 127.1, 126.7, 126.0 (d, J_{CP} = 14.3 Hz), 125.6, 125.5, 124.2 (d, J_{CP} = 126.7 Hz), 121.1, 107.9 (d, J_{CP} = 7.8 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 19.00; **HRMS (ESI)** calculated for $C_{35}H_{26}N_2OP$ $[M+H]^+$: 521.1777, found: 521.1716.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	26.574	39636915	52.72	293722
2	W2489 ChB 210nm	33.310	35551728	47.28	228618

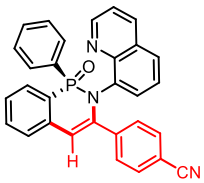
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	26.506	104641230	99.39	765985
2	W2489 ChB 210nm	33.678	642650	0.61	4531

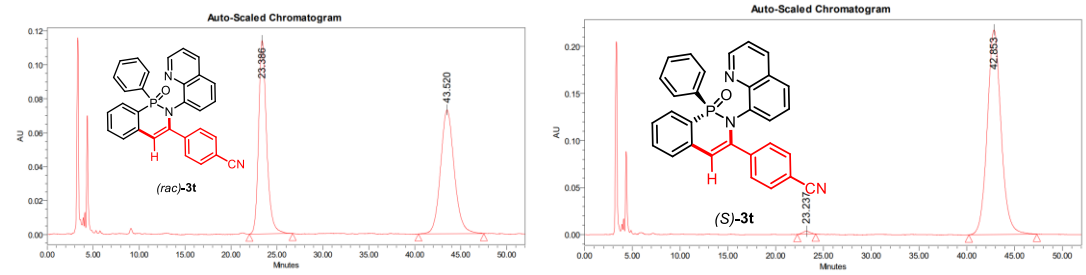
Synthetic Procedure and Characterization of 3t

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2t** (0.30 mmol, 1.5 eq.), $Co(OAc)_2·4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 2:1 v/v) to give the desired product **3t** (84.4 mg) in 90% yield as a light-yellow foam with 98% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-4-(1-Oxido-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphinin-3-yl)benzonitrile (3t)



M.p.: 133 - 135 ℃; $[\alpha]_D^{20}$ = +486.0 (c = 0.4, $CHCl_3$), 98% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 23.237 min, t (mjaor) = 42.853 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (d, *J* = 4.0 Hz, 1H), 8.15 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.65 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.52-7.46 (m, 3H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.31-7.26 (m, 2H), 7.16 (t, *J* = 4.4 Hz, 2H), 7.15 (d, *J* = 4.1 Hz, 0H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.97 (td, *J* = 7.6, 3.3 Hz, 2H), 6.34 (s, 1H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 149.4, 143.5 (d, J_{CP} = 2.9 Hz), 143.4, 143.1 (d, J_{CP} = 4.4 Hz), 137.3 (d, J_{CP} = 4.7 Hz), 137.2 (d, J_{CP} = 2.6 Hz), 135.7, 133.0 (d, J_{CP} = 10.5 Hz), 131.9 (d, J_{CP} = 2.4 Hz), 131.6 (d, J_{CP} = 2.6 Hz), 131.0 (d, J_{CP} = 12.4 Hz), 130.8, 130.0 (d, J_{CP} = 2.8 Hz), 129.7 (d, J_{CP} = 118.7 Hz), 129.4, 128.5, 127.6, 127.2 (d, J_{CP} = 13.6 Hz), 126.96 (d, J_{CP} = 9.1 Hz), 126.60 (d, J_{CP} = 14.4 Hz), 125.6, 123.9 (d, J_{CP} = 126.9 Hz), 121.3, 118.5, 110.9, 108.7 (d, J_{CP} = 7.7 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.58; **HRMS (ESI)** calculated for $C_{30}H_{21}N_3OP$ $[M + H]^+$: 470.1417, found: 470.1412.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	23.386	6881271	47.61	114050
2	W2489 ChA 254nm	43.520	7573469	52.39	73022

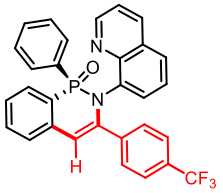
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	23.237	168796	0.77	3127
2	W2489 ChA 254nm	42.853	21879044	99.23	217561

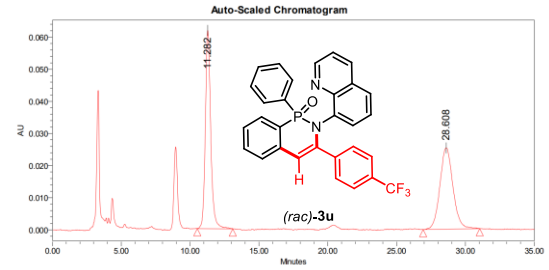
Synthetic Procedure and Characterization of 3u

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2u** (0.30 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product **3u** (86.1 mg) in 84% yield as a light-yellow foam with 99% ee. Product exists as a 9:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1-Phenyl-2-(quinolin-8-yl)-3-(4-(trifluoromethyl)phenyl)-2*H*- benzo[*c*][1,2]aza-phosphinine 1-oxide (3u)

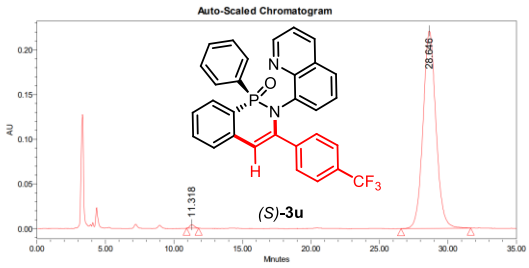


M.p.: 112 - 113 °C; $[\alpha]_D^{20}$ = +559.0 (c = 0.4, $CHCl_3$), 99% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 11.318 min, t (mjaor) = 28.646 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.14 (d, *J* = 7.8 Hz), 7.77 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.71-7.61 (m, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.52-7.43 (m, 4H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.29-7.24 (m, 2H), 7.17 (m, 3H), 7.13-7.08 (m, 1H), 6.97 (td, *J* = 7.6, 3.6 Hz, 2H), 6.34 (d, *J* = 2.0 Hz, 1H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 149.4, 143.9, 143.81 (d, J_{CP} = 3.3 Hz), 142.1, 137.6 (d, J_{CP} = 4.9 Hz), 137.4 (d, J_{CP} = 2.6 Hz), 135.7, 133.0 (d, J_{CP} = 10.6 Hz), 132.0 (d, J_{CP}= 2.5 Hz), 131.6 (d, J_{CP}= 2.9 Hz), 131.60(d, J_{CP} = 136.1 Hz), 131.0 (d, J_{CP}= 12.2 Hz), 130.2 (d, J_{CP} = 2.9 Hz), 129.2, 128.5, 127.6, 127.3, 127.1, 126.9 (d, J_{CP} = 9.3 Hz), 126.5 (d, J_{CP} = 14.5 Hz), 125.6, 123.9 (q, J_{CF} = 270.5), 123.8(d, J_{CP} = 126.7), 124.0 (q, J_{CF} = 3.7 Hz), 121.3, 108.5 (d, J_{CP} = 8.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ 62.71 ; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.74; **HRMS (ESI)** calculated for $C_{30}H_{21}F_3N_2OP$ $[M+H]^+$: 513.1338, found: 513.1340.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	11.282	1674359	50.07	61739
2	W2489 ChA 254nm	28.608	1669841	49.93	25318



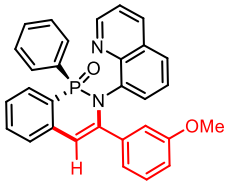
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	11.318	93104	0.64	3861
2	W2489 ChA 254nm	28.646	14501647	99.36	220998

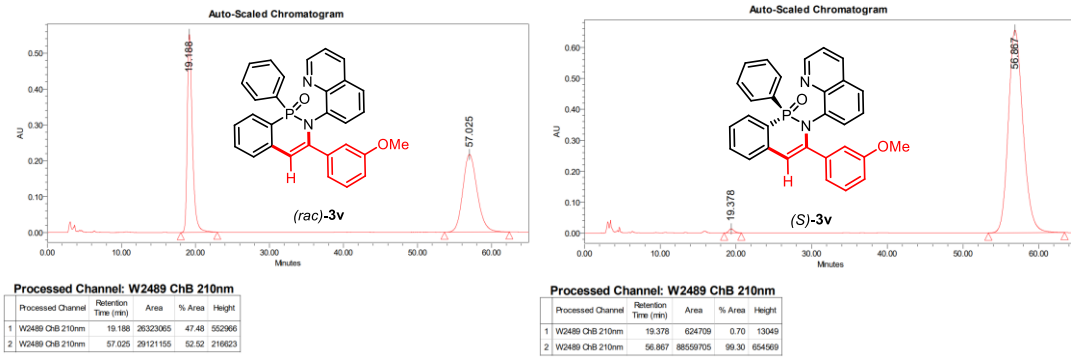
Synthetic Procedure and Characterization of 3v

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2v** (0.30 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3v** (86.4 mg) in 91% yield as a light-yellow foam with 99% ee. Product exists as a 8:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(3-Methoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphini-ne 1-oxide (3v)



M.p.: 93 - 94 °C; $[\alpha]_D^{20}$ = +310.4 (c = 0.9, $CHCl_3$), 99% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (minor) = 19.378 min, t (mjaor) = 57.867 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.77-7.66 (m, 3H), 7.56-7.42 (m, 3H), 7.38-7.30 (m, 1H), 7.27 -7.18 (m, 2H), 7.17-7.03 (m, 3H), 7.03-6.94 (m, 2H), 6.91 (s, 1H), 6.82 (t, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 6.36 (s, 1H), 3.48 (s, 3H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 158.23, 149.3, 145.0, 144.2 (d, J_{CP} = 3.2 Hz), 139.6 (d, J_{CP} = 4.3 Hz), 138.0 (d, J_{CP} = 5.0 Hz), 137.8 (d, J_{CP} = 2.1 Hz), 135.5, 132.9 (d, J_{CP} = 10.5 Hz), 131.8 (d, J_{CP} = 2.3 Hz), 131.4 (d, J_{CP} = 2.7 Hz), 130.8 (d, J_{CP} = 11.9 Hz), 130.3 (d, J_{CP} = 2.7 Hz), 128.4, 128.0, 127.3, 127.2 (d, J_{CP} = 13.6 Hz), 126.7 (d, J_{CP} = 9.3 Hz), 126.3 (d, J_{CP} = 75.9 Hz), 126.0 (d, J_{CP} = 14.4 Hz), 125.4, 124.1 (d, J_{CP} = 126.5 Hz), 121.6, 121.0, 114.8 (d, J_{CP} = 175.2 Hz), 114.1 (d, J_{CP} = 15.5 Hz), 107.9 (d, J_{CP} = 7.7 Hz), 55.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 19.12; **HRMS (ESI)** calculated for $C_{30}H_{24}N_2O_2P$ $[M+H]^+$: 475.1570, found: 475.1569.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	19.188	26323065	47.48	552966
2	W2489 ChB 210nm	57.025	29121155	52.52	216623

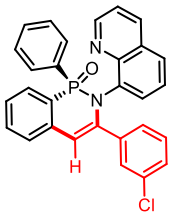
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	19.378	624709	0.70	13049
2	W2489 ChB 210nm	56.867	88559705	99.30	654569

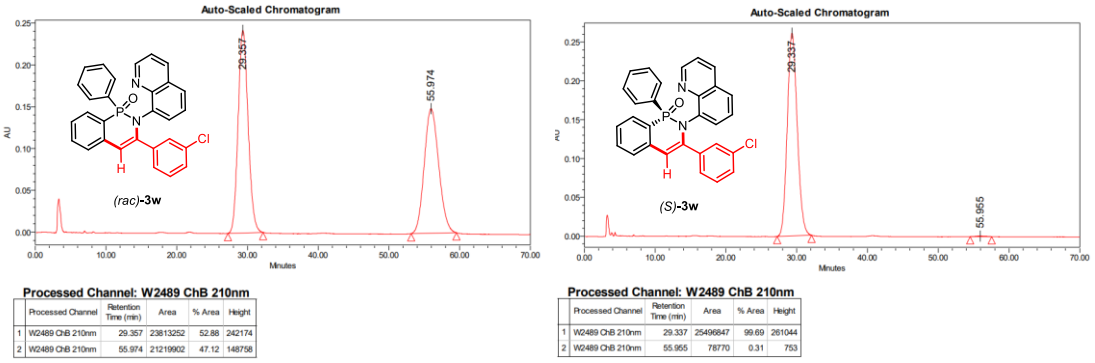
Synthetic Procedure and Characterization of 3w

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2w** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3w** (78.3 mg) in 82% yield as a light-yellow foam with 99% ee. Product exists as a 9:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(3-Chlorophenyl)-1-Phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3w)



M.p.: 108 - 110 °C, $[\alpha]_D^{20}$ = +461.6 (c = 0.5, $CHCl_3$), 99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 29.257 min, t (minor) = 55.974 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.12 (d, *J* = 7.2 Hz, 1H), 7.77 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.72 – 7.61 (m, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.42 (m, 2H), 7.44 – 7.34 (m, 2H), 7.30 – 7.20 (m, 3H), 7.16 (dd, *J* = 8.2, 4.4 Hz, 2H), 7.15 – 7.06 (m, 1H), 6.97 (td, *J* = 7.2, 3.6 Hz, 2H), 6.90 – 6.77 (m, 2H), 6.32 (d, *J* = 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.4, 143.8 (d, J_{CP} = 3.4 Hz), 143.8, 140.2 (d, J_{CP} = 4.5 Hz), 137.7 (d, J_{CP} = 4.8 Hz), 137.4 (d, J_{CP} = 2.5 Hz), 135.5, 133.1, 133.0, 132.8, 131.8 (d, J_{CP} = 2.4 Hz), 131.5 (d, J_{CP} = 2.8 Hz), 131.0, 130.8, 130.3 (d, J_{CP} = 2.9 Hz), 129.1, 128.5, 128.1, 127.5, 127.2, 127.1, 126.8 (d, J_{CP} = 9.3 Hz), 126.2 (d, J_{CP} = 14.4 Hz), 125.5, 123.7 (d, J_{CP} = 127.8 Hz), 121.2, 108.0 (d, J_{CP} = 7.8 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.67; **HRMS (ESI)** calculated for $C_{29}H_{21}ClN_2OP$ $[M + H]^+$: 479.1075, found: 479.1075.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	29.357	23813252	52.88	242174
2	W2489 ChB 210nm	55.974	21219902	47.12	148758

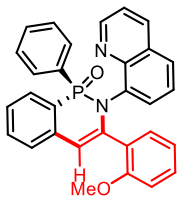
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	29.337	25496847	99.69	261044
2	W2489 ChB 210nm	55.955	78770	0.31	753

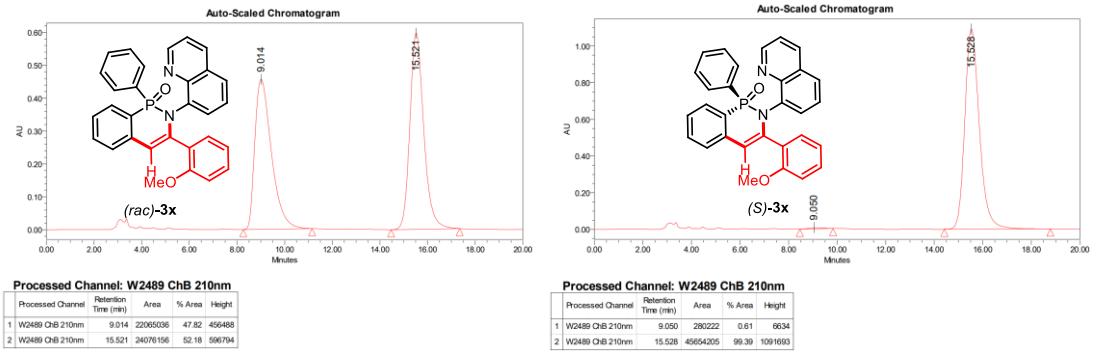
Synthetic Procedure and Characterization of 3x

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2x** (0.30 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was proformed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 2:1 v/v) to give the desired product **3x** (88.3 mg) in 93% yield as a light-yellow foam with 99% ee. Product exists as a 7:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(2-Methoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphini-ne 1-oxide (3x)



M.p.: 117 - 119 °C; $[\alpha]_D^{20}$ = +208.0 (c = 0.4, $CHCl_3$), 99% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (minor) = 9.050 min, t (mjaor) = 15.528 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.23 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.75-7.65 (m, 3H), 7.56-7.36 (m, 4H), 7.33 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.26 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.25-7.14 (m, 2H), 7.12 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.11-7.02 (m, 1H), 6.93 (td, *J* = 7.6, 3.6 Hz, 2H), 6.86 (td, *J* = 7.8, 2.0 Hz, 1H), 6.48-6.33 (m, 2H), 6.24 (d, *J* = 2.0 Hz, 1H), 3.71 (s, 3H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 156.2, 149.2, 144.4 (d, J_{CP} = 3.7 Hz), 143.3, 138.2 (d, J_{CP} = 4.7 Hz), 137.2 (d, J_{CP} = 2.4 Hz), 135.3, 133.3 (d, J_{CP} = 10.5 Hz), 131.7, 131.5 (d, J_{CP} = 2.5 Hz), 131.3 (d, J_{CP} = 2.9 Hz), 130.9 (d, J_{CP} = 11.0 Hz), 130.8, 129.5, 127.9, 127.5, 127.1 (d, J_{CP} = 4.1 Hz), 127.0 (d, J_{CP} = 13.5 Hz), 126.6 (d, J_{CP} = 9.2 Hz), 125.6 (d, J_{CP} = 14.4 Hz), 124.9, 124.1 (d, J_{CP} = 128.3 Hz), 121.1 (d, J_{CP} = 180.5 Hz), 120.7, 119.0, 109.3, 106.6 (d, J_{CP} = 7.3 Hz), 54.9; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 17.38; **HRMS (ESI)** calculated for $C_{30}H_{24}N_2O_2P$ $[M+H]^+$: 475.1570, found: 475.1574.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	9.014	22065036	47.82	456488
2	W2489 ChB 210nm	15.521	24076156	52.18	596794

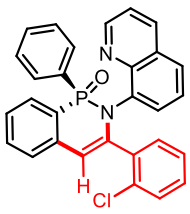
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	9.050	280222	0.61	6634
2	W2489 ChB 210nm	15.528	45654205	99.39	1091693

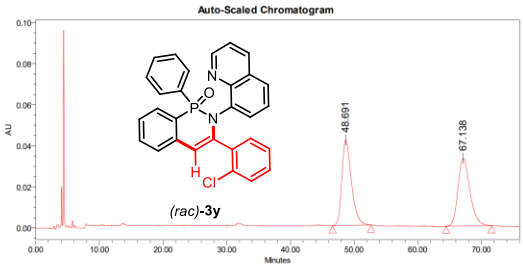
Synthetic Procedure and Characterization of 3y

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2y** (0.30 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product **3y** (88.1 mg) in 92% yield as a light-yellow foam with 99% ee. Product exists as a 8:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(2-Chlorophenyl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphini-ne 1-oxide (3y)

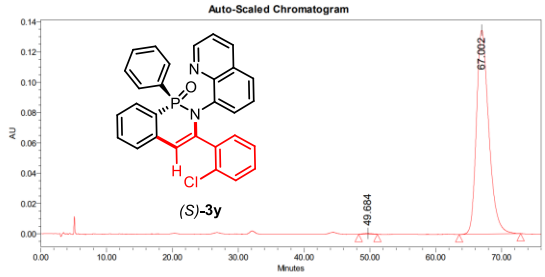


M.p.: 113 - 115 °C; $[\alpha]_D^{20}$ = +224.0 (c = 0.4, $CHCl_3$),99% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 48.684 min, t (mjaor) = 67.002 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.79 (dd, *J* = 4.4, 1.6Hz, 1H), 8.36 (d, *J* = 7.2 Hz, 1H), 7.74 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.71-7.63 (m, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.48-7.40 (m, 2H), 7.37-7.31 (m, 2H), 7.25-7.19 (m, 2H), 7.16 (dd, *J* = 8.2, 4.4 Hz, 1H), 7.09-7.02 (m, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.92 (td, *J* = 8.0, 3.2 Hz, 2H), 6.83 (td, *J* = 7.8, 1.6 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.25 (d, *J* = 2.4 Hz, 1H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 149.3, 144.3 (d, J_{CP} = 3.5 Hz), 142.5, 137.7 (d, J_{CP} = 4.7 Hz), 136.6 (d, J_{CP} = 4.1 Hz), 136.5 (d, J_{CP} = 2.5 Hz), 135.4, 133.7, 133.3 (d, J_{CP} = 10.6 Hz), 132.0, 131.7 (d, J_{CP} = 2.4 Hz), 131.4 (d, J_{CP} = 2.8 Hz), 131.0 (d, J_{CP} = 12.6 Hz), 130.7 (d, J_{CP} = 2.8 Hz), 129.2 (d, J_{CP} = 132.2), 129.1, 128.7, 128.0, 127.8, 127.0 (d, J_{CP} = 13.5 Hz), 126.8 (d, J_{CP} = 9.3 Hz), 126.1 (d, J_{CP} = 14.4 Hz), 125.4, 125.0, 123.78 (d, J_{CP} = 127.9 Hz), 121.0, 107.5 (d, J_{CP} = 7.5 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 17.51; **HRMS (ESI)** calculated for $C_{29}H_{21}ClN_2OP$ $[M + H]^+$: 479.1075, found: 479.1071.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	48.691	4366894	50.42	41665
2	W2489 ChA 254nm	67.138	4294049	49.58	32979



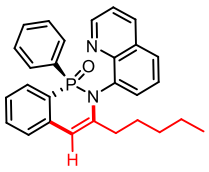
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	49.684	58538	0.33	626
2	W2489 ChA 254nm	67.002	17528194	99.67	134659

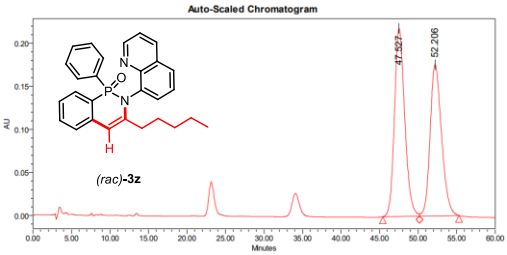
Synthetic Procedure and Characterization of 3z

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2z** (0.3 mmol, 1.5 eq.), $Co(OAc)_2{\bullet}4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the mixured **3z** and **3z'** (8:1, 76.2 mg) in 87% yield as a yellow oil with >99% ee. Major product exists as a 17:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-Pentyl-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3z)

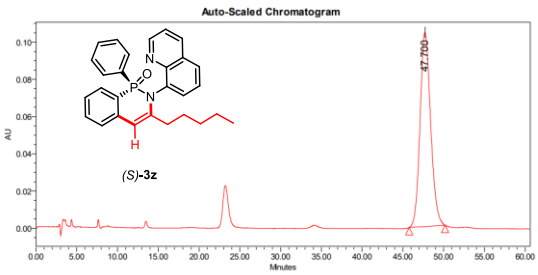


$[\alpha]_D^{20}$ = +399.9 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 230 nm, t_1 (major) = 47.527 min, t_1 (minor) = 52.206 min, t_2 (major) = 23.138 min, t_2 (minor) = 34.071 min..**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.82 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.48 (dd, *J* = 14.0, 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.14 (m, 9H), 7.12 – 7.01 (m, 2H), 6.99 – 6.95 (m, 4H), 6.56 – 6.53 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.3, 144.4 (d, J_{CP} = 3.6 Hz), 142.6, 139.3 (d, J_{CP} = 3.6 Hz), 138.7 (d, J_{CP} = 1.4 Hz), 137.6 (d, J_{CP} = 2.3 Hz), 136.6 (d, J_{CP} = 3.9 Hz), 135.5, 133.4 (d, J_{CP} = 10.5 Hz), 132.4, 131.6 (d, J_{CP} = 2.9 Hz), 131.4 (d, J_{CP} = 2.9 Hz), 131.4 (d, J_{CP} = 1.6 Hz), 131.0, 131.0, 130.2 (d, J_{CP} = 124.8 Hz), 128.2, 127.7, 127.4, 127.0 (d, J_{CP} = 13.6 Hz), 126.5, 126.4, 126.3, 125.8, 125.7 (d, J_{CP} = 14.6 Hz), 125.4, 123.7 (d, J_{CP} = 129.3 Hz), 121.0, 117.7 (d, J_{CP} = 7.3 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.12, 16.30; **HRMS (ESI)** calculated for $C_{28}H_{28}N_2OP$ $[M + H]^+$: 439.1934, found: 439.1932.



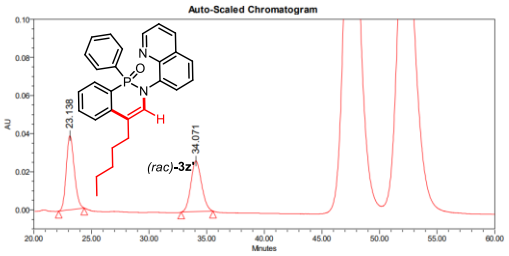
Processed Channel: W2489 ChB 230nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 230nm	47.527	20282990	52.71	218593
2	W2489 ChB 230nm	52.206	18194249	47.29	175832



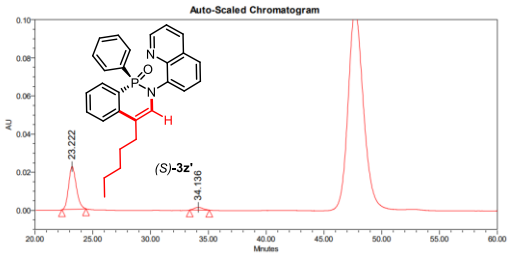
Processed Channel: W2489 ChB 230nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 230nm	47.700	9407308	100.00	104283



Processed Channel: W2489 ChB 230nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 230nm	23.138	1881591	52.23	38924
2	W2489 ChB 230nm	34.071	1720972	47.77	26586



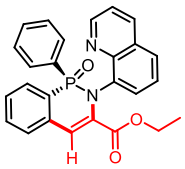
Processed Channel: W2489 ChB 230nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 230nm	23.222	1039365	93.34	22431
2	W2489 ChB 230nm	34.136	74150	6.66	1420

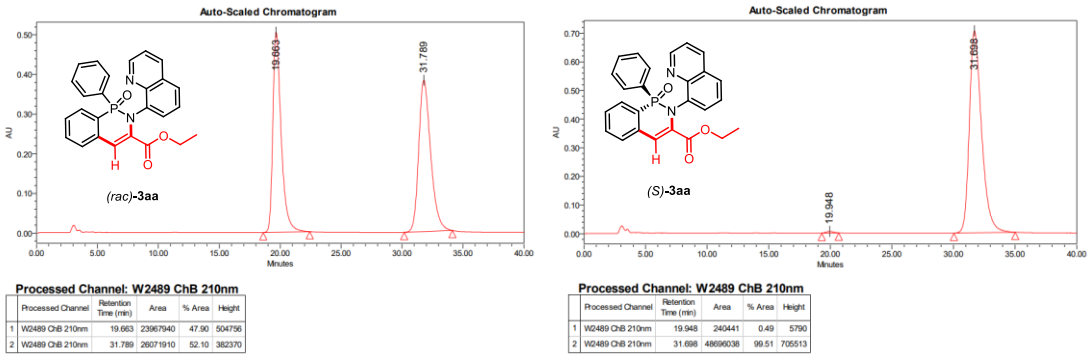
Synthetic Procedure and Characterization of 3aa

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2aa** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3aa** (70.4 mg) in 80% yield as a yellow oil with 99% ee.

Ethyl (*S*)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine-3-carboxylate 1-oxide (3aa)



$[\alpha]_D^{20}$ = +431.2 (c = 1.0, $CHCl_3$), 99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (minor) = 19.663min, t (major) = 31.789 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.15 (s, 1H), 7.96 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.62 – 7.54 (m, 4H), 7.53 – 7.42 (m, 2H), 7.38 – 7.29 (m, 2H), 7.28 – 7.25 (m, 1H),7.22 (s, 1H), 7.14 – 7.10 (m, 1H), 6.98 (s, 2H), 3.77 (q, *J* = 7.2 Hz, 2H), 0.68 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.0 (d, J_{CP} = 6.5 Hz), 149.4, 144.1 (d, J_{CP} = 1.4 Hz), 138.3, 135.8, 135.7 (d, J_{CP} = 4.5 Hz), 135.01, 132.8 (d, J_{CP} = 10.6 Hz), 131.9 (d, J_{CP} = 2.3 Hz), 131.6 (d, J_{CP} = 2.9 Hz), 131.02 (d, J_{CP} = 11.6 Hz), 128.3, 128.1, 128.0, 127.9, 127.3, 127.2, 126.4, 125.9 (d, J_{CP} = 125.7 Hz), 125.9, 121.1, 60.9, 13.4; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.02; **HRMS (ESI)** calculated for $C_{26}H_{22}N_2O_3P$ $[M + H]^+$: 441.1363, found: 441.1364.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	19.663	23967940	47.90	504756
2	W2489 ChB 210nm	31.789	26071910	52.10	382370

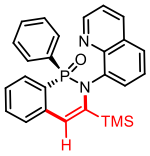
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	19.948	240441	0.49	5790
2	W2489 ChB 210nm	31.698	48696038	99.51	705513

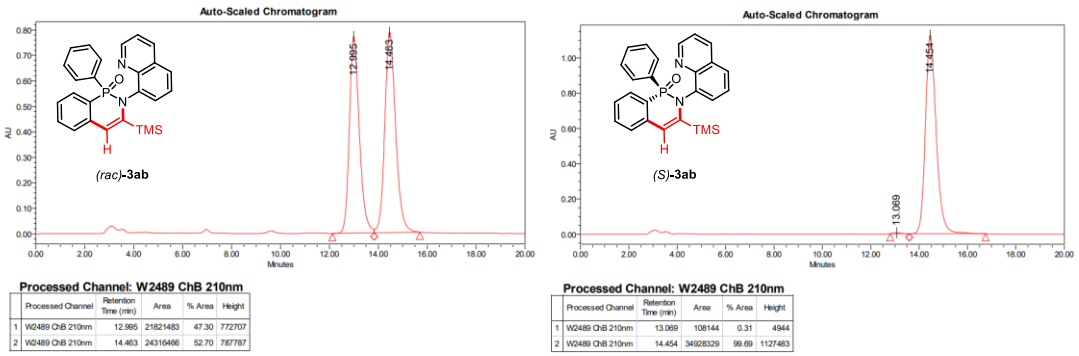
Synthetic Procedure and Characterization of 3ab

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2ab** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3ab** (67.7 mg) in 77% yield as a colorless oil with >99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1-Phenyl-2-(quinolin-8-yl)-3-(trimethylsilyl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3ab)



$[\alpha]_D^{20}$ = +462.0 (c = 0.5, $CHCl_3$), >99% ee, lit[1d]: $[\alpha]_D^{20}$ = +537.7 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (minor) = 12.995 min, t (major) = 14.463 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.22 (d, *J* = 7.2 Hz, 1H), 7.95 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.66 – 7.48 (m, 4H), 7.48 – 7.35 (m, 3H), 7.28 – 7.20 (m, 2H), 7.04 (td, *J* = 7.2, 1.2 Hz, 1H), 6.90 (td, *J* = 7.6, 3.2 Hz, 2H), -0.34 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.9, 148.4 (d, J_{CP} = 4.6 Hz), 146.1 (d, J_{CP} = 3.4 Hz), 138.0 (d, J_{CP} = 2.2 Hz), 137.1 (d, J_{CP} = 3.6 Hz), 135.6, 133.4, 133.3, 132.5 (d, J_{CP} = 2.6 Hz), 131.4 (d, J_{CP} = 1.9 Hz), 131.1 (d, J_{CP} = 2.3 Hz), 130.4 (d, J_{CP} = 12.0 Hz), 128.7, 128.3, 126.7, 126.6, 126.5, 126.2 (d, J_{CP} = 14.4 Hz), 125.6, 123.9 (d, J_{CP} = 128.6 Hz), 121.2, 115.1 (d, J_{CP} = 11.3 Hz), 0.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.27; **HRMS (ESI)** calculated for$C_{26}H_{26}N_2OPSi$ $[M + H]^+$: 441.1547, found: 441.1551.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	12.995	21821483	47.30	772707
2	W2489 ChB 210nm	14.463	24316466	52.70	787787

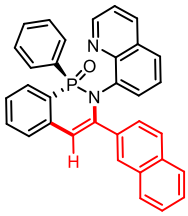
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	13.069	108144	0.31	4944
2	W2489 ChB 210nm	14.454	34928329	99.69	1127483

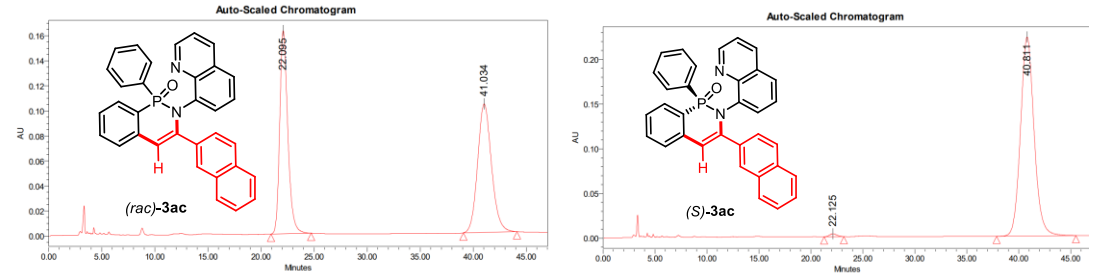
Synthetic Procedure and Characterization of 3ac

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2ac** (0.30 mmol, 1.5 eq.), $Co(OAc)_2·4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **3ac** (88.0 mg) in 89% yield as a light-yellow foam with 98% ee. Product exists as a 8:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(Naphthalen-2-yl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphini-ne 1-oxide (3ac)



M.p.: 120 - 122 °C; $[\alpha]_D^{20}$ = +288.0 (c = 0.2, $CHCl_3$), 99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 22.125 min, t (mjaor) = 40.811 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.74 (dd, *J* = 4.4 1.6 Hz, 1H), 8.18 (d, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 1.6 Hz, 1H), 7.76-7.65 (m, 2H), 7.66 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.59-7.52 (m, 4H), 7.51-7.47 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.32-7.25 (m, 4H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.14-7.08 (m, 1H), 7.08-7.05 (m, 1H), 6.98 (td, *J* = 7.8, 3.6 Hz, 2H), 6.44 (d, *J* = 2.0 Hz, 1H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 149.2, 145.1, 144.1 (d, J_{CP} = 3.1 Hz), 138.0 (d, J_{CP} = 5.1 Hz), 137.7 (d, J_{CP} = 1.9 Hz), 136.0 (d, J_{CP} = 4.4 Hz), 135.4, 133.03 132.9, 132.4 (d, J_{CP} = 5.4 Hz), 131.8 (d, J_{CP} = 2.4 Hz), 131.6 (d, J_{CP} = 135.8 Hz), 131.4 (d, J_{CP} = 2.9 Hz), 130.9 (d, J_{CP} = 12.4 Hz), 130.3 (d, J_{CP} = 2.8 Hz), 128.4, 128.2 (d, J_{CP} = 20.5 Hz), 127.3, 127.2, 127.1 (d, J_{CP} = 13.6 Hz), 126.8, 126.7, 126.6, 126.4, 126.1, 125.9, 125.7, 125.4, 124.2 (d, J_{CP} = 126.7 Hz), 1201.0, 108.4 (d, J_{CP} = 7.7 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.98; **HRMS (ESI)** calculated for $C_{33}H_{24}N_2OP$ $[M+H]^+$: 495.1621, found: 495.1618.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	22.095	8561767	47.85	162334
2	W2489 ChA 254nm	41.034	9331572	52.15	102686

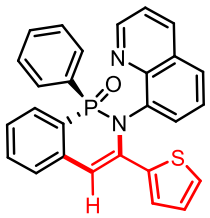
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	22.125	153273	0.75	3126
2	W2489 ChA 254nm	40.811	20241493	99.25	222677

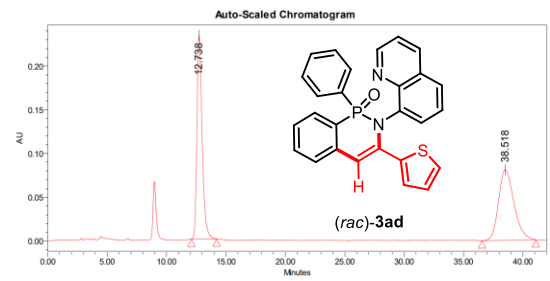
Synthetic Procedure and Characterization of 3ad

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2ad** (0.30 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product **3ad** (63.1 mg) in 70% yield as a light-yellow foam with 99% ee. Product exists as a 8:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1-Phenyl-2-(quinolin-8-yl)-3-(thiophen-2-yl)-*2H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3ad)

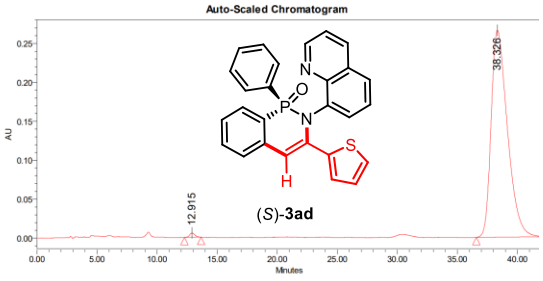


M.p.: 105 - 107 °C; $[\alpha]_D^{20}$ = +378.7 (c = 0.5, $CHCl_3$), 99% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 12.915 min, t (mjaor) = 38.326 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (d, *J* = 4.4 Hz, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.70 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.53 – 7.44 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.26 – 7.18 (m, 2H), 7.13 – 7.09 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 4.8 Hz, 1H), 6.78 (s, 1H), 6.53 (s, 1H), 6.46 (d, *J* = 4.4 Hz, 1H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 149.6, 144.5 (d, J_{CP} = 3.0 Hz), 140.4z (d, J_{CP} = 4.9 Hz), 138.3, 137.7 (d, J_{CP} = 5.4 Hz), 137.42 (d, J_{CP} = 1.8 Hz), 135.5, 133.0 (d, J_{CP} = 10.6 Hz), 131.8 (d, J_{CP} = 2.2 Hz), 131.56 (d, J_{CP} = 2.6 Hz), 130.8 (d, J_{CP} = 12.0 Hz), 130.4 (d, J_{CP} = 2.6 Hz), 130.1 (d, J_{CP} = 135.8 Hz), 128.4, 127.8, 127.6, 127.2 (d, J_{CP} = 13.7 Hz), 126.9 (d, J_{CP} = 9.1 Hz), 126.3 (d, J_{CP} = 14.0 Hz), 125.9, 125.6 (d, J_{CP} = 12.4 Hz), 1234.1 (d, J_{CP} = 126.3 Hz), 121.2, 111.7 (d, J_{CP} = 7.2 Hz), 108.5 (d, J_{CP} = 7.5 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 19.30; **HRMS (ESI)** calculated for $C_{27}H_{20}N_2OPS$ $[M + H]^+$: 451.1028, found: 451.1025.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	12.738	7091135	49.48	233024
2	W2489 ChA 254nm	38.518	7238936	50.52	80620



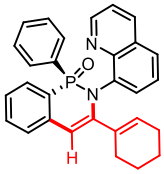
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	12.915	161904	0.64	5421
2	W2489 ChA 254nm	38.326	25018902	99.36	265556

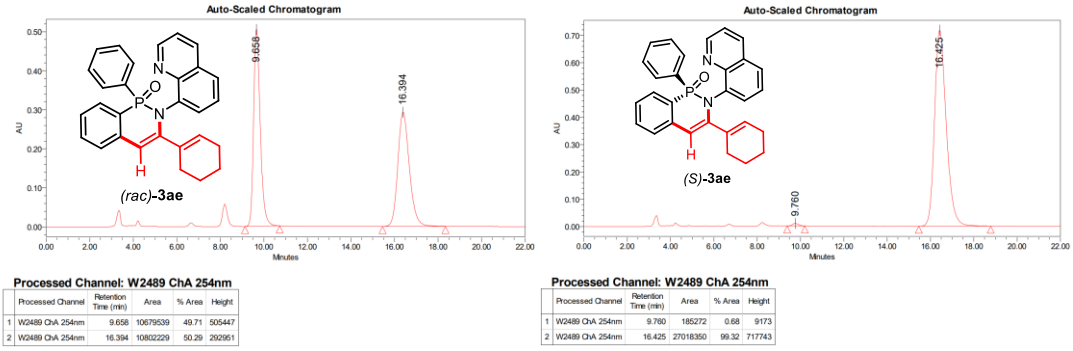
Synthetic Procedure and Characterization of 3ae

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2ae** (0.30 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3ae** (79.8 mg) in 89% yield as a light-yellow foam with 99% ee. Product exists as a 7:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(Cyclohex-1-en-1-yl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphi-nine 1-oxide (3ae)



M.p.: 85 - 86 °C; $[\alpha]_D^{20}$ = +331.6 (c = 0.2, $CHCl_3$), 99% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 9.760 min, t (mjaor) = 16.425 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (d, *J* = 4.0 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.54—7.44 (m, 2H), 7.43-7.36 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.24 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.21-7.14 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.98 (td, *J* = 7.8, 3.2 Hz, 2H), 6.18 (d, *J* = 2.0 Hz, 1H), 5.72 (t, *J* = 4.0 Hz, 1H), 2.07-1.96 (m, 2H), 1.67-1.38 (m, 2H), 1.17-0.96(m, 4H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 149.3, 147.4, 144.8 (d, J_{CP} = 3.4 Hz), 138.3 (d, J_{CP} = 5.0 Hz), 138.0 (d, J_{CP} = 2.4 Hz), 135.5, 135.3 (d, J_{CP} = 4.0 Hz), 133.1 (d, J_{CP} = 10.5 Hz), 131.6 (d, J_{CP} = 2.5 Hz), 131.4 (d, J_{CP} = 121.2 Hz), 131.3 (d, J_{CP} = 2.7 Hz), 130.7 (d, J_{CP} = 12.2 Hz), 130.4, 130.3 (d, J_{CP} = 2.9 Hz), 128.5, 127.1, 126.9, 126.4 (d, J_{CP} = 9.4 Hz), 125.5, 125.4, 124.0 (d, J_{CP} = 127.5 Hz), 121.0, 104.8 (d, J_{CP} = 7.7 Hz), 28.1, 25.0, 22.3, 21.6; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.61; **HRMS (ESI)** calculated for $C_{29}H_{26}N_2OP$ $[M + H]^+$: 449.1777, found: 449.1776.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	9.658	10679539	49.71	505447
2	W2489 ChA 254nm	16.394	10802229	50.29	292951

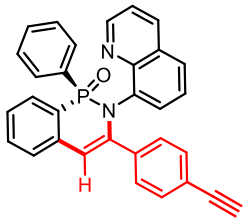
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	9.760	185272	0.68	9173
2	W2489 ChA 254nm	16.425	27018350	99.32	717743

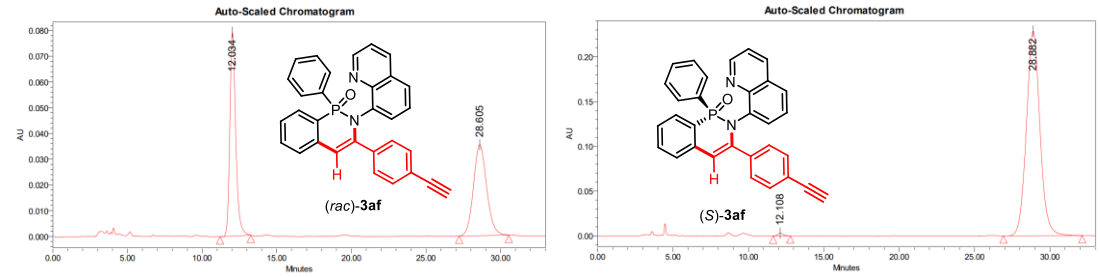
Synthetic Procedure and Characterization of 3af

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2af** (0.30 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 5:1 v/v) to give the desired product **3af** (60.9 mg) in 65% yield as a light-yellow foam with 99% ee. Product exists as a 9:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(4-Ethynylphenyl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphini-ne 1-oxide (3af)



M.p.: 197 - 200 °C; $[\alpha]_D^{20}$ = +341.2 (c = 0.5, $CHCl_3$), 99% ee; The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 12.108 min, t (mjaor) = 28.882 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.75 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.66 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.49-7.43 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.26-7.21 (m, 2H), 7.15-7.08 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.97 (td, *J* = 7.8, 3.2 Hz, 2H), 6.32 (d, *J* = 2.0 Hz, 1H), 2.94 (s, 1H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 149.3, 144.4, 143.8 (d, J_{CP} = 3.2 Hz), 139.0 (d, J_{CP} = 4.3 Hz), 137.8 (d, J_{CP} = 4.8 Hz), 137.5, 135.5, 133.0 (d, J_{CP} = 10.5 Hz), 131.8 (d, J_{CP} = 2.1 Hz), 131.6 (d, J_{CP} = 136.0 Hz), 131.5 (d, J_{CP} = 2.9 Hz), 130.9, 130.8, 130.2 (d, J_{CP} = 2.8 Hz), 128.8, 128.4, 127.4, 127.2 (d, J_{CP} = 13.5 Hz), 126.8 (d, J_{CP} = 9.1 Hz), 126.2 (d, J_{CP} = 14.4 Hz), 125.5, 124.3 (d, J_{CP} = 127.3 Hz), 121.1, 120.9, 108.0 (d, J_{CP} = 7.6 Hz), 83.3, 77.6; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.76; **HRMS (ESI)** calculated for $C_{31}H_{22}N_2OP$ $[M+H]^+$: 469.1464, found: 469.1465.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	12.034	2167344	49.92	79201
2	W2489 ChA 254nm	28.605	2174490	50.08	35353

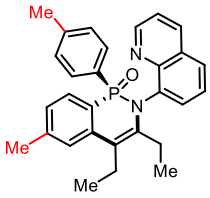
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	12.108	81682	0.57	3085
2	W2489 ChA 254nm	28.882	14330399	99.43	228554

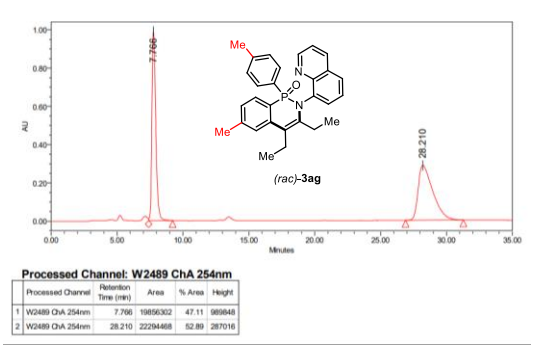
Synthetic Procedure and Characterization of 3ag

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1b** (0.2 mmol, 1.0 eq.), alkyne **2l** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product (*S*)-**3ag** (68.7 mg) in 76% yield as a white solid with 99% ee. Product exists as a 9:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Diethyl-6-methyl-2-(quinolin-8-yl)-1-(*p*-tolyl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3ag)

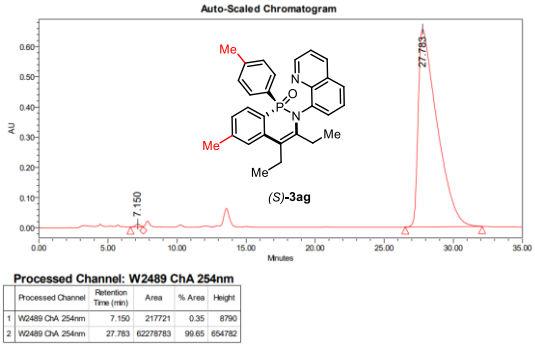


M.p.: 65 - 71 °C, 99% ee; $[\alpha]_D^{20}$ = +397.1 (c = 0.5, $CHCl_3$), lit[1d]: $[\alpha]_D^{20}$ = +399.9 [c = 0.5, $CHCl_3$, 99% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 27.783 min, t (minor) = 7.150 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 7.95 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.52 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.33 – 7.25 (m, 2H), 7.19 (dd, *J* = 14.4, 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.0, 3.2 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.49 – 2.43 (m, 4H), 2.07 (s, 3H), 1.76 (dq, *J* = 14.8, 7.2 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.0, 145.4 (d, J_{CP} = 3.5 Hz), 142.3, 141.4 (d, J_{CP} = 2.9 Hz), 141.3 (d, J_{CP} = 2.5 Hz), 139.0 (d, J_{CP} = 4.5 Hz), 137.7 (d, J_{CP} = 2.5 Hz), 135.8, 133.3 (d, J_{CP} = 10.5 Hz), 130.8 (d, J_{CP} = 13.0 Hz), 130.5 (d, J_{CP} = 3.4 Hz), 128.5, 127.7 (d, J_{CP} = 13.6 Hz), 127.5 (d, J_{CP} = 137.9 Hz), 127.2, 125.9 (d, J_{CP} = 15.0 Hz), 125.8, 123.8 (d, J_{CP} = 9.8 Hz), 122.4 (d, J_{CP} = 132.0 Hz), 121.2, 114.0 (d, J_{CP} = 8.4 Hz), 24.8 (d, J_{CP} = 2.5 Hz), 22.4, 22.2, 21.3, 15.0, 13.2; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.70; **HRMS (ESI)** calculated for $C_{29}H_{30}N_2OP$ $[M+H]^+$: 453.2090, found: 453.2091.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	7.766	19856302	47.11	989848
2	W2489 ChA 254nm	28.210	22294468	52.89	287016



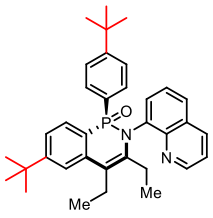
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	7.150	217721	0.35	8790
2	W2489 ChA 254nm	27.783	62278783	99.65	654782

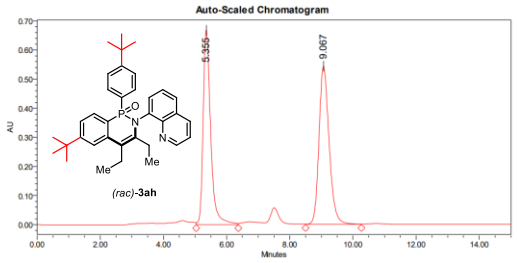
Synthetic Procedure and Characterization of 3ah

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1c** (0.2 mmol, 1.0 eq.), alkyne **2l** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 2:1 v/v) to give the desired product (*S*)-**3ah** (101.8 mg) in 95% yield as a yellow foam with 99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-6-(*tert*-Butyl)-1-(4-(*tert*-butyl)phenyl)-3,4-diethyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3ah)

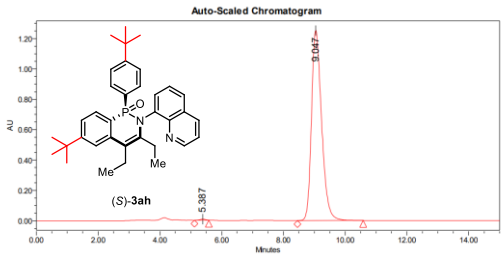


M.p.: 87 - 91 °C, 99% ee; $[\alpha]_D^{20}$ = +204.4 (c = 0.5, $CHCl_3$). The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 9.047 min, t (minor) = 5.387 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.74 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.08 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.92 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.69 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.41 (dd, *J* = 12.4, 8.4 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.25 – 7.22 (m, 2H), 6.88(dd, *J* = 8.4, 3.2 Hz, 2H), 2.83 – 2.77 (m, 2H), 2.53 – 2.43 (m, 1H), 1.88 – 1.78 (m, 1H), 1.38 (s, 9H), 1.34 (t, *J* = 7.6 Hz, 3H), 1.04 (s, 9H), 0.95 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.4 (d, J_{CP} = 2.9 Hz), 154.3 (d, J_{CP} = 2.5 Hz), 150.0, 145.4 (d, J_{CP} = 3.4 Hz), 142.2, 138.7 (d, J_{CP} = 4.5 Hz), 137.4 (d, J_{CP} = 2.3 Hz), 135.7, 133.1 (d, J_{CP} = 10.5 Hz), 131.2 (d, J_{CP} = 3.3 Hz), 130.6 (d, J_{CP} = 13.0 Hz), 128.6, 127.4 (d, J_{CP} = 138.0 Hz), 127.3, 125.8, 123.6 (d, J_{CP} = 13.6 Hz), 122.4 (d, J_{CP} = 14.6 Hz), 121.5 (d, J_{CP} = 131.2 Hz), 121.1, 120.2 (d, J_{CP} = 9.7 Hz), 113.7 (d, J_{CP} = 8.2 Hz), 35.2, 34.6, 31.3, 30.9, 24.9 (d, J_{CP} = 2.6 Hz), 22.4, 15.0, 13.4.; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.85; **HRMS (ESI)** calculated for $C_{35}H_{42}N_2OP$ $[M + H]^+$: 537.3029, found: 537.3027.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	5.355	11045550	47.66	669952
2	W2489 ChA 254nm	9.067	12131763	52.34	543156



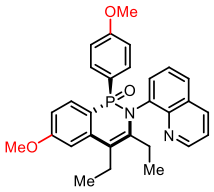
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	5.387	85670	0.30	6882
2	W2489 ChA 254nm	9.047	28503749	99.70	1252299

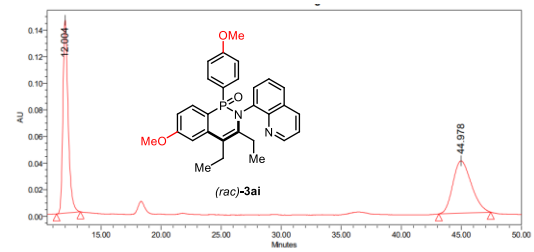
Synthetic Procedure and Characterization of 3ai

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1d** (0.2 mmol, 1.0 eq.), alkyne **2l** (0.3 mmol, 1.5 eq.), $Co(OAc)_2·4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:2 v/v) to give the desired product (*S*)-**3ai** (83.3 mg) in 86 % yield as a white solid with >99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Diethyl-6-methoxy-1-(4-methoxyphenyl)-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3ai)

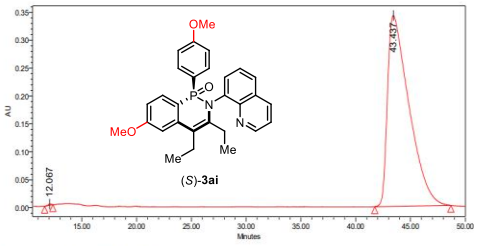


M.p.: 67 - 72 °C; >99% ee; $[\alpha]_D^{20}$ = +499.5 (c = 0.5, $CHCl_3$), lit[1d]: $[\alpha]_D^{20}$ = +502.4 [c = 0.5, $CHCl_3$, >99% ee (*S*)] The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 43.437 min, t (minor) = 12.067 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.75 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.47 (dd, *J* = 12.4, 8.8 Hz, 2H), 7.32 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.13 (dd, *J* = 4.4, 2.4 Hz, 1H), 6.73 (dt, *J* = 8.4, 2.0 Hz, 1H), 6.40 (dd, *J* = 8.8, 2.4 Hz, 2H), 3.85 (s, 3H), 3.57 (s, 3H), 2.75 – 2.69 (m, 2H), 2.47 – 2.41 (m, 1H), 1.75 (dq, *J* = 14.8, 7.2 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.0 (d, J_{CP} = 2.9 Hz), 161.8 (d, J_{CP} = 2.9 Hz), 150.0, 145.3 (d, J_{CP} = 2.9 Hz), 142.9, 141.0 (d, J_{CP} = 5.3 Hz), 137.5 (d, J_{CP} = 1.4 Hz), 135.8, 135.1 (d, J_{CP} = 11.6 Hz), 132.6 (d, J_{CP} = 13.9 Hz), 130.6 (d, J_{CP} = 2.6 Hz),, 128.5, 127.4, 125.8, 122.0 (d, J_{CP} = 143.0 Hz), 121.2, 117.7 (d, J_{CP} = 135.9 Hz), 113.4 (d, J_{CP} = 8.0 Hz), 112.4 (d, J_{CP} = 14.5 Hz), 111.3 (d, J_{CP} = 15.3 Hz), 108.2 (d, J_{CP} = 10.4 Hz), 55.2, 55.0, 24.9, 22.5, 14.9, 13.3.; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.54; **HRMS (ESI)** calculated for $C_{29}H_{30}N_2O_3P$ $[M + H]^+$: 485.1989, found: 485.1976;



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	12.004	4381771	51.08	145170
2	W2489 ChA 254nm	44.978	4195759	48.92	39259



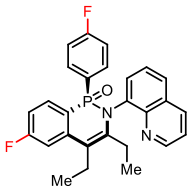
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	12.067	46605	0.10	2287
2	W2489 ChA 254nm	43.437	46576516	99.90	341907

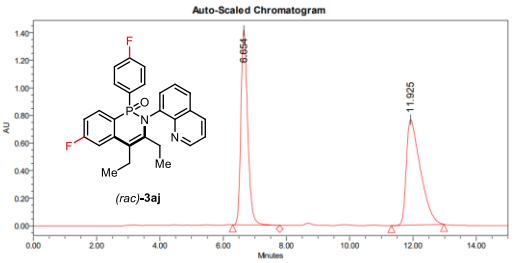
Synthetic Procedure and Characterization of 3aj

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1e** (0.2 mmol, 1.0 eq.), alkyne **2l** (0.3 mmol, 1.5 eq.), $Co(OAc)_2 \cdot 4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 8 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product (*S*)-**3aj** (89.3 mg) in 97% yield as a white foam with 99% ee. Product exists as a 12:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Diethyl-6-fluoro-1-(4-fluorophenyl)-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3aj)

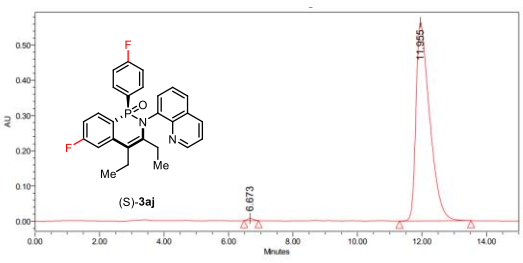


M. p.: 164 - 166 °C; 99% ee; $[\alpha]_D^{20}$ = +451.2 (c = 0.5, $CHCl_3$), lit[1d]: $[\alpha]_D^{20}$ = +472.8 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 11.955 min, t (minor) = 6.673 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.06 (dt, *J* = 7.6, 1.6 Hz, 1H) , 7.99 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60 – 7.51 (m, 3H), 7.38 – 7.27 (m, 4H), 6.90 (tt, *J* = 8.4, 2.0 Hz, 1H), 6.59 (td, *J* = 8.8, 2.4 Hz, 2H), 2.77 – 2.67 (m, 2H), 2.46 (ddd, *J* = 14.8, 7.6, 2.0 Hz, 1H), 1.79 (dq, *J* = 14.8, 7.6 Hz, 1H), 1.31 (t, *J* = 7.6 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.2 (dd, J_{CF} = 247.7, J_{CP} = 3.2 Hz), 164.7 (dd, J_{CF} = 251.4, J_{CP} = 3.4 Hz), 150.3, 145.2 (d, J_{CP} = 3.6 Hz), 143.9, 142.1 (dd, J_{CF} = 8.4, J_{CP} = 5.5 Hz), 137.0 (d, J_{CP} = 2.6 Hz), 136.0, 135.7 (dd, J_{CF} = 11.7, J_{CP} = 8.8 Hz), 133.3 (dd, J_{CF} = 13.8, J_{CP} = 9.5 Hz), 130.9 (d, J_{CP} = 3.1 Hz), 128.7, 127.9, 126.5 (dd, J_{CP} = 140.4, J_{CF} = 3.0 Hz), 125.8, 121.5, 120.5 (dd, J_{CP} = 133.2, J_{CF} = 2.3 Hz), 114.3 (dd, J_{CF} = 21.2, J_{CP} = 14.6 Hz), 113.3 (dd, J_{CF} = 7.8, J_{CP} = 2.3 Hz), 112.8 (dd, J_{CF} = 22.5, J_{CP} =14.7 Hz), 110.0 (dd, J_{CF} = 22.3, J_{CP} = 10.6 Hz), 25.0 (d, J_{CP} = 2.7 Hz), 22.5, 14.7, 13.3.; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -107.39, -107.52 (d, J_{FP} = 1.5 Hz), **^{31}P NMR (162 MHz, $CDCl_3$)** δ 14.66; **HRMS (ESI)** calculated for $C_{27}H_{24}F_2N_2OP$ $[M + H]^+$: 461.1589, found: 461.1591;



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	6.654	21147734	47.14	1413808
2	W2489 ChA 254nm	11.925	23710811	52.86	766522



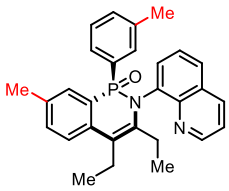
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	6.673	80414	0.48	5928
2	W2489 ChA 254nm	11.955	16779984	99.52	564242

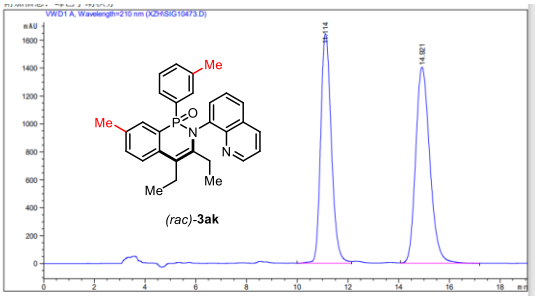
Synthetic Procedure and Characterization of 3ak

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1f** (0.2 mmol, 1.0 eq.), alkyne **2l** (0.3 mmol, 1.5 eq.), $Co(OAc)_2·4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of *t*-BuOH / H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product (*S*)-**3ak** (74.2 mg) in 82% yield as a light-yellow foam with 99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Diethyl-7-methyl-2-(quinolin-8-yl)-1-(*m*-tolyl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3ak)



M. p.: 189 - 190 °C; 99% ee; $[\alpha]_D^{20}$ = +620.9 (c = 0.5, $CHCl_3$). The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 14.940 min, t (minor) = 11.165 min.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.43 – 7.25 (m, 5H), 7.15 (d, *J* = 15.6 Hz, 1H), 6.88 – 6.80 (m, 2H), 2.76 (q, *J* = 7.2 Hz, 2H), 2.49 – 2.43 (m, 1H), 2.24 (s, 3H), 1.93 (s, 3H), 1.93 – 1.77 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.9, 145.5, 141.3, 137.6 (d, J_{CP} = 2.6 Hz), 136.4 (d, J_{CP} = 18.3 Hz), 136.4, 135.8, 134.5 (d, J_{CP} = 14.6 Hz), 133.7 (d, J_{CP} = 10.3 Hz), 132.5 (d, J_{CP} = 2.6 Hz), 131.9 (d, J_{CP} = 2.9 Hz), 130.7 (d, J_{CP} = 8.1 Hz), 130.6 (d, J_{CP} = 2.3 Hz), 130.5 (d, J_{CP} = 135.0 Hz), 130.4 (d, J_{CP} = 10.1 Hz), 128.5, 127.3, 126.68 (d, J_{CP} = 14.0 Hz), 125.8, 124.7 (d, J_{CP} = 128.7 Hz), 123.5 (d, J_{CP} = 10.0 Hz), 121.1, 114.0 (d, J_{CP} = 8.2 Hz), 24.7, 22.4, 20.9, 20.8, 14.9, 13.4.; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.72; **HRMS (ESI)** calculated for $C_{29}H_{30}N_2OP$ $[M + H]^+$: 453.2090, found: 453.2081;

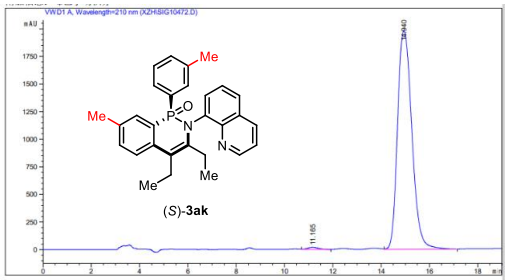


面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, Wavelength=210 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.114	BV	0.4567	4.80692e4	1641.24426	46.8883
2	14.921	VB	0.6027	5.44493e4	1403.01135	53.1117
总量 :				1.02518e5	3044.25562	



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

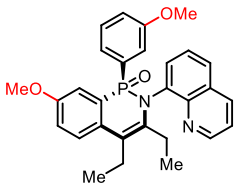
信号 1: VWD1 A, Wavelength=210 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.165	VV	0.4462	604.42206	20.56963	0.7378
2	14.940	VB	0.6490	8.13230e4	1976.06885	99.2622
总量 :				8.19274e4	1996.63848	

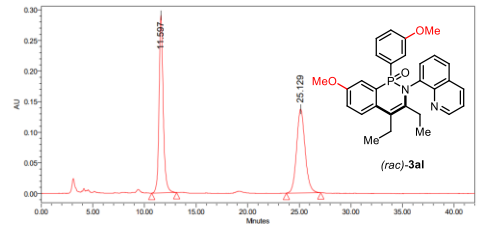
Synthetic Procedure and Characterization of 3al

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1g** (0.2 mmol, 1.0 eq.), alkyne **2l** (0.3 mmol, 1.5 eq.), $Co(OAc)_2 \cdot 4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 8 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product (*S*)-**3al** (90.0 mg) in 93 % yield as a light-yellow foam with 97% ee. Product exists as a 11:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Diethyl-7-methoxy-1-(3-methoxyphenyl)-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]-azaphosphinine 1-oxide (3al)

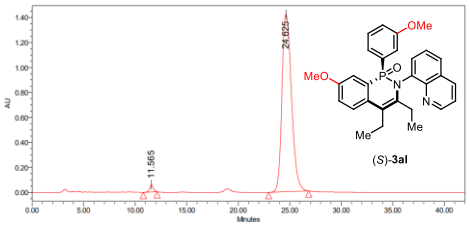


M. p.: 154 - 156 °C; 97% ee; $[\alpha]_D^{20}$ = +530.7 (c = 0.5, $CHCl_3$). The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 24.625 min, t (minor) = 11.565 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.79 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.96 – 7.94 (m, 1H), 7.62 – 7.54 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.18 (m, 2H), 7.15 – 7.11 (m, 1H), 6.90 (td, *J* = 8.0, 4.0 Hz, 1H), 6.84(dd, *J* = 15.6, 2.8 Hz, 1H),6.66 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.67 (s, 3H), 3.39 (s, 3H), 2.76 – 2.70 (m, 2H), 2.41 – 2.35 (m, 1H), 1.80 (dq, *J* = 14.8, 7.6 Hz, 1H), 1.27 (t, *J* = 7.6 Hz, 3H), 0.92 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 158.4 (d, J_{CP} = 16.3 Hz), 157.1 (d, J_{CP} = 17.6 Hz), 150.0, 145.6 (d, J_{CP} = 3.7 Hz), 139.8, 137.6 (d, J_{CP} = 2.6 Hz), 136.0, 132.4 (d, J_{CP} = 4.1 Hz), 132.2 (d, J_{CP} = 133.8 Hz), 130.4 (d, J_{CP} = 3.5 Hz), 128.7, 128.2 (d, J_{CP} = 15.9 Hz), 127.3, 126.1 (d, J_{CP} = 10.3 Hz),126.0 (d, J_{CP} = 128.8Hz) 125.9, 125.4 (d, J_{CP} = 11.5 Hz), 121.2, 119.1 (d, J_{CP} = 2.6 Hz), 118.8 (d, J_{CP} = 2.8 Hz), 116.6 (d, J_{CP} = 11.4 Hz), 115.2 (d, J_{CP} = 8.2 Hz), 113.6 (d, J_{CP} = 13.6 Hz), 55.5, 55.1, 24.5 (d, J_{CP} = 2.5 Hz), 22.5, 15.0, 13.4.; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.61; **HRMS (ESI)** calculated for $C_{29}H_{30}N_2O_3P$ $[M + H]^+$: 485.1989, found: 485.1995;



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	11.597	8083975	50.83	290176
2	W2489 ChB 210nm	25.129	7821088	49.17	136812



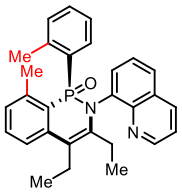
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	11.565	1465570	1.58	58097
2	W2489 ChB 210nm	24.625	91540338	98.42	1417944

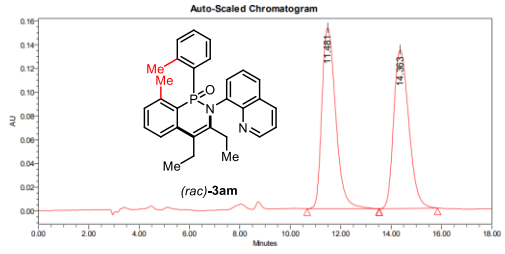
Synthetic Procedure and Characterization of 3am

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1h** (0.2 mmol, 1.0 equiv), alkyne **2l** (0.3 mmol, 1.5 equiv), $Co(OAc)_2·4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 equiv) were placed in a 15 mL cell and dissolved in 4.0 mL of *t*-BuOH / H_2O (3.0:1.0). Electrocatalysis was performed at 70 °C with a constant current of 3 mA maintained for 20 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product (*S*)-**3am** (61.5 mg) in 68% yield as a white foam with >99% ee. Product exists as a 16:1 mixture of atropisomers due to the hindered rotation about the N-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Diethyl-8-methyl-2-(quinolin-8-yl)-1-(*o*-tolyl)-2H-benzo[*c*][1,2]azaphosphinine 1-oxide (3am)

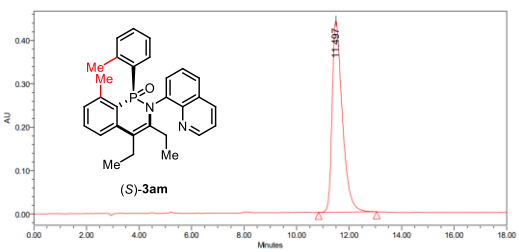


M. p.: 188 - 190 °C; >99% ee; $[\alpha]_D^{20}$ = +459.6 (c = 0.5, $CHCl_3$), lit[1d]: $[\alpha]_D^{20}$ = +452.4 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, t (single peak) = 11.497 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.64 (d, *J* = 2.4 Hz, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.55 – 7.52 (m, 1H), 7.48 – 7.40 (m, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 8.4, 4.4 Hz, 1H), 6.94 (dd, *J* = 7.6, 4.4 Hz, 1H), 6.87 – 6.78 (m, 2H), 6.50 (t, *J* = 6.4 Hz, 1H), 2.82 – 2.65 (m, 1H), 2.56 – 2.48 (m, 2H), 2.06 (s, 3H), 1.82 – 1.73 (m, 4H), 1.30 (t, *J* = 7.6 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.4, 145.3 (d, J_{CP} = 2.6 Hz), 142.1 (d, J_{CP} = 2.2 Hz), 141.9 (d, J_{CP} = 10.2 Hz), 140.4 (d, J_{CP} = 11.7 Hz), 139.6 (d, J_{CP} = 4.7 Hz), 137.1 (d, J_{CP} = 3.3 Hz), 135.6, 134.7 (d, J_{CP} = 9.5 Hz), 131.2 (d, J_{CP} = 2.3 Hz), 131.1 (d, J_{CP} = 2.0 Hz), 130.9 (d, J_{CP} = 130.5 Hz), 130.8, 130.4 (d, J_{CP} = 12.4 Hz), 128.3, 127.5 (d, J_{CP} = 12.9 Hz), 127.2, 125.5, 124.3 (d, J_{CP} = 13.0 Hz), 124.1 (d, J_{CP} = 128.1 Hz), 122.0 (d, J_{CP} = 9.6 Hz), 121.0, 112.6 (d, J_{CP} = 8.4 Hz), 25.0, 23.0, 21.5, 21.4, 15.1, 13.3; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 11.81; **HRMS (ESI)** calculated for $C_{29}H_{30}N_2OP$ $[M + H]^+$: 453.2090, found: 453.2099;



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	11.481	5825811	51.10	152430
2	W2489 ChA 254nm	14.363	5574764	48.90	133659



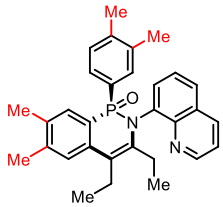
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	11.497	11919591	100.00	441220

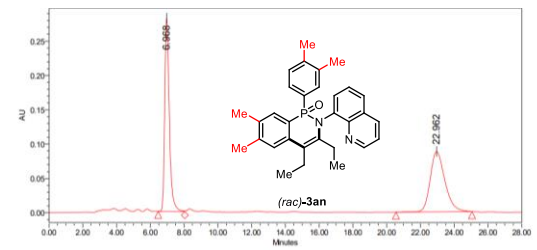
Synthetic Procedure and Characterization of 3an

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1i** (0.2 mmol, 1.0 equiv), alkyne **2l** (0.3 mmol, 1.5 equiv), $Co(OAc)_2·4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 equiv) were placed in a 15 mL cell and dissolved in 4.0 mL of *t*-BuOH / H_2O (3.0:1.0). Electrocatalysis was performed at 60 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 2:1 v/v) to give the desired product (*S*)-**3an** (80.6 mg) in 84% yield as a light-yellow foam with >99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1-(3,4-Dimethylphenyl)-3,4-diethyl-6,7-dimethyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]-azaphosphinine 1-oxide (3an)

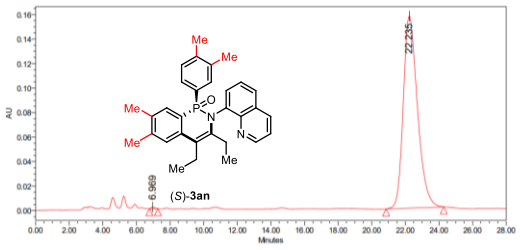


M. p.: 89 - 90 °C; >99% ee; $[\alpha]_D^{20}$ = +390.2 (c = 0.5, $CHCl_3$), lit[1d]: $[\alpha]_D^{20}$ = +377.4 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 22.235 min, t (minor) = 6.969 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.02 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.94 (dt, *J* = 8.4, 1.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 4.8 Hz, 1H), 7.34 – 7.24 (m, 4H), 7.08 (d, *J* = 14.4 Hz, 1H), 6.69 (dd, *J* = 8.4, 3.6 Hz, 1H), 2.78 – 2.72 (m, 2H), 2.48 – 2.42 (m, 1H), 2.35 (s, 3H), 2.14 (s, 3H), 1.98 (s, 3H), 1.83 – 1.75 (m, 4H), 1.32 (t, *J* = 7. Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.9, 145.5 (d, J_{CP} = 3.6 Hz), 141.3, 140.2 (d, J_{CP} = 2.5 Hz), 140.0 (d, J_{CP} = 2.9 Hz), 137.8 (d, J_{CP} = 2.5 Hz), 136.7 (d, J_{CP} = 4.1 Hz), 135.7, 135.2 (d, J_{CP} = 13.6 Hz), 134.2 (d, J_{CP} = 10.7 Hz), 133.6 (d, J_{CP} = 14.9 Hz), 131.2 (d, J_{CP} = 13.0 Hz), 130.9 (d, J_{CP} = 10.0 Hz), 130.5 (d, J_{CP} = 3.2 Hz), 128.4, 128.2 (d, J_{CP} = 14.0 Hz), 127.7 (d, J_{CP} = 137.3 Hz), 127.2, 125.8, 124.4 (d, J_{CP} = 10.0 Hz), 122.6 (d, J_{CP} = 130.9 Hz), 121.0, 113.6 (d, J_{CP} = 8.1 Hz), 24.7 (d, J_{CP} = 2.5 Hz), 22.4, 20.7, 19.7, 19.3, 19.0, 15.1, 13.4; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.97; **HRMS (ESI)** calculated for $C_{31}H_{34}N_2OP$ $[M + H]^+$: 481.2403, found: 481.2401;



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	6.968	5344975	50.09	281678
2	W2489 ChA 254nm	22.962	5326128	49.91	87815



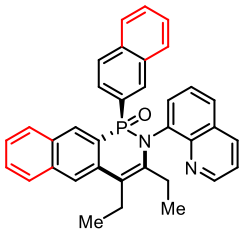
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	6.969	20714	0.23	1411
2	W2489 ChA 254nm	22.235	9161065	99.77	156515

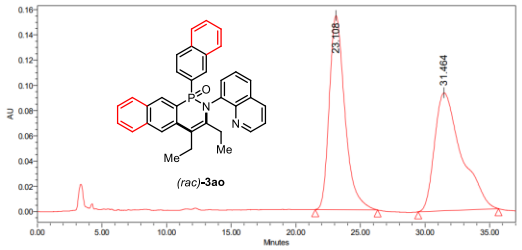
Synthetic Procedure and Characterization of 3ao

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1j** (0.2 mmol, 1.0 equiv), alkyne **2l** (0.3 mmol, 1.5 equiv), $Co(OAc)_2·4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 equiv) were placed in a 15 mL cell and dissolved in 4.0 mL of *t*-BuOH / H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product (*S*)-**3ao** (79.6 mg) in 76% yield as a white foam with >99% ee. Product exists as a 8:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Diethyl-1-(naphthalen-2-yl)-2-(quinolin-8-yl)-2*H*-naphtho[2,3-*c*][1,2]azaphosphi-nine 1-oxide (3ao)

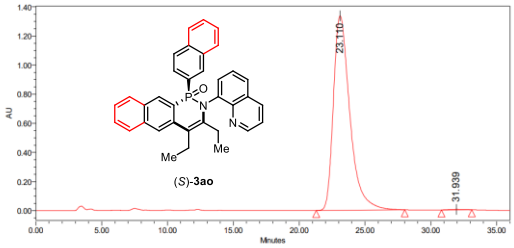


M.p.: 106 - 107 °C; >99% ee; $[\alpha]_D^{20}$ = +523.3 (c = 0.5, $CHCl_3$), lit[1d]: $[\alpha]_D^{20}$ = +518.7 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 23.110 min, t (minor) = 31.939 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.84 (d, *J* = 4.0 Hz, 1H), 8.52 (d, *J* = 14.8 Hz, 1H), 8.12 (d, *J* = 4.4 Hz, 1H), 8.00 – 7.89 (m, 4H), 7.72 (d, *J* = 7.6 Hz, 1H),7.66 – 7.32 (m, 9H), 7.28 – 7.23 (m, 2H), 2.92 (q, *J* = 7.2 Hz, 2H), 2.46 (dd, *J* = 14.8, 7.6 Hz, 1H), 1.92 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.41 (t, *J* = 7.6 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.0, 145.6 (d, J_{CP} = 2.3 Hz), 142.1, 137.7, 135.8, 135.5 (d, J_{CP} = 10.0 Hz), 135.1, 135.0 (d, J_{CP} = 3.6 Hz), 134.5 (d, J_{CP} = 2.5 Hz), 131.9, 131.9 (d, J_{CP} = 28.3 Hz), 130.9 (d, J_{CP} = 15.1 Hz), 130.1 (d, J_{CP} = 2.0 Hz), 128.8, 128.6, 128.5 (d, J_{CP} = 135.6 Hz), 128.3, 128.1, 127.8, 127.7, 127.6, 127.5, 127.2, 126.6 (d, J_{CP} = 10.2 Hz), 126.2, 125.8, 125.7 (d, J_{CP} = 127.8 Hz), 125.5, 121.9 (d, J_{CP} = 9.1 Hz), 121.2, 116.6 (d, J_{CP} = 7.2 Hz), 24.9, 22.8, 14.9, 13.3; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.91; **HRMS (ESI)** calculated for $C_{35}H_{30}N_2OP$ $[M + H]^+$: 525.2090, found: 525.2075;



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	23.108	12916982	48.96	153846
2	W2489 ChB 210nm	31.464	13464042	51.04	93493



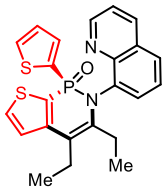
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	23.110	116266506	99.81	1335630
2	W2489 ChB 210nm	31.939	225888	0.19	2734

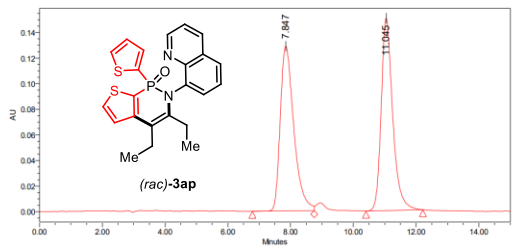
Synthetic Procedure and Characterization of 3ap

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1k** (0.2 mmol, 1.0 eq.), alkyne **2l** (0.3 mmol, 1.5 eq.), $Co(OAc)_2·4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of *t*-BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product (*S*)-**3ap** (68.2 mg) in 78% yield as a white foam with >99% ee. Product exists as a 13:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3,4-Diethyl-2-(quinolin-8-yl)-1-(thiophen-2-yl)-2*H*-thieno[2,3-*c*][1,2]azaphosphinine 1-oxide (3ap)

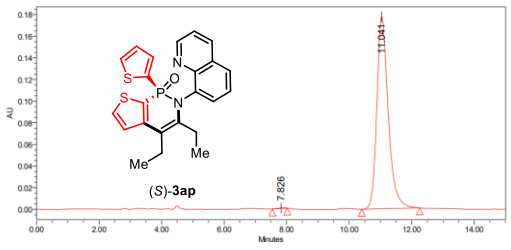


M.p.: 226 - 227 °C; >99% ee; $[\alpha]_D^{20}$ = +685.6 (c = 0.5, $CHCl_3$). The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 11.041 min, t (minor) = 7.826 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 8.00 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.22 (t, *J* = 4.8 Hz, 1H), 7.17 (dd, *J* = 8.4, 3.6 Hz, 1H), 6.61 – 6.58 (m, 1H), 2.74 – 2.68 (m, 2H), 2.50 – 2.40 (m, 1H), 1.82 – 1.73 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.2, 148.3 (d, J_{CP} = 6.7 Hz), 145.4 (d, J_{CP} = 3.3 Hz), 142.4, 137.5 (d, J_{CP} = 12.1 Hz), 136.4 (d, J_{CP} = 2.6 Hz), 135.8, 133.9 (d, J_{CP} = 6.5 Hz),133.0 (d, J_{CP} = 163.4 Hz),132.1 (d, J_{CP} = 11.9 Hz), 132.1, 128.6, 128.3, 126.8 (d, J_{CP} = 16.5 Hz), 125.9, 124.7 (d, J_{CP} = 12.4 Hz), 121.3, 118.7 (d, J_{CP} = 148.9 Hz), 111.7 (d, J_{CP} = 6.4 Hz), 24.0 (d, J_{CP} = 3.3 Hz), 23.8, 15.2, 13.9; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 4.34; **HRMS (ESI)** calculated for $C_{23}H_{22}N_2OPS_2$ $[M + H]^+$: 437.0906, found: 437.0901;



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	7.847	3860662	50.19	128831
2	W2489 ChA 254nm	11.045	3831157	49.81	150602



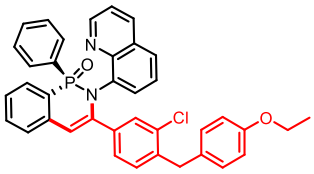
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	7.826	8546	0.19	540
2	W2489 ChA 254nm	11.041	4493502	99.81	177919

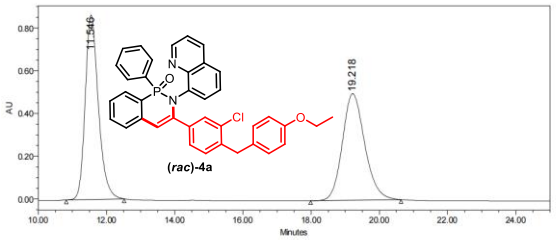
Synthetic Procedure and Characterization of 4a

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2aq** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH / H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product (*S*)-**4a** (47.7 mg) in 78% yield as a yellow solid with 99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(3-chloro-4-(4-ethoxybenzyl)phenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo-[1,2]-aza-phosphinine 1-oxide (4a)

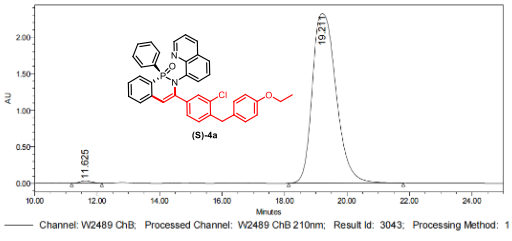


M.p.: 89 - 90 ºC; $[\alpha]_D^{20}$ = +389.8 (c = 0.8, $CHCl_3$); The 99% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 19.211 min, t (minor) = 11.625 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.61 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.0Hz, 1H), 7.63 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.47 – 7.36 (m, 3H), 7.23 – 7.21 (m, 3H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.12 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.95 (dt, *J* = 7.6, 2.8 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 2.0 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.73 (s, 2H), 1.42 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.3, 149.3, 144.2, 143.7 (d, J_{CP} = 2.0 Hz), 137.8 (d, J_{CP} = 4.0 Hz), 137.5, 137.5, 137.3 (d, J_{CP} = 4.0 Hz), 135.5, 133.3, 133.0 (d, J_{CP} = 11.0 Hz), 131.8, 131.7, 131.5, 131.0, 131.0 (d, J_{CP} = 12.0 Hz), 130.2, 130.0, 129.6, 129.0, 128.4, 128.3 (d, J_{CP} = 6.0 Hz), 127.3, 127.2 (d, J_{CP} = 14.0 Hz), 126.8 (d, J_{CP} = 9.0 Hz), 126.1 (d, J_{CP} = 15.0 Hz), 125.6, 124.1 (d, J_{CP} = 128.0 Hz), 121.1, 114.3, 107.5 (d, J_{CP} = 8.0 Hz), 63.4, 38.1, 15.0.; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.71; **HRMS (ESI)** calculated for $C_{38}H_{31}ClN_2O_2P$ $[M + H]^+$: 613.1806, found: 613.1816.



Processed Channel Descr.: W2489 ChB 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 210nm	11.546	23062261	50.38	862346
2	W2489 ChB 210nm	19.218	22713074	49.62	498655



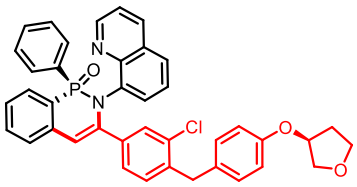
Processed Channel Descr.: W2489 ChB 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 210nm	11.625	833505	0.67	33049
2	W2489 ChB 210nm	19.211	123022189	99.33	2317951

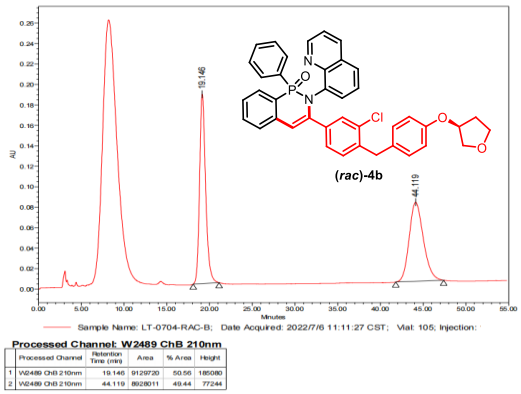
Synthetic Procedure and Characterization of 4b

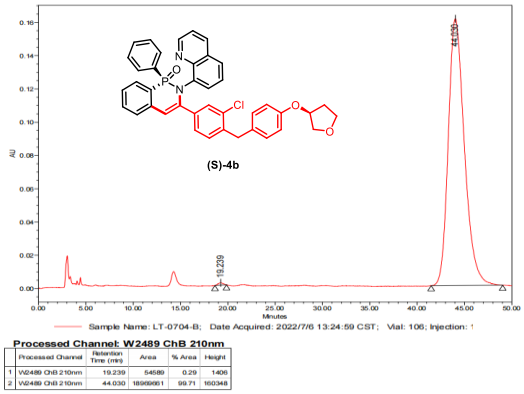
The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2ar** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product (*S*)-**4b** (52.3 mg) in 81% yield as a light-yellow solid with 99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(3-chloro-4-(4-(((*S*)-tetrahydrofuran-3-yl)oxy)benzyl)phenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (4b)



M.p.: 105 - 106 ºC; $[\alpha]_D^{20}$ = +326.0 (c = 0.8, $CHCl_3$); The 99% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 44.030 min, t (minor) = 19.239 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.61 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.62 (dd, *J* = 12.8, 7.2 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.37 (t, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 2.0 Hz, 2H), 7.18 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.11 (dd, *J* = 8.0, 4.4 Hz, 1H), 6.96 – 6.89 (m, 3H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 1.6 Hz, 1H), 4.91 – 4.87 (m, 1H), 4.00 – 3.95 (m, 3H), 3.91 – 3.86 (m, 1H), 3.72 (s, 2H), 2.21 – 2.14 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.7, 149.3, 144.1, 143.7 (d, J_{CP} = 3.0 Hz), 137.7 (d, J_{CP} = 5.0 Hz), 137.4 (d, J_{CP} = 1.0 Hz), 137.3, 137.2 (d, J_{CP} = 4.0 Hz), 135.4, 133.2, 132.9 (d, J_{CP} = 10.0 Hz), 131.8, 131.6, 131.4, 130.9 (d, J_{CP} = 12.0 Hz), 130.1, 129.7, 128.3, 128.2, 128.2, 127.3, 127.1, 127.0, 126.7 (d, J_{CP} = 9.0 Hz), 126.1 (d, J_{CP} = 14.0 Hz), 125.5, 124.0 (d, J_{CP} = 137.0 Hz), 121.1, 115.1, 115.0, 107.5 (d, J_{CP} = 8.0 Hz),77.2, 73.1, 67.2, 38.0, 33.0. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.75; **HRMS (ESI)** calculated for $C_{40}H_{33}ClN_2O_3P$ $[M + H]^+$: 655.1912, found: 655.1921.

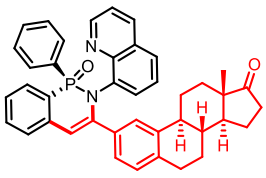




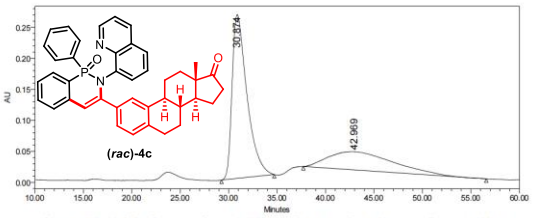
Synthetic Procedure and Characterization of 4c

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2as**(0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product (*S*)-**4c** (46.5 mg) in 75% yield as a light-yellow solid with > 99:1 ee. Product exists as a 7:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-2-((S)-1-oxido-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinin-3-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4c)

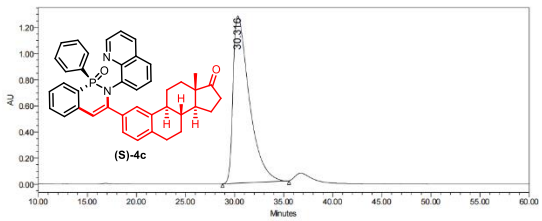


M.p.: 178 -179 ºC; $[\alpha]_D^{20}$ = +273.4 (c = 0.5, $CHCl_3$), lit[1d]: $[\alpha]_D^{20}$ = +266.5 (c = 0.5, $CHCl_3$) The >99% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (single peak) = 30.316 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (dd, *J* = 4.0, 2.0 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.69 (dd, *J* = 13.2, 7.2 Hz, 2H), 7.53 – 7.42 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.25-7.21 (m, 2H), 7.18 – 7.08 (m, 5H), 6.97 (td, *J* = 7.6, 3.2 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.32 (d, *J* = 2.0 Hz, 1H), 2.62 – 2.58 (m, 2H), 2.44 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.19 – 2.15 (m, 1H), 2.11 – 1.93 (m, 4H), 1.84 (dd, *J* = 9.2, 3.2 Hz, 2H), 1.57 – 1.47 (m, 1H), 1.40 – 1.34 (m, 4H), 1.27 – 1.23 (m, 1H), 0.80 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.2, 145.1, 144.4 (d, J_{CP} = 3.0 Hz), 139.0, 138.2 (d, J_{CP} = 5.0 Hz), 138.0 (d, J_{CP} = 2.0 Hz), 135.9 (d, J_{CP} = 5.0 Hz), 135.4, 135.0, 132.9 (d, J_{CP} = 11.0 Hz), 132.0, 131.7 (d, J_{CP} = 3.0 Hz), 131.4 (d, J_{CP} = 3.0 Hz), 130.8 (d, J_{CP} = 12.0 Hz), 130.3 (d, J_{CP} = 3.0 Hz), 129.5, 128.5 (d, J_{CP} = 130.0 Hz), 127.1, 127., 126.6 (d, J_{CP} = 9.0 Hz), 126.2, 125.9 (d, J_{CP} = 14.0 Hz), 125.4, 124.6 (d, J_{CP} = 177.0 Hz), 124.1, 121.0, 107.9 (d, J_{CP} = 8.0 Hz), 50.5, 47.9, 44.1, 37.8, 35.8, 31.5, 29.0, 26.3, 25.4, 21.5, 13.8; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 19.08; **HRMS (ESI)** calculated for $C_{41}H_{38}N_2O_2P$ $[M+H]^+$: 621.2665, found: 621.2675.



Processed Channel Descr.: W2489 ChB 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 210nm	30.874	28201084	67.09	263940
2	W2489 ChB 210nm	42.969	13834435	32.91	29394



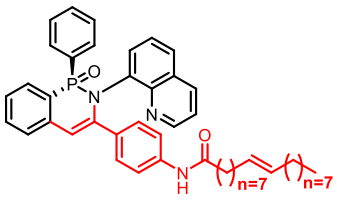
Processed Channel Descr.: W2489 ChB 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 210nm	30.316	147416746	100.00	1278419

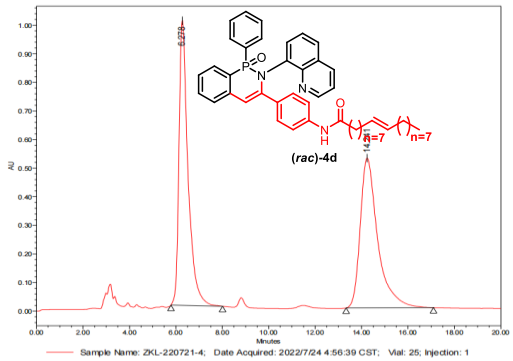
Synthetic Procedure and Characterization of 4d

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2at** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product (*S*)-**4d** (52.8 mg) in 73% yield as a light-yellow solid with 97% ee. Product exists as a 7:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-2-((*S*)-1-oxido-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinin-3-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4d)

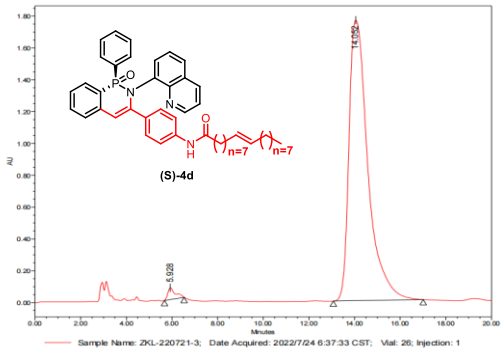


M.p.: 78 - 79 ℃; $[\alpha]_D^{20}$ = +336.0 (c = 0.5, $CHCl_3$); The 97% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 14.052min, t (minor) = 5.928 min. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.68 (s, 1H), 8.78 (d, *J* = 4.0 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.61 – 7.53 (m, 5H), 7.34 – 7.29 (m, 4H), 7.22 (q, *J* = 8.4 Hz, 5H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.42 (s, 1H), 5.29 (t, *J* = 4.8 Hz, 2H), 2.14 (t, *J* = 7.6 Hz, 2H), 1.94 (d, *J* = 6.8 Hz, 4H), 1.46 (t, *J* = 7.2 Hz, 2H), 1.20 (s, 21H), 0.81 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 171.1, 149.6, 144.3, 143.5 (d, J_{CP} = 3.0 Hz), 138.7, 137.5, 137.4, 135.8, 132.4 (d, J_{CP} = 4.0 Hz), 132.2 (d, J_{CP} = 10.0 Hz), 131.8, 131.7, 131.4 (d, J_{CP} = 10.0 Hz), 130.0 (d, J_{CP} = 11.0 Hz), 129.6 (d, J_{CP} = 3.0 Hz), 129.4, 129.1 (d, J_{CP} = 12.0 Hz), 128.8, 128.7, 128.1 (d, J_{CP} = 154.0 Hz), 128.0, 127.4, 127.4 (d, J_{CP} = 13.0 Hz), 125. 5, 124.1 (d, J_{CP} = 126.0 Hz), 121.5, 117.5, 107.1 (d, J_{CP} = 7.0 Hz), 36.3, 31.3, 29.1, 28.8, 28.7, 28.6, 28.6, 28.6, 28.5, 26.6, 25.0, 22.1, 13.9; **^{31}P NMR (162 MHz, DMSO-*d*$_6$)** δ 17.43; **HRMS (ESI)** calculated for $C_{47}H_{55}N_3O_2P$ $[M + H]^+$: 724.4026, found: 724.4045.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	6.278	27078415	49.76	996001
2	W2489 ChB 210nm	14.241	27342860	50.24	523786



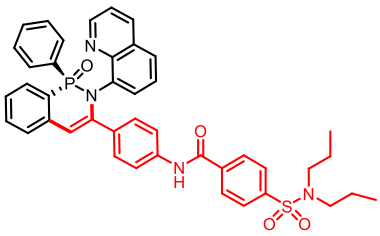
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	5.928	1684478	1.63	73641
2	W2489 ChB 210nm	14.052	101534957	98.37	1763413

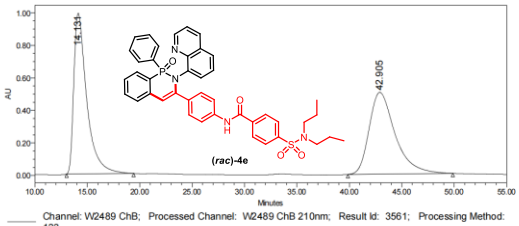
Synthetic Procedure and Characterization of 4e

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2au** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 2:1 v/v) to give the desired product (*S*)-**4e** (58.8 mg) in 81% yield as a light-yellow solid with 94% ee. Product exists as a 7:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-4-(*N*,*N*-dipropylsulfamoyl)-*N*-(4-(1-oxido-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinin-3-yl)phenyl)benzamide (4e)



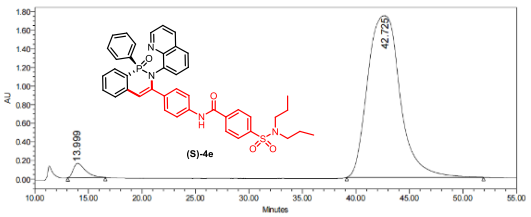
M.p.: 167 - 168 ºC; $[\alpha]_D^{20}$ = +487.0 (c = 0.5, $CHCl_3$); The 94% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 42.725min, t (minor) = 13.999 min. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.29 (s, 1H), 8.81 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.89 (t, *J* = 10.0 Hz, 3H), 7.64 (d, *J* = 5.6 Hz, 2H), 7.60 – 7.52 (m, 3H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.30 (m, 5H), 7.27 – 7.20 (m, 2H), 7.11 – 7.07 (m, 2H), 6.48 (s, 1H), 3.02 (t, *J* = 7.6 Hz, 4H), 1.50 – 1.42 (m, 4H), 0.79 (t, *J* = 7.6 Hz, 6H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 164.3, 149.7, 144.2, 144.0, 143.5 (d, J_{CP} = 4.0 Hz), 141.9, 138.3 (d, J_{CP} = 13.0 Hz), 137.4 (d, J_{CP} = 3.0 Hz), 136.7 (d, J_{CP} = 60.0 Hz), 135.9, 133.5 (d, J_{CP} = 4.0 Hz), 132.9, 132.2 (d, J_{CP} = 11.0 Hz), 131.9, 131.7 (d, J_{CP} = 3.0 Hz), 131.6, 131.4 (d, J_{CP} = 10.0 Hz), 130.3 (d, J_{CP} = 6.0 Hz), 130.0 (d, J_{CP} = 12.0 Hz), 129.5, 129.1 (d, J_{CP} = 13.0 Hz), 128.7, 128.6, 128.1, 127.4, 127.3, 126.8, 126.1 (d, J_{CP} = 13.0 Hz), 124.2 (d, J_{CP} = 126.0 Hz), 121.5, 118.9, 107.4 (d, J_{CP} = 8.0 Hz), 49.6, 21.6, 10.9; **^{31}P NMR (162 MHz, DMSO-*d*$_6$)** δ 17.34; **HRMS (ESI)** calculated for $C_{42}H_{40}N_4O_4PS$ $[M+H]^+$: 727.2502, found: 727.2514.



Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3561; Processing Method: 123

Processed Channel Descr.: W2489 ChB 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 210nm	14.131	84696473	49.48	987257
2	W2489 ChB 210nm	42.905	86473708	50.52	503207



Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3558; Processing Method: 123

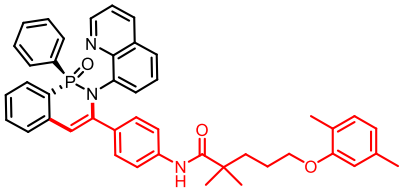
Processed Channel Descr.: W2489 ChB 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 210nm	13.999	12014363	3.16	152831
2	W2489 ChB 210nm	42.725	367771141	96.84	1737166

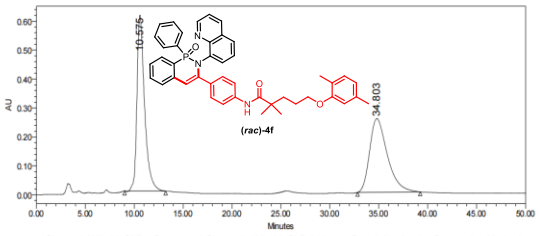
Synthetic Procedure and Characterization of 4f

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2av** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product (*S*)-**4f** (38.0 mg) in 55% yield as a light-yellow solid with 97% ee. Product exists as a 6:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-5-(2,5-dimethylphenoxy)-2,2-dimethyl-*N*-(4-(1-oxido-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinin-3-yl)phenyl)pentanamide (4f)

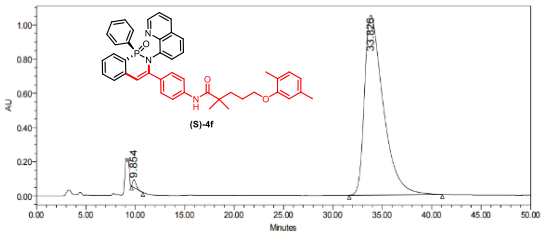


M.p.: 135 -137 ℃; $[\alpha]_D^{20}$ = +289.2 (c = 0.5, $CHCl_3$); The 97% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 33.826min, t (minor) = 9.854 min; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.04 (s, 1H), 8.80 (d, *J* = 4.0 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 12.0 Hz, 3H), 7.58 – 7.54 (m, 2H), 7.35 – 7.29 (m, 8H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 10.8 Hz, 2H), 6.45 (s, 1H), 3.83 (t, *J* = 6.0 Hz, 2H), 2.18 (s, 3H), 1.99 (s, 3H), 1.67 – 1.53 (m, 4H), 1.12 (s, 6H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 175.5, 156.4, 149.7, 144.3, 143.6 (d, J_{CP} = 3.0 Hz), 138.6, 137.4 (d, J_{CP} = 2.0 Hz), 136.0, 135.8, 132.8 (d, J_{CP} = 5.0 Hz), 132.1 (d, J_{CP} = 11.0 Hz), 131.8 (d, J_{CP} = 14.0 Hz), 130.4, 130.0, 129.4, 128.4, 128.1, 127.9, 127.4 (d, J_{CP} = 5.0 Hz), 127.3, 126.7 (d, J_{CP} = 5.0 Hz), 126.1 (d, J_{CP} = 15.0 Hz), 125.5, 124.1 (d, J_{CP} = 125.0 Hz), 122.4, 121.5, 120.4, 119.3, 119.0, 111.9, 107.4 (d, J_{CP} = 8.0 Hz), 67.4, 42.2, 36.5, 25.0, 24.9, 24.6, 21.0, 15.5; **^{31}P NMR (162 MHz, DMSO-*d*$_6$)** δ 17.59; **HRMS (ESI)** calculated for $C_{44}H_{43}N_3O_3P$ $[M + H]^+$: 692.3037, found: 692.3045



Processed Channel Descr.: W2489 ChB 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 210nm	10.575	32958500	50.71	607642
2	W2489 ChB 210nm	34.803	32034463	49.29	254510



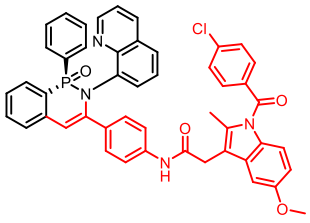
Processed Channel Descr.: W2489 ChB 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 210nm	9.854	1115651	0.79	45060
2	W2489 ChB 210nm	33.826	139232095	99.21	1052431

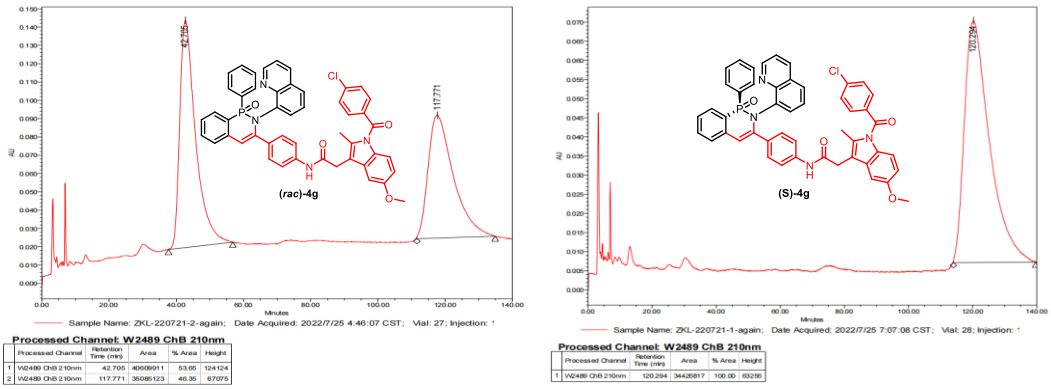
Synthetic Procedure and Characterization of 4g

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2aw** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 2:1 v/v) to give the desired product (*S*)-**4g** (37.5 mg) in 47% yield as a yellow solid with >99% ee. Product exists as a 6:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-*N*-(4-(1-oxido-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinin-3-yl)phenyl)acetamide (4g)



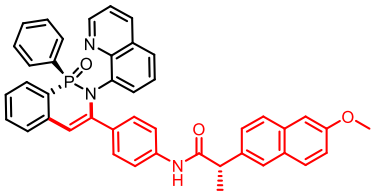
M.p.: 165 - 166 ºC; $[\alpha]_D^{20}$ = +236.0 (c = 0.5, $CHCl_3$); The >99% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (single peak) = 120.294 min; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.08 (s, 1H), 8.78 (d, *J* = 3.9 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.3 Hz, 1H), 7.66 – 7.60 (m, 7H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.25 (m, 8H), 7.20 (t, *J* = 9.2 Hz, 1H), 7.08 (d, *J* = 12.0 Hz, 3H), 6.91 (d, *J* = 9.2 Hz, 1H), 6.67 (d, *J* = 9.2 Hz, 1H), 6.44 (s, 1H), 3.67 (s, 3H), 3.63 (s, 2H), 2.20 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 168.2, 167.7, 155.4, 149.5, 144.1, 143.3 (d, J_{CP} = 3.0 Hz), 138.3, 137. 5, 137.3, 137.3, 135.7, 135.2 (d, J_{CP} = 120.0 Hz), 132.7 (d, J_{CP} = 4.0 Hz), 132.1 (d, J_{CP} = 11.0 Hz), 131.7 (d, J_{CP} = 14.0 Hz), 131.0, 130.7, 130.2, 130.1, 129.9 (d, J_{CP} = 11.0 Hz), 129.3, 128.9, 128.6, 128.4, 127.9, 127.3 (d, J_{CP} = 5.0 Hz), 127.2, 126.5 (d, J_{CP} = 9.0 Hz), 126.0 (d, J_{CP}= 14.0 Hz), 125.3, 124.0 (d, J_{CP} = 125.0 Hz), 121.3, 117.9, 117.6, 114.4, 113.7, 111.0, 107.0 (d, J_{CP} = 8.0 Hz), 101.7, 55.2, 31.8, 13.2; **^{31}P NMR (162 MHz, DMSO-*d*$_6$)** δ 17.67; **HRMS (ESI)** calculated for $C_{48}H_{37}ClN_4O_4P$ $[M + H]^+$: 799.2235, found: 799.2246.



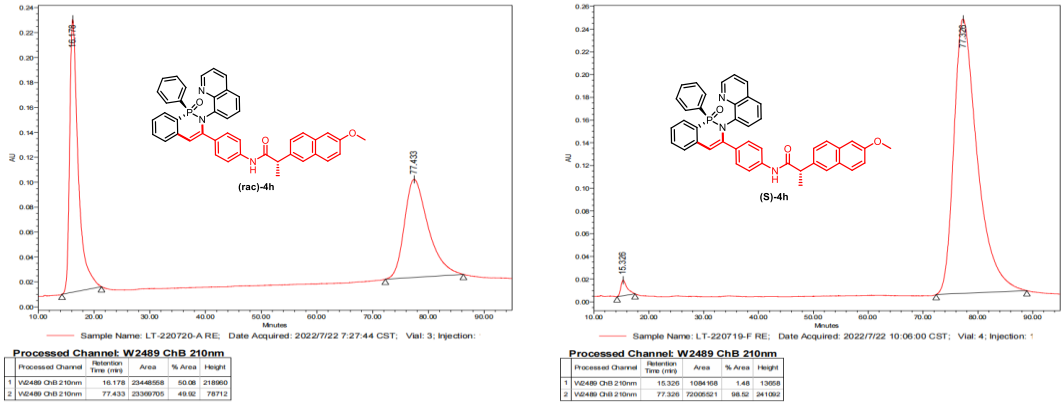
Synthetic Procedure and Characterization of 4h

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2ax** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH / H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product (*S*)-**4h** (50.3 mg) in 75% yield as a yellow solid with >99: 1 dr. Product exists as a 6:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-2-(6-methoxynaphthalen-2-yl)-*N*-(4-((*S*)-1-oxido-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinin-3-yl)phenyl)propenamide (4h)



M.p.: 102 - 103 ºC; $[\alpha]_D^{20}$ = +268.4 (c = 0.5, $CHCl_3$); The > 99:1 dr was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 77.326min, t (minor) = 15.326 min; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.97 (s, 1H), 8.78 (d, *J* = 4.0 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.71 (m, 3H), 7.61 – 7.51 (m, 5H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.33 – 7.19 (m, 10H), 7.14 – 7.05 (m, 3H), 6.43 (s, 1H), 3.83 (s, 4H), 1.40 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 172.3, 157.1, 149.7, 144.2, 143.5 (d, J_{CP} = 2.0 Hz), 138.5, 137.4 (d, J_{CP} = 5.0 Hz), 136.7, 135.9, 133.2, 132.8 (d, J_{CP} = 4.0 Hz), 132.4, 132.2 (d, J_{CP} = 10.0 Hz), 131.9 (d, J_{CP} = 13.0 Hz), 131.6, 131.4 (d, J_{CP} = 10.0 Hz), 131.1, 130.3, 130.0 (d, J_{CP} = 12.0 Hz), 129.5, 129.1, 128.7, 128.1, 127.5, 127.3, 126.8 (d, J_{CP} = 153.0 Hz), 126.7 (d, J_{CP} = 9.0 Hz), 126.2, 125.5, 125.4, 124.2 (d, J_{CP} = 125.0 Hz), 121.5, 118.7, 117.8, 107.2 (d, J_{CP} = 7.0 Hz), 105.6, 55.1, 45.8, 18.5. **^{31}P NMR (162 MHz, DMSO-*d*$_6$)** δ 17.43; **HRMS (ESI)** calculated for $C_{43}H_{35}N_3O_3P$ $[M + H]^+$: 672.2411, found: 672.2420.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	16.178	23448558	50.08	218960
2	W2489 ChB 210nm	77.433	23369705	49.92	78712

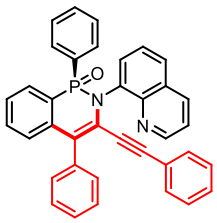
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	15.326	1084168	1.48	13958
2	W2489 ChB 210nm	77.326	72006521	98.52	241092

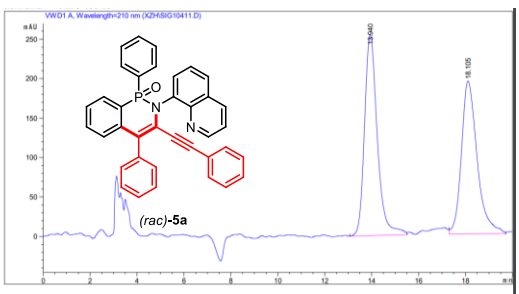
Synthetic Procedure and Characterization of 5a

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a**(0.2 mmol, 1.0 eq.), alkyne **2az** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product (*S*)-**5a** (90.9 mg) in 82% yield as a white solid with >99% ee. Product exists as a 16:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1,4-diphenyl-3-(phenylethynyl)-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (5a)



M.p.: 104 - 105 °C, $[\alpha]_D^{20}$ = +32.0 (c = 0.65, $CHCl_3$), >99% ee, lit[1d]: $[\alpha]_D^{20}$ = +76.5 (c = 0.5, $CHCl_3$). The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 14.028 min, t (minor) = 18.105 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.84 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.30 (d, *J* = 7.2 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.91 – 7.77 (m, 2H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60 – 7.34 (m, 8H), 7.32 – 7.21 (m, 2H), 7.20 – 7.11 (m, 2H), 7.04 (td, *J* = 7.6, 3.6 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.16 – 6.09 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.0, 145.3 (d, J_{CP} = 3.9 Hz), 138.8, 138.3 (d, J_{CP} = 4.4 Hz), 137.8 (d, J_{CP} = 1.5 Hz), 135.6, 133.7 (d, J_{CP} = 10.5 Hz), 131.9, 131.7 (d, J_{CP} = 3.0 Hz), 131.4 (d, J_{CP} = 2.5 Hz), 131.1, 131.0, 130.9, 130.8 (d, J_{CP} = 139.0Hz), 130.7, 128.5, 128.2, 128.0 (d, J_{CP} = 12.8 Hz), 127.8, 127.4, 127.3 (d, J_{CP} = 13.7 Hz), 126.8 (d, J_{CP} = 2.0 Hz), 126.7 (d, J_{CP} = 8.9 Hz), 126.4 (d, J_{CP} = 14.5 Hz), 125.9, 125.5 (d, J_{CP} = 127.9 Hz), 123.7 (d, J_{CP} = 6.9 Hz), 122.1, 121.2, 97.4, 87.0 (d, J_{CP} = 6.5 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.51; **HRMS (ESI)** calculated for $C_{37}H_{26}N_2OP$ $[M + H]^+$: 545.1777, found: 545.1776.

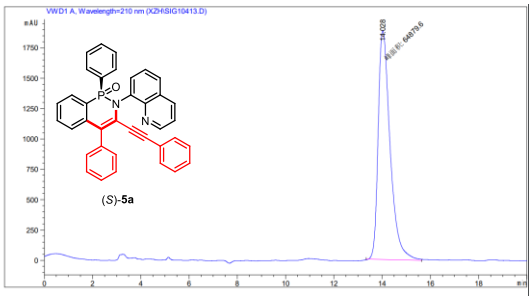


面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, Wavelength=210 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.940	BV	0.5841	9630.06836	254.53618	51.7197
2	18.105	VV	0.7196	8989.65039	193.53291	48.2803
总量 :				1.86197e4	448.06909	



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

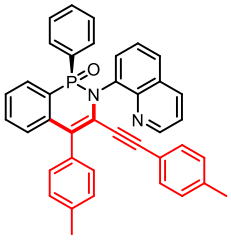
信号 1: VWD1 A, Wavelength=210 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.028	MM	0.5736	6.48796e4	1885.02893	100.0000
总量 :				6.48796e4	1885.02893	

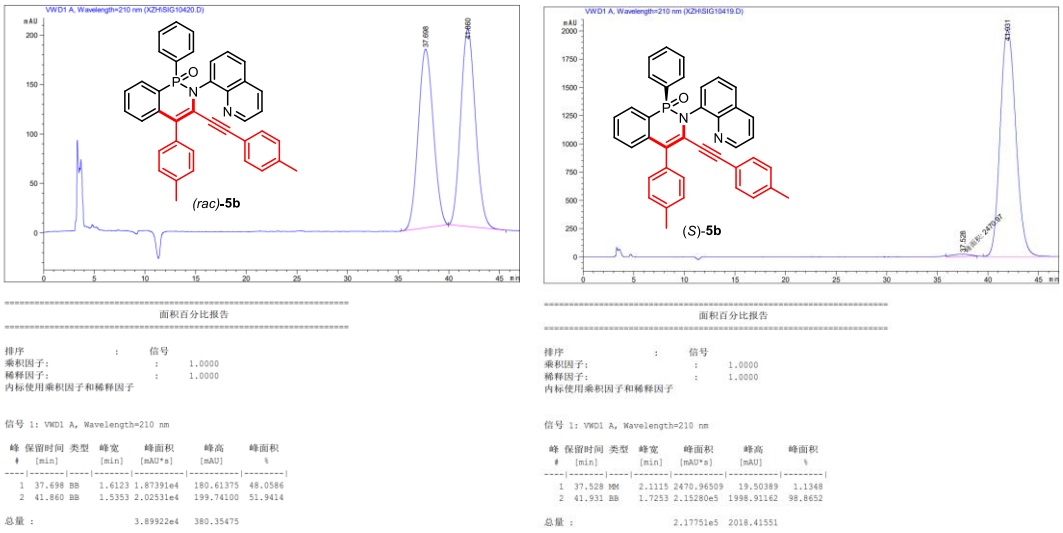
Synthetic Procedure and Characterization of 5b

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2ba** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product (*S*)-**5b** (97.3 mg) in 85% yield as a white solid with 98% ee. Product exists as a 17:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1-Phenyl-2-(quinolin-8-yl)-4-(p-tolyl)-3-(p-tolylethynyl)-*2H*-benzo[*c*][1,2]azaphosphinine 1-oxide (5b)



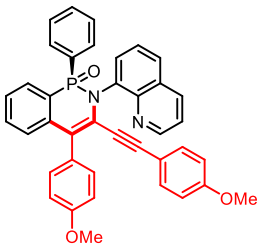
M.p.: 113 - 115 °C, $[\alpha]_D^{20}$ = +68.9 (c = 0.65, $CHCl_3$), 97% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (minor) = 37.528 min, t (mjaor) = 41.931 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 7.98 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.64 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.51 – 7.36 (m, 5H), 7.29 – 7.17 (m, 5H), 7.15 (td, *J* = 7.6, 1.6 Hz, 1H), 7.04 (td, *J* = 8.0, 3.6 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 2H), 6.06 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 2.13 (s, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.9, 148.1, 145.3 (d, J_{CP} = 3.6 Hz), 138.6 (d, J_{CP} = 4.5 Hz), 138.1, 138.0 (d, J_{CP} = 1.5), 136.8, 135.8, 135.6, 133.7 (d, J_{CP} = 10.5 Hz), 131.9 (d, J_{CP} = 10.2 Hz), 131.8, 131.6 (d, J_{CP} = 2.9 Hz), 131.3 (d, J_{CP} = 2.6 Hz), 131.1 (d, J_{CP} = 2.9 Hz), 131.0, 130.9, 130.6, 129.5 (d, J_{CP} = 56.6 Hz), 128.8, 128.5, 127.8 (d, J_{CP} = 182,7Hz), 127.2 (d, J_{CP} = 13.5 Hz), 126.7 (d, J_{CP} = 9.1 Hz), 126.2 (d, J_{CP} = 14.6 Hz), 125.5 (d, J_{CP} = 128.0 Hz), 123.3 (d, J_{CP} = 6.9 Hz), 121.1, 119.2, 97.5, 86.6 (d, J_{CP} = 6.5 Hz), 21.3, 21.3; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.49; **HRMS (ESI)** calculated for $C_{39}H_{30}N_2OP$ $[M + H]^+$: 573.2090, found: 573.2090.



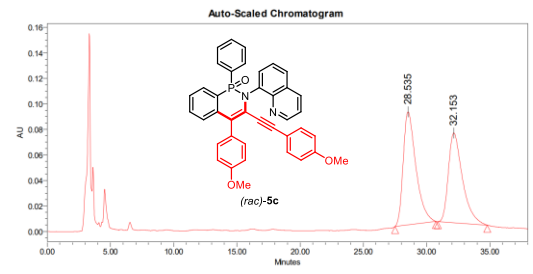
Synthetic Procedure and Characterization of 5c

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2bb** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product (*S*)-**5c** (105.2 mg) in 87% yield as a white solid with >99% ee. Product exists as a 14:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-4-(4-Methoxyphenyl)-3-((4-methoxyphenyl)ethynyl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphinine 1-oxide (5c)

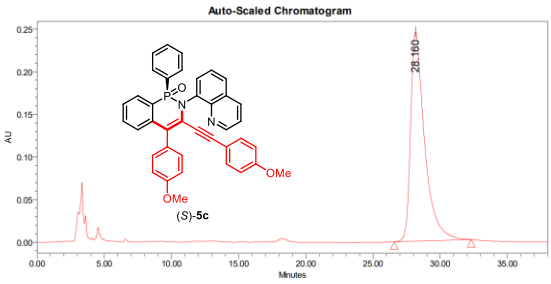


M.p.: 120 - 122 °C, $[\alpha]_D^{20}$ = +32.0 (c = 1.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 28.160 min, t (minor) = 32.163 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.82 (s, 1H), 8.30 (d, *J* = 6.4 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 10.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.33 (m, 5H), 7.29 – 7.08 (m, 4H), 7.08-6.94 (m, 4H), 6.43 (d, *J* = 8.4 Hz, 2H), 6.12 (d, *J* = 8.2 Hz, 2H), 3.83 (s, 3H), 3.58 (s, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.4, 158.9, 149.9 (d, J_{CP} = 2.7 Hz), 145.3 (d, J_{CP} = 3.4 Hz), 138.7 (d, J_{CP} = 7.7 Hz), 138.0, 135.6, 133.6 (d, J_{CP} = 11.8 Hz), 133.1 (d, J_{CP} = 7.3 Hz), 132.2, 131.7 (d, J_{CP} = 4.7 Hz), 131.3 (d, J_{CP} = 7.4 Hz), 131.0, 129.6 (d, J_{CP} = 114.3 Hz), 128.5, 127.8 (d, J_{CP} = 3.3 Hz), 127.2, 127.1 (d, J_{CP} = 4.6 Hz), 126.6 (d, J_{CP} = 11.0 Hz), 126.2 (d, J_{CP} = 8.7 Hz), 125.9 (d, J_{CP} = 9.7 Hz), 125.5 (d, J_{CP} = 123.8 Hz), 124.8, 122.5, 121.2, 114.3, 113.75 (d, J_{CP} = 3.6 Hz), 97.5, 86.1 (d, J_{CP} = 5.9 Hz),97.5, 86.1, 55.3, 55.1; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.43; **HRMS (ESI)** calculated for $C_{39}H_{30}N_2O_3P$ $[M + H]^+$: 605.1989, found: 605.1986.



Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	28.535	6194119	53.08	88617
2	W2489 ChB 210nm	32.153	5474730	46.92	70469



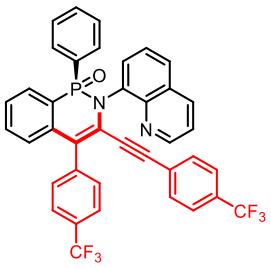
Processed Channel: W2489 ChB 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 210nm	28.160	17751576	100.00	245235

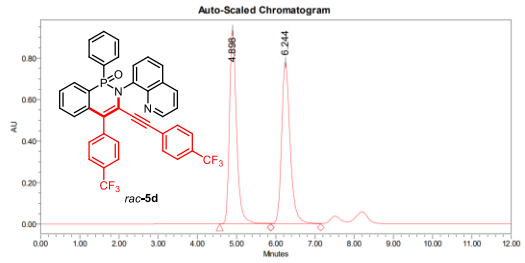
Synthetic Procedure and Characterization of 5d

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 equiv), alkyne **2bc** (0.3 mmol, 1.5 equiv), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 equiv) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH / H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product (*S*)-**5d** (117.0 mg) in 86% yield as a white solid with 99% ee. Product exists as a 14:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(S)-1-Phenyl-2-(quinolin-8-yl)-4-(4-(trifluoromethyl)phenyl)-3-((4-(trifluoromethyl)phenyl)ethynyl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (5d)

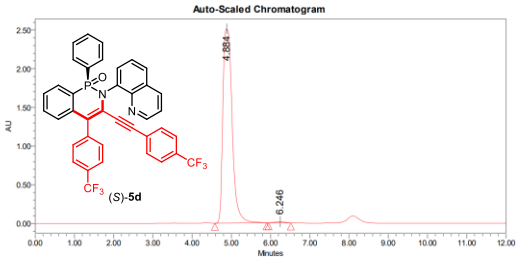


M.p.: 114.8 – 116.5 °C, $[\alpha]_D^{20}$ = +45.0 (c = 0.4, $CHCl_3$), 99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 4.884 min, t (major) = 6.246 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.89 (d, *J* = 3.2 Hz, 1H), 8.34 (d, *J* = 7.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.70 (m, 7H), 7.52 – 7.47 (m, 3H), 7.34 – 7.28 (m, 2H), 7.21 – 7.08 (m, 6H), 6.20 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.1, 145.1 (d, J_{CP} = 3.5 Hz), 142.7, 137.5 (d, J_{CP} = 3.4 Hz), 137.4 (d, J_{CP} = 4.2 Hz), 135.7, 133.6 (d, J_{CP} = 10.6 Hz), 132.0 (d, J_{CP} = 2.5 Hz), 131.7 (d, J_{CP} = 1.7 Hz), 131.3, 131.2, 130.9, 130.9, 130.7, 130.3, 130.0 (d, J_{CP} = 4.8 Hz), 129.7 (d, J_{CP} = 4.5 Hz), 128.5, 128.1, 127.4, 127.3, 127.0 (d, J_{CP} = 14.7 Hz), 126.7 (q, J_{CF} = 128.0 Hz), 126.4 (d, J_{CP} = 9.0 Hz), 126.0, 125.8 (d, J_{CP} = 13.0 Hz), 125.6 (q, J_{CF} = 220.6 Hz), 125.2, 124.9 (q, J_{CP} = 7.2 Hz), 123.2 (q, J_{CP} = 6.8 Hz), 123.1, 123.0, 121.4, 96.1, 88.7 (d, J_{CP} = 6.4 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ 62.44, 63.08; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.51; **HRMS (ESI)** calculated for $C_{39}H_{24}F_6N_2OP$ $[M + H]^+$:681.1525, found: 681.1523.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	4.898	11828821	50.00	935441
2	W2489 ChA 254nm	6.244	11827249	50.00	780909



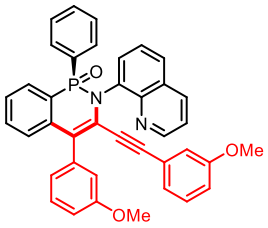
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	4.884	41469587	99.34	2511333
2	W2489 ChA 254nm	6.246	275535	0.66	16504

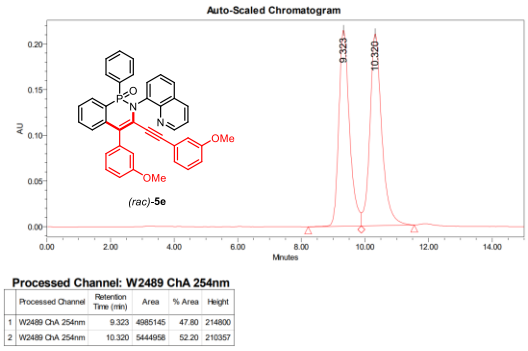
Synthetic Procedure and Characterization of 5e

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2bd** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product (*S*)-**5e** (81.0 mg) in 67% yield as a white solid with >99% ee. Product exists as a 20:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-4-(3-Methoxyphenyl)-3-((3-methoxyphenyl)ethynyl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphinine 1-oxide (5e)

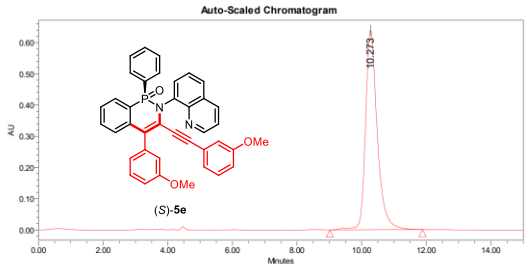


M.p.: 98 – 100 °C, $[\alpha]_D^{20}$ = +44.5 (c = 1.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 9.323 min, t (major) = 10.273 min. **^{1}H NMR (400 MHz, $CDCl_3$)** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 8.31 (d, *J* = 7.2 Hz, 1H), 7.95 (t, *J* = 7.8 Hz, 1H), 7.86 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.63 (t, *J* = 6.4 Hz, 1H), 7.51 – 7.32 (m, 5H), 7.25 – 7.09 (m, 5H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.84 – 6.77 (m, 1H), 6.55 (d, *J* = 9.2Hz, 1H), 5.80 (d, *J* = 7.8 Hz, 1H), 5.64 (s, 1H), 3.78 (s, 3H), 3.52 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.6, 158.8, 150.0, 145.3 (d, J_{CP} = 3.2 Hz), 140.1, 138.2 (d, J_{CP} = 4.2 Hz), 137.8, 135.6, 133.7 (d, J_{CP} = 10.5 Hz), 131.8 (d, J_{CP} = 2.4 Hz), 131.4, 131.1, 131.0, 130.9, 129.1, 128.9, 128.5, 127.9, 127.3 (d, J_{CP} = 11.6 Hz), 127.2, 126.7 (d, J_{CP} = 3.5 Hz), 126.6, 126.4 (d, J_{CP} = 10.5 Hz), 126.3, 125.9, 125.5 (d, J_{CP} = 114.6 Hz), 124.3, 123.5 (d, J_{CP} = 6.8 Hz), 123.1, 123.1, 121.3, 115.3, 114.9, 113.6, 97.4, 86.8 (d, J_{CP} = 6.2 Hz), 55.3, 55.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.53; **HRMS (ESI)** calculated for $C_{39}H_{30}N_2O_3P$ $[M + H]^+$: 605.1989, found: 605.1991.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	9.323	4985145	47.80	214800
2	W2489 ChA 254nm	10.320	5444958	52.20	210357



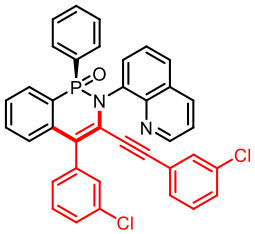
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	10.273	16142359	100.00	639494

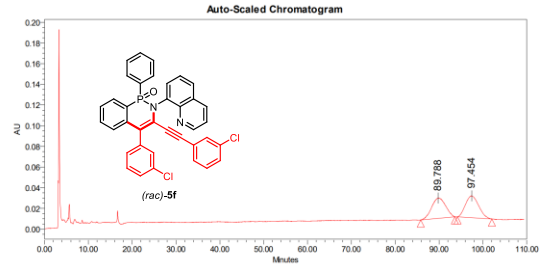
Synthetic Procedure and Characterization of 5f

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2be** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product (*S*)-**5f** (38.0 mg) in 31% yield as a white solid with 99% ee. Product exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-4-(3-Chlorophenyl)-3-((3-chlorophenyl)ethynyl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphinine 1-oxide (5f)

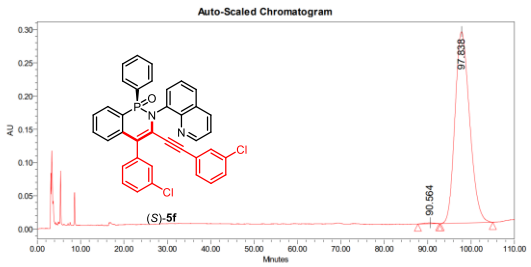


M.p.: 100 - 103 °C, $[\alpha]_D^{20}$ = +111.0 (c = 0.2, $CHCl_3$), 99% ee. The e e was determined by Daicel Chiralcel IC, Hexanes/IPA = 95/5, 1.0 m L/min, λ = 210 nm, t (minor) = 90.564 min, t (major) = 97.838 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.85 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.02 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.69 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.51 – 7.40 (m, 6H), 7.33 – 7.24 (m, 3H), 7.23 – 7.13 (m, 2H), 7.05 (td, *J* = 8.0, 3.6 Hz, 2H), 7.02 – 6.99 (m, 1H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.11 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.1, 145.1 (d, J_{CP} = 3.6 Hz), 140.4, 137.6 (d, J_{CP} = 4.4 Hz), 137.6 (d, J_{CP} = 1.5 Hz), 135.7, 133.6, 133.5, 131,9 (d, J_{CP} = 2.9 Hz),131,8 (d, J_{CP} = 2.7 Hz), 131.6 (d, J_{CP} = 2.3 Hz), 131.2, 131.1 (d, J_{CP} = 4.9 Hz), 131.0, 130.5, 130.4, 130.1, 129.5, 129.1, 128.7, 128.5, 128.4, 128.0, 127.7, 127.4 (d, J_{CP} = 13.7 Hz), 126.8 (d, J_{CP} = 13.4 Hz), 126,8(d, J_{CP} = 4.7 Hz), 126.7 (d, J_{CP} = 2.2 Hz), 126.4 (d, J_{CP} = 9.1 Hz), 126.0, 125.7 (d, J_{CP} = 127,7 Hz), 123.5, 122.7 (d, J_{CP} = 6.9 Hz), 121.3, 96.2, 87.6 (d, J_{CP} = 7.2 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.47; **HRMS (ESI)** calculated for $C_{37}H_{24}Cl_2N_2OP$ $[M + H]^+$: 613.0998, found: 613.0993



Processed Channel: W2489 ChA 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 210nm	89.788	4320381	49.60	19570
2	W2489 ChA 210nm	97.454	4390741	50.40	21141



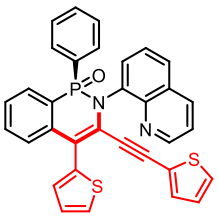
Processed Channel: W2489 ChA 210nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 210nm	90.564	224322	0.33	1461
2	W2489 ChA 210nm	97.838	67465435	99.67	287804

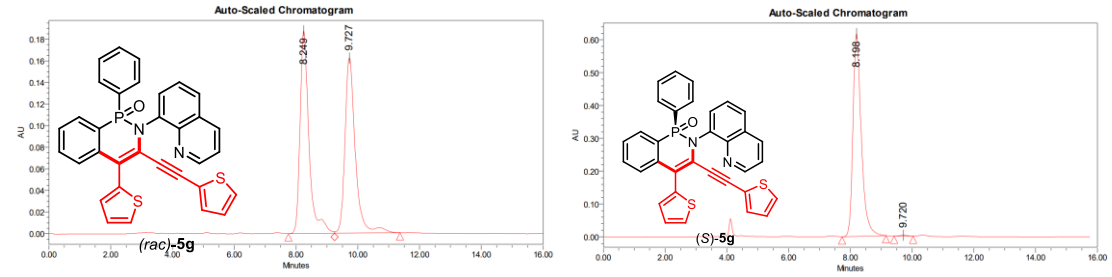
Synthetic Procedure and Characterization of 5g

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2bh** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product (*S*)-**5g** (112.2 mg) in 99% yield as a white solid with 99% ee. Product exists as a 48:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-1-Phenyl-2-(quinolin-8-yl)-4-(thiophen-2-yl)-3-(thiophen-2-ylethynyl)-*2H*-benzo[*c*][1,2]azaphosphinine 1-oxide (5g)



M.p.: 120 - 122 °C, $[\alpha]_D^{20}$ = +39.5 (c = 1.0, $CHCl_3$), 99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 8.198 min, t (minor) = 9.720 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.79 (d, *J* = 4.4 Hz, 1H), 8.28 (d, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.83 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.33 (m, 5H), 7.29 – 7.19 (m, 3H), 7.12 (m, 2H), 7.03 (td, *J* = 7.2, 3.2 Hz, 2H), 6.93 (d, *J* = 5.2 Hz, 1H), 6.60 (t, *J* = 4.4 Hz, 1H), 6.20 (d, *J* = 3.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.0, 145.1 (d, J_{CP} = 3.4 Hz), 139.3, 138.7 (d, J_{CP} = 4.3 Hz), 137.3, 135.7, 133.6 (d, J_{CP} = 10.6 Hz), 131.8, 131.8, 131.6 (d, J_{CP} = 2.3 Hz), 131.1 (d, J_{CP} = 2.8 Hz), 130.9 (d, J_{CP} = 12.3 Hz), 130.6 (d, J_{CP} = 138.6 Hz), 129.9, 128.8 (d, J_{CP} = 2.2 Hz), 128.6, 128.2, 127.9, 127.3 (d, J_{CP} = 13.8 Hz), 127.0 (d, J_{CP} = 3.3 Hz), 126.8 (d, J_{CP} = 2.5 Hz), 126.6 (d, J_{CP} = 2.0 Hz), 126.5, 126.4 (d, J_{CP} = 3.1 Hz), 125.9, 124.9 (d, J_{CP} = 127.1 Hz), 121.8, 121.2, 115.2 (d, J_{CP} = 6.9 Hz), 91.8, 90.1 (d, J_{CP} = 6.4 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.78; **HRMS (ESI)** calculated for $C_{33}H_{22}N_2OPS_2$ $[M + H]^+$: 557.0906, found: 557.0901.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	8.249	3797308	50.15	187787
2	W2489 ChA 254nm	9.727	3775180	49.85	162426

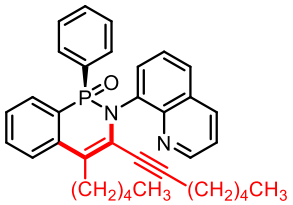
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	8.198	11612218	99.63	617517
2	W2489 ChA 254nm	9.720	42752	0.37	2415

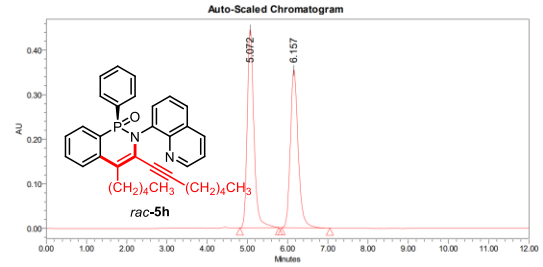
Synthetic Procedure and Characterization of 5h

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2bh** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product (*S*)-**5h** (47.9 mg) in 45% yield as a white solid with 99% ee. Product exists as a 16:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(Hept-1-yn-1-yl)-4-pentyl-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphinine 1-oxide (5h)

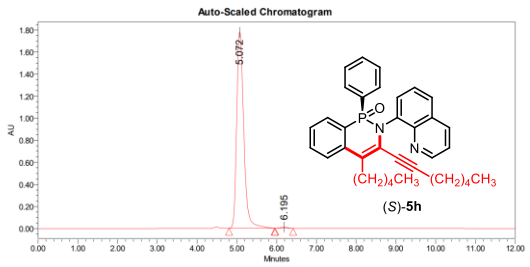


M.p.: 75 - 76 °C, $[\alpha]_D^{20}$ = +208.5 (c = 1.5, $CHCl_3$), 99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 5.072 min, t (minor) = 6.195 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.94 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.65 (dd, *J* = 8.3, 4.8 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.42 – 7.31 (m, 2H), 7.24 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.19 (dt, *J* = 7.8, 2.8 Hz, 1H), 7.09 (td, *J* = 7.2, 1.6 Hz, 1H), 6.96 (td, *J* = 7.8, 3.6 Hz, 2H), 2.96 (t, *J* = 8.0 Hz, 2H), 1.77 – 1.67 (m, 4H), 1.49 – 1.33 (m, 5H), 0.98 (q, *J* = 6.8 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.77 – 0.67 (m, 7H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.6, 145.5 (d, J_{CP} = 3.8 Hz), 138.2 (d, J_{CP} = 1.9 Hz), 137.5 (d, J_{CP} = 4.7 Hz), 135.5, 133.5 (d, J_{CP} = 10.4 Hz), 131.4 (d, J_{CP} = 3.1 Hz), 131.4 (d, J_{CP} = 3.0), 131.2 (d, J_{CP} = 12.6 Hz), 131.1 (d, J_{CP} = 138.1 Hz), 130.8 (d, J_{CP} = 3.1 Hz), 128.4, 127.4, 127.1 (d, J_{CP} = 13.5 Hz), 125.9 (d, J_{CP} = 128.0 Hz), 125.9 (d, J_{CP} = 2.0 Hz), 125.8, 125.6, 124.0 (d, J_{CP} = 9.5 Hz), 120.9, 119.8 (d, J_{CP} = 6.8 Hz), 98.6, 32.0, 31.1, 30.4, 29.7, 29.2, 27.5, 22.6, 22.0, 18.9, 14.1, 13.7; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.24; **HRMS (ESI)** calculated for $C_{35}H_{38}N_2OP$ $[M + H]^+$: 533.2716, found: 533.2715.



Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	5.072	5124105	51.69	445829
2	W2489 ChA 254nm	6.157	4789057	48.31	354658



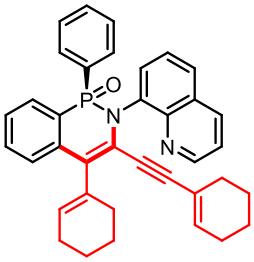
Processed Channel: W2489 ChA 254nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChA 254nm	5.072	21924227	99.49	1784798
2	W2489 ChA 254nm	6.195	111580	0.51	8958

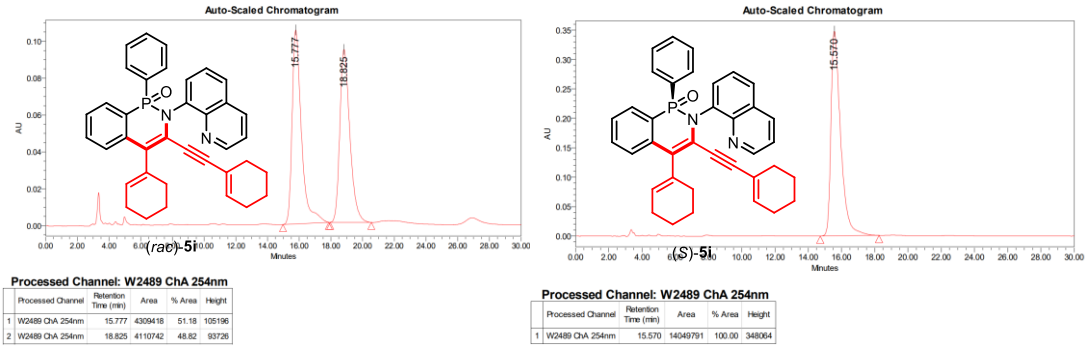
Synthetic Procedure and Characterization of 5i

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2bi** (0.3 mmol, 1.5 eq.), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 °C with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product (*S*)-**5i** (66.3 mg) in 60% yield as a white solid with >99% ee. Product exists as a 16:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-4-(Cyclohex-1-en-1-yl)-3-(cyclohex-1-en-1-ylethynyl)-1-phenyl-2-(quinolin-8-yl)-*2H*-benzo[*c*][1,2]azaphosphinine 1-oxide (5i)

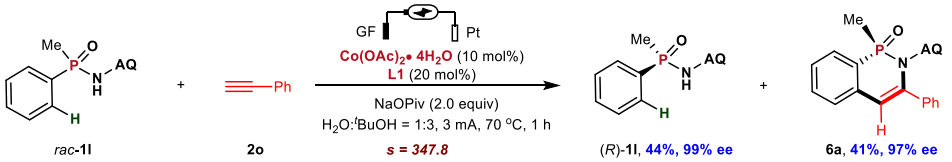


M.p.: 138 - 140 °C, $[\alpha]_D^{20}$ = +63.0 (c = 1.0, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 15.570 min, t (minor) = 18.825 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (d, *J* = 4.4 Hz, 1H), 8.19 (d, *J* = 7.2Hz), 7.95 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.78 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.62 – 7.53 (m, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.24 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.18 (td, *J* = 7.2, 2.4 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.99 (td, *J* = 8.0, 3.6 Hz, 2H), 5.91 (s, 1H), 5.30 – 5.23 (m, 1H), 2.25 (d, *J* = 36.6 Hz, 4H), 1.85 – 1.66 (m, 6H), 1.38 – 1.22 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.7, 145.3 (d, J_{CP} = 3.9 Hz), 137.9 (d, J_{CP} = 1.1 Hz), 135.4, 134.7, 133.6 (d, J_{CP} = 10.5 Hz), 131.5 (d, J_{CP} = 2.8 Hz), 131.4 (d, J_{CP} = 2.5 Hz), 131.1 (d, J_{CP} = 138.4 Hz), 131.0, 131.0, 130.9, 129.6, 128.4, 127.5, 127.1 (d, J_{CP} = 13.7 Hz), 125.9, 125.8, 125.7 (d, J_{CP} = 9.2 Hz), 125.5 (d, J_{CP} = 139.7 Hz), 124.6 (d, J_{CP} = 4.6 Hz), 121.0, 120.2, 84.4 (d, J_{CP} = 6.1 Hz), 31.6, 29.4, 28.0, 25.8, 25.5, 23.4, 22.6, 22.3, 21.9, 21.2, 14.1; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 15.42; **HRMS (ESI)** calculated for $C_{34}H_{34}N_2OP$ $[M + H]^+$: 553.2403, found: 553.2406.



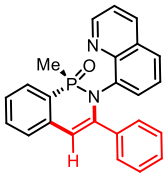
Kinetic Resolution of *(rac)*-1l

Kinetic Resolution of *(rac)*-1l with 6a

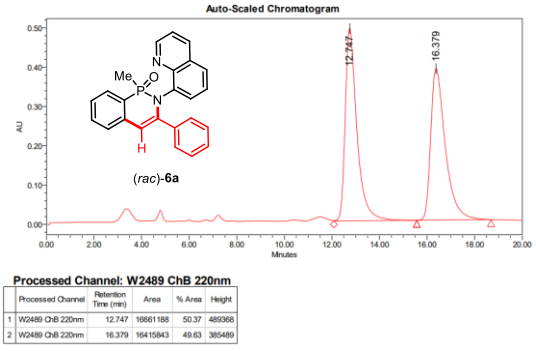


The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide *rac*-**1l** (0.2 mmol, 1.0 eq.), alkyne **2o** (0.3 mmol, 1.5 eq.), $Co(OAc)_2 \cdot 4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 °C with a constant current of 3 mA maintained for 1 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **6a** (31.3 mg) in 41% yield as a light-yellow foam with 97% ee. **6a** exists as a 8:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown and recovered the *(R)*-**1l** in 44% yield with >99% ee.

(*S*)-1-Methyl-3-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (6a)

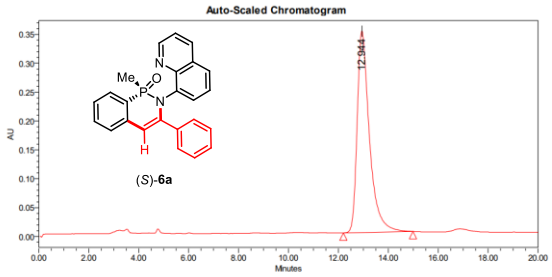


M.p.: 115 - 117 °C, $[\alpha]_D^{20}$ = -99.3 (c = 0.5, $CHCl_3$), 97% ee, lit[1d] $[\alpha]_D^{20}$ = -97.9 [c = 0.5, $CHCl_3$, 98% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (major) = 12.747 min, t (minor) = 16.379 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.96 (d, *J* = 4.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 12.4, 8.0 Hz, 1H), 7.63 – 7.47 (m, 4H), 7.42 – 7.35 (m, 4H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.05 – 6.87 (m, 3H), 6.40 (s, 1H), 1.95 (d, *J* = 14.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.9, 145.3, 144.5 (d, J_{CP} = 1.3 Hz), 137.8, 137.8 (d, J_{CP} = 4.8 Hz), 137.1 (d, J_{CP} = 6.7 Hz), 135.9, 131.8 (d, J_{CP} = 2.4 Hz), 131.4 (d, J_{CP} = 10.6 Hz), 130.1 (d, J_{CP} = 2.6 Hz), 129.1, 129.0, 128.8, 128.0, 127.6, 126.9 (d, J_{CP} = 13.0 Hz), 126.8, 126.4 (d, J_{CP} = 9.3 Hz), 126.0, 124.1 (d, J_{CP} = 117.7 Hz), 121.4, 110.6 (d, J_{CP} = 8.1 Hz), 16.3 (d, J_{CP} = 96.1 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.27; **HRMS (ESI)** calculated for $C_{24}H_{20}N_2OP$ $[M + H]^+$: 383.1308, found: 383.1311.



Processed Channel: W2489 ChB 220nm

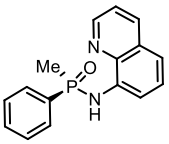
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	12.747	16661188	50.37	489368
2	W2489 ChB 220nm	16.379	16415843	49.63	385489



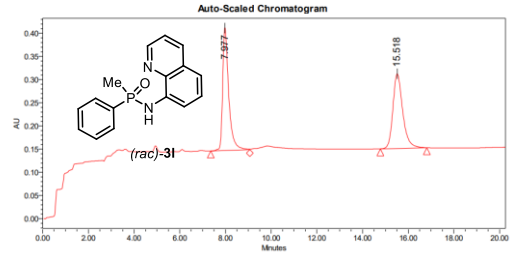
Processed Channel: W2489 ChB 220nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	12.944	11926118	100.00	348962

(*R*)-P-Methyl-P-phenyl-*N*-(quinolin-8-yl)phosphinic amide [(*R*)-1l]

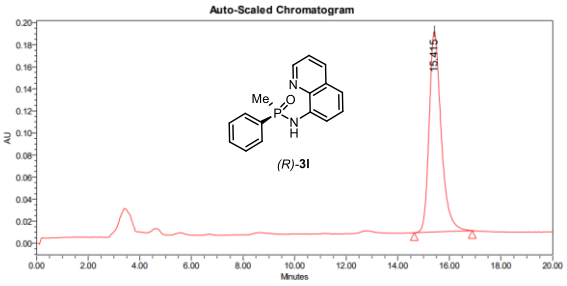


$[\alpha]_D^{20}$ = +198.3 (c = 0.5, $CHCl_3$), lit[1d] $[\alpha]_D^{20}$ = +172 [c = 0.25, $CHCl_3$, 99% ee (*R*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (minor) = 7.977 min, t (major) = 15.518 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (dd, *J* = 4.4, 2.0 Hz,1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.85 (m, 3H), 7.53 – 7.50 (m, 1H), 7.47 – 7.40 (m, 3H), 7.37 – 7.37 (m, 1H), 7.30 – 7.24 (m, 2H), 1.95 (d, *J* = 14.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.9, 138.6 (d, J_{CP} = 6.9 Hz), 137.7, 136.4, 132.1 (d, J_{CP} = 125.2 Hz), 131.5, 131.4, 128.9 (d, J_{CP} = 12.9 Hz), 128.8, 127.2, 121.7, 119.2, 113.2 (d, J_{CP} = 3.9 Hz), 18.0 (d, J_{CP} = 92.2 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 25.65; **HRMS (ESI)** calculated for $C_{16}H_{16}N_2OP$ $[M + H]^+$: 283.0995, found: 283.0994.



Processed Channel: W2489 ChB 220nm

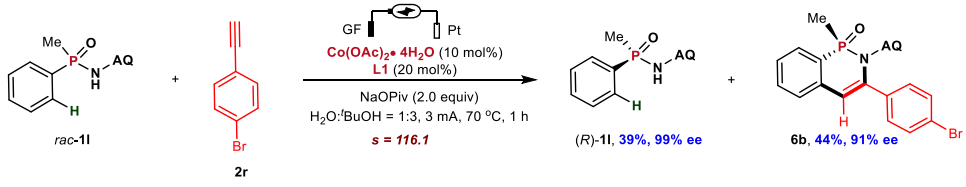
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	7.977	4873218	50.39	265184
2	W2489 ChB 220nm	15.518	4798541	49.61	161090



Processed Channel: W2489 ChB 220nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	15.415	5863153	100.00	181894

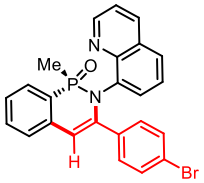
Kinetic Resolution of *(rac)*-1l with 6b



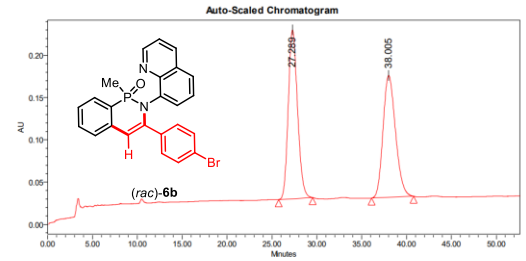
The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide *rac*-**1l** (0.2 mmol, 1.0 equiv), alkyne **2r** (0.3 mmol, 1.5 equiv), $Co(OAc)_2 \cdot 4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.4 mmol, 2.0 equiv) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH / H_2O (3.0:1.0). Electrocatalysis was performed at 70 °C with a constant current of 3 mA maintained for 1 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on

silica gel (PE/Acetone = 3:1 v/v) to give the desired product **6b** (40.6 mg) in 44% yield as a light-yellow foam with 91% ee. **6b** exists as a 10:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown and recovered the *(R)*-**1l** in 39% yield with >99% ee.

(*S*)-3-(4-Bromophenyl)-1-methyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (6b)

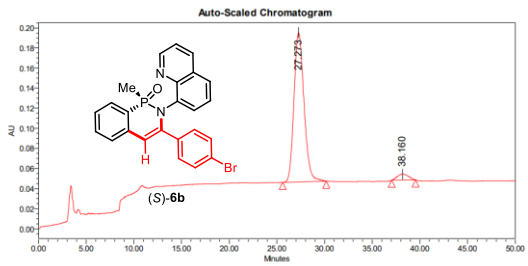


M.p.: 123 - 125 °C, $[\alpha]_D^{20}$ = -100.3 (c = 1.0, $CHCl_3$), 91% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (major) = 27.289 min, t (minor) = 38.005 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.94 (d, *J* = 4.2 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 12.0, 7.2 Hz, 1H), 7.66 – 7.50 (m, 3H), 7.47 – 7.36 (m, 3H), 7.36 – 7.29 (m, 1H), 7.27 (d, *J* = 7.6, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 1.92 (d, *J* = 14.7 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.1, 145.2, 143.5, 137.6, 136.9 (d, J_{CP} = 1.6 Hz), 136.8 (d, J_{CP} = 4.5 Hz), 136.0, 131.9 (d, J_{CP} = 2.4 Hz), 130.9, 130.1 (d, J_{CP} = 2.6 Hz), 129.6, 129.1 (d, J_{CP} = 9.9 Hz), 128.1 (d, J_{CP} = 169.7 Hz), 127.1 (d, J_{CP} = 6.3 Hz), 126.6 (d, J_{CP} = 9.2 Hz), 126.1, 124.3 (d, J_{CP} = 117.8 Hz), 122.2, 121.6, 110.7 (d, J_{CP} = 8.2 Hz), 16.3 (d, J_{CP} = 96.3 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 28.76; **HRMS (ESI)** calculated for $C_{24}H_{19}BrN_2OP$ $[M + H]^+$: 461.0418, found: 461.0422.



Processed Channel: W2489 ChB 220nm

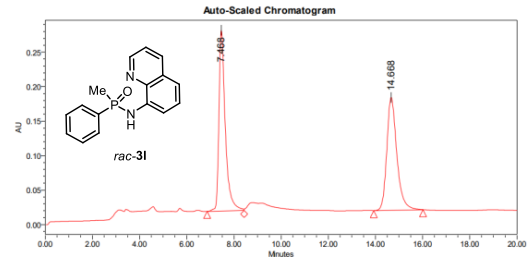
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	27.289	14294628	50.63	199833
2	W2489 ChB 220nm	38.005	13940407	49.37	144348



Processed Channel: W2489 ChB 220nm

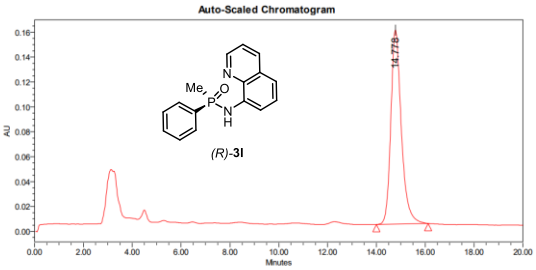
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	27.273	10845111	95.67	148700
2	W2489 ChB 220nm	38.160	490279	4.33	5947

HPLC Condition The enantiomeric excess was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (minor) = 7.468 min, t (major) = 14.668 min.



Processed Channel: W2489 ChB 220nm

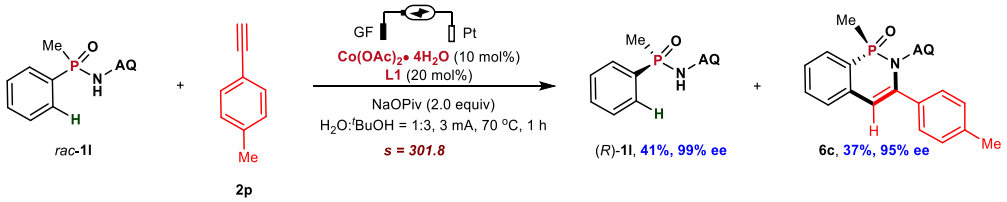
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	7.468	4912735	50.37	262331
2	W2489 ChB 220nm	14.668	4839755	49.63	163639



Processed Channel: W2489 ChB 220nm

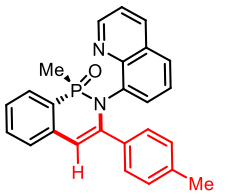
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	14.778	4645959	100.00	156019

Kinetic Resolution of *(rac)*-1l with 6c

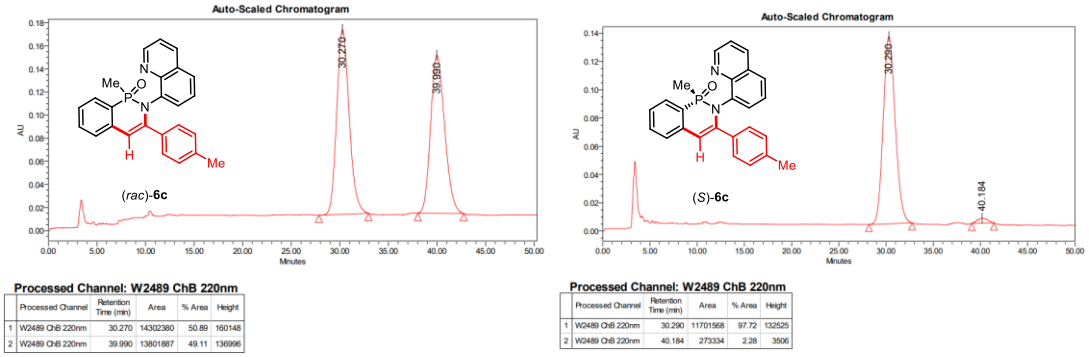


The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide *rac*-**1l** (0.2 mmol, 1.0 eq.), alkyne **2ap** (0.3 mmol, 1.5 eq.), $Co(OAc)_2 \cdot 4H_2O$ (10 mol %), (*S*)-**L1** (15 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of $^tBuOH/H_2O$ (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 1 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 3:1 v/v) to give the desired product **6c** (29.3 mg) in 37% yield as a light-yellow foam with 95% ee. **6c** exists as a 12:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown and recovered the *(R)*-**1l** in 41% yield with >99% ee.

(*S*)-1-Methyl-2-(quinolin-8-yl)-3-(*p*-tolyl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (6c)



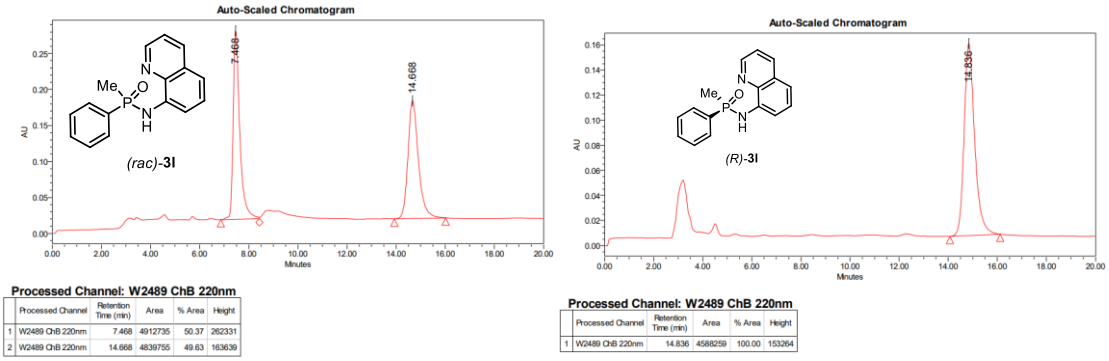
M.p.: 110 - 113 °C, $[\alpha]_D^{20}$ = -140.3 (c = 1.0, $CHCl_3$), 95% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220 nm, t (major) = 30.270 min, t (minor) = 39.990 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.97 (d, *J* = 4.4 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 12.0, 7.6 Hz, 1H), 7.53 (t, *J* = 8.4, 3.6 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.29 – 7.26 (m, 3H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H), 2.11 (s, 3H), 1.96 (d, *J* = 14.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.9, 145.4, 144.5, 138.0 (d, J_{CP} = 7.0 Hz), 137.2 (d, J_{CP} = 6.9 Hz), 135.9, 135.0 (d, J_{CP} = 4.7 Hz), 131.8 (d, J_{CP} = 2.3 Hz), 130.0 (d, J_{CP} = 2.5 Hz), 129.0 (d, J_{CP} = 9.6 Hz), 128.8, 128.4, 127.8, 126.8 (d, J_{CP} = 12.7 Hz), 126.7, 126.3 (d, J_{CP} = 9.4 Hz), 126.0, 124.2 (d, J_{CP} = 117.6 Hz), 121.4, 110.4 (d, J_{CP} = 8.2 Hz), 21.1, 16.2 (d, J_{CP} = 95.8 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 29.49; **HRMS (ESI)** calculated for $C_{25}H_{22}N_2OP$ $[M + H]^+$: 397.1470, found: 397.1475.



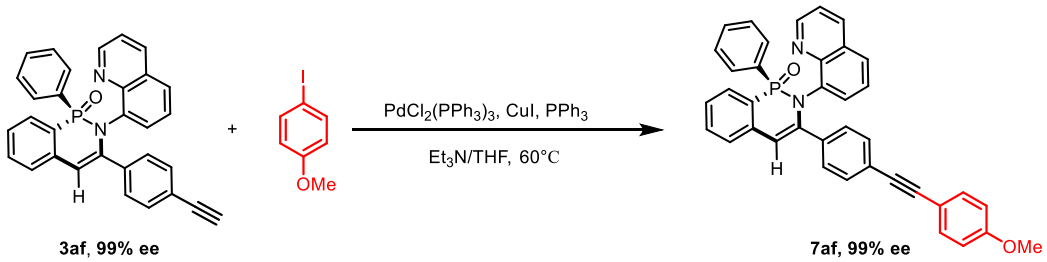
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	30.270	14302380	50.89	160148
2	W2489 ChB 220nm	39.990	13801887	49.11	136996

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	W2489 ChB 220nm	30.290	11701568	97.72	132525
2	W2489 ChB 220nm	40.184	273334	2.28	3506

HPLC Condition The enantiomeric excess was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 220nm, t (minor) = 7.468 min, t (major) = 14.668 min.

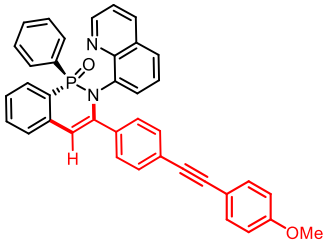


Synthetic Procedure and Characterization of 7af



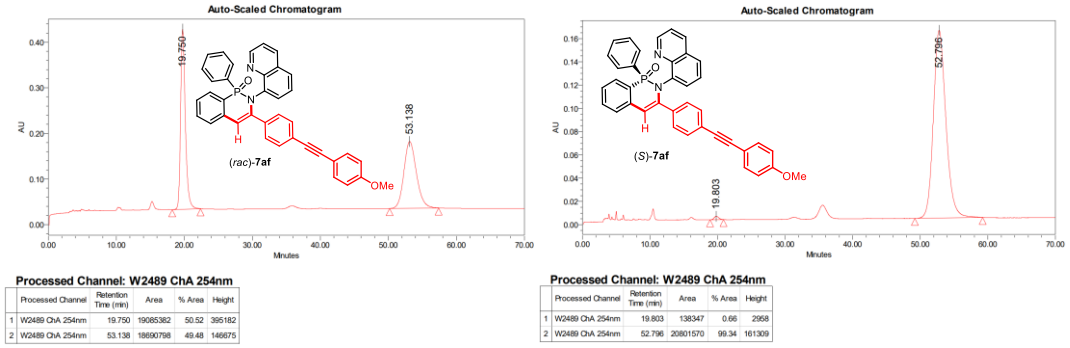
An oven-dried Schlenk flask was charged with CuI (0.04 mmol, 0.02 equiv.), PPh_3 (0.004 mmol, 0.02 equiv.), $Pd(PPh_3)_3Cl_2$ (0.004 mmol, 0.02 equiv.) and *p*-iodoanisole (0.2 mmol, 1.0 equiv.). The vessel was evacuated and backfilled with argon three times. Subsequently, dry THF (2 ml), **3af** (0.2 mmol, 1.0 equiv.), and dry Et_3N (2 ml) were added and the mixture was stirred at 60 °C. After completion of the reaction, which was indicated by TLC, the mixture was quenched with water and the aqueous phase was extracted three times with AcOEt (3×5 ml). The combined extracts were dried over MgSO4 and the solvents were evaporated under reduced pressure. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product **7af** (95.4 mg) in 83% yield as a light-yellow foam with 99% ee. Product exists as a 8:1 mixture of atropisomers due to the hindered rotation about the *N*-quinoline bond and the structure of major isomer was shown.

(*S*)-3-(4-((4-methoxyphenyl)ethynyl)phenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*benzo[*c*][1,2]azaphosphinine 1-oxide (7af)

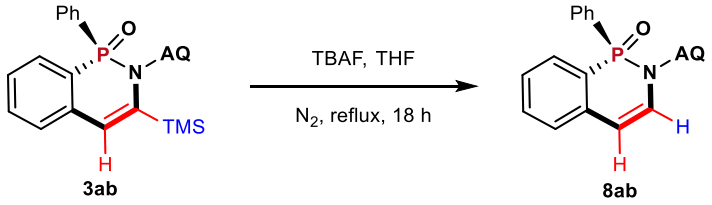


M.p.: 125 - 127 °C; $[\alpha]_D^{20}$ = +385.3 (c = 0.2, $CHCl_3$), 99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 19.803 min, t (mjaor) = 52.796 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.74 (s, 1H), 8.15 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.71 (dd, *J* = 12.8, 7.6 Hz, 2H), 7.59 – 7.44 (m, 4H), 7.40 - 7.32 (m, 5H), 7.29 (s, 1H), 7.18 - 7.11 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.03 – 6,95 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.37 (s, 1H), 3.78 (s, 3H); **^{13}C MR (100 MHz, $CDCl_3$)** δ 159.6, 149.3, 144.6, 143.8 (d, J_{CP} = 3.1 Hz), 138.1 (d, J_{CP} = 4.2 Hz), 137.8 (d, J_{CP} = 5.0 Hz), 137.6 (d, J_{CP} = 2.4 Hz), 135.6, 133.0, 132.9, 132.9, 131.8 (d, J_{CP} = 2.5 Hz), 131.5, 131.5, 130.9, 130.8, 130.1, 128.8, 128.4, 128.2 (d, J_{CP} = 30.7 Hz), 127.4, 127.1 (d, J_{CP} = 13.8 Hz), 126.8 (d, J_{CP} = 9.0 Hz), 126.1 (d, J_{CP} = 14.5 Hz), 125.5,

123.6 (d, J_{CP} = 126.8 Hz), 122.4, 121.1, 115.1, 114.0, 107.8 (d, J_{CP} = 7.9 Hz), 90.1, 87.9, 55.3; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 18.79; **HRMS (ESI)** calculated for $C_{38}H_{27}N_2O_2P$ [M+ H]$^+$: 575.1883, found: 575.1884.

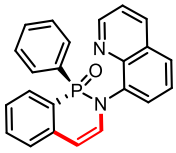


Synthetic Procedure and Characterization of 8ab

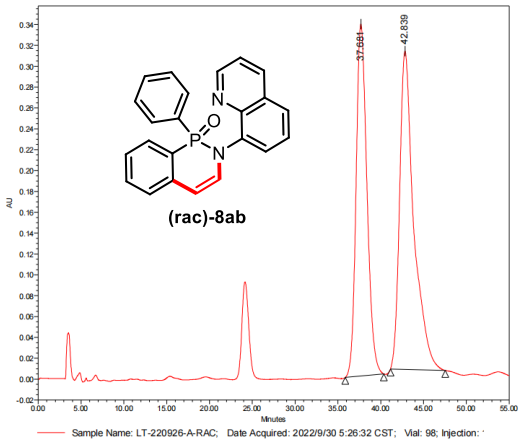


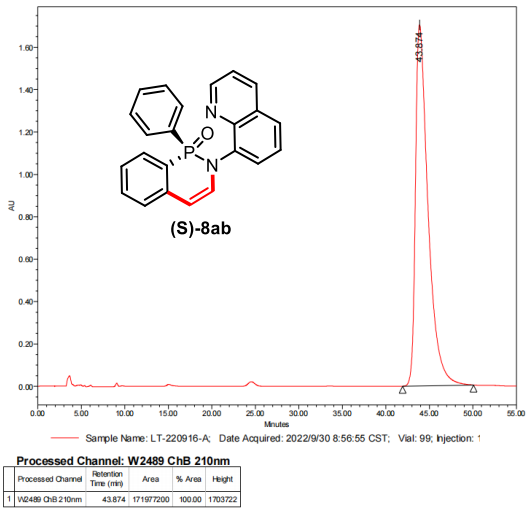
Adding TBAF (2.4 mmol, 627.5 mg, 4 equiv.) into a THF solution of **3ab** (0.51 mmol, 225 mg) under a nitrogen atmosphere. The mixture was stirred at 60°C for 18 h and cooled to room temperature. Next, adding water to the mixture, add separating the phases and washing the aqueous phase with diethyl ether (3 × 25 mL). Then, the combined organic phases were dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. The mixture was subjected to column chromatography on silica gel (PE/Acetone = 2:1 v/v) to give the desired product **8ab** (156.0 mg) in 83% yield as a white solid with >99% ee.

(*S*)-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine 1-oxide (8ab)

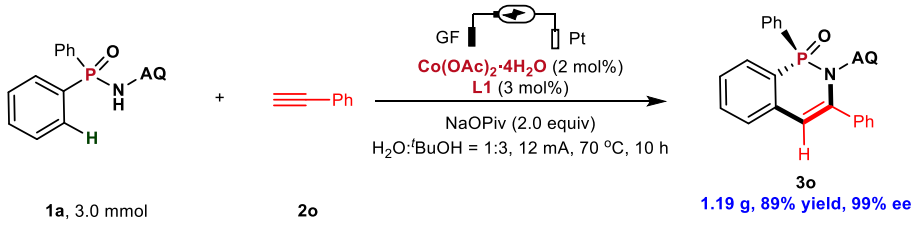


M.p.: 77 – 79°C, > 99% ee; $[\alpha]_D^{20}$ = +394.4 (c = 0.5, $CHCl_3$), lit[1d] $[\alpha]_D^{20}$ = +400.9 [c = 0.5, $CHCl_3$, >99% ee (*S*)]. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 90/10, 1.0 mL/min, λ = 210 nm, t (single) = 43.874 min; **(400 MHz, $CDCl_3$)** δ 8.84 (s, 1H), 8.23 (d, *J* = 7.2 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 13.2 Hz, 1H), 7.73 (d, *J* = 13.2 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.40 – 7.29 (m, 3H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.06 (s, 2H), 6.82 (dd, *J* = 16.0, 8.0 Hz, 1H), 6.04 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.0, 143.7 (d, J_{CP} = 3.8 Hz), 137.9, 137.5 (d, J_{CP} = 4.3 Hz), 136.1 (d, J_{CP} = 4.6 Hz), 132.8 (d, J_{CP} = 10.7 Hz), 131.7 (d, J_{CP} = 2.5 Hz), 131.6 (d, J_{CP} = 2.9 Hz), 131.1 (d, J_{CP} = 136.5 Hz), 130.9 (d, J_{CP} = 12.0 Hz), 129.2, 129.0, 127.6, 127.4 (d, J_{CP} = 13.7 Hz), 126.0, 125.9, 125.9, 125.6 (d, J_{CP} = 14.4 Hz), 123.3 (d, J_{CP} = 125.6 Hz), 121.3, 102.2 (d, J_{CP} = 8.8 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)** δ 16.80; **HRMS (ESI)** calculated for $C_{27}H_{24}F_2N_2OP$ [M + H]$^+$: 369.1151, found: 369.1159.



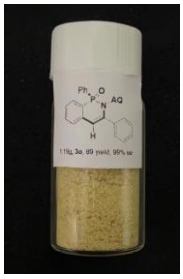


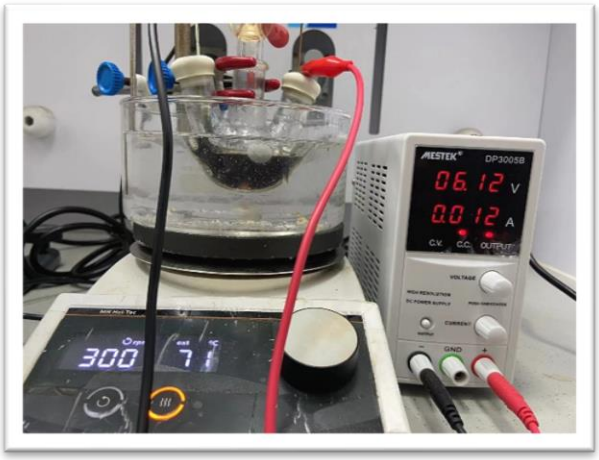
Gram-Scale Synthesis of (*S*)-3o with Reduced Catalyst Loading

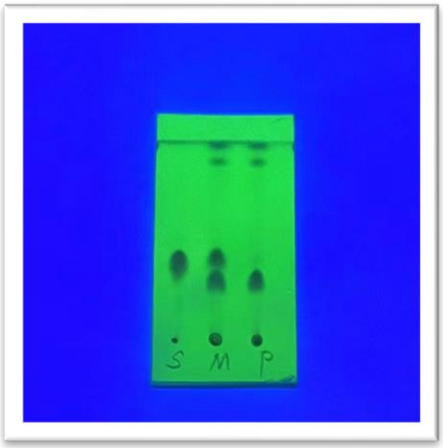


1a, 3.0 mmol **2o**

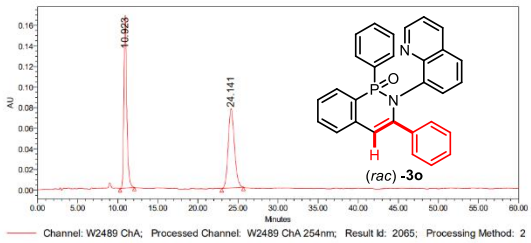
3o
1.19 g, 89% yield, 99% ee





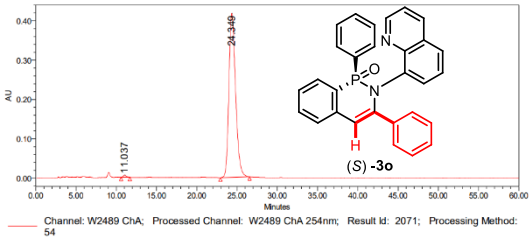


The electrocatalysis was carried out in an undivided cell, with a GF anode (20 mm ×30 mm ×6 mm) and a platinum cathode (20 mm ×30 mm ×0.25 mm). Phosphinic amid **1a** (3.0 mmol), phenylacetylene **2o** (4.5 mmol), $Co(OAc)_2·4H_2O$ (2 mol%), (*S*)-L1 (3.0 mol%), NaOPiv (6 mmol), ^{t}BuOH (15 mL) and H_2O (5 mL) were added to an oven dried vial equipped with stirring bars. Electrocatalysis was performed at 70 °C with a constant current of 12 mA maintained for 10 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the desired product (*S*)-**3o** (1.19 g) in 89% yield as a light-yellow foam with 99% ee. The enantiomeric excess was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254nm, t (minor) = 11.037 min, t (major) = 24.349 min.



Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	10.923	4181797	50.37	167709
2	W2489 ChA 254nm	24.141	4121153	49.63	76799

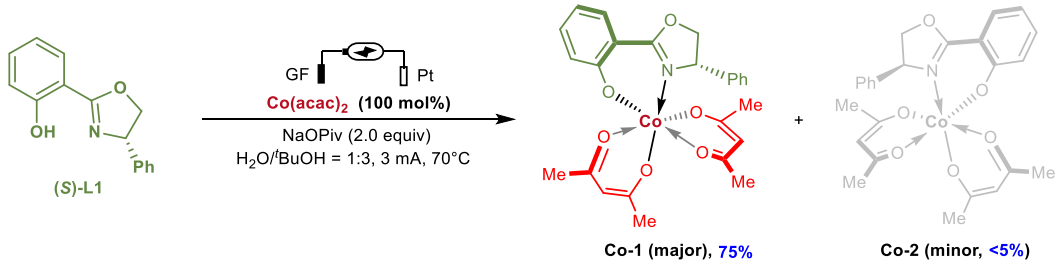


Processed Channel Descr.: W2489 ChA 254nm

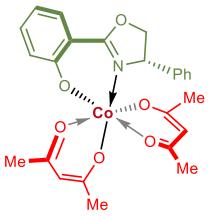
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.037	147293	0.61	5717
2	W2489 ChA 254nm	24.349	23937109	99.39	416479

Mechanistic Studies

Synthesis of Octahedral Co(III)-Complex via Stoichiometric Reaction of $Co(acac)_2$ and L1

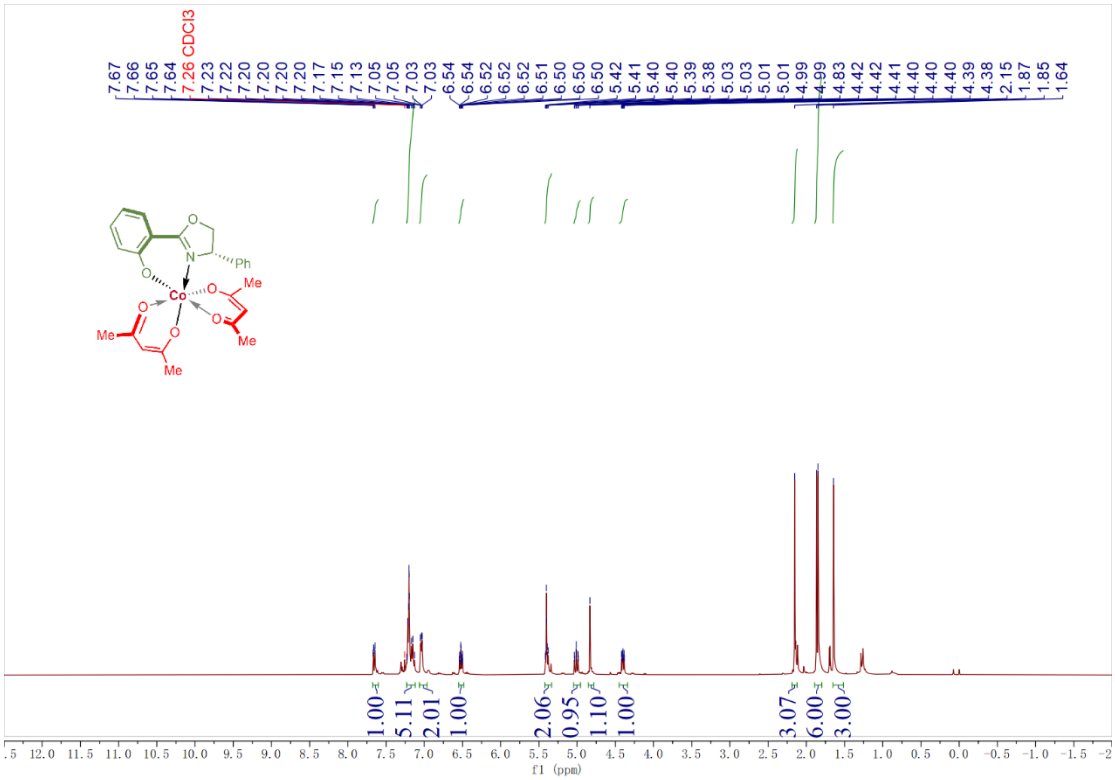


The reaction was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). (*S*)-**L1** (0.2 mmol), $Co(acac)_2$ (0.2 mmol) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). The reaction was performed at 70 ℃ with a constant current of 3 mA maintained for 3 h. Every reaction mixture was diluted with DCM and concentrated in vacuo. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with DCM and concentrated in vacuo.Then the mixture was subjected to column chromatography on silica gel (PE/EtOAc/DCM = 10:1:2 v/v/v) to give the desired complex **Co-1**.

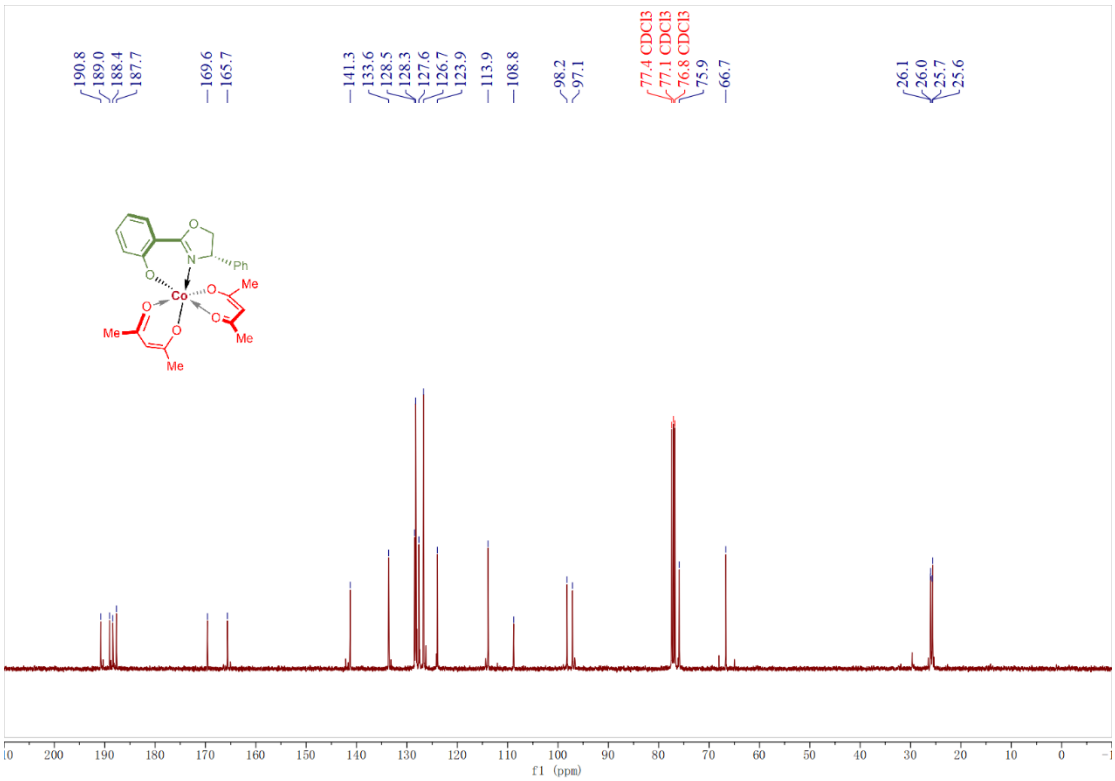


Co-1: dark green solid, (74.3 mg, 75% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (dd, J = 8.0, 1.6 Hz, 1H), 7.23 – 7.13 (m, 5H), 7.05 – 7.03 (m, 2H), 6.52 (ddd, J = 8.4, 6.8, 1.6 Hz, 1H), 5.42 – 5.38 (m, 2H), 5.04 – 4.99 (m, 1H), 4.83 (s, 1H), 4.42 – 4.38 (m, 1H), 2.15 (s, 3H), 1.87 (s, 3H), 1.85 (s, 3H), 1.64 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.8, 189.0, 188.4, 187.7, 169.6, 165.7, 141.3, 133.6, 128.5, 128.3, 127.6, 126.7, 124.0, 113.9, 108.8, 98.2, 97.1, 75.9, 66.7, 26.1, 26.0, 25.7, 25.6.; HRMS (MALDI-TOF) calculated for $C_{25}H_{26}CoNO_6$ $[M]^+$: 495.1092, found: 495.1091. The data was in accordance with refer 1d.

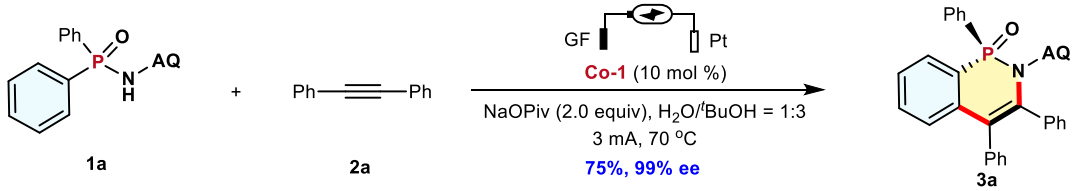
^{1}H-NMR of **Co-1**



^{13}C-NMR of **Co-1**



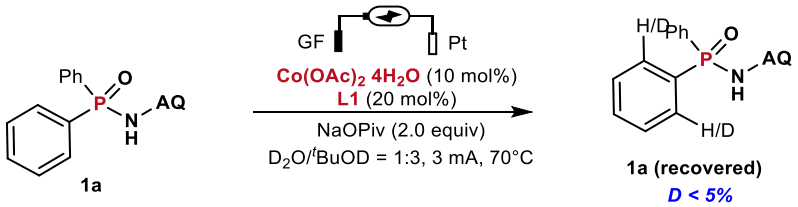
Cobalt-based Intermediate Co-1 Used as a Catalyst in [4+2] Annulation of 1a and 2a



The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), alkyne **2a** (0.3 mmol, 1.5 eq.), **Co-1** (10 mol %), NaOPiv (0.4 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 2:1 v/v) to give the desired product (*S*)-**3a** (37.5 mg) in 75% yield with 99% ee.

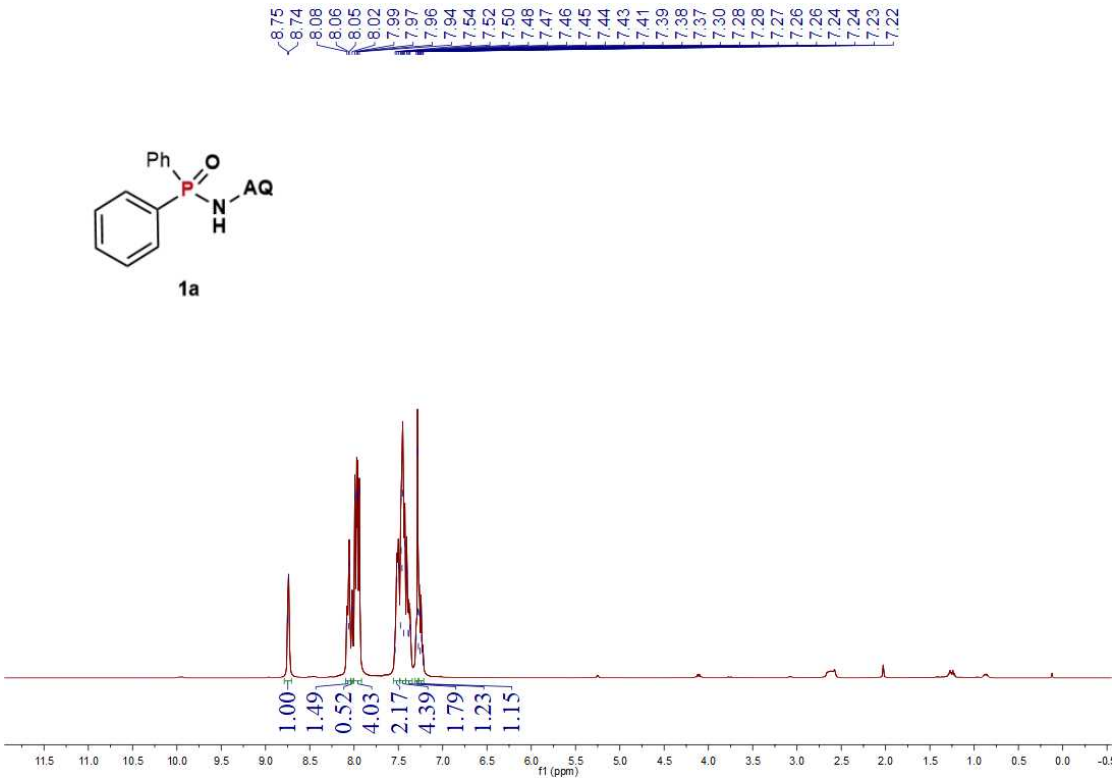
Kinetic Isotope Effect

D/H Exchange Experiment of 1a

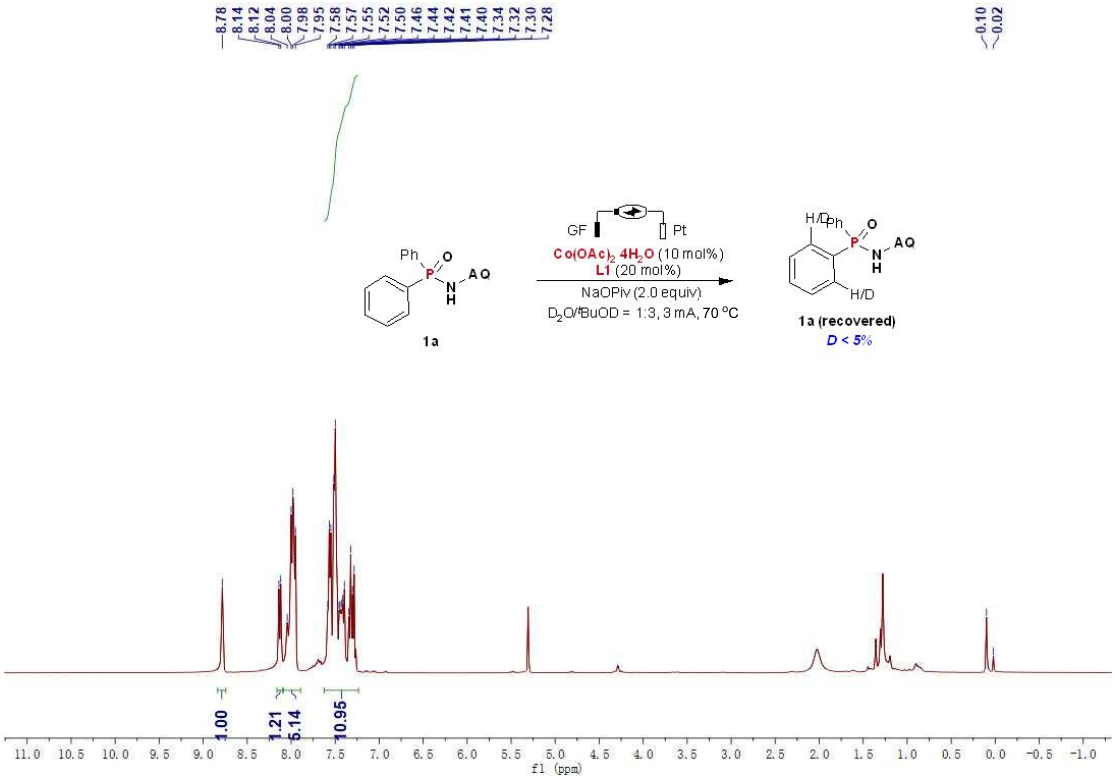


The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 equiv), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 equiv) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOD/D_2O (3.0:1.0). Electrocatalysis was performed at 70 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the recovered starting material. No obvious H/D exchange was observed.

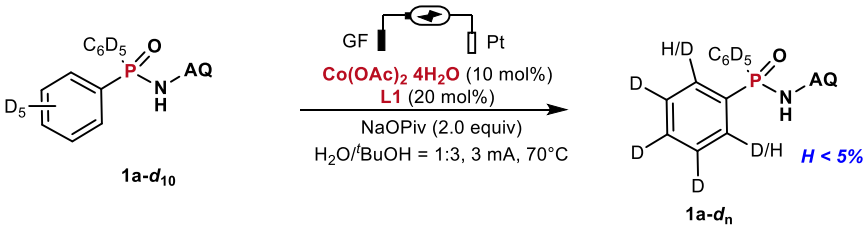
^{1}H-NMR of **1a**



^{1}H-NMR of recovered **1a** from the D/H exchange experiment

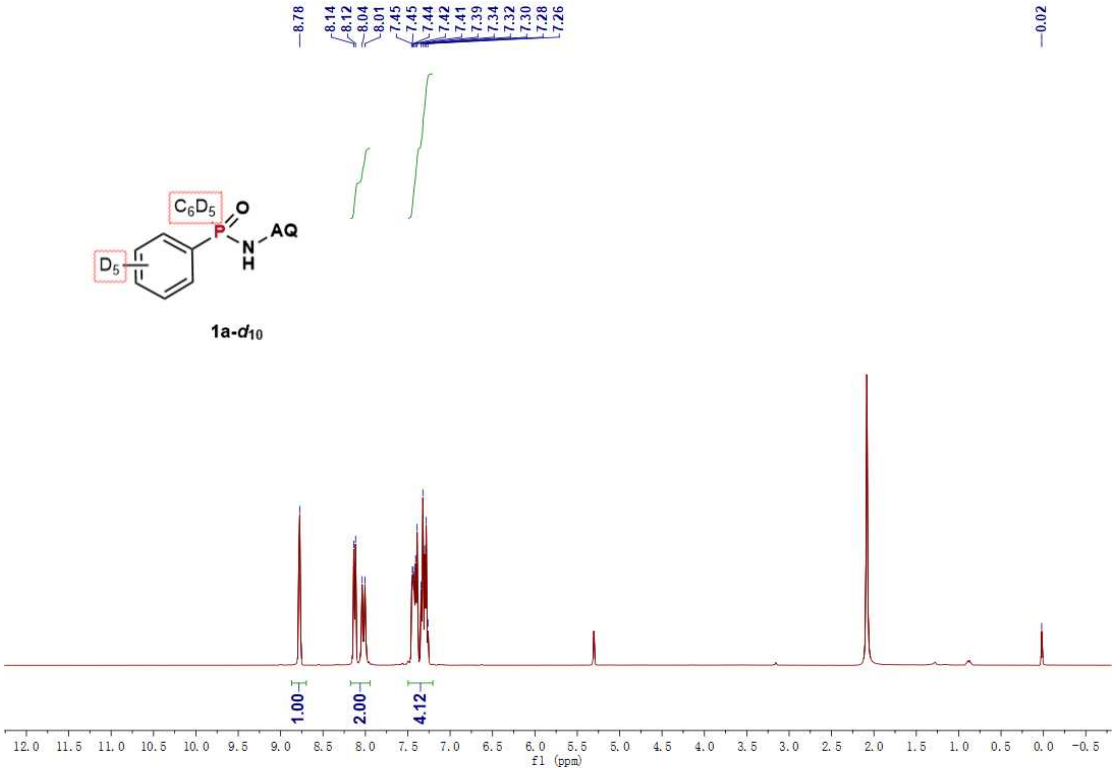


D/H Exchange Experiment of 1a-d_{10}

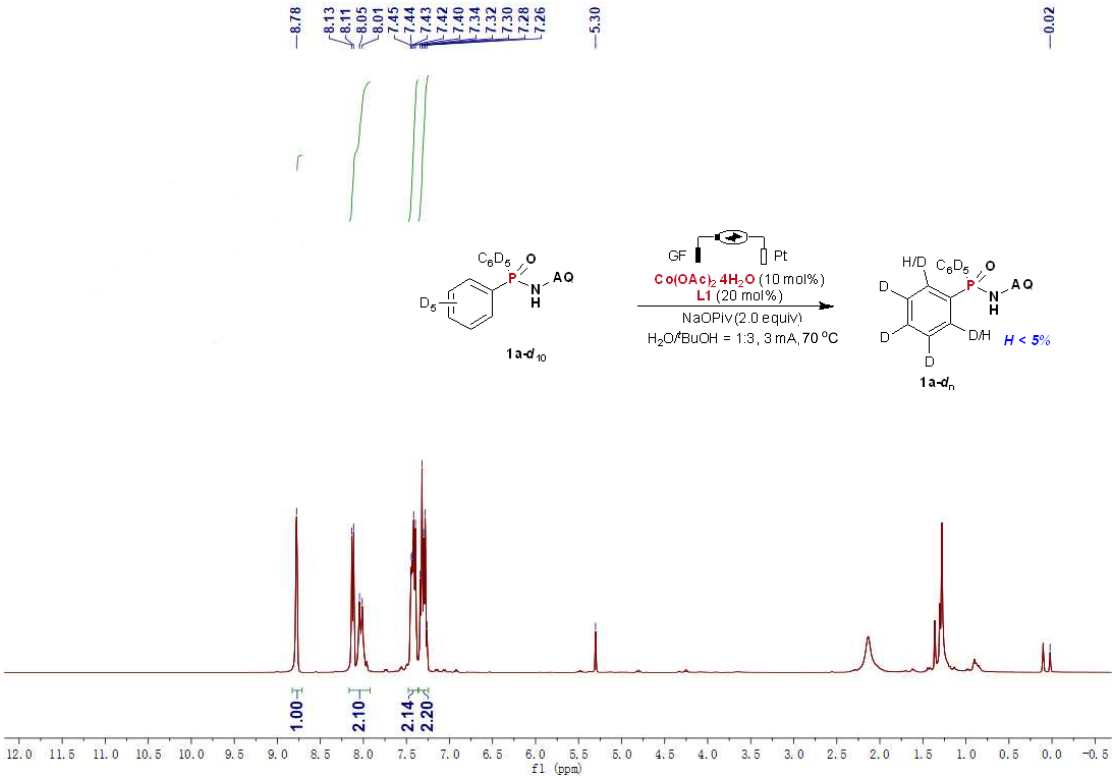


The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a-*d*$_{10}$** (0.2 mmol, 1.0 equiv), $Co(OAc)_2$•$4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.4 mmol, 2.0 equiv) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 °C with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 1:1 v/v) to give the recovered deuterium labelling starting material. No obvious D/H exchange was observed.

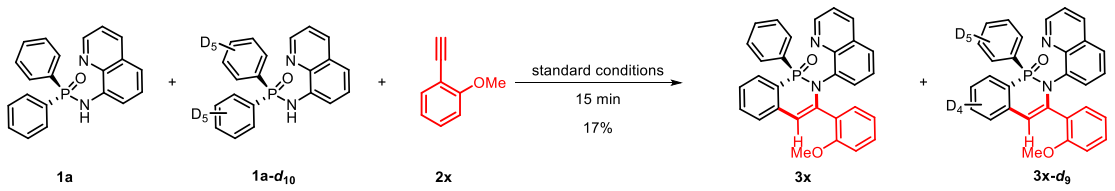
^{1}H-NMR of recovered **1a-*d*$_{10}$**



^{1}H-NMR of recovered **1a-*d*$_{10}$** from the D/H exchange experiment

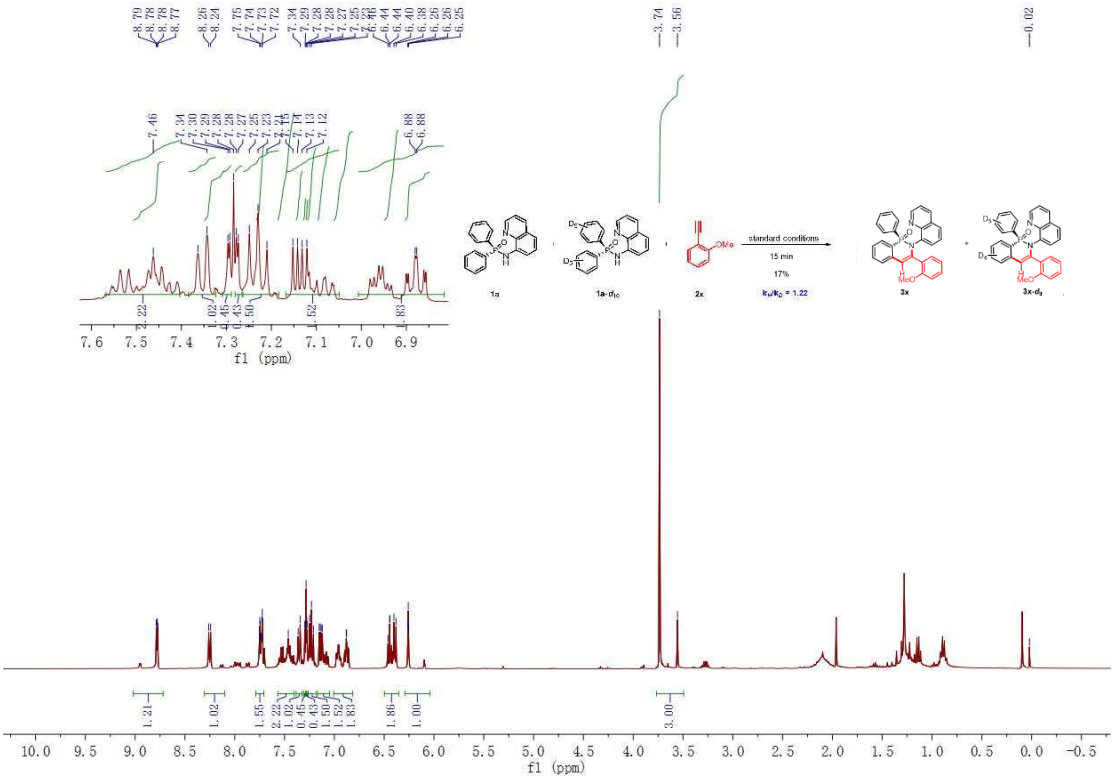


Competing Experiment

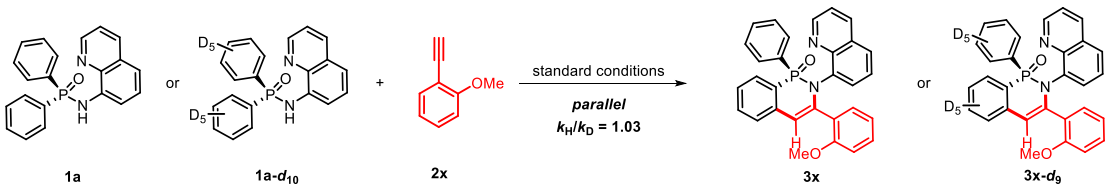


The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** (0.2 mmol, 1.0 eq.), **1a-*d*$_{10}$** (0.2 mmol, 1.0eq.), alkyne **2x** (0.3 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was proformed at 70 °C with a constant current of 3 mA maintained for 15 min. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na_2CO_3, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel (PE/Acetone = 4:1 v/v) to give the desired product (35.2 mg) in 17% yield. (k_H/k_D = 1.22). The ratio of product **3x**/**3x-*d*$_9$** was analyzed by ^{1}H NMR.

^{1}H-NMR of mixtured **3x** and **3x-*d*$_9$** from the competing experiment



Parallel Experiments



The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm ×20 mm ×6 mm) and a platinum cathode (10 mm ×20 mm ×0.25 mm). Phosphinic amide **1a** or **1a-*d*$_{10}$** (0.2 mmol, 1.0 eq.), alkyne **2x** (0.3 mmol, 1.5 eq.), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), (*S*)-**L1** (20 mol %), NaOPiv (0.2 mmol, 2.0 eq.) were placed in a 15 mL cell and dissolved in 4.0 mL of ^{t}BuOH/H_2O (3.0:1.0). Electrocatalysis was performed at 70 °C with a constant current of 3 mA for 10 min, 12 min, 14 min, 16 min, 18 min, and immediately quenched with EA and monitored by HPLC (Figure S1). The KIE was determined as k_H/k_D = 1.86/1.81 = 1.03.

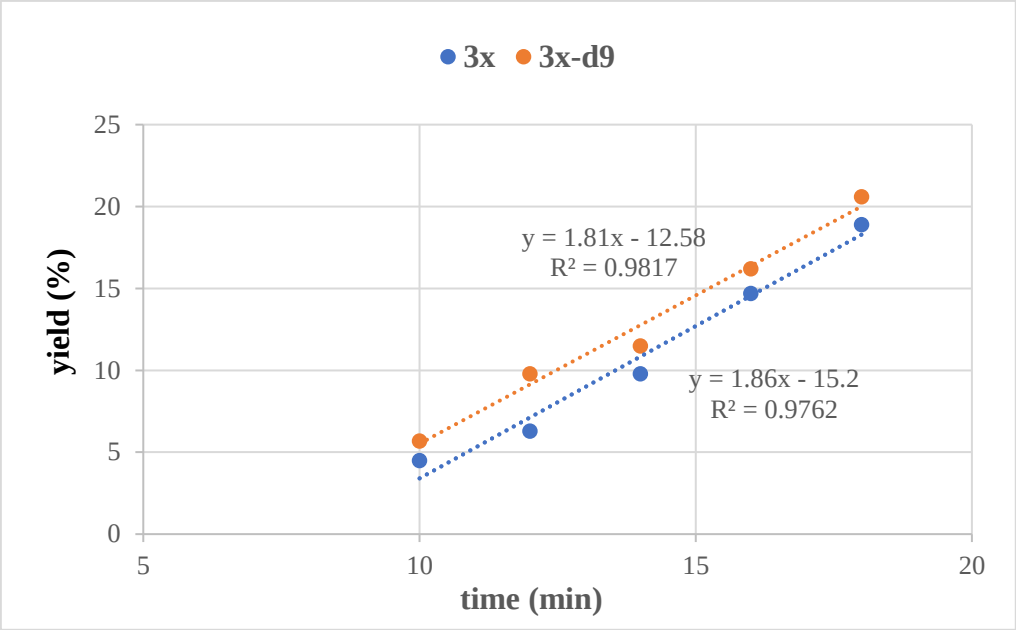
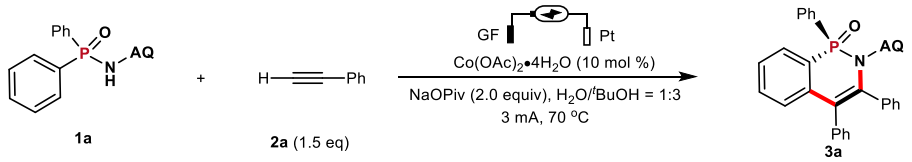


Figure S1 Parallel KIE experiments

Linear Effects between ee of 3a and ee of L1



The results were obtained using general procedure with a mixture of *(rac)*-**L1** and *(S)*-**L1** in different ratio (Table S1 and Figure S2). The mixtures were prepared using mother solution (C = 10 mg/mL in ^{t}BuOH) of *(rac)*-**L1** and *(S)*-**L1**. And the ee value of the mixtures and alkynylation product **3a** were determined by chiral HPLC.

Table S1 Linear Effects Studies

Entry	Ee value of ligand **L** (%)	Ee value of **3a** (%)
1	-2.30	7.92
2	28.24	31.54
3	34.32	37.10
4	46.54	49.32
5	56.68	58.56
6	61.90	64.94

7	78.74	79.52
8	88.78	96.62
9	99.90	99.90

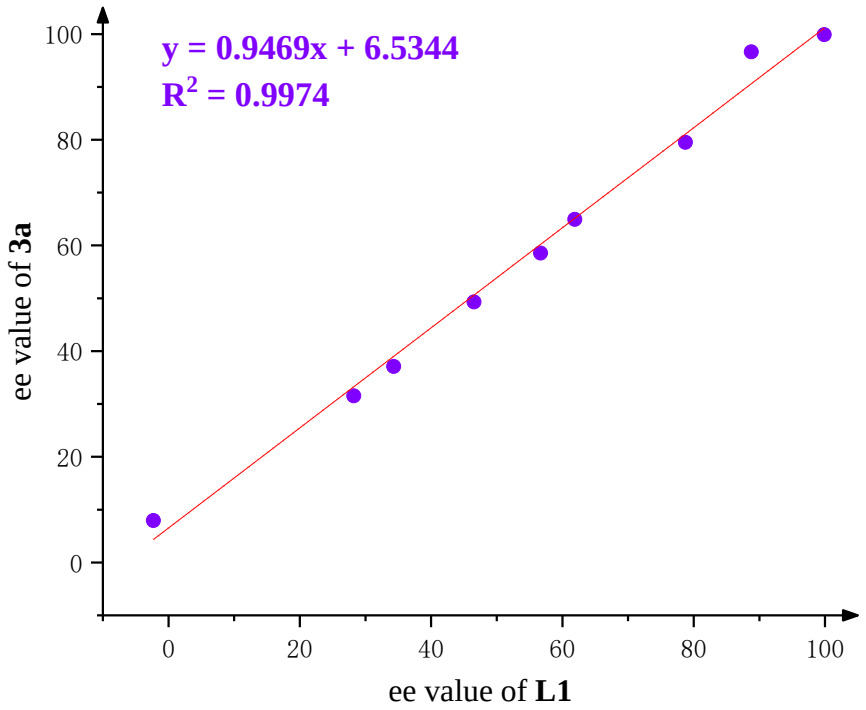


Figure S2 Linear effects between ee of **3a** and ee of **L1**

Cyclic Voltammetry (C-V) Studies

The cyclic voltammograms were recorded on a CHI 600E instrument using a glassy-carbon working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode, with electrolyte solution of *n*-Bu_4NBF_4 (1 mmol, 329 mg) in MeCN (6 mL) and H_2O (4 mL) at room temperature. A scan rate of 100 mV/s (Figure S3).

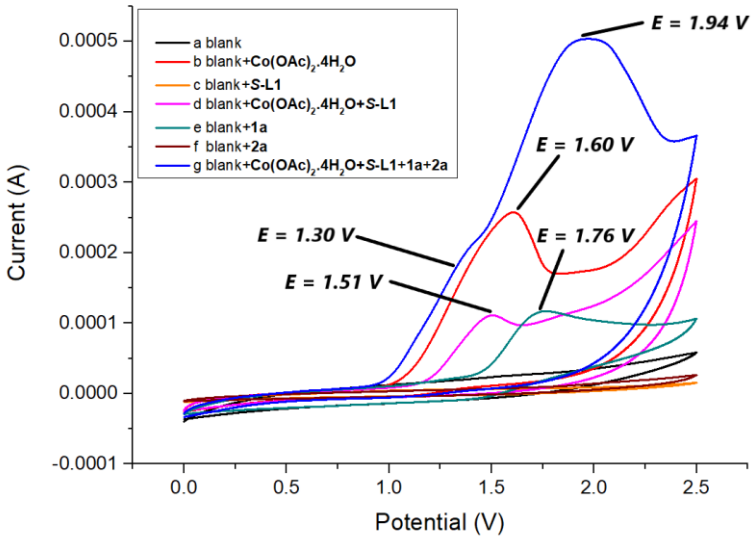


Figure S3. a) background; **b)** adding **Co(OAc)$_2$.4H$_2$O** (0.3 mmol, 75 mg) into background; **c)** adding ***S*-L1** (0.3 mmol, 72 mg) into background; **d)** adding **Co(OAc)$_2$.4H$_2$O** (0.3 mmol, 75 mg) and ***S*-L1** (0.3 mmol, 72 mg) into background; **e)** adding **1a** (0.3 mmol, 103 mg) into background; **f)** adding **2a** (0.3 mmol, 53 mg) into background; **g)** adding **Co(OAc)$_2$.4H$_2$O** (0.3 mmol, 75 mg), ***S*-L1** (0.3 mmol, 72 mg), **1a** (0.3 mmol, 103 mg) and **2a** (0.3 mmol, 53 mg) into background.

A mixture of Co(OAc)$_2$•4H$_2$O in a solution of H$_2$O and MeCN (red curve) showed an oxidation peak of 1.60 V for the oxidation of Co(II) species to Co(III) species. Dipenylphosphinamide **1a** featured a higher onset potential of 1.76 V, while no obviously oxidative peak of ligand **L1** or alkyne **2a** (green curve) was found, suggesting the preferential oxidation of Co-catalyst over substrates and ligand. Notably, the combination of Co(OAc)$_2$•4H$_2$O with ligand **L1** (pink curve) highlighted a shift forward of the oxidation wave with a potential of 1.51 V, might owing to the *in situ* coordination of Co(II) salt with **L1**. Besides, an oxidation potential of 1.31 V was observed when mixturing Co(OAc)$_2$•4H$_2$O, **1a** and **L1** together (Fig. 6d, blue curve), being indicative of an oxidation of cobalt(II) to cobalt(III) in the presence of the substrate at significantly lower potential.

DFT Calculations[3]

Computational Details

Density functional theory (DFT) calculations were performed with Gaussian 09. [1] The geometry of each species was optimized using the B3LYP/{[6-31G(d)] (for C, H, N, O, P) + sdd (for Co) SCRF = (SMD, solvent = dimethylbenzene)} level of theory with the corresponding effective core potential for Co. Frequency calculations were also conducted at the same level of theory to obtain vibrational frequencies to determine the identity of stationary points as intermediates or transition states, as well as obtaining the thermal corrections to enthalpy ($H_{correction}$) and free energy ($G_{correction}$) at the temperature of 298 K. All DFT calculations were with an ultrafine integration grid. All structural figures were generated with CYLview[4]. Distances in structural figures are shown in Å and energies are in kcal/mol.

IRC Scan Data

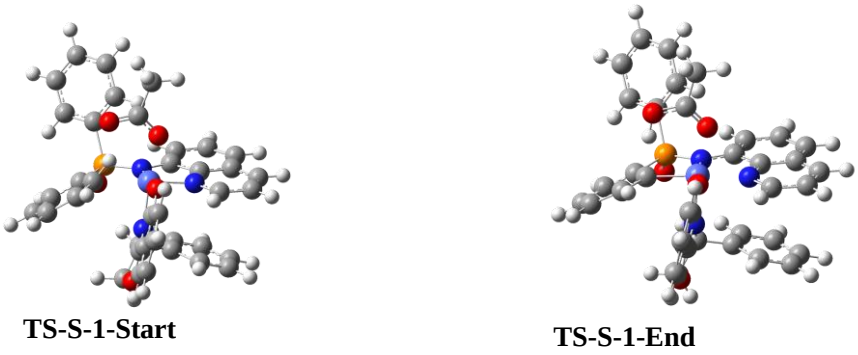


Figure S4. IRC scan of **TS-S-1**.

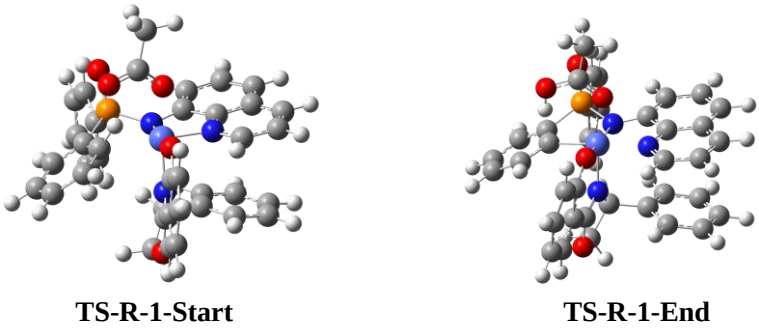


Figure S5. IRC scan of **TS-R-1**.

Cartesian Coordinates and Energies of Calculated Structures

1 **L1**			
E= -1336.613473			
Zero-point correction= 0.331423			
Thermal correction to Energy= 0.351648			
Thermal correction to Enthalpy= 0.352592			
Thermal correction to Gibbs Free Energy= 0.280722			
P	-2.1060710	1.2263540	0.5175640
O	-1.9572770	0.7589540	1.9421980
C	-3.0259360	0.0531440	-0.5263120
C	-3.1394700	-1.2752860	-0.0913650
C	-3.5627070	0.4205300	-1.7695290
C	-3.7843170	-2.2228350	-0.8874670
H	-2.7310520	-1.5614660	0.8730350
C	-4.2085260	-0.5293220	-2.5621130
H	-3.4886380	1.4467840	-2.1162250
C	-4.3194420	-1.8512500	-2.1231500
H	-3.8702640	-3.2491580	-0.5417450
H	-4.6273360	-0.2359810	-3.5206850

H	-4.8230400	-2.5888440	-2.7418520
C	-0.4520980	1.4343010	-0.2399970
C	-0.2675650	1.9164890	-1.5462330
C	0.6673830	1.0677780	0.5203060
C	1.0171740	2.0366860	-2.0762720
H	-1.1236170	2.1958570	-2.1540540
C	1.9522570	1.1887240	-0.0126930
H	0.5266090	0.6940170	1.5294150
C	2.1284400	1.6734450	-1.3100790
H	1.1504890	2.4119650	-3.0870050
H	2.8135280	0.9055570	0.5859660
H	3.1281810	1.7668730	-1.7251040
N	-2.7328230	2.7820810	0.2185550
H	-2.0127090	3.4312830	-0.0842080
C	-4.0207590	3.3380170	0.1395430
C	-5.1699620	2.7090090	0.7173370
C	-4.1785090	4.5616700	-0.4985710
C	-6.4469690	3.3476110	0.6008850
C	-5.4396090	5.1860410	-0.5934160
H	-3.3084100	5.0459620	-0.9347540
C	-6.0672070	0.9441220	1.8976230
C	-7.5576880	2.6807460	1.1817480
C	-6.5647680	4.5945870	-0.0624040
H	-5.5119490	6.1435200	-1.1013710
C	-7.3737510	1.4810220	1.8269160
H	-5.8975300	0.0002510	2.4126450
H	-8.5427180	3.1343690	1.1079380
H	-7.5404760	5.0657870	-0.1392150
H	-8.2022030	0.9473970	2.2817130
N	-5.0058300	1.5258570	1.3700560

2 **$Co(OAc)_2•4H_2O$**

E= -1386.945951

Zero-point correction= 0.344475

Thermal correction to Energy= 0.369175

Thermal correction to Enthalpy= 0.370119

Thermal correction to Gibbs Free Energy= 0.287856

Co	-0.5976810	-0.4556210	0.0095910
O	-2.0114840	-0.3150500	-1.3321250
O	-2.1867850	0.5068380	0.6617350
C	-2.7042840	0.3768080	-0.5040230
C	-3.9891290	1.0267010	-0.8919840
H	-3.7568960	1.9568380	-1.4254930
H	-4.5520950	0.3766980	-1.5660910

H	-4.5812050	1.2660480	-0.0067710
O	0.2560540	1.2944730	-0.3180080
O	0.6889730	0.0227900	1.3798020
C	0.9295870	1.1206710	0.7539110
C	1.9463590	2.0972940	1.2383650
H	1.9317280	2.1463450	2.3302910
H	2.9392190	1.7524490	0.9245090
H	1.7627730	3.0837620	0.8076270
N	-1.1589400	-2.1388090	0.7377630
C	-2.4136790	-2.4291460	1.4801980
C	-2.0219840	-3.7201840	2.2376680
H	-1.7542010	-3.5272770	3.2794200
H	-2.7686330	-4.5113540	2.1791350
C	-0.3668130	-3.1730770	0.8053270
O	-0.8233490	-4.1899610	1.5566300
O	0.7102880	-1.2483970	-1.0617610
C	1.3693870	-2.3565720	-0.7701820
C	0.9102430	-3.3394560	0.1522430
C	2.5936020	-2.6005950	-1.4389110
C	1.6782880	-4.5000410	0.3951170
C	3.3251190	-3.7507790	-1.1905010
H	2.9420100	-1.8561970	-2.1486180
C	2.8762950	-4.7104330	-0.2646050
H	1.3108800	-5.2296310	1.1087340
H	4.2641170	-3.9059980	-1.7154930
H	3.4607190	-5.6037930	-0.0697110
C	-3.6281680	-2.5903670	0.5805930
C	-4.8263440	-1.9526460	0.9244760
C	-3.5954640	-3.4108360	-0.5567040
C	-5.9751300	-2.1293200	0.1478520
H	-4.8590590	-1.3149800	1.8045390
C	-4.7405300	-3.5849090	-1.3347970
H	-2.6749490	-3.9159990	-0.8379080
C	-5.9338450	-2.9445250	-0.9849000
H	-6.8975660	-1.6276580	0.4271550
H	-4.7017750	-4.2216160	-2.2143680
H	-6.8242900	-3.0816870	-1.5920790
H	-2.6022540	-1.6212220	2.1882720

3 $Co(OAc)_2 \cdot 4H_2O$ + L1

E= -2494.442793

Zero-point correction= 0.614479

Thermal correction to Energy= 0.654930

Thermal correction to Enthalpy= 0.655874

Thermal correction to Gibbs Free Energy= 0.540515			
Co	-0.7847020	-0.1058920	1.0191870
O	-0.5556610	-0.8383790	2.8553220
O	-2.3834250	0.1333090	2.2050210
C	-1.7225190	-0.4124780	3.1560700
C	-2.2709600	-0.5162620	4.5423490
H	-2.0362090	0.4107890	5.0798220
H	-3.3573520	-0.6318070	4.5143270
H	-1.8104800	-1.3518390	5.0744630
N	-1.4053370	0.7673300	-0.6071750
C	-2.3367720	0.2176190	-1.6289800
C	-2.0701820	1.1646330	-2.8158110
H	-1.3223010	0.7634330	-3.5059090
H	-2.9656280	1.4638380	-3.3591440
C	-1.0663450	1.9771300	-0.9702860
O	-1.5077420	2.3486390	-2.1905470
O	-0.1711910	1.5321270	1.7346020
C	0.0328150	2.6777240	1.1351430
C	-0.3396040	2.9603500	-0.2104300
C	0.6551940	3.7188220	1.8760060
C	-0.0500970	4.2223790	-0.7806980
C	0.9134980	4.9493810	1.3001910
H	0.9318450	3.5103730	2.9050410
C	0.5704410	5.2117920	-0.0414120
H	-0.3326620	4.4063480	-1.8115890
H	1.3969380	5.7218490	1.8931260
H	0.7858200	6.1778600	-0.4866040
C	-3.7926790	0.2116250	-1.1828670
C	-4.6300210	-0.8244250	-1.6187730
C	-4.3404080	1.2479110	-0.4145920
C	-5.9882440	-0.8280850	-1.2941570
H	-4.2140140	-1.6336050	-2.2139330
C	-5.6980080	1.2429840	-0.0856560
H	-3.7094750	2.0592180	-0.0630930
C	-6.5259420	0.2061720	-0.5240610
H	-6.6229130	-1.6402600	-1.6381850
H	-6.1077600	2.0510850	0.5141220
H	-7.5813650	0.2037670	-0.2662540
H	-2.0412950	-0.7963600	-1.8976740
P	2.4232070	-0.1047170	0.6532220
O	2.4957670	0.3584880	2.0903620
C	3.6519170	-1.4445070	0.4155870
C	3.4827590	-2.6363760	1.1410290
C	4.8163440	-1.2673820	-0.3448870

C	4.4521270	-3.6372380	1.0898870
H	2.5905230	-2.7842960	1.7437010
C	5.7888050	-2.2703730	-0.3911360
H	4.9690940	-0.3498670	-0.9045290
C	5.6071980	-3.4564610	0.3221000
H	4.3075180	-4.5572450	1.6494610
H	6.6871050	-2.1216800	-0.9839750
H	6.3627730	-4.2363400	0.2840000
C	2.8815040	1.2494730	-0.4854720
C	2.5302820	1.2367420	-1.8450860
C	3.6153470	2.3328550	0.0216850
C	2.9148730	2.2855270	-2.6824300
H	1.9519950	0.4145910	-2.2550130
C	3.9936310	3.3841100	-0.8160680
H	3.8768770	2.3549420	1.0747970
C	3.6468110	3.3599310	-2.1690000
H	2.6386150	2.2666910	-3.7330610
H	4.5557970	4.2212410	-0.4117270
H	3.9416680	4.1777220	-2.8208490
N	0.9109230	-0.6979860	0.1931790
C	0.6941880	-1.7838170	-0.6469680
C	-0.5575630	-2.4494170	-0.4591240
C	1.5272810	-2.3029340	-1.6417720
C	-0.8972600	-3.6486760	-1.1459680
C	1.1865280	-3.4828740	-2.3405980
H	2.4647460	-1.8169100	-1.8782780
C	-2.5900940	-2.4289500	0.6899610
C	-2.1463350	-4.2413850	-0.8297270
C	0.0133110	-4.1679240	-2.1001050
H	1.8820100	-3.8527820	-3.0890880
C	-2.9780360	-3.6447140	0.0920580
H	-3.2420730	-1.9115510	1.3823040
H	-2.4357020	-5.1637410	-1.3257760
H	-0.2333070	-5.0795490	-2.6352770
H	-3.9383080	-4.0752780	0.3529520
N	-1.4224850	-1.8581410	0.4199120

4 **Complex of Co+1a+L1**			
E= -2494.405804			
Zero-point correction= 0.608903			
Thermal correction to Energy= 0.648949			
Thermal correction to Enthalpy= 0.649893			
Thermal correction to Gibbs Free Energy= 0.536628			
P	-2.1494730	-0.1347780	-1.3254440

O	-2.3408120	0.6180110	-2.6291990
C	-1.2652380	-1.7067910	-1.5572960
C	-1.3375600	-2.3661190	-2.7872070
C	-0.4228230	-2.1740240	-0.5182170
C	-0.5815470	-3.5229980	-3.0002630
H	-1.9655330	-1.9730570	-3.5821610
C	0.3304050	-3.3400510	-0.7670940
H	-0.9455840	-2.3334460	0.6969540
C	0.2490670	-4.0123090	-1.9878350
H	-0.6407840	-4.0398480	-3.9540990
H	0.9649190	-3.7417910	0.0179350
H	0.8308970	-4.9153520	-2.1519350
C	-3.7830770	-0.4791530	-0.5776670
C	-4.0357770	-0.2913960	0.7891850
C	-4.8178800	-0.9431220	-1.4079290
C	-5.3004880	-0.5634920	1.3169250
H	-3.2496580	0.0791220	1.4381480
C	-6.0771310	-1.2237030	-0.8771670
H	-4.6411040	-1.0799680	-2.4711360
C	-6.3202040	-1.0340830	0.4865290
H	-5.4883320	-0.4049780	2.3753470
H	-6.8689340	-1.5853430	-1.5272930
H	-7.3023120	-1.2487800	0.8987100
N	-1.1427220	0.5385000	-0.1805060
C	-1.2162220	1.8284250	0.3072710
C	-0.1457940	2.1935720	1.1840300
C	-2.1790660	2.8002590	0.0325770
C	-0.0433880	3.4942400	1.7508350
C	-2.0813450	4.0896810	0.6019520
H	-3.0057260	2.5773800	-0.6333430
C	1.8177100	1.4800320	2.2249590
C	1.0740480	3.7418340	2.5895560
C	-1.0447980	4.4499080	1.4411090
H	-2.8521950	4.8167620	0.3606780
C	1.9972010	2.7451850	2.8222660
H	2.5144620	0.6677110	2.3958080
H	1.1910500	4.7230070	3.0415890
H	-0.9821580	5.4466780	1.8666920
H	2.8598890	2.9102400	3.4584730
N	0.7836190	1.2248250	1.4395760
Co	0.2912300	-0.5043280	0.6198410
O	-0.8226070	-0.6586460	2.2524160
O	-1.5390890	-2.7161940	1.7667520
C	-1.4552750	-1.7140220	2.5535980

C	-2.1551350	-1.7949630	3.8835620
H	-1.8027500	-2.6791910	4.4245230
H	-1.9730680	-0.8985800	4.4780830
H	-3.2305320	-1.9158440	3.7141270
N	1.5587880	-0.2332550	-0.8479240
C	1.3809220	0.6363820	-2.0455480
C	2.4118630	0.0257360	-3.0145320
H	1.9614610	-0.7086750	-3.6886680
H	2.9827850	0.7602470	-3.5811430
C	2.6874110	-0.8751440	-0.9691150
O	3.3325660	-0.6825530	-2.1414830
O	1.5650690	-1.5064120	1.6290560
C	2.7288560	-1.9845200	1.2584340
C	3.3333620	-1.7400170	-0.0093500
C	3.4397950	-2.8061030	2.1747070
C	4.5822020	-2.3242920	-0.3256610
C	4.6640280	-3.3597050	1.8434340
H	2.9842140	-2.9926460	3.1430680
C	5.2481540	-3.1259880	0.5835230
H	5.0168040	-2.1296310	-1.3000710
H	5.1768030	-3.9875380	2.5679080
H	6.2067210	-3.5668570	0.3292480
C	1.6193540	2.1137520	-1.7692430
C	0.7097880	3.0589930	-2.2596520
C	2.7645910	2.5609640	-1.0937230
C	0.9348990	4.4260430	-2.0767570
H	-0.1840380	2.7202240	-2.7768280
C	2.9894880	3.9260080	-0.9081450
H	3.4844920	1.8443690	-0.7069250
C	2.0753330	4.8629520	-1.3999590
H	0.2171300	5.1461100	-2.4599940
H	3.8797840	4.2580330	-0.3809140
H	2.2515330	5.9252630	-1.2544860
H	0.3754620	0.5089550	-2.4432130

5 **TS-R-1**

E= -2494.402146

Zero-point correction= 0.608815

Thermal correction to Energy= 0.648948

Thermal correction to Enthalpy= 0.649892

Thermal correction to Gibbs Free Energy= 0.536081

P	-1.9233270	-1.6855130	0.6516910
O	-2.2404800	-2.2687220	2.0168440
C	-3.4637730	-1.6084110	-0.3368530

C	-4.6734350	-1.9170290	0.3053770
C	-3.4856340	-1.2644870	-1.6984380
C	-5.8810360	-1.8681310	-0.3942350
H	-4.6631010	-2.1950110	1.3542850
C	-4.6927010	-1.2217870	-2.3984240
H	0.9910060	-2.4063530	1.3487970
C	-5.8927070	-1.5188670	-1.7462950
H	-6.8097100	-2.1068590	0.1164910
H	-4.6950240	-0.9592150	-3.4525670
H	-6.8313480	-1.4834590	-2.2922210
C	-0.6798710	-2.6238520	-0.2816160
C	0.6679940	-2.3433300	0.0645030
C	-0.9947370	-3.5632490	-1.2661820
C	1.6777320	-3.0412180	-0.6281770
C	0.0322200	-4.2370680	-1.9359260
H	-2.0297400	-3.7697180	-1.5223810
C	1.3675520	-3.9770080	-1.6166940
H	2.7184440	-2.8739190	-0.3657760
H	-0.2125180	-4.9679480	-2.7016560
H	2.1630870	-4.5095890	-2.1307840
N	-1.1229800	-0.2115170	0.6300450
C	-1.6093730	0.9750510	1.1580340
C	-0.6118540	1.9654470	1.4282660
C	-2.9351310	1.3255310	1.4143320
C	-0.9433500	3.2700090	1.8904600
C	-3.2651470	2.6177480	1.8810850
H	-3.7336660	0.6130000	1.2432550
C	1.6736370	2.4441310	1.4398960
C	0.1325830	4.1691740	2.1059820
C	-2.3080450	3.5861250	2.1101470
H	-4.3127210	2.8465420	2.0581020
C	1.4292730	3.7614180	1.8798550
H	2.6806290	2.0804810	1.2733770
H	-0.0801420	5.1765800	2.4532330
H	-2.5775230	4.5766720	2.4634120
H	2.2691270	4.4286840	2.0397700
N	0.6859670	1.5895960	1.2259750
Co	0.8336050	-0.3104550	0.7308540
O	0.6380030	-0.5848240	2.6725980
O	1.2319450	-2.7343970	2.5768480
C	0.9235610	-1.6860120	3.2345100
C	0.8516860	-1.7708410	4.7349390
H	-0.1340150	-2.1668840	5.0078470
H	1.6119130	-2.4583260	5.1133940

H	0.9702460	-0.7837920	5.1858220
N	1.1286620	0.1614130	-1.1420520
C	0.0947460	0.5754990	-2.1275940
C	0.8153630	0.2825630	-3.4579300
H	0.5696440	-0.7067880	-3.8550660
H	0.6708490	1.0440820	-4.2232430
C	2.2759150	0.0820420	-1.7553470
O	2.2227230	0.2750300	-3.0932920
O	2.7142980	-0.3924280	1.0681820
C	3.7158720	-0.3647100	0.2220620
C	3.5785890	-0.1625060	-1.1830490
C	5.0303920	-0.5510320	0.7296290
C	4.7193600	-0.1760620	-2.0190850
C	6.1313190	-0.5516410	-0.1088430
H	5.1411890	-0.7020810	1.7996360
C	5.9859620	-0.3669610	-1.4975030
H	4.5858850	-0.0285710	-3.0853110
H	7.1213510	-0.7020130	0.3144660
H	6.8540390	-0.3726040	-2.1488710
C	-0.3379720	2.0287630	-1.9905690
C	-1.7015790	2.3475290	-2.0056140
C	0.5998270	3.0696450	-1.9195380
C	-2.1240900	3.6782140	-1.9453910
H	-2.4378010	1.5498320	-2.0589720
C	0.1795980	4.3992610	-1.8572230
H	1.6634040	2.8460180	-1.9093770
C	-1.1841440	4.7078330	-1.8701530
H	-3.1862040	3.9071650	-1.9541520
H	0.9176960	5.1947020	-1.8000620
H	-1.5099060	5.7432080	-1.8210220
H	-0.7747320	-0.0668920	-2.0106140
H	-2.5628900	-1.0463970	-2.2258490

6 **TS-S-1**

E= -2494.436776

Zero-point correction= 0.613336

Thermal correction to Energy= 0.653947

Thermal correction to Enthalpy= 0.654892

Thermal correction to Gibbs Free Energy= 0.538097

P	-2.0760390	-0.5252830	-1.3631420
O	-2.2344810	0.1461340	-2.7185530
C	-1.1260790	-2.0628950	-1.3794550
C	-1.5416580	-3.1629140	-2.1461940
C	0.0447440	-2.1074650	-0.5963150

C	-0.7929770	-4.3386730	-2.1361420
H	-2.4508880	-3.1009680	-2.7406000
C	0.7756970	-3.3051410	-0.5916380
H	1.4595320	-2.0762330	2.3696610
C	0.3629420	-4.4058630	-1.3526090
H	-1.1081370	-5.1948670	-2.7261830
H	1.6755230	-3.4010390	0.0076260
H	0.9495850	-5.3214800	-1.3303330
C	-3.7352500	-0.9050920	-0.6858990
C	-3.9005090	-1.3528550	0.6348210
C	-4.8617750	-0.7726490	-1.5108860
C	-5.1727210	-1.6597120	1.1193190
H	-3.0348080	-1.4567330	1.2823980
C	-6.1344820	-1.0816990	-1.0243410
H	-4.7393600	-0.4213970	-2.5307870
C	-6.2911790	-1.5252290	0.2906830
H	-5.2924710	-2.0021200	2.1436740
H	-7.0008610	-0.9749840	-1.6714080
H	-7.2808890	-1.7646880	0.6700480
N	-1.1788250	0.2850330	-0.2116250
C	-1.5198530	1.4807790	0.3856360
C	-0.5602580	1.9977800	1.3200820
C	-2.6735930	2.2398830	0.1721010
C	-0.7629040	3.2346480	1.9967350
C	-2.8746920	3.4604130	0.8534260
H	-3.4252240	1.9052900	-0.5344490
C	1.5061800	1.6703320	2.3376280
C	0.2634650	3.6568560	2.8813460
C	-1.9525370	3.9661440	1.7486980
H	-3.7879900	4.0149380	0.6533600
C	1.3907350	2.8824870	3.0506100
H	2.3768370	1.0315000	2.4477510
H	0.1478840	4.5954300	3.4170380
H	-2.1189610	4.9085460	2.2617410
H	2.1898820	3.1852800	3.7188920
N	0.5647620	1.2469160	1.5094330
Co	0.4680030	-0.5128760	0.4247790
O	-0.6551900	-1.2378620	1.9543740
O	0.8328000	-2.5207630	3.0561510
C	-0.3733800	-2.0443070	2.8634490
C	-1.4284020	-2.5554590	3.7956630
H	-0.9994060	-2.7885040	4.7726100
H	-2.2331240	-1.8247660	3.8938110
H	-1.8449560	-3.4784240	3.3734530

N	1.5536310	0.1587760	-1.0525580
C	1.1238450	1.1068810	-2.1220120
C	2.1723880	0.8267190	-3.2157670
H	1.8170710	0.1056080	-3.9576850
H	2.5544060	1.7194780	-3.7094140
C	2.7662030	-0.2342770	-1.3211510
O	3.2718760	0.2099490	-2.4924350
O	2.0619030	-1.2045100	1.2899280
C	3.2456400	-1.4979120	0.7713290
C	3.6464180	-1.0600720	-0.5179140
C	4.1585390	-2.2643670	1.5311930
C	4.9228110	-1.4070000	-1.0119130
C	5.4093990	-2.5885330	1.0266210
H	3.8531340	-2.5960860	2.5195290
C	5.8015880	-2.1633380	-0.2534410
H	5.2098240	-1.0690940	-2.0013220
H	6.0890040	-3.1824800	1.6320600
H	6.7797000	-2.4230690	-0.6453010
C	1.1035710	2.5598090	-1.6715880
C	0.0255740	3.3735240	-2.0425870
C	2.1669510	3.1275390	-0.9550880
C	0.0052170	4.7283780	-1.7015120
H	-0.8051330	2.9387760	-2.5922810
C	2.1457490	4.4798960	-0.6089790
H	3.0145890	2.5144630	-0.6602910
C	1.0650010	5.2846800	-0.9820720
H	-0.8405850	5.3449190	-1.9932340
H	2.9748190	4.9057100	-0.0502330
H	1.0496980	6.3371260	-0.7122510
H	0.1311310	0.8303210	-2.4732980

7 **AcO**			
E= -228.414651			
Zero-point correction= 0.047757			
Thermal correction to Energy= 0.052317			
Thermal correction to Enthalpy= 0.053261			
Thermal correction to Gibbs Free Energy= 0.019275			
O	-0.8564770	1.9897080	0.0633550
O	-2.0383800	0.4428080	-0.6603990
C	-1.7989550	1.1870560	0.3379490
C	-2.4955390	1.1075220	1.6454850
H	-1.9584270	0.3973330	2.2855550
H	-2.4945770	2.0874250	2.1305500
H	-3.5183800	0.7481010	1.5036540

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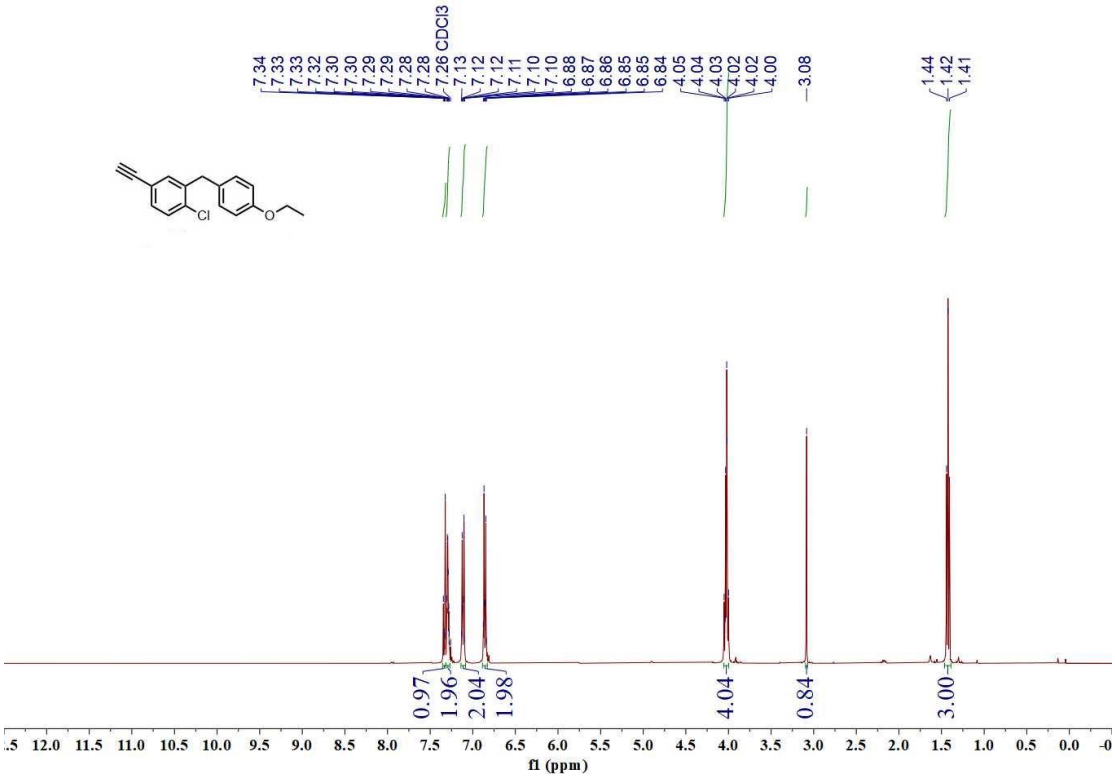
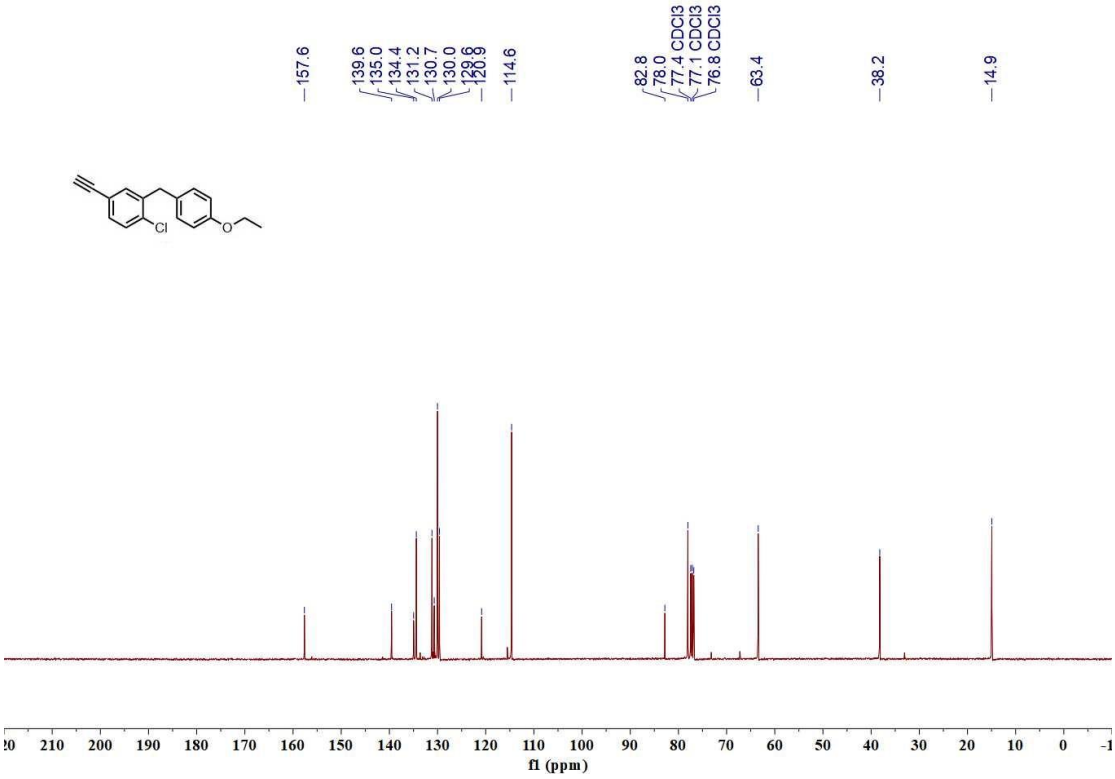
NMR Spectrum

^{1}H-NMR of **2aq**



^{13}C-NMR of **2aq**



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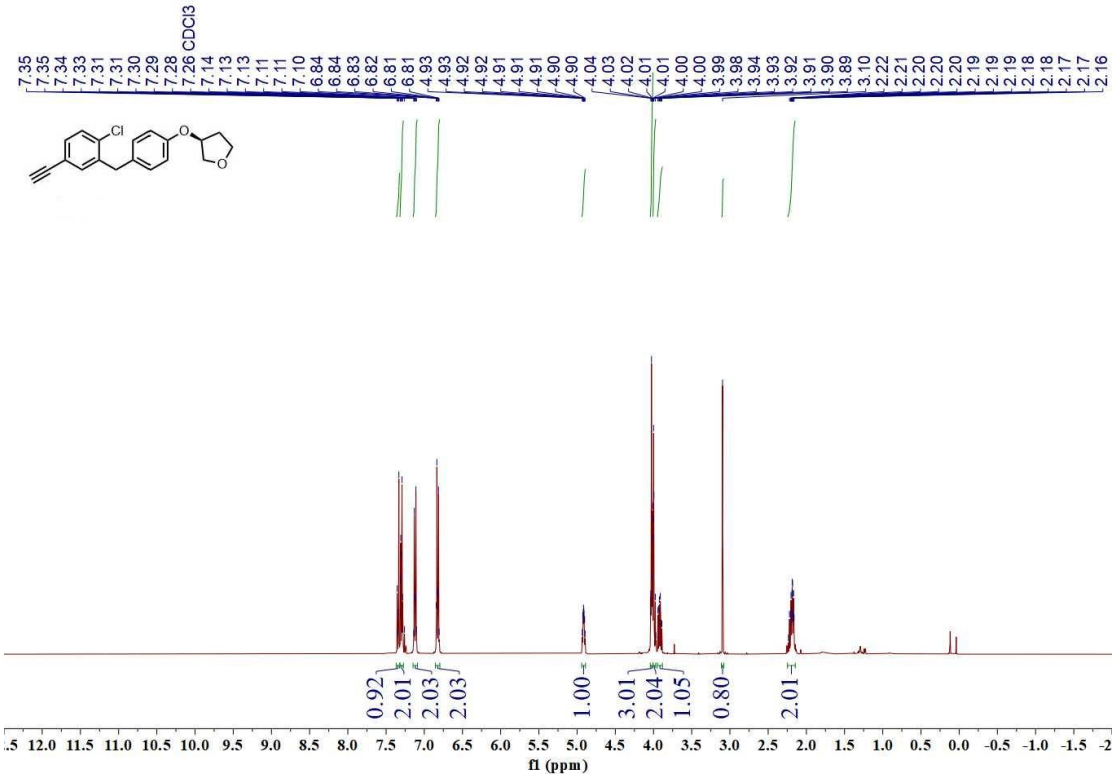

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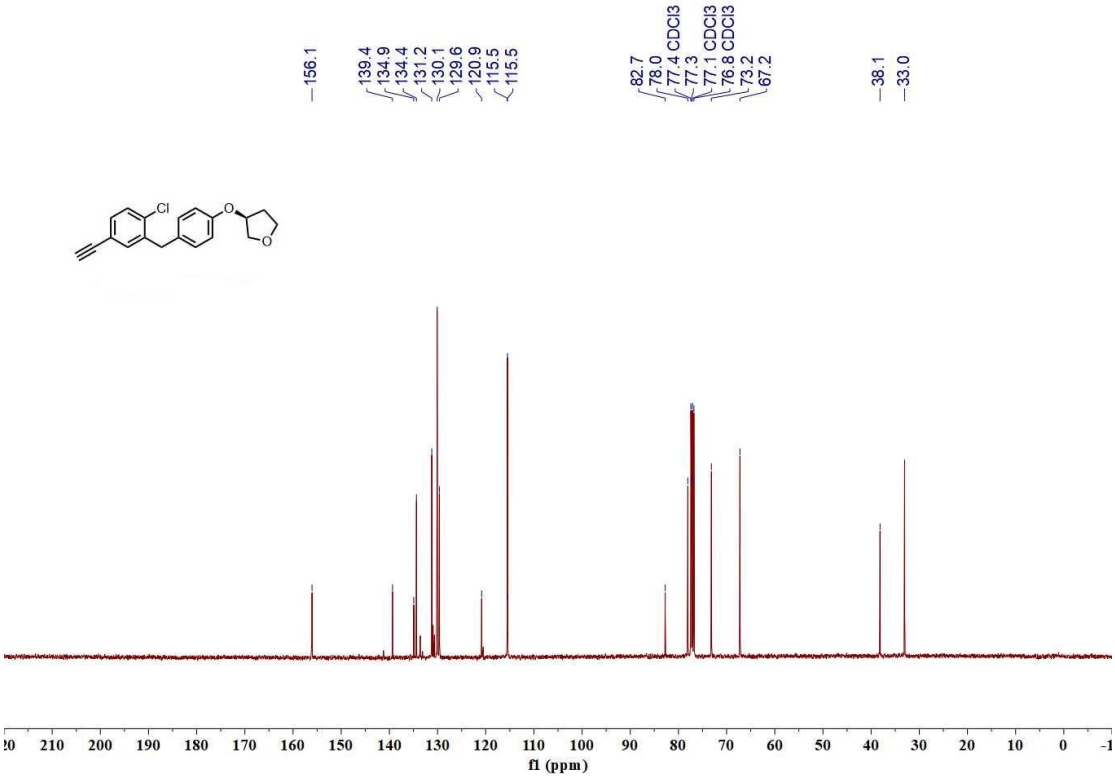

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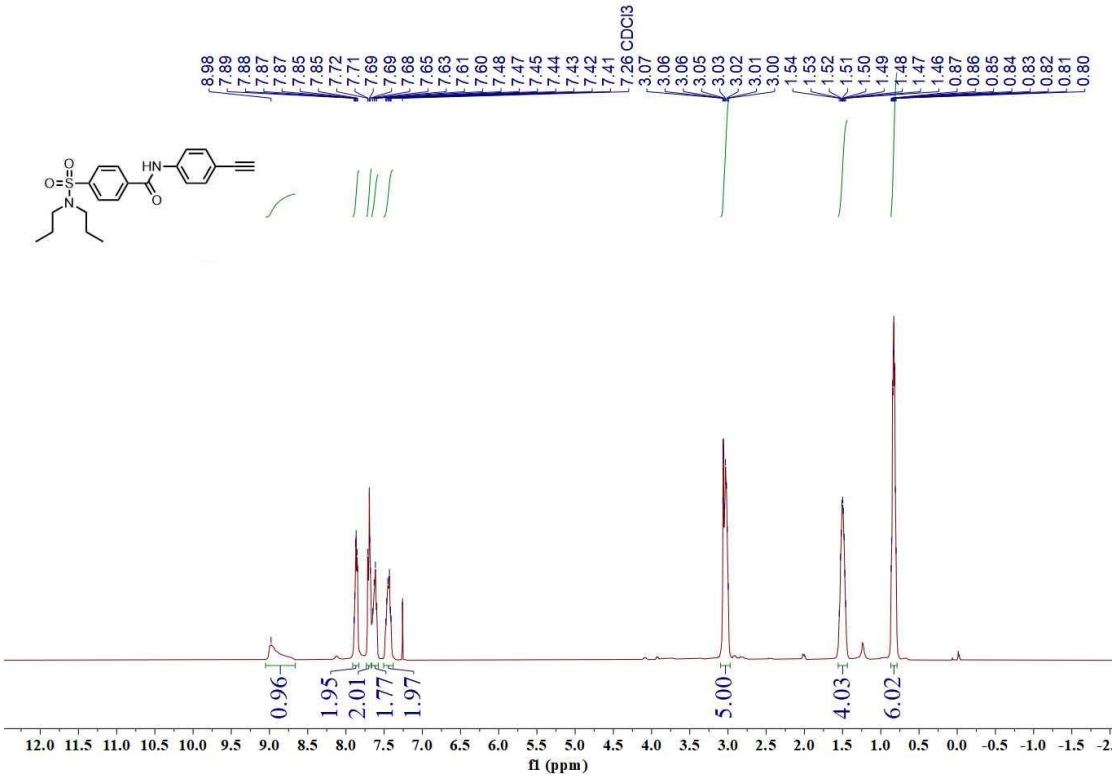

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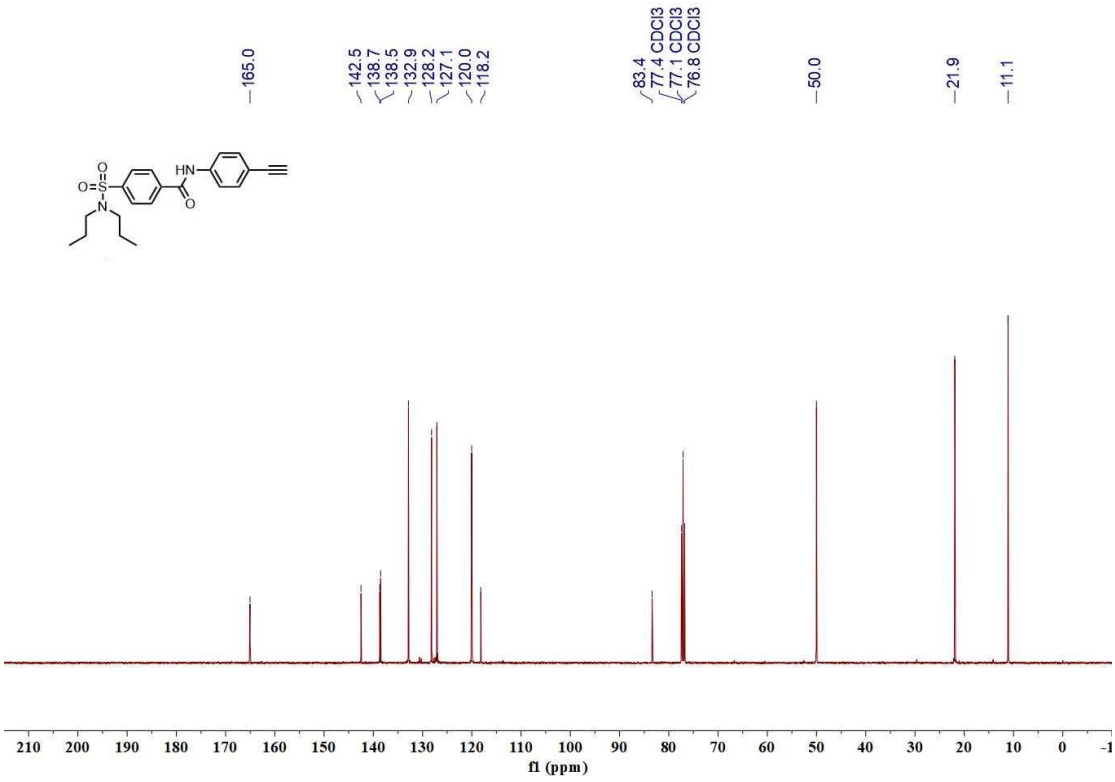

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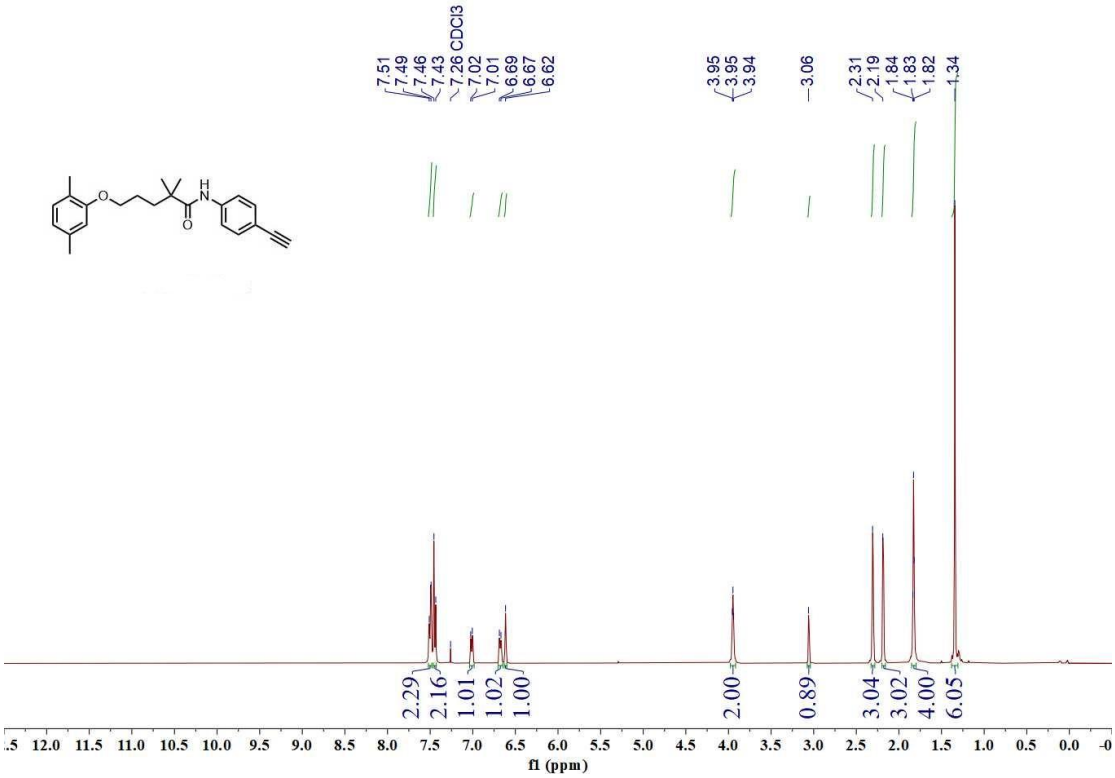

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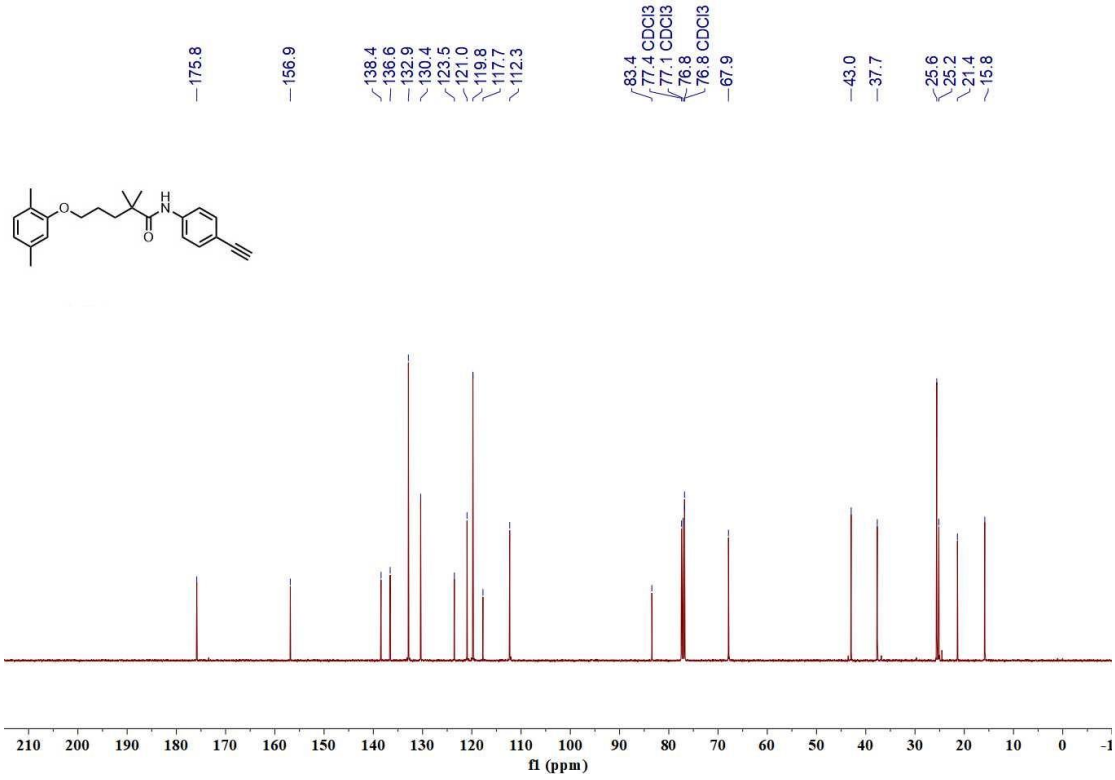

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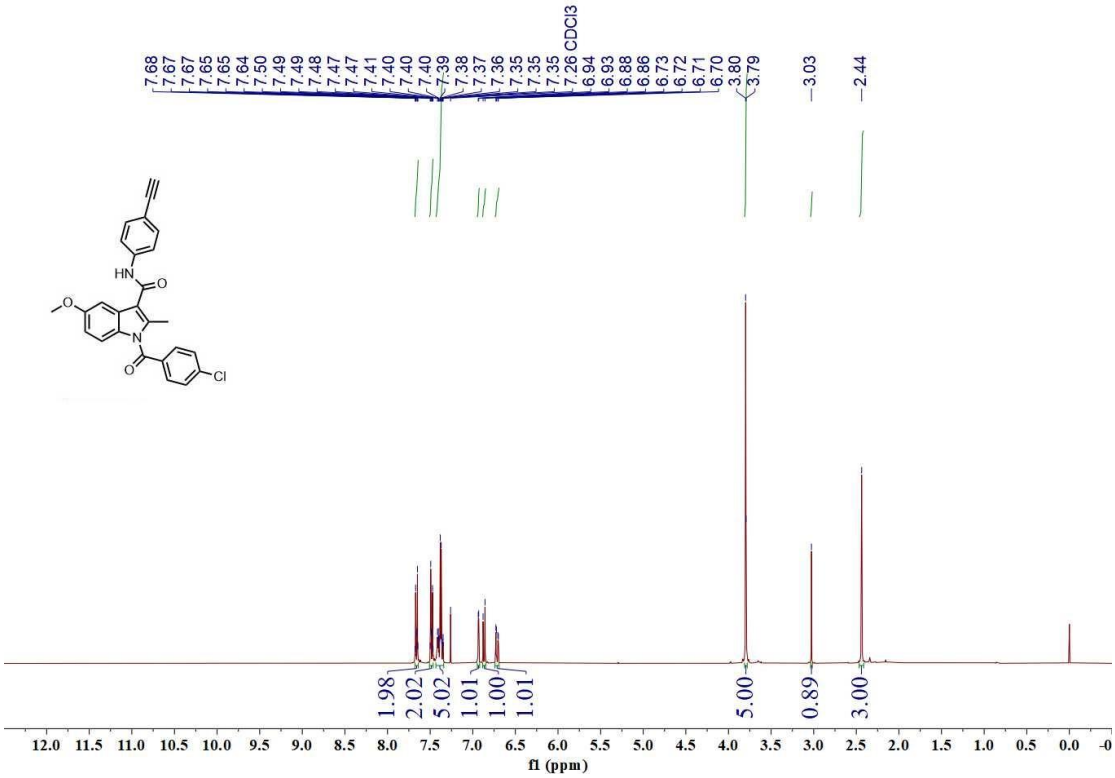

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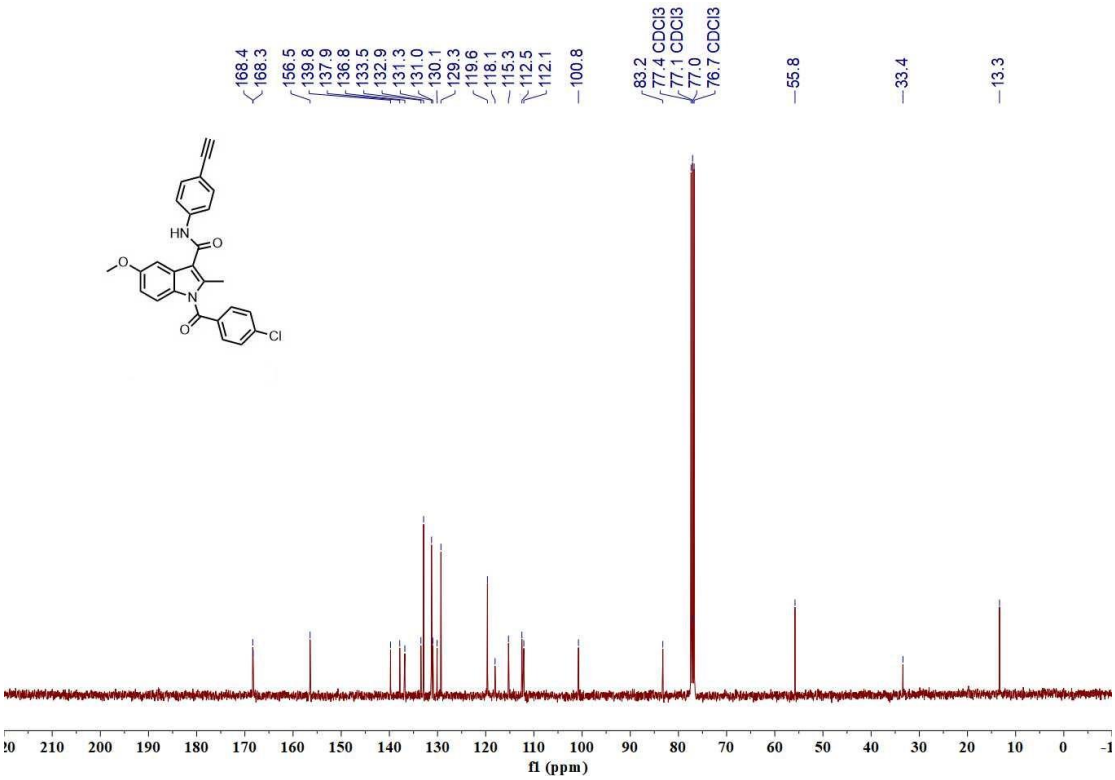

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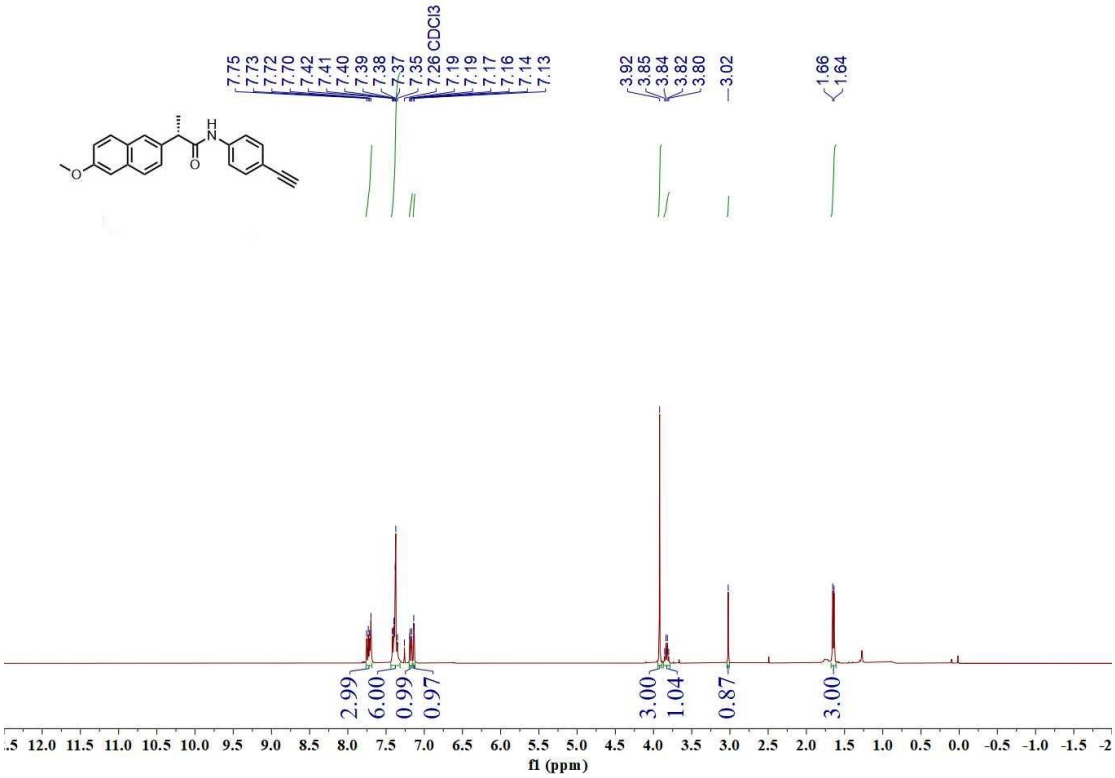

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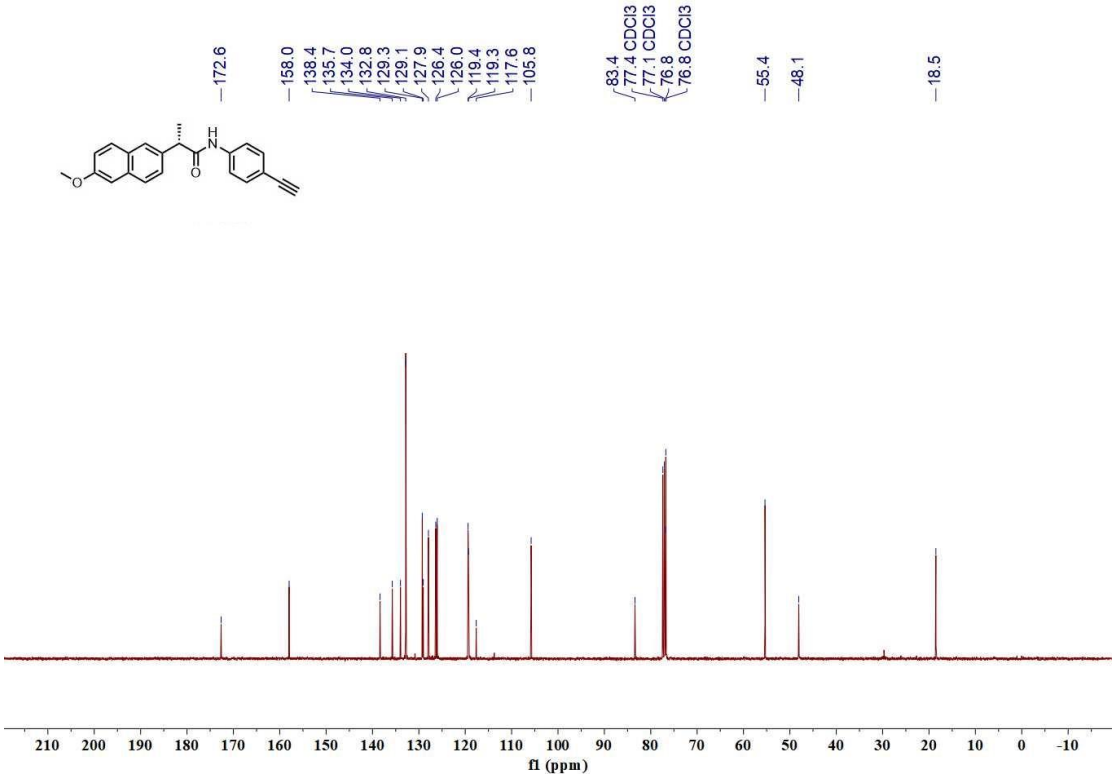

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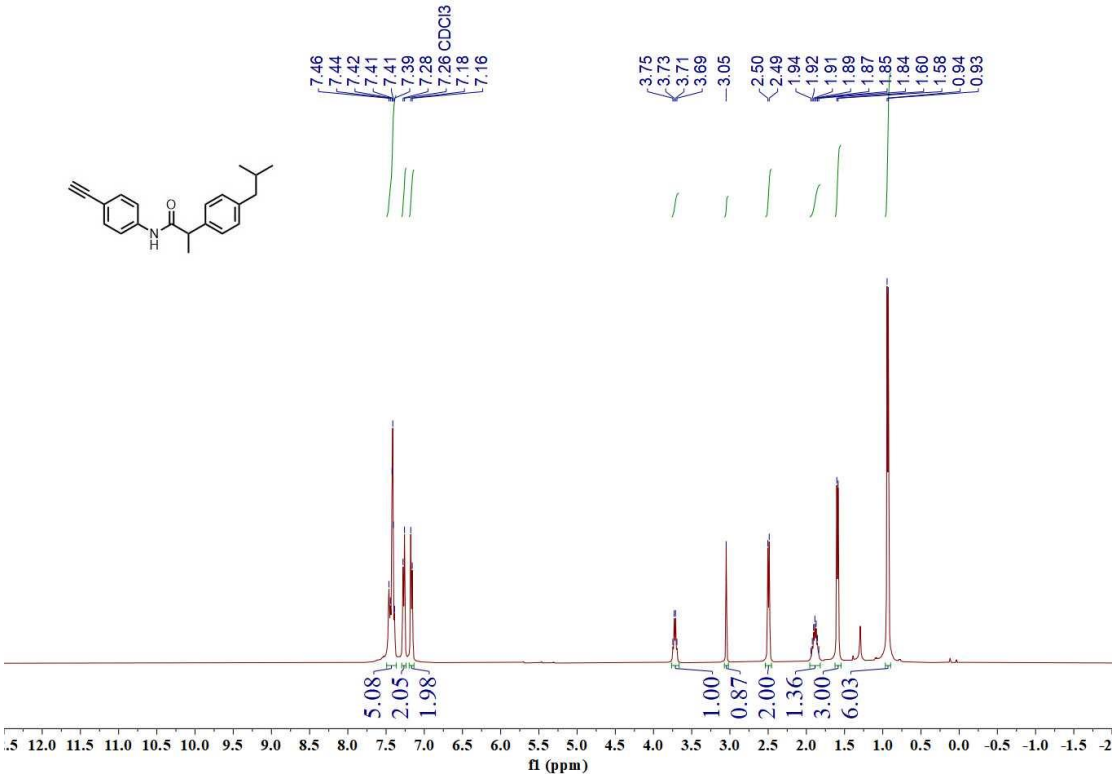

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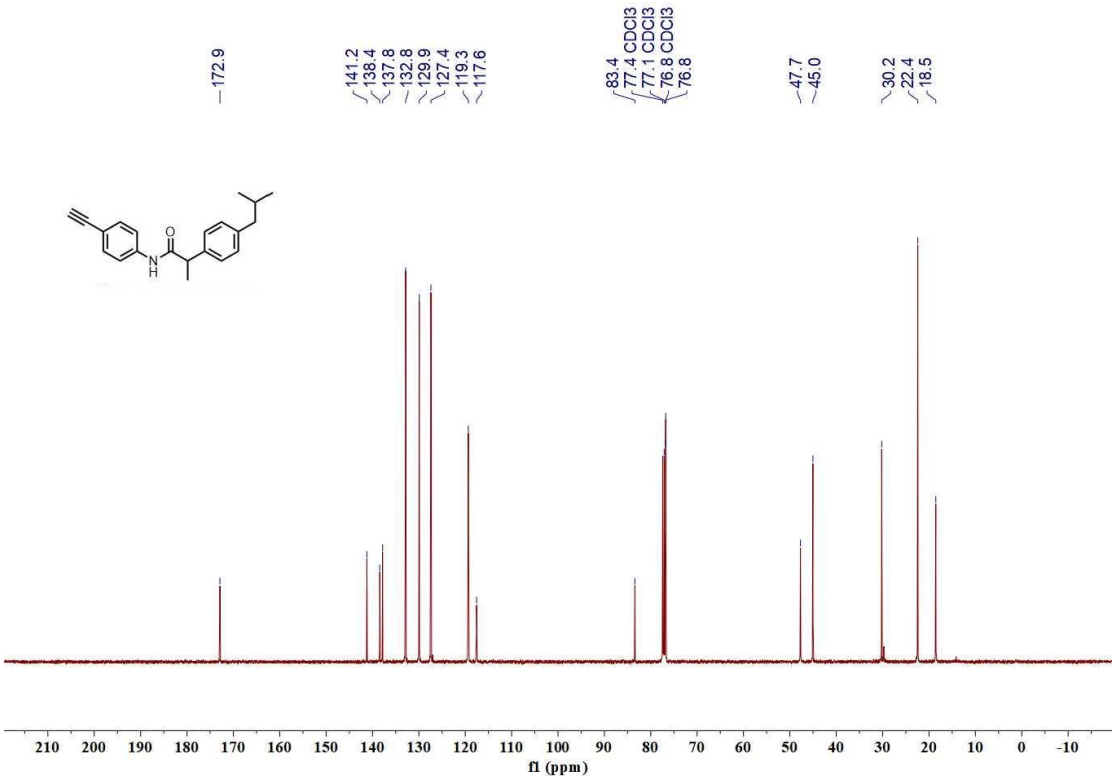

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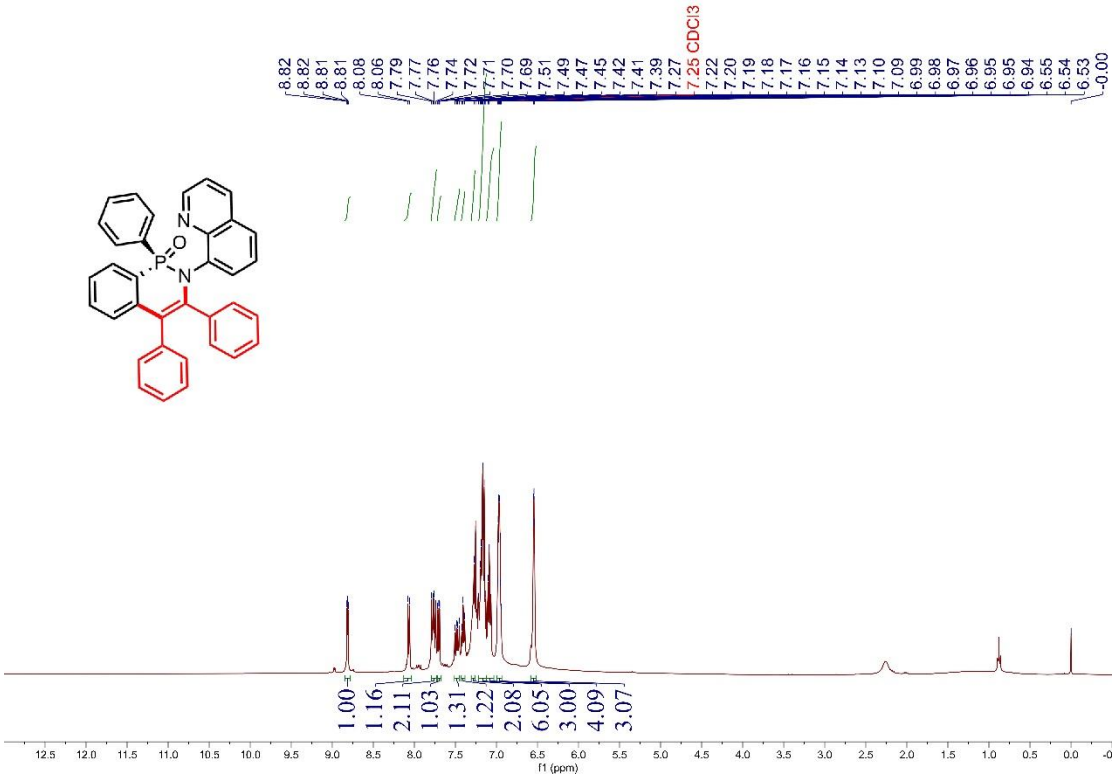

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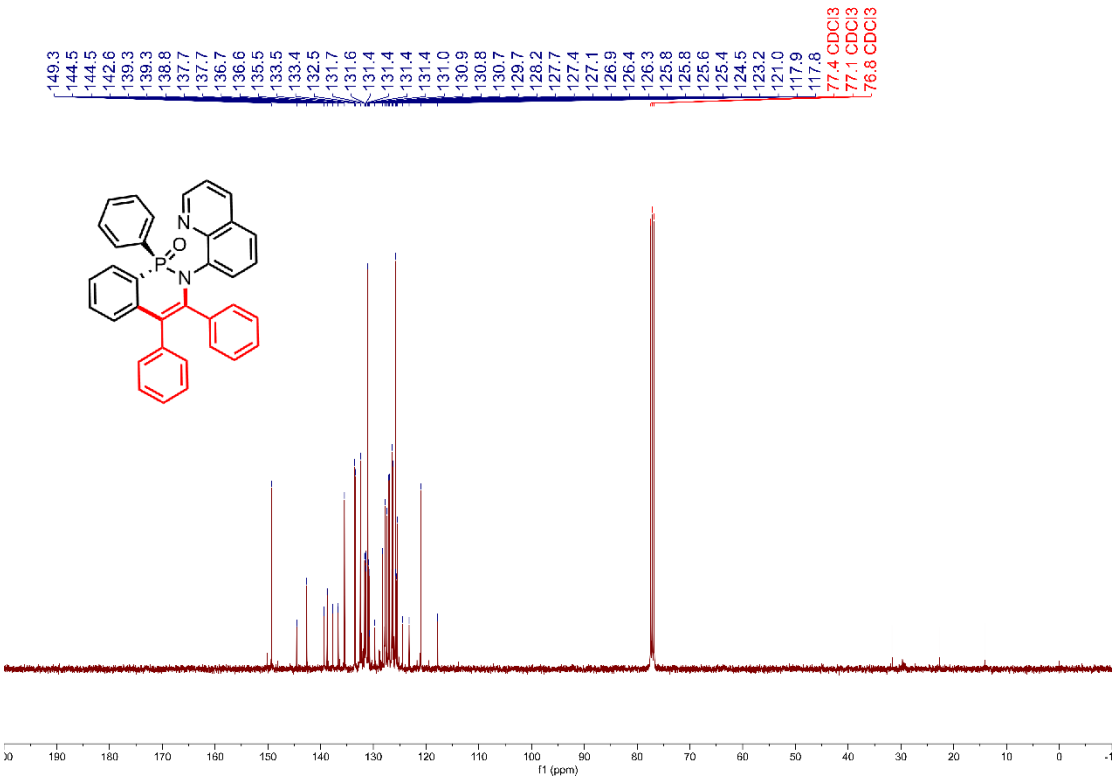
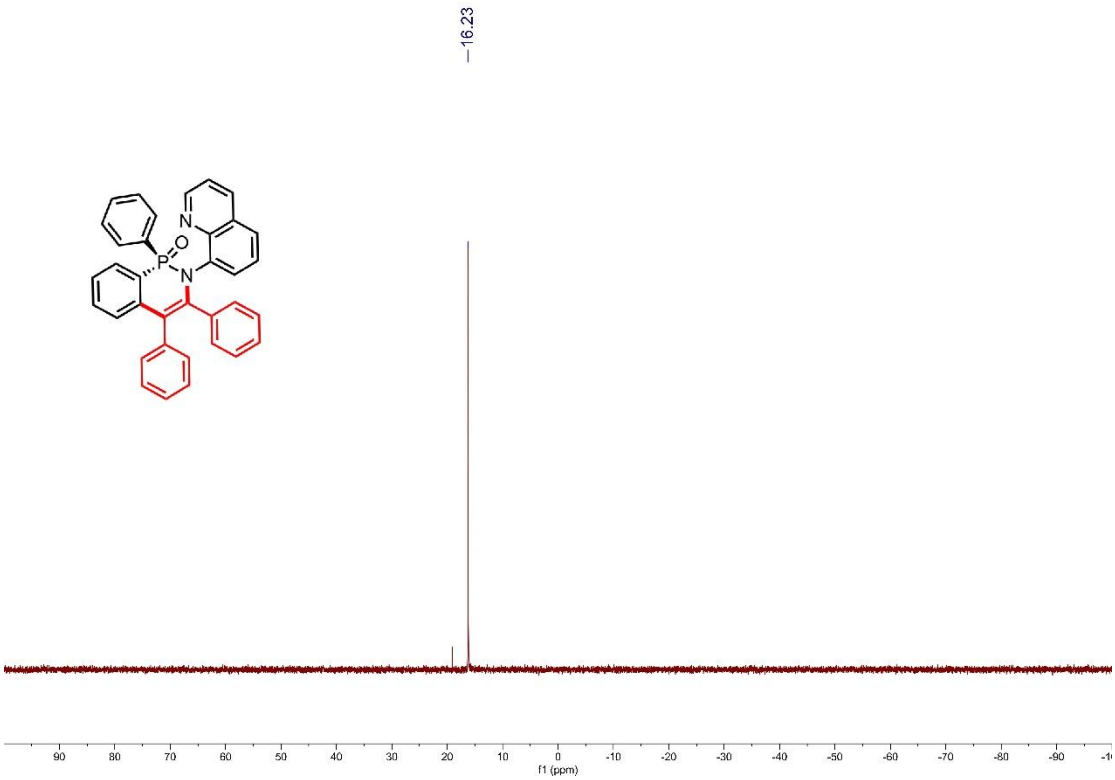


^{31}P-NMR of **3a**



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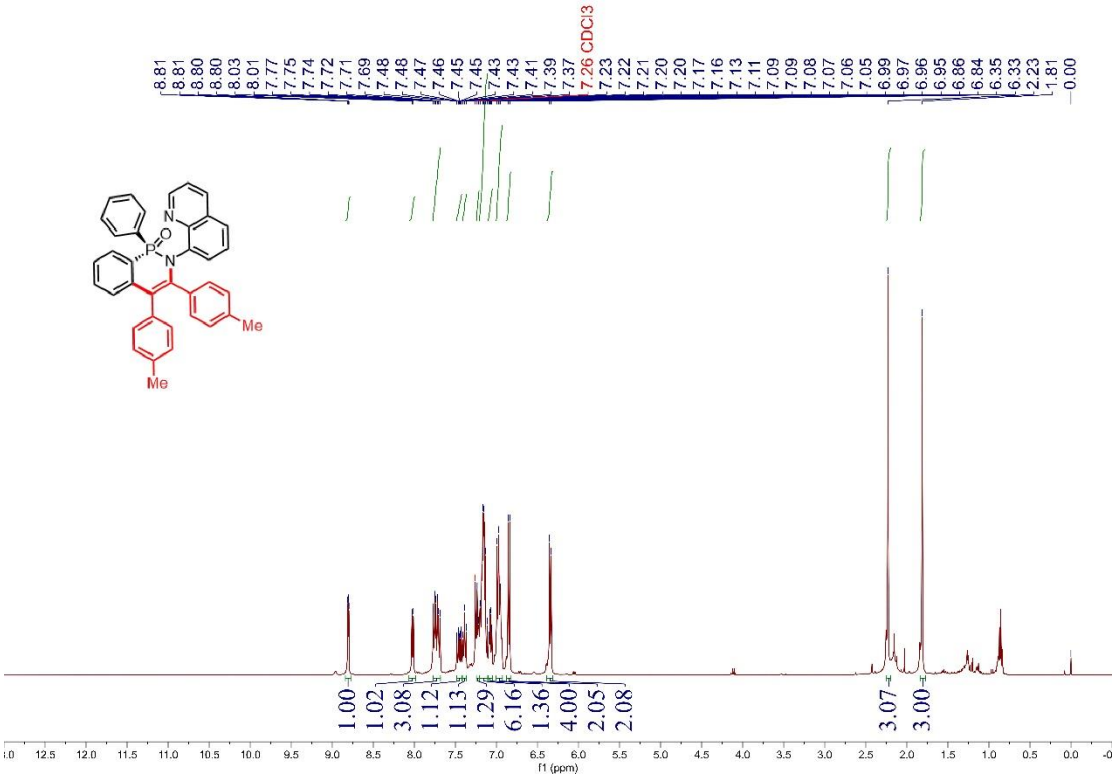

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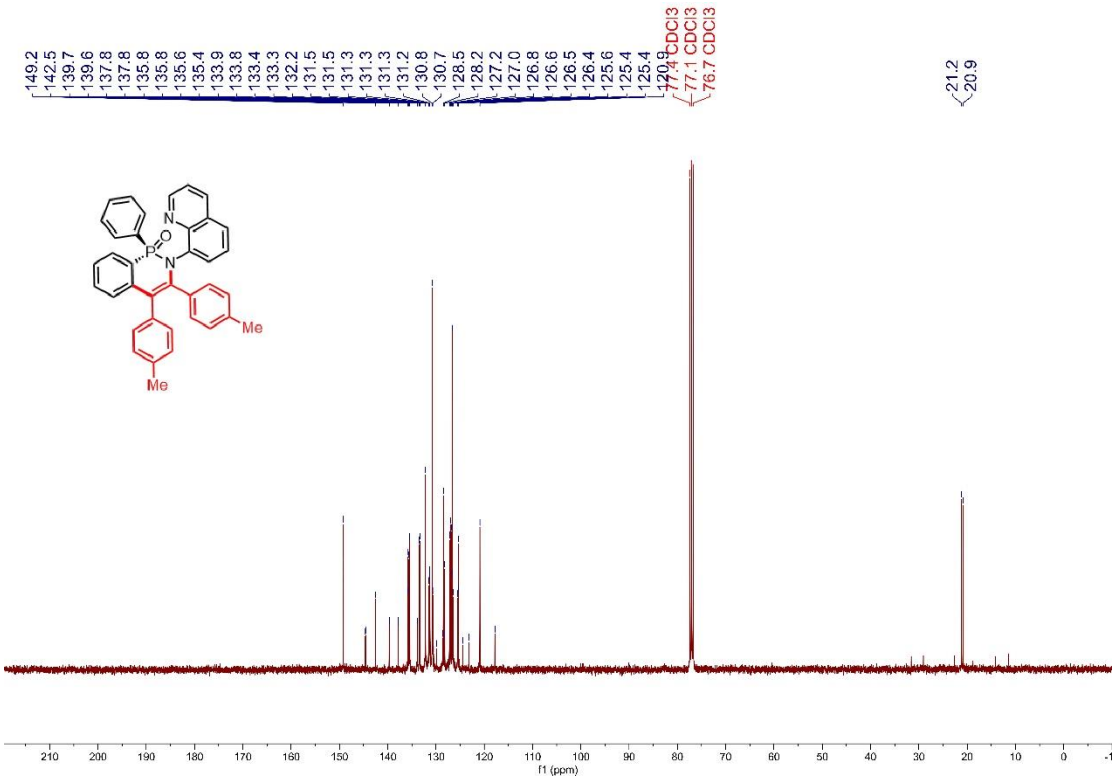

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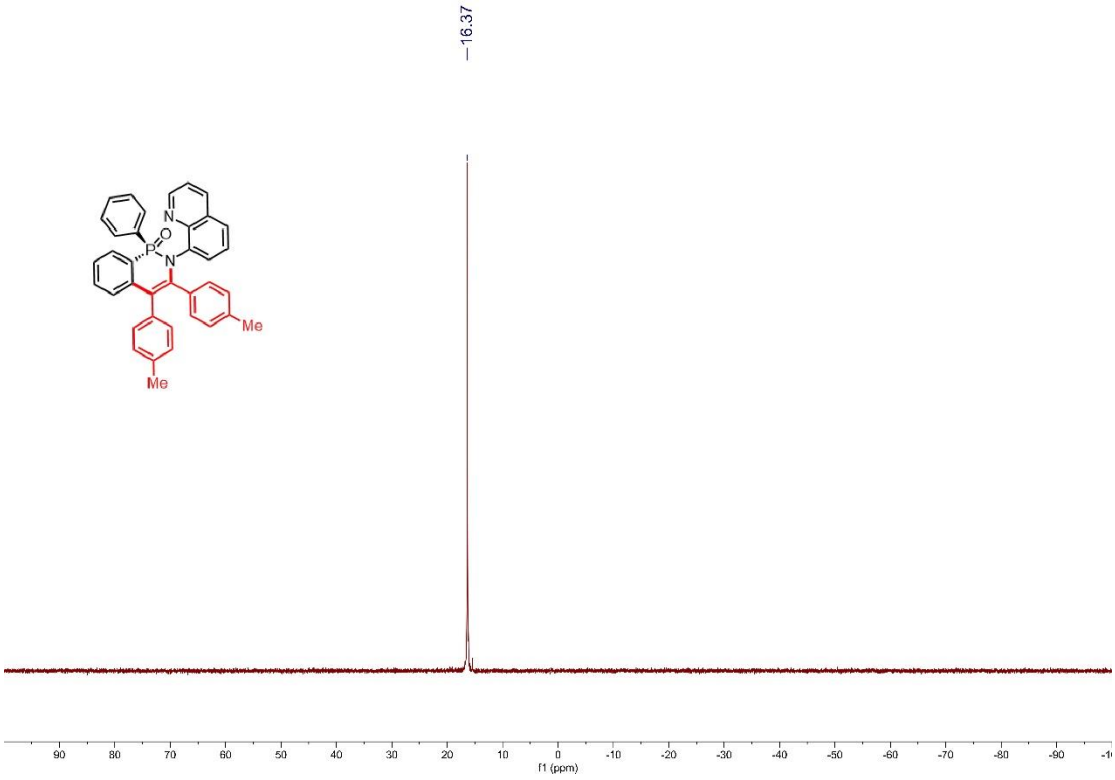

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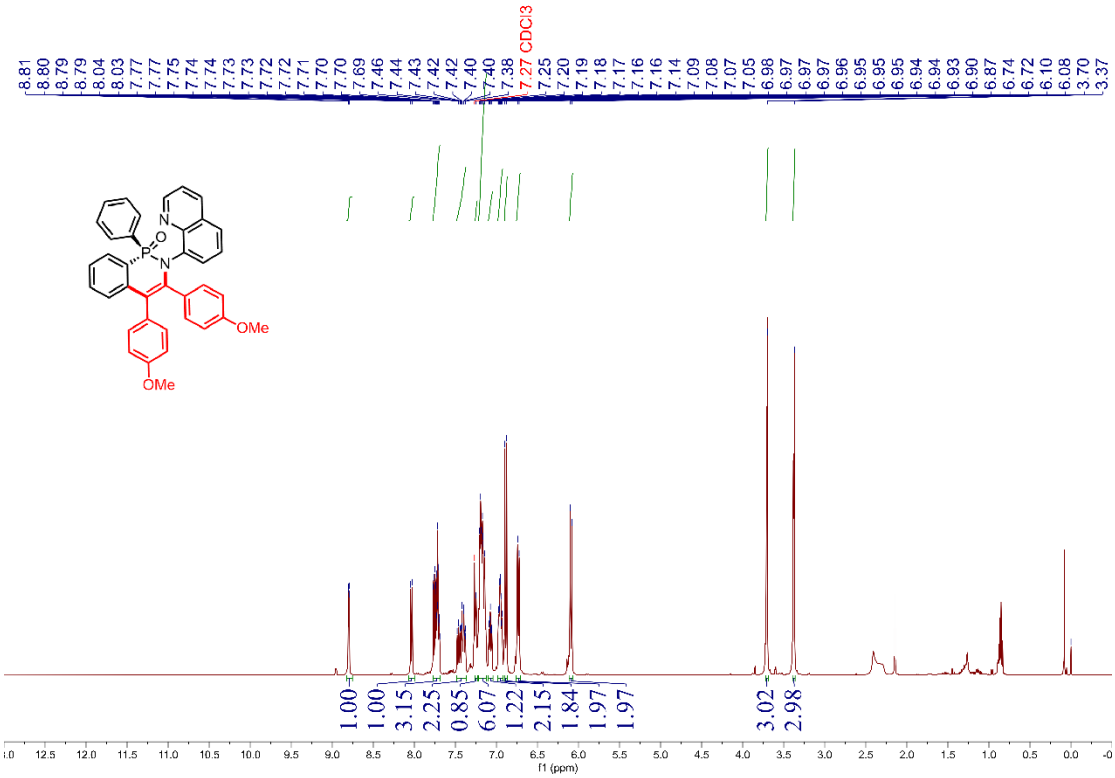

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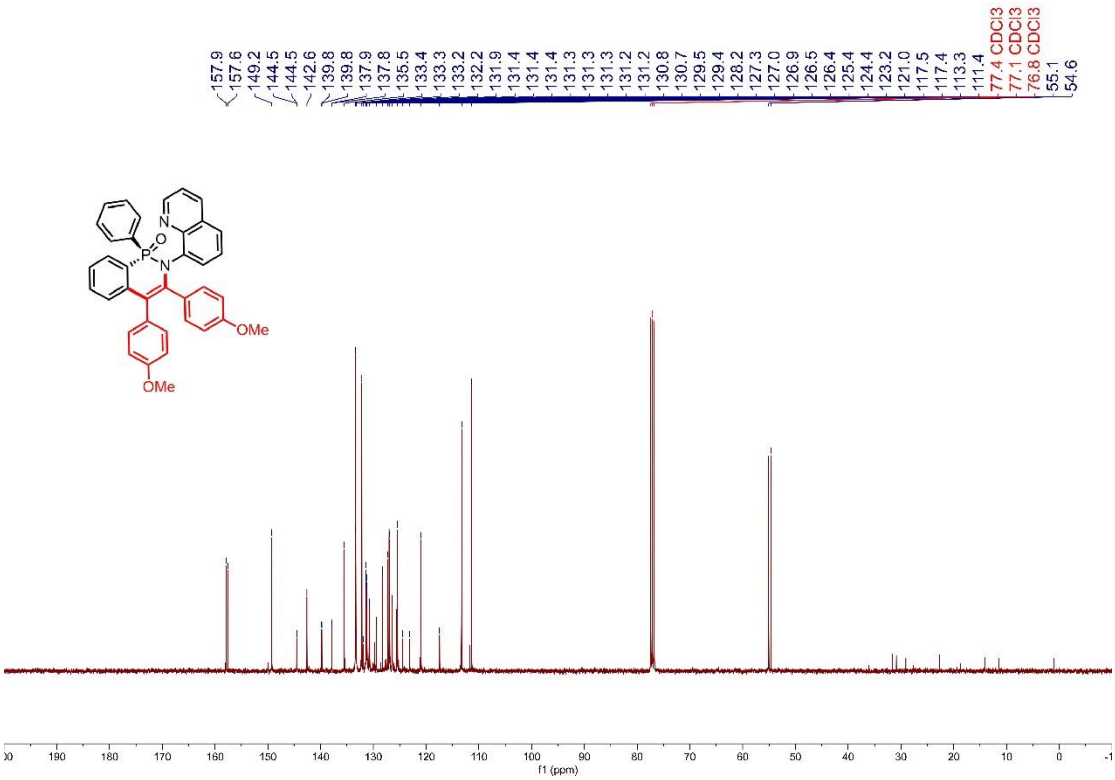

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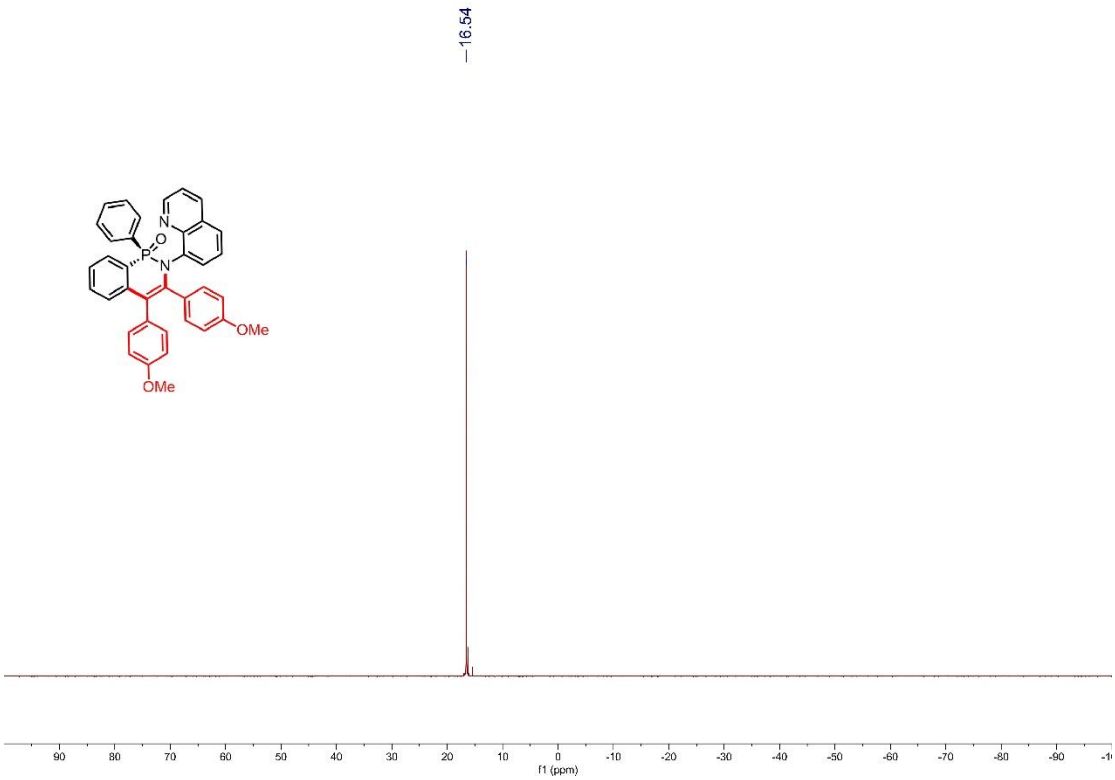

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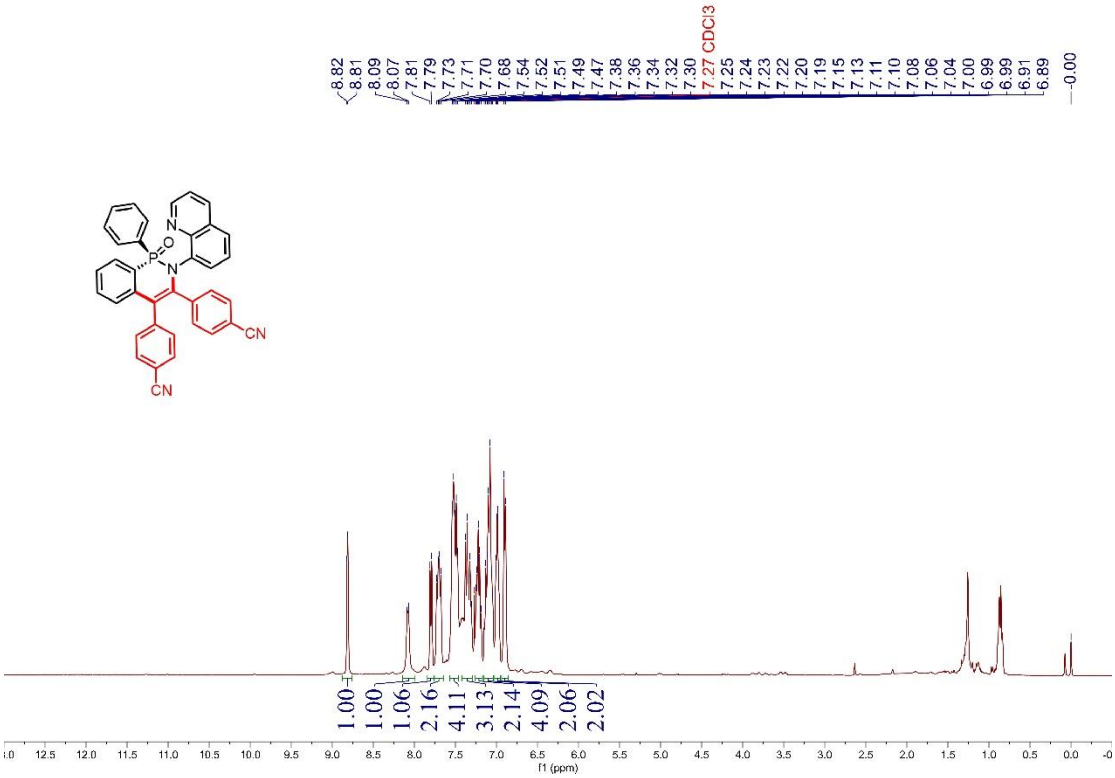

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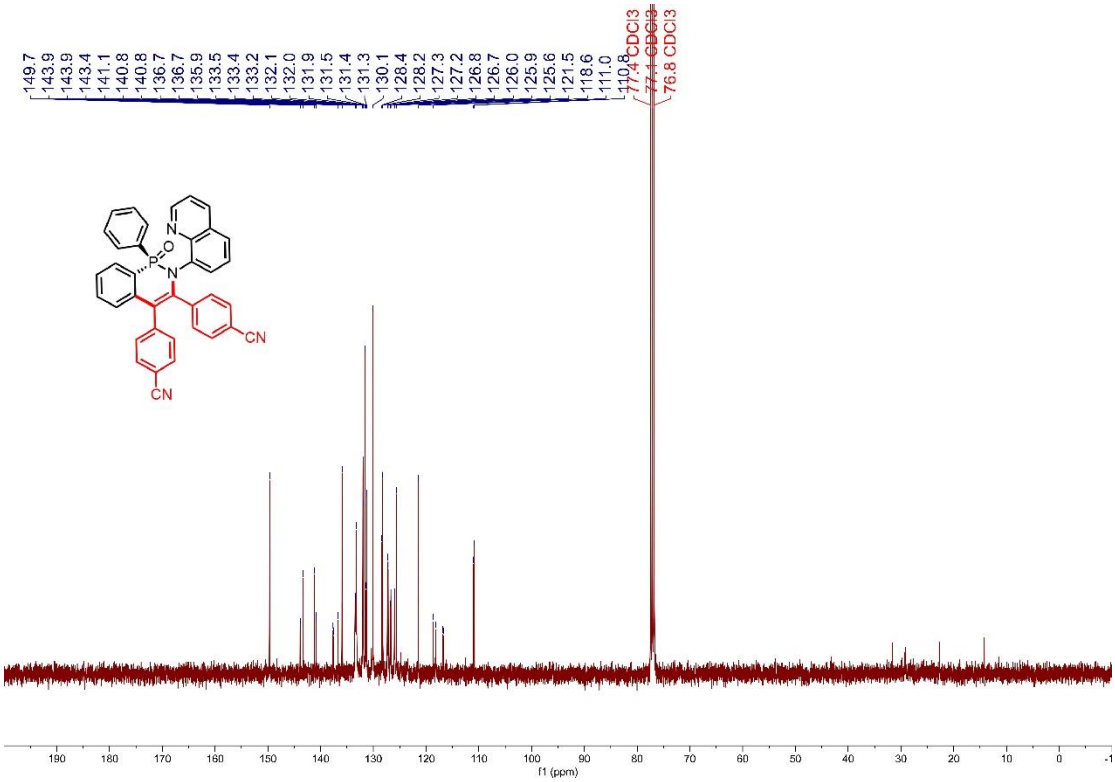

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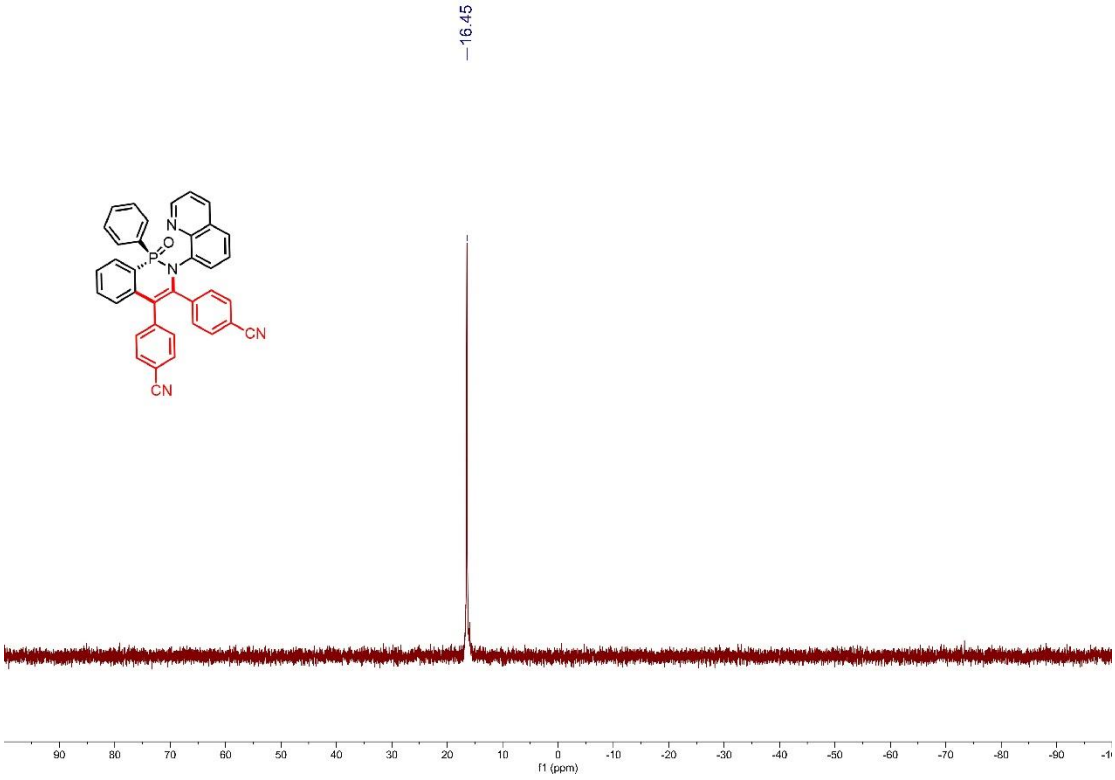

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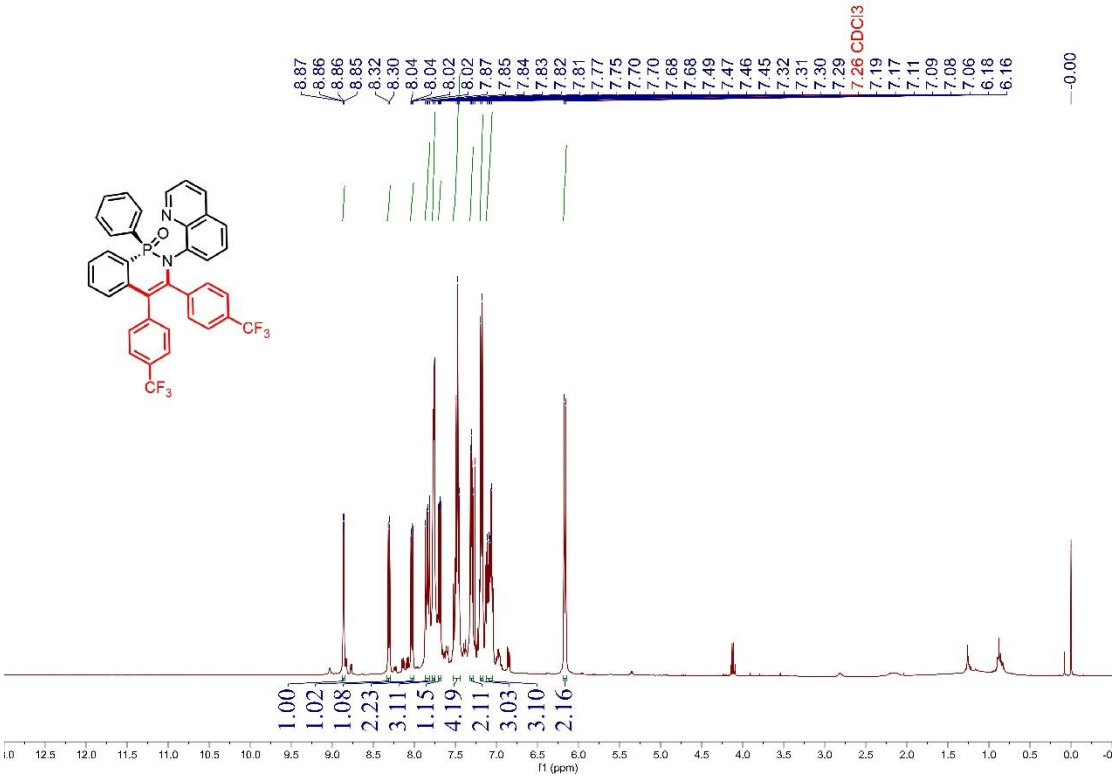

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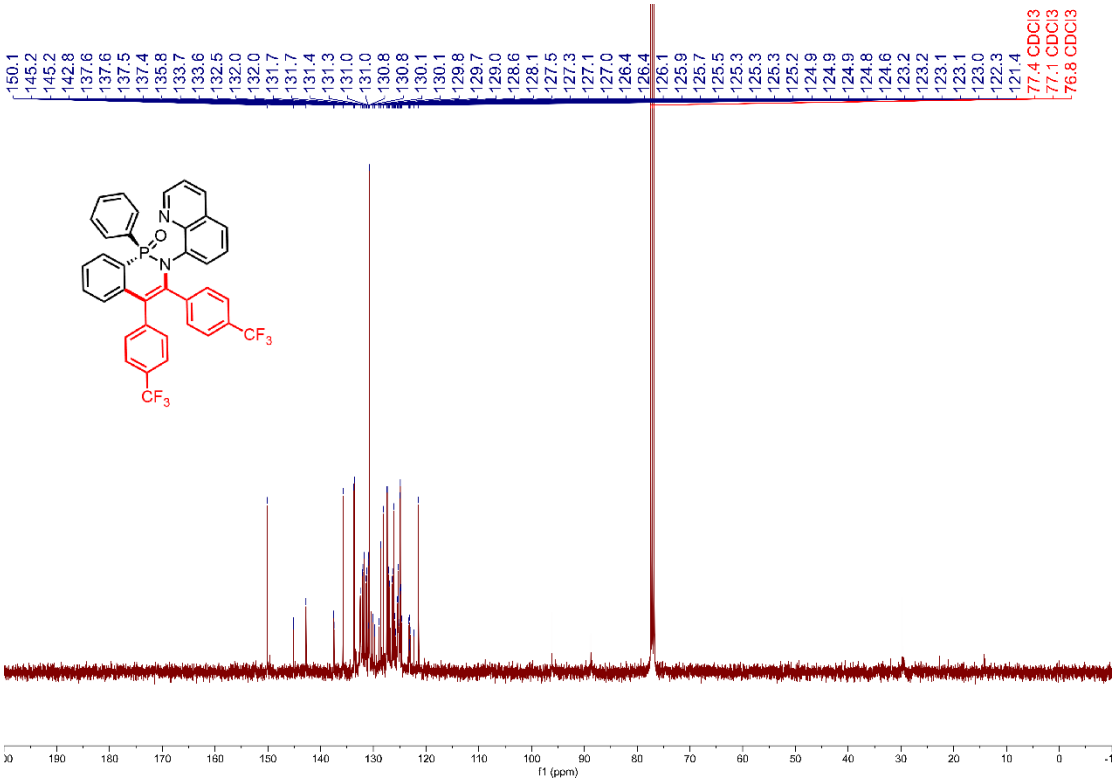
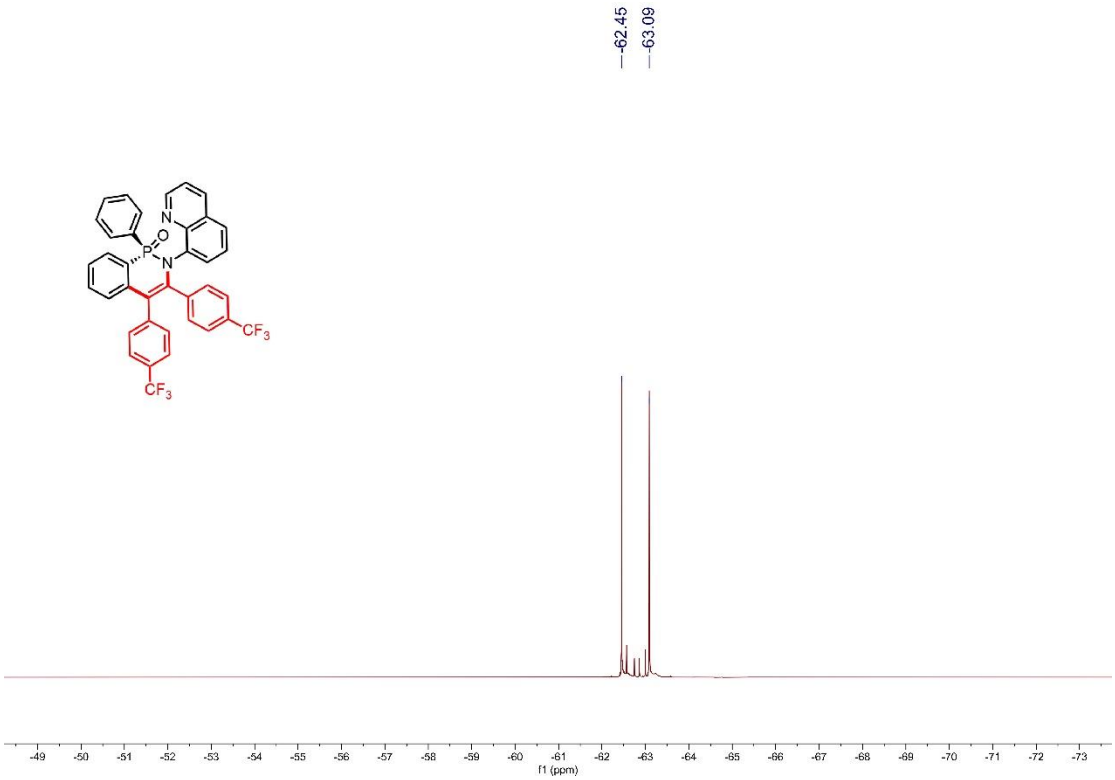


^{19}F-NMR of **3e**



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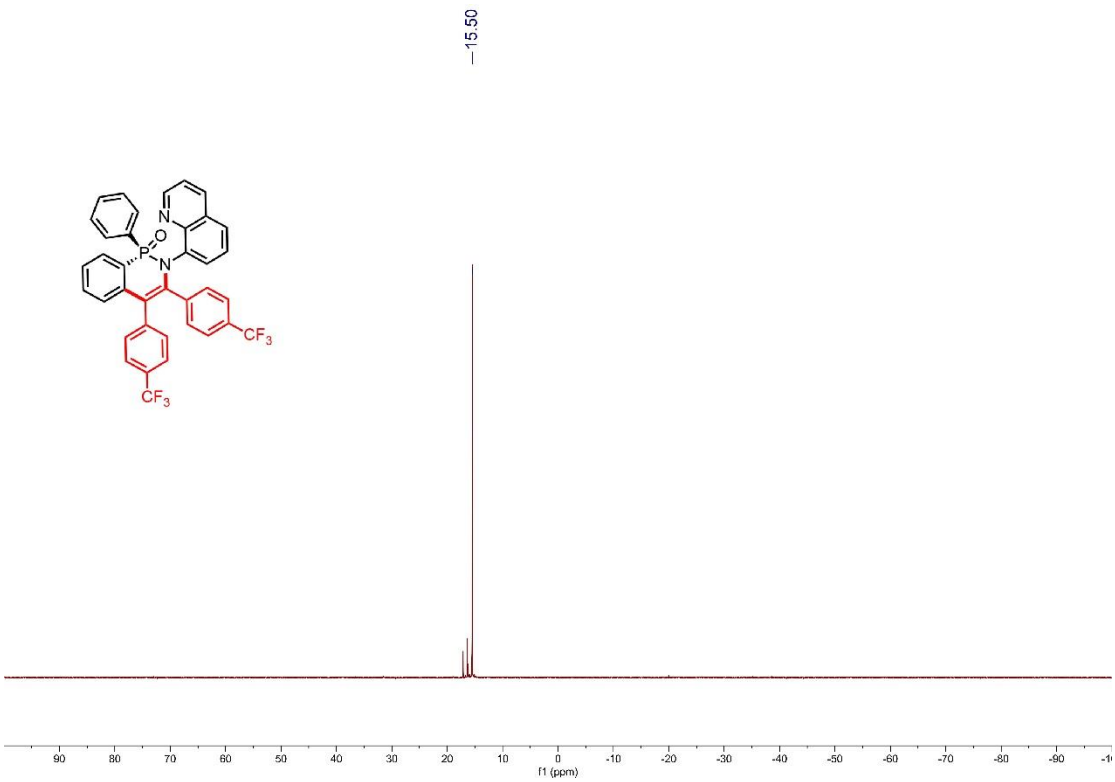

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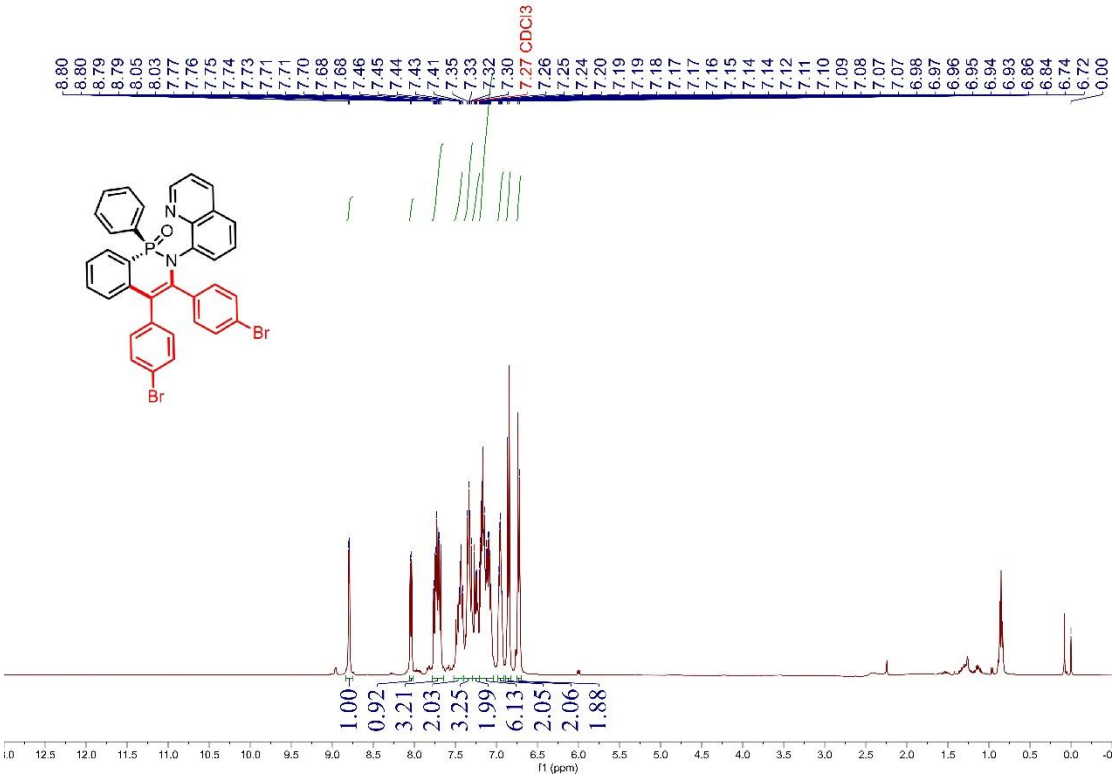

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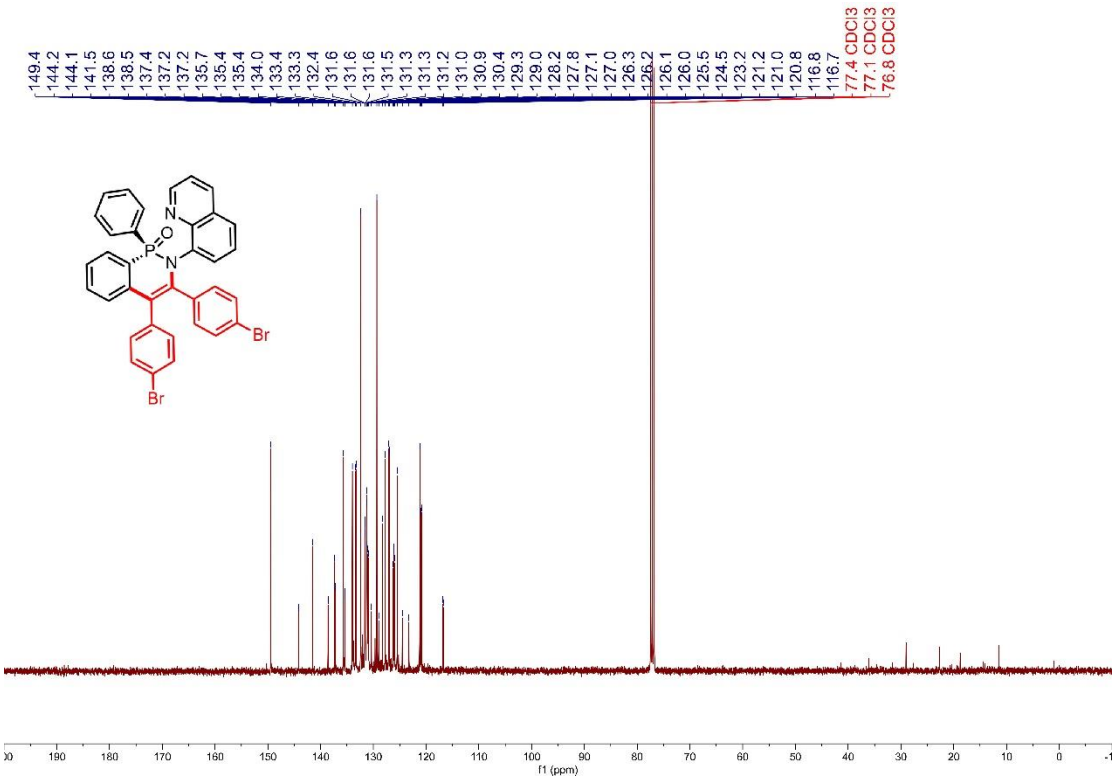

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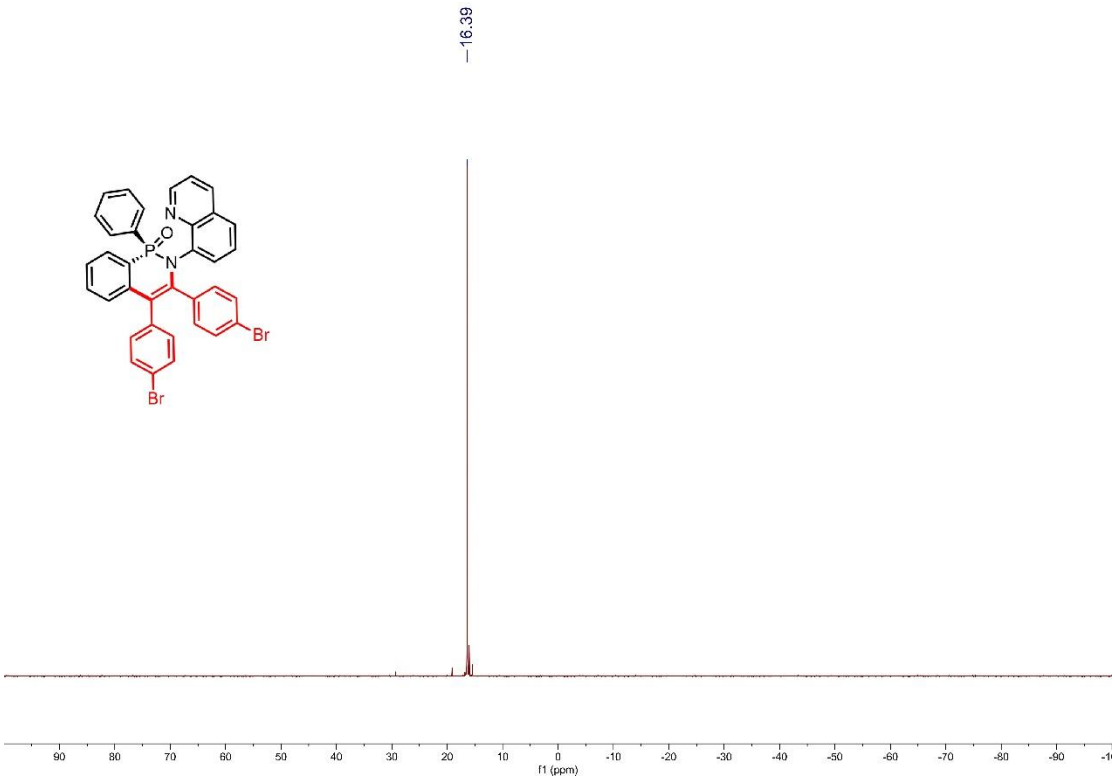

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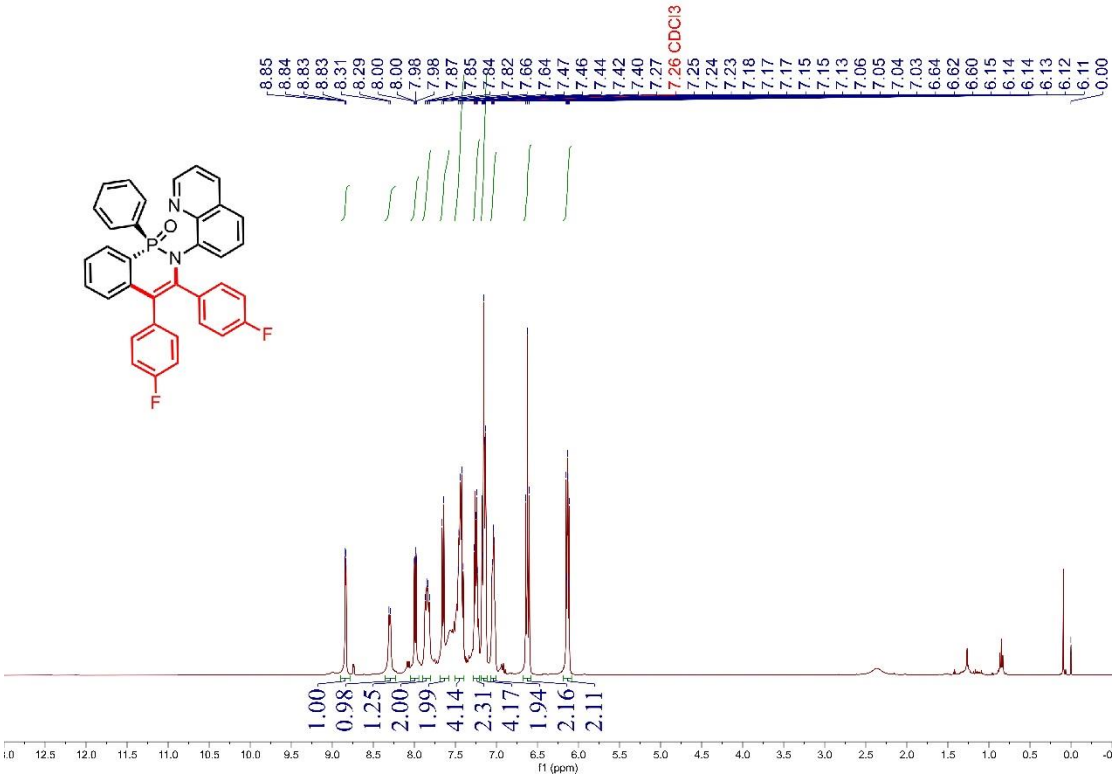

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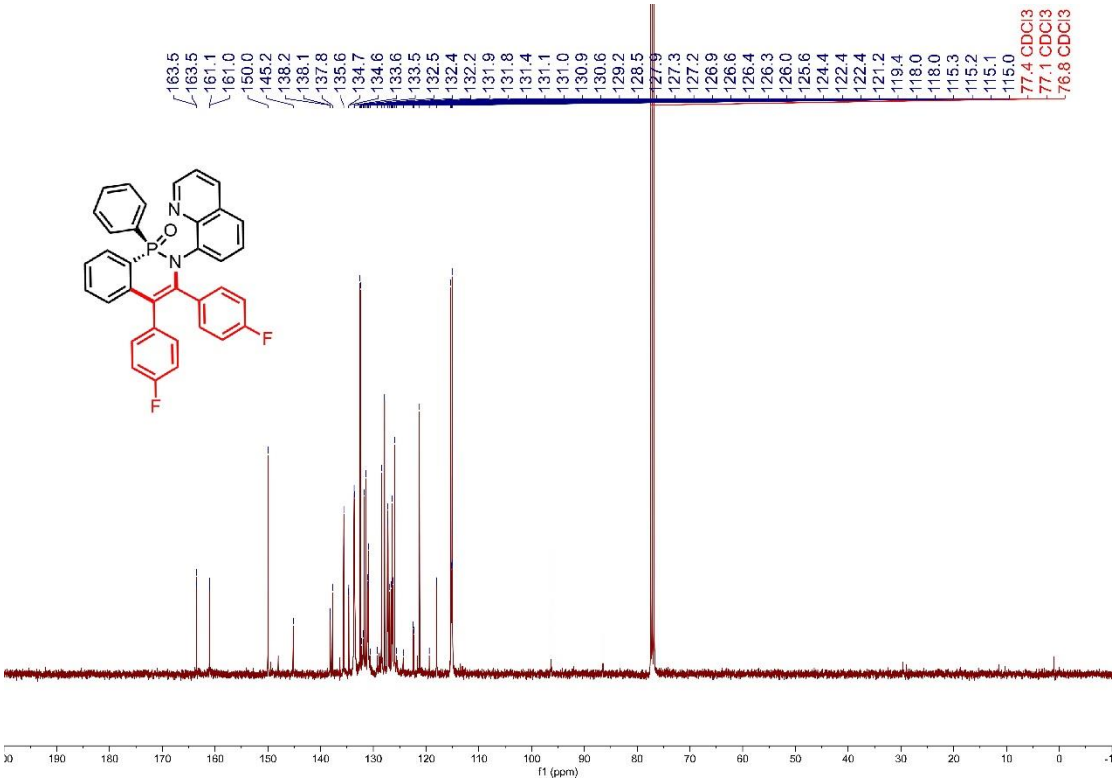

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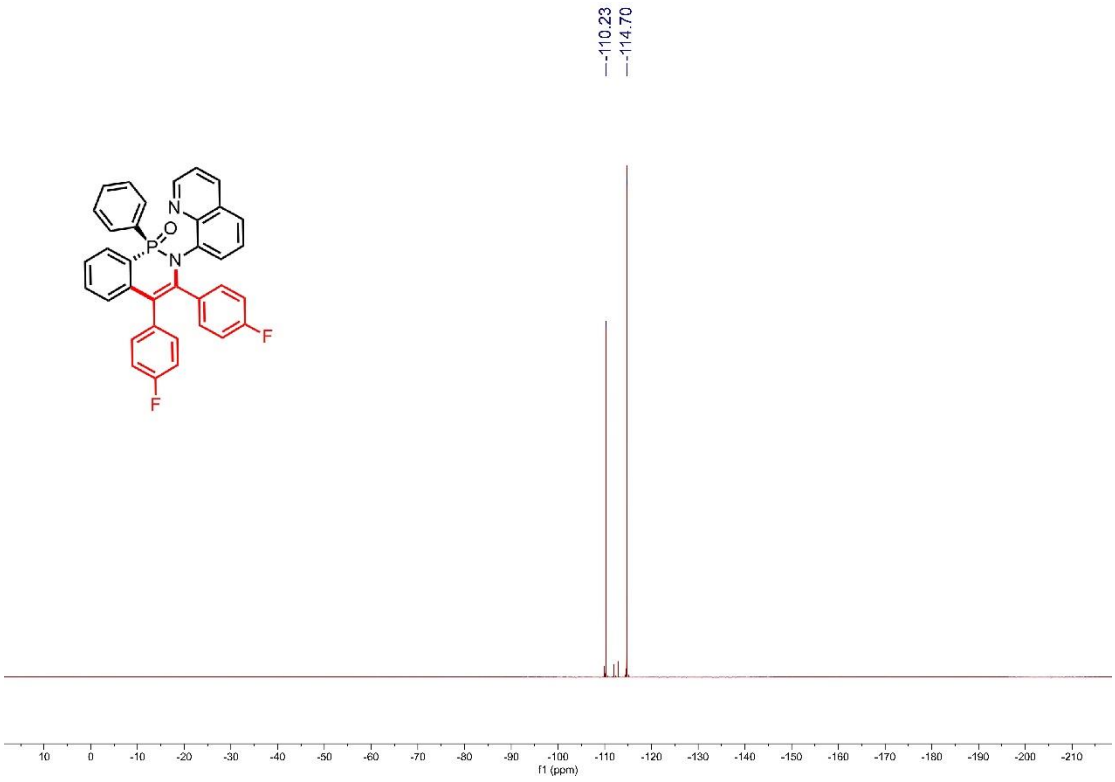

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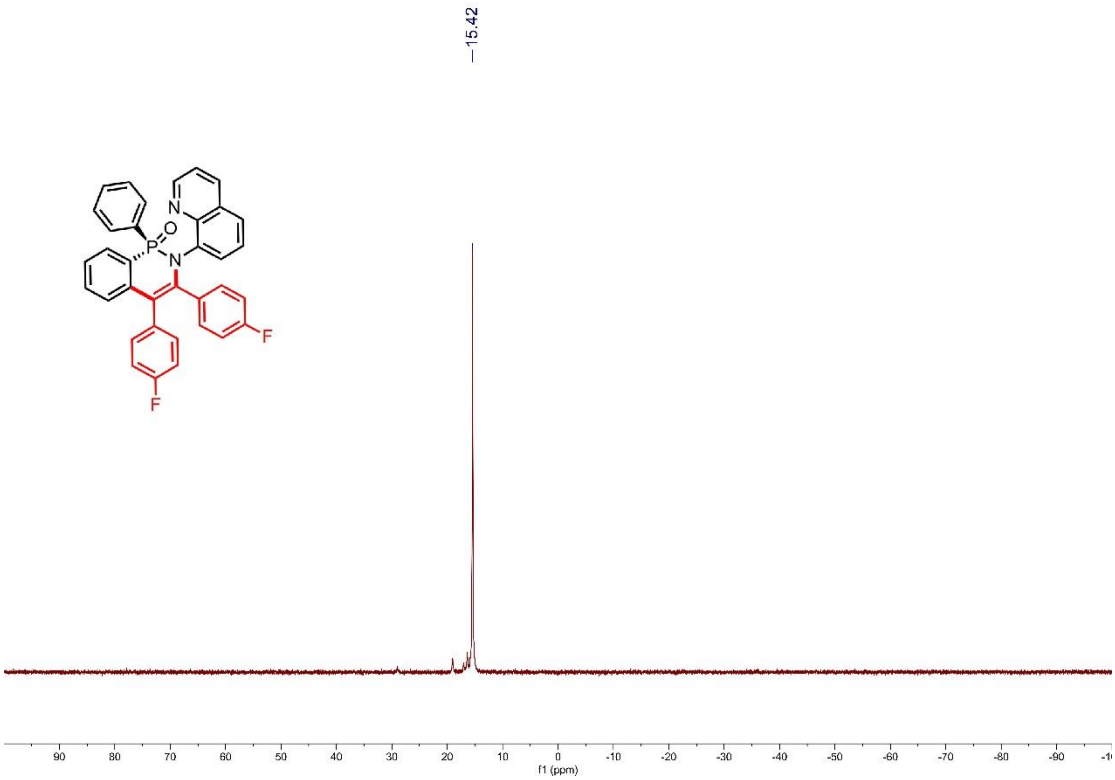

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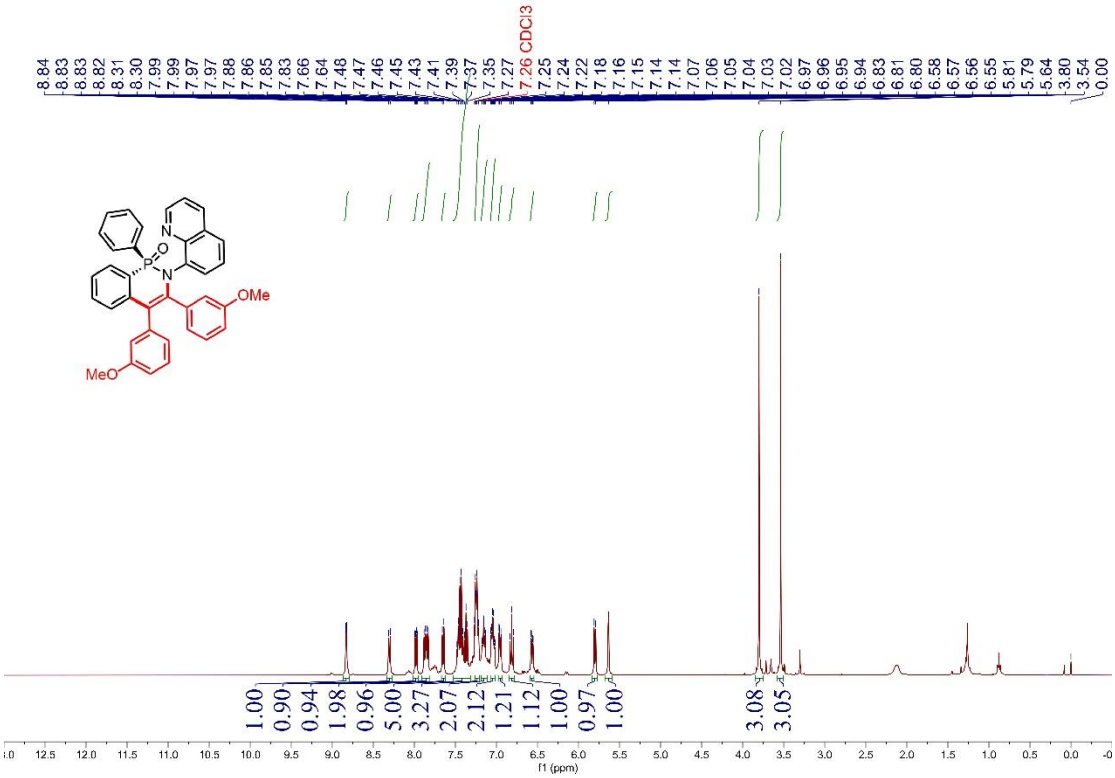

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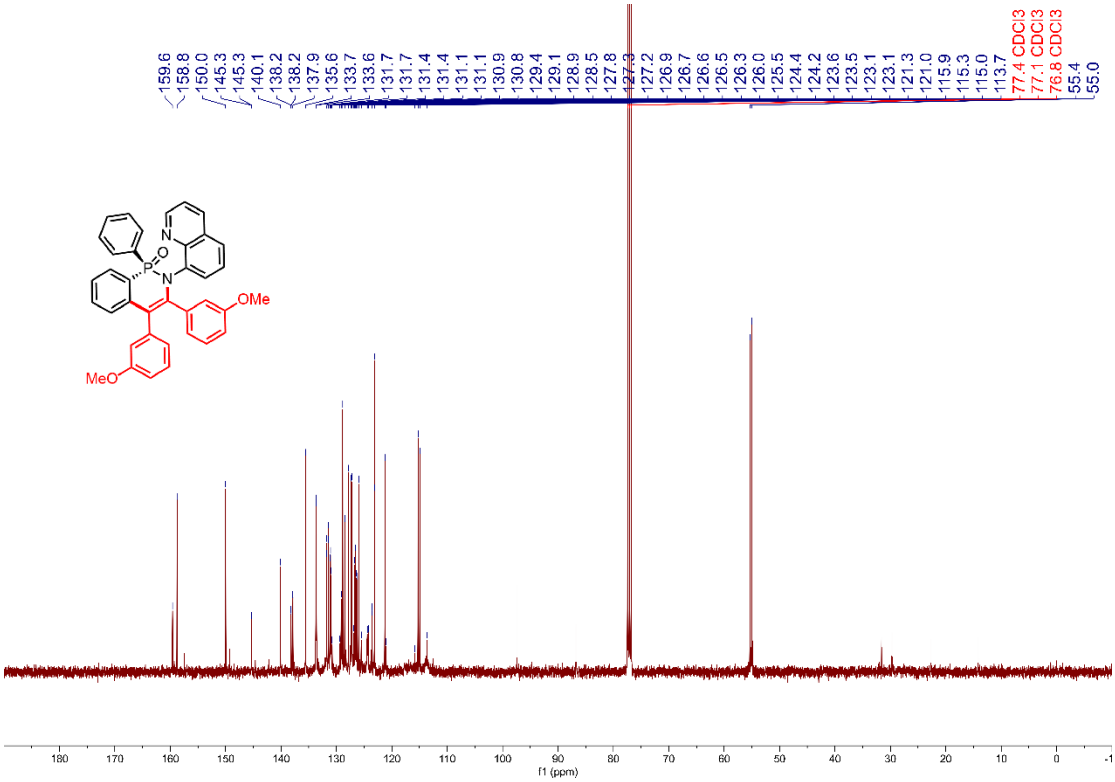

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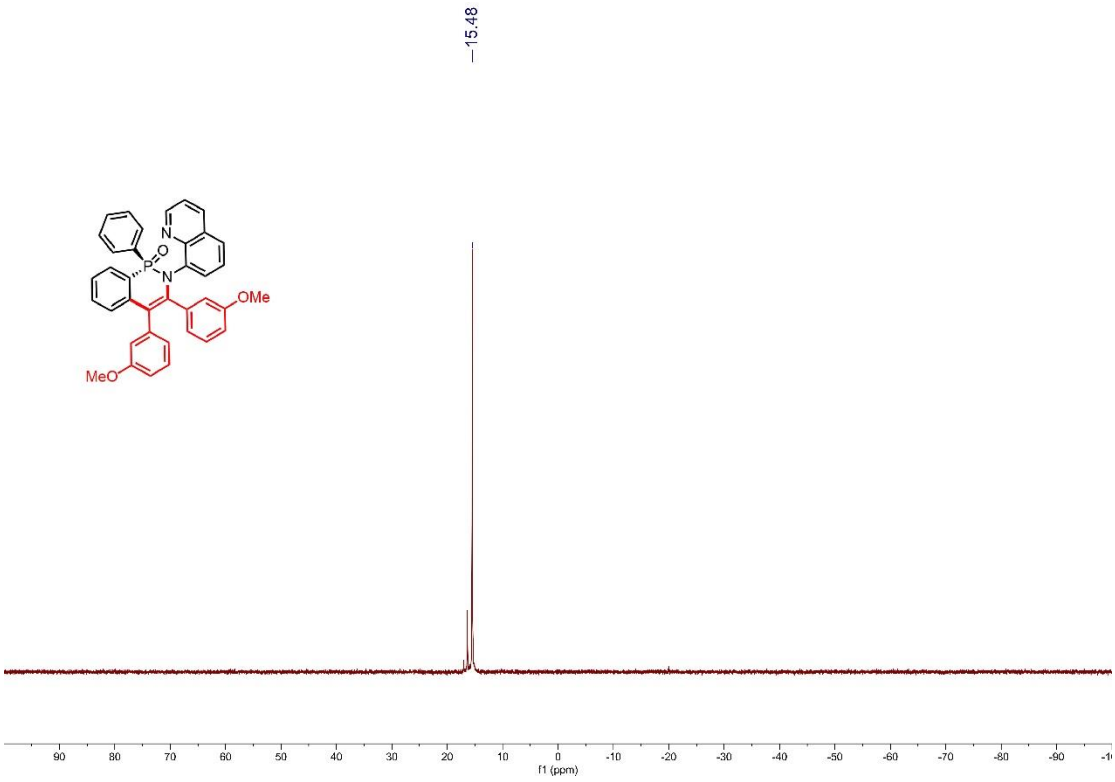

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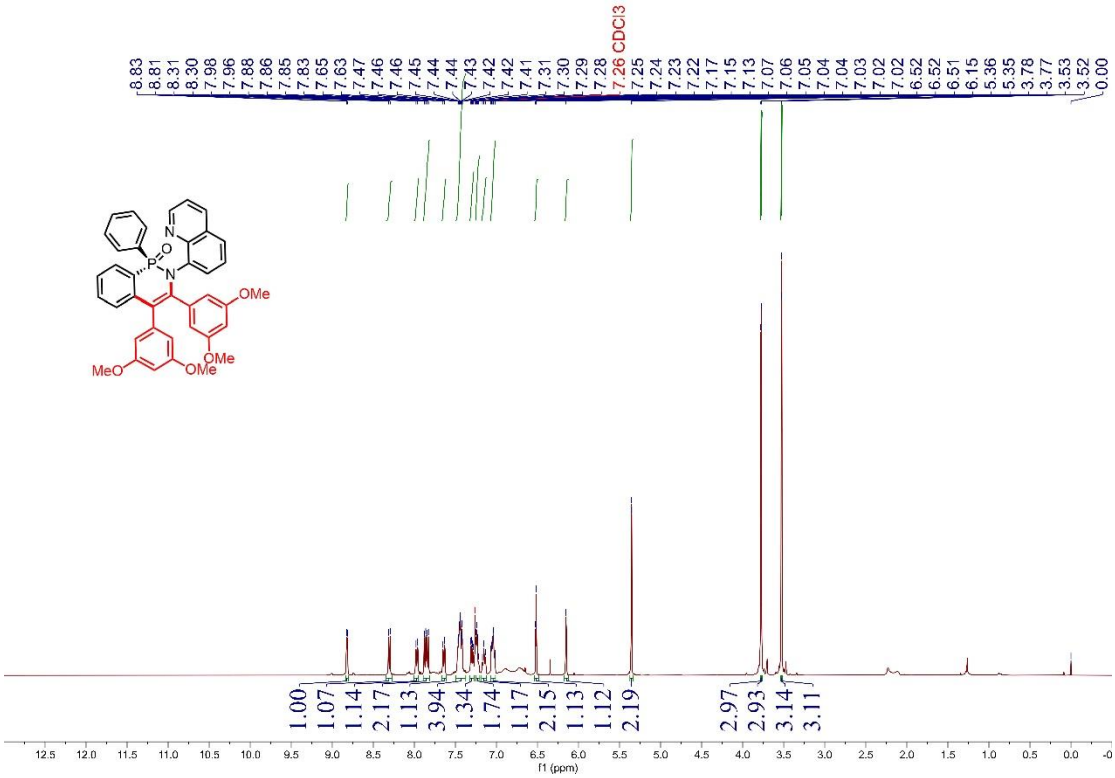

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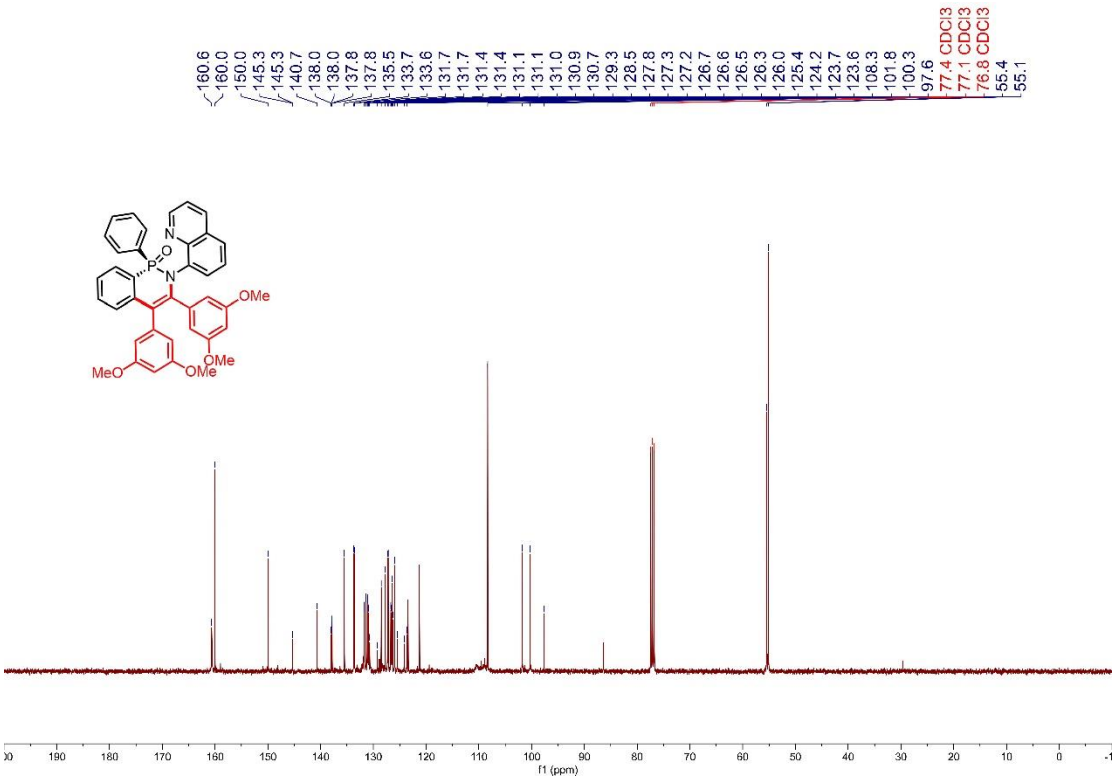

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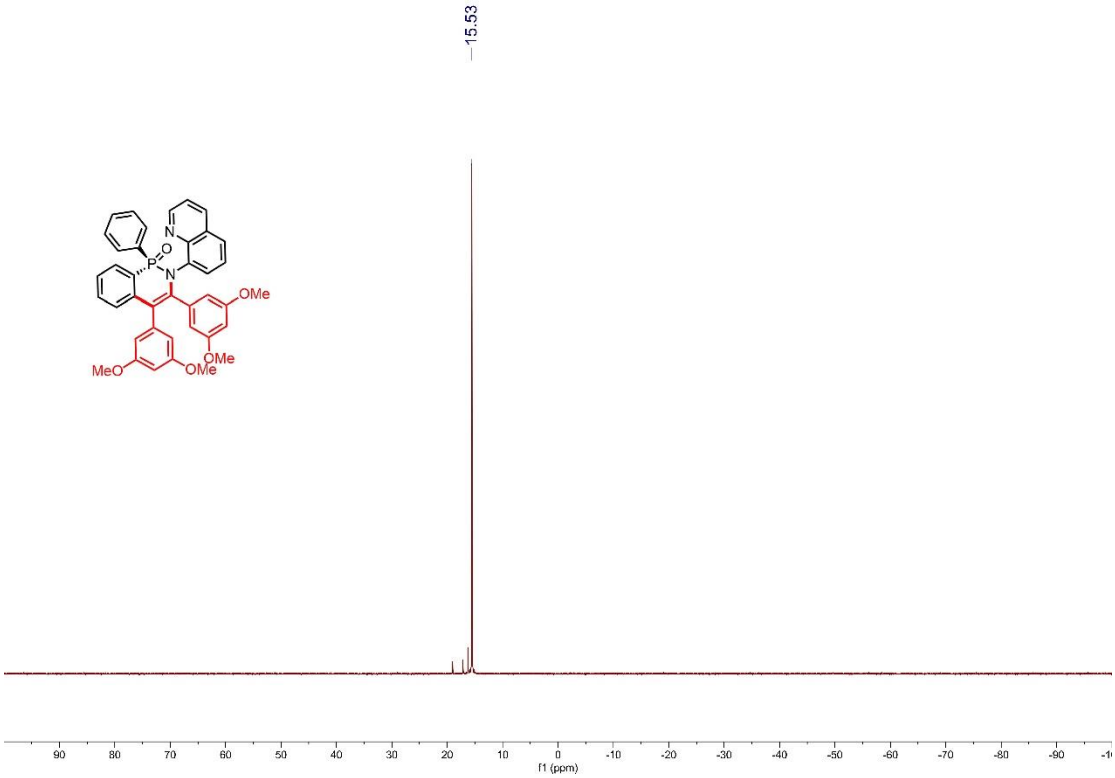

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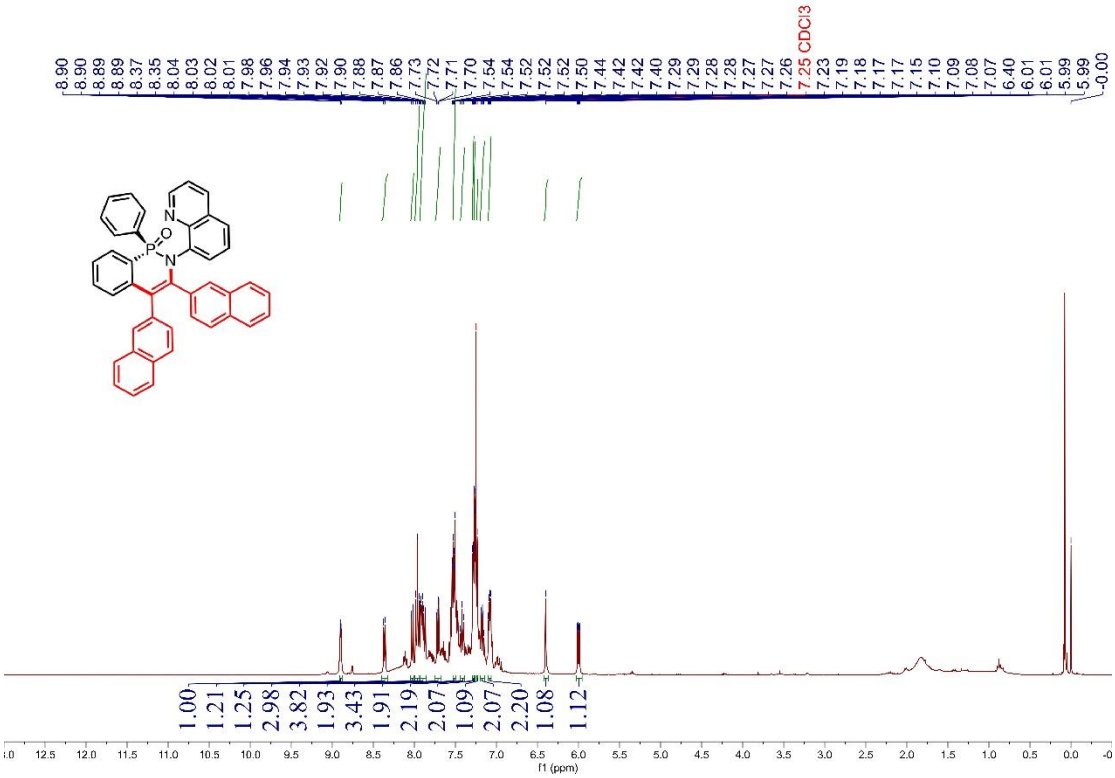

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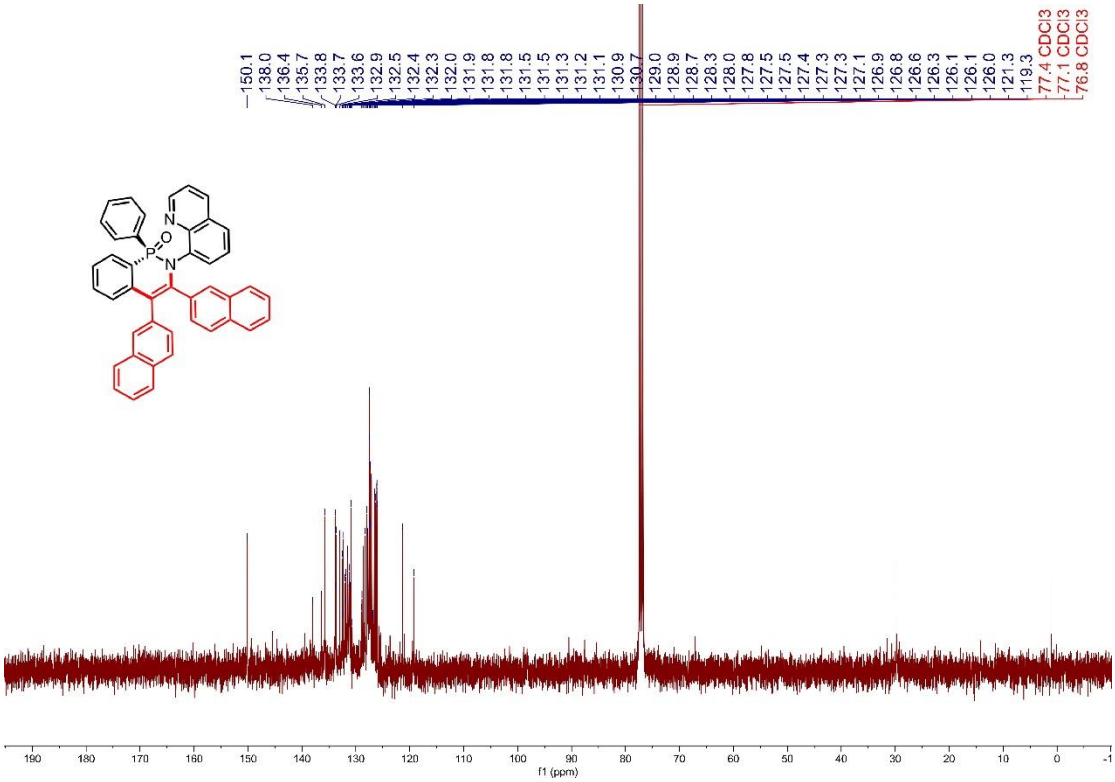

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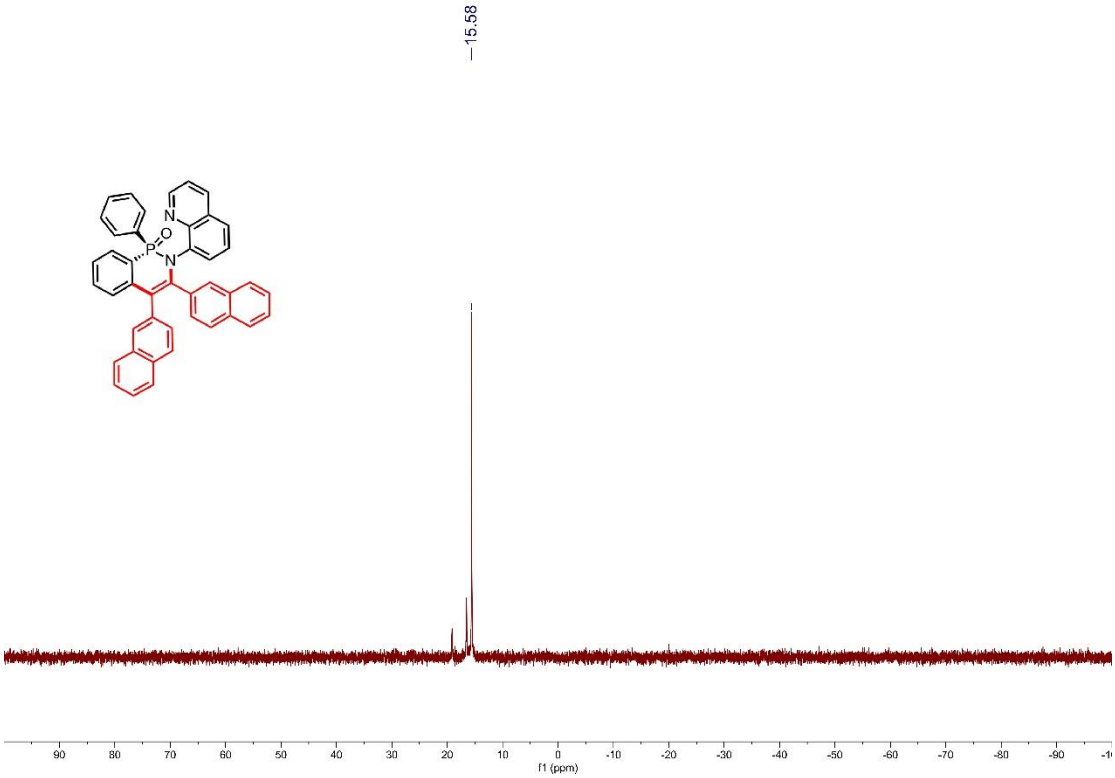

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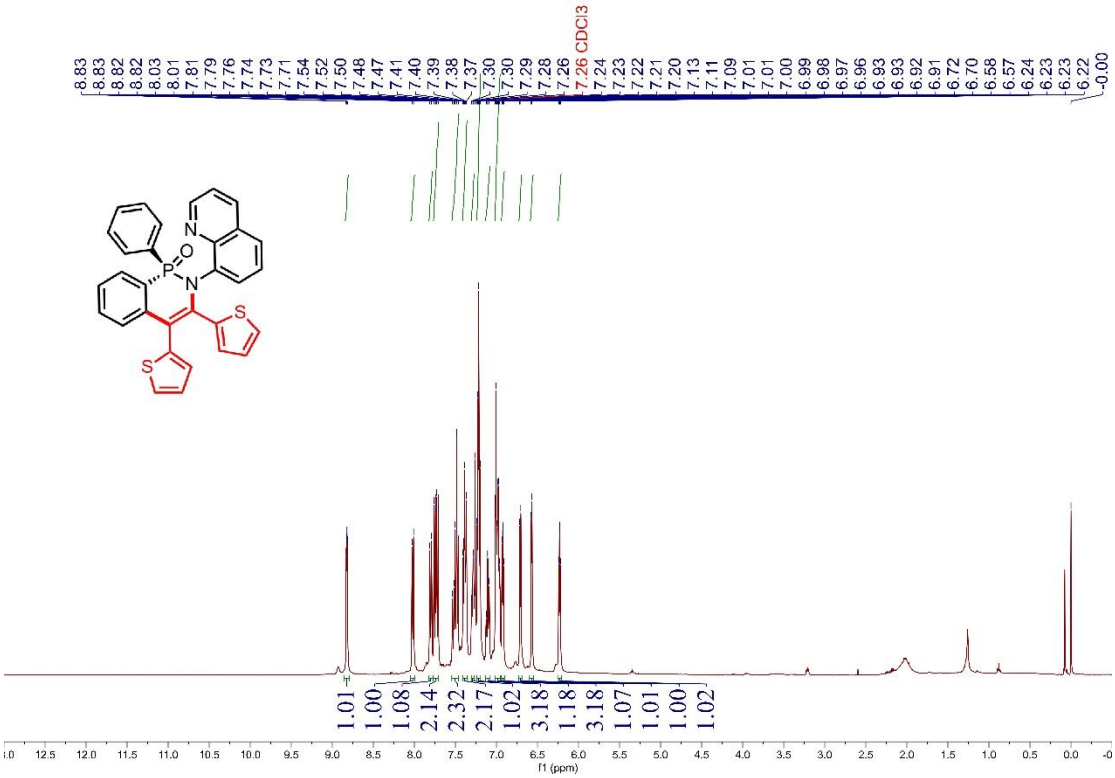

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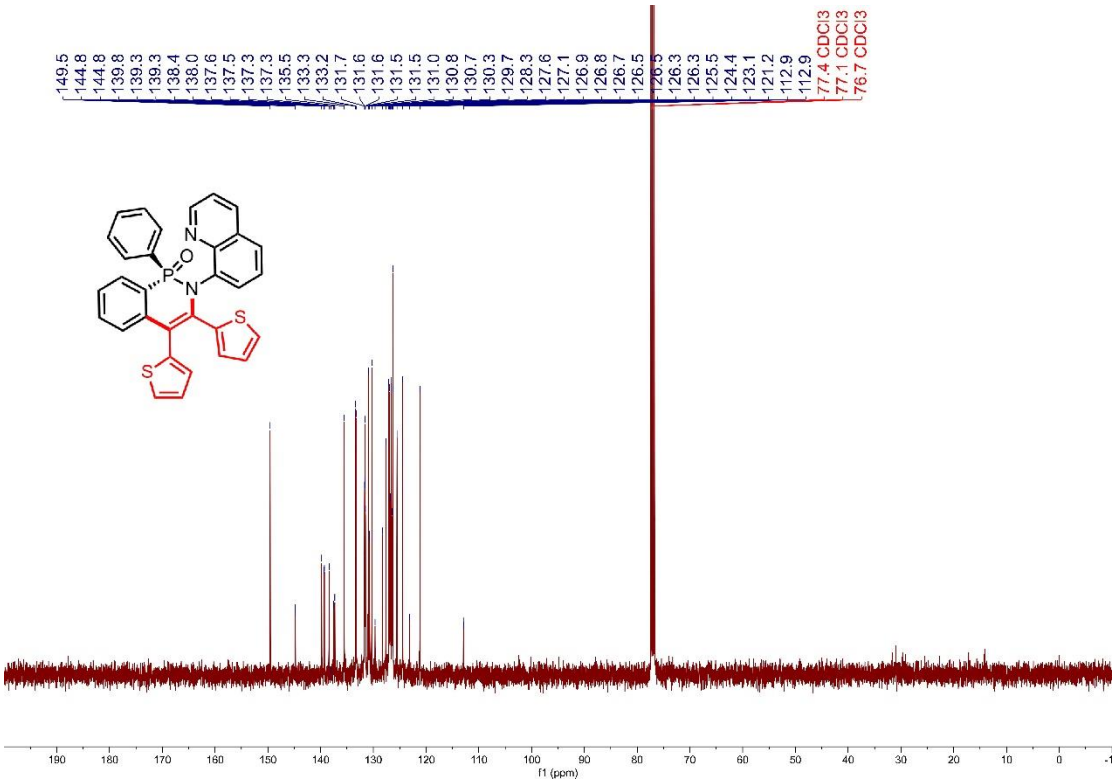

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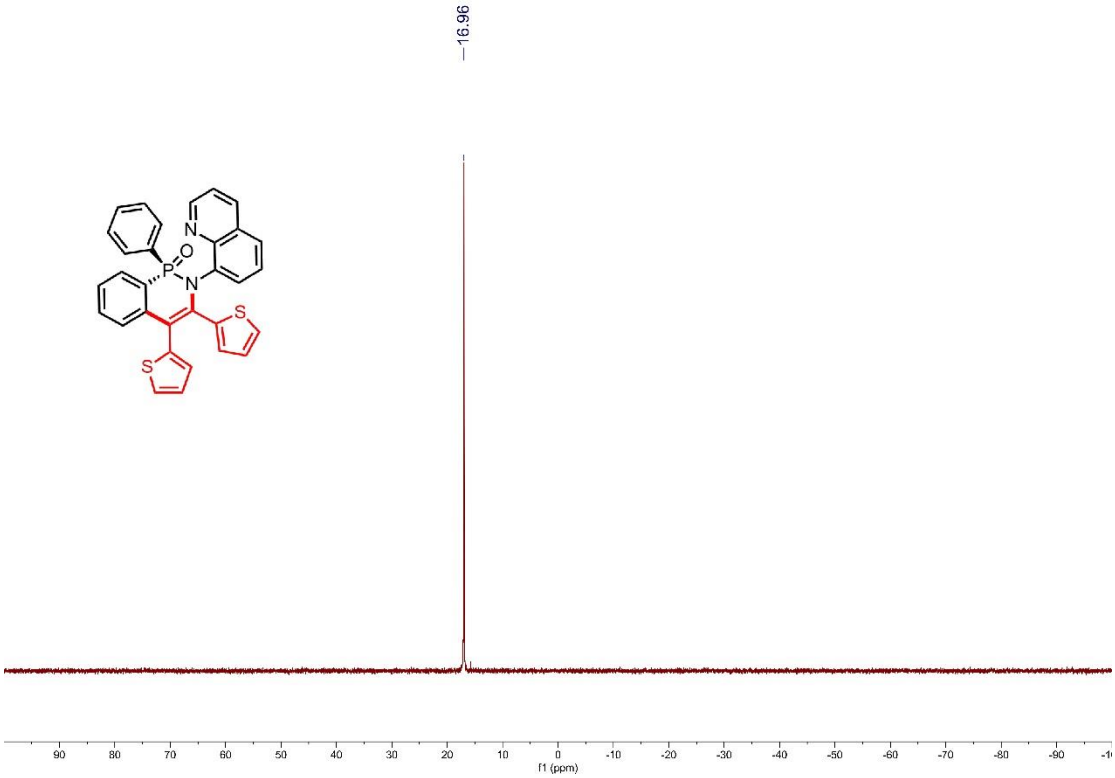

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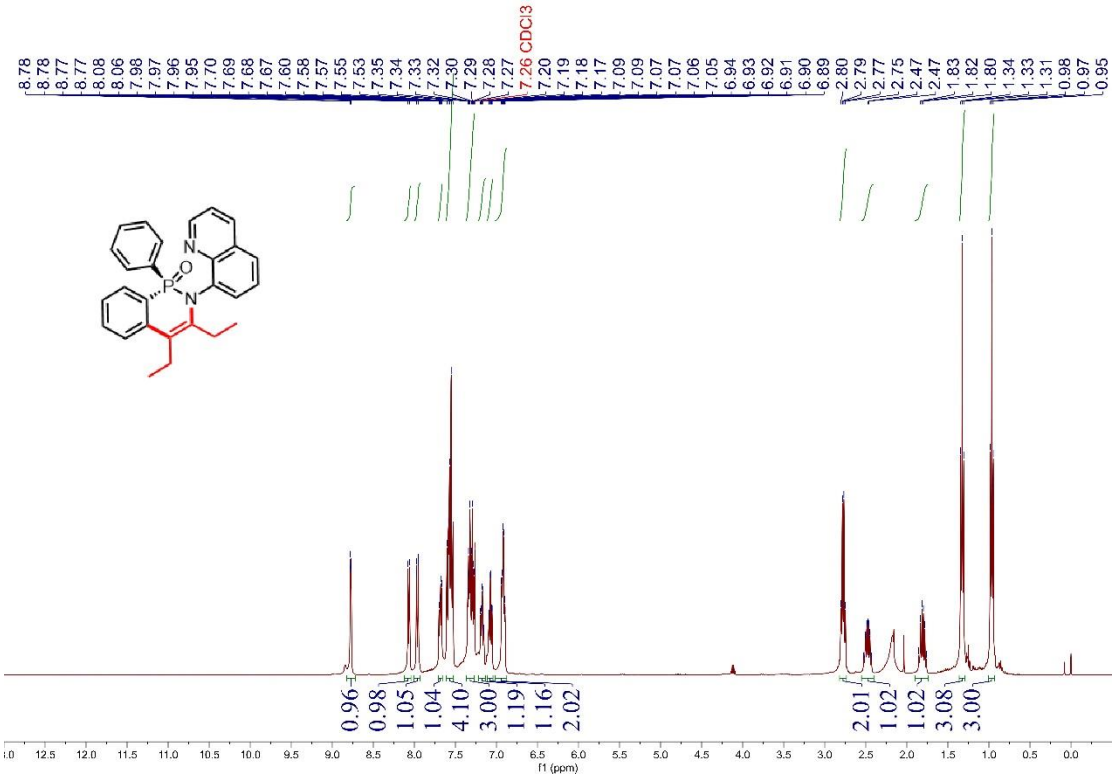

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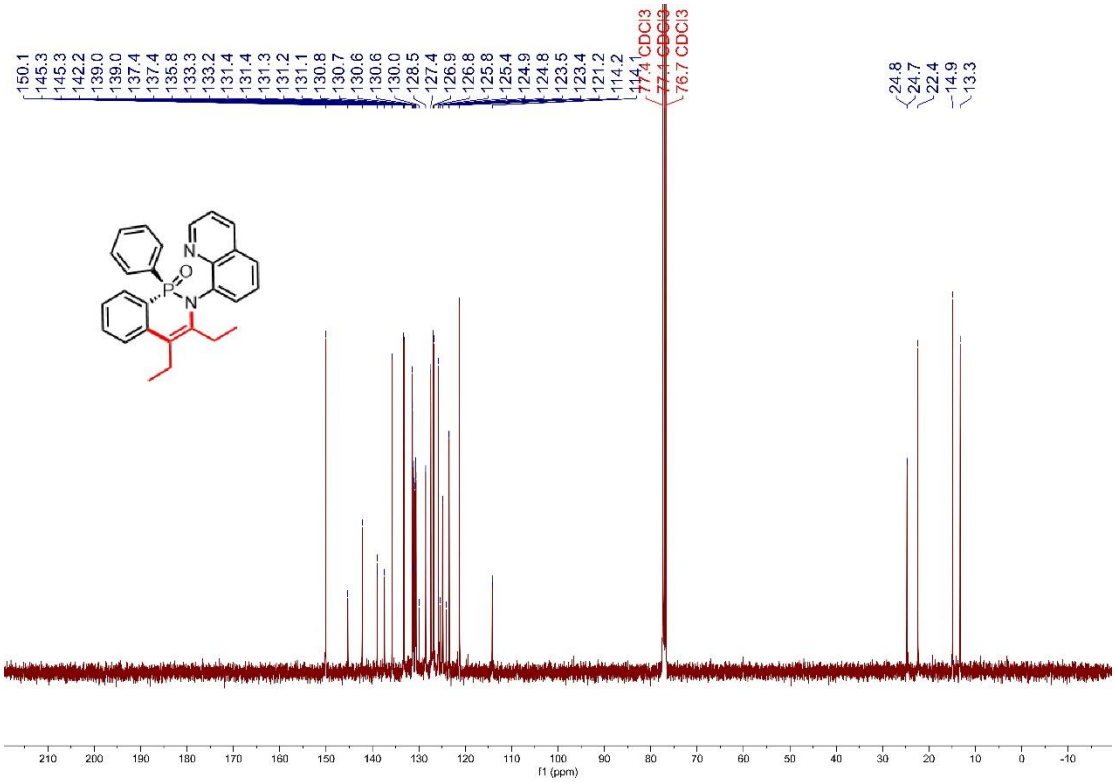
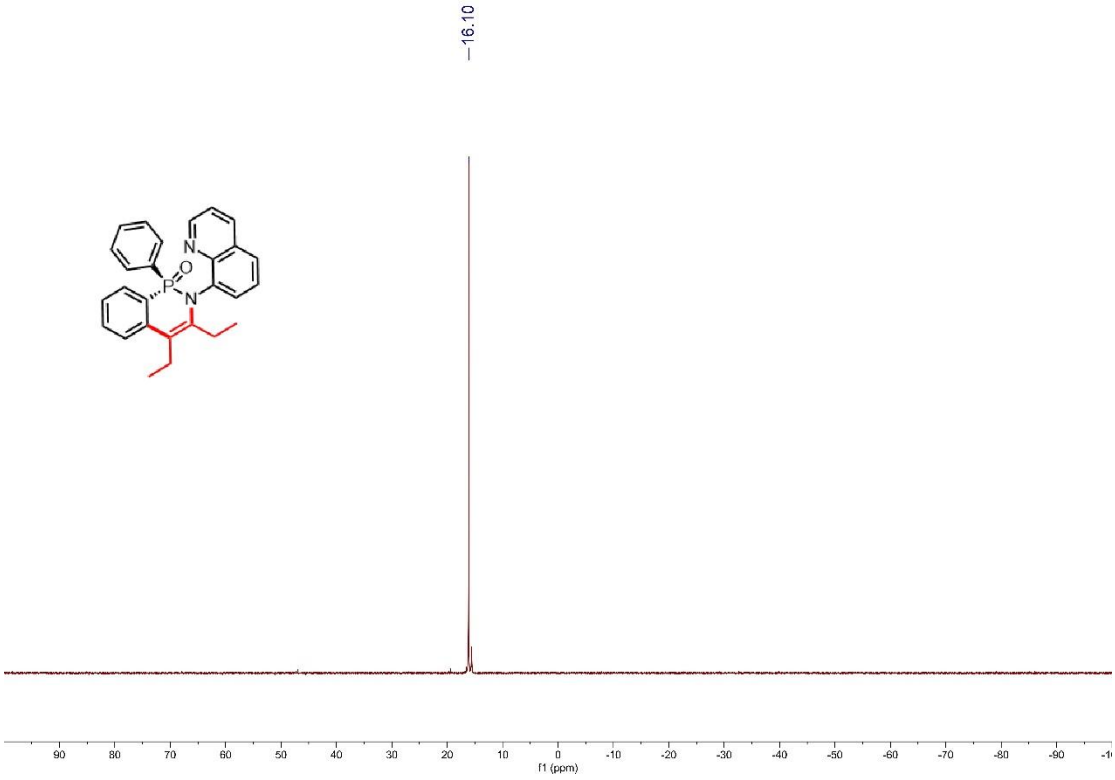
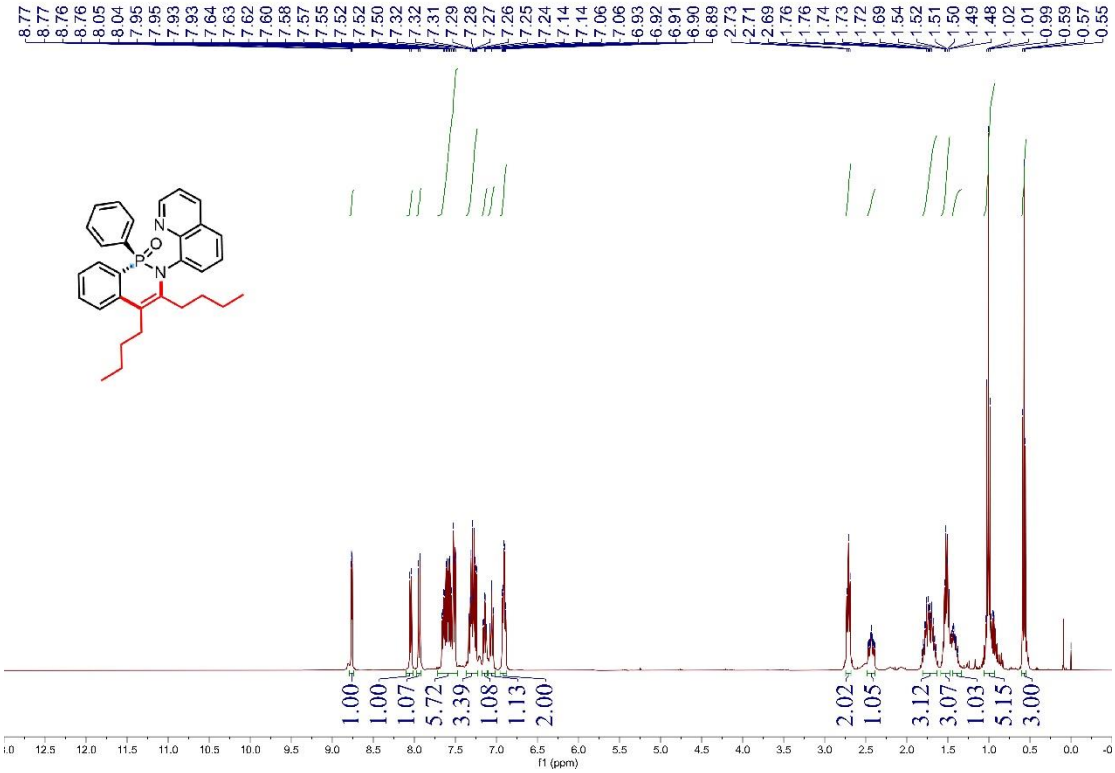


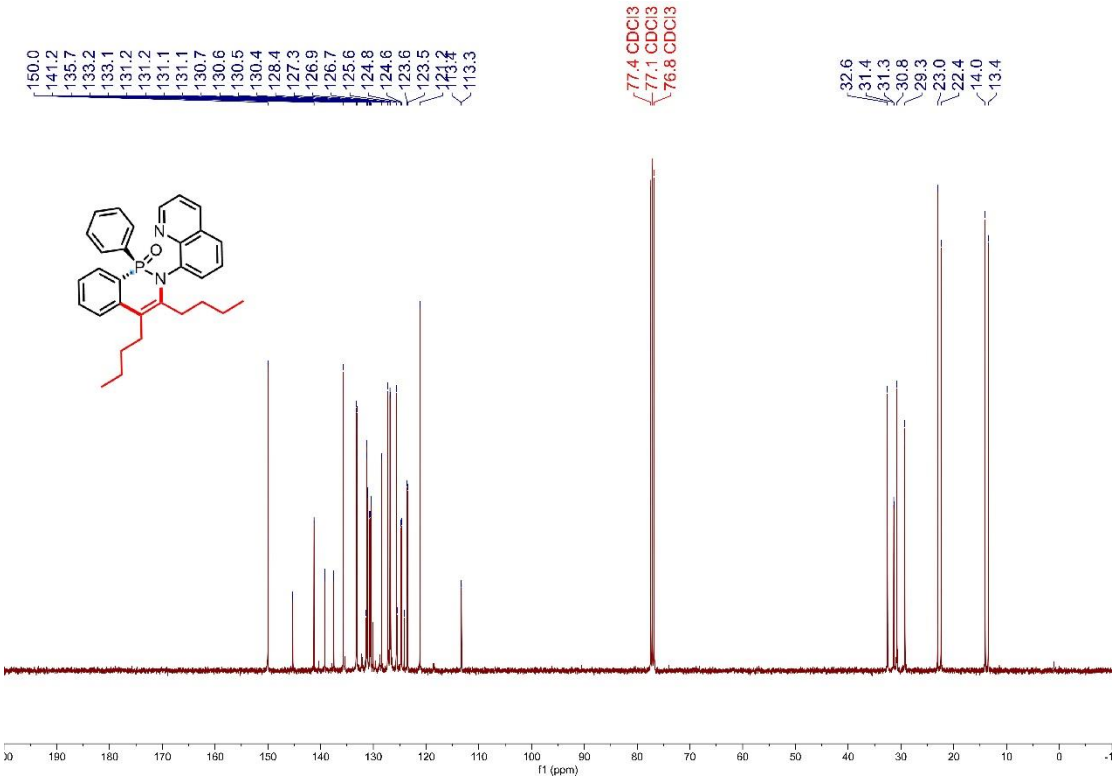
^{31}P-NMR of **3l**



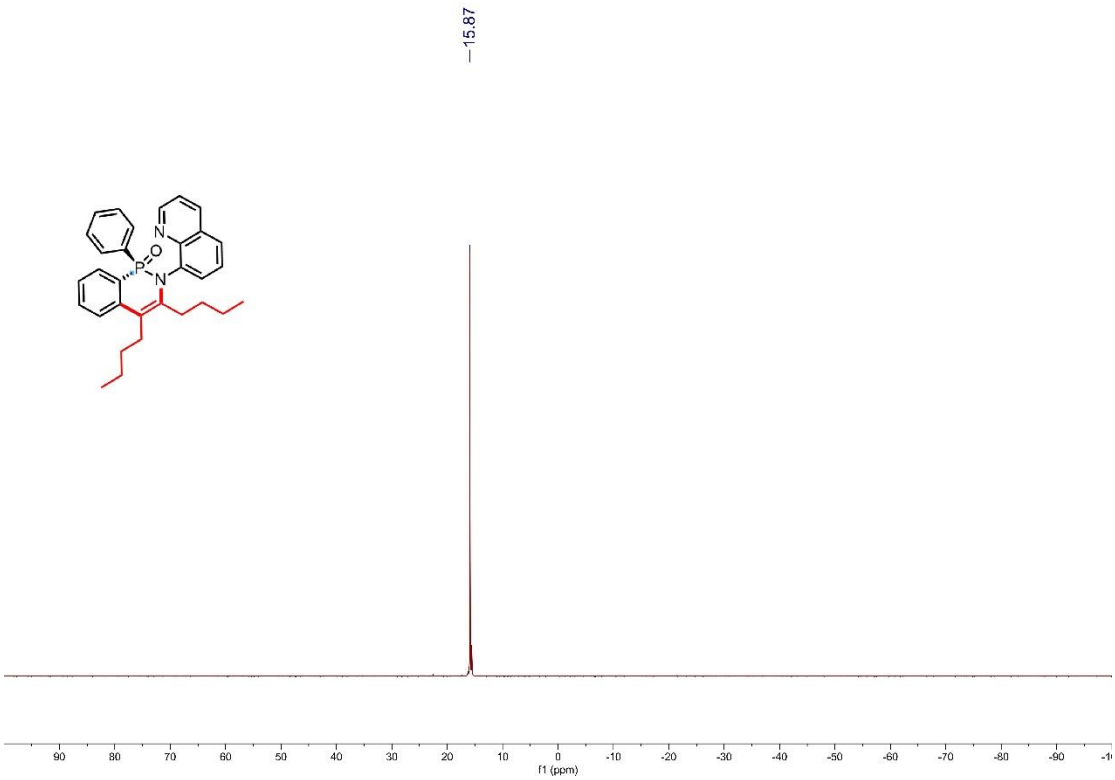
^{1}H-NMR of **3m**



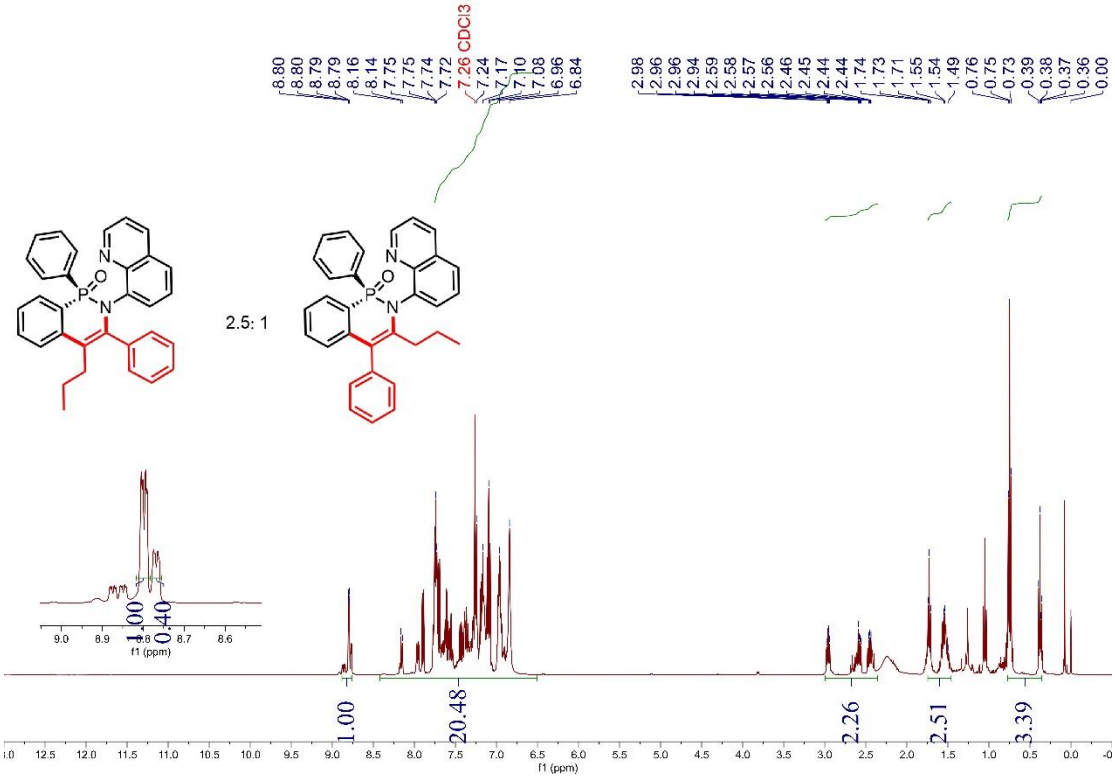
^{13}C-NMR of **3m**



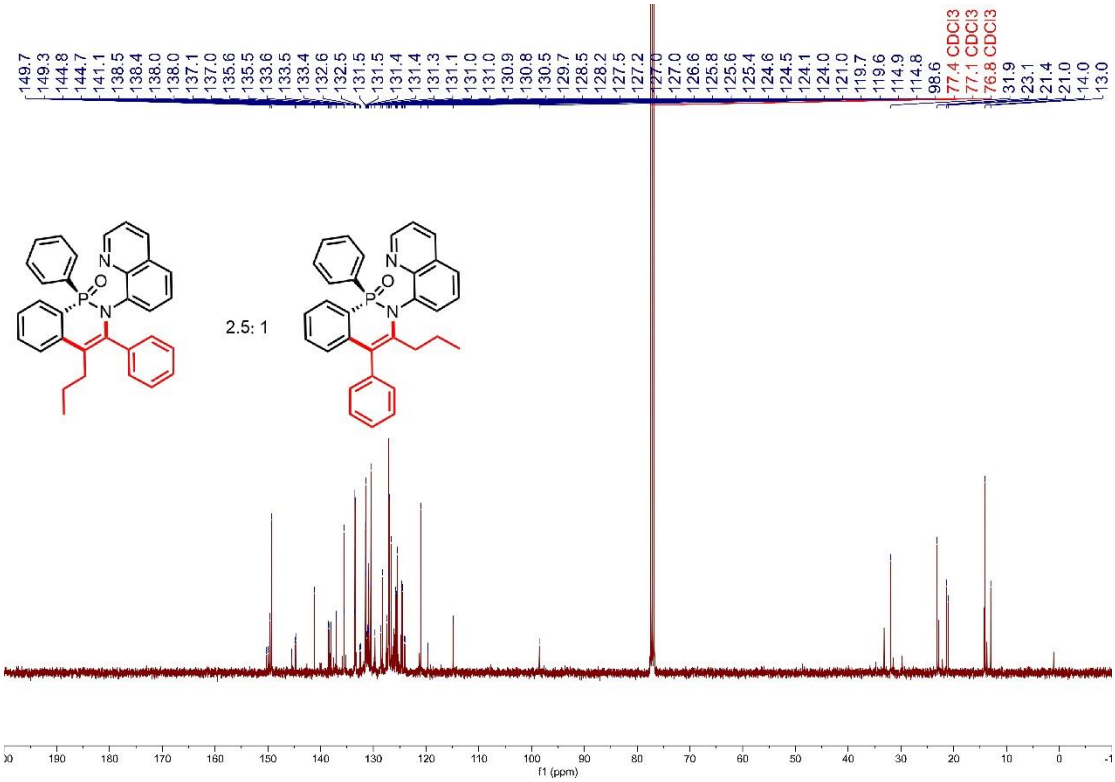
^{31}P-NMR of **3m**



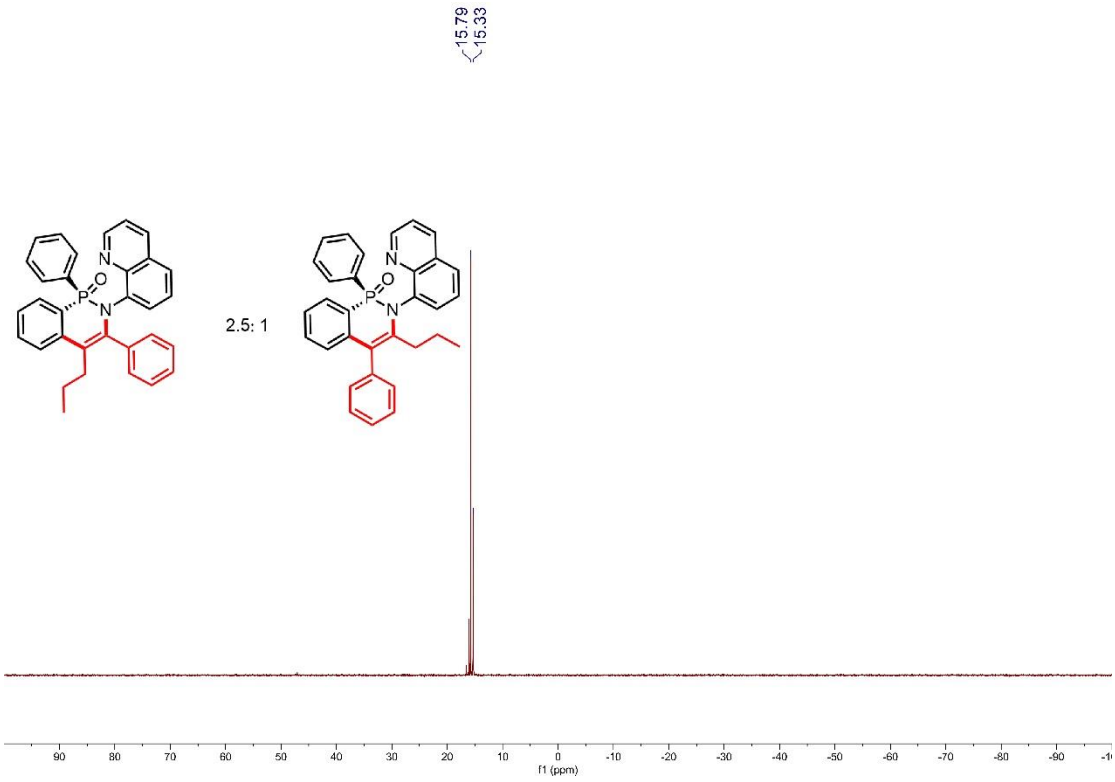
^{1}H-NMR of **3n**



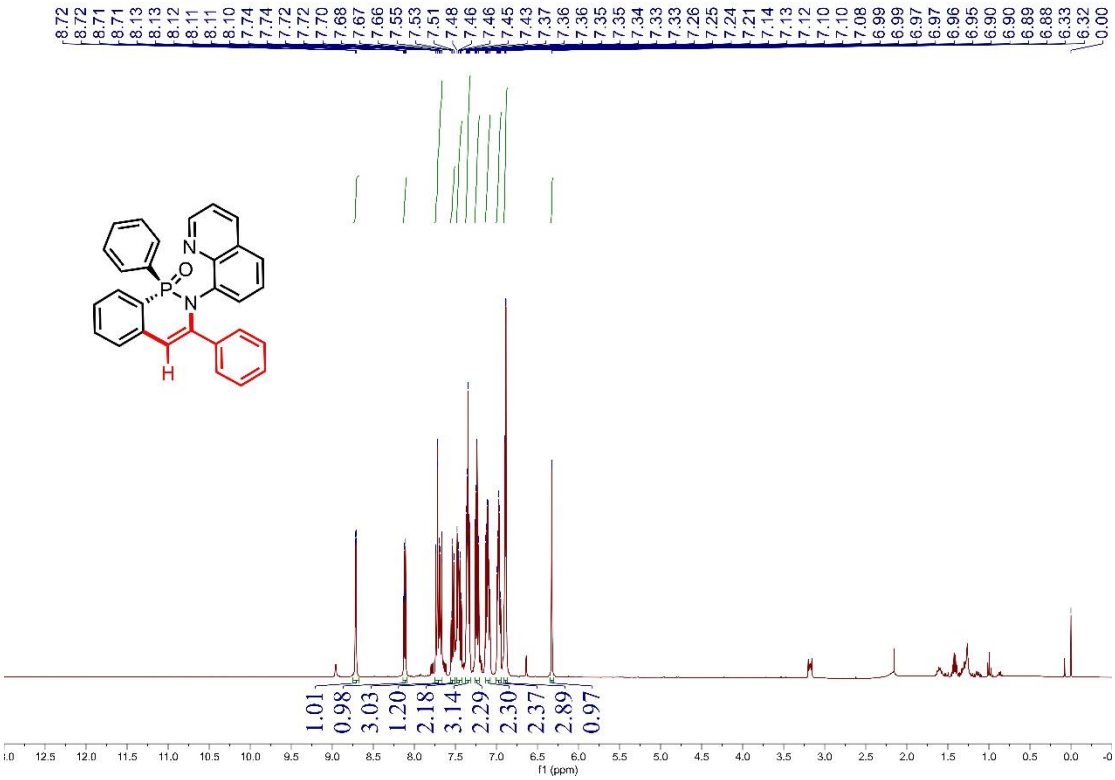
^{13}C-NMR of **3n**



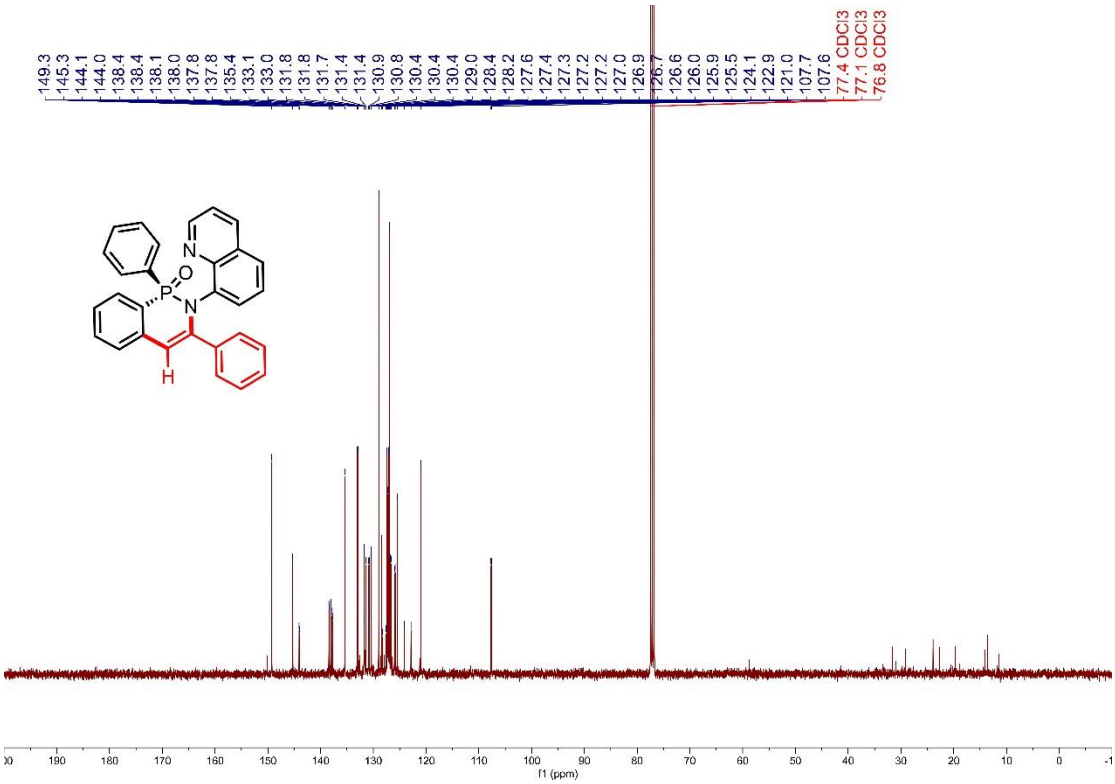
^{31}P-NMR of **3n**



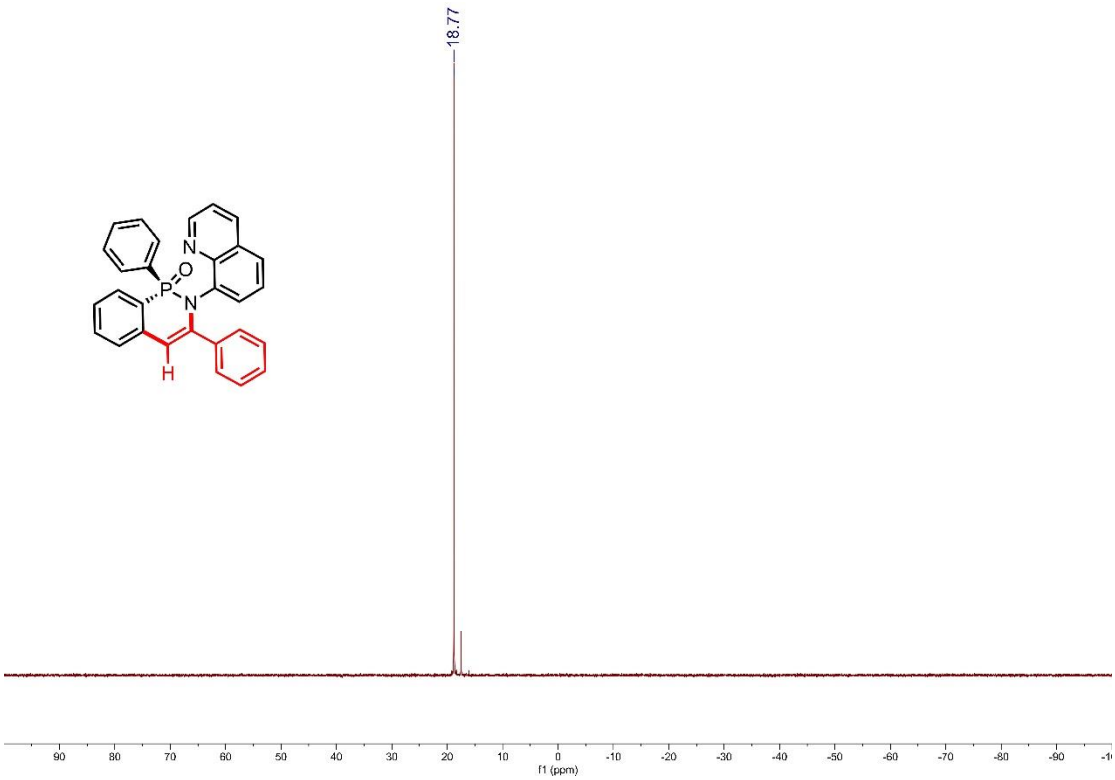
^{1}H-NMR of **3o**



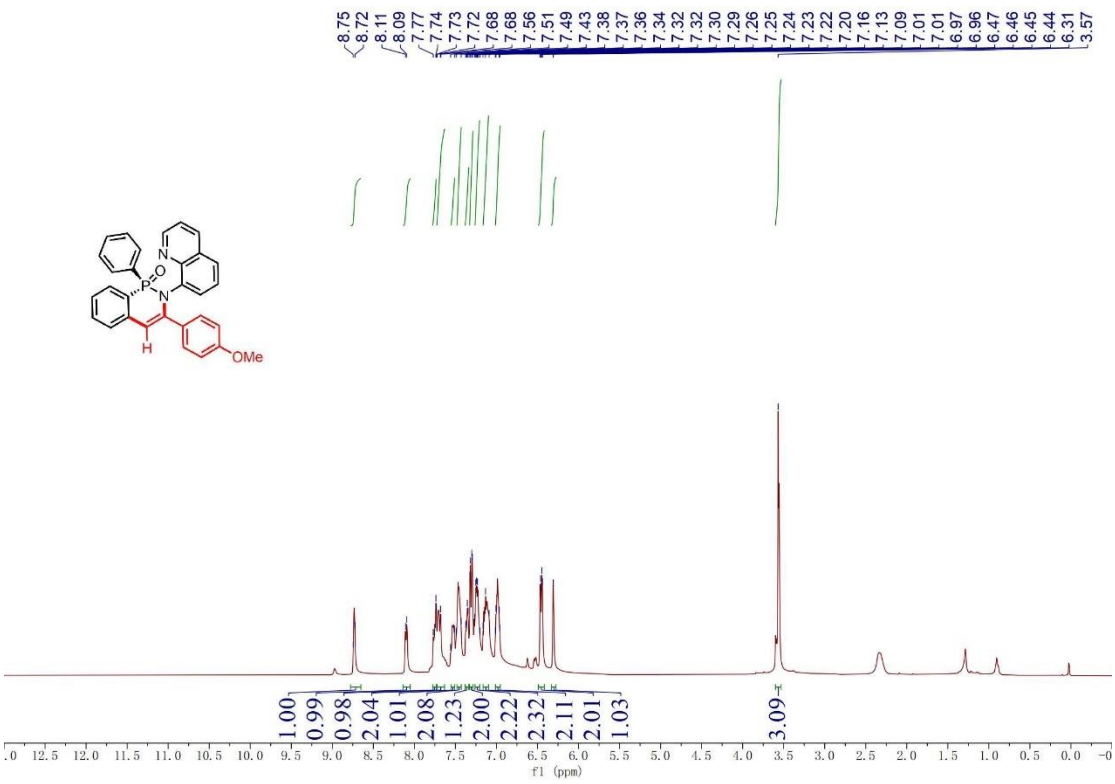
^{13}C-NMR of **3o**



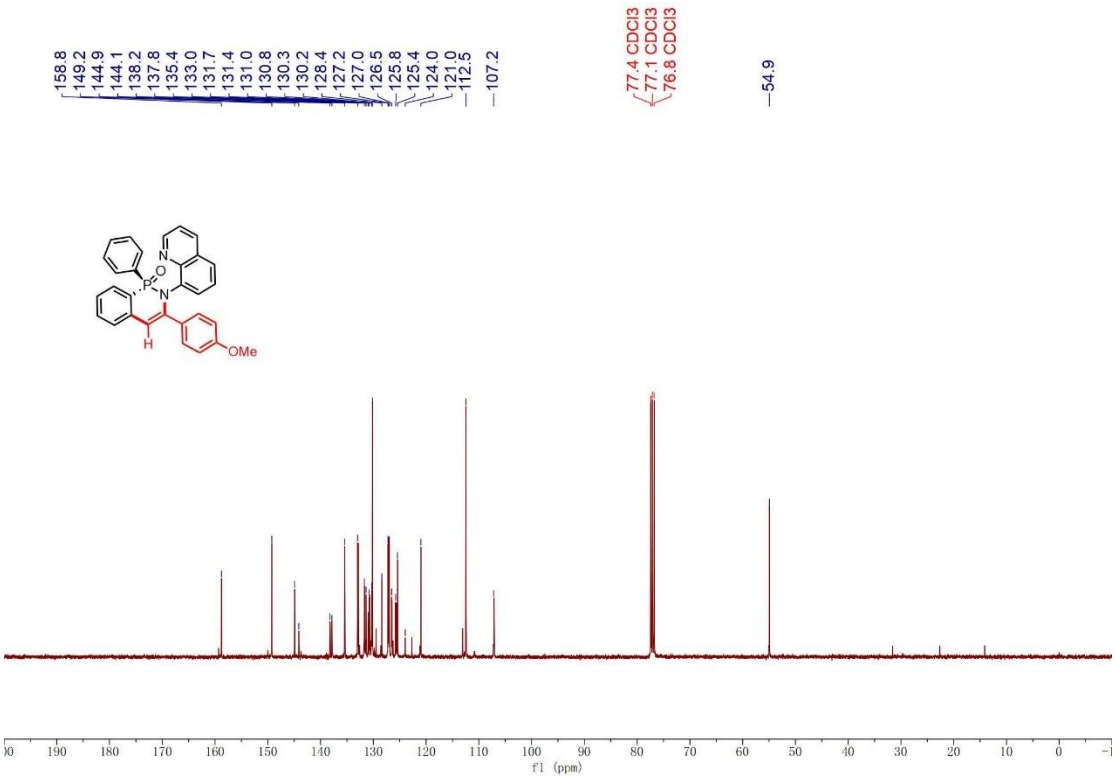
^{31}P-NMR of **3o**



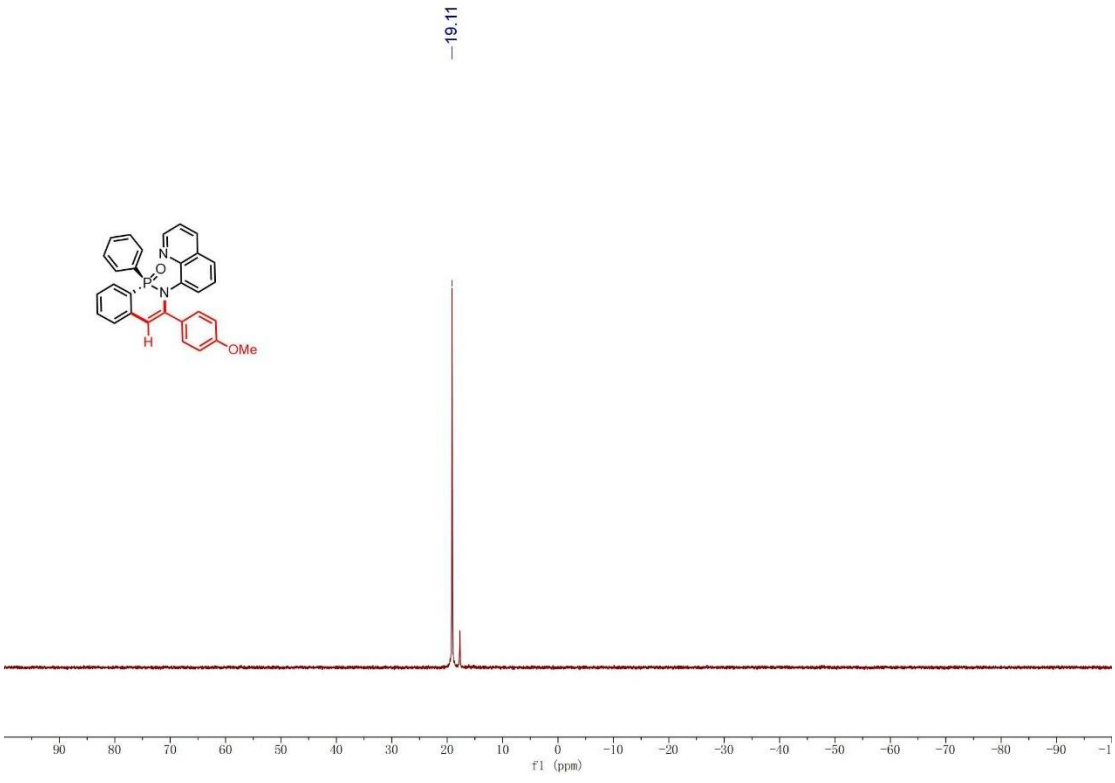
^{1}H-NMR of **3p**



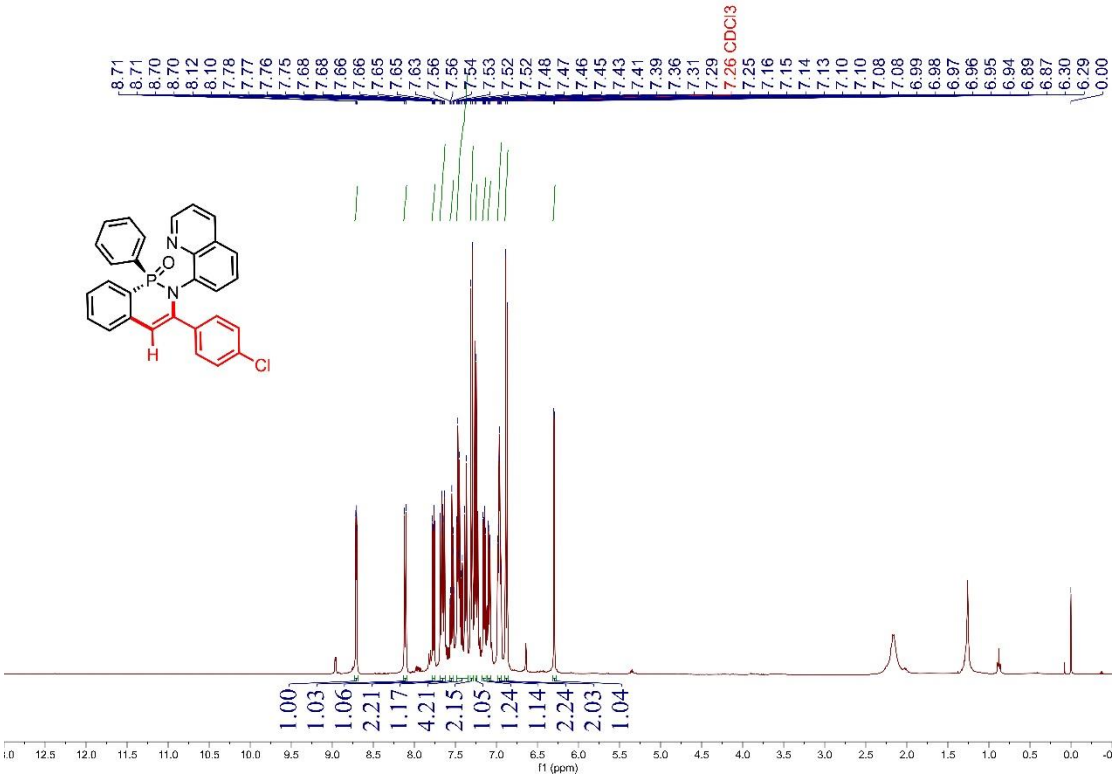
^{13}C-NMR of **3p**



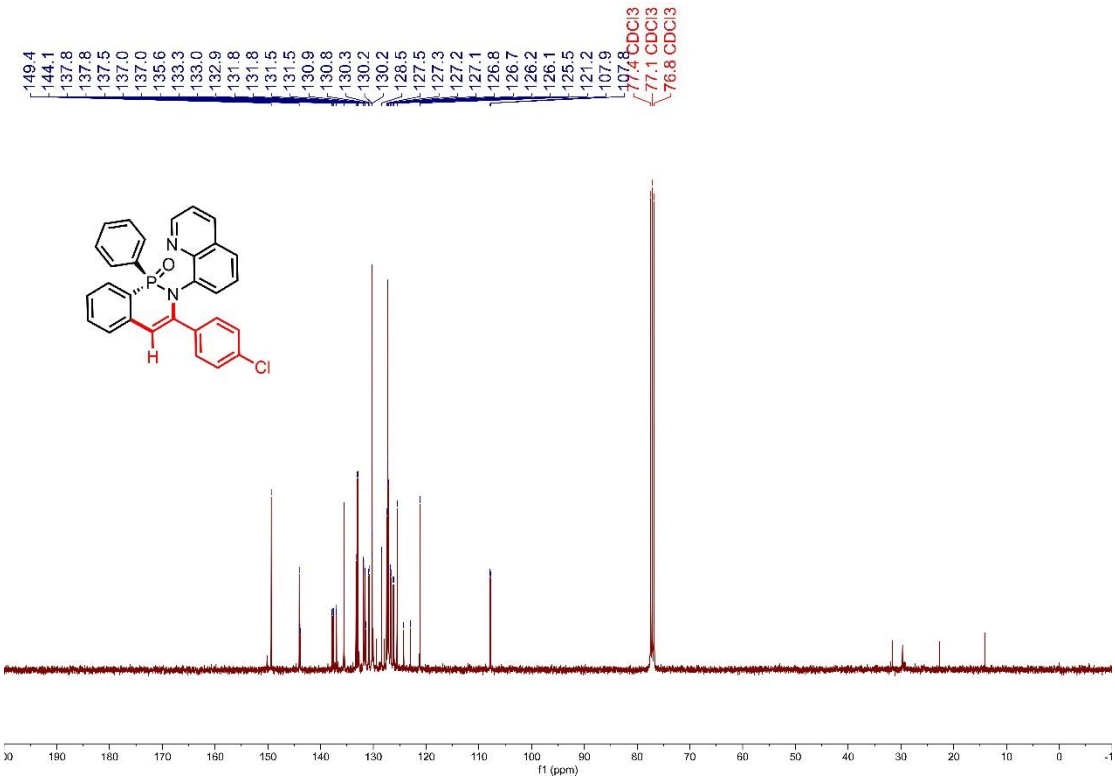
^{31}P-NMR of **3p**



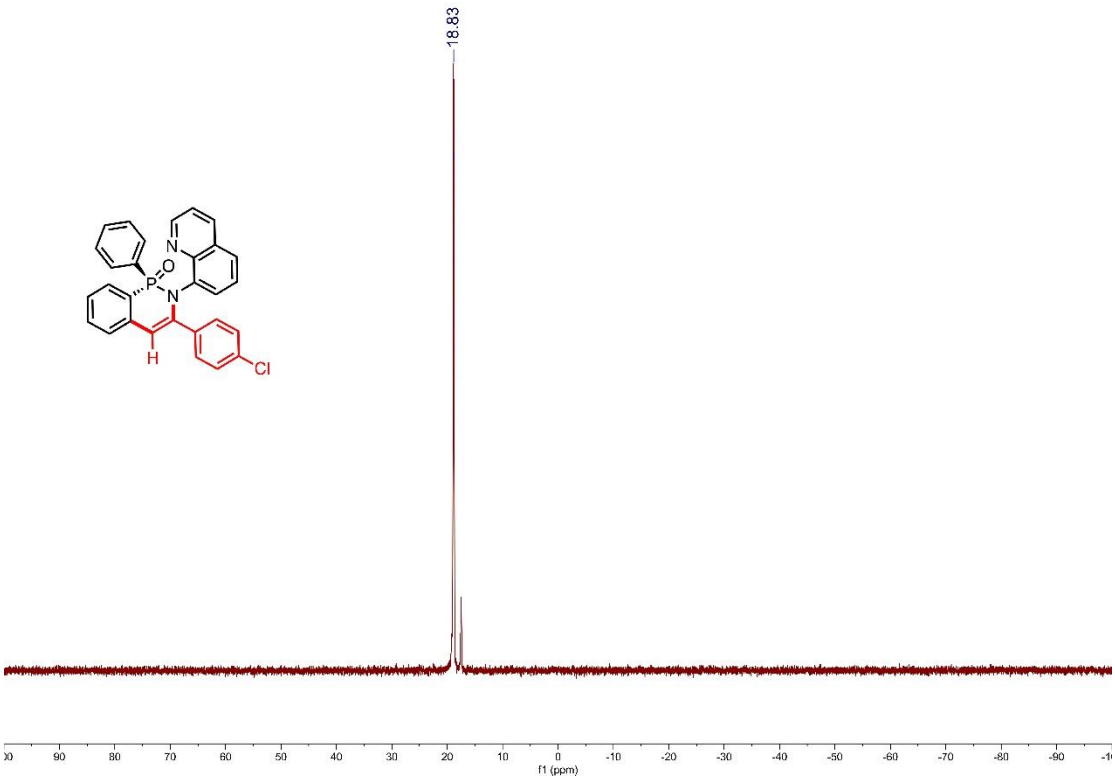
^{1}H-NMR of **3q**



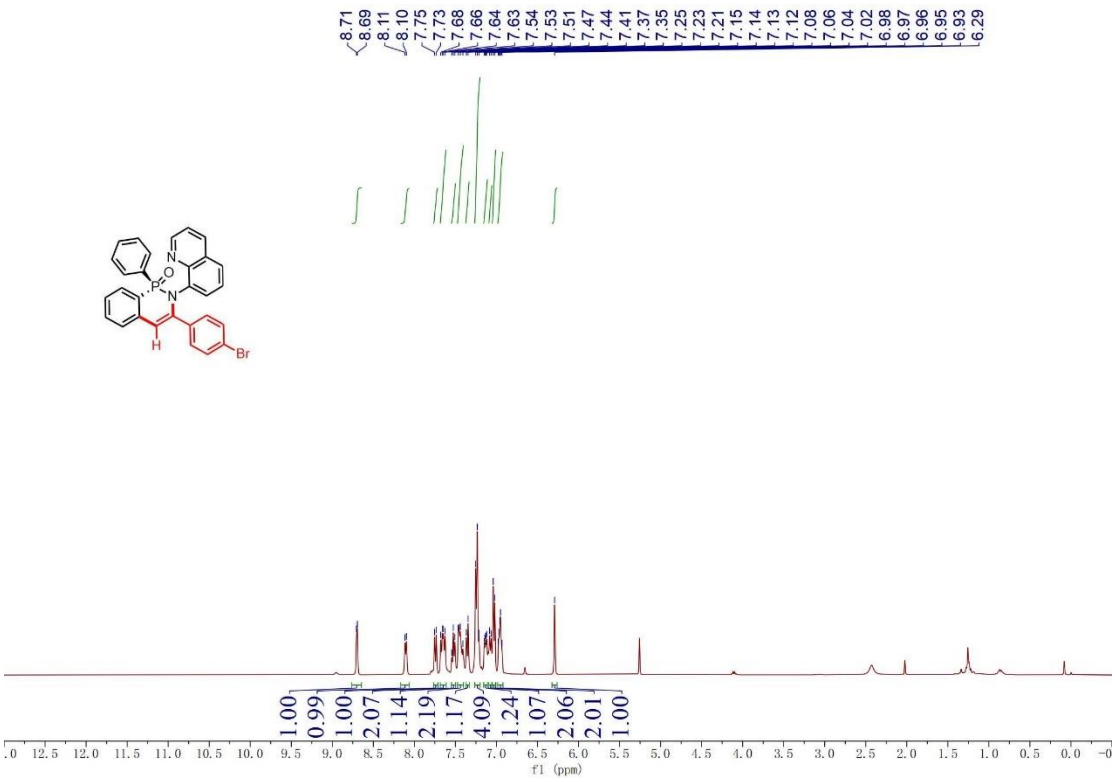
^{13}C-NMR of **3q**



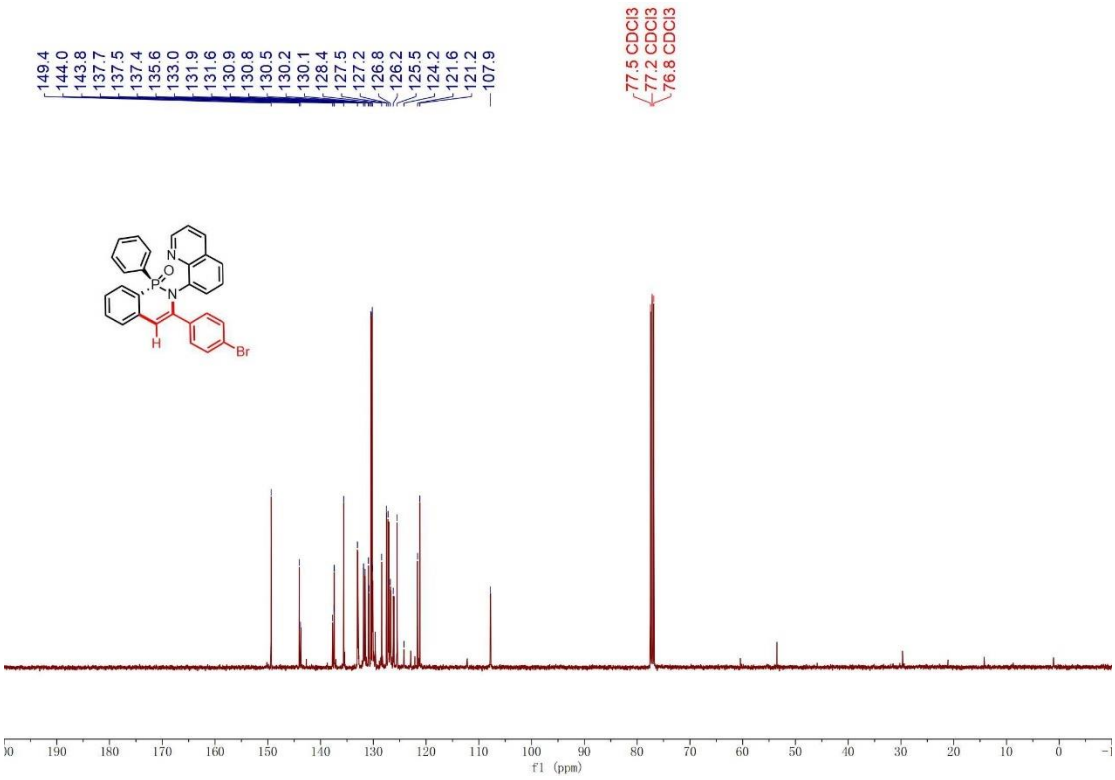
^{31}P-NMR of **3q**



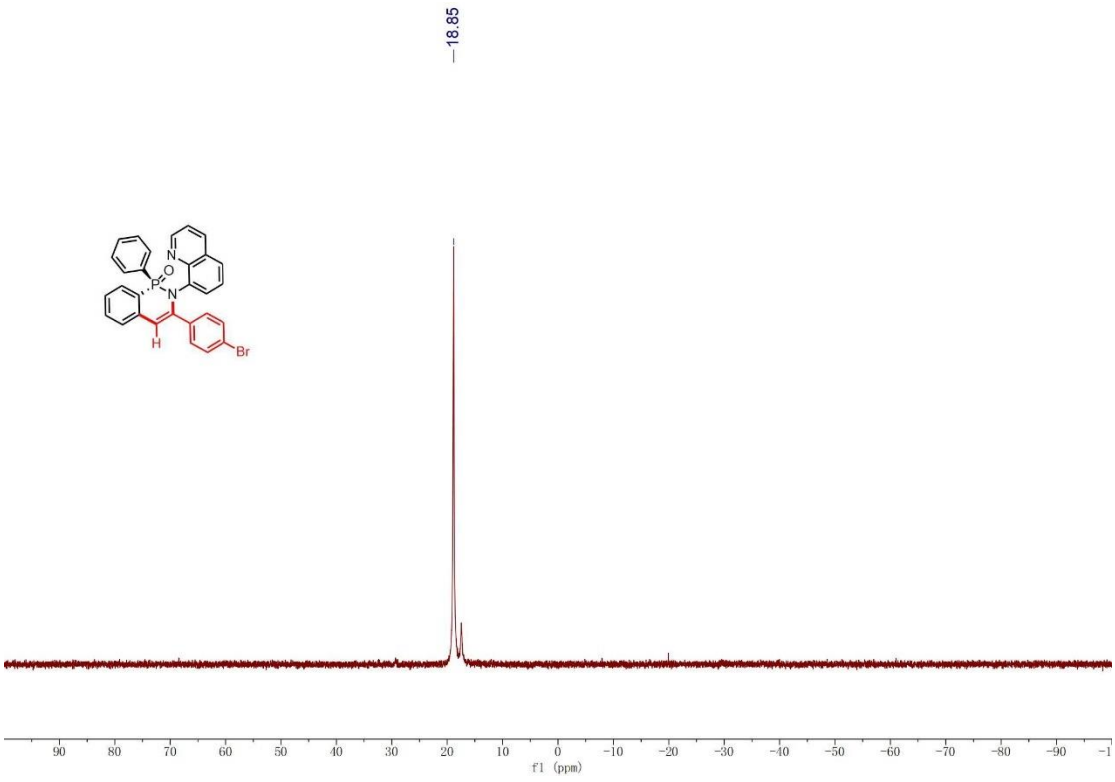
^{1}H-NMR of **3r**



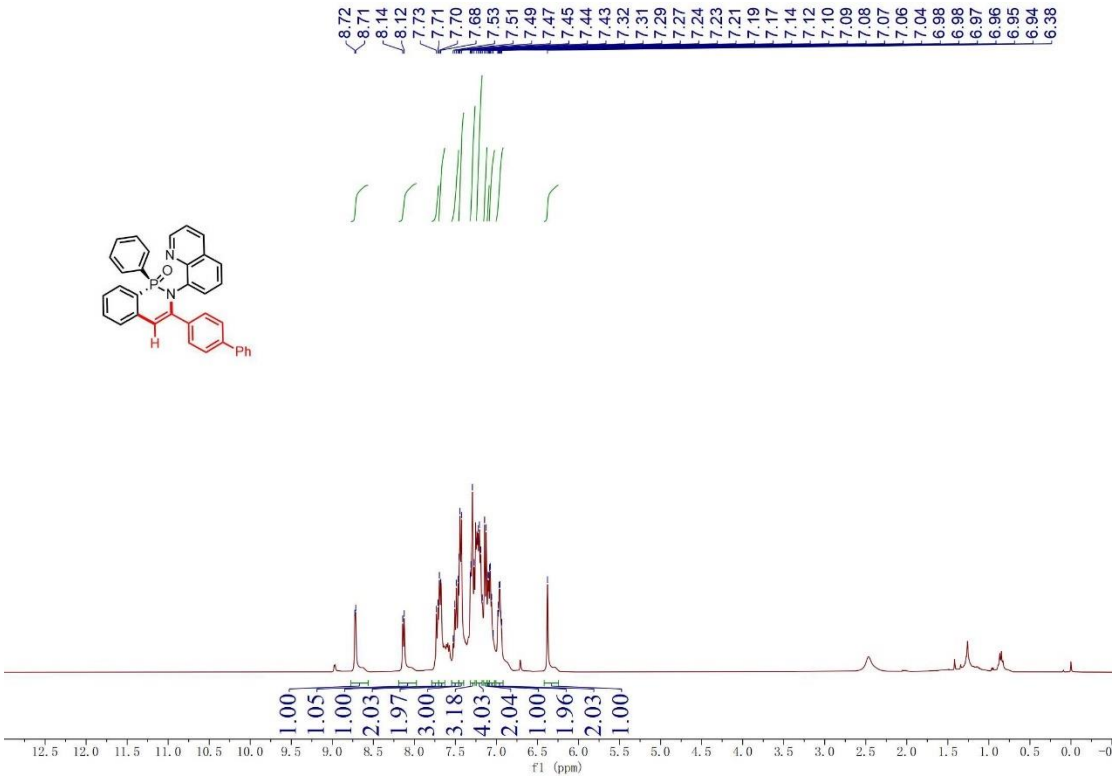
^{13}C-NMR of **3r**



^{31}P-NMR of **3r**



^{1}H-NMR of **3s**



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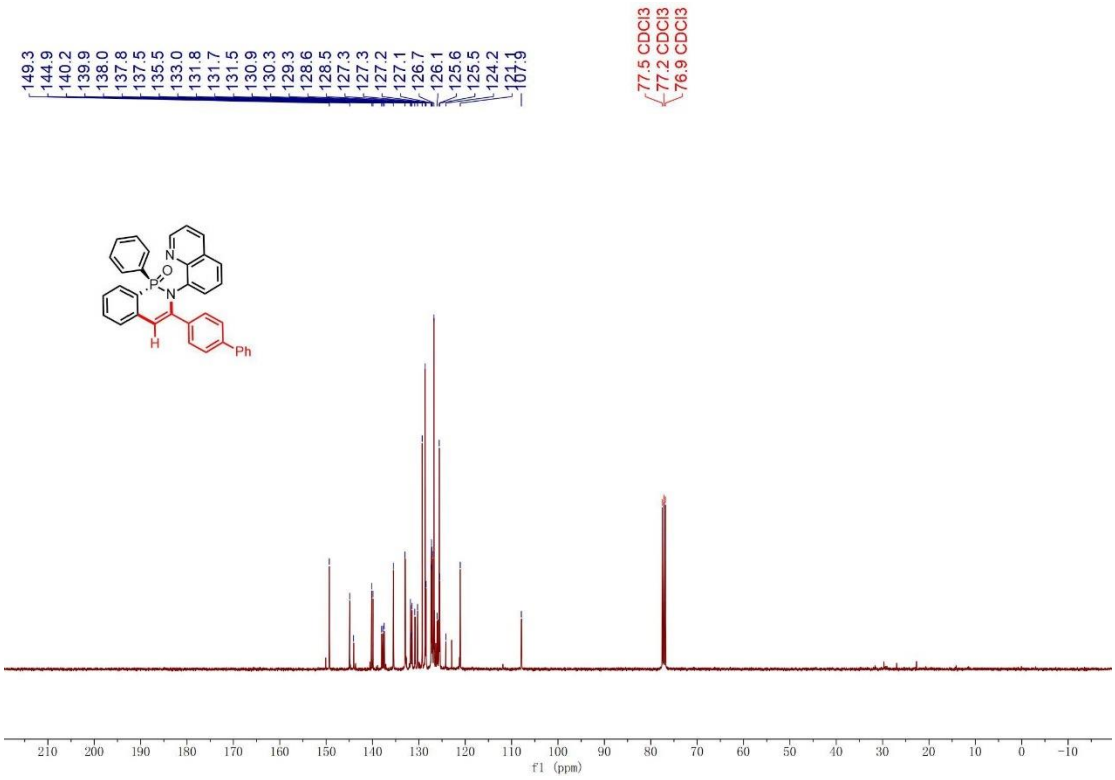

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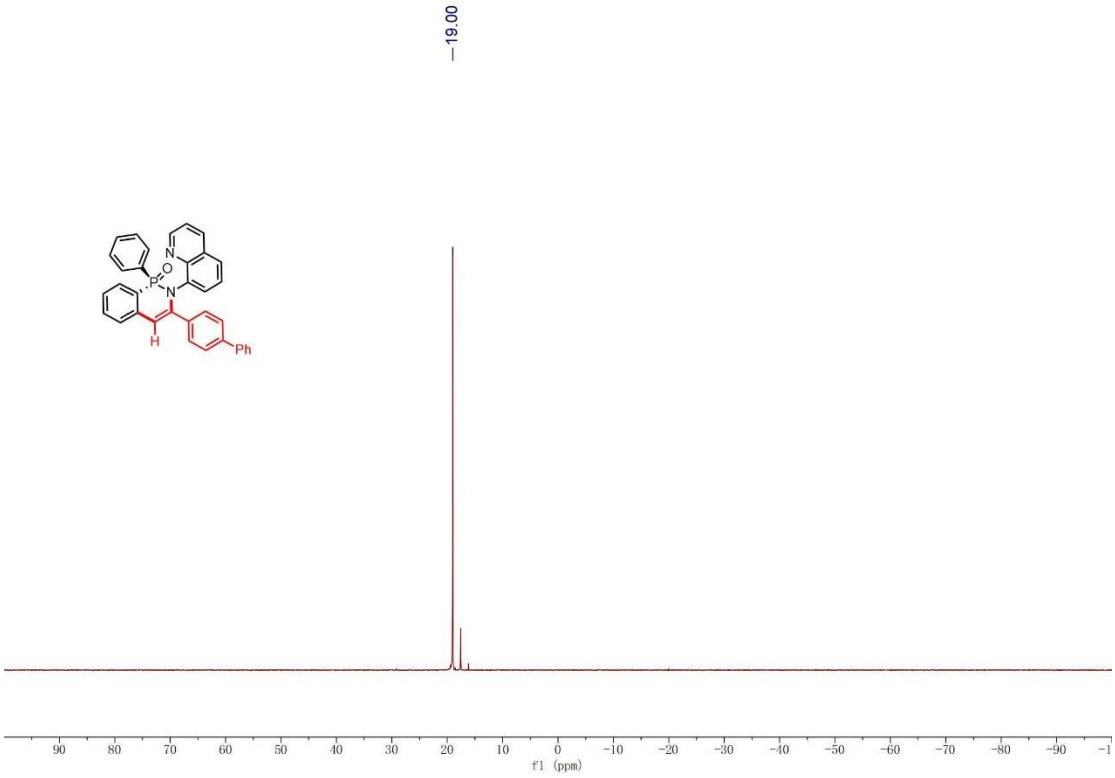
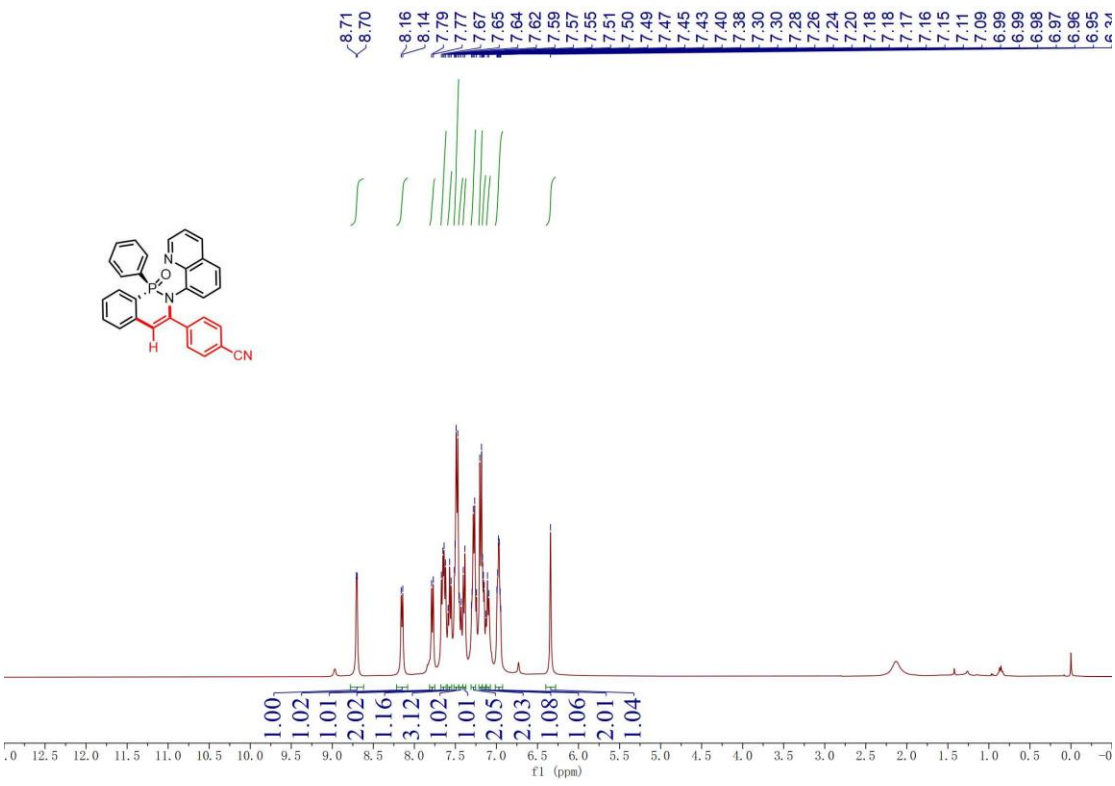
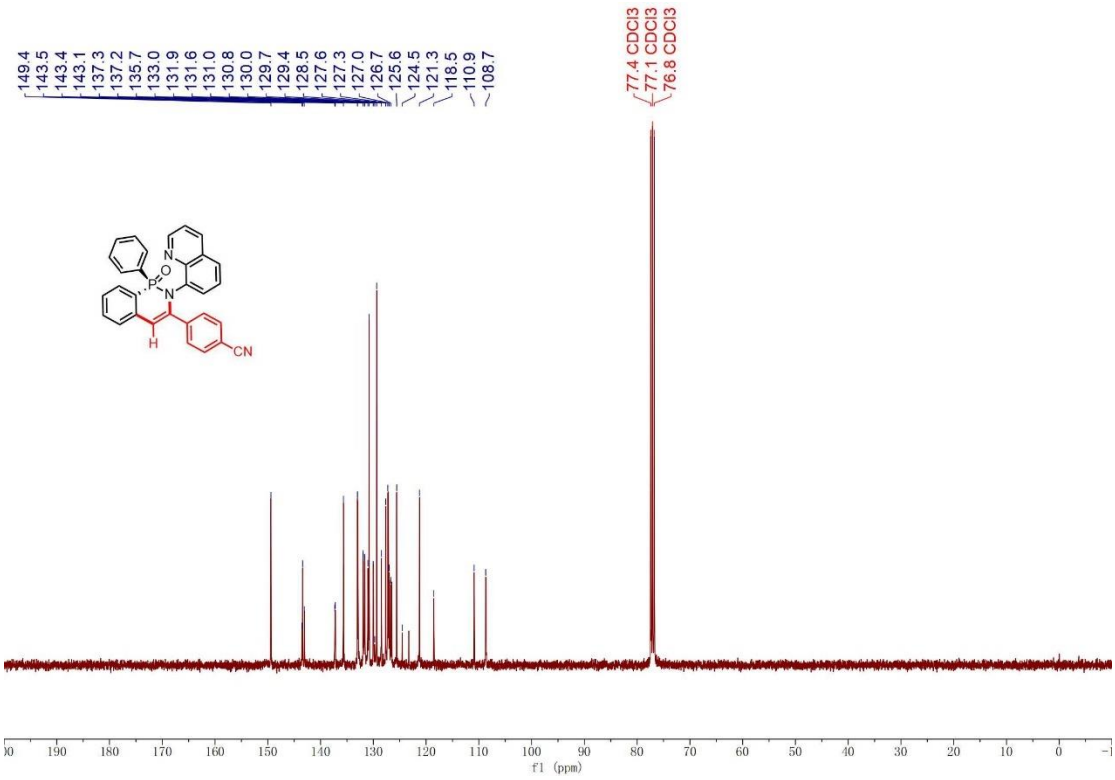


^{1}H-NMR of **3t**



^{13}C-NMR of **3t**



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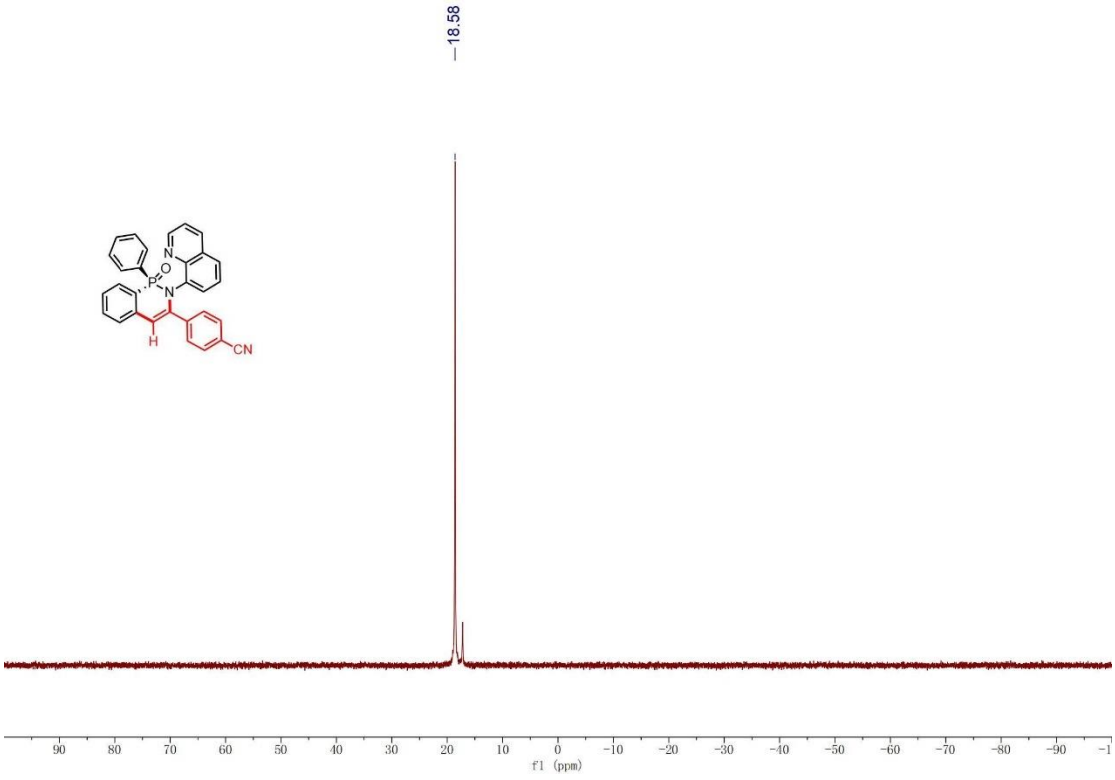
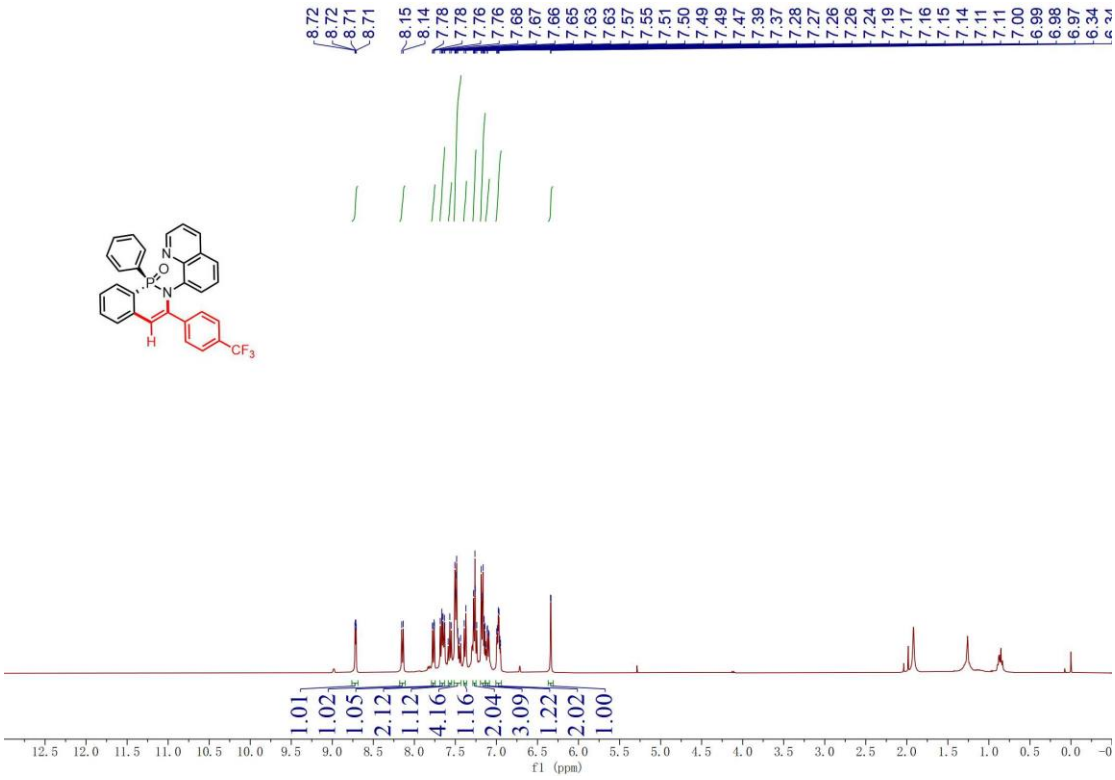
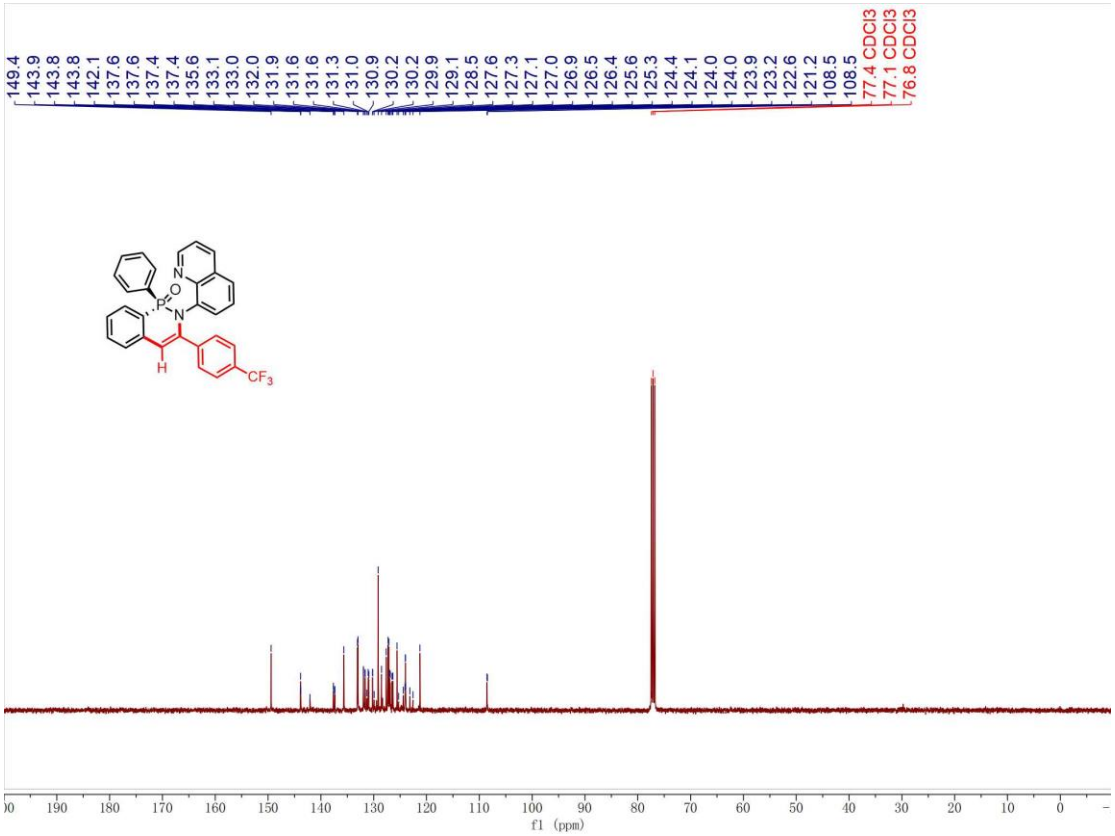


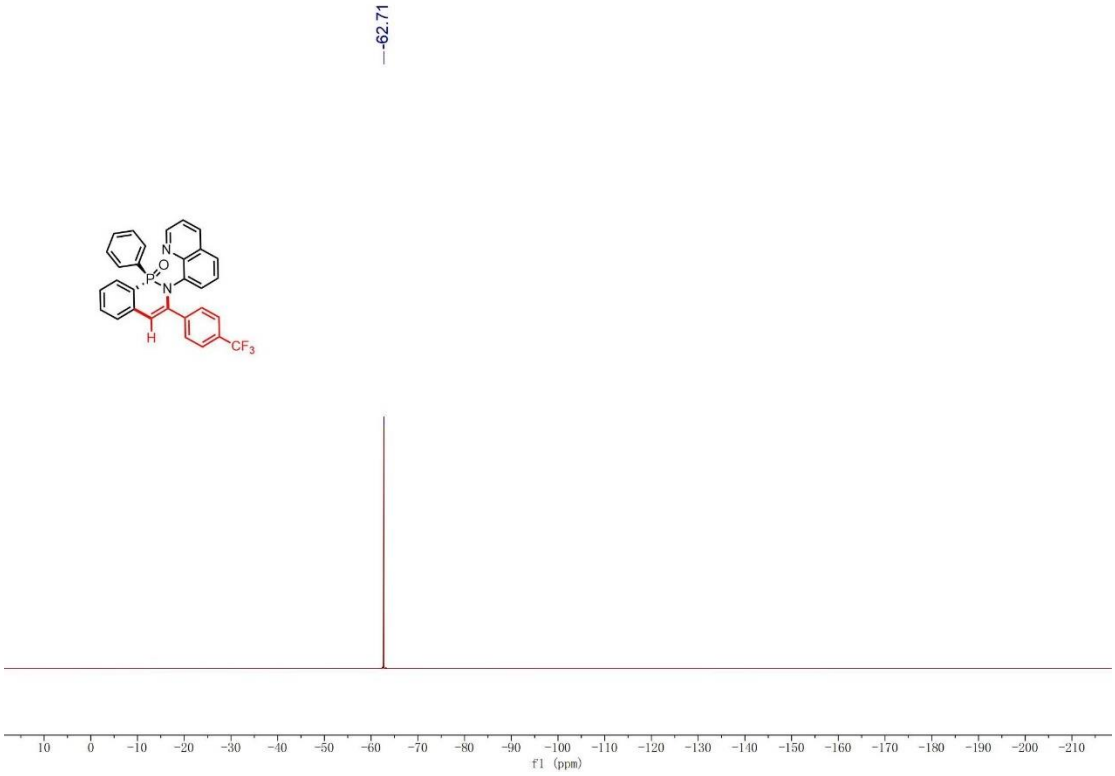
^{1}H-NMR of **3u**



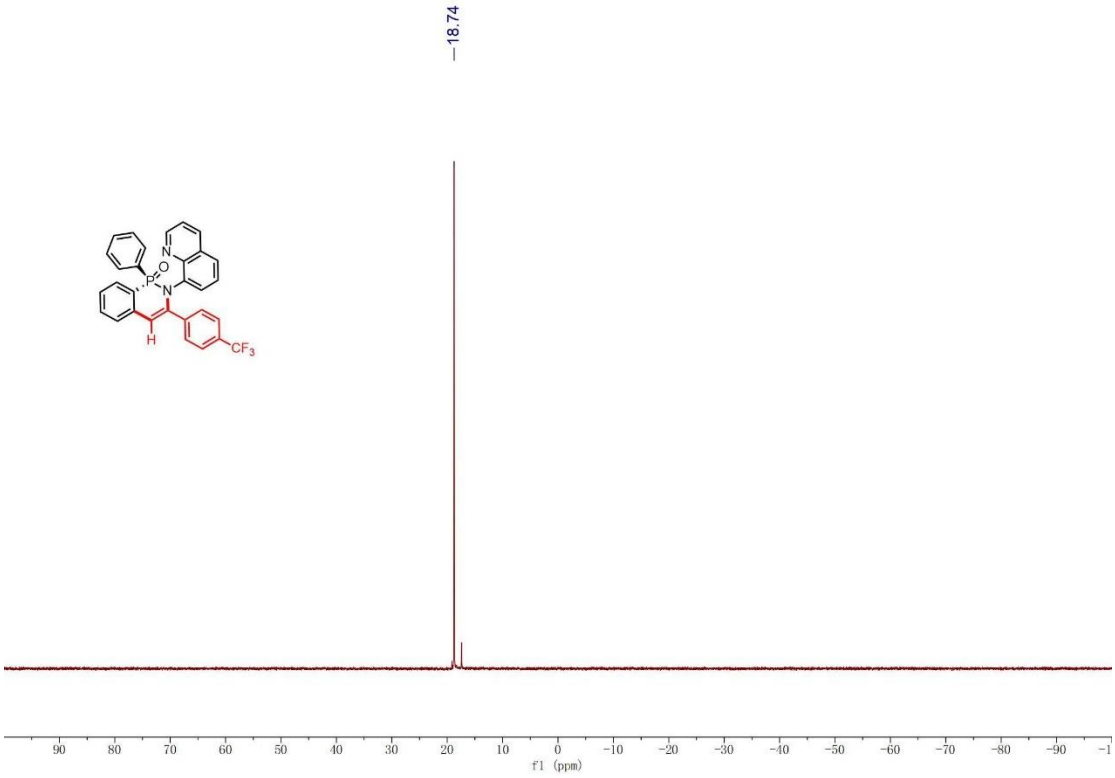
^{13}C-NMR of **3u**



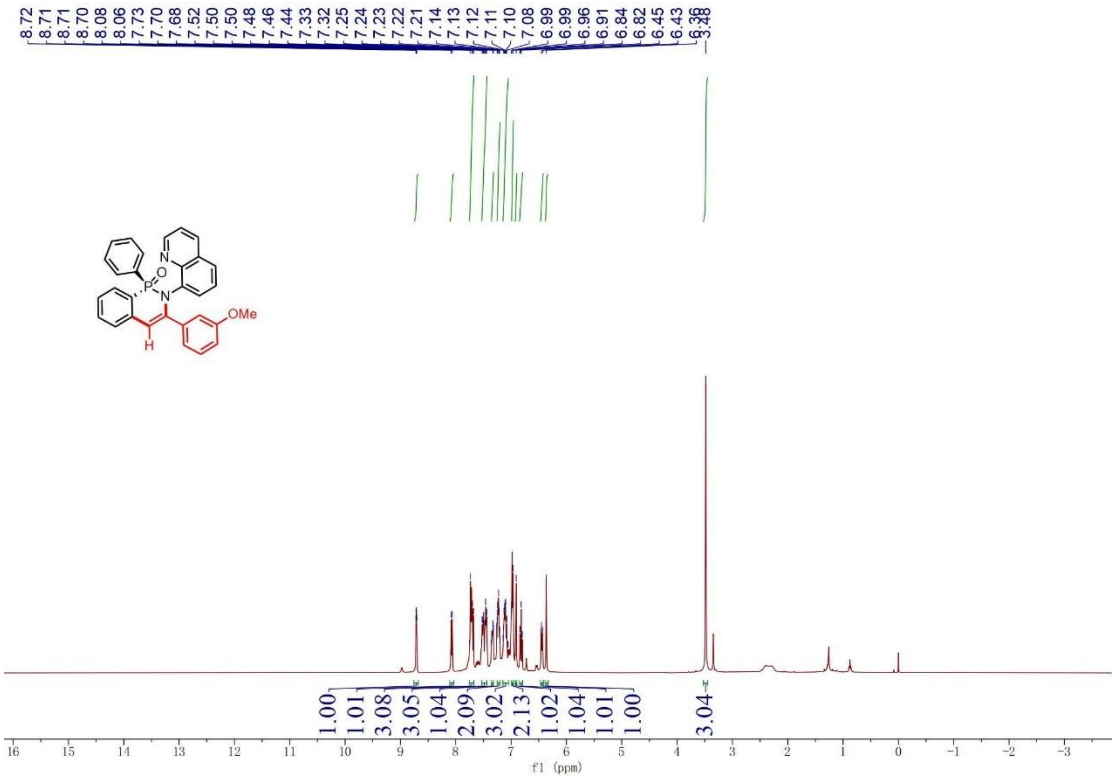
^{19}F-NMR of **3u**



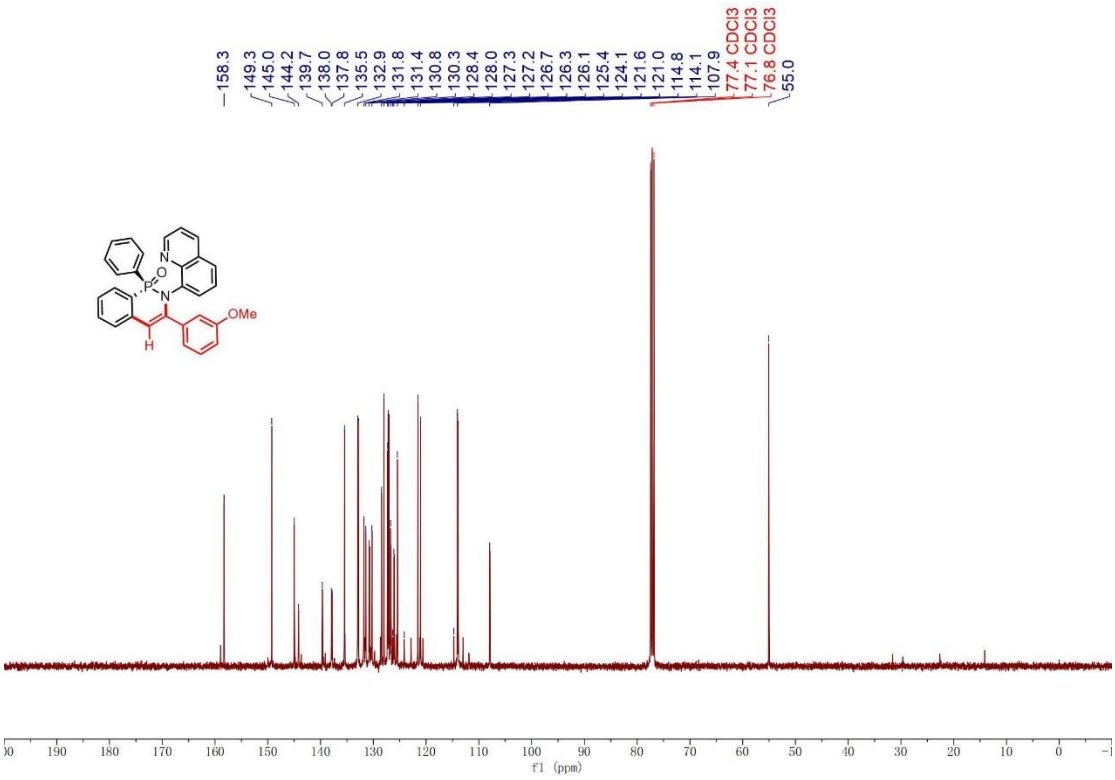
^{31}P-NMR of **3u**



^{1}H-NMR of **3v**



^{13}C-NMR of **3v**



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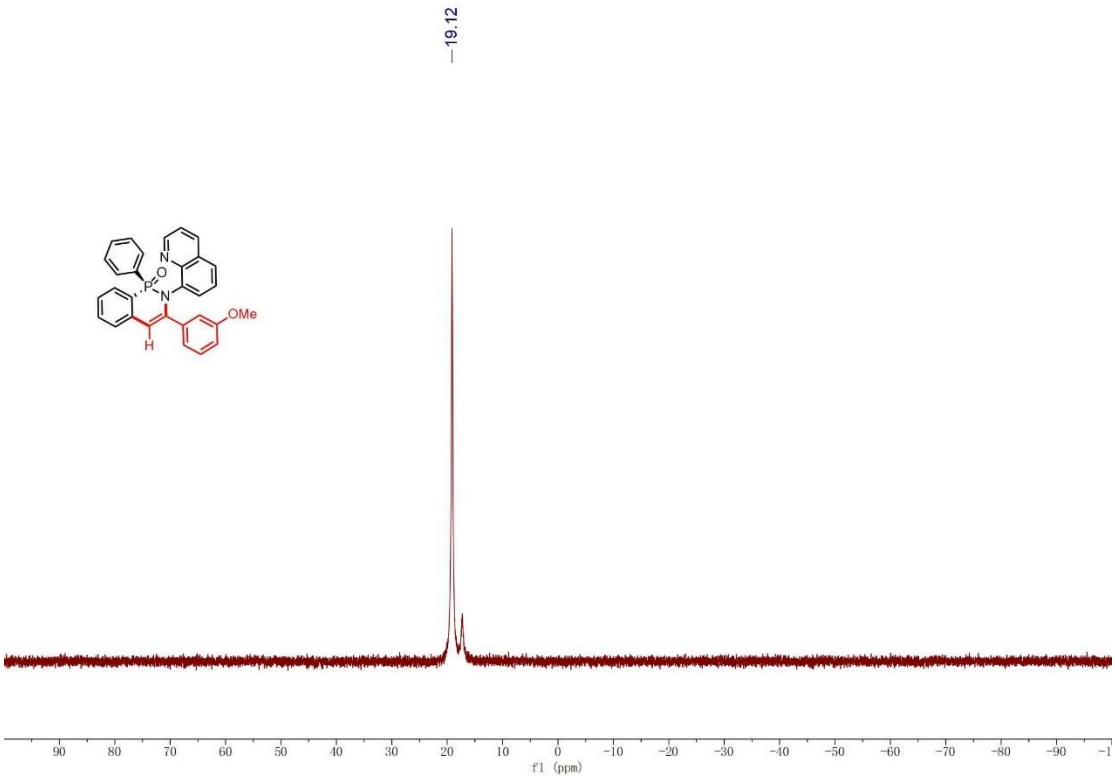
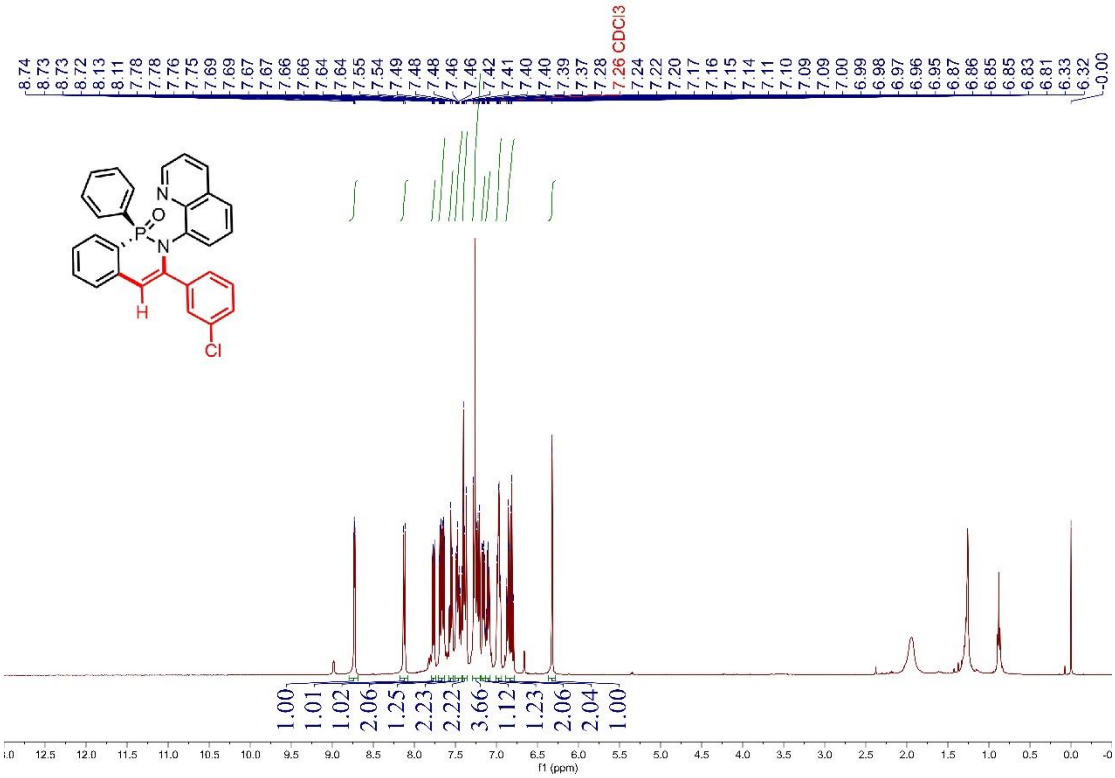
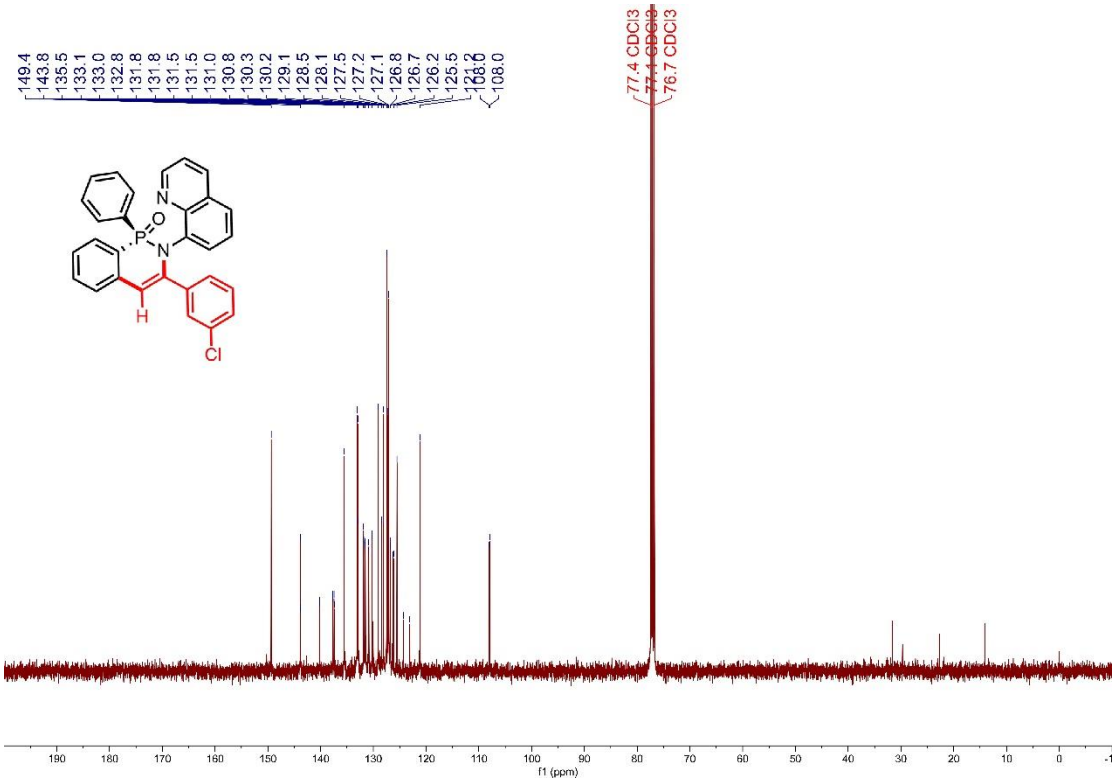


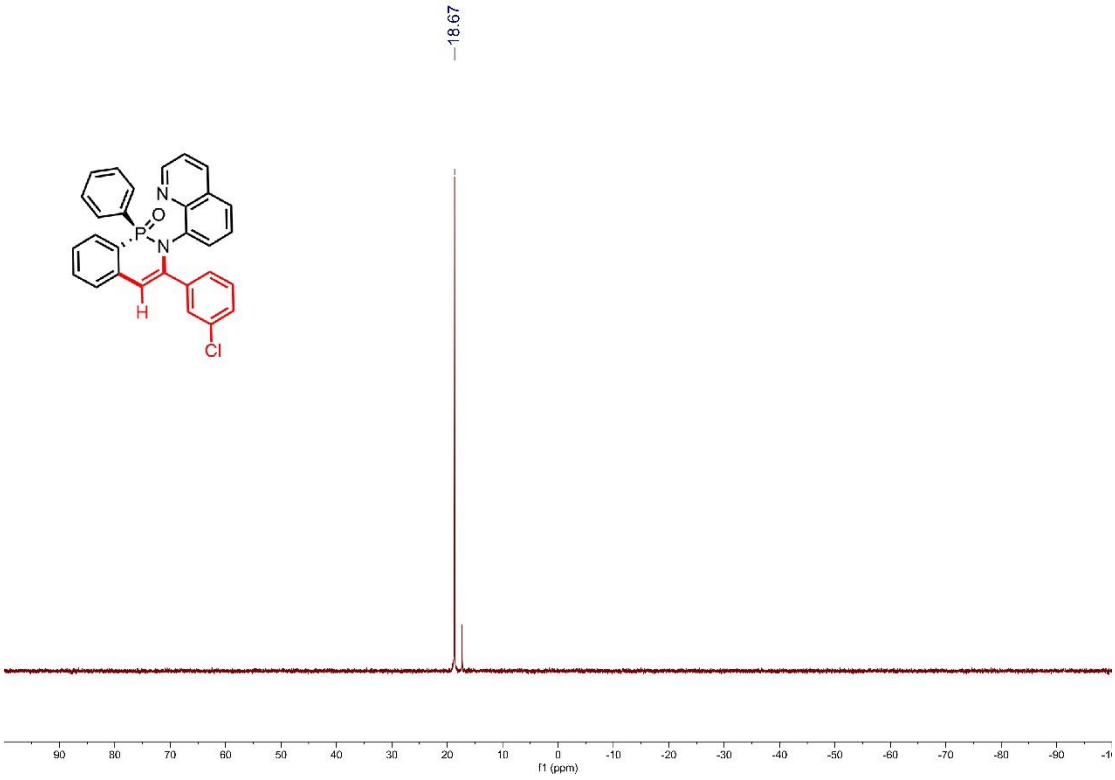
^{1}H-NMR of **3w**



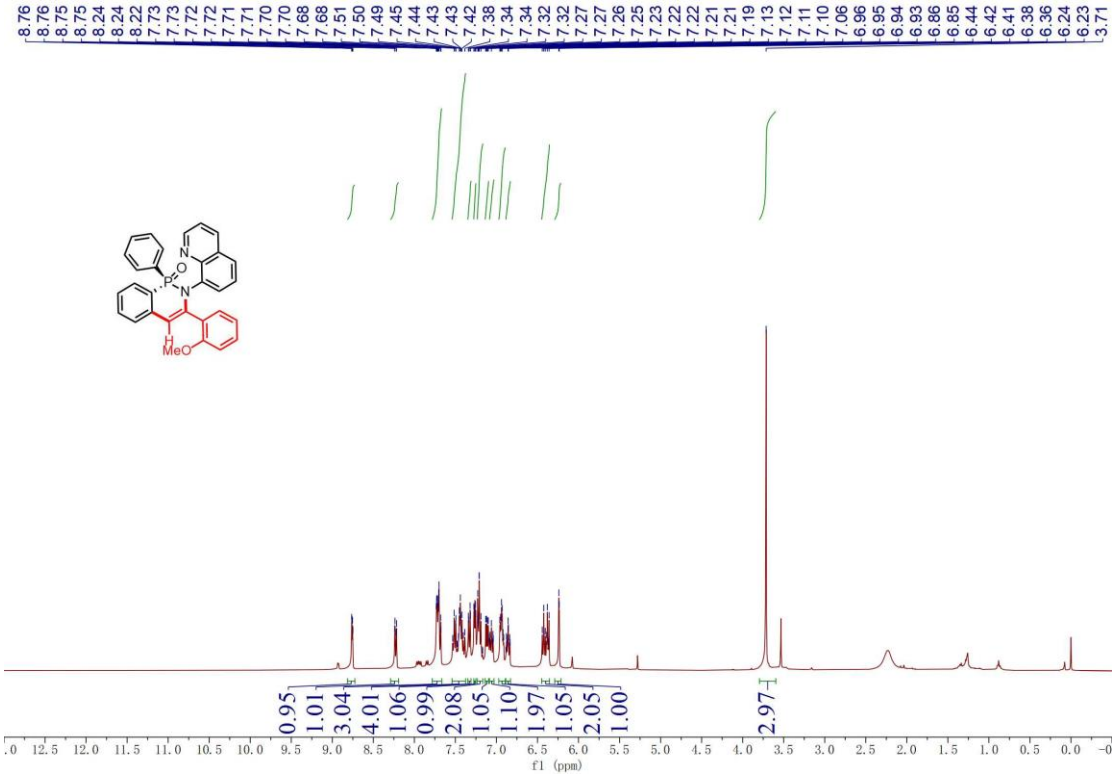
^{13}C-NMR of **3w**



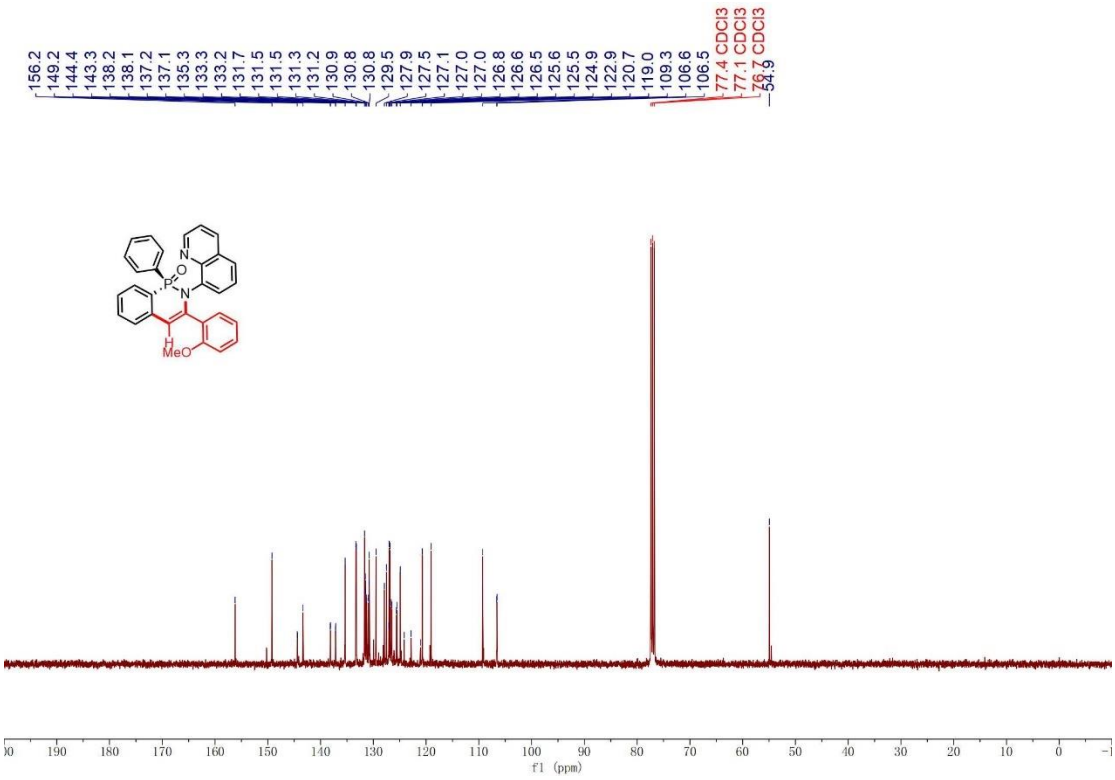
^{31}P-NMR of **3w**



^{1}H-NMR of **3x**



^{13}C-NMR of **3x**



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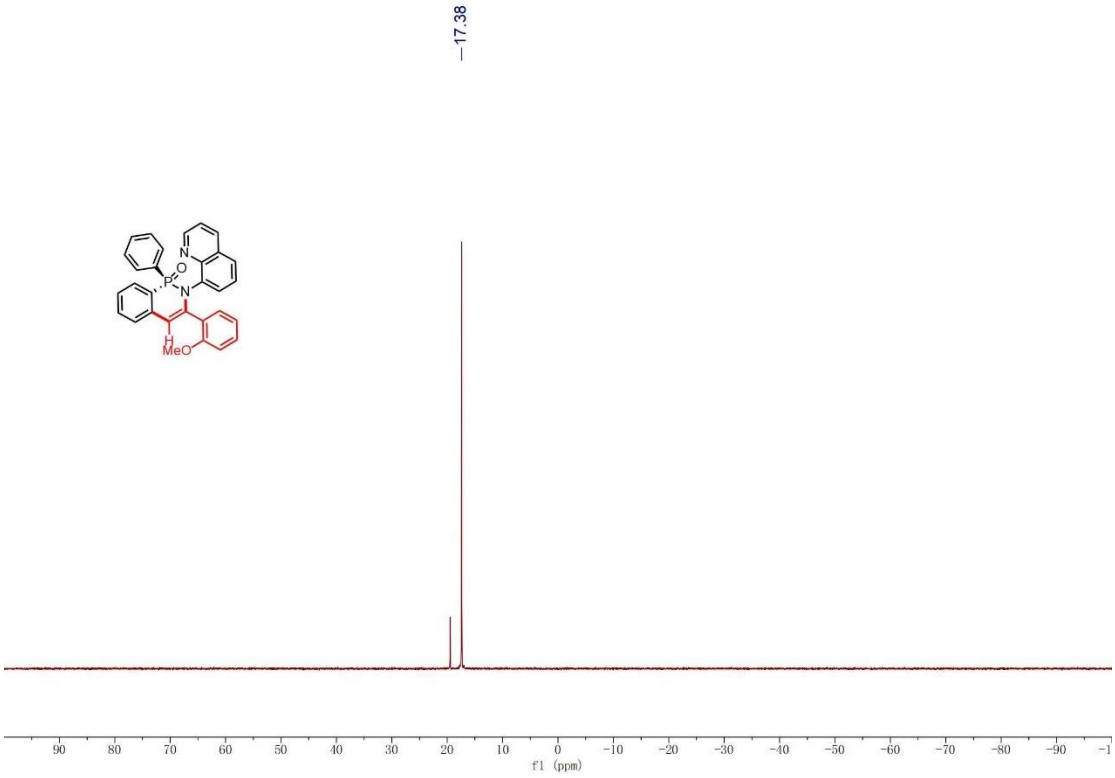
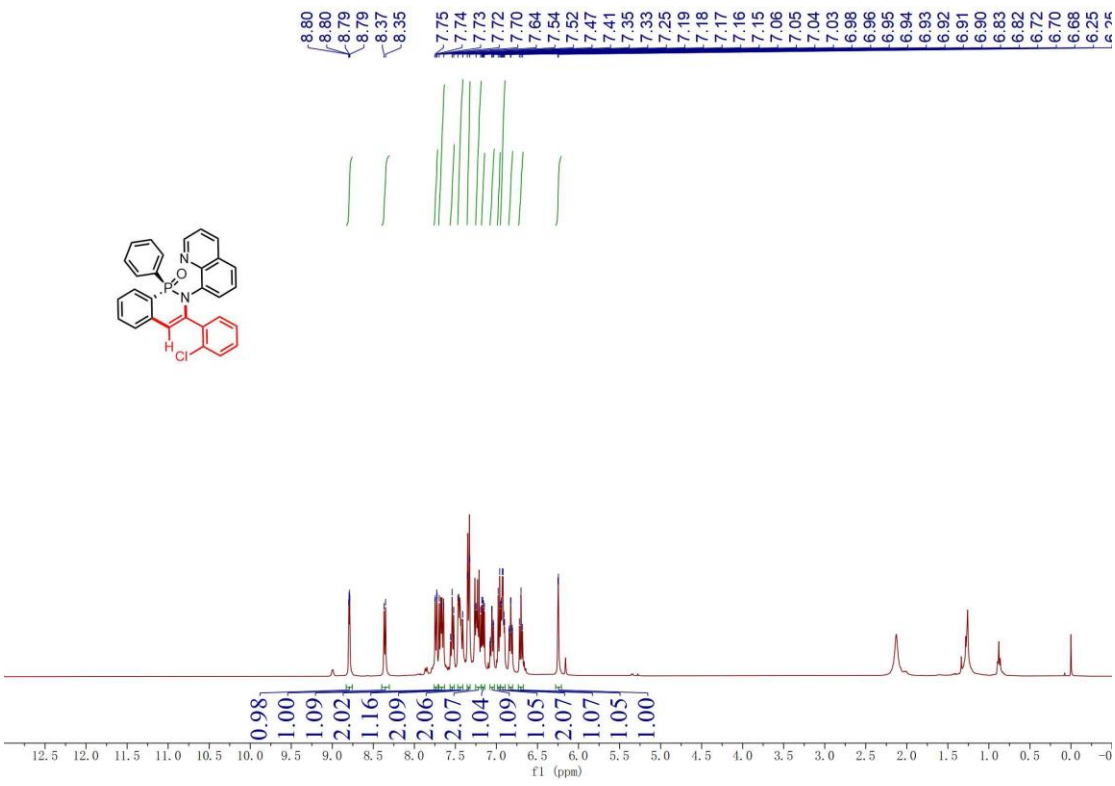


^{1}H-NMR of **3y**



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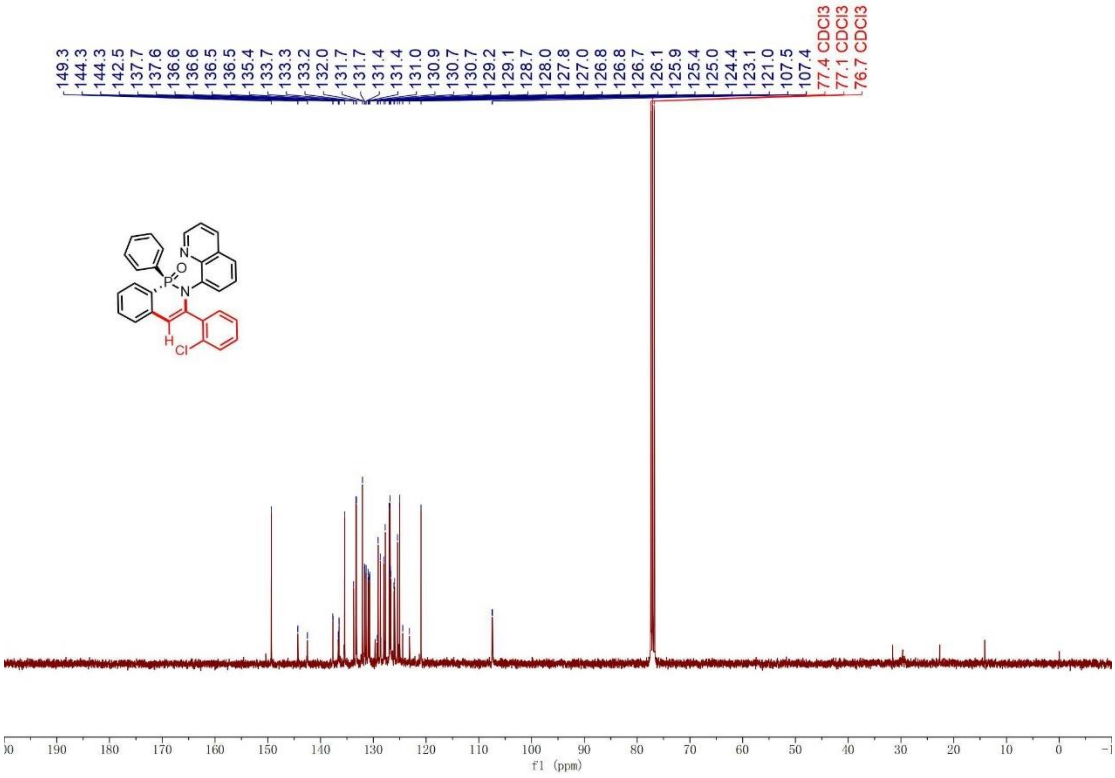
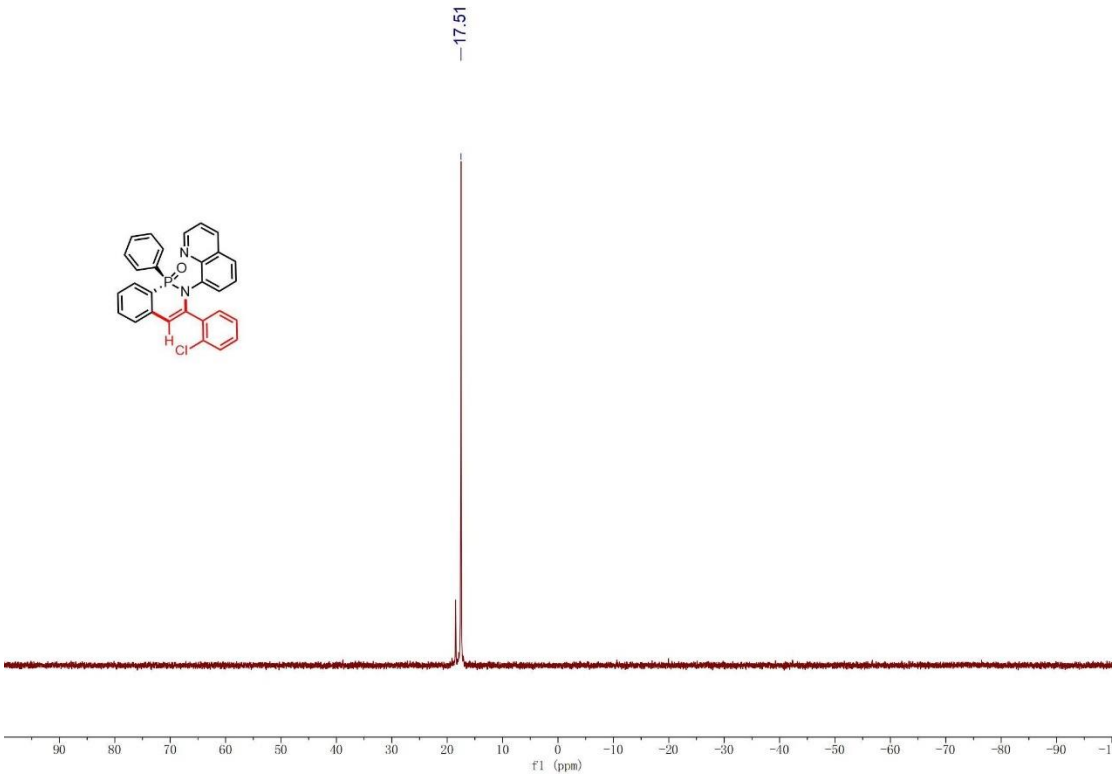
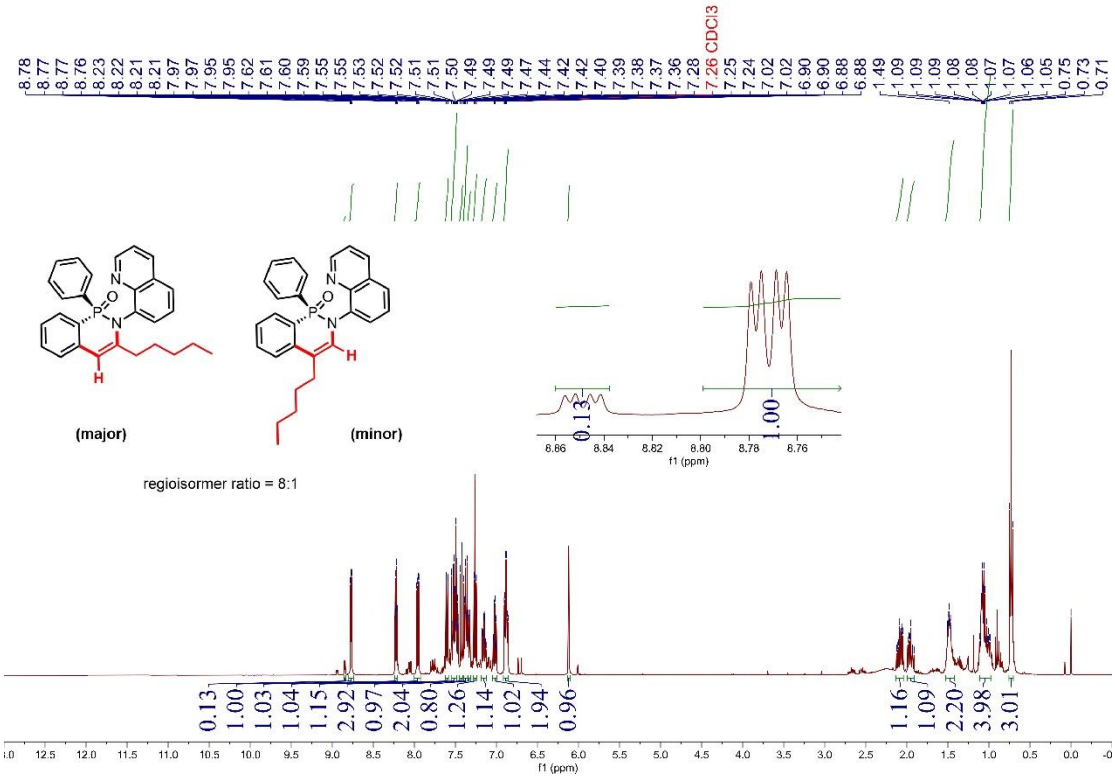


^{31}P-NMR of **3y**



^{1}H-NMR of **3z**



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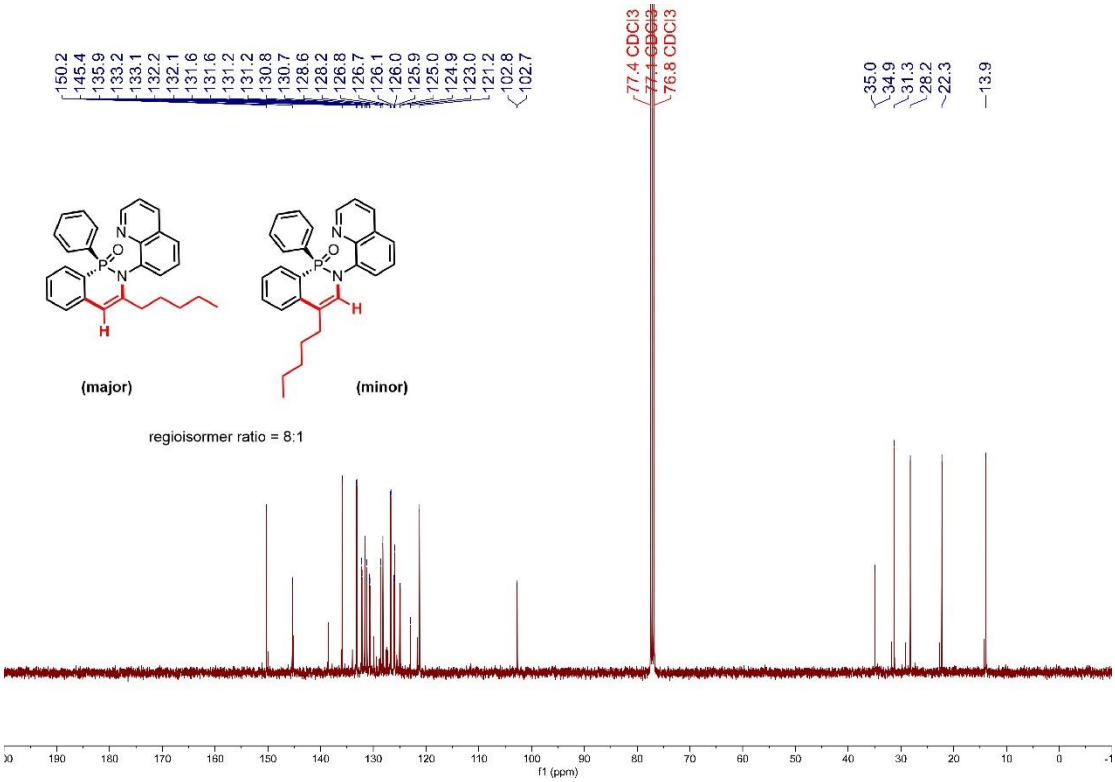

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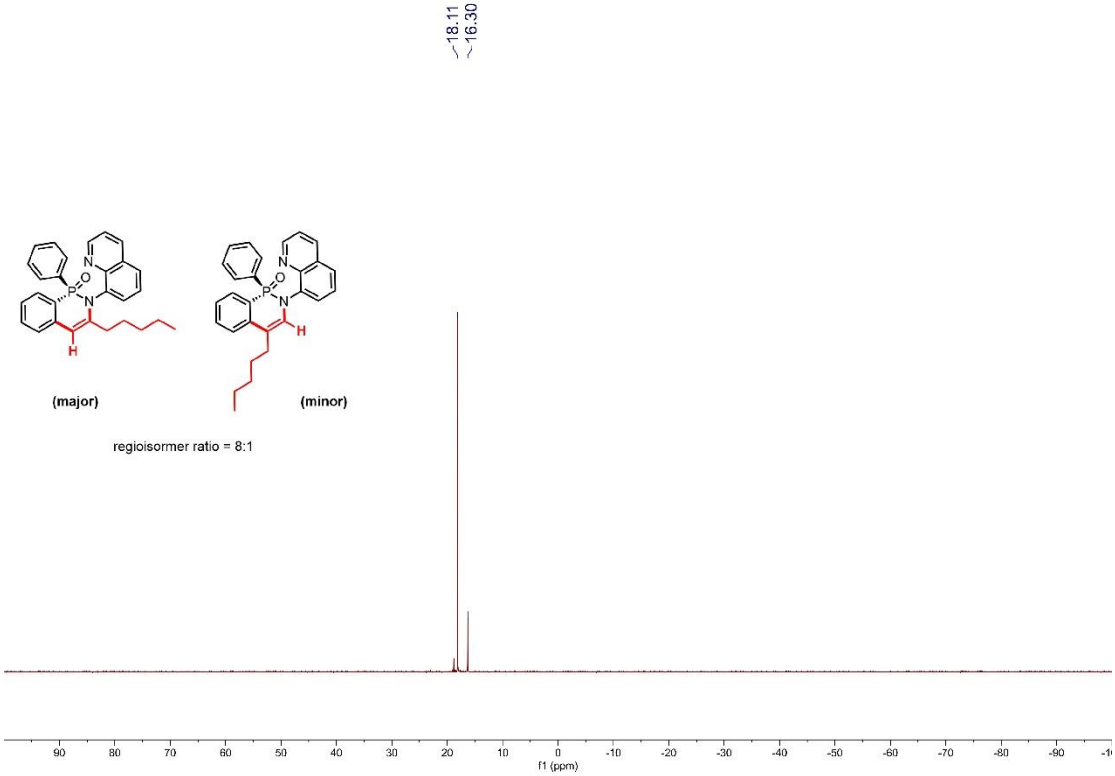
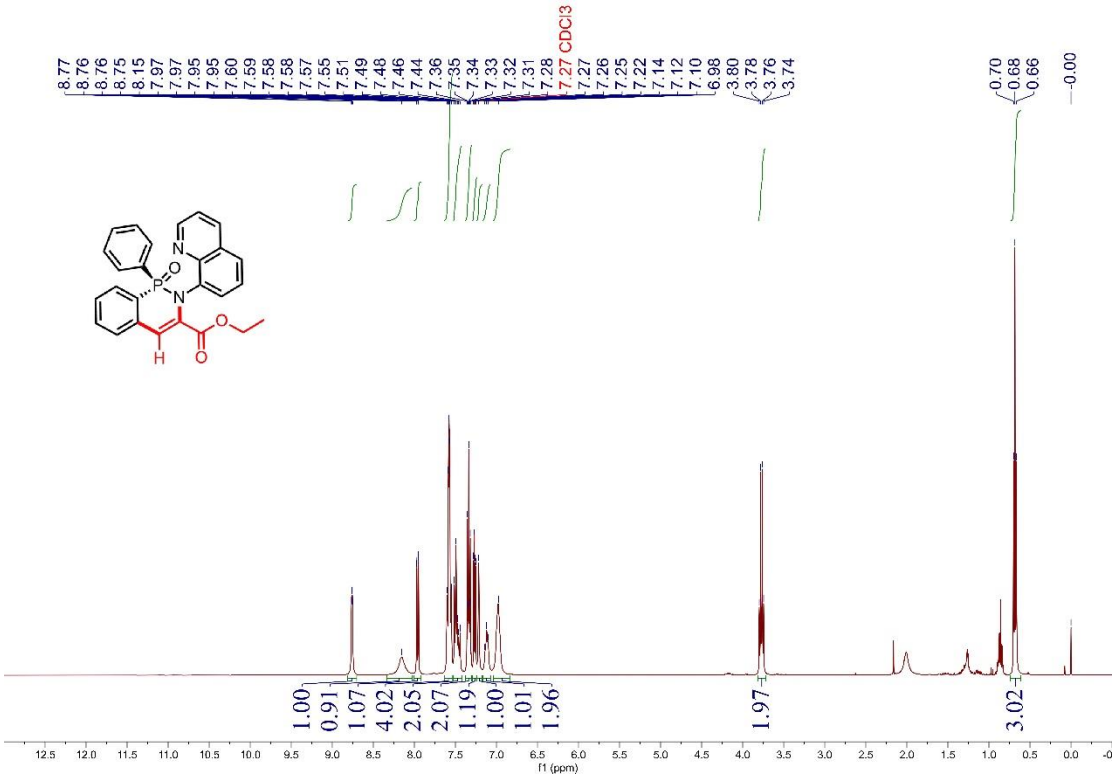


^{1}H-NMR of **3aa**



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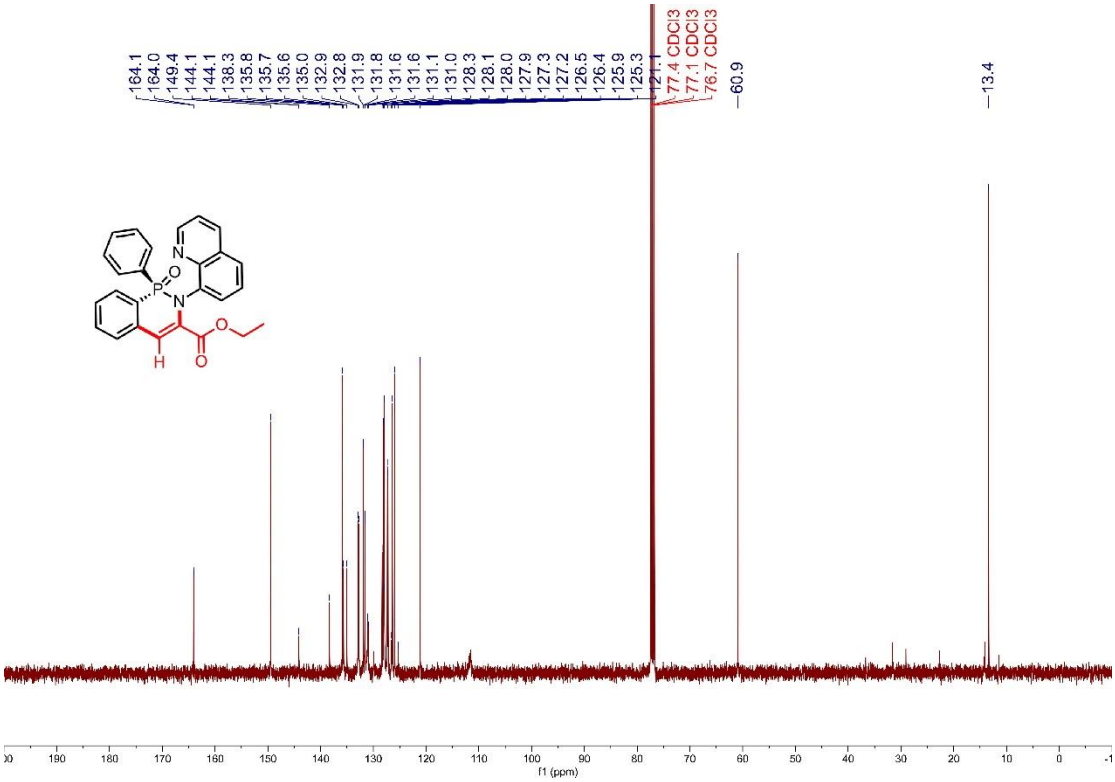
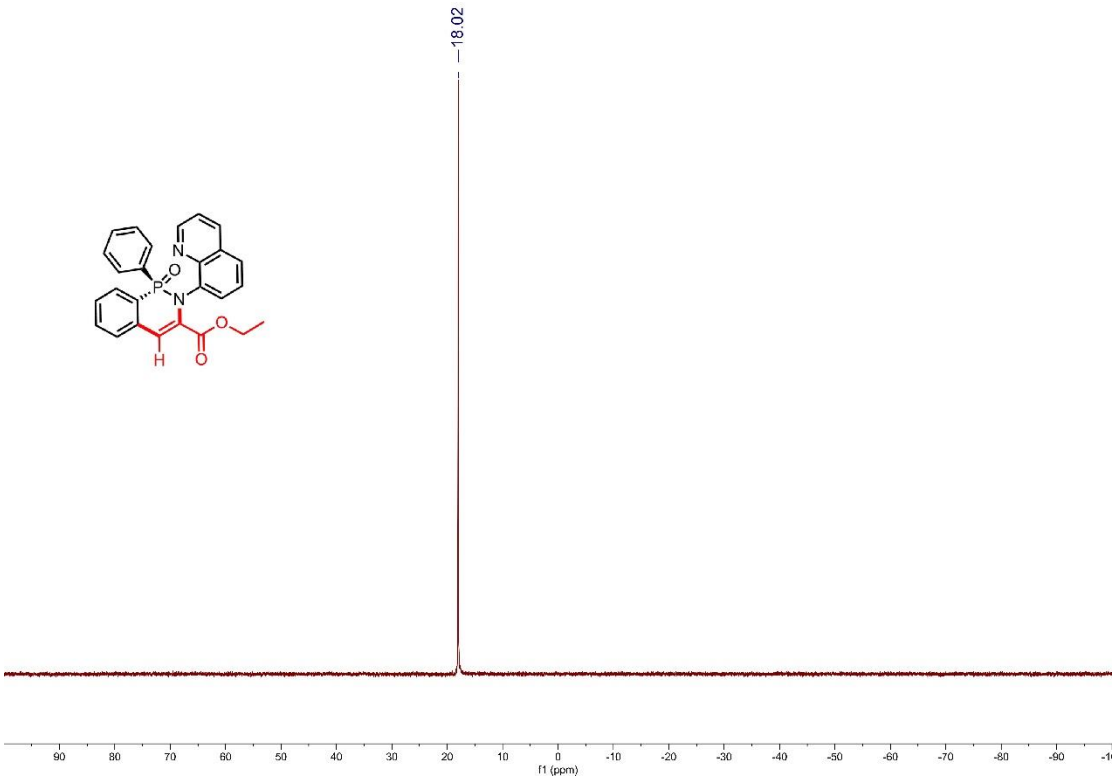
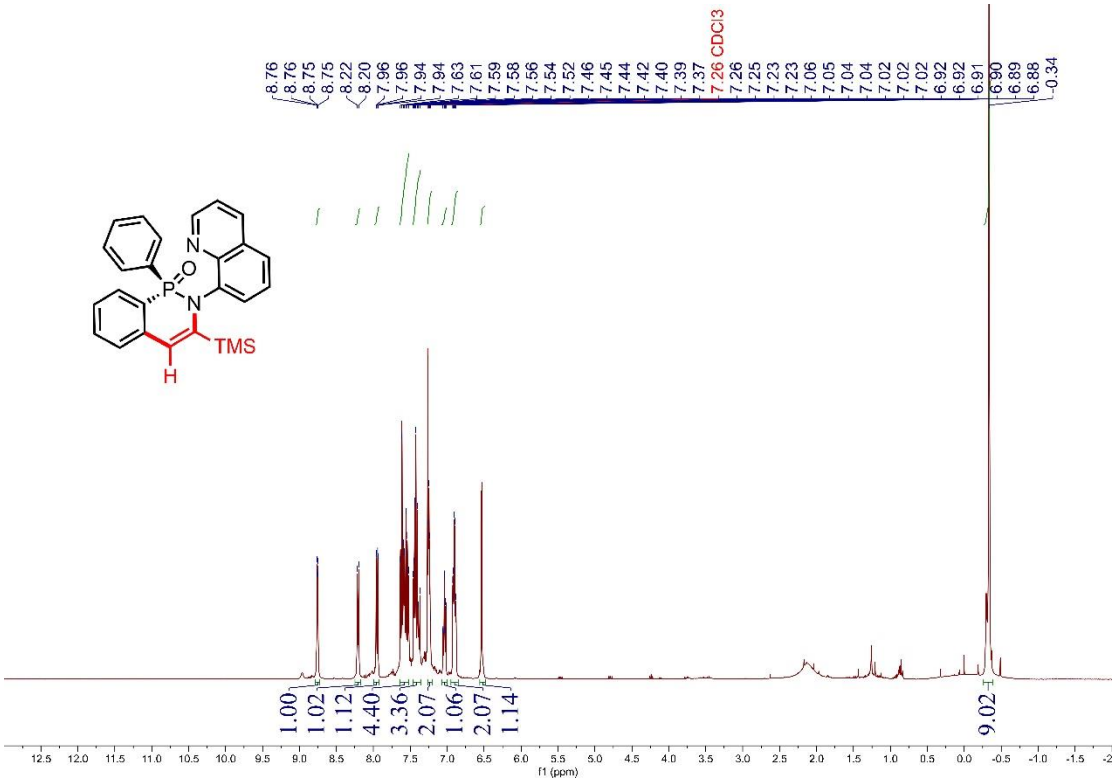


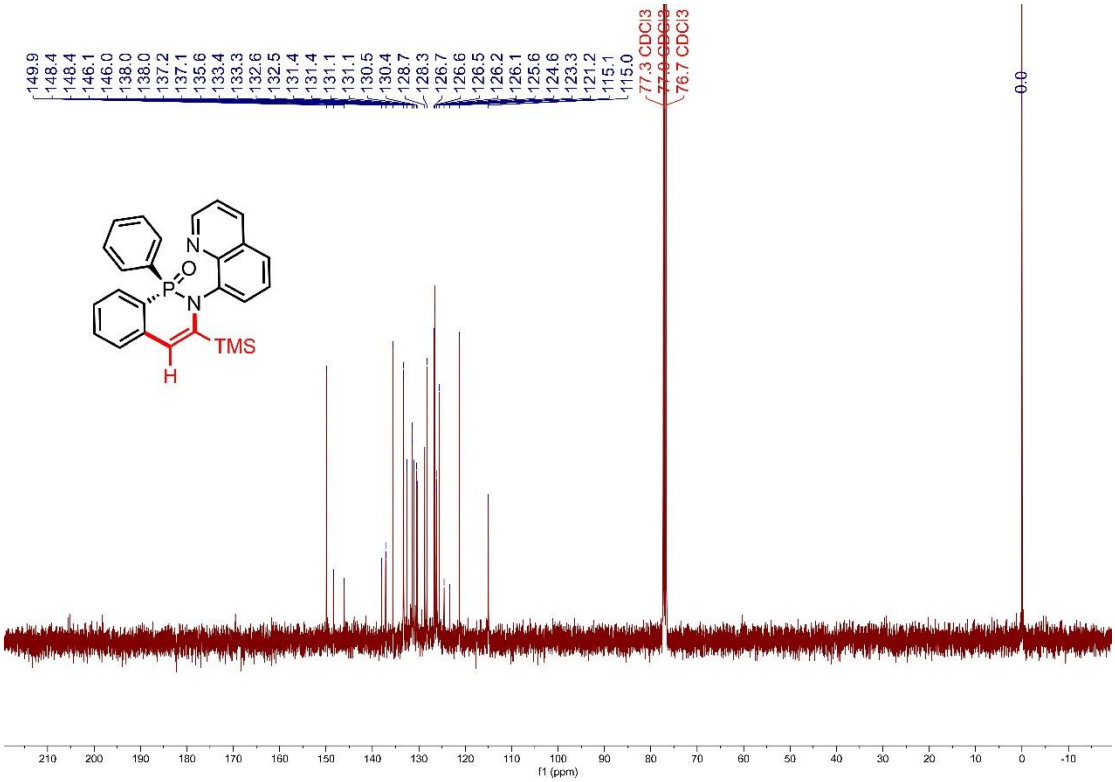
^{31}P-NMR of **3aa**



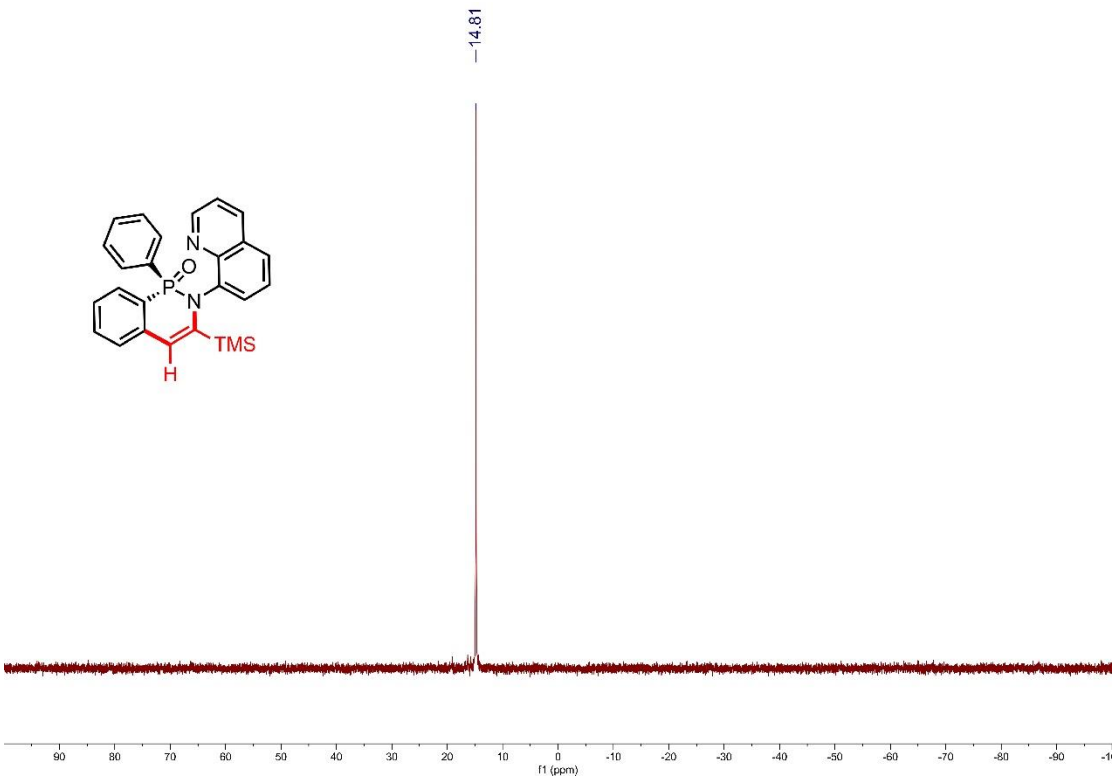
^{1}H-NMR of **3ab**



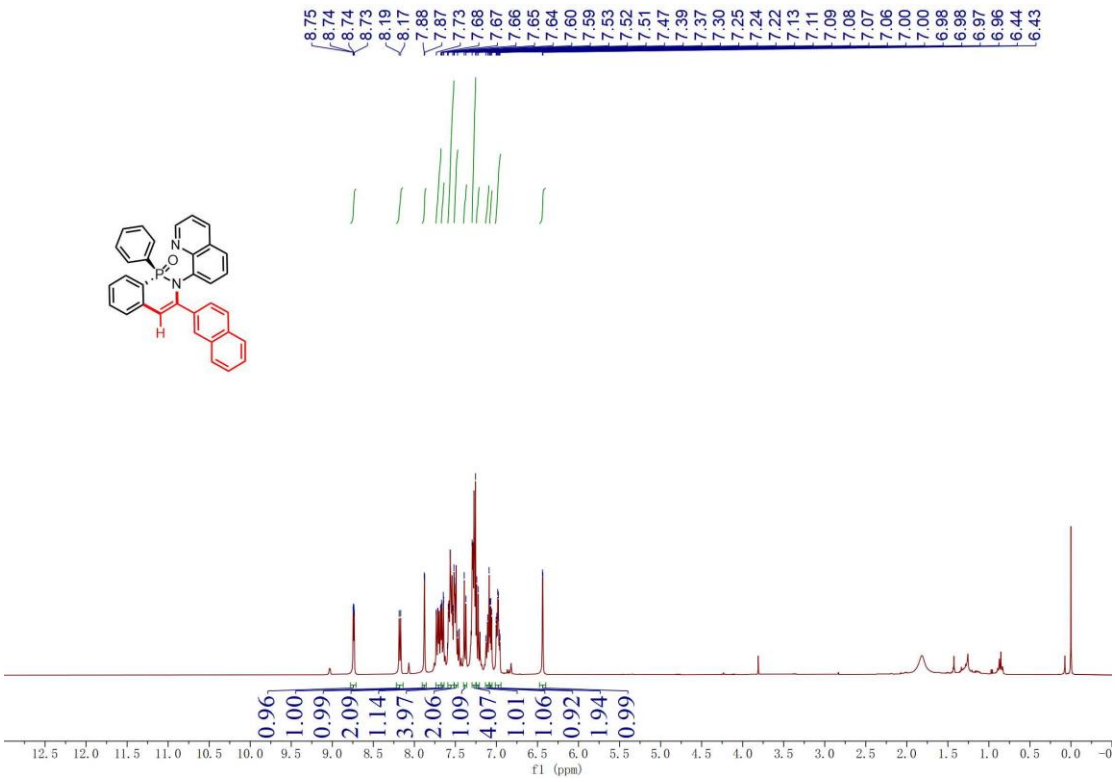
^{13}C-NMR of **3ab**



^{31}P-NMR of **3ab**



^{1}H-NMR of **3ac**



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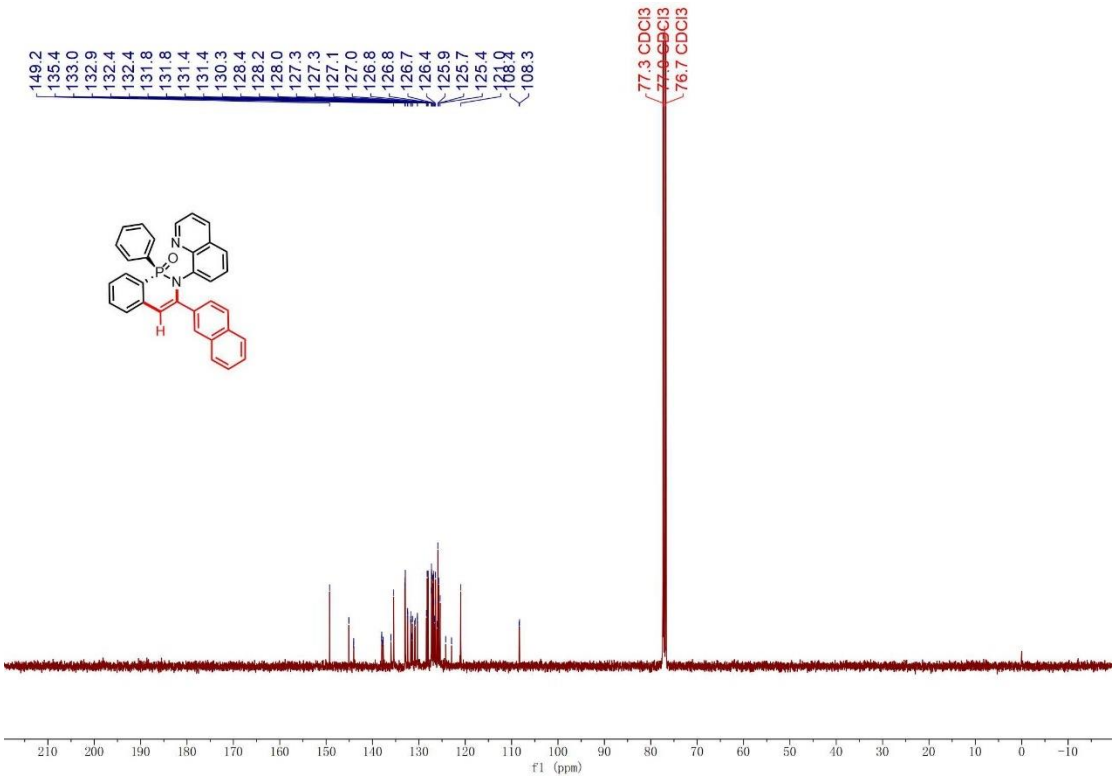
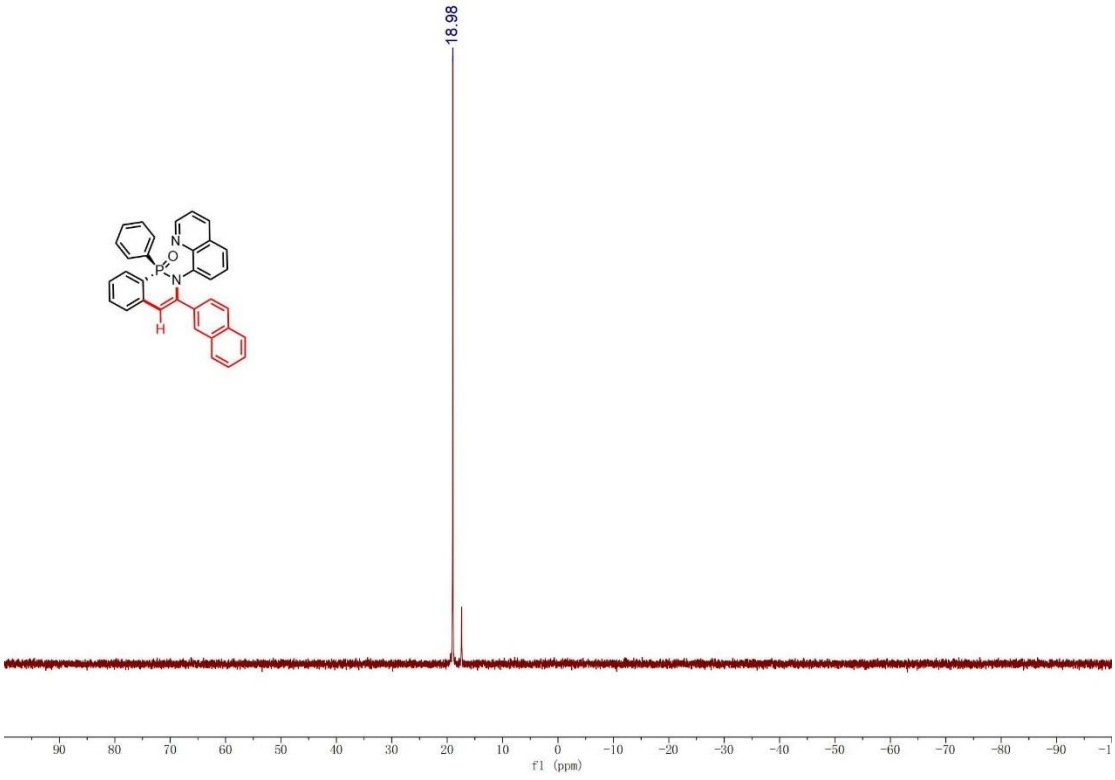
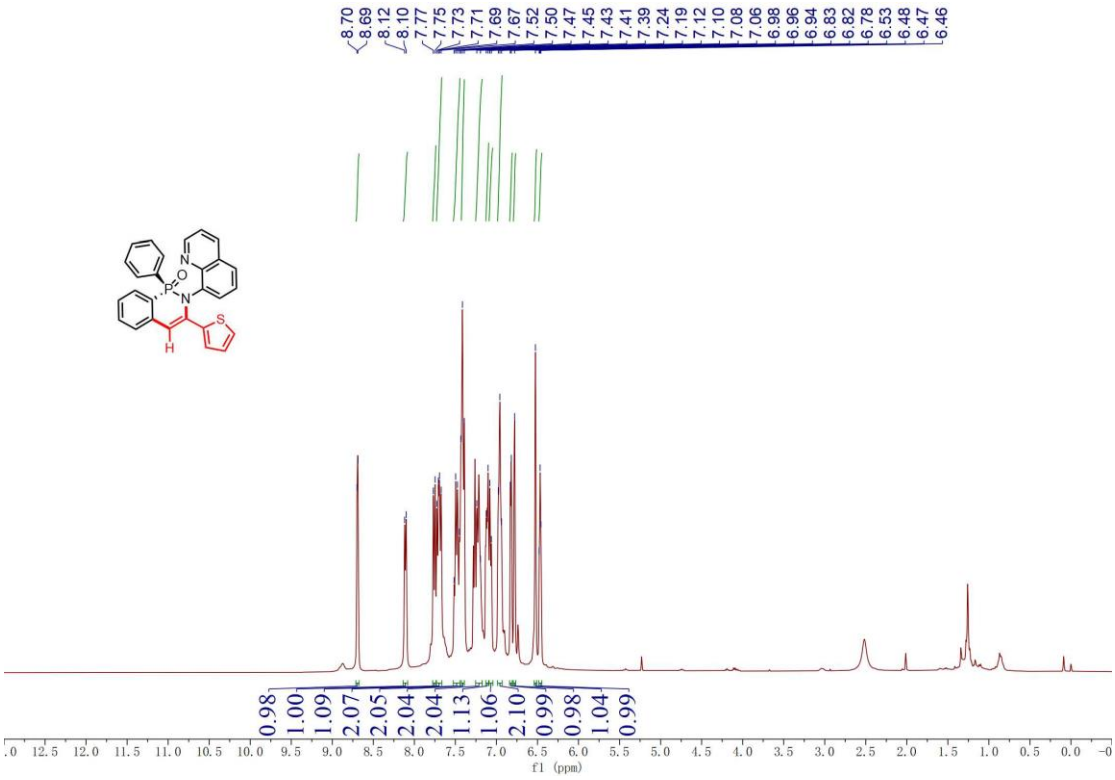


^{31}P-NMR of **3ac**



^{1}H-NMR of **3ad**



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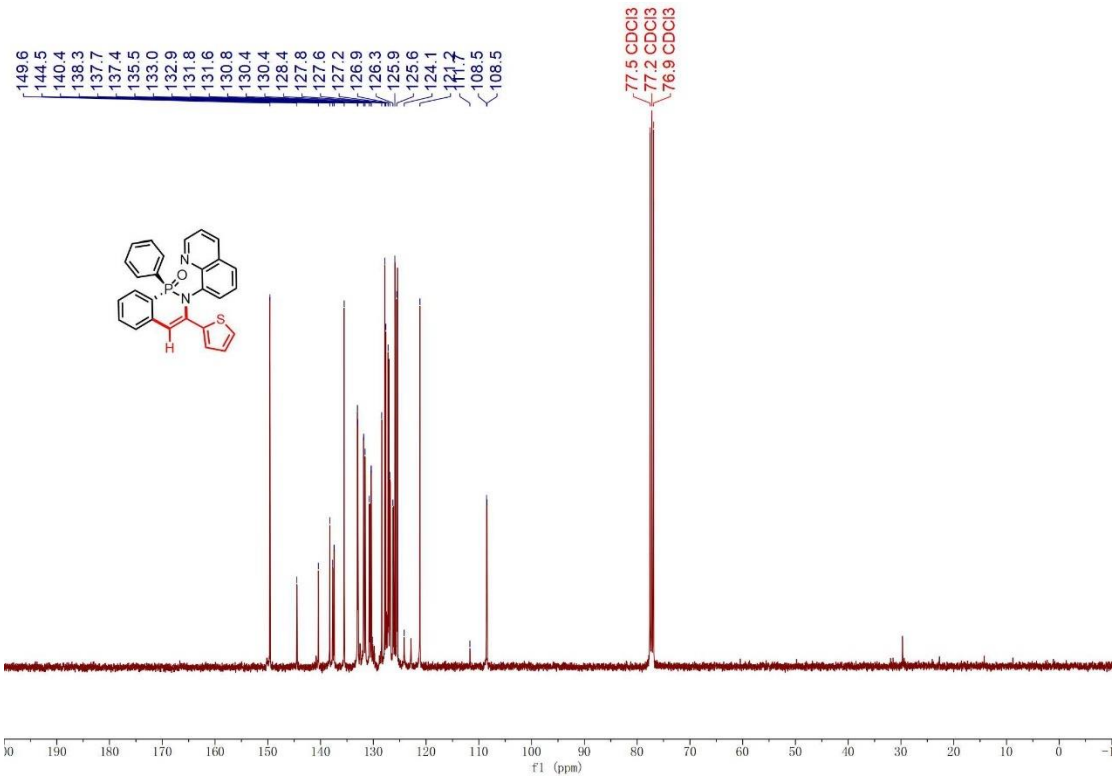
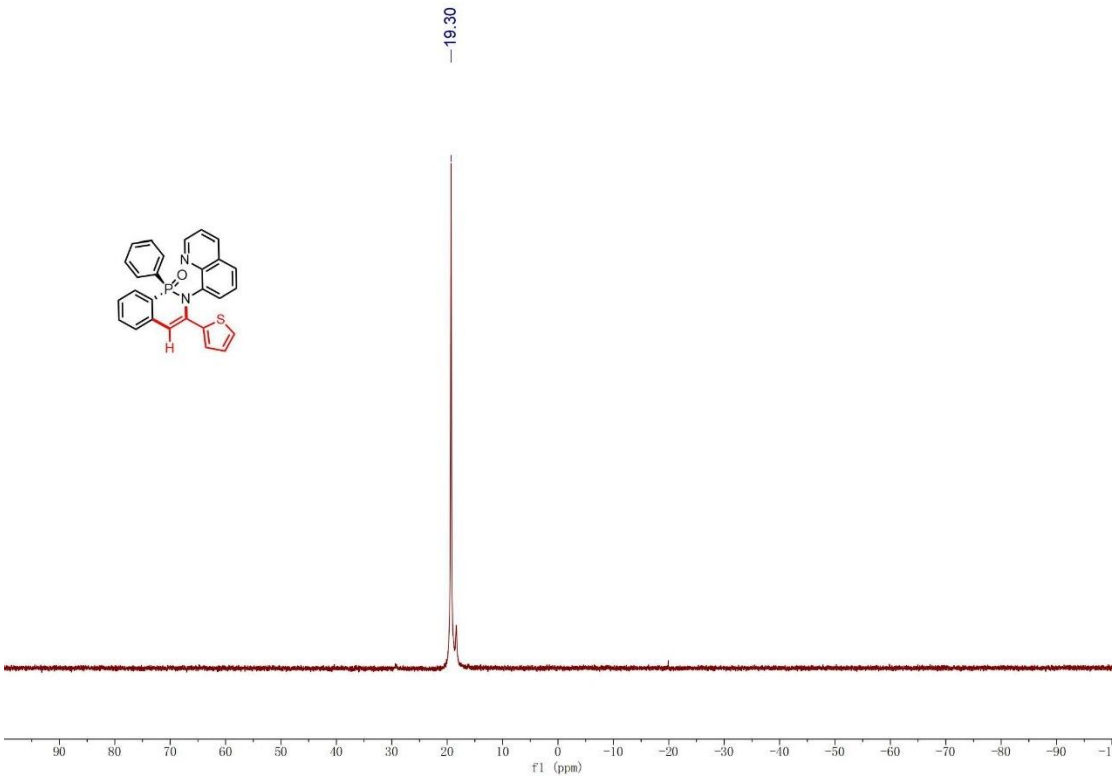
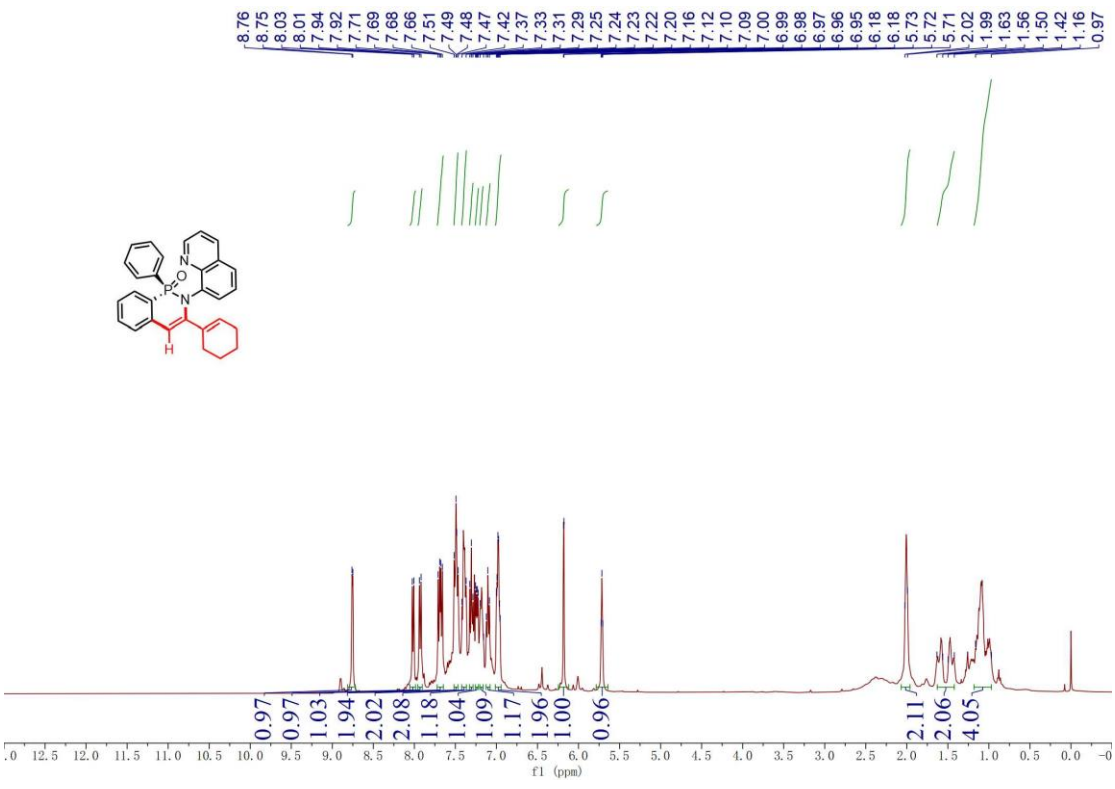


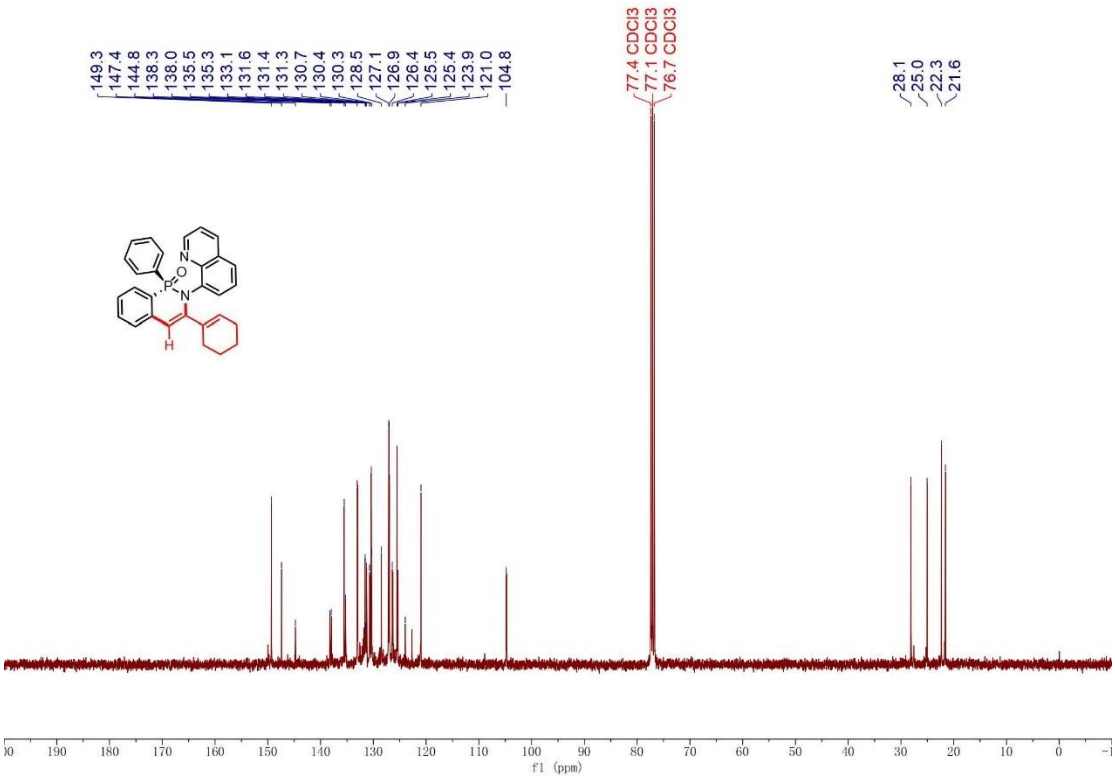
^{31}P-NMR of **3ad**



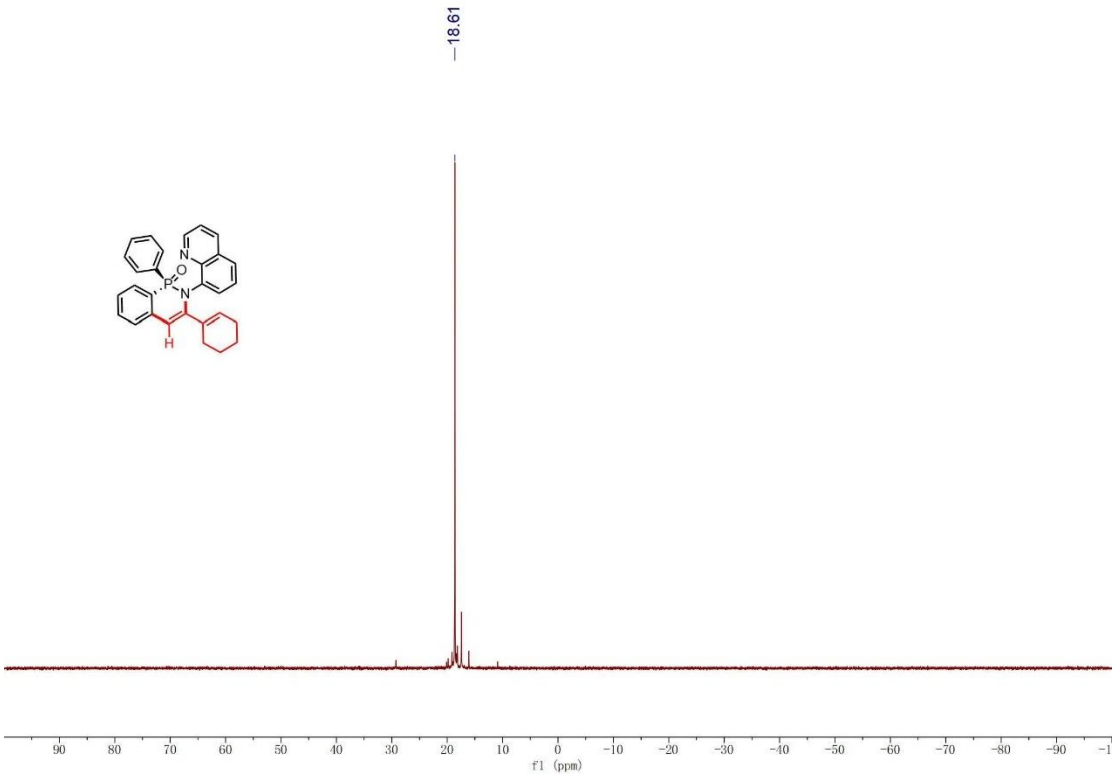
^{1}H-NMR of **3ae**



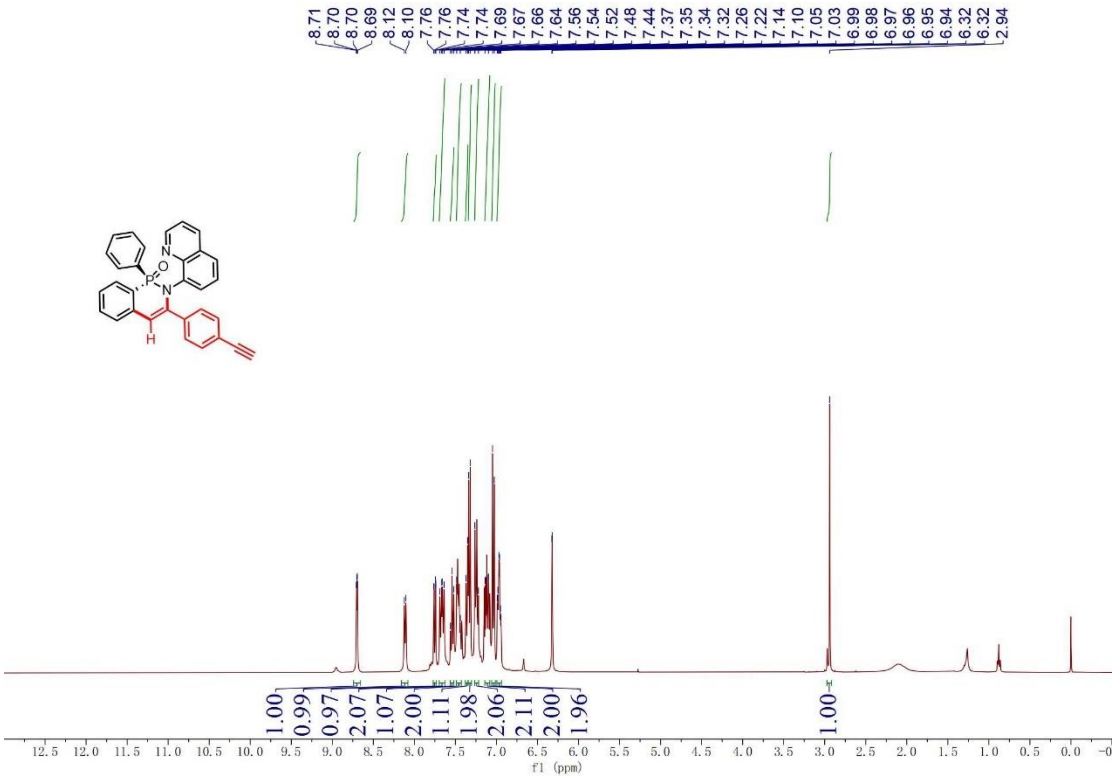
^{13}C-NMR of **3ae**



^{31}P-NMR of **3ae**



^{1}H-NMR of **3af**



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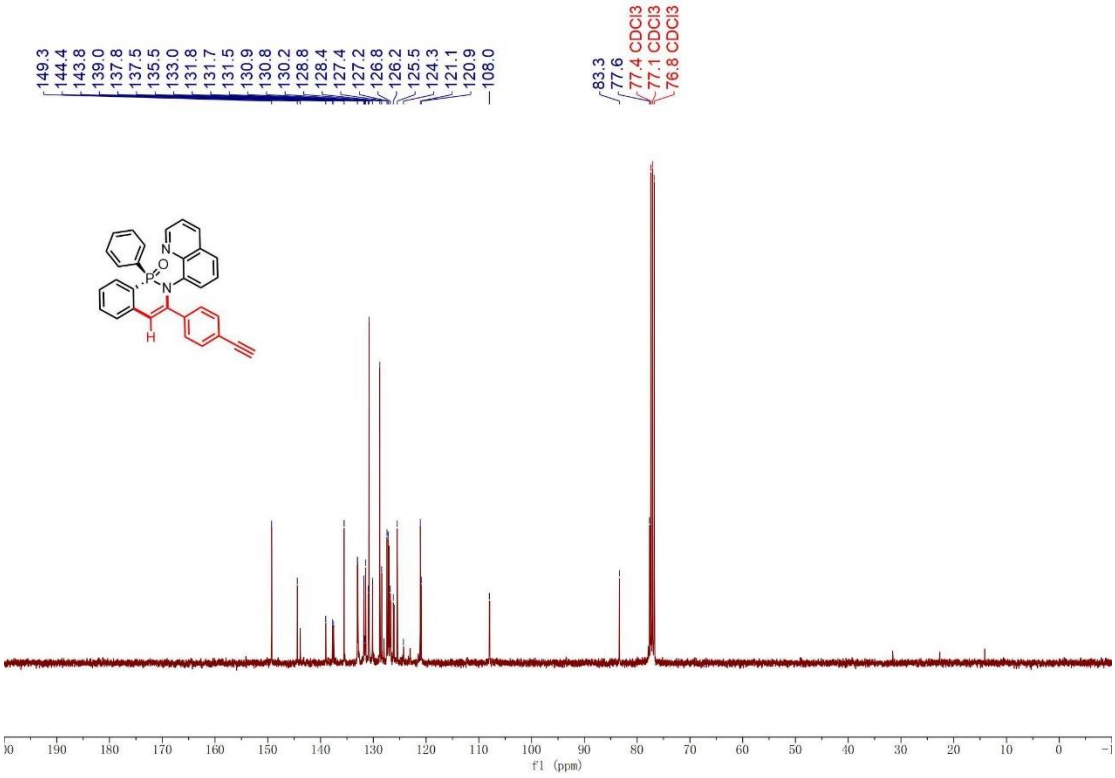

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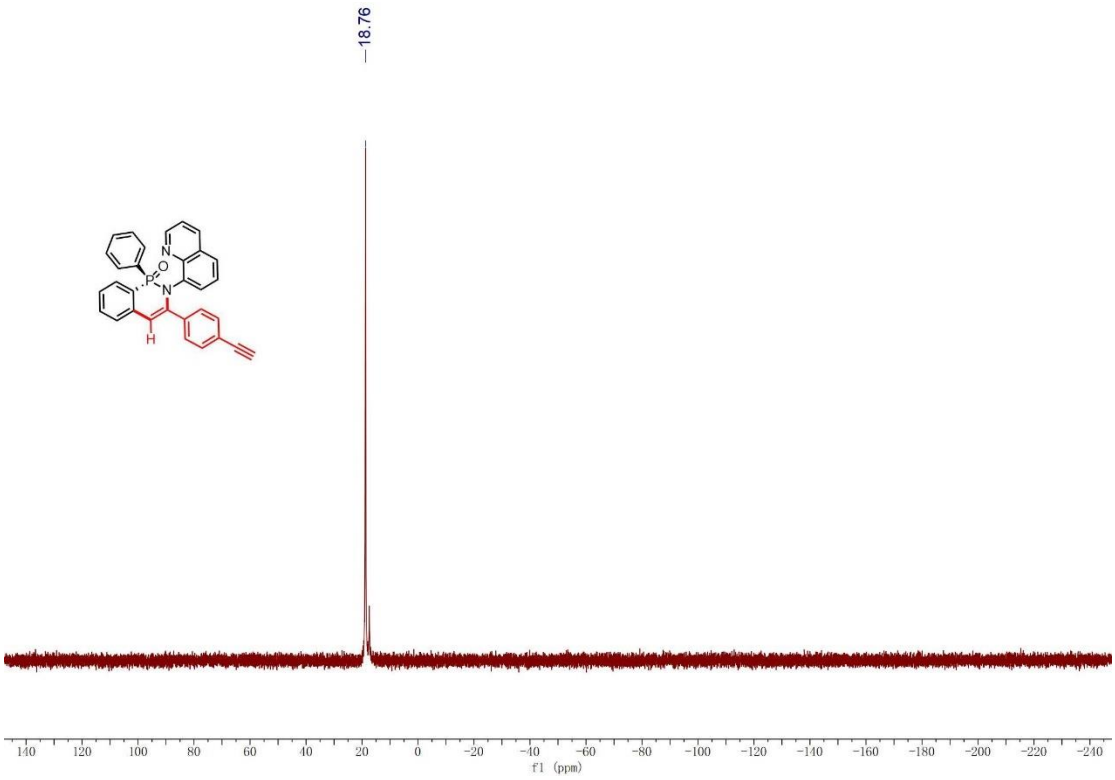
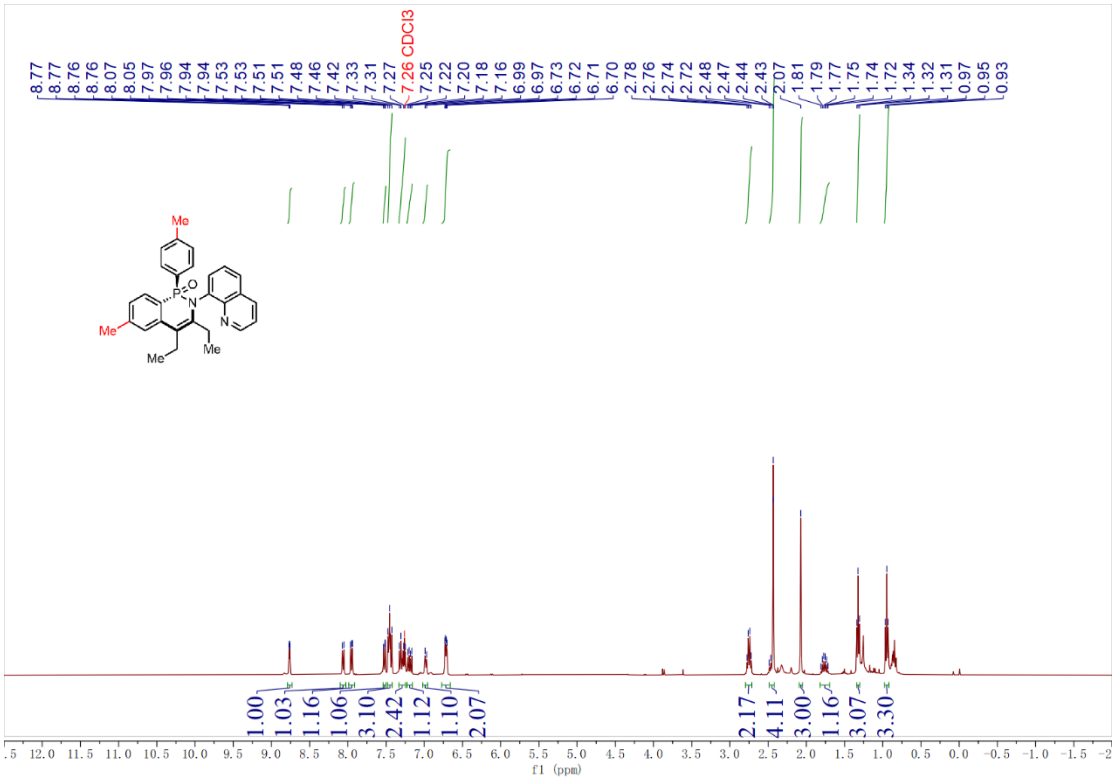
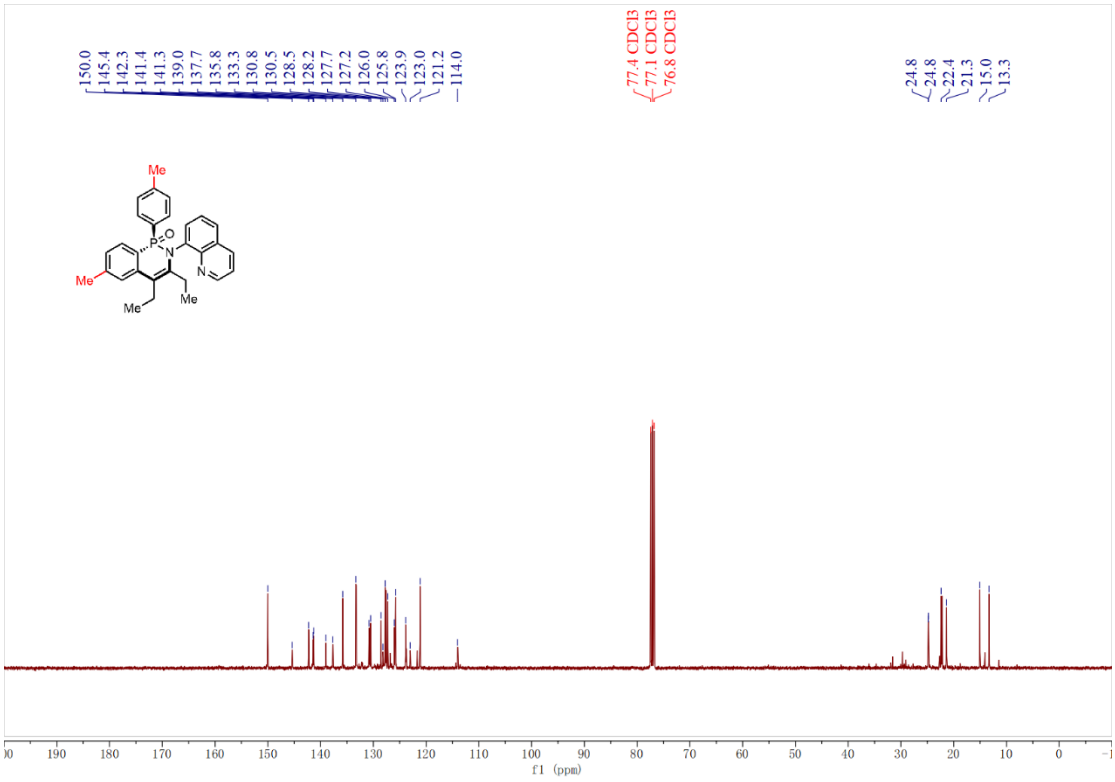


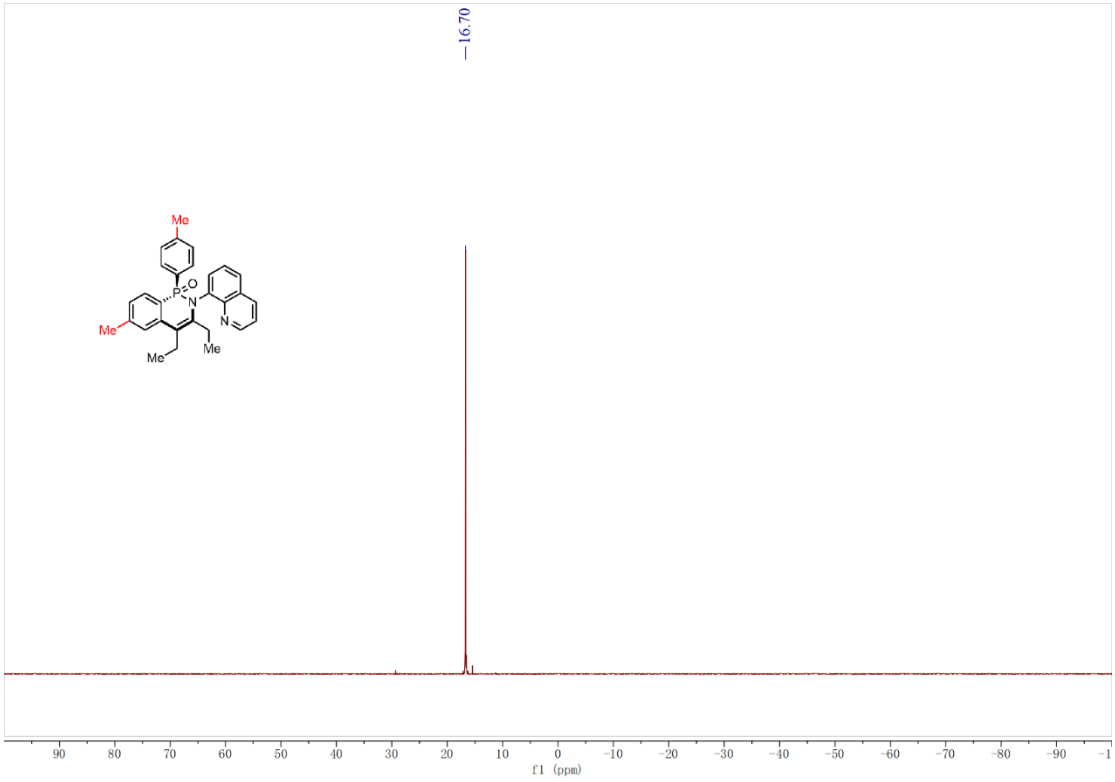
^{1}H-NMR of **3ag**



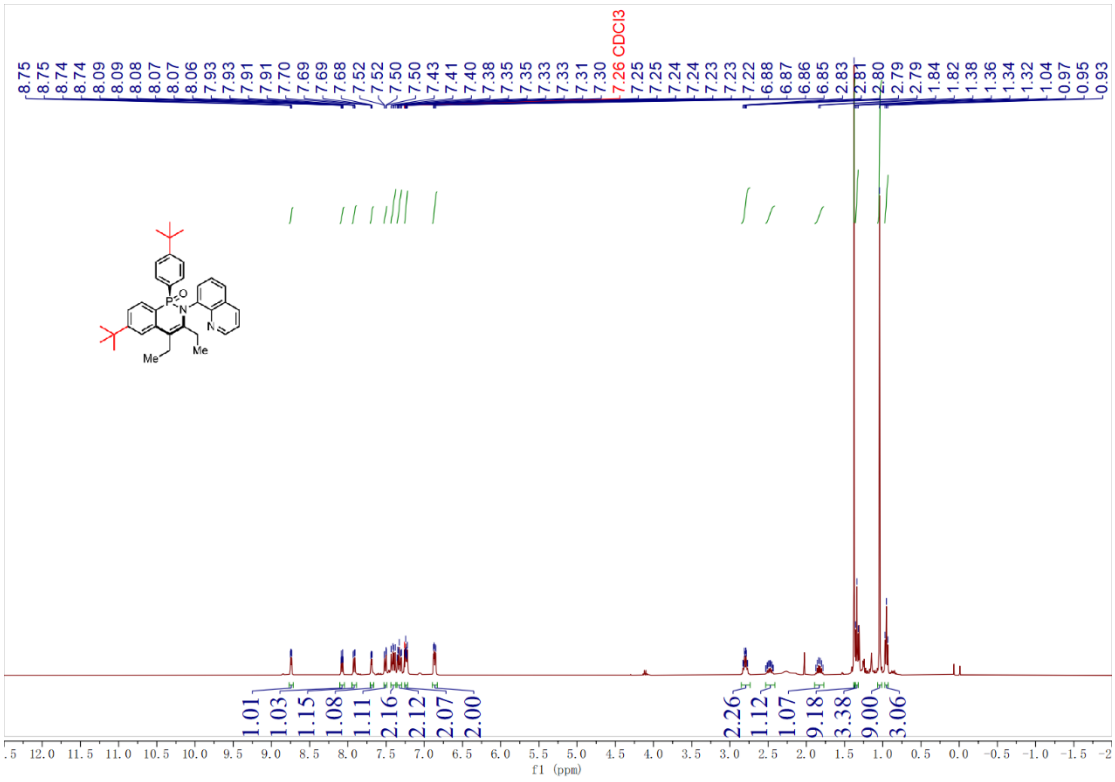
^{13}C-NMR of **3ag**



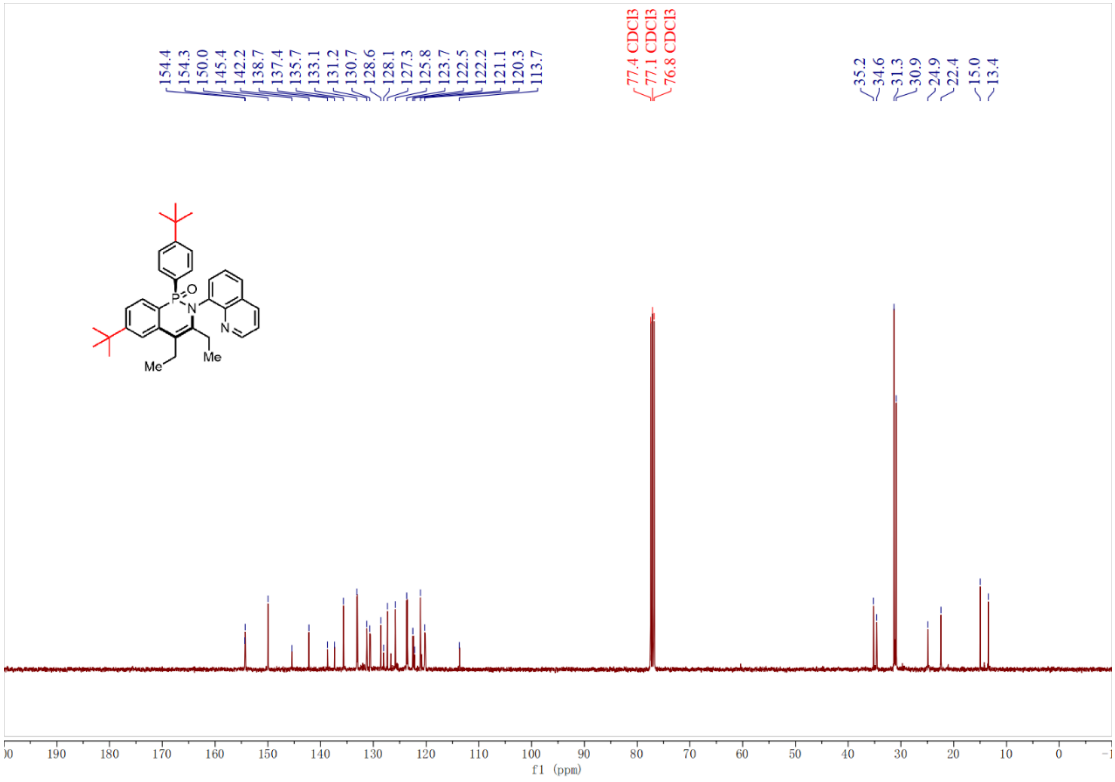
^{31}P – NMR of **3ag**



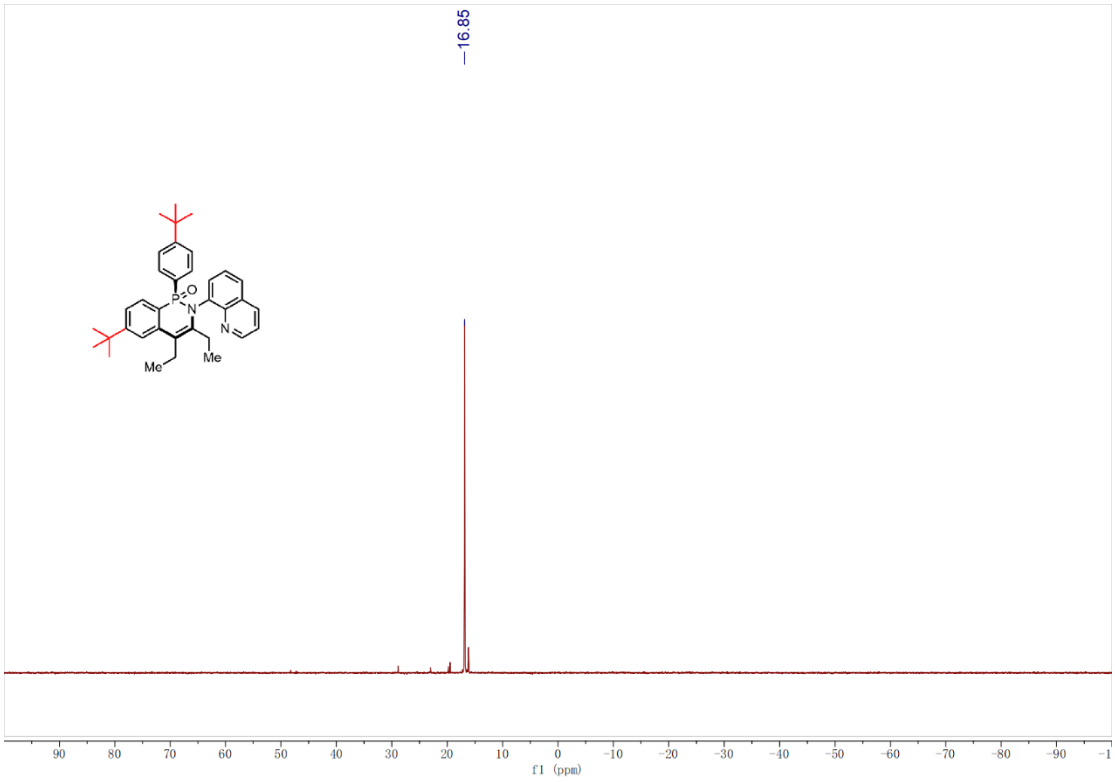
^{1}H-NMR of **3ah**



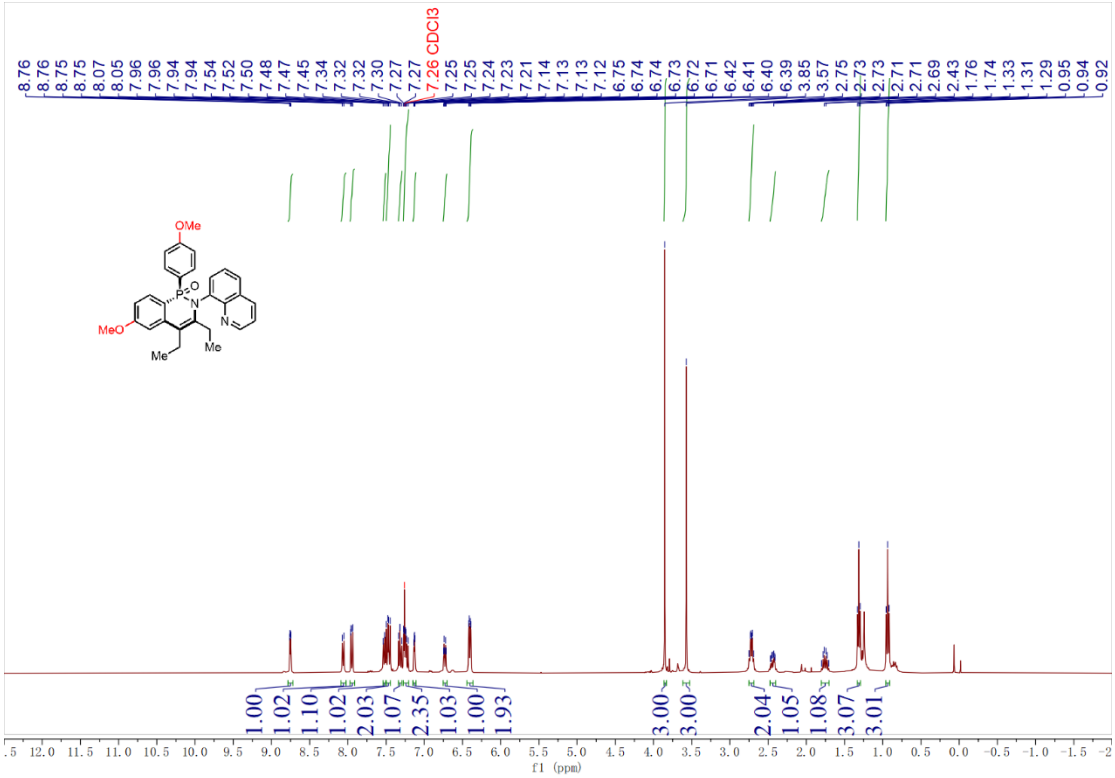
^{13}C-NMR of **3ah**



^{31}P-NMR of **3ah**



^{1}H-NMR of **3ai**



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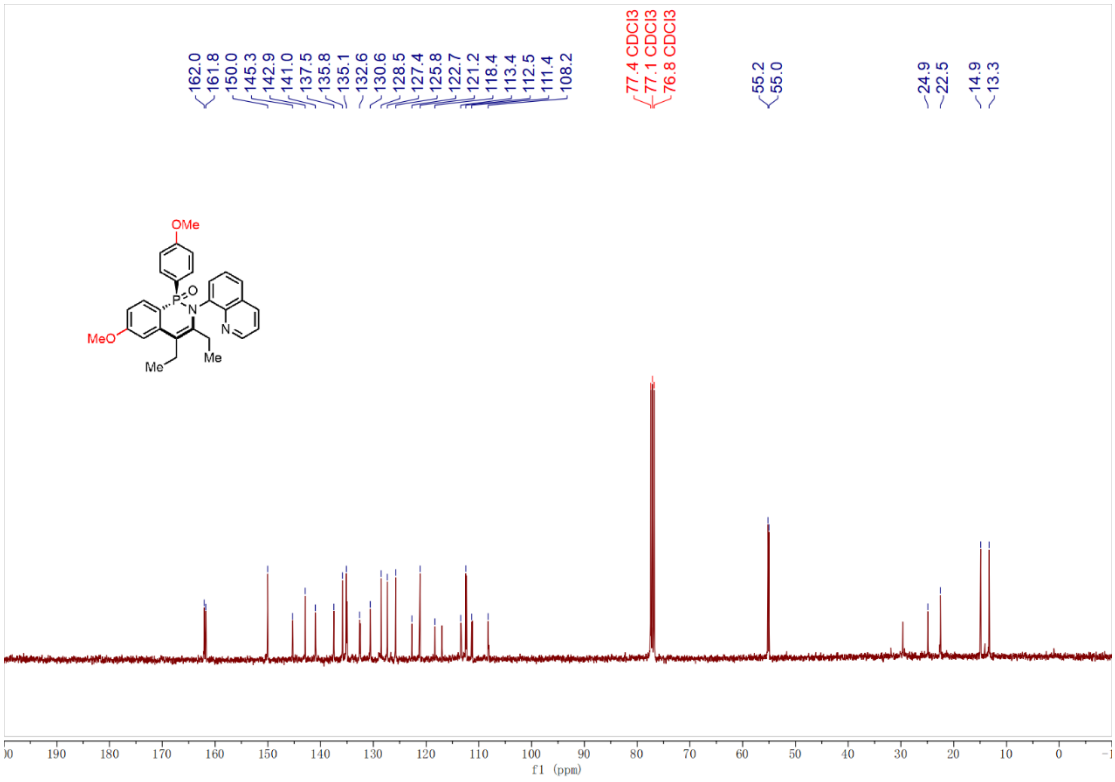

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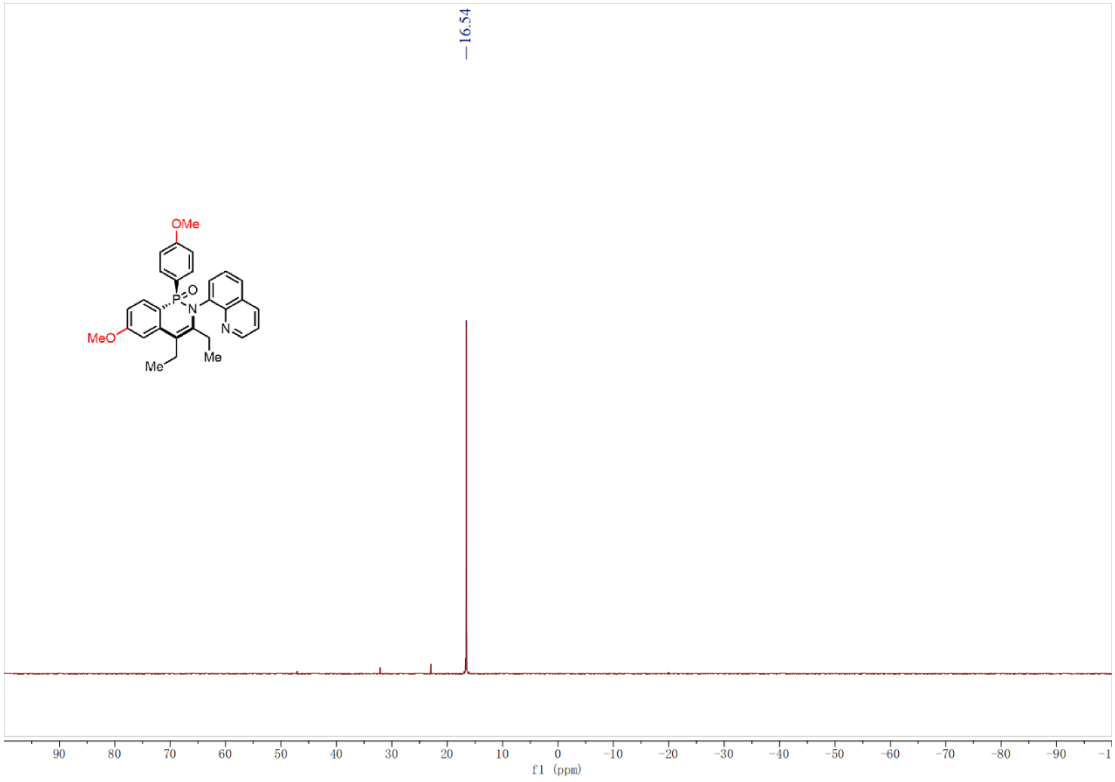
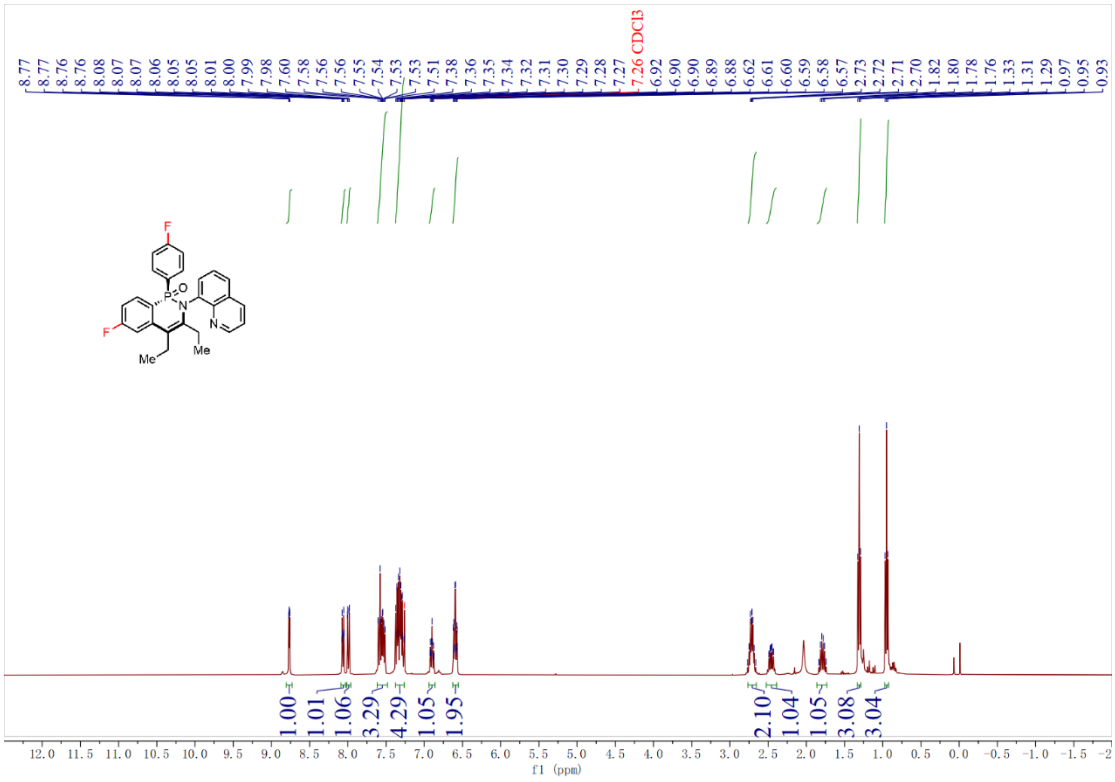
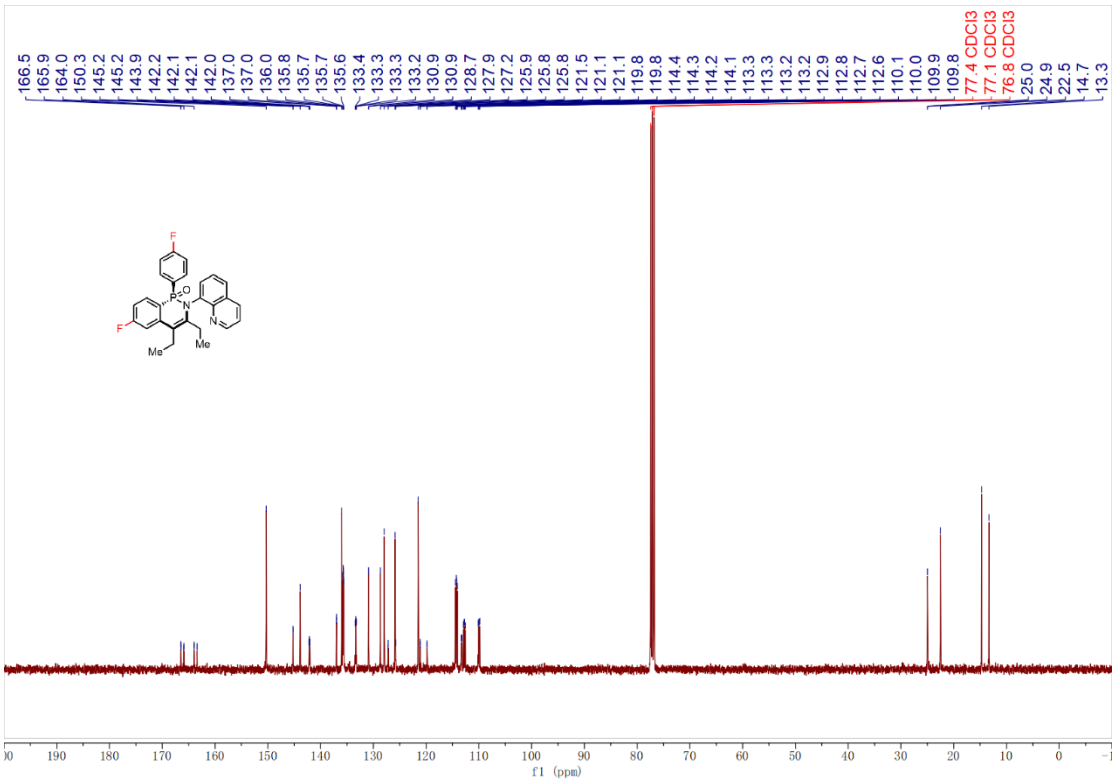


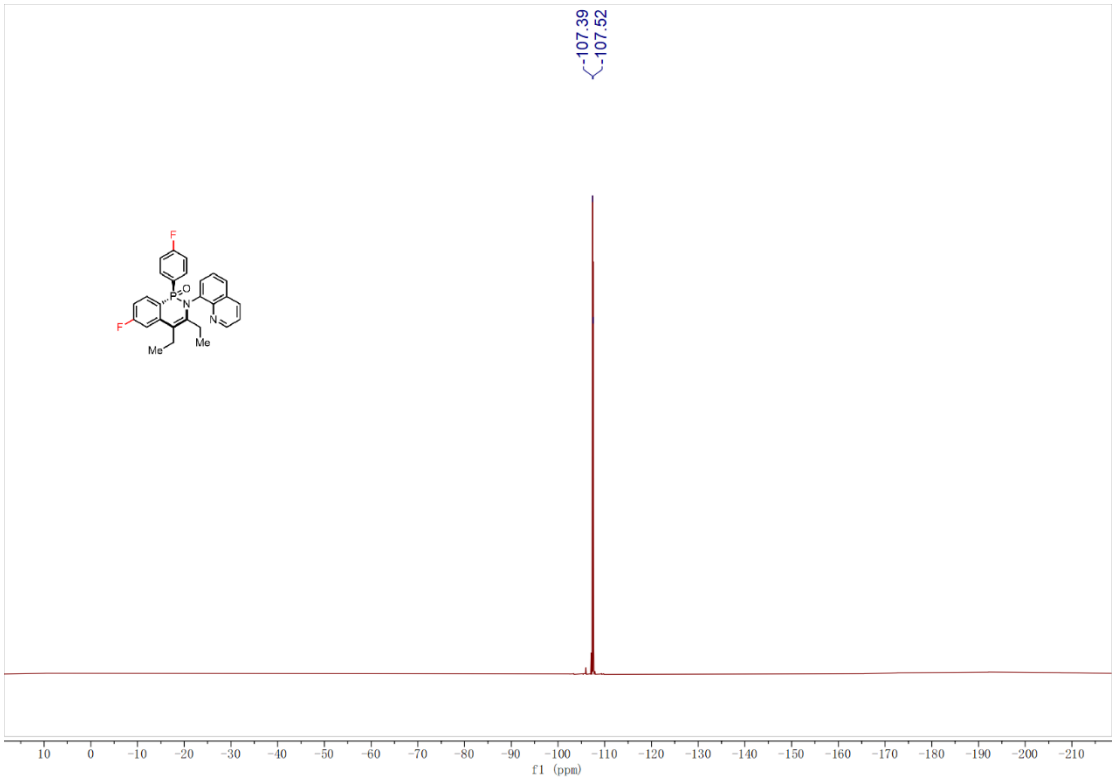
^{1}H-NMR of **3aj**



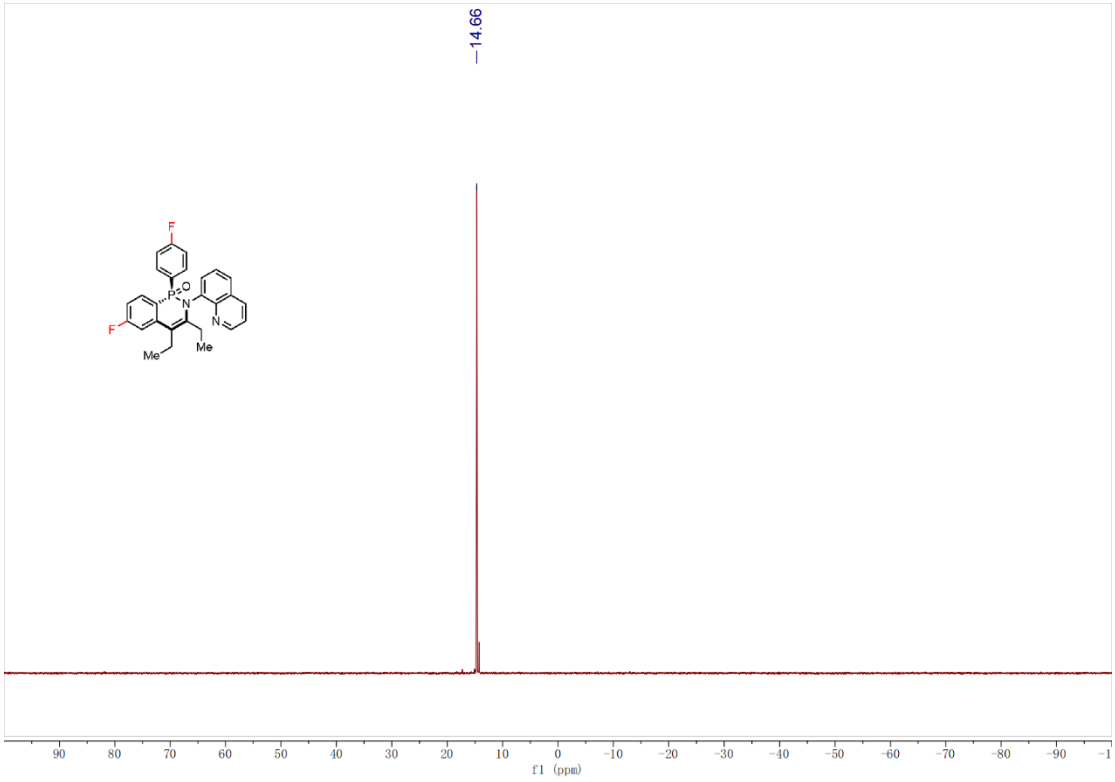
^{13}C-NMR of **3aj**



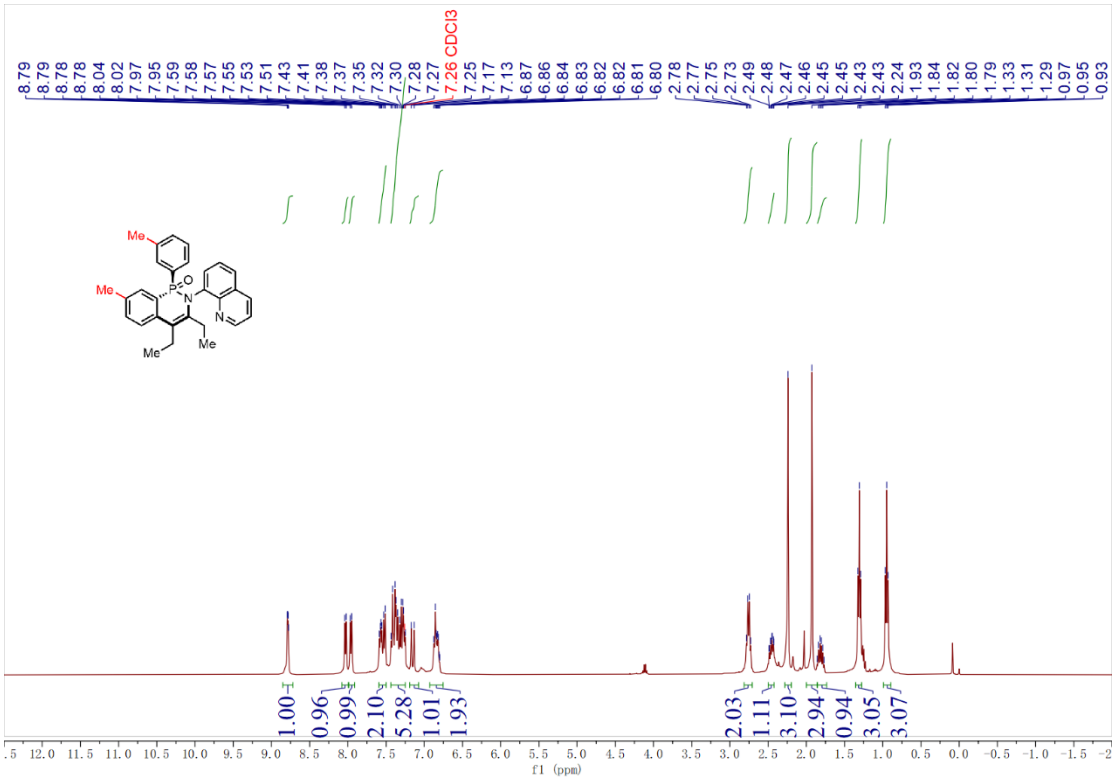
^{19}F-NMR of **3aj**



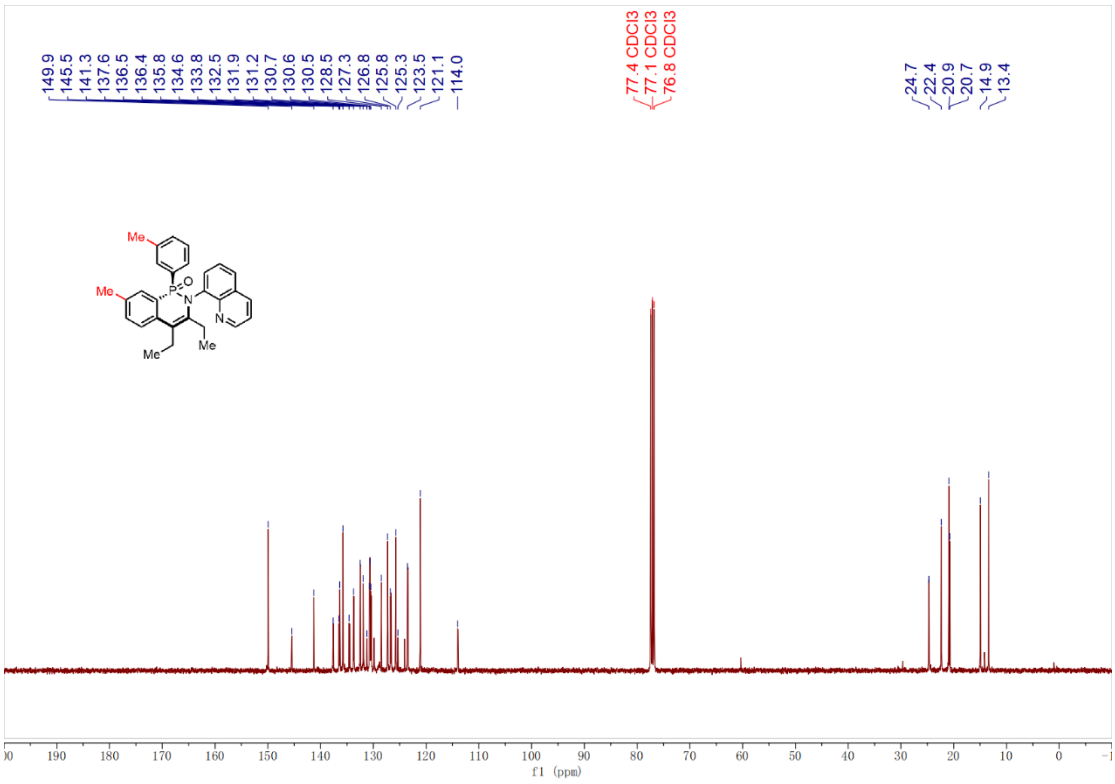
^{31}P-NMR of **3aj**



^{1}H-NMR of **3ak**



^{13}C-NMR of **3ak**



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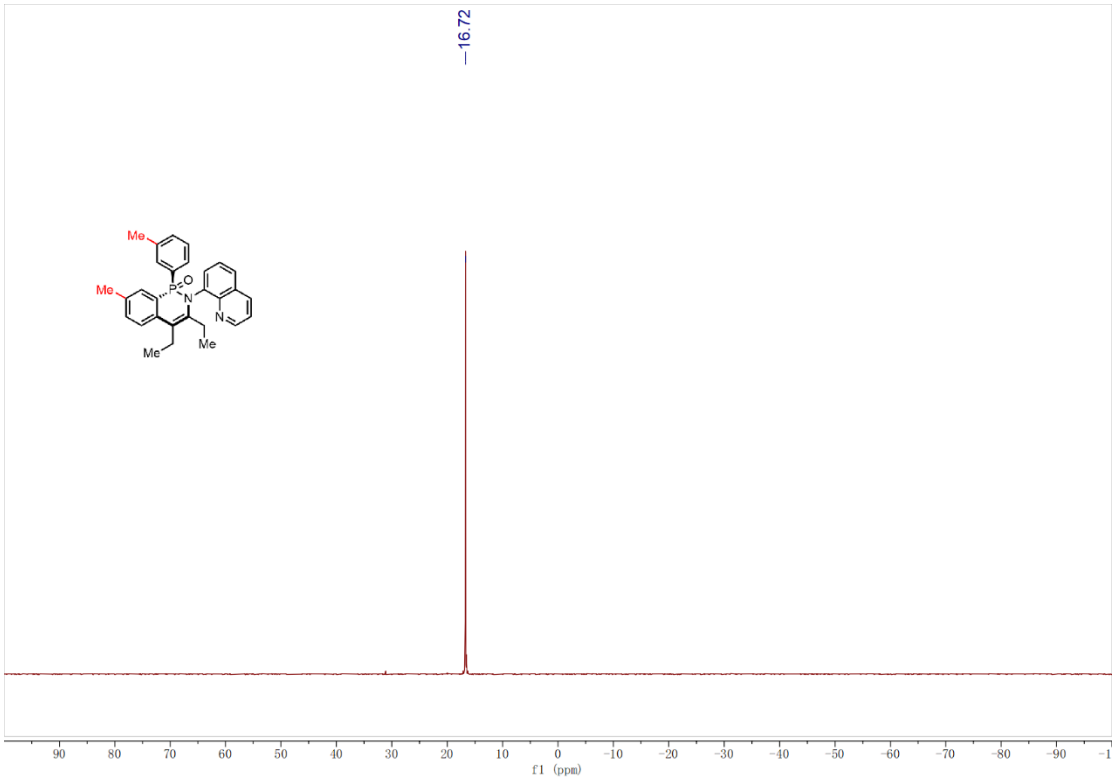
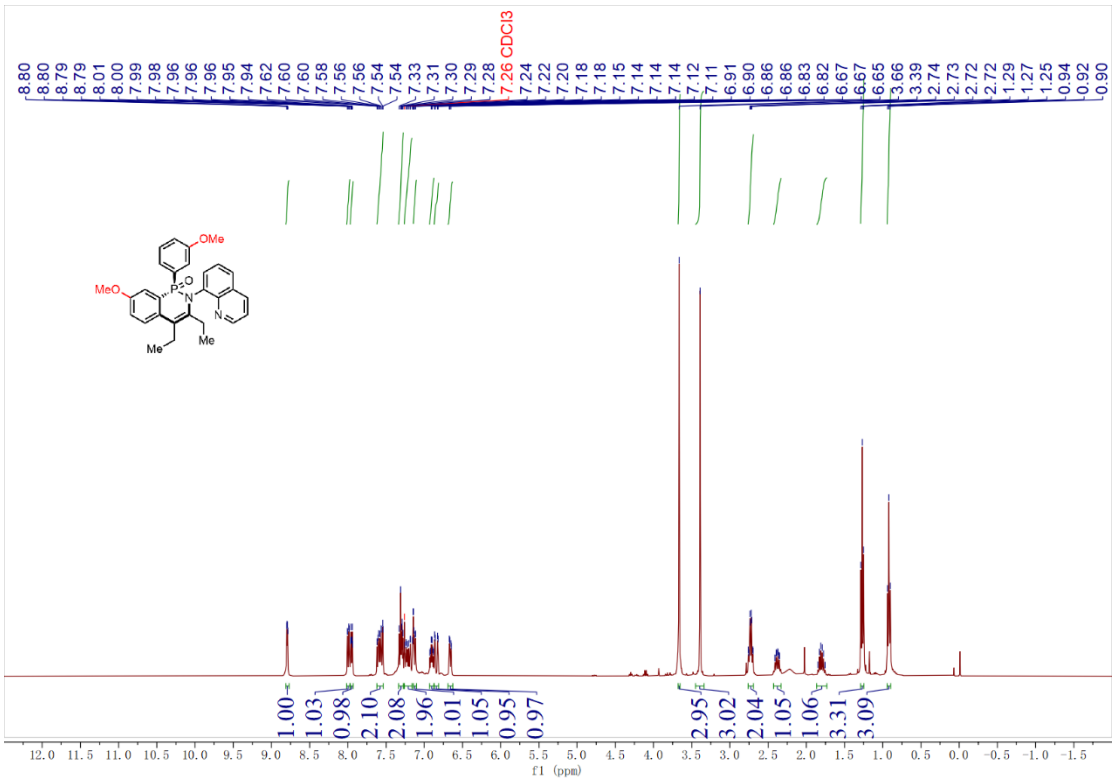
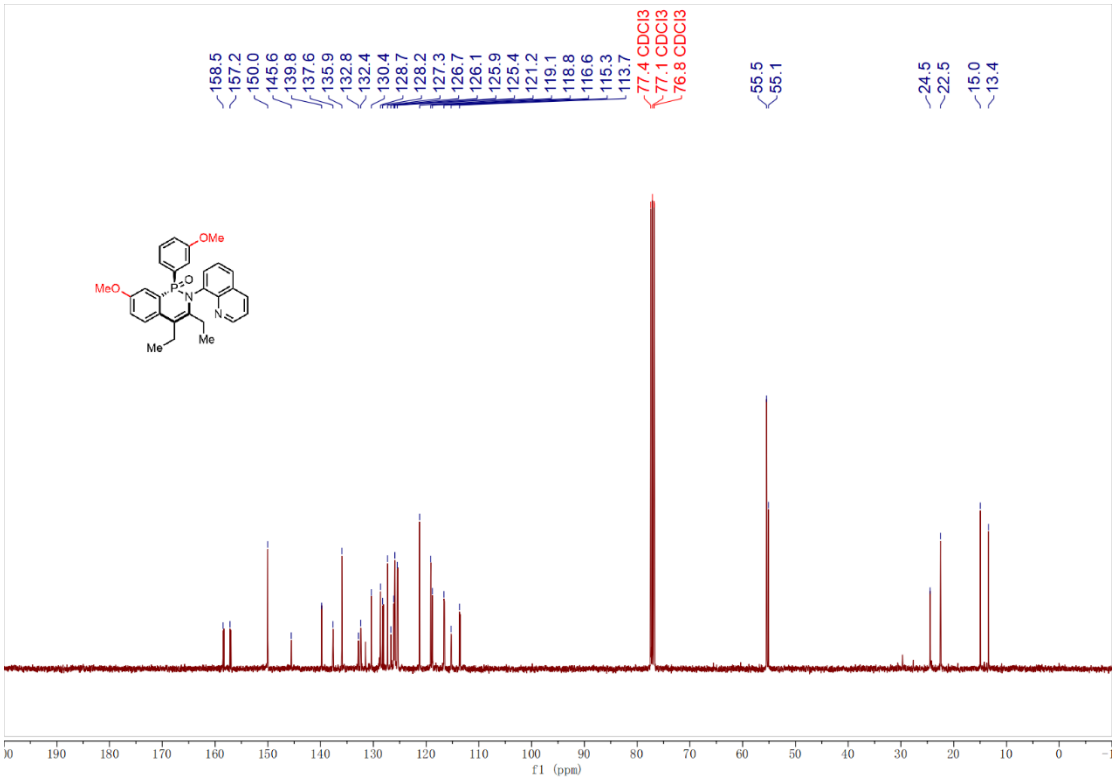


^{1}H-NMR of **3al**



^{13}C-NMR of **3al**



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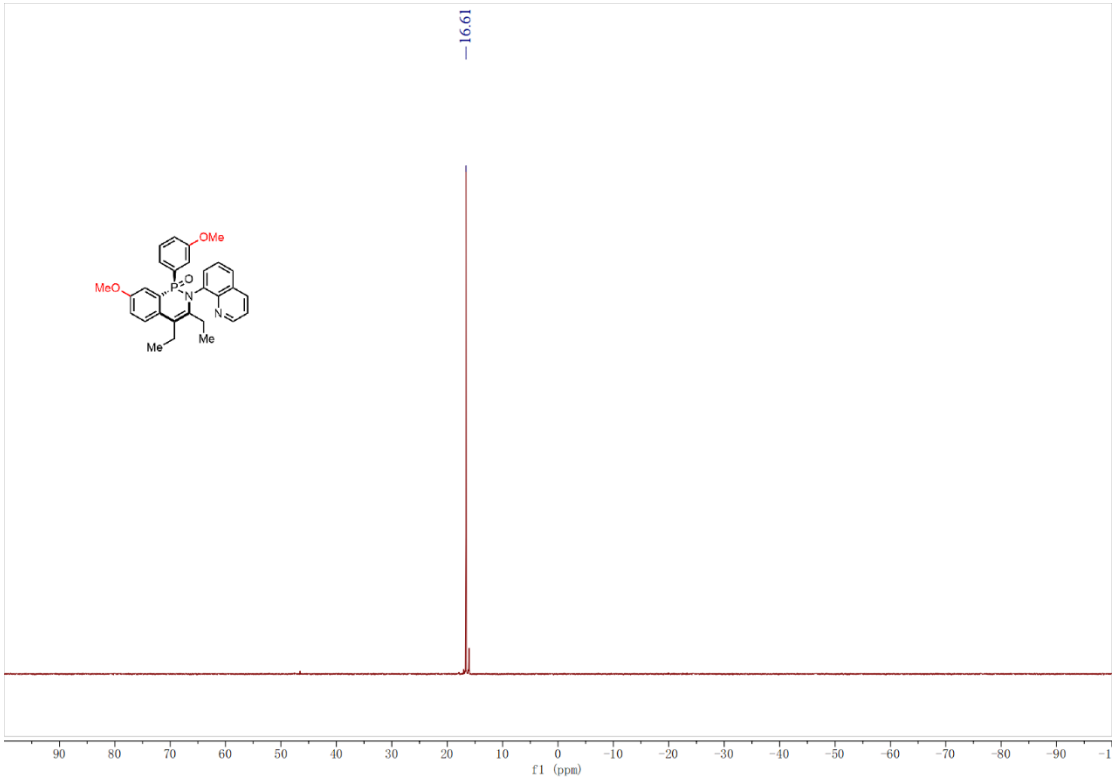
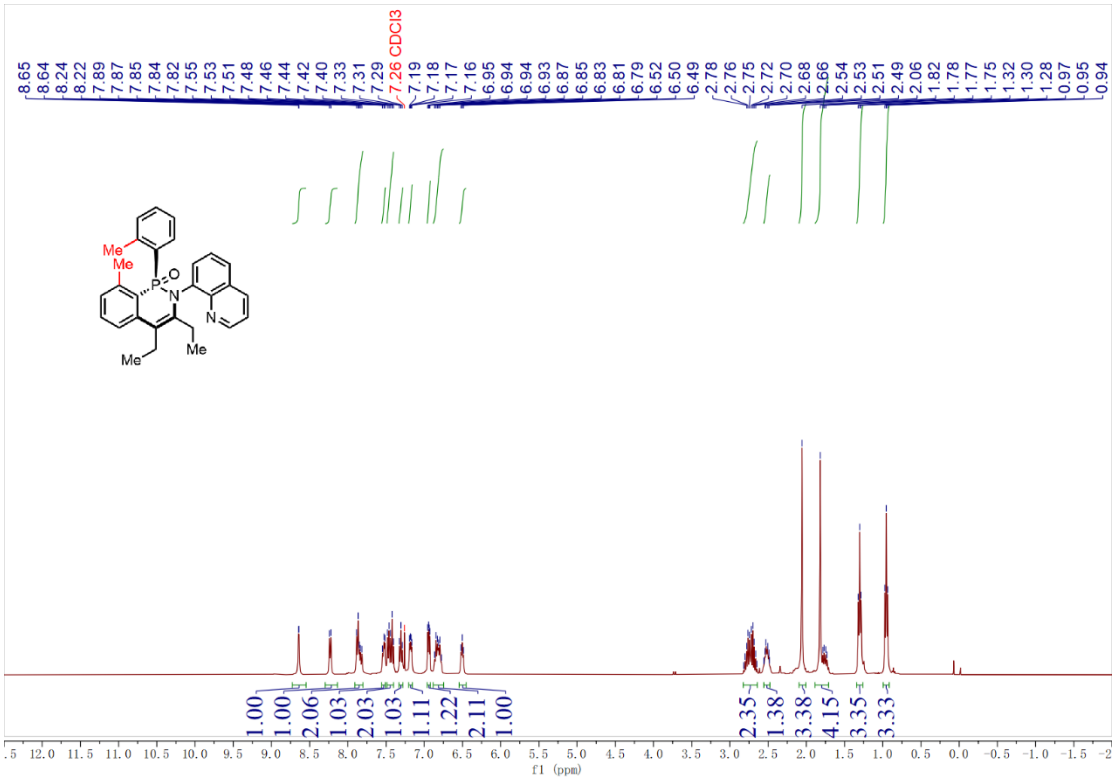


^{1}H-NMR of **3am**



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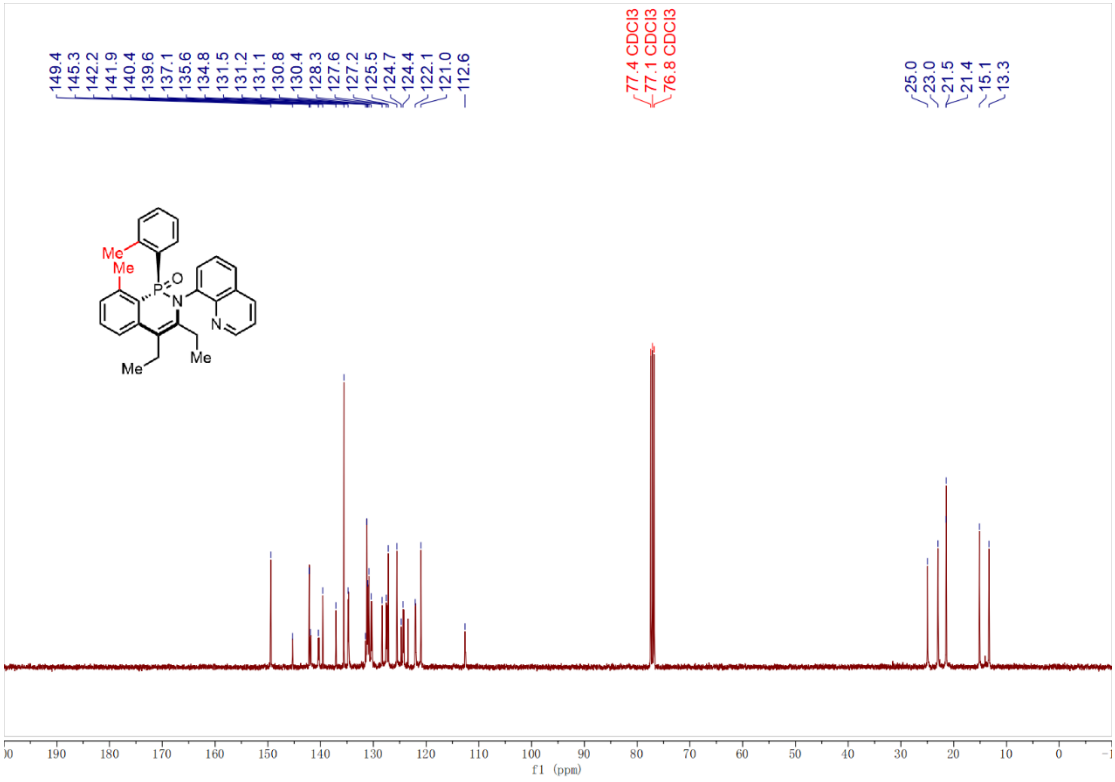

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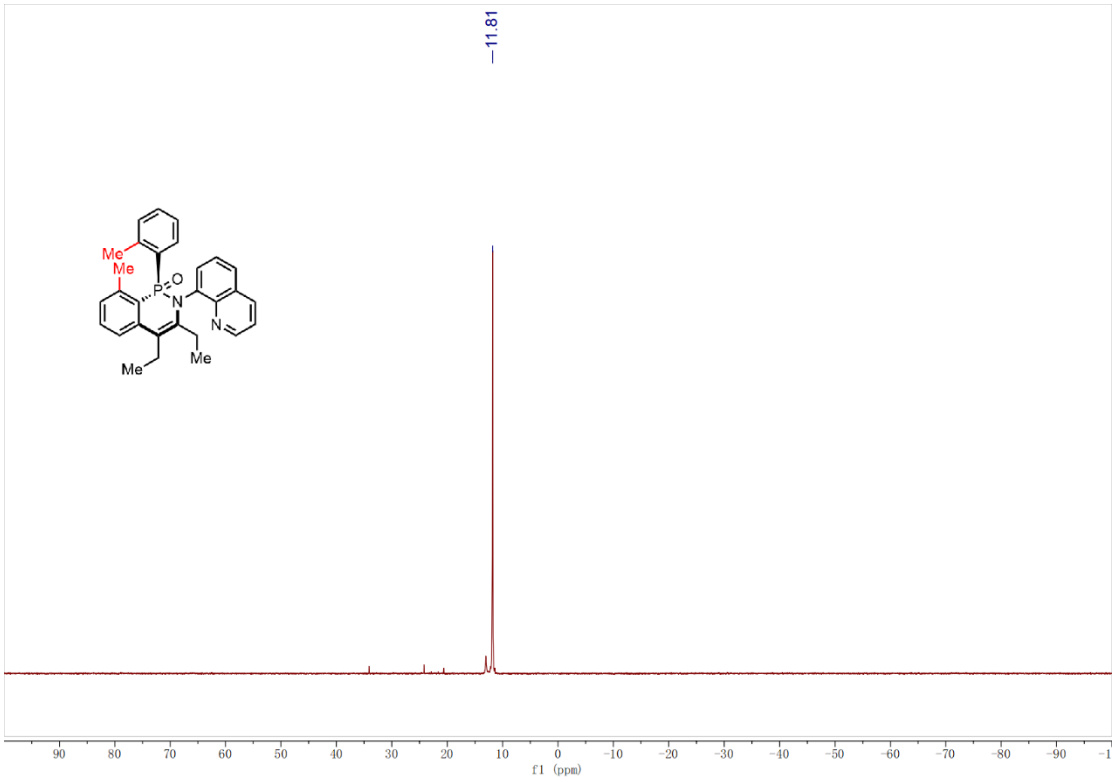
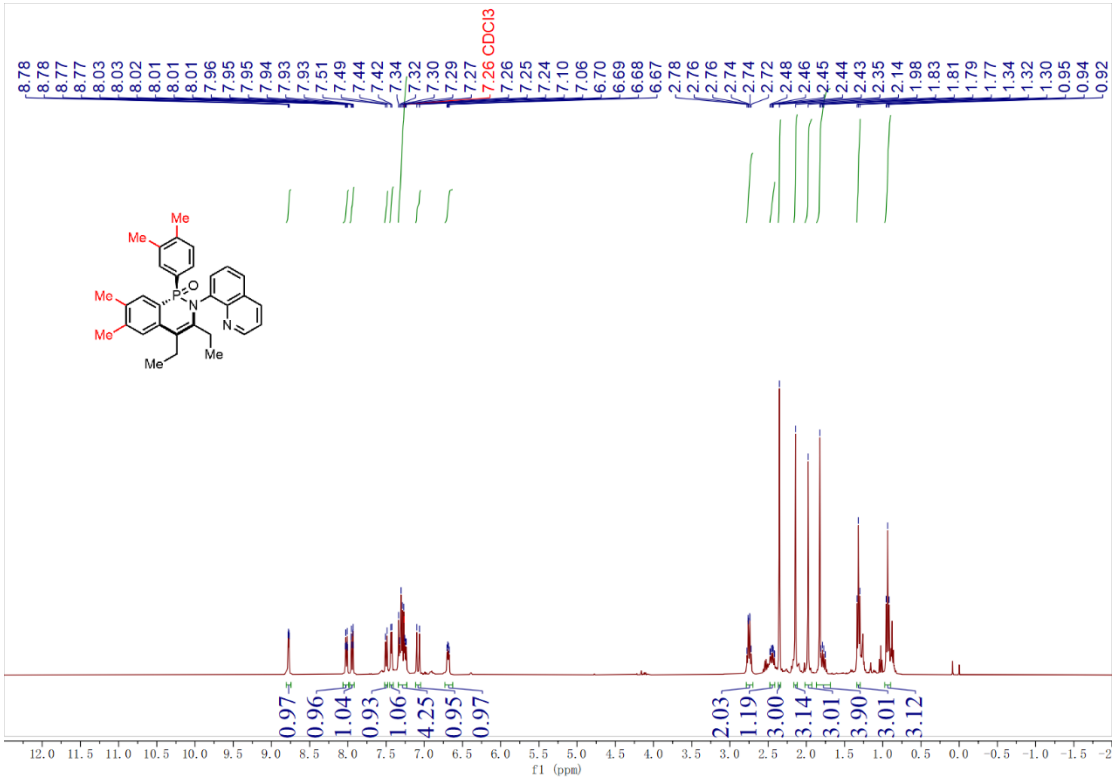


^{1}H-NMR of **3an**



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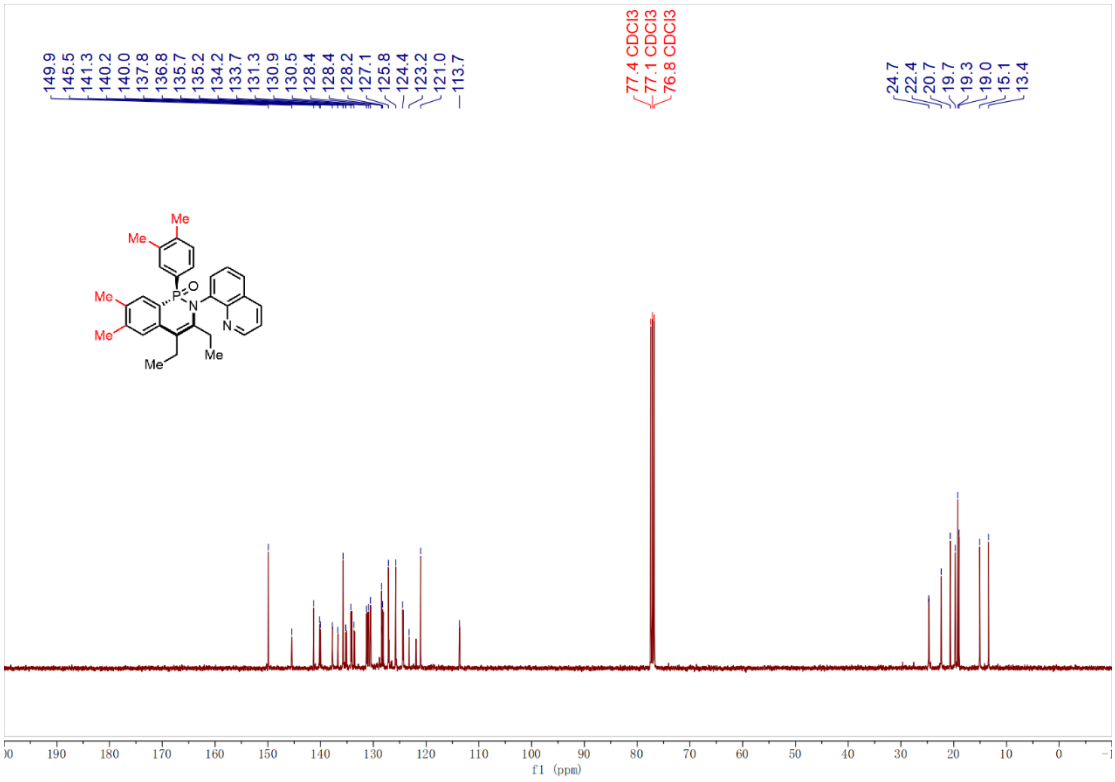

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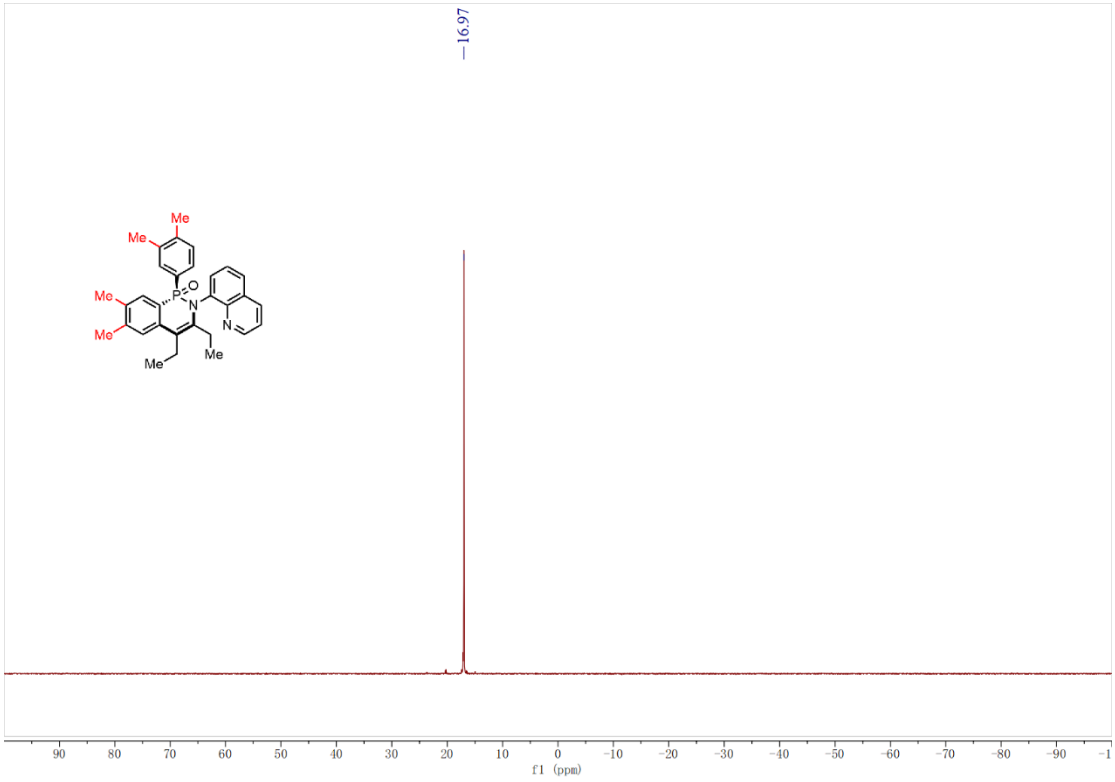
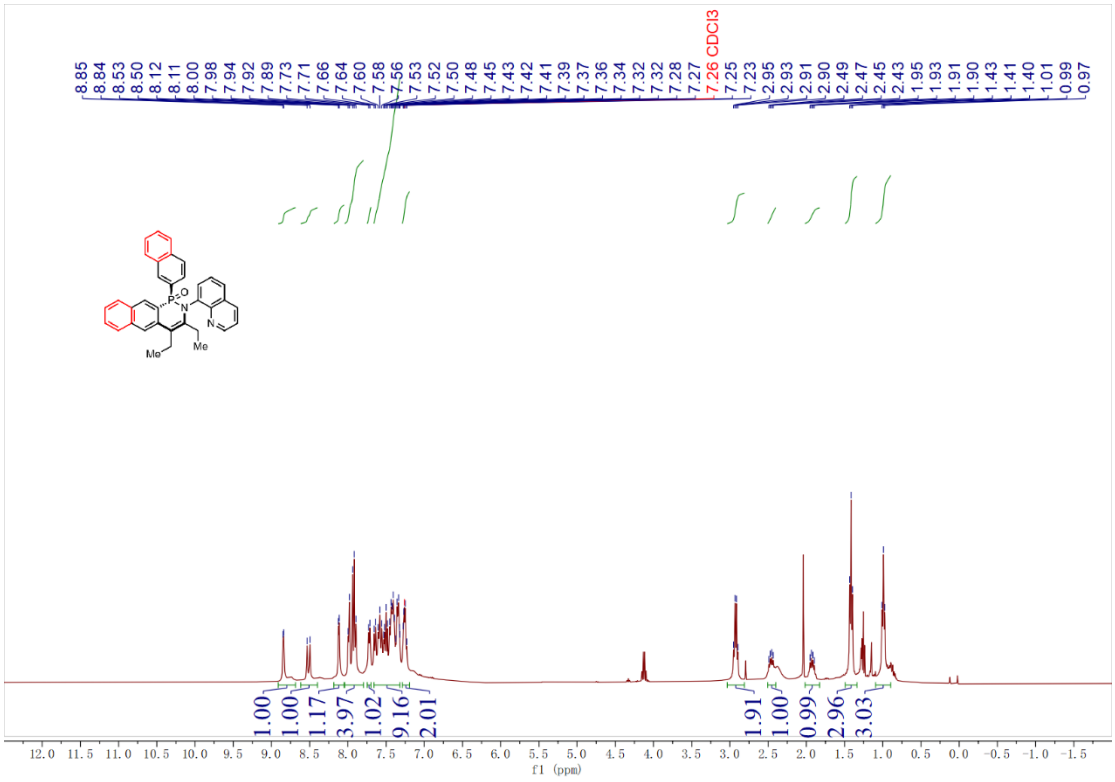


^{1}H-NMR of **3ao**



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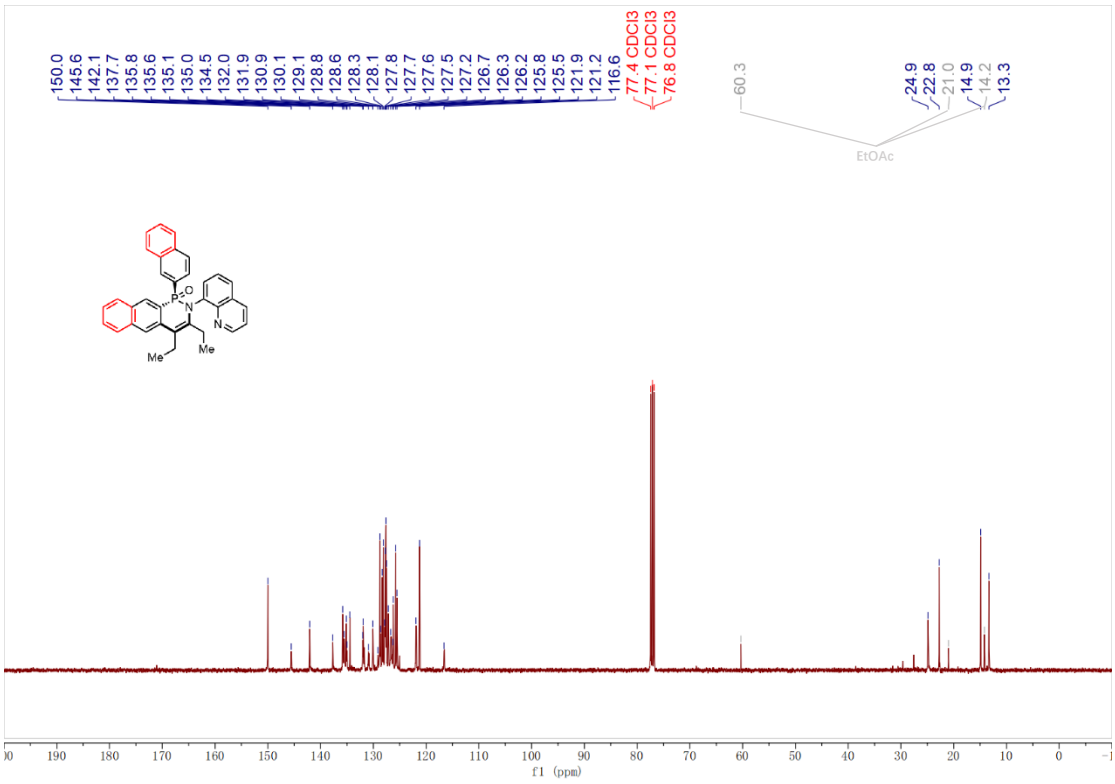

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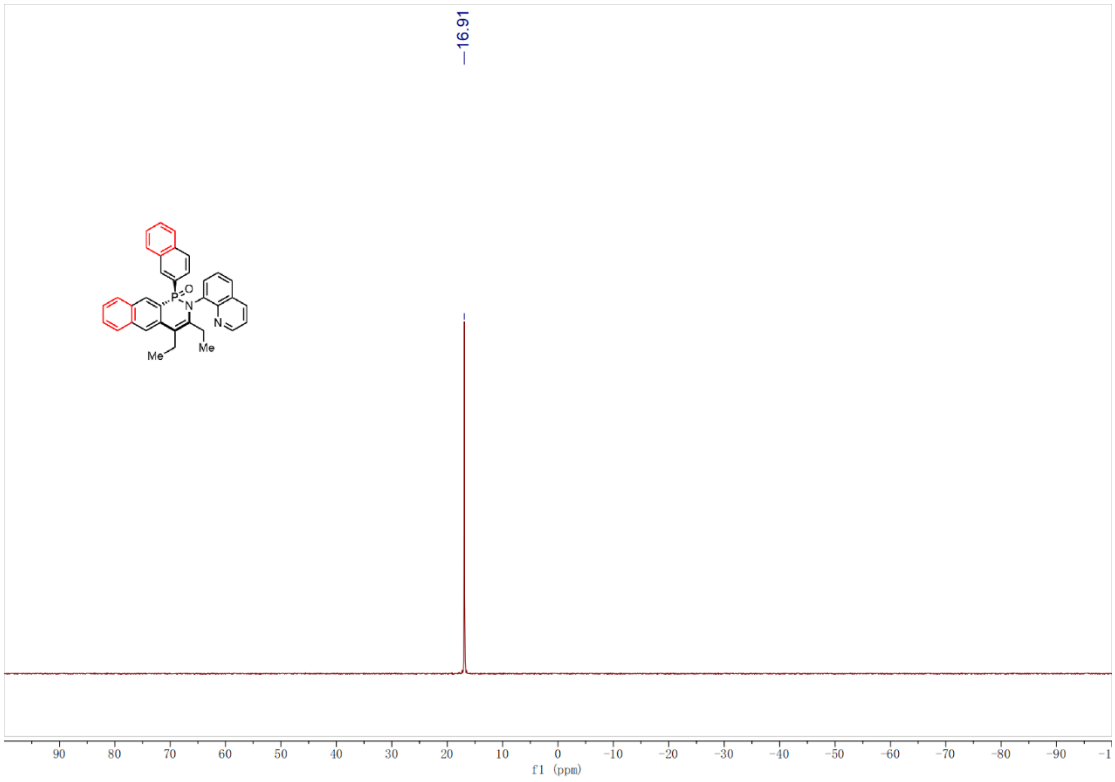
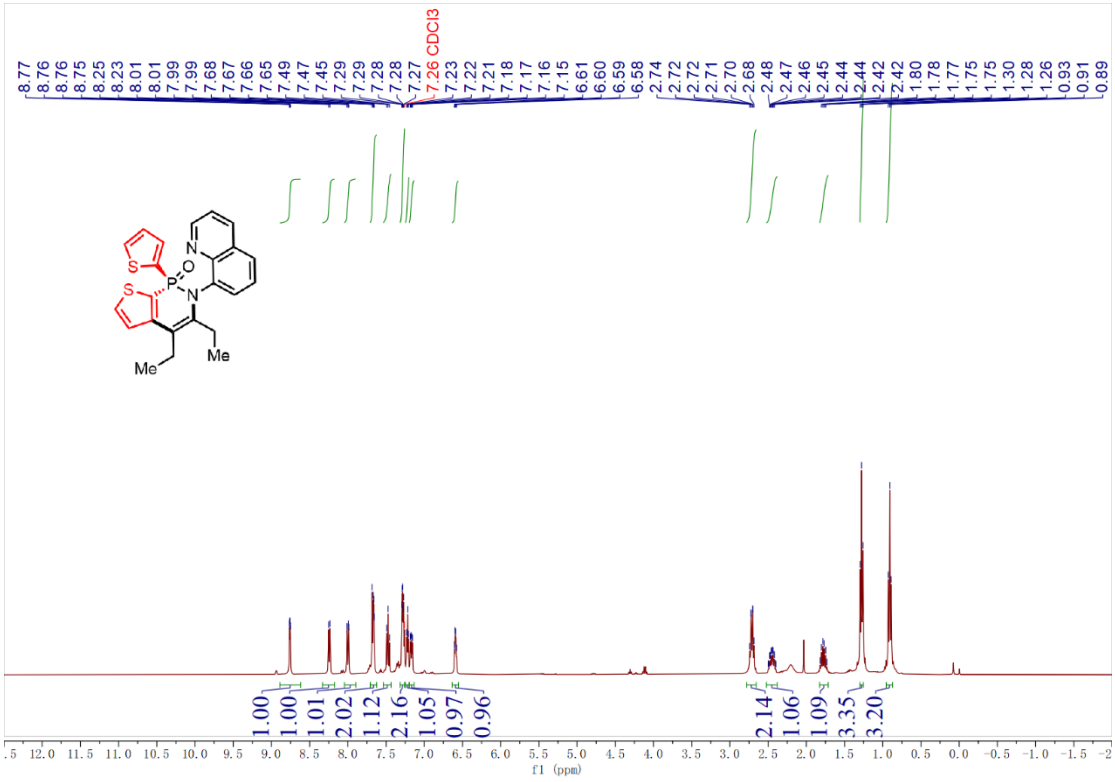
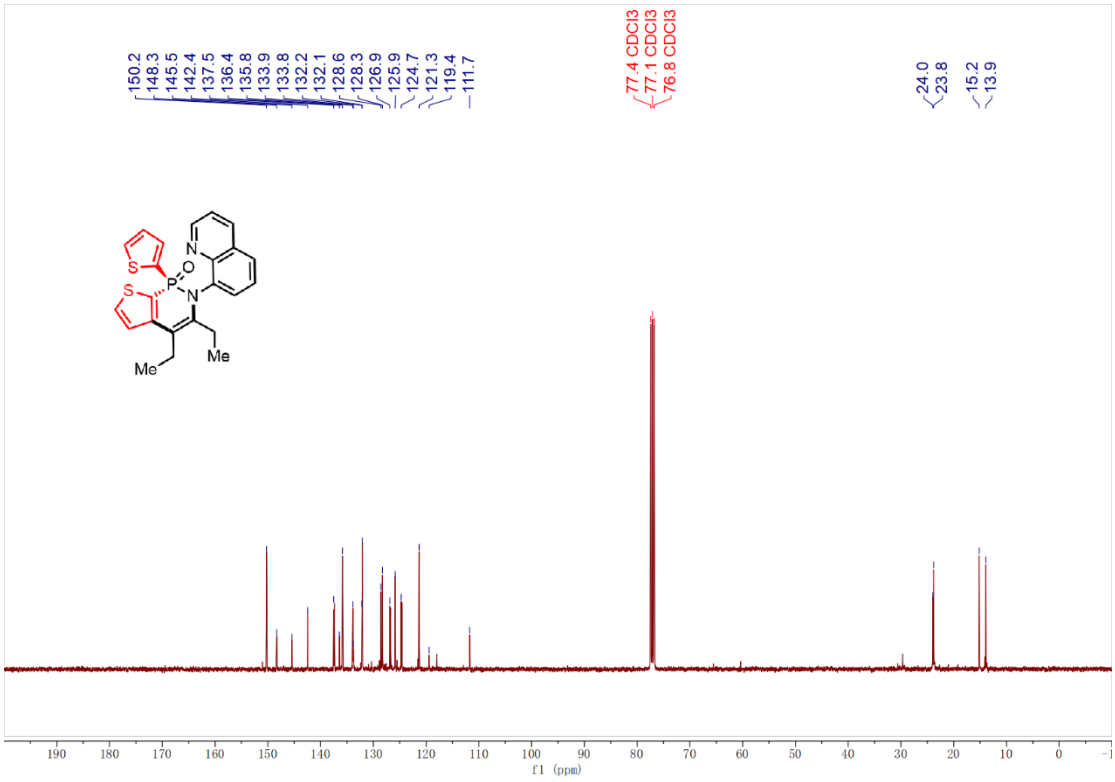


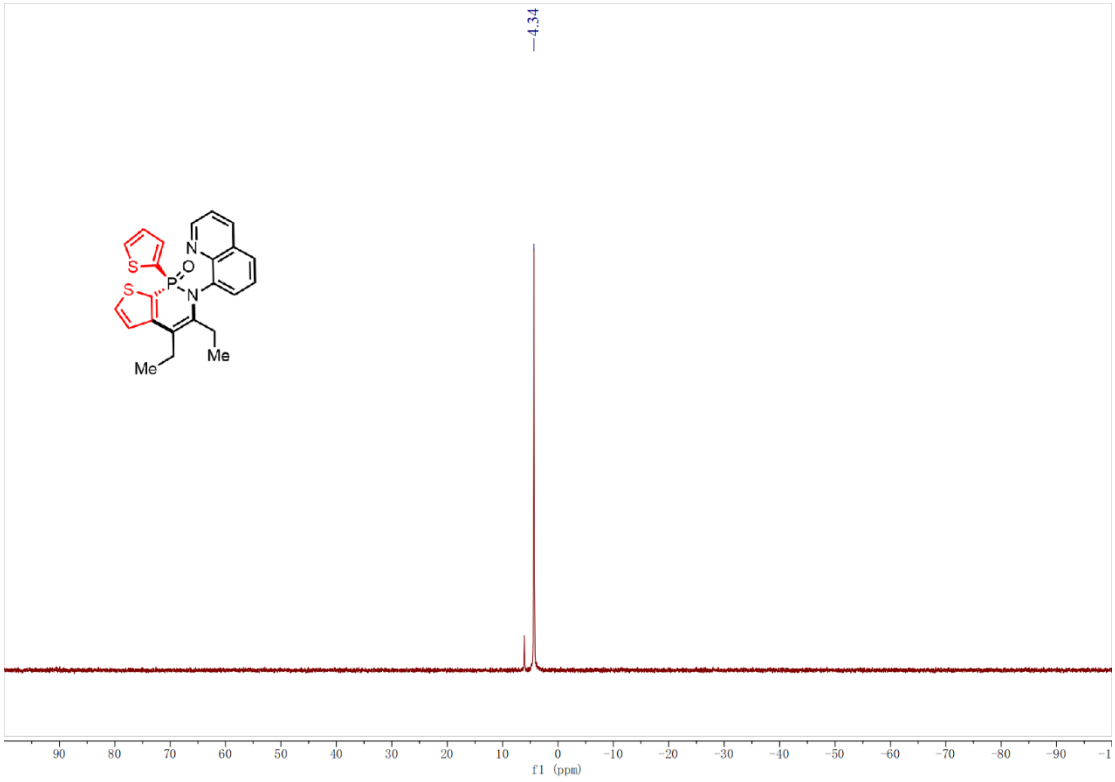
^{1}H-NMR of **3ap**



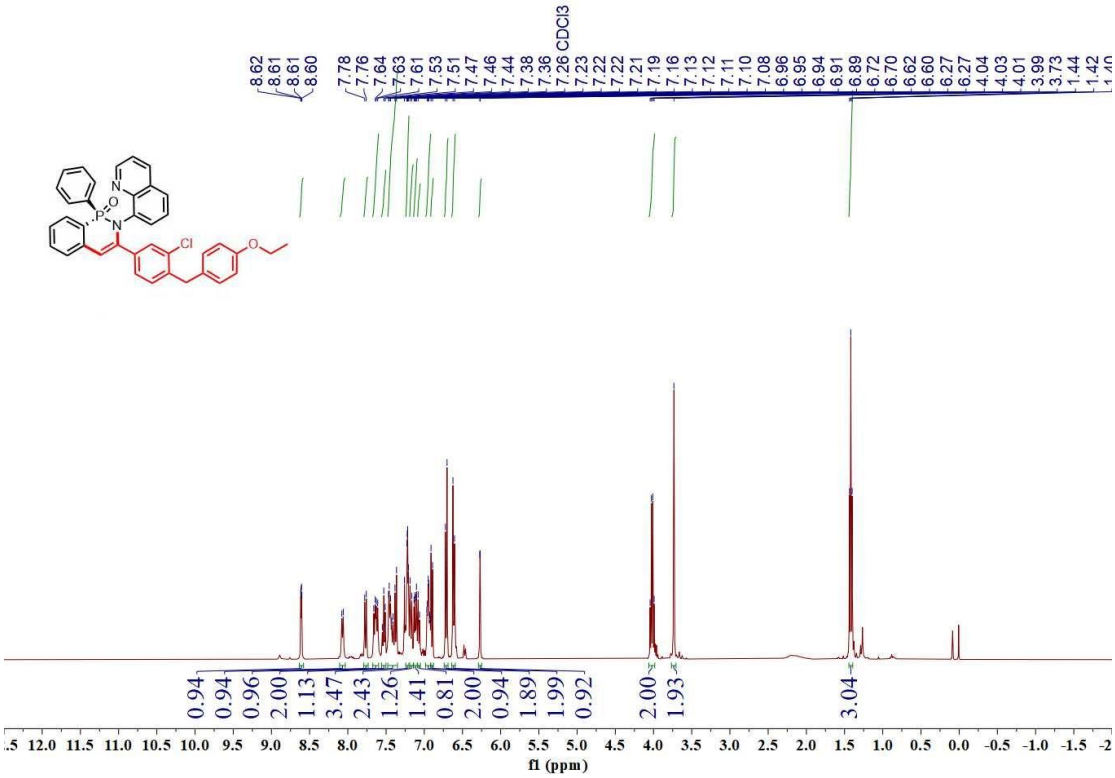
^{13}C-NMR of **3ap**



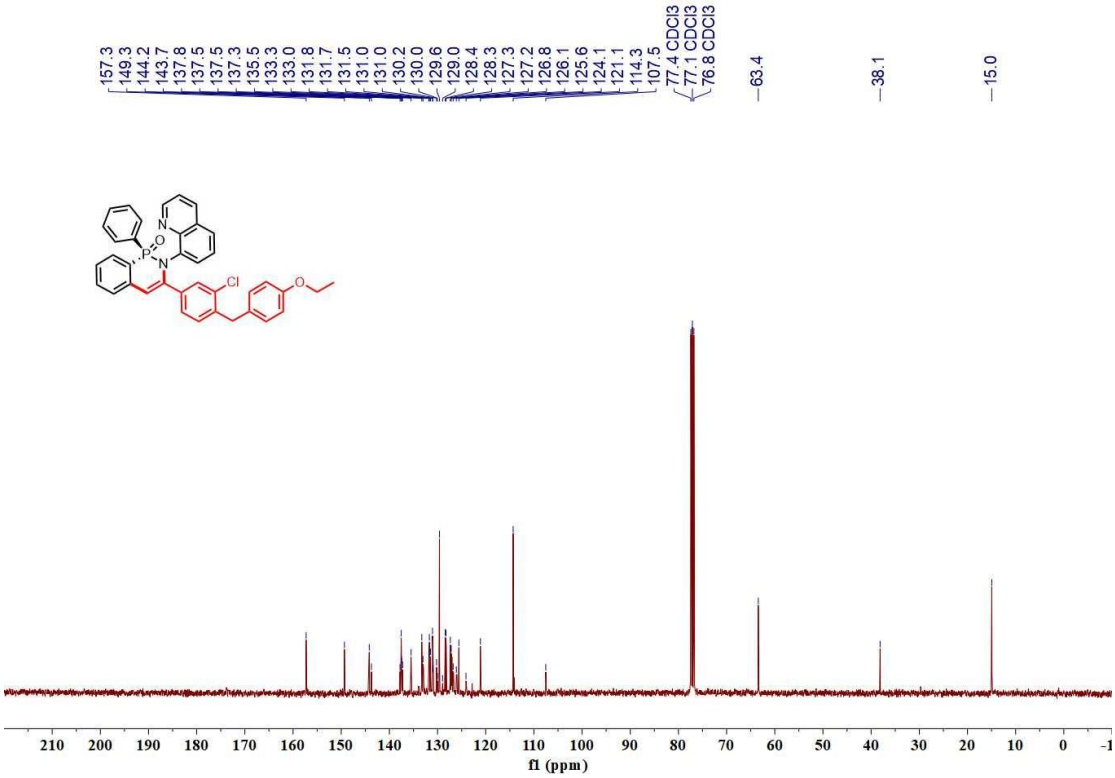
^{31}P-NMR of **3ap**



^{1}H-NMR of **4a**



^{13}C-NMR of **4a**



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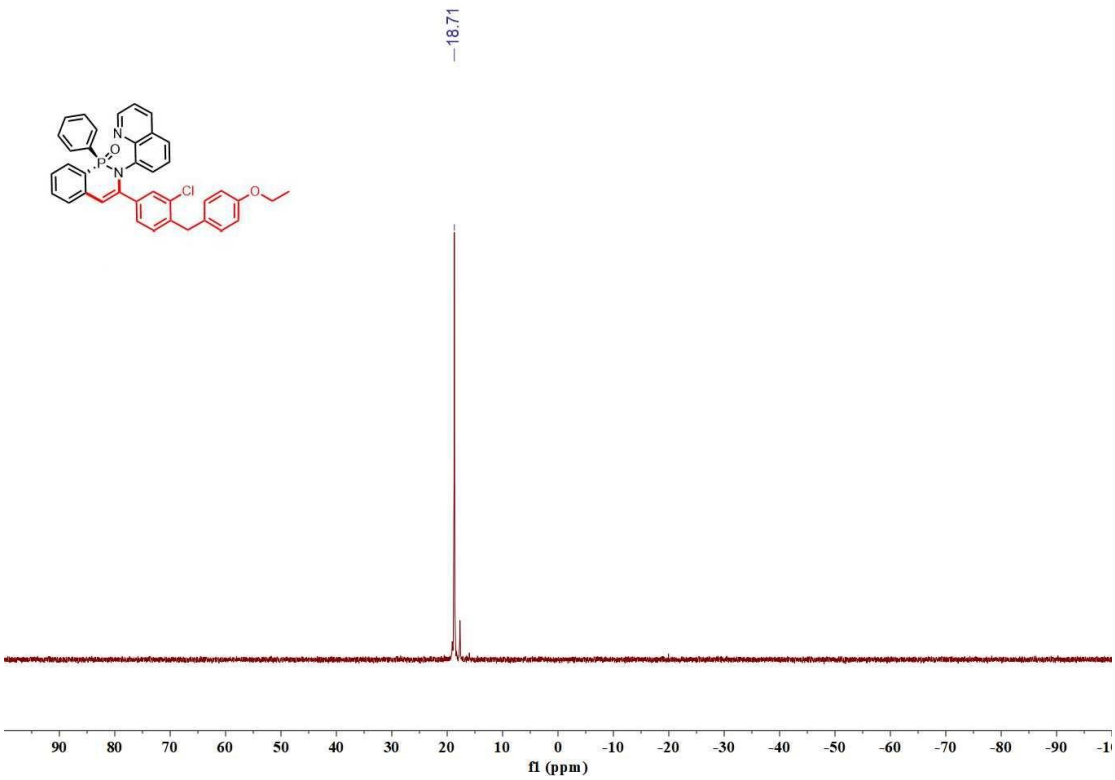
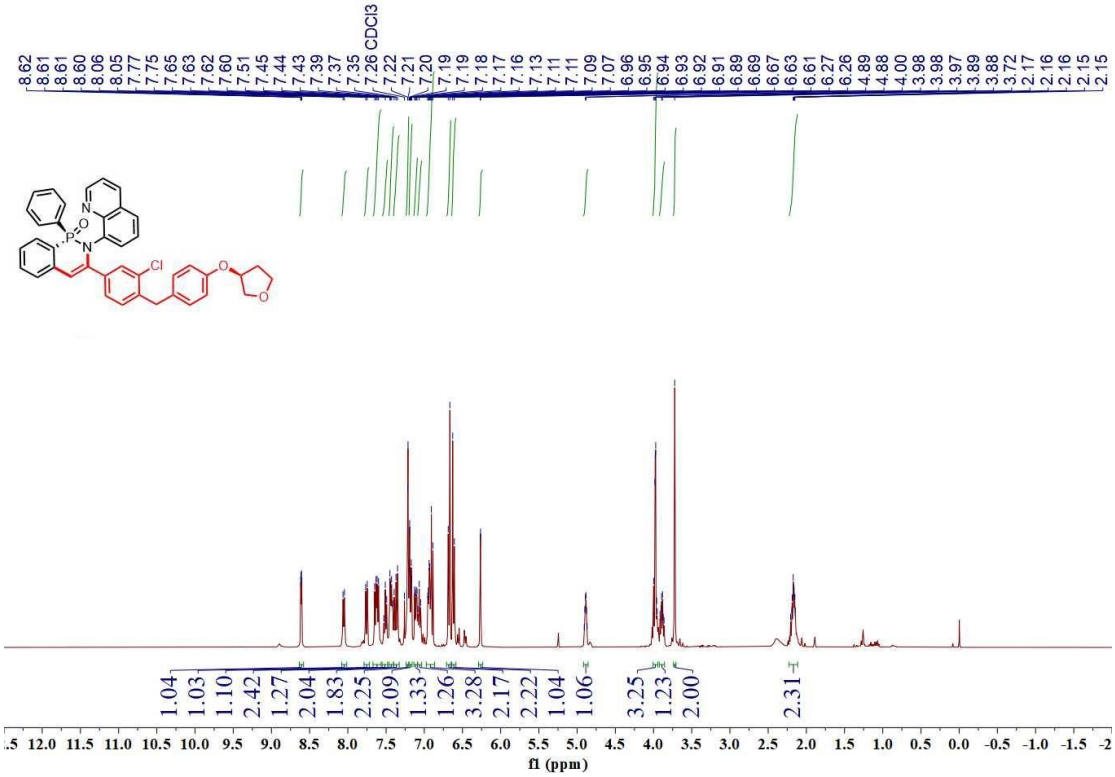
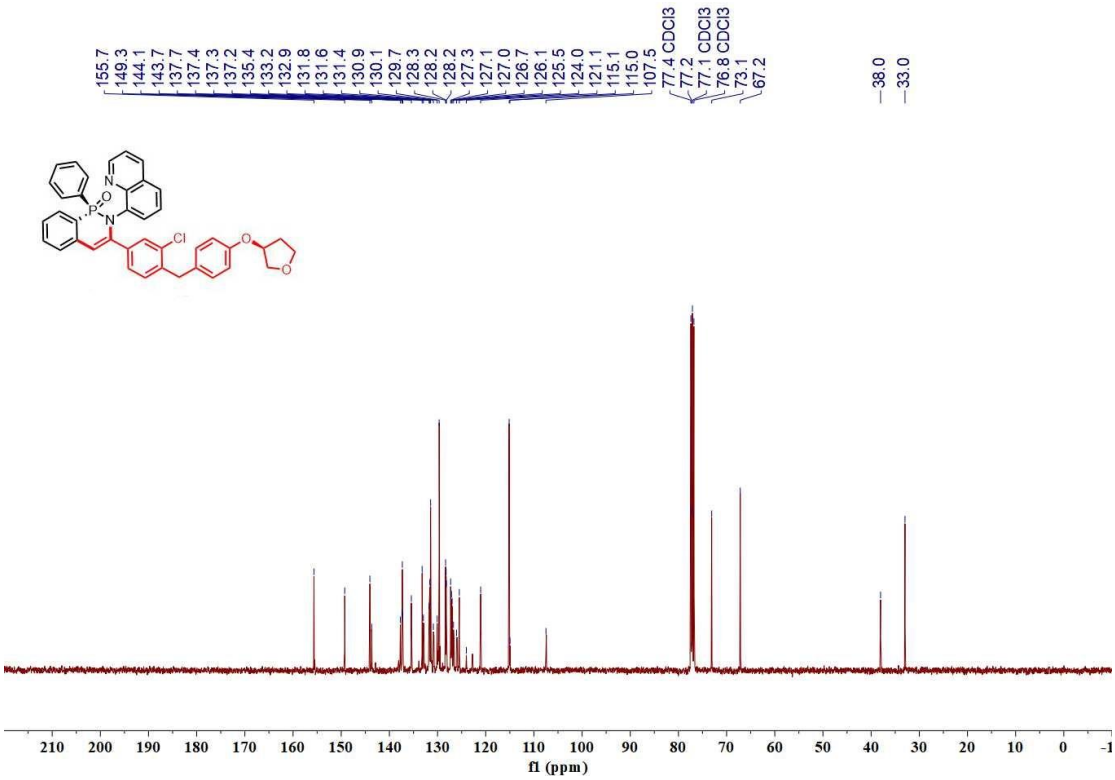


^{1}H-NMR of **4b**



^{13}C-NMR of **4b**



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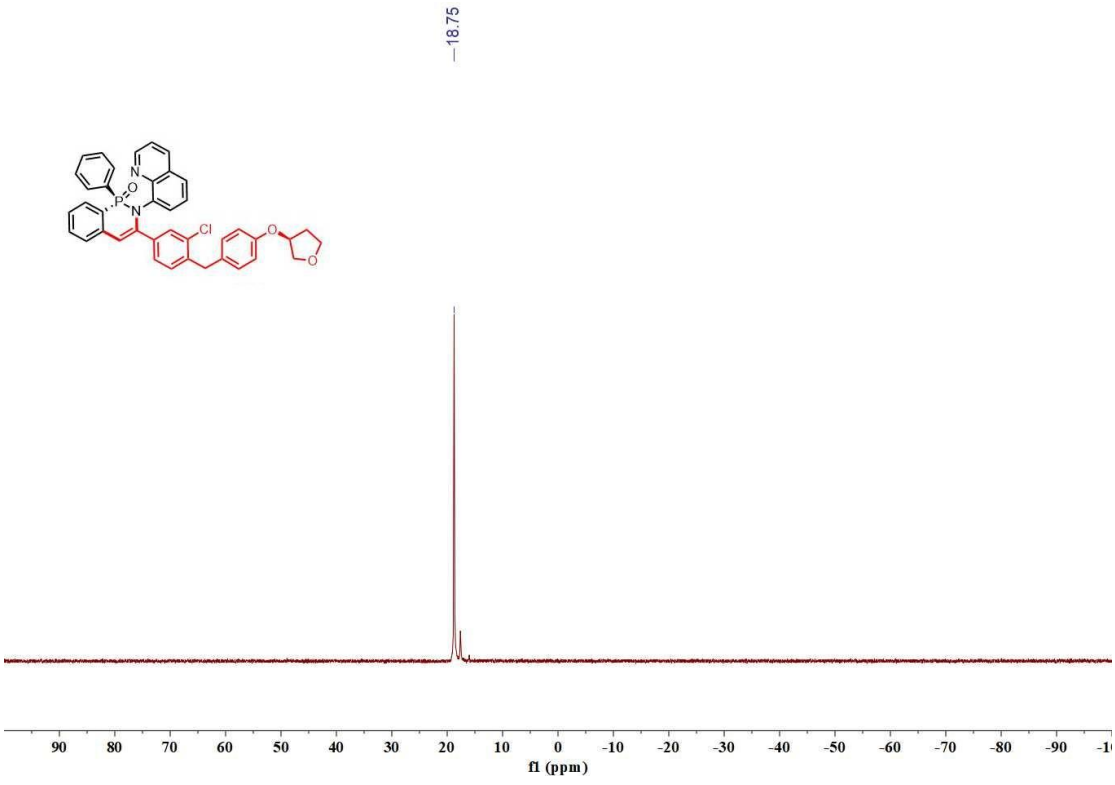
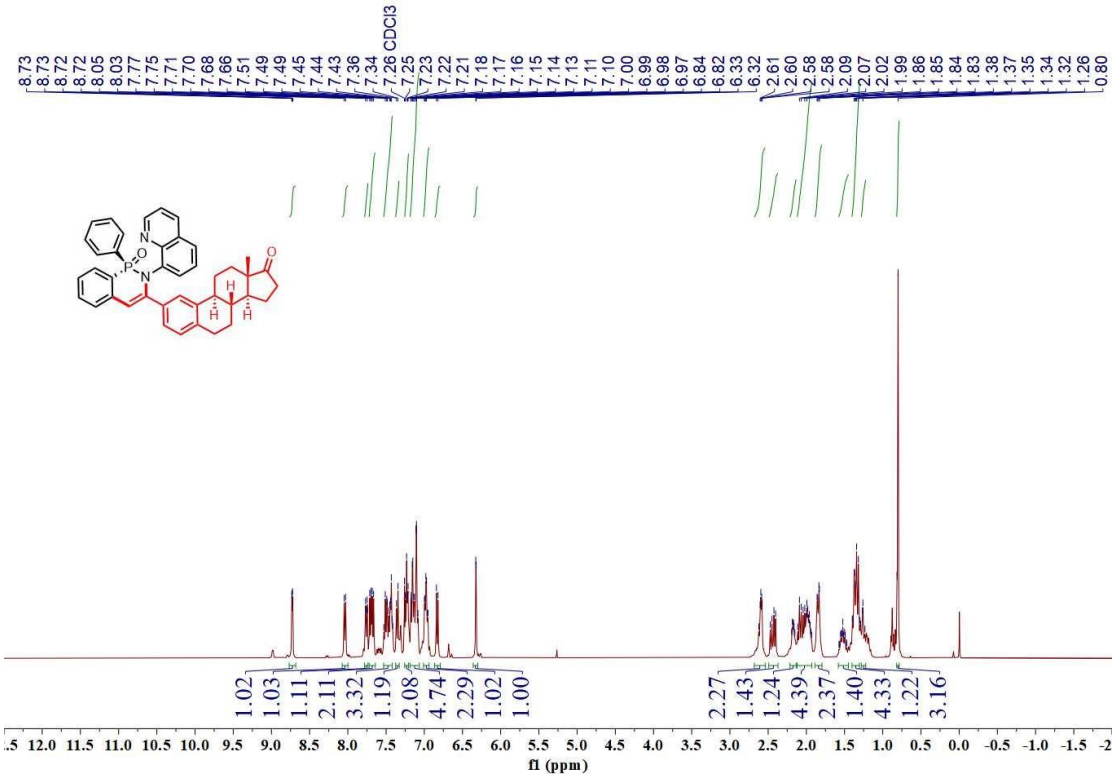


^{1}H-NMR of **4c**



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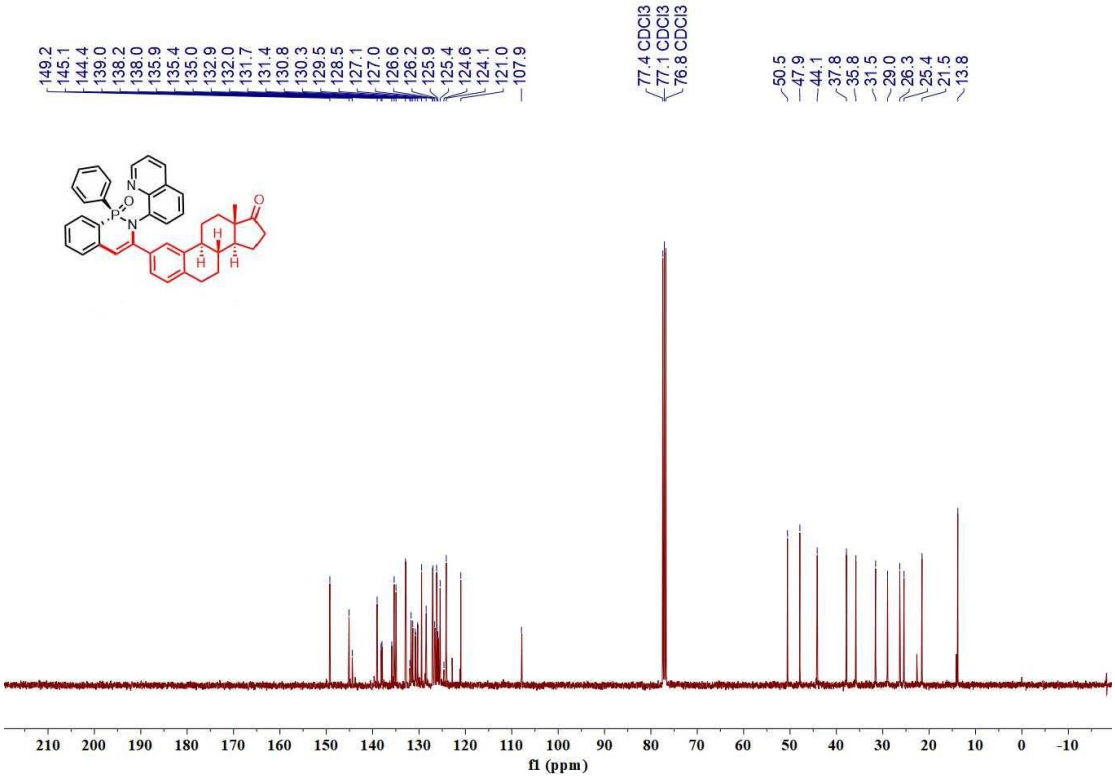

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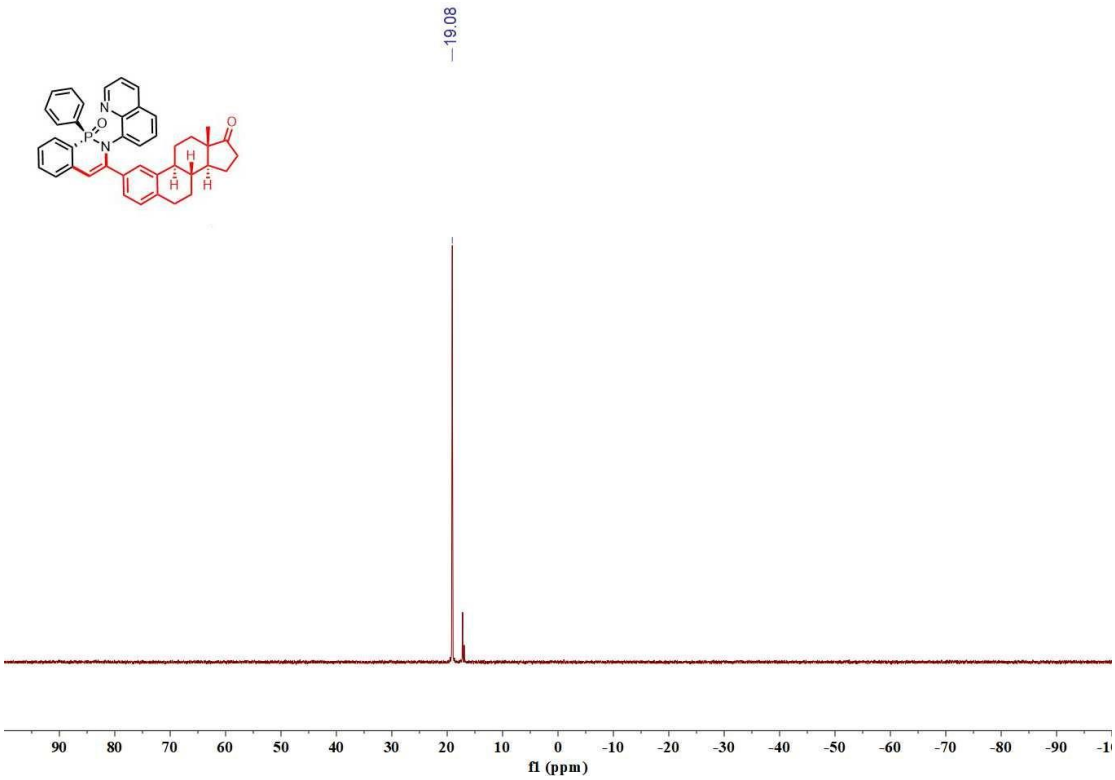

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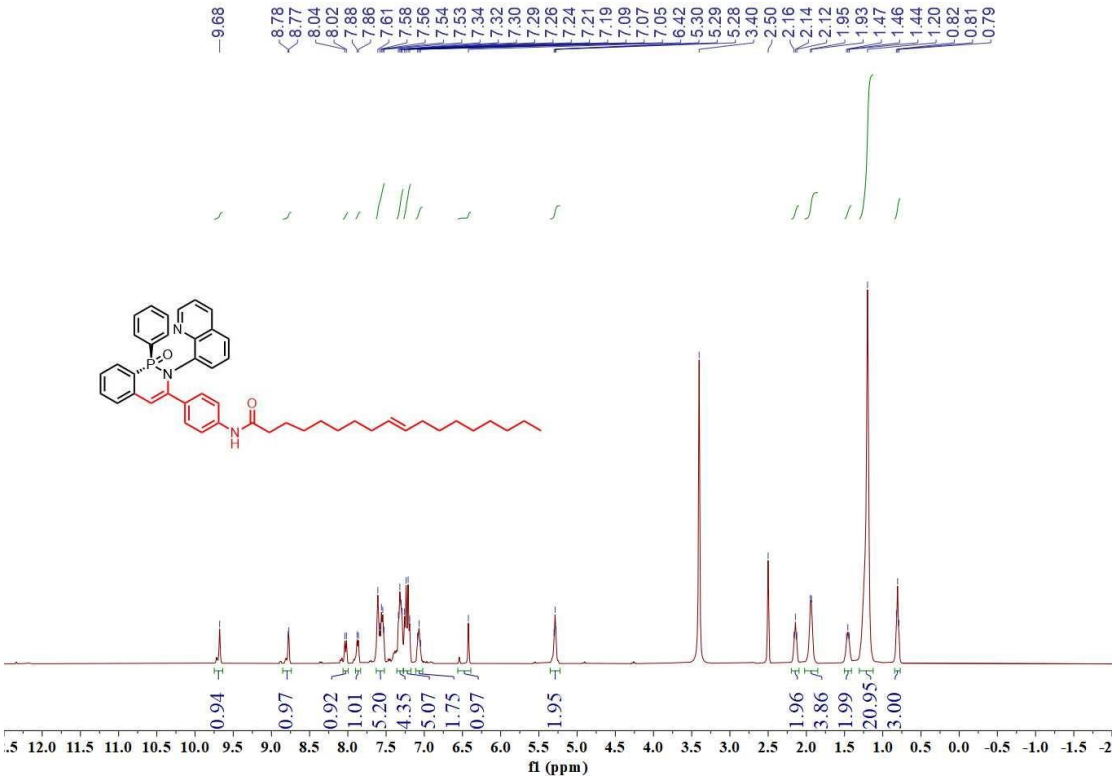

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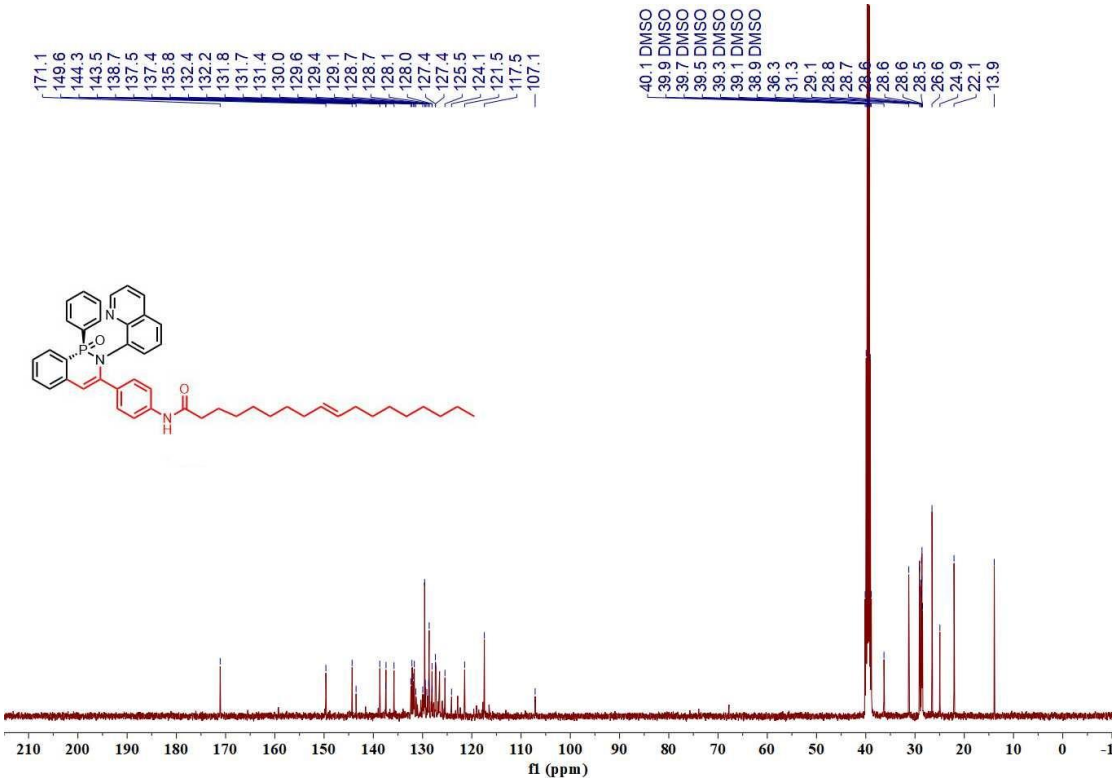

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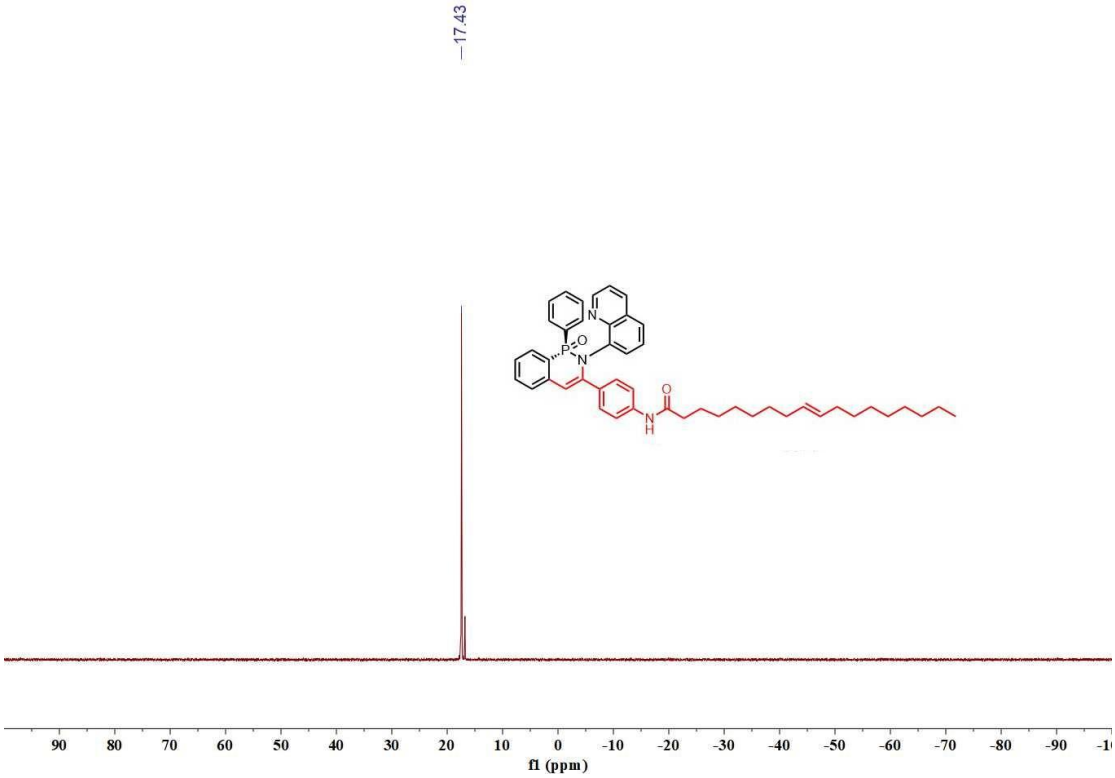

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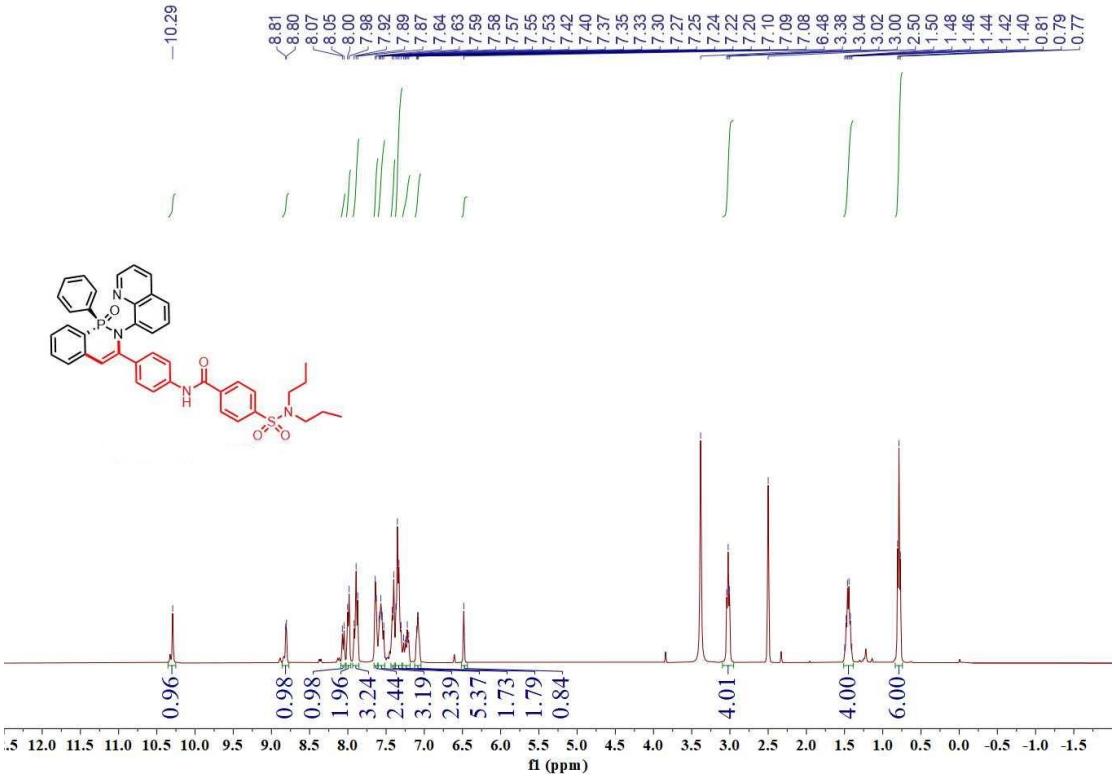

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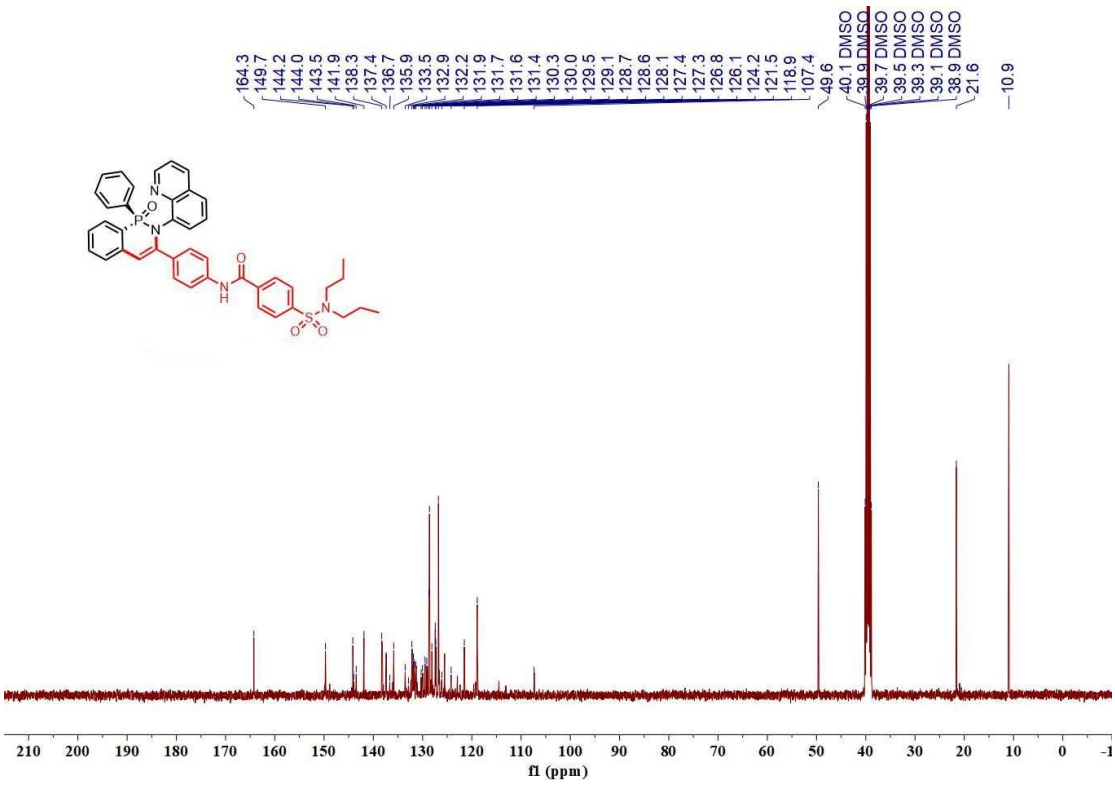

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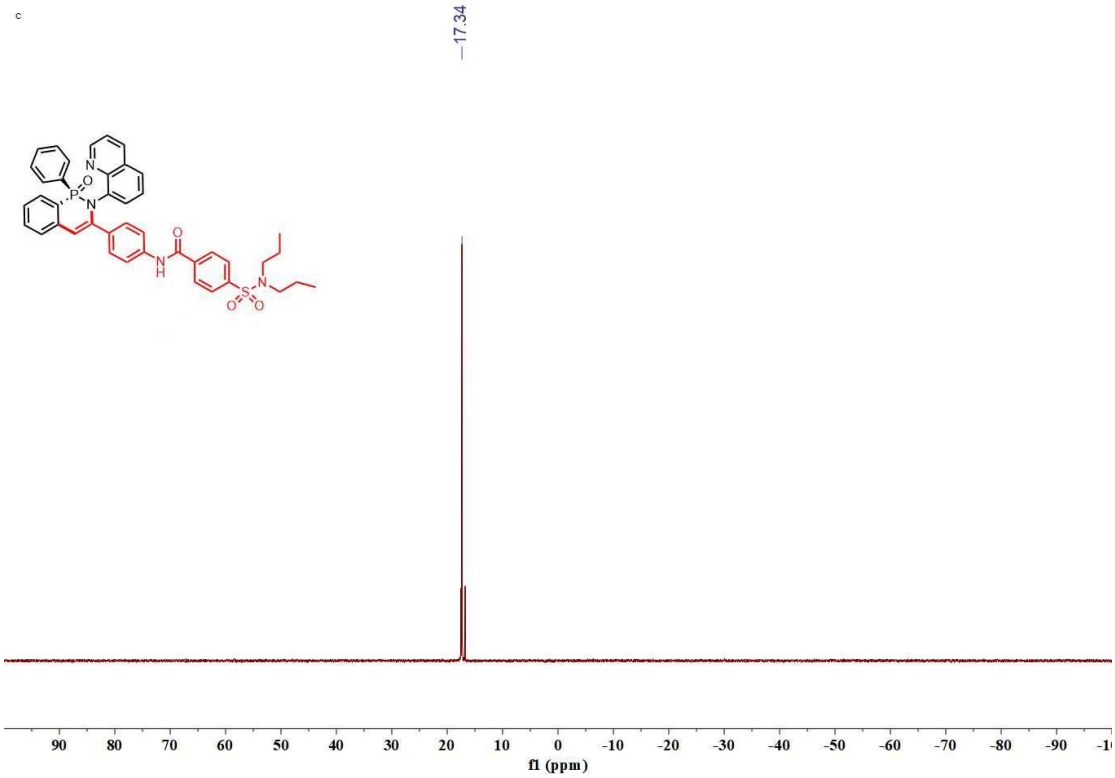
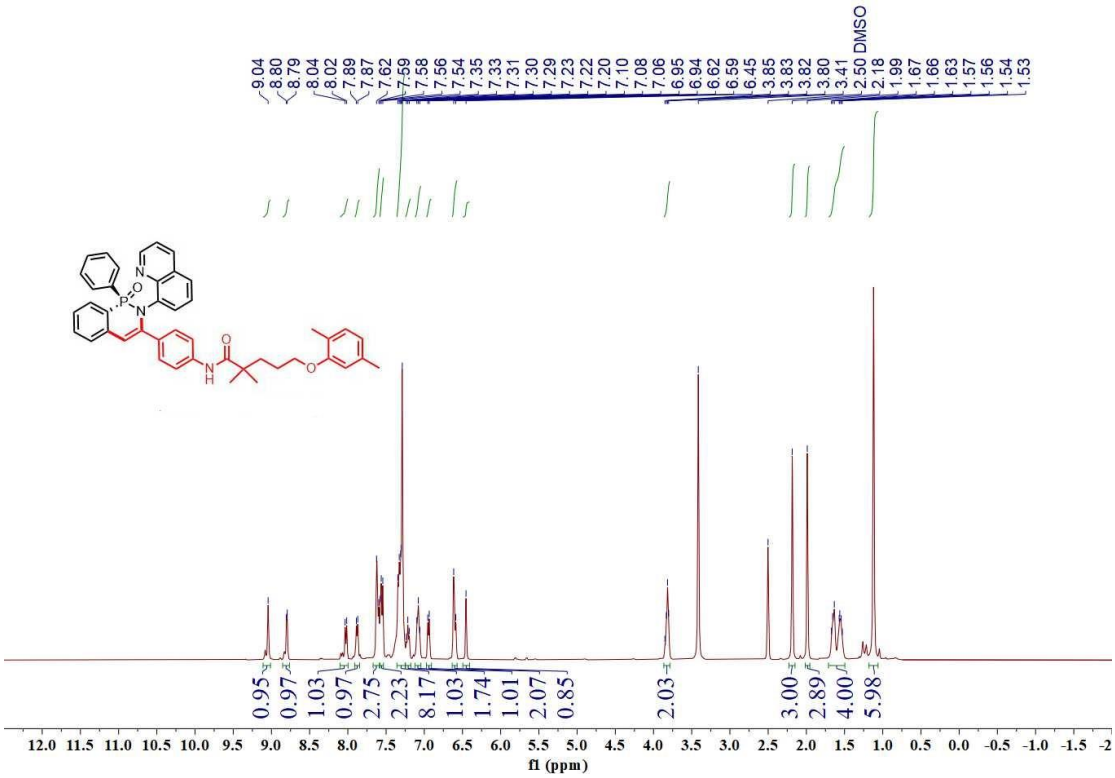


^{1}H-NMR of **4f**



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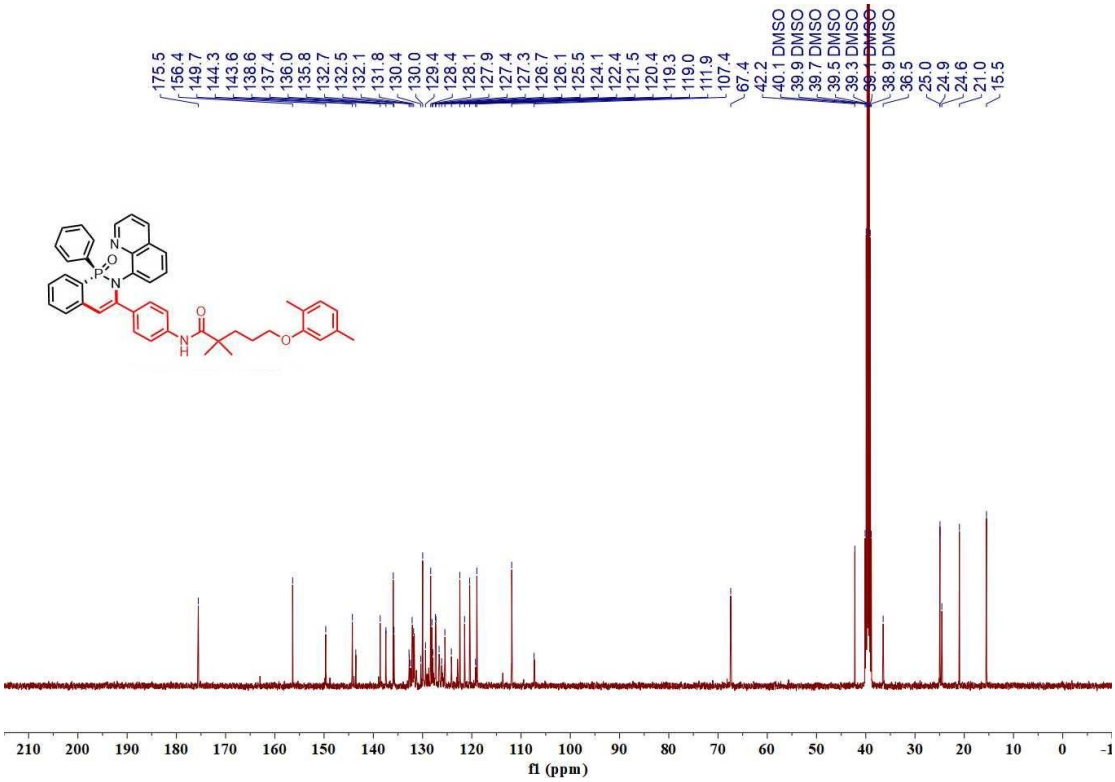

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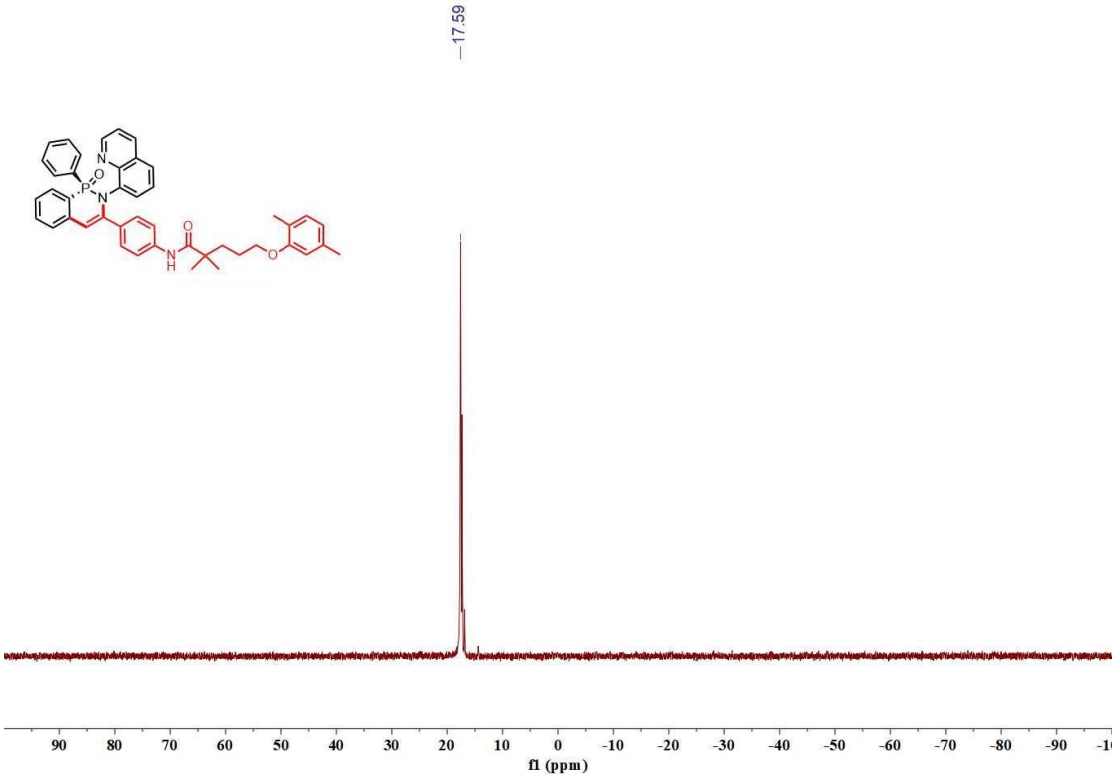
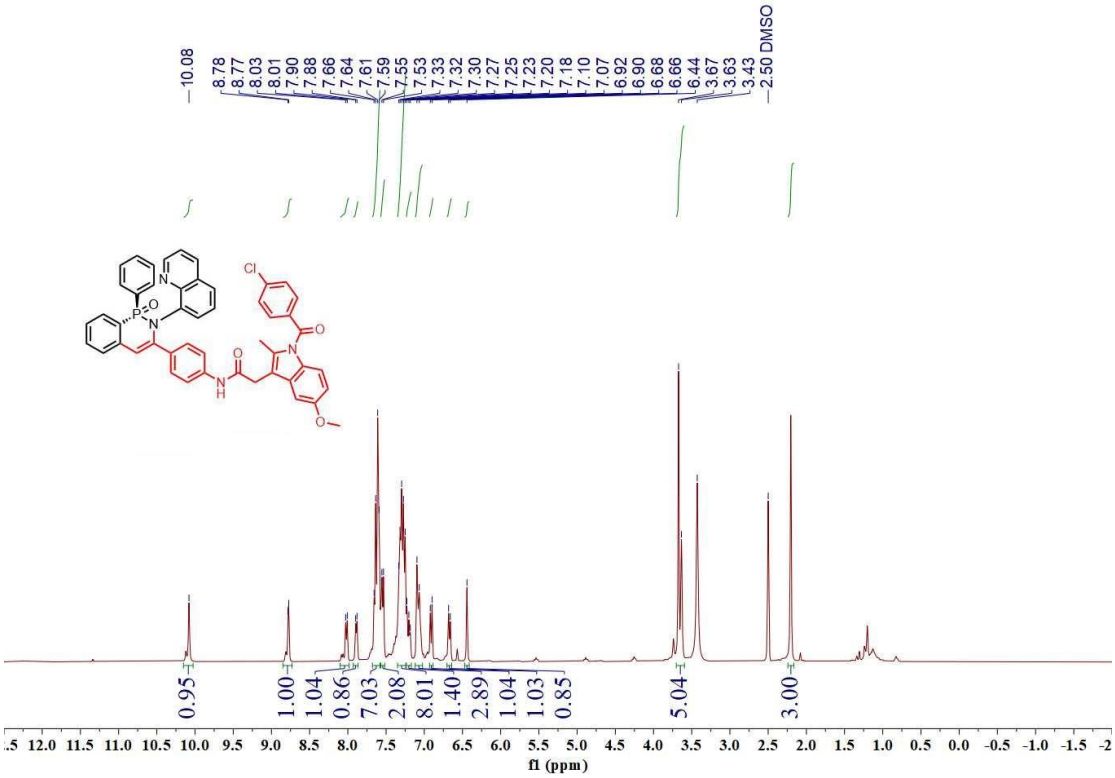
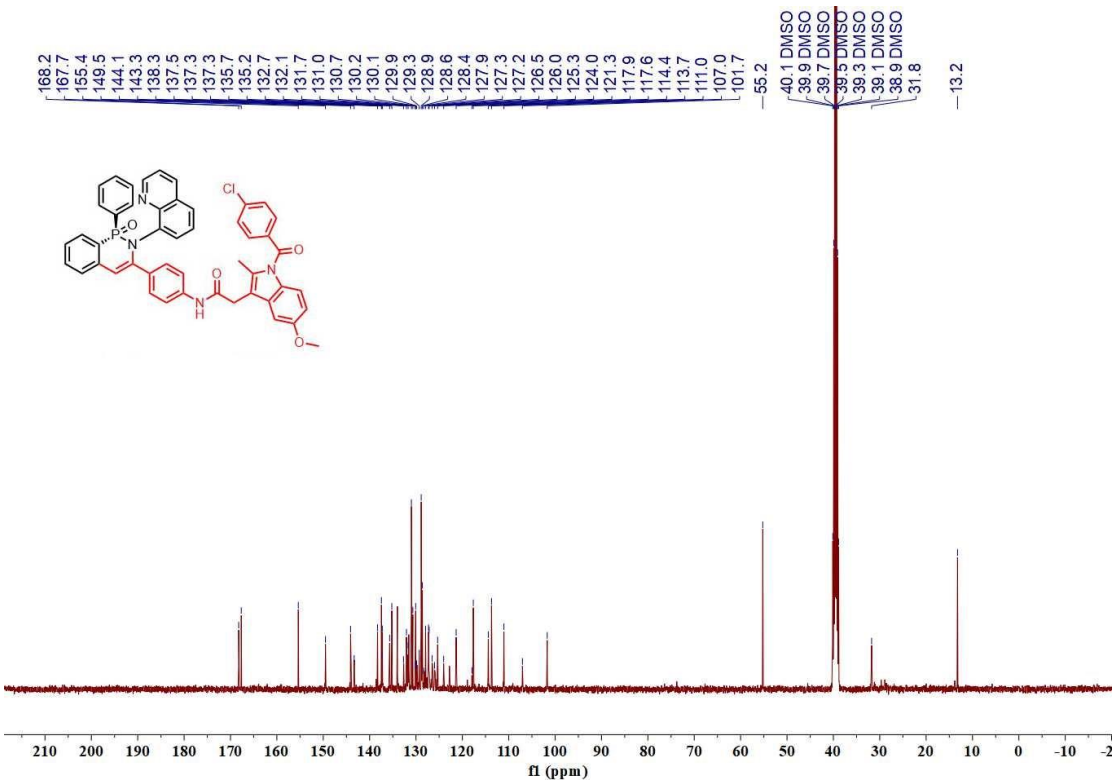


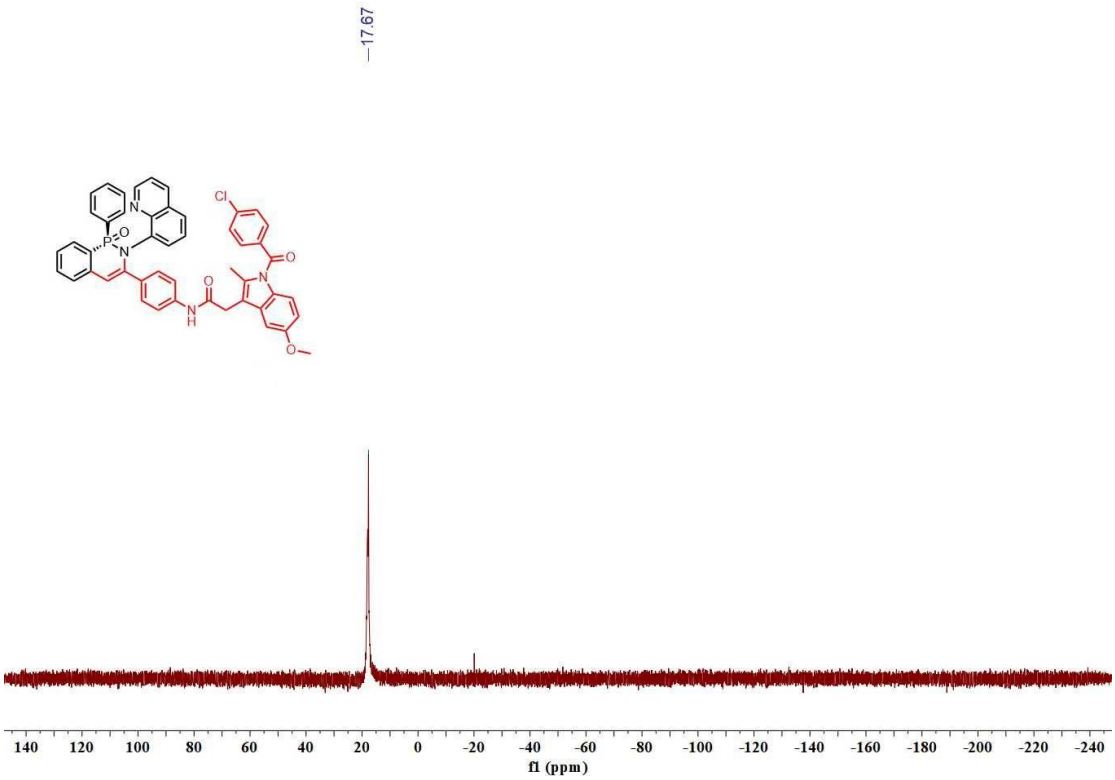
^{1}H-NMR of **4g**



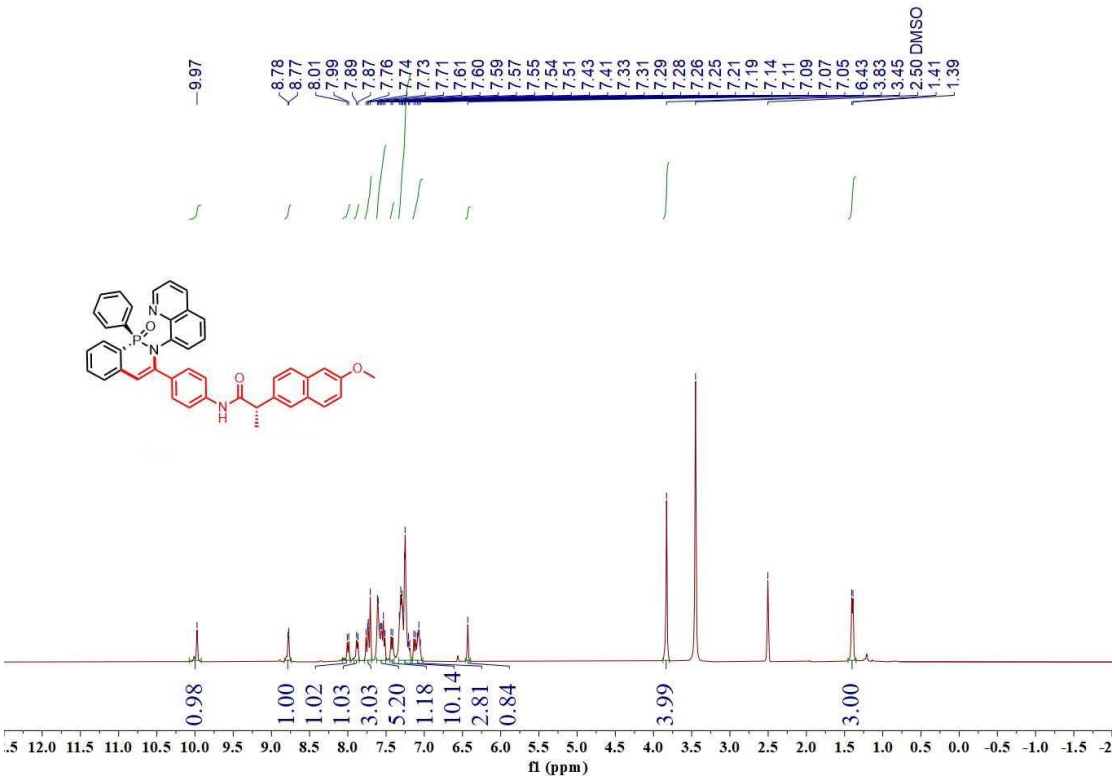
^{13}C-NMR of **4g**



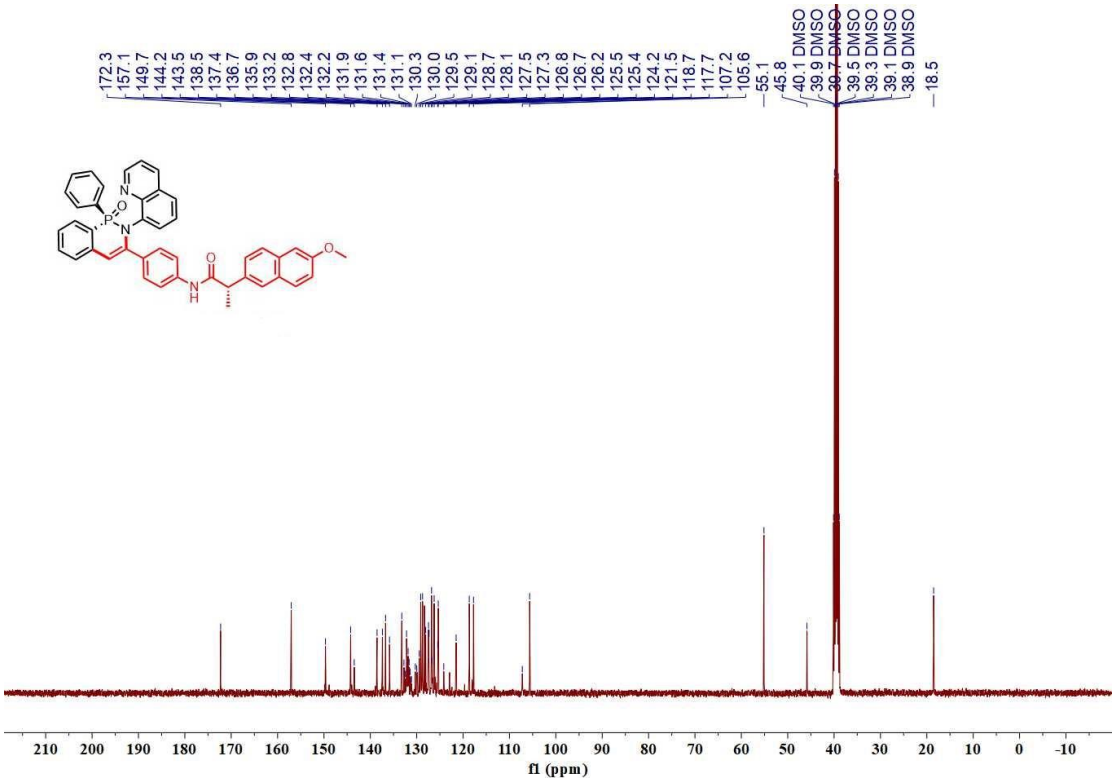
^{31}P-NMR of **4g**



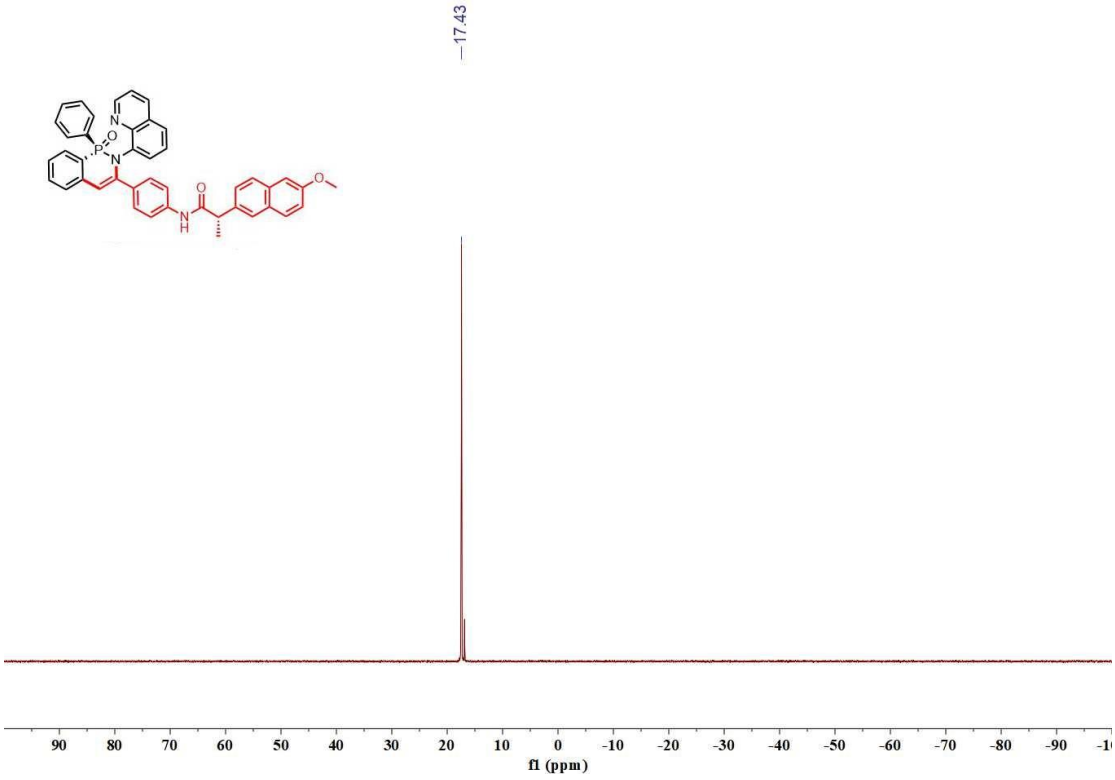
^{1}H-NMR of **4h**



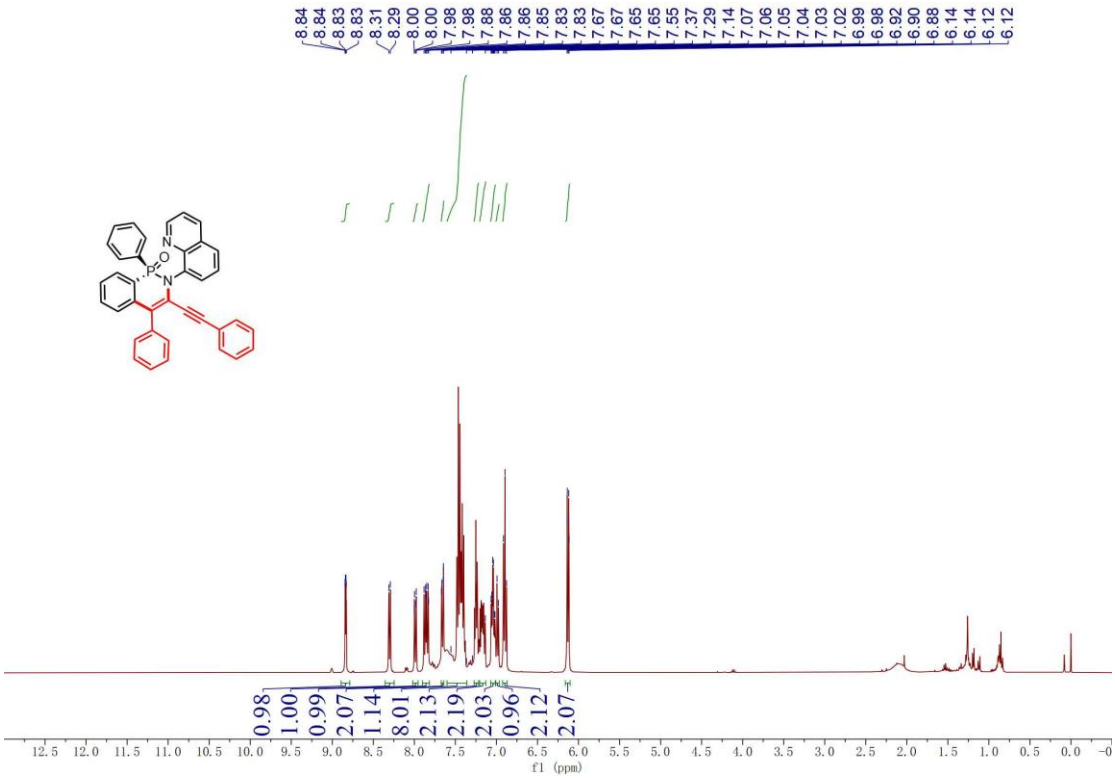
^{13}C-NMR of **4h**



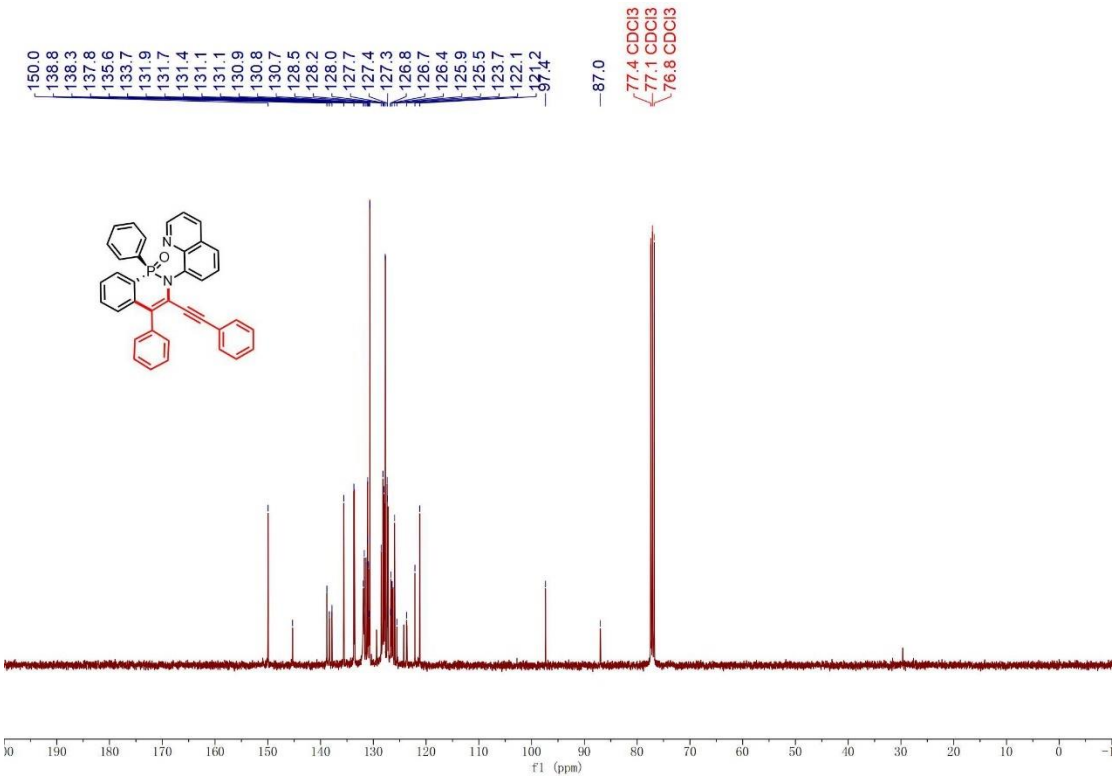
^{31}P-NMR of **4h**



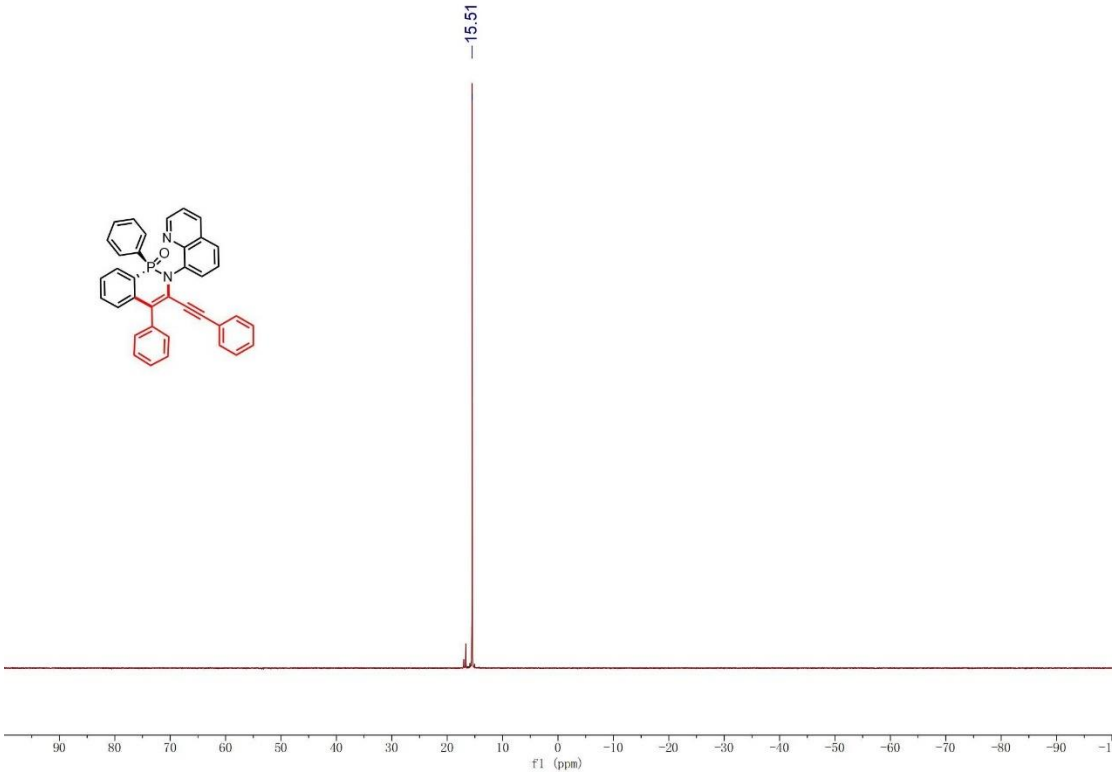
^{1}H-NMR of **5a**



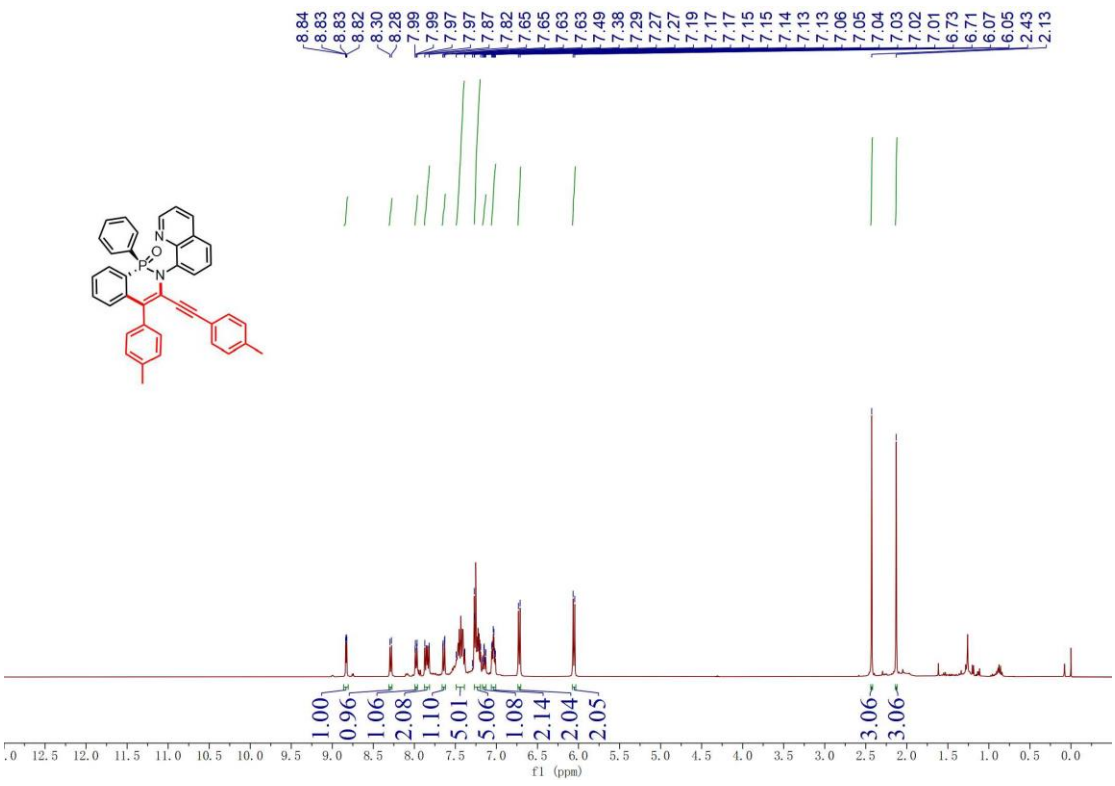
^{13}C-NMR of **5a**



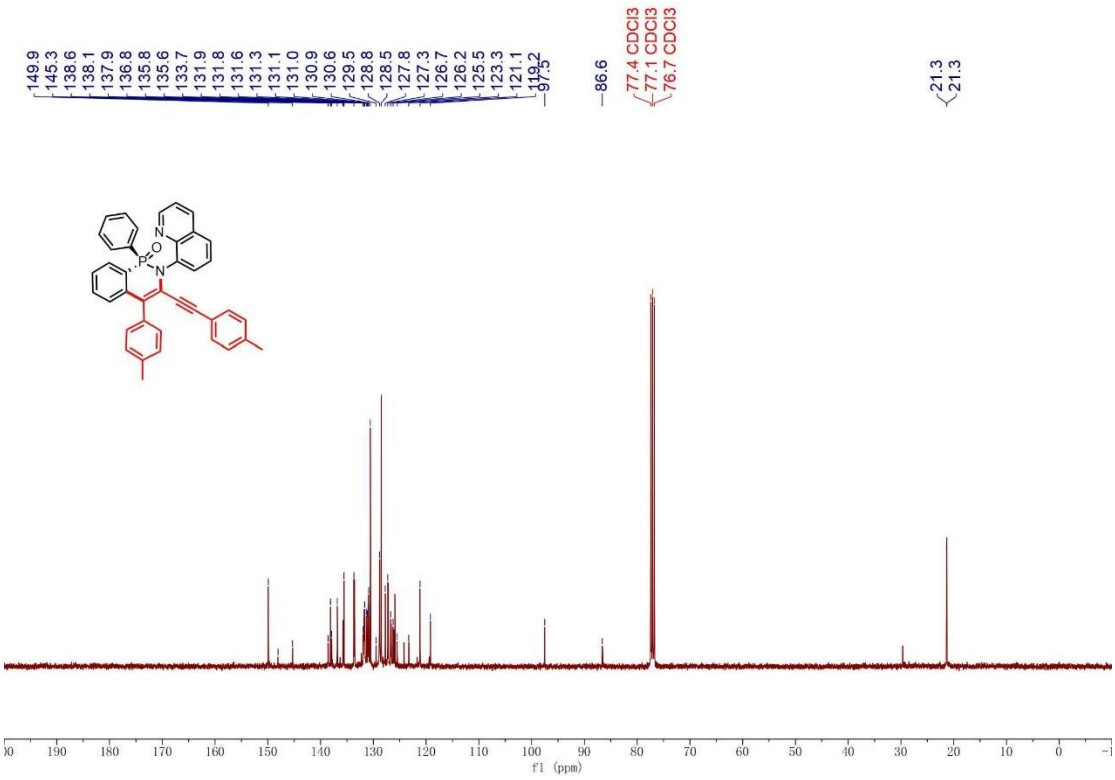
^{31}P-NMR of **5a**



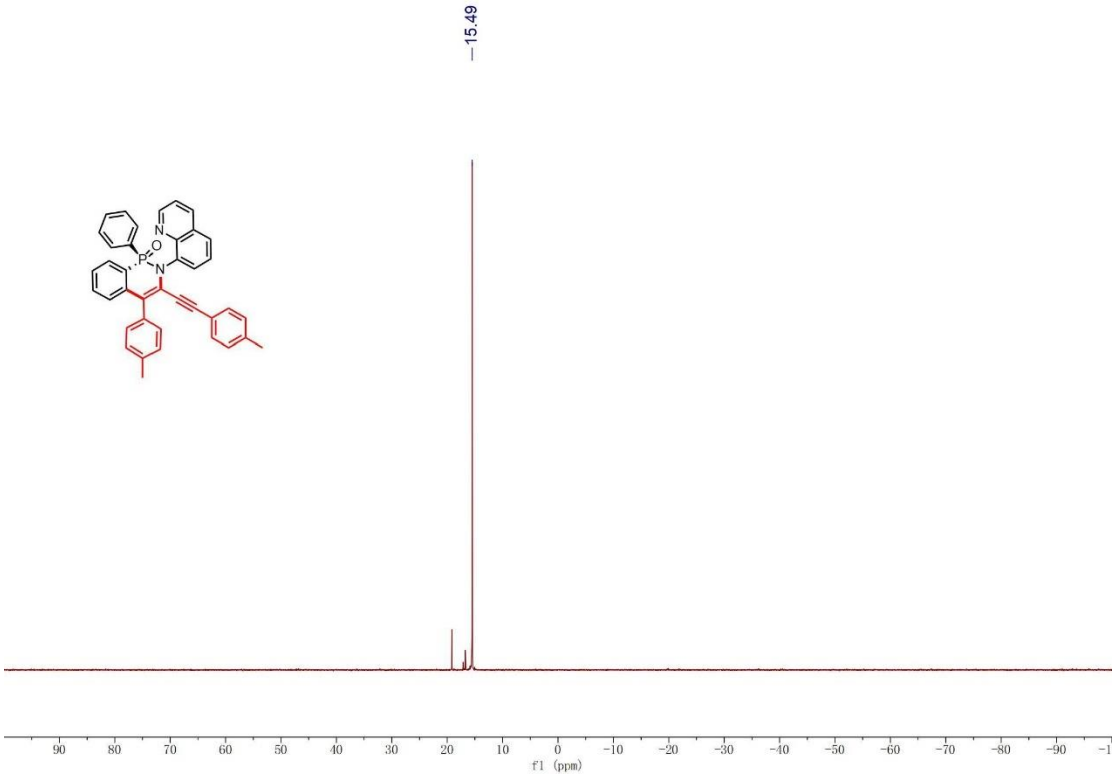
^{1}H-NMR of **5b**



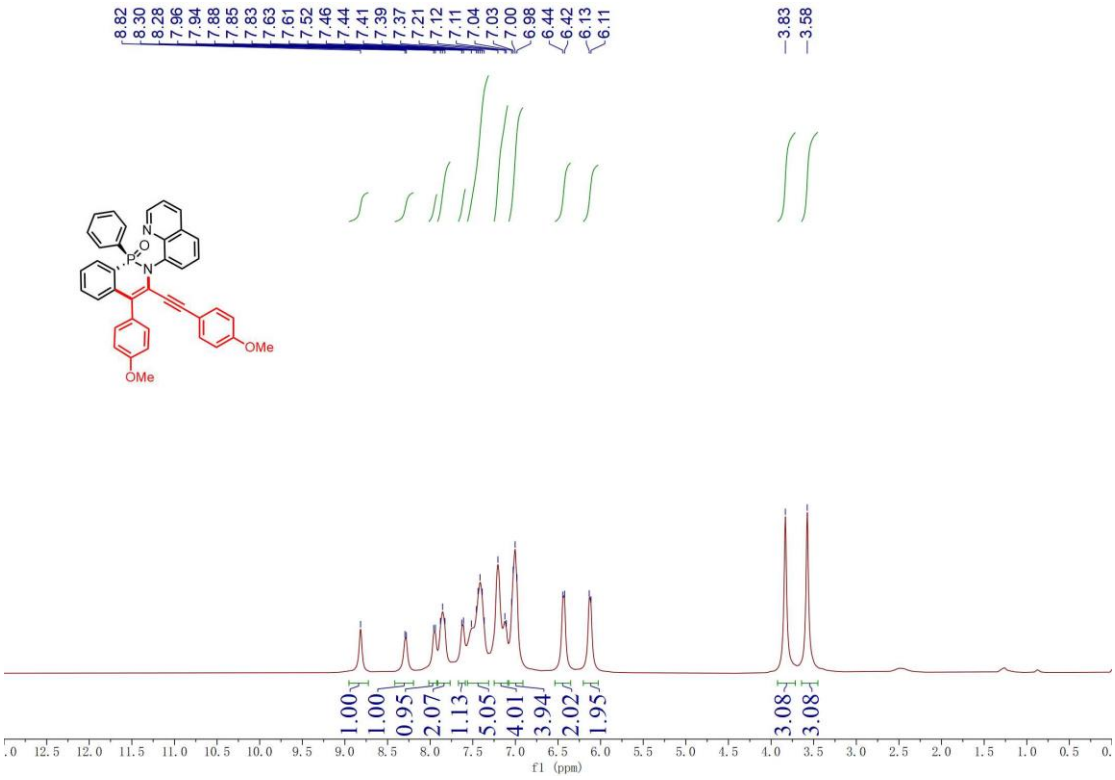
^{13}C-NMR of **5b**



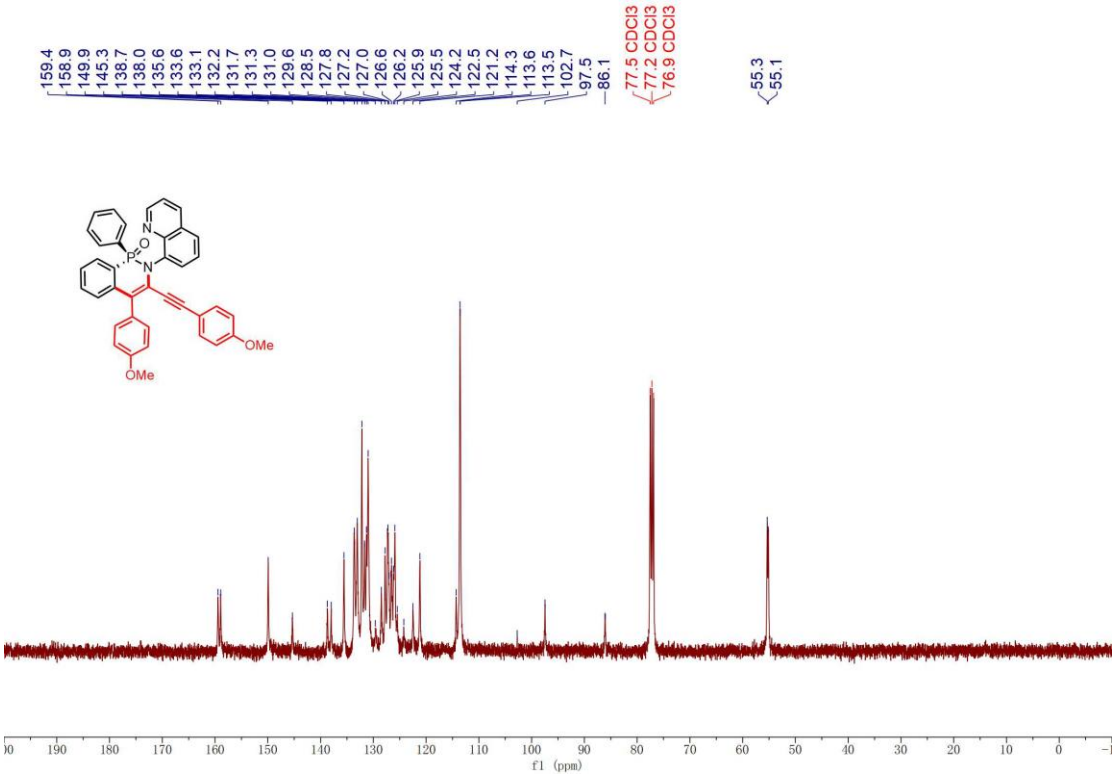
^{31}P-NMR of **5b**



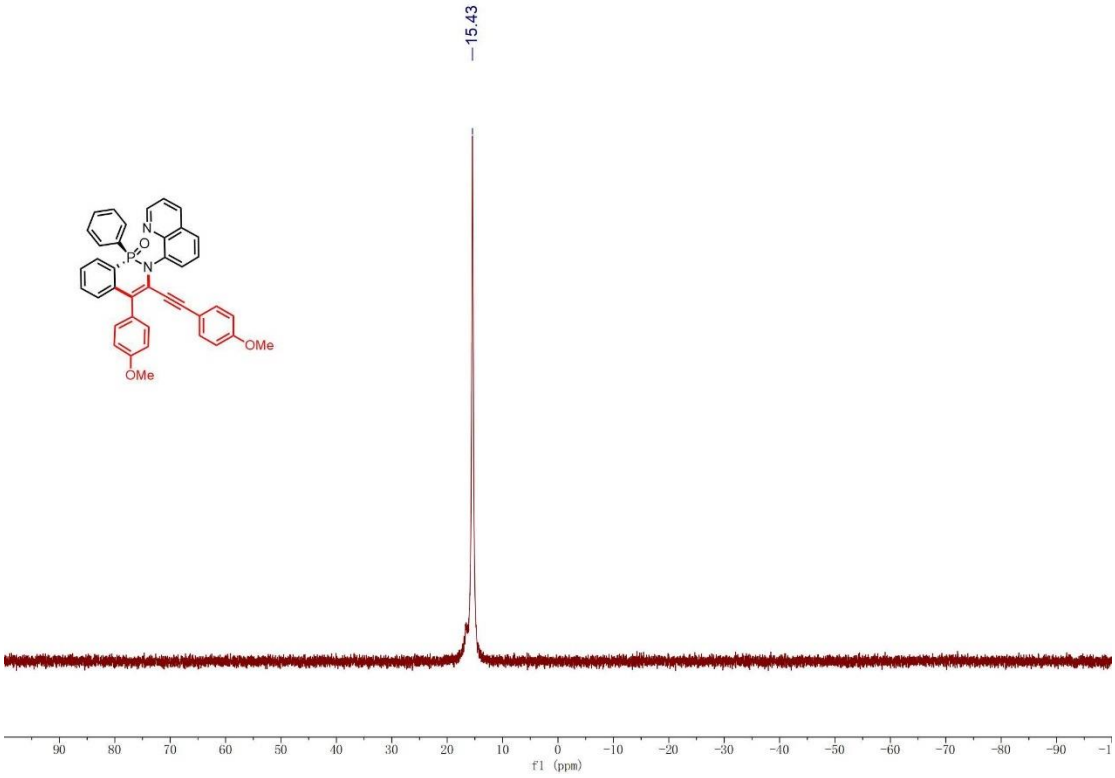
^{1}H-NMR of **5c**



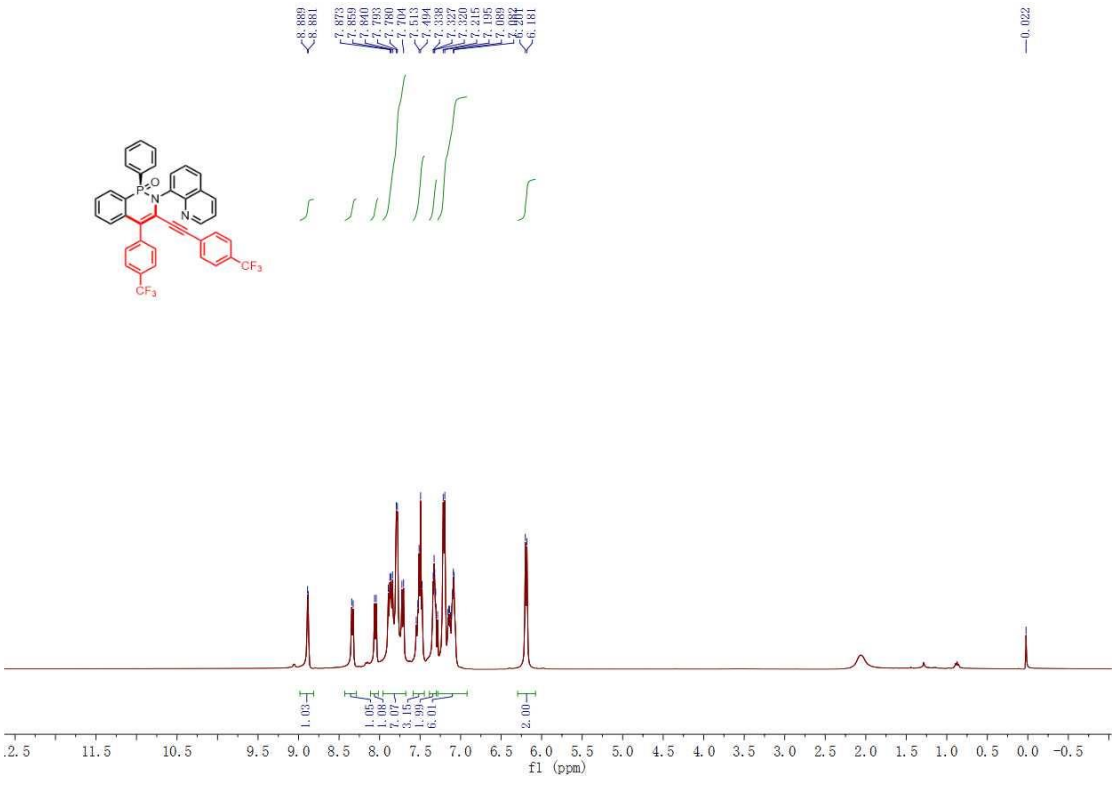
^{13}C-NMR of **5c**



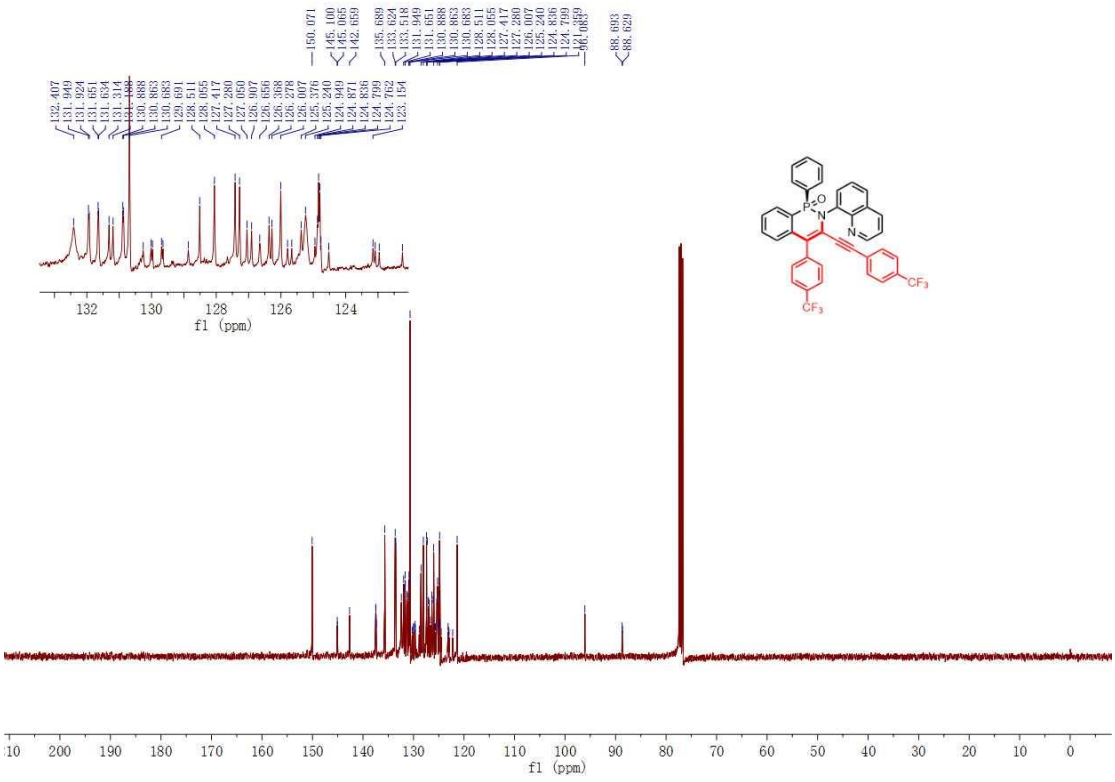
^{31}P-NMR of **5c**



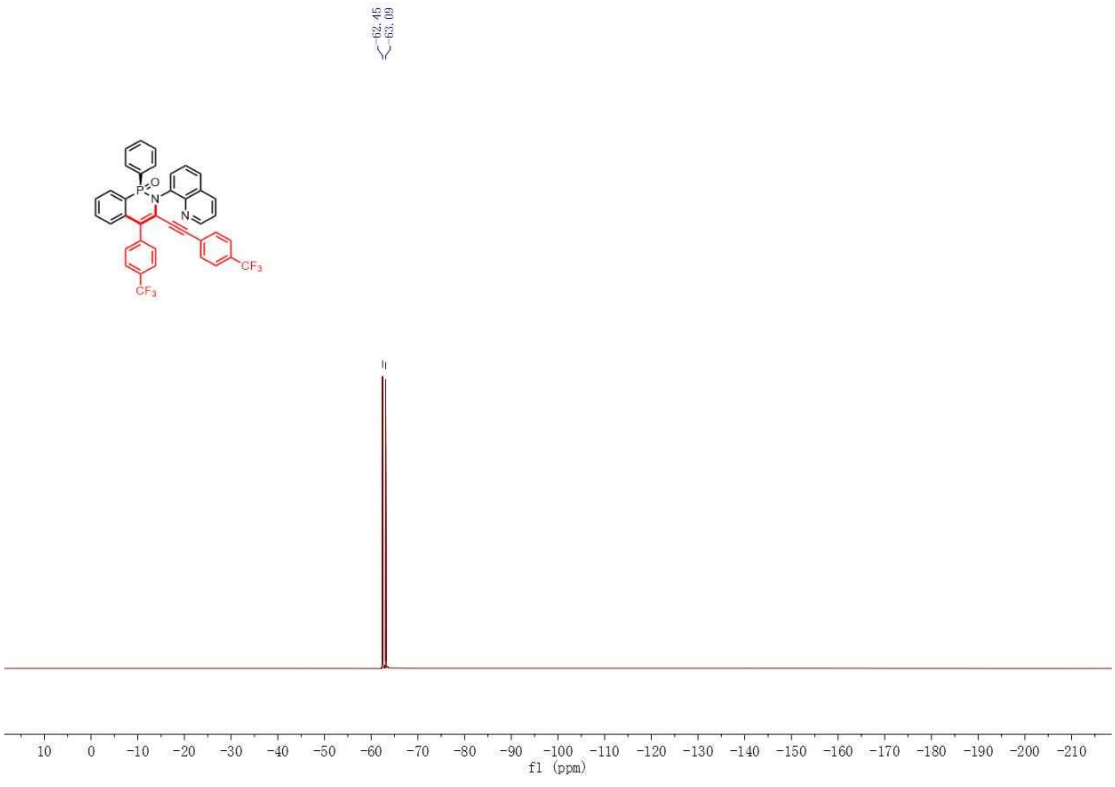
^{1}H-NMR of **5d**



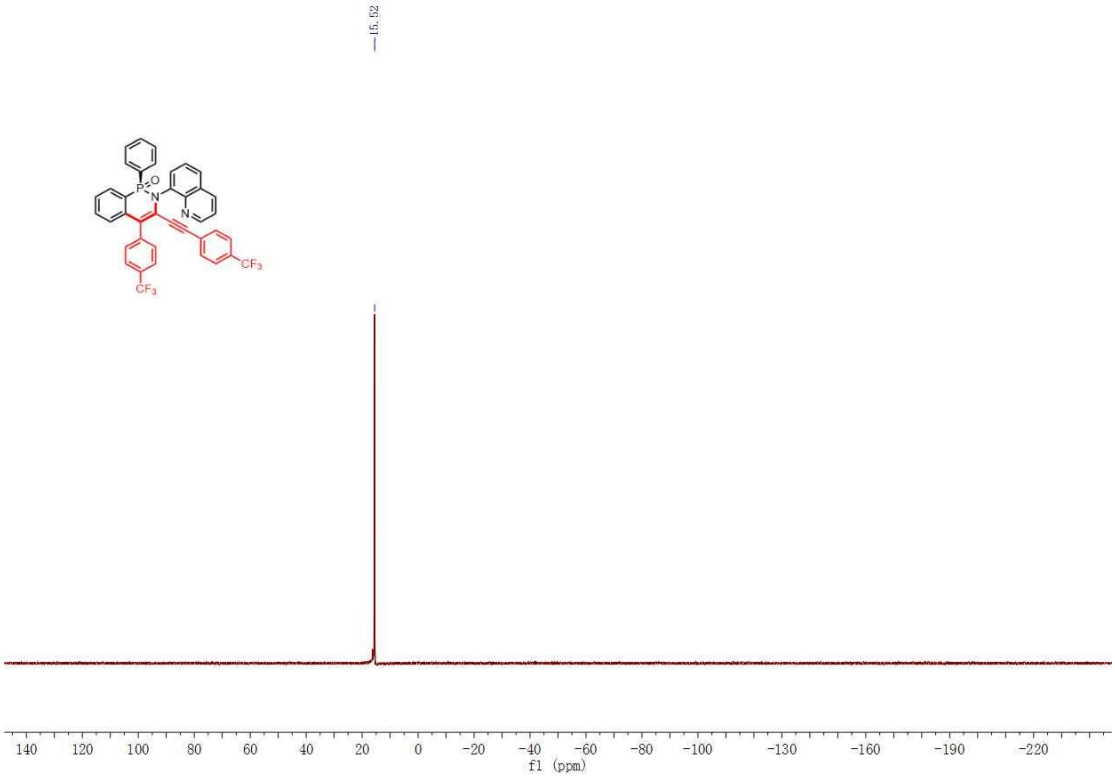
^{13}C-NMR of **5d**



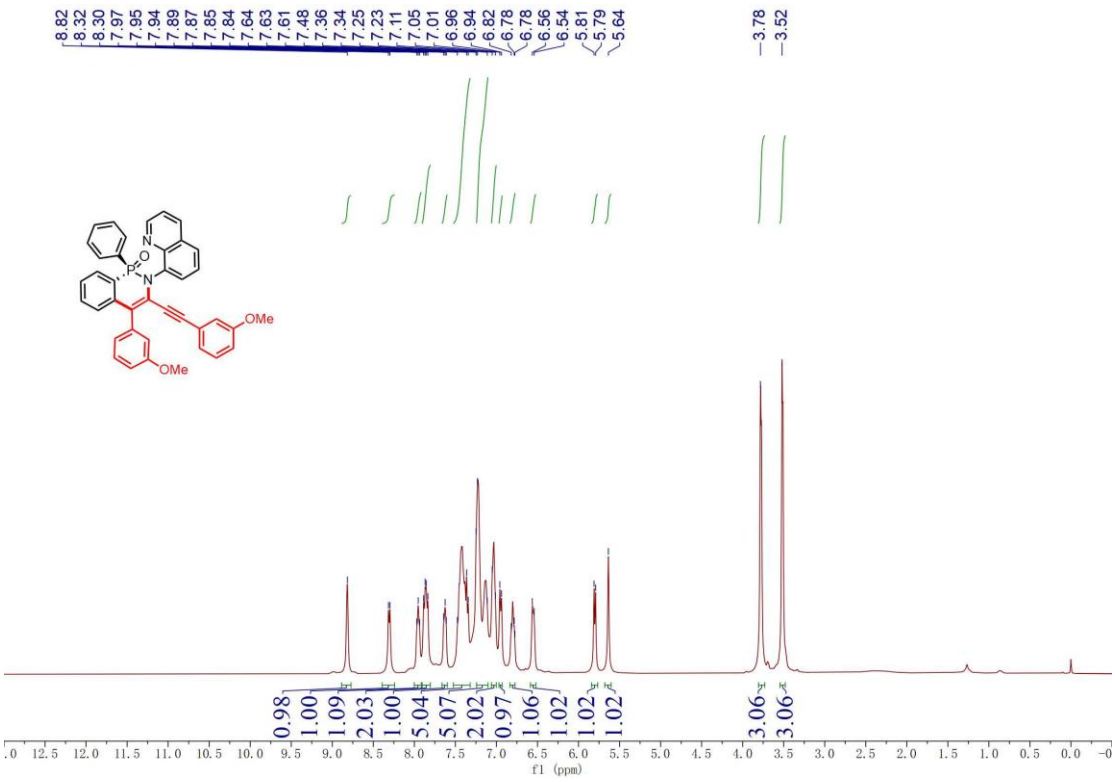
^{19}F-NMR of **5d**



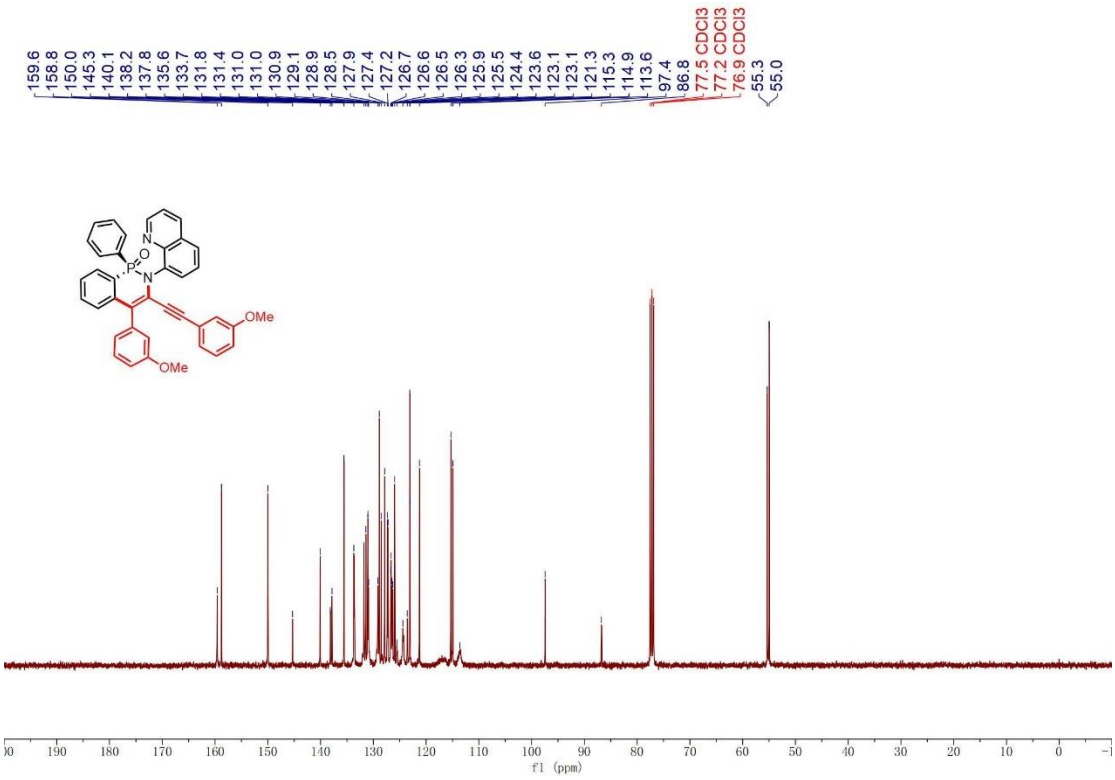
^{31}P-NMR of **5d**



^{1}H-NMR of **5e**



^{13}C-NMR of **5e**



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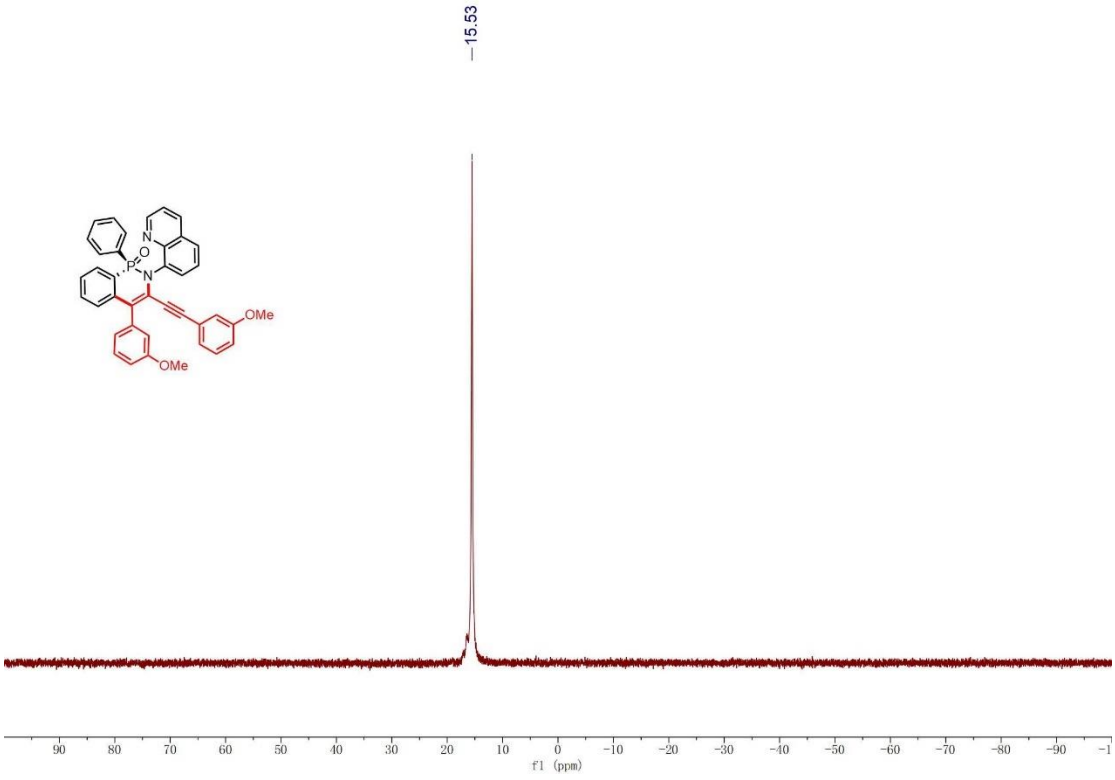
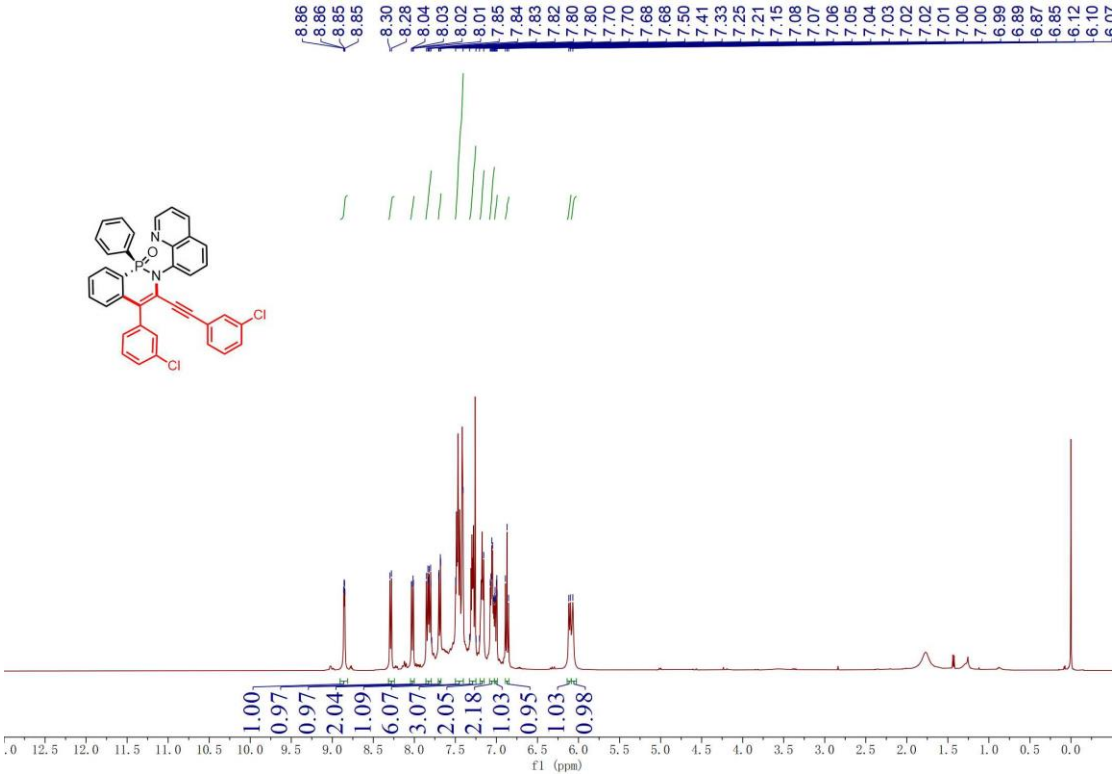
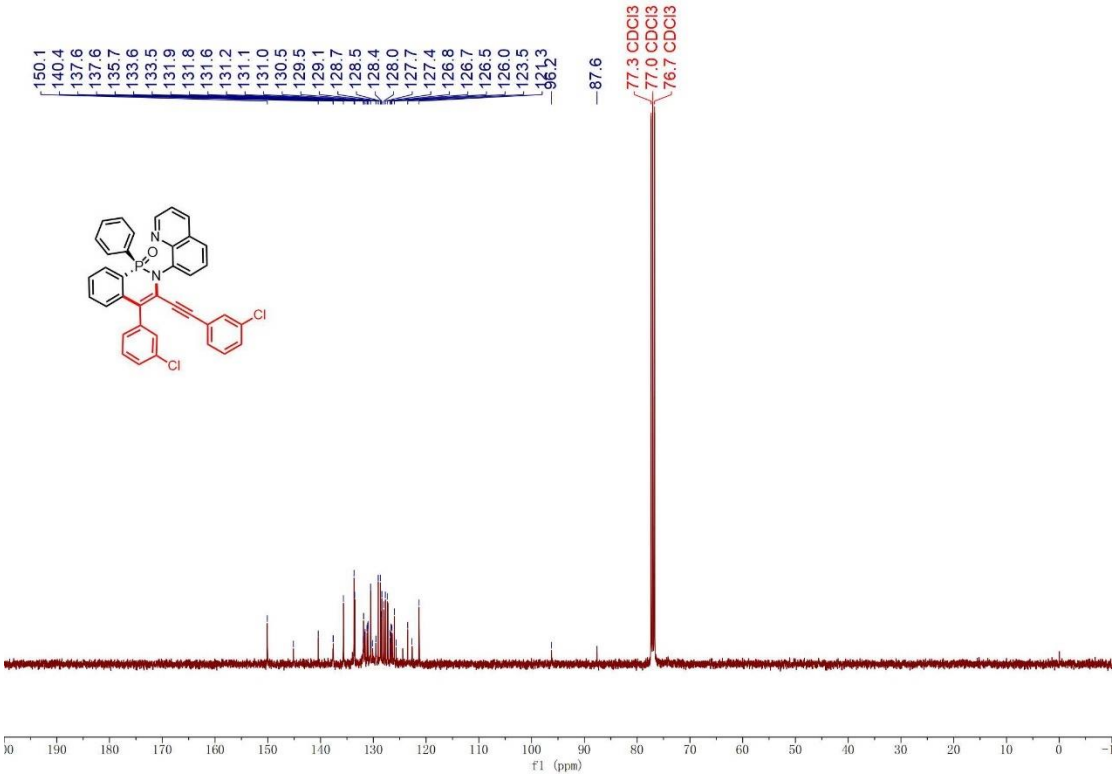


^{1}H-NMR of **5f**



^{13}C-NMR of **5f**



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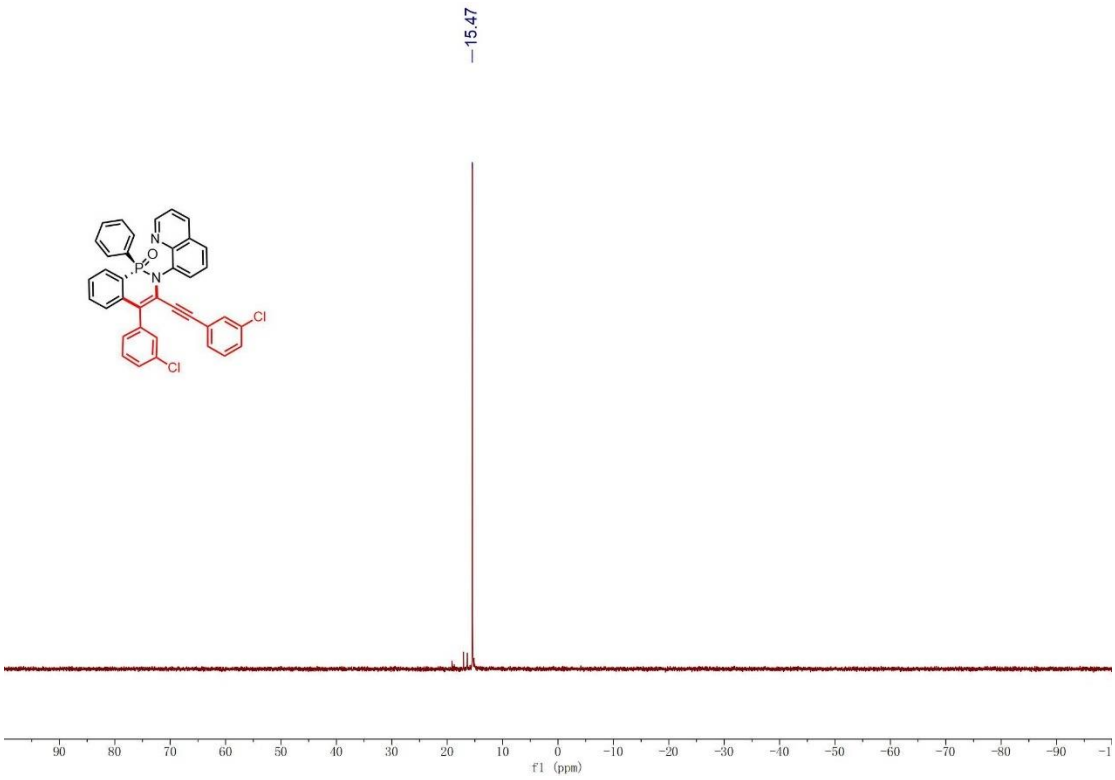
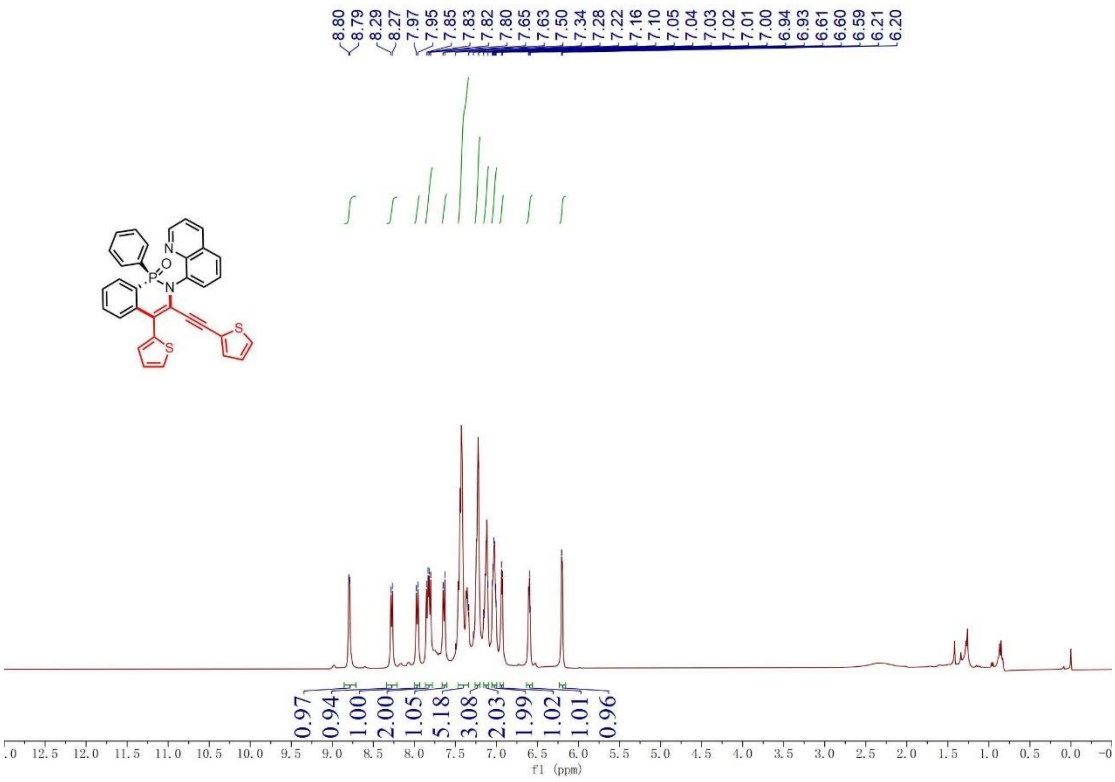
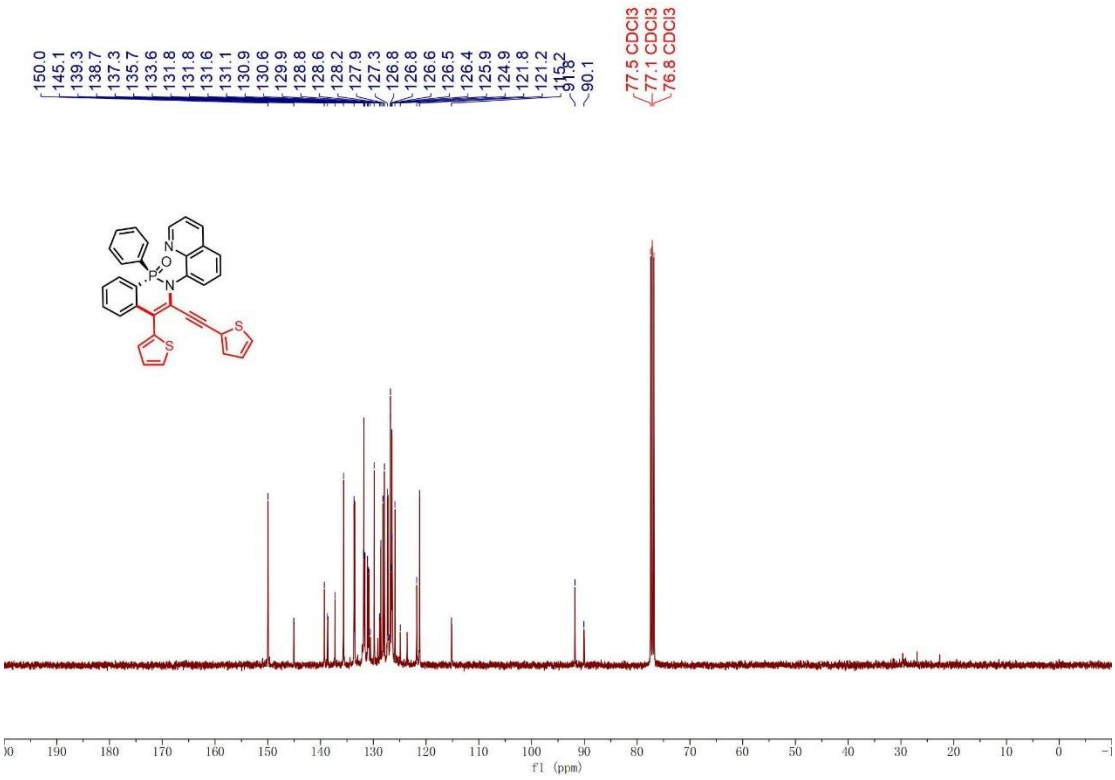


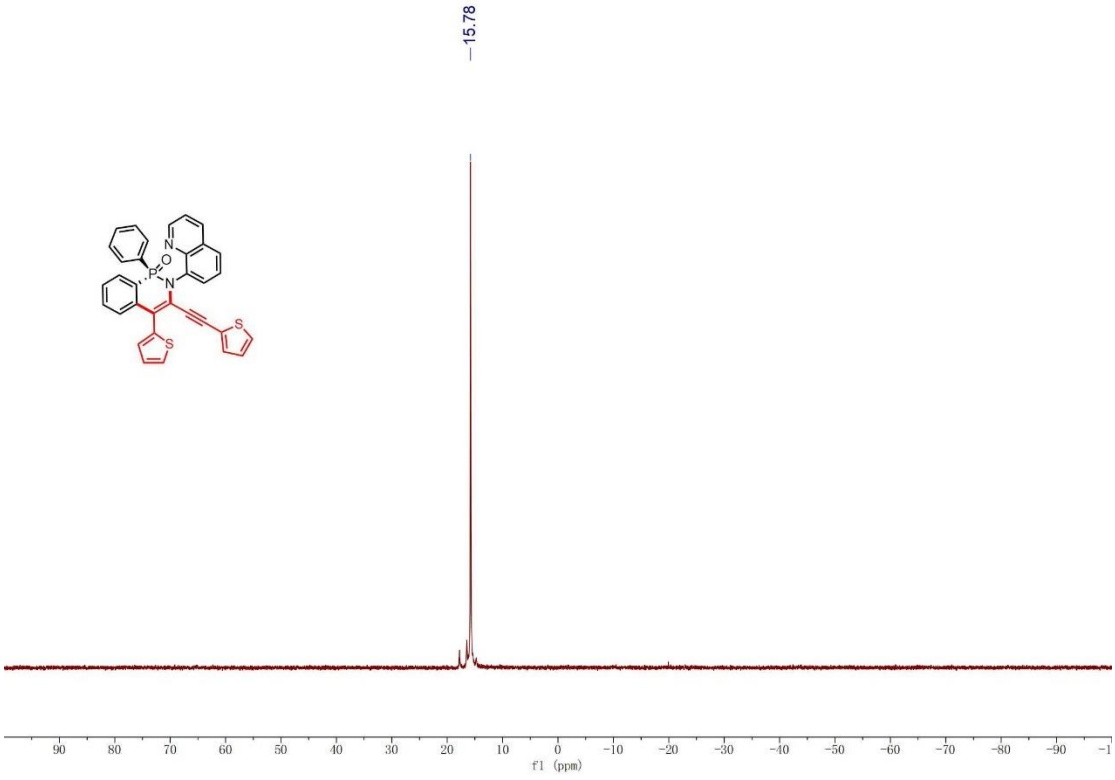
^{1}H-NMR of **5g**



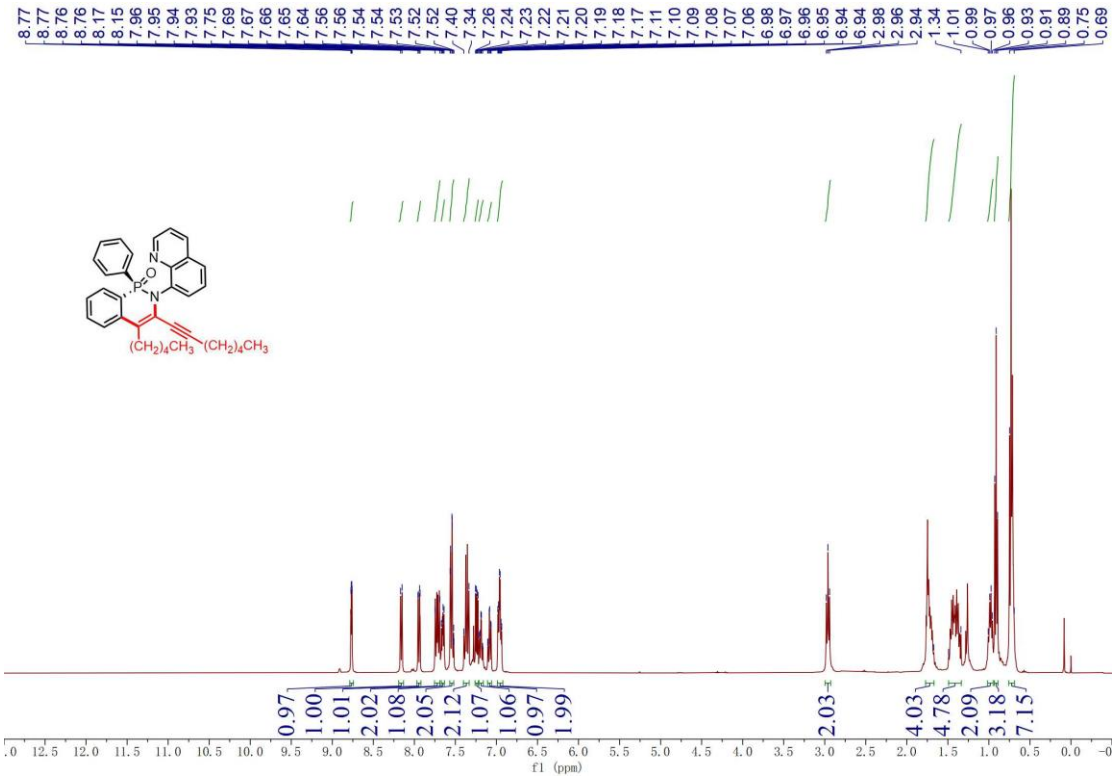
^{13}C-NMR of **5g**



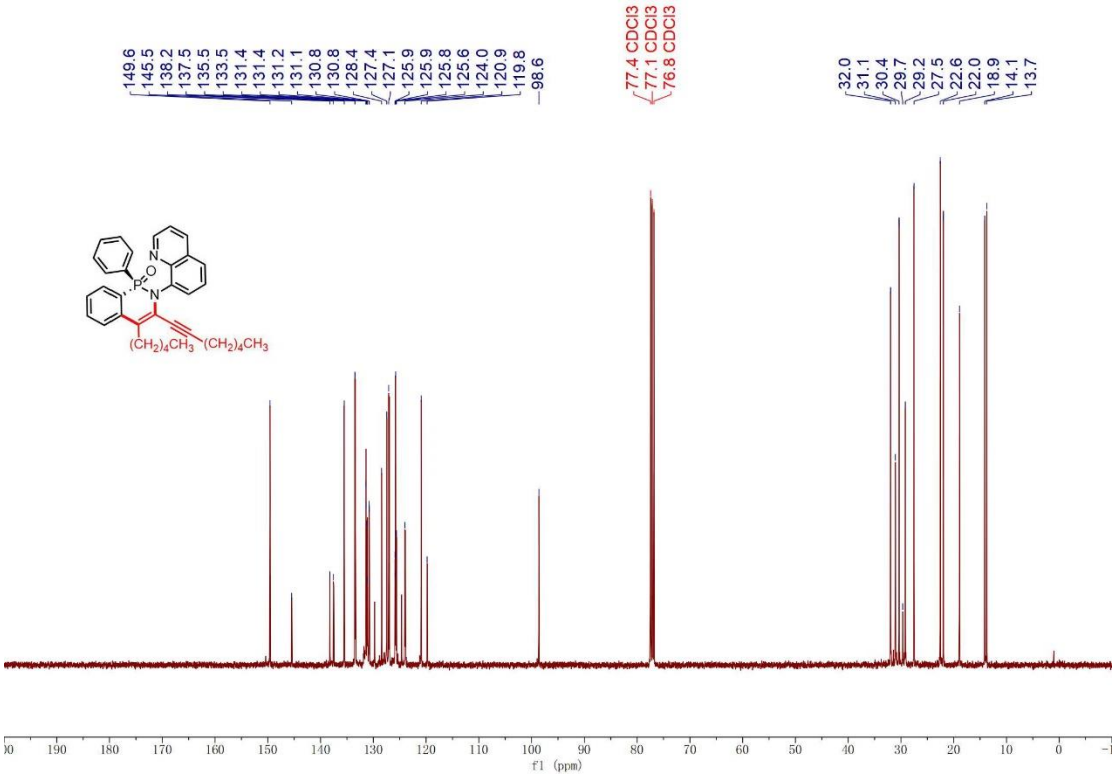
^{31}P-NMR of **5g**



^{1}H-NMR of **5h**



^{13}C-NMR of **5h**



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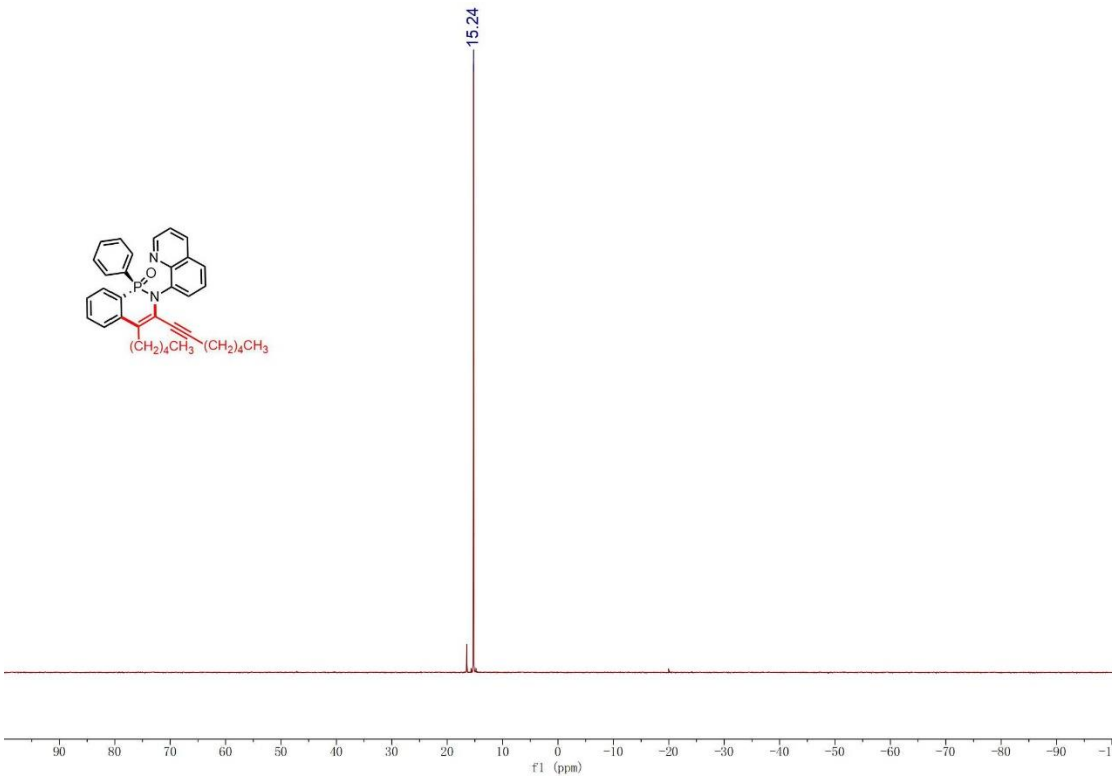
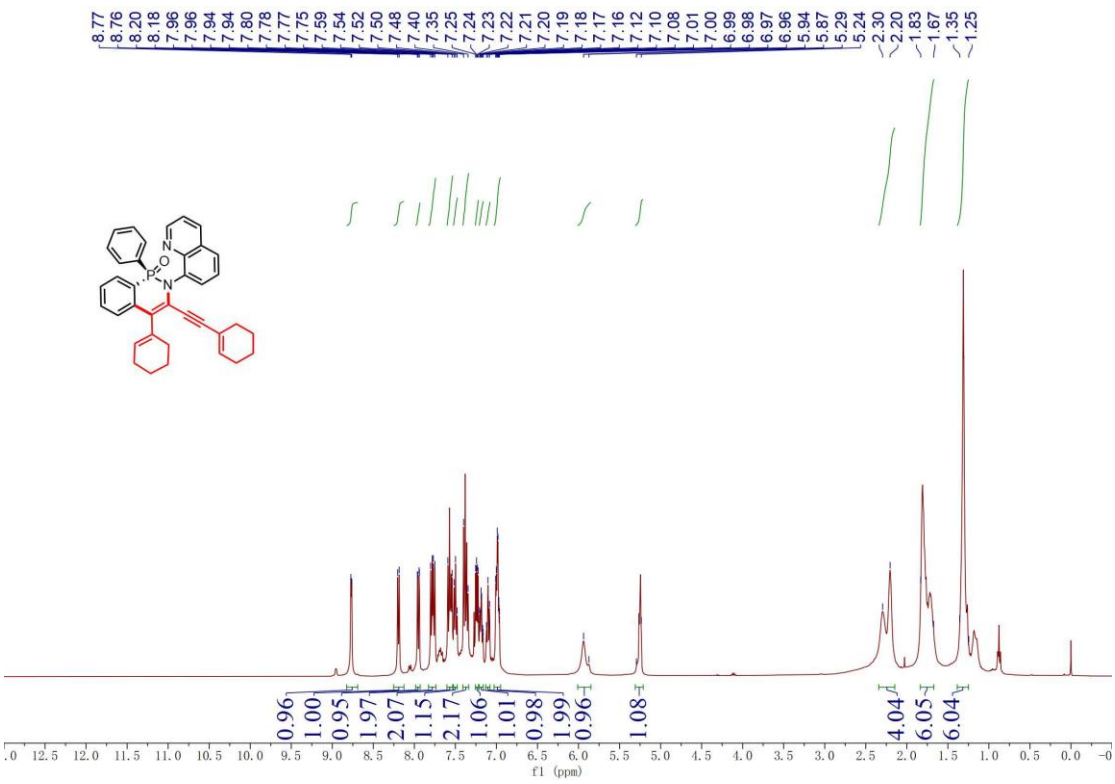
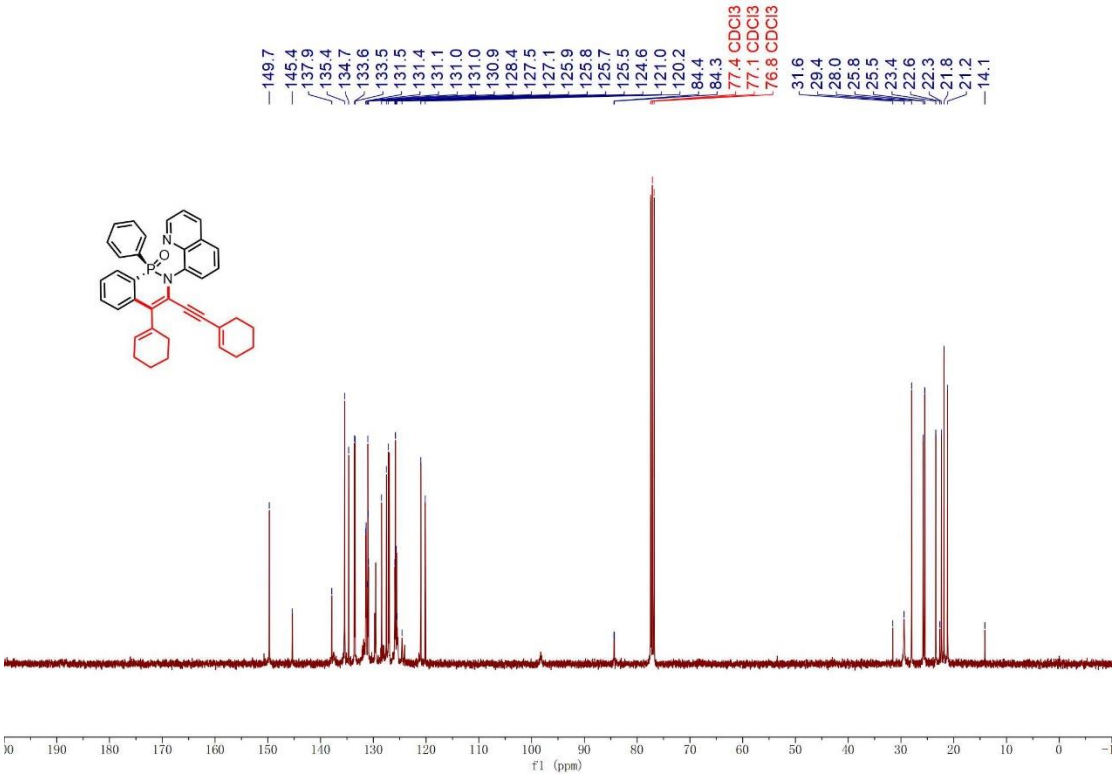


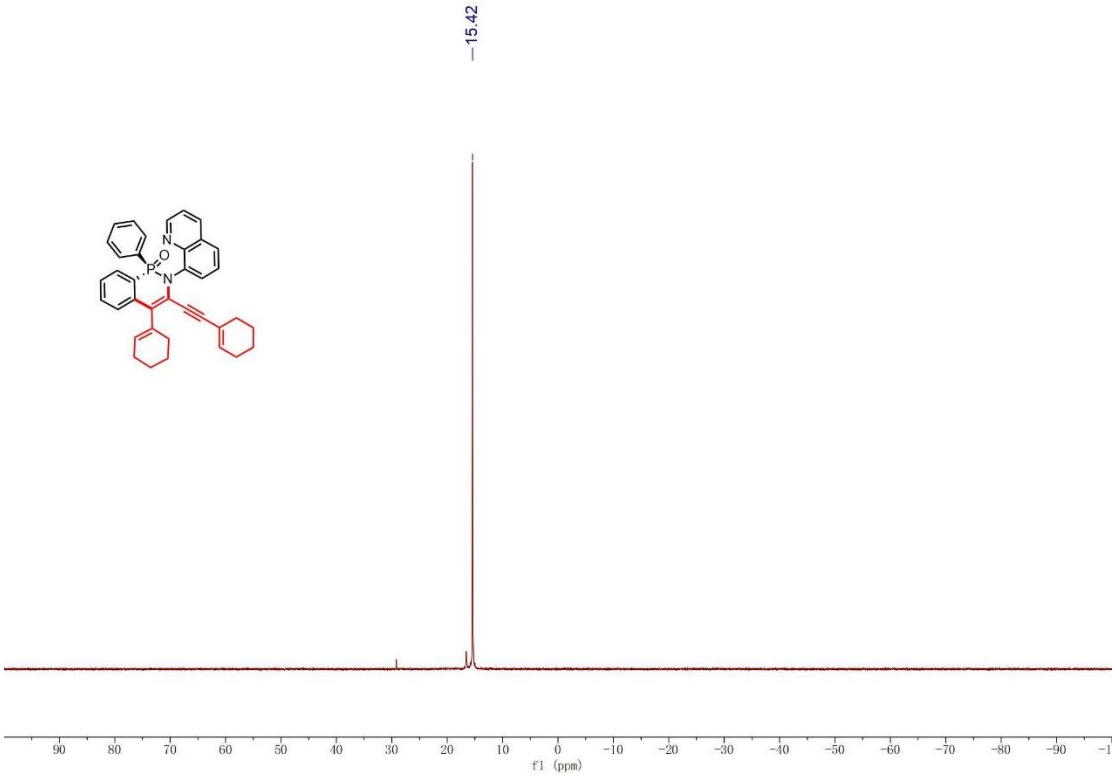
^{1}H-NMR of **5i**



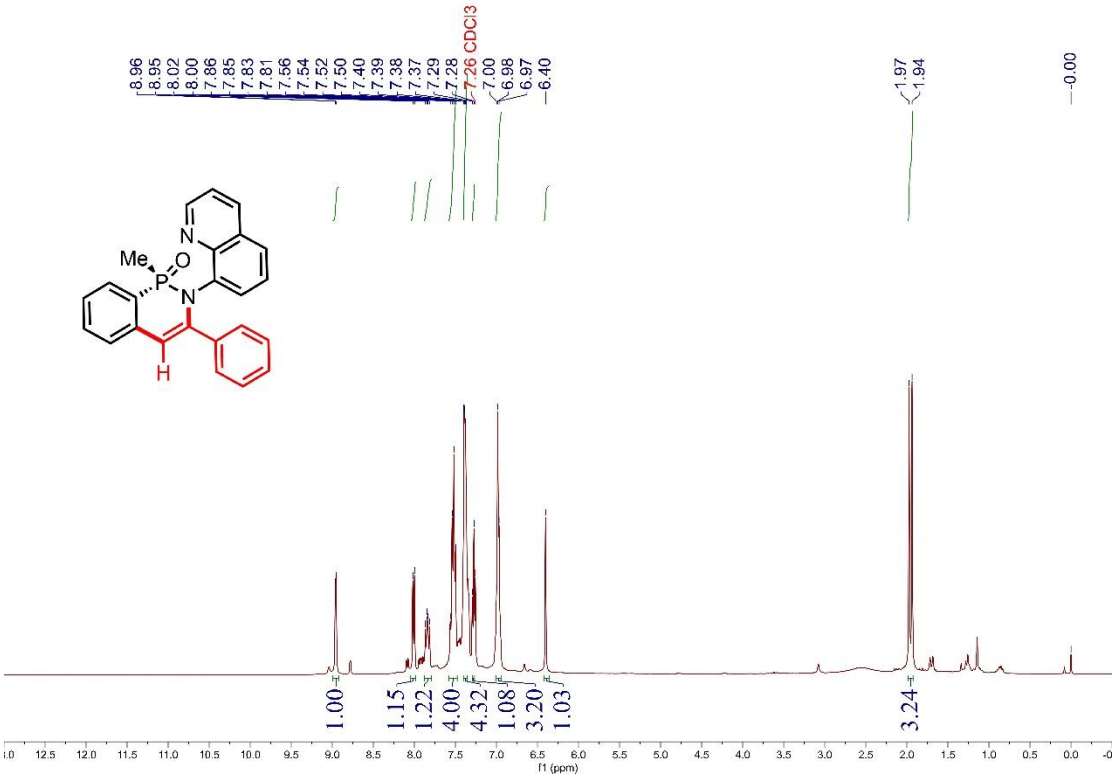
^{13}C-NMR of **5i**



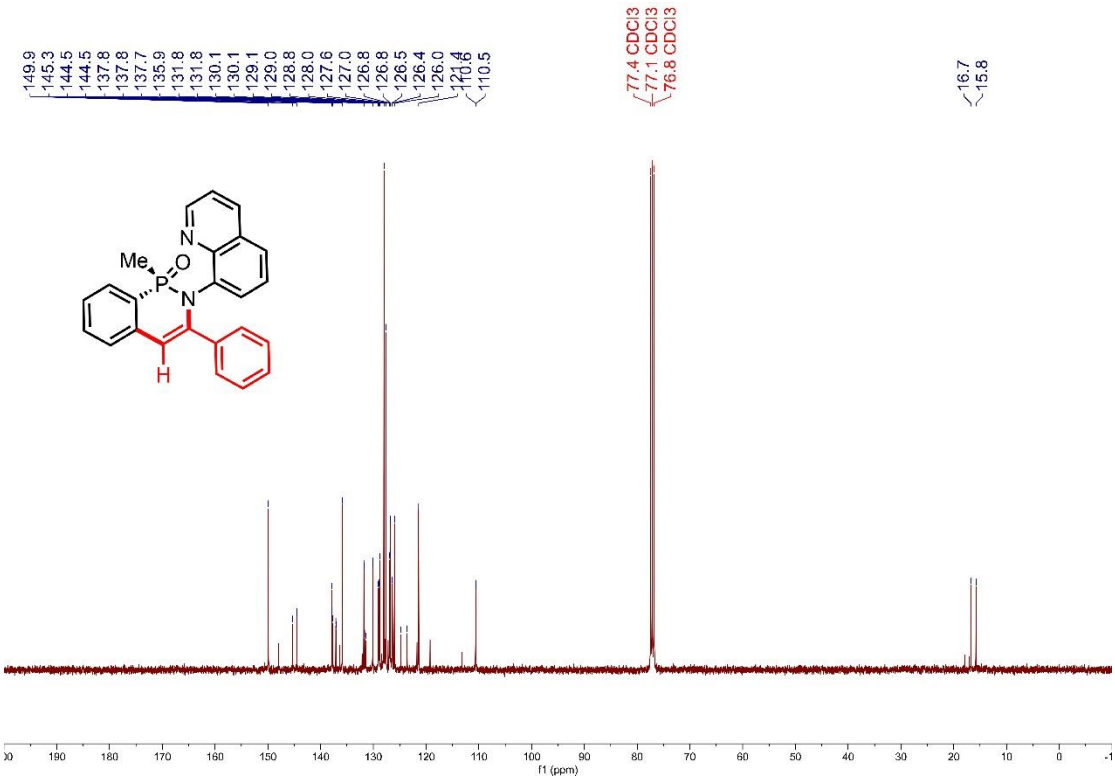
^{31}P-NMR of **5i**



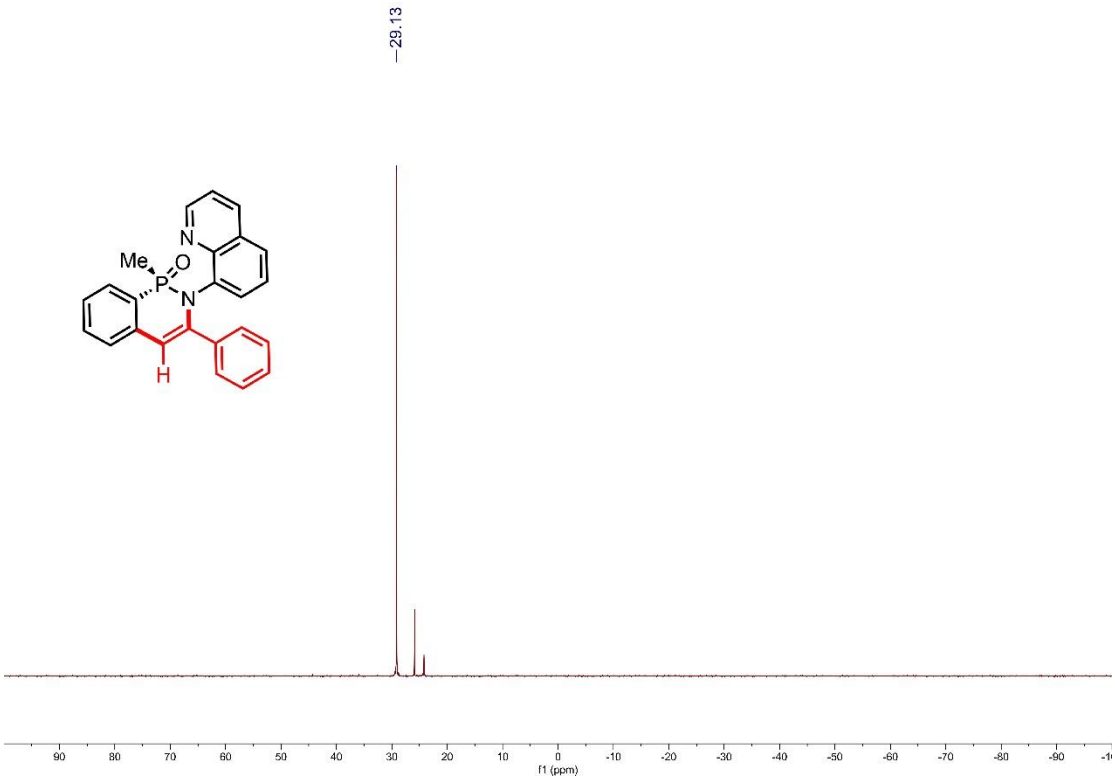
^{1}H-NMR of **6a**



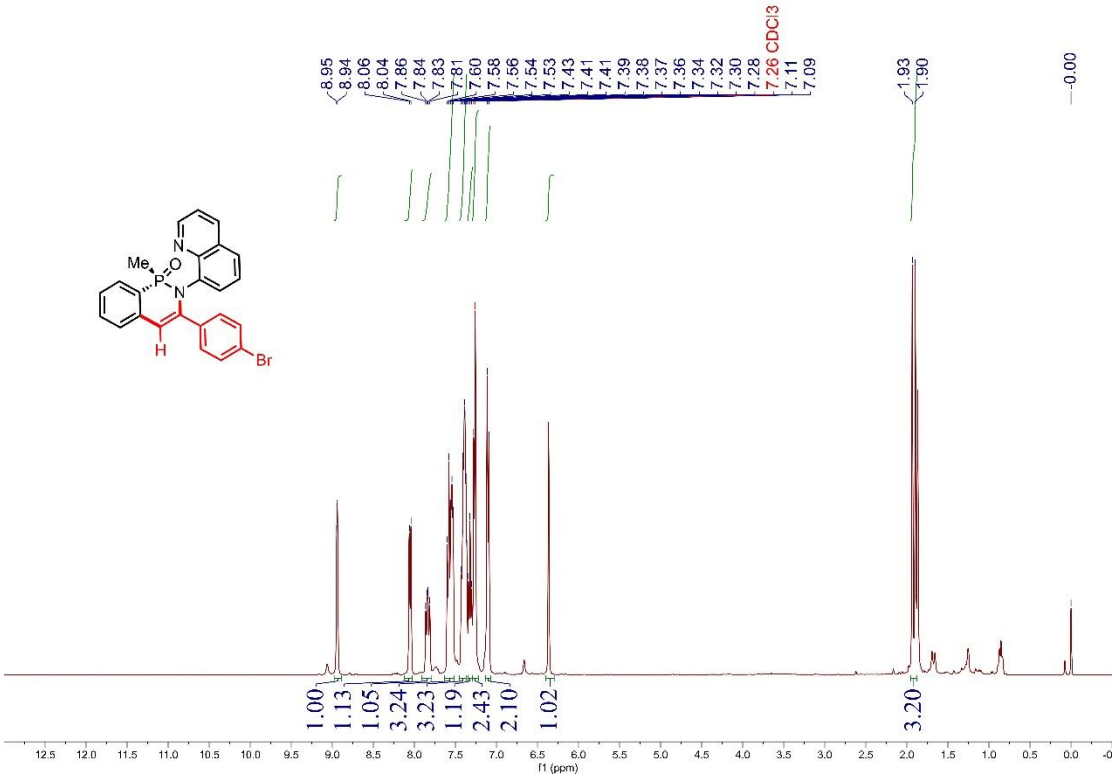
^{13}C-NMR of **6a**



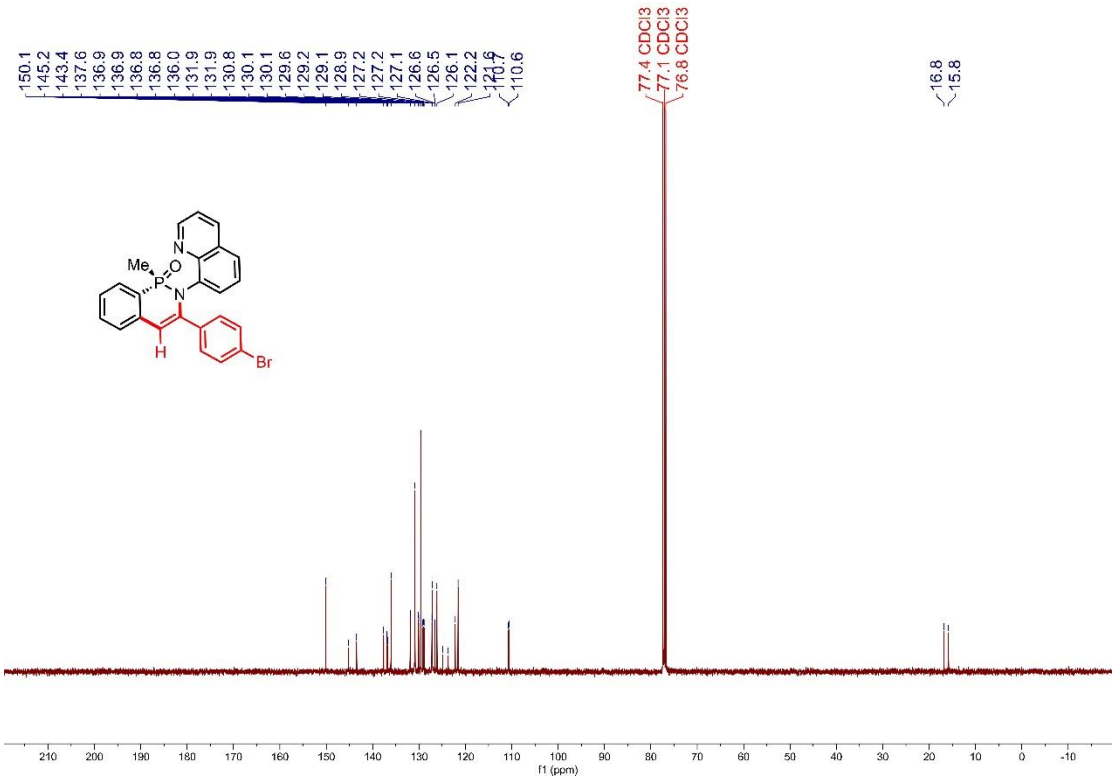
^{31}P-NMR of **6a**



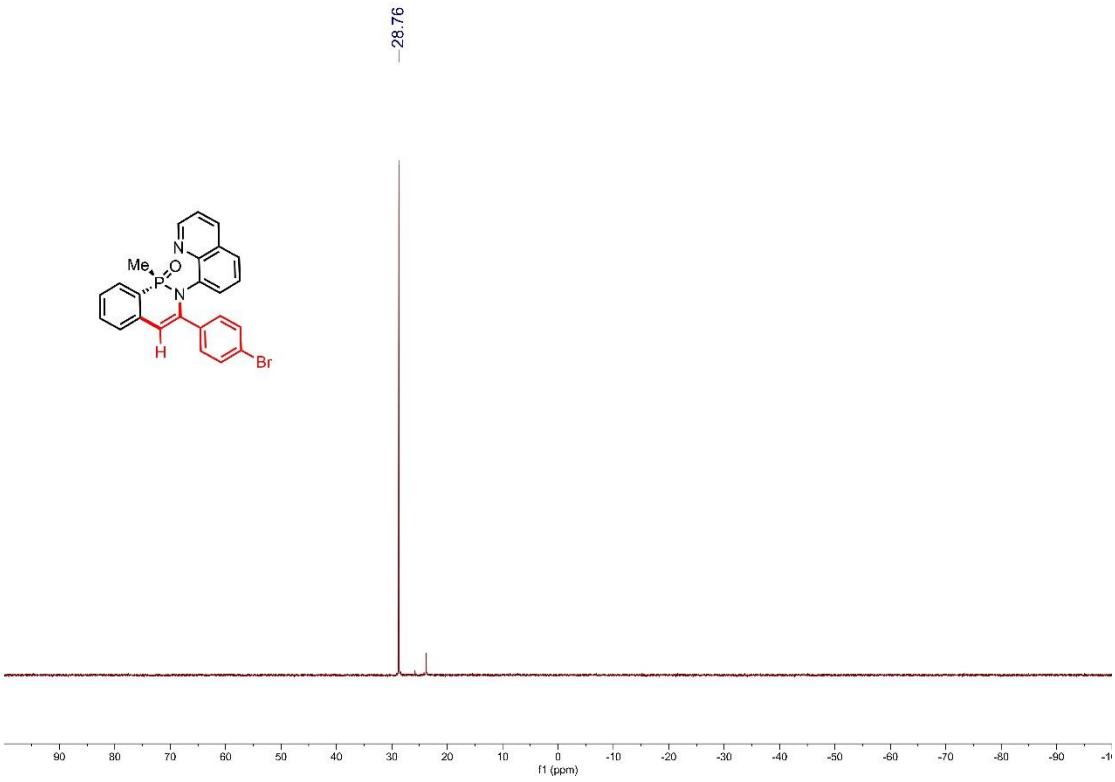
^{1}H-NMR of **6b**



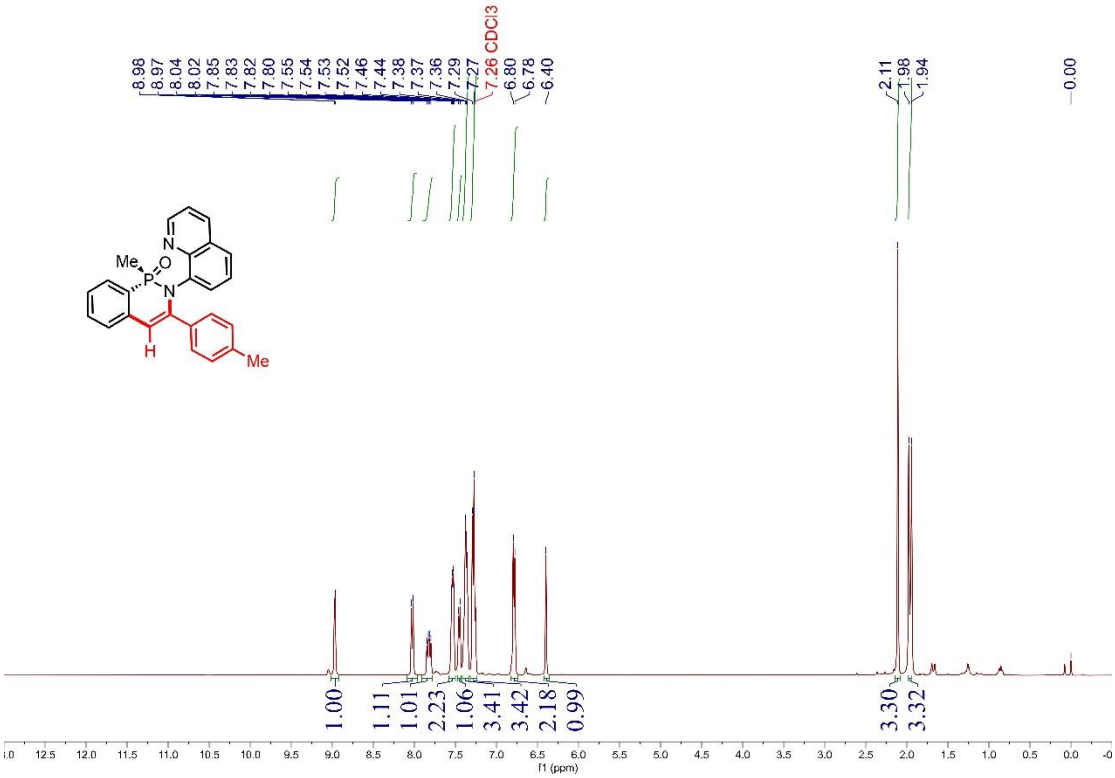
^{13}C-NMR of **6b**



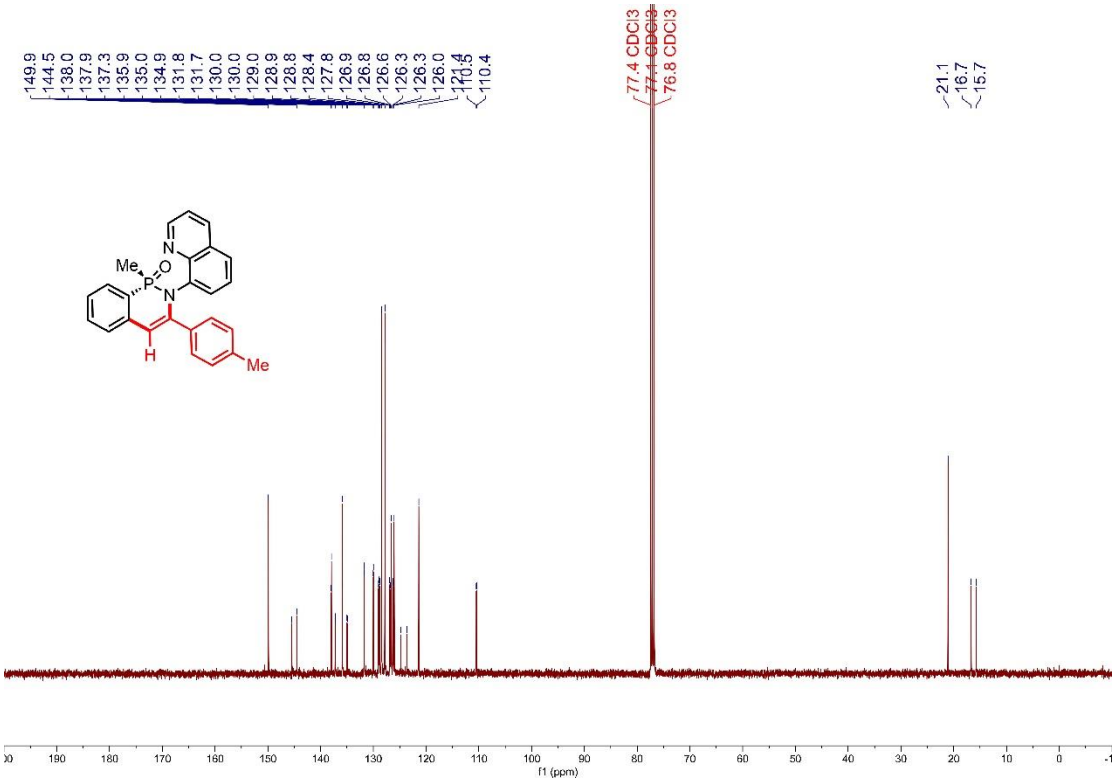
^{31}P-NMR of **6b**



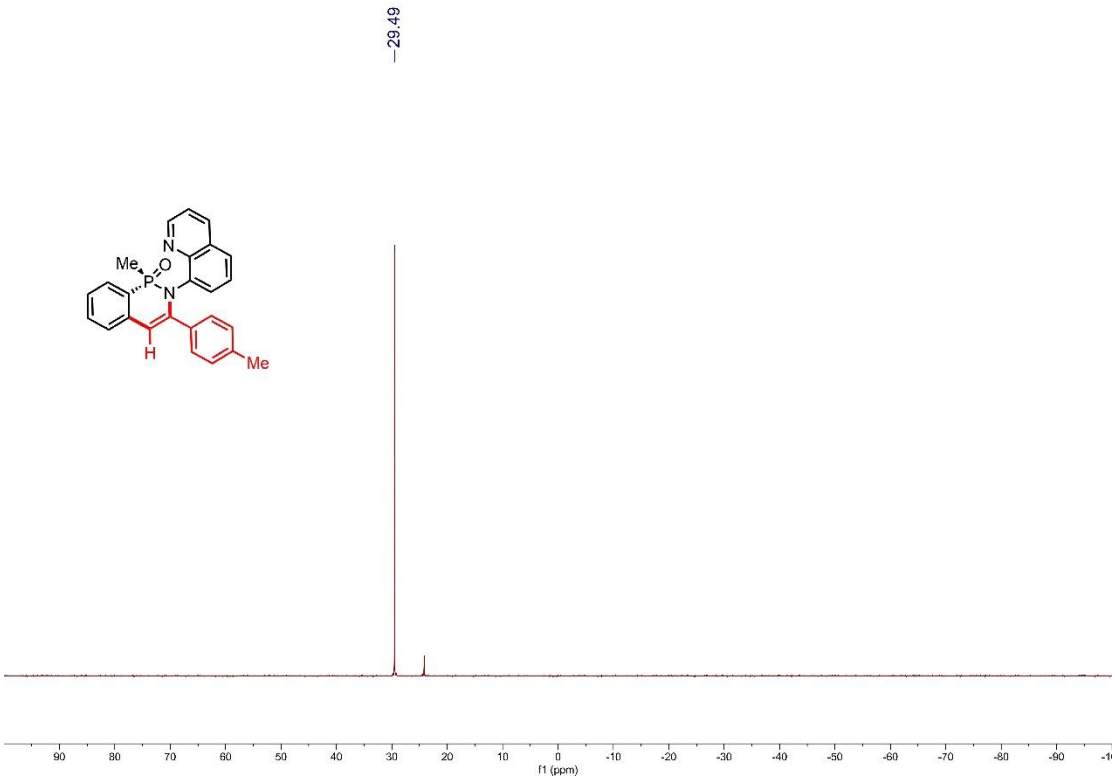
^{1}H-NMR of **6c**



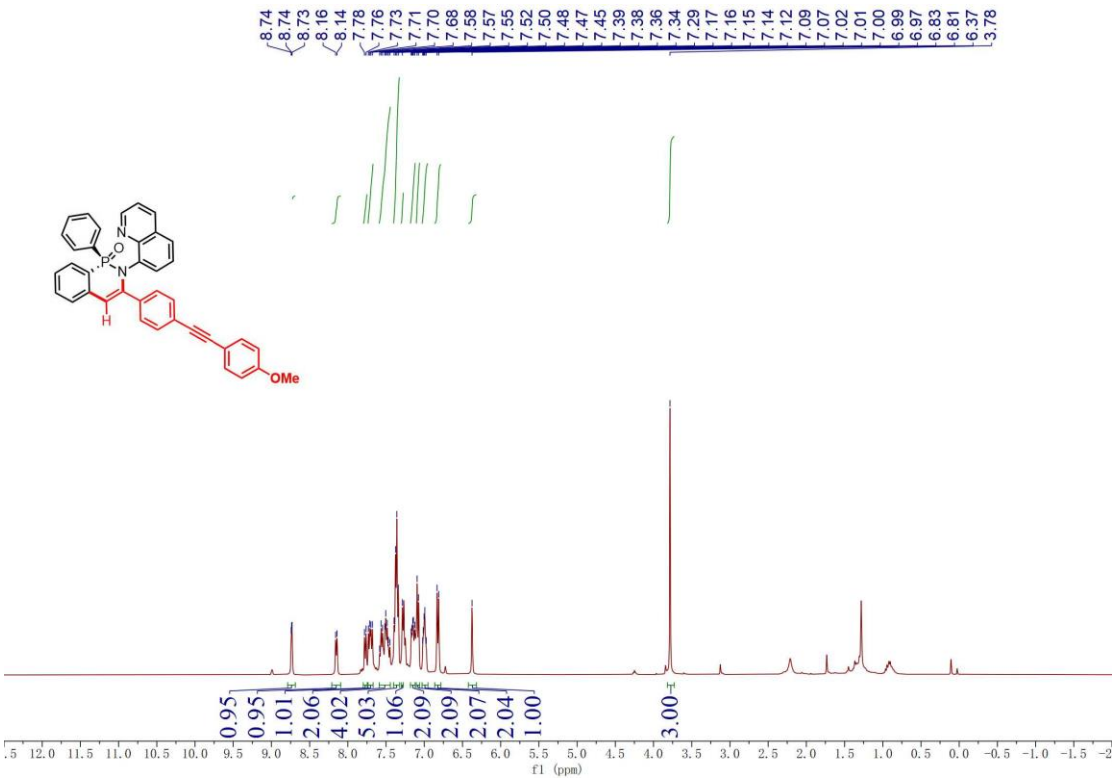
^{13}C-NMR of **6c**



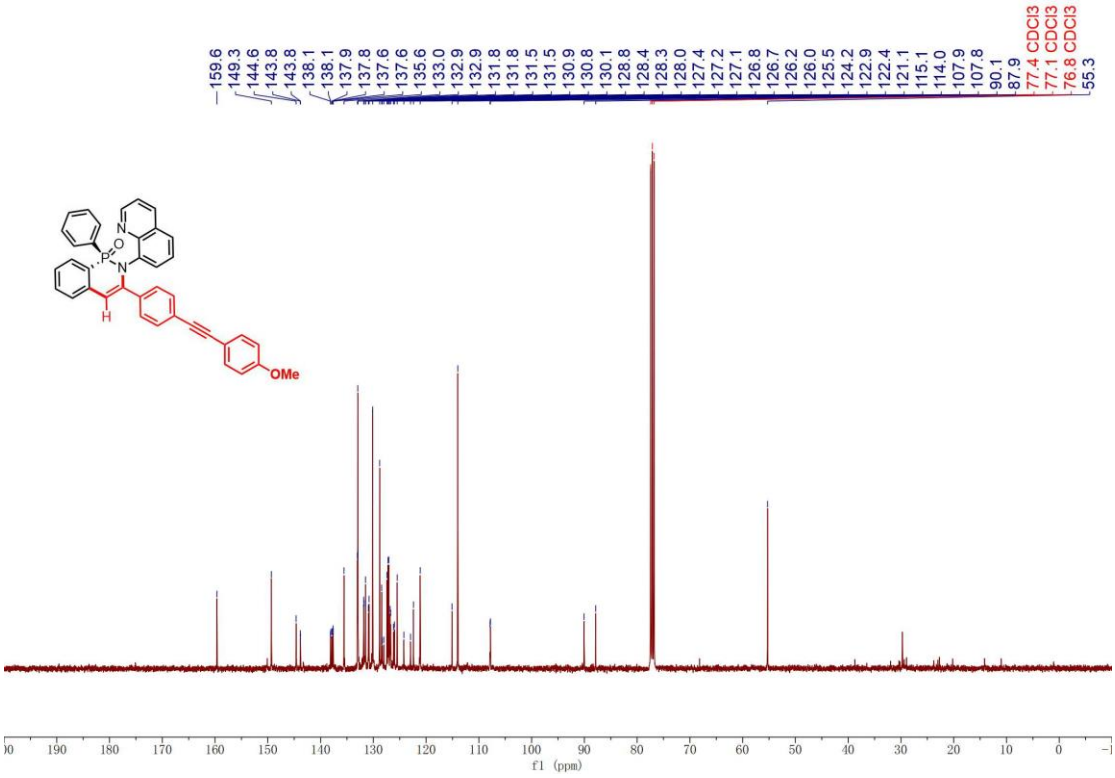
^{31}P-NMR of **6c**



^{1}H-NMR of **7af**



^{13}C-NMR of **7af**



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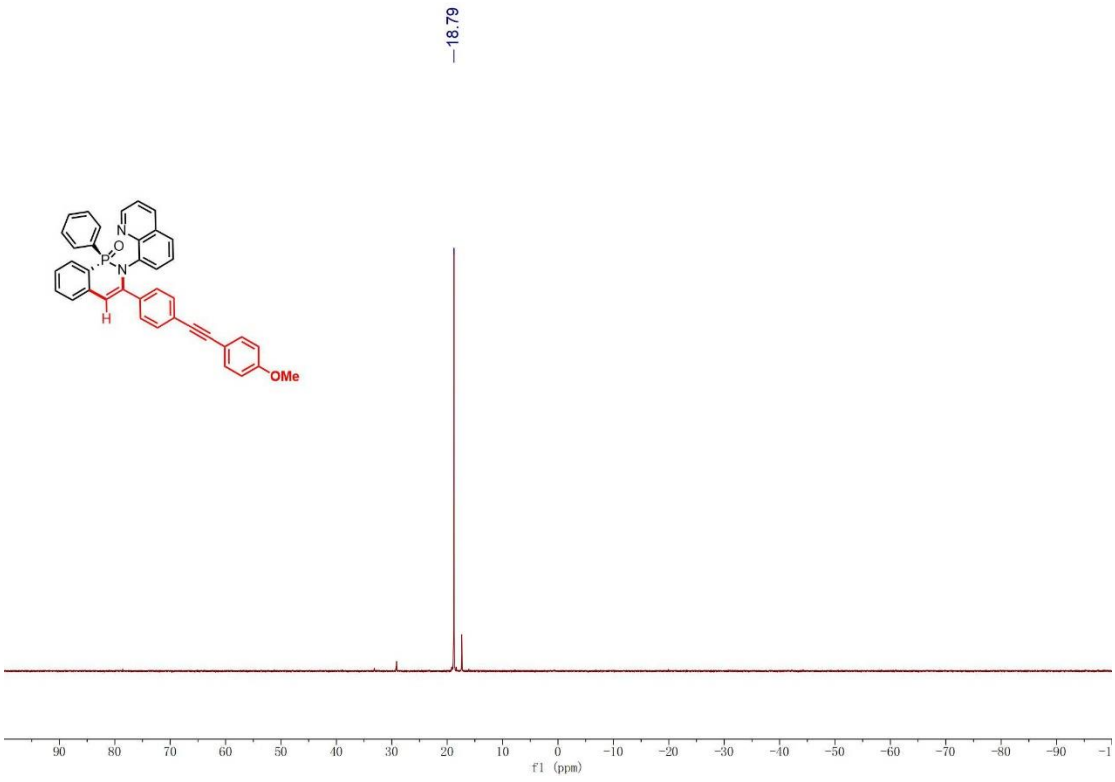
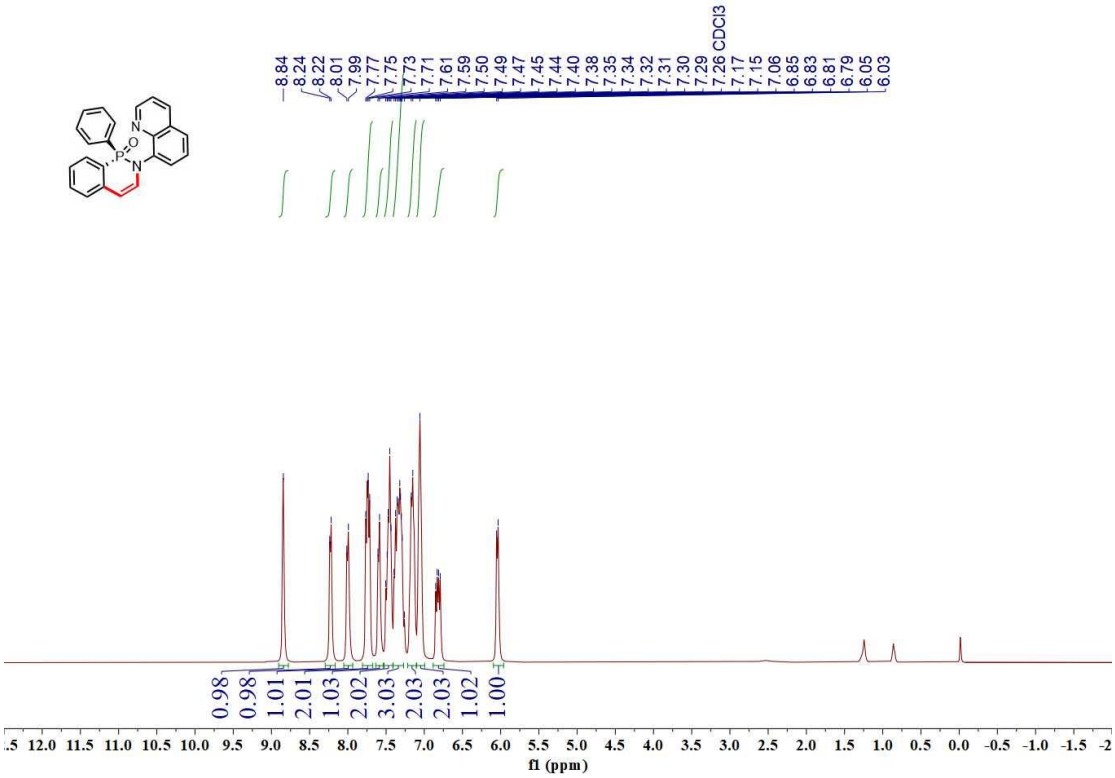
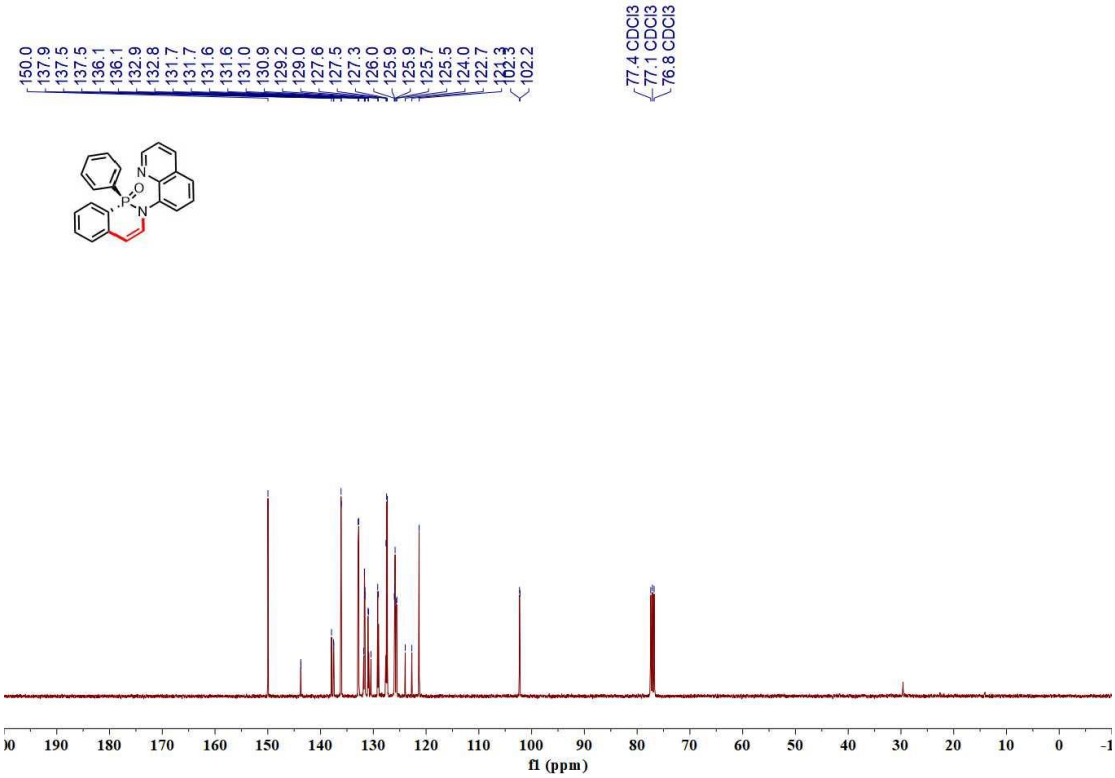


^{1}H-NMR of **8ab**



^{13}C-NMR of **8ab**



^{31}P-NMR of **8ab**