# Supporting Information

## Electrochemical enabled cobalt catalyzed enantioselective C-H acyloxylation of aryl phosphamide with carboxylic acid

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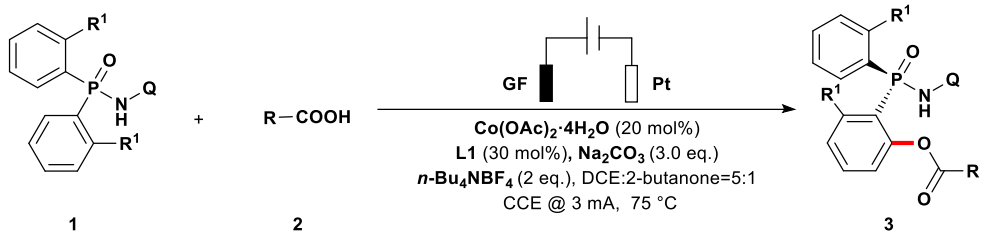
### Table of Contents

## 1. General Information

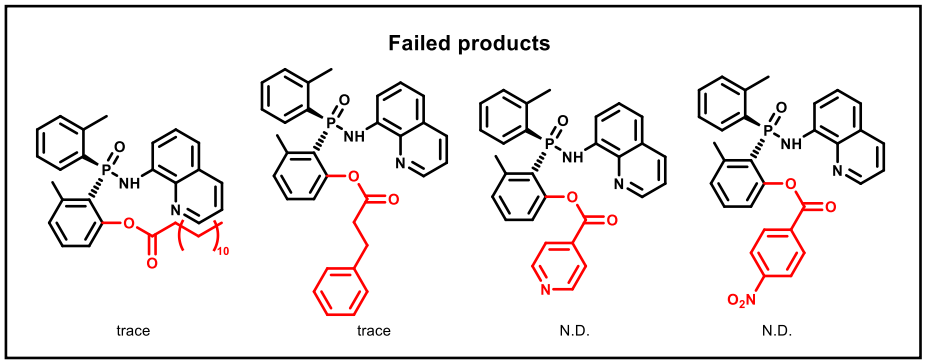
Commercial reagents were purchased from Adamas-beta, Aladdin, Bidepharm, Energy Chemical and TCI. All air-sensitive manipulations were carried out with standard Schlenk techniques under argon. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried 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 $^{31}$P). Chemical shifts were reported in δ (ppm) referenced to the residual solvent peak of $CDCl_3$ (δ 7.26), DMSO-*d6* (δ 2.50) for $^{1}$H NMR and $CDCl_3$ (δ 77.1), DMSO-*d6* (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. The crystal was measured by Bruker D8 VENTURE Metaljet PHOTON II.

Aryl phosphinamides and ligands were synthesized according to previously published works.[1]

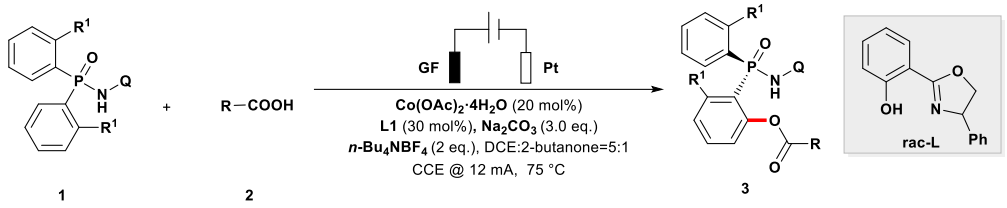
## 2. General Procedure for the Electrochemical Enantioselective C-H Acyloxylation




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.), carboxylic acid **2** (0.60 mmol, 3.0 eq.), $Co(OAc)_2$•$4H_2O$ (20 mol%), **L1** (30 mol%), $Na_2CO_3$ (0.6 mmol, 3.0 eq.) were placed in a 15 mL cell and dissolved in 6 mL of DCE/2-Butanone (5.0:1.0). Electrocatalysis was performed at 75 ℃ 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**.



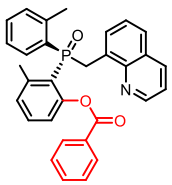

## Preparation pathway of racemic products




The reaction for racemic product 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** (0.05 mmol, 1.0 eq.), carboxylic acid **2** (0.15 mmol, 3.0 eq.), $Co(OAc)_2$•$4H_2O$ (20 mol%), rac-**L1** (30 mol%), $Na_2CO_3$ (0.14 mmol, 3.0 eq.), n-Bu4NBF4 (0.2 mmol) were placed in a 15 mL cell and dissolved in 6 mL of DCE/2-Butanone (5.0:1.0). Electrocatalysis was performed at 75 ℃ with a constant current of 3 mA maintained for 6 h. After the reaction was completed, the desired racemic product was obtained.

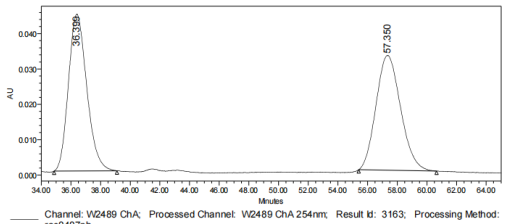
## Analytic Data of product 3

### (S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl benzoate (3a)



White foam, 68.9 mg, 70% yield. M.p.: 154 - 156 °C, $[\alpha]_D^{20}$ = +173.6 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 36.894 min, t (minor) = 57.350 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.76 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.24 (d, *J* = 14.4 Hz, 1H), 8.12 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.93 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.87 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.50 – 7.41 (m, 3H), 7.39 – 7.31 (m, 3H), 7.25 – 7.18 (m, 3H), 7.15 – 7.09 (m, 2H), 7.00 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.51 – 6.46 (m, 1H), 2.98 (s, 3H), 2.48 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 164.0, 152.4 (d, $J_{C-P}$ = 4.0 Hz), 147.6, 146.4 (d, $J_{C-P}$ = 7.0 Hz), 141.6 (d, $J_{C-P}$ = 11.0 Hz), 138.9, 138.7 (d, $J_{C-P}$ = 8.0 Hz), 136.4, 133.4, 132.7 (d, $J_{C-P}$ = 2.0 Hz), 132.6 (d, $J_{C-P}$ = 120.0 Hz), 131.7 (d, $J_{C-P}$ = 12.0 Hz), 131.5 (d, $J_{C-P}$ = 3.0 Hz), 131.3 (d, $J_{C-P}$ = 11.0 Hz), 130.3, 130.1 (d, $J_{C-P}$ = 11.0 Hz), 128.9, 128.5, 128.1, 127.7, 125.1 (d, $J_{C-P}$ = 13.0 Hz), 123.6 (d, $J_{C-P}$ = 119.0 Hz), 121.6, 121.5 (d, $J_{C-P}$ = 6.0 Hz), 118.9, 113.8 (d, $J_{C-P}$ = 3.0 Hz), 22.4 (d, $J_{C-P}$ = 3.0 Hz), 20.9 (d, $J_{C-P}$

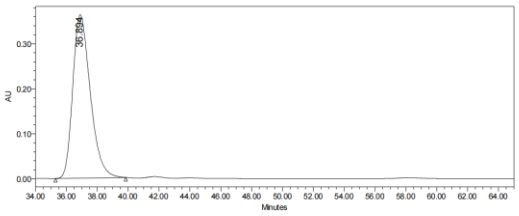
= 5.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.18. **HRMS (ESI)** calculated for $C_{30}H_{26}N_2O_3P$ $[M + H]^+$ : 493.1676, found: 493.1674.




Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3163; Processing Method: rac0407ph

**Processed Channel Descr.: W2489 ChA 254nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 36.399 | 3809273 | 50.44 | 44339 |
| 2 | W2489 ChA 254nm | 57.350 | 3742859 | 49.56 | 32477 |

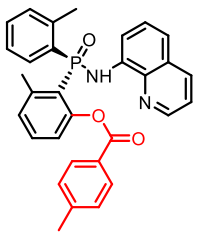



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3167; Processing Method: chiraxxyph

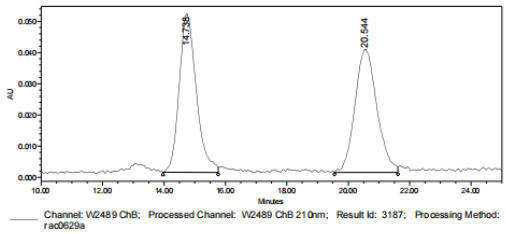
**Processed Channel Descr.: W2489 ChA 254nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 36.894 | 28666670 | 100.00 | 363222 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-methylbenzoate (3b)**



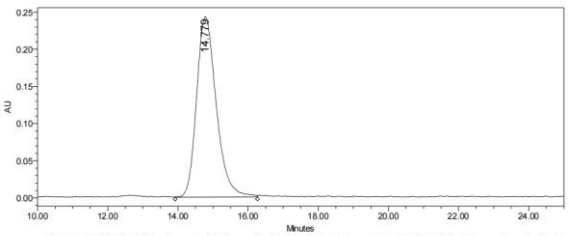
White foam, 64.8 mg, 64% yield. M.p.: 147 - 148 °C, $[\alpha]_D^{20}$ = +319.6 (c = 0.6, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 14.779 min, t (minor) = 20.544 min.z **$^1$H NMR (400 MHz, $CDCl_3$)**δ 8.76 (d, *J* = 4.4 Hz, 1H), 8.25 (d, *J* = 14.0 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H) , 7.48 – 7.42 (m, 2H) , 7.39 – 7.31 (m, 3H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.18 – 7.09 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 3H), 6.57 – 6.41 (m, 1H), 2.98 (s, 3H), 2.48 (s, 3H), 2.33 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 164.0, 152.6 (d, $J_{C-P}$ = 4.0 Hz), 147.7, 146.5 (d, $J_{C-P}$ = 7.0 Hz), 144.3, 141.6 (d, $J_{C-P}$ = 12.0 Hz), 139.0, 138.7 (d, $J_{C-P}$ = 7.0 Hz), 136.4, 132.8 (d, $J_{C-P}$ = 2.0 Hz), 132.6 (d, $J_{C-P}$ = 128.0 Hz), 131.7 (d, $J_{C-P}$ = 13.0 Hz), 131.5 (d, $J_{C-P}$ = 3.0 Hz), 131.4 (d, $J_{C-P}$ = 12.0 Hz), 130.4, 130.1 (d, $J_{C-P}$ = 44.0 Hz), 128.8, 128.6, 127.7, 126.2, 125.2 (d, $J_{C-P}$ = 14.0 Hz), 123.6 (d, $J_{C-P}$ = 119.0 Hz), 121.6, 121.5, 118.9, 113.9 (d, $J_{C-P}$ = 2.0 Hz), 22.5 (d, $J_{C-P}$ = 3.0 Hz), 21.8, 21.0 (d, $J_{C-P}$ = 5.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.41. **HRMS (ESI)** calculated for $C_{31}H_{28}N_2O_3P$ $[M + H]^+$ : 507.1832, found: 507.1829.




Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3187; Processing Method: rac0629a

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 14.738 | 1968028 | 49.97 | 50632 |
| 2 | W2489 ChB 210nm | 20.544 | 1970052 | 50.03 | 39347 |

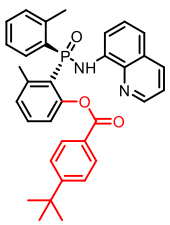



Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3189; Processing Method: chiraxxy0613c

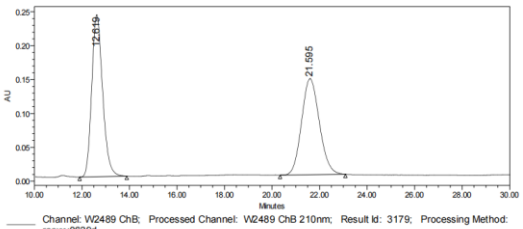
**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 14.779 | 9461967 | 100.00 | 242557 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-(tert-butyl)benzoate (3c)**

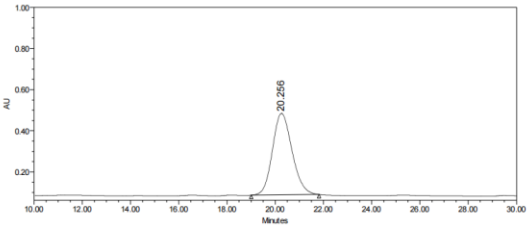


Light-yellow foam, 73.4 mg, 67% yield. M.p.: 164 - 168 °C, $[\alpha]_D^{20}$ = +184.0 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 20.256 min, t (minor) = 12.619 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.73 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.22 (d, *J* = 14.0 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.92 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.29 (m, 5H), 7.26 – 7.16 (m, 3H), 7.17 – 7.10 (m, 2H), 6.97 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.56 – 6.50 (m, 1H), 2.96 (s, 3H), 2.50 (s, 3H), 1.29 (s, 9H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 164.1, 157.3, 152.6 (d, $J_{C-P}$ = 4.0 Hz), 147.7, 146.4 (d, $J_{C-P}$ = 6.0 Hz), 141.7 (d, $J_{C-P}$ = 11.0 Hz), 139.0, 138.8 (d, $J_{C-P}$ = 7.0 Hz), 136.4, 132.7 (d, $J_{C-P}$ = 3.0 Hz), 132.6 (d, $J_{C-P}$ = 129.0 Hz), 131.7 (d, $J_{C-P}$ = 12.0 Hz), 131.6 (d, $J_{C-P}$ = 2.0 Hz), 131.5 (d, $J_{C-P}$ = 6.0 Hz), 130.3, 130.0 (d, $J_{C-P}$ = 11.0 Hz), 128.6, 127.7, 126.1, 125.2 (d, $J_{C-P}$ = 13.0 Hz), 125.0, 123.8 (d, $J_{C-P}$ = 119.0 Hz), 121.6 (d, $J_{C-P}$ = 7.0 Hz), 121.6, 118.9, 113.9 (d, $J_{C-P}$ = 2.0 Hz), 35.2, 31.2, 22.5 (d, $J_{C-P}$ = 3.0 Hz), 21.0 (d, $J_{C-P}$ = 5.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.17. **HRMS (ESI)** calculated for $C_{34}H_{34}N_2O_3P$ $[M + H]^+$ : 549.2302, found: 549.2297.




**Processed Channel Descr.: W2489 ChB 210nm**

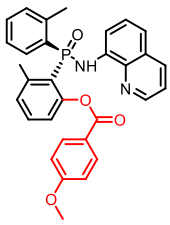
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 12.619 | 7618783 | 50.80 | 239227 |
| 2 | W2489 ChB 210nm | 21.595 | 7378579 | 49.20 | 141856 |




**Processed Channel Descr.: W2489 ChB 210nm**

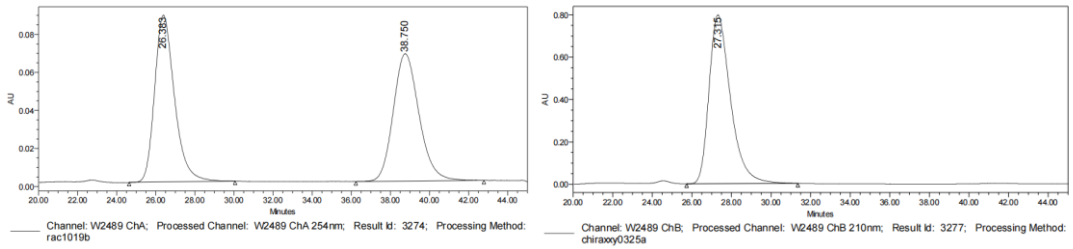
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 20.256 | 22431367 | 100.00 | 396676 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-methoxybenzoate (3d)**



white foam, 78.3 mg, 75% yield. M.p.: 123 - 126 °C, $[\alpha]_D^{20}$ = +223.7 (c = 0.6, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 27.315 min, t (minor) = 38.750 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.75 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.23 (d, *J* = 14.0 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.93 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.39 – 7.31 (m, 3H), 7.22 (dd, *J* = 7.6, 3.2 Hz, 1H), 7.14 (td, *J* = 3.6, 0.8 Hz, 2H), 6.98 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.58 – 6.53 (m, 1H), 3.79 (s, 3H), 2.98 (s, 3H), 2.49 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 163.7 (d, $J_{C-P}$ = 10.0 Hz), 152.5 (d, $J_{C-P}$ = 3.0 Hz), 147.6, 146.4 (d, $J_{C-P}$ = 7.0 Hz), 141.5 (d, $J_{C-P}$ = 11.0 Hz), 138.9, 138.7 (d, $J_{C-P}$ = 7.0 Hz), 136.4, 136.3, 132.7 (d, $J_{C-P}$ = 2.0 Hz), 132.6 (d, $J_{C-P}$ = 128.0 Hz), 132.4, 131.6 (d, $J_{C-P}$ = 22.0 Hz), 131.4, 131.4 (d, $J_{C-P}$ = 14.0 Hz), 129.9 (d, $J_{C-P}$ = 12.0 Hz), 128.5, 127.6, 125.0 (d, $J_{C-P}$ = 14.0 Hz), 123.6 (d, $J_{C-P}$ = 120.0 Hz), 121.5 (d, $J_{C-P}$ = 7.0 Hz), 121.5, 121.3, 118.9, 113.8 (d, $J_{C-P}$ = 3.0 Hz), 113.3, 55.4, 22.4 (d, $J_{C-P}$ = 3.0 Hz), 20.9 (d, $J_{C-P}$ = 5.0 Hz).

**$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.41. **HRMS (ESI)** calculated for $C_{31}H_{28}N_2O_4P$ $[M + H]^+$ : 523.1781, found: 523.1778.




**Processed Channel Descr.: W2489 ChA 254nm**

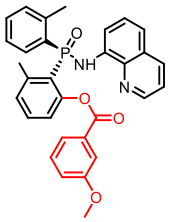
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 26.383 | 6209408 | 50.29 | 87755 |
| 2 | W2489 ChA 254nm | 38.750 | 6137667 | 49.71 | 66999 |



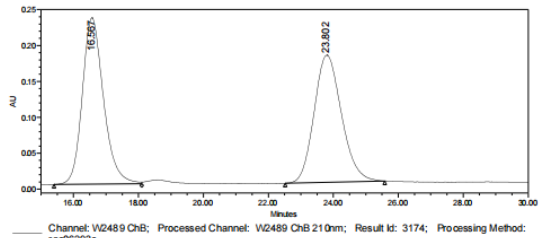

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 27.315 | 60224593 | 100.00 | 796681 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 3-methoxybenzoate (3e)**

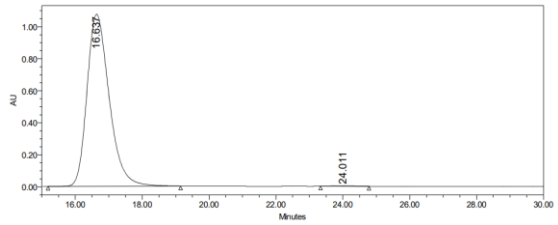


White foam, 59.5 mg, 57% yield. M.p.: 124 °C, $[\alpha]_D^{20}$ = +96.5 (c = 0.4, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 16.637 min, t (minor) = 24.011 min. **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.73 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.20 (d, *J* = 14.4 Hz, 1H), 8.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.88 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.51 – 7.35 (m, 5H), 7.35 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 7.15 (t, *J* = 4.0 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.02 – 6.95 (m, 2H), 7.00 – 6.96 (m, 1H), 3.64 (s, 3H), 2.96 (s, 3H), 2.50 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 164.0, 159.3, 152.5 (d, $J_{C-P}$ = 4.5 Hz), 147.8, 146.5 (d, $J_{C-P}$ = 7.5 Hz), 141.7 (d, $J_{C-P}$ = 12.0 Hz), 138.8, 138.7 (d, $J_{C-P}$ = 7.5 Hz), 136.3, 132.9 (d, $J_{C-P}$ = 129.0 Hz), 132.8 (d, $J_{C-P}$ = 1.5 Hz), 131.7 (d, $J_{C-P}$ = 13.5 Hz), 131.5 (d, $J_{C-P}$ = 3.0 Hz), 131.4 (d, $J_{C-P}$ = 12.0 Hz), 130.2 (d, $J_{C-P}$ = 3.0 Hz), 130.1, 129.1, 128.5, 127.6, 125.2 (d, $J_{C-P}$ = 13.5 Hz), 123.7 (d, $J_{C-P}$ = 120 Hz), 122.9, 121.6, 121.5, 120.0, 119.0, 114.6, 113.8 (d, $J_{C-P}$ = 3.0 Hz), 55.4, 22.5 (d, $J_{C-P}$ = 3.0 Hz), 21.0 (d, $J_{C-P}$ = 4.5 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 21.93. **HRMS (ESI)** calculated for $C_{31}H_{28}N_2O_4P$ $[M + H]^+$ : 523.1781, found: 523.1780.




**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 16.567 | 10503044 | 50.29 | 231460 |
| 2 | W2489 ChB 210nm | 23.802 | 10381072 | 49.71 | 177101 |

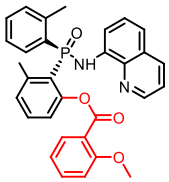



**Processed Channel Descr.: W2489 ChB 210nm**

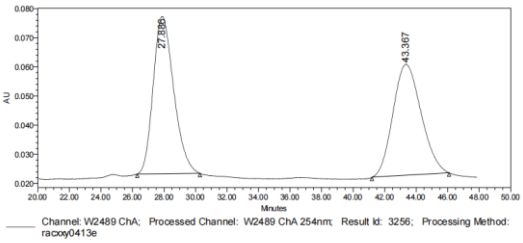
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 16.637 | 49410244 | 99.72 | 1073616 |
| 2 | W2489 ChB 210nm | 24.011 | 140401 | 0.28 | 2967 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 2-methoxybenzoate (3f)**

White foam, 69.9 mg, 67% yield. M.p.: 127 °C, $[\alpha]_D^{20}$ = +171.0 (c = 0.3, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major)

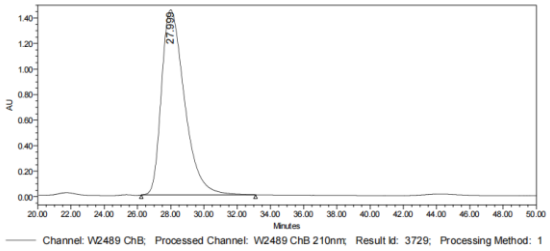


= 27.999 min, t (minor) = 43.367 min. **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.68 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.17 (d, *J* = 14.4 Hz, 1H), 8.08 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.84 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.45 (t, *J* = 8.4 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.29 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.20 (dd, *J* = 7.8, 3.0 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.05 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.79 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.67 (td, *J* = 7.8, 1.2 Hz, 1H) , 6.60 – 6.57 (m, 1H), 3.66 (s, 3H), 2.94 (s, 3H), 2.50 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 162.3, 160.3, 152.6 (d, $J_{C-P}$ = 4.0 Hz), 147.6, 146.2 (d, $J_{C-P}$ = 7.0 Hz), 141.6 (d, $J_{C-P}$ = 11.0 Hz), 138.9, 138.8 (d, $J_{C-P}$ = 7.0 Hz), 136.3, 134.6, 133.0, 132.8 (d, $J_{C-P}$ = 129.0 Hz), 132.6 (d, $J_{C-P}$ = 2.0 Hz), 131.6 (d, $J_{C-P}$ = 12.0 Hz), 131.4, 131.3 (d, $J_{C-P}$ = 2.0 Hz), 129.8 (d, $J_{C-P}$ = 11.0 Hz), 128.5, 127.6, 125.0 (d, $J_{C-P}$ = 13.0 Hz), 123.4 (d, $J_{C-P}$ = 119.0 Hz), 121.6 (d, $J_{C-P}$ = 7.0 Hz), 121.5, 119.7, 118.8, 117.7, 113.9 (d, $J_{C-P}$ = 2.0 Hz), 111.7, 55.6, 22.5 (d, $J_{C-P}$ = 3.0 Hz), 21.0 (d, $J_{C-P}$ = 5.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.50. **HRMS (ESI)** calculated for $C_{31}H_{28}N_2O_4P$ $[M + H]^+$ : 523.1781, found: 523.1777.




**Processed Channel Descr.: W2489 ChA 254nm**

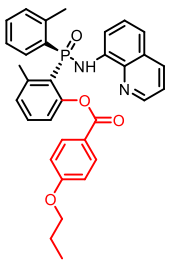
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 27.886 | 4891311 | 50.82 | 54006 |
| 2 | W2489 ChA 254nm | 43.367 | 4734387 | 49.18 | 38065 |



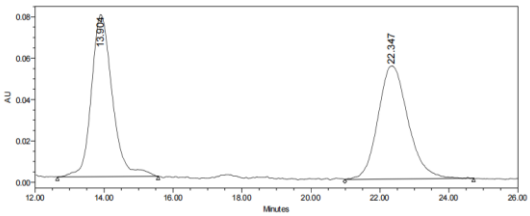

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 27.999 | 139800739 | 100.00 | 1449667 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-propoxybenzoate (3g)**

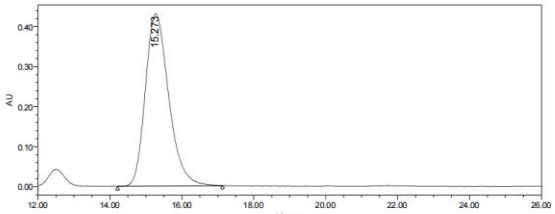


White foam, 61.6 mg, 56% yield. M.p.: 134 °C, $[\alpha]_D^{20}$ = +305.5 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 15.234 min, t (minor) = 22.347 min. **$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.76 (d, *J* = 4.4 Hz, 1H), 8.24 (d, *J* = 14.0 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.50 – 7.29 (m, 5H), 7.22 (dd, *J* = 8.0, 3.6 Hz, 1H), 7.13 (t, *J* = 3.6 Hz, 2H), 6.98 (dd, *J* = 8.0, 4.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.57 – 6.52 (m, 1H), 3.90 (t, *J* = 6.8 Hz, 2H), 2.98 (s, 3H), 2.48 (s, 3H), 1.80 (q, *J* = 6.8 Hz, 2H), 1.03 (t, *J* = 7.6 Hz, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 163.7, 163.4, 152.6 (d, $J_{C-P}$ = 4.0 Hz), 147.6, 146.5 (d, $J_{C-P}$ = 7.0 Hz) 141.6 (d, $J_{C-P}$ = 11.0 Hz), 139.0, 138.7 (d, $J_{C-P}$ = 8.0 Hz), 136.4, 132.7 (d, $J_{C-P}$ = 2.0 Hz), 132.7 (d, $J_{C-P}$ = 129.0 Hz), 132.5, 131.7 (d, $J_{C-P}$ = 12.0 Hz), 131.5, 131.5 (d, $J_{C-P}$ = 9.0 Hz), 129.9 (d, $J_{C-P}$ = 12.0 Hz), 128.6, 127.7, 125.1 (d, $J_{C-P}$ = 13.0 Hz), 123.7 (d, $J_{C-P}$ = 120.0 Hz), 121.6 (d, $J_{C-P}$ = 7.0 Hz), 121.6, 121.1, 118.9, 113.9 (d, $J_{C-P}$ = 2.0 Hz), 113.8, 69.8, 22.5, 22.4 (d, $J_{C-P}$ = 3.0 Hz), 21.0 (d, $J_{C-P}$ = 5.0 Hz), 10.6. **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.50. **HRMS (ESI)** calculated for $C_{33}H_{32}N_2O_4P$ $[M + H]^+$ : 551.2094, found: 551.2090.




Processed Channel Descr.: W2489 ChA 254nm

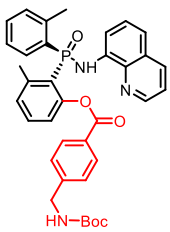
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 13.904 | 3299948 | 49.89 | 78331 |
| 2 | W2489 ChA 254nm | 22.347 | 3313876 | 50.11 | 54769 |



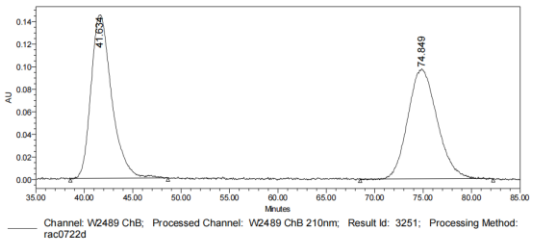

Processed Channel Descr.: W2489 ChA 254nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 15.273 | 19494653 | 100.00 | 430649 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-(((tert-butoxycarbonyl) amino)methyl)benzoate (3h)**

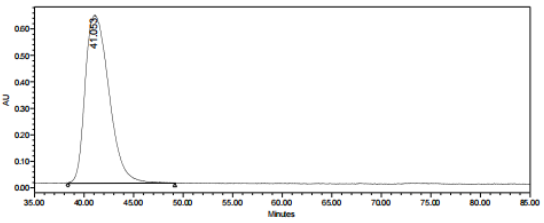



Yellow foam, 60.9 mg, 49% yield. M.p.: 111 °C, $[\alpha]_D^{20}$ = +258.8 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 41.053 min, t (minor) = 74.849 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.72 (d, *J* = 4.0 Hz, 1H), 8.20 (d, *J* = 12.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 4.0 Hz, 2H), 7.48 – 7.40 (m, 2H) , 7.38 – 7.30 (m, 3H), 7.22 (dd, *J* = 8.0, 3.2 Hz, 1H), 7.12 (t, *J* = 3.2 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.98 (dd, *J* = 8.4, 5.2 Hz, 1H), 6.53 – 6.50 (m, 1H), 5.06 (t, *J* = 6.4 Hz, 1H), 4.26 (d, *J* = 6.4 Hz, 2H), 2.96 (s, 3H), 2.48 (s, 3H), 1.45 (s, 9H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 163.7, 155.9, 152.4 (d, $J_{C-P}$ = 4.0 Hz), 147.6, 146.4 (d, $J_{C-P}$ = 7.0 Hz), 145.0, 141.5 (d, $J_{C-P}$ = 12.0 Hz), 138.8, 138.6 (d, $J_{C-P}$ = 7.0 Hz), 136.3, 132.7 (d, $J_{C-P}$ = 2.0 Hz), 132.5 (d, $J_{C-P}$ = 128.0 Hz), 131.7, 131.6, 131.5 (d, $J_{C-P}$ = 2.0 Hz), 131.3 (d, $J_{C-P}$ = 11.0 Hz), 130.6, 130.1 (d, $J_{C-P}$ = 11.0 Hz), 128.5, 127.8, 127.6, 126.8, 125.1 (d, $J_{C-P}$ = 13.0 Hz), 124.2, 123.6 (d, $J_{C-P}$ = 119.0 Hz), 121.5, 121.4 (d, $J_{C-P}$ = 7.0 Hz), 118.9, 113.8 (d, $J_{C-P}$ = 3.0 Hz), 28.4, 22.4 (d, $J_{C-P}$ = 3.0 Hz), 20.9 (d, $J_{C-P}$ = 5.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.10. **HRMS (ESI)** calculated for $C_{36}H_{37}N_3O_5P$ $[M + H]^+$ : 622.2465, found: 622.2461.




Processed Channel Descr.: W2489 ChB 210nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 41.634 | 21531379 | 51.16 | 144825 |
| 2 | W2489 ChB 210nm | 74.849 | 20554862 | 48.84 | 97319 |

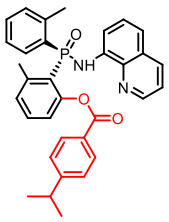



Processed Channel Descr.: W2489 ChB 210nm

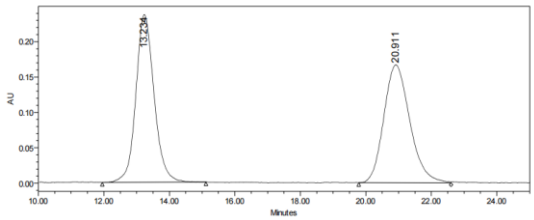
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 41.053 | 106314222 | 100.00 | 634140 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-isopropylbenzoate (3i)**

White foam, 64.1 mg, 60% yield. M.p.: 159- 161 °C, $[\alpha]_D^{20}$ = +297.5 (c = 0.5, $CHCl_3$), 95.1% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t

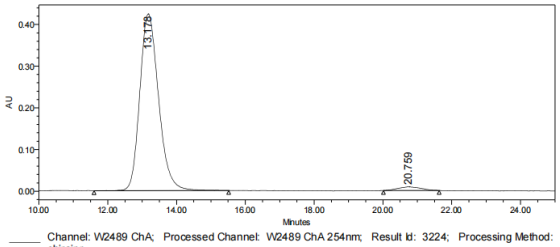


(major) = 13.178 min, t (minor) = 20.759 min. **$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.74 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.23 (d, *J* = 14.4 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.92 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.37 (m, 3H), 7.40 – 7.33 (m, 1H), 7.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.23 (dd, *J* = 7.6, 3.6 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.97 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.59 – 6.46 (m, 1H), 2.96 (s, 3H), 2.91 – 2.84 (m, 1H), 2.50 (s, 3H), 1.22 (dd, *J* = 7.2, 2.0 Hz, 6H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 164.1, 155.1, 152.6 (d, $J_{C-P}$ = 4.0 Hz), 147.7, 146.4 (d, $J_{C-P}$ = 7.0 Hz), 141.6 (d, $J_{C-P}$ = 11.0 Hz), 139.0, 138.8 (d, $J_{C-P}$ = 8.0 Hz), 136.4, 133.0 (d, $J_{C-P}$ = 128.0 Hz) 132.7 (d, $J_{C-P}$ = 2.0 Hz), 131.7(d, $J_{C-P}$ = 13.0 Hz), 131.5, 131.5(d, $J_{C-P}$ = 15.0 Hz), 130.6, 130.1 (d, $J_{C-P}$ = 11.0 Hz), 128.6, 127.7, 126.5, 126.2, 125.2 (d, $J_{C-P}$ = 33.0 Hz), 123.7 (d, $J_{C-P}$ = 119.0 Hz), 121.6, 121.5, 118.9, 113.9 (d, $J_{C-P}$ = 3.0 Hz), 34.3, 23.8, 23.7, 22.5 (d, $J_{C-P}$ = 3.0 Hz), 21.0 (d, $J_{C-P}$ = 4.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.30. **HRMS (ESI)** calculated for $C_{33}H_{32}N_2O_3P$ $[M + H]^+$ : 535.2145 found: 535.2143.




**Processed Channel Descr.: W2489 ChA 254nm**

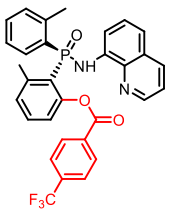
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 13.234 | 9171729 | 49.91 | 236667 |
| 2 | W2489 ChA 254nm | 20.911 | 9202992 | 50.09 | 166605 |



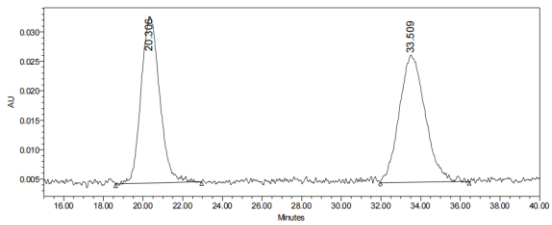

**Processed Channel Descr.: W2489 ChA 254nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 13.178 | 16064638 | 97.55 | 424406 |
| 2 | W2489 ChA 254nm | 20.759 | 403468 | 2.45 | 8530 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-(trifluoromethyl)benzoate (3j)**

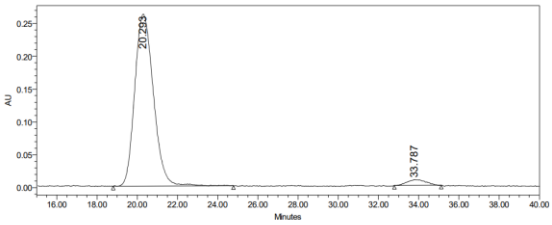


Light-yellow foam, 59.4 mg, 53% yield. M.p.: 137- 138 °C, $[\alpha]_D^{20}$ = + 179.2 (c = 0.5, $CHCl_3$), 93.72% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 85/15, 1.0 mL/min, λ = 254 nm, t (major) = 20.293 min, t (minor) = 33.767 min. **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ 8.67 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.14 – 8.06 (m, 2H), 7.87 (dd, *J* = 12.0, 7.8 Hz, 3H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.35 (m, 5H), 7.34 – 7.26 (m, 2H), 7.25 – 7.16 (m, 2H), 7.00 (dd, *J* = 7.8, 4.8 Hz, 1H) , 6.64 – 6.61 (m, 1H), 2.90 (s, 3H), 2.52 (s, 3H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 163.1, 152.2 (d, $J_{C-P}$ = 3.0 Hz), 147.7, 146.6 (d, $J_{C-P}$ = 6.0 Hz), 141.9 (d, $J_{C-P}$ = 12.0 Hz), 138.7, 138.6, 136.5, 136.4, 134.8 (q, $J_{C-F}$ = 16.5 Hz), 133.0, 132.9, 132.2 (q, $J_{C-F}$ = 16.5 Hz), 131.9 (d, $J_{C-P}$ = 12.0 Hz), 131.8 (d, $J_{C-P}$ = 15.0 Hz), 131.4 (d, $J_{C-P}$ = 12.0 Hz), 130.6, 130.5, 129.5 (d, $J_{C-P}$ = 291.0 Hz), 127.7, 125.3 (d, $J_{C-P}$ = 13.5 Hz), 125.0 (q, $J_{C-F}$ = 3.0 Hz), 124.4(d, $J_{C-P}$ = 12.0 Hz), 121.7, 121.4 (d, $J_{C-P}$ = 7.5 Hz), 119.9(q, $J_{C-F}$ = 268.5 Hz), 114.0 (d, $J_{C-P}$ = 3.0 Hz), 22.6 (d, $J_{C-P}$ = 3.0 Hz), 21.1 (d, $J_{C-P}$ = 6.0 Hz). **$^{19}$F NMR (564 MHz, CDCl3)** δ -63.2. **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 21.09. **HRMS (ESI)** calculated for $C_{31}H_{25}F_3N_2O_3P$ $[M + H]^+$ : 561.1549, found: 561.1547.




Processed Channel Descr.: W2489 ChA 254nm

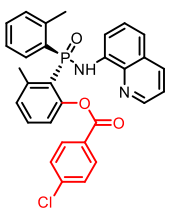
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 20.306 | 1843945 | 48.33 | 28316 |
| 2 | W2489 ChA 254nm | 33.509 | 1971230 | 51.67 | 21631 |



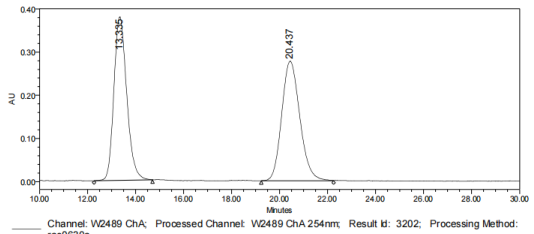

Processed Channel Descr.: W2489 ChA 254nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 20.293 | 16969692 | 96.86 | 261899 |
| 2 | W2489 ChA 254nm | 33.787 | 549932 | 3.14 | 8697 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-chlorobenzoate (3k)**

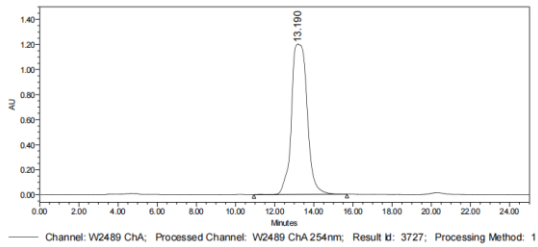


Light-yellow foam, 49.4 mg, 47% yield. M.p.: 166- 167°C, $[\alpha]_D^{20}$ = + 179.0 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 13.190 min, t (minor) = 20.437 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.72 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.19 – 8.08 (m, 2H), 7.91 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.39 (m, 2H), 7.42 – 7.29 (m, 3H), 7.27 – 7.18 (m, 1H), 7.20 – 7.10 (m, 4H), 6.99 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.64 – 6.54 (m, 1H), 2.94 (s, 3H), 2.49 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 163.3, 152.3 (d, $J_{C-P}$ = 4.0 Hz), 147.7, 146.6 (d, $J_{C-P}$ = 7.0 Hz), 141.8 (d, $J_{C-P}$ = 11.0 Hz), 139.9, 138.8, 138.7 (d, $J_{C-P}$ = 8.0 Hz), 136.5, 133.3, 132.8 (d, $J_{C-P}$ = 2.0 Hz), 131.8 (d, $J_{C-P}$ = 12.0 Hz), 131.6, 131.3 (d, $J_{C-P}$ = 12.0 Hz), 130.4 (d, $J_{C-P}$ = 11.0 Hz), 128.6, 128.4, 127.7, 127.4, 125.3 (d, $J_{C-P}$ = 14.0 Hz), 123.7 (d, $J_{C-P}$ = 119 Hz), 121.7, 121.6, 121.4 (d, $J_{C-P}$ = 7 Hz), 119.1, 113.9 (d, $J_{C-P}$ = 2.0 Hz), 22.5 (d, $J_{C-P}$ = 4.0 Hz), 21.0 (d, $J_{C-P}$ = 5.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 21.66. **HRMS (ESI)** calculated for $C_{30}H_{25}ClN_2O_3P$ $[M + H]^+$ : 527.1286, found: 527.1285.




Processed Channel Descr.: W2489 ChA 254nm

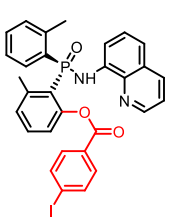
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 13.335 | 14052371 | 49.12 | 378578 |
| 2 | W2489 ChA 254nm | 20.437 | 14556894 | 50.88 | 277029 |




Processed Channel Descr.: W2489 ChA 254nm

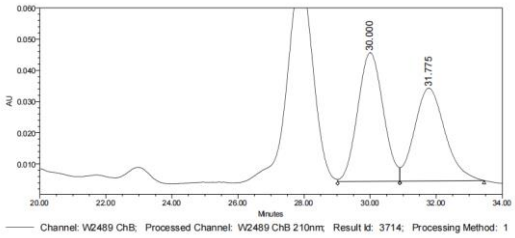
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 13.190 | 67197580 | 100.00 | 1200111 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-iodobenzoate (3l)**



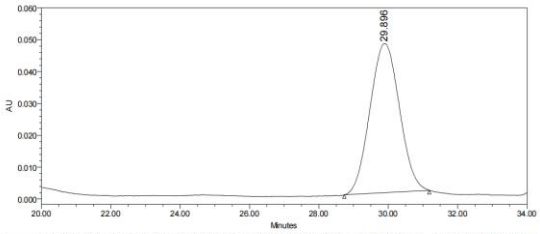
Light-yellow foam, 48.1 mg, 39% yield. M.p.: 171- 172°C, $[\alpha]_D^{20}$ = +219.7 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 29.896 min, t (minor) = 31.775 min. **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.70 (dd, *J* = 3.6, 1.2Hz, 1H), 8.16 – 8.08 (m, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.40 (m, 6H), 7.40 – 7.32 (m, 3H),

7.27 – 7.12 (m, 3H), 6.98 (dd, $J$ = 8.4, 4.2 Hz, 1H), 6.63 – 6.60 (m, 1H), 2.93 (s, 3H), 2.50 (s, 3H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 163.7, 152.3, 147.7, 146.6 (d, $J_{C-P}$ = 7.5 Hz), 141.8 (d, $J_{C-P}$ = 10.5 Hz), 138.7, 138.6 (d, $J_{C-P}$ = 7.5 Hz), 137.4, 136.5, 133.1, 132.8, 131.9, 131.7 (d, $J_{C-P}$ = 3.0 Hz), 131.7, 131.6, 131.4 (d, $J_{C-P}$ = 12.0 Hz), 130.3 (d, $J_{C-P}$ = 12.0 Hz), 128.4 (d, $J_{C-P}$ = 24.0 Hz), 127.7, 125.4 (d, $J_{C-P}$ = 13.5 Hz), 123.7 (d, $J_{C-P}$ = 118.5 Hz), 121.7, 121.4 (d, $J_{C-P}$ = 6.0 Hz), 119.1, 113.9 (d, $J_{C-P}$ = 3.0 Hz), 101.6, 22.5 (d, $J_{C-P}$ = 3.0 Hz), 21.0 (d, $J_{C-P}$ = 4.5 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 21.62. **HRMS (ESI)** calculated for $C_{30}H_{25}IN_2O_3P$ $[M + H]^+$ : 619.0642, found: 619.0640.




Processed Channel Descr.: W2489 ChB 210nm

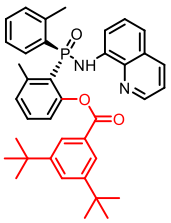
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 30.000 | 2216267 | 53.67 | 41291 |
| 2 | W2489 ChB 210nm | 31.775 | 1913036 | 46.33 | 29756 |



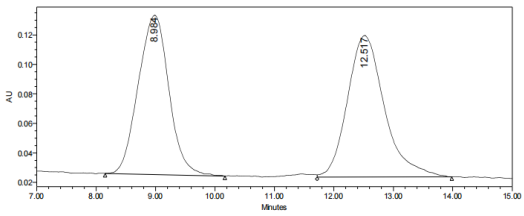

Processed Channel Descr.: W2489 ChB 210nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 29.896 | 2769493 | 100.00 | 46850 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 3,5-di-tert-butylbenzoate (3m)**



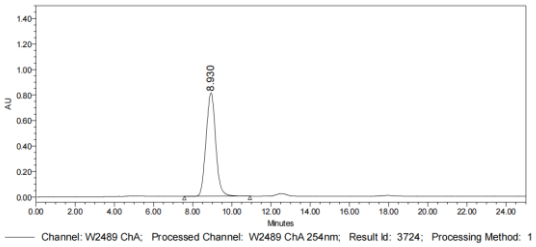
Light-yellow foam, 78.5 mg, 65% yield. M.p.: 169 - 170 °C, $[\alpha]_D^{20}$ = +200.0 (c = 0.5, $CHCl_3$), 94.3% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 8.930 min, t (minor) = 12.513 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.66 (dd, $J$ = 4.4, 2.0 Hz, 1H), 8.16 (d, $J$ = 14.4 Hz, 1H), 8.09 (dd, $J$ = 8.0, 1.6 Hz, 1H), 7.77 (dd, $J$ = 7.2, 1.2 Hz, 1H), 7.57 (d, $J$ = 1.6 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.45 – 7.39 (m, 1H), 7.39 – 7.33 (m, 2H), 7.30 (dd, $J$ = 8.0, 1.2 Hz, 1H) , 7.26 – 7.24 (m, 1H), 7.12 (dd, $J$ = 7.6, 4.8 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.41 – 6.36 (m, 1H), 2.98 (s, 3H), 2.51 (s, 3H), 1.15 (s, 18H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 164.7, 152.8 (d, $J_{C-P}$ = 3.0 Hz), 150.7, 147.9, 146.5 (d, $J_{C-P}$ = 6.0 Hz), 141.5 (d, $J_{C-P}$ = 10.5 Hz), 138.7 (d, $J_{C-P}$ = 7.5 Hz), 138.6, 136.2, 132.7 (d, $J_{C-P}$ = 1.5 Hz), 132.4 (d, $J_{C-P}$ = 130.5 Hz), 131.6 (d, $J_{C-P}$ = 7.5 Hz), 131.5, 131.5, 131.3 (d, $J_{C-P}$ = 3.0 Hz), 130.1 (d, $J_{C-P}$ = 12.0 Hz), 128.3 (d, $J_{C-P}$ = 34.5 Hz), 127.5, 127.3, 124.9 (d, $J_{C-P}$ = 13.5 Hz), 124.6, 123.4 (d, $J_{C-P}$ = 118.5 Hz), 121.8 (d, $J_{C-P}$ = 6.0 Hz), 121.4, 118.8, 113.8 (d, $J_{C-P}$ = 3.0 Hz), 34.7, 31.2, 22.4 (d, $J_{C-P}$ = 3.0 Hz), 21.0 (d, $J_{C-P}$ = 4.5 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.01. **HRMS (ESI)** calculated for $C_{38}H_{42}N_2O_3P$ $[M + H]^+$ : 605.2928, found: 605.2926.




Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3236; Processing Method: rac04313a

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 8.984 | 3871385 | 48.30 | 107917 |
| 2 | W2489 ChB 210nm | 12.517 | 4144590 | 51.70 | 95914 |

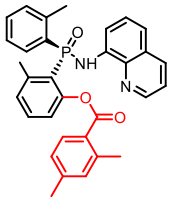



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3724; Processing Method: 1

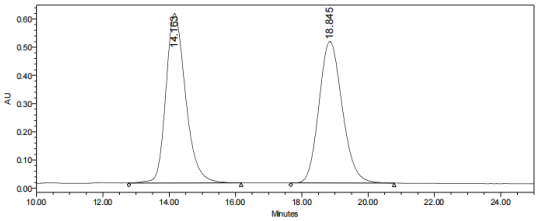
**Processed Channel Descr.: W2489 ChA 254nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 8.930 | 27747342 | 100.00 | 810052 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 2,4-dimethylbenzoate (3n)**



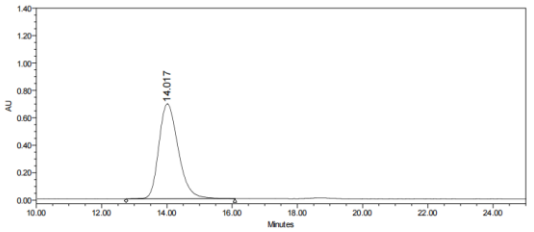
Light-yellow foam, 62.4 mg, 60% yield. M.p.: 150-152 °C, $[\alpha]_D^{20}$ = +453.0 (c = 0.5, $CHCl_3$), >% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 14.017 min, t (minor) = 18.723 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.79 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.25 (d, *J* = 14.0 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.92 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 7.22 (dd, *J* = 7.6, 3.2 Hz, 1H), 7.15 – 7.13 (m, 2H), 6.99 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.89 (s, 1H), 6.74 (dd, *J* = 8.0, 2.0 Hz, 1H) , 6.51 – 6.45 (m, 1H), 3.00 (s, 3H), 2.48 (s, 3H), 2.28 (s, 3H), 2.19 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 163.8, 152.5 (d, $J_{C-P}$ = 4.0 Hz), 147.6, 146.5 (d, $J_{C-P}$ = 6.0 Hz), 143.6, 142.4, 141.5 (d, $J_{C-P}$ = 12.0 Hz), 139.0, 138.7 (d, $J_{C-P}$ = 48.0 Hz), 136.3, 132.8 (d, $J_{C-P}$ = 129.0 Hz), 132.6 (d, $J_{C-P}$ = 2.0 Hz), 132.4, 131.9, 131.4 (d, $J_{C-P}$ = 36.0 Hz), 131.4, 131.3 (d, $J_{C-P}$ = 2.0 Hz), 129.8 (d, $J_{C-P}$ = 11.0 Hz), 128.6, 127.7, 126.3, 125.0 (d, $J_{C-P}$ = 13.0 Hz), 124.5, 123.7 (d, $J_{C-P}$ = 119.0 Hz), 121.6, 121.5, 118.8, 113.8 (d, $J_{C-P}$ = 3.0 Hz), 22.3 (d, $J_{C-P}$ = 3.0 Hz), 22.0, 21.5, 20.9 (d, $J_{C-P}$ = 5.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.56. **HRMS (ESI)** calculated for $C_{32}H_{30}N_2O_3P$ $[M + H]^+$ : 521.1989, found: 521.1989.




Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3231; Processing Method: rac0413f

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 14.163 | 24785549 | 50.24 | 600565 |
| 2 | W2489 ChB 210nm | 18.845 | 24549928 | 49.76 | 502337 |



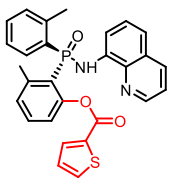

Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3721; Processing Method: 1

**Processed Channel Descr.: W2489 ChB 210nm**

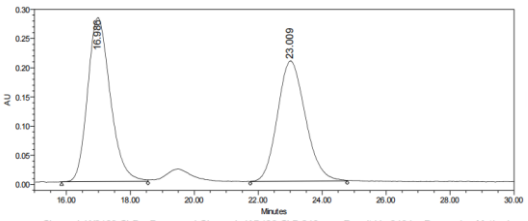
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 14.017 | 28594095 | 100.00 | 692024 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl thiophene-2-carboxylate (3o)**

Light-yellow foam, 45.8 mg, 46% yield. M.p.: 132-134 °C, $[\alpha]_D^{20}$ = +171.3 (c = 0.6, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm,

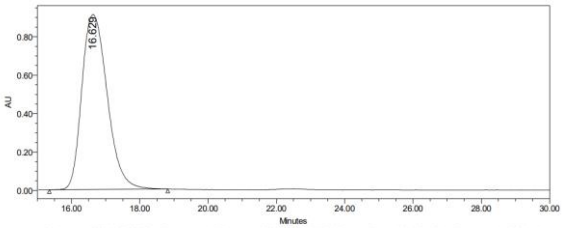


t (major) = 16.629 min, t (minor) = 23.009 min. **$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.74 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.22 (d, *J* = 14.4 Hz, 1H), 8.11 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.92 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.71 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.42 – 7.39 (m, 1H), 7.37 – 7.31 (m, 2H), 7.23 (dd, *J* = 7.6, 3.2 Hz, 1H), 7.21 – 7.13 (m, 2H), 7.00 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.89 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.67 – 6.63 (m, 1H), 2.97 (s, 3H), 2.50 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 159.3, 152.0 (d, $J_{C-P}$ = 4.0 Hz), 147.6, 146.5 (d, $J_{C-P}$ = 6.0 Hz), 141.6 (d, $J_{C-P}$ = 11.0 Hz), 138.8, 138.7 (d, $J_{C-P}$ = 8.0 Hz), 136.3, 134.8, 133.7, 132.7 (d, $J_{C-P}$ = 2.0 Hz), 132.5 (d, $J_{C-P}$ = 129.0 Hz), 132.6, 131.7, 131.6 (d, $J_{C-P}$ = 3.0 Hz), 131.6, 131.3 (d, $J_{C-P}$ = 11.0 Hz), 130.2 (d, $J_{C-P}$ = 12.0 Hz), 128.5, 127.6 (d, $J_{C-P}$ = 6.0 Hz), 125.0 (d, $J_{C-P}$ = 13.0 Hz), 123.6 (d, $J_{C-P}$ = 120.0 Hz), 121.6, 121.4 (d, $J_{C-P}$ = 7.0 Hz), 118.9, 113.8 (d, $J_{C-P}$ = 2.0 Hz), 22.4 (d, $J_{C-P}$ = 3.0 Hz), 20.9 (d, $J_{C-P}$ = 5.0 Hz) . **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.20. **HRMS (ESI)** calculated for $C_{28}H_{24}N_2O_3PS$ $[M + H]^+$ : 499.1240, found: 499.1237.




Processed Channel Descr.: W2489 ChB 210nm

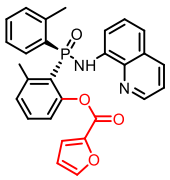
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 16.986 | 13810120 | 52.46 | 280952 |
| 2 | W2489 ChB 210nm | 23.009 | 12512996 | 47.54 | 206204 |



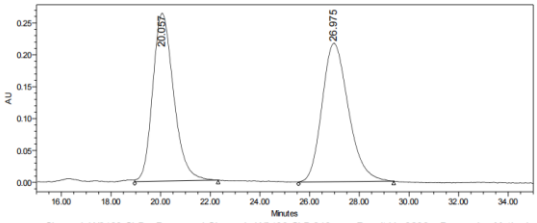

Processed Channel Descr.: W2489 ChB 210nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 16.629 | 47010695 | 100.00 | 910311 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl furan-2-carboxylate (3p)**



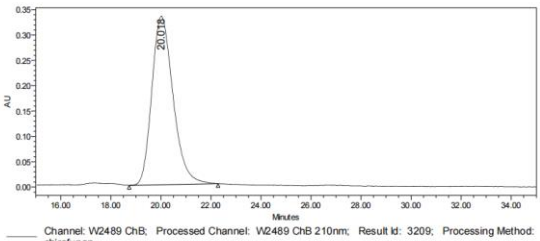
Light-yellow foam, 42.4 mg, 44% yield. M.p.: 129 -130 °C, $[\alpha]_D^{20}$ = +129.0 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 210 nm, t (major) = 20.018 min, t (minor) = 26.975 min. **$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.74 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.21 (d, *J* = 14.0 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.94 (dd, *J* = 4.4, 1.6 Hz, 1H), 7.52 – 7.32 (m, 6H), 7.27 – 7.12 (m, 4H), 7.00 (dd, *J* = 8.4, 4.8 Hz, 1H) , 6.75 – 6.70 (m, 1H), 6.33 (dd, *J* = 3.6, 1.6 Hz, 1H), 2.96 (s, 3H), 2.50 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 155.4, 151.4 (d, $J_{C-P}$ = 4.0 Hz), 147.8, 147.0, 146.6 (d, $J_{C-P}$ = 6.0 Hz), 143.5, 141.8 (d, $J_{C-P}$ = 11.0 Hz), 138.9, 138.8 (d, $J_{C-P}$ = 8.0 Hz), 136.5, 132.8 (d, $J_{C-P}$ = 2.0 Hz), 132.5 (d, $J_{C-P}$ = 125.0 Hz), 131.9, 131.8 (d, $J_{C-P}$ = 2.0 Hz), 131.5 (d, $J_{C-P}$ = 12.0 Hz), 130.3 (d, $J_{C-P}$ = 11.0 Hz), 128.6, 127.7, 124.7 (d, $J_{C-P}$ = 14.0 Hz), 123.8 (d, $J_{C-P}$ = 119.0 Hz), 121.6, 121.2 (d, $J_{C-P}$ = 6.0 Hz), 119.7, 119.0, 113.9 (d, $J_{C-P}$ = 2.0 Hz), 112.0, 22.5 (d, $J_{C-P}$ = 3.0 Hz), 21.0 (d, $J_{C-P}$ = 5.0 Hz). **$^{31}$PI NMR (162 MHz, $CDCl_3$)** δ 22.20. **HRMS (ESI)** calculated for $C_{28}H_{24}N_2O_4P$ $[M + H]^+$ : 483.1468, found: 483.1465.




Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3206; Processing Method: rac funan

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 20.057 | 15422678 | 49.00 | 263100 |
| 2 | W2489 ChB 210nm | 26.975 | 16050297 | 51.00 | 216920 |

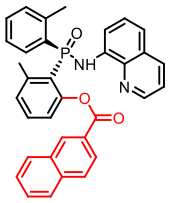



Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3209; Processing Method: chirafunan

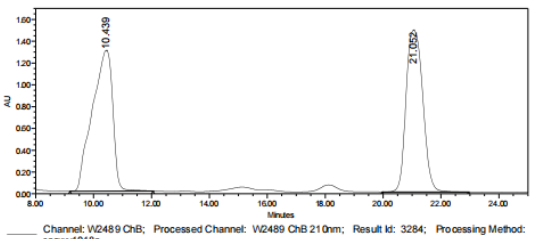
**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 20.018 | 19626827 | 100.00 | 332372 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 2-naphthoate (3q)**



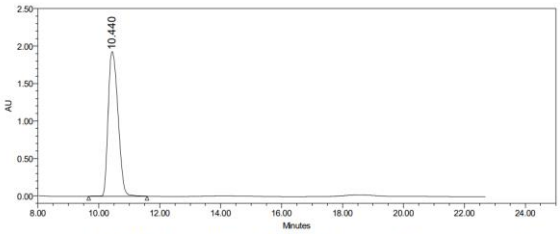
white foam, 65.0 mg, 60% yield. M.p.: 145- 146 °C, $[\alpha]_D^{20}$ = + 220.0 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 10.440 min, t (minor) = 21.052 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.68 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.35 – 8.22 (m, 2H), 8.04 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.83 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.28 (m, 8H), 7.31 – 7.23 (m, 1H), 7.20 – 7.03 (m, 3H) , 6.47 – 6.43 (m, 1H), 2.99 (s, 3H), 2.54 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 164.2, 152.6 (d, $J_{C-P}$ = 3.0 Hz), 147.7, 146.5 (d, $J_{C-P}$ = 7.0 Hz), 141.7 (d, $J_{C-P}$ = 11.0 Hz), 138.8, 138.6 (d, $J_{C-P}$ = 7.0 Hz), 136.3, 135.6, 132.8 (d, $J_{C-P}$ = 3.0 Hz) 132.5 (d, $J_{C-P}$ = 129.0 Hz), 131.9, 131.7 (d, $J_{C-P}$ = 12.0 Hz), 131.5 (d, $J_{C-P}$ = 3.0 Hz), 131.5, 131.4 (d, $J_{C-P}$ = 12.0 Hz), 130.2 (d, $J_{C-P}$ = 11.0 Hz), 129.4, 128.6, 128.5, 127.8, 127.7, 127.6, 126.6, 126.1, 125.6, 125.3 (d, $J_{C-P}$ = 14.0 Hz), 123.7 (d, $J_{C-P}$ = 119.0 Hz), 121.6 (d, $J_{C-P}$ = 7.0 Hz), 121.4, 119.0, 113.7 (d, $J_{C-P}$ = 3.0 Hz), 22.5 (d, $J_{C-P}$ = 3.0 Hz), 21.0 (d, $J_{C-P}$ = 12.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 21.93. **HRMS (ESI)** calculated for $C_{34}H_{28}N_2O_3P$ $[M + H]^+$ : 543.1832, found: 543.1830.




Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3284; Processing Method: racoxy1018a

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 10.439 | 63455468 | 51.60 | 1290687 |
| 2 | W2489 ChB 210nm | 21.052 | 59523957 | 48.40 | 1484310 |

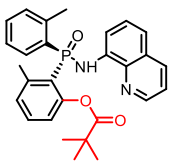



Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3288; Processing Method: chiraxxy0824a

**Processed Channel Descr.: W2489 ChB 210nm**

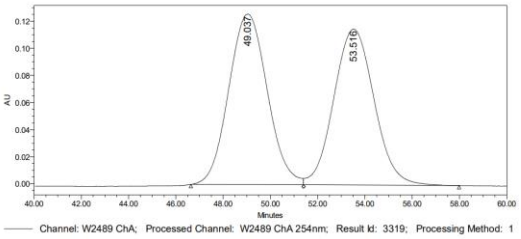
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 10.440 | 43493602 | 100.00 | 1930886 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl pivalate (3r)**



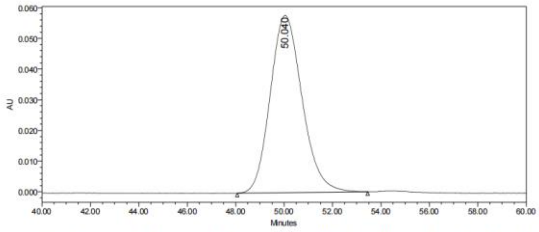
white foam, 59.5 mg, 63% yield. M.p.: 109- 111 °C, $[\alpha]_D^{20}$ = +161.1 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 0.6 mL/min, λ = 254 nm, t (major) = 50.040 min, t (minor) = 53.516 min. **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.71 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.18 (d, *J* = 13.8

Hz, 1H), 8.10 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.92 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.57 (dd, *J* = 15.6, 7.2Hz, 1H), 7.42 – 7.34 (m, 4H), 7.31 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.16-7.12 (m, 2H), 6.81 (dd, *J* = 8.4, 4.8 Hz, 1H), 2.85 (s, 3H), 2.59 (s, 3H), 1.06 (s, 9H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 176.5, 154.1 (d, $J_{C-P}$ = 3.0 Hz), 147.6, 146.2 (d, $J_{C-P}$ = 7.5 Hz), 142.0 (d, $J_{C-P}$ = 9.0 Hz), 139.0, 138.9 (d, $J_{C-P}$ = 7.5 Hz), 136.4, 133.5, 132.6 (d, $J_{C-P}$ = 3.0 Hz), 132.0 (d, $J_{C-P}$ = 150.0 Hz), 132.0, 131.5 (d, $J_{C-P}$ = 15.0 Hz), 129.8 (d, $J_{C-P}$ = 12.0 Hz), 128.6, 127.8, 125.5 (d, $J_{C-P}$ = 15.0 Hz), 123.1 (d, $J_{C-P}$ = 120.0 Hz), 121.6, 121.0 (d, $J_{C-P}$ = 7.5 Hz), 118.8, 113.6 (d, $J_{C-P}$ = 3.0 Hz), 39.2, 26.8, 22.8 (d, $J_{C-P}$ = 3.0 Hz), 21.2 (d, $J_{C-P}$ = 6.0 Hz). **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 23.48. **HRMS (ESI)** calculated for $C_{28}H_{30}N_2O_3P$ $[M + H]^+$ : 473.1989, found: 473.1986.




**Processed Channel Descr.: W2489 ChA 254nm**

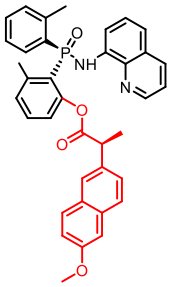
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 49.037 | 14267262 | 51.06 | 125929 |
| 2 | W2489 ChA 254nm | 53.516 | 13676733 | 48.94 | 115159 |



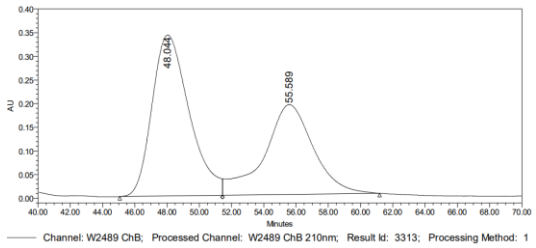

**Processed Channel Descr.: W2489 ChA 254nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 50.040 | 5289046 | 100.00 | 57806 |

**3-methyl-2-((S)-(quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (3s)**

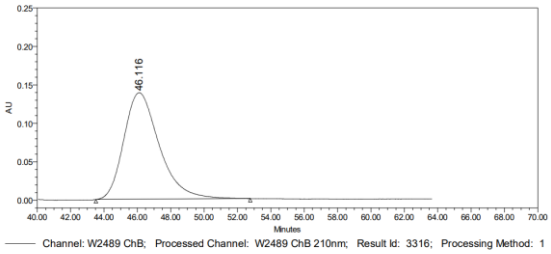


Light-yellow foam, 50.4 mg, 42% yield. M.p.: 177 - 178 °C, $[\alpha]_D^{20}$ = +171.1 (c = 0.2, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 46.116 min, t (minor) = 55.583 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.75 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.25 (d, *J* = 14.0 Hz, 1H), 8.17 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.96 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.77 -7.74 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.58 (s, 1H),7.47 – 7.38 (m, 5H), 7.30 -7.27 (m, 1H), 7.26 – 7.25 (m, 1H), 7.22 – 7.15 (m, 1H), 7.18 – 7.07 (m, 3H), 6.52 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.92 (s, 3H), 3.58 (q, *J* = 7.2 Hz, 1H), 2.88 (s, 3H), 2.50 (s, 3H), 1.18 (d, *J* = 6.8 Hz, 3H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 171.9, 158.0, 148.0, 146.2 (d, $J_{C-P}$ = 7.5 Hz), 142.1, 139.1, 136.6, 134.8, 134.2, 134.0, 132.6 (d, $J_{C-P}$ = 4.5 Hz), 132.2 (d, $J_{C-P}$ = 12.0 Hz), 131.9 (d, $J_{C-P}$ = 3.0 Hz), 131.9, 131.0, 131.0, 130.9, 129.9 (d, $J_{C-P}$ = 10.5 Hz), 129.4, 128.9 (d, $J_{C-P}$ = 57.0 Hz), 127.9, 127.5, 126.3 (d, $J_{C-P}$ = 6.0 Hz), 125.6 (d, $J_{C-P}$ = 13.5 Hz), 122.8, 121.7, 120.7 (d, $J_{C-P}$ = 7.5 Hz), 120.7, 119.2 (d, $J_{C-P}$ = 19.5 Hz), 114.3, 114.2, 105.8, 55.5, 45.1, 34.1, 22.3, 21.1 (d, $J_{C-P}$ = 4.5 Hz). **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 22.43. **HRMS (ESI)** calculated for $C_{37}H_{34}N_2O_4P$ $[M + H]^+$ : 601.2251, found: 601.2247.




Processed Channel Descr.: W2489 ChB 210nm

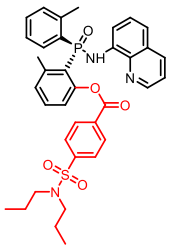
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 48.044 | 54415275 | 57.45 | 339971 |
| 2 | W2489 ChB 210nm | 55.589 | 40309201 | 42.55 | 189672 |



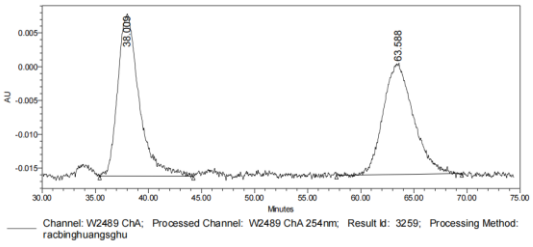

Processed Channel Descr.: W2489 ChB 210nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 46.116 | 20473376 | 100.00 | 138512 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl 4-(N,N-dipropylsulfamoyl) benzoate (3t)**

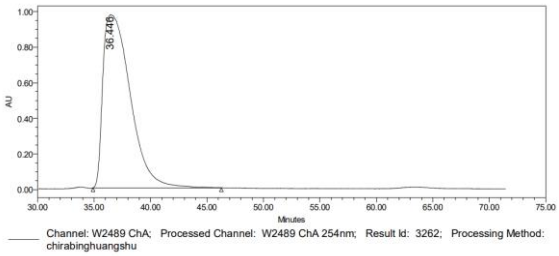


Light-yellow foam, 47.2 mg, 36% yield. M.p.: 139 °C, $[\alpha]_D^{20}$ = +305.5 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 36.446 min, t (minor) = 63.588 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.70 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.16 – 8.08 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.86 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.29 – 7.25 (m, 1H), 7.17 (t, *J* = 3.6 Hz, 2H), 7.00 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.62 – 6.57 (m, 1H), 3.08 – 3.00 (m, 4H), 2.90 (s, 3H), 2.50 (s, 3H), 1.50 (h, *J* = 7.6 Hz, 4H), 0.83 (t, *J* = 7.6 Hz, 6H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 163.0, 152.3 (d, $J_{C-P}$ = 3.0 Hz), 147.8, 146.5 (d, $J_{C-P}$ = 7.0 Hz), 144.7, 141.9 (d, $J_{C-P}$ = 11,0 Hz), 138.6, 136.6, 133.2, 132.9 (d, $J_{C-P}$ = 2.0 Hz), 132.1, 132.0, 131.9, 131.8 (d, $J_{C-P}$ = 3.0 Hz), 131.3(d, $J_{C-P}$ = 12.0 Hz), 130.8, 130.6 (d, $J_{C-P}$ = 11.0 Hz), 128.6, 127.7, 126.6, 125.2 (d, $J_{C-P}$ = 14.0 Hz), 123.7 (d, $J_{C-P}$ = 119.0 Hz), 121.8, 121.4 (d, $J_{C-P}$ = 7.0 Hz), 119.3, 113.9 (d, $J_{C-P}$ = 3.0 Hz), 49.9, 22.5 (d, $J_{C-P}$ = 3.0 Hz), 21.9, 21.0 (d, $J_{C-P}$ = 5.0 Hz), 11.2. **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 21.16. **HRMS (ESI)** calculated for $C_{36}H_{39}N_3O_5PS$ $[M + H]^+$ : 656.2343 found: 656.2343.




Processed Channel Descr.: W2489 ChA 254nm

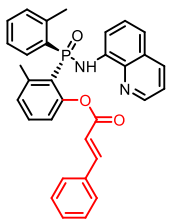
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 38.009 | 3374156 | 50.72 | 23988 |
| 2 | W2489 ChA 254nm | 63.588 | 3278299 | 49.28 | 16489 |



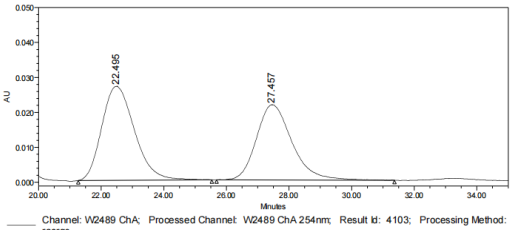

Processed Channel Descr.: W2489 ChA 254nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 36.446 | 163720347 | 100.00 | 972438 |

**(S)-3-methyl-2-((quinolin-8-ylamino)(o-tolyl)phosphoryl)phenyl cinnamate (3u)**



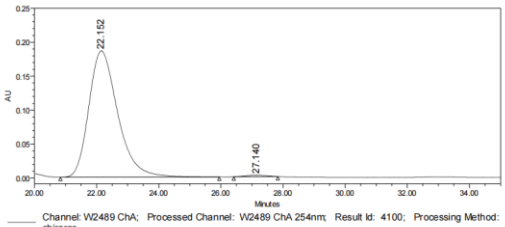
Light-yellow foam, 44.5 mg, 43% yield. M.p.: 127 - 128 °C, $[\alpha]_D^{20}$ = +86.0 (c = 0.2, $CHCl_3$), 98.4% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 22.152 min, t (minor) = 27.140 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.73 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.20 (d, *J* = 14.4 Hz, 1H), 8.08 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.63 (dd, *J* = 15.2, 6.8 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.40 – 7.27 (m, 7H), 7.25 – 7.18 (m, 4H), 7.04 – 6.93 (m, 2H), 6.04 (d, *J* = 16.0 Hz, 1H), 2.91 (s, 3H), 2.53 (s, 3H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 164.3, 152.3 (d, $J_{C-P}$ = 4.5 Hz), 147.9, 146.4 (d, $J_{C-P}$ = 7.5 Hz), 146.2, 142.0 (d, $J_{C-P}$ = 10.5 Hz), 138.9 (d, $J_{C-P}$ = 7.5 Hz), 138.9, 136.5, 134.2, 133.1 (d, $J_{C-P}$ = 129.0 Hz), 132.7, 132.0 (d, $J_{C-P}$ = 12.0 Hz), 131.8, 131.8 (d, $J_{C-P}$ = 7.5 Hz), 130.1, 130.0, 129.0, 128.7, 128.2, 127.7, 125.5, 125.4, 121.6, 121.3(d, $J_{C-P}$ = 6.0 Hz), 119.1, 117.1, 114.1(d, $J_{C-P}$ = 3.0 Hz), 22.6(d, $J_{C-P}$ = 3.0 Hz), 21.2(d, $J_{C-P}$ = 4.5 Hz). **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 21.76. **HRMS (ESI)** calculated for $C_{32}H_{27}N_2O_3P$ [M + H]$^+$ : 519.1832 found: 519.1831.




Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4103; Processing Method: racrgs

**Processed Channel Descr.: W2489 ChA 254nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 22.495 | 1954988 | 53.43 | 26922 |
| 2 | W2489 ChA 254nm | 27.457 | 1703929 | 46.57 | 21568 |

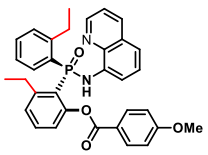



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4100; Processing Method: chirargs

**Processed Channel Descr.: W2489 ChA 254nm**

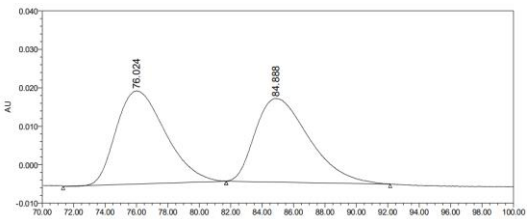
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 22.152 | 12033318 | 99.20 | 186008 |
| 2 | W2489 ChA 254nm | 27.140 | 96534 | 0.80 | 1963 |

**(S)-3-ethyl-2-((2-ethylphenyl)(quinolin-8-ylamino)phosphoryl)phenyl 4-methoxybenzoate (3v)**



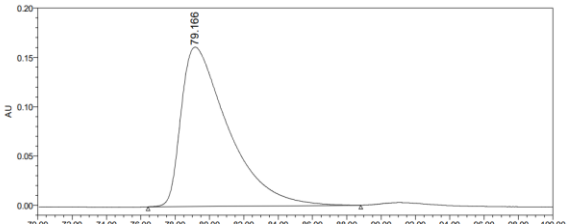
Light-yellow foam, 68.2 mg, 62% yield. M.p.: 124 - 125 °C, $[\alpha]_D^{20}$ = +267.6 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 79.166 min, t (minor) = 84.888 min. **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.74 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.19 (d, *J* = 14.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.30 (dd, *J* = 7.8, 3.6 Hz, 1H), 7.23 – 7.19 (m, 2H), 6.98 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.66 (d, *J* = 9.0 Hz, 2H), 6.53 – 6.51 (m, 1H), 3.80 (s, 3H), 3.75 – 3.69 (m, 1H), 3.38 – 3.32 (m, 1H), 3.04 – 2.97 (m, 1H), 2.91 – 2.85 (m, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.8 Hz, 3H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 163.8, 163.6, 152.9 (d, $J_{C-P}$ = 7.5 Hz), 152.6 (d, $J_{C-P}$ = 4.5 Hz), 147.8 (d, $J_{C-P}$ = 10.5 Hz), 147.6, 139.2, 138.8 (d, $J_{C-P}$ = 7.5 Hz), 136.4, 132.8 (d, $J_{C-P}$ = 130.5 Hz), 132.8, 132.6, 131.6, 131.5 (d, $J_{C-P}$ = 6.0 Hz), 129.9 (d, $J_{C-P}$ = 12.0 Hz), 128.7, 128.6 (d, $J_{C-P}$ = 10.5 Hz), 127.9, 125.2 (d, $J_{C-P}$ = 12.0 Hz), 123.9(d, $J_{C-P}$ = 120.0 Hz), 121.6, 121.5, 121.4 (d, $J_{C-P}$ = 7.5 Hz), 118.8,

114.1 (d, $J_{C-P}$ = 2.0 Hz), 113.4, 55.5, 27.3 (d, $J_{C-P}$ = 3.0 Hz), 27.0 (d, $J_{C-P}$ = 4.5 Hz), 17.0, 15.2. **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 22.46. **HRMS (ESI)** calculated for $C_{33}H_{32}N_2O_4P$ $[M + H]^+$ : 551.2094, found: 551.2090.




Processed Channel Descr.: W2489 ChA 254nm

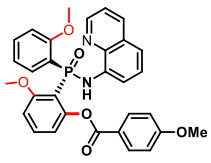
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 76.024 | 5267962 | 50.39 | 24202 |
| 2 | W2489 ChA 254nm | 84.888 | 5186105 | 49.61 | 21744 |



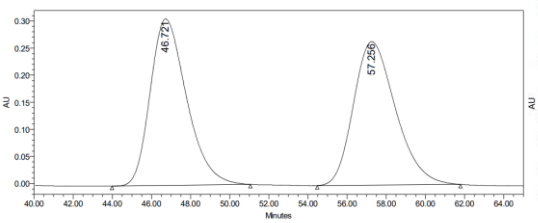

Processed Channel Descr.: W2489 ChA 254nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 79.166 | 30813807 | 100.00 | 161555 |

**(S)-3-methoxy-2-((2-methoxyphenyl)(quinolin-8-ylamino)phosphoryl)phenyl 4-methoxybenzoate (3w)**

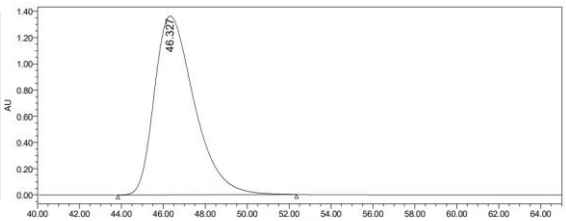


Light-yellow foam, 35.5 mg, 32% yield. M.p.: 109 - 111 °C, $[\alpha]_D^{20}$ = +211.1 (c = 0.2, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 0.6 mL/min, λ = 254 nm, t (major) = 46.327 min, t (minor) = 57.256 min. **$^1$H NMR (600 MHz, $CDCl_3$)** δ 9.53 (d, *J* = 12.0 Hz, 1H), 8.71 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.00 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.98 – 7.89 (m, 3H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.32 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.85 (dd, *J* = 9.0, 4.8 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.78 – 6.76 (m, 1H), 6.76 – 6.70 (m, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 3.61 (s, 3H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 164.3, 163.5, 161.5, 160.1 (d, $J_{C-P}$ = 3.0 Hz), 154.4, 147.4, 139.4, 139.3 (d, $J_{C-P}$ = 9.0 Hz), 135.9, 134.8, 134.7, 133.1, 132.8, 132.5, 128.3, 127.5, 122.7, 121.8, 121.0, 120.1 (d, $J_{C-P}$ = 13.5 Hz), 118.1, 116.8 (d, $J_{C-P}$ = 6.0 Hz), 113.6 (d, $J_{C-P}$ = 3.0 Hz), 113.3, 111.1 (d, $J_{C-P}$ = 7.5 Hz), 108.8 (d, $J_{C-P}$ = 6.0 Hz), 56.2, 55.6, 55.4. **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 13.66. **HRMS (ESI)** calculated for $C_{31}H_{28}N_2O_6P$ $[M + H]^+$ : 555.1679, found: 555.1677.




Processed Channel Descr.: W2489 ChB 210nm

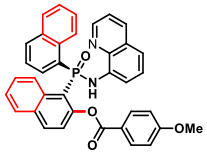
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 46.721 | 39761578 | 50.12 | 307440 |
| 2 | W2489 ChB 210nm | 57.256 | 39576742 | 49.88 | 264861 |



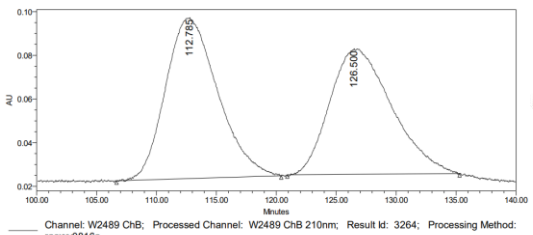

Processed Channel Descr.: W2489 ChB 210nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 46.327 | 180202471 | 100.00 | 1363086 |

**(S)-1-(naphthalen-1-yl(quinolin-8-ylamino)phosphoryl)naphthalen-2-yl 4-methoxybenzoate (3x)**

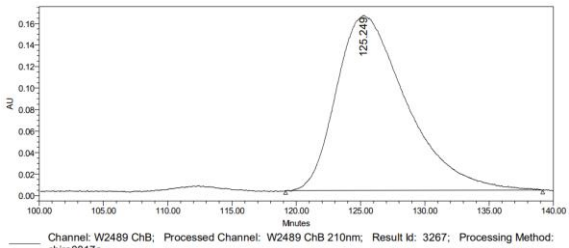


yellow foam, 77.2 mg, 65% yield. M.p.: 190- 191 °C, $[\alpha]_D^{20}$ = +326.5 (c = 0.5, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 85/15, 1.0 mL/min, λ = 210 nm, t (major) = 125.249 min, t (minor) = 112.785 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.94 (d, *J* = 8.8 Hz, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 8.63 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.40 (d, *J* = 14.8 Hz, 1H), 8.09 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.99 – 7.91 (m, 2H), 7.82 – 7.75 (m, 2H), 7.74 – 7.71 (m, 1H), 7.70 – 7.66 (m, 1H), 7.60 – 7.56 (m, 3H), 7.47 – 7.42 (m, 1H), 7.40 – 7.32 (m, 4H), 7.17 (dd, *J* = 8.8, 4.8 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.60 – 6.58 (m, 2H), 3.80 (s, 3H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 163.8 (d, $J_{C-P}$ = 6.0 Hz), 152.1 (d, $J_{C-P}$ = 1.5 Hz), 147.6, 138.7, 138.7, 136.2, 135.7(d, $J_{C-P}$ = 9.0 Hz), 134.9, 134.9, 133.9 (d, $J_{C-P}$ = 10.5 Hz), 133.2 (d, $J_{C-P}$ = 10.5 Hz), 132.6 (d, $J_{C-P}$ = 3.0 Hz), 132.3, 132.1 (d, $J_{C-P}$ = 10.5 Hz), 131.7(d, $J_{C-P}$ = 12.0 Hz), 130.0 (d, $J_{C-P}$ = 129.0 Hz), 128.7, 128.7, 128.5, 128.1, 127.6 (d, $J_{C-P}$ = 3.0 Hz), 127.5, 127.4, 126.7( d, $J_{C-P}$ = 6.0 Hz), 126.3, 126.2, 124.2 (d, $J_{C-P}$ = 15.0 Hz), 122.1 (d, $J_{C-P}$ = 7.5 Hz), 121.4, 120.9, 119.4 (d, $J_{C-P}$ = 120.0 Hz), 119.1, 114.1 (d, $J_{C-P}$ = 3.0 Hz), 113.3, 55.4. **$^{31}$P NMR (243 MHz, $CDCl_3$)** δ 22.53. **HRMS (ESI)** calculated for $C_{37}H_{28}N_2O_4P$ $[M + H]^+$ : 595.1781, found: 595.1777.




**Processed Channel Descr.: W2489 ChB 210nm**

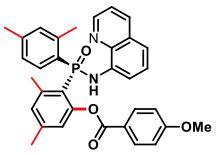
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 112.785 | 22261126 | 51.91 | 73483 |
| 2 | W2489 ChB 210nm | 126.500 | 20619333 | 48.09 | 57419 |




**Processed Channel Descr.: W2489 ChB 210nm**

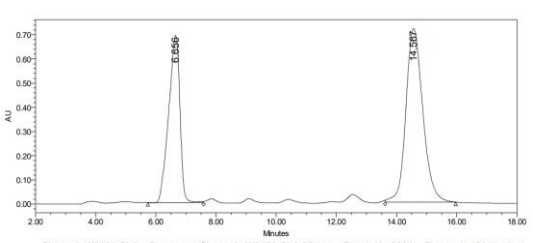
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 125.249 | 61581564 | 100.00 | 162521 |

**(S)-2-((2,4-dimethylphenyl)(quinolin-8-ylamino)phosphoryl)-3,5-dimethylphenyl 4-methoxybenzoate (3y)**



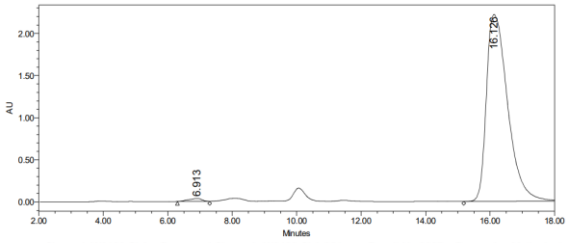
Light-yellow foam, 56.1 mg, 51% yield. M.p.: 130 - 131 °C, $[\alpha]_D^{20}$ = +434.3 (c = 0.5, $CHCl_3$), 97.98% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 16.126 min, t (minor) = 6.913 min. **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.72 (dd, *J* = 4.2, 1.2 Hz, 1H), 8.15 – 8.08 (m, 2H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 2H), 7.40 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.04 (s, 1H), 6.94 (d, *J* = 4.8 Hz, 1H), 6.79 (d, *J* = 4.2 Hz, 1H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.36 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 2.90 (s, 3H), 2.47 (s, 3H), 2.35 (s, 3H), 2.15 (s, 3H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 163.9, 163.7, 152.7 (d, $J_{C-P}$ = 4.5 Hz), 147.6, 146.1 (d, $J_{C-P}$ = 6.0 Hz), 143.4, 141.7 (d, $J_{C-P}$ = 8.0 Hz), 141.6 (d, $J_{C-P}$ = 3.0 Hz), 139.2, 138.9 (d, $J_{C-P}$ = 9.0 Hz), 136.3, 132.5 (d, $J_{C-P}$ = 13.5 Hz), 132.4, 131.8 (d, $J_{C-P}$ = 12.0 Hz), 131.1(d, $J_{C-P}$ = 10.5 Hz), 129.8 (d, $J_{C-P}$ = 132.0 Hz), 128.6, 127.8, 125.8 (d, $J_{C-P}$ = 13.5 Hz),

122.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 121.7, 121.5, 120.9 (d, $J_{C\text{-}P}$ = 121.5 Hz), 118.7, 113.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 113.3, 55.5, 22.5 (d, $J_{C\text{-}P}$ = 4.5 Hz), 21.4, 21.4, 21.0 (d, $J_{C\text{-}P}$ = 4.5 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.29. **HRMS (ESI)** calculated for $C_{33}H_{32}N_2O_4P$ $[M + H]^+$ : 551.2094, found: 551.2088.




Processed Channel Descr.: W2489 ChA 254nm

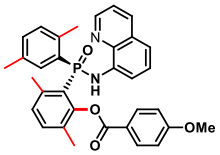
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 6.656 | 17923201 | 38.95 | 690974 |
| 2 | W2489 ChA 254nm | 14.567 | 28090049 | 61.05 | 717512 |



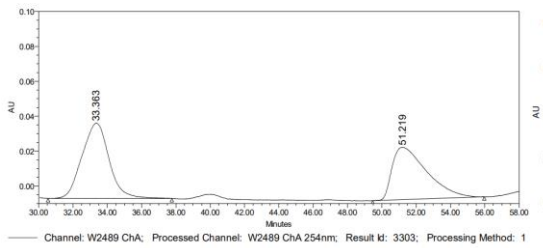

Processed Channel Descr.: W2489 ChA 254nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 6.913 | 1044809 | 1.01 | 35986 |
| 2 | W2489 ChA 254nm | 16.126 | 101927040 | 98.99 | 2219433 |

**(S)-2-((2,5-dimethylphenyl)(quinolin-8-ylamino)phosphoryl)-3,6-dimethylphenyl 4-methoxybenzoate (3z)**

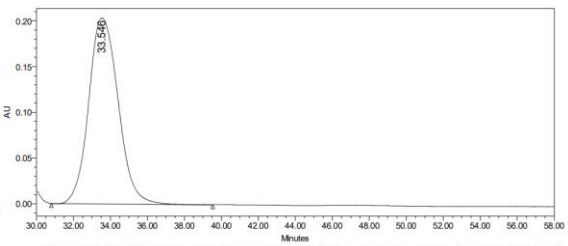



Light-yellow foam, 49.6 mg, 45% yield. M.p.: 128- 129 °C, $[\alpha]_D^{20}$ = +304.7 (c = 0.3, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 85/15, 0.6 mL/min, λ = 254 nm, t (major) = 33.546 min, t (minor) = 51.219 min. **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.87 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.30 (d, *J* = 13.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 2H), 7.47 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.40 (t, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.21 – 7.10 (m, 2H), 7.02 - 6.96 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 2.96 (s, 3H), 2.41 (s, 3H), 2.02 (s, 3H), 1.47 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 163.6, 162.0, 151.0 (d, $J_{C\text{-}P}$ = 4.0 Hz), 147.6, 143.9 (d, $J_{C\text{-}P}$ = 7.0 Hz), 139.4, 138.8, 136.6, 134.9, 134.8 (d, $J_{C\text{-}P}$ = 7.0 Hz), 134.7 (d, $J_{C\text{-}P}$ = 2.0 Hz), 132.5, 132.4, 132.2 (d, $J_{C\text{-}P}$ = 2.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.3 (d, $J_{C\text{-}P}$ = 13.0 Hz), 129.3 (d, $J_{C\text{-}P}$ = 7.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 76.0 Hz), 124.9, 121.6 (d, $J_{C\text{-}P}$ = 10.0 Hz), 118.8, 114.2 (d, $J_{C\text{-}P}$ = 2.0 Hz), 113.6, 113.4, 55.6, 29.4, 22.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 20.4, 20.3 (d, $J_{C\text{-}P}$ = 5.0 Hz), 16.8. **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 23.93. **HRMS (ESI)** calculated for $C_{33}H_{32}N_2O_4P$ $[M + H]^+$ : 551.2094, found: 551.2086.




Processed Channel Descr.: W2489 ChA 254nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 33.363 | 4736844 | 52.95 | 43144 |
| 2 | W2489 ChA 254nm | 51.219 | 4209578 | 47.05 | 30077 |

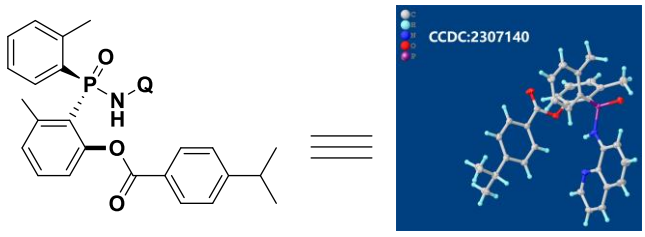



Processed Channel Descr.: W2489 ChA 254nm

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 33.546 | 22536499 | 100.00 | 203181 |

## 3. X-Ray Crystallographic Analysis of 3i

30 mg of **3i** was dissolved in 2 mL of acetone and filtrated into a 15 mL vial. Subsequently, 4 mL of hexane was added slowly along the wall of the vial. The vial was sealed with parafilm which was pricked a few small holes. Then, the vial was placed in an empty room at 25 ℃. The crystal was grown with the gradual volatilization of the solvent.




**3i**

**Figure S1** X-Ray Crystallographic Analysis of **3i.** The ellipsoids drawn at 30% probability level.

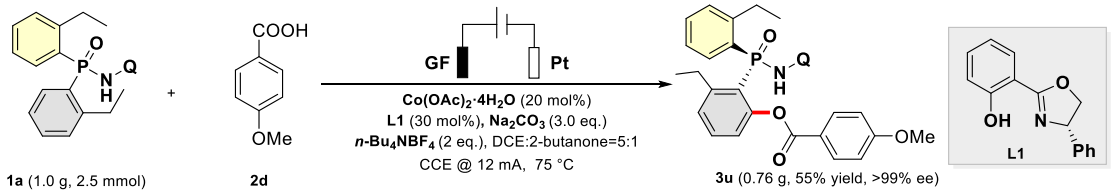
Crystal data and structure refinement for **3i**:

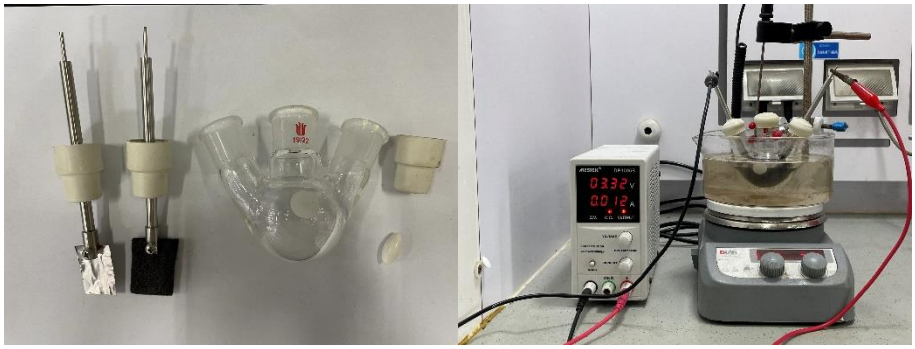
| | |
|---|---|
| Identification code | 230629ZH_ZHCZ255386_0m |
| Empirical formula | $C_{33}H_{31}N_2O_3P$ |
| Formula weight | 534.57 |
| Temperature/K | 193.00 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.7228(3) |
| b/Å | 15.2917(5) |
| c/Å | 19.0023(5) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2825.23(15) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.257 |
| μ/mm$^{-1}$ | 0.745 |
| F(000) | 1128.0 |
| Crystal size/mm$^3$ | 0.13 × 0.12 × 0.1 |
| Radiation | GaKα (λ = 1.34139) |
| 2Θ range for data collection/° | 6.454 to 120.58 |
| Index ranges | -12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -24 ≤ l ≤ 23 |
| Reflections collected | 41702 |
| Independent reflections | 6329 [$R_{int}$ = 0.0399, $R_{sigma}$ = 0.0267] |
| Data/restraints/parameters | 6329/0/356 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.034 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0312, $wR_2$ = 0.0759 |
| Final R indexes [all data] | $R_1$ = 0.0367, $wR_2$ = 0.0790 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.16/-0.20 |
| Flack parameter | 0.023(7) |

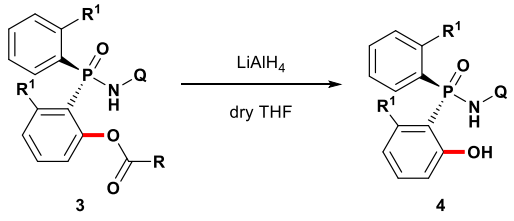
## 4. Gram Scale Experiment

The experiment was carried out in a 50 mL three-necked flask, with a GF anode (30 mm ×25 mm ×6 mm) and a platinum cathode (30 mm ×25 mm ×0.25 mm). Phosphinic amide **1a** (2.5 mmol, 1.0 eq.), carboxylic acid **2d** (7.5 mmol, 3.0 eq.), $Co(OAc)_2$•$4H_2O$ (20 mol%), **L1** (30 mol%), $Na_2CO_3$ (7.5 mmol, 3.0 eq.), n-$Bu_4NBF_4$ (0.7 mmol) were placed in the flask and dissolved in 21 mL of DCE/2-Butanone (5.0:1.0). Electrocatalysis was performed at 75 ℃ with a constant current of 12 mA maintained for 26 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 **3u** in 0.76 g, 55% yield, >99% ee).



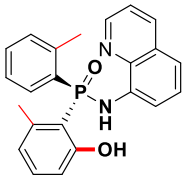
## 5. General Procedure for the Late-Stage Product Derivation



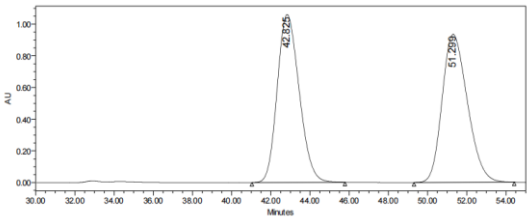

To an overdried double- necked round bottom flask, **3** (0.2 mmol) in dry THF (5 mL) was added under nitrogen protection. Then, $LiAlH_4$ (14.8 mg,0.4 mmol) was added to the mixture at 0℃. After the reaction was completed, the reaction mixture was quenched by water and extracted with 10 mL

of EtOAc three times. The organic layer was dried over anhydrous $Na_2SO_4$ and subjected to column chromatography on silica gel to give the desired product **4**.

**(S)-P-(2-hydroxy-6-methylphenyl)-N-(quinolin-8-yl)-P-(o-tolyl)phosphinic amide (4a)**



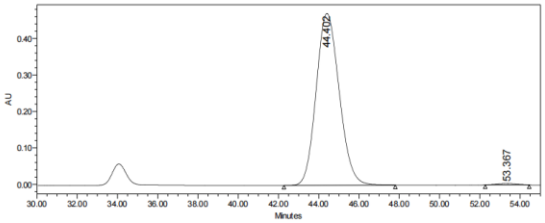
light yellow foam, 84.2% yield. M.p.: 108- 109 °C, $[\alpha]_D^{20}$ = +220.6 (c = 1.0, $CHCl_3$), 98.70% ee. The ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 44.404 min, t (minor) = 53.367 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 12.45 (s, 1H), 8.77 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.29 (d, *J* = 14.8 Hz, 1H), 8.14 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.64 (dd, *J* = 14.8, 7.6Hz, 1H), 7.57 (dd, *J* = 5.6, 3.2 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.39 – 7.36 (m, 3H), 7.31 (t, *J* = 7.2Hz, 1H), 7.25 – 7.21 (m, 1H), 6.90 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.60 (dd, *J* = 7.2, 4.4 Hz, 1H), 2.73 (s, 3H), 2.12 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 165.9 (d, $J_{C-P}$ = 6.0 Hz), 148.2, 142.8 (d, $J_{C-P}$ = 11.0 Hz), 141.2 (d, $J_{C-P}$ = 9.0 Hz), 138.6 (d, $J_{C-P}$ = 8.0 Hz), 137.0, 136.4, 134.5 (d, $J_{C-P}$ = 2.0 Hz), 132.7 (d, $J_{C-P}$ = 3.0 Hz), 132.5 (d, $J_{C-P}$ = 12.0 Hz), 131.8 (d, $J_{C-P}$ = 14.0 Hz), 129.9 (d, $J_{C-P}$ = 128.0 Hz), 128.5, 127.4, 125.7 (d, $J_{C-P}$ = 14.0 Hz), 122.3 (d, $J_{C-P}$ = 11.0 Hz), 121.8, 119.8, 116.7 (d, $J_{C-P}$ = 9.0 Hz), 113.3 (d, $J_{C-P}$ = 3.0 Hz), 108.6 (d, $J_{C-P}$ = 121.0 Hz), 22.2 (d, $J_{C-P}$ = 5.0 Hz), 21.3 (d, $J_{C-P}$ = 4.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 31.81. **HRMS (ESI)** calculated for $C_{23}H_{22}N_2O_2P$ $[M + H]^+$ : 389.1413, found: 389.1411.




Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3269; Processing Method: rachuanyuan

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 42.825 | 82534406 | 49.66 | 1059157 |
| 2 | W2489 ChB 210nm | 51.299 | 83651974 | 50.34 | 934079 |

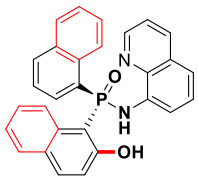



Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3272; Processing Method: chirahuanyuan

**Processed Channel Descr.: W2489 ChB 210nm**

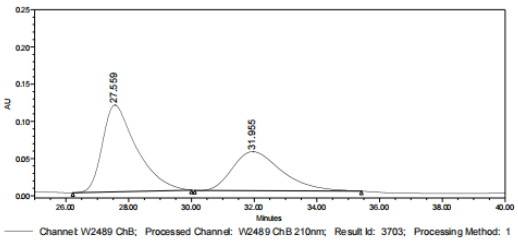
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 44.402 | 37454952 | 99.35 | 471034 |
| 2 | W2489 ChB 210nm | 53.367 | 244039 | 0.65 | 3354 |

**(S)-P-(2-hydroxynaphthalen-1-yl)-P-(naphthalen-1-yl)-N-(quinolin-8-yl)phosphinic amide (4w)**



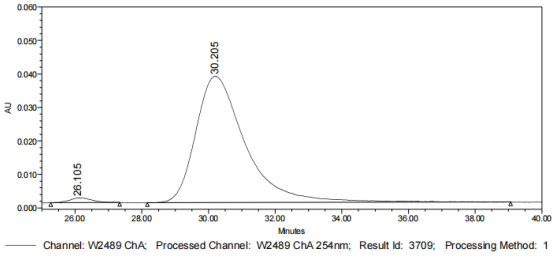
Light-yellow foam, 66.8% yield. M.p.: 135 - 136 °C, $[\alpha]_D^{20}$ = +332.9 (c = 1.0, $CHCl_3$), 96.7% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 30.205 min, t (minor) = 26.105 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 13.36 (s, 1H), 9.02 (d, *J* = 8.4 Hz, 1H), 8.66 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.61 (d, *J* = 15.2 Hz, 1H), 8.07 – 8.05(m, 2H), 8.03 – 7.90 (m, 3H), 7.80 (dd, *J* = 18.0, 7.2Hz, 1H), 7.69 – 7.56 (m, 4H), 7.39 – 7.34(m, 2H), 7.33 – 7.27 (m, 3H), 7.15 – 7.10 (m, 2H). **$^{13}$C{1H} NMR (150 MHz, $CDCl_3$)** δ 152.1 (d, $J_{C-P}$ = 1.5 Hz), 147.6, 138.7, 136.2, 135.7 (d, $J_{C-P}$ = 9.0 Hz), 134.9, 134.9, 133.9 (d, $J_{C-P}$ = 10.5 Hz), 133.2 (d, $J_{C-P}$ = 10.5 Hz), 132.6, 132.1 (d, $J_{C-P}$ = 10.5 Hz), 131.7 (d, $J_{C-P}$ = 12.0 Hz), 130.0 (d, $J_{C-P}$ = 129.0 Hz), 129.2, 128.7, 128.5, 128.1, 127.6 (d, $J_{C-P}$ = 3.0 Hz), 127.5, 126.7 (d, $J_{C-P}$ = 6.0 Hz), 126.3, 126.2, 124.2 (d, $J_{C-P}$ = 15.0 Hz), 122.1 (d, $J_{C-P}$ = 7.5 Hz), 121.4, 119.4 (d, $J_{C-P}$ = 120.0 Hz), 119.1, 114.1

(d, $J_{C\text{-}P}$ = 3.0 Hz), 113.3. **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 33.14. **HRMS (ESI)** calculated for $C_{29}H_{22}N_2O_2P$ $[M + H]^+$ : 461.1413, found: 461.1411.




**Processed Channel Descr.: W2489 ChB 210nm**

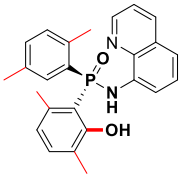
| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 27.559 | 8811721 | 60.61 | 116691 |
| 2 | W2489 ChB 210nm | 31.955 | 5726229 | 39.39 | 52437 |



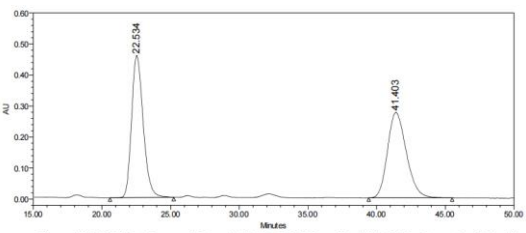

**Processed Channel Descr.: W2489 ChA 254nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChA 254nm | 26.105 | 65497 | 1.65 | 1372 |
| 2 | W2489 ChA 254nm | 30.205 | 3900817 | 98.35 | 37708 |

**(S)-P-(2,5-dimethylphenyl)-P-(2-hydroxy-3,6-dimethylphenyl)-N-(quinolin-8-yl)phosphinic amide (4y)**

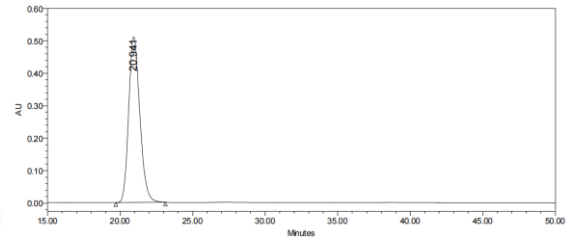


Light-yellow foam, 81.7% yield. M.p.: 112- 113 °C, $[\alpha]_D^{20}$ = +205.4 (c = 1.0, $CHCl_3$), >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 20.941 min, t (minor) = 41.403 min. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 12.63 (s, 1H), 8.75 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.23 (d, *J* = 14.8 Hz, 1H), 8.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.56 (dd, *J* = 5.6, 3.2 Hz, 1H), 7.47 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.50 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.68 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H), 2.09 (s, 3H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 164.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 148.3, 139.6 (d, $J_{C\text{-}P}$ = 10.0 Hz), 138.5 (d, $J_{C\text{-}P}$ = 8.0 Hz), 137.4, 136.5, 135.4 (d, $J_{C\text{-}P}$ = 4.0 Hz), 135.3 (d, $J_{C\text{-}P}$ = 7.0 Hz), 132.7, 132.5, 132.3, 132.2, 130.1 (d, $J_{C\text{-}P}$ = 127.0 Hz), 128.6, 127.6, 125.2, 121.9, 121.7, 121.6, 119.7, 113.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 22.2 (d, $J_{C\text{-}P}$ = 5.0 Hz), 21.2, 21.0 (d, $J_{C\text{-}P}$ = 5.0 Hz), 16.4 (d, $J_{C\text{-}P}$ = 2.0 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 32.83. **HRMS (ESI)** calculated for $C_{25}H_{26}N_2O_2P$ $[M + H]^+$ : 417.1726, found: 417.1722.



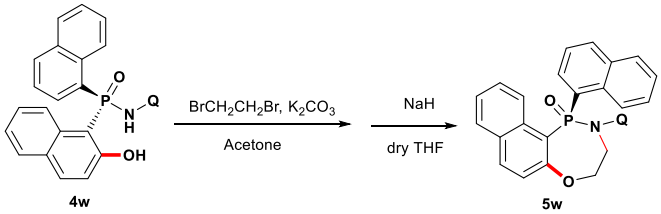

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 22.534 | 27068965 | 50.69 | 458222 |
| 2 | W2489 ChB 210nm | 41.403 | 26331226 | 49.31 | 275767 |



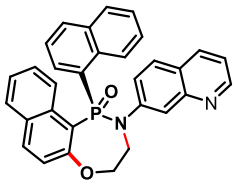

**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 20.941 | 27329124 | 100.00 | 510477 |

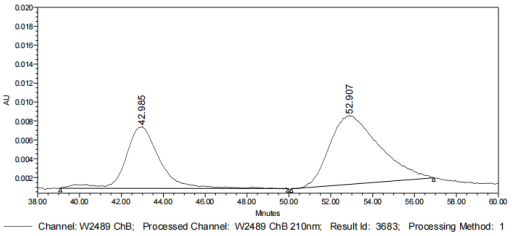


To a round bottom flask, **4w** (0.2 mmol) and $BrCH_2CH_2Br$ (2 mmol) was added in acetone (5 mL) followed with anhydrous $K_2CO_3$ (40 mmol) at room temperature. The reaction mixture was reflux for 24h. Then, the reaction mixture was concentrated in vacuo and subjected to column chromatography on silica gel to give the O-protected intermediate. To an overdried double- necked round bottom flask, the O-protected intermediate in dry THF (5 mL) was added under nitrogen protection. Then, NaH (0.56 mmol) was added to the mixture at 0℃. After the reaction was completed, the reaction mixture was quenched by water and extracted with 10 mL of EtOAc for three times. The organic layer was dried over anhydrous $Na_2SO_4$ and subjected to column chromatography on silica gel to give the desired product **5w**.

**(S)-1-(naphthalen-1-yl)-2-(quinolin-7-yl)-2,3,4-trihydronaphtho[1,2 f][1,4,5]oxazaphosphepine 1-oxide (5w)**

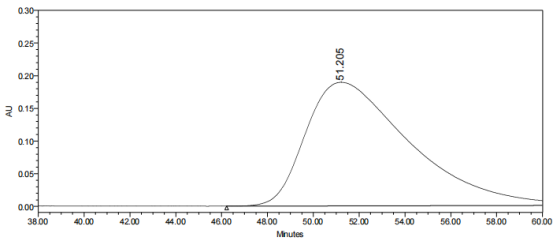


yellow oil, 42% yield. >99% ee. The ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, λ = 210 nm, t (major) = 42.985 min, t (minor) = 51.205 min. **$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.98 (dd, *J* = 22.2, 7.2 Hz, 2H), 8.87 (d, *J* = 4.2 Hz, 1H), 8.08 – 7.95 (m, 3H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.33(m, 5H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.25 – 7.19 (m, 2H), 4.77 – 4.73(m, 1H), 4.63 – 4.59(m, 1H), 4.09 – 3.93 (m, 2H). **$^{13}$C{1H} NMR (100 MHz, $CDCl_3$)** δ 164.2, 152.6 (d, $J_{C-P}$ = 3.0 Hz), 147.7, 146.5 (d, $J_{C-P}$ = 7.0 Hz), 141.7 (d, $J_{C-P}$ = 11.0 Hz), 138.8, 138.6 (d, $J_{C-P}$ = 7.0 Hz), 136.3, 135.6, 132.8 (d, $J_{C-P}$ = 3.0 Hz) 132.5 (d, $J_{C-P}$ = 129.0 Hz), 131.9, 131.7 (d, $J_{C-P}$ = 12.0 Hz), 131.5(d, $J_{C-P}$ = 3.0 Hz), 131.5, 131.4 (d, $J_{C-P}$ = 12.0 Hz), 130.2 (d, $J_{C-P}$ = 11.0 Hz), 129.4, 128.5, 127.8, 127.6, 126.6, 125.6, 125.3 (d, $J_{C-P}$ = 14.0 Hz), 123.7 (d, $J_{C-P}$ = 119.0 Hz), 121.6 (d, $J_{C-P}$ = 7.0 Hz), 121.4, 119.0, 113.7 (d, $J_{C-P}$ = 3.0 Hz), 22.5, 21.0. **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 29.87. **HRMS (ESI)** calculated for $C_{31}H_{24}N_2O_2P$ $[M + H]^+$ : 487.1570, found: 487.1572.




**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 42.985 | 744651 | 38.29 | 6525 |
| 2 | W2489 ChB 210nm | 52.907 | 1200019 | 61.71 | 7254 |

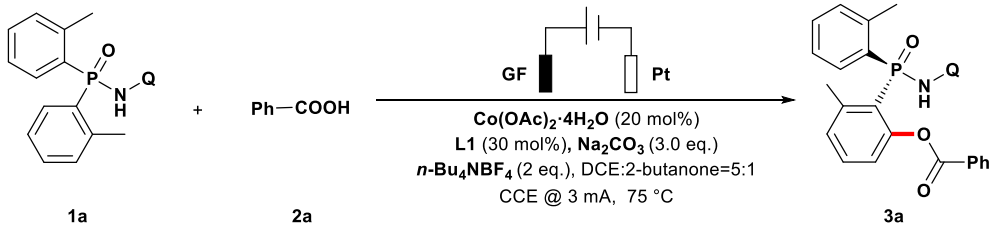



**Processed Channel Descr.: W2489 ChB 210nm**

| | Processed Channel Descr. | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | W2489 ChB 210nm | 51.205 | 60519214 | 100.00 | 189314 |

## 6. Mechanistic Studies

### 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 DCE) 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 (%) of L1 | ee (%) of 3a |
|---|---|---|
| **1** | **20.00** | **20.19** |
| **2** | **40.22** | **33.79** |
| **3** | **58.66** | **55.04** |
| **4** | **79.17** | **65.50** |
| **5** | **>99** | **>99** |

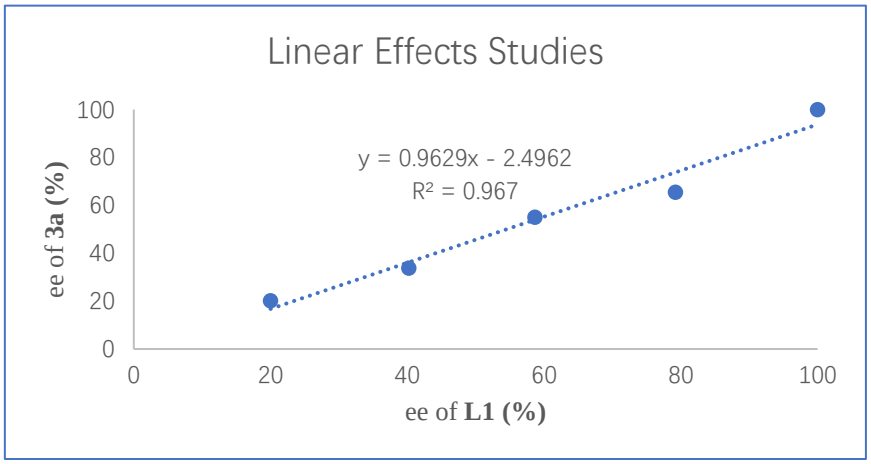



**Figure S2** Linear Effects Studies

### 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*-$Bu_4NBF_4$ (0.5 mmol, 165 mg) in MeCN (5 mL) and H2O (5 mL) at room temperature. A scan rate of 100 mV/s.

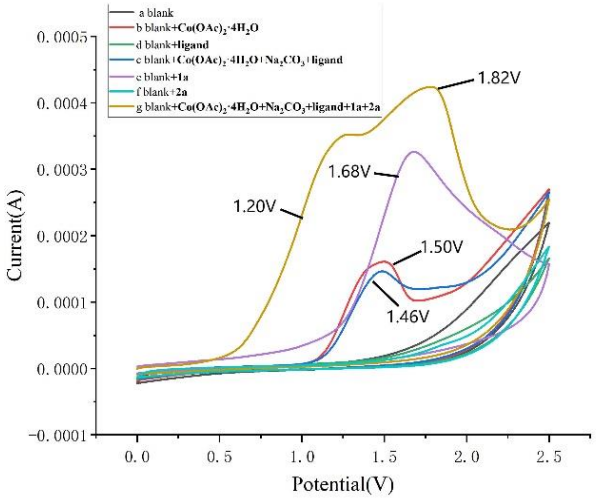



**Figure S3.** Cyclic voltammetry (C-V) studies: **a)** background; **b)** adding **$Co(OAc)_2$•$4H_2O$** (0.1 mmol, 25 mg) into background; **c)** adding **$Co(OAc)_2$•$4H_2O$** (0.1 mmol, 25 mg), **$Na_2CO_3$** (0.1 mmol, 11 mg) and **L1** (0.1 mmol, 24 mg) into background; **d)** adding **L1** (0.1 mmol, 24 mg) into background; **e)** adding **1a** (0.1 mmol, 37 mg) into background; **f)** adding **2a** (0.1 mmol, 12 mg) into background; **g)** adding **$Co(OAc)_2$•$4H_2O$** (0.3 mmol, 75 mg), **$Na_2CO_3$** (0.1 mmol, 11 mg), **L1** (0.3 mmol, 72 mg), **1a** (0.3 mmol, 103 mg) and **2a** (0.3 mmol, 53 mg) into background.

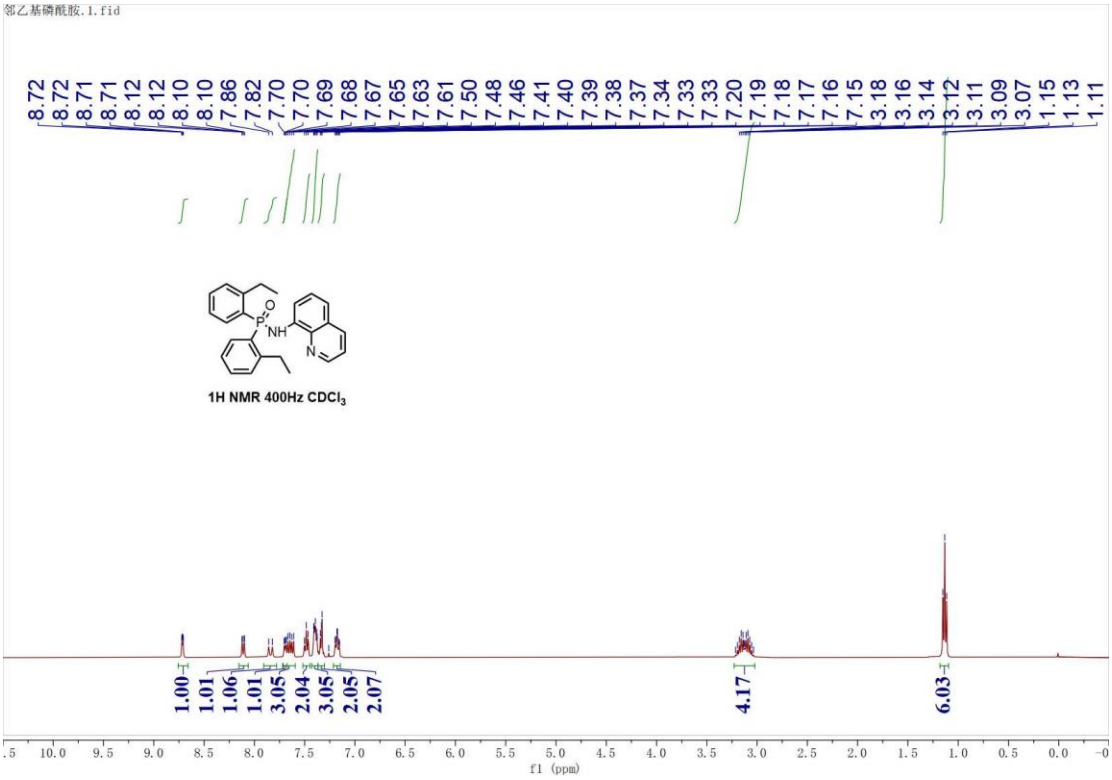
A mixture of $Co(OAc)_2$•$4H_2O$ in a solution of $H_2O$ and MeCN (red curve) showed an oxidation peak of 1.50 V for the oxidation of Co(II) species to Co(III) species. Aryl phosphinamide **1a** featured a higher onset potential of 1.68 V, while no obviously oxidative peak of ligand **L1** or alkyne **2a** (green curve) was found, suggesting the preferential oxidation of Co-catalyst over substrates and ligand. Notably, the combination of $Co(OAc)_2$•$4H_2O$ with ligand **L1** (pink curve) highlighted a shift forward of the oxidation wave with a potential of 1.46 V, might owing to the *in situ* coordination of Co(II) salt with **L1**. Besides, When mixing $Co(OAc)_2$·$4H_2O$, **1a**, **2a**, **L1** and $Na_2CO_3$ together, one oxidation potential of 1.20V was observed, being indicative of an oxidation of cobalt(II) to cobalt(III) in the presence of the substrate at significantly lower potential.

## 7. Reference

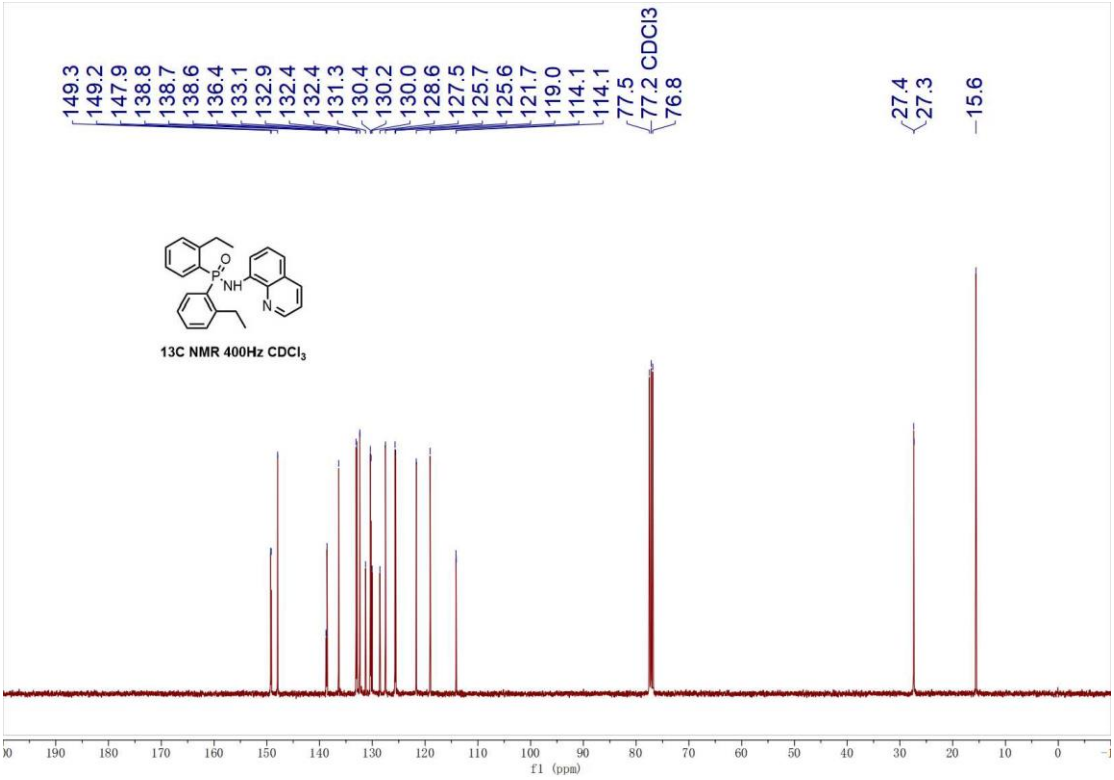
1 (a) T. Liu, W. Zhang, C. Xu, Z. Xu, D. Song, W. Qian, G. Lu, C.-J. Zhang, W. Zhong and F. Ling, Synthesis of P-stereogenic cyclicphosphinic amide via electrochemical enabled cobalt-catalyzed enantioselective C-H annulation. *Green. Chem.*, 2023, **25**, 3606-3614. (b) Zhou, G.; Chen, J.-H.; Yao, Q.-J.; Huang, F.-R.; Wang, Z.-K.; Shi, B.-F. Base-Promoted Electrochemical Co(II)-Catalyzed Enantioselective C-H Oxygenation. *Angew. Chem. Int. Ed.* **2023**, *62*, e202302964.

## 8. NMR Spectrum

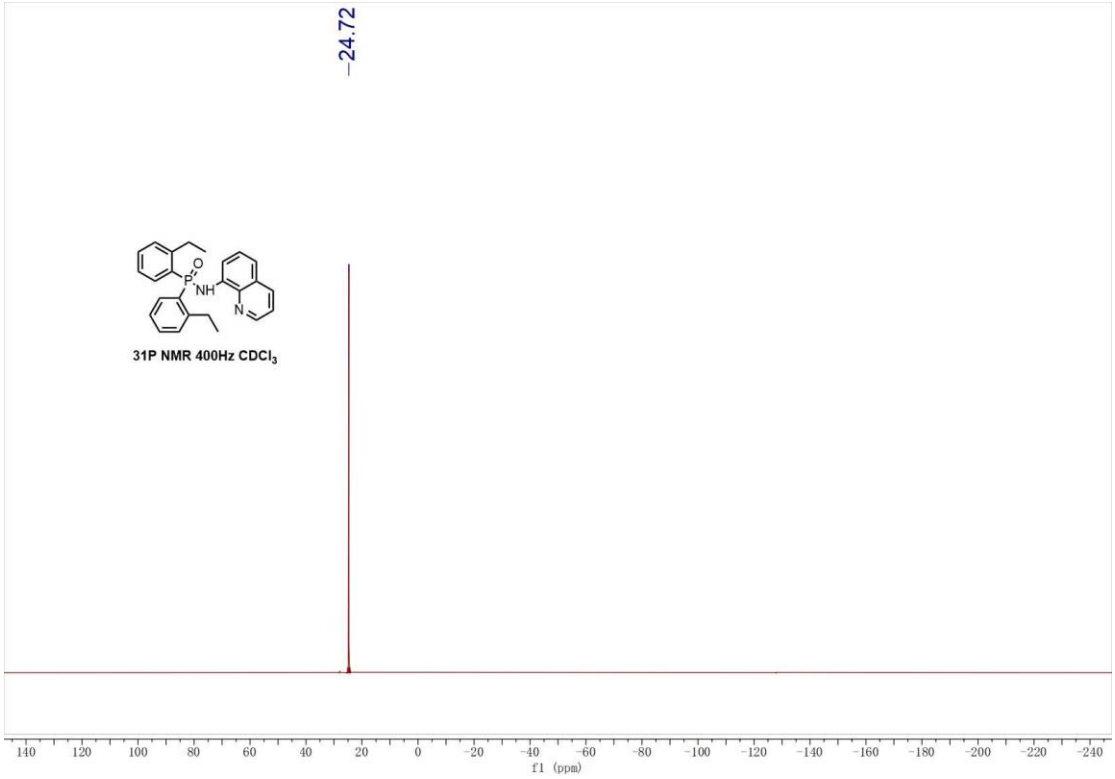
### $^{1}$H NMR of 1a



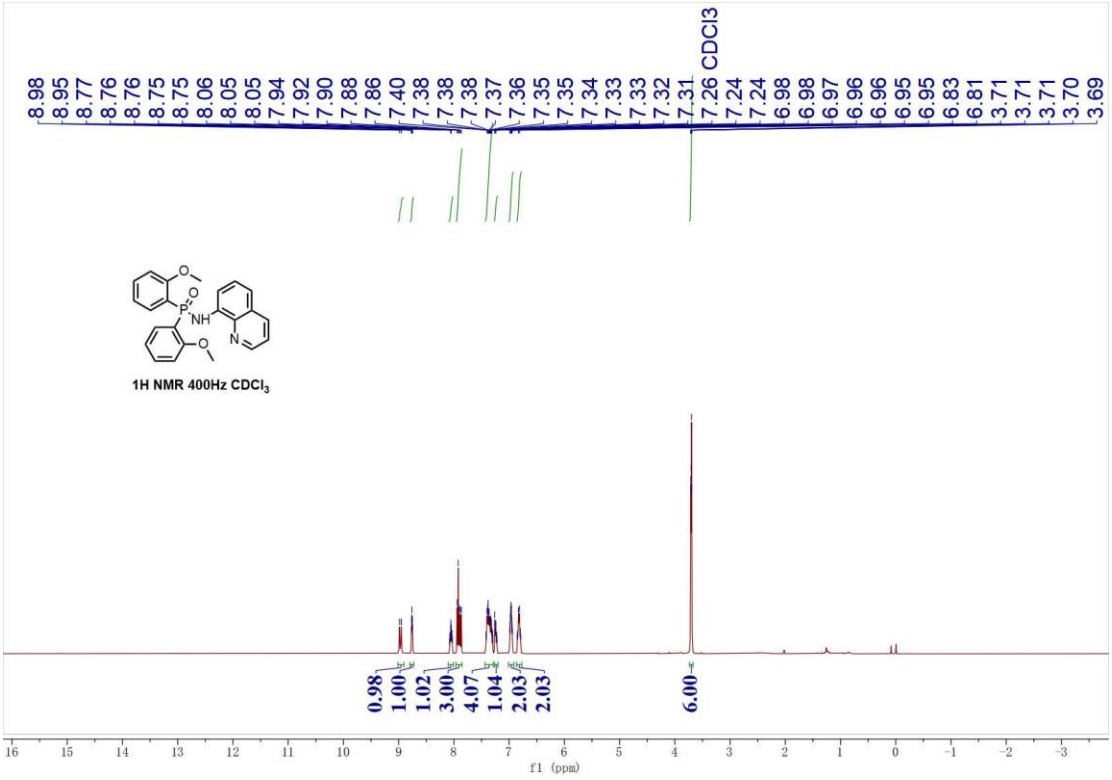

### $^{13}$C{$^{1}$H} NMR of 1a



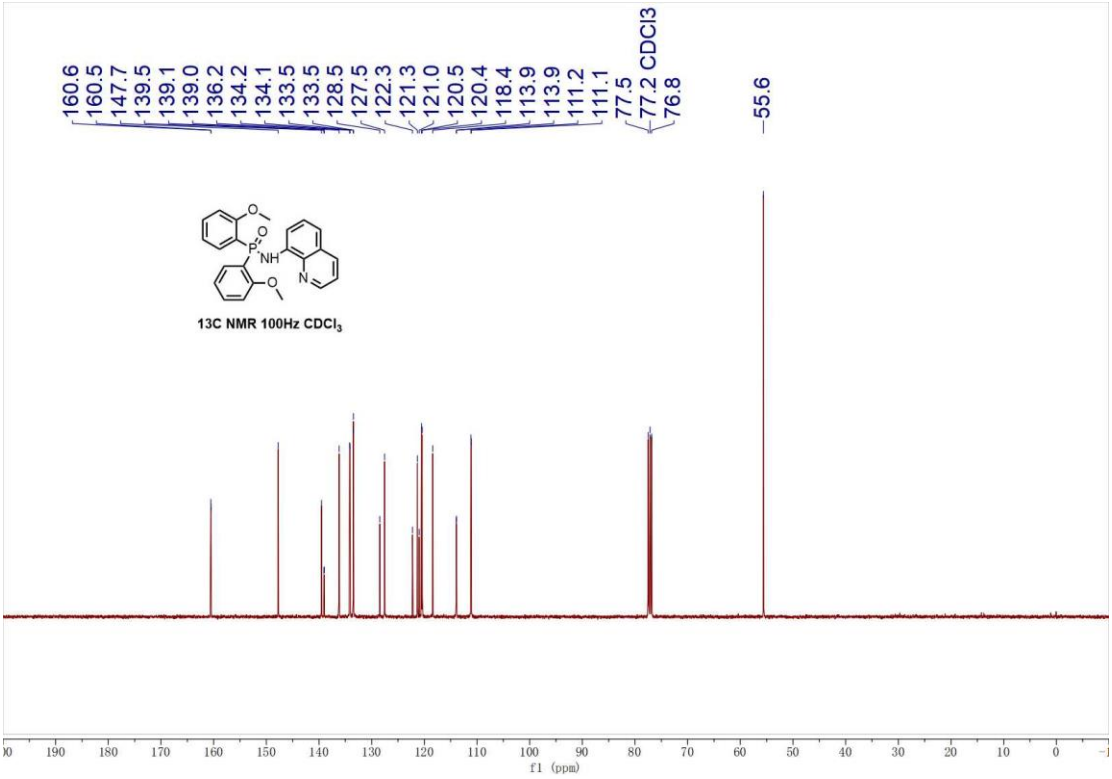
## $^{31}$P NMR of 1a



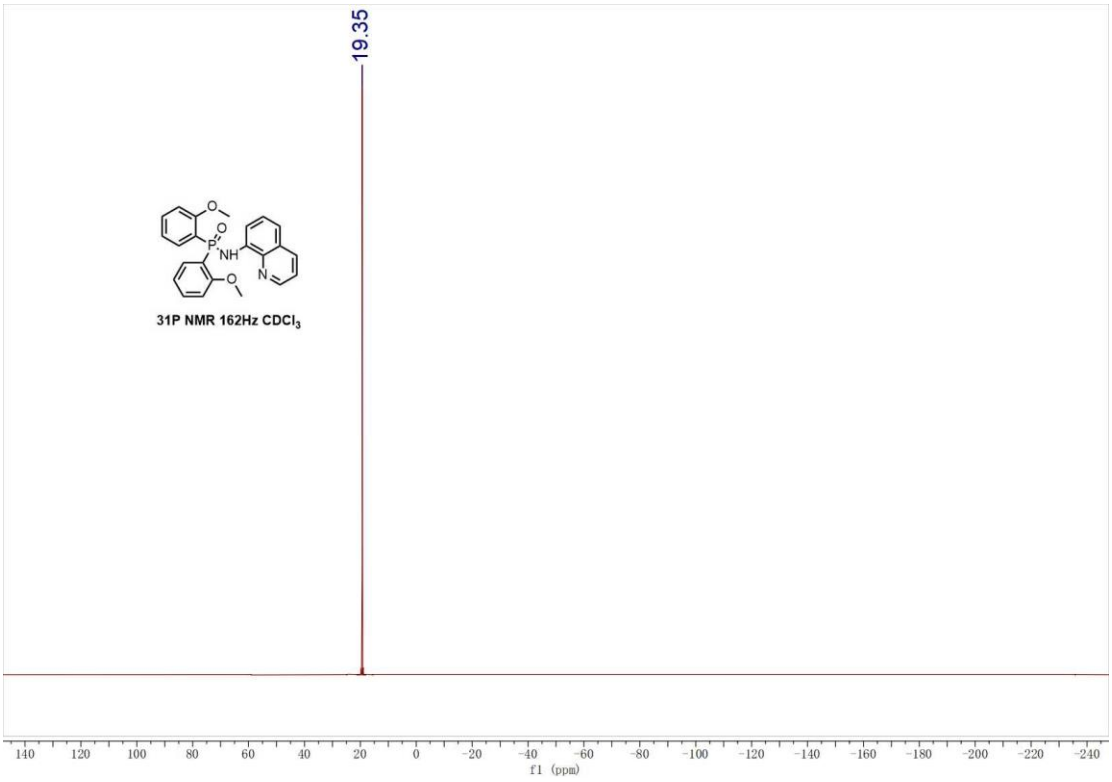

## $^{1}$H NMR of 1b



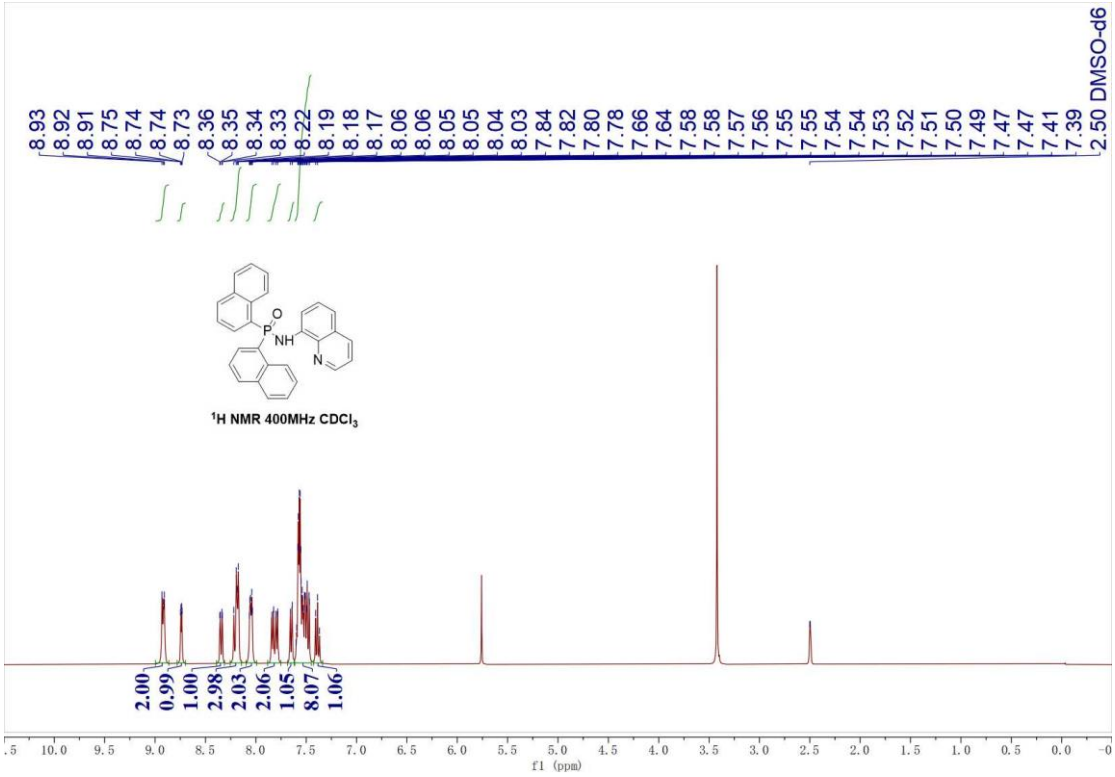
## $^{13}C\{^{1}H\}$ NMR of 1b



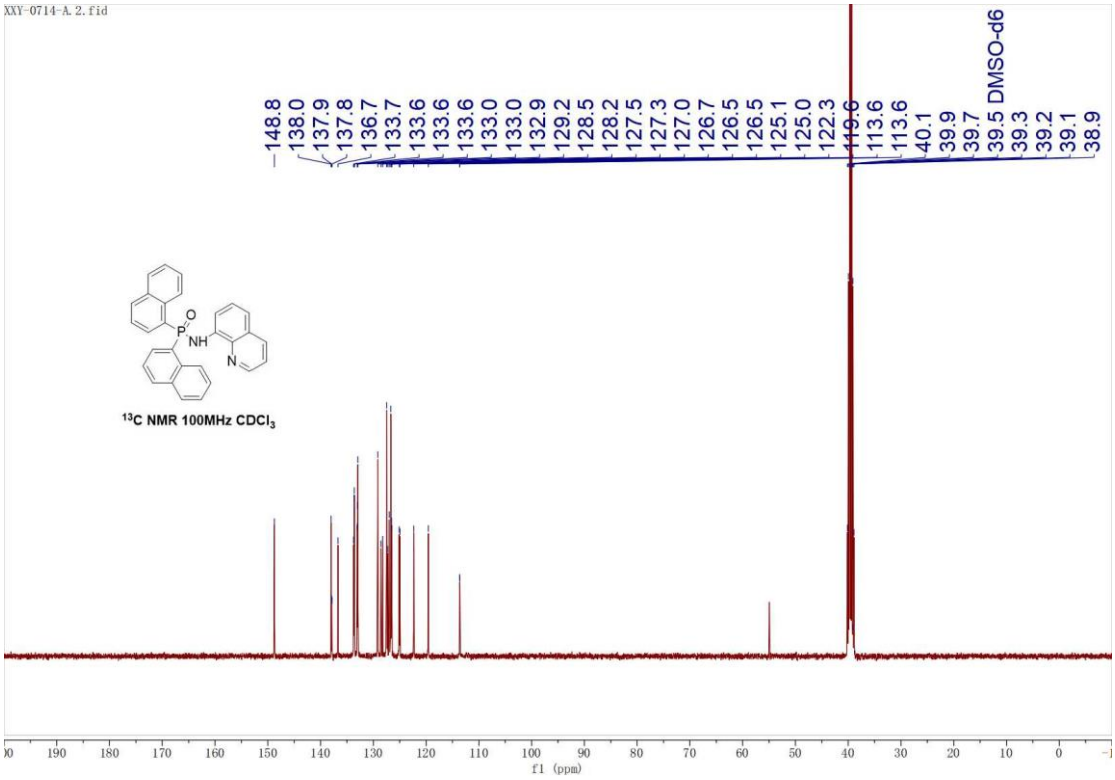

## $^{31}P$ NMR of 1b



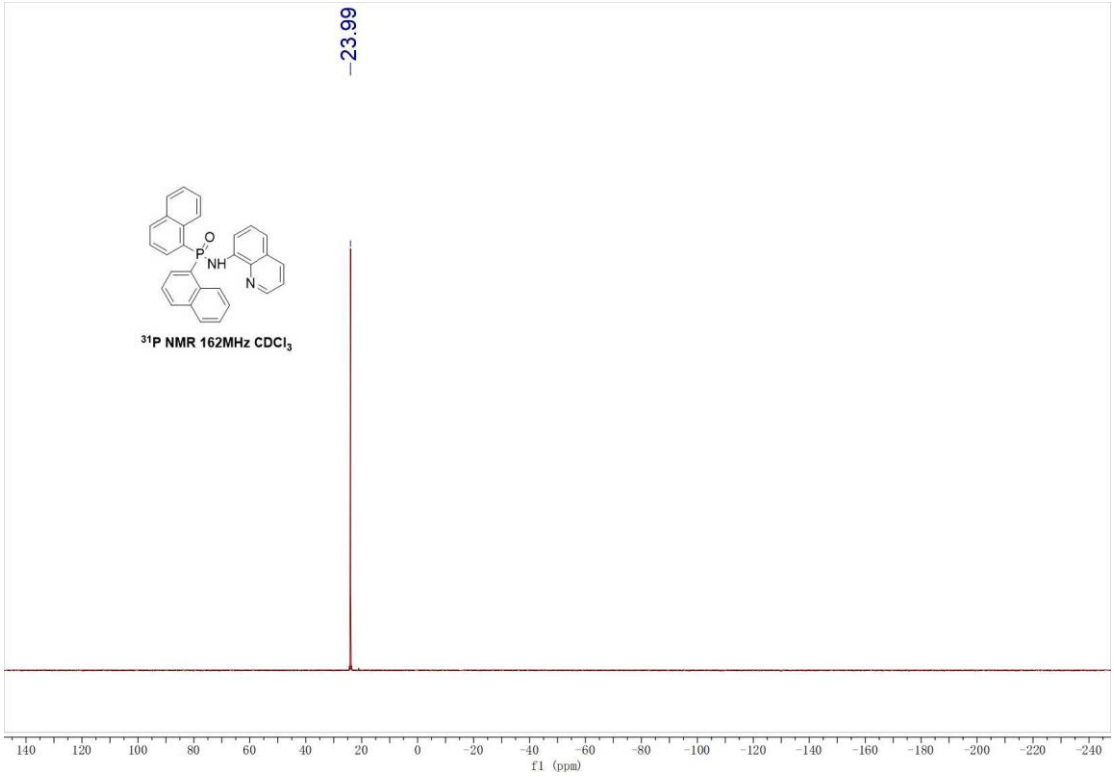
**$^{1}$H NMR of 1c**



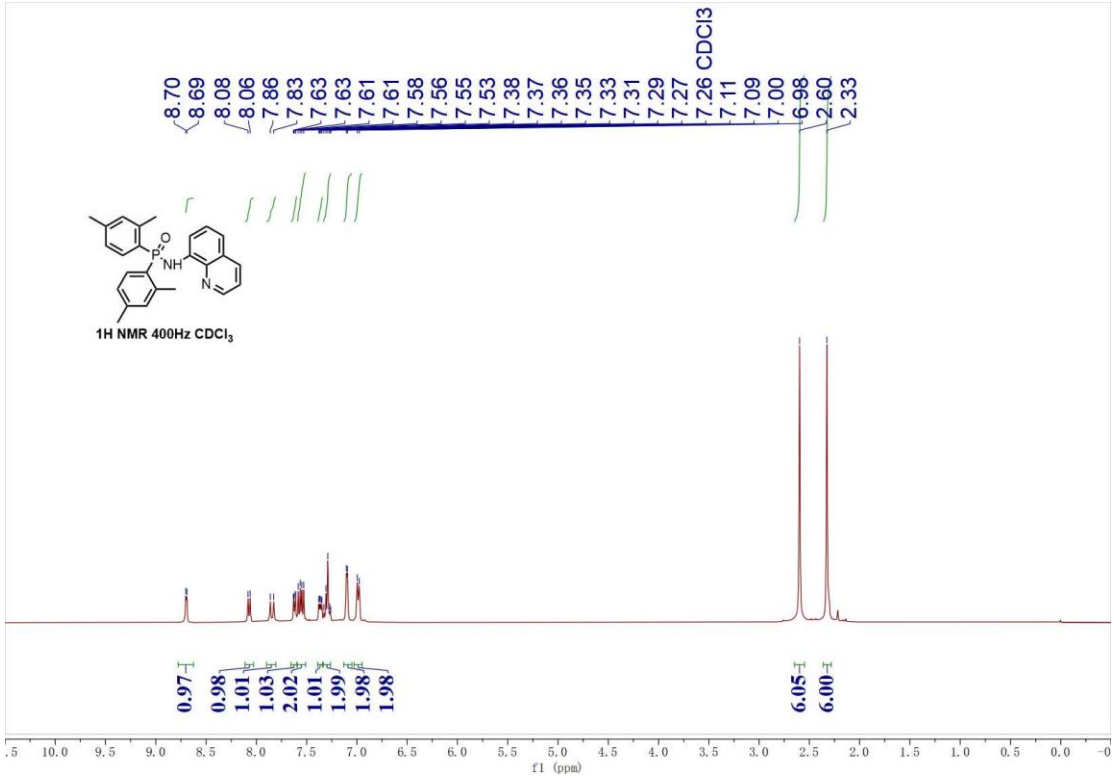

**$^{13}$C{$^{1}$H} NMR of 1c**



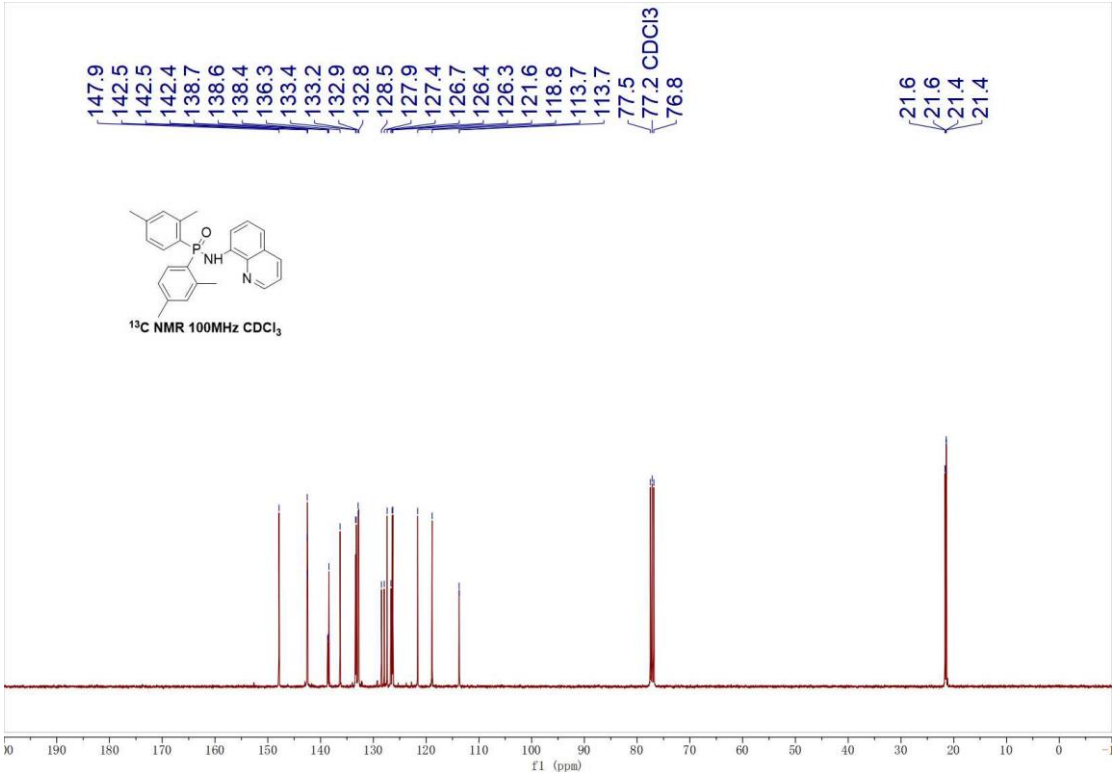
## $^{31}$P NMR of 1c



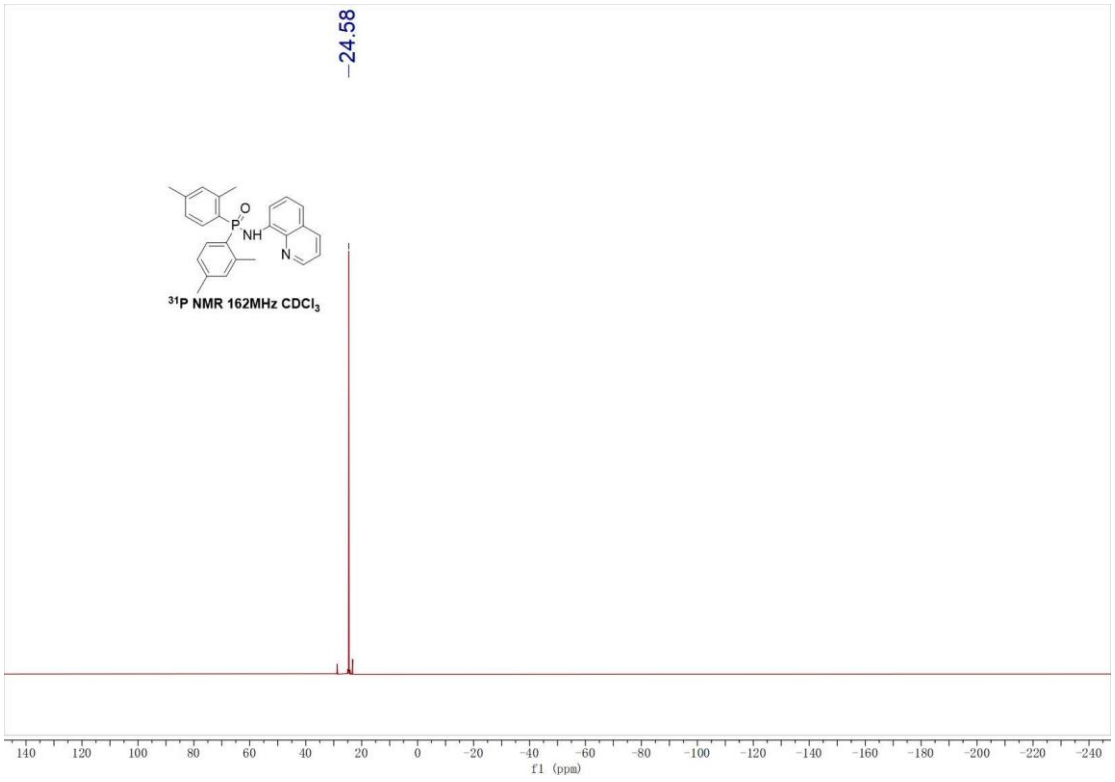

## $^{1}$H NMR of 1d



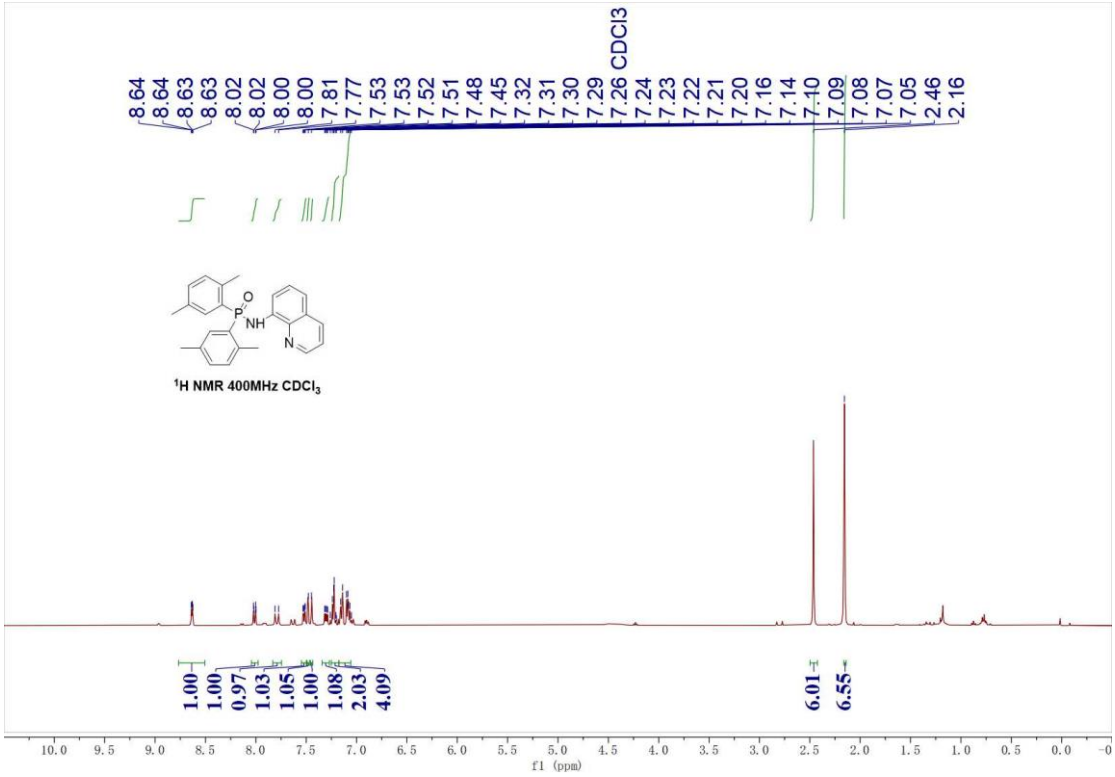
## $^{13}C\{^{1}H\}$ NMR of 1d



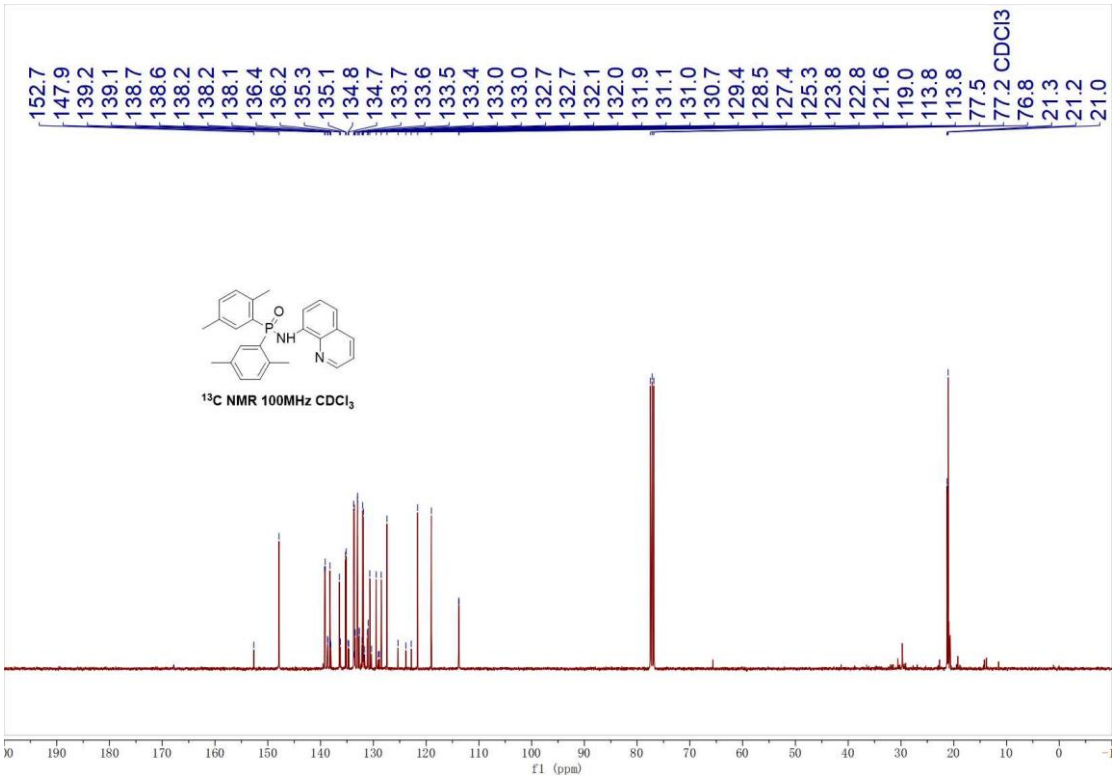

## $^{31}P$ NMR of 1d



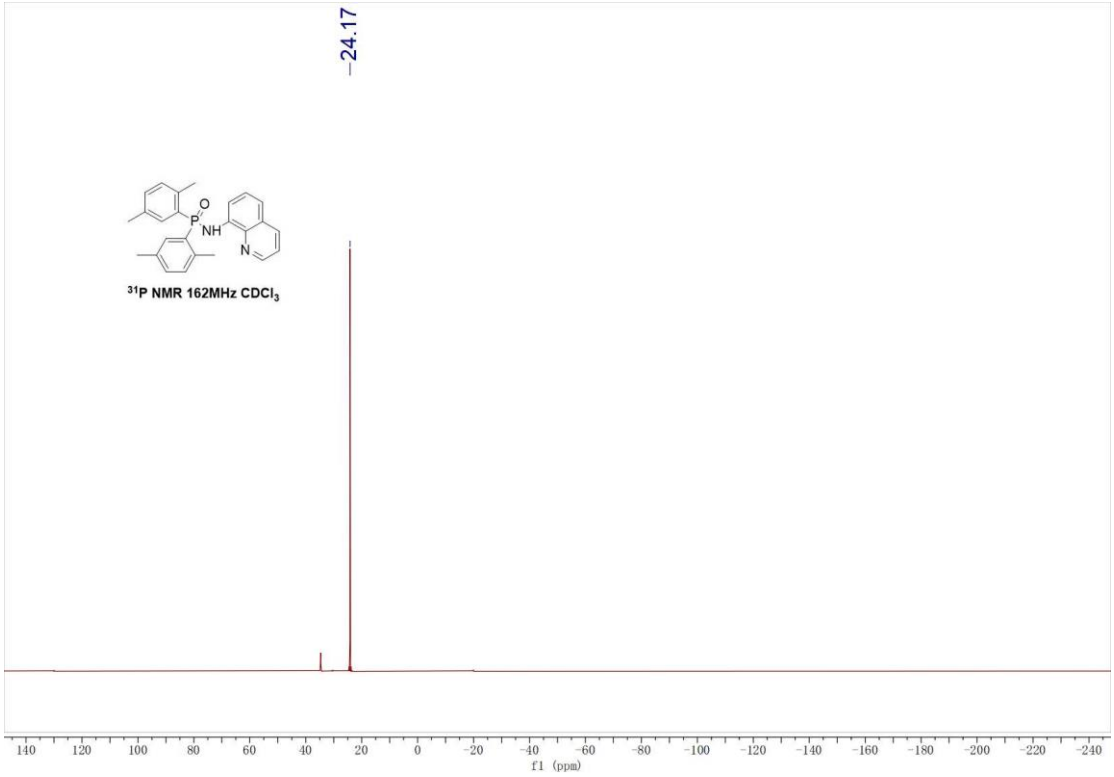
**$^{1}$H NMR of 1e**



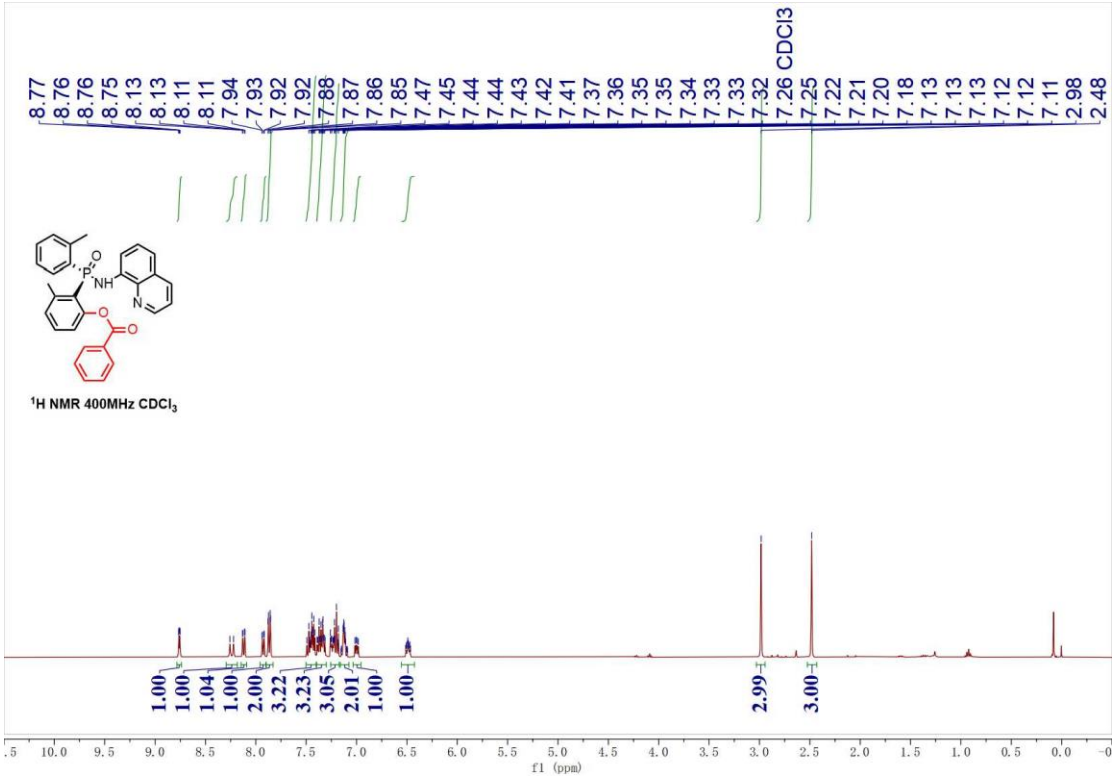

**$^{13}$C{$^{1}$H} NMR of 1e**



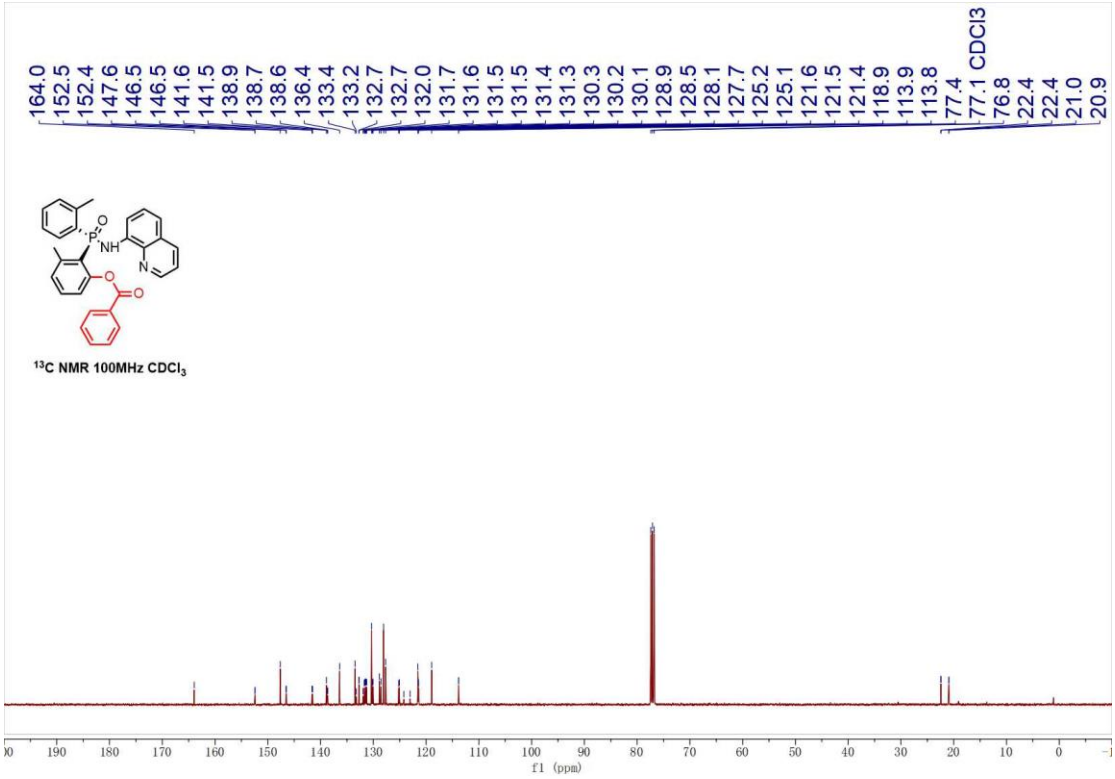
## $^{31}$P NMR of 1e



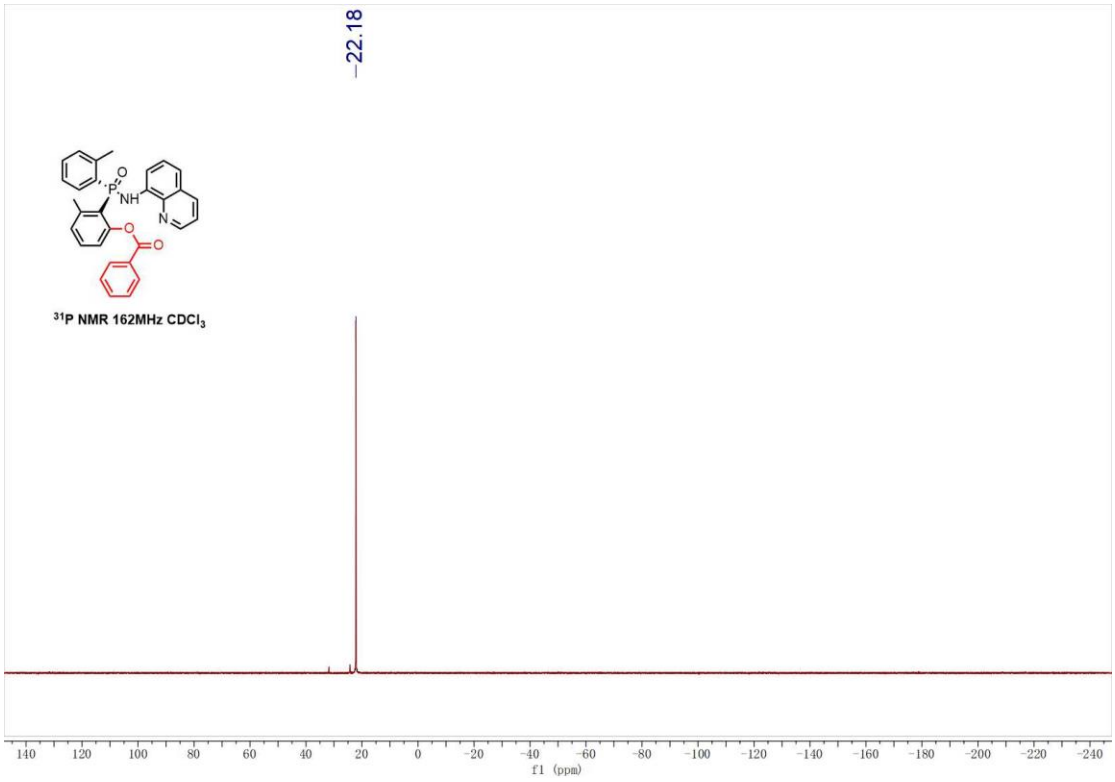

## $^{1}$H NMR of 3a



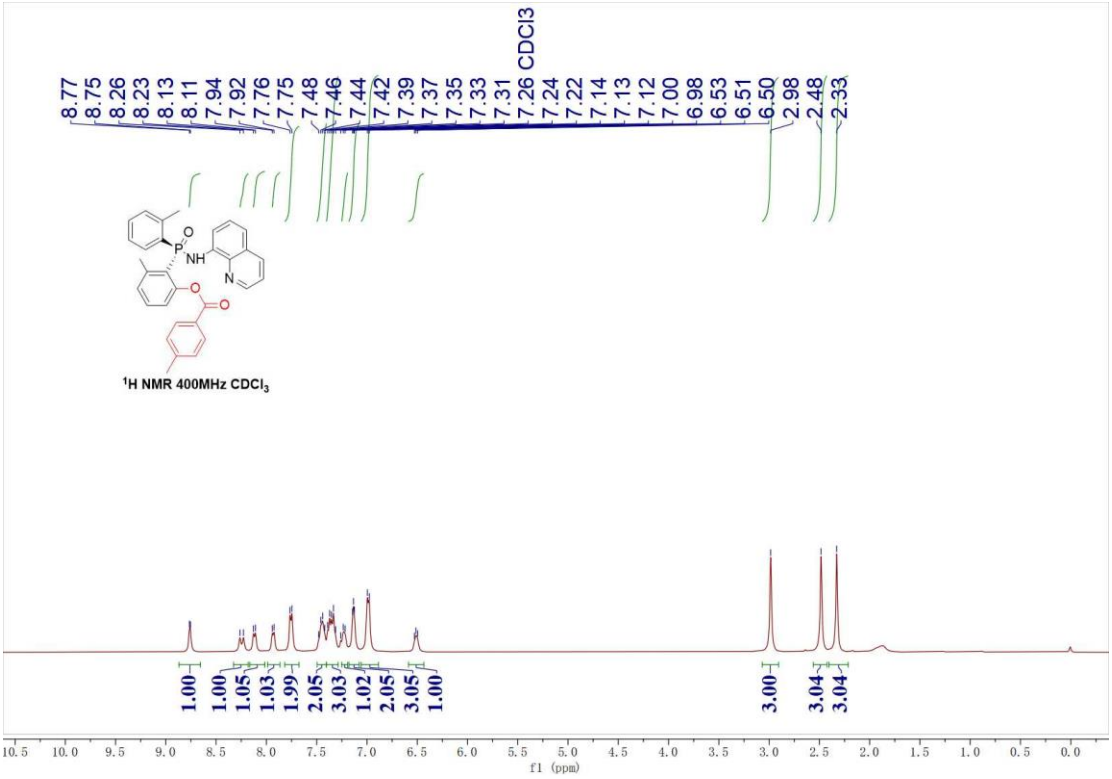
## $^{13}C\{^{1}H\}$ NMR of 3a




## $^{31}P$ NMR of 3a

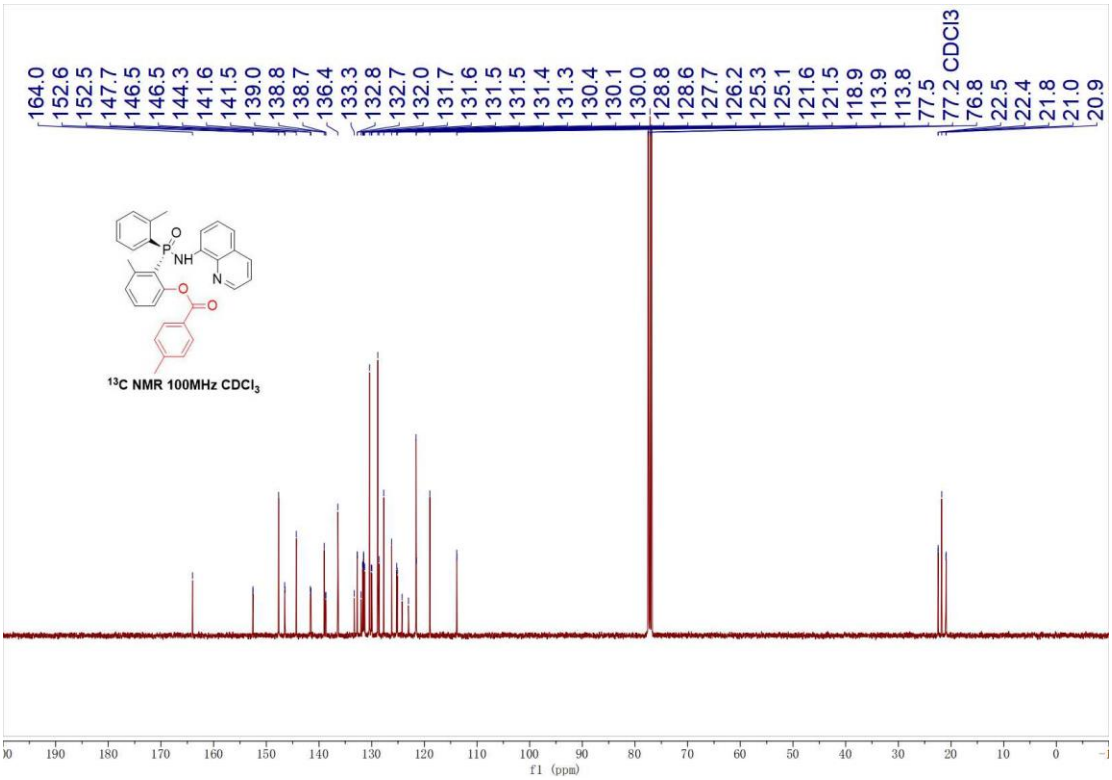


## $^{1}$H NMR of 3b



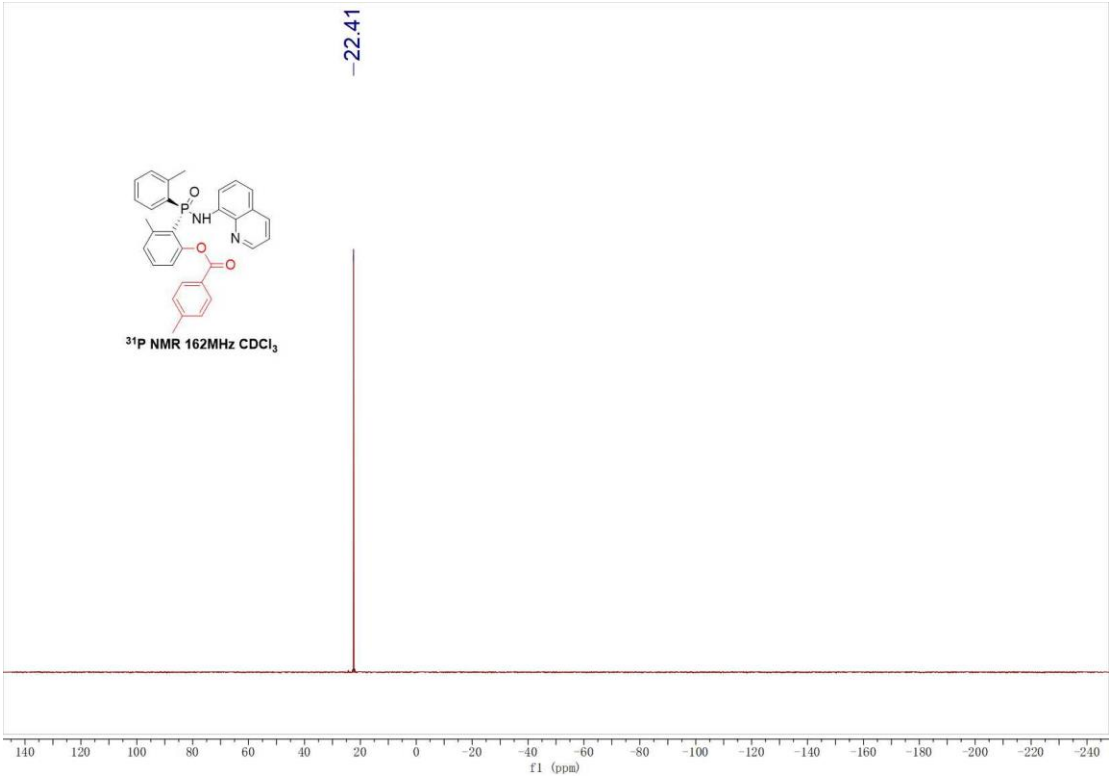

$^{1}$H NMR 400MHz $CDCl_3$

## $^{13}$C{$^{1}$H} NMR of 3b

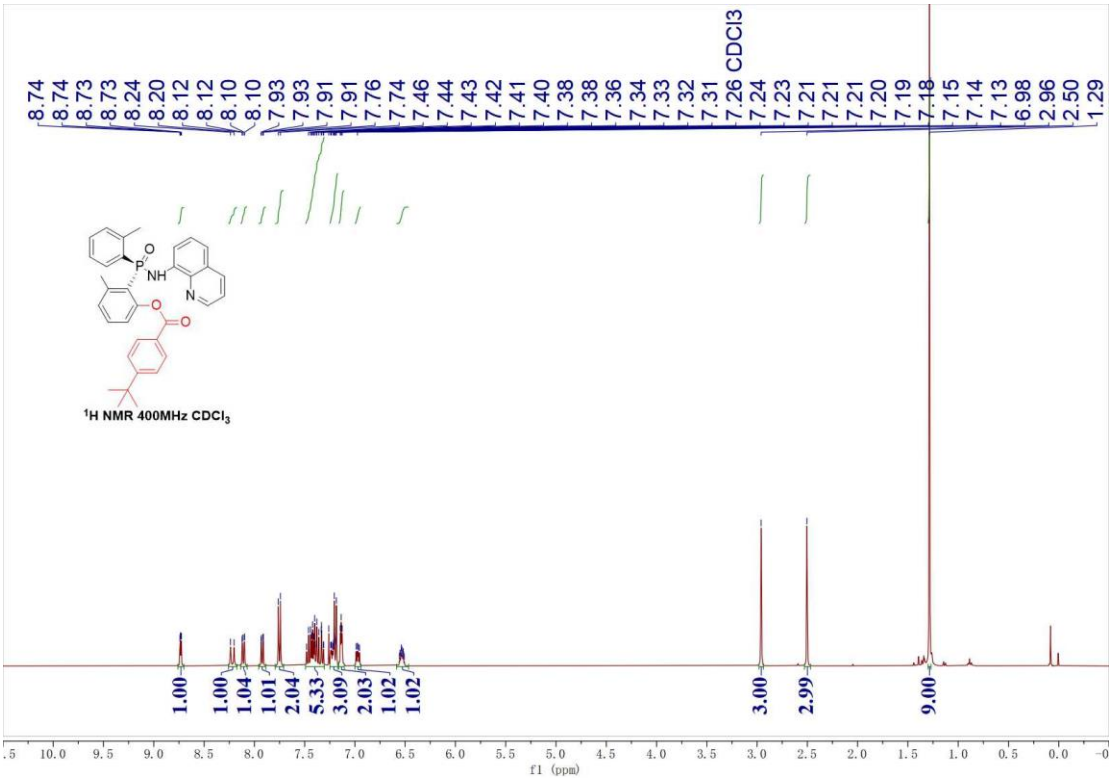



$^{13}$C NMR 100MHz $CDCl_3$

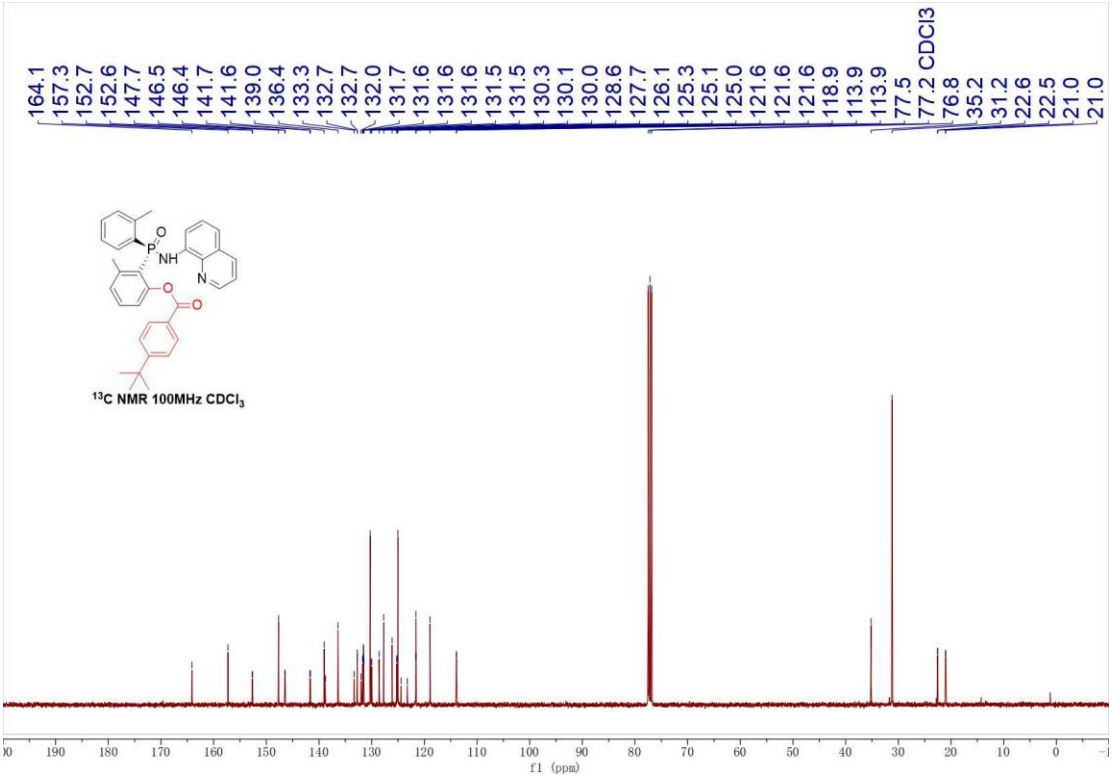
## $^{31}$P NMR of 3b



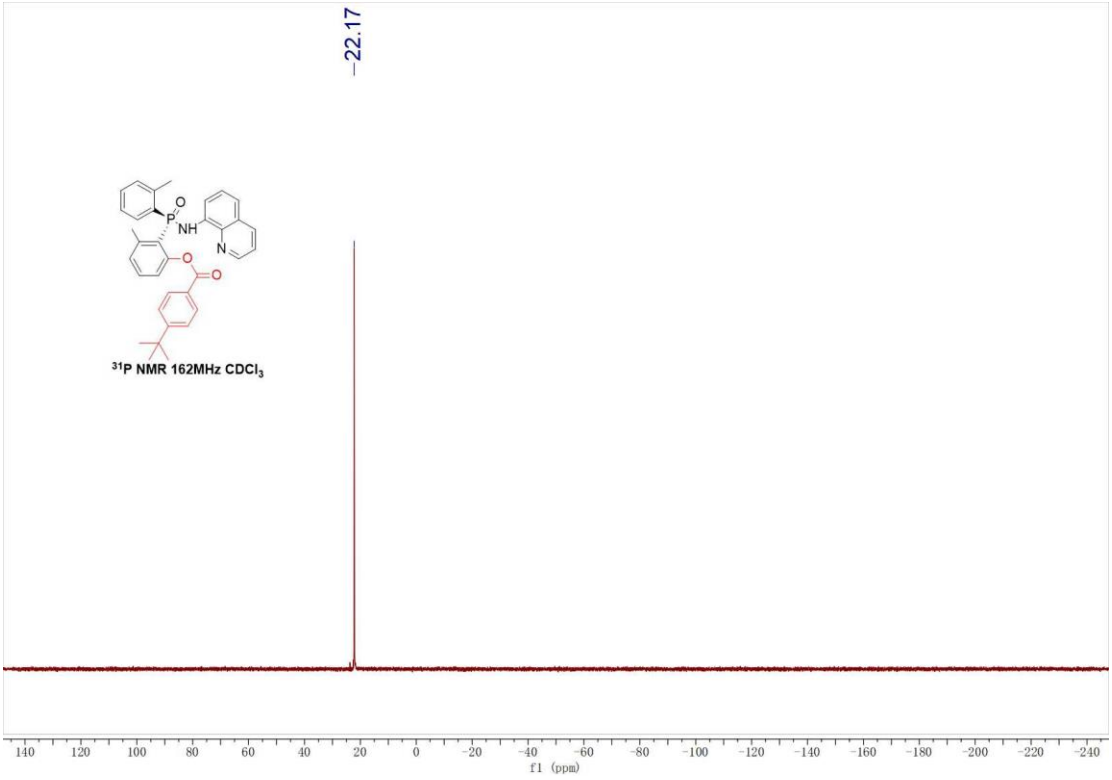

## $^{1}$H NMR of 3c



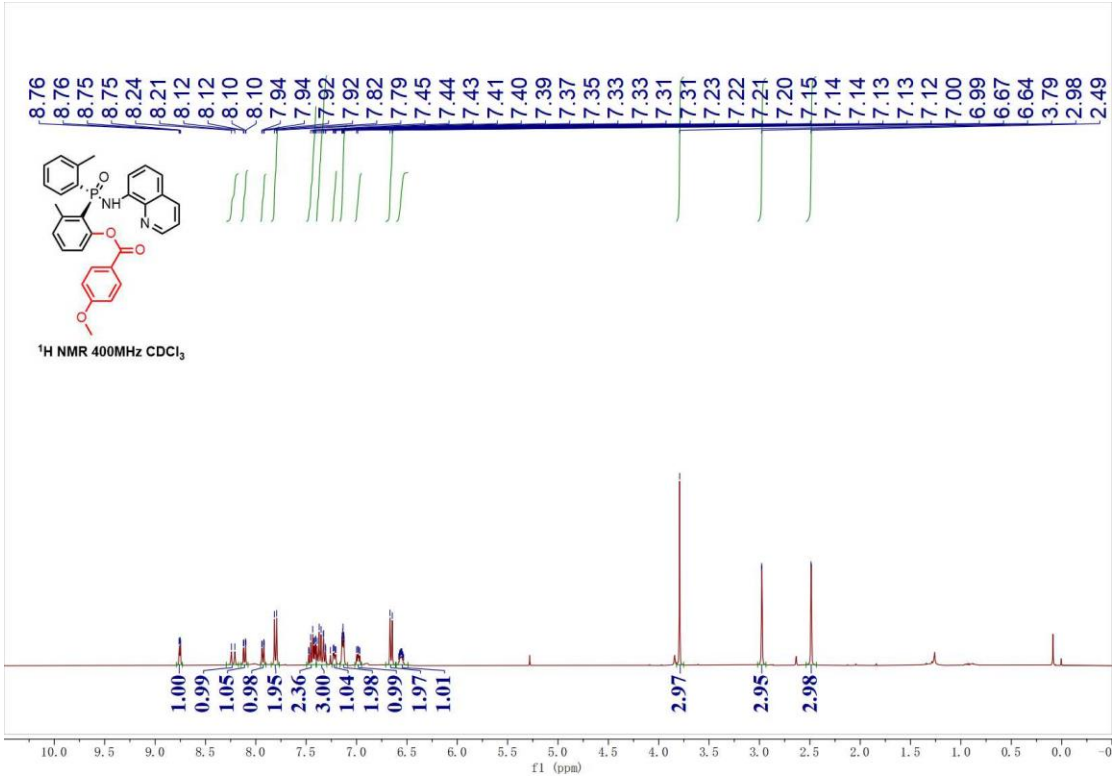
## $^{13}C\{^{1}H\}$ NMR of 3c




## $^{31}P$ NMR of 3c

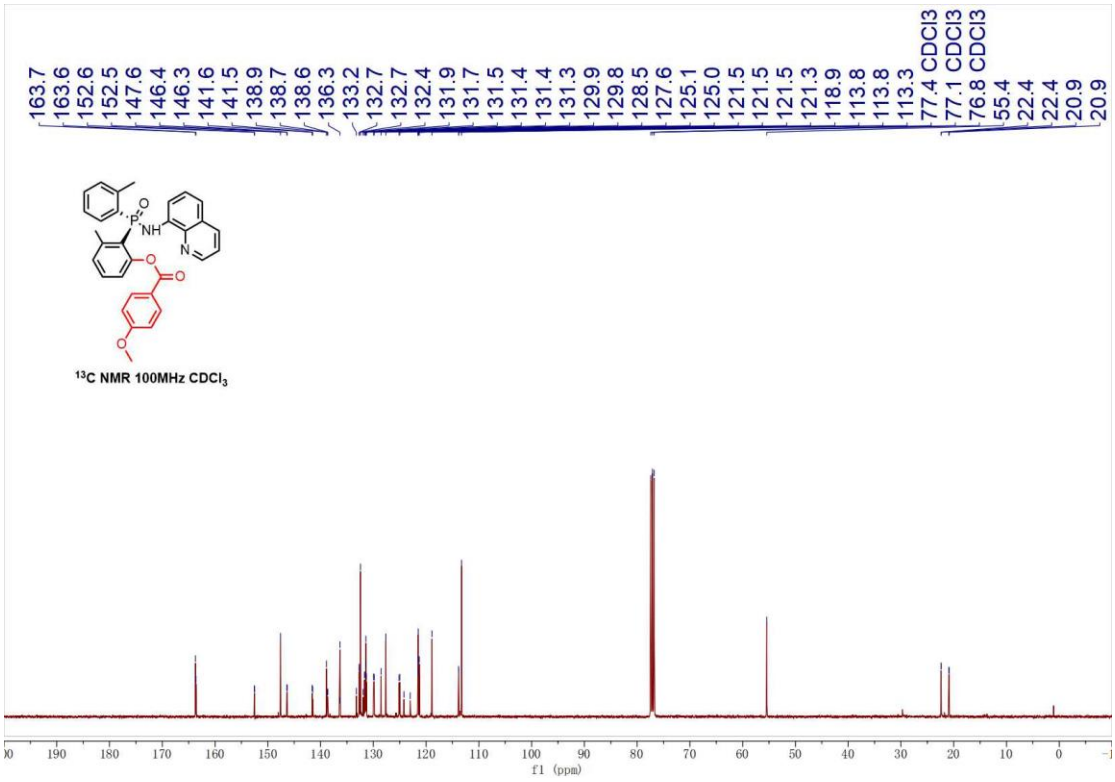


## $^{1}$H NMR of 3d



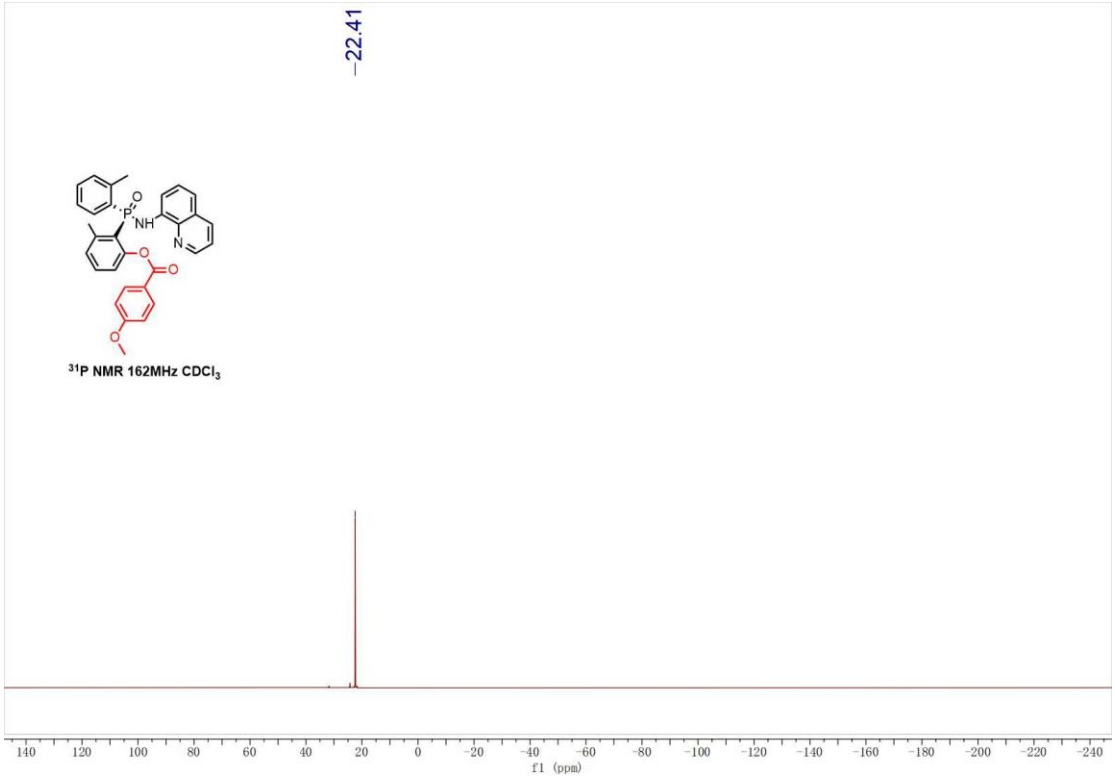

$^{1}$H NMR 400MHz $CDCl_3$

## $^{13}$C{$^{1}$H} NMR of 3d

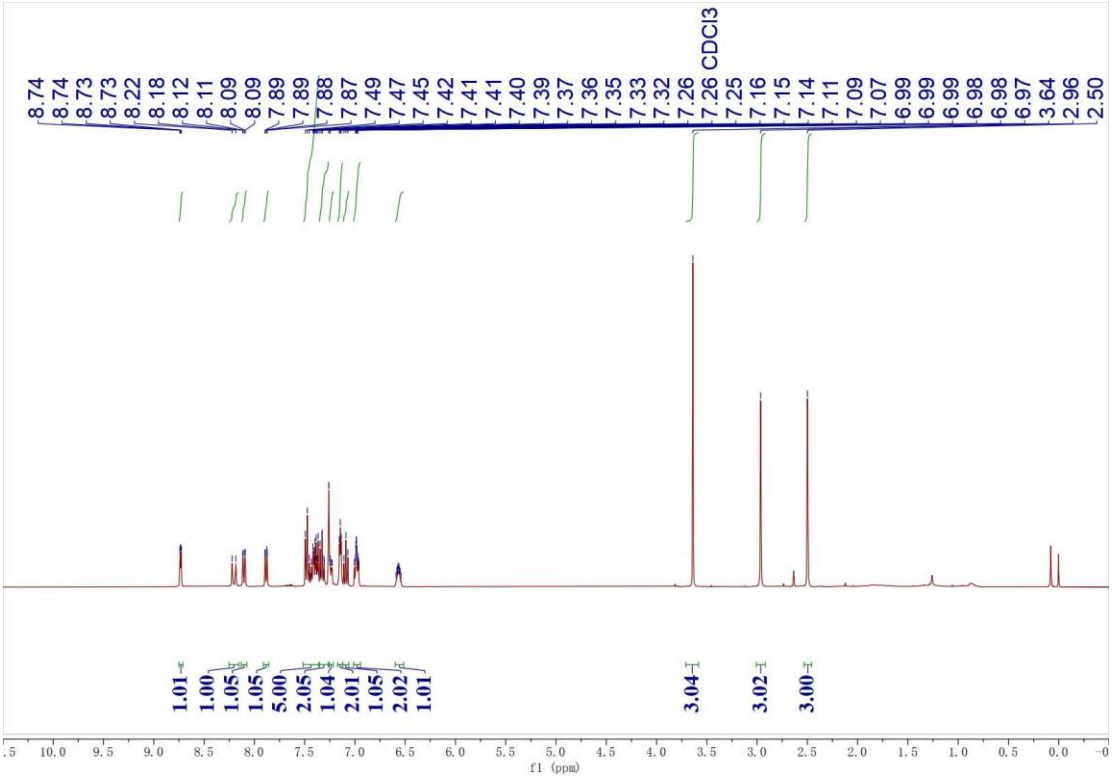



$^{13}$C NMR 100MHz $CDCl_3$

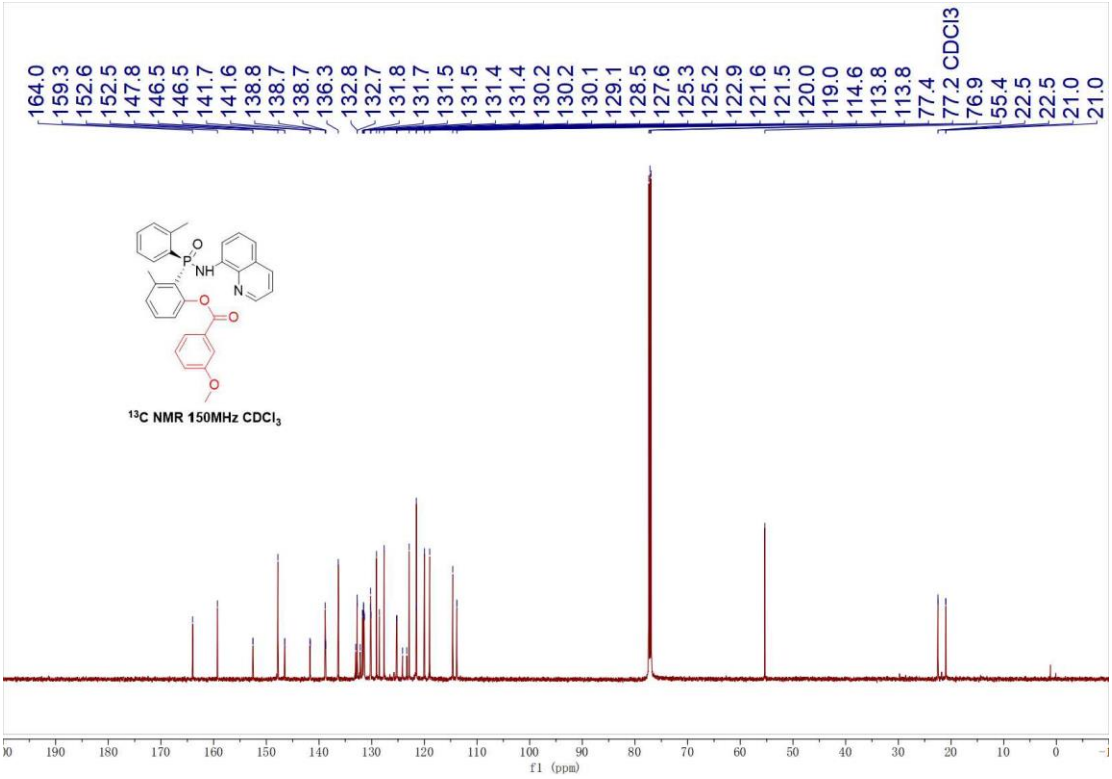
## $^{31}$P NMR of 3d



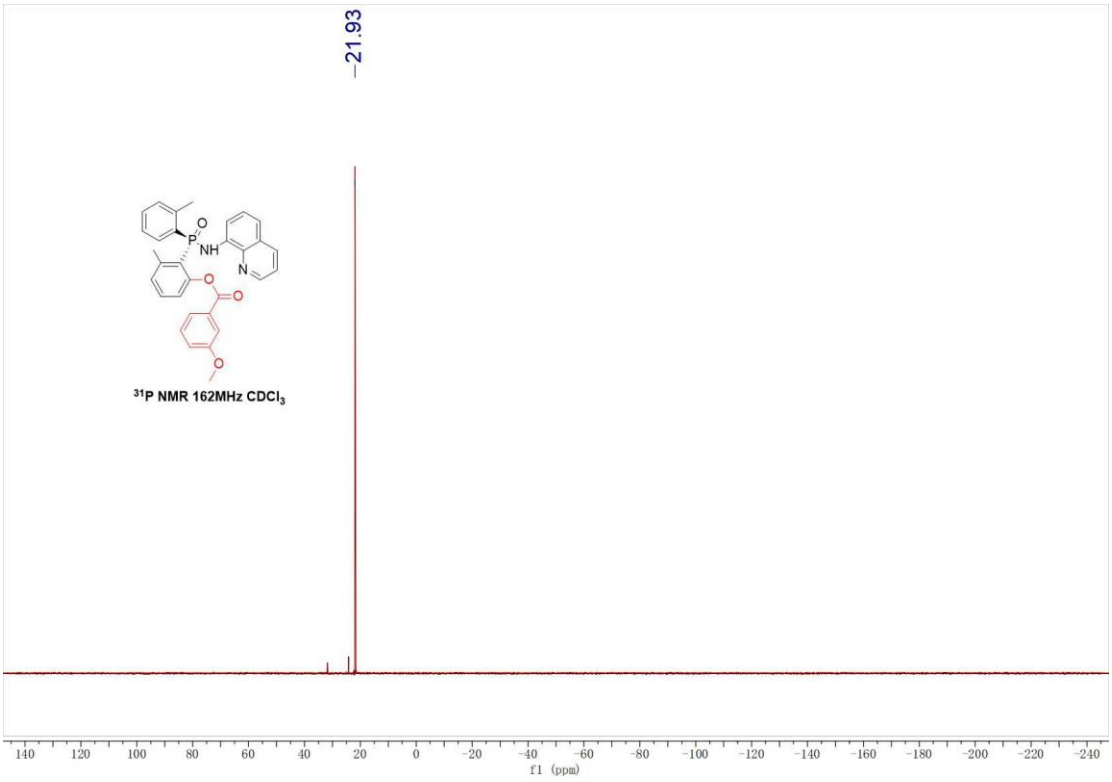

## $^{1}$H NMR of 3e



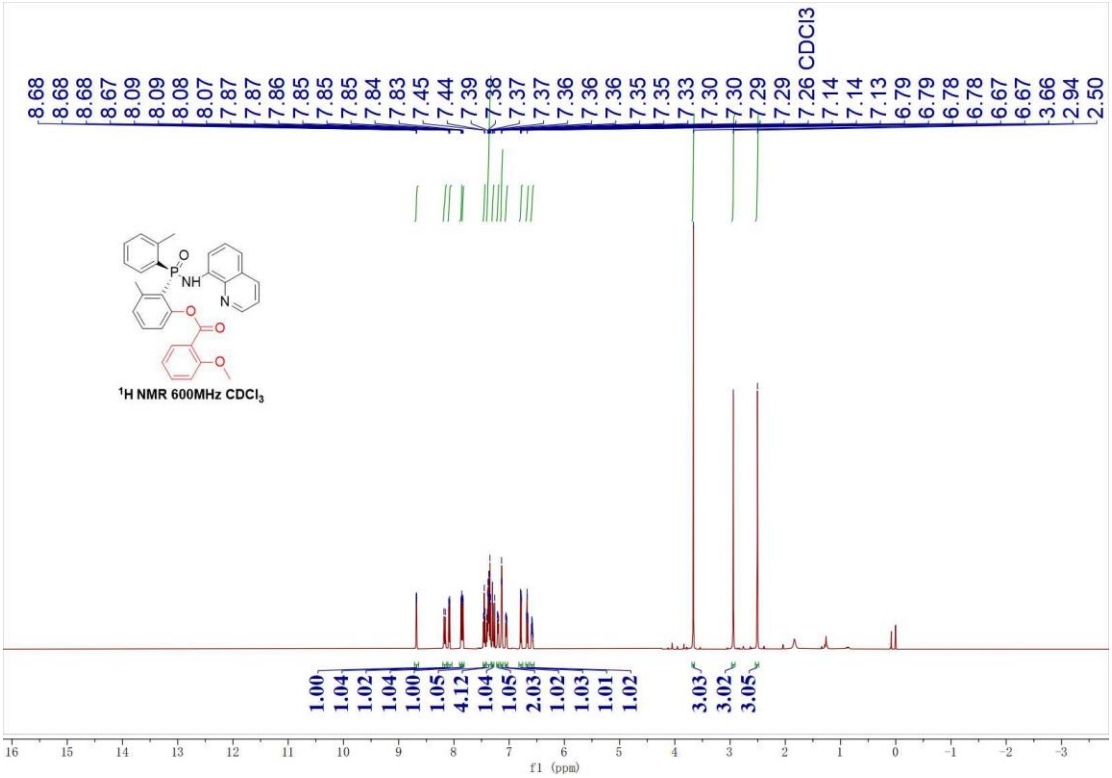
## $^{13}C\{^{1}H\}$ NMR of 3e



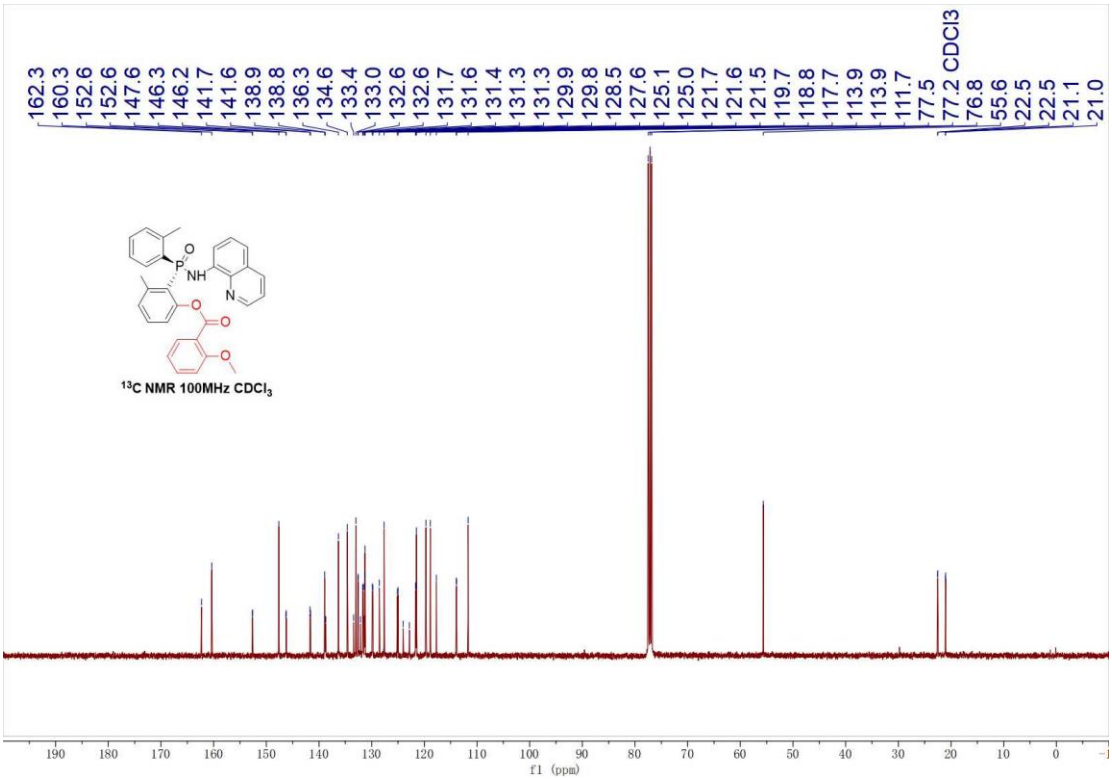

## $^{31}P$ NMR of 3e



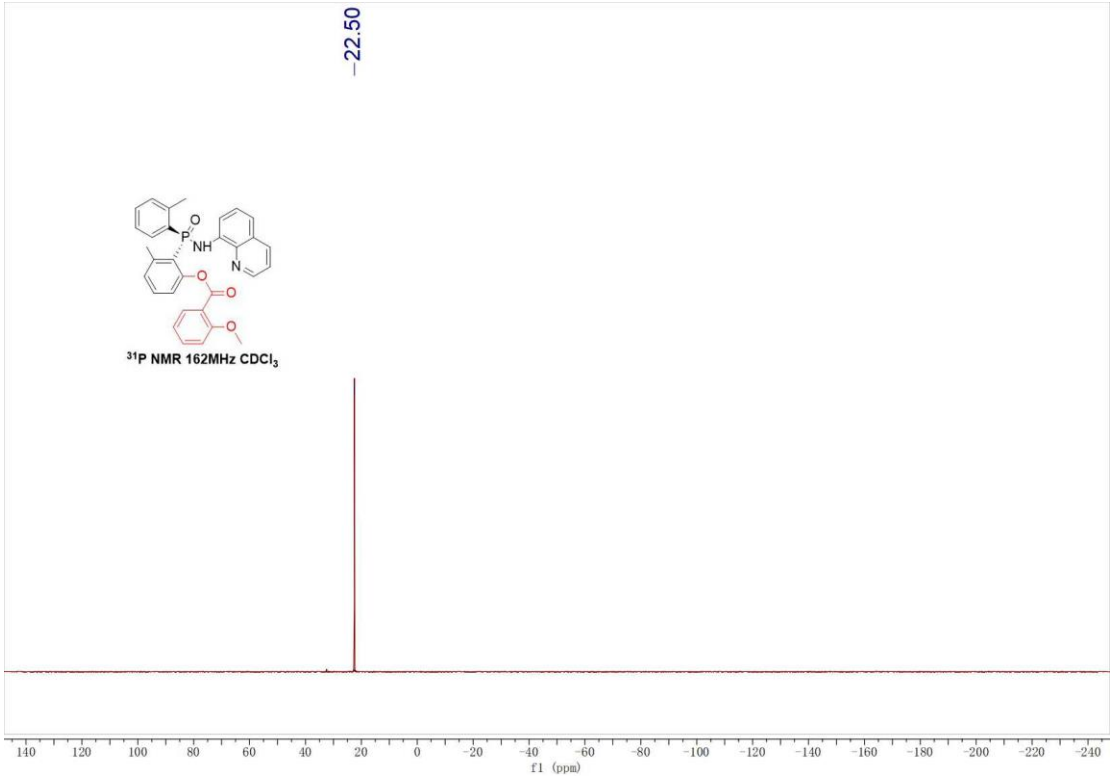
**$^{1}$H NMR of 3f**



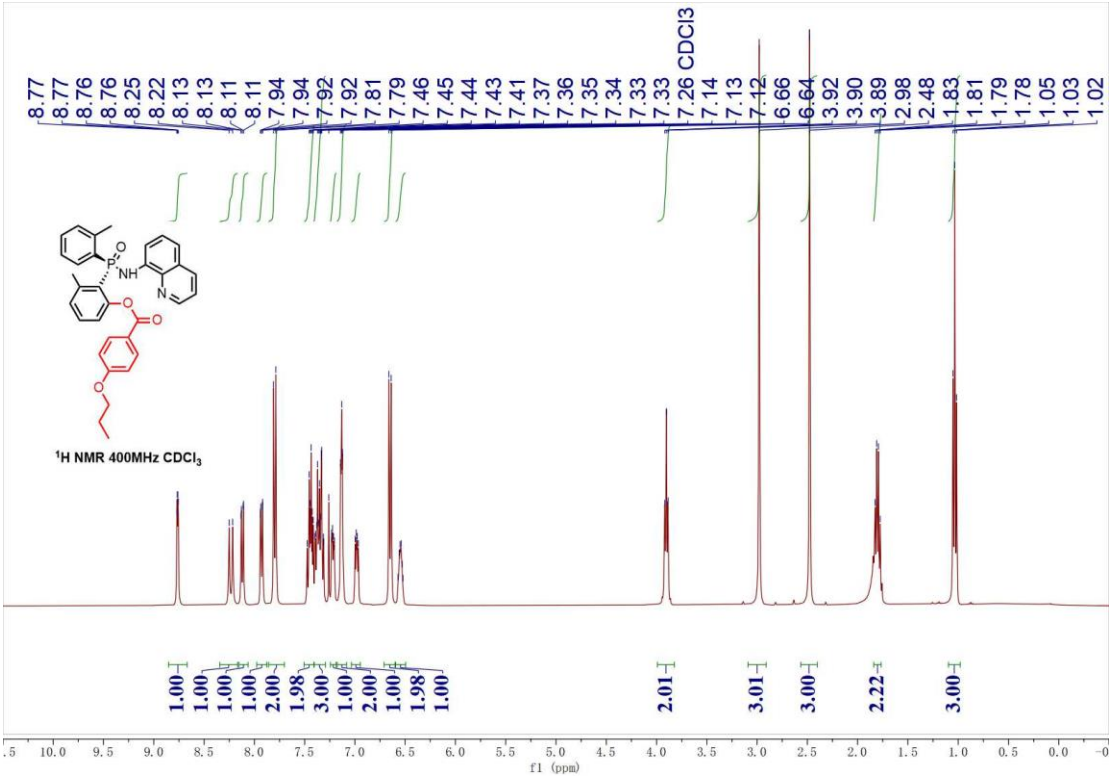

**$^{13}$C{$^{1}$H} NMR of 3f**



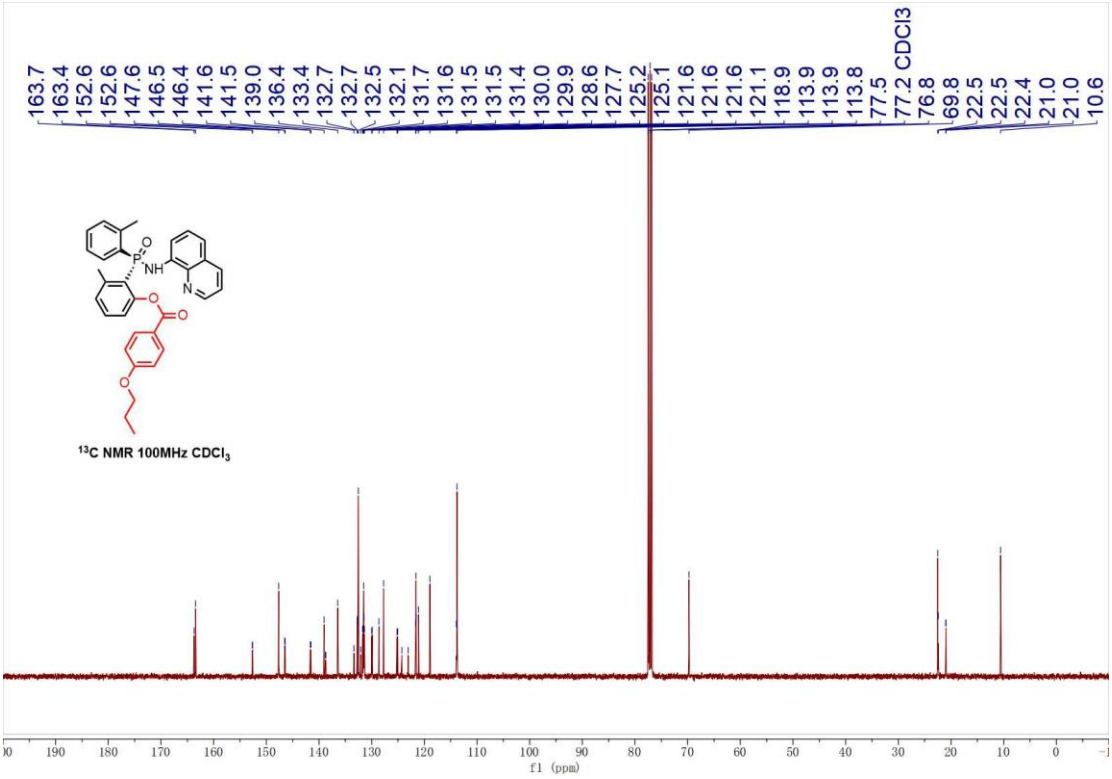
## $^{31}$P NMR of 3f



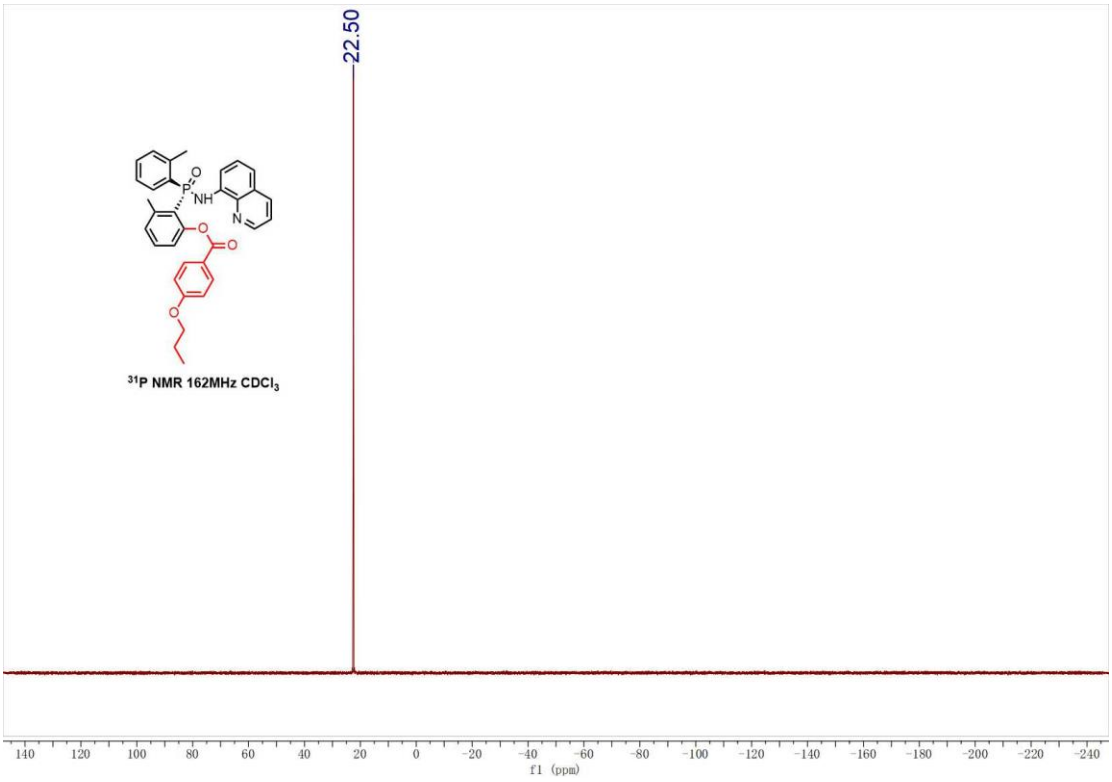

## $^{1}$H NMR of 3g



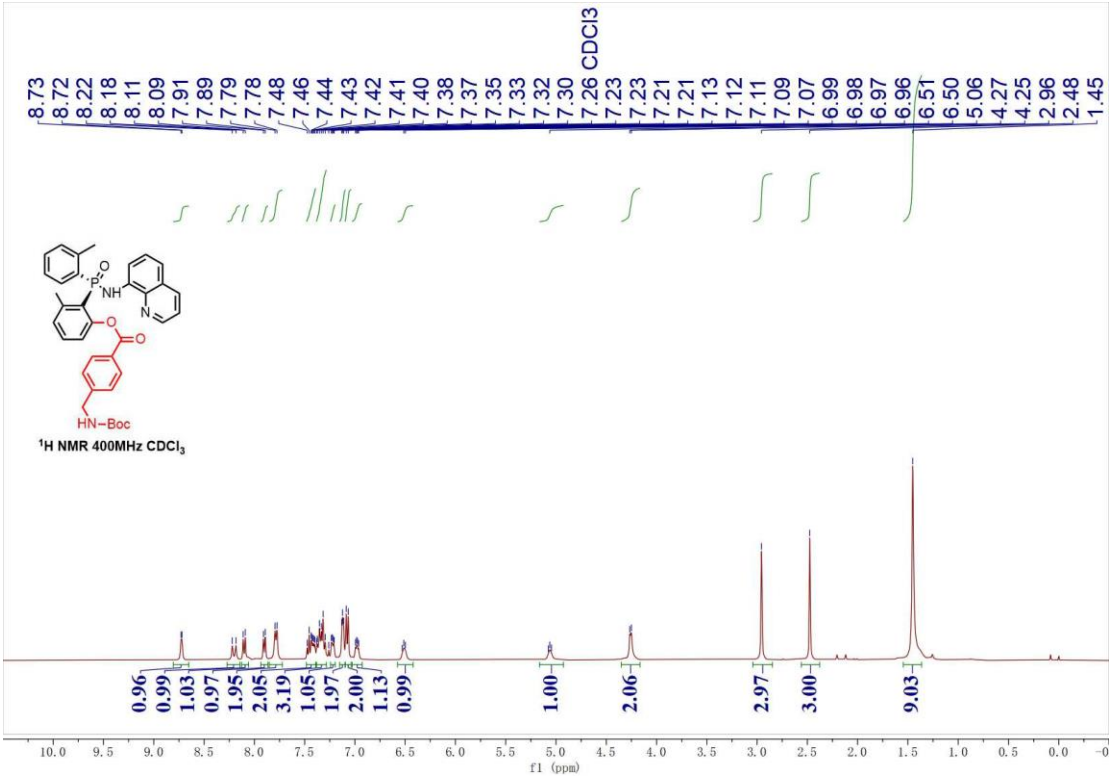
**$^{13}C\{^{1}H\}$ NMR of 3g**



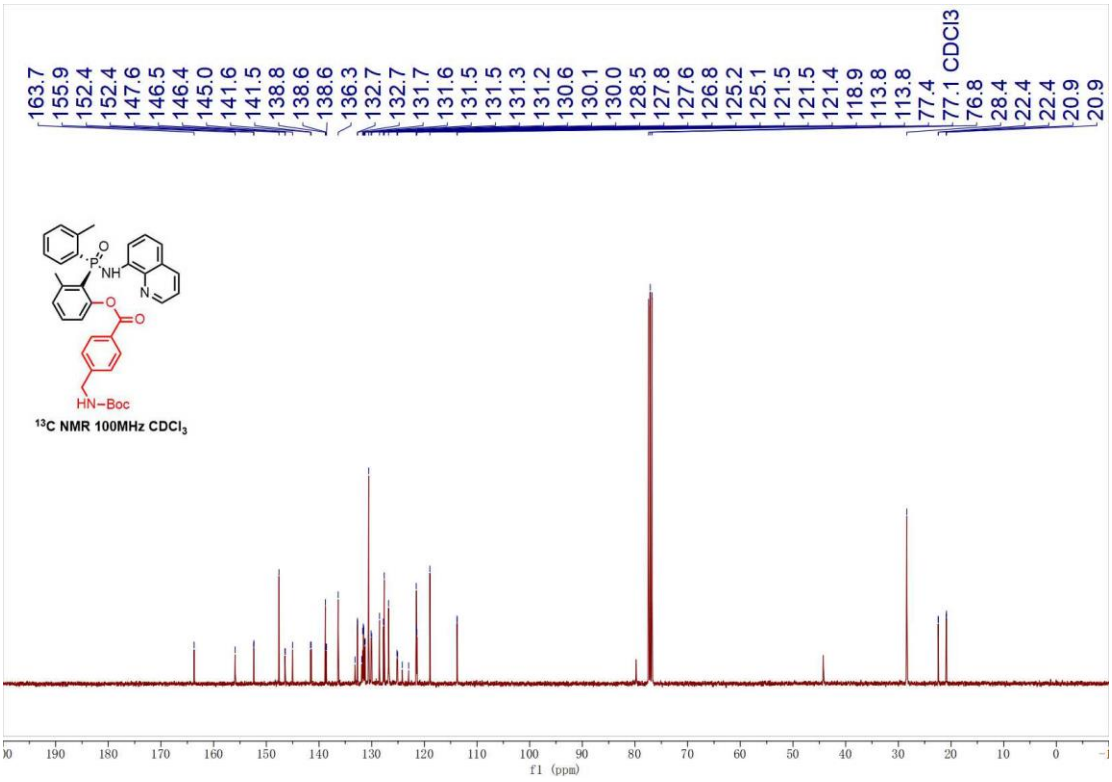

**$^{31}P$ NMR of 3g**



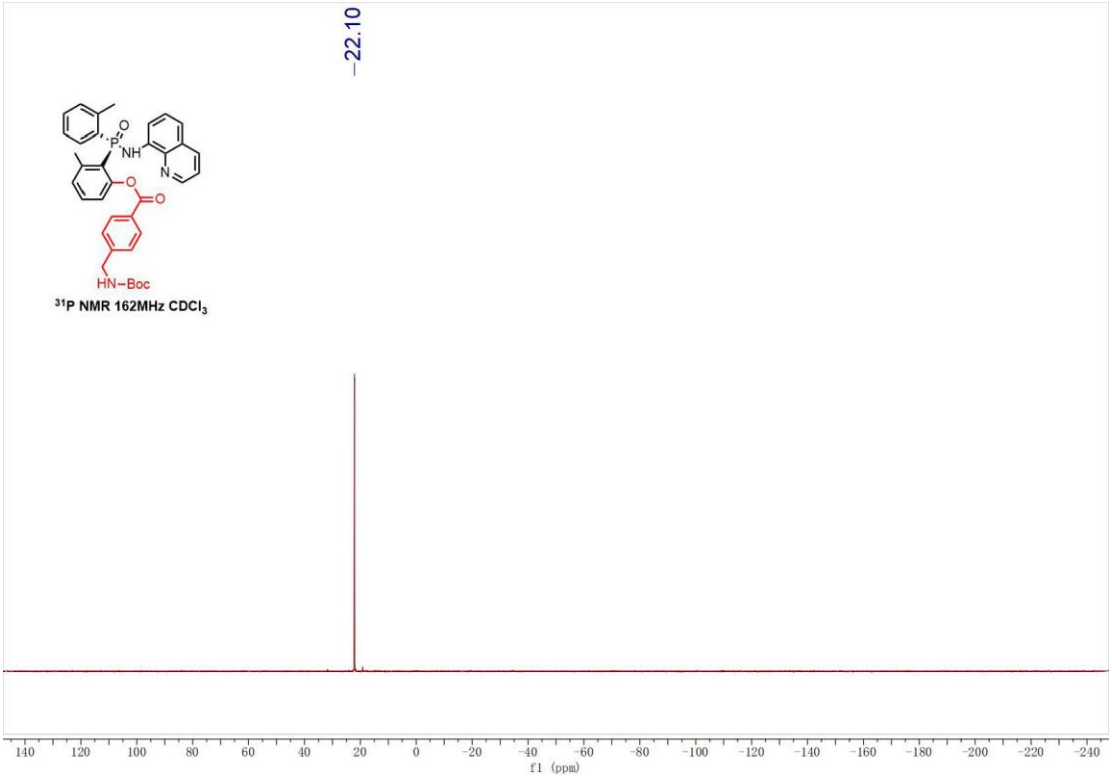
## $^{1}$H NMR of 3h



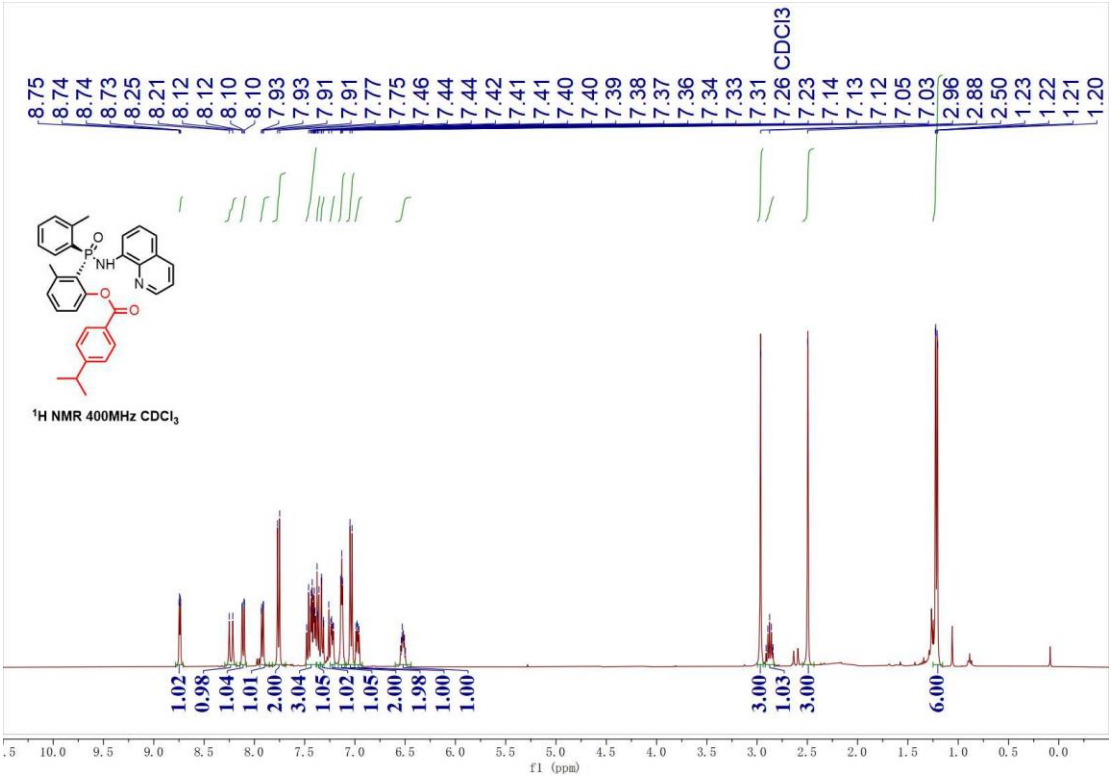

## $^{13}$C{$^{1}$H} NMR of 3h



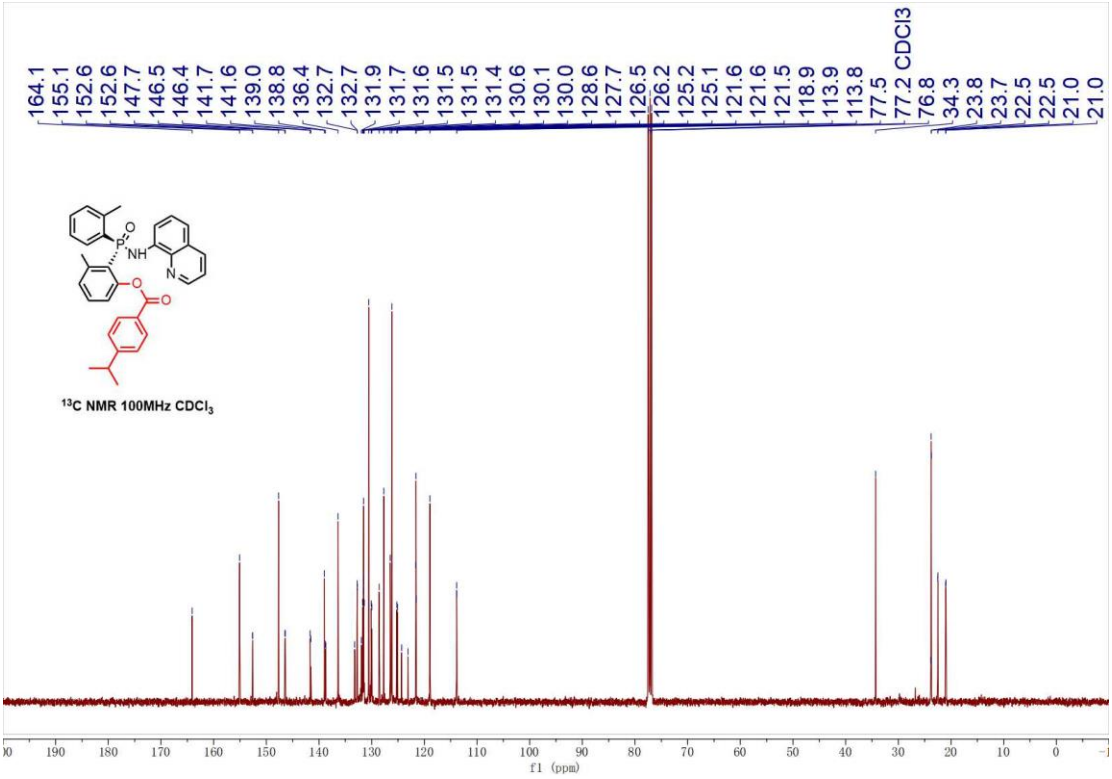
## $^{31}$P NMR of 3h



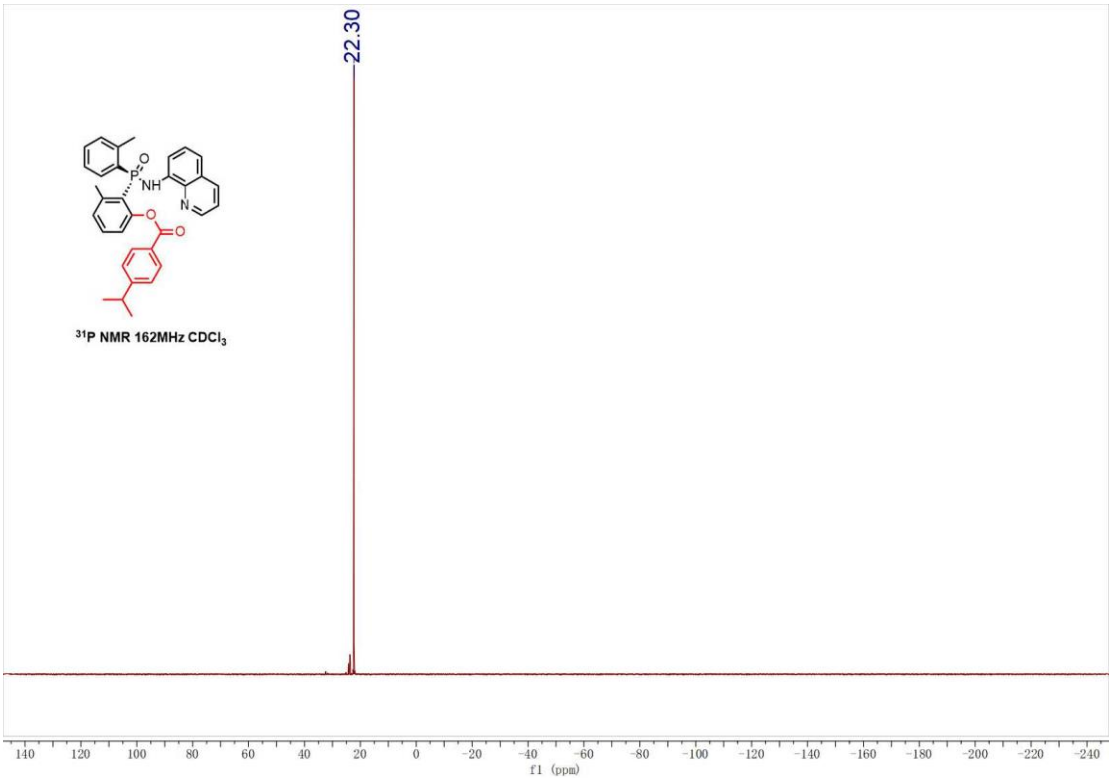

## $^{1}$H NMR of 3i



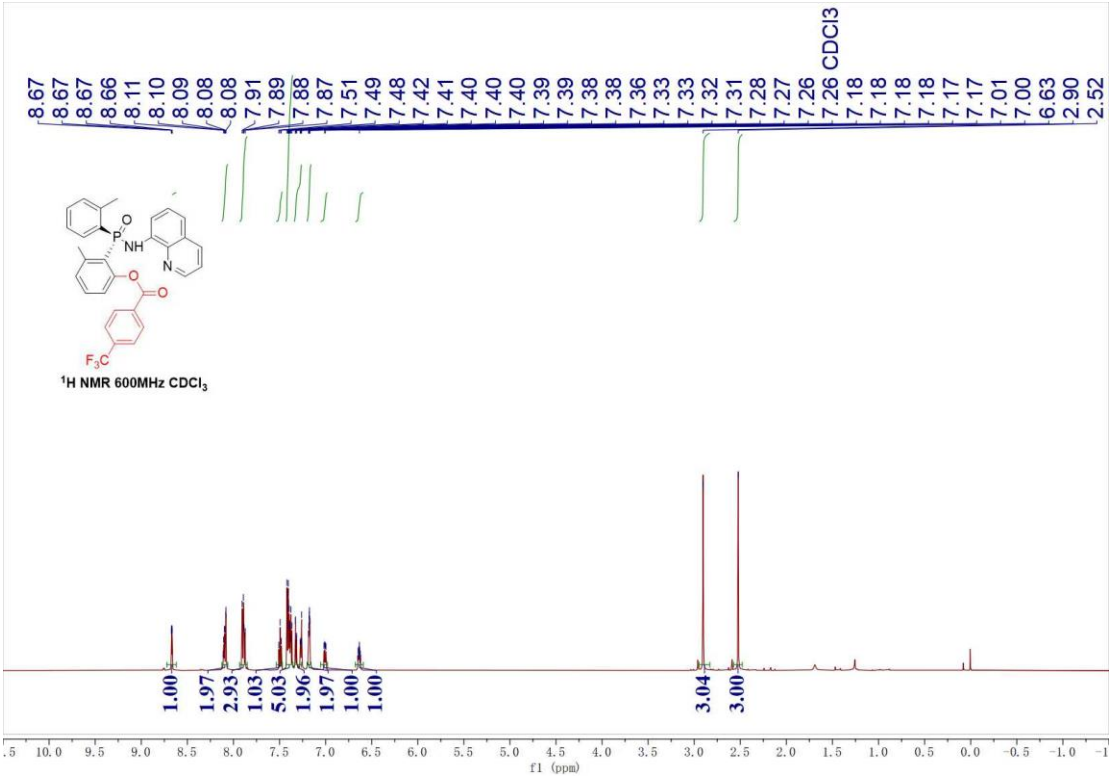
**$^{13}C\{^{1}H\}$ NMR of 3i**



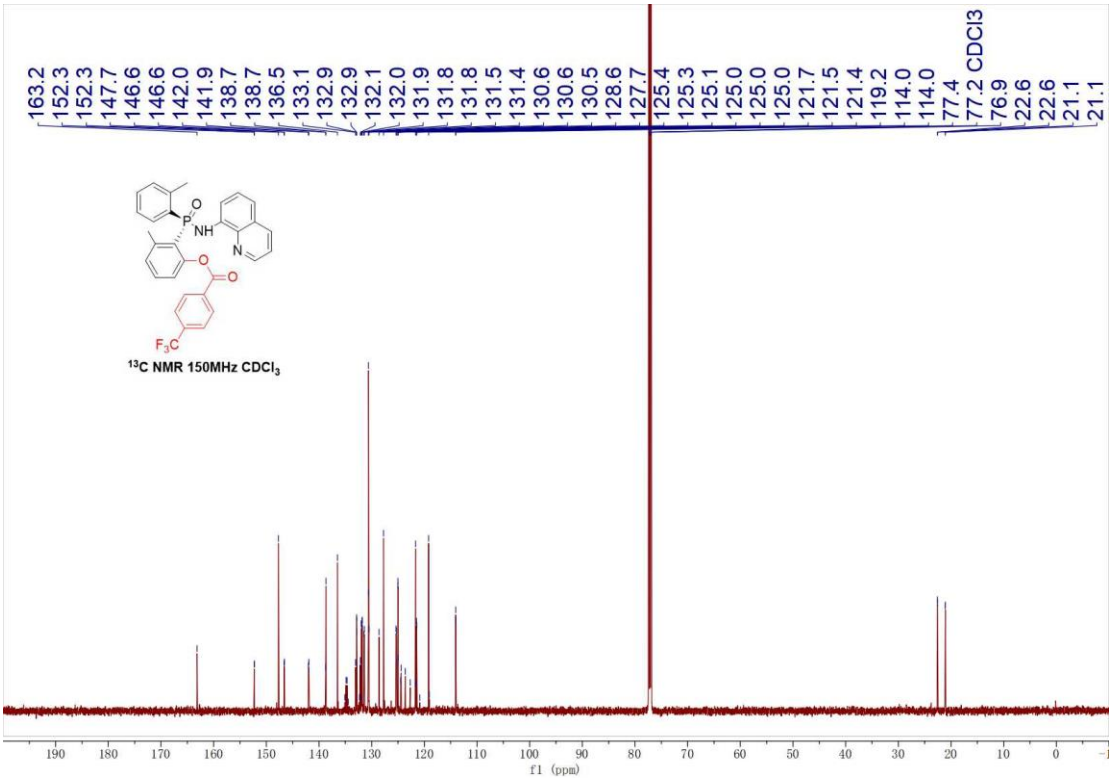

**$^{31}P$ NMR of 3i**



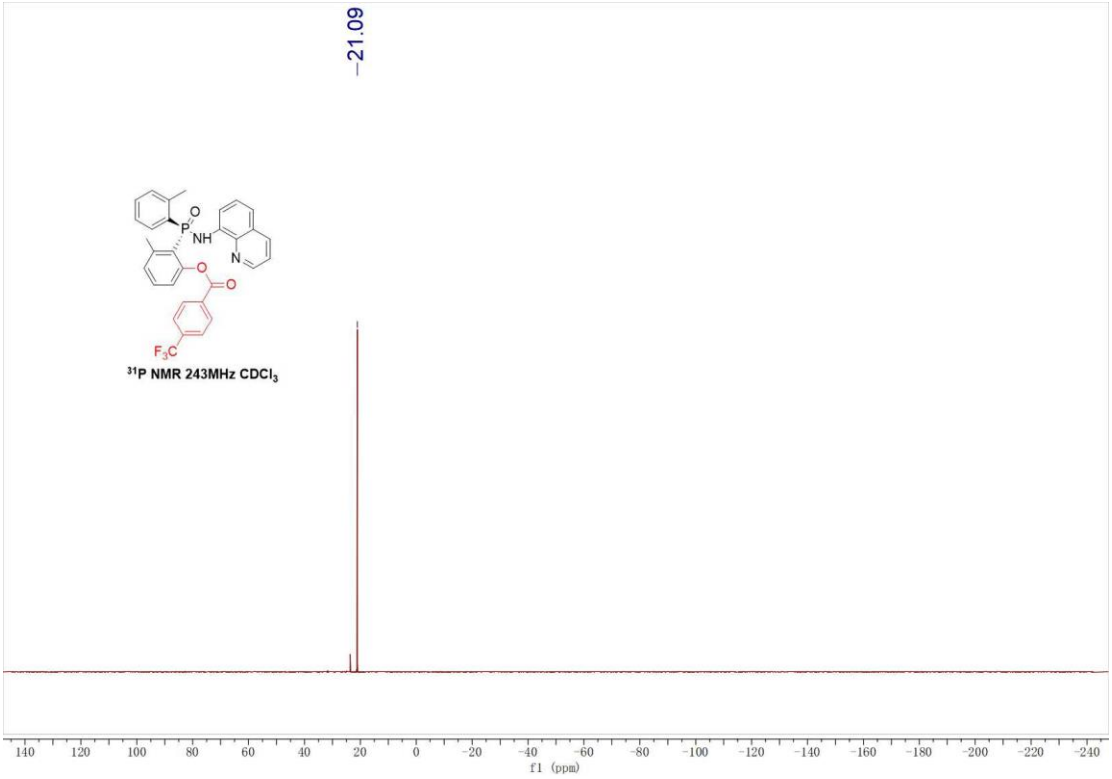
## $^{1}$H NMR of 3j



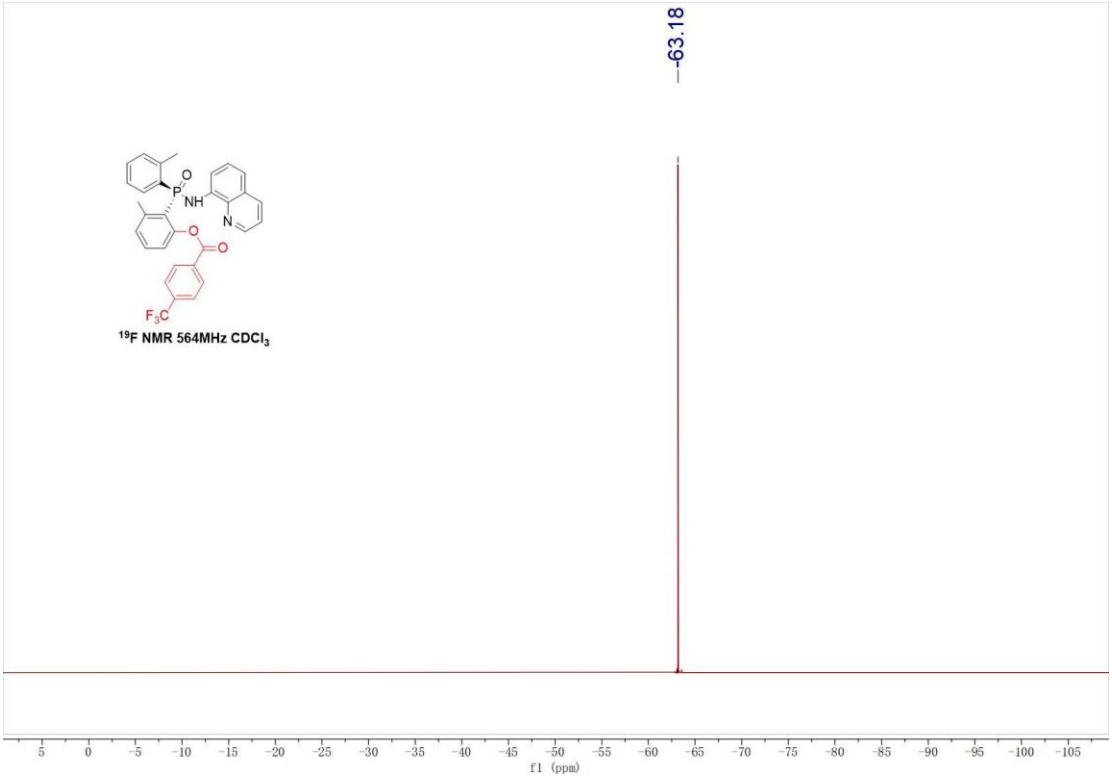

## $^{13}$C{$^{1}$H} NMR of 3j



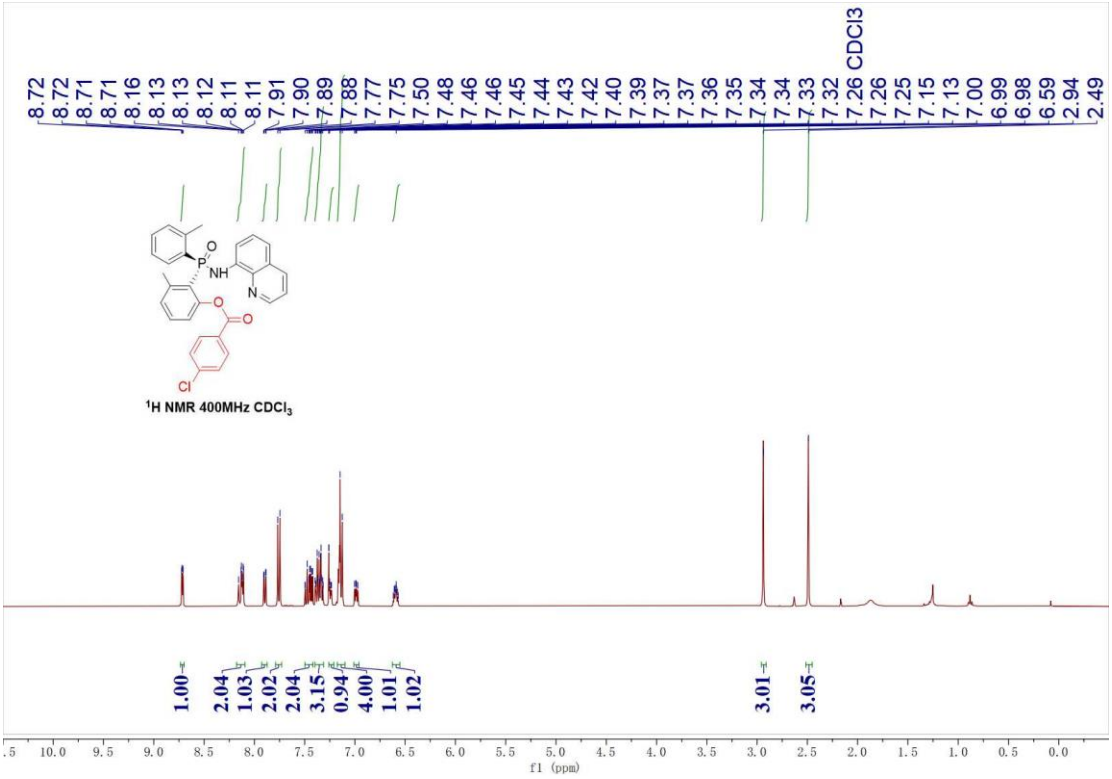
## $^{31}$P NMR of 3j



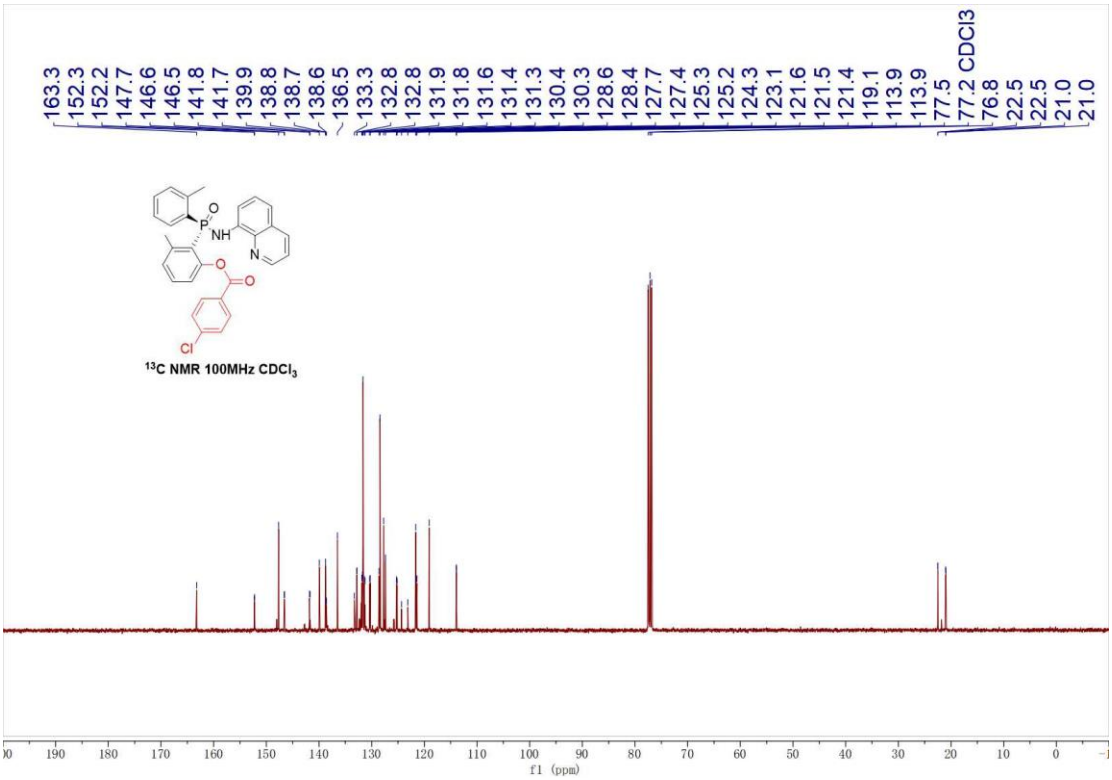

## $^{19}$F NMR of 3j



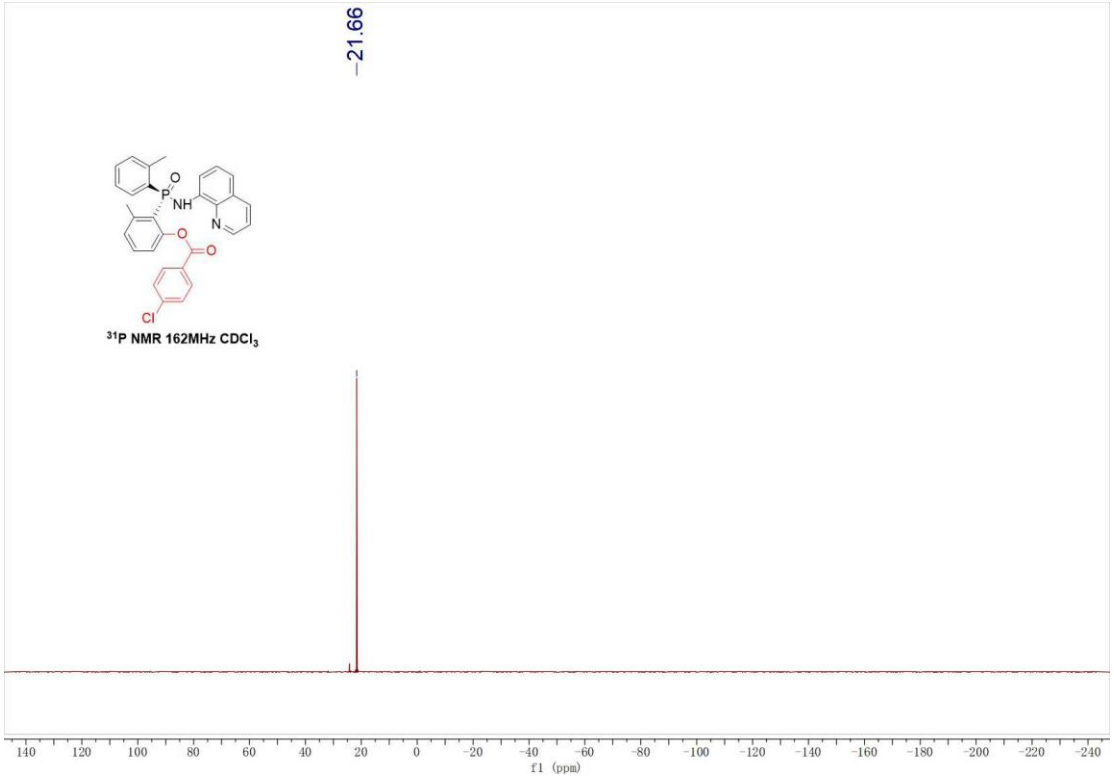
## $^{1}$H NMR of 3k



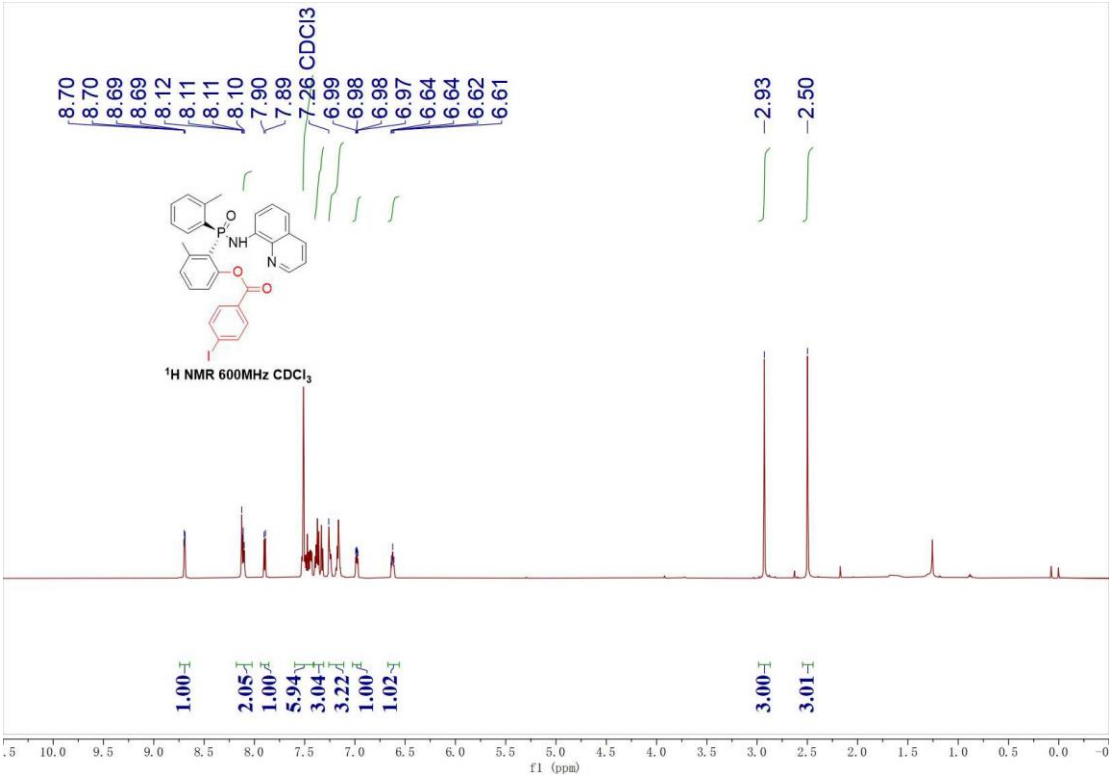

## $^{13}$C{$^{1}$H} NMR of 3k



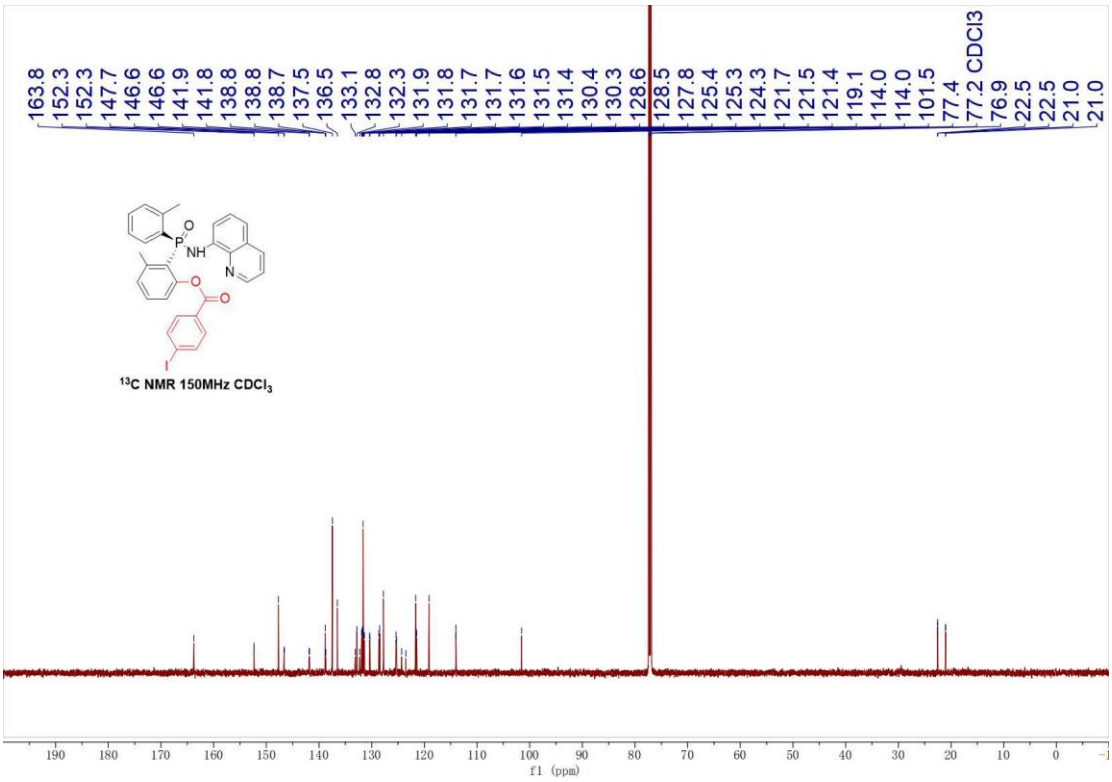
## $^{31}$P NMR of 3k



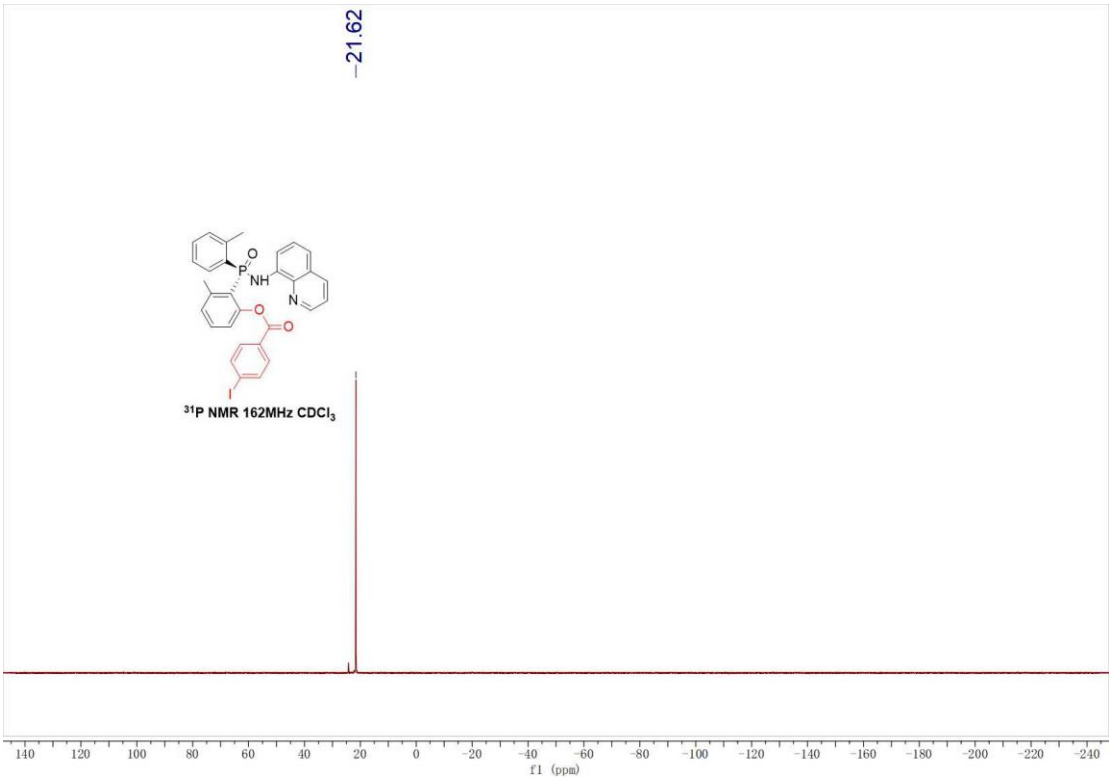

## $^{1}$H NMR of 3l



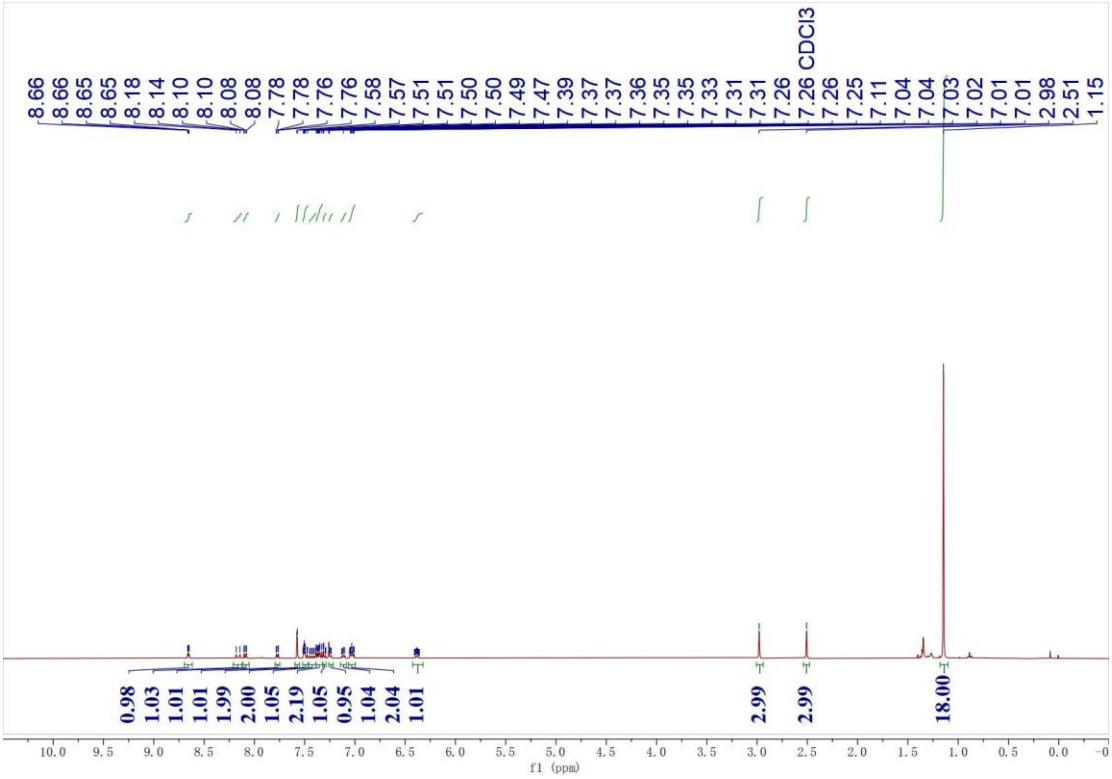
**$^{13}C\{^{1}H\}$ NMR of 3l**



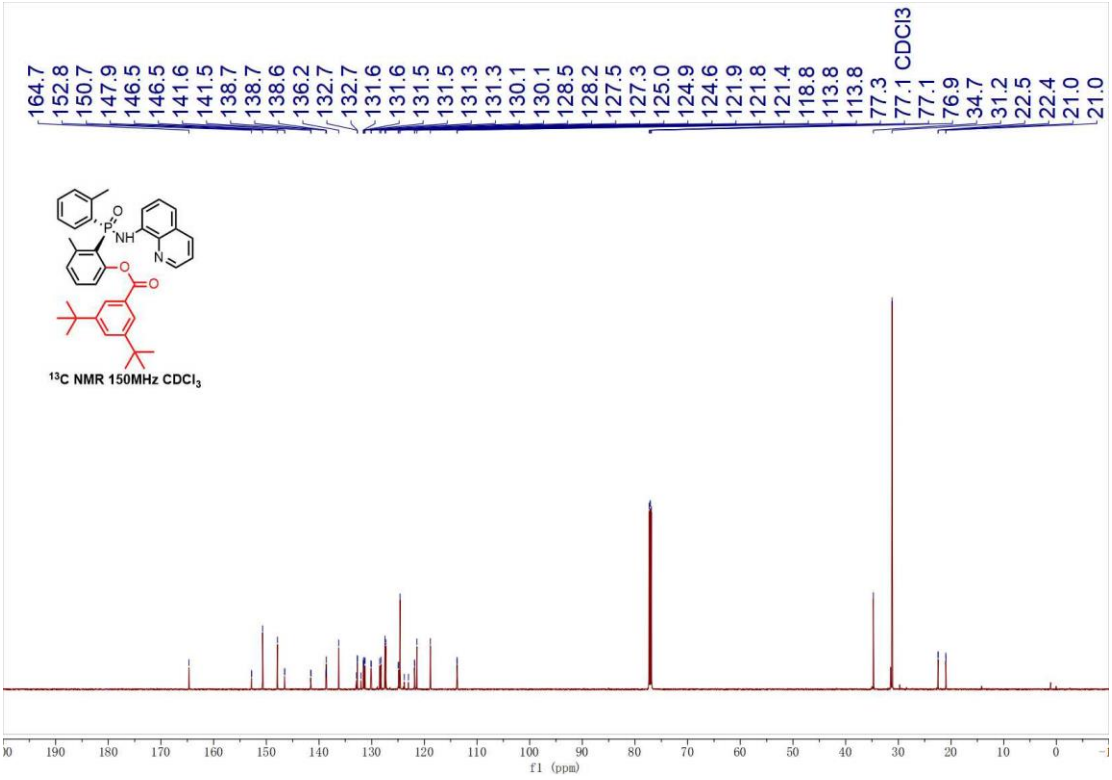

**$^{31}P$ NMR of 3l**



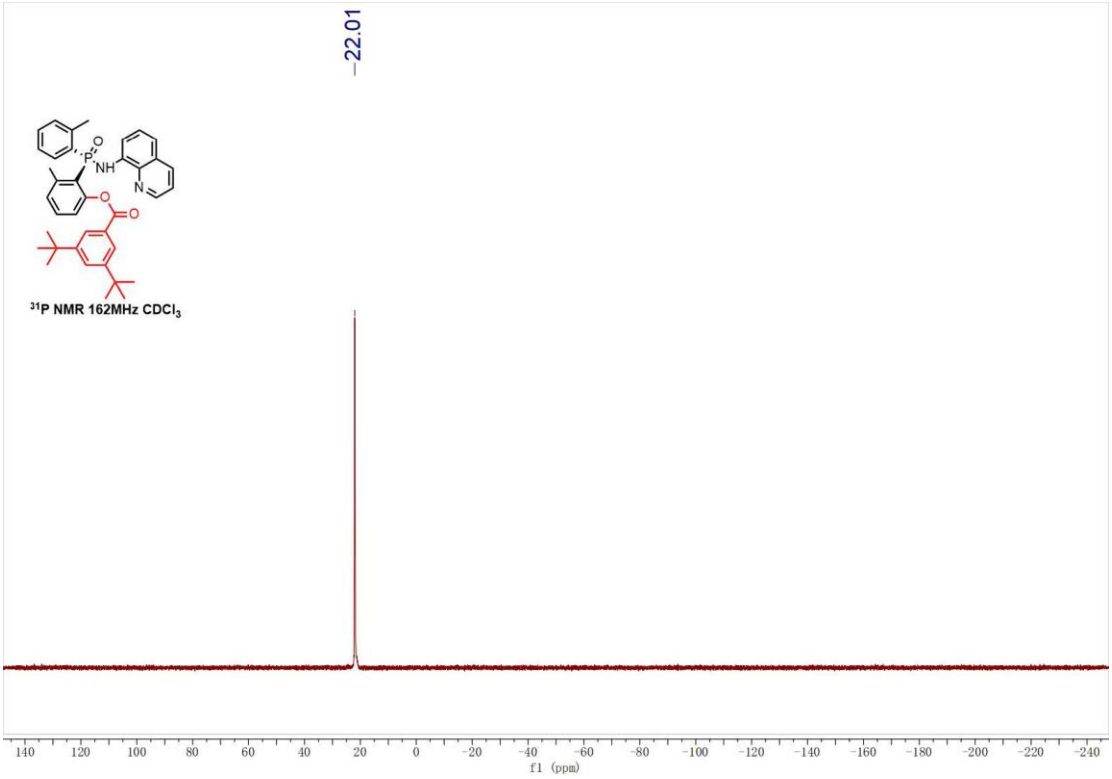
## $^{1}$H NMR of 3m



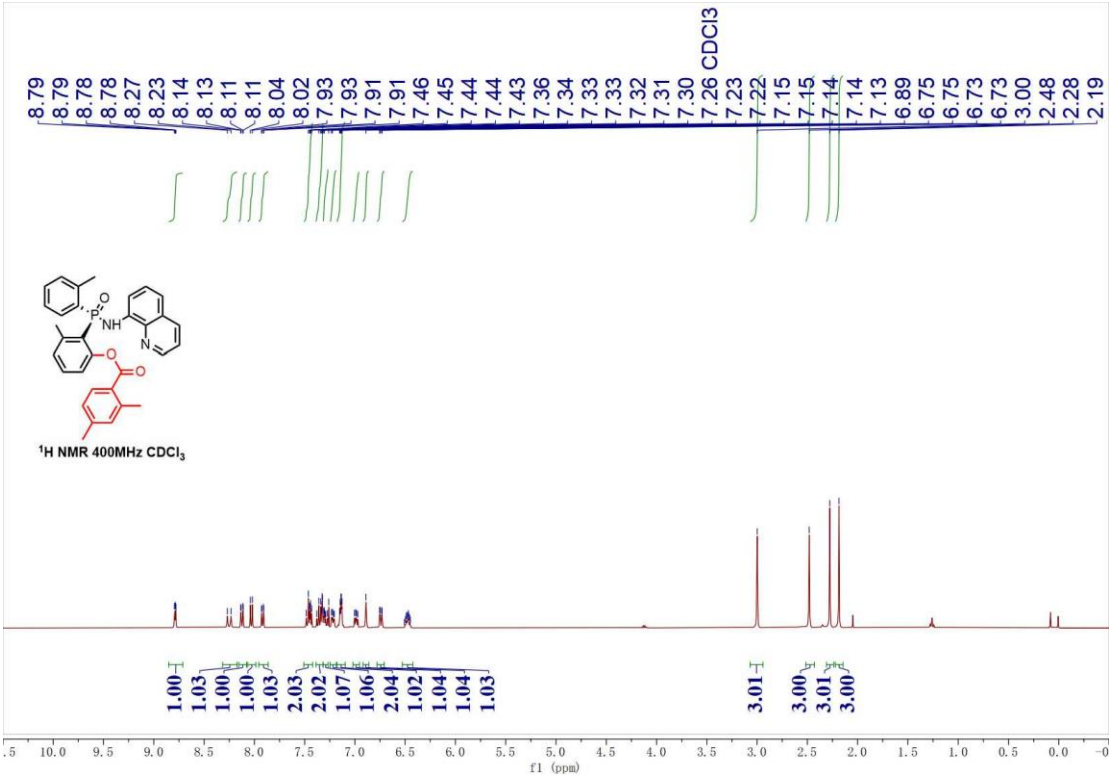

## $^{13}$C{$^{1}$H} NMR of 3m



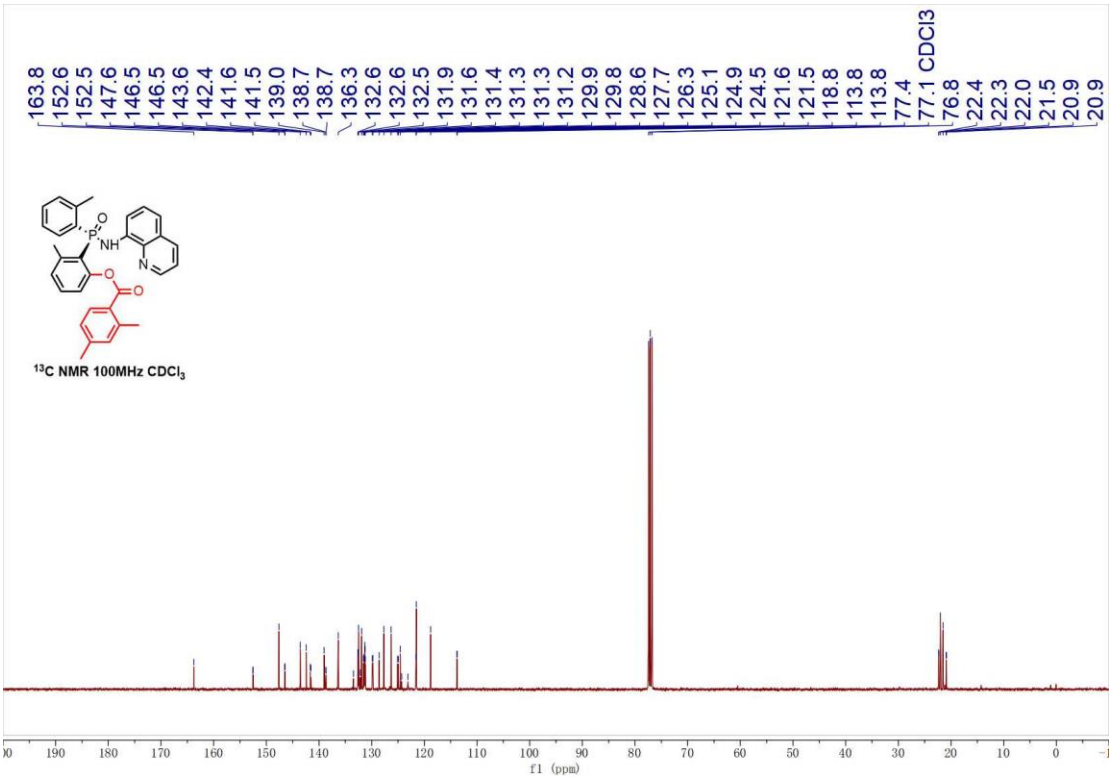
## $^{31}$P NMR of 3m



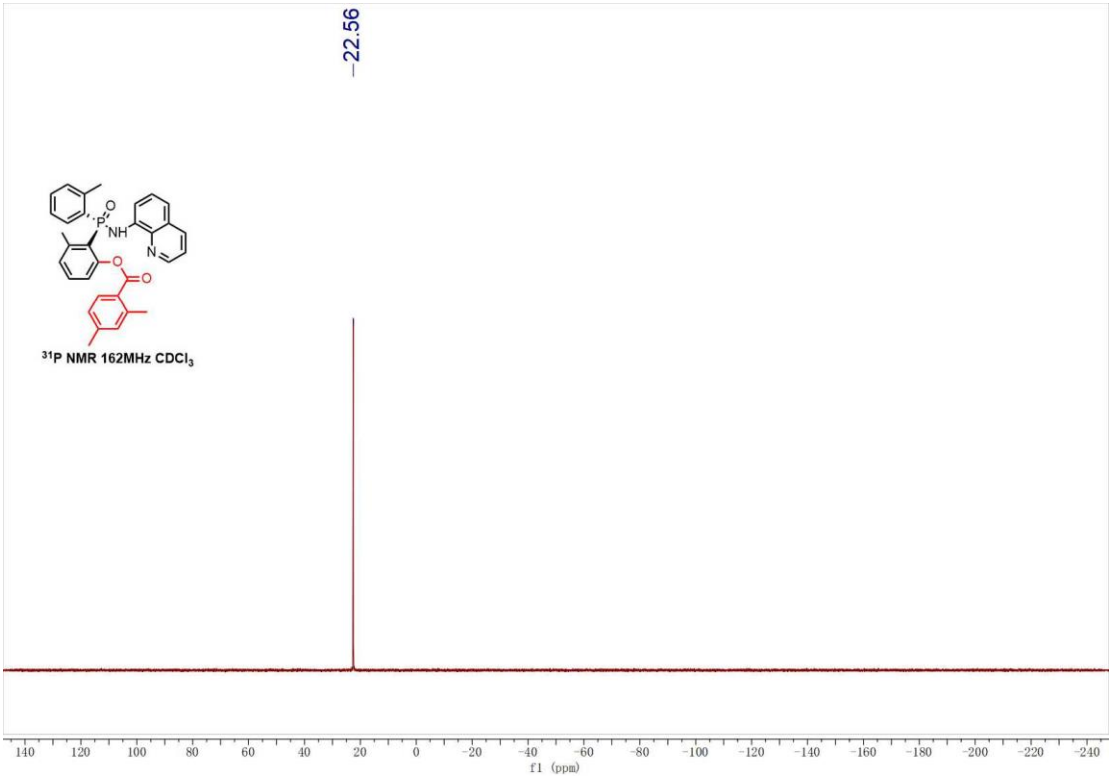

## $^{1}$H NMR of 3n



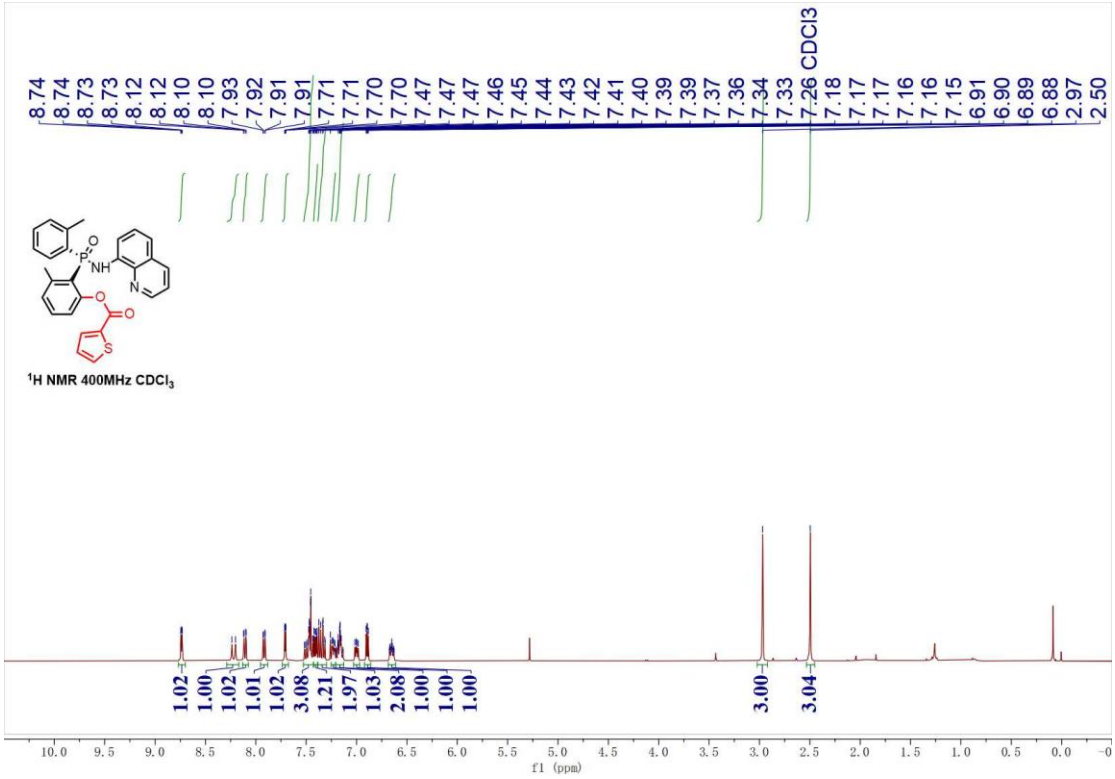
## $^{13}C\{^{1}H\}$ NMR of 3n



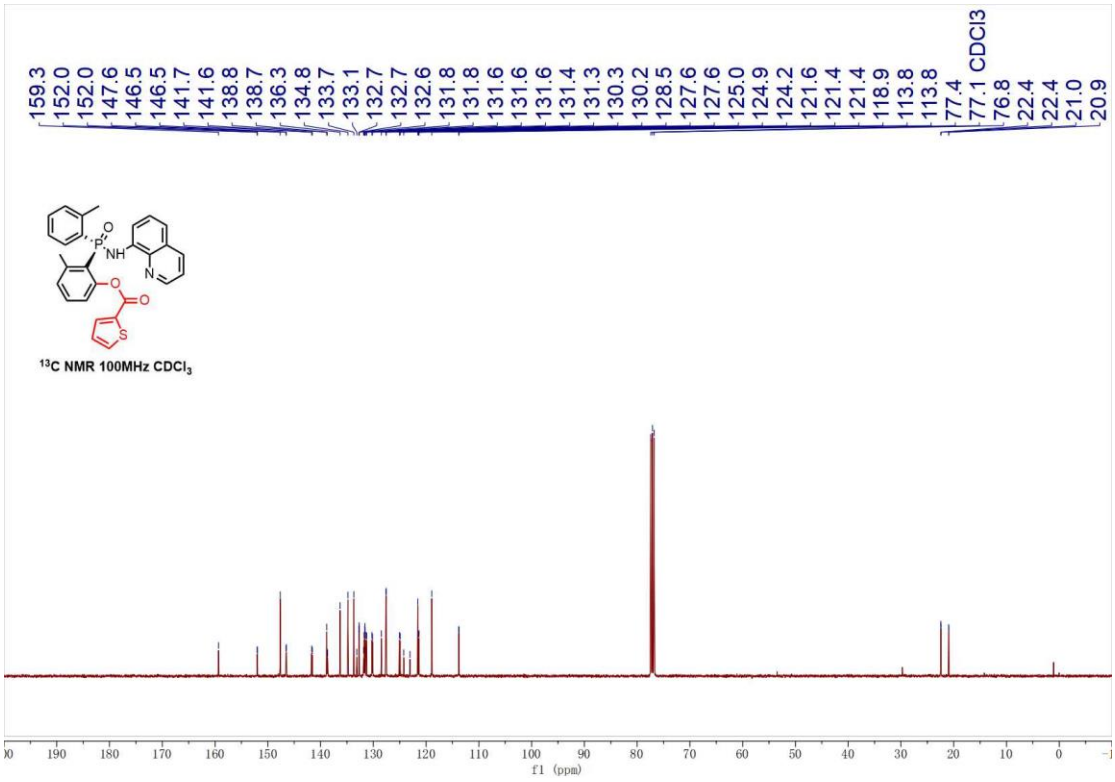

## $^{31}P$ NMR of 3n



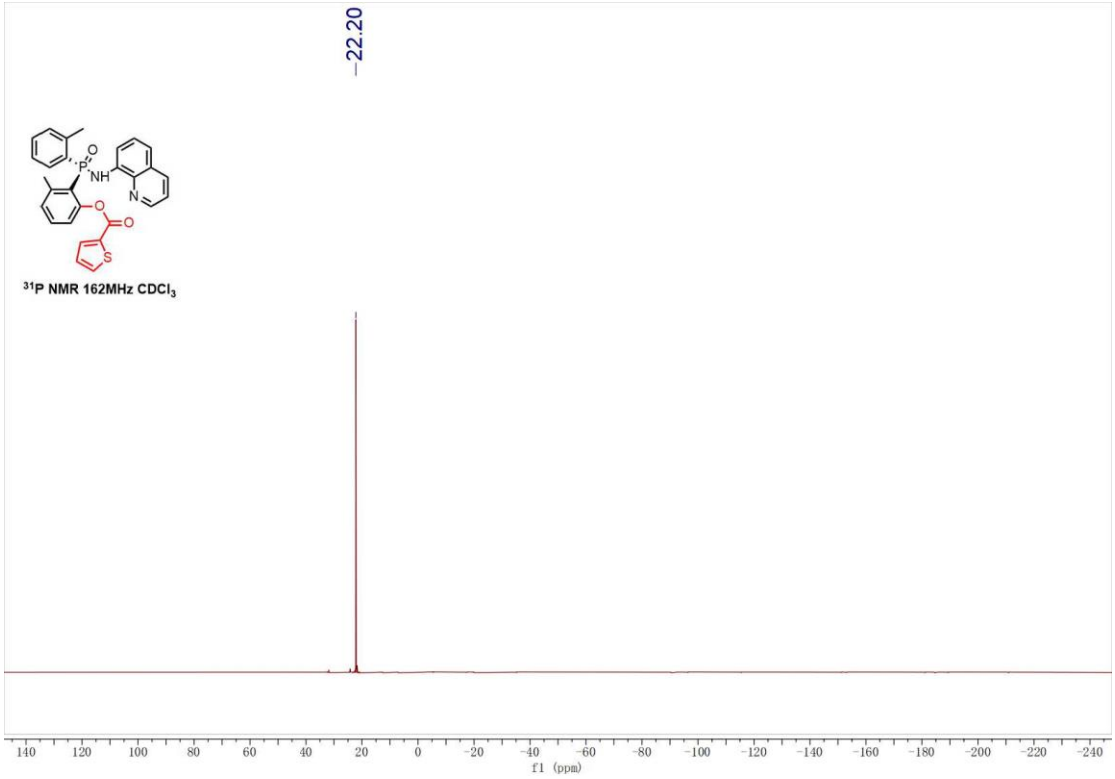
## $^{1}$H NMR of 3o



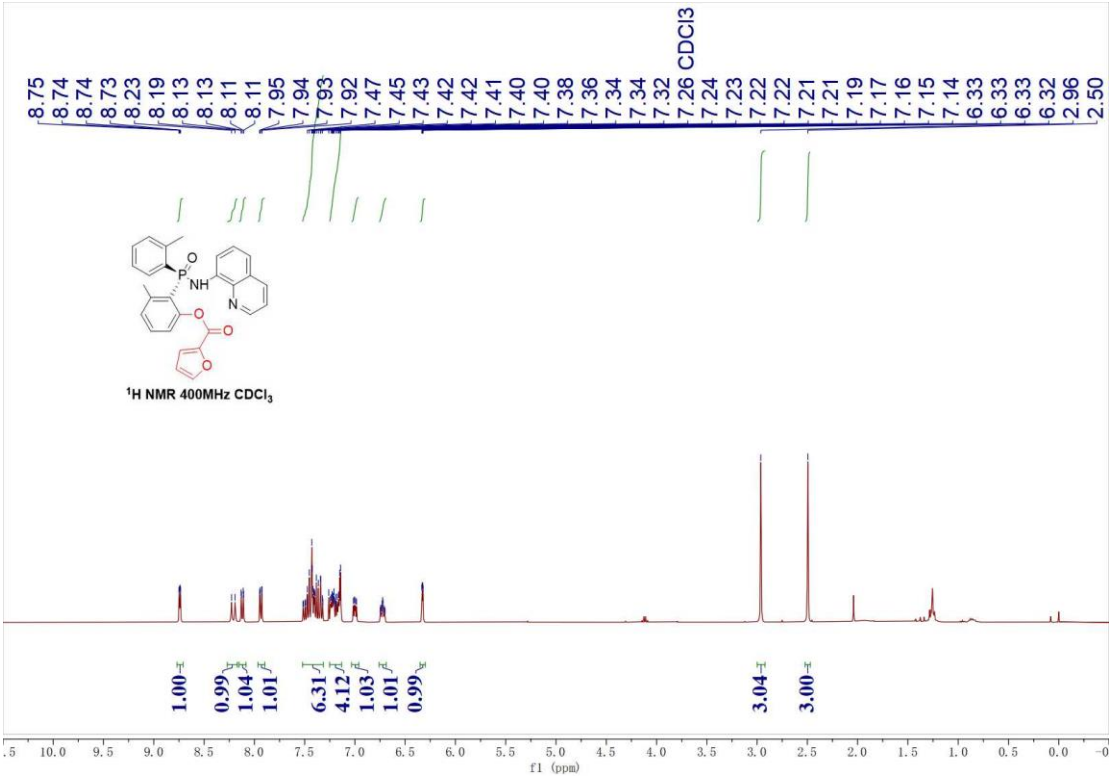

## $^{13}$C{$^{1}$H} NMR of 3o



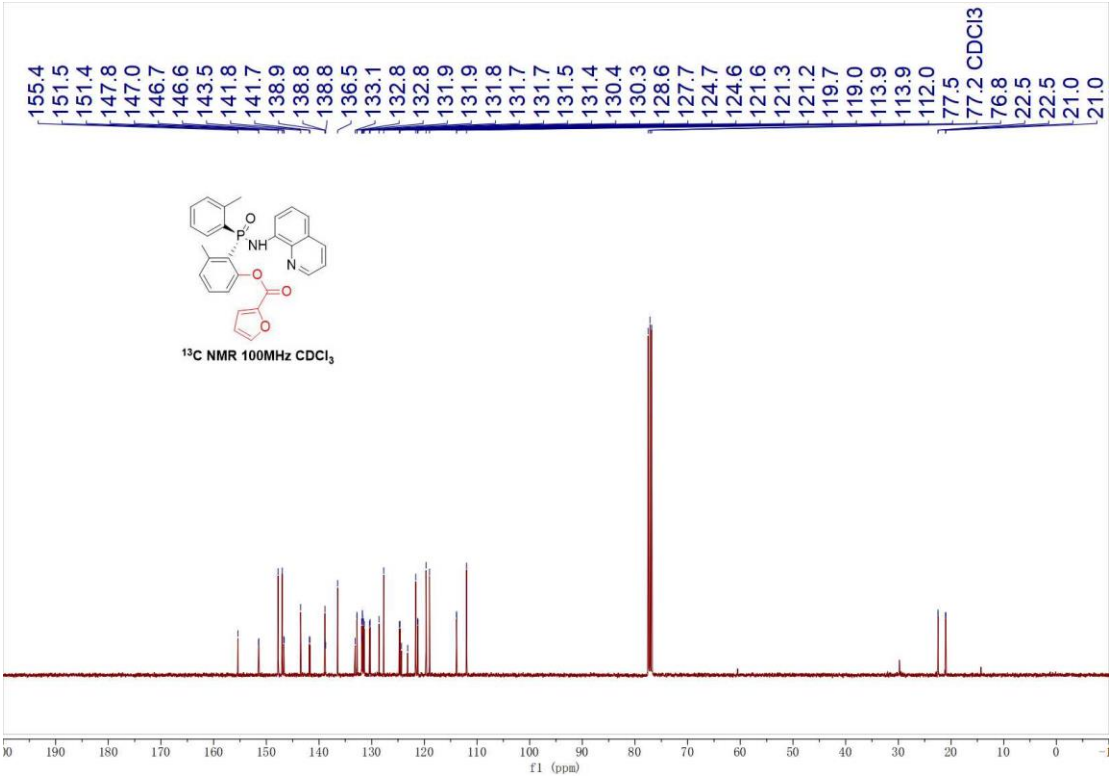
## $^{31}$P NMR of 3o



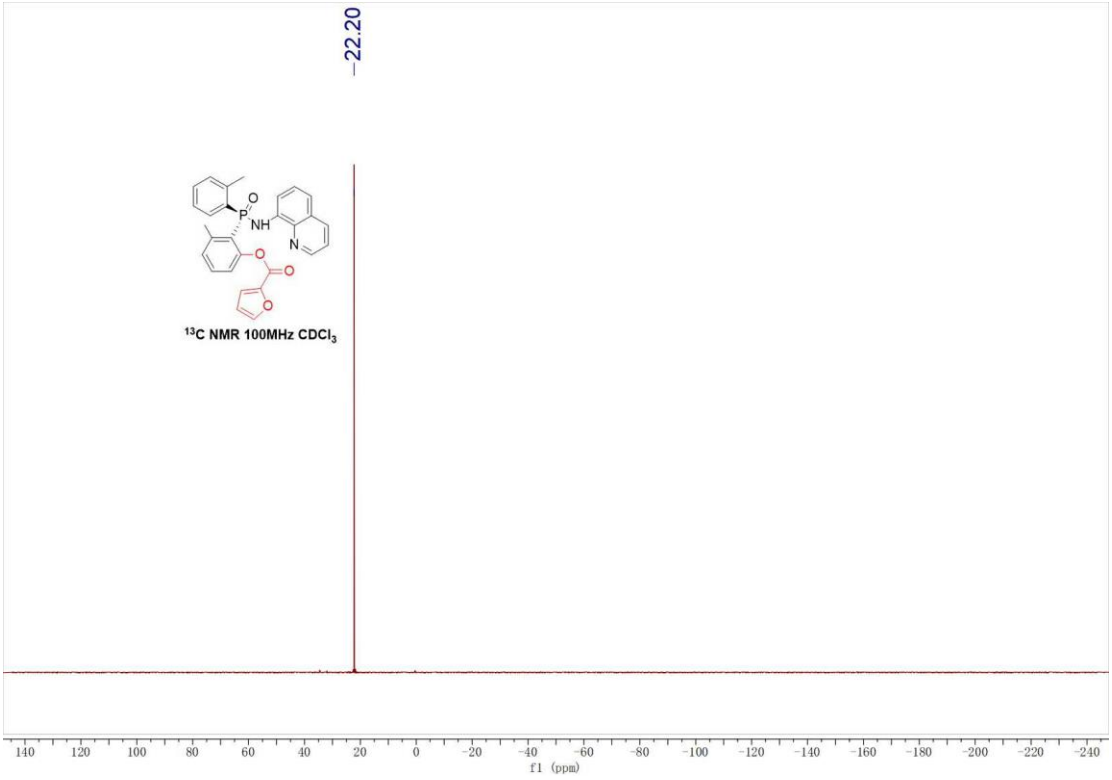

## $^{1}$H NMR of 3p



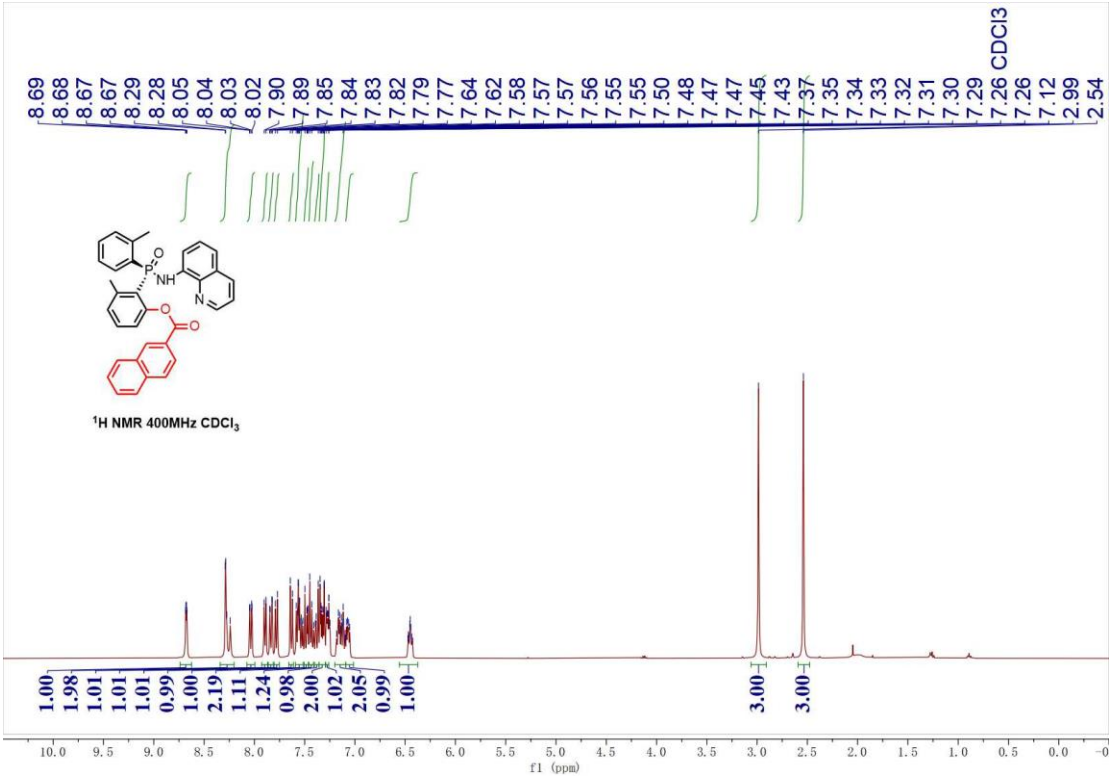
## $^{13}C\{^{1}H\}$ NMR of 3p



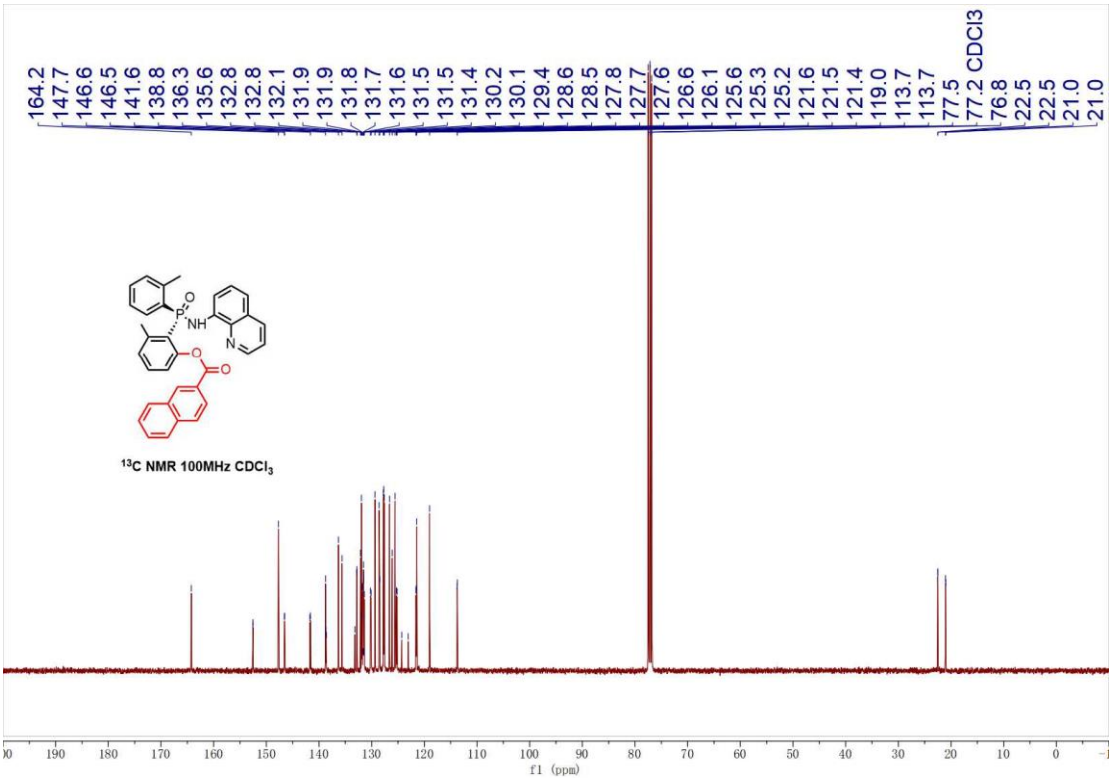

## $^{31}P$ NMR of 3p



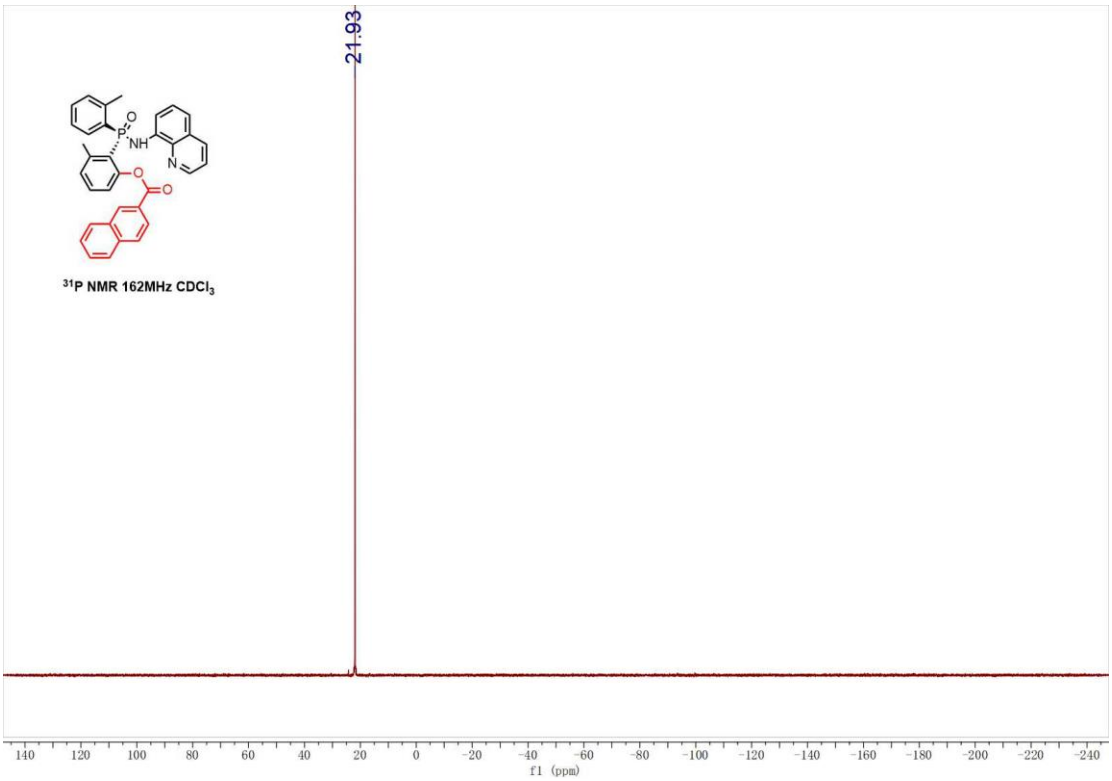
## $^{1}$H NMR of 3q



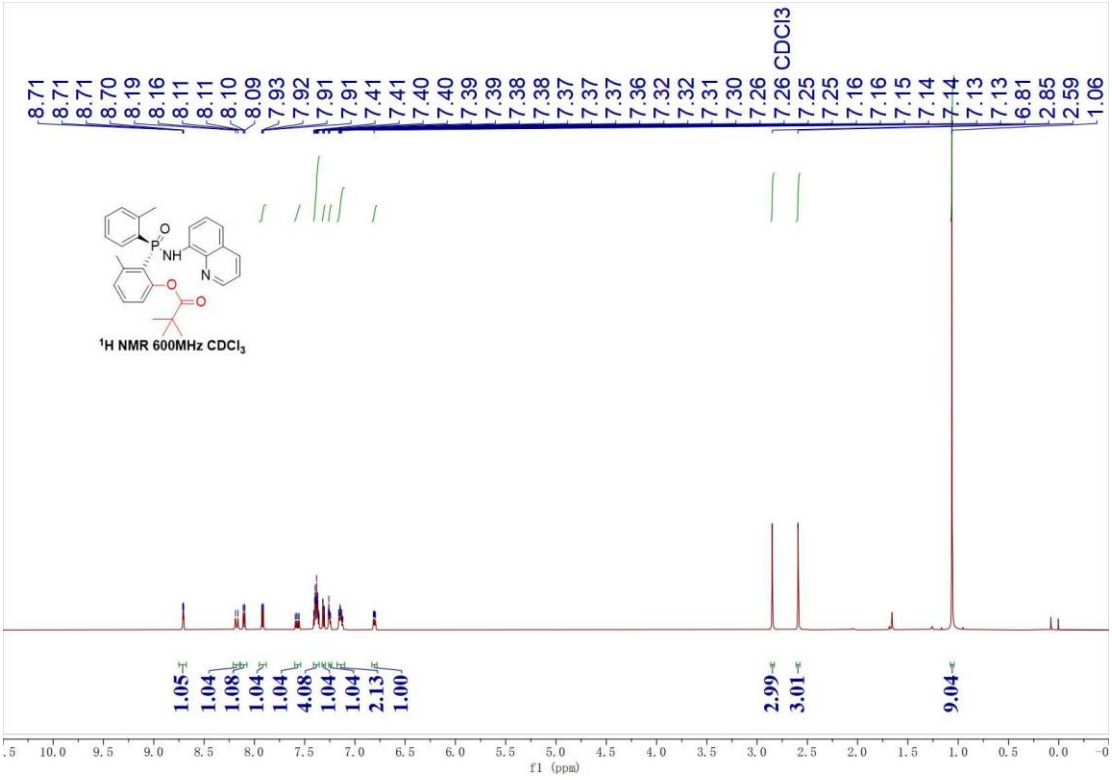

## $^{13}$C{$^{1}$H} NMR of 3q



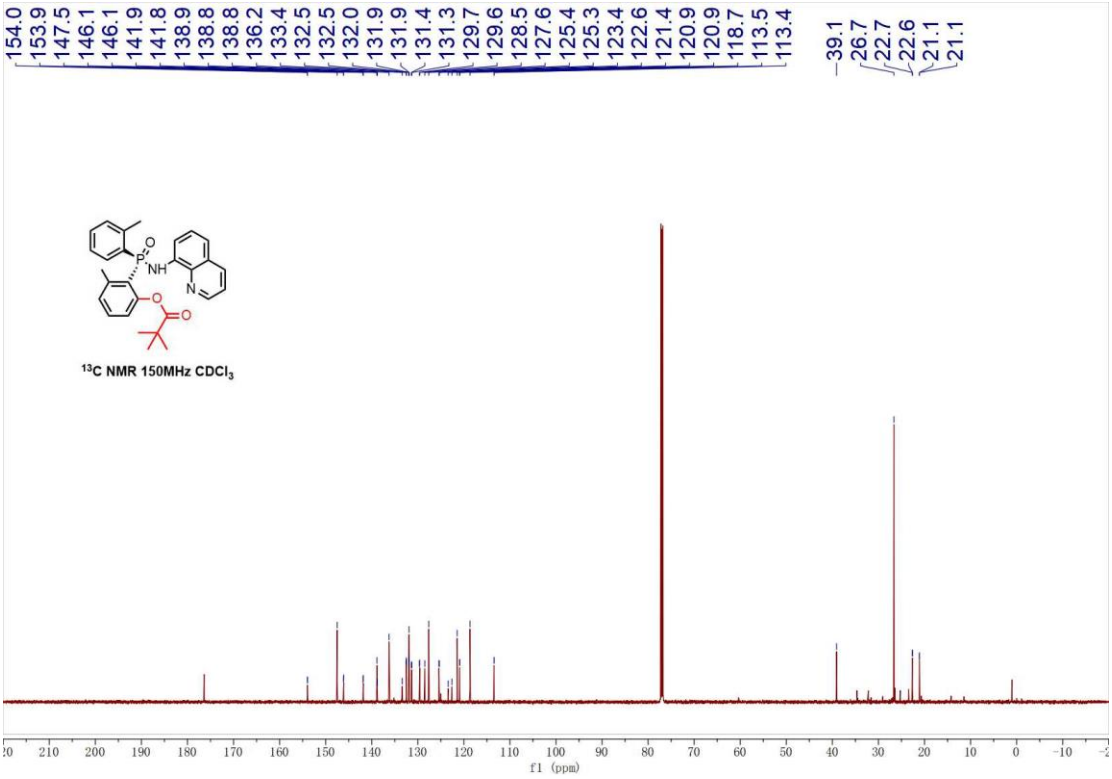
## $^{31}$P NMR of 3q



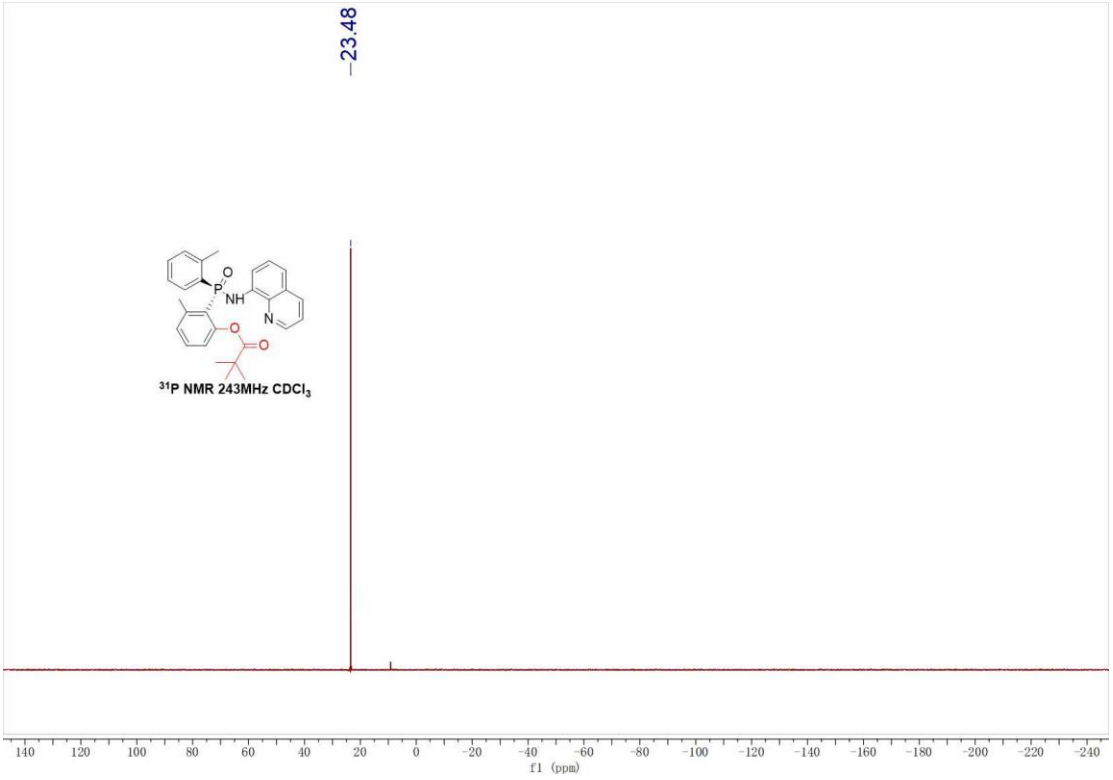

## $^{1}$H NMR of 3r



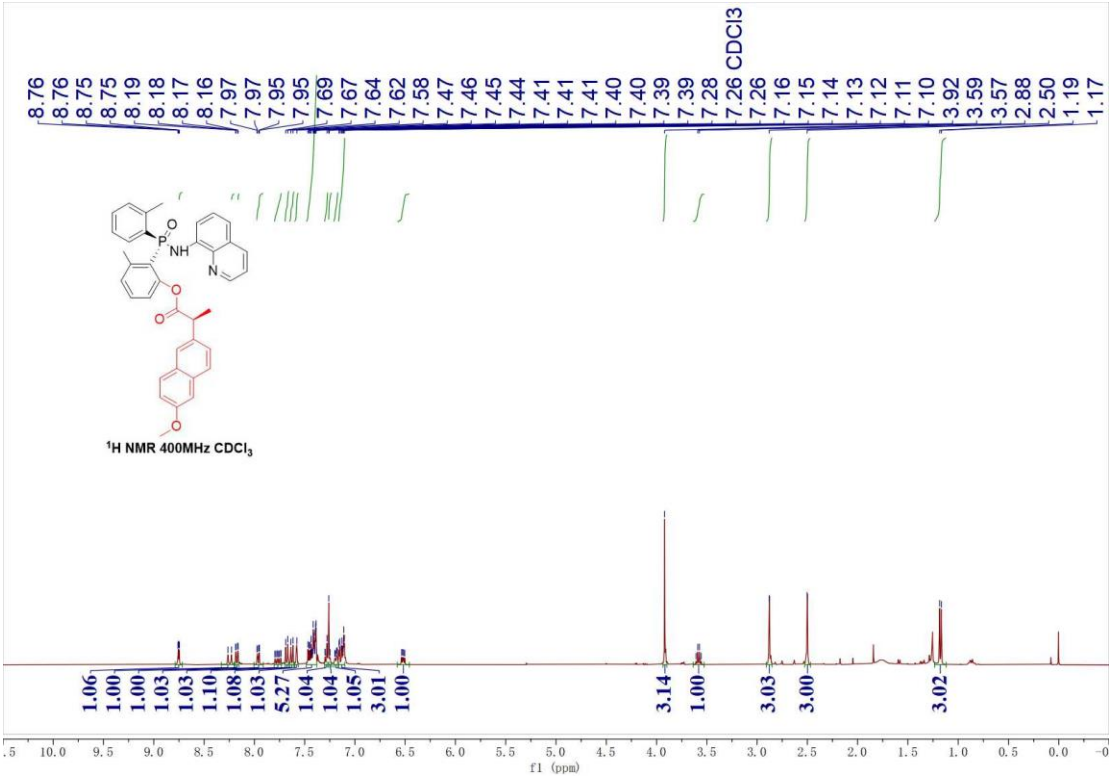
## $^{13}C\{^{1}H\}$ NMR of 3r




## $^{31}P$ NMR of 3r

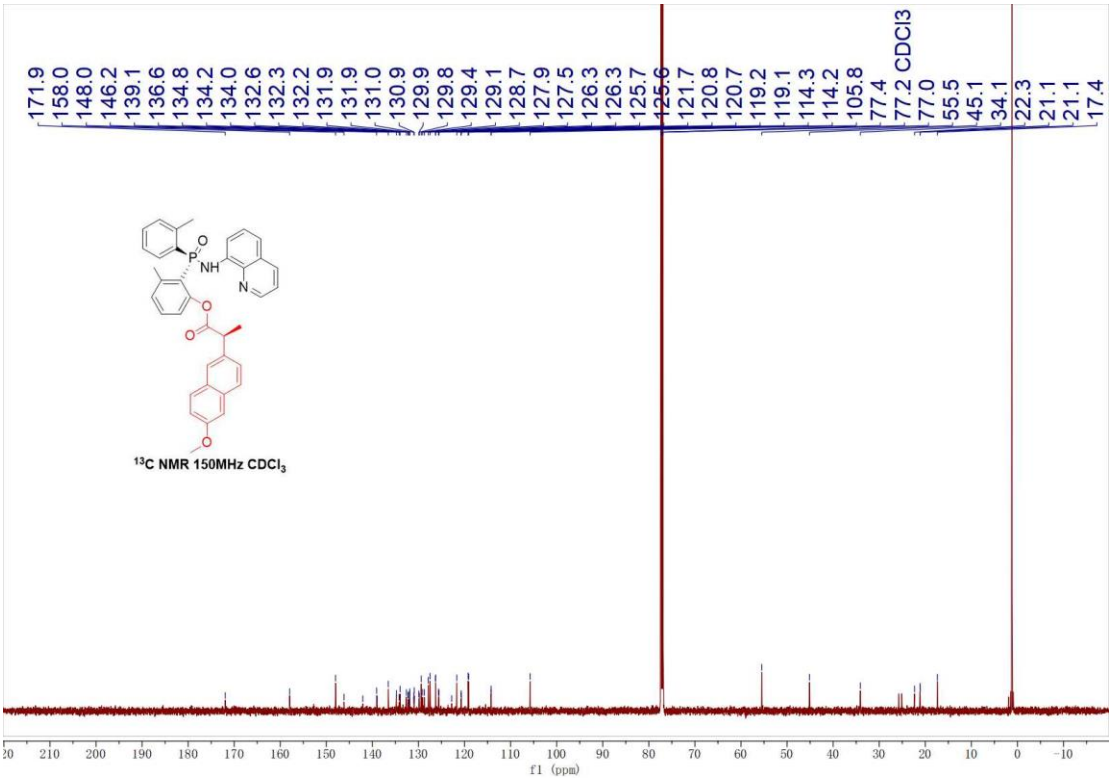


## $^{1}$H NMR of 3s



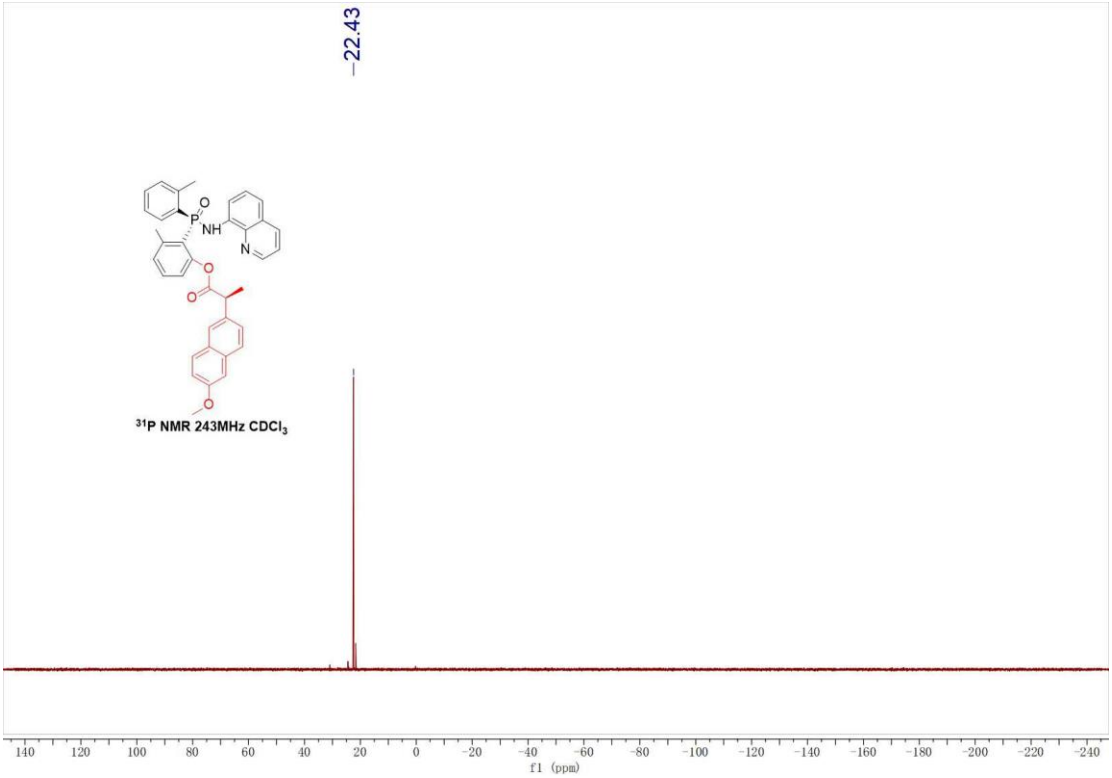

$^{1}$H NMR 400MHz $CDCl_3$

## $^{13}$C{$^{1}$H} NMR of 3s

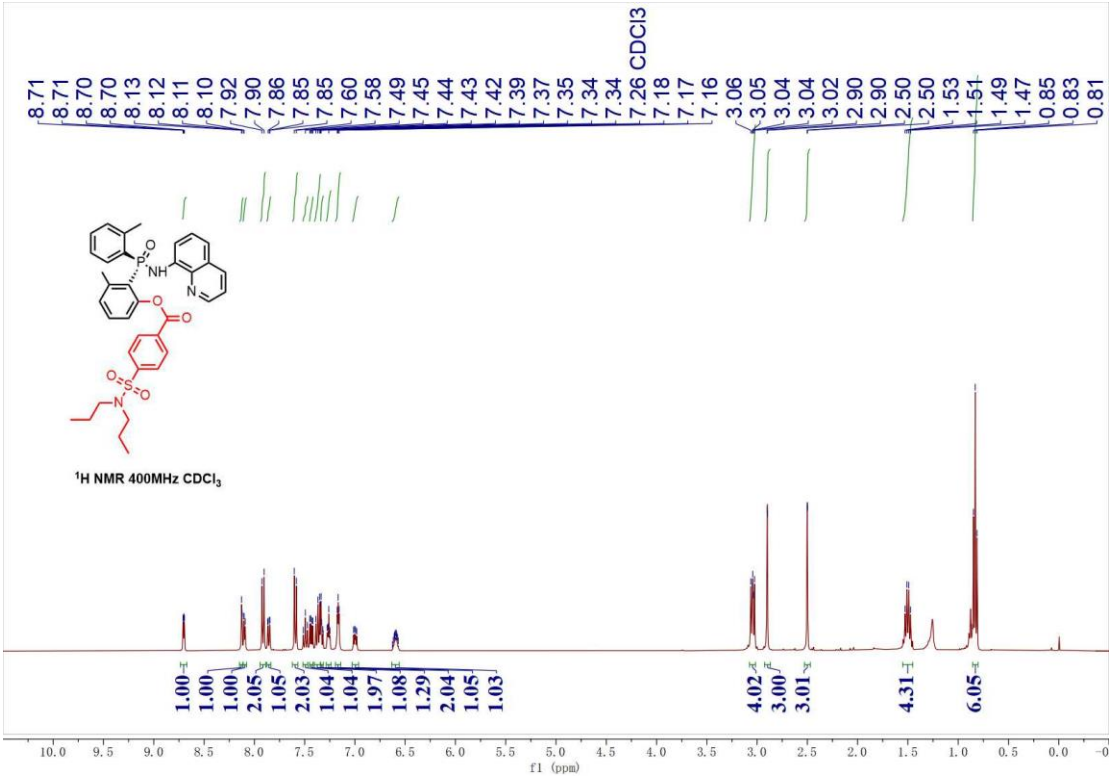



$^{13}$C NMR 150MHz $CDCl_3$

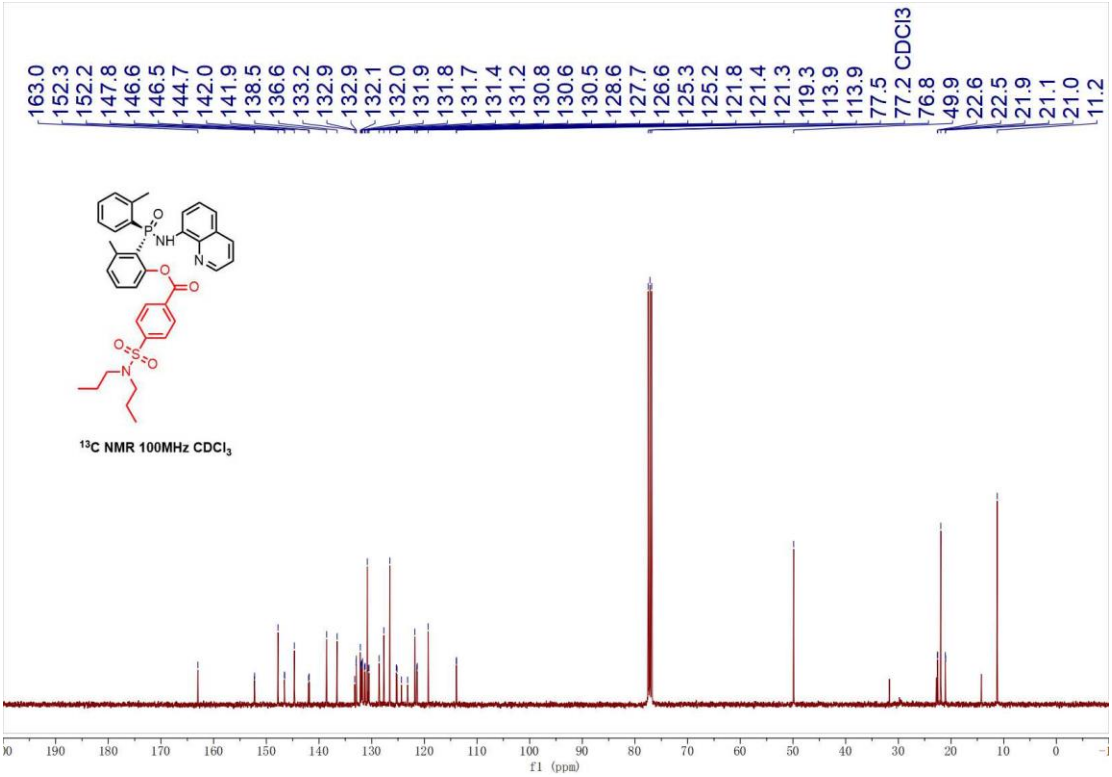
## $^{31}$P NMR of 3s



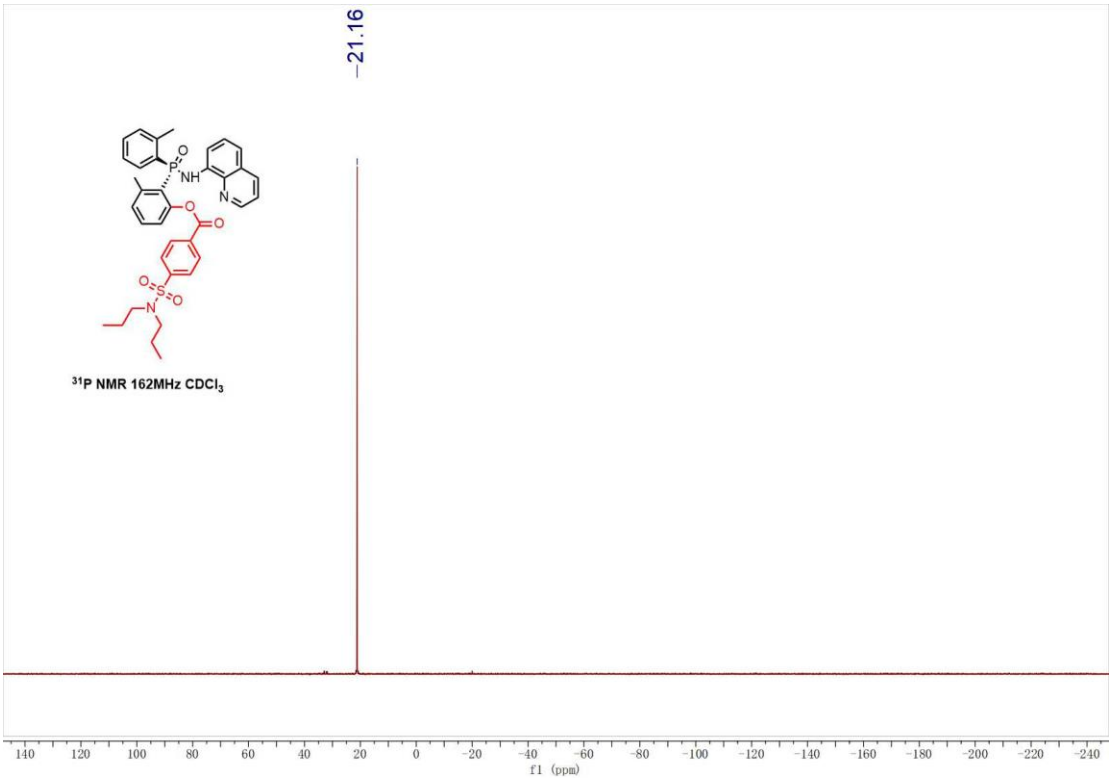

## $^{1}$H NMR of 3t



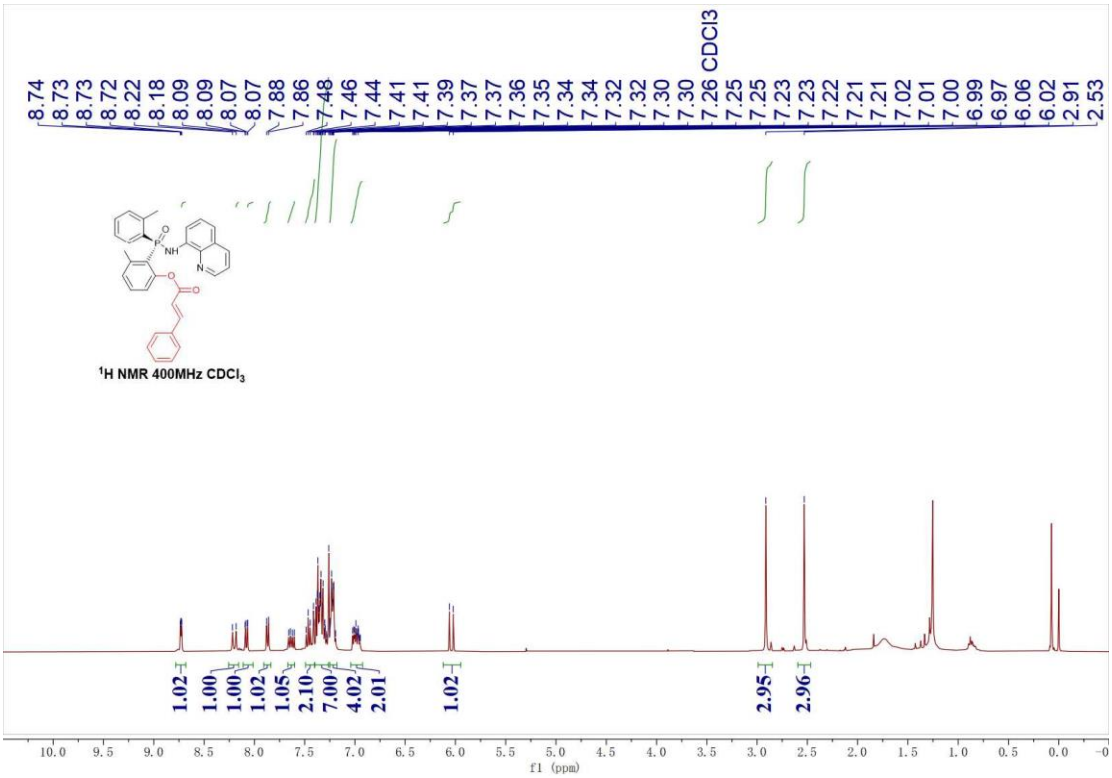
**$^{13}C\{^{1}H\}$ NMR of 3t**



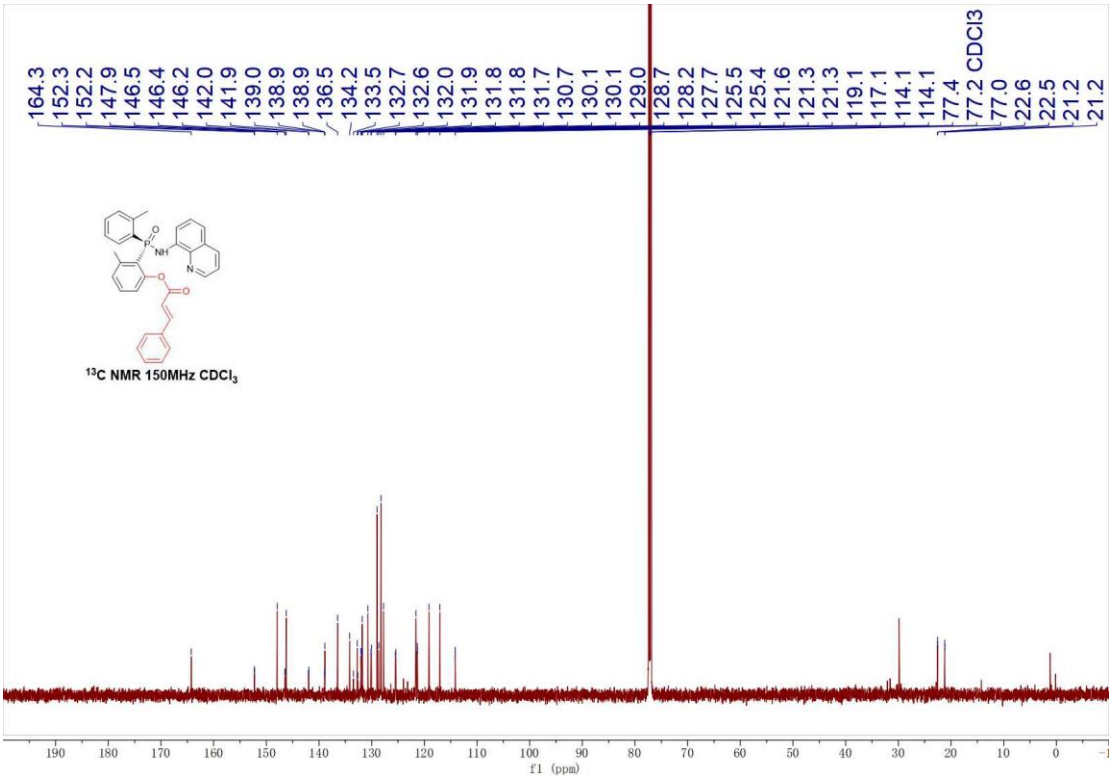

**$^{31}P$ NMR of 3t**



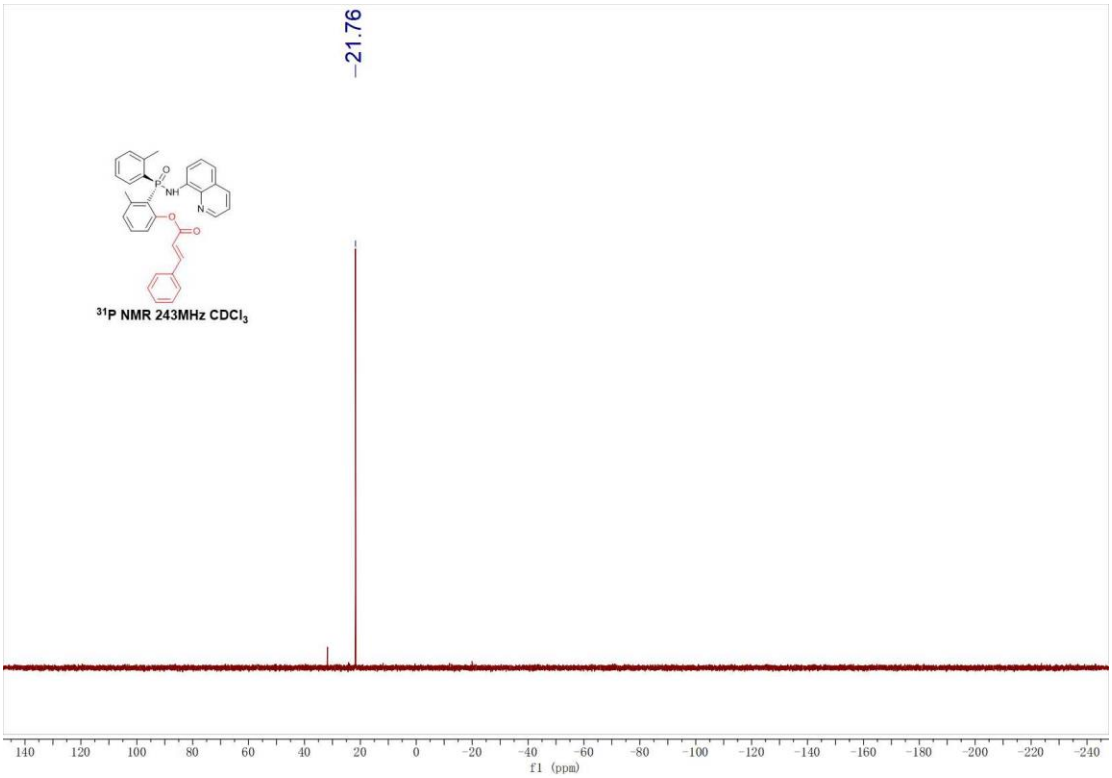

**$^{1}H$ NMR of 3u**



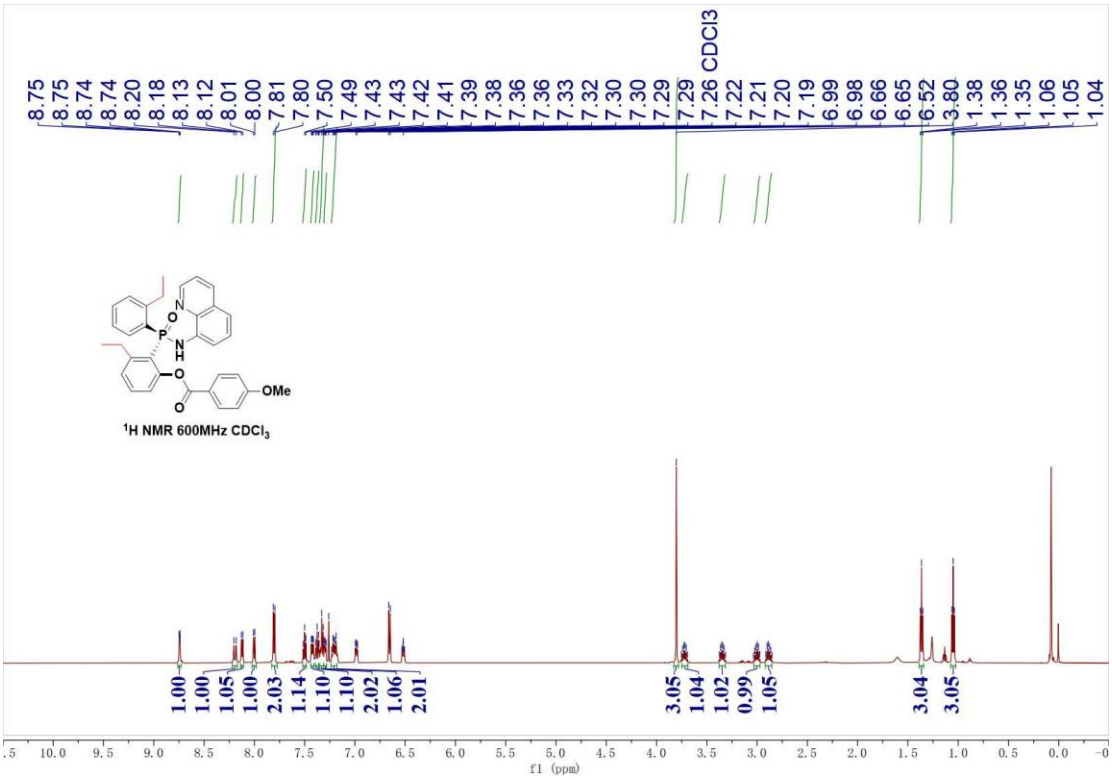

**$^{13}C\{^{1}H\}$ NMR of 3u**



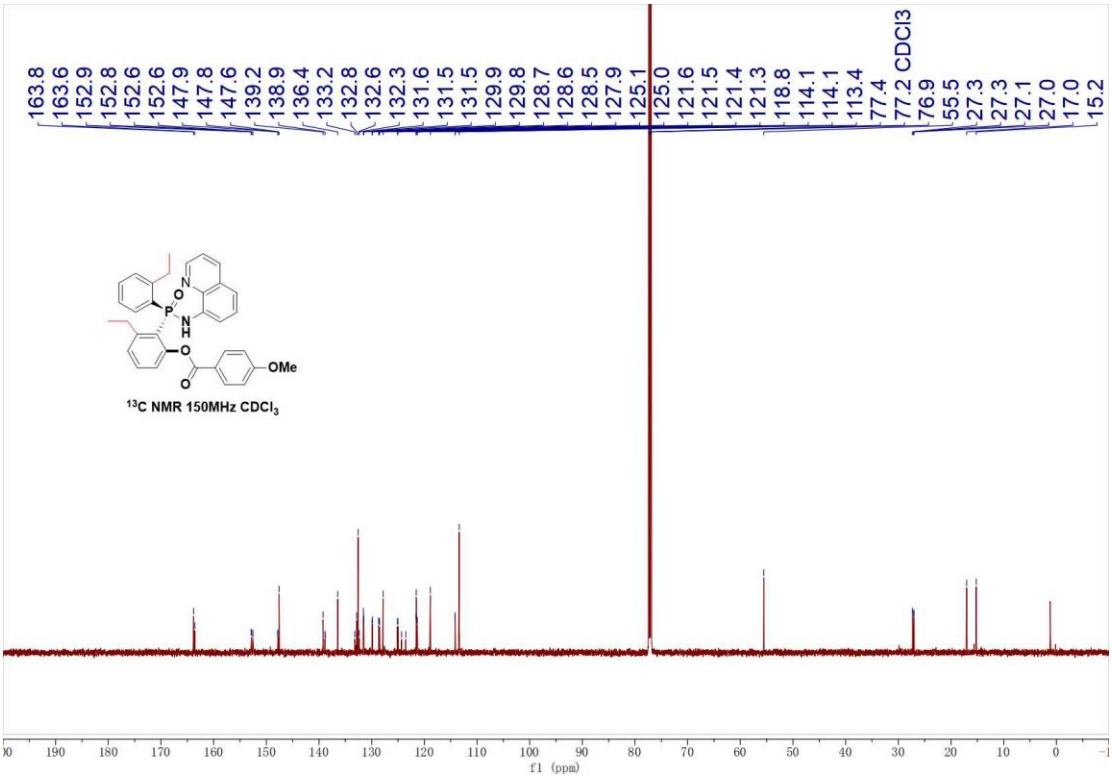

**$^{31}P$ NMR of 3u**



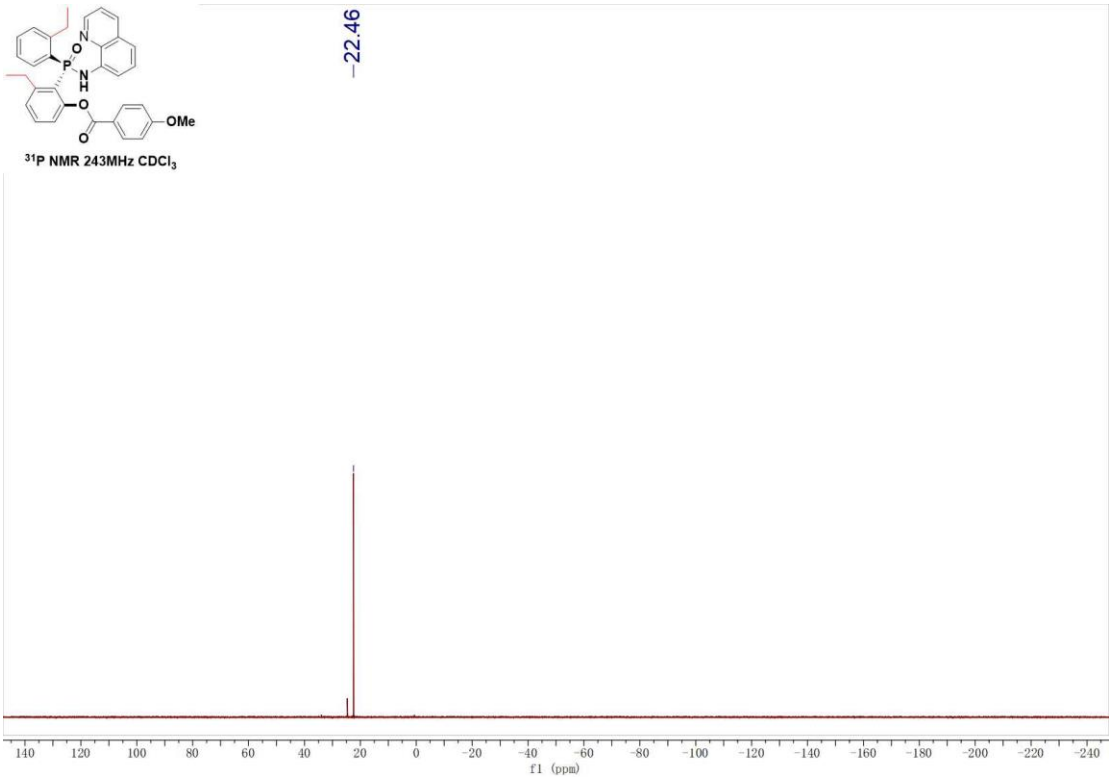

**$^{1}$H NMR of 3v**



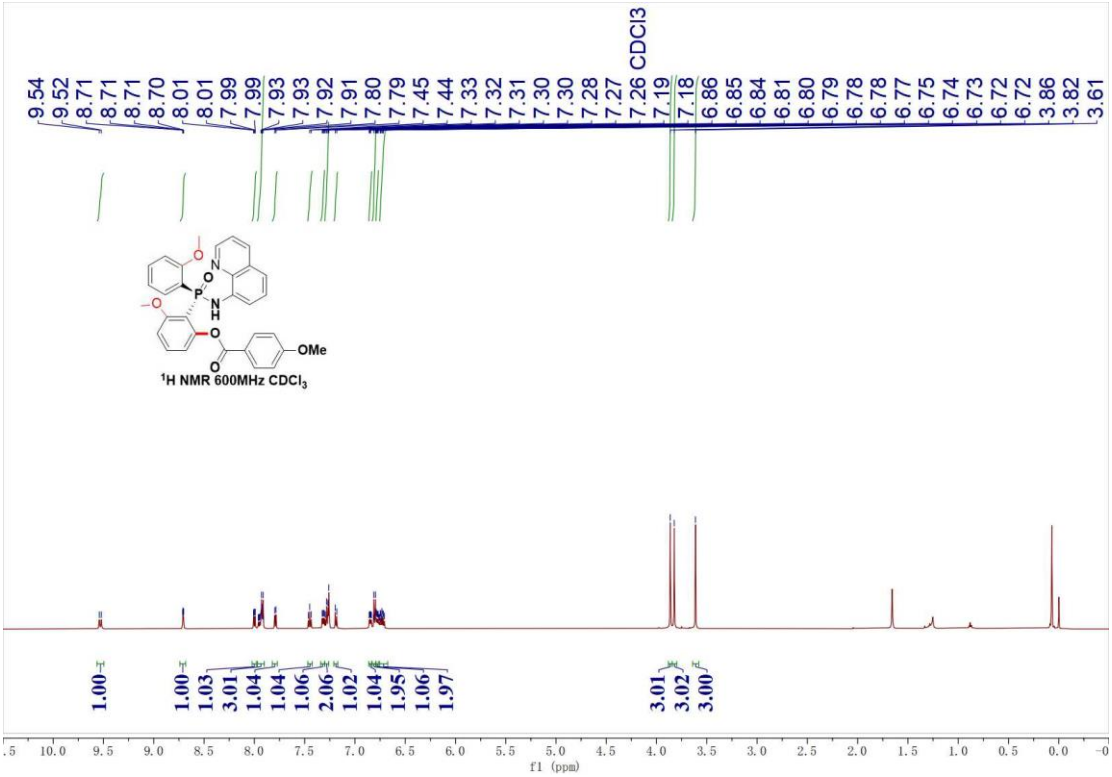

**$^{13}$C{$^{1}$H} NMR of 3v**


163.8
163.6
152.9
152.8
152.6
152.6
147.9
147.8
147.6
139.2
138.9
136.4
133.2
132.8
132.6
132.3
131.6
131.5
131.5
129.9
129.8
128.7
128.6
128.5
127.9
125.1
125.0
121.6
121.5
121.4
121.3
118.8
114.1
114.1
113.4
77.4
77.2 CDCl3
76.9
55.5
27.3
27.3
27.1
27.0
17.0
15.2
OMe
13C NMR 150MHz CDCl3
f1 (ppm)

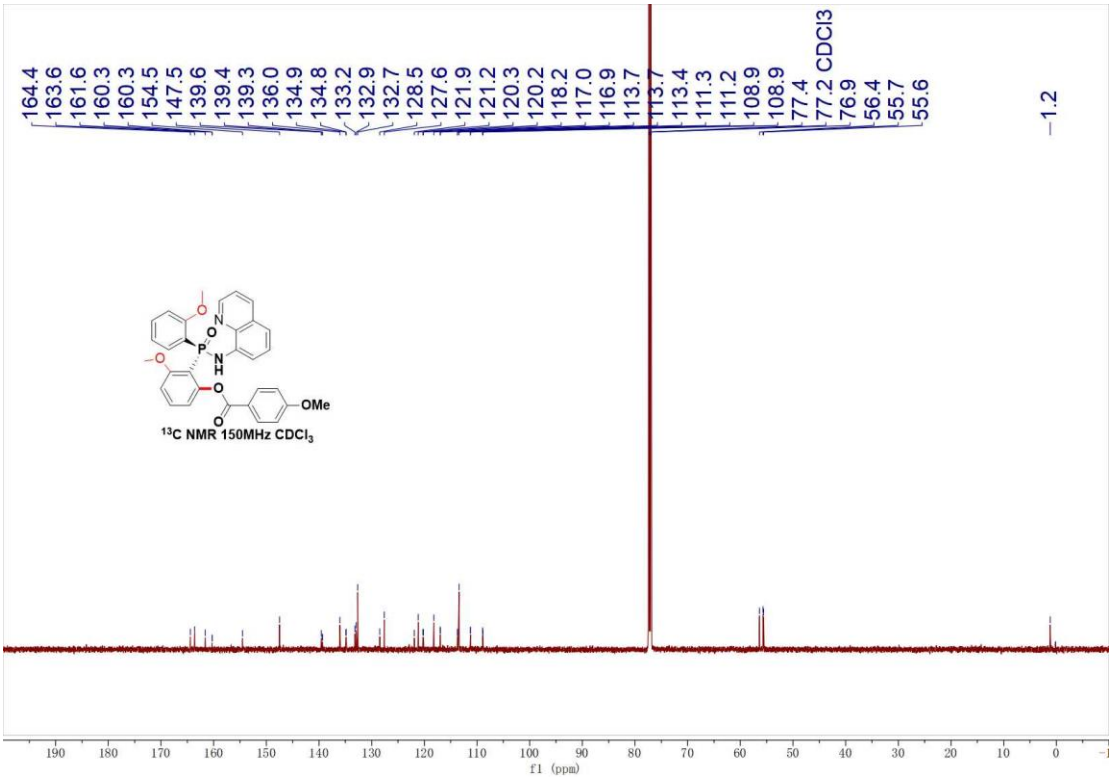
**$^{31}$P NMR of 3v**


-22.46
OMe
31P NMR 243MHz CDCl3
f1 (ppm)

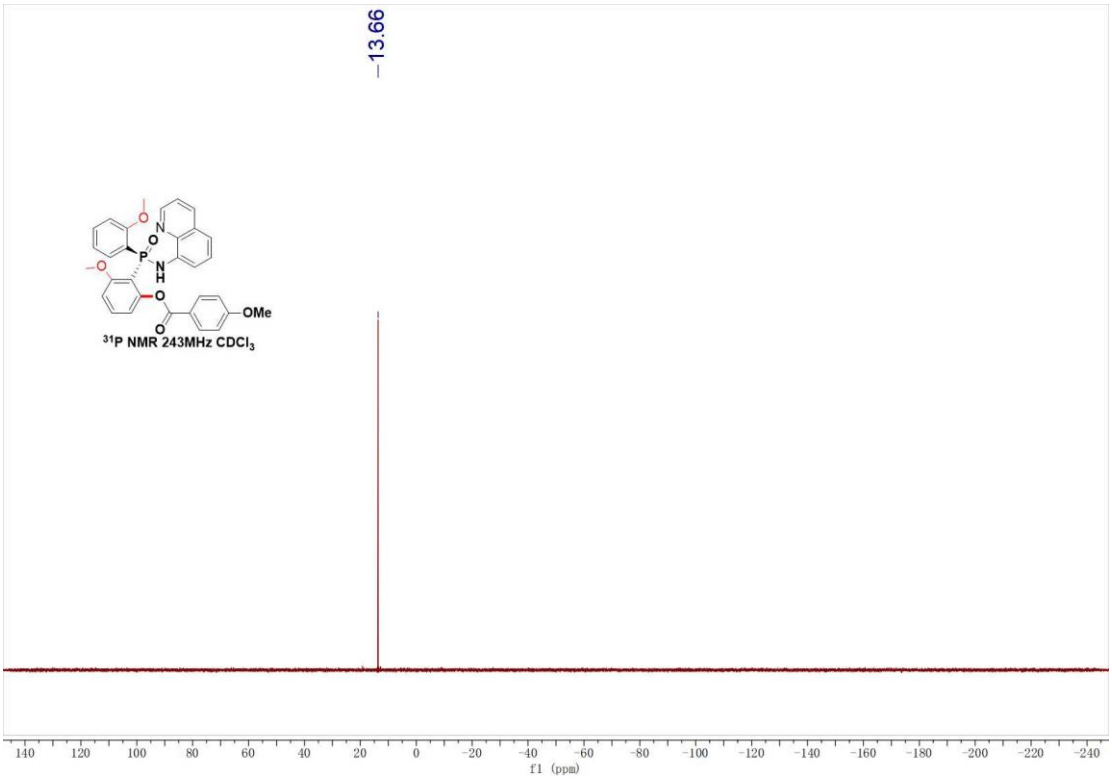
**$^{1}$H NMR of 3w**



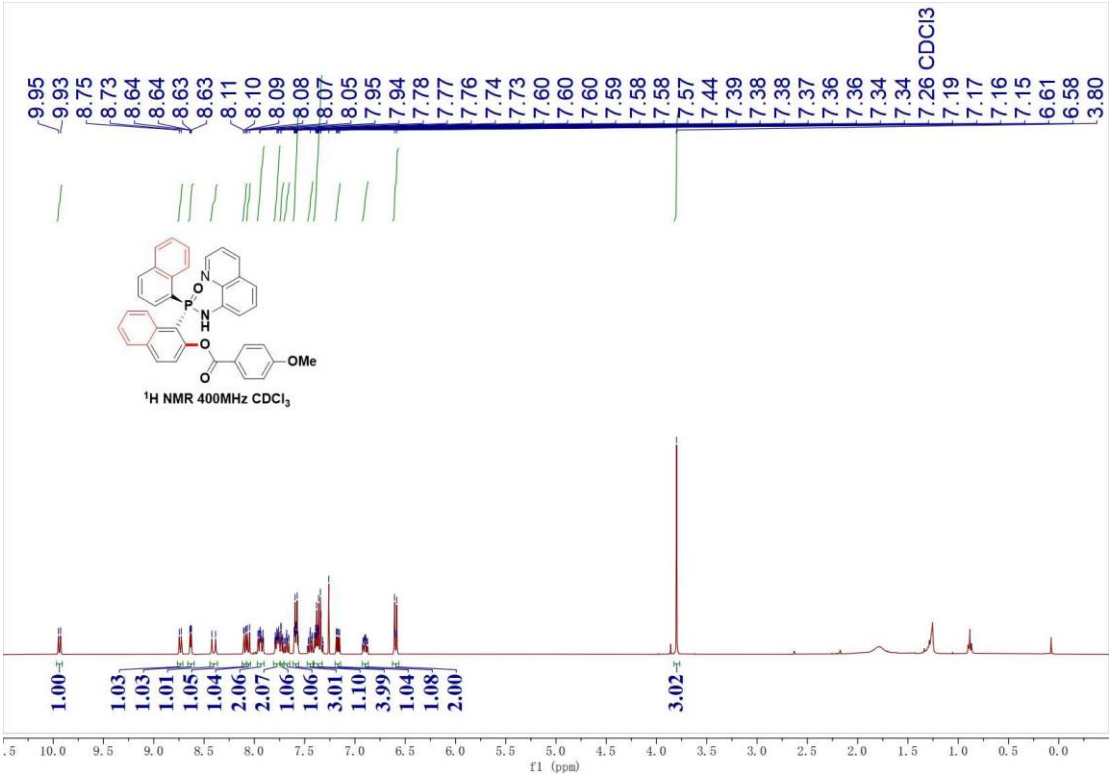

**$^{13}$C{$^{1}$H} NMR of 3w**



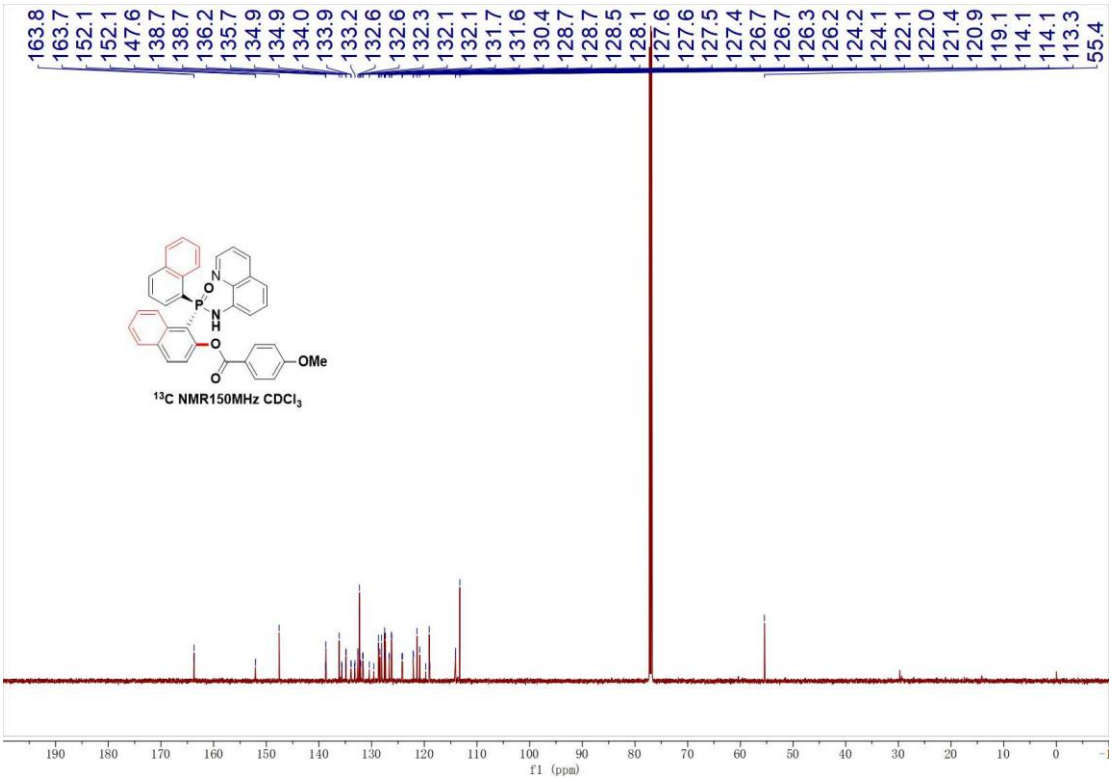

**$^{31}$P NMR of 3w**


-13.66
OMe
31P NMR 243MHz CDCl3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

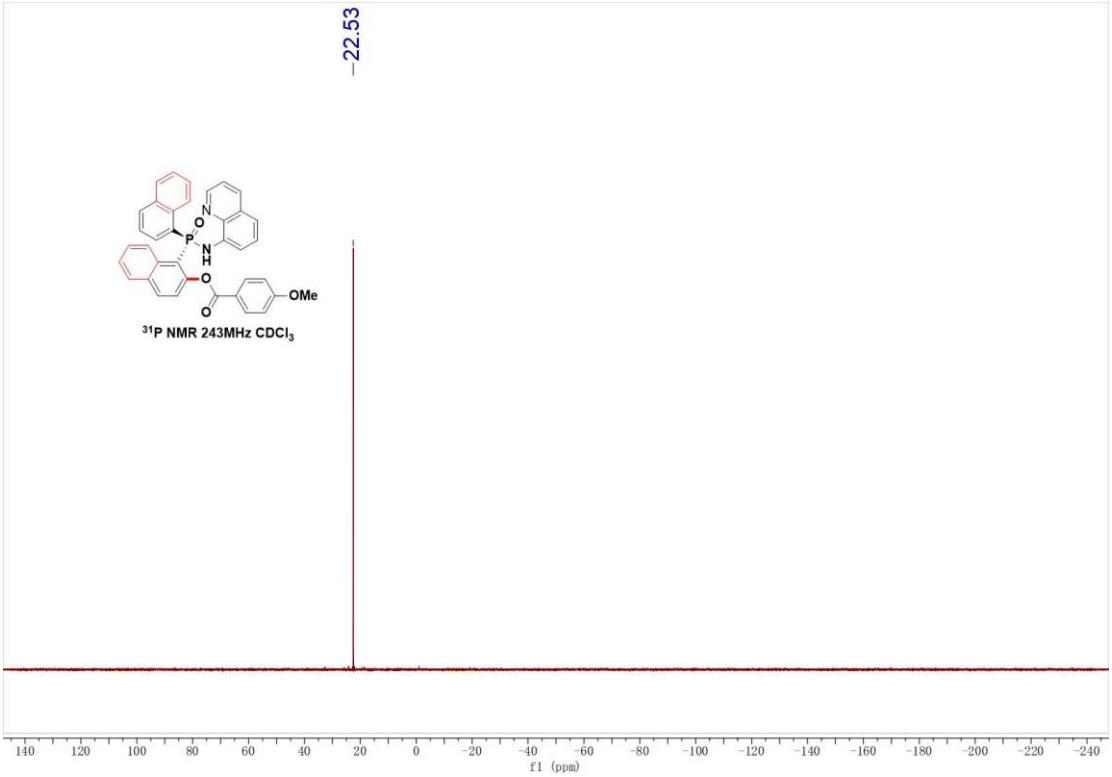
## $^{1}$H NMR of 3x



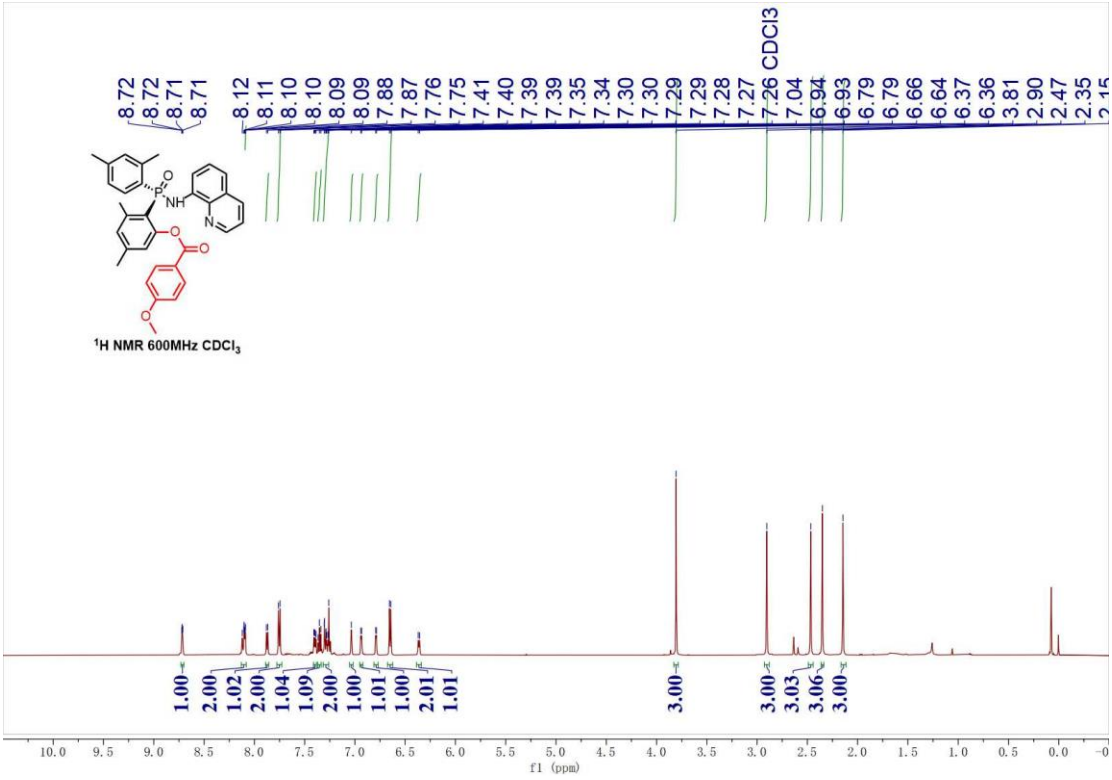

## $^{13}$C{$^{1}$H} NMR of 3x



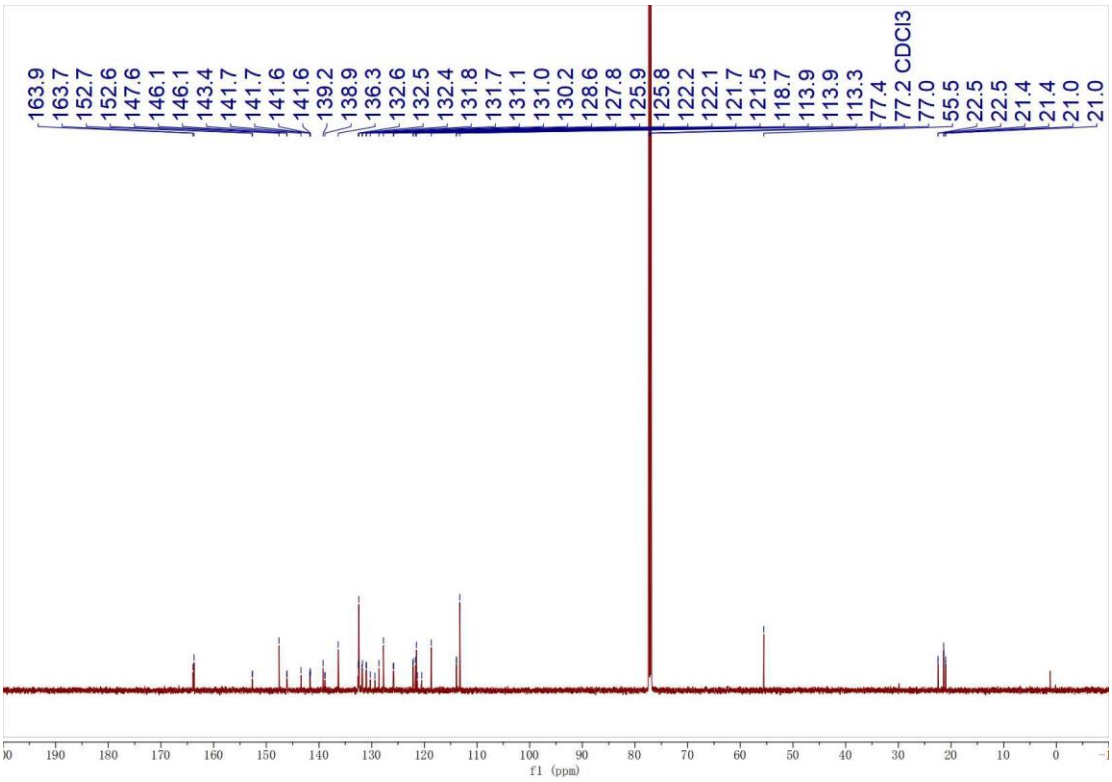
## $^{31}$P NMR of 3x



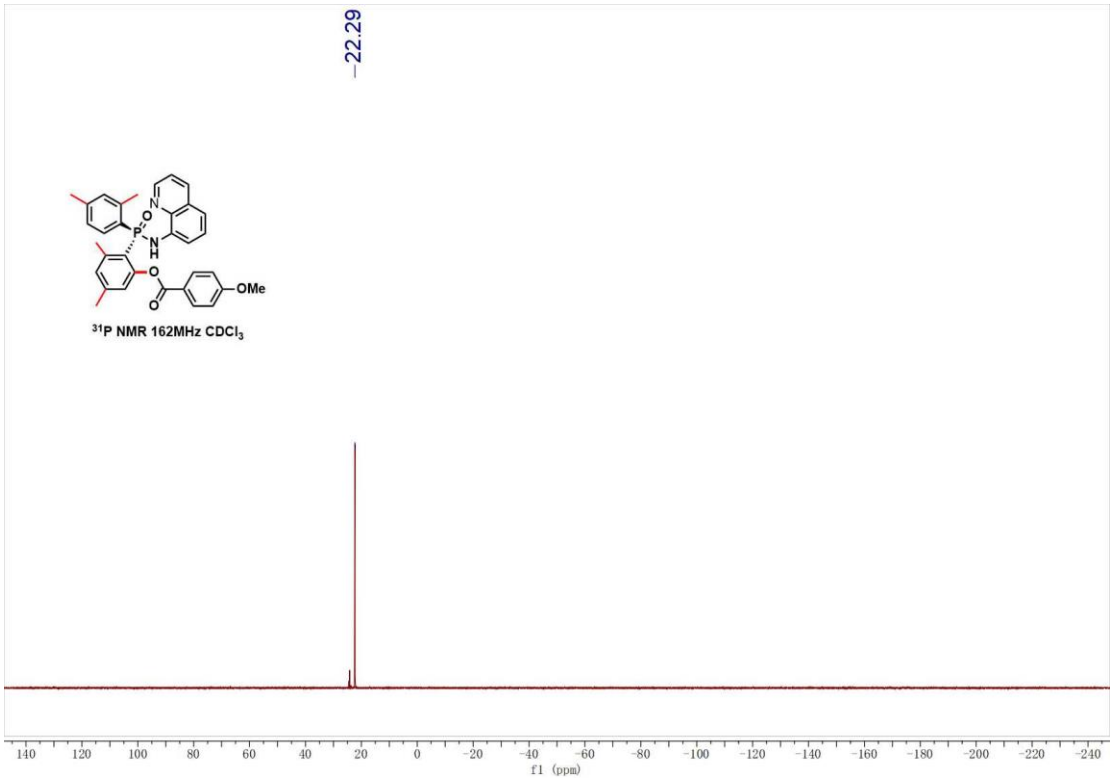

## $^{1}$H NMR of 3y



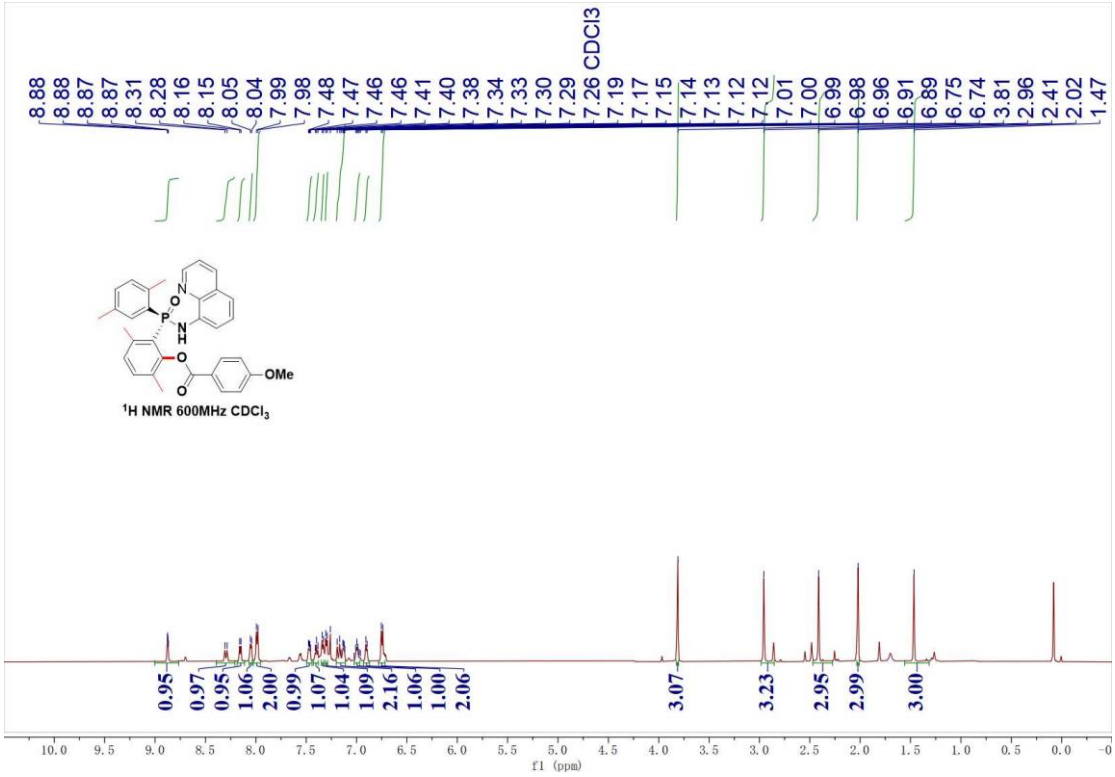
## $^{13}C\{^{1}H\}$ NMR of 3y



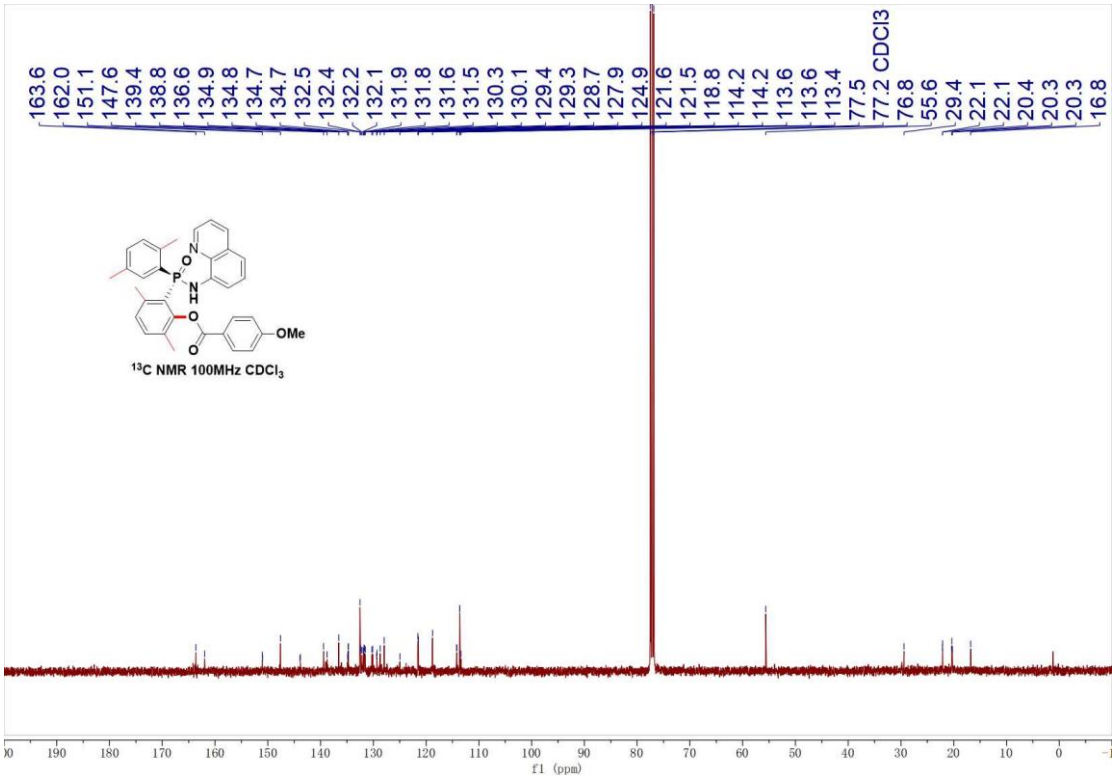

## $^{31}P$ NMR of 3y



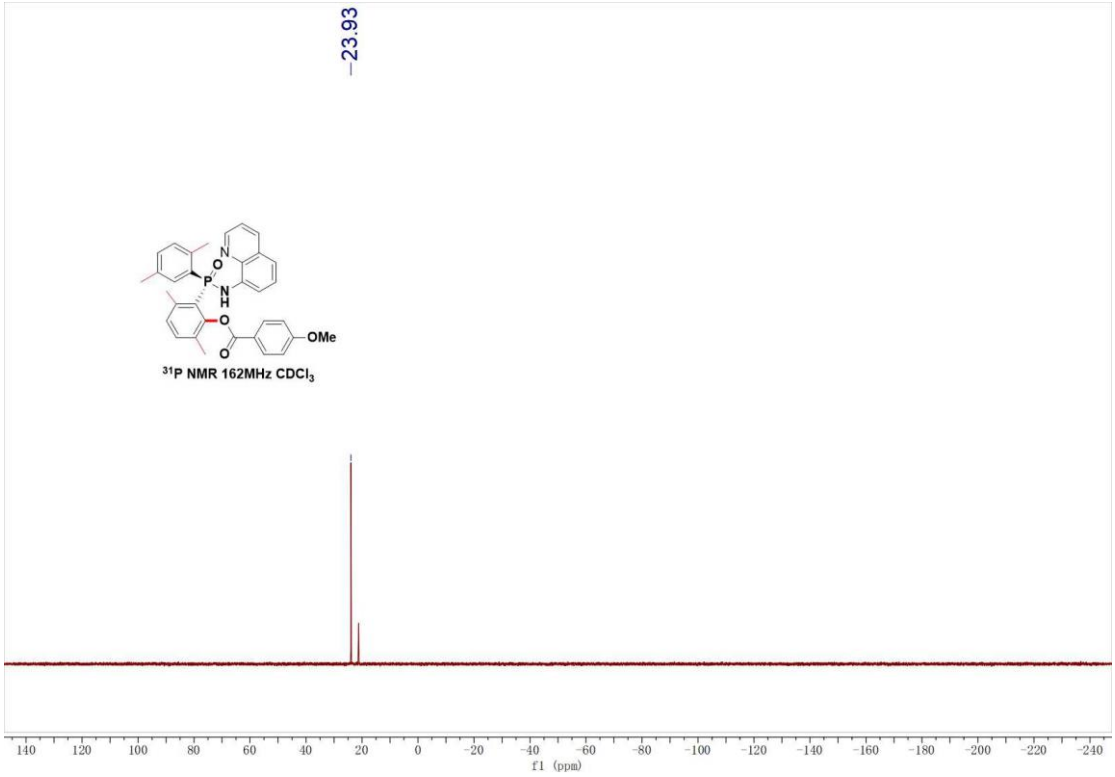
## $^{1}$H NMR of 3z



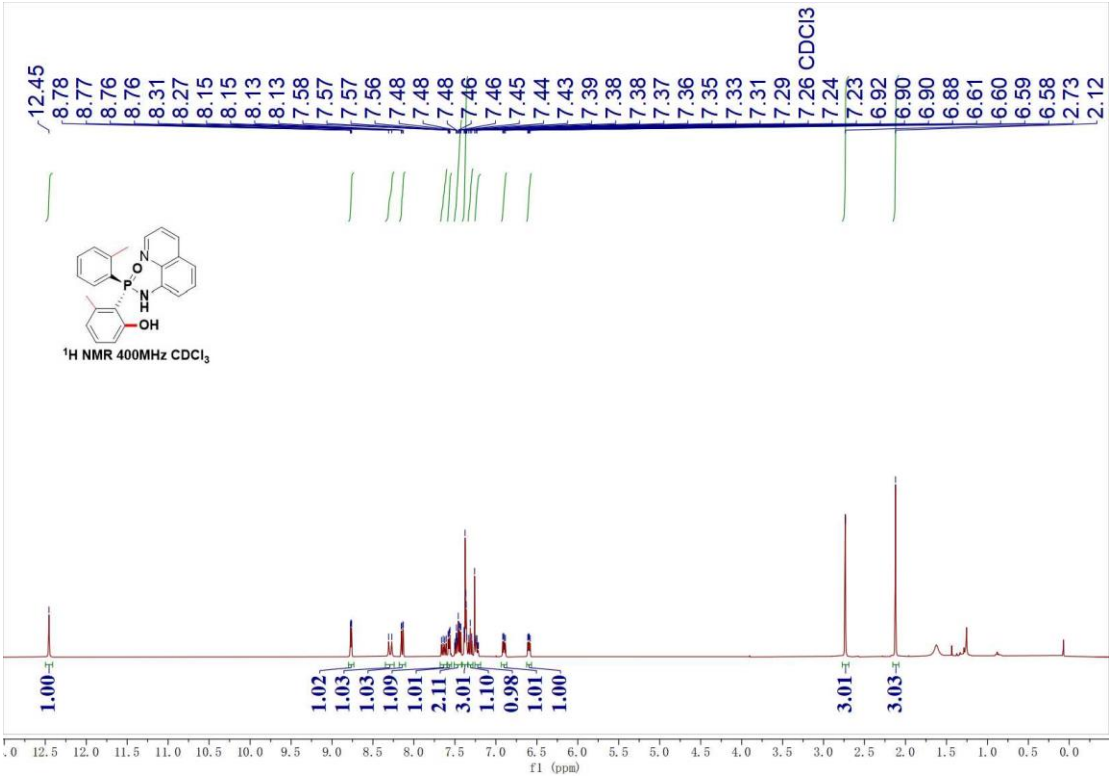

## $^{13}$C{$^{1}$H} NMR of 3z



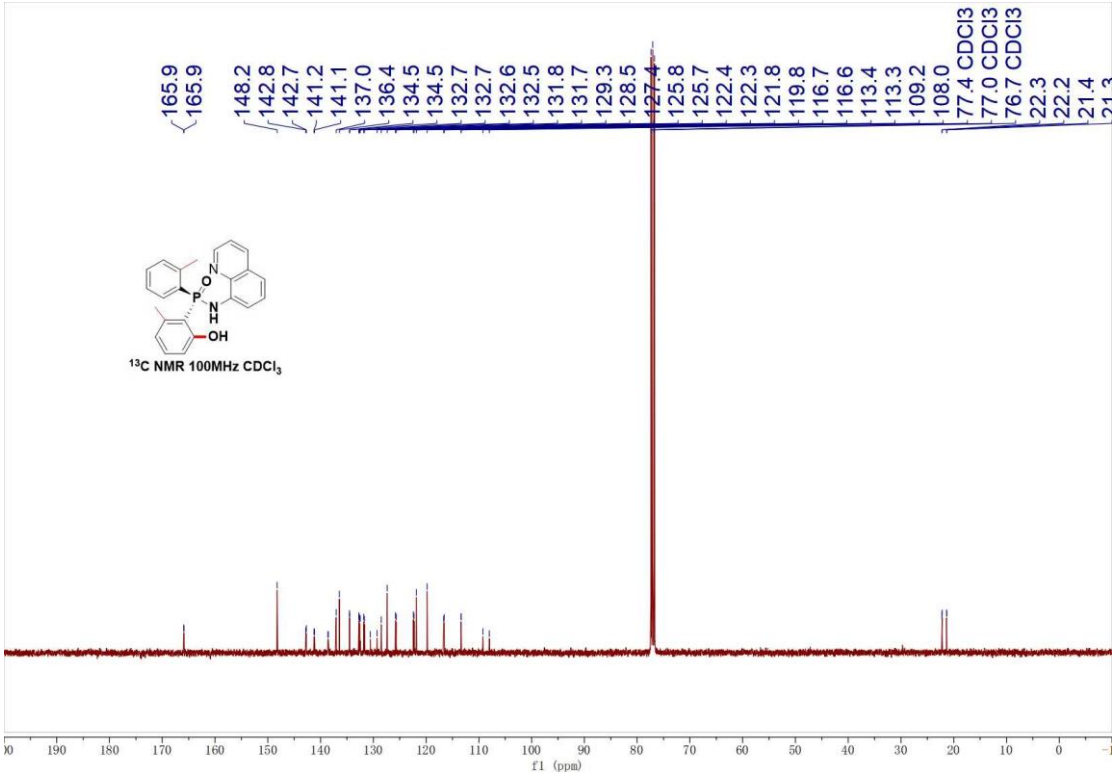
## $^{31}$P NMR of 3z



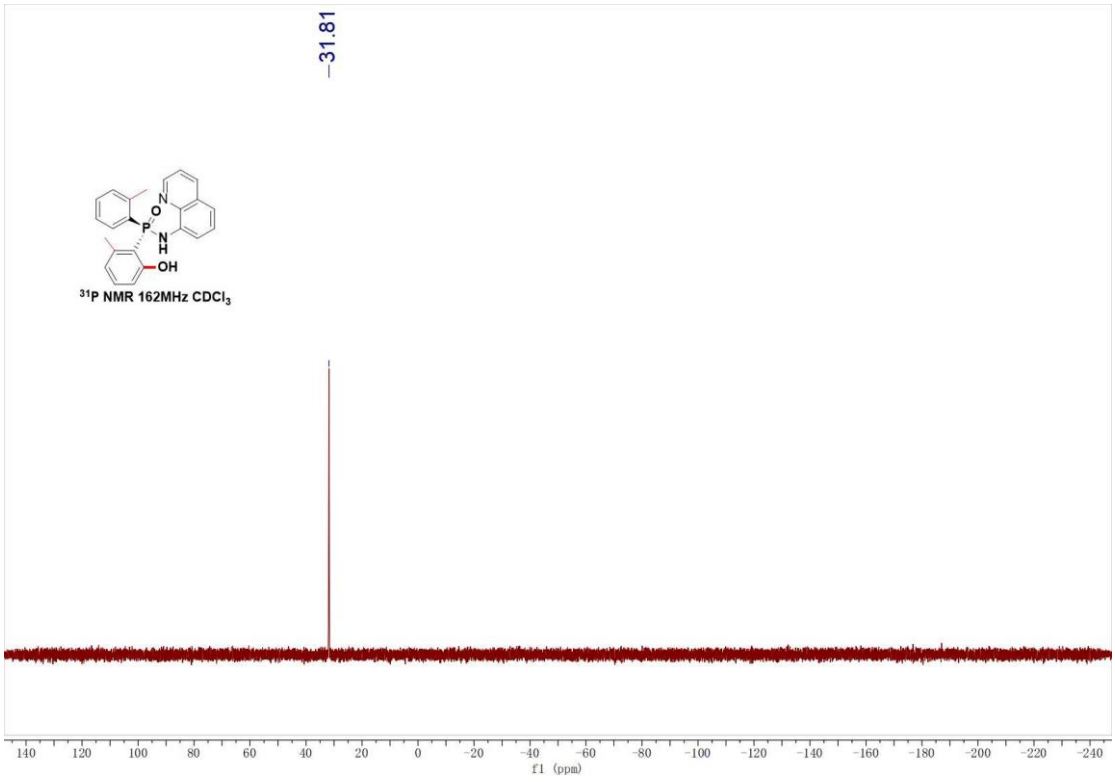

## $^{1}$H NMR of 4a



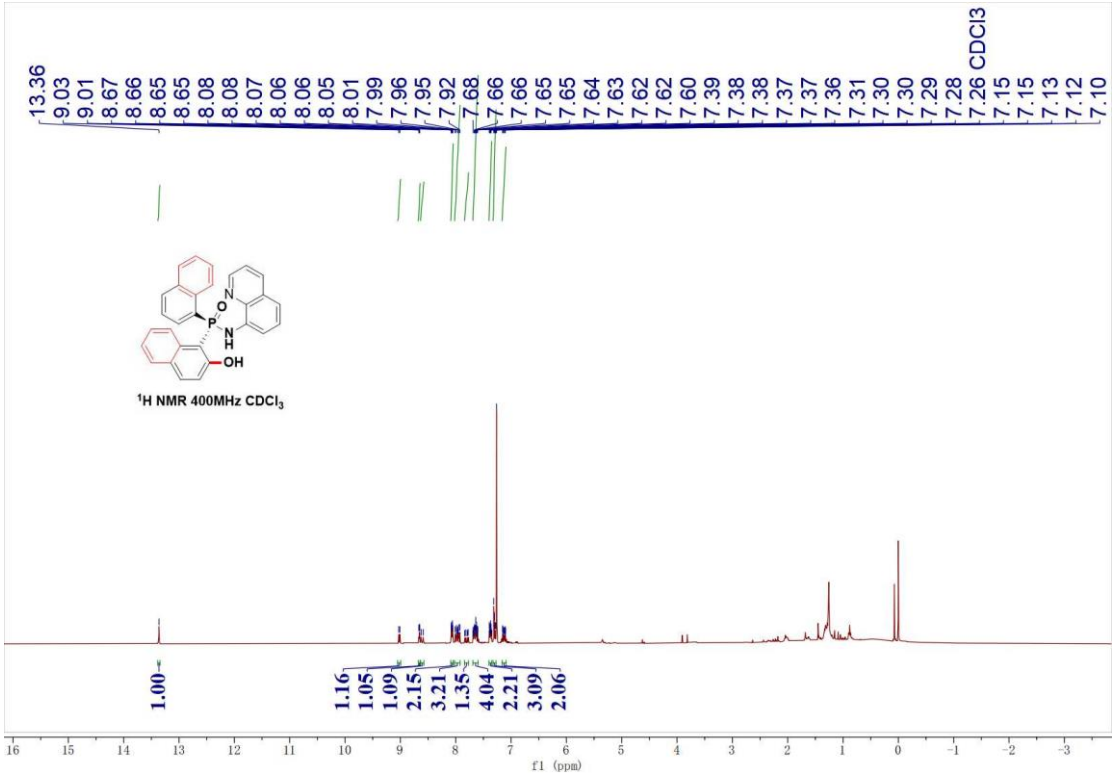
**$^{13}C\{^{1}H\}$ NMR of 4a**



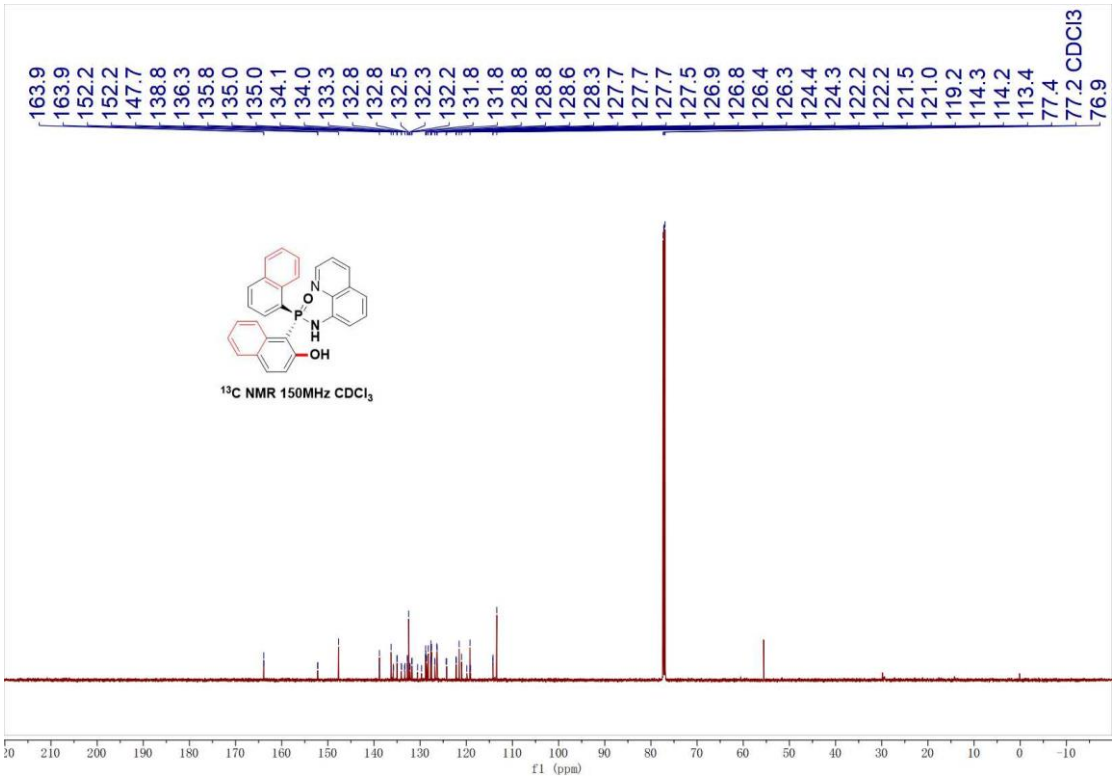

**$^{31}P$ NMR of 4a**



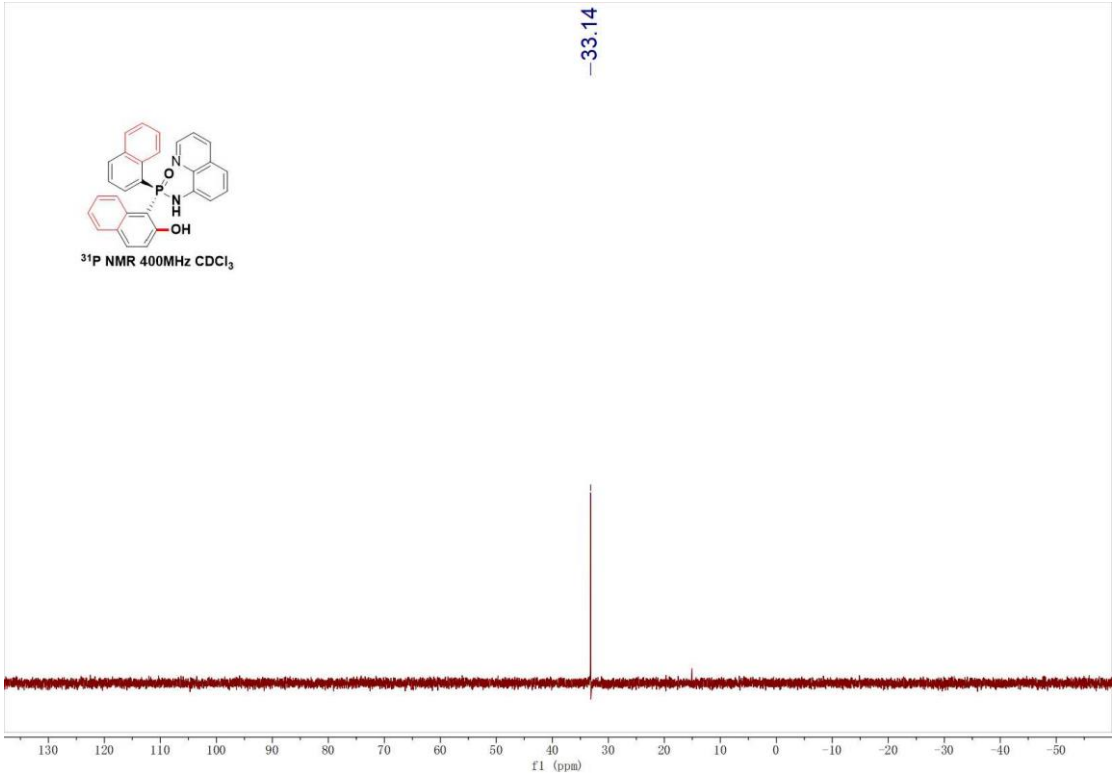
## $^{1}$H NMR of 4w



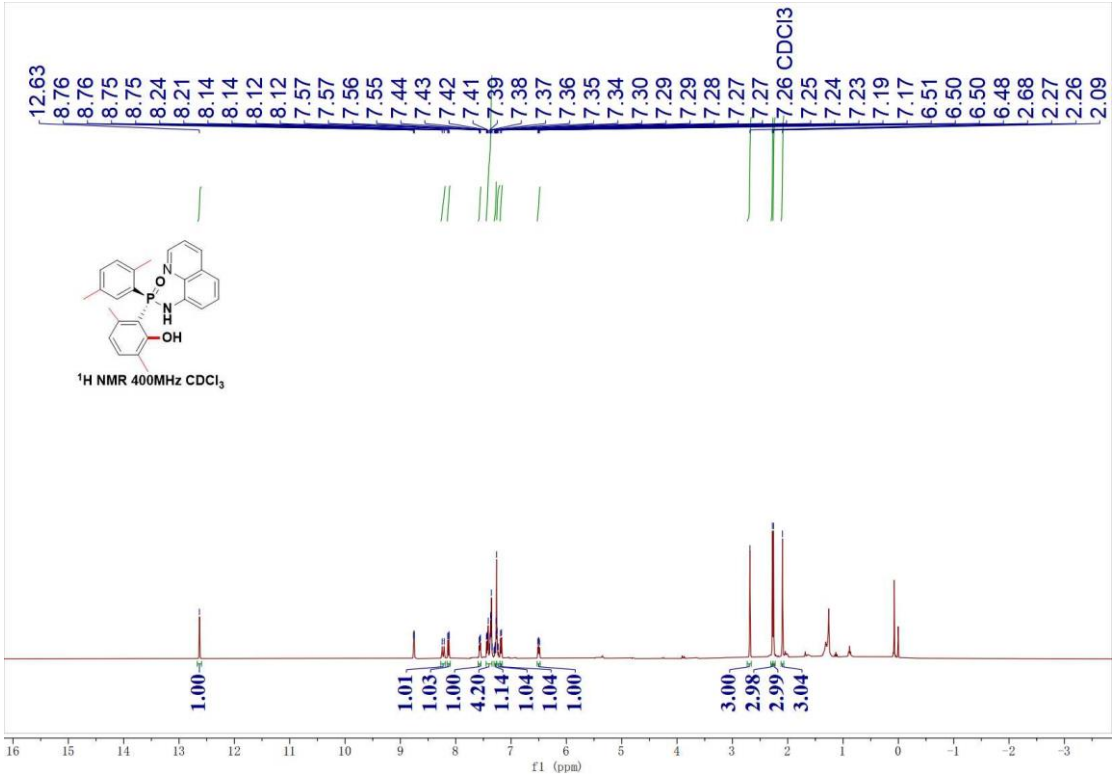

## $^{13}$C{$^{1}$H} NMR of 4w



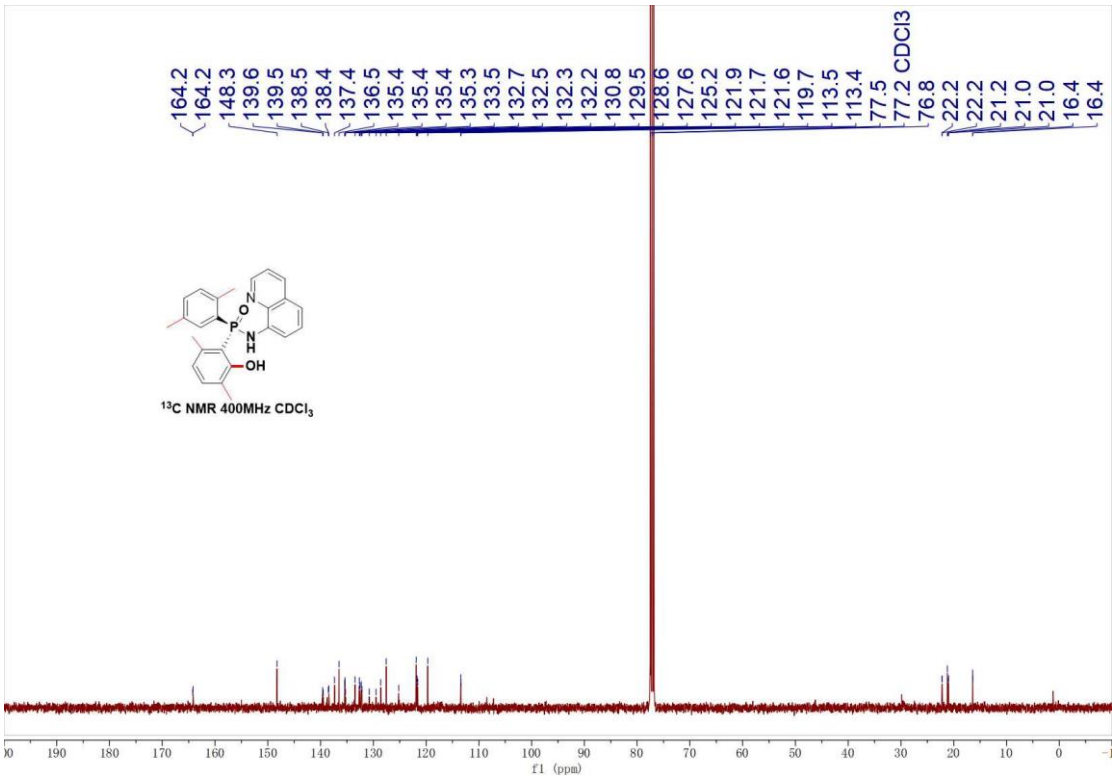
## $^{31}$P NMR of 4w



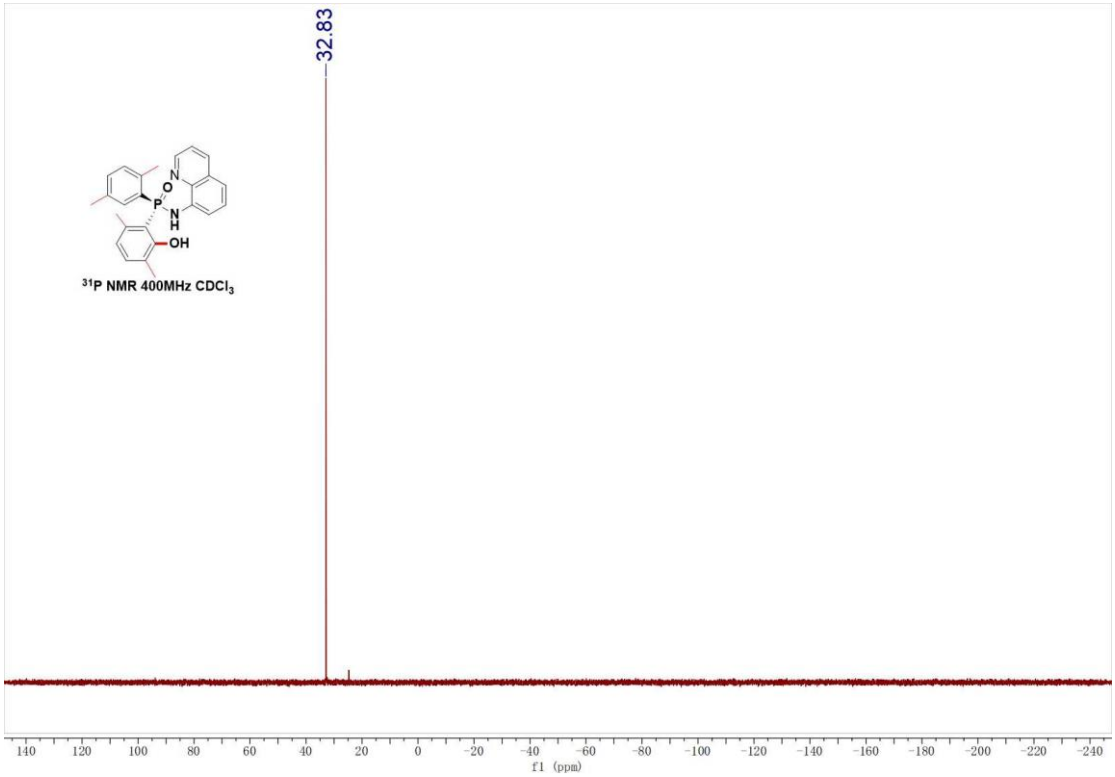

## $^{1}$H NMR of 4y



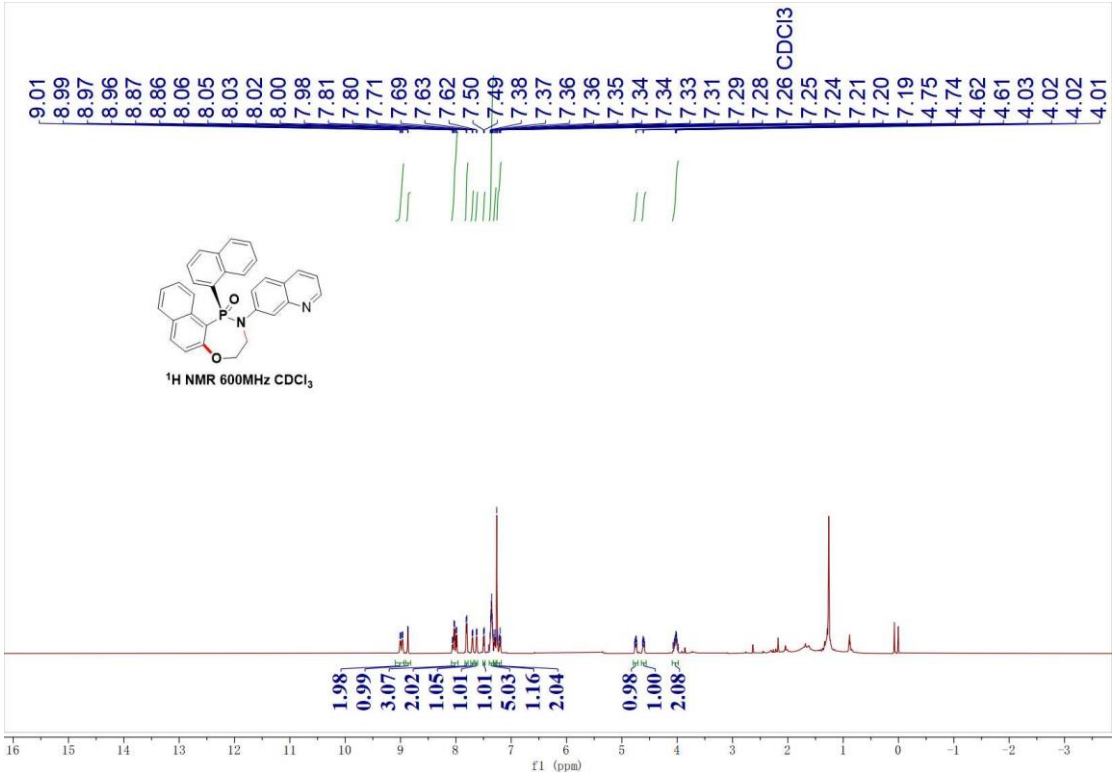
## $^{13}C\{^{1}H\}$ NMR of 4y



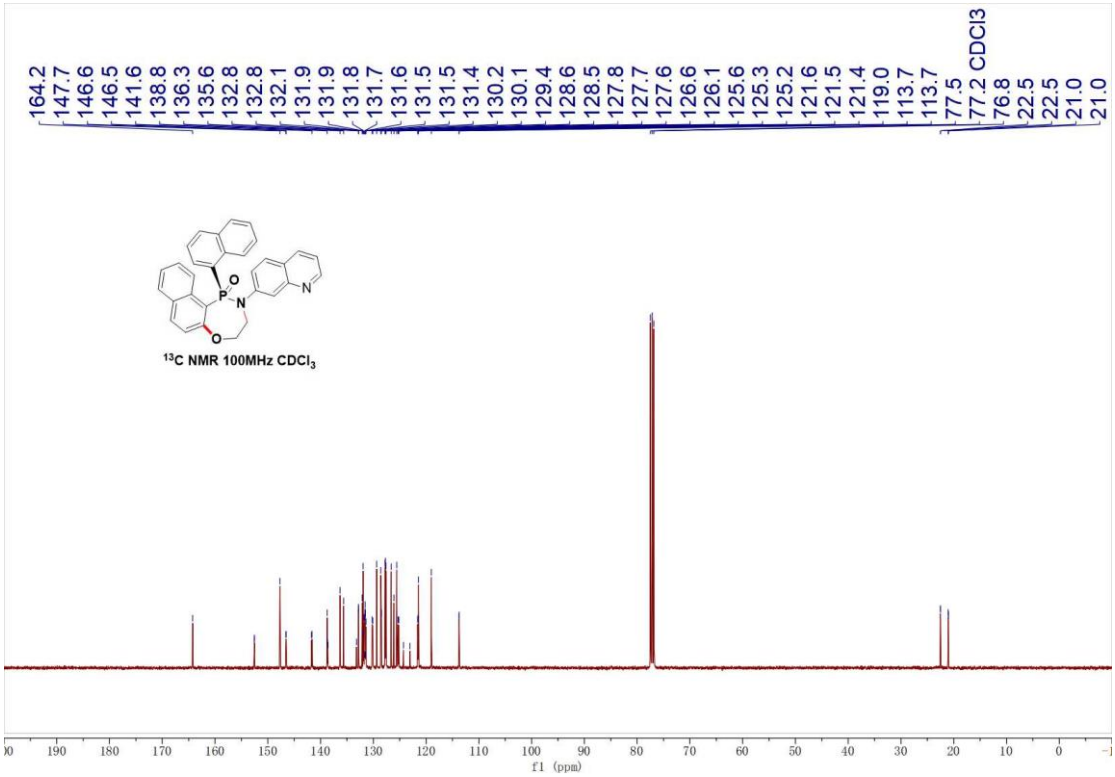

## $^{31}P$ NMR of 4y



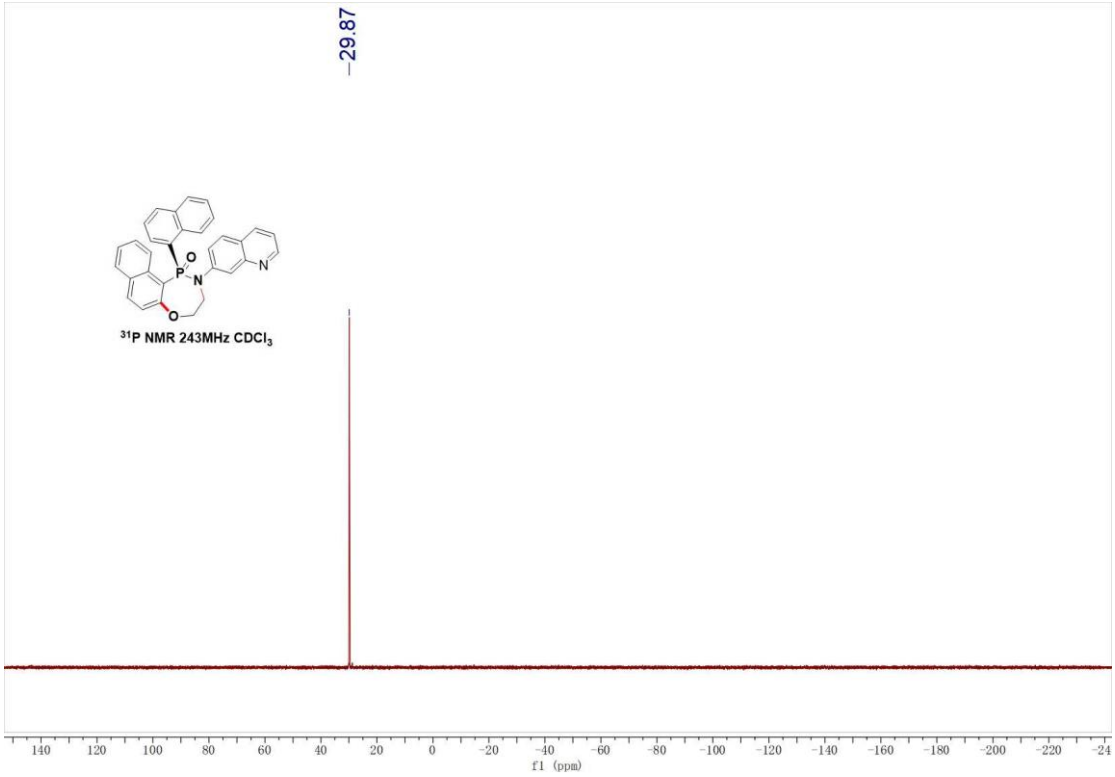
## $^{1}$H NMR of 5w




## $^{13}$C{$^{1}$H} NMR of 5w



## $^{31}$P NMR of 5w


29.87
31P NMR 243MHz CDCl3
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-24
f1 (ppm)