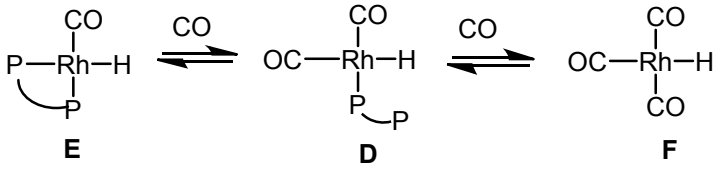
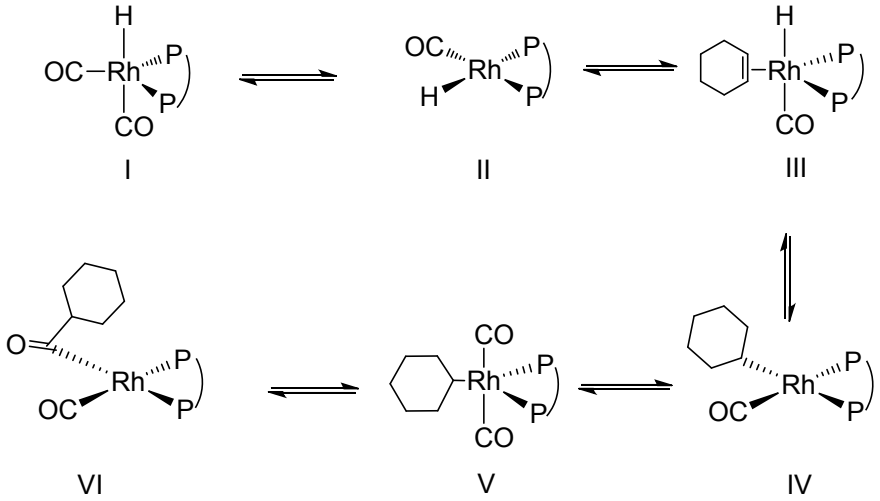
Electronic Supplementary Material (ESI) for RSC Advances.


# Support information

## Content




**Scheme S1**. Ligand dissociation in Rh-catalyzed hydroformylation




**Scheme S2**. The geometric evolution of the ligand-Rh intermediates

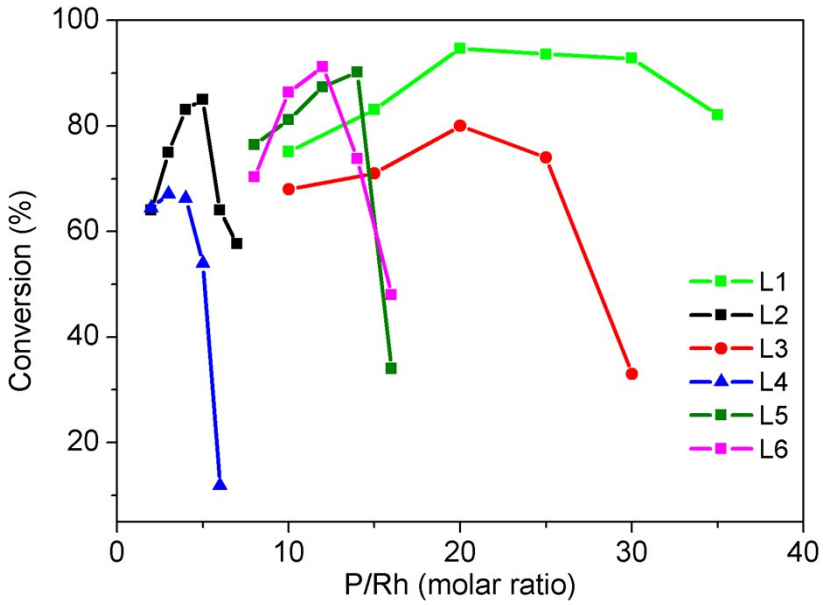
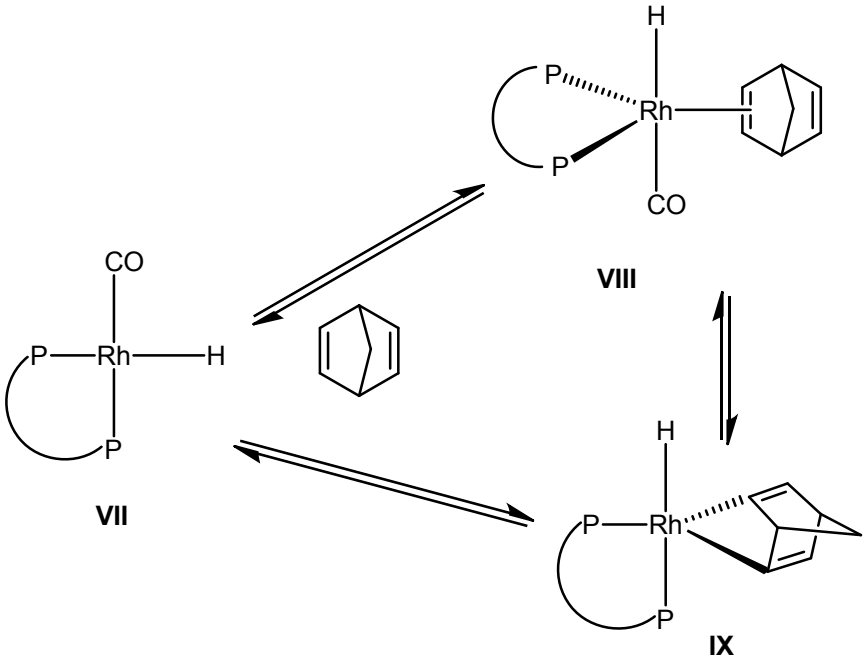
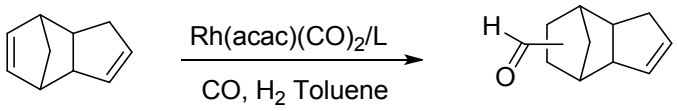



**Figure S1.**The impact of different P/Rh molar ratios on the conversion of cyclohexene (**L1-L6**)




**Scheme S3.** Proposed mechanism of NBD hydroformylation catalyzed by Rh-Ligand.[1]

**Table S1** Hydroformylation of DCPD using ligands L1-L6




DCPD TCDMA

| Entry | L | P/Rh | P (Mp) | Temp. (°C) | Time (h) | Conv.%[a] | TCDMA %[b] |
|---|---|---|---|---|---|---|---|
| 1 | **L1** | 20 | 1 | 80 | 2 | 99.9 | 99.0 |
| 2 | **L2** | 5 | 1 | 100 | 2 | / | / |
| 3 | **L3** | 20 | 1 | 80 | 2 | 99.9 | 96.2 |
| 4 | **L4** | 3 | 1 | 80 | 4 | 77.6 | 99.2 |
| 5 | **L5** | 14 | 1 | 100 | 2 | / | / |
| 6 | **L6** | 12 | 1 | 80 | 2 | 99.9 | 99.1 |

Reaction conditions: S/C=1000, [Rh] = $2.12\times10^{-3}$ mol/L, Toluene: 3 mL,

[a] The conversion of DCPD based on GC.

[b] Selectivity for TCDMA of in the products of DCPD hydroformylation.

## Experimental

### General Information

Solvents were dried with standard methods and freshly distilled prior to use if needed. Unless otherwise noted, all synthetic processes were performed in argon atmosphere and all the starting materials were commercially available and used without further purification. $Rh(acac)(CO)_2$ was prepared according to the literatures.[2] The $^{1}H$, $^{13}C$, and $^{31}P$ NMR spectra were recorded on a Bruker ARX400 NMR instrument. Mass spectra were recorded with an AMD 40223 (Interambulacra) spectrometer.

**procedure of hydroformylation experiments**

All the hydroformylation reactions were carried out in a stainless steel autoclave of 60 ml with a magnetic stirrer. A typical procedure was conducted as follows: toluene solution of $Rh(acac)(CO)_2$, the ligand and cycloolefins were added to the autoclave, which was immediately evacuated and purged with syngas for three times. The autoclave was pressurized by syngas to the desired pressure and stirred under the designed conditions. After the reaction was completed, the autoclave was cooled quickly to room temperature in a water bath, and then vented slowly. The reaction mixture was immediately analyzed by GC.

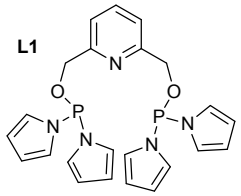
### Synthesis of pyridine-2,6-dimethanol (C)

To a solution of pyridine-2, 6-dicarboxylic acid (28 g, 0.168mol) in ethanol (300 mL) was added slowly acetyl-chloride (15 mL, 0.212 mol).The mixture was stirred at room temperature for 24 h. After that the ethanol was evaporated under reduced pressure, and then the residue was dissolved in water (30 mL) and neutralized by solid $Na_2CO_3$. The aqueous solution was extracted with ether three times, dried over $MgSO_4$, and evaporated to dryness to give diethyl pyridine-2,6-dicarboxylate (**B**) (30 g, 80%) as a colorless solid. m. p: 42−43 °C (literature: 42−43 °C)[3].

To a stirring solution of the diethyl ester (17.84 g, 0.08mol) in 400 mL anhydrous ethanol, $NaBH_4$ (3.55g, 0.09mol) was added in portions at room temperature. A drying tube was placed on the apparatus. Finely powdered $CaCl_2$ (10.67g, 0.096mol) was added in small portions, and the evolution of $H_2$ was allowed to cease before each further addition. The reaction mixture was then stirred at room temperature for 4 h. When the reaction was completed, the solvent was removed and saturated potassium carbonate solution (100 mL) was added to the residue. The aqueous mixture was stirred for a period of time. After removal of the solvent, the residue was dried, and purified by flash chromatography to give white solid of pyridine-2,6-dimethanol (**C**) (10 g, yield: 89.2%). m.p.114–116 °C (literature: 114-116 °C)[4] $^{1}H$ NMR (400 MHz, DMSO-$d_6$) δ 7.78 (t, $J$ = 7.7 Hz, 1H), 7.32 (d, $J$ = 7.6 Hz, 2H), 5.37 (td, $J$ = 5.9, 2.5 Hz, 2H), 4.53 (d, $J$ = 5.6 Hz, 4H).

**Synthesis of L1**

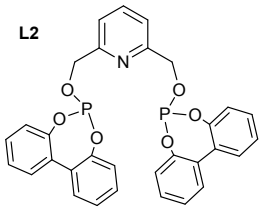
An excess of $Et_3N$ (10 mL) was added to a Schlenk apparatus containing **pyridine-2,6-dimethanol (C)** (0.8g, 5.76mmol) and DMAP (0.14g, 1.15mmol)**,** in dry THF (20 mL). After the solution was stirred at -78 $^oC$ for 30 min. And then a solution of chlorodipyrrolylphosphine (2.27mL, 11.51mmol),[5] in dry THF (10 mL) was slowly added within 30 min. The mixture was warmed to room temperature and then stirred for 4 h. The triethylamine hydrochloride salt were filtered under nitrogen atmosphere, and the filtrate was evaporated under reduced pressure to yield yellow pale residues. And the resulting thick oil was extracted three times with 25 mL of pentane. Evaporation of the pentane solutions to dryness generated **L1** as a colorless oil. Yield: 52%.




$^1H$ NMR (400 MHz, DMSO-$d_6$) δ 7.81 (t, $J$ = 7.8 Hz, 1H), 7.34 (d, $J$ = 7.8 Hz, 2H), 7.10 (dt, $J$ = 4.2, 2.2 Hz, 8H), 6.27 (t, $J$ = 2.2 Hz, 8H), 4.99 (d, $J$ = 10.9 Hz, 4H). $^{31}P$ NMR (162 MHz, DMSO-$d_6$) δ 112.01 .$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 156.24 (d, $J$ = 7.3 Hz), 137.80, 121.58 (d, $J$ = 15.4 Hz), 120.19, 112.35 (dd, $J$ = 4.7, 1.9 Hz), 69.36 (d, $J$ = 18.8 Hz). MS (EI): $[M+Na]^+$, cal.: 486.1225, found: 486.1209, ($C_{23}H_{23}N_5O_2P_2$): 463.4085.

**Synthesis of L2**

An excess of $Et_3N$ (10 ml) was added to a Schlenk apparatus containing **pyridine-2,6-dimethanol (C)** (0.72g, 5.2mmol) and DMAP (0.13g, 1.04mmol)**,** and dry THF (20 mL). After the solution was stirred at -78 $^oC$ for 30 min, a solution of phosphorochloridite in dry THF (10 mL), which prepared from [1,1'-biphenyl]-2,2'-diol and $PCl_3$ in a stoichiometric ratio,[6] was slowly added into the cooled solution over a period of 30 min. And then warmed to room temperature to stirred for 4 h. The triethylamine hydrochloride salt were filtered under nitrogen atmosphere, and the filtrate was evaporated under reduced pressure producing yellow pale residues. And the resulting thick oil was extracted three times with15 mL of pentane. Evaporation of the pentane solutions to dryness yield **L2** as a colorless oil. Yield: 47%.




$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.68 (t, $J$ = 7.8 Hz, 1H), 7.39 (dd, $J$ = 7.6, 1.9 Hz, 4H), 7.34 (d, $J$ = 7.8 Hz, 2H), 7.26 (td, $J$ = 7.6, 1.9 Hz, 4H), 7.22 – 7.15 (m, 4H), 7.07 (dt, $J$ = 7.9, 1.2 Hz, 4H), 4.98 (d, $J$ = 7.7 Hz, 4H).

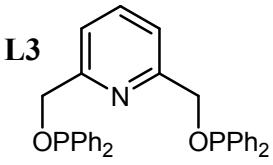
$^{31}$P NMR (162 MHz, $CDCl_3$) δ 137.21. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.76 (d, *J* = 4.0 Hz), 148.68 (d, *J* = 5.5 Hz), 136.52, 129.89 (d, *J* = 3.2 Hz), 128.99 (d, *J* = 1.2 Hz), 128.33, 124.20 , 120.86 (d, *J* = 1.3 Hz), 118.92 , 65.41 (d, *J* = 4.1 Hz).

MS (EI): $[M+Na]^+$ , cal.: 590.0898, found: 590.0859, ($C_{31}H_{23}NO_6P_2$): 567.1001.

**Synthesis of L3 and L5**

An excess of $Et_3N$ (10 mL) was added to a Schlenk apparatus containing **pyridine-2,6-dimethanol (C)** (0.8g, 5.76 mmol) and dry THF (20 mL). After the solution was stirred at -78 $^oC$ for 30 min, a solution of $PPh_2Cl$ (2.10 mL,11.51mmol) in dry THF(10 mL) was slowly added over a period of 30min.The mixture was warmed to room temperature and stirred for 4 h. The triethylamine hydrochloride salt was filtered under nitrogen atmosphere, and the filtrate was evaporated under reduced pressure producing yellow pale residues. And the resulting thick oil was extracted three times with 25 mL of pentane. Evaporation of the pentane solutions to dryness led to **L3** as a colorless oil [7]. Yield: 60%.And **L5** was synthesized according to literature.[8] Yield: 65%.

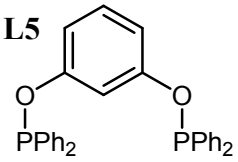
**L3**




**L3**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.38 (m, 8H), 7.33 – 7.20 (m, 14H), 4.85 (dd, *J* = 9.2, 1.9 Hz, 4H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 116.54 .

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.03 (d, *J* = 8.4 Hz), 141.41 (d, *J* = 18.3 Hz), 137.25 , 130.64 (d, *J* = 21.9 Hz), 129.51 , 128.39 (d, *J* = 6.7 Hz), 119.74 , 72.04 (d, *J* = 18.7 Hz).

**L5**




**L5:** $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.56 (ddt, *J* = 7.7, 5.4, 2.5 Hz, 8H), 7.45 (dt, *J* = 5.3, 1.8 Hz, 12H), 7.25 (t, *J* = 8.2 Hz, 1H), 6.94 (t, *J* = 2.1 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 110.86. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.27 (d, *J* = 10.0 Hz), 140.69 (d, *J* = 17.4 Hz), 130.69 (d, *J* = 1.3 Hz), 130.46 (d, *J* = 1.3 Hz), 129.77 (d, *J* = 1.5 Hz), 128.50 (dd, *J* = 7.1, 1.5 Hz), 112.84 (d, *J* = 12.0 Hz), 109.88 ,

**Synthesis of L4 and L6**

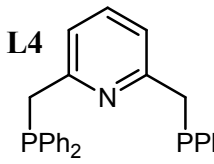
**Synthesis of 2,6-Bis(bromomethyl)pyridine**

48% HBr (30 mL) was slowly added to pyridine-2,6-diyldimethanol (**C**) (2g, 14mmol). The mixture was heated at 125 °C for 6 h and then cooled to room temperature. The resulting residue was dissolved in $H_2O$ (50 mL) to give a yellow solution. To this solution was added saturated $K_2CO_3$ to pH=8. The resulting aqueous solution was extracted with $CH_2Cl_2$ (4×50

mL), and the combined organic layers were dried by $Na_2SO_4$. The solvent was removed by rotary evaporation, and the residue was purified by flash column chromatography (PE/EA, 2:1) to yield **2,6-bis(bromomethyl)pyridine** (1.6 g, 43%) as a white solid.[9] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 4.56 (s, 4H).

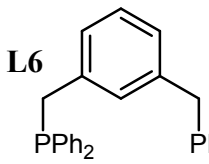
Triphenylphosphine (3.91 g, 14.9mmol) and lithium （0.45 g，65mmol) in 20 mL THF were stirred for 2 h at room temperature, and the orange-red solution was filtered to remove the unreacted lithium. *t*Butyl-chloride (1.6 mL, 14.9mmol) in THF (10 mL) was slowly added to the filtrate cooling in an ice-bath, and then the solution was heated to reflux for 10 min. The solution was cooled to 0 °C in an ice-bath again, and **2,6-Bis(bromomethyl)pyridine** (1.8 g 6.79mmol) or 1,3-bis(bromomethyl)benzene (1.8 g, 6.82mmol) in THF (20 mL) was added slowly into the cooled solution over a period of 50 min, while the color of the solution changed from orange-red to pale yellow. The reaction mixture was heated to reflux for 30 min before the solvents were evaporated to give a yellow sticky solid under vacuum. $CH_2Cl_2$ (30 mL) and water (20 mL) were added to dissolve the solid, and then it was allowed to separate in a separatory funnel. The organic layer was collected and reduced to 5 mL under vacuum. Methanol (20ml) was added to the $CH_2Cl_2$ solution, and a lot of white needle crystals were formed after an hour. The product was filtered, washed with methanol and dried under vacuum to give **L4** and **L6** as white needles. [10,11].

**L4**




**L4**: $^1$H NMR (400 MHz, Benzene-$d_6$) δ 7.33 – 7.18 (m, 8H), 6.91 – 6.75 (m, 12H), 6.59 (t, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 7.7 Hz, 2H), 3.35 (s, 4H). $^{31}$P NMR (162 MHz, Benzene-$d_6$) δ-10.69 .

**L6**




**L6**:$^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 20H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.89 (s, 1H), 6.80 (d, *J* = 5.8 Hz, 2H), 3.32 (s, 4H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ -10.16 .

**NMR Spectra**

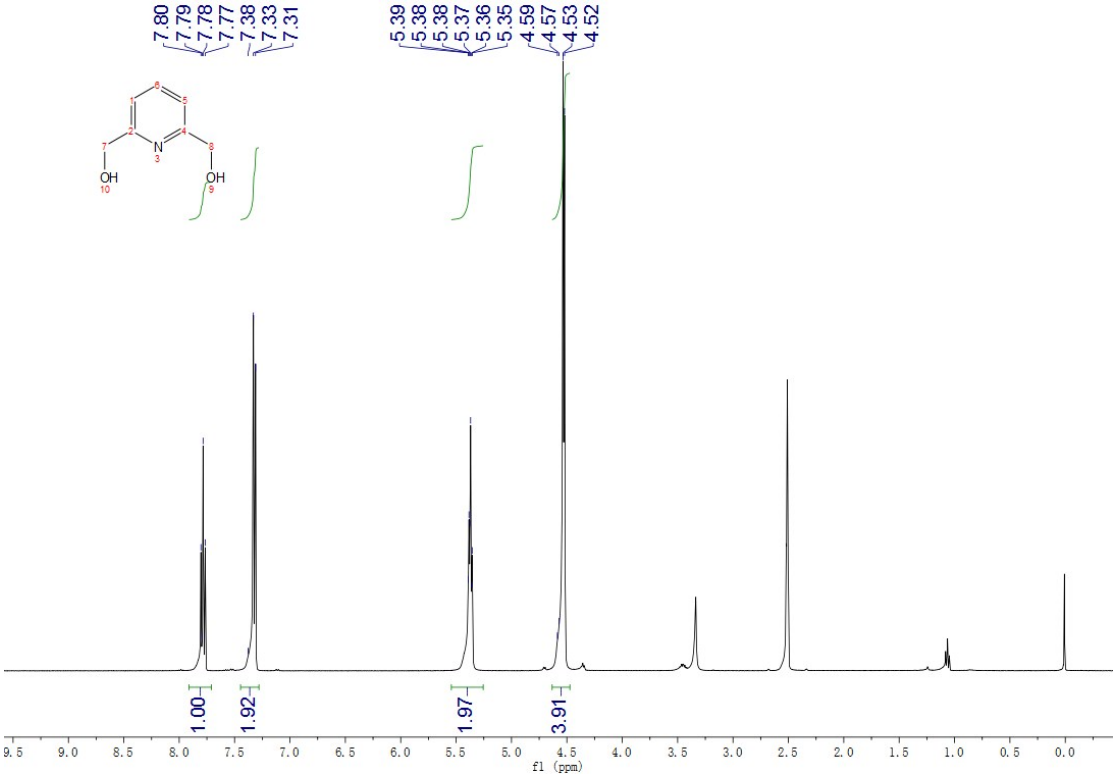
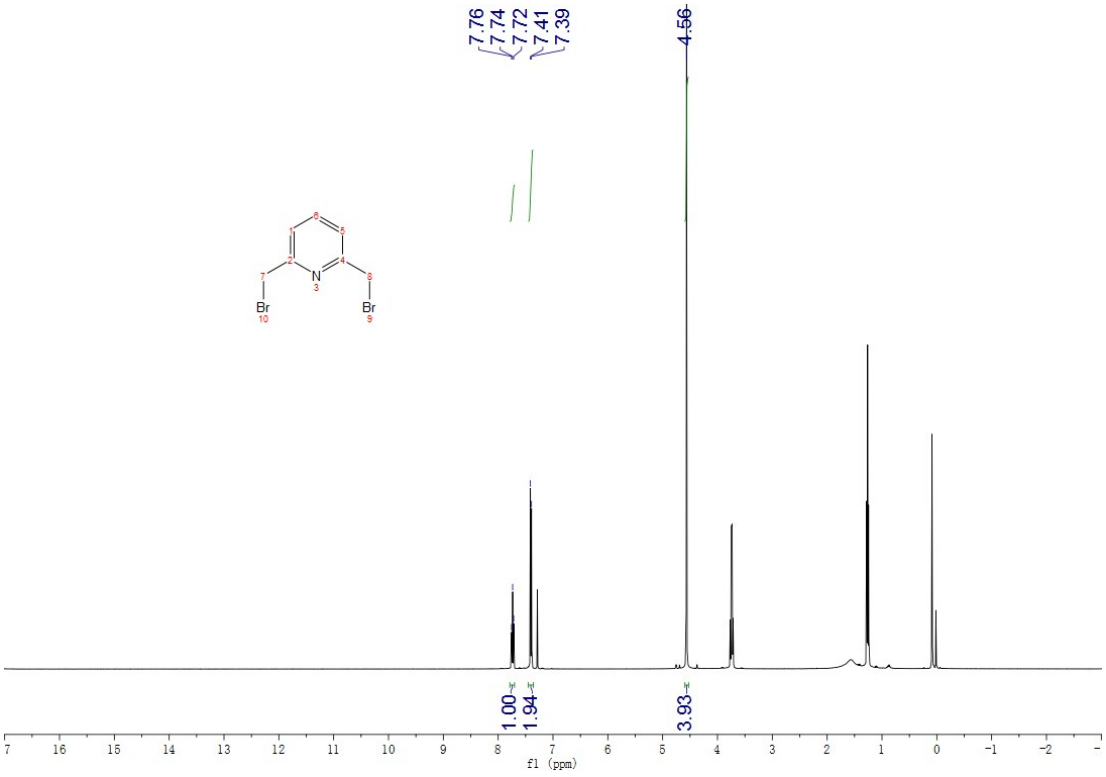



Figure S2. $^{1}$H NMR spectrum of **C**




FigureS3.$^{1}$H NMR spectrum of **2,6-Bis(bromomethyl)pyridine**

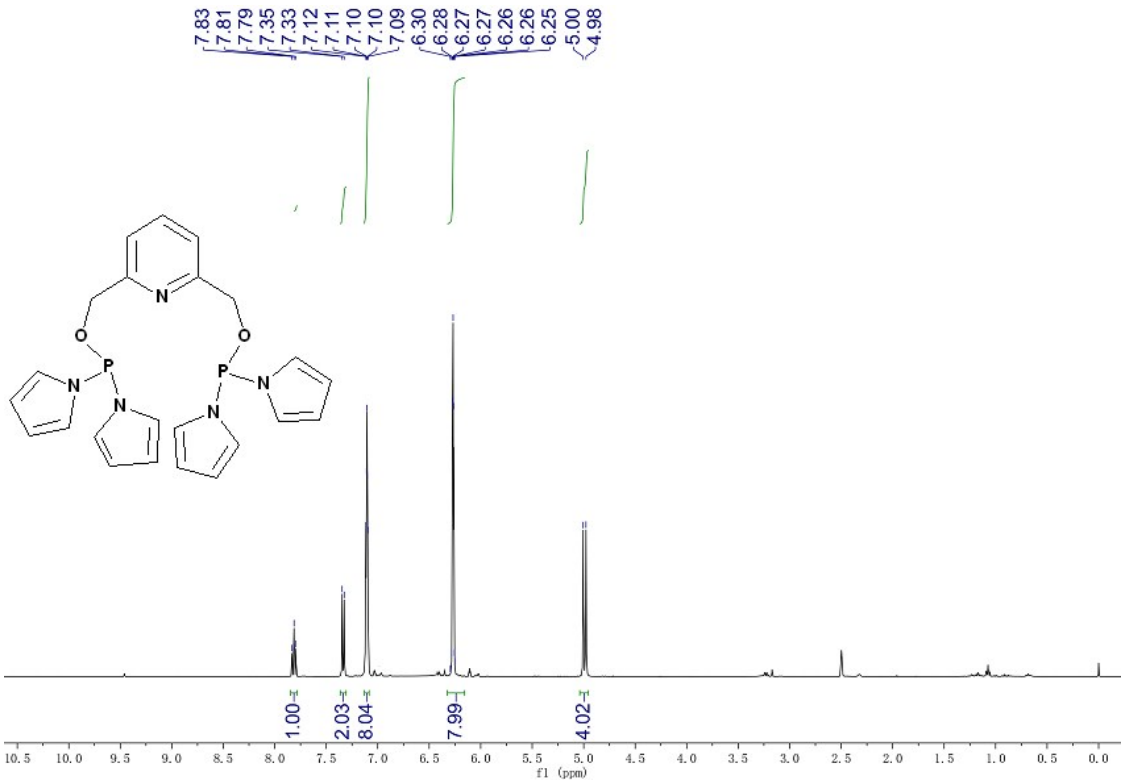



Figure S4. $^{1}$H NMR spectrum of **L1**

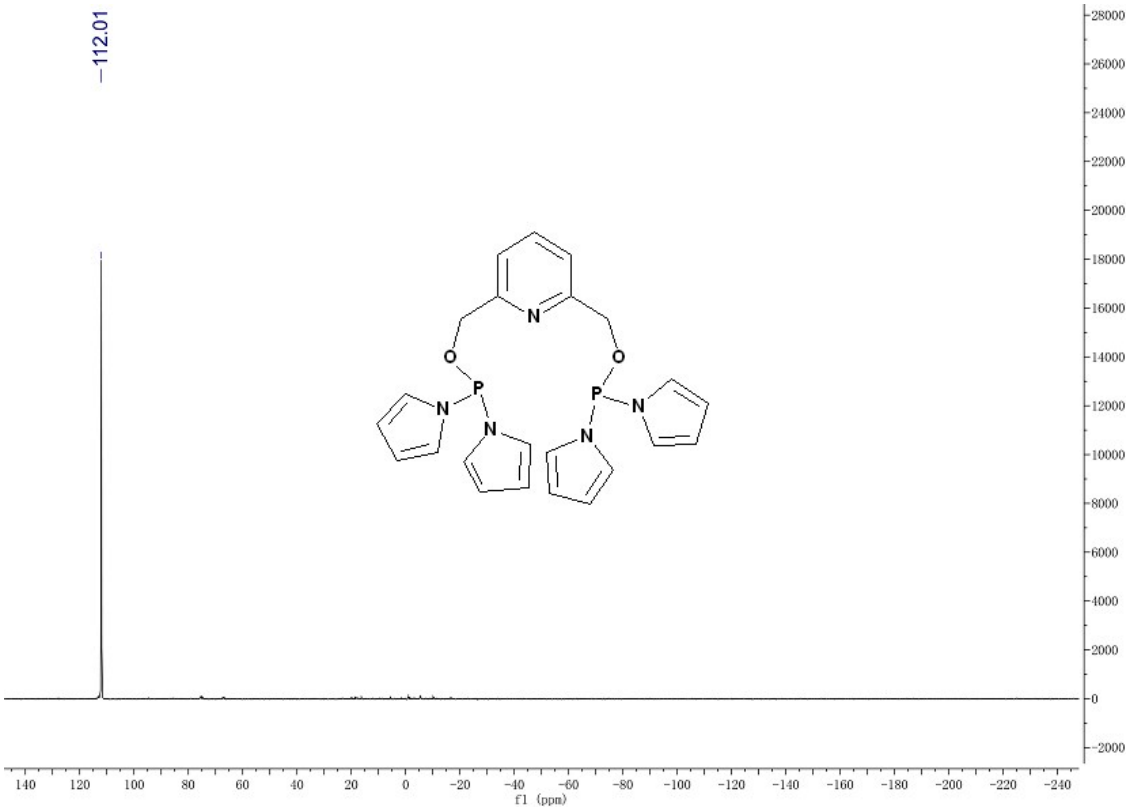



Figure S5. $^{31}$P NMR spectrum of **L1**

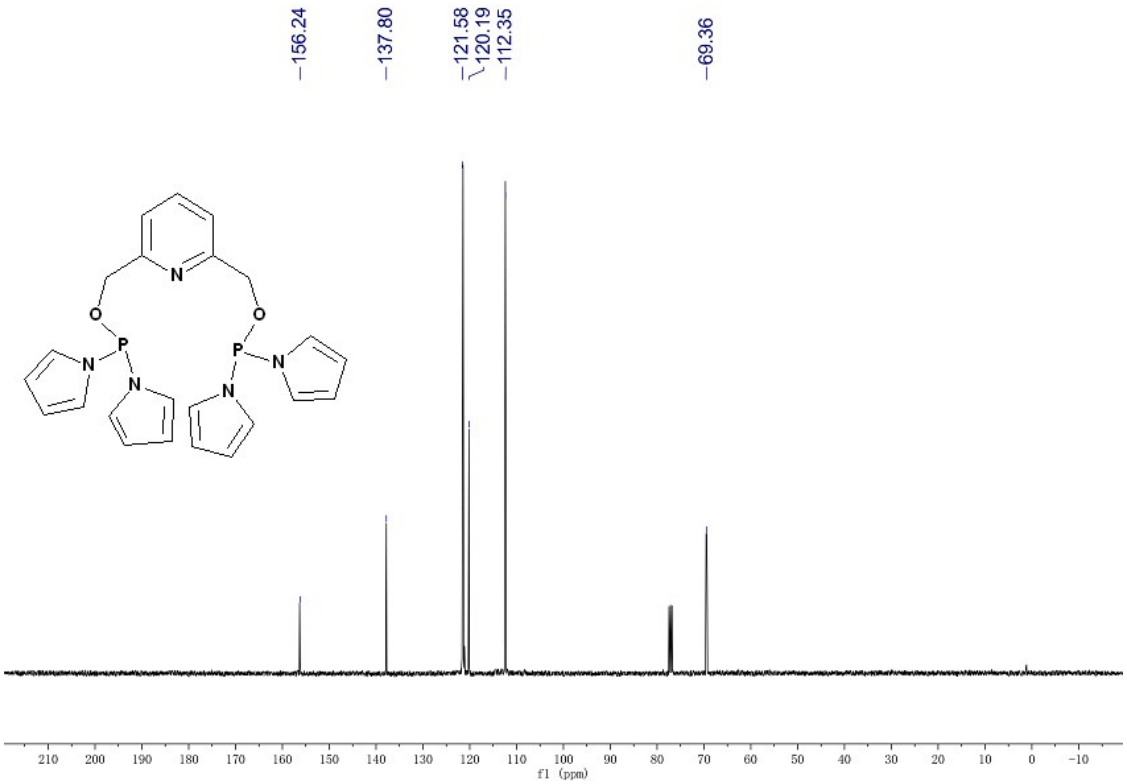



Figure S6.[13]C NMR spectrum of **L1**

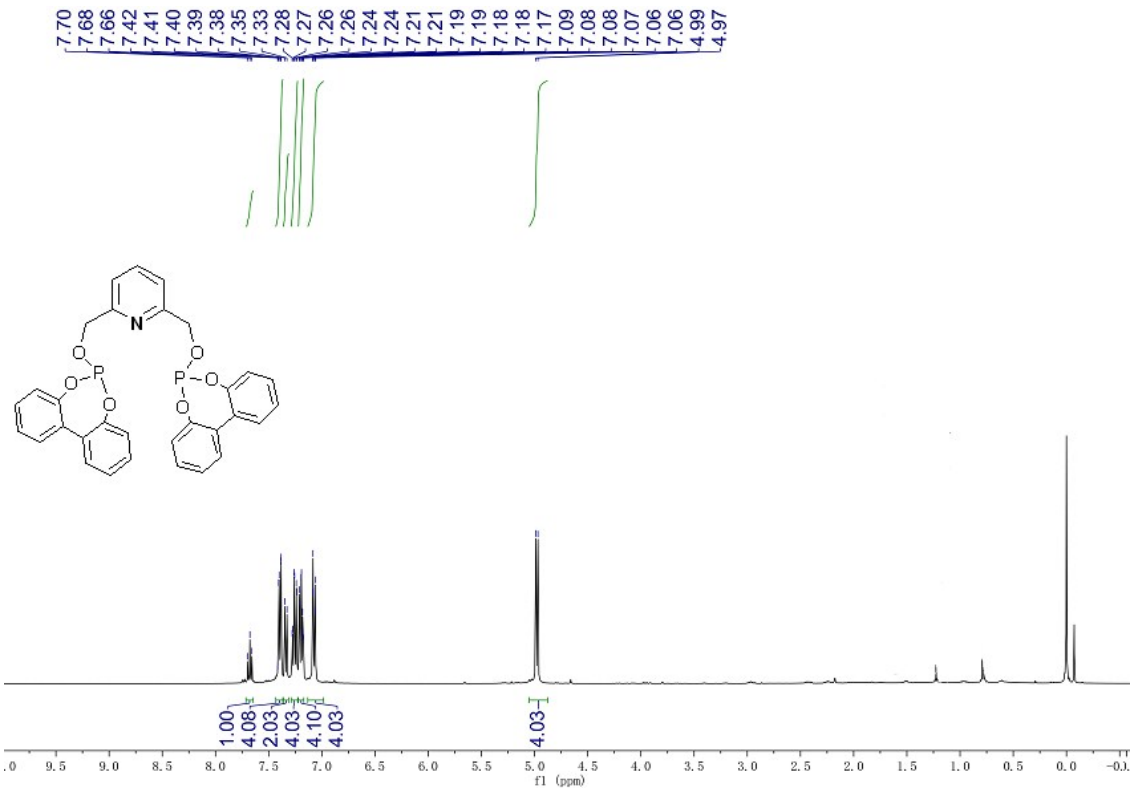



Figure S7. [1]H NMR spectrum of **L2**

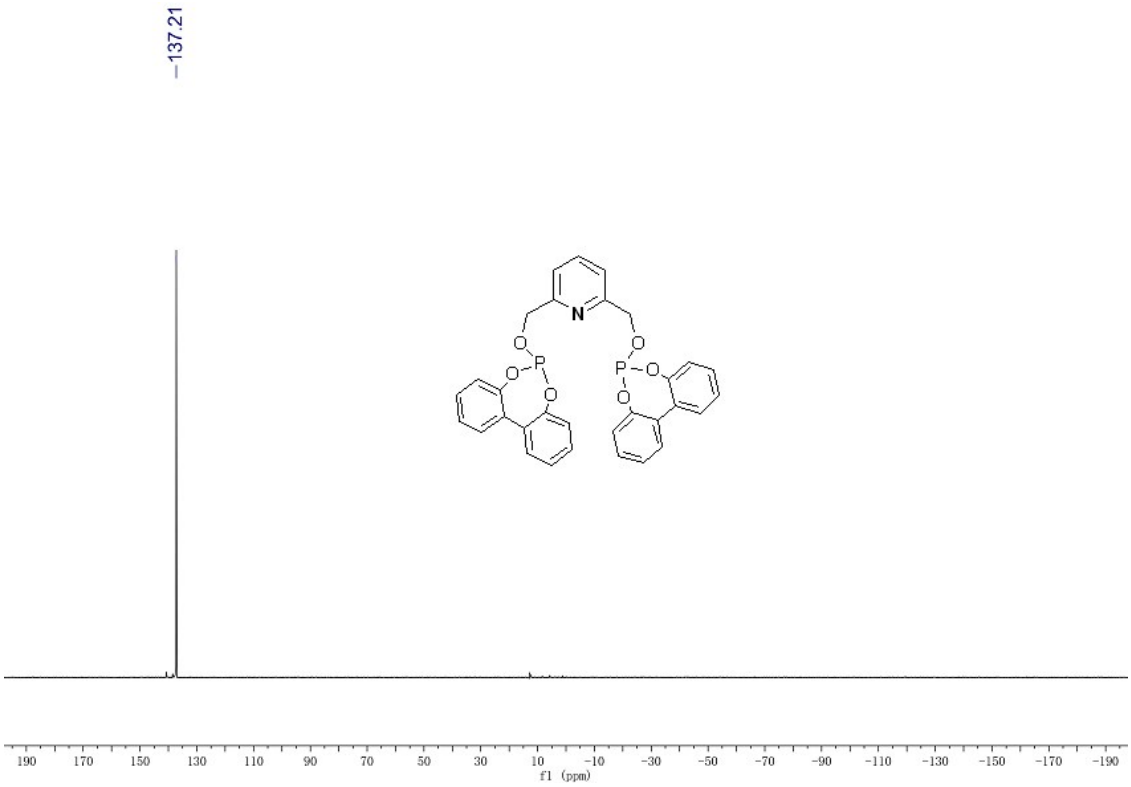



Figure S8. $^{31}$P NMR spectrum of **L2**

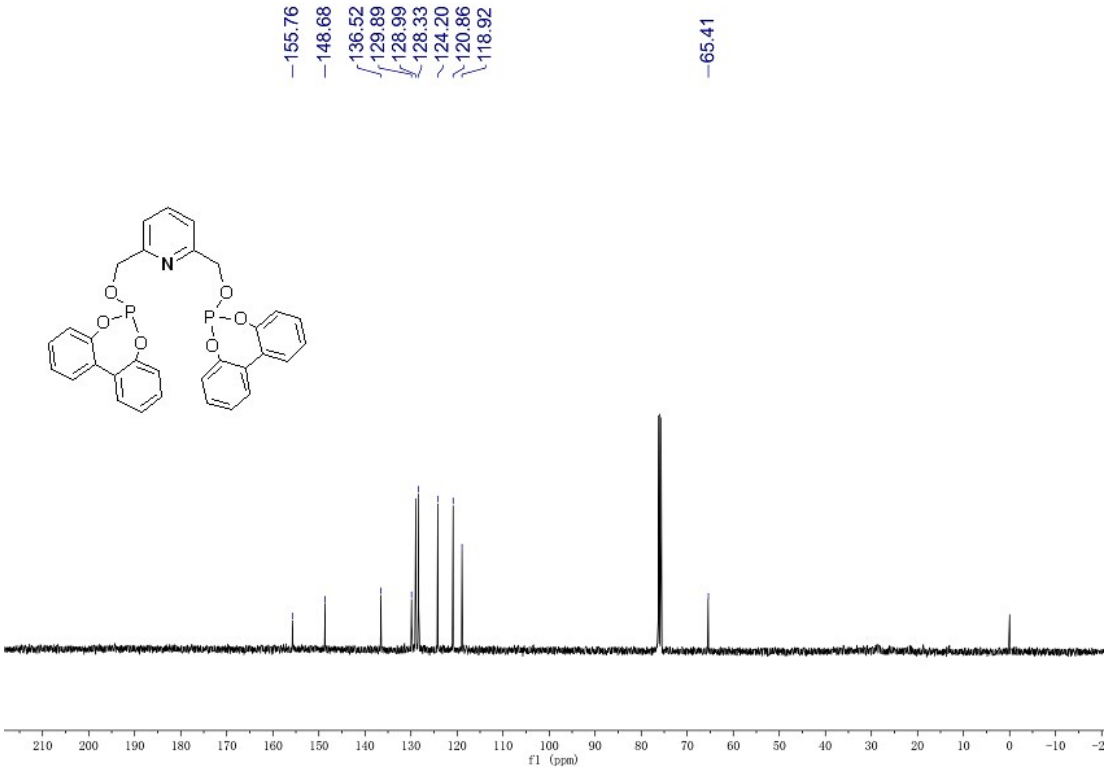



Figure S9. $^{13}$CNMR spectrum of **L2**

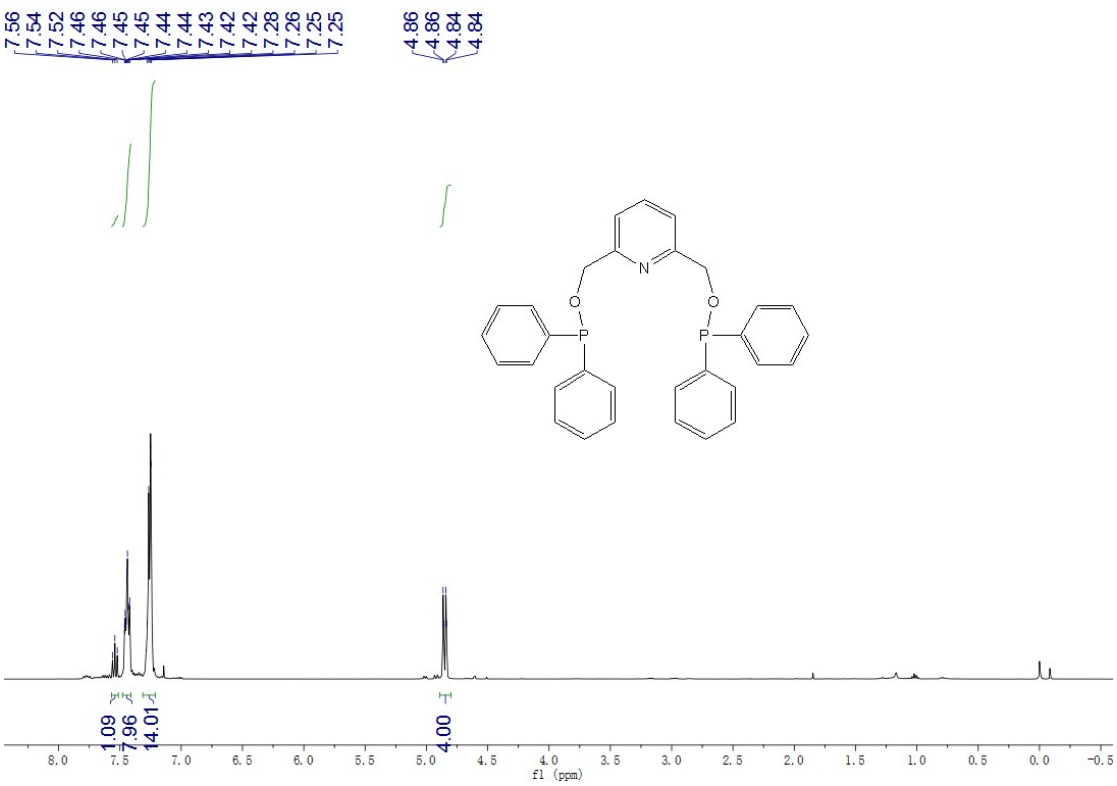



Figure S10. $^{1}$H NMR spectrum of **L3**

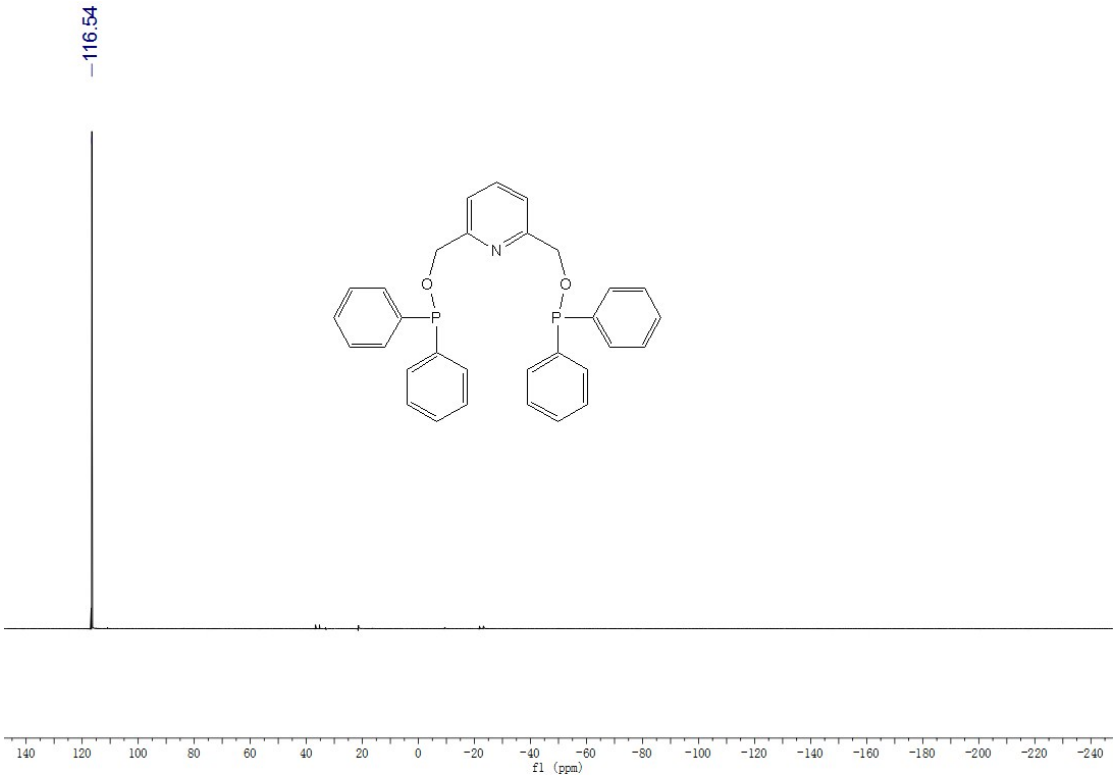



Figure S11. $^{31}$P NMR spectrum of **L3**

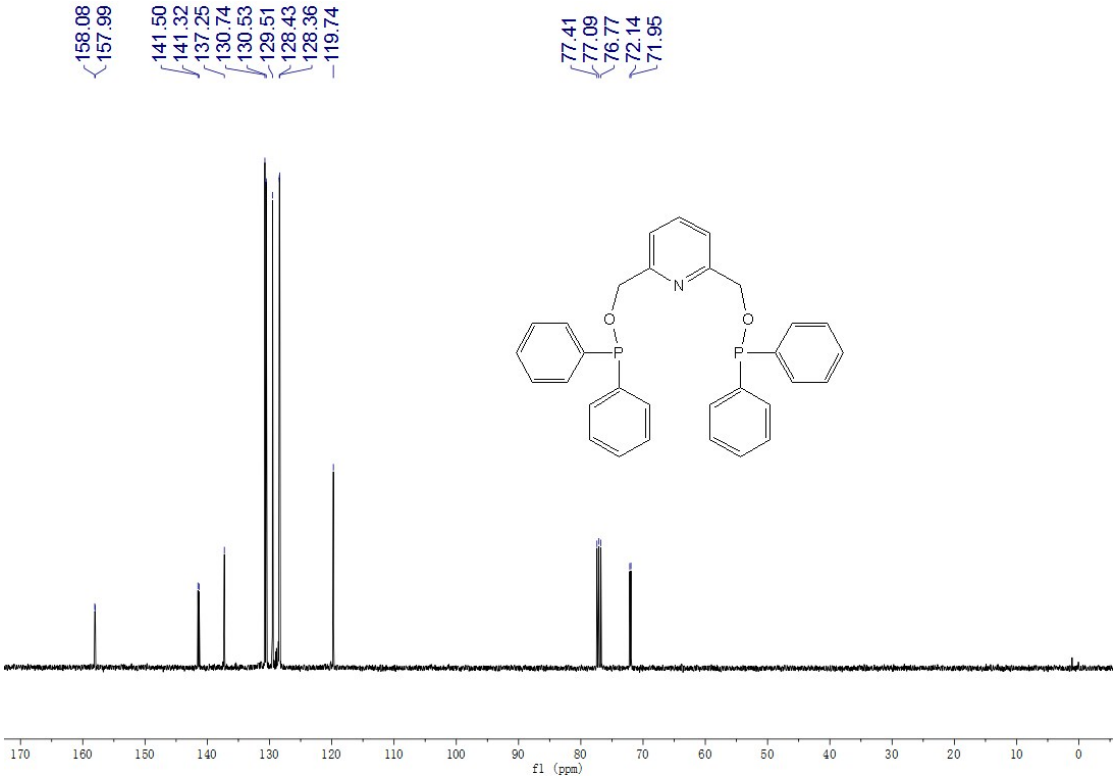



Figure S12. $^{13}C$ NMR spectrum of **L3**

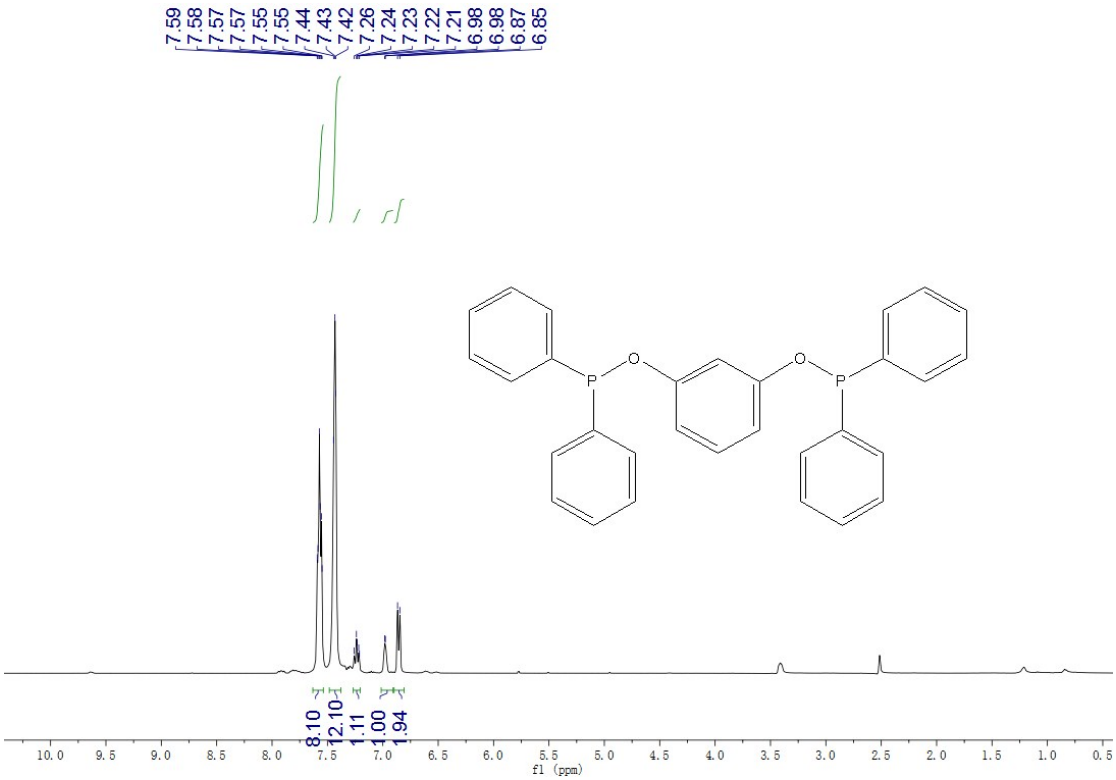



Figure S13. $^{1}H$ NMR spectrum of **L5**

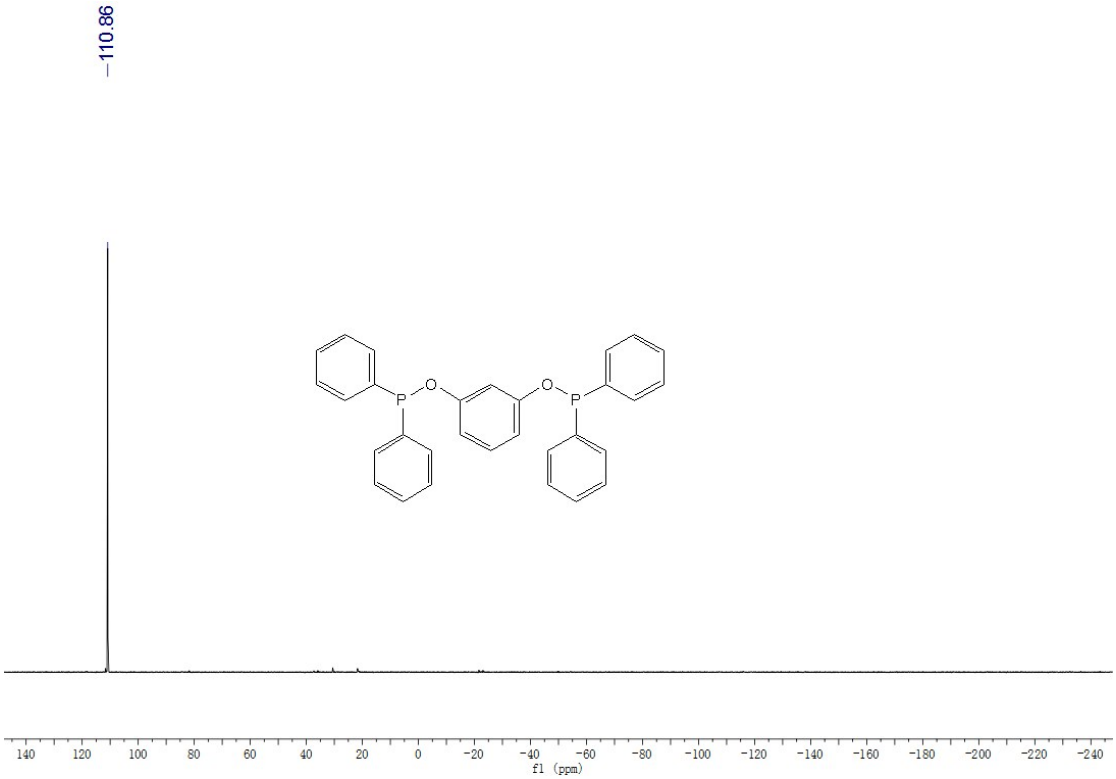



Figure S14.$^{31}$P NMR spectrum of **L5**

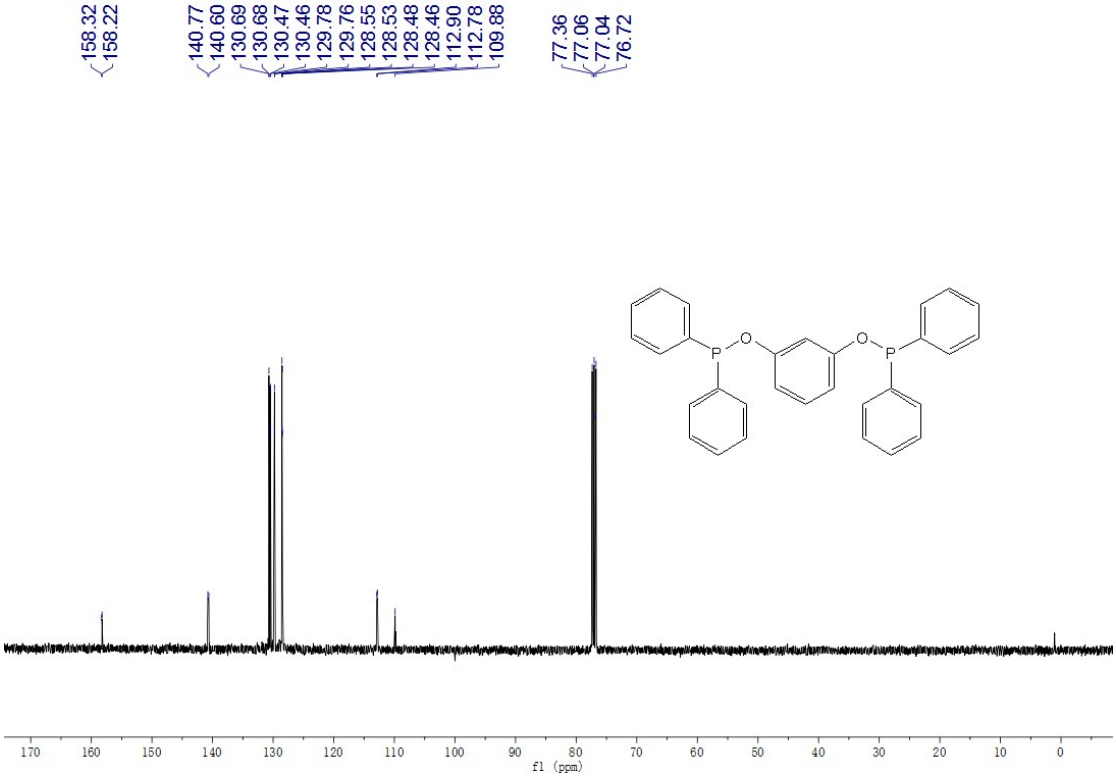



Figure S15. $^{13}$C NMR spectrum of **L5**

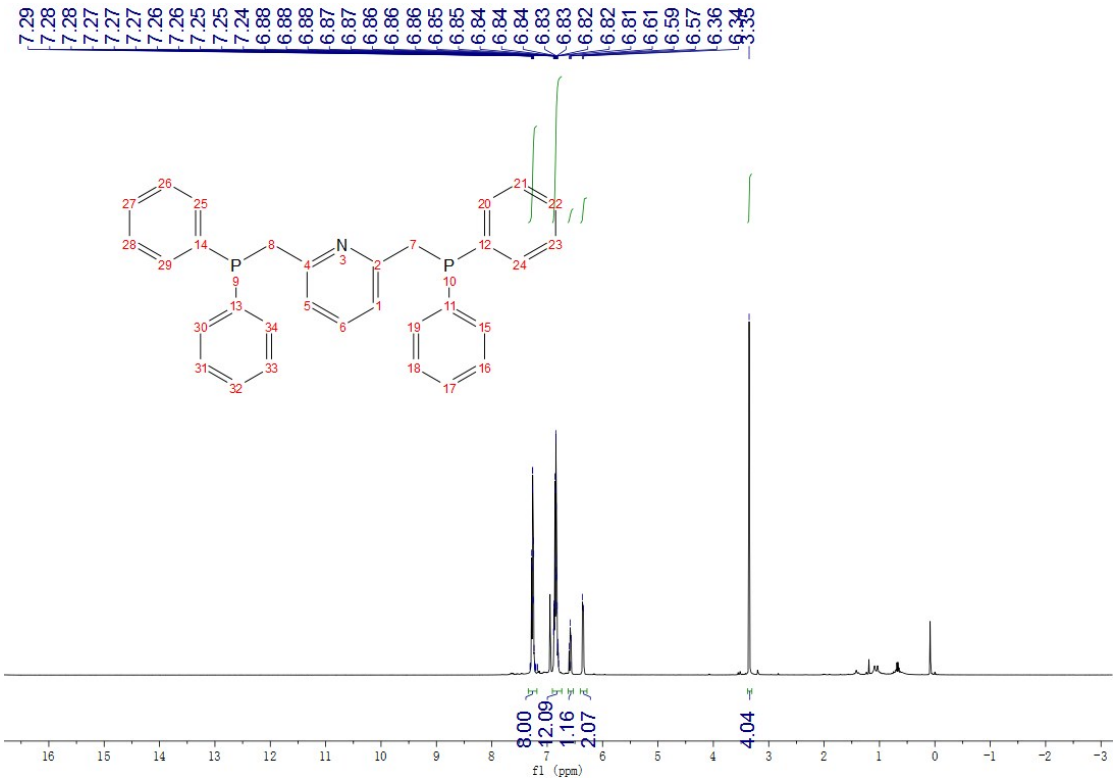



Figure S16. $^{1}$H NMR spectrum of **L4**

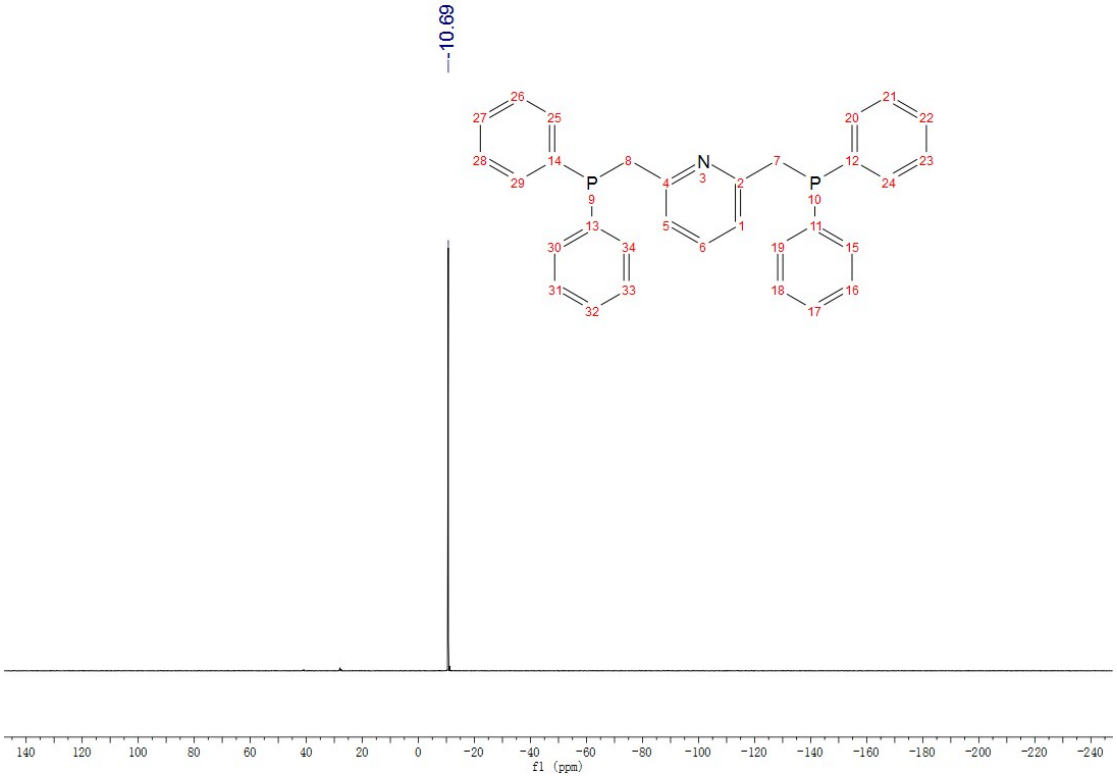



Figure S17. $^{31}$P NMR spectrum of **L4**

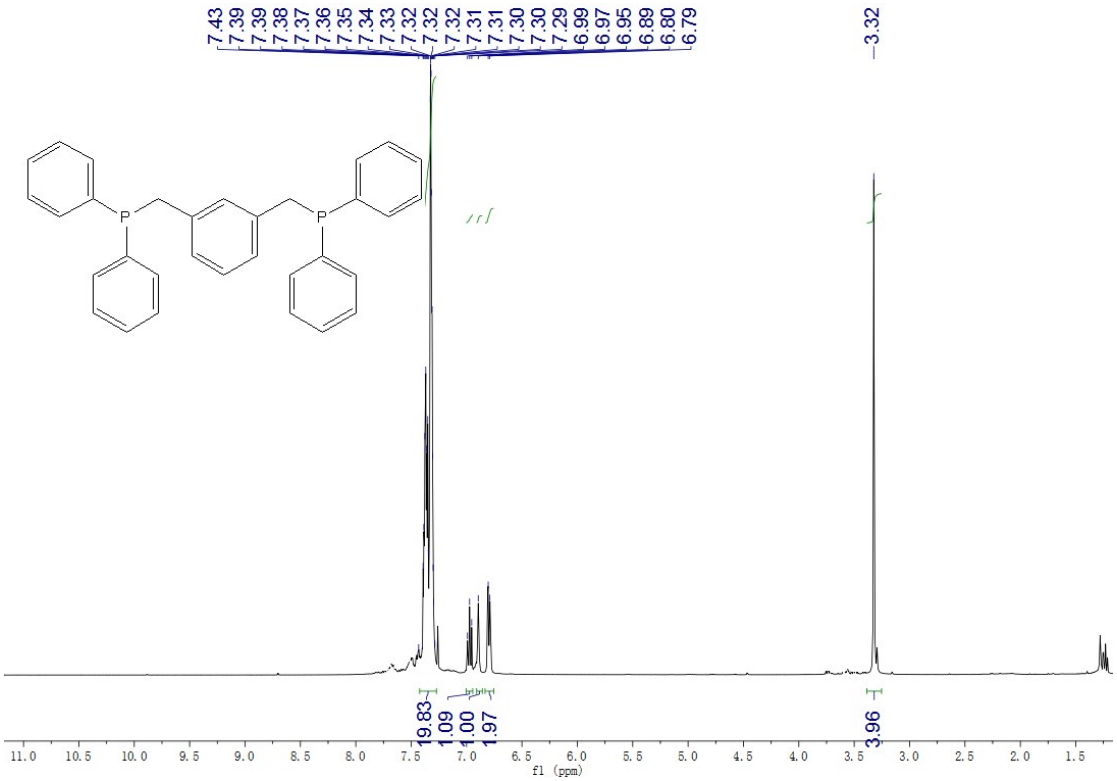



Figure S18. $^{1}$H NMR spectrum of **L6**


Figure S19.$^{31}$P NMR spectrum of **L6**

## Reference


[1]X. Yang, H. Liang, H. Fu, X. Zheng, M. Yuan, R. Li, H. Chen. *Appl. Organometal. Chem*. **2016**, *30*, 335-340.

[2] F. Bonati, G. Wilkison, *J. Chem. Soc.* **1964**, *1*,179-181.

[3] A. W. Singer, S. M. Mcelvain, *J. Am. Chem. Soc*. **1935**, *57*, 1135-1137

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