Supporting Information

Ni-catalyzed C−F activation to construct C−P bond with P−P(O) and P(O)OR mediation

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1. General Information

All reactions were carried out in oven-dried Schlenk tubes under N_2 atmosphere. Dry solvents were obtained by purification according to standard methods or purchased from commercial suppliers. Reagents were used as received unless otherwise noted. All solvents and bases were stored inside a N_2-filled glove box. Column chromatography was performed using Silica Gel 60 (particle size 38–75 μm). The pure products were obtained by means of column chromatography. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR data were acquired on a 400 MHz spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P NMR spectroscopy and 377 MHz for ^{19}F NMR spectroscopy). Chemical shifts for ^{1}H NMR are referred to internal Me_4Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{31}P NMR were relative to H_3PO_4 (85% solution in D_2O, 0 ppm). Gas chromatography monitoring was performed using Shimadzu GC-2014C spectrometer (FID). Mass spectra were measured on a Shimadzu GCMS-QP2010 plus spectrometer (EI). The high resolution ESI mass spectra were recorded on a Waters Xevo G2-XS.

2. Synthesis of the Starting Materials

P(O)−H compounds **1a-1g** are commercially available. Aryl fluorides **2a-2e**, **2g-2n** and **2o** are commercially available. **2f**[1] and **2p**[2] were known compounds which were synthesized according to the reported method. Aryl fluoride **2f** was prepared by the $Pd(OAc)_2$-catalyzed Mizoroki-Heck arylation using styrene and 4-fluoroiodobenzene.

N-Bn-protected paroxetine **2o** was prepared through the reaction of Paroxetine hydrochloride hemihydrate (1 mmol, 365.5 mg), benzyl bromide (1.5 equiv.) and K_2CO_3 (4.0 equiv.) in MeCN. The reaction mixture in pressure vessel was placed in an oil bath at 100 °C and was allowed to stir for 12 hours. Upon completion (monitored by TLC), the solution was cooled to 22 °C. H_2O was then added and the organic material was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The unpurified product mixture was subjected to flash silica gel column chromatography (EtOAc:hexane = 1:4) to afford **2o** as a white solid.[2]

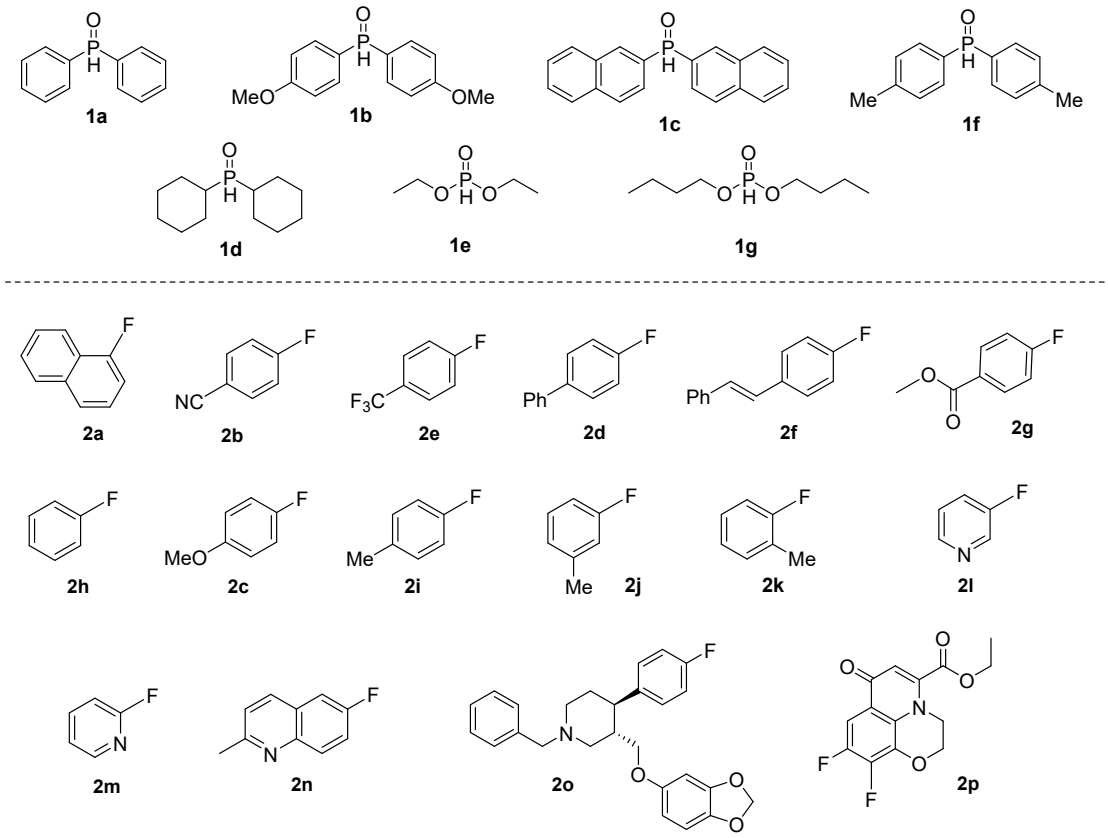
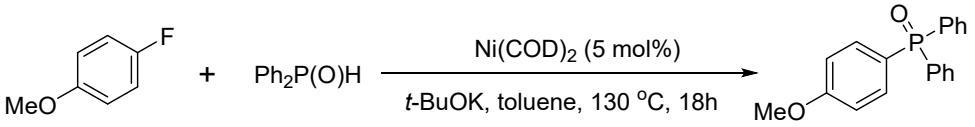


Figure S1. List of substrates for catalytic reactions

(3S, 4R)-3-((benzo[d][1, 3]dioxol-5-yloxy)methyl)-1-benzyl-4-(4-fluorophenyl)piperidine (2o). White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 4H), 7.28–7.25 (m, 1H), 7.17–7.14 (m, 2H), 6.98–6.93 (m, 2H), 6.61 (d, J = 9.2 Hz, 1H), 6.31 (s, 1H), 6.11–6.09 (m, 1H), 5.87 (d, J = 1.0 Hz, 2H), 3.65–3.42 (m, 4H), 3.24 (d, J = 10.8 Hz, 1H), 2.99 (d, J = 10.8 Hz, 1H), 2.50–2.45 (m, 1H), 2.22 (s, 1H), 2.12–2.04 (m,2H), 1.90–1.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, $J_{C\text{-}F}$ = 246.2 Hz), 154.4, 148.1, 141.6, 139.9 (d, J_{C-F} = 2.9 Hz), 138.2, 129.3, 128.8 (d, J_{C-F} = 7.6 Hz), 128.3, 127.1, 115.3 (d, J_{C-F} = 20.9 Hz), 107.8, 105.6, 101.1, 98.0, 69.7, 63.4, 57.6, 53.9, 44.1, 42.2, 34.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.7.

3. Experimental Procedures

Typical procedure for C−F phosphorylation of aryl fluorides



Under N_2 atmosphere, 0.2 mmol diphenylphosphine oxide **1a**, 0.4 mmol 4-fluoroanisole **2c**, 5 mol% $Ni(COD)_2$, 0.3 mmol *t*-BuOK and 2.0 mL toluene were charged into a 10 mL schlenk tube, and

the mixture was stirred at 130 ºC for 18 h. After removal of the volatile, the residues were passed through a short silica chromatography (particle size 38–75 μm, pether/ethyl acetate as eluent) to afford analytically pure organophosphorus compounds **3ac**.

Preparation of 3ac at 5 mmol scale

Under N_2 atmosphere, 10 mmol (1.261 g) 4-fluoroanisole **2c**, 5 mmol (1.011 g) diphenylphosphine oxide **1a**, 5 mol% (68.8 mg) $Ni(COD)_2$, 7.5 mmol (0.841 g) *t*-BuOK and 20 mL toluene were heated at 130 ºC for 18 h. After removal of the volatile, the crude product was passed through a short SiO_2 column using EtOAc as an eluent to give the spectroscopically pure **3ac** in 75% yield (1.156 g).

Preparation of tetraphenyldiphosphine monoxide

To a 50 mL round bottom schlenk flask, 20 mmol (4.320g) methoxydiphenylphosphine and 20 mmol (4.400g) chlorodiphenylphosphine dissolved in degassed benzene (10 mL) was added under an argon atmosphere, and the mixture was refluxed for 3 h. The reaction mixture was filtered and washed with benzene under an argon atmosphere to give the product in 86% yield.[3]

Preparation of $Ph_2P(O)OBu$-*t*

Potassium tert-butoxide (5.5 mL, 1.0 M in THF) was added dropwise to diphenylphosphine chloride (1.0 mL, 1.22 g, 5.5 mmol) at 0 ºC, the ice bath was removed and stirring continued at room temperature After 2 hours, the reaction solution was separated by filtration and then added with 30% hydrogen peroxide solution for oxidation. The mixture was extracted with CH_2Cl_2. After removing the volatiles, the crude product was passed through a short SiO_2 column using EtOAc/PE as an eluent to give the spectroscopically pure $Ph_2P(O)OBu$-*t* in 75% yield (0.452g).[4]

4. Mechanistic Studies

^{31}P NMR spectra of intermediate and product 3 in toluene/ C_7D_8

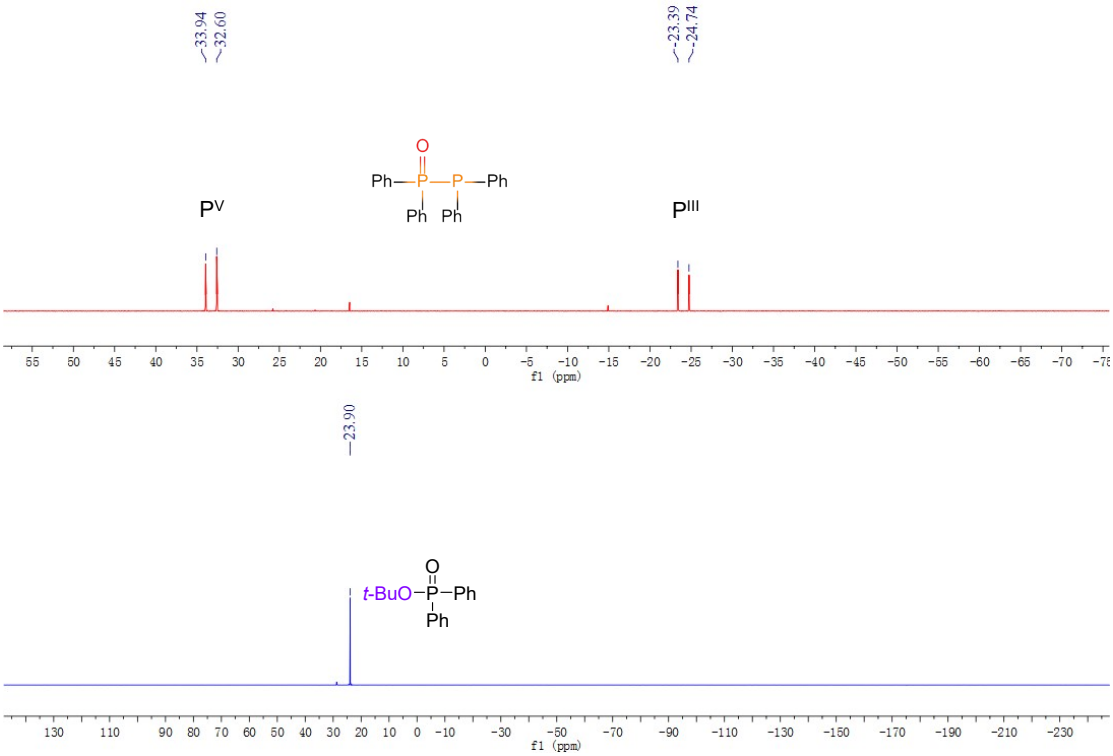


Figure S2. ^{31}P NMR spectra of tetraphenyldiphosphine monoxide **A** and $Ph_2P(O)OBu$-*t* **B** in toluene/C_7D_8

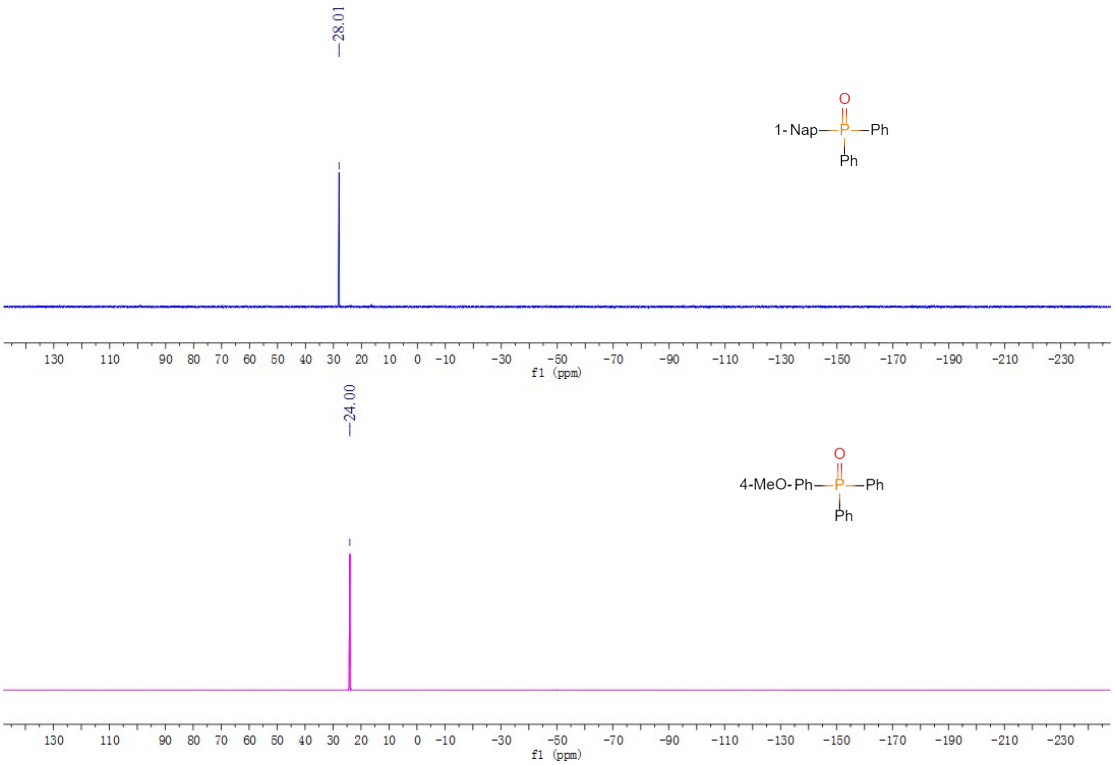


Figure S3. ^{31}P NMR spectra of naphthalen-1-yldiphenylphosphine oxide **3aa** and (4-

Methoxyphenyl)diphenylphosphine oxide **3ac** in toluene/C_7D_8

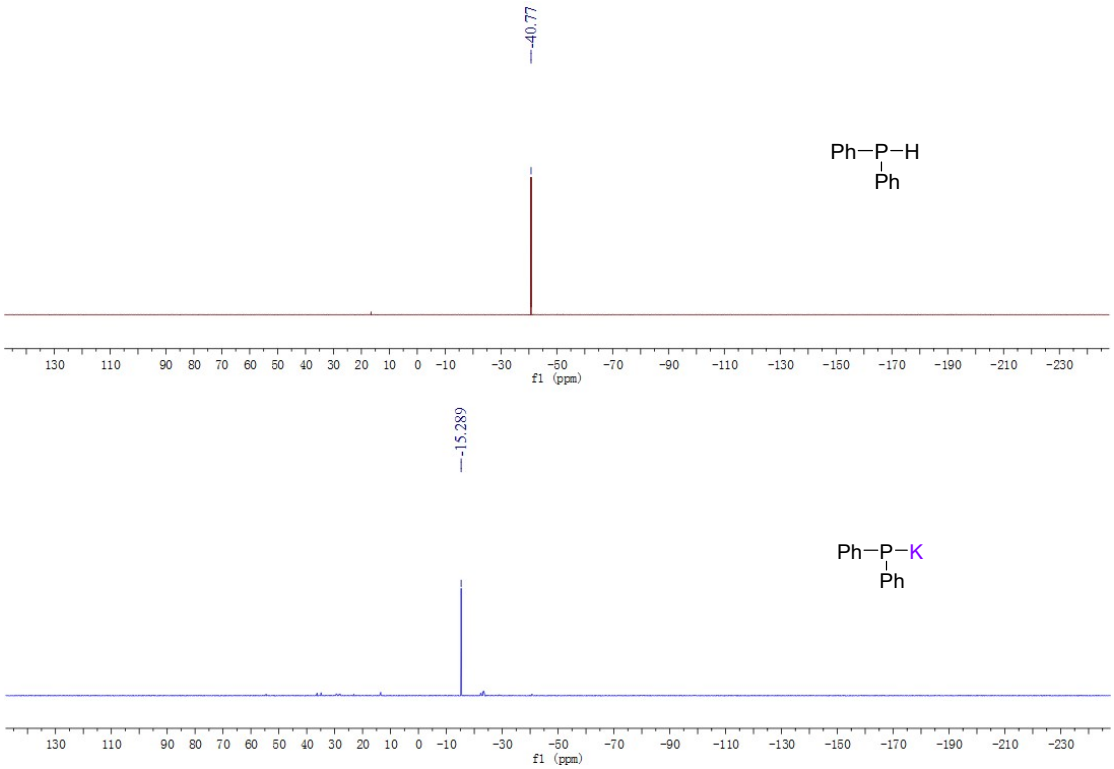


Figure S4. ^{31}P NMR spectra of diphenylphosphine (Ph_2PH) and diphenylphosphine potassium salt (Ph_2PK) in THF/C_7D_8

^{31}P NMR spectra of the reaction mixture in toluene/ C_7D_8

General procedure: Under N_2 atmosphere, 0.1 mmol **1**, 0.15 mmol **2**, 5 mol% $Ni(COD)_2$, 0.15 mmol *t*-BuOK and 1.0 mL toluene were charged into a 10 mL schlenk tube, and part of the reaction solution was added to the NMR tube with the adjunction of appropriate amount of deuterated toluene in the glove box for NMR monitor experiment.

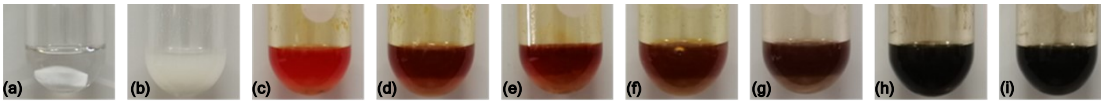


Figure S5. (a) **1a**; (b) **1a** with *t*-BuOK; (c) **1a**, 5 mol% $Ni(COD)_2$ with *t*-BuOK; (d) **1a**, 5 mol% $Ni(COD)_2$ with *t*-BuOK and **2a** at RT; (e) **1a**, 5 mol% $Ni(COD)_2$ with *t*-BuOK and **2a** at RT for 2 h; (f) **1a**, 5 mol% $Ni(COD)_2$ with *t*-BuOK and **2a** at 50 °C for 3 min; (g) **1a**, 5 mol% $Ni(COD)_2$ with *t*-BuOK and **2a** at 100 °C for 3 min; (h) **1a**, 5 mol% $Ni(COD)_2$ with *t*-BuOK and **2a** at 120 °C for 3 min; (i) **1a**, 5 mol% $Ni(COD)_2$ with *t*-BuOK and **2a** at 130 °C for 2 h.

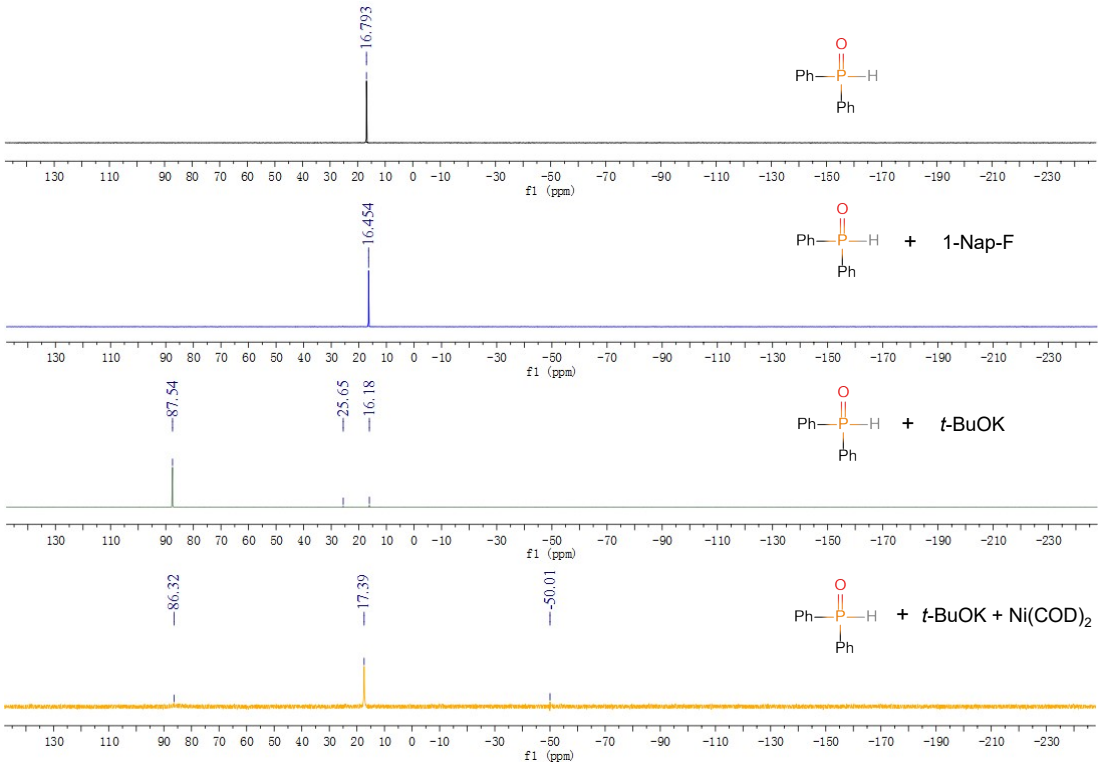


Figure S6. ^{31}P NMR spectra of the control experiments in toluene/C_7D_8

Several control experiments were conducted, and the reactions were monitored by ^{31}P NMR spectroscopy (Figure S7−S9). As shown in Figure S5b, the treatment of **1a** (0.1 mmol, δ 16.8 ppm) with *t*-BuOK (1.5 equiv) caused the formation of white precipitates in toluene at room temperature. The ^{31}P NMR analysis of the suspension was clearly indicative of the formation of potassium phosphinite (δ 87.5 ppm) (Figure S6).[5] The addition of Ni catalyst (5 mol% $Ni(COD)_2$) causes the decomposition of potassium phosphinite back to **1a**, with the gradual disappearance of solids in the reaction solution and the color from colorless transparent to orange (Figure S5,S6).

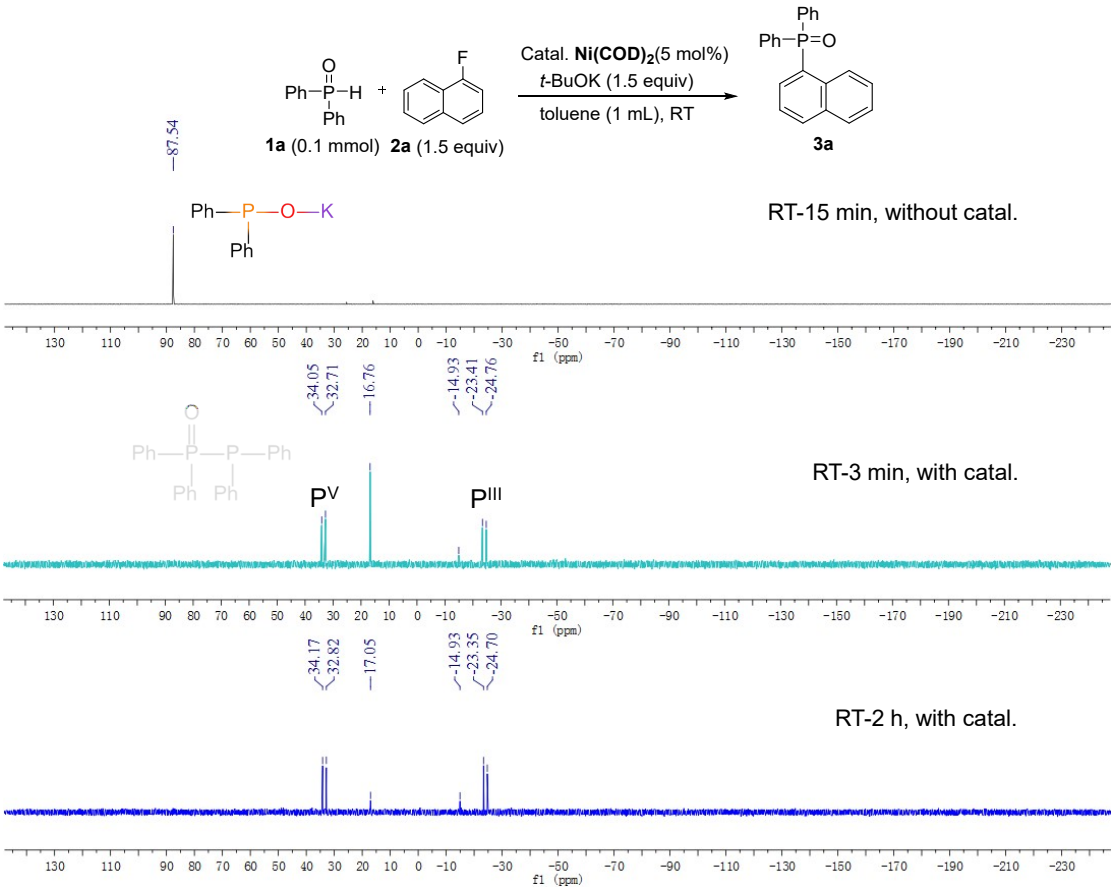


Figure S7. ^{31}P NMR spectra of the reaction mixture in toluene/C_7D_8 at room temperature

Further addition of 1-fluoronaphthalene **2a** to the reaction solution resulted in the rapidly formation of tetraphenyldiphosphine monoxide **A** with two doublets at 33.4 and -24.1 ppm appearing in the ^{31}P NMR spectrum (Figure S7). When the reaction time was extended to 2 hours at room temperature, intermediate **A** remained stable and the peak of **1a** decreased. Heating the reaction mixture at 50 ºC for 3 min lead to the decomposition of **A**, with the signals of Ph_2POK and Ph_2PK appeared in ^{31}P NMR spectrum (Figure S8). When the temperature was raised to 100 ºC, the C−F phosphorylation products **3aa** of appeared on the phosphorus spectrum, and a new peak at 24.3 ppm was observed which could be $Ph_2P(O)OBu$-*t*.

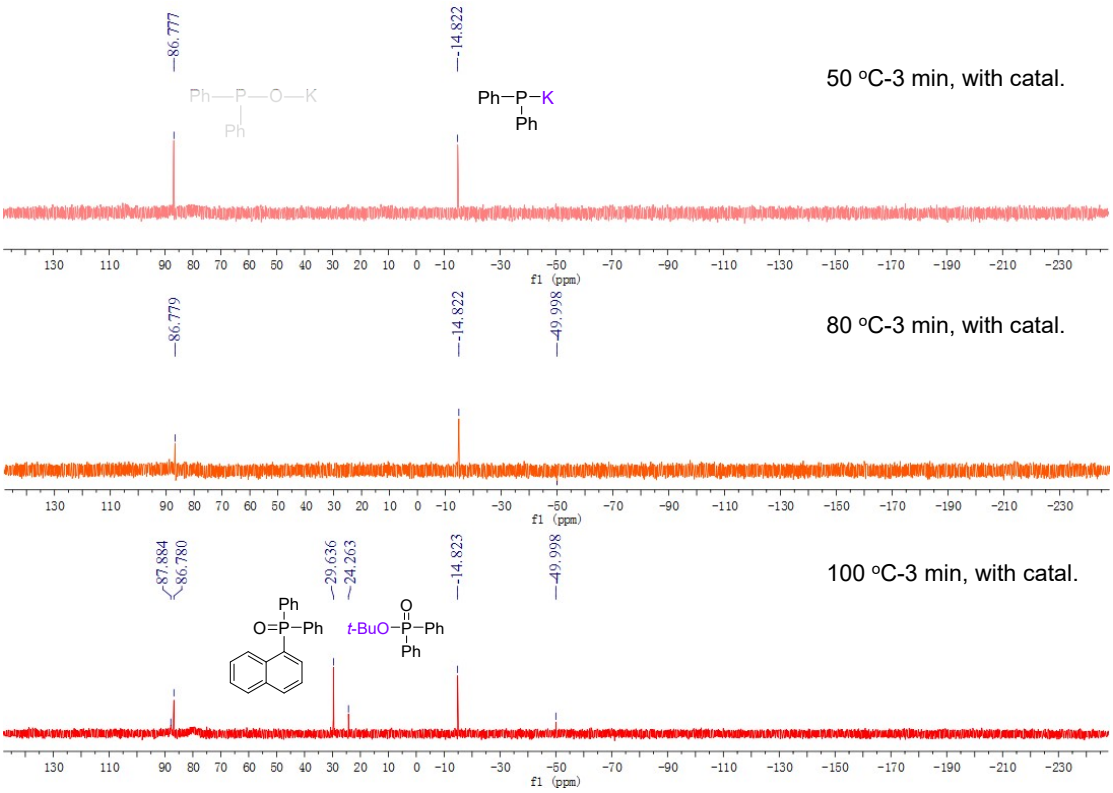


Figure S8. ^{31}P NMR spectra of the reaction mixture at different temperature for 3min

When the reaction temperature is above 120 ºC, the main signal peak in the ^{31}P NMR spectra is the product **3aa** (Figure S9).

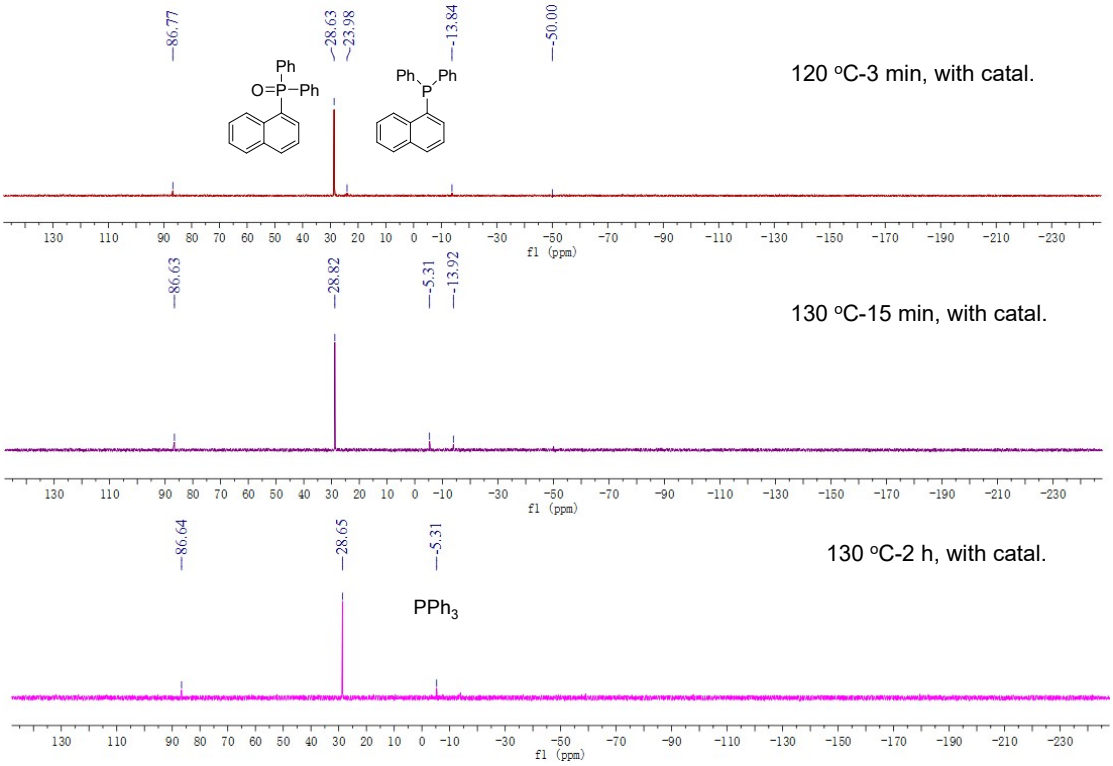


Figure S9. ^{31}P NMR spectra of the reaction mixture at 120 ºC and 130 ºC

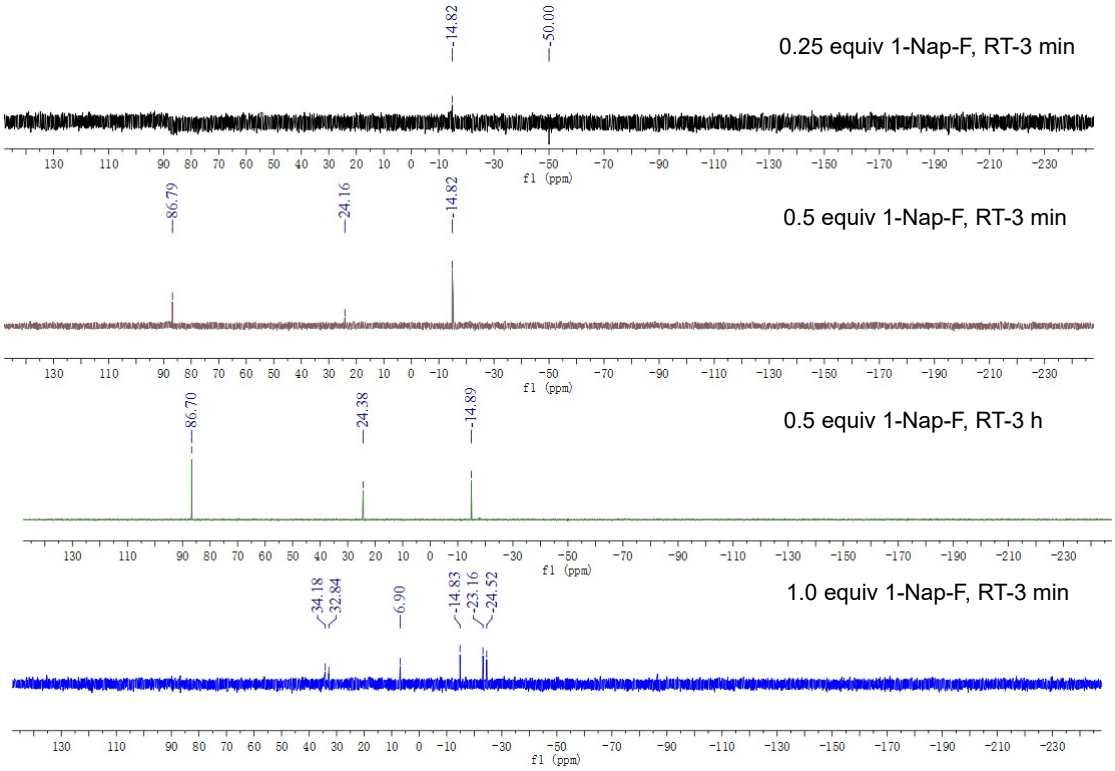


Figure S10. Effects of different fluorobenzene dosage on the formation of intermediates (0.25-0.5-1.0 equiv 1-Nap-F)

Effect of the amount of aryl fluoride on the formation of intermediate A. As can be seen from Figure S10, when the dosage of fluorobenzene is less than 1 equivalent, no signals of intermediate **A** were appeared even if the reaction time is prolonged to 3 h.

Effect of different aryl fluorides on the formation of intermediate. When **2a** was replaced by 4-fluorobenzonitrile **2b**, intermediate **A** can also be produced smoothly, accompanied with the signals of $Ph_2P(O)OBu$-*t* appeared in the ^{31}P NMR spectrum (Figure S11).

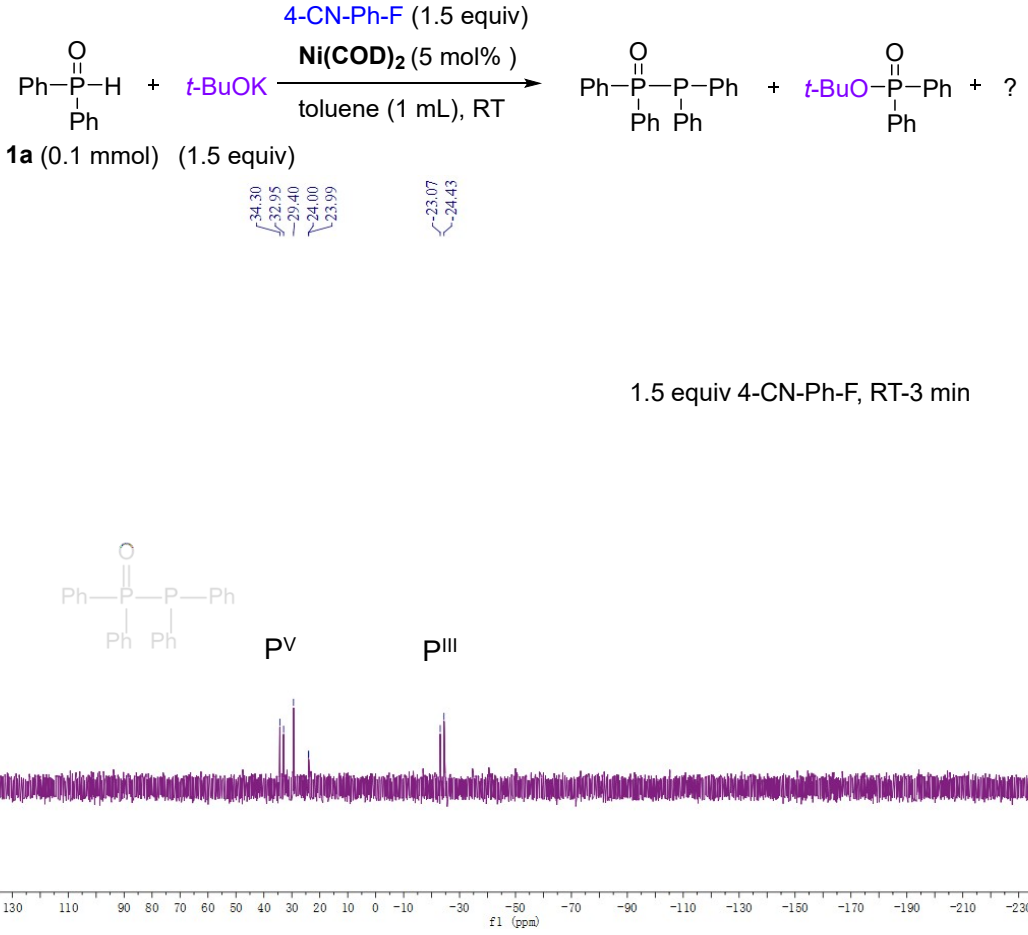
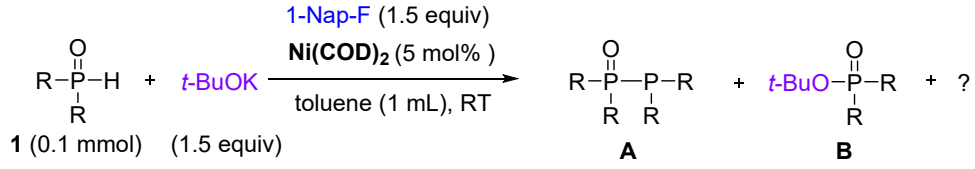


Figure S11. The formation of intermediates **A** promoted by 4-F-PhCN

Effect of different P(O)H compounds on the formation of intermediate. When **1a** was replaced by **1b** or **1c**, kinds of tetraarylphosphine monoxide were produced in the promotion of **2a**, *t*-BuOK and $Ni(COD)_2$. Furthermore, dicyclohexylphosphine oxide **1d** transformed to tetracyclohexylphosphine monoxide smoothly in similar conditions (Figure S12).



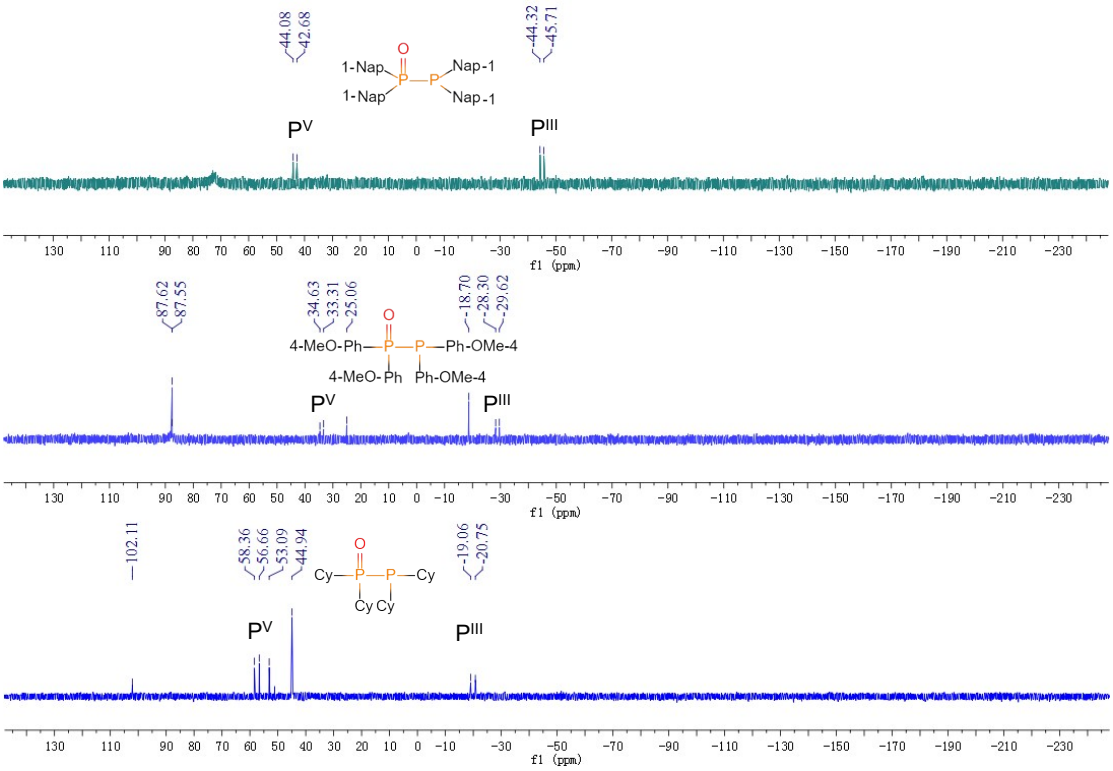


Figure S12. The production of phosphine monoxide through different secondary phosphine oxide

The formation of intermediate B from inactive aryl fluorides. For the inactive monocyclic aryl fluoride, 4-fluoroanisole **2c**, only one peak of the signals of $Ph_2P(O)OBu$-*t* **B** was detected by prolonging the reaction time to 2h at room temperature (Figure S13, S14).

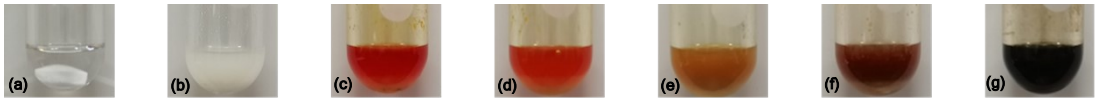
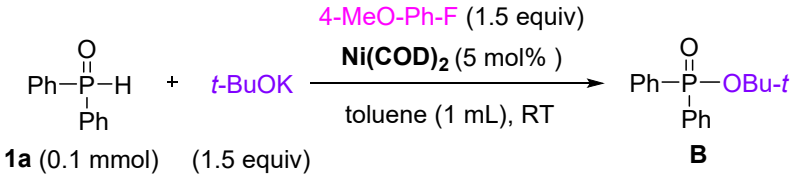


Figure S13. (a) **1a**; (b) **1a** with 1.5 equiv *t*-BuOK; (c) **1a**, 5 mol% $Ni(COD)_2$ with 1.5 equiv *t*-BuOK; (d) **1a**, 5 mol% $Ni(COD)_2$ with 1.5 equiv *t*-BuOK and **2c** at RT; (e) **1a**, 5 mol% $Ni(COD)_2$ with 1.5 equiv *t*-BuOK and **2c** at 50 °C for 3 min; (f) **1a**, 5 mol% $Ni(COD)_2$ with 1.5 equiv *t*-BuOK and **2c** at 100 °C for 3 min; (g) **1a**, 5 mol% $Ni(COD)_2$ with 1.5 equiv *t*-BuOK and **2c** at 130 °C for 10 h.



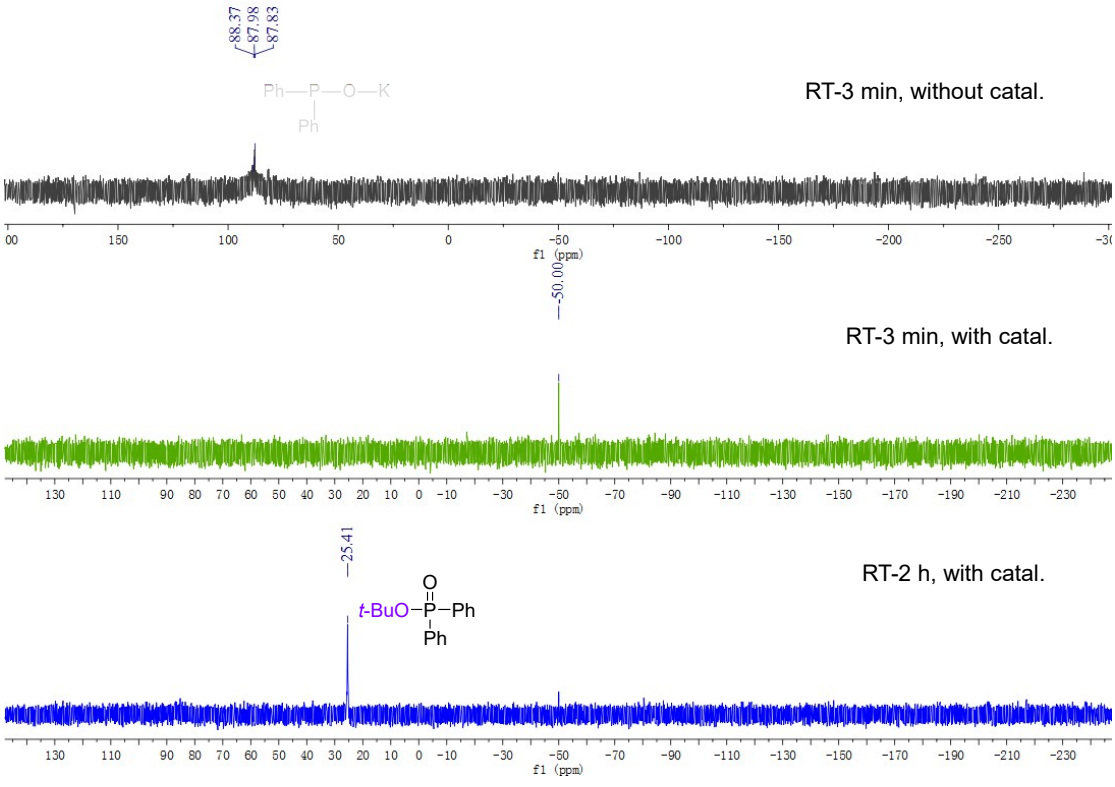


Figure S14. Reaction mixture of **1a**, **2c**, *t*-BuOK with or without Ni catalyst

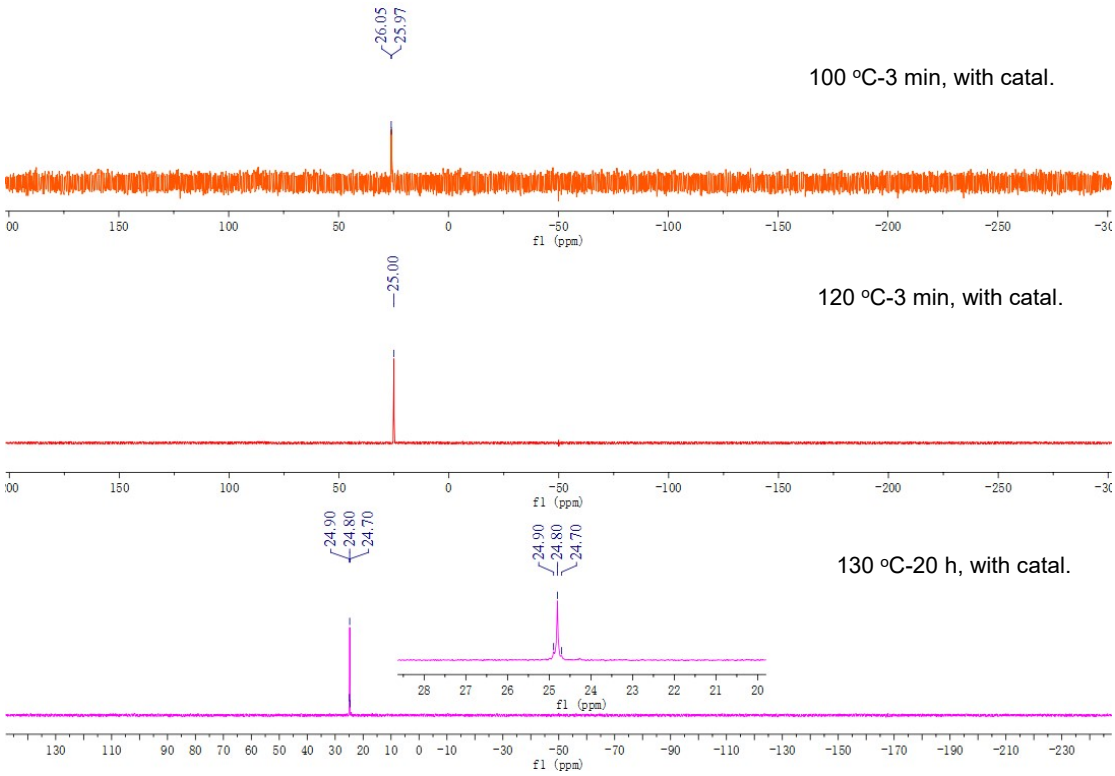


Figure S15. Reaction mixture of **1a**, **2c**, *t*-BuOK with Ni catalyst at different temperature

(4-Methoxyphenyl)diphenyl-phosphine oxide **3ac** was afforded at 130 ºC via the catalytic C−F/P−H cross-coupling reactions (Figure S15).

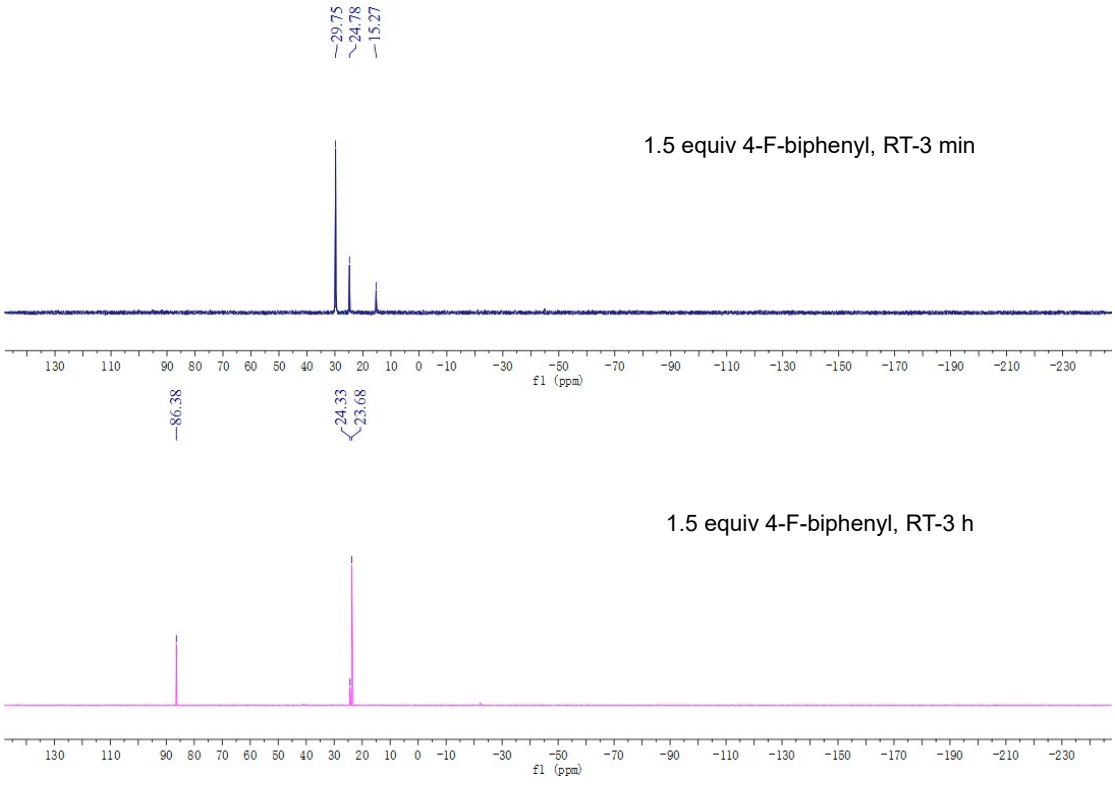


Figure S16. The formation of $Ph_2P(O)OBu$-*t* through 4-F-biphenyl

Similar to **2c**, 4-F-biphenyl **2d** could promote the formation of $Ph_2P(O)OBu$-*t* at room temperature or 50 ºC (Figure S16). In addition, the formation of $(EtO)_2P(O)OBu$-*t* took place in the presence of **1e**, **2a**, *t*-BuOK and $Ni(COD)_2$ (Figure S17).[5]

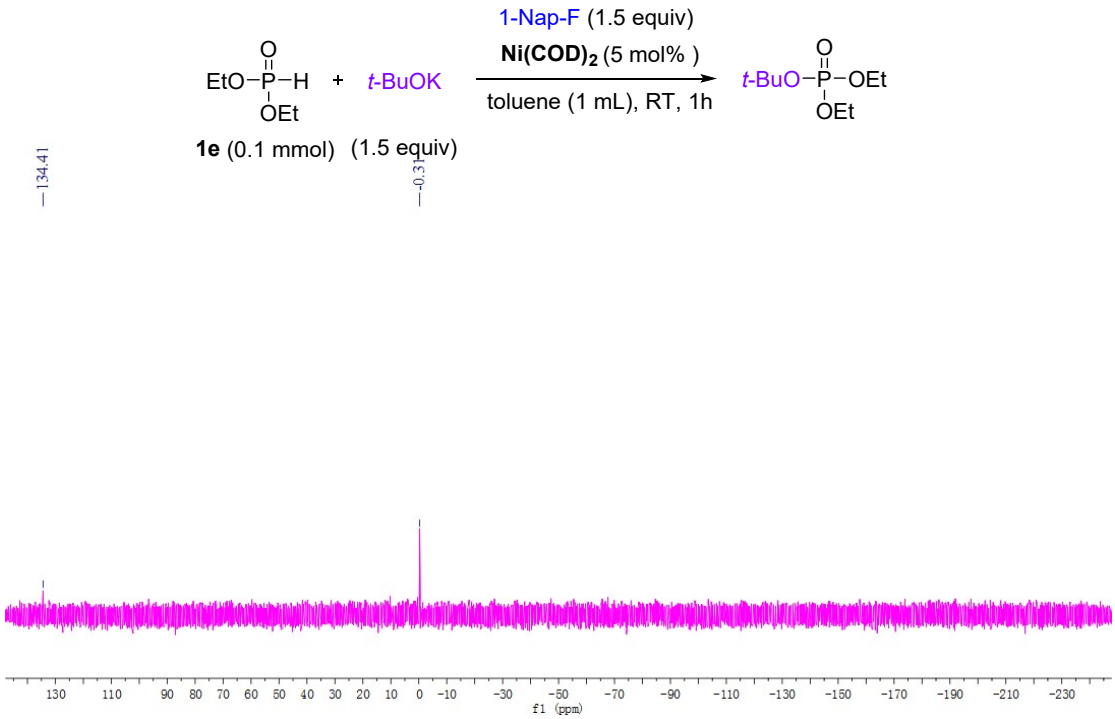


Figure S17. The formation of phosphate through diethyl phosphite at RT for 1h

Decomposition and formation of A

Coordination experiments between intermediate and Ni catalyst. When the catalytic amount $Ni(COD)_2$ of is used, the ^{31}P NMR spectrum is almost unchanged compared with that of pure intermediate **A**. A new signal peak appeared at 124.3 ppm through the addition of 1 equivalent catalyst. Further increasing the temperature to 60 ºC could enhance the coordination between **A** and Ni catalyst (Figure S18).

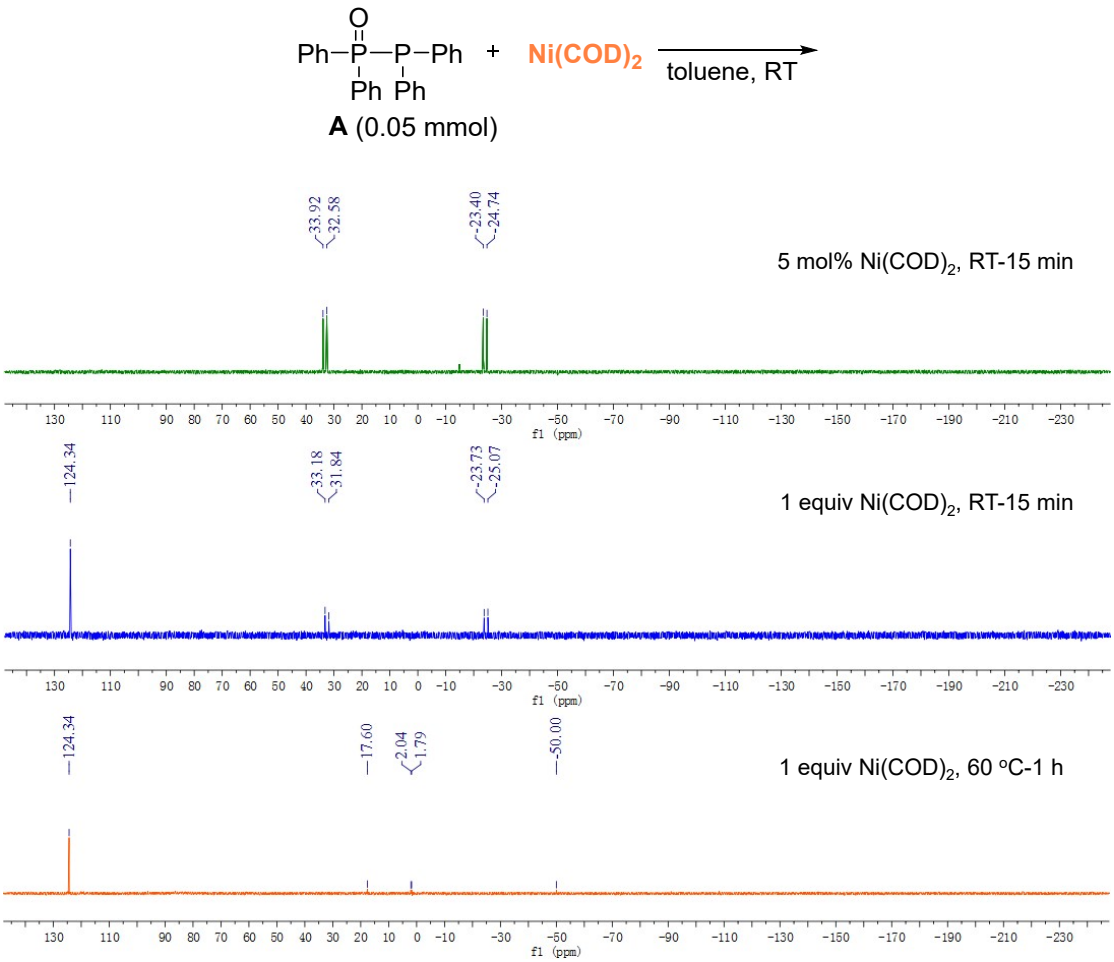


Figure S18. The reaction of **A** with catalyst

Decomposition of A. At room temperature, tetraphenyldiphosphine monoxide decomposed rapidly in the promotion of *t*-BuOK, forming Ph_2POK, $Ph_2P(O)OBu$-*t*, Ph_2PK and $Ph_2P(O)Bu$-*t*. When **2a**, and catalytic amount of $Ni(COD)_2$ was added, a slight change was observed in the ^{31}P NMR spectroscopy. Signals of $Ph_2P(O)Bu$-*t* disappeared and a new peak at -22.2 ppm was appeared which may be the coordinative complex of $Ni(COD)_2$ with Ph_2PK (Figure S19).

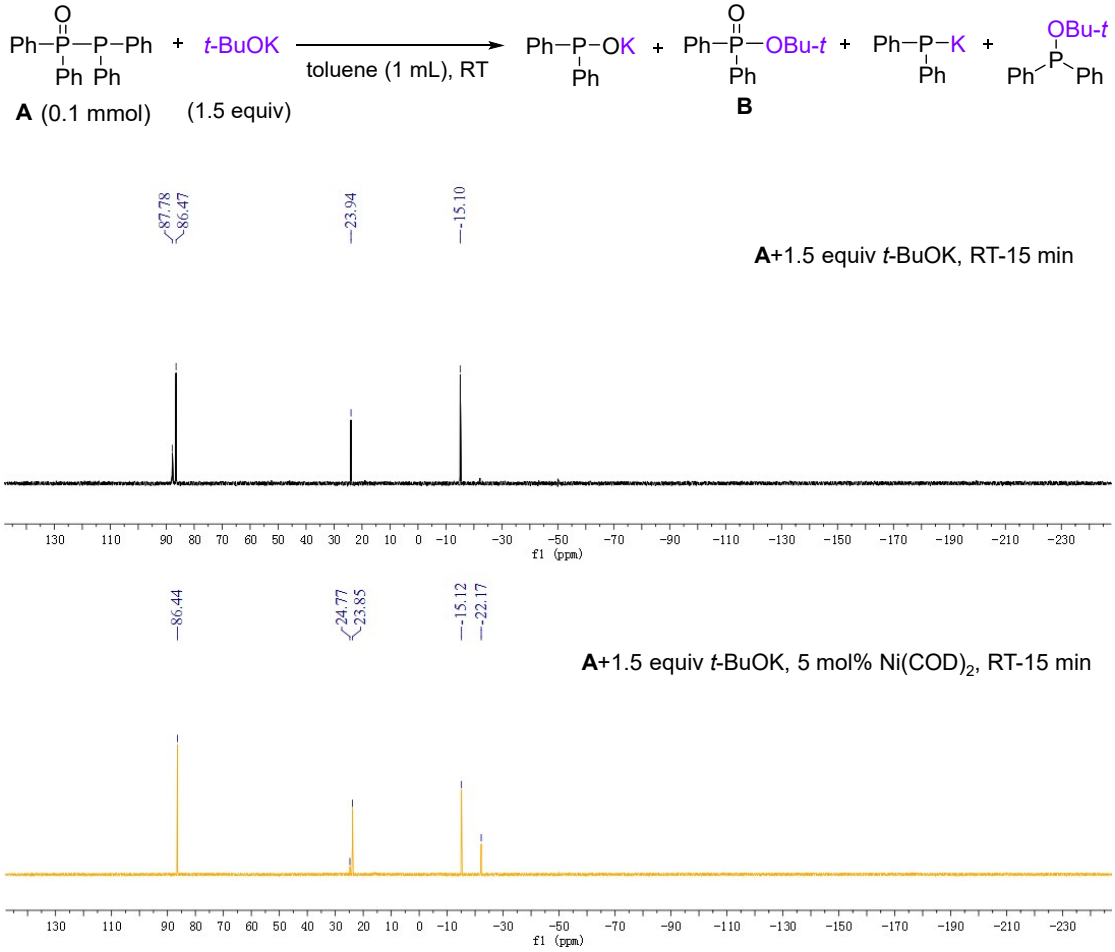
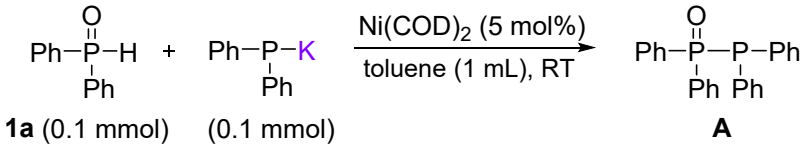


Figure S19. The decomposition of **A**

Formation of A. Ph_2PK reacted with **1a** could produce trace amount of tetraphenyldiphosphine monoxide **A**, while when $Ni(COD)_2$ was added, the reaction efficiency was improved, demonstrating Ni catalyst performed crucial impact in the production of **A** (Figure S20).



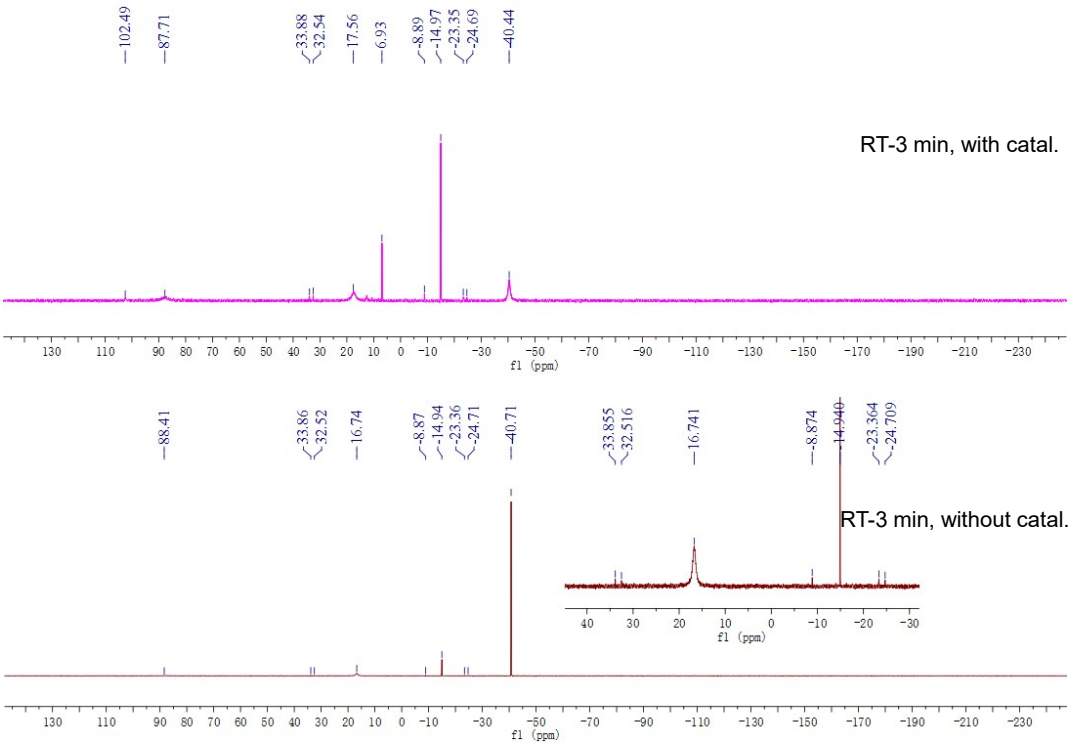
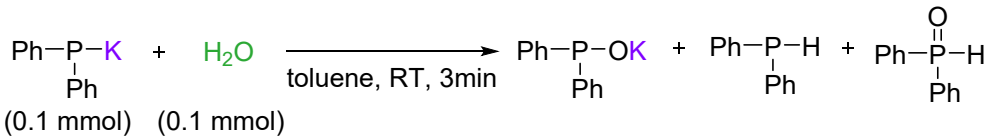


Figure S20. The formation of intermediate A through **1a** and Ph_2PK



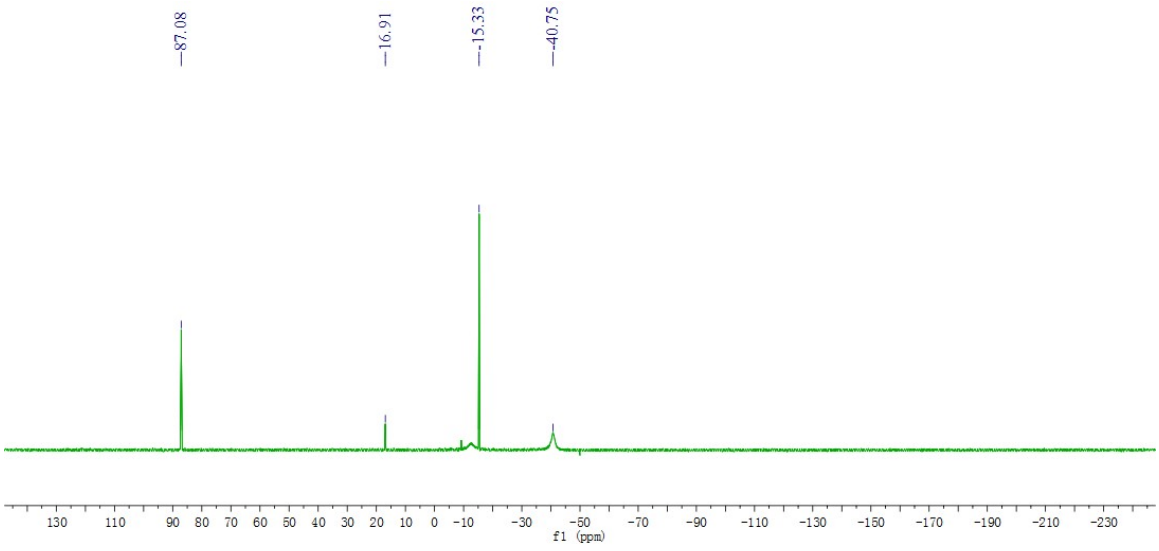


Figure S21. The reaction of H_2O and Ph_2PK

The reaction of Ph_2PK with H_2O was monitored by ^{31}P NMR spectroscopy, Ph_2POK, $Ph_2P(O)H$ and Ph_2PH were observed (Figure S21).

Intermediate **A** can be formed when Ph_2PK and $Ph_2P(O)OBu$-*t* was mixed in toluene for a few minutes, which decomposed with the prolongation of reaction time (Figure S22).

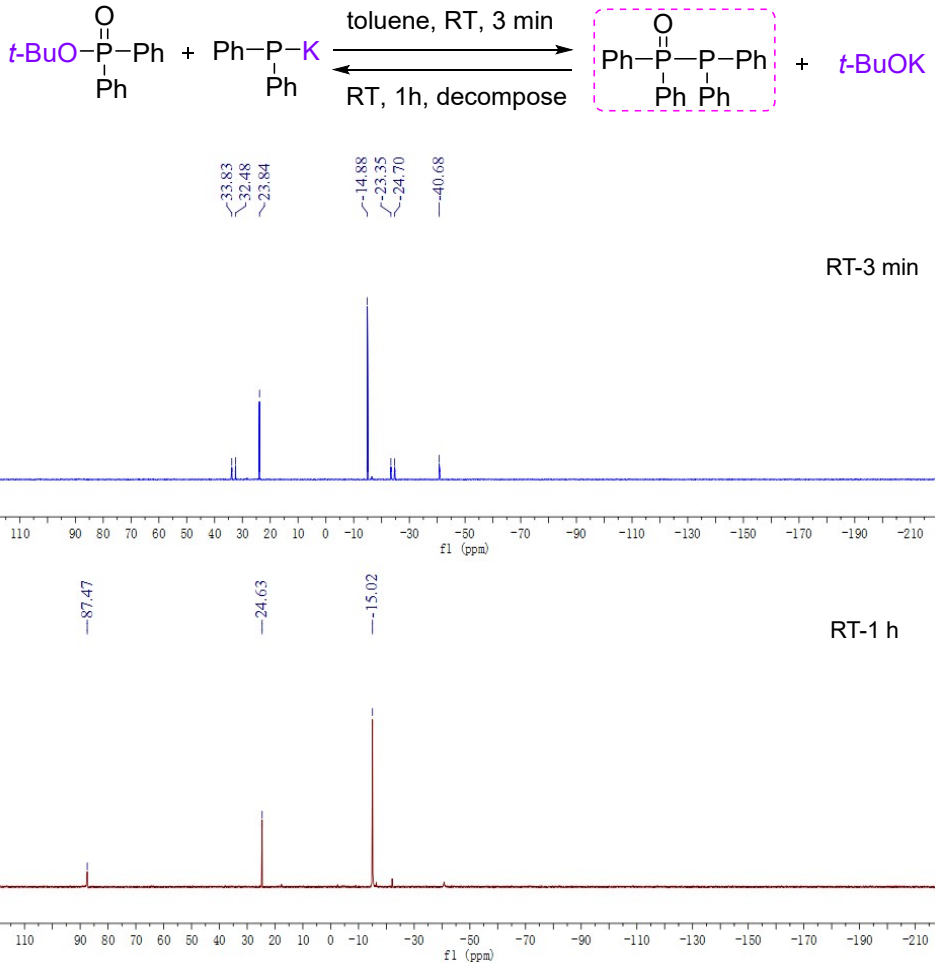
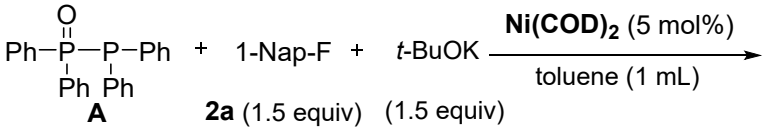


Figure S22. The reaction of $Ph_2P(O)OBu$-*t* with Ph_2PK

Reaction of A with 2a.

A decomposed rapidly in the presence of *t*-BuOK, and the cross-coupling reaction took place between **A** and **2a** with trace amount of the C−F phosphorylation product were detected at room temperature for 15 min. When the temperature was improved to 130 ºC, both pentavalent and trivalent phosphorus product peaks appear in the ^{31}P NMR spectrum. In addition to the corresponding C−F functionalization products, a small amount of triphenyl phosphine was detected under the conditions of Ni catalysis (Figure S23).



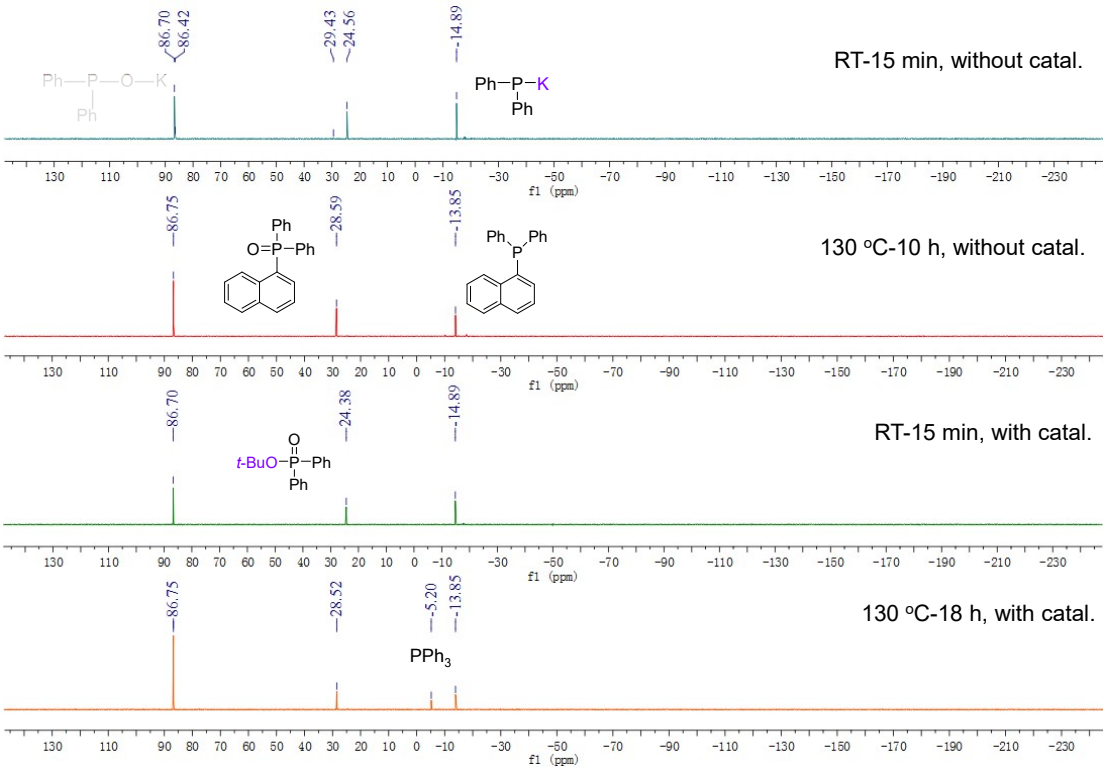
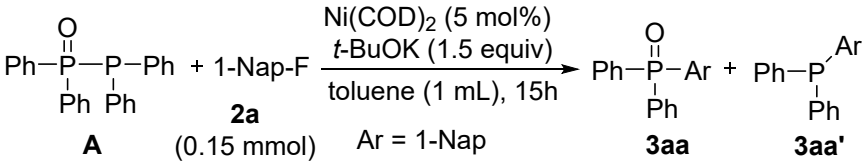


Figure S23. The reaction of **A**, **2a** and *t*-BuOK with or without catalyst

Performing the reaction of **A** (0.05 mmol), **2a** (0.15 mmol), and *t*-BuOK (0.15 mmol) in toluene at room temperature, trace amount of C−F activation products were prepared. Raising the temperature to 130 ºC delivered product **3aa** in 42% yield, **3aa'** in 9% yield, respectively. Similar results were obtained in the presence of $Ni(COD)_2$, indicating that Ni catalyst presented unconspicuous promotion in the C−F phosphorylation between **A** and **2a** (Table S1).

Table S1 Reaction of **A** with aryl fluorides

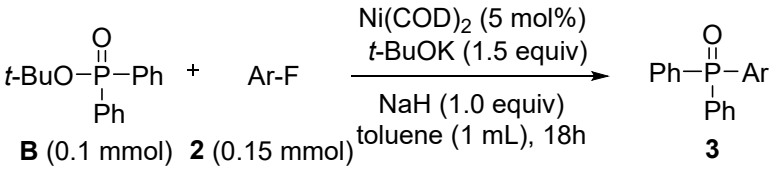


entry	Ni cat.	**A**	Temp.	yield (%)	
				3aa	**3aa'**
1	---	0.1 mmol	RT	trace	trace
2	$Ni(COD)_2$	0.1 mmol	130°C	39%	19%
3[a]	---	0.05 mmol	130°C	41%	12%
4[a]	$Ni(COD)_2$	0.05 mmol	130°C	42%	9%

[a] 3.0 equiv *t*-BuOK.

In addition, intermediate **B** reacted with **2a** smoothly in the promotion of *t*-BuOK and NaH with $Ni(COD)_2$, afforded **3aa** in 75% yield (Table S2, entry 1). However, 48% yield of C-F phosphorylation product **3ac** was prepared via the reaction of **1a** with 4-fluoroanisole **2c**, which exhibited a significant decrease of the reactivity without the use of $Ni(COD)_2$, indicating that Ni catalyst could reduce the activation energy of the inactive C–F bond (Table S2).

Table S2 Reaction of **B** with aryl fluorides

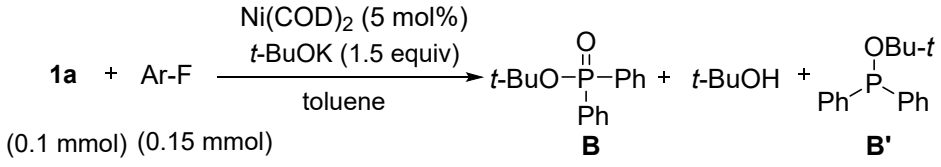


B (0.1 mmol) **2** (0.15 mmol) **3**

entry	Ni cat.	Ar	Temp.	**3**
1	$Ni(COD)_2$	1-Nap	130°C	75%
2	---	1-Nap	130°C	72%
3	$Ni(COD)_2$	1-Nap	30°C	trace
4	$Ni(COD)_2$	4-MeO-Ph	130°C	48%
5	---	4-MeO-Ph	130°C	9%
6	$Ni(COD)_2$	4-MeO-Ph	30°C	n.d.

Through gas chromatography monitoring, it was found that tert butyl alcohol could be detected in the reaction solution at room temperature or 120 ºC (Table S3).

Table S3 Detection of **B**, **B'** and *t*-BuOH



(0.1 mmol) (0.15 mmol) **B** **B'**

entry	Ni cat. (5 mol%)	Ar	Temp.	**B**	**B'**	*t*-BuOH
1	$Ni(COD)_2$	1-Nap	RT, 10min	trace	---	√
2	$Ni(COD)_2$	1-Nap	120°C, 2h	trace	√	√
3	$Ni(COD)_2$	4-MeO-Ph	RT, 10min	√	---	√
4	$Ni(COD)_2$	4-MeO-Ph	120°C, 2h	√	---	√

Competitive experiment.

The mixture of 0.1 mmol **1a**, 0.1 mmol **1e**, 0.3 mmol **2a**, 10 mol% $Ni(COD)_2$, 0.3 mmol *t*-BuOK in 2 mL toluene was heated in 130 °C for 18 h, and the yield of the two corresponding products decreased significantly (**3aa** in 25% GC yield, **3aa'** in 8% GC yield, **3ea** in 3% GC yield). The presence of the two P(O)–H compounds is not conductive to the formation of the intermediate and

the activation of C−F bond. ^{31}P NMR detection of the competitive reaction showed that the signals of Ph_2POK is dominant when the reaction mixture was heated in 130°C for 2 h or 18 h, while trace amount of Ph_2POK was presented in NMR spectra without the addition of $(EtO)_2P(O)H$ (Figure S9). In terms of the effect of competitive reaction, the reaction between diphenyl phosphine oxide and 1-Nap-F is dominant in this competitive system, and the role of diethyl phosphite in the mixed system will continue to be explored.

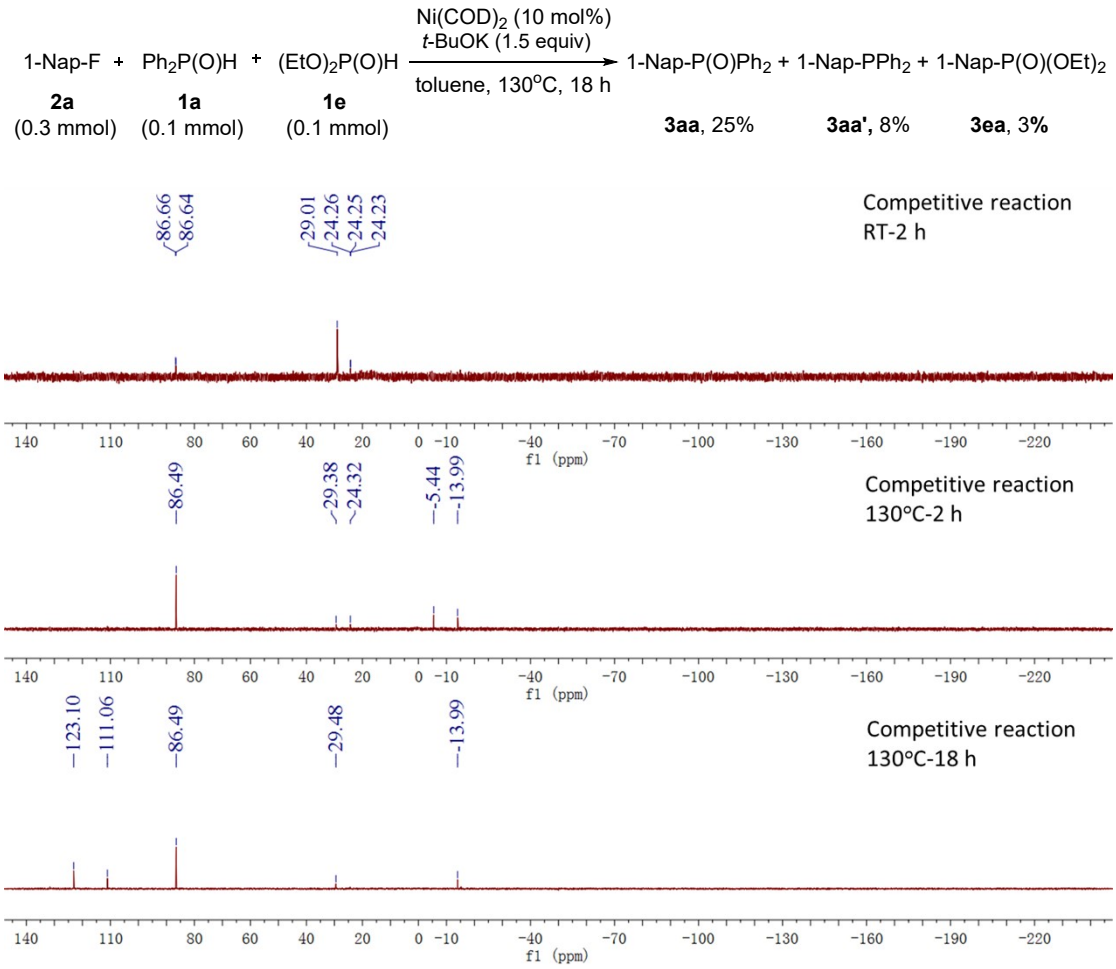
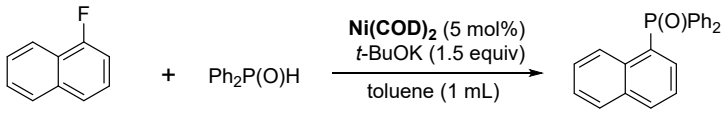


Figure S24. ^{31}P NMR spectra of competitive reactions

5. Reaction Optimization

Table S4 Ni-catalyzed cross-coupling reactions of **1a** with **2a**

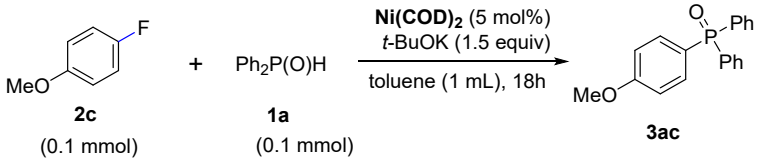


2a (0.15 mmol) **1a** (0.1 mmol) **3aa**

Entry	Catalyst	Base	Time	Temp(ºC)	Yield(%)
1	--	*t*-BuOK	18	140	77
2	--	*t*-BuOK	18	130	78
3	--	*t*-BuOK	18	110	67
4	--	*t*-BuOK	18	90	26
5	--	*t*-BuOK	18	60	n.d.
6	--	*t*-BuOK	12	130	51
7	--	*t*-BuOK	6	130	17
8	--	*t*-BuOK	2	130	6
9	--	*t*-BuONa	18	130	n.d.
10	$Ni(COD)_2$	--	18	130	n.d.
11	**$Ni(COD)_2$**	***t*-BuOK**	**18**	**130**	**91**
12	$Ni(COD)_2$	*t*-BuOK	18	110	85
13	$Ni(COD)_2$	*t*-BuOK	18	100	83
14	$Ni(COD)_2$	*t*-BuOK	18	80	65
15	$Ni(COD)_2$	*t*-BuOK	18	40	trace
16	$Ni(COD)_2$	*t*-BuOK	12	130	83
17	$Ni(COD)_2$	*t*-BuOK	10	130	71
18	$Ni(COD)_2$	*t*-BuOK	6	130	58
19	$Ni(COD)_2$	*t*-BuOK	2	130	37
20	$Ni(COD)_2$	*t*-BuOK	1	130	27
21	$Ni(COD)_2$	*t*-BuOK	15min	130	13
22[a]	$Ni(COD)_2$	*t*-BuOK	18	130	80
23[b]	$Ni(COD)_2$	*t*-BuOK	18	130	35

[a] 1.0 equiv base. [b] 0.5equiv base.

Table S5 Ni-catalyzed cross-coupling reactions of 4-fluoroanisole with **1a**

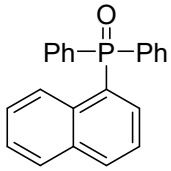


2c (0.1 mmol) + **1a** (0.1 mmol) → **3ac**

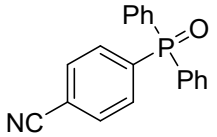
Entry	Catalyst	Base	Solvent	Temp(ºC)	Yield(%)[b]
1	$Ni(COD)_2$	*t*-BuONa	toluene	120	46
2	$Ni(COD)_2/PPh_3$	*t*-BuONa	toluene	120	46
3	$Ni(COD)_2$/dppp	*t*-BuONa	toluene	120	33
4	$Ni(COD)_2$/dppf	*t*-BuONa	toluene	120	40
5	--	*t*-BuONa	toluene	120	n.d.
6	$Ni(COD)_2$	--	toluene	120	n.d.
7	$Ni(COD)_2$	*t*-BuOK	toluene	120	65
8	$Ni(COD)_2$	*t*-BuOLi	toluene	120	14
9	$Ni(COD)_2$	Cs_2CO_3	toluene	120	n.d.
10	$Ni(COD)_2$	K_3PO_4	toluene	120	n.d.
11	$Ni(COD)_2$	*t*-BuOK	dioxane	120	57
12	$Ni(COD)_2$	*t*-BuOK	THF	120	46
13	$Ni(COD)_2$	*t*-BuOK	DMA	120	n.d.
14	$Ni(COD)_2$	*t*-BuOK	DMF	120	n.d.
15	$Ni(COD)_2$	*t*-BuOK	toluene	100	18
16	$Ni(COD)_2$	*t*-BuOK	toluene	130	70
17	$Ni(COD)_2$	*t*-BuOK	toluene	140	66
18[a]	$Ni(COD)_2$	*t*-BuOK	toluene	130	76
19[b]	**$Ni(COD)_2$**	***t*-BuOK**	**toluene**	**130**	**81**
20	--	*t*-BuOK	toluene	150	n.d.

[a] 0.15 mmol of **2a**. [b] 0.2 mmol of **2a**.

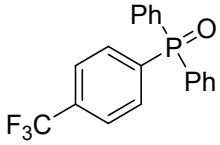
6. Characterization and Analytical Data of Products 3



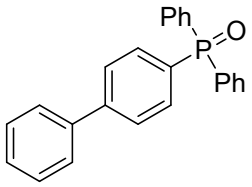
Naphthalen-1-yldiphenylphosphine oxide (3aa).[6] Yield: 91%, 60 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.58 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.71–7.66 (m, 4H), 7.57–7.44 (m, 8H), 7.42–7.36 (m, 1H), 7.337.27 (m, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 132.9 (d, $J_{C\text{-}P}$ = 10.2 Hz), 132.8 (d, $J_{C\text{-}P}$ = 11.9 Hz), 132.7 (d, $J_{C\text{-}P}$ = 8.0 Hz), 132.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 104.3 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.8 Hz), 130.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 127.84 (d, $J_{C\text{-}P}$ = 101.6 Hz), 127.75 (d, $J_{C\text{-}P}$ = 0.9 Hz), 127.6 (d, $J_{C\text{-}P}$ = 12.1 Hz), 126.6 (d, $J_{C\text{-}P}$ = 5.7 Hz), 126.3, 125.5, 123.1 (d, $J_{C\text{-}P}$ = 14.2 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 32.49. MS (EI): 328.



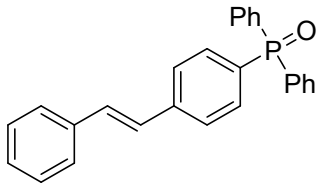
4-(Diphenylphosphoryl)benzonitrile (3ab).[7] Yield: 50%, 30 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ7.75–7.66 (m, 4H), 7.59–7.49 (m, 6H), 7.43–7.39 (m, 4H). ^{13}C NMR (100 MHz $CDCl_3$): δ 138.4 (d, $J_{C\text{-}P}$ = 98.7 Hz), 132.63 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.60 (d, $J_{C\text{-}P}$ = 3.1 Hz), 132.03 (d, $J_{C\text{-}P}$ = 12.0 Hz), 131.99 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 104.9 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.2 Hz), 117.9, 115.6 (d, $J_{C\text{-}P}$ = 1.9 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 28.00. MS (EI): 302.



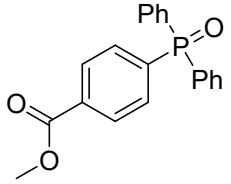
Diphenyl(4-(trifluoromethyl)phenyl)phosphine oxide (3ae).[6] Yield: 26%, 18 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.85–7.80 (m, 2H), 7.74–7.64 (m, 6H), 7.60–7.56 (m, 2H), 7.51–7.47 (m, 4H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.2 (d, $J_{C\text{-}P}$ = 100.5 Hz), 133.7 (dq, $J_{C\text{-}P}$ = 2.8 Hz, $J_{C\text{-}F}$ = 32.6 Hz), 132.6 (d, $J_{C\text{-}P}$ = 10.0 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.6 (d, $J_{C\text{-}P}$ = 104.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.3 Hz), 125.3 (dq, $J_{C\text{-}P}$ = 11.5 Hz, $J_{C\text{-}F}$ = 3.7 Hz), 123.6 (q, $J_{C\text{-}F}$ = 271.4 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 28.08. MS (EI): 345.



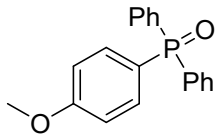
(1,1'-Biphenyl)-4-yldiphenylphosphine oxide (3ad).[6] Yield: 76%, 54 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.77–7.64 (m, 8H), 7.61–7.52 (m, 4H), 7.50–7.43 (m, 6H), 7.40–7.36 (m, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 144.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 139.9 (d, $J_{C\text{-}P}$ = 0.9 Hz), 132.6 (d, $J_{C\text{-}P}$ = 10.1 Hz), 132.6 (d, $J_{C\text{-}P}$ = 105.4 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.8 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 104.6 Hz), 129.0, 128.6 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.7 (d, $J_{C\text{-}P}$ = 104.8 Hz), 127.3 (d, $J_{C\text{-}P}$ = 13.7 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 29.05. MS (EI): 354.



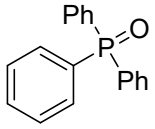
(E)-diphenyl(4-styrylphenyl)phosphine oxide (3af).[8] Yield: 67%, 51 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.61–7.52 (m, 6H), 7.47–7.32 (m, 10H), 7.23 (d, J = 7.6 Hz, 2H), 7.17–7.13 (m, 1H), 7.10–6.96 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 141.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 136.7, 132.6 (d, $J_{C\text{-}P}$ = 103.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 10.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.4, 131.2 (d, $J_{C\text{-}P}$ = 105.1 Hz), 128.8, 128.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.3, 127.4 (d, $J_{C\text{-}P}$ = 1.4 Hz), 126.8, 126.5 (d, $J_{C\text{-}P}$ = 12.4 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 28.99. MS (EI): 380.



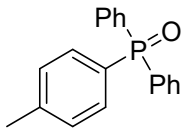
Methyl 4-(diphenylphosphoryl)benzoate (3ag).[9] Yield: 63%, 42 mg. Yellow liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.13–8.11 (m, 2H), 7.77 (dd, J = 8.4 Hz, J = 11.2 Hz, 2H), 7.69–7.64 (m, 4H), 7.59–7.55 (m, 2H), 7.50–7.47 (m, 4H), 3.94 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 166.2, 137.6 (d, $J_{C\text{-}P}$ =100.4 Hz), 133.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 132.2, 132.0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.8 (d, $J_{C\text{-}P}$ = 105.5 Hz), 129.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.2 Hz), 52.5. ^{31}P NMR (162 MHz $CDCl_3$): δ 28.43. MS (EI): 336.



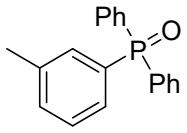
(4-Methoxyphenyl)diphenylphosphine oxide (3ac).[6] Yield: 81%, 50 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.60–7.55 (m, 4H), 7.52–7.48 (m, 2H), 7.46–7.42 (m, 2H), 7.38–7.34 (m, 4H), 6.88 (dd, J = 2.0 Hz, J = 8.8 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 162.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 134.0 (d, $J_{C\text{-}P}$ = 11.2 Hz), 132.8 (d, $J_{C\text{-}P}$ = 103.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 9.8 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 123.4 (d, $J_{C\text{-}P}$ = 109.9 Hz), 114.1 (d, $J_{C\text{-}P}$ = 13.1 Hz), 55.4. ^{31}P NMR (162 MHz $CDCl_3$): δ 29.33. MS (EI): 307.



Triphenylphosphine oxide (3ah).[6] Yield: 75%, 42 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.70–7.65 (m, 6H), 7.53–7.49 (m, 3H), 7.45–7.41 (m, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ 132.5 (d, $J_{C\text{-}P}$ = 103.5 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.9, 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 28.97. MS (EI): 277.

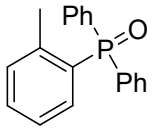


Diphenyl(p-tolyl)phosphine oxide (3ai).[6] Yield: 77%, 45 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.69–7.64 (m, 4H), 7.58–7.51 (m, 4H), 7.47–7.43 (m, 4H), 7.28–7.26 (m, 2H) , 2.40 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 142.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.9 (d, $J_{C\text{-}P}$ = 103.4 Hz), 132.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 129.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 129.2 (d, $J_{C\text{-}P}$ = 105.9 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 21.6 (d, $J_{C\text{-}P}$ = 1.2 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 29.10. MS (EI): 291.

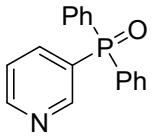


Diphenyl(o-tolyl)phosphine oxide (3aj).[6] Yield: 60%, 35 mg.White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.69–7.65 (m, 4H), 7.59–7.52 (m, 3H), 7.48–7.43 (m, 4H), 7.40–7.32 (m, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 138.5 (d, $J_{C\text{-}P}$ = 11.9 Hz), 132.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.7 (d,

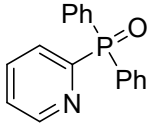
$J_{C\text{-}P}$ = 105.1 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.4 Hz), 132.3 (d, $J_{C\text{-}P}$ = 103.1 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.8 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.6 Hz), 129.2 (d, $J_{C\text{-}P}$ = 10.2 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.9 Hz), 21.4. ^{31}P NMR (162 MHz $CDCl_3$): δ 29.36. MS (EI): 291.



Diphenyl(o-tolyl)phosphine oxide (3ak).[6] Yield: 78%, 45 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.57 (dd, J = 6.8 Hz, J = 12.0 Hz, 4H), 7.48–7.45 (m, 2H), 7.41–7.37 (m, 4H), 7.36–7.32 (m, 1H), 7.20 (dd, J = 4.8 Hz, J = 7.2 Hz, 1H), 7.05 (t, J = 7.2 Hz, 1H), 6.94 (dd, J = 7.6 Hz, J = 14.0 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 143.3 (d, $J_{C\text{-}P}$ = 8.1 Hz), 133.5 (d, $J_{C\text{-}P}$ = 12.8 Hz), 132.6 (d, $J_{C\text{-}P}$ = 103.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.3 Hz), 131.9 (d, $J_{C\text{-}P}$ = 9.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.7 (d, $J_{C\text{-}P}$ = 102.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.1 Hz), 125.2 (d, $J_{C\text{-}P}$ = 12.8 Hz), 21.7 (d, $J_{C\text{-}P}$ = 4.7 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 31.84. MS (EI): 291.

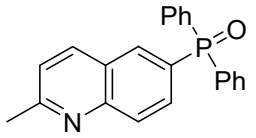


Diphenyl(pyridin-2-yl)phosphine oxide (3al).[10] Yield: 93%, 52 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.78–8.77 (m, 2H), 8.08–8.03 (m, 1H), 7.71–7.66 (m, 4H), 7.59–7.56 (m, 2H), 7.52–7.47 (m, 4H), 7.44–7.41 (m, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 152.6 (d, $J_{C\text{-}P}$ = 1.8 Hz), 152.5 (d, $J_{C\text{-}P}$ = 11.9 Hz), 139.7 (d, $J_{C\text{-}P}$ = 7.8 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.9 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.5 (d, $J_{C\text{-}P}$ = 105.1 Hz), 129.1 (d, $J_{C\text{-}P}$ = 100.3 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.3 Hz), 123.5 (d, $J_{C\text{-}P}$ = 9.0 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 26.61. MS (EI): 278.

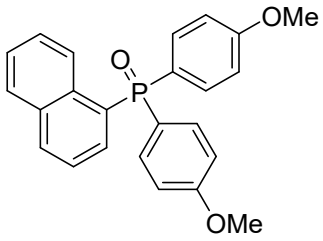


Diphenyl(pyridin-2-yl)phosphine oxide (3am).[7] Yield: 90%, 50 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.75 (d, J = 4.4 Hz, 1H), 8.29 (t, J = 6.8 Hz, 1H), 7.91–7.86 (m, 4H), 7.84–7.80 (m, 1H), 7.52–7.41 (m, 6H), 7.37–7.34 (m, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 156.4 (d, $J_{C\text{-}P}$ = 131.1 Hz), 150.1 (d, $J_{C\text{-}P}$ = 19.1 Hz), 136.2 (d, $J_{C\text{-}P}$ = 9.2 Hz), 132.2 (d, $J_{C\text{-}P}$ = 103.5 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 128.35 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.31 (d, $J_{C\text{-}P}$ = 18.7 Hz),

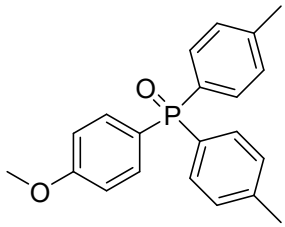
125.3 (d, $J_{C\text{-}P}$ = 3.1 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 20.97. MS (EI): 278.



Diphenyl(quinolin-3-yl)phosphine oxide (3an).[11] Yield: 65%, 45 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.23 (d, J = 13.2 Hz, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.74–7.69 (m, 1H), 7.65–7.60 (m, 4H), 7.49–7.44 (m, 2H), 7.41–7.37 (m, 4H), 7.27 (d, J = 8.4 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 161.6, 148.7 (d, $J_{C\text{-}P}$ = 1.9 Hz), 137.2, 133.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 132.2 (d, $J_{C\text{-}P}$ = 104.0 Hz), 132.18 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.8 (d, $J_{C\text{-}P}$ = 11.0 Hz), 129.5, 129.8 (d, $J_{C\text{-}P}$ = 103.0 Hz), 128.8 (d, $J_{C\text{-}P}$ = 14.2 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.1 Hz), 125.8 (d, $J_{C\text{-}P}$ = 13.6 Hz), 123.2, 25.4. ^{31}P NMR (162 MHz $CDCl_3$): δ 28.58. MS (EI): 343.

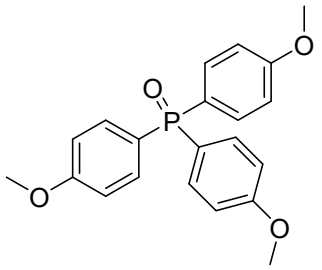


Bis(4-methoxyphenyl)(naphthalen-1-yl)phosphine oxide (3ba).[12] Yield: 70%, 54 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.61 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.61–7.56 (m, 4H), 7.50–7.29 (m, 4H), 6.96–6.94 (m, 4H), 3.82 (s, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ 162.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.93, 133.87 (d, $J_{C\text{-}P}$ = 11.2 Hz), 133.8 (d, $J_{C\text{-}P}$ = 13.4 Hz), 133.6 (d, $J_{C\text{-}P}$ = 11.7 Hz), 133.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 129.8 (d, $J_{C\text{-}P}$ = 101.9 Hz), 128.7 (d, $J_{C\text{-}P}$ = 0.8 Hz), 127.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 127.2, 126.4, 124.4 (d, $J_{C\text{-}P}$ = 110.5 Hz), 124.2 (d, $J_{C\text{-}P}$ = 14.1 Hz), 114.2 (d, $J_{C\text{-}P}$ = 13.2 Hz), 55.3. ^{31}P NMR (162 MHz $CDCl_3$): δ 32.21. MS (EI): 388.

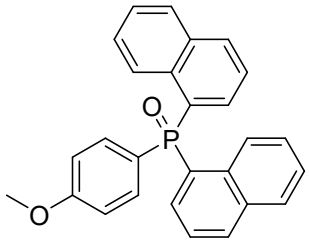


(4-Mehoxyphenyl)di-p-tolylphosphine oxide (3fc). Yield: 50%, 34 mg. White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.59–7.51 (m, 6H), 7.27–7.24 (m, 4H), 6.96–6.93 (m, 2H), 3.83 (s, 3H), 2.39 (s, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ 162.4 (d, $J_{C\text{-}P}$ = 1.0 Hz), 142.2 (d, $J_{C\text{-}P}$ = 0.9 Hz), 133.9 (d, $J_{C\text{-}P}$ = 11.2 Hz), 132.1 (d, $J_{C\text{-}P}$= 9.5 Hz), 129.9 (d, $J_{C\text{-}P}$ = 106.3 Hz), 129.2 (d, $J_{C\text{-}P}$ = 12.5 Hz), 124.2

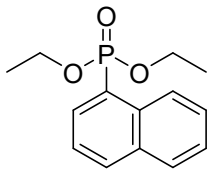
(d, $J_{C\text{-}P}$ = 109.7 Hz), 114.0 (d, $J_{C\text{-}P}$ = 13.0 Hz), 55.3 (d, $J_{C\text{-}P}$ = 0.9 Hz), 21.6. ^{31}P NMR (162 MHz $CDCl_3$): δ 29.19. MS (EI): 336.



Tris(4-methoxyphenyl)phosphine oxide (3bc).[13] Yield: 65%, 48 mg. White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, J = 8.8 Hz, J = 11.2 Hz, 6H), 6.95–6.93 (m, 6H), 3.81 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 133.8 (d, $J_{C\text{-}P}$ = 11.2 Hz), 124.3 (d, $J_{C\text{-}P}$ = 110.5 Hz), 114.0 (d, $J_{C\text{-}P}$ = 13.1 Hz), 55.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.27. MS (EI): 368.

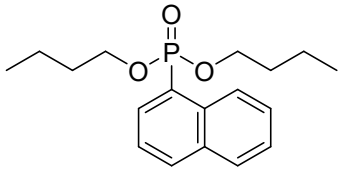


(4-Methoxyphenyl)di(naphthalen-1-yl)phosphine oxide (3cc). Yield: 51%, 41 mg. White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.62 (dd, J = 8.4 Hz, J = 11.2 Hz, 2H), 7.51–7.43 (m, 4H), 7.33–7.23 (m, 4H), 6.96–6.93 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 134.2 (d, $J_{C\text{-}P}$ = 11.1 Hz), 134.07 (d, $J_{C\text{-}P}$ = 3.0 Hz), 133.98 (d, $J_{C\text{-}P}$ = 4.0 Hz), 133.4 (d, $J_{C\text{-}P}$ = 11.9 Hz), 133.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 129.5 (d, $J_{C\text{-}P}$ = 102.0 Hz), 128.7, 128.0 (d, $J_{C\text{-}P}$ = 5.4 Hz), 127.4, 126.5, 124.3 (d, $J_{C\text{-}P}$ = 14.3 Hz), 123.8 (d, $J_{C\text{-}P}$ = 110.2 Hz), 114.3 (d, $J_{C\text{-}P}$ = 13.2 Hz), 55.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.07.

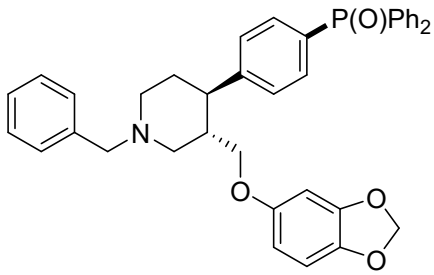


Diethyl naphthalen-1-ylphosphonate (3ea).[12] Yield: 82%, 43 mg. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 8.4 Hz, 1H), 8.26 (dd, J = 16.4, 7.2 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.60 (dd, J = 8.0Hz, J = 7.2Hz, 1H), 7.55-7.49 (m, 2H), 4.27-4.16 (m, 2H), 4.13–4.03 (m,2H) 1.30 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7 (d, $J_{C\text{-}P}$ =

9.1 Hz), 133.6 (d, $J_{C\text{-}P}$ = 3.5 Hz), 133.5, 132.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 128.8 (d, $J_{C\text{-}P}$ = 1.8 Hz), 127.4 (d, $J_{C\text{-}P}$=5.2 Hz), 126.6 (d, $J_{C\text{-}P}$ = 4.1 Hz), 126.4, 124.6 (d, $J_{C\text{-}P}$ = 181.5 Hz), 124.5 (d, $J_{C\text{-}P}$ = 16.5 Hz), 62.2 (d, $J_{C\text{-}P}$ = 5.2 Hz), 16.3 (d, $J_{C\text{-}P}$ = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.13. MS (EI): 264.

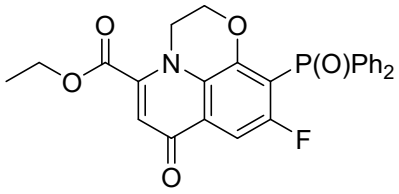


Dibutyl naphthalen-1-ylphosphonate (3ga).[12] Yield: 85%, 55 mg. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, J = 8.4 Hz, 1H), 8.24 (dd, J = 7.2, J =16.4Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.62–7.50 (m, 3H), 4.18–4.10 (m, 2H), 4.04–3.96 (m, 2H), 1.67−1.60 (m, 4H), 1.41–1.32 (m, 4H), 0.86 (t, J = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6 (d, $J_{C\text{-}P}$ = 9.2Hz), 133.7, 133.6 (d, $J_{C\text{-}P}$ = 3.5 Hz), 132.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 128.7 (d, $J_{C\text{-}P}$ = 1.7 Hz), 127.3, 126.7 (d, $J_{C\text{-}P}$ = 4.1 Hz), 126.3, 124.7 (d, $J_{C\text{-}P}$ = 181.7 Hz), 124.5 (d, $J_{C\text{-}P}$ = 16.5 Hz), 65.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 32.4 (d, $J_{C\text{-}P}$ = 6.6 Hz), 18.8, 13.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.32. MS (EI): 321.



(4-((3S,4R)-3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-1-benzylpiperidin-4-yl)phenyl)diphenylphosphine oxide (3ao). Yield: 55%, 33 mg. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.63 (m, 4H), 7.58–7.44 (m, 9H), 7.35–7.29 (m, 6H), 6.60 (d, J = 8.4 Hz, 1H), 6.29 (d, J = 2.4 Hz, 1H), 6.08 (dd, J = 2.4 Hz, J = 8.4 Hz, 1H), 5.87 (s, 2H), 3.69–3.53 (m, 3H), 3.44 (dd, J = 6.4 Hz, J = 8.8 Hz, 1H), 3.26 (d, J = 10.0 Hz, 1H), 3.04 (d, J = 10.4 Hz, 1H), 2.60–2.55 (m, 1H), 2.30 (br, 1H), 2.23–2.09 (m, 2H), 1.93–1.80 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 154.3, 148.2, 141.6, 132.6 (d, $J_{C\text{-}P}$ = 5.3 Hz), 132.5 (d, $J_{C\text{-}P}$ = 105.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.6, 130.0 (d, $J_{C\text{-}P}$ = 102.5 Hz), 130.0, 129.4, 128.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.3, 127.9 (d, $J_{C\text{-}P}$ = 12.3 Hz), 127.3 (d, $J_{C\text{-}P}$ = 4.0 Hz), 107.8, 105.5, 101.1, 98.0, 69.5, 63.2, 57.3, 53.6, 44.8, 41.6, 33.8. ^{31}P NMR (162 MHz $CDCl_3$): δ 29.07. HRMS

(ESI): Cal. for $C_{38}H_{36}N_1O_4P_1$ ([M+H]$^+$): 602.2382. Found: 602.2350.



Ethyl-10-(diphenylphosphoryl)-9-fluoro-7-oxo-2,3-dihydro-7H-[1,4]oxazino[2,3,4-i*J*]quinoline-5-carboxylate (3ap). Yield: 50%, 24 mg. Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.78–7.69 (m, 4H), 7.61–7.45 (m, 7H), 4.36 (d, J = 6.8 Hz, 2H). 4.11–3.99 (m, 2H), 1.46 (d, J = 8.0 Hz, 2H), 1.39 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2 (d, $J_{C\text{-}P}$ = 2.3 Hz), 165.1, 160.0 (d, $J_{C\text{-}F}$ = 251.9 Hz), 149.8 (d, $J_{C\text{-}P}$ = 7.0 Hz), 145.5, 133.4 (d, $J_{C\text{-}P}$ = 110.2 Hz), 133.1 (d, $J_{C\text{-}P}$ = 9.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (dd, $J_{C\text{-}P}$ = 10.3 Hz, $J_{C\text{-}F}$ = 11.5 Hz), 131.0 (t, $J_{C\text{-}P}$ = 10.2 Hz), 128.6 (dd, $J_{C\text{-}F}$ = 4.1 Hz, $J_{C\text{-}F}$ = 12.8 Hz), 123.1 (dd, $J_{C\text{-}F}$ = 2.1 Hz, $J_{C\text{-}P}$ = 7.9 Hz), 113.0 (dd, $J_{C\text{-}F}$ = 21.6 Hz, $J_{C\text{-}P}$ = 92.1 Hz), 111.1, 105.7 (dd, $J_{C\text{-}P}$ = 5.2 Hz, $J_{C\text{-}F}$ = 26.7 Hz), 68.3, 61.1, 54.5, 18.2, 14.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.96. ^{19}F NMR (377 MHz, $CDCl_3$): δ -101.31. HRMS (ESI): Cal. for $C_{26}H_{22}F_1N_1O_5P_1$ ([M+H]$^+$) : 478.1214. Found: 478.1208.

7. Rerferences

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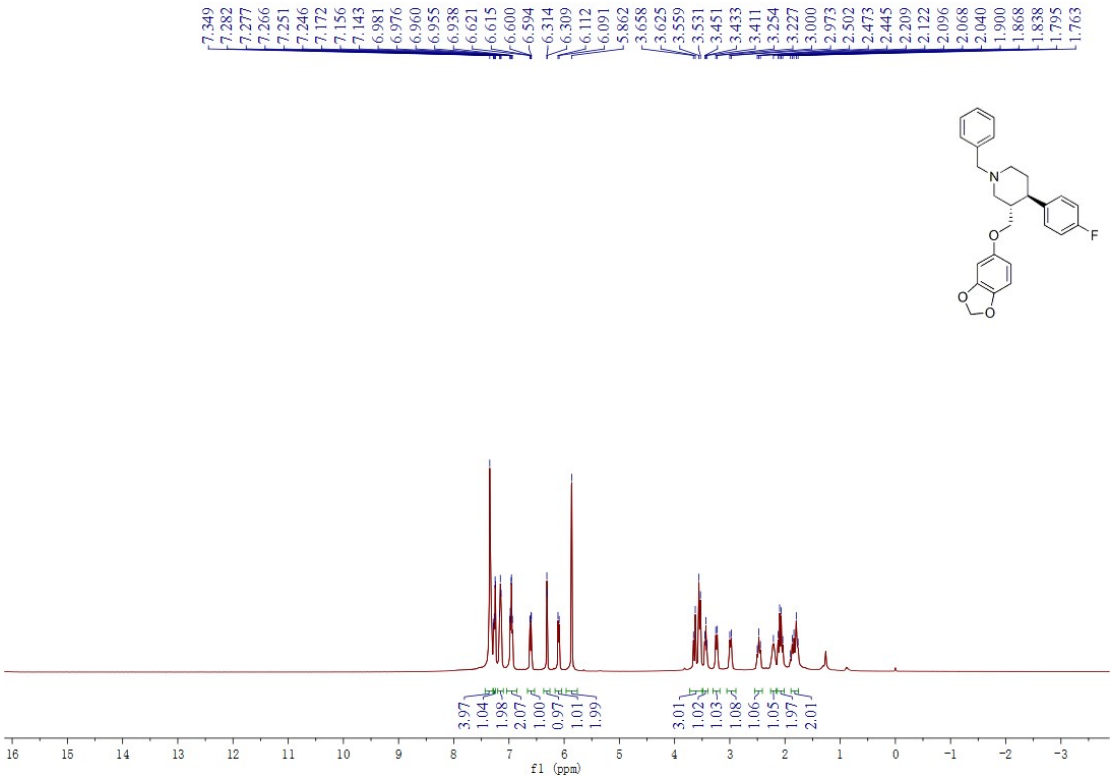
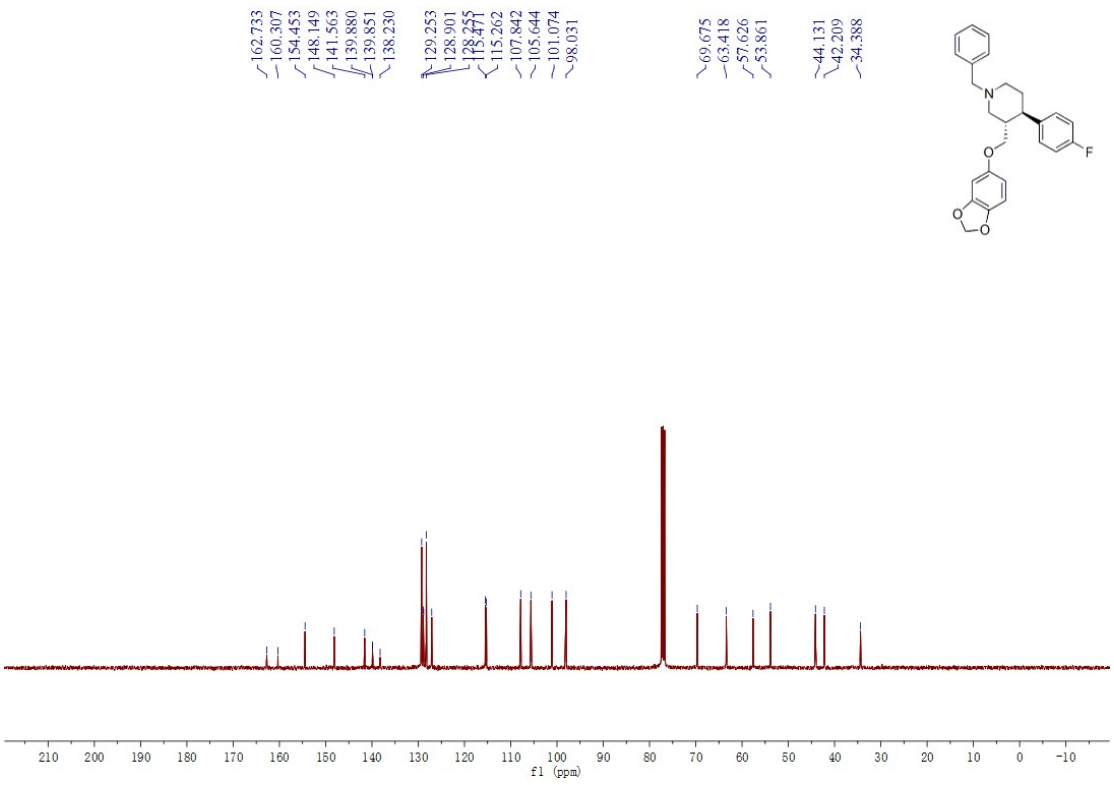
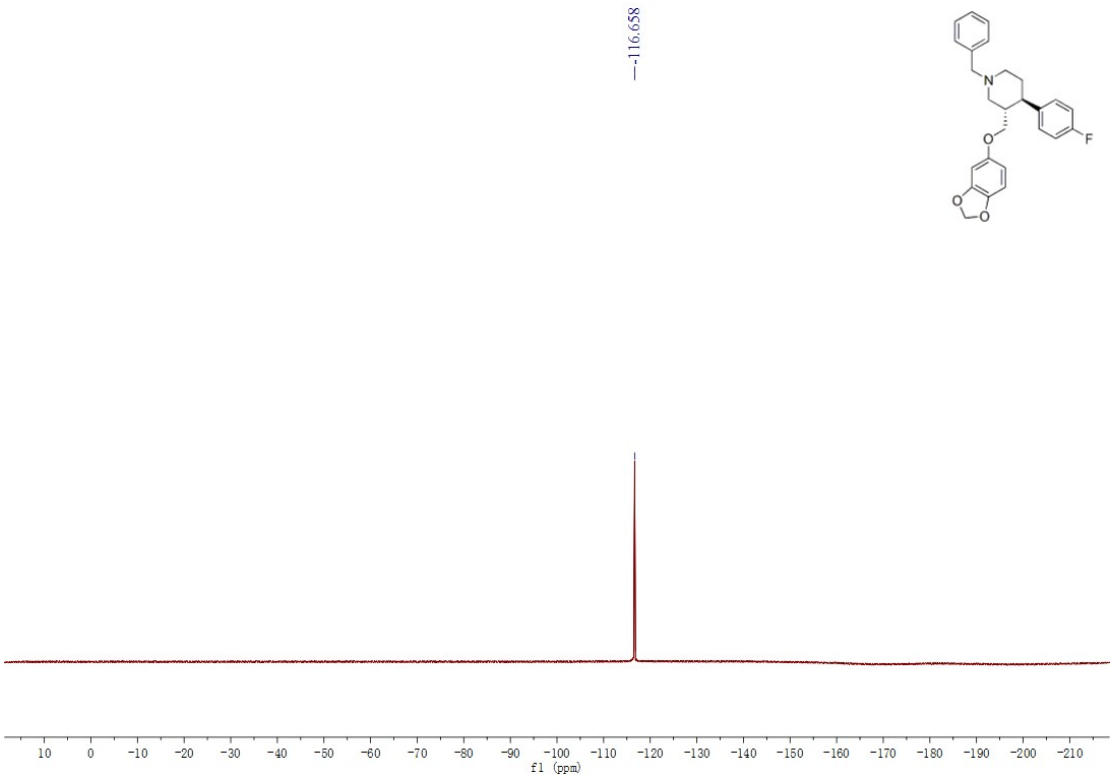
8. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra



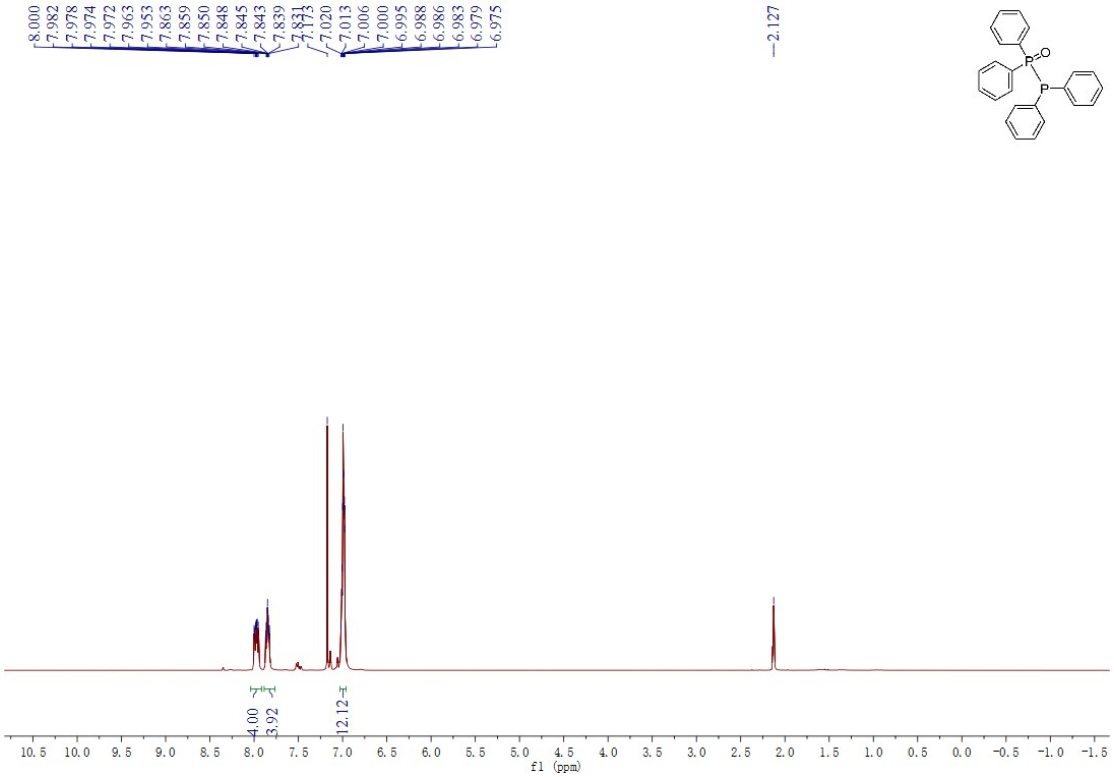
^{1}H NMR spectrum of **2o** in $CDCl_3$



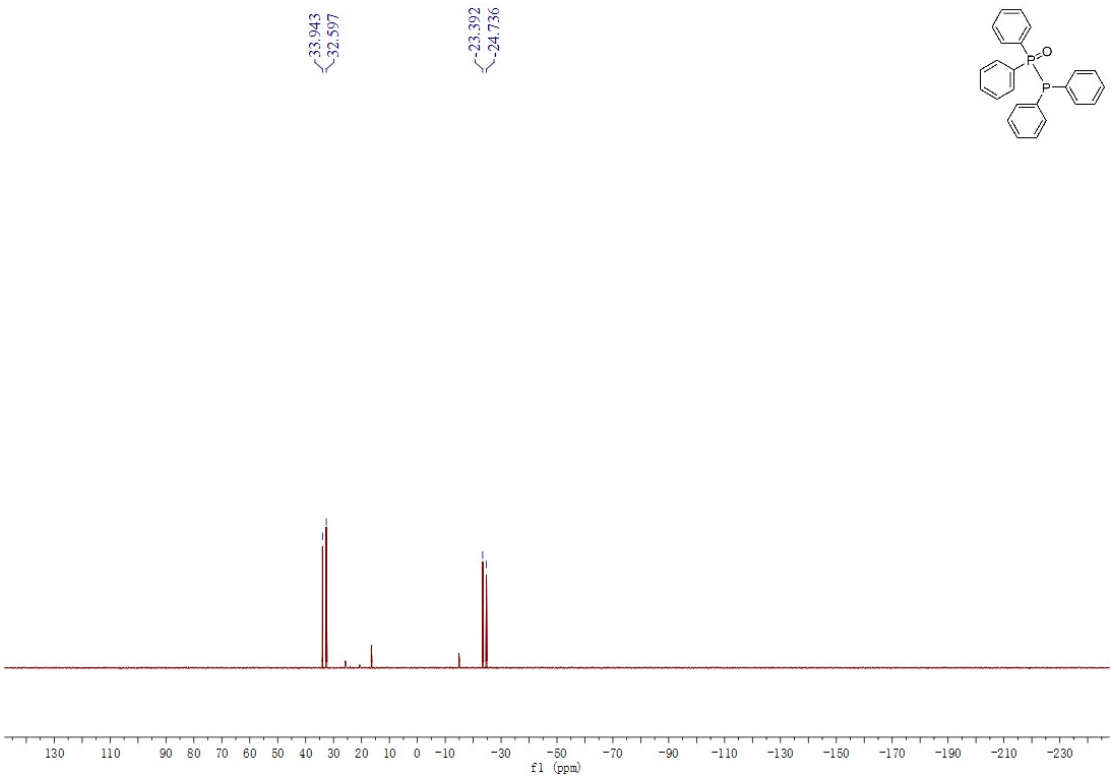
^{13}C NMR spectrum of **2o** in $CDCl_3$



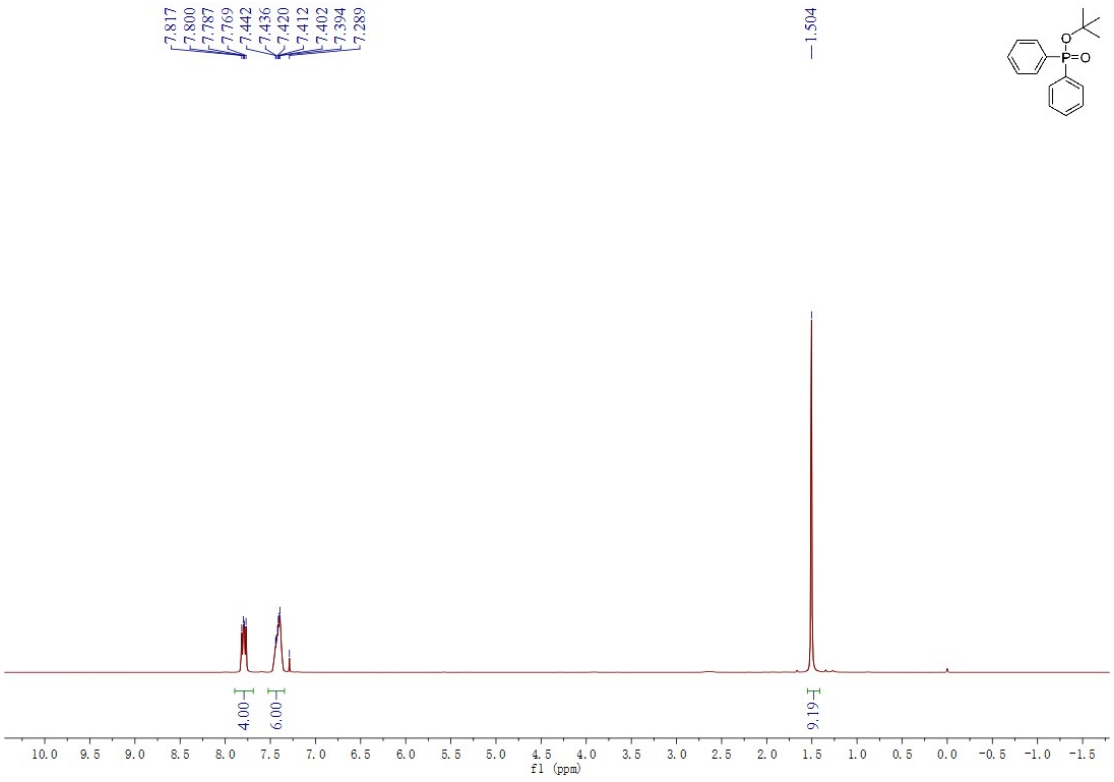
^{19}F NMR spectrum of **2o** in $CDCl_3$



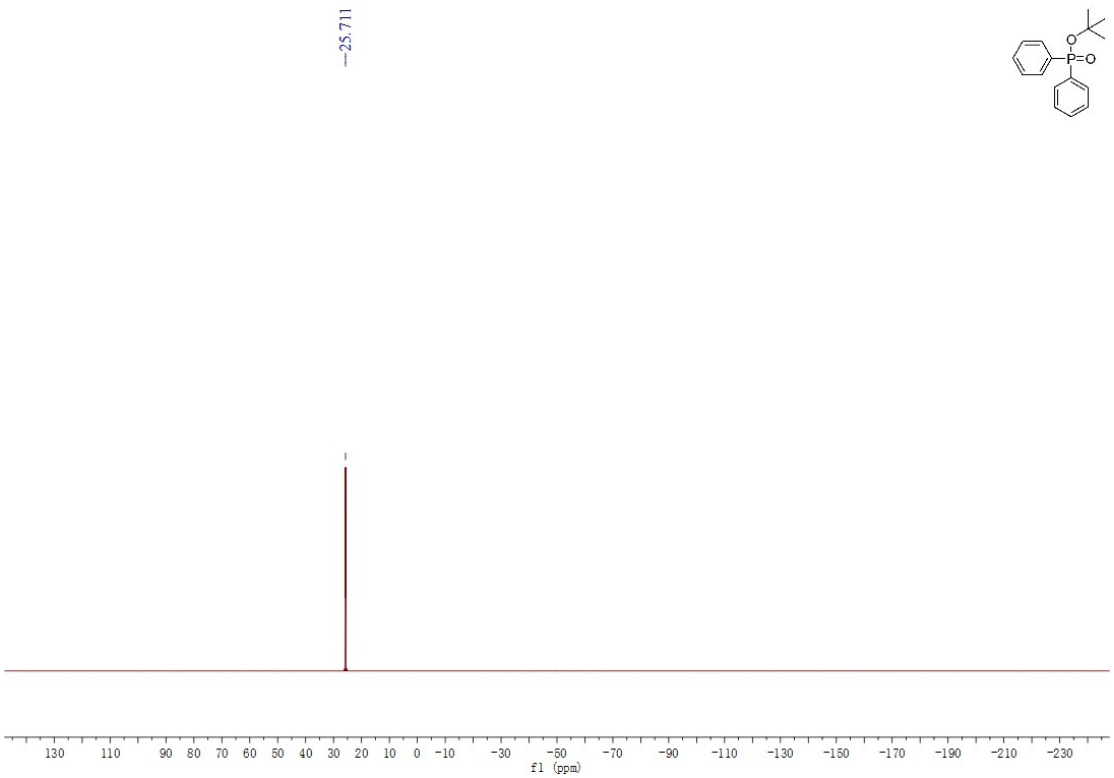
^{1}H NMR spectrum of tetraphenyldiphosphine monoxide **A** in Toluene-d_8



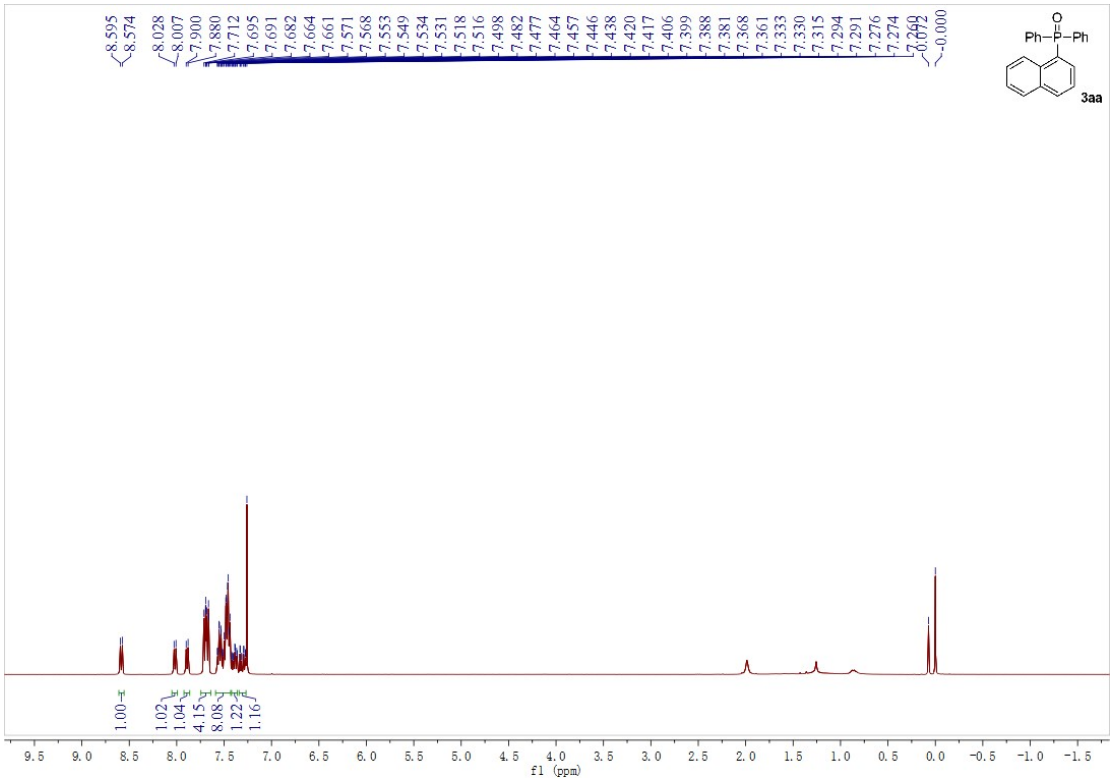
^{31}P NMR spectrum of tetraphenyldiphosphine monoxide **A** in Toluene-d_8



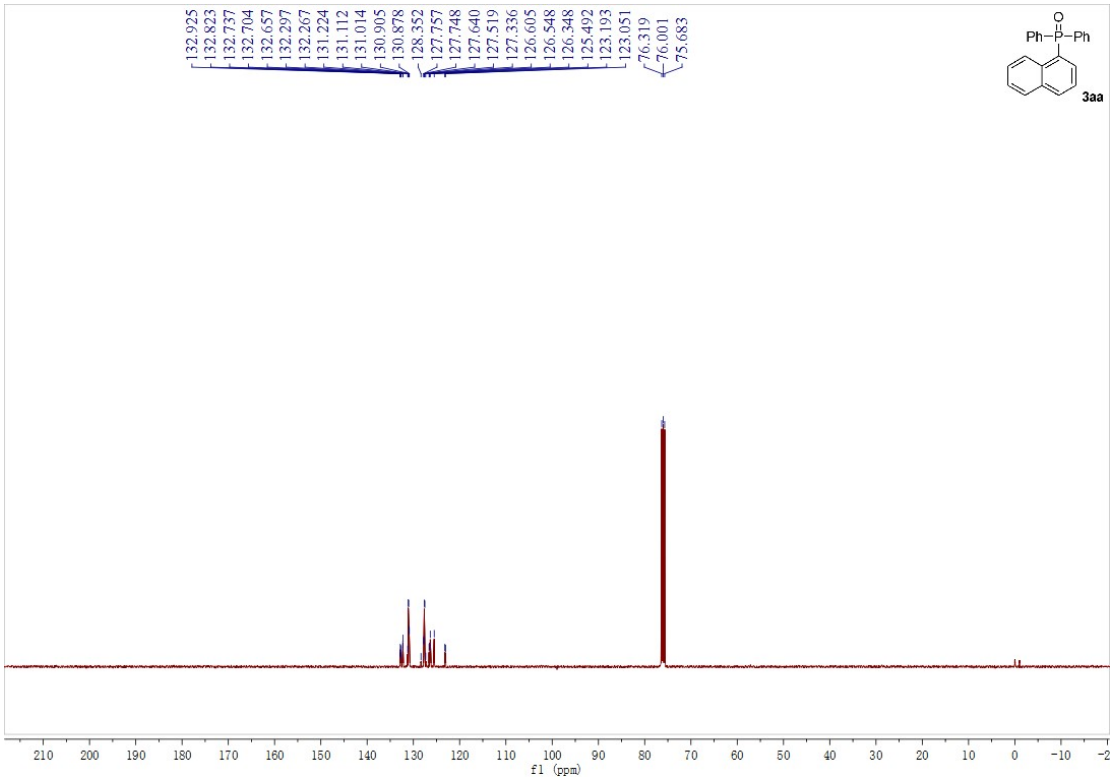
^{1}H NMR spectrum of $Ph_2P(O)OBu$-*t* **B** in $CDCl_3$



^{31}P NMR spectrum of $Ph_2P(O)OBu$-*t* **B** in $CDCl_3$



^{1}H NMR spectrum of **3aa** in $CDCl_3$



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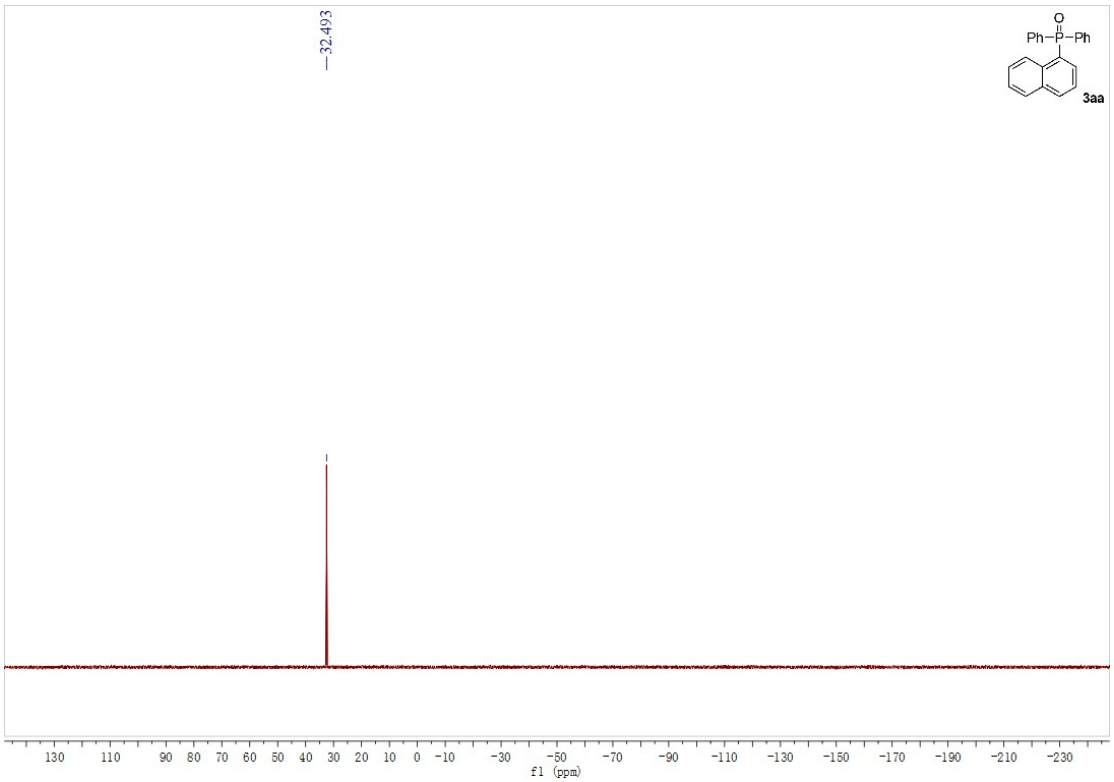
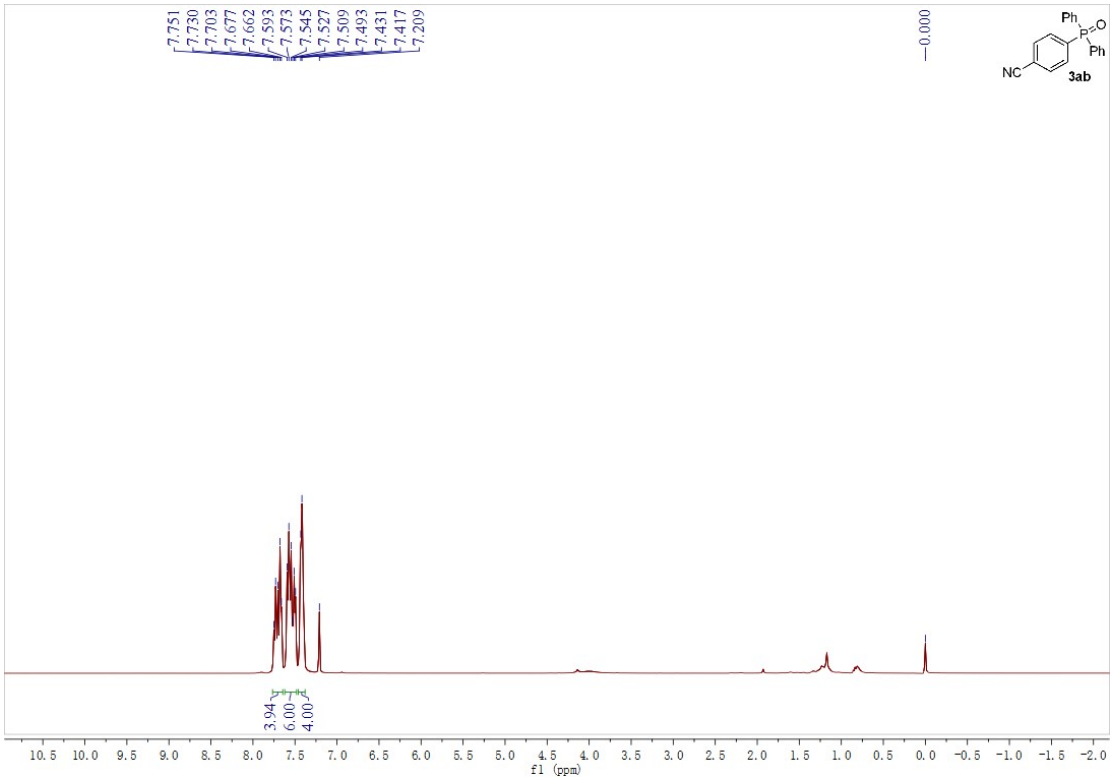


^{31}P NMR spectrum of **3aa** in $CDCl_3$



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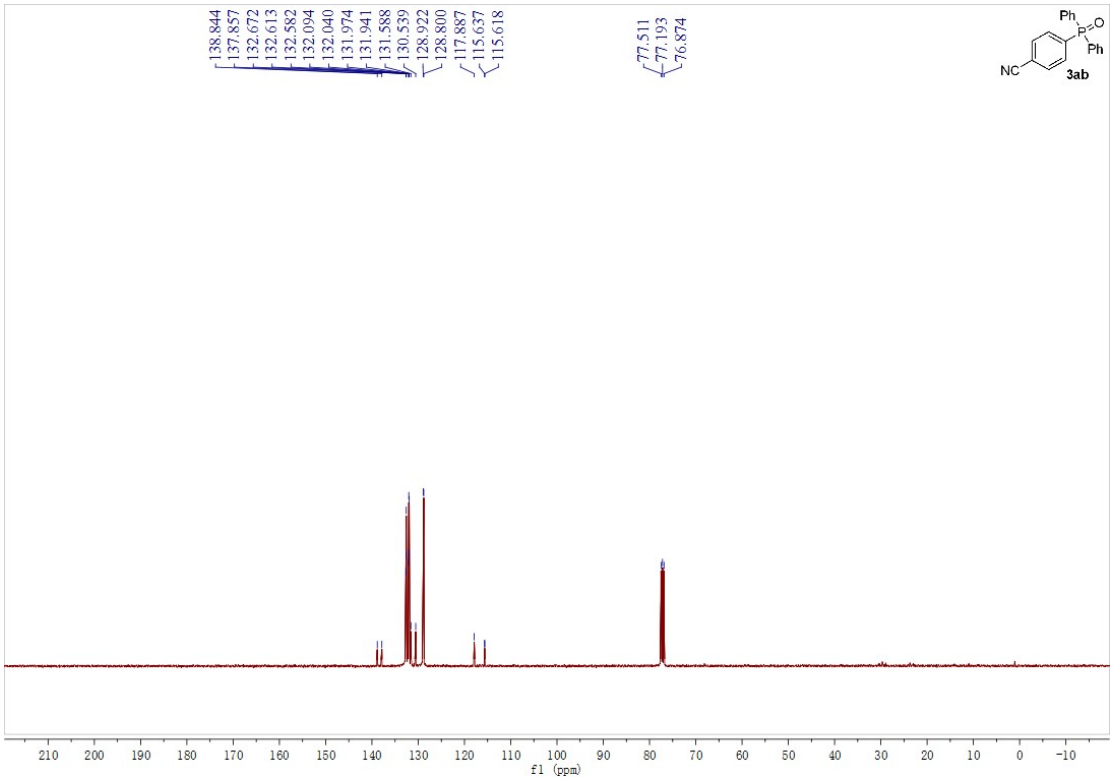
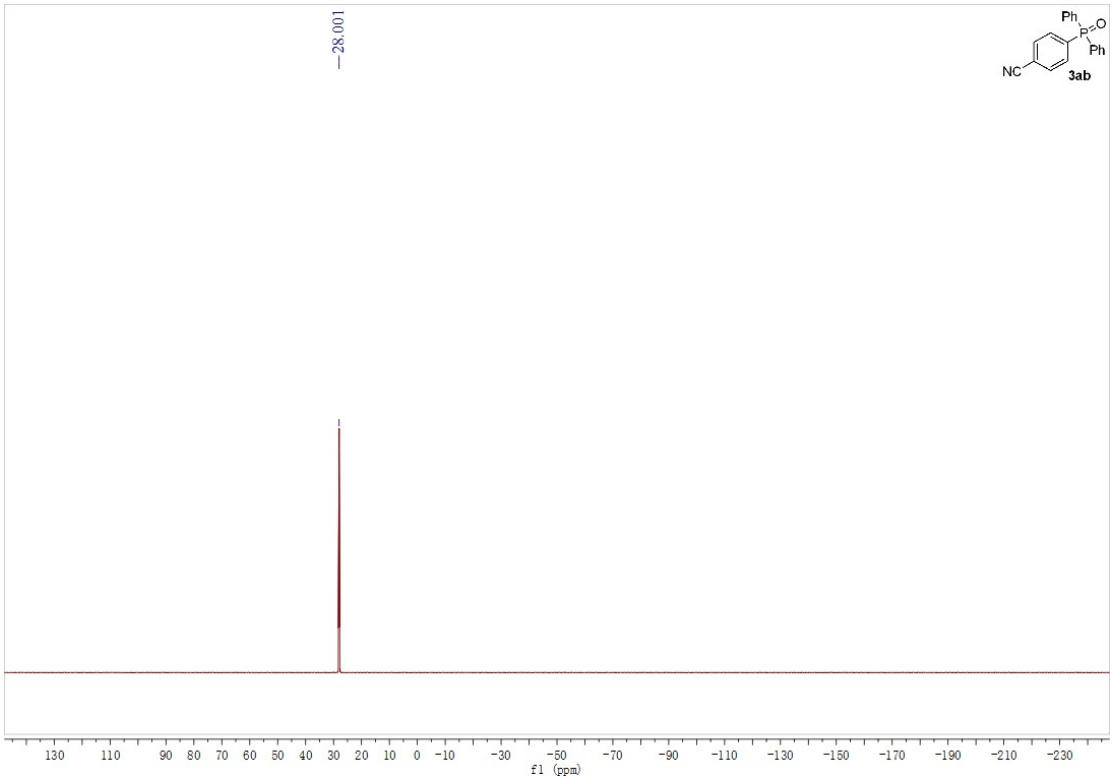
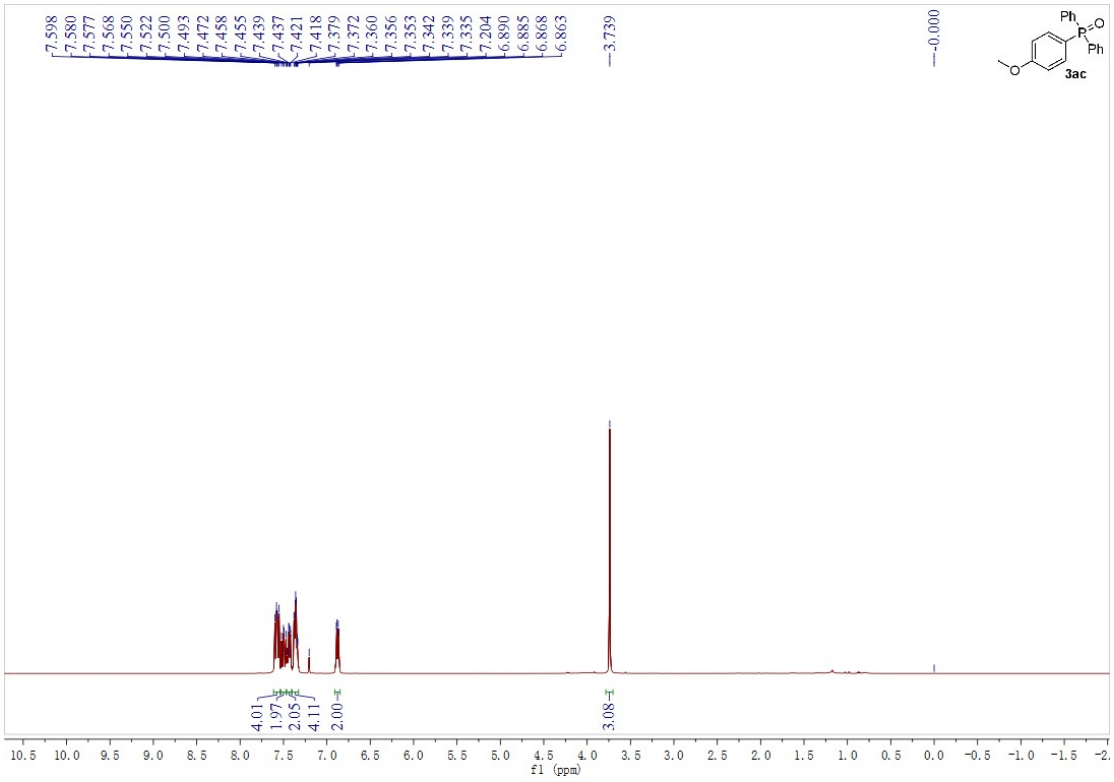


^{13}C NMR spectrum of **3ab** in $CDCl_3$



^{31}P NMR spectrum of **3ab** in $CDCl_3$



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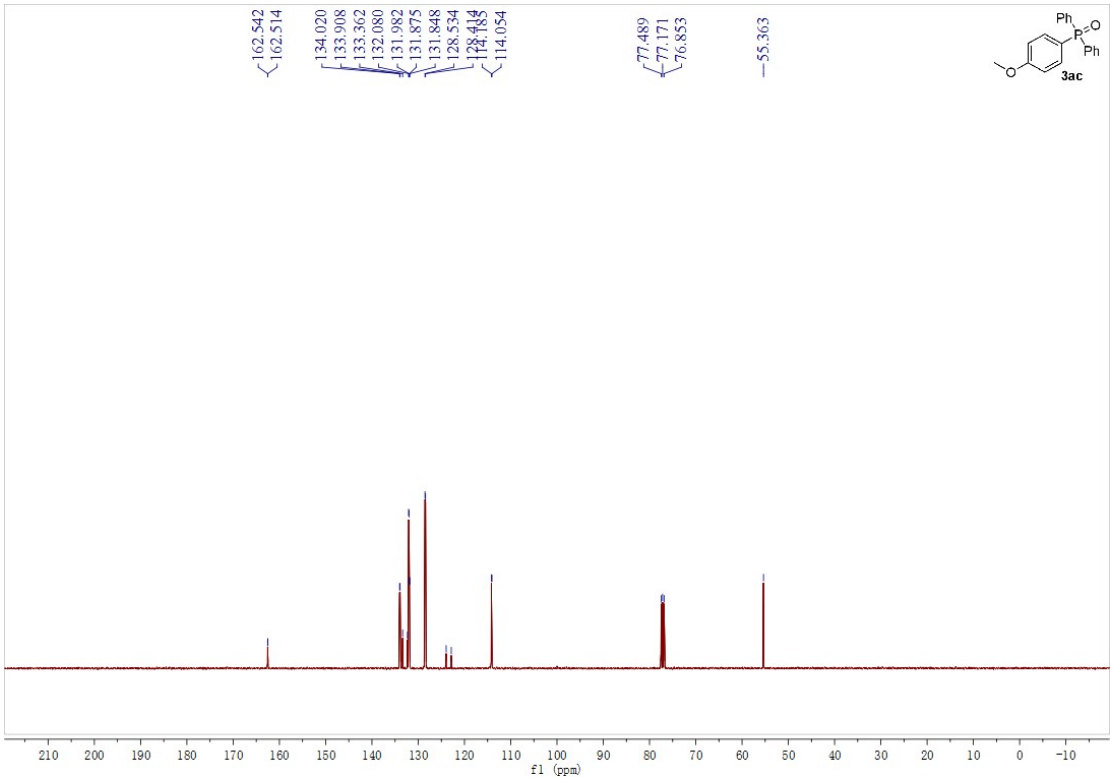
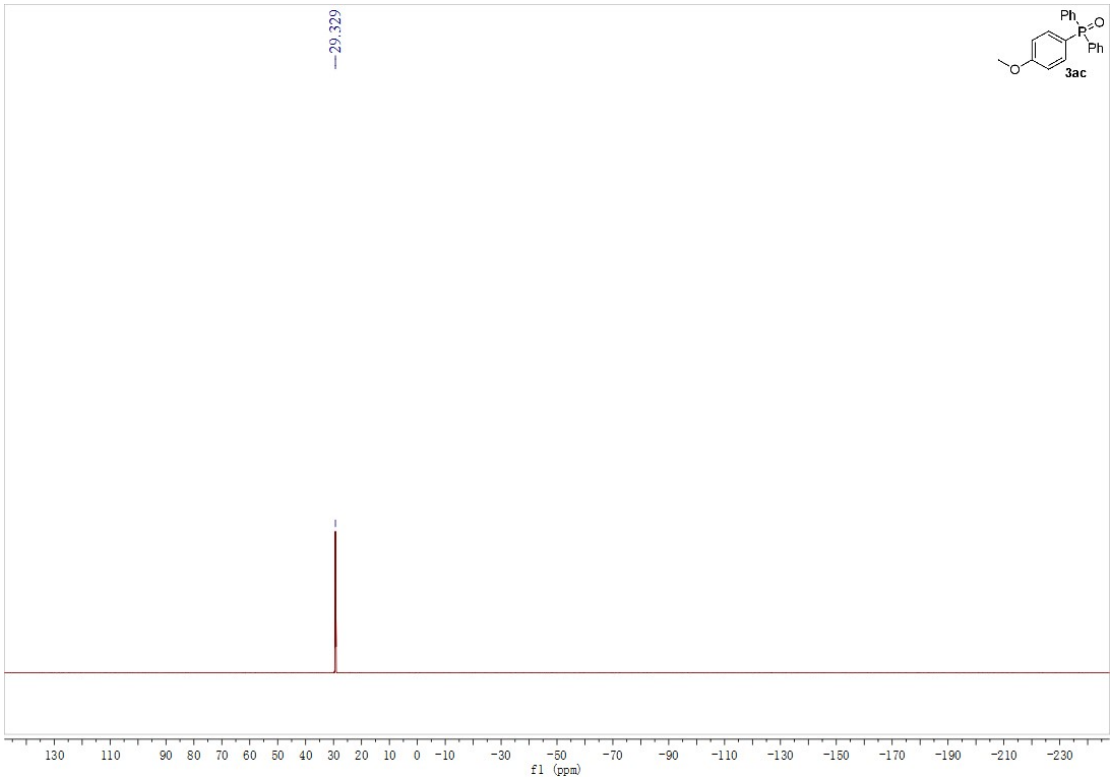


^{13}C NMR spectrum of **3ac** in $CDCl_3$



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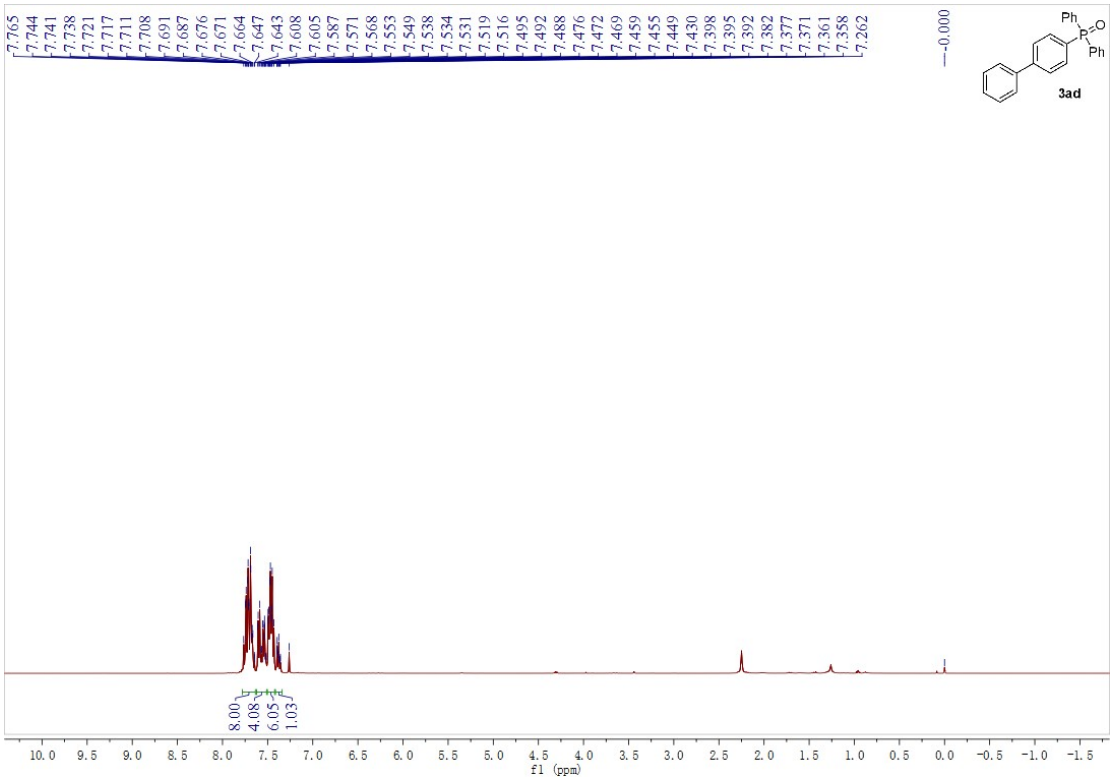

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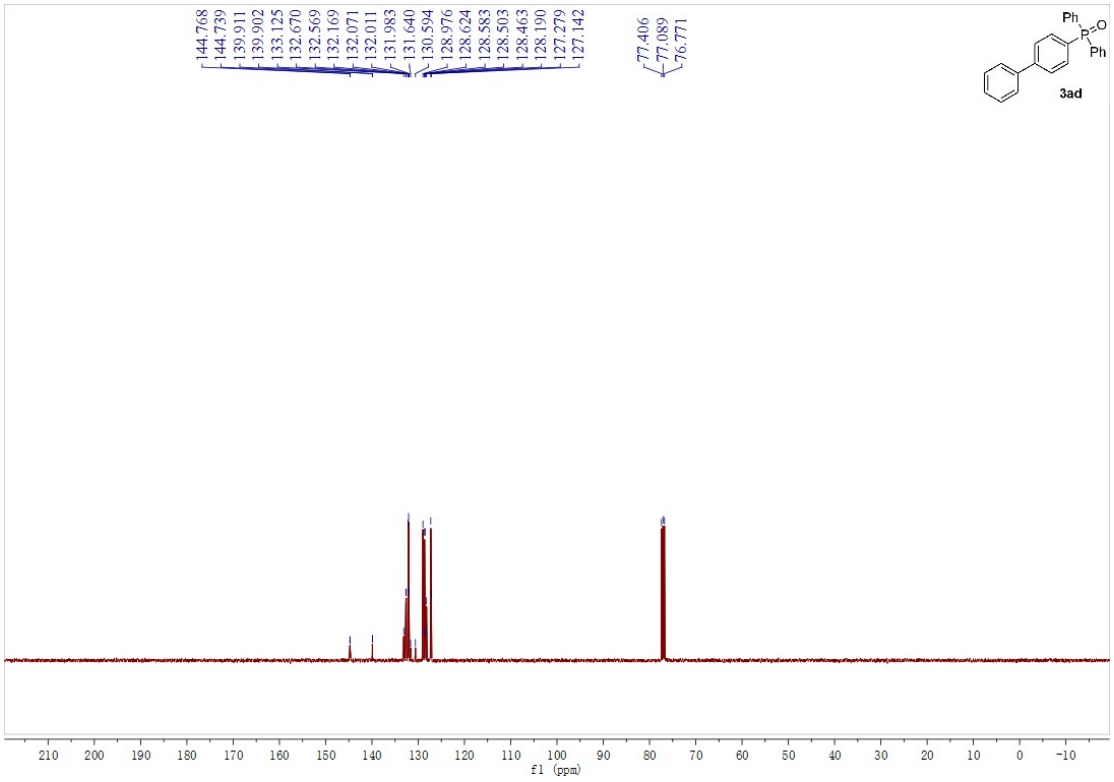

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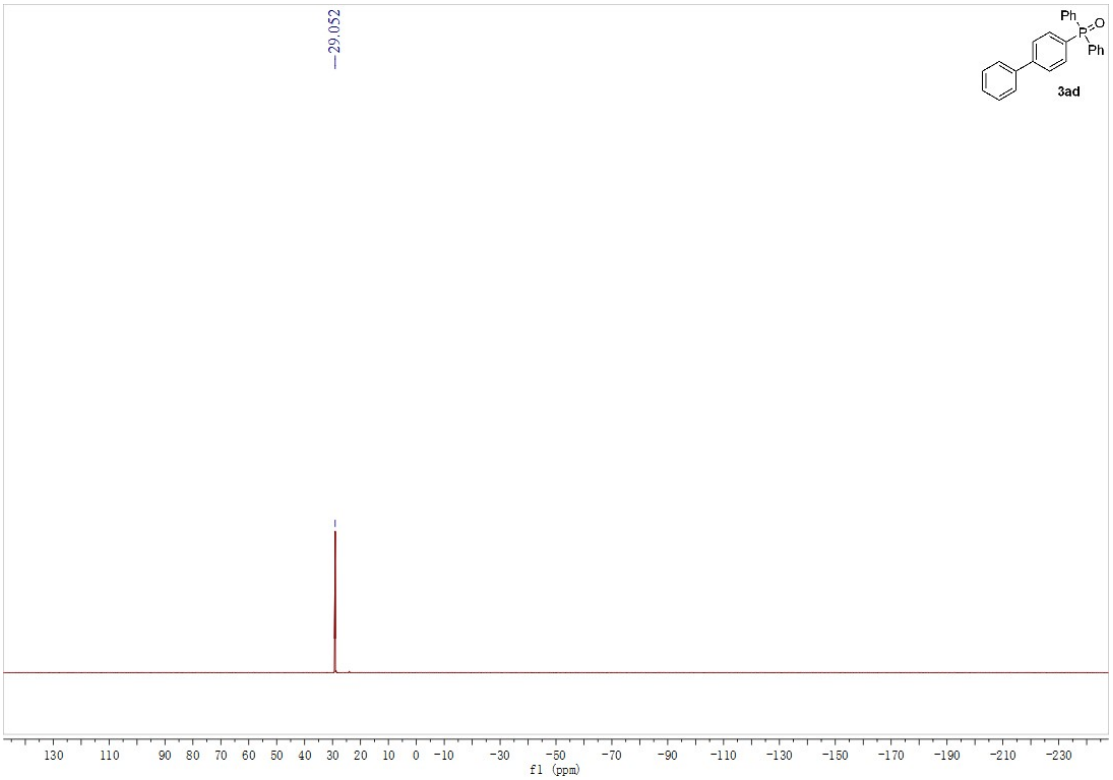

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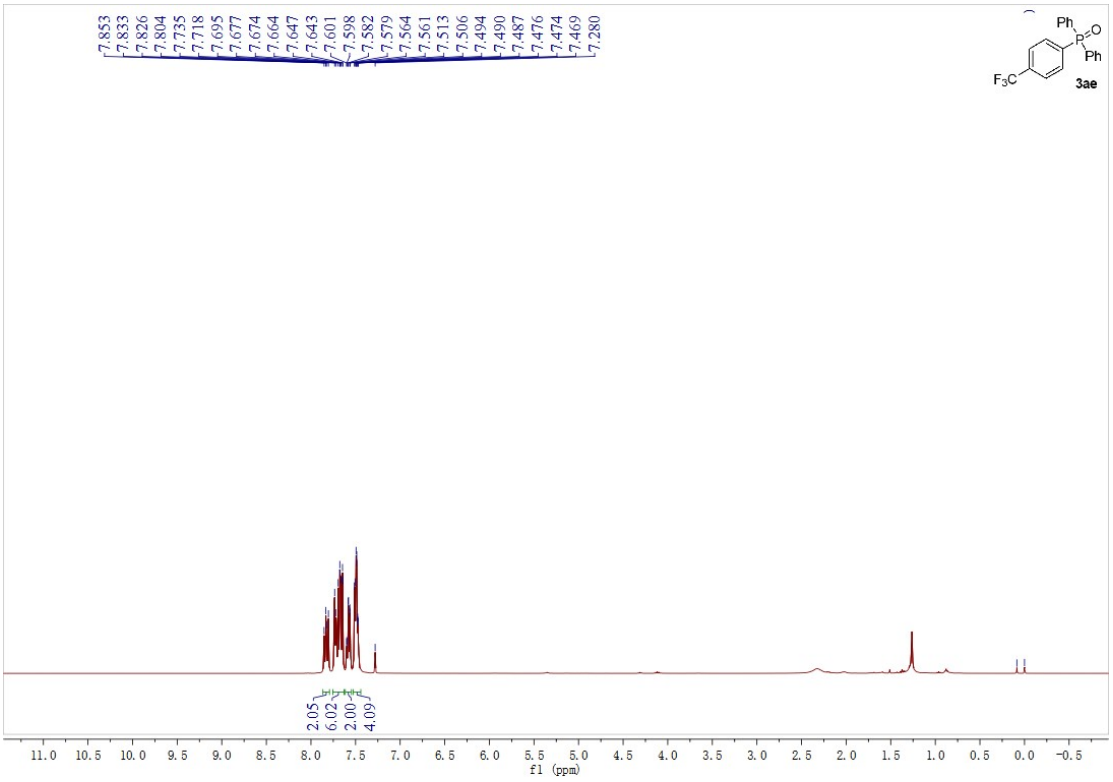

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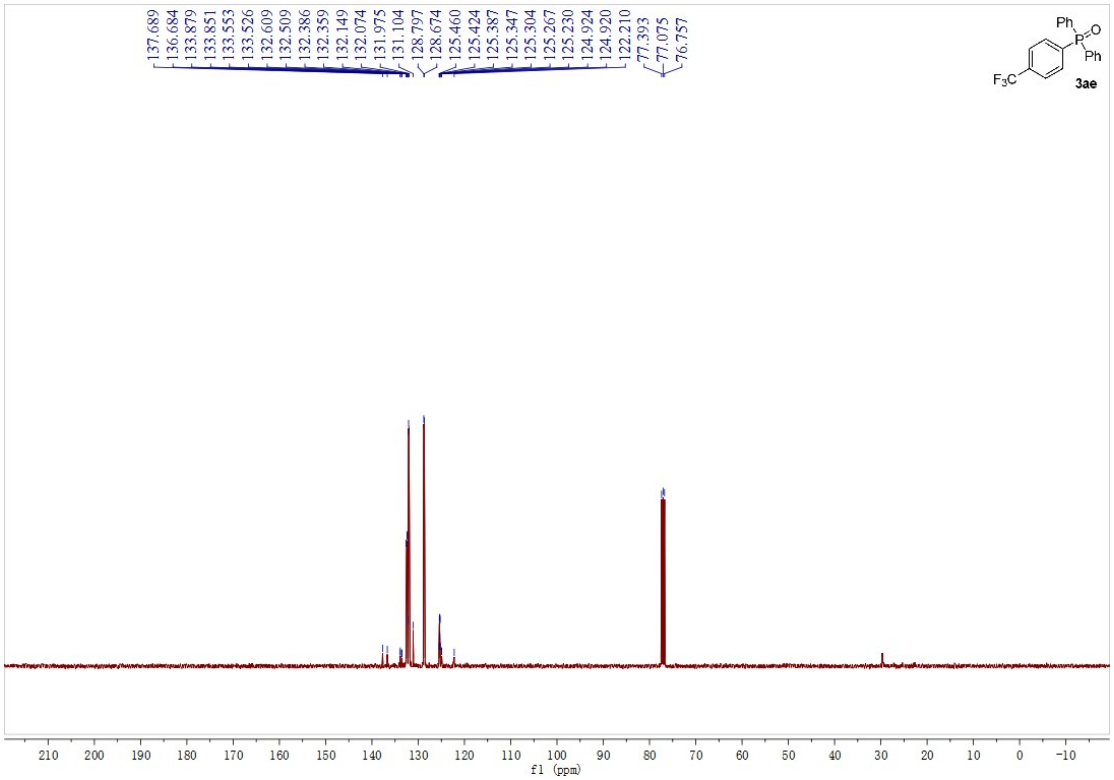

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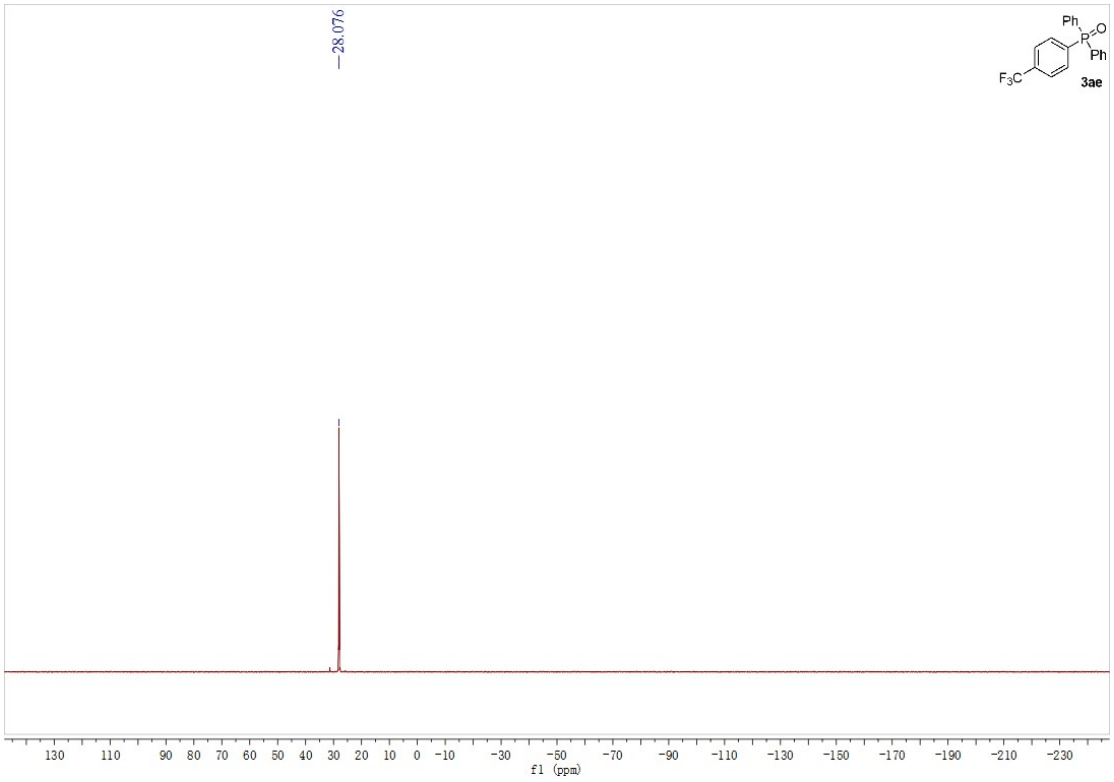

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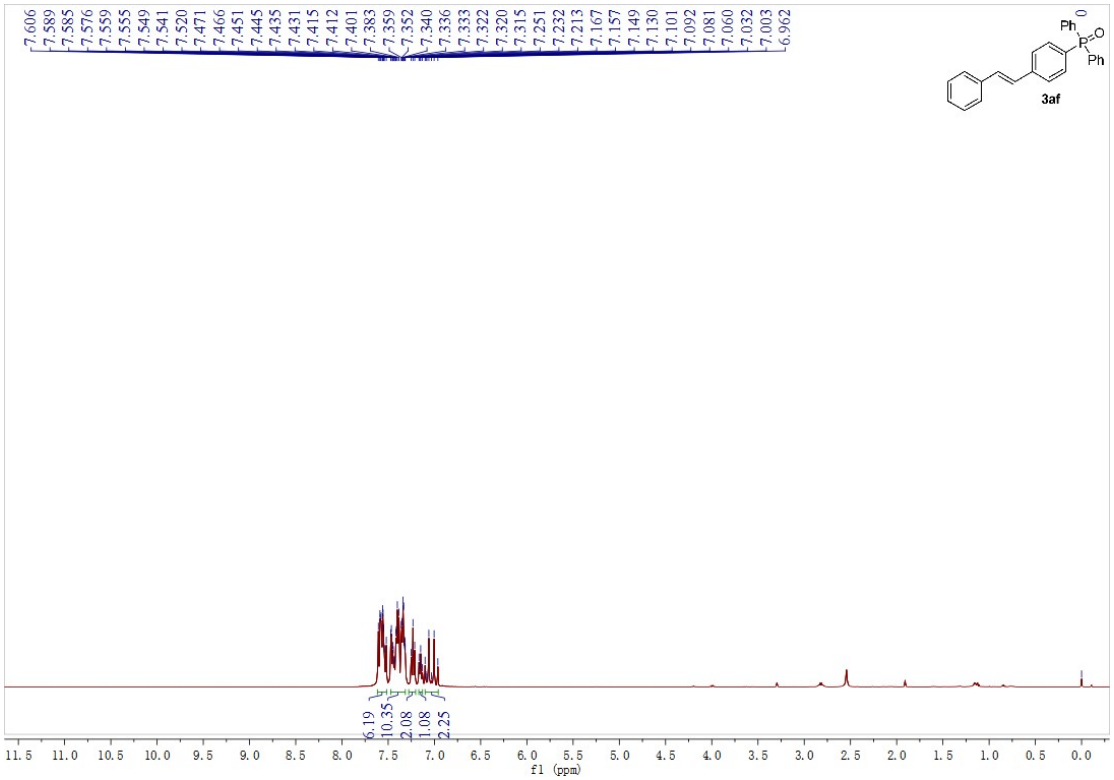

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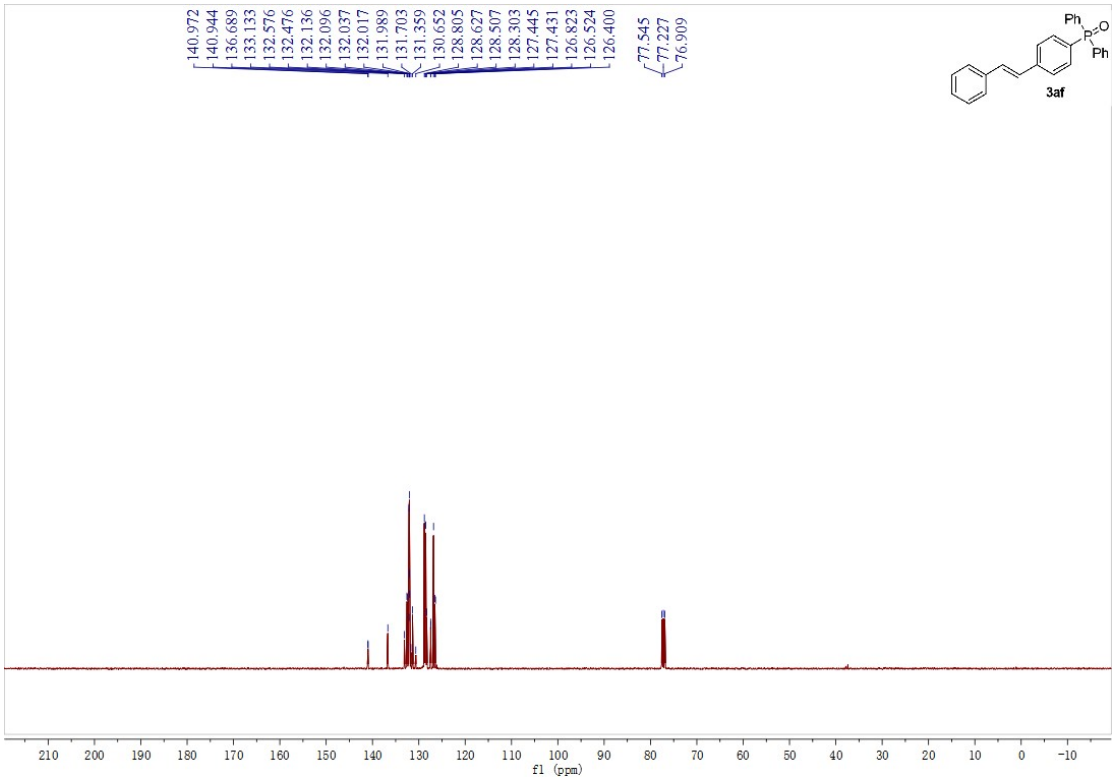

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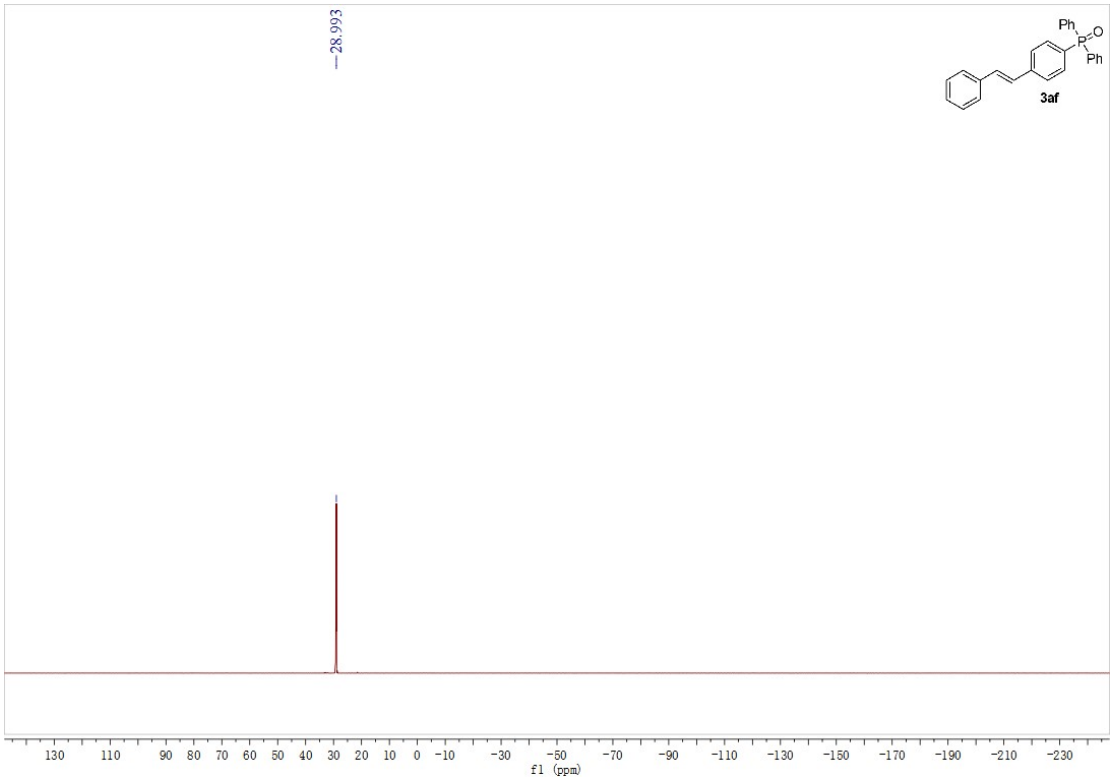

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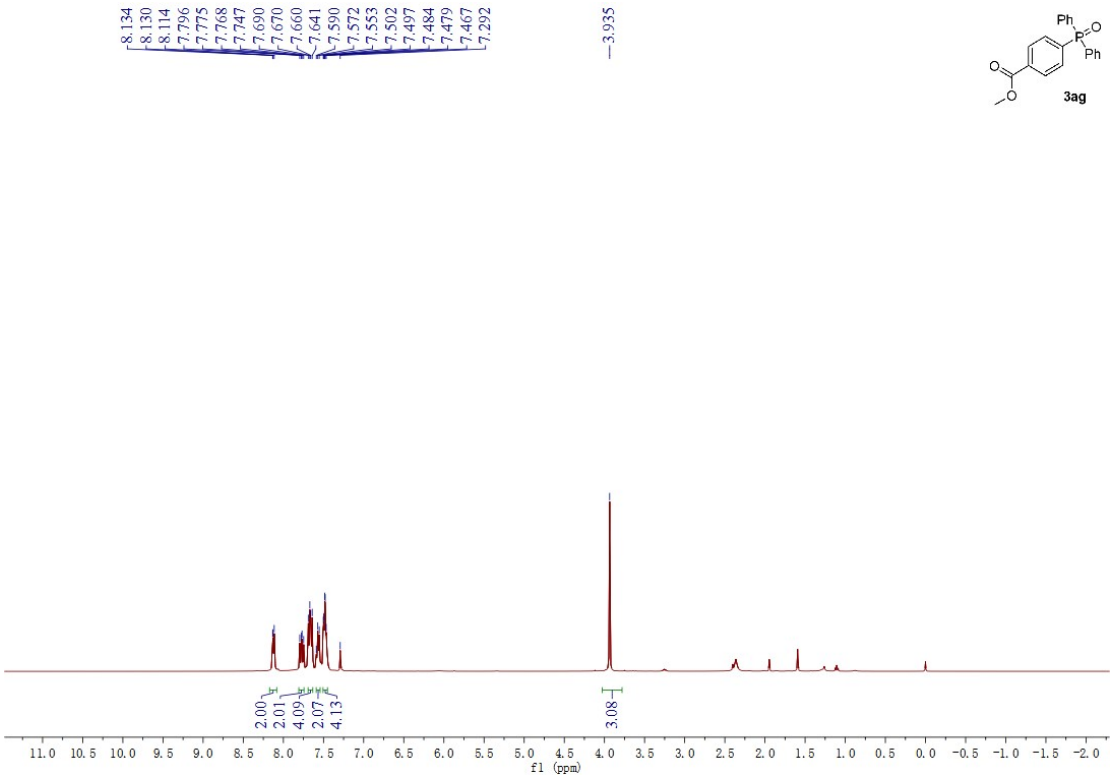

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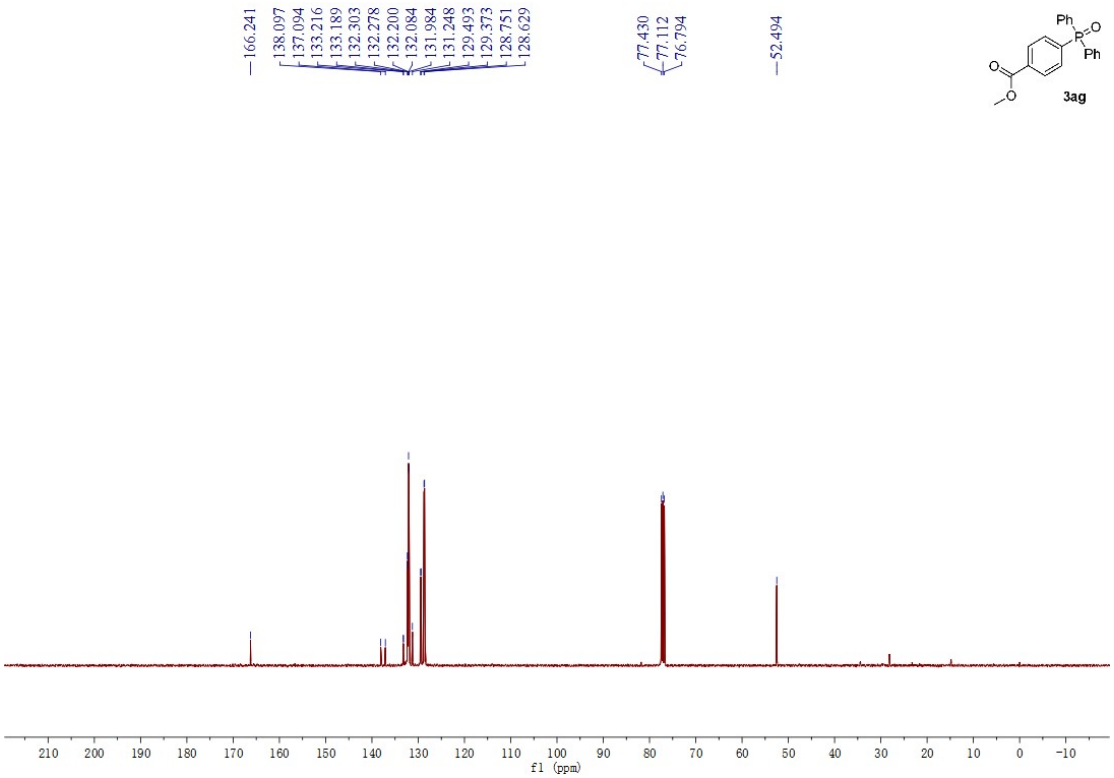
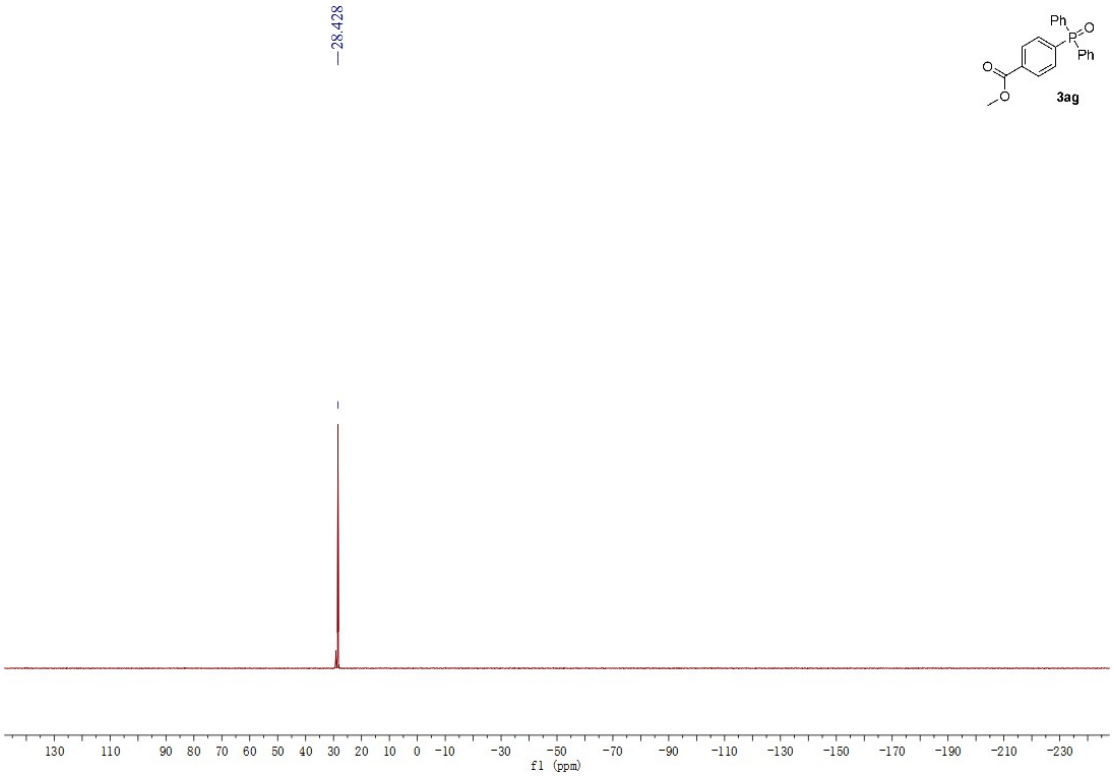


^{13}C NMR spectrum of **3ag** in $CDCl_3$



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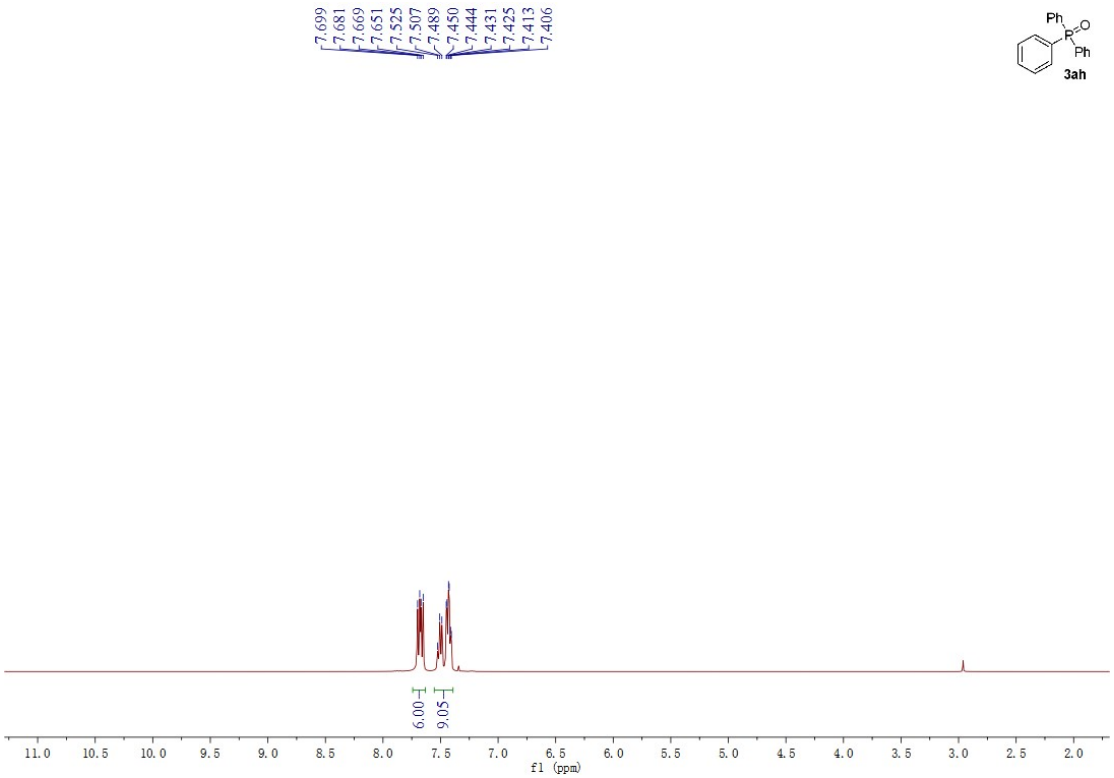

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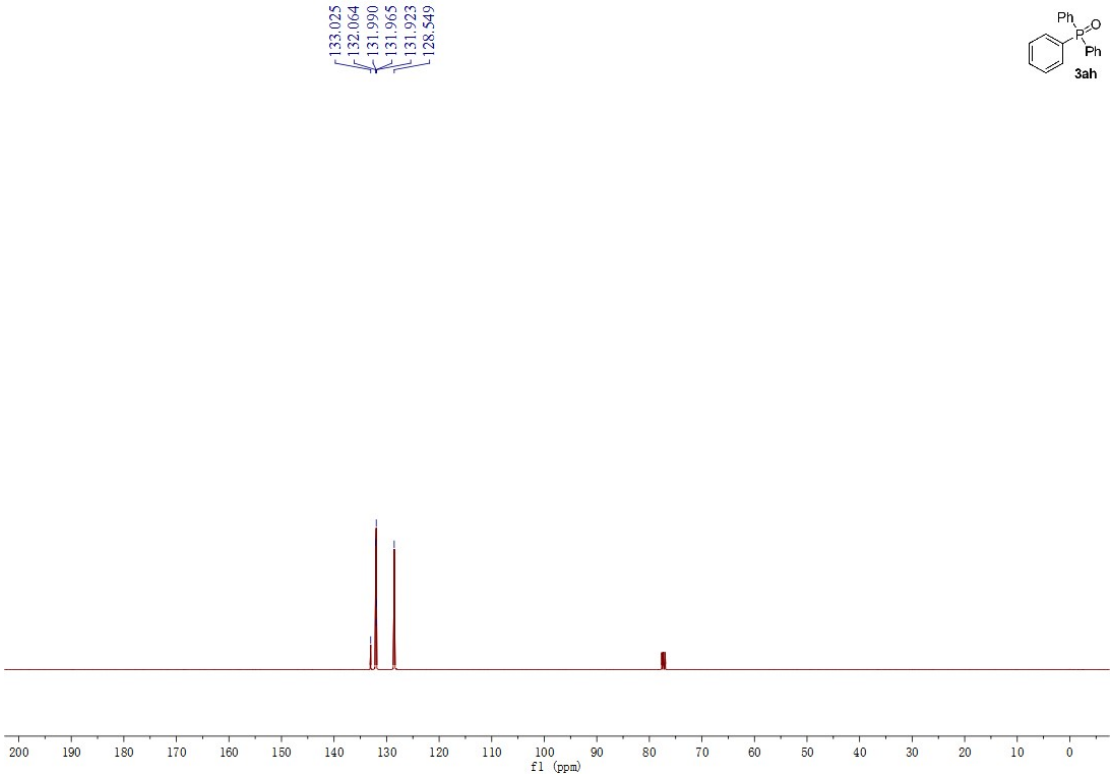
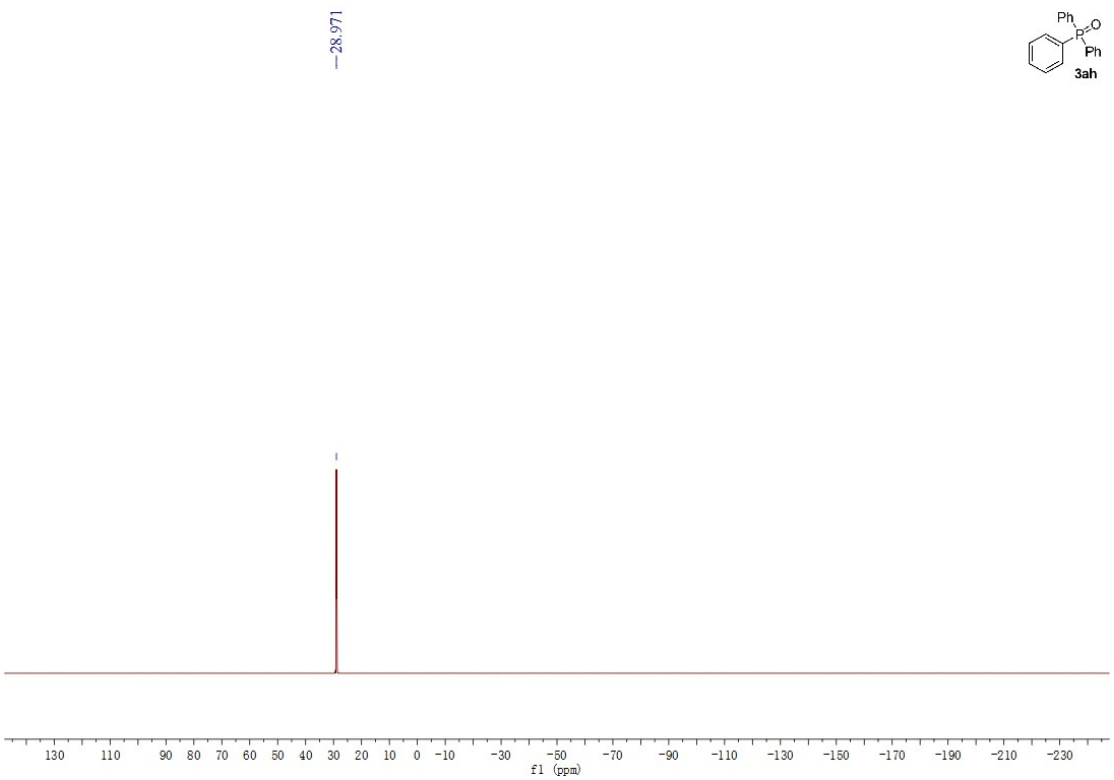
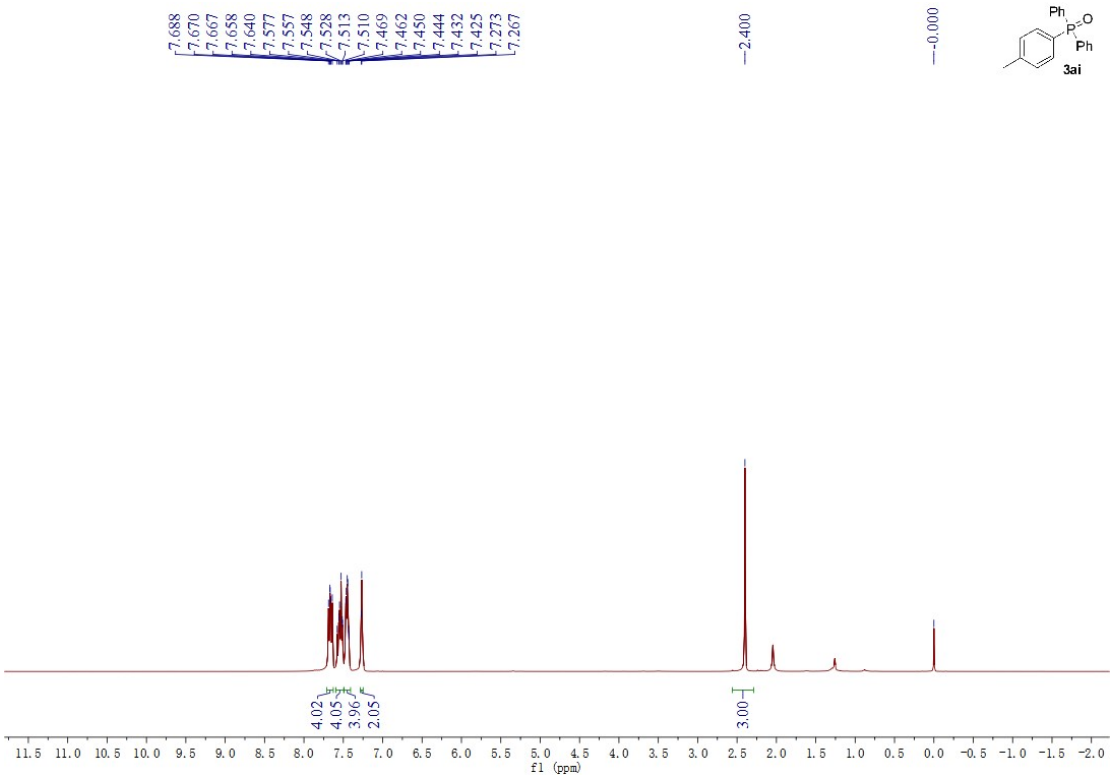


^{13}C NMR spectrum of **3ah** in $CDCl_3$



^{31}P NMR spectrum of **3ah** in $CDCl_3$



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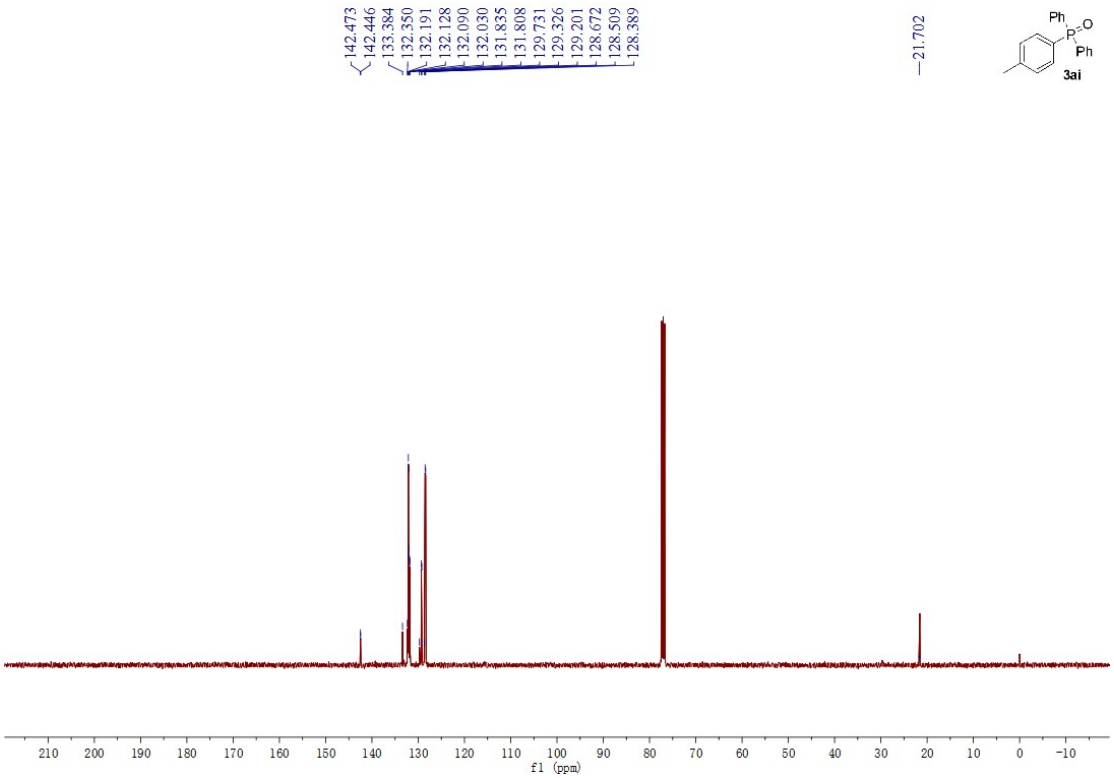

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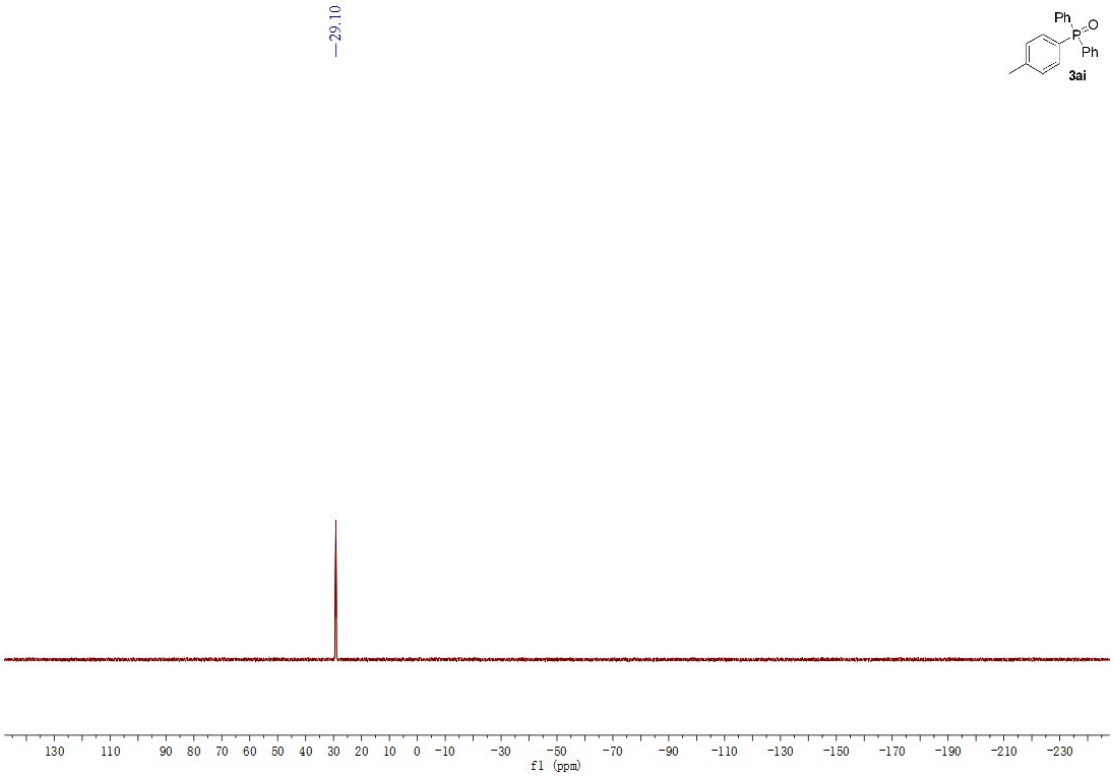

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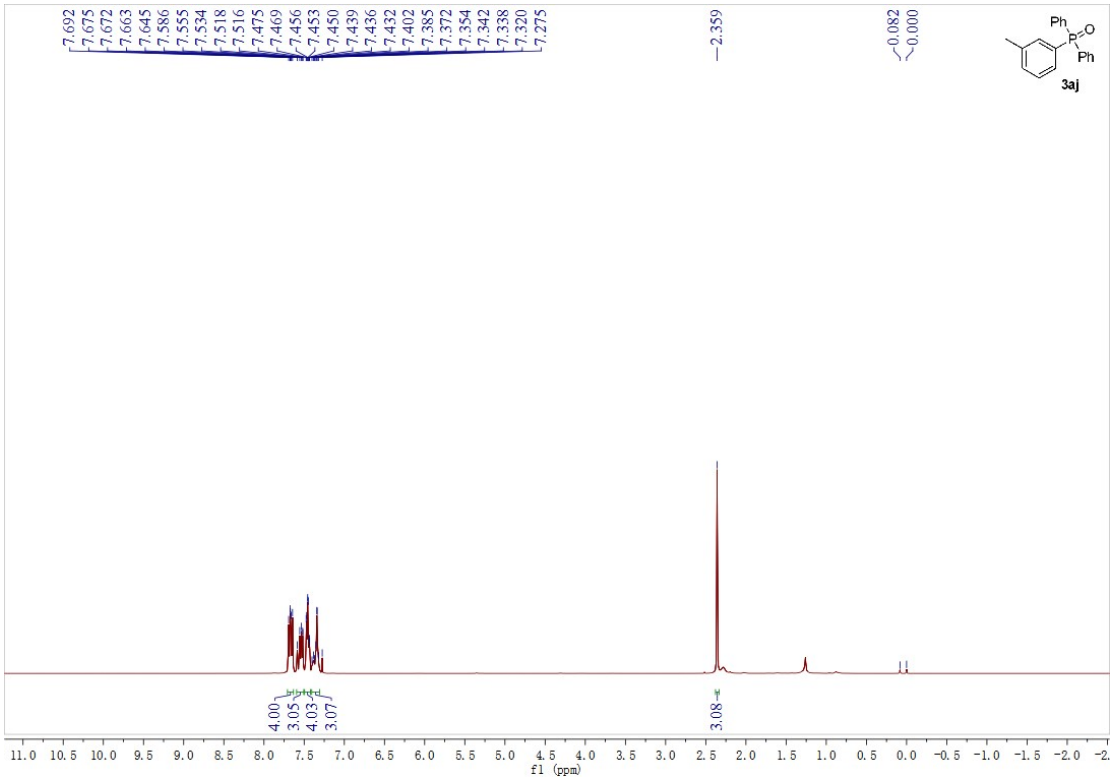

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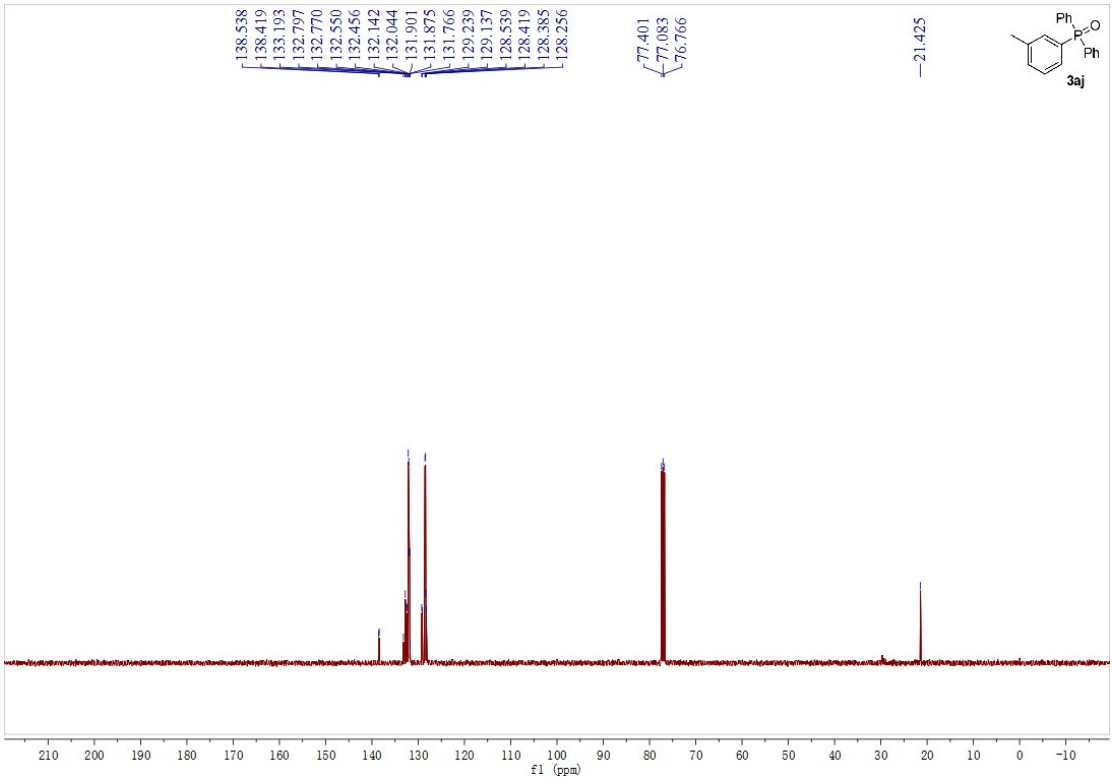

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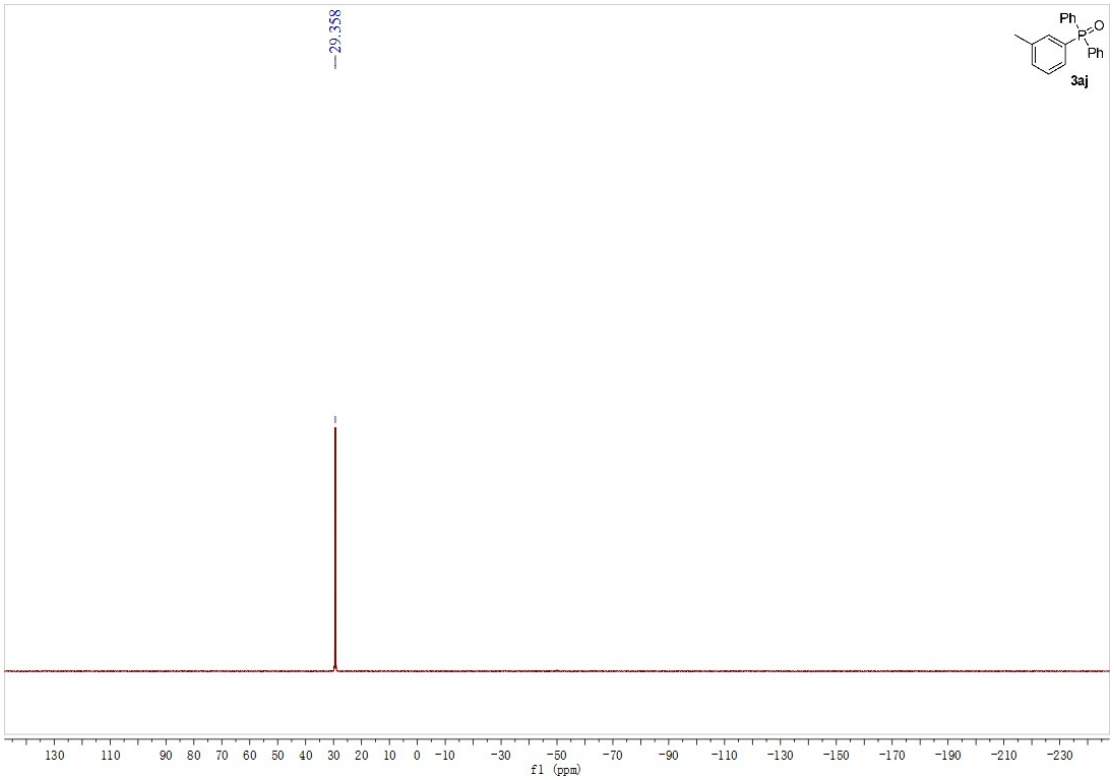

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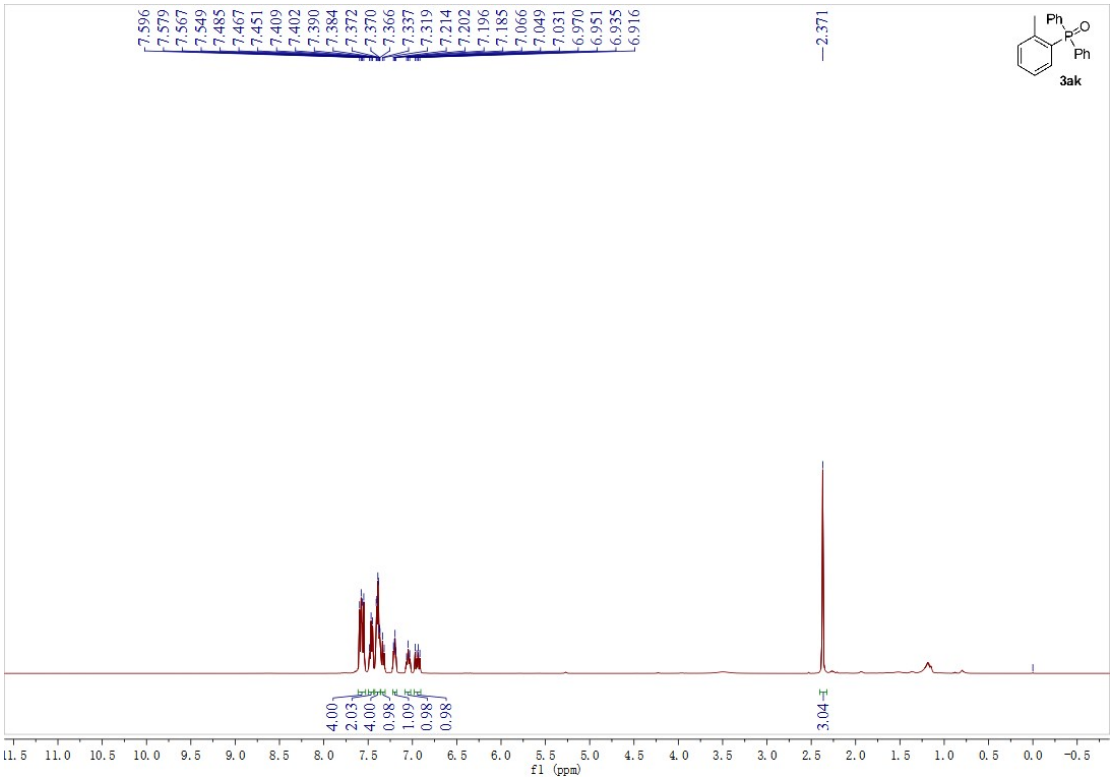

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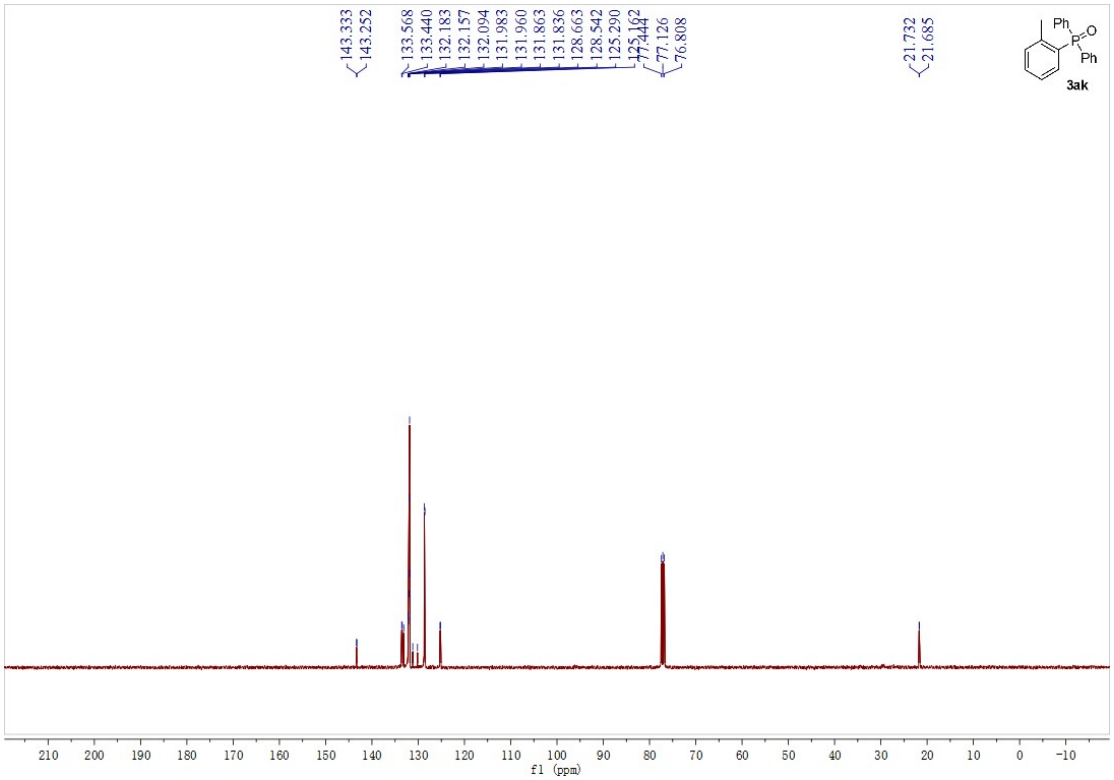

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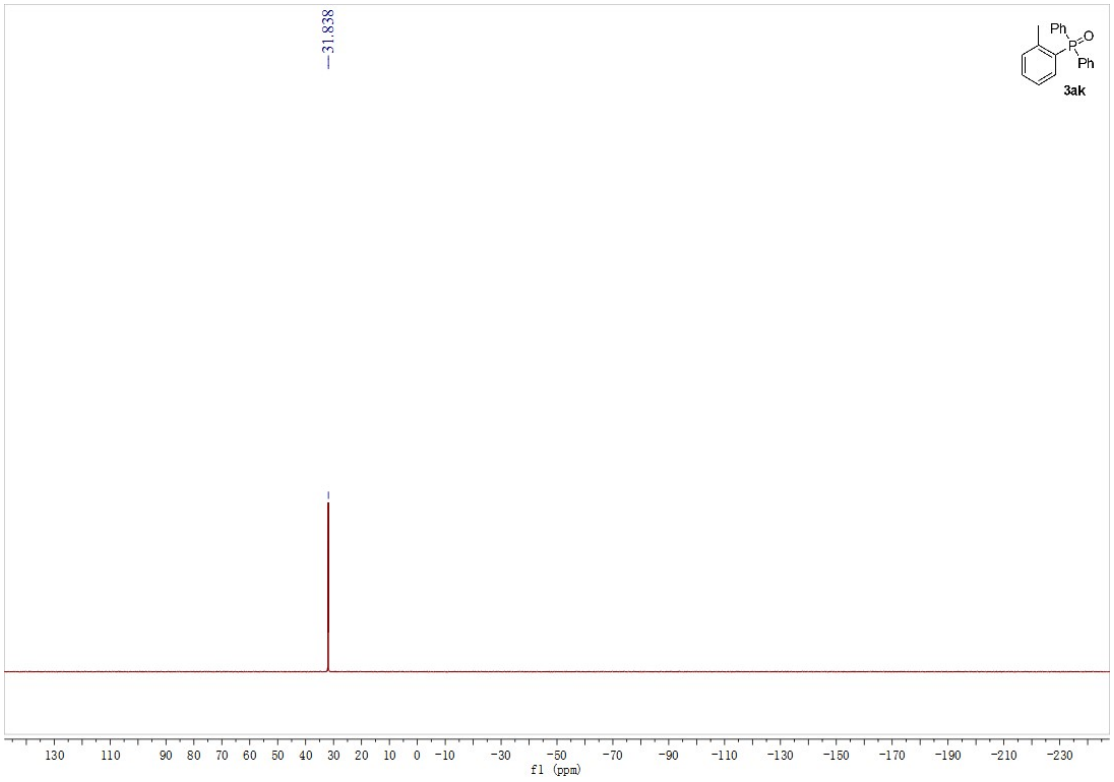

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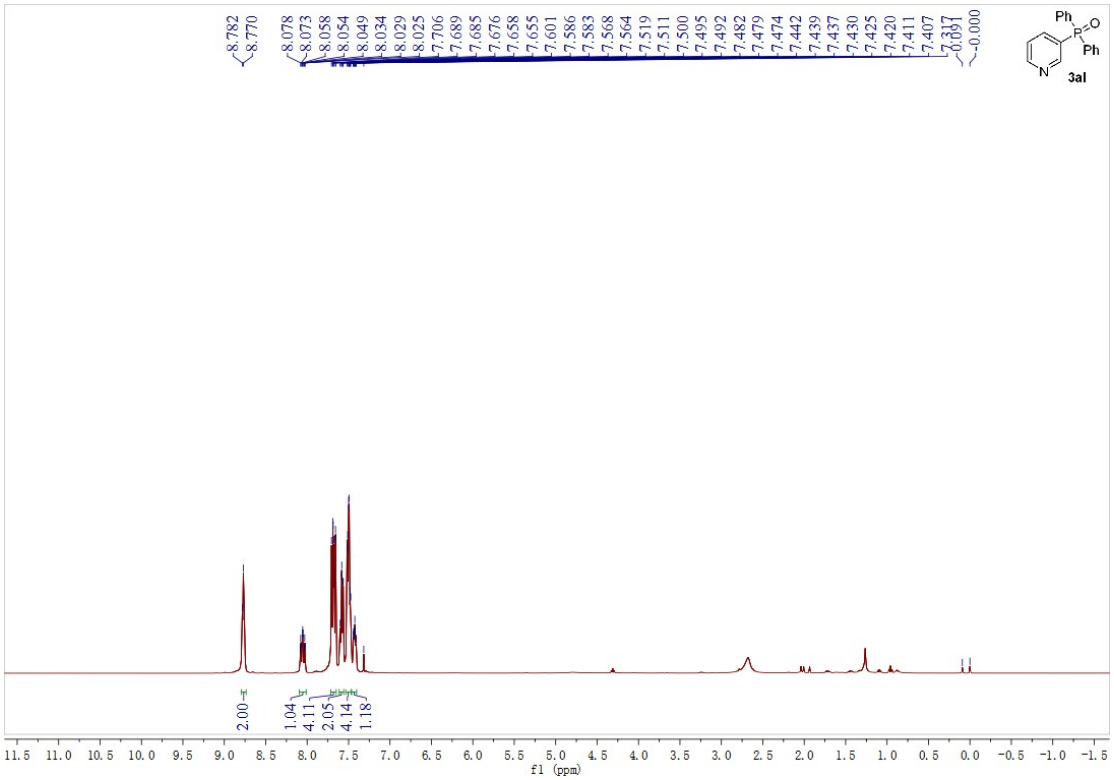

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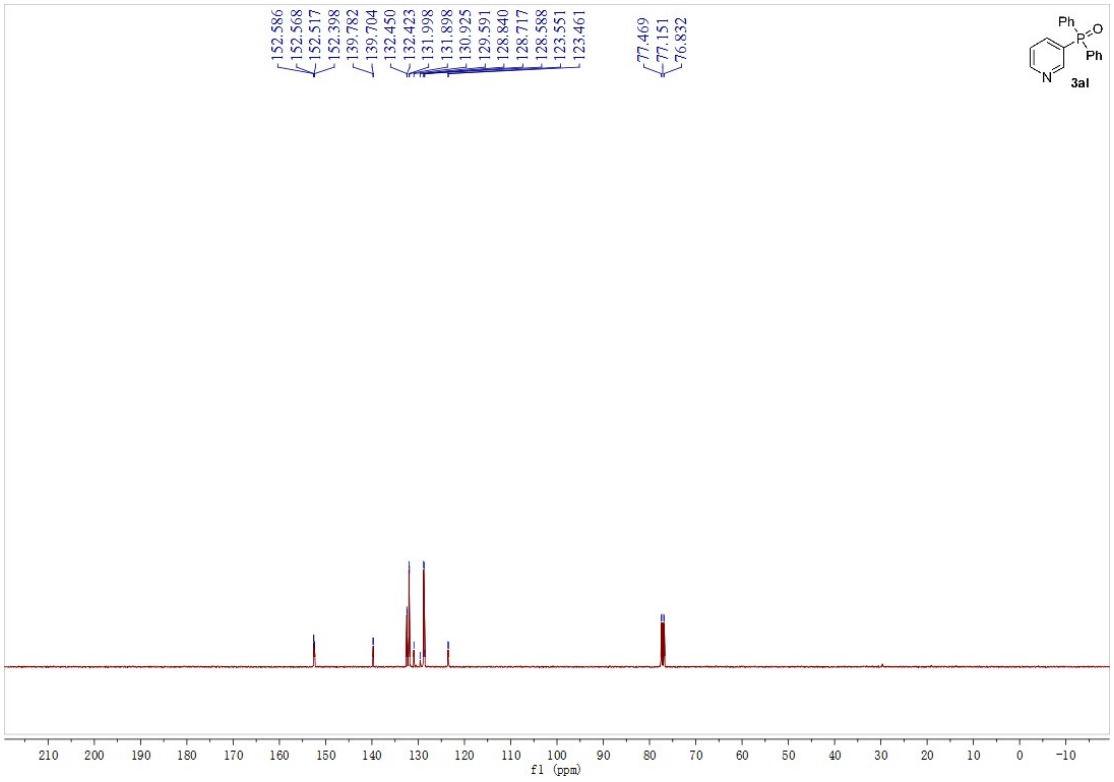

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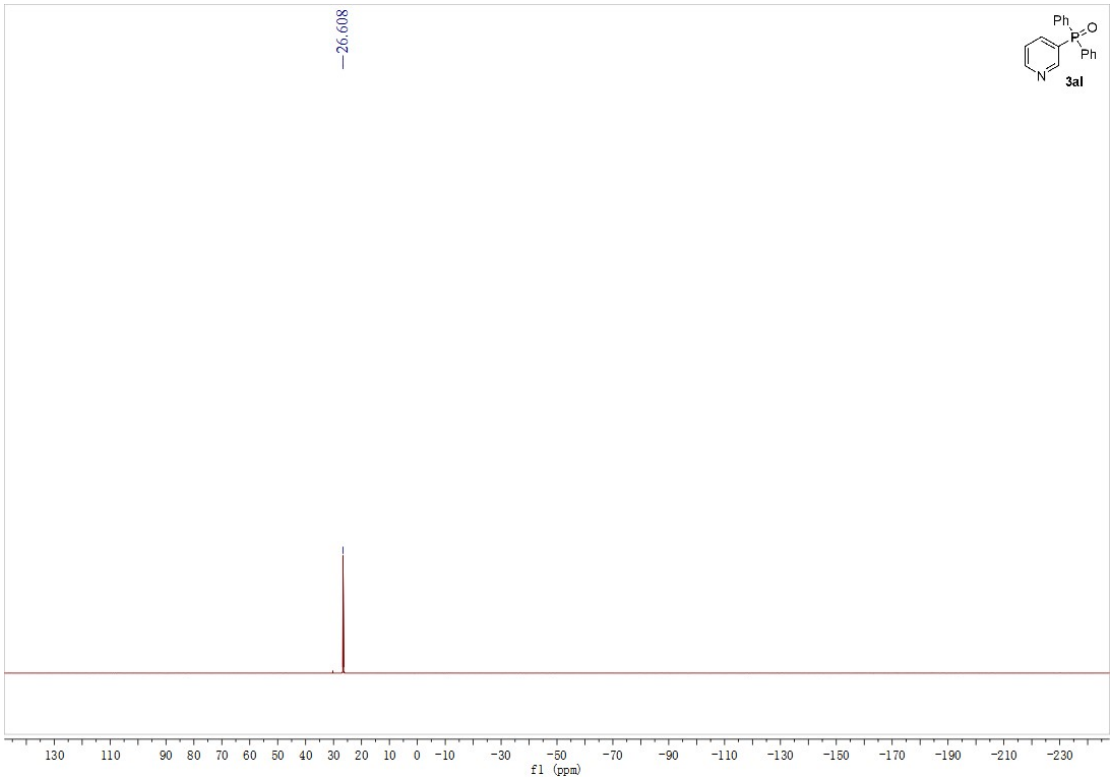

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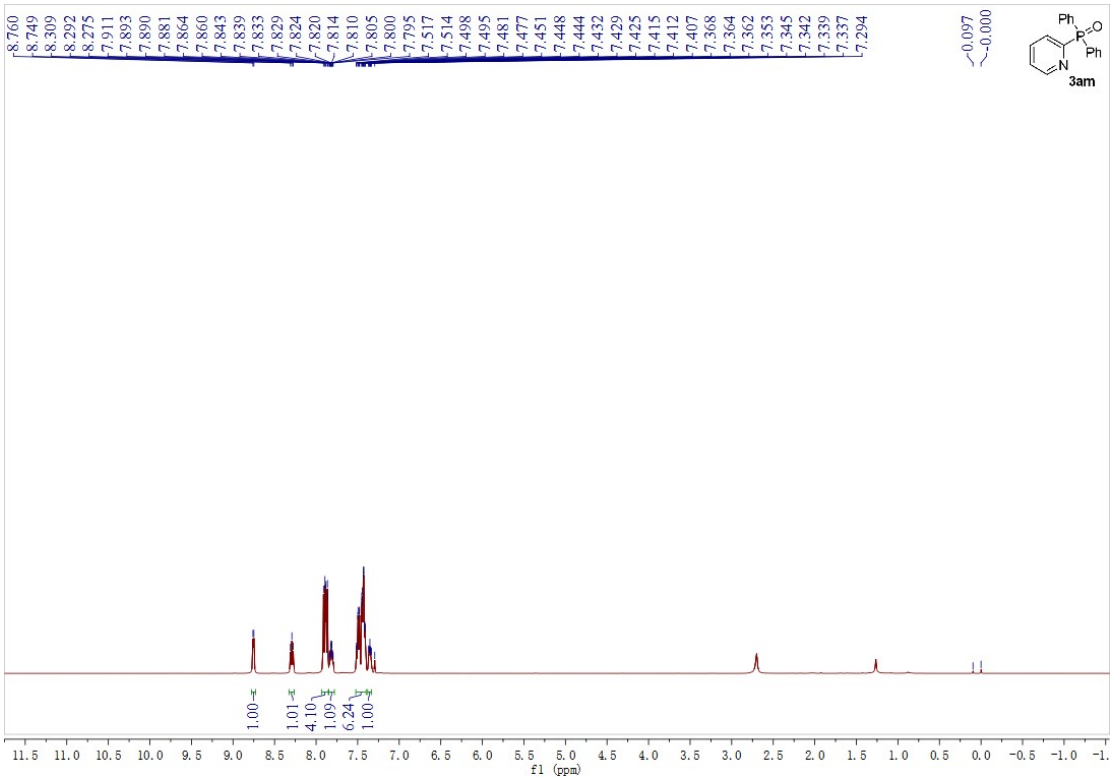

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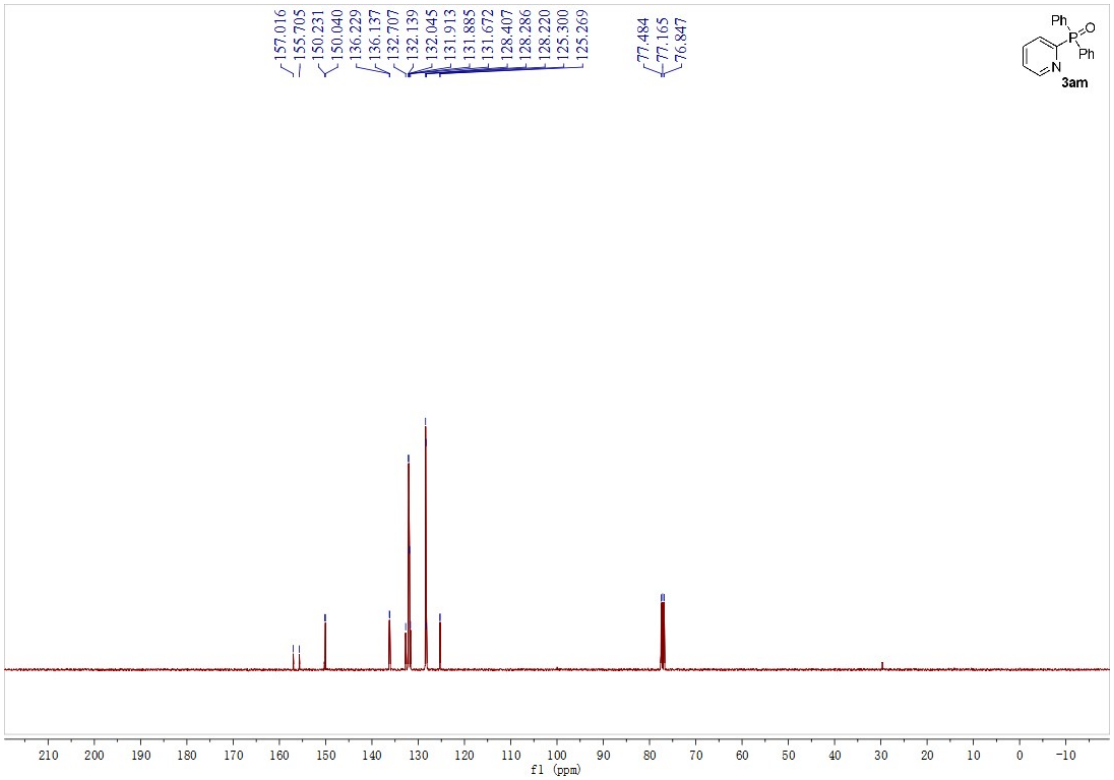
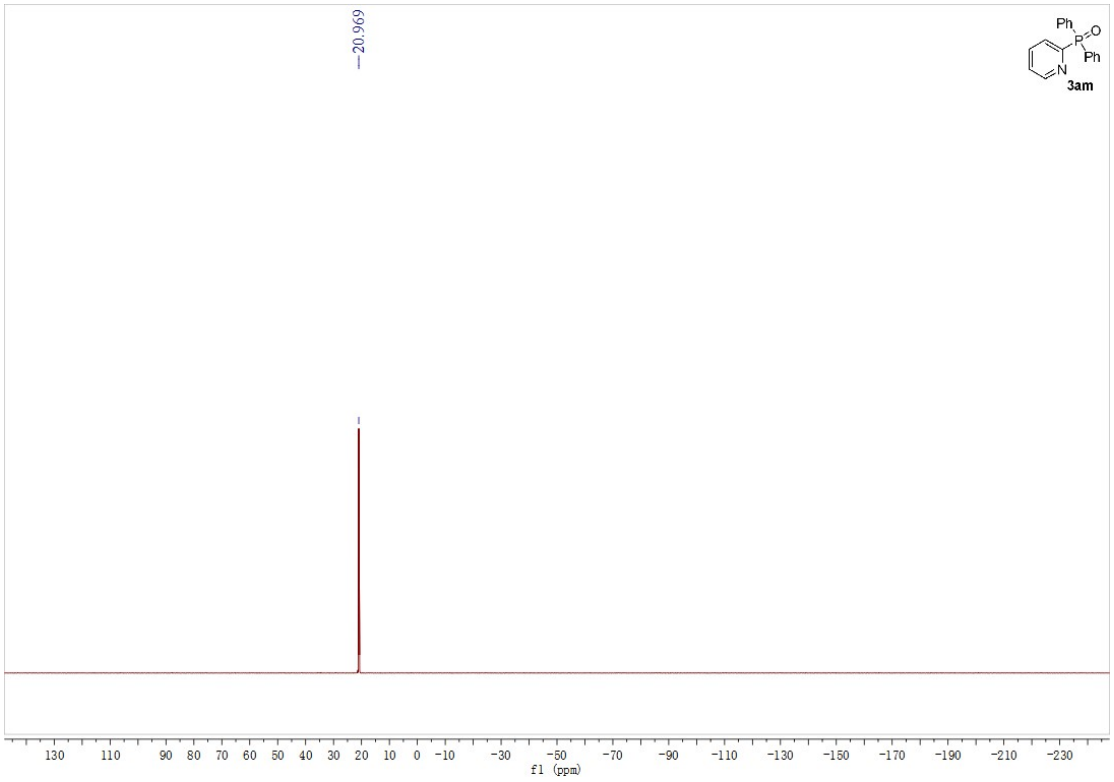


^{13}C NMR spectrum of **3am** in $CDCl_3$



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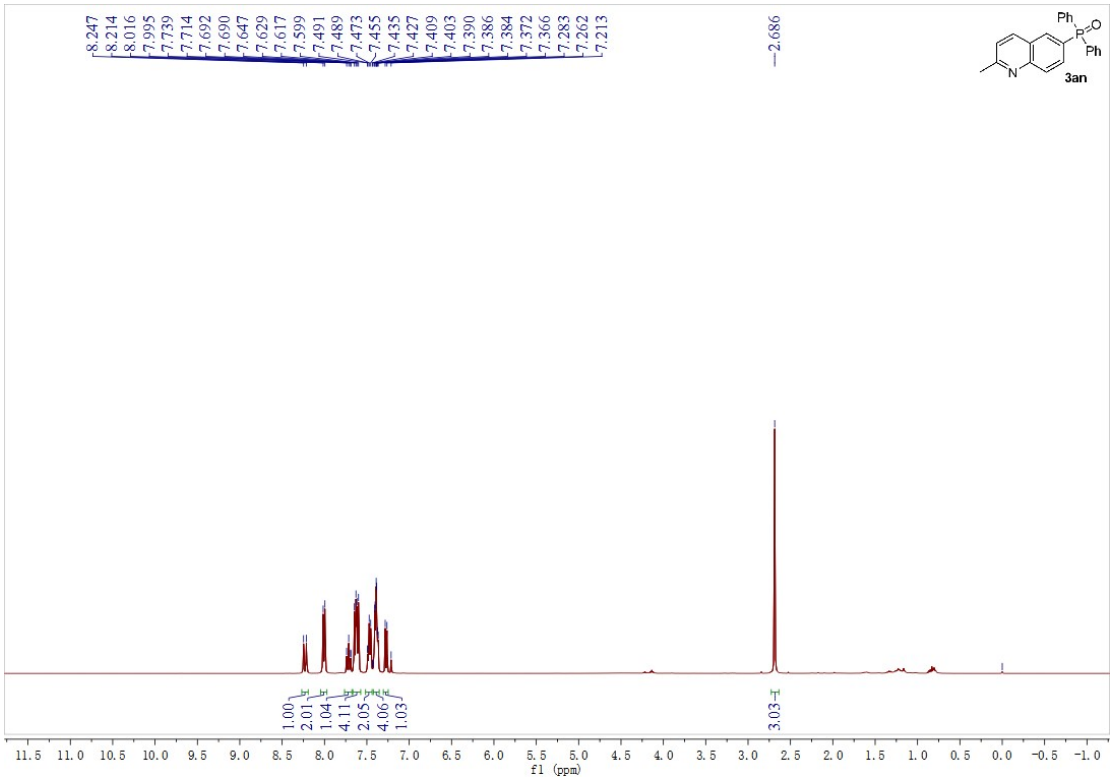
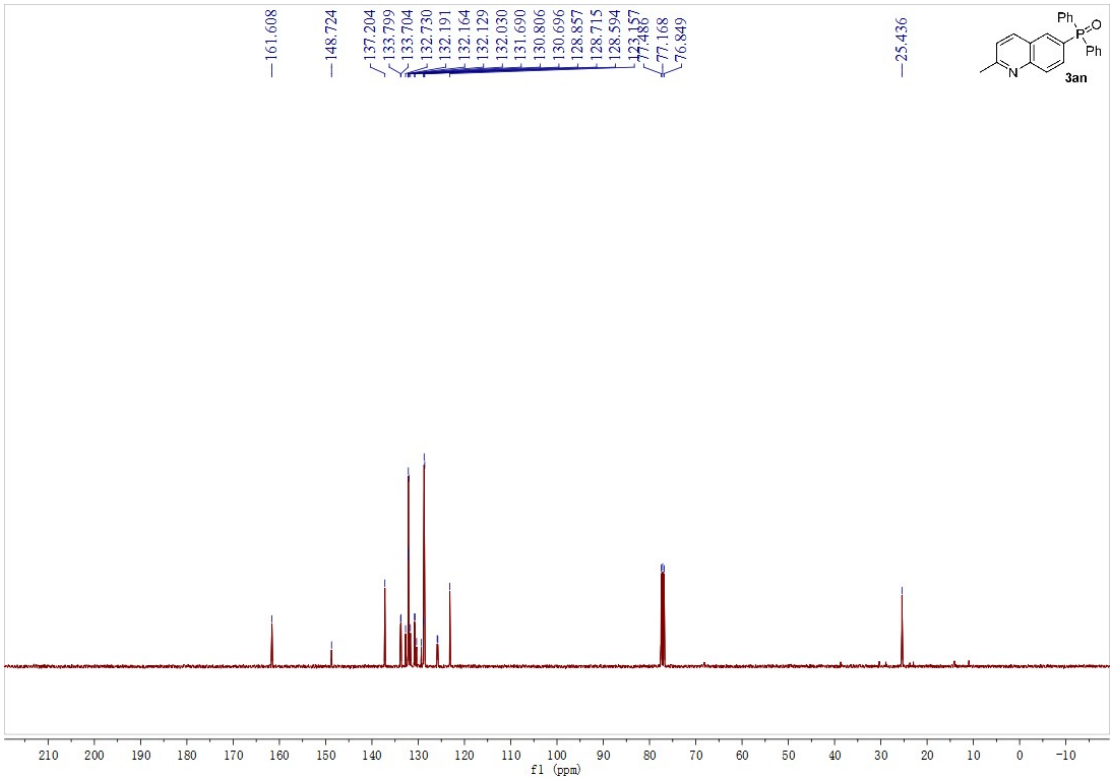
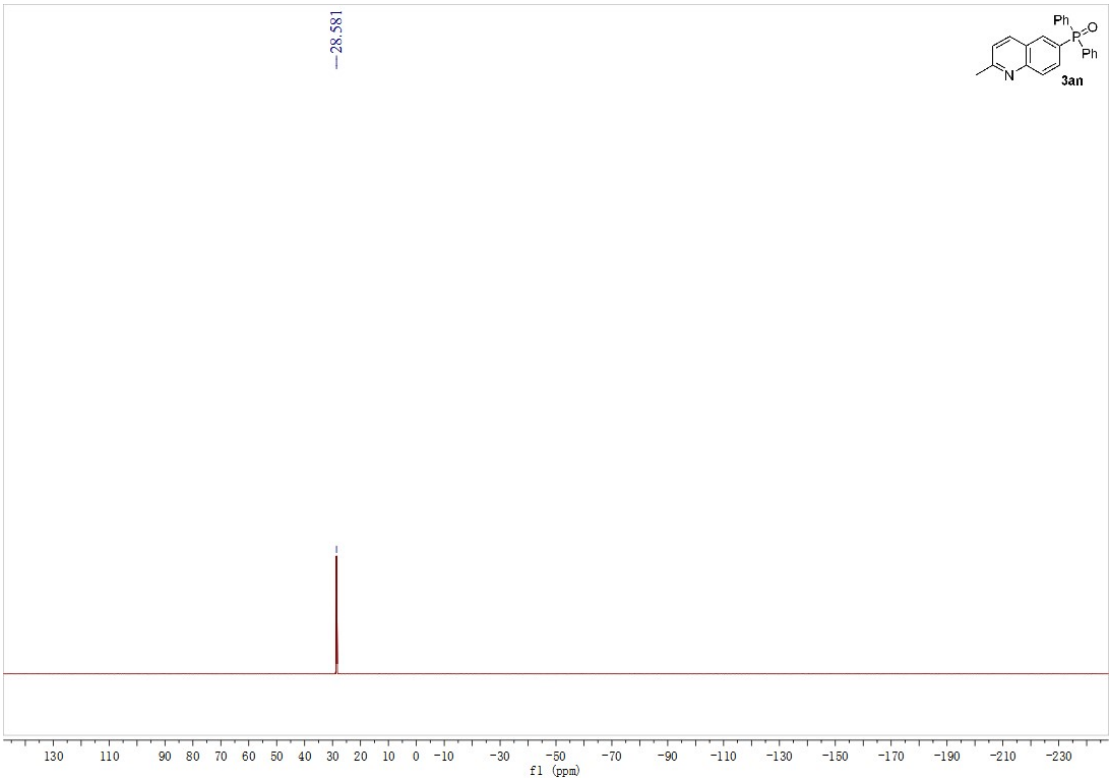


^{1}H NMR spectrum of **3an** in $CDCl_3$



^{13}C NMR spectrum of **3an** in $CDCl_3$



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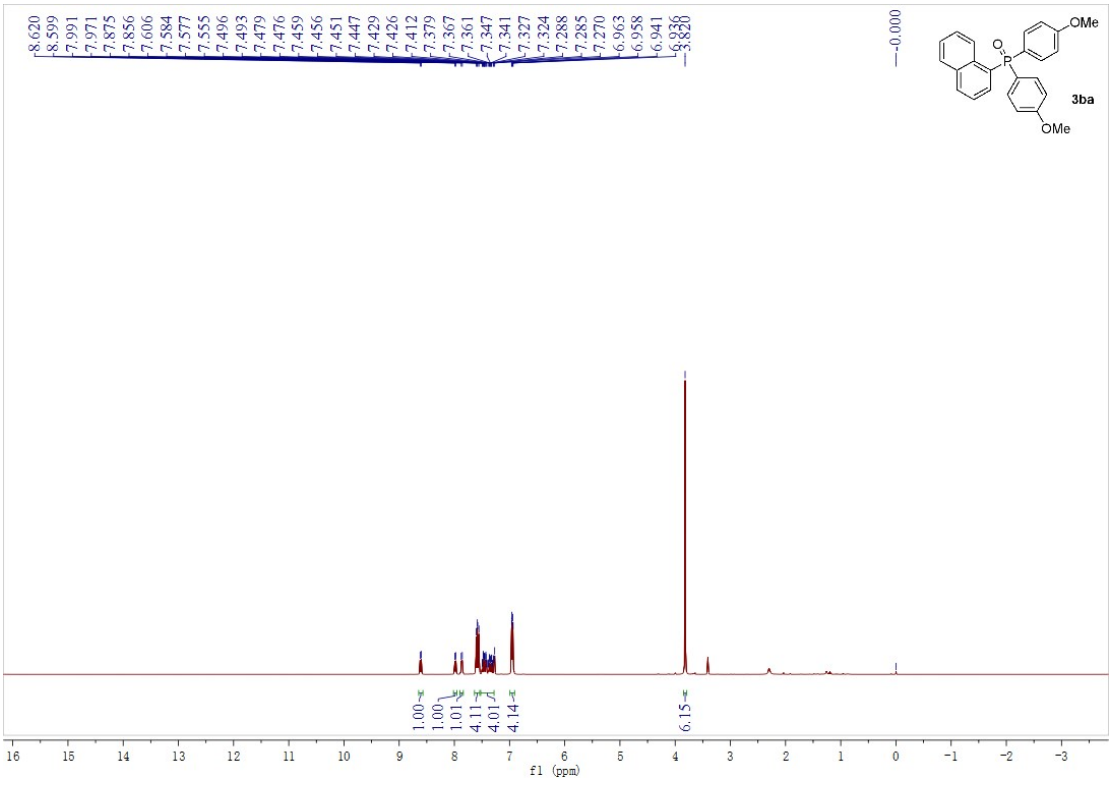
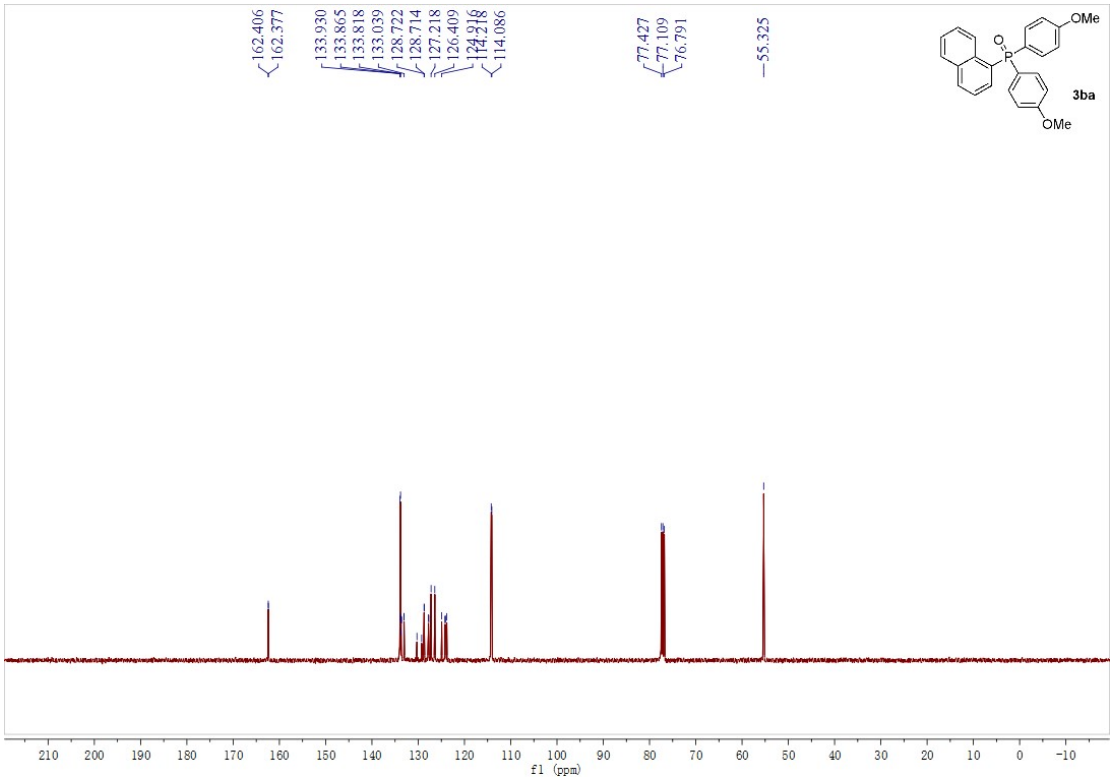
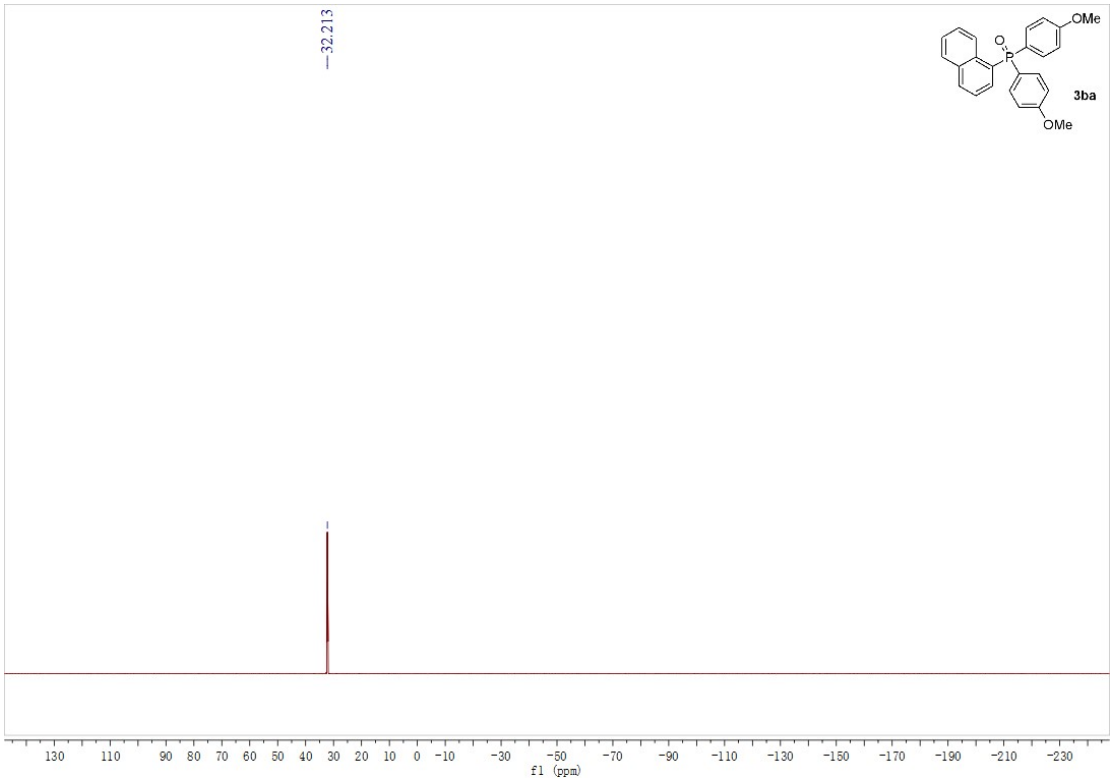


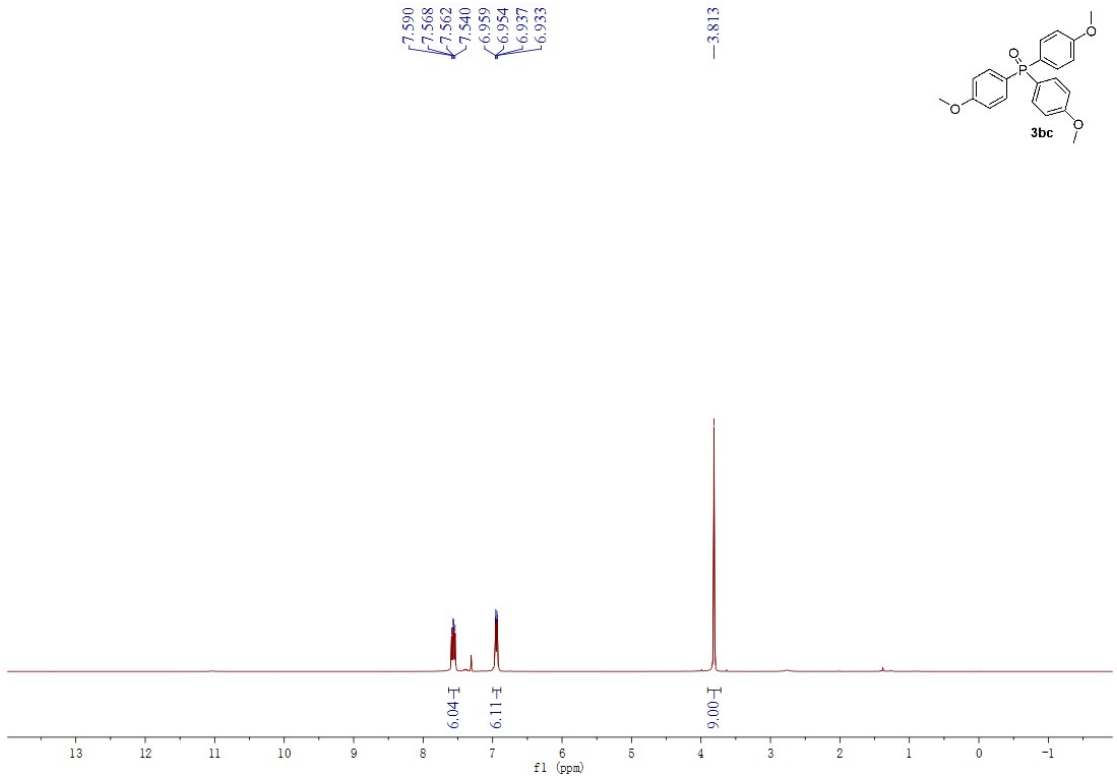
^{1}H NMR spectrum of **3ba** in $CDCl_3$



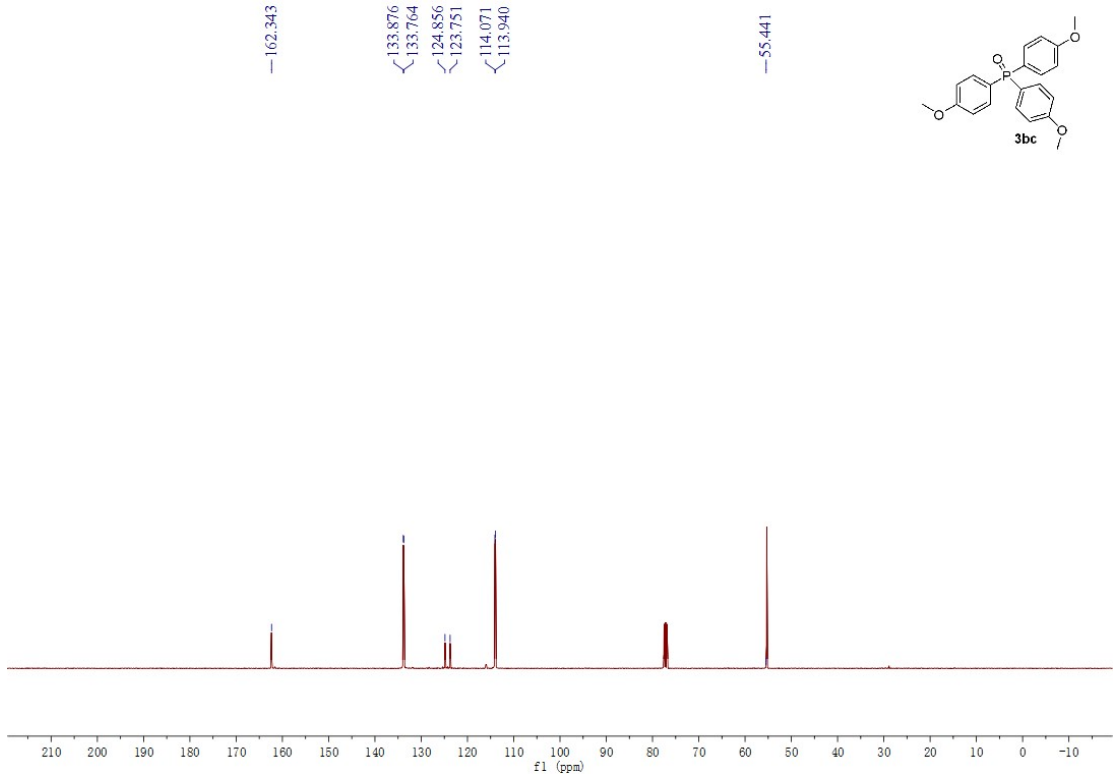
^{13}C NMR spectrum of **3ba** in $CDCl_3$



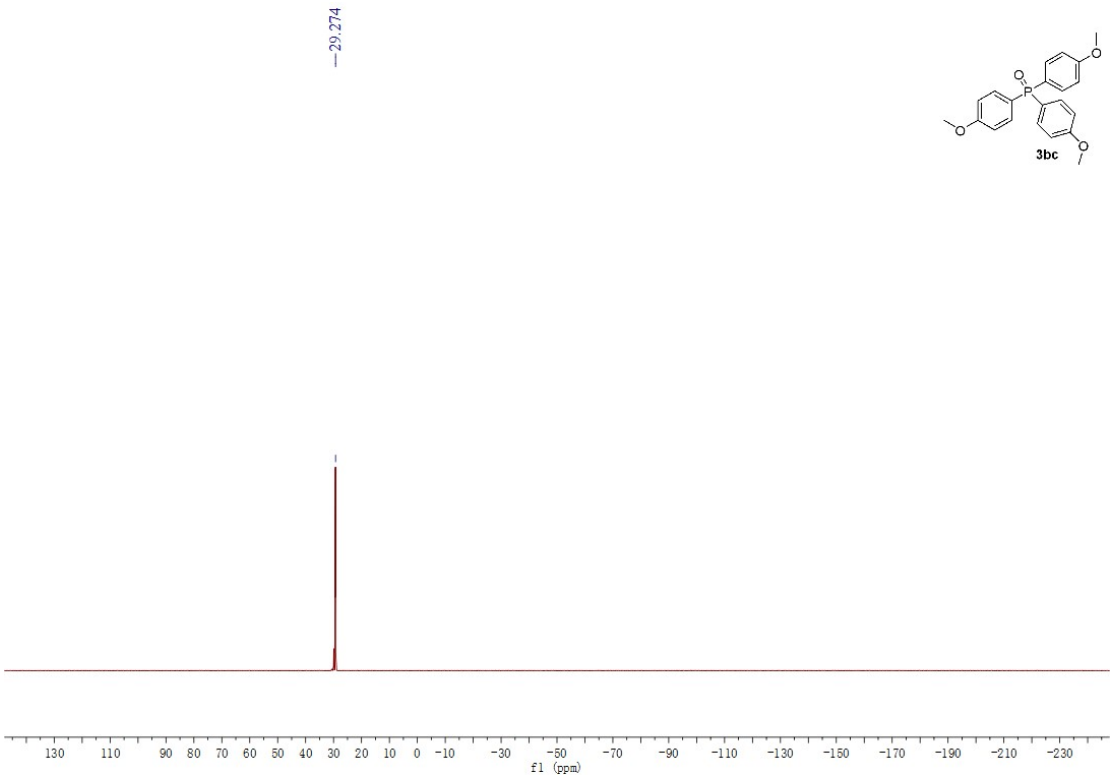
^{31}P NMR spectrum of **3ba** in $CDCl_3$



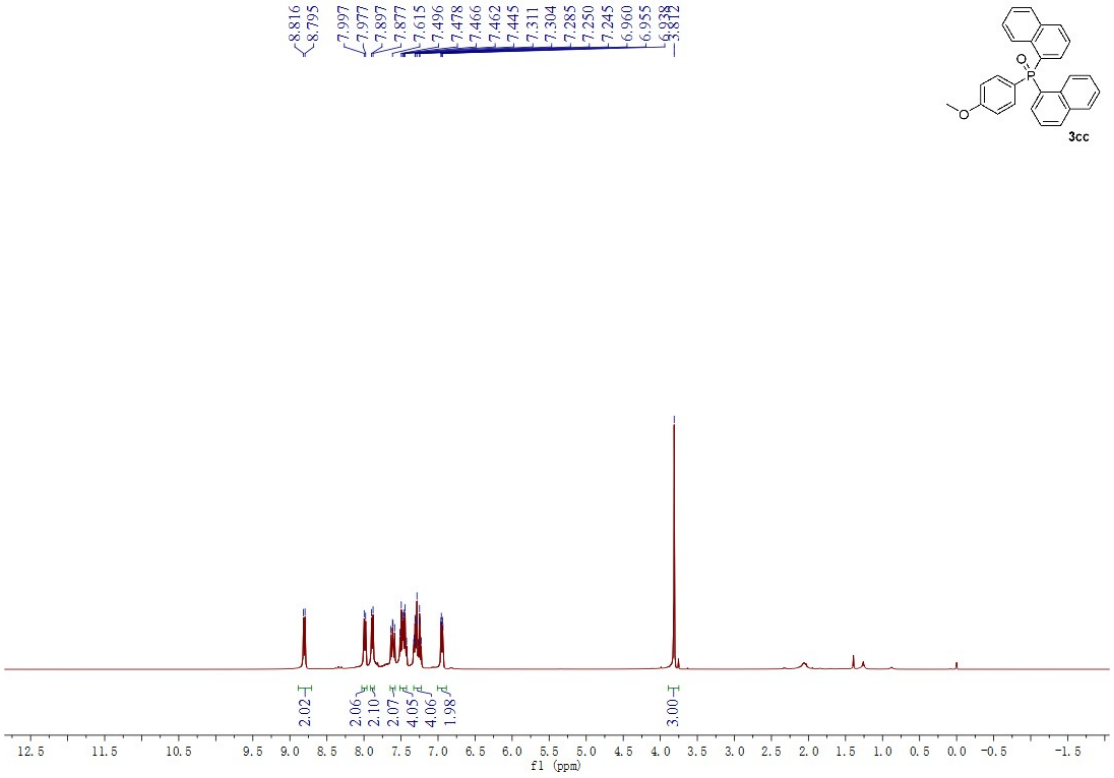
^{1}H NMR spectrum of **3bc** in $CDCl_3$



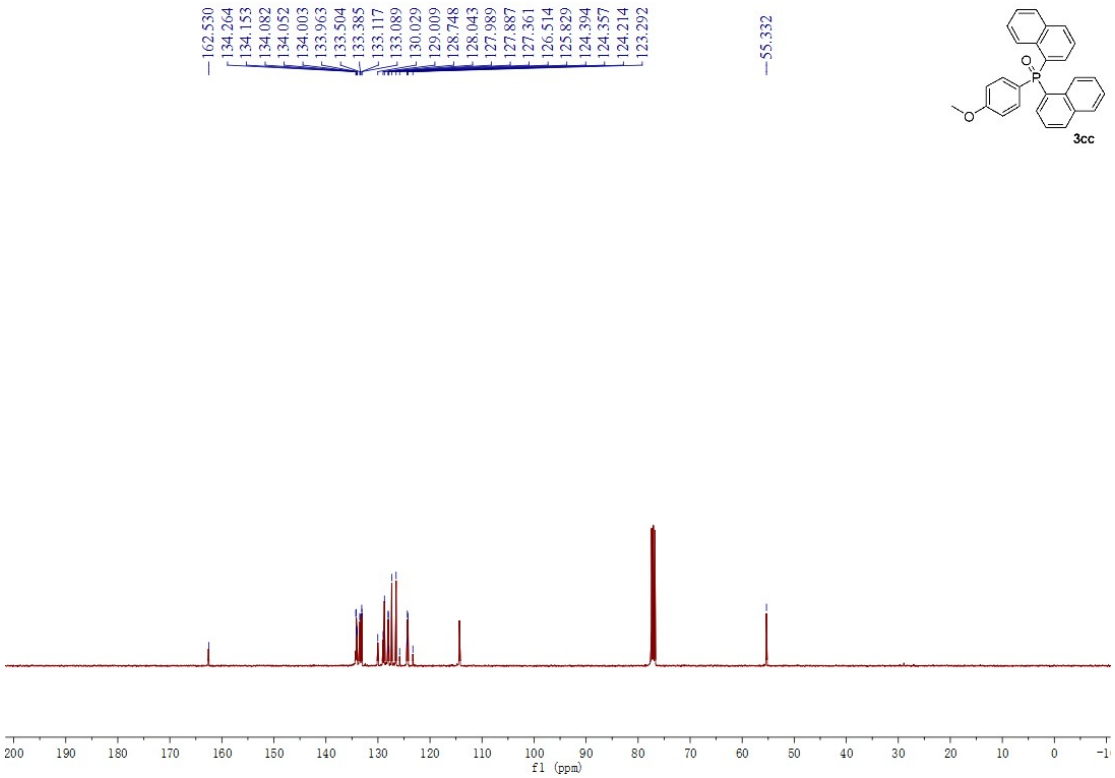
^{13}C NMR spectrum of **3bc** in $CDCl_3$



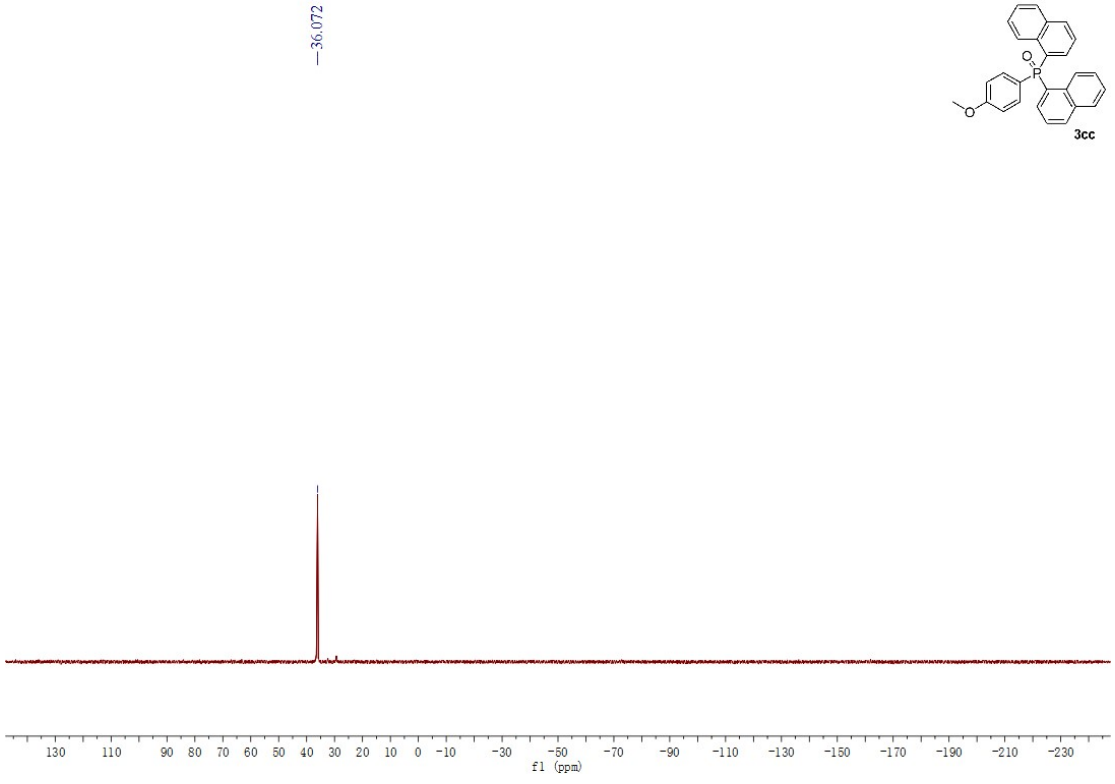
^{31}P NMR spectrum of **3bc** in $CDCl_3$



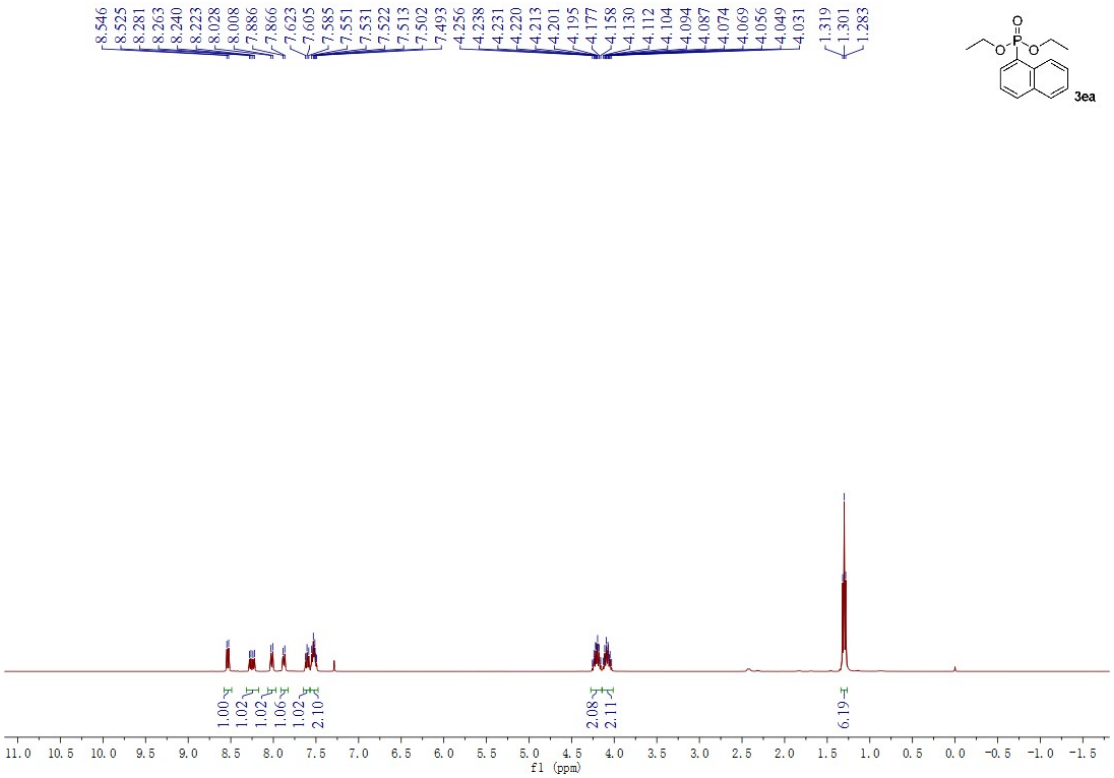
^{1}H NMR spectrum of **3cc** in $CDCl_3$



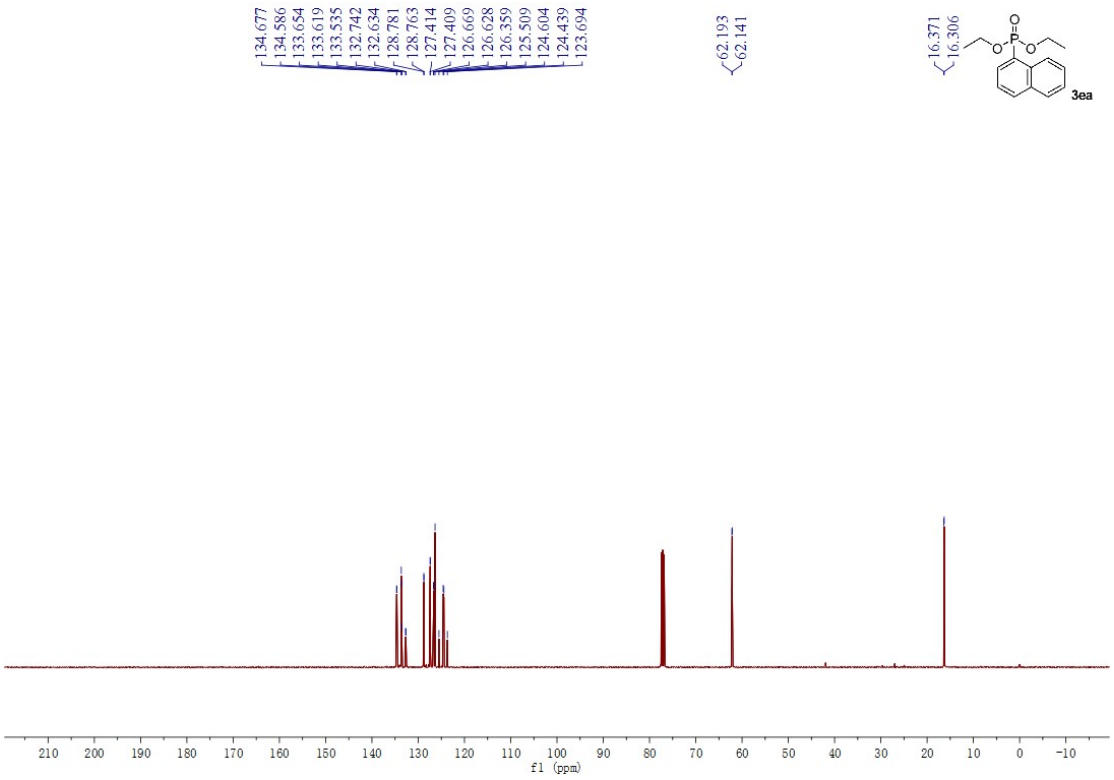
^{13}C NMR spectrum of **3cc** in $CDCl_3$



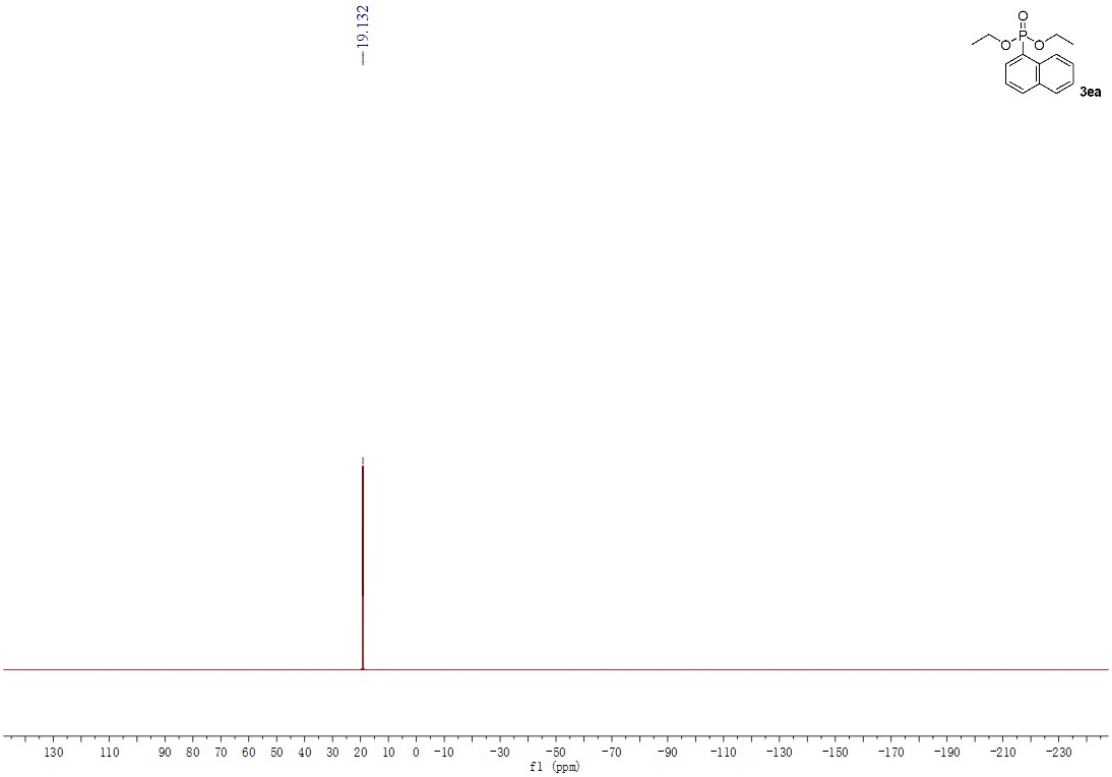
^{31}P NMR spectrum of **3cc** in $CDCl_3$



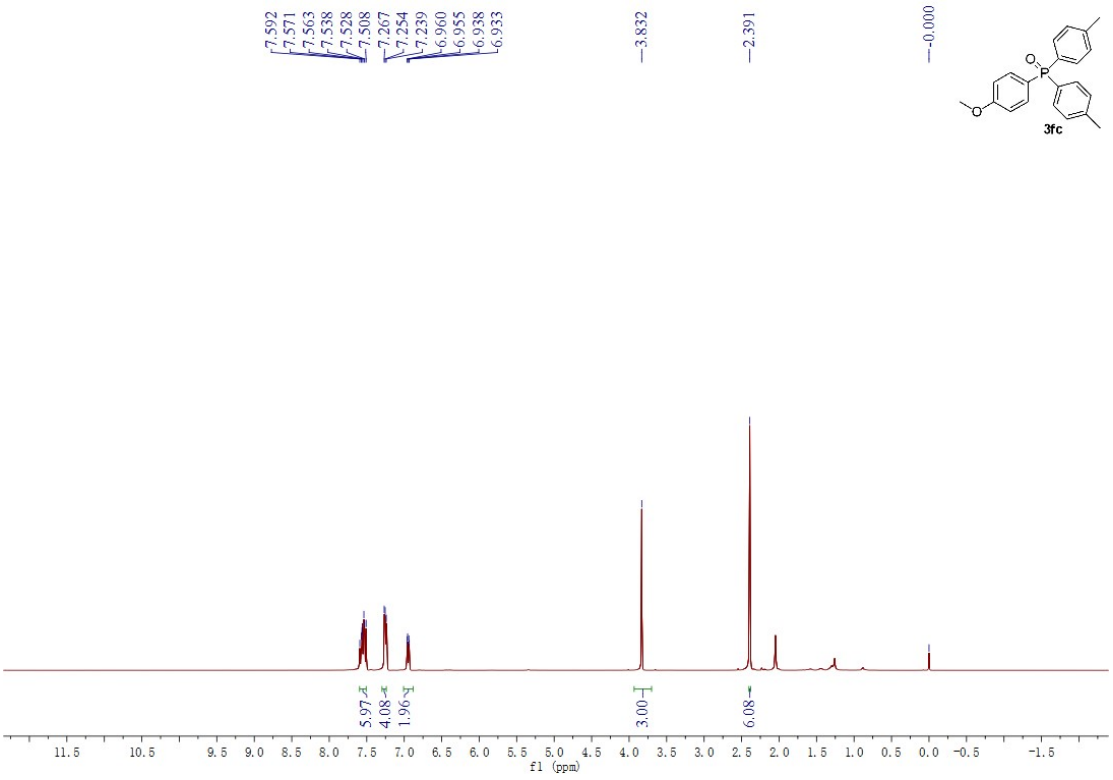
^{1}H NMR spectrum of **3ea** in $CDCl_3$



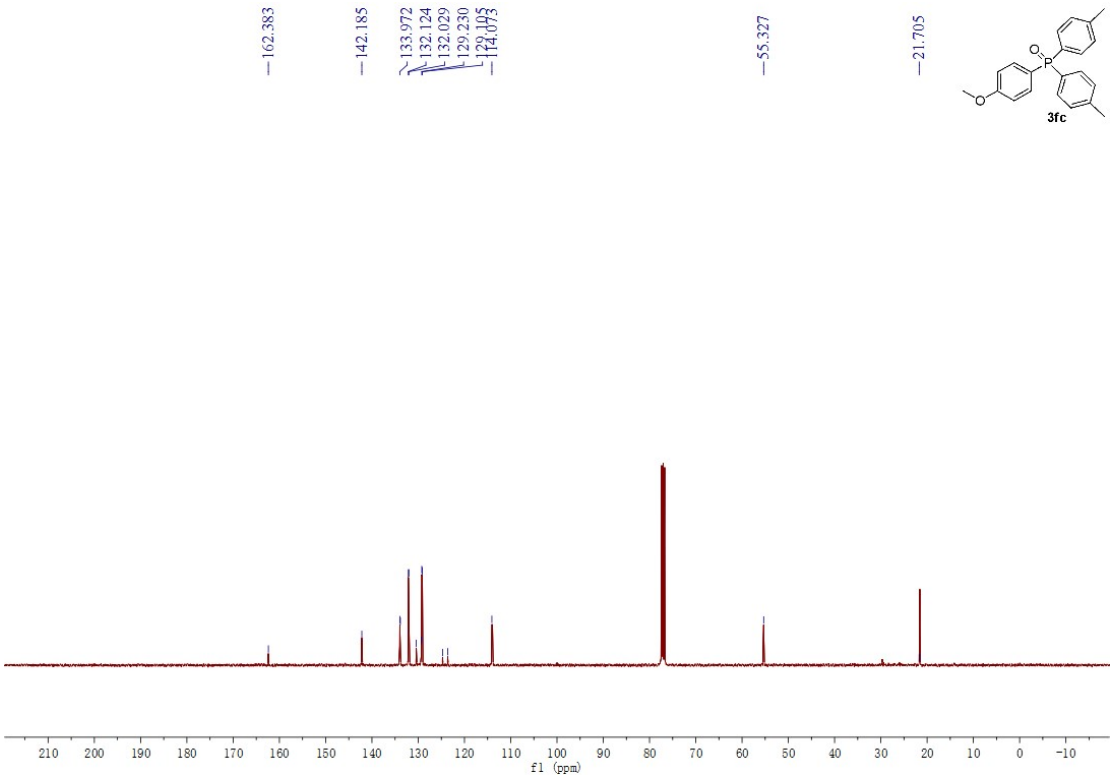
^{13}C NMR spectrum of **3ea** in $CDCl_3$



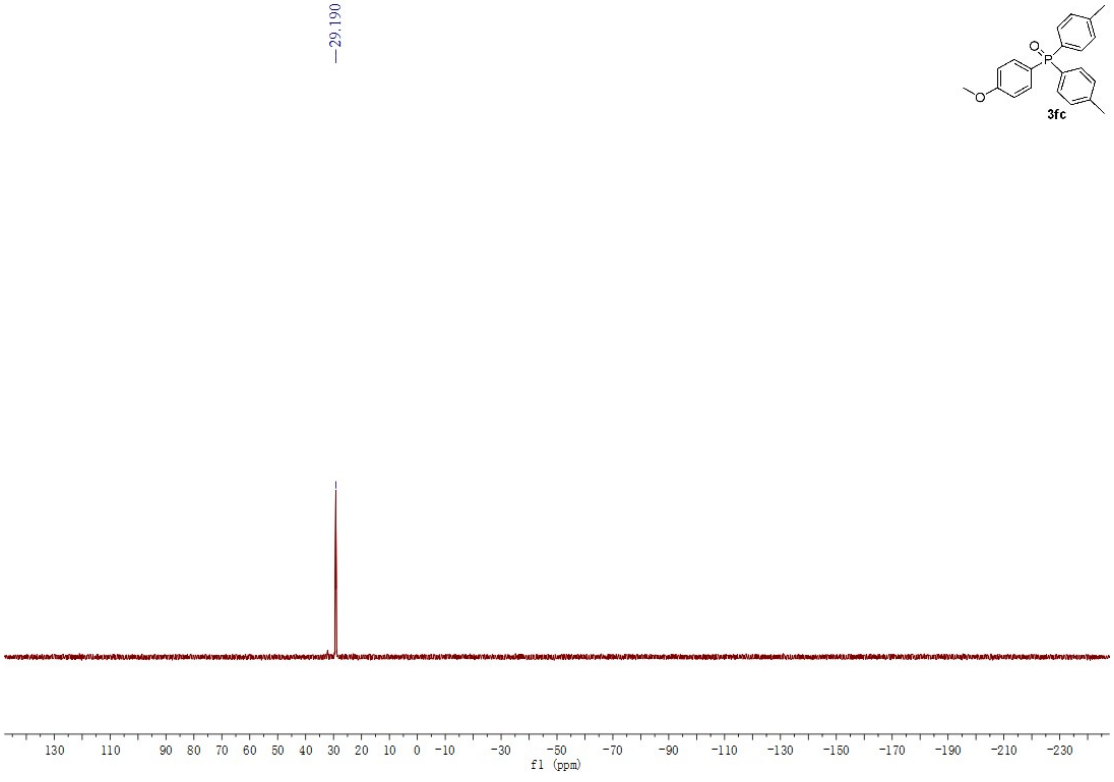
^{31}P NMR spectrum of **3ea** in $CDCl_3$



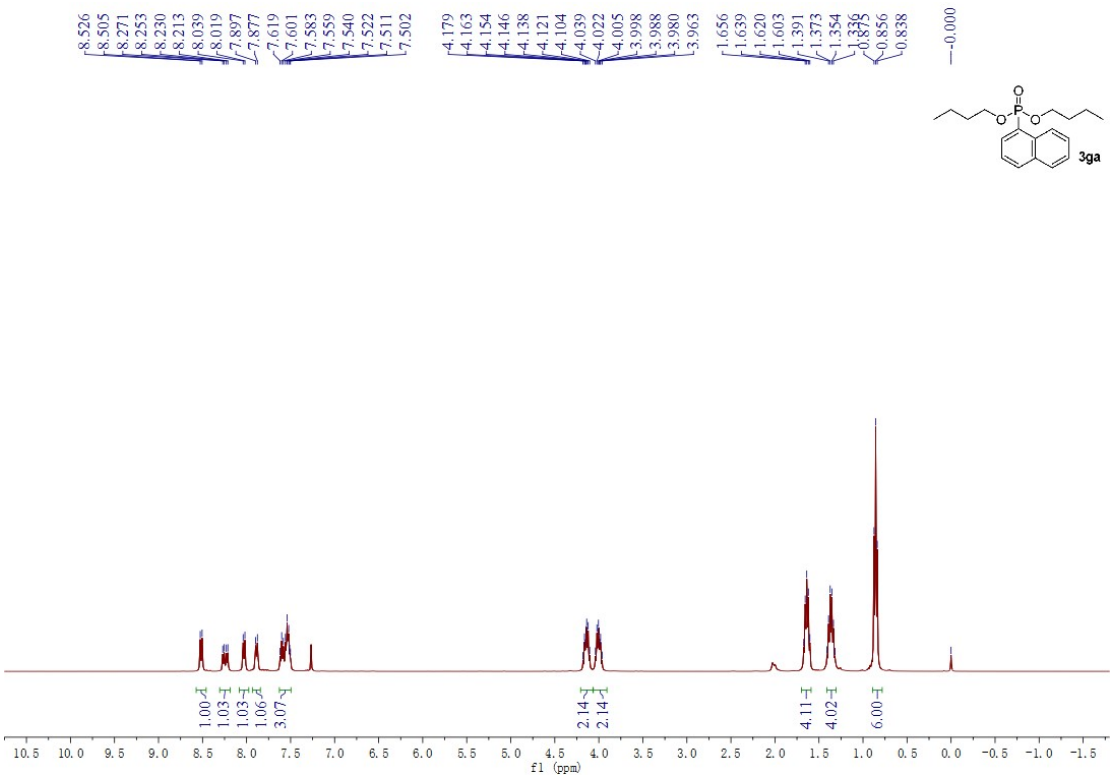
^{1}H NMR spectrum of **3fc** in $CDCl_3$



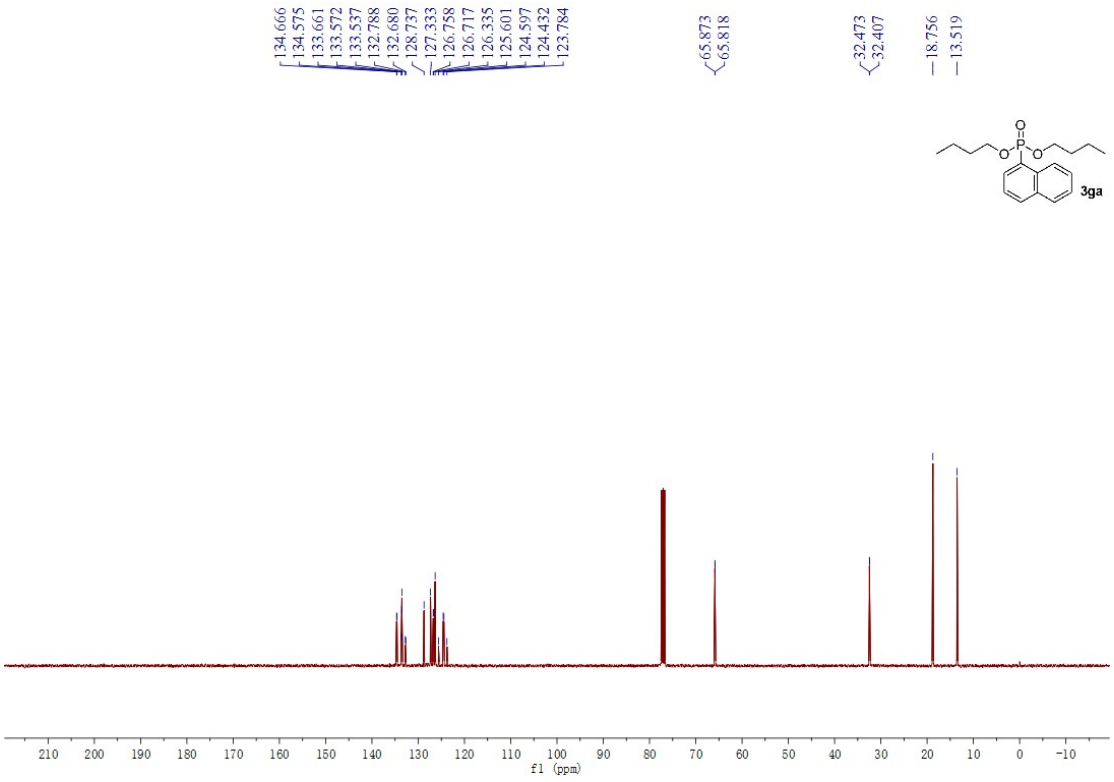
^{13}C NMR spectrum of **3fc** in $CDCl_3$



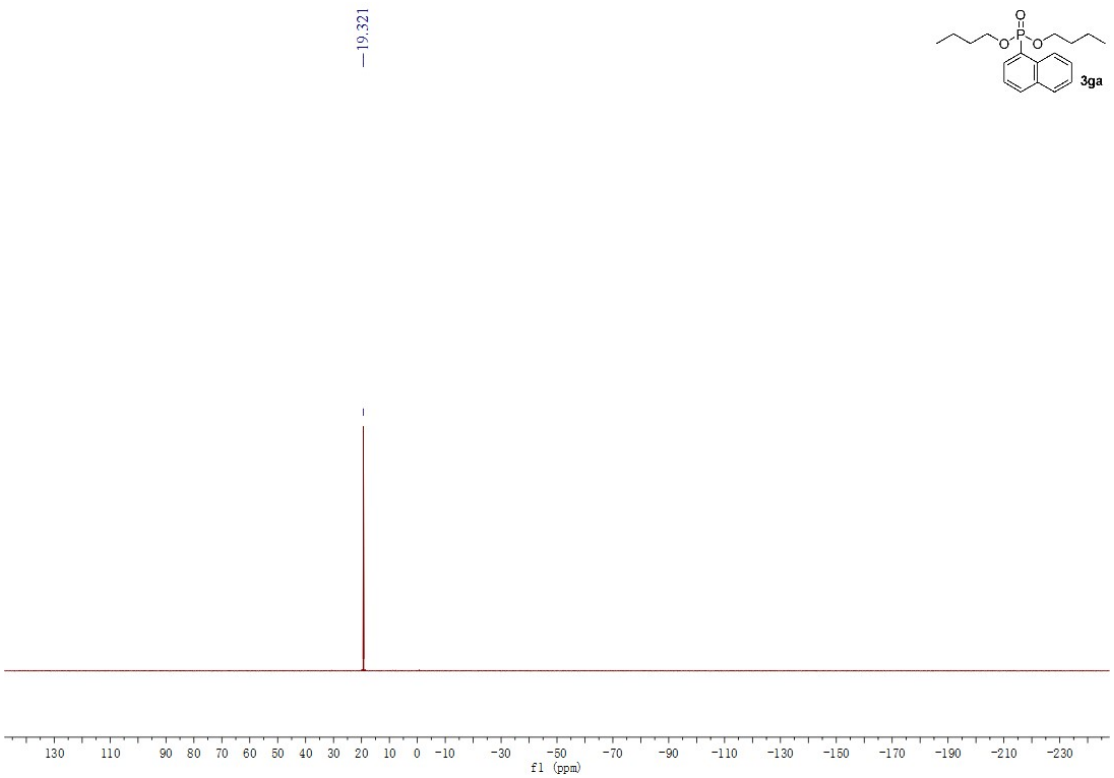
^{31}P NMR spectrum of **3fc** in $CDCl_3$



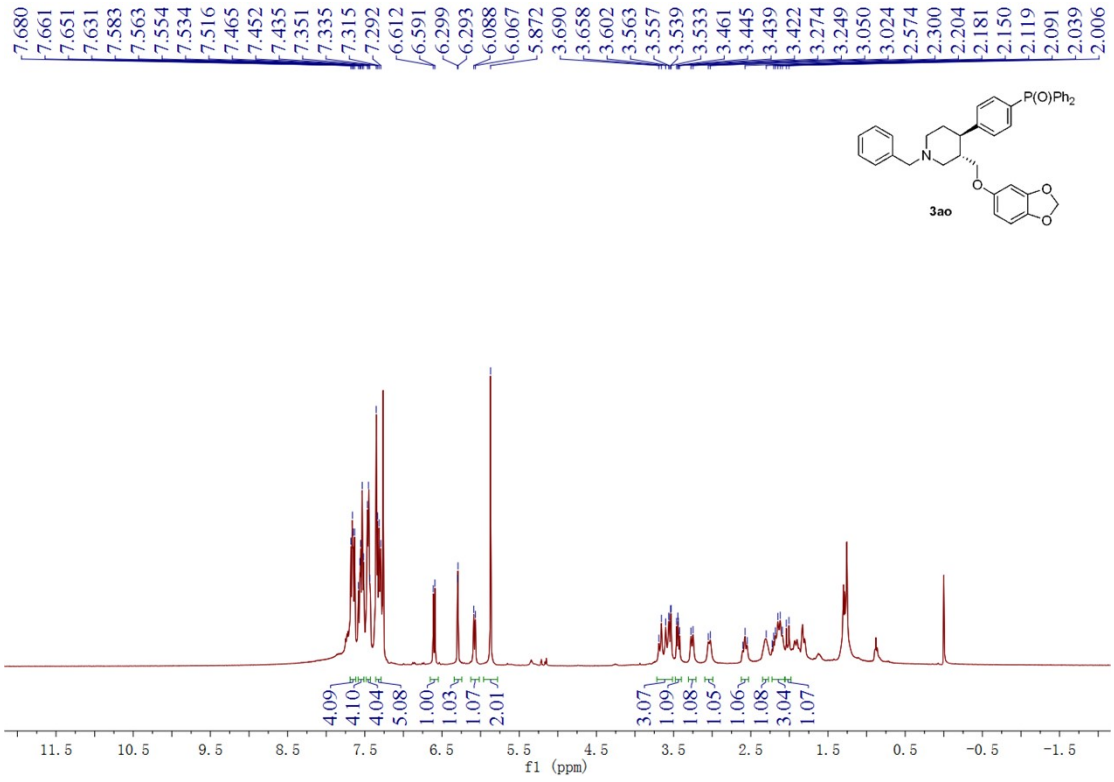
^{1}H NMR spectrum of **3ga** in $CDCl_3$



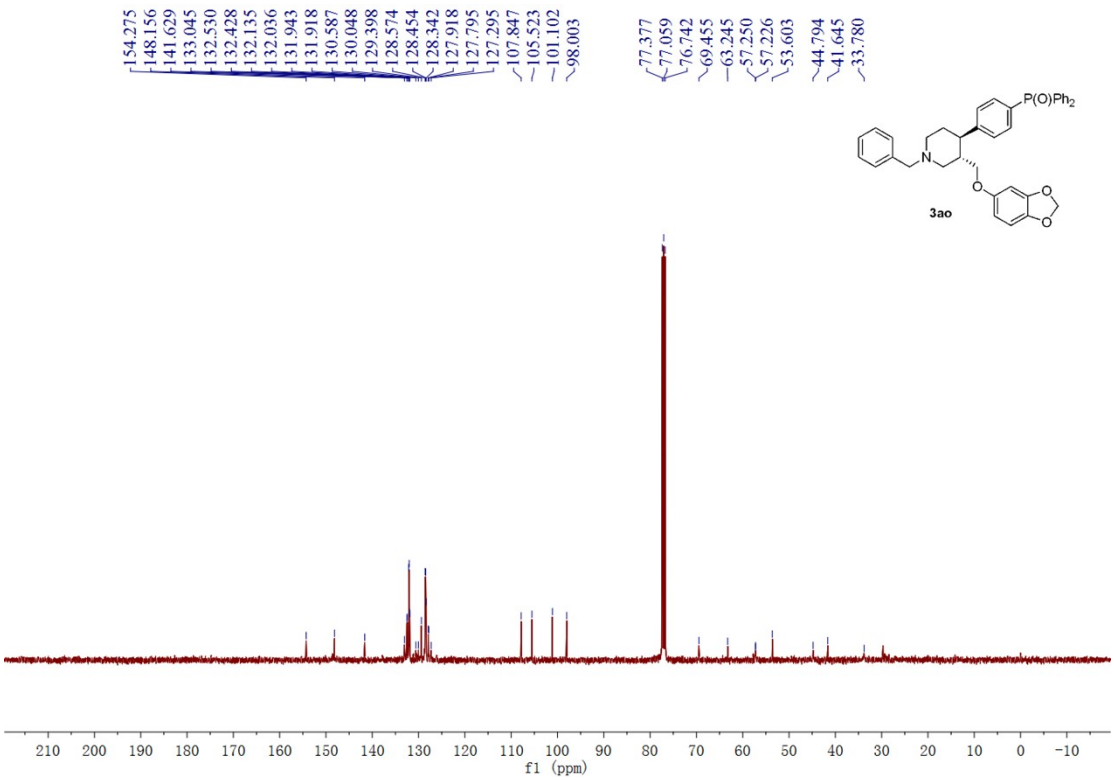
^{13}C NMR spectrum of **3ga** in $CDCl_3$



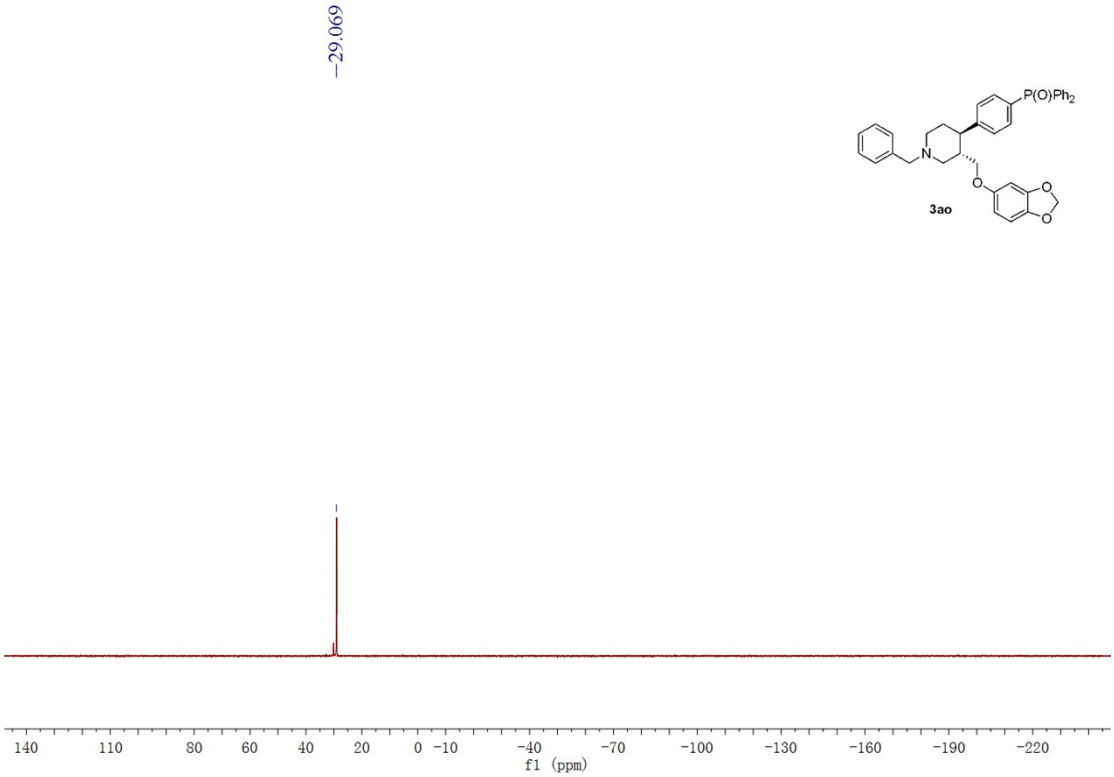
^{31}P NMR spectrum of **3ga** in $CDCl_3$



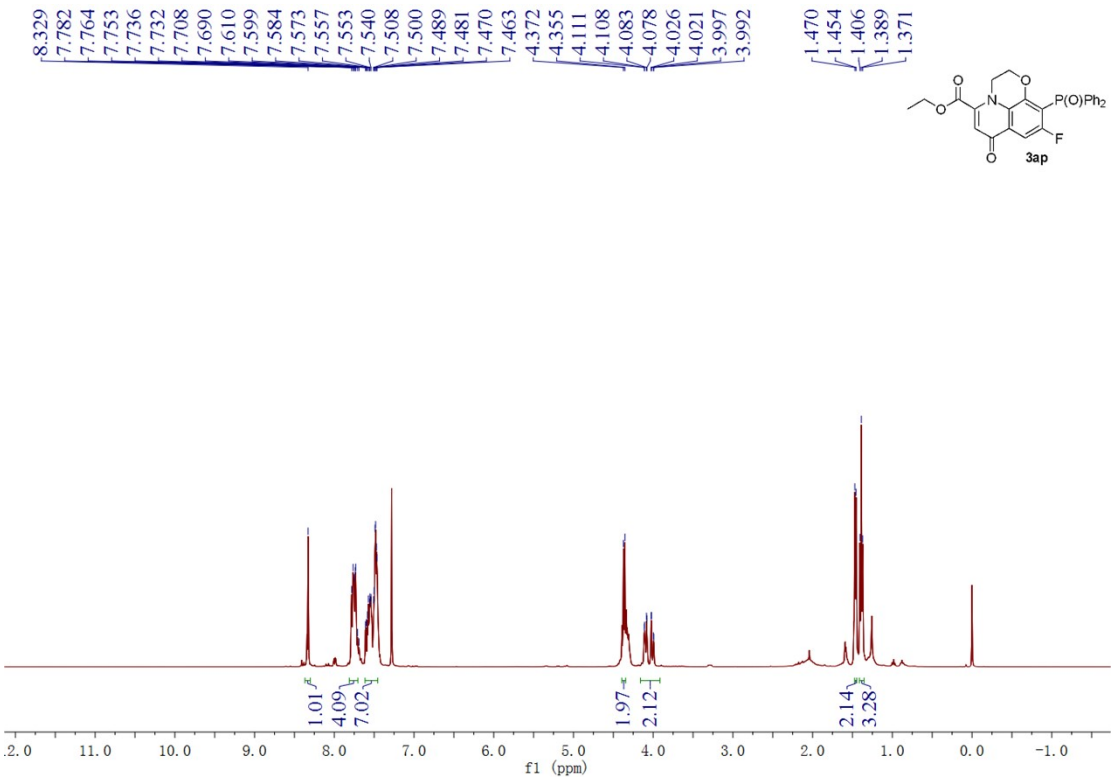
^{1}H NMR spectrum of **3ao** in $CDCl_3$



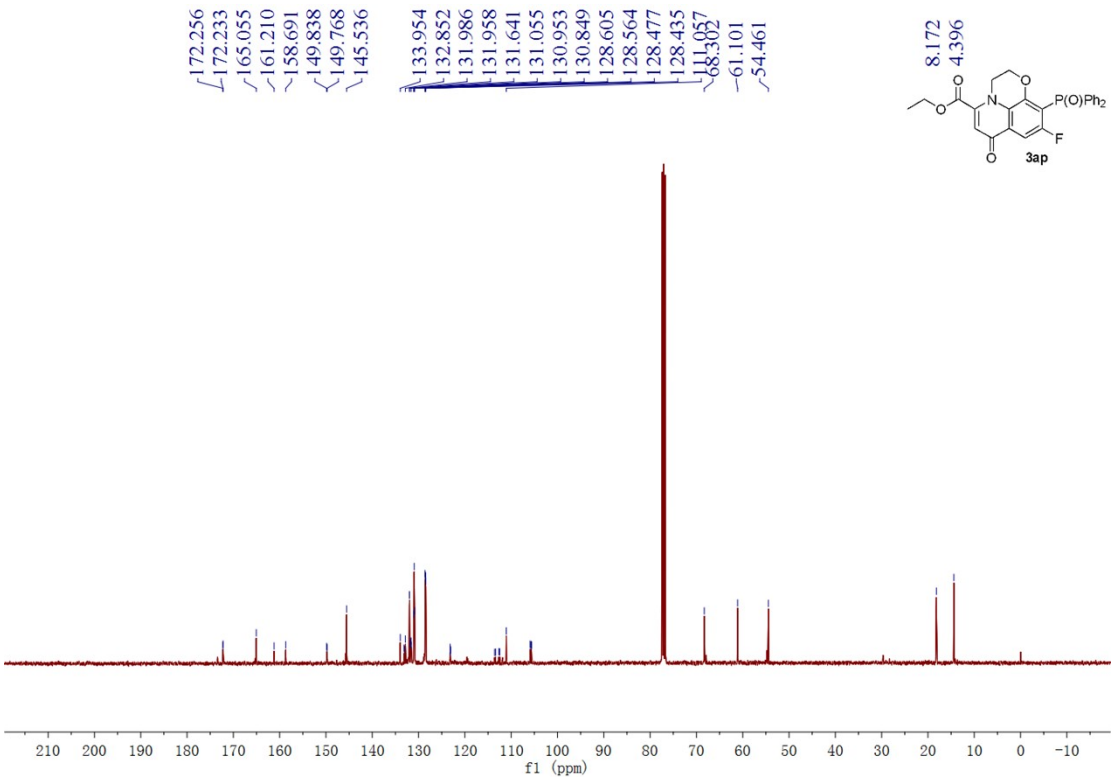
^{13}C NMR spectrum of **3ao** in $CDCl_3$



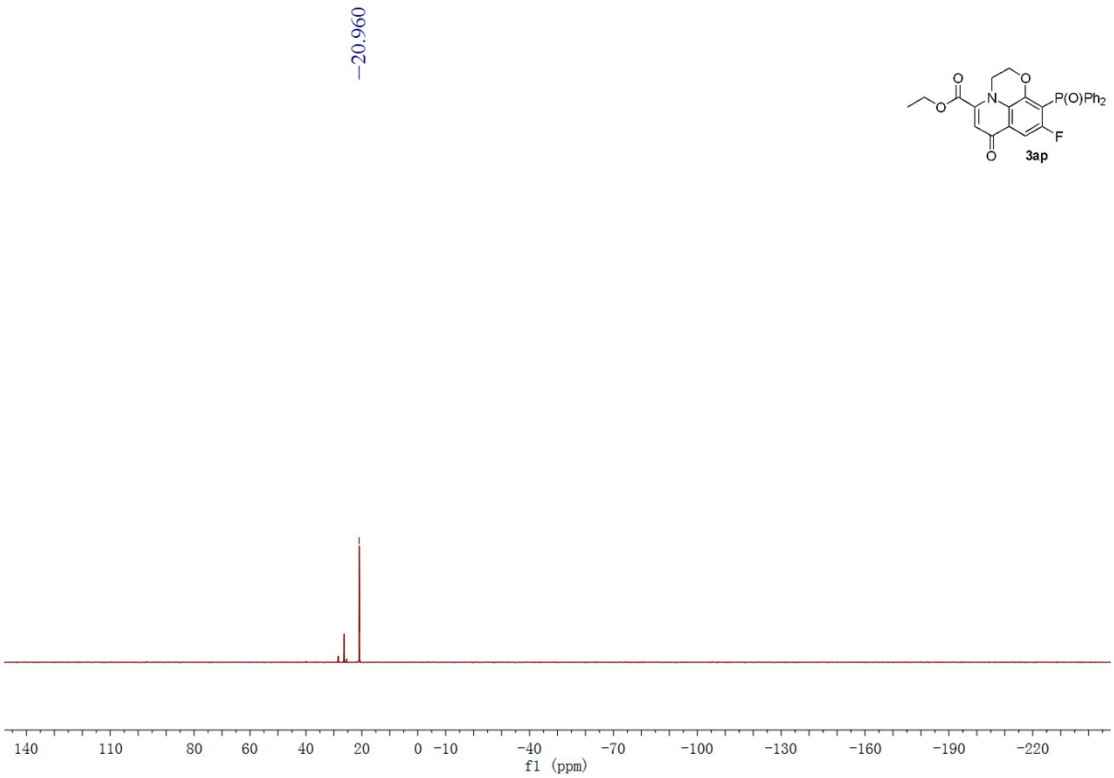
^{31}P NMR spectrum of **3ao** in $CDCl_3$



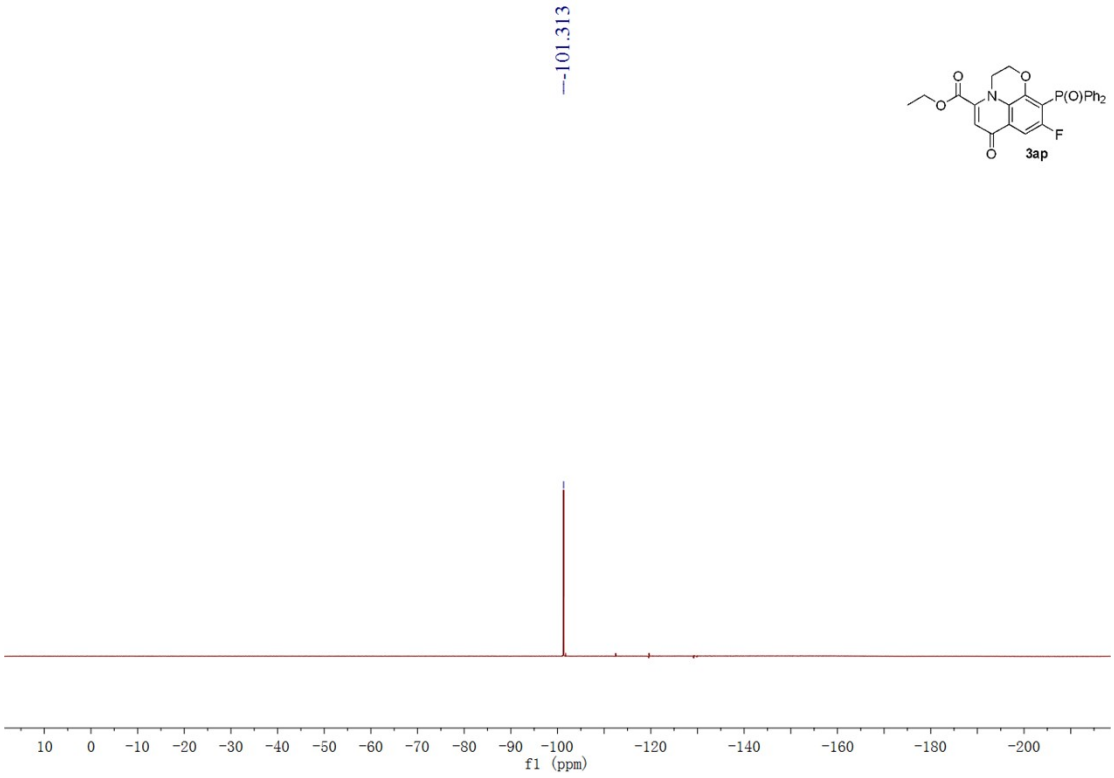
^{1}H NMR spectrum of **3ap** in $CDCl_3$



^{13}C NMR spectrum of **3ap** in $CDCl_3$



^{31}P NMR spectrum of **3ap** in $CDCl_3$



^{19}F NMR spectrum of **3ap** in $CDCl_3$