Supporting Information

Phosphoric acid activation, reduction and transformation processes: efficient preparation of triarylphosphines

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Content

1. General Information

1.1 General Remarks

All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. [TBA][H_2PO_4] was used after vacuum-drying at 80 °C for 12 h. Diatomaceous earth, 4 Å molecular sieve and basic alumina were all dried by dynamic vacuum heating to 200 °C for at least 48 h before usage.

All manipulations were performed in a MO-40M glove box under vacuum with an Argon inert atmosphere or using standard Schlenk techniques. Benzene and Tetrahydrofuran were dried over Na and stored with molecular sieves (4 Å). Acetonitrile and dichloromethane were distilled at the present of CaH_2 and stored with molecular sieves (4 Å). $CDCl_3$ was stored with molecular sieves (4 Å). All solvents used were anhydrous and oxygen-free, obtained by bubble degassing with argon. To ensure proper usage, it is recommended that all glassware be oven-dried for a minimum of 6 hours at temperatures exceeding 150 °C. All the other materials unless otherwise mentioned were used as received.

^1H NMR, ^{31}P NMR and ^{13}C NMR data analyses were performed with Varian Mercuryplus-400 instrument and plus-600 instrument respectively. $CDCl_3$ was employed as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by specifying TMS resonance in the ^1H NMR spectrum as 0.00 ppm. The data of ^1H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shift for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Melting points were measured with an XT-4 apparatus. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer. Column chromatography was generally performed on silica gel (200–300 mesh) and TLC analyses were conducted on silica gel GF254 plates.

1.2. Notes

1.2.1 Precautions related to the synthesis of [TBA][$P(SiCl_3)_2$].

Research has shown that [TBA][$P(SiCl_3)_2$] can release toxic phosphine (PH_3) gas when it comes into contact with water. To ensure safety, contaminated glassware should be placed in a well-ventilated fume hood overnight and rinsed with water. When removing the contaminated glassware from the glove box, it is important to use a well-sealed secondary container and transport it to a fume hood for disposal in order to prevent exposure to foul odors and potentially toxic vapors. For large quantities of reactions, it is recommended to remove volatile substances on the Schlenk line in a fume hood and connect it to an exhaust gas treatment unit to avoid contaminating the laboratory environment. Inside the glove box, glassware contaminated with [TBA][$P(SiCl_3)_2$] should be immediately stored in a second sealed container. Long-term storage of contaminated glassware in glove boxes has been found to result in the production of a fine white powder, which can subsequently contaminate the internal environment of the glove box.

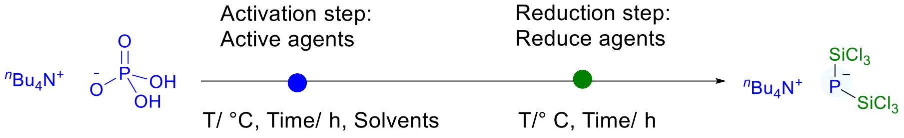
1.2.2 Treatment method of the extra trichlorosilane

As per the method described by Cummins[1], the collected trichlorosilane should be slowly added to isopropanol at 0 °C with rapid stirring in a fume hood. The temperature should be kept below 40 °C and the mixture should be stirred overnight. The resulting solution should be added proportionally to an aqueous solution of sodium hydroxide. The addition process is exothermic and results in gas production. It should be carried out slowly at a temperature not exceeding 40 °C. After the addition was completed, the resultant mixture should be stirred overnight and then discarded. If any residue remains in the glassware, it can be cleaned using a 1.0 M aqueous solution of sodium hydroxide.

2 Experimental Procedures

2.1 Optimize reaction conditions.

Table S1 The screening and optimization of the reaction conditions for both the first-step activation and second-step reduction reactions.[a]

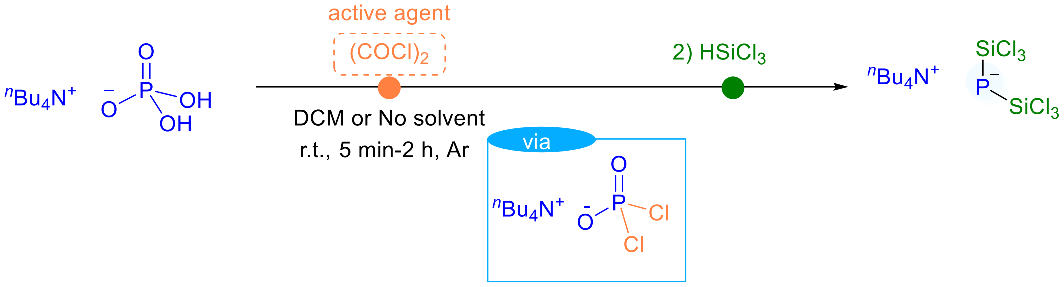


Entry	Activation step		Reduction step			
	Active agent (3 eq.)	solvent	Reductant	T / °C	Time / h	Yield/%
1	$(COCl)_2$	CH_2Cl_2	$HSiCl_3$	60	24	75
2[b]	Tf_2O	CH_2Cl_2	$HSiCl_3$	60	24	--
3	Oxalic acid	CH_2Cl_2	$HSiCl_3$	60	24	n.r.
4	$SOCl_2$	CH_2Cl_2	$HSiCl_3$	60	24	trace
5	PVCl	CH_2Cl_2	$HSiCl_3$	60	24	trace
6	CCl_4	CH_2Cl_2	$HSiCl_3$	60	24	trace
7	TCCA	CH_2Cl_2	$HSiCl_3$	60	24	trace
8	\	CH_2Cl_2	$HSiCl_3$	60	24	\
9	$(COCl)_2$(1 eq.)	CH_2Cl_2	$HSiCl_3$	60	24	21
10	$(COCl)_2$(2 eq.)	CH_2Cl_2	$HSiCl_3$	60	24	50
11[c]	$(COCl)_2$ (3 eq.)	CH_2Cl_2	H-M	60	24	n.r.
12	$(COCl)_2$ (3 eq.)	CH_2Cl_2	$HSiCl_3$ (5 eq.)	60	24	n.r.
13	$(COCl)_2$ (3 eq.)	CH_2Cl_2	$HSiCl_3$ (15 eq.)	60	24	51
14	$(COCl)_2$ (3 eq.)	CH_2Cl_2	$HSiCl_3$ (25 eq.)	60	24	75
15	$(COCl)_2$ (3 eq.)	THF	$HSiCl_3$	60	24	6
16	$(COCl)_2$ (3 eq.)	TBMe	$HSiCl_3$	60	24	29
17	$(COCl)_2$ (3 eq.)	CH_3CN	$HSiCl_3$	60	24	52
18	$(COCl)_2$ (3 eq.)	PhMe	$HSiCl_3$	60	24	35
19	$(COCl)_2$ (3 eq.)	DME	$HSiCl_3$	60	24	32
20	$(COCl)_2$ (3 eq.)	\	$HSiCl_3$	60	24	70
21	$(COCl)_2$ (3 eq.)	CH_2Cl_2	$HSiCl_3$	rt	24	n.r.
22	$(COCl)_2$ (3 eq.)	CH_2Cl_2	$HSiCl_3$	80	24	80
23	$(COCl)_2$ (3 eq.)	CH_2Cl_2	$HSiCl_3$	110	12	77

[a]. Standard conditions: [TBA][H_2PO_4] (0.2 g, 0.6 mmol), $(COCl)_2$ (0.015 mL, 1.8 mmol, 3 eq.), DCM (4 mL) at room temperature for up to 2 hours. Then $HSiCl_3$ (1.7 mL, 18 mmol, 20 eq.) at 60 °C for 24 h under argon atmosphere; PVCl = Trimethylacetyl chloride, TCCA = Trichloroisocyanuric acid, PMHS = Poly(methylhydrosiloxane), TMDS = 1,1,3,3-Tetramethyldisiloxane, AL-H = diisobutyl aluminum hydride. [b] $(COCl)_2$ was replaced by Tf_2O, which produced a new shift of -150 ppm, but the compound was not isolated. [c] $HSiCl_3$ was replaced by PMHS, TMDS, $(Et)_3SiH$, $PhSiH_3$, Ph_3SiH, and Al-H, but no reaction occurred.

2.2 Standard reaction procedure for the synthesis of [TBA] [P($SiCl_3$)$_2$]

Note: The compound [TBA][P($SiCl_3$)$_2$] is extremely sensitive to moisture and air. Therefore, it is necessary to use dry solvents and glassware during the preparative procedures. To purify impure material, recrystallization can be carried out using DCM and pentane at a temperature of −35 °C. The purification method reported by Cummins[1-3] previously and can be referred to for more information.

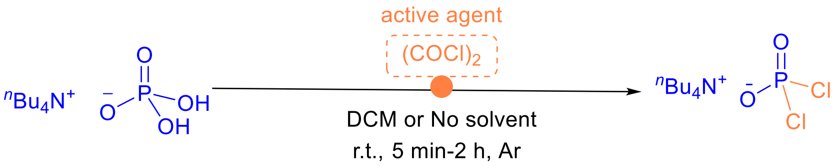


Standard reaction procedure: To a 50 mL Schlenk tube placed in the glove box, which was oven-dried overnight at 80 °C and cooled down to ambient temperature under Argon atmosphere, a magnets and dried dichloromethane (DCM, 5 mL) were added, followed by tetrabutylphosphonic acid ([TBA][H_2PO_4] (3 mmol, 1 g), oxalyl chloride (3 eq, 9 mmol, 0.75 mL). The Schlenk tube was sealed properly and moved out the glove box. The mixture was then reacted at room temperature for two hours. After removing the solvent, unreacted oxalyl chloride (COCl)$_2$, and volatile substances in the mixture through the connection to an oil bubbler, water bubbler and vacuum line equipped with potassium permanganate drying tower, trichlorosilane (60 mmol, 20 eq., 6 mL,) was added in the residual mixture in the Schlenk tube under argon (Ar) atmosphere and quickly degassed with Argon three times. The resultant mixture was then reacted at 60 °C for 24 h. After cooled down to room temperature, the reaction tube was then placed in a cold trap at -78 °C for 30 minutes to accelerate the precipitation of solid compounds. The reaction tube was then connected to the oil bubbler and water bubbler again to remove the possible gaseous substances generated during the reaction as well as unreacted trichlorosilane. The resulted mixture in the Schlenk tube was then moved into glove box. The supernatant of the reaction mixture was then quickly transfer to a flask (50 mL) for consequent special workup process. The remaining solids in the reaction tube were dissolved with dichloromethane DCM (3 × 5 mL), and collected the solution by a disposable syringe containing diatomaceous earth (3 cm) into a flask (50 mL). Then the resultant solution was recrystallized with dried diethyl ether (15 mL) and sealed, followed by moving out of the glove box and placement in a cold trap at -35 °C for overnight. A white powder was obtained from the recrystallization. The powder was then washed with pre-cooled diethyl ether at -35 °C for 3 times and dried under vacuum to give the isolated yield. Of important note is that the filtration must be as quick as possible while the solid at low temperature, otherwise, it will transform into yellow oil in the solution at ambient temperature for a bit longer time. The recrystallization process required once again to obtain the white solid product.

All products were characterized on 400 MHz and 600 MHz NMR instrument at 25 °C by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy in $CDCl_3$.

2.3 General procedure for the preparation of [TBA][PO_2Cl_2].

Note: Experiments in this section (S2.3.) were performed under the General Conditions described in Section S2.2.



To a 50 mL Schlenk tube placed in the glove box, which was oven-dried overnight and cooled down to ambient temperature under Argon atmosphere, a magnets and dried dichloromethane (DCM, 5 mL) were added, followed by tetrabutylphosphonic acid ([TBA][H_2PO_4] (3 mmol, 1 g), oxalyl chloride (3 eq., 9 mmol, 0.75 mL). The Schlenk tube was sealed properly and moved out the glove box. The mixture was then reacted at room temperature for two hours. After removing the solvent, unreacted oxalyl chloride $(COCl)_2$, and volatile substances in the mixture through the connection to an oil bubbler, water bubbler and vacuum line equipped with potassium permanganate drying tower, the resulting yellow slime was then dissolved with dried acetone (4 mL) and go through a short column containing diatomaceous earth, followed by the addition of dried ether (16 mL) and recrystallization at -35 °C. The resulted white solid is pure compound of [TBA][PO_2Cl_2] with 87% isolated yield. It is worth noting that the atmosphere of recrystallization should be engaged with Ar as a protective gas in order to prevent any possible moisture in the air causing a potential decomposition of resultant product during the recrystallization process.

Characterization data for [TBA][PO_2Cl_2]

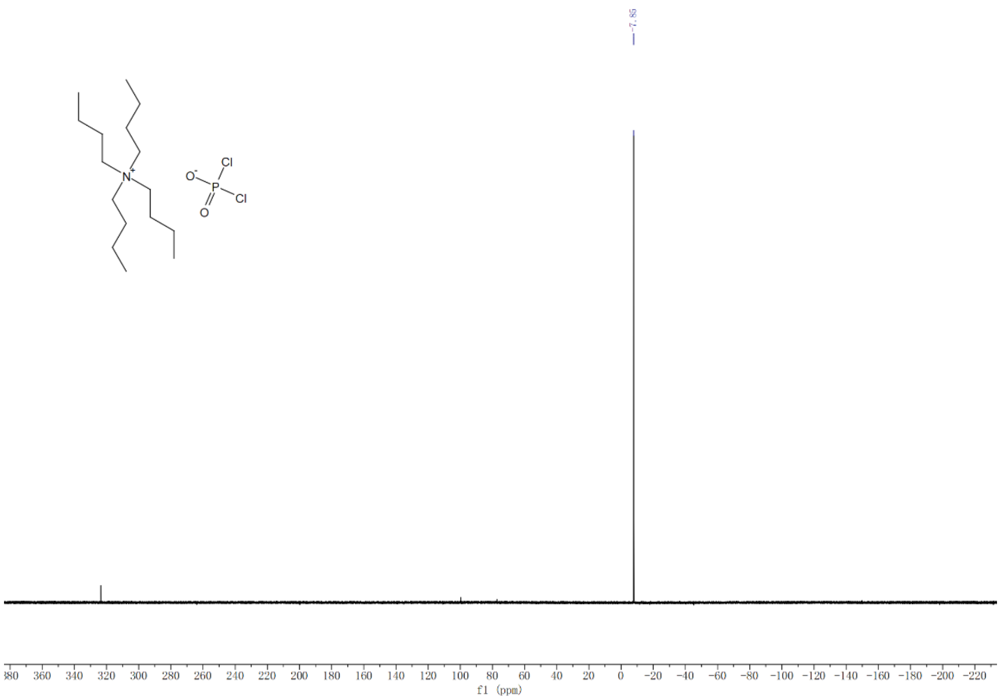


Figure S1. ^{31}P NMR spectrum of [TBA][PO_2Cl_2] in $CDCl_3$ at 25 °C, recorded at 400 MHz. Silicone grease was present in the $CDCl_3$. ^{31}P NMR (162 MHz, $CDCl_3$) δ = -7.85 ppm.

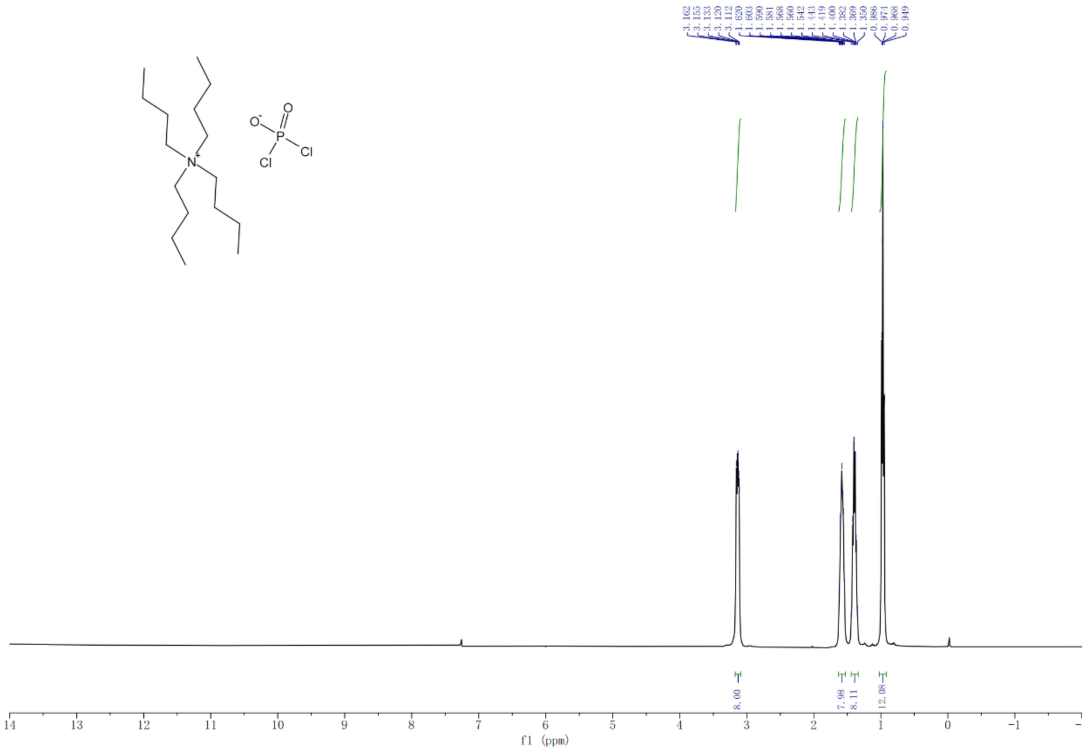


Figure S2. ^{1}H NMR spectrum of [TBA][PO_2Cl_2] in $CDCl_3$ at 25 °C, recorded at 400 MHz. Silicone grease was present in the $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.51 – 3.42 (m, 8H), 1.89 – 1.78 (m, 8H), 1.67 – 1.56 (m, 8H), 1.17 (t, *J*=8.0, 12H) ppm.

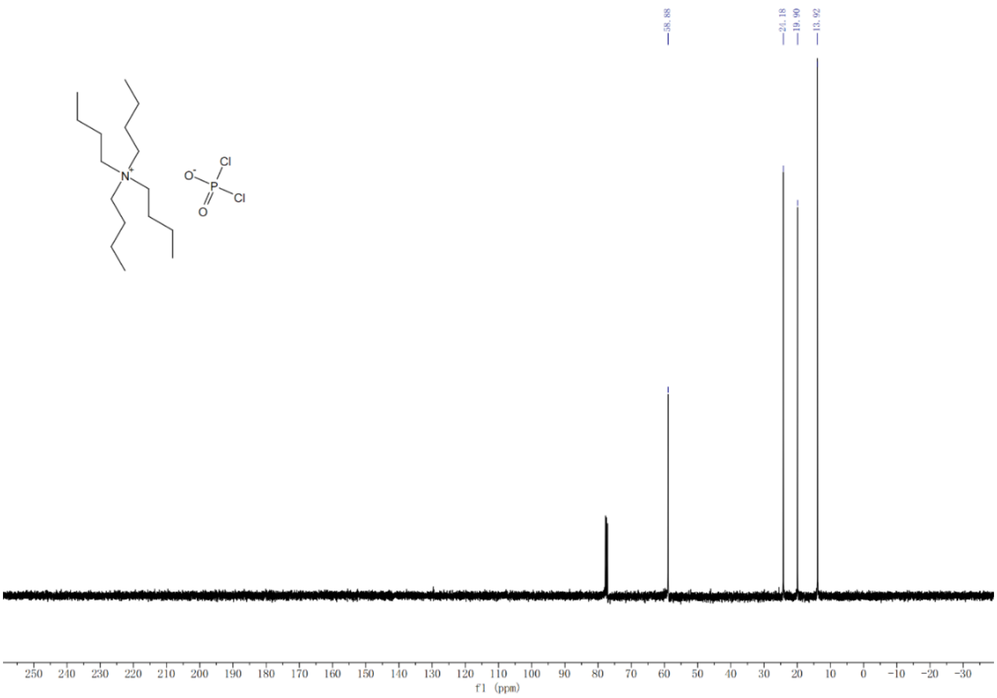


Figure S3. ^{13}C NMR spectrum of [TBA][PO_2Cl_2] in $CDCl_3$ at 25 °C, recorded at 400 MHz. Silicone grease was present in the $CDCl_3$. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 58.8, 24.1, 19.9, 13.9 ppm.

2.4 Preparation of [TBA][$P(SiCl_3)_2$].

To a 50 mL Schlenk tube placed in the glove box, which was oven-dried overnight and cooled down to ambient temperature under Argon atmosphere, a magnets and dried dichloromethane (DCM, 5 mL) were added, followed by tetrabutylphosphonic acid ([TBA][H_2PO_4] (3 mmol, 1 g), oxalyl chloride (3 eq., 9 mmol, 0.75 mL). The Schlenk tube was sealed properly and moved out the glove box. The mixture was then reacted at room temperature for two hours. After removing the solvent, unreacted oxalyl chloride $(COCl)_2$, and volatile substances in the mixture through the connection to an oil bubbler, water bubbler and vacuum line equipped with potassium permanganate drying tower, trichlorosilane (60 mmol, 20 eq., 6 mL,) was added in the residual mixture in the Schlenk tube under argon (Ar) atmosphere and quickly degassed with Argon three times. The resultant mixture was then reacted at 60 °C for 24 h. After cooled down to room temperature, the reaction tube was then placed in a cold trap at -78 °C for 30 minutes to accelerate the precipitation of solid compounds.

Characterization data for [TBA][P(SiCl$_3$)$_2$]

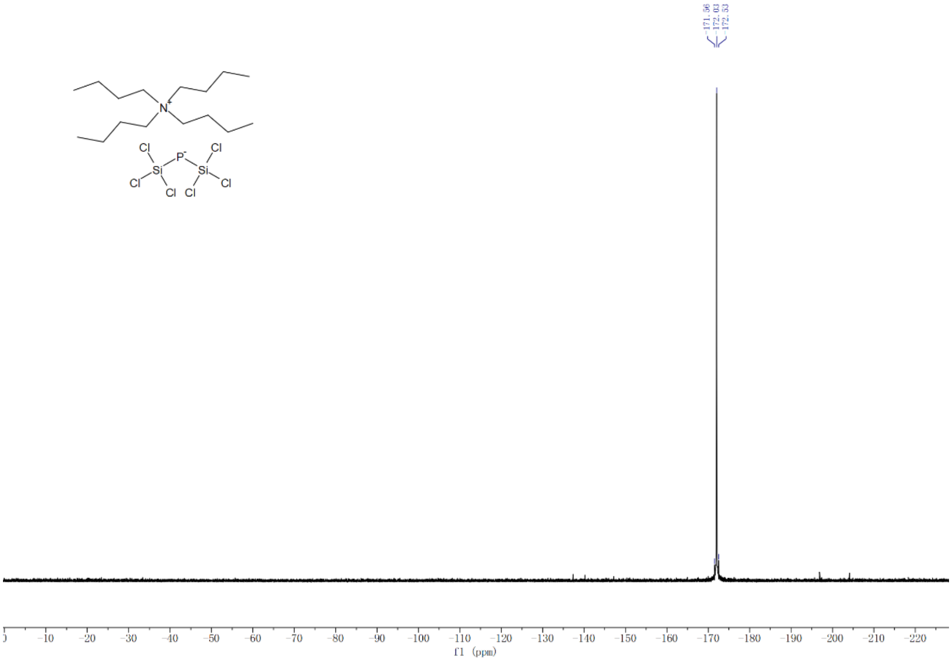


Figure S5. ^{31}P NMR spectrum of [TBA][P(SiCl$_3$)$_2$] in CDCl$_3$ at 25 °C, recorded at 400 MHz. Silicone grease was present in the CDCl$_3$. ^{31}P NMR (162 MHz, CDCl$_3$) δ = -172.03 ppm.

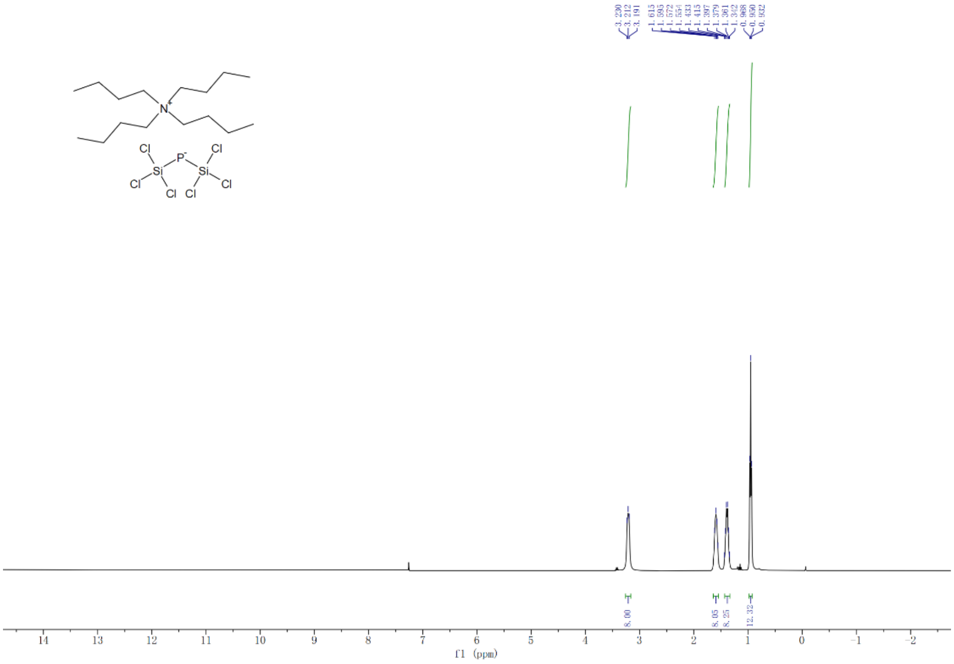


Figure S6. ^{1}H NMR spectrum of [TBA][P(SiCl$_3$)$_2$] in CDCl$_3$ at 25 °C, recorded at 400 MHz. Silicone grease was present in the CDCl$_3$. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.26 – 3.16 (m, 8H), 1.64 – 1.54 (m, 8H), 1.43 – 1.33 (m, 8H), 0.95 (t, *J* = 7.1, 12H).

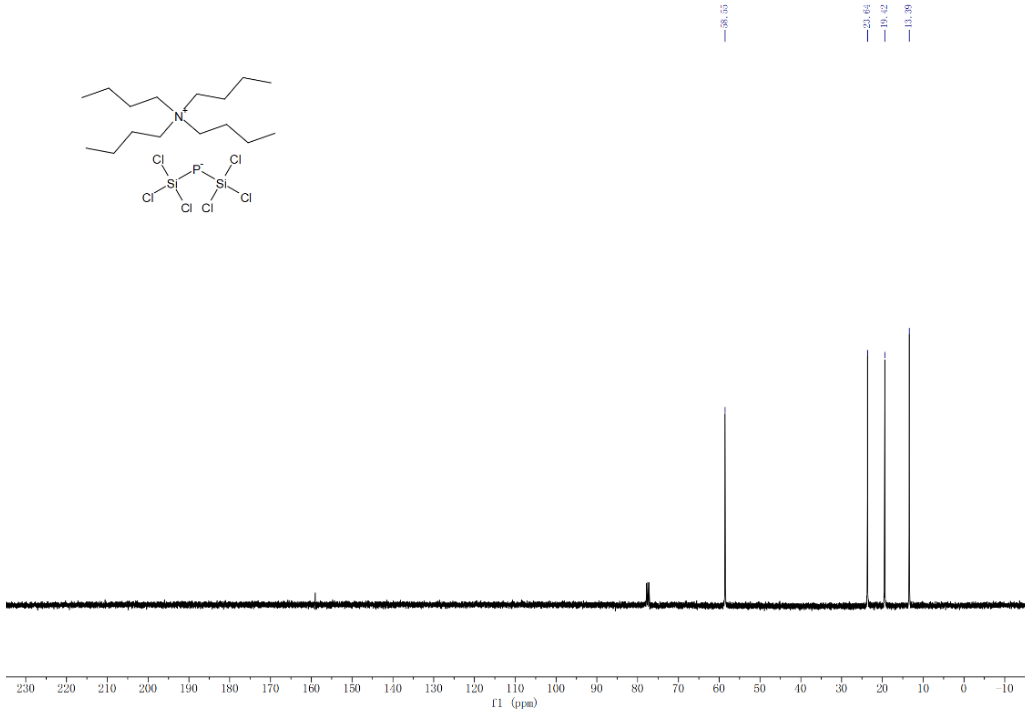
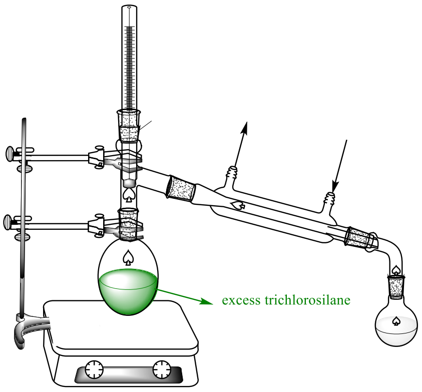


Figure S7. ^{13}C NMR spectrum of [TBA][P($SiCl_3$)$_2$] in $CDCl_3$ at 25 °C, recorded at 400 MHz. Silicone grease was present in the $CDCl_3$. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 58.5, 23.6, 19.4, 13.3 ppm.

2.4.1 Recycle and reuse of excess trichlorosilane

Note: Experiments in this section (S2.5.1) were performed under the General Conditions described in Section S2.2. and Section S1.2.2.



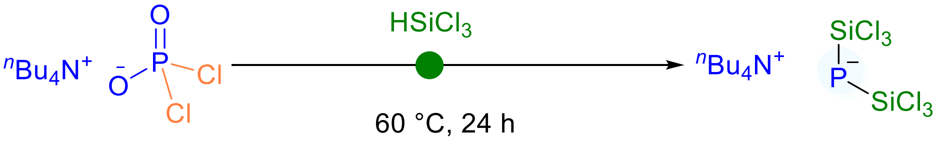
The excess silane remaining in the reaction to [TBA][P($SiCl_3$)$_2$] was collected and treated by simple distillation to test its reducing capacity. The experiment was conducted following the procedure outlined in Section S2.2. The results showed that the yield of [TBA][$P(SiCl_3)_2$] obtained from the first repeated use was 54%. The yield from the second repeated use was found to be 43%. Due to the volatile nature and susceptibility to hydrolysis of silane, the experiment was repeated only three times.

3 Experimental sections

3.1 Optimization of reduction step to produce [TBA][$P(SiCl_3)_2$]

Note: Experiments in this section (S3.1) were performed under the General Conditions described in Section S2.2.

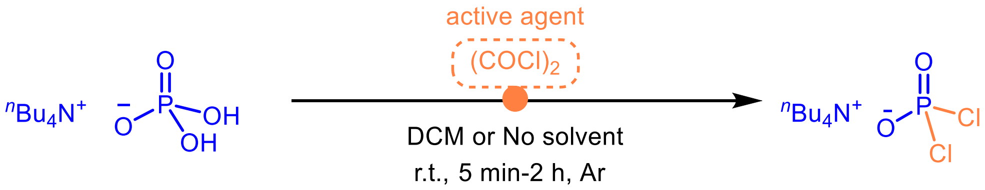
3.2 Reduction of pure intermediates with silanes



The direct reduction of the resultant intermediate [TBA][PO_2Cl_2] with $HSiCl_3$ was conducted subsequently. In a glove box under Ar atmosphere, the intermmediate [TBA][PO_2Cl_2] (3 mmol, 1.125 g) was added into an oven-dried Schlenk tube and sealed the tube, then $HSiCl_3$ (60 mmol, 6 mL) was quickly add into the tube. The sealed tube with the mixture was then taken out of the glove box and reacted at 60°C for 24 h. After cooled down to room temperature, the resultant mixture was used for the next step reaction without any further treatment, proceeding in accordance with the general conditions described in Section S2.2.

3.3 Reaction intermediates and mechanism verification of [TBA][$P(SiCl_3)_2$]

3.3.1 Monitoring the actication step of the addition of oxalyl chloride to [TBA][H_2PO_4] by ^{31}P NMR spectrum



Following the standard procedure, 0.6 mmol (1 eq.) of [TBA][H_2PO_4] was added in an overn-dried Schlenk tube, then 1.8 mmol (3 eq.) of oxalyl chloride was added into it at once. The reaction was then monitored by ^{31}P NMR spectroscopy at different reaction time to capture possible intermmediates by new appearing chemical shifts. At the different time spot, after removing the solvent and volatiles by vacuum, the residue of the reaction mixture was dissolved in $CDCl_3$ (0.5 mL) for ^{31}P NMR experimental monitoring.

Table S2 Monitoring of the possible intermediates generated during the activation step by ^{31}P NMR.[a]

Entry	[TBA][H_2PO_4]	$(COCl)_2$	T/ ℃	**Time**
1	0.6 mmol	\	\	****
2	0.6 mmol	$(COCl)_2$	rt	**5 min**
3	0.6 mmol	$(COCl)_2$	rt	**15 min**
4	0.6 mmol	$(COCl)_2$	rt	**30min**
5	0.6 mmol	$(COCl)_2$	rt	**60 min**
6	0.6 mmol	$(COCl)_2$	rt	**3 h**
7	0.6 mmol	$(COCl)_2$	rt	**5 h**
8	0.6 mmol	$(COCl)_2$	rt	**10 h**
9	0.6 mmol	$(COCl)_2$	rt	**15 h**
10	0.6 mmol	$(COCl)_2$	rt	**24 h**

[a] Standard conditions: Reaction conditions: [TBA][H_2PO_4](0.6 mmol,1 eq.), $(COCl)_2$ (3 eq., 1.8 mmol), at rt for 5 min-24 h under argon atmosphere.

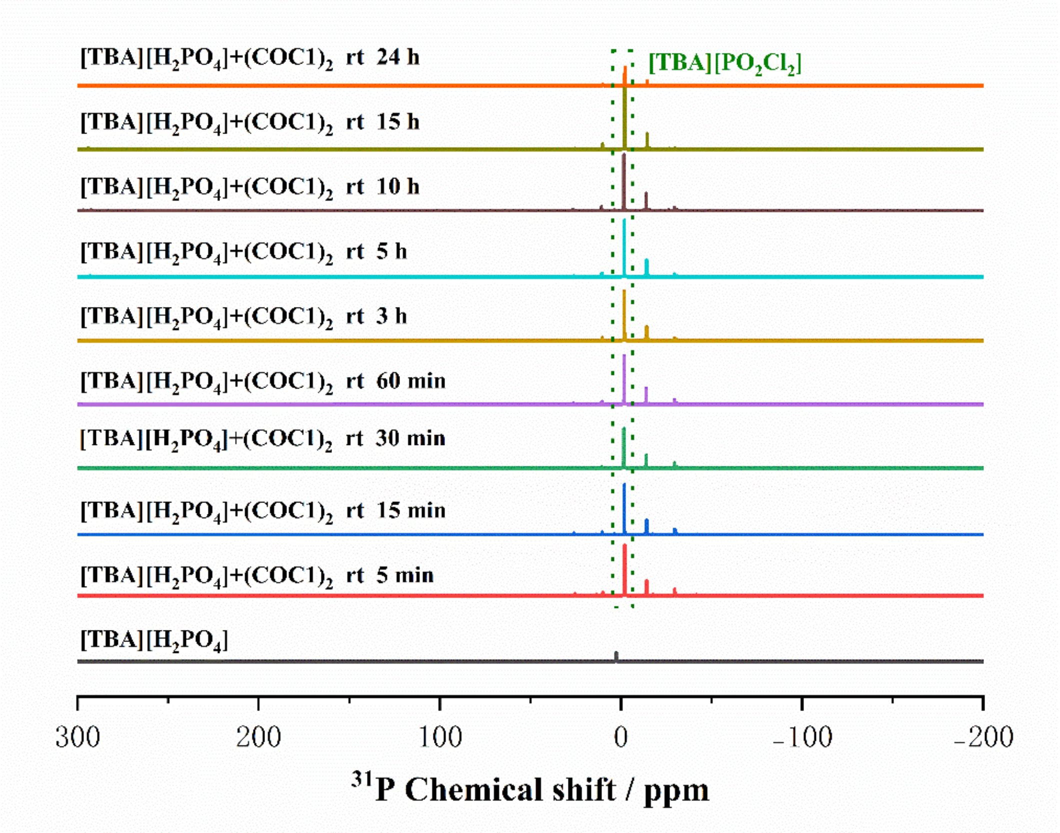


Figure S8. ^{31}P NMR spectra of the reaction mixture at different reaction time for the activation step with $(COCl)_2$.

Table S3. Various of cations of phosphoric acid salts.[a]

"P" source	$CaHPO_4$	$NH_4H_2PO_4$	$Ca(H_2PO_4)_2 \cdot H_2O$
^{31}P NMR	N.R.	N.R.	N.R.

[a] ^{31}P NMR spectrum in $CDCl_3$ at 25 °C, recorded at 400 MHz. Silicone grease was present in the $CDCl_3$.

In the glove box, add other phosphates to the 50 mL sealed tube, such as calcium hydrogenphosphate ($CaHPO_4$) (3 mmol, 0.408 g), ammonium dihydrogen phosphate anhydrous ($NH_4H_2PO_4$) (3 mmol, 0.345 g), calcium phosphate monobasic monohydrate $Ca(H_2PO_4)_2 \cdot H_2O$ (3 mmol, 0.756 g), and oxalyl chloride (3 eq., 9 mmol, 0.75 mL). Properly seal the Schlenk tube and move it out of the glove box. Allow the mixture to react at room temperature for two hours. After removing the solvent, unreacted oxalyl chloride $(COCl)_2$, and volatile substances in the mixture through the connection to an oil bubbler, water bubbler, and vacuum line equipped with a potassium permanganate drying tower, add trichlorosilane (60 mmol, 20 eq., 6 mL) to the residual mixture in the Schlenk tube under an argon (Ar) atmosphere and quickly degas it with argon three times. Then, react the resulting mixture at 60 °C for 24 hours. Cool it to room temperature and extract the reaction mixture in $CDCl_3$, and detect it by ^{31}P NMR.

3.3.2 Monitoring of phosphine chemical displacement during silane reduction

Following the standard procedure, the reactants [TBA][H_2PO_4] (0.6 mmol, 1 eq.) and oxalyl chloride (1.8 mmol, 3 eq.) were added to the reaction tube in a glove box under Ar atmosphere. The resultant mixture was then stirred at room temperature for 2 h. After removing the solvents and volatile substances by vacuum, $HSiCl_3$ (12 mmol, 20 eq.) was added to the reaction mixture at once. The sealed reaction mixture was then stirred at 110 °C (Table S4) or 60 °C (Table S5) for the specific reaction time to monitor the reaction process. After removing the solvent and volatiles substances by vacuum, the residue of the reaction mixture was dissolved t in $CDCl_3$ (0.5 mL) for ^{31}P NMR experimental monitoring (Figure S9, Figure S10).

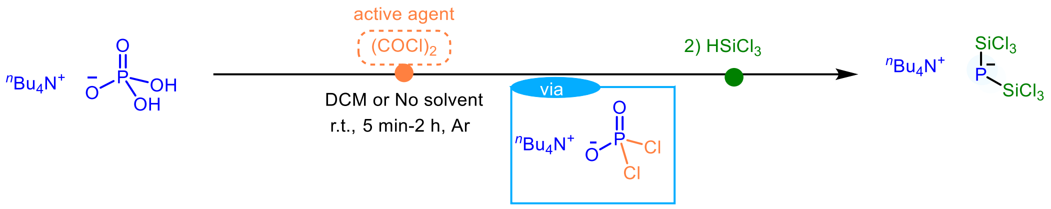


Table S4. ^{31}P **NMR data of the reaction mixture of** $HSiCl_3$ **reduction of [TBA][**H_2PO_4**] at 110 °C**[a]

Entry	[TBA][H_2PO_4]	$(COCl)_2$	$HSiCl_3$	T/°C	Time	^{31}P NMR/ppm
1	0.6 mmol	$(COCl)_2$	$HSiCl_3$	110	5min	-7.85
2	0.6 mmol	$(COCl)_2$	$HSiCl_3$	110	15min	-171.92
3	0.6 mmol	$(COCl)_2$	$HSiCl_3$	110	30min	-171.92
4	0.6 mmol	$(COCl)_2$	$HSiCl_3$	110	1 h	-171.92
5	0.6 mmol	$(COCl)_2$	$HSiCl_3$	110	2 h	-171.92
6	0.6 mmol	$(COCl)_2$	$HSiCl_3$	110	3 h	-171.92
7	0.6 mmol	$(COCl)_2$	$HSiCl_3$	110	5 h	-171.92
8	0.6 mmol	$(COCl)_2$	$HSiCl_3$	110	12 h	-171.92
9	0.6 mmol	$(COCl)_2$	$HSiCl_3$	110	24 h	-171.92

[a] Standard conditions: Reaction conditions: [TBA][H_2PO_4](0.6 mmol,1 eq.), $(COCl)_2$(3 eq., 1.8 mmol), $HSiCl_3$(12 mmol, 20 eq.), at 110 °C for 5 min-24 h in glove box under argon atmosphere.

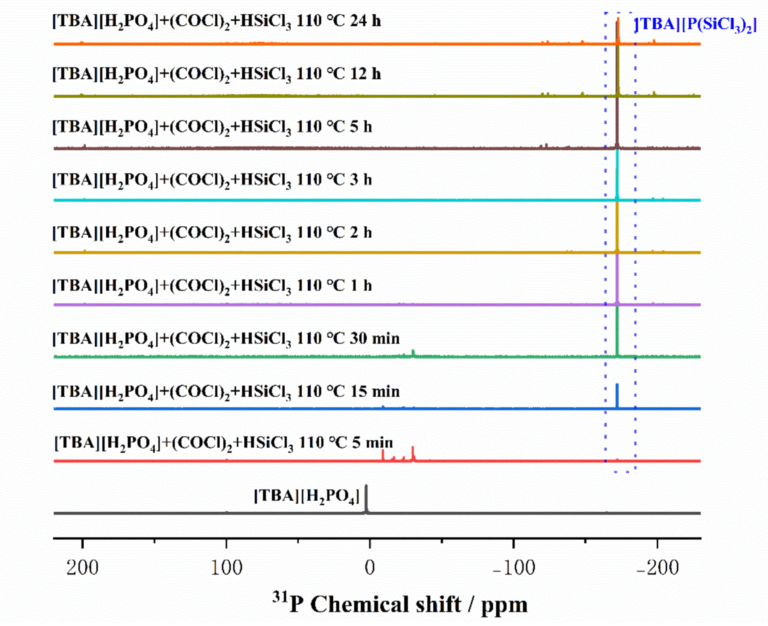


Figure S9. [TBA] [$P(SiCl_3)_2$] ^{31}P NMR over time at 110 °C.

Table S5. ^{31}P NMR data of the reaction mixture of $HSiCl_3$ reduction of [TBA][H_2PO_4] at 60 °C[a]

Entry	[TBA][H_2PO_4]	$HSiCl_3$	T/ °C	Time	^{31}P NMR/ppm
1	0.6mmol	$HSiCl_3$	60	0.5 h	-7.85,-20.37
2	0.6mmol	$HSiCl_3$	60	1 h	-7.85,-16.53,-31.79,-171.92
3	0.6mmol	$HSiCl_3$	60	2 h	-7.85,-16.53,-31.79,-171.92
4	0.6mmol	$HSiCl_3$	60	3 h	-7.85,-16.53,-31.79, -171.92
5	0.6mmol	$HSiCl_3$	60	12 h	-171.92
6	0.6mmol	$HSiCl_3$	60	24 h	-171.92

[a] Standard conditions: Reaction conditions:[TBA][H_2PO_4](0.6 mmol,1 eq.), $(COCl)_2$ (3 eq., 1.8 mmol), $HSiCl_3$ (12 mmol, 20 eq.), at 60 °C for 5 min-24 h under argon atmosphere.

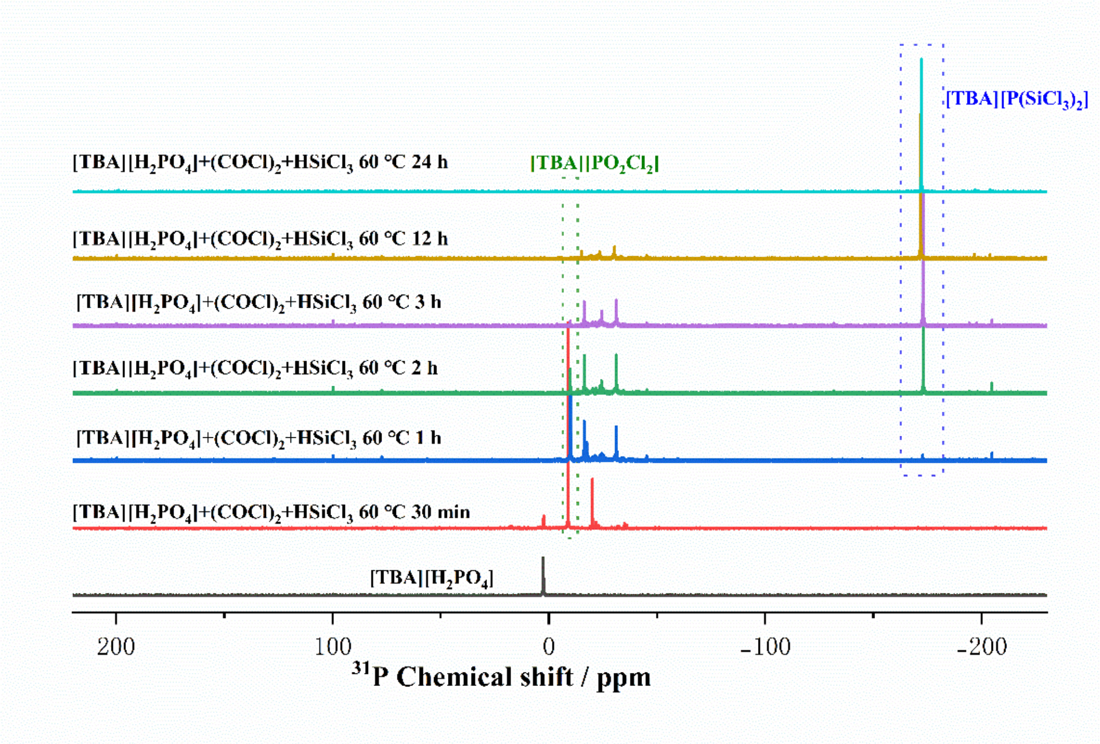
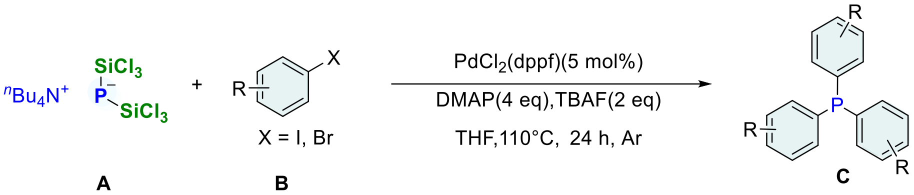


Figure S10. [TBA] [P($SiCl_3$)$_2$] ^{31}P NMR over time at 60 °C.

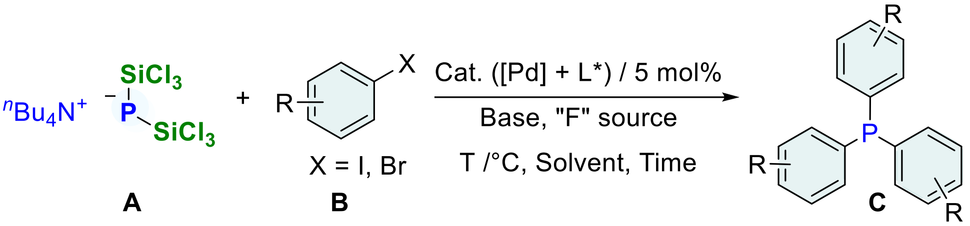
4. Synthesis of triarylphosphine compounds with bis(trichlorosilyl)phosphating anion $[P(SiCl_3)_2]^-$

4.1. General procedure for the synthesis of triphenylphosphine



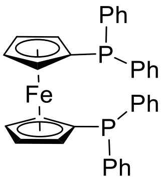
All reaction operations were carried out in a glove box under argon atmosphere. To an oven-dried 25 mL Schlenk tube, $[TBA][P(SiCl_3)_2]$ (0.2 mmol, 0.108 g), $PdCl_2(dppf)$ (5 mol%, 0.001 mmol, 0.007 g), iodobenzene (0.6 mmol, 67 µl, 3 eq.), DMAP (0.8 mmol, 0.098 g, 4 eq.), and $TBAF\cdot 3H_2O$ (0.4 mmol, 0.126 g, 2 eq.) were added in order. With the addition of THF (2 mL) as solvent, the reaction tube was sealed and taken out of the glove box. The reaction mixture was then stirred at 110° C for 24 hours. After cooled down to room temperature, the reaction mixture was extracted with dichloromethane (3×20 mL), collected all the organic layers, dried over anhydrous sodium sulfate, evaporated the solvents by vacuum rotator to afford white solid as crude product. The crude product was then purified by using a chromatographic column (Silica gel, eluent petroleum ether (PE): DCM = 10:1~3:1) to obtain the pure desired product, it was characterized by NMR and HRMS.

Table S6: Optimization of the reaction conditions for the synthesis of triphenylphosphine.[a]



Entry	[Metal precursor] / 5 mol%	L*[b]	Solvent	F source[c]	Base[d] / 4 eq.	T / °C	Time / h	Yield[e] / %
1	$PdCl_2$	DPPF	THF	TBAF	DMAP	110	24	69
2	$PdBr_2$	DPPF	THF	TBAF	DMAP	110	24	n.r.
3	$Pd(dba)_2$	DPPF	THF	TBAF	DMAP	110	24	n.r.
4	$Pd(acac)_2$	DPPF	THF	TBAF	DMAP	110	24	n.r.
5	$Pd(PPh_3)_4$	DPPF	THF	TBAF	DMAP	110	24	n.r.
6	$NiCl_2$	DPPF	THF	TBAF	DMAP	110	24	trace
7	$PdCl_2$	**L1**	THF	TBAF	DMAP	110	24	n.r.
8	$PdCl_2$	**L2**	THF	TBAF	DMAP	110	24	n.r.
9	$PdCl_2$	**L3**	THF	TBAF	DMAP	110	24	24
10	$PdCl_2$	**L4**	THF	TBAF	DMAP	110	24	15
11	$PdCl_2$	**L5**	THF	TBAF	DMAP	110	24	n.r.
12	$PdCl_2$	**L6**	THF	TBAF	DMAP	110	24	n.r.
13	$PdCl_2$	**L7**	THF	TBAF	DMAP	110	24	trace
14	$PdCl_2$	**L8**	THF	TBAF	DMAP	110	24	26
15	$PdCl_2$	DPPF	CH_3CN	TBAF	DMAP	110	24	35
16	$PdCl_2$	DPPF	DME	TBAF	DMAP	110	24	26
17	$PdCl_2$	DPPF	PhMe	TBAF	DMAP	110	24	53
18	$PdCl_2$	DPPF	MTBE	TBAF	DMAP	110	24	n.r.
19	$PdCl_2$	DPPF	THF	/	DMAP	110	24	19
20	$PdCl_2$[f]	DPPF[f]	THF	/	DMAP	110	24	58
21	$PdCl_2$	DPPF	THF	NFSI	DMAP	110	24	trace
22	$PdCl_2$	DPPF	THF	KF	DMAP	110	24	trace
23	$PdCl_2$	DPPF	THF	CsF	DMAP	110	24	trace
24	$PdCl_2$	DPPF	THF	$TBAF\cdot3(H_2O)$	DMAP	110	24	68
25	$PdCl_2$	DPPF	THF	TBAF	NEt_3	110	24	34
26	$PdCl_2$	DPPF	THF	TBAF	Py	110	24	53
27	$PdCl_2$	DPPF	THF	TBAF	^{t}Bu-Py	110	24	43
28	$PdCl_2$	DPPF	THF	TBAF	DBU	110	24	19
29	$PdCl_2$	DPPF	THF	TBAF	DABCO	110	24	11
30	$PdCl_2$	DPPF	THF	TBAF	^{t}BuOK	110	24	32
31	$PdCl_2$	DPPF	THF	TBAF	KOH	110	24	n.r.

32	$PdCl_2$	DPPF	THF	TBAF	NaOH	110	24	19
33	$PdCl_2$	DPPF	THF	TBAF	K_2CO_3	110	24	28
34	$PdCl_2$	DPPF	THF	TBAF	Na_2CO_3	110	24	trace
35	$PdCl_2$	DPPF	THF	TBAF	Cs_2CO_3	110	24	n.r.
36	$PdCl_2$	DPPF	THF	TBAF	DMAP[g]	110	24	trace
37	$PdCl_2$	DPPF	THF	TBAF	DMAP[h]	110	24	50
38	$PdCl_2$	DPPF	THF	TBAF	DMAP[i]	110	24	61
39	$PdCl_2$	DPPF	THF	TBAF	DMAP[j]	110	24	68
40	$PdCl_2$	DPPF	THF	TBAF	DMAP	110	12	19
41	$PdCl_2$	DPPF	THF	TBAF	DMAP	110	36	44
42	$PdCl_2$	DPPF	THF	TBAF	DMAP	110	48	59
43	$PdCl_2$	DPPF	THF	TBAF	DMAP	60	24	n.r.
44	$PdCl_2$	DPPF	THF	TBAF	DMAP	80	24	49
45	$PdCl_2$	DPPF	THF	TBAF	DMAP	120	24	53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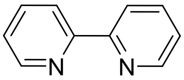
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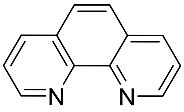
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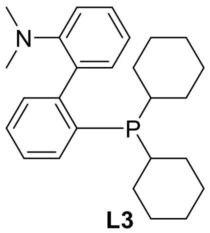
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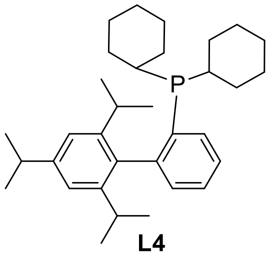
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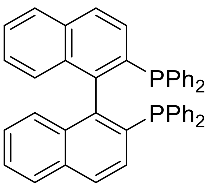
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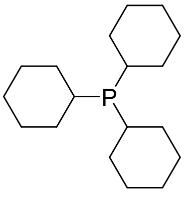
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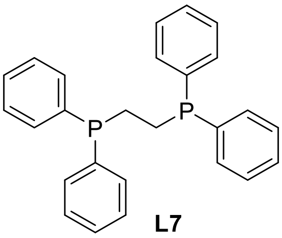
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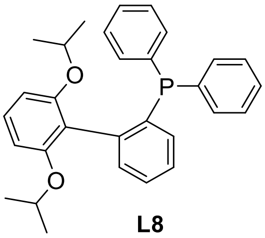
L8

[a] Standard conditions: $[TBA][P(SiCl_3)_2]$ (0.108 g, 0.2 mmol), PhI (0.067 mL, 0.6 mmol, 3 eq.), $PdCl_2(DPPF)$ (0.007 g, 0.001 mmol, 5 mol%), DMAP (0.097 g, 0.8 mmol), TBAF (0.4 mL, 1 M in THF), 0.4 mmol) or $TBAF\cdot 3(H_2O)$ (0.126 g, 0.4 mmol), in THF (2 mL), at 110 °C for 24 h under argon atmosphere. [b] L^* = ligands screened for the synthetic reaction of OPCs; **DPPF** = 1,1'-bis(diphenylphosphino)ferrocene; The structures of the ligands **L1**-**L8** present at the bottom of the table. [c] F source refers to fluorine-containing desilyl reagents, 2 eqv. of TBAF is the optimal; the use of $TBAF\cdot 3H_2O$ gives the same performance; MTBE = tert-butyl methyl ether. [d] 4 eqv. of base was used in general as otherwise specified; Py = pyridine, ^{t}Bu-Py = 4-tert-butylpyridine, DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, DABCO = 1,4-Diazabicyclo[2.2.2]octane. [e] isolated yield. [f] 20 mol% ($PdCl_2$+DPPF) was used. [g] 1 eq. of base was applied. [h] 2 eq. of base was applied. [i] 3 eq. of base was applied. [j] 5 eq. of base was applied.

4.2 Control experiments of “F“ source for the synthesis of triphenylphosphine

Performed under the conditions described in Section S4.1., the synthesis of triphenylphosphine was monitored by ^{31}P NMR. The reaction was stopped and cooled to room temperature, then 0.5 mL of the reaction mixture was pipetted out and added into the ^{31}P NMR tube for NMR experiments with the addition of $CDCl_3$. As shown in Table S7-S8 and Figure S11-S12, there were new peaks observed in the ^{31}P NMR spectrum (14.36 ppm) from 1 h to 5 h reaction time prior to the final product peaks appeared (-4.22 ppm), presumably the intermmediate during the transformation. Of important note is that there is an obvious accelerate of the reaction rate at the presence of “F“ source, generating the desired product in 3 h with it instead of 12 h without it (Entry B, Table S8 vs Entry 5, Table S7). The isolated yield of the desired product promoted significantly with the addition of “F” source (69% vs 19% in 24 h). Interestingly, the same effect was achieved with TBAF·$3H_2O$ as “F” source for the same reaction.

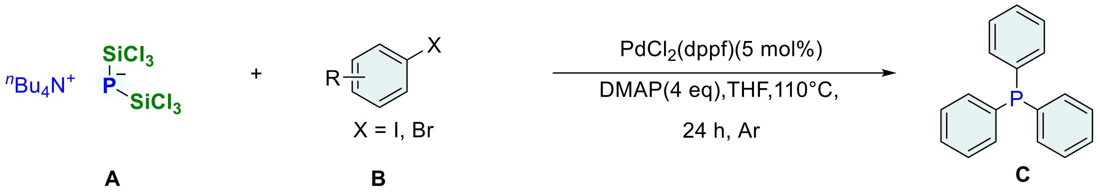

Table S7. No "F" source for phosphine spectroscopy[a]

Entry	[cat.] (5 mol%)	Solvent (2 mL)	" F " source	Base (4 eq.)	T/ °C	**Time**	**^{31}P NMR/ppm[b]**
A	PdCl$_2$(dppf)	THF	\	DMAP	110	**1 h**	**-14.36**
B	PdCl$_2$(dppf)	THF	\	DMAP	110	**3 h**	**-14.36**
C	PdCl$_2$(dppf)	THF	\	DMAP	110	**5 h**	**-14.36**
D	PdCl$_2$(dppf)	THF	\	DMAP	110	**10 h**	**-14.36**
E	PdCl$_2$(dppf)	THF	\	DMAP	110	**12 h**	**-4.22**
F	PdCl$_2$(dppf)	THF	\	DMAP	110	**24 h**	**-4.22, 25.64**

[a] Standard conditions: [TBA][P(SiCl$_3$)$_2$] (0.108 g, 0.2 mmol), PhI (0.067 mL, 0.6 mmol, 3 eq.), PdCl$_2$(DPPF) (0.007 g, 0.001 mmol, 5 mol%), DMAP (0.097 g, 0.8 mmol), at 110 °C for 24 h under argon atmosphere. [b]The peak of DPPF is not marked.

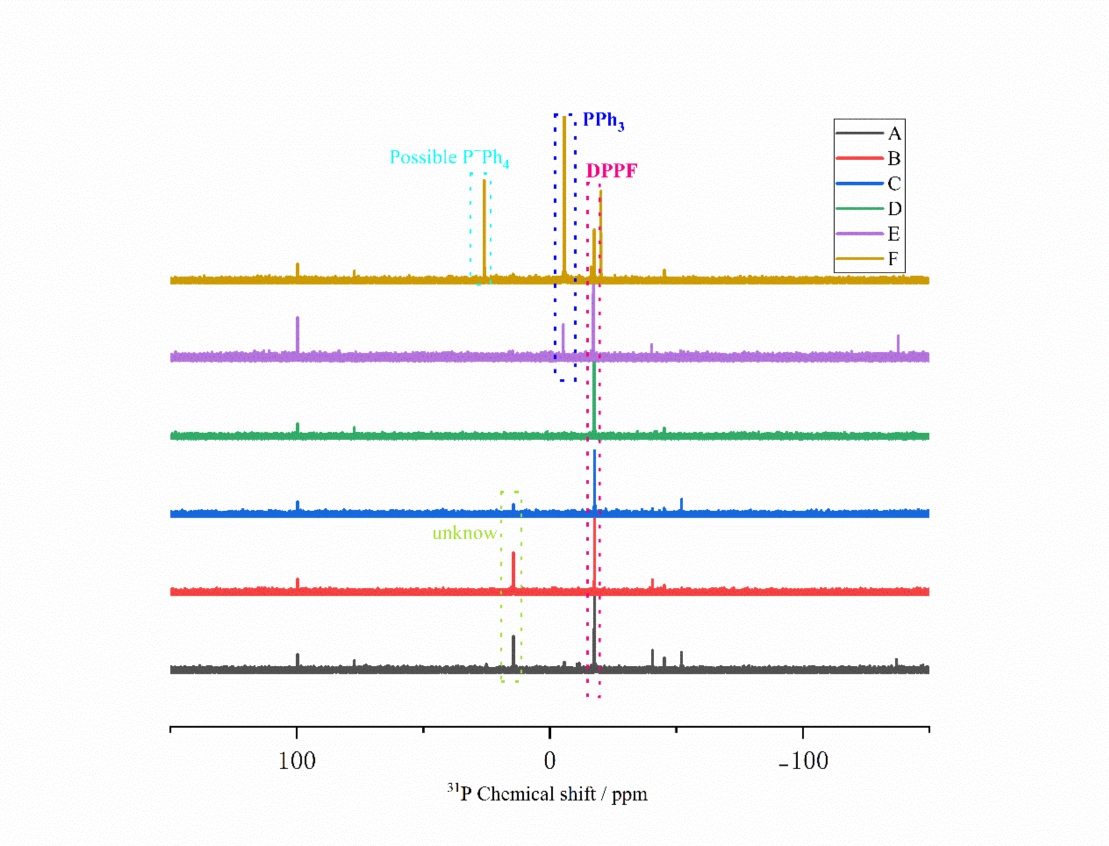

Figure S11. ^{31}P NMR spectra for the monitor of the synthesis reaction without "F" source at different reaction time.

Table S8. Add "F" source for phosphine spectroscopy[a]

Entry	[cat.] (5 mol%)	Solvent (2 mL)	“ F ” source	Base (4 eq)	T /°C	**Time**	**^{31}P NMR/ppm[b]**
A	$PdCl_2$(dppf)	THF	TBAF or TBAF·$3H_2O$	DMAP	110	**1 h**	**14.36**
B	$PdCl_2$(dppf)	THF	TBAF·$3H_2O$	DMAP	110	**3 h**	**14.36, 4.22**
C	$PdCl_2$(dppf)	THF	TBAF·$3H_2O$	DMAP	110	**5 h**	**14.36, 4.22**
D	$PdCl_2$(dppf)	THF	TBAF·$3H_2O$	DMAP	110	**12 h**	**-4.22, 25.64**
E	$PdCl_2$(dppf)	THF	TBAF·$3H_2O$	DMAP	110	**24 h**	**-4.22, 25.64**

[a] Standard conditions: [TBA][$P(SiCl_3)_2$] (0.108 g, 0.2 mmol), PhI (0.067 mL, 0.6 mmol, 3 eq.), $PdCl_2$(DPPF) (0.007 g, 0.001 mmol, 5 mol%), DMAP (0.097 g, 0.8 mmol), TBAF (0.4 mL, 1 M in THF), 0.4 mmol) or TBAF·3(H_2O) (0.126 g, 0.4 mmol), in THF (2 mL), at 110 °C for 24 h under argon atmosphere.

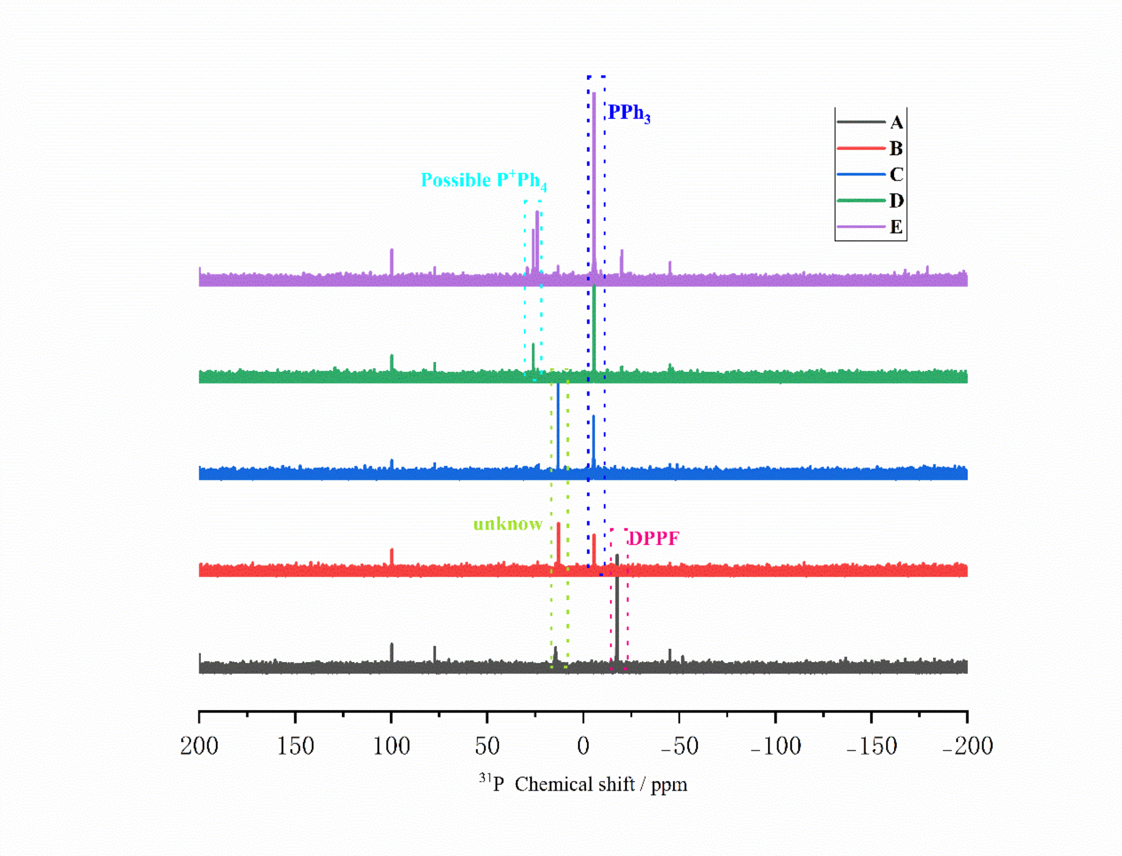

Figure S12. ^{31}P NMR spectra for the monitor of the synthesis reaction with "F" source at different reaction time.

5. Mechanism study

5.1 DFT calculation for the activation step:

All structures were optimized at CAM-B3LYP/Def2SVP level[4-6] (Implemented in the Gaussian16 package[7]) followed by harmonic vibration frequencies calculations (0 imaginary frequency for reactants, intermediates (INTs) and products, only 1 imaginary frequency for each of transition states (TS)). Moreover, intrinsic reaction coordination (IRC) calculations were performed to investigate the validity of all optimized transition state structures.

The DFT calculations were conducted to elucidate the reaction path involved in the formation of intermediate **3** from one $[H_2PO_4]^-$ and two $(COCl)_2$ molecules as reactants in the activation step. A plausible pathway consisting of three main steps was proposed as illustrated (Figure S13). It has been found that a stable dimer (reactants), formed by one $(COCl)_2$ molecule reacting with one $[H_2PO_4]^-$, is energy feasible initially, followed by **TS1**/**TS2** with an energy barrier of 0.23 eV to generate an active PO_3^- species (**INT2**). It then involves the attack of the second $(COCl)_2$ molecule onto the PO_3^- group, leading to the formation of **TS3** with an activation energy of 0.12 eV. The most complex stage of the activation involves several transition states (**TS4** to **TS8**) in which ring opening/closing and chlorine atom transformations, as well as the rate-determining step (activation energy is 0.71 eV), occur. Upon the release of CO_2 and CO gas molecules, the active intermediate **3** (products) is formed exothermally with an active energy of -1.0 Ev. Partially assisted by simulation, There could be two reasonable reaction pathways for the activation of phosphorus salts by oxalyl chloride with two oxalyl chloride molecules reacting with one phosphate salt molecule (Figure 2C, Pathway I) or one-to-one in a simultaneously concerted way (Figure 2C, Pathway II, which has been approved as unfavorable by DFT calculation shown above). The resultant intermediates (**1** or **2)** are supposed to lose two molecules of carbon dioxide and carbon monoxide by intramolecular rearrangement, or ring-opening to generate the active substance intermediate **3**.

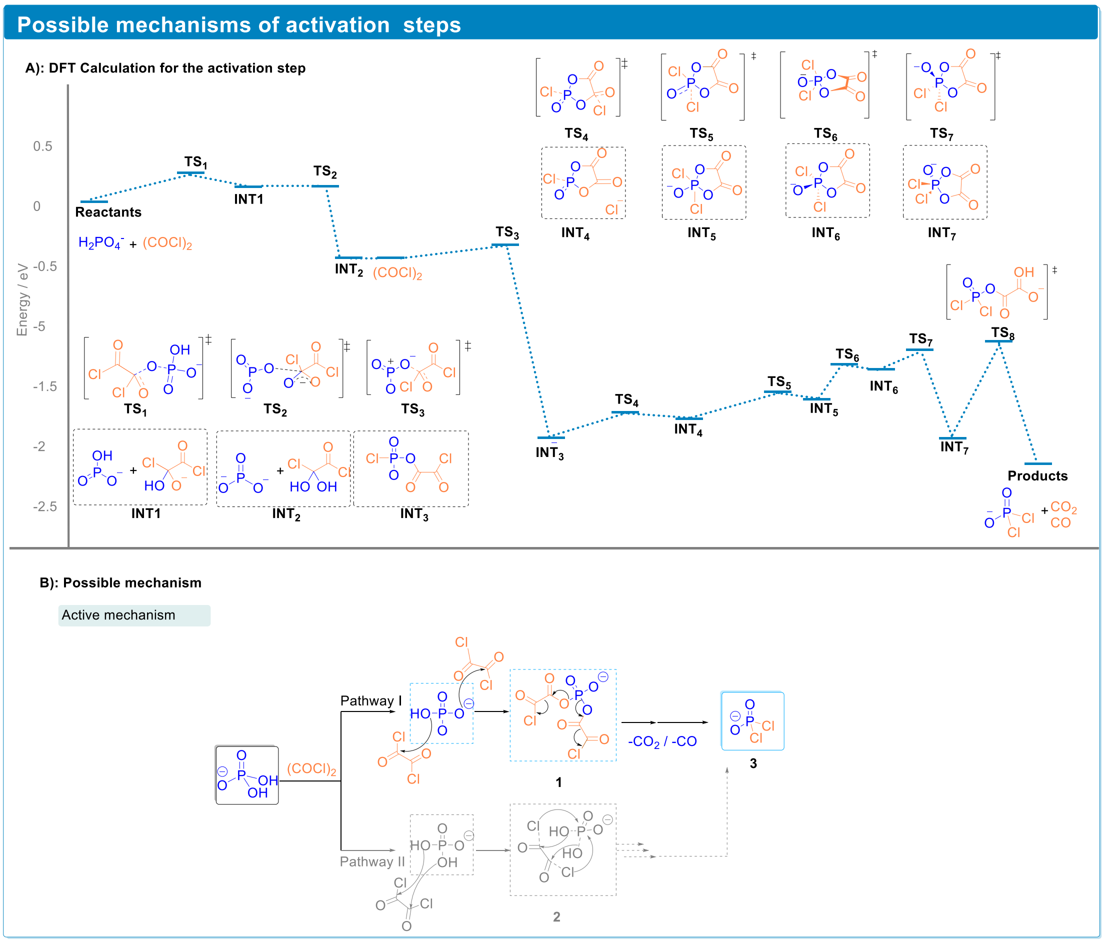

Figure S13 Proposed mechanisms of the activation of inorganic phosphate salts and the subsequent reduction. A): Calculated energy profiles for the formation of the active $[PO_2Cl_2]^-$ by $(COCl)_2$ and $[H_2PO_4]^-$. B): Proposed mechanisms.

5.2 ^{31}P NMR tracking experiment for the reaction process

However, further investigation of this initial step is needed for a more comprehensive understanding of the mechanisms. The structure of the proposed intermediate **3** has been established through a process of scientific inquiry. To elucidate the role of $(COCl)_2$ for the activation of $[TBA][H_2PO_4]$ via the unique double chlorination of hydroxyl groups on the phosphorus, an in situ ^{31}P NMR spectroscopy experiment was conducted to disclose the reaction process and identify possible intermediates generated and involved during the first step (Figures S8 in SI). As previously stated, the activation reaction occurred quickly upon the addition of oxalyl chloride into the phosphate salts solution, indicated by the complete disappearance of phosphate peaks within 5 minutes. Building upon these observations, subsequent experiments were conducted to further investigate the reduction reaction pathway of $[TBA][PO_2Cl_2]$ to form $[P(SiCl_3)_2]^-$. An in situ and real-time observation of phosphine spectroscopy (^{31}P NMR) of the following silane reduction step was attempted to monitor the intermediates and the reaction process, clarifying the possible reaction pathway for the formation of $[P(SiCl_3)_2]^-$ ion (Figures S4-S5, S9-S10 in SI).

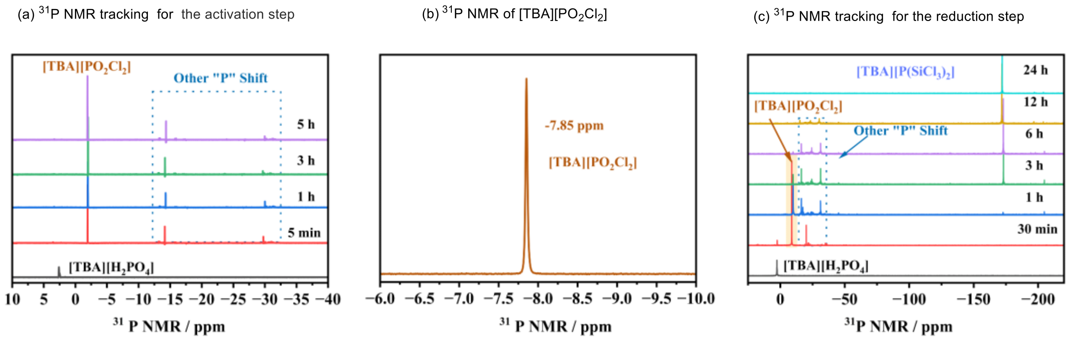

Figure S14 The reaction of activation of inorganic phosphate salts by oxalyl chloride; (a) Real-time ^{31}P NMR spectrum of activation of inorganic phosphate salts ($[TBA][H_2PO_4]$) with oxalyl chloride under standard conditions (b) ^{31}P NMR spectrum of activated intermediate of [TBA][PO_2Cl_2]. (c) Real-time ^{31}P NMR spectrum of the reduction of resultant intermediate with trichlorosilane to generate [TBA][$P(SiCl_3)_2$] under standard conditions.

5.3. Possible mechanisms for the reduction of activated interemmediate with trichlorosilane

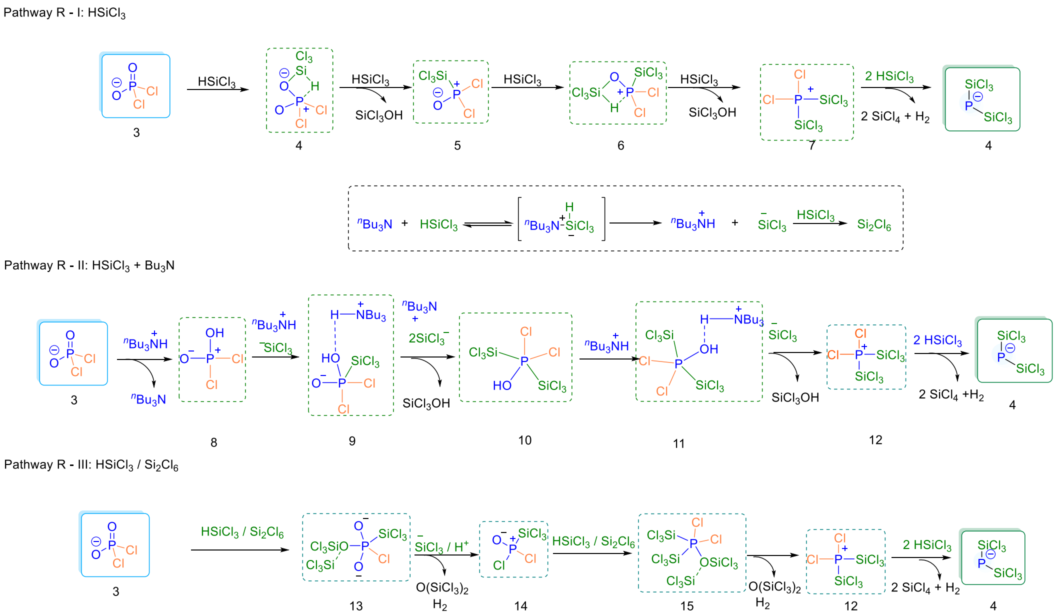

Figure S15. Proposed mechanisms for the reduction of activated intermediate by trichlorosilane.

Previous literature has proposed a possible mechanism for the formation of $[P(SiCl_3)_2]^-$ Initially, the silane interacts with the P=O double bond in the oxalyl-activated inorganic phosphate **3**, resulting in the formation of a positively charged phosphorus intermediate. The silane then reacts with this intermediate, leading to the elimination of a silanol molecule. This intermediate is subsequently reduced through the action of excess silane, gradually resulting in the formation of compound **4**. However, the reduction process with the other active substances could not be ruled out decisively. Possible mechanisms were proposed for the formation of $[P(SiCl_3)_2]$ according to the previous literature reports: It is hypothesized that the product generation may be due to protonated trichlorosilyl nucleophilic attack (pathway R-I) by intermediate **3** or coordination of hexachlorodisilane with oxygen (pathway R-II). It is hypothesized that the product may be produced due to the direct coordination of intermediate **3** with silane (pathway R-I) or **3** being attacked by trichlorosilane nucleophile by protonation (pathway R-II), and the coordination of hexachlorodisilane with oxygen (pathway R-III) (Figure S16). It couldn't role out the involvement of the more active silane dimer (Si_2Cl_6) to coordinate with oxygen (pathway R-III). Therefore, the cationic cleavage of tetrabutylamine in the reaction mixture forms tributylamine during the reaction, and the original silane compound could be transferred to the intermediate silamine [$^{n}Bu_3N^{+}Si\text{-}Cl_3H$] by reaction with tributylamine. The dimers (hexachlorodisilanes) were then produced by subsequent cleavage of trichlorosilyl anion combined with another silane molecule, which maybe the dominant and more active reducing substance.

Pathway R-I: The oxalyl activated inorganic phosphate salts, intermediate **3** was firstly protonated by the $^{n}Bu_4NH^{+}$ cations, generating possible intermediates **4**, **5**, **6**, **7** in a stepwise procedure with the coordination and/or interaction with corresponding reagents such as silane, in-situ-generated trichlorosilyl anion (Cl_3Si^{-}), *etc.* (Figure S16, Pathway R-I). The targeted intermediate, tetrabutylamine cation with bisiliphosphine anion species ($^{n}Bu_4N^{+}[P(SiCl_3)_2]^{-}$), were generated by the elimination of H_2 and release of $SiCl_4$ from intermediate **7**, which has been solid-proved by the single crystal structure of desired complex along with spectroscopic identification of both product and by-products in the literature previously. Whilst for the possible pathway with more active dimer, hexachlorodisilane, two plausible pathways could undergo to generate the desired reduction products (Figures S14).

Pathway R-II：The intermediate **3** could also be protonated by $^{n}Bu_3NH^+$ to generate the possible intermediate **8**, existing as an ammonium cation species. The trichlorosilyl anion $SiCl_3^-$ could then nucleophilic attacks **8** to produce possible intermediate **9**. A further nucleophilic attack could occur to the intermediate **9** by another molecule of trichlorosilyl anion $SiCl_3^-$ under the same mechanism. It could then lead to the generation of the possible intermediate **10.** Repeated similar process to the intermediate **10** through possible intermediates **11**, **12** to generate the same bisilylphosphine anion $[PCl_2(SiCl_3)_2]^+$as in the pathway R-I.

Pathway R-III: The intermediate **3** could also be protonated under the action of hexachlorodisilane to provide possible pentavalent *n*-phosphine intermediate **13**, upon the elimination of a molecule of methyl silyl ether from **13** together with H_2 release, a possible intermediate **14** could be generated. Again, repeated similar process to the possible intermediate **14** to obtain possible orthophosphine intermediates **15**, and then **12.** With further reduction, a same bisilylphosphine anion $[P(SiCl_3)_2]^-$ could be afforded as the desIt is speculated here that the catalytic pathway for the subsequence synthesis of organic phosphine compounds, triarylphosphines aligned with the well-established coupling reaction with palladium catalysis. The R-DPPF-linked Pd(0) complex undergoes oxidative addition preferentially to ArI to form ArPd(II)I species. Subsequent coordination of the $P(SiCl_3)_2$ anion leads to the formation of complex **5**, which then undergoes reductive elimination to yield the compound

$ArP(SiCl_3)_2$. This process regenerates the Pd(0) species, thereby completing the catalytic cycle. Furthermore, the resulting bistrichlorosilylarylphosphine compound **6** is converted to the fluorinated orthophosphate **7** by TBAF, followed by the removal of a $SiFCl_3$ molecule to yield a silylphosphine anion **8**. This intermediate then participates in the corresponding palladium-catalyzed process, ultimately leading to the formation of the desired triarylphosphine product. It can thus be proposed that the arylsilylphosphine intermediate 6 plays a pivotal role in the catalytic step of the stepwise arylation in the palladium-catalyzed process. To gain further insight into the mechanism, we performed ^{31}P NMR experiments, which revealed the appearance of new phosphorus species at 13 ppm over time, gradually converting into the triarylphosphine product. Unfortunately, we were unable to isolate this intermediateired product.

5.4. Possible mechanisms for the synthesis of OPCs by Palladium-catalyzed coupling reaction bisilylphosphine salts [TBA][P(SiCl₃)₂] with aryl halides

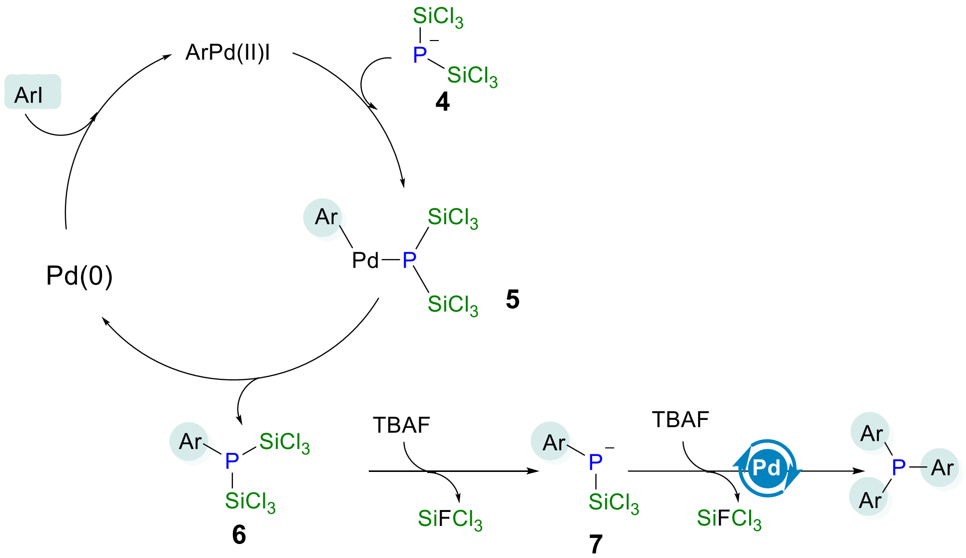

Figure S16. Proposed reaction pathways for Pd-catalysed coupling step.

It is speculated here that the catalytic pathway for the subsequence synthesis of organic phosphine compounds, triarylphosphines aligned with the well-established coupling reaction with palladium catalysis. The R-DPPF-linked Pd(0) complex undergoes oxidative addition preferentially to ArI to form ArPd(II)I species. Subsequent coordination of the $P(SiCl_3)_2$ anion leads to the formation of complex **5**, which then undergoes reductive elimination to yield the compound $ArP(SiCl_3)_2$. This process regenerates the Pd(0) species, thereby completing the catalytic cycle. Furthermore, the resulting bistrichlorosilylarylphosphine compound **6** is converted to the fluorinated orthophosphate **7** by TBAF, This intermediate then participates in the corresponding palladium-catalyzed process, ultimately leading to the formation of the desired triarylphosphine product. It can thus be proposed that the arylsilylphosphine intermediate **6** plays a pivotal role in the catalytic step of the stepwise arylation in the palladium-catalyzed process. To gain further insight into the mechanism, we performed ^{31}P NMR experiments, which revealed the appearance of new phosphorus species at 13 ppm over time, gradually converting into the triarylphosphine product. Unfortunately, we were unable to isolate this intermediate.

6. References

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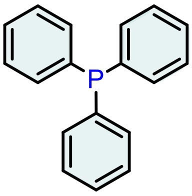
7. Copies of NMR Spectra



Triphenylphosphane(C1,C2)[9] (CAS: 603-35-0)

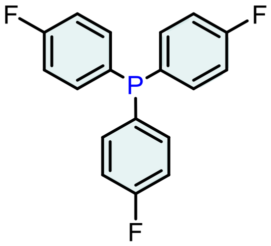
X= I, yield: 69%; X = Br, yield: 48%, White solid, m.p. 80-81 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 – 7.40 (m, 15H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 137.3 (d, J = 10.8), 133.8 (d, J = 19.5), 128.8, 128.6 (d, J=6.9).

^{31}P NMR (162 MHz, $CDCl_3$) δ= -4.22.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C18H16P^+$ 263.0984, found 263.0984.



Tris(4-fluorophenyl)phosphane(C3)[9] (CAS: 18437-78-0)

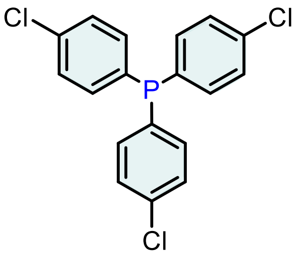
Yield: 68% , White solid, m.p. 79-80 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.21 (m, 6H), 7.05 (t, *J* = 8.5, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.4 (d, *J* = 249.4), 135.4 (dd, *J* = 21.2, 8.2), 132.4, 115.9 (dd, *J*=20.9, 6.9).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -7.99.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C18H13F3P^+$317.0707, found317.0712.



Tris(4-chlorophenyl)phosphane (C4)[10](CAS: 1159-54-2)

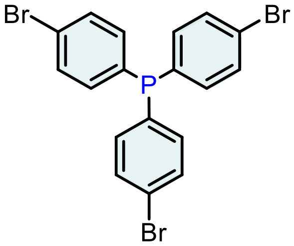
Yield: 63% White solid, m.p. 103 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.3, 6H), 7.20 (t, *J* = 7.8, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 135.5, 134.9, 134.8, 129.0 (d, *J* = 7.4).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -7.47.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C18H13Cl3P^+$364.9815, found 364.9816.



Tris(4-bromophenyl)phosphane(C5)[10] (CAS: 29949-81-3)

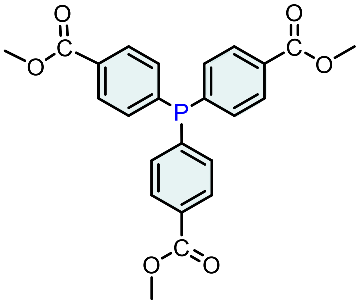
Yield: 72% White solid, m.p. 117-118 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 8.0, 6H), 7.13 (t, *J* = 7.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 135.2 (d, *J* = 12.5), 135.0 (d, *J* = 20.4), 131.9 (d, *J* = 7.3), 123.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ = -7.42.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C18H13Br3P^+$ 498.8279, found 498.8281.



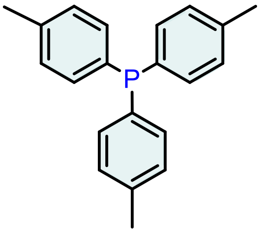
1,1',1''-(phosphanetriyltris(benzene-4,1-diyl))tris(propan-2-one)(C6)[10] (CAS: 66417-54-7)

Yield: 77% White solid, m.p. 111-112 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 (d, *J*=8.4, 6H), 7.36 – 7.31 (m, 6H), 3.88 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 166.5, 141.6 (d, *J* = 13.8), 133.5 (d, *J* = 19.8), 130.8, 129.6 (d, *J*=6.9), 52.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ = -4.22.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C24H22O6P^+$ 437.1149, found 437.1158.



Tri-p-tolylphosphane(C7)[9] (CAS: *1038-95-5*)

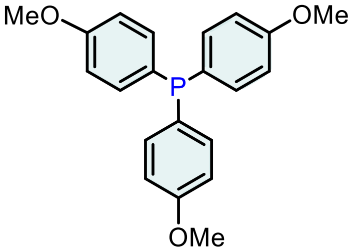
Yield: 48% White solid, m.p. 143-144 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.28 (t, *J* = 8.0, 6H), 7.20 (d, *J* = 7.5, 6H), 2.40 (s, 9H).

^{13}C NMR (151 MHz, CDCl$_3$): δ = 138.5, 134.1 (d, *J* = 9.0), 133.7 (d, *J* = 19.6), 129.3 (d, *J* = 6.0), 21.3.

^{31}P NMR (162 MHz, CDCl$_3$): δ = -6.79.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for C21H22P$^+$ 305.1454, found: 305.1454.



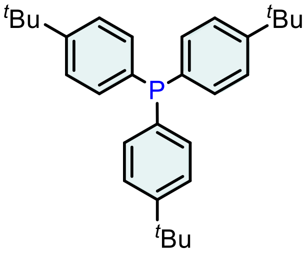
Tris(4-methoxyphenyl)phosphane(C8)[9] (CAS: *855-38-9*)

Yield: 33% White solid, m.p. 135 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.38 – 7.21 (m, 6H), 6.91 (d, *J*=8.8, 6H), 3.81 (s, 9H). **^{13}C NMR** (151 MHz, CDCl$_3$): δ = 160.1, 134.9 (d, *J* = 21.1), 128.9 (d, *J* = 7.6), 114.1 (d, *J* = 7.6), 55.1.

^{31}P NMR (162 MHz, CDCl$_3$): δ = -9.09.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for C21H22O3P$^+$ 353.1310, found 353.1310.



Tris(4-(tert-butyl)phenyl)phosphane(C9)[10] (CAS: *54409-77-7*)

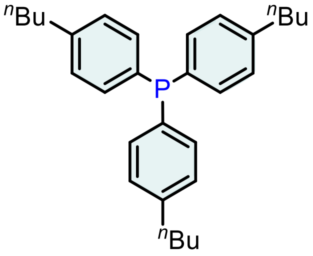
Yield: 22% White oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.37 (d, *J* = 6.8, 6H), 7.30 (t, *J* = 8.0, 6H), 1.31 (s, 27H).

^{13}C NMR (151 MHz, CDCl$_3$): δ = 151.7, 133.4 (d, *J* = 19.6), 125.4 (d, *J* = 6.0), 34.6, 31.2.

^{31}P NMR (162 MHz, CDCl$_3$): δ = -7.81.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for C30H40P$^+$ 431.2862, found 431.2862.



Tris(4-butylphenyl)phosphane(C10)[10] (CAS: *76287-43-9*)

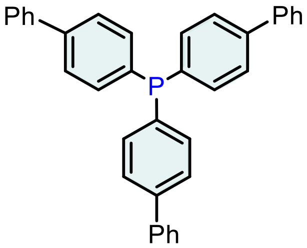
Yield: 54% White solid, m.p. 252 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.21 (t, *J* = 7.6, 6H), 7.14 (d, *J* = 7.6, 6H), 2.60 (t, *J* = 7.7, 6H), 1.62 – 1.55 (m, 6H), 1.40 – 1.31 (m, 6H), 0.92 (t, *J* = 8, 9H).

^{13}C NMR (151 MHz, CDCl$_3$): δ = 144.0, 133.6 (d, *J* = 18.1), 132.1 (d, *J* = 10.6), 128.6 (d, *J* = 7.6), 35.4, 33.3, 22.3, 13.9.

^{31}P NMR (162 MHz, CDCl$_3$): *δ = -6.70.*

HRMS (ESI): (m/z): [M + H]$^+$ calc. for $C30H40P^+$ 431.2862, found 431.2862.



Tri([1,1'-biphenyl]-4-yl)phosphane(C11)[10] (CAS: *13885-05-7*)

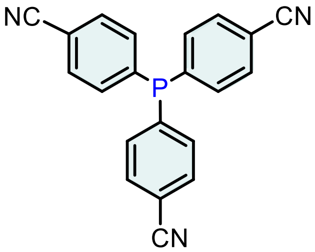
Yield: 73% White solid, m.p. 185-186 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.65 (m, 12H), 7.56 – 7.45 (m, 12H), 7.39 (t, *J* = 4.8, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ = 141.6, 140.5, 136.0 (d, *J* = 10.8), 134.2 (d, *J* = 19.6), 128.8, 127.5, 127.2 (d, *J* = 7.1), 127.1.

^{31}P NMR (162 MHz, CDCl$_3$): δ = -6.41.

HRMS (ESI): (m/z): [M + H]$^+$ calc. for $C36H28P^+$ 491.1923, found 491.1926.



4,4',4''-phosphanetriyltribenzonitrile(C12,C13)[11] (CAS: *22836-30-2*)

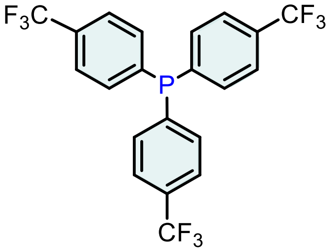
X= I,Yield: 74%;X = Br,Yield: 55% White solid, m.p.187-188 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.6, 6H), 7.36 (t, *J* =7.2, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.9 (d, *J* = 16.6), 134.1 (d, *J* = 21.1), 132.4 (d, *J* = 6.0), 118.0, 113.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ = - 2.99.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C21H13N3P^+$338.0847, found338.0852.



Tris(4-(trifluoromethyl)phenyl)phosphane(C14,C15)[11] (CAS: *13406-29-6*)

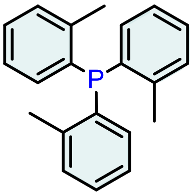
X= I,Yield: 49%;X = Br,Yield: 48% White solid, m.p.70-72 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.1, 6H), 7.47 (t, *J* = 7.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.3 (d, *J* = 13.6), 133.9 (d, *J* = 19.6), 131.5 (q, *J* = 64.9,33.2), 126.3 – 125.1 (m), 123.8 (q, *J* = 545.1,271.8).

^{31}P NMR (162 MHz, $CDCl_3$): δ = -4.98.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C21H13F9P^+$467.0606, found 467.0611.



Tri-o-tolylphosphane(C16)[11] (CAS: *6163-58-2*)

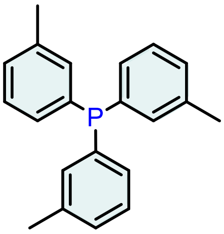
Yield: 46% White solid, m.p. 128-129 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.20 (m, 3H), 7.09 (t, *J* = 5.6, 3H), 6.79 – 6.71 (m, 6H), 2.41 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 137.9 (d, *J* = 7.6), 137.1 (d, *J* = 10.6), 134.5 (d, *J* = 22.7), 130.7 (d, *J* = 16.6), 129.5, 128.3 (d, *J* = 6.0), 21.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ = -4.12.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C21H22P^+$ 305.1454, found: 305.1454.



Tri-m-tolylphosphane(C17)[11] (CAS: *6224-63-1*)

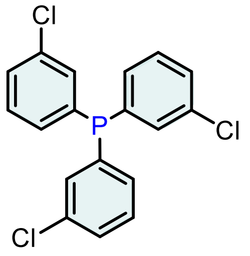
Yield: 52% White solid, m.p. 98-100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.27 (m, 6H), 7.26 – 7.15 (m, 6H), 2.39 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 138.0 (d, *J* = 9.0), 137.2 (d, *J* = 9.0), 134.5 (d, *J* = 22.7), 130.8 (d, *J* = 16.6), 129.5, 128.4 (d, *J* = 6.0), 21.5.

^{31}P NMR (162 MHz, $CDCl_3$): δ = -4.09.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C21H22P^+$ 305.1454, found: 305.1454.



Tris(3-chlorophenyl)phosphane(C18)[11] (CAS: *29949-85-7*)

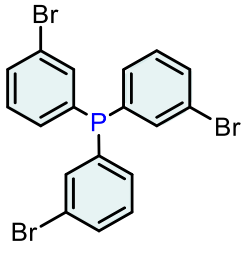
Yield: 55% White solid, m.p. 67 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.1, 3H), 7.32 (d, *J* = 7.5, 3H), 7.27 (d, *J* = 7.5, 3H), 7.18 (t, *J* = 7.4, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 138.2 (d, *J* = 15.1), 135.0 (d, *J* = 9.0), 133.2 (d, *J* = 21.1), 131.7 (d, *J* = 19.6), 130.0 (d, *J* = 6.0), 129.5.

^{31}P NMR (162 MHz, $CDCl_3$): δ = -3.55.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C18H13Cl3P^+$364.9815, found 364.9816.



Tris(3-bromophenyl)phosphane(C19)[11] (CAS: *464928-06-1*)

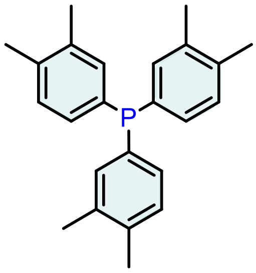
Yield: 62% White solid, m.p. 117-119 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 – 7.50 (m, 3H), 7.47 – 7.40 (m, 3H), 7.34 – 7.18 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 138.5 (d, *J* = 15.1), 136.1 (d, *J* = 21.1), 132.4, 132.1(d, *J* = 18.1), 130.3 (d, *J* = 7.6), 123.3 (d, *J* = 7.6).

^{31}P NMR (162 MHz, $CDCl_3$): δ = -3.02.

HRMS (ESI): (m/z): [M + H]+ calc. for $C18H13Br3P^+$496.8305, found496.8300.



Tris(3,4-dimethylphenyl)phosphane(C20)[11] (CAS: 69227-46-9)

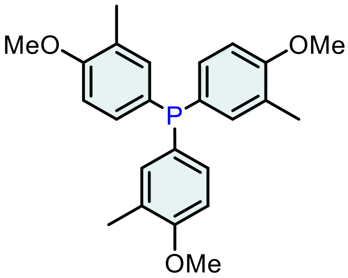
Yield: 60% White solid, m.p. 77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 (d, *J* = 8.6, 3H), 7.10 (d, *J* = 7.6, 3H), 7.02 (t, *J* = 8.2, 3H), 2.27 (s, 9H), 2.22 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 137.1, 135.6, 133.6 (d, *J* = 21.2), 132.3, 131.7 (d, *J*=19.6), 131.3 (d, *J*=7.2), 29.7, 19.9 (d, *J*=29.0).

^{31}P NMR (162 MHz, $CDCl_3$): δ = -7.80.

HRMS (ESI): (m/z): [M + H]+ calc. for C24H28P^{+} 347.1923, found 347.1923.



(4-methoxy-3-methylphenyl)bis(3-methoxy-4-methylphenyl)phosphane(C21) (New Compound)

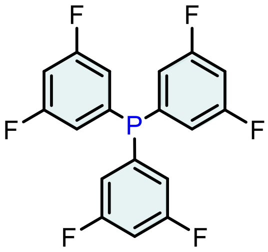
Yield: 47% White solid, m.p. 112-113 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (q, *J* = 8.2, 7.7, 6H), 6.79 (d, *J* = 8.3, 3H), 3.82 (s, 9H), 2.17 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.2, 135.2, 135.7, 132.4 (d, *J* = 18.7), 126.7 (d, *J* = 8.1), 109.9 (d, *J* = 7.6).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -9.88.

HRMS (ESI): (m/z): [M + H]$^{+}$ calc. for C24H28O3P^{+} 359.1771, found: 359.1772.



Tris(3,5-difluorophenyl)phosphane(C22)[11] (CAS: 132698-61-4)

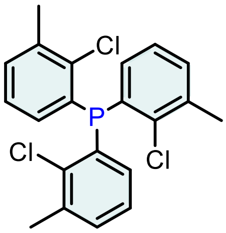
Yield: 50% White solid, m.p. 102-104 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.90 – 6.84 (m, 3H), 6.83 – 6.77 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 164.5 – 163.4 (m), 163.0 – 161.0 (m), 139.0 (d, *J* = 16.2), 139.0 (dd, *J*=16.3, 13.2), 116.3 – 115.6 (m), 105.5 (t, *J* = 25.2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -0.65.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C18H10F6P^+$ 371.0419, found 371.0420.



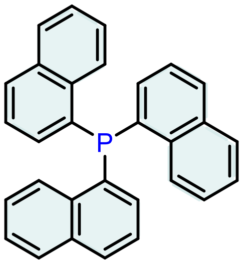
Tris(2-chloro-3-methylphenyl)phosphane(C23) (New Compound)

Yield: 56% White solid, m.p. 82-83 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 – 7.19 (m, 4H), 7.07 (t, *J*=7.5, 2H), 2.38 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 137.2, 135.5 (d, *J* = 12.9), 135.0 (d, *J* = 8.2), 133.6 (d, *J* = 21.2), 131.7 (d, *J* = 19.6), 131.3 (d, *J* = 7.2), 20.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ = -7.54.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C21H19Cl3P^+$ 407.0284, found:407.0287.



Tri(naphthalen-1-yl)phosphane(C24)[11] (CAS: *3411-48-1*)

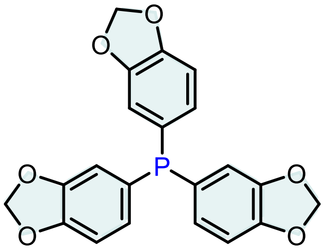
Yield: 59% White solid, m.p. 281-282 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.69 – 8.49 (m, 3H), 7.89 (dd, *J* = 20.1, 8.2, 6H), 7.63 – 7.41 (m, 6H), 7.27 (t, *J* = 7.7, 3H), 7.13 – 6.94 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 135.6 (d, *J* = 23.7), 133.5 (d, *J* = 4.7), 133.4, 132.7 (d, *J* = 11.0), 129.6, 128.6 (d, *J* = 1.9), 126.4 (d, *J* = 27.2), 126.3 (d, *J* = 2.3), 126.0 (d, *J* = 1.3), 125.8 (d, *J* = 1.7).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -32.00.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C30H22P^+$ 413.1454, found 413.1455.



Tris(benzo[d][1,3]dioxol-5-yl)phosphane(C25) (New Compound)

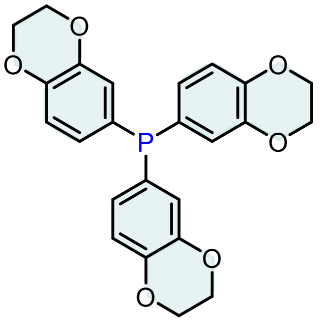
Yield: 57% White solid, m.p. 132-133 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.92 – 6.81 (m, 3H), 6.79 (d, *J* = 7.9, 3H), 6.72 (d, *J* = 6.4, 3H), 5.95 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.4, 148.0 (d, *J* = 8.6), 130.3 (d, *J* = 9.8), 128.1 (d, *J* = 26.5), 112.8 (d, *J* = 17.7), 108.7 (d, *J* = 10.3), 101.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.67.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C21H16O6P^+$ 359.0679, found:359.0681.



Tris(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)phosphane(C26) (New Compound)

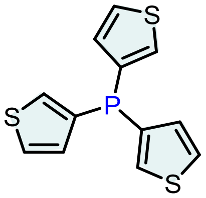
Yield: 63% colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.85 – 6.80 (m, 6H), 6.79 – 6.74 (m, 3H), 4.28 – 4.20 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.2, 143.6, 129.5 (d, *J* = 7.3), 127.0 (d, *J* = 23.3), 122.2 (d, *J* = 18.8), 117.5 (d, *J* = 9.2), 64.3 (d, *J* = 15.7).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -7.24.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C24H22O6P^+$ 437.1149, found 437.1149.



Tri(thiophen-3-yl)phosphane(C27)[9] (CAS: *23415-53-4*)

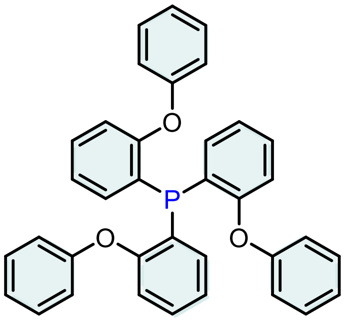
Yield: 32% White solid, m.p. 67-68 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.37 (dd, *J* = 4.9, 2.9, 3H), 7.27 – 7.24 (m, 3H), 7.05 (d, *J* = 3.4, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 137.1 (d, *J* = 12.2), 130.8 (d, *J* = 17.9), 130.6, 126.5 (d, *J* = 6.3).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -43.53.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C12H10PS3^+$ 280.9677, found:280.9677.



Tris(4-phenoxyphenyl)phosphane(C28) (New Compound)

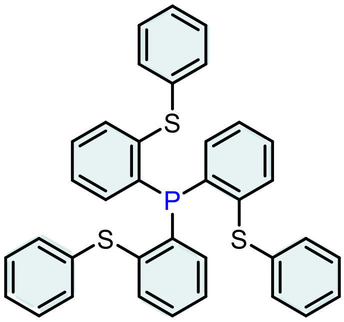
yield: 57% White solid, m.p. 119-120 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.25 (m, 3H), 7.23 – 7.17 (m, 6H), 7.15 – 7.10 (m, 3H), 7.09 – 7.00 (m, 6H), 6.88 – 6.79 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.8 (d, *J* = 18.0), 156.8, 134.8 (d, *J* = 2.2), 130.2, 129.4, 127.1 (d, *J* = 15.5), 123.3, 123.2, 119.4, 117.4 (d, *J* = 1.6).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -37.21.

HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C36H28O3P^+$ 539.1771, found: 359.1774.



Tris(4-(phenylthio)phenyl)phosphane(C29) (New Compound)

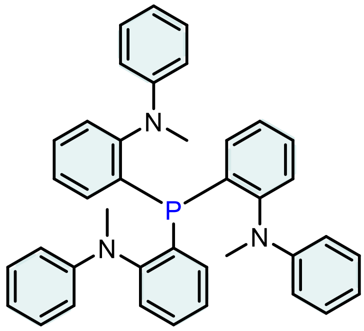
Yield: 52% colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.24 (m, 12H), 7.22 – 7.12 (m, 12H), 6.85 (d, *J*=7.7, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.8 (d, *J* = 31.2), 139.4 (d, *J* = 11.1), 136.3 (d, *J* = 5.7), 134.0, 132.7 (d, *J* = 3.1), 131.4, 129.5, 128.9, 127.5, 126.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ = -23.97.

HRMS (ESI): (m/z): [M + H]$^+$ calc. for C36H28PS3$^+$ 587.1085, found:587.1090.



4,4',4''-phosphanetriyltris(N-methyl-N-phenylaniline)(C30) (New Compound)

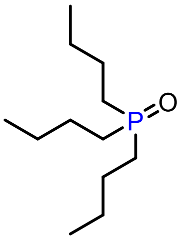
Yield: 54% colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (t, *J* = 7.5, 3H), 7.24 (t, *J* = 8.2, 3H), 7.14 (d, *J* = 7.8, 3H), 7.08 – 7.00 (m, 3H), 6.92 (t, *J* = 7.7, 6H), 6.57 (t, *J* = 7.2, 3H), 6.24 (d, *J* = 8.1, 6H), 2.80 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.0 (d, *J* = 26.3), 149.2, 138.4 (d, *J* = 15.9), 135.8 (d, *J* = 1.5), 130.5, 128.6, 128.2, 126.5, 116.7, 113.5, 39.8 (d, *J* = 6.3).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -37.00.

HRMS (ESI): (m/z): [M + H]$^+$ calc. for C38H34N3P$^+$ 536.2490, found:536.2497.



Tributylphosphine(C31) (CAS: 814-29-9)

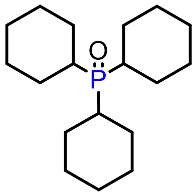
Yield: 57% White solid, m.p. 65-66 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.24 – 3.20 (m, 6H), 1.68 – 1.54 (m, 6H), 1.43 – 1.37 (m, 6H), 0.96 (t, *J*=7.3, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 57.4, 22.6, 18.4, 12.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ = 38.70.

HRMS (ESI): (m/z): [M + H]$^+$ calc. for C12H27OP$^+$ 218.1794, found: 218.17945.



Tricyclohexyl phosphine(C32)[9] (CAS: 13689-19-5)

Yield: 69% White solid, m.p. 155-156 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ = 1.83 – 1.67 (m, 15H), 1.66 – 1.61 (m, 3H), 1.31 – 1.11 (m, 15H).

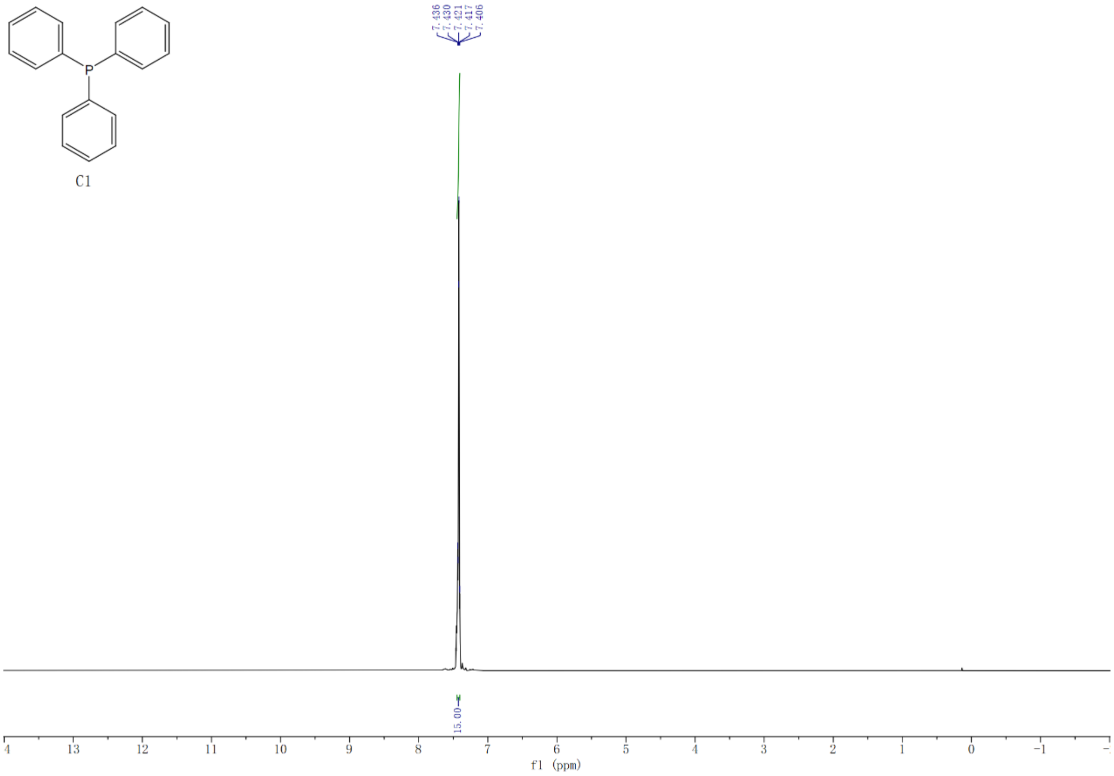
^{13}C NMR (101 MHz, DMSO-d6) δ = 34.9 (d, *J*=60.8), 26.7 (d, *J*=11.5), 26.3 (d, *J*=2.8), 26.2.

^{31}P NMR (162 MHz, DMSO-d6) δ = 48.39.

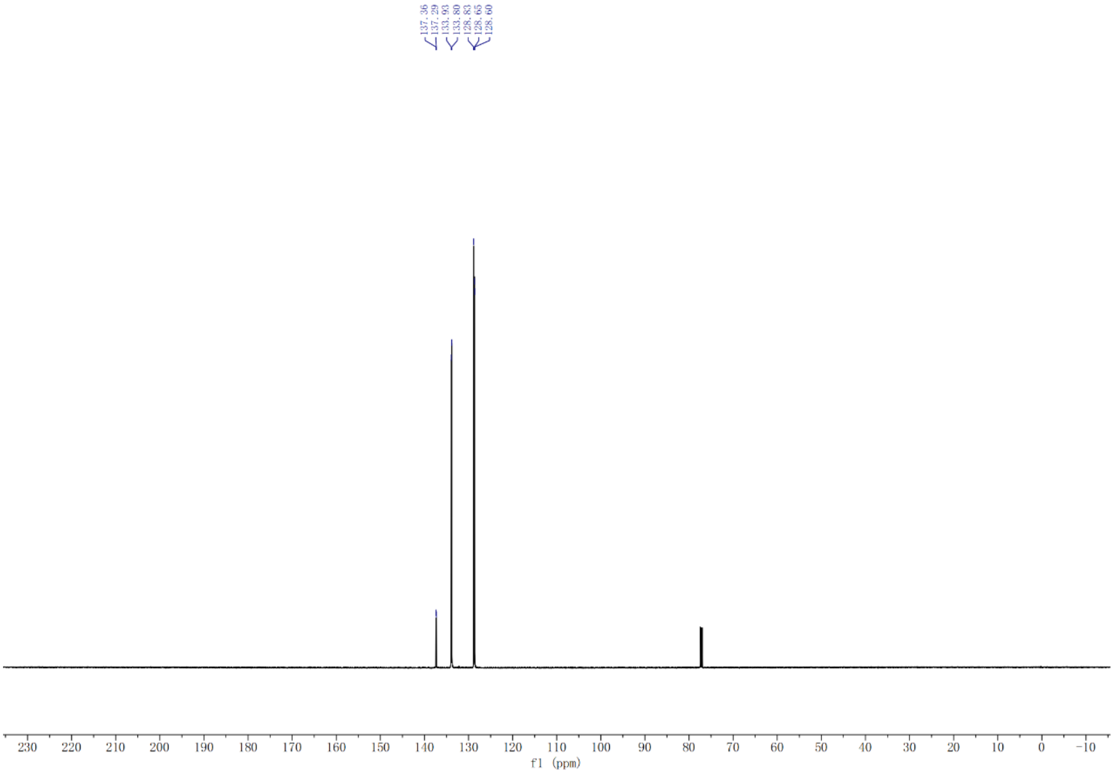
HRMS (ESI): (m/z): $[M + H]^+$ calc. for $C18H33OP^+$ 296.2264, found: 296.2266.

8. ^{1}H NMR, ^{31}P NMR, and ^{13}C NMR Spectra trace of the OPC products

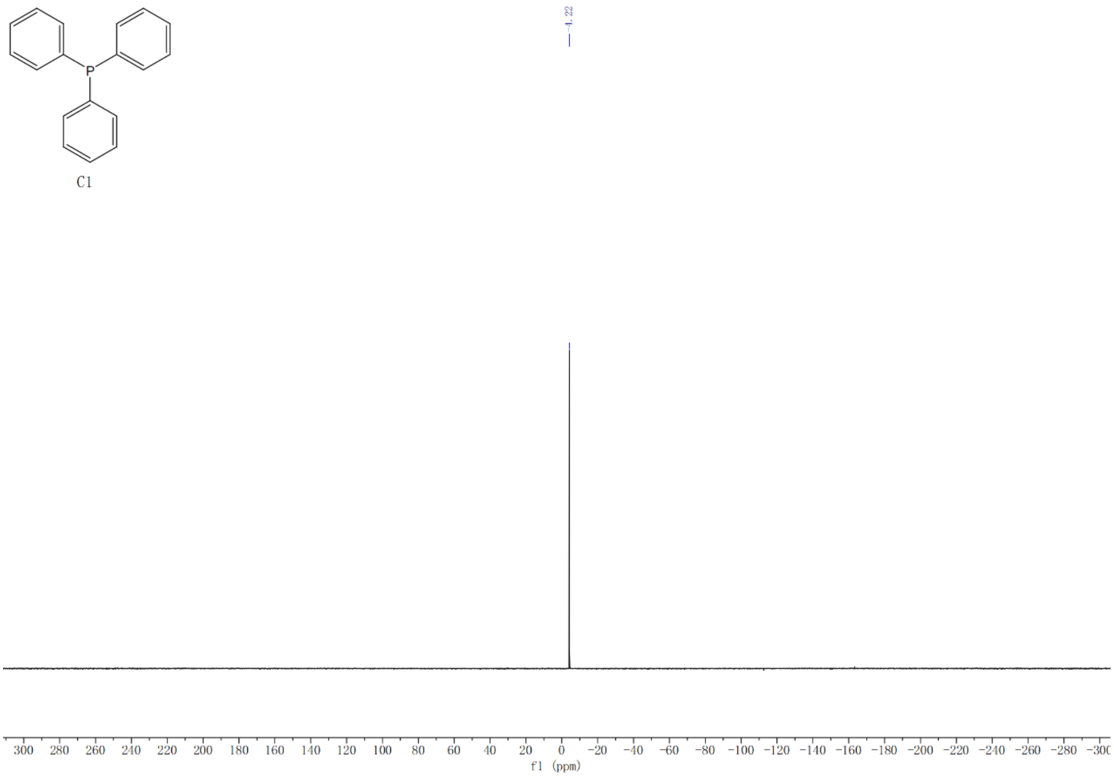
^{1}H NMR spectrum of **C1**



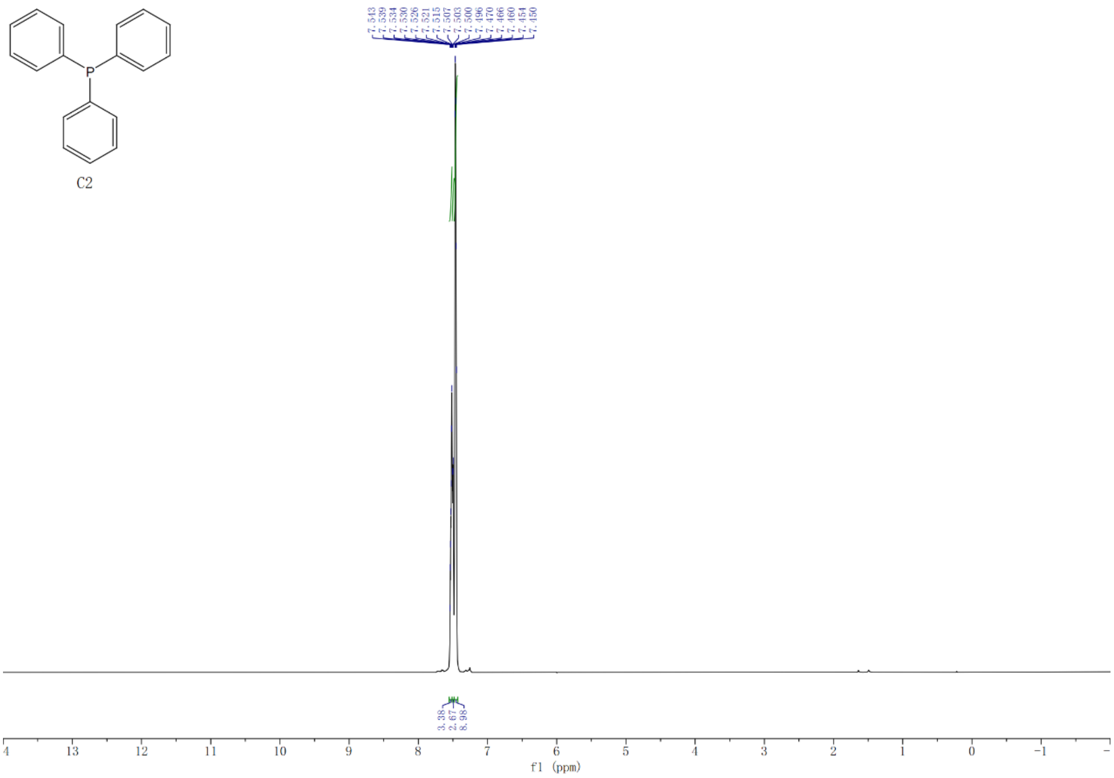
^{13}C NMR spectrum of **C1**



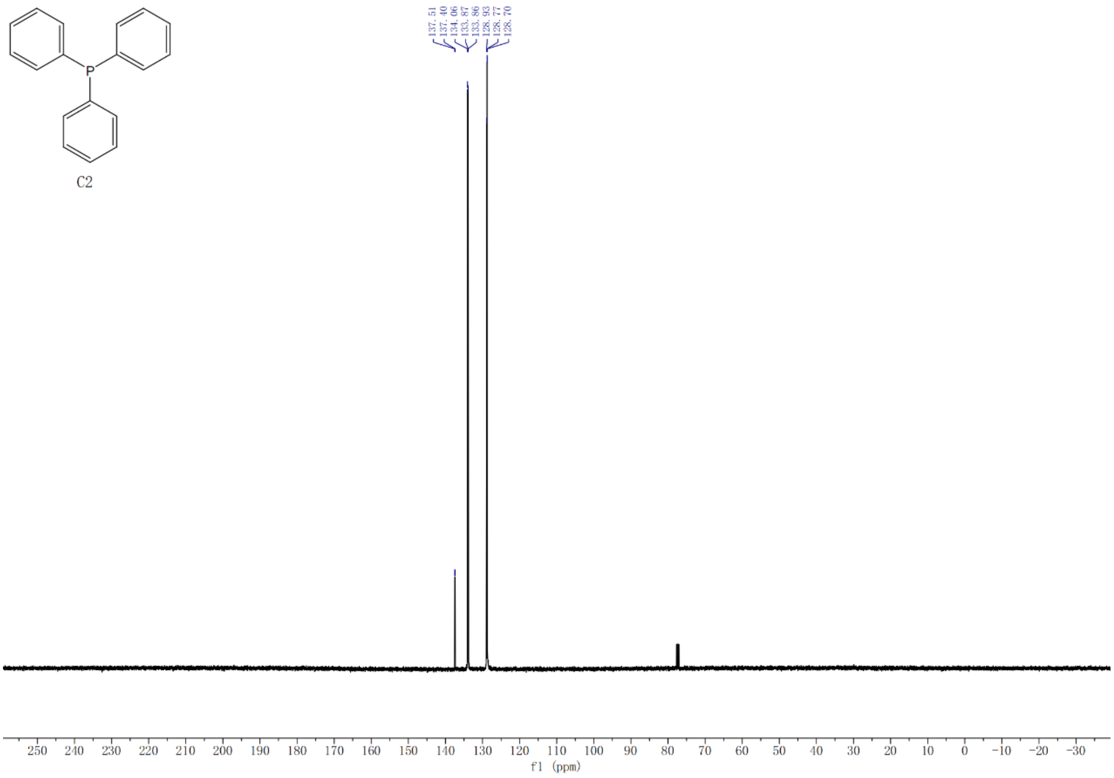
^{31}P NMR spectrum of **C1**



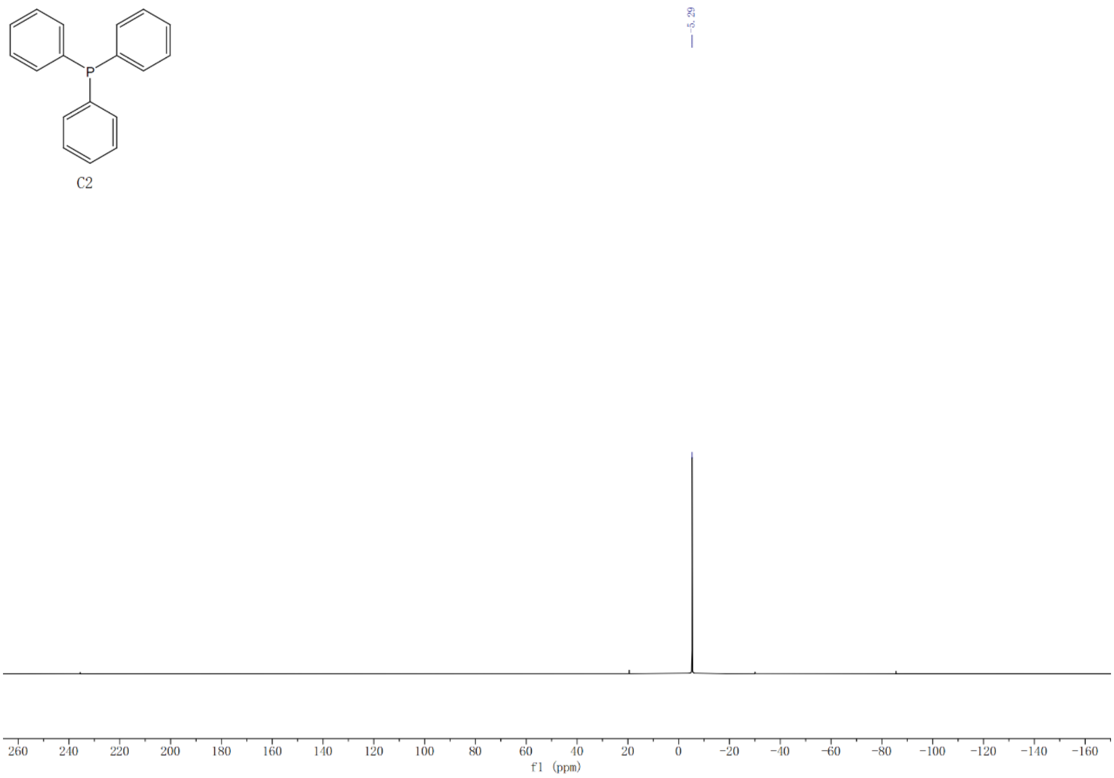
^{1}H NMR spectrum of **C2**



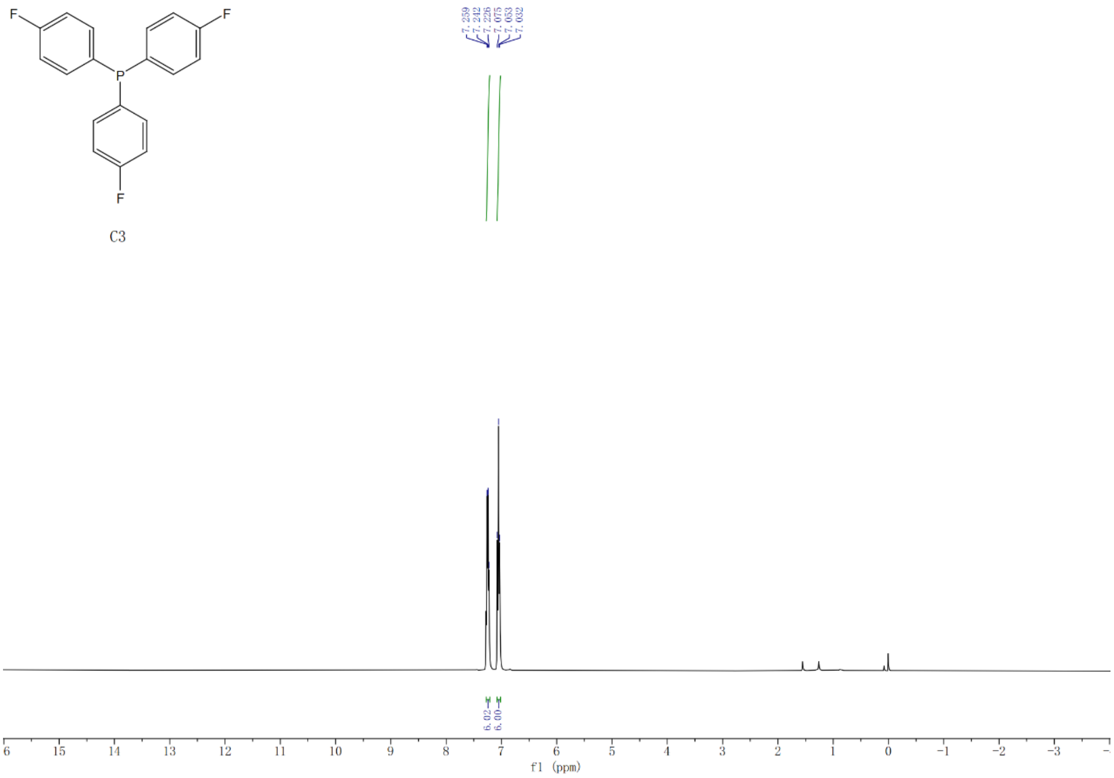
^{13}C NMR spectrum of **C2**



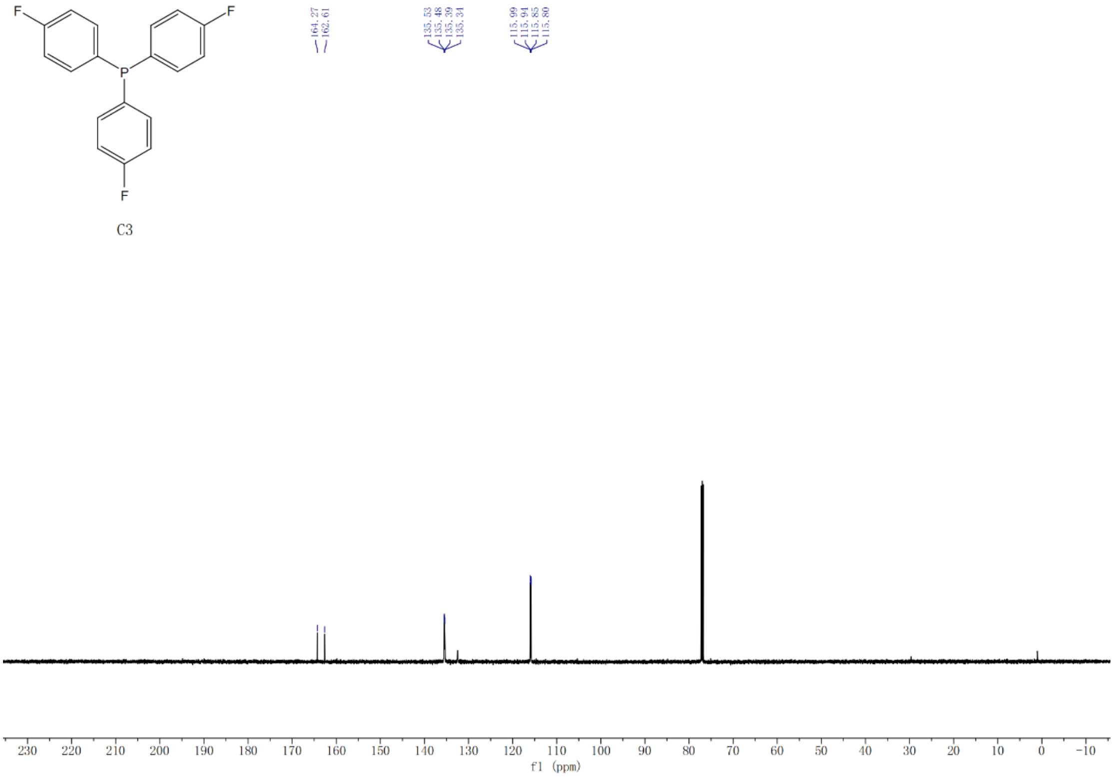
^{31}P NMR spectrum of **C2**



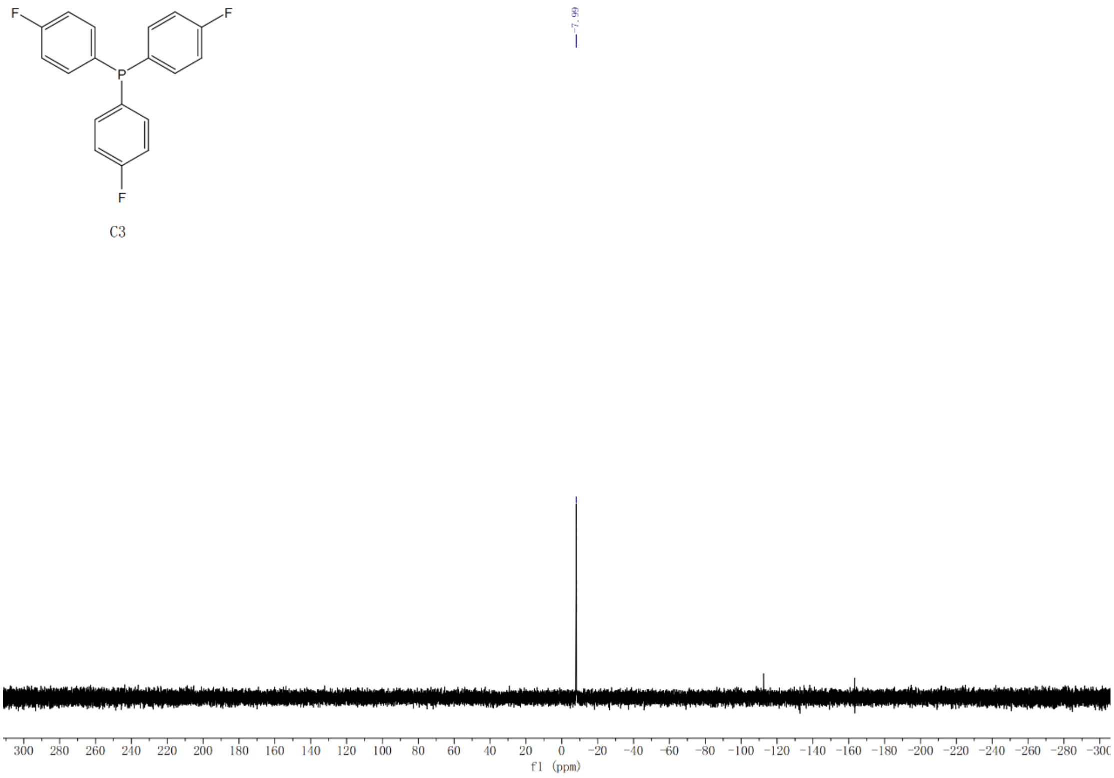
^{1}H NMR spectrum of **C3**



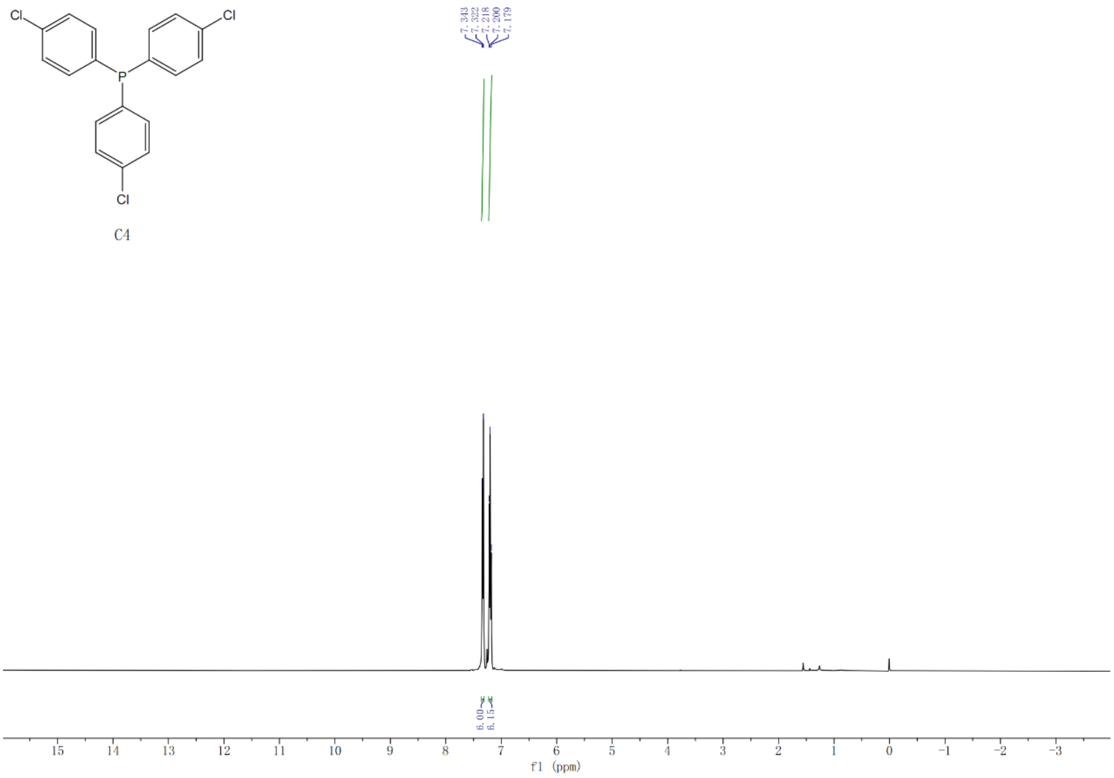
^{13}C NMR spectrum of **C3**



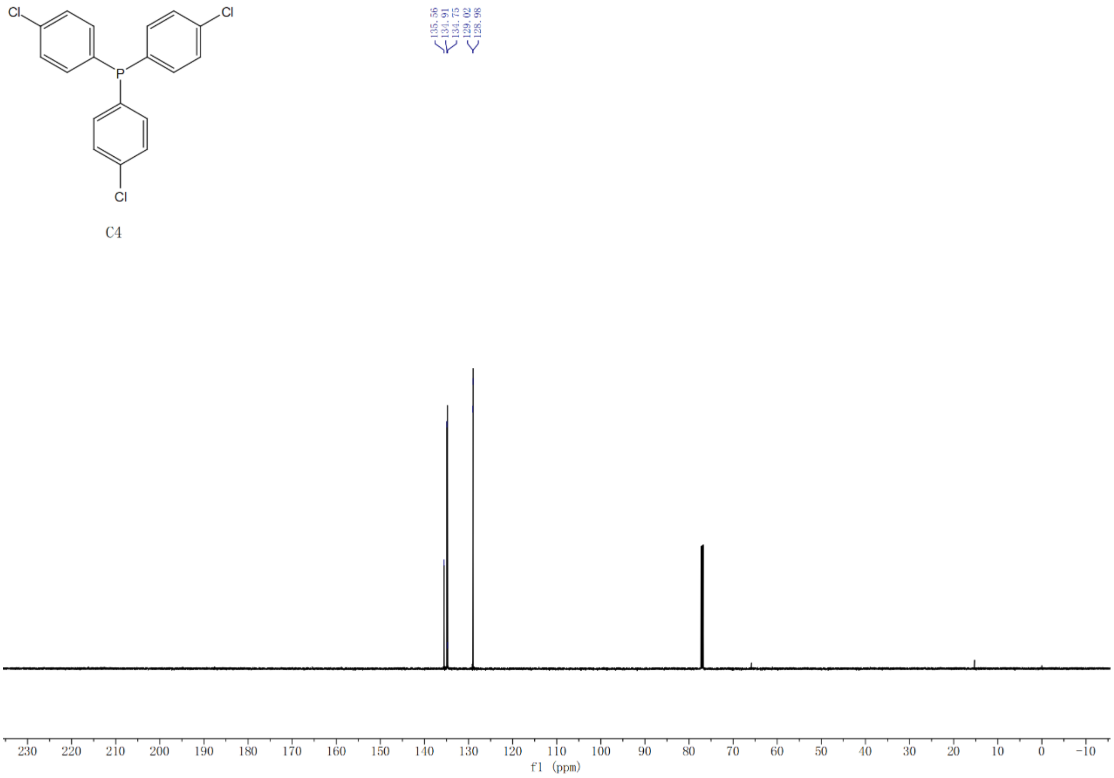
^{31}P NMR spectrum of **C3**



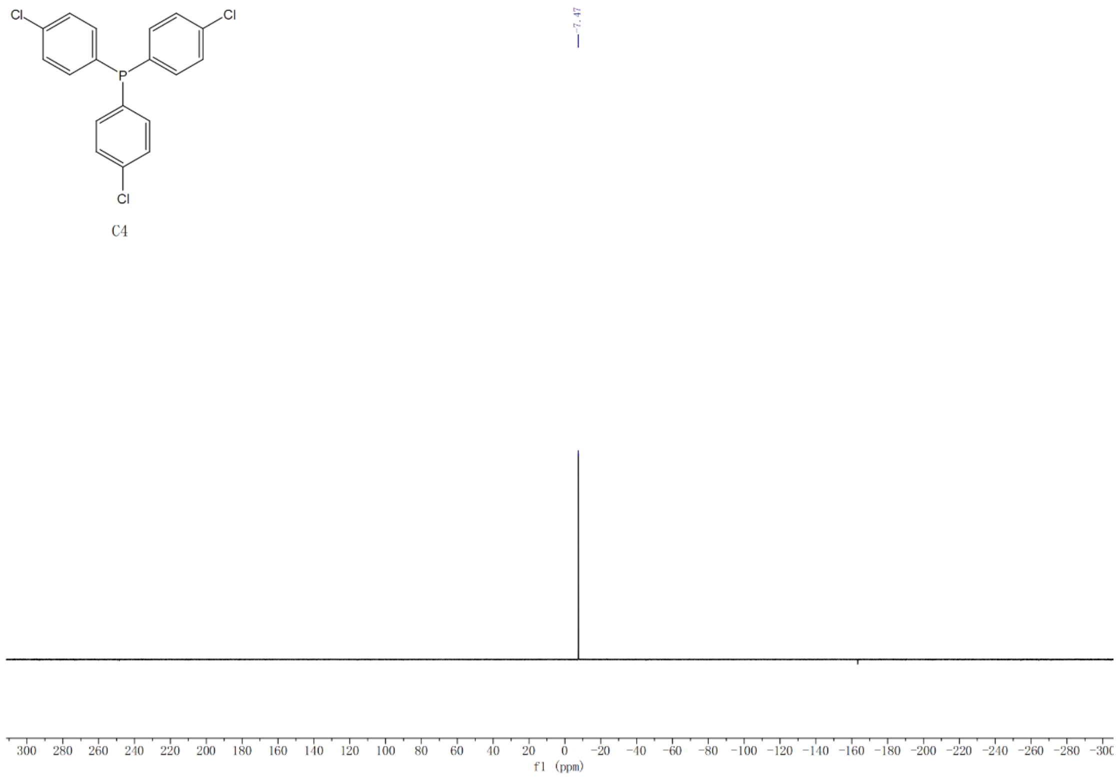
^{1}H NMR spectrum of **C4**



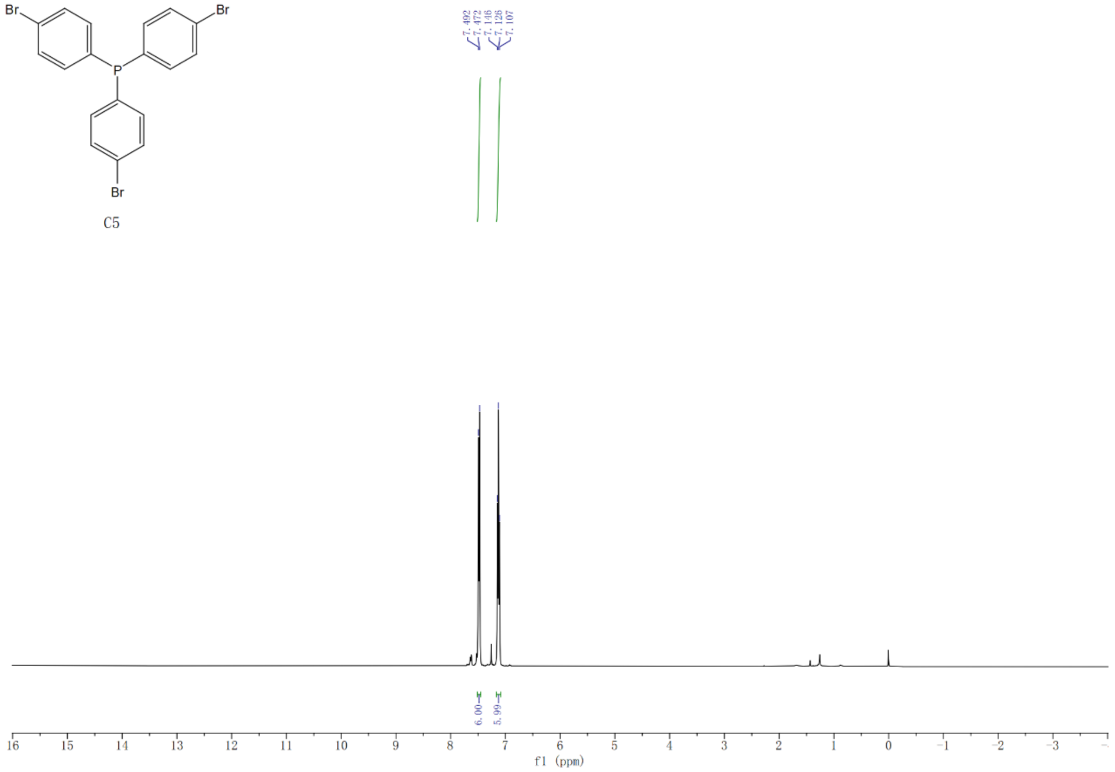
^{13}C NMR spectrum of **C4**



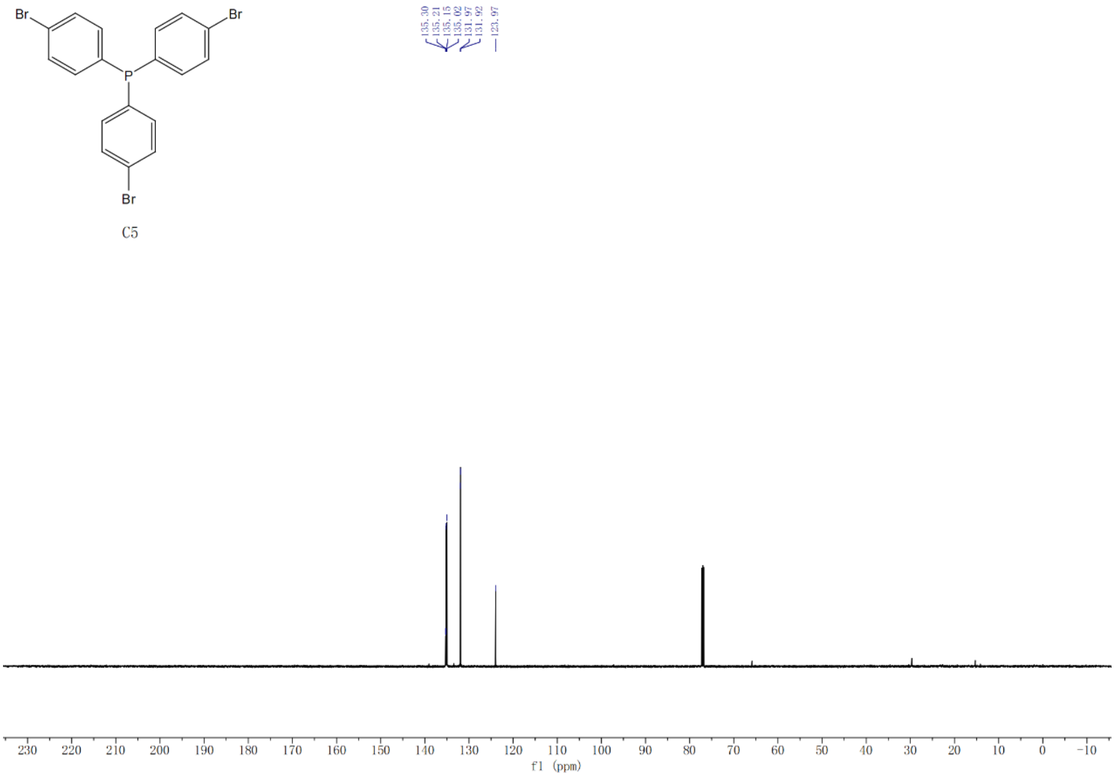
^{31}P NMR spectrum of **C4**



^{1}H NMR spectrum of **C5**

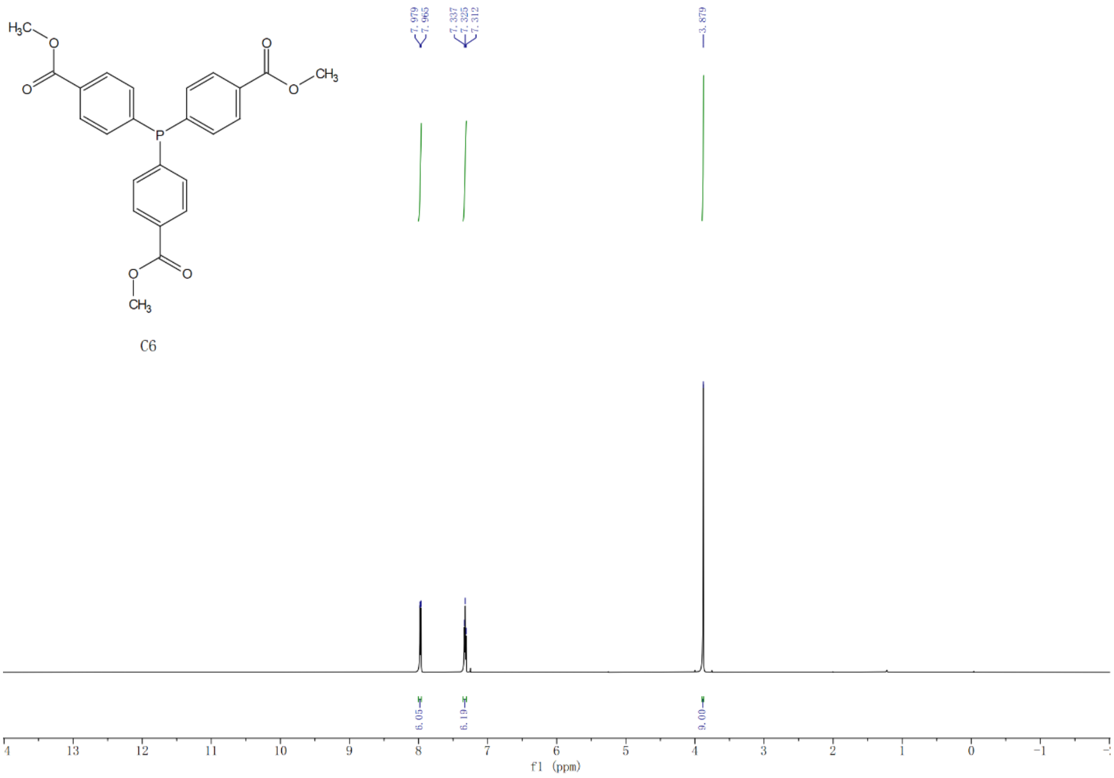


^{13}C NMR spectrum of **C5**

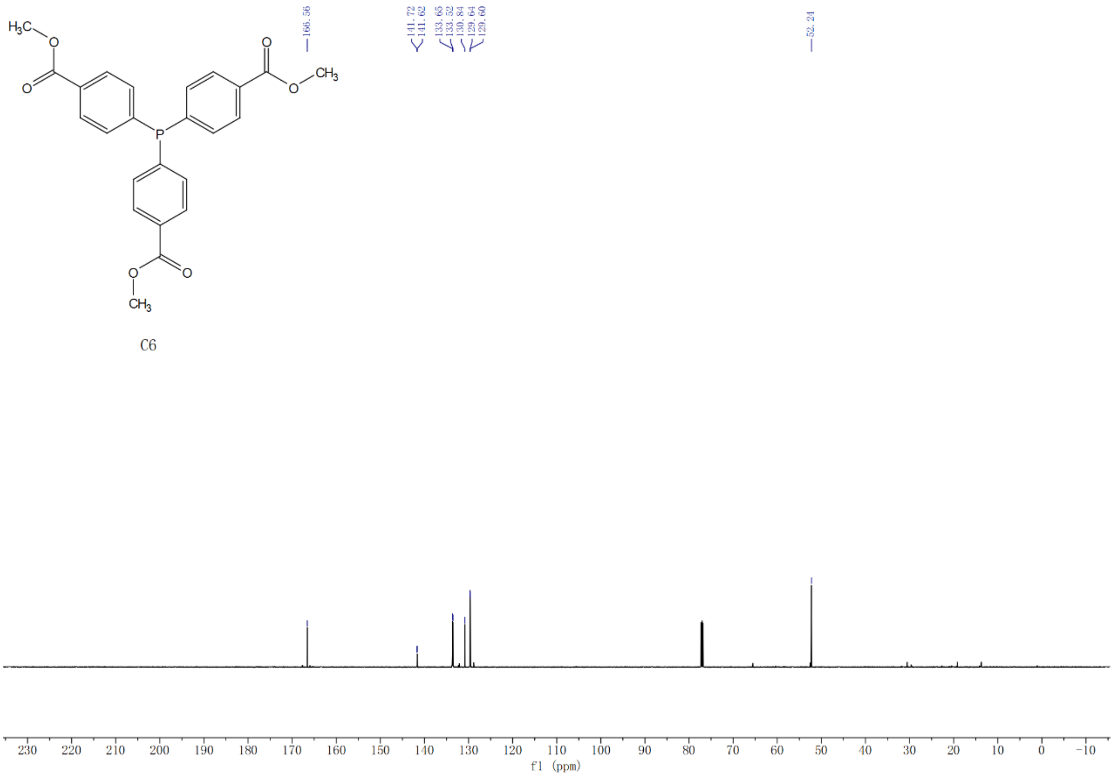


^{31}P NMR spectrum of **C5**

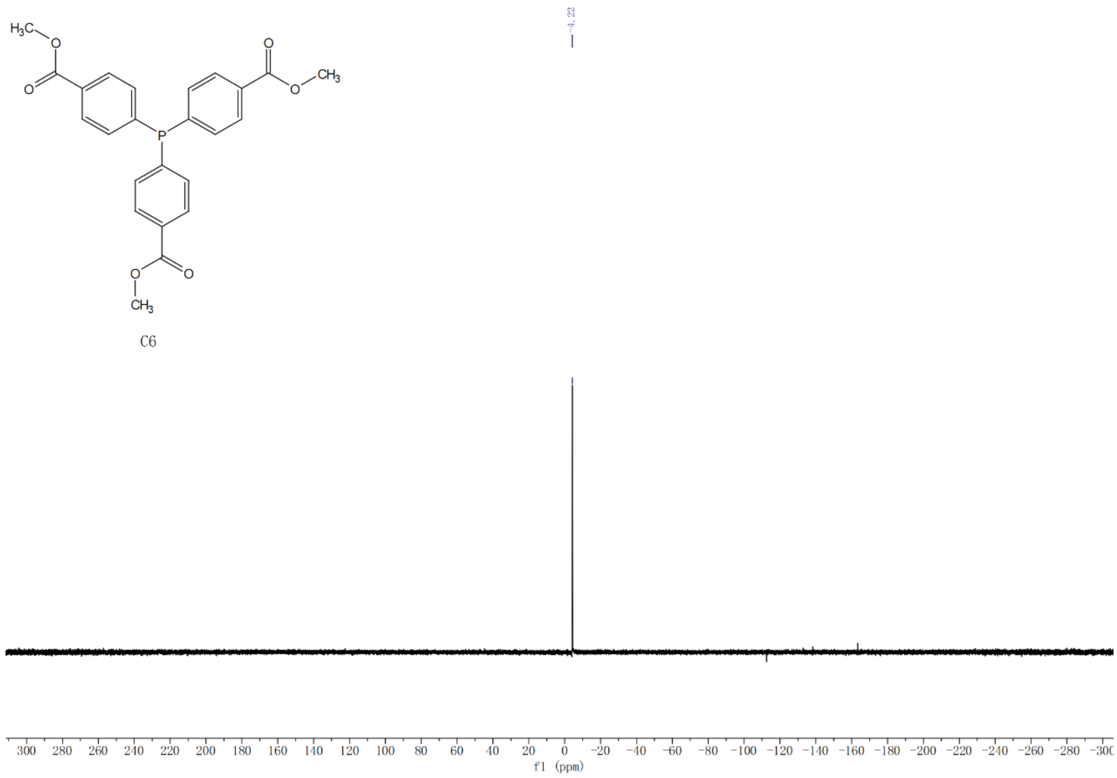
^{1}H NMR spectrum of **C6**



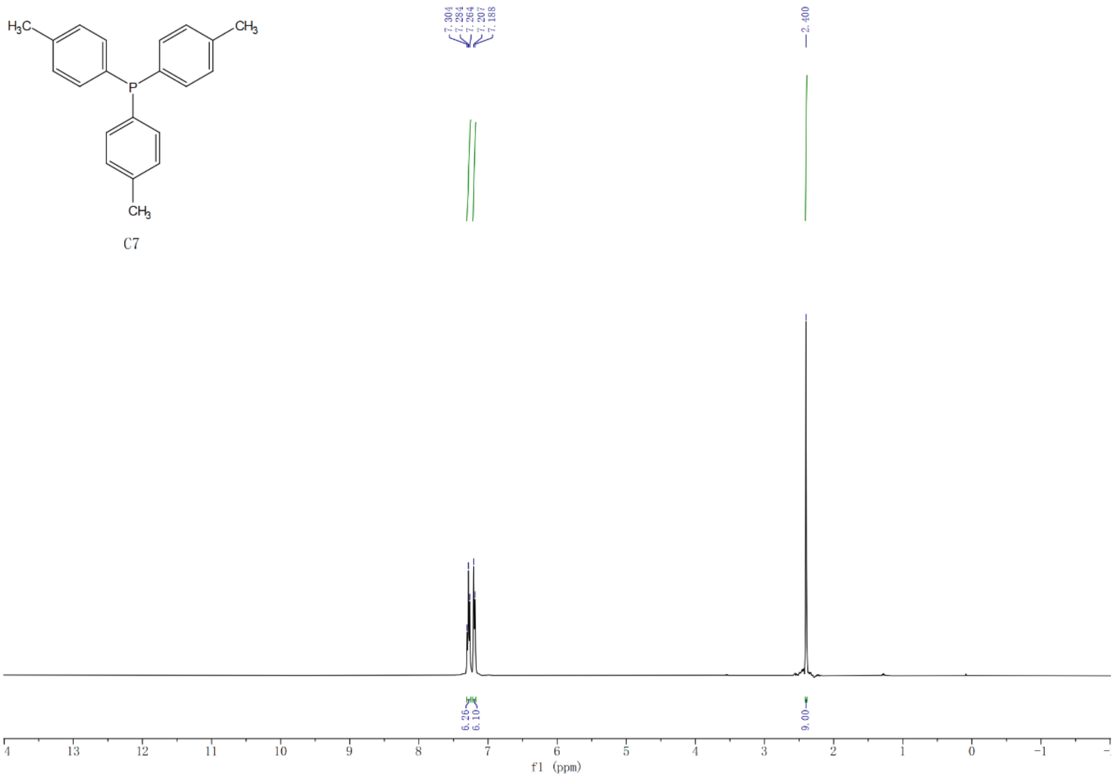
^{13}C NMR spectrum of **C6**



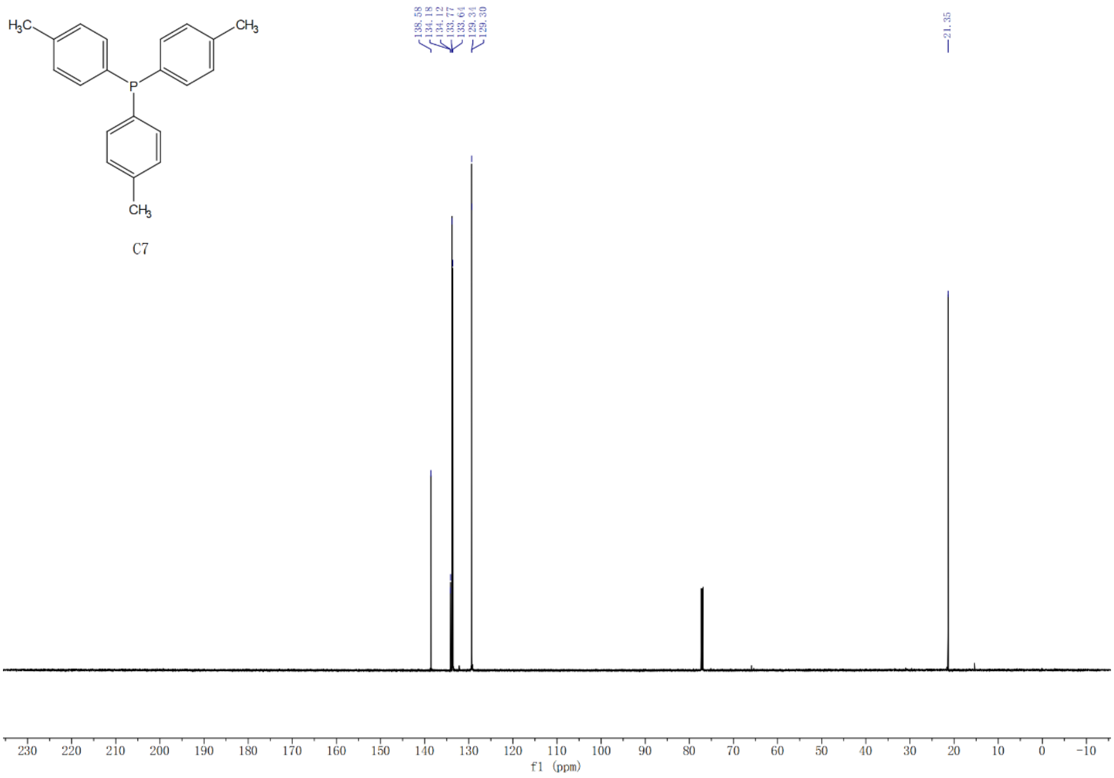
^{31}P NMR spectrum of **C6**



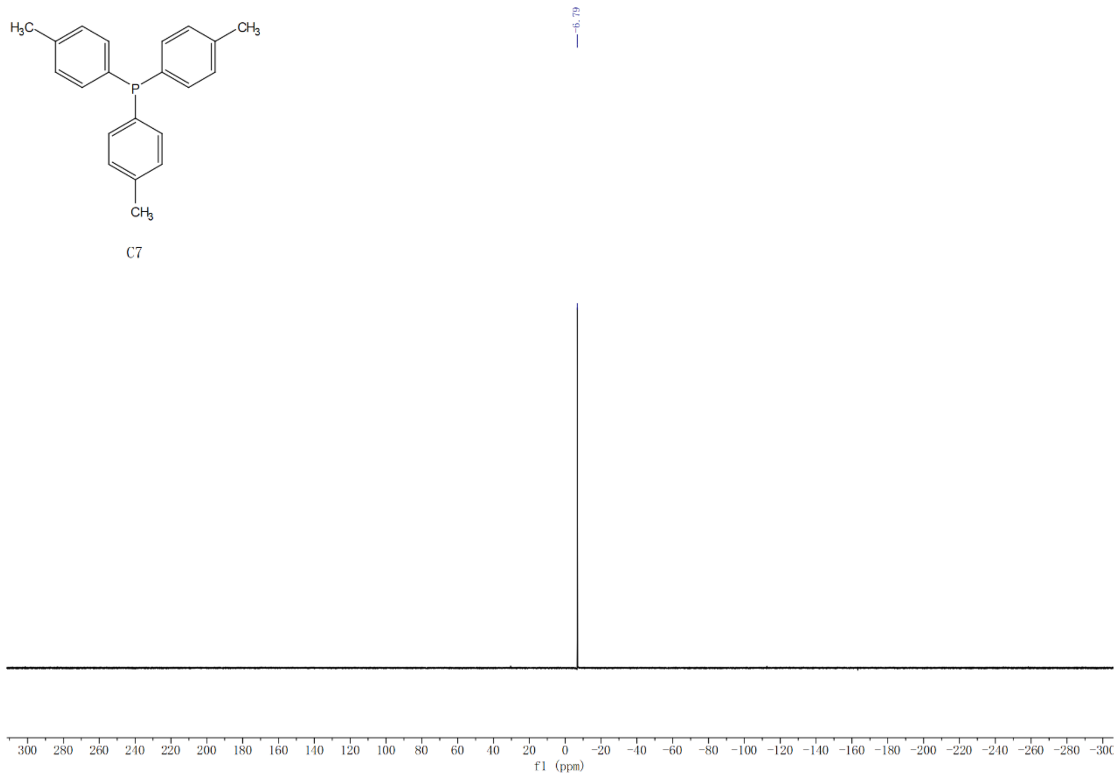
^{1}H NMR spectrum of **C7**



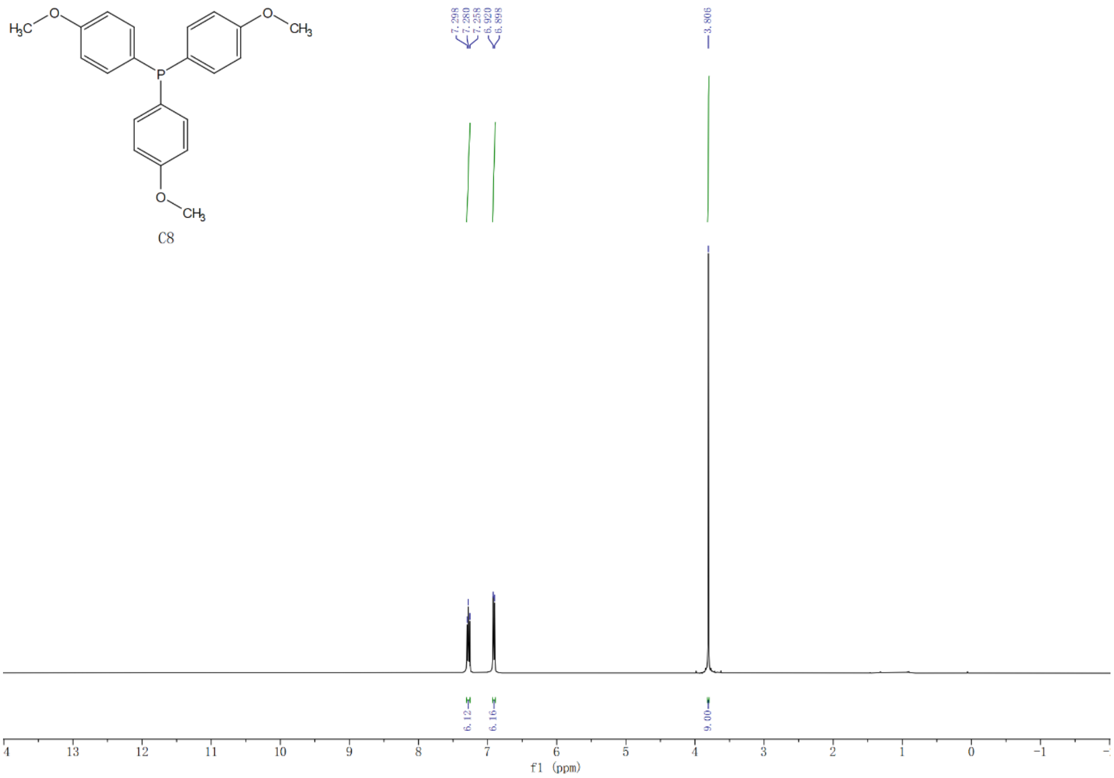
^{13}C NMR spectrum of **C7**



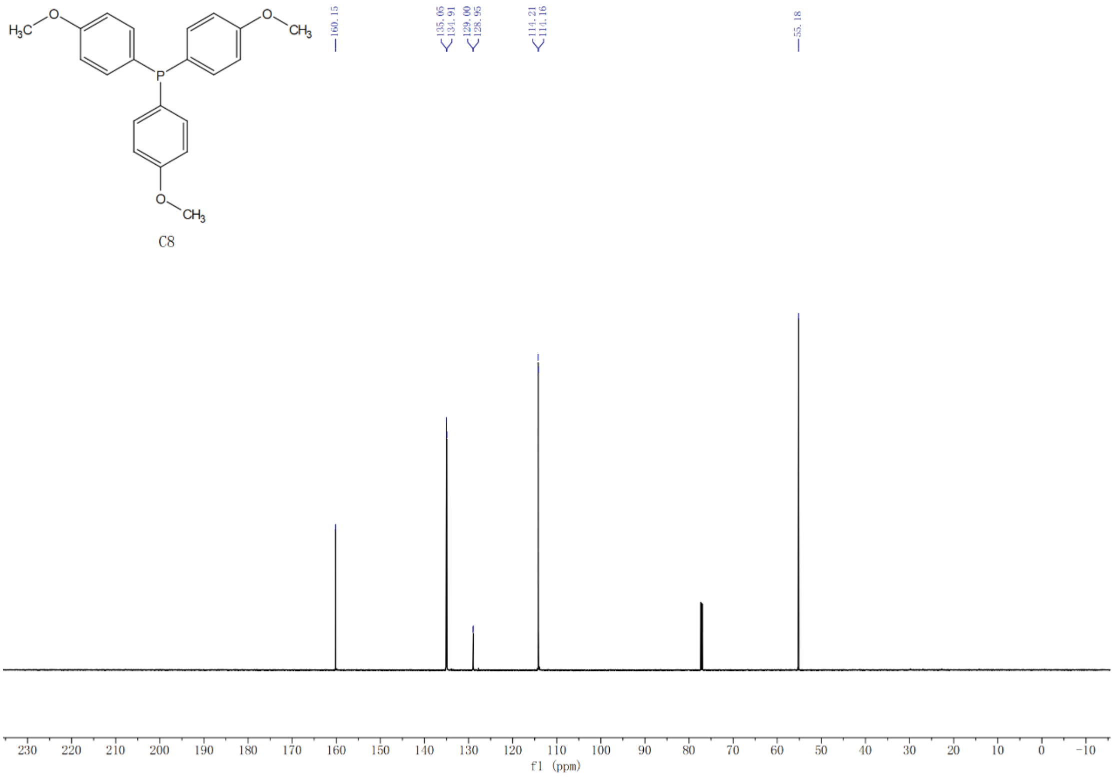
^{31}P NMR spectrum of **C7**



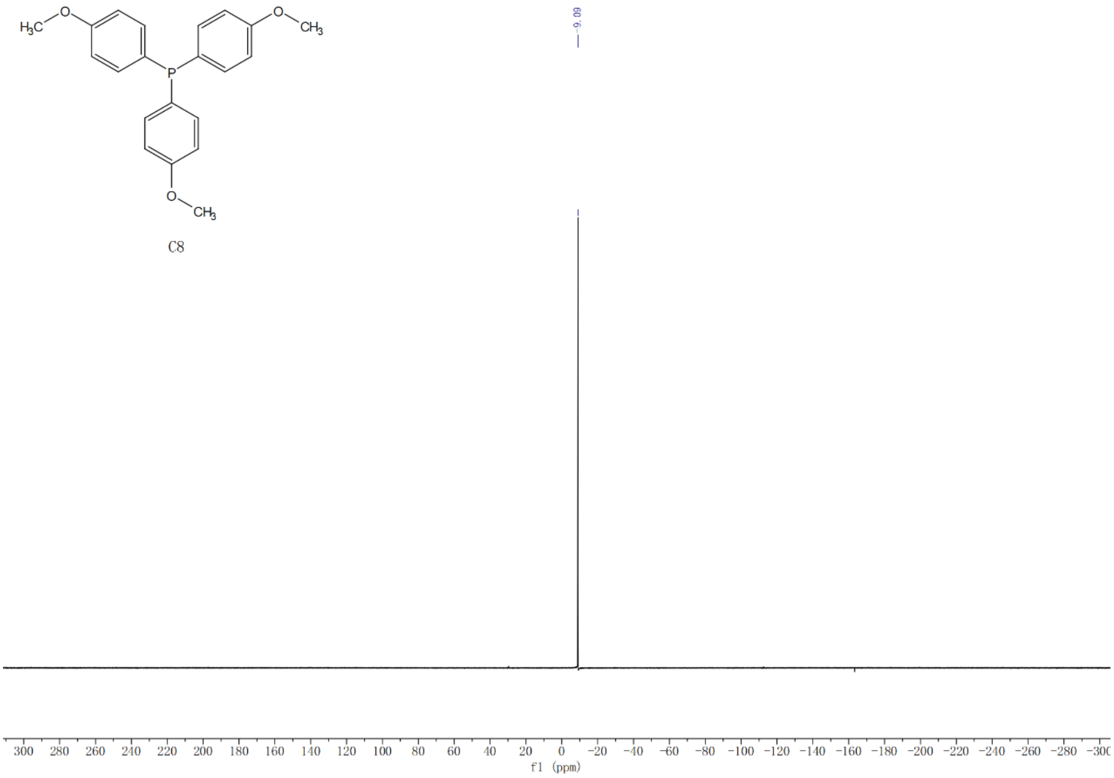
^{1}H NMR spectrum of **C8**



^{13}C NMR spectrum of **C8**

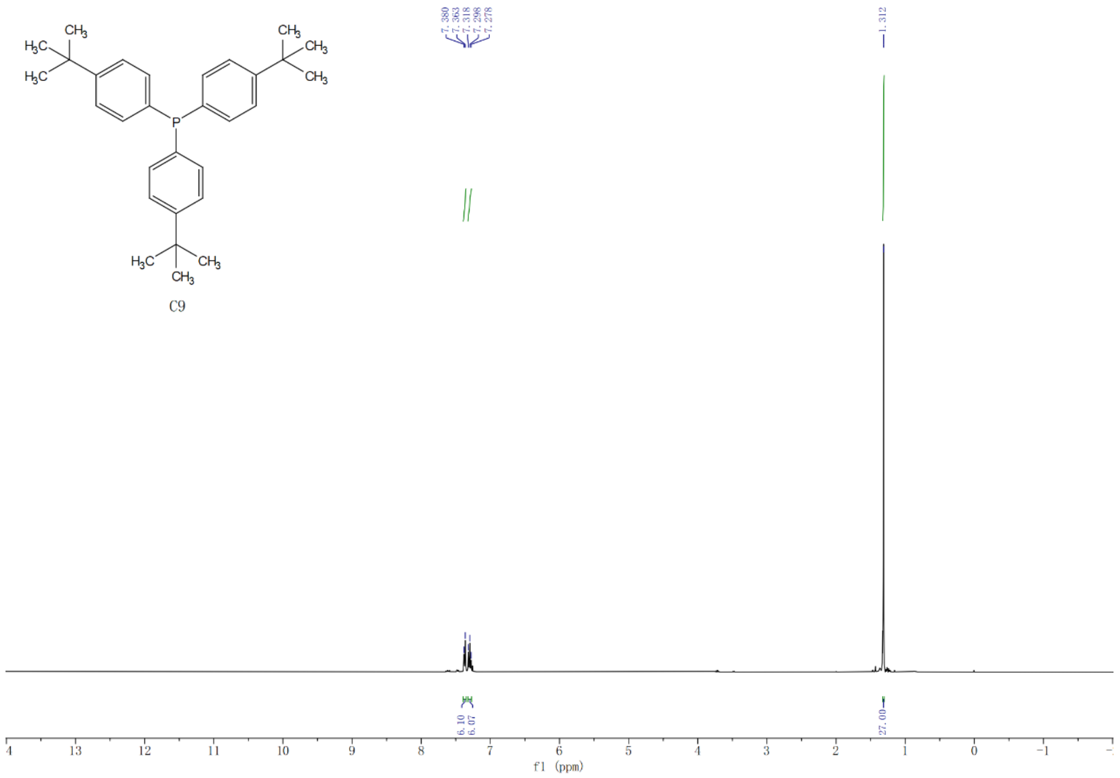


^{31}P NMR spectrum of **C8**

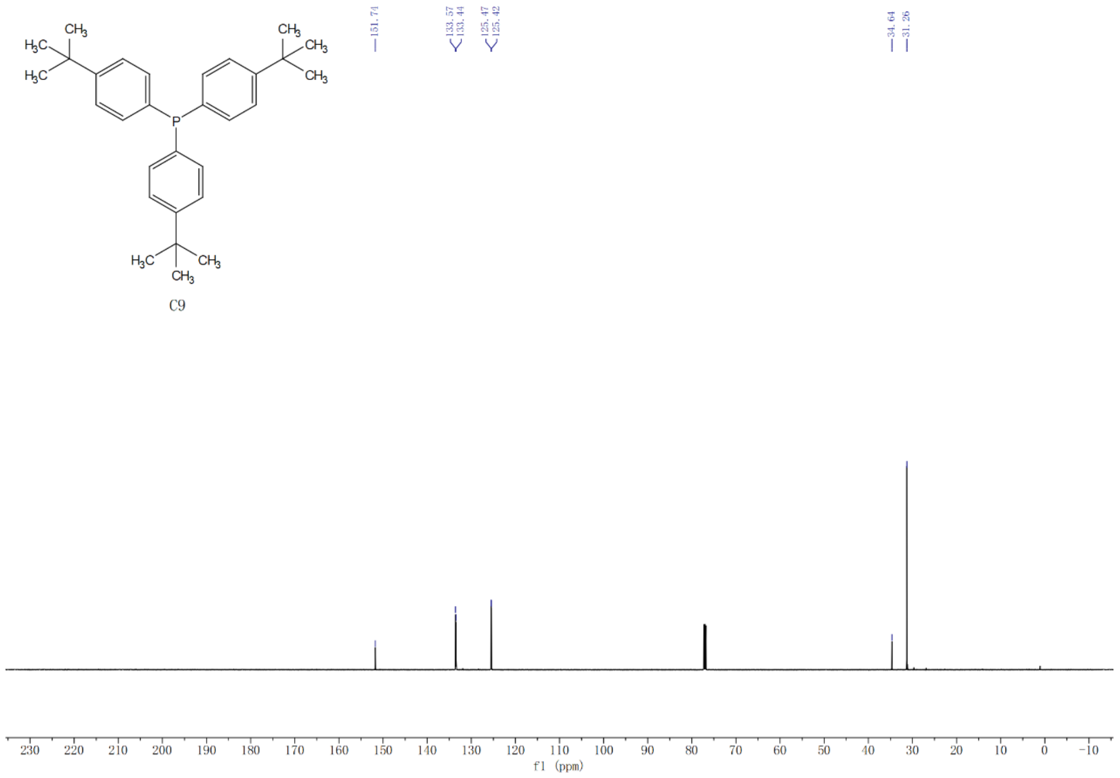


C8

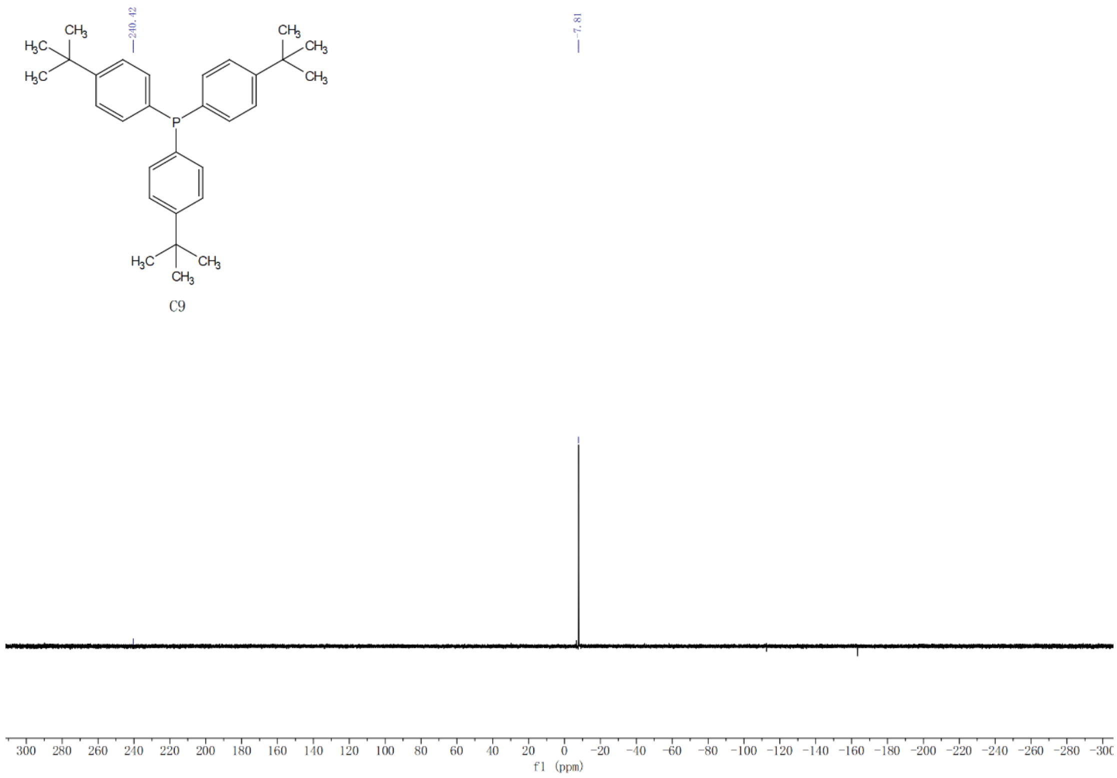
^{1}H NMR spectrum of **C9**



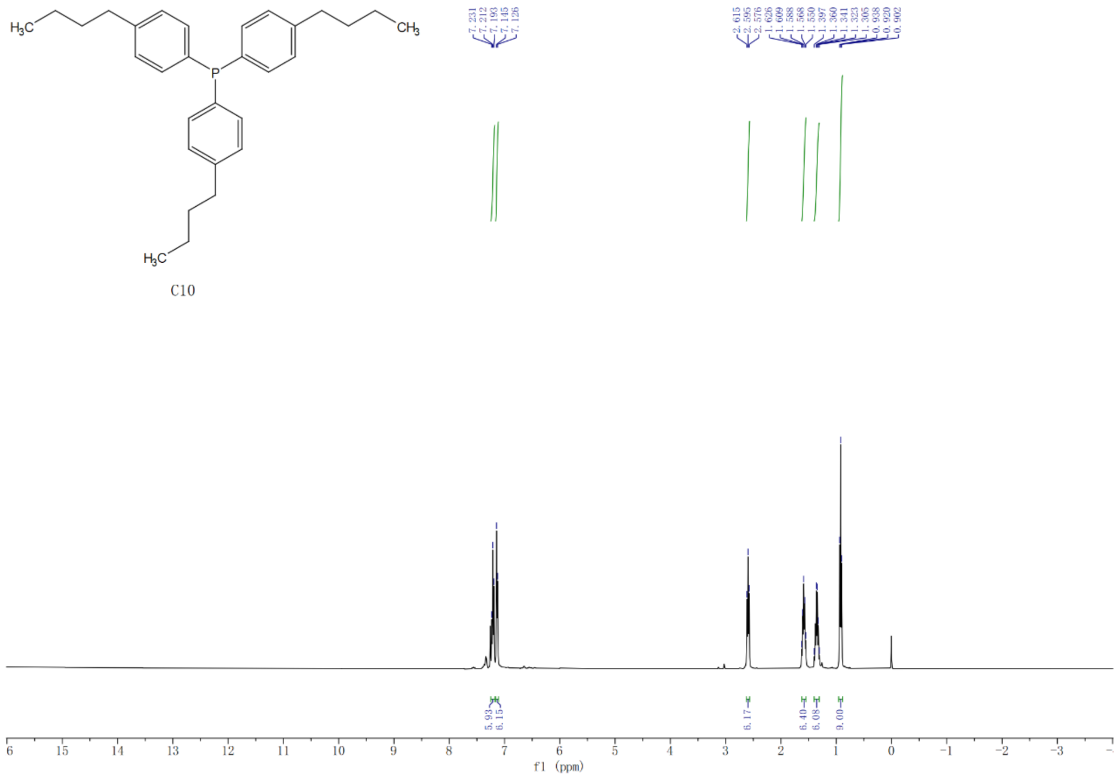
^{13}C NMR spectrum of **C9**



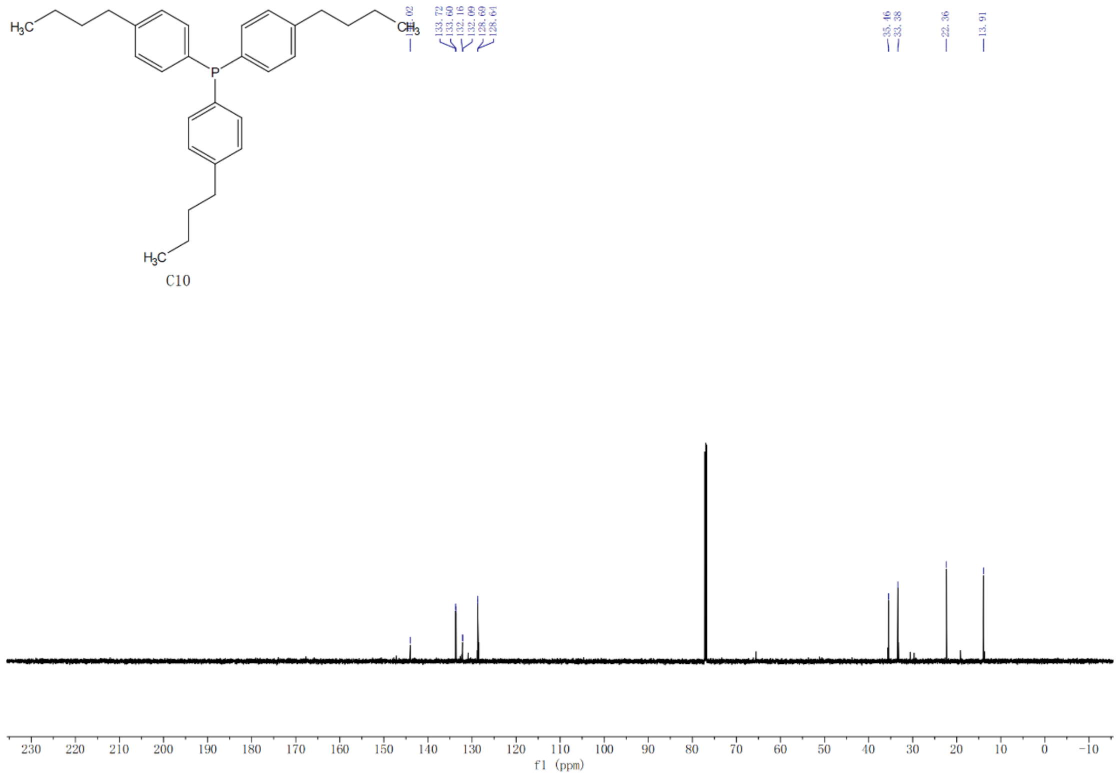
^{31}P NMR spectrum of **C9**



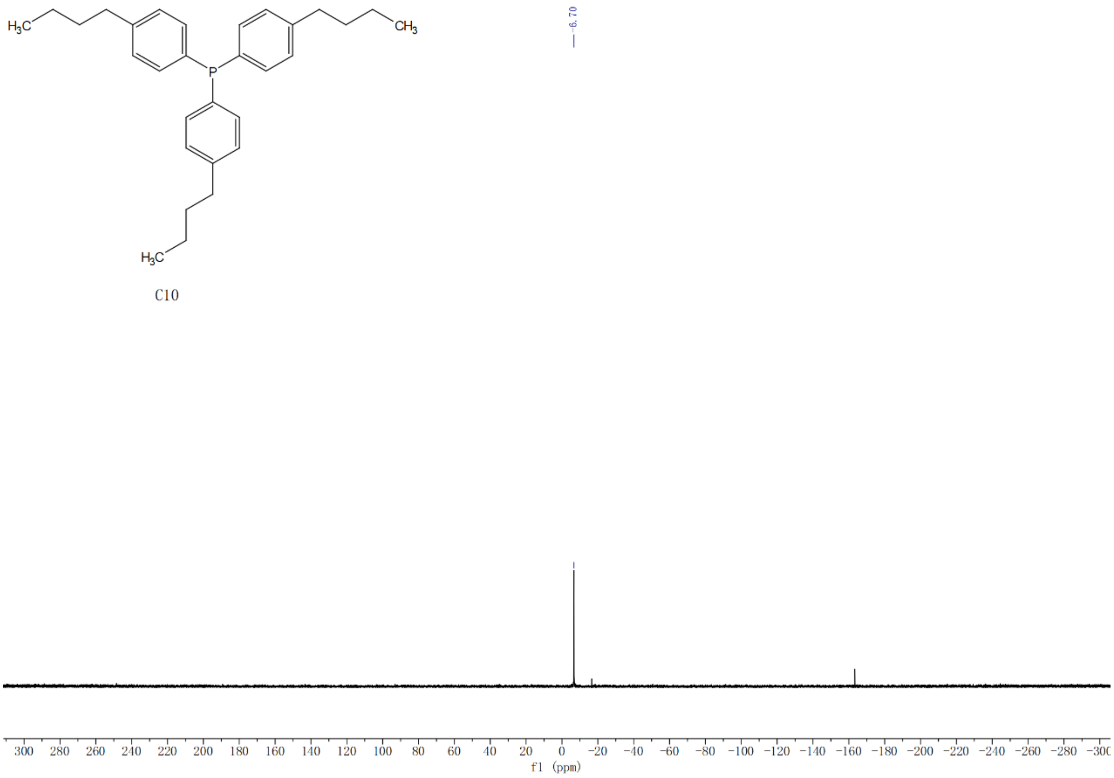
^{1}H NMR spectrum of **C10**



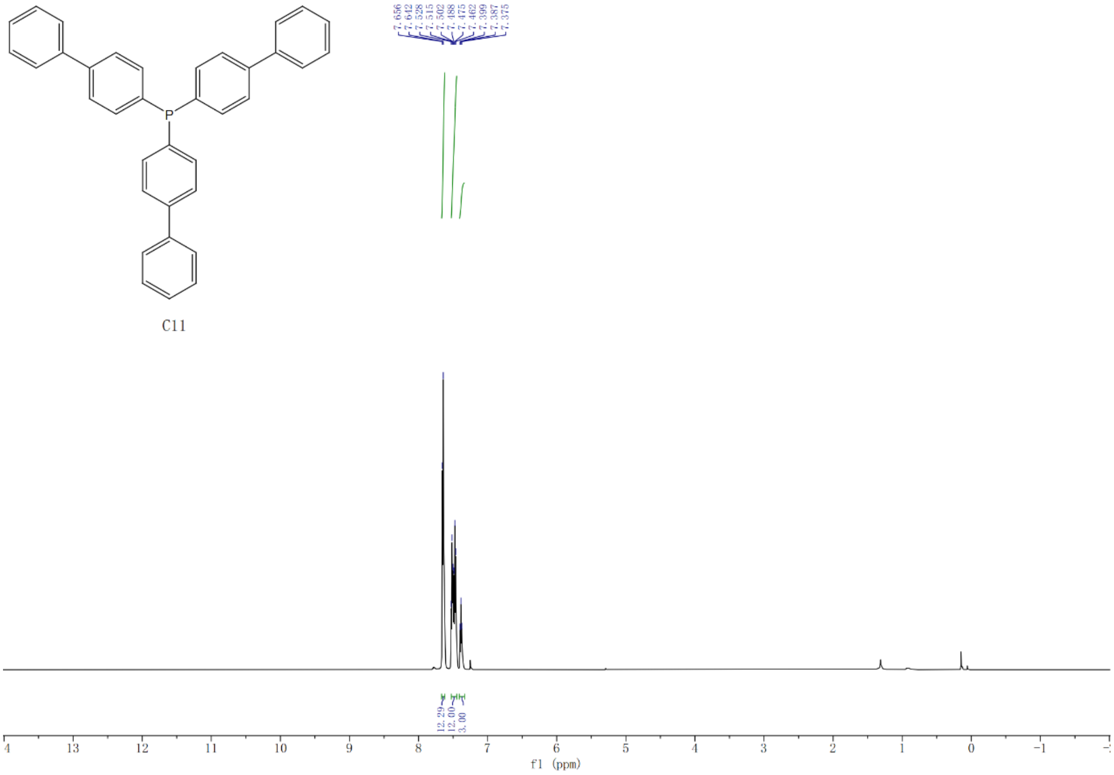
^{13}C NMR spectrum of **C10**



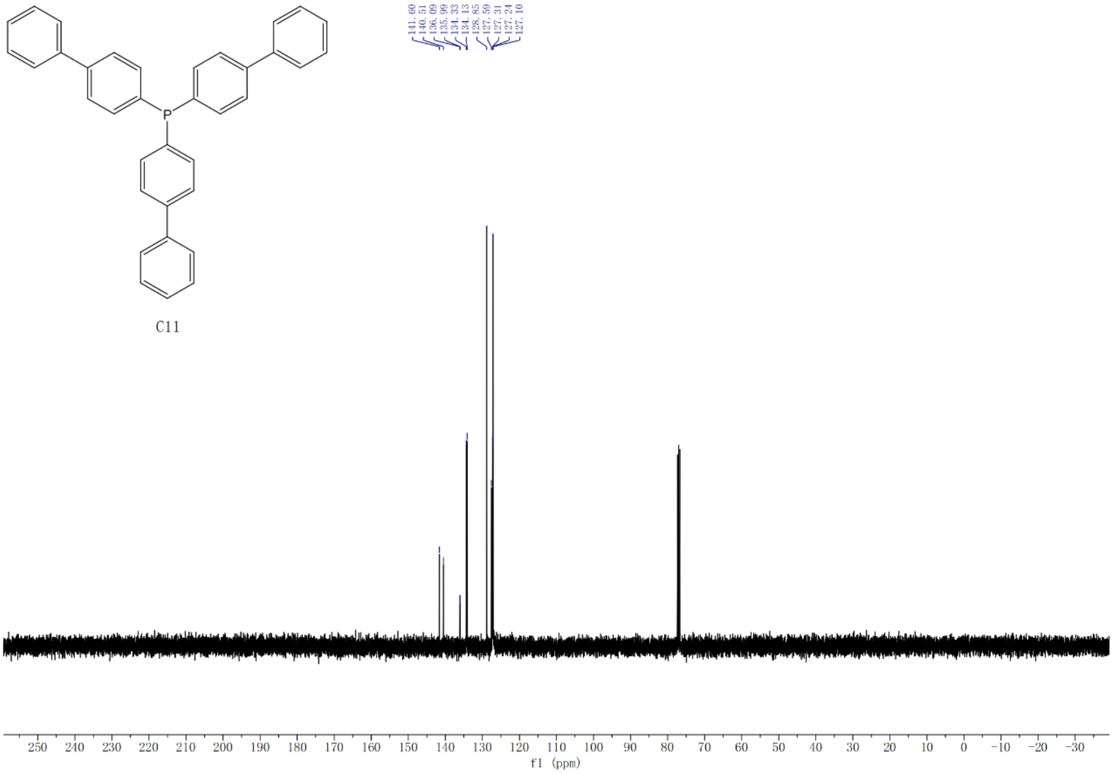
^{31}P NMR spectrum of **C10**



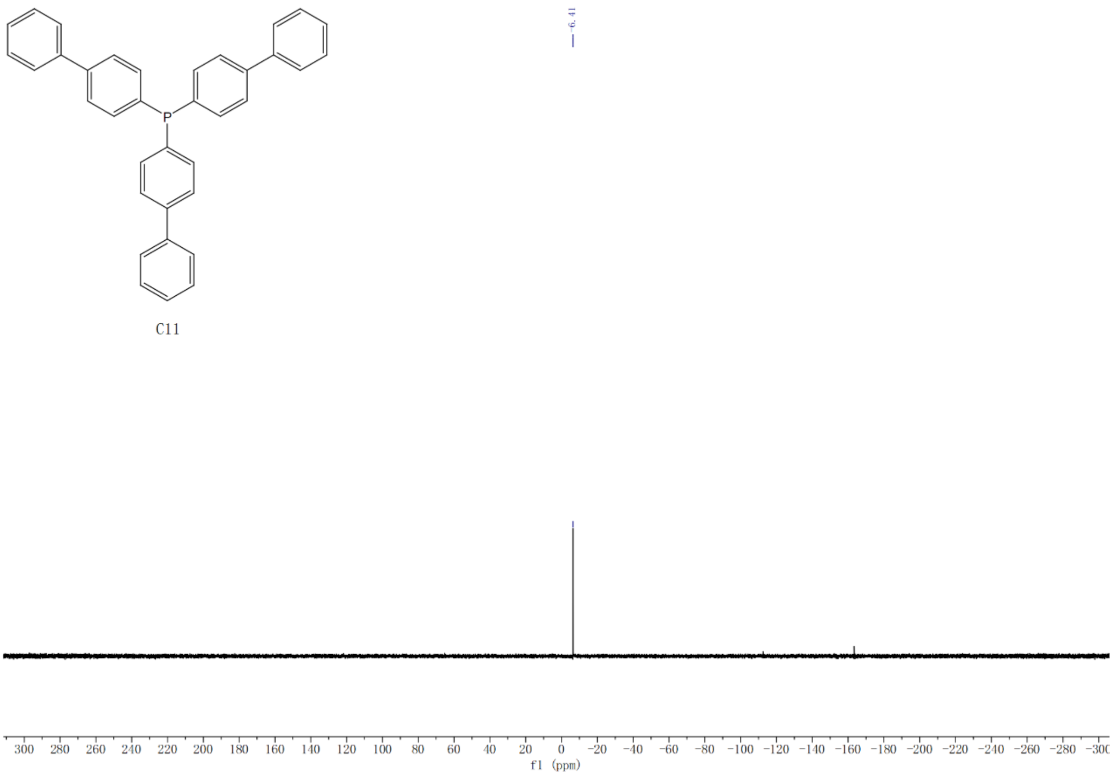
^{1}H NMR spectrum of **C11**



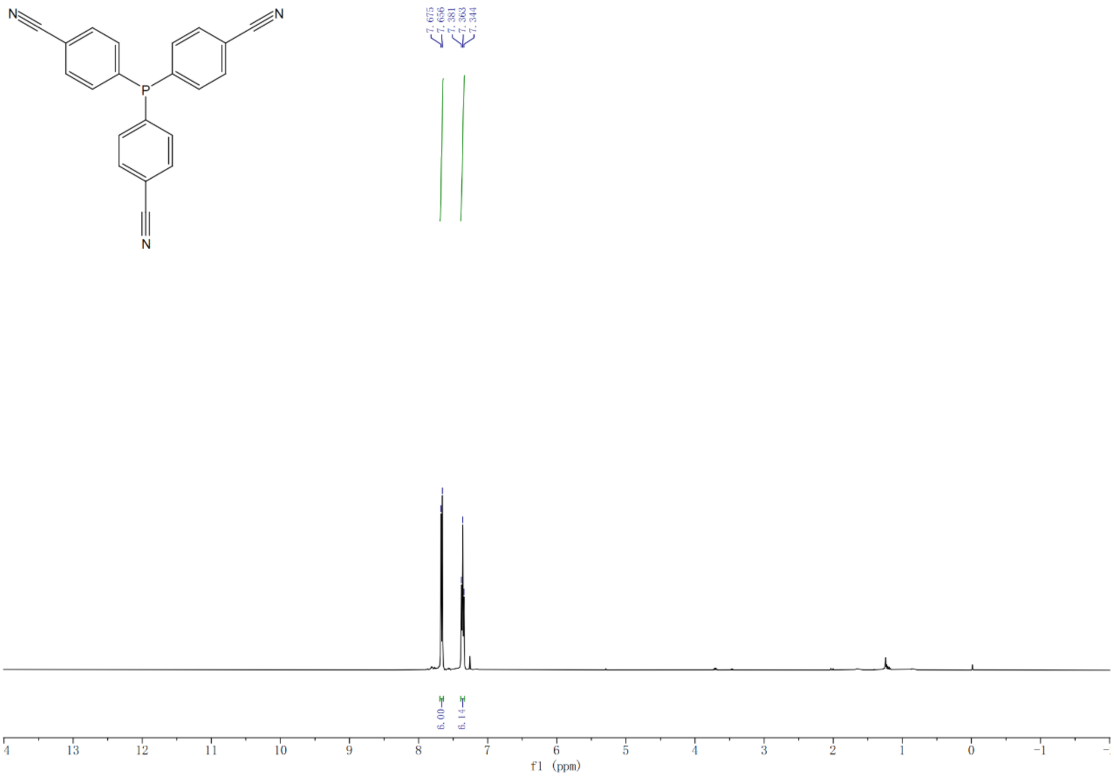
^{13}C NMR spectrum of **C11**



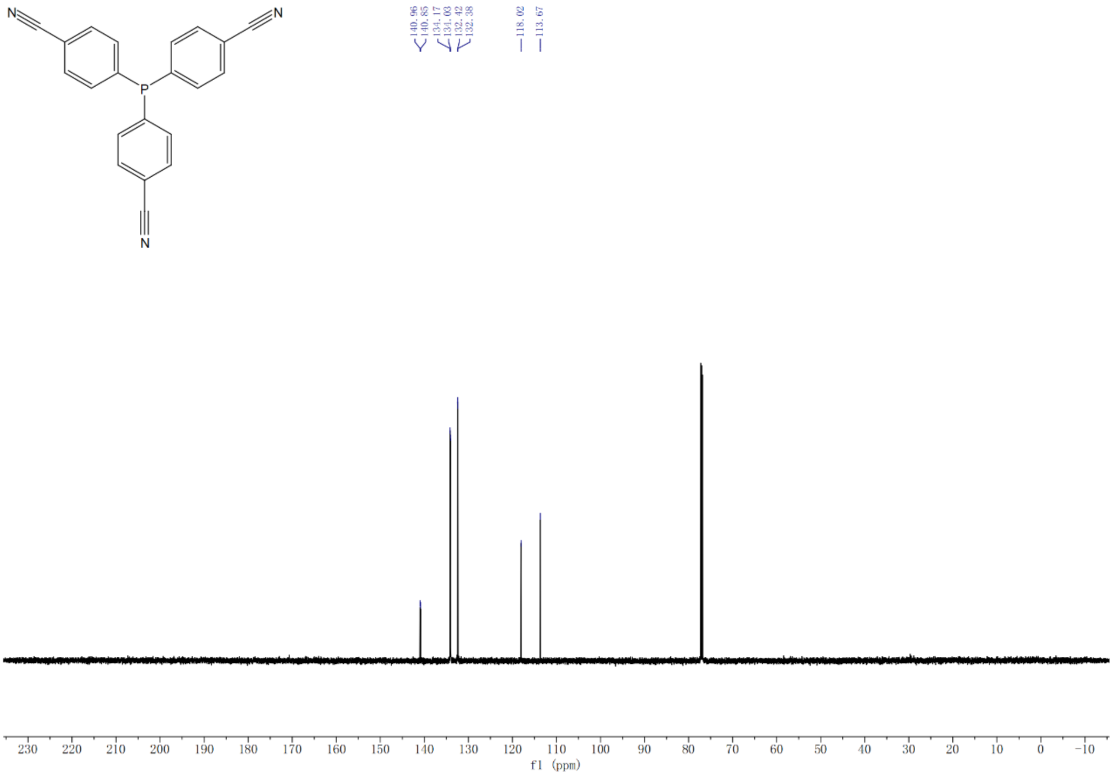
^{31}P NMR spectrum of **C11**



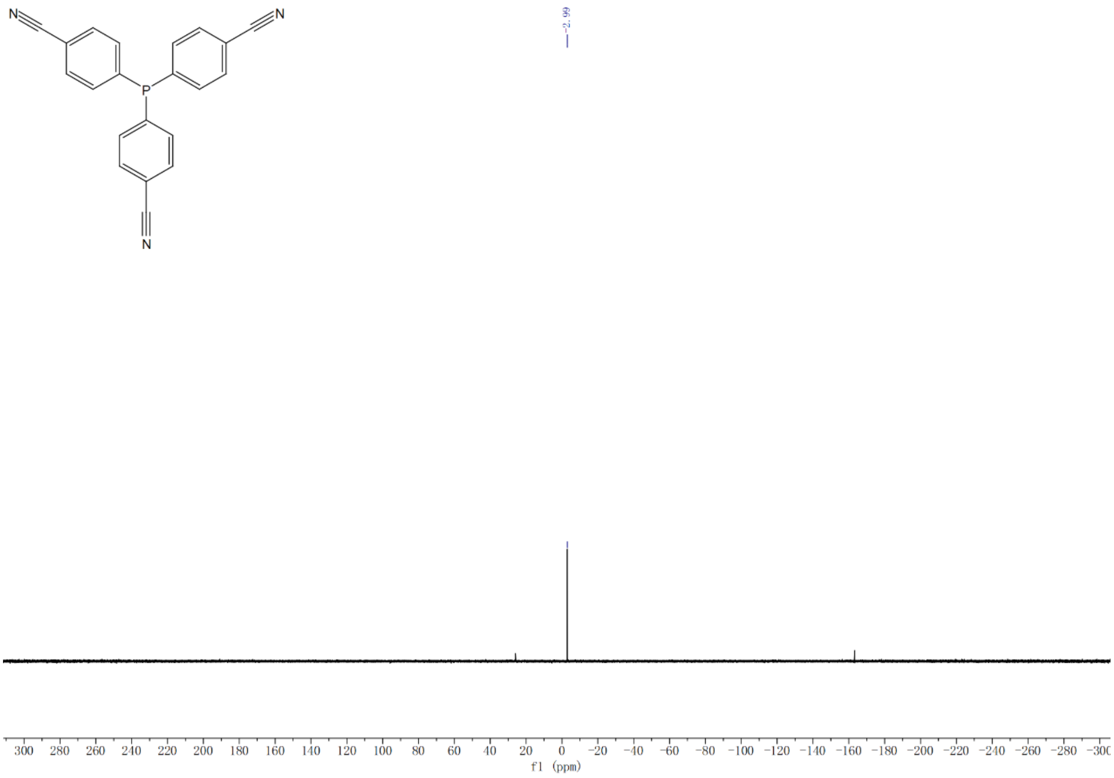
^{1}H NMR spectrum of **C12,C13**



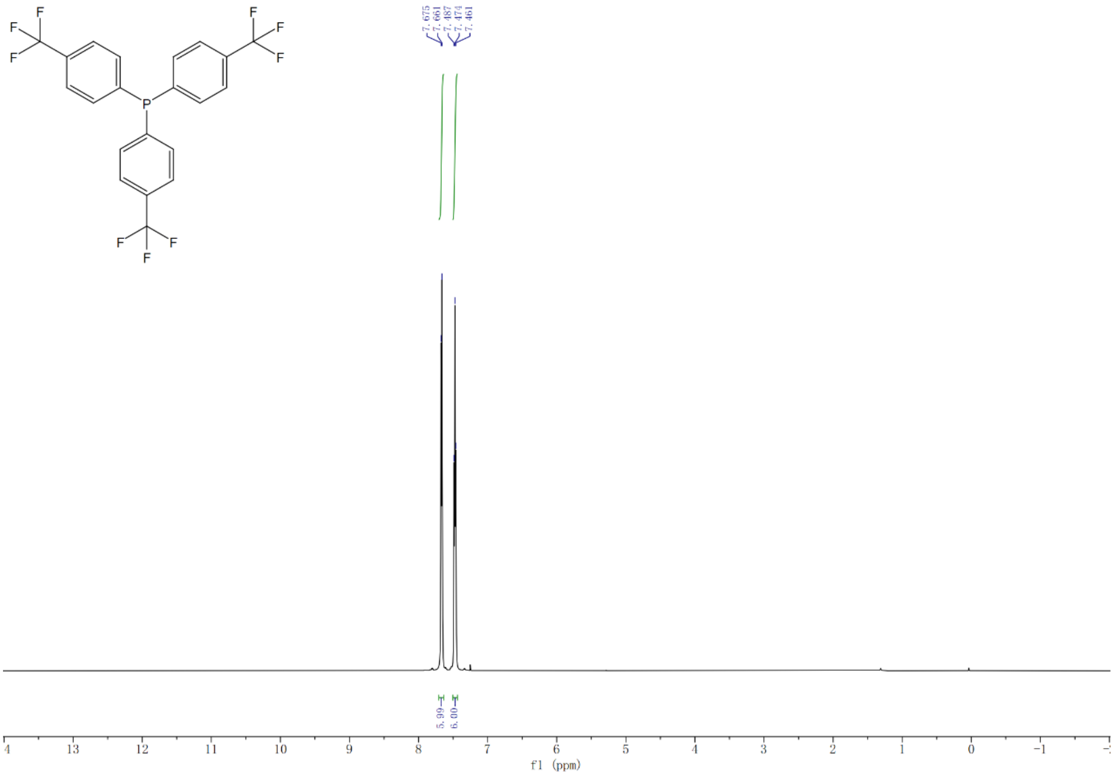
^{13}C NMR spectrum of **C12,C13**



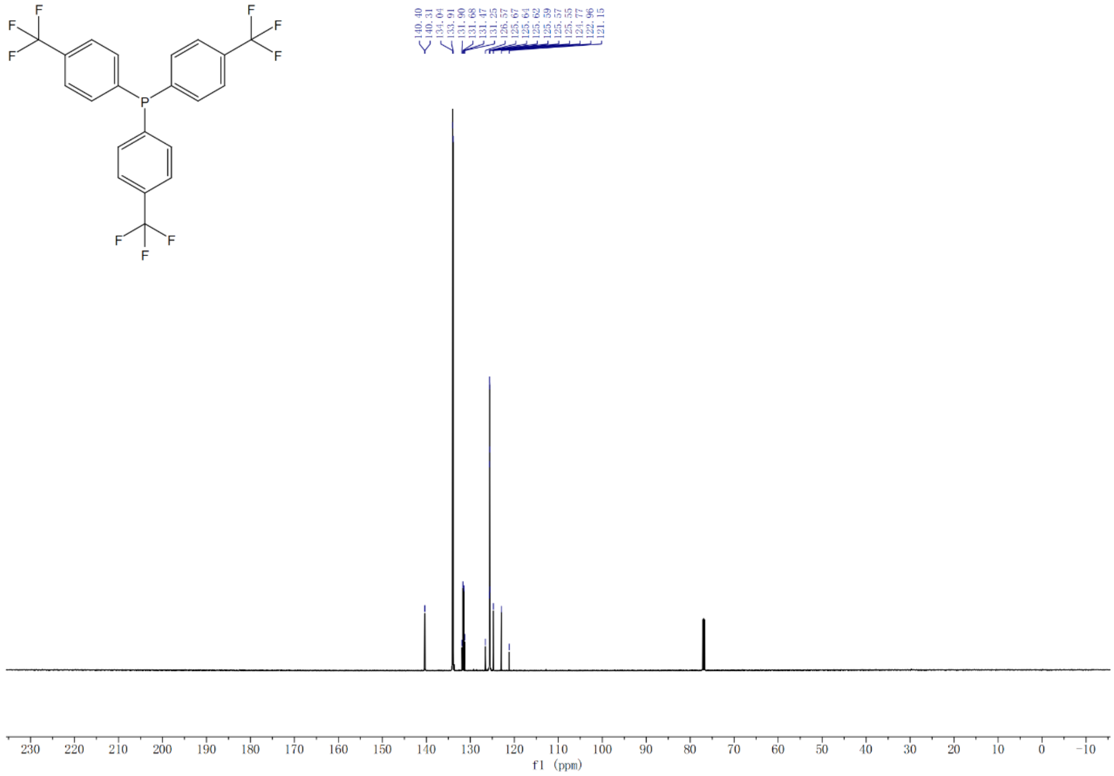
^{31}P NMR spectrum of **C12,C13**



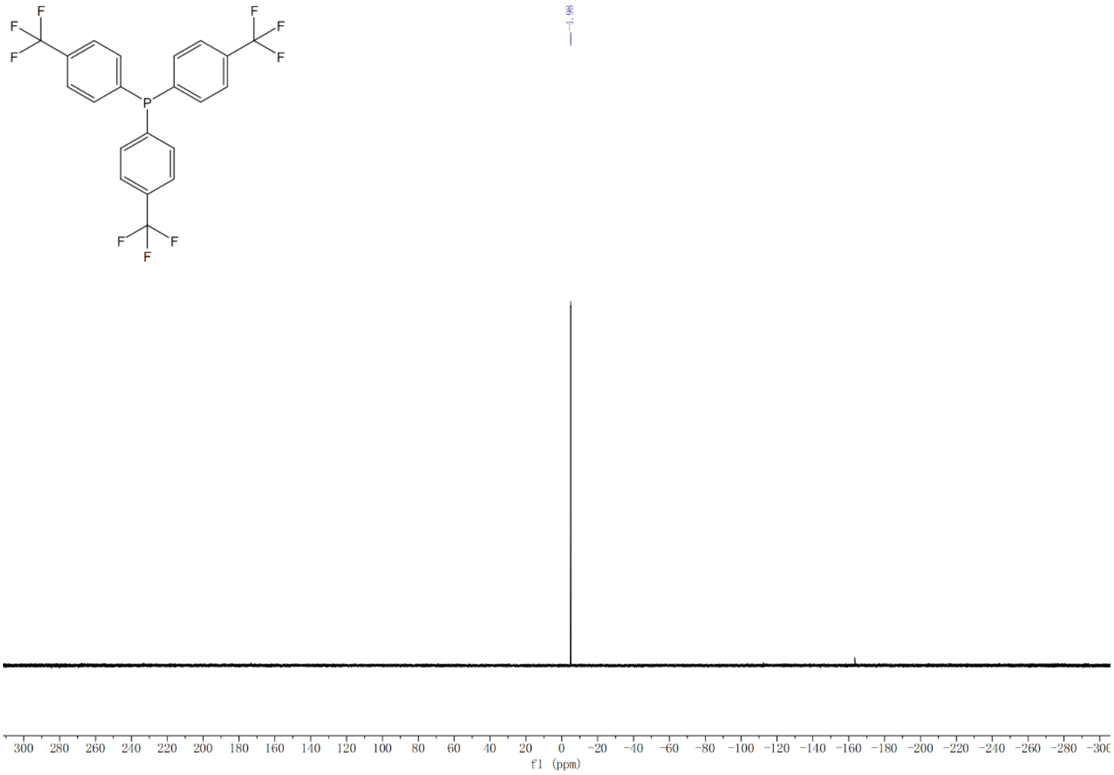
^{1}H NMR spectrum of **C14,C15**



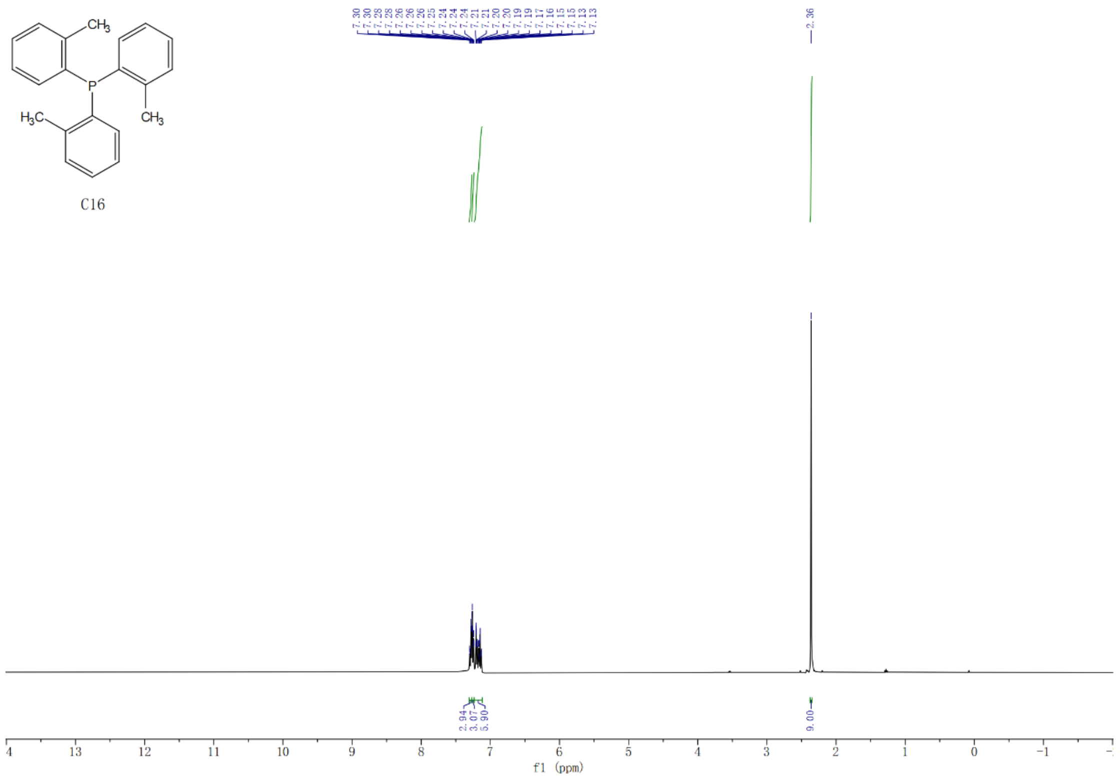
^{13}C NMR spectrum of **C14,C15**



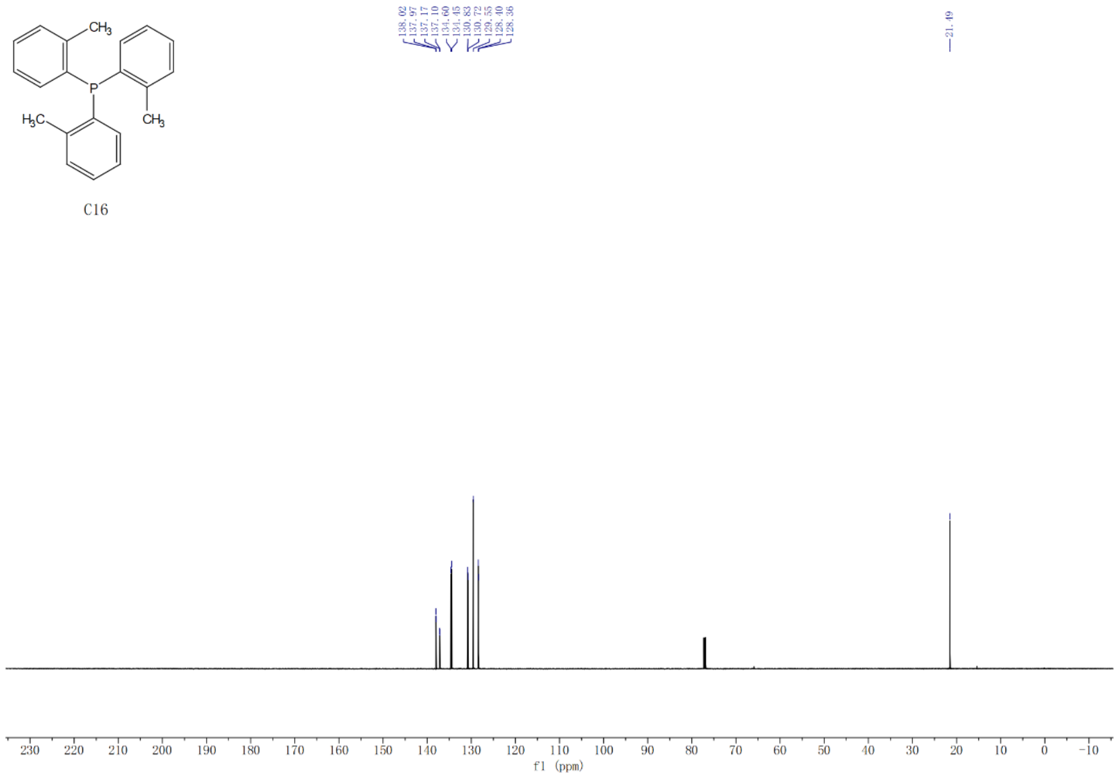
^{31}P NMR spectrum of **C14,C15**



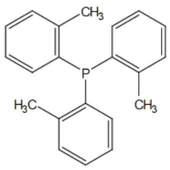
^{1}H NMR spectrum of **C16**



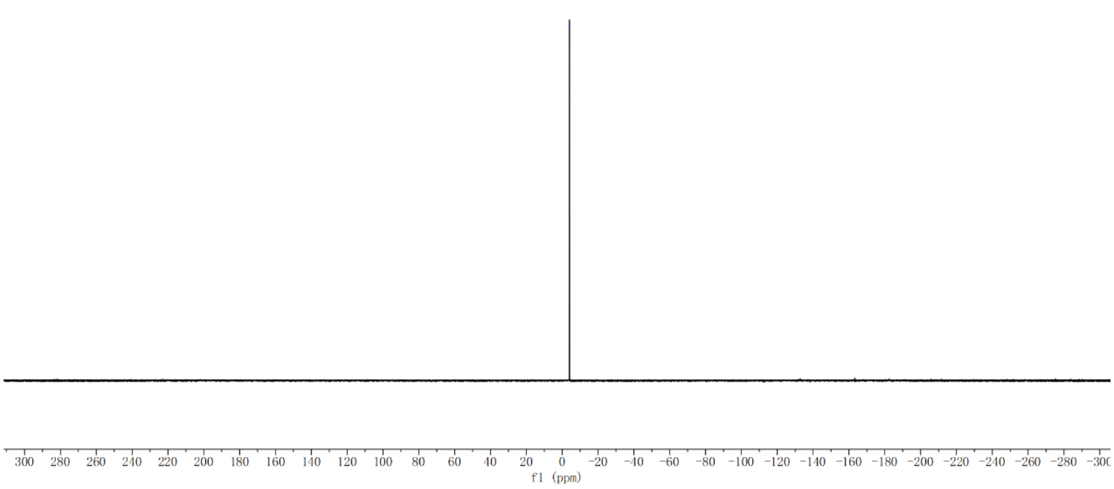
^{13}C NMR spectrum of **C16**



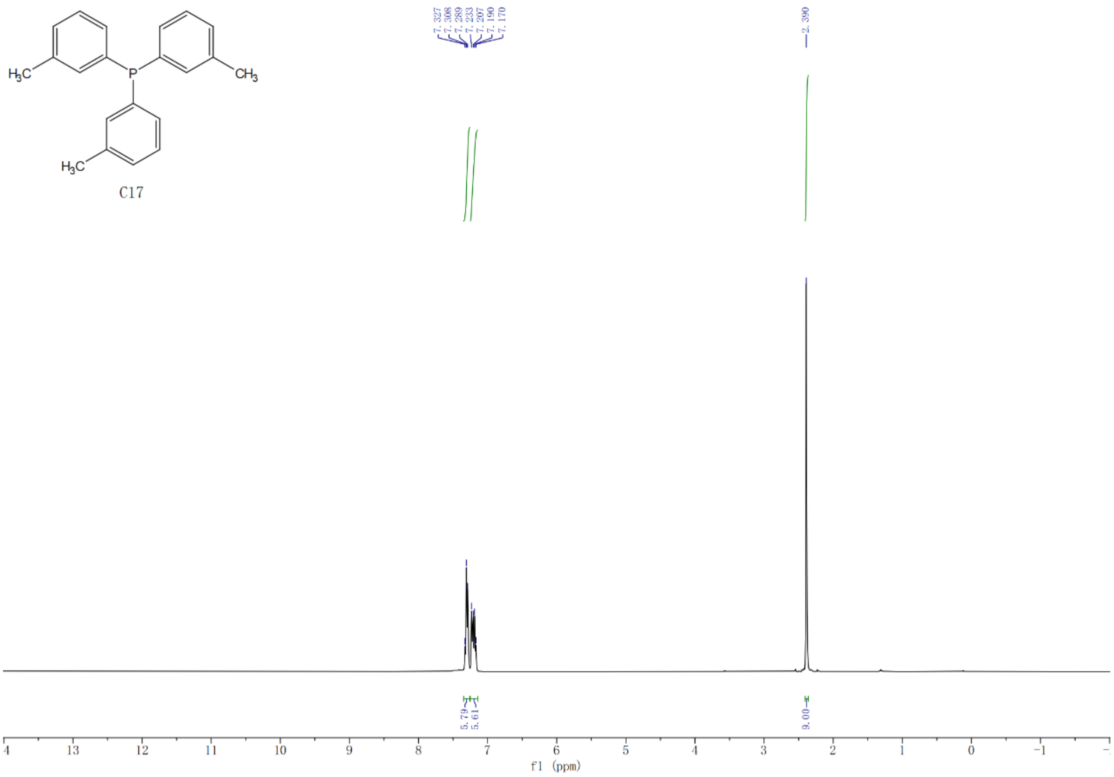
^{31}P NMR spectrum of **C16**



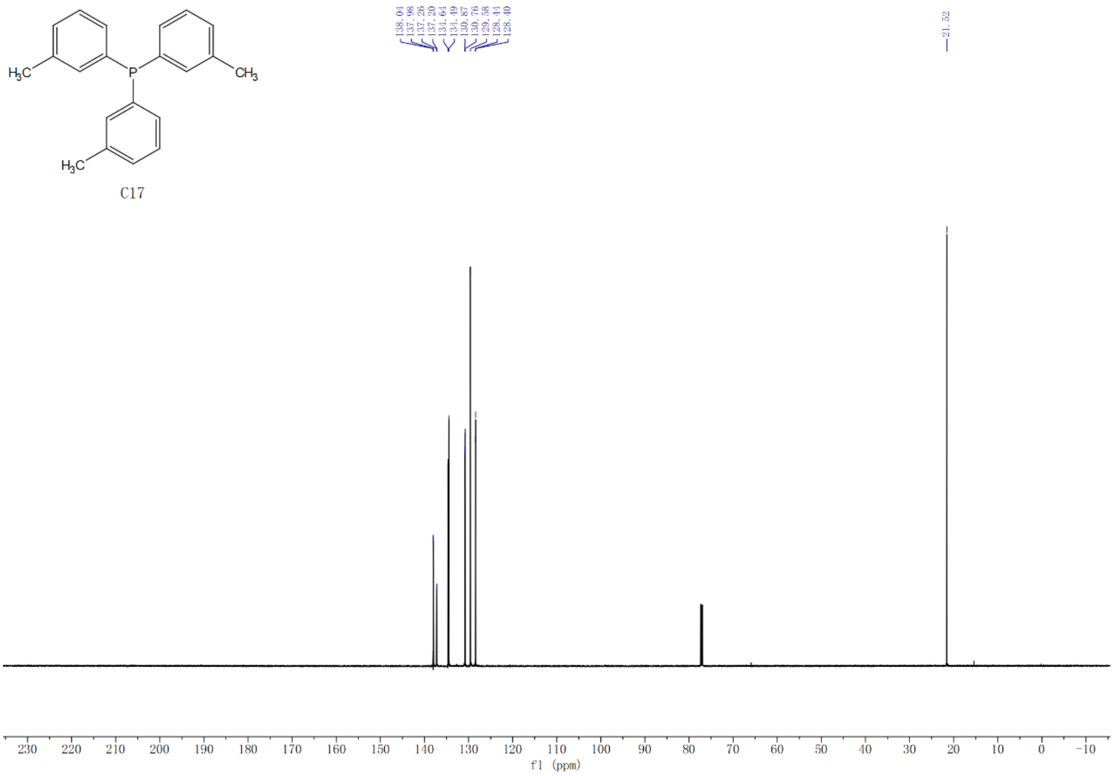
C16



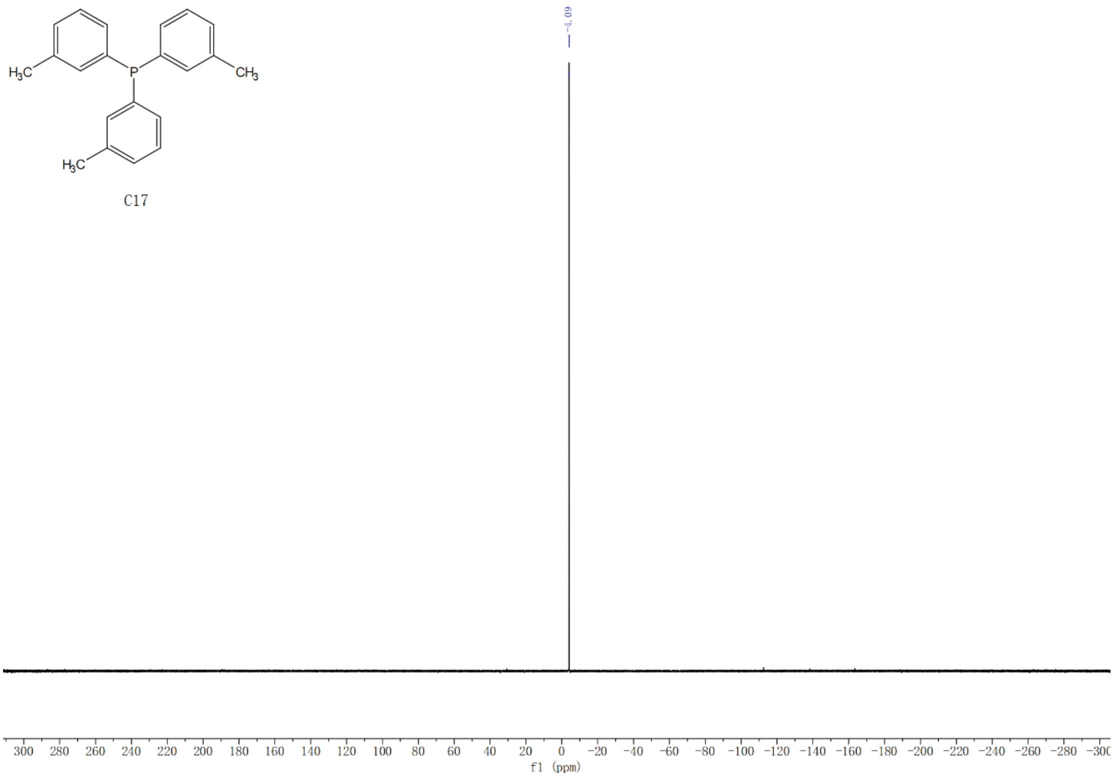
^{1}H NMR spectrum of **C17**



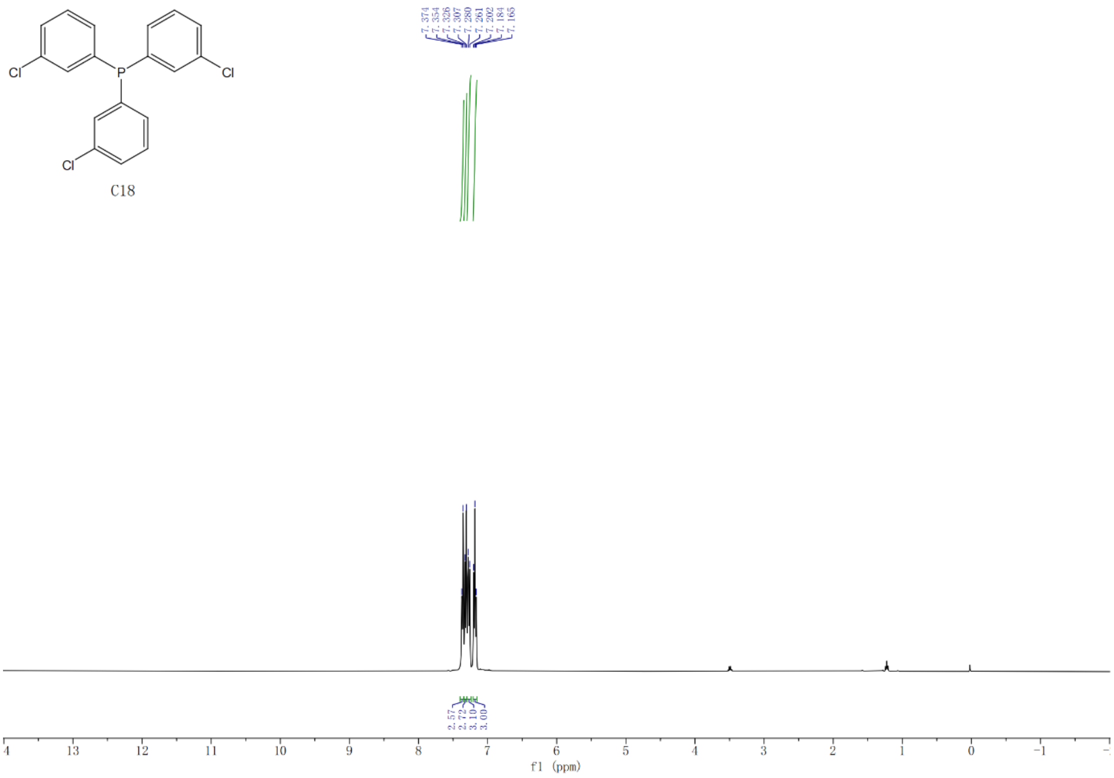
^{13}C NMR spectrum of **C17**



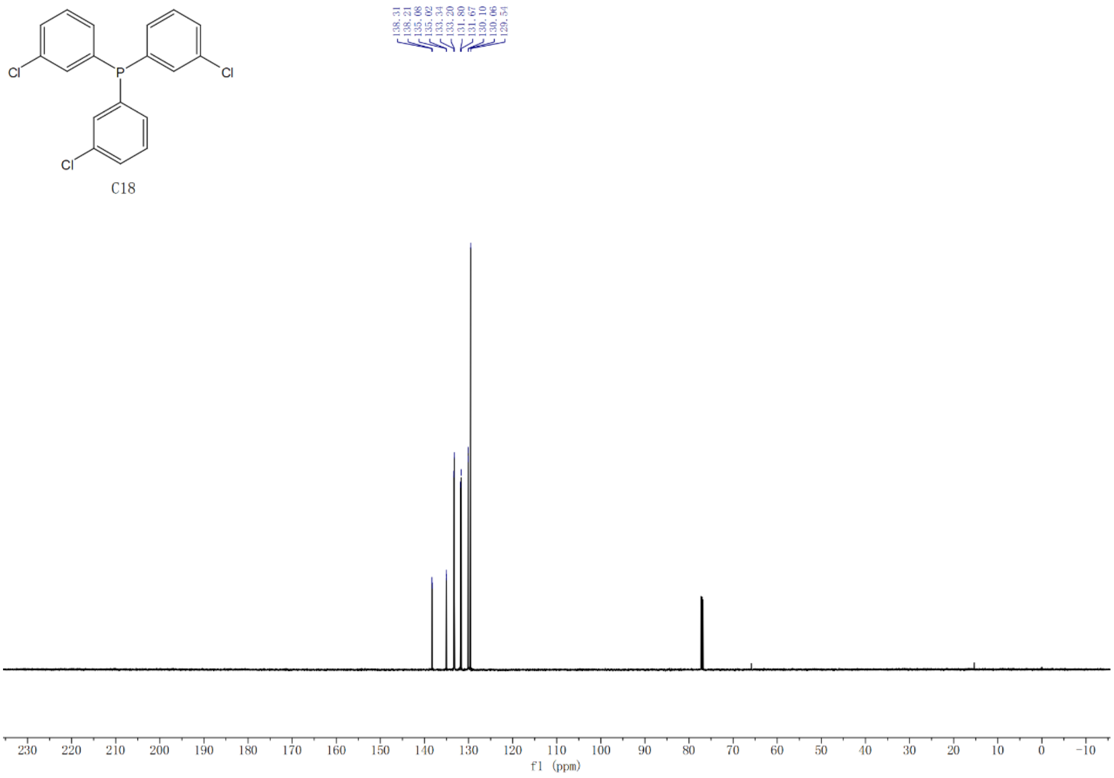
^{31}P NMR spectrum of **C17**



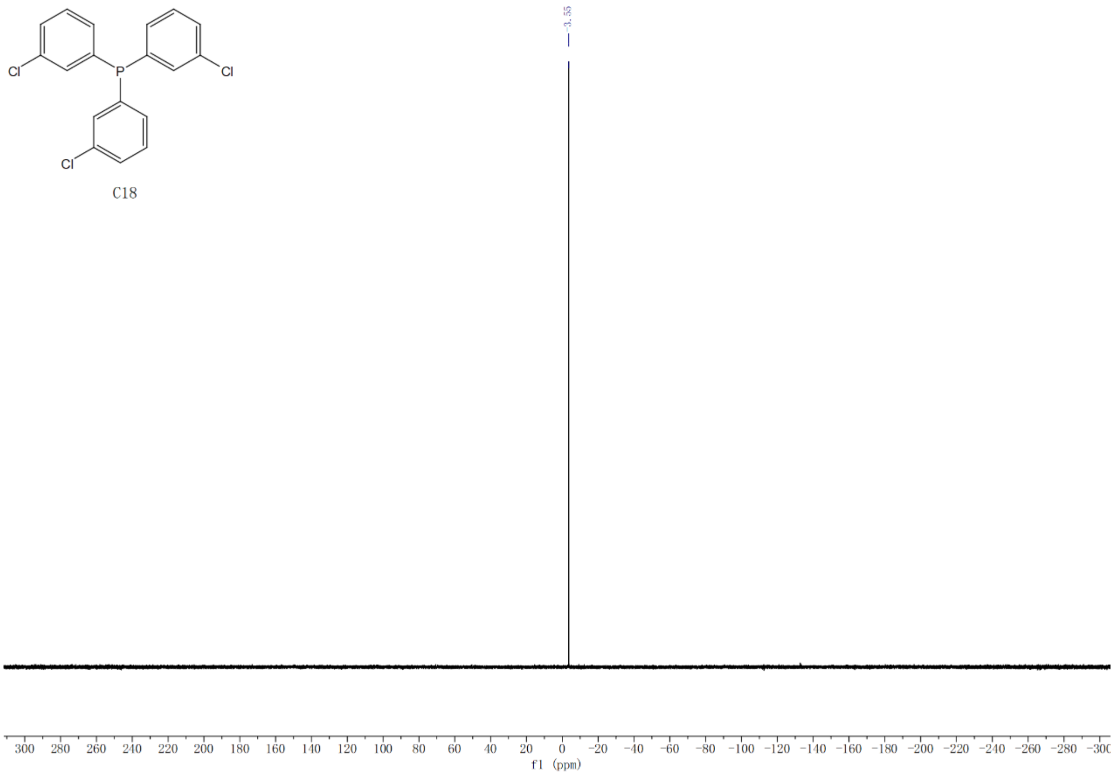
^{1}H NMR spectrum of **C18**



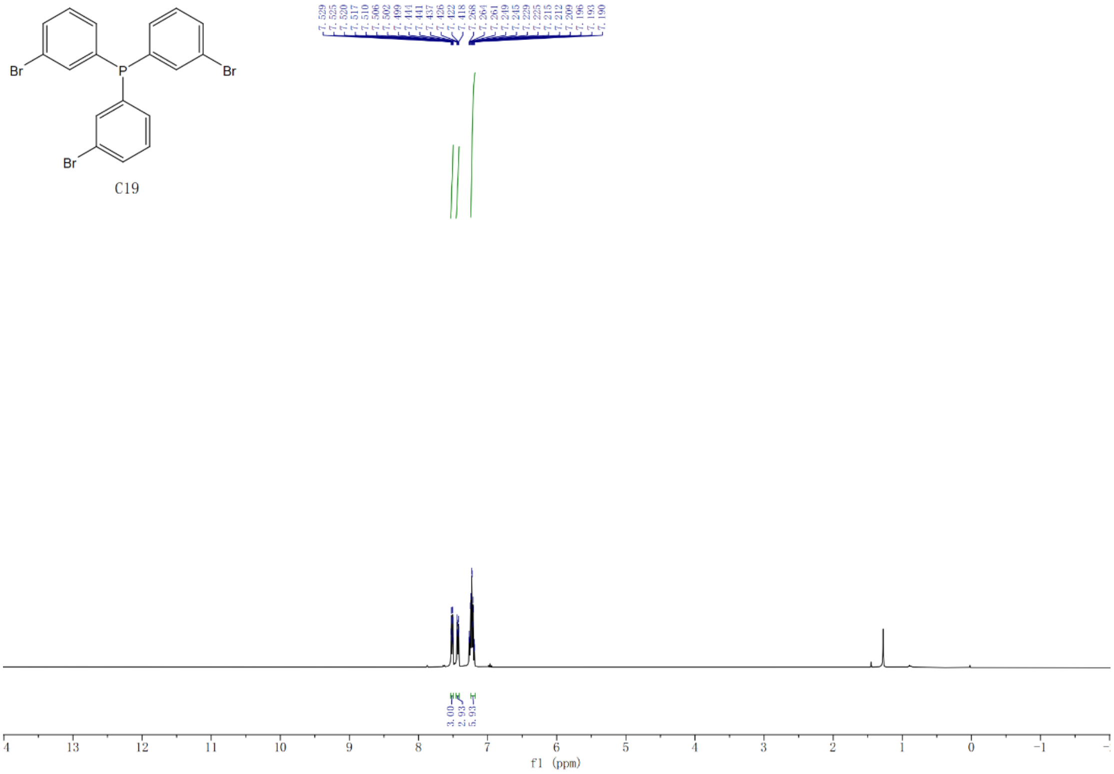
^{13}C NMR spectrum of **C18**



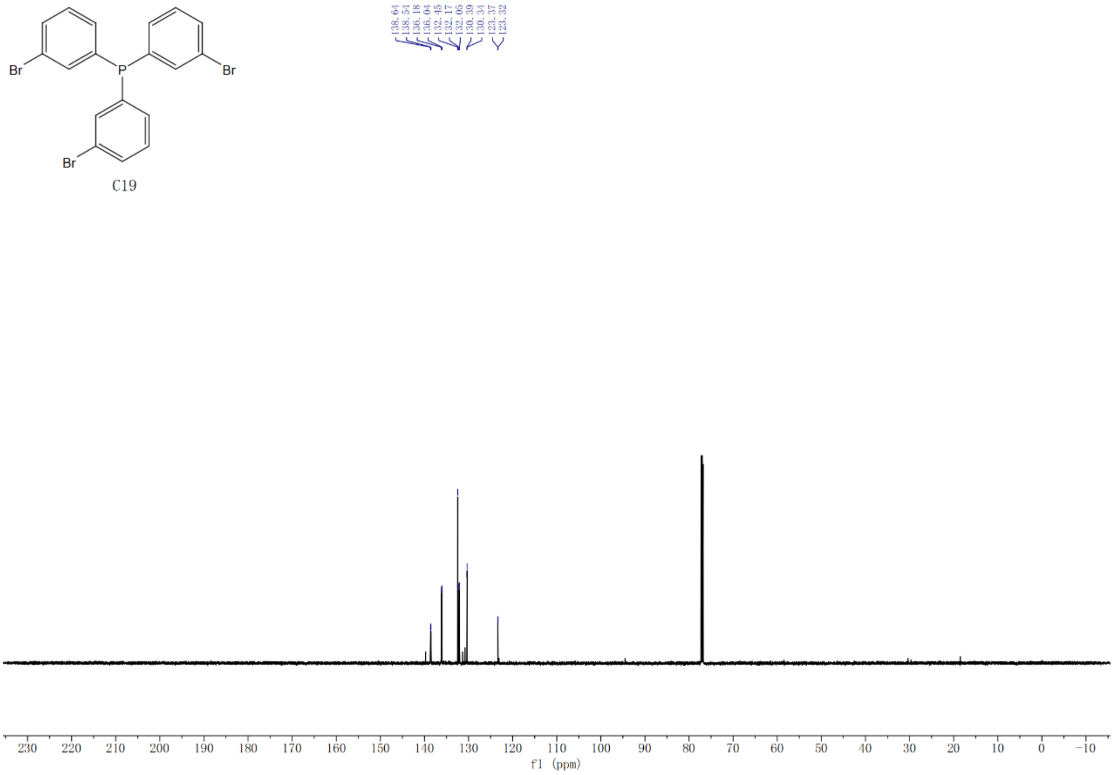
^{31}P NMR spectrum of **C18**



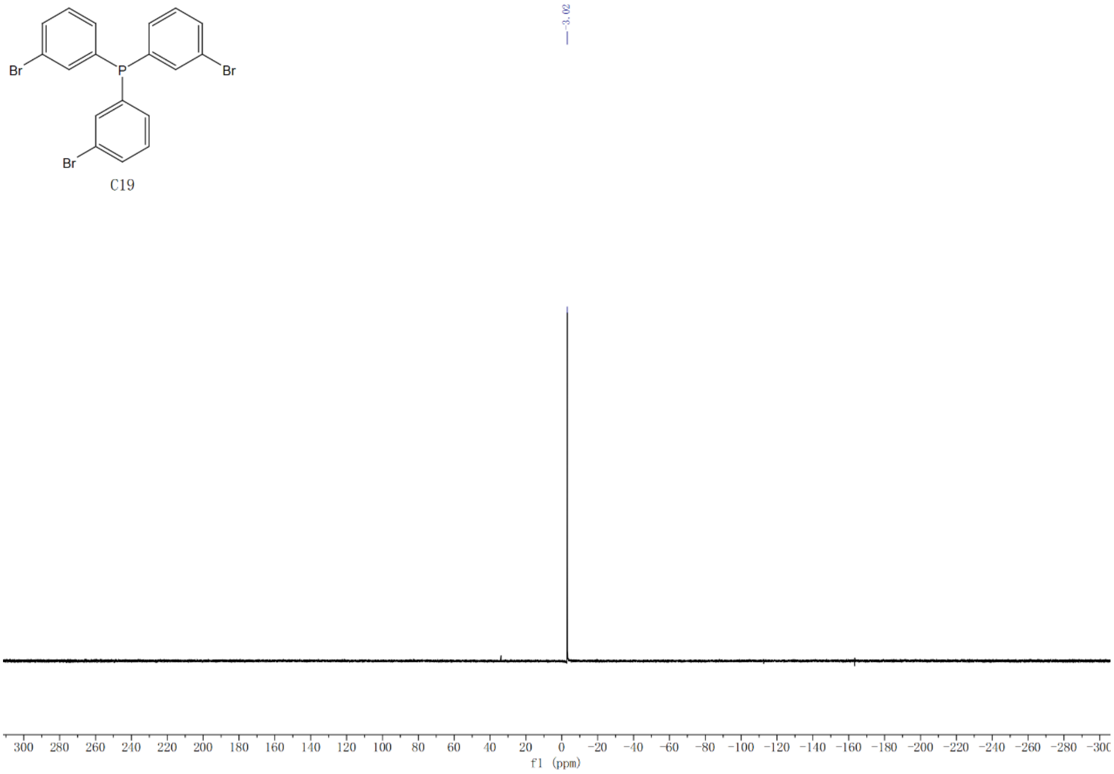
^{1}H NMR spectrum of **C19**


C19

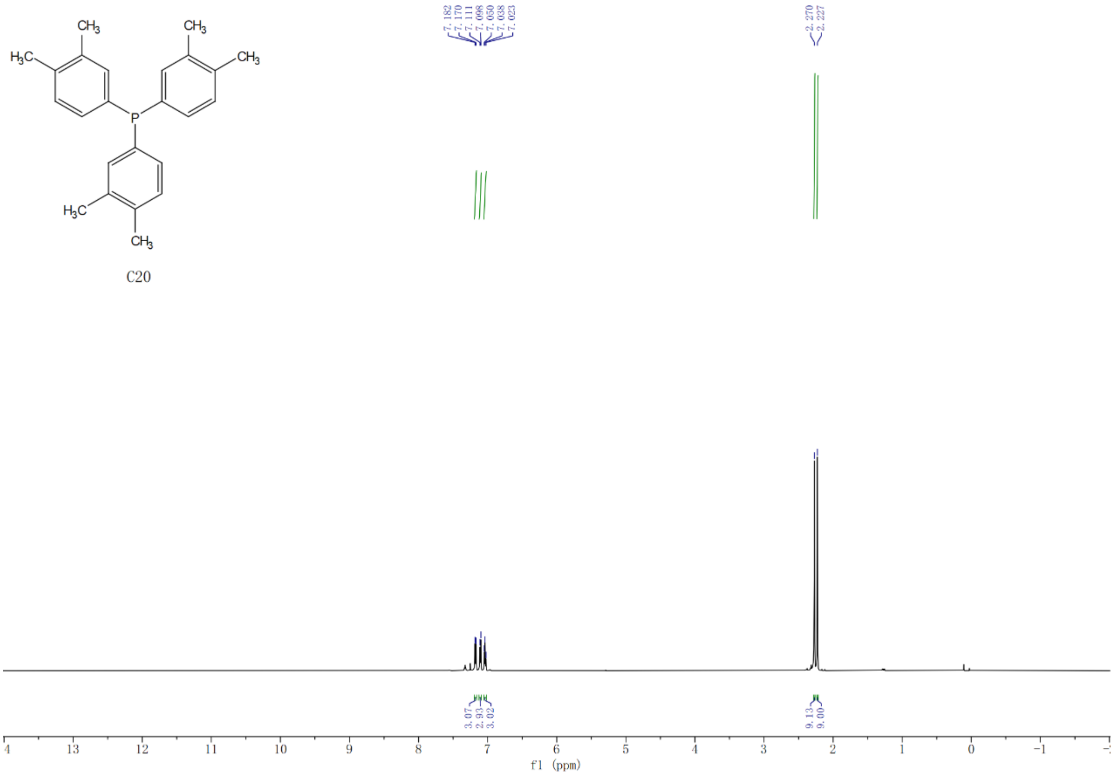
^{13}C NMR spectrum of **C19**


C19

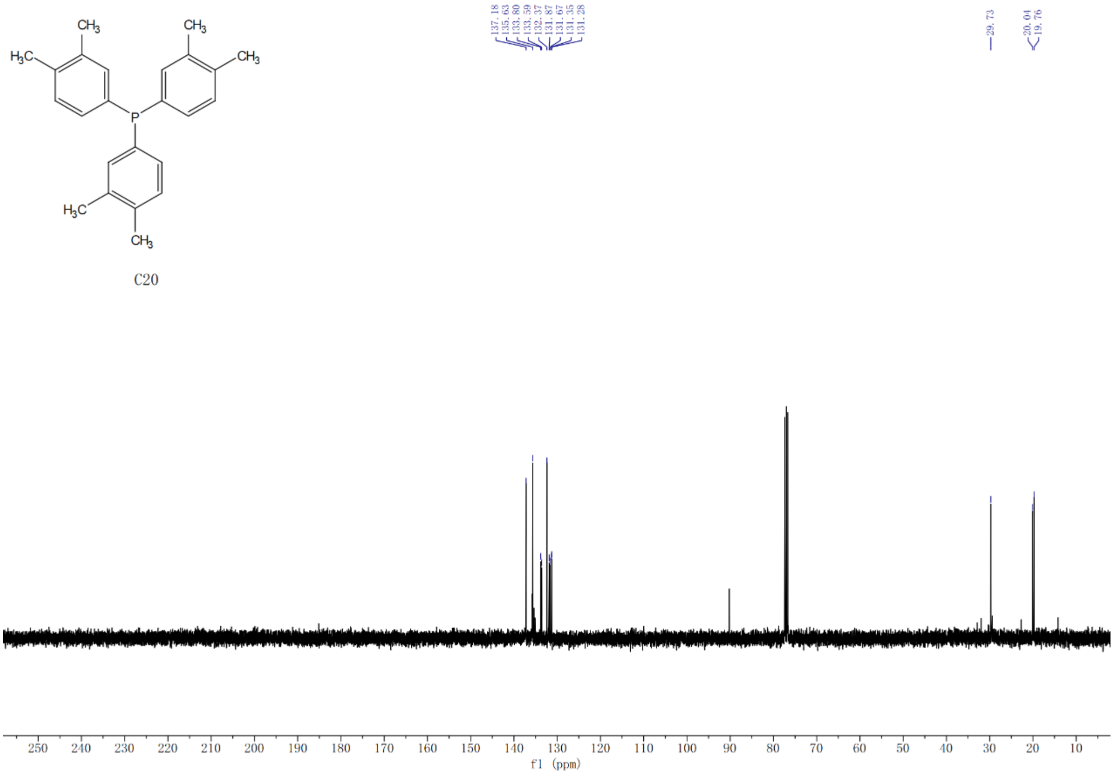
^{31}P NMR spectrum of **C19**



^{1}H NMR spectrum of **C20**



^{13}C NMR spectrum of **C20**



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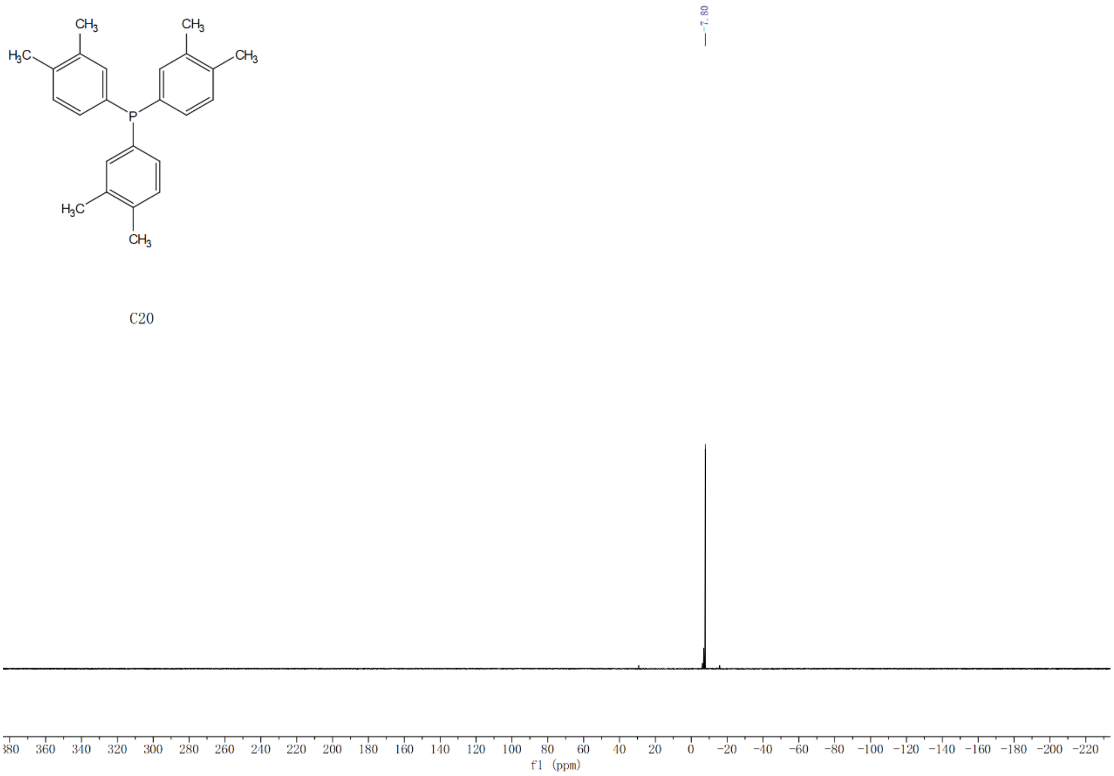
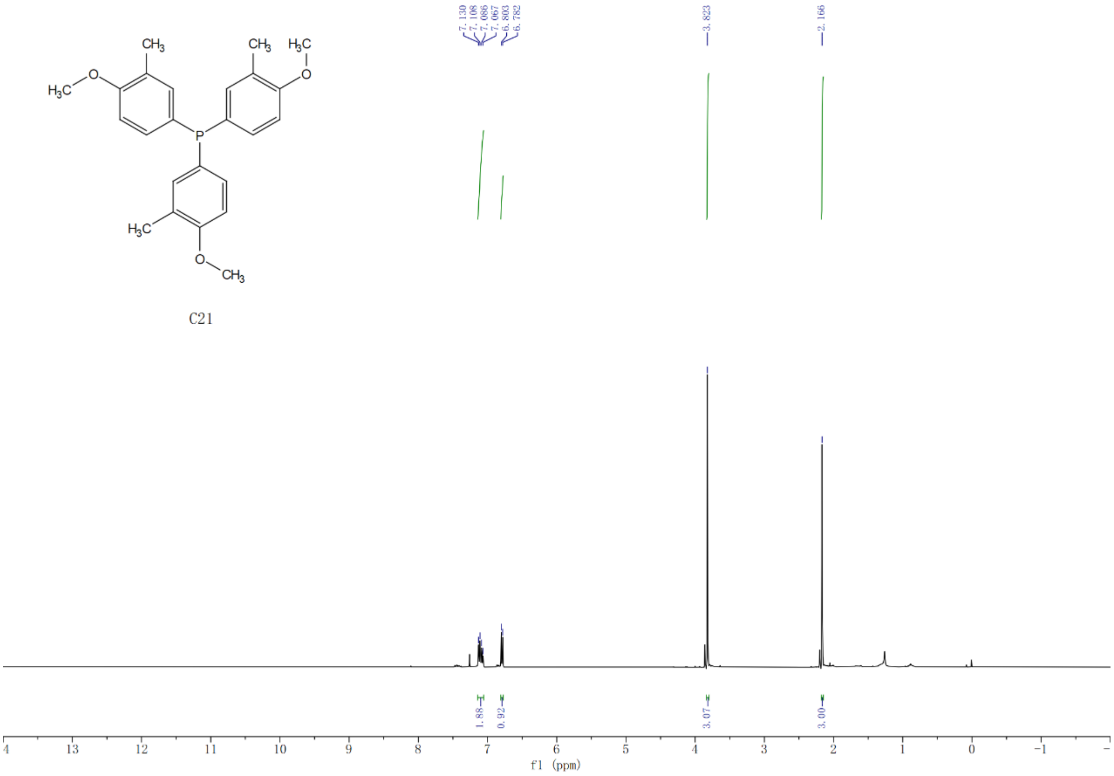
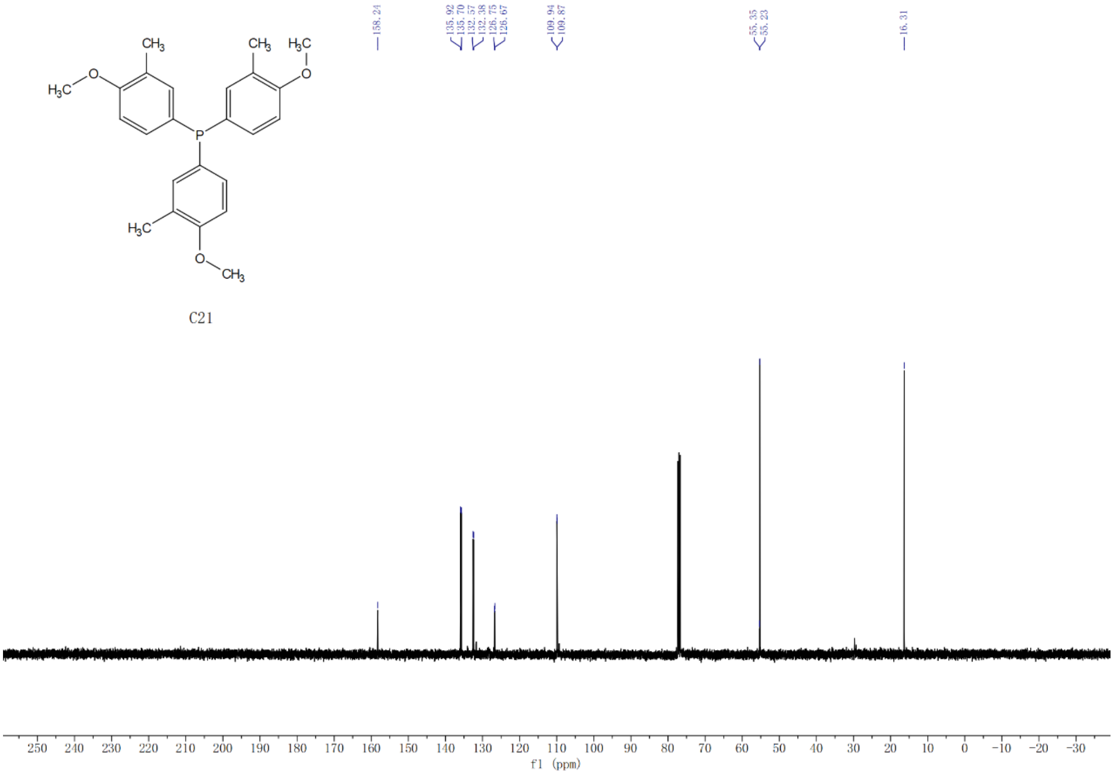


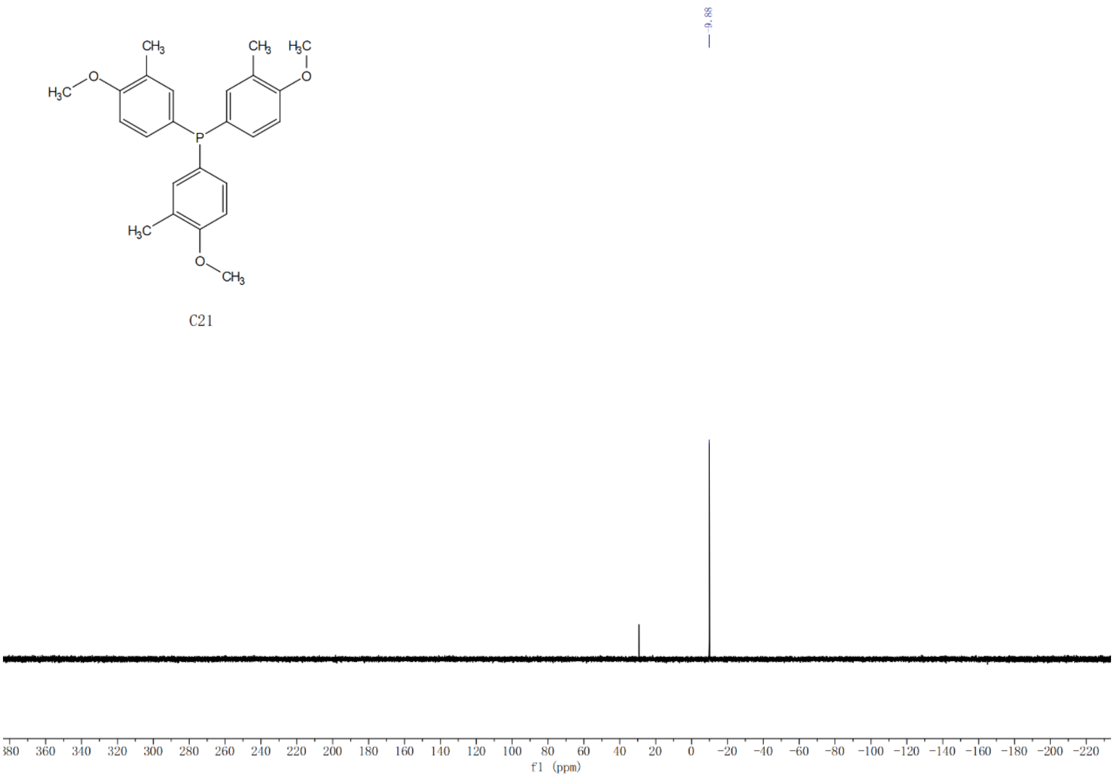
^{1}H NMR spectrum of **C21**



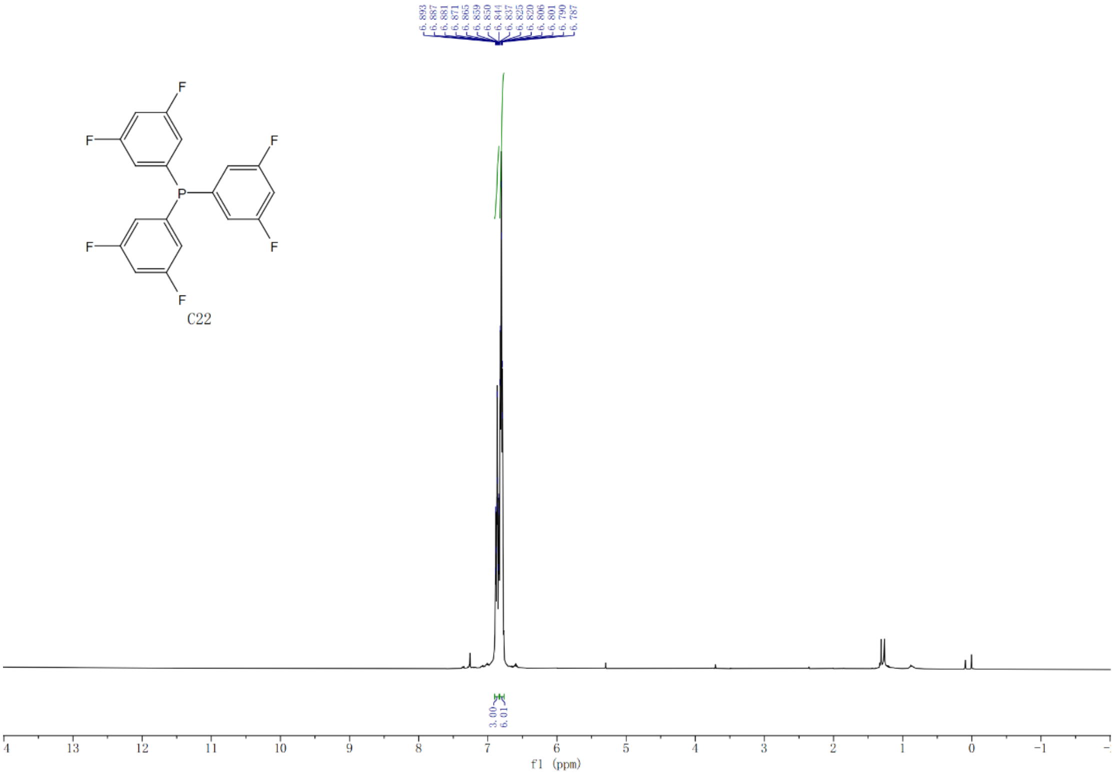
^{13}C NMR spectrum of **C21**



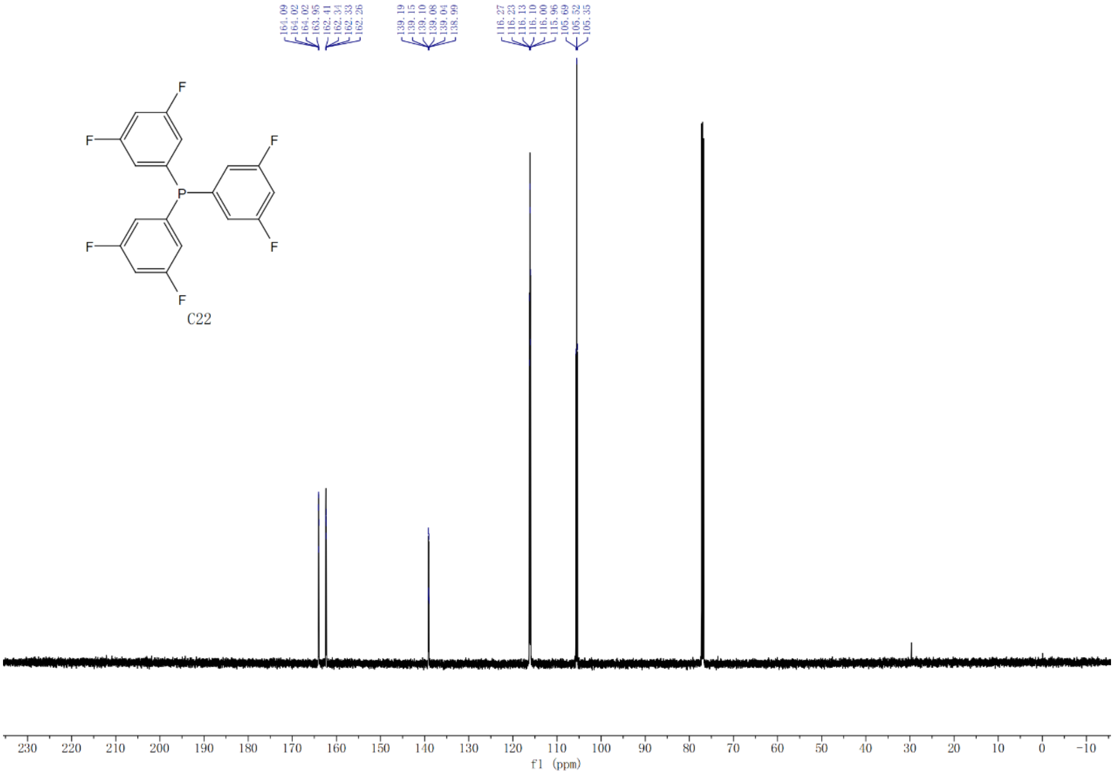
^{31}P NMR spectrum of **C21**



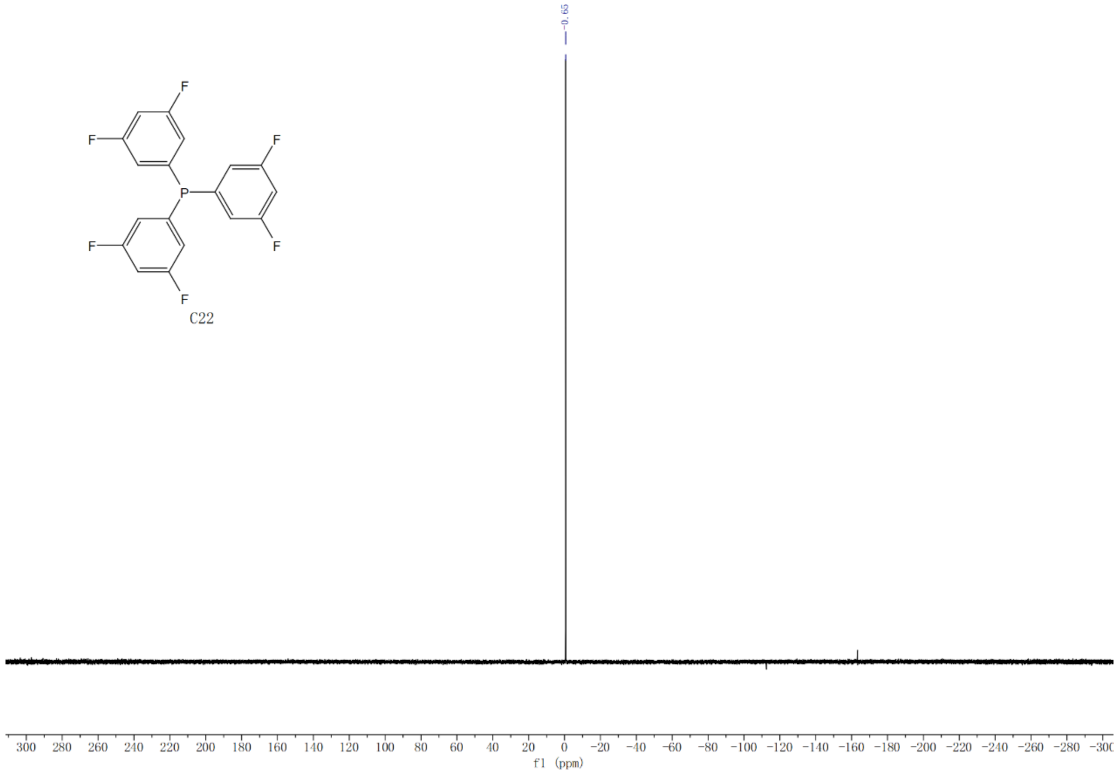
^{1}H NMR spectrum of **C22**



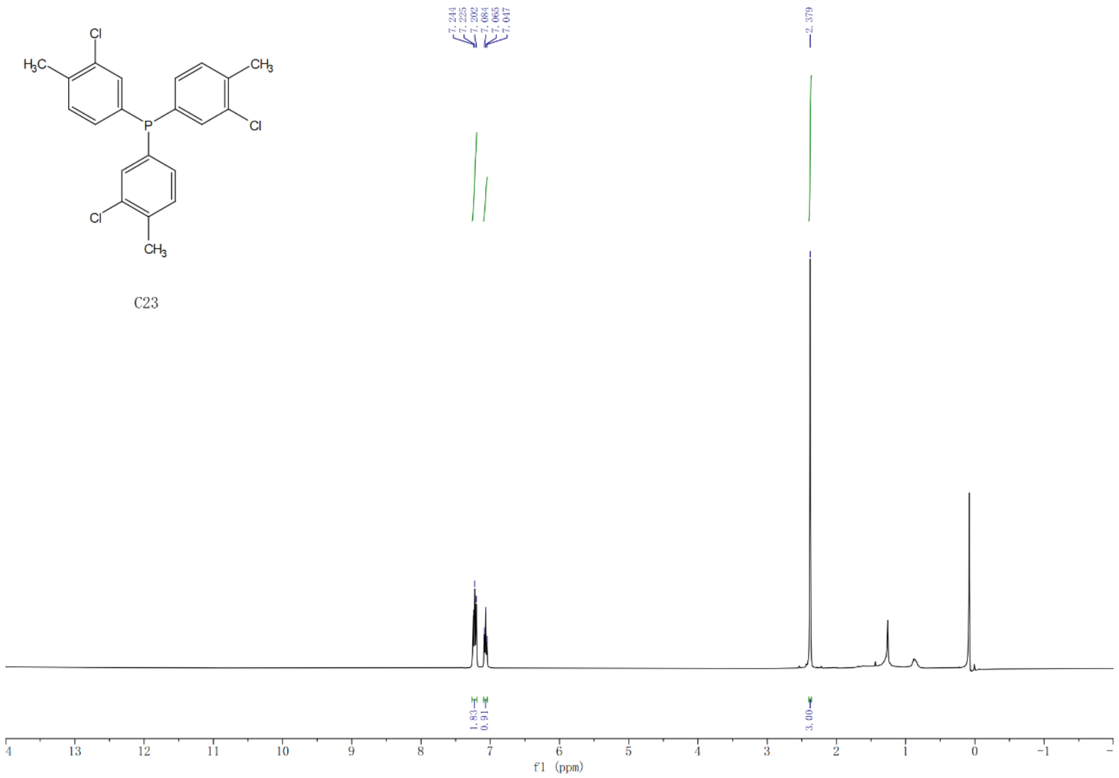
^{13}C NMR spectrum of **C22**



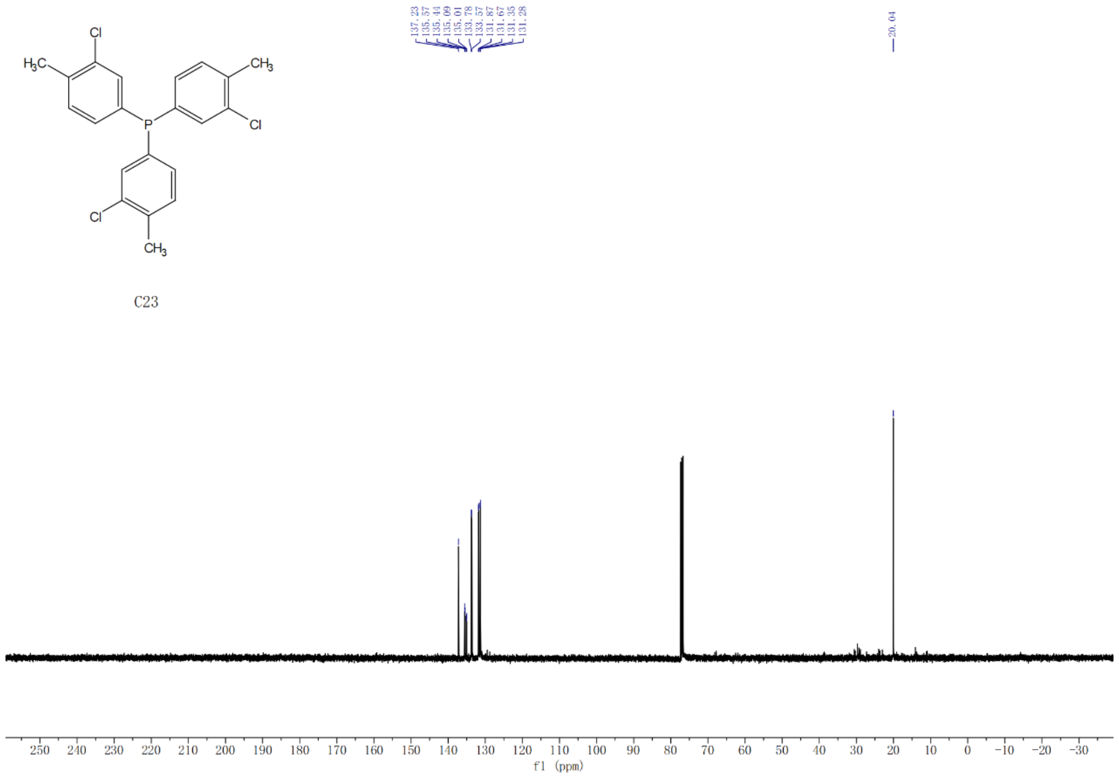
^{31}P NMR spectrum of **C22**



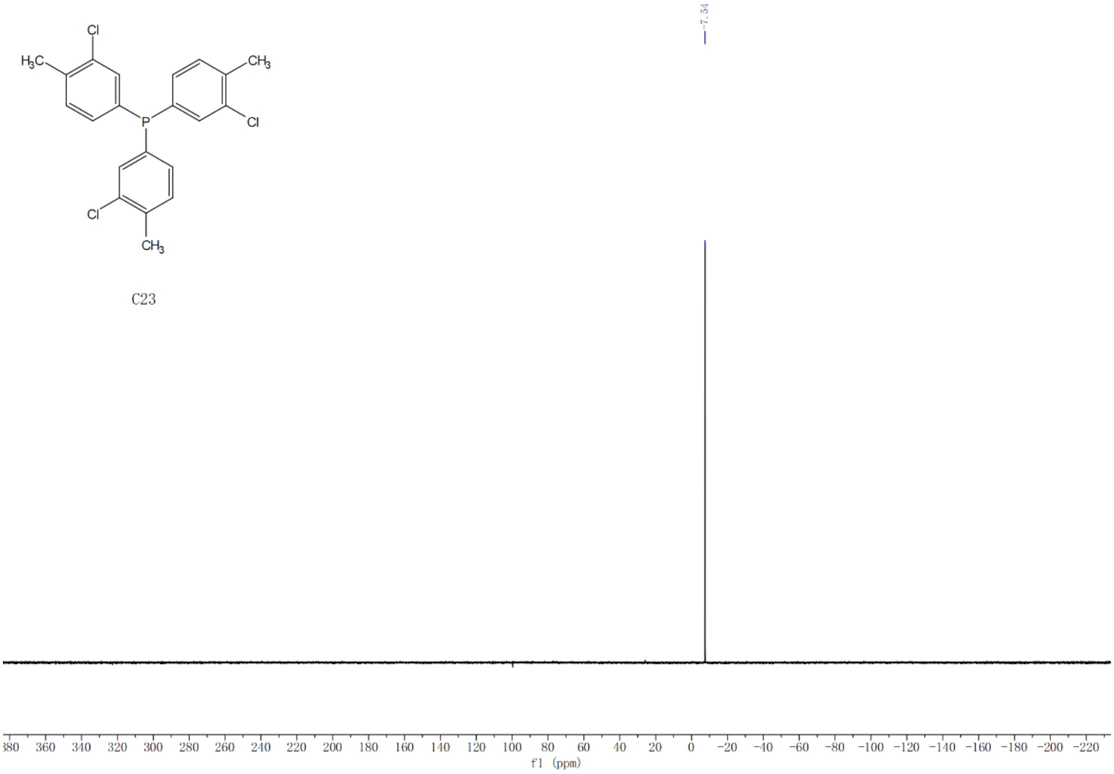
^{1}H NMR spectrum of **C23**



^{13}C NMR spectrum of **C23**



^{31}P NMR spectrum of **C23**



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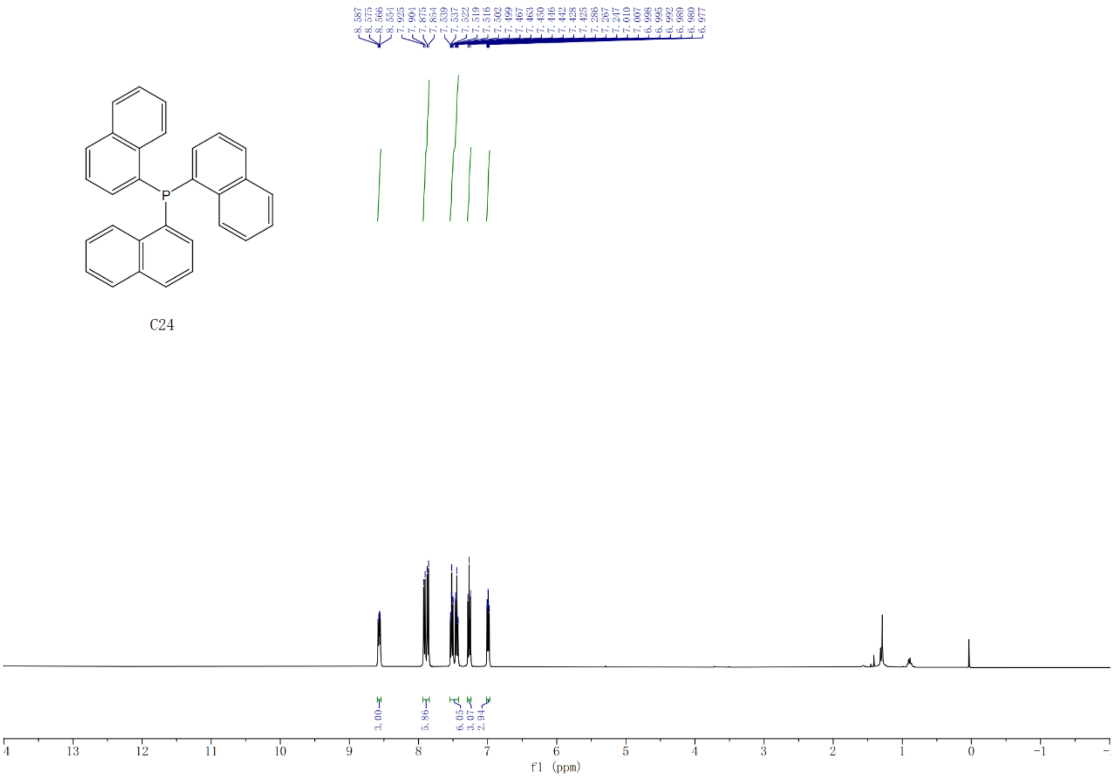
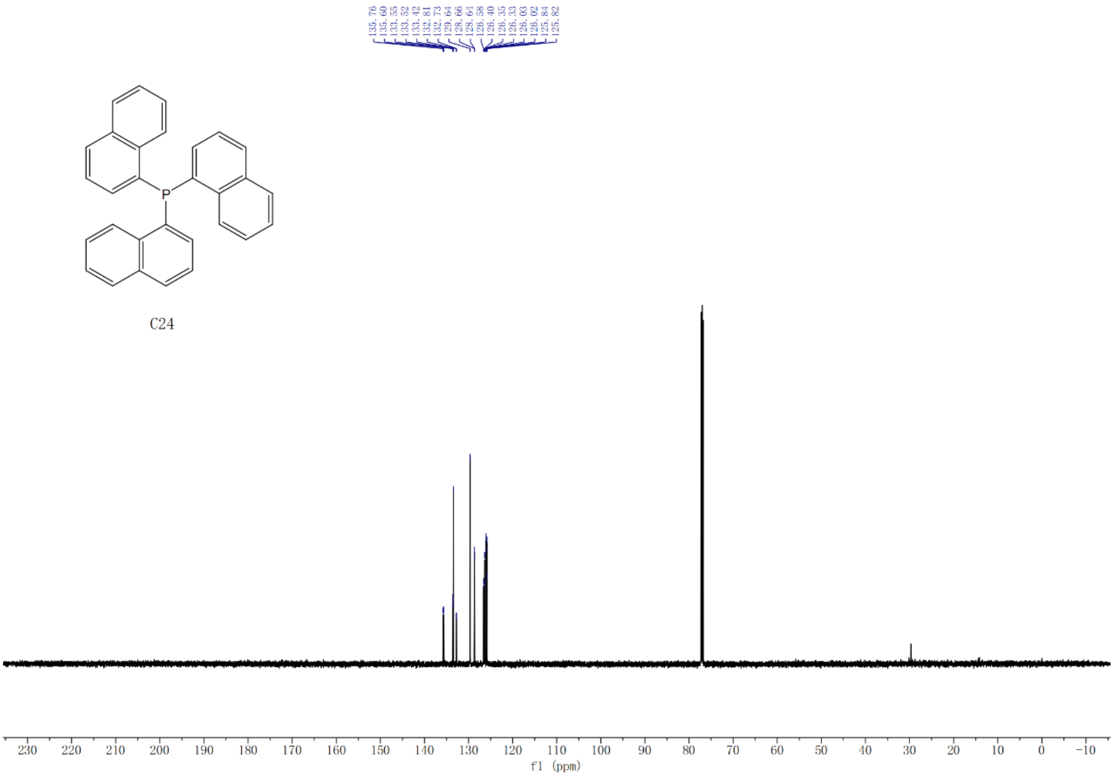
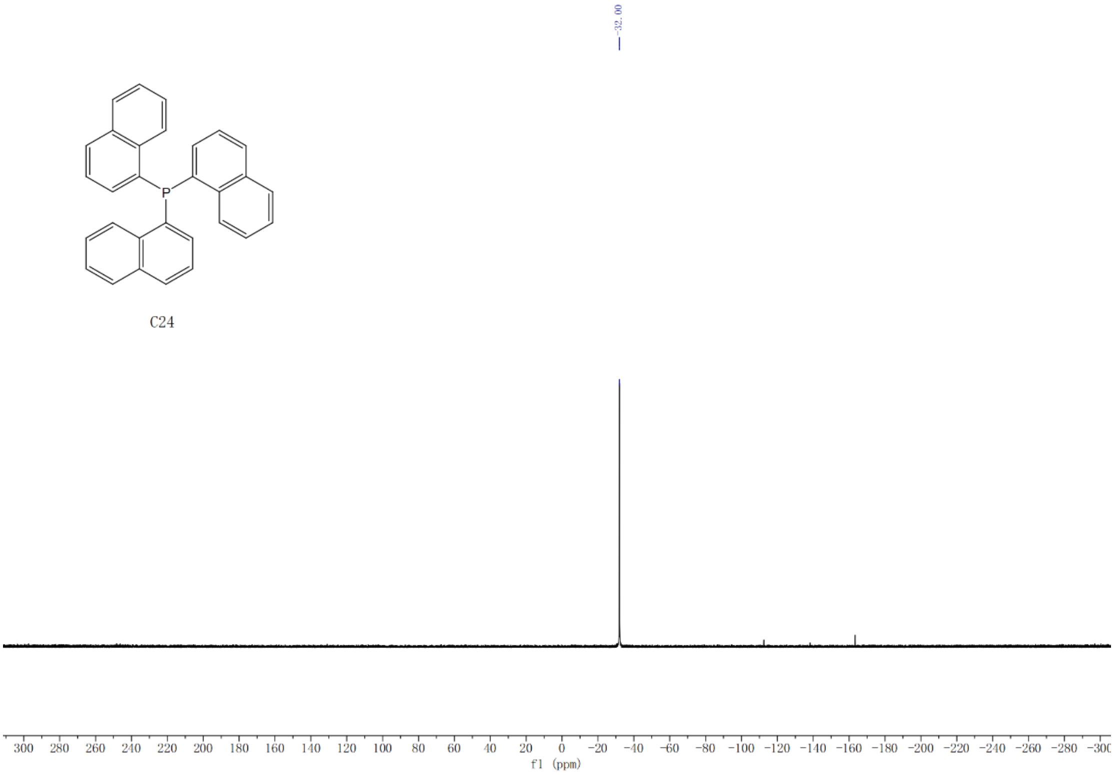


^{13}C NMR spectrum of **C24**



^{31}P NMR spectrum of **C24**



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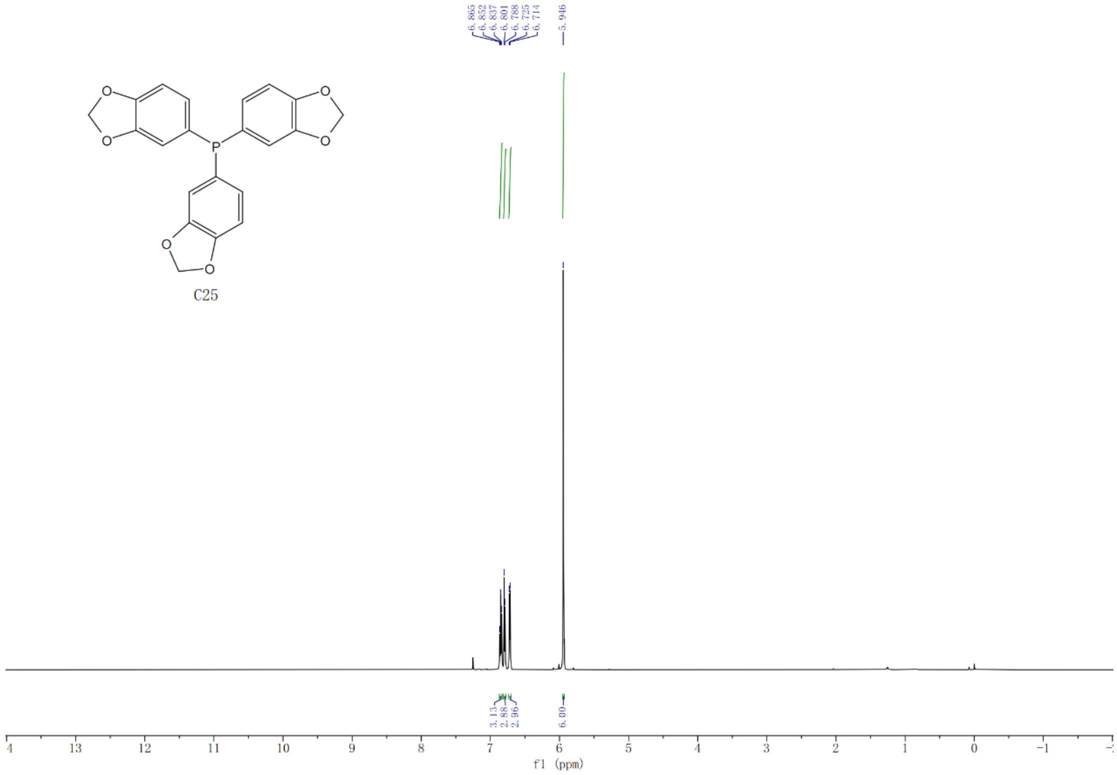

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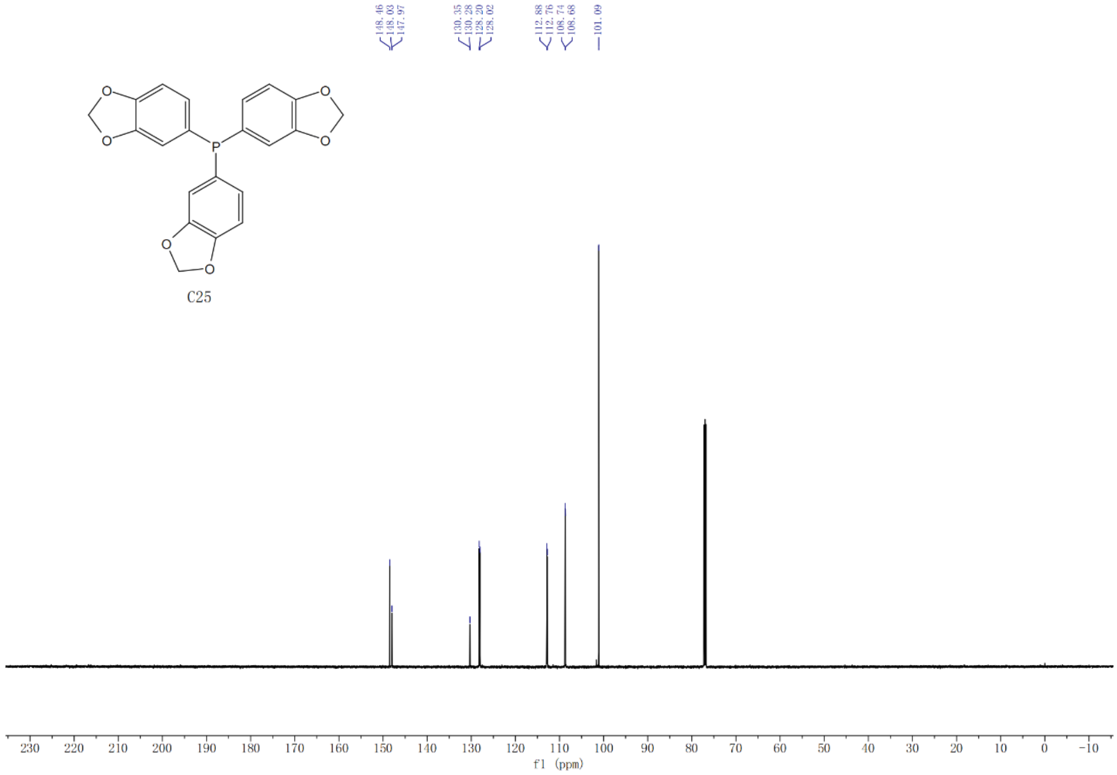

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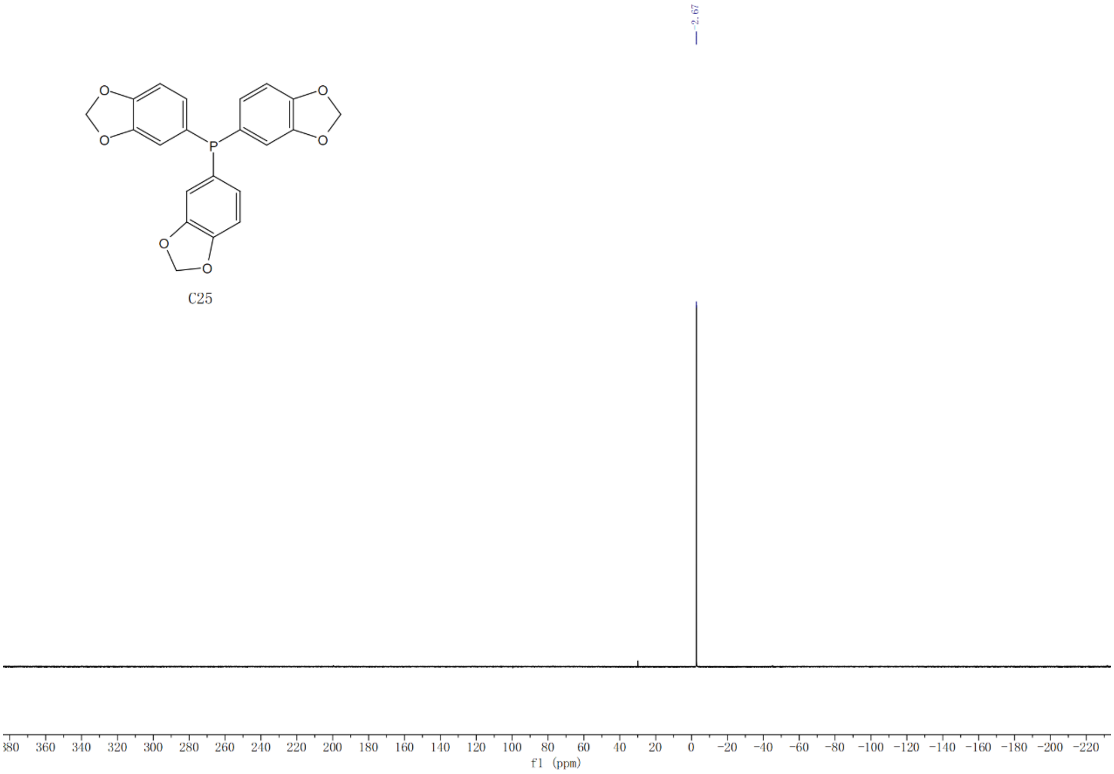

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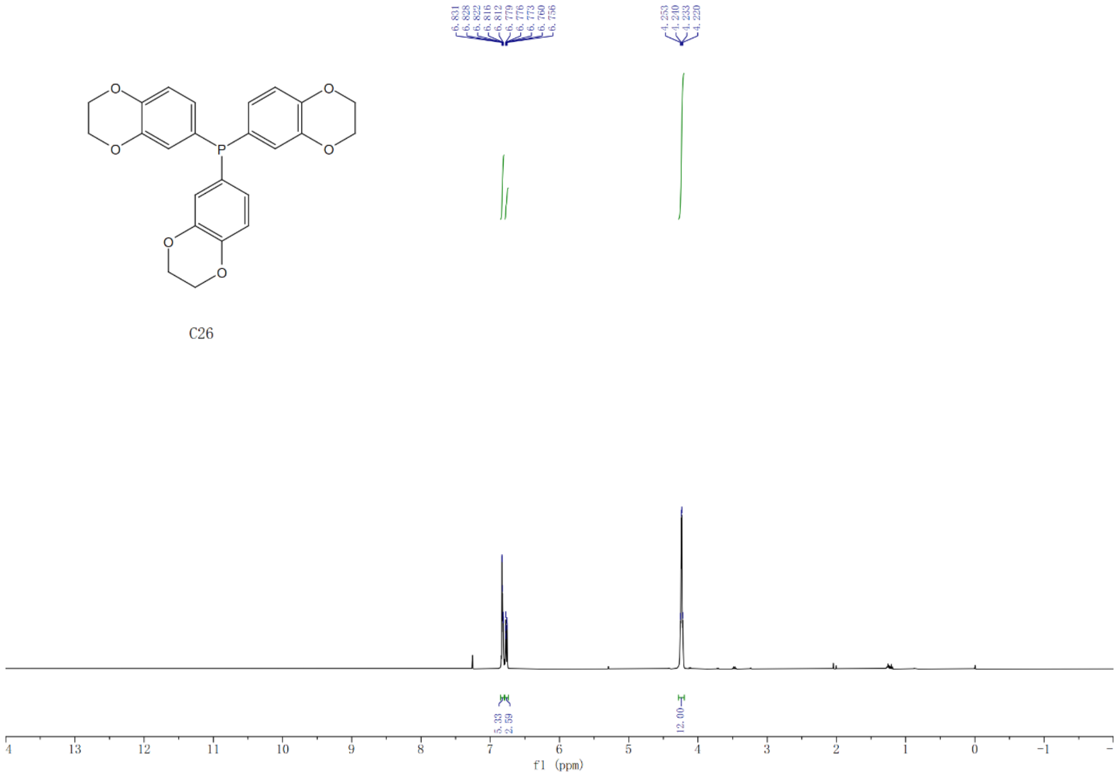
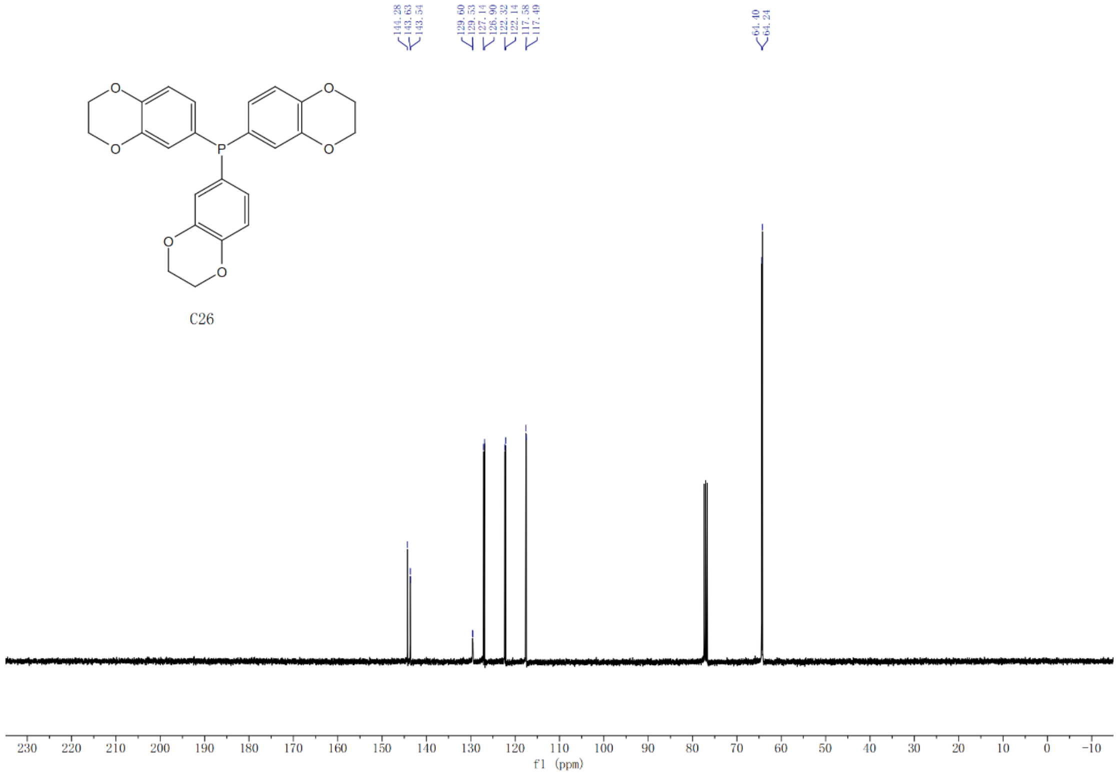
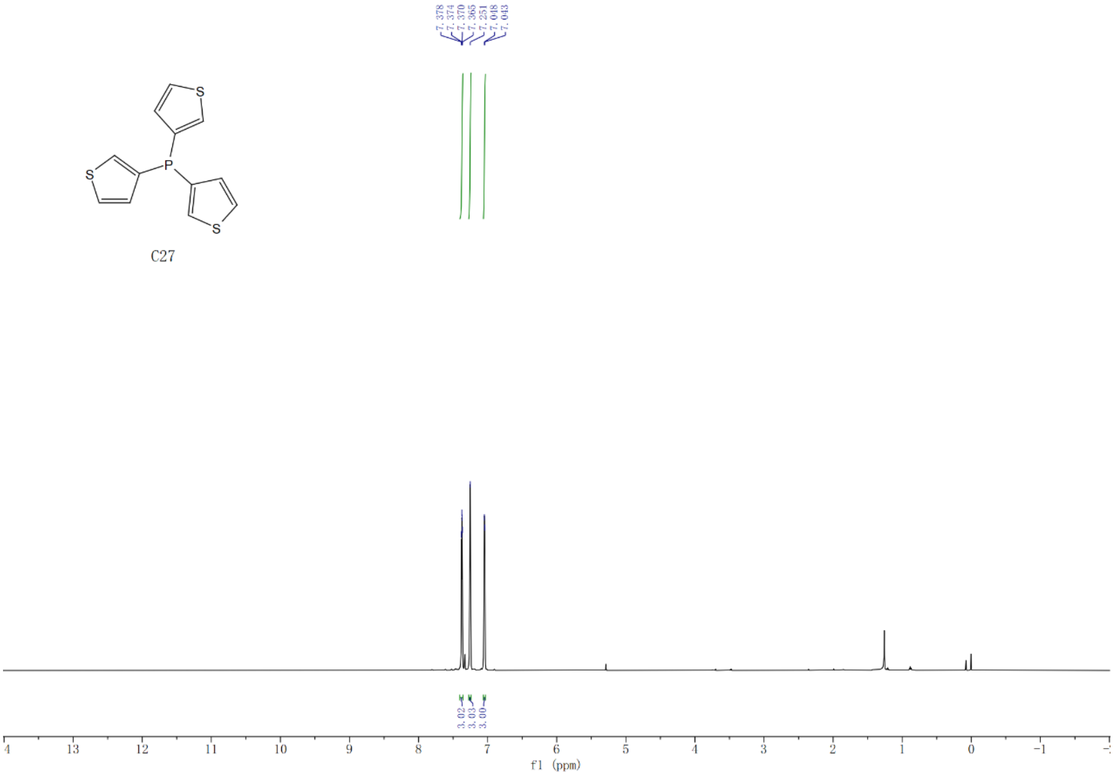


^{13}C NMR spectrum of **C26**

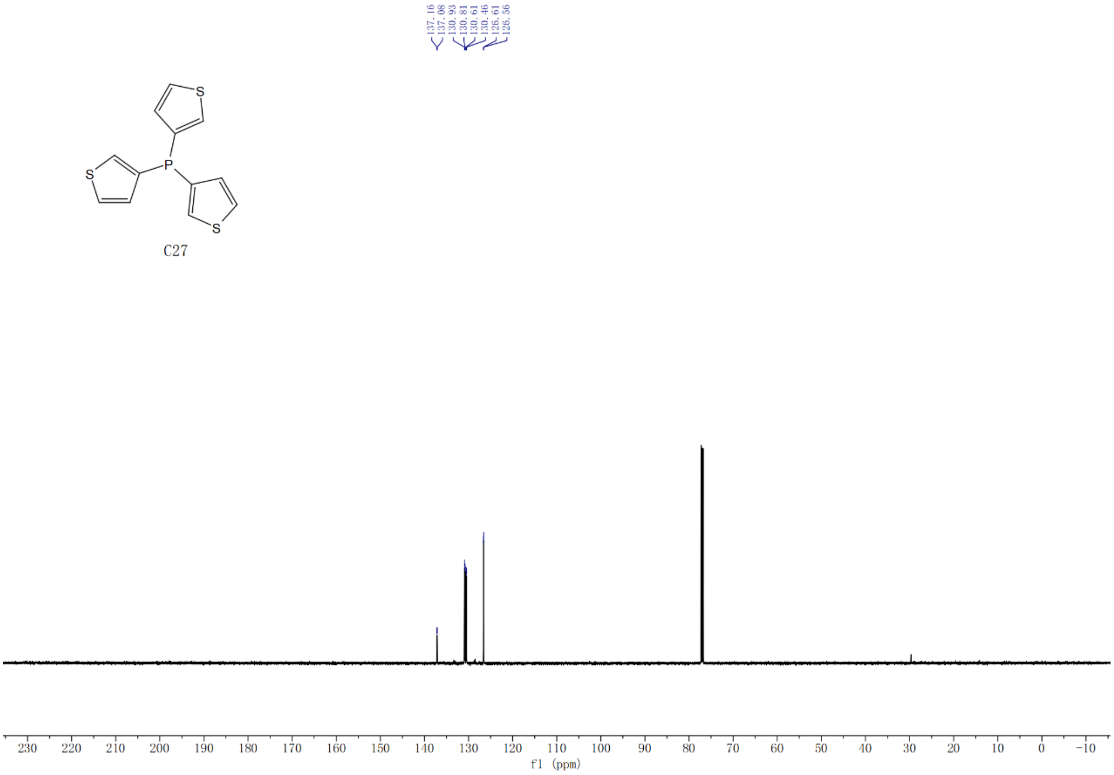


^{31}P NMR spectrum of **C26**

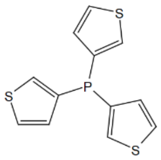
^{1}H NMR spectrum of **C27**



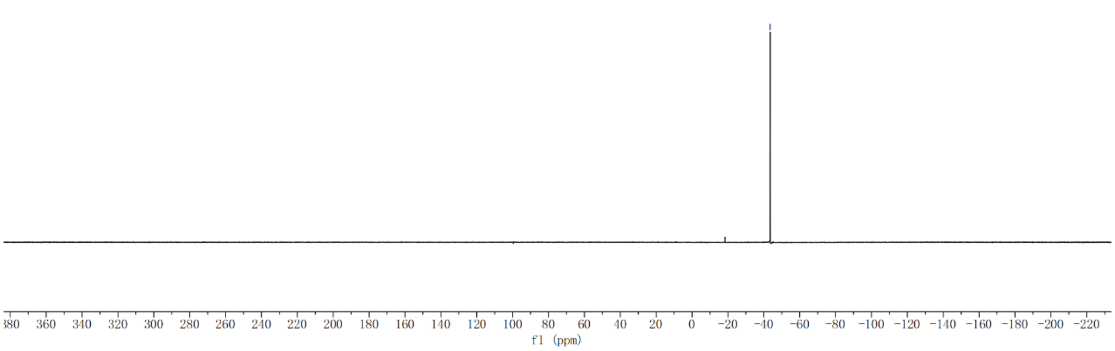
^{13}C NMR spectrum of **C27**



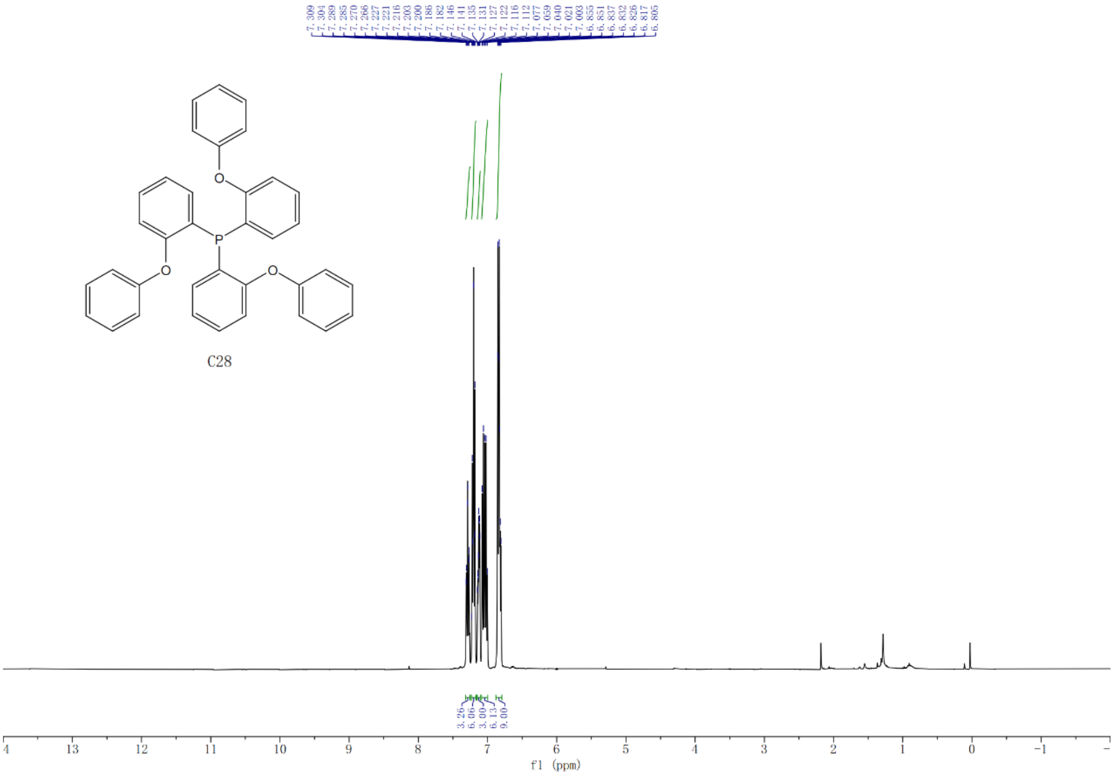
^{31}P NMR spectrum of **C27**



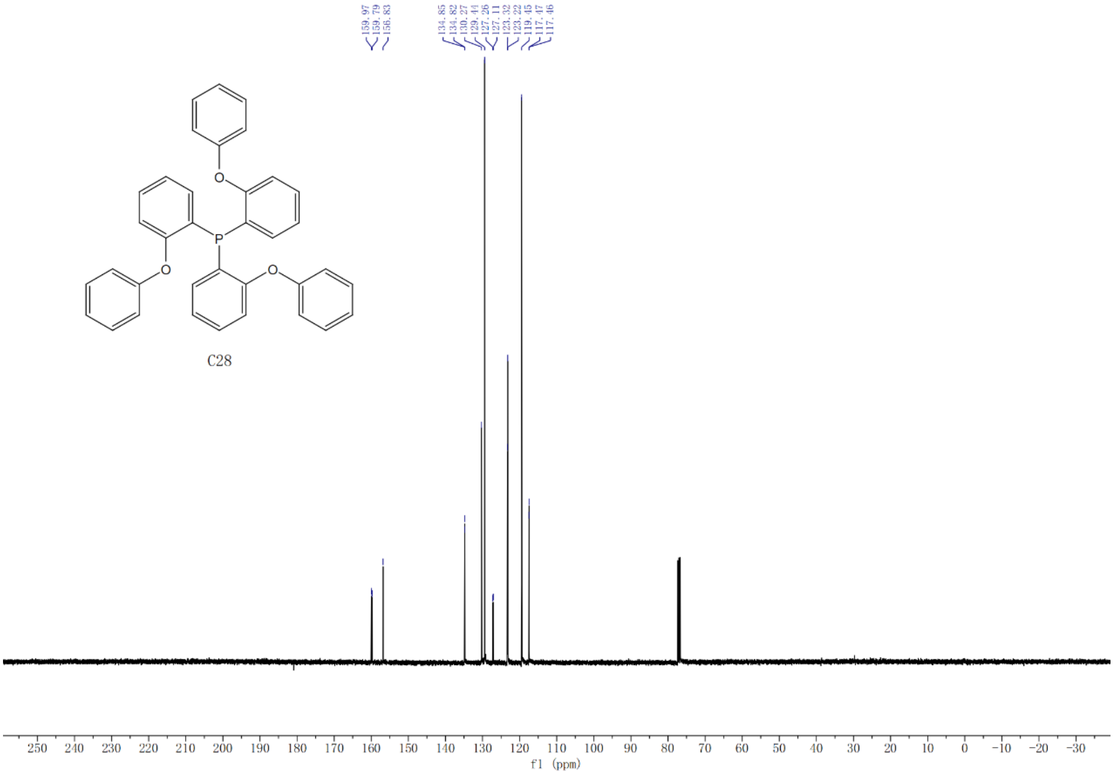
C27



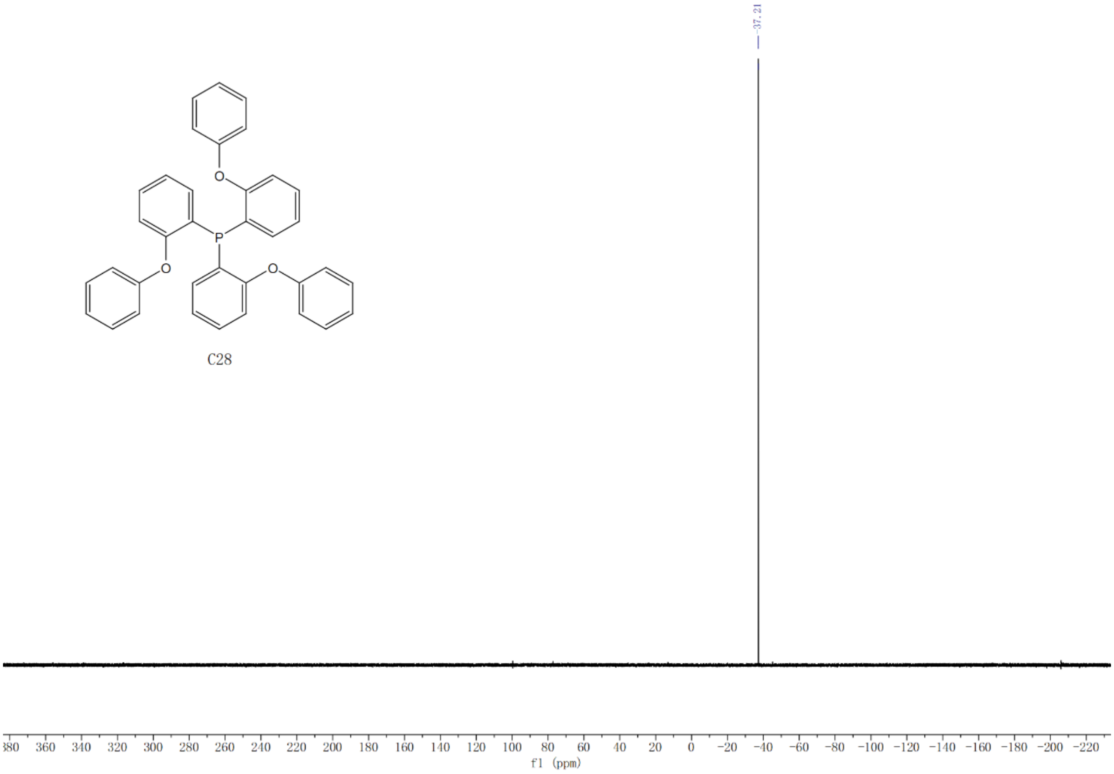
^{1}H NMR spectrum of **C28**



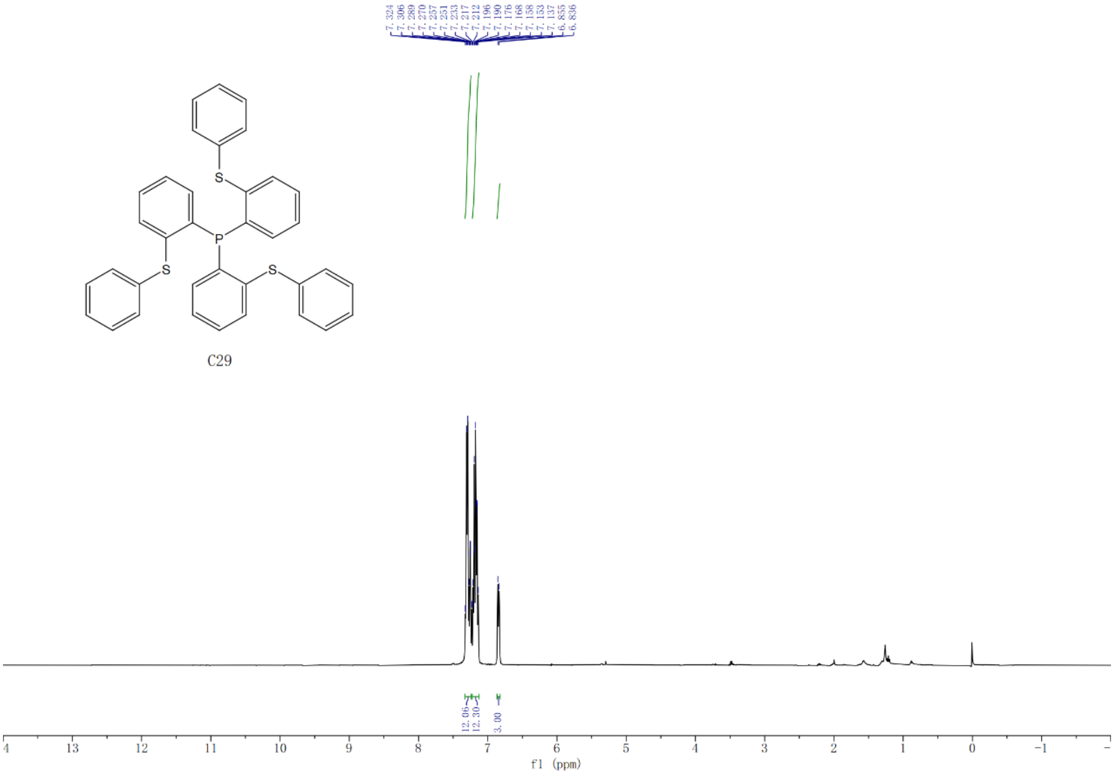
^{13}C NMR spectrum of **C28**



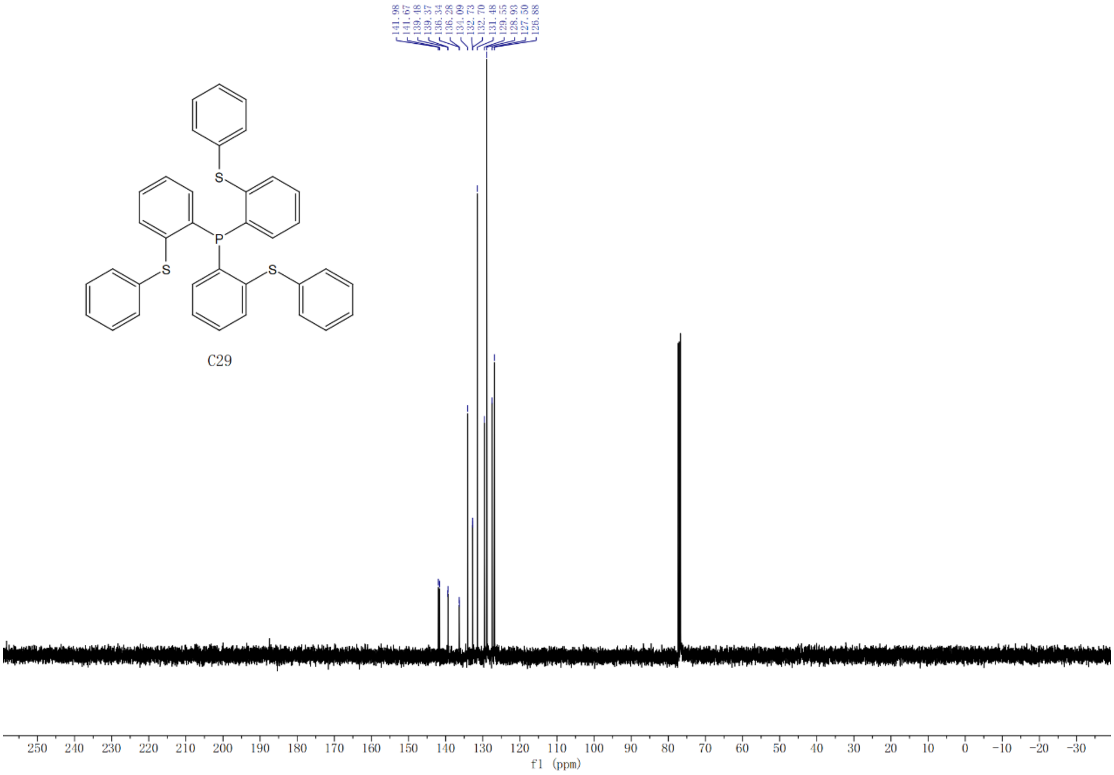
^{31}P NMR spectrum of **C28**



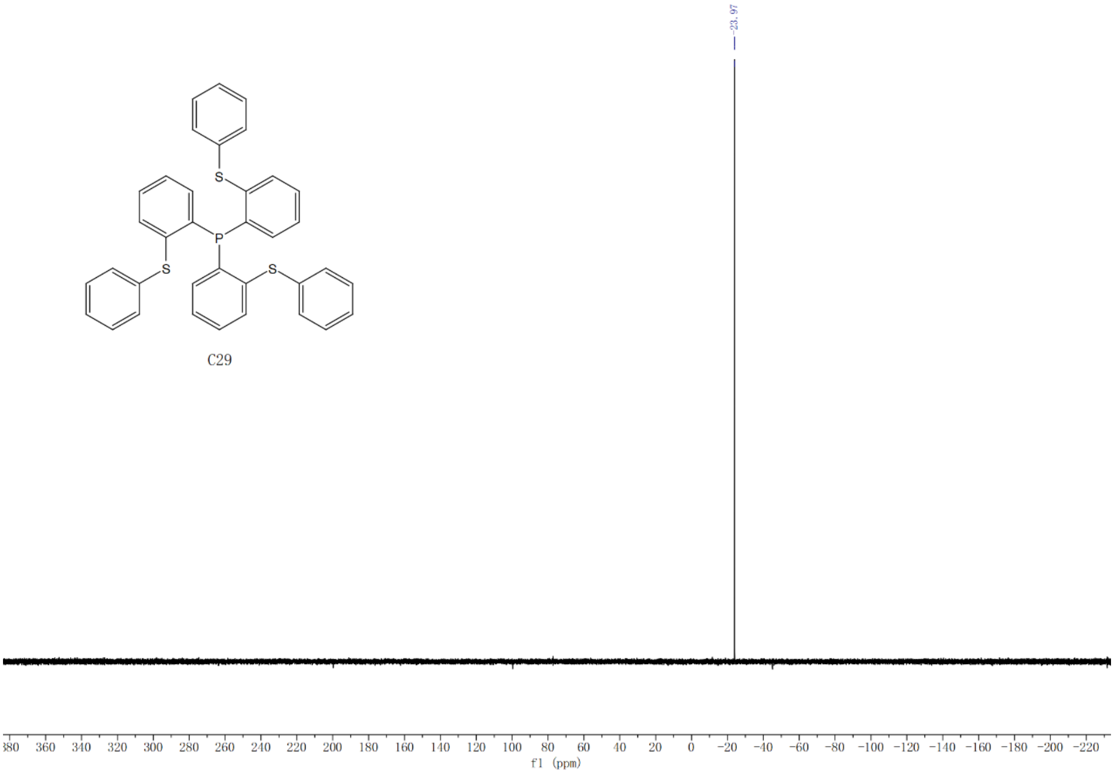
^{1}H NMR spectrum of **C29**



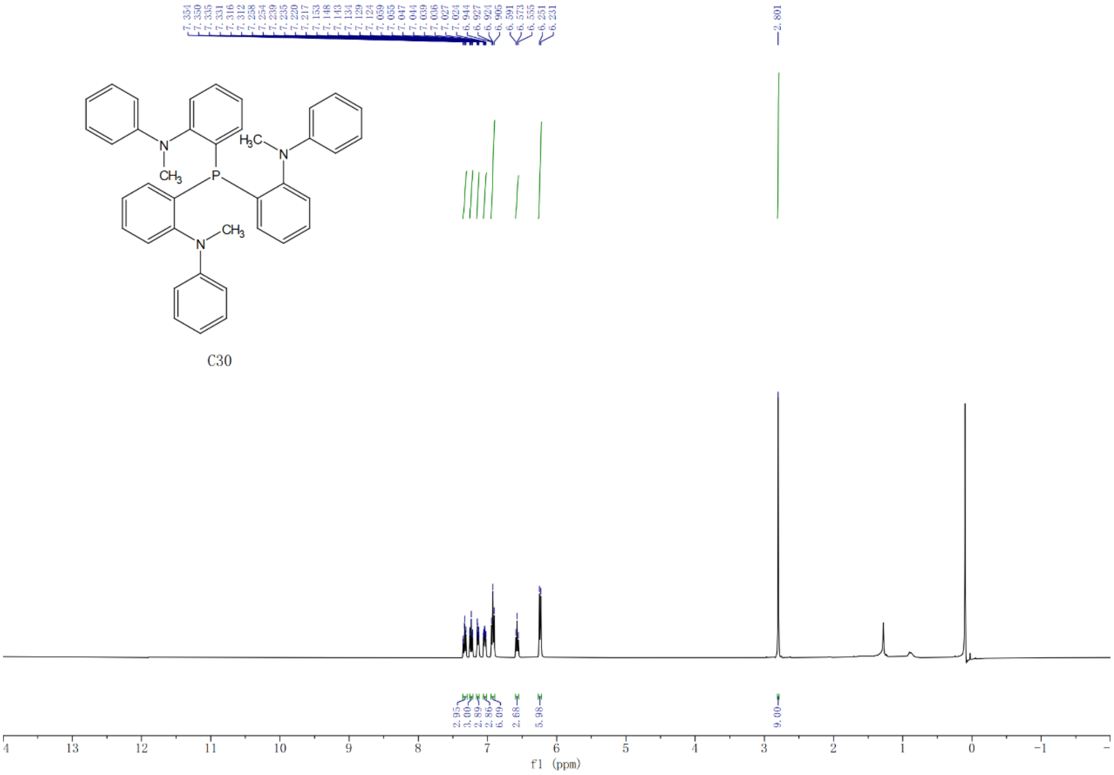
^{13}C NMR spectrum of **C29**



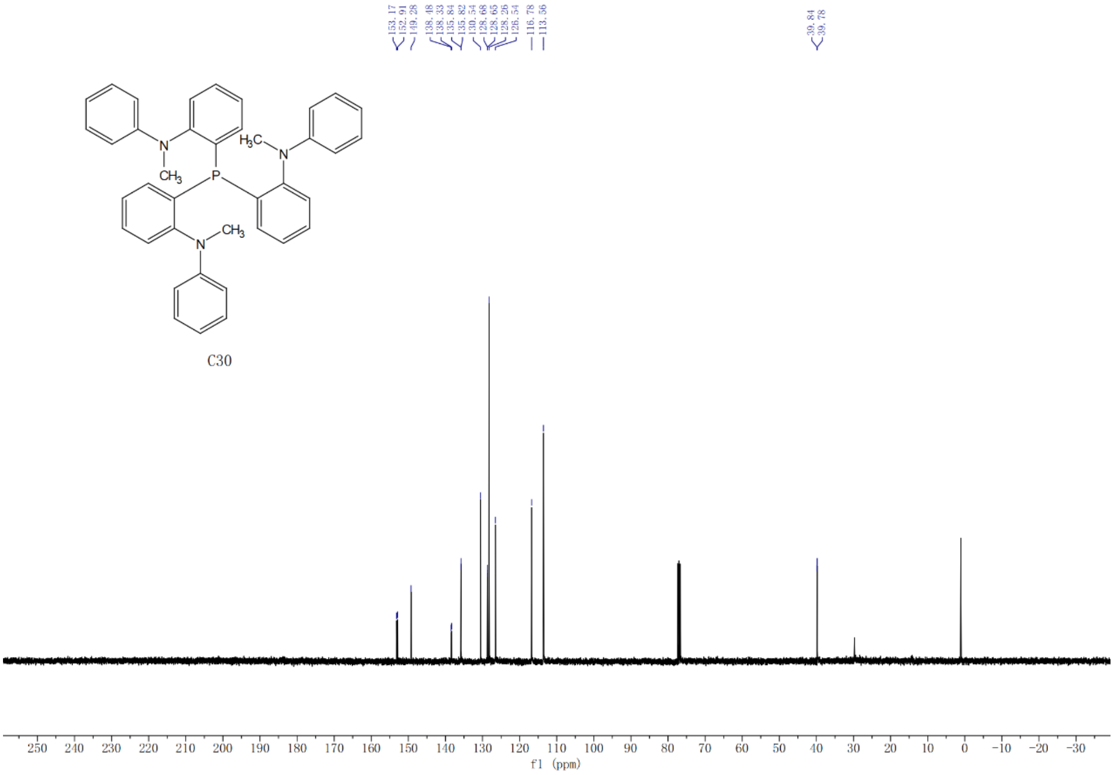
^{31}P NMR spectrum of **C29**



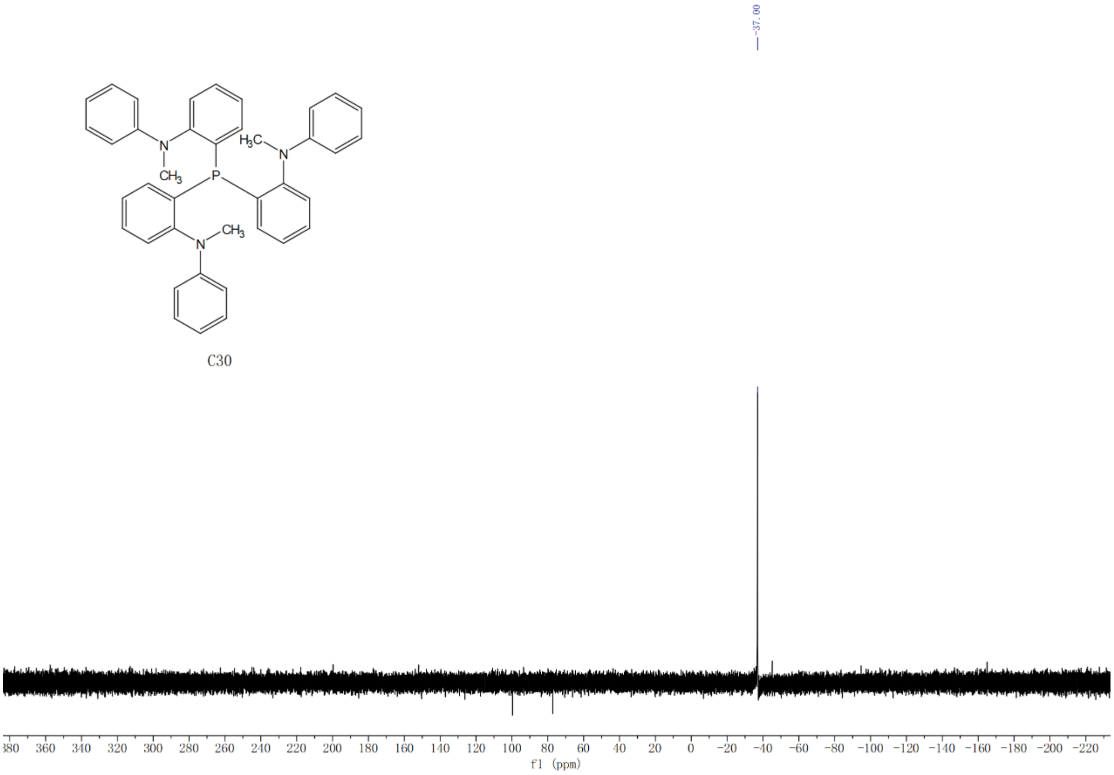
^{1}H NMR spectrum of **C30**



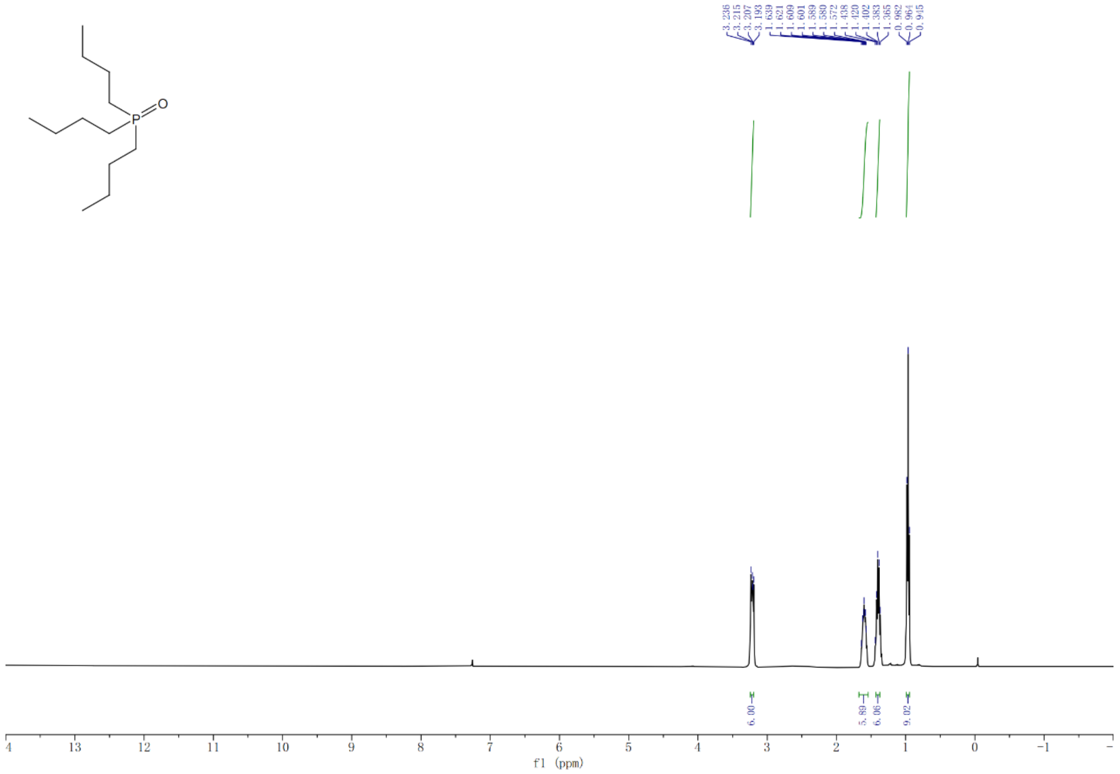
^{13}C NMR spectrum of **C30**



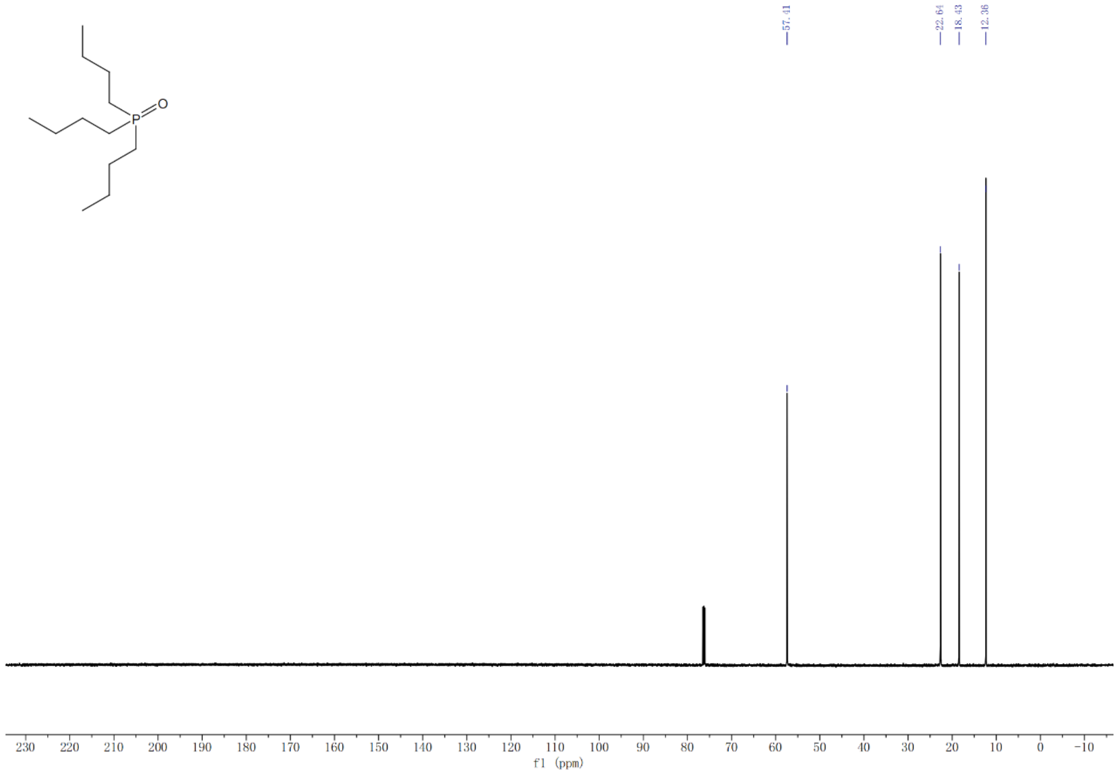
^{31}P NMR spectrum of **C30**



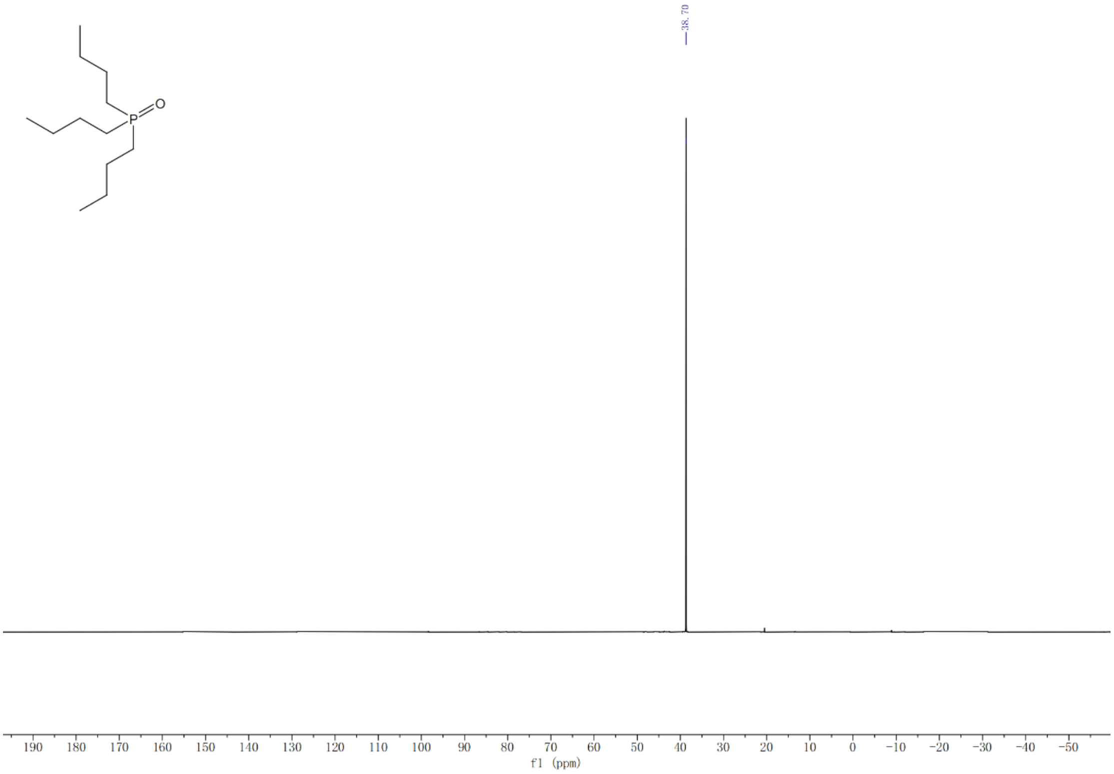
^{1}H NMR spectrum of **C31**



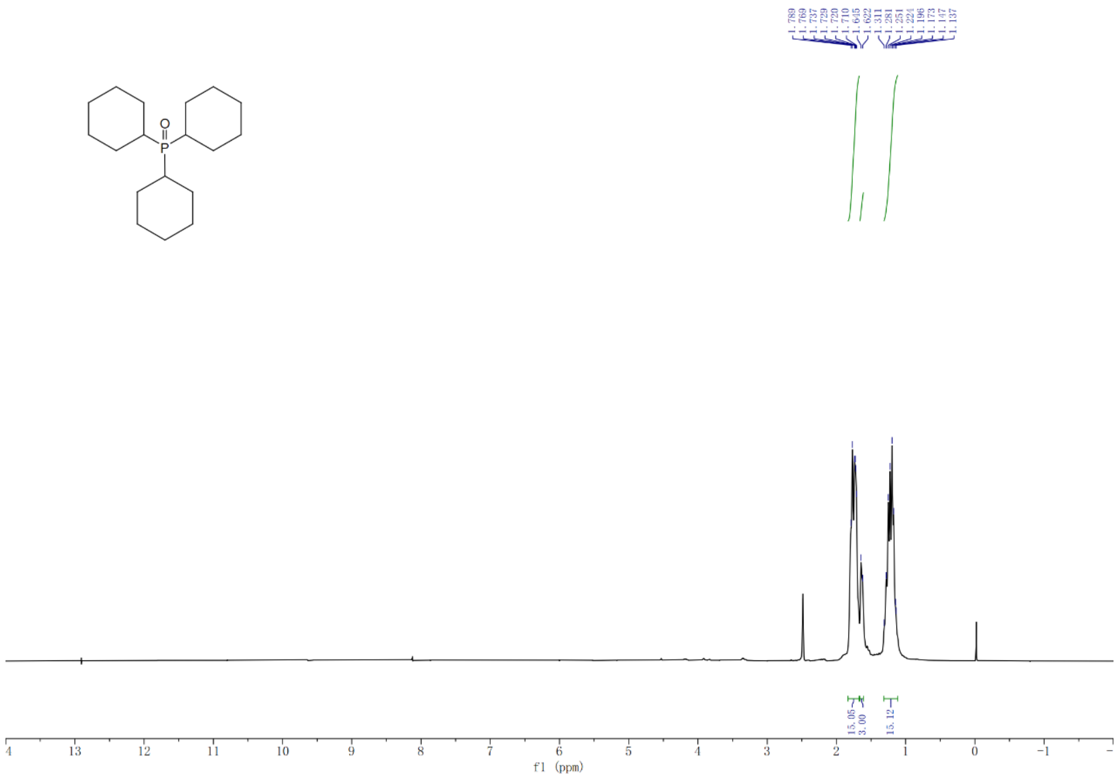
^{13}C NMR spectrum of **C31**



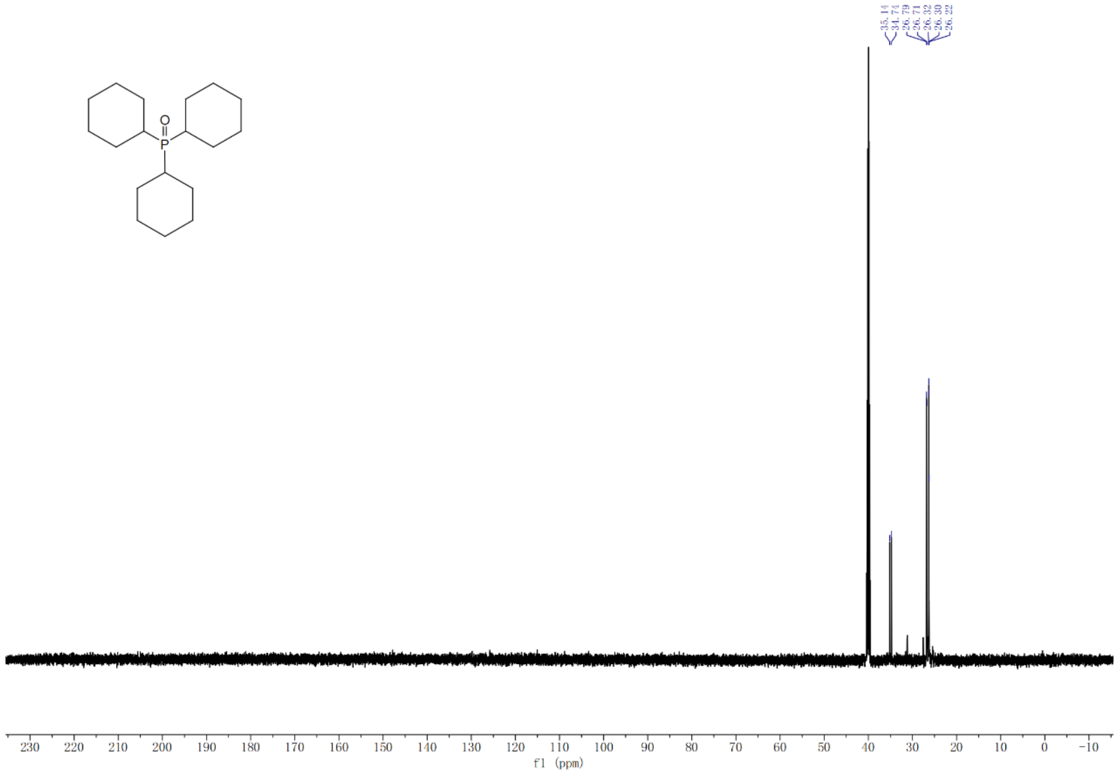
^{31}P NMR spectrum of **C31**



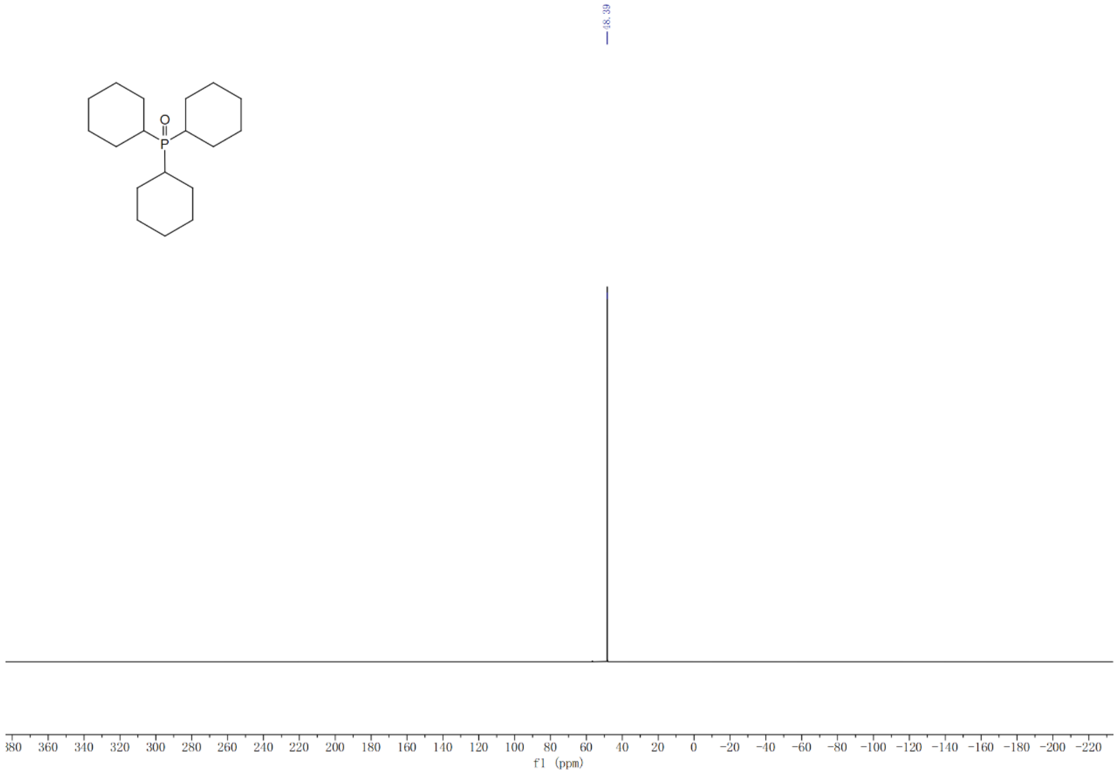
^{1}H NMR spectrum of **C32**



^{13}C NMR spectrum of **C32**



^{31}P NMR spectrum of **C32**



9. DFT Calculation data

Table S7. DFT data

Reactants.xyz

13

P	2.066607	-0.098074	-0.125289
O	1.803053	0.956386	1.122345
O	0.640539	0.169113	-1.022895
O	1.931059	-1.483383	0.413084
H	1.291521	0.476166	1.786152
H	0.855419	0.863219	-1.659299
O	3.159780	0.455182	-0.975277
C	-1.696889	0.537942	-0.415488
C	-1.264498	-0.572769	0.560023
O	-2.296056	0.369874	-1.418937
Cl	-1.427404	2.144399	0.270531
Cl	-1.511581	-2.162417	-0.120235
O	-0.915247	-0.386297	1.672960

TS1.xyz

13

P	2.145257	0.282358	-0.185986
O	1.908256	0.791332	1.337132
O	0.346915	0.238745	-0.624680
O	2.565828	-1.132608	-0.267377
H	1.217683	0.253239	1.769502
H	0.113510	1.182972	-0.664068
O	2.592374	1.427997	-1.014910
C	-2.082551	0.037977	-0.218850
C	-0.795546	-0.524435	0.444995
O	-2.968817	-0.542608	-0.726102
Cl	-2.170126	1.836001	-0.004281
Cl	-0.601979	-2.246764	-0.123772
O	-0.584014	-0.254092	1.608985

INT1.xyz

13

P	2.251260	0.379283	-0.092131
O	2.049464	-0.437826	1.248351
O	0.215232	0.223010	-0.623322
O	3.005176	-0.354206	-1.122967

H	1.099188	-0.347848	1.591211
H	0.077980	1.183429	-0.492178
O	2.109060	1.852648	0.031567
C	-2.149312	-0.003832	-0.089677
C	-0.713397	-0.448598	0.309298
O	-3.129296	-0.635349	-0.219596
Cl	-2.237237	1.826694	-0.158456
Cl	-0.582999	-2.234903	-0.296443
O	-0.477860	-0.257113	1.523280

TS2.xyz
13

P	-2.337134	-0.361264	-0.058785
O	-2.025547	0.426153	1.261561
O	-0.166694	-0.172731	-0.700543
O	-3.150712	0.376266	-1.040083
H	-1.019973	0.334809	1.531222
H	-0.099183	-1.137397	-0.554847
O	-2.104840	-1.826453	-0.016922
C	2.175364	-0.025041	-0.064015
C	0.726738	0.440874	0.255979
O	3.174404	0.586222	-0.134760
Cl	2.228457	-1.855122	-0.159700
Cl	0.678062	2.247132	-0.308950
O	0.442481	0.243340	1.470831

INT2.xyz
13

P	-2.888031	-0.324403	-0.000137
O	-2.100098	-0.372013	1.279701
O	0.477573	-0.314943	-1.153714
O	-4.365278	-0.259038	-0.000795
H	-0.536294	-0.333169	1.205037
H	-0.532641	-0.329283	-1.213705
O	-2.098481	-0.360868	-1.279223
C	2.450479	0.135687	0.000403
C	0.903663	0.214722	-0.000998
O	3.244390	1.004848	0.001527
Cl	2.986362	-1.576987	-0.000529
Cl	0.496318	2.071896	0.003775
O	0.474270	-0.321412	1.147394

```
+(COCl)2.xyz
     10

P         2.080130       -0.441874       -0.102942
O         0.666272       -0.519032       -0.651850
O         3.190325       -0.200211       -1.062484
O         2.293265       -0.630136        1.356174
C        -1.190903        0.851340       -0.428791
C        -1.337913       -0.318620        0.551868
O        -1.699663        0.936816       -1.488999
Cl       -0.379472        2.236572        0.341550
Cl       -2.106044       -1.715797       -0.233401
O        -1.172108       -0.265109        1.718053
```

```
TS3.xyz
     10

P         1.895854       -0.706997       -0.021726
O         0.398368       -0.798361       -0.418469
O         2.851796       -0.301288       -1.072992
O         2.246494       -1.172233        1.337501
C        -0.628089        0.640071       -0.552957
C        -1.599739        0.091945        0.510678
O        -0.943169        0.892521       -1.669085
Cl        0.518604        1.885324        0.361705
Cl       -2.758650       -1.042786       -0.247449
O        -1.677248        0.365576        1.652697
```

```
INT3.xyz
     10

P         1.206486       -0.624468       -0.079530
O         0.302625        0.509595       -1.007310
O         1.792551       -1.590548       -1.027364
O         0.350637       -0.903504        1.107219
C        -0.837498        1.037820       -0.626575
C        -1.648826        0.374861        0.501296
O        -1.333846        2.000833       -1.143557
Cl        2.704510        0.722690        0.507031
Cl       -2.492090       -1.091471       -0.132831
O        -1.960776        0.878651        1.518914
```

```
TS4.xyz
     10
```

P	1.084358	-0.560245	-0.109748
O	0.312971	0.442595	-1.174173
O	1.567461	-1.816136	-0.695539
O	0.093115	-0.462769	1.073512
C	-0.824557	1.014064	-0.684455
C	-1.277977	0.402799	0.655563
O	-1.385521	1.895384	-1.250291
Cl	2.689966	0.630050	0.417384
Cl	-2.355300	-1.139732	-0.080510
O	-1.755460	1.011813	1.558078

INT4.xyz
10

P	1.005811	-0.544628	-0.000332
O	0.167094	0.106998	-1.212469
O	1.377280	-1.957382	-0.001186
O	0.166461	0.105276	1.212390
C	-0.971942	0.808853	-0.761240
C	-0.972658	0.807338	0.761516
O	-1.604969	1.493894	-1.491676
Cl	2.697960	0.627253	0.000784
Cl	-2.193252	-1.300951	-0.000355
O	-1.605817	1.491856	1.492445

TS5.xyz
10

P	-0.832895	0.476877	-0.000164
O	0.007476	-0.256885	-1.240210
O	-1.712245	1.653113	-0.000433
O	0.007746	-0.256302	1.240128
C	1.147096	-0.819953	-0.773377
C	1.147316	-0.819193	0.773521
O	1.966331	-1.339251	-1.458051
Cl	-2.313898	-1.079844	0.000492
Cl	1.186615	1.960853	-0.000278
O	1.967039	-1.337605	1.458310

INT5.xyz
10

P	-0.943376	0.002459	-0.000178

O	0.190565	-0.000830	-1.252949
O	-2.417144	0.007474	-0.000833
O	0.190828	-0.001045	1.252808
C	1.441523	-0.003693	-0.775483
C	1.441578	-0.004162	0.775229
O	2.424402	-0.005976	-1.446690
Cl	-0.761939	-2.245567	0.000203
Cl	-0.747162	2.249838	0.000752
O	2.424693	-0.007416	1.446159

TS6.xyz
10

P	0.873287	-0.000469	0.256921
O	-0.363753	0.001051	-1.101558
O	2.055185	-0.001673	1.154529
O	-0.443949	0.000237	1.317375
C	-1.612771	0.001236	-0.723865
C	-1.683522	0.000575	0.810688
O	-2.580633	0.001953	-1.434963
Cl	1.141720	2.028823	-0.459156
Cl	1.137972	-2.030017	-0.460138
O	-2.676387	0.000491	1.471273

INT6.xyz
10

P	0.805904	0.002077	0.382903
O	-0.391185	-0.007194	-1.062997
O	1.774361	0.007898	1.507877
O	-0.637008	0.005002	1.316988
C	-1.660794	-0.005996	-0.786793
C	-1.837267	0.001797	0.735330
O	-2.576110	-0.010197	-1.568075
Cl	1.363661	1.847840	-0.525223
Cl	1.373139	-1.847847	-0.511683
O	-2.873283	0.003760	1.330286

TS7.xyz
10

P	0.945182	0.001533	-0.435790
O	-0.645756	-0.004293	1.225137
O	1.977302	0.005223	-1.494737

O	-0.470715	0.004796	-1.266641
C	-1.815962	-0.002758	0.753670
C	-1.761767	0.003120	-0.794168
O	-2.904070	-0.005100	1.299619
Cl	1.323100	-1.737781	0.616489
Cl	1.323506	1.733118	0.629016
O	-2.669718	0.006137	-1.562595

INT7.xyz

10

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P	-0.459893	0.305422	-0.536459
O	1.368195	0.347446	-0.778034
O	-0.719336	1.570129	-1.258317
O	-0.097896	0.208135	1.121411
C	2.103597	0.343112	0.289651
C	1.186641	0.269117	1.518774
O	3.303773	0.389890	0.363687
Cl	-2.501537	-0.171912	0.064126
Cl	-0.334055	-1.554534	-1.499656
O	1.519171	0.259678	2.663493

TS8.xyz

10

P	-1.029233	-0.160873	-0.427638
O	1.868102	-1.272045	-0.705729
O	-1.298668	-1.068800	-1.553740
O	-0.026581	0.994240	-0.459900
C	2.603974	-0.472431	-0.216595
C	1.669364	1.133587	0.068244
O	3.714431	-0.237949	0.169823
Cl	-2.810753	0.801288	0.107980
Cl	-0.677366	-1.189695	1.336572
O	1.879779	2.215689	0.392960

Products.xyz

10

P	-1.035100	0.340283	-0.534851
O	2.067272	-1.924536	-0.777938
O	-1.899961	0.675749	-1.687820
O	0.445543	0.500673	-0.469571
C	1.870368	-1.589196	0.314623

C	3.079609	1.380559	-0.082633
O	1.759744	-1.352985	1.444524
Cl	-1.837802	1.276296	1.176889
Cl	-1.440360	-1.676989	0.012405
O	2.821826	2.471018	-0.207591