Supporting Information

Replacing Low-Boiling-Point Amines: Electrocatalytic Phosphinamide Synthesis with Liquid Formamide Reagents

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1. General information

All the reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. All the reactions were carried out under air in ovendried glassware with magnetic stirring. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded on Bruker-AV (400, 100, 162, and 377 MHz, respectively) at ambient temperature. HRMS were made by means of ESI with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. IR spectra were recorded on a new Fourier transform infrared spectroscopy. Unless otherwise noted, all reagents were weighed and handled in air. Oil bath was used for reactions that require heating. The melting points were measured on micro melting point apparatus.

2. Reaction apparatus diagram

Figure S1. Diagram of reaction device.

3. Comparison of methods

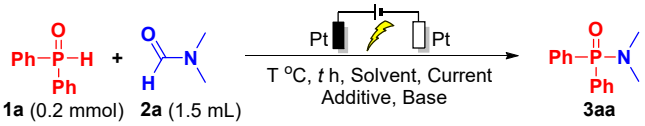
Table S1 Comprehensive comparison between the proposed method and existing methods.

Method	P	N	Time /h	T /°C	AE /%	FE /%	Drawbacks
Thermal[20]	$R_2P(O)Cl$	RNH_2	—	0	79.6	—	Low efficiency, $R_2P(O)Cl$, HCl
Thermal[21]	$R_2P(O)Cl$	R_2NH	4	50	85.5	—	Low efficiency, $R_2P(O)Cl$, HCl
Thermal[23]	$R_2P(O)Cl$	R_2N_3	4	25	86.1	—	Low efficiency, $R_2P(O)Cl$, HCl
Thermal[3]	$R_2P(O)OH$	RNH_2	25.5	rt	86.8	—	Low efficiency, HCl, slow
Thermal[24]	$R_2P(O)Cl$	RC=NR'	24	60	91.5	—	Low efficiency, $R_2P(O)Cl$, HCl, slow
Thermal[25]	R_2PCl	RNHOH	1	0	89.4	—	Low efficiency, $R_2P(O)Cl$, HCl, low temp.
Thermal[27]	R_2PH	RNH_2	0.5	rt	99.4	—	Metal (Cu/Co), low efficiency
Thermal[28]	R_2PH	$R_2N\text{-}O_2CR$	12	rt	73.9	—	Metal (Cu), low efficiency, slow
Thermal[30]	$R_2P(O)H$	R_2NH	1	25	93.5	—	ZnI_2/TBHP, low efficiency
Thermal[31]	$R_2P(O)H$	R_2NHCO_3R	3	80	67.5	—	Metal (Cu), low efficiency, high T.
Thermal[32]	$R_2P(O)H$	R_2NNH	12	rt	99.4	—	Metal (Cu) & Ligand, low efficiency, slow
Thermal[33]	$R_2P(O)H$	$PhNO_2$	18	120	90.2	—	Metal (Ni/Zn) & Ligand, TMSCl, high T., low efficiency, slow
Thermal[34]	$R_2P(O)H$	$PhNO_2$	3	80	49.1	—	Metal (Cu) & Ligand, [Si]-H, high T., low efficiency
Thermal[35]	$R_2P(O)H$	NH_2OH HCl	28	80	39.3	—	Metal (Fe), $Ph(IOAc)_2$, high T., low efficiency, HCl, slow
Photo[36]	$R_2P(O)H$	ArN_3	24	rt	91.6	—	Metal (Ir/Cu), ArN_3, slow
Photo[37]	$R_2P(S)H$	R_2NH	48	rt	99.3	—	Metal (Ru), slow
Photo[38]	$R_2P(O)H$	RNH_2	10	rt	76.9	—	Metal (Cu) & 4CzIPN, ^{t}BuOOH, slow
Photo[39]	$R_2P(O)H$	RNH_2	12	25	99.3	—	Cat. (Acid red), slow
Photo[40]	$R_2P(O)H$	$PhNH_2$	16	rt	74.3	—	Add. (IsoamyIONO), slow
Electronic[41]	$R_2P(O)H$	$PhNH_2$	4	rt	99.4	43.8	HFIP
Electronic[42]	$R_2P(O)H$	R_2NH	4	rt	99.3	7.7	Low FE
Electronic[43]	$R_2P(O)H$	R_2NH	3	rt	99.4	50.7	Add. (DMMI)
Electronic[44]	$(RO)_3P$	R_2NH	6	rt	89.4	32.9	Unstable P-source, slow
Electronic[45]	$R_2P(O)H$	$R_2S(O)NH$	15	40	99.5	10.0	Low FE, slow, Specific N-source
Electronic[46]	$R_2P(O)H$	R_2NH	Slow	rt	99.3	43.4	Slow
	$R_2P(O)H$	**DMF**	**1**	**30**	**89.1**	**39.5**	**DMF**
Electronic (This work)	**Relative advantages**						**Alternative gaseous N-source, stable P-source, rapid, high AE, moderate FE, rt.**

Note: See references in the manuscript.

4. Optimization experiments

Table S2 Optimization of reaction conditions.[a]



1a (0.2 mmol) **2a** (1.5 mL) **3aa**

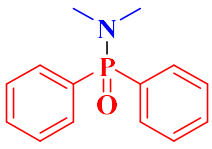
Entry	Anode/ Cathode	Base (equiv)	Additive (equiv)	t/h	Current/mA	T/°C	Yield/%
1	Pt/Pt	^{t}BuOK (3)	KI (1)	1	20	30	67
2	Pt/Pt	^{t}BuOK (3)	KI (2)	1	20	30	66
3	Pt/Pt	^{t}BuOK (3)	KI (3)	1	20	30	67
4	Pt/Pt	^{t}BuOK (3)	Me_4NI (1)	1	20	30	61
5	Pt/Pt	^{t}BuOK (3)	Et_4NI (1)	1	20	30	59
6	Pt/Pt	^{t}BuOK (3)	Pr_4NI (1)	1	20	30	64
7	Pt/Pt	^{t}BuOK (3)	^{n}Bu$_4$NI (1)	1	20	30	56
8	Pt/Pt	^{t}BuOK (3)	^{n}Bu$_4$NOAc (1)	1	20	30	n.d.
9	Pt/Pt	^{t}BuOK (3)	NaI (1)	1	20	30	59
10	Pt/Pt	^{t}BuOK (3)	$LiClO_4$ (1)	1	20	30	trace
11	Pt/Pt	^{t}BuOK (3)	KI (1)	0.5	20	30	59
12	**Pt/Pt**	^{t}BuOK (3)	**KI (1)**	**1**	**20**	**30**	**67**
13	Pt/Pt	^{t}BuOK (3)	KI (1)	3	20	30	63
14	Pt/Pt	^{t}BuOK (3)	KI (1)	4	20	30	57
15	Pt/Pt	^{t}BuOK (3)	KI (1)	1	15	30	55
16	Pt/Pt	^{t}BuOK (3)	KI (1)	1	25	30	60
17	C/Pt	^{t}BuOK (3)	KI (1)	1	20	30	62
18	Pt/C	^{t}BuOK (3)	KI (1)	1	20	30	57
19	C/C	^{t}BuOK (3)	KI (1)	1	20	30	62
20	Pt/Ni	^{t}BuOK (3)	KI (1)	1	20	30	62
21	Pt/Ag	^{t}BuOK (3)	KI (1)	1	20	30	54
22	Pt/Al	^{t}BuOK (3)	KI (1)	1	20	30	52
23	Pt/Cu	^{t}BuOK (3)	KI (1)	1	20	30	44
24	C/Ag	^{t}BuOK (3)	KI (1)	1	20	30	58
25	C/Al	^{t}BuOK (3)	KI (1)	1	20	30	59
26	C/Cu	^{t}BuOK (3)	KI (1)	1	20	30	58
27	Pt/Pt	^{t}BuOK (3)	KI (1)	1	20	0	55
28	Pt/Pt	^{t}BuOK (3)	KI (1)	1	20	20	63
29	Pt/Pt	^{t}BuOK (3)	KI (1)	1	20	40	59
30[b]	Pt/Pt	^{t}BuOK (3)	KI (1)	1	20	30	58
31[c]	Pt/Pt	^{t}BuOK (3)	KI (1)	1	20	30	55
32	Pt/Pt	^{t}BuOK (3)	KI (1)	1	0	30	N.D.
33	Pt/Pt	Cs_2CO_3 (3)	KI (1)	1	20	30	22
34	Pt/Pt	Et_3N (3)	KI (1)	1	20	30	8

35	Pt/Pt	$KHCO_3$ (3)	KI (1)	1	20	30	trace
36	Pt/Pt	DIPEA (3)	KI (1)	1	20	30	trace
37	Pt/Pt	DBU (3)	KI (1)	1	20	30	n.d.
38	Pt/Pt	KOH (3)	KI (1)	1	20	30	17
39	Pt/Pt	K_2CO_3 (3)	KI (1)	1	20	30	trace
40	Pt/Pt	Na_2CO_3 (3)	KI (1)	1	20	30	trace
41	Pt/Pt	K_3PO_3 (3)	KI (1)	1	20	30	n.d.
42	Pt/Pt	NaOAc (3)	KI (1)	1	20	30	n.d.
43	Pt/Pt	CH_3ONa (3)	KI (1)	1	20	30	16
44	Pt/Pt	^{t}BuONa (3)	KI (1)	1	20	30	32
45	Pt/Pt	Li_2CO_3 (3)	KI (1)	1	20	30	n.d.
46	Pt/Pt	^{t}BuOK (2)	KI (1)	1	20	30	50
47	Pt/Pt	^{t}BuOK (1)	KI (1)	1	20	30	33

[a] Platinum anode (10 mm × 10 mm × 0.1 mm), platinum cathode (10 mm × 10 mm × 0.1 mm), electrode distance (~0.5 cm), **1a** (0.2 mmol), KI (0.2 mmol), ^{t}BuOK (0.6 mmol), DMF (1.5 mL), H_2O (0.5 mL), 10 mL reaction tube, undivided cell, current = 20 mA, 30 °C, 1 h in a 10 mL three-neck flask. NMR yield (CH_2Br_2 as an internal standard); [b] In an O_2 atmosphere; [c] In an Ar atmosphere.

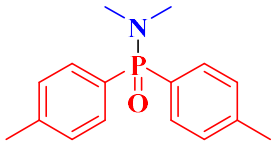
5. Experimental procedure and characterization data for products

A typical experimental procedure: Diphenylphosphine oxide (0.2 mmol, 1.0 equiv), KI (0.2 mmol, 1.0 equiv), and ^{t}BuOK (0.6 mmol, 3.0 equiv.) were added to an undivided cell (a 10 mL three-necked flask) equipped with a platinum plate anode and a platinum plate cathode (both 10 × 10 × 0.1 mm). The cell was then charged with a DMF/H_2O mixture (3:1 v/v, 2.0 mL). The two electrodes were positioned parallel to each other with a distance of approximately 0.5 cm. No pretreatment was applied to the electrode. The reaction was performed at 30 °C for 1 h under constant-current electrolysis (20 mA) with stirring at 500 rpm. At the end of the reaction, the electrode was removed, the reaction solution was diluted in saturated salt water (10 mL), extracted with ethyl acetate (10 mL × 3), and the organic phase was combined and washed with saturated salt water (10 mL × 3). The organic phase was dried with anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel thin layer chromatography (EA) to obtain pure target compounds.

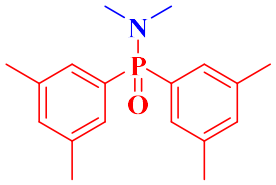


***N,N*-Dimethyl-*P,P*-diphenylphosphinic amide (3aa)** [1]**:** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 58% (28.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ

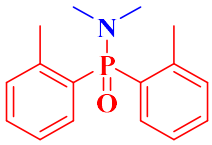
7.80-7.75 (m, 4H), 7.40-7.35 (m, 6H), 2.59 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.3 (d, J = 9.2 Hz), 131.8 (d, J = 2.7 Hz), 131.1, 128.6 (d, J = 12.2 Hz), 37.1 (d, J = 2.3 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.42.



***N,N*-Dimethyl-*P,P*-di-*p*-tolylphosphinic amide (3ba):** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 66% (36.0 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76-7.71 (m, 4H), 7.26-7.23 (m, 4H), 2.66 (s, 3H), 2.63 (s, 3H), 2.37 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.1 (d, J = 2.9 Hz), 132.3 (d, J = 9.5 Hz), 129.3 (d, J = 12.7 Hz), 128.0, 37.1 (d, J = 2.4 Hz), 21.6; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.98; IR: 3714, 3634, 3519, 2528, 2055, 1275, 751, 567; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{20}NOPNa$: 296.1175, found 296.1178.

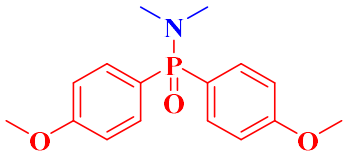


***P,P*-Bis(3,5-dimethylphenyl)-*N,N*-dimethylphosphinic amide (3ca):** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 72% (43.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 12.0 Hz, 4H), 7.10 (s, 2H), 2.66 (s, 3H), 2.64 (s, 3H), 2.33 (s, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.2 (d, J = 13 Hz), 133.4 (d, J = 2.9 Hz), 131.5 (d, J = 127.4 Hz), 129.9 (d, J = 9.1 Hz), 37.2 (d, J = 2.2 Hz), 21.3; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 32.32; IR: 3724, 3439, 2915, 2308, 1599, 1454, 1273, 966, 852, 750; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{24}NOPNa$: 324.1488, found 324.1491.

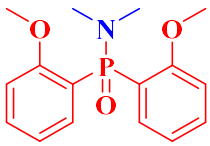


***N,N*-Dimethyl-*P,P*-di-*o*-tolylphosphinic amide (3da):** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 39% (21.3 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42-7.39 (m, 2H), 7.34-7.26 (m, 4H), 7.22-7.18 (m, 2H), 2.76 (s, 3H), 2.73 (s, 3H), 2.54 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.0 (d, J = 8.6 Hz), 132.6 (d, J = 12 Hz), 131.8 (d, J = 11.2 Hz), 131.7 (d, J = 2.7 Hz), 130. 6 (d, J = 122.2 Hz), 125.4 (d,

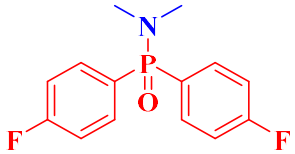
J = 13 Hz), 36.8 (d, J = 4.2 Hz), 21.4 (d, J = 3.7 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 37.15; IR: 2923, 2823, 1593, 1451, 1187, 982, 806, 765, 707; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{20}NOPNa$: 296.1175, found 296.1178.



***P,P*-Bis(4-methoxyphenyl)-*N,N*-dimethylphosphinic amide (3ea):** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 85% (51.9 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 11.2, 8.3 Hz, 4H), 6.95 (d, *J* = 7.4 Hz, 4H), 3.82 (s, 6H), 2.65 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.2 (d, J = 2.9 Hz), 134.0 (d, J = 10.3 Hz), 123.3 (d, J = 135.7 Hz), 114.0 (d, J = 13.3 Hz), 55.3, 37.0 (d, J = 2.4 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.57; IR: 3793, 3556, 2010, 1275, 750, 551; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{20}NO_3PNa$: 328.1073, found 328.1076.

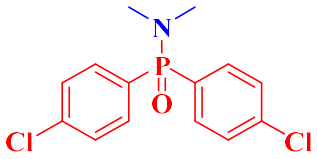


***P,P*-Bis(2-methoxyphenyl)-*N,N*-dimethylphosphinic amide (3fa) :** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 68% (41.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 14.4, 7.4 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.96 (dt, *J* = 28.7, 7.6 Hz, 4H), 3.75 (s, 6H), 2.69 (s, 3H), 2.66 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.2 (d, J = 2.6 Hz), 134.7 (d, J = 8.1 Hz), 133.3, 120.5 (d, J = 12.7 Hz), 110.8 (d, J = 7 Hz), 55.6, 36.8 (d, J = 5.1 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.84; IR: 2909, 1955, 1589, 1476, 1273, 1188, 981, 802, 757; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{20}NO_3PNa$: 328.1073, found 328.1076.

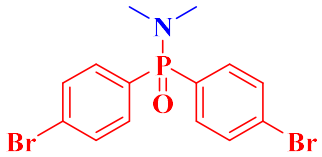


***P,P*-Bis(4-fluorophenyl)-*N,N*-dimethylphosphinic amide (3ga):** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 70% (39.3mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90-7.81 (m, 4H), 7.16 (tt, *J* = 8.8, 2.1 Hz, 4H), 2.67 (d, *J* = 1.7 Hz, 3H), 2.64 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0 (dd, J = 251.9, 3.5 Hz), 134.8 (dd, J = 10.4, 8.6 Hz), 127.5 (dd, J = 133.0, 3.4 Hz), 116.0 (dd, J

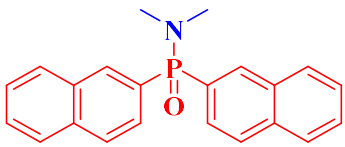
= 21.2, 13.6 Hz), 37.0 (d, J = 2.3 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.67; ^{19}F NMR (377 MHz, $CDCl_3$) δ -106.95; IR: 3627, 2891, 2323, 1590, 1498, 1157, 970, 831, 750; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}F_2NOPNa$: 304.0673, found 304.0676.



***P,P*-Bis(4-chlorophenyl)-*N,N*-dimethylphosphinic amide (3ha):** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 75% (47.0 mg); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (dd, J = 11.1, 8.5 Hz, 4H), 7.45 (dd, J = 8.3, 2.6 Hz, 4H), 2.67 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.6 (d, J = 3.7 Hz), 133.7 (d, J = 9.9 Hz), 130.5, 129.1 (d, J = 12.8 Hz), 37.1 (d, J = 2.4 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.77; IR: 3553, 2927, 2221, 1583, 1480, 1180, 1085, 968, 823, 757, 718; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}Cl_2NOPNa$: 336.0082, found 336.0082.

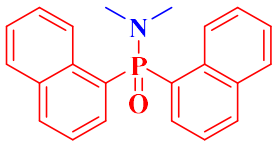


***P,P*-Bis(4-bromophenyl)-*N,N*-dimethylphosphinic amide (3ia):** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 58% (46.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (ddt, *J* = 11.4, 8.1, 2.9 Hz, 4H), 7.60 (ddd, *J* = 8.1, 4.4, 2.4 Hz, 4H), 2.66 (d, *J* = 4.1 Hz, 3H), 2.63 (d, *J* = 4.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.8 (d, J = 9.9 Hz), 132.1 (d, J = 12.8 Hz), 130.3 (d, J = 131.0 Hz), 127.3 (d, J = 3.6 Hz), 37.1 (d, J = 2.3 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.05; IR: 2920, 2324, 1574, 1475, 1384, 1166, 1009, 967, 816, 742, 688; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}Br_2NOPNa$: 423.9072, found 423.9070.

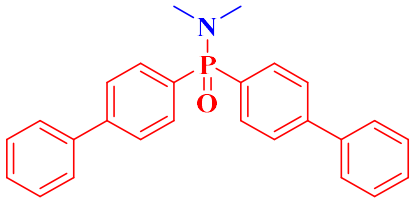


***N,N*-Dimethyl-*P,P*-di(naphthalen-2-yl)phosphinic amide (3ja):** Purified by PTLC; R_f = 0.5 (EA); Light yellow solid; M.p. = 123-124 °C; Isolated yield 76% (52.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 13.9 Hz, 2H), 7.88 (td, *J* = 20.3, 18.8, 7.9 Hz, 8H), 7.53 (p, *J* = 6.5 Hz, 4H), 2.76 (s, 3H), 2.73 (s, 3H); ^{13}C NMR (101 MHz,

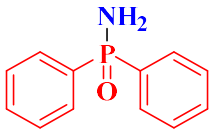
Chloroform-*d*) δ 134.8 (d, J = 9.1 Hz), 134.7 (d, J = 2.3 Hz), 132.7 (d, J = 13.7 Hz), 129.5, 129.0, 128.5 (d, J = 11.9 Hz), 128.1, 127.7, 126.9 (d, J = 9.4 Hz), 126.8, 37.2 (d, J = 2.2 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.43; IR: 3052, 2924, 1590, 1455, 1271, 1185, 1087, 968, 819, 745; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{22}H_{20}NOPNa$: 368.1175, found 368.1172.



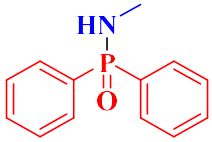
***N,N*-Dimethyl-*P,P*-di(naphthalen-1-yl)phosphinic amide (3ka):** Purified by PTLC; R_f = 0.5 (EA); Light yellow solid; M.p. = 130-131 ℃; Isolated yield 75% (51.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.85-8.79 (m, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.93-7.86 (m, 2H), 7.60-7.48 (m, 7H), 7.42-7.35 (m, 2H), 2.85 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.0 (dd, J = 8.6, 5.6 Hz), 133.0, 133.0 (d, J = 14.9 Hz), 129.4, 128.7 (d, J = 1.5 Hz), 128.2, 127.6 (d, J = 4.8 Hz), 127.5, 126.5, 124.5 (d, J = 15 Hz), 37.1 (d, J = 4.4 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 37.71; IR: 3056, 2925, 2325, 1504, 1194, 989, 833, 775; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{22}H_{20}NOPNa$: 368.1175, found 368.1175.



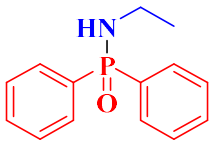
***P,P*-Di([1,1'-biphenyl]-4-yl)-*N,N*-dimethylphosphinic amide (3la):** Purified by PTLC; R_f = 0.5 (EA); Light yellow solid; M.p. = 101-102 ℃; Isolated yield 69% (54.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 11.3, 8.2 Hz, 4H), 7.68 (dd, *J* = 8.2, 2.9 Hz, 4H), 7.58 (d, *J* = 7.2 Hz, 4H), 7.43 (t, *J* = 7.4 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 2H), 2.74 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6 (d, J = 2.8 Hz), 140.0, 132.9 (d, J = 9.4 Hz), 130.4 (d, J = 130.3 Hz), 128.9, 128.1, 127.4 (d, J = 12.7 Hz), 127.3, 37.2 (d, J = 2.3 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.40; IR: 3029, 2926, 1597, 1481, 1185, 966, 820, 760, 672; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{24}NOPNa$: 420.1488, found 420.1486.



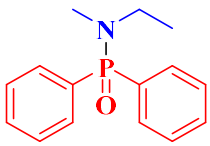
***P,P*-Diphenylphosphinic amide (3ab)** [2]**:** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 49% (21.3 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88-7.83 (m, 4H), 7.46-7.35 (m, 6H), 3.63 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.0, 132.7, 131.8 (d, J = 9.7 Hz), 128.5 (d, J = 12.6 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 22.51.



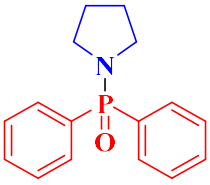
***N*-Methyl-*P,P*-diphenylphosphinic amide (3ac)** [2]**:** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 58% (26.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88-7.83 (m, 4H), 7.50-7.37 (m, 6H), 3.00 (s, 1H), 2.63 (dd, *J* = 12.4, 5.9 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.1 (d, J = 128.7 Hz), 132.1 (d, J = 9.4 Hz), 131.8 (d, J = 2.8 Hz), 128.6 (d, J = 12.4 Hz), 26.8 (d, J = 2.1 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.42.



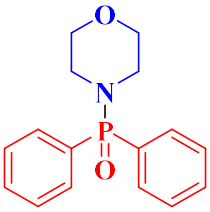
***N*-Ethyl-*P,P*-diphenylphosphinic amide (3ad)** [3]**:** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 56% (27.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93-7.87 (m, 4H), 7.53-7.40 (m, 6H), 3.05-2.09 (m, 2H), 2.89 (s, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.4 (d, J = 128.9 Hz), 132.1 (d, J = 9.4 Hz), 131.8 (d, J = 2.8 Hz), 128.6 (d, J = 12.5 Hz), 35.7 (d, J = 1.8 Hz), 17.7 (d, J = 7.5 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 23.85.



***N*-Ethyl-*N*-methyl-*P,P*-diphenylphosphinic amide (3ae)** [4]**:** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 54% (28.0 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 11.7, 7.5 Hz, 4H), 7.52-7.39 (m, 6H), 2.99 (p, *J* = 7.3 Hz, 2H), 2.64 (d, *J* = 11.2 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.3 (d, J = 9.2 Hz), 132.0 (d, J = 128.7 Hz), 131.7 (d, J = 2.4 Hz), 128.6 (d, J = 12.3 Hz), 43.8, 33.3, 13.6 (d, J = 5.4 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.34.

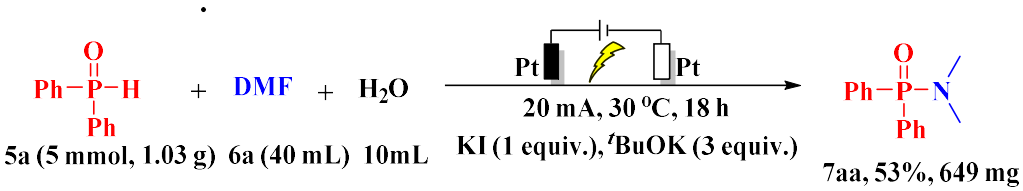


Diphenyl(pyrrolidin-1-yl)phosphine oxide (3af) [2]**:** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 63% (34.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92-7.82 (m, 4H), 7.50-7.41 (m, 6H), 3.12 (dd, *J* = 9.1, 4.3 Hz, 4H), 1.92-1.82 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.6 (d, J = 129.0 Hz), 132.2 (d, J = 9.3 Hz), 131.6 (d, J = 2.8 Hz), 128.5 (d, J = 12.3 Hz), 46.9 (d, J = 2.2 Hz), 26.7 (d, J = 6.7 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.57.



Morpholinodiphenylphosphine oxide (3ag) [5]**:** Purified by PTLC; R_f = 0.5 (EA); Yellow oil; Isolated yield 58% (33.3 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91-7.86 (m, 4H), 7.57-7.43 (m, 6H), 3.72 (t, *J* = 4.6 Hz, 4H), 3.10-3.06 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.4 (d, J = 9.1 Hz), 132.0 (d, J = 2.7 Hz), 130.8 (d, J = 128.3 Hz), 128.8 (d, J = 12.4 Hz), 67.2 (d, J = 6.9 Hz), 45.0; ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.16.

6. Gram-scale preparation of 3aa



Diphenylphosphine oxide (5 mmol), KI (5 mmol), ^{t}BuOK (15 mmol) and DMF: H_2O mixture (4:1 v/v, 50 mL) were added into a 100 mL three-neck flask. Platinum plate anode and cathode (both 10 mm × 10 mm × 0.1 mm) were placed with an inter-electrode distance of ~0.5 cm, and electrolyzed with a constant current of 20 mA at 30 °C for 18 h with stirring at 700 rpm. No pretreatment was applied to the electrode. At the end of the reaction, the electrode was removed, the reaction solution was diluted in saturated salt water (50 mL), extracted with ethyl acetate (30 mL × 3), and the organic phase was

combined and washed with saturated salt water (40 mL × 3). The organic phase was dried with anhydrous sodium sulfate and concentrated under reduced pressure. The mixture was subjected to column chromatography to obtain the target product.

7. Green chemistry metrics

Atom Economy (AE) Calculation for the Model Reaction (synthesis of **3aa**):

The AE is calculated based on the incorporation of all atoms from the stoichiometric reactants (diphenylphosphine oxide and DMF) into the target product.

AE (%) = (Molecular weight of product **3aa** / Sum of molecular weights of reactants) × 100% = [245.3 / (202.2 + 73.1)] × 100% = 89.1%

Faradaic Efficiency (FE) Calculation:

The FE, representing the efficiency of charge utilization for product formation, was determined for both scales, n=2 electrons transferred per molecule of product formed, consistent with the proposed radical-radical coupling mechanism.

Model Reaction (0.2 mmol scale):

Charge passed (Q) = Current (I) × Time (t) = 0.020 A × 1.0 h × 3600 s/h = 72.0 C

Moles of **3aa** produced (N)=0.2×10^{-3} mol×58% (isolated yield)=1.16×10^{-4} mol

FE (%)=(n×F×N/Q)×100% = (2×96485 C/mol×1.16×10^{-4} mol)/72.0 C×100%=31.1%

Gram-scale Reaction (5 mmol scale):

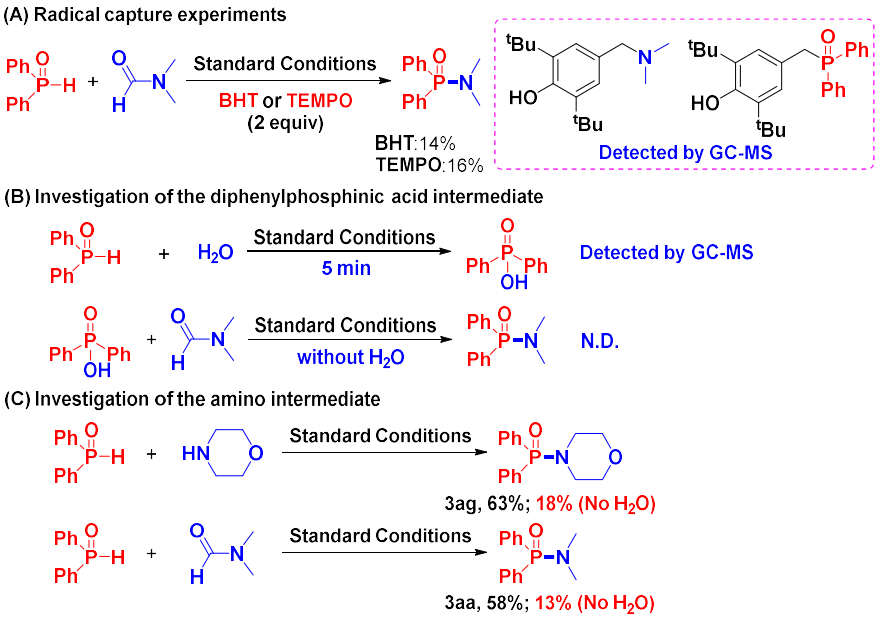
Charge passed (Q) = 0.020 A × 18.0 h × 3600 s/h = 1296.0 C

Moles of **3aa** produced (N)= 5.0×10^{-3}mol×53%(isolated yield) = 2.65×10^{-3} mol

FE (%) = (2 × 96485 C/mol × 2.65×10^{-3} mol) / 1296.0 C × 100% = 39.5%

These quantitative metrics demonstrate that the developed method possesses a high Atom Economy (~89%) and moderate FE, which improved upon scale-up. The moderate FE values are characteristic of indirect electrolysis systems employing a redox mediator ($I^-/I\bullet$), where charge consumption is shared with competing processes such as mediator over-oxidation.

8. Control experiments



For (A): Diphenylphosphine oxide (0.2 mmol), KI (0.2 mmol), ^{t}BuOK (0.6 mmol), TEMPO (0.4 mmol) or BHT (0.4 mmol) and DMF: H_2O mixture (3:1 v/v, 2 mL) were added into a 10 mL three-neck flask. The platinum bipolar electrode (10 mm × 10 mm × 0.1 mm) was immersed into the reaction system, and electrolyzed with a constant current of 20 mA at 30 °C for 1 h. At the end of the reaction, the electrode was removed, the reaction solution was diluted in saturated salt water (10 mL), extracted with ethyl acetate (10 mL × 3), and the organic phase was combined and washed with saturated salt water (10 mL × 3). The organic phase was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The yield was NMR yield, related compounds are detected by GC-MS.

For (B): Diphenylphosphinic acid (0.2 mmol), KI (0.2 mmol), ^{t}BuOK (0.6 mmol) and DMF: H_2O mixture (3:1 v/v, 2 mL) were added into a 10 mL three-neck flask. The platinum bipolar electrode (10 mm × 10 mm × 0.1 mm) was immersed into the reaction system, and electrolyzed with a constant current of 20 mA at 30 °C for 1 h. At the end of the reaction, the electrode was removed, the reaction solution was diluted in saturated salt water (10 mL), extracted with ethyl acetate (10 mL × 3), and the organic phase was combined and washed with saturated salt water (10 mL × 3). The organic phase was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The yield was NMR yield, related compounds are detected by GC-MS.

For (C): Procedure for Strictly Anhydrous Reactions.

DMF was rendered anhydrous by refluxing over calcium hydride (CaH_2) for 12 h

followed by distillation under argon prior to use. All glassware was flame-dried under vacuum and subjected to three vacuum-argon refill cycles. Solid reagents (KI, ^{t}BuOK) and electrodes were dried in vacuo overnight. Diphenylphosphinic acid (0.2 mmol), KI (0.2 mmol), ^{t}BuOK (0.6 mmol), and anhydrous morpholine or the freshly distilled DMF (2 mL) were added into the pre-dried 10 mL three-neck flask inside a glovebox. The reaction setup was then transferred out and conducted under a continuous flow of high-purity argon (99.999%). The platinum bipolar electrode (10 mm × 10 mm × 0.1 mm) was immersed into the reaction system, and electrolyzed with a constant current of 20 mA at 30 °C for 1 h. At the end of the reaction, the electrode was removed, the reaction solution was diluted in saturated salt water (10 mL), extracted with ethyl acetate (10 mL × 3), and the organic phase was combined and washed with saturated salt water (10 mL × 3). The organic phase was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The yields were isolated yield.

9. References

[1] R. Zhu, C. Pan, Z. Gu, A catalyst-free synthesis of phosphinic amides using *O*-benzoylhydroxylamines, *Org. Lett.* **2015**, *17*, 5862-5865.

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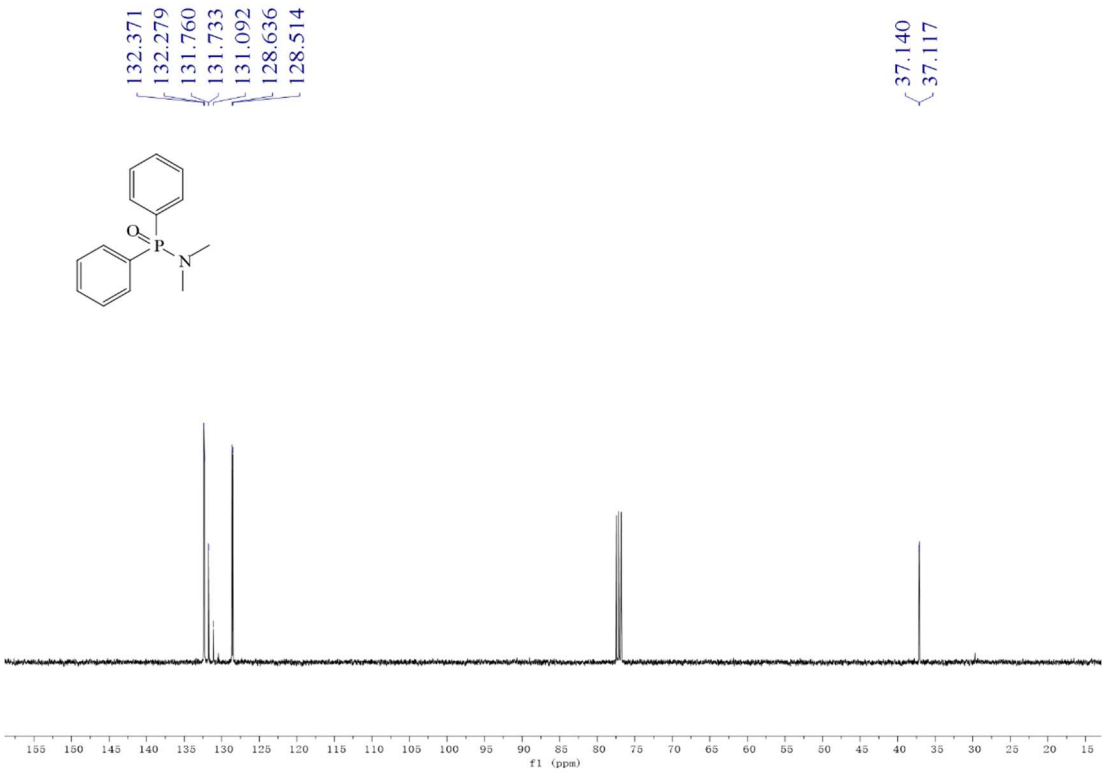
[4] N. A. Bondarenko, A. V. Kharlamov, A. G. Vendilo, Synthesis of nonsymmetrical dialkylamines on the basis of diphenylphosphinic amides, *Russ. Chem. Bull.* **2009**, *58*, 1872-1885.

[5] Y. Wang, P. Qian, J.-H. Su, Y. Li, M. Bi, Z. Zha, Z. Wang, Efficient electrosynthesis of phosphinic amides via oxidative cross-coupling between N–H/P–H, *Green Chem.* **2017**, *19*, 4769-4773.

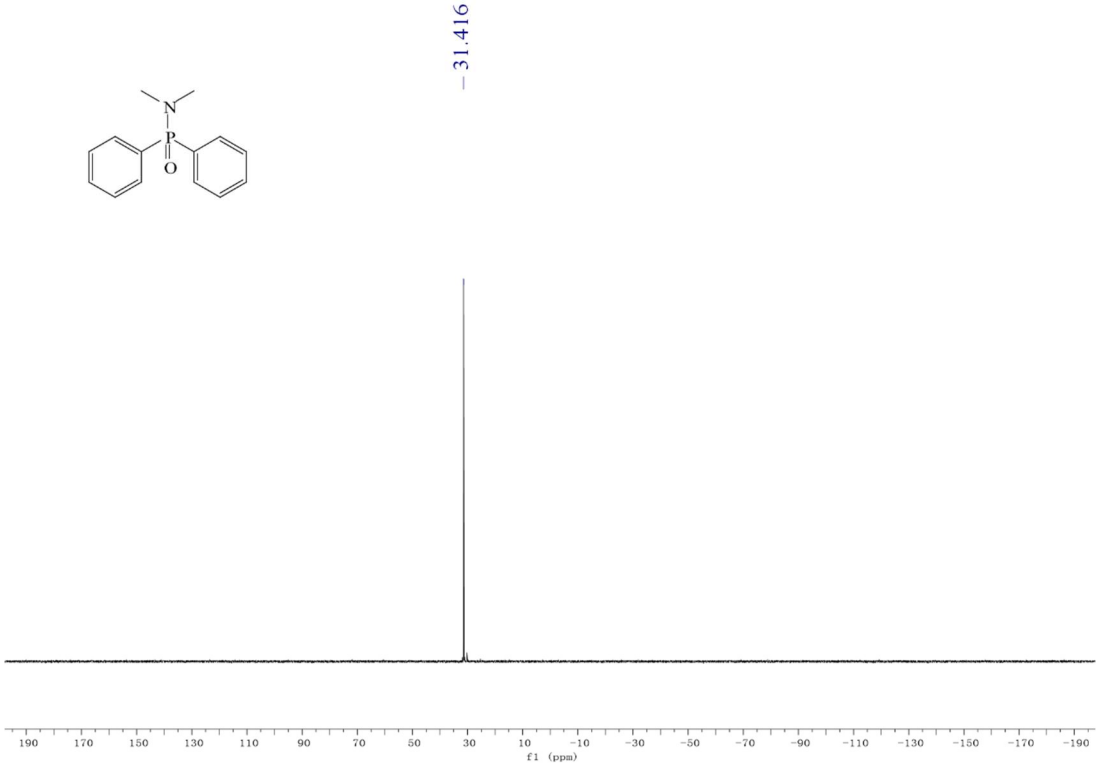
10. Copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra

^{1}H NMR spectrum of 3aa (400 MHz, $CDCl_3$)

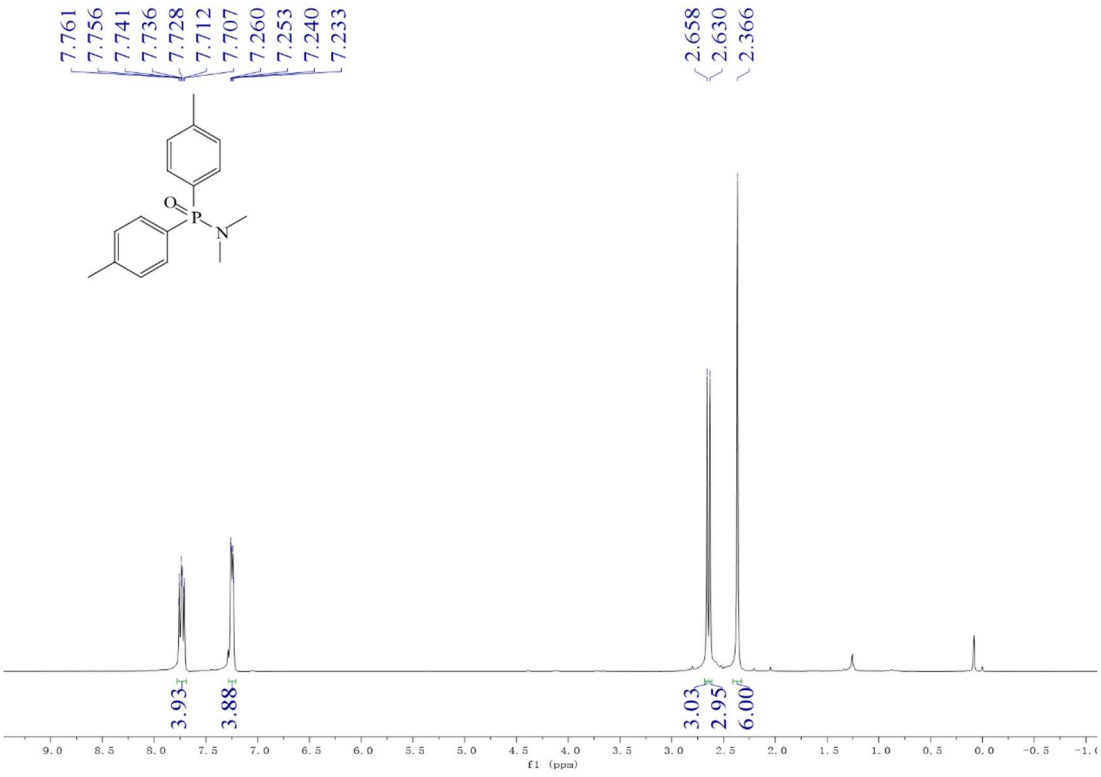
^{13}C NMR spectrum of 3aa (100 MHz, $CDCl_3$)



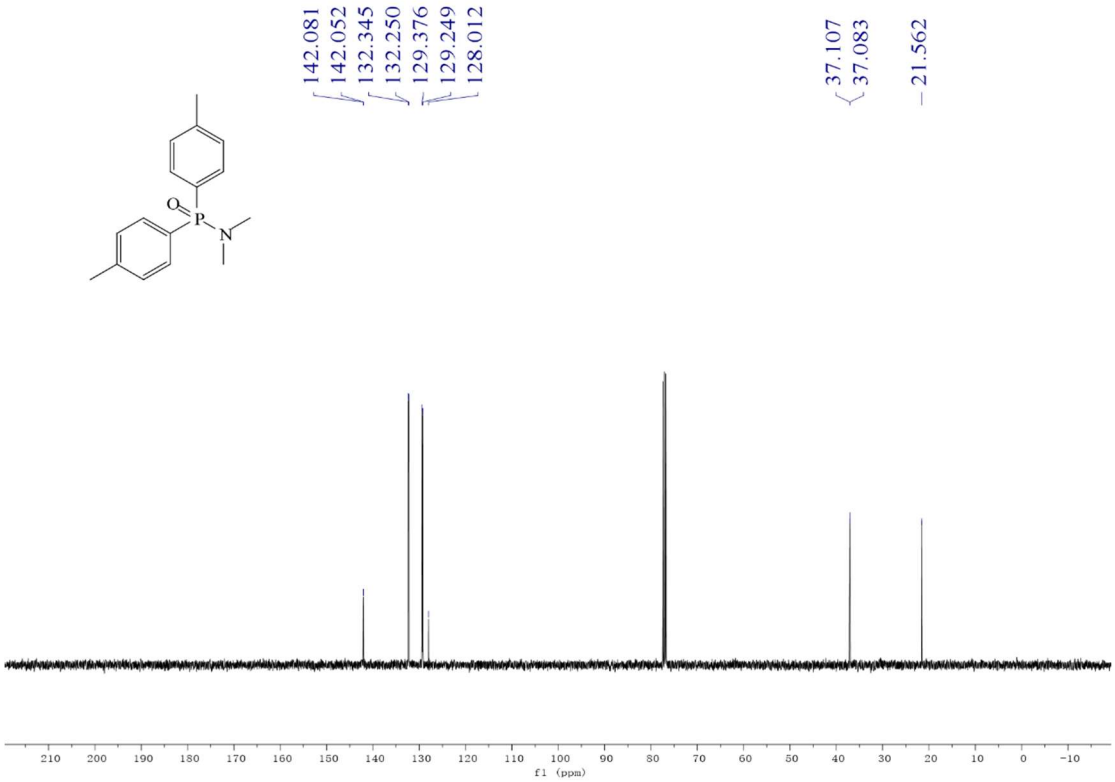
^{31}P NMR spectrum of 3aa (162 MHz, $CDCl_3$)



^{1}H NMR spectrum of 3ba (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3ba (100 MHz, $CDCl_3$)



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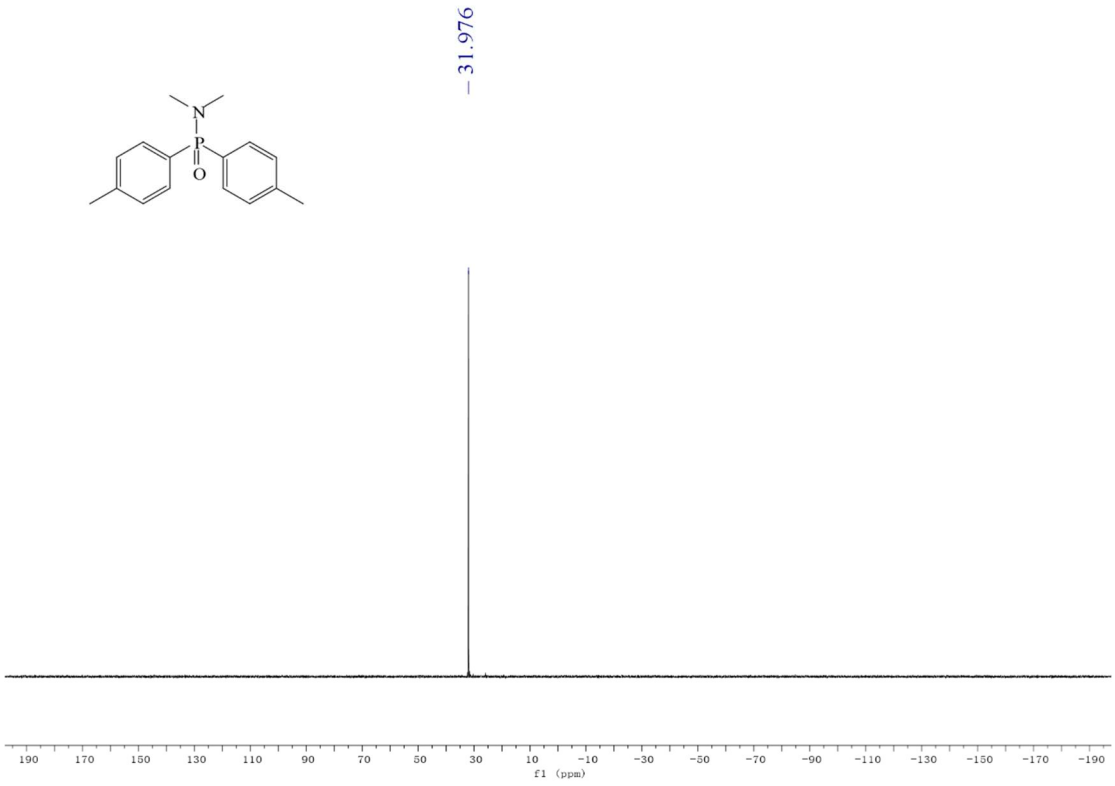
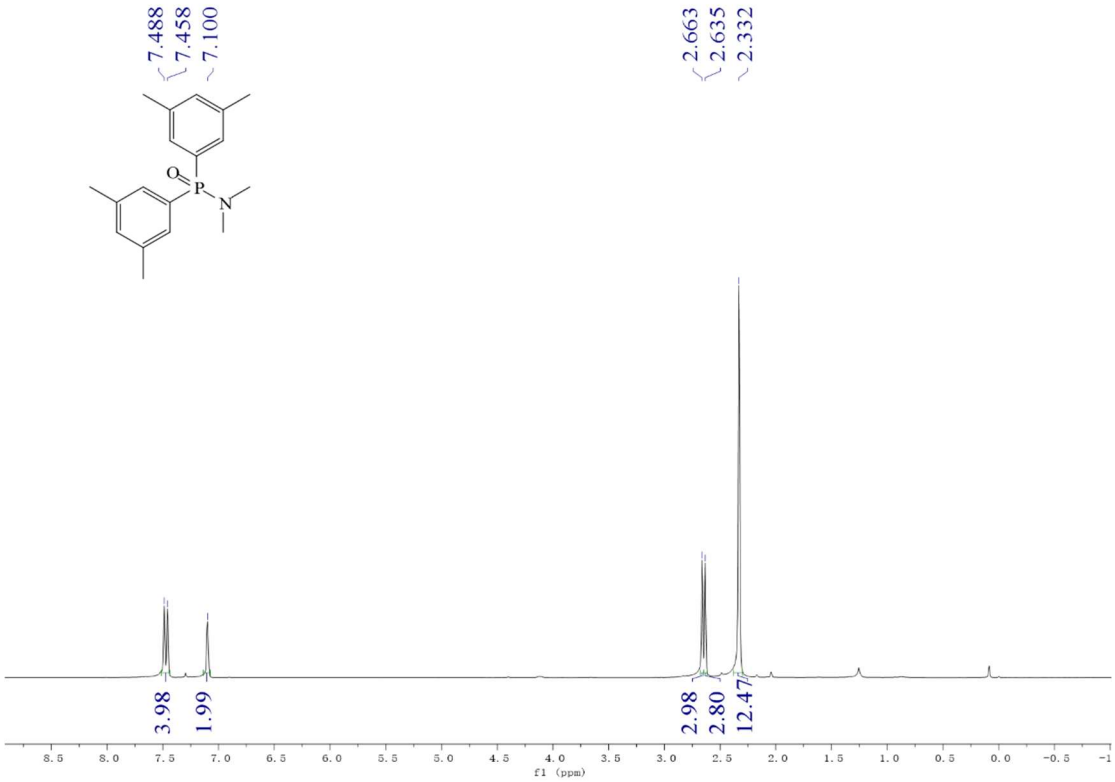
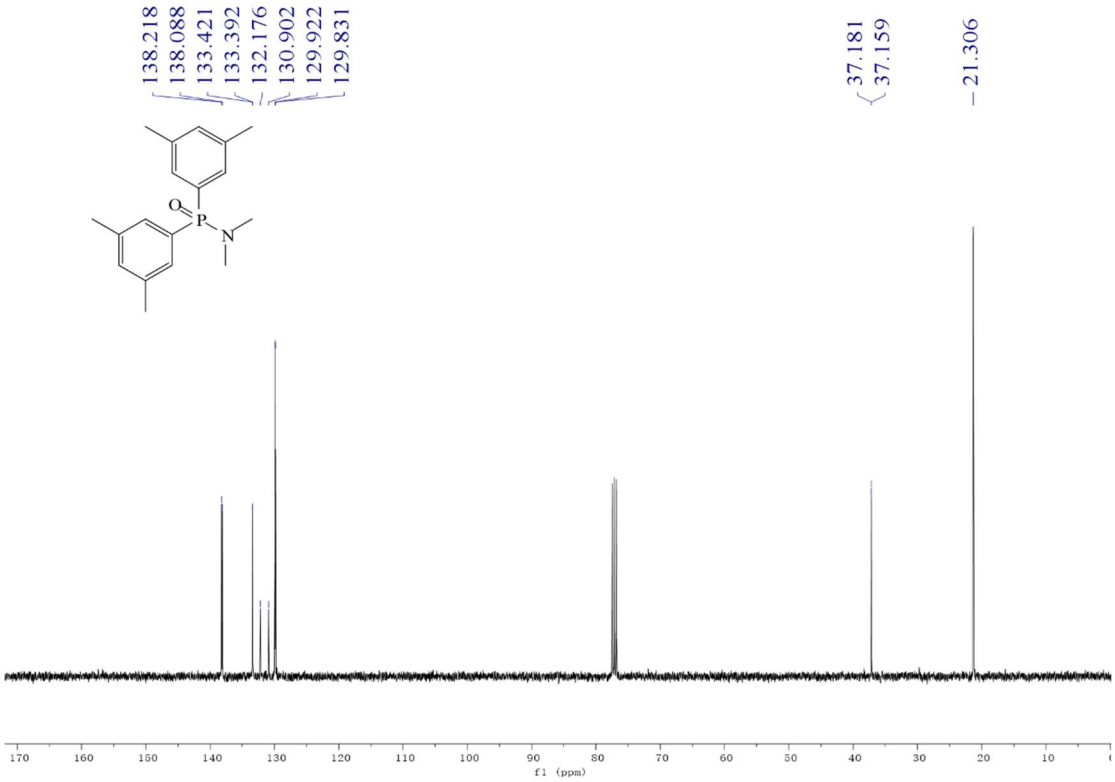


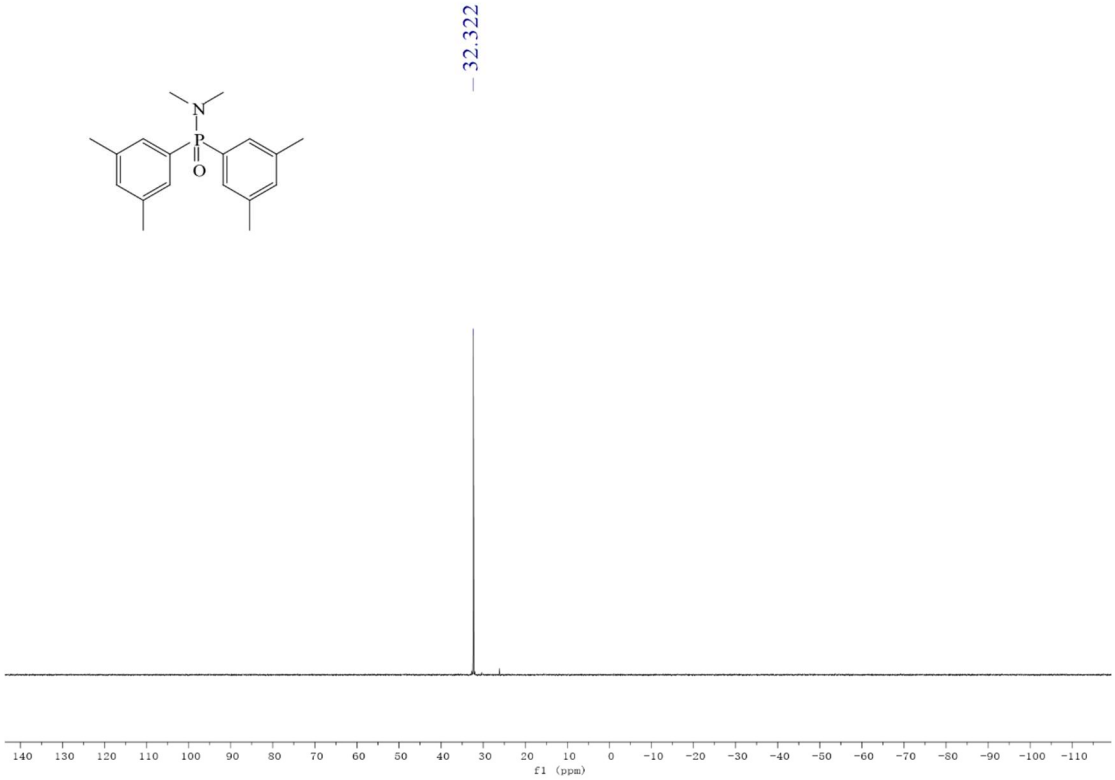
^{1}H NMR spectrum of 3ca (400 MHz, $CDCl_3$)



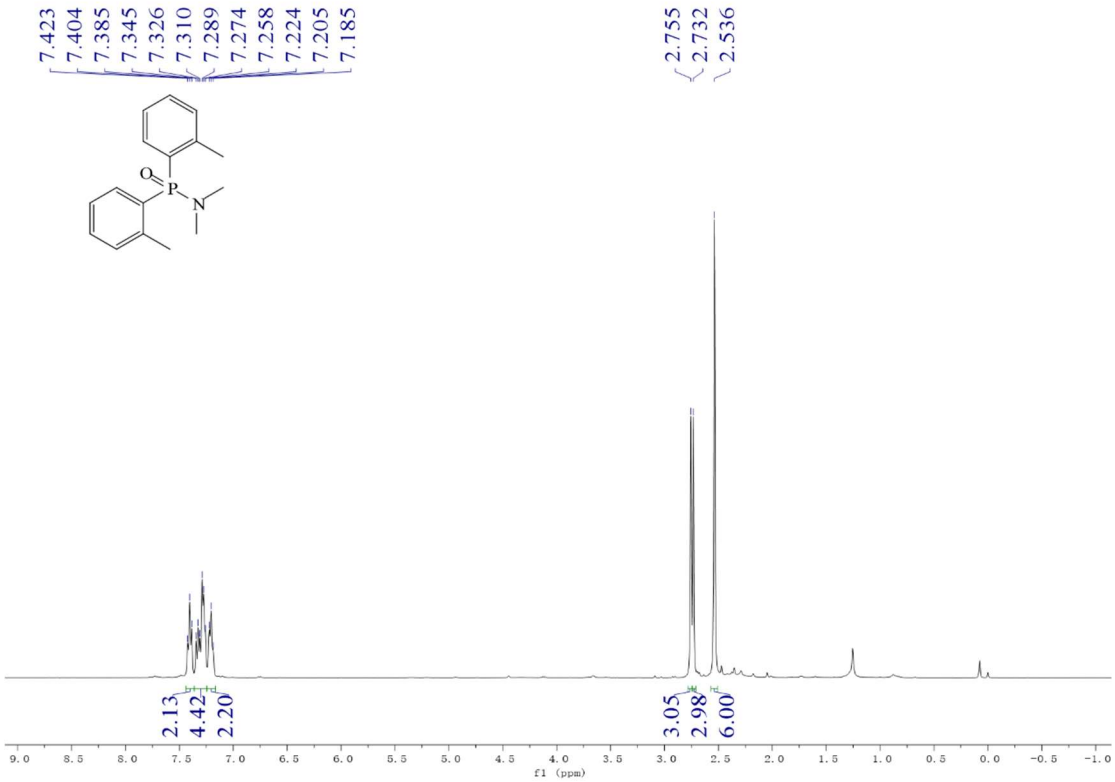
^{13}C NMR spectrum of 3ca (100 MHz, $CDCl_3$)



^{31}P NMR spectrum of 3ca (162 MHz, $CDCl_3$)



^{1}H NMR spectrum of 3da (400 MHz, $CDCl_3$)



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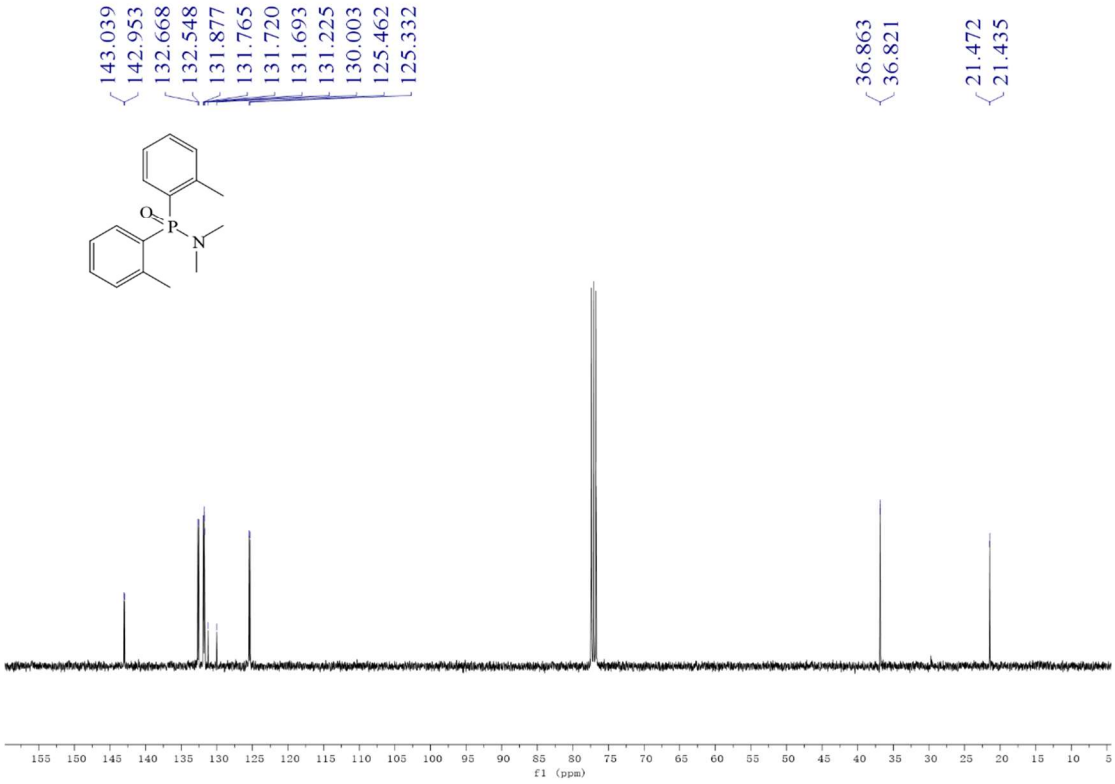

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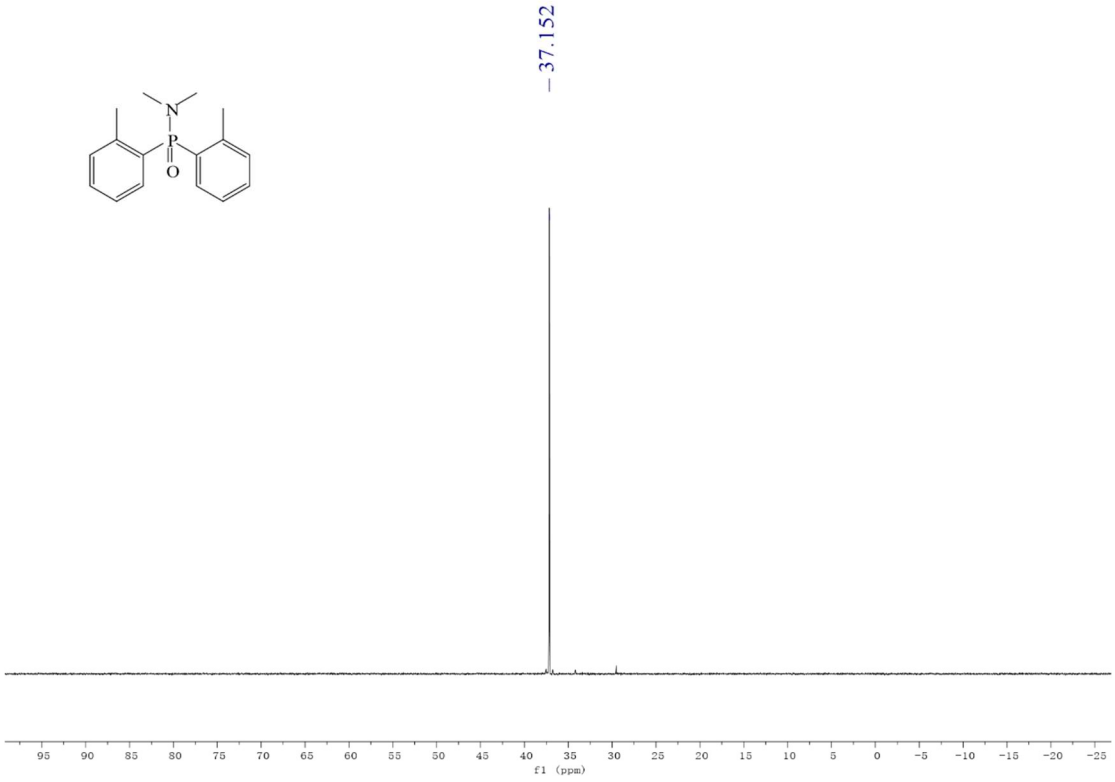
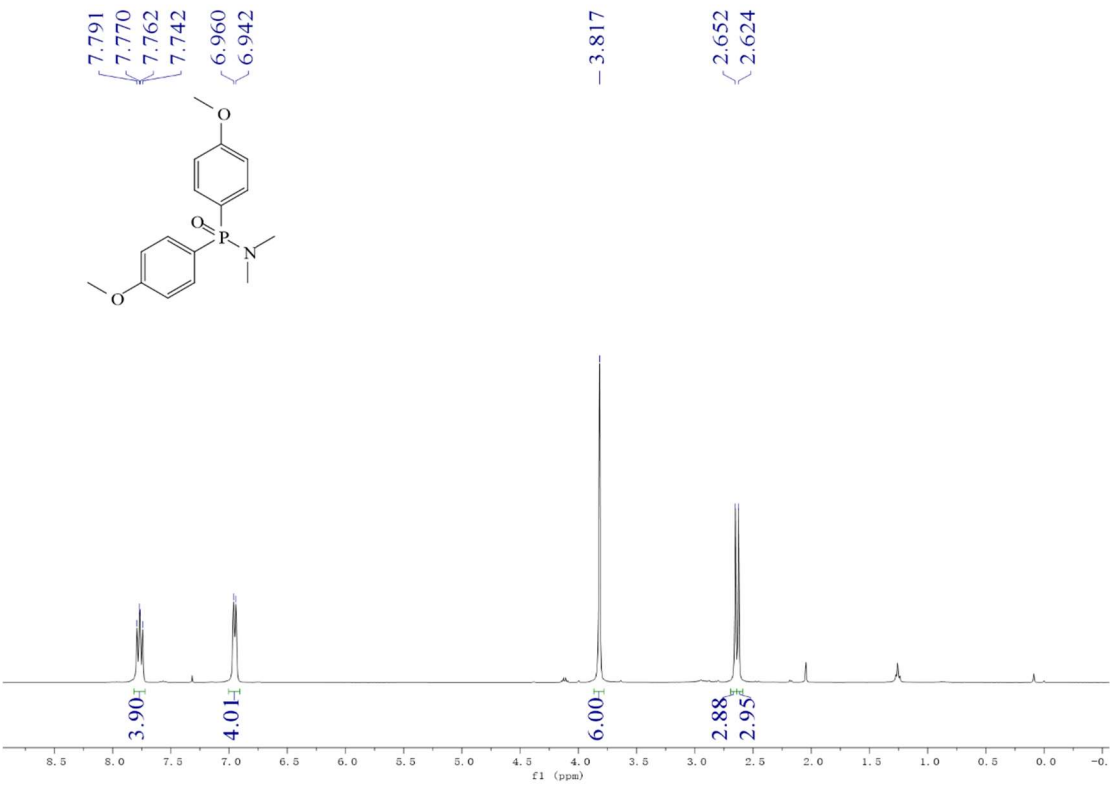
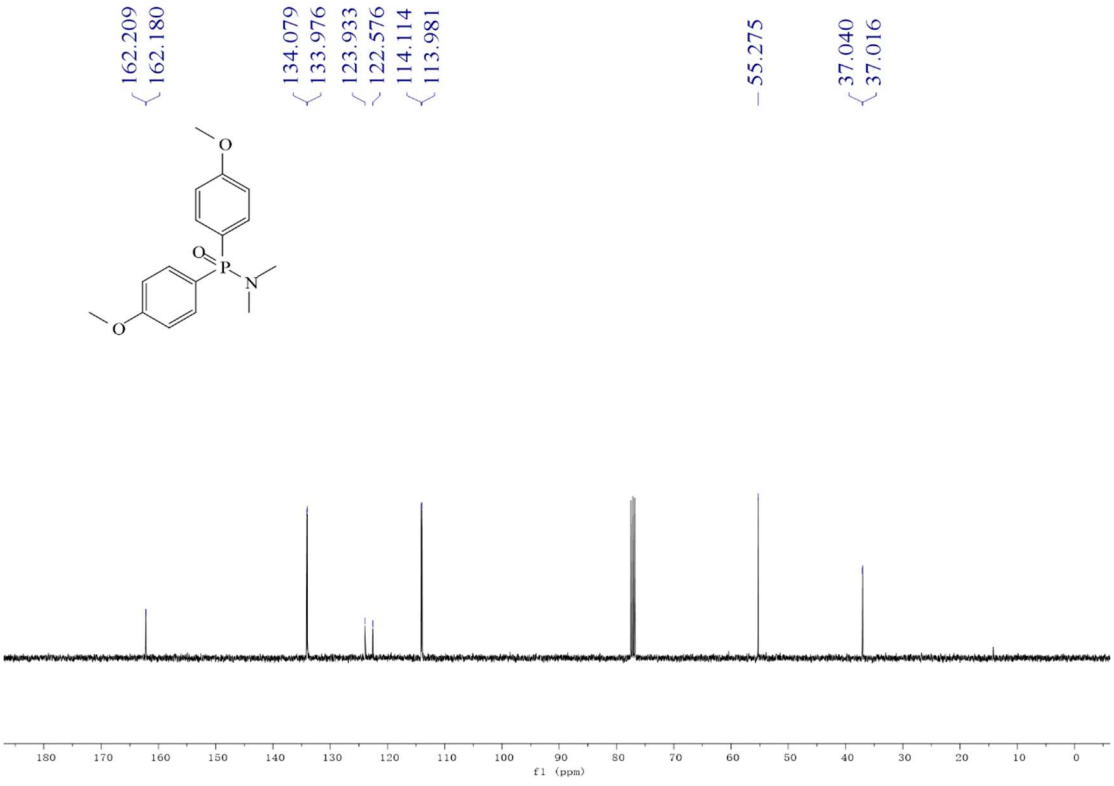


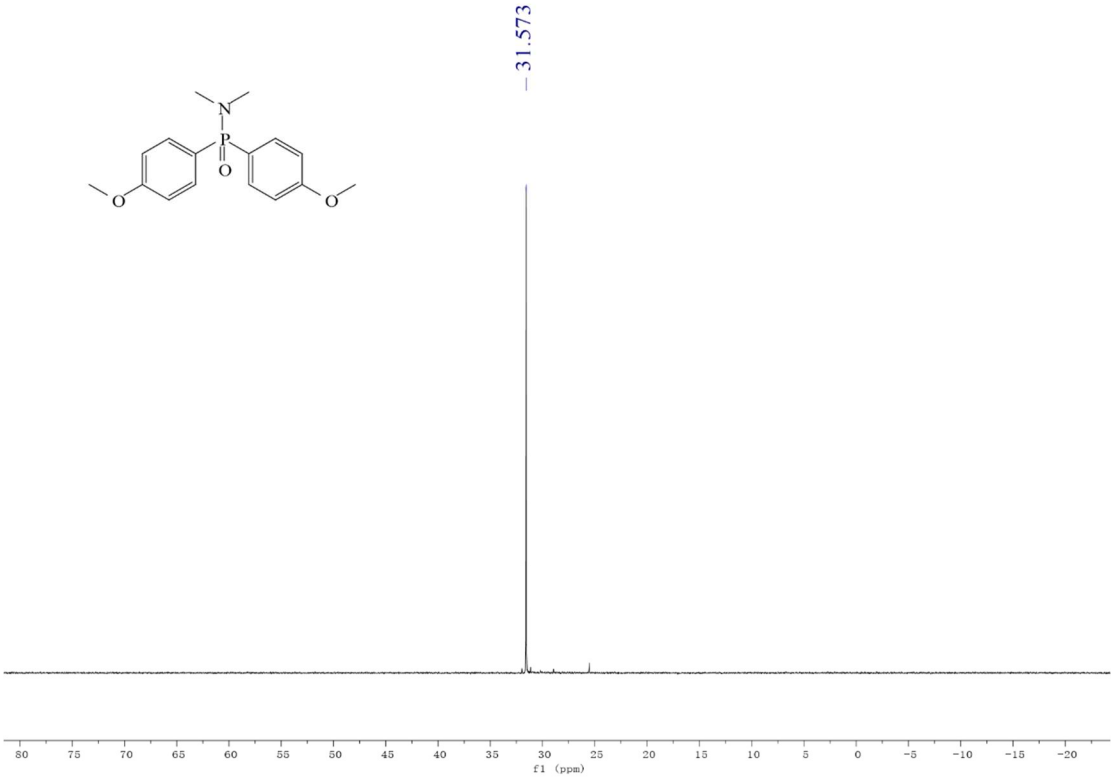
^{1}H NMR spectrum of 3ea (400 MHz, $CDCl_3$)



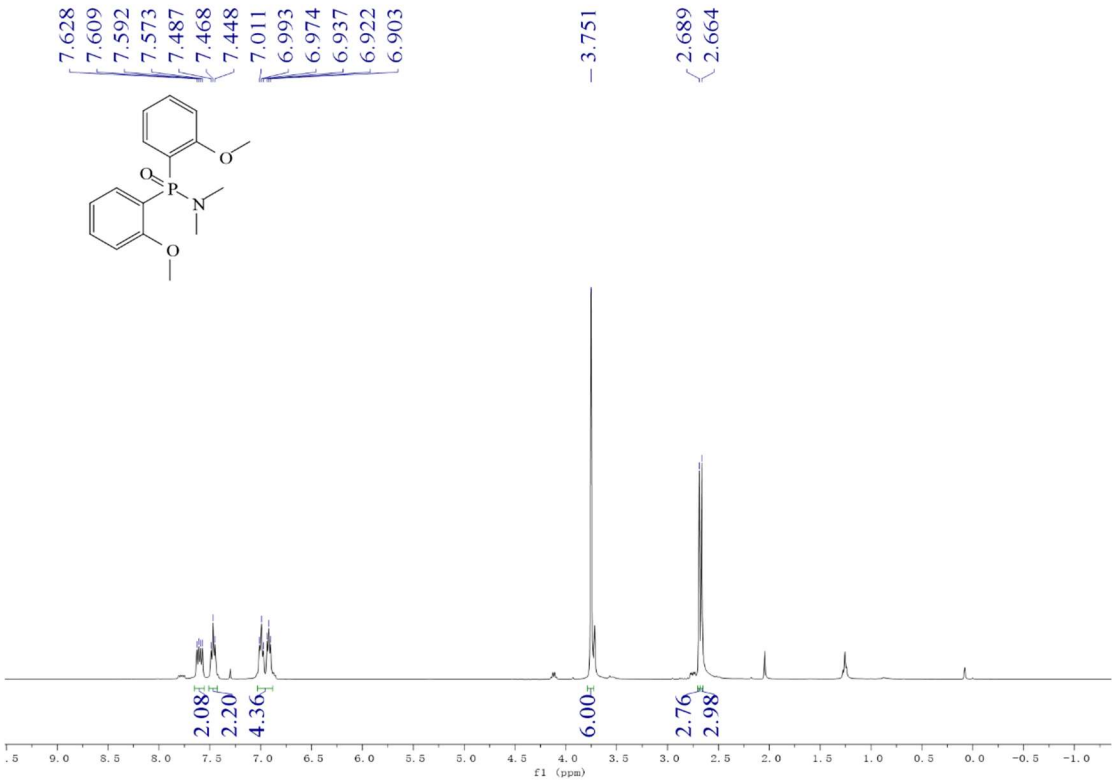
^{13}C NMR spectrum of 3ea (100 MHz, $CDCl_3$)



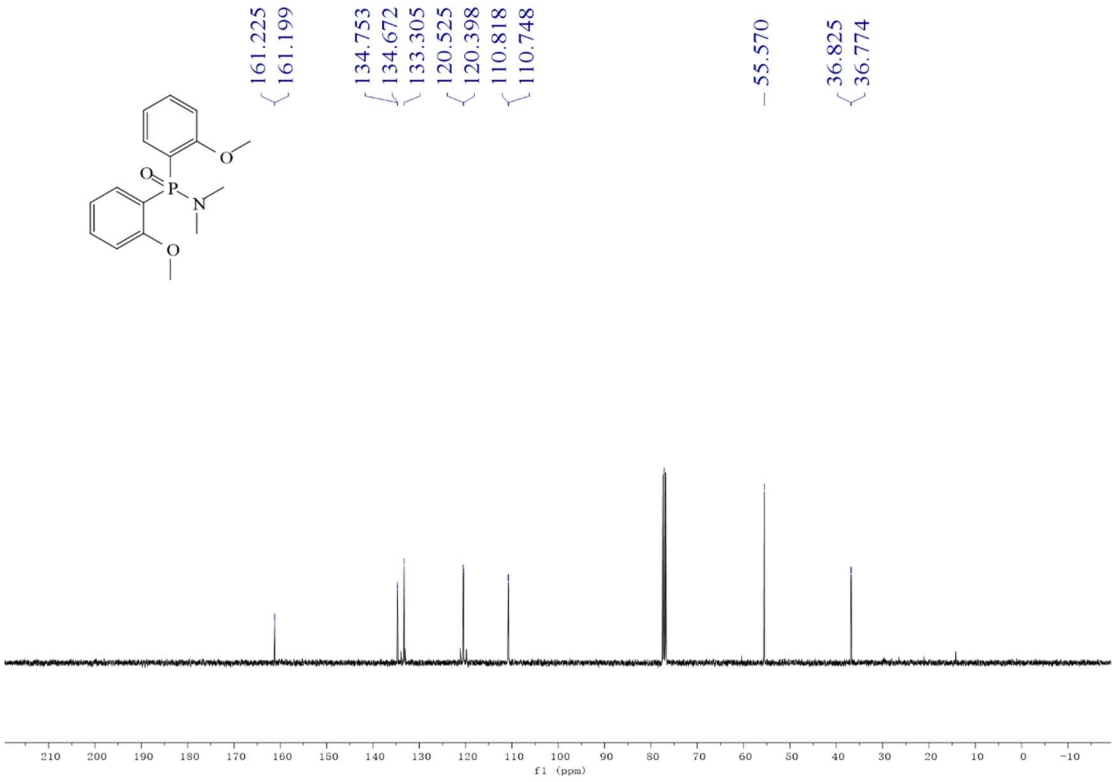
^{31}P NMR spectrum of 3ea (162 MHz, $CDCl_3$)



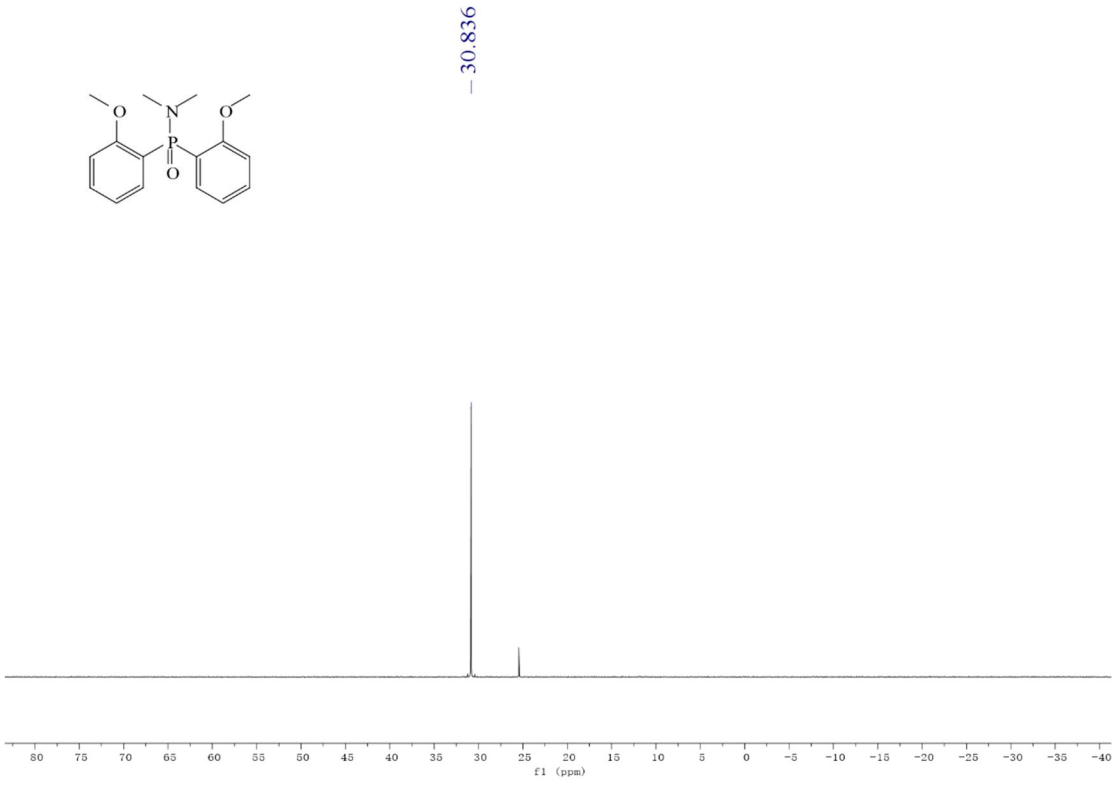
^{1}H NMR spectrum of 3fa (400 MHz, $CDCl_3$)



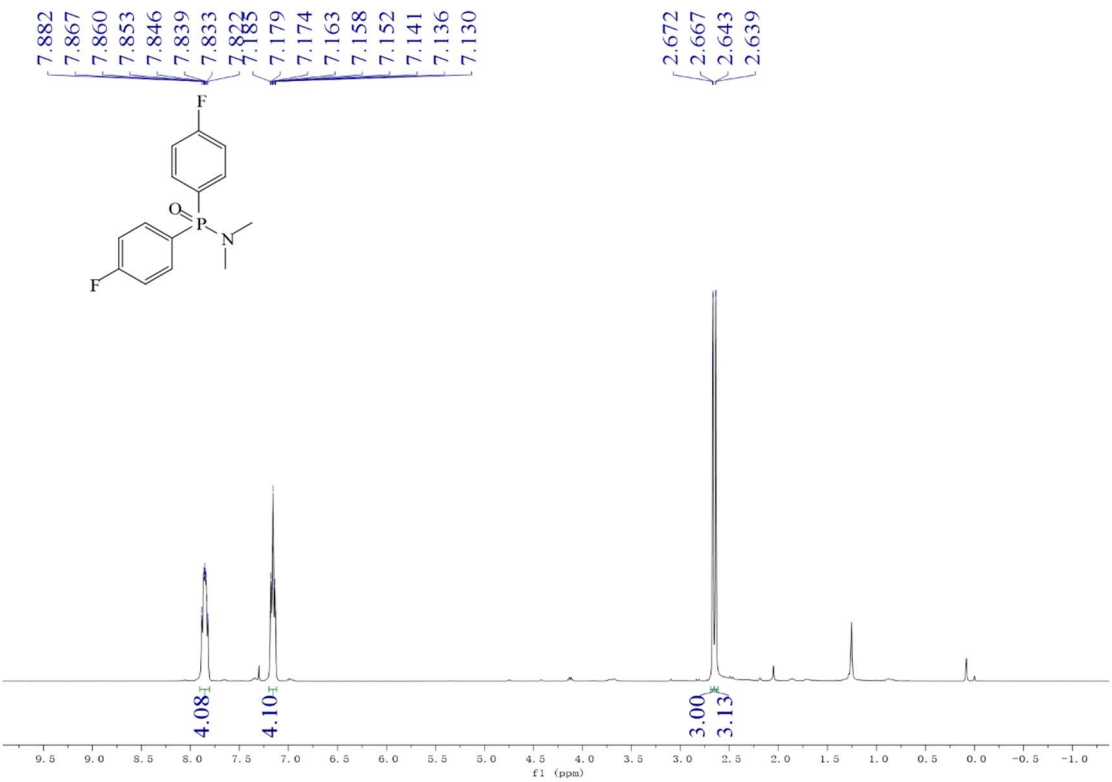
^{13}C NMR spectrum of 3fa (100 MHz, $CDCl_3$)



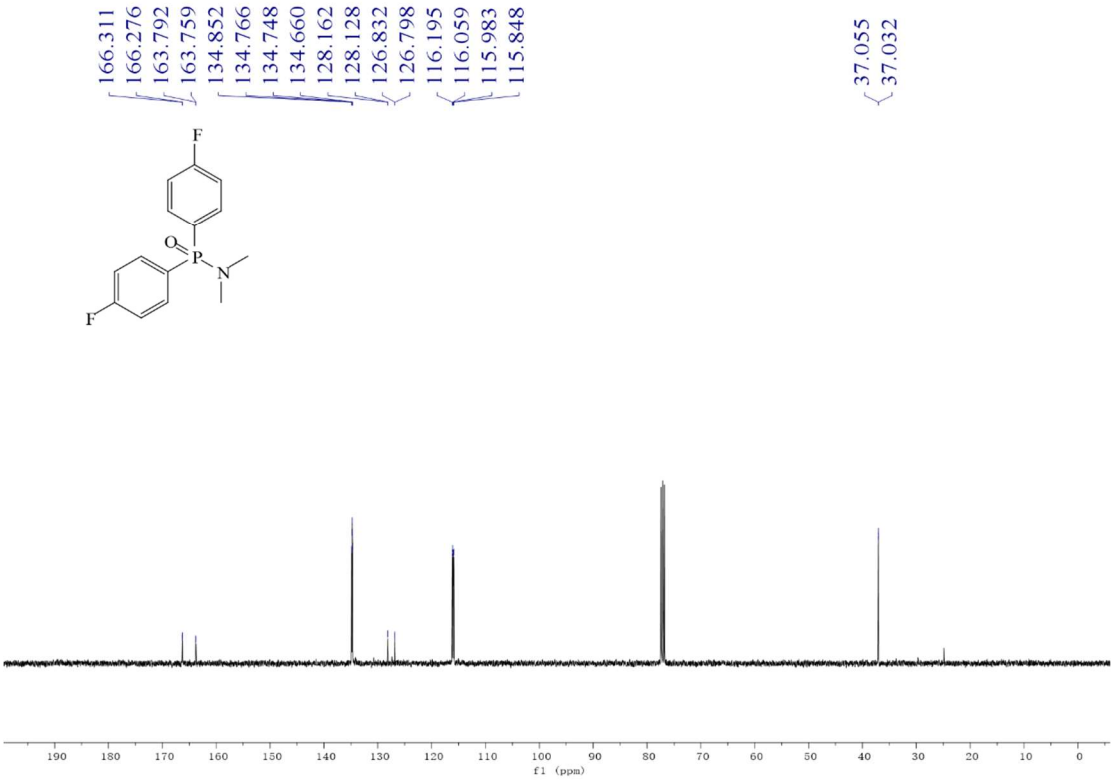
^{31}P NMR spectrum of 3fa (162 MHz, $CDCl_3$)



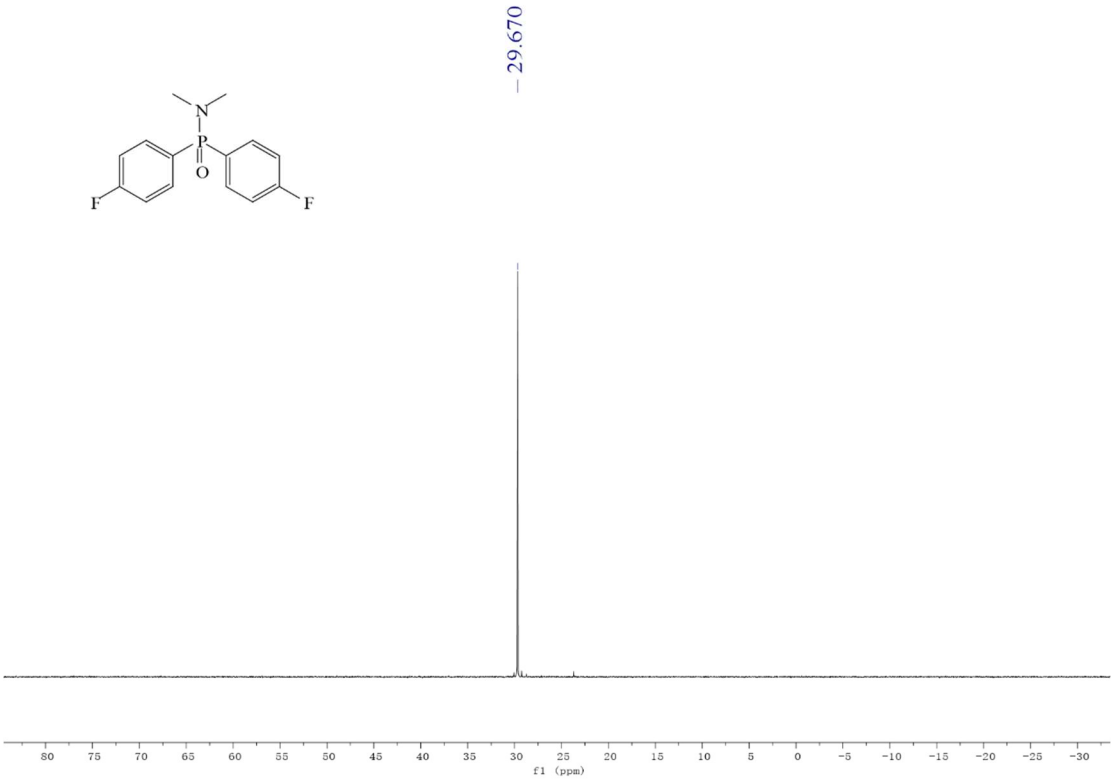
^{1}H NMR spectrum of 3ga (400 MHz, $CDCl_3$)



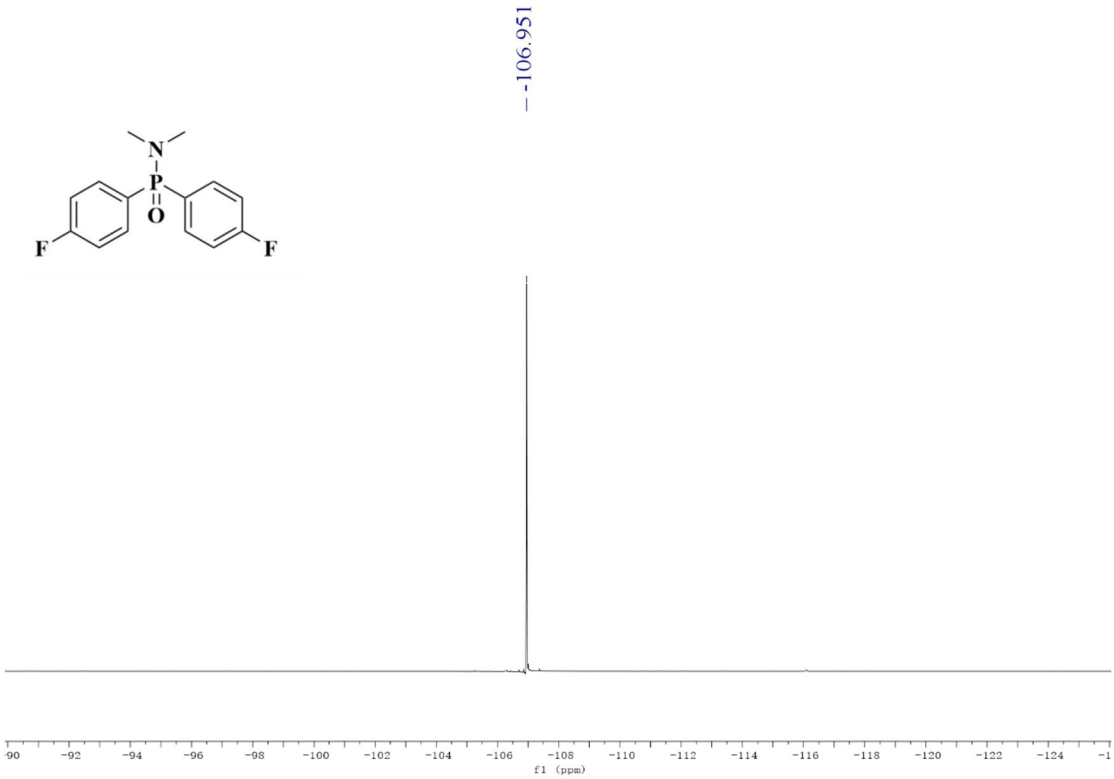
^{13}C NMR spectrum of 3ga (100 MHz, $CDCl_3$)



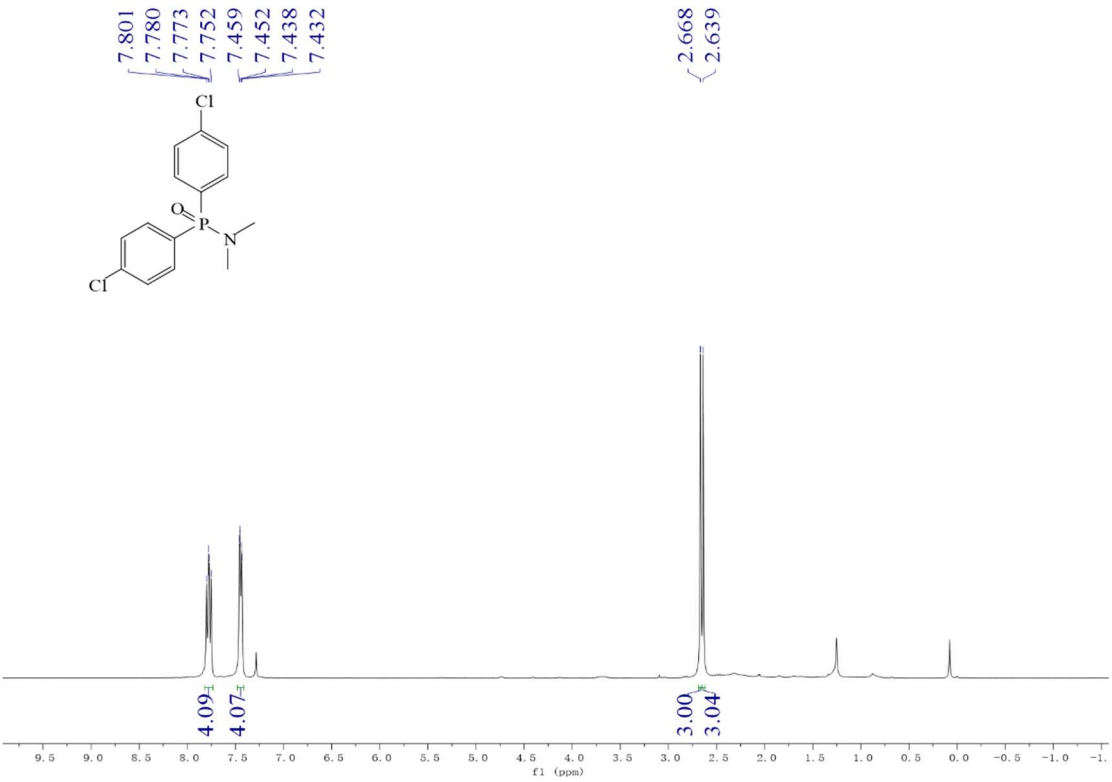
^{31}P NMR spectrum of 3ga (162 MHz, $CDCl_3$)



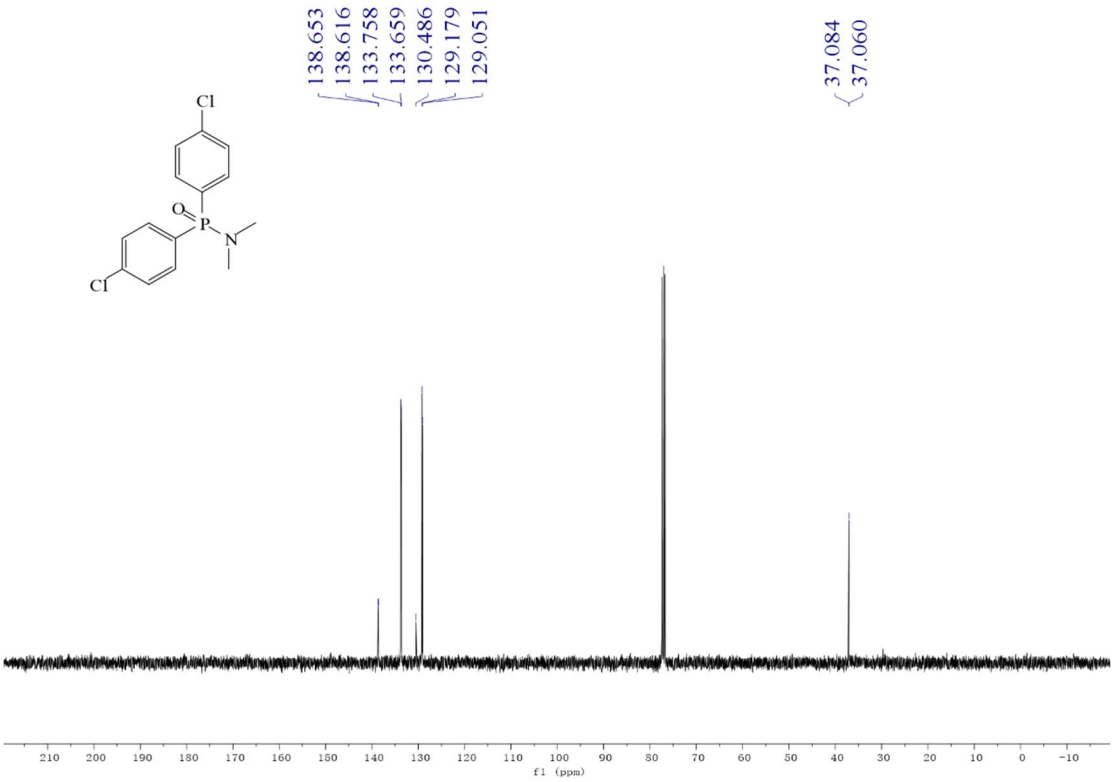
^{19}F NMR spectrum of 3ga (376 MHz, $CDCl_3$)



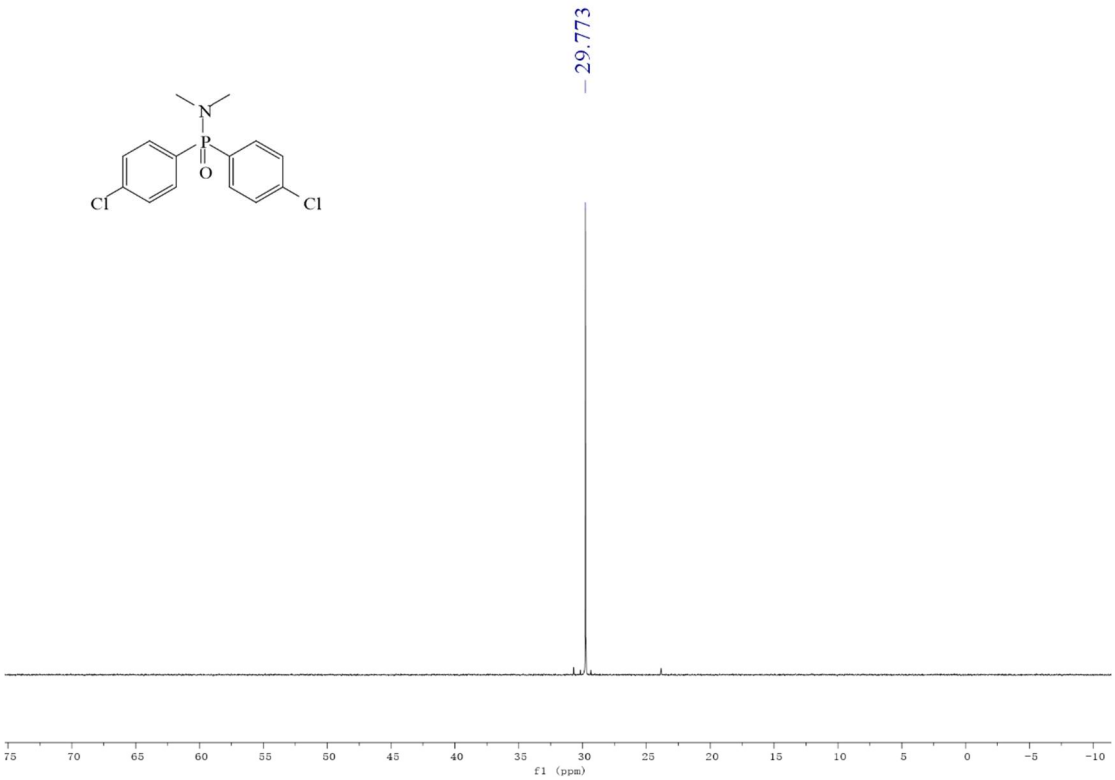
^{1}H NMR spectrum of 3ha (400 MHz, $CDCl_3$)



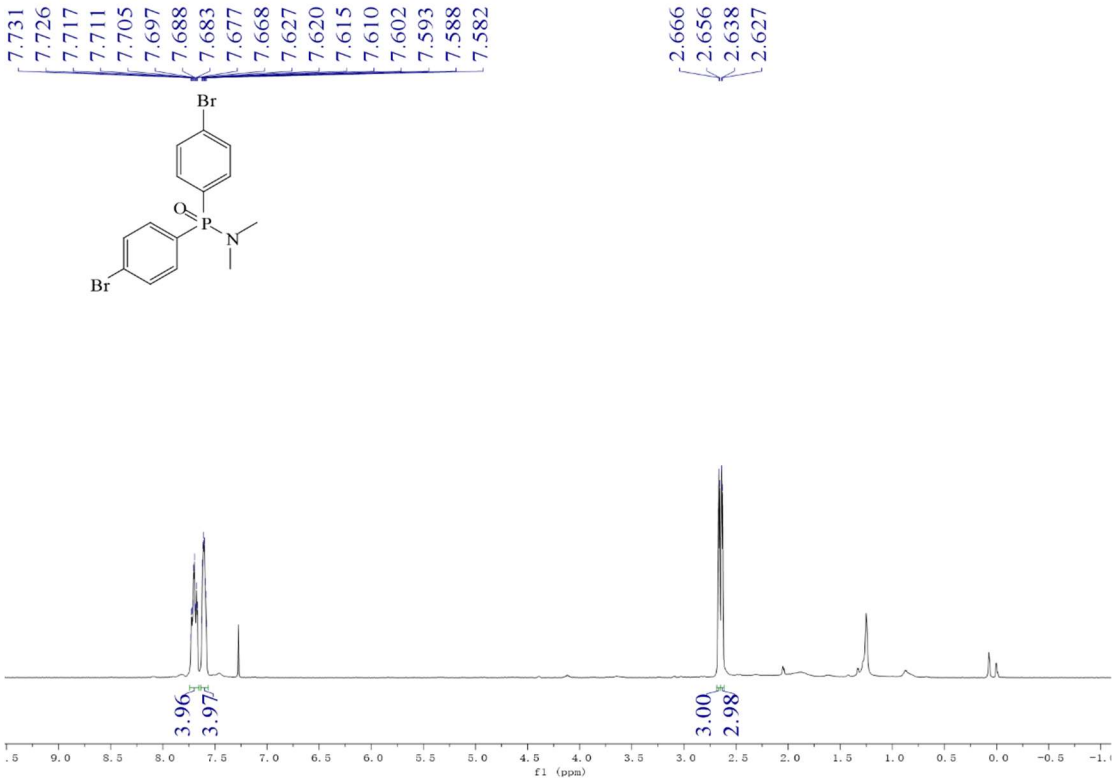
^{13}C NMR spectrum of 3ha (100 MHz, $CDCl_3$)



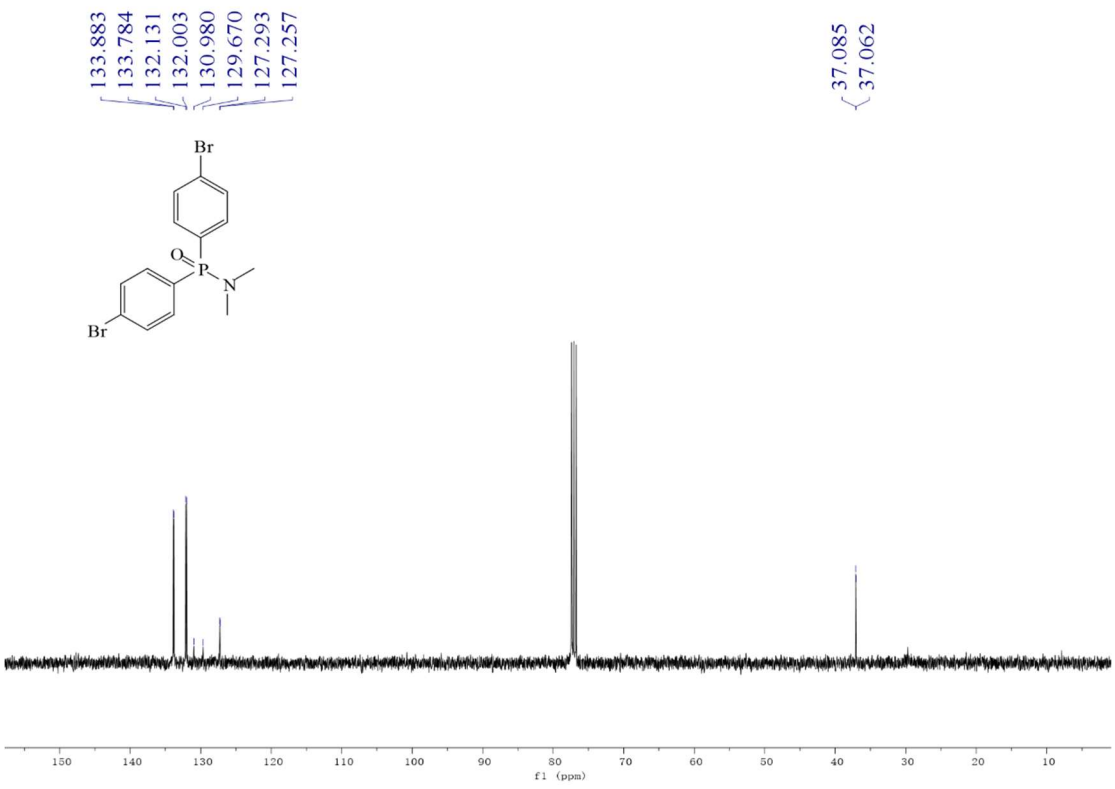
^{31}P NMR spectrum of 3ha (162 MHz, $CDCl_3$)



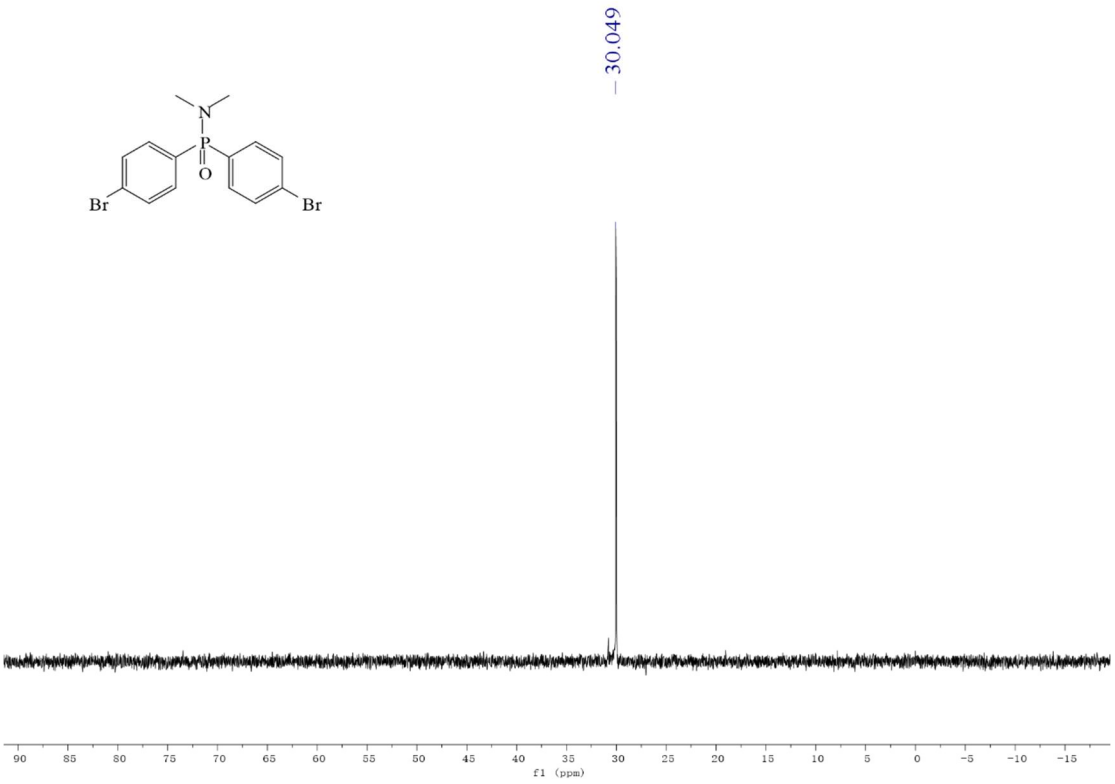
^{1}H NMR spectrum of 3ia (400 MHz, $CDCl_3$)



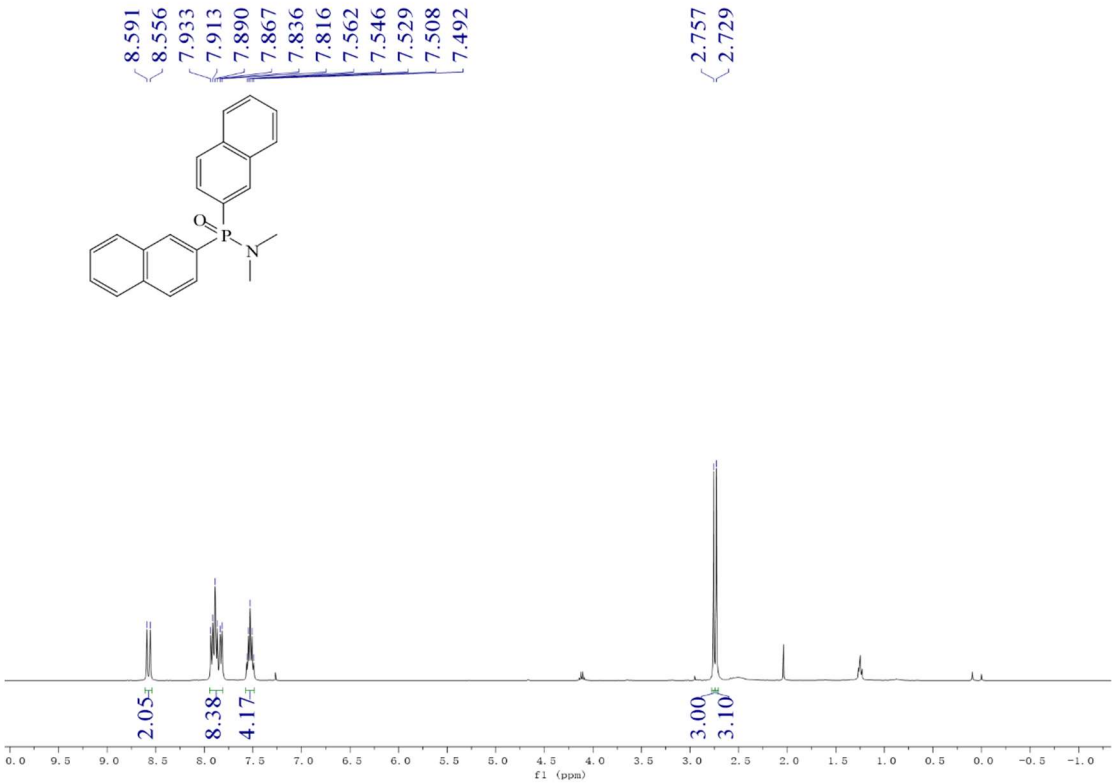
^{13}C NMR spectrum of 3ia (100 MHz, $CDCl_3$)



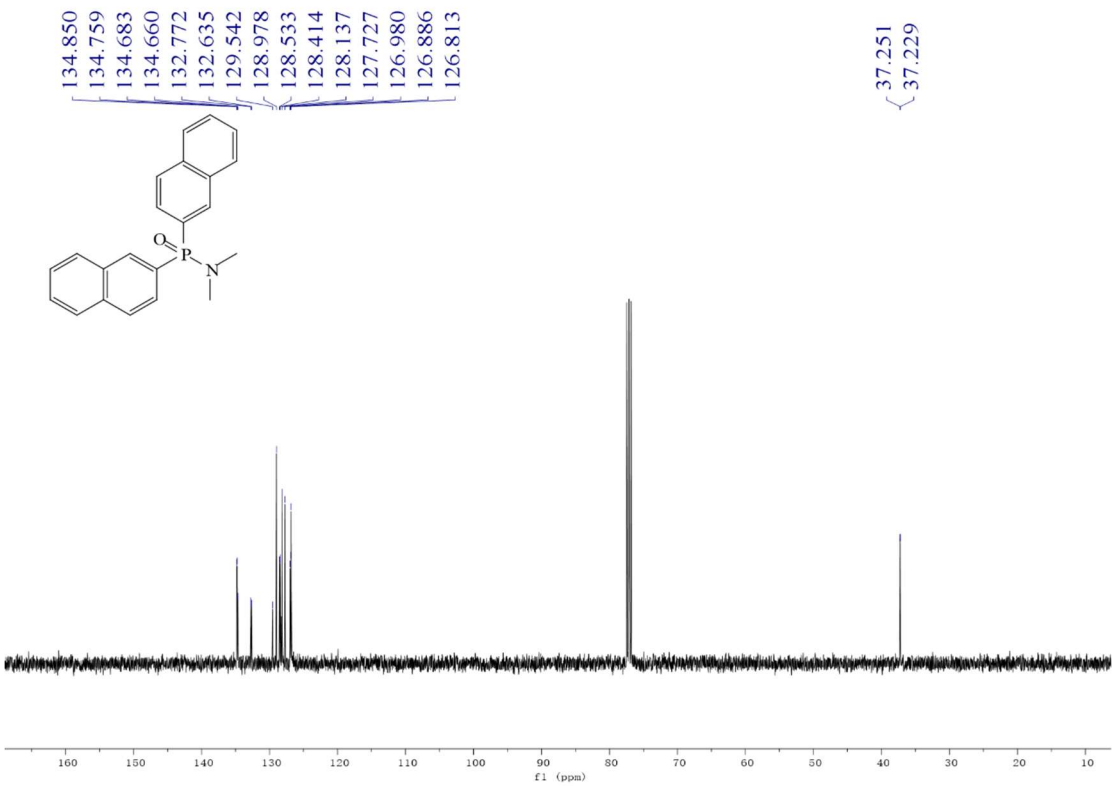
^{31}P NMR spectrum of 3ia (162 MHz, $CDCl_3$)



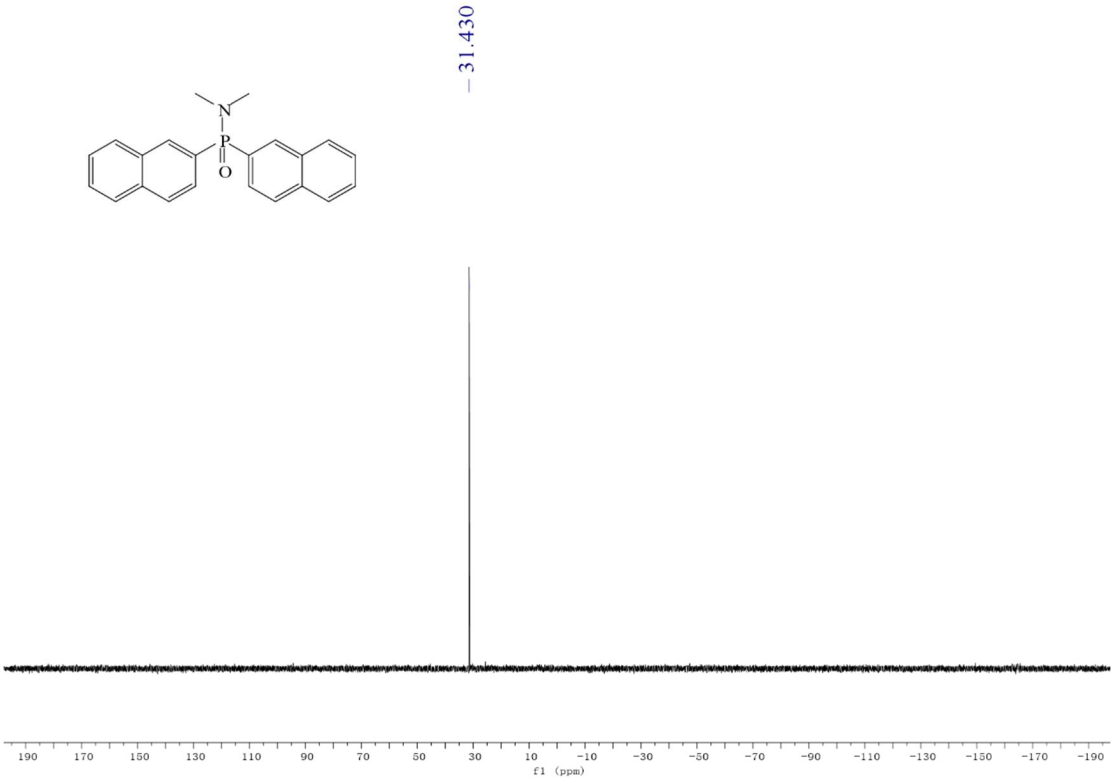
^{1}H NMR spectrum of 3ja (400 MHz, $CDCl_3$)



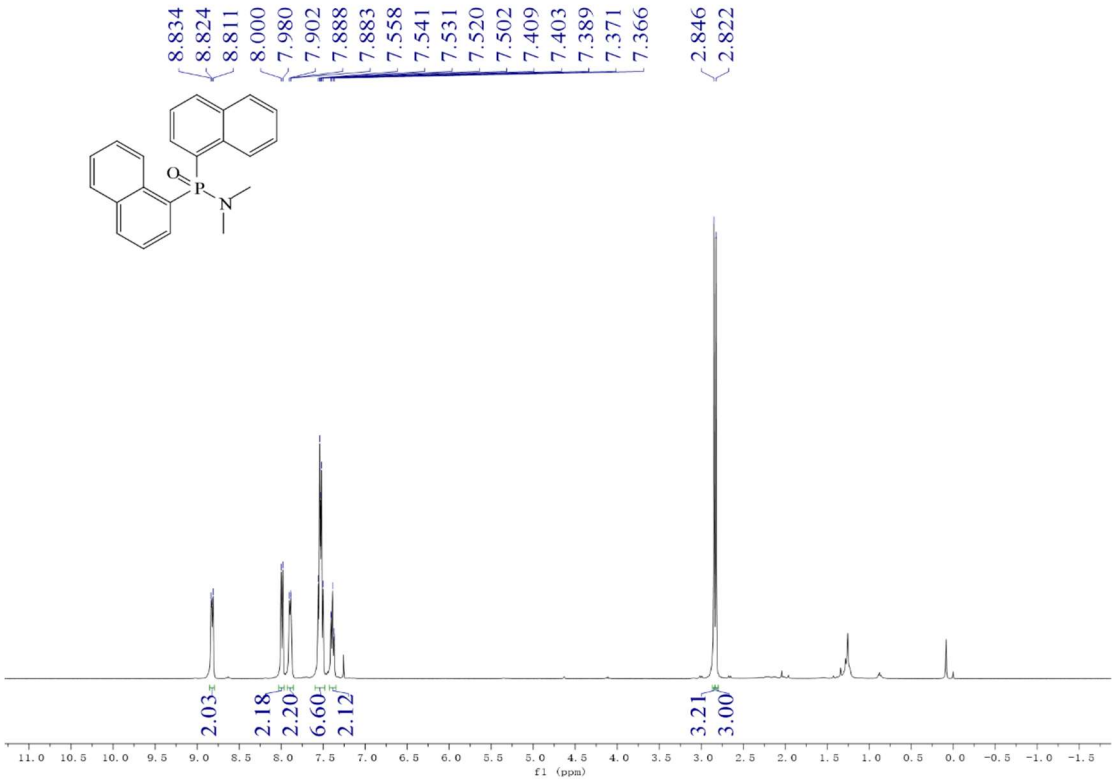
^{13}C NMR spectrum of 3ja (100 MHz, $CDCl_3$)



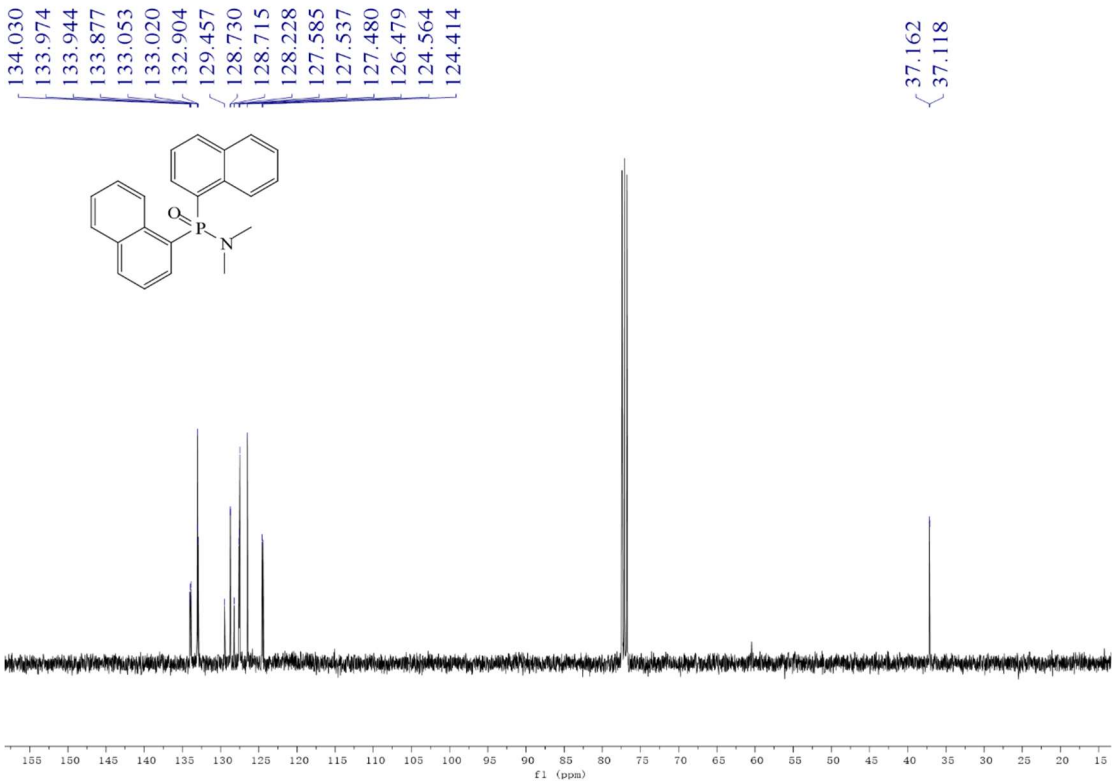
^{31}P NMR spectrum of 3ja (162 MHz, $CDCl_3$)



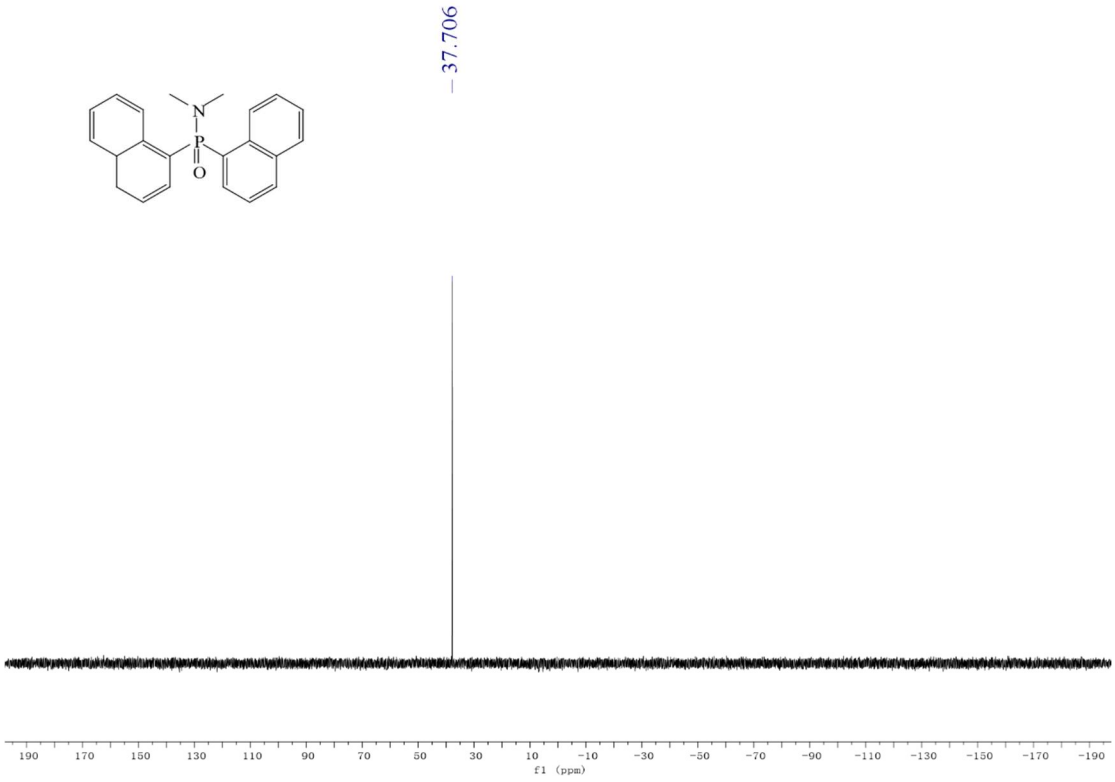
^{1}H NMR spectrum of 3ka (400 MHz, $CDCl_3$)



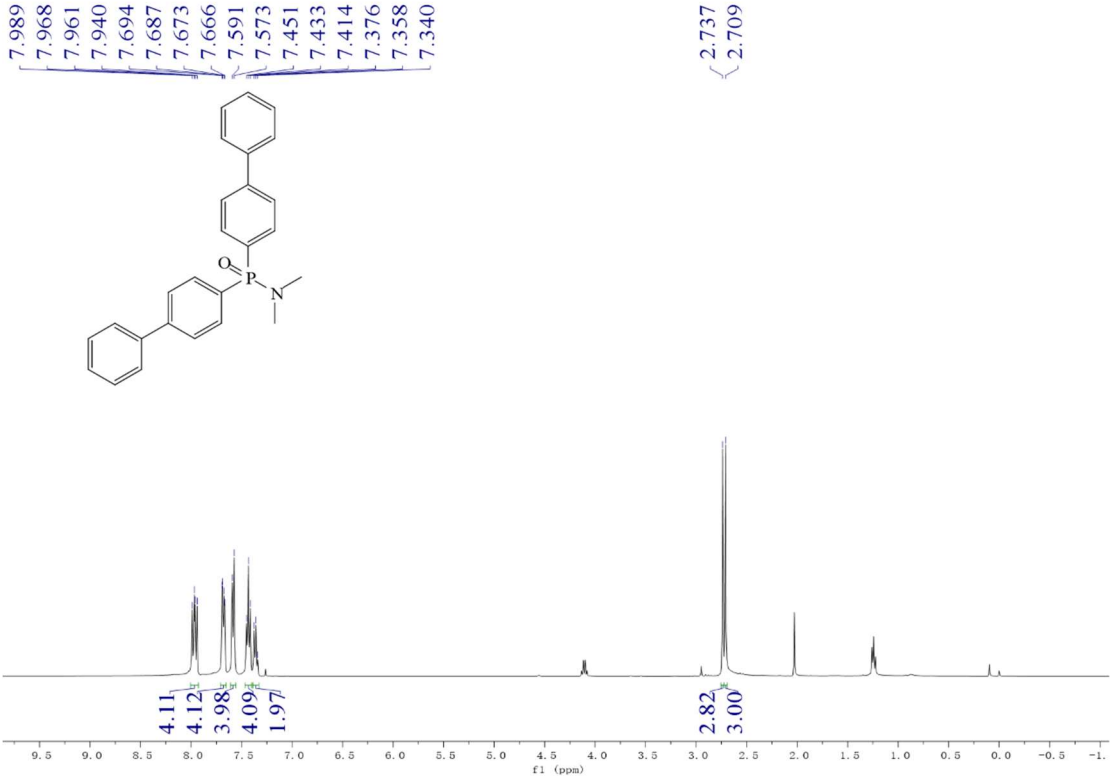
^{13}C NMR spectrum of 3ka (100 MHz, $CDCl_3$)



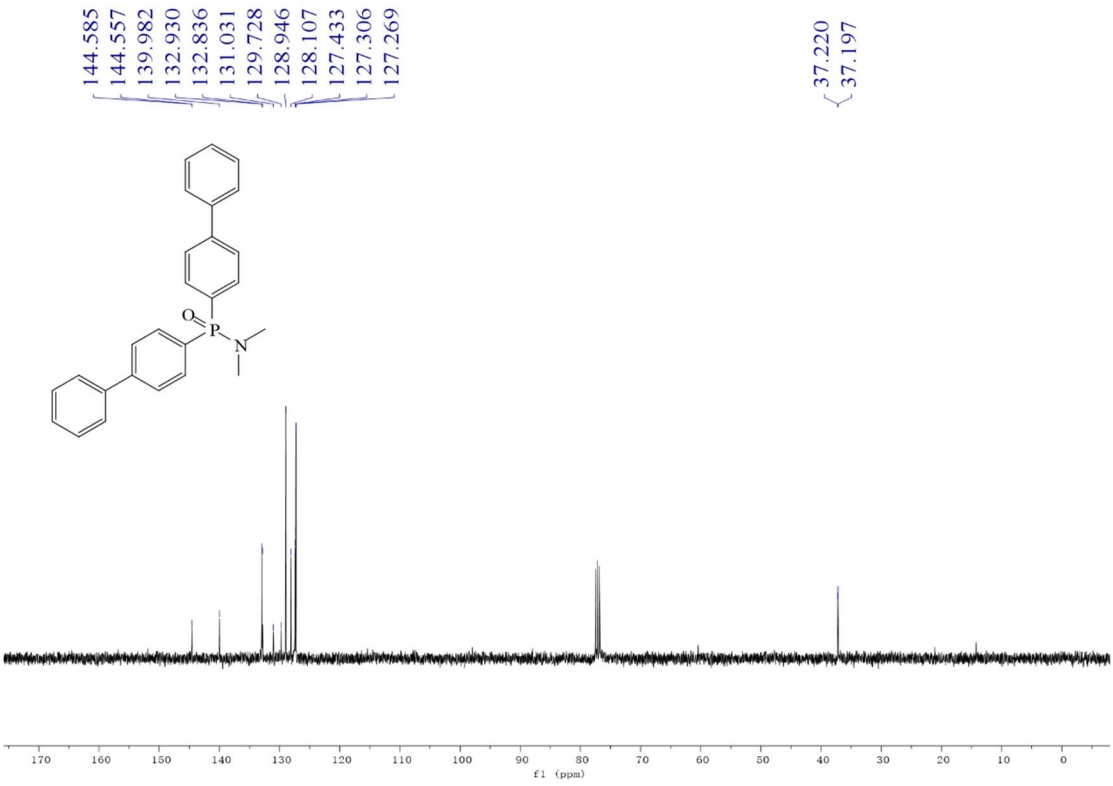
^{31}P NMR spectrum of 3ka (162 MHz, $CDCl_3$)



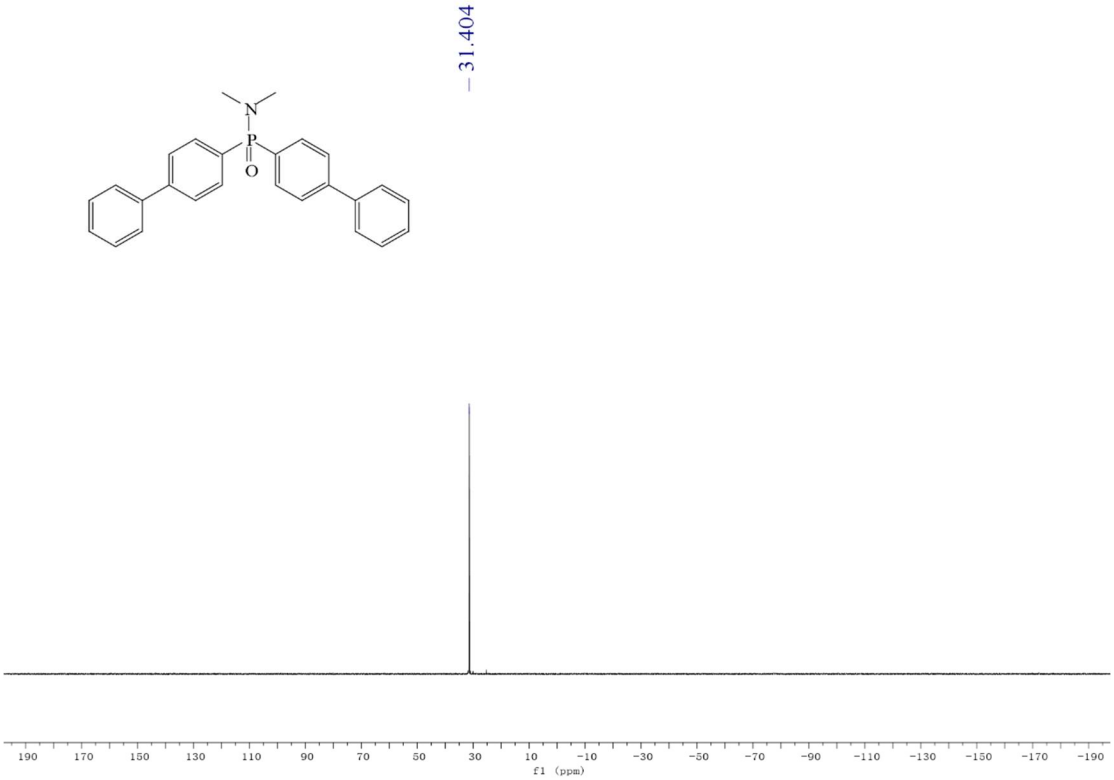
^{1}H NMR spectrum of 3la (400 MHz, $CDCl_3$)



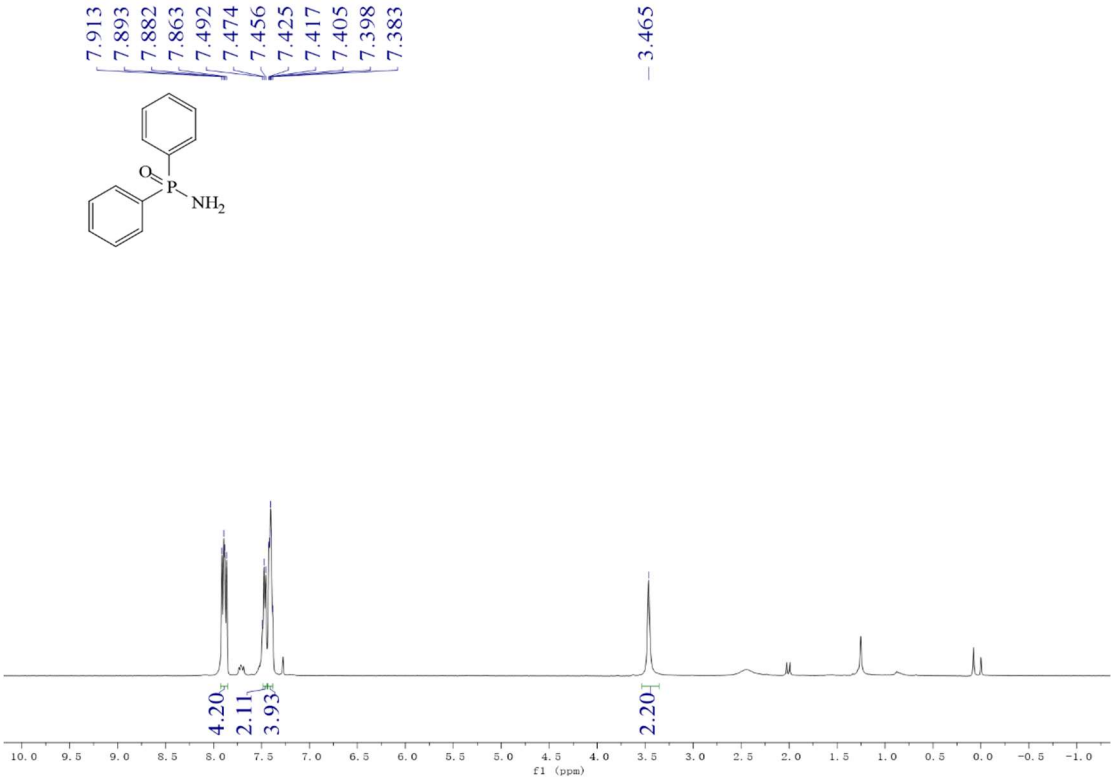
^{13}C NMR spectrum of 3la (100 MHz, $CDCl_3$)



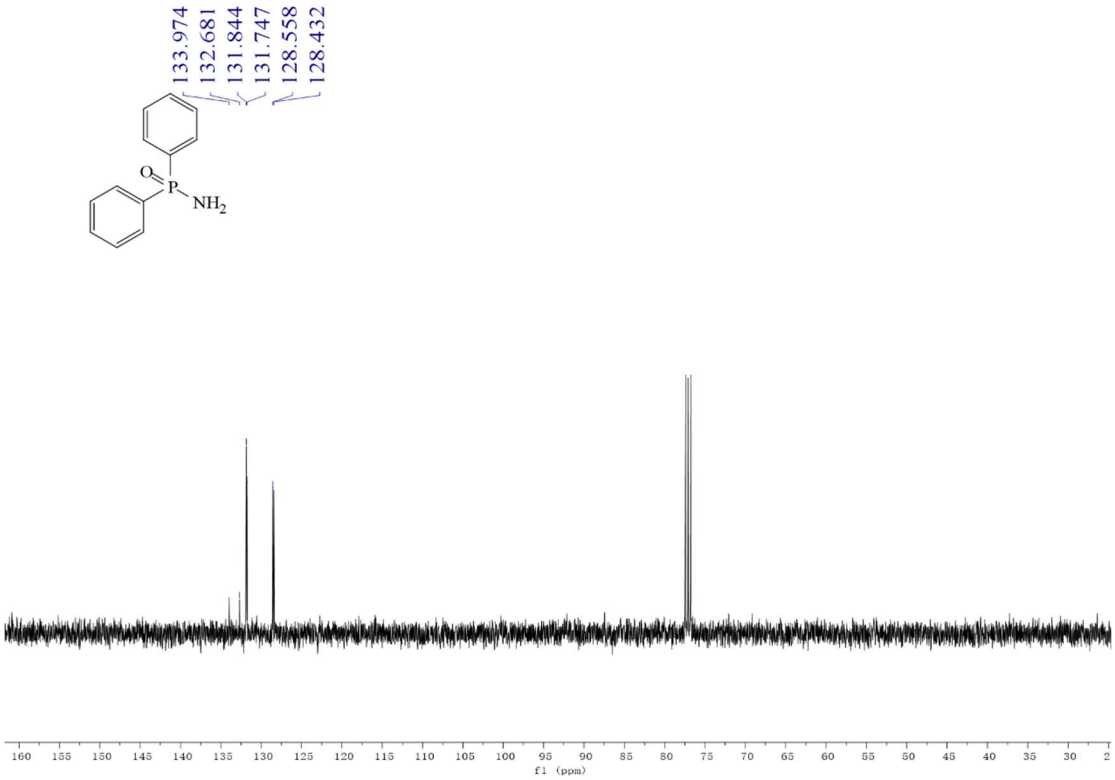
^{31}P NMR spectrum of 3la (162 MHz, $CDCl_3$)



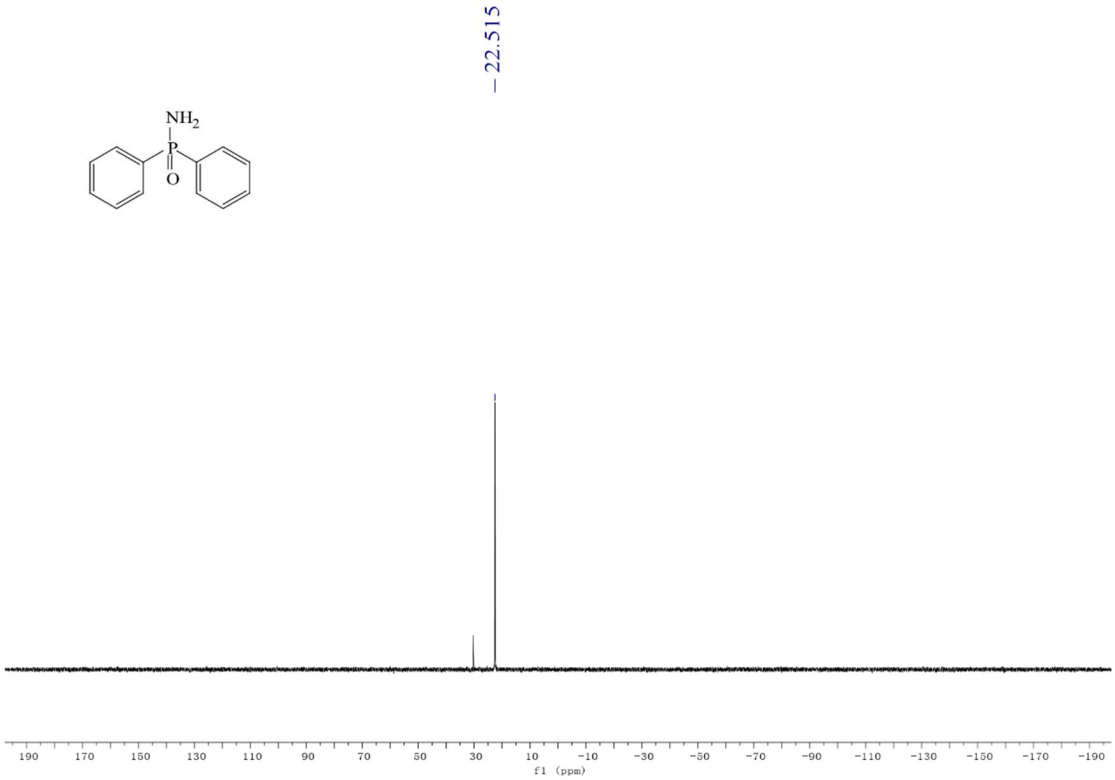
^{1}H NMR spectrum of 3ab (400 MHz, $CDCl_3$)



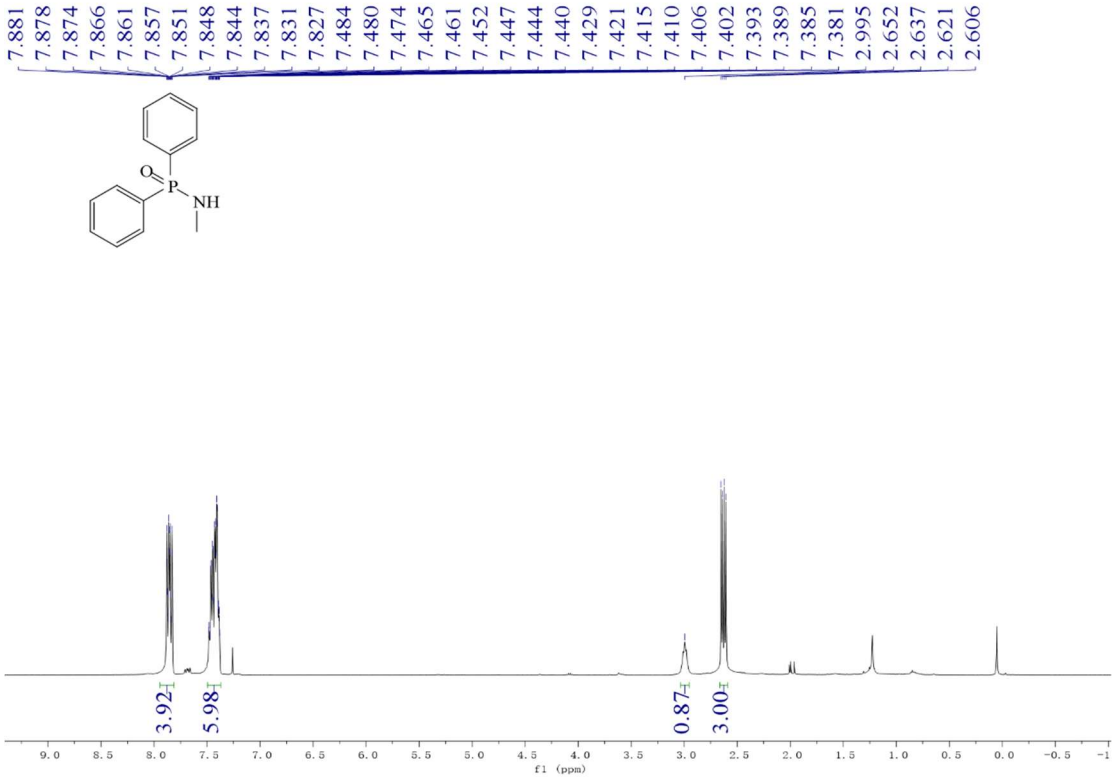
^{13}C NMR spectrum of 3ab (100 MHz, $CDCl_3$)



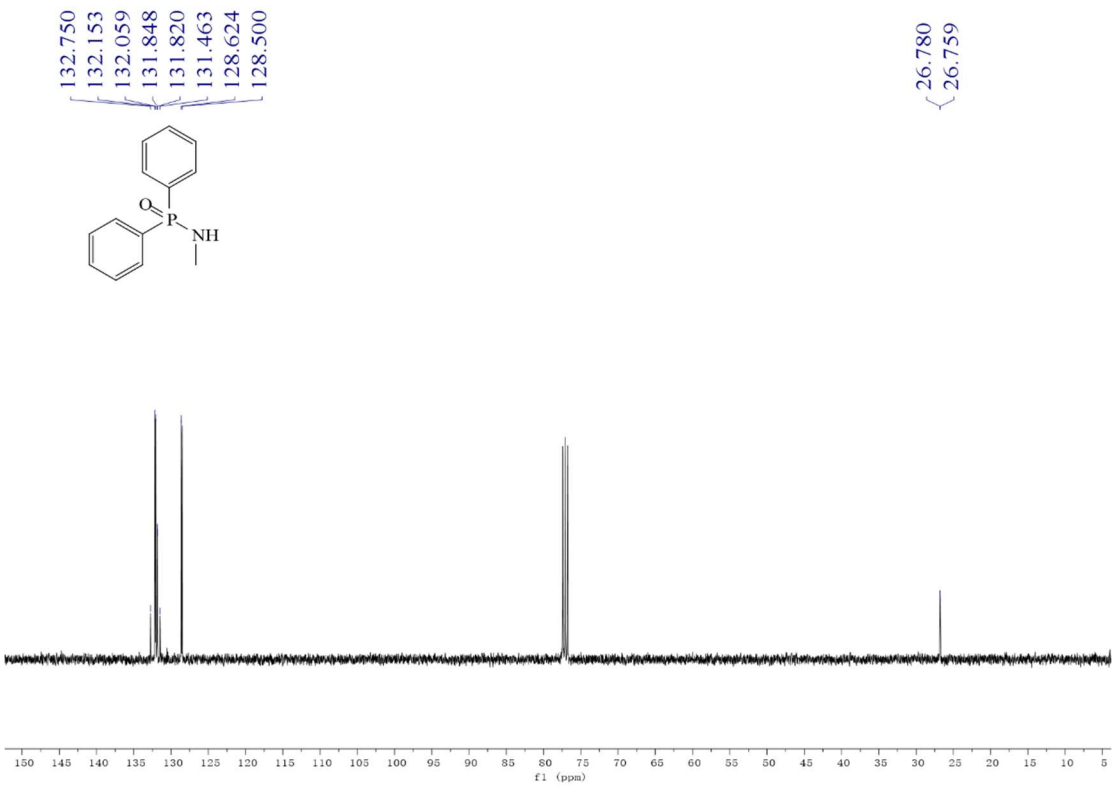
^{31}P NMR spectrum of 3ab (162 MHz, $CDCl_3$)



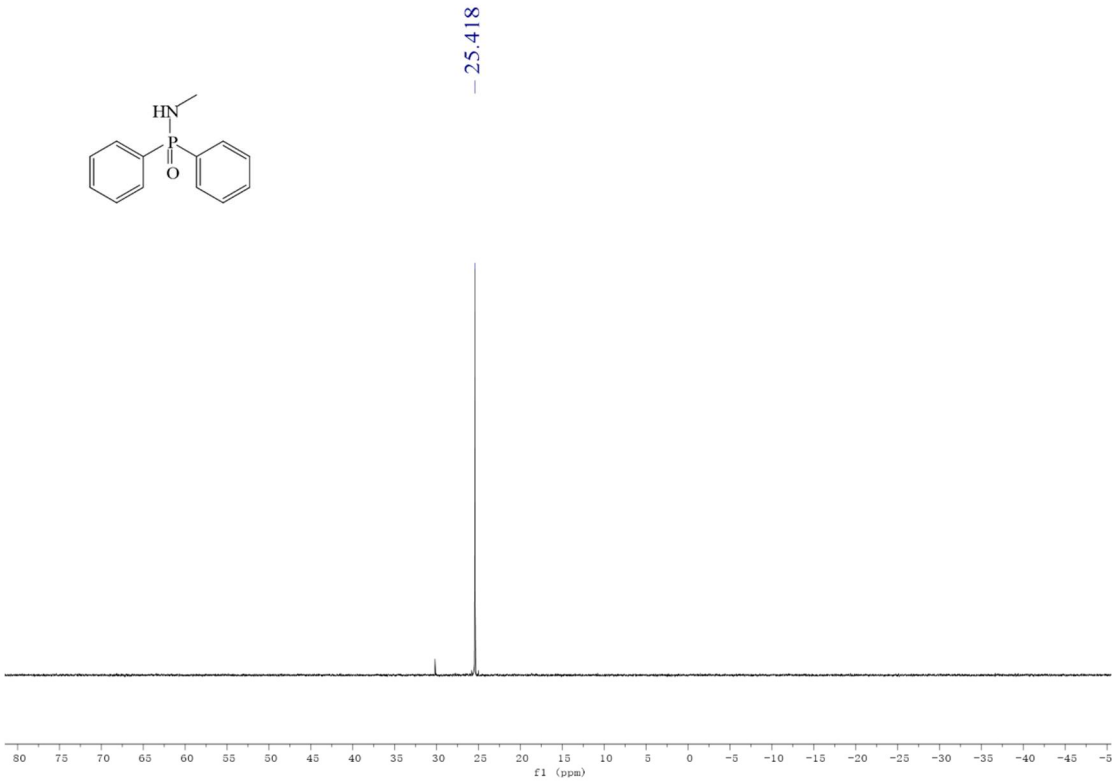
^{1}H NMR spectrum of 3ac (400 MHz, $CDCl_3$)



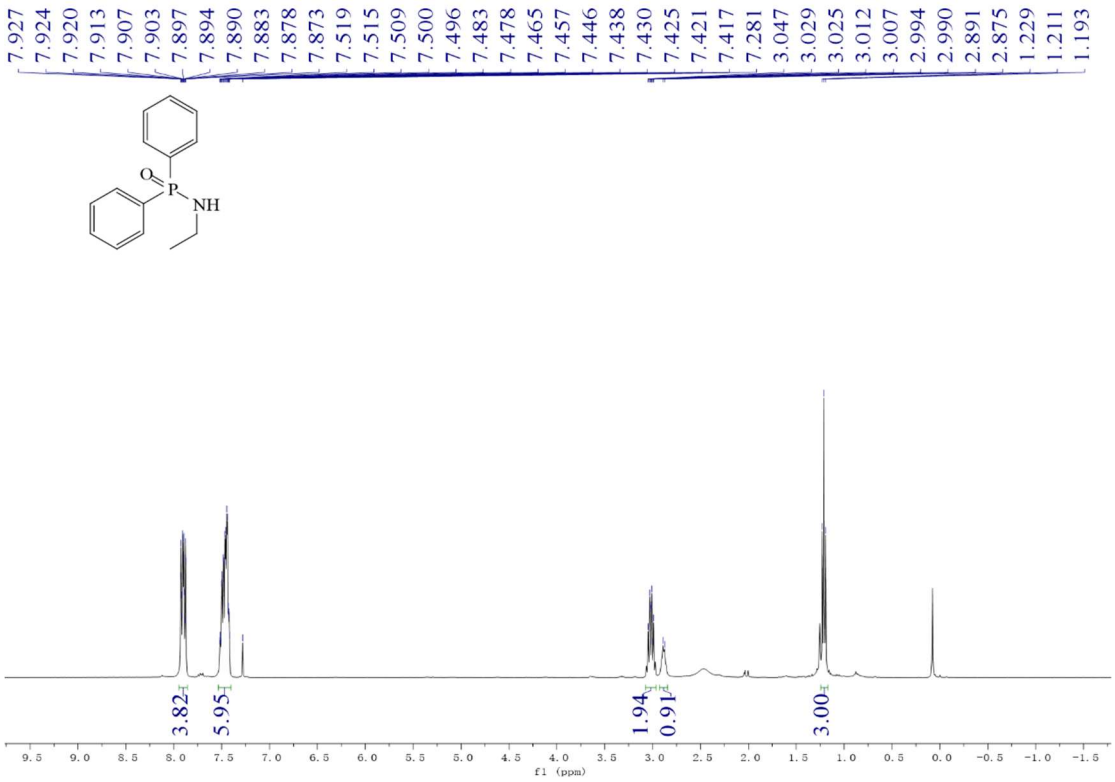
^{13}C NMR spectrum of 3ac (100 MHz, $CDCl_3$)



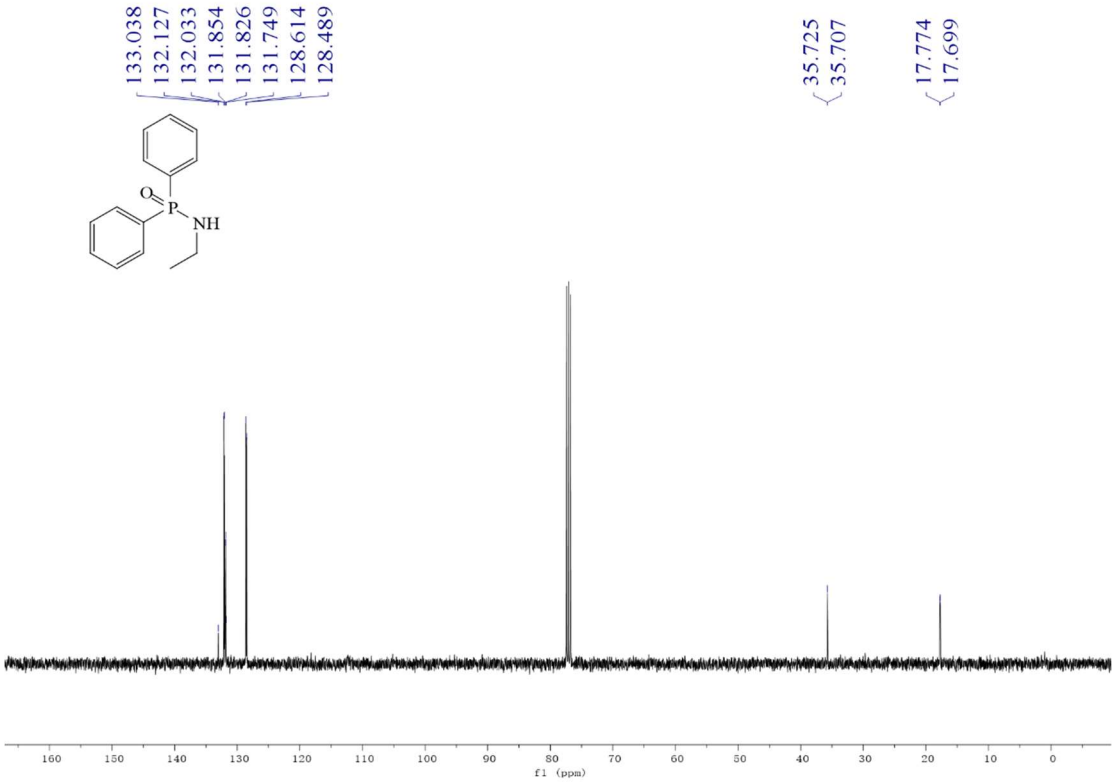
^{31}P NMR spectrum of 3ac (162 MHz, $CDCl_3$)



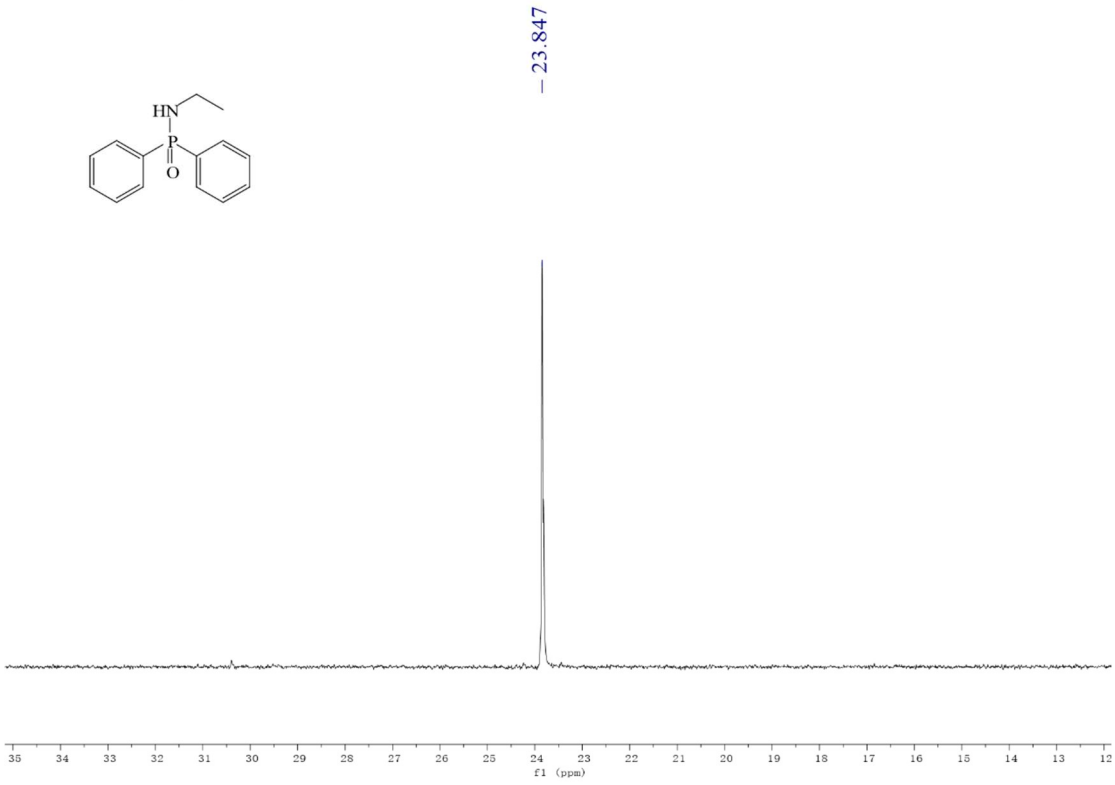
^{1}H NMR spectrum of 3ad (400 MHz, $CDCl_3$)



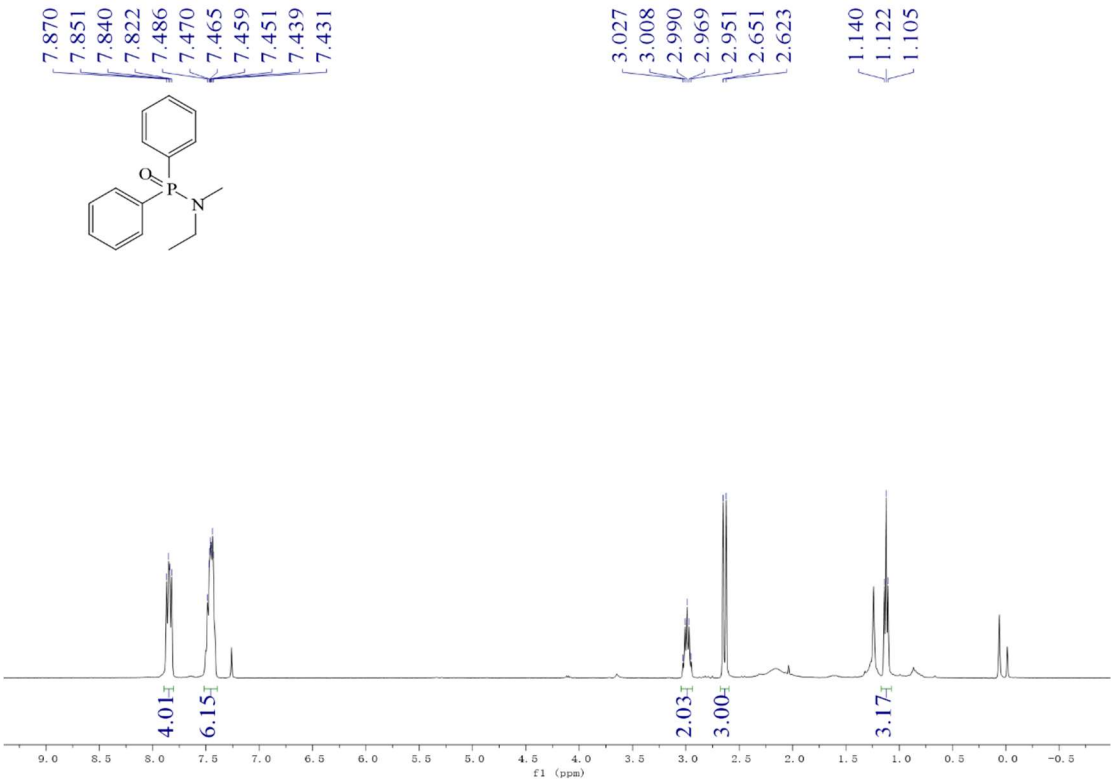
^{13}C NMR spectrum of 3ad (100 MHz, $CDCl_3$)



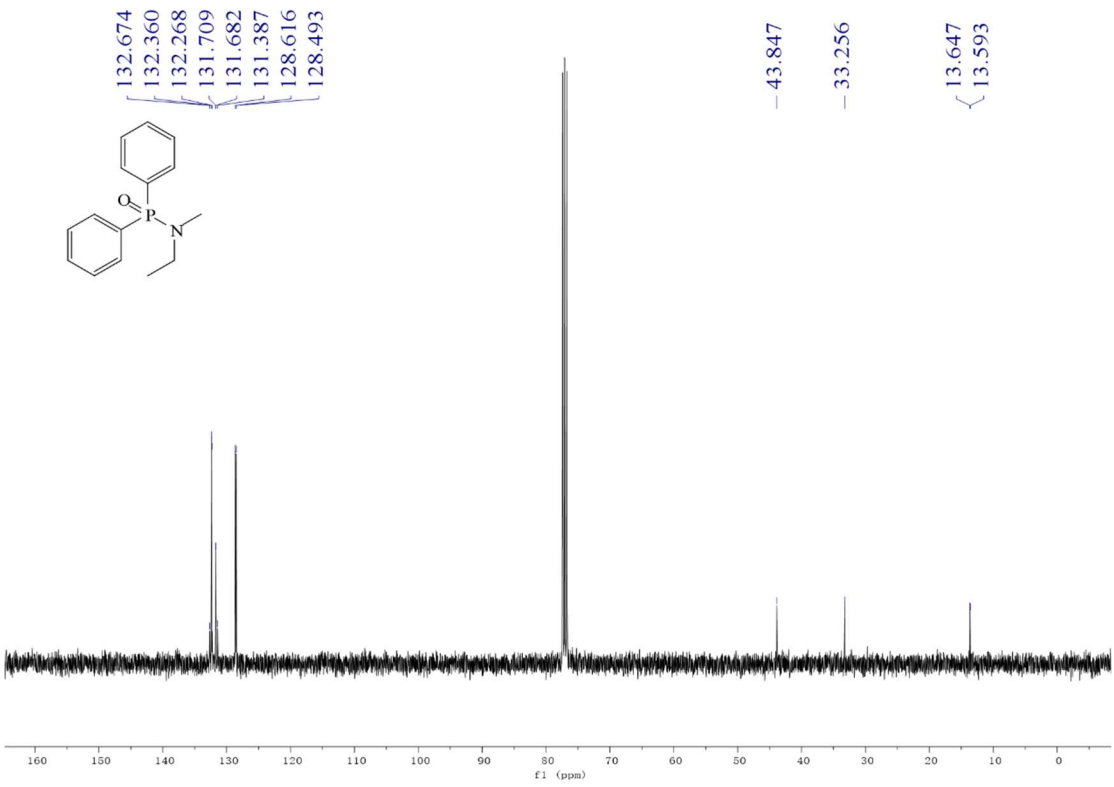
^{31}P NMR spectrum of 3ad (162 MHz, $CDCl_3$)



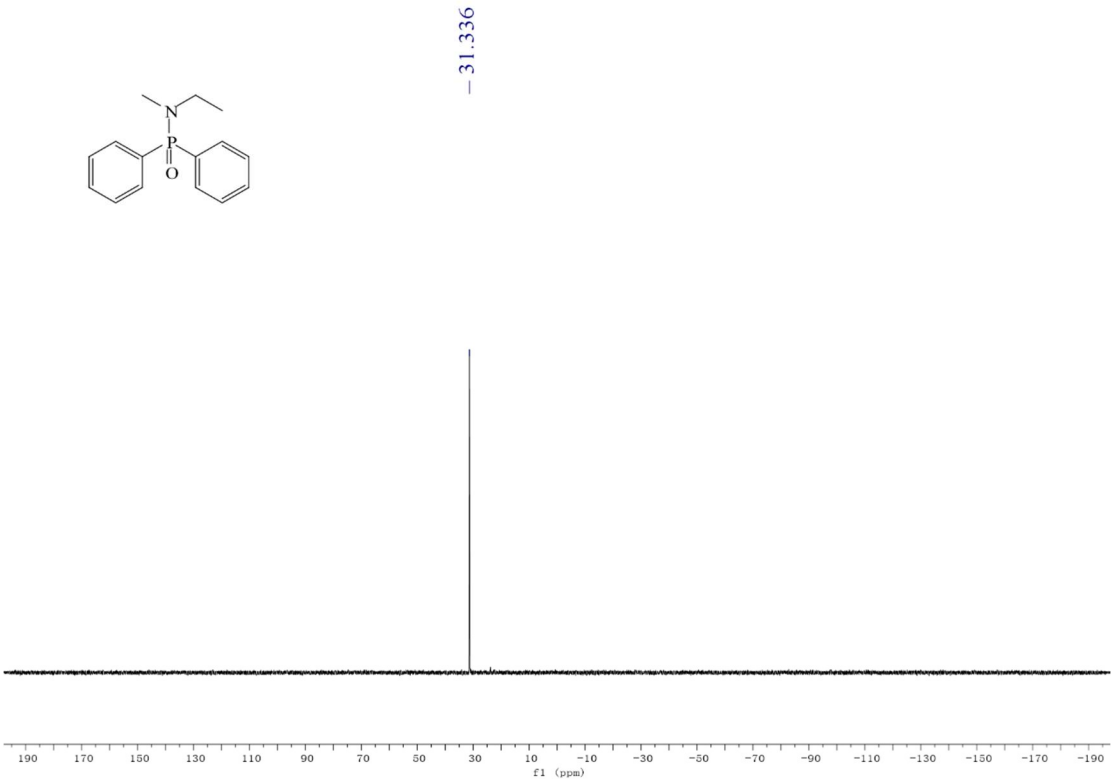
^{1}H NMR spectrum of 3ae (400 MHz, $CDCl_3$)



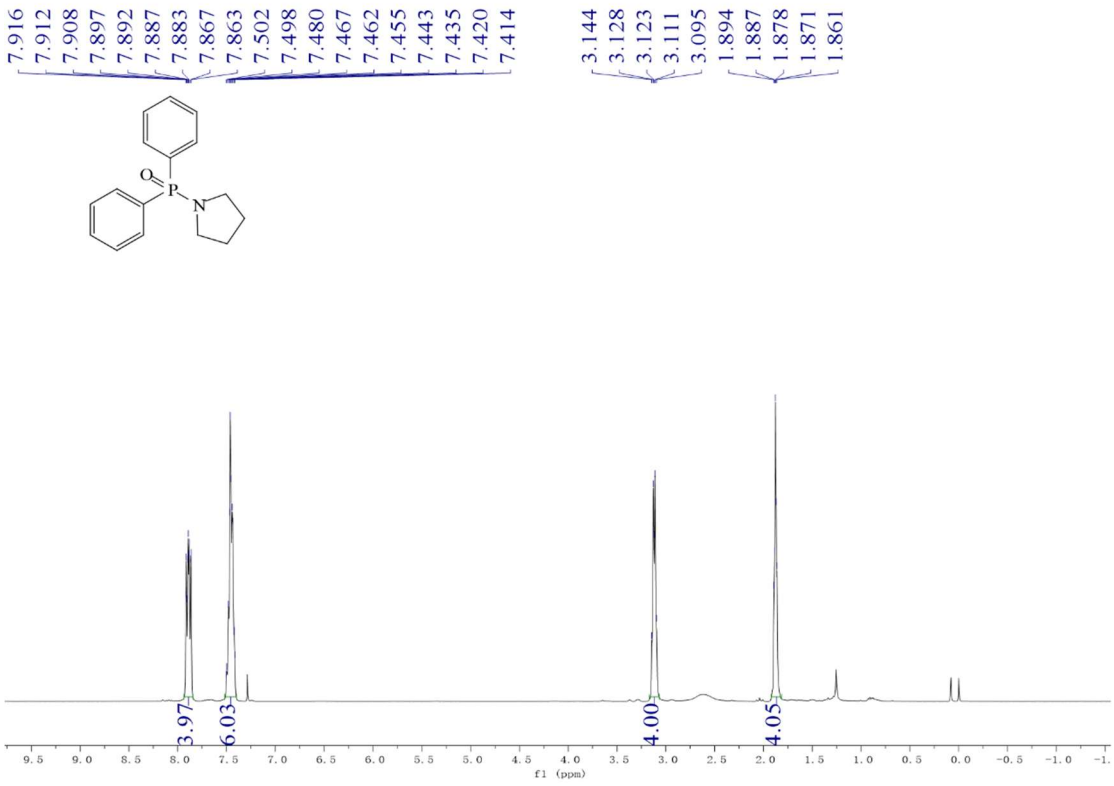
^{13}C NMR spectrum of 3ae (100 MHz, $CDCl_3$)



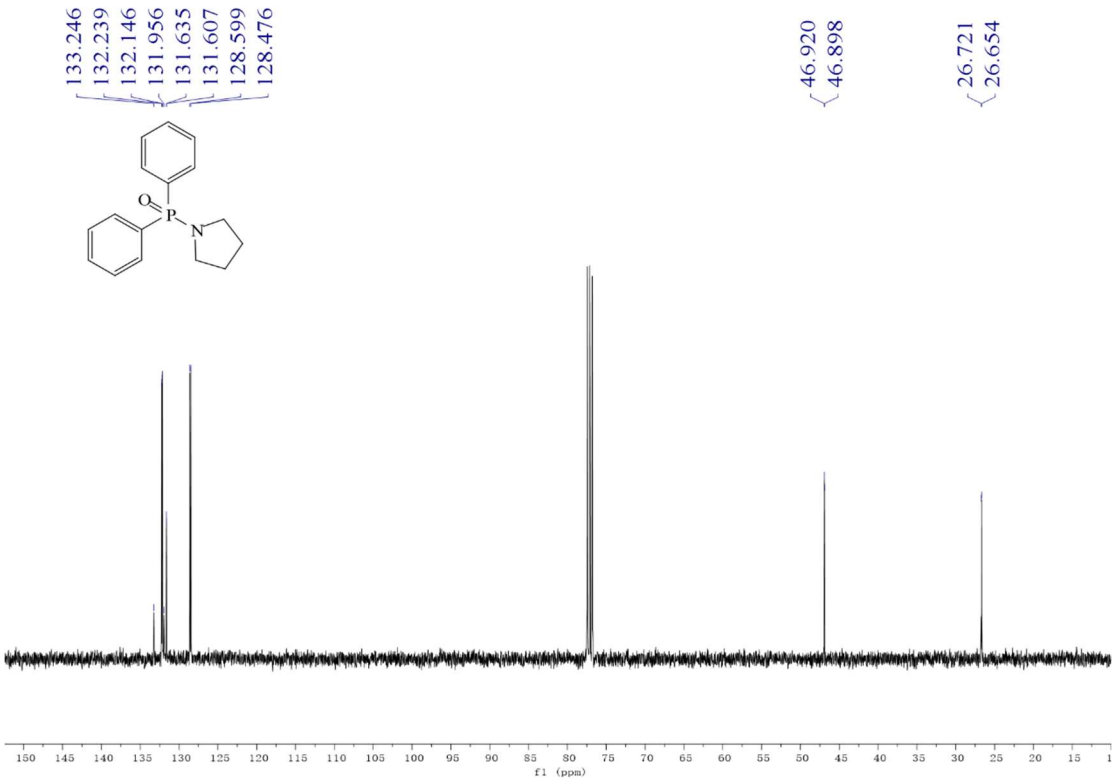
^{31}P NMR spectrum of 3ae (162 MHz, $CDCl_3$)



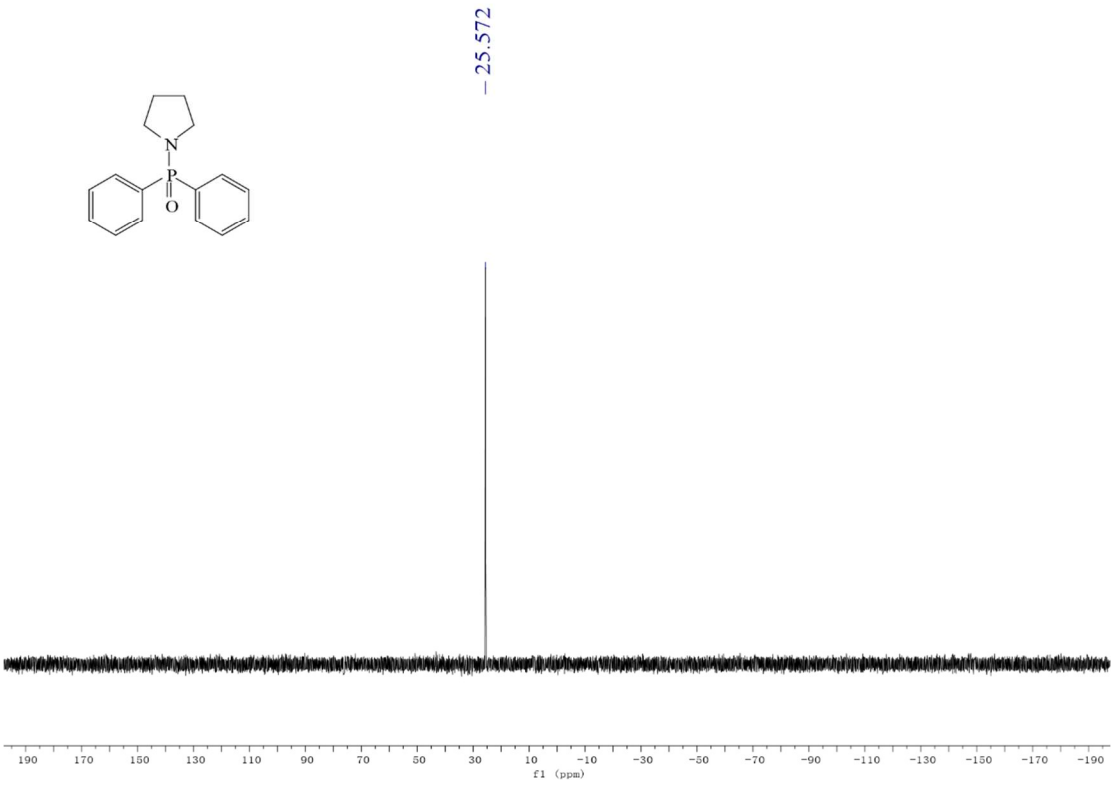
^{1}H NMR spectrum of 3af (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3af (100 MHz, $CDCl_3$)

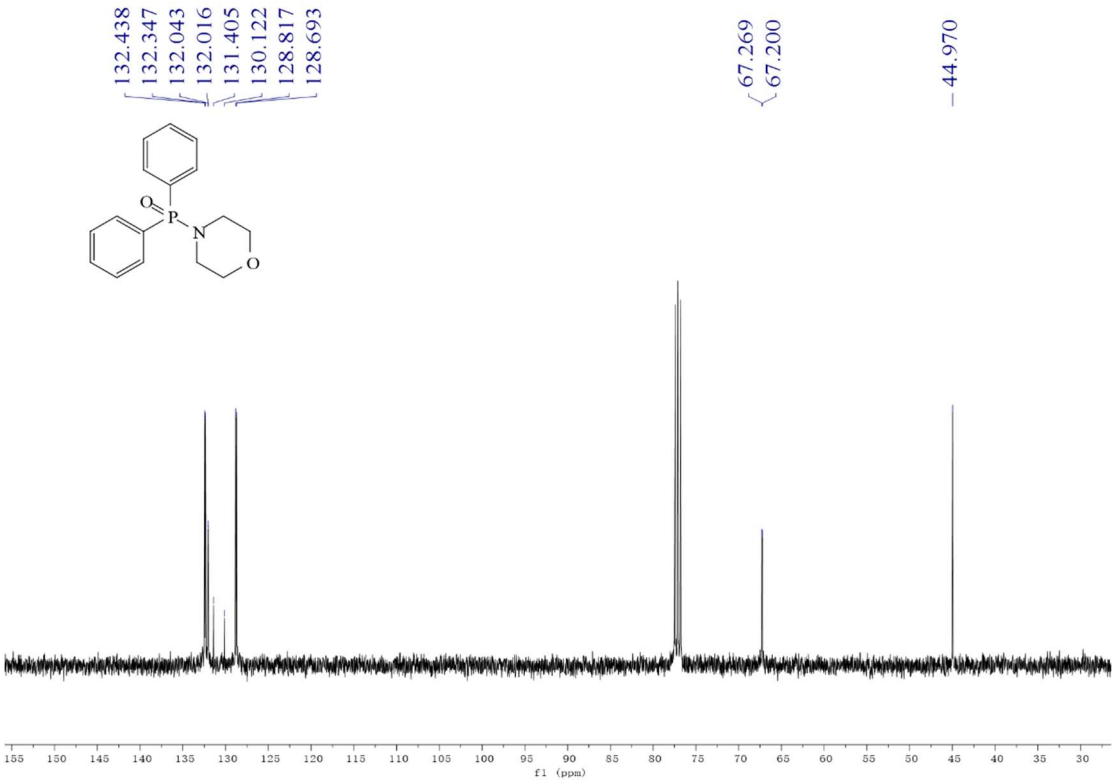


^{31}P NMR spectrum of 3af (162 MHz, $CDCl_3$)



^{1}H NMR spectrum of 3ag (400 MHz, $CDCl_3$)

^{13}C NMR spectrum of 3ag (100 MHz, $CDCl_3$)



^{31}P NMR spectrum of 3ag (162 MHz, $CDCl_3$)