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Supporting Information

Efficient C(sp^3)-P(V) Bond Cleavage and Reconstruction of Free α-Aminophosphonates via Palladium Catalysis

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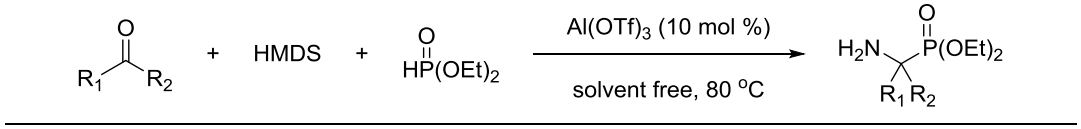
1. General information

^{1}H and ^{13}C NMR spectra were recorded on Bruker advance III 600 MHz and Varian 400 MHz spectrometer in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal tandard. ^{31}P NMR spectra were recorded on a Bruker advance III 600 and 400 spectrometer. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants are reported in Hertz (Hz). High resolution mass spectroscopic (HRMS) and mass spectra were measured using Bruker micro TOF-Q mass spectrometer and Thermo Scientific DS II mass spectrometer. Analytical thin layer chromatography (TLC) was carried out using commercial silica-gel plates, spots were detected with UV light (254 nm) and revealed with phosphomolybdic acid solutions. Melting points were determined by the BÜCHI Melting Point B-540. The aminophosphonates were synthesized by reported methods, and the halides were purchased from Sigma-Aldrich, J&K Chemicals, bidepharm and Adamas, and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. General procedure for the preparation of free diethyl α-aminophosphonates



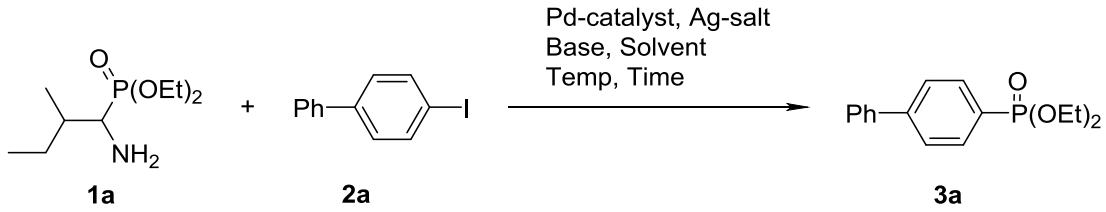
1a **1b** **1c** **1d** **1e**

1f **1g** **1h** **1i**

General procedure[1]: A mixture of an aldehyde/ketone (2.0 mmol, 1.7 equiv), HMDS (249.6 μL, 1.2 mmol, 1.0 equiv), diethyl phosphite (154.4 μL, 1.2 mmol, 1.0 equiv), and $Al(OTf)_3$ (5.7 mg, 0.012 mmol, 1 mol %) was stirred in an oil bath at 80 °C overnight. The reaction mixture was then cooled and acidified to pH = 1 by HCl (aq). The solution was washed with EtOAc (2 × 10 mL). The aqueous phase was then made alkaline with NaOH (aq) and the product was extracted with EtOAc (2 × 10 mL). All the organic extracts were collected, combined in a vial and evaporated under reduced pressure and the resulting mixture was purified by silica gel chromatography (PE/EA = 1:3) to afford the diethyl α-aminophosphonates.

3. Optimization of the reaction conditions

Table S1. Optimization of conditions for Pd-catalyzed C-P bond arylation of α-aminophosphonate **1a**[a]

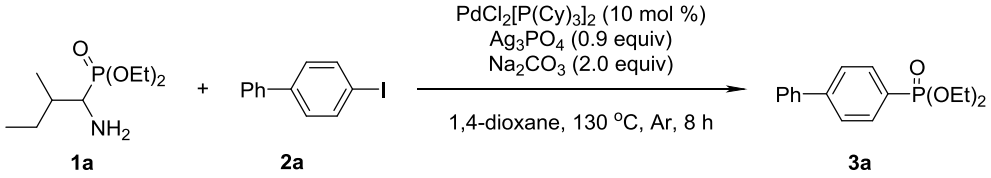


1a **2a** **3a**

Entry	Pd-catalyst (mol %)	Ag-salt (equiv)	Base (equiv)	Solvent	T (^{o}C)	Yield (%)
1	$Pd(OAc)_2$ (10)	AgOTs (2)	$KHCO_3$ (2)	TFE	130	35
2	$Pd(OAc)_2$ (10)	AgOTs (2)	$KHCO_3$ (2)	HFIP	130	35
3	$Pd(OAc)_2$ (10)	AgOTs (2)	$KHCO_3$ (2)	1,4-dioxane	130	48
4	$Pd(OAc)_2$ (10)	AgOTs (2)	$KHCO_3$ (2)	CH_3CN	130	21
5	$Pd(OAc)_2$ (10)	AgOTs (2)	$KHCO_3$ (2)	DCE	130	38
6	$Pd(OAc)_2$ (10)	AgOTs (2)	$KHCO_3$ (2)	Toluene	130	36
7	$Pd(OAc)_2$ (10)	AgOTs (2)	$KHCO_3$ (2)	DME	130	38
8	$Pd(OAc)_2$ (10)	AgOTs (2)	$KHCO_3$ (2)	DMF	130	35
9	$Pd(OAc)_2$ (10)	AgOAc (2)	$KHCO_3$ (2)	1,4-dioxane	130	52
10	$Pd(OAc)_2$ (10)	Ag_2CO_3 (2)	$KHCO_3$ (2)	1,4-dioxane	130	48
11	$Pd(OAc)_2$ (10)	Ag_3PO_4 (2)	$KHCO_3$ (2)	1,4-dioxane	130	69
12	$Pd(OAc)_2$ (10)	$AgNO_3$ (2)	$KHCO_3$ (2)	1,4-dioxane	130	38
13	$Pd(OAc)_2$ (10)	AgTFA (2)	$KHCO_3$ (2)	1,4-dioxane	130	45
14	$PdCl_2$ (10)	Ag_3PO_4 (2)	$KHCO_3$ (2)	1,4-dioxane	130	59
15	$[PdCl(C_3H_5)]_2$ (10)	Ag_3PO_4 (2)	$KHCO_3$ (2)	1,4-dioxane	130	52
16	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (2)	$KHCO_3$ (2)	1,4-dioxane	130	93
17	$Pd_2(dba)_3$ (10)	Ag_3PO_4 (2)	$KHCO_3$ (2)	1,4-dioxane	130	48
18	$Pd(TFA)_2$ (10)	Ag_3PO_4 (2)	$KHCO_3$ (2)	1,4-dioxane	130	49
19	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (2)	$NaHCO_3$ (2)	1,4-dioxane	130	93
20	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (2)	Na_2CO_3 (2)	1,4-dioxane	130	97
21	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (2)	KOAc (2)	1,4-dioxane	130	52
22	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (2)	K_2HPO_4 (2)	1,4-dioxane	130	69
23	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (2)	K_2CO_3 (2)	1,4-dioxane	130	93
24	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (2)	Na_2CO_3 (2)	1,4-dioxane	110	83
25	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (2)	Na_2CO_3 (2)	1,4-dioxane	90	55
26	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (0.3)	Na_2CO_3 (2)	1,4-dioxane	130	52
27	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (0.6)	Na_2CO_3 (2)	1,4-dioxane	130	79
28	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (0.9)	Na_2CO_3 (2)	1,4-dioxane	130	97
29	$PdCl_2[P(Cy)_3]_2$ (5)	Ag_3PO_4 (0.9)	Na_2CO_3 (2)	1,4-dioxane	130	69
30	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (0.9)	Na_2CO_3 (1)	1,4-dioxane	130	69
31	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (0.9)	Na_2CO_3 (1.5)	1,4-dioxane	130	86
32	$PdCl_2[P(Cy)_3]_2$ (10)	Ag_3PO_4 (0.9)	Na_2CO_3 (2)	1,4-dioxane	130	76[b]

[a] **1a** (0.2 mmol), **2a** (0.4 mmol), Pd-catalyst, Ag-salt, Base, solvent (2 mL) at T ℃ under Ar; isolated yields; [b] In air.

4. General procedure for Pd-catalyzed C-P bond arylation of α-aminophosphonates

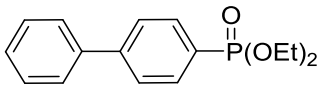


1a **2a** **3a**

General procedure (3a as example)

In a 10 mL Schlenk tube containing a magnetic stir bar, **1a** (44.6 mg, 0.2 mmol, 1.0 equiv), **2a** (112.0 mg, 0.4 mmol, 2.0 equiv), $PdCl_2[P(Cy)_3]_2$ (14.8 mg, 0.02 mmol, 10 mol %), Ag_3PO_4 (75.3 mg, 0.18 mmol, 0.9 equiv), Na_2CO_3 (42.4 mg, 0.4 mmol, 2 equiv) were added. The tube was evacuated and backfilled with Ar for 3 times, then 1,4-dioxane (2 mL) was added with a syringe under Ar and stirred on a pie-block preheated to 130 ℃ for 8 h. Upon completion, the reaction mixture was cooled to room temperature and concentrated under vacuum, and the residue was purified by silica gel chromatography (PE/EA = 2/1) to afford the product **3a** (56.3 mg, 97%).

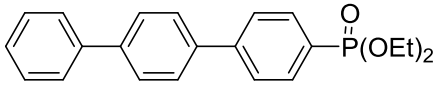
5. Characterization data of products



diethyl [1,1'-biphenyl]-4-ylphosphonate (**3a**)[2]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (56.3 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 13.0, 8.1 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 4.23 – 4.06 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (d, *J* = 3.3 Hz), 139.9 (d, *J* = 0.9 Hz), 132.3 (d, *J* = 10.2 Hz), 128.9, 128.1, 127.2, 127.1 (d, *J* = 15.3 Hz), 126.8 (d, *J* = 188.8 Hz), 62.1 (d, *J* = 5.6 Hz), 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.98. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{19}O_3PNa$, 313.0970; found, 313.0968.

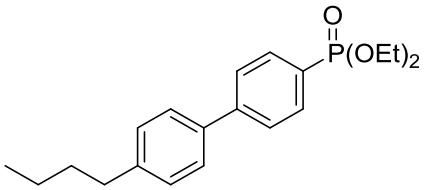


diethyl [1,1':4',1"-terphenyl]-4-ylphosphonate (**3b**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); colorless oil (70.3 mg, 96%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 13.0, 8.0 Hz, 2H), 7.81 (s, 1H), 7.74 (dd, *J* = 8.0, 3.7 Hz, 2H), 7.63 (dd, *J* = 12.0, 7.7 Hz, 3H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 4.23 – 4.09 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 142.0, 140.8, 140.5, 132.3 (d, *J* = 10.1 Hz), 129.3, 128.8, 127.5, 127.3, 127.2, 127.1 (d, *J* = 190.7 Hz), 126.9, 126.1 (d, *J* = 5.0 Hz), 62.1 (d, *J* = 5.3 Hz), 16.3 (d, *J* = 6.4 Hz). ^{31}P NMR (243

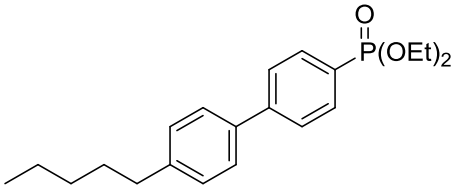
MHz, $CDCl_3$) δ 18.91. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{23}O_3PNa$, 389.1283; found, 389.1286.



diethyl (4'-butyl-[1,1'-biphenyl]-4-yl)phosphonate (**3c**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (62.3 mg, 90%).

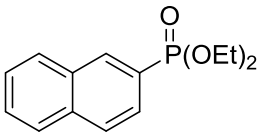
^1H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 13.0, 7.9 Hz, 2H), 7.67 (dd, *J* = 7.8, 3.7 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 4.21 – 4.06 (m, 4H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.39 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 6H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1 (d, *J* = 3.1 Hz), 143.1, 137.2, 132.2 (d, *J* = 10.4 Hz), 129.0, 127.0, 126.9 (d, *J* = 15.3 Hz), 126.6 (d, *J* = 190.6 Hz), 62.0 (d, *J* = 5.3 Hz), 35.2, 33.5, 22.3, 16.3 (d, *J* = 6.3 Hz), 13.8. ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.07. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{27}O_3PNa$, 369.1596; found, 369.1600.



diethyl (4'-pentyl-[1,1'-biphenyl]-4-yl)phosphonate (**3d**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (61.2 mg, 85%).

^1H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 13.0, 8.1 Hz, 2H), 7.59 (dd, *J* = 8.1, 3.8 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 4.13 – 3.98 (m, 4H), 2.60 – 2.54 (m, 2H), 1.61 – 1.53 (m, 2H), 1.31 – 1.23 (m, 10H), 0.82 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1 (d, *J* = 3.0 Hz), 143.1, 137.2, 132.2 (d, *J* = 10.3 Hz), 129.0, 127.0, 126.9 (d, *J* = 15.3 Hz), 126.5 (d, *J* = 190.8 Hz), 62.0 (d, *J* = 5.3 Hz), 35.5, 31.5, 31.0, 22.5, 16.3 (d, *J* = 6.4 Hz), 13.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.12. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{29}O_3PNa$, 383.1752; found, 383.1757.

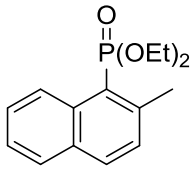


diethyl naphthalen-2-ylphosphonate (**3e**)[3]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); colorless oil (45.9 mg, 87%).

^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 15.5 Hz, 1H), 7.95 – 7.84 (m, 3H), 7.79 – 7.71 (m, 1H), 7.62 – 7.51 (m, 2H), 4.24 – 4.04 (m, 4H), 1.32 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9 (d, *J* = 2.7 Hz), 134.0 (d, *J* = 10.2 Hz), 132.3 (d, *J* = 16.5 Hz), 128.8, 128.3 (d, *J* = 14.3 Hz),

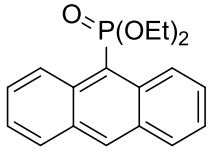
128.2, 127.7 (d, *J* = 0.7 Hz), 126.8 (d, *J* = 1.1 Hz), 126.4 (d, *J* = 9.9 Hz), 125.3 (d, *J* = 187.9 Hz), 62.1 (d, *J* = 5.3 Hz), 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.09. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{17}O_3PNa$, 287.0813; found, 287.0814.



diethyl (2-methylnaphthalen-1-yl)phosphonate (**3f**)

The title compound was purified by silica gel chromatography (PE/EA = 3/1); yellow oil (52.8 mg, 95%).

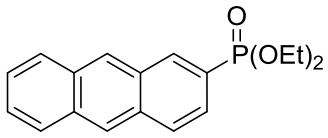
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.34 (dd, *J* = 8.4, 4.6 Hz, 1H), 4.26 – 4.15 (m, 2H), 4.09 – 3.99 (m, 2H), 2.88 (d, *J* = 2.3 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.86 (d, *J* = 10.1 Hz), 134.5(d, *J* = 12.8 Hz), 132.9, 132.1(d, *J* = 12.7 Hz), 130.1(d, *J* = 17.4 Hz), 128.3, 127.0, 125.2, 121.6 (d, *J* = 177.9 Hz), 61.5 (d, *J* = 5.2 Hz), 23.8, 16.3(d, *J* = 6.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.63. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{19}O_3PNa$, 301.0970; found, 301.0974.



diethyl anthracen-9-ylphosphonate (**3g**)

The title compound was purified by silica gel chromatography (PE/EA = 4/1); yellow oil (53.4 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (d, *J* = 9.2 Hz, 2H), 8.65 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.54 – 7.45 (m, 2H), 4.32 – 4.21 (m, 2H), 4.10 – 3.83 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0 (d, *J* = 11.5 Hz), 134.6 (d, *J* = 4.1 Hz), 131.0 (d, *J* = 15.2 Hz), 129.0 (d, *J* = 1.3 Hz), 127.4 (d, *J* = 1.4 Hz), 127.3, 125.1, 118.7 (d, *J* = 177.4 Hz), 61.8 (d, *J* = 4.9 Hz), 16.3 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.61. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{19}O_3PNa$, 337.0970; found, 337.0967.

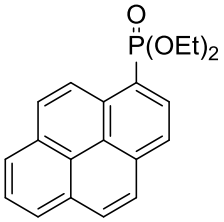


diethyl anthracen-2-ylphosphonate (**3h**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (48.4 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 16.4 Hz, 1H), 8.52 (s, 1H), 8.42 (s, 1H), 8.07 – 7.98 (m, 3H), 7.67 (t, *J* = 9.5 Hz, 1H), 7.51 (p, *J* = 7.0 Hz, 2H), 4.28 – 4.08 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4 (d, *J* = 10.0 Hz), 132.9, 132.1 (d, *J* = 2.6 Hz), 132.0 (d, *J* = 1.4 Hz),

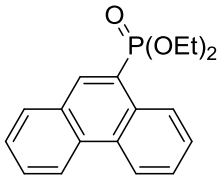
130.0 (d, *J* = 17.4 Hz), 128.7 (d, *J* = 13.9 Hz), 128.4, 128.1 (d, *J* = 2.5 Hz), 126.5, 126.3, 125.9, 124.8, 124.70 (d, *J* = 188.6 Hz), 124.69, 62.2 (d, *J* = 5.3 Hz), 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.11. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{19}O_3PNa$, 337.0970; found, 337.0967.



diethyl pyren-1-ylphosphonate (**3i**)[4]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); white solid (56.1 mg, 83%). mp = 71-72 °C.

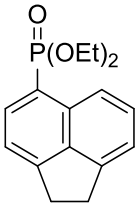
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 9.3 Hz, 1H), 8.68 (dd, *J* = 14.3, 7.9 Hz, 1H), 8.28 – 8.16 (m, 4H), 8.12 (d, *J* = 8.9 Hz, 1H), 8.02 (t, *J* = 8.2 Hz, 2H), 4.33 – 4.21 (m, 2H), 4.20 – 4.07 (m, 2H), 1.33 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5 (d, *J* = 3.1 Hz), 132.8 (d, *J* = 10.9 Hz), 131.8 (d, *J* = 9.4 Hz), 130.9, 130.3, 129.7, 129.0, 127.1, 126.3, 126.23, 126.17, 125.6 (d, *J* = 5.0 Hz), 124.6 (d, *J* = 14.4 Hz), 124.1 (d, *J* = 1.6 Hz), 123.9 (d, *J* = 15.5 Hz), 120.9 (d, *J* = 184.5 Hz), 62.2 (d, *J* = 5.1 Hz), 16.3 (d, *J* = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.88. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{19}O_3PNa$, 361.0970; found, 361.0972.



diethyl phenanthren-9-ylphosphonate (**3j**)[5]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); colorless oil (62.2 mg, 99%).

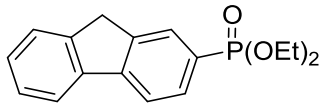
^{1}H NMR (400 MHz,$CDCl_3$) δ 8.71 (d, *J* = 7.3 Hz, 1H), 8.69 – 8.61 (m, 2H), 8.59 – 8.50 (m, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.61 (m, 4H), 4.30 – 4.19 (m, 2H), 4.16 – 4.04 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1 (d, *J* = 8.8 Hz), 132.2 (d, *J* = 2.8 Hz), 130.5 (d, *J* = 11.9 Hz), 130.0, 129.9 (d, *J* = 2.8 Hz), 129.7 (d, *J* = 3.4 Hz), 129.1, 127.4 (d, *J* = 3.6 Hz), 127.1, 127.1, 126.9, 123.2 (d, *J* = 182.4 Hz), 122.9 (d, *J* = 1.6 Hz), 122.5, 62.2 (d, *J* = 5.1 Hz), 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.36. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{19}O_3PNa$, 337.0970; found, 337.0974.



diethyl (1,2-dihydroacenaphthylen-5-yl)phosphonate (**3k**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (56.3 mg, 97%).

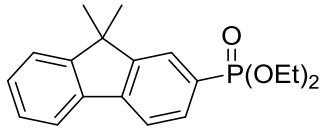
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 15.9, 7.1 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.34 – 7.31 (m, 1H), 4.18 (dp, *J* = 10.1, 7.2 Hz, 2H), 4.07 – 4.00 (m, 2H), 3.41 (s, 4H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 146.4, 139.1 (d, *J* = 14.1 Hz), 136.5 (d, *J* = 11.3 Hz), 131.1 (d, *J* = 10.8 Hz), 129.3, 122.0, 120.1, 119.4 (d, *J* = 187.9 Hz), 118.4 (d, *J* = 16.8 Hz), 61.8 (d, *J* = 5.0 Hz), 30.4, 30.2, 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.92. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{19}O_3PNa$, 313.0970; found, 313.0975.



diethyl (9H-fluoren-2-yl)phosphonate (**3l**)[5]

The title compound was purified by silica gel chromatography (PE/EA = 3/1); yellow oil (51.3 mg, 85%).

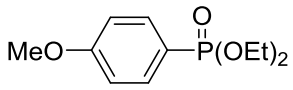
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 13.1 Hz, 1H), 7.88 – 7.81 (m, 3H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.42 – 7.35 (m, 2H), 4.21 – 4.07 (m, 4H), 3.94 (s, 2H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 143.9, 143.1 (d, *J* = 16.4 Hz), 140.5, 130.6 (d, *J* = 10.8 Hz), 128.4 (d, *J* = 10.5 Hz), 128.0, 127.0, 125.9 (d, *J* = 187.6 Hz), 125.2, 120.7, 119.8 (d, *J* = 16.5 Hz), 62.0 (d, *J* = 5.2 Hz), 36.8, 16.3 (d, *J* = 6.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.96. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{17}H_{19}O_3PNa$, 325.0970; found, 325.0975.



diethyl (9,9-dimethyl-9H-fluoren-2-yl)phosphonate (**3m**)[5]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (55.4 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 13.2 Hz, 1H), 7.76 (dd, *J* = 12.2, 6.5 Hz, 3H), 7.44 (d, *J* = 5.1 Hz, 1H), 7.39 – 7.31 (m, 2H), 4.23 – 4.03 (m, 4H), 1.49 (s, 6H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 153.4 (d, *J* = 15.4 Hz), 143.3 (d, *J* = 3.1 Hz), 137.8, 130.7 (d, *J* = 10.8 Hz), 128.4, 127.1, 126.3 (d, *J* = 188.2 Hz), 126.2 (d, *J* = 10.7 Hz), 122.7, 120.7, 119.8 (d, *J* = 16.3 Hz), 62.0 (d, *J* = 5.4 Hz), 47.0 (d, *J* = 1.8 Hz), 26.8, 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.05. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{24}O_3P$, 331.1463; found, 331.1459.

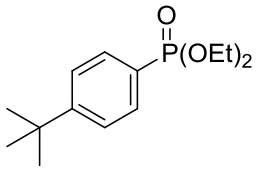


diethyl (4-methoxyphenyl)phosphonate (**3n**)[7]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); colorless oil (41.5 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 12.7, 8.7 Hz, 2H), 6.96 (dd, *J* = 8.5, 2.9 Hz, 2H), 4.18 – 3.98 (m, 4H), 3.84 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 133.8 (d, *J* =

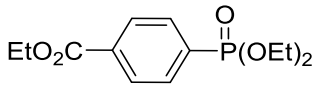
11.3 Hz), 119.5 (d, *J* = 194.1 Hz), 114.0 (d, *J* = 16.0 Hz), 61.88 (d, *J* = 5.2 Hz), 55.3, 16.31 (d, *J* = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.73. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{11}H_{17}O_4PNa$, 267.0762; found, 267.0764.



diethyl (4-(tert-butyl)phenyl)phosphonate (**3o**)[2]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); colorless oil (50.2 mg, 93%).

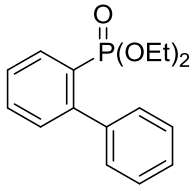
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 13.0, 8.4 Hz, 2H), 7.48 – 7.41 (m, 2H), 4.15 – 3.98 (m, 4H), 1.33 – 1.26 (m, 15H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 131.6 (d, *J* = 10.5 Hz), 125.4 (d, *J* = 15.2 Hz), 124.9 (d, *J* = 189.8 Hz), 61.9 (d, *J* = 5.2 Hz), 35.0, 31.0, 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.47. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{23}O_3PNa$, 293.1283; found, 293.1288.



ethyl 4-(diethoxyphosphoryl)benzoate (**3p**)[3]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); colorless oil (52.1 mg, 91%).

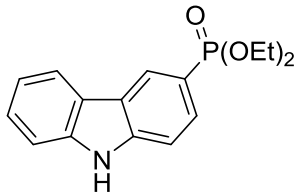
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.8, 3.6 Hz, 2H), 7.85 (dd, *J* = 12.9, 8.1 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.10 (qd, *J* = 17.2, 9.7 Hz, 4H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 133.8 (d, *J* = 3.3 Hz), 131.7 (d, *J* = 10.0 Hz), 129.3 (d, *J* = 15.0 Hz), 133.0 (d, *J* = 186.4 Hz), 62.3 (d, *J* = 5.4 Hz), 61.34, 16.2 (d, *J* = 6.4 Hz), 14.18. ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.08. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{13}H_{19}O_5PNa$, 309.0868; found, 309.0865.



diethyl [1,1'-biphenyl]-2-ylphosphonate (**3q**)[8]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (51.0 mg, 88%).

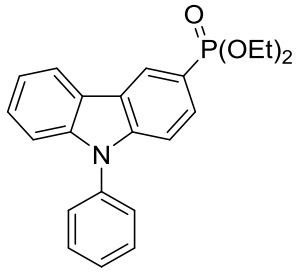
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (ddd, *J* = 14.3, 7.7, 1.0 Hz, 1H), 7.55 (dd, *J* = 10.7, 4.4 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.40 – 7.34 (m, 3H), 7.32 (dd, *J* = 9.7, 3.4 Hz, 1H), 3.92 (dp, *J* = 10.1, 7.1 Hz, 2H), 3.86 – 3.79 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.0 (d, *J* = 9.7 Hz), 141.4 (d, *J* = 4.2 Hz), 133.8 (d, *J* = 9.8 Hz), 131.9, 131.30 (d, *J* = 14.1 Hz), 129.3, 127.42, 127.37, 127.0 (d, *J* = 187.7 Hz), 126.9, 126.8, 61.7 (d, *J* = 6.0 Hz), 16.0 (d, *J* = 6.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.12. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{19}O_3PNa$, 313.0970; found, 313.0974.



diethyl (9H-carbazol-3-yl)phosphonate (**3r**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (27.9 mg, 46%).

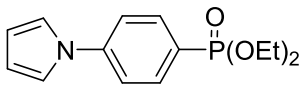
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.59 (d, *J* = 13.9 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.77 (m, 1H), 7.52 – 7.39 (m, 3H), 7.26 (dd, *J* = 8.4, 6.3 Hz, 1H), 4.24 – 4.04 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0 (d, *J* = 2.8 Hz), 139.9, 128.7 (d, *J* = 11.8 Hz), 126.6, 125.2 (d, *J* = 11.7 Hz), 123.2 (d, *J* = 17.6 Hz), 122.8 (d, *J* = 1.7 Hz), 120.6, 120.1, 119.0 (d, *J* = 181.9 Hz), 111.0, 110.9 (d, *J* = 16.5 Hz), 62.0 (d, *J* = 5.1 Hz), 16.4 (d, *J* = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.78. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{18}NO_3PNa$, 326.0922; found, 326.0924.



diethyl (9-phenyl-9H-carbazol-3-yl)phosphonate (**3s**)[9]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (65.9 mg, 87%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 13.8 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.56 – 7.49 (m, 3H), 7.47 – 7.42 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 4.24 – 4.15 (m, 2H), 4.11 (dp, *J* = 10.0, 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 141.4, 137.0, 130.0, 129.0 (d, *J* = 11.9 Hz), 128.0, 127.1, 126.7, 125.3 (d, *J* = 11.7 Hz), 123.2 (d, *J* = 17.5 Hz), 122.9, 120.8, 120.6, 118.3 (d, *J* = 191.6 Hz), 110.1, 109.9 (d, *J* = 16.2 Hz), 61.9 (d, *J* = 5.0 Hz), 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 21.25. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{22}NO_3PNa$, 402.1235; found, 402.1240.

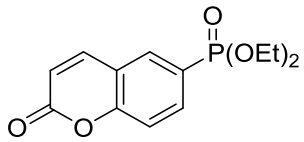


diethyl (4-(1H-pyrrol-1-yl)phenyl)phosphonate (**3t**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (46.9 mg, 84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 12.8, 8.5 Hz, 2H), 7.46 (dd, *J* = 8.5, 3.2 Hz, 2H), 7.15 – 7.11 (m, 2H), 6.39 – 6.33 (m, 2H), 4.19 – 4.05 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.5 (d, *J* = 3.3 Hz), 133.4 (d, *J* = 10.7 Hz), 124.9 (d, *J* = 193.3 Hz), 119.5 (d, *J* = 15.6 Hz),

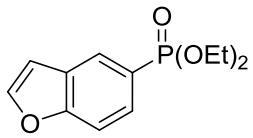
118.9, 111.4, 62.1 (d, J = 5.3 Hz), 16.3 (d, J = 6.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.21. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{18}NO_3PNa$, 302.0922; found, 302.0927.



diethyl (2-oxo-2H-chromen-6-yl)phosphonate (**3u**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); colorless oil (44.0 mg, 78%).

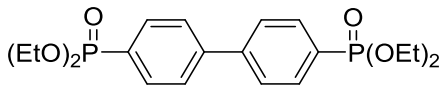
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 13.5 Hz, 1H), 7.92 – 7.84 (m, 1H), 7.73 (d, J = 9.6 Hz, 1H), 7.38 (dd, J = 8.5, 2.9 Hz, 1H), 6.47 (d, J = 9.6 Hz, 1H), 4.11 (tdd, J = 17.2, 9.8, 7.7 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 156.4 (d, J = 3.4 Hz), 142.8, 134.5 (d, J = 10.4 Hz), 132.4 (d, J = 11.5 Hz), 125.0 (d, J = 192.8 Hz), 118.7 (d, J = 16.9 Hz), 117.6, 117.3 (d, J = 15.0 Hz), 62.4 (d, J = 5.5 Hz), 16.3 (d, J = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.60. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{13}H_{15}O_5PNa$, 305.0555; found, 305.0554.



diethyl benzofuran-5-ylphosphonate (**3v**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (40.6 mg, 80%).

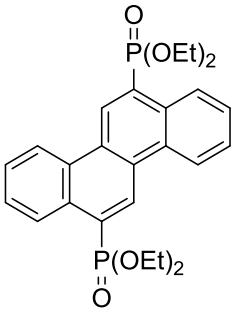
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 13.8 Hz, 1H), 7.78 – 7.66 (m, 2H), 7.58 (dd, J = 8.2, 2.0 Hz, 1H), 6.83 (s, 1H), 4.11 (tdd, J = 17.2, 9.9, 7.7 Hz, 4H), 1.32 (t, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0 (d, J = 3.3 Hz), 146.1, 127.6 (d, J = 11.9 Hz), 127.5 (d, J = 18.6 Hz), 126.2 (d, J = 11.6 Hz), 122.4 (d, J = 190.1 Hz), 111.8 (d, J = 16.7 Hz), 106.8, 62.1 (d, J = 5.3 Hz), 16.3 (d, J = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.96. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{12}H_{15}O_4PNa$, 277.0606; found, 277.0609.



tetraethyl [1,1'-biphenyl]-4,4'-diylbis(phosphonate) (**3w**)[10]

The title compound was purified by silica gel chromatography (PE/EA = 1/1); white solid (27.3 mg, 32%). mp = 45-46 ^{o}C.

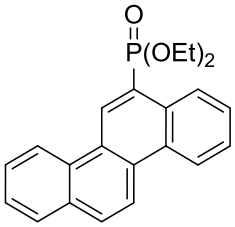
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 12.8, 8.2 Hz, 4H), 7.68 (dd, J = 11.4, 9.7 Hz, 4H), 4.24 – 4.01 (m, 8H), 1.32 (t, J = 7.0 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8 (d, J = 3.3 Hz), 132.3 (d, J = 10.2 Hz), 127.9 (d, J = 189.5 Hz), 127.2 (d, J = 15.2 Hz), 62.1 (d, J = 5.5 Hz), 16.3 (d, J = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.41. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{28}O_6P_2Na$, 449.1259; found, 449.1254.



tetraethyl chrysene-6,12-diylbis(phosphonate) (**3xa**)

The title compound was purified by silica gel chromatography (PE/EA = 1/1); yellow oil (27.0 mg, 27%).

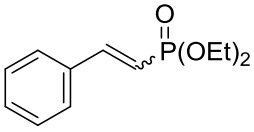
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 18.5 Hz, 2H), 8.98 (d, *J* = 8.2 Hz, 2H), 8.65 (d, *J* = 8.2 Hz, 2H), 7.78 (dt, *J* = 15.0, 7.2 Hz, 4H), 4.36 – 4.23 (m, 4H), 4.20 – 4.06 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.1, 131.0, 130.8, 130.4 (d, *J* = 10.6 Hz), 129.1 (d, *J* = 3.1 Hz), 128.9 (d, *J* = 3.0 Hz), 127.7 (d, *J* = 6.1 Hz), 127.4 (d, *J* = 3.8 Hz), 126.4 (d, *J* = 181.7 Hz), 123.8, 62.5 (d, *J* = 5.2 Hz), 16.4 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.96. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{30}O_6P_2Na$, 523.1415; found, 523.1412.



diethyl chrysen-6-ylphosphonate (**3xb**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (31.3 mg, 43%).

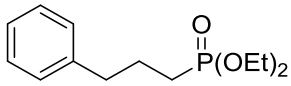
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 18.5 Hz, 1H), 8.93 (d, *J* = 8.4 Hz, 1H), 8.83 (d, *J* = 7.8 Hz, 1H), 8.68 (dd, *J* = 18.3, 8.7 Hz, 2H), 8.11 (d, *J* = 9.1 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.75 (dd, *J* = 15.0, 7.5 Hz, 3H), 7.67 (t, *J* = 7.4 Hz, 1H), 4.35 – 4.23 (m, 2H), 4.20 – 4.08 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.6, 132.1(d, *J* = 0.9 Hz), 131.7 (d, *J* = 9.9 Hz), 131.1 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 12.5 Hz), 130.6, 130.4 (d, *J* = 10.6 Hz), 130.1, 128.5, 127.4, 127.4, 127.1, 126.9 (d, *J* = 13.6 Hz), 126.2 (d, *J* = 16.7 Hz), 123.6 (d, *J* = 1.6 Hz), 123.29, 123.25 (d, *J* = 182.8 Hz), 120.7, 62.3 (d, *J* = 5.1 Hz), 16.4 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.86. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{21}O_3PNa$, 387.1126; found, 387.1125.



diethyl styrylphosphonate (**3y**)[11]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (35.0 mg, 73%), *E-Z* stereoselectivity determinded by ^{31}P NMR (E/Z = 8:5).

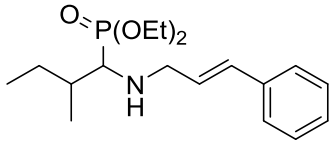
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.0 Hz, 2H), 7.57 – 7.32 (m, 10H), 6.26 (t, *J* = 17.6 Hz, 1H), 5.81 (t, *J* = 14.9 Hz, 1H), 4.18 – 4.09 (m, 4H), 4.06 – 3.93 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H), 1.19 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9 (d, *J* = 6.9 Hz), 148.4 (d, *J* = 1.6 Hz), 135.2 (d, *J* = 8.9 Hz), 134.8 (d, *J* = 22.8 Hz), 130.2, 129.5, 129.3, 128.8, 128.1, 127.7, 116.5 (d, *J* = 185.4 Hz), 113. 8 (d, *J* = 191.3 Hz), 61.82 (d, *J* = 7.5 Hz), 61.76 (d, *J* = 5.9 Hz), 16.4(d, *J* = 6.5 Hz), 16.1 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.56, 16.03. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{12}H_{17}O_3NaP$, 263.0813; found, 263.0817.



diethyl (3-phenylpropyl)phosphonate (**3z**)[12]

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (17.4 mg, 34%).

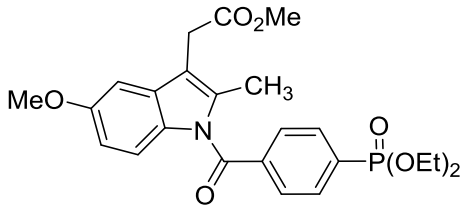
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 9.3 Hz, 3H), 4.07 (dt, *J* = 7.1, 6.1 Hz, 4H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.00 – 1.85 (m, 2H), 1.79 – 1.67 (m, 2H), 1.30 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 128.4, 128.4, 126.0, 61.4 (d, *J* = 6.5 Hz), 36.4 (d, *J* = 17.2 Hz), 25.0 (d, *J* = 141.0 Hz), 24.1 (d, *J* = 4.8 Hz), 16.4 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.16. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{13}H_{21}O_3PNa$, 279.1126; found, 279.1123.



diethyl (1-(cinnamylamino)-2-methylbutyl)phosphonate (**4**)

The title compound was purified by silica gel chromatography (PE/EA = 3/1); yellow oil (40.0 mg, 59%, dr = 4:3); diastereoselectivity determinded by ^{31}P NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.4 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.28 – 6.09 (m, 1H), 4.23 – 4.04 (m, 4H), 3.67 – 3.54 (m, 1H), 3.47 (dd, *J* = 13.9, 6.6 Hz, 1H), 2.87 (ddd, *J* = 19.5, 15.7, 2.9 Hz, 1H), 1.83 (dd, *J* = 14.1, 6.9 Hz, 1H), 1.74 – 1.61 (m, 1H), 1.61 – 1.38 (m, 1H), 1.38 – 1.22 (m, 7H), 1.01 (dd, *J* = 22.8, 6.8 Hz, 3H), 0.88 (q, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 131.5, 128.4, 128.3, 127.3, 126.1, 61.6 (d, *J* = 7.3 Hz), 61.5 (d, *J* = 7.4 Hz), 58.9 (d, *J* = 143.8 Hz), 56.8 (d, *J* = 141.4 Hz), 51.4 (d, *J* = 3.6 Hz), 51.1 (d, *J* = 5.5 Hz), 36.1 (d, *J* = 5.2 Hz), 35.7 (d, *J* = 5.1 Hz), 27.3, 27.1, 16.53 (d, *J* = 2.8 Hz), 16.47 (d, *J* = 2.8 Hz), 14.9, 12.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.05, 28.14. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{30}NO_3PNa$, 362.1861; found, 362.1858.



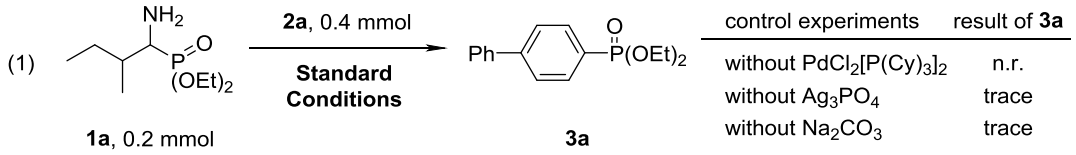
methyl 2-(1-(4-(diethoxyphosphoryl)benzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**3bb**)

The title compound was purified by silica gel chromatography (PE/EA = 2/1); yellow oil (39.8 mg, 42%).

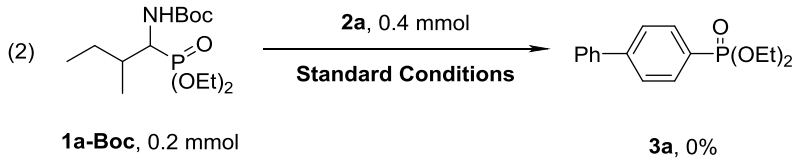
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 12.9, 7.9 Hz, 2H), 7.78 (dd, *J* = 7.8, 3.7 Hz, 2H), 6.96 (d, *J* = 2.2 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.2 Hz, 1H), 4.24 – 4.12 (m, 4H), 3.84 (s, 3H), 3.71 (s, 3H), 3.67 (s, 2H), 2.35 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 168.4, 156.2, 139.2, 135.8, 133.1 (d, *J* = 187.5 Hz), 132.0 (d, *J* = 9.9 Hz), 130.7 (d, *J* = 9.3 Hz), 129.2 (d, *J* = 14.9 Hz), 115.1, 112.9, 111.7, 101.4, 62.5 (d, *J* = 5.6 Hz), 55.7, 52.1, 30.1, 16.3 (d, *J* = 6.0 Hz), 13.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ 16.48. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{29}NO_7P$, 474.1682; found, 474.1687.

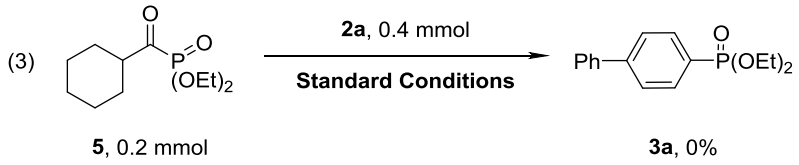
6. Preliminary mechanistic studies

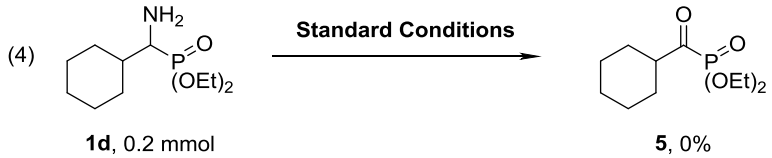
6.1 Control experiments



control experiments	result of **3a**
without $PdCl_2[P(Cy)_3]_2$	n.r.
without Ag_3PO_4	trace
without Na_2CO_3	trace

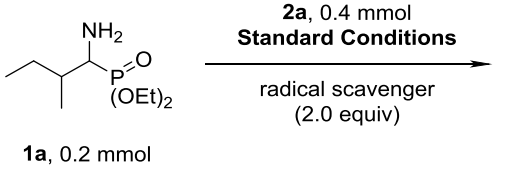






Controlled experiments 1-4 were carried out with **1a**, **1a-Boc**, or **1d** (0.2 mmol, 1.0 equiv) under Standard Conditions. The procedure was performed as in General procedure, but the results were monitored by TLC.

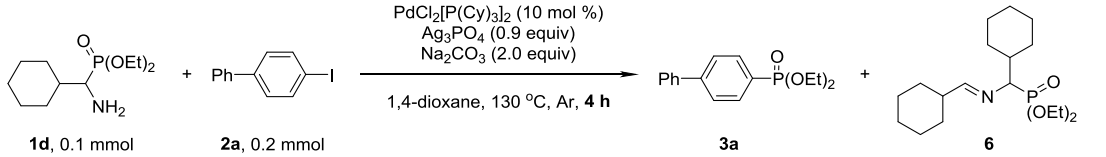
6.2 Radical-trapping experiments



radical scavenger	yield of **3a**
TEMPO	93%
DDNU	79%

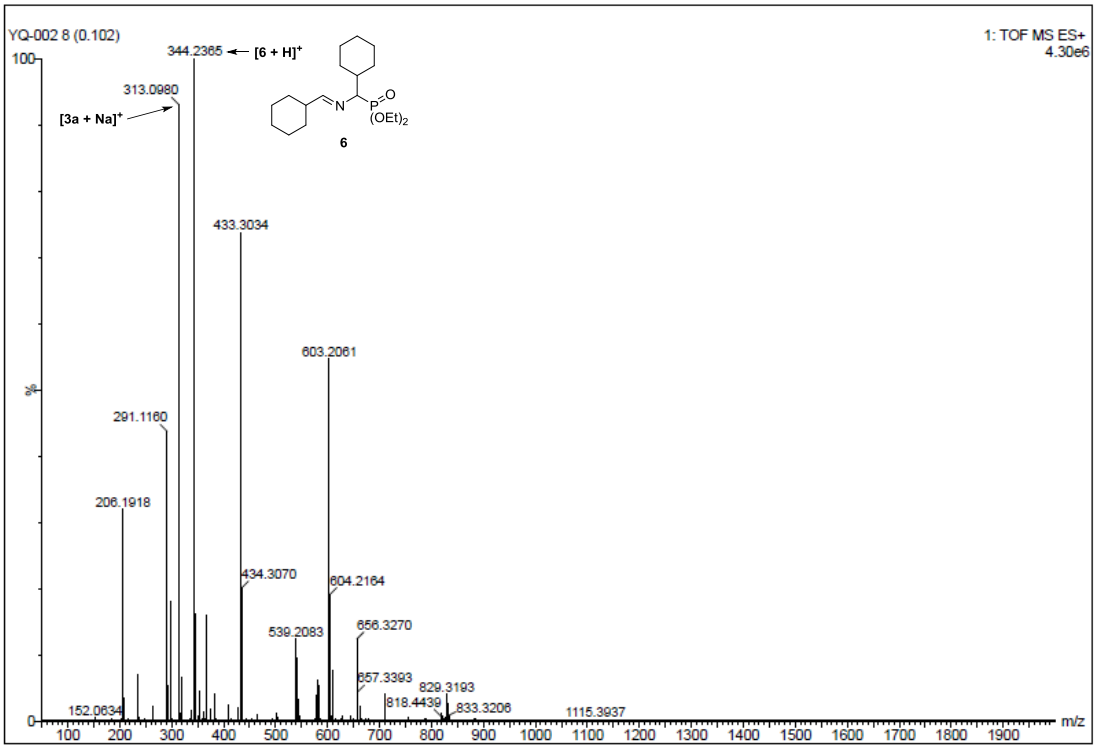
Under the Standard Conditions, 2.0 equivalents of radical scavengers were added into the mixture. After the reaction finished, the mixture was concentrated under vacuum, and the residue was purified by silica gel chromatography (PE/EA = 2/1) to afford the product **3a**, respectively.

6.3 Analytical data of ESI-MS



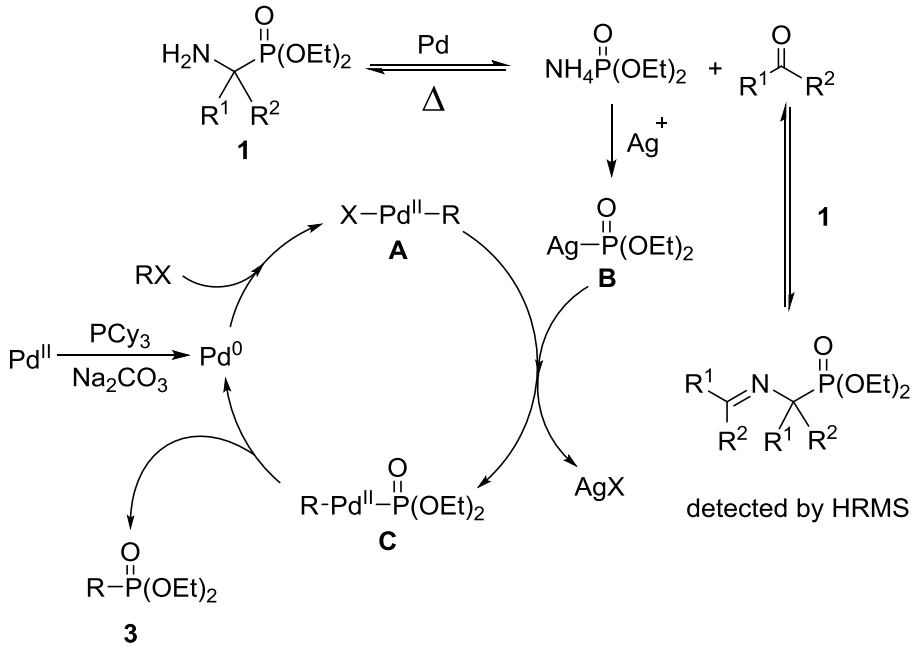
HRMS (ESI, m/z) $[M+H]^+$
cacld: 344.2355;
found,344.2365

In a 10 mL Schlenk tube containing a magnetic stir bar, **1d** (24.9mg, 0.1 mmol, 1.0 equiv), **2a** (56.0 mg, 0.2 mmol, 2.0 equiv), $PdCl_2[P(Cy)_3]_2$ (7.4 mg, 0.01 mmol, 10 mol %), Ag_3PO_4 (37.7 mg, 0.09 mmol, 0.9 equiv), Na_2CO_3 (21.2 mg, 0.2 mmol, 2 equiv) were added. The tube was evacuated and backfilled with Ar for 3 times, then 1,4-dioxane (1 mL) was added with a syringe under Ar and stirred on a pie-block preheated to 130 ℃ for 4 h. The reaction was cooled to room temperature, concentrated under vacuum, and diluted with CH_3CN prior to the injection into the mass spectrometer.



6.4 Proposed mechanism

Based on these results and previous reports on C-P bonds cleavage,[13] a reaction mechanism was proposed. Firstly, Pd^{II} was reduced to form Pd^0 *in situ*, followed by oxidative addition with halogenates to produce **Int-A**. On the other hand, the aminophosphonate was decomposed to phosphonate amine salt and aldehyde or ketone. Subsequently, the phosphonate amine salt immediately generated **Int-B** with silver salt, which was transmetallized with **Int-A** to give **Int-C**. Ultimately, reductive elimination produced Pd^0 and C-P bond functionalized product **3**.



7. References

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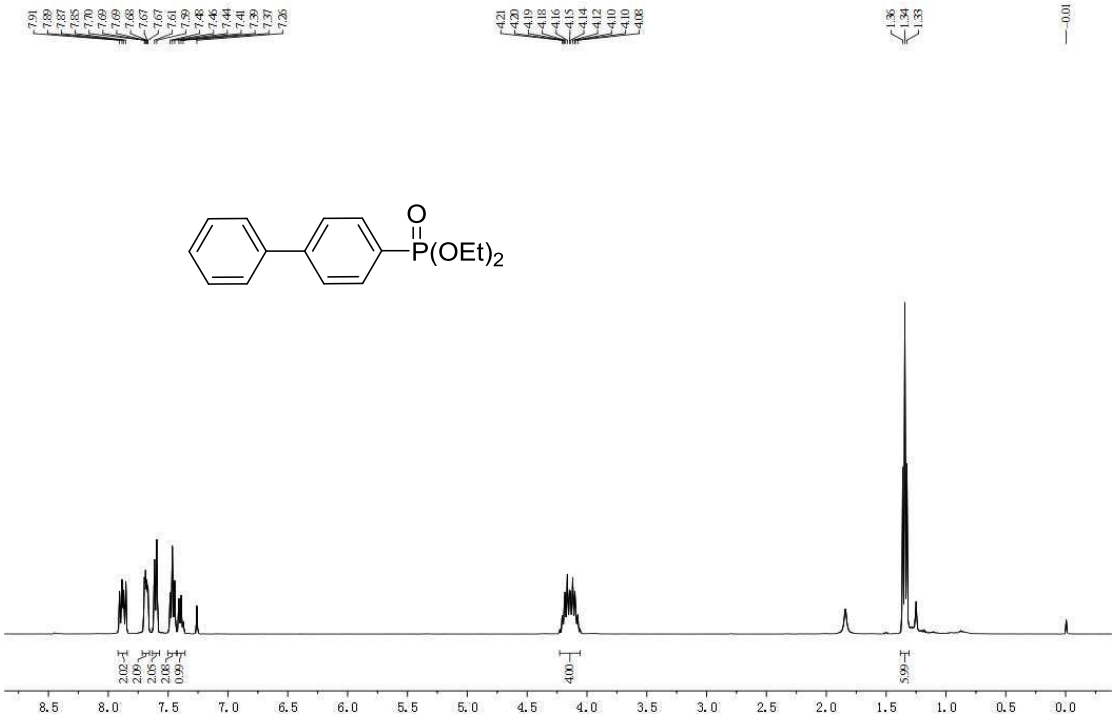
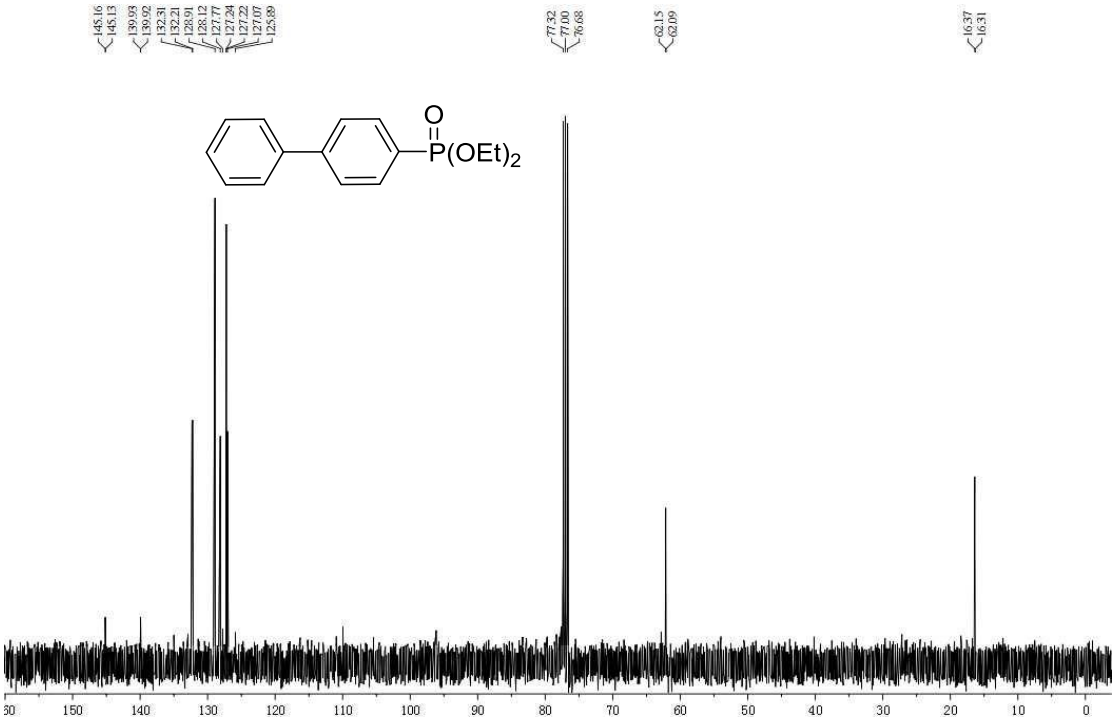
8. Copies of NMR spectra

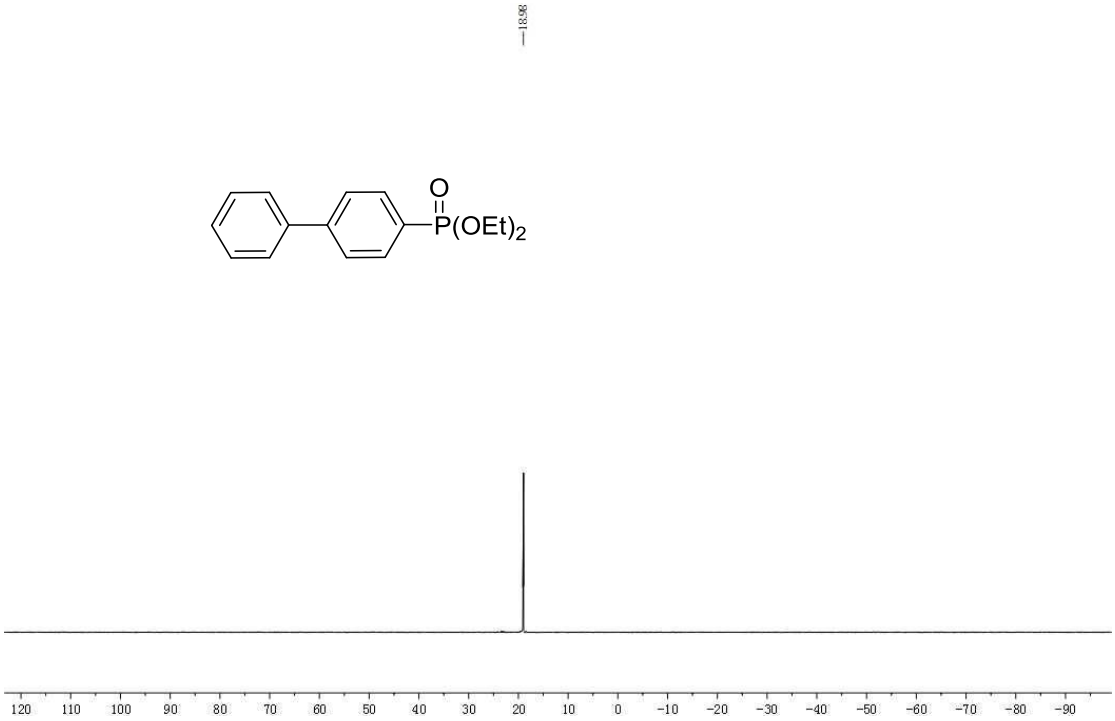
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3a



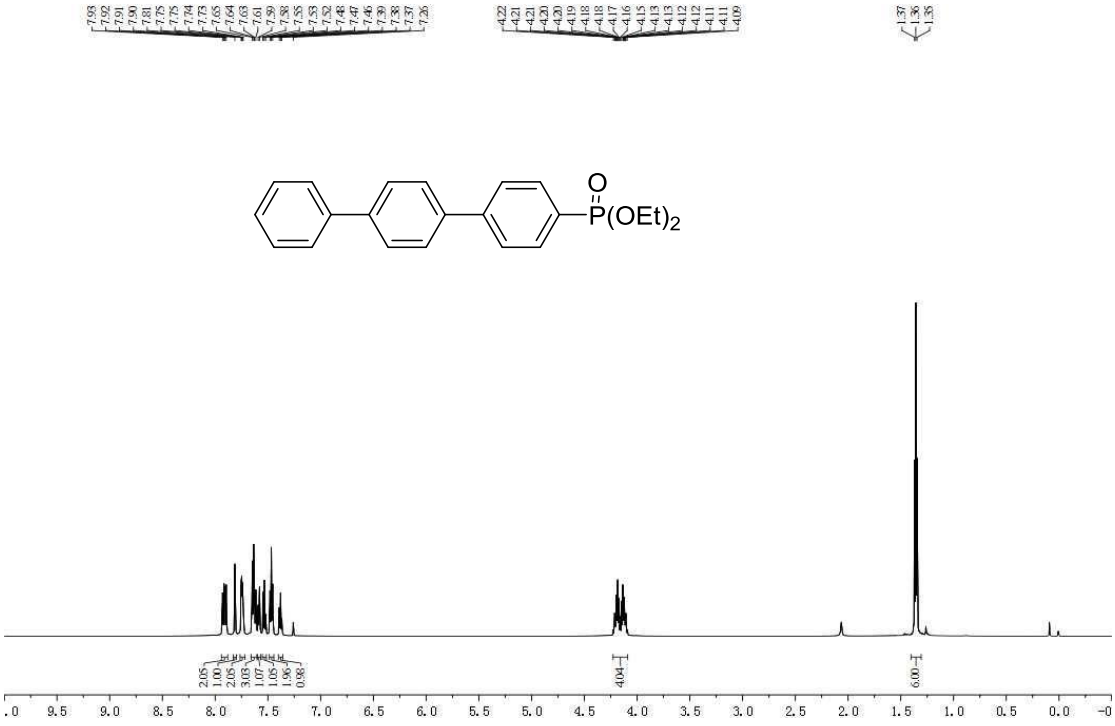
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3a



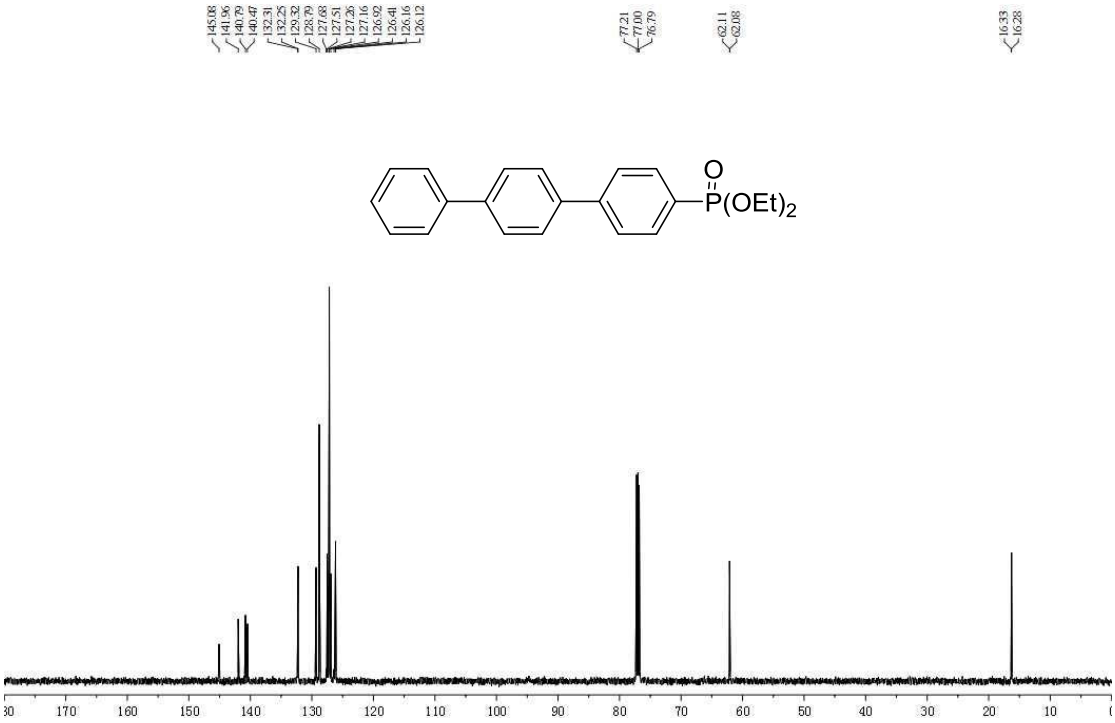
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3a



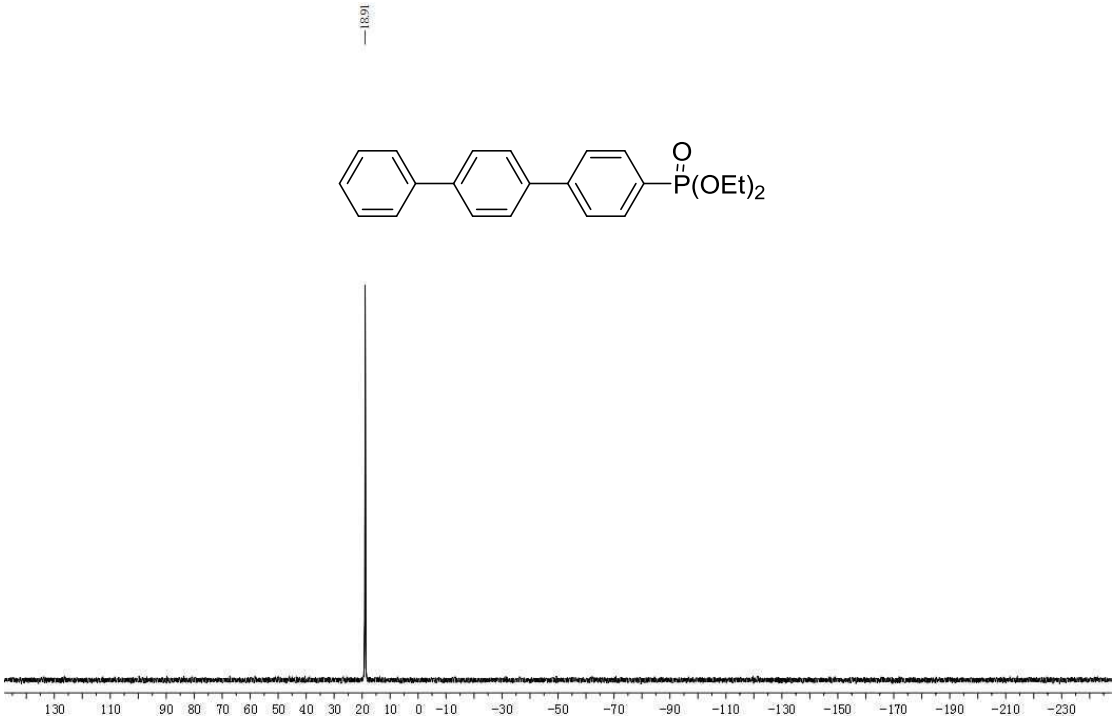
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3b



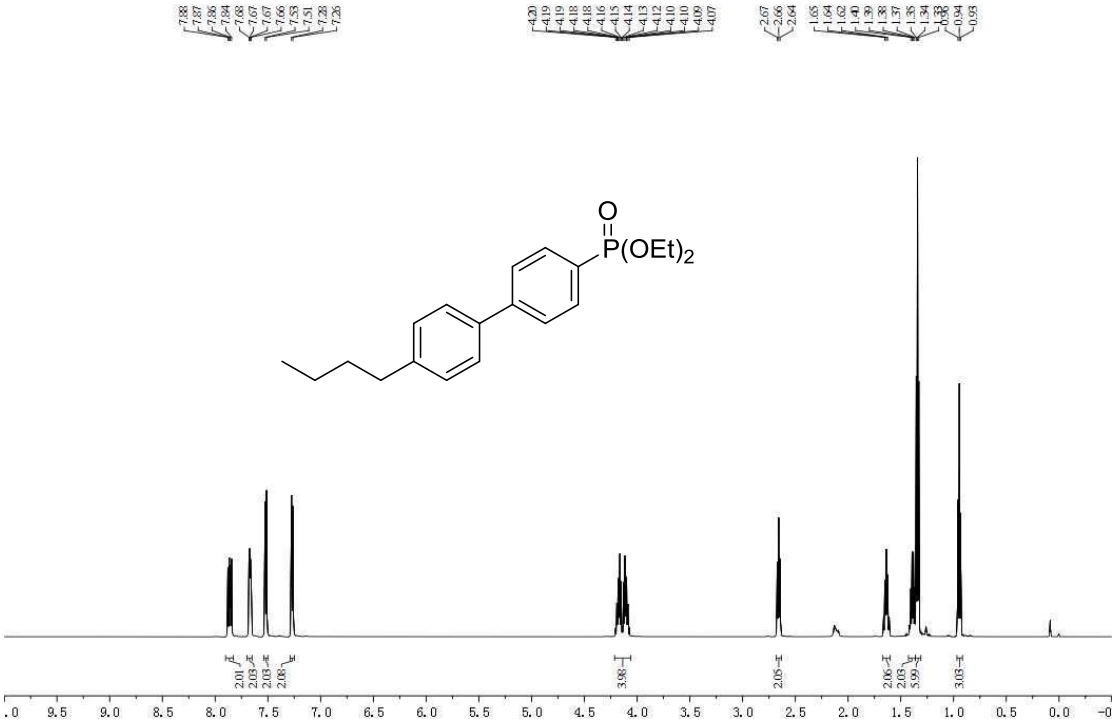
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3b



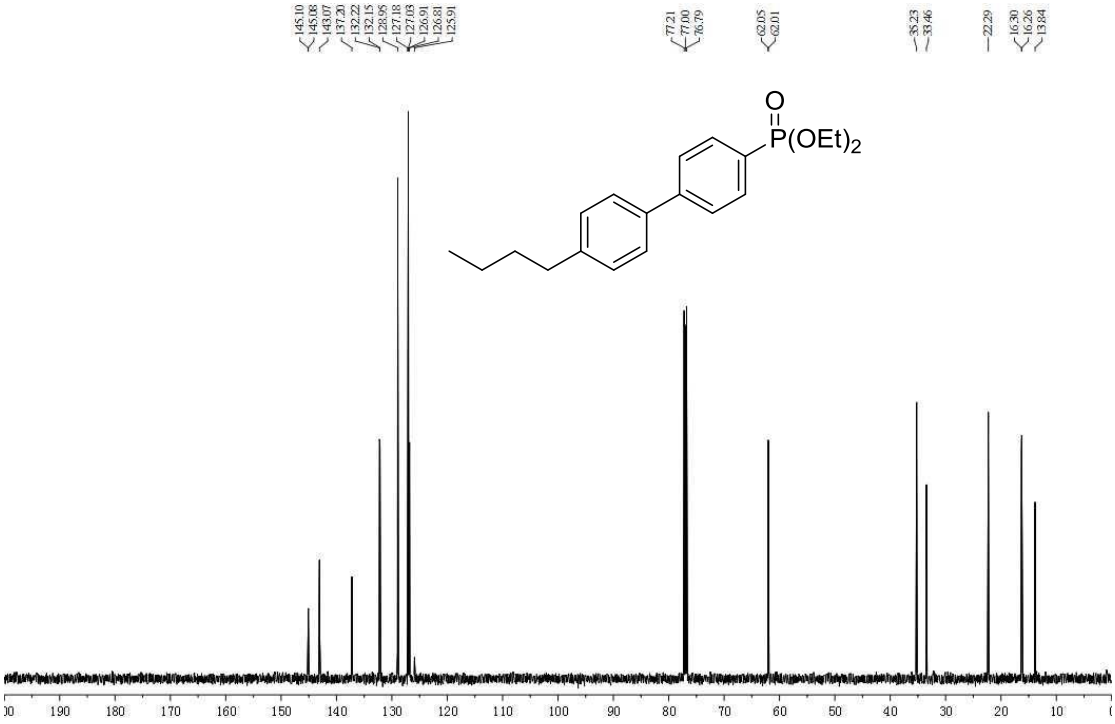
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3b



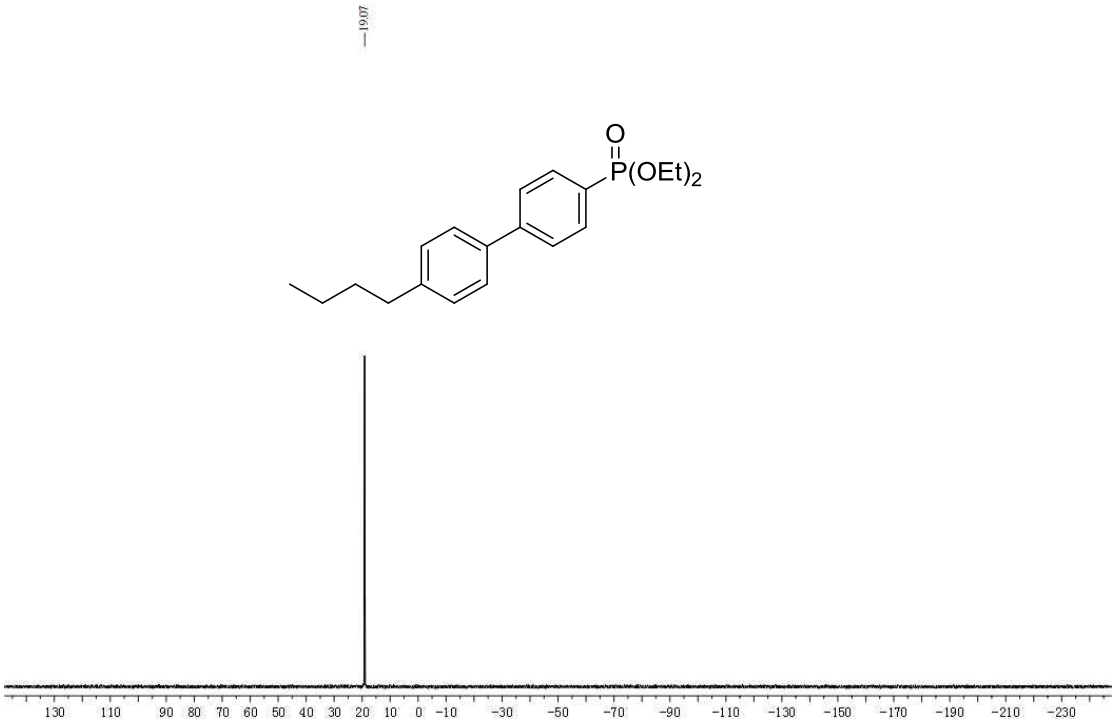
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3c



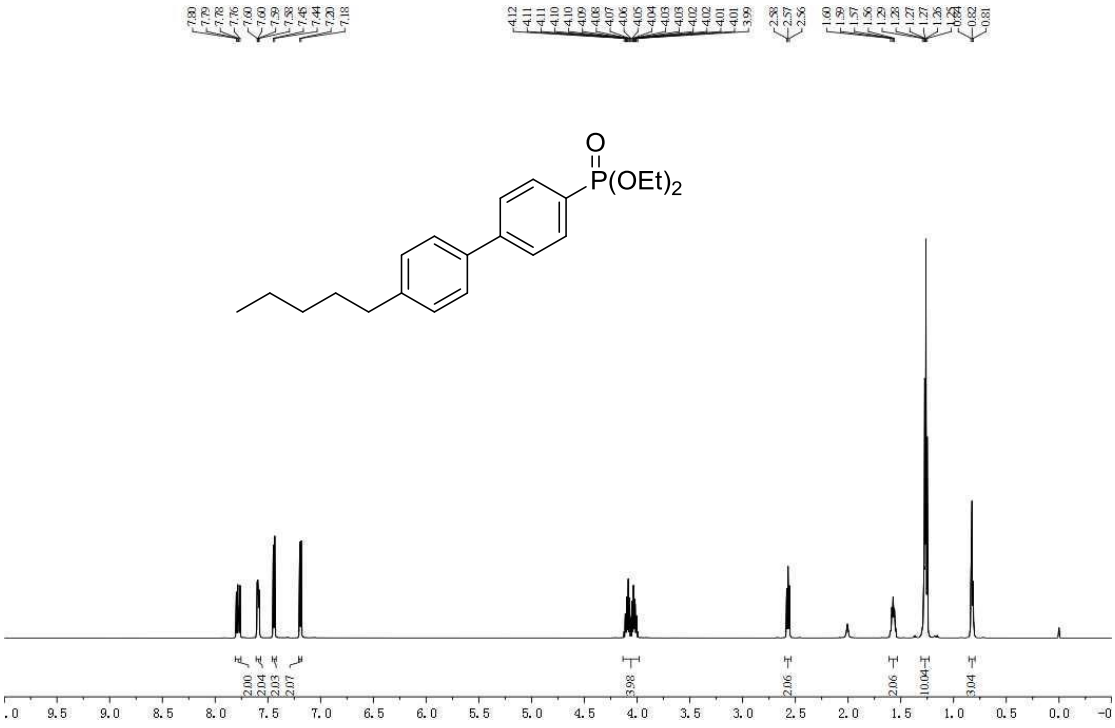
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3c



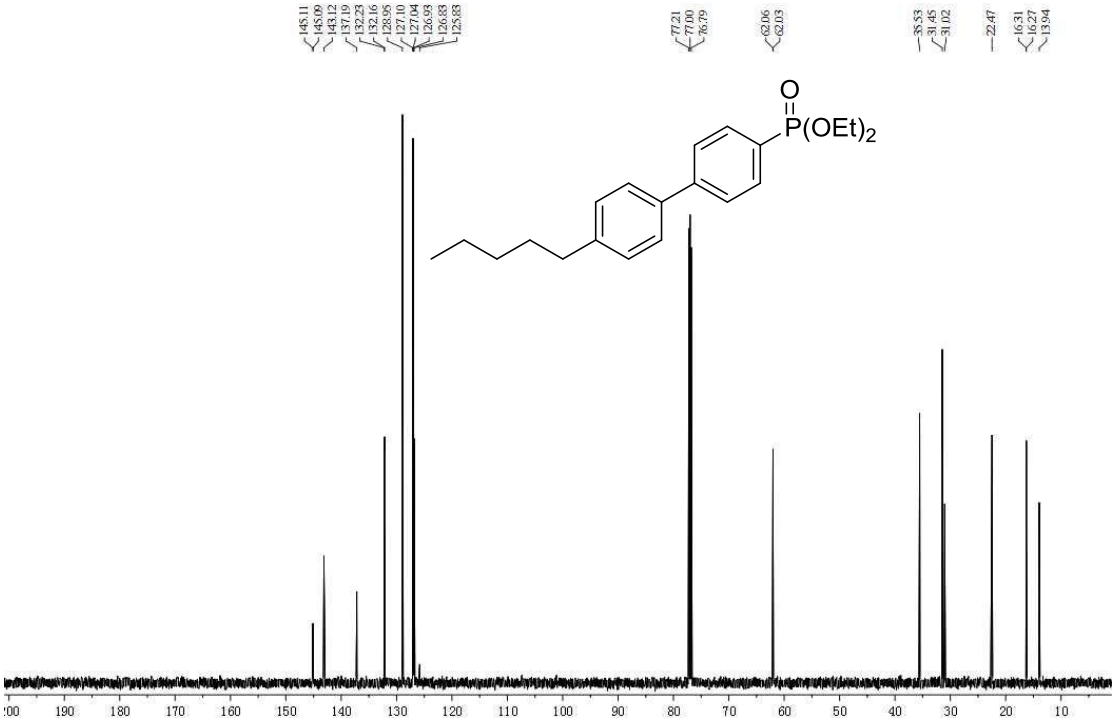
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3c



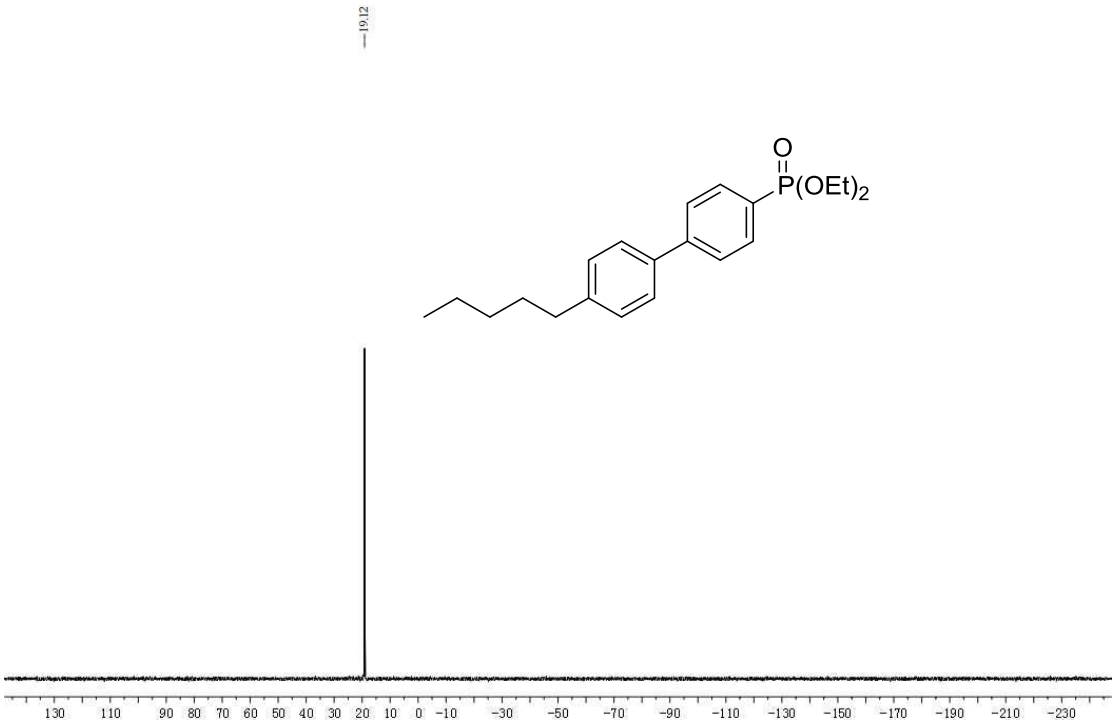
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3d



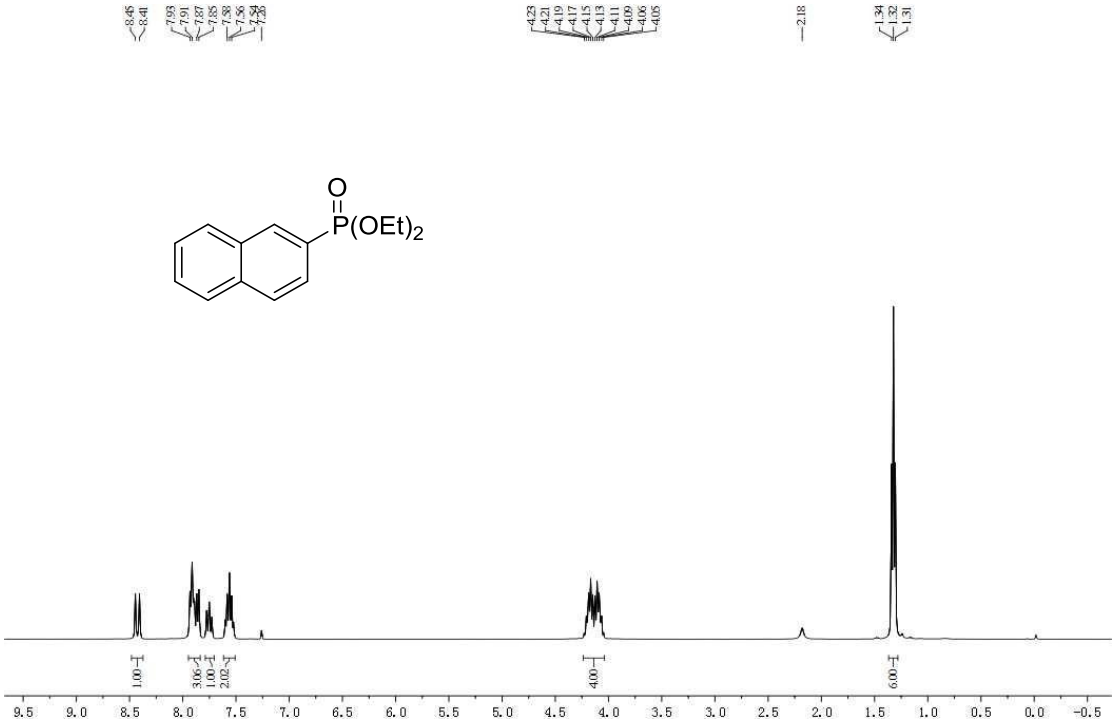
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3d



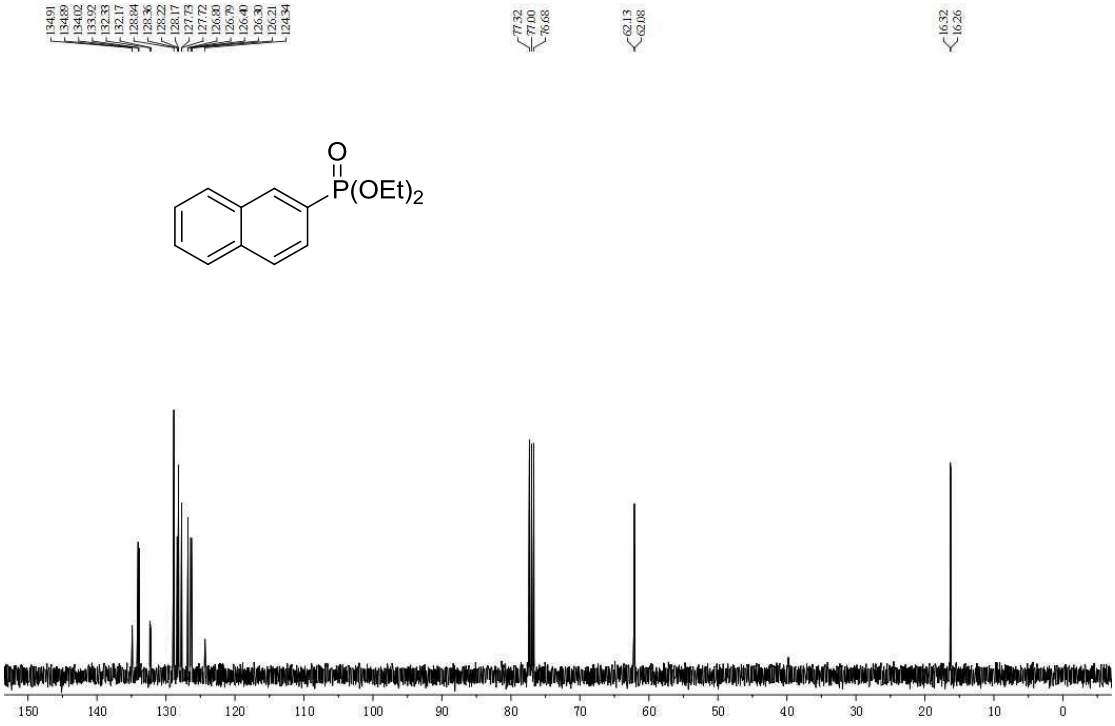
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3d



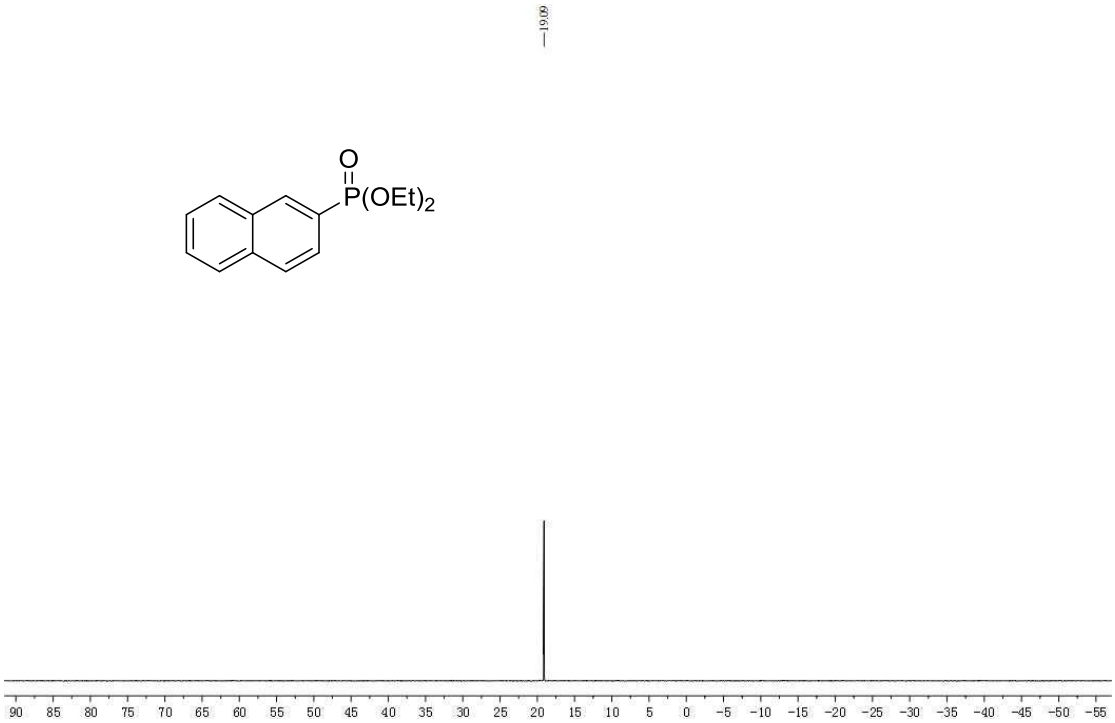
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3e



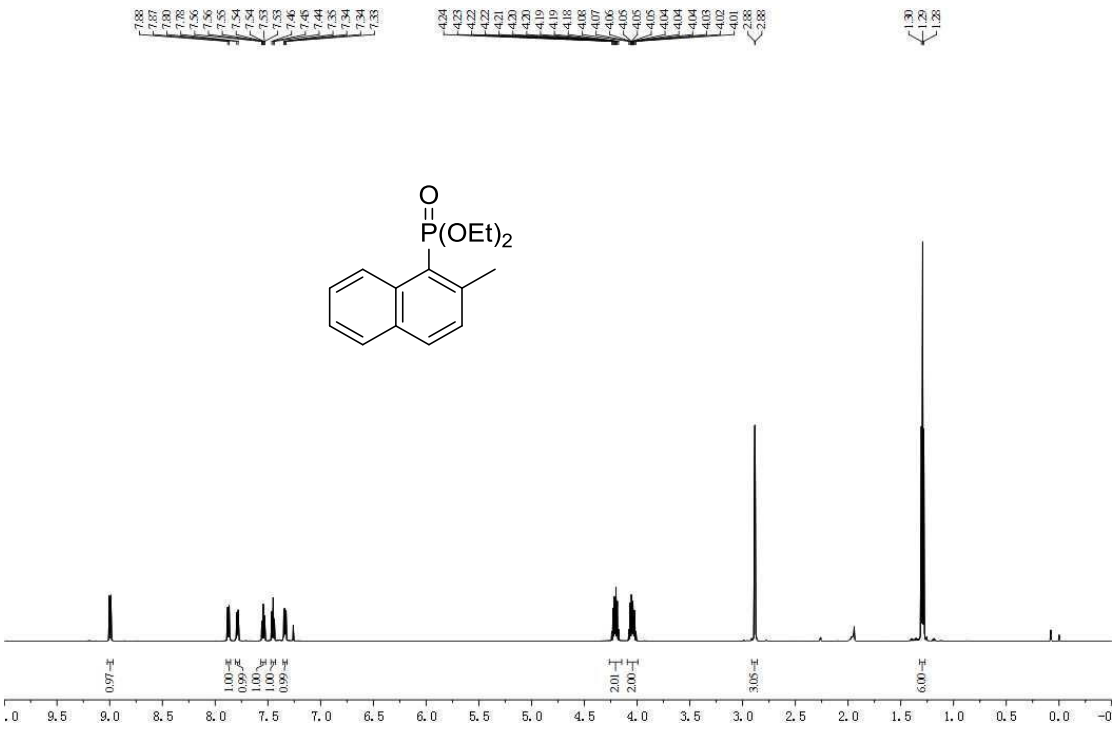
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3e



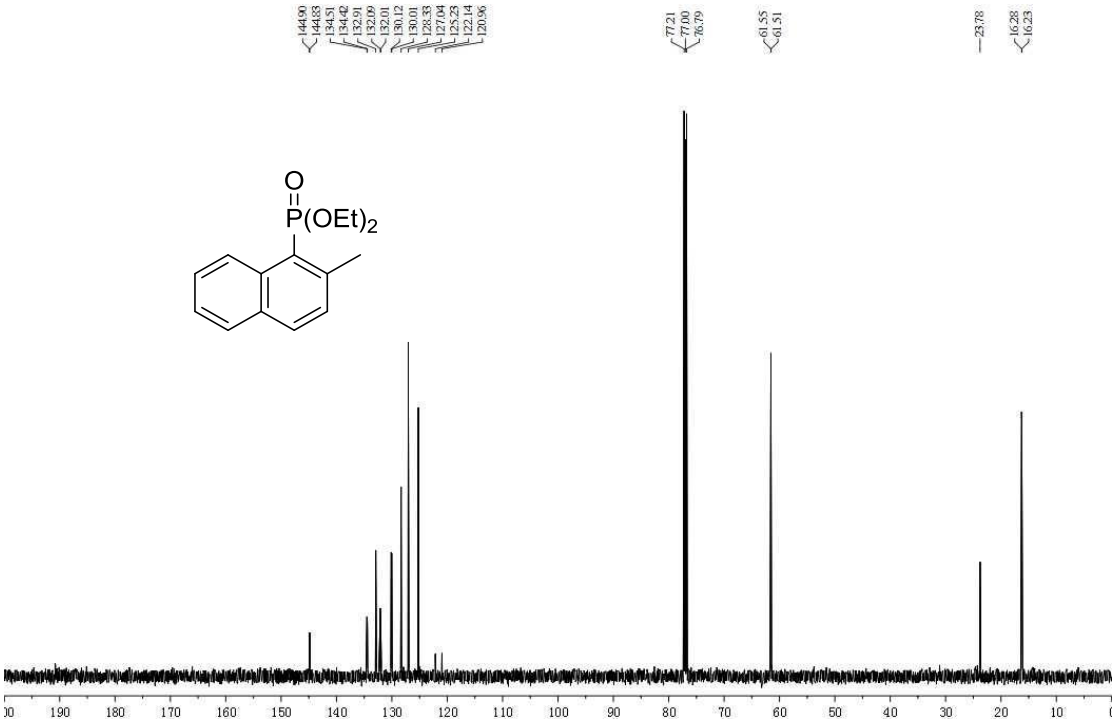
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3e



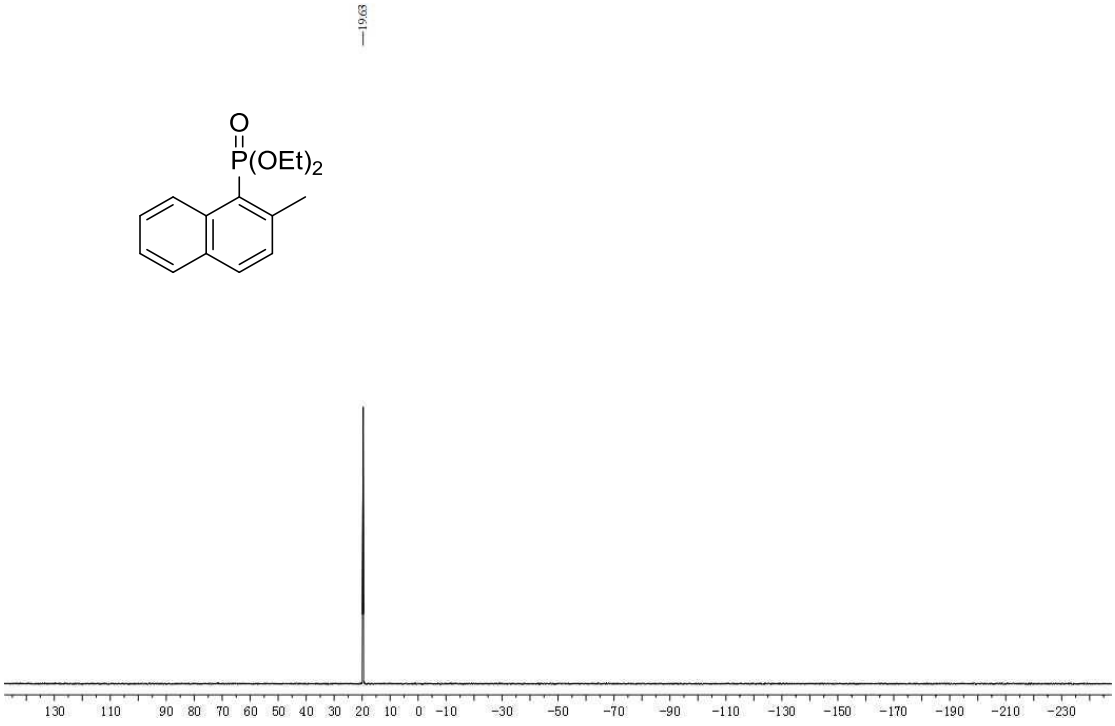
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3f



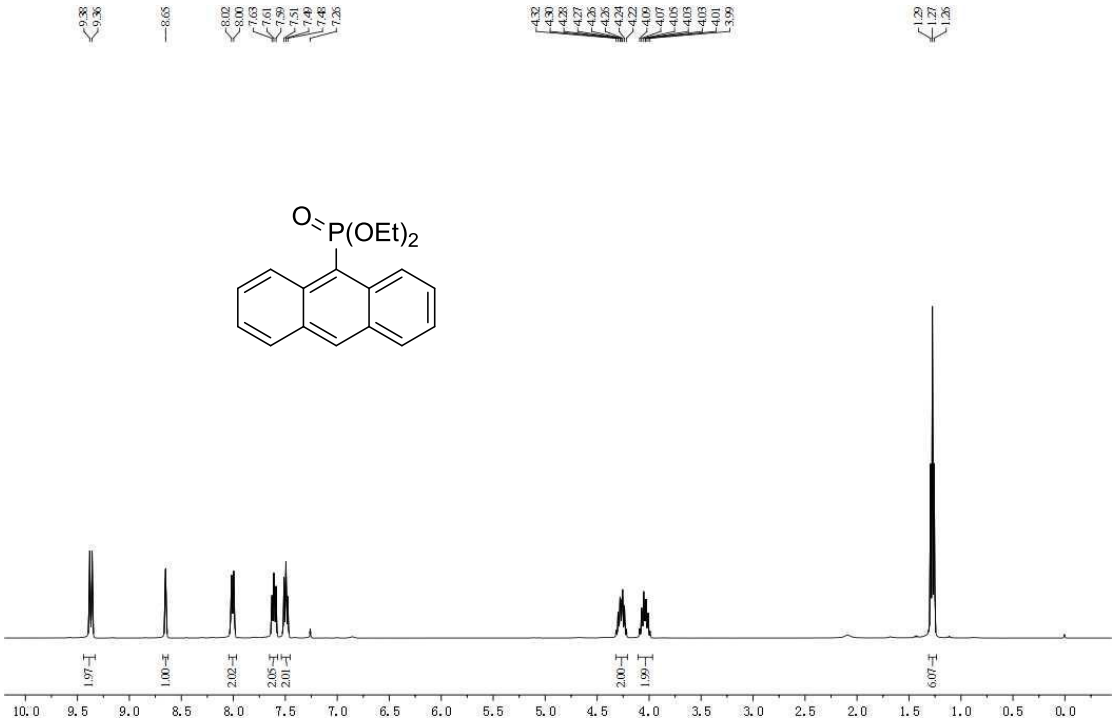
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3f



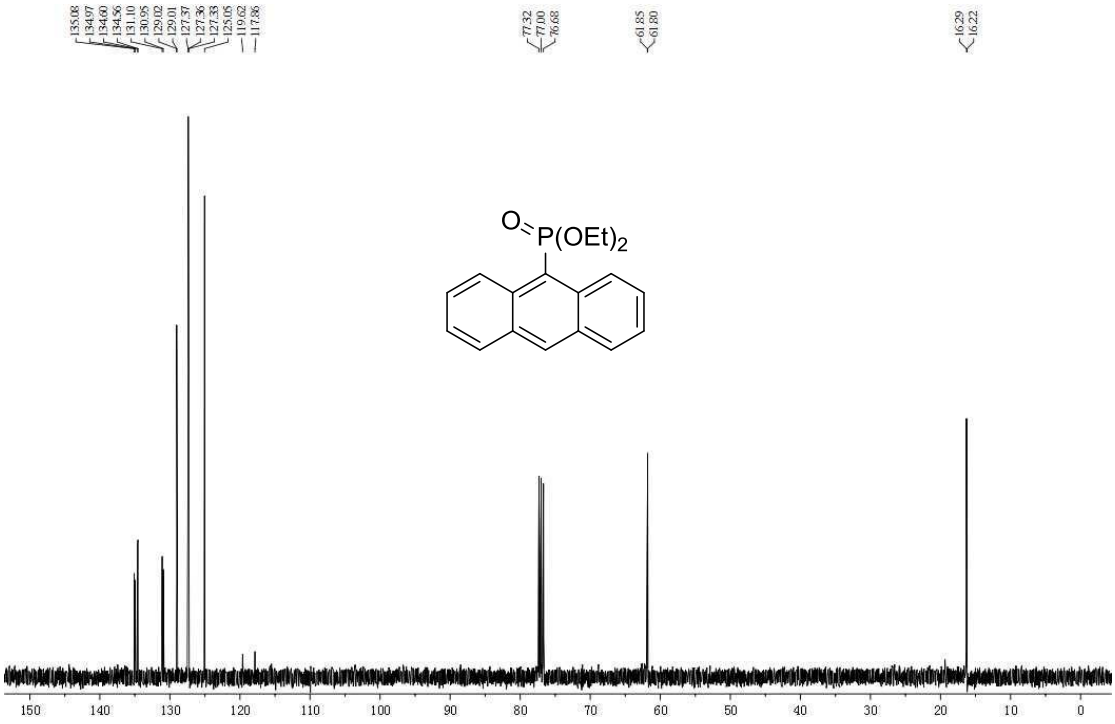
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3f



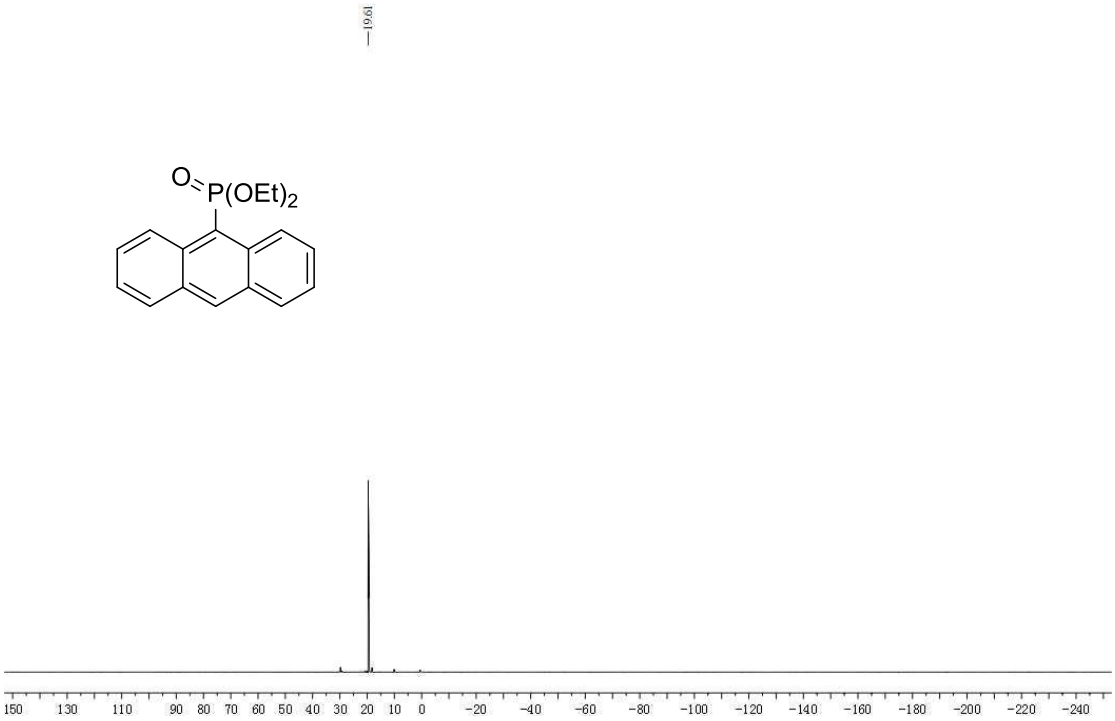
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3g



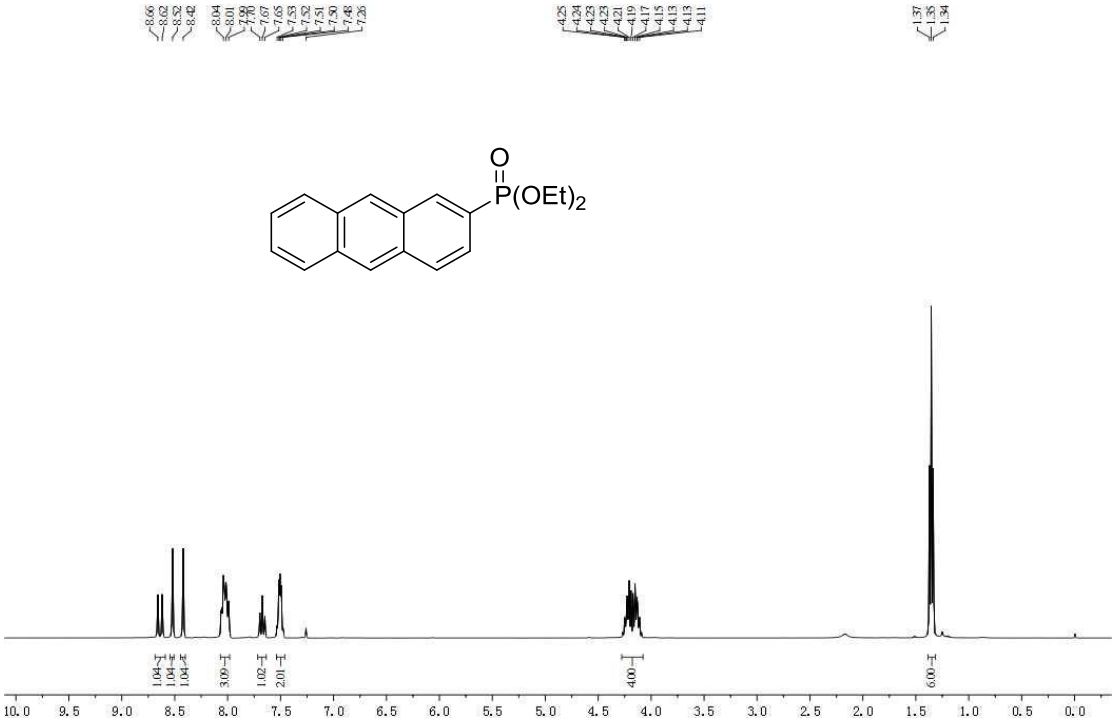
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3g



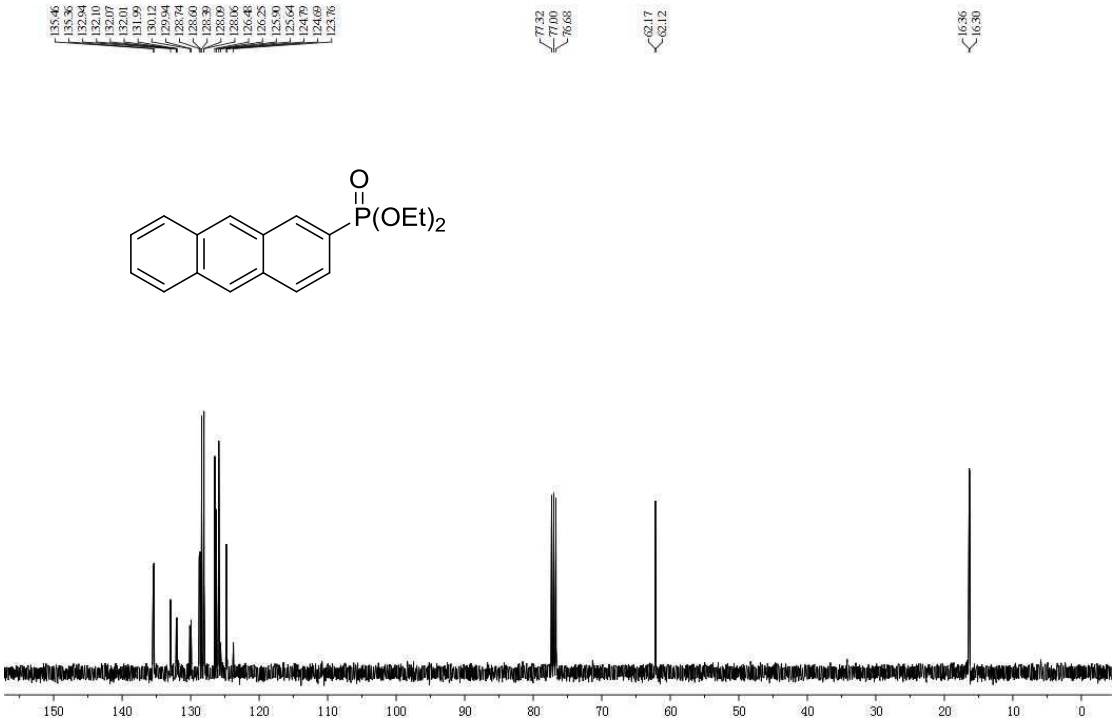
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3g



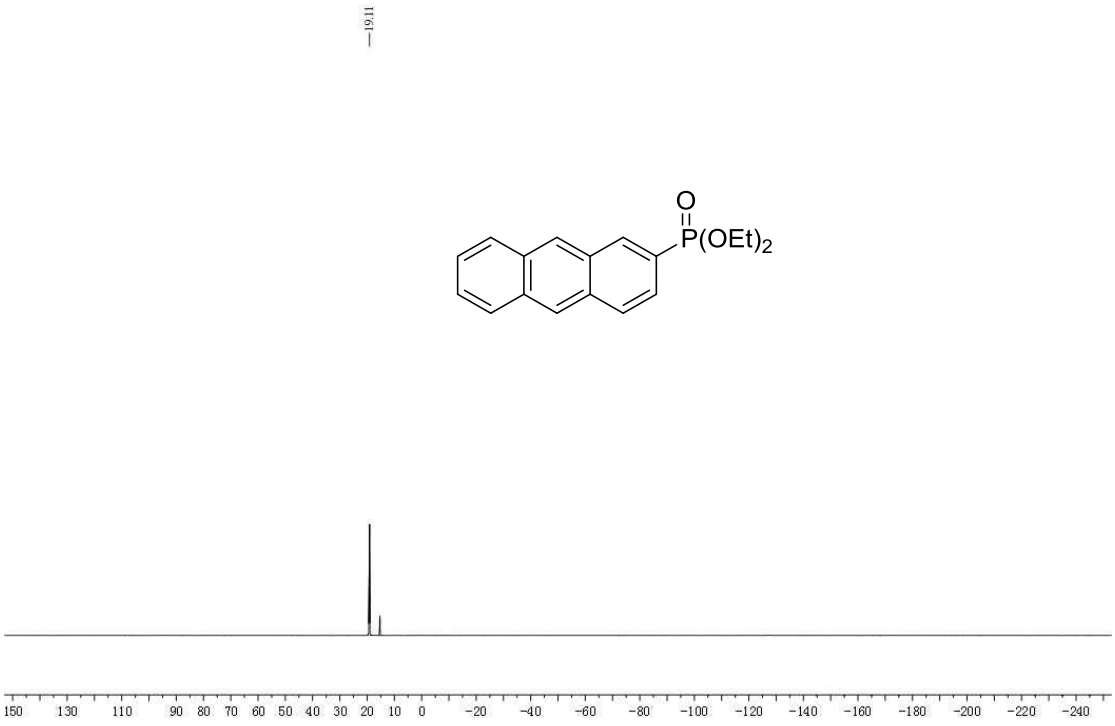
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3h



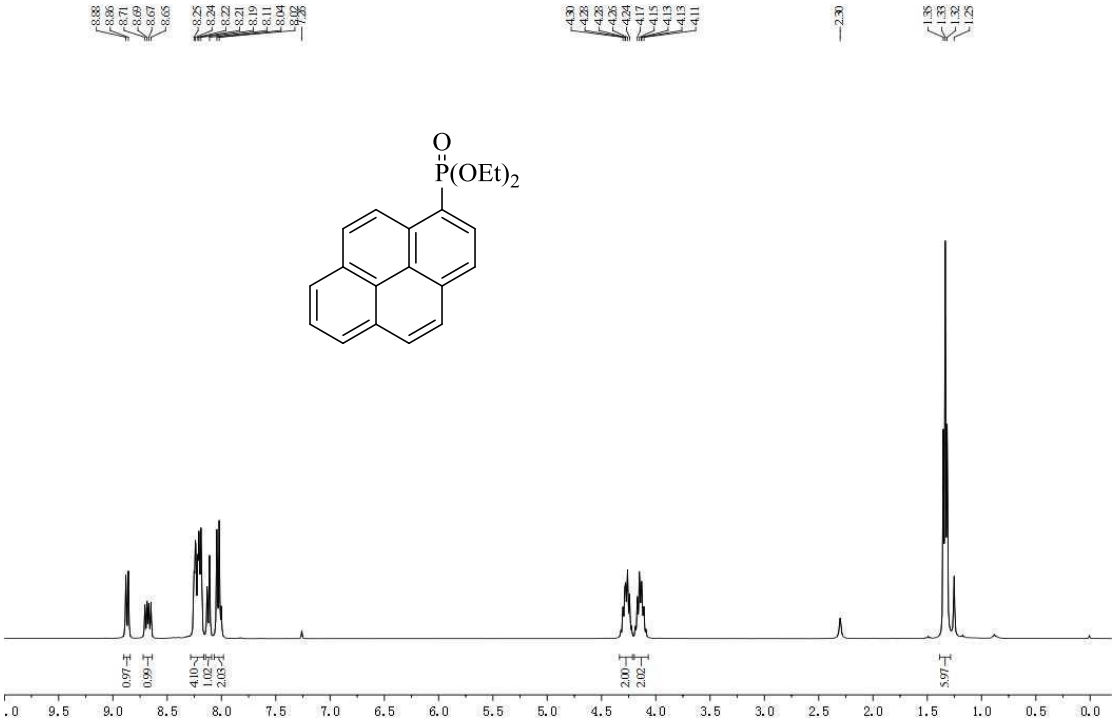
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3h



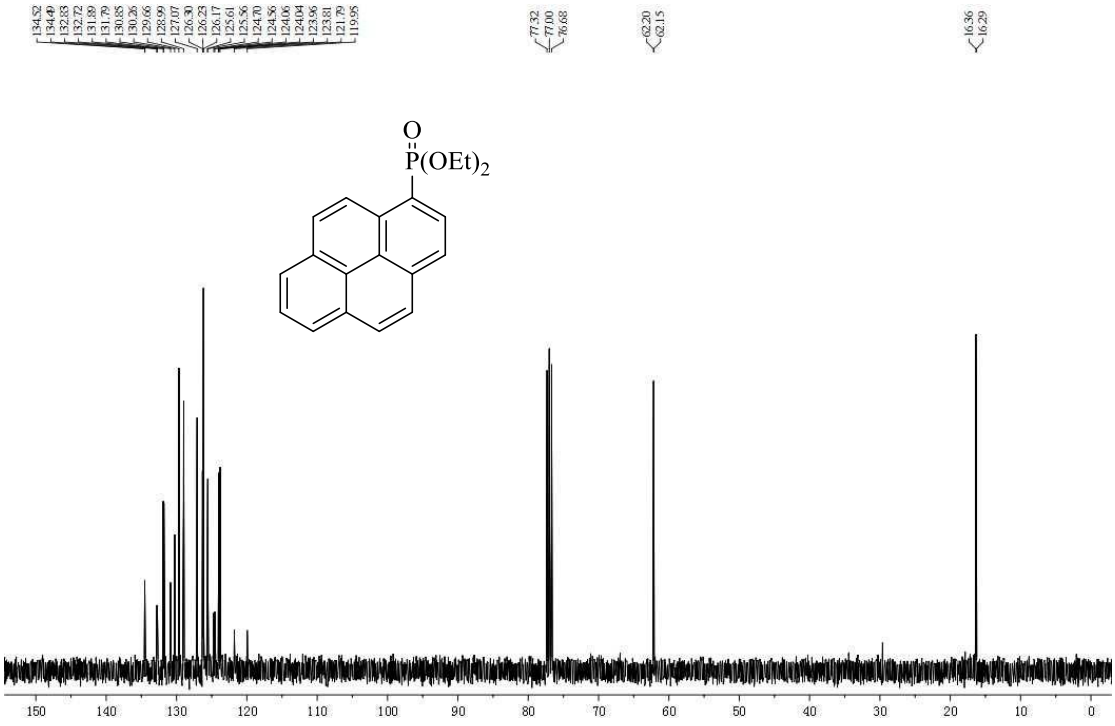
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3h



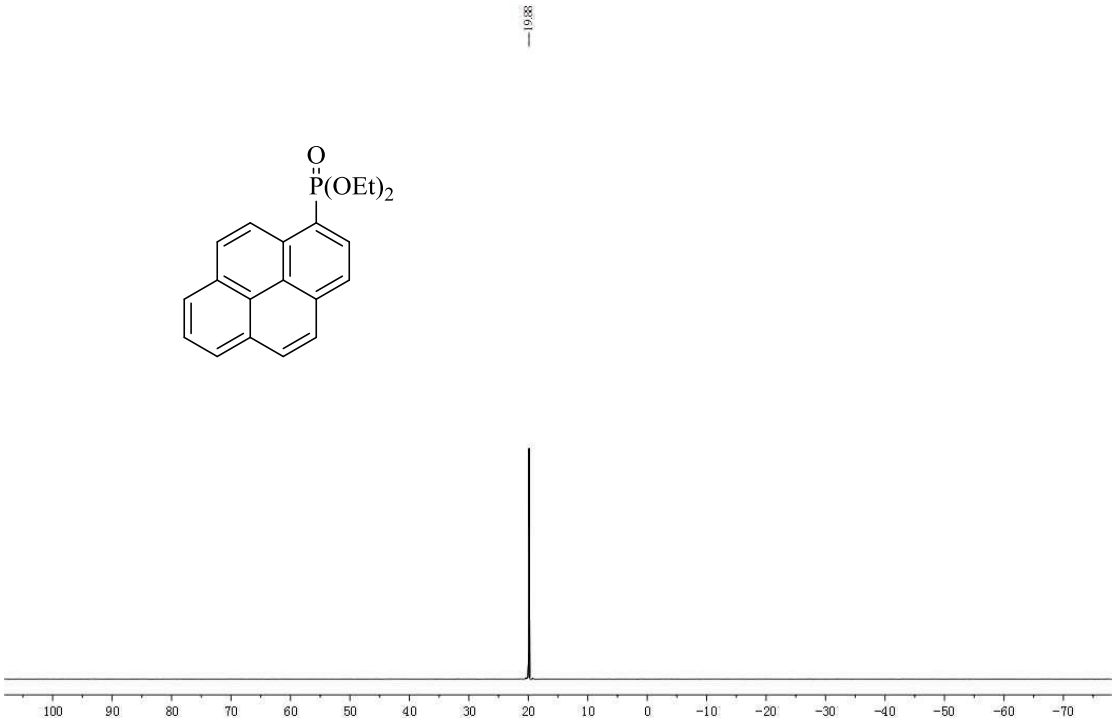
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3i



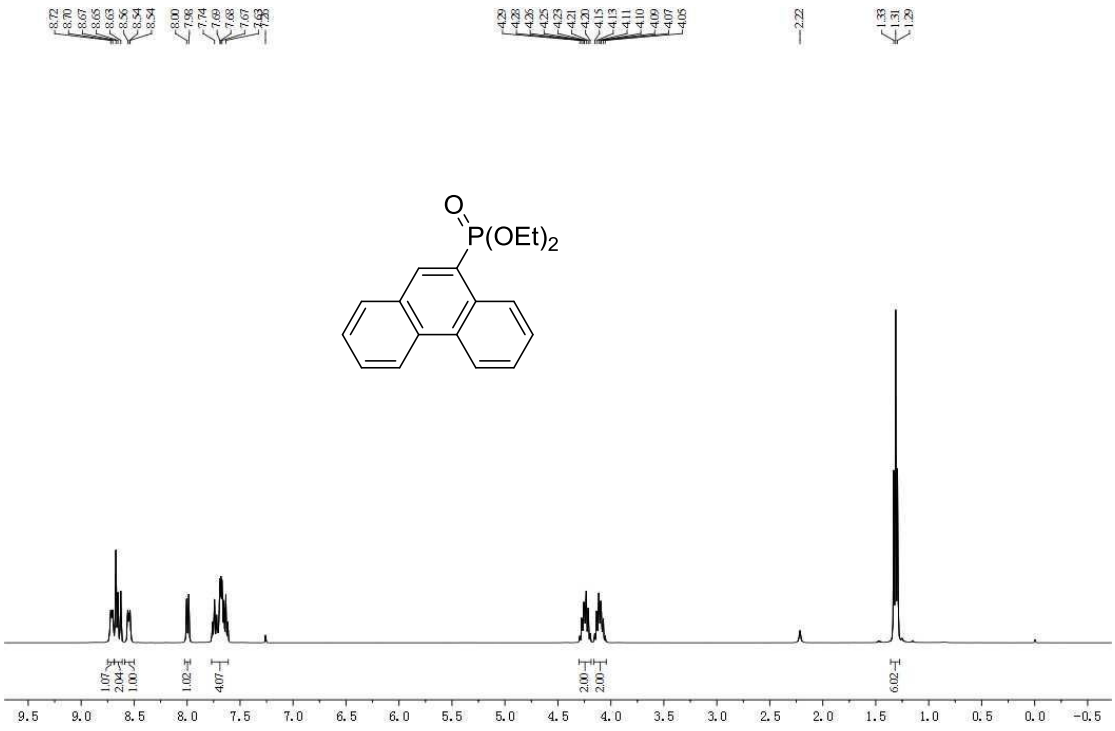
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3i



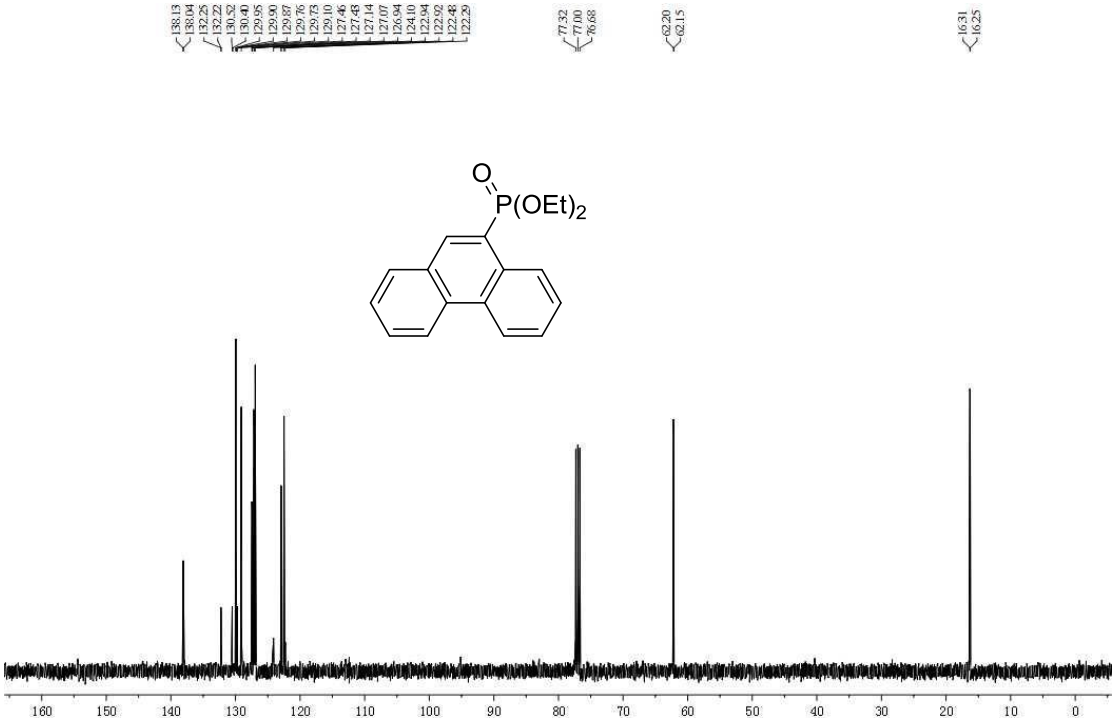
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3i



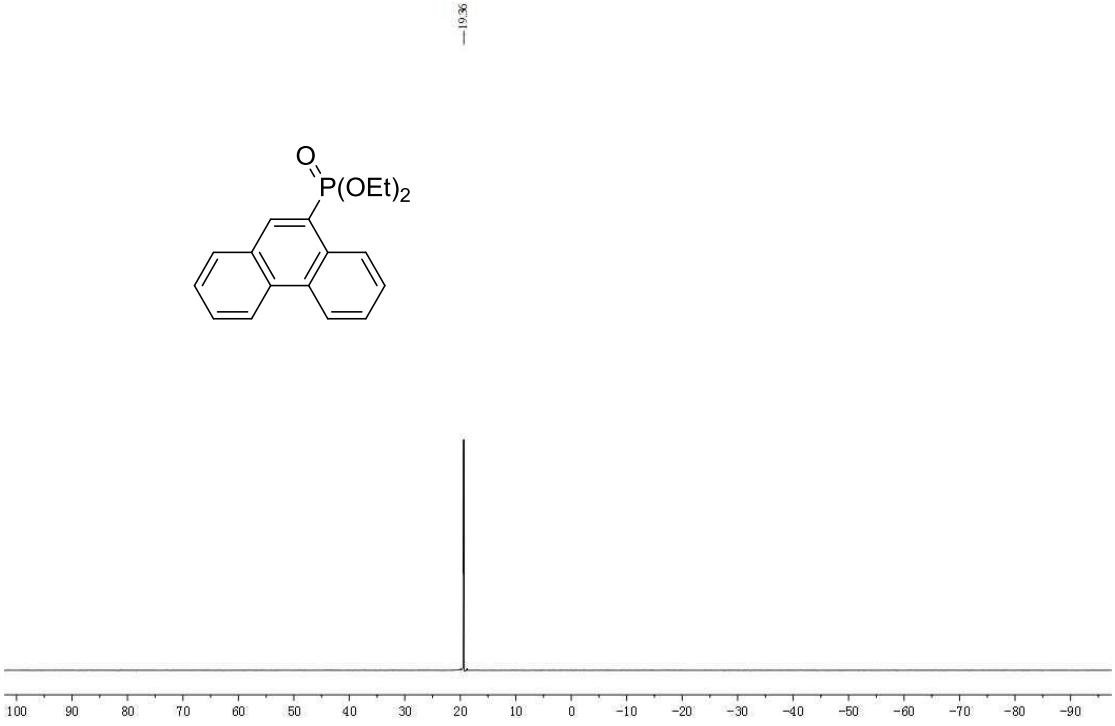
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3j



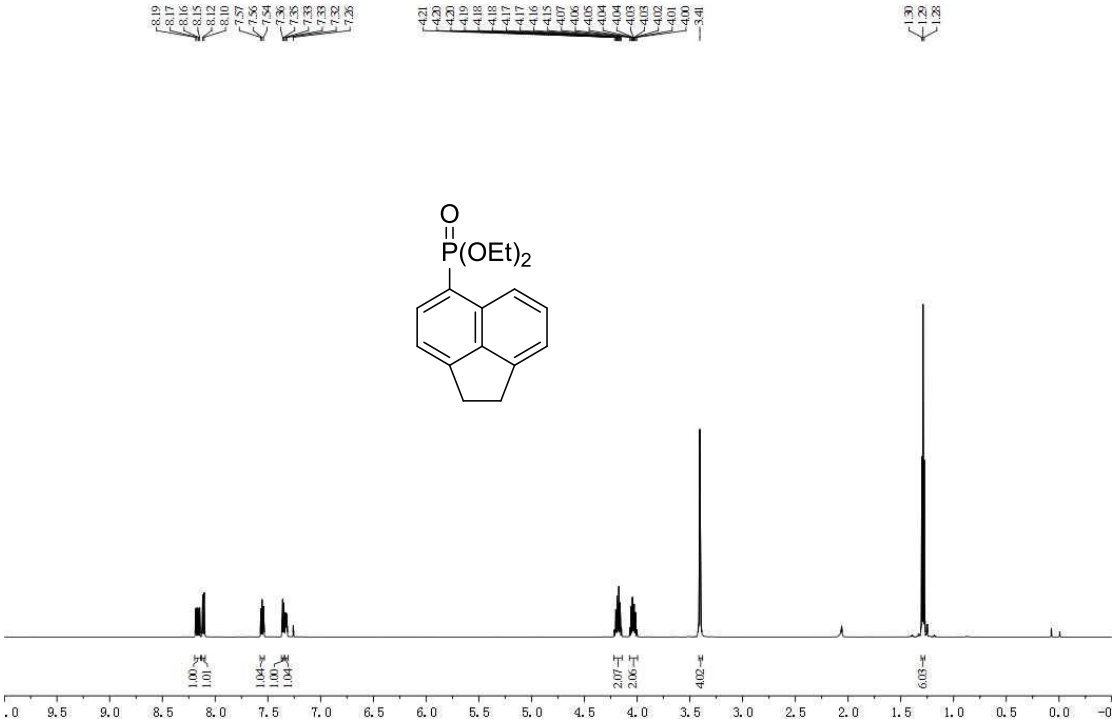
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3j



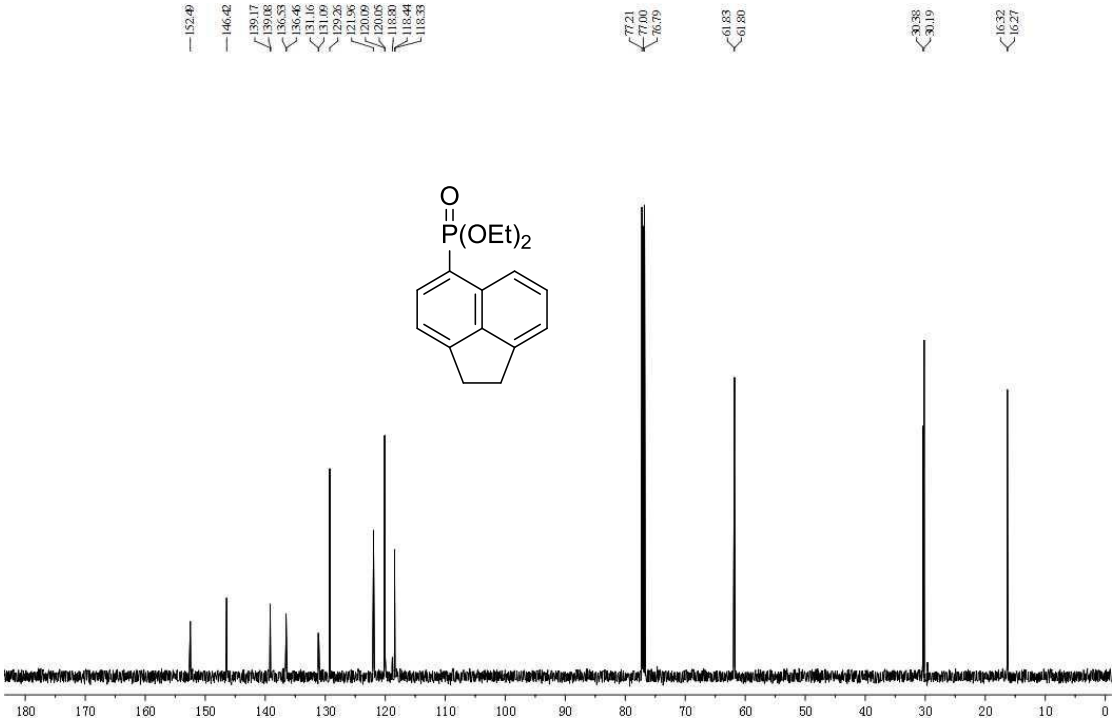
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3j



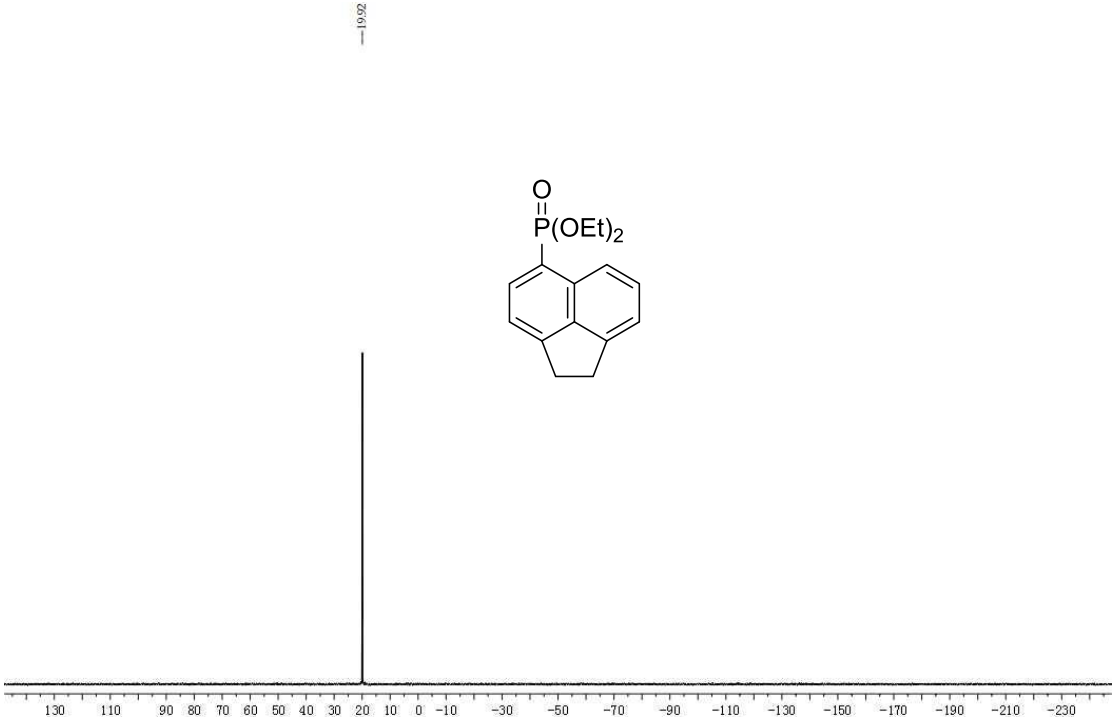
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3k



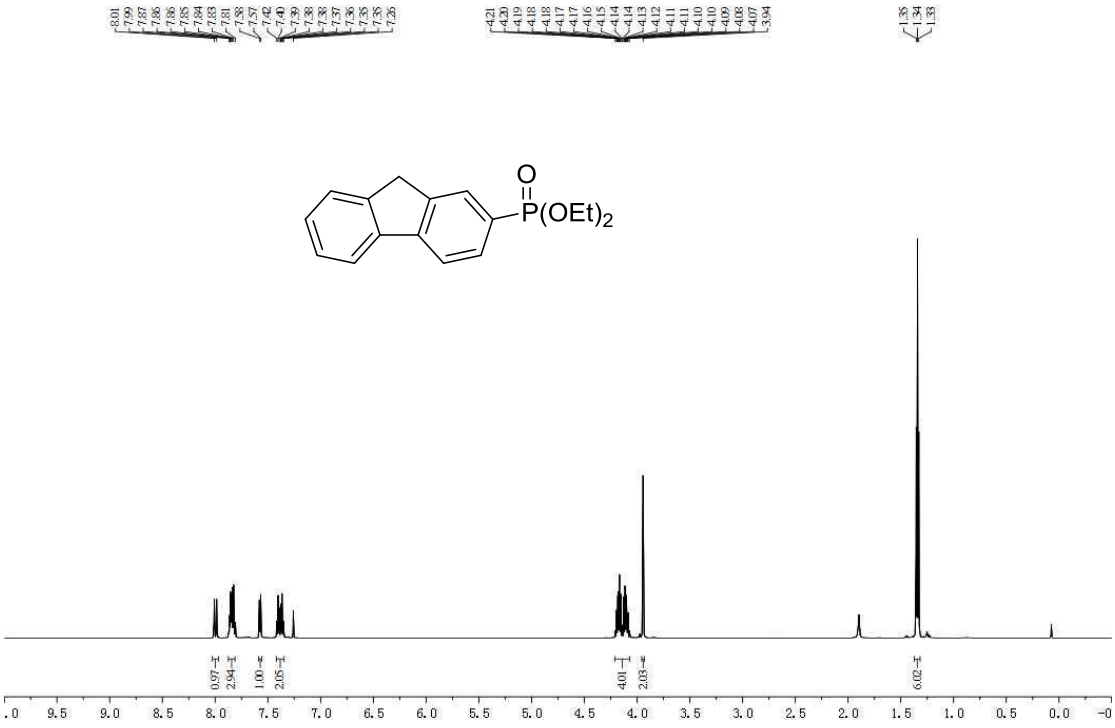
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3k



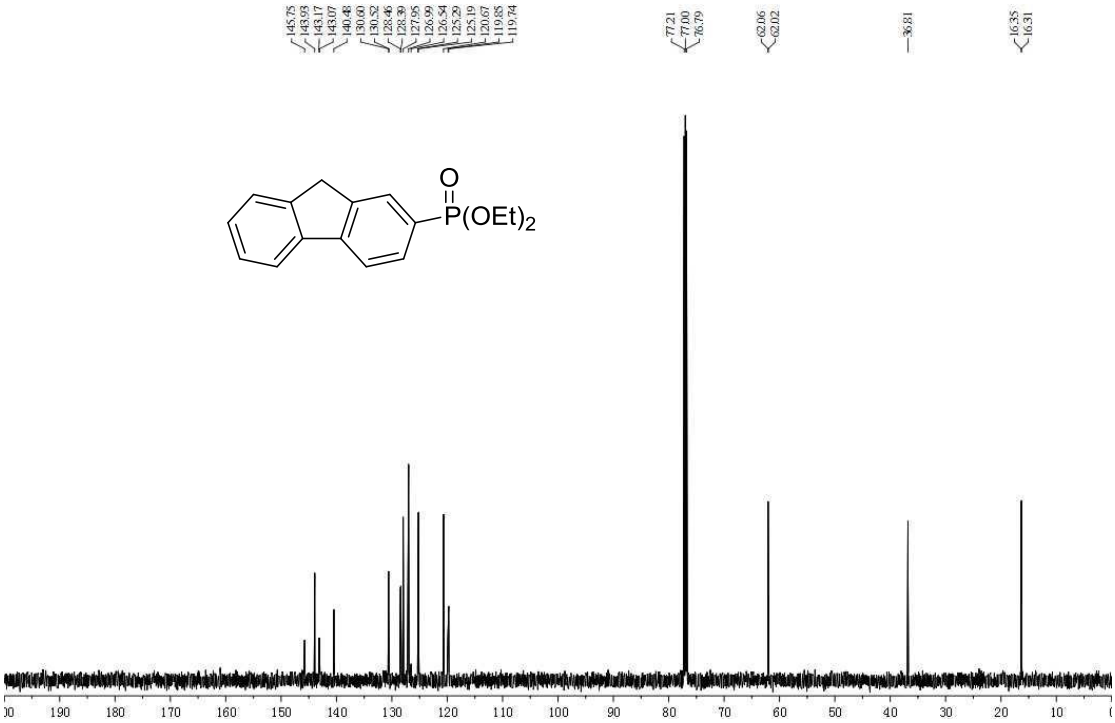
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3k



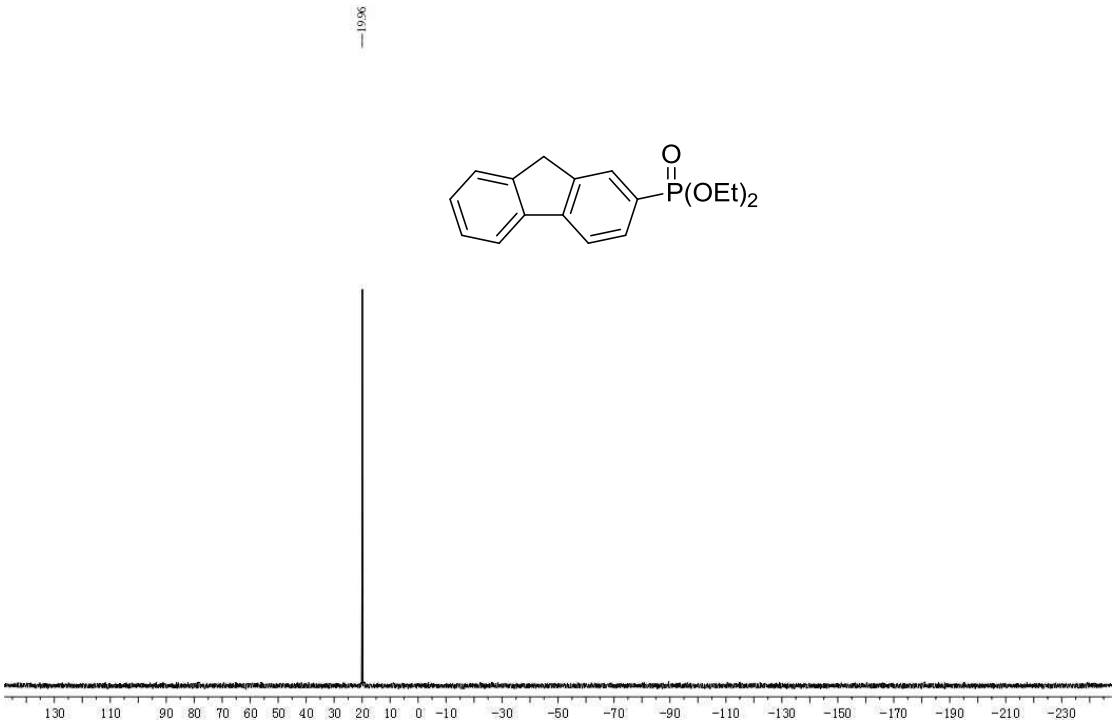
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3l



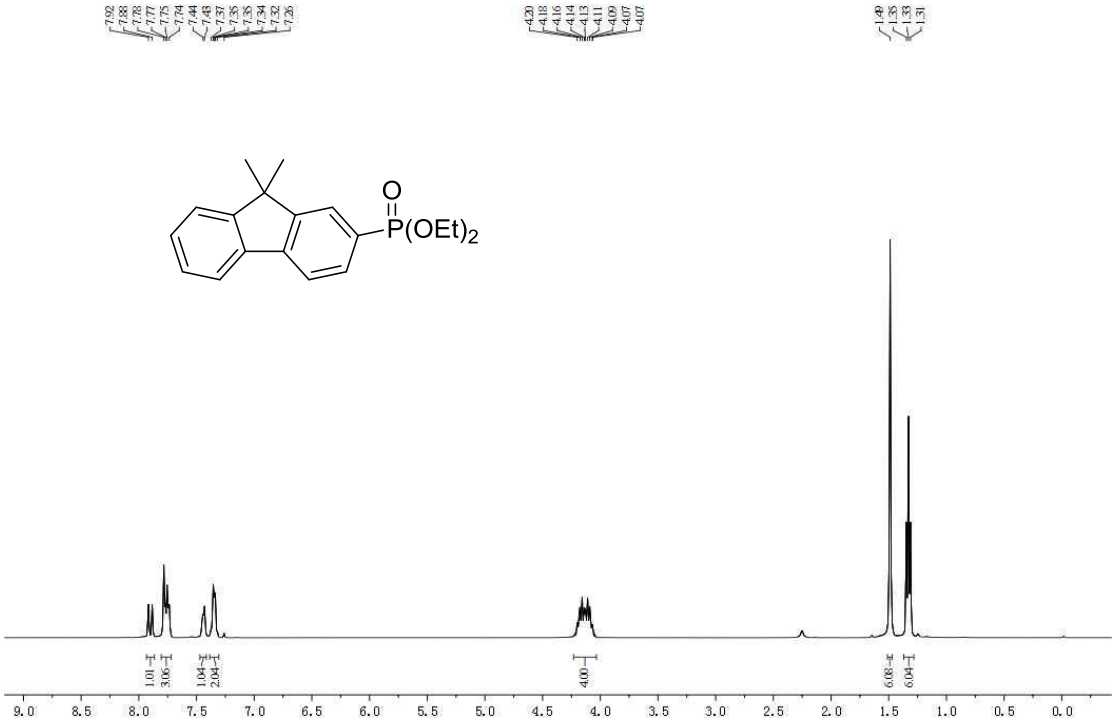
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3l



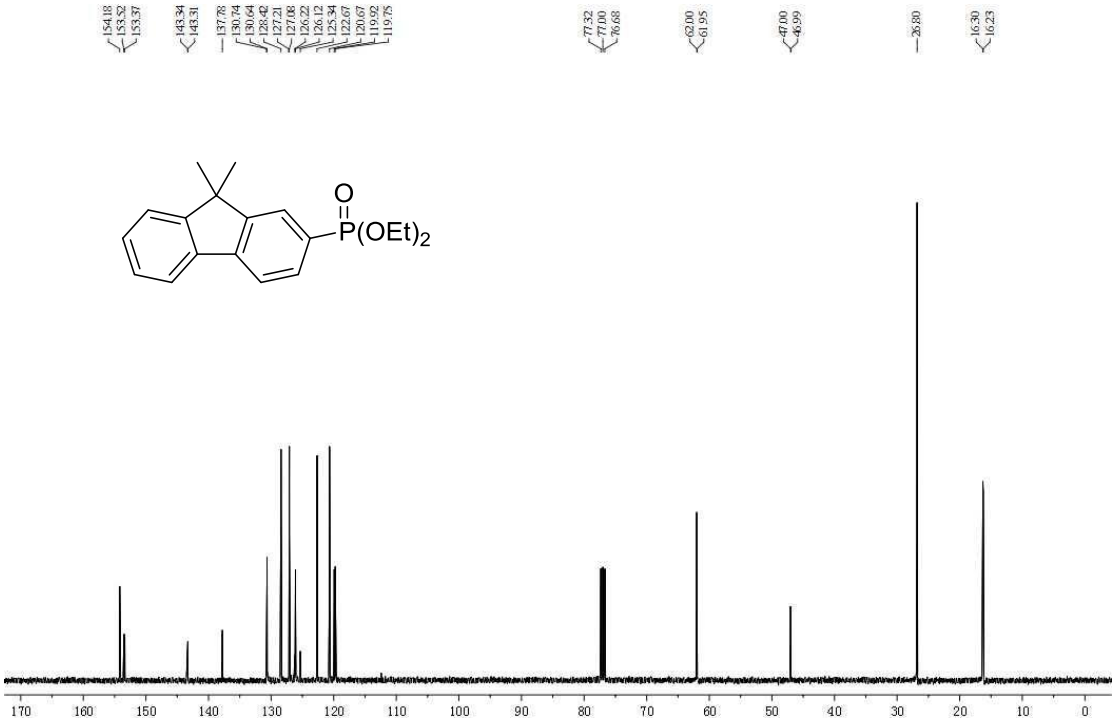
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3l



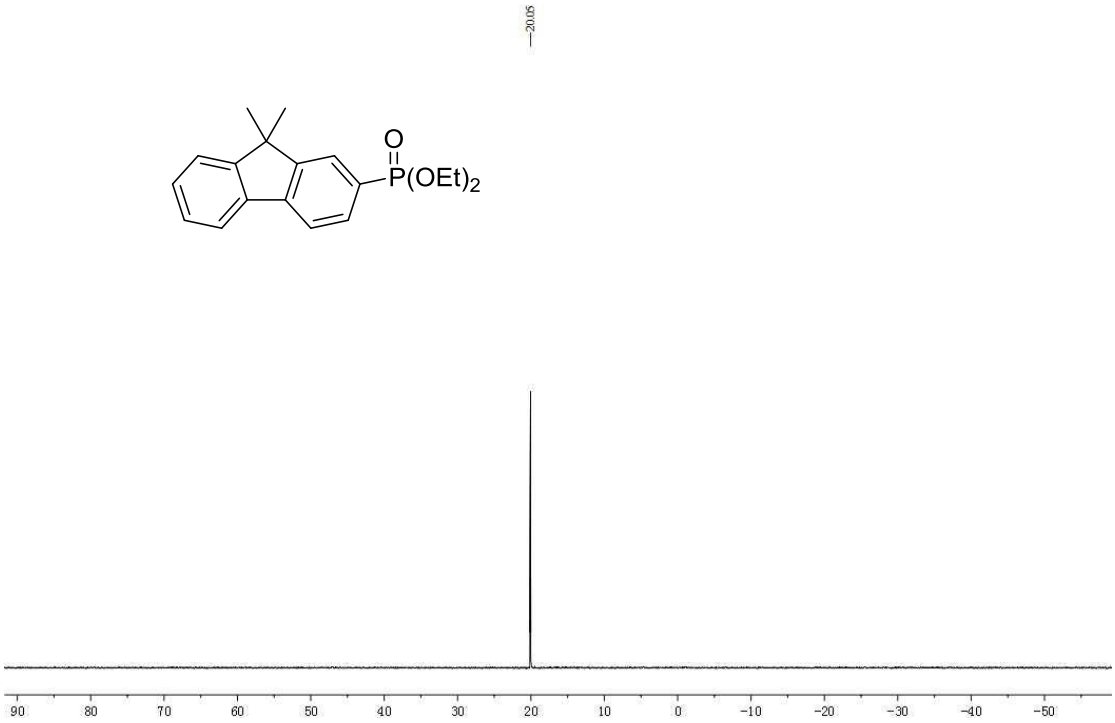
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3m



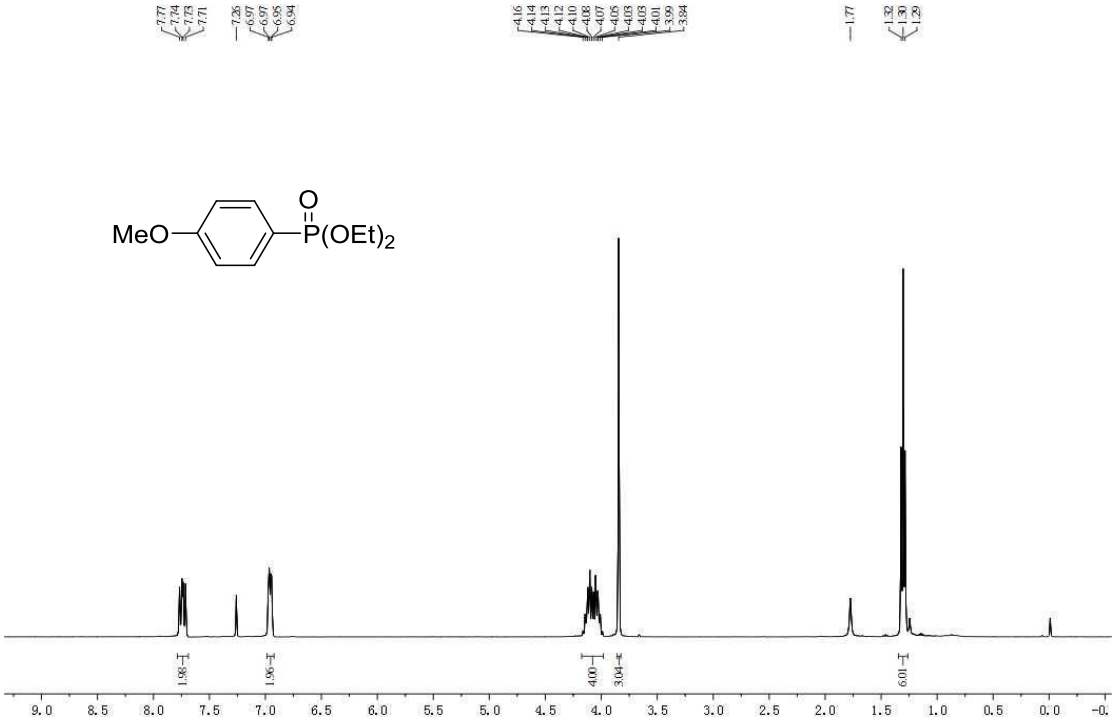
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3m



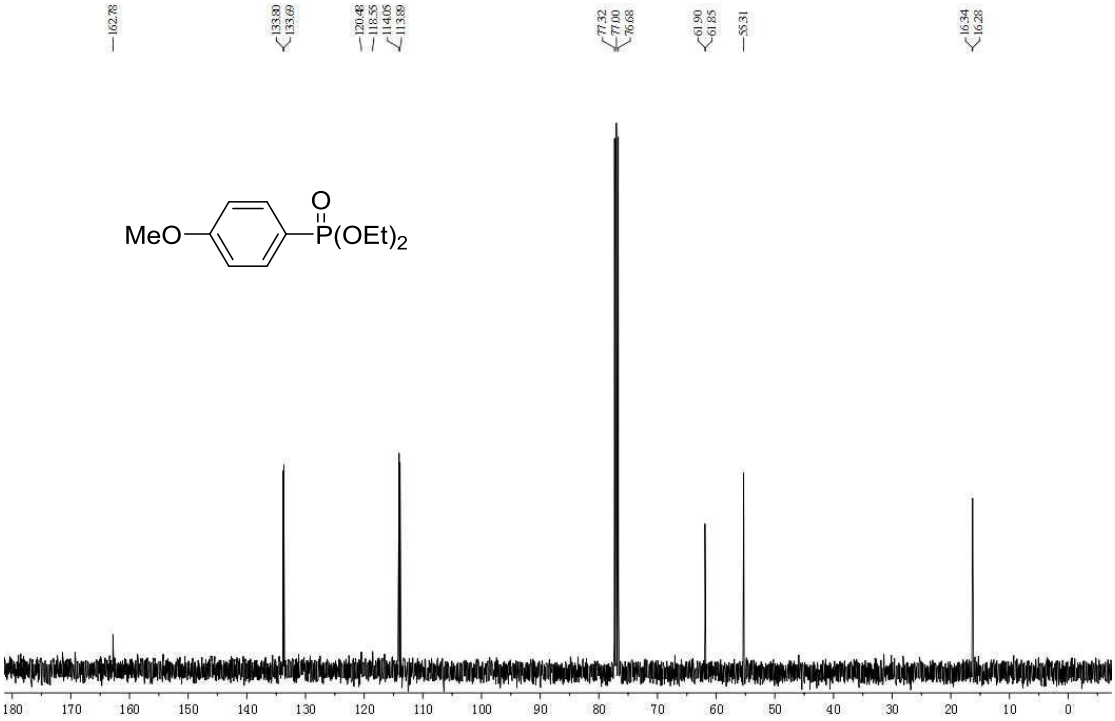
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3m



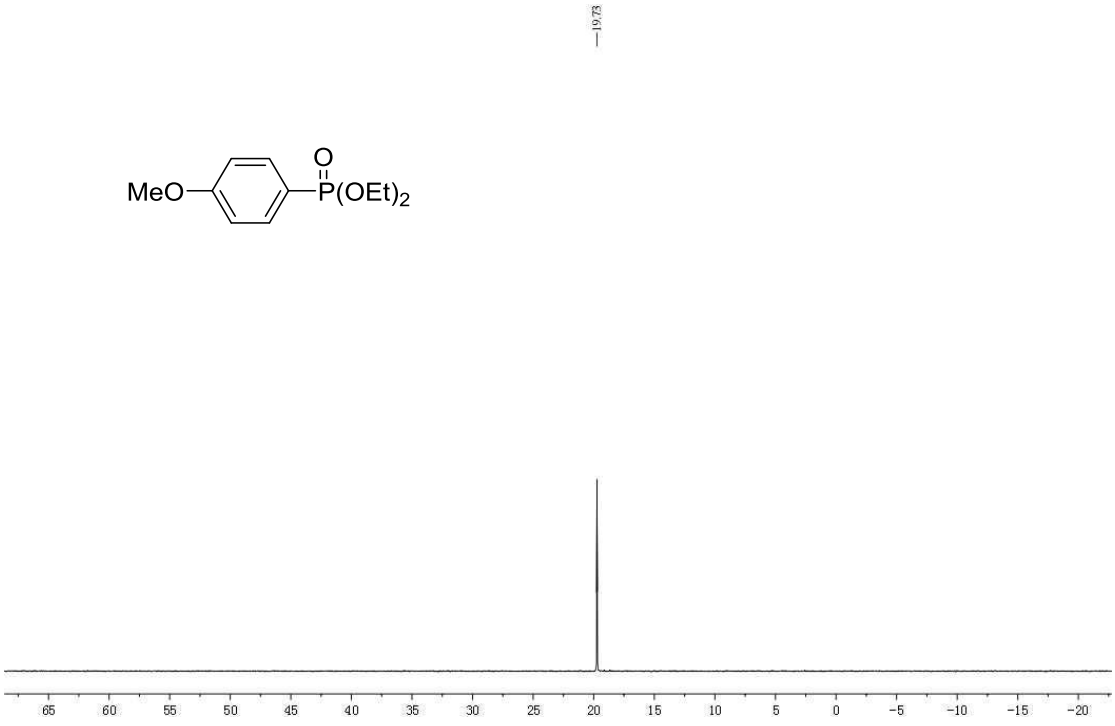
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3n



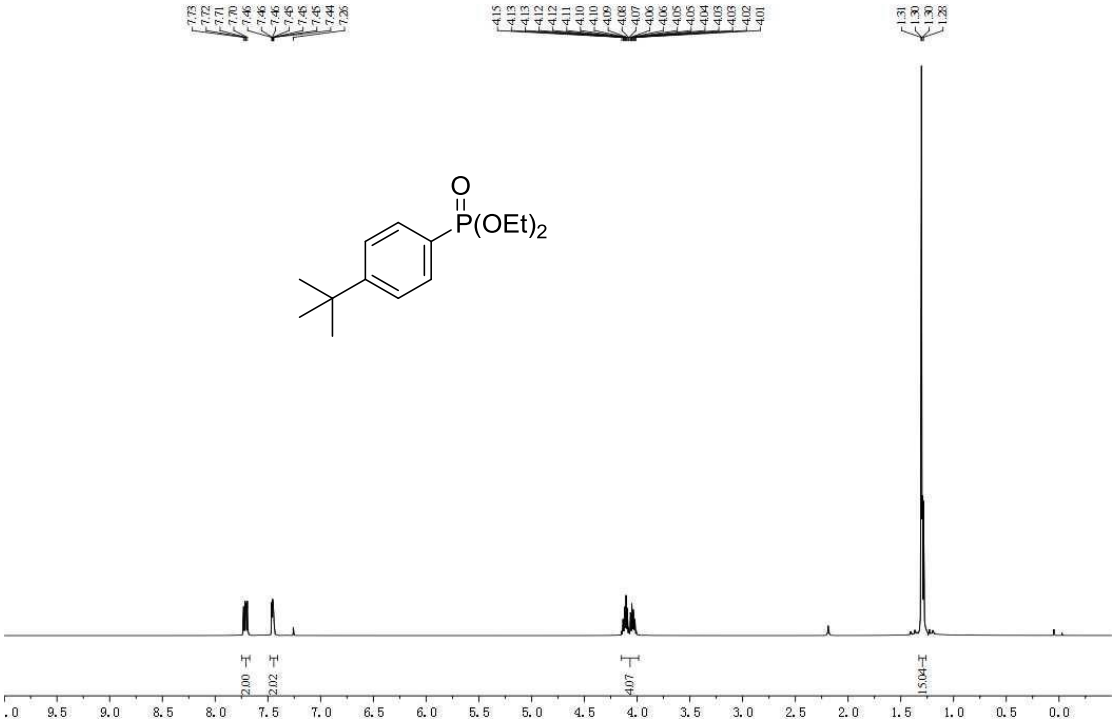
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3n



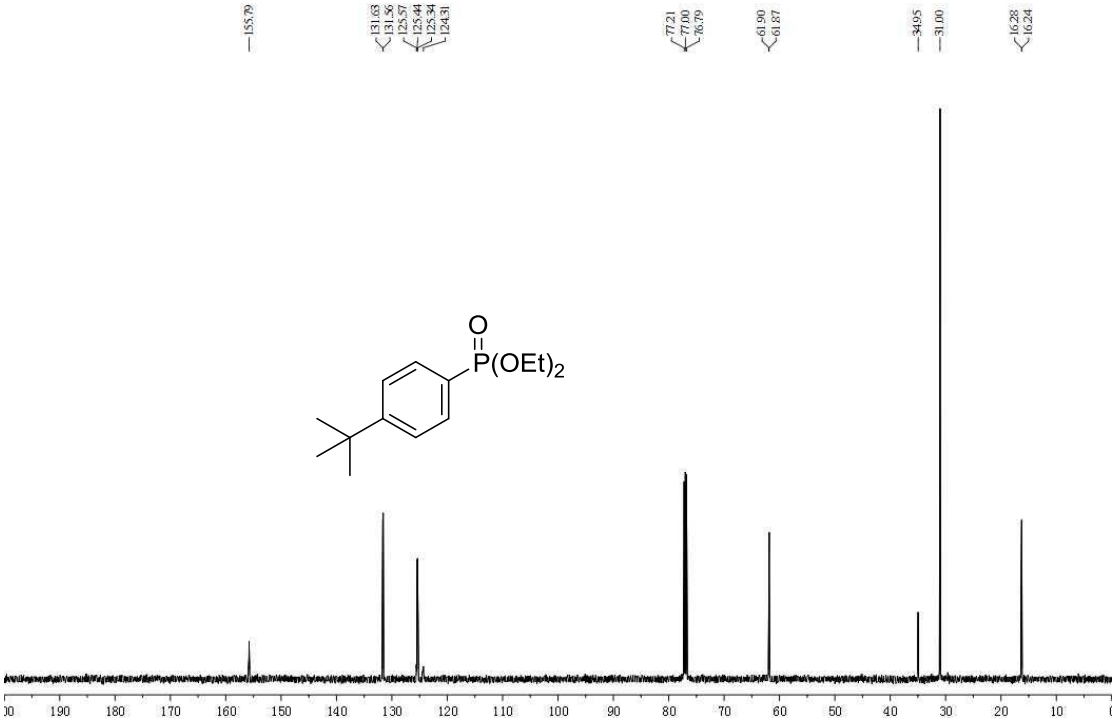
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3n



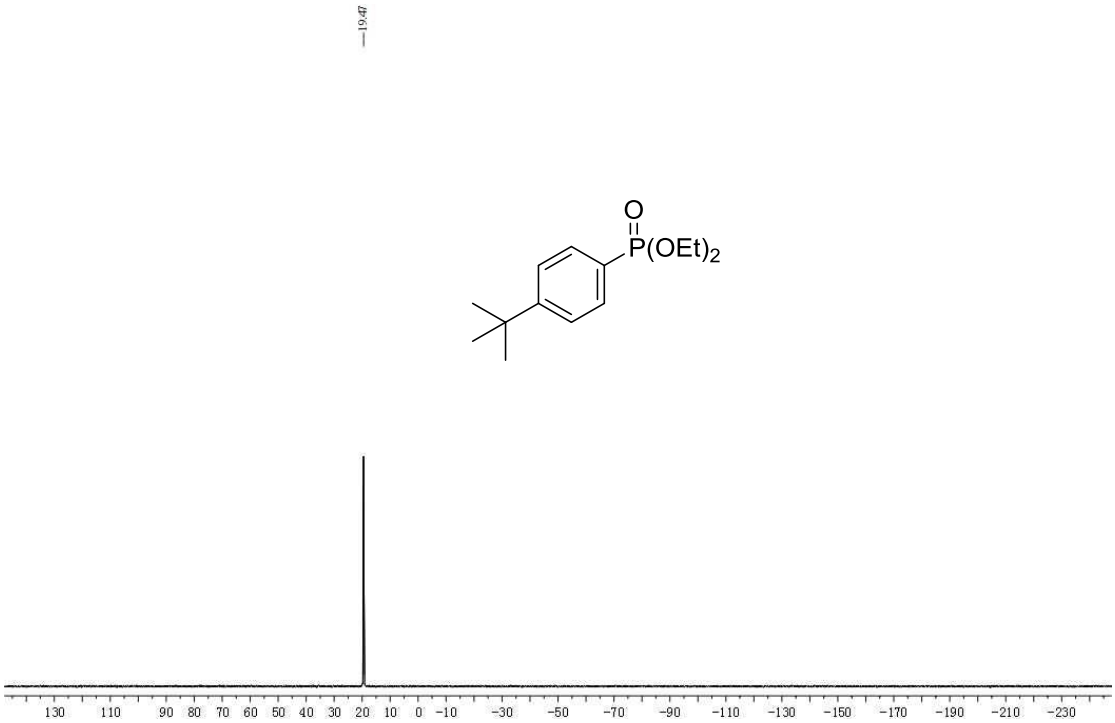
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3o



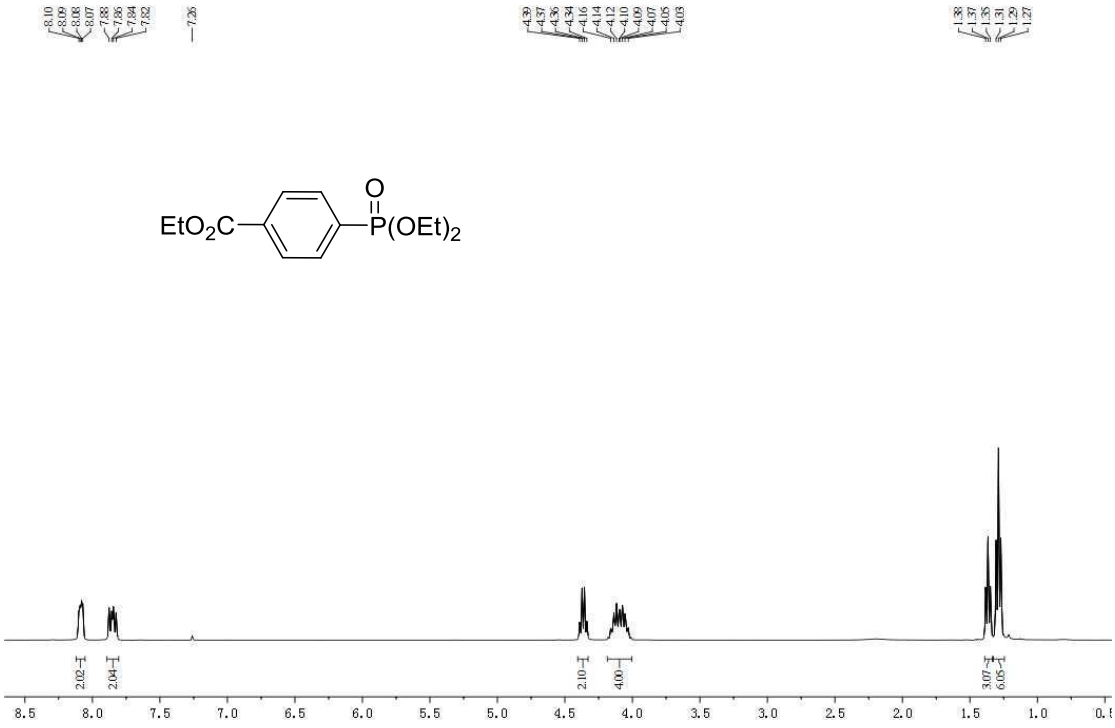
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3o



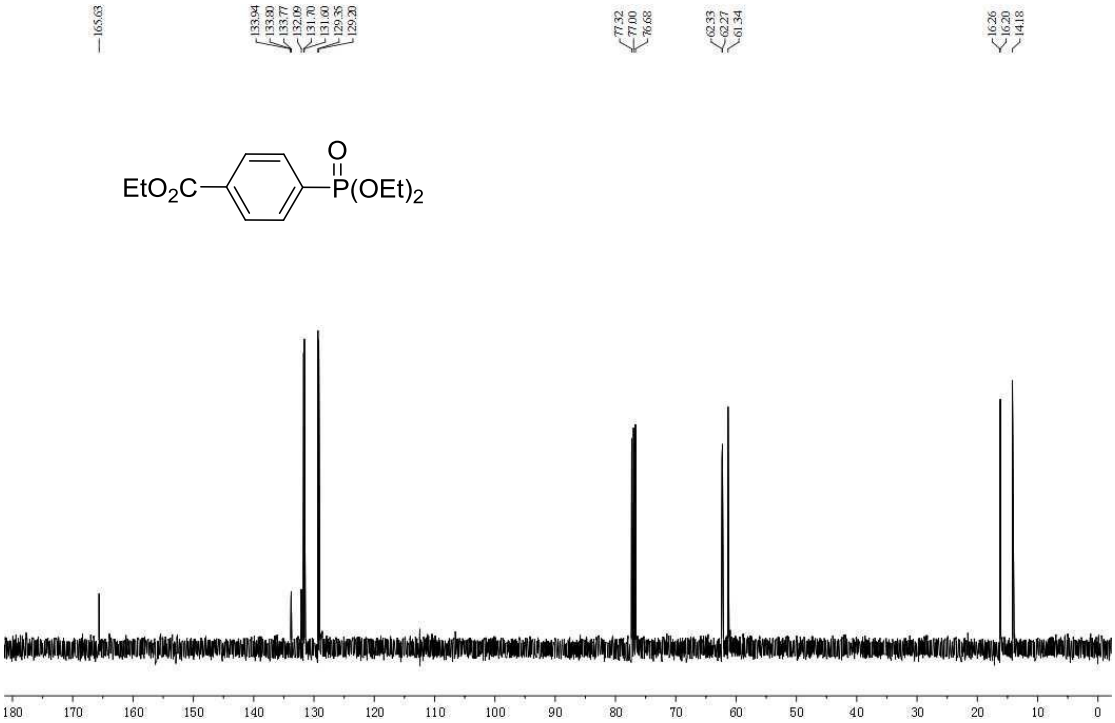
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3o



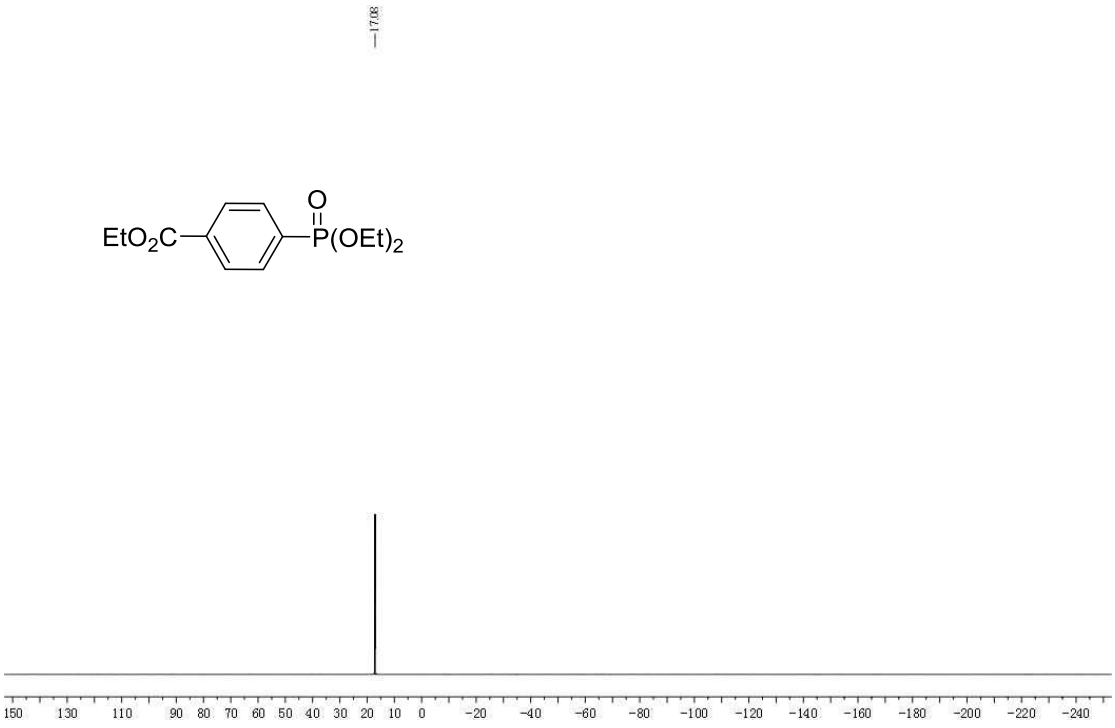
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3p



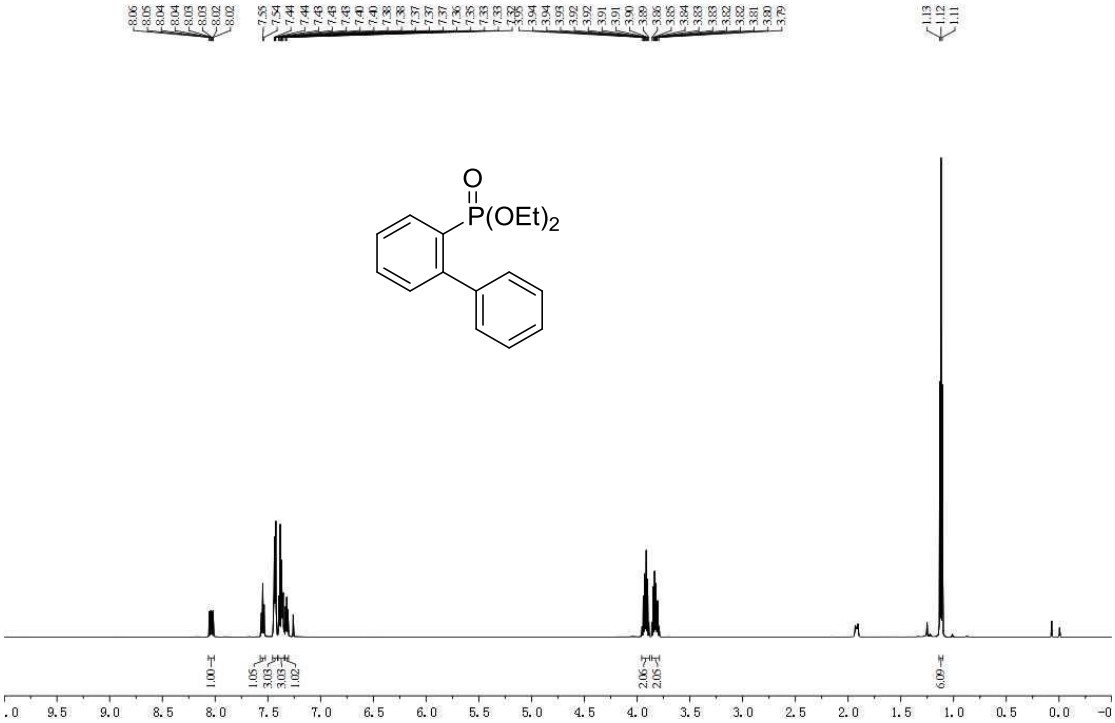
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3p



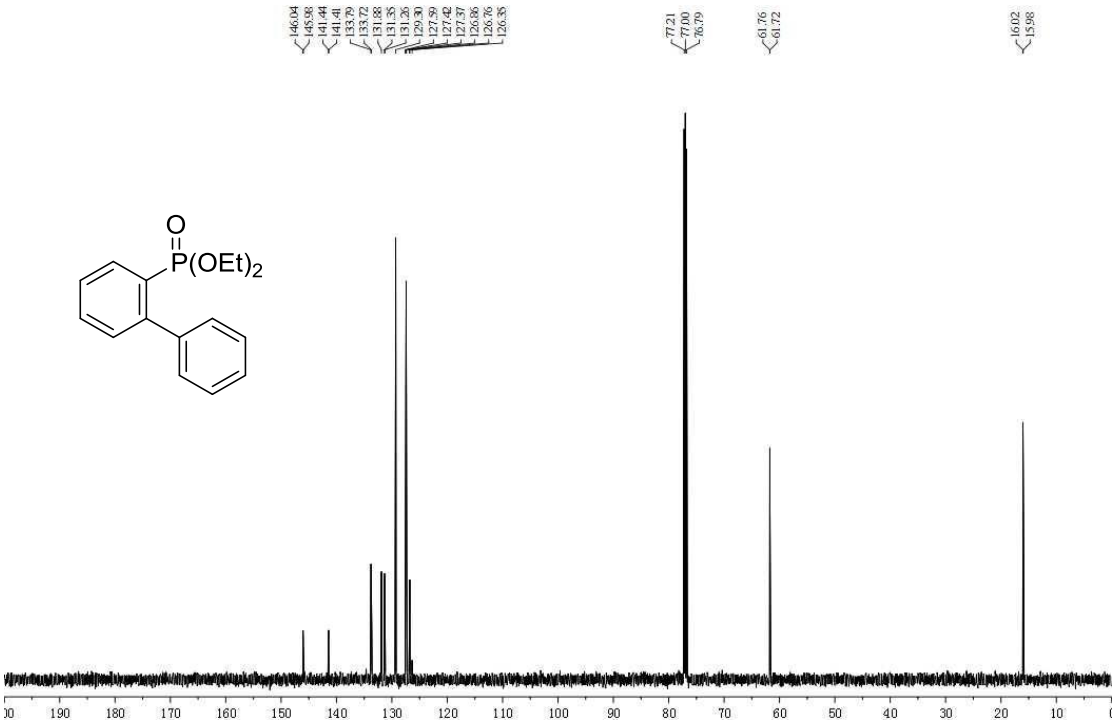
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3p



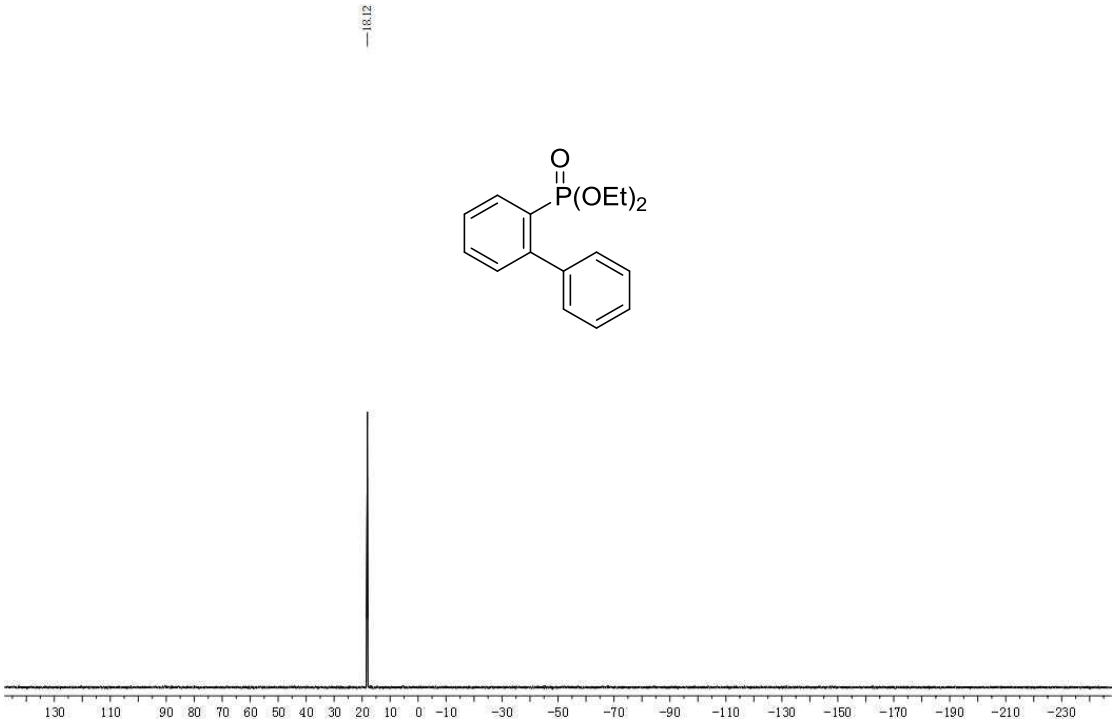
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3q



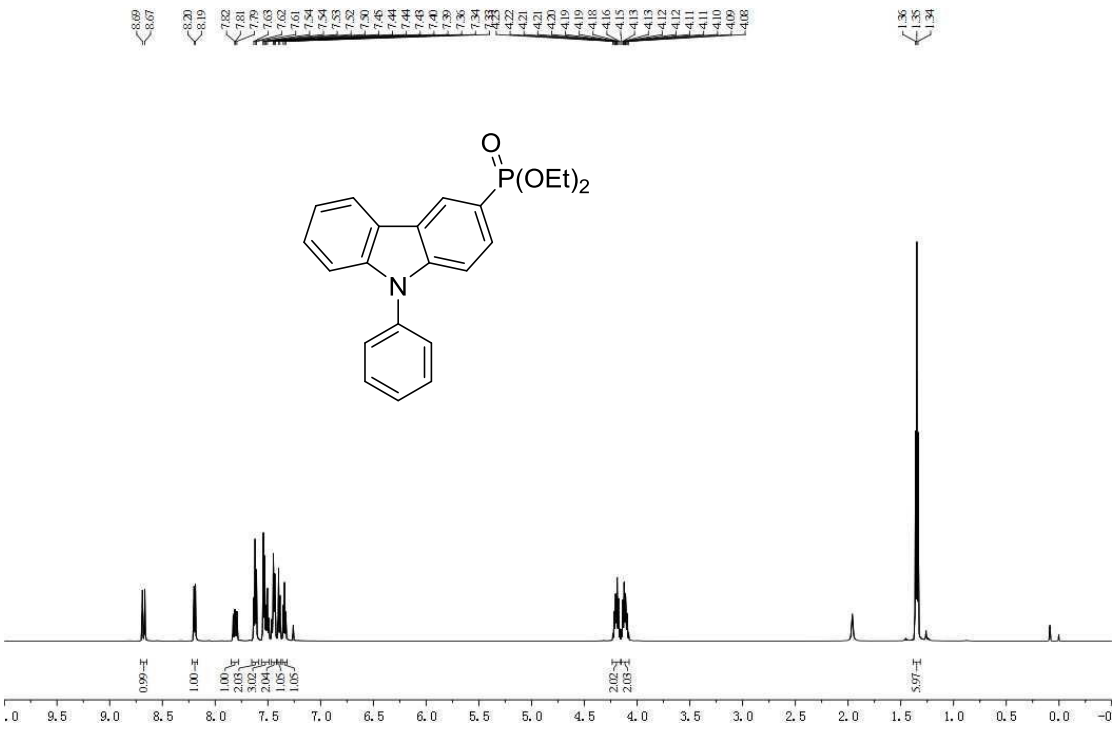
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3q



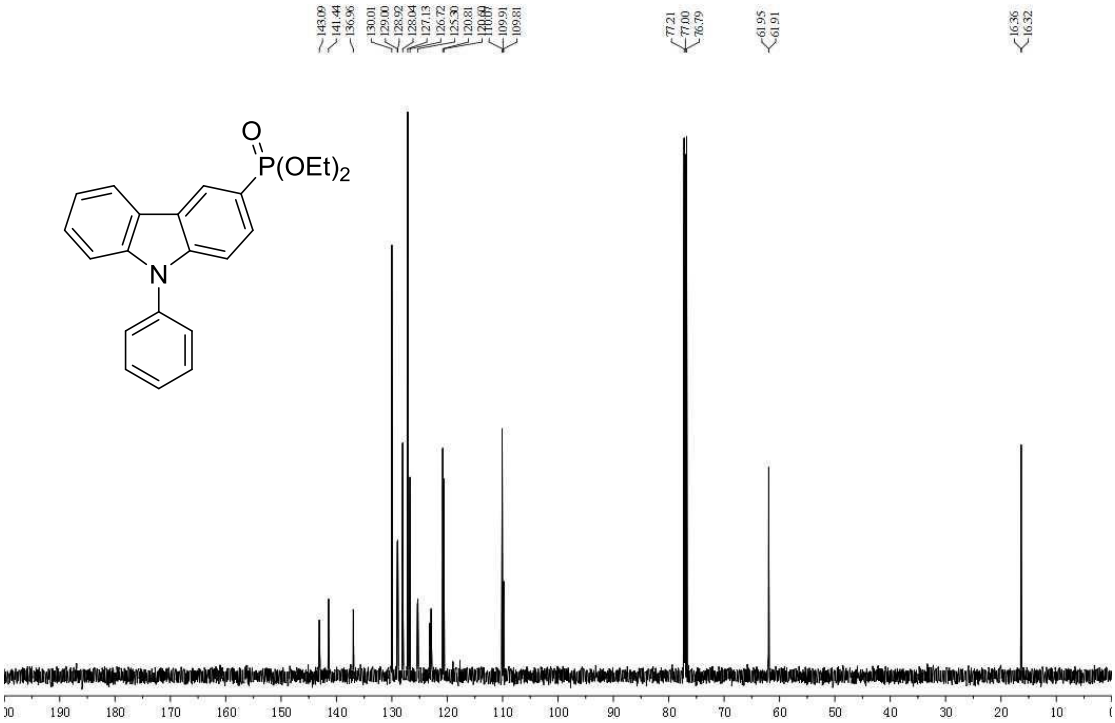
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3q



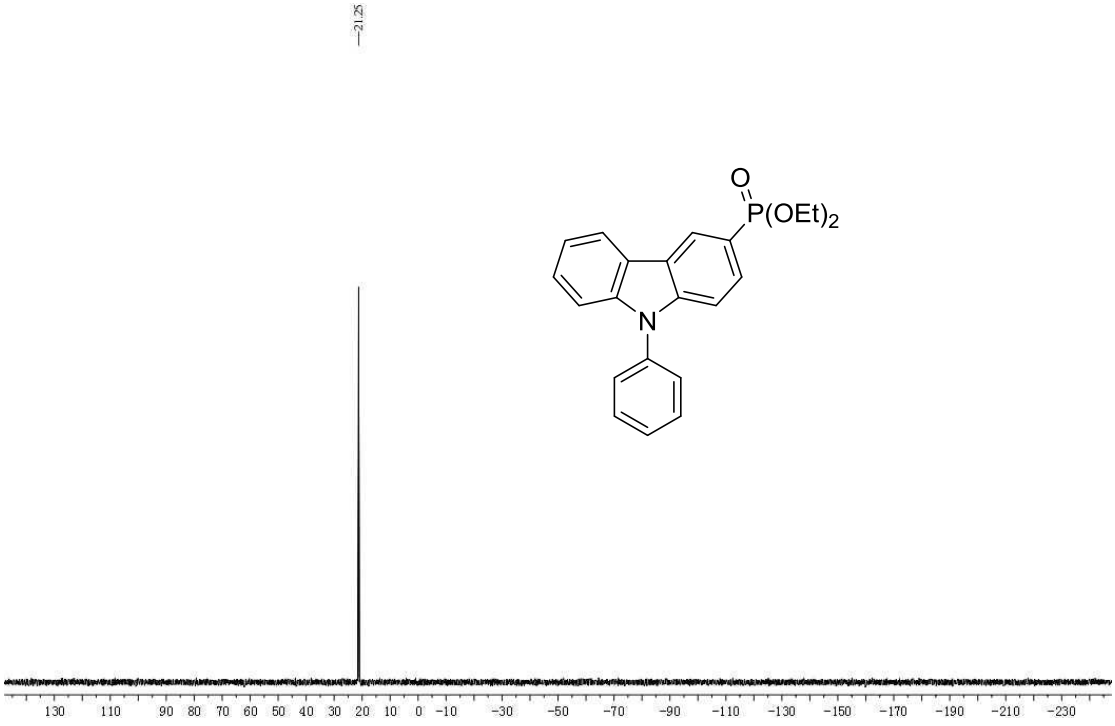
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3r



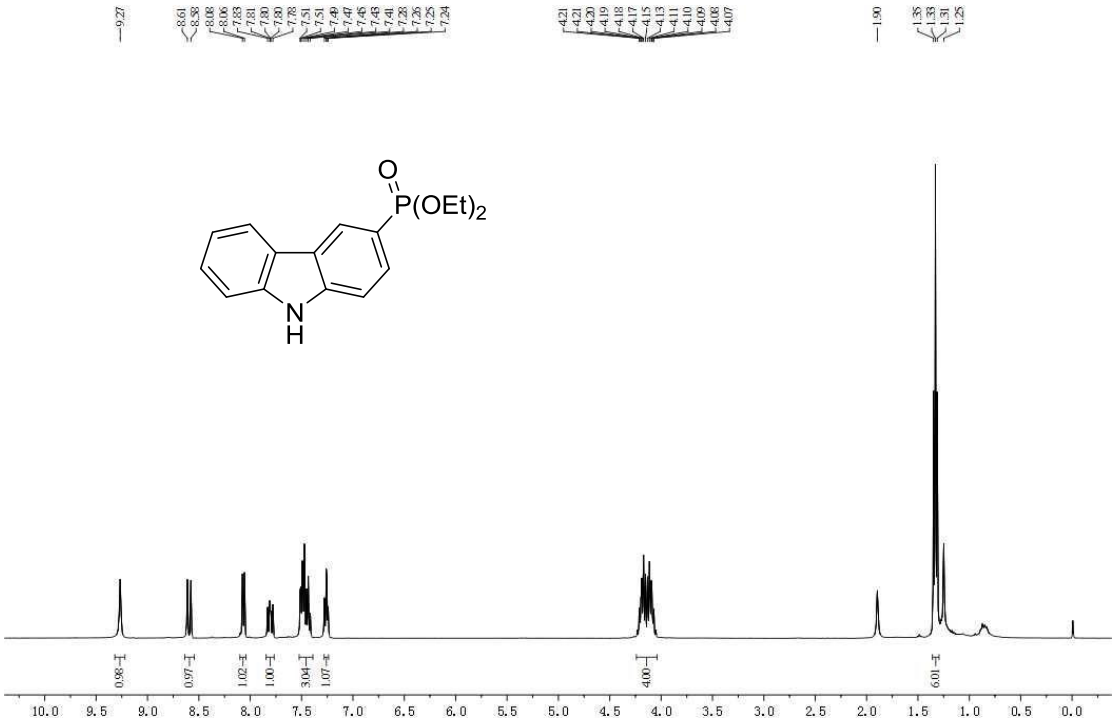
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3r



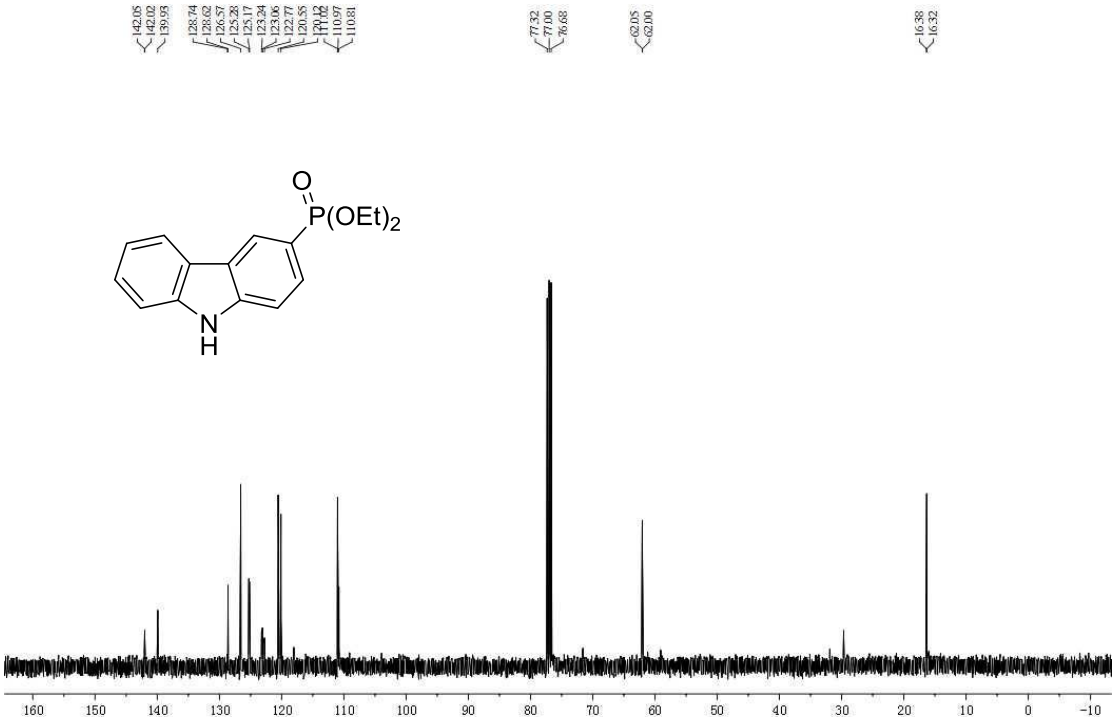
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3r



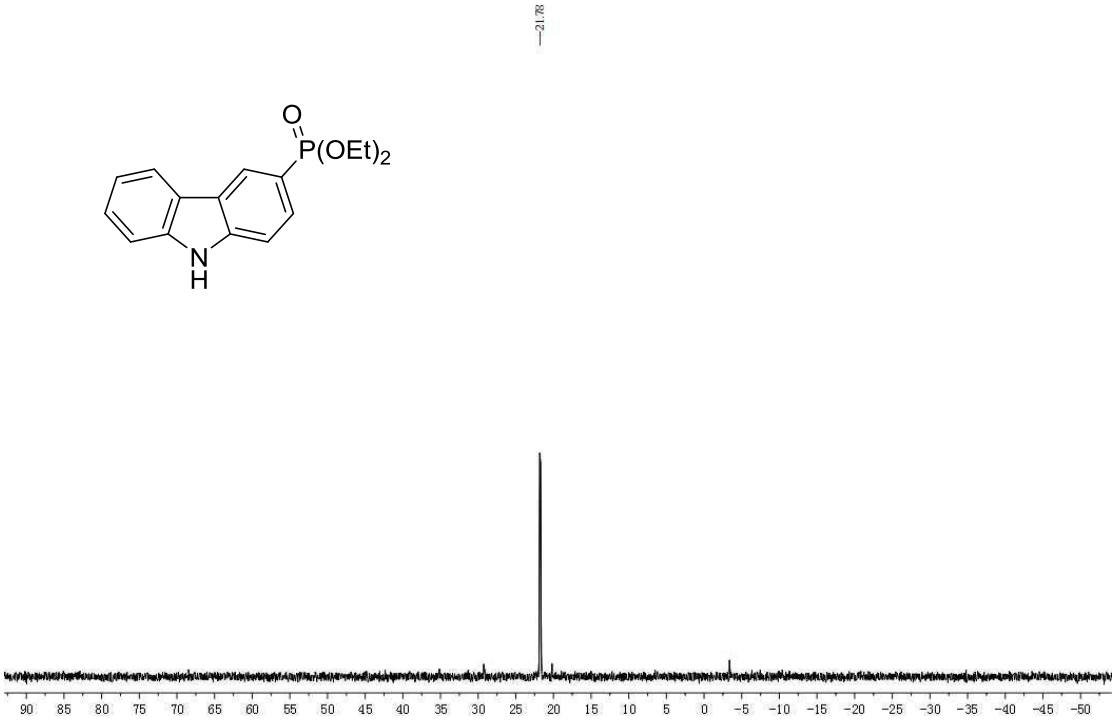
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3s



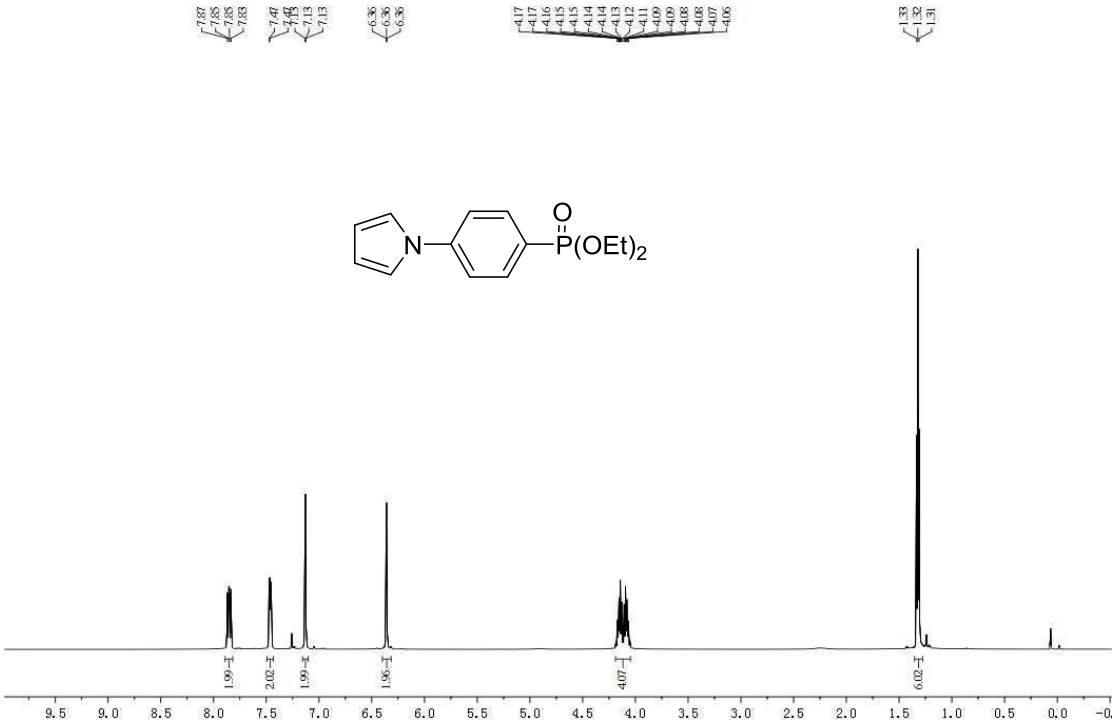
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3s



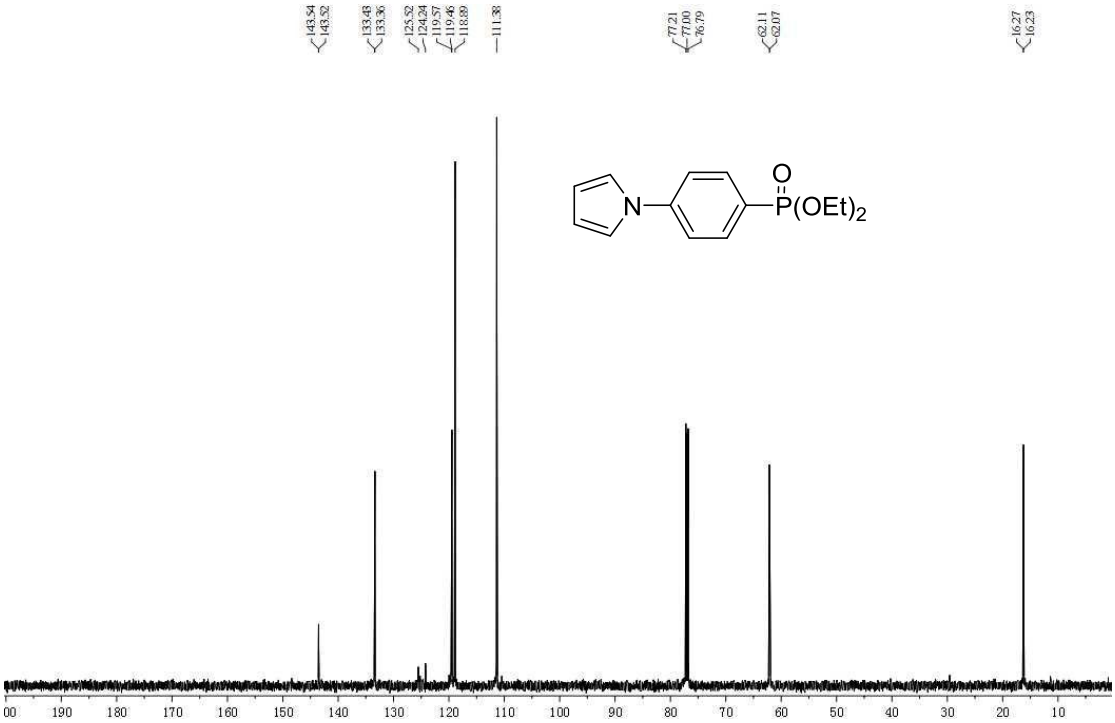
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3s



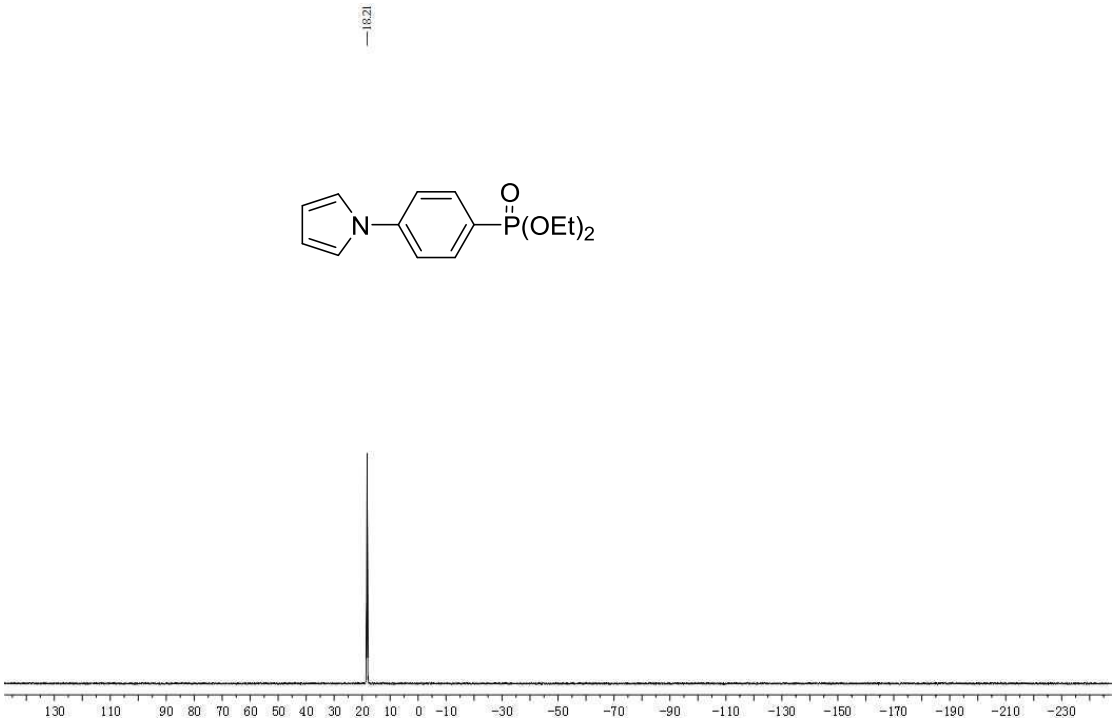
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3t



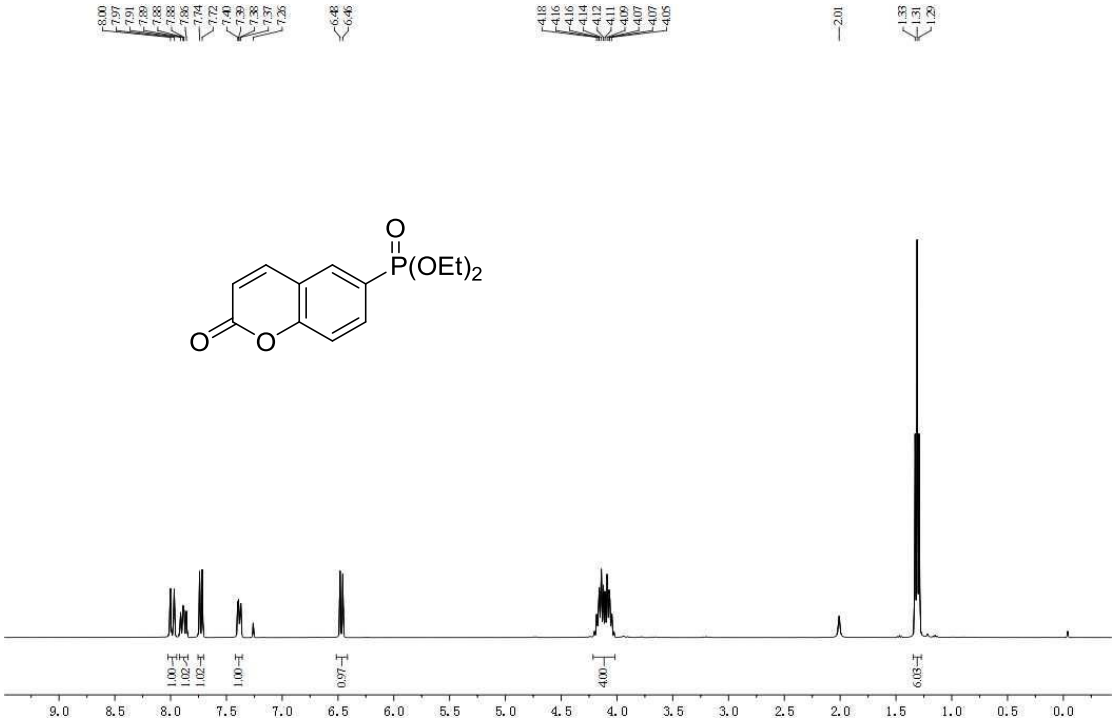
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3t



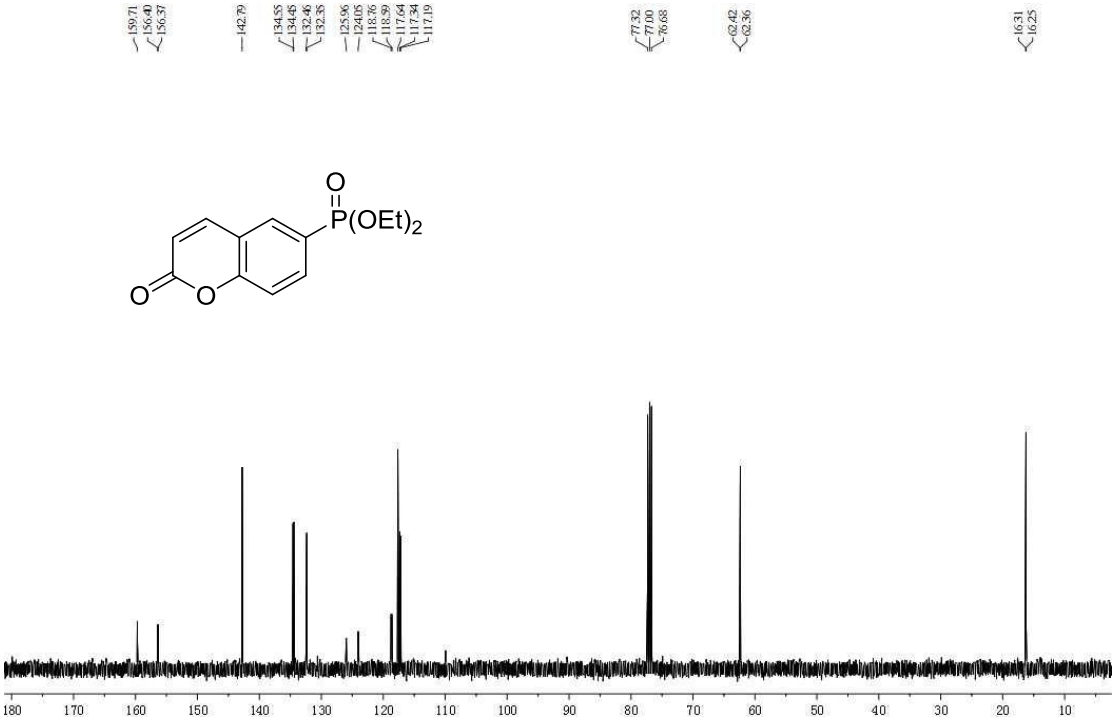
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3t



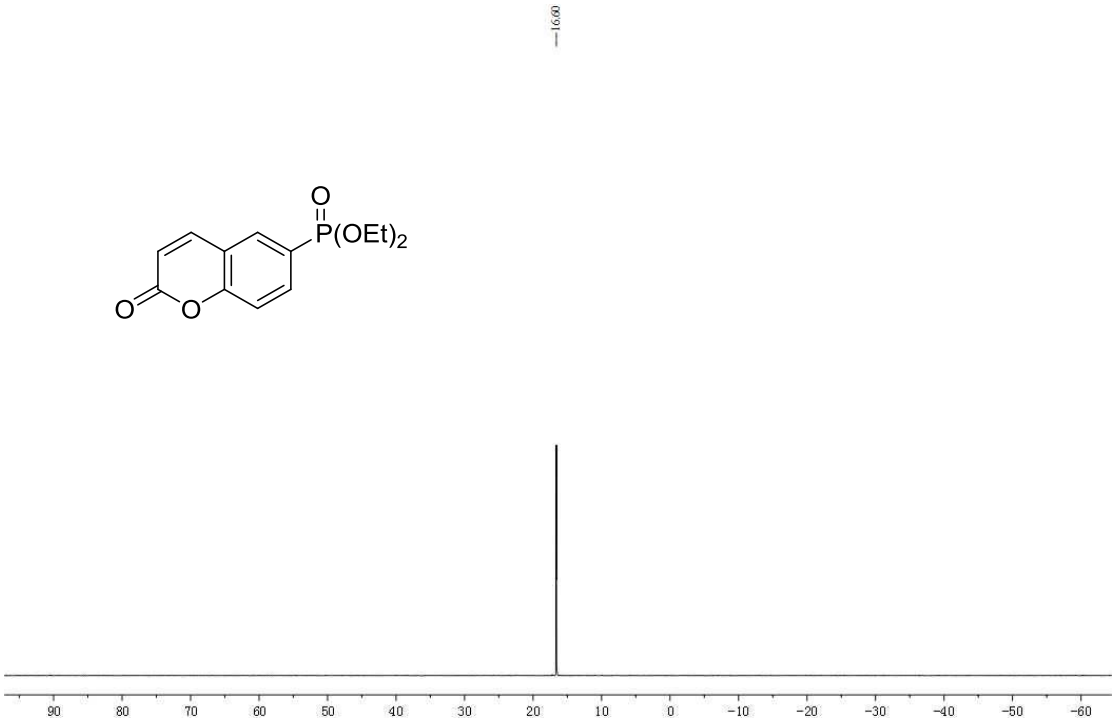
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3u



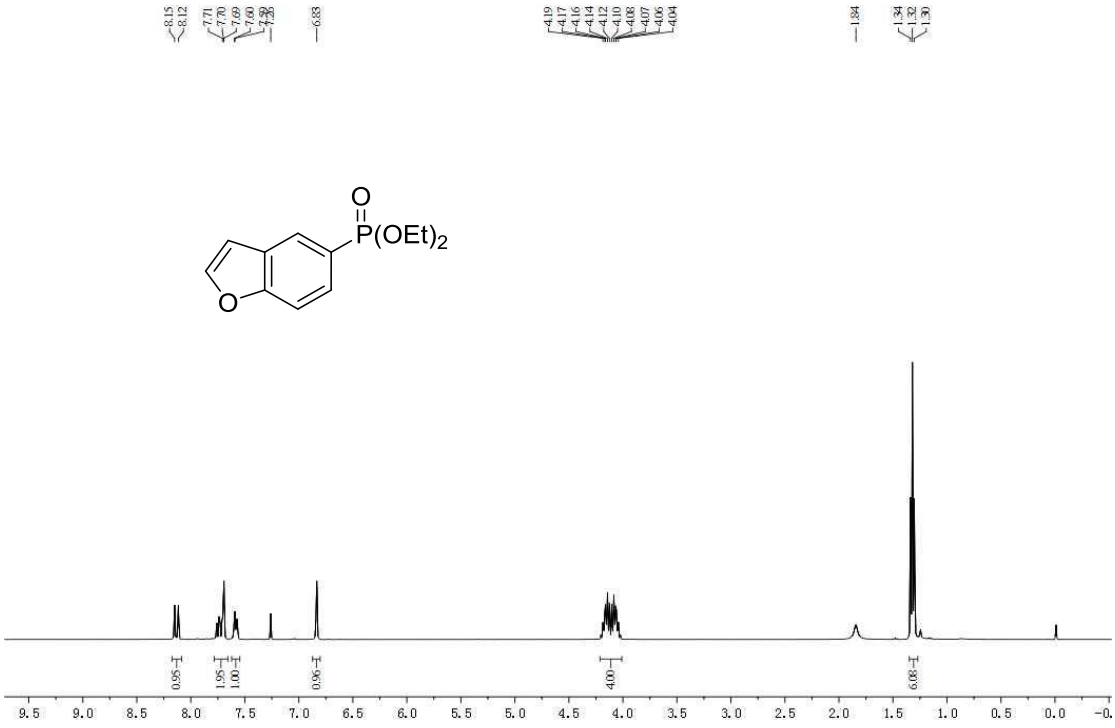
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3u



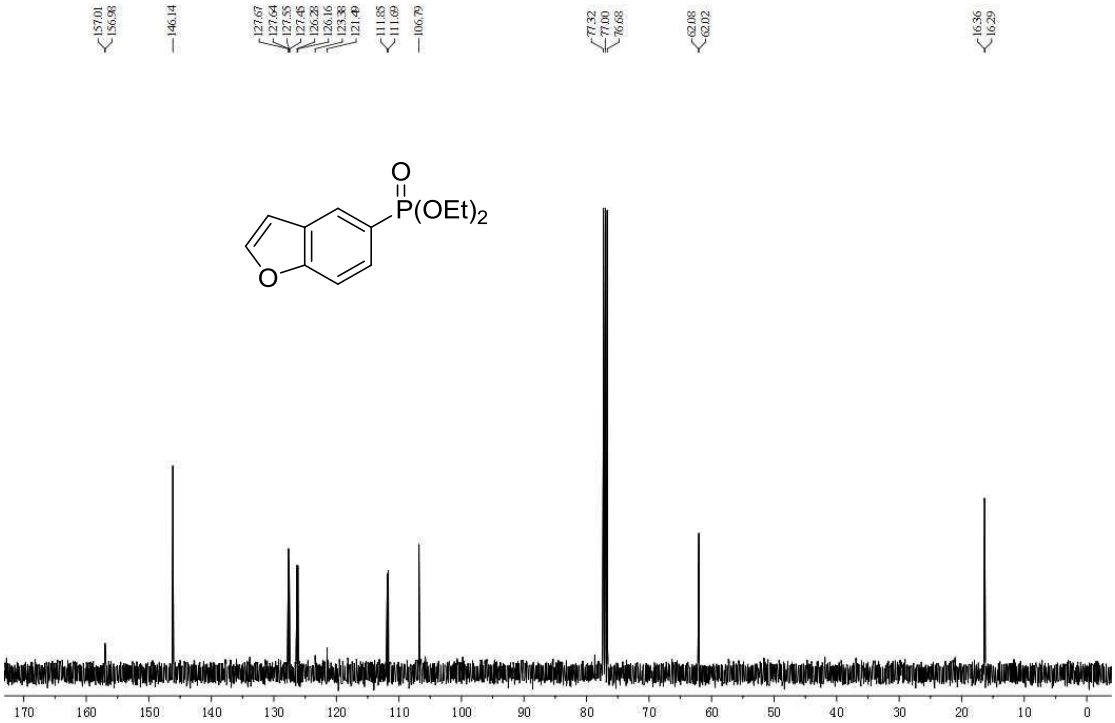
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3u



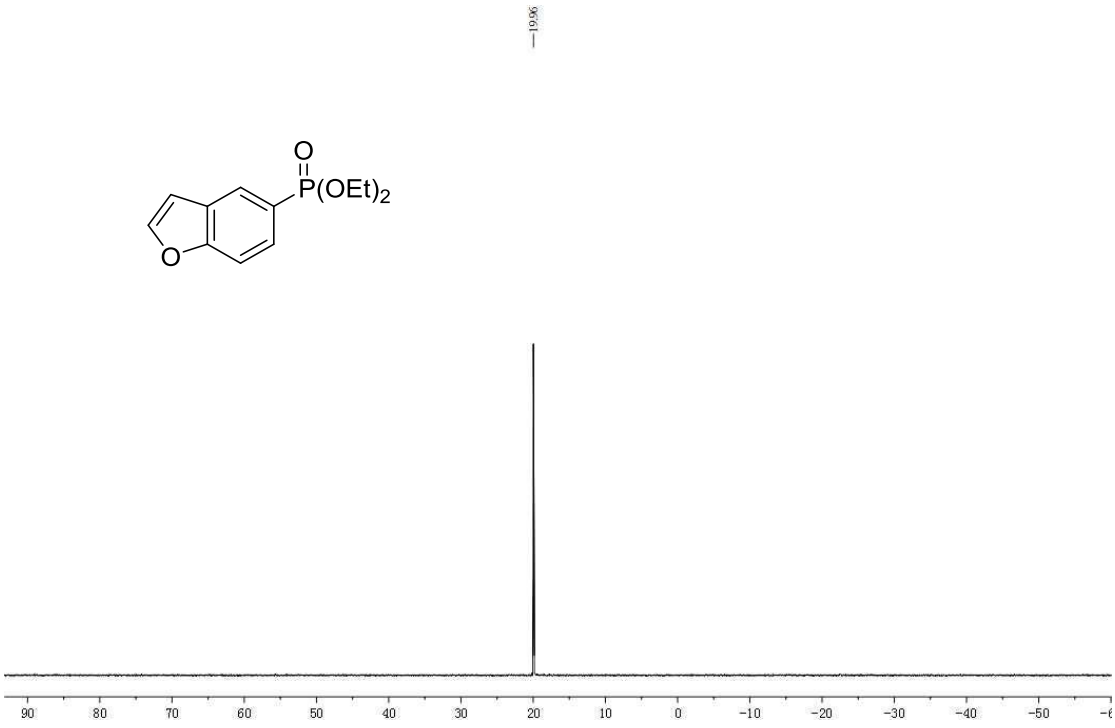
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3v



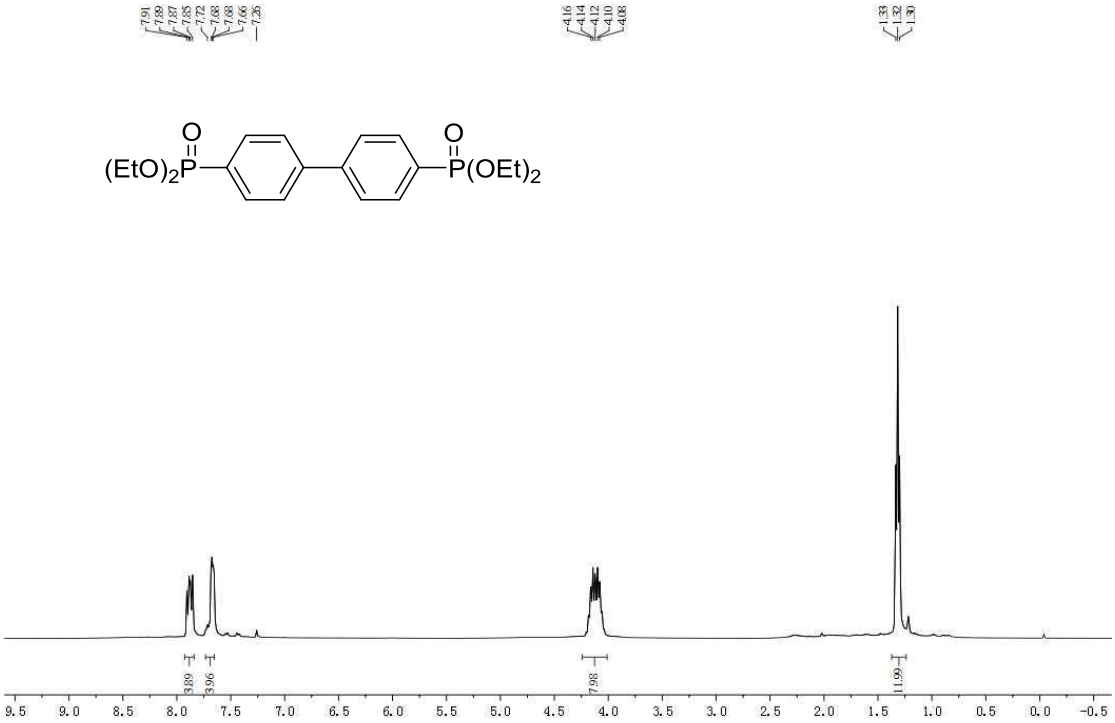
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3v



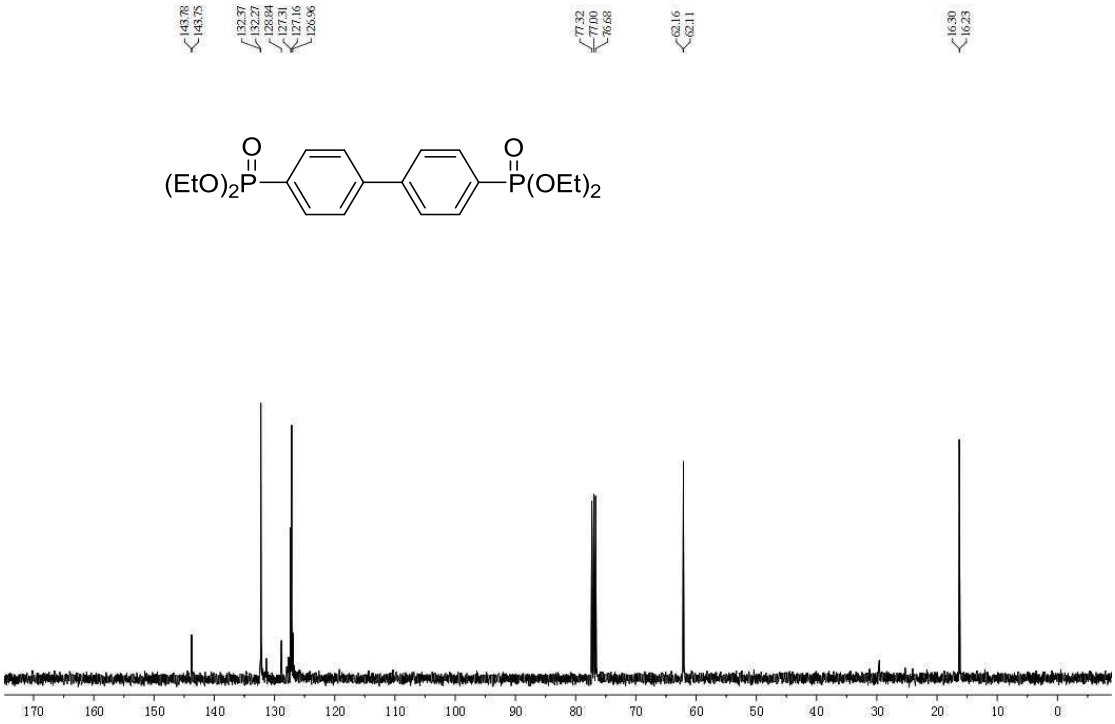
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3v



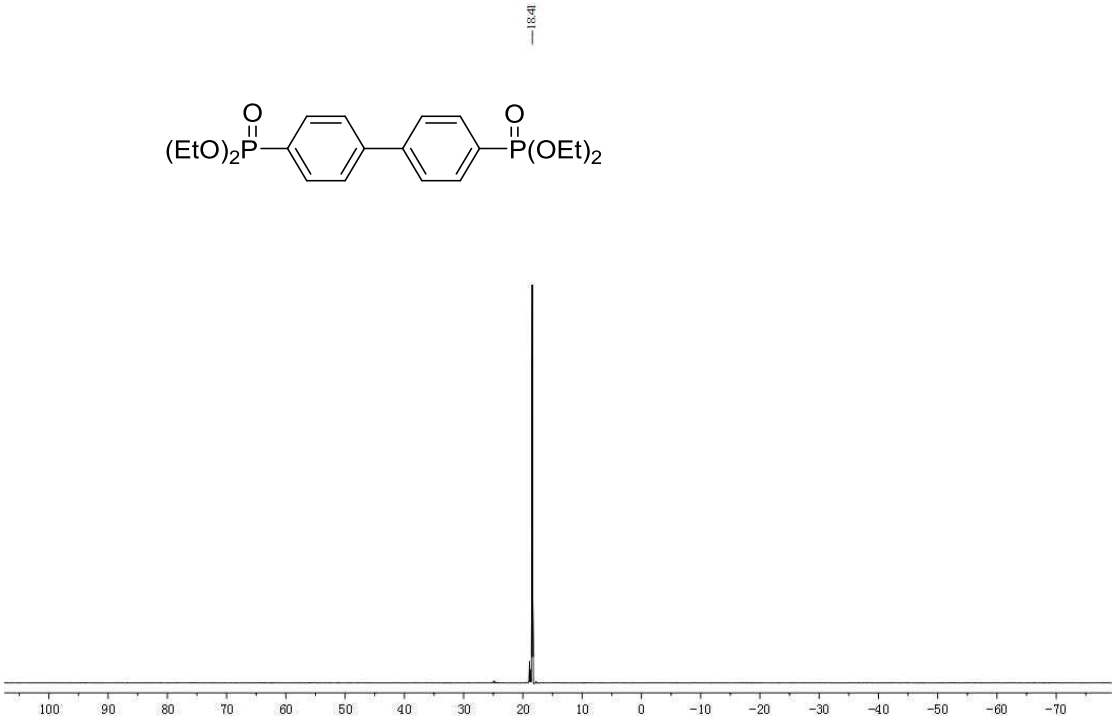
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3w



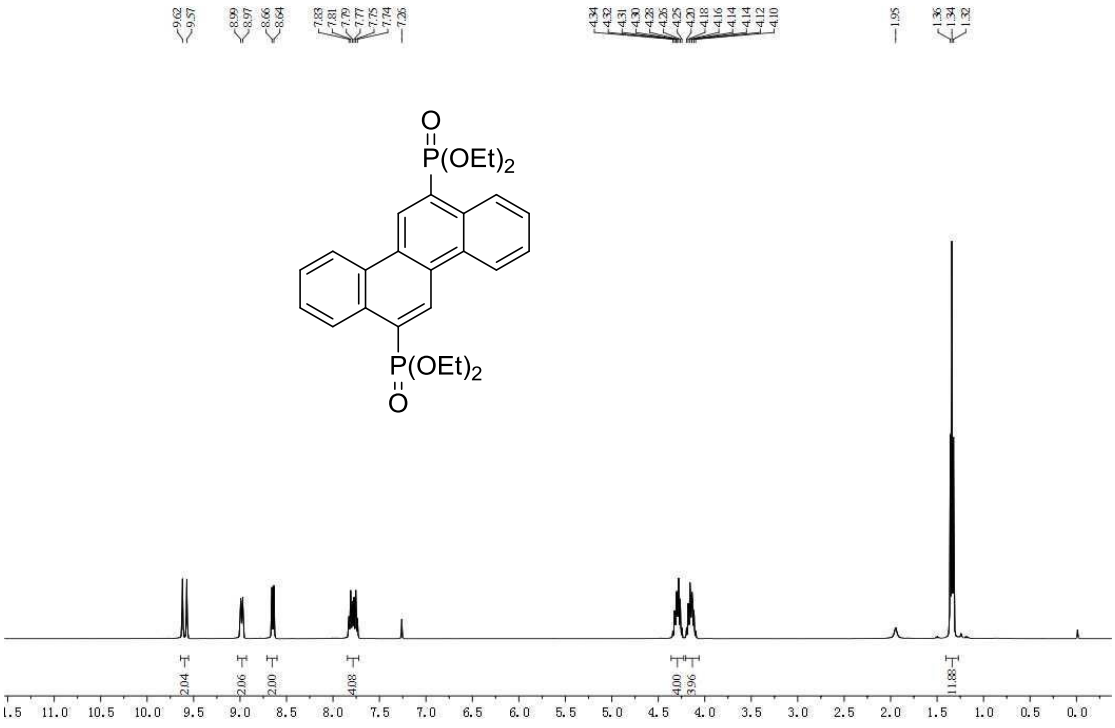
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3w



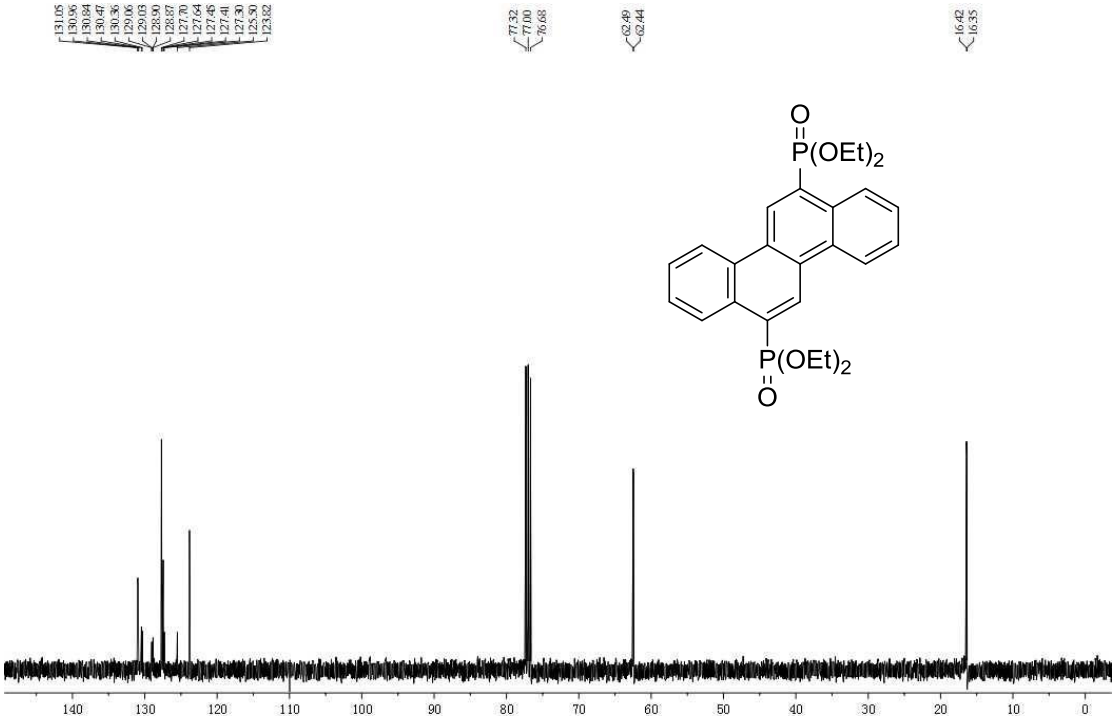
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3w



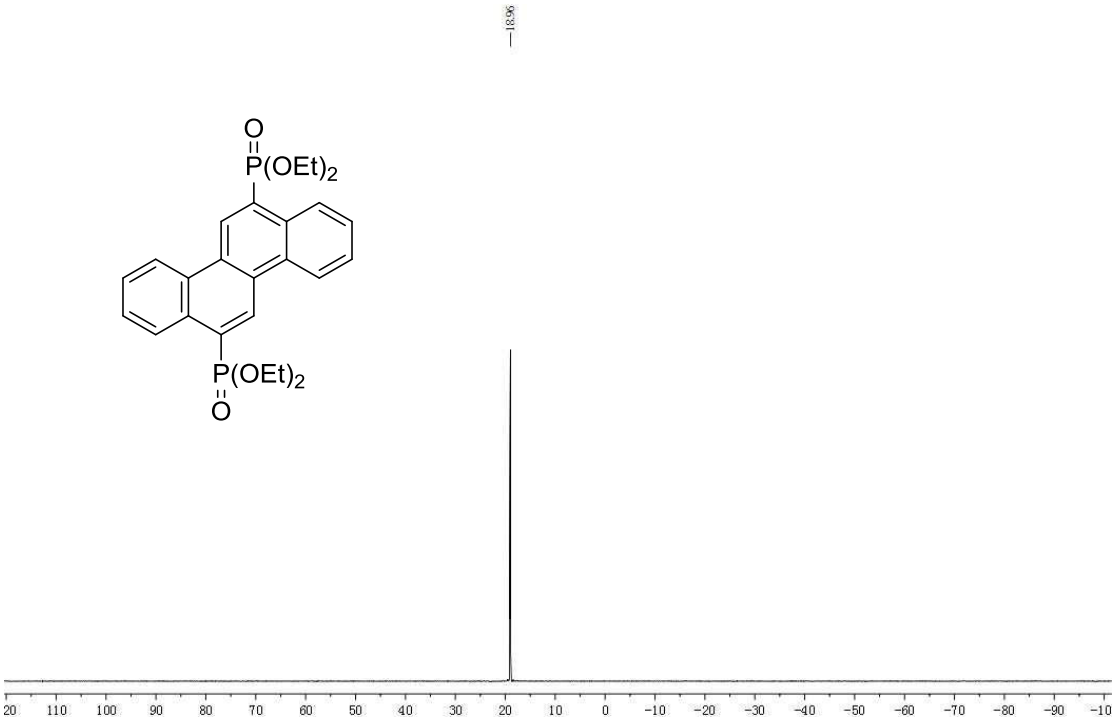
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3xa



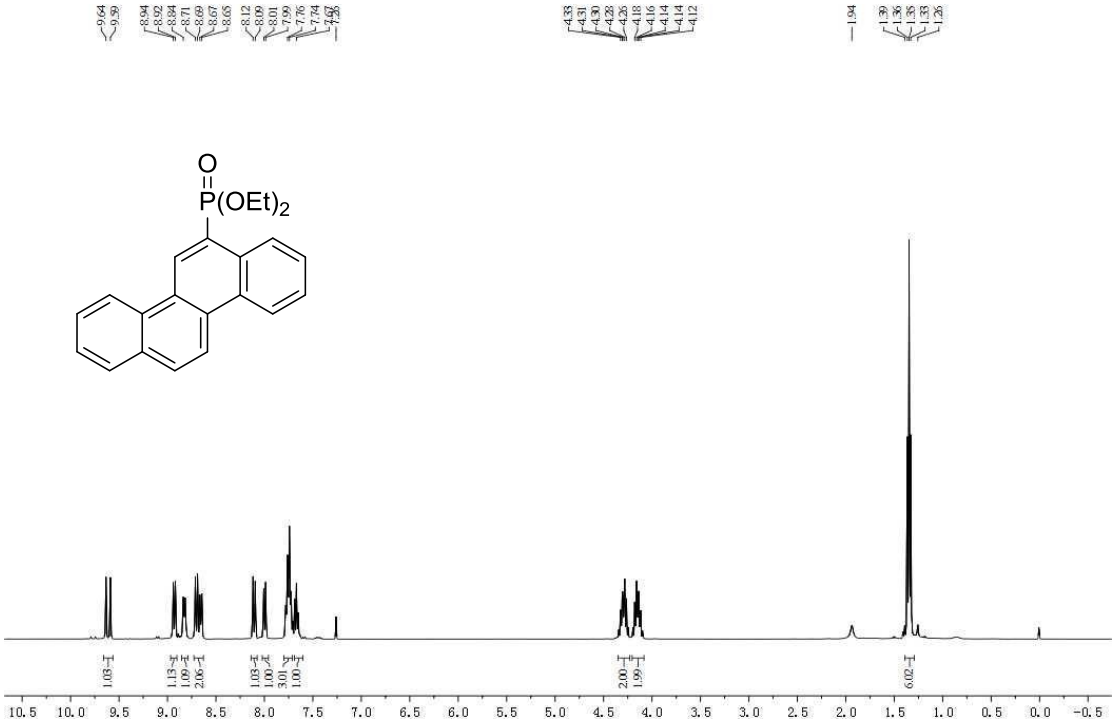
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3xa



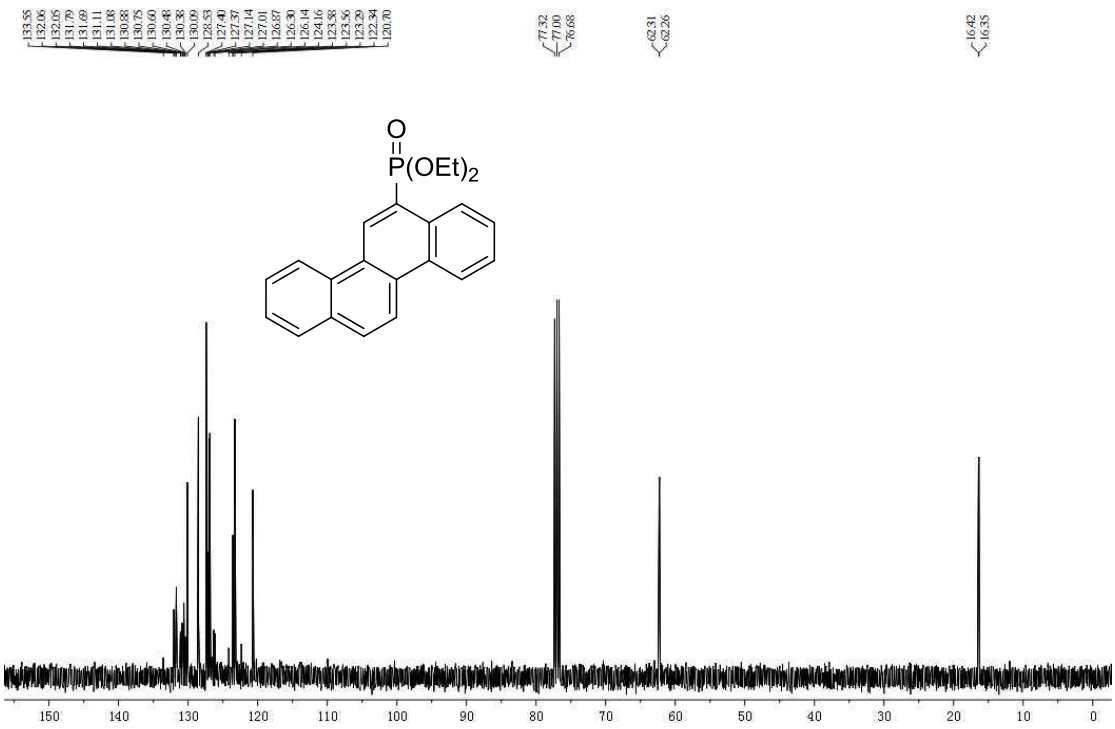
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3xa



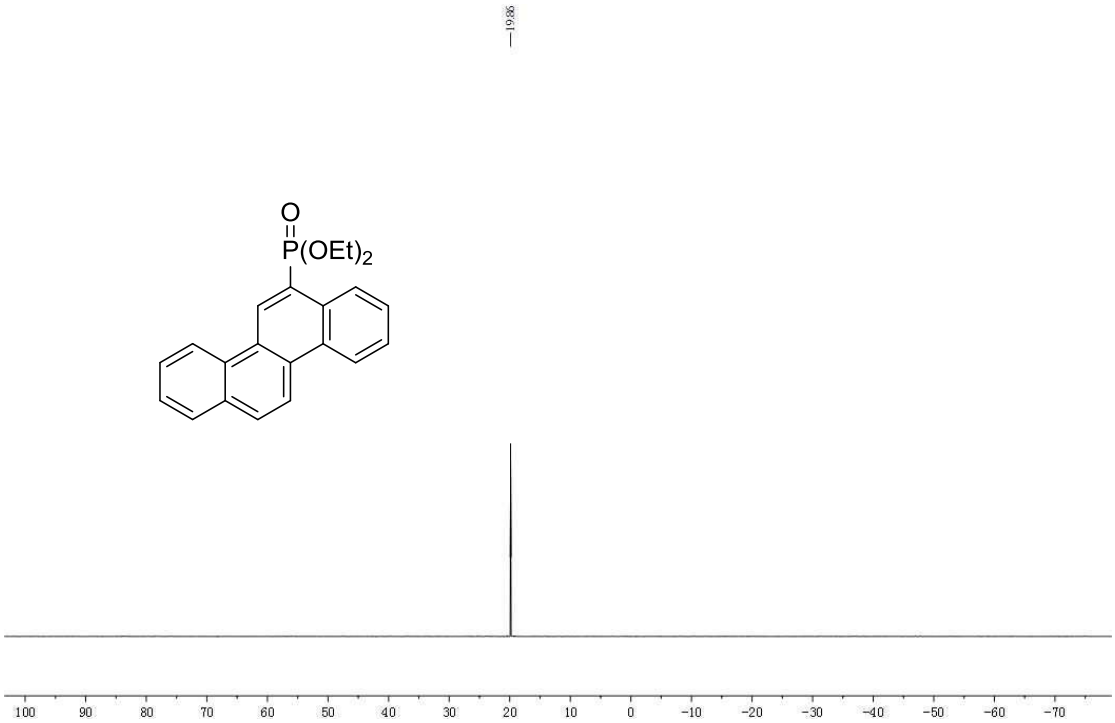
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3xb



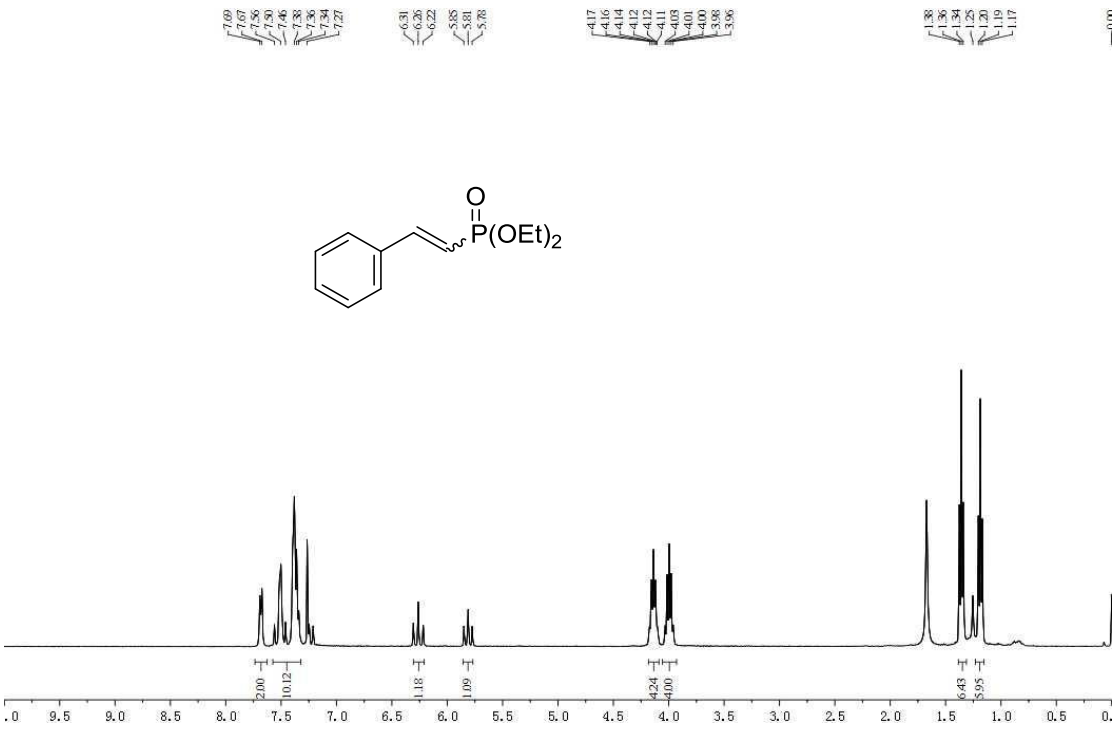
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3xb



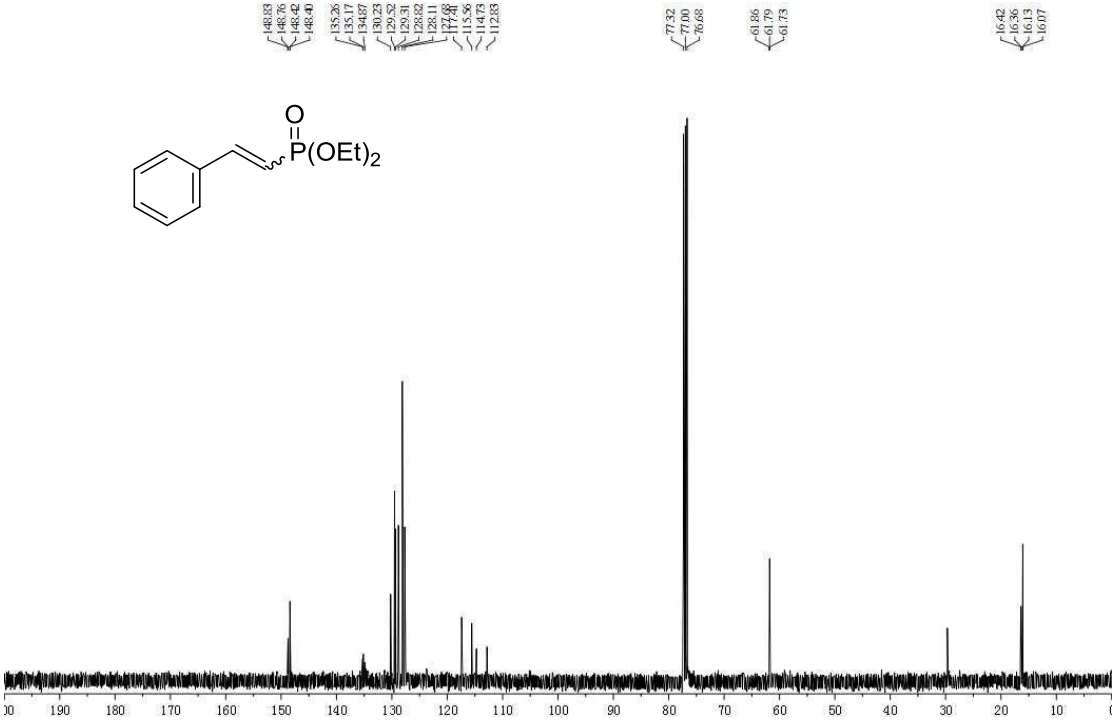
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3xb



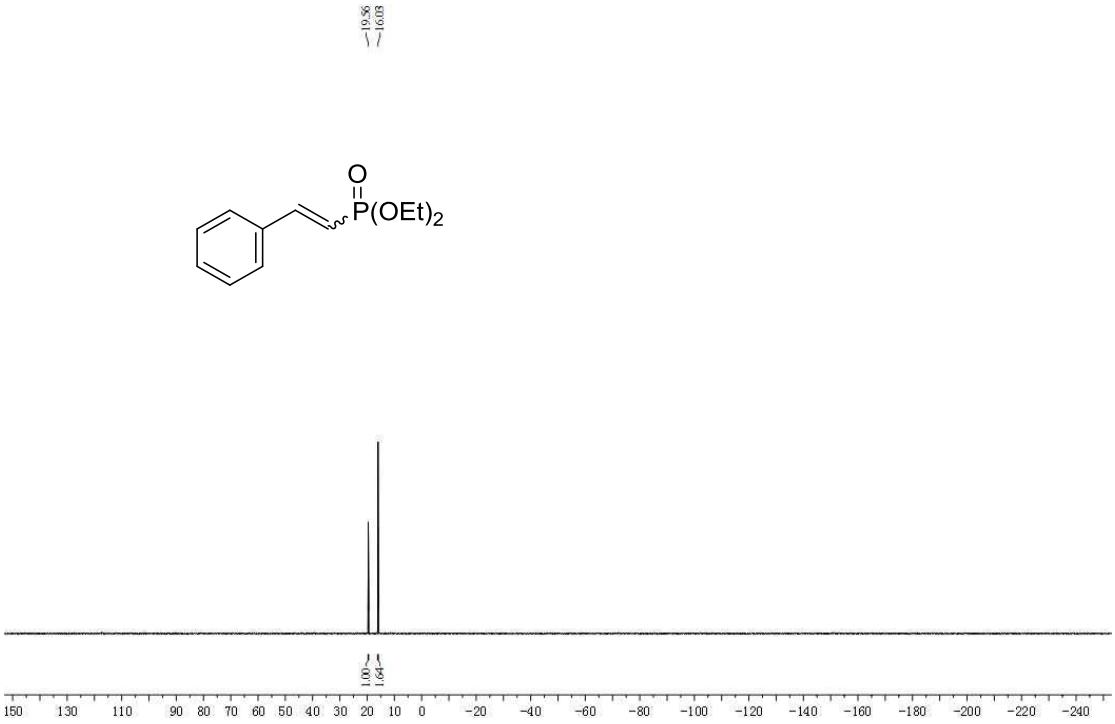
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3y



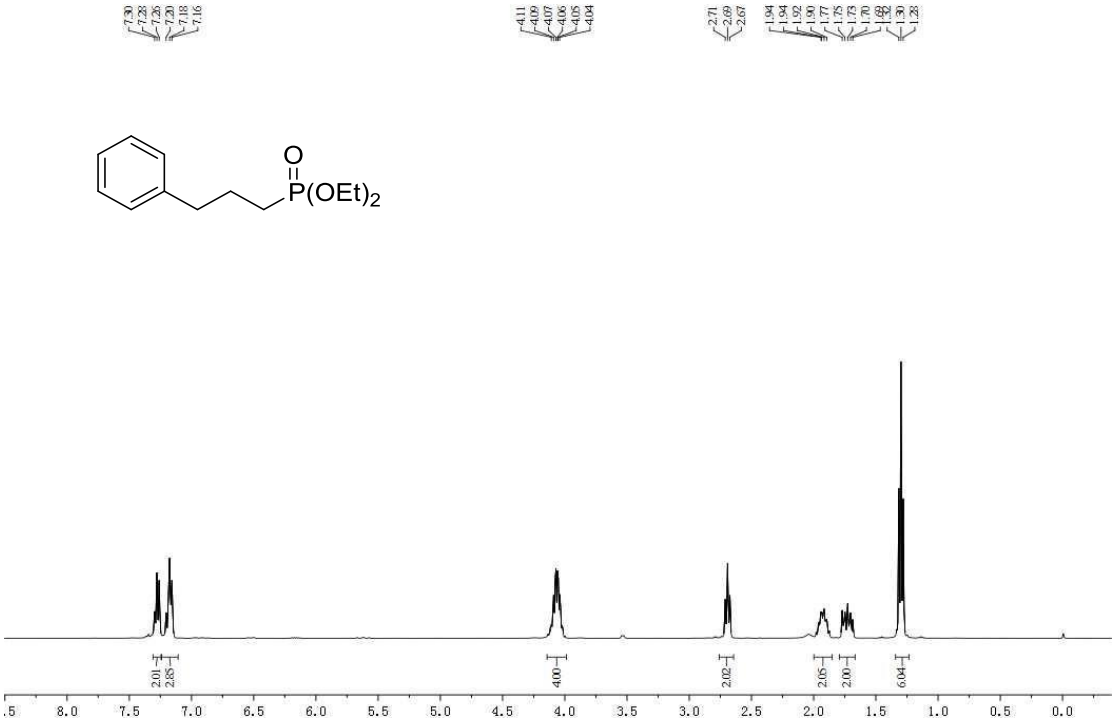
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3y



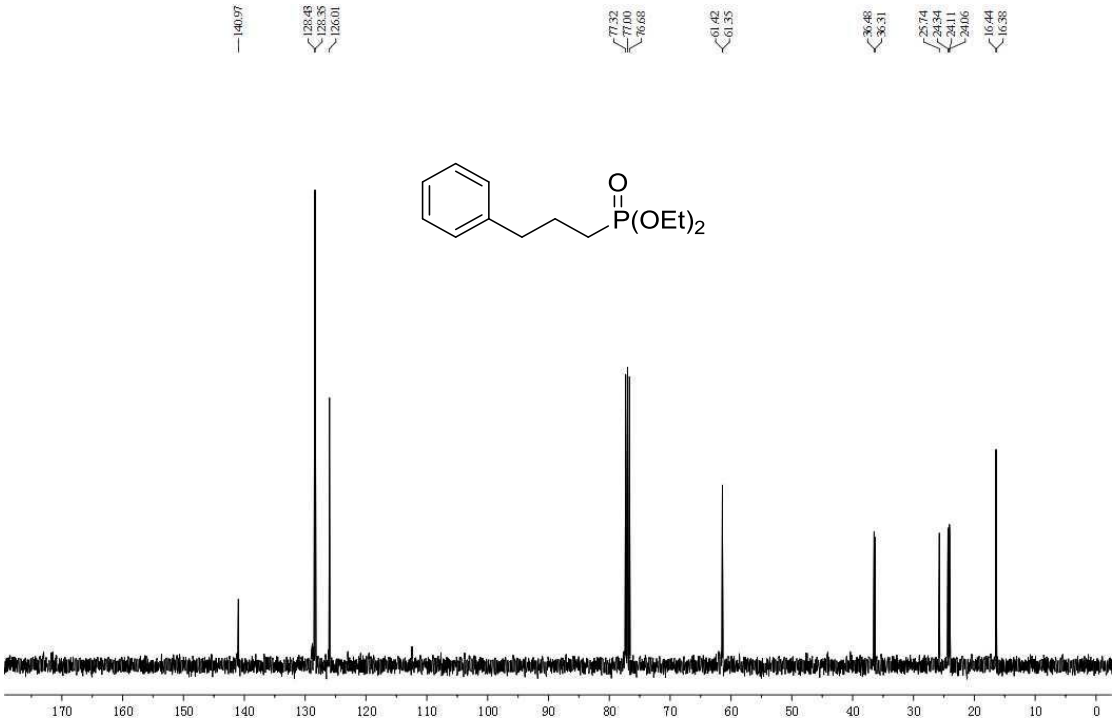
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3y



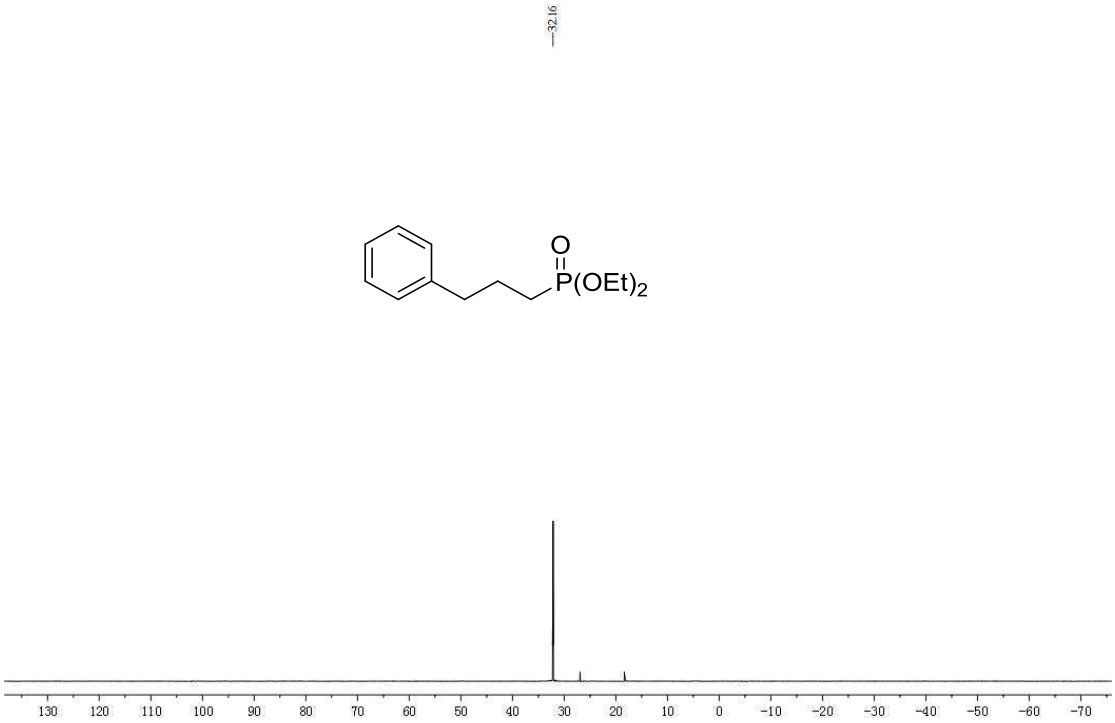
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3z



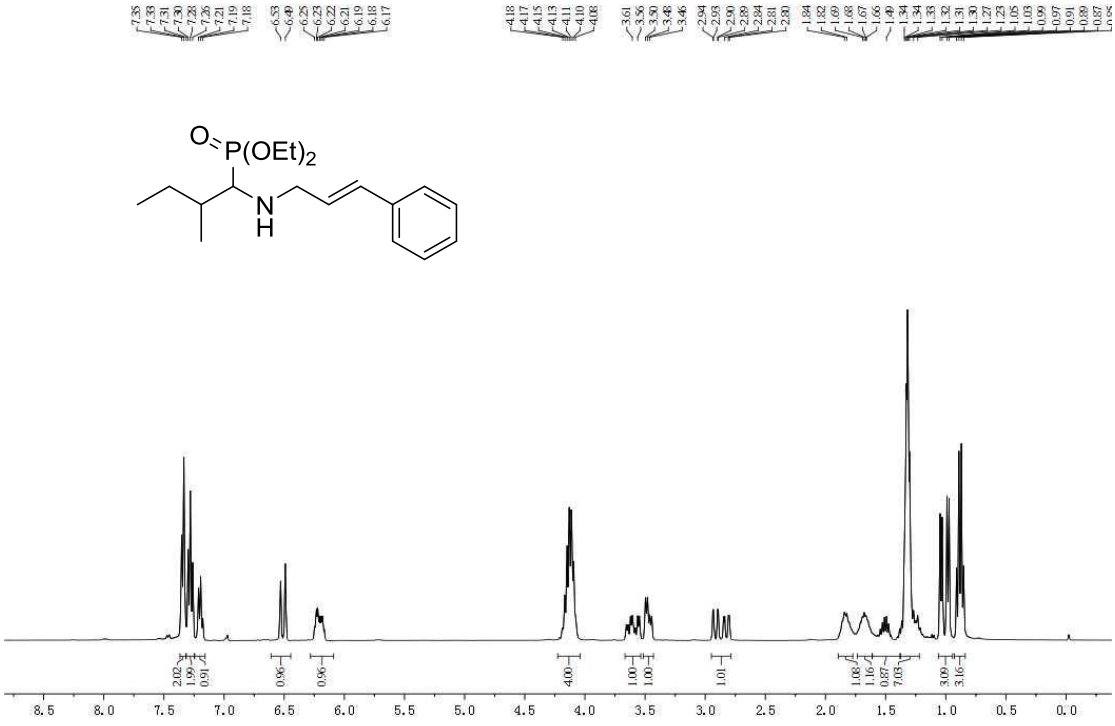
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3z



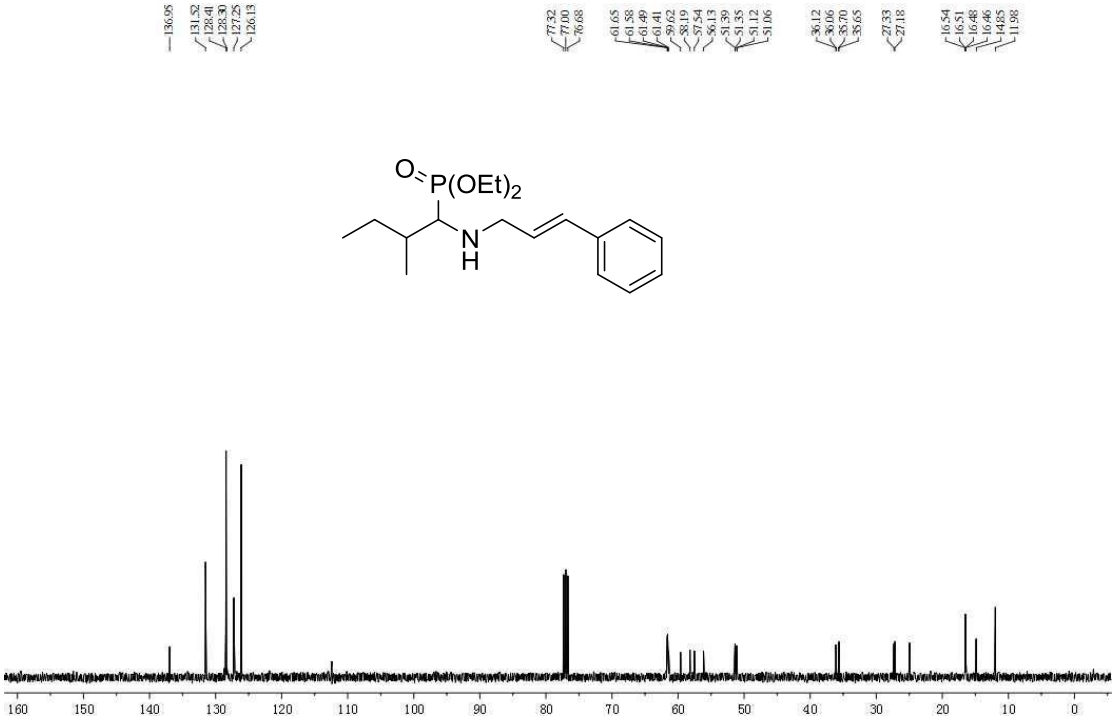
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3z



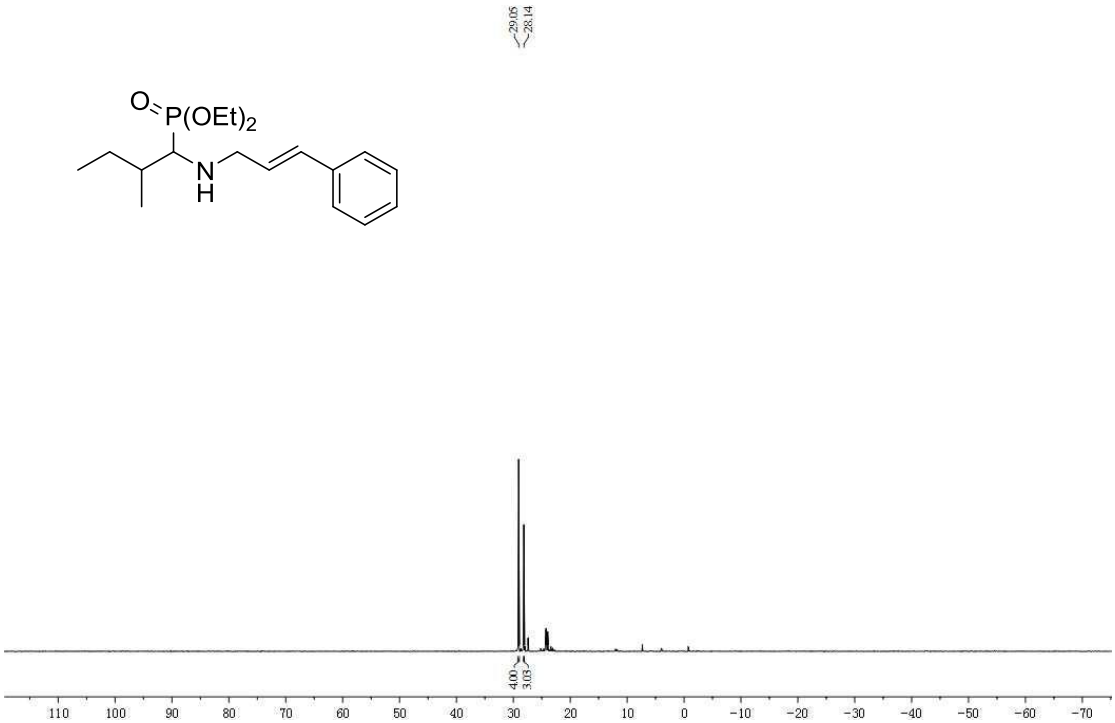
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4



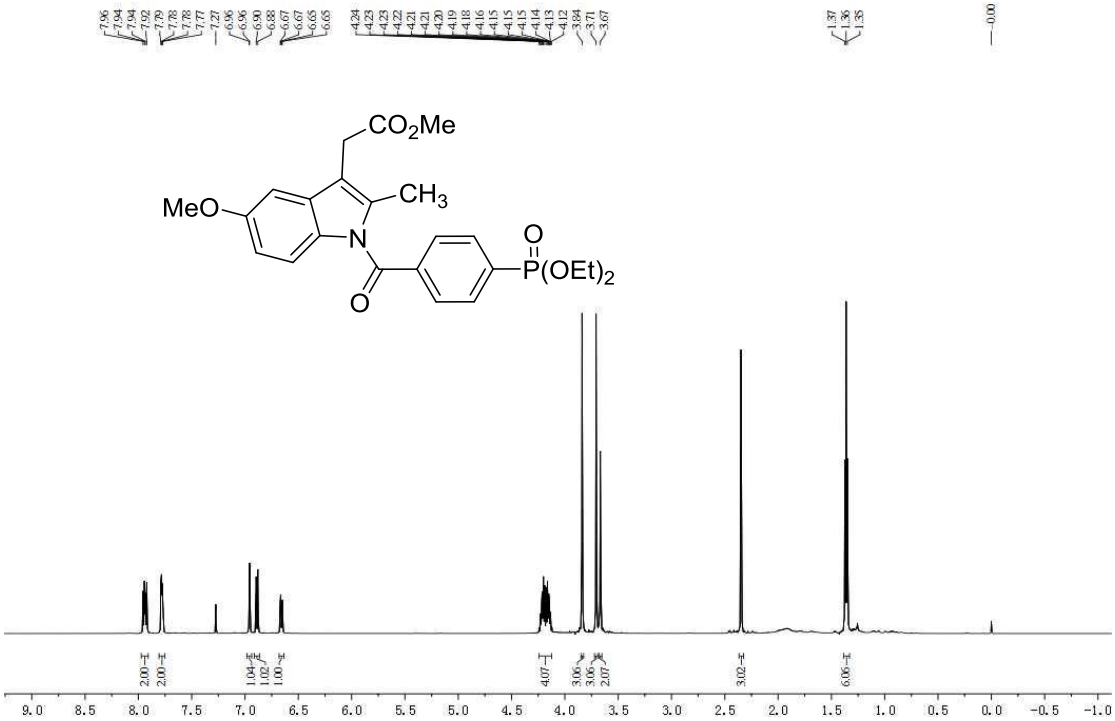
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4



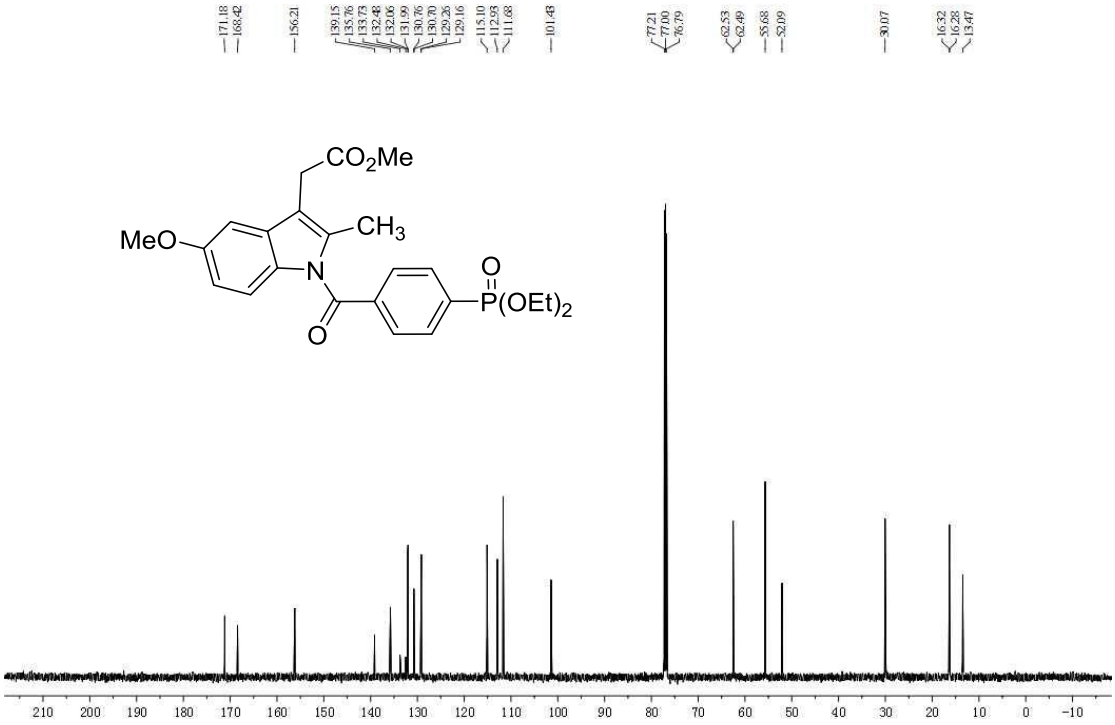
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 4



^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3bb



^{13}C NMR (151 MHz, $CDCl_3$) spectrum for 3bb



^{31}P NMR (243 MHz, $CDCl_3$) spectrum for 3bb