Supporting Information

Tandem Arbuzov-Perkow reaction: General synthesis of α-substituted vinyl P(V)-compounds

Kuo Zhao[a,b], Wenjie Liu[b], Yu Huang[b], Qian Wu[b], Yingle Liu*[a], Huichuang Guo*[b], Enxue Shi*[b]

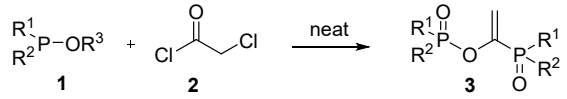
[a]College of Chemistry and Environmental Engineering, Sichuan University of Science and Engineering, Zigong 643002, China.
[b]State Key Laboratory of Chemistry for NBC Hazards Protection, Beijing 102205, China.
* Corresponding authors: *784943812@qq.com*; *liuyingleyou@163.com*; *exshi@sina.com*

Table of Contents

1. General information

All reactions were carried out in oven-dried glassware with a magnetic stirring bar. Dry solvents were obtained by a solvent purification system under argon. All commercially available reagents were used as received without further purification. Purification of products was carried out by flash column chromatography using silica gel 200-300 mesh. Visualization was accompanied by UV light and/or $KMnO_4$ solution. High-resolution mass spectra (HRMS) were recorded on an Agilent LC/Xevo G2-XS QTOF mass spectrometer by electrospray ionization time of flight reflectron experiments. ^1H NMR spectra were recorded in $CDCl_3$ on a 300 MHz NMR spectrometer. The ^1H chemical shifts are referenced to residual solvent signals at δ 7.26 ($CHCl_3$) or δ 0.00 (TMS). ^1H NMR coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), tt (triplet of triplets). ^{13}C NMR spectra were proton decoupled and recorded in $CDCl_3$ on 75 MHz NMR or 151 NMR spectrometer. The ^{13}C chemical shifts are referenced to solvent signals at δ 77.16 ($CDCl_3$). ^{31}P NMR spectra were proton decoupled and recorded in $CDCl_3$ on a 121 MHz NMR spectrometer. ^{19}F NMR spectra were proton decoupled and recorded in $CDCl_3$ on a 282 MHz NMR spectrometer.

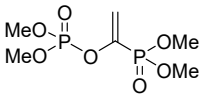
2. General procedure for the synthesis of enol bisphosphorus compounds



1 **2** **3**

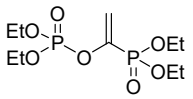
A mixture of chloroacetyl chloride **2** (1 mmol) and P(III)-reagents **1** (2.2 mmol) was stirred at 25 °C under solvent-free conditions for 1 h. The reaction progress was monitored by TLC (visualization with $KMnO_4$ staining). Upon completion, the crude product was purified by column chromatography (hexane/ethyl acetate = 1:1) to afford the target compound **3** as a colorless oil.

1-(dimethoxyphosphoryl)vinyl dimethyl phosphate (3a)



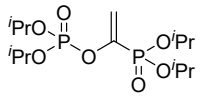
92% yield, oily liquid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 2:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.93 (ddd, *J* = 2.9, 1.4 Hz, 1H), 5.83 (ddd, *J* = 2.9, 2.3 Hz, 1H), 3.84 (s, 3H), 3.80 (d, *J* = 0.6 Hz, 6H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 146.25 (d, *J* = 10.4 Hz), 143.19 (d, *J* = 10.5 Hz), 116.59 (d, *J* = 4.1 Hz), 116.26 (d, *J* = 4.2 Hz), 55.14 (d, *J* = 6.3 Hz), 53.47 (d, *J* = 5.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 9.74 (d, *J* = 23.9 Hz), -4.27 (d, *J* = 25.0 Hz). HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_6H_{14}O_7P_2$ 261.0288; found 261.0286.

1-(diethoxyphosphoryl)vinyl diethyl phosphate (3b)



95% yield, oily liquid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 2:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.79 (dd, *J* = 2.7, 1.3 Hz, 1H), 5.69 – 5.66 (m, 1H), 5.64 (t, *J* = 2.5 Hz, 1H), 4.10 – 3.99 (m, 8H), 1.26 – 1.20 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 147.31 (d, *J* = 10.7 Hz), 144.27 (d, *J* = 10.6 Hz), 114.56 (d, *J* = 4.0 Hz), 114.24 (d, *J* = 4.1 Hz), 64.54 (d, *J* = 6.3 Hz), 62.80 (d, *J* = 5.4 Hz), 15.97 (d, *J* = 6.2 Hz), 15.73 (d, *J* = 6.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 6.9 (d, *J* = 26.6 Hz), -6.7 (d, *J* = 26.6 Hz). HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{10}H_{22}O_7P_2$ 317.0914, found 317.0915.

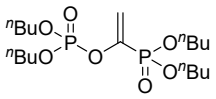
1-(diisopropoxyphosphoryl)vinyl diisopropyl phosphate (3c)



82% yield, oily liquid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 2:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.87 – 5.73 (m,

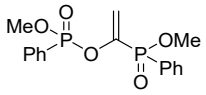
1H), 5.70 (s, 1H), 4.73 – 4.62 (m, 4H), 1.32 (s, 3H), 1.31 (s, 6H), 1.30 (d, J = 2.8 Hz, 12H), 1.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 148.54 (d, J = 11.2 Hz), 145.47 (d, J = 11.2 Hz), 113.21 (d, J = 3.9 Hz), 112.89 (d, J = 4.0 Hz), 73.93 (d, J = 6.4 Hz), 72.14 (d, J = 5.7 Hz), 24.11 (d, J = 3.9 Hz), 23.80 (d, J = 5.0 Hz), 23.68 (d, J = 5.0 Hz), 23.54 (d, J = 5.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 4.9 (d, J = 31.5 Hz), - 8.7 (d, J = 31.5 Hz). HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{14}H_{30}O_6P_2$ 373.1540, found 373.1547.

(1-(dibutoxyphosphoryl)vinyl) dibutyl phosphate (3d)



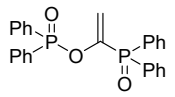
89% yield, oily liquid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 2:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.93 – 5.71 (m, 2H), 4.13 – 4.01 (m, 8H), 1.71 – 1.61 (m, 8H), 1.39 (dd, J = 15.2, 7.3 Hz, 8H), 0.91 (td, J = 7.3, 2.0 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 147.48 (d, J = 10.7 Hz), 144.43 (d, J = 10.7 Hz), 114.68 (d, J = 4.1 Hz), 114.36 (d, J = 4.0 Hz), 68.54 (d, J = 6.5 Hz), 66.78 (d, J = 5.7 Hz), 32.43 (d, J = 6.4 Hz), 32.21 (d, J = 6.9 Hz), 18.71 (d, J = 3.7 Hz), 13.63 (d, J = 3.2 Hz). ^{31}P NMR (121 MHz, Chloroform-d) δ= 7.3 (d, J = 28.5 Hz), -6.4 (d, J = 28.6 Hz). HRMS (ESI) (m/z) $[M+H]^+$ Calcd for $C_{18}H_{38}O_7P_2$ 429.2166, found 429.2165.

1-(methoxy(phenyl)phosphonate)vinyl methyl phenylphosphonate (3e)



87% yield, oily liquid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 2:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.83 – 7.73 (m, 2H), 7.72 – 7.63 (m, 1H), 7.60 – 7.48 (m, 3H), 7.48 – 7.38 (m, 3H), 7.38 – 7.29 (m, 1H), 6.14 – 5.65 (m, 2H), 3.79 (dd, J = 19.8, 11.4 Hz, 3H), 3.67 (dd, J = 11.4, 2.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 133.23 (dd, J = 5.6, 3.1 Hz), 133.08 (d, J = 2.9 Hz), 132.26 – 131.99 (m), 131.90 (d, J = 1.9 Hz), 128.74 (t, J = 2.6 Hz), 128.54 (d, J = 2.8 Hz), 126.94, 124.84 (d, J = 19.5 Hz), 115.03 – 114.42 (m), 53.19 (d, J = 6.1 Hz), 52.13 (d, J = 6.3 Hz), 51.97 (d, J = 6.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 23.73 (dd, J = 19.7, 4.1 Hz), 17.49 (dd, J = 41.6, 19.6 Hz). HRMS (ESI) (m/z) $[M+H]^+$ Calcd for $C_{16}H_{18}O_5P_2$ 353.0702, found 353.0704.

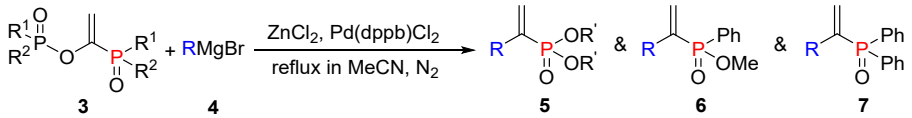
1-(diphenylphosphinate)vinyl diphenylphosphinate (3f)



85% yield, oily liquid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 2:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.76 (dd, J = 11.6, 7.7 Hz, 4H), 7.63 – 7.55 (m, 2H), 7.55 – 7.42 (m, 10H), 7.35 (dd, J = 7.6, 3.8 Hz, 4H), 6.05 (dd, J = 29.5, 3.4 Hz, 1H), 5.70 (d, J = 8.1 Hz, 1H). ^{13}C NMR (75 MHz,

$CDCl_3$) δ= 149.32 (d, *J* = 15.6 Hz), 132.77 (d, *J* = 3.0 Hz), 132.69 (d, *J* = 2.9 Hz), 132.32 (d, *J* = 10.2 Hz), 131.72 (d, *J* = 10.7 Hz), 131.34 (d, *J* = 10.5 Hz), 130.82 (d, *J* = 24.4 Hz), 129.20 (d, *J* = 5.5 Hz), 128.82 (d, *J* = 4.3 Hz), 128.65 (d, *J* = 5.5 Hz), 128.54, 128.37, 113.97 (dd, *J* = 17.1, 5.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 32.25 (d, *J* = 16.5 Hz), 22.40 (d, *J* = 16.5 Hz).. HRMS (ESI) (m/z) $[M+H]^+$ Calcd for $C_{26}H_{22}O_3P_2$ 445.1117, found 445.1118.

3. General procedure for the synthesis of α-substituted vinyl P(V)-compounds

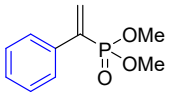


3 **4** **5** **6** **7**

A solution of RMgBr (1 M, 0.8 mmol) in THF was added to a stirred suspension of $ZnCl_2$ (1.6 mmol) in CH_3CN (3.0 mL) at 0~5 °C under N_2 atmosphere. The mixture was stirred at the same temperature for 1 h, then substrate **3** (0.4 mmol) in CH_3CN (5 mL) and Pd(dppb)Cl_2 (0.04 mmol) in CH_3CN (2 mL) were successively added and stirred for 2 h. After cooling down, aq. HCl solution (1 M) was added to the mixture, which was extracted twice with EtOAc. The combined organic phase was washed with brine, dried (Na_2SO_4), and concentrated. Upon completion, the crude product was purified by column chromatography (hexane/ethyl acetate = 10:1 - 1:1) to give the desired product **5**, **6**, or **7**.

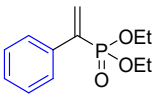
3.1 Characterizations of α-substituted vinyl phosphonates (5a-5z)

Dimethyl (1-phenylvinyl)phosphonate (5a)



87% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.49 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.39 – 7.30 (m, 3H), 6.34 (dd, *J* = 22.1, 1.5 Hz, 1H), 6.19 (dd, *J* = 46.2, 1.5 Hz, 1H), 3.73 (d, *J* = 11.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 138.67 (d, *J* = 177.5 Hz), 136.58 (d, *J* = 11.8 Hz), 132.67 (d, *J* = 8.1 Hz), 128.69, 128.57, 127.51 (d, *J* = 5.8 Hz), 52.88 (d, *J* = 5.8 Hz).^{31}P NMR (121 MHz, $CDCl_3$) δ= 20.00 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{13}O_3P$ 213.0602; Found 213.0608.

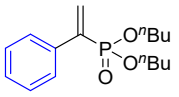
Diethyl (1-phenylvinyl)phosphonate (5b)



90% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.54 – 7.48 (m,

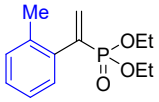
2H), 7.38 – 7.31 (m, 3H), 6.33 (dd, J = 22.0, 1.6 Hz, 1H), 6.15 (dd, J = 45.9, 1.6 Hz, 1H), 4.17 – 4.04 (m, 4H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 139.80 (d, J = 174.5 Hz), 136.78 (d, J = 11.8 Hz), 131.91 (d, J = 7.9 Hz), 128.53, 128.38 (d, J = 1.3 Hz), 127.55 (d, J = 5.7 Hz), 62.37 (d, J = 5.7 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 17.10 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{17}O_3P$ 241.0915; Found 241.0922.

Dibutyl (1-phenylvinyl)phosphonate (5c)



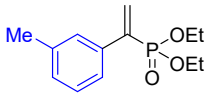
82% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 7:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.50 (d, J = 6.3 Hz, 2H), 7.32 (d, J = 5.8 Hz, 3H), 6.31 (dd, J = 22.0, 1.6 Hz, 1H), 6.14 (dd, J = 45.7, 1.6 Hz, 1H), 4.01 (dtt, J = 13.7, 6.8, 3.5 Hz, 4H), 1.63 – 1.53 (m, 4H), 1.36 – 1.25 (m, 4H), 0.85 (t, J = 7.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 139.69 (d, J = 174.7 Hz), 136.72 (d, J = 11.8 Hz), 131.69 (d, J = 8.0 Hz), 128.39, 128.25 (d, J = 1.3 Hz), 127.45 (d, J = 5.7 Hz), 65.93 (d, J = 6.0 Hz), 32.37 (d, J = 6.4 Hz), 18.70, 13.55. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 17.20 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{26}O_3P$ 297.1614; Found 297.1620.

Diethyl (1-(o-tolyl)vinyl)phosphonate (5d)



84% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.30 – 7.10 (m, 4H), 6.42 (dd, J = 22.5, 2.0 Hz, 1H), 5.96 – 5.76 (m, 1H), 4.07 (p, J = 7.2 Hz, 4H), 2.31 (s, 3H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 139.99 (d, J = 176.9 Hz), 136.54 (d, J = 9.8 Hz), 136.07 (d, J = 5.5 Hz), 132.98 (d, J = 8.4 Hz), 130.30 (d, J = 1.2 Hz), 129.11 (d, J = 3.7 Hz), 127.92 (d, J = 2.2 Hz), 125.38 (d, J = 1.9 Hz), 62.38 (d, J = 6.3 Hz), 28.48, 19.99 (d, J = 1.3 Hz), 16.29 (d, J = 6.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 15.90 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}O_3P$ 255.1145; Found 255.1146.

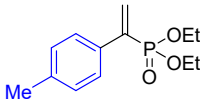
Diethyl (1-(m-tolyl)vinyl)phosphonate (5e)



92% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.27 – 7.08 (m, 4H), 6.40 (dd, J = 22.5, 2.0 Hz, 1H), 5.94 – 5.73 (m, 1H), 4.05 (p, J = 7.2 Hz, 4H), 2.29 (s, 3H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 139.82 (d, J = 173.9 Hz), 138.05, 136.69 (d, J = 11.7 Hz), 131.65 (d, J = 8.0 Hz), 129.08, 128.34, 128.12 (d,

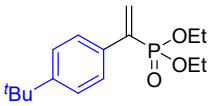
J = 5.9 Hz), 124.62 (d, J = 5.6 Hz), 62.24 (d, J = 5.7 Hz), 21.53, 16.33 (d, J = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 17.26 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}O_3P$ 255.1145; Found 255.1146.

Diethyl (1-(p-tolyl)vinyl)phosphonate (5f)



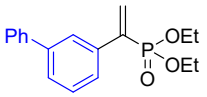
88% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1).^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.41 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 7.5 Hz, 2H), 6.27 (dd, J = 22.0, 1.6 Hz, 1H), 6.12 (dd, J = 45.9, 1.6 Hz, 1H), 4.19 – 3.97 (m, 4H), 2.33 (s, 3H), 1.26 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 139.43 (d, J = 173.8 Hz), 138.23 (d, J = 1.3 Hz), 133.77 (d, J = 11.8 Hz), 131.13 (d, J = 8.2 Hz), 129.20, 127.34 (d, J = 5.9 Hz), 62.23 (d, J = 5.7 Hz), 21.23, 16.34 (d, J = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 16.76 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}O_3P$ 255.1145; Found 255.1146.

Diethyl (1-(4-(tert-butyl)phenyl)vinyl)phosphonate (5g)



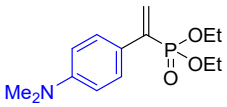
82% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.46 (d, J = 7.6 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 6.29 (dd, J = 22.0, 1.5 Hz, 1H), 6.15 (dd, J = 45.9, 1.4 Hz, 1H), 4.19 – 4.01 (m, 4H), 1.33 – 1.23 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 151.31, 139.27 (d, J = 173.6 Hz), 133.59 (d, J = 11.9 Hz), 131.10 (d, J = 8.1 Hz), 127.06 (d, J = 5.9 Hz), 125.37, 62.15 (d, J = 5.6 Hz), 34.55, 31.25, 16.29 (d, J = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 17.60 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{25}O_3P$ 297.1614; Found 297.1620.

Diethyl (1-([1,1'-biphenyl]-3-yl)vinyl)phosphonate (5h)



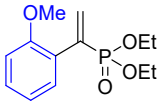
87% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.76 (d, J = 1.8 Hz, 1H), 7.62 – 7.50 (m, 4H), 7.46 – 7.33 (m, 4H), 6.38 (dd, J = 22.0, 1.5 Hz, 1H), 6.22 (dd, J = 45.8, 1.6 Hz, 1H), 4.20 – 4.08 (m, 4H), 1.30 (t, J = 7.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 141.43, 140.85 (d, J = 2.9 Hz), 138.55, 137.23 (d, J = 11.8 Hz), 132.13 (d, J = 8.1 Hz), 128.90 (d, J = 4.0 Hz), 127.53, 127.19, 127.14 (d, J = 1.3 Hz), 126.38, 62.40 (d, J = 5.8 Hz), 16.35 (d, J = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 17.04 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}O_3P$ 317.1301; Found 317.1310.

Diethyl (1-(4-(dimethylamino)phenyl)vinyl)phosphonate (5i)



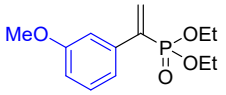
83% yield, dark brown oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.45 (d, *J* = 9.9 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.18 (dd, *J* = 12.0, 1.5 Hz, 1H), 6.06 (dd, *J* = 36.3, 1.5 Hz, 1H), 4.16 – 3.99 (m, 4H), 2.96 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 150.47, 138.69 (d, *J* = 171.8 Hz), 128.32, 128.24, 124.22 (d, *J* = 12.3 Hz), 112.08, 62.12 (d, *J* = 5.5 Hz), 40.44, 16.40 (d, *J* = 6.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 18.56 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}NO_3P$ 284.1410; Found 284.1414.

Diethyl (1-(2-methoxyphenyl)vinyl)phosphonate (5j)



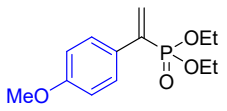
80% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.22 – 7.14 (m, 2H), 6.83 (dd, *J* = 13.3, 7.4 Hz, 2H), 6.35 (dd, *J* = 22.3, 2.0 Hz, 1H), 5.96 (dd, *J* = 46.9, 2.0 Hz, 1H), 3.99 (td, *J* = 7.4, 3.0 Hz, 4H), 3.71 (s, 3H), 1.17 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 156.79 (d, *J* = 5.4 Hz), 136.63 (d, *J* = 177.5 Hz), 134.47 (d, *J* = 7.8 Hz), 130.43 (d, *J* = 4.3 Hz), 129.42, 126.38 (d, *J* = 10.4 Hz), 120.48, 111.07, 62.18 (d, *J* = 5.7 Hz), 55.60, 16.38 (d, *J* = 6.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 16.76 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}O_4P$ 271.1094; Found 271.1104.

Diethyl (1-(3-methoxyphenyl)vinyl)phosphonate (5k)



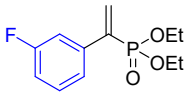
87% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 9.4 Hz, 1H), 6.31 (dd, *J* = 21.9, 1.6 Hz, 1H), 6.14 (dd, *J* = 45.6, 1.6 Hz, 1H), 4.14 – 4.01 (m, 4H), 3.78 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 159.49, 139.61 (d, *J* = 174.8 Hz), 138.09 (d, *J* = 11.8 Hz), 132.00 (d, *J* = 8.0 Hz), 129.48, 119.96 (d, *J* = 5.8 Hz), 113.87, 113.13 (d, *J* = 5.8 Hz), 62.29 (d, *J* = 5.8 Hz), 55.25, 16.34 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ=16.99 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}O_4P$ 271.1094; Found 271.1104.

Diethyl (1-(4-methoxyphenyl)vinyl)phosphonate (5l)



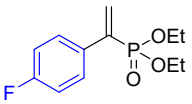
83% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.47 (s, 2H), 6.86 (s, 2H), 6.28 (s, 1H), 6.19 (d, *J* = 9.0 Hz, 1H), 4.09 (dd, *J* = 16.5, 7.6 Hz, 4H), 3.81 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 159.79, 138.98 (d, *J* = 174.0 Hz), 130.30 (d, *J* = 8.1 Hz), 129.10 (d, *J* = 12.0 Hz), 128.78 (d, *J* = 5.8 Hz), 113.92, 62.29 (d, *J* = 5.2 Hz), 16.40 (d, *J* = 6.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 17.65 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}O_4P$ 271.1094; Found 271.1104.

Diethyl (1-(3-fluorophenyl)vinyl)phosphonate (5m)



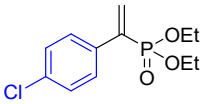
76% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1).^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.30 – 7.16 (m, 3H), 6.96 (t, *J* = 6.7 Hz, 1H), 6.30 (dd, *J* = 21.7, 1.3 Hz, 1H), 6.12 (dd, *J* = 45.3, 1.3 Hz, 1H), 4.12 – 3.97 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 162.68 (d, *J* = 245.9 Hz), 140.10 (d, *J* = 2.1 Hz), 138.87 (dd, *J* = 12.1, 7.9 Hz), 137.76 (d, *J* = 2.3 Hz), 132.59 (d, *J* = 7.7 Hz), 130.03 (d, *J* = 8.3 Hz), 123.28 (dd, *J* = 5.8, 3.0 Hz), 115.26 (d, *J* = 21.3 Hz), 114.74 (d, *J* = 5.7 Hz), 114.44 (d, *J* = 5.7 Hz), 62.44 (d, *J* = 5.7 Hz), 16.34 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 16.34 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ= -112.84 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}FO_3P$ 259.0894; Found 259.0897.

Diethyl (1-(4-fluorophenyl)vinyl)phosphonate (5n)



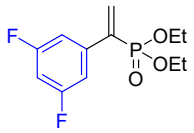
85% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.49 (dd, *J* = 8.8, 6.6 Hz, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 6.28 (dd, *J* = 21.9, 1.3 Hz, 1H), 6.09 (dd, *J* = 45.5, 1.4 Hz, 1H), 4.14 – 4.02 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ= 164.50, 161.21, 138.81 (d, *J* = 175.7 Hz), 132.89, 132.73, 131.61 (d, *J* = 8.0 Hz), 129.33 (dd, *J* = 8.1, 5.7 Hz), 115.45 (d, *J* = 21.6 Hz), 62.38 (d, *J* = 5.8 Hz), 16.34 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 16.78 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ= -113.62 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}FO_3P$ 259.0894; Found 259.0897.

Diethyl (1-(4-chlorophenyl)vinyl)phosphonate (5o)



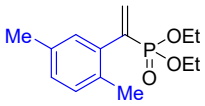
75% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.40 (d, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.26 (dd, *J* = 21.9, 1.3 Hz, 1H), 6.08 (dd, *J* = 45.4, 1.3 Hz, 1H), 4.10 – 3.97 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 138.89 (d, *J* = 175.9 Hz), 135.26 (d, *J* = 12.0 Hz), 134.47, 132.06 (d, *J* = 7.8 Hz), 128.93 (d, *J* = 5.8 Hz), 128.76, 62.47 (d, *J* = 5.7 Hz), 16.42 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 16.52 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}ClO_3P$ 275.0593; Found 275.0607.

Diethyl (1-(3,5-difluorophenyl)vinyl)phosphonate (5p)



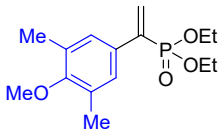
70% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.06 (d, *J* = 7.4 Hz, 2H), 6.79 (s, 1H), 6.38 (dd, *J* = 21.7, 1.2 Hz, 1H), 6.18 (dd, *J* = 44.6, 1.2 Hz, 1H), 4.12 (q, *J* = 7.6 Hz, 4H), 1.30 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 164.55 (d, *J* = 13.0 Hz), 161.26 (d, *J* = 12.9 Hz), 140.18 – 139.45 (m), 137.17, 133.29 (d, *J* = 7.6 Hz), 110.86 (d, *J* = 5.7 Hz), 110.69 (d, *J* = 3.5 Hz), 110.52 (d, *J* = 5.8 Hz), 103.78 (t, *J* = 25.4 Hz), 62.62 (d, *J* = 5.8 Hz), 16.37 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 15.58 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ= -109.45 (t, *J* = 8.4 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}F_2O_3P$ 277.0800; Found 277.0805.

Diethyl (1-(2,5-dimethylphenyl)vinyl)phosphonate (5q)



78% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.08 (d, *J* = 7.7 Hz, 1H), 7.00 (dd, *J* = 11.3, 3.3 Hz, 2H), 6.40 (dd, *J* = 22.5, 2.0 Hz, 1H), 5.81 (dd, *J* = 47.8, 2.0 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 4H), 2.27 (d, *J* = 15.0 Hz, 6H), 1.27 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 16.3 (d, *J*= 6.75 Hz), 19.5, 20.9, 62.3 (d, *J*= 6.0 Hz), 128.6, 129.7 (d, *J*=3.75 Hz), 130.2, 132.8 (d, *J*=9.0 Hz), 134.7, 136.4 (d, *J*= 9.75 Hz) ,140.1 (d, *J*=174.8 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 16.11 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}O_3P$ 269.1301; Found 269.1310.

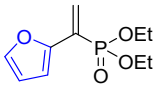
Diethyl (1-(4-methoxy-3,5-dimethylphenyl)vinyl)phosphonate (5r)



77% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1).^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.16 (s, 2H),

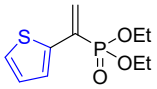
6.22 (dd, J = 21.9, 1.6 Hz, 1H), 6.07 (dd, J = 45.9, 1.6 Hz, 1H), 4.08 (q, J = 7.0 Hz, 4H), 3.70 (s, 3H), 2.26 (s, 6H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 157.25 (d, J = 1.4 Hz), 139.21 (d, J = 173.8 Hz), 132.64 (d, J = 10.5 Hz), 132.13 (d, J = 12.1 Hz), 131.48 (d, J = 16.5 Hz), 130.93, 130.85, 128.00 (d, J = 5.9 Hz), 62.25 (d, J = 5.7 Hz), 59.71, 16.34 (d, J = 6.1 Hz), 16.25. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 17.42 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{23}O_4P$ 299.1407; Found 299.1414.

Diethyl (1-(furan-2-yl)vinyl)phosphonate (5s)



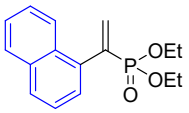
80% yield, brown oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.39 (s, 1H), δ= 6.64 (s, 1H), δ= 6.50 – 6.31 (m, 2H), δ= 6.14 (d, J = 24.0 Hz, 1H), δ= 4.11 (s, 4H), δ= 1.31 (t, J = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 149.59 (d, J = 26.2 Hz), 142.90, 129.52, 126.72 (d, J = 4.0 Hz), 111.77, 110.68, 62.48 (d, J = 5.3 Hz), 16.39 (d, J = 6.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 15.40 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}O_4P$ 231.0781; Found 231.0784.

Diethyl (1-(thiophen-2-yl)vinyl)phosphonate (5t)



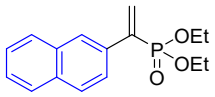
75% yield, dark brown oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.33 (s, 1H), 7.23 (d, J = 5.1 Hz, 1H), 6.99 (d, J = 8.8 Hz, 1H), 6.33 – 6.12 (m, 2H), 4.23 – 4.01 (m, 4H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 138.99 (d, J = 16.8 Hz), 132.59 (d, J = 176.6 Hz), 129.23 (d, J = 7.2 Hz), 127.86, 127.44 (d, J = 3.3 Hz), 125.71, 62.50 (d, J = 5.4 Hz), 16.37 (d, J = 6.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ =15.52 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}O_3PS$ 247.0552; Found 247.0553.

Diethyl (1-(naphthalen-1-yl)vinyl)phosphonate (5v)



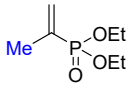
75% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.74 (d, J = 7.2 Hz, 2H), 7.59 – 7.47 (m, 5H), 6.37 (dd, J = 18.9, 17.3 Hz, 2H), 4.19 (p, J = 7.2 Hz, 4H), 1.39 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 171.31 (d, J = 3.8 Hz), 140.52, 139.6 (d, J = 121.5 Hz), 129.87, 129.25 – 128.79 (m), 128.33, 128.02, 126.60 (d, J = 5.2 Hz), 123.51 – 122.24 (m), 60.54 (d, J = 1.9 Hz), 21.19 (d, J = 2.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 18.90 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}O_3P$ 291.1145; Found 291.1151.

Diethyl (1-(naphthalen-2-yl)vinyl)phosphonate (5w)



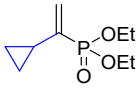
77% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 8.04 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 3H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.47 (m, 2H), 6.43 (dd, *J* = 22.0, 1.5 Hz, 1H), 6.30 (dd, *J* = 45.7, 1.5 Hz, 1H), 4.20 – 4.10 (m, 4H), 1.30 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 139.73 (d, *J* = 174.6 Hz), 134.12 (d, *J* = 11.7 Hz), 133.21 (d, *J* = 12.1 Hz), 132.23 (d, *J* = 8.0 Hz), 128.53, 128.20, 127.70, 126.97 (d, *J* = 6.1 Hz), 126.49 (d, *J* = 5.8 Hz), 125.28 (d, *J* = 5.9 Hz), 62.48 (d, *J* = 5.6 Hz), 16.44 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 16.42 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}O_3P$ 291.1145; Found 291.1151.

Diethyl prop-1-en-2-ylphosphonate (5x)



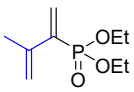
86% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.96 (d, *J* = 22.2 Hz, 1H), 5.75 (d, *J* = 48.2 Hz, 1H), 4.09 (d, *J* = 7.2 Hz, 4H), 1.93 (d, *J* = 14.0 Hz, 3H), 1.31 (d, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 135.36, 125.17, 32.34, 29.84, 26.54, 23.58. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 19.58 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_{15}O_3P$ 179.0832; Found 179.0840.

Diethyl (1-cyclopropylvinyl) phosphonite (5y)



78% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.90 (dd, *J* = 22.3, 1.3 Hz, 1H), 5.55 (d, *J* = 47.8 Hz, 1H), 4.09 (dq, *J* = 7.0, 3.7 Hz, 4H), 1.59 – 1.48 (m, 1H), 1.36 – 1.31 (m, 6H), 0.79 (dd, *J* = 8.3, 2.2 Hz, 2H), 0.57 (dd, *J* = 5.2, 2.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 141.13 (d, *J* = 173.8 Hz), 125.60, 62.04 (d, *J* = 5.6 Hz), 16.49 (d, *J* = 6.4 Hz), 12.64 (d, *J* = 15.5 Hz), 7.51 (d, *J* = 4.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 19.17 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{17}O_2P$ 205.0988; Found 205.0989.

Diethyl (3-methylbuta-1,3-dien-2-yl) phosphonate (5z)

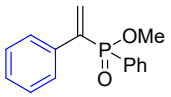


78% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 2:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 6.22 (d, *J* =

22.3 Hz, 1H), 5.99 (d, J = 46.1 Hz, 1H), 5.52 (s, 1H), 5.20 (s, 1H), 4.17 – 4.02 (m, 4H), 1.95 (s, 3H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 139.85 (d, J = 125.3 Hz), 138.81, 138.36, 130.59 (d, J = 7.7 Hz), 118.35 (d, J = 4.4 Hz), 62.15 (d, J = 5.5 Hz), 21.84 (d, J = 8.4 Hz), 16.44 (d, J = 6.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 17.93ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{17}O_3P$ 205.0988; Found 205.0988.

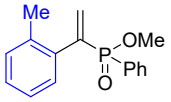
3.2 Characterizations of α-substituted vinyl phosphinates (6a-6t)

Methyl phenyl(1-phenylvinyl)phosphinate (6a)



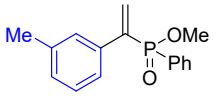
84% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.71 – 7.60 (m, 2H), 7.47 – 7.29 (m, 5H), 7.21 (d, J = 3.0 Hz, 3H), 6.21 (dd, J = 20.1, 1.5 Hz, 1H), 6.07 (dd, J = 41.0, 1.5 Hz, 1H), 3.68 (d, J = 11.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 142.82 (d, J = 124.9 Hz), 137.12 (d, J = 11.6 Hz), 132.43 (d, J = 2.8 Hz), 132.02 (d, J = 10.0 Hz), 131.82, 130.78, 128.98, 128.55 (d, J = 13.2 Hz), 128.27 (d, J = 1.4 Hz), 127.96 (d, J = 4.9 Hz), 51.64 (d, J = 6.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 32.74 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}O_2P$ 259.0882; Found 259.0886.

Methyl phenyl(1-(m-tolyl)vinyl)phosphinate (6b)



83% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.33 (m, 5H), 6.97 (d, J = 4.7 Hz, 4H), 6.42 (dd, J = 20.6, 1.9 Hz, 1H), 5.84 (dd, J = 42.3, 1.9 Hz, 1H), 3.68 (d, J = 11.1 Hz, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 143.03 (d, J = 125.3 Hz), 136.46 (d, J = 2.5 Hz), 136.36 (d, J = 2.7 Hz), 132.81 (d, J = 8.8 Hz), 132.41 (d, J = 4.0 Hz), 132.25, 130.17, 130.09, 129.43 (d, J = 3.2 Hz), 128.38 (d, J = 12.7 Hz), 127.91 (d, J = 2.1 Hz), 125.24, 51.51 (d, J = 6.3 Hz), 19.70. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 31.51 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O_2P$ 273.1039; Found 273.1042.

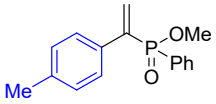
Methyl phenyl(1-(m-tolyl)vinyl)phosphinate (6c)



85% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.81 – 7.64 (m, 2H), 7.56 – 7.36 (m, 3H), 7.28 – 7.03 (m, 4H), 6.46 – 5.94 (m, 2H), 3.74 (d, J = 11.1 Hz, 3H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 142.90 (d, J = 124.9 Hz), 138.06, 137.07 (d, J = 11.5 Hz), 132.40 (d, J = 2.8 Hz), 132.07 (d, J = 10.1 Hz), 131.68 (d, J = 8.6 Hz), 130.85, 129.05, 128.63 (d, J = 3.4 Hz), 128.37 (d, J = 9.6 Hz), 125.06 (d, J =

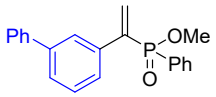
4.8 Hz), 51.63 (d, J = 6.2 Hz), 21.50. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 32.98 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O_2P$ 273.1039; Found 273.1042.

Methyl phenyl(1-(p-tolyl)vinyl)phosphinate (6d)



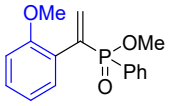
79% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.78 – 7.66 (m, 2H), 7.48 (d, J = 9.0 Hz, 1H), 7.40 (d, J = 3.6 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.5 Hz, 2H), 6.28 – 6.03 (m, 2H), 3.73 (d, J = 11.0 Hz, 3H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 142.45 (d, J = 124.9 Hz), 138.10 (d, J = 1.4 Hz), 134.10 (d, J = 11.8 Hz), 132.32 (d, J = 2.8 Hz), 131.93 (d, J = 10.0 Hz), 131.20 (d, J = 8.8 Hz), 130.88, 129.13, 128.48 (d, J = 13.1 Hz), 127.73 (d, J = 5.0 Hz), 51.55 (d, J = 6.1 Hz), 21.19. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 33.06 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O_2P$ 273.1039; Found 273.1042.

Methyl phenyl(1-([1,1'-biphenyl]-3-yl)vinyl)phosphinate (6e)



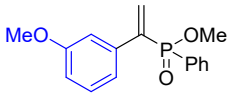
73% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.79 – 7.71 (m, 2H), 7.58 – 7.48 (m, 5H), 7.46 – 7.32 (m, 7H), 6.37 – 6.08 (m, 2H), 3.77 (d, J = 11.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 142.87 (d, J = 124.9 Hz), 141.35, 140.79, 137.65 (d, J = 11.7 Hz), 132.51 (d, J = 2.8 Hz), 132.11 (d, J = 10.0 Hz), 128.89, 128.64 (d, J = 13.1 Hz), 127.57, 127.23, 127.06, 126.91 (d, J = 4.7 Hz), 126.80 (d, J = 5.1 Hz), 51.71 (d, J = 6.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 32.58 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}O_2P$ 335.1195; Found 335.1197.

Methyl phenyl(1-(2-methoxyphenyl)vinyl)phosphinate (6f)



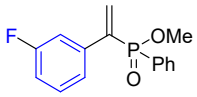
80% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.72 – 7.64 (m, 2H), 7.49 (d, J = 9.0 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.25 (d, J = 6.4 Hz, 1H), 7.10 (d, J = 9.3 Hz, 1H), 6.89 (t, J = 7.0 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 6.46 (s, 1H), 6.01 (d, J = 1.8 Hz, 1H), 3.74 (d, J = 11.1 Hz, 3H), 3.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 156.64 (d, J = 3.8 Hz), 140.30 (d, J = 126.3 Hz), 133.58 (d, J = 7.9 Hz), 131.97 (d, J = 3.0 Hz), 131.86, 130.50 (d, J = 4.4 Hz), 129.76, 129.54 (d, J = 1.9 Hz), 128.09 (d, J = 13.1 Hz), 126.61 (d, J = 10.2 Hz), 120.43, 110.76, 55.03, 51.53 (d, J = 6.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 31.91 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O_3P$ 289.0988; Found 289.0993.

Methyl phenyl(1-(3-methoxyphenyl)vinyl)phosphinate (6g)



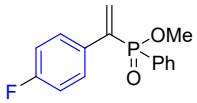
83% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.76 – 7.67 (m, 2H), 7.51 – 7.38 (m, 3H), 7.18 (t, *J* = 7.9 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.26 (dd, *J* = 19.9, 1.5 Hz, 1H), 6.21 – 6.05 (m, 1H), 3.73 (d, *J* = 11.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 159.40, 142.61 (d, *J* = 124.8 Hz), 138.42 (d, *J* = 11.8 Hz), 132.41 (d, *J* = 2.9 Hz), 132.05, 131.91, 130.78, 129.44, 128.99, 128.53 (d, *J* = 13.2 Hz), 120.38 (d, *J* = 4.9 Hz), 113.97 (d, *J* = 1.3 Hz), 113.40 (d, *J* = 5.0 Hz), 55.22, 51.60 (d, *J* = 6.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 32.50 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O_3P$ 289.0988; Found 289.0993.

Methyl phenyl(1-(3-fluorophenyl)vinyl)phosphinate (6h)



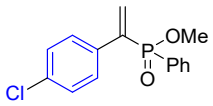
72% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.74 – 7.65 (m, 2H), 7.52 – 7.46 (m, 1H), 7.39 (d, *J* = 1.4 Hz, 2H), 7.23 (dd, *J* = 8.9, 3.0 Hz, 1H), 7.10 (ddd, *J* = 10.0, 2.5, 1.3 Hz, 1H), 6.96 (s, 1H), 6.25 (d, *J* = 19.9 Hz, 1H), 6.12 (d, *J* = 39.1 Hz, 1H), 3.73 (d, *J* = 11.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 164.21, 160.95, 141.95 (d, *J* = 128.0 Hz), 139.18 (dd, *J* = 12.0, 7.9 Hz), 132.61 (d, *J* = 2.8 Hz), 132.40 (d, *J* = 8.2 Hz), 131.99 (d, *J* = 10.0 Hz), 130.39, 129.98 (d, *J* = 8.4 Hz), 128.64 (d, *J* = 13.1 Hz), 123.75 (dd, *J* = 4.8, 3.0 Hz), 115.34, 115.17, 115.13 – 115.04 (m), 114.84 (d, *J* = 5.0 Hz), 51.70 (d, *J* = 6.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 33.34 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ= -112.75. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}FO_2P$ 277.0788; Found 277.0788.

Methyl phenyl(1-(4-fluorophenyl)vinyl)phosphinate (6i)



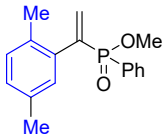
70% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.67 (d, *J* = 12.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 15.7 Hz, 4H), 6.95 (s, 2H), 6.17 (s, 1H), 6.14 (s, 1H), 3.73 (d, *J* = 11.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 161.12, 141.84 (d, *J* = 126.0 Hz), 133.12 (d, *J* = 3.4 Hz), 132.97 (d, *J* = 3.3 Hz), 132.51 (d, *J* = 2.9 Hz), 131.95 (d, *J* = 9.9 Hz), 131.54 (d, *J* = 8.3 Hz), 130.43, 129.72 (dd, *J* = 8.2, 4.9 Hz), 128.58 (d, *J* = 13.2 Hz), 115.38 (d, *J* = 21.5 Hz), 51.63 (d, *J* = 6.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 32.55 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ= -113.66. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}FO_2P$ 277.0788; Found 277.0788.

Methyl phenyl(1-(4-chlorophenyl)vinyl)phosphinate (6j)



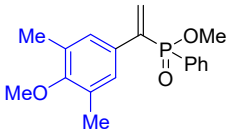
79% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.64 – 7.55 (m, 2H), 7.40 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.33 (dd, *J* = 7.5, 3.6 Hz, 2H), 7.26 – 7.11 (m, 4H), 6.13 (dd, *J* = 20.0, 1.3 Hz, 1H), 6.00 (dd, *J* = 40.7, 1.3 Hz, 1H), 3.64 (d, *J* = 11.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 141.90 (d, *J* = 126.0 Hz), 135.55 (d, *J* = 11.9 Hz), 134.39 (d, *J* = 1.6 Hz), 133.18 (d, *J* = 11.0 Hz), 132.07, 131.89 (d, *J* = 6.5 Hz), 130.40, 129.31 (d, *J* = 4.9 Hz), 128.71 (d, *J* = 5.4 Hz), 128.57, 51.71 (d, *J* = 6.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 32.41 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}ClO_2P$ 293.0493; Found 293.0499.

Methyl phenyl(1-(2,5-dimethylphenyl)vinyl)phosphinate (6k)



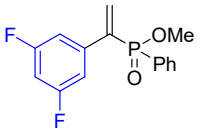
80% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.62 – 7.47 (m, 3H), 7.42 – 7.34 (m, 2H), 6.99 (s, 2H), 6.77 (s, 1H), 6.39 (dd, *J* = 20.6, 1.9 Hz, 1H), 5.83 (dd, *J* = 42.5, 1.9 Hz, 1H), 3.70 (d, *J* = 11.1 Hz, 3H), 2.24 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 143.25 (d, *J* = 125.2 Hz), 136.31 (d, *J* = 9.6 Hz), 134.66 (d, *J* = 1.8 Hz), 133.26 (d, *J* = 4.6 Hz), 132.72 (d, *J* = 9.0 Hz), 132.53, 132.41, 130.27, 130.15 (d, *J* = 3.2 Hz), 130.09, 128.69 (d, *J* = 2.2 Hz), 128.39 (d, *J* = 12.8 Hz), 51.59 (d, *J* = 6.3 Hz), 20.95, 19.26. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 31.69 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O_3P$ 289.0988; Found 289.0998.

Methyl phenyl(1-(4-methoxy-3,5-dimethylphenyl)vinyl)phosphinate (6l)



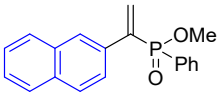
75% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.73 (dd, *J* = 12.1, 6.8 Hz, 2H), 7.54 – 7.39 (m, 3H), 7.02 (s, 2H), 6.21 – 5.88 (m, 2H), 3.76 – 3.66 (m, 6H), 2.21 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 157.16, 142.29 (d, *J* = 125.1 Hz), 132.52, 132.34 (d, *J* = 3.1 Hz), 132.04 (d, *J* = 10.0 Hz), 130.95, 130.81 (d, *J* = 4.1 Hz), 129.07, 128.49 (d, *J* = 9.8 Hz), 128.37 (d, *J* = 1.8 Hz), 59.67, 51.57 (d, *J* = 6.2 Hz), 16.16. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 33.34 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}O_3P$ 317.1301; Found 317.1304.

Methyl phenyl(1-(3,5-difluorophenyl)vinyl)phosphinate (6m)



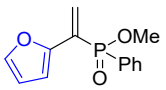
75% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.75 – 7.67 (m, 2H), 7.58 – 7.50 (m, 1H), 7.45 (dd, *J* = 7.5, 3.6 Hz, 2H), 6.96 (d, *J* = 6.1 Hz, 2H), 6.77 – 6.69 (m, 1H), 6.27 (d, *J* = 18.6 Hz, 1H), 6.14 (d, *J* = 39.8 Hz, 1H), 3.76 (d, *J* = 11.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 164.47 (d, *J* = 13.0 Hz), 161.17 (d, *J* = 12.9 Hz), 141.39 (d, *J* = 127.1 Hz), 132.96 (d, *J* = 7.9 Hz), 132.84 (d, *J* = 2.9 Hz), 132.05 (d, *J* = 10.1 Hz), 130.06, 128.80 (d, *J* = 13.2 Hz), 128.25, 111.40 – 110.90 (m), 103.79 (t, *J* = 25.6 Hz), 51.85 (d, *J* = 6.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 31.73 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ= -109.35 (t, *J* = 8.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}F_2O_2P$ 295.0694; Found 295.0699.

Methyl phenyl(1-(naphthalen-2-yl)vinyl)phosphinate (6n)



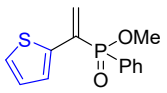
73% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 6:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.90 – 7.34 (m, 12H), 6.45 – 6.10 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 142.82 (d, *J* = 125.1 Hz), 134.55 (d, *J* = 11.6 Hz), 133.13 (d, *J* = 13.8 Hz), 132.50 (d, *J* = 2.8 Hz), 132.07 (d, *J* = 10.1 Hz), 130.82, 129.03, 128.71, 128.49 (d, *J* = 6.7 Hz), 128.14, 127.68, 127.31 (d, *J* = 5.4 Hz), 126.44 (d, *J* = 5.6 Hz), 125.76 (d, *J* = 4.8 Hz), 51.75 (d, *J* = 6.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 32.79 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}O_2P$ 309.1039; Found 309.1042.

Methyl (1-(furan-2-yl)vinyl)(phenyl)phosphinate (6o)



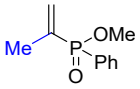
70% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.86 – 7.77 (m, 2H), 7.55 – 7.49 (m, 1H), 7.44 (ddd, *J* = 8.6, 6.4, 3.6 Hz, 2H), 7.36 (s, 1H), 6.58 (d, *J* = 3.4 Hz, 1H), 6.47 (dd, *J* = 39.0, 1.4 Hz, 1H), 6.34 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.15 (dd, *J* = 20.1, 1.3 Hz, 1H), 3.79 (d, *J* = 11.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 149.43 (d, *J* = 25.2 Hz), 142.78, 132.49 (d, *J* = 2.9 Hz), 131.71, 131.46 (d, *J* = 10.4 Hz), 131.10, 129.62 (d, *J* = 57.2 Hz), 128.56 (d, *J* = 13.5 Hz), 126.69 (d, *J* = 4.0 Hz), 111.67, 110.70, 51.72 (d, *J* = 6.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 30.55ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}O_3P$ 249.0675; Found 249.0675.

Methyl phenyl(1-(thiophen-2-yl)vinyl)phosphinate (6p)



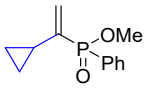
75% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 5:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.83 – 7.73 (m, 2H), 7.55 – 7.48 (m, 1H), 7.46 – 7.38 (m, 2H), 7.26 – 7.22 (m, 1H), 7.19 (d, *J* = 5.2 Hz, 1H), 6.92 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.37 – 6.14 (m, 2H), 3.80 (d, *J* = 11.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 138.94 (d, *J* = 16.3 Hz), 135.26 (d, *J* = 125.3 Hz), 132.58 (d, *J* = 2.9 Hz), 131.70 (d, *J* = 10.4 Hz), 130.91, 129.59 (d, *J* = 7.3 Hz), 129.07, 128.65 (d, *J* = 13.4 Hz), 127.87, 127.46 (d, *J* = 3.5 Hz), 125.89, 51.81 (d, *J* = 6.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 31.23ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}O_2PS$ 265.0447; Found 265.0448.

Methyl phenyl(prop-1-en-2-yl)phosphinate (6r)



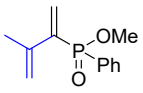
77% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.80 – 7.72 (m, 2H), 7.55 – 7.43 (m, 3H), 5.94 (d, *J* = 20.8 Hz, 1H), 5.78 (d, *J* = 44.5 Hz, 1H), 3.70 (d, *J* = 11.0 Hz, 3H), 1.87 (d, *J* = 13.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 137.61 (d, *J* = 125.0 Hz), 132.43 (d, *J* = 2.8 Hz), 131.91 (d, *J* = 9.9 Hz), 130.42, 130.13 (d, *J* = 9.3 Hz), 128.67 (d, *J* = 12.8 Hz), 51.41 (d, *J* = 6.1 Hz), 18.75. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 34.69 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{13}O_2P$ 197.0726; Found 197.0732.

Methyl phenyl(1-cyclopropylvinyl)phosphinate (6s)



70% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 4:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.85 – 7.77 (m, 2H), 7.55 – 7.43 (m, 3H), 5.94 (dd, *J* = 20.2, 1.1 Hz, 1H), 5.58 (d, *J* = 42.2 Hz, 1H), 3.74 (d, *J* = 11.0 Hz, 3H), 1.48 (d, *J* = 6.5 Hz, 1H), 0.79 – 0.59 (m, 2H), 0.56 – 0.34 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 143.85 (d, *J* = 124.8 Hz), 132.36 (d, *J* = 2.8 Hz), 131.93 (d, *J* = 10.2 Hz), 131.19, 129.43, 128.58 (d, *J* = 12.9 Hz), 125.36 (d, *J* = 9.9 Hz), 51.49 (d, *J* = 6.1 Hz), 12.40 (d, *J* = 16.9 Hz), 7.76 (d, *J* = 4.4 Hz), 7.50 (d, *J* = 4.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 34.29 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}O_2P$ 223.0882; Found 223.0886.

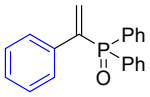
Methyl (3-methylbuta-1,3-dien-2-yl)(phenyl)phosphinate (6t)



52% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 2:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.81 – 7.73 (m, 2H), 7.54 – 7.42 (m, 3H), 6.21 – 5.96 (m, 2H), 5.26 (d, *J* = 91.5 Hz, 2H), 3.74 (d, *J* = 11.1 Hz, 3H), 1.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 142.01 (d, *J* = 122.8 Hz), 139.24 (d, *J* = 11.5 Hz), 132.32 (d, *J* = 2.9 Hz), 131.65 (d, *J* = 10.4 Hz), 130.22 (d, *J* = 7.7 Hz), 129.93, 128.60 (d, *J* = 13.2 Hz), 118.55 (d, *J* = 4.8 Hz), 51.54 (d, *J* = 6.1 Hz), 22.26 (d, *J* = 6.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 33.47ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}O_2P$ 223.0882; Found 223.0883.

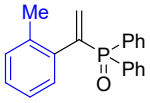
3.3 Characterizations of α-substituted vinyl phosphine oxides (7a-7q)

Diphenyl(1-phenylvinyl)phosphine oxide (7a)



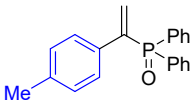
78% yield, white solid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.76 – 7.66 (m, 4H), 7.45 (dtd, *J* = 14.2, 7.1, 2.4 Hz, 9H), 7.24 – 7.22 (m, 2H), 6.25 (dd, *J* = 40.3, 1.1 Hz, 1H), 5.74 (dd, *J* = 19.8, 1.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 144.31 (d, *J* = 92.4 Hz), 137.56 (d, *J* = 10.0 Hz), 132.23 (d, *J* = 7.3 Hz), 132.12, 132.01 (d, *J* = 2.5 Hz), 131.71 (d, *J* = 10.1 Hz), 130.91, 128.64, 128.49 (d, *J* = 1.6 Hz), 128.29, 128.18 (d, *J* = 4.7 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 30.32 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}OP$ 305.1090; Found 305.1096.

Diphenyl(1-(o-tolyl)vinyl)phosphine oxide (7b)



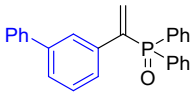
73% yield, white solid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.81 – 7.70 (m, 5H), 7.63 (d, *J* = 5.7 Hz, 2H), 7.53 (s, 3H), 7.22 (d, *J* = 13.1 Hz, 2H), 7.09 (s, 1H), 6.95 (d, *J* = 6.3 Hz, 1H), 6.51 (d, *J* = 19.1 Hz, 1H), 6.19 (d, *J* = 37.5 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 144.31 (d, *J* = 90.0 Hz), 136.94 (d, *J* = 4.2 Hz), 136.71 (d, *J* = 9.5 Hz), 133.52 (d, *J* = 8.0 Hz), 132.16 (d, *J* = 9.5 Hz), 130.42, 129.05 (d, *J* = 3.2 Hz), 128.41 (d, *J* = 11.9 Hz), 127.99 (d, *J* = 1.9 Hz), 125.33 (d, *J* = 1.5 Hz), 20.00. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 26.80 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}OP$ 319.1246; Found 319.1254.

Diphenyl(1-(p-tolyl)vinyl)phosphine oxide (7c)



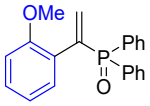
75% yield, white solid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.65 – 7.58 (m, 4H), 7.42 – 7.25 (m, 8H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.13 (d, *J* = 39.5 Hz, 1H), 5.59 (d, *J* = 18.8 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 144.04 (d, *J* = 93.7 Hz), 138.25, 134.62 (d, *J* = 10.2 Hz), 132.10 (d, *J* = 9.7 Hz), 131.52 (d, *J* = 10.2 Hz), 129.26, 128.59 (d, *J* = 12.1 Hz), 128.07 (d, *J* = 4.8 Hz), 21.27. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 30.41 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}OP$ 319.1246; Found 319.1254.

Diphenyl(1-([1,1'-biphenyl]-3-yl)vinyl)phosphine oxide (7d)



70% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.75 – 7.64 (m, 4H), 7.56 (d, *J* = 1.6 Hz, 1H), 7.51 – 7.23 (m, 14H), 6.32 (s, 1H), 5.83 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 144.38 (d, *J* = 92.2 Hz), 141.01 (d, *J* = 46.6 Hz), 138.08 (d, *J* = 10.1 Hz), 132.44 (d, *J* = 9.5 Hz), 132.20, 132.10 (d, *J* = 4.1 Hz), 130.85, 128.90 (d, *J* = 10.7 Hz), 128.65 (d, *J* = 12.1 Hz), 127.52, 127.23 (d, *J* = 4.1 Hz), 127.03 (d, *J* = 5.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 29.90 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}OP$ 381.1403; Found 381.1408.

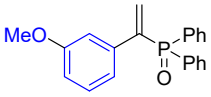
Diphenyl(1-(2-methoxyphenyl)vinyl)phosphine oxide (7e)



63% yield, white solid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.70 (dd, *J* = 11.8, 6.8 Hz, 4H), 7.44 (dd, *J* = 20.7, 7.5 Hz, 6H), 7.23 (d, *J* = 5.7 Hz, 2H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 6.32 – 6.07 (m, 2H), 3.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 156.52 (d, *J* = 3.6 Hz), 142.04 (d, *J* = 93.7 Hz), 134.22 (d, *J* = 8.8 Hz), 133.04, 131.98 (d, *J* = 9.6 Hz), 131.65 (d, *J* = 2.8 Hz), 130.56 (d, *J* = 4.2 Hz), 129.66 (d, *J* = 1.6 Hz), 128.17 (d, *J* = 12.1 Hz), 126.82 (d, *J* = 9.1 Hz), 120.56, 110.68, 54.85.

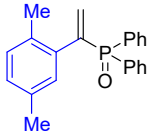
^{31}P NMR (121 MHz, $CDCl_3$) δ= 29.09 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}O_2P$ 335.1195; Found 335.1195.

Diphenyl(1-(3-methoxyphenyl)vinyl)phosphine oxide (7f)



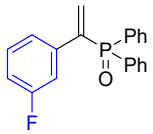
70% yield, white solid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.82 – 7.76 (m, 3H), 7.56 (dd, *J* = 15.2, 6.5 Hz, 7H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.87 (d, *J* = 5.7 Hz, 1H), 6.33 (d, *J* = 39.9 Hz, 1H), 5.88 (d, *J* = 20.8 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 159.45, 144.29 (d, *J* = 91.5 Hz), 139.01 (d, *J* = 10.0 Hz), 132.30 (d, *J* = 8.8 Hz), 132.10 (d, *J* = 9.6 Hz), 131.76 (d, *J* = 10.2 Hz), 130.96, 129.56, 128.61 (d, *J* = 12.1 Hz), 120.75 (d, *J* = 4.7 Hz), 114.35, 113.47 (d, *J* = 4.6 Hz), 55.26. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 29.78 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}O_2P$ 335.1195; Found 335.1195.

Diphenyl(1-(2,5-dimethylphenyl)vinyl)phosphine oxide (7g)



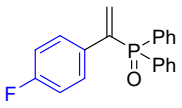
67% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.69 – 7.61 (m, 4H), 7.52 (td, *J* = 7.2, 1.5 Hz, 2H), 7.41 (td, *J* = 7.3, 3.0 Hz, 4H), 6.94 (d, *J* = 4.4 Hz, 2H), 6.62 (s, 1H), 6.40 (dd, *J* = 19.1, 1.7 Hz, 1H), 6.04 (dd, *J* = 39.0, 1.7 Hz, 1H), 2.11 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 144.54 (d, *J* = 89.4 Hz), 136.63 (d, *J* = 9.4 Hz), 134.67 (d, *J* = 1.6 Hz), 133.67 (d, *J* = 4.3 Hz), 133.25 (d, *J* = 8.0 Hz), 132.22 (d, *J* = 9.4 Hz), 131.97 (d, *J* = 2.8 Hz), 131.77, 130.36 (d, *J* = 8.0 Hz), 129.91 (d, *J* = 3.1 Hz), 128.69 (d, *J* = 2.0 Hz), 128.34 (d, *J* = 11.9 Hz), 20.91, 19.54. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 26.66 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}OP$ 333.1403; Found 333.1410.

Diphenyl(1-(3-fluorophenyl)vinyl)phosphine oxide (7h)



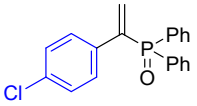
75% yield, white solid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.76 – 7.66 (m, 4H), 7.54 – 7.41 (m, 6H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.16 (m, 2H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 39.7 Hz, 1H), 5.75 (d, *J* = 20.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 162.63 (d, *J* = 246.2 Hz), 132.79 (d, *J* = 9.7 Hz), 132.23 (d, *J* = 2.8 Hz), 132.06 (d, *J* = 9.7 Hz), 130.56, 130.08 (d, *J* = 8.4 Hz), 128.71 (d, *J* = 12.2 Hz), 124.08, 115.42 (d, *J* = 6.8 Hz), 115.24 (d, *J* = 9.8 Hz), 115.04 (d, *J* = 5.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 30.21 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ= -112.48 – -112.59 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FOP$ 323.0996; Found 323.1000.

Diphenyl(1-(4-fluorophenyl)vinyl)phosphine oxide (7i)



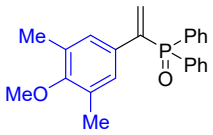
72% yield, white solid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.76 – 7.65 (m, 4H), 7.53 – 7.40 (m, 8H), 6.93 (t, *J* = 8.7 Hz, 2H), 6.20 (d, *J* = 39.3 Hz, 1H), 5.68 (d, *J* = 19.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 162.83 (d, *J* = 247.9 Hz), 143.41 (d, *J* = 92.9 Hz), 133.69 (d, *J* = 3.4 Hz), 133.55 (d, *J* = 3.4 Hz), 132.12 (d, *J* = 3.1 Hz), 131.97, 131.81, 130.72, 130.04 (d, *J* = 4.6 Hz), 129.94 (d, *J* = 4.7 Hz), 128.65 (d, *J* = 12.1 Hz), 115.52 (d, *J* = 21.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 30.49 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ= -113.49 (tdd, *J* = 10.6, 5.3, 1.7 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}FOP$ 323.0996; Found 323.1000.

Diphenyl(1-(4-chlorophenyl)vinyl)phosphine oxide (7j)



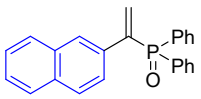
77% yield, white solid. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.80 – 7.67 (m, 4H), 7.48 (d, *J* = 7.5 Hz, 8H), 7.23 (s, 2H), 6.26 (d, *J* = 40.0 Hz, 1H), 5.73 (d, *J* = 20.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 143.35 (d, *J* = 92.8 Hz), 136.01 (d, *J* = 10.0 Hz), 134.43, 132.34, 132.19 (d, *J* = 2.9 Hz), 131.99 (d, *J* = 9.7 Hz), 131.87, 130.49, 129.49 (d, *J* = 4.7 Hz), 128.74 (d, *J* = 1.8 Hz), 128.59. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 30.34 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}ClOP$ 339.0700; Found 339.0702.

Diphenyl(1-(4-methoxy-3,5-dimethylphenyl)vinyl)phosphine oxide (7k)



62% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.74 – 7.67 (m, 4H), 7.50 – 7.43 (m, 6H), 7.08 (s, 2H), 6.17 (d, *J* = 39.5 Hz, 1H), 5.66 (d, *J* = 19.8 Hz, 1H), 3.66 (s, 3H), 2.17 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 171.30, 156.2, 132.15 (d, *J* = 9.7 Hz), 132.00, 131.77 (d, *J* = 10.1 Hz), 130.90, 128.82 (d, *J* = 4.6 Hz), 128.69 (d, *J* = 7.5 Hz), 128.52 (d, *J* = 6.3 Hz), 60.13 (d, *J* = 59.5 Hz), 16.24. ^{31}P NMR (121 MHz, $CDCl_3$) ^{31}P NMR (121 MHz, $CDCl_3$) δ= 30.38 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{23}O_2P$ 363.1508; Found 363.1512.

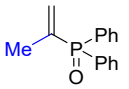
Diphenyl(1-(naphthalen-2-yl)vinyl)phosphine oxide (7l)



65% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 8.01 (s, 1H),

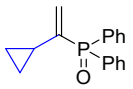
7.75 (dd, J = 11.9, 6.8 Hz, 7H), 7.57 – 7.41 (m, 9H), 6.37 (d, J = 41.2 Hz, 1H), 5.84 (d, J = 19.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 133.12 (d, J = 12.8 Hz), 132.16 (d, J = 8.8 Hz), 128.67 (d, J = 11.3 Hz), 128.24, 127.71 (d, J = 12.1 Hz), 126.41 (d, J = 10.5 Hz), 125.92. ^{31}P NMR (121 MHz, $CDCl_3$) δ= 30.34 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}OP$ 355.1246; Found 355.1251.

Diphenyl(prop-1-en-2-yl)phosphine oxide (7o)



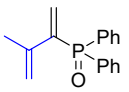
73% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.74 – 7.63 (m, 4H), 7.55 – 7.41 (m, 6H), 5.93 (d, J = 39.7 Hz, 1H), 5.61 (d, J = 18.6 Hz, 1H), 1.99 (d, J = 13.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 139.15 (d, J = 93.1 Hz), 132.02 (d, J = 2.7 Hz), 131.85 (d, J = 9.7 Hz), 131.39, 130.64 (d, J = 9.8 Hz), 130.04, 128.58 (d, J = 12.0 Hz), 19.12 (d, J = 11.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 31.59 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}OP$ 243.0933; Found 243.0937.

Diphenyl(1-cyclopropylvinyl)phosphine oxide (7p)



60% yield, yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 10:1–2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.79 – 7.71 (m, 4H), 7.56 – 7.44 (m, 6H), 5.69 (d, J = 26.7 Hz, 1H), 5.59 (d, J = 5.1 Hz, 1H), 1.59 – 1.51 (m, 1H), 0.76 (dd, J = 8.4, 2.4 Hz, 2H), 0.58 (dd, J = 5.2, 2.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 145.91 (d, J = 98.0 Hz), 132.15 (d, J = 9.8 Hz), 132.00 (d, J = 2.7 Hz), 131.00 (d, J = 7.4 Hz), 128.57 (d, J = 12.0 Hz), 124.74 (d, J = 9.9 Hz), 29.84, 12.97 (d, J = 16.2 Hz), 9.03 (d, J = 3.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 31.34 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}OP$ 269.1090; Found 269.1095.

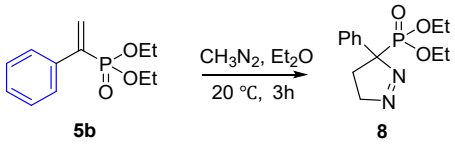
Diphenyl (3-methylbuta-1,3-dien-2-yl) phosphine oxide (7q)



40% yield, pale yellow oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 2:1–1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.70 (dd, J = 11.0, 7.6 Hz, 4H), 7.50 (dd, J = 14.1, 6.1 Hz, 6H), 6.07 (d, J = 42.2 Hz, 1H), 5.53 (s, 1H), 5.42 (d, J = 20.8 Hz, 1H), 5.18 (s, 1H), 1.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ= 144.03 (d, J = 92.2 Hz), 139.46, 132.53, 132.17 – 131.76 (m), 130.23 (d, J = 10.3 Hz), 129.95, 128.64 (d, J = 12.1 Hz), 128.08, 120.35, 116.12, 22.62 (d, J = 52.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 31.25 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}OP$ 269.1090; Found 269.1088.

4. Synthetic transformations of 5b

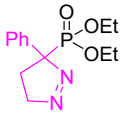
4.1 Method and characterizations of 8



5b **8**

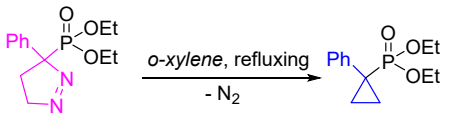
To a solution of **5b** (120 mg, 0.5 mmol) in anhydrous diethyl ether (5 mL) was added 0.1 M solution of diazomethane (9 mL, 1 mmol) in anhydrous ether. The mixture was stirred at 20 °C for 3 h. Volatile components were removed firstly in a rotary evaporator and then under high vacuum, giving compound **8** as a pale yellow oil.

Diethyl (3-phenyl-4,5-dihydro-3H-pyrazol-3-yl)phosphonate (8)



83% yield, pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.59 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.33 – 7.20 (m, 3H), 4.78 – 4.62 (m, 1H), 4.57 – 4.41 (m, 1H), 4.03 – 3.71 (m, 4H), 2.68 – 2.53 (m, 1H), 1.85 – 1.64 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.09 – 1.03 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 137.86 (d, *J* = 5.3 Hz), 128.37 (d, *J* = 2.9 Hz), 127.89 (d, *J* = 3.2 Hz), 127.25 (d, *J* = 4.9 Hz), 99.31, 97.35, 64.01 (d, *J* = 7.4 Hz), 63.18 (d, *J* = 7.4 Hz), 27.69 (d, *J* = 1.5 Hz), 16.28 (d, *J* = 1.7 Hz), 16.20 (d, *J* = 1.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 19.10 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}N_2O_3P$ 283.1206; Found 283.1208.

4.2 Method and characterizations of 9

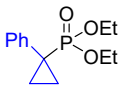


8 **9**

A solution of compound **8** (201 mg, 0.715 mmol) in anhydrous *o*-xylene (16 mL) was refluxed for 3 h. After removal of the solvent, the residue was dissolved in acetone (5 mL) and then a saturated solution of $KMnO_4$ (25 mL) in aqueous acetone was added dropwise with stirring for 7 h. Upon completion, the excess of $KMnO_4$ was decomposed by adding saturated aqueous Na_2SO_3 until the violet color vanished. The brown precipitate that formed was filtered off and washed with acetone. The combined filtrates were concentrated and the product was extracted with diethyl ether (3×20 mL). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced

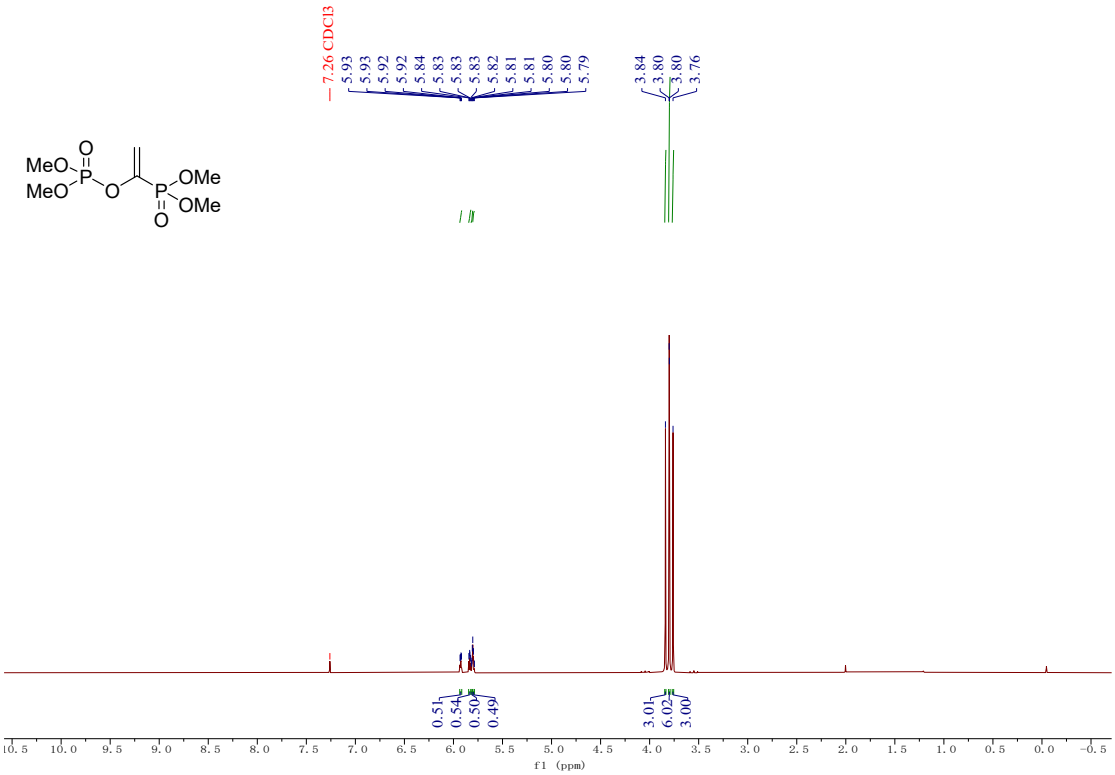
pressure. The crude product was purified by column chromatography (hexane/ethyl acetate = 15:1 - 10:1) to give the desired product **9**.

Diethyl (1-phenylcyclopropyl)phosphonate (9)

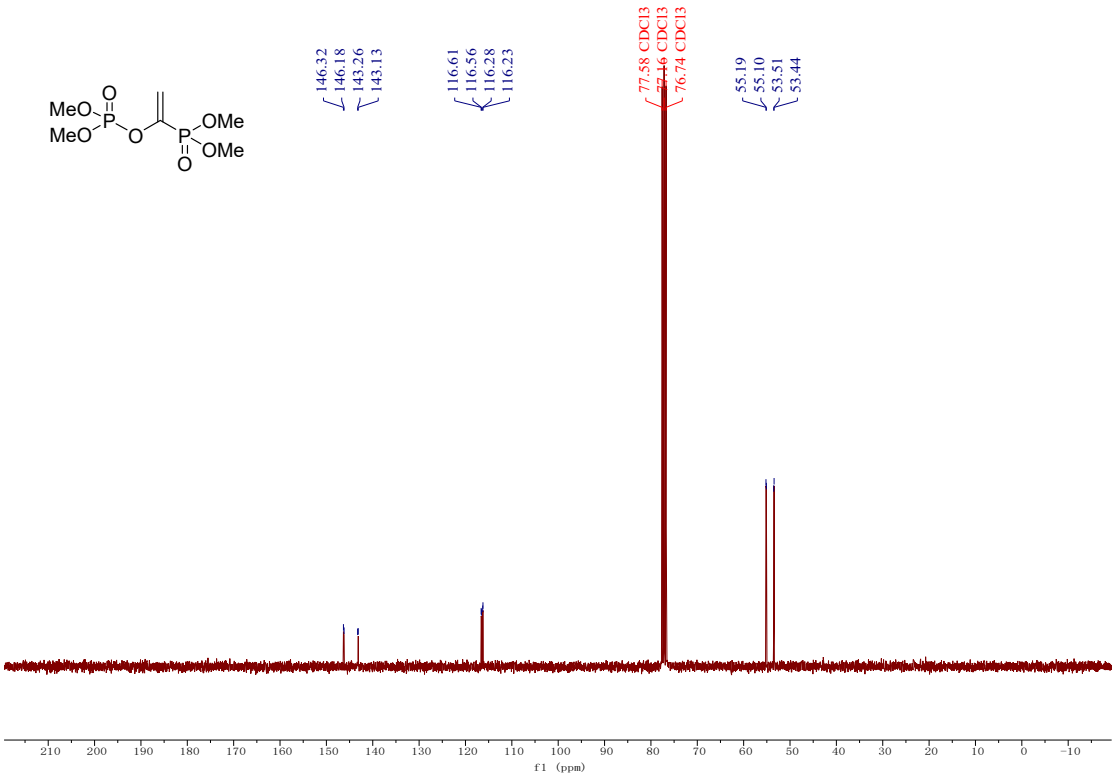


70% yield, colorless oil. The residue was purified by silica gel chromatography with hexane and EtOAc (gradually 15:1–10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.37 (d, *J* = 7.7 Hz, 2H), 7.21 (dd, *J* = 10.7, 7.4 Hz, 3H), 4.06 – 3.92 (m, 4H), 1.49 – 1.39 (m, 2H), 1.20 (t, *J* = 7.4 Hz, 6H), 1.05 – 0.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 138.78 (d, *J* = 2.4 Hz), 131.14 (d, *J* = 3.8 Hz), 128.19 (d, *J* = 2.2 Hz), 127.26 (d, *J* = 2.7 Hz), 62.31 (d, *J* = 6.5 Hz), 22.54, 20.02, 16.41 (d, *J* = 6.1 Hz), 11.50 (d, *J* = 2.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ= 28.13 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}O_3P$ 255.1145; Found 255.1153.

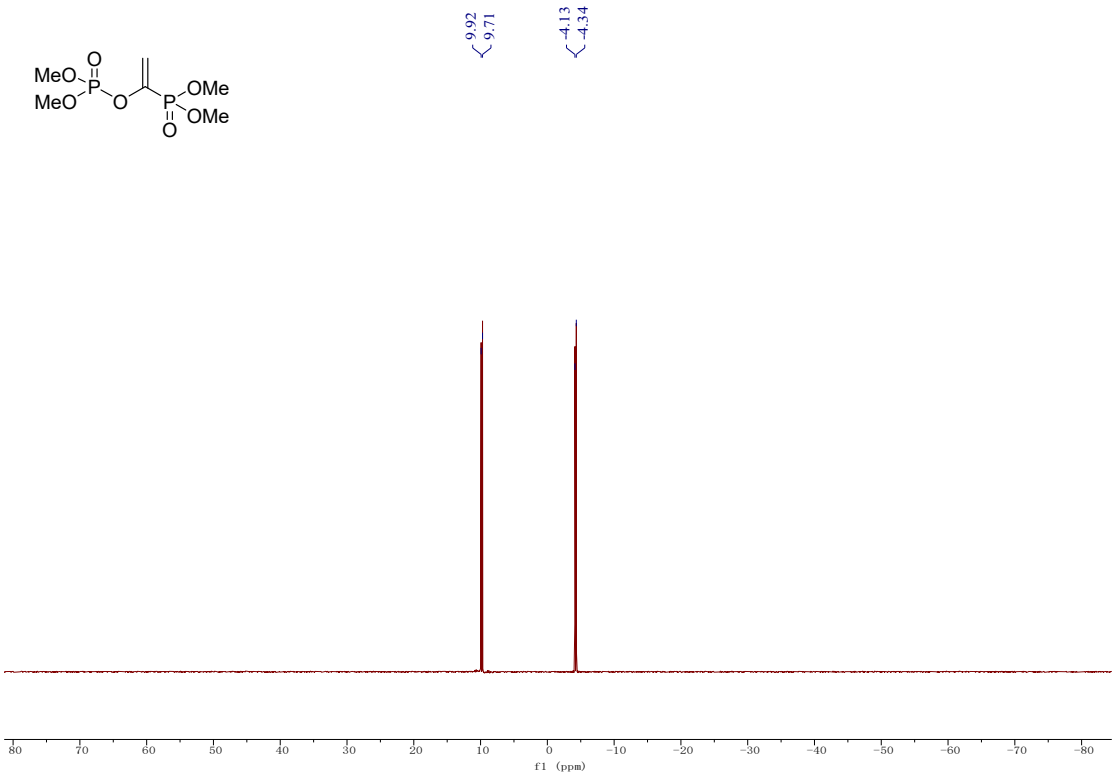
5. Spectra of products 3, 5-9



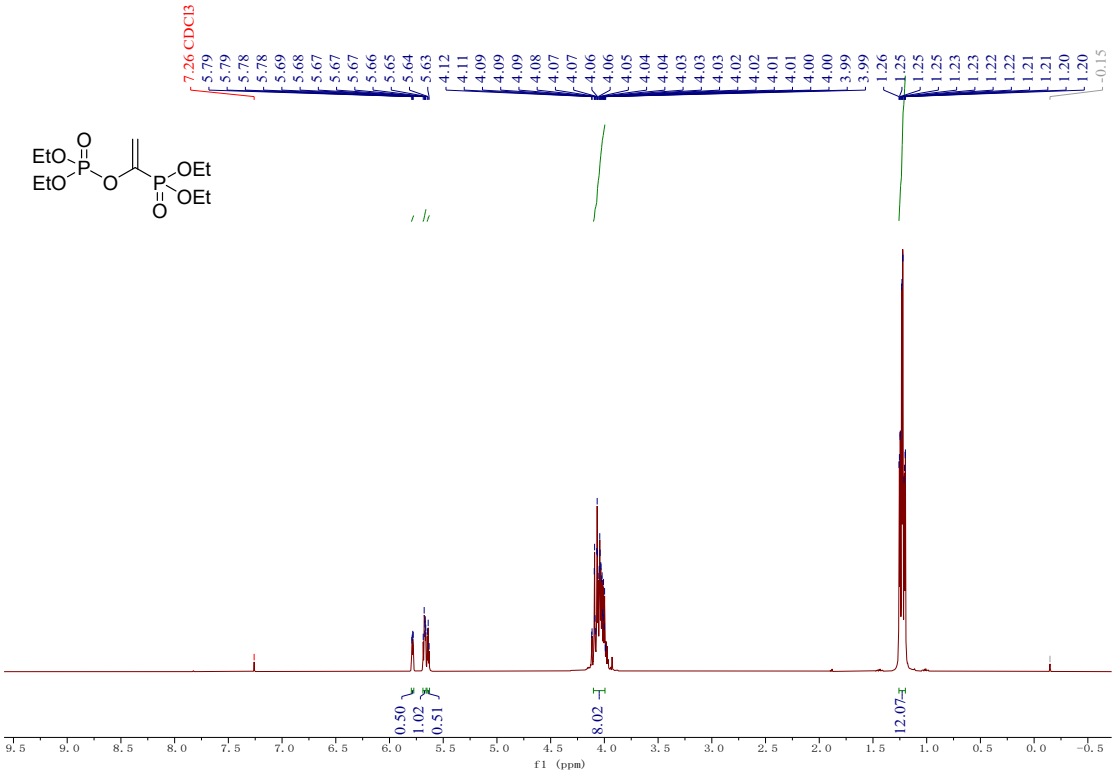
^{1}H NMR (300 MHz, $CDCl_3$) of **3a**



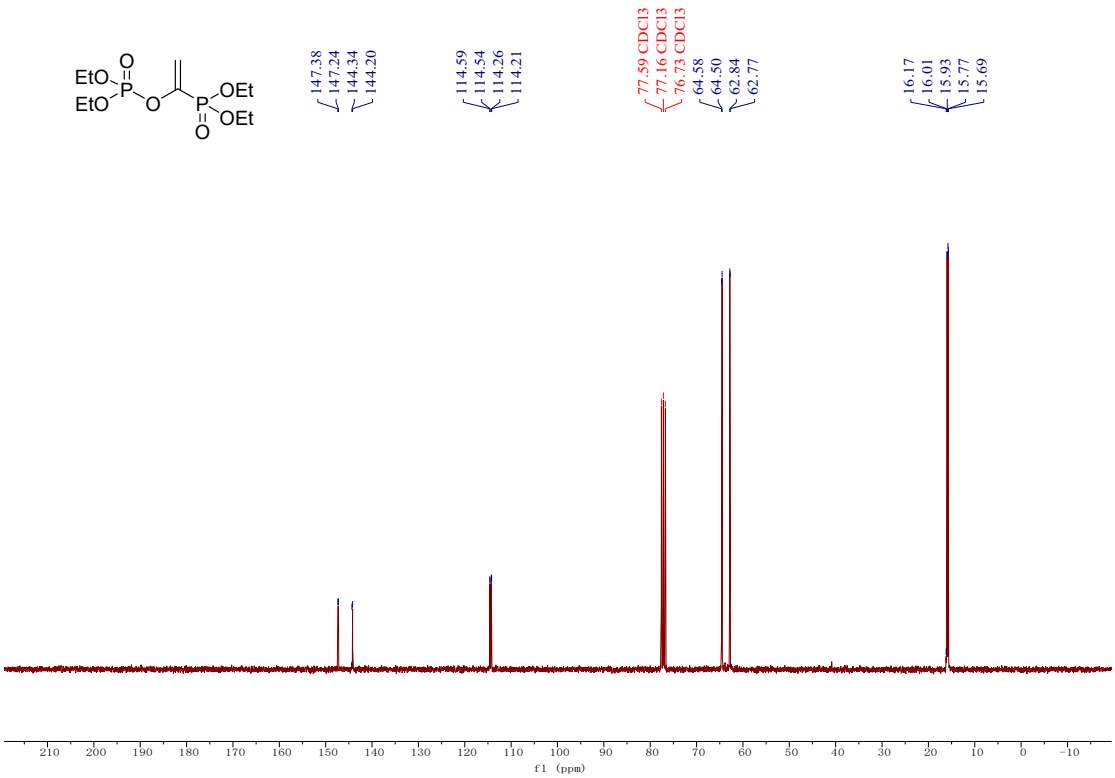
^{13}C NMR (75 MHz, $CDCl_3$) of **3a**



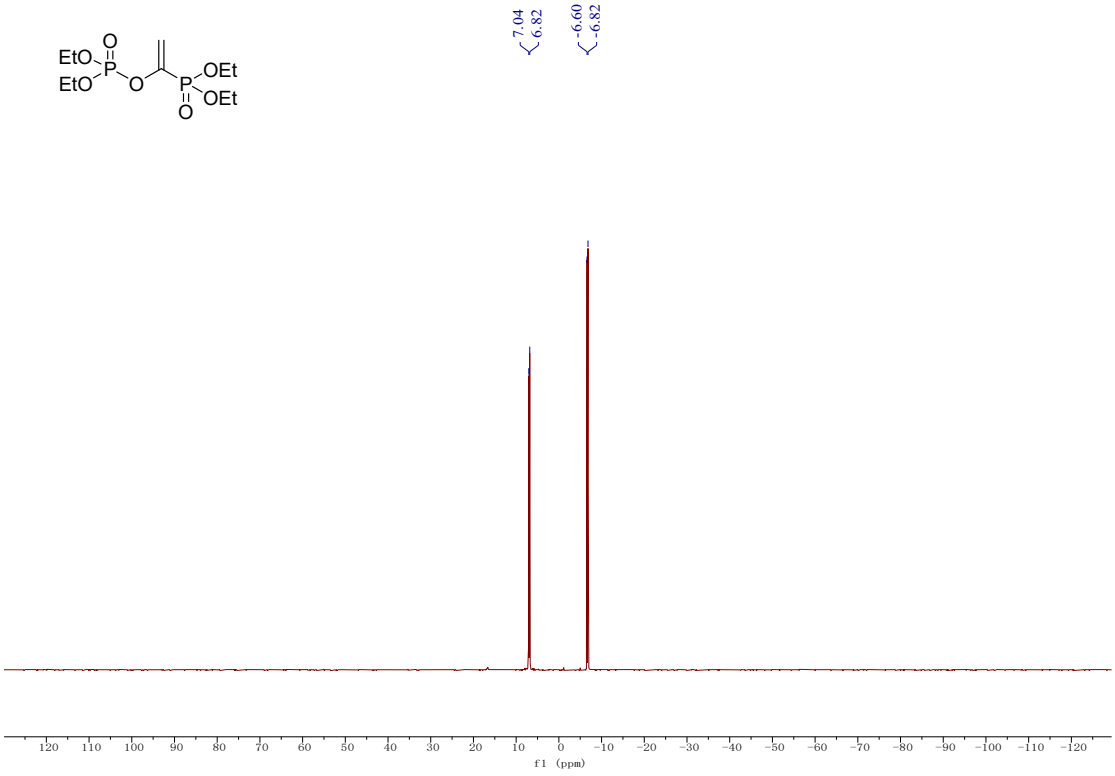
^{31}P NMR (121 MHz, $CDCl_3$) of **3a**



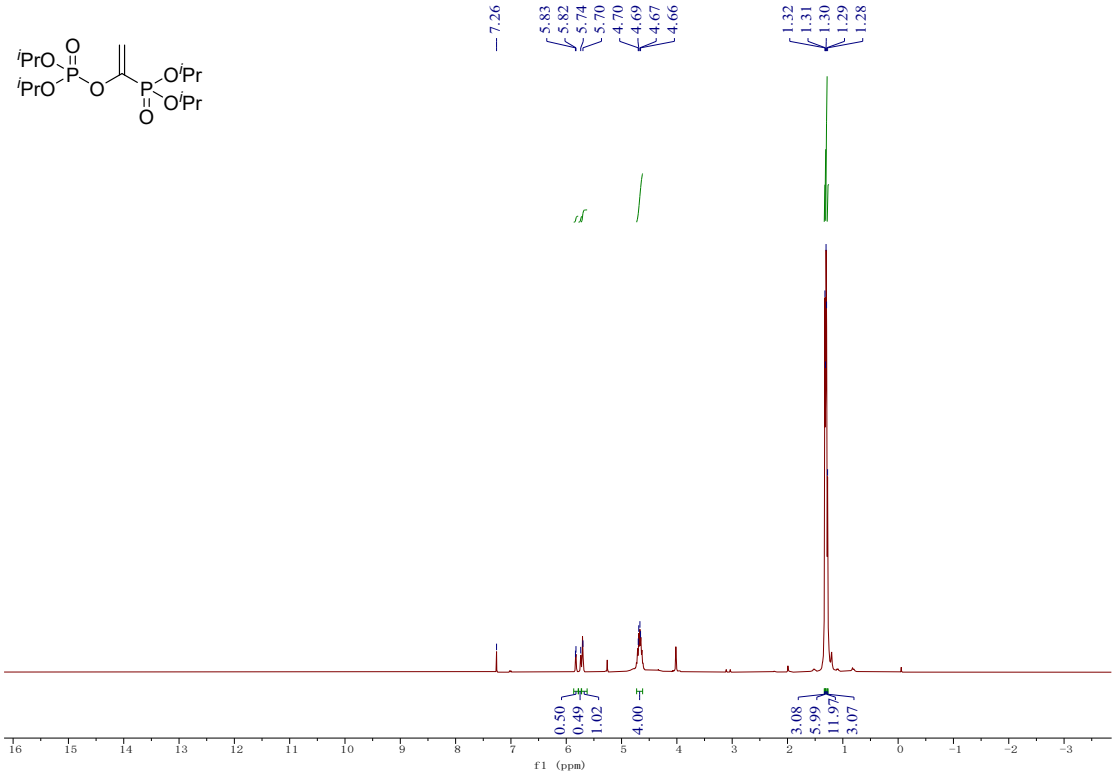
^{1}H NMR (300 MHz, $CDCl_3$) of **3b**



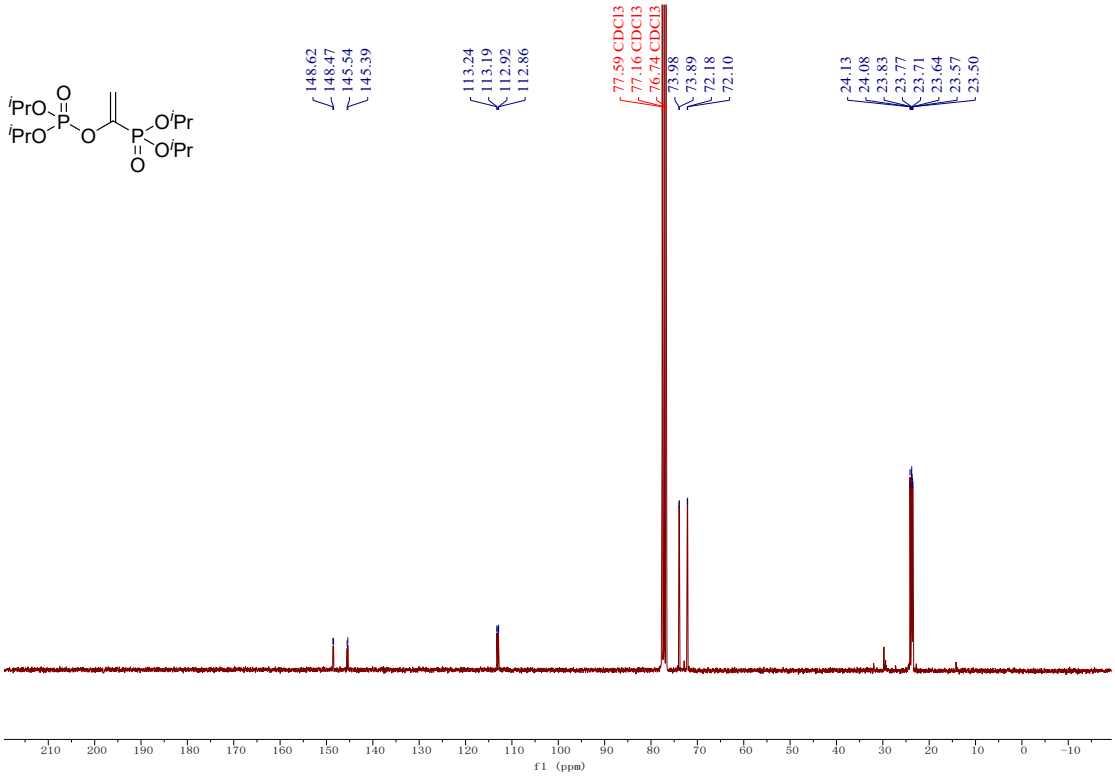
^{13}C NMR (75 MHz, $CDCl_3$) of **3b**



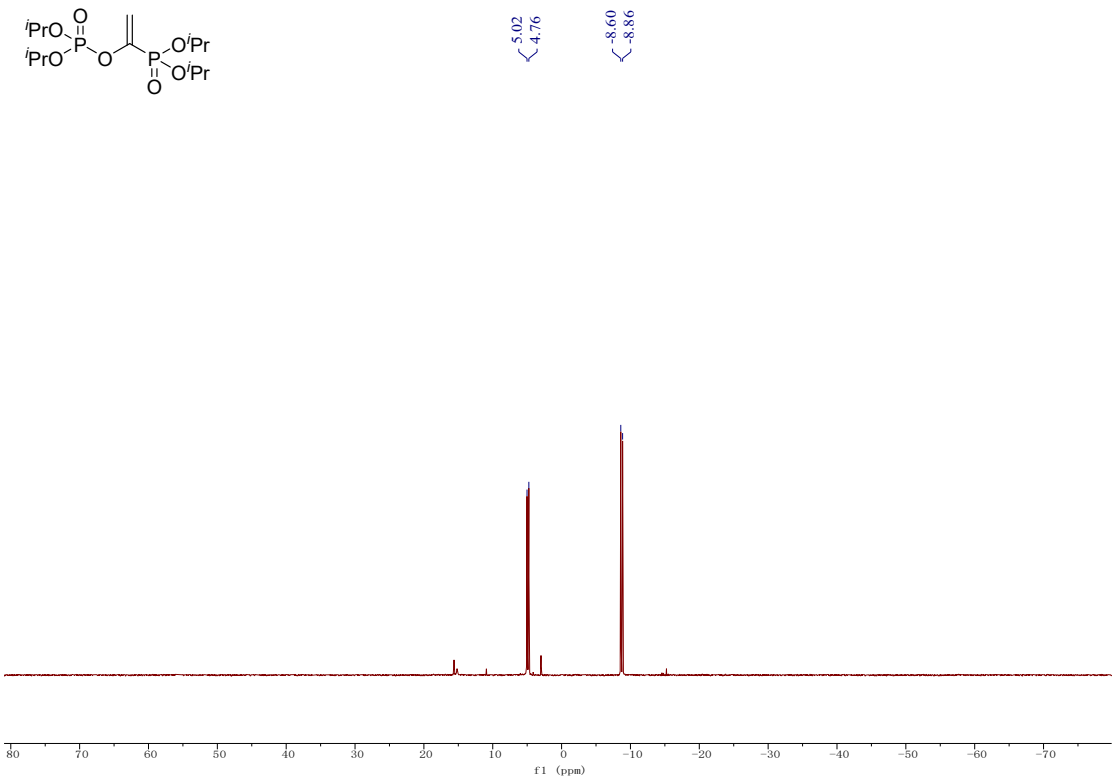
^{31}P NMR (121 MHz, $CDCl_3$) of **3b**



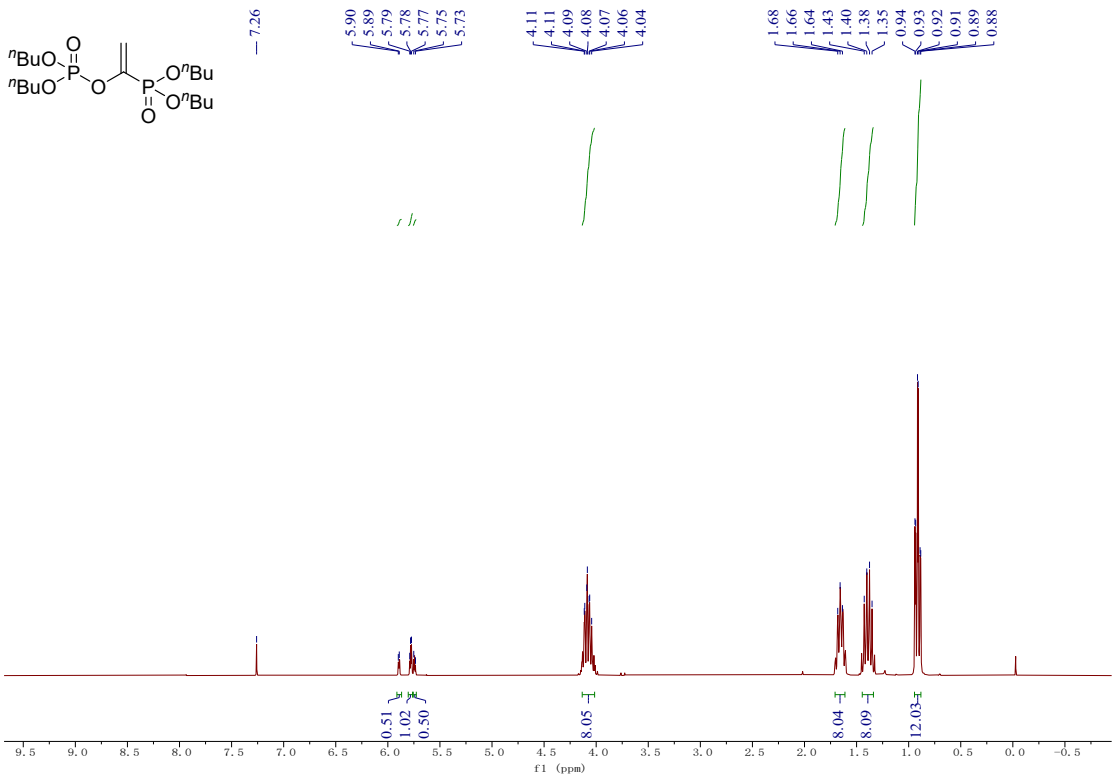
^{1}H NMR (300 MHz, $CDCl_3$) of **3c**



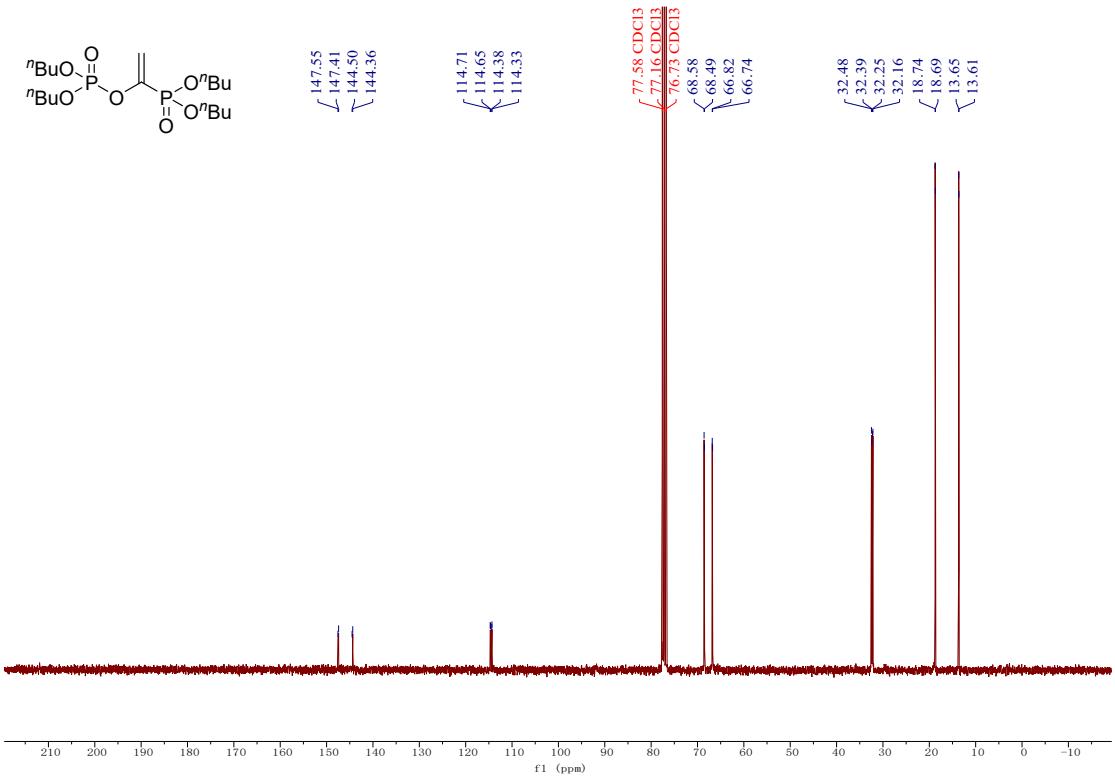
^{13}C NMR (75 MHz, $CDCl_3$) of **3c**



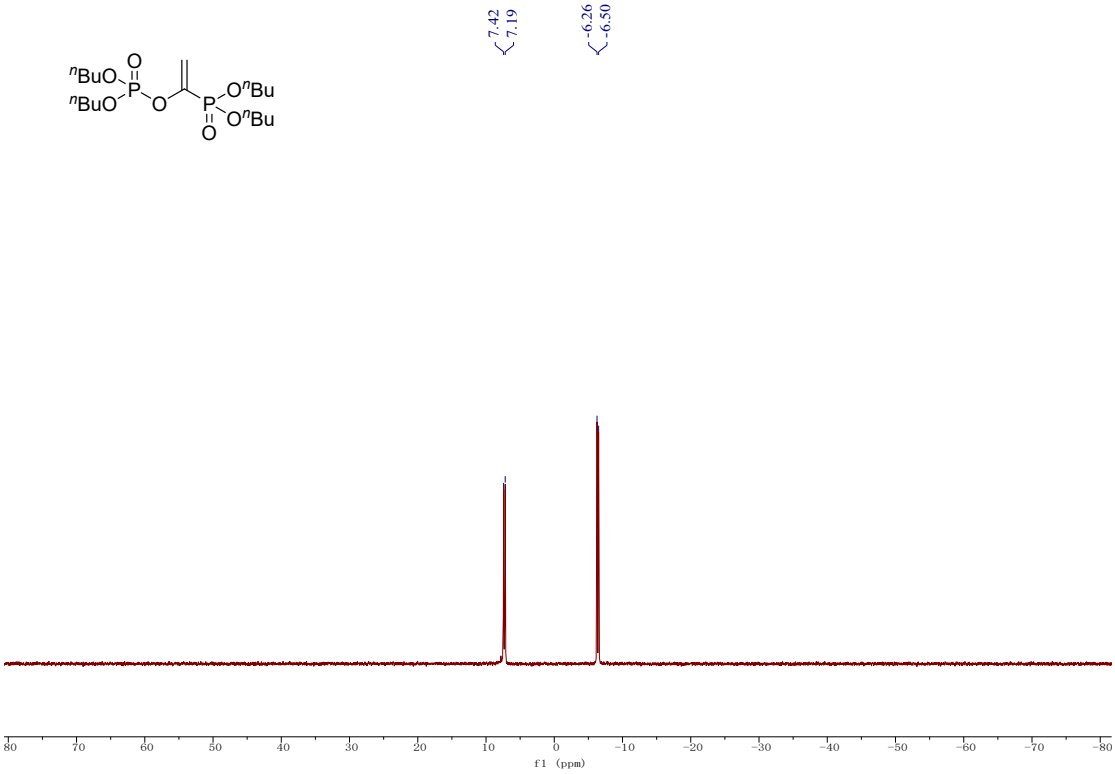
^{31}P NMR (121 MHz, $CDCl_3$) of **3c**



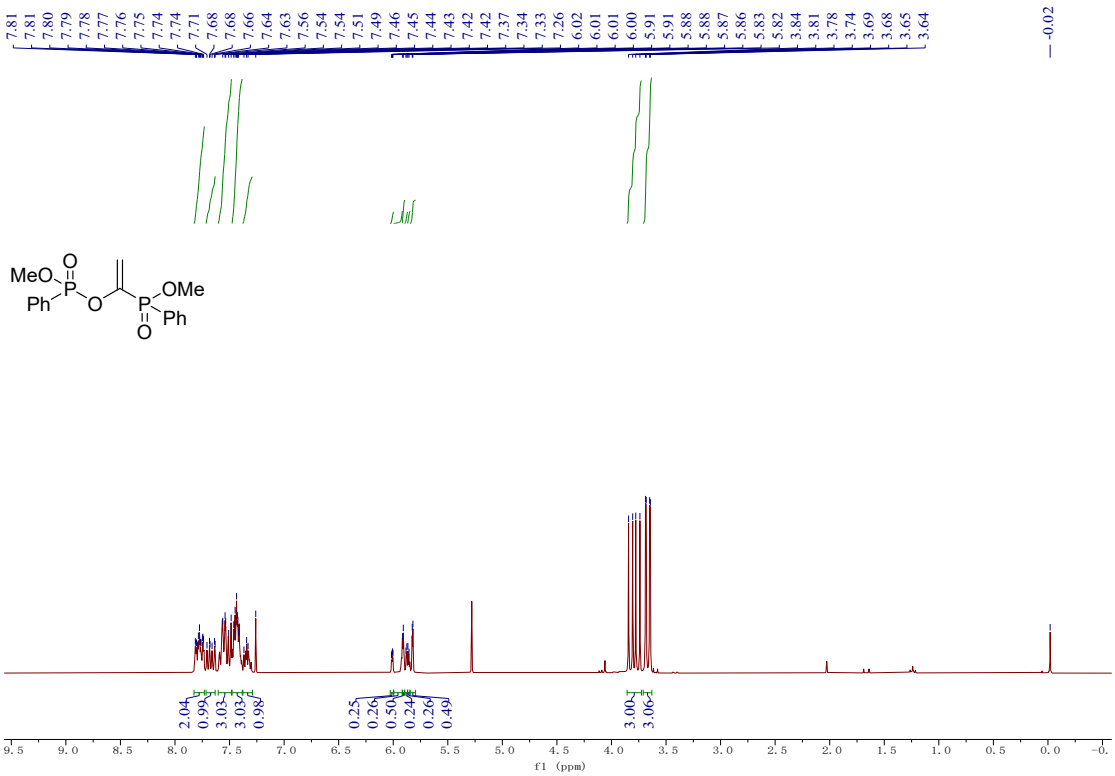
^{1}H NMR (300 MHz, $CDCl_3$) of **3d**



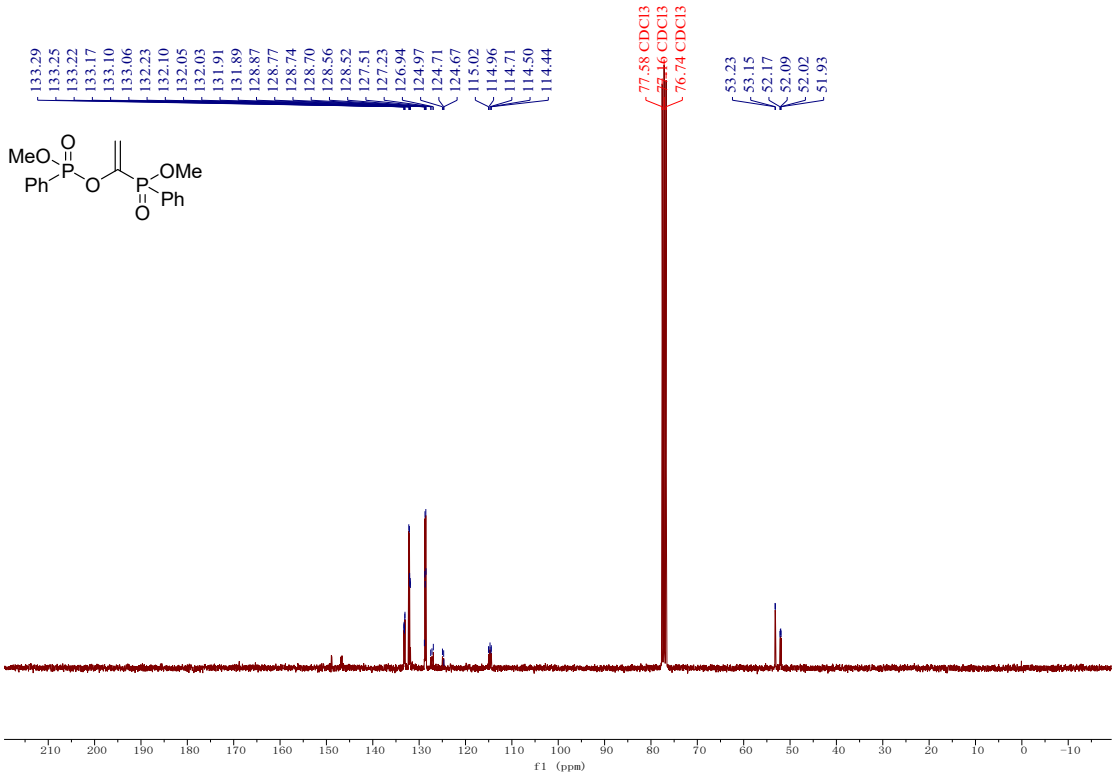
^{13}C NMR (75 MHz, $CDCl_3$) of **3d**



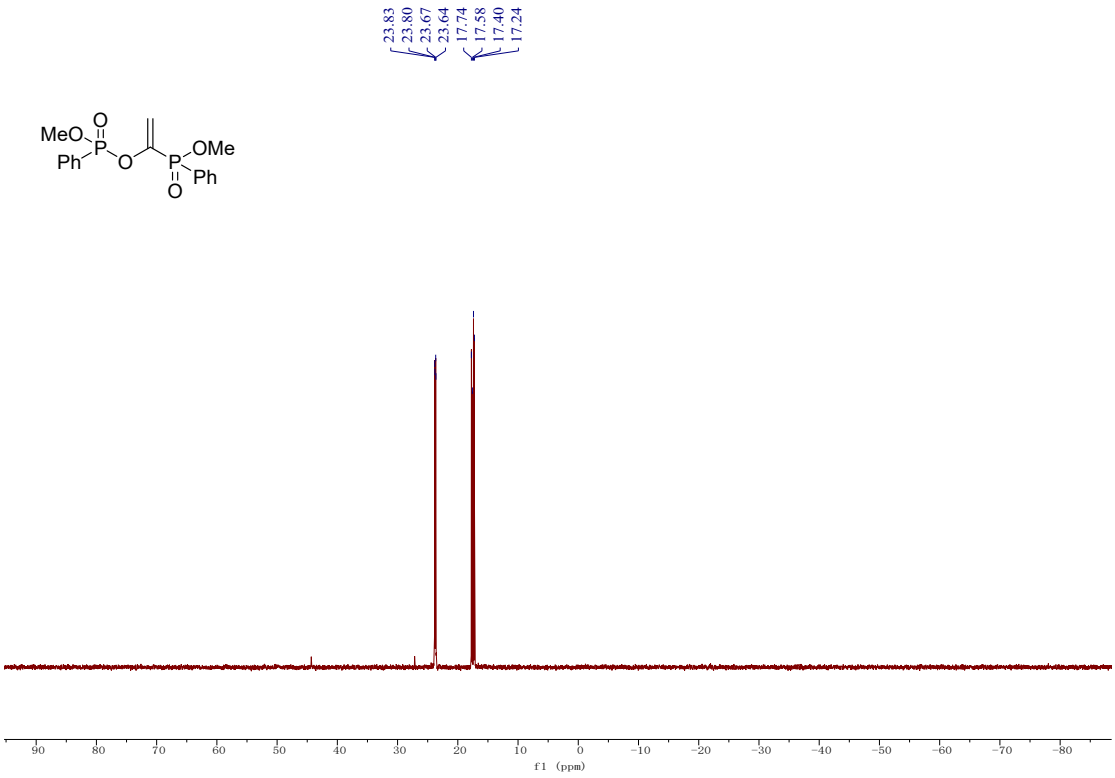
^{31}P NMR (121 MHz, $CDCl_3$) of **3d**



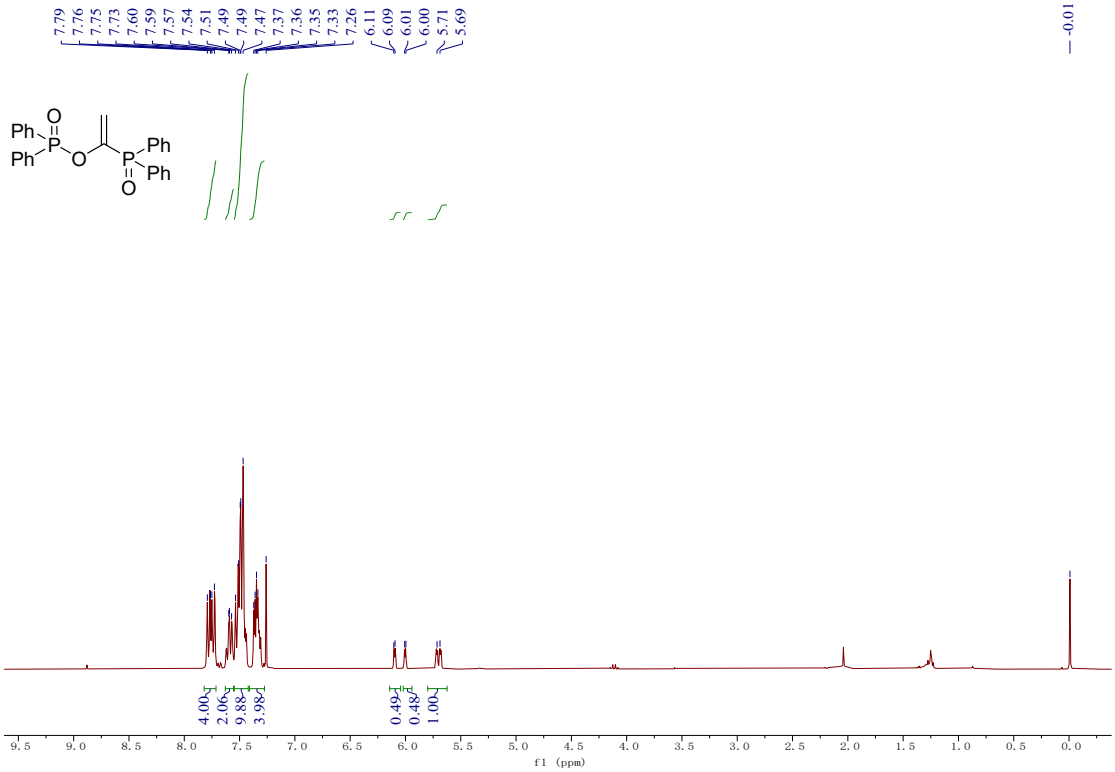
^{1}H NMR (300 MHz, $CDCl_3$) of **3e**



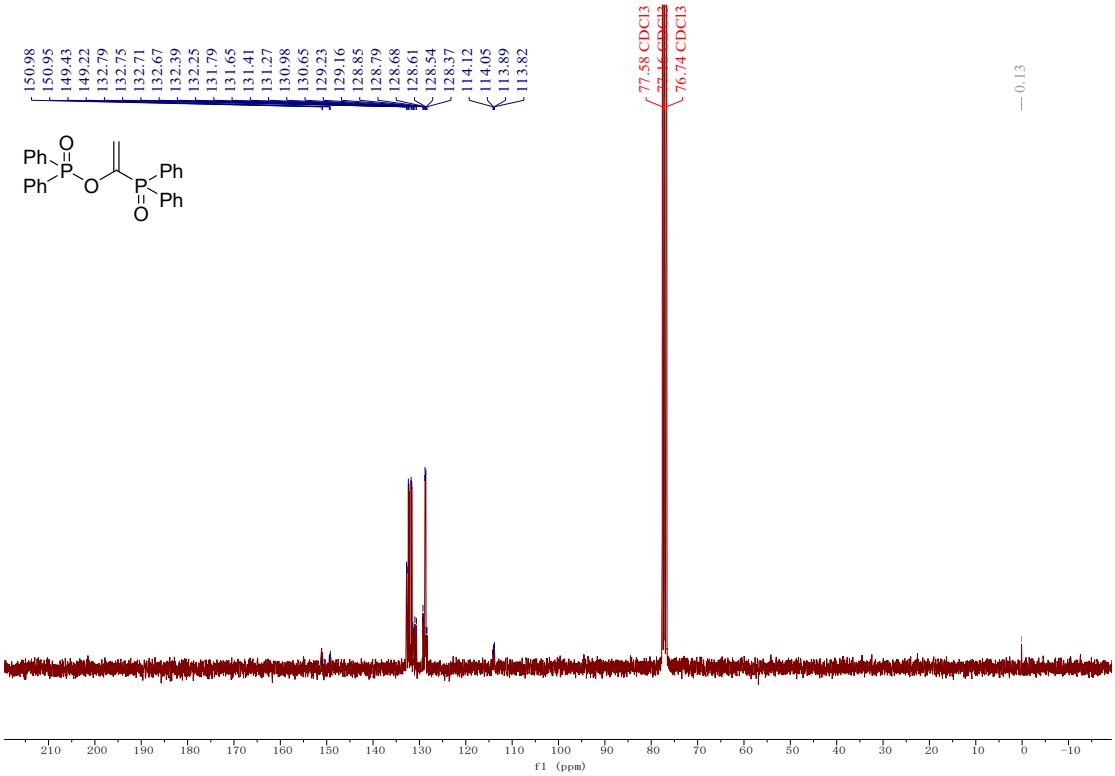
^{13}C NMR (75 MHz, $CDCl_3$) of **3e**



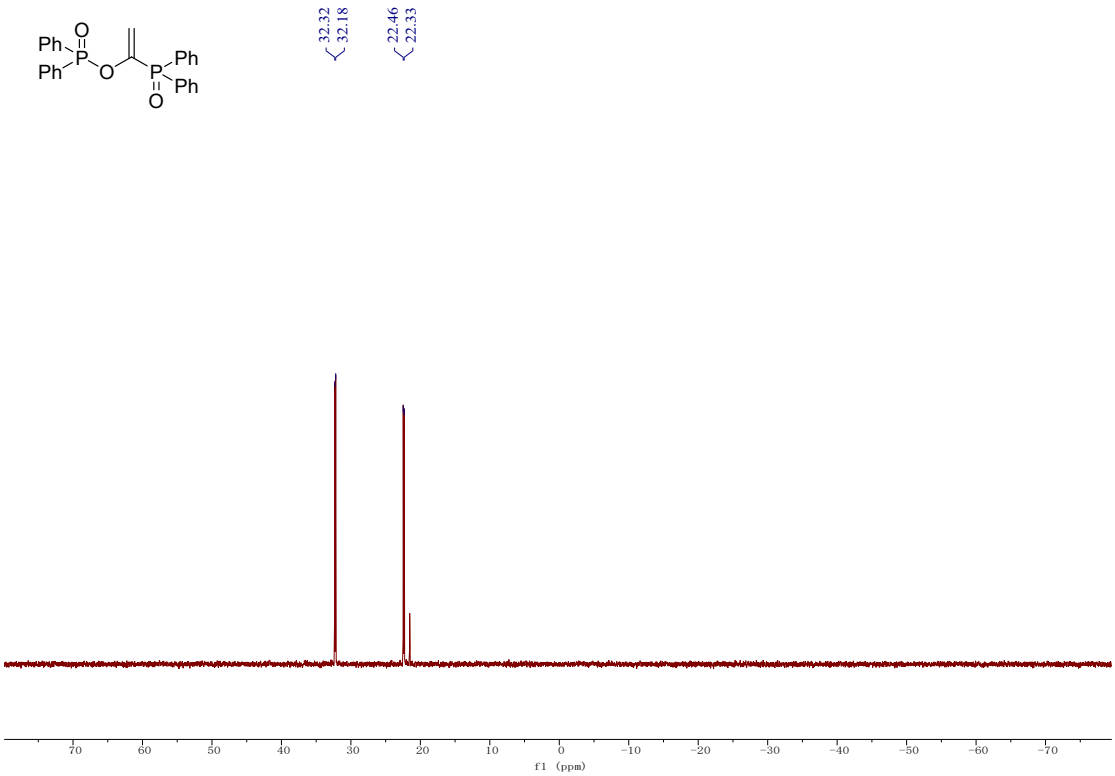
^{31}P NMR (121 MHz, $CDCl_3$) of **3e**



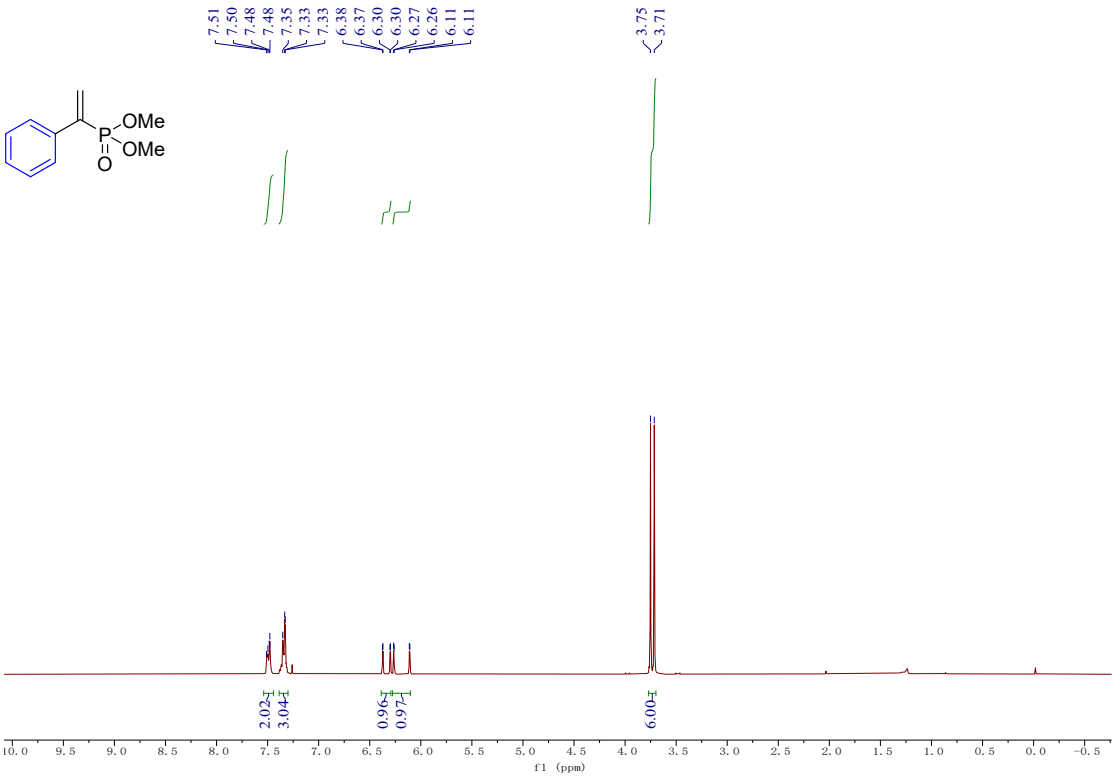
^{1}H NMR (300 MHz, $CDCl_3$) of **3f**



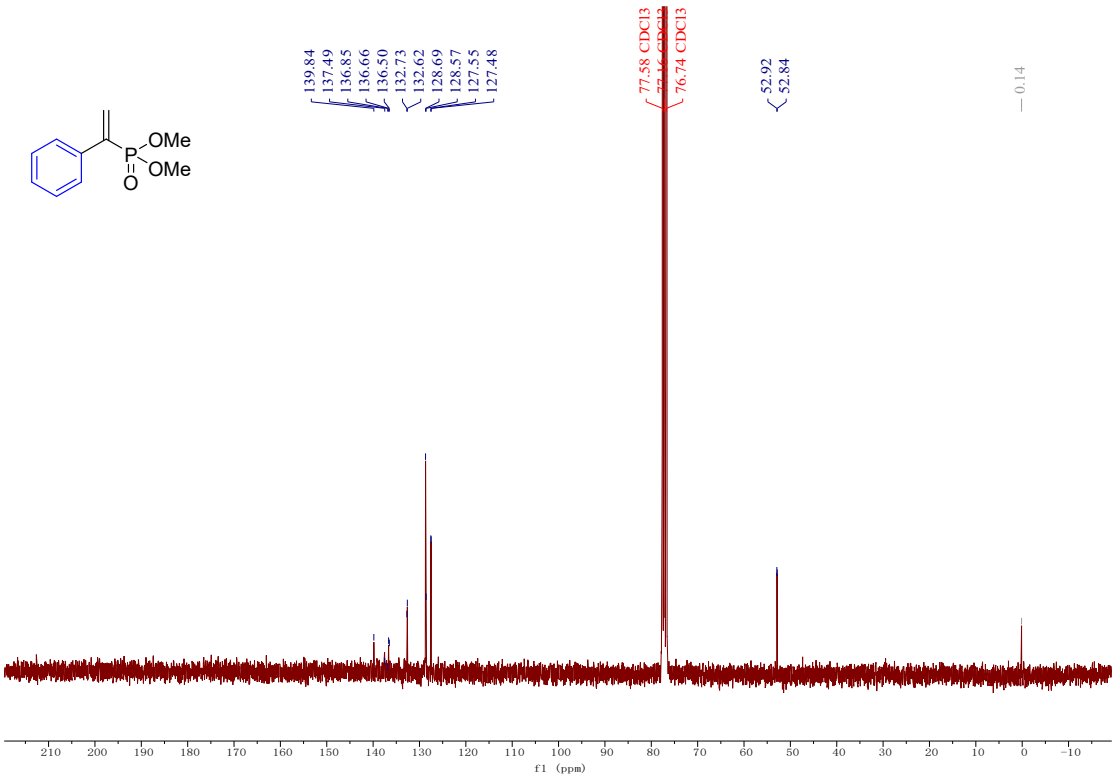
^{13}C NMR (75 MHz, $CDCl_3$) of **3f**



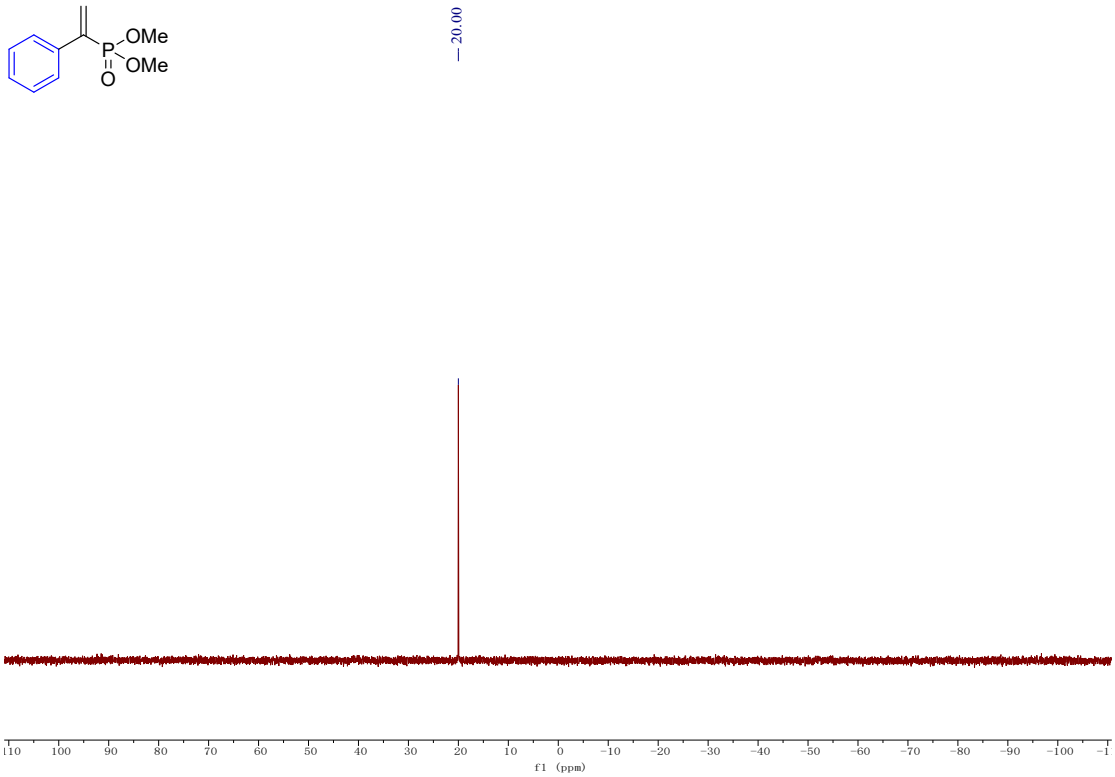
^{31}P NMR (121 MHz, $CDCl_3$) of **3f**



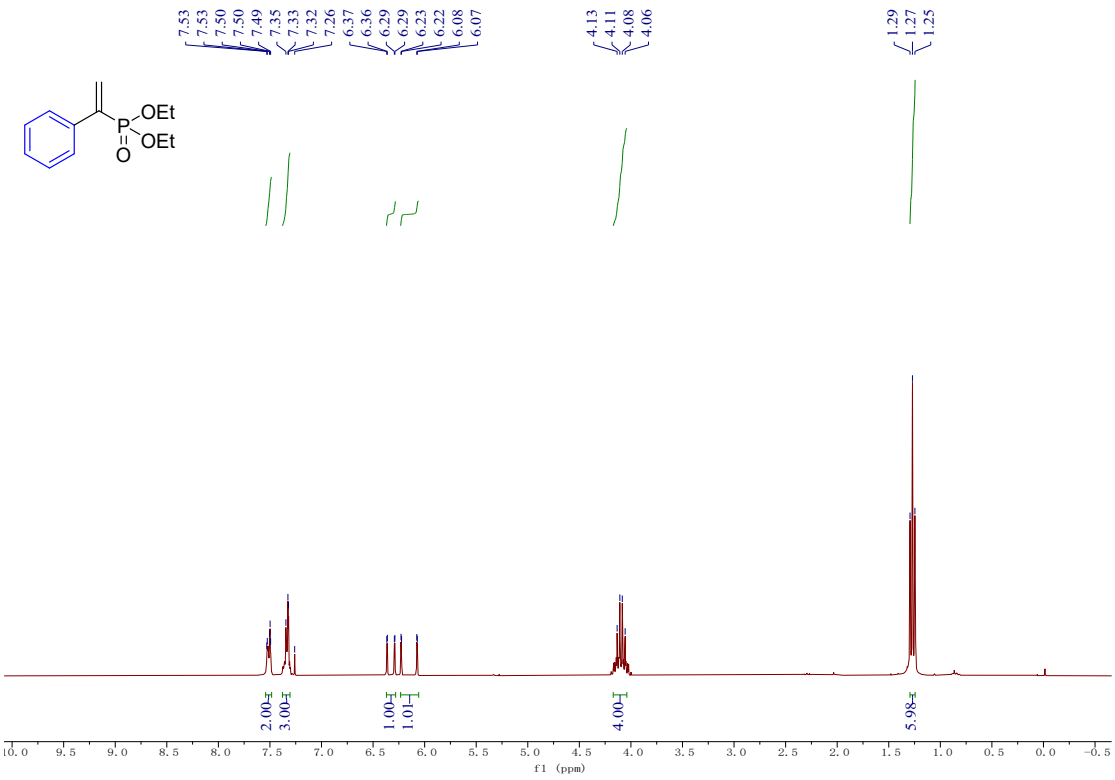
^{1}H NMR (300 MHz, $CDCl_3$) of **5a**



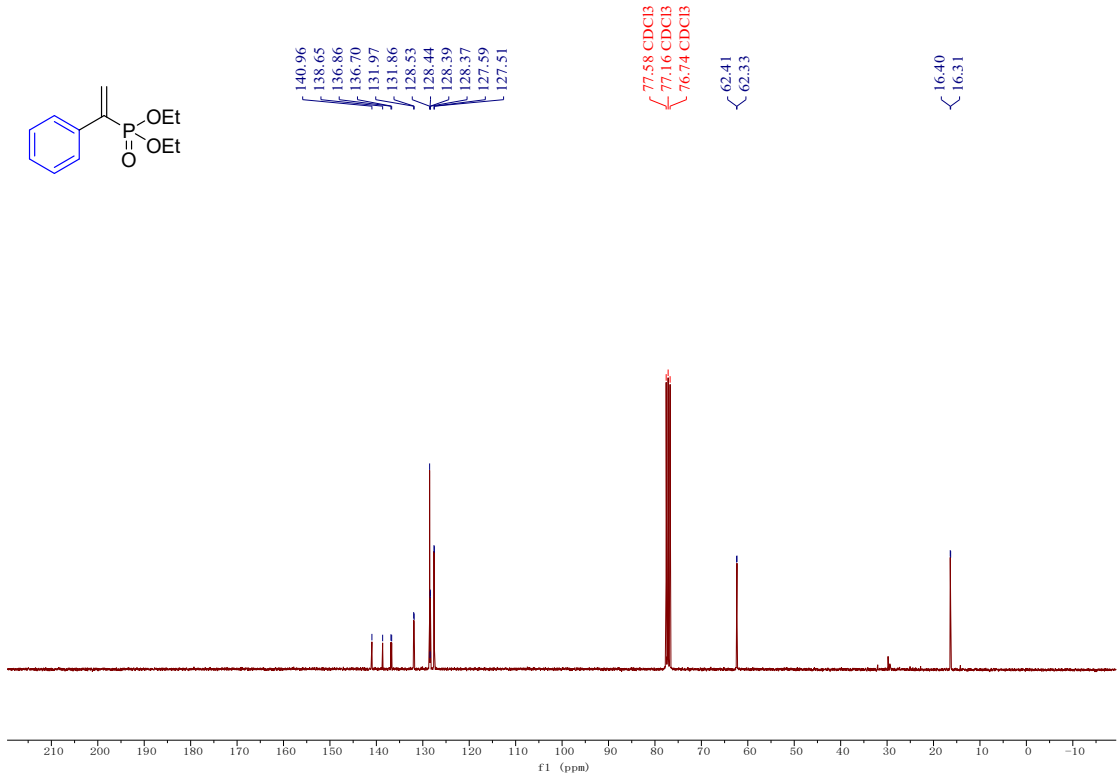
^{13}C NMR (75 MHz, $CDCl_3$) of **5a**



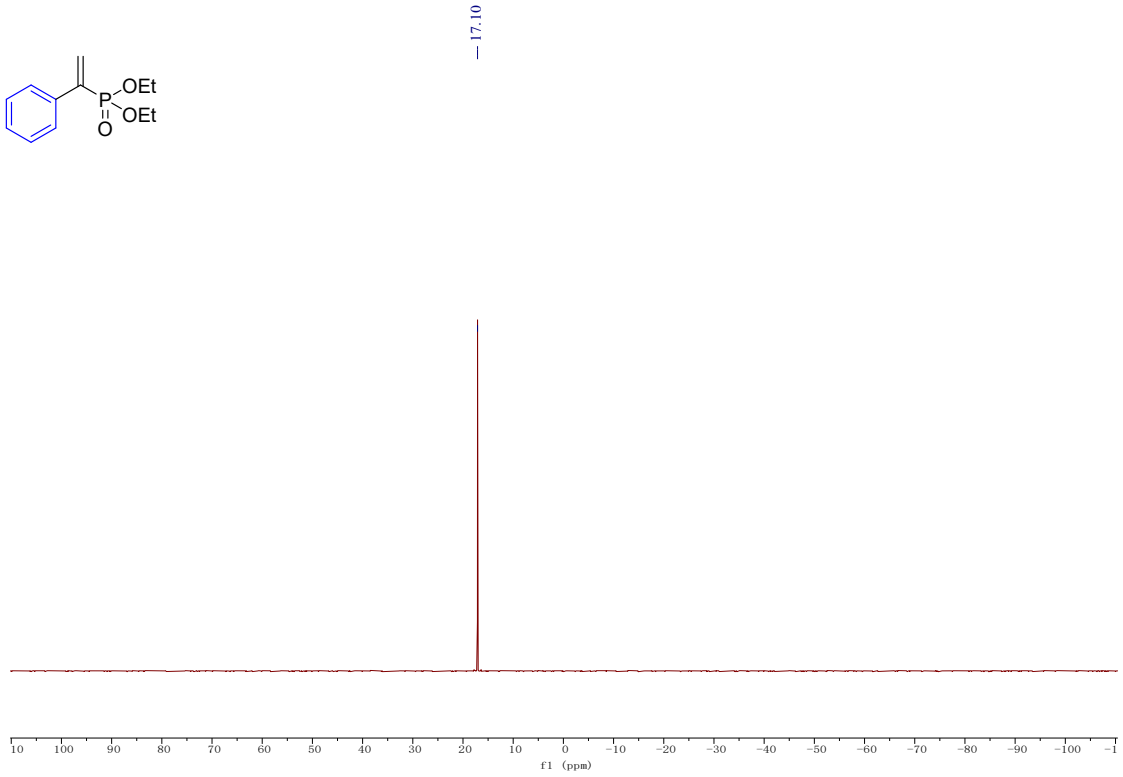
^{31}P NMR (121 MHz, $CDCl_3$) of **5a**



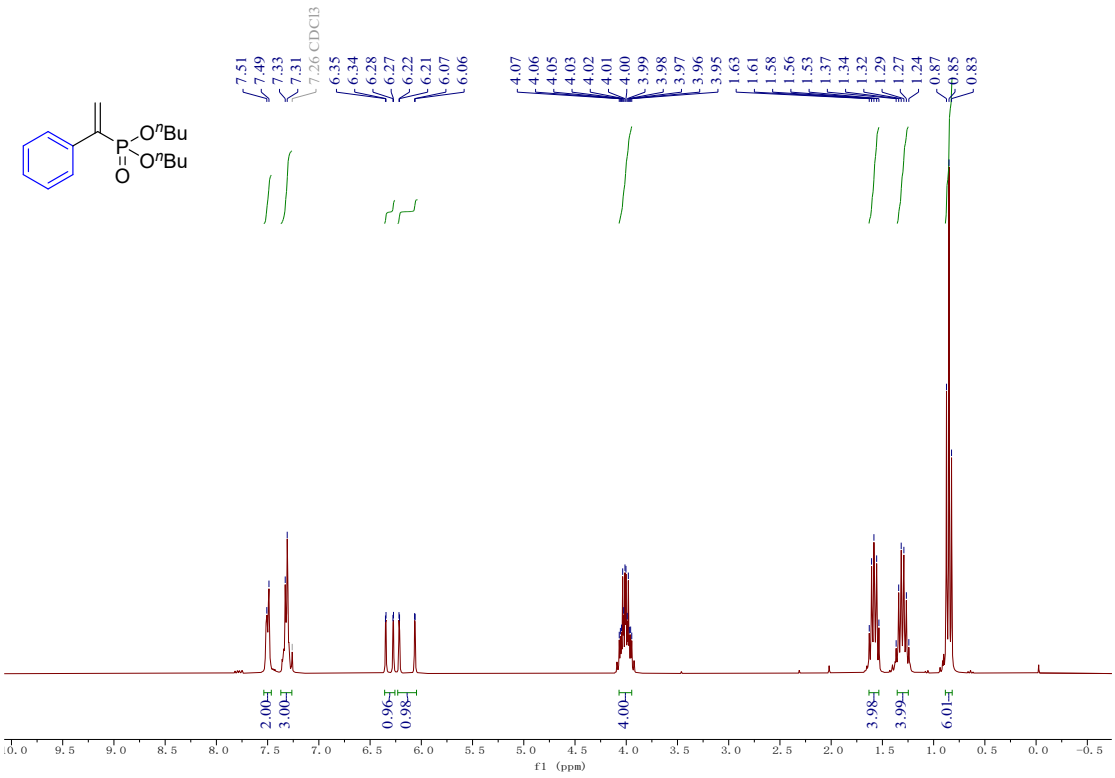
^{1}H NMR (300 MHz, $CDCl_3$) of **5b**



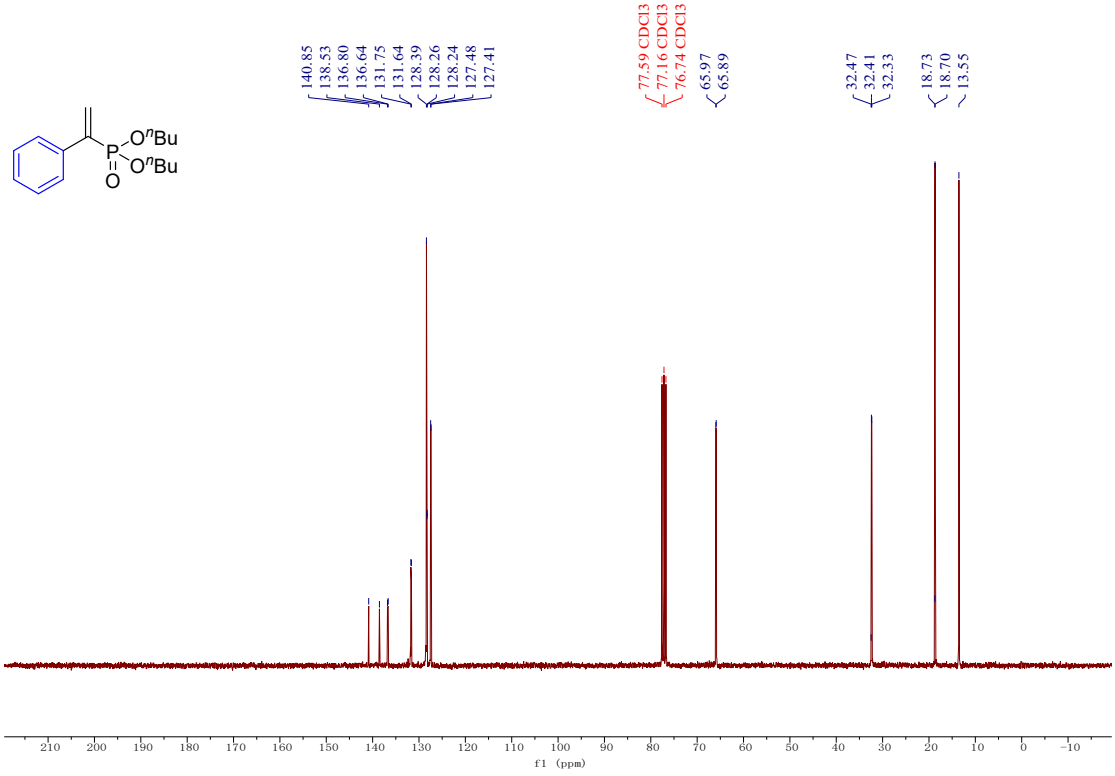
^{13}C NMR (75 MHz, $CDCl_3$) of **5b**



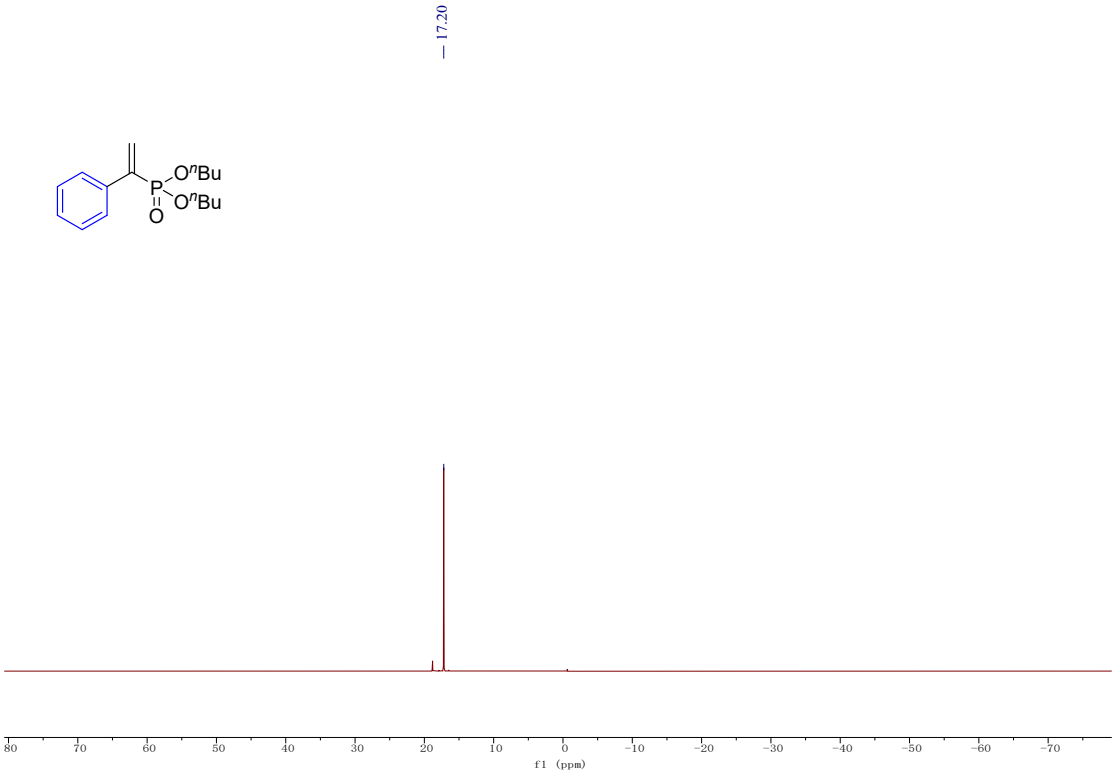
^{31}P NMR (121 MHz, $CDCl_3$) of **5b**



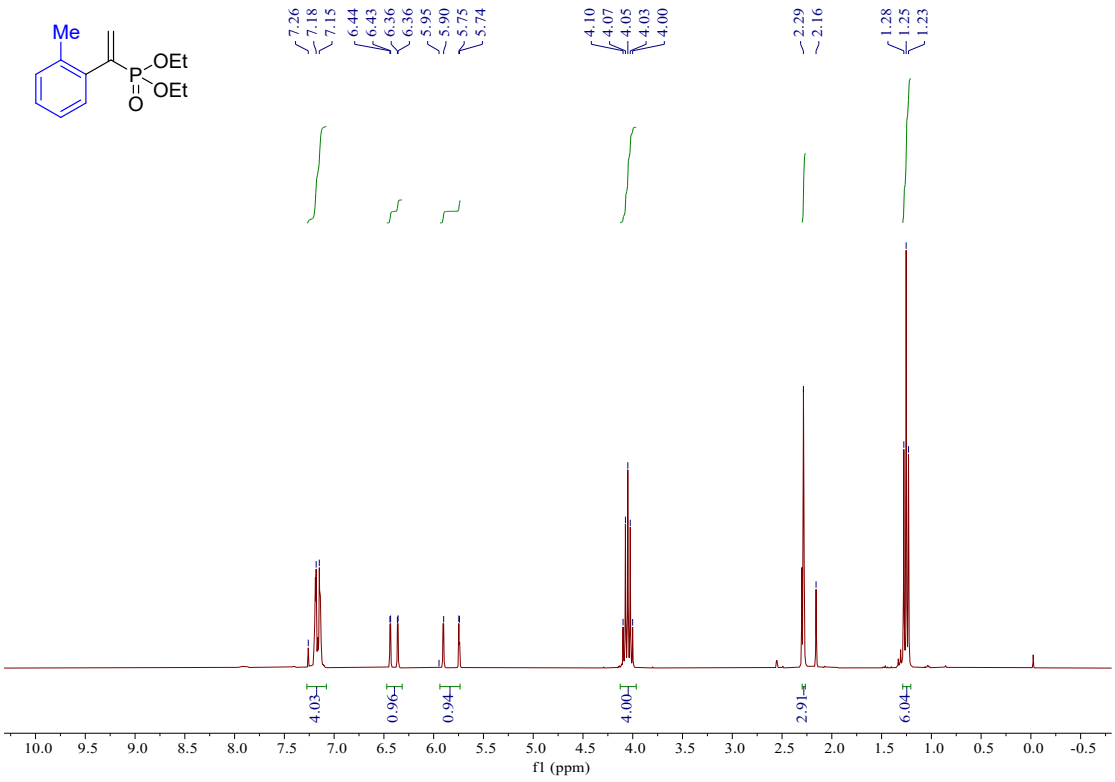
^{1}H NMR (300 MHz, $CDCl_3$) of **5c**



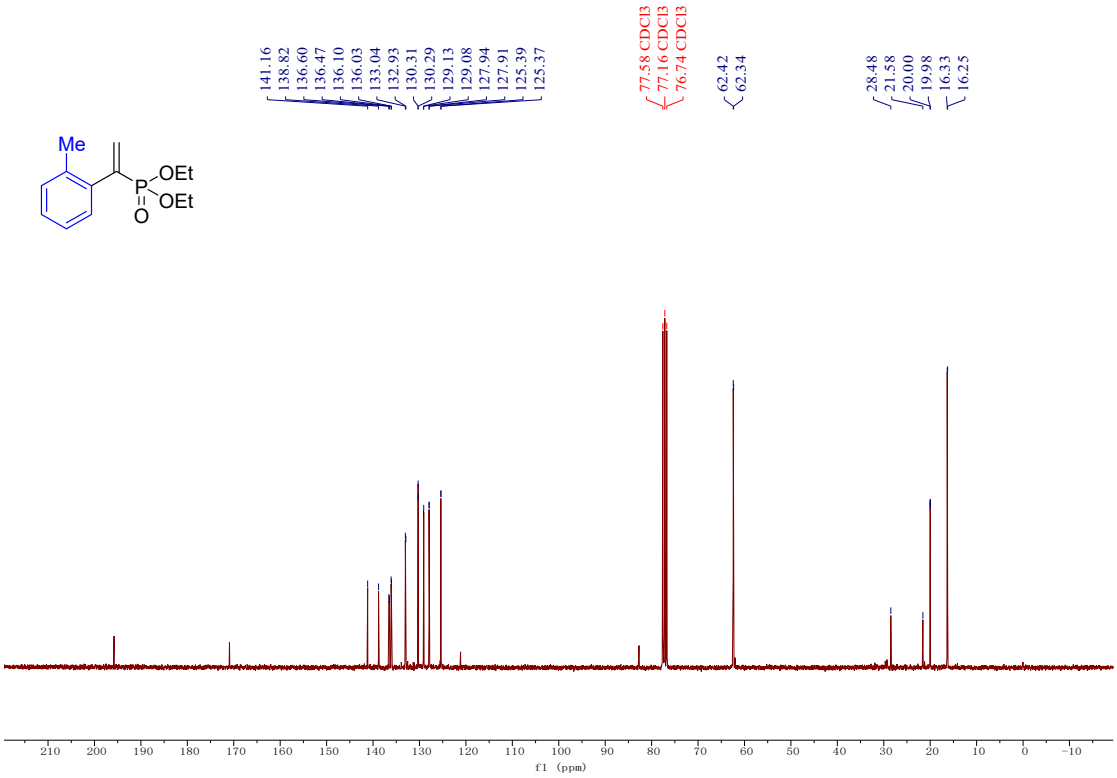
^{13}C NMR (75 MHz, $CDCl_3$) of **5c**



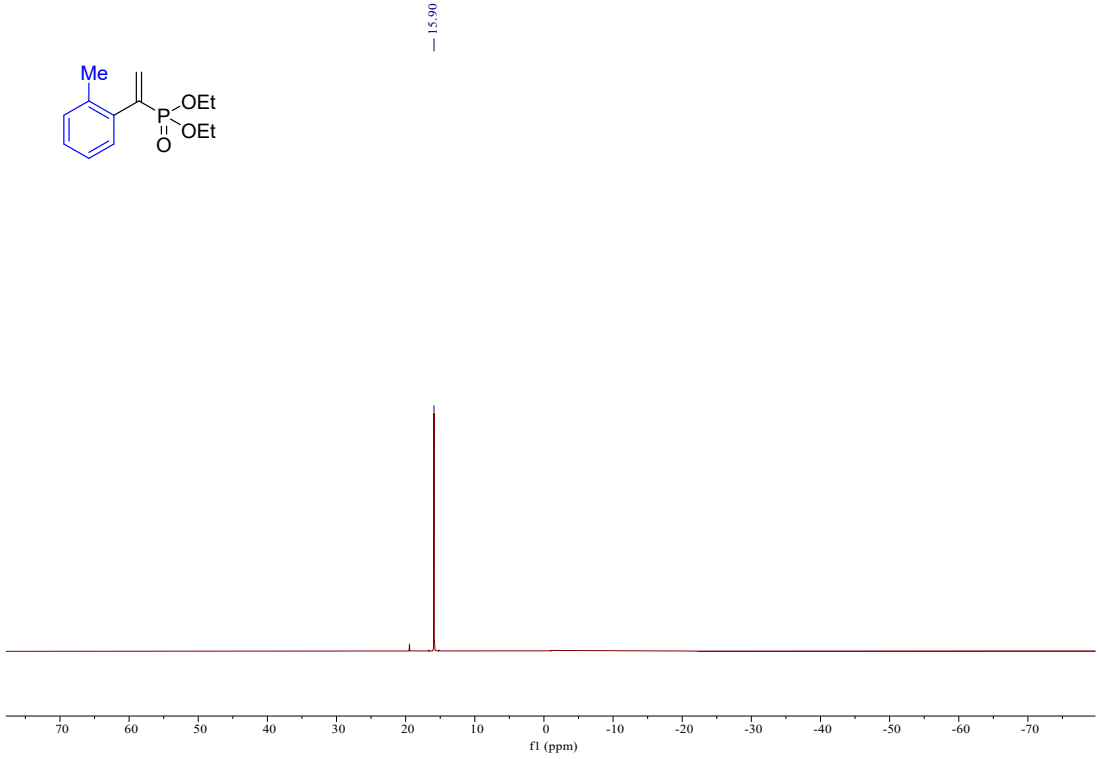
^{31}P NMR (121 MHz, $CDCl_3$) of **5c**



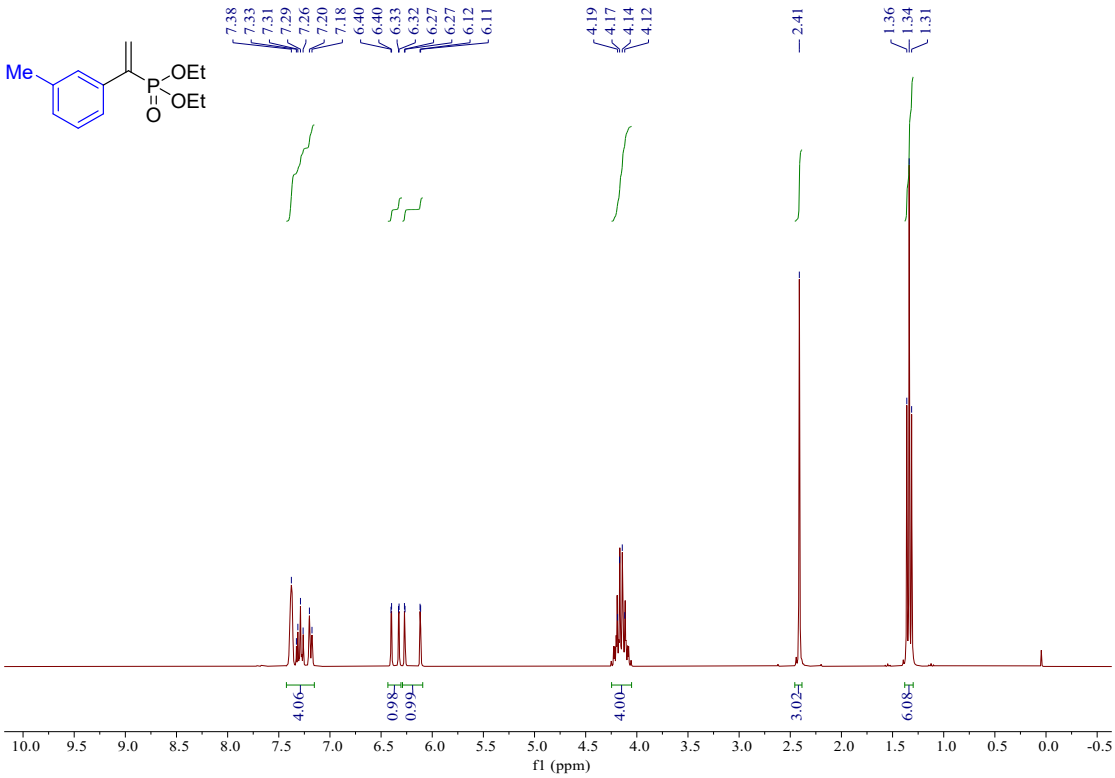
^{1}H NMR (300 MHz, $CDCl_3$) of **5d**



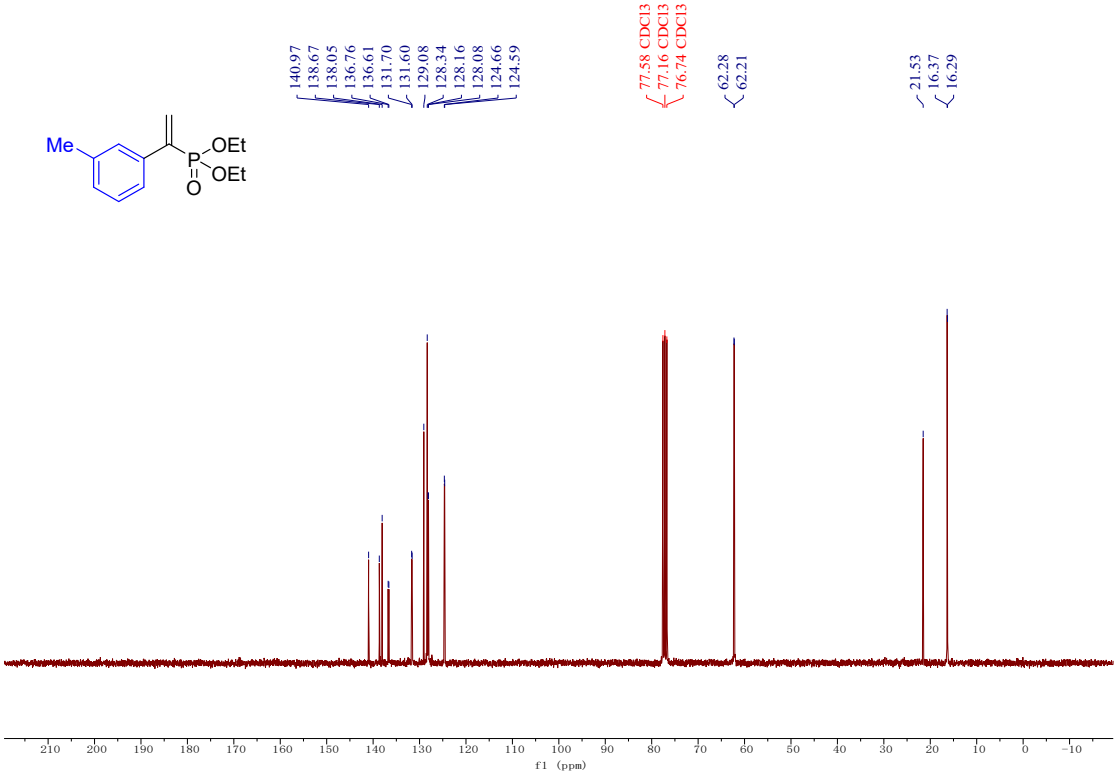
^{13}C NMR (75 MHz, $CDCl_3$) of **5d**



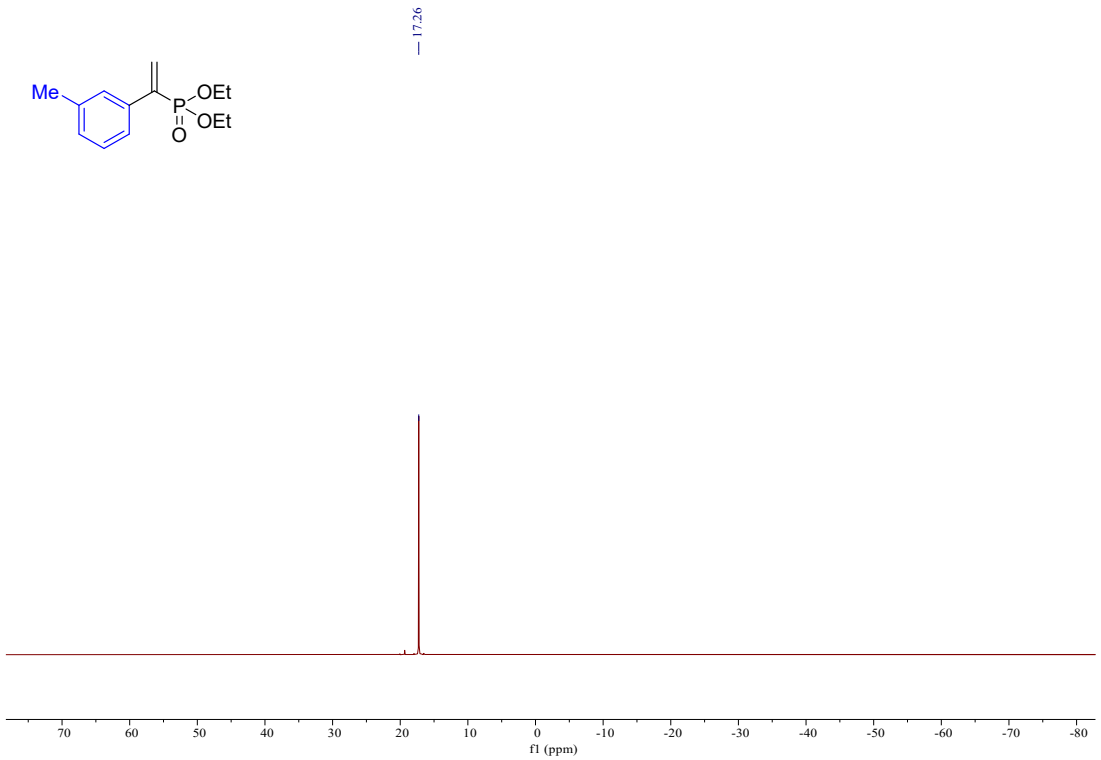
^{31}P NMR (121 MHz, $CDCl_3$) of **5d**



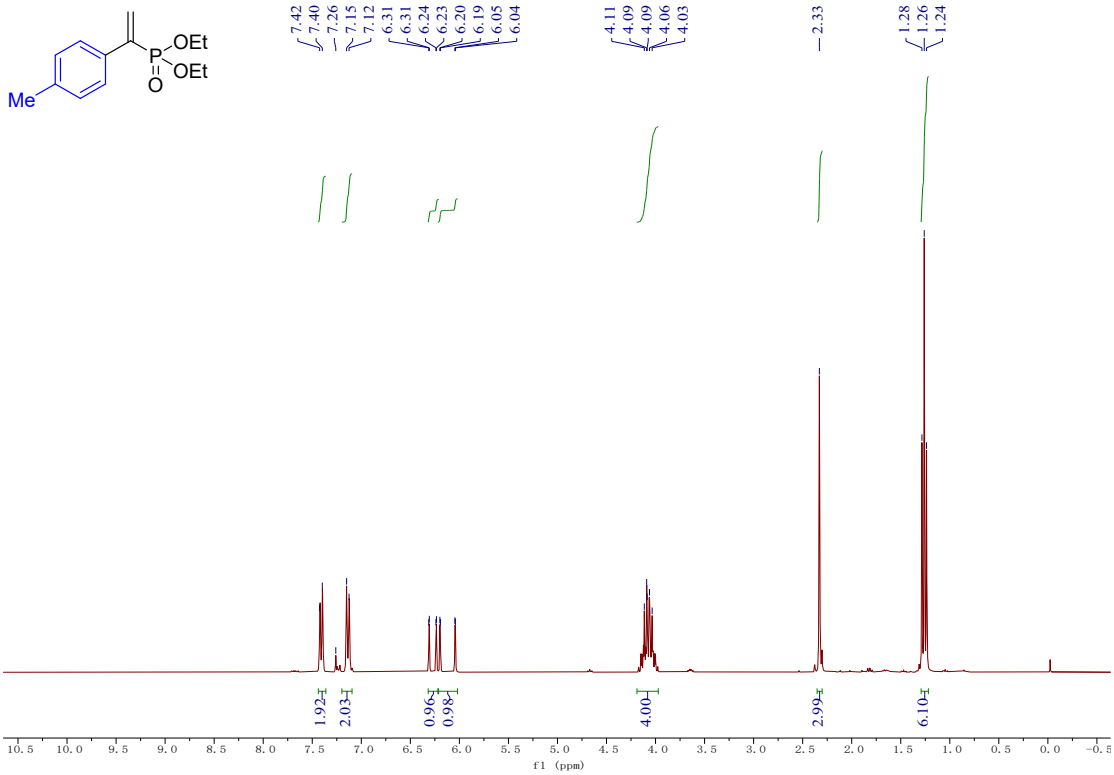
^{1}H NMR (300 MHz, $CDCl_3$) of **5e**



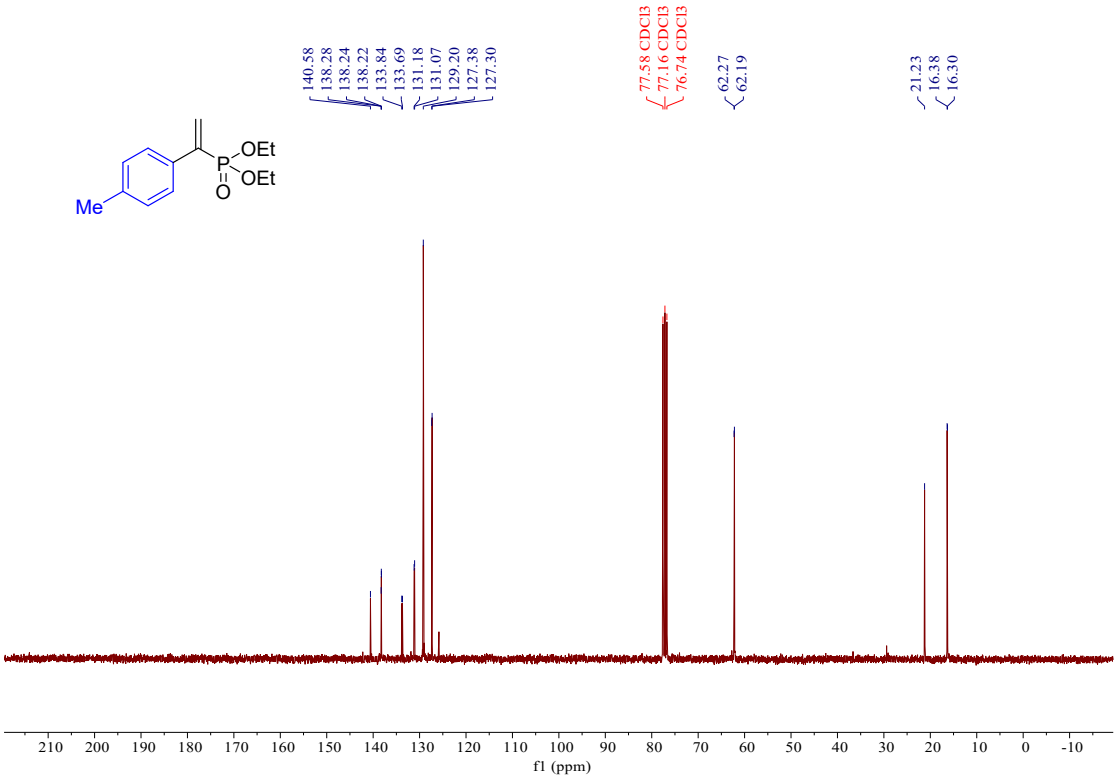
^{13}C NMR (75 MHz, $CDCl_3$) of **5e**



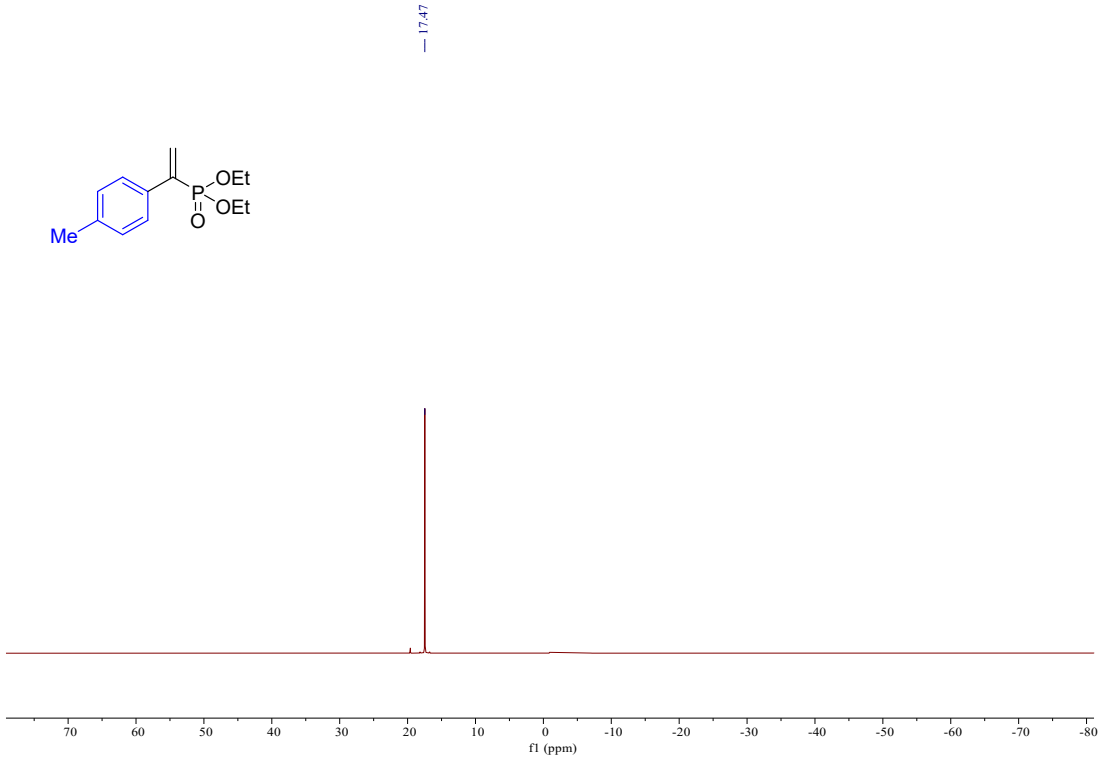
^{31}P NMR (121 MHz, $CDCl_3$) of **5e**



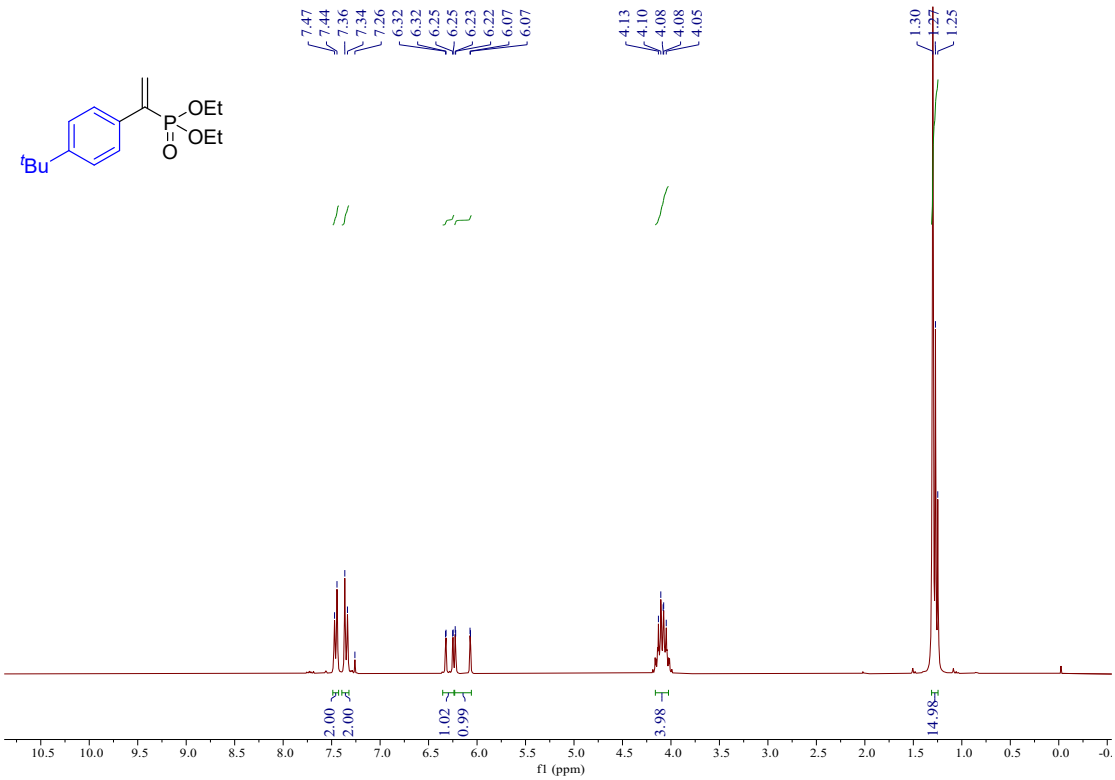
^{1}H NMR (300 MHz, $CDCl_3$) of **5f**



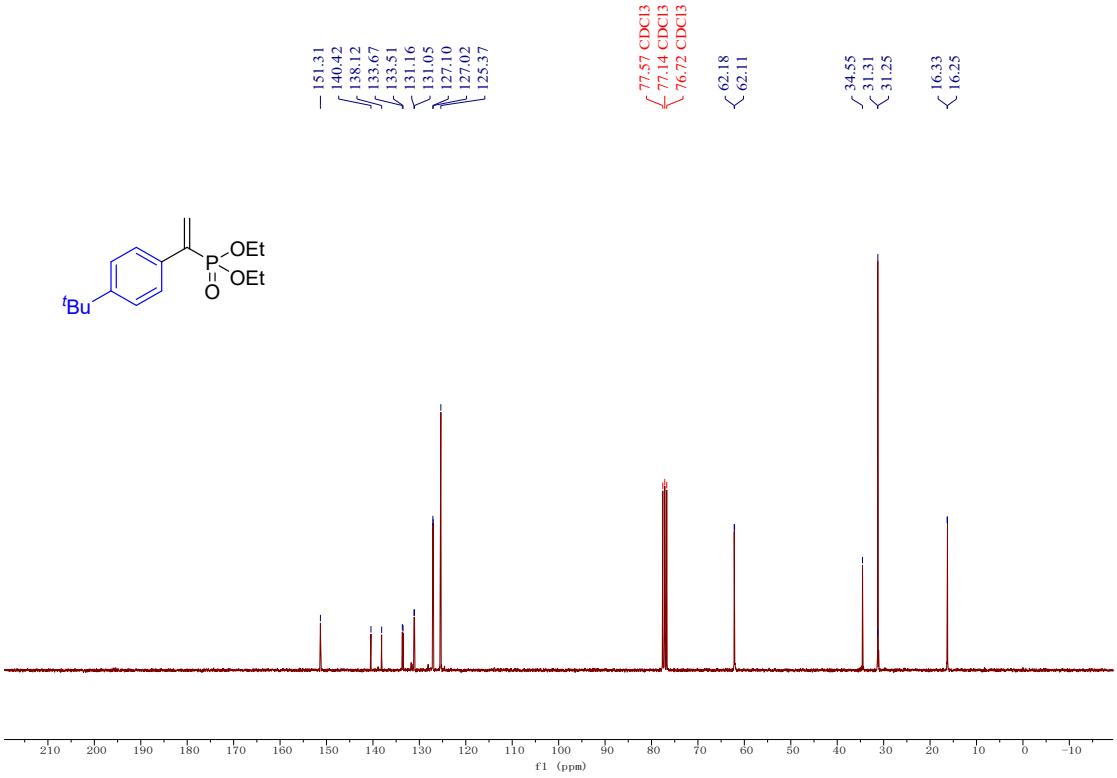
^{13}C NMR (75 MHz, $CDCl_3$) of **5f**



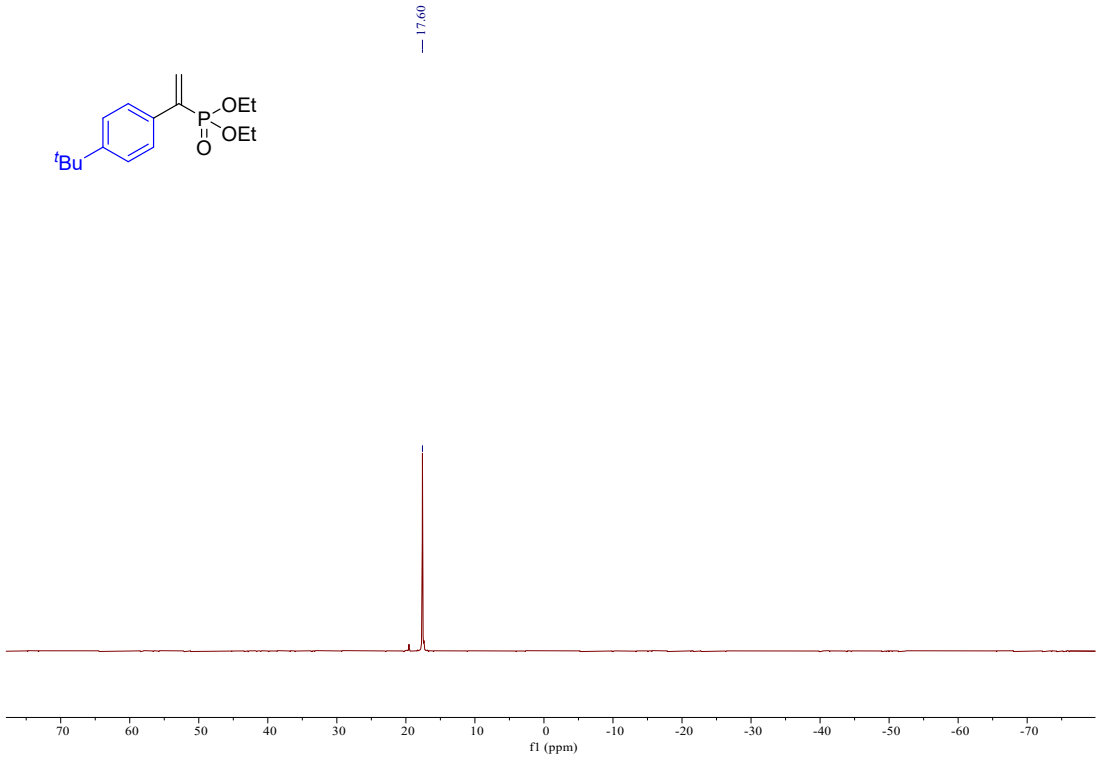
^{31}P NMR (121 MHz, $CDCl_3$) of **5f**



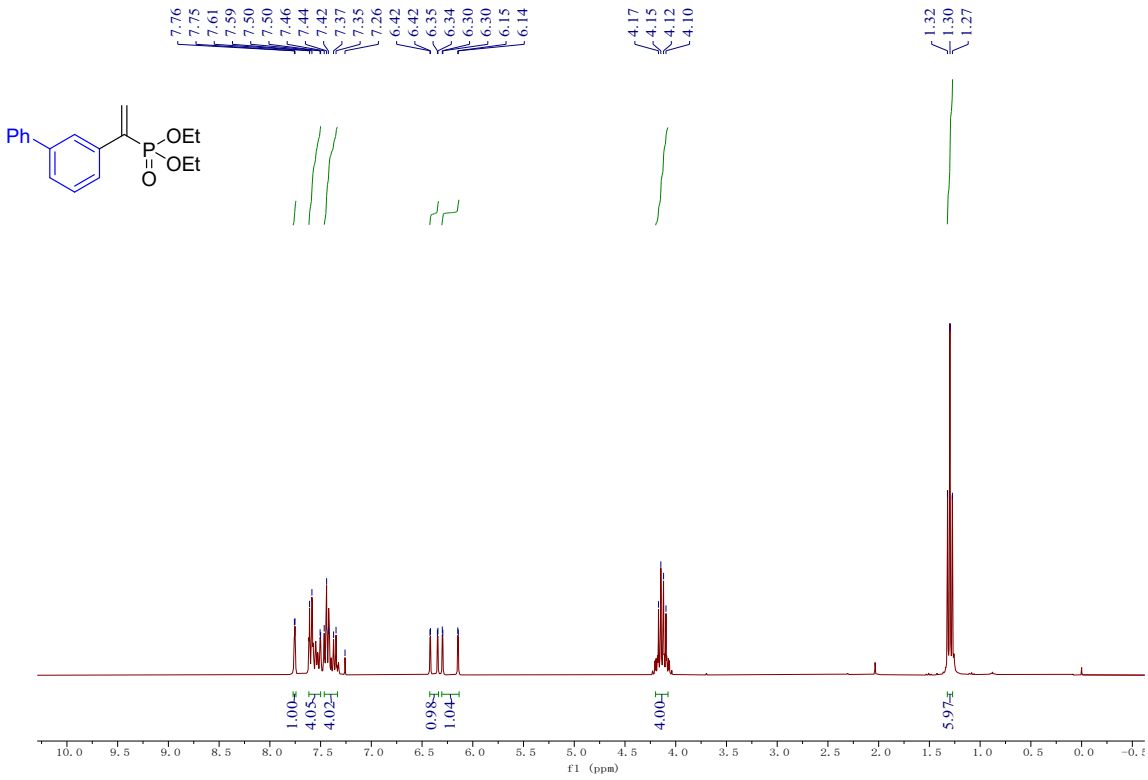
^{1}H NMR (300 MHz, $CDCl_3$) of **5g**



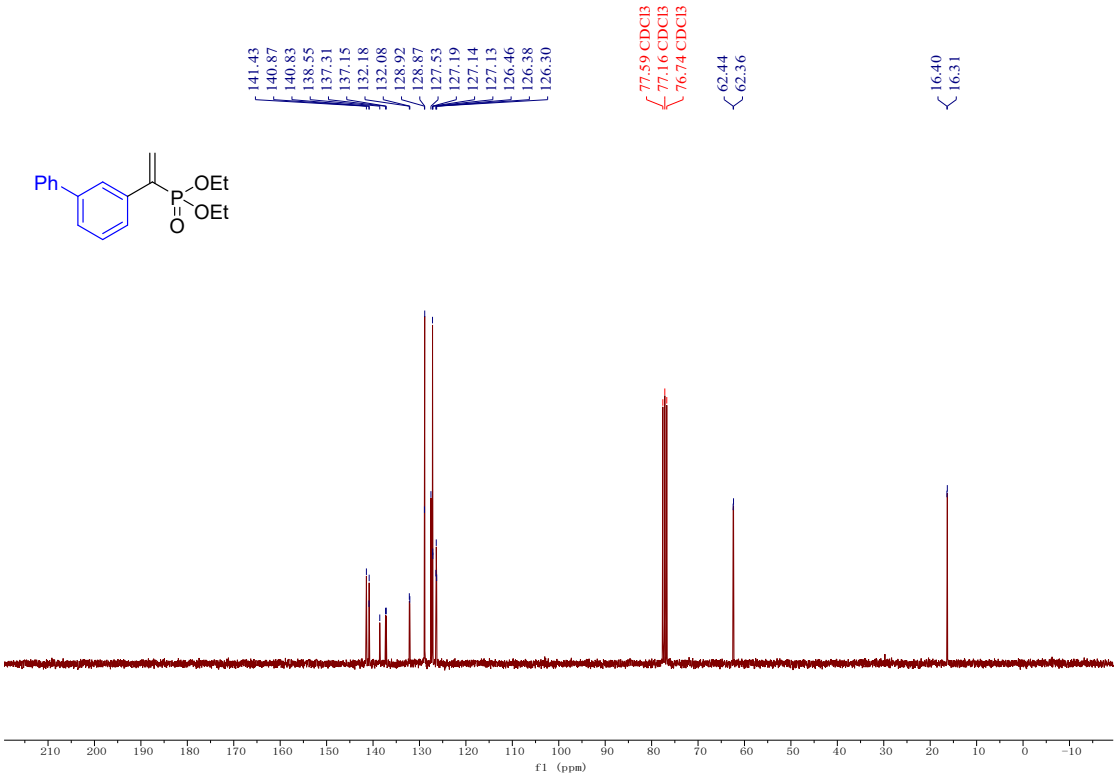
^{13}C NMR (75 MHz, $CDCl_3$) of **5g**



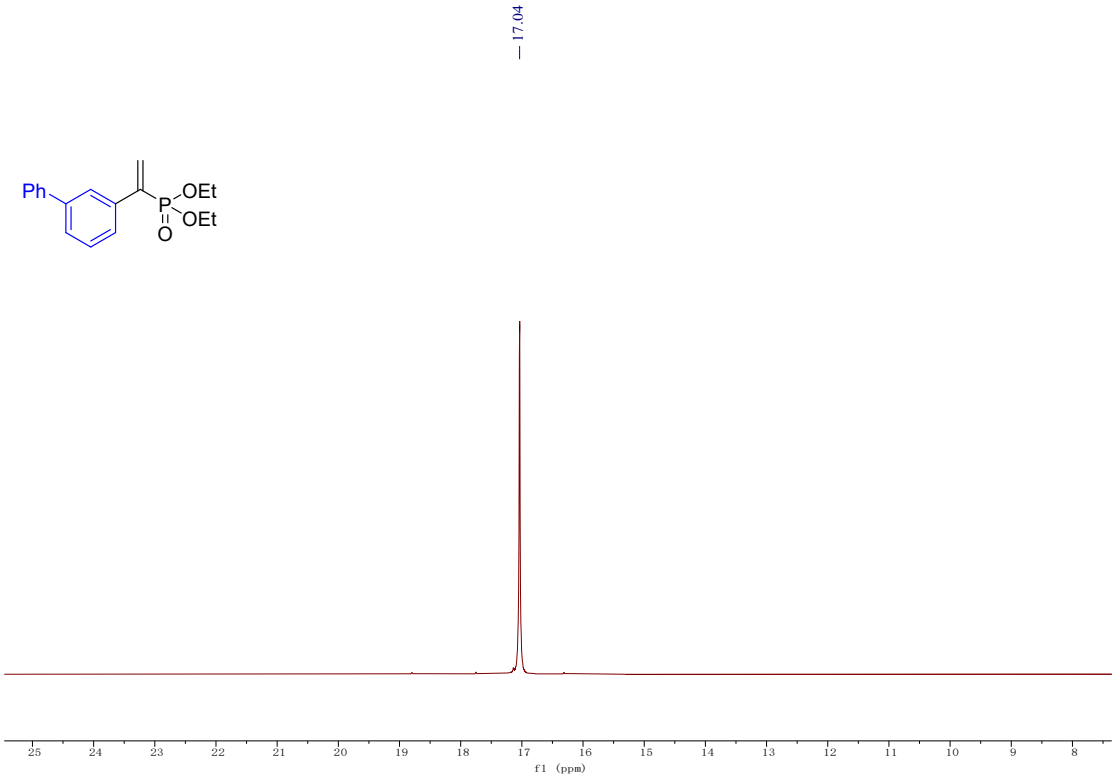
^{31}P NMR (121 MHz, $CDCl_3$) of **5g**



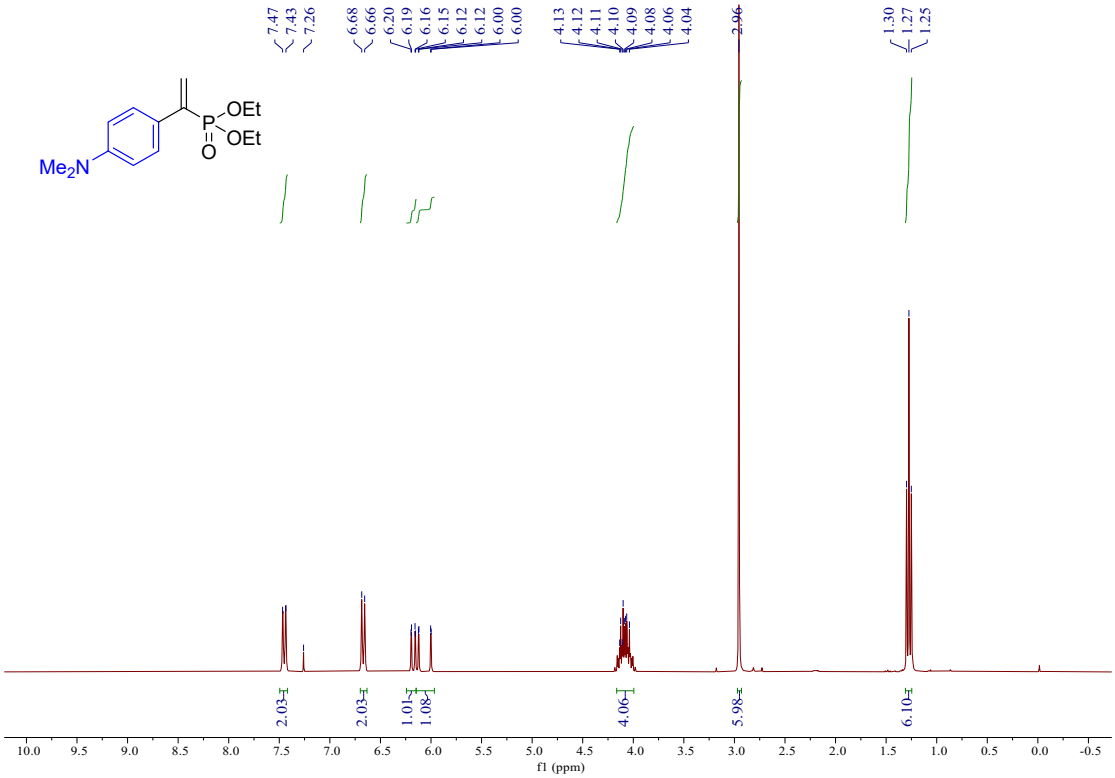
^{1}H NMR (300 MHz, $CDCl_3$) of **5h**



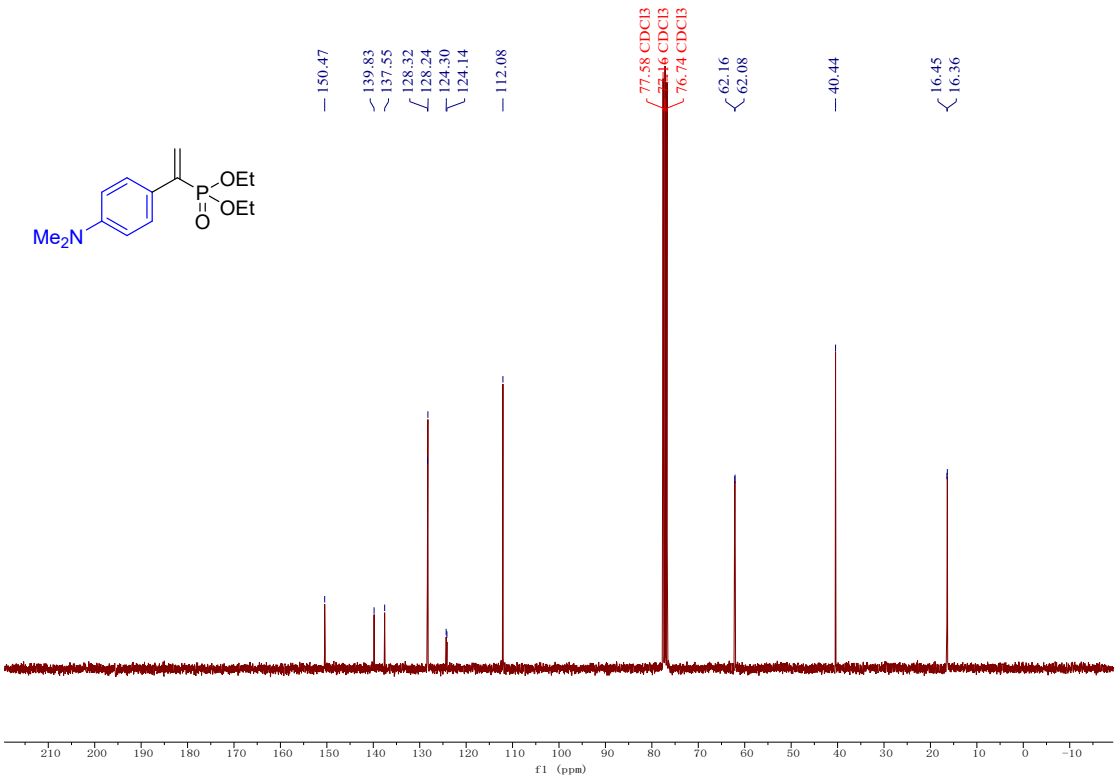
^{13}C NMR (75 MHz, $CDCl_3$) of **5h**



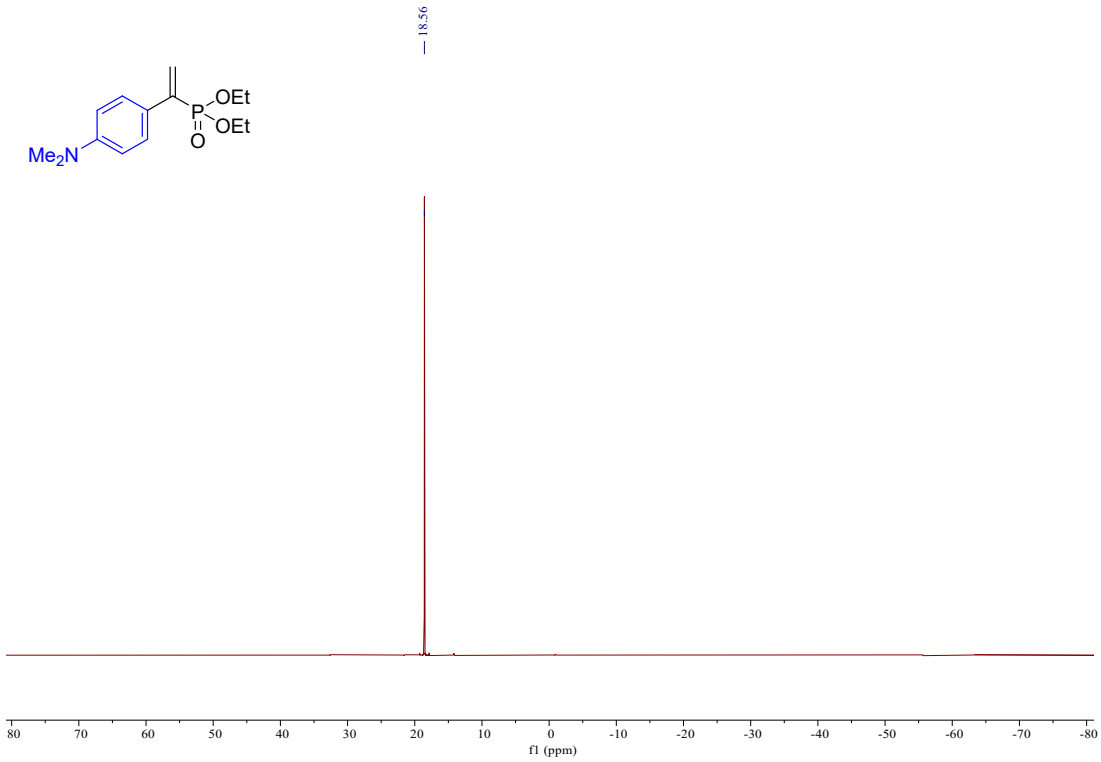
^{31}P NMR (121 MHz, $CDCl_3$) of **5h**



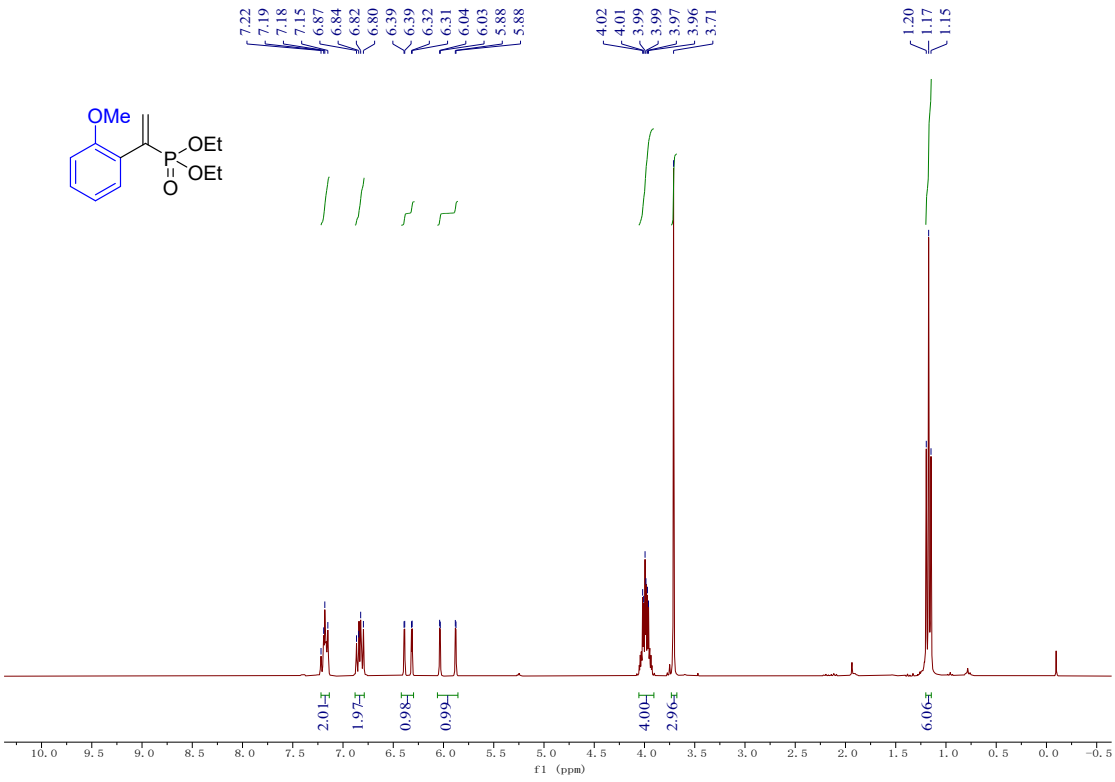
^{1}H NMR (300 MHz, $CDCl_3$) of **5i**



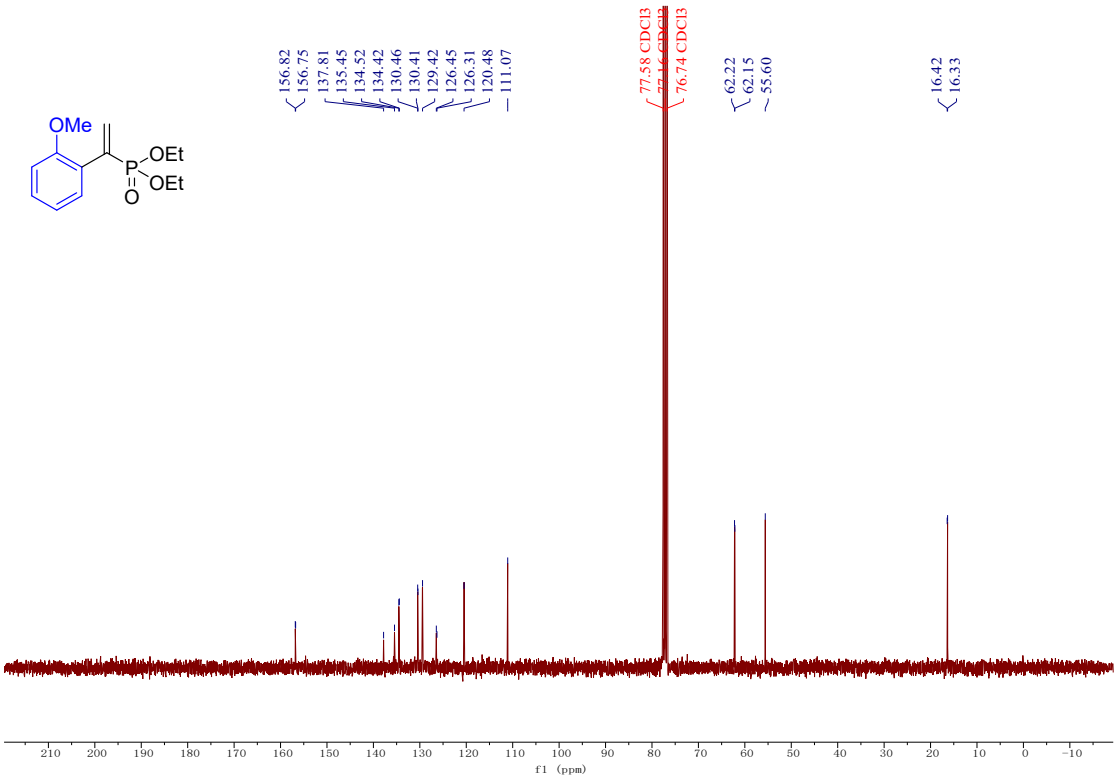
^{13}C NMR (75 MHz, $CDCl_3$) of **5i**



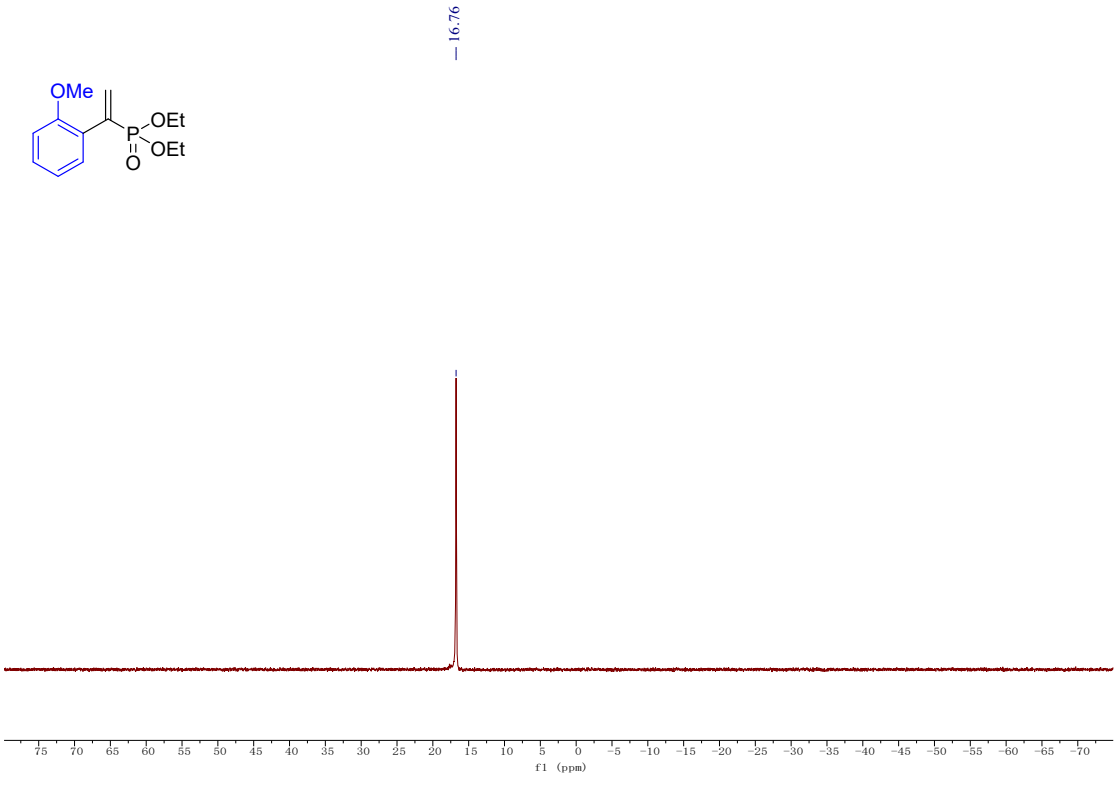
^{31}P NMR (121 MHz, $CDCl_3$) of **5i**



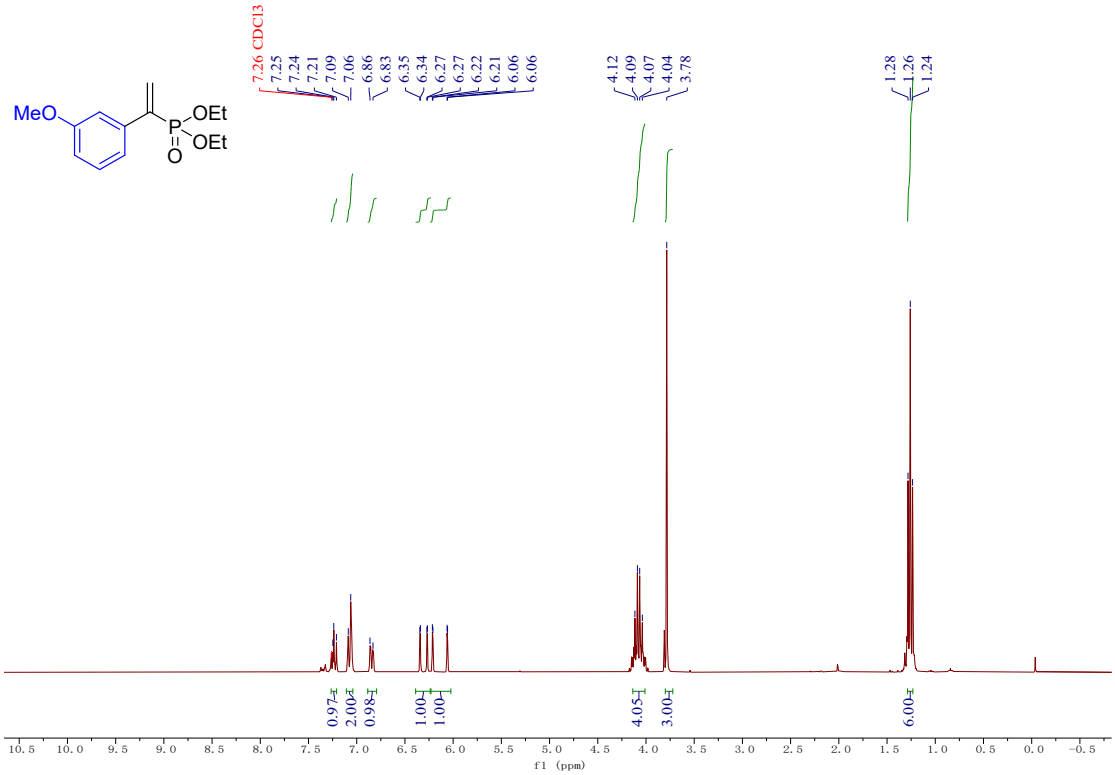
^{1}H NMR (300 MHz, $CDCl_3$) of **5j**



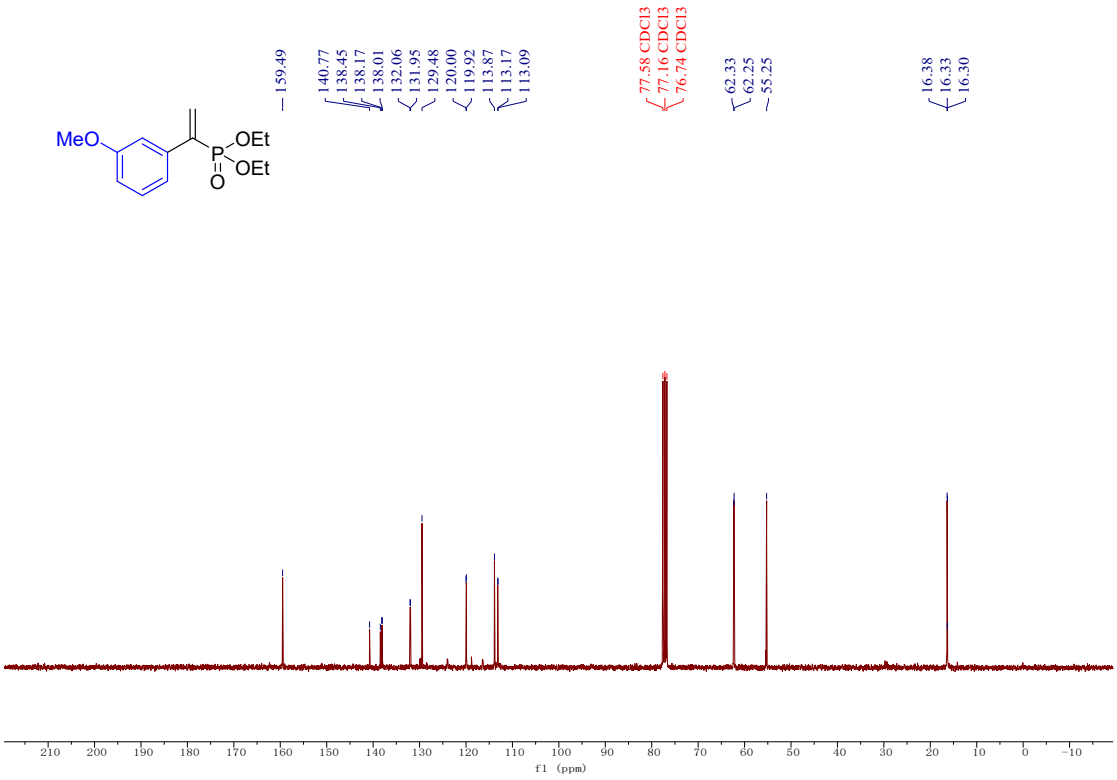
^{13}C NMR (75 MHz, $CDCl_3$) of **5j**



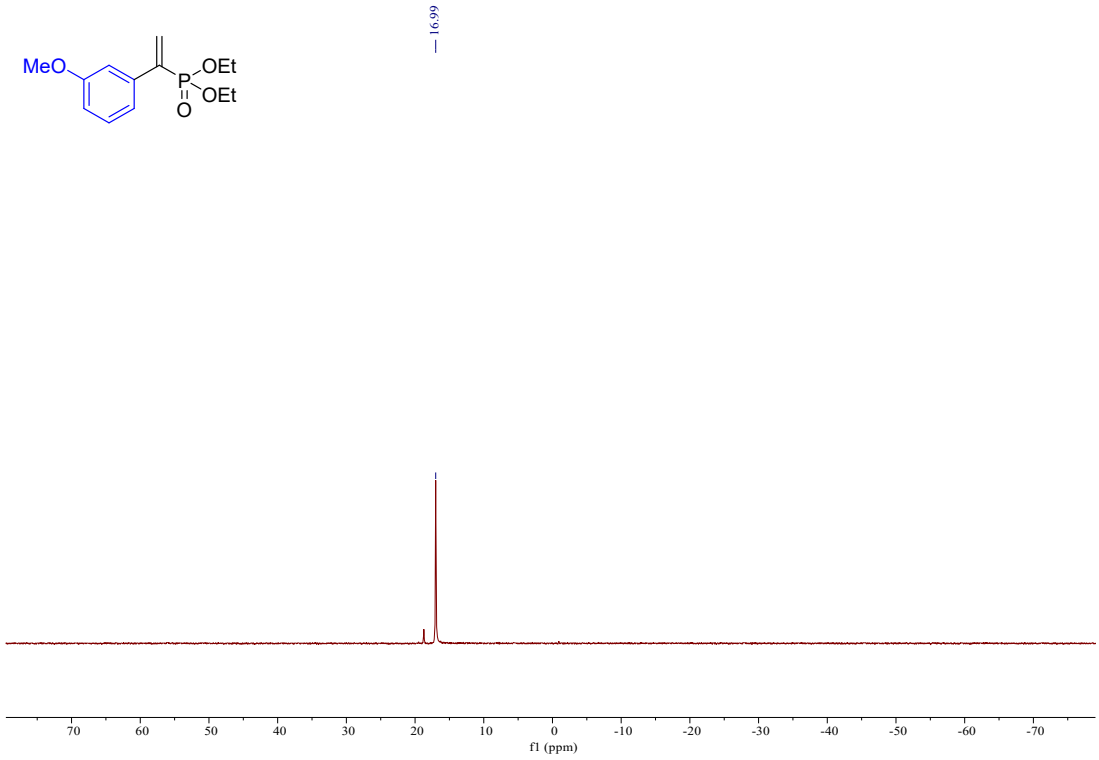
^{31}P NMR (121 MHz, $CDCl_3$) of **5j**



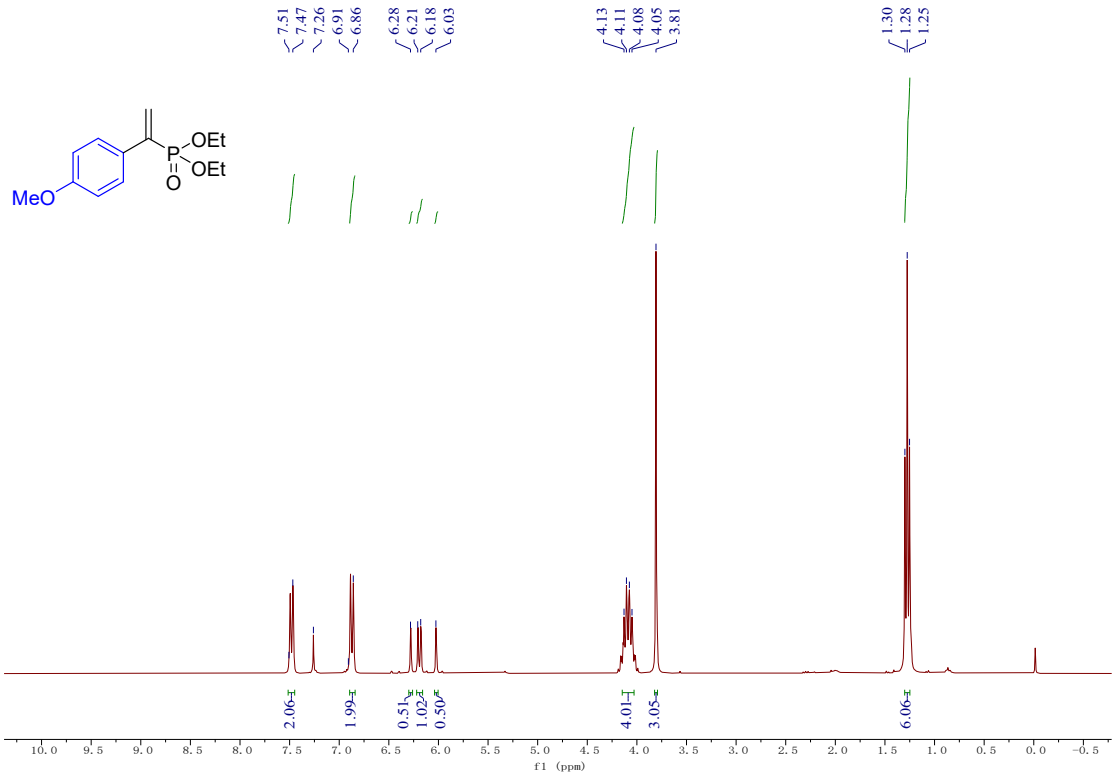
^{1}H NMR (300 MHz, $CDCl_3$) of **5k**



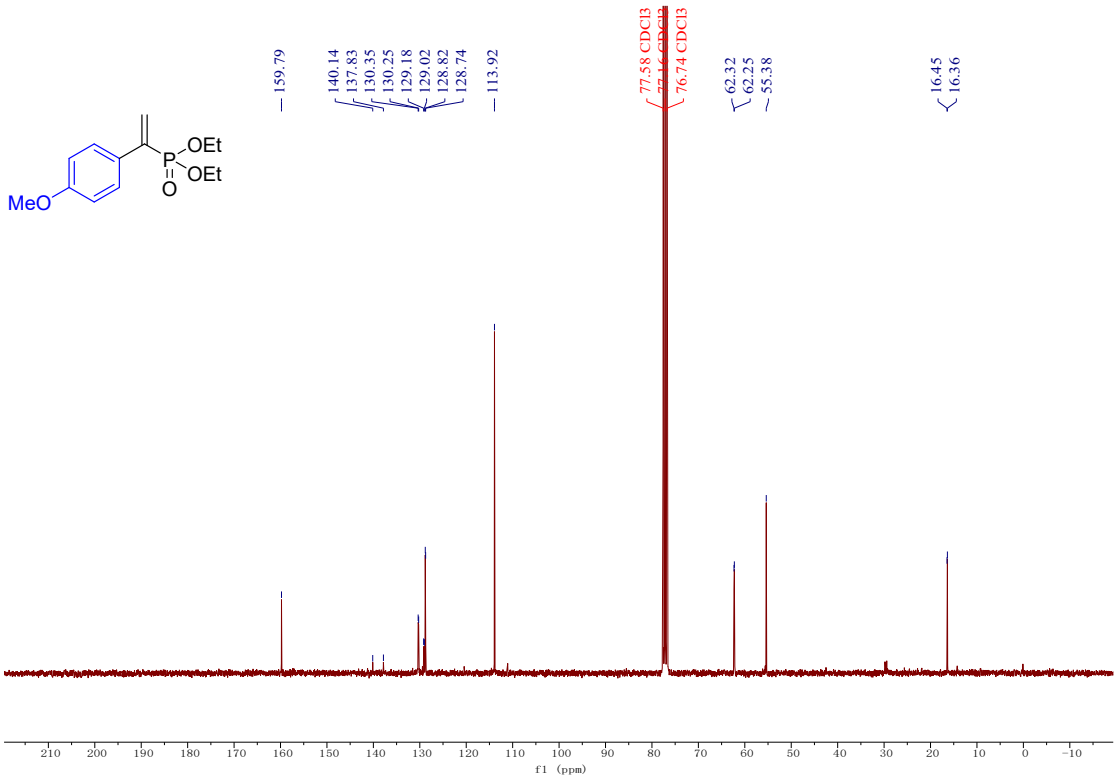
^{13}C NMR (75 MHz, $CDCl_3$) of **5k**



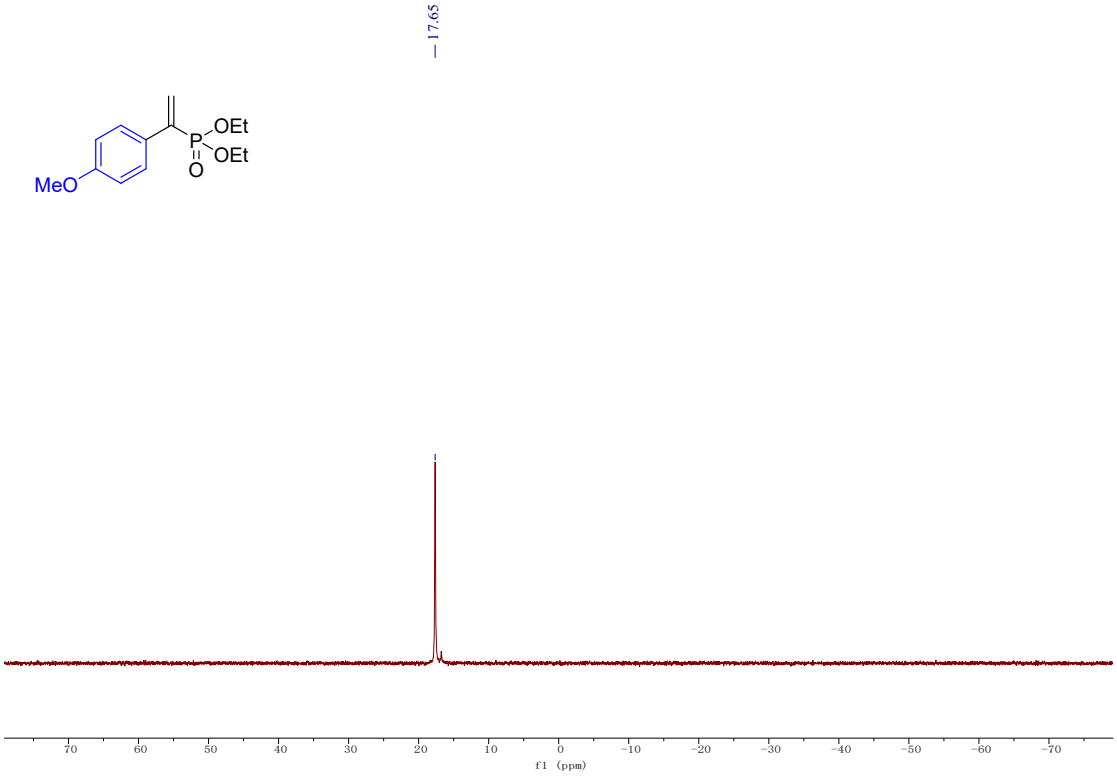
^{31}P NMR (121 MHz, $CDCl_3$) of **5k**



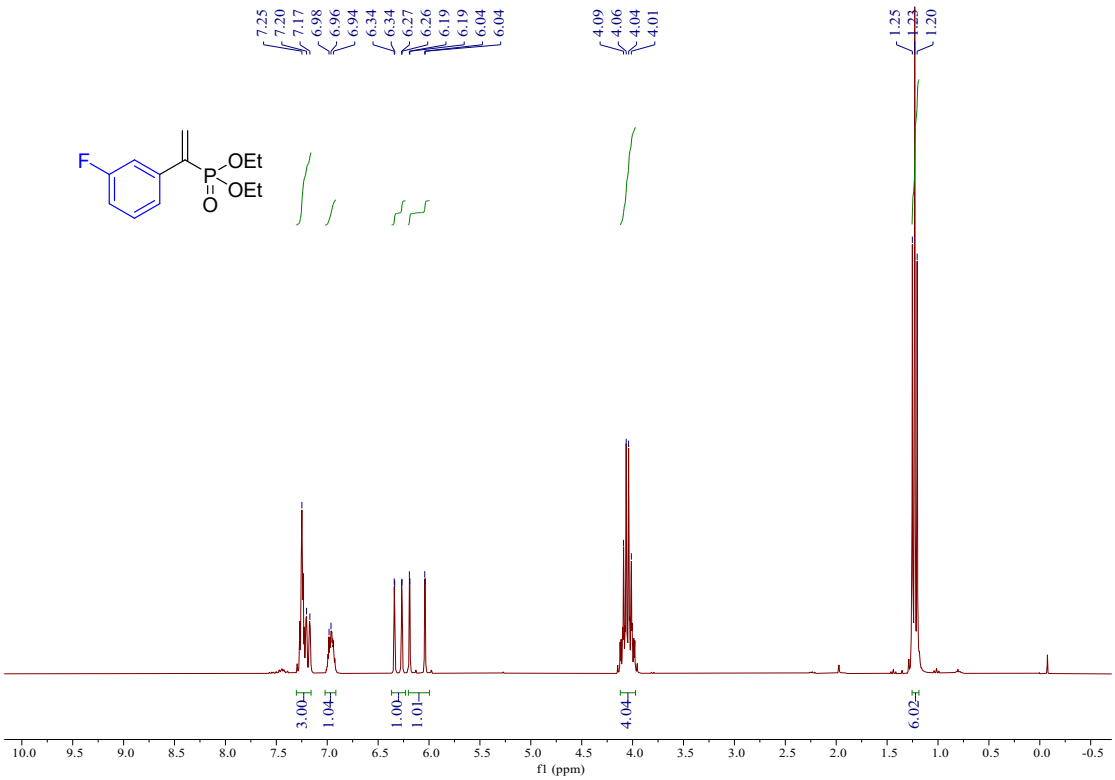
^{1}H NMR (300 MHz, $CDCl_3$) of **5l**



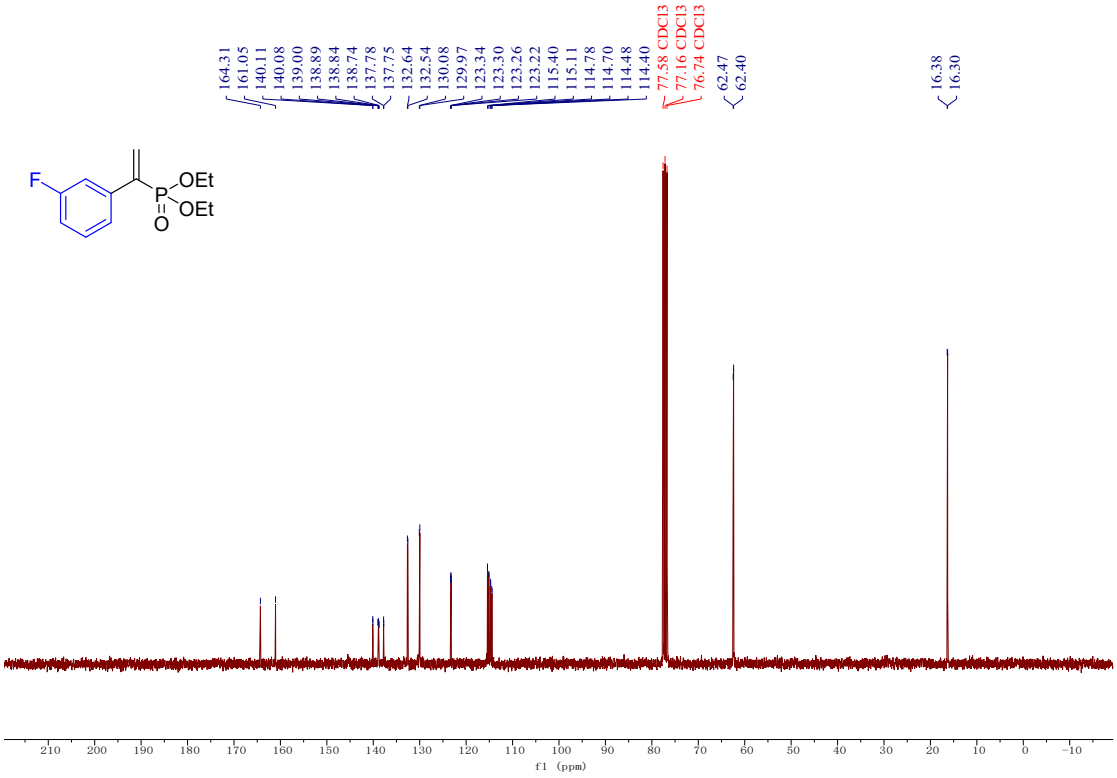
^{13}C NMR (75 MHz, $CDCl_3$) of **5l**



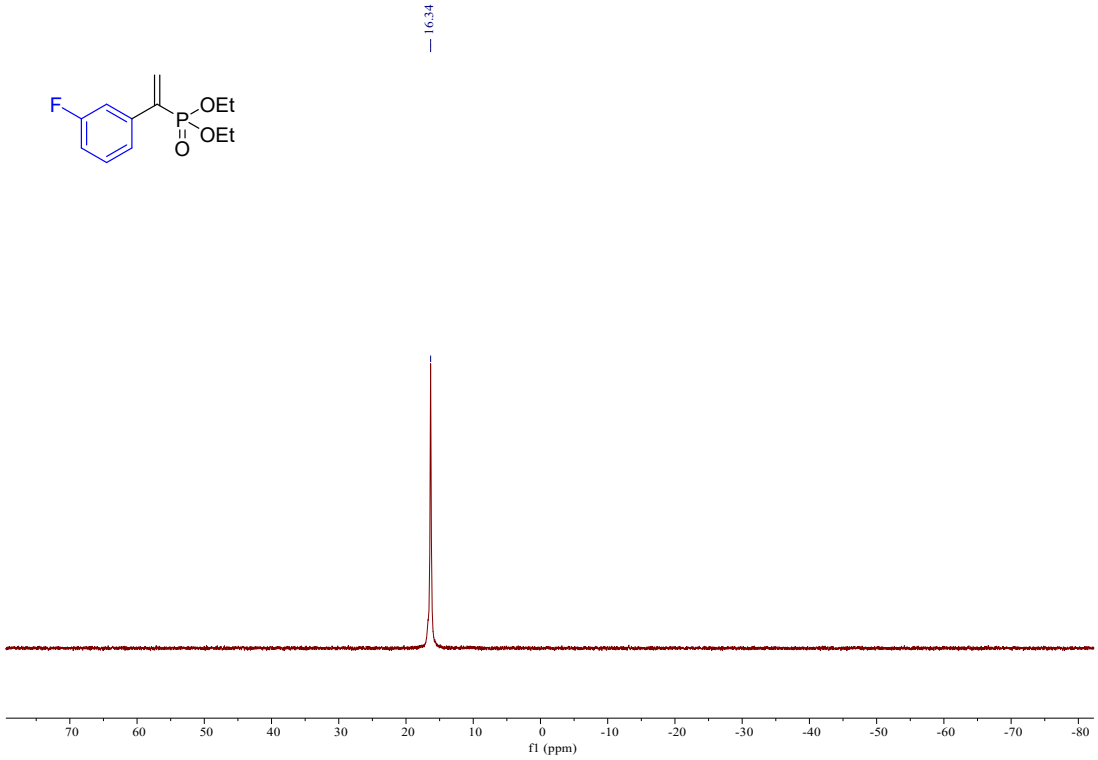
^{31}P NMR (121 MHz, $CDCl_3$) of **5l**



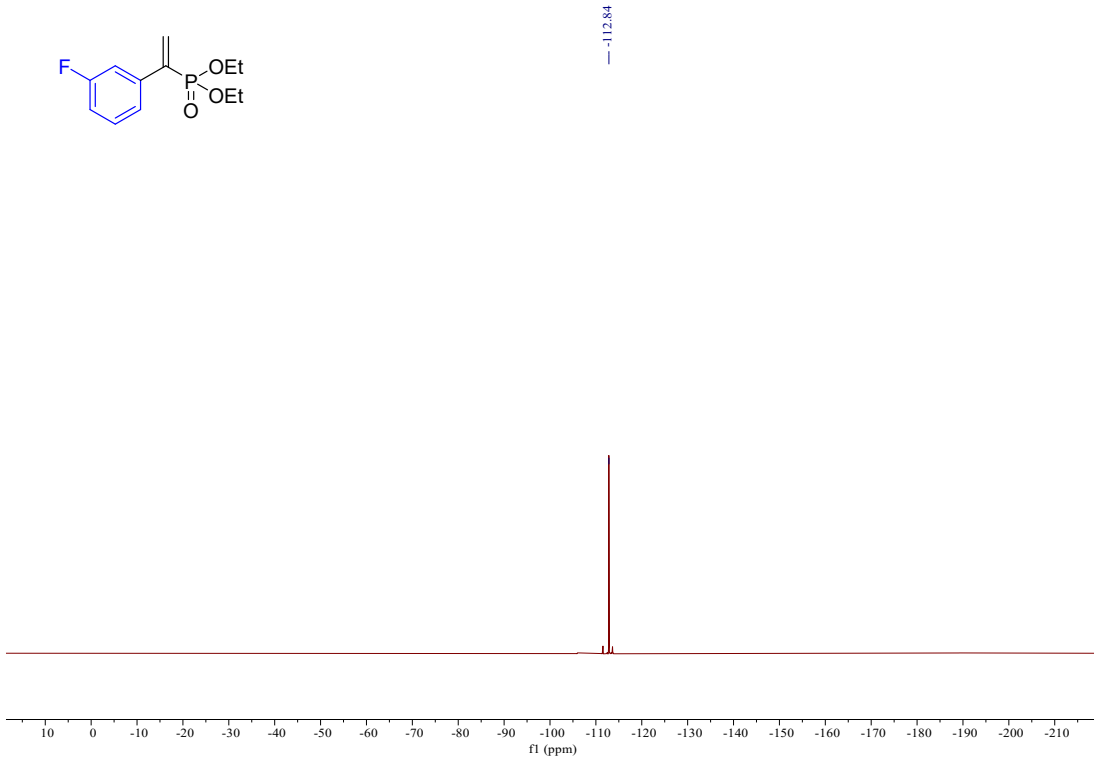
^{1}H NMR (300 MHz, $CDCl_3$) of **5m**



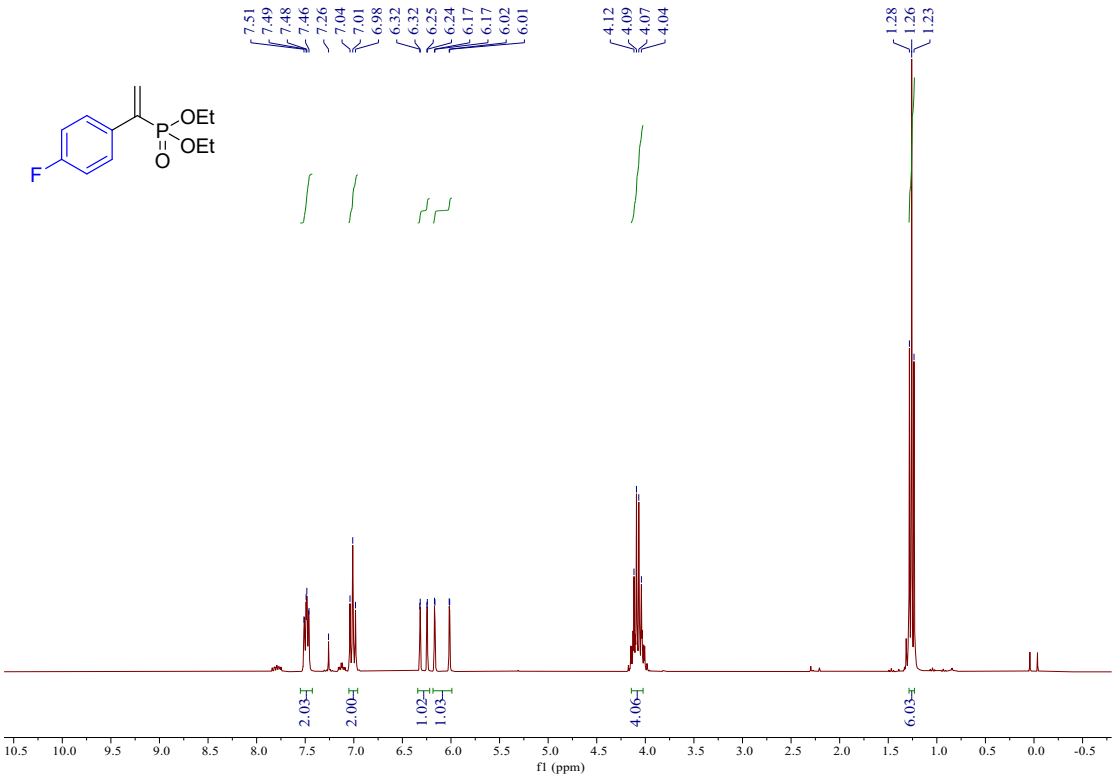
^{13}C NMR (75 MHz, $CDCl_3$) of **5m**



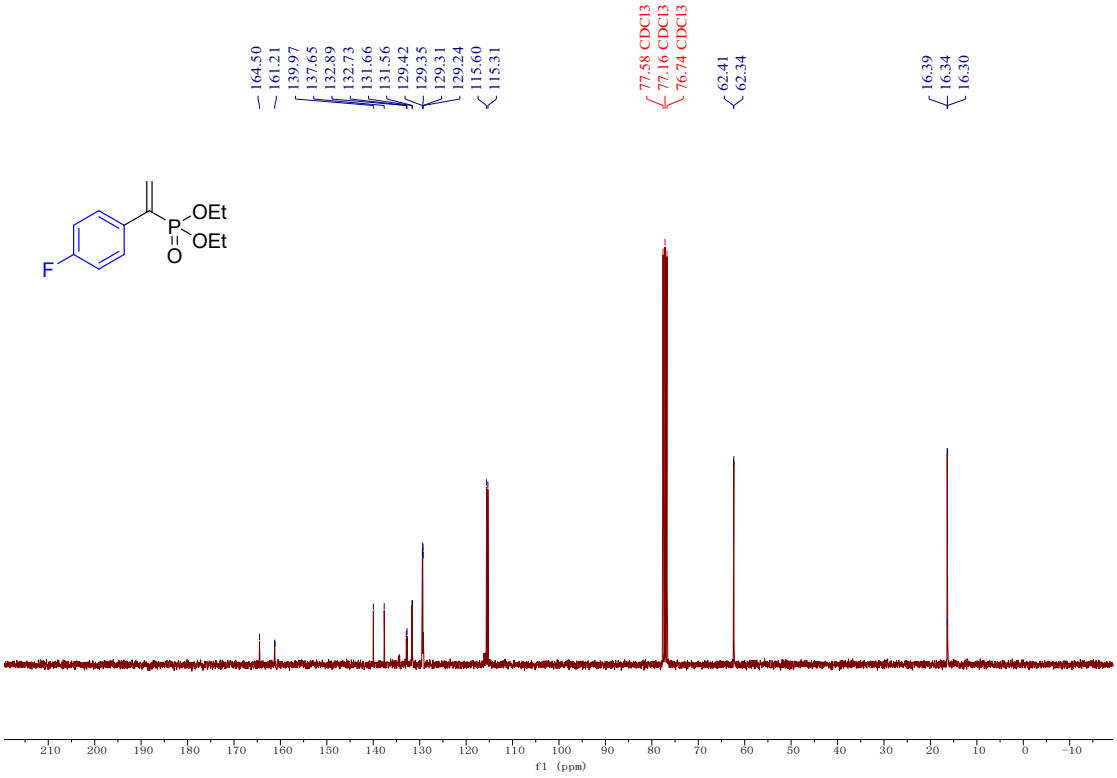
^{31}P NMR (121 MHz, $CDCl_3$) of **5m**



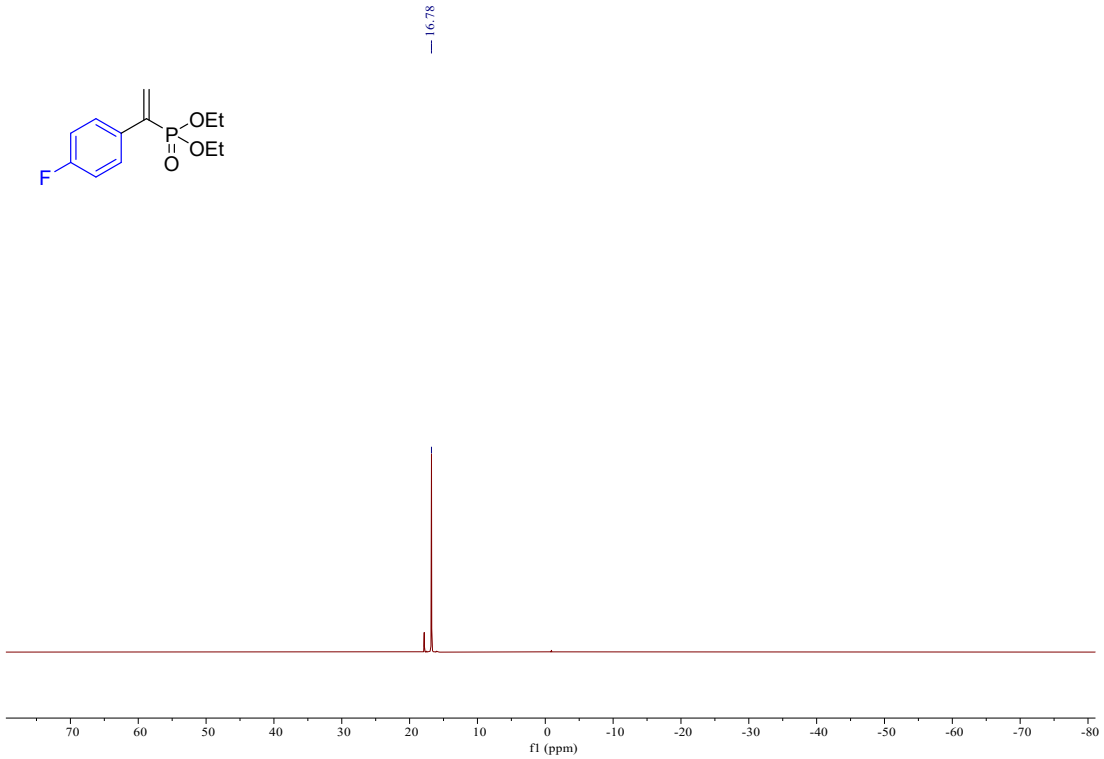
^{19}F NMR (282 MHz, $CDCl_3$) of **5m**



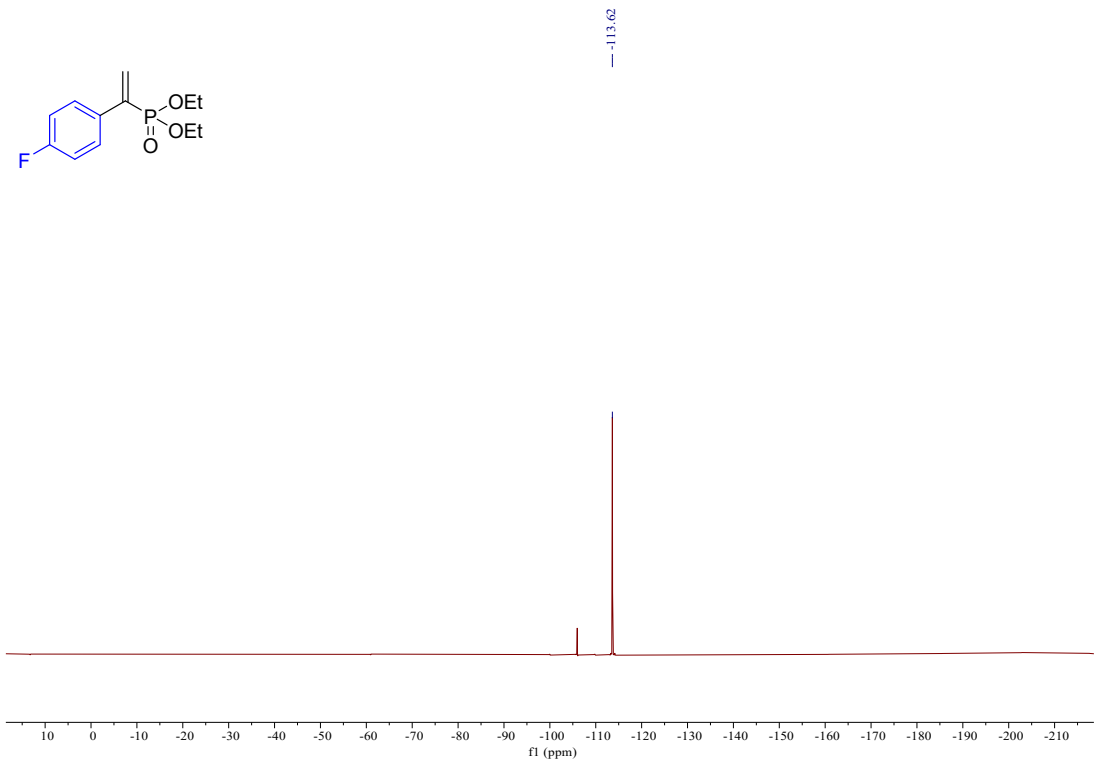
^{1}H NMR (300 MHz, $CDCl_3$) of **5n**



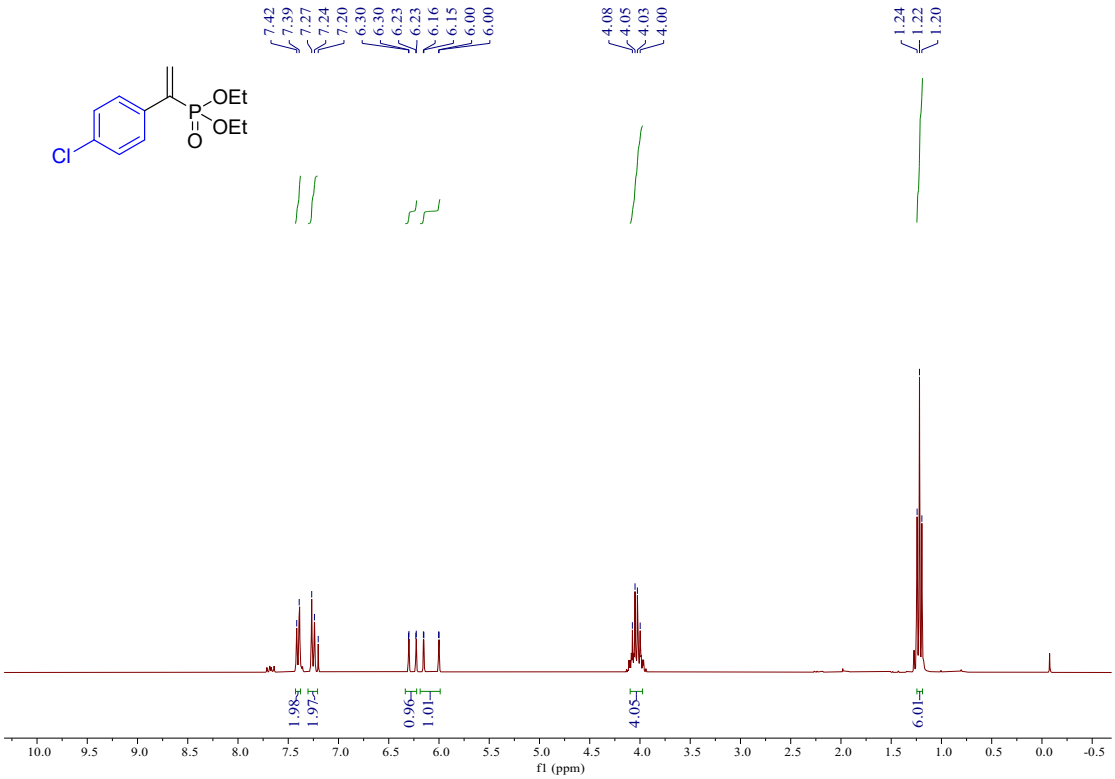
^{13}C NMR (75 MHz, $CDCl_3$) of **5n**



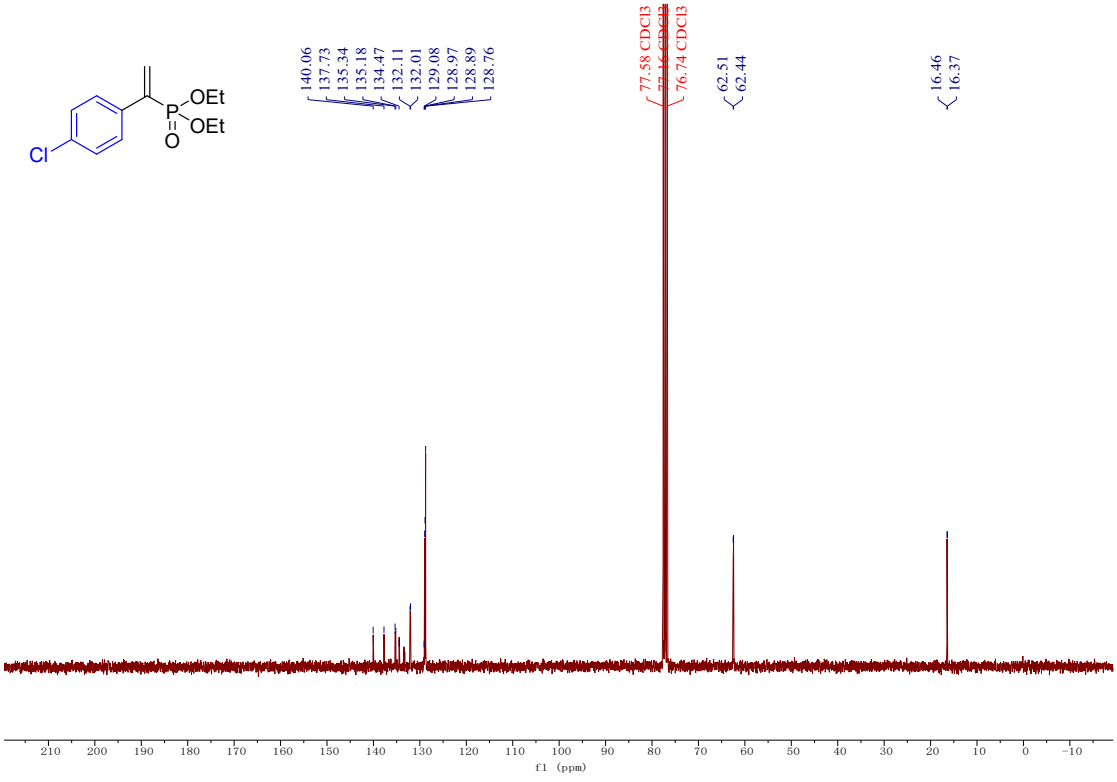
^{31}P NMR (121 MHz, $CDCl_3$) of **5n**



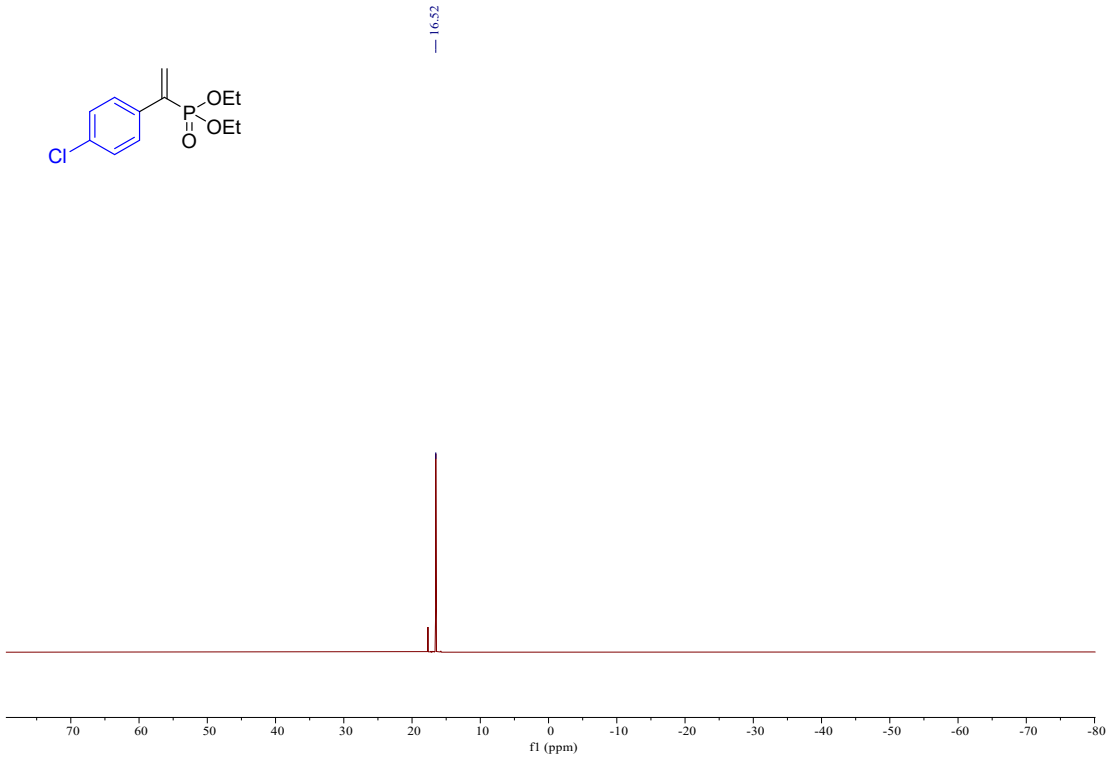
^{19}F NMR (282 MHz, $CDCl_3$) of **5n**



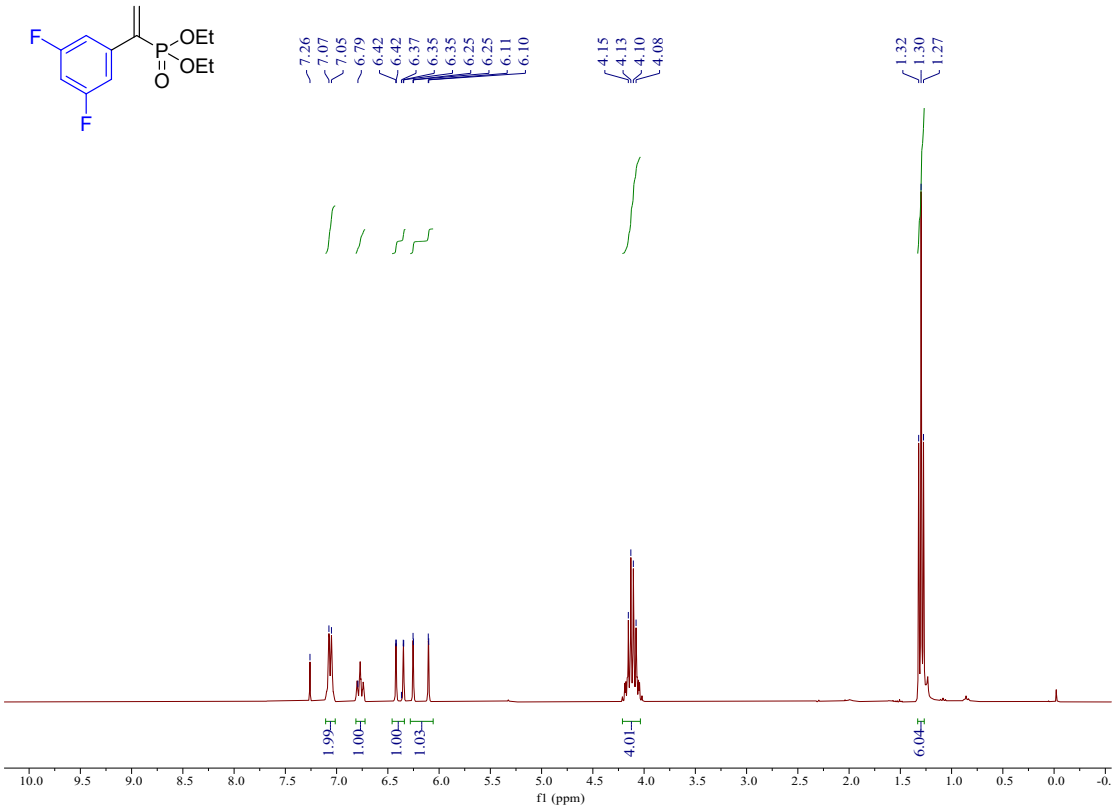
^{1}H NMR (300 MHz, $CDCl_3$) of **5o**



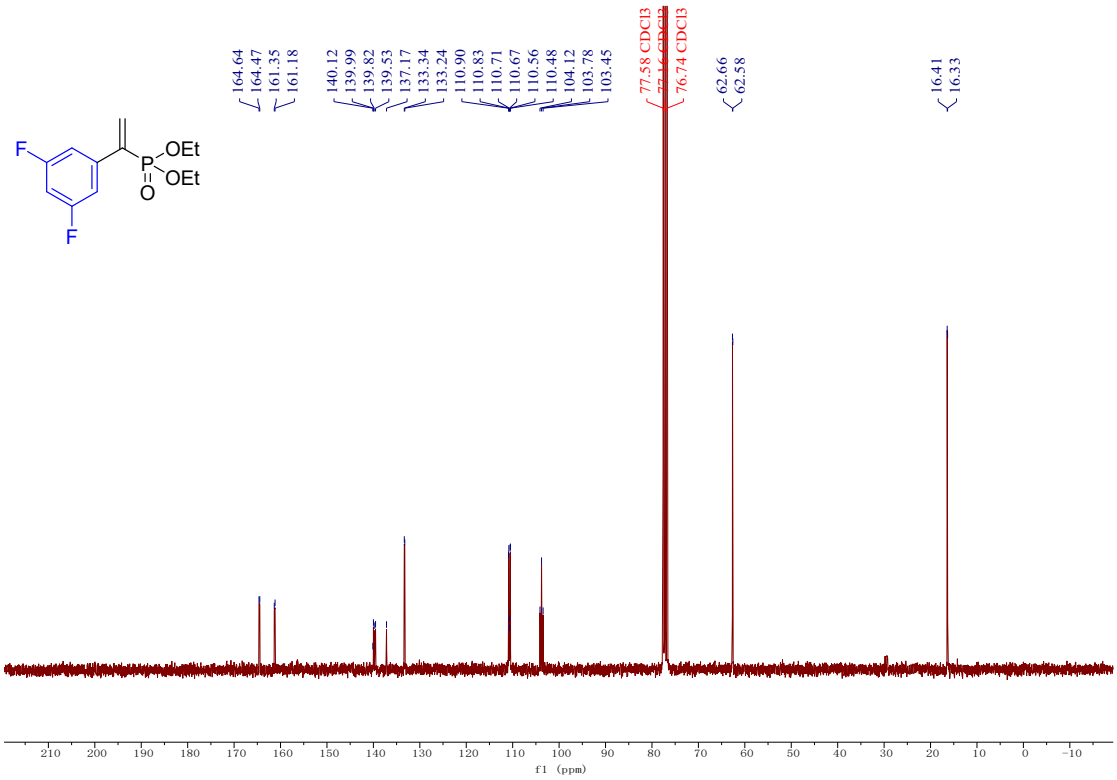
^{13}C NMR (75 MHz, $CDCl_3$) of **5o**



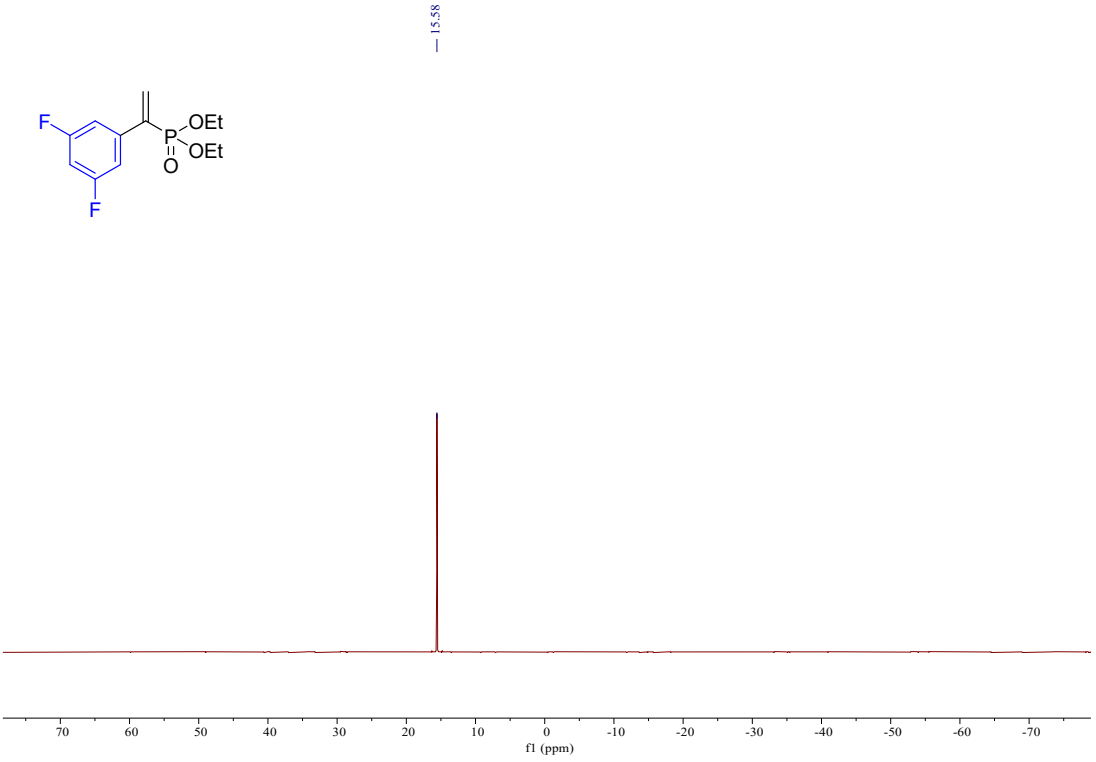
^{31}P NMR (121 MHz, $CDCl_3$) of **5o**



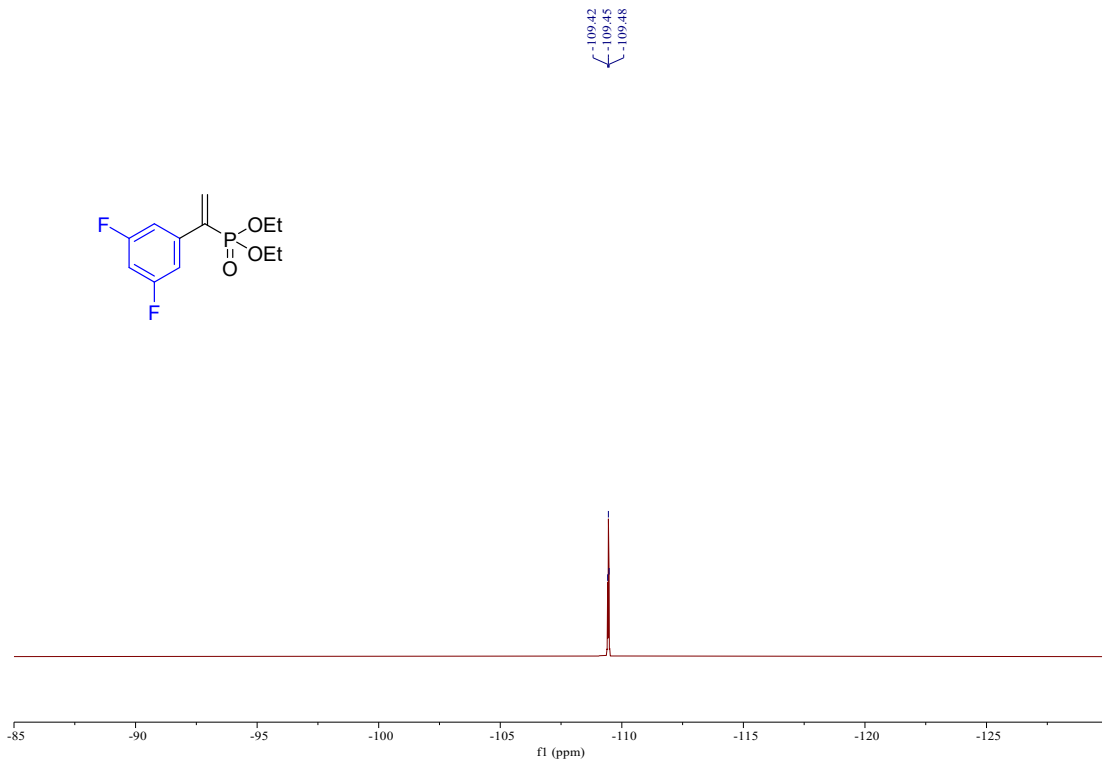
^{1}H NMR (300 MHz, $CDCl_3$) of **5p**



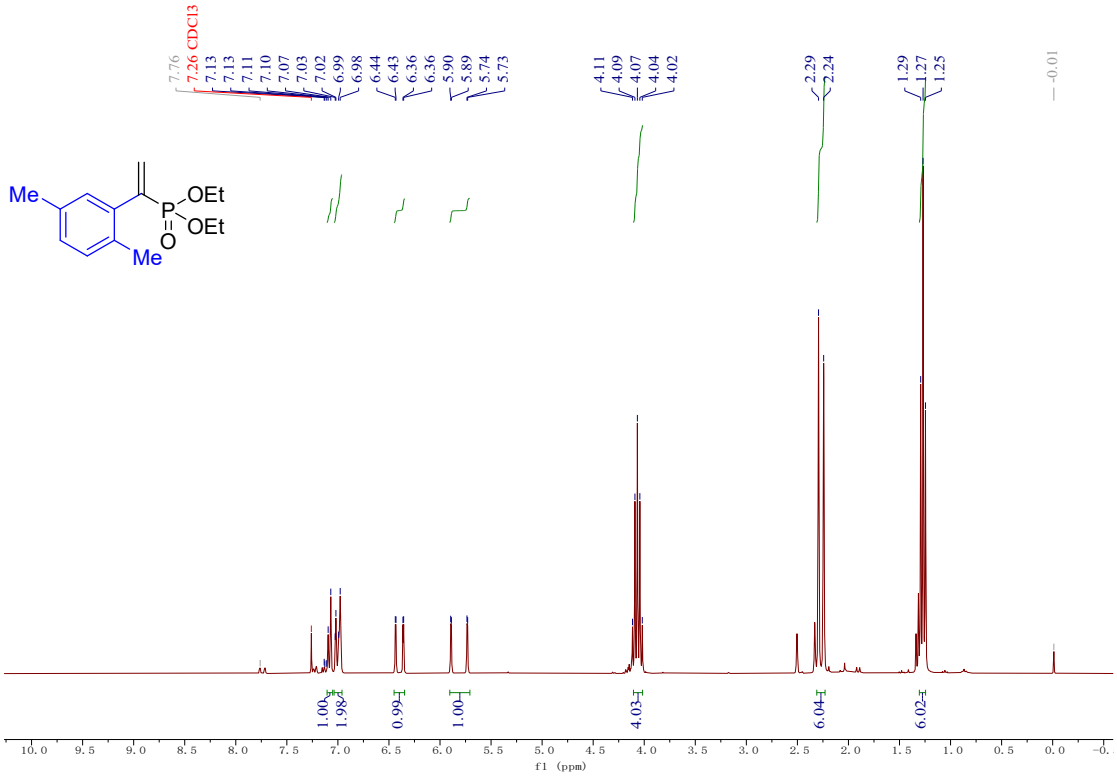
^{13}C NMR (75 MHz, $CDCl_3$) of **5p**



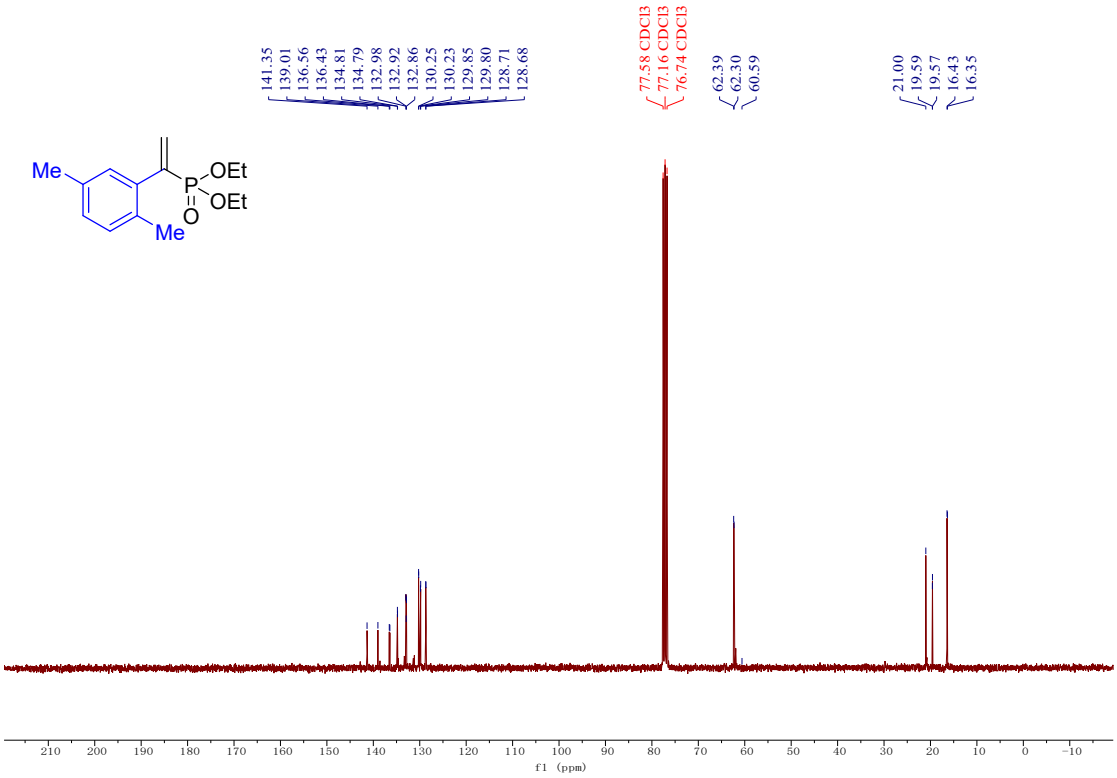
^{31}P NMR (121 MHz, $CDCl_3$) of **5p**



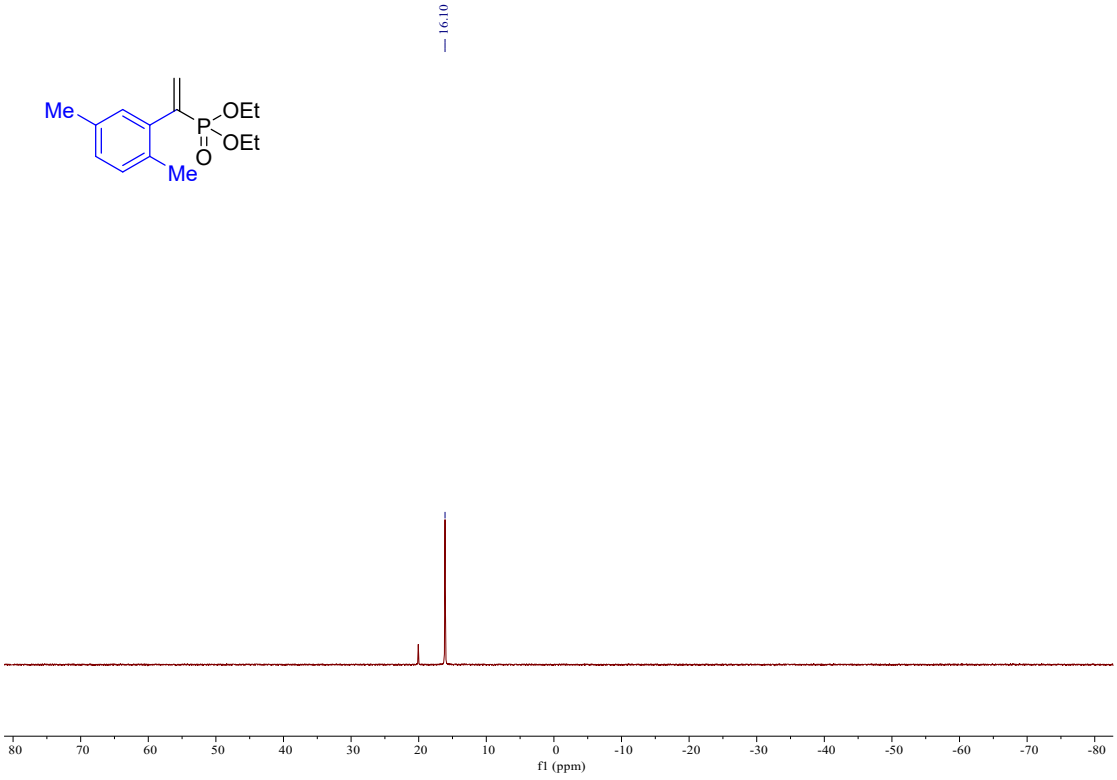
^{19}F NMR (282 MHz, $CDCl_3$) of **5p**



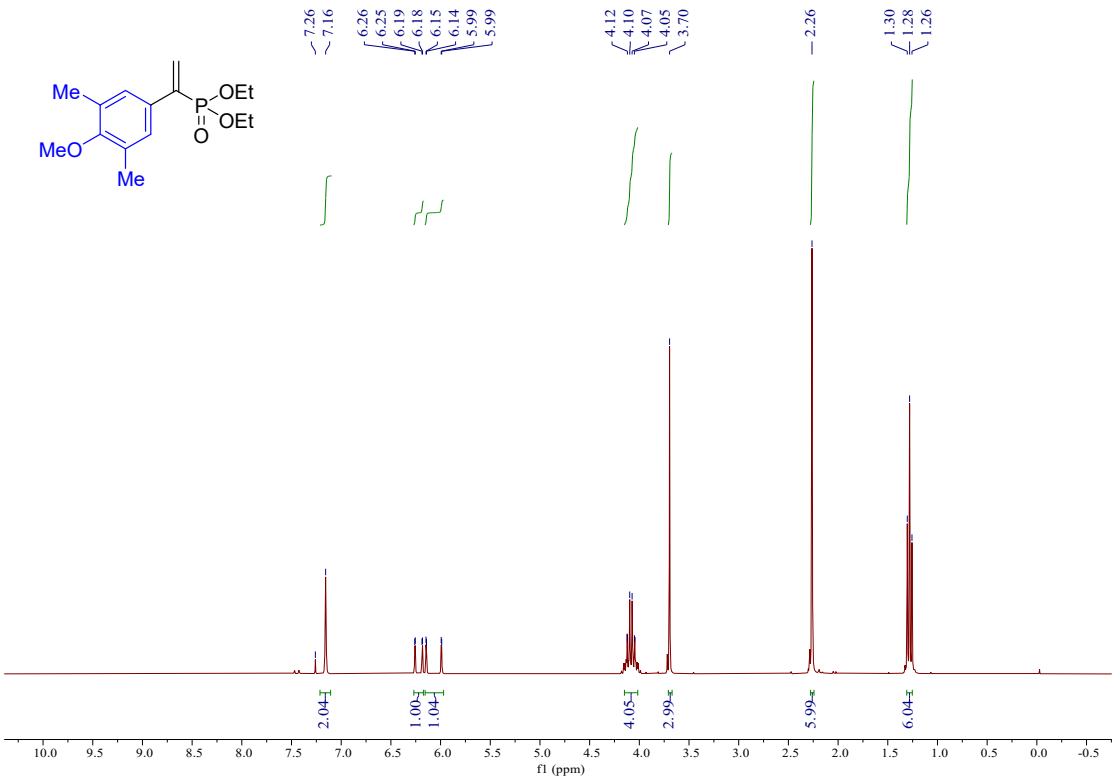
^{1}H NMR (300 MHz, $CDCl_3$) of **5q**



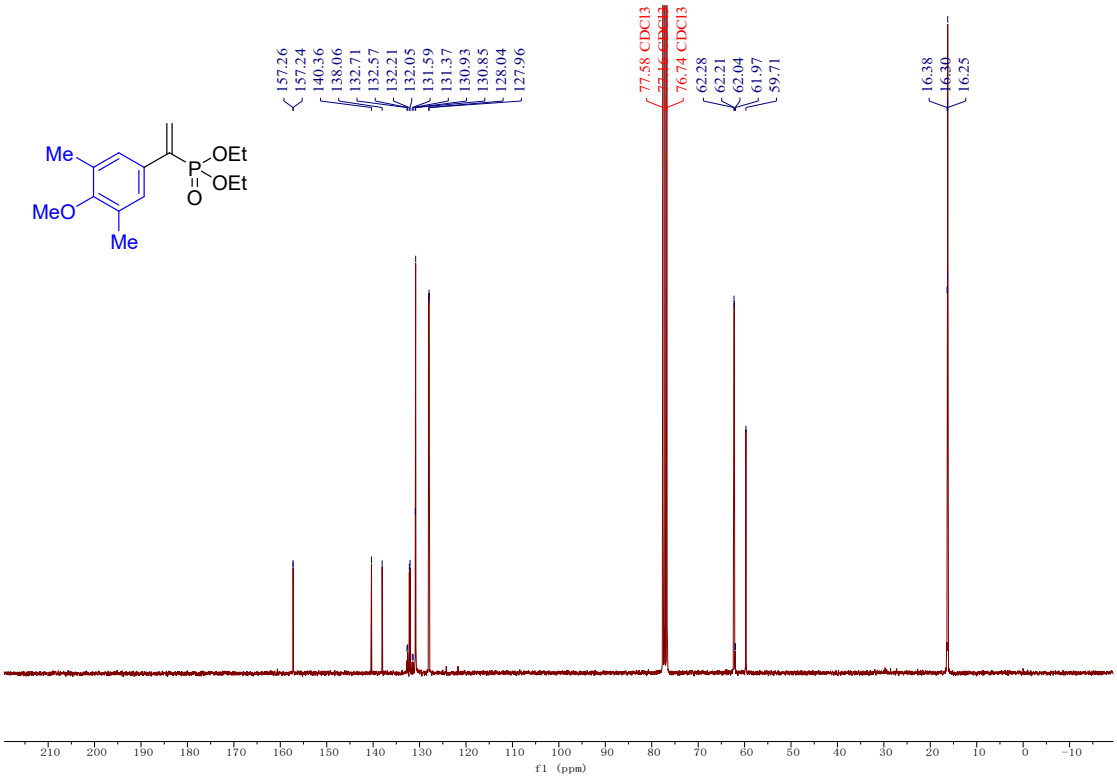
^{13}C NMR (75 MHz, $CDCl_3$) of **5q**



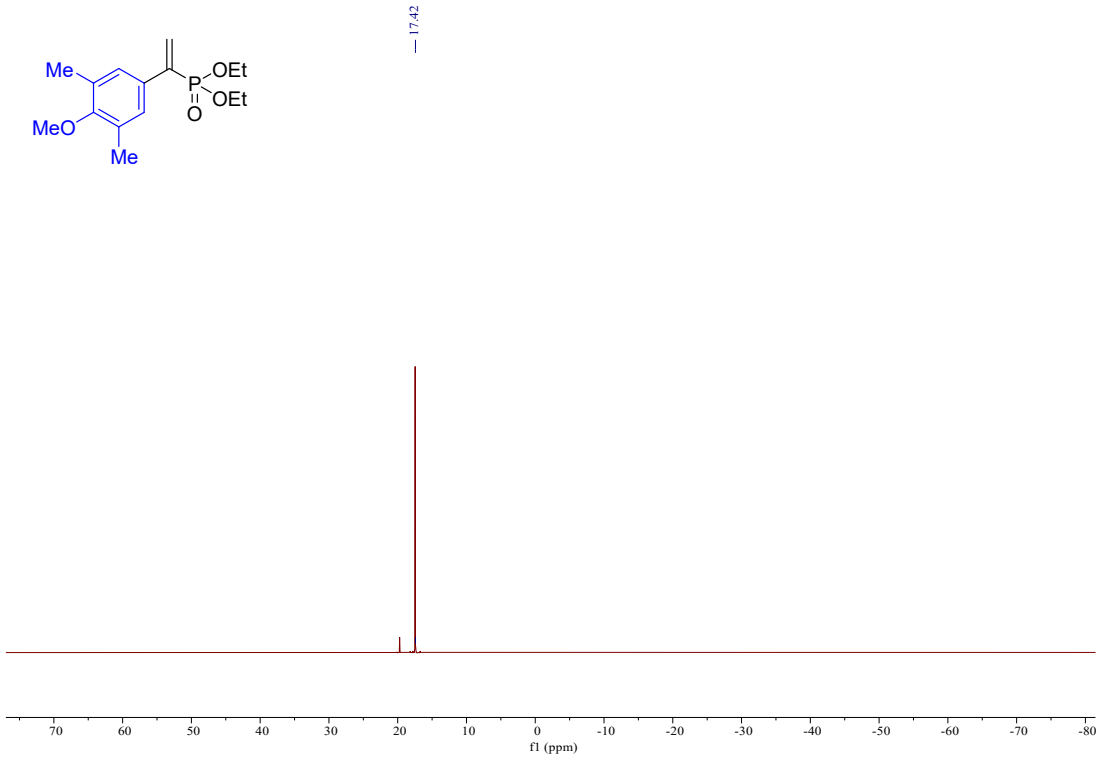
^{31}P NMR (121 MHz, $CDCl_3$) of **5q**



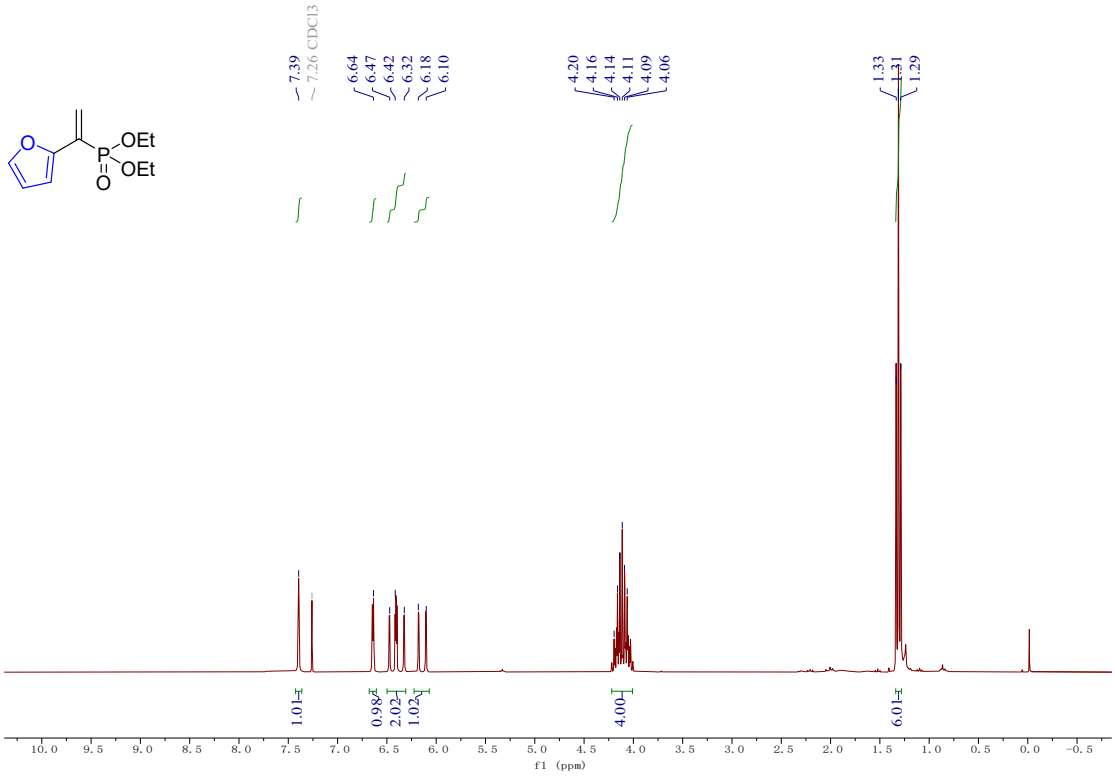
^{1}H NMR (300 MHz, $CDCl_3$) of **5r**



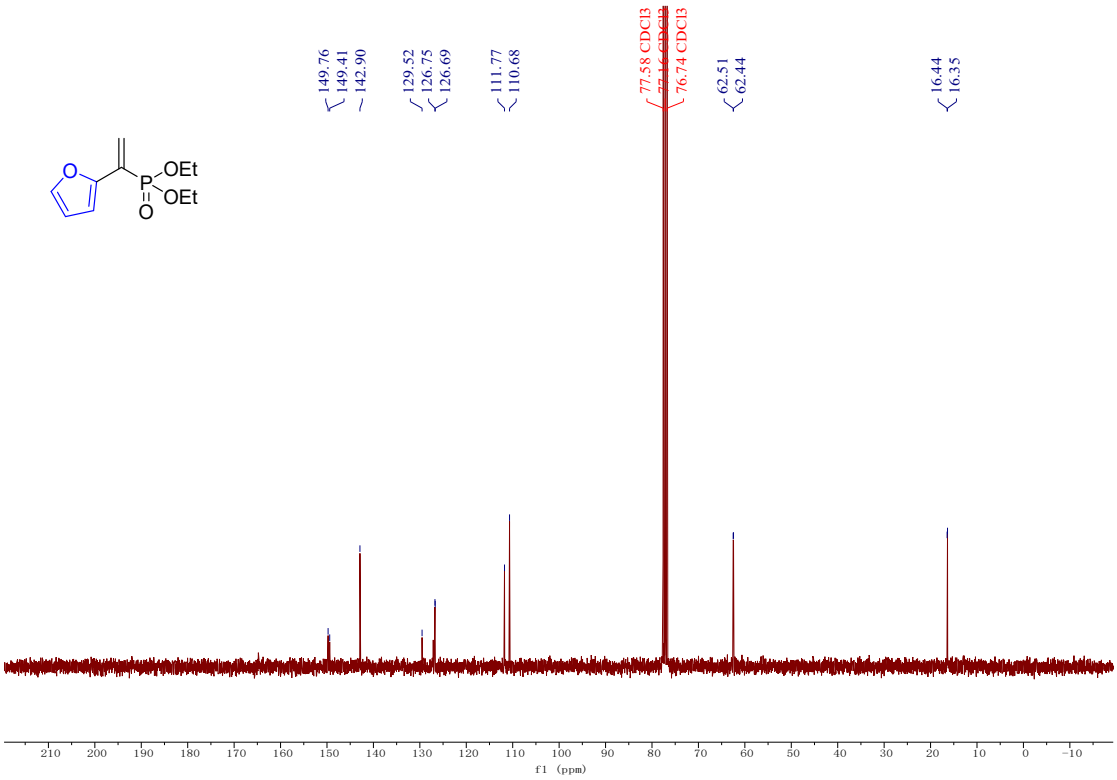
^{13}C NMR (75 MHz, $CDCl_3$) of **5r**



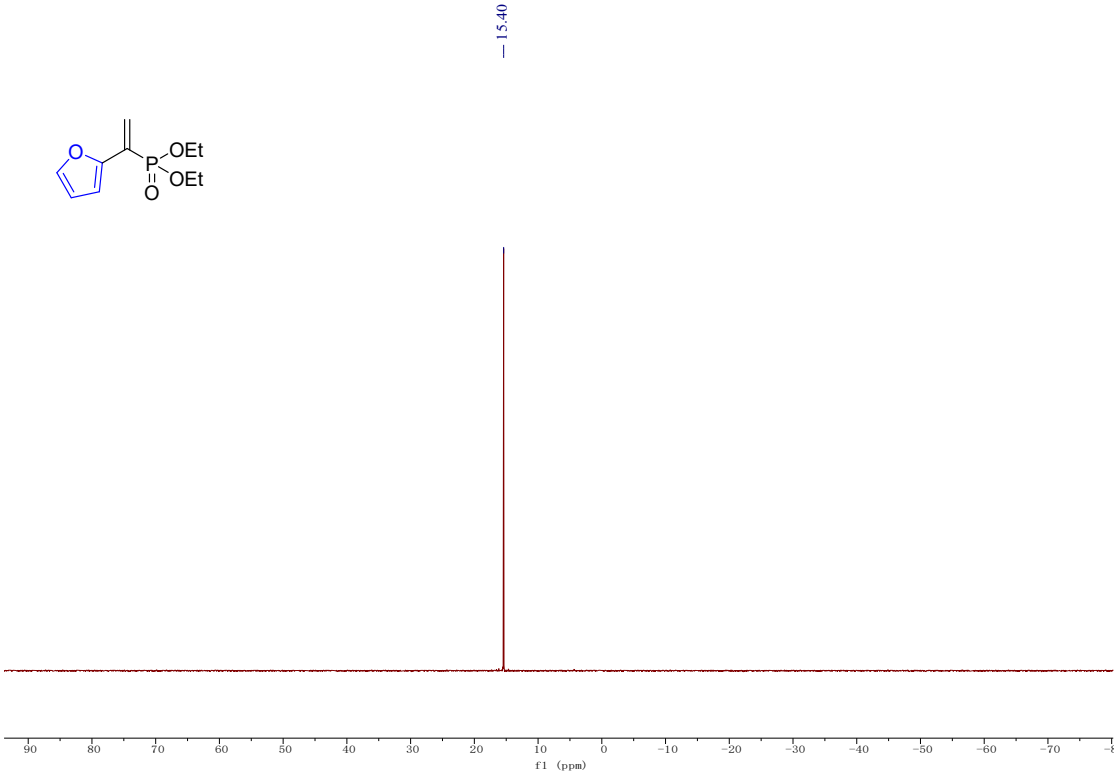
^{31}P NMR (121 MHz, $CDCl_3$) of **5r**



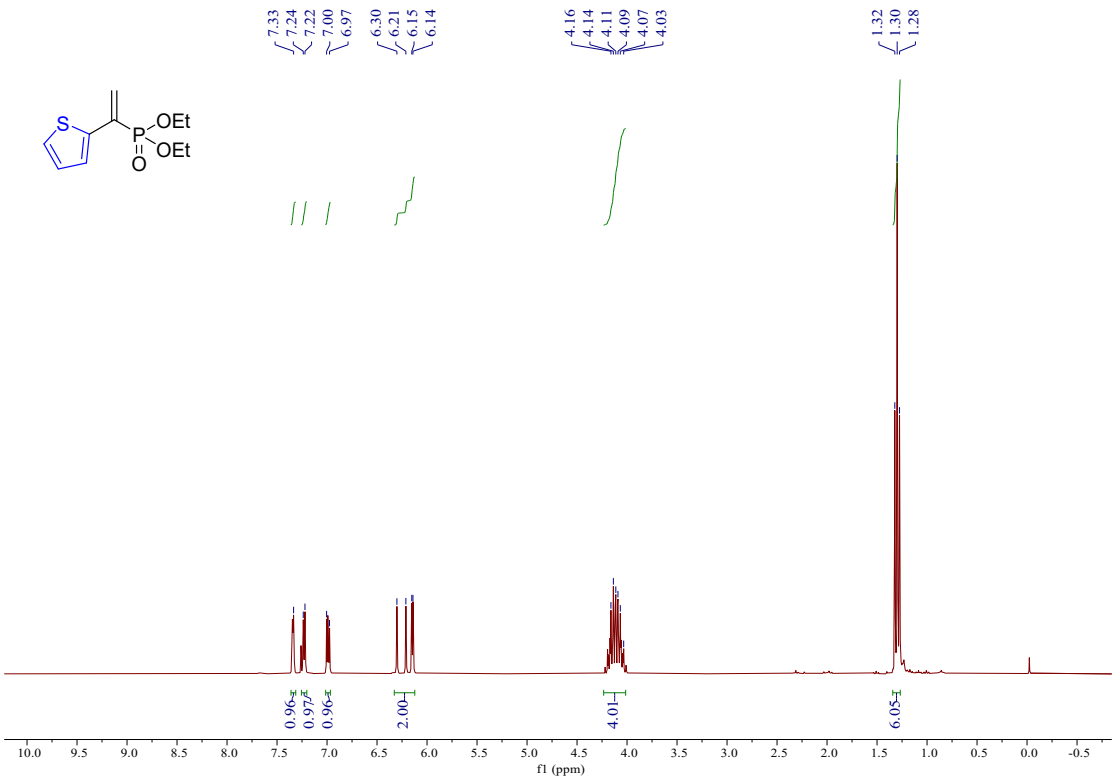
^{1}H NMR (300 MHz, $CDCl_3$) of **5s**



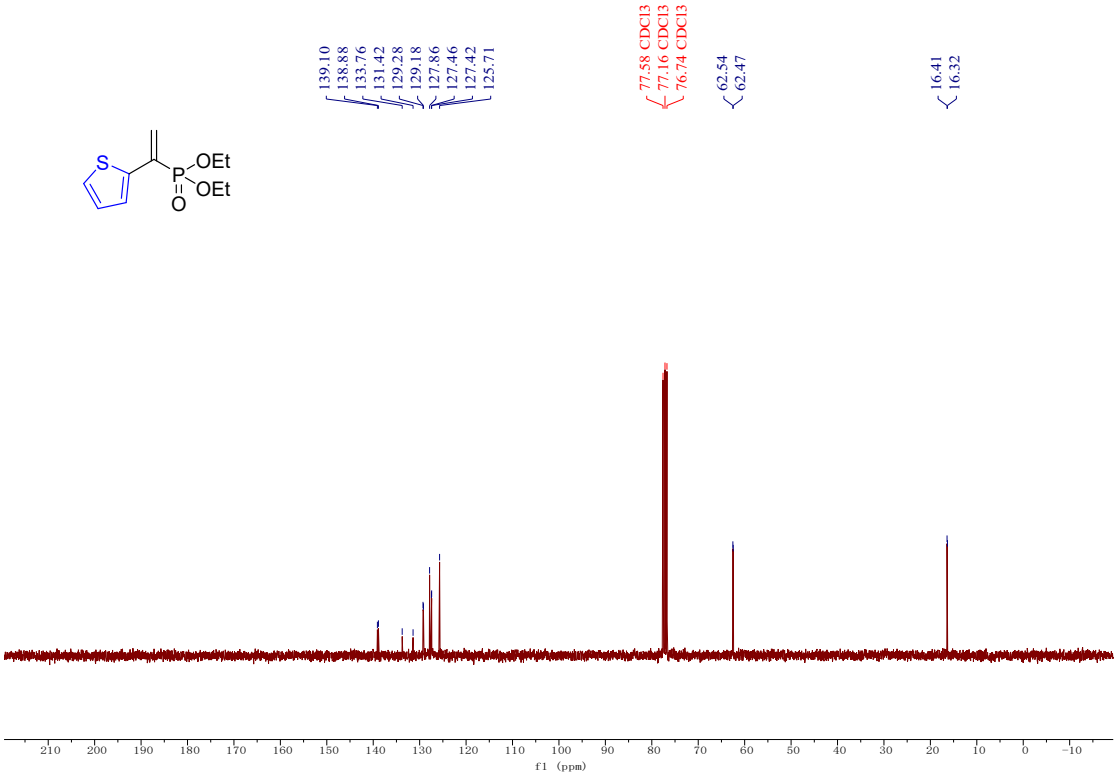
^{13}C NMR (75 MHz, $CDCl_3$) of **5s**



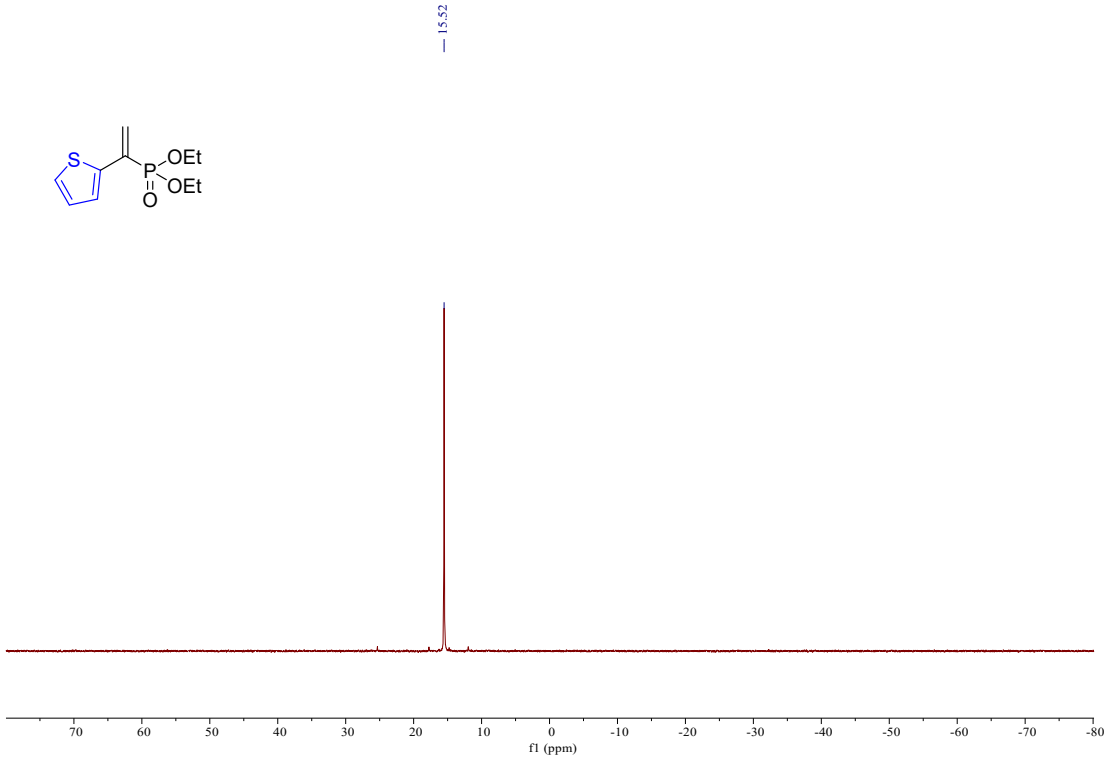
^{31}P NMR (121 MHz, $CDCl_3$) of **5s**



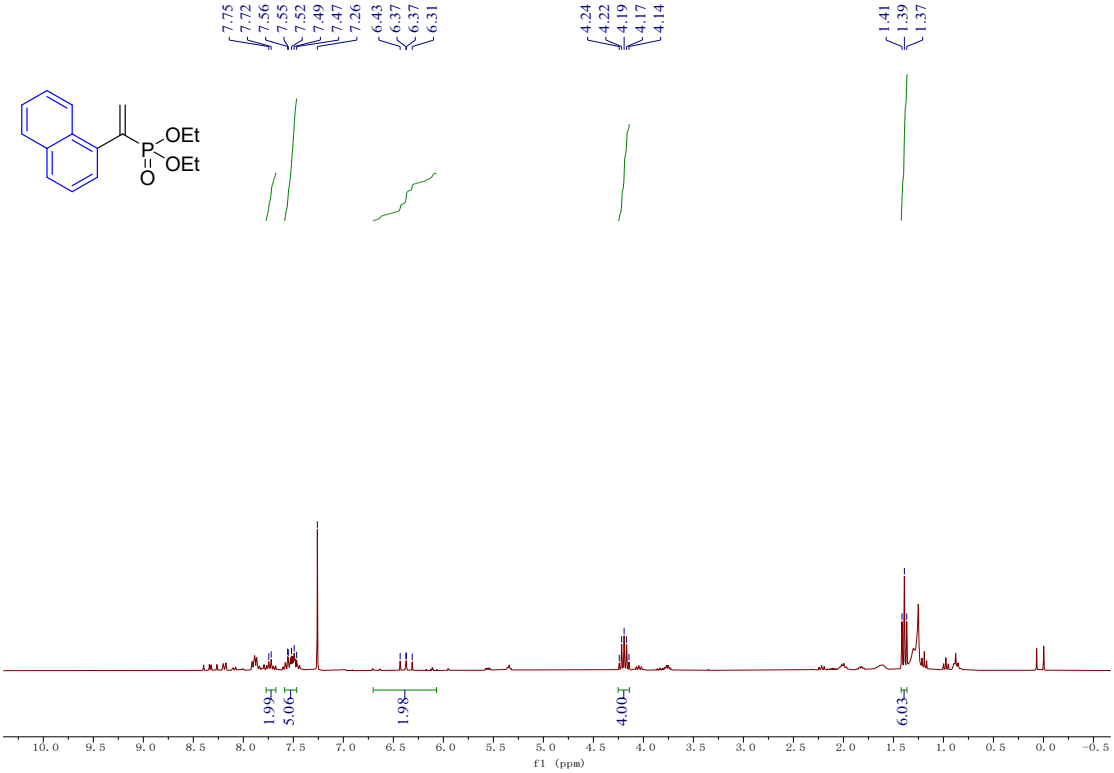
^{1}H NMR (300 MHz, $CDCl_3$) of **5t**



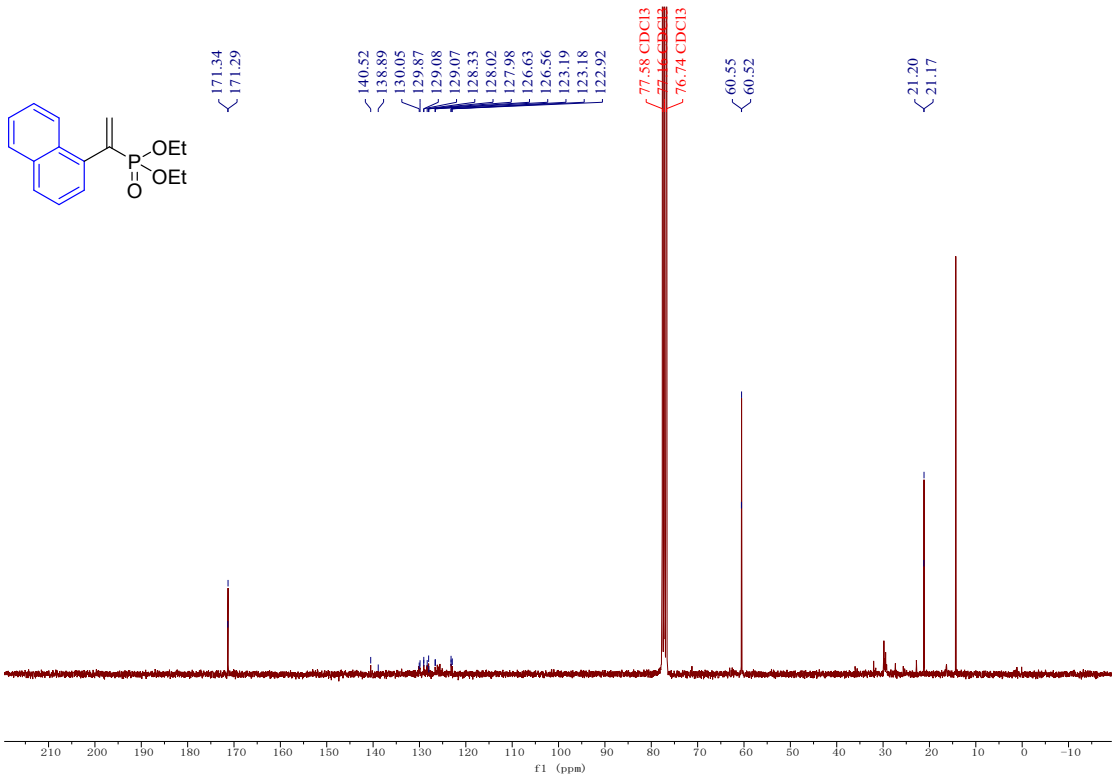
^{13}C NMR (75 MHz, $CDCl_3$) of **5t**



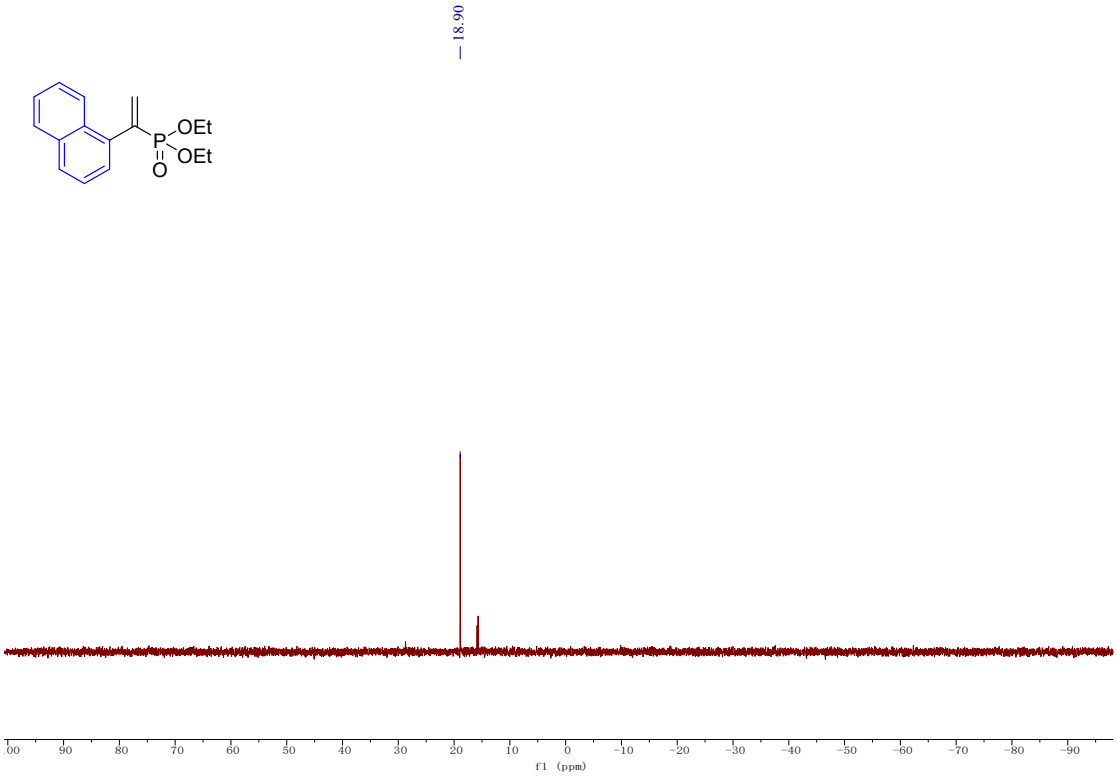
^{31}P NMR (121 MHz, $CDCl_3$) of **5t**



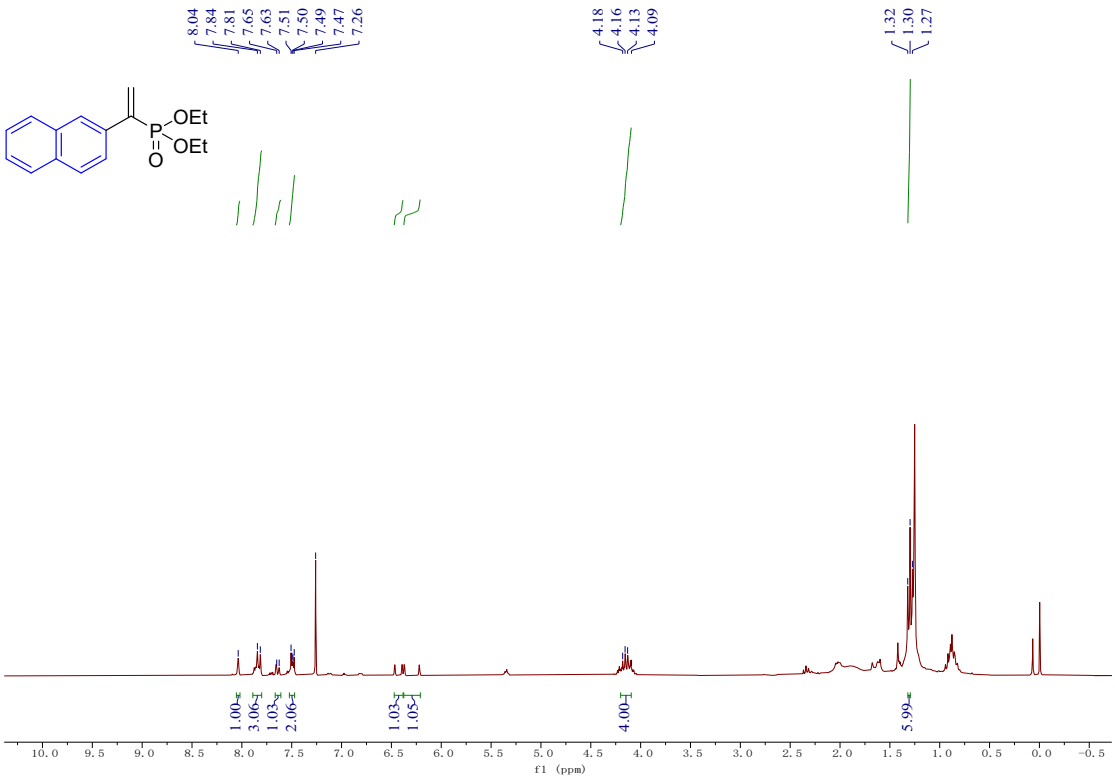
^{1}H NMR (300 MHz, $CDCl_3$) of **5v**



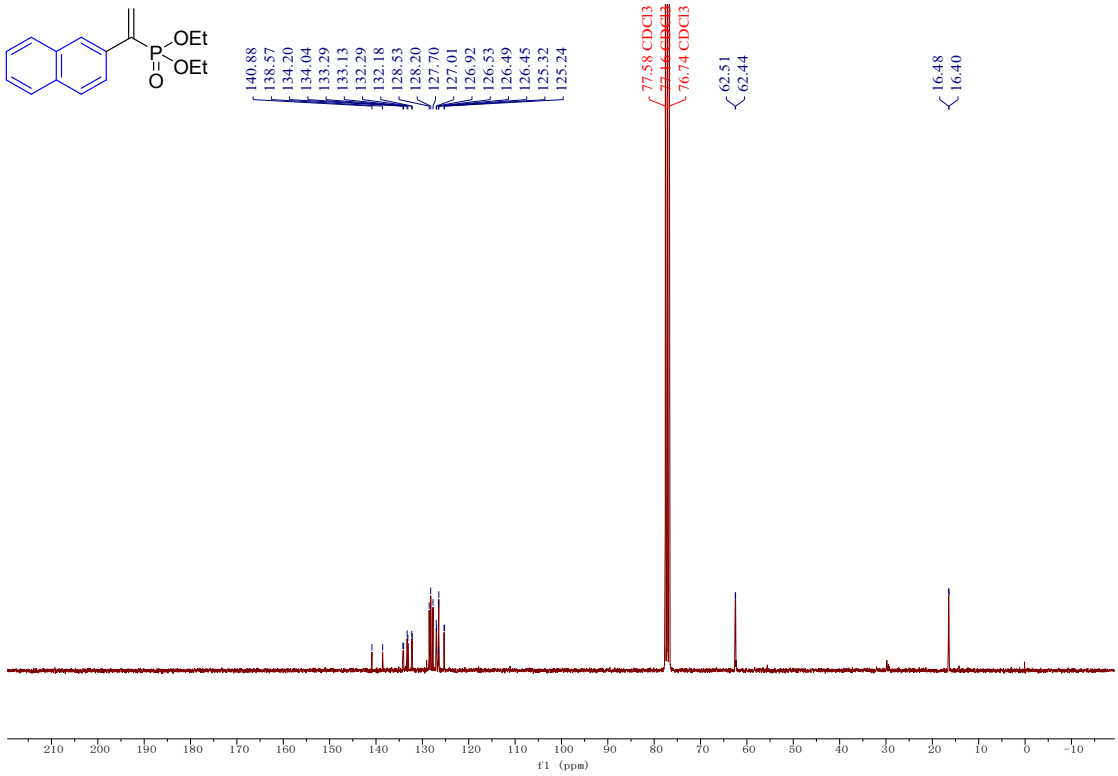
^{13}C NMR (75 MHz, $CDCl_3$) of **5v**



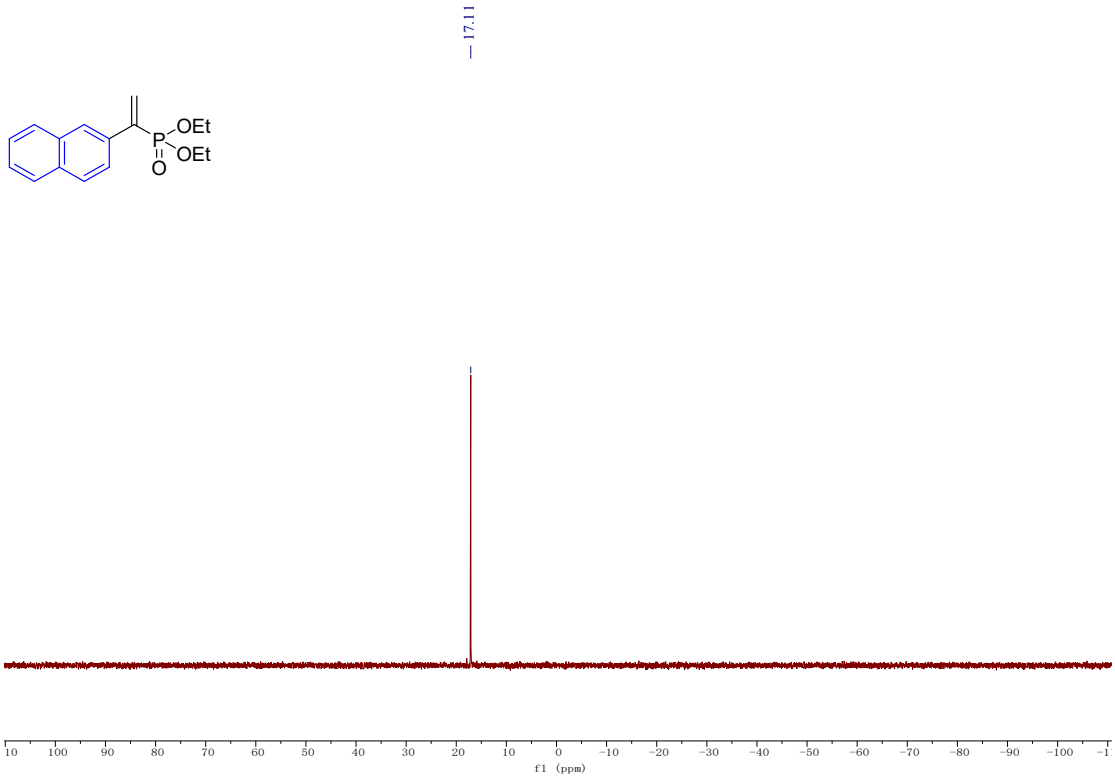
^{31}P NMR (121 MHz, $CDCl_3$) of **5v**



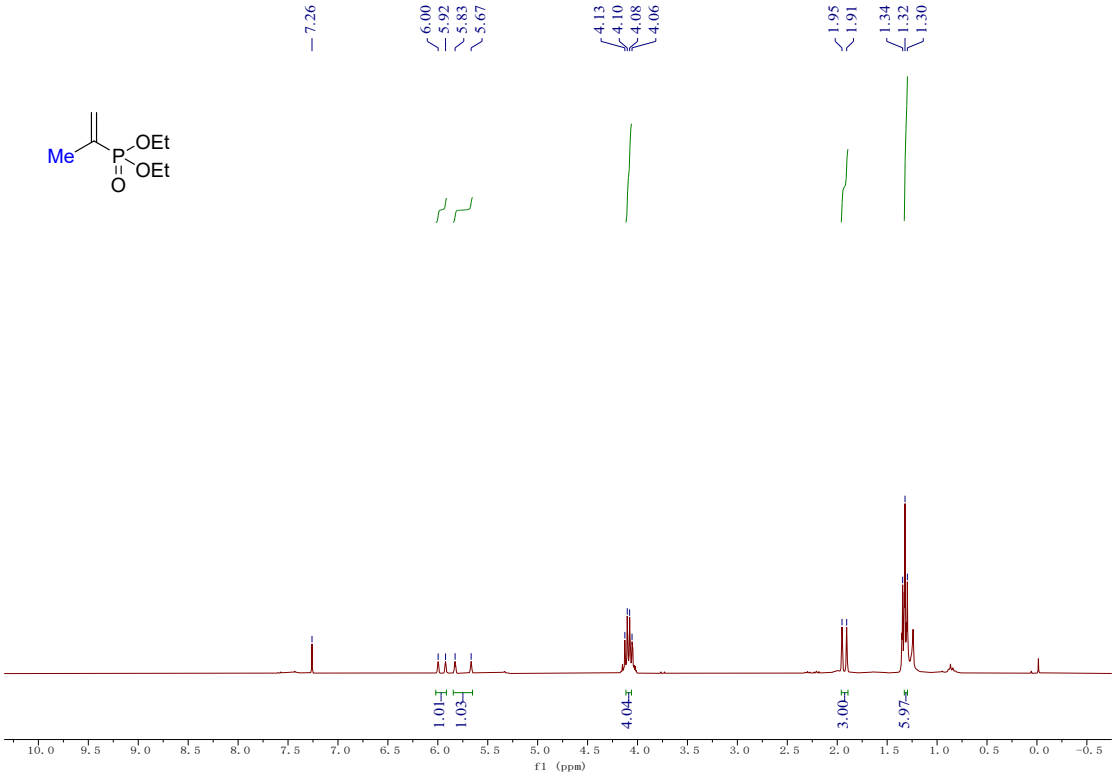
^{1}H NMR (300 MHz, $CDCl_3$) of **5w**



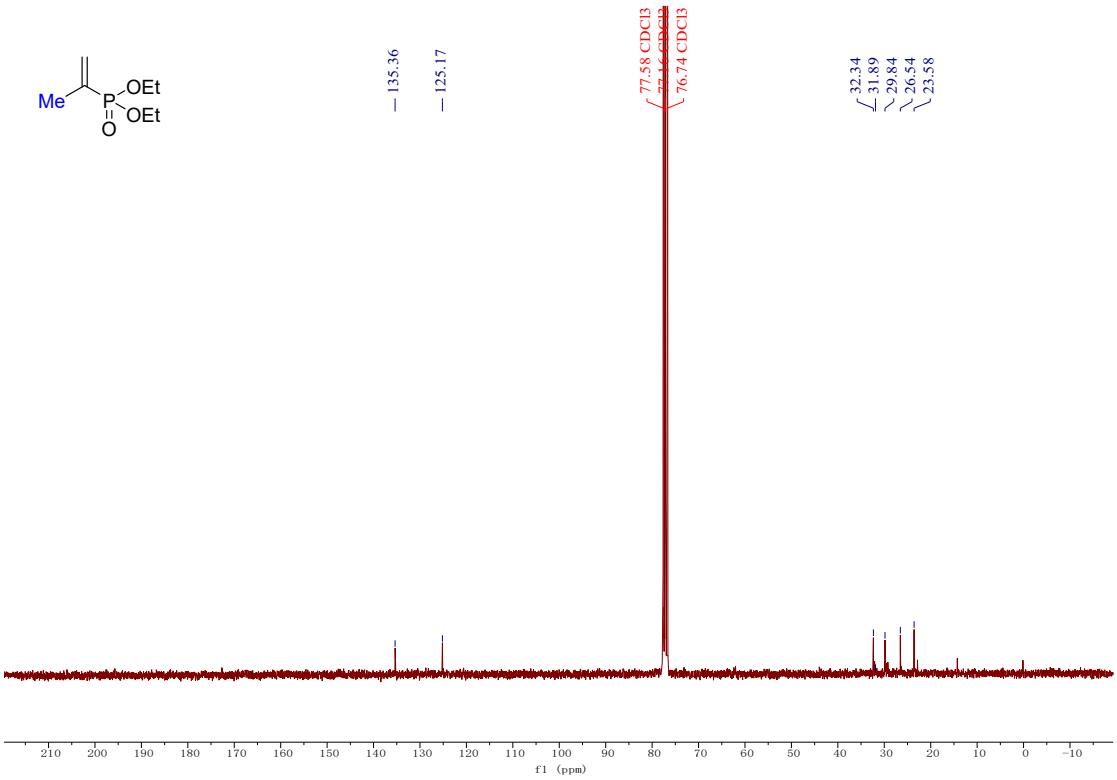
^{13}C NMR (75 MHz, $CDCl_3$) of **5w**



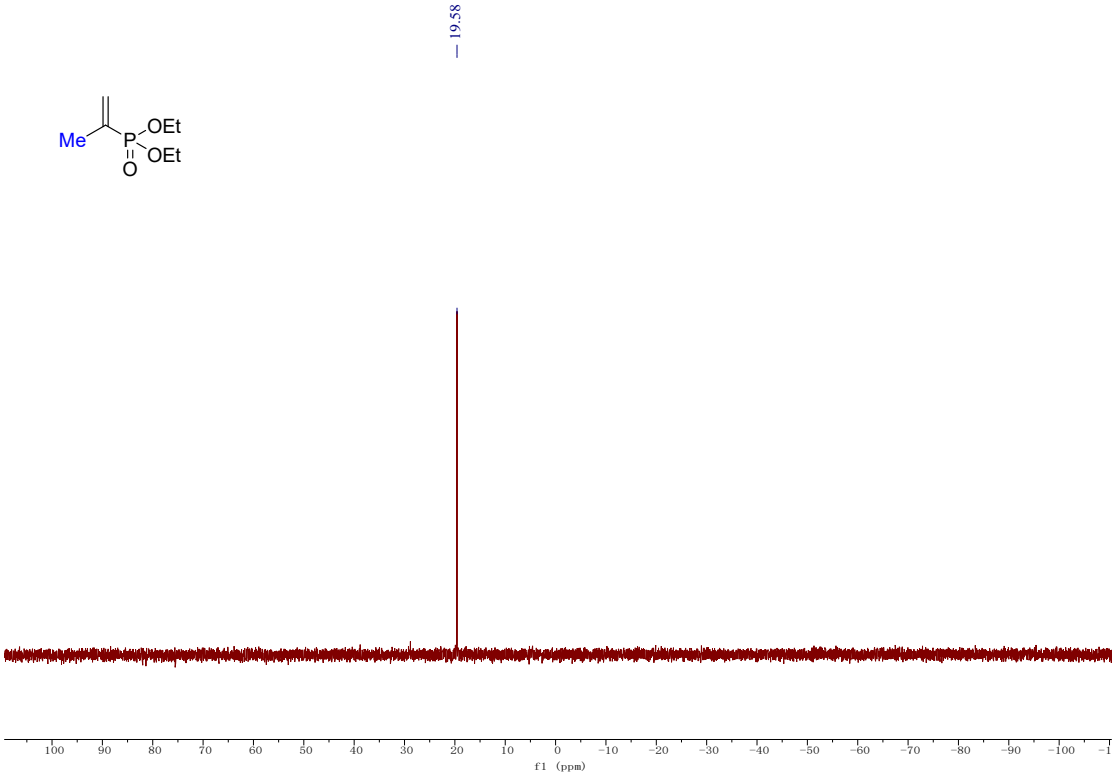
^{31}P NMR (121 MHz, $CDCl_3$) of **5w**



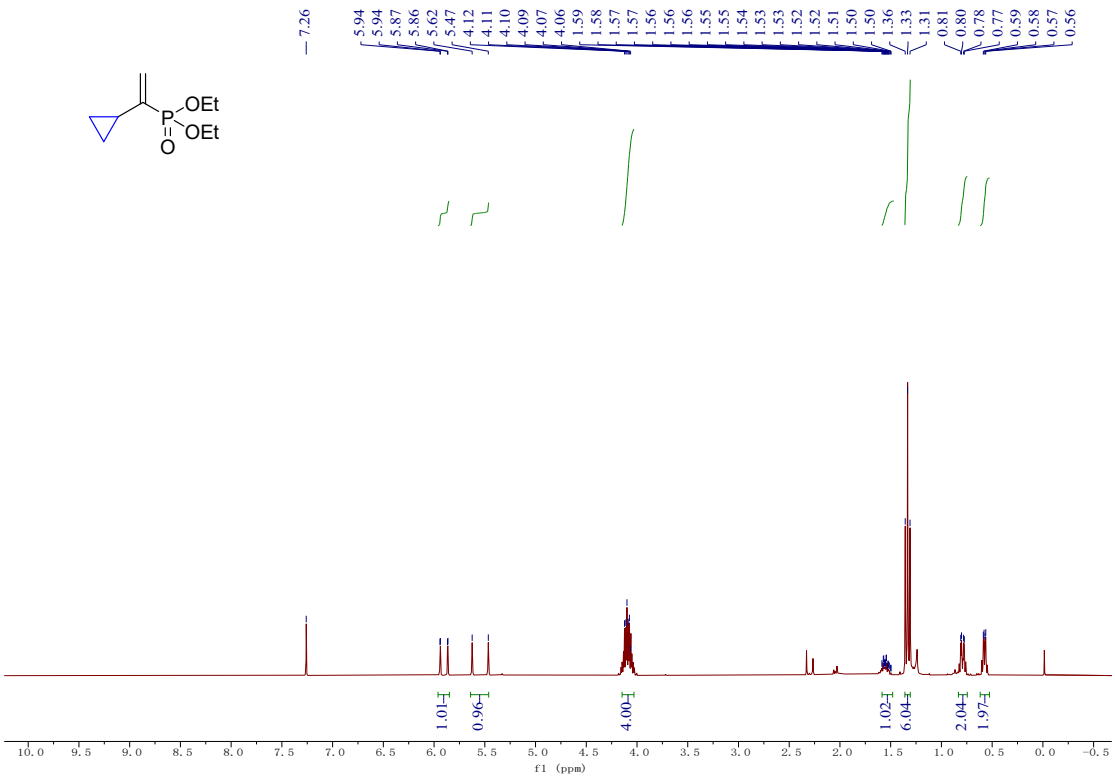
^{1}H NMR (300 MHz, $CDCl_3$) of **5x**



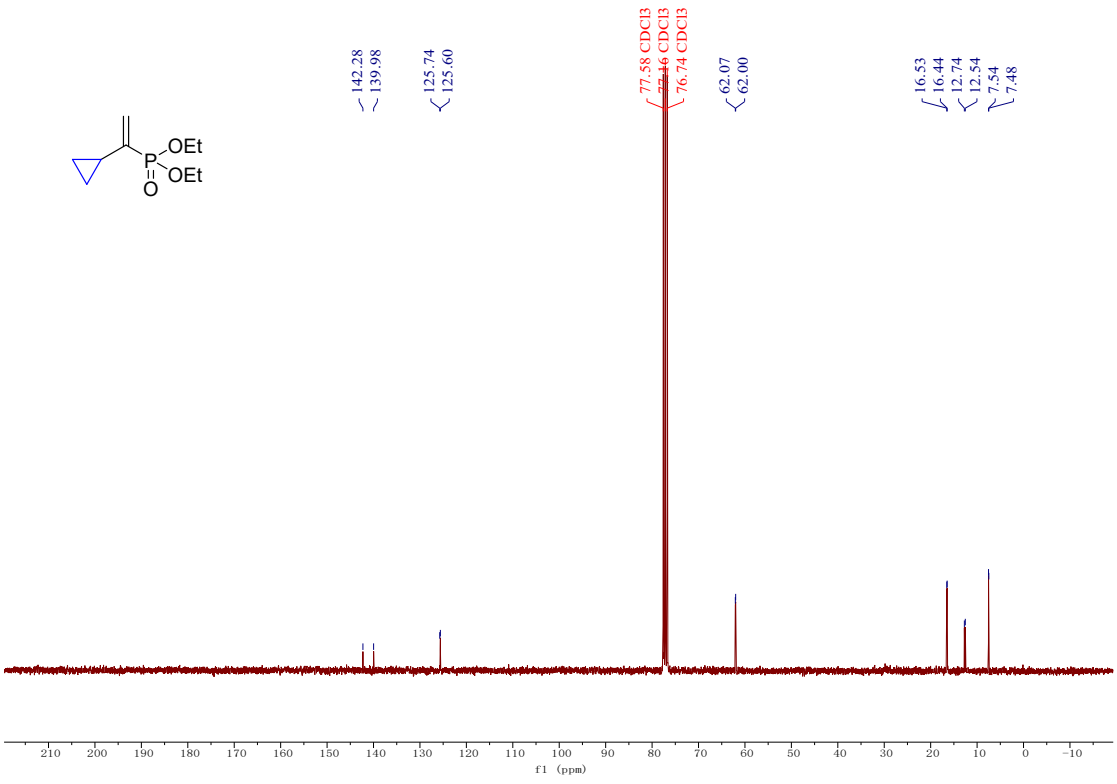
^{13}C NMR (75 MHz, $CDCl_3$) of **5x**



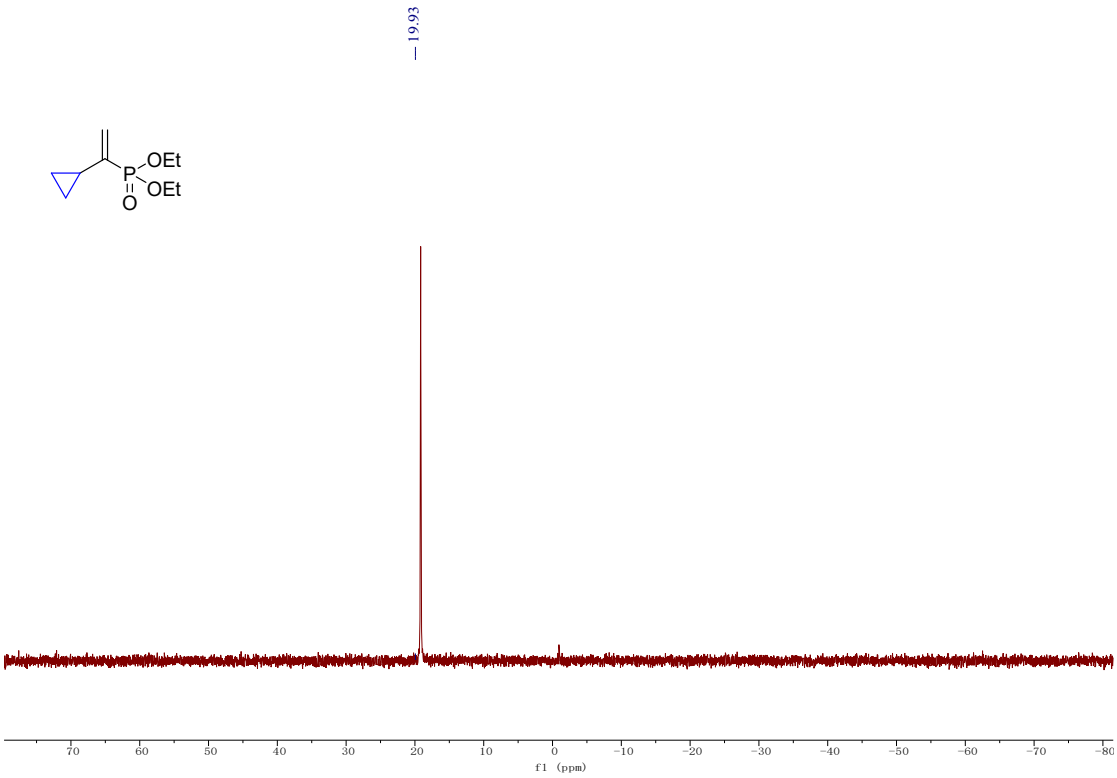
^{31}P NMR (121 MHz, $CDCl_3$) of **5x**



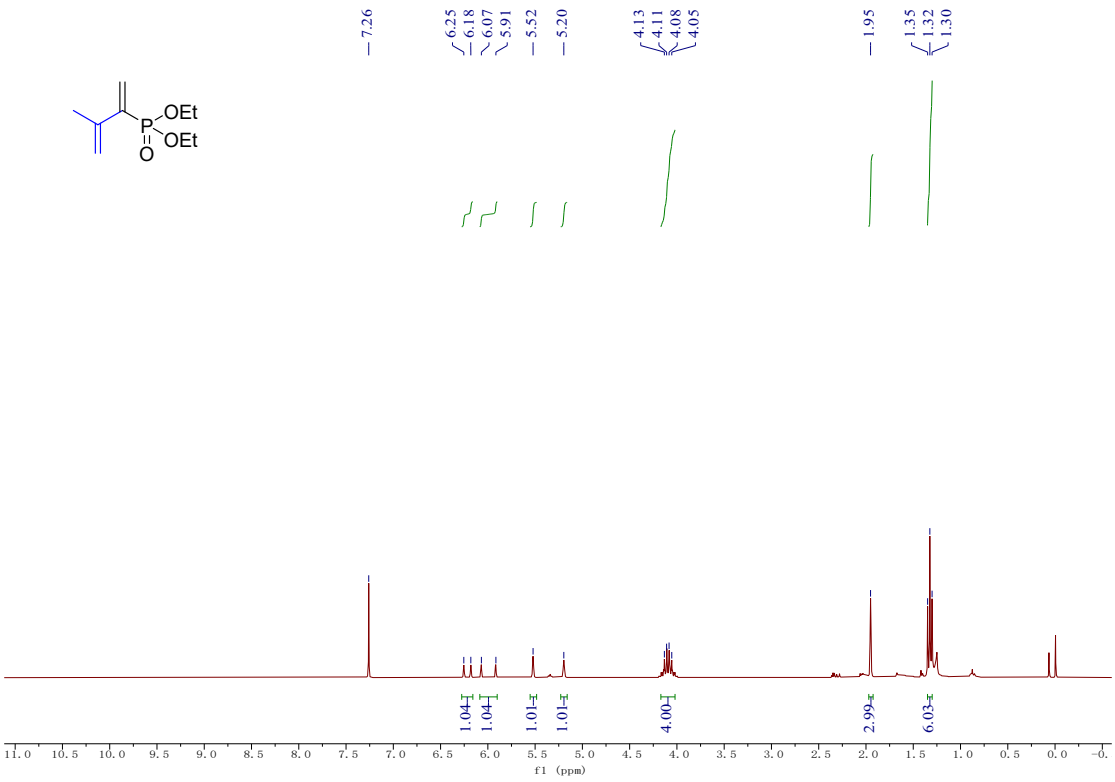
^{1}H NMR (300 MHz, $CDCl_3$) of **5y**



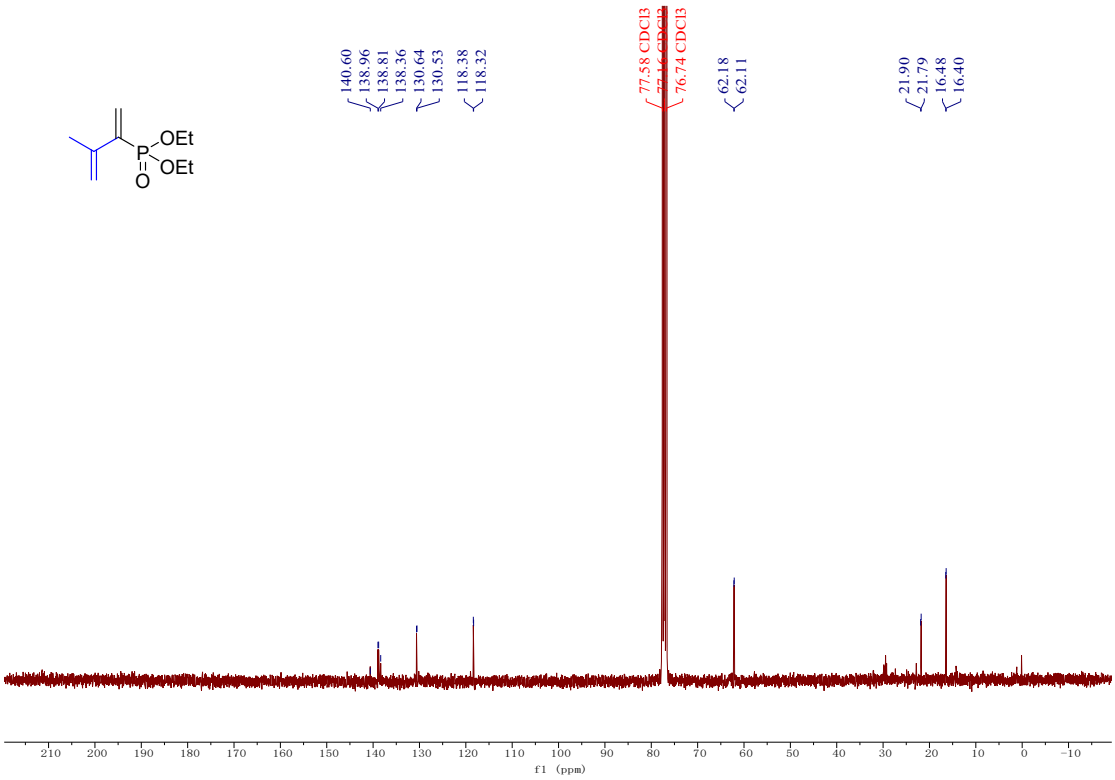
^{13}C NMR (75 MHz, $CDCl_3$) of **5y**



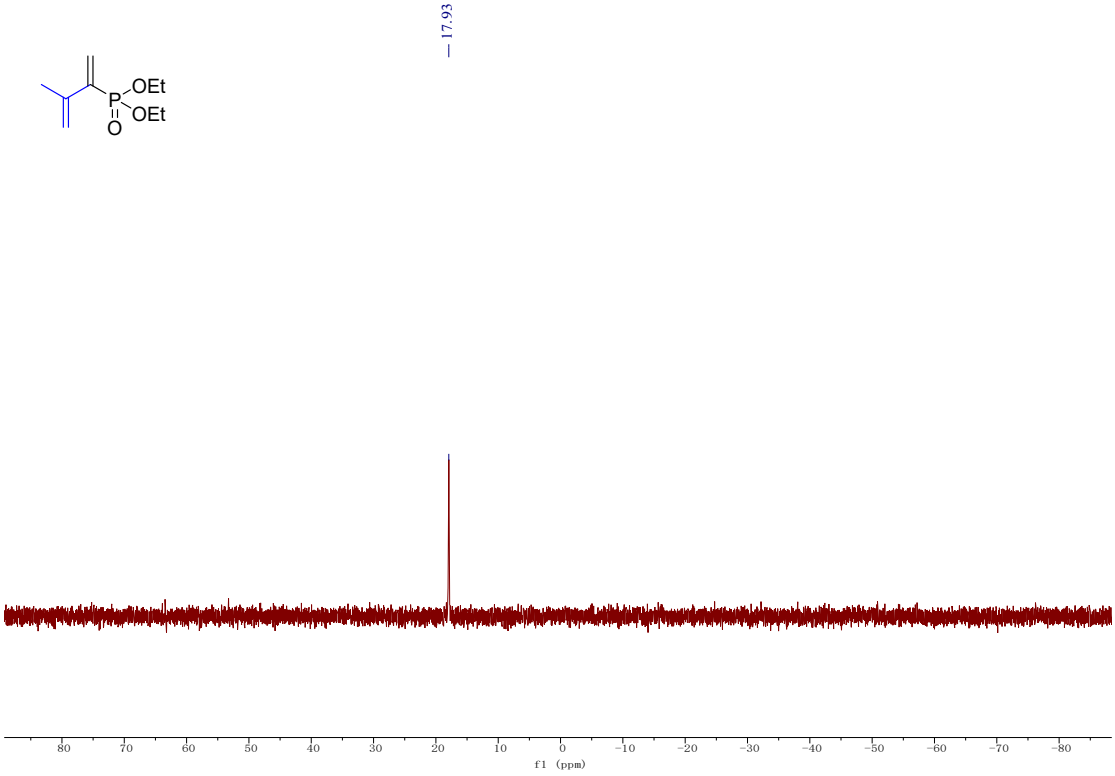
^{31}P NMR (121 MHz, $CDCl_3$) of **5y**



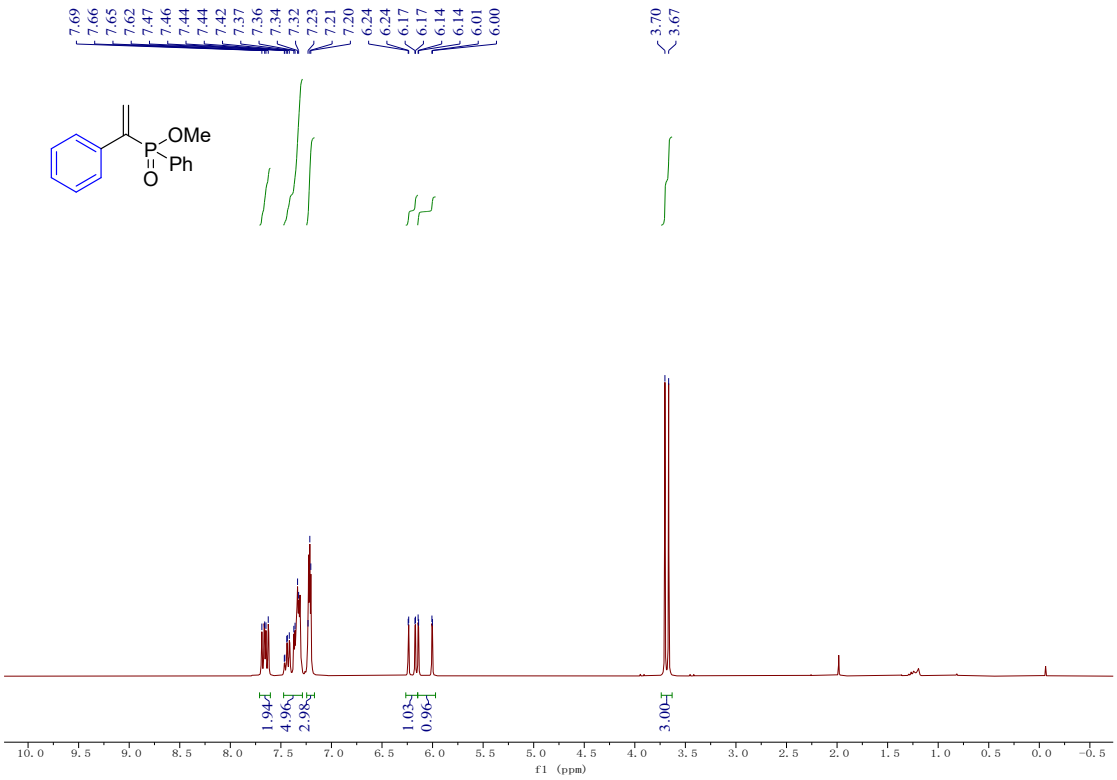
^{1}H NMR (300 MHz, $CDCl_3$) of **5z**



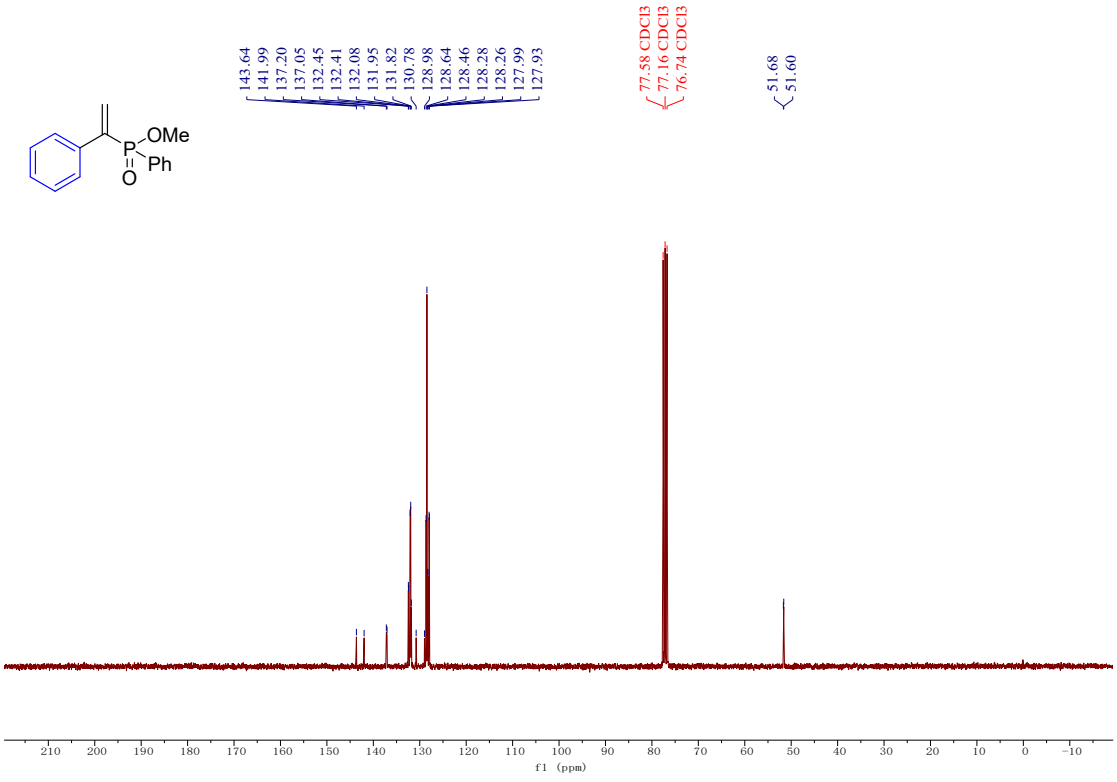
^{13}C NMR (75 MHz, $CDCl_3$) of **5z**



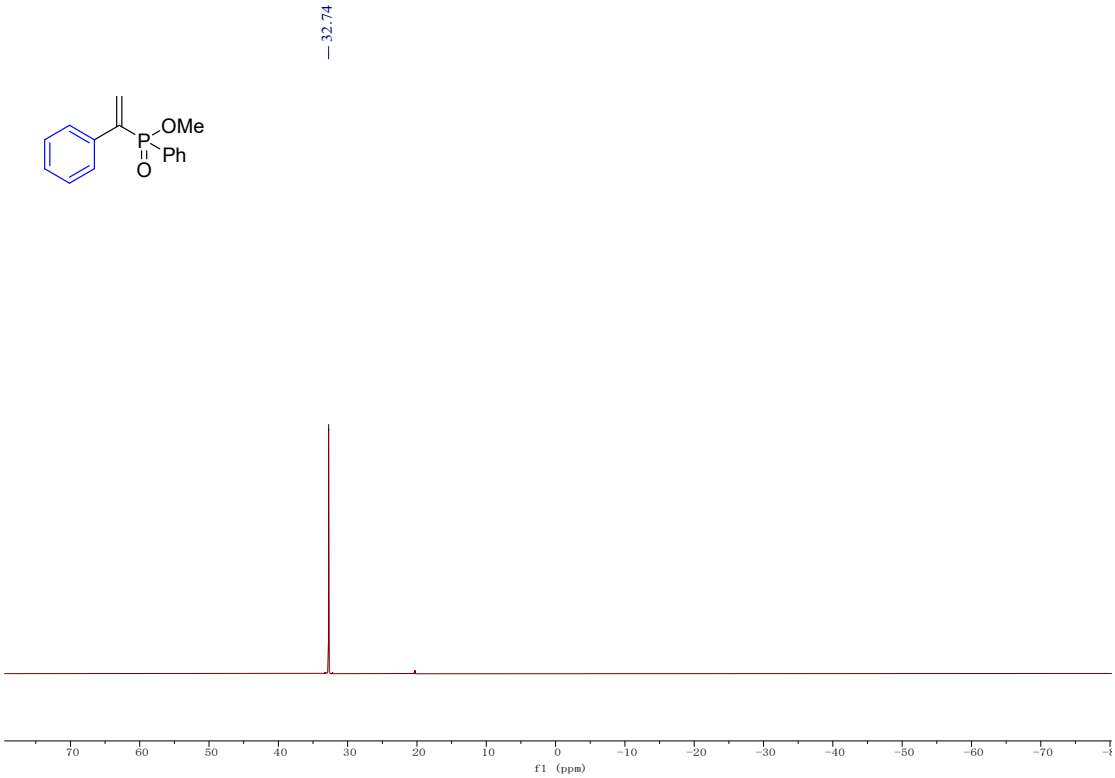
^{31}P NMR (121 MHz, $CDCl_3$) of **5z**



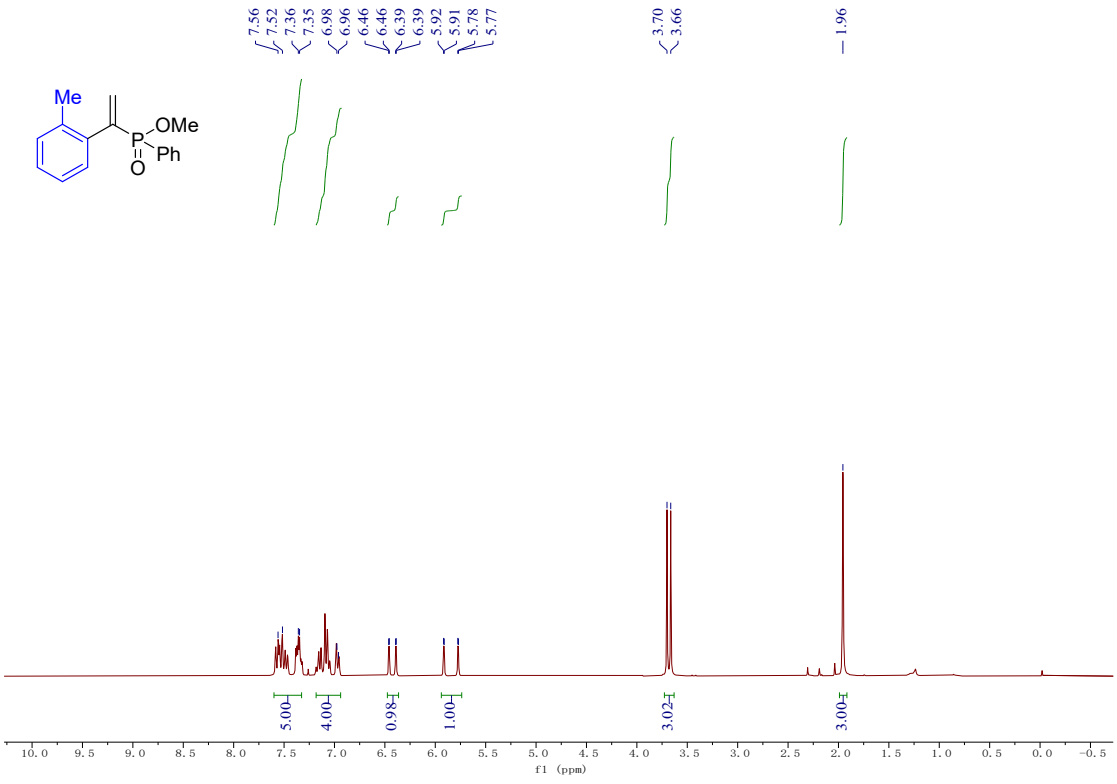
^{1}H NMR (300 MHz, $CDCl_3$) of **6a**



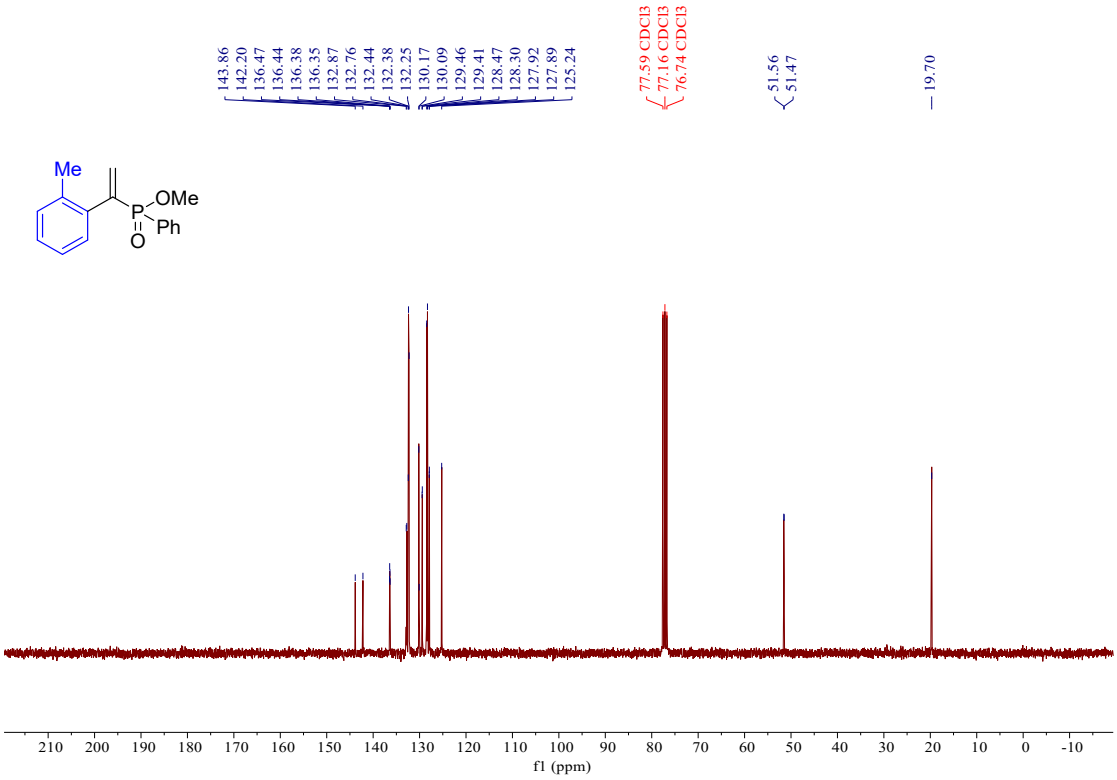
^{13}C NMR (75 MHz, $CDCl_3$) of **6a**



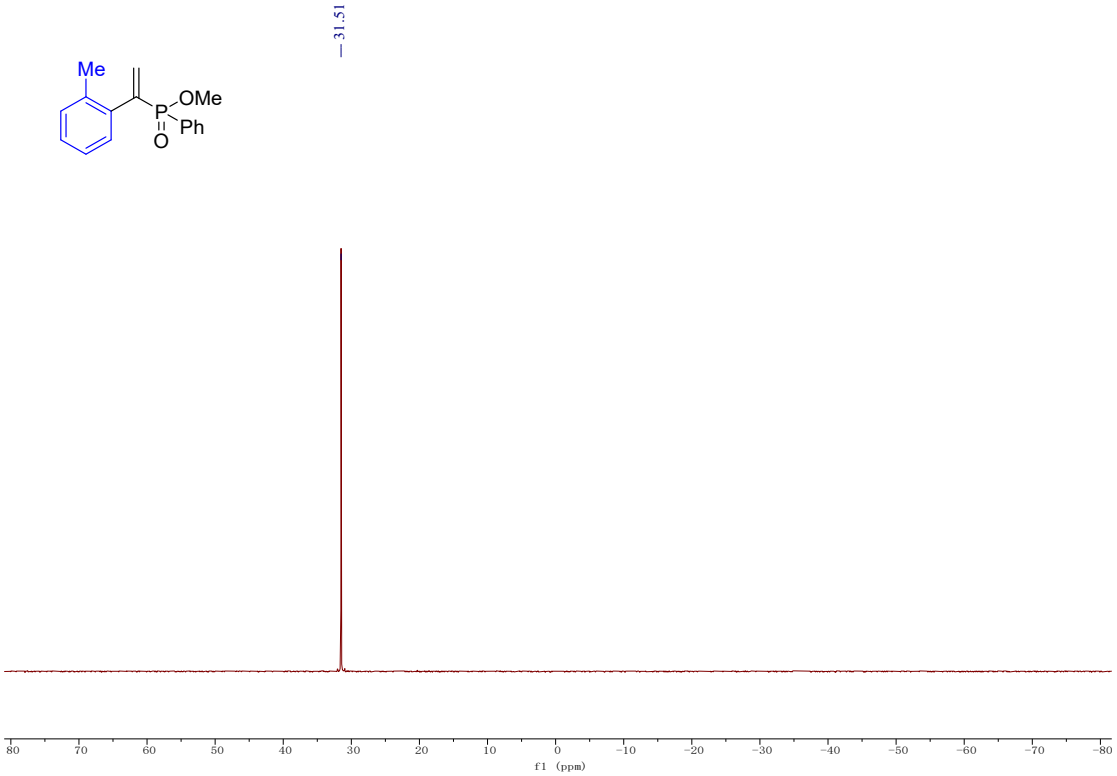
^{31}P NMR (121 MHz, $CDCl_3$) of **6a**



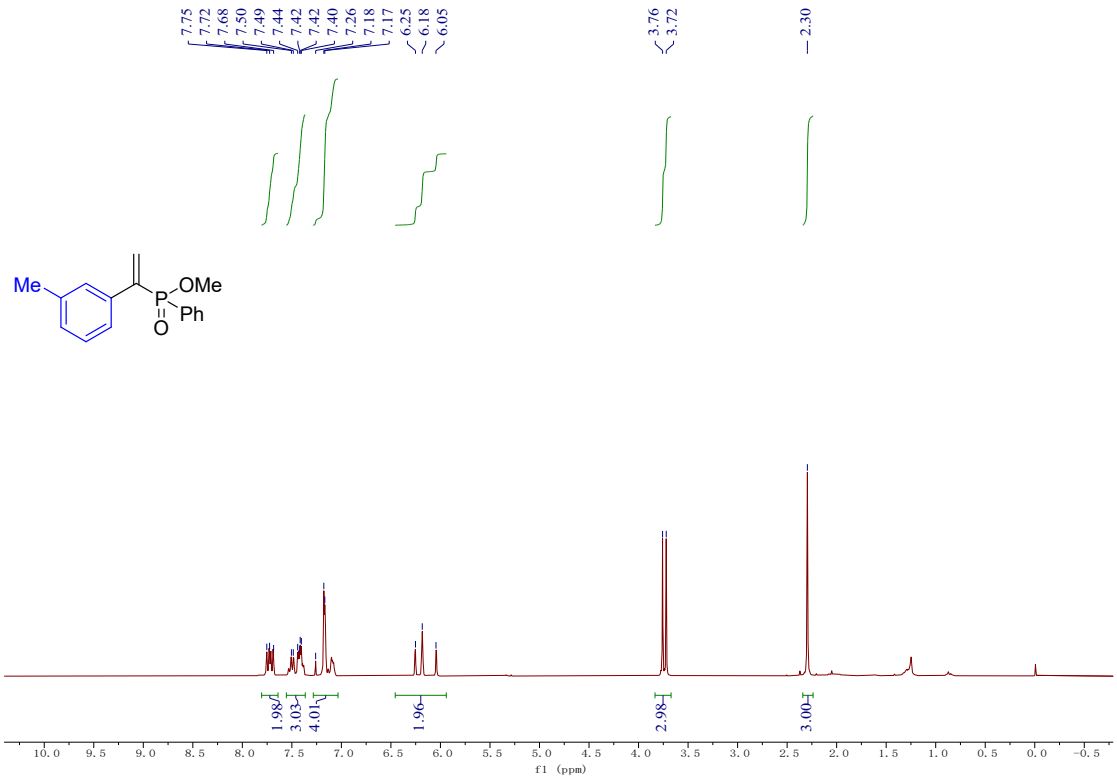
^{1}H NMR (300 MHz, $CDCl_3$) of **6b**



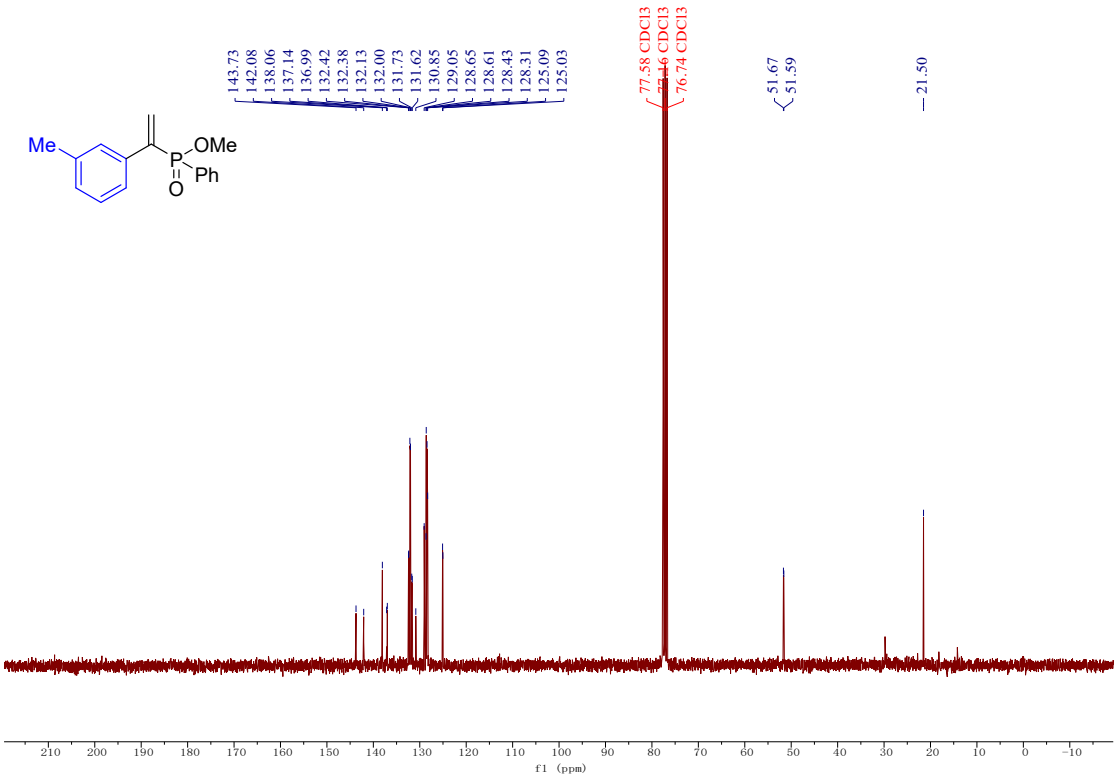
^{13}C NMR (75 MHz, $CDCl_3$) of **6b**



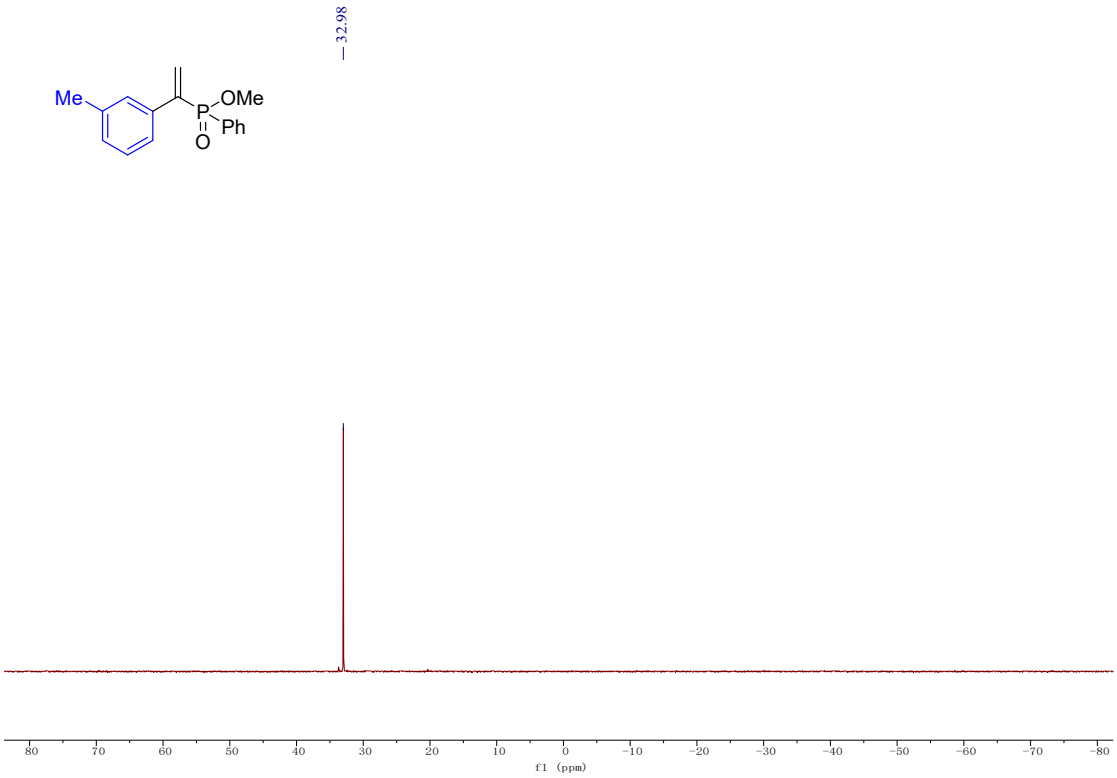
^{31}P NMR (121 MHz, $CDCl_3$) of **6b**



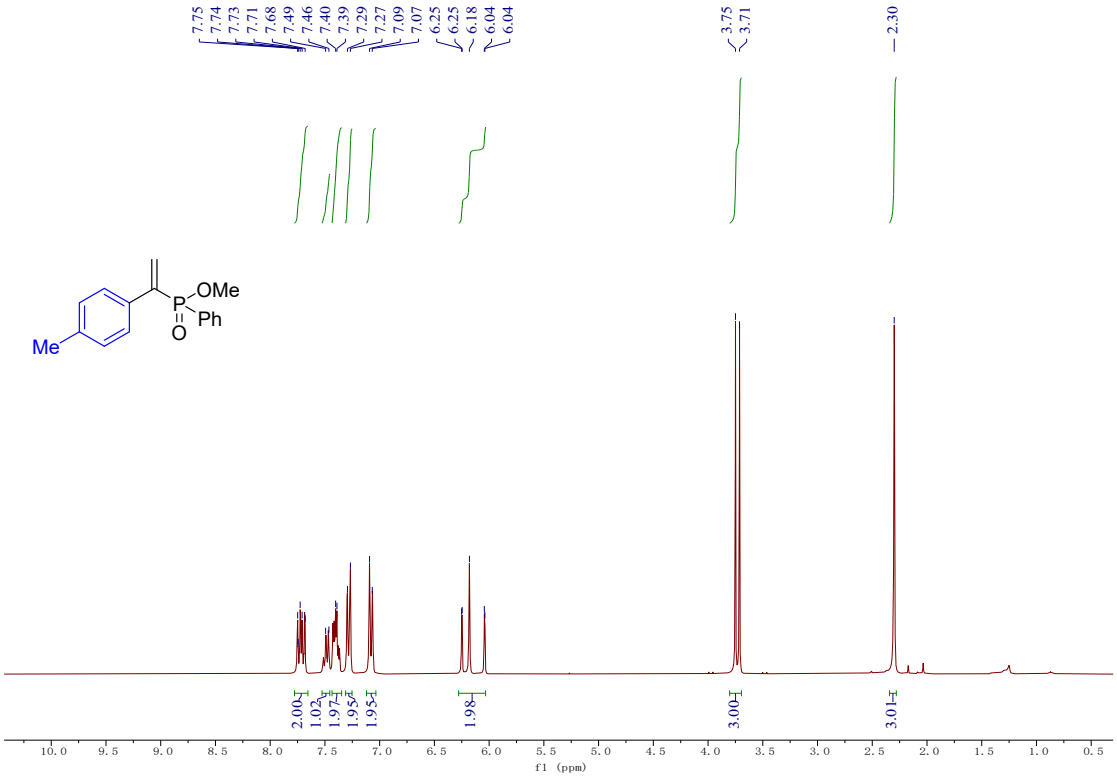
^{1}H NMR (300 MHz, $CDCl_3$) of **6c**



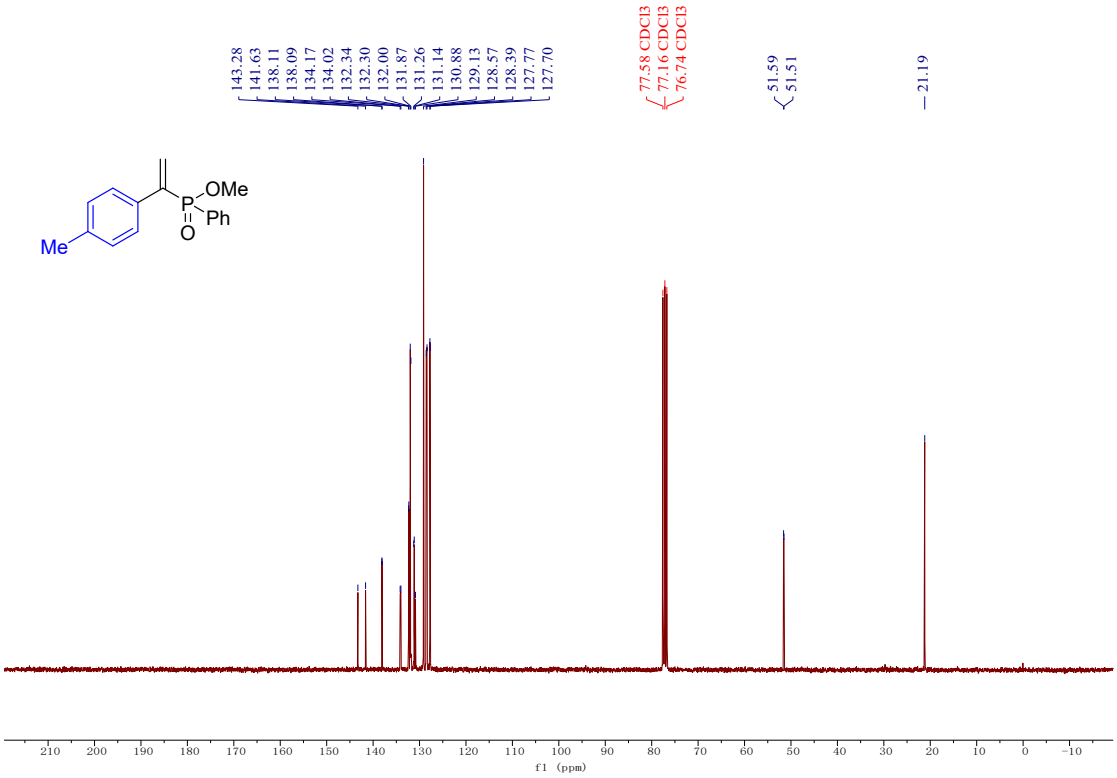
^{13}C NMR (75 MHz, $CDCl_3$) of **6c**



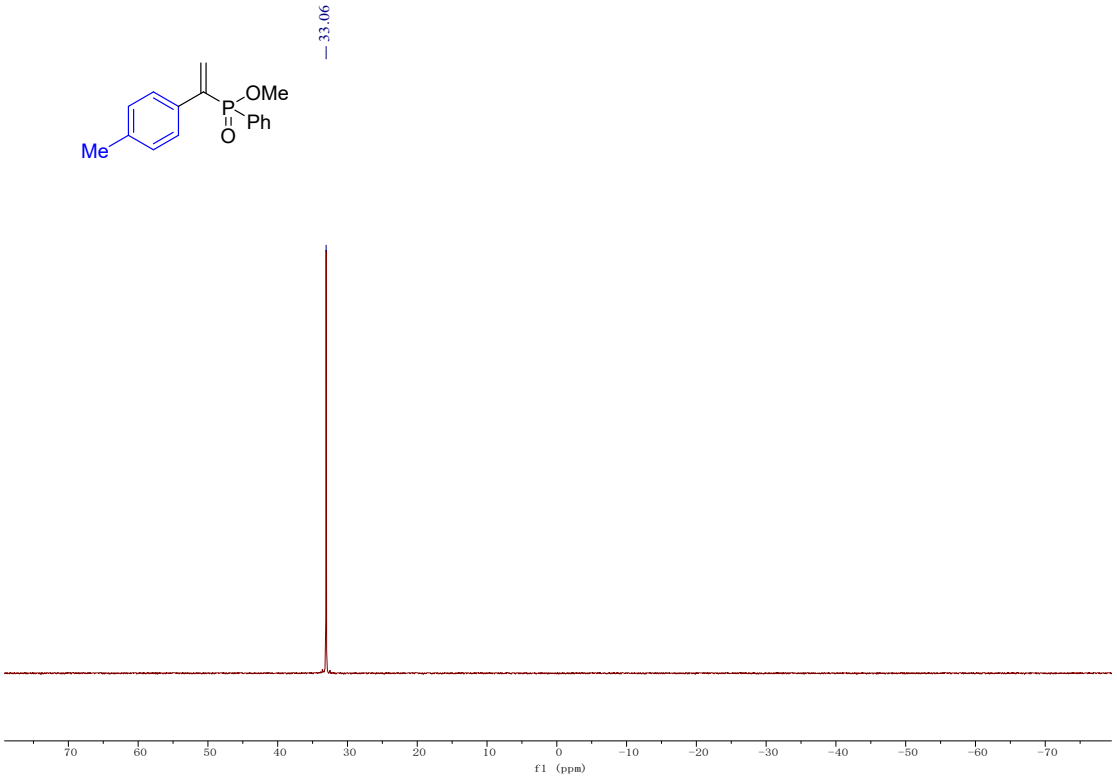
^{31}P NMR (121 MHz, $CDCl_3$) of **6c**



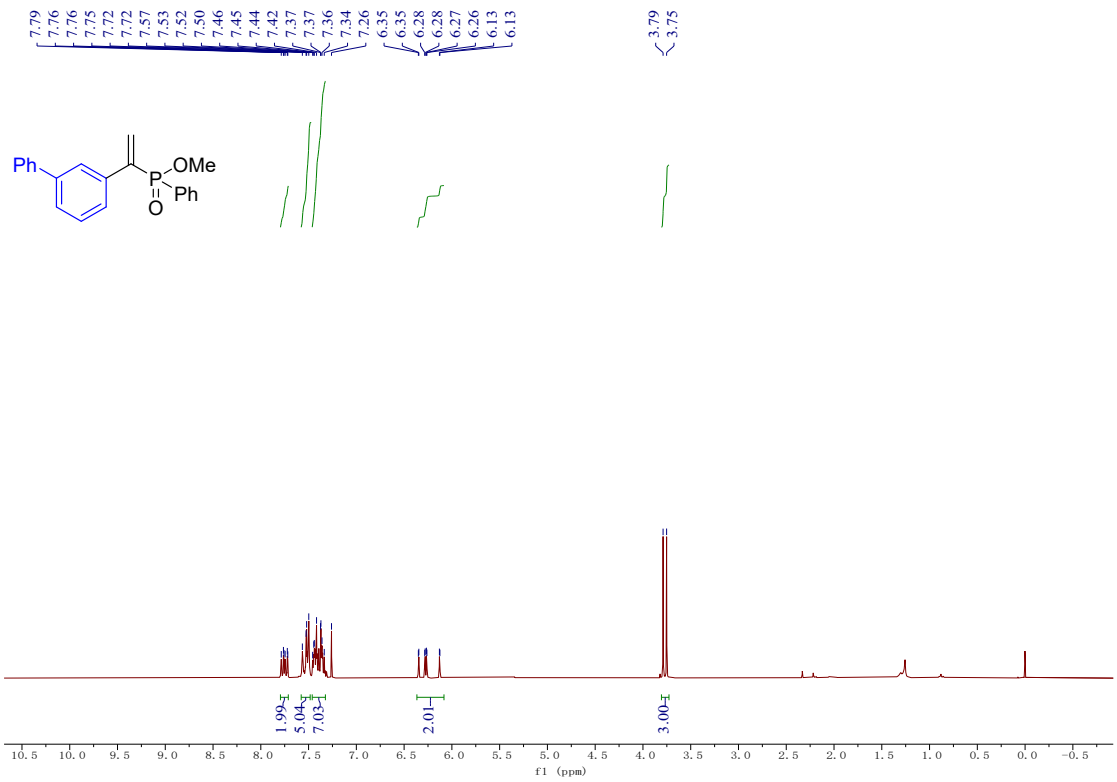
^{1}H NMR (300 MHz, $CDCl_3$) of **6d**



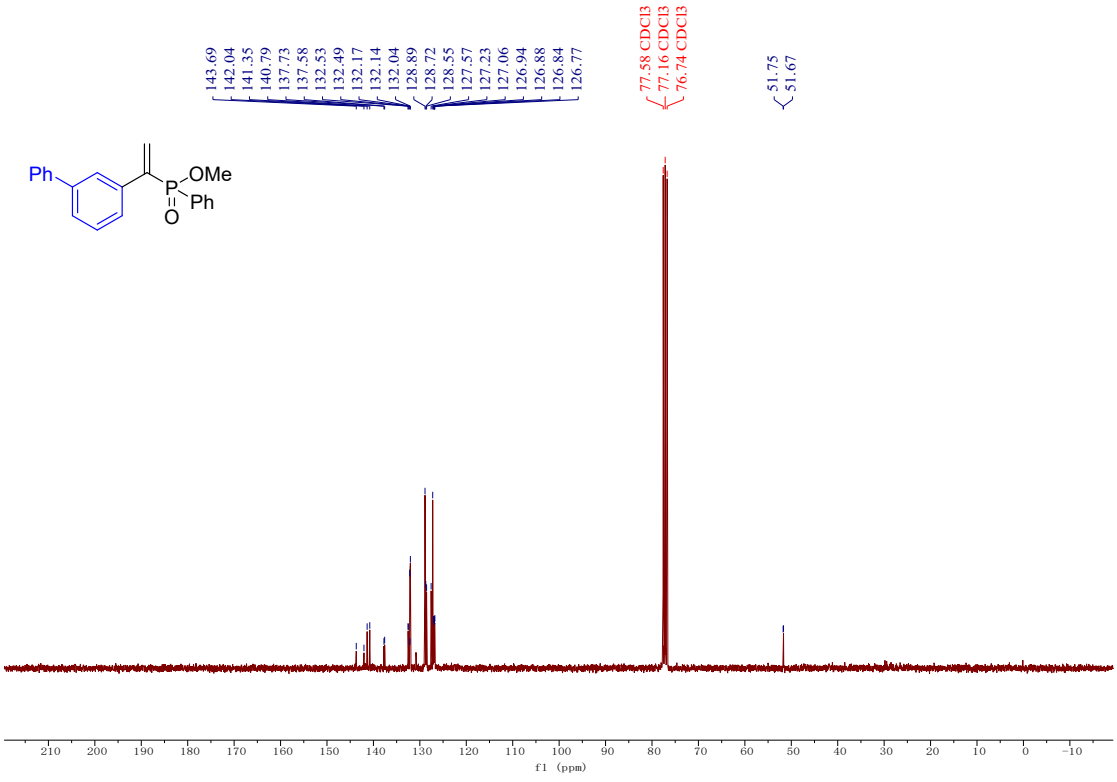
^{13}C NMR (75 MHz, $CDCl_3$) of **6d**



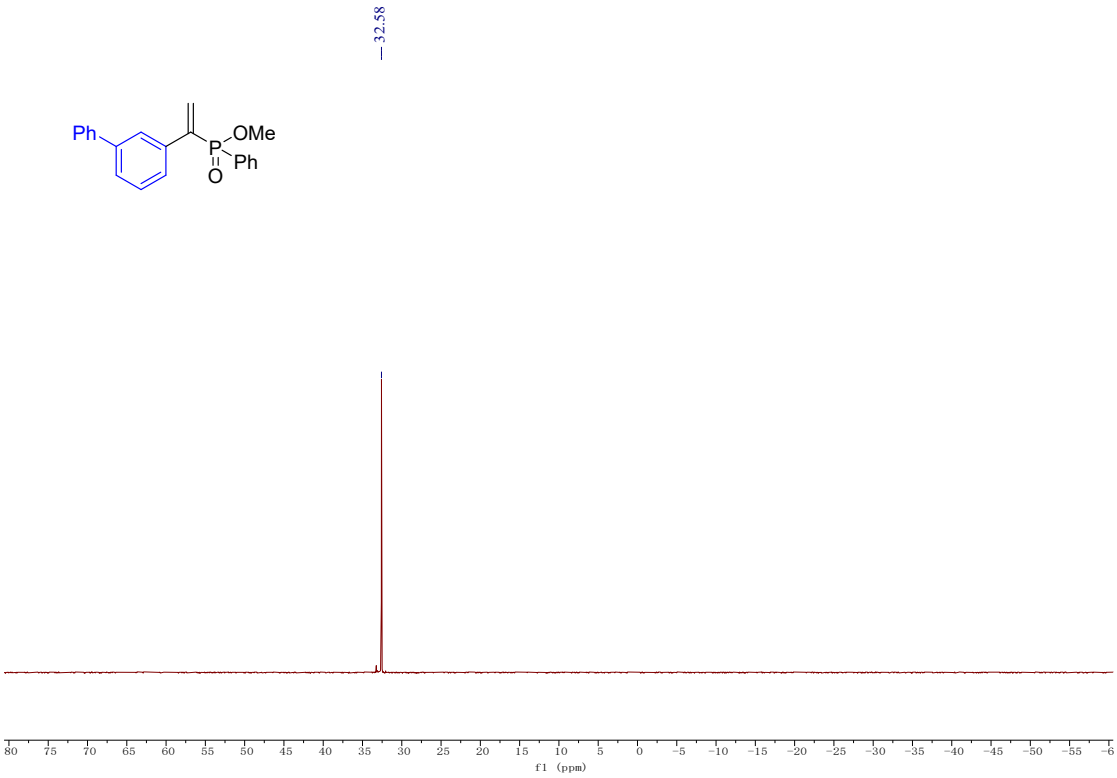
^{31}P NMR (121 MHz, $CDCl_3$) of **6d**



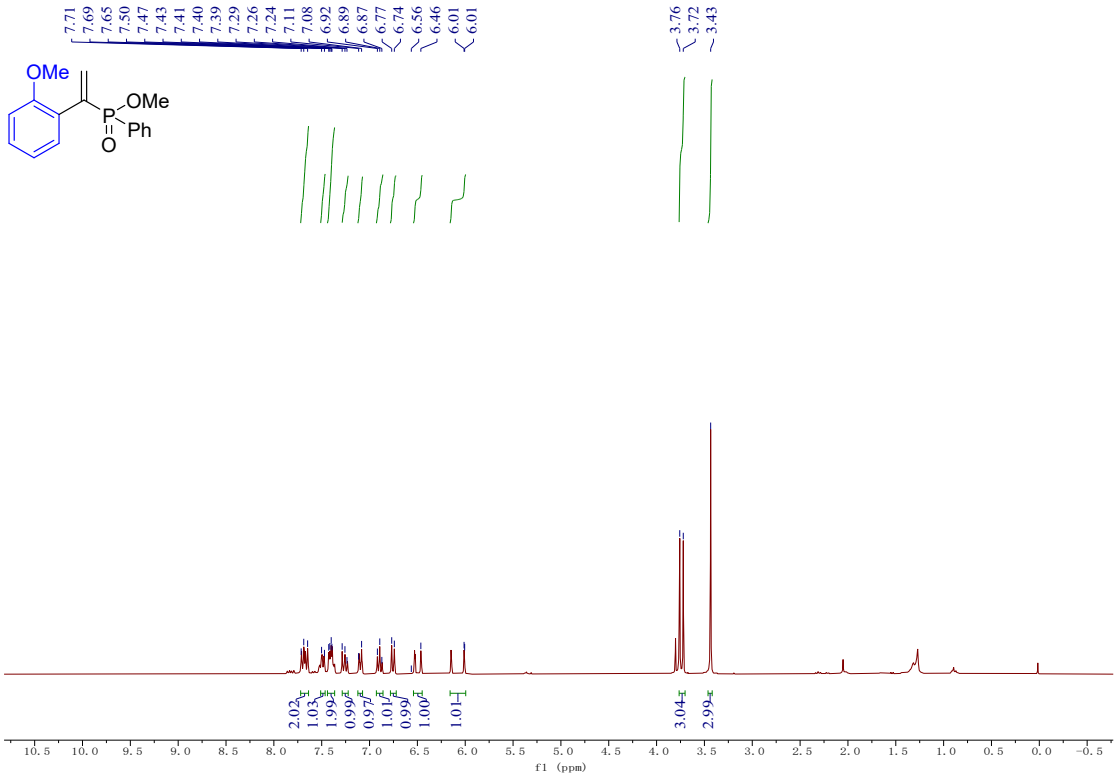
^{1}H NMR (300 MHz, $CDCl_3$) of **6e**



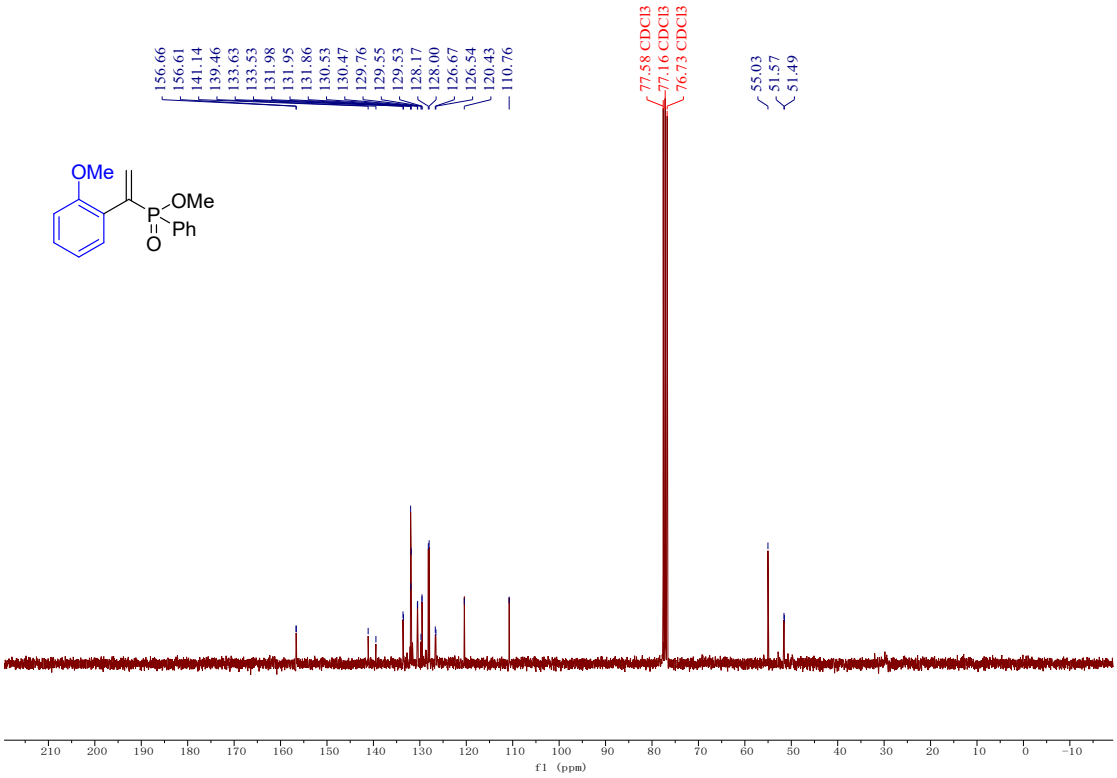
^{13}C NMR (75 MHz, $CDCl_3$) of **6e**



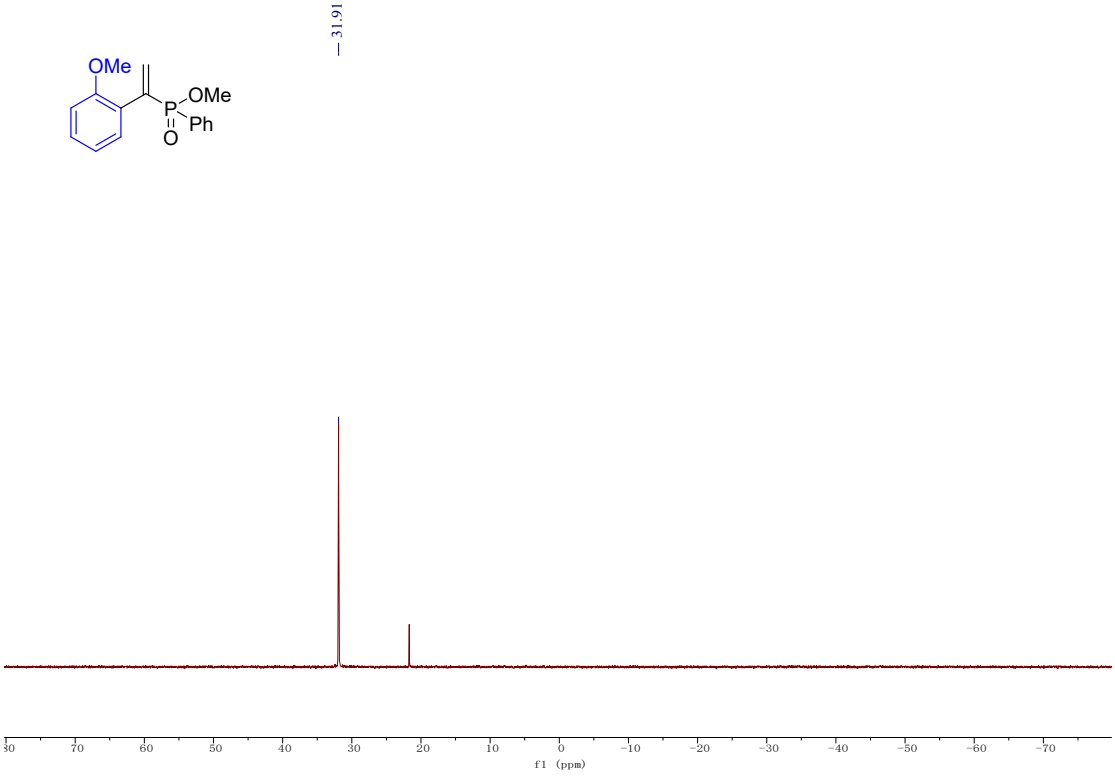
^{31}P NMR (121 MHz, $CDCl_3$) of **6e**



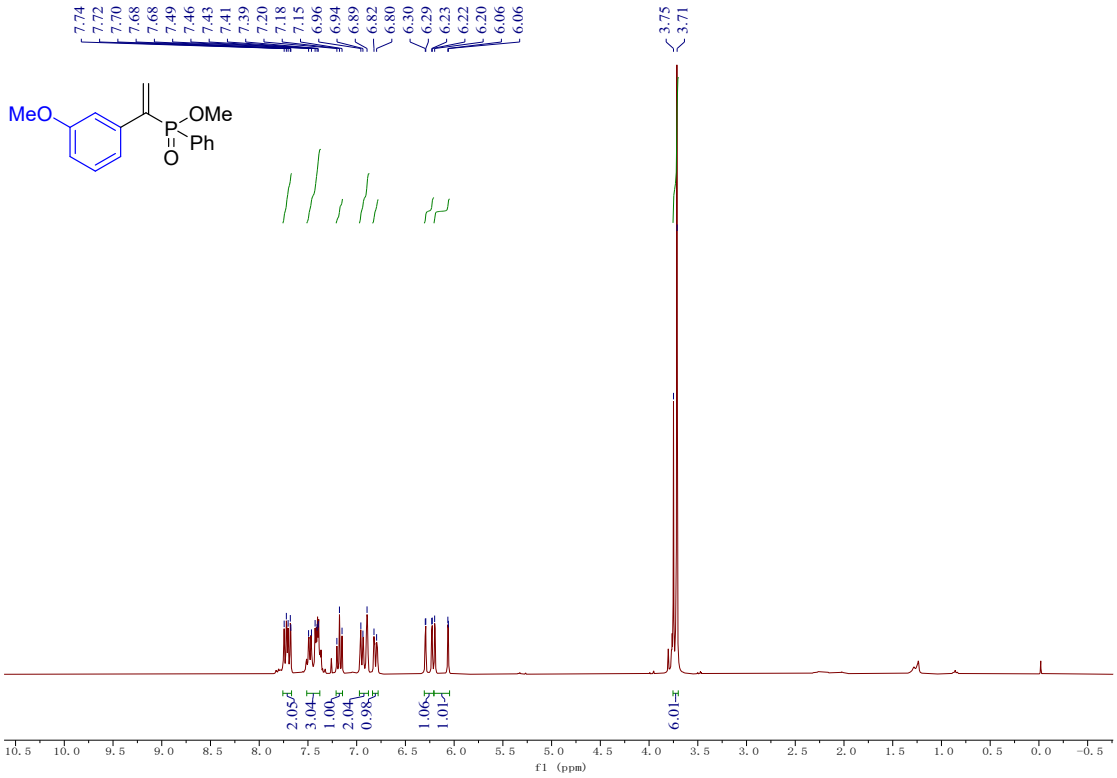
^{1}H NMR (300 MHz, $CDCl_3$) of **6f**



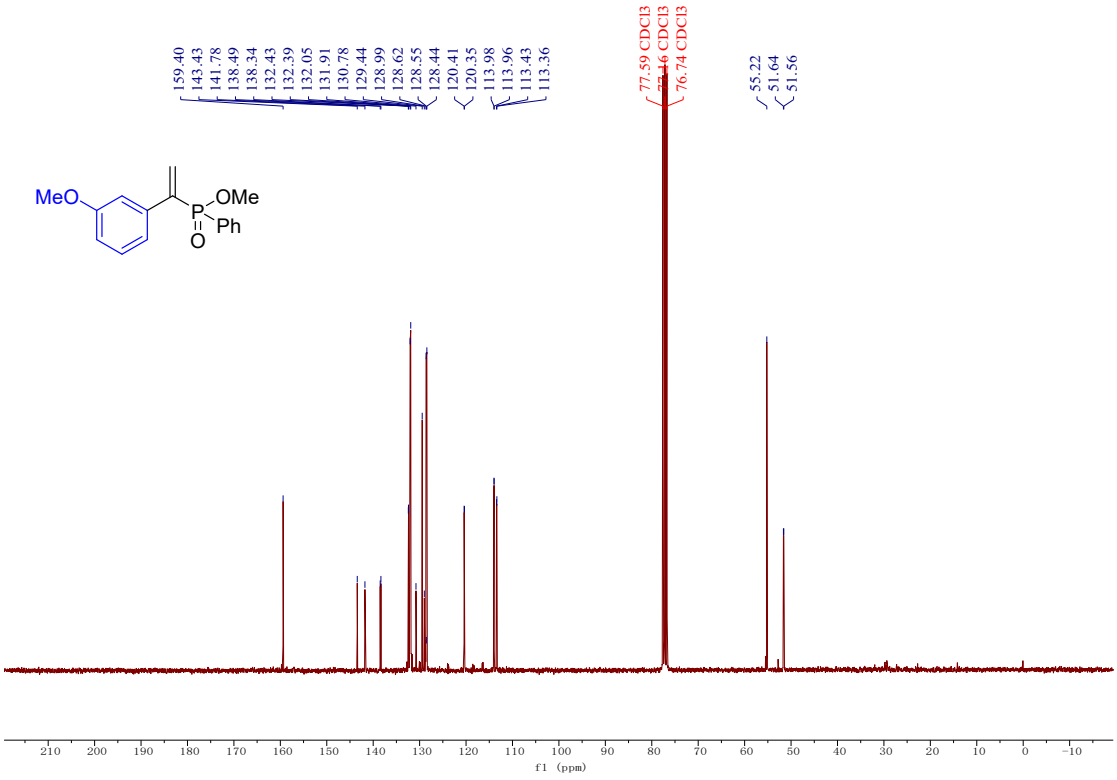
^{13}C NMR (75 MHz, $CDCl_3$) of **6f**



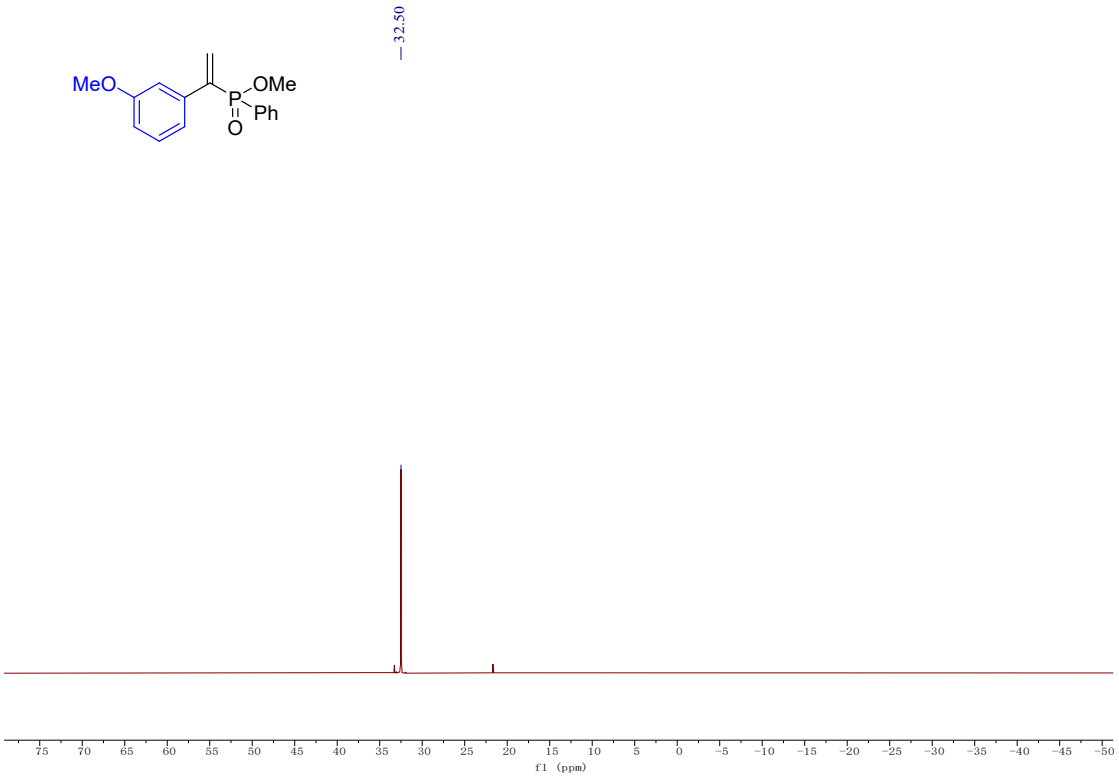
^{31}P NMR (121 MHz, $CDCl_3$) of **6f**



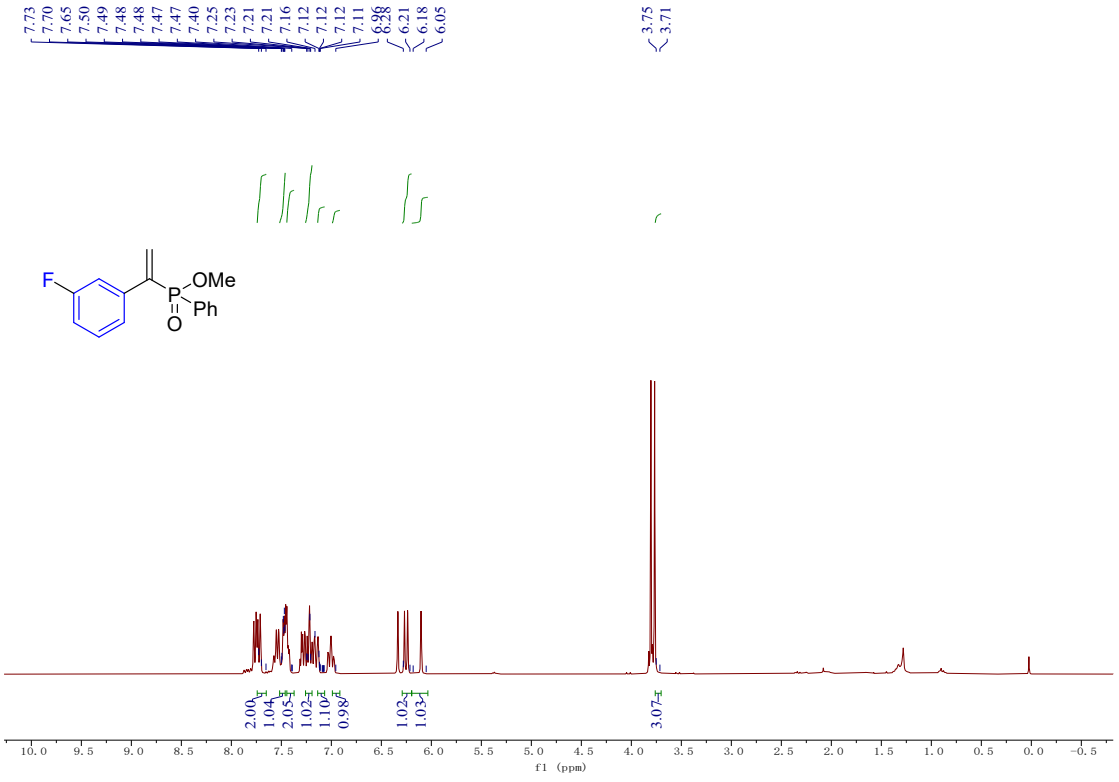
^{1}H NMR (300 MHz, $CDCl_3$) of **6g**



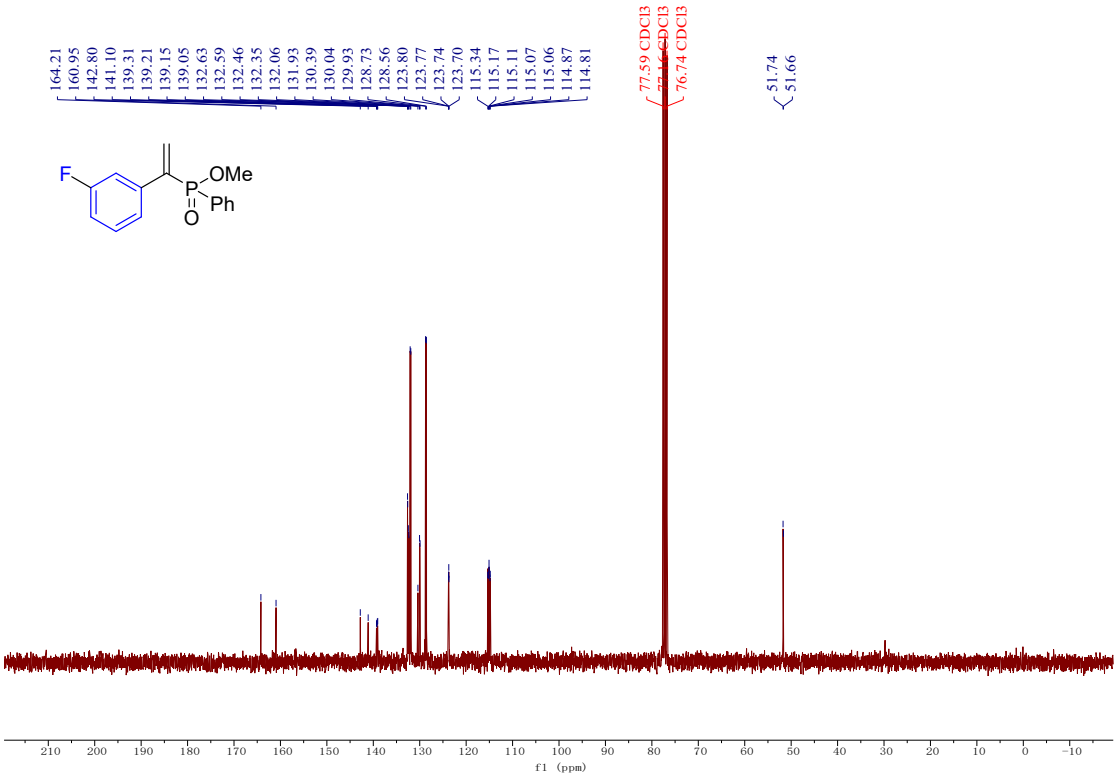
^{13}C NMR (75 MHz, $CDCl_3$) of **6g**



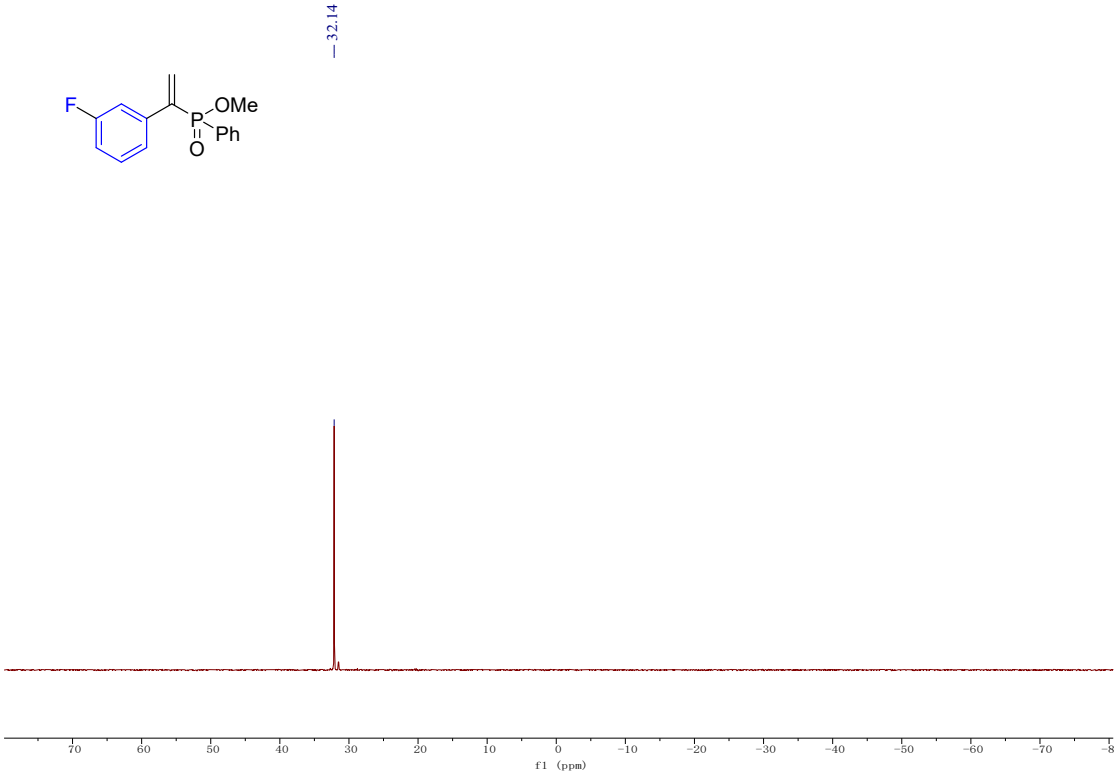
^{31}P NMR (121 MHz, $CDCl_3$) of **6g**



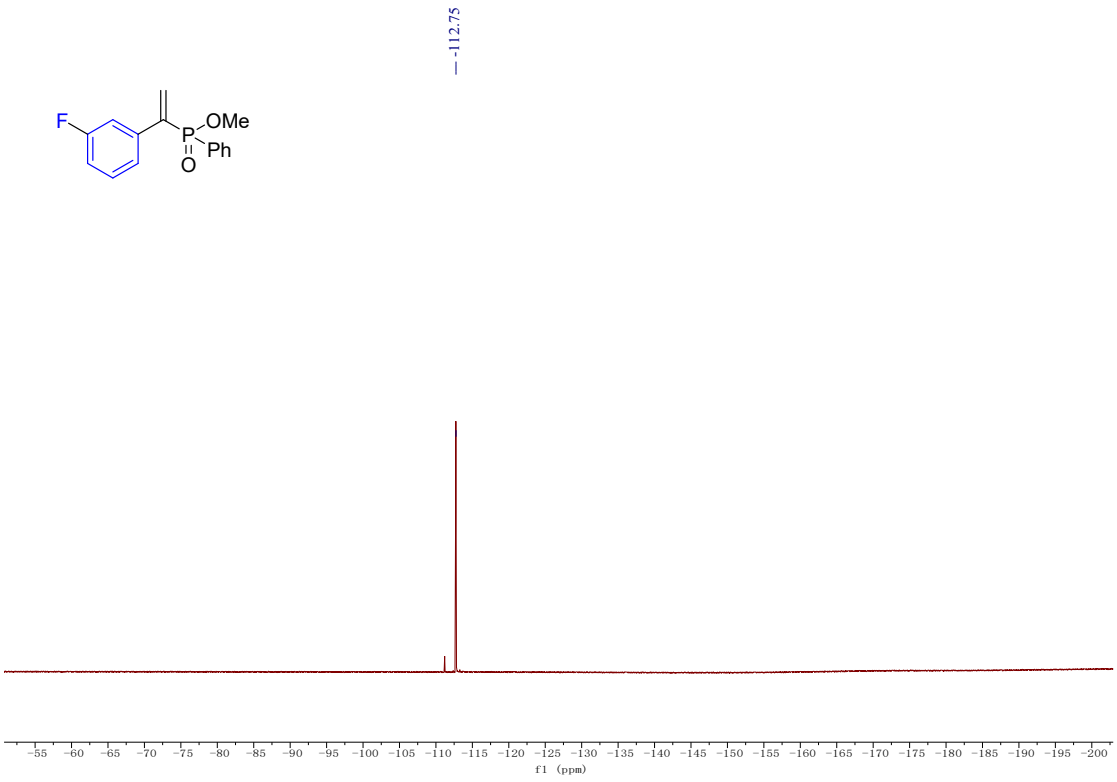
^{1}H NMR (300 MHz, $CDCl_3$) of **6h**



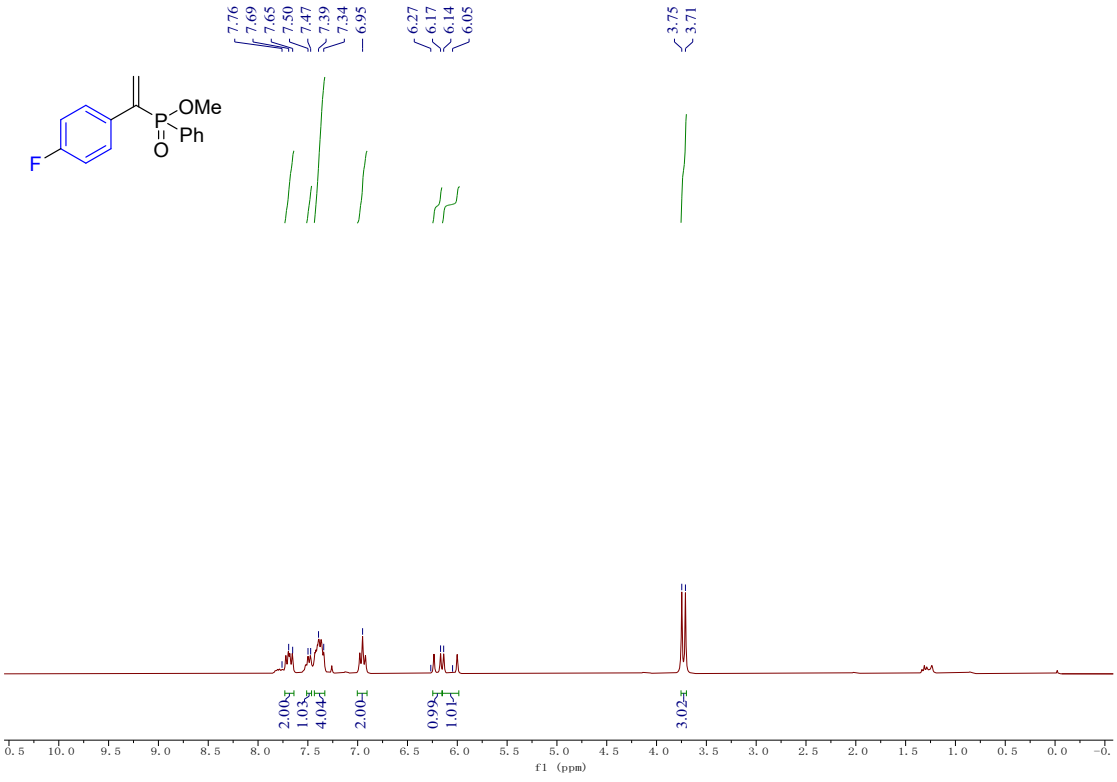
^{13}C NMR (75 MHz, $CDCl_3$) of **6h**



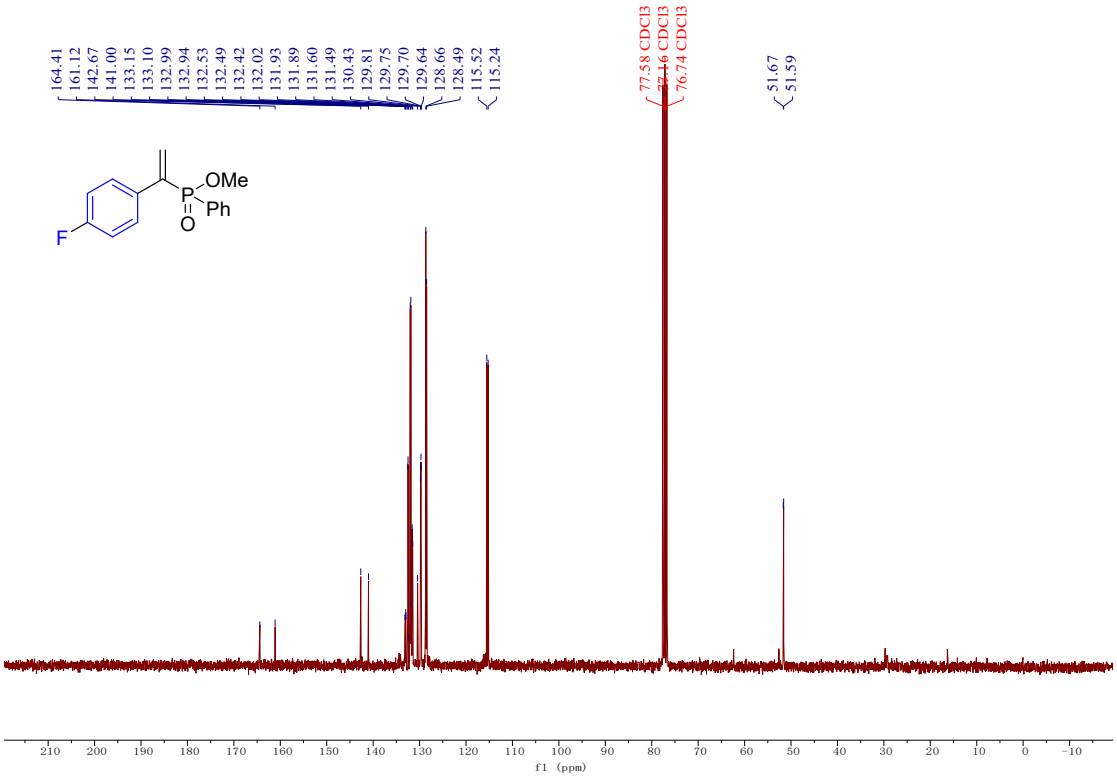
^{31}P NMR (121 MHz, $CDCl_3$) of **6h**



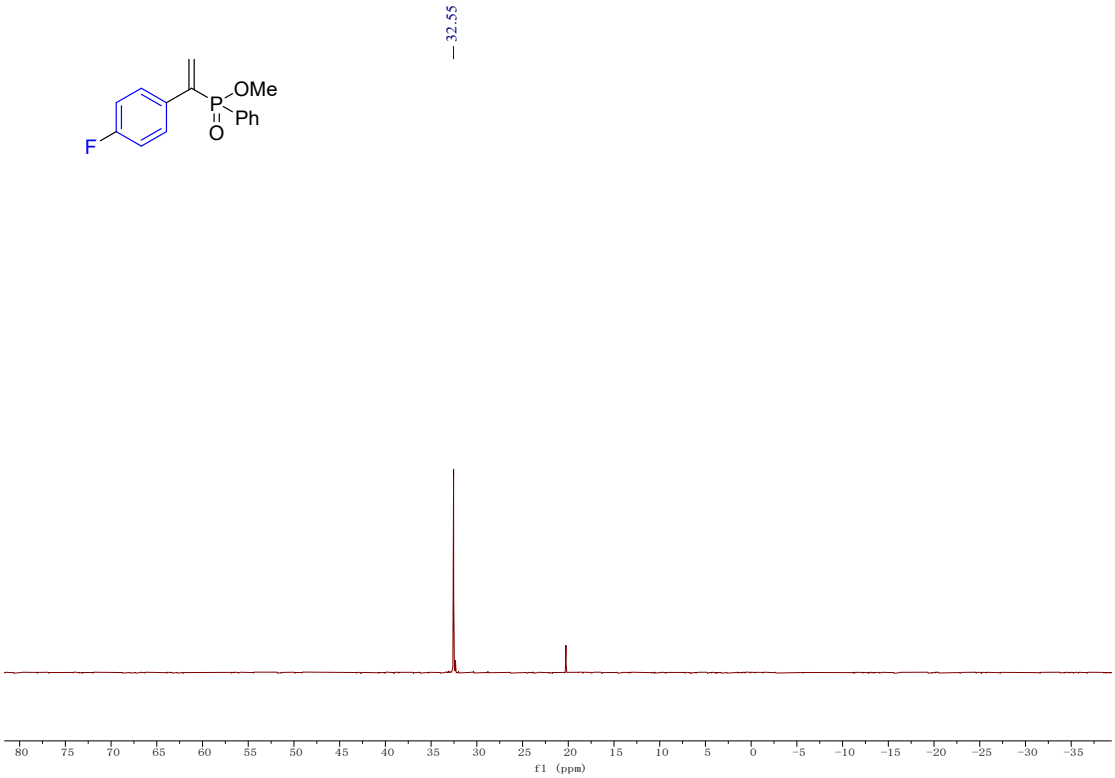
^{19}F NMR (282 MHz, $CDCl_3$) of **6h**



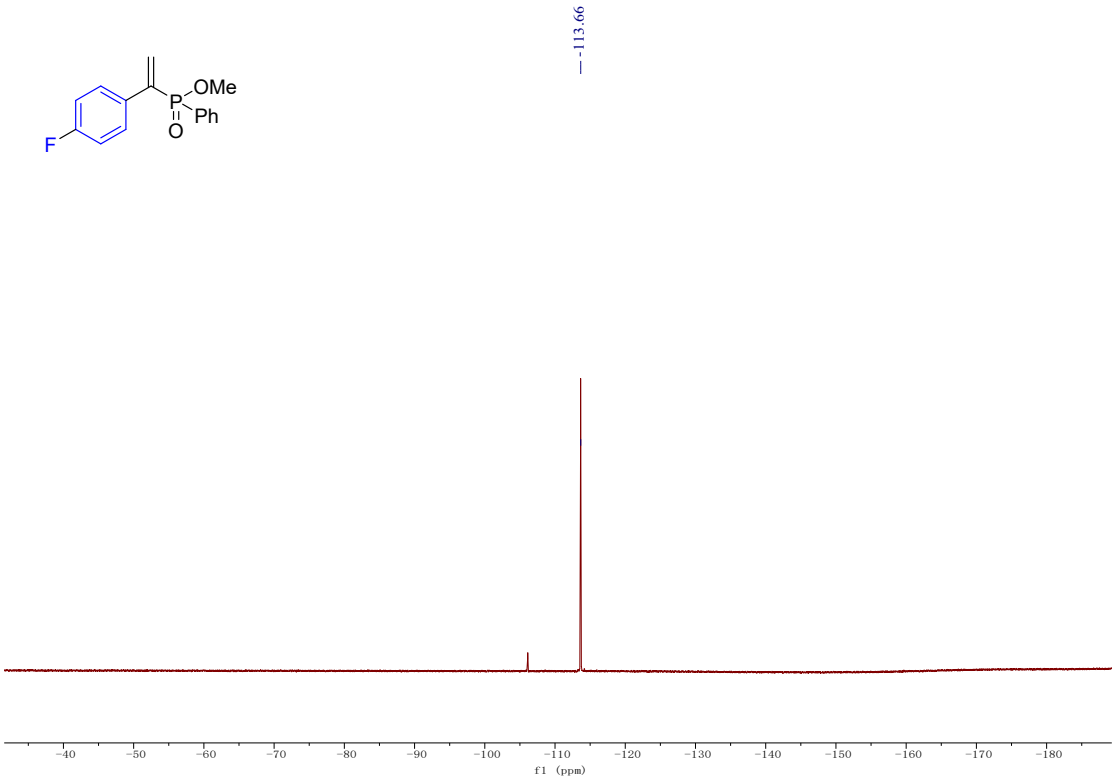
^{1}H NMR (300 MHz, $CDCl_3$) of **6i**



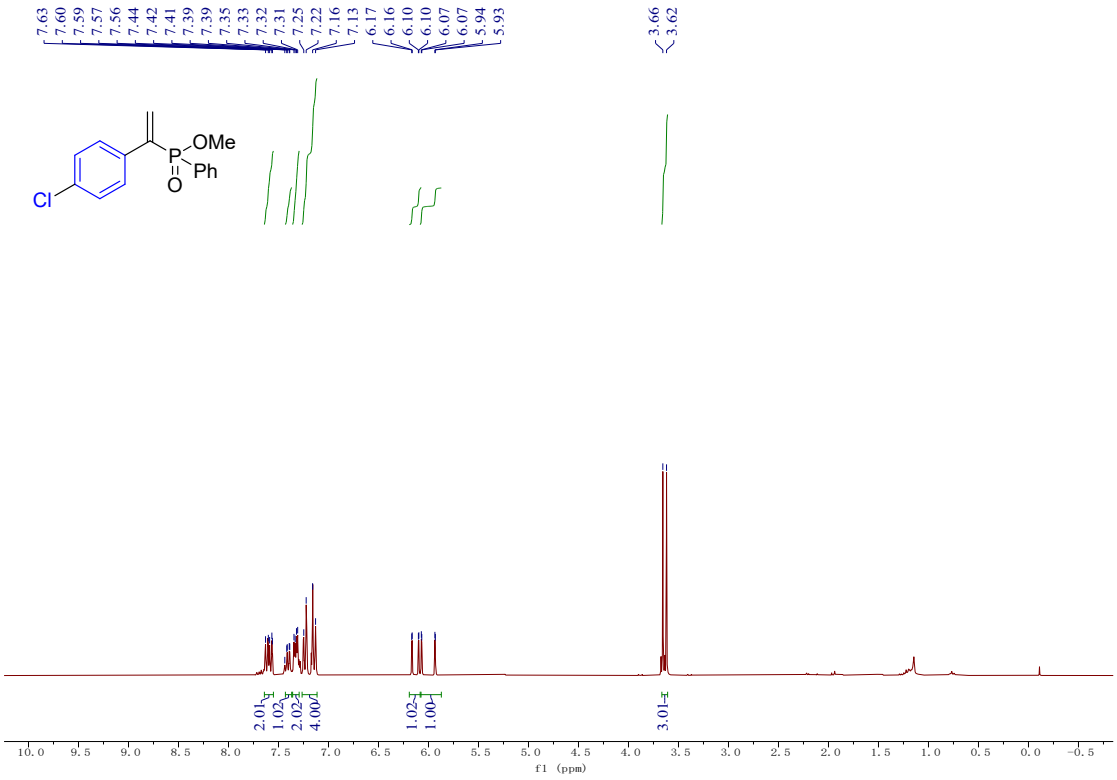
^{13}C NMR (75 MHz, $CDCl_3$) of **6i**



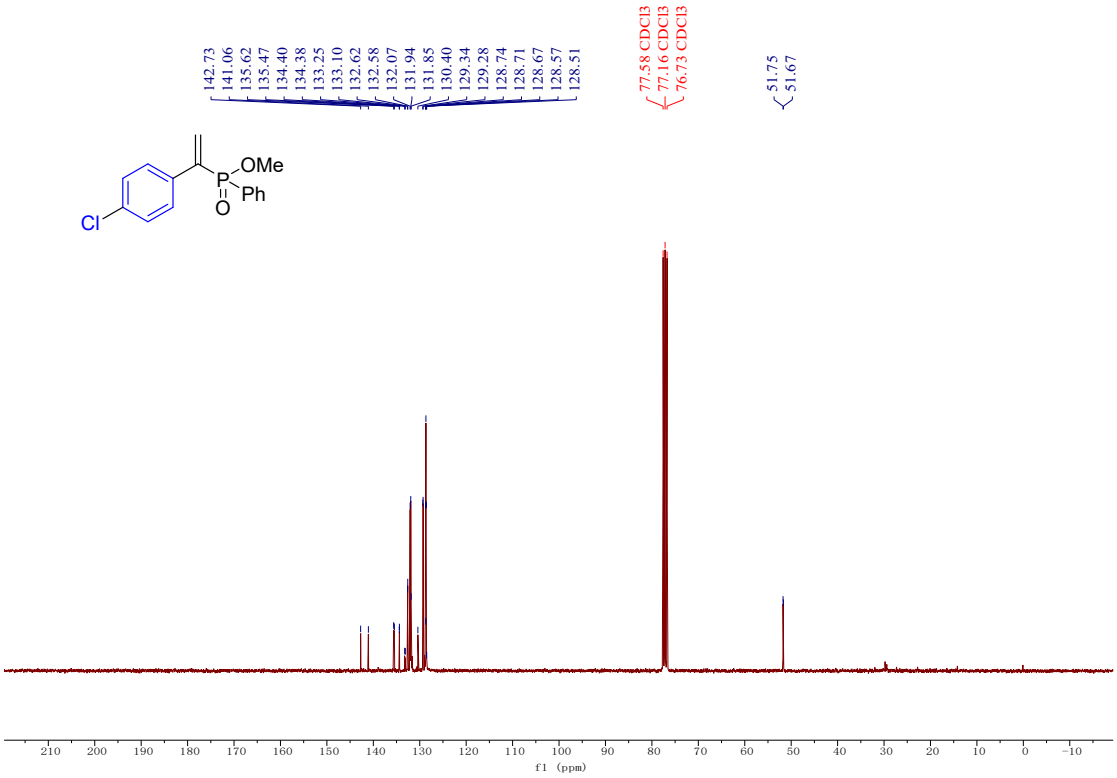
^{31}P NMR (121 MHz, $CDCl_3$) of **6i**



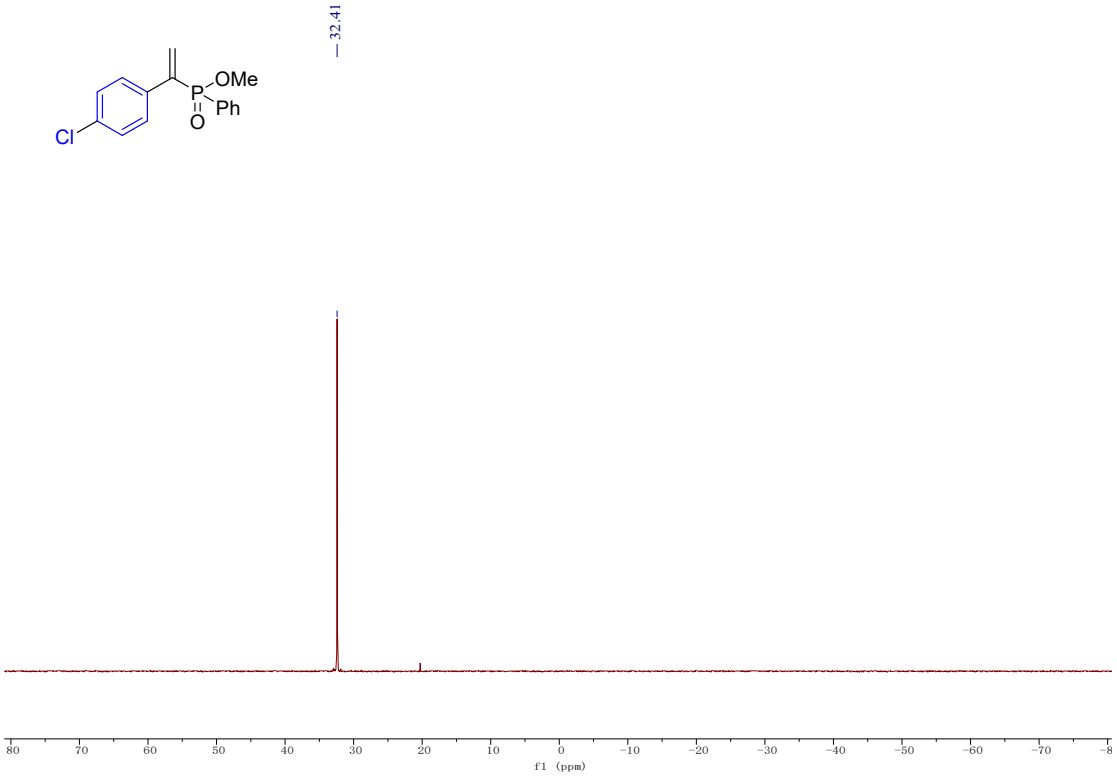
^{19}F NMR (282 MHz, $CDCl_3$) of **6i**



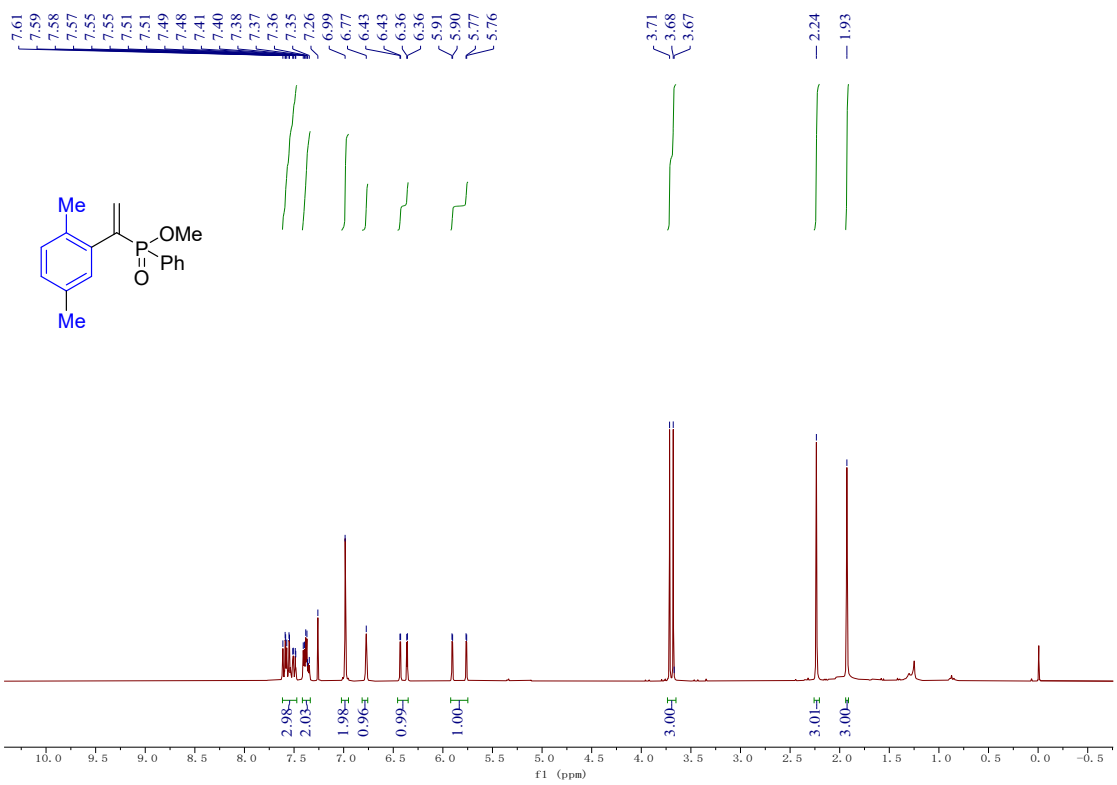
^{1}H NMR (300 MHz, $CDCl_3$) of **6j**



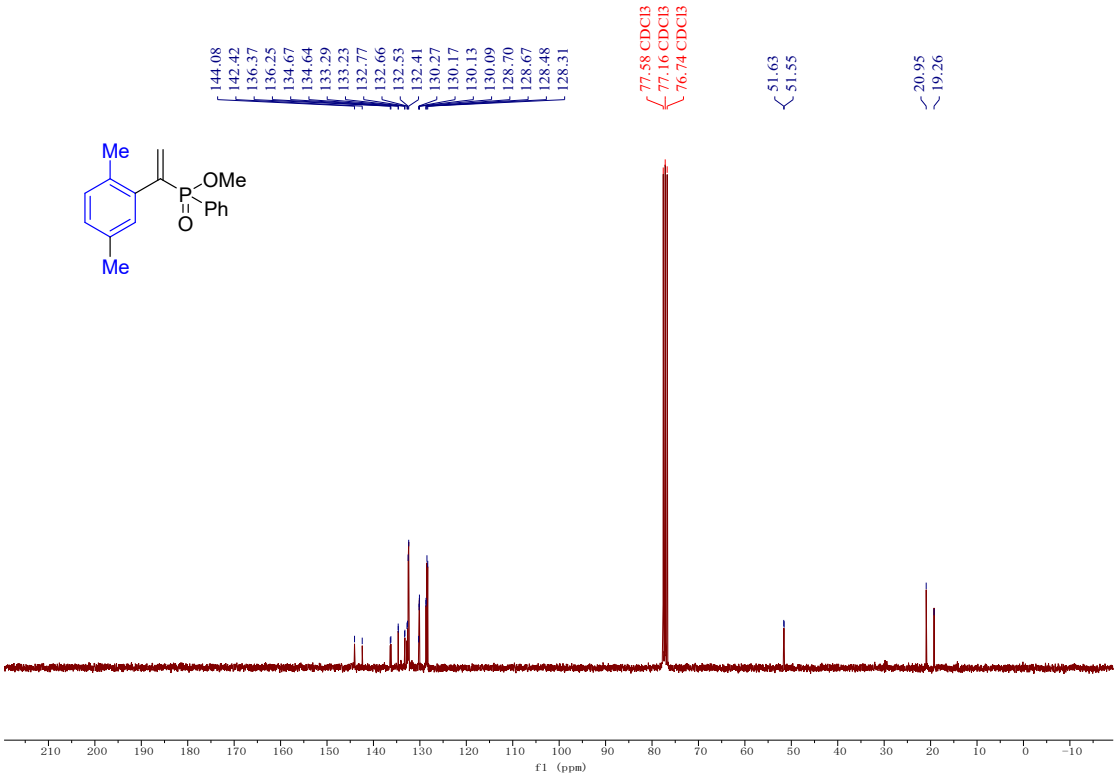
^{13}C NMR (75 MHz, $CDCl_3$) of **6j**



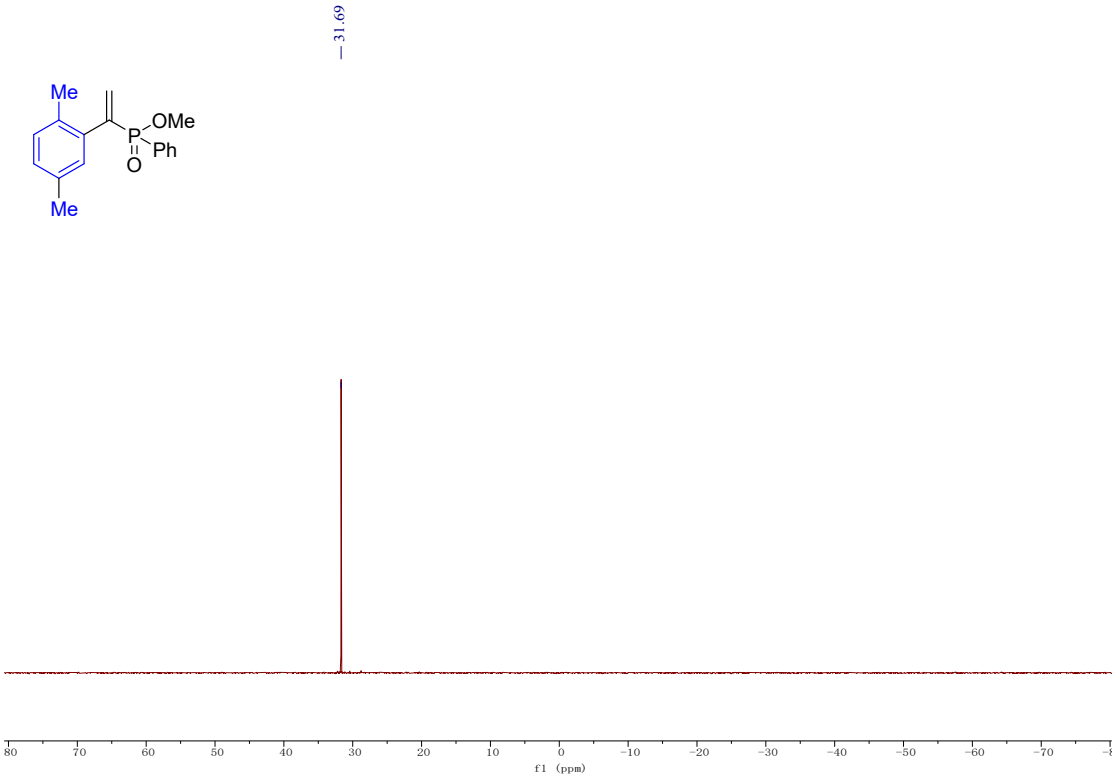
^{31}P NMR (121 MHz, $CDCl_3$) of **6j**



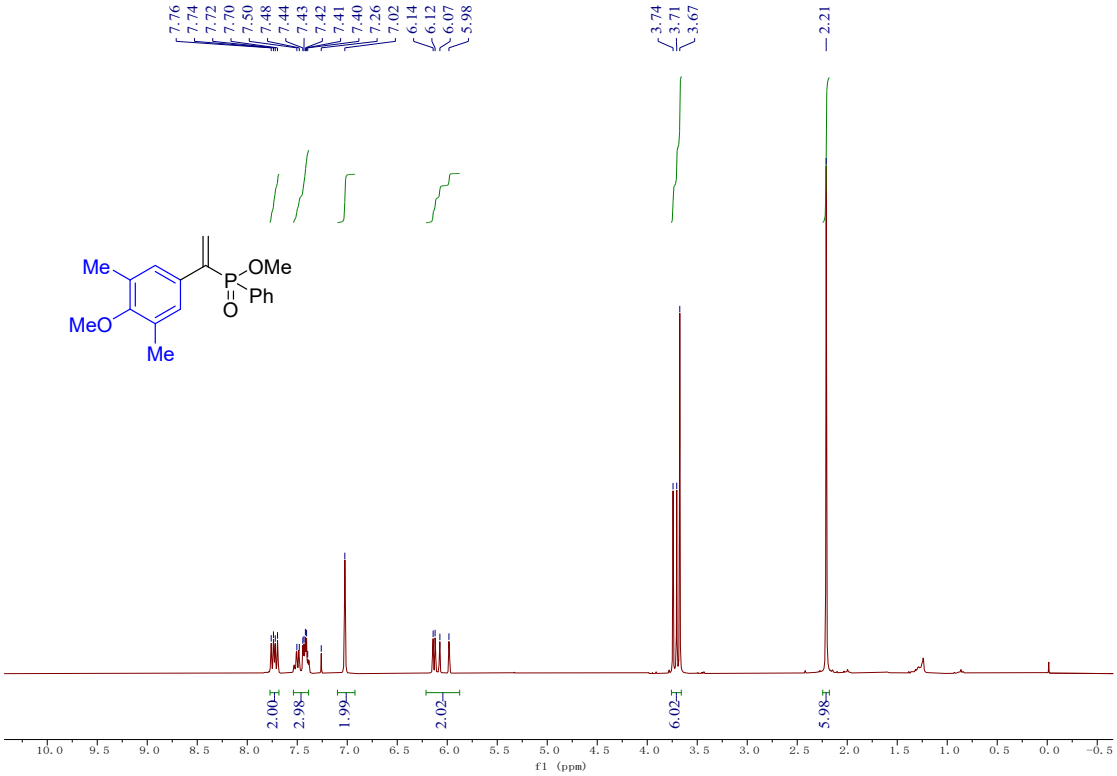
^{1}H NMR (300 MHz, $CDCl_3$) of **6k**



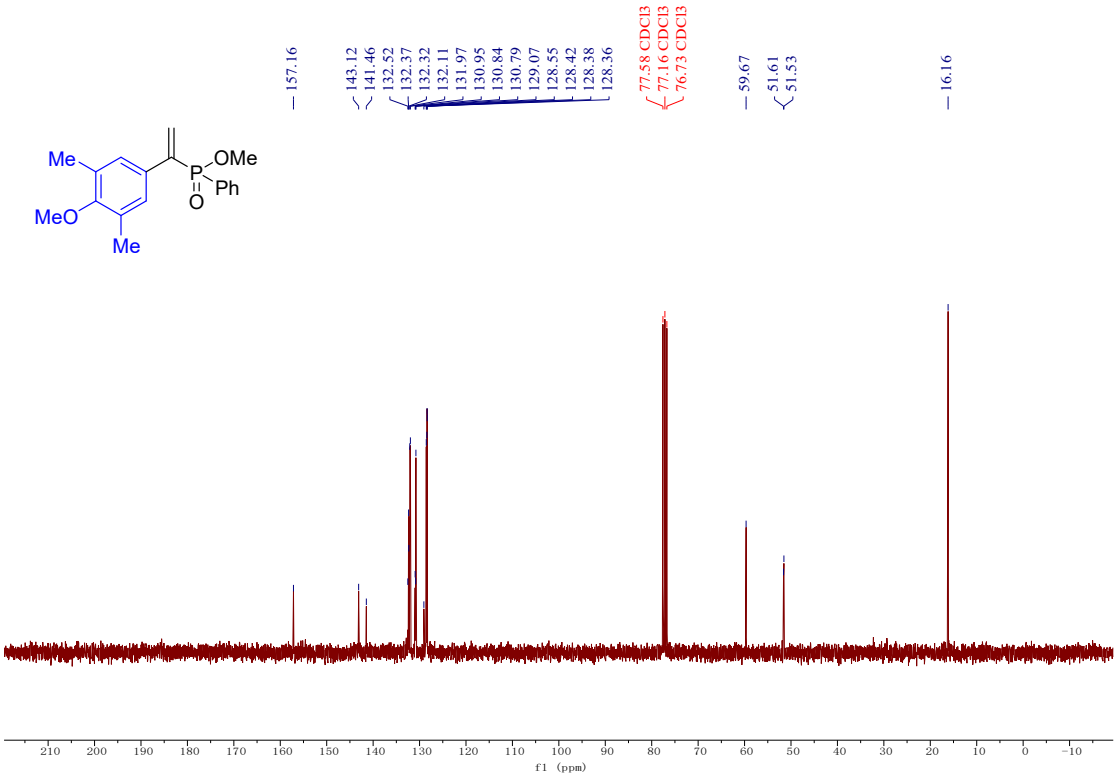
^{13}C NMR (75 MHz, $CDCl_3$) of **6k**



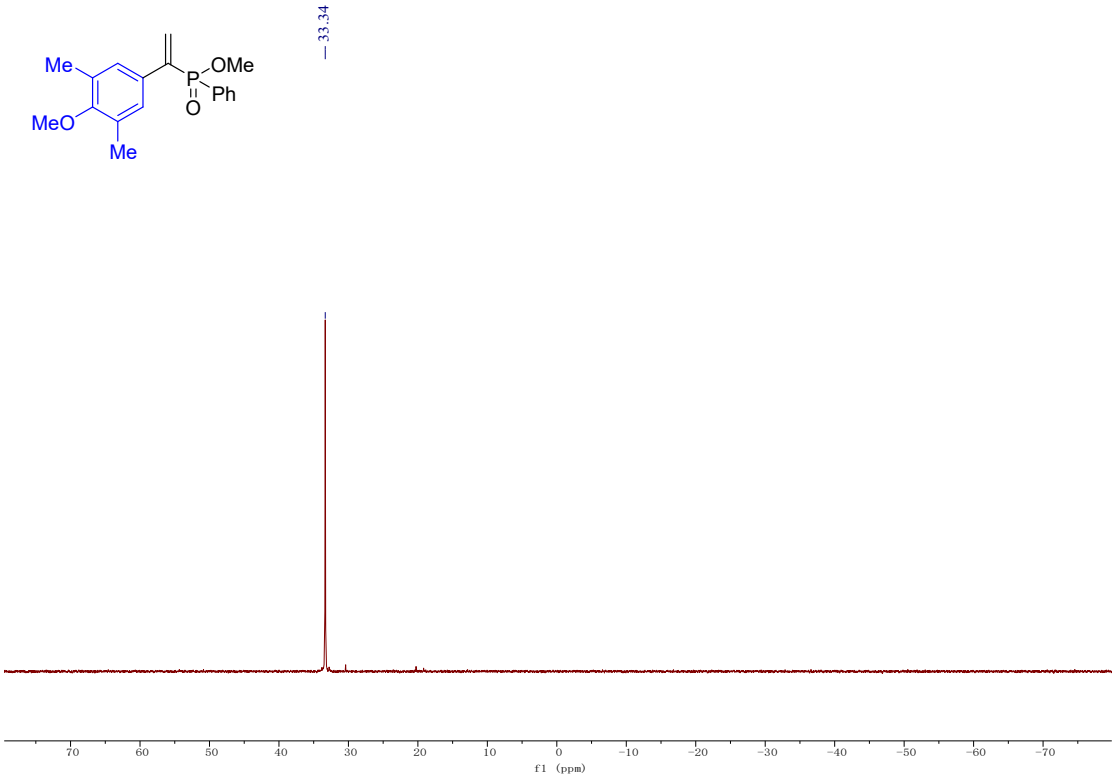
^{31}P NMR (121 MHz, $CDCl_3$) of **6k**



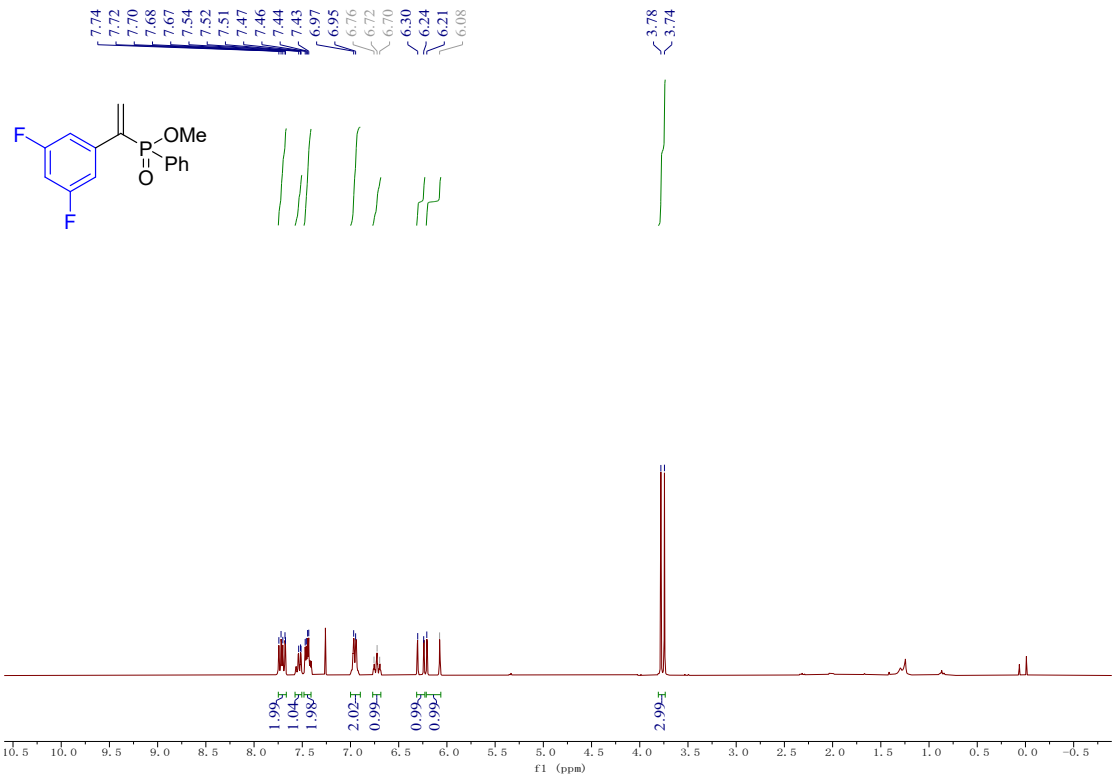
^{1}H NMR (300 MHz, $CDCl_3$) of **6l**



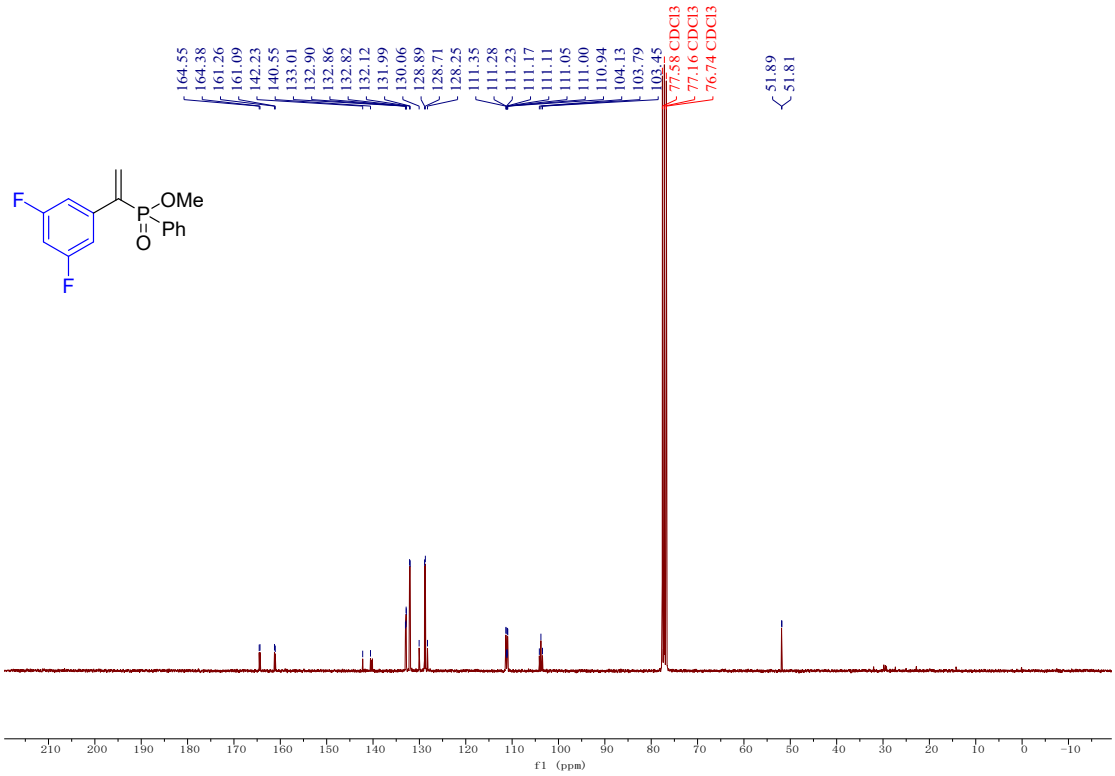
^{13}C NMR (75 MHz, $CDCl_3$) of **6l**



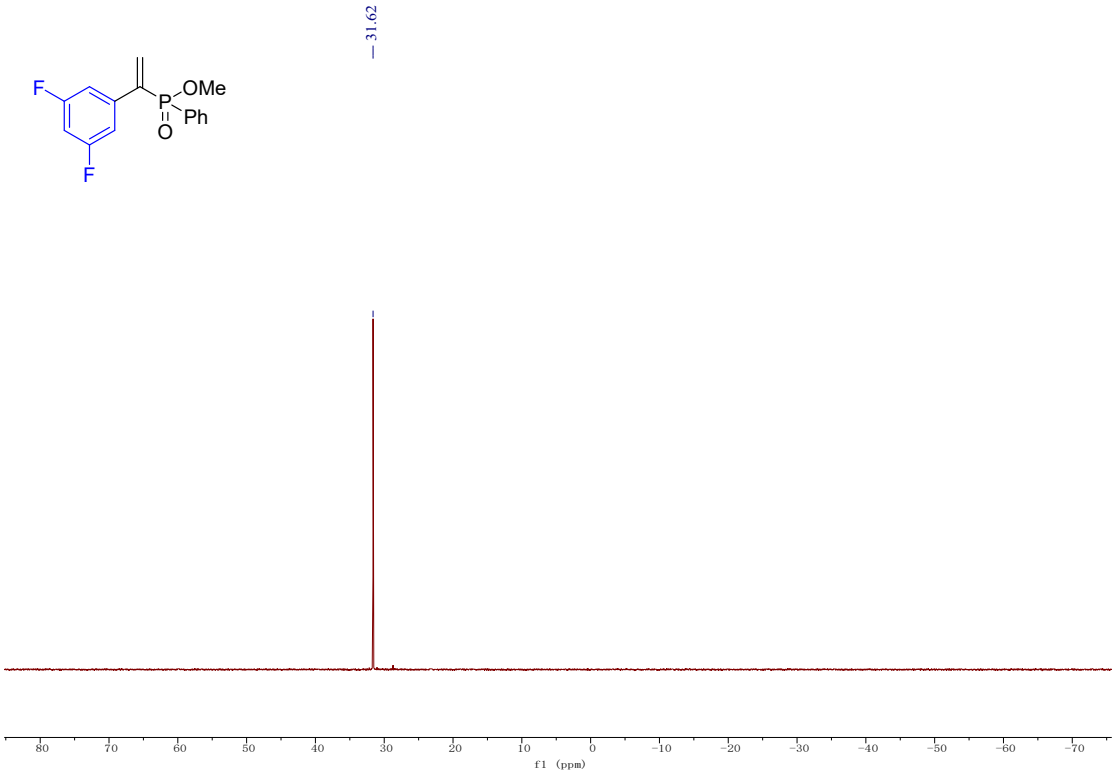
^{31}P NMR (121 MHz, $CDCl_3$) of **6l**



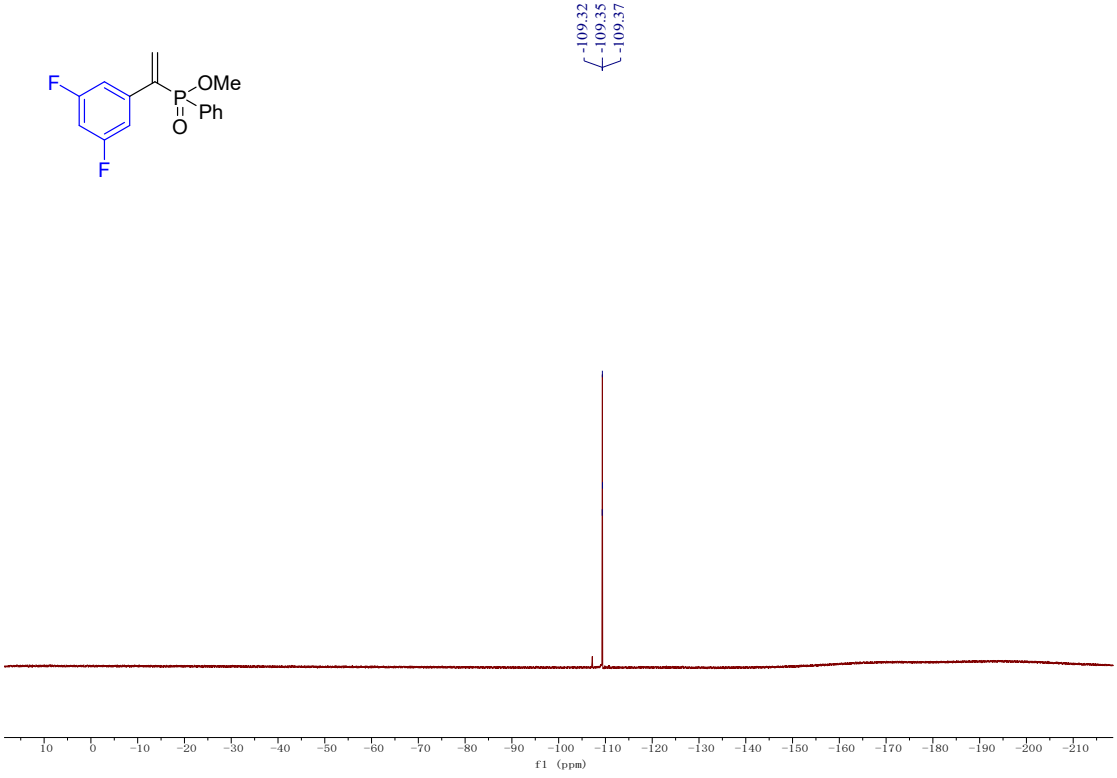
^{1}H NMR (300 MHz, $CDCl_3$) of **6m**



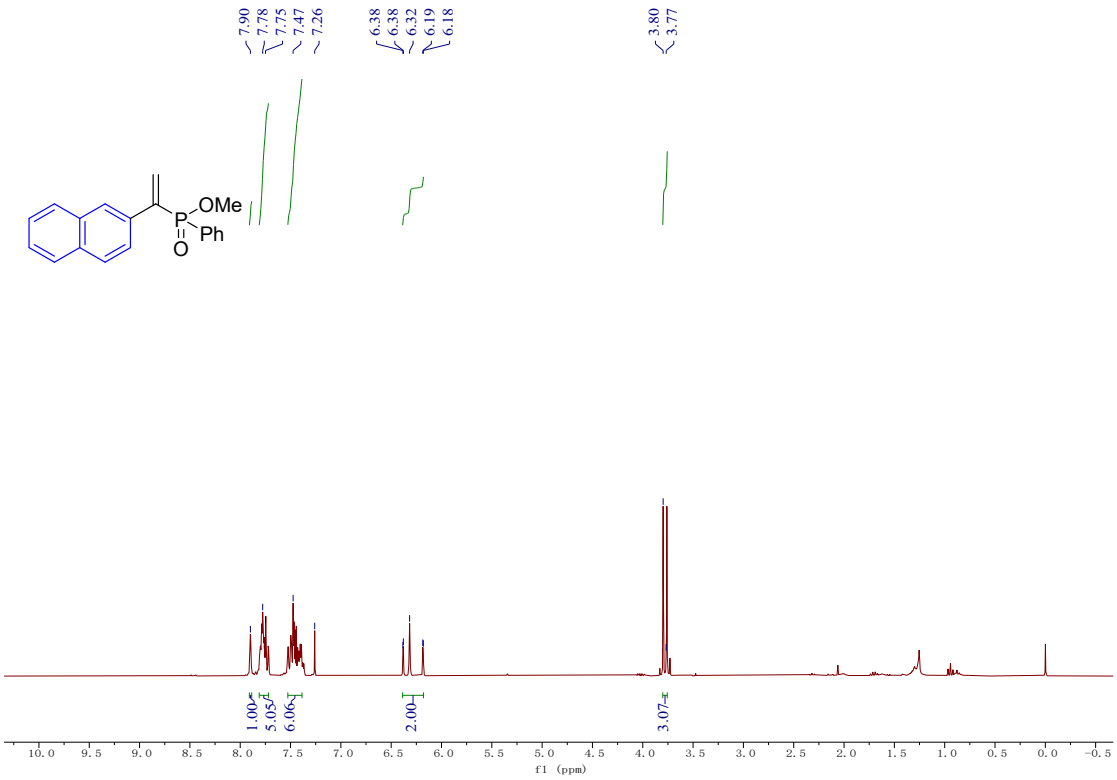
^{13}C NMR (75 MHz, $CDCl_3$) of **6m**



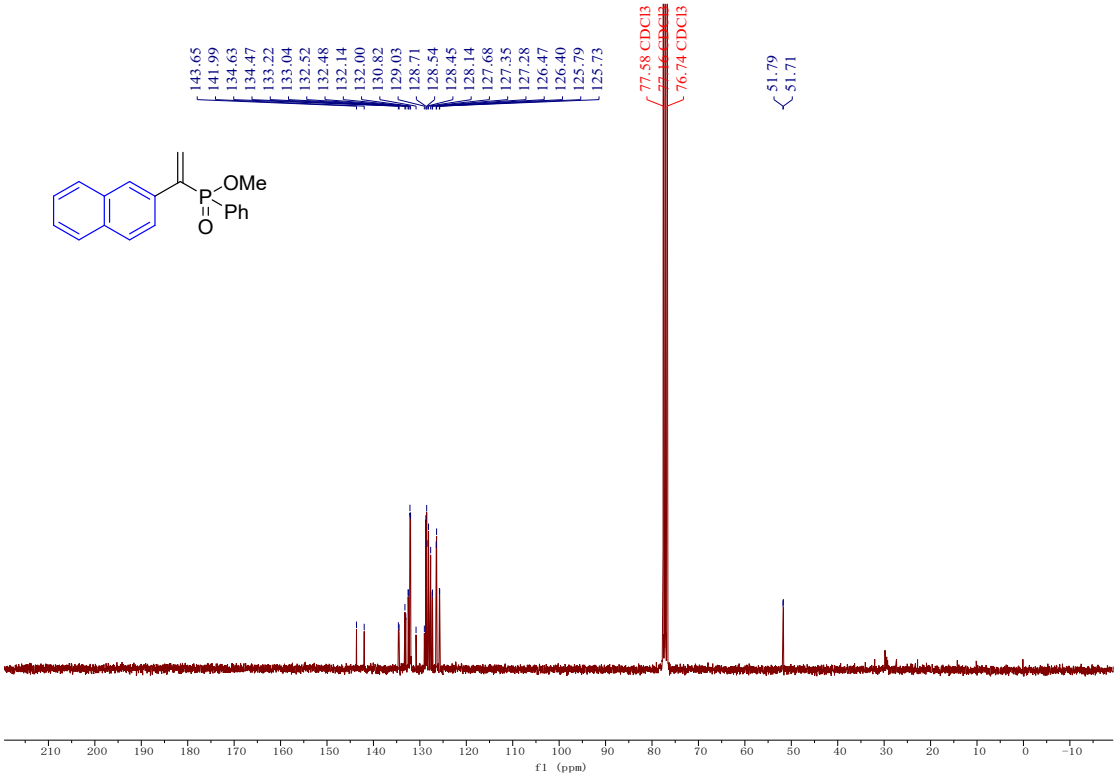
^{31}P NMR (121 MHz, $CDCl_3$) of **6m**



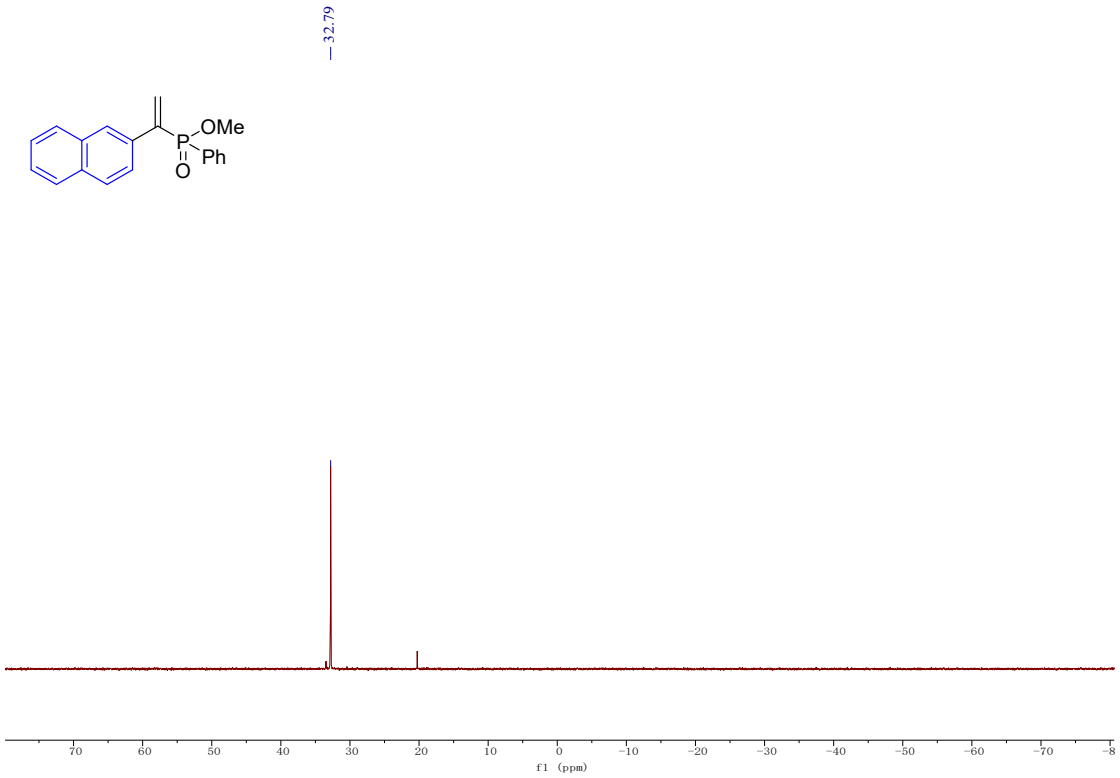
^{19}F NMR (282 MHz, $CDCl_3$) of **6m**



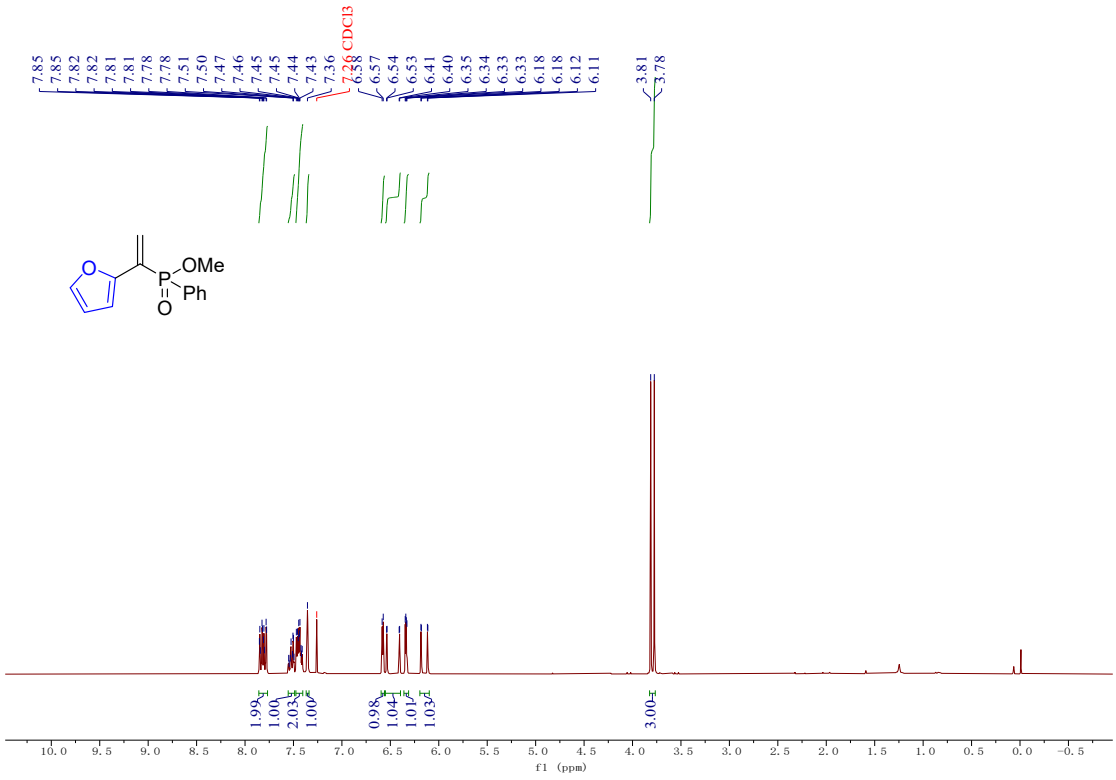
^{1}H NMR (300 MHz, $CDCl_3$) of **6n**



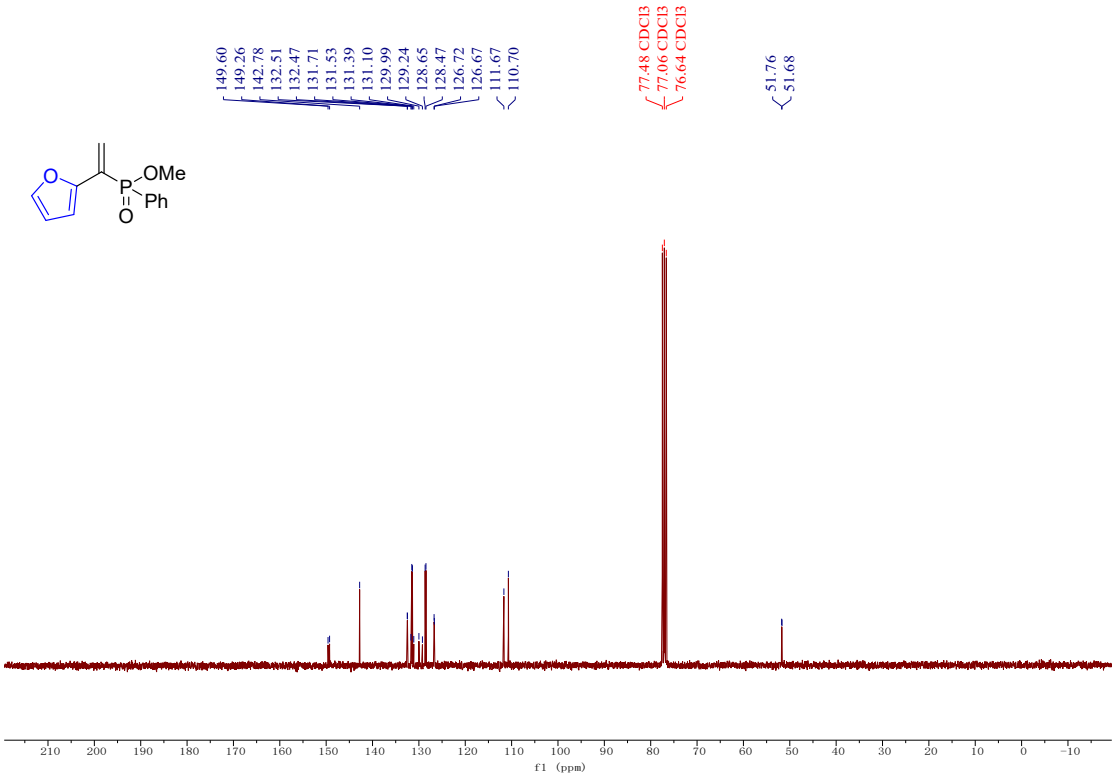
^{13}C NMR (75 MHz, $CDCl_3$) of **6n**



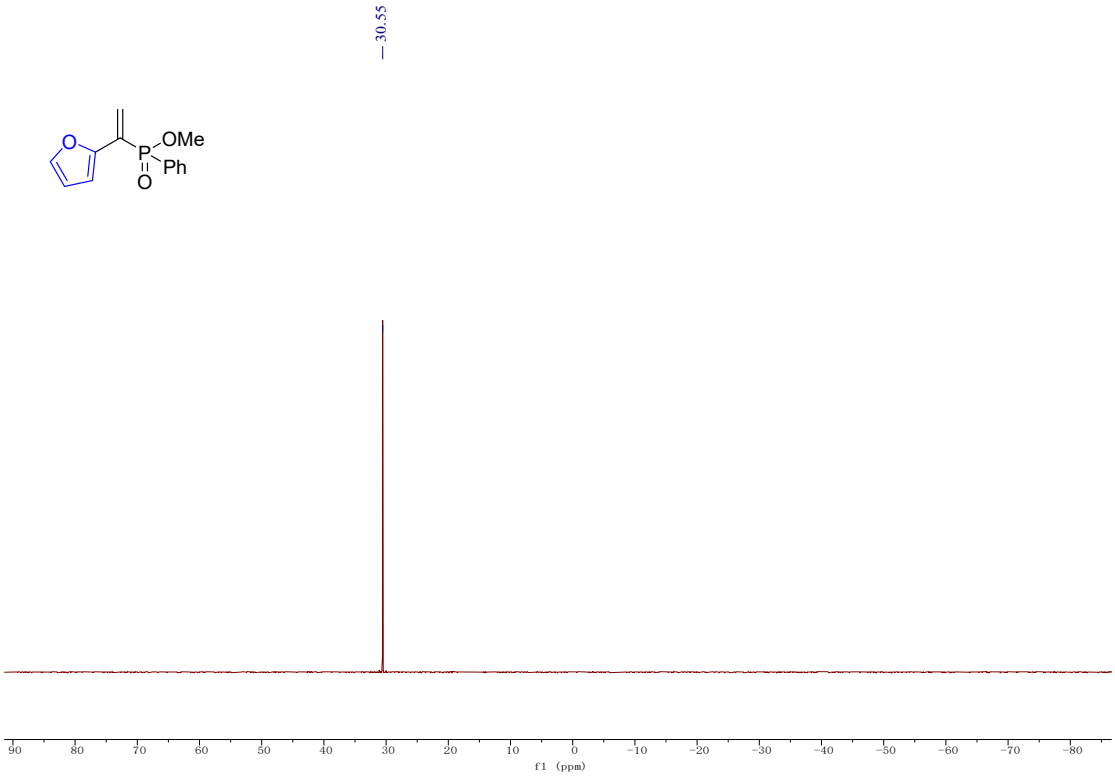
^{31}P NMR (121 MHz, $CDCl_3$) of **6n**



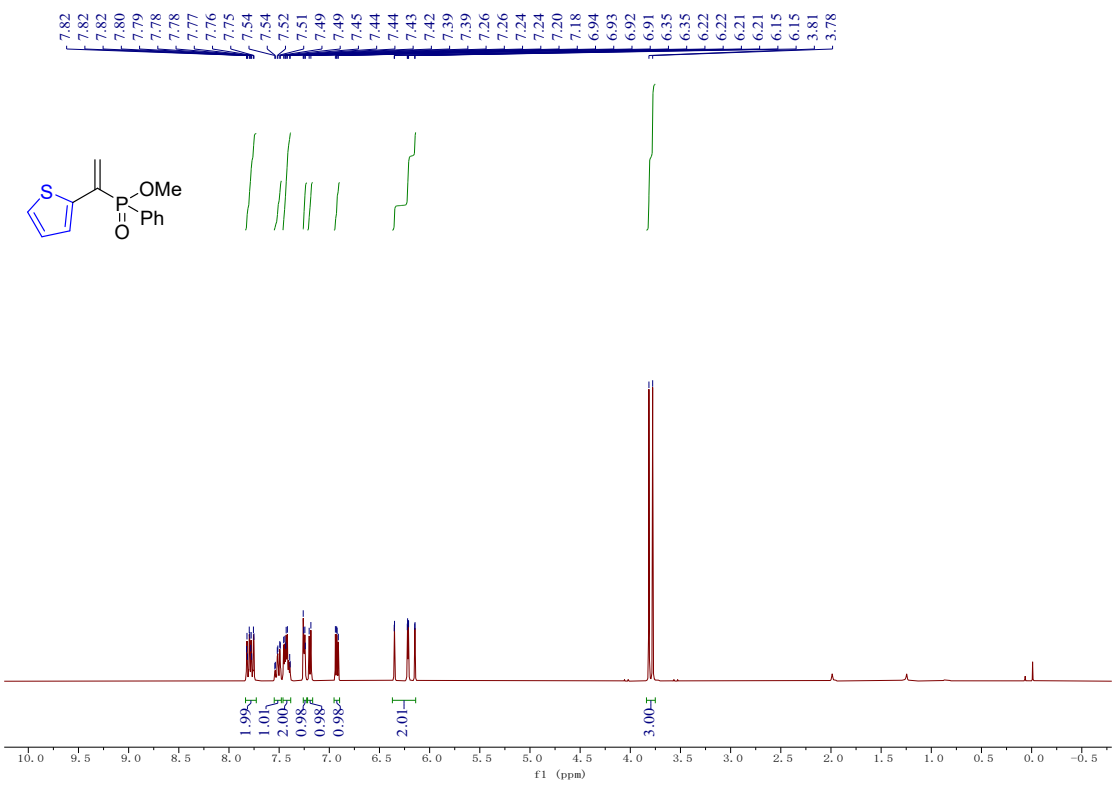
^{1}H NMR (300 MHz, $CDCl_3$) of **6o**



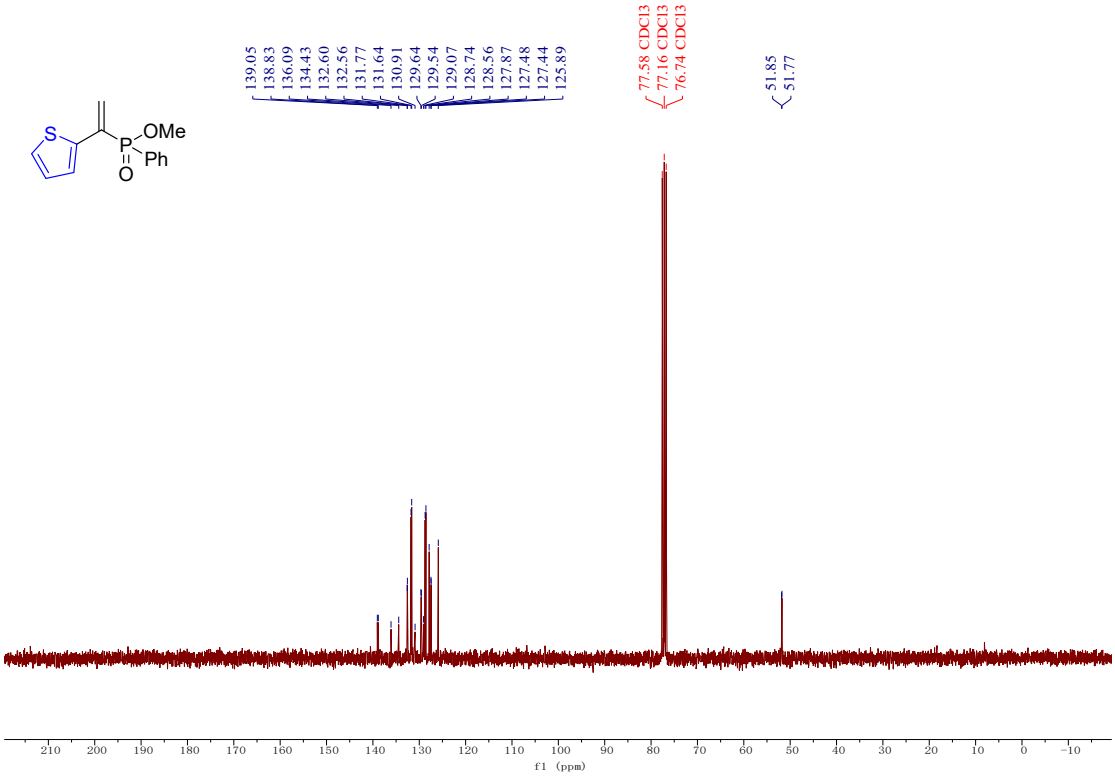
^{13}C NMR (75 MHz, $CDCl_3$) of **6o**



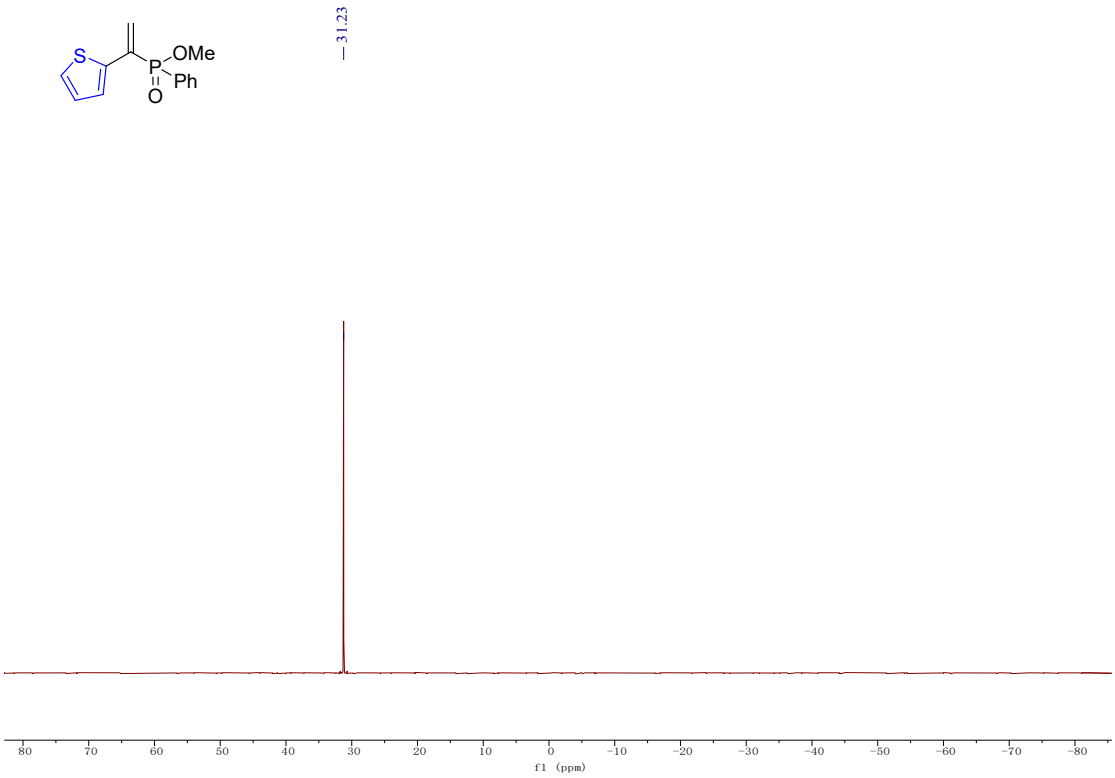
^{31}P NMR (121 MHz, $CDCl_3$) of **6o**



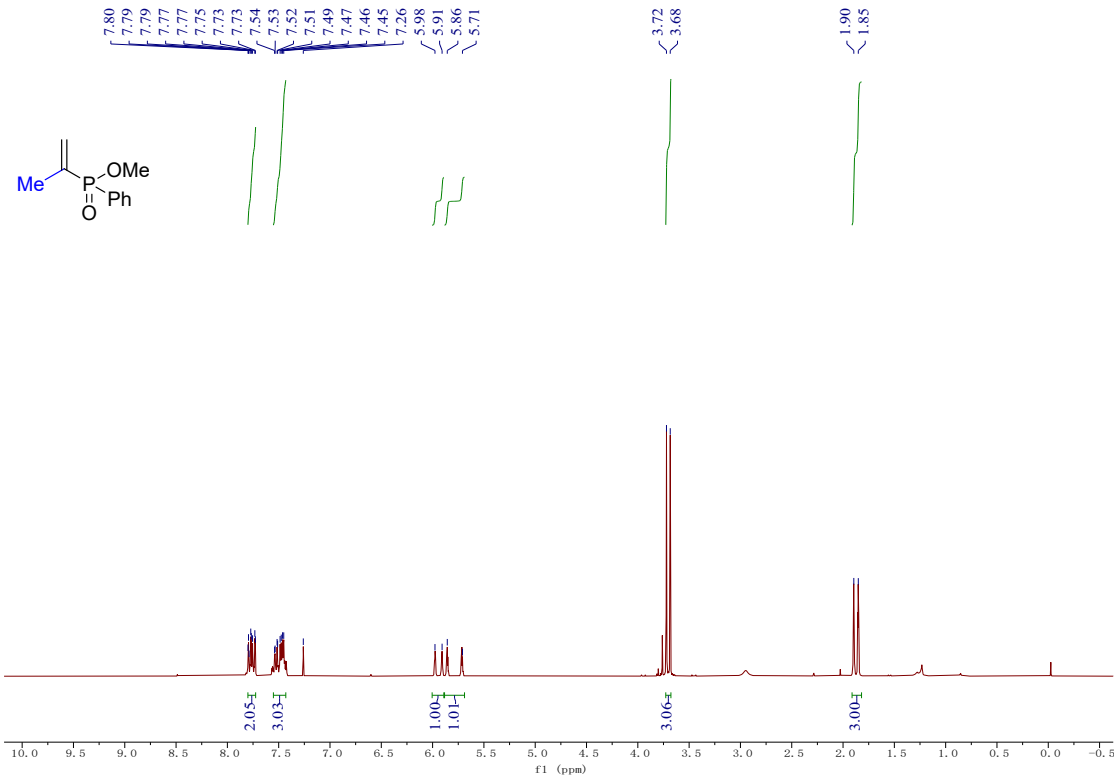
^{1}H NMR (300 MHz, $CDCl_3$) of **6p**



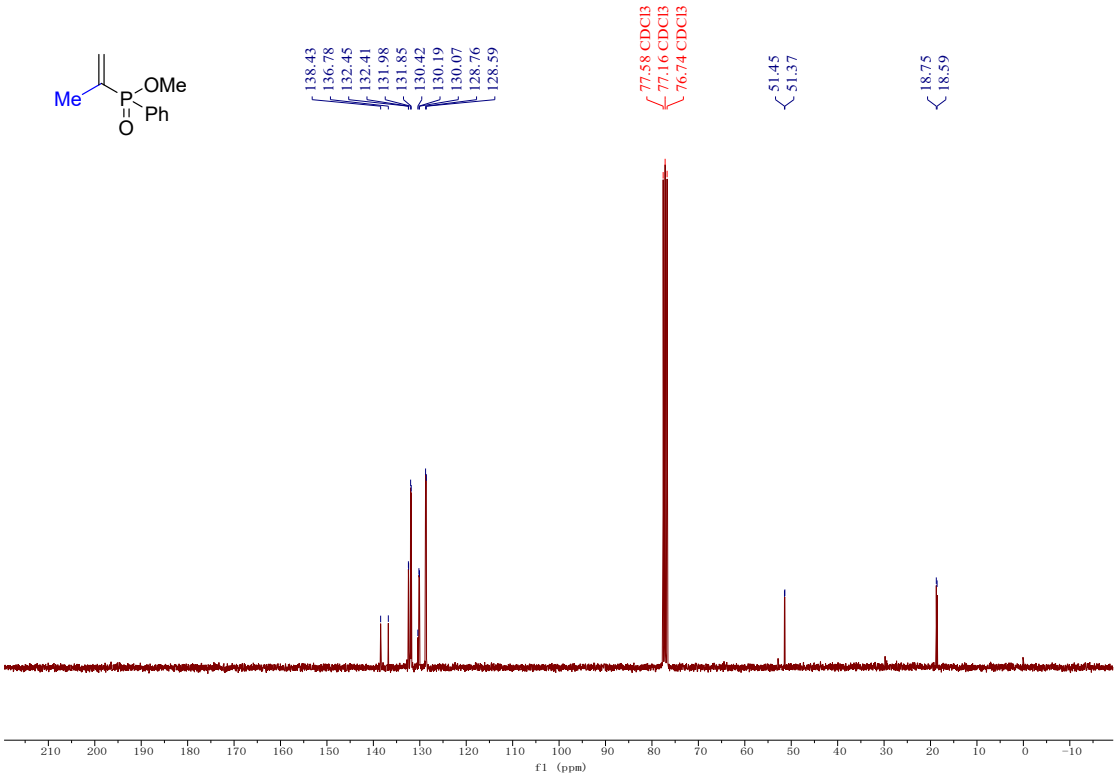
^{13}C NMR (75 MHz, $CDCl_3$) of **6p**



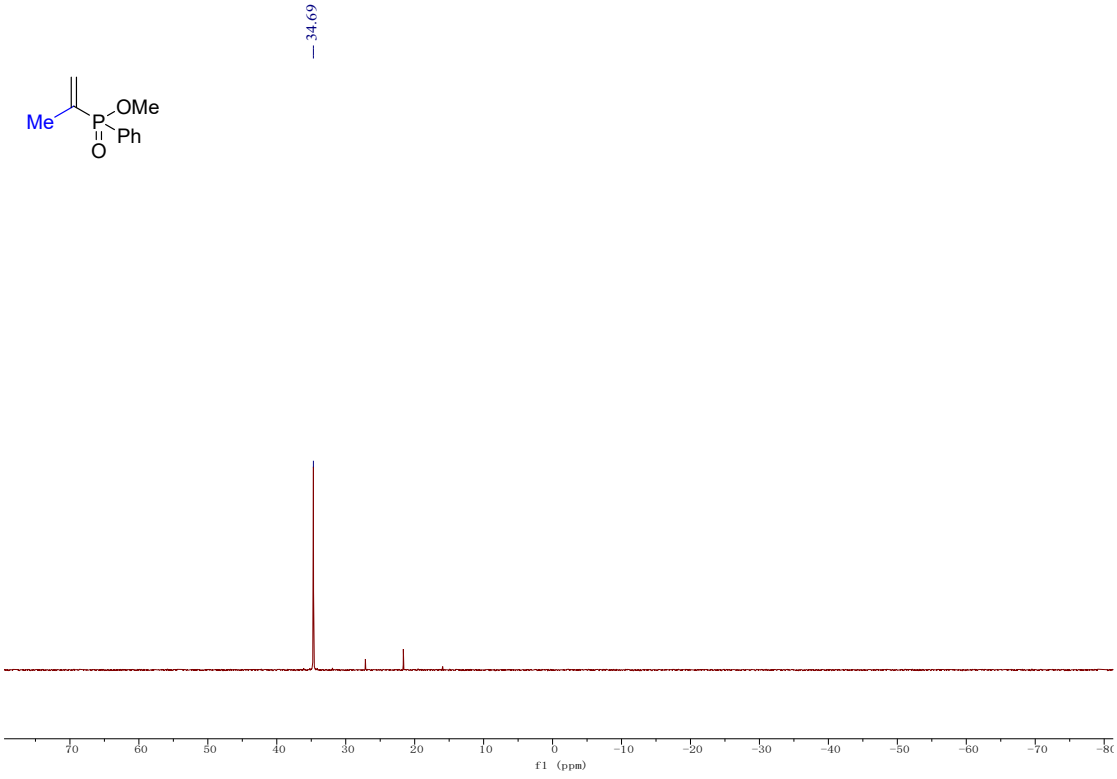
^{31}P NMR (121 MHz, $CDCl_3$) of **6p**



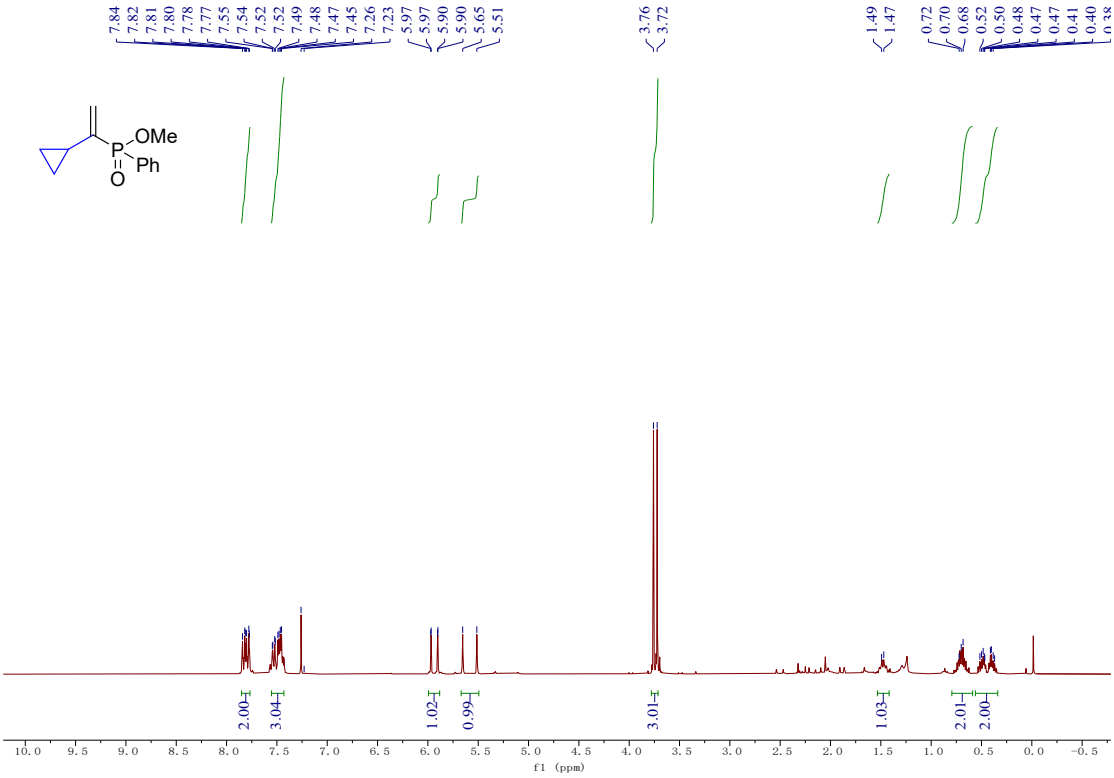
^{1}H NMR (300 MHz, $CDCl_3$) of **6r**



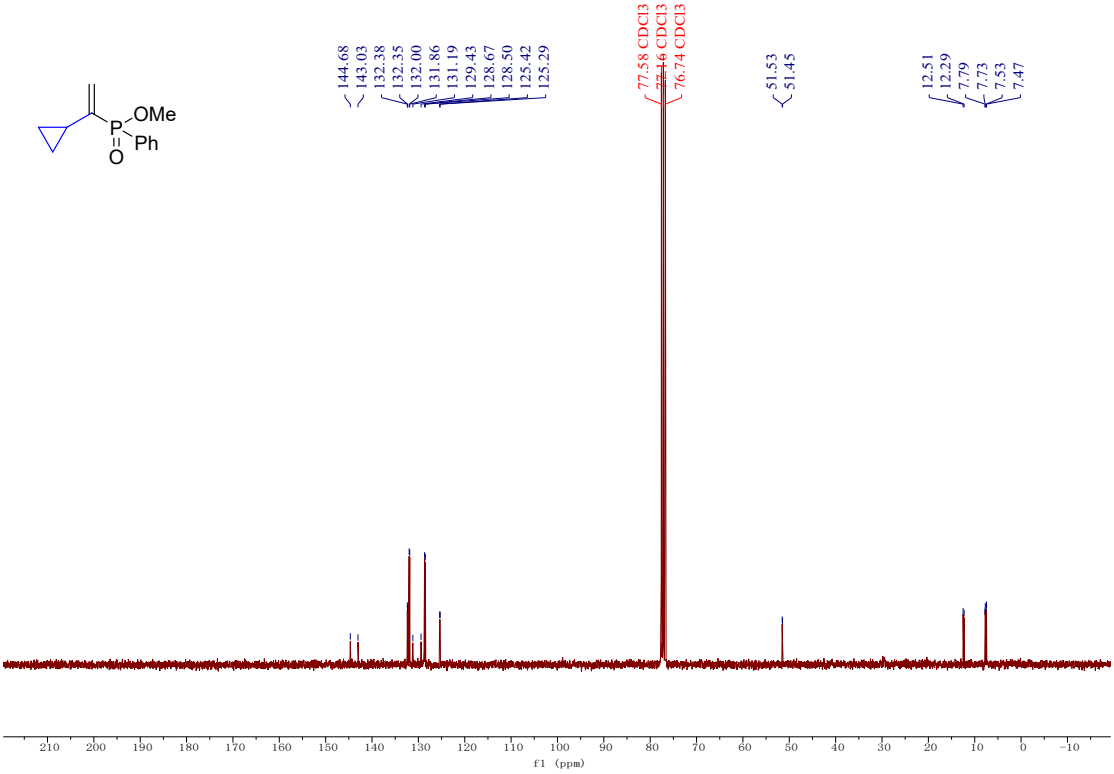
^{13}C NMR (75 MHz, $CDCl_3$) of **6r**



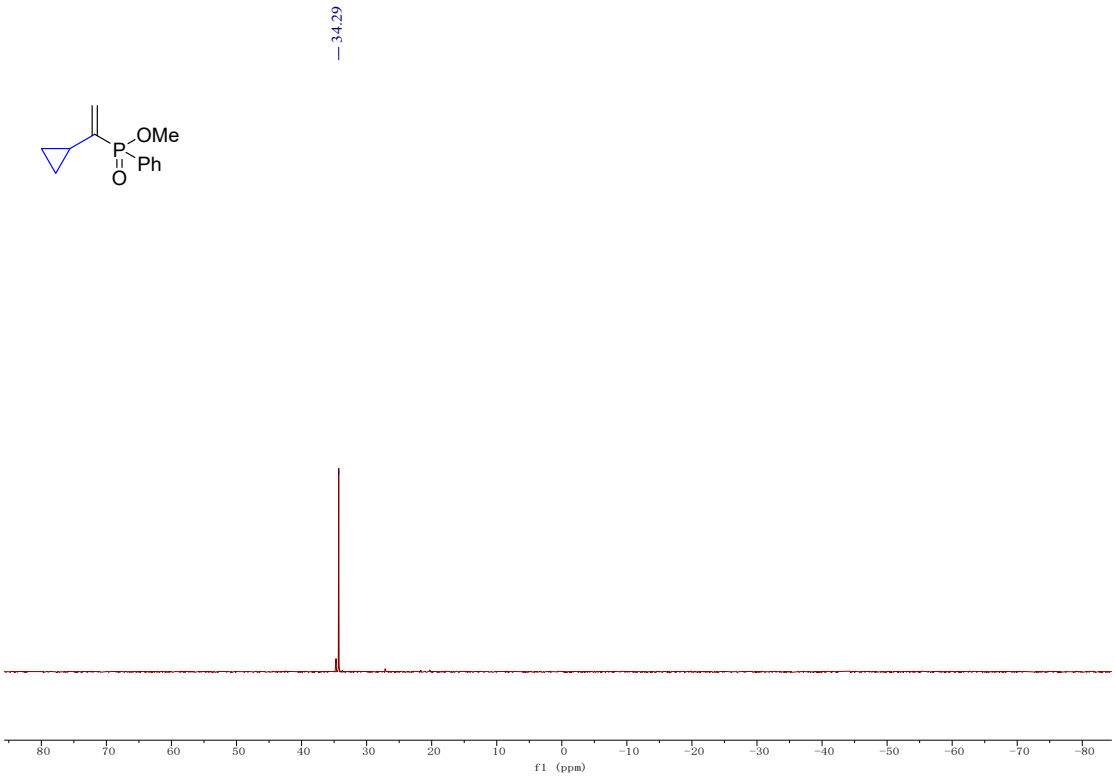
^{31}P NMR (121 MHz, $CDCl_3$) of **6r**



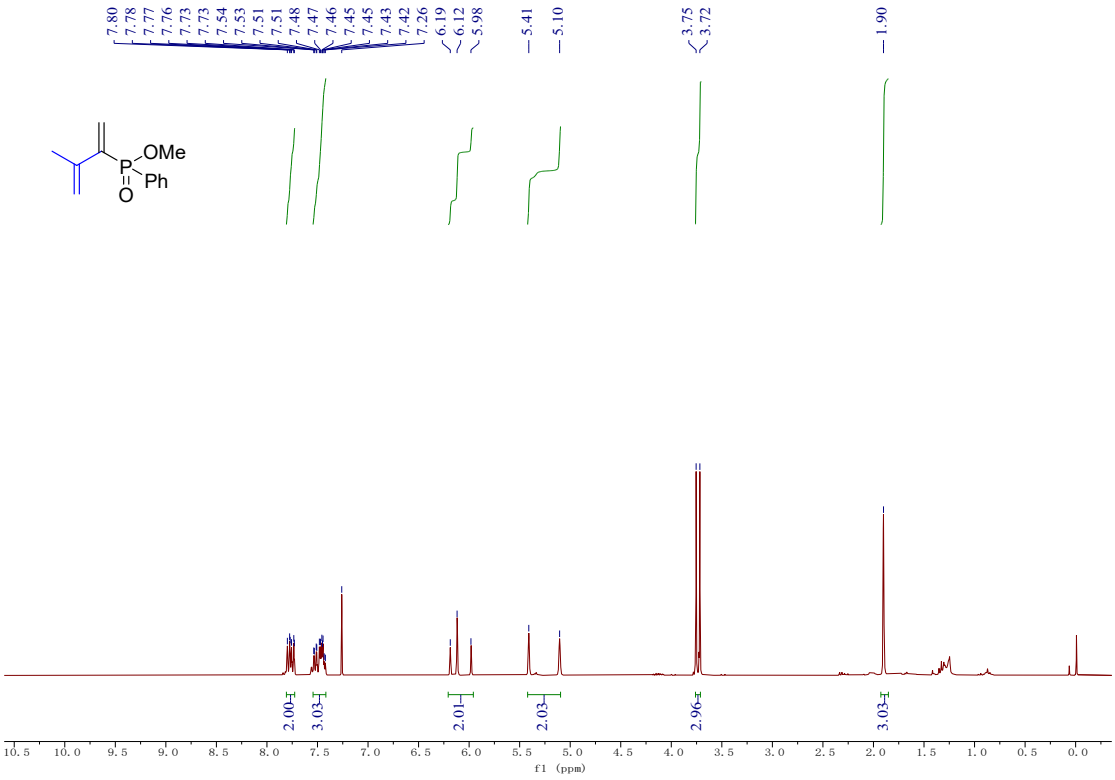
^{1}H NMR (300 MHz, $CDCl_3$) of **6s**



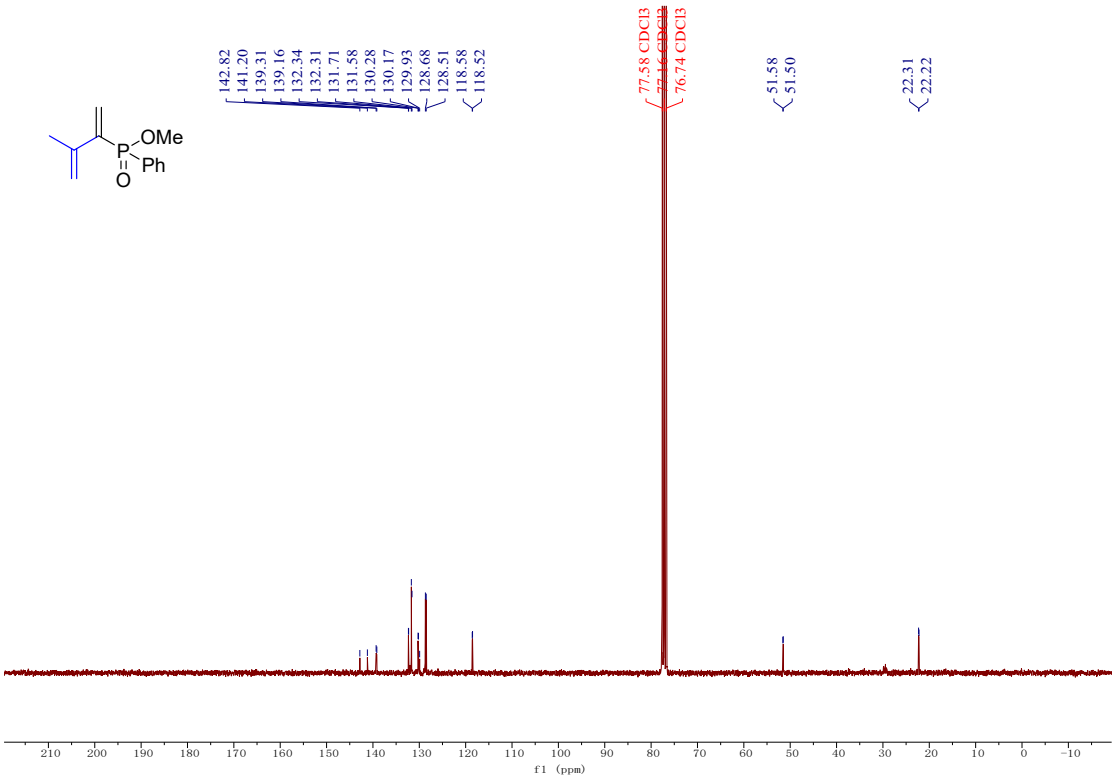
^{13}C NMR (75 MHz, $CDCl_3$) of **6s**



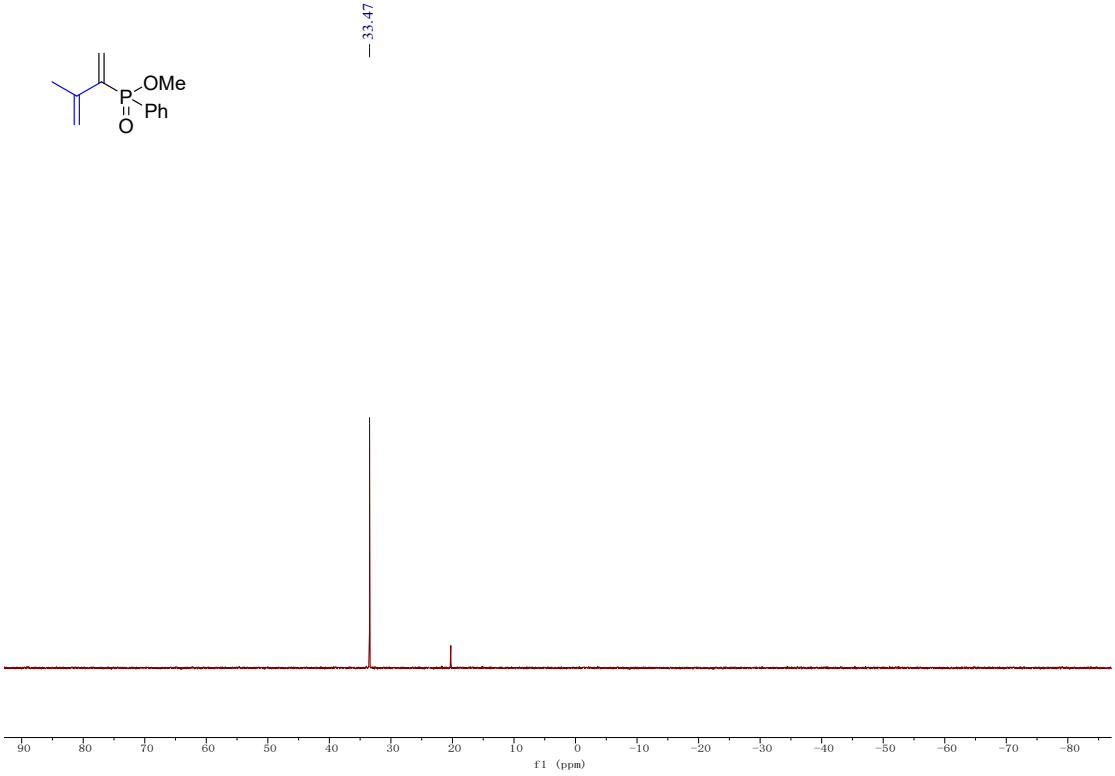
^{31}P NMR (121 MHz, $CDCl_3$) of **6s**



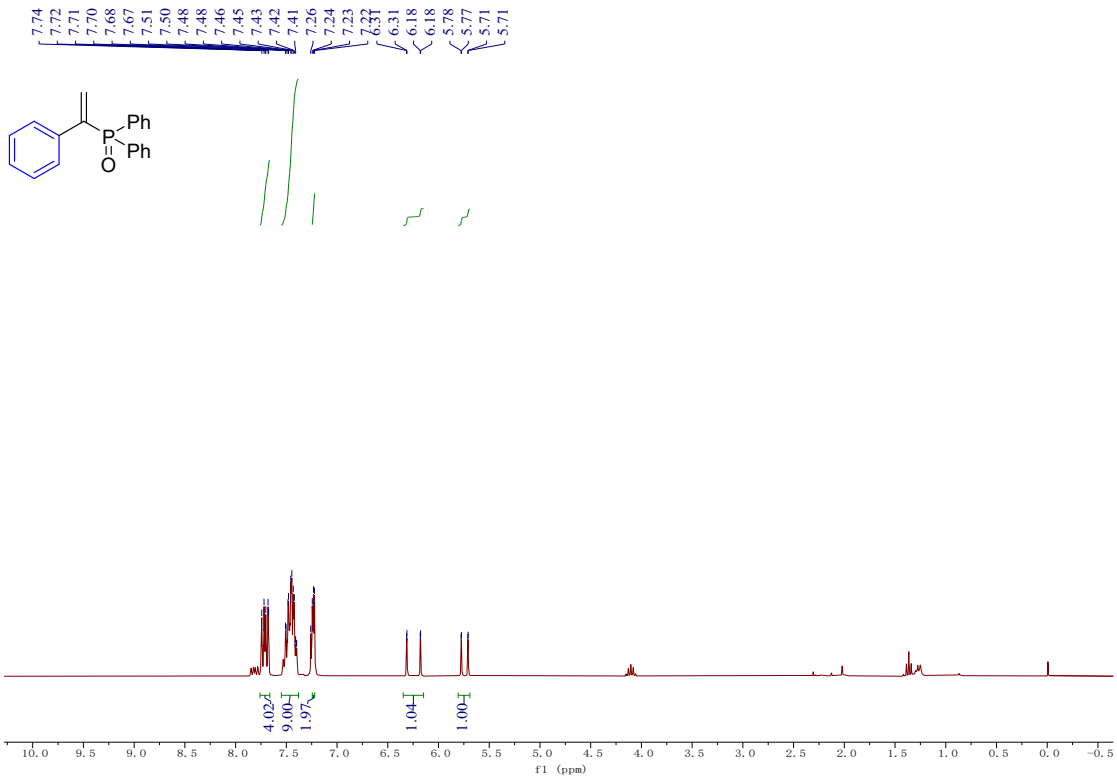
^{1}H NMR (300 MHz, $CDCl_3$) of **6t**



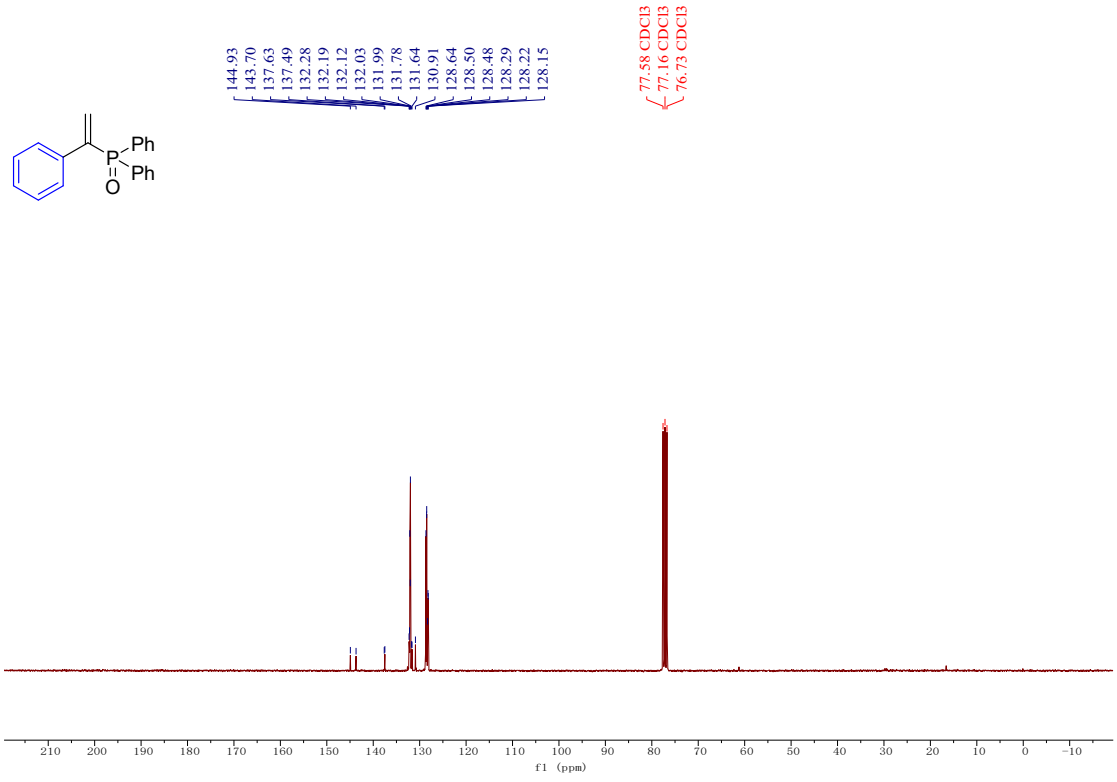
^{13}C NMR (75 MHz, $CDCl_3$) of **6t**



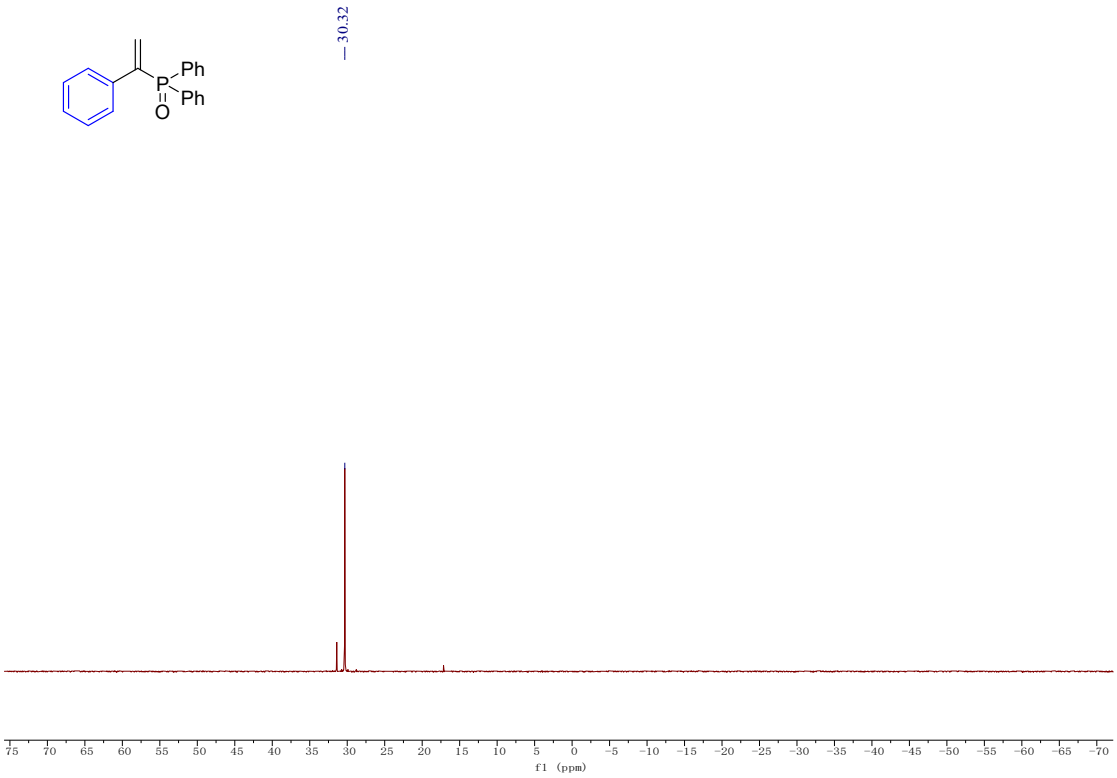
^{31}P NMR (121 MHz, $CDCl_3$) of **6t**



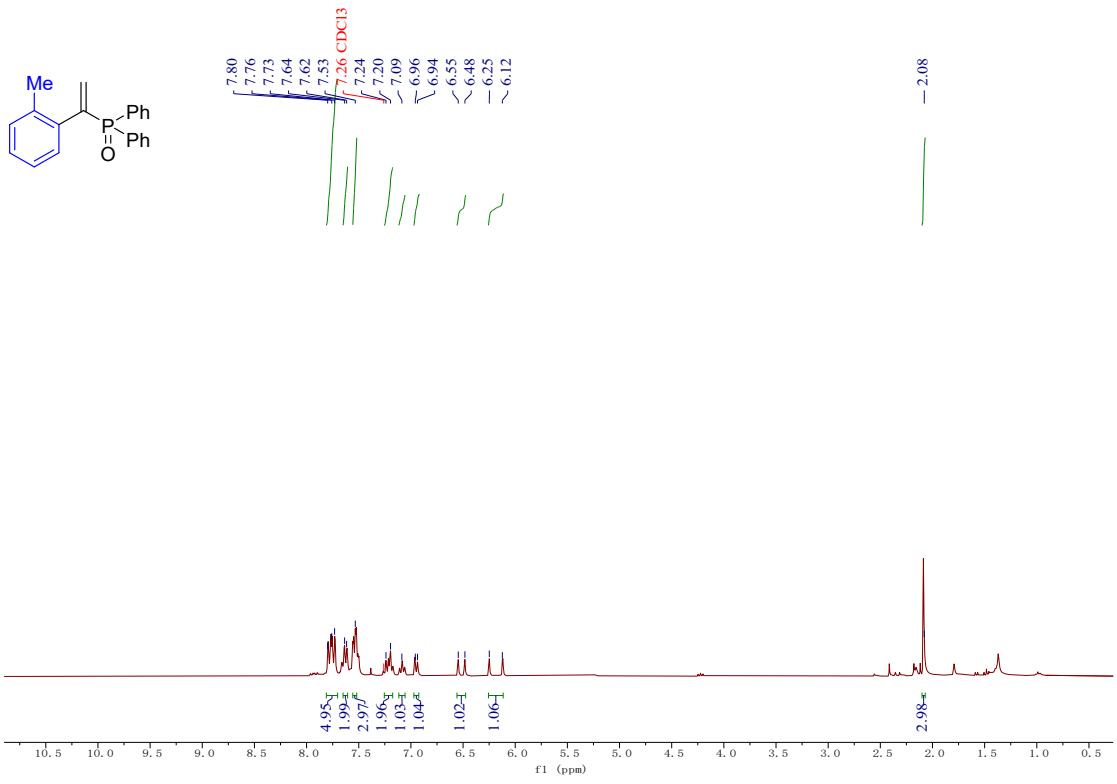
^{1}H NMR (300 MHz, $CDCl_3$) of **7a**



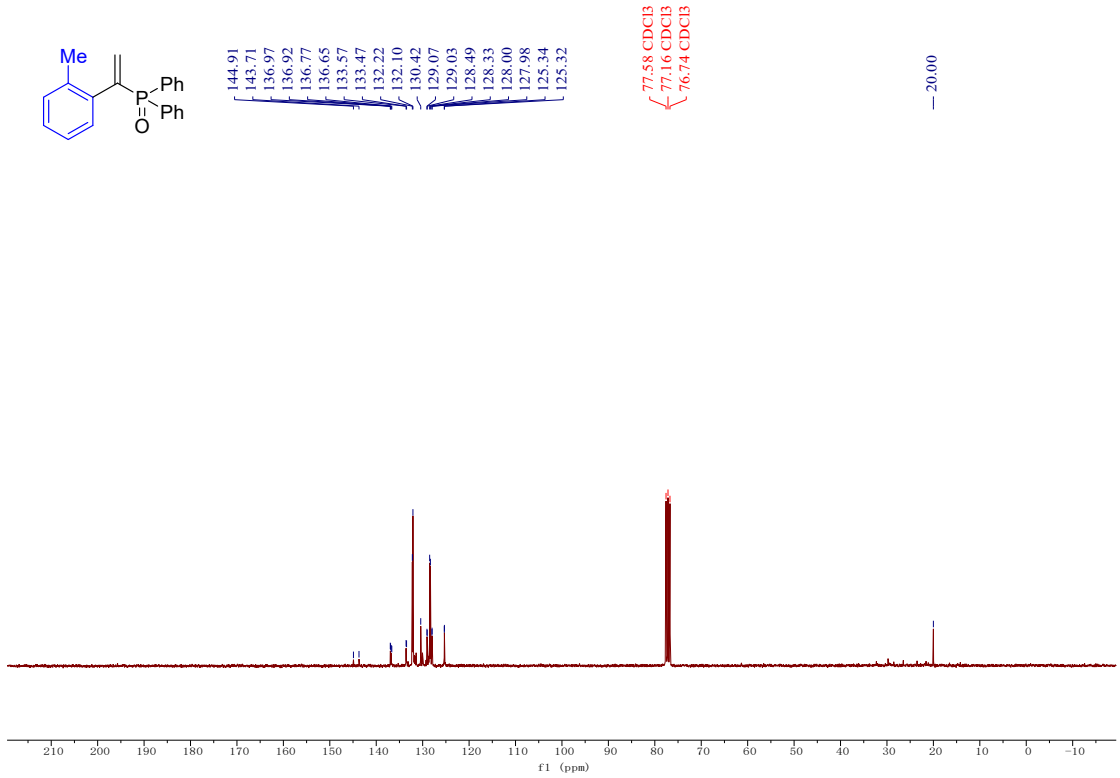
^{13}C NMR (75 MHz, $CDCl_3$) of **7a**



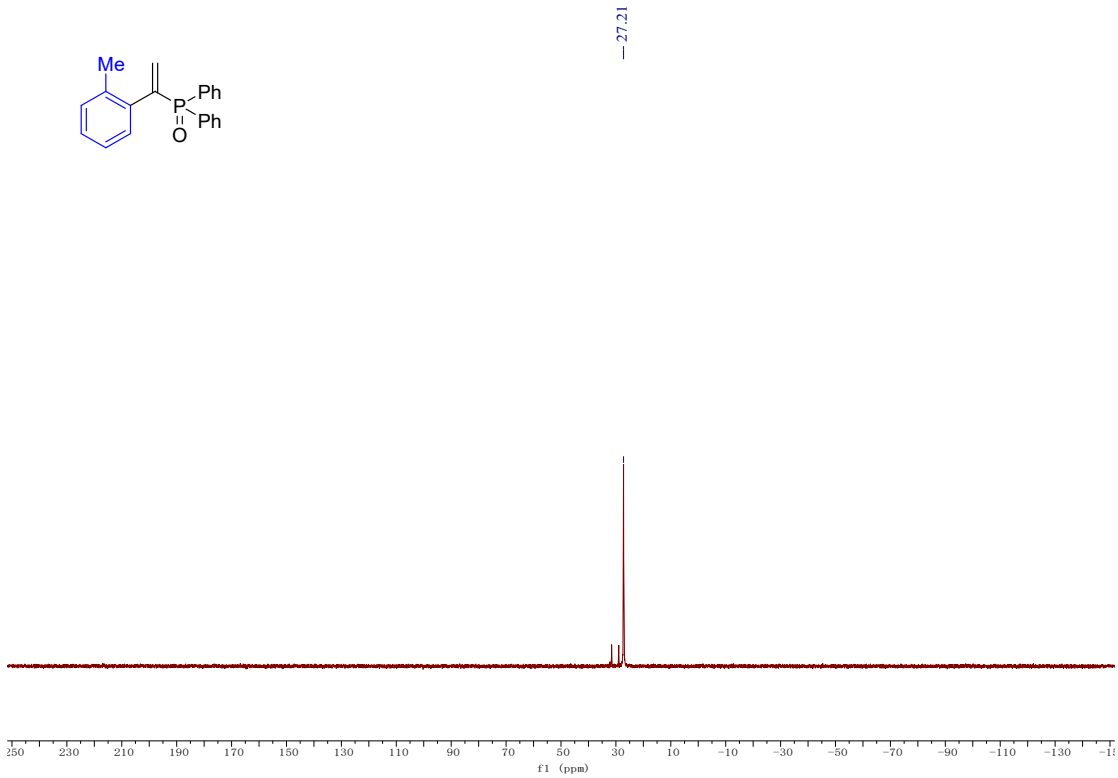
^{31}P NMR (121 MHz, $CDCl_3$) of **7a**



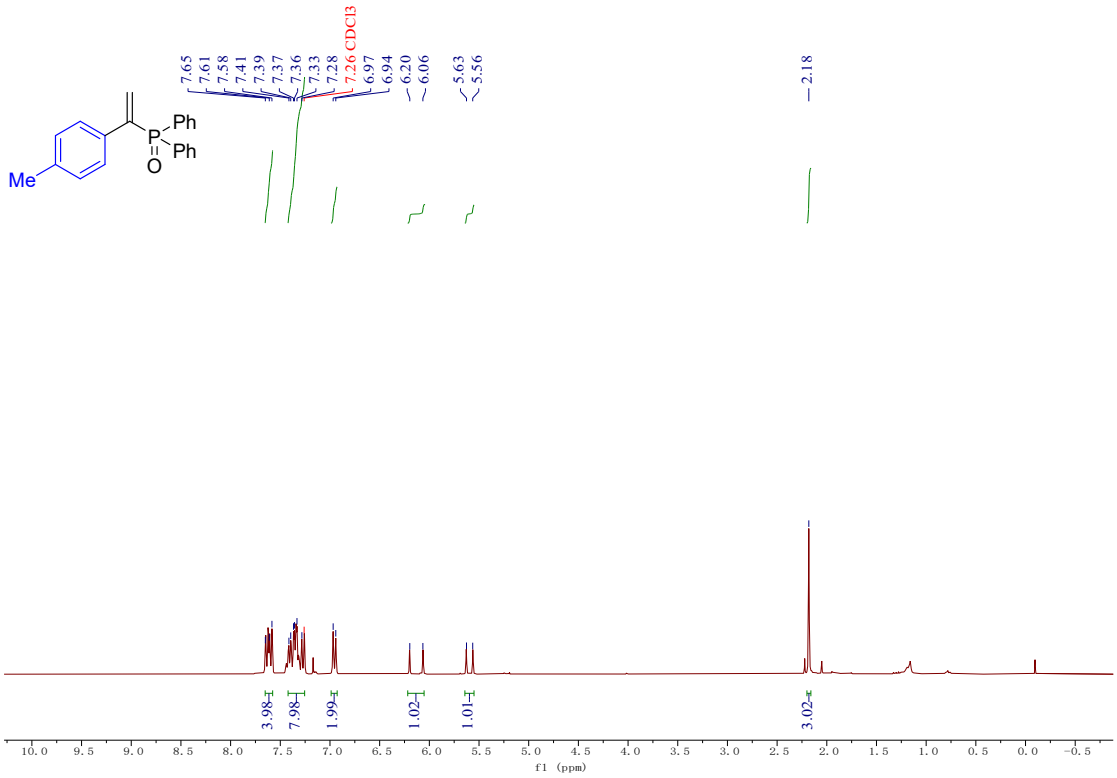
^{1}H NMR (300 MHz, $CDCl_3$) of **7b**



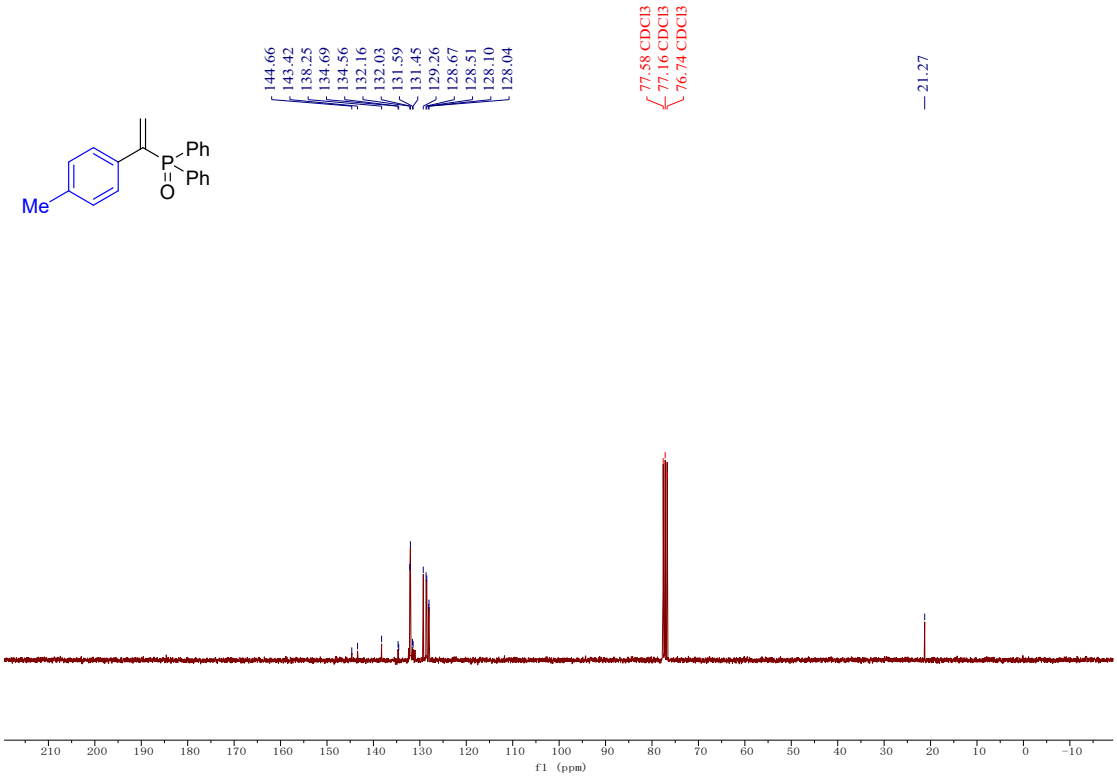
^{13}C NMR (75 MHz, $CDCl_3$) of **7b**



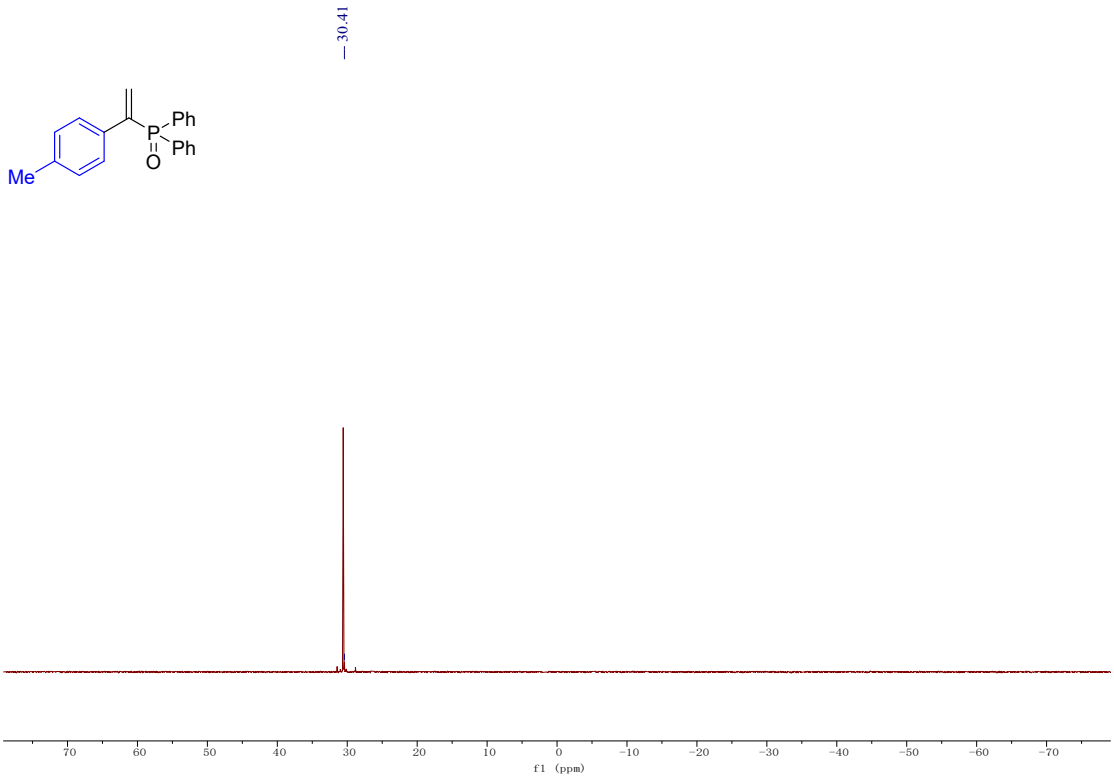
^{31}P NMR (121 MHz, $CDCl_3$) of **7b**



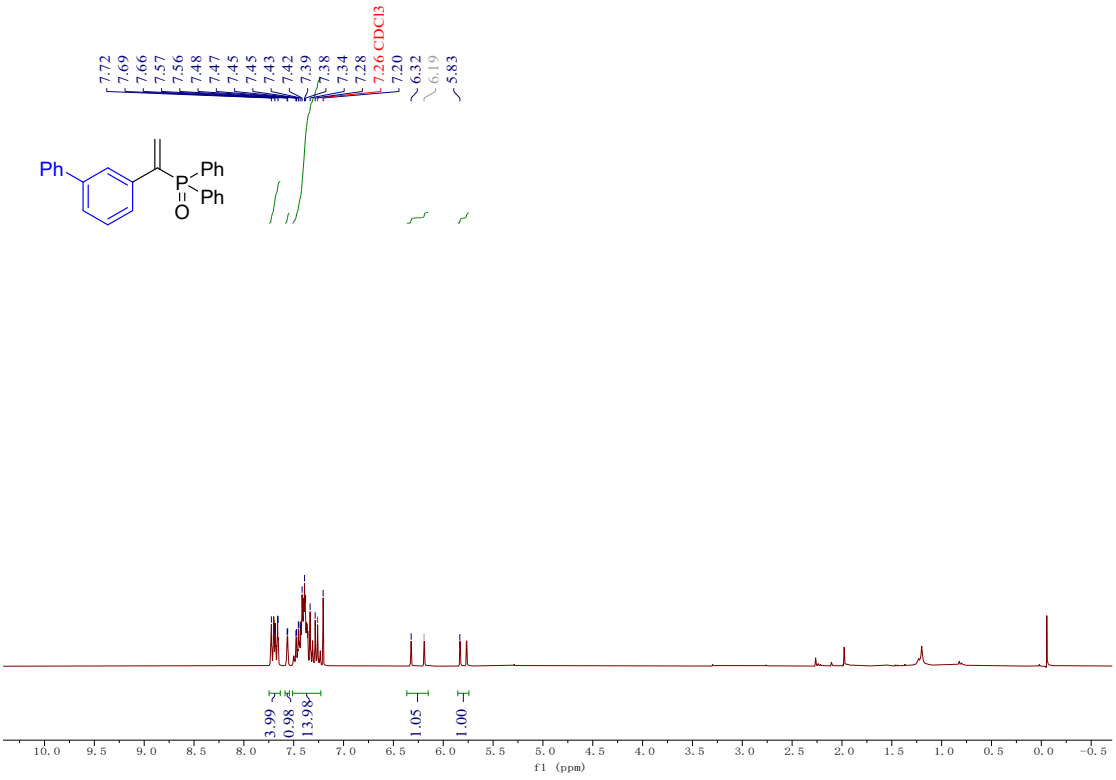
^{1}H NMR (300 MHz, $CDCl_3$) of **7c**



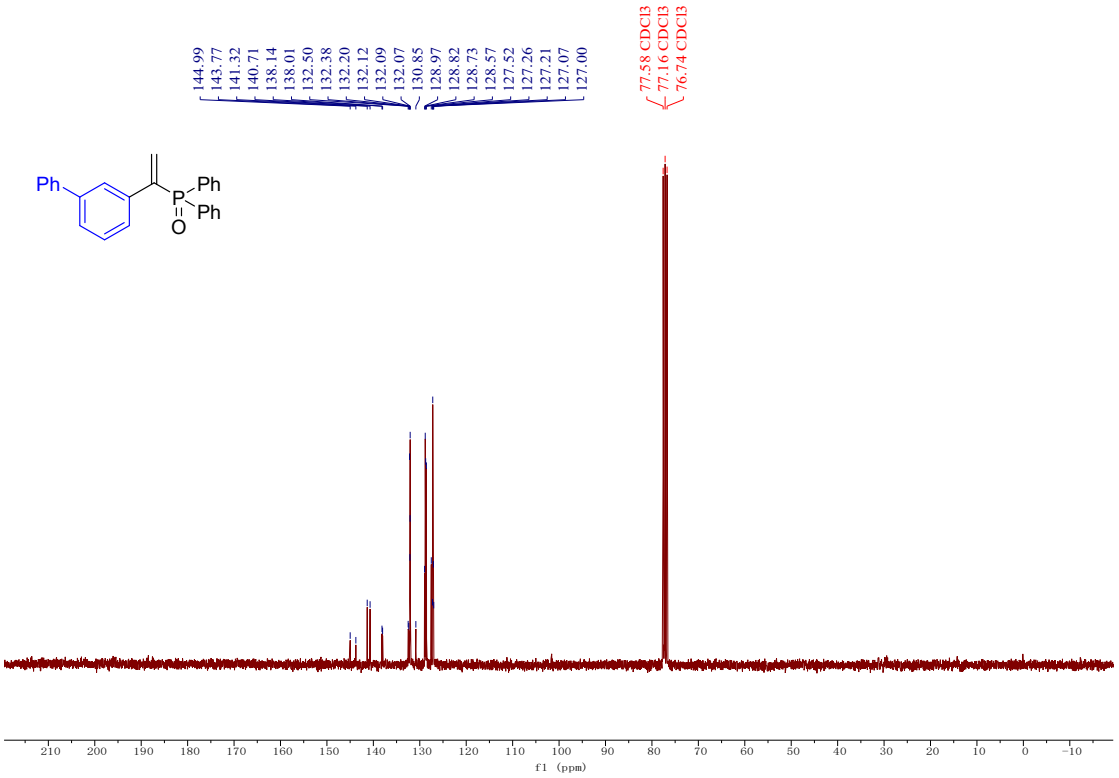
^{13}C NMR (75 MHz, $CDCl_3$) of **7c**



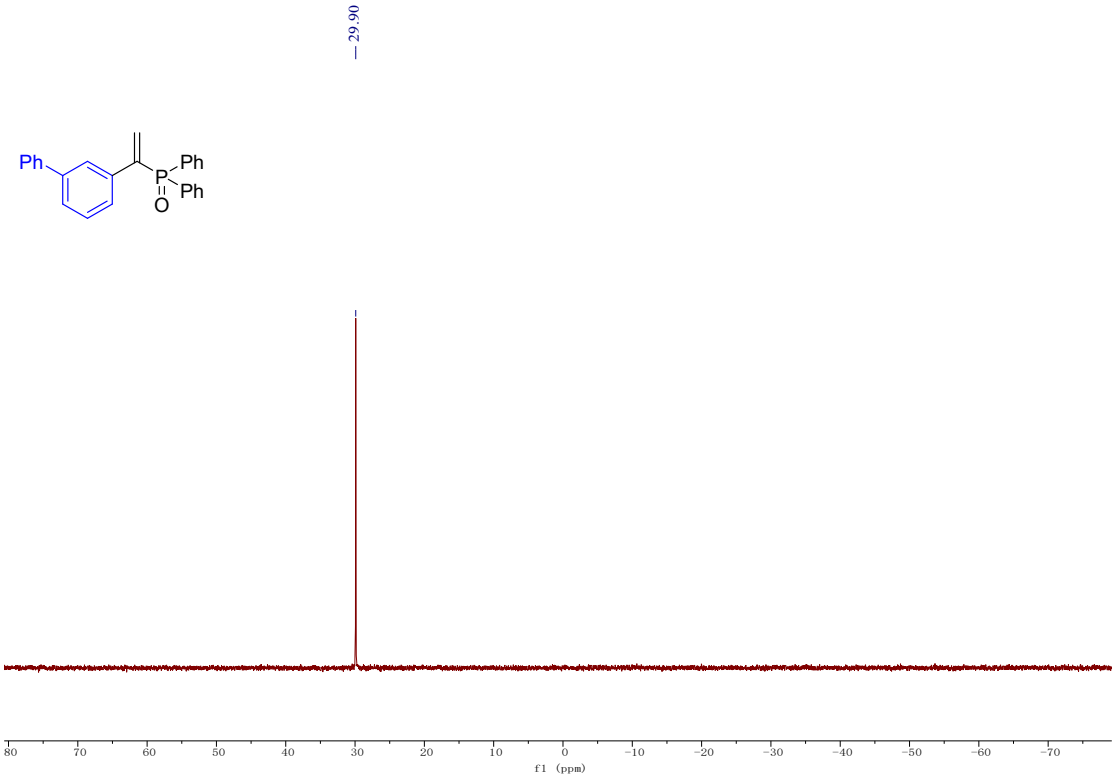
^{31}P NMR (121 MHz, $CDCl_3$) of **7c**



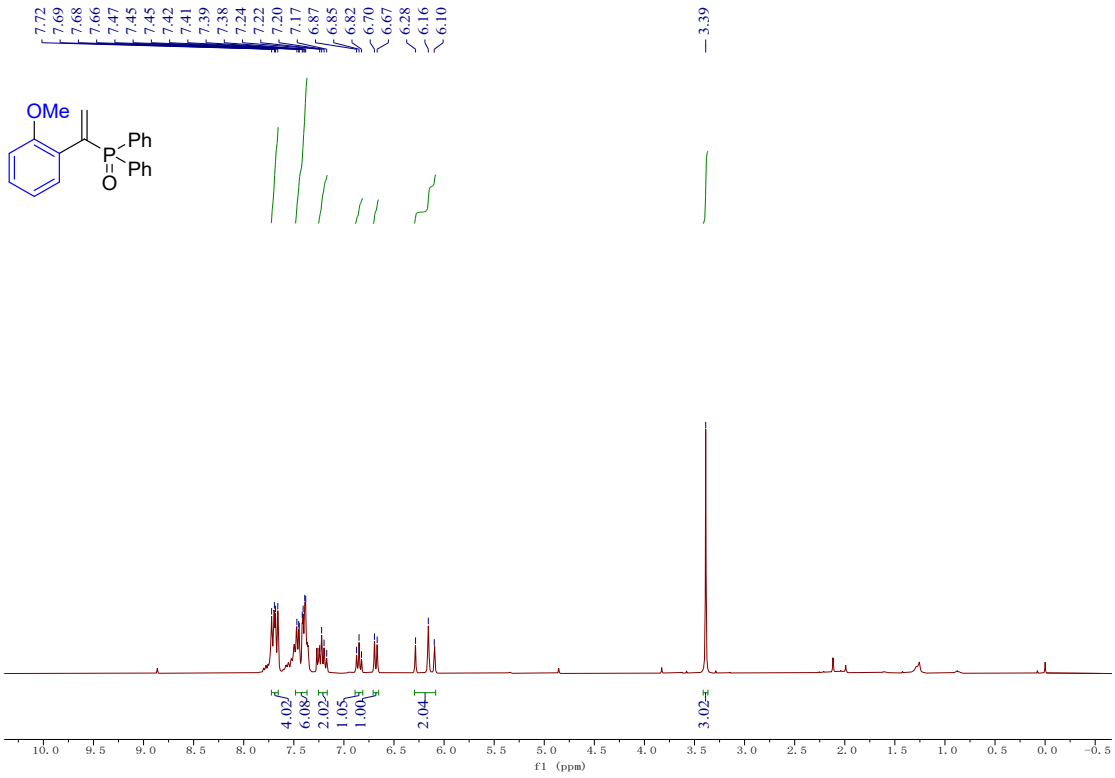
^{1}H NMR (300 MHz, $CDCl_3$) of **7d**



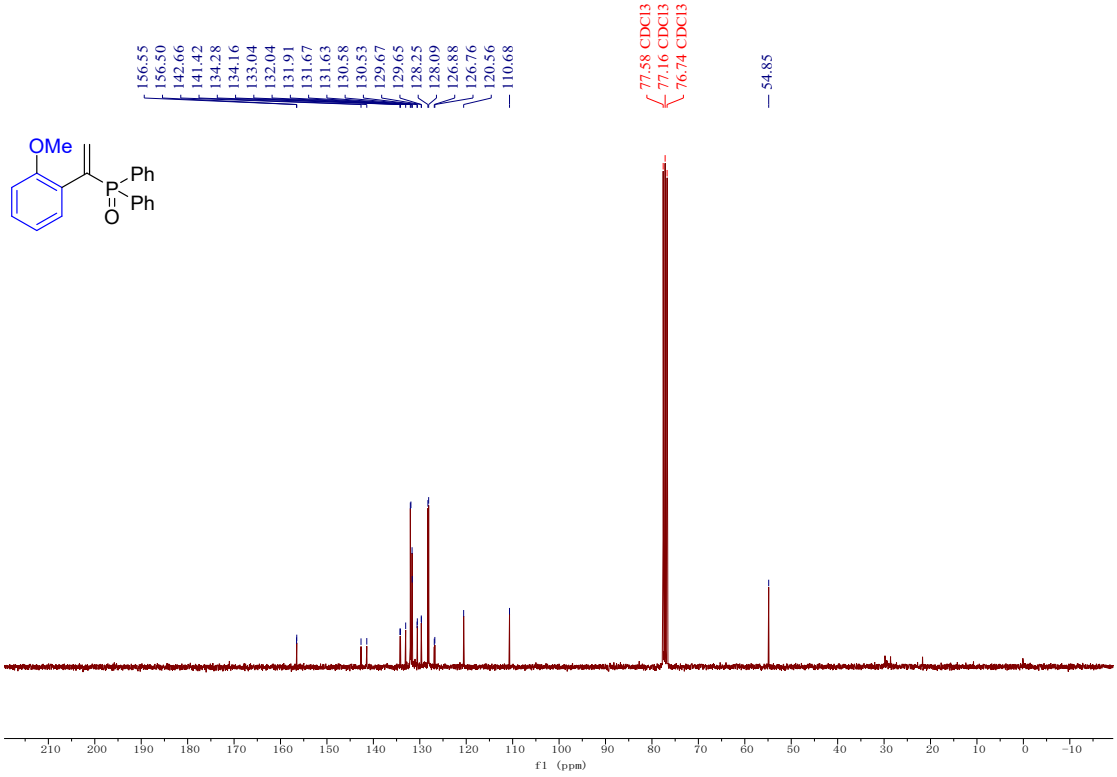
^{13}C NMR (75 MHz, $CDCl_3$) of **7d**



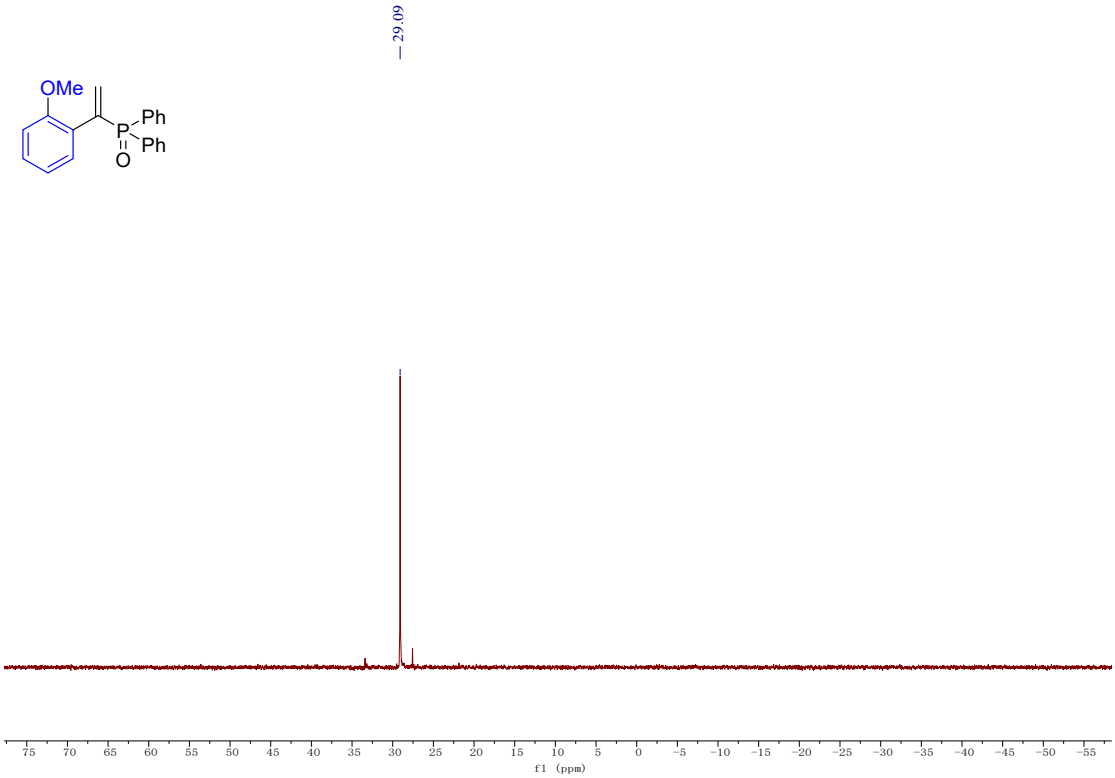
^{31}P NMR (121 MHz, $CDCl_3$) of **7d**



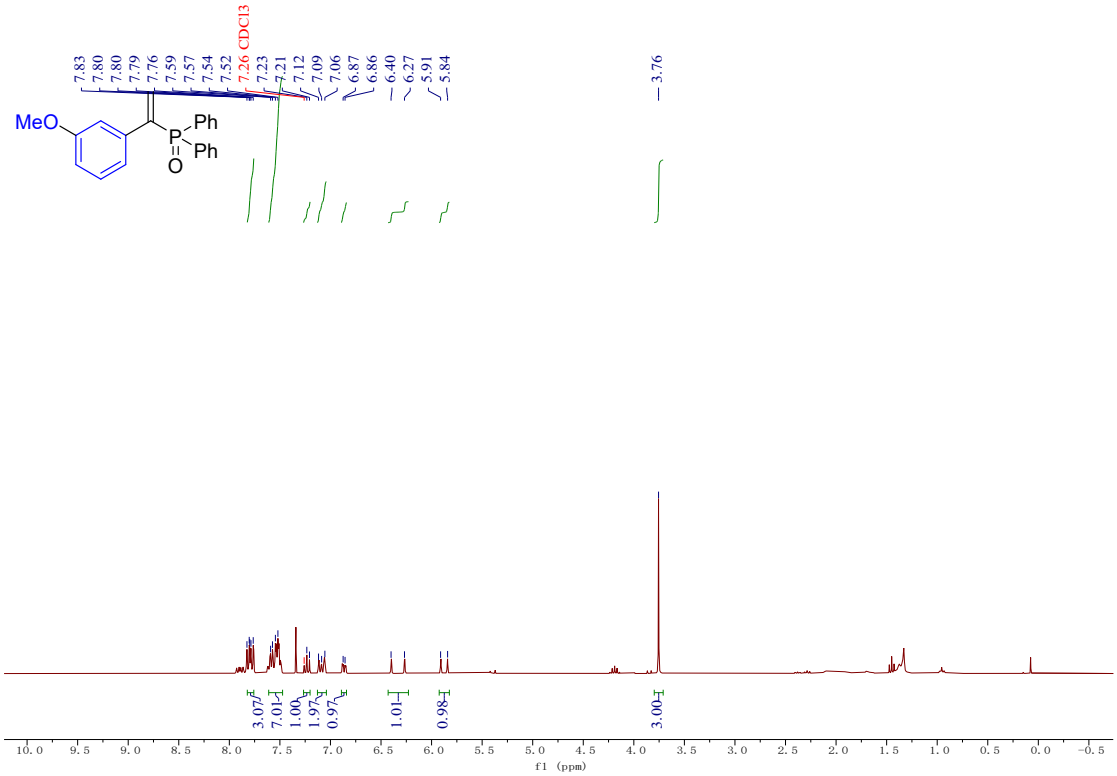
^{1}H NMR (300 MHz, $CDCl_3$) of **7e**



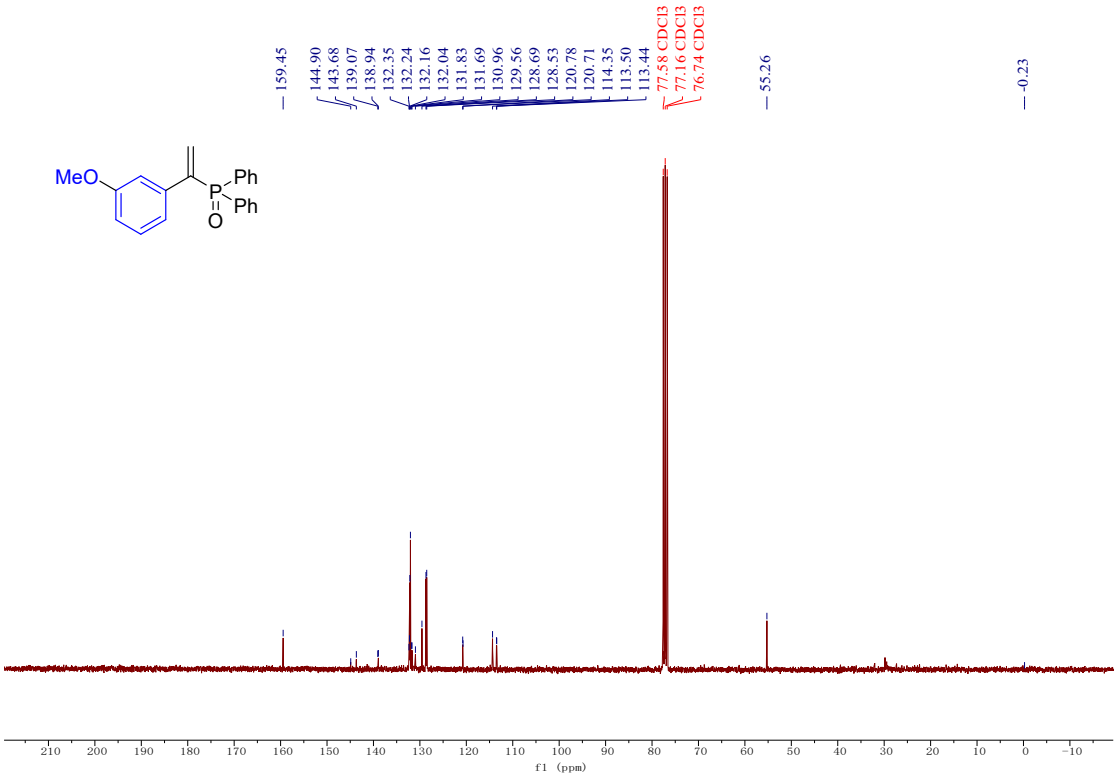
^{13}C NMR (75 MHz, $CDCl_3$) of **7e**



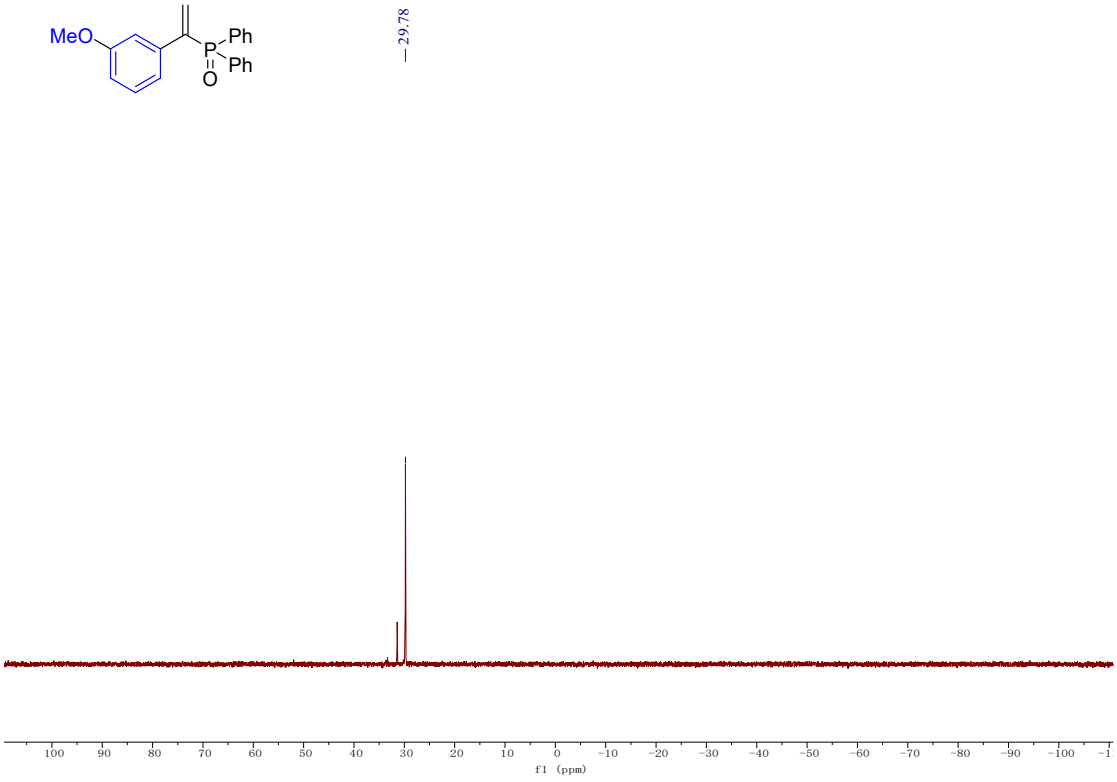
^{31}P NMR (121 MHz, $CDCl_3$) of **7e**



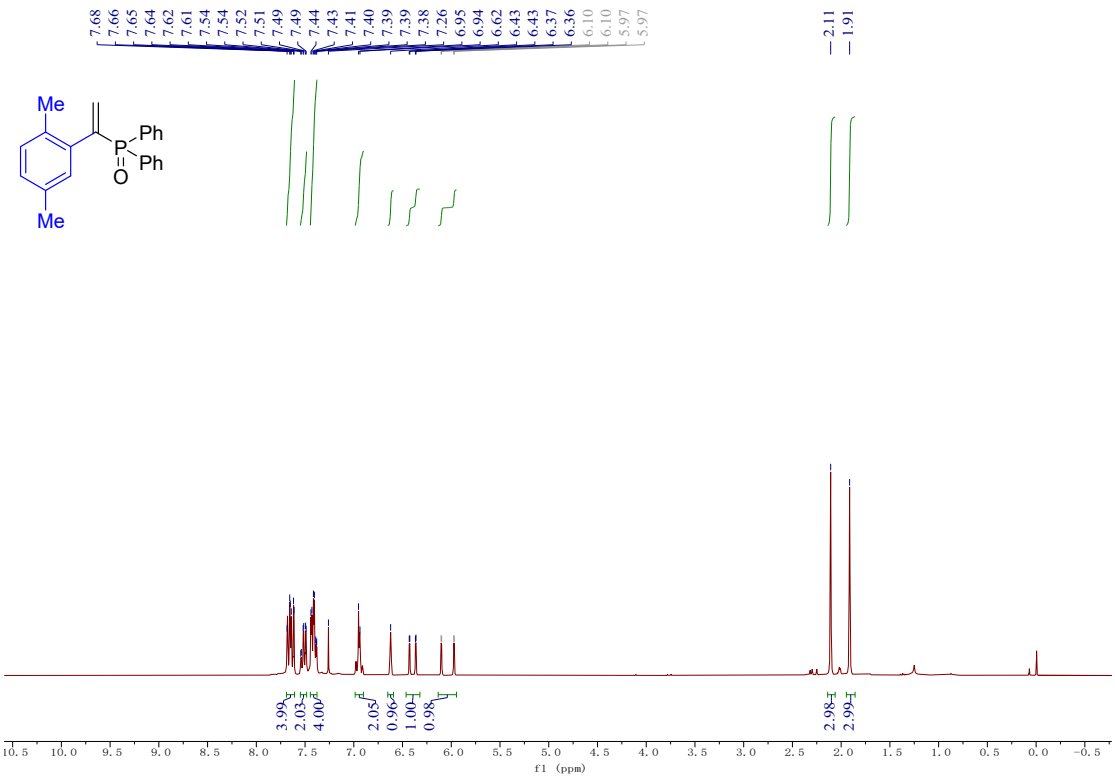
^{1}H NMR (300 MHz, $CDCl_3$) of **7f**



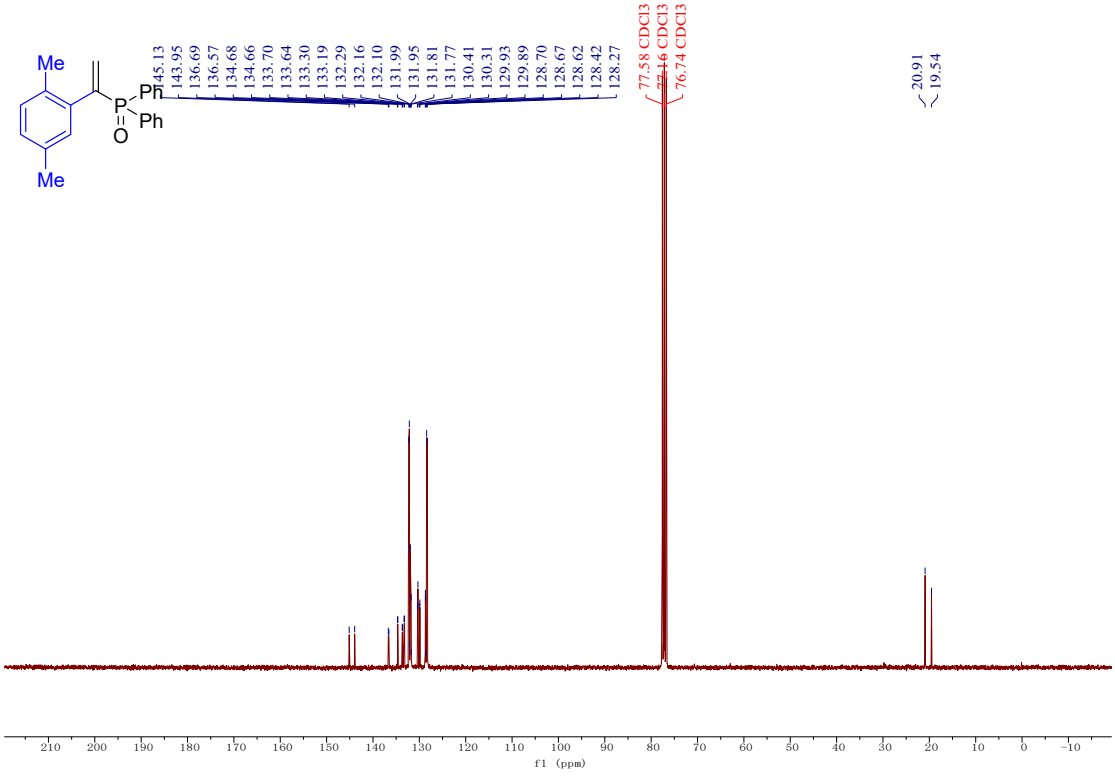
^{13}C NMR (75 MHz, $CDCl_3$) of **7f**



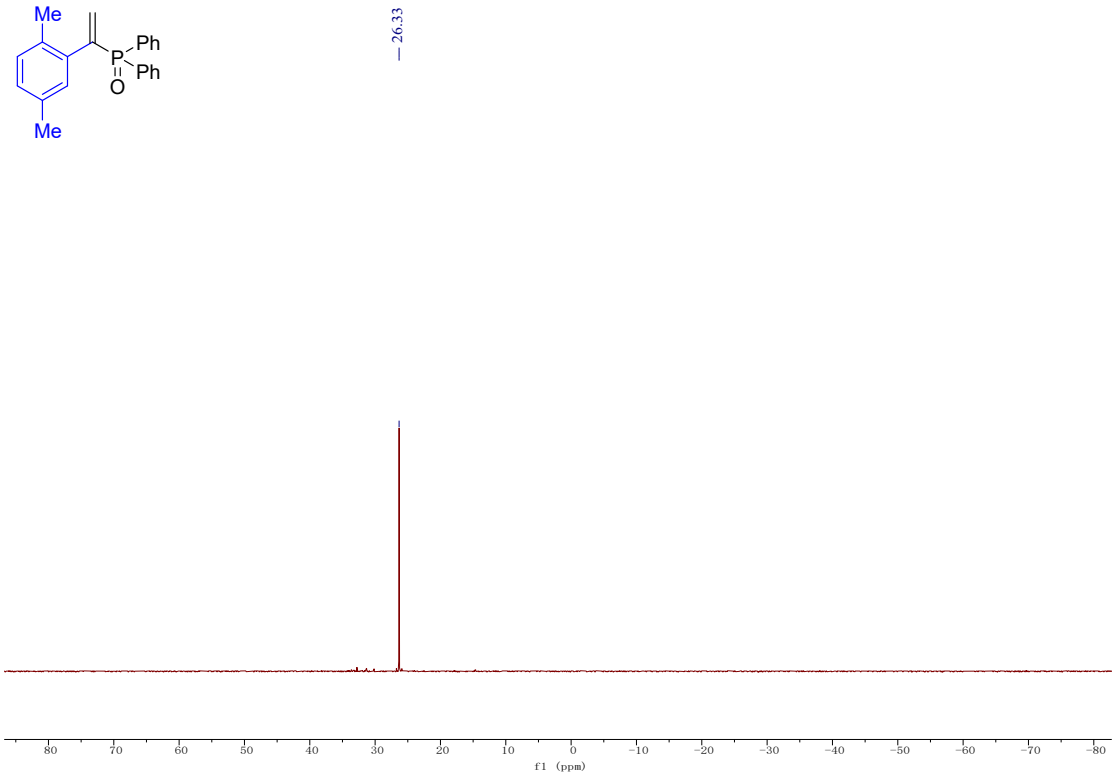
^{31}P NMR (121 MHz, $CDCl_3$) of **7f**



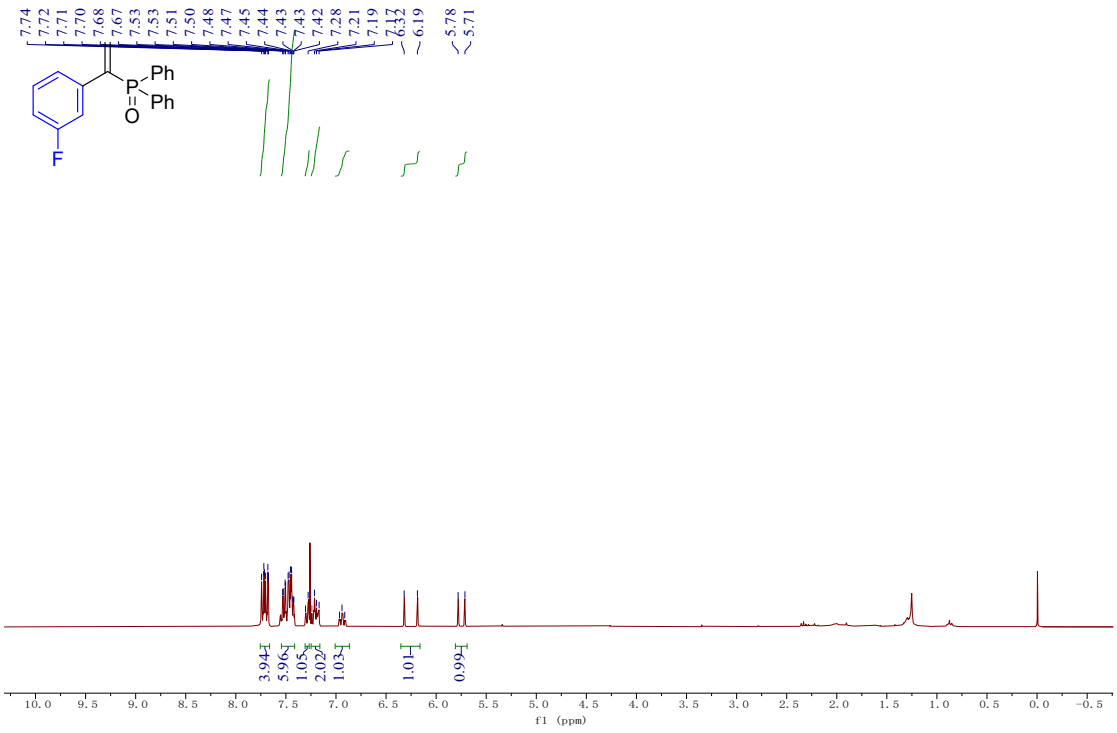
^{1}H NMR (300 MHz, $CDCl_3$) of **7g**



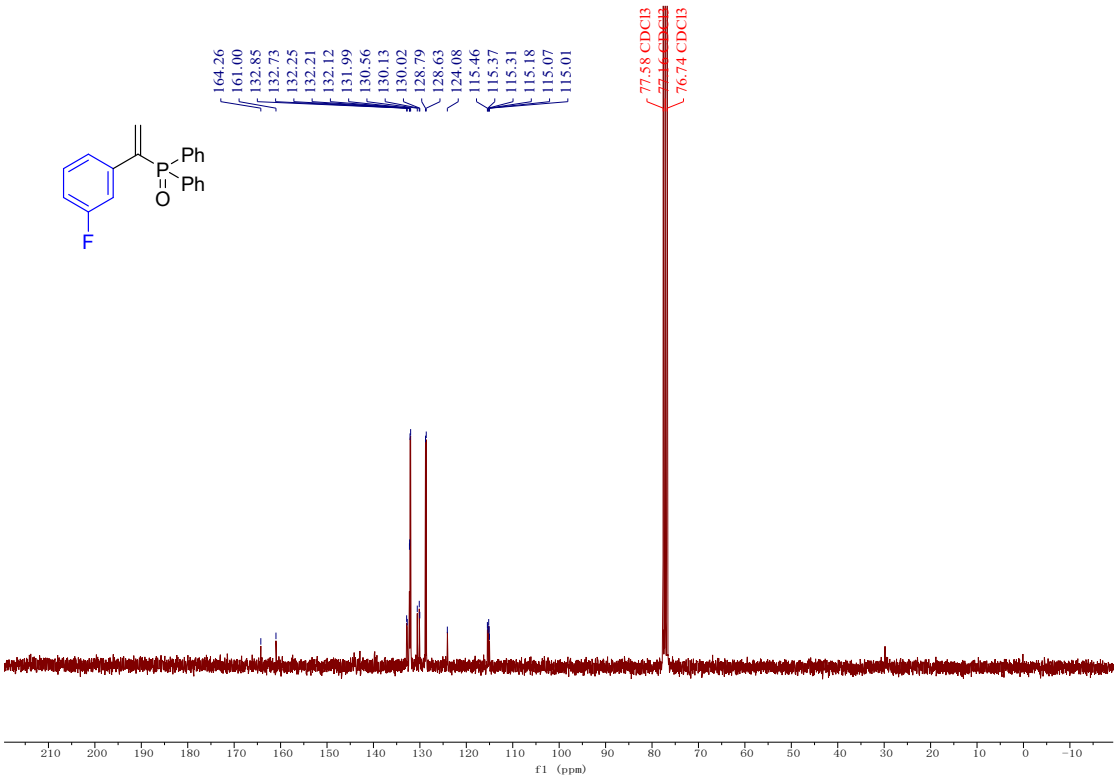
^{13}C NMR (75 MHz, $CDCl_3$) of **7g**



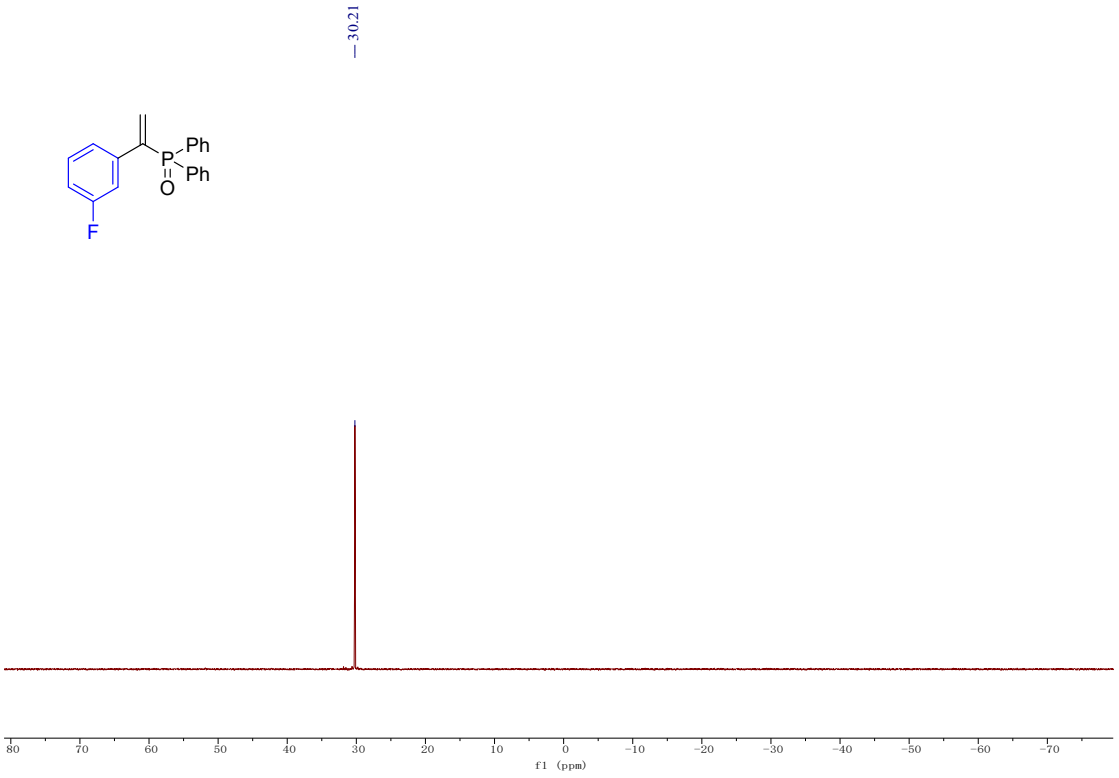
^{31}P NMR (121 MHz, $CDCl_3$) of **7g**



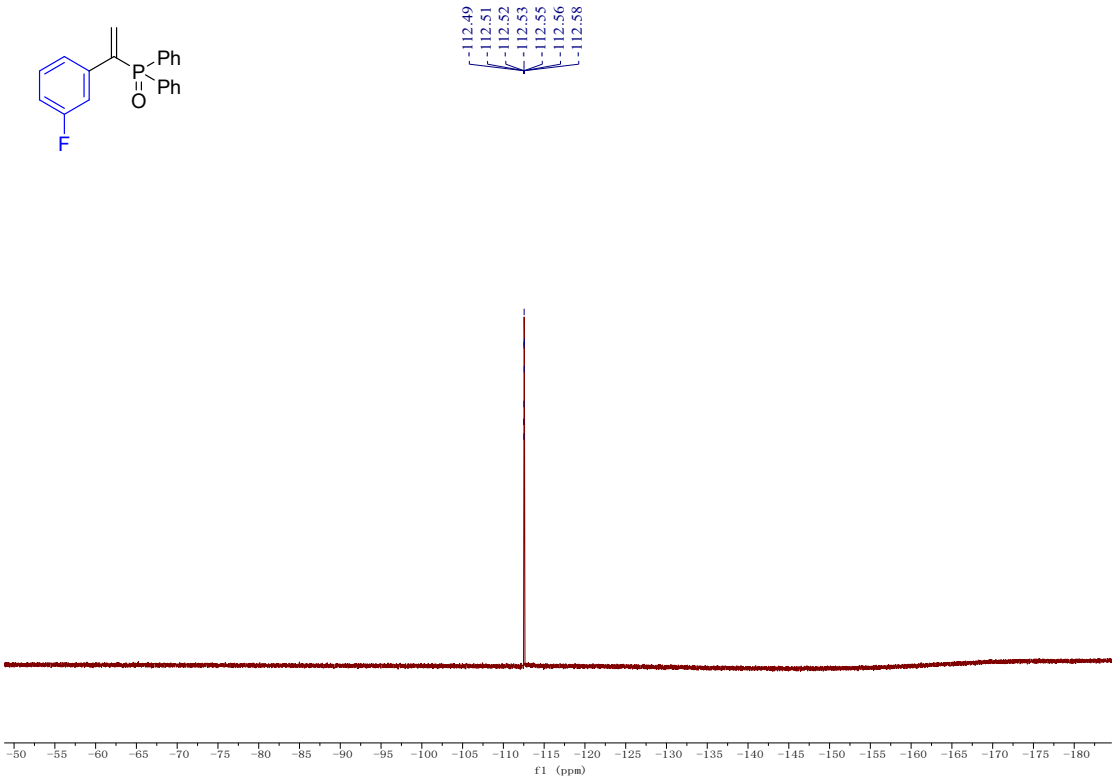
^{1}H NMR (300 MHz, $CDCl_3$) of **7h**



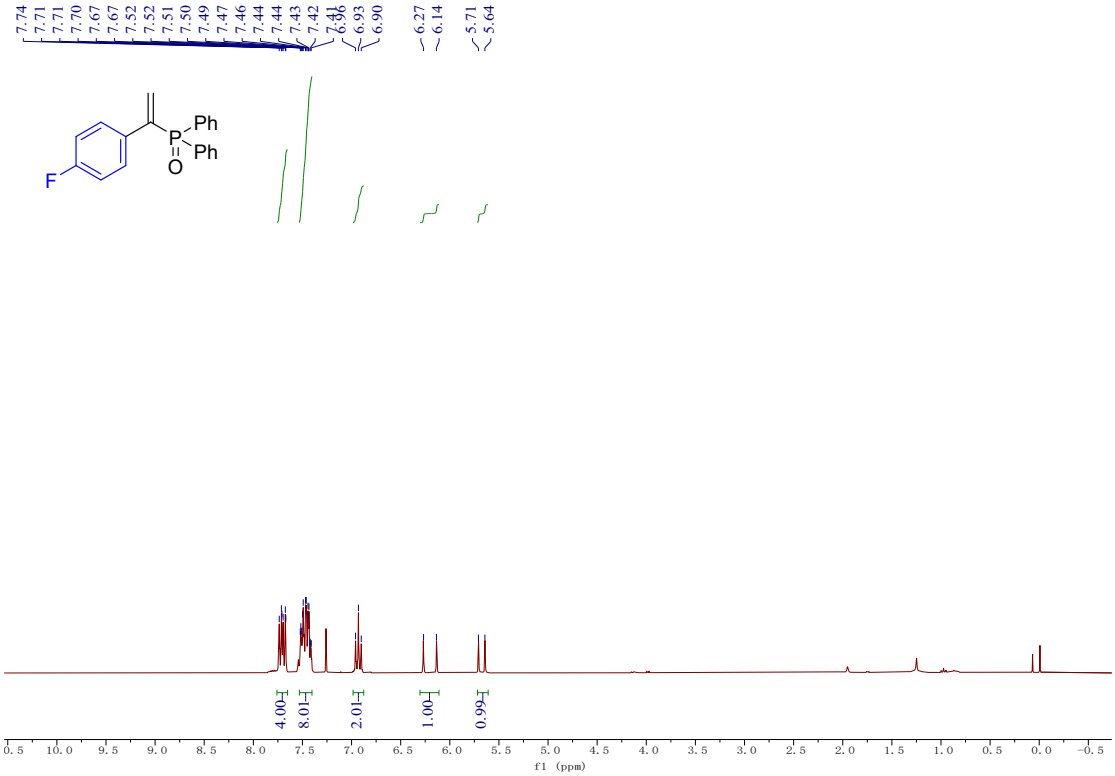
^{13}C NMR (75 MHz, $CDCl_3$) of **7h**



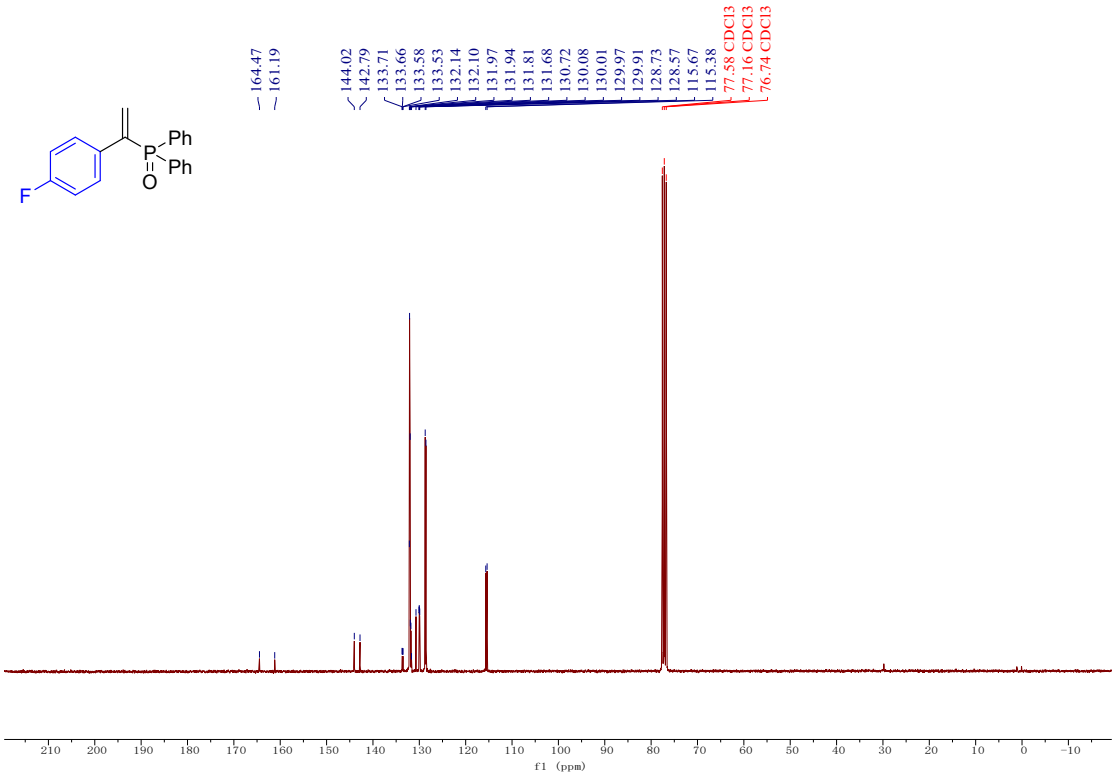
^{31}P NMR (121 MHz, $CDCl_3$) of **7h**



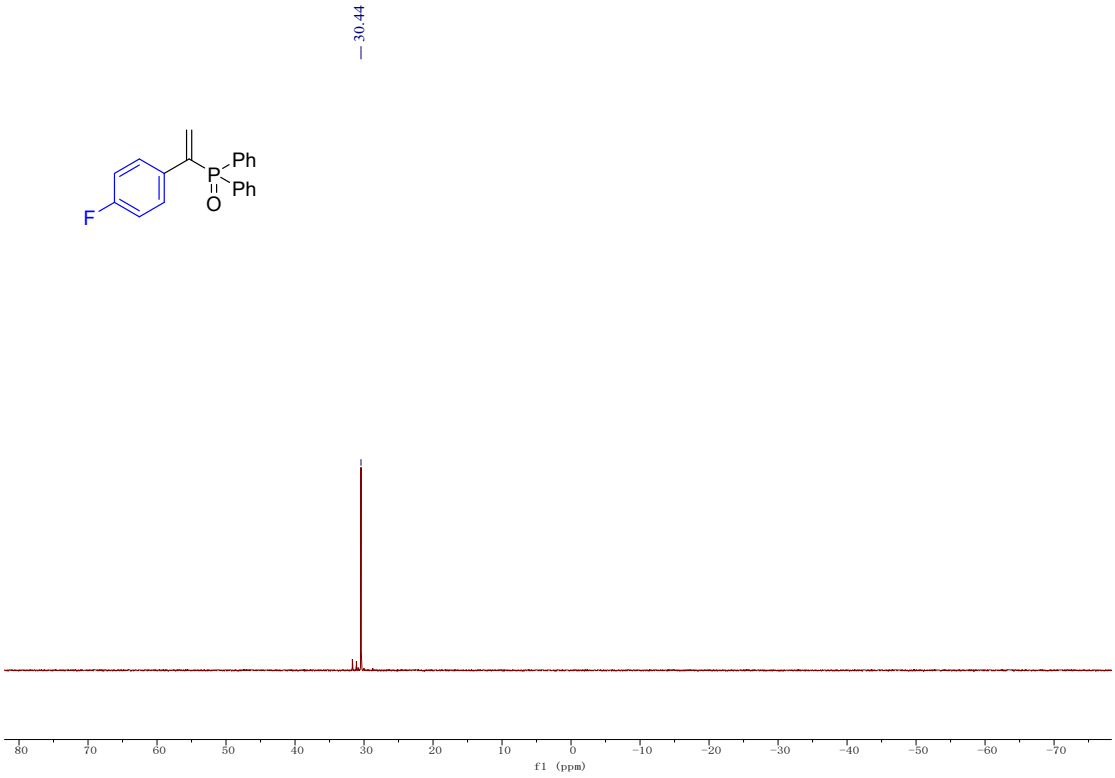
^{19}F NMR (282 MHz, $CDCl_3$) of **7h**



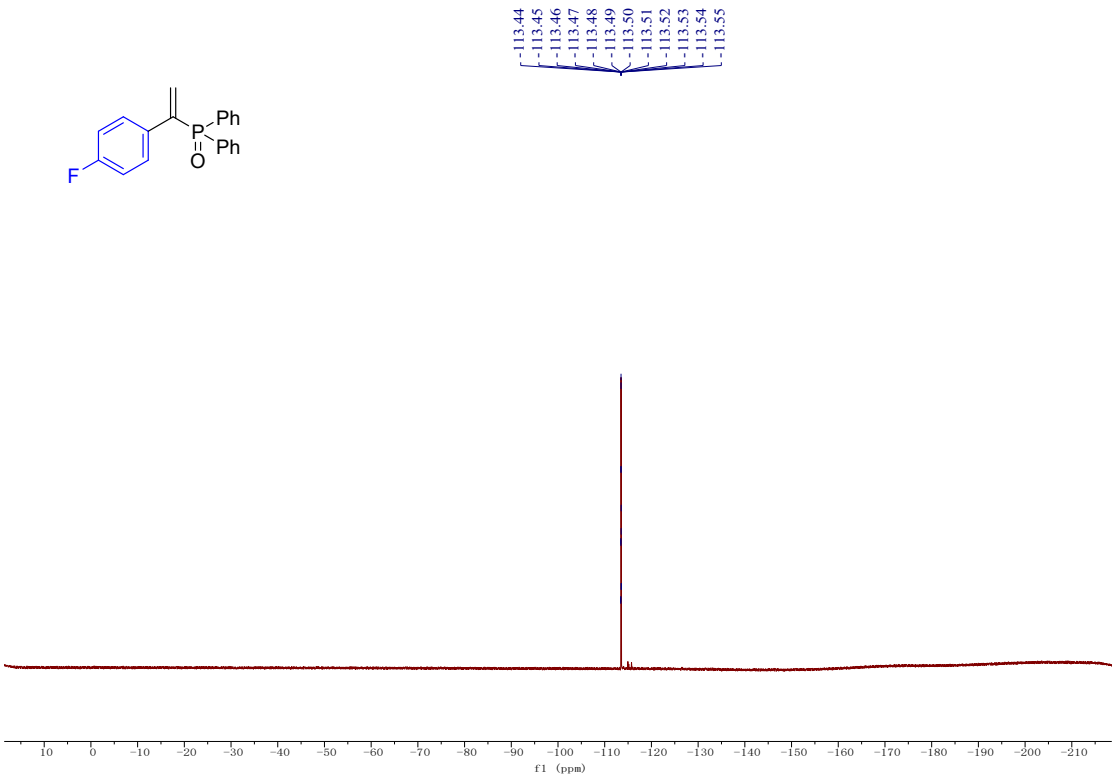
^{1}H NMR (300 MHz, $CDCl_3$) of **7i**



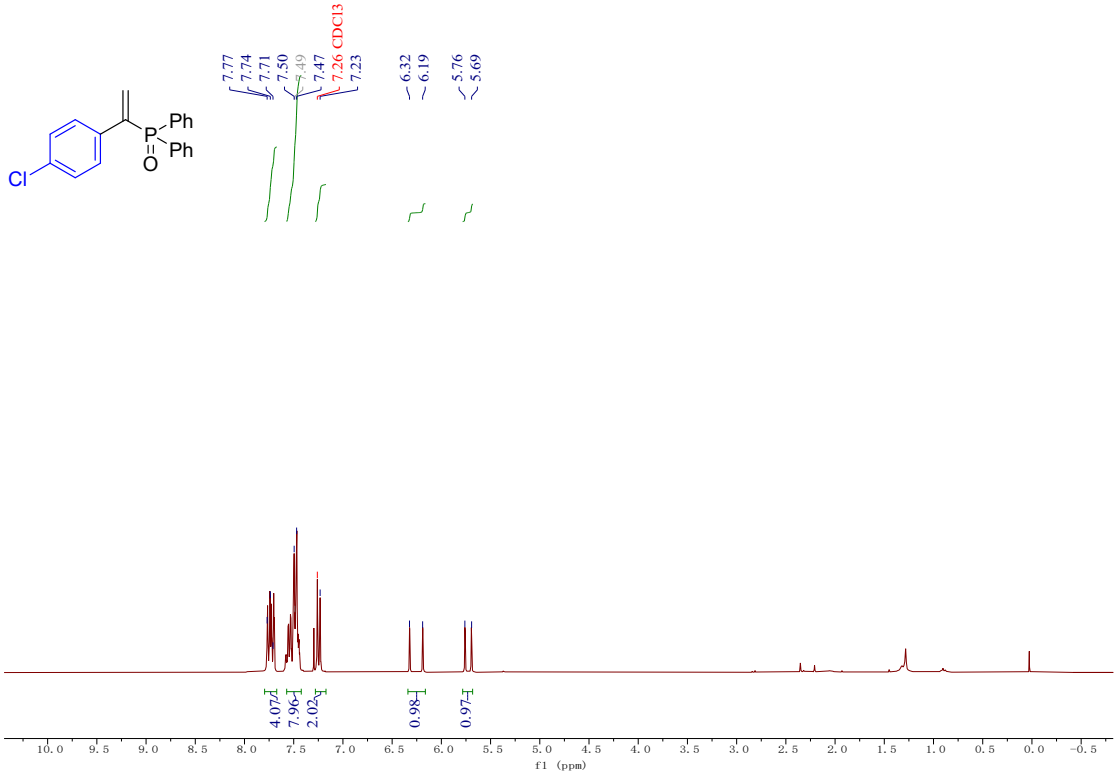
^{13}C NMR (75 MHz, $CDCl_3$) of **7i**



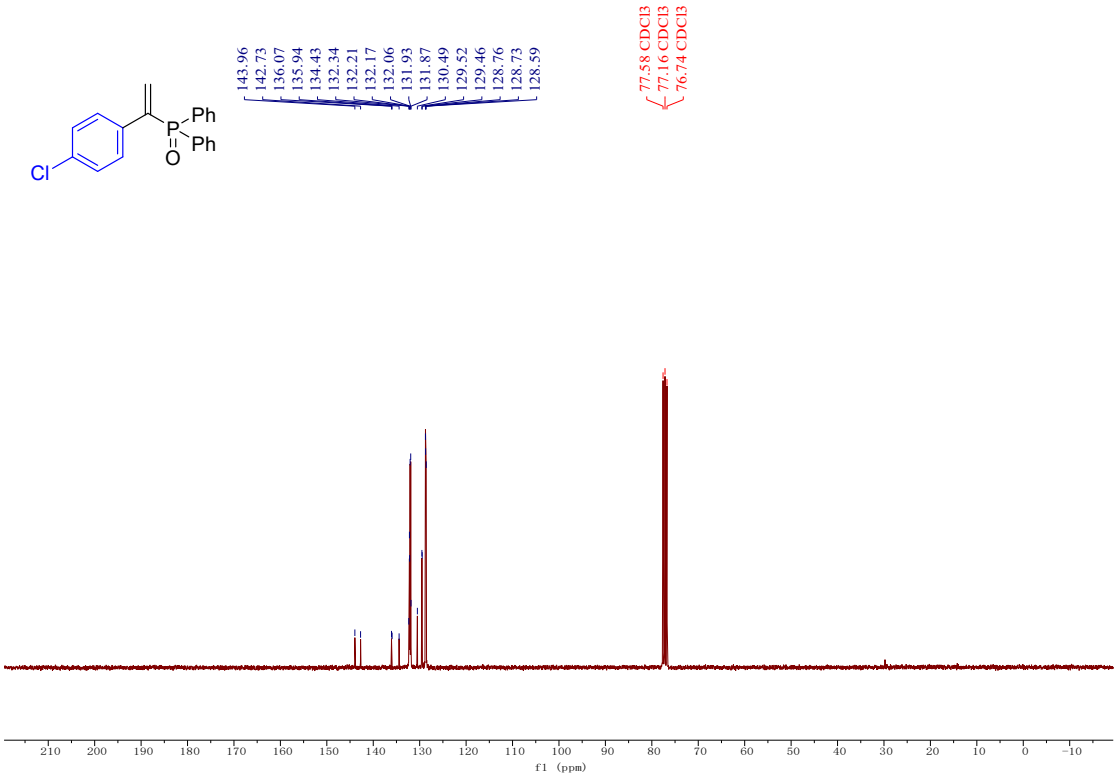
^{31}P NMR (121 MHz, $CDCl_3$) of **7i**



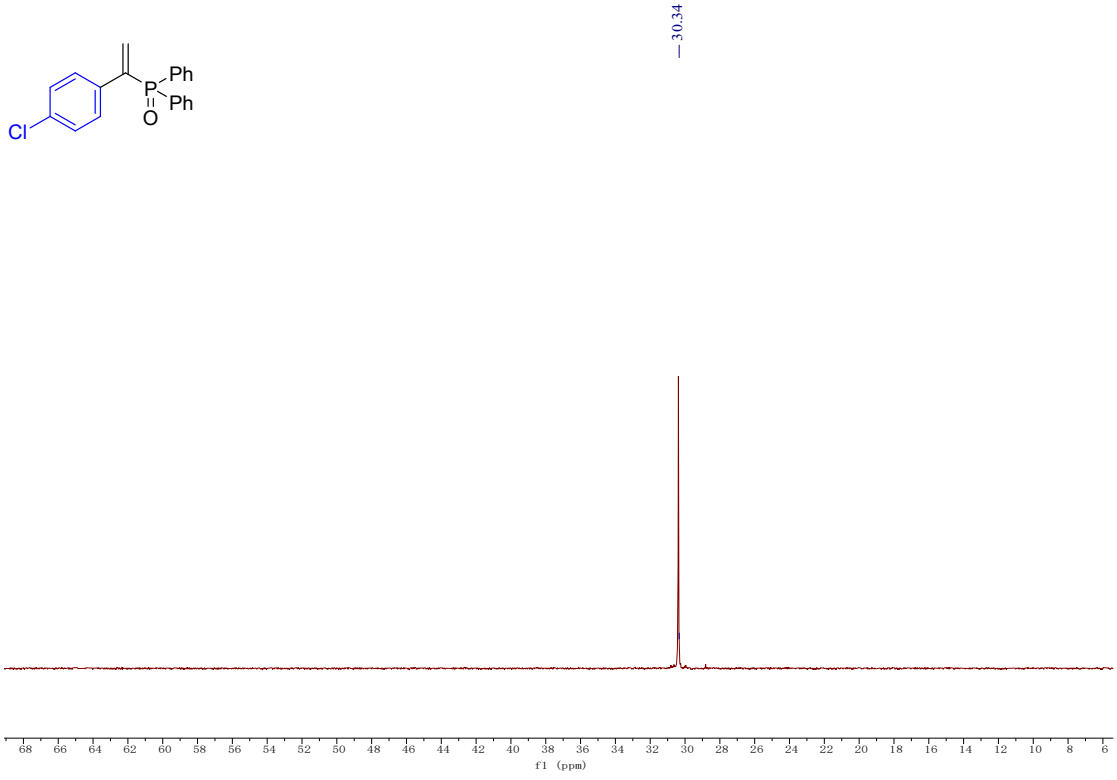
^{19}F NMR (282 MHz, $CDCl_3$) of **7i**



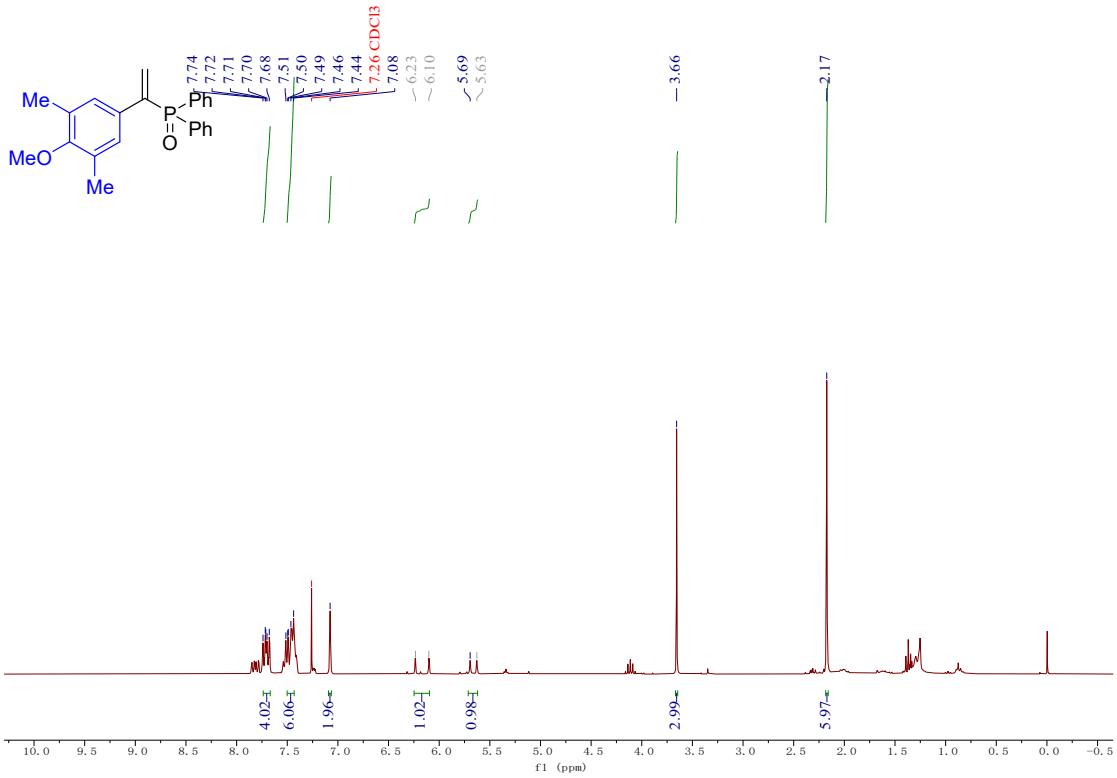
^{1}H NMR (300 MHz, $CDCl_3$) of **7j**



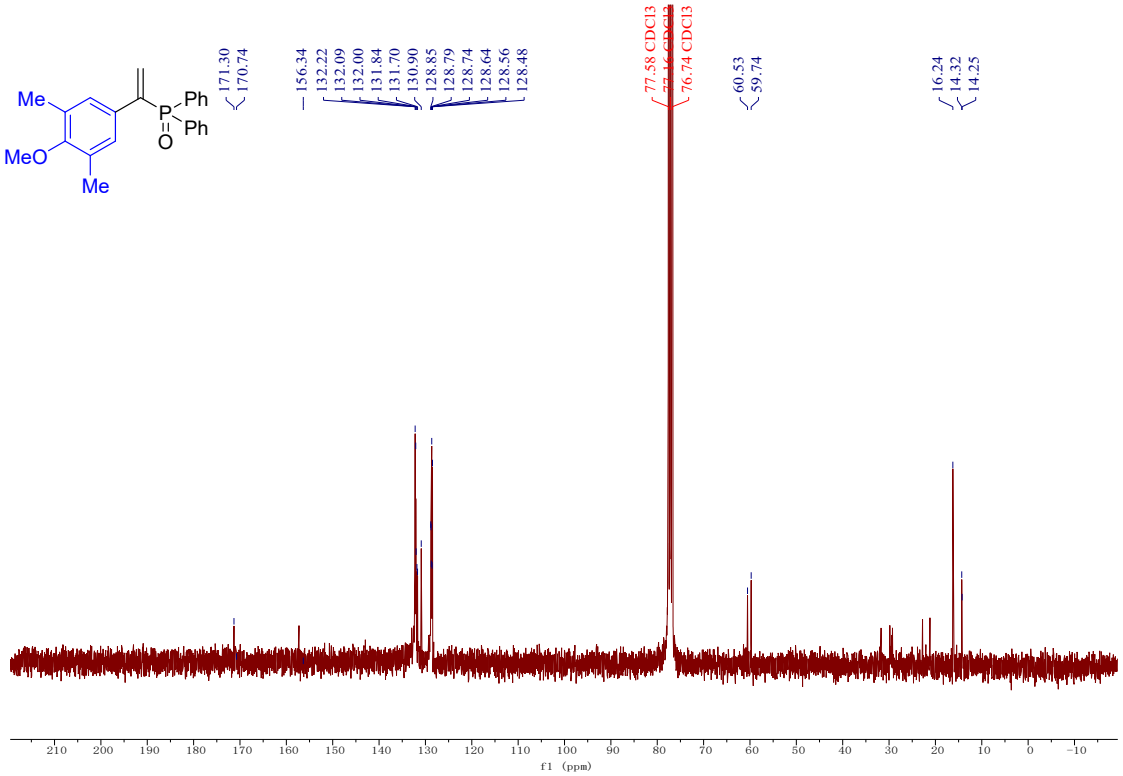
^{13}C NMR (75 MHz, $CDCl_3$) of **7j**



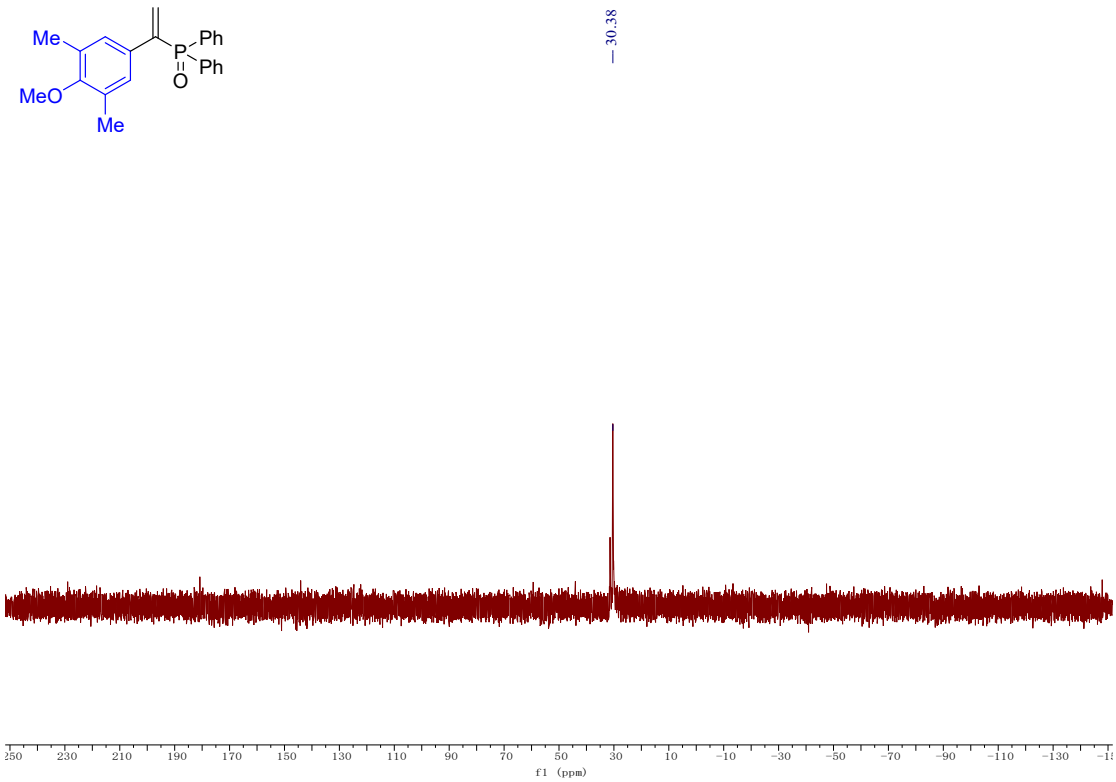
^{31}P NMR (121 MHz, $CDCl_3$) of **7j**



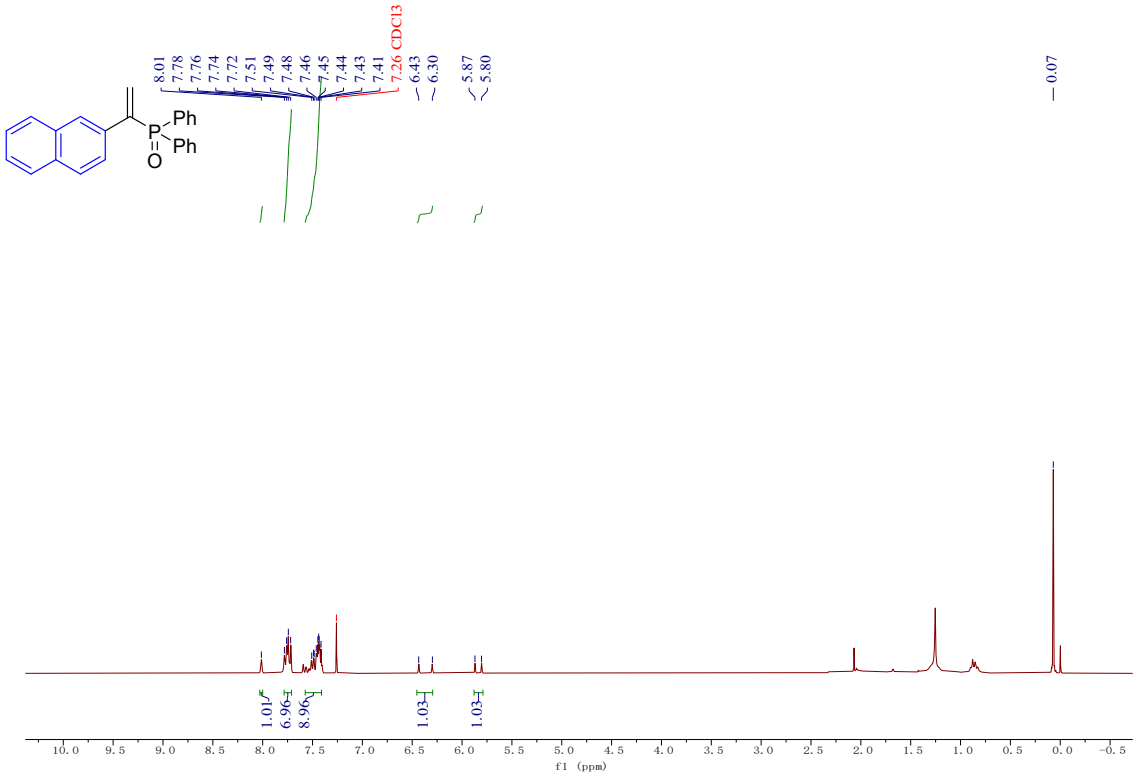
^{1}H NMR (300 MHz, $CDCl_3$) of **7k**



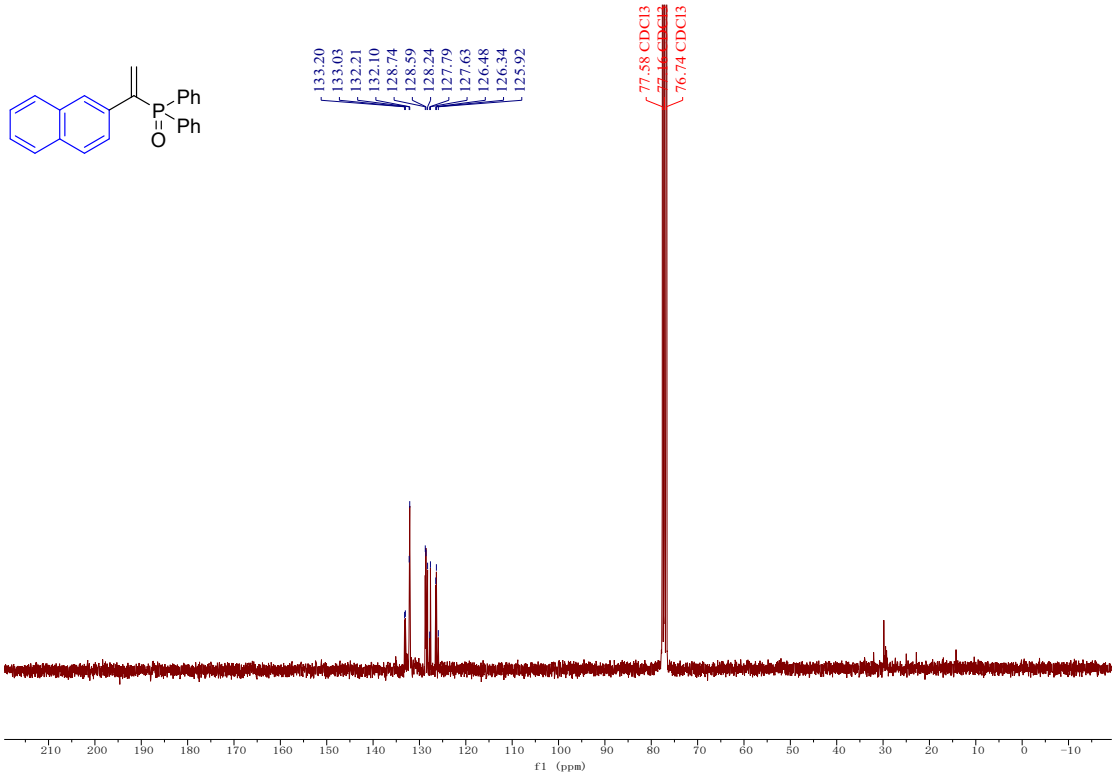
^{13}C NMR (75 MHz, $CDCl_3$) of 7**k**



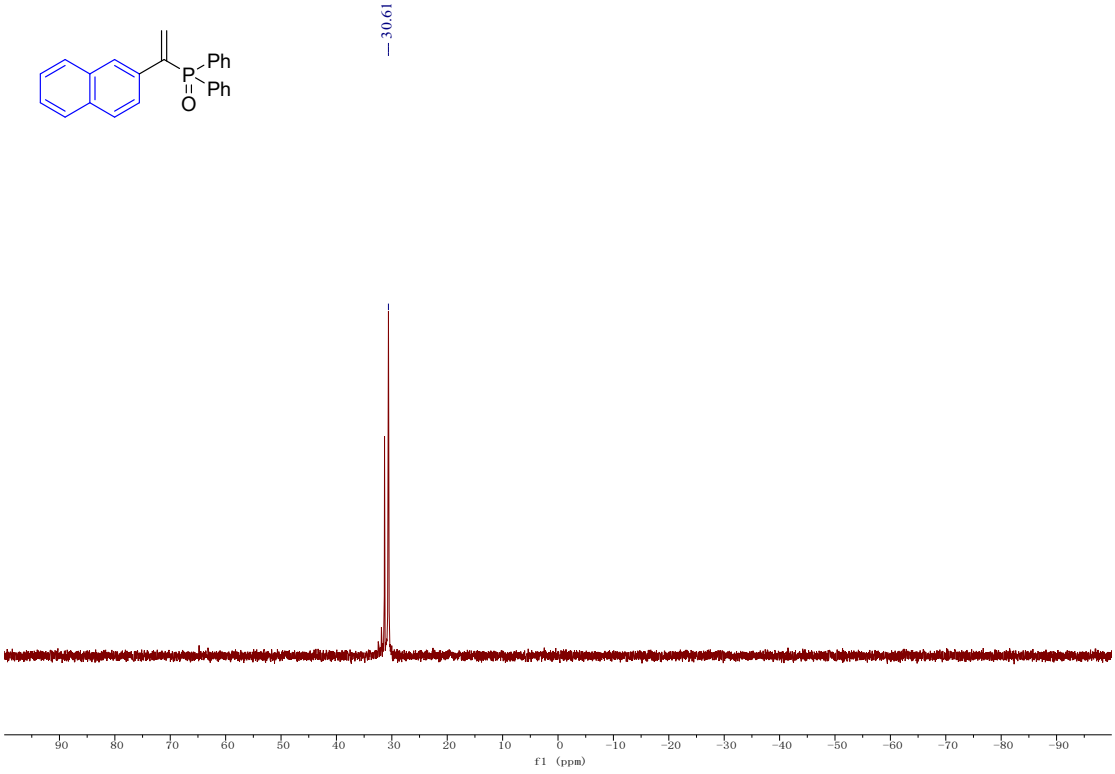
^{31}P NMR (121 MHz, $CDCl_3$) of 7**k**



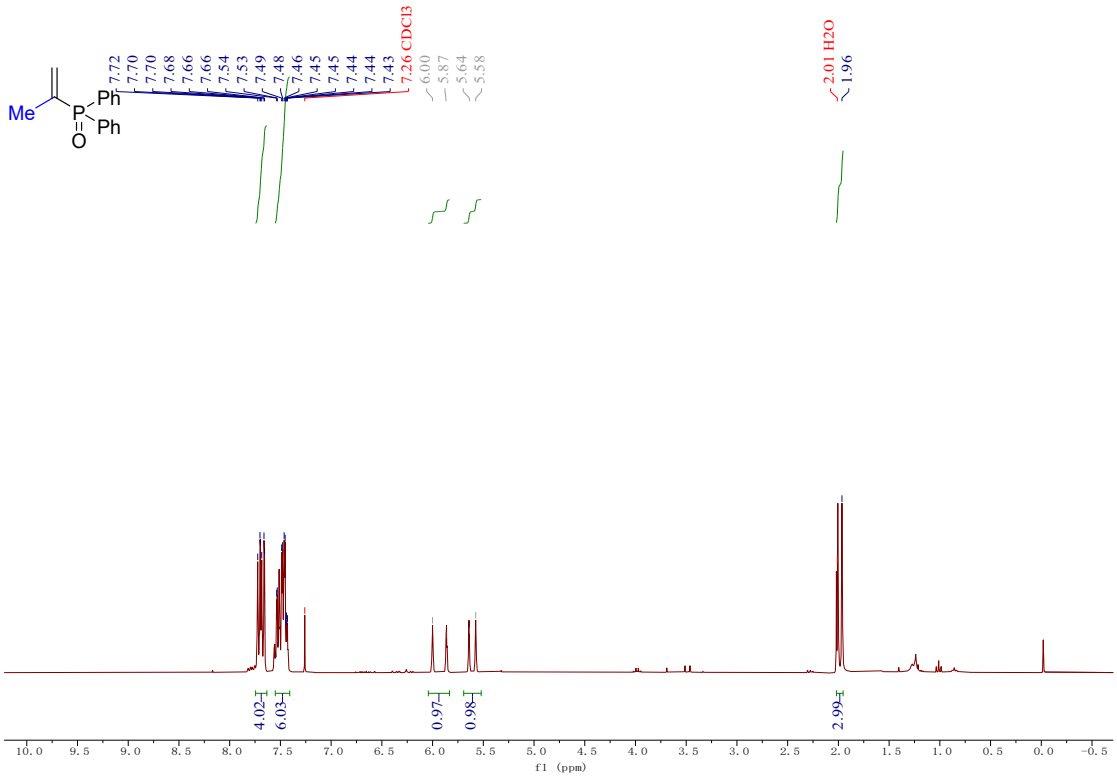
^{1}H NMR (300 MHz, $CDCl_3$) of **7l**



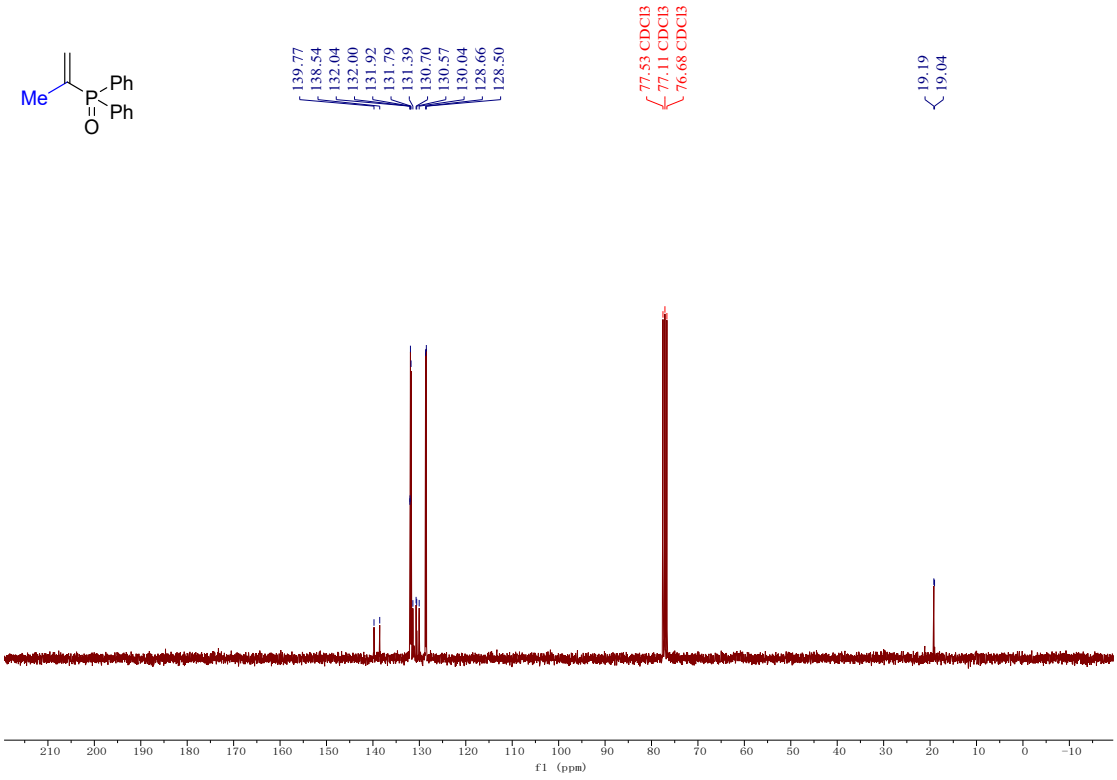
^{13}C NMR (75 MHz, $CDCl_3$) of **7l**



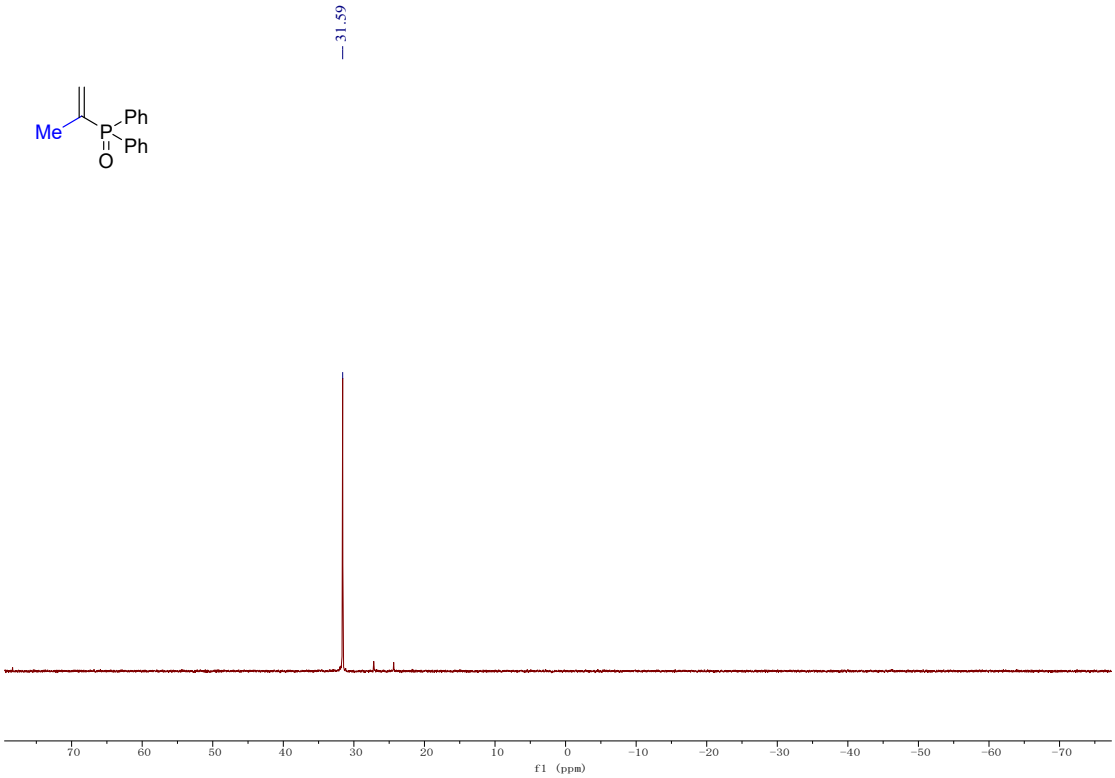
^{31}P NMR (121 MHz, $CDCl_3$) of **7l**



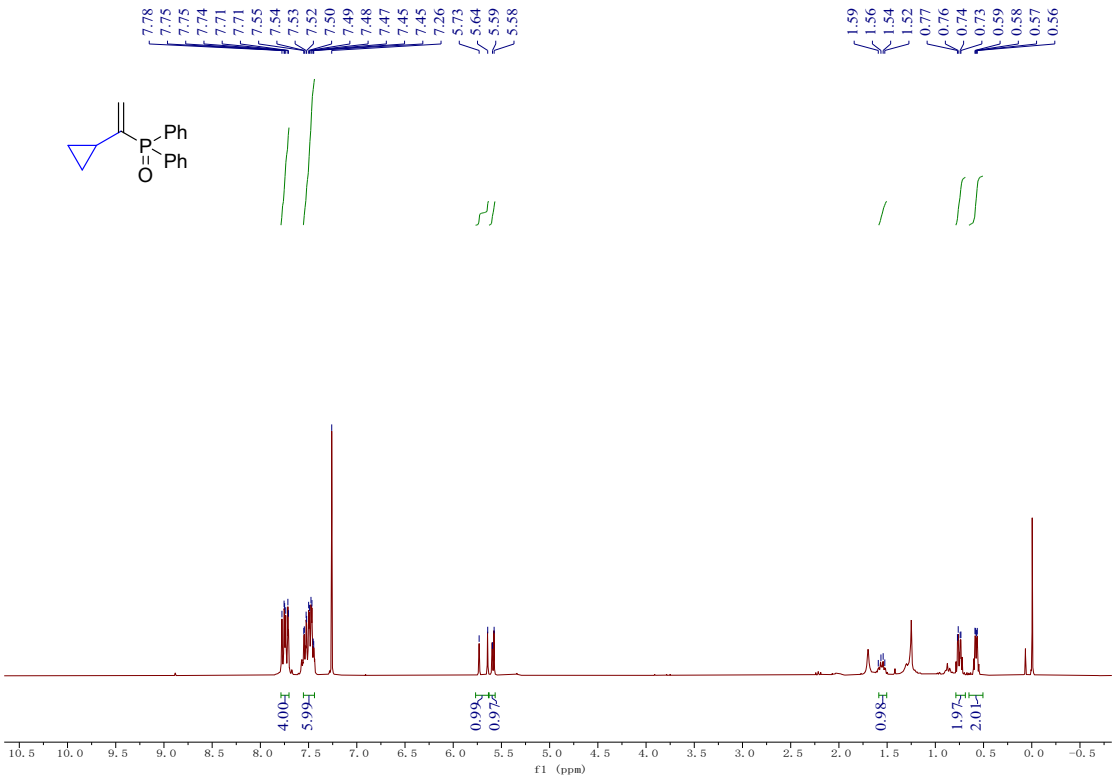
^{1}H NMR (300 MHz, $CDCl_3$) of **7o**



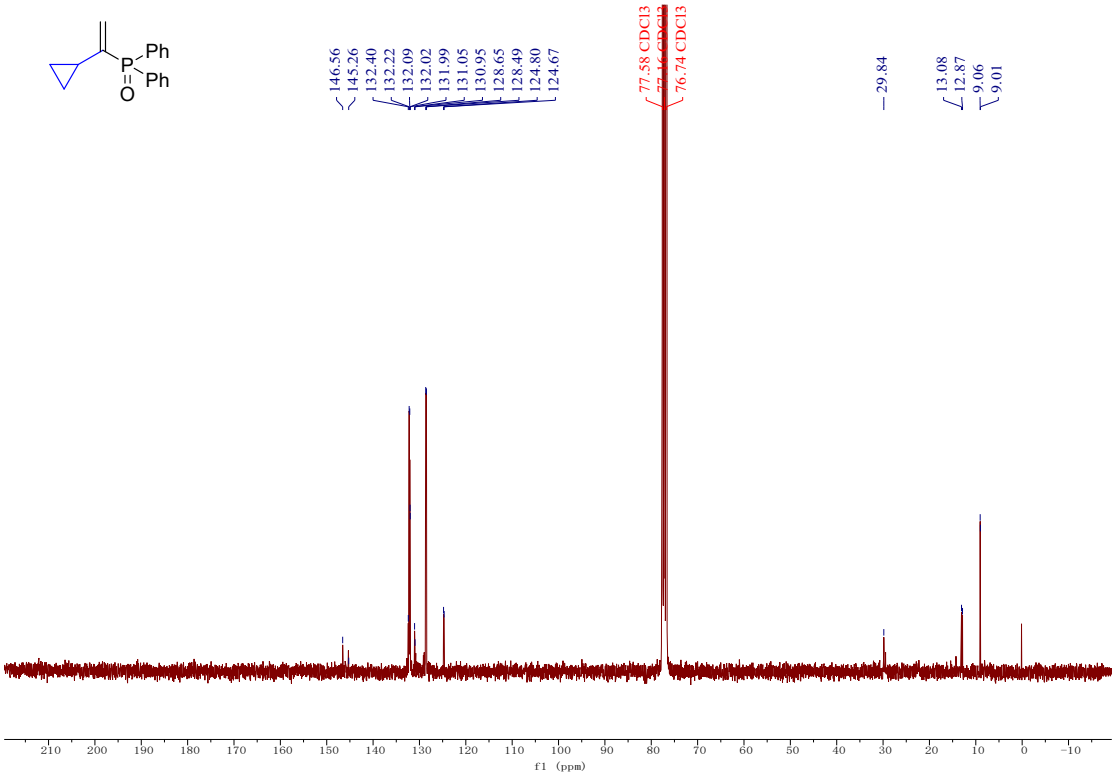
^{13}C NMR (75 MHz, $CDCl_3$) of **7o**



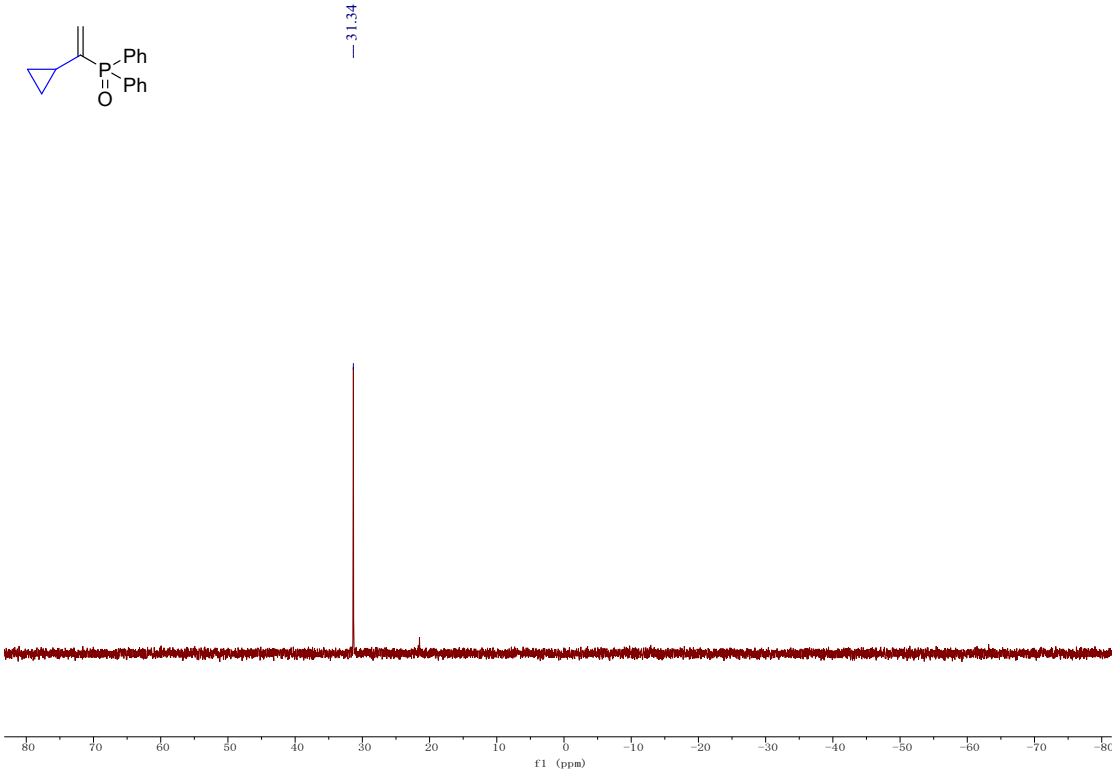
^{31}P NMR (121 MHz, $CDCl_3$) of **7o**



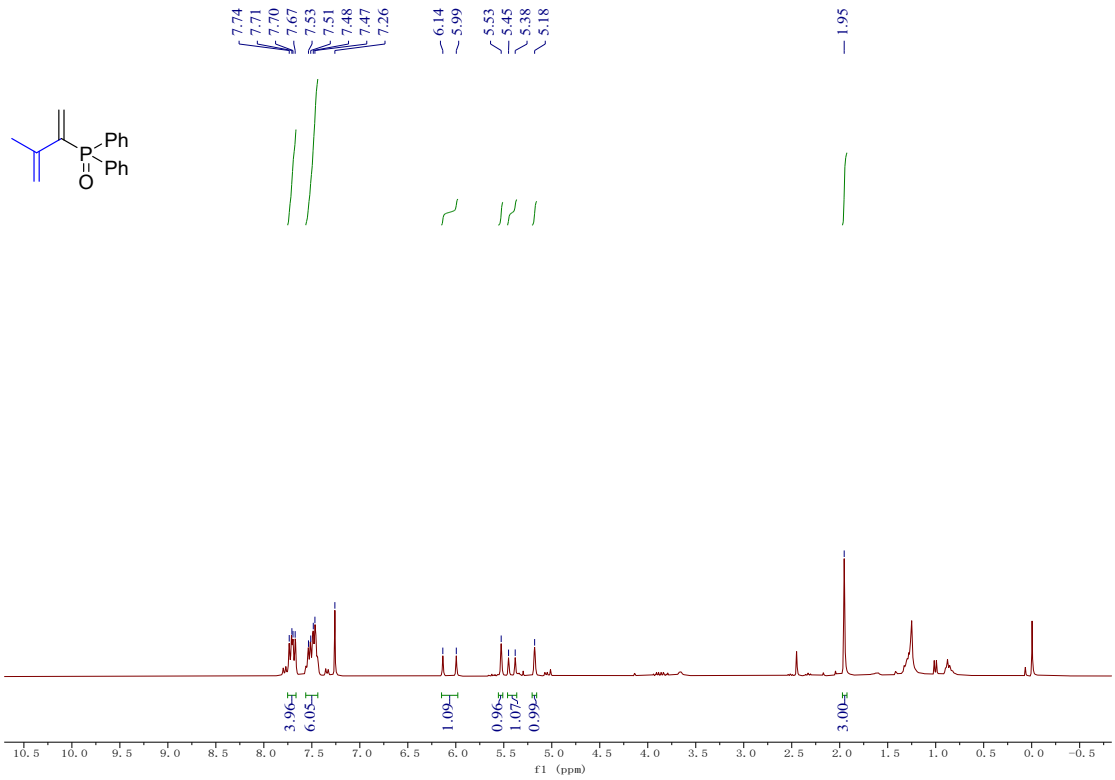
^{1}H NMR (300 MHz, $CDCl_3$) of **7p**



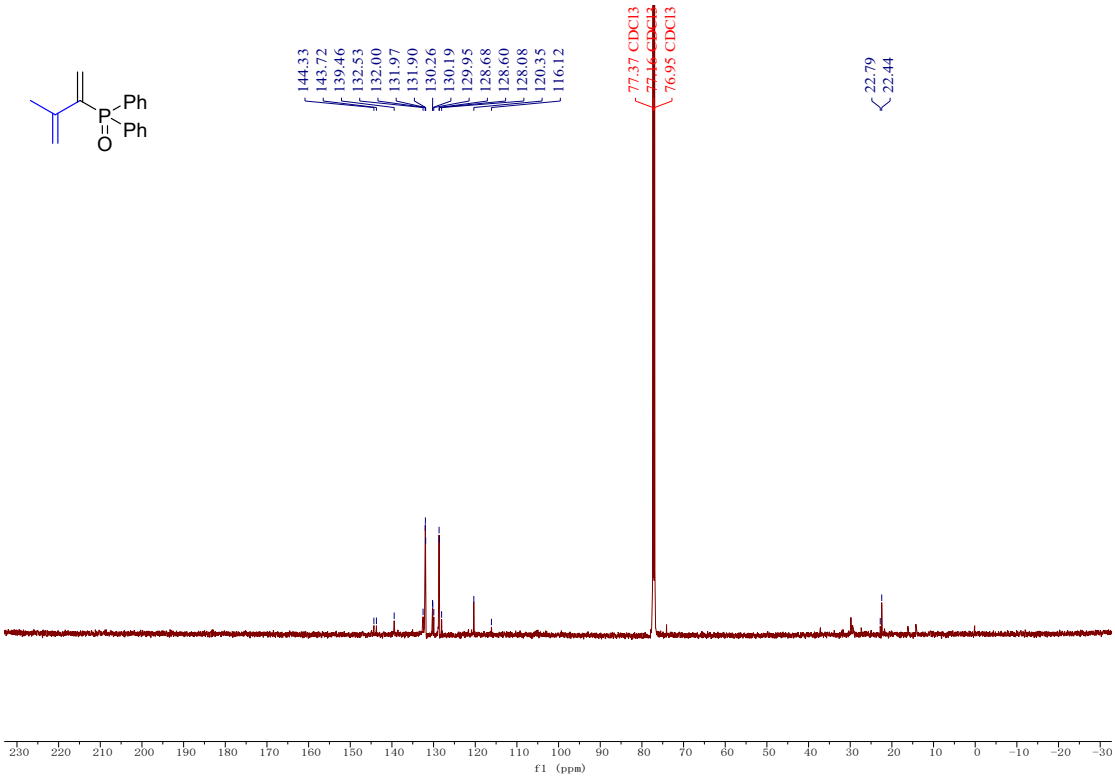
^{13}C NMR (75 MHz, $CDCl_3$) of **7p**



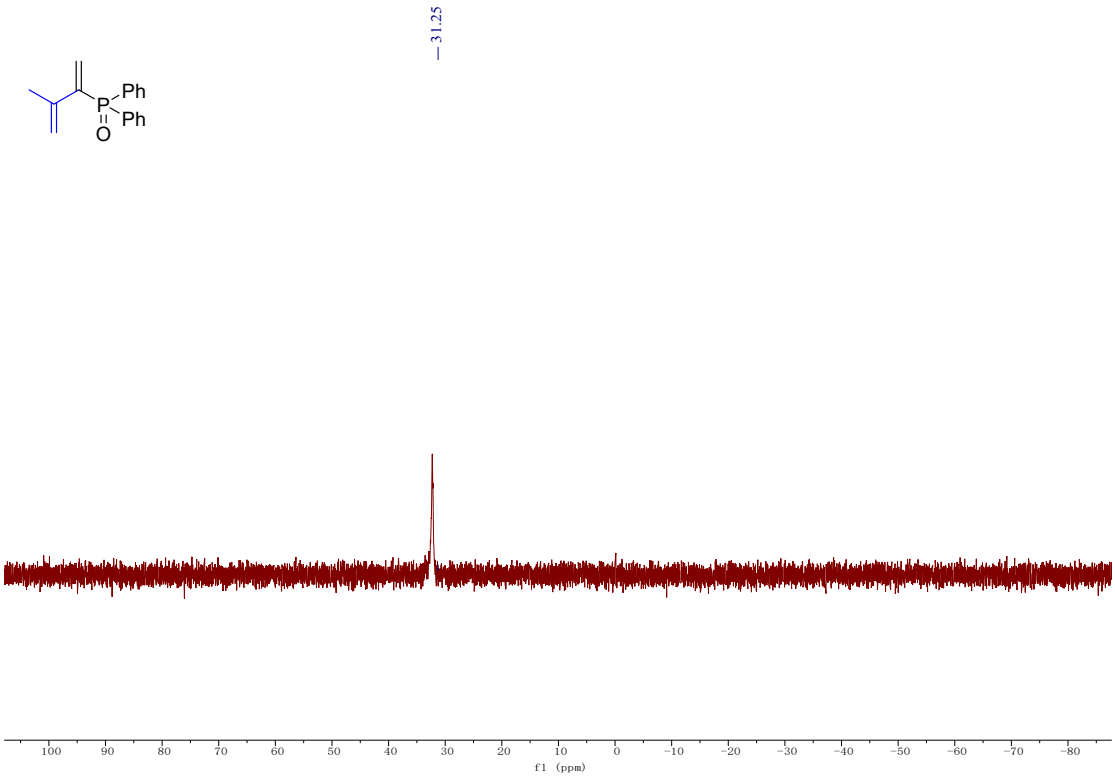
^{31}P NMR (121 MHz, $CDCl_3$) of **7p**



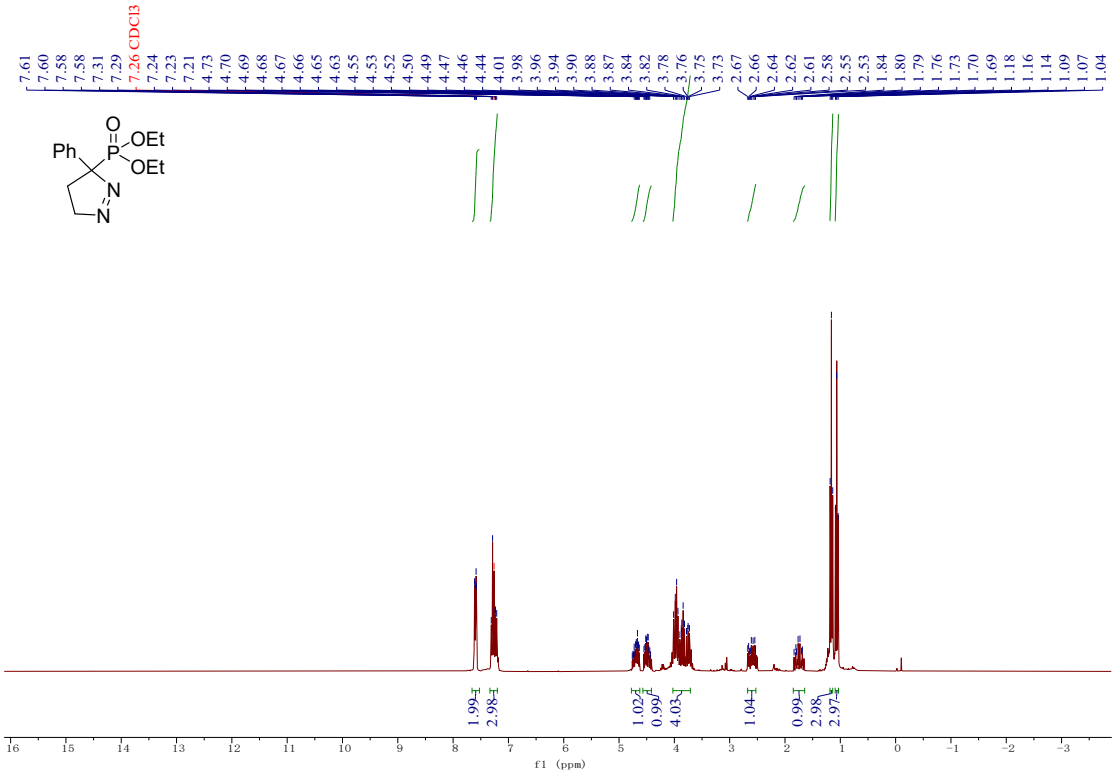
^{1}H NMR (300 MHz, $CDCl_3$) of **7q**



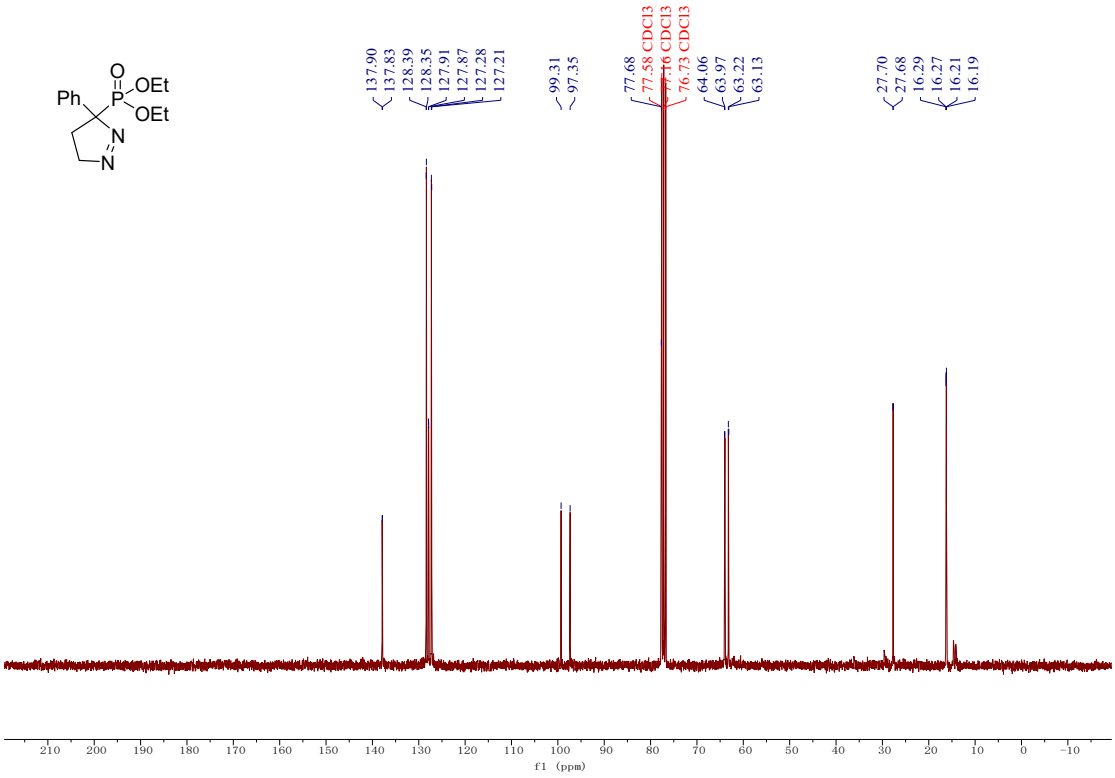
^{13}C NMR (151 MHz, $CDCl_3$) of **7q**



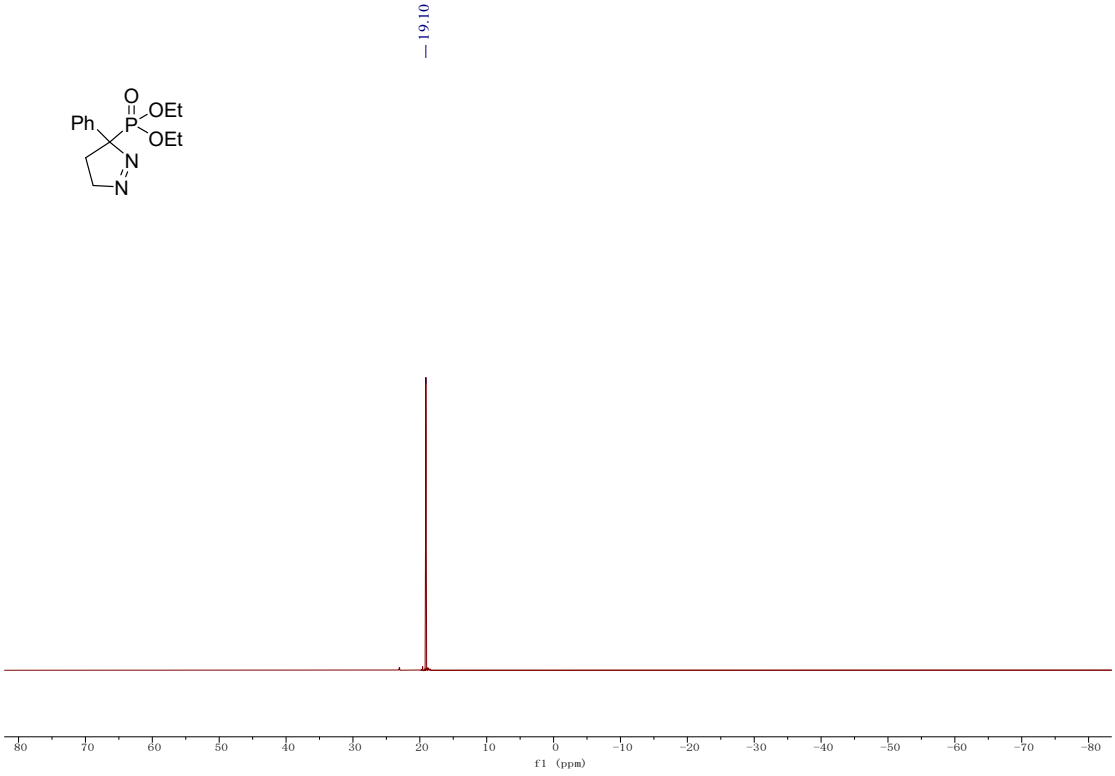
^{31}P NMR (121 MHz, $CDCl_3$) of **7q**



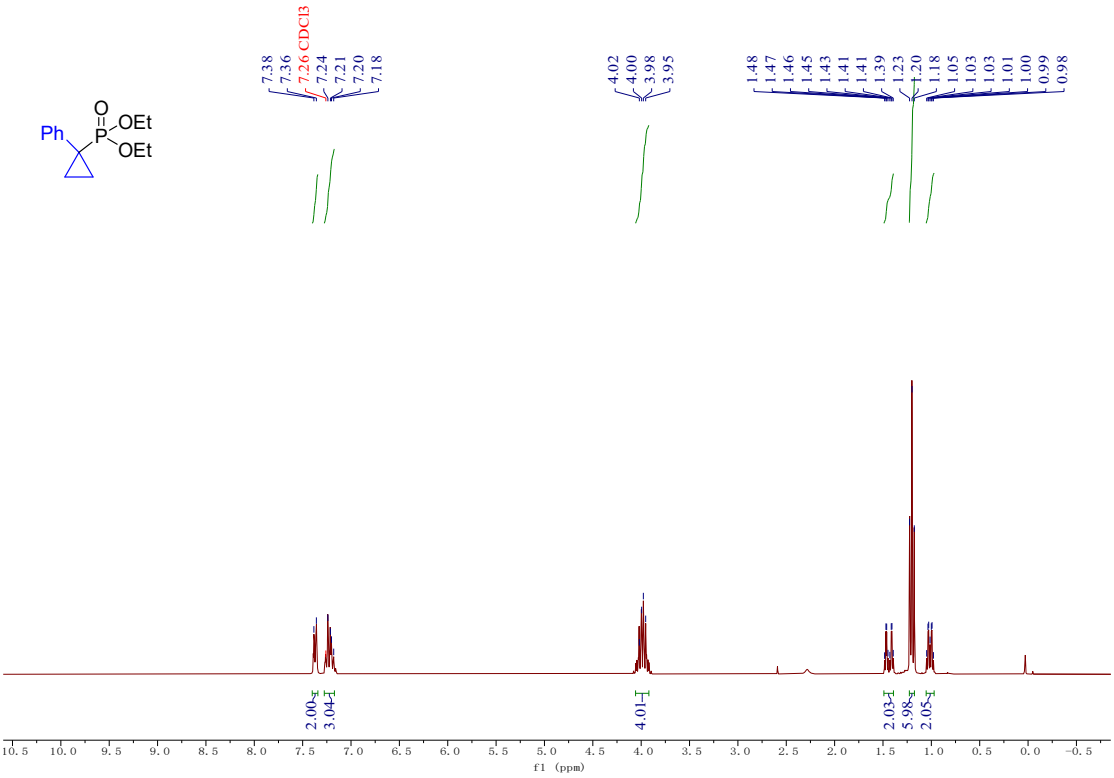
^{1}H NMR (300 MHz, $CDCl_3$) of **8**



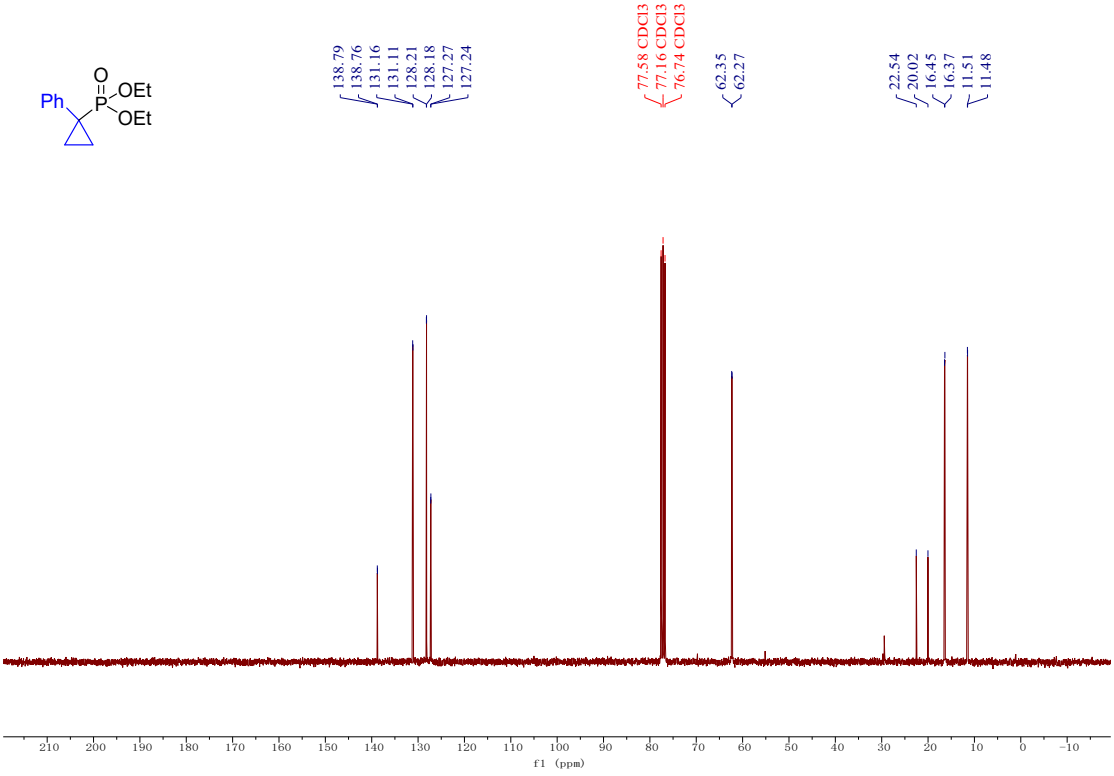
^{13}C NMR (75 MHz, $CDCl_3$) of **8**



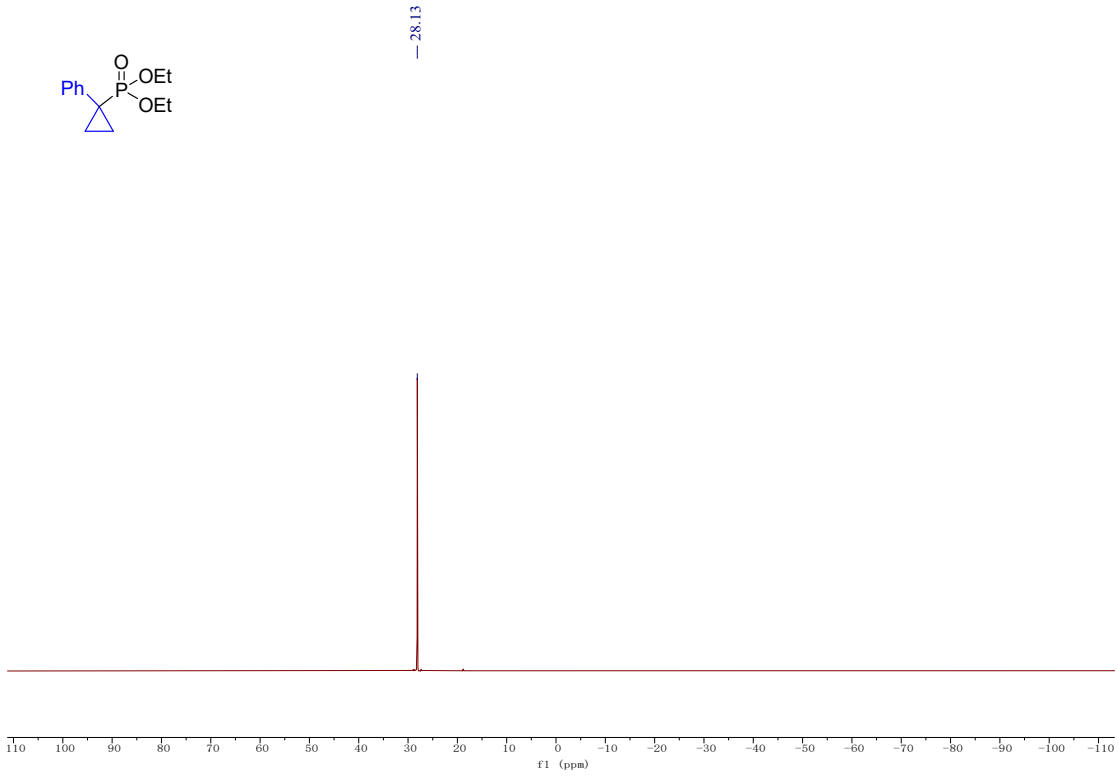
^{31}P NMR (121 MHz, $CDCl_3$) of **8**



^{1}H NMR (300 MHz, $CDCl_3$) of **9**



^{13}C NMR (75 MHz, $CDCl_3$) of **9**



^{31}P NMR (121 MHz, $CDCl_3$) of **9**