Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

## Efficient Synthesis of Benzophosphole Oxides by Ag-Promoted Radical Cycloisomerization

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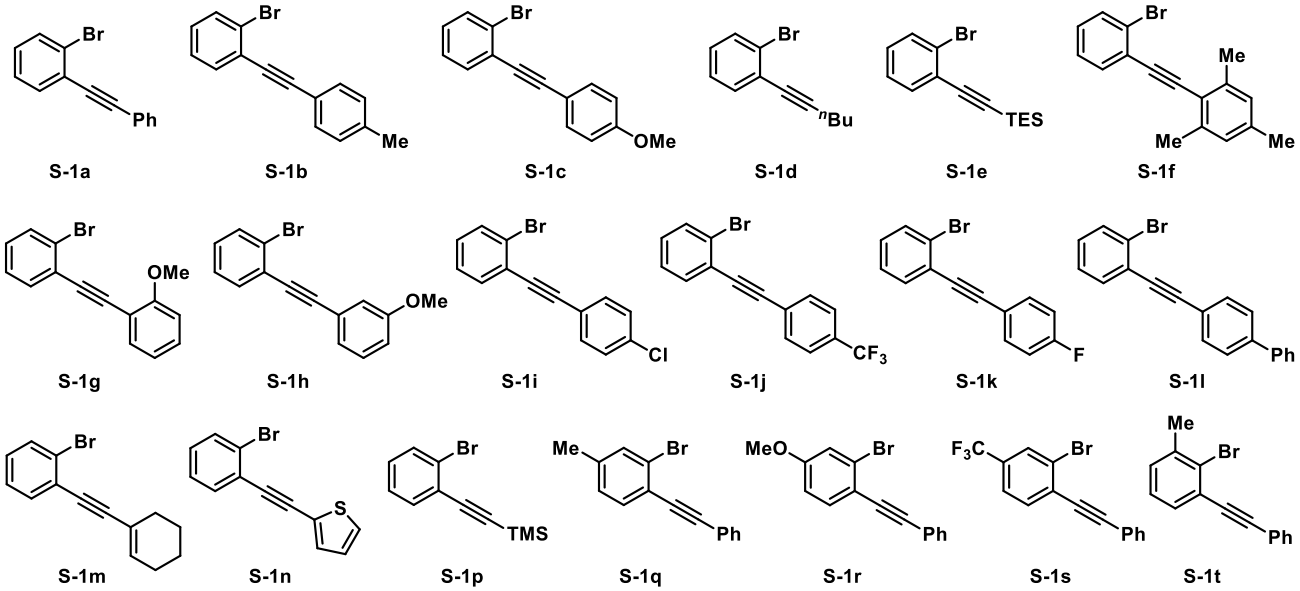
## 1. General information

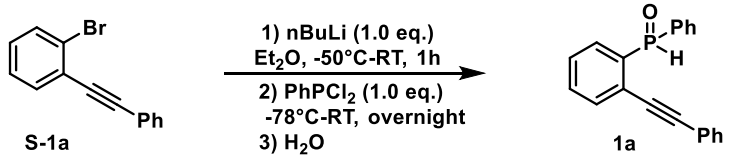
Unless otherwise indicated, all reactions were performed under an atmosphere of Argon. Dry and degassed solvents were employed. All organic reagents were obtained from commercial sources and used as received or prepared from known literature procedures. $^{1}H$ NMR, $^{13}C$ NMR, $^{31}P$ NMR and $^{19}F$ NMR spectra were obtained on Bruker Avance 300, 400 or 500 MHz spectrometers at 293 K. Chemical shifts are given in ppm relative to residual solvent as an internal standard for $^{1}H$ and $^{13}C$ NMR ($CDCl_3$: $\delta$ = 7.26 ppm for $^{1}H$ and $\delta$ = 77.0 ppm for $^{13}C$), $CCl_3F$ and $H_3PO_4$ as external references for $^{19}F$ and $^{31}P$ NMR spectra, respectively. Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets). Coupling constants (*J*) are reported in Hertz (Hz). The number of proton atoms (n) for a given resonance was indicated by *n*H. The number of carbon atoms (n) for a given resonance was indicated by *n*C. High resolution mass spectra were obtained using high resolution DCI-$CH_4$-TOF or ESI-TOF mass spectrometer.

**General experimental procedures and characterization data for the substrates.**

General procedures for the synthesis of 2-alkynylaryl bromobenzene are based on reported literature. **S-1a**, **S-1b**, **S-1c**, **S-1l**, **S-1i**, **S-1q**;[1] **S-1d**;[2] **S-1j**, **S-1r**;[3] **S-1k**, **S-1p**, **S-1s**, **S-1t**;[4] **S-1e**;[5] **S-1f**;[15] **S-1g**;[16] **S-1h**;[17] **S-1m**;[18] **S-1n**.[6]




**General procedure A**[6]**:**




A 50 mL Schlenk tube equipped with a magnetic stirrer was charged under Ar atmosphere with 1-bromo-2-(phenylethynyl)benzene **S-1a** (5.0 mmol, 1.29 g) and $Et_2O$ (10 mL). A solution of 1.60 M

$^n$BuLi (5.0 mmol, 3.13 mL) in hexane was added dropwise at –50 °C, the resulting solution was slowly warmed to RT and stirred for 1 h. Then, the mixture solution was cooled to –78°C and dichlorophenylphosphine (5.0 mmol, 0.68 mL) was added dropwise. The resulting reaction mixture was warmed at RT and stirred overnight. After adding $H_2O$ (20 mL), the biphasic mixture was extracted with Ethyl Acetate (EA) (15 mL×3) and the combined organic fractions were dried over anhydrous $Na_2SO_4$, the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (Pentane/EA = 2/1 to 1/1) to afford the desired product **1a** as a light yellow oil (yield 72%, 1.09 g).

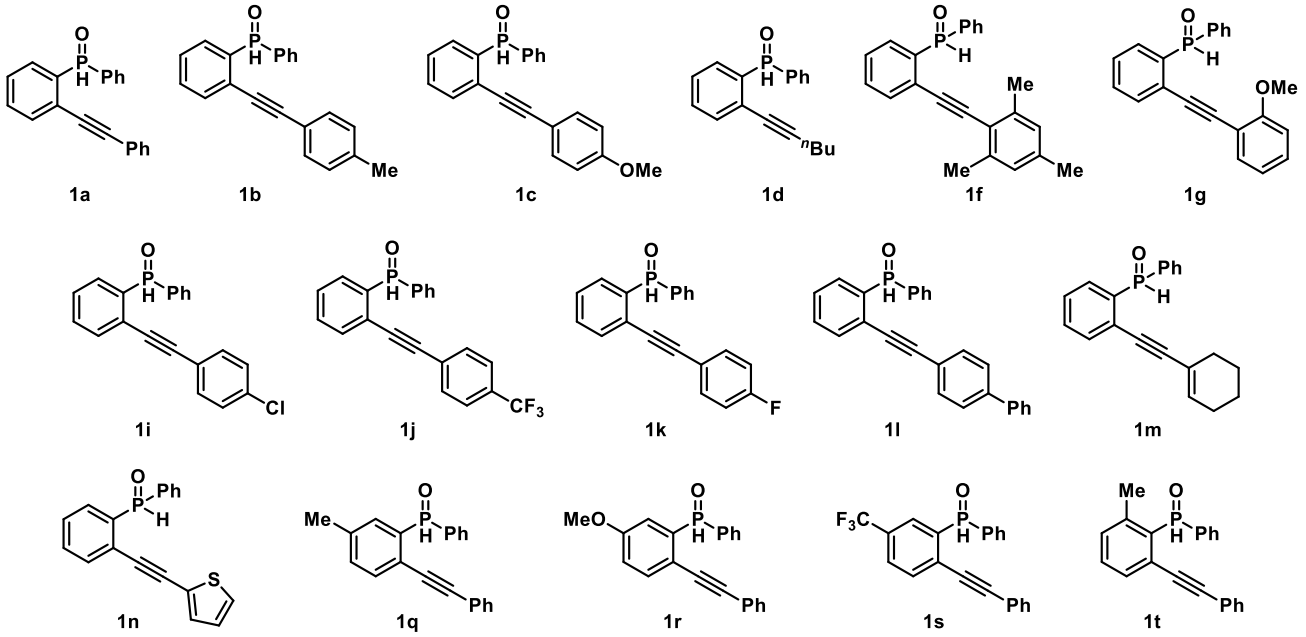
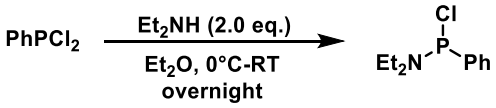


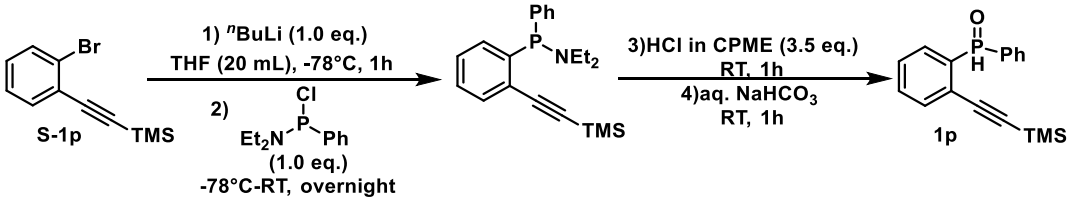

**Figure S1.** Secondary phosphine oxides synthesized according to General procedure **A**.

**General procedure B:**

**Step I:** Prepare aminochlorophosphine according to reference.[7]




**Step II:**




(2-Bromophenyl)ethynyl)trimethylsilane **S-1p** (10 mmol, 2.53 g) was dissolved in dry THF (20 mL) and cooled to –78°C. A solution of 1.6 M $^n$BuLi (10 mmol, 6.3 mL) was added dropwise over 5 minutes under stirring, resulting in a deep yellow/dark orange color. After stirring at the same temperature for 1 h, a solution of $Ph(NEt_2)PCl$ (10 mmol, 2.15 g, 2.0 mL) in 5 mL of dry THF was added dropwise via syringe at –78°C. The reaction mixture was allowed to warm at RT overnight. The resulting mixture was treated with 4.0 M HCl in cyclopentyl methyl ether (CPME) (35 mmol, 8.8 mL) for 1 h, followed

by quenching with aqueous $NaHCO_3$ (20 mL) and stirring for 1 h. The residue was extracted with EA (20 mL×3) and the combined organic fractions were dried over anhydrous $Na_2SO_4$, the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (Pentane/EA = 2/1 to 1/1) to afford the desired product **1p** as a light yellow oil (yield 65%, 1.93 g).

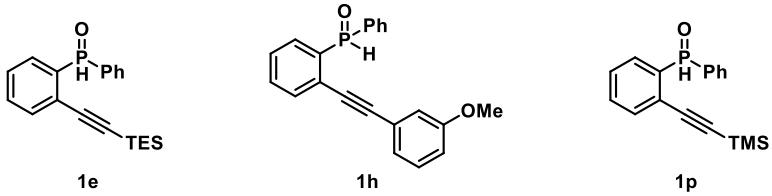
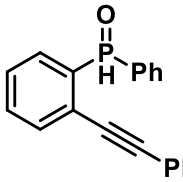


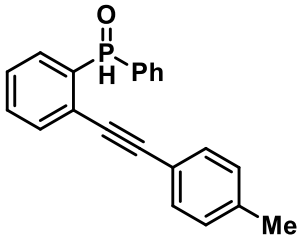

**Figure S2.** Secondary phosphine oxides synthesized according to General procedure **B**.

**Phenyl(2-(phenylethynyl)phenyl)phosphine oxide (1a)**[6]



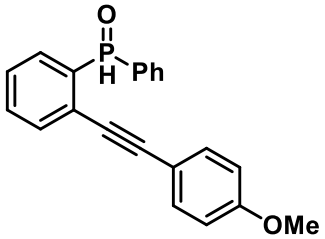

The general procedure **A** was used to obtain **1a**: total yield 72% (1.09 g, scale: 5.0 mmol), light yellow oil. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.34 (d, $J_{PH}$ = 496.5Hz, 1H), 7.97 – 7.90 (m, 1H), 7.68 – 7.61(m, 2H), 7.50 – 7.19 (m, 11H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 132.7 (d, $J_{PC}$=8.3 Hz), 132.5, 132.1, 132.1, 132.1 (d, $J_{PC}$=6.5 Hz), 131.3,131.0 (d, $J_{PC}$=31.4 Hz), 130.6 (d, $J_{PC}$=11.6 Hz), 128.9, 128.5 (d, $J_{PC}$=12.9 Hz), 128.4 (d, $J_{PC}$=11.4 Hz), 128.2, 124.8 (d, $J_{PC}$=9.8 Hz), 121.8, 96.7, 85.8 (d, $J_{PC}$=8.4 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 16.8. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ15.8 (dq, $J_1$=498.0 Hz, $J_2$ =14.0 Hz).

**Phenyl(2-(p-tolylethynyl)phenyl)phosphine oxide (1b)**




The general procedure **A** was used to obtain **1b**: total yield 62% (0.98 g, scale: 5.0 mmol), yellow solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.43 (d, $J_{PH}$ = 497.7 Hz,1H), 8.06 – 7.96 (m, 1H), 7.77 – 7.70 (m, 2H), 7.58 – 7.39 (m, 6H), 7.23 – 7.20 (m, 2H), 7.13 – 7.10 (m, 2H), 2.34 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 139.3, 132.7 (d, $J_{PC}$ = 8.3 Hz), 132.4, 132.2, 132.2 (d, $J_{PC}$ = 4.0 Hz), 132.1, 131.3, 131.0 (d, $J_{PC}$ = 14.5 Hz), 130.7 (d, $J_{PC}$ = 11.5 Hz), 129.1, 128.6 (d, $J_{PC}$ = 13.0 Hz), 128.3 (d, $J_{PC}$ = 11.2 Hz), 125.0 (d, $J_{PC}$ = 9.9 Hz), 118.8, 97.1, 85.3 (d, $J_{PC}$ = 8.6 Hz), 21.5. **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 17.0. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ17.0 (dq, $J_1$=496.6 Hz, $J_2$ =14.3 Hz). **HRMS (DCI-$CH_4$):** m/z calcd for $C_{21}H_{18}OP$ $[M + H]^+$: 317.1095, Found: 317.1094.

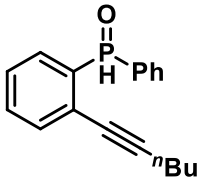
**(2-((4-methoxyphenyl)ethynyl)phenyl)(phenyl)phosphine oxide (1c)** [6]




The general procedure **A** was used to obtain **1c**: total yield 72% (1.19 g, scale: 5.0 mmol), light yellow oil. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.44 (d, $J_{PH}$ = 496.8Hz, 1H), 8.06 – 7.99 (m, 1H), 7.79– 7.71 (m, 2H), 7.60 – 7.40 (m, 6H), 7.30 – 7.25 (m, 2H), 6.87 – 6.82 (m, 2H), 3.80 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 160.1, 132.9, 132.6 (d, $J_{PC}$ = 8.4 Hz), 132.4 (d, $J_{PC}$ = 1.7 Hz), 132.2 (d, $J_{PC}$ = 2.5 Hz), 132.09 (d, $J_{PC}$ = 5.2 Hz), 132.08, 131.0 (d, $J_{PC}$ = 2.2 Hz), 130.7 (d, $J_{PC}$ = 11.6 Hz), 128.6 (d, $J_{PC}$ = 12.8 Hz), 128.1 (d, $J_{PC}$ = 11.3 Hz), 125.2 (d, $J_{PC}$ = 9.8 Hz), 114.0, 113.9,

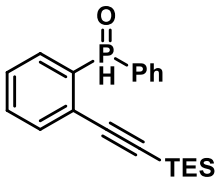
97.1, 84.8 (d, $J_{PC}$ = 8.6 Hz), 55.2. **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ16.9. **$^{31}P$ NMR (121 MHz, $CDCl_3$)** δ16.9 (dq, $J_1$=495.7 Hz, $J_2$ =14.3 Hz).

**(2-(hex-1-yn-1-yl)phenyl)(phenyl)phosphine oxide (1d)**



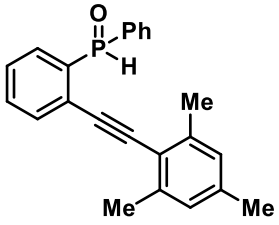

The general procedure **A** was used to obtain **1d**: total yield 42% (352 mg, scale: 3.0 mmol), light yellow oil. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 8.33 (d, $J$ = 499.2 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.73 – 7.65 (m, 2H), 7.55 – 7.42 (m, 6H), 2.29 (t, $J$ = 6.9 Hz, 2H), 1.45 – 1.28 (m, 4H), 0.86 (t, $J$ = 7.2 Hz, 3H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 132.8 (d, $J_{PC}$ = 8.6 Hz), 132.3, 132.1 (d, $J_{PC}$ = 5.0 Hz), 132.1, 132.0 (d, $J_{PC}$ = 3.5 Hz), 130.8 (d, $J_{PC}$ = 14.1 Hz), 130.6 (d, $J_{PC}$ = 11.4Hz), 128.5 (d, $J_{PC}$ = 12.8 Hz), 127.8 (d, $J_{PC}$ = 11.3 Hz), 125.8 (d, $J_{PC}$ = 10.1 Hz), 98.9, 77.5 (d, $J_{PC}$ = 8.6 Hz), 30.2, 21.9, 19.1, 13.5. **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 17.2. **$^{31}P$ NMR (121 MHz, $CDCl_3$)** δ17.3 (dq, $J_1$=497.3 Hz, $J_2$ =13.8 Hz). **HRMS (DCI-$CH_4$):** m/z calcd for $C_{18}H_{20}OP$ $[M + H]^+$: 283.1252, Found: 283.1246.

**phenyl(2-((triethylsilyl)ethynyl)phenyl)phosphine oxide (1e)**



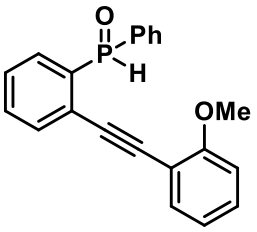

The general procedure **B** was used to obtain **1e**: total yield 57% (1.93 g, scale: 10.0 mmol), light yellow oil. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 8.43 (d, J = 500.4 Hz, 1H), 8.00 – 7.90 (m, 1H), 7.72 – 7.65 (m, 2H), 7.54 – 7.35 (m, 6H), 0.90 (t, J = 8.1 Hz, 9H), 0.59 – 0.51 (m, 6H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 133.4 (d, $J_{PC}$ = 8.3 Hz), 132.4 (d, $J_{PC}$ = 26.0 Hz), 132.1 (d, $J_{PC}$ = 2.9 Hz), 131.9 (d, $J_{PC}$ = 2.5 Hz), 131.8 (d, $J_{PC}$ = 2.7 Hz), 131.0 (d, $J_{PC}$ = 26.7 Hz), 130.5 (d, $J_{PC}$ = 11.3 Hz), 128.6 (d, $J_{PC}$ = 11.0 Hz), 128.5 (d, $J_{PC}$ = 12.8 Hz), 124.7 (d, $J_{PC}$ = 10.3 Hz), 102.1 (d, $J_{PC}$ = 8.1 Hz), 100.7, 7.2, 3.9. **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 15.5. **$^{31}P$ NMR (121 MHz, $CDCl_3$)** δ15.5 (dq, $J_1$=498.4 Hz, $J_2$ =13.3 Hz). **HRMS (ESI):** m/z calcd for $C_{20}H_{26}OPSi$ $[M + H]^+$: 341.1491, Found: 341.1492.

**(2-(mesitylethynyl)phenyl)(phenyl)phosphine oxide (1f)**



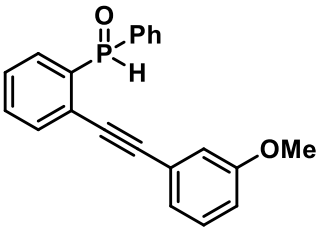

The general procedure **A** was used to obtain **1f**: total yield 68% (0.94 g, scale: 4.0 mmol), white solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 8.56 (d, J = 496.5 Hz, 1H), 7.99 – 7.92 (m, 1H), 7.75 – 7.61 (m, 3H), 7.56 – 7.35 (m, 5H), 6.84 (d, J = 0.6 Hz, 2H), 2.30 (s, 6H), 2.26 (s, 3H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 140.3, 138.6, 133.0 (d, $J_{PC}$ = 8.5 Hz), 132.1 (d, $J_{PC}$ = 2.9 Hz), 132.0 (d, $J_{PC}$ = 1.6 Hz), 132.0 (d, $J_{PC}$ = 12 Hz), 132.0 (d, $J_{PC}$ = 2.8 Hz), 130.6 (d, $J_{PC}$ = 11.3 Hz), 130.6 (d, $J_{PC}$ = 1.5 Hz), 128.5 (d, $J_{PC}$ = 12.8 Hz), 128.2 (d, $J_{PC}$ = 11.1 Hz), 127.6, 125.7 (d, $J_{PC}$ = 9.9 Hz), 118.7, 95.0, 93.1 (d, $J_{PC}$ = 8.6 Hz), 21.2, 20.8. **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ15.9. **$^{31}P$ NMR (121 MHz, $CDCl_3$)** δ16.1 (dq, $J_1$=494.8 Hz, $J_2$ =13.9 Hz). **HRMS (DCI-$CH_4$):** m/z calcd for $C_{23}H_{22}OP$ $[M + H]^+$: 345.1408, Found: 345.1408.

**(2-((2-methoxyphenyl)ethynyl)phenyl)(phenyl)phosphine oxide (1g)**



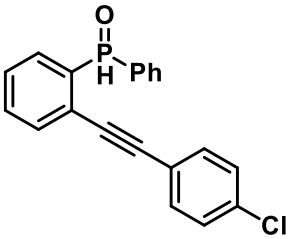
The general procedure **A** was used to obtain **1g**: total yield 61% (1.71 g, scale: 8.5 mmol), light yellow oil. **$^{1}$H NMR (300 MHz, CDCl$_3$)** δ 8.61 (d, $J$ = 506.4, 1H)，δ 8.06 – 7.99 (m, 1H), 7.87 – 7.80 (m, 2H), 7.64 – 7.31 (m, 8H), 6.95 – 6.87 (m, 2H), 3.83 (s, 3H). **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 159.8, 132.9, 132.4 (d, $J_{PC}$ = 8.3 Hz), 132.0, 131.9 (d, $J_{PC}$ = 2.9 Hz), 131.8 (d, $J_{PC}$ = 2.4 Hz), 131.4 (d, $J_{PC}$ = 7.6 Hz), 130.9 (d, $J_{PC}$ = 29.0 Hz), 130.4, 130.2, 128.3 (d, $J_{PC}$ = 12.9 Hz), 128.2 (d, $J_{PC}$ = 11.0 Hz), 124.8 (d, $J_{PC}$ = 10.4 Hz), 120.2, 110.9, 110.4, 93.5, 89.7 (d, $J_{PC}$ = 8.6 Hz), 55.2. **$^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$)** δ 15.8. **$^{31}$P NMR (121 MHz, CDCl$_3$)** δ16.3 (dq, $J_1$ = 504.3 Hz, $J_2$ = 13.4 Hz). **HRMS (DCI-CH$_4$):** m/z calcd for $C_{21}H_{18}O_2P$ $[M + H]^+$: 333.1044, Found: 333.1043.

**(2-((3-methoxyphenyl)ethynyl)phenyl)(phenyl)phosphine oxide (1h)**



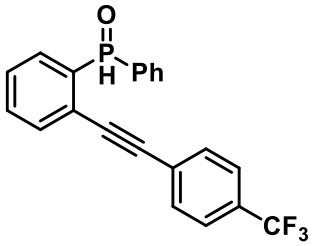
The general procedure **B** was used to obtain **1h**: total yield 89% (1.18 g, scale: 4.0 mmol), light yellow oil.**$^{1}$H NMR (300 MHz, CDCl$_3$)** δ 8.36 (d, $J$ = 493.8, 1H), 8.09 – 7.86 (m, 1H),7.76 – 7.68 (m, 2H), 7.57 – 7.36 (m, 6H), 7.28 (dd, $J_1$ = 5.4 Hz, $J_2$ = 1.2 Hz, 1H), 7.12 (dd, $J_1$ = 3.9 Hz, $J_2$ = 1.2 Hz, 1H), 6.97 – 6.94 (m, 1H). **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 159.1, 132.7 (d, $J_{PC}$ = 8.5 Hz), 132.6, 132.2 (d, $J_{PC}$ = 1.8 Hz), 132.1, 132.1 (d, $J_{PC}$ = 6.0 Hz), 131.0 (d, $J_{PC}$ = 29.0 Hz), 130.6 (d, $J_{PC}$ = 11.6 Hz), 129.3, 128.5 (d, $J_{PC}$ = 13.0 Hz), 128.5 (d, $J_{PC}$ = 11.3 Hz), 124.7 (d, $J_{PC}$ = 9.8 Hz), 123.8, 122.9, 116.1, 115.4, 96.6, 85.6 (d, $J_{PC}$ = 7.8 Hz), 55.1.**$^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$)** δ 16.8. **$^{31}$P NMR (121 MHz, CDCl$_3$)** δ16.8 (dq, $J_1$ = 495.0 Hz, $J_2$ = 13.6 Hz). **HRMS (DCI-CH$_4$):** m/z calcd for $C_{21}H_{18}O_2P$ $[M + H]^+$: 333.1044, Found: 333.1030.

**(2-((4-chlorophenyl)ethynyl)phenyl)(phenyl)phosphine oxide (1i)**



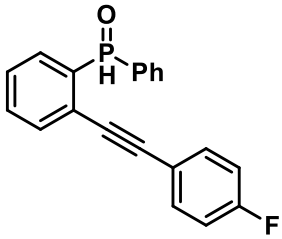
The general procedure **A** was used to obtain **1i**: total yield 65% (1.09 g, scale: 4.7 mmol), white solid. **$^{1}$H NMR (300 MHz, CDCl$_3$)** δ 8.39 (d, $J_{PH}$ = 495.3 Hz, 1H), 8.05 – 7.97 (m, 1H), 7.76 – 7.68 (m, 2H), 7.61 – 7.49 (m, 4H), 7.46 – 7.39 (m, 2H), 7.31 – 7.21 (m, 4H). **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 135.0, 132.8 (d, $J_{PC}$ = 8.4 Hz), 132.6, 132.5, 132.3 (d, $J_{PC}$ = 6.3 Hz), 132.2 (d, $J_{PC}$ = 2.3 Hz), 132.2, 132.7 (d, $J_{PC}$ = 56.9 Hz), 130.6 (d, $J_{PC}$ = 11.5 Hz), 128.7 (d, $J_{PC}$ = 11.4 Hz), 128.6, 128.6 (d, $J_{PC}$ = 13.1 Hz), 124.5 (d, $J_{PC}$ = 9.4 Hz), 120.3, 95.5, 86.9 (d, $J_{PC}$ = 8.3 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$)** δ 17.0. **$^{31}$P NMR (121 MHz, CDCl$_3$)** δ17.1 (dq, $J_1$=493.8 Hz, $J_2$ =14.2 Hz). **HRMS (DCI-CH$_4$):** m/z calcd for $C_{20}H_{15}OPCl$ $[M + H]^+$: 337.0549, Found: 337.0545.

**Phenyl(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)phosphine oxide (1j)**[2]



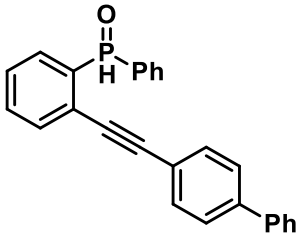
The general procedure **A** was used to obtain **1j**: total yield 66% (487 mg, scale: 2.0 mmol), light yellow solid. **$^{1}$H NMR (300 MHz, $CDCl_3$)** δ 8.35 (d, $J$ = 499.5 Hz, 1H), 8.03 – 7.93 (m, 1H), 7.74 – 7.64 (m, 2H), 7.61 – 7.45 (m, 6H), 7.42 – 7.36 (m, 4H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 132.9 (d, $J_{PC}$ = 8.3 Hz), 132.4, 132.4 (d, $J_{PC}$ = 68.3 Hz), 132.3 (t, $J_{PC}$ = 1.5 Hz), 132.2 (d, $J_{PC}$ = 2.3 Hz), 131.5, 131.0 (d, $J_{PC}$ = 70.1 Hz), 130.6 (d, $J_{PC}$ = 11.6 Hz), 130.4 (q, $J_{FC}$ = 32.7 Hz), 128.9 (d, $J_{PC}$ = 11.4 Hz), 128.6 (d, $J_{PC}$ = 12.8 Hz), 125.6 (d, $J_{PC}$ = 1.5 Hz), 125.1 (q, $J_{FC}$ = 3.8 Hz), 124.1 (d, $J_{PC}$ = 9.3 Hz), 123.6 (q, $J_{FC}$ = 270.7 Hz), 94.9, 88.0 (d, $J_{PC}$ = 8.3 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, $CDCl_3$)** δ17.0. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ17.1 (dq, $J_1$=493.2 Hz, $J_2$ =13.6 Hz). **$^{19}$F NMR (282 MHz, $CDCl_3$)** δ -62.9.

**(2-((4-fluorophenyl)ethynyl)phenyl)(phenyl)phosphine oxide (1k)**



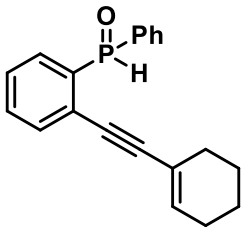
The general procedure **A** was used to obtain **1k**: total yield 72% (1.19 g, scale: 5.0 mmol), light yellow oil.**$^{1}$H NMR (300 MHz, $CDCl_3$)** δ 8.39 (d, $J$ = 495.6 Hz, 1H), 8.04 – 7.94 (m, 1H), 7.75 – 7.67 (m, 2H), 7.56 – 7.47 (m, 4H), 7.44 – 7.38 (m, 2H), 7.30 – 7.23 (m, 2H), 7.02 – 6.95 (m, 2H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 162.7 (d, $J_{FC}$ = 249.4 Hz), 133.3 (d, $J_{PC}$ = 8.6 Hz), 132.7 (d, $J_{PC}$ = 8.4Hz), 132.3 (d, $J_{PC}$ = 35.9 Hz), 132.2 (d, $J_{PC}$ = 9.9 Hz), 132.1, 132.1 (d, $J_{PC}$ = 7.6 Hz), 132.9 (d, $J_{PC}$ = 37.1 Hz), 130.6 (d, $J_{PC}$ = 11.5 Hz), 128.5 (d, $J_{PC}$ = 13.05 Hz), 128.5 (d, $J_{PC}$ = 11.4 Hz), 124.6 (d, $J_{PC}$ = 9.6 Hz), 117.9 (d, $J_{PC}$ = 3.5 Hz), 115.6 (d, $J_{PC}$ = 22.1 Hz) , 95.6, 85.6 (dd, $J_{PC1}$ = 8.6 Hz, $J_{PC2}$ = 1.6 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, $CDCl_3$)** δ 17.0. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ17.1 (dq, $J_1$=493.9 Hz, $J_2$ =14.2 Hz). **$^{19}$F NMR (282 MHz, $CDCl_3$)** δ -109.4. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{20}H_{15}OFP$ $[M + H]^+$: 321.0845, Found: 321.0840.

**(2-([1,1'-biphenyl]-4-ylethynyl)phenyl)(phenyl)phosphine oxide (1l)**



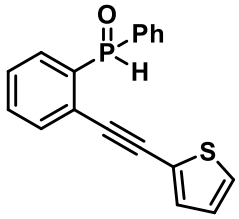
The general procedure **A** was used to obtain **1l**: total yield 35% (1.34 g, scale: 10.0 mmol), white solid. **$^{1}$H NMR (300 MHz, $CDCl_3$)** δ 8.47 (d, $J$ = 497.1 Hz, 1H), 8.09 – 8.02 (m, 1H), 7.81 – 7.73 (m, 2H), 7.65 – 7.34 (m, 15H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 141.7, 139.9, 132.8 (d, $J_{PC}$= 8.3 Hz), 132.6, 132.3, 132.3, 132.3, 132.2, 132.2, 132.2, 131.8, 131.0 (d, $J_{PC}$= 26.0 Hz), 130.7 (d, $J_{PC}$= 11.5 Hz), 128.8, 128.7 (d, $J_{PC}$= 12.9 Hz), 128.5 (d, $J_{PC}$= 11.4 Hz), 127.8, 127.0 (d, $J_{PC}$= 5.9 Hz), 124.9 (d, $J_{PC}$= 9.7 Hz), 120.7, 96.8, 86.6 (d, $J_{PC}$= 8.5 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, $CDCl_3$)** δ16.9. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ17.0 (dq, $J_1$=495.0 Hz, $J_2$ =13.4 Hz). **HRMS (DCI-$CH_4$):** m/z calcd for $C_{26}H_{20}OP$ $[M + H]^+$: 379.1252, Found: 379.1245.

**2-(cyclohex-1-en-1-yl)-1-phenylphosphindole 1-oxide (1m)**



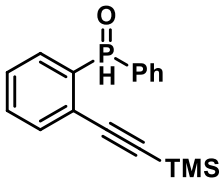
The general procedure **A** was used to obtain **1m**: total yield 83% (2.54 g, scale: 10.0 mmol), white solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.26 (d, *J* = 497.7 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.66 – 7.58 (m, 2H), 7.42 – 7.26 (m, 6H), 5.99 – 5.96 (m, 1H), 2.01 – 1.91 (m, 4H), 1.53 – 1.40 (m, 4H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 136.4, 132.3 (d, $J_{PC}$ = 8.3 Hz), 132.0 (d, $J_{PC}$ = 8.3 Hz), 131.8 (d, $J_{PC}$ = 2.9 Hz), 131.8, 131.7 (d, $J_{PC}$ = 5.2 Hz), 130.6 (d, $J_{PC}$ = 8.2 Hz), 130.3 (d, $J_{PC}$ =11.3 Hz), 128.2 (d, $J_{PC}$ = 12.8 Hz), 127.6 (d, $J_{PC}$ = 11.3 Hz), 125.2 (d, $J_{PC}$ = 9.9 Hz), 119.6, 98.7, 83.3 (d, $J_{PC}$ = 8.8 Hz), 28.2, 25.3, 21.7, 20.9. **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ16.5. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ16.6 (dq, $J_1$=496.3 Hz, $J_2$ =13.2 Hz). **HRMS (DCI-$CH_4$):** m/z calcd for $C_{20}H_{20}OP$ $[M + H]^+$: 307.1252, Found: 307.1248.

**phenyl(2-(thiophen-2-ylethynyl)phenyl)phosphine oxide (1n)**



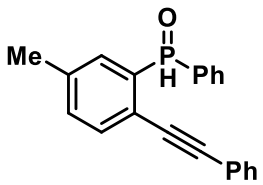
The general procedure **A** was used to obtain **1n**: total yield 77% (1.89 g, scale: 8.0 mmol), light yellow oil. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.36 (d, *J* = 493.8, 1H), 8.09 – 7.86 (m, 1H),7.76 – 7.68 (m, 2H), 7.57 – 7.36 (m, 6H), 7.28 (dd, $J_1$ = 5.4 Hz, $J_2$ = 1.2 Hz, 1H), 7.12 (dd, $J_1$ = 3.9 Hz, $J_2$ = 1.2 Hz, 1H), 6.97 – 6.94 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 132.5, 132.5 (d, $J_{PC}$ = 8.3 Hz), 132.2 (d, $J_{PC}$ = 1.5 Hz), 132.1 (d, $J_{PC}$ = 6.5 Hz), 132.1, (d, $J_{PC}$ = 2.4 Hz), 132.1, 130.9 (d, $J_{PC}$ = 25.2 Hz), 130.6 (d, $J_{PC}$ = 11.6 Hz), 128.6 (d, $J_{PC}$ = 12.8 Hz), 128.6 (d, $J_{PC}$ = 11.2 Hz), 128.2, 127.1, 124.3 (d, $J_{PC}$ = 9.7 Hz), 121.6, 90.2, 89.5 (d, $J_{PC}$ = 8.6 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ17.1. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ17.2 (dq, $J_1$ = 494.8 Hz, $J_2$ = 14.0 Hz). **HRMS (DCI-$CH_4$):** m/z calcd for $C_{18}H_{14}OPS$ $[M + H]^+$: 309.0503, Found: 309.0496.

**Phenyl(2-((trimethylsilyl)ethynyl)phenyl)phosphine oxide (1p)**



The general procedure **B** was used to obtain **1p**: total yield 65% (1.93 g, scale: 10.0 mmol), light yellow oil. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.37 (d, *J* = 501.3 Hz, 1H), 8.04 – 7.95 (m, 1H), 7.75 – 7.66 (m, 2H), 7.51 – 7.29 (m, 6H), 0.13 (s, 9H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 132.9 (d, $J_{PC}$ = 8.3 Hz), 132.3, 132.0 (d, $J_{PC}$ = 2.9 Hz), 131.8, 131.8 (d, $J_{PC}$ = 4.6 Hz), 130.7 (d, $J_{PC}$ = 33.8 Hz), 130.5 (d, $J_{PC}$ = 11.5 Hz), 128.6 (d, $J_{PC}$ = 11.0 Hz), 128.3 (d, $J_{PC}$ = 12.8 Hz), 124.3 (d, $J_{PC}$ = 10.1 Hz), 102.8, 100.8 (d, $J_{PC}$ = 8.2 Hz), 0.8. **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 16.3. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ16.3 (dq, $J_1$=499.6 Hz, $J_2$ =13.7 Hz). **HRMS (DCI-$CH_4$):** m/z calcd for $C_{17}H_{20}OSiP$ $[M + H]^+$: 299.1021, Found: 299.1014.

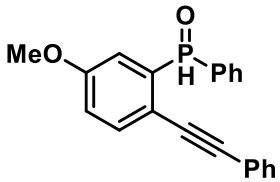
**(5-methyl-2-(phenylethynyl)phenyl)(phenyl)phosphine oxide (1q)**



The general procedure **A** was used to obtain **1q**: total yield 69% (1.05 g, scale: 4.8 mmol), white solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.40 (d, *J* = 496.5 Hz, 1H), 7.86 (d, *J* = 1.8 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.46 – 7.36 (m, 4H), 7.29 – 7.26 (m, 6H), 2.36 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 138.8 (d, $J_{PC}$ = 11.2

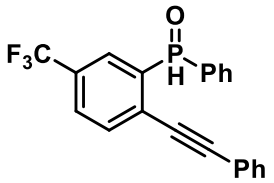
Hz), 132.7 (d, $J_{PC}$ = 2.4 Hz), 132.5 (d, $J_{PC}$ = 17.6 Hz), 132.5, 132.1 (d, $J_{PC}$ = 13.4 Hz), 131.9 (d, $J_{PC}$ = 2.9 Hz), 131.0, 130.7 (d, $J_{PC}$ = 12.4 Hz), 130.4 (d, $J_{PC}$ = 11.5 Hz), 128.5, 128.4 (d, $J_{PC}$ = 12.8 Hz), 128.1, 121.8, 121.5 (d, $J_{PC}$ = 9.8 Hz), 95.80, 85.8 (d, $J_{PC}$ = 8.4 Hz), 21.10. **$^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$)** δ 16.7. **$^{31}$P NMR (121 MHz, CDCl$_3$)** δ16.8 (dq, $J_1$=494.6 Hz, $J_2$ =13.6 Hz). **HRMS (DCI-CH$_4$):** m/z calcd for $C_{21}H_{18}OP$ $[M + H]^+$: 317.1095, Found: 317.1093.

**(5-methoxy-2-(phenylethynyl)phenyl)(phenyl)phosphine oxide (1r)**



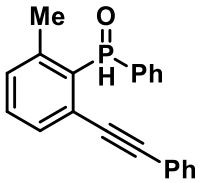

The general procedure **A** was used to obtain **1r**: total yield 73% (486 mg, scale: 2.0 mmol), white solid. **$^{1}$H NMR (300 MHz, CDCl$_3$)** δ 8.40 (d, $J$ = 500.1 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.59 – 7.35 (m, 5H), 7.26 (s, 5H), 7.01 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.4 Hz, 1H), 3.81 (s, 3H). **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 159.5 (d, $J_{PC}$ = 13.5 Hz), 134.2 (d, $J_{PC}$ = 10.0 Hz), 133.2 (d, $J_{PC}$ = 100.4 Hz), 132.1 (d, $J_{PC}$ = 2.8 Hz), 131.3 (d, $J_{PC}$ = 102.7 Hz), 131.0, 130.5 (d, $J_{PC}$ = 11.6 Hz), 128.4, 128.4 (d, $J_{PC}$ = 12.9 Hz), 128.1, 122.0, 118.6 (d, $J_{PC}$ = 2.4 Hz), 116.3 (d, $J_{PC}$ = 9.8 Hz), 116.3 (d, $J_{PC}$ = 8.6 Hz), 95.1, 85.7 (d, $J_{PC}$ = 8.4 Hz), 55.4. **$^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$)** δ 16.7. **$^{31}$P NMR (121 MHz, CDCl$_3$)** δ16.8 (dq, $J_1$=498.3 Hz, $J_2$ =14.0 Hz). **HRMS (DCI-CH$_4$):** m/z calcd for $C_{21}H_{18}O_2P$ $[M + H]^+$: 333.1044, Found: 333.1039.

**Phenyl(2-(phenylethynyl)-5-(trifluoromethyl)phenyl)phosphine oxide (1s)**



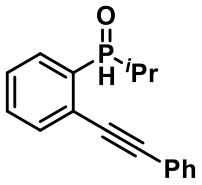

The general procedure **A** was used to obtain **1s**: total yield 12% (86 mg, scale: 2.0 mmol), yellow oil. **$^{1}$H NMR (300 MHz, CDCl$_3$)** δ 8.44 (d, $J$ = 502.8 Hz, 1H), 8.34 (d, $J$ = 12.6 Hz, 1H), 7.81 – 7.69 (m, 4H), 7.58 – 7.26 (m, 8H). **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 133.2 (d, $J_{PC}$ = 8.2 Hz), 132.7 (d, $J_{PC}$ = 2.9 Hz), 131.9 (q, $J_{FC}$ = 100.1 Hz), 131.5, 130.7 (d, $J_{PC}$ = 11.7 Hz), 130.3 (d, $J_{PC}$ = 11.6 Hz), 129.3 (m, $J_{FC}$ = 5.1 Hz), 128.9, 128.9, 128.8, 128.8, 128.5, 128.5, 123.3 (d, $J_{PC}$ = 271.8 Hz), 121.2, 99.5, 84.9 (d, $J_{PC}$ = 8.5 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$)** δ 15.9. **$^{31}$P NMR (121 MHz, CDCl$_3$)** δ16.0 (dq, $J_1$=500.1 Hz, $J_2$ =13.3 Hz). **$^{19}$F NMR (282 MHz, CDCl$_3$)** δ -62.8. **HRMS (DCI-CH$_4$):** m/z calcd for $C_{21}H_{15}F_3OP$ $[M + H]^+$: 371.0831, Found: 371.0812.

**(2-methyl-6-(phenylethynyl)phenyl)(phenyl)phosphine oxide (1t)**



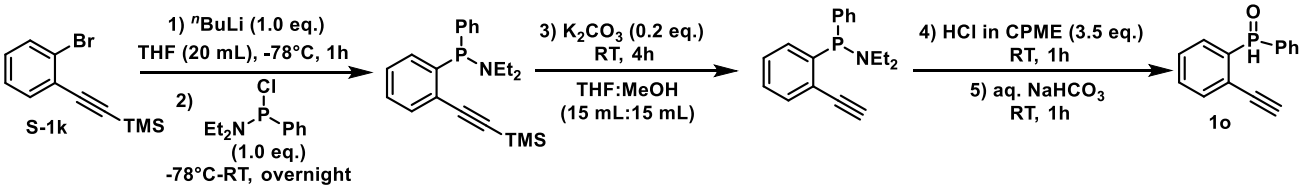

The general procedure **A** was used to obtain **1t**: total yield 51% (320 mg, scale: 2.0 mmol), yellow oil. **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 9.09 (d, $J$ = 506.1 Hz, 1H), 7.81 – 7.73 (m, 2H), 7.54 – 7.30 (m, 10H), 7.20 – 7.16 (m, 1H), 7.24 – 7.17 (m, 1H), 2.51 (s, 3H). **$^{1}$H NMR (300 MHz, CDCl$_3$)** δ 143.5 (d, $J_{PC}$ = 7.3 Hz), 132.0 (d, $J_{PC}$ = 3.0 Hz), 131.8 (d, $J_{PC}$ = 1.9 Hz), 131.7 (d, $J_{PC}$ = 5.6 Hz), 131.5 (d, $J_{PC}$ = 98.2 Hz), 131.3, 131.0 (d, $J_{PC}$ = 7.7 Hz), 130.3 (d, $J_{PC}$ = 11.3 Hz), 130.0 (d, $J_{PC}$ = 101.4 Hz), 128.8 (d, $J_{PC}$ = 10.1 Hz), 128.6, 128.4, 126.0 (d, $J_{PC}$ = 11.3 Hz), 122.1, 96.5, 86.7 (d, $J_{PC}$ = 11.2 Hz), 20.8 (d, $J_{PC}$ = 5.2 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$)** δ 15.0. **$^{31}$P NMR (121 MHz, CDCl$_3$)** δ16.0 (dt, $J_1$=504.3 Hz, $J_2$ =13.7 Hz). **HRMS (DCI-CH$_4$):** m/z calcd for $C_{21}H_{18}OP$ $[M + H]^+$: 317.1095, Found: 317.1087.

**Isopropyl(2-(phenylethynyl)phenyl)phosphine oxide (1v)**



The general procedure **A** was used with dichloroisopropylphoshine instead of dichlorophenylphosphine to obtain **1v**: total yield 80% (1.07 g, scale: 5.0 mmol), light yellow oil. **$^{1}$H NMR (300 MHz, CDCl$_3$)** δ 7.67 (d, *J* = 473.7 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.57 – 7.53 (m, 1H), 7.52 – 7.41 (m, 4H), 7.35 – 7.29 (m, 3H), 6.88 (s, 1H), 2.44 – 7.36 (m, 1H), 1.29 (dd, *J1* = 18.9 Hz, *J2* =7.2 Hz, 3H), 1.07 (dd, $J_1$ = 17.4 Hz, $J_2$ =7.2 Hz Hz, 3H). **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 132.5 (d, $J_{PC}$ = 8.0 Hz), 132.2 (d, $J_{PC}$ = 6.8 Hz), 131.7 (d, $J_{PC}$ = 2.4 Hz), 131.1 (d, $J_{PC}$ = 91.8 Hz), 131.1, 129.0, 128.4, 128.3 (d, $J_{PC}$ = 10.4 Hz), 123.8 (d, $J_{PC}$ = 9.2 Hz), 121.8, 96.3, 85.8 (d, $J_{PC}$ = 7.4 Hz), 27.5 (d, $J_{PC}$ = 69.5 Hz), 15.9 (d, $J_{PC}$ = 1.4 Hz), 13.8 (d, $J_{PC}$ = 3.0 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$)** δ 33.1. **$^{31}$P NMR (121 MHz, CDCl$_3$)** δ33.1 (dm, *J*=472.1 Hz). **HRMS (DCI-CH$_4$):** m/z calcd for $C_{17}H_{18}OP$ $[M + H]^+$: 269.1095, Found: 269.1088.

**(2-ethynylphenyl)(phenyl)phosphine oxide (1o)**



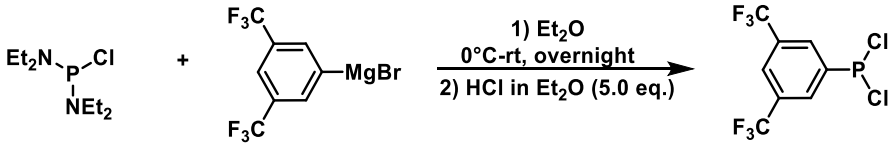

(2-Bromophenyl)ethynyl)trimethylsilane **S-1k** (8.3 mmol, 2.11 g) was dissolved in dry THF (15 mL) and cooled to -78°C. A solution of 1.6 M $^{n}$BuLi (8.3 mmol, 5.2 mL) was added dropwise over 5 minutes with stirring, resulting in a deep yellow/dark orange color. After stirring at the same temperature for 1 h, a solution of Ph(NEt$_2$)PCl (8.3 mmol, 1.8 g, 1.6 mL) in 5 mL of dry THF was added dropwise via syringe. The reaction mixture was allowed to warm to RT overnight. The mixture was filtered through celite, the solvent was evaporated under reduced pressure and the residue was dissolved in a mixture of THF:MeOH (15 mL:15 mL) and treated with $K_2CO_3$ (1.7 mmol, 235 mg) stirred for 4h, The progress of was monitored by $^{31}$P NMR (58.2 ppm to 57.1 ppm), Once the reaction was complete, the mixture was immediately filtered by cannula under Ar and the solvent was removed under vacuum. The resulting mixture was dissolved in THF (20 mL) treated with 4.0 M HCl in cyclopentyl methyl ether (CPME) (29 mmol, 7.3 mL) for 1 h, followed by quenching with aqueous $NaHCO_3$ (20 mL) and stirring for 1 h. The residue was extracted with EA (20 mL×3) and the combined organic fractions were dried over anhydrous $Na_2SO_4$, the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (Pentane/EA = 2/1 to 1/1) to afford the desired product **1o** as a light yellow oil, yield 45%, 848 mg.

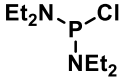
**$^{1}$H NMR (300 MHz, CDCl$_3$)** δ 8.29 (d, J = 499.5 Hz, 1H), 7.90 – 7.80 (m, 1H), 7.66 – 7.59 (m, 2H), 7.47 – 7.29 (m, 6H), 3.36 (s, 1H). **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 133.3 (d, $J_{PC}$ = 8.5 Hz), 132.6 (d, $J_{PC}$ = 100.3 Hz), 132.0 (d, $J_{PC}$ = 2.9 Hz), 131.8 (d, $J_{PC}$ = 2.4 Hz), 131.6 (d, $J_{PC}$ = 8.2 Hz), 130.9 (d, $J_{PC}$ = 102.5 Hz), 130.4 (d, $J_{PC}$ = 11.4 Hz), 128.8 (d, $J_{PC}$ = 11.3 Hz), 128.3 (d, $J_{PC}$ = 13.0 Hz), 123.3 (d, $J_{PC}$ = 9.6 Hz), 85.0, 79.8 (d, $J_{PC}$ = 8.3 Hz).**$^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$)** δ 16.4 (s). **$^{31}$P NMR (121**

**MHz, $CDCl_3$)** δ16.5 (dq, $J_1$=497.9 Hz, $J_2$ =13.8 Hz). **HRMS (DCI-$CH_4$):** m/z calcd for $C_{14}H_{12}OP$ [M + H]$^+$: 227.0626, Found: 227.0618.

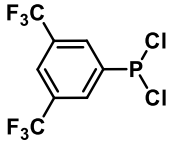
**(3,5-bis(trifluoromethyl)phenyl)(2-(phenylethynyl)phenyl)phosphine oxide (1u)**

**Step I:** Prepare (3,5-bis(trifluoromethyl)phenyl)dichlorophosphine according to reference.[8]



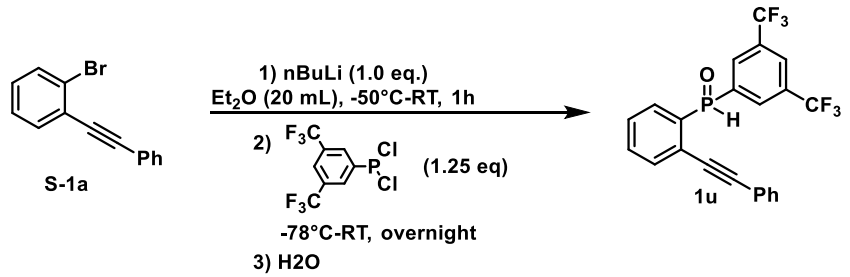




**Bis(diethylamino)chlorophosphine** was prepared by slow addition of a solution of trichlorophosphine (20 mmol, 1.74 mL) to a stirring solution of diethylamine (80 mmol, 8.24 mL) in 50 mL dry heptane at 0 °C. A large quantity of white precipitate was formed immediately. The reaction solution was stirred at 0 °C for 30 min, allowed to warm to RT and heat to 70 °C for 48 h. The reaction vessel was cooled and the solution filtered rapidly through a cannula under Ar and washed with dry heptane. Solvent removed in vacuo to give crude Bis(diethylamino)chlorophosphine as a pale yellow viscous liquid (yield 97%, 4.1 g), which was used without purification.**$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 159.8 ppm (consistent with literature).[8]




**(3,5-bis(trifluoromethyl)phenyl)dichlorophosphine** was prepared by using the Grignard reagent formed from reaction of magnesium turnings (30.8 mmol, 0.75 g, 1.4 equiv.) and 1-bromo-3,5-bis(trifluoromethyl)benzene (22 mmol, 3.8 mL, 1.0 equiv.) in 22 mL dry diethyl ether. The Grignard reagent (21.6 mmol, 0.98 M solution, 22 mL, 1.1 equiv.) was reacted with N,N,N',N'-Tetraethylphosphorodiamidous chloride (19.4 mmol, 4.1 g, 1.0 eq.) and the resultant solution treated using hydrogen chloride solution (97 mmol, 48.5 mL, 2.0 M in diethyl ether; 5.0 equiv.). Crude (3,5-bis(trifluoromethyl)phenyl)dichlorophosphane was obtained as a brown-orange liquid (yield 78%, 4.8 g), which was used without purification. **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 160.0 ppm, **$^{19}$F NMR (282 MHz, $CDCl_3$)** δ -63.0 (consistent with literature).[8]

**Step II:**

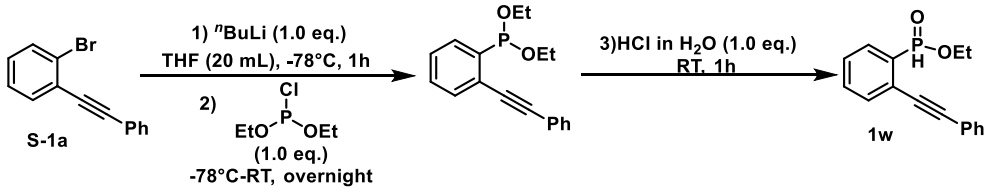



A 100 mL Schlenk tube equipped with a magnetic stirrer under Ar atmosphere was charged with 1-bromo-2-(phenylethynyl)benzene (13 mmol, 3.34 g) and $Et_2O$ (20 mL). A solution of 1.60 M $^n$BuLi (13.0 mmol, 8.10 mL) in hexane was added dropwise at a temperature of -50 °C, the resulting solution was slowly returned to RT and stirred for 1 h. Then the mixture solution was cooled to -78°C and (3,5-

bis(trifluoromethyl)phenyl)dichlorophosphane (15.0 mmol) was added slowly. The resulting reaction mixture was allowed to reach RT and stirred overnight. After adding $H_2O$ (40 mL), the residue was extracted with EA (15 mL×3) and the combined organic fractions were dried over anhydrous $Na_2SO_4$, the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (Pentane/EA = 2/1 to 1/1) to afford the desired product **1u** as a light yellow oil (yield 48%, 2.67 g).

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.51(d, *J* = 509.1 Hz, 1H), 8.21 (d, *J* = 12.9 Hz, 2H), 8.09 – 8.02 (m, 1H), 7.96 (s, 1H), 7.65 – 7.53 (m, 3H), 7.36 – 7.31 (m, 5H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 135.3 (d, *J*pc = 98.8 Hz), 133.1 (d, *J*pc = 2.5 Hz), 132.8 (dd, $J_{FC1}$ = 67.7 Hz, $J_{FC2}$ = 8.7 Hz), 132.1 (dd, $J_{FC1}$ = 33.8 Hz, $J_{FC2}$ = 12.7 Hz),132.1 (dd, $J_{FC1}$ = 101.4 Hz, $J_{FC2}$ = 12.8 Hz),131.3, 130.8, 130.6 (d, *J*pc = 3.2 Hz), 129.4, 128.9 (d, *J*pc = 11.8 Hz),128.5, 125.8 (q, $J_{FC}$ = 3.3 Hz), 124.9 (d, *J*pc = 10.0 Hz), 122.6 (d, *J*pc = 271.5 Hz), 121.2, 97.8, 85.5 (d, *J*pc = 8.7 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ13.8. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ14.0 (dt, $J_1$=507.4 Hz, $J_2$ =13.1 Hz). **$^{19}$F NMR (282 MHz, $CDCl_3$)** δ -63.1. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{22}H_{14}F_6OP$ $[M + H]^+$: 439.0686, Found: 439.0689.

**Ethyl (2-(phenylethynyl)phenyl)phosphinate (1w)**

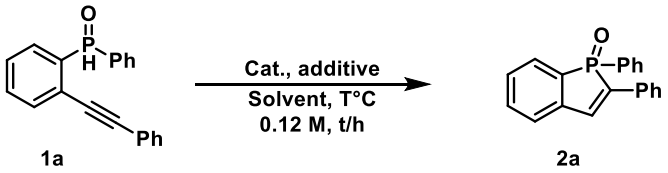



1-Bromo-2-(phenylethynyl)benzene **S-1a** (10 mmol, 2.6 g) was dissolved in dry THF (20 mL) and cooled to -78°C. A solution of 1.6 M $^n$BuLi (10 mmol, 6.3 mL) was added dropwise over 5 minutes with stirring, resulting in a deep yellow/dark orange color. After stirring at the same temperature for 1 h, then $(EtO)_2PCl$ (10 mmol, 1.57g, 1.5 mL) was added dropwise via syringe. The reaction mixture was allowed to slowly return to RT overnight. The resulting mixture was treated with 1.0 M HCl in $H_2O$ (10 mmol, 10 mL) stirring for 1 h. The residue was extracted with EA (20 mL×3) and the combined organic fractions were dried over anhydrous $Na_2SO_4$, the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (Pentane/EA = 2/1 to 1/1) to afford the desired product **1w** as a light yellow oil (yield 51%, 1.37 g).

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.01 – 7.94 (m, 1H), 7.83 (d, *J* = 579.6 Hz, 1H), 7.61 – 7.41 (m, 5H), 7.37 – 7.31 (m, 3H), 4.20 – 4.06 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 132.7 (d, $J_{PC}$ = 9.7 Hz), 132.5 (d, $J_{PC}$ = 2.5 Hz), 132.4 (d, $J_{PC}$ = 8.5 Hz), 131.3, 129.9 (d, $J_{PC}$ = 224.0 Hz), 129.6, 128.9, 128.0 (d, $J_{PC}$ = 12.2 Hz), 125.1 (d, $J_{PC}$ = 10.9 Hz), 122.2, 95.9, 85.5 (d, $J_{PC}$ = 9.0 Hz), 62.2 (d, $J_{PC}$ = 6.5 Hz), 16.2 (d, $J_{PC}$ = 6.8 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 22.1. **$^{31}$P NMR (121 MHz, $CDCl_3$)** δ 22.1 (dm, *J*=577.5 Hz). **HRMS (ESI):** m/z calcd for $C_{16}H_{16}O_2P$ $[M + H]^+$: 271.0888, Found: 271.0887.

## 2. Optimization of the reaction conditions

**Table S1** [a]




1a 2a

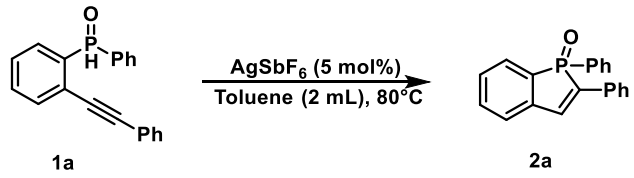
| entry | Cat. | additive | T°C | Solvent | t/h | Conv.% | Yield% |
|---|---|---|---|---|---|---|---|
| 1 | $Pd_2(dba)_3$ (0.5 mol%) | -- | 120 | Toluene | 11 | >96 | 36 |
| 2 | $Pd_2(dba)_3$ (0.5 mol%) | dppe (1.0 mol%) | 120 | Toluene | 24 | >96 | 44 |
| 3 | $AuPPh_3Cl$ (5 mol%) | -- | 120 | Toluene | 20 | >96 | 40 |
| 4 | $AuPPh_3Cl$ (5 mol%) | $AgSbF_6$ (5 mol%) | 120 | Toluene | 18 | >96 | 77 |
| 5 | Under air | -- | 80 | Toluene | 20 | 15 | 10(4)[c] |
| 6 | $AgSbF_6$ (5 mol%) Under air | -- | 80 | Toluene | 9 | 87 | 67(15)[c] |
| **7** | $AgSbF_6$ (5 mol%) | -- | 120 | Toluene | 2 | >96 | 93 |
| 8 | **$AgSbF_6$ (5 mol%)** | -- | **80** | **Toluene** | **9** | **>96** | **96(91)[b]** |
| 9 | $AgSbF_6$ (20 mol%) | -- | 80 | Toluene | 4 | >96 | 96 |
| 10 | $AgSbF_6$ (100 mol%) | -- | 80 | Toluene | 1 | >96 | 27(49)[c] |
| 11 | -- | -- | 80 | Toluene | 9 | 9 | 7 |
| 12 | $AgNTf_2$ (5 mol%) | -- | 80 | Toluene | 9 | 51 | 49 |
| 13 | AgOTf (5 mol%) | -- | 80 | Toluene | 9 | 61 | 60 |
| 14 | $AgBF_4$ (5 mol%) | -- | 80 | Toluene | 9 | 44 | 44 |
| 15 | $AgNO_3$ (5 mol%) | -- | 80 | Toluene | 9 | >96 | 20 |
| 16 | $Mn(OAc)_3$ (100 mol%) | | 80 | Toluene | 4 | >96 | 20 |
| 17 | TBHP (20 mol%) | -- | 80 | Toluene | 9 | 24 | 3(20)[c] |
| 18 | AIBN (20 mol%) | -- | 80 | Toluene | 9 | 8 | 5 |
| 19 | TBPB (20 mol%) | -- | 80 | Toluene | 9 | 33 | 9(8)[c] |
| 20 | $K_2S_2O_8$ (20 mol%) | -- | 80 | Toluene | 9 | 13 | 6(5)[c] |
| 21 | $K_2S_2O_8$ (20 mol%) | -- | 80 | $CH_3CN$ | 9 | 45 | 10(27)[c] |
| 22 | $AgSbF_6$ (5 mol%) | -- | 80 | Benzene | 9 | >96 | 96 |
| 23 | $AgSbF_6$ (5 mol%) | -- | 80 | $^t$BuPh | 9 | 85 | 83 |
| 24 | $AgSbF_6$ (5 mol%) | -- | 80 | DCM | 22 | >96 | 84 |
| 25 | $AgSbF_6$ (5 mol%) | -- | 80 | $CH_3CN$ | 33 | >96 | 86 |
| 26 | $AgSbF_6$ (5 mol%) | -- | 80 | DCE | 47 | >96 | 82 |
| 27 | $AgSbF_6$ (5 mol%) | -- | 80 | DMF | 9 | >61 | 48 |
| 28 | Under air | -- | 90 | DMF | 9 | >93 | 30(40)[c] |
| 29 | $AgSbF_6$ (5 mol%) | $Ph_2P(O)OH$ (5 mol%) | 80 | Toluene | 13 | >96 | 92 |
| 30 | $AgSbF_6$ (5 mol%) | $C_6H_3(OH)_3$ (5 mol%) | 80 | Toluene | 14 | >96 | 96 |
| 31 | $AgSbF_6$ (5 mol%) | HFIP (0.5 mL) | 80 | Toluene | 45 | >96 | 11 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 32 | $AgSbF_6$ (5 mol%) | $Et_3N$ (10 mol%) | 80 | Toluene | 16 | 23 | 10 |
| 33 | $AgSbF_6$ (5 mol%) | 2,6-Dibutylpyridine (10 mol%) | 80 | Toluene | 16 | > 96 | 96 |
| 34 | $AgSbF_6$ (5 mol%) | $K_2CO_3$ (10 mol%) | 80 | Toluene | 16 | 31 | 2 |
| 35 | $AgSbF_6$ (5 mol%) | $PPh_3$ (10 mol%) | 80 | Toluene | 16 | 11 | 10 |

[a] Reaction conditions: **1a** (0.25 mmol), **solvent** (2 mL). Yield estimated by $^{31}P$ NMR, [b]isolated Yield, [c]Phosphaisocoumarin **3a** by-product.

## 3. General procedures for catalysis and characterization data

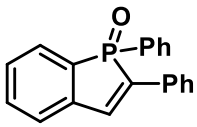
### General catalytic procedure C:




1a 2a

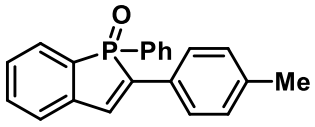
An oven-dried Schlenk tube under Ar atmosphere was charged with secondary phosphine oxide **1a** (0.25 mmol, 1.0 eq., 75.6 mg), $AgSbF_6$ (5 mol%, 4.3 mg) and toluene (2 mL). The mixture was stirred at 80°C and the progress of the reaction was monitored by $^{31}P$ NMR. Upon completion, the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (Pentane/EA = 2/1 to 1/1) to afford the desired light yellow solid benzophosphole oxide **2a,** yield 91%, 68.9 mg.

### 1,2-diphenylphosphindole 1-oxide (2a)[2]



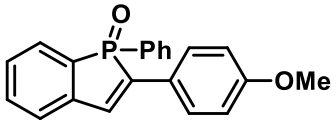

The general procedure **C** was used to obtain **2a**: yield 91% (68.9 mg), 9h, white solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.82 – 7.26 (m, 15H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 141.6 (d, $J_{PC}$ = 28.1 Hz), 138.8 (d, $J_{PC}$ = 94.1 Hz), 136.5 (d, $J_{PC}$ = 20.0 Hz), 133.1 (d, $J_{PC}$ = 2.0 Hz), 133.0 (d, $J_{PC}$ = 65.6 Hz), 132.2 (d, $J_{PC}$ = 32.0 Hz), 132.2 (d, $J_{PC}$ = 2.9 Hz), 130.7 (d, $J_{PC}$ = 10.7 Hz), 129.9 (d, $J_{PC}$ = 97.7 Hz), 129.1 (d, $J_{PC}$ = 1.4 Hz), 128.9, 128.9, 128.8, 128.8, 126.6 (d, $J_{PC}$ = 6.3 Hz), 124.6 (d, $J_{PC}$ = 9.6 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 39.2.

### 1-phenyl-2-(p-tolyl)phosphindole 1-oxide (2b)



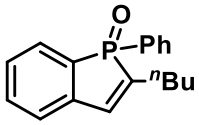

The general procedure **C** was used to obtain **2b**: yield 95% (75.0 mg), 8h, light yellow solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.81 – 7.74 (m, 2H), 7.66 – 7.60 (m, 3H), 7.50 – 7.28 (m, 7H), 7.14 (d, $J$ = 8.1 Hz, 2H), 2.32 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 141.8 (d, $J_{PC}$ = 28.3 Hz), 138.9, 138.6 (d, $J_{PC}$ = 94.1 Hz), 135.4 (d, $J_{PC}$ = 20.0 Hz), 133.1 (d, $J_{PC}$ = 2.1 Hz), 132.6 (d, $J_{PC}$ = 108.2 Hz), 132.1 (d, $J_{PC}$ = 3.0 Hz), 130.7 (d, $J_{PC}$ = 10.7 Hz), 130.2 (d, $J_{PC}$ = 73.9 Hz), 129.6, 129.4 (d, $J_{PC}$ = 13.0 Hz), 128.8 (d, $J_{PC}$ = 1.9 Hz), 128.8 (d, $J_{PC}$ = 22.7 Hz), 128.8 (d, $J_{PC}$ = 12.2 Hz), 126.4 (d, $J_{PC}$ = 6.4 Hz), 124.4 (d, $J_{PC}$ = 9.4 Hz), 21.3. **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 39.3. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{21}H_{18}OP$ $[M + H]^+$: 317.1095, Found: 317.1089.

**2-(4-methoxyphenyl)-1-phenylphosphindole 1-oxide (2c)**[2]



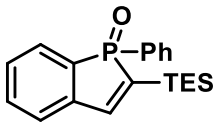
The general procedure **C** was used to obtain **2c**: yield 93% (76.9 mg), 4h, light yellow solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.78 – 7.23 (m, 12H), 6.83 (d, $J$ = 8.4 Hz, 2H), 3.75 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 160.1, 141.9 (d, $J_{PC}$ = 28.3 Hz), 138.2 (d, $J_{PC}$ = 94.0 Hz), 134.1 (d, $J_{PC}$ = 20.2 Hz), 133.1 (d, $J_{PC}$ = 2.1 Hz), 132.3 (d, $J_{PC}$ = 108.2 Hz), 132.1 (d, $J_{PC}$ = 2.9 Hz), 130.6 (d, $J_{PC}$ = 10.7 Hz), 130.1 (d, $J_{PC}$ = 97.4 Hz), 128.9 (d, $J_{PC}$ = 10.3 Hz), 128.8 (d, $J_{PC}$ = 12.3 Hz), 128.5 (d, $J_{PC}$ = 10.7 Hz), 128.0 (d, $J_{PC}$ = 6.6 Hz), 125.1 (d, $J_{PC}$ = 10.8 Hz), 124.2 (d, $J_{PC}$ = 9.6 Hz), 114.3, 55.2. **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ39.4.

**2-butyl-1-phenylphosphindole 1-oxide (2d)**



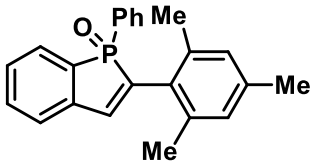
The general procedure **C** was used to obtain **2d**: yield 81% (45.8 mg), 4h, light yellow oil. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.72 – 7.64 (m, 2H), 7.59 – 7.38 (m, 5H), 7.30 – 7.23 (m, 2H), 7.05 – 6.91 (m, 1H), 2.51 – 2.23 (m, 2H), 1.56 – 1.46 (m, 2H), 1.37 – 1.24 (m, 2H), 0.83 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 142.5 (q, $J_{PC}$ = 29.8 Hz), 137.6 (d, $J_{PC}$ = 21.0 Hz), 133.0 (d, $J_{PC}$ = 2.1 Hz), 132.1 (d, $J_{PC}$ = 2.7 Hz), 131.9, 130.7 (q, $J_{PC}$ = 101.0 Hz), 130.8 (d, $J_{PC}$ = 10.7 Hz), 128.9 (d, $J_{PC}$ = 9.9 Hz), 128.7 (d, $J_{PC}$ = 10.1 Hz), 128.4 (d, $J_{PC}$ = 12.1 Hz), 128.2 (d, $J_{PC}$ = 10.2 Hz), 123.6 (d, $J_{PC}$ = 9.9 Hz), 29.7 (d, $J_{PC}$ = 5.1 Hz), 27.2 (d, $J_{PC}$ = 10.1 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 40.5. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{18}H_{20}OP$ $[M + H]^+$: 283.1252, Found: 283.1255.

**1-phenyl-2-(triethylsilyl)phosphindole 1-oxide (2e)**



The general procedure **C** was used to obtain **2e**: yield 53% (45.3 mg), 3h, white solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.67 – 7.26 (m, 10H), 0.84 (t, $J$ = 7.8 Hz, 9H), 0.74 – 0.47 (m, 6H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 152.6 (d, $J_{PC}$ = 7.6 Hz), 143.2 (d, $J_{PC}$ = 37.2 Hz), 139.2 (d, $J_{PC}$ = 57.5 Hz), 135.2 (d, $J_{PC}$ = 101.5 Hz), 132.7 (d, $J_{PC}$ = 2.1 Hz), 131.8 (d, $J_{PC}$ =2.9 Hz), 130.8 (d, $J_{PC}$ = 10.4 Hz), 130.3 (d, $J_{PC}$ = 95.6 Hz), 129.4 (d, $J_{PC}$ = 9.7 Hz), 128.8 (d, $J_{PC}$ = 9.9 Hz), 128.5 (d, $J_{PC}$ = 12.0 Hz), 124.1 (d, $J_{PC}$ = 11.6 Hz), 7.0, 3.2 (d, $J_{PC}$ = 1.7 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ48.7. **HRMS (ESI):** m/z calcd for $C_{20}H_{26}OPSi$ $[M + H]^+$: 341.1491, Found: 341.1498.

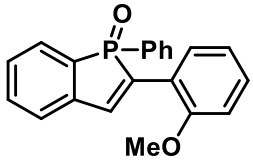
**2-mesityl-1-phenylphosphindole 1-oxide (2f)**



The general procedure **C** was used to obtain **2f**: yield 96% (82.6 mg), 12 h, white solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.75 (t, $J$ = 8.4 Hz, 1H), 7.61 – 7.29 (m, 8H), 6.96 (d, $J$ = 39.6 Hz, 1H), 6.80 (s, 2H), 2.24 (s, 3H), 1.94 (bs, 6H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 142.6 (d, $J_{PC}$ = 89.9 Hz), 142.4 (d, $J_{PC}$ = 28.7 Hz), 140.3 (d, $J_{PC}$ = 22.3 Hz), 137.1 (d, $J_{PC}$ = 2.0 Hz), 133.2 (d, $J_{PC}$ = 2.1 Hz), 132.2 (d, $J_{PC}$ = 2.9 Hz), 131.0 (d, $J_{PC}$ = 40.7 Hz), 131.0 (d, $J_{PC}$ = 10.5 Hz), 129.9, 129.6, 129.4, 129.2 (d, $J_{PC}$ = 7.5 Hz), 128.8 (d, $J_{PC}$ = 10.1 Hz), 128.5 (d, $J_{PC}$ = 12.1 Hz), 128.1, 124.3 (d, $J_{PC}$

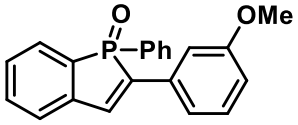
= 9.5 Hz), 20.8, 20.2. **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 40.5. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{23}H_{22}OP$ $[M + H]^+$: 345.1408, Found: 345.1408.

**2-(2-methoxyphenyl)-1-phenylphosphindole 1-oxide (2g)**



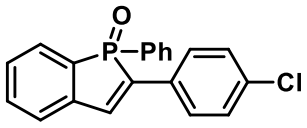

The general procedure **C** was used to obtain **2g**: yield 92% (76.3 mg), 16 h, light yellow solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 8.90 – 7.96 (m, 1H), 7.87 – 7.74 (m, 3H), 7.59 – 7.53 (m, 1H), 7.46 – 7.32 (m, 5H), 7.29 – 7.17 (m, 2H), 6.91 – 6.84 (m, 2H), 3.73 (s, 3H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 157.7 (d, $J_{PC}$ = 7.7 Hz), 141.9 (d, $J_{PC}$ = 29.0 Hz), 140.1 (d, $J_{PC}$ = 18.5 Hz), 134.9 (d, $J_{PC}$ = 92.7 Hz), 132.7 (d, $J_{PC}$ = 2.0 Hz), 132.3 (d, $J_{PC}$ = 108.3 Hz), 131.6 (d, $J_{PC}$ = 2.6 Hz), 130.3, 130.2 (d, $J_{PC}$ = 10.7 Hz), 129.5, 129.5 (d, $J_{PC}$ = 5.9 Hz), 128.6 (d, $J_{PC}$ = 10.4 Hz), 128.5 (d, $J_{PC}$ = 12.3 Hz), 128.4 (d, $J_{PC}$ = 10.4 Hz), 124.4 (d, $J_{PC}$ = 9.4 Hz), 121.4 (d, $J_{PC}$ = 10.7 Hz), 120.7, 111.1, 54.9. **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 41.5. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{21}H_{18}O_2P$ $[M + H]^+$: 333.1044, Found: 333.1041.

**2-(3-methoxyphenyl)-1-phenylphosphindole 1-oxide (2h)**



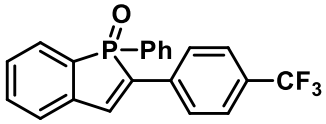

The general procedure **C** was used to obtain **2h**: yield 99% (83.0 mg), 10 h, light yellow solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 7.80 – 7.72 (m, 2H), 7.63 – 7.18 (m, 11H), 6.83 – 6.79 (m, 1H), 3.73 (s, 3H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 159.6, 141.4 (d, $J_{PC}$ = 27.9 Hz), 138.5 (d, $J_{PC}$ = 94.2 Hz), 136.7 (d, $J_{PC}$ = 20.0 Hz), 133.6 (d, $J_{PC}$ = 10.7 Hz), 133.1 (d, $J_{PC}$ = 2.1 Hz), 132.5 (d, $J_{PC}$ = 108.2 Hz), 132.1 (d, $J_{PC}$ = 2.9 Hz), 130.6 (d, $J_{PC}$ = 10.7 Hz), 129.8, 129.2, 128.9 (d, $J_{PC}$ = 18.7 Hz), 128.9 (d, $J_{PC}$ = 2.3 Hz), 128.7 (d, $J_{PC}$ = 12.3 Hz), 124.5 (d, $J_{PC}$ = 9.5 Hz), 119.1 (d, $J_{PC}$ = 6.2 Hz), 114.7, 111.5 (d, $J_{PC}$ = 6.6 Hz), 55.0. **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 38.9. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{21}H_{18}O_2P$ $[M + H]^+$: 333.1044, Found: 333.1037.

**2-(4-chlorophenyl)-1-phenylphosphindole 1-oxide (2i)**



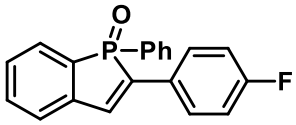

The general procedure **C** was used to obtain **2i** yield 90% (75.7 mg), 15h, light yellow solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 7.79 – 7.70 (m, 2H), 7.67 – 7.27 (m, 12H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 141.4 (d, $J_{PC}$ = 27.8 Hz), 138.2, 137.0, 135.6 (d, $J_{PC}$ = 152.6 Hz), 133.2 (d, $J_{PC}$ = 2.2 Hz), 133.2, 132.3 (d, $J_{PC}$ = 2.9Hz), 131.4 (d, $J_{PC}$ = 51.7 Hz), 130.6 (d, $J_{PC}$ = 7.5 Hz), 130.5 (d, $J_{PC}$ = 52.7 Hz), 129.3, 129.0 (d, $J_{PC}$ = 13.3 Hz), 129.1, 128.9 (d, $J_{PC}$ = 12.5 Hz), 127.7 (d, $J_{PC}$ = 6.4 Hz), 124.7 (d, $J_{PC}$ = 9.6 Hz). **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 39.0. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{20}H_{15}OPCl$ $[M + H]^+$: 337.0549, Found: 337.0545.

**1-phenyl-2-(4-(trifluoromethyl)phenyl)phosphindole 1-oxide (2j)**[2]



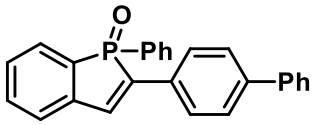
The general procedure **C** was used to obtain **2j**: yield 79% (73.4 mg), 23h, white solid. **$^{1}$H NMR (300 MHz, $CDCl_3$)** δ 7.82 – 7.35 (m, 14H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 141.1 (d, $J_{PC}$ = 27.4 Hz), 138.6 (d, $J_{PC}$ = 19.8 Hz), 137.6 (d, $J_{PC}$ = 94.7 Hz), 136.0 (d, $J_{PC}$ = 10.9 Hz), 133.4 (d, $J_{PC}$ = 2.2 Hz), 132.5 (d, $J_{PC}$ = 2.9 Hz), 132.7 (d, $J_{PC}$ = 108.6 Hz), 130.2, 129.9 (d, *J1* = 123.2 Hz, *J2* = 10.8 Hz), 129.9, 129.7 (d, $J_{PC}$ = 10.6 Hz), 129.3, 128.6, 126.7 (d, $J_{PC}$ = 6.1 Hz), 125.9 (q, $J_{PC}$ = 3.8 Hz), 125.1 (d, $J_{PC}$ = 9.5 Hz), 123.9 (d, $J_{PC}$ = 270.2 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, $CDCl_3$)** δ 38.9. **$^{19}$F NMR (282 MHz, $CDCl_3$)** δ 62.8.

**2-(4-fluorophenyl)-1-phenylphosphindole 1-oxide (2k)**



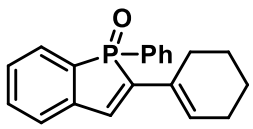
The general procedure **C** was used to obtain **2k**: yield 89% (71.3 mg), 15h, white solid. **$^{1}$H NMR (300 MHz, $CDCl_3$)** δ 7.77 – 7.26 (m, 12H), 6.99 (t, *J* = 8.7 Hz, 2H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 162.9 (d, $J_{PC}$ = 248.1 Hz), 141.5 (d, $J_{PC}$ = 27.9 Hz), 137.7 (d, $J_{PC}$ = 94.0 Hz), 136.3 (d, $J_{PC}$ = 2.3 Hz), 136.0 (d, $J_{PC}$ = 2.3 Hz), 133.2 (d, $J_{PC}$ = 2.1 Hz), 131.0 (q, $J_{FC}$ = 108.5 Hz), 132.3 (d, $J_{PC}$ = 2.9 Hz), 130.7 (d, $J_{PC}$ = 10.7 Hz), 129.0 (d, $J_{PC}$ = 10.1 Hz), 128.9 (d, $J_{PC}$ = 12.2 Hz), 128.7 (d, $J_{PC}$ = 3.4 Hz), 128.4 (d, $J_{PC}$ = 6.2 Hz), 128.3 (d, $J_{PC}$ = 6.2 Hz), 124.6 (d, $J_{PC}$ = 9.7 Hz), 116.0 (d, $J_{PC}$ = 21.8 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, $CDCl_3$)** δ 39.1.**$^{19}$F NMR (282 MHz, $CDCl_3$)** δ-111.5. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{20}H_{15}OFP$ $[M + H]^+$: 321.0845, Found: 321.0839.

**2-([1,1'-biphenyl]-4-yl)-1-phenylphosphindole 1-oxide (2l)**



The general procedure **C** was used to obtain **2l**: yield 97% (91.5 mg), 18h, light yellow solid. **$^{1}$H NMR (300 MHz, $CDCl_3$)** δ 7.83 – 7.76 (m, 4H), 7.69 – 7.29 (m, 15H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 141.6 (d, $J_{PC}$ = 30.0 Hz), 140.8 (d, $J_{PC}$ = 94.7 Hz), 138.2 (d, $J_{PC}$ = 94.1 Hz), 136.3, 136.1, 133.2 (d, $J_{PC}$ = 2.0 Hz), 132.6 (d, $J_{PC}$ = 108.3 Hz), 132.2 (d, $J_{PC}$ = 3.0 Hz), 131.4 (d, $J_{PC}$ = 12.2 Hz), 130.7 (d, $J_{PC}$ = 10.7 Hz), 129.9 (d, $J_{PC}$ = 97.5 Hz), 129.0, 128.9, 128.9 (d, $J_{PC}$ = 12.2 Hz), 128.7, 127.5, 127.5, 126.9 (d, $J_{PC}$ = 6.5 Hz), 126.8, 124.6 (d, $J_{PC}$ = 9.5 Hz). **$^{31}$P{$^{1}$H} NMR (121 MHz, $CDCl_3$)** δ 39.2. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{26}H_{20}OP$ $[M + H]^+$: 379.1252, Found: 379.1245.

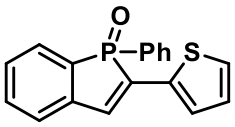
**2-(cyclohex-1-en-1-yl)-1-phenylphosphindole 1-oxide (2m)**



The general procedure **C** was used to obtain **2m**: yield 94% (71.6 mg), 4 h, white solid. **$^{1}$H NMR (300 MHz, $CDCl_3$)** δ 7.70 – 7.62 (m, 2H), 7.49 – 7.32 (m, 5H), 7.26 – 7.14 (m, 2H), 6.98 (d, *J* = 36.6 Hz, 1H), 6.29 (s, 1H), 2.31 – 1.93 (m, 4H), 1.72 – 1.43 (m, 4H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 141.9 (d, $J_{PC}$ = 28.5 Hz), 140.5 (d, $J_{PC}$ = 92.6 Hz), 133.0 (d, $J_{PC}$ = 5.5 Hz), 132.8 (d, $J_{PC}$ = 2.0 Hz), 132.8 (d, $J_{PC}$ = 20.7 Hz), 132.4 (d, $J_{PC}$ = 124.8 Hz), 131.8 (d, $J_{PC}$ = 2.9 Hz), 130.6 (d, $J_{PC}$ = 8.8 Hz), 130.3, 130.3 (d, $J_{PC}$ = 10.8 Hz), 128.6 (d, $J_{PC}$ = 12.2 Hz), 128.5 (d, $J_{PC}$ = 10.2 Hz), 128.2 (d, $J_{PC}$ = 10.5 Hz), 124.0 (d,

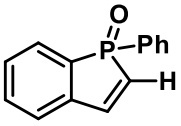
$J_{PC}$ = 9.5 Hz), 25.9, 25.6 (d, $J_{PC}$ = 7.2 Hz), 22.0, 21.6. **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 39.1. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{20}H_{20}OP$ $[M + H]^+$: 307.1252, Found: 307.12459.

**phenyl-2-(thiophen-2-yl)phosphindole 1-oxide (2n)**



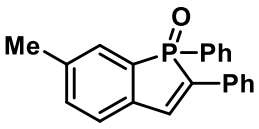
The general procedure **C** was used to obtain **2n** yield 73% (56.3 mg), 60 h, light yellow solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 7.80 – 7.72 (m, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.21 (m, 9H), 6.94 – 6.91 (m, 1H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 141.9 (d, $J_{PC}$ = 27.5 Hz), 135.9 (d, $J_{PC}$ = 14.6 Hz), 134.1 (d, $J_{PC}$ = 19.1 Hz), 133.5 (d, $J_{PC}$ = 94.0 Hz), 133.3 (d, $J_{PC}$ = 2.2 Hz), 132.3 (d, $J_{PC}$ = 3.0 Hz), 131.8 (d, $J_{PC}$ = 108.6 Hz), 130.8 (d, $J_{PC}$ = 11.0 Hz), 130.2, 129.1 (d, $J_{PC}$ = 10.5 Hz), 128.9, 128.9 (d, $J_{PC}$ = 12.4 Hz), 128.7 (d, $J_{PC}$ = 10.7 Hz), 127.6 (d, $J_{PC}$ = 3.8 Hz), 127.2 (d, $J_{PC}$ = 140.9 Hz), 124.4 (d, $J_{PC}$ = 9.6 Hz). **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 38.3. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{18}H_{14}OPS$ $[M + H]^+$: 309.0503, Found: 309.0512.

**1-phenylphosphindole 1-oxide (2o)**[3]



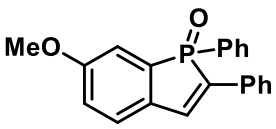
The general procedure **C** was used to obtain **2o**: yield 40% (21.8 mg), 4h, light yellow oil. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 7.75 – 7.68 (m, 2H), 7.61 (t, $J$ = 6.9Hz, 1H), 7.52 – 7.33 (m, 7H), 6.45 (dd, $J_1$ = 25.8 Hz, $J_2$ = 8.4 Hz, 1H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 145.3 (d, $J_{PC}$ = 13.0 Hz), 141.9 (d, $J_{PC}$ = 31.1 Hz), 132.9 (d, $J_{PC}$ = 1.95 Hz), 132.2 (d, $J_{PC}$ = 2.9 Hz), 132.1 (d, $J_{PC}$ = 107.3 Hz), 130.7 (d, $J_{PC}$ = 10.8 Hz), 129.6, 129.2 (d, $J_{PC}$ = 40.7 Hz), 128.8, 128.6, 126.4 (d, $J_{PC}$ = 95.7 Hz), 124.8 (d, $J_{PC}$ = 9.9 Hz). **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 41.2.

**6-methyl-1,2-diphenylphosphindole 1-oxide (2q)**



The general procedure **C** was used to obtain **2q**: yield 93% (73.2 mg), 12h, light yellow solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 7.82 – 7.75 (m, 2H), 7.70 (d, $J$ = 7.8 Hz, 1H), 7.59 (d, $J$ = 36.3 Hz, 1H), 7.50 – 7.23 (m, 9H), 2.33 (s, 3H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 139.3 (d, $J_{PC}$ = 10.6 Hz), 138.9 (d, $J_{PC}$ = 27.9 Hz), 137.6 (d, $J_{PC}$ = 94.4 Hz), 136.5 (d, $J_{PC}$ = 20.1 Hz), 133.5 (d, $J_{PC}$ = 2.1 Hz), 132.6 (d, $J_{PC}$ = 10.5 Hz), 132.0 (d, $J_{PC}$ = 2.9 Hz), 131.5 (d, $J_{PC}$ = 99.2 Hz), 130.6 (d, $J_{PC}$ = 10.7 Hz), 129.7 (d, $J_{PC}$ = 10.3 Hz), 129.5, 128.8 (d, $J_{PC}$ = 12.2 Hz), 128.8, 128.5, 126.4 (d, $J_{PC}$ = 6.3 Hz), 124.4 (d, $J_{PC}$ = 10.1 Hz), 21.3 (d, $J_{PC}$ = 1.1 Hz). **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 39.2. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{21}H_{18}OP$ $[M + H]^+$: 317.1095, Found: 317.1098.

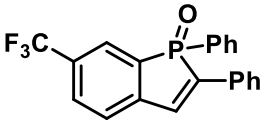
**6-methoxy-1,2-diphenylphosphindole 1-oxide (2r)**



The general procedure **C** was used to obtain **2r**: yield 97% (80.9 mg), 15h, light yellow solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 7.82 – 7.74 (m, 2H), 7.68 – 7.17 (m, 11H), 6.98 (dd, $J_1$ = 8.1 Hz, $J_2$ = 1.8 Hz, 1H), 3.78 (s, 3H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 160.6 (d, $J_{PC}$ = 13.4 Hz), 136.6 (d, $J_{PC}$ = 20.0 Hz), 136.2 (d, $J_{PC}$ = 95.8 Hz), 134.6

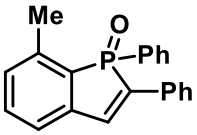
(d, $J_{PC}$ = 107.3 Hz), 133.9 (d, $J_{PC}$ = 27.9 Hz), 132.6 (d, $J_{PC}$ = 10.7 Hz), 132.1 (d, $J_{PC}$ = 2.9 Hz), 130.6 (d, $J_{PC}$ = 10.7 Hz), 129.9 (d, $J_{PC}$ = 97.5 Hz), 128.8 (d, $J_{PC}$ = 12.3 Hz), 128.77, 128.3, 126.1 (d, $J_{PC}$ = 6.5 Hz), 125.7 (d, $J_{PC}$ = 11.3 Hz), 118.1 (d, $J_{PC}$ = 2.0 Hz), 114.8 (d, $J_{PC}$ = 11.7 Hz), 55.5. **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 39.4. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{21}H_{18}O_2P$ $[M + H]^+$: 333.1044, Found: 333.1054.

**1,2-diphenyl-6-(trifluoromethyl)phosphindole 1-oxide (2s)**



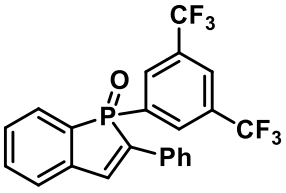
The general procedure **C** was used to obtain **2s**: yield 89% (66.3 mg), 13h, light yellow solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 9.6 Hz, 1H), 7.80 – 7.69 (m, 5H), 7.57 – 7.29 (m, 8H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 144.8 (d, $J_{PC}$ = 27.2 Hz), 141.6 (d, $J_{PC}$ = 93.4 Hz), 134.9 (d, $J_{PC}$ = 18.8 Hz), 133.8 (d, $J_{PC}$ = 107.6 Hz), 132.7 (d, $J_{PC}$ = 2.9 Hz), 131.9 (d, $J_{PC}$ = 10.4 Hz), 130.7 (d, $J_{PC}$ = 10.8 Hz), 130.4 (q, $J_{PC}$ = 1.7 Hz), 130.1 (q, $J_{PC}$ = 11.0 Hz), 129.6, 129.3, 129.1, 127.9, 126.8 (d, $J_{PC}$ = 6.4 Hz), 126.6 (q, $J_{PC}$ = 179.6 Hz) 125.8 (q, $J_{PC}$ = 3.8 Hz), 124.6 (d, $J_{PC}$ = 9.4 Hz). **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ38.3. **$^{19}F$ NMR (282 MHz, $CDCl_3$)** δ-62.6. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{21}H_{15}F_3OP$ $[M + H]^+$: 371.0831, Found: 371.0806.

**7-methyl-1,2-diphenylphosphindole 1-oxide (2t)**



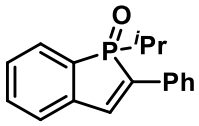
The general procedure **C** was used to obtain **2t**: yield 93% (73.1 mg), 3h, white solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 7.73 – 7.66 (m, 2H), 7.61 – 7.10 (m, 11H), 6.97 (dd, $J_1$ = 7.5 Hz, $J_2$ = 5.1 Hz, 1H), 2.26 (s, 3H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 141.7 (d, *J* = 28.4 Hz), 141.1 (d, *J* = 9.5 Hz), 138.4 (d, *J* = 94.3 Hz), 136.5 (d, *J* = 20.3 Hz), 133.2 (d, *J* = 1.8 Hz), 132.5 (d, *J* = 10.7 Hz), 132.0 (d, *J* = 2.8 Hz), 130.8, 130.7 (d, *J* = 107.5 Hz), 130.7, 130.6, 128.8 (d, *J* = 12.2 Hz),128.8, 128.6, 126.5 (d, *J* = 6.2 Hz), 122.1 (d, *J* = 9.6 Hz), 19.1 (d, *J* = 4.4 Hz). **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 39.3. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{21}H_{18}OP$ $[M + H]^+$: 317.1095, Found: 317.1097.

**1-(3,5-bis(trifluoromethyl)phenyl)-2-phenylphosphindole 1-oxide (2u)**



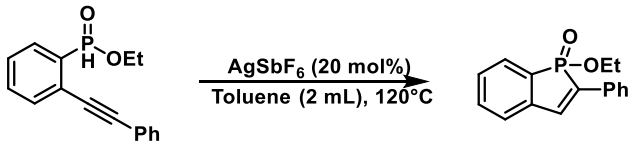
The general procedure **C** was used to obtain **2u**: yield 97% (106.0 mg), 9h, white solid. **$^{1}H$ NMR (300 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 11.7 Hz, 2H), 7.87 (s, 1H), 7.87 – 7.18 (m, 10H). **$^{13}C$ NMR (75 MHz, $CDCl_3$)** δ 141.4 (d, $J_{PC}$ = 29.6 Hz), 137.6 (d, $J_{PC}$ = 21.1 Hz), 135.9 (dd, $J_{Fc1}$ = 233.9 Hz, $J_{Fc2}$ = 95.9 Hz), 134.2 (d, $J_{PC}$ = 2.0 Hz), 133.0 (dd, $J_{Fc1}$ = 101.2 Hz, $J_{Fc2}$ = 12.1 Hz), 132.4 (dd, $J_{Fc1}$ = 33.6 Hz, $J_{Fc2}$ = 12.1 Hz), 131.6 (t, $J_{PC}$ = 9.9 Hz), 130.9 (m), 130.0,129.5 (t, $J_{PC}$ = 10.9 Hz), 129.4, 129.2, 129.1, 126.4 (d, $J_{PC}$ = 6.5 Hz), 126.0 (m), 125.2 (d, $J_{PC}$ = 9.9 Hz), 122.7 (d, $J_{PC}$ = 271.6 Hz). **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ35.9. **$^{19}F$ NMR (282 MHz, $CDCl_3$)** δ-62.9. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{22}H_{14}F_6OP$ $[M + H]^+$: 439.0681, Found: 439.0703.

**1-isopropyl-2-phenylphosphindole 1-oxide (2v)**



The general procedure **C** was used to obtain **2v**: yield 99% (67.0 mg), 33h, white solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.30 (m, 7H), 2.39 – 2.24 (m, 1H), 1.27 (dd, $J_1$ = 16.5 Hz, $J_2$ = 7.2 Hz, 3H), 0.85 (dd, $J_1$ = 18.3 Hz, $J_2$ = 7.2 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 141.9 (d, $J_{PC}$ = 25.7 Hz), 136.8 (d, $J_{PC}$ = 86.1 Hz), 136.4 (d, $J_{PC}$ = 17.9 Hz), 133.7 (d, $J_{PC}$ = 10.4 Hz), 132.9 (d, $J_{PC}$ = 2.0 Hz), 129.5 (d, $J_{PC}$ = 98.6 Hz), 129.2 (d, $J_{PC}$ = 9.3 Hz), 128.9, 128.8, 128.4 (d, $J_{PC}$ = 9.6 Hz), 126.5 (d, $J_{PC}$ = 5.7 Hz), 124.5 (d, $J_{PC}$ = 8.9 Hz), 28.0 (d, $J_{PC}$ = 66.6 Hz), 15.4, 15.1 (d, $J_{PC}$ = 2.4 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 57.5. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{17}H_{18}OP$ $[M + H]^+$: 269.1095, Found: 269.1093.

**1-ethoxy-2-phenylphosphindole 1-oxide (2w)**



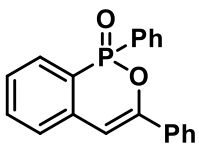

1w 2w

An oven -dried Schlenk tube under Ar atmosphere was charged with secondary phosphine oxide **1w** (0.25 mmol, 1.0 eq., 67.6 mg), $AgSbF_6$ (20 mol%, 17.2 mg) and toluene (2 mL). The mixture was stirred at 120°C for 16h. Upon completion, the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (Pentane/EA = 2/1 to 1/1) to afford the desired light yellow oil benzophosphorous product **2w** (yield 52%, 34.9 mg).

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.81 – 7.78 (m, 2H), 7.70 – 7.64 (m, 1H), 7.51 – 7.26 (m, 7H), 4.09 – 3.99 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 139.8 (d, $J_{PC}$ = 35.4 Hz), 135.5 (d, $J_{PC}$ = 25.8 Hz), 134.4 (d, $J_{PC}$ = 122.7 Hz), 133.3 (d, $J_{PC}$ = 2.2 Hz), 132.2 (d, $J_{PC}$ = 10.0 Hz), 129.0, 129.0 (d, $J_{PC}$ = 11.0 Hz), 127.8 (d, $J_{PC}$ = 9.5 Hz), 126.5 (d, $J_{PC}$ = 6.8 Hz), 124.8 (d, $J_{PC}$ = 11.5 Hz), 62.1 (d, $J_{PC}$ = 6.3 Hz), 16.4 (d, $J_{PC}$ = 6.5 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 46.0. **HRMS (ESI):** m/z calcd for $C_{16}H_{16}O_2P$ $[M + H]^+$: 271.0888, Found: 271.0888.

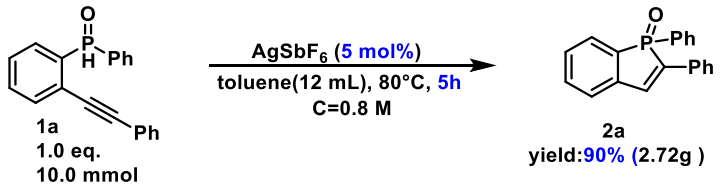
**By-product: Phosphaisocoumarin**

**1,3-diphenylbenzo[c][1,2]oxaphosphinine 1-oxide (3a)**



**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.89 – 7.78 (m, 4H), 7.62 – 7.34 (m, 10H), 6.77 (d, *J* = 1.8 Hz, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 149.6 (d, $J_{PC}$ = 10.4 Hz), 136.4 (d, $J_{PC}$ = 5.6 Hz), 133.2 (d, $J_{PC}$ = 5.6 Hz), 132.8 (d, $J_{PC}$ = 3.4 Hz), 131.8 (d, $J_{PC}$ = 11.2 Hz), 131.4, 130.3 (d, $J_{PC}$ = 12.2 Hz), 129.5, 128.4 (d, $J_{PC}$ = 14.0 Hz), 128.4, 127.7 (d, $J_{PC}$ = 14.2 Hz), 127.0 (d, $J_{PC}$ = 9.4 Hz), 125.1, 123.3, 121.6, 103.6 (d, $J_{PC}$ = 11.5 Hz). **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 26.3. **HRMS (DCI-$CH_4$):** m/z calcd for $C_{20}H_{15}O_2P$ $[M + H]^+$: 319.0888, Found: 319.0886.

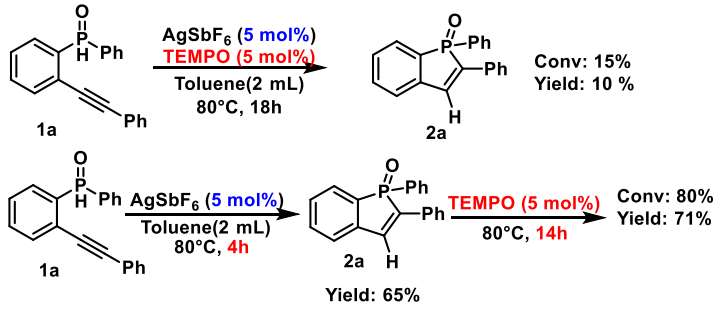
## 4. Scale-up experiment




An oven-dried Schlenk tube under Ar atmosphere was charged with secondary phosphine oxide **1a** (10.0 mmol, 1.0 eq., 3.02 g), $AgSbF_6$ (5 mol%, 171.8 mg) and toluene (12 mL). The mixture was stirred at 80°C for 5h. Upon completion, the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel to afford the BPO **2a** (yield: 90%, 2.72 g).

## 5. Mechanistic studies

### *a. Radical quenching experiments:*



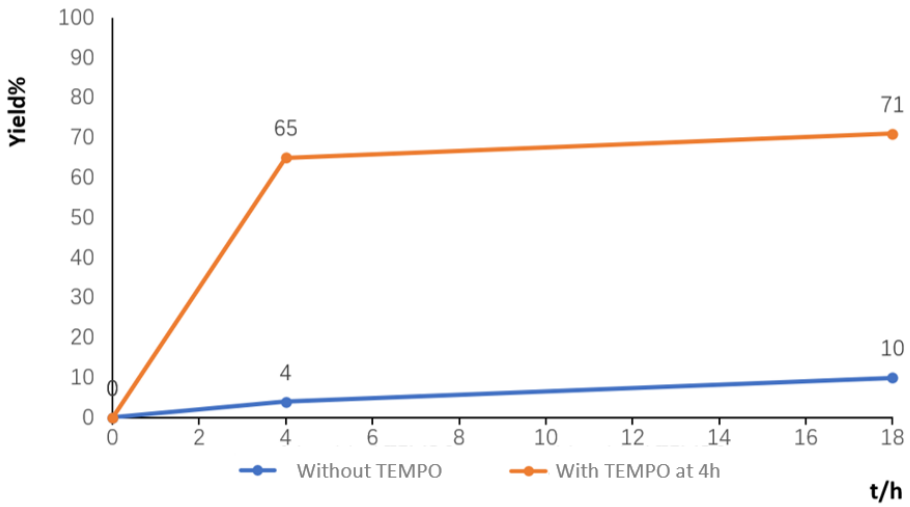




**Figure S3.** The effect of adding TEMPO on the reaction.

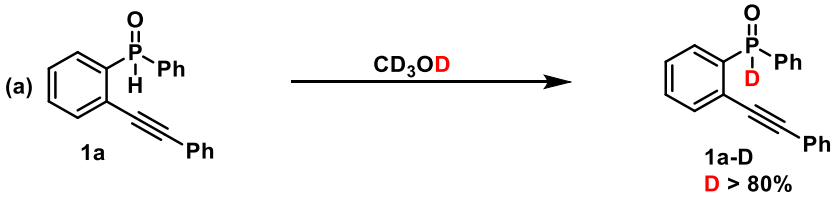
Control experiment **1:** (blue line): An oven-dried Schlenk tube under Ar atmosphere was charged with secondary phosphine oxide **1a** (0.25 mmol, 1.0 eq., 75.6 mg), $AgSbF_6$ (5 mol%, 4.3 mg), TEMPO (5 mol%, 2.0 mg) and toluene (2 mL). The mixture was stirred at 80°C and the progress of the reaction was controlled by $^{31}P\{H\}$ NMR.

Control experiment **2:** (orange line): An oven-dried Schlenk tube under Ar atmosphere was charged with secondary phosphine oxide **1a** (0.25 mmol, 1.0 eq., 75.6 mg), $AgSbF_6$ (5 mol%, 4.3 mg) and

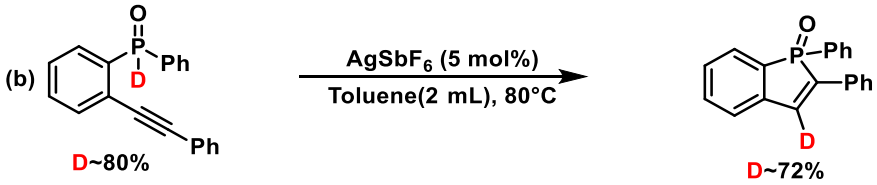
toluene (2 mL). The mixture was stirred at 80°C for 4 h. Then, TEMPO (5 mol%, 2.0 mg) was added to the reaction mixture and the progress of the reaction at 80°C was monitoreded by $^{31}P\{H\}$ NMR.

### *b. Deuterium labeling experiments*

Preparation of **1a-D** according to reference.[9]




(a): A dried flask (25 mL) was rinsed with $CD_3OD$ twice, and then charged with **1a** (75.6 mg, 0.25 mmol). $CD_3OD$ (99.8 % D, 2 mL) was added and the mixture was slowly concentrated using rotatory evaporator. The residual solvent was evaporated with high vacuum, this process was repeated six times, the product was used directly in the next step (b).




(b): An oven-dried Schlenk tube under Ar atmosphere was charged with **D-1a** (0.25 mmol, 1.0 eq., 75.8 mg), $AgSbF_6$ (5 mol%, 4.3 mg) and toluene (2 mL). The mixture was stirred at 80°C and the progress of the reaction was monitored by $^{31}P$ NMR. Upon completion, the solvent was evaporated under reduced pressure and the residue was purified by filtration to afford the desired light yellow solid product **D-2a,** yield 92%, 69.5 mg, ~72% **D**.

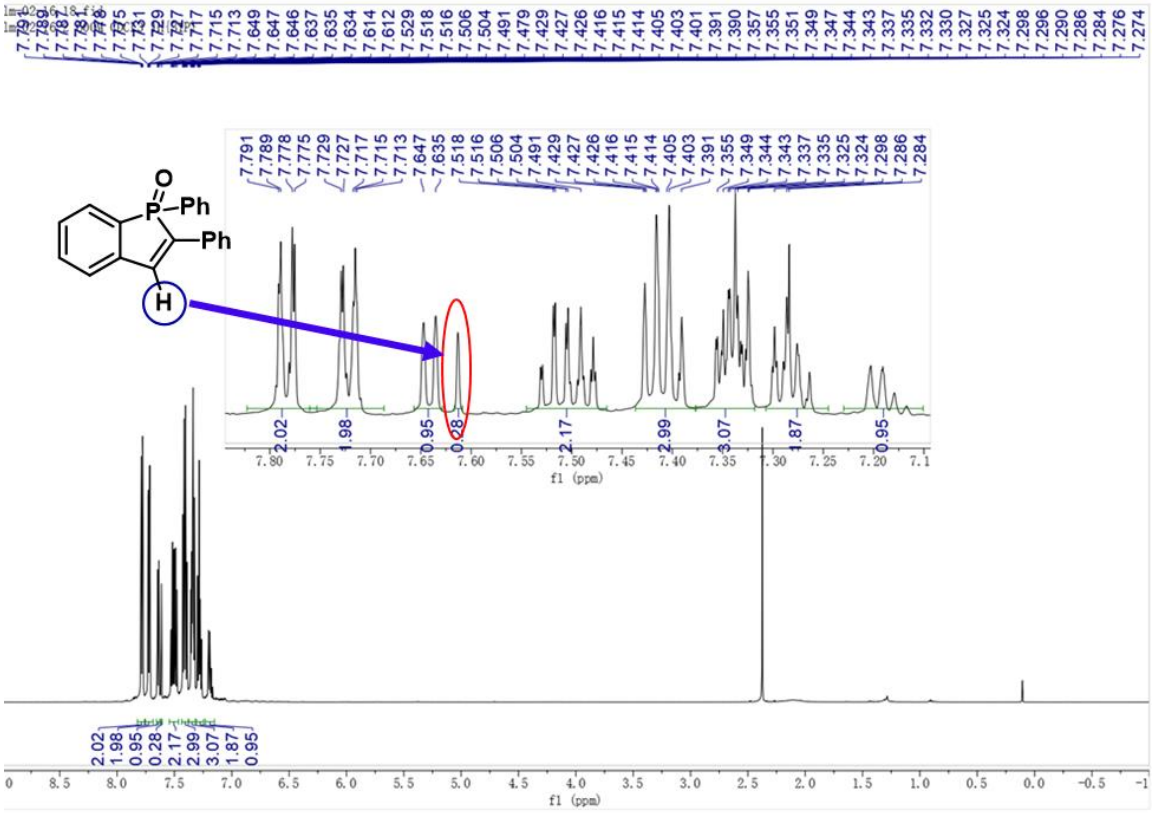
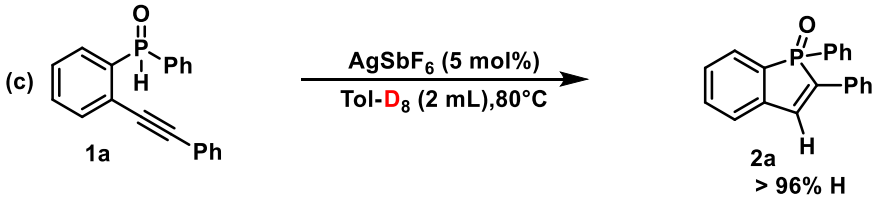


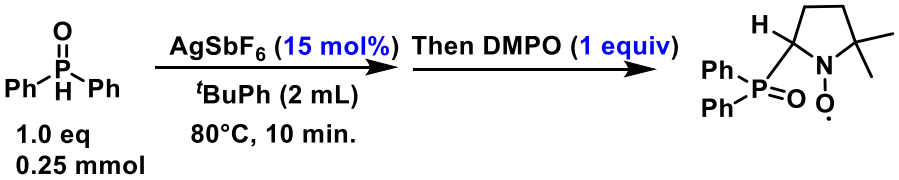

**Figure S4.** $^{1}H$ NMR spectrum of **2a** with the identified H3 in the red circle**.**




(c): An oven-dried Schlenk tube under Ar atmosphere was charged with secondary phosphine oxide **1a** (0.25 mmol, 1.0 eq., 75.6 mg), $AgSbF_6$ (5 mol%, 4.3 mg) and toluene-$D_8$ (2 mL). The mixture was stirred at 80°C and the progress of the reaction was monitored by $^{31}P$ NMR. Upon completion, the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (Pentane/EA = 2/1 to 1/1) to afford the desired light yellow solid product **2a,** yield 93%, 70.1 mg, >96% H.

### *c. General procedure for the radical trapping experiments:*


An oven-dried Schlenk tube under Ar atmosphere was charged with **1a** (0.25 mmol, 1.0 eq., 75.6 mg), $AgSbF_6$ (15 mol%, 12.9 mg) and $^t$BuPh (2 mL). The mixture was stirred at 80°C for 1h, followed by the addition of DMPO (0.25 mmol, 1.0 eq., 28.3mg) and stirred at RT for 5 min. Then, the reaction was taken out some samples and was analyzed by ESR at RT. This result was shown in Figure 2 in the main text.



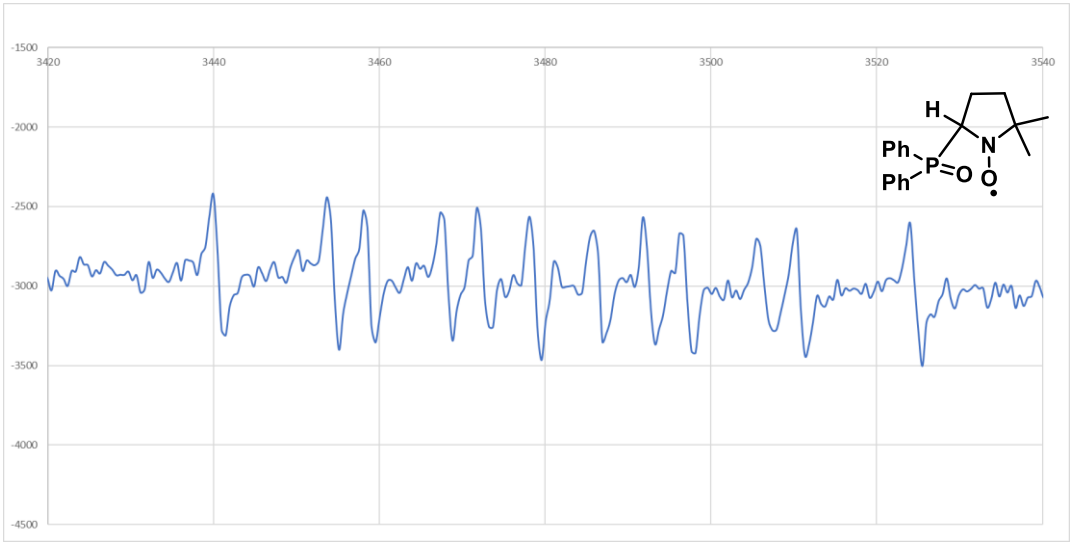




**Figure S5.** Electron spin resonance (ESR) spectra of the adduct between Diphenylphosphine oxide and DMPO.

## 6. Figures complementary to main text

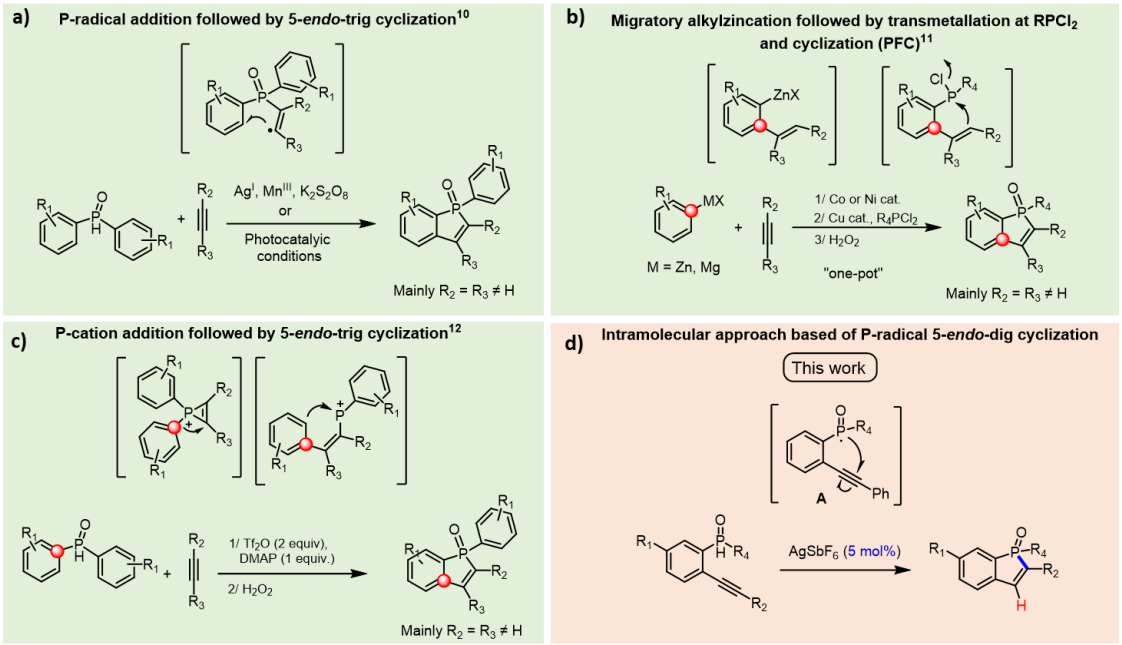



**Figure S6.** Comparison of the main synthetic routes developed to access benzophosphole oxides with schematic representation of the key intermediates involved in each case.

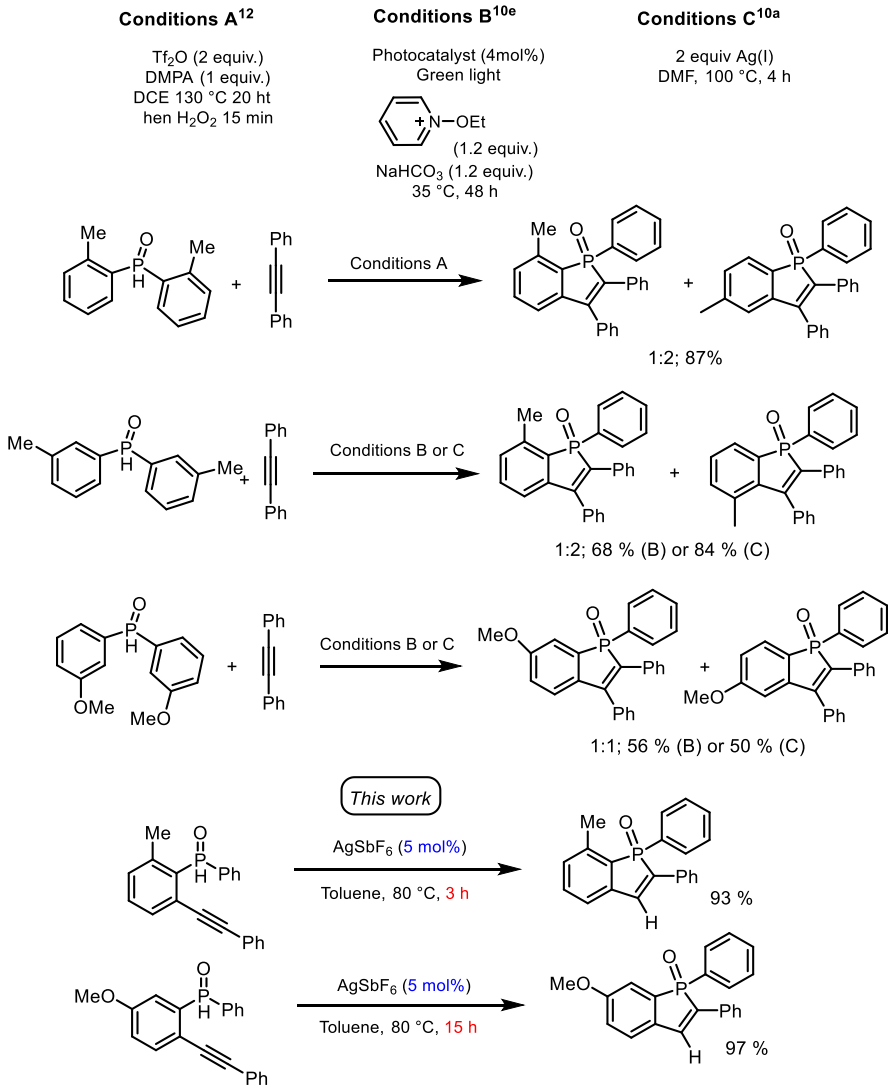



**Figure S7.** Representative examples comparing the intermolecular and intramolecular routes to benzophosphole oxides in terms of regioselectity.

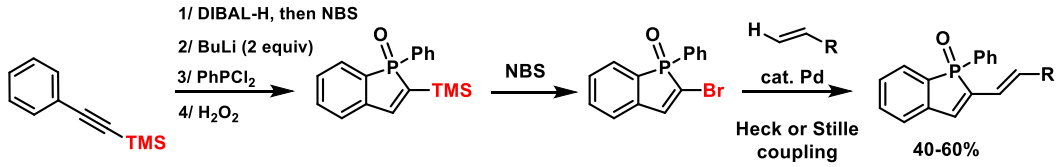
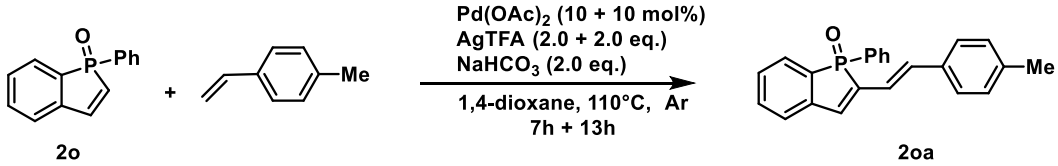


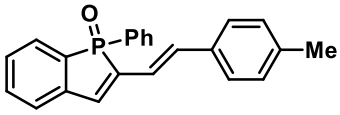

**Figure S8.** Derivatization of benzophosphole oxide brominated at C-2 by Pd-catalyzed CC coupling.[13]

## 7. General procedures for the C-H vinylation reaction[14]



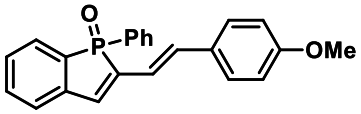

An oven-dried Schlenk tube under Ar atmosphere was charged with 1-phenylphosphindole 1-oxide **2j** (0.25 mmol, 1.0 eq., 56.6 mg), 4-Methylstyrene (0.5 mmol, 2.0 eq., 66 uL), $Pd(OAc)_2$ (0.025 mmol, 10 mol%, 5.6 mg), AgTFA (0.5 mmol, 2.0 eq., 110 mg), $NaHCO_3$ (0.5 mmol, 2.0 eq., 42.0 mg) and 1,4-dioxane (2 mL). The mixture was stirred at 110°C for 7 h, Add $Pd(OAc)_2$ (0.025 mmol, 10 mol%, 5.6 mg), AgTFA (0.5 mmol, 2.0 eq., 110 mg) again, continue stirring the mixture at 110°C for 13 h. The resulting mixture was cooled to room temperature and then quenched with water and brine, the residue was extracted with EA (15 mL×3) and the combined organic fractions were dried over anhydrous $Na_2SO_4$, the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (Pentane/EA = 2/1 to 1/1) to afford the desired product **2ja** as a yellow solid, yield 90%, 77.4 mg.

**(E)-2-(4-methylstyryl)-1-phenylphosphindole 1-oxide (2oa)**



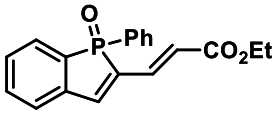

Yield 90% (77.4 mg), yellow solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.83 – 7.76 (m, 2H), 7.64 – 7.59 (m, 1H), 7.52 – 7.43 (m, 4H), 7.36 – 6.92 (m, 9H), 2.33 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 142.2 (d, *J*pc = 27.4 Hz), 139.1, 138.4, 138.2, 137.9, 135.2 (d, *J*pc = 5.0 Hz), 133.8, 133.1 (d, *J*pc = 2.2 Hz), 132.2 (d, *J*pc = 2.9 Hz), 131.5 (q, *J*pc = 98.2 Hz), 130.6 (d, *J*pc = 10.8 Hz), 129.3, 128.9 (d, *J*pc = 10.2 Hz), 128.8 (d, *J*pc = 12.2 Hz), 128.7 (d, *J*pc = 10.7 Hz), 126.7, 124.3 (d, *J*pc = 9.5 Hz), 120.9 (d, *J*pc = 9.9 Hz), 21.2. **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 38.0. **HRMS (DCI-CH4):** m/z calcd for $C_{23}H_{20}OP$ $[M + H]^+$: 343.1252, Found: 343.1247.

**(E)-2-(4-methoxystyryl)-1-phenylphosphindole 1-oxide (2ob)**




Yield 94% (84.5 mg), yellow solid. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.83 – 7.82 (m, 2H), 7.64 – 7.57 (m, 1H), 7.55– 7.40 (m, 4H), 7.39 – 6.82 (m, 9H), 3.81 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 159.9, 142.3 (d, *J*pc = 27.6 Hz), 138.6 (d, *J*pc = 92.6 Hz), 137.6, 137.3, 134.8 (d, *J*pc = 5.2 Hz), 133.1 (d, *J*pc = 2.0 Hz), 132.2 (d, *J*pc = 2.9 Hz), 131.5 (q, *J*pc = 97.7 Hz), 130.6 (d, *J*pc = 10.7 Hz), 129.4, 128.9 (d, *J*pc = 10.2 Hz), 128.8 (d, *J*pc = 12.3 Hz), 128.6 (d, *J*pc = 10.6 Hz), 128.2, 124.2 (d, *J*pc = 9.4 Hz), 119.8 (d, *J*pc = 9.9 Hz), 114.0, 55.3. **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 38.0. **HRMS (DCI-CH4):** m/z calcd for $C_{23}H_{20}O_2P$ $[M + H]^+$: 359.1201, Found: 359.1216.

**ethyl (E)-3-(1-oxido-1-phenylphosphindol-2-yl)acrylate (2oc)**




Yield 73% (59.4 mg), light yellow oil.**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.72 – 7.36 (m, 11H), 6.24 (d, *J* = 15.9 Hz, 1H), 4.20 – 4.10 (m, 2H), 1.24 (t, *J* = 6.9 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 166.3, 145.5 (d, $J_{PC}$ = 20.0 Hz), 141.0 (d, $J_{PC}$ = 26.6 Hz), 136.2 (d, $J_{PC}$ = 9.5 Hz), 134.9 (q, $J_{PC}$ = 107.5 Hz), 133.3 (d, $J_{PC}$ = 2.0 Hz), 132.6 (d, $J_{PC}$ = 2.9 Hz), 131.2 (d, $J_{PC}$ = 10.8 Hz), 130.6 (d, $J_{PC}$ = 11.0 Hz), 130.4 (d, $J_{PC}$ = 10.7 Hz), 129.2 (d, $J_{PC}$ = 10.3 Hz), 129.0 (d, $J_{PC}$ = 12.5 Hz), 128.9 (d, $J_{PC}$ = 99.2 Hz), 125.6 (d, $J_{PC}$ = 9.3 Hz), 123.6 (d, $J_{PC}$ = 4.2 Hz), 60.6, 14.1. **$^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$)** δ 41.4. **HRMS (DCI-CH4):** m/z calcd for $C_{19}H_{18}O_3P$ $[M + H]^+$: 325.0994, Found: 325.1002.

## 8. Crystallographic Data

Crystallographic data were collected at low temperature (193(2) K) on a Bruker D8 VENTURE diffractometer equipped with a PHOTON III detector, using $MoK_\alpha$ radiation ($\lambda = 0.71073$ Å). Phi and Omega scans were performed for data collection. An empirical absorption correction was applied[15] and the structures were solved by intrinsic phasing method (ShelXT).[16] All non-hydrogen atoms were refined anisotropically by means of least-squares procedures on $F^2$ with ShelXL.[17]
Crystallographic data (excluding structure factors) have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication CCDC 2332940. These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

**Procedure for preparation of the crystals**: The product **2l** (50 mg) was dissolved in DCM and filtered through a pad of filter paper. The filtrate was then transferred into several test-tubes by different volumes. Then to these solutions was added hexane in dropwise. These samples were allowed to be evaporated slowly at room temperature, which would eventually give crystals on the surface of the tubes.

Crystal Data, Data Collection, and Structure Refinement for **2l**.

| ID | **2l** |
|---|---|
| formula | $C_{26}H_{19}OP$ |
| $M_r$ | 378.38 |
| crystal system | monoclinic |
| space group | $P2_1/c$ |
| $a$ (Å) | 9.5610(7) |
| $b$ (Å) | 8.7992(7) |
| $c$ (Å) | 23.2962(14) |
| α (°) | 90 |
| β (°) | 90.14(3) |
| γ (°) | 90 |
| $V$ (Å$^3$) | 1959.9(2) |
| $Z$ | 4 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.559 |
| $\mu$ (mm$^{-1}$) | 3.459 |
| $F$(000) | 2144 |
| crystal size (mm$^3$) | 0.34 x 0.22 x 0.20 |
| $T$/K | 193(2) |
| measd reflns | 27187 |
| Unique reflns (Rint) | 3910 (0.0308) |
| Data/restraints/parameters | 3910 / 0 / 253 |
| GOF on $F^2$ | 1.031 |
| $R_1$[a] [I>2σ(I)] | 0.0376 |
| $wR_2$[b] [all data] | 0.1102 |

[a] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma |F_o|$. [b] $wR_2 = [\Sigma[ w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$.

## 9. References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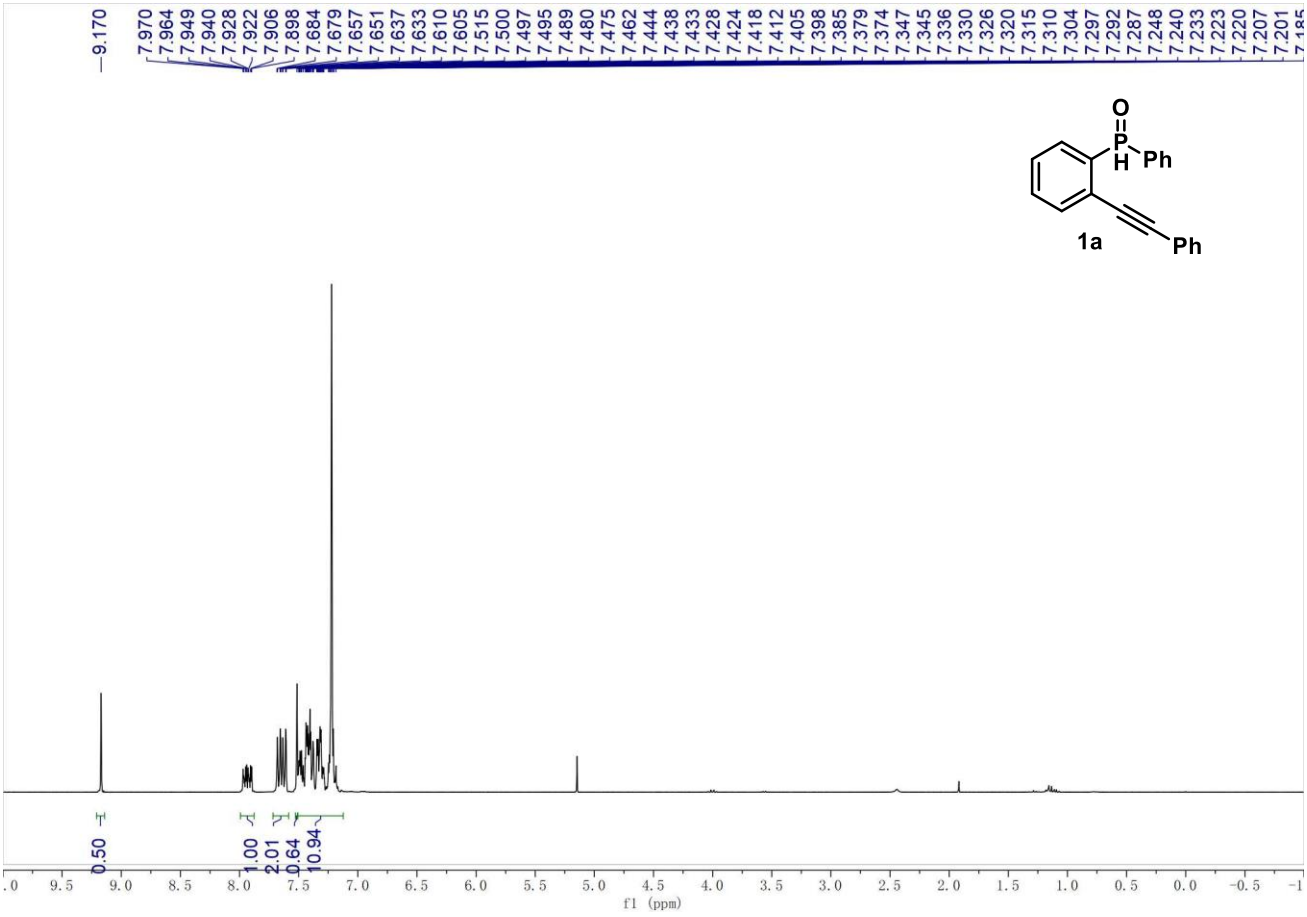
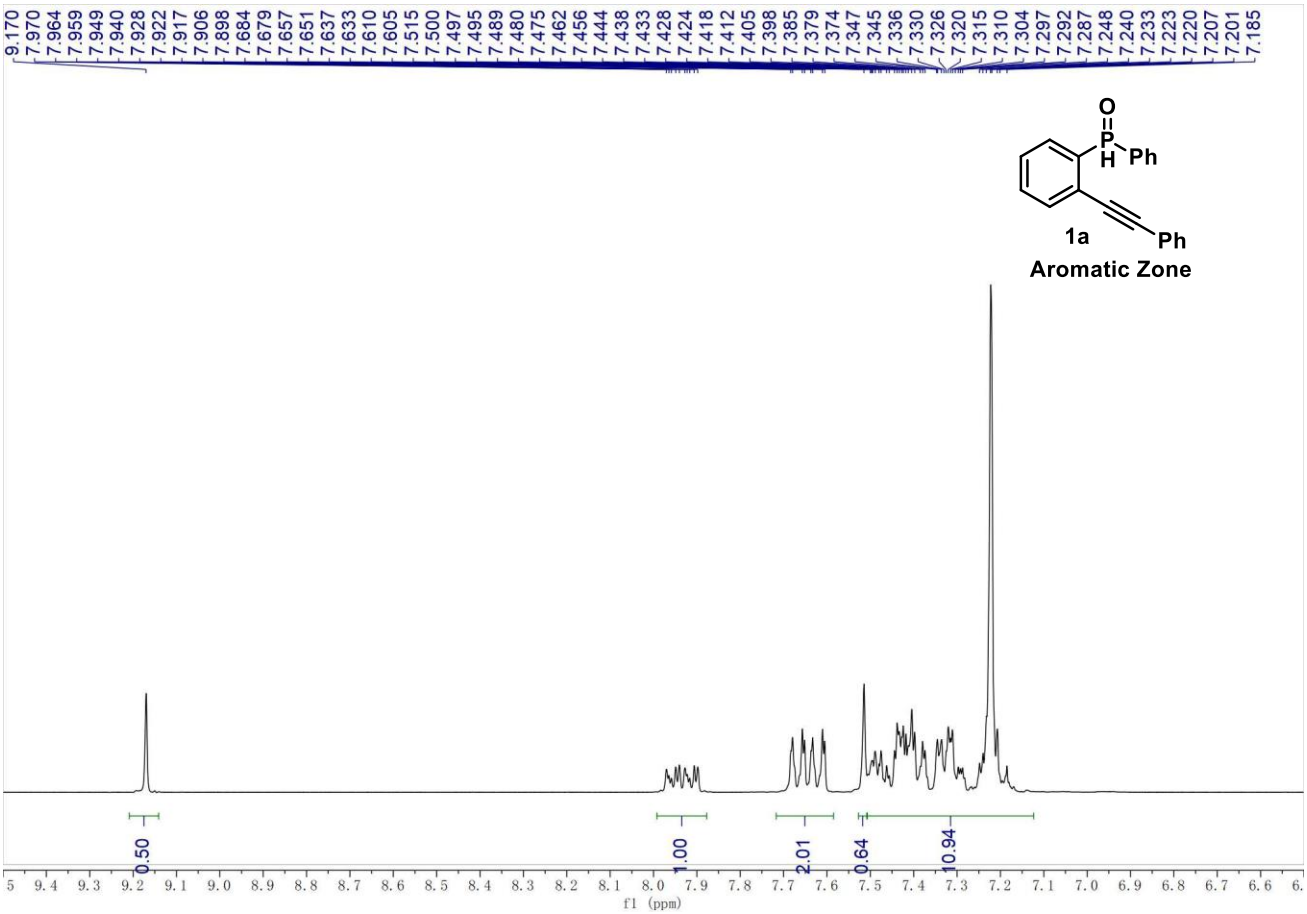
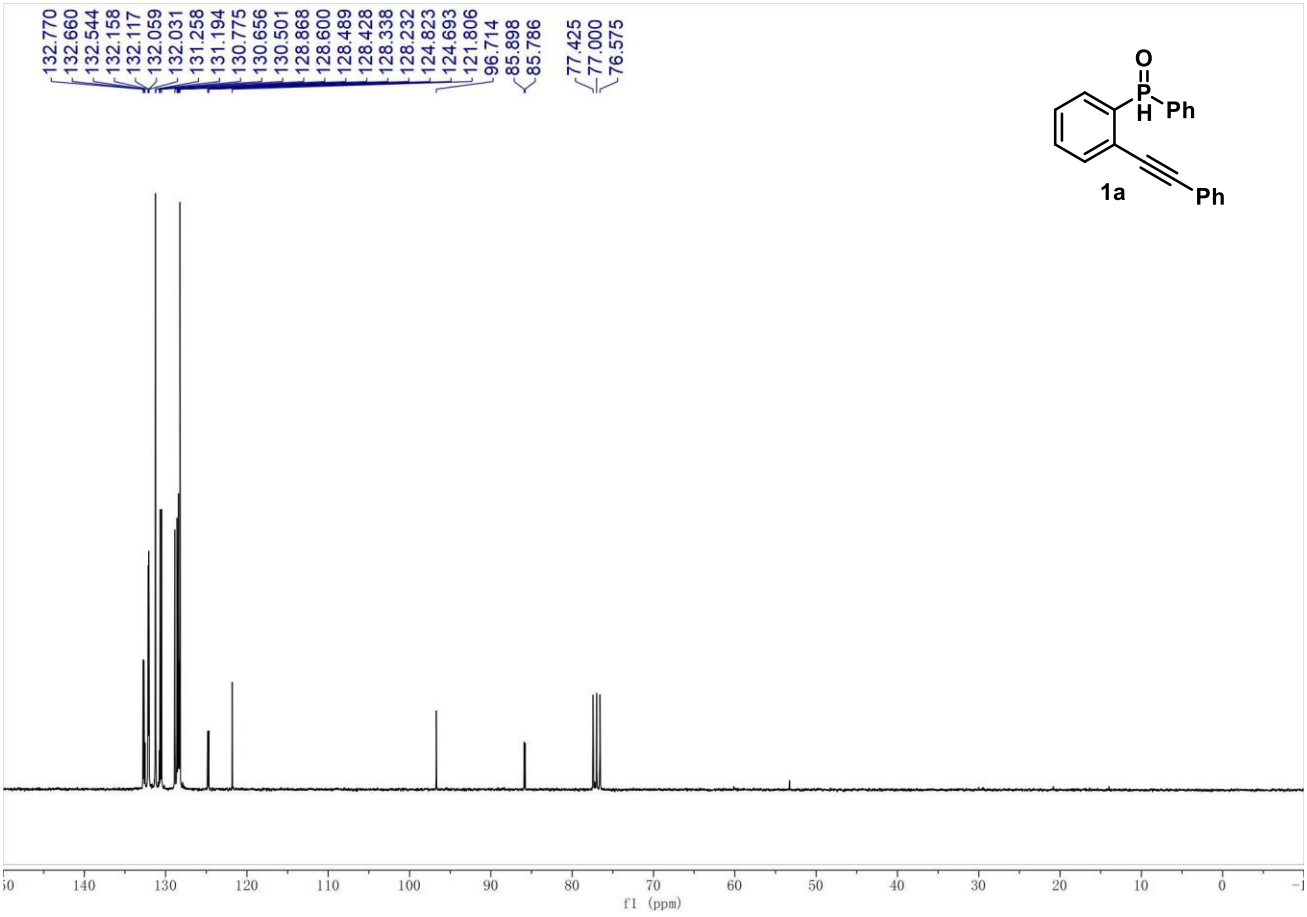
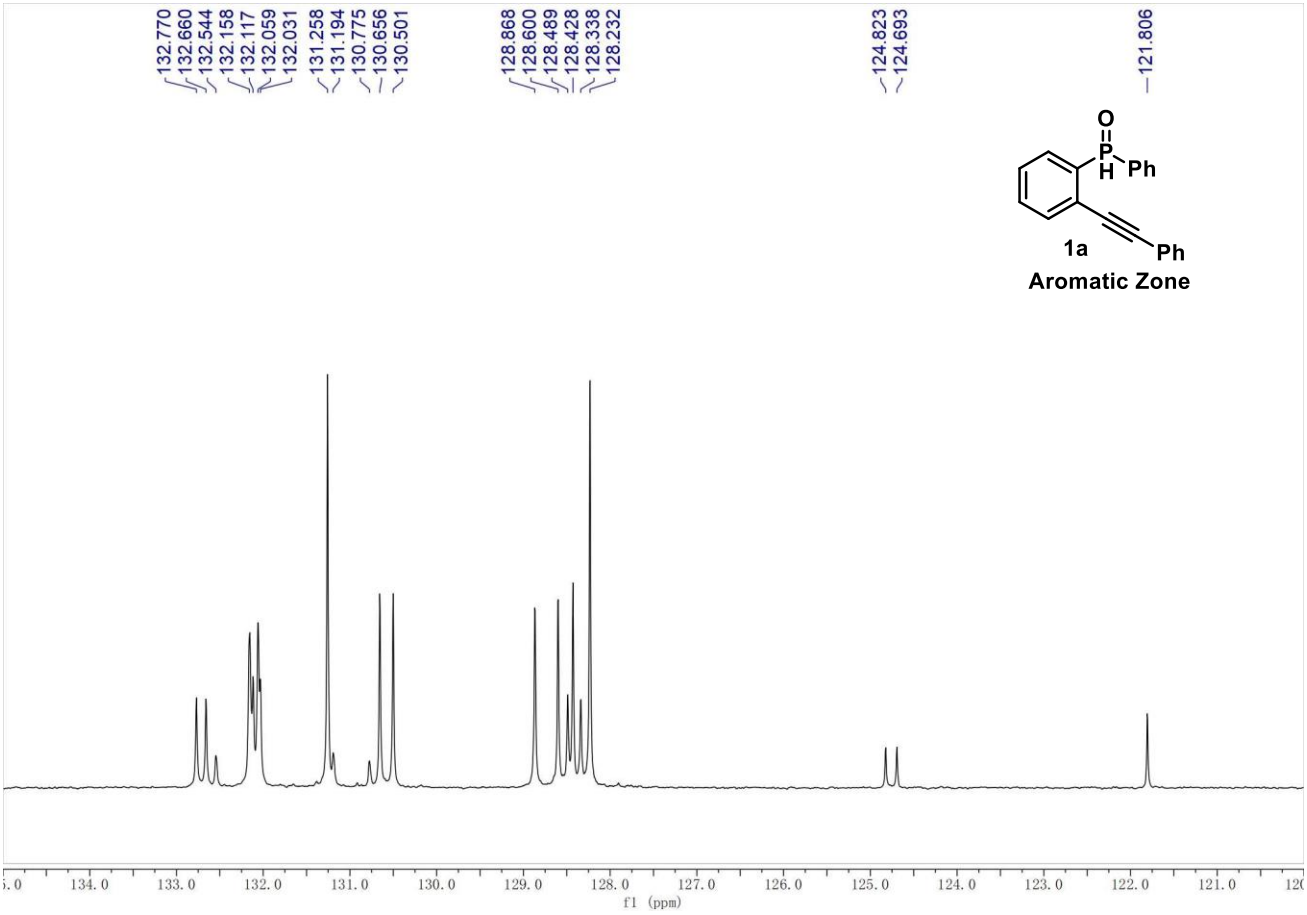
**$^1$H NMR spectrum of 1a (300 MHz, $CDCl_3$)**



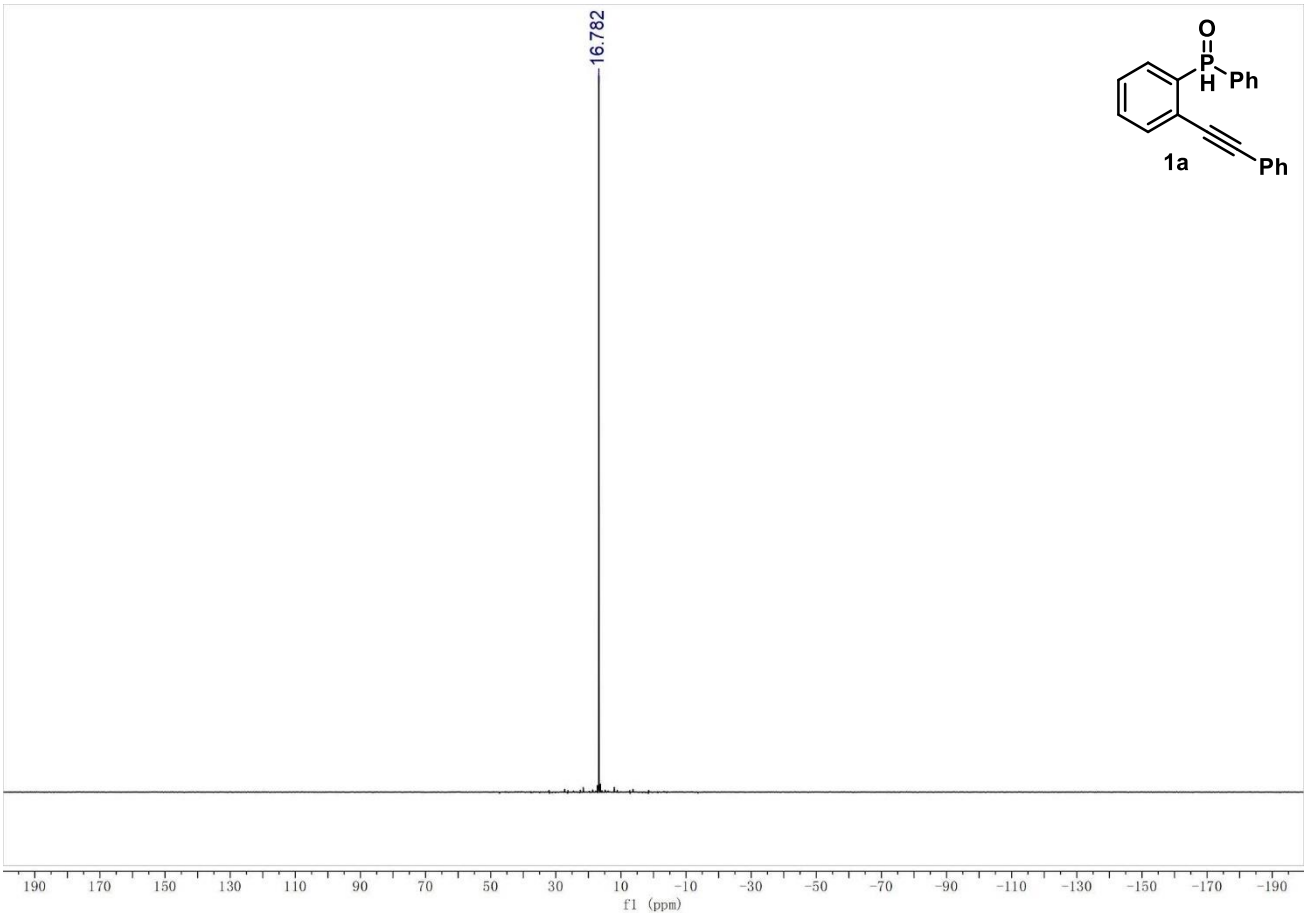



**$^{13}$C NMR spectrum of 1a (75 MHz, $CDCl_3$)**



**$^{31}P\{^{1}H\}$ NMR spectrum of 1a (121 MHz, $CDCl_3$)**

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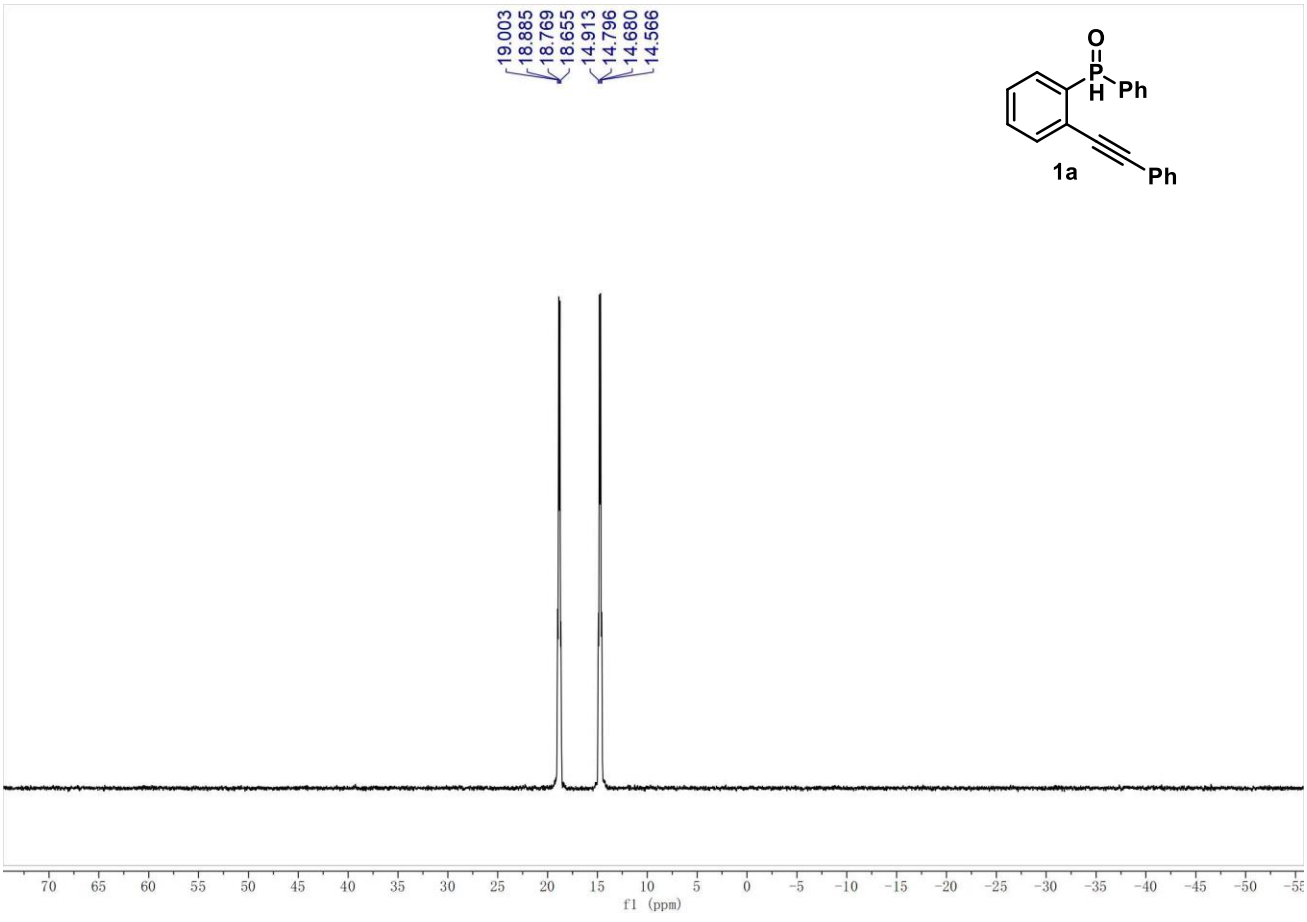

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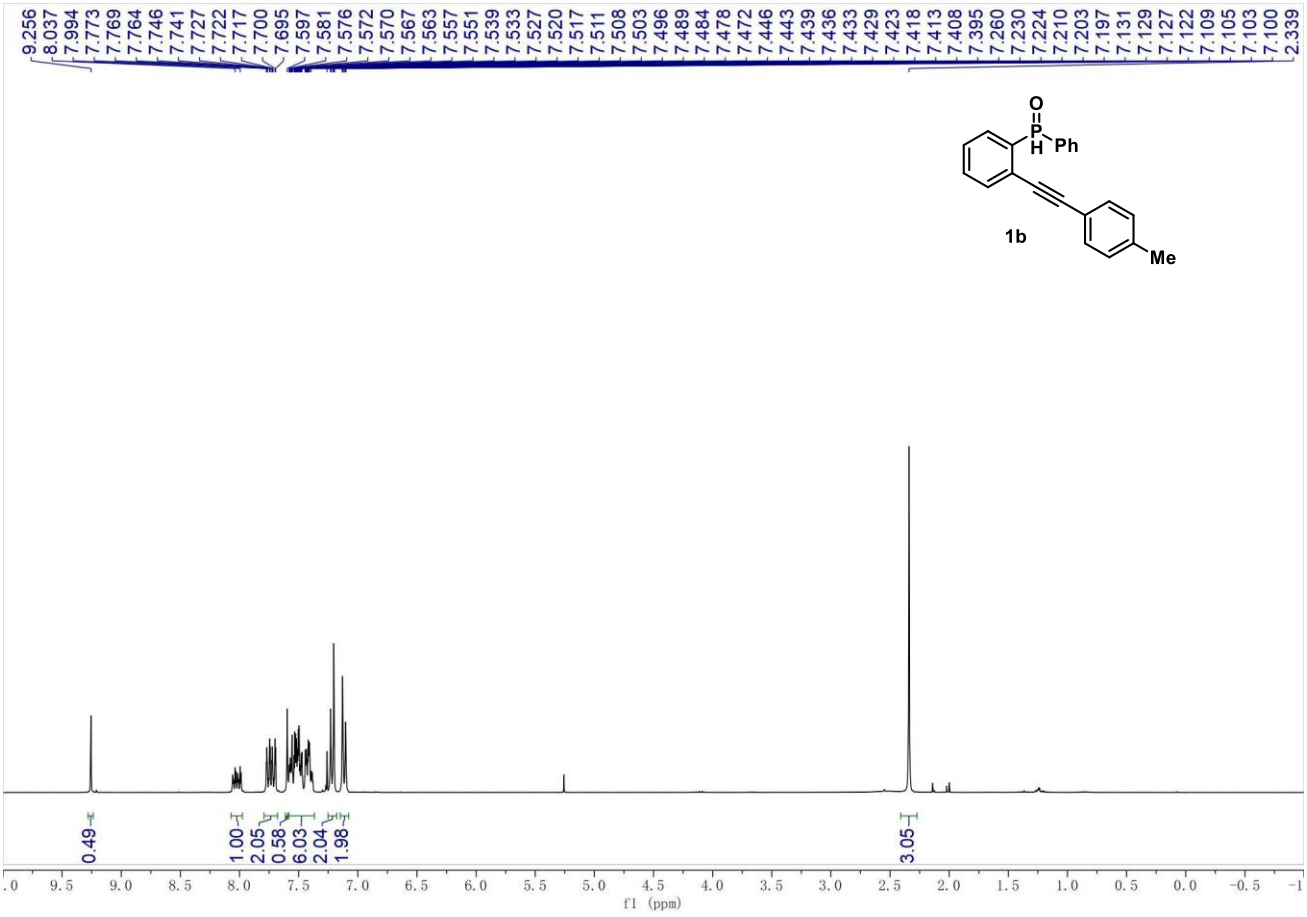


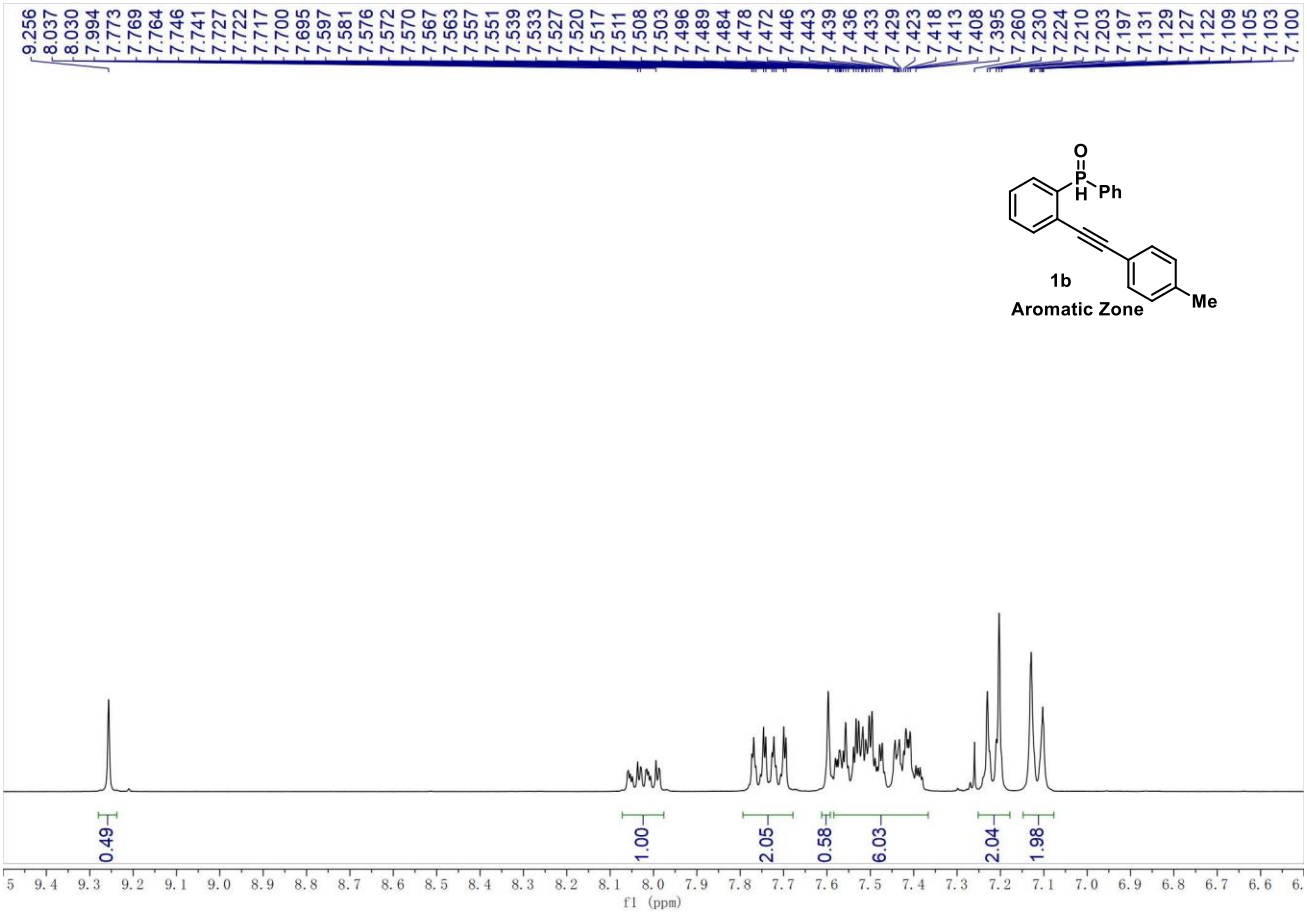

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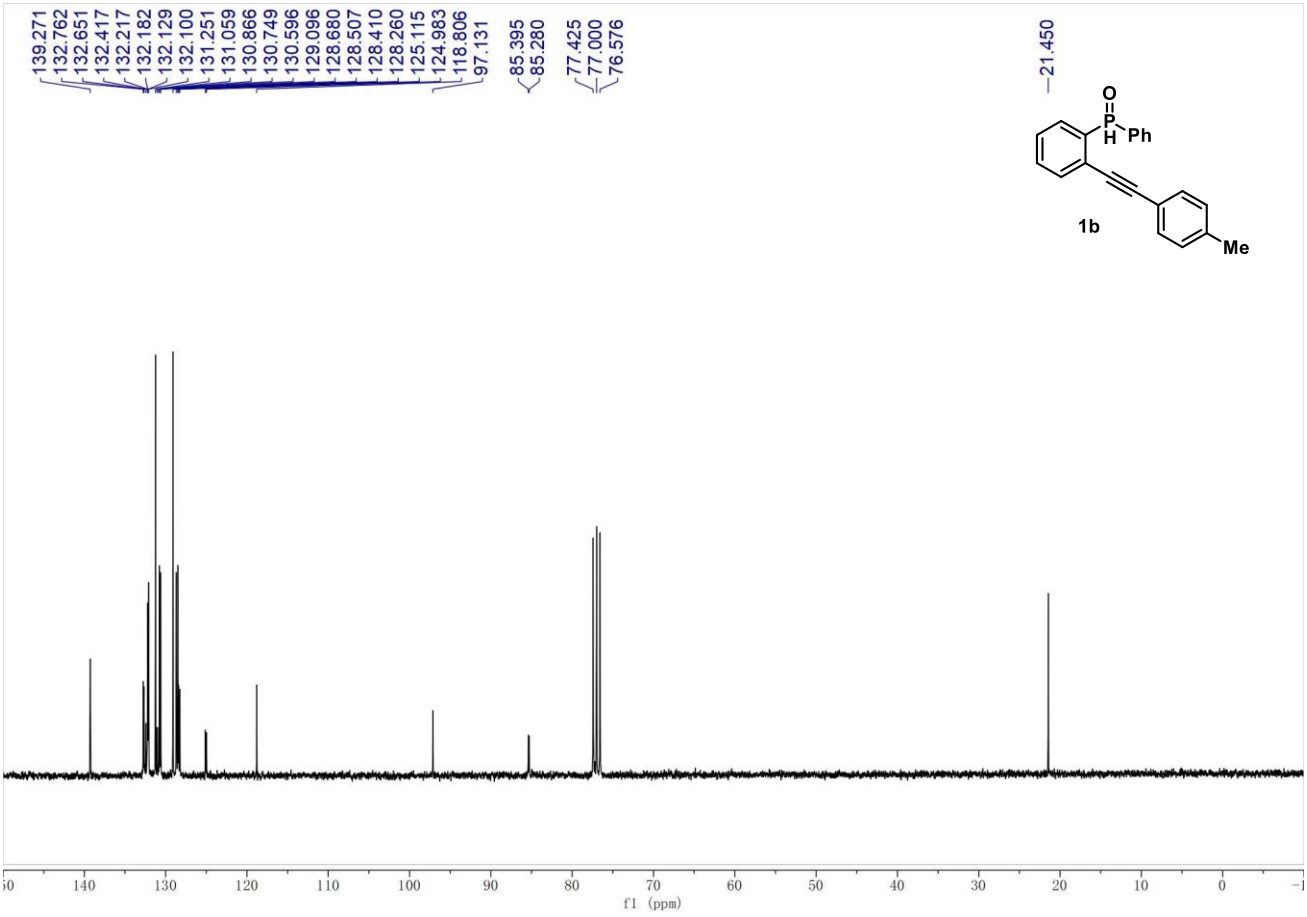


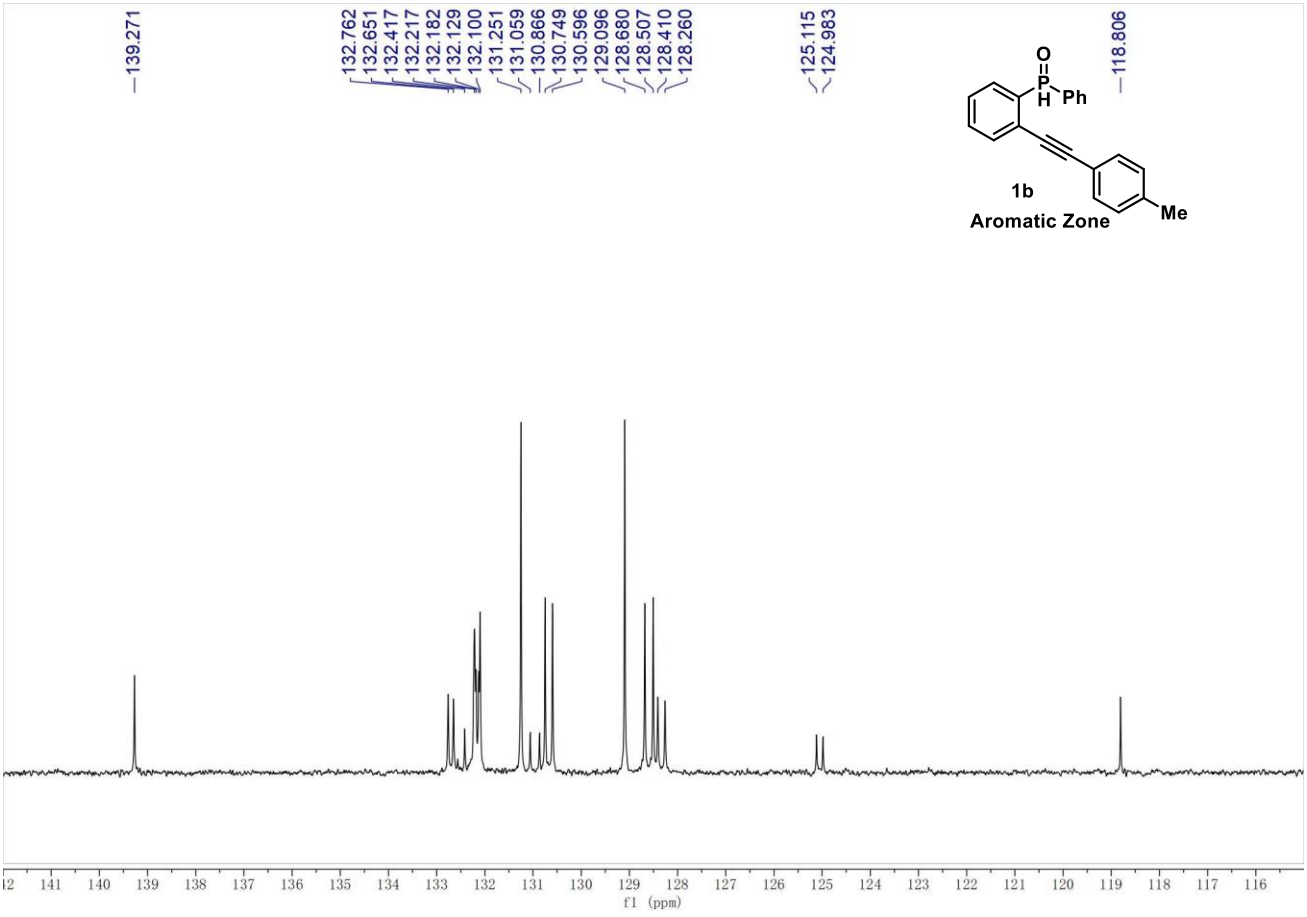

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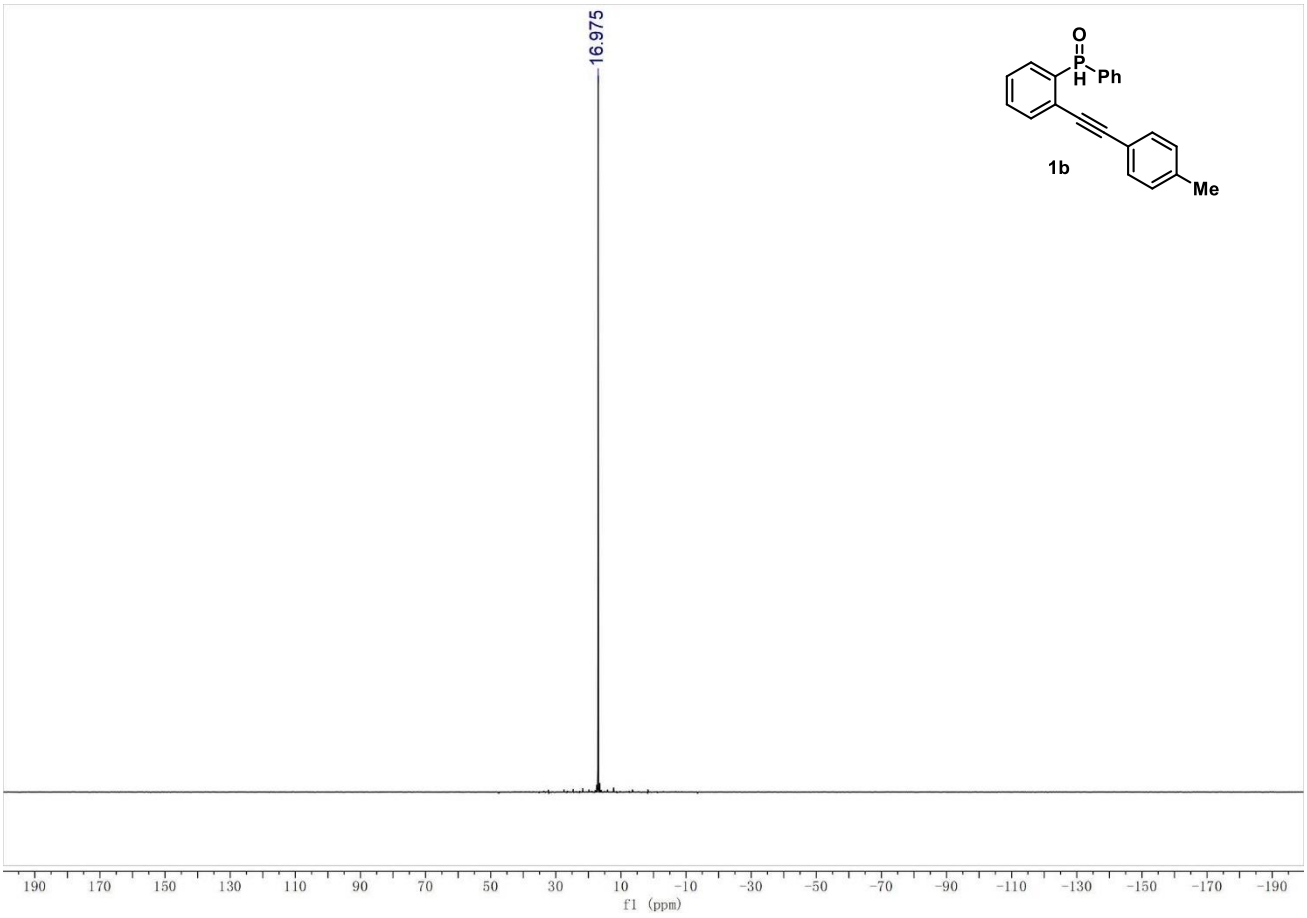


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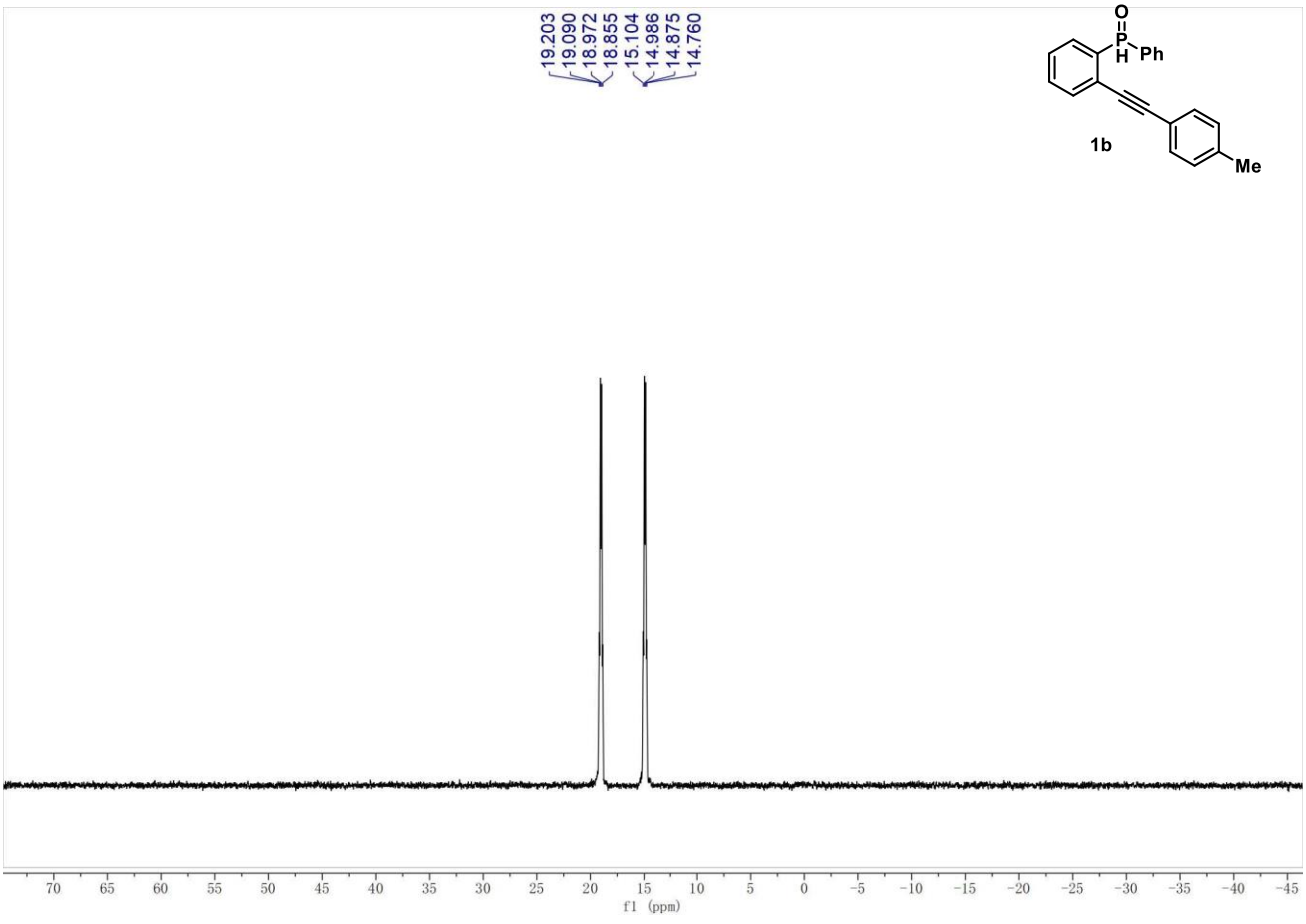

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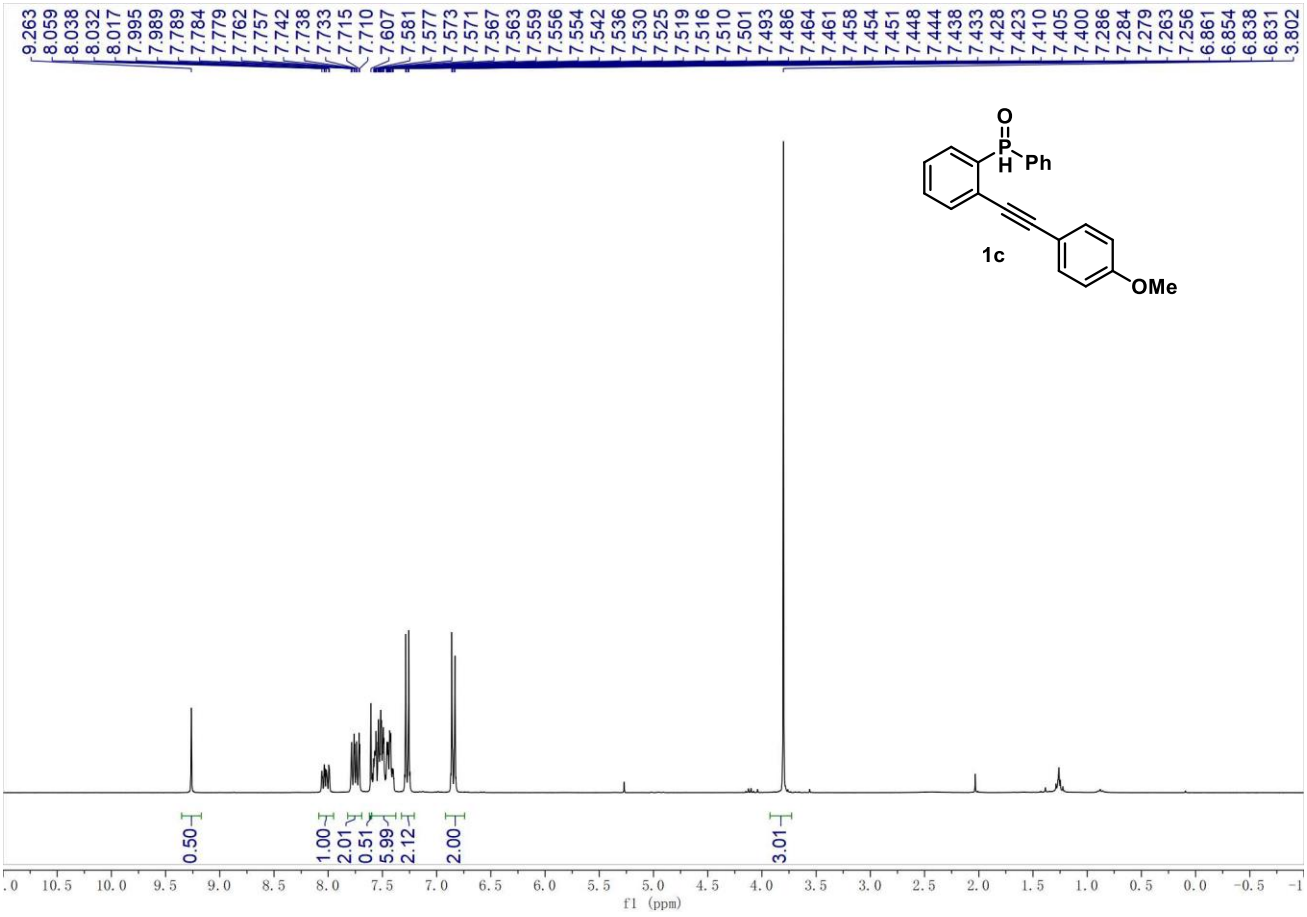


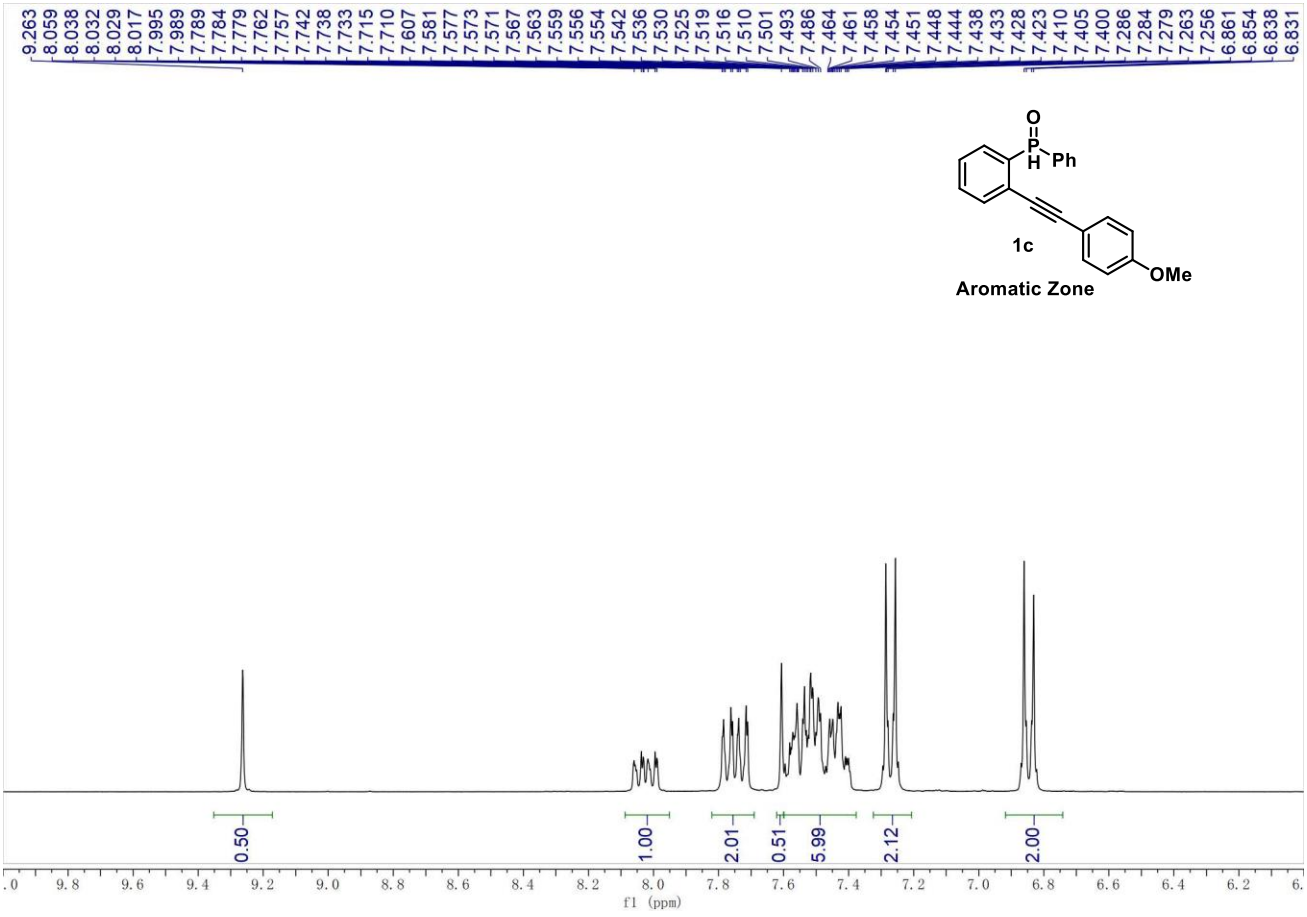

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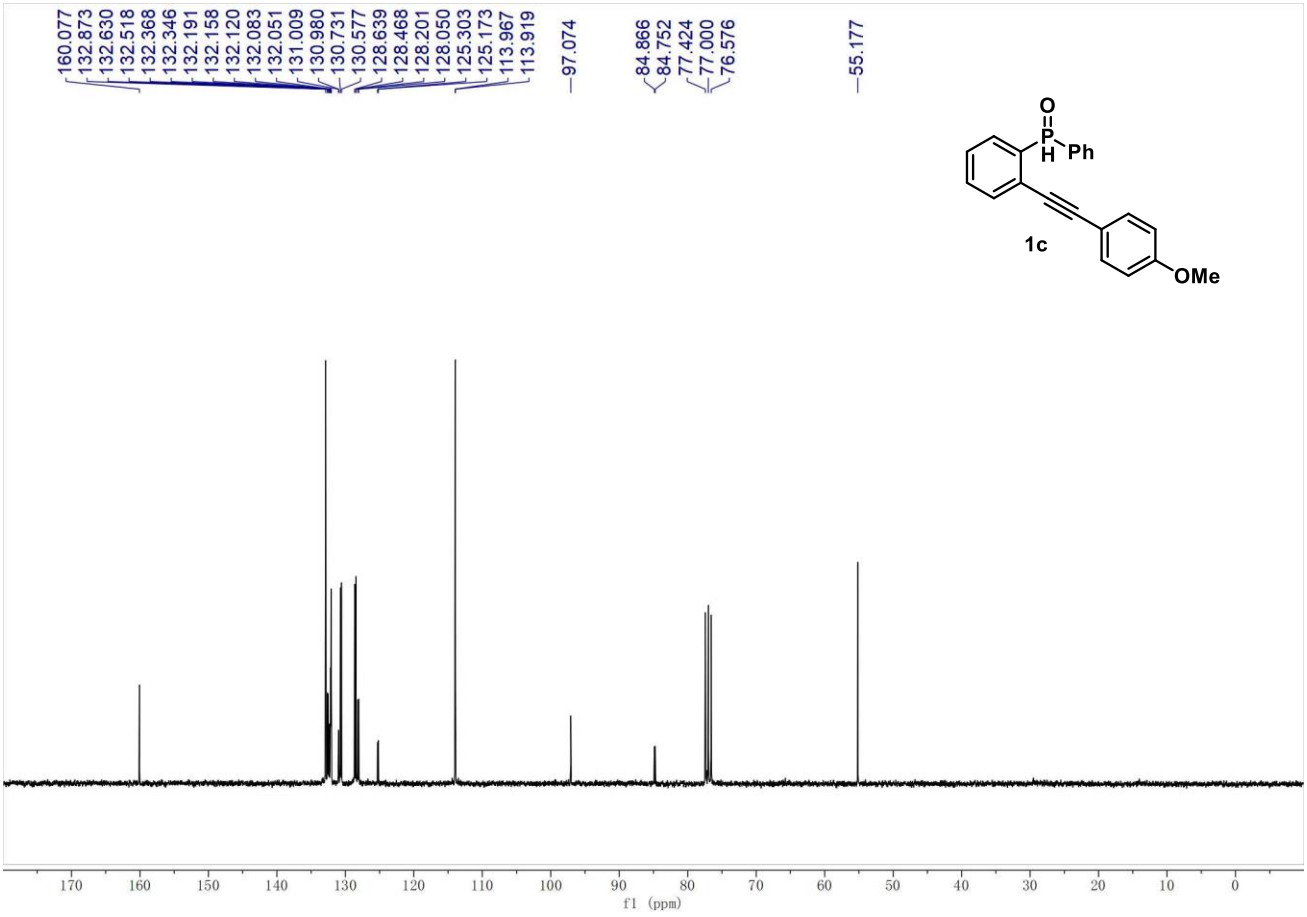


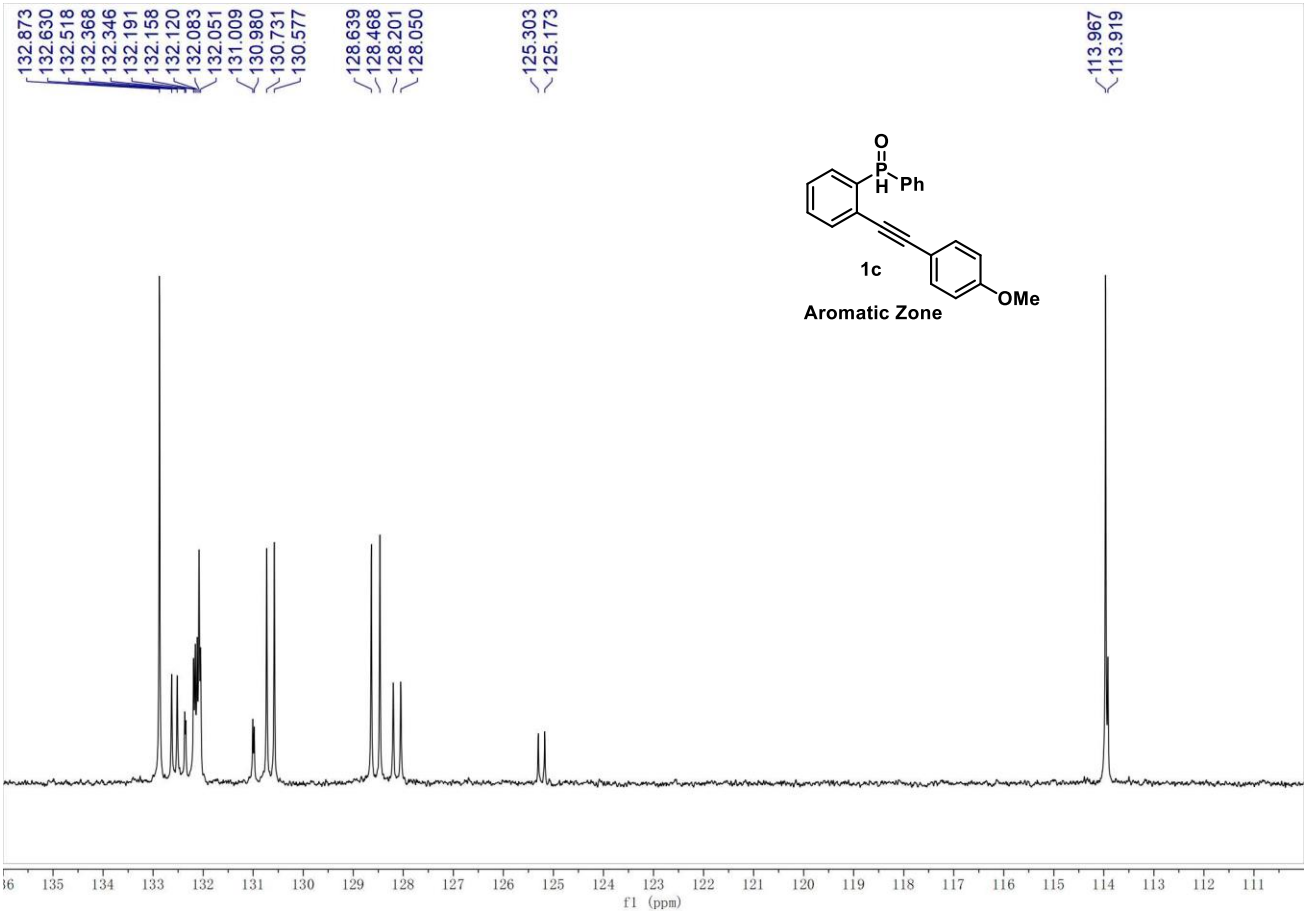

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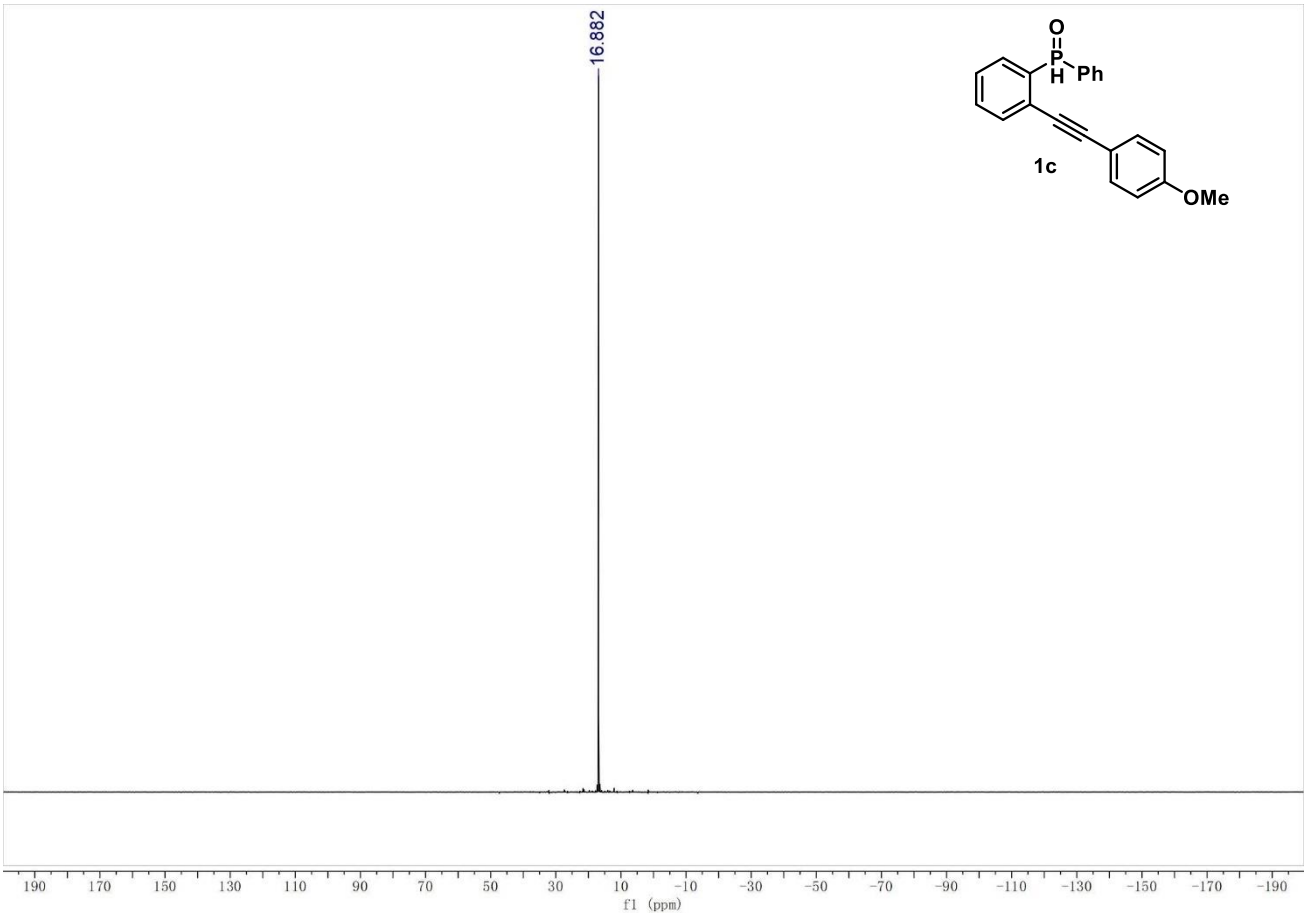


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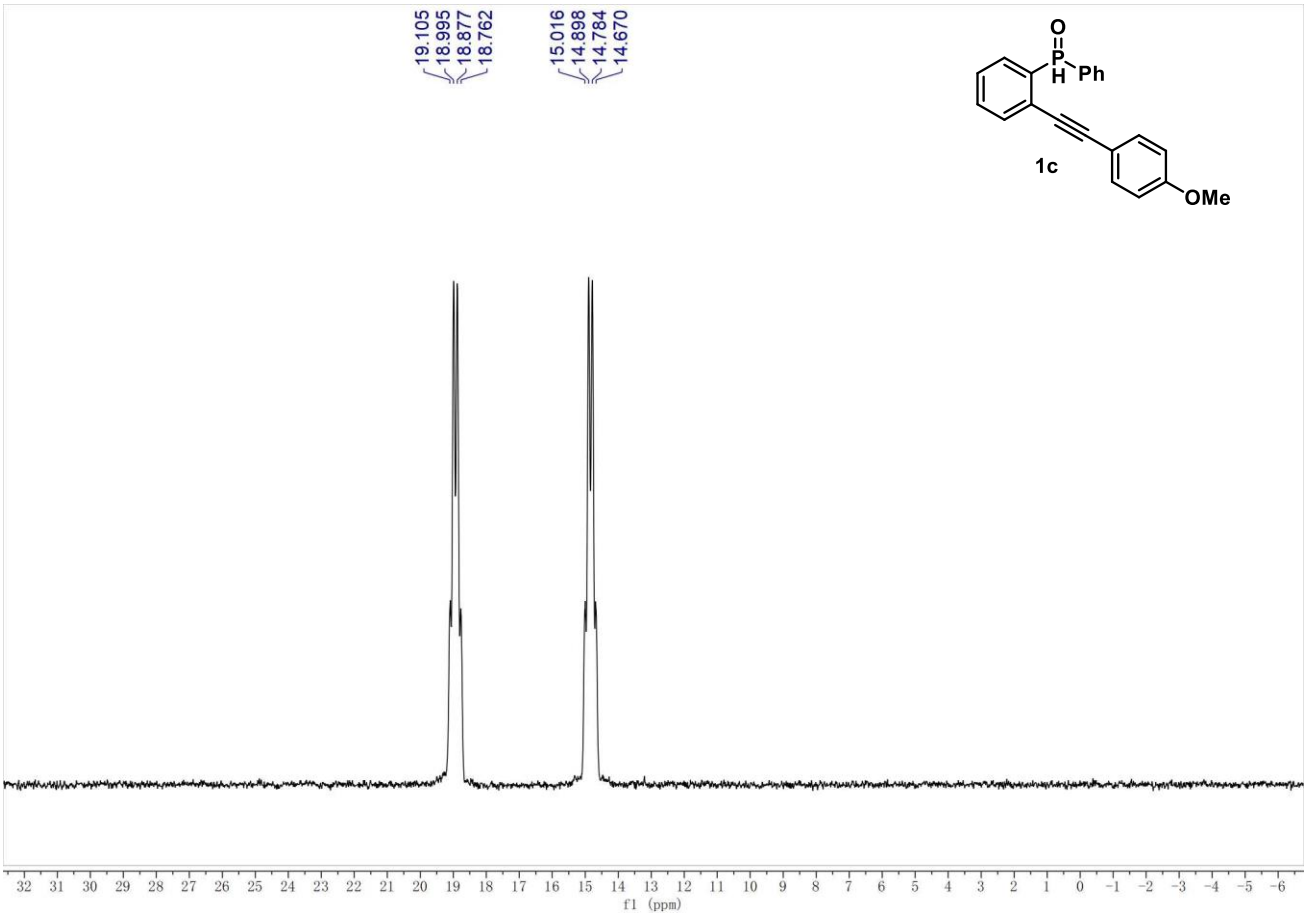

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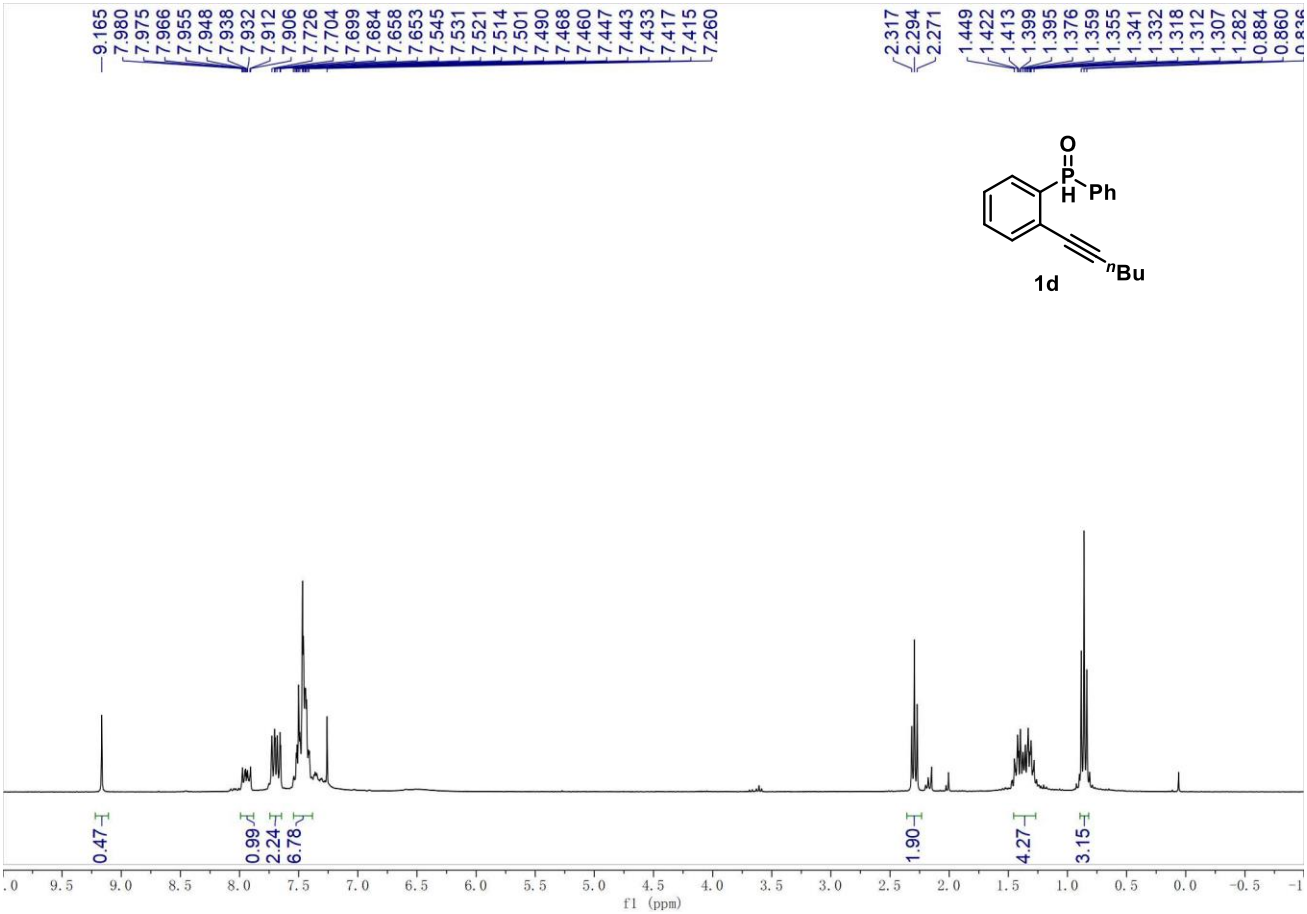


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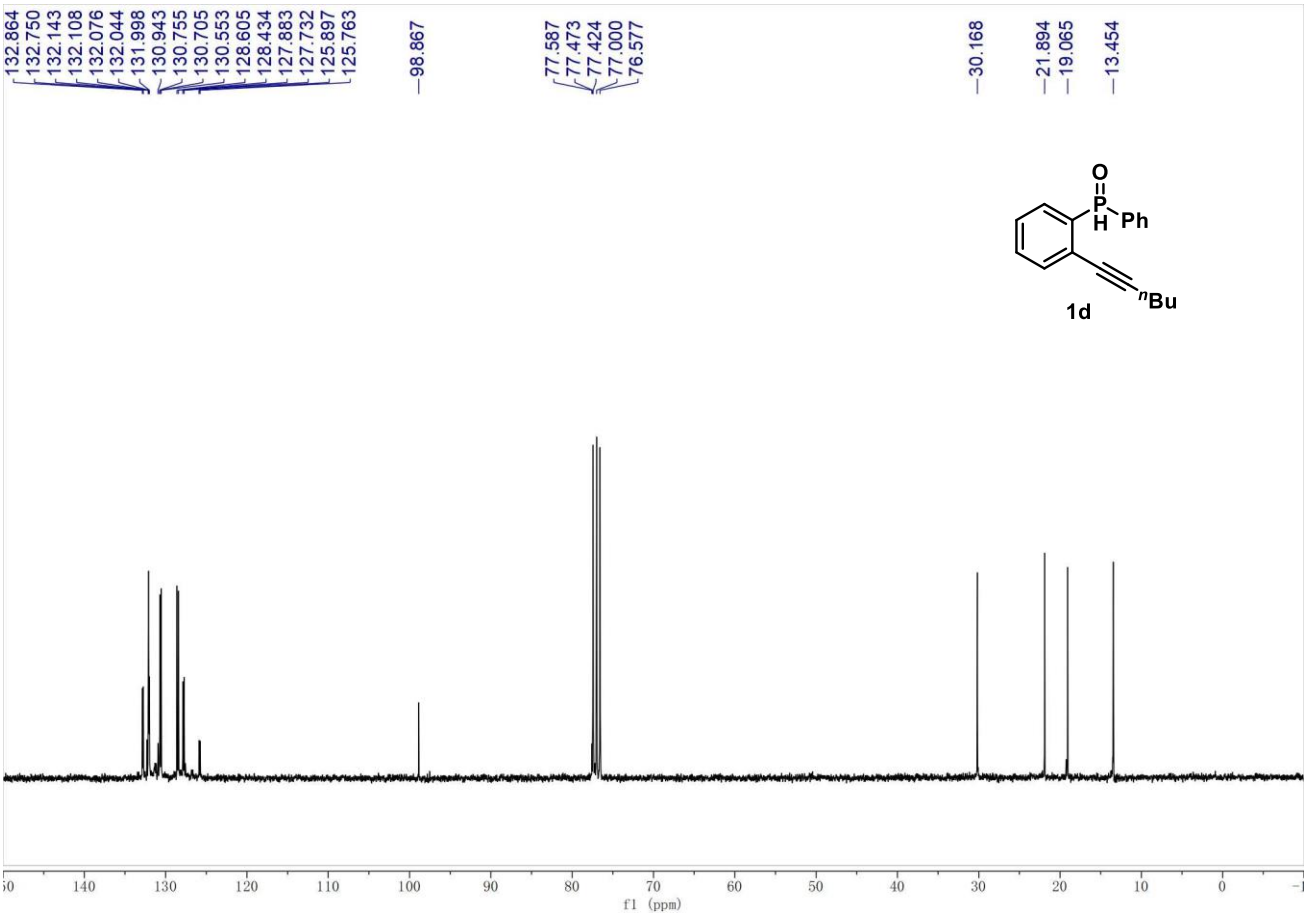

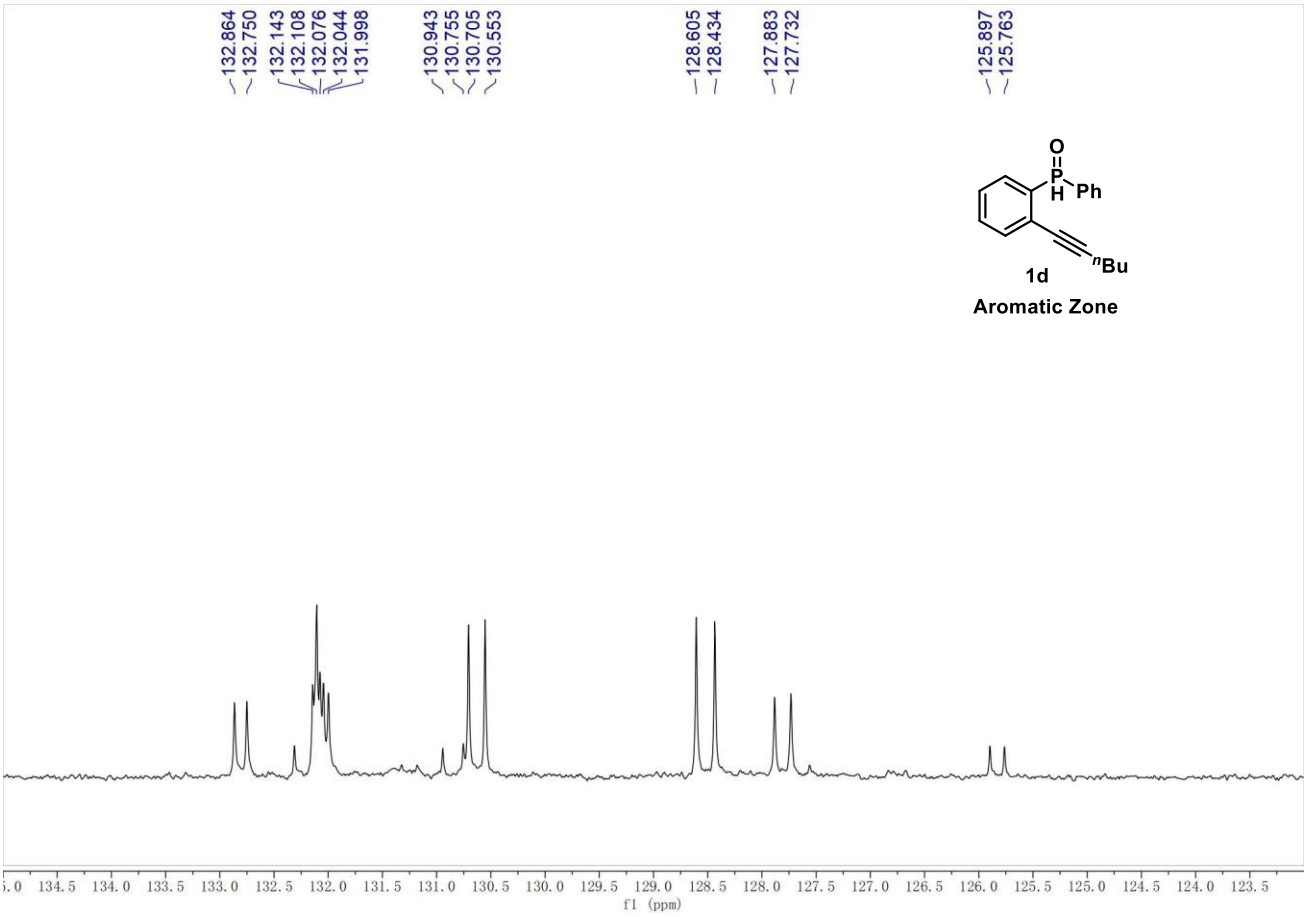


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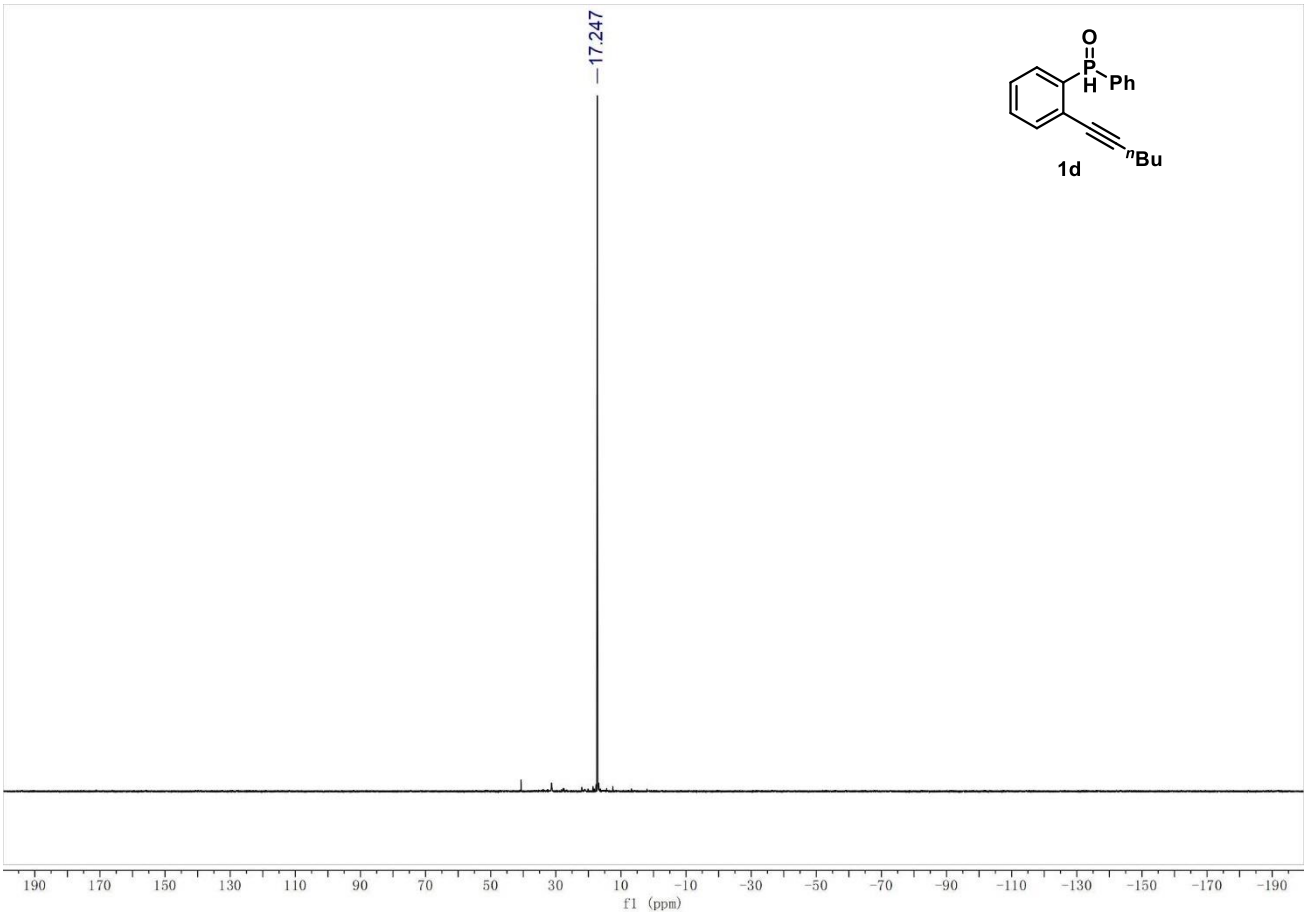

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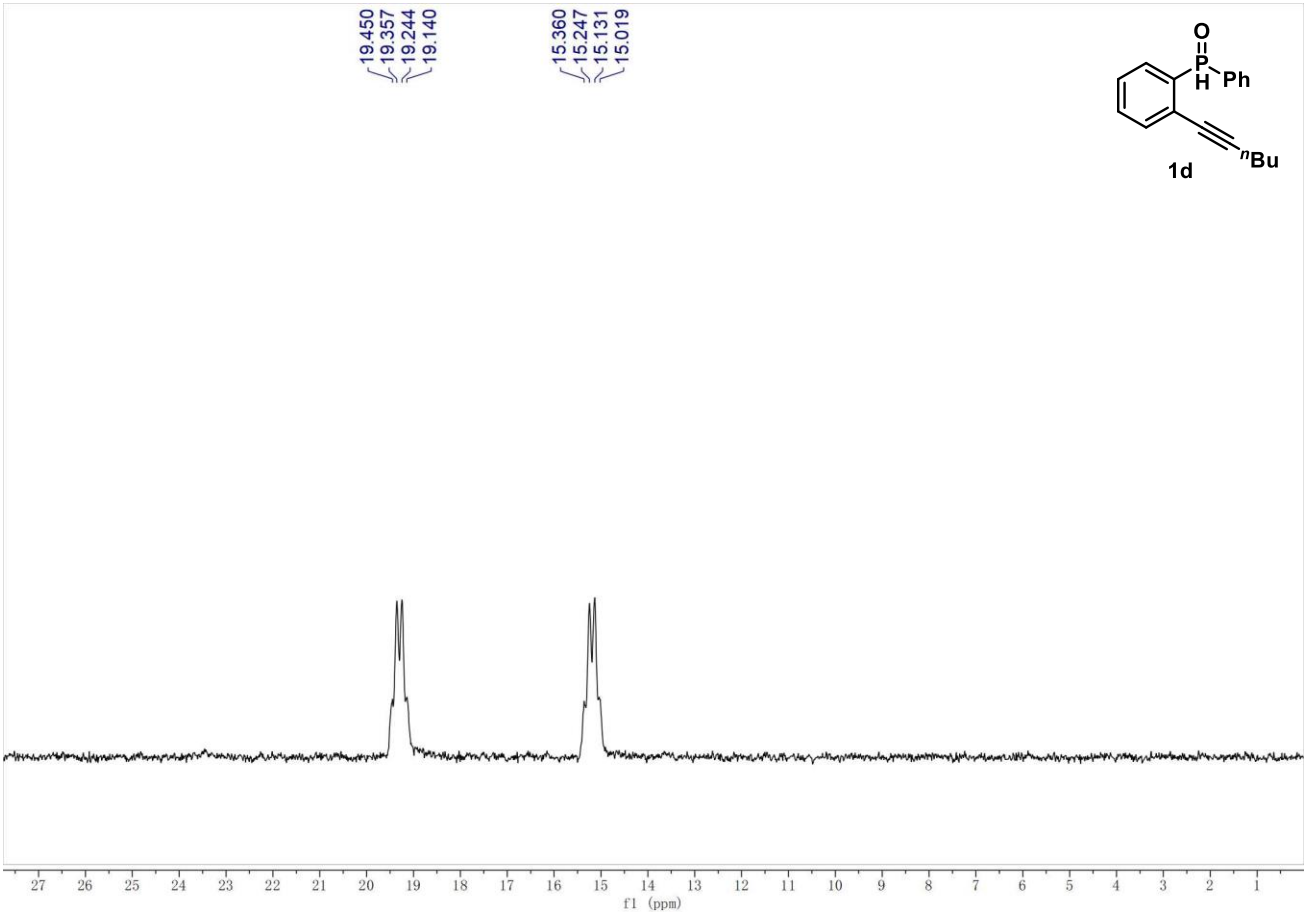


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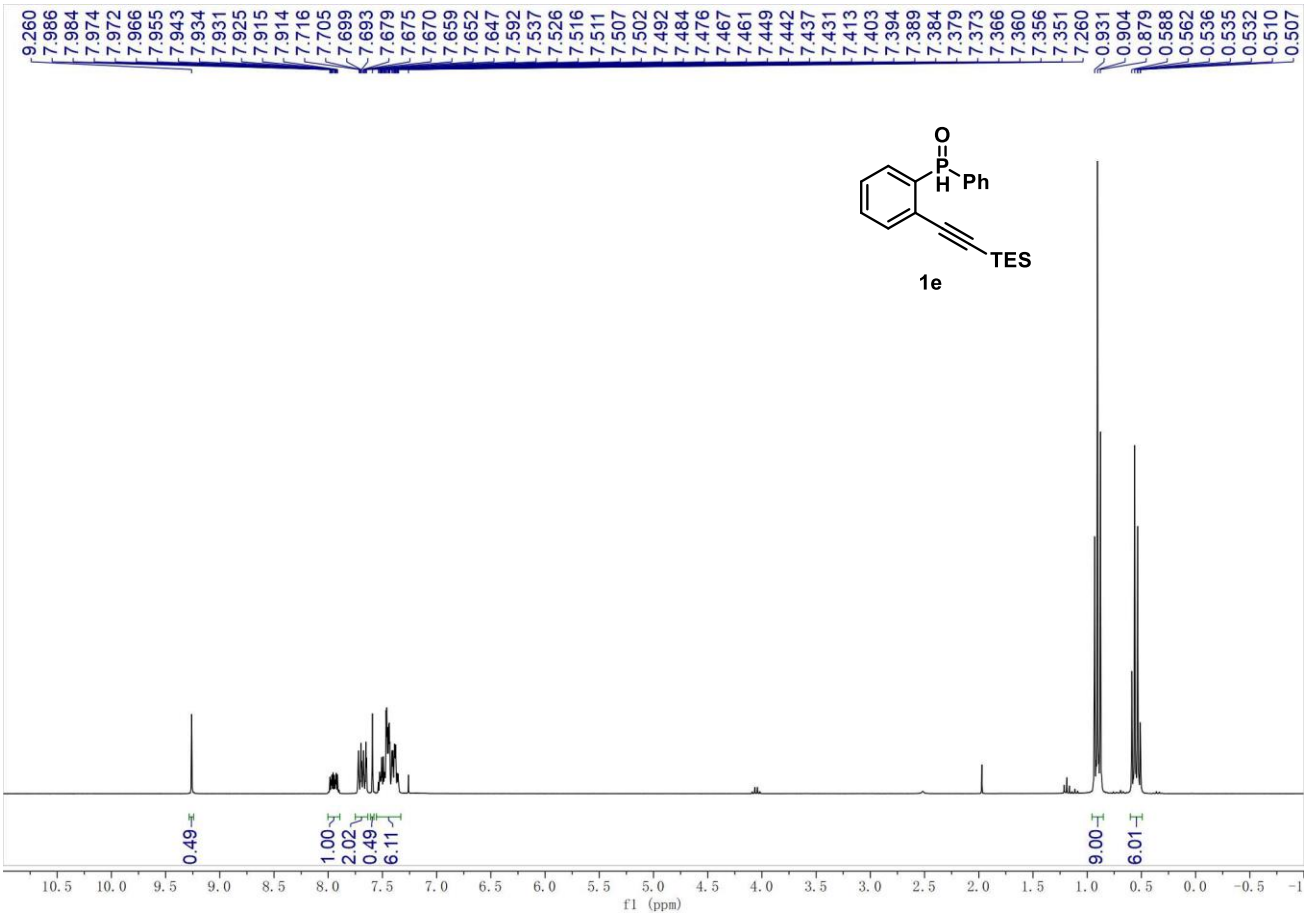

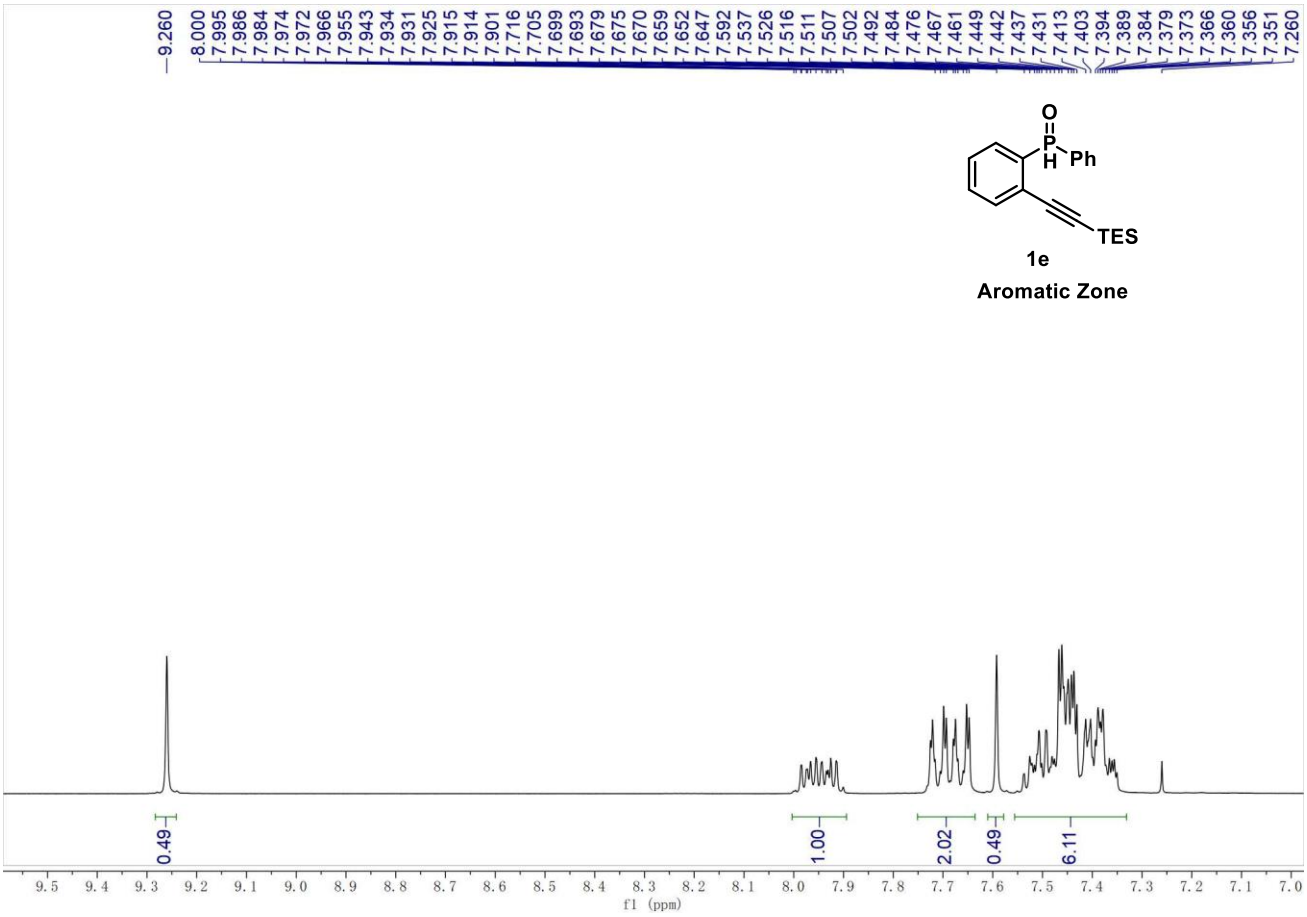


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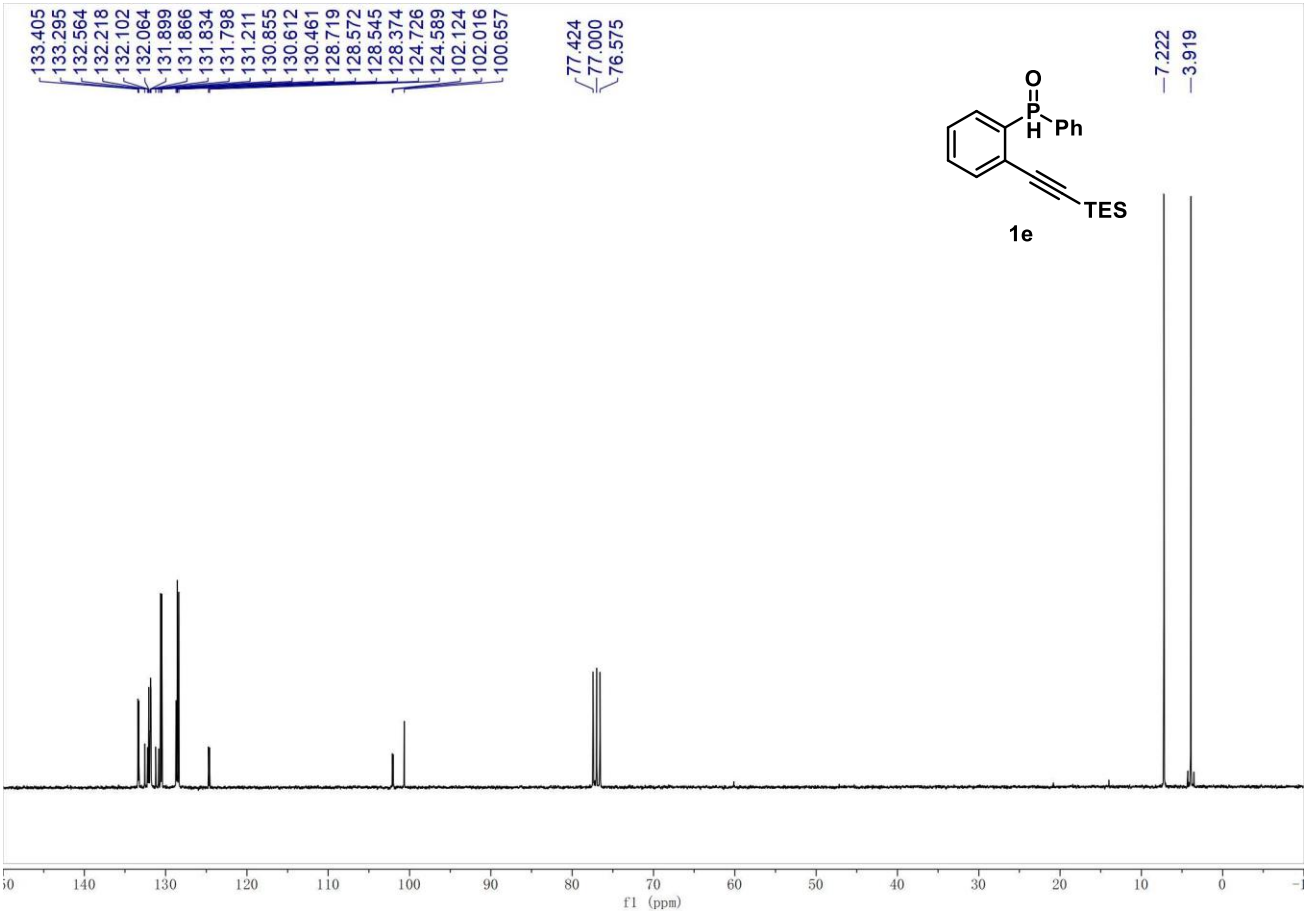

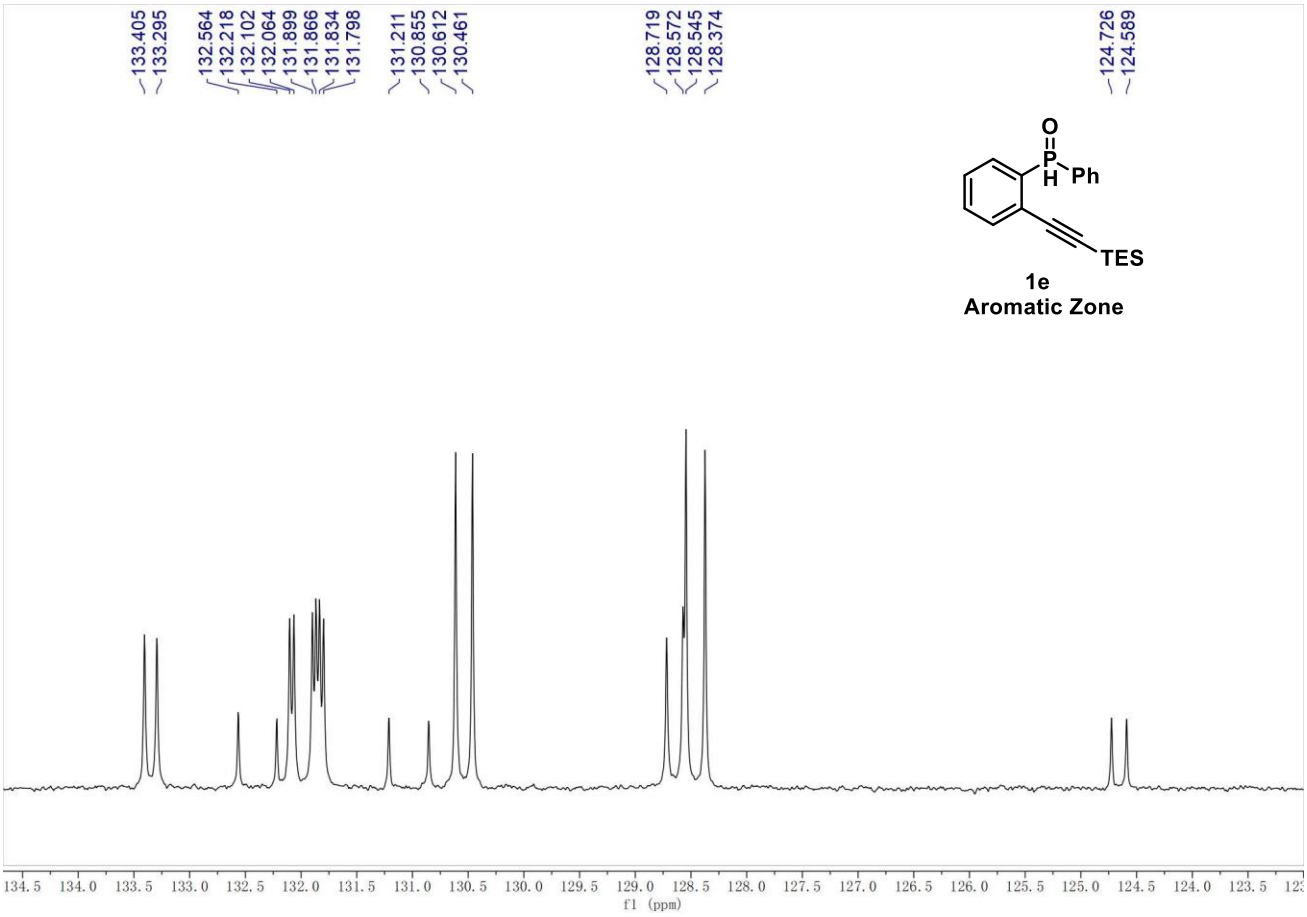


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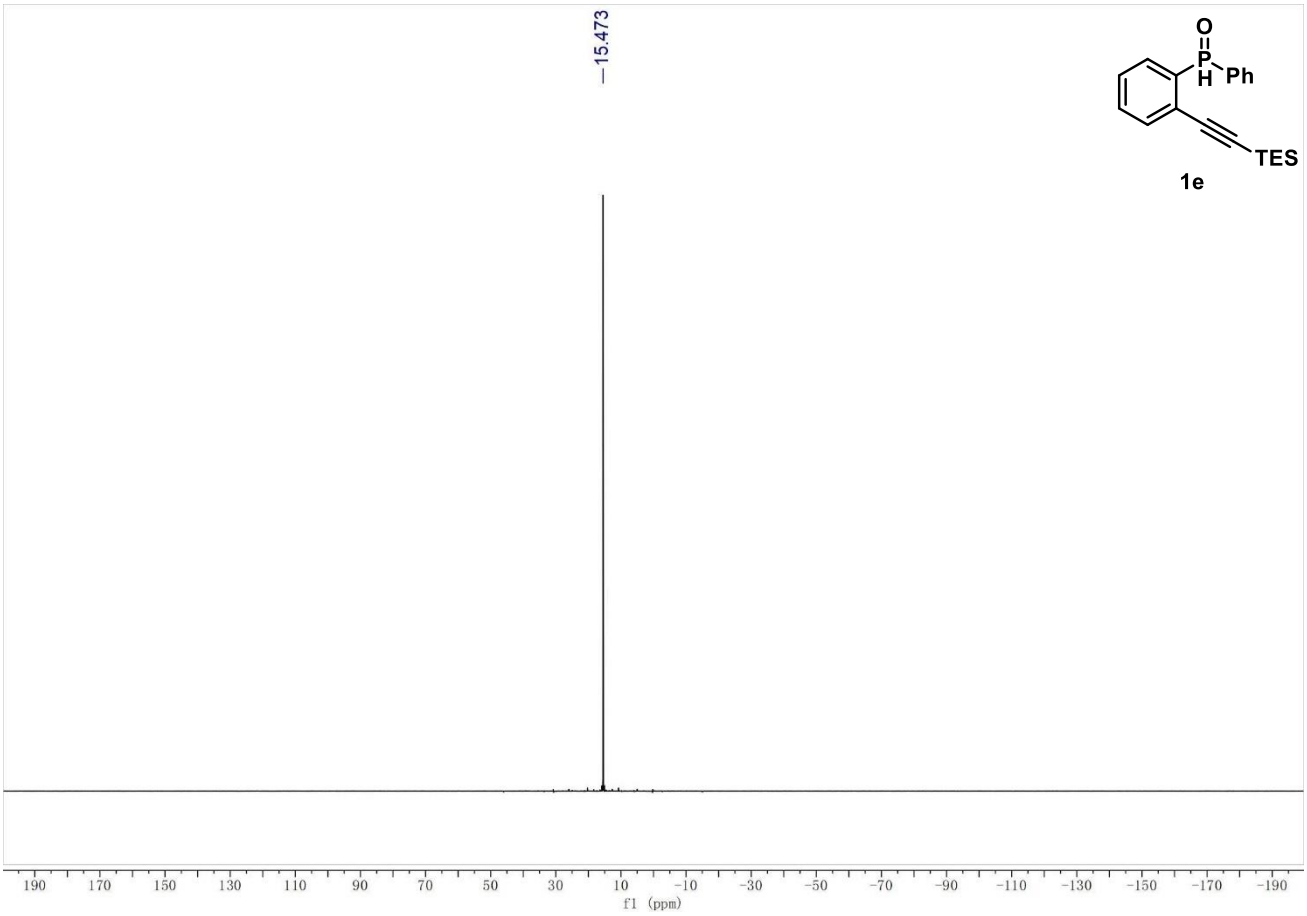

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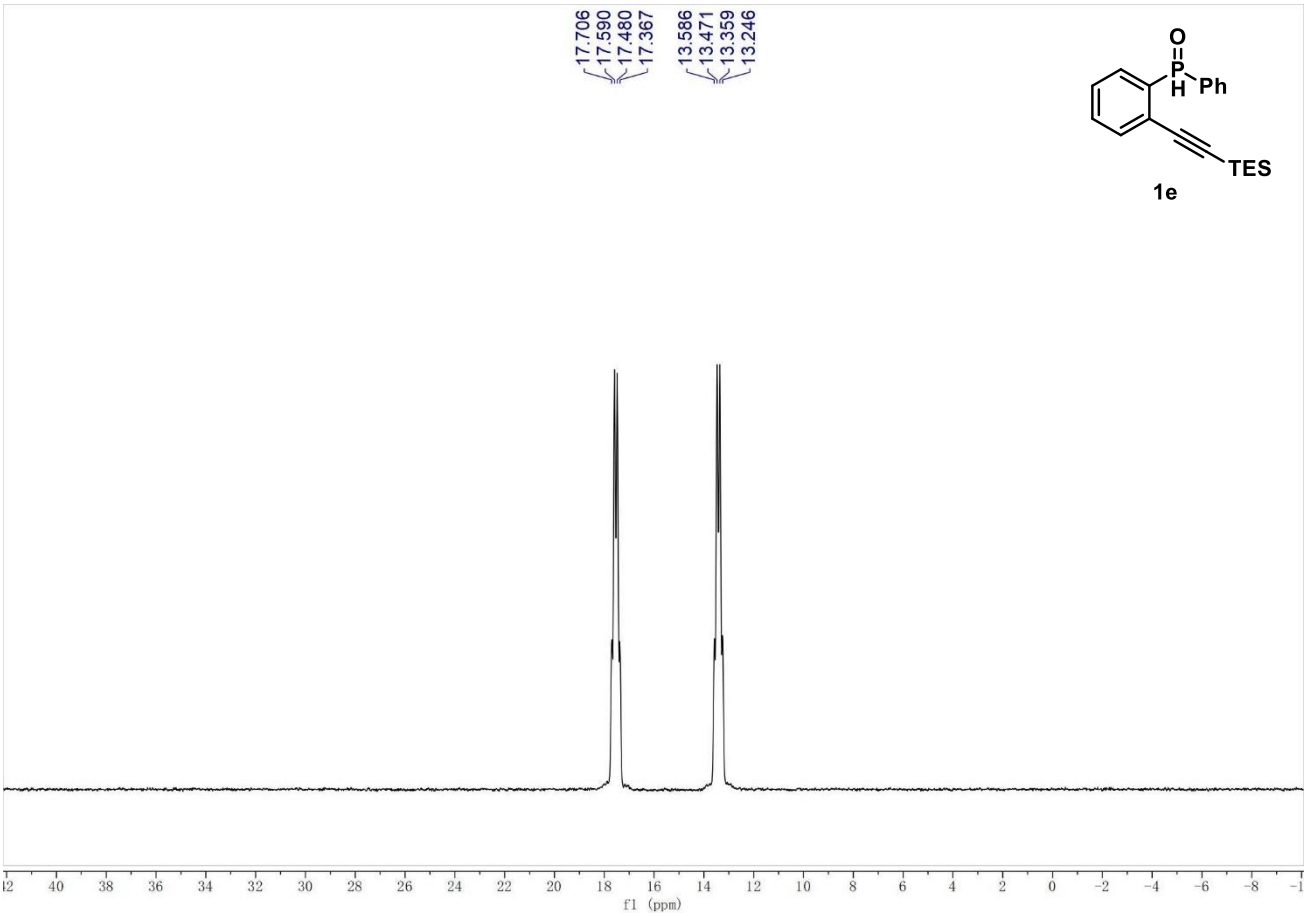


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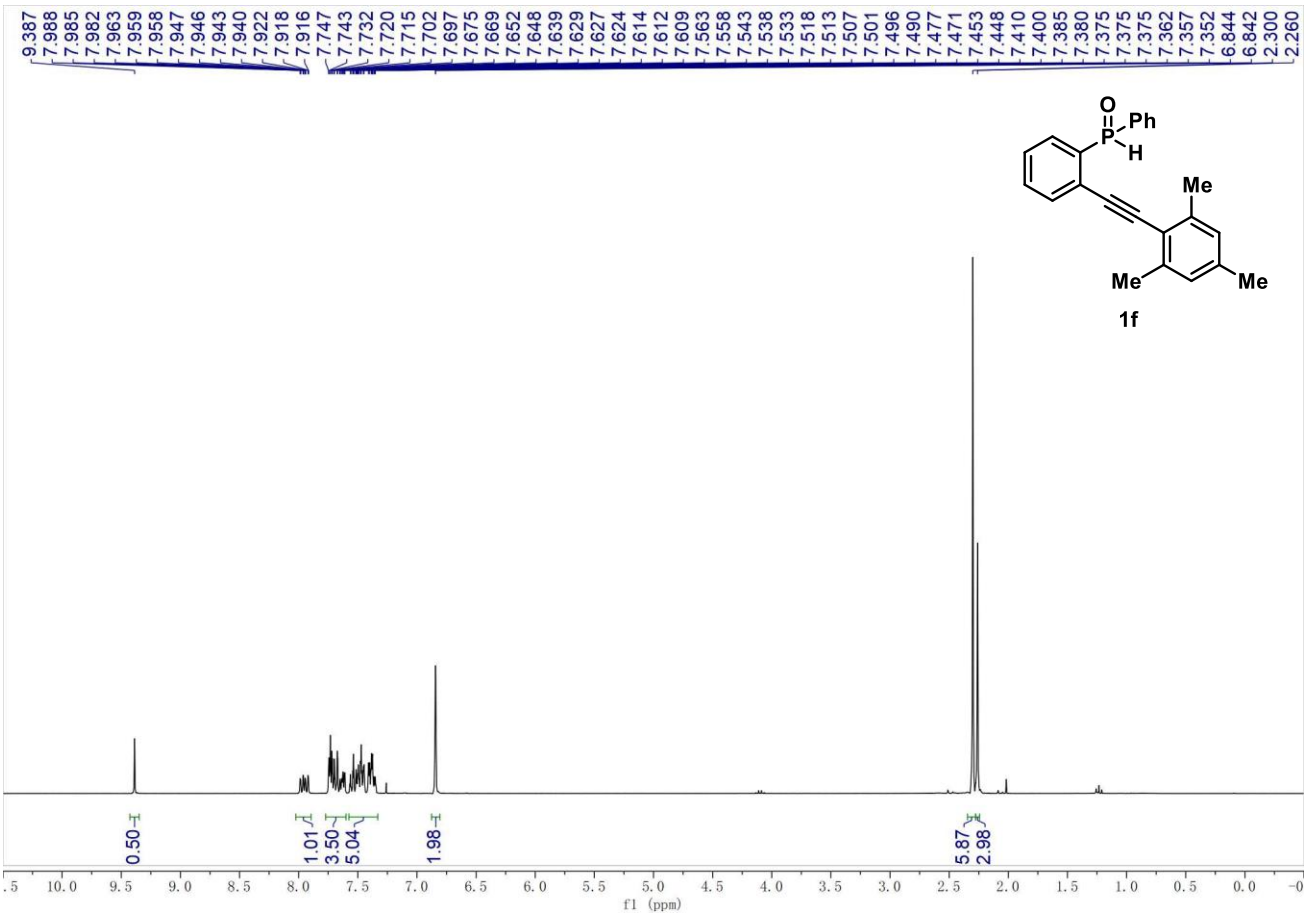

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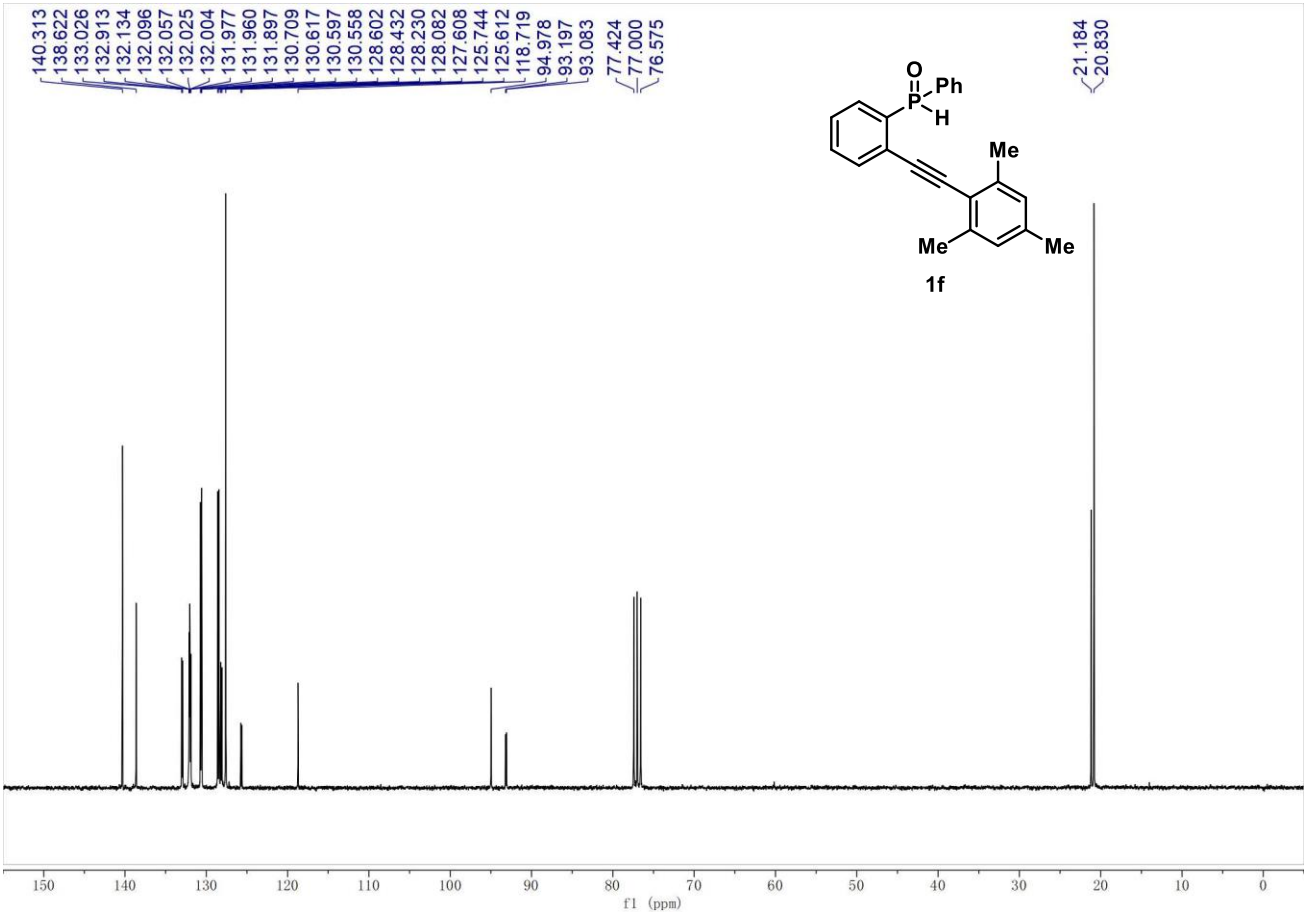


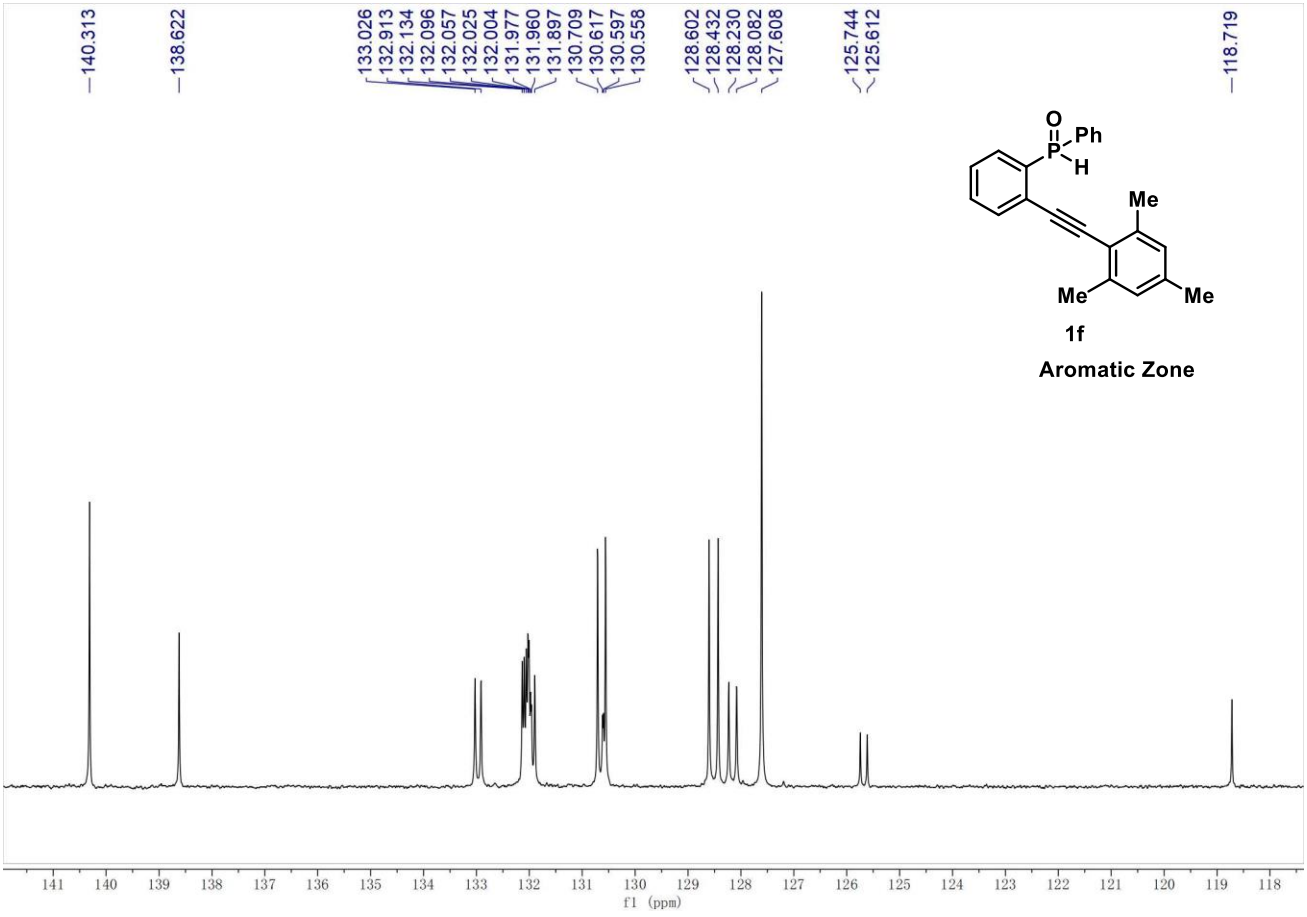

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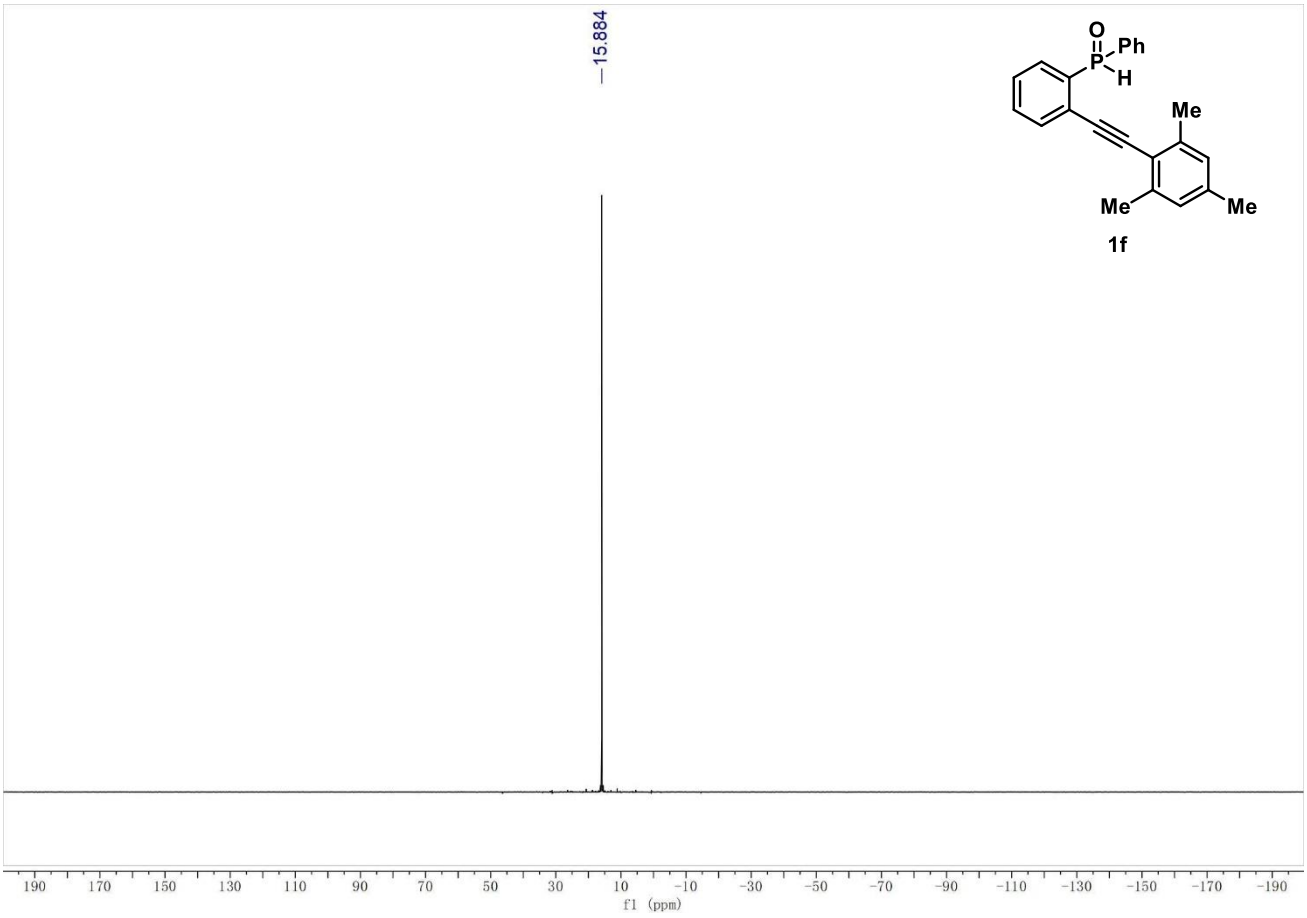


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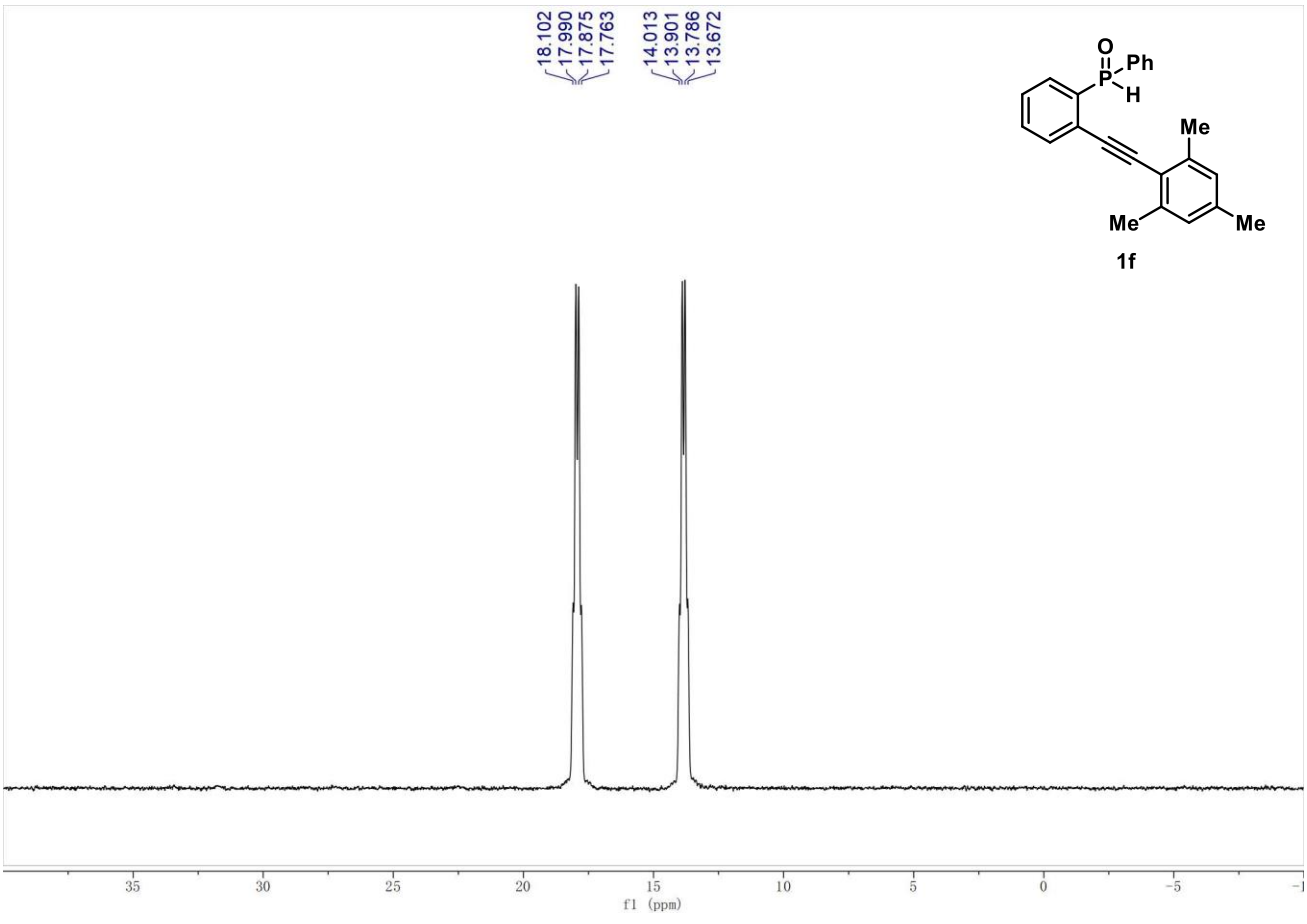

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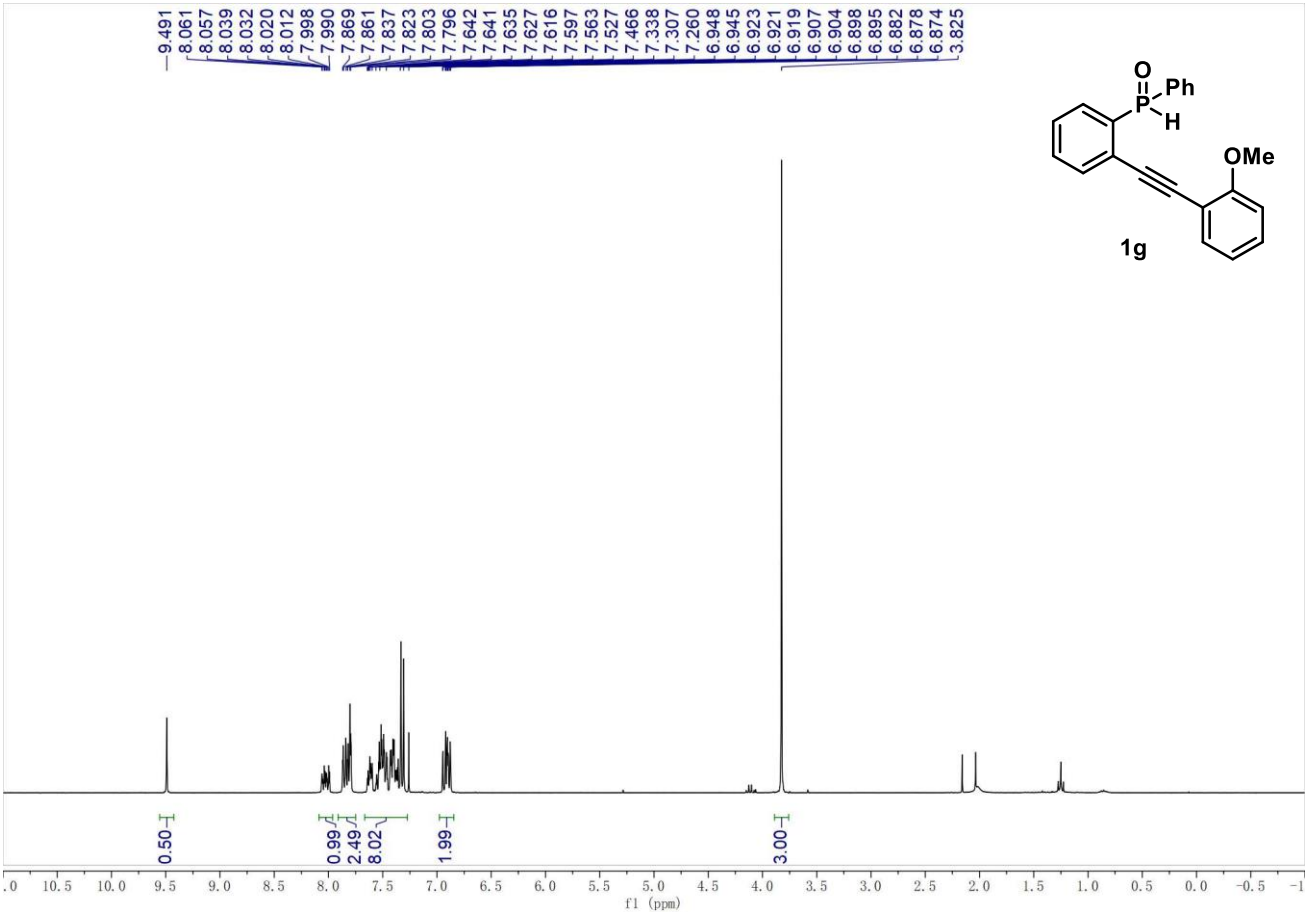


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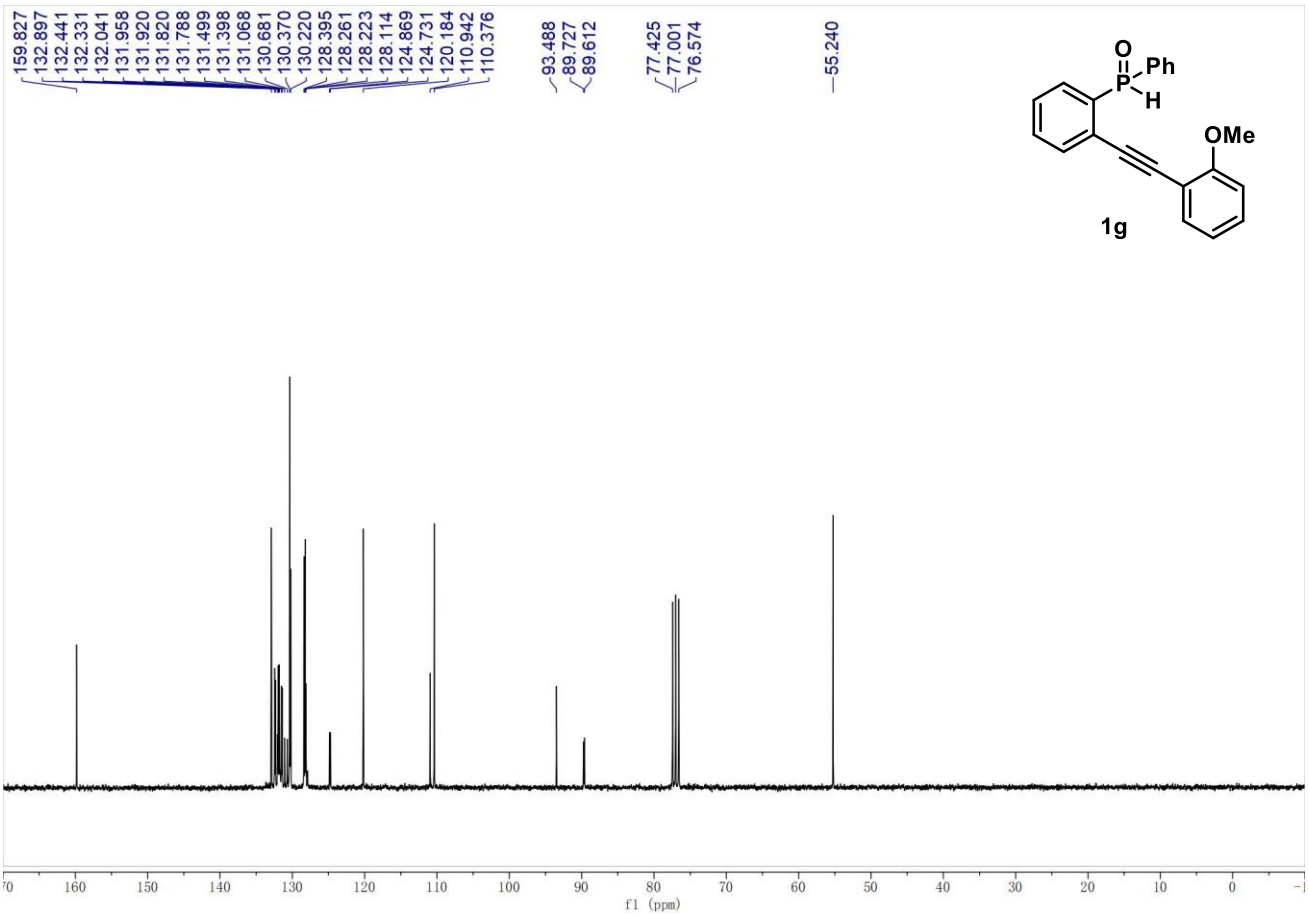

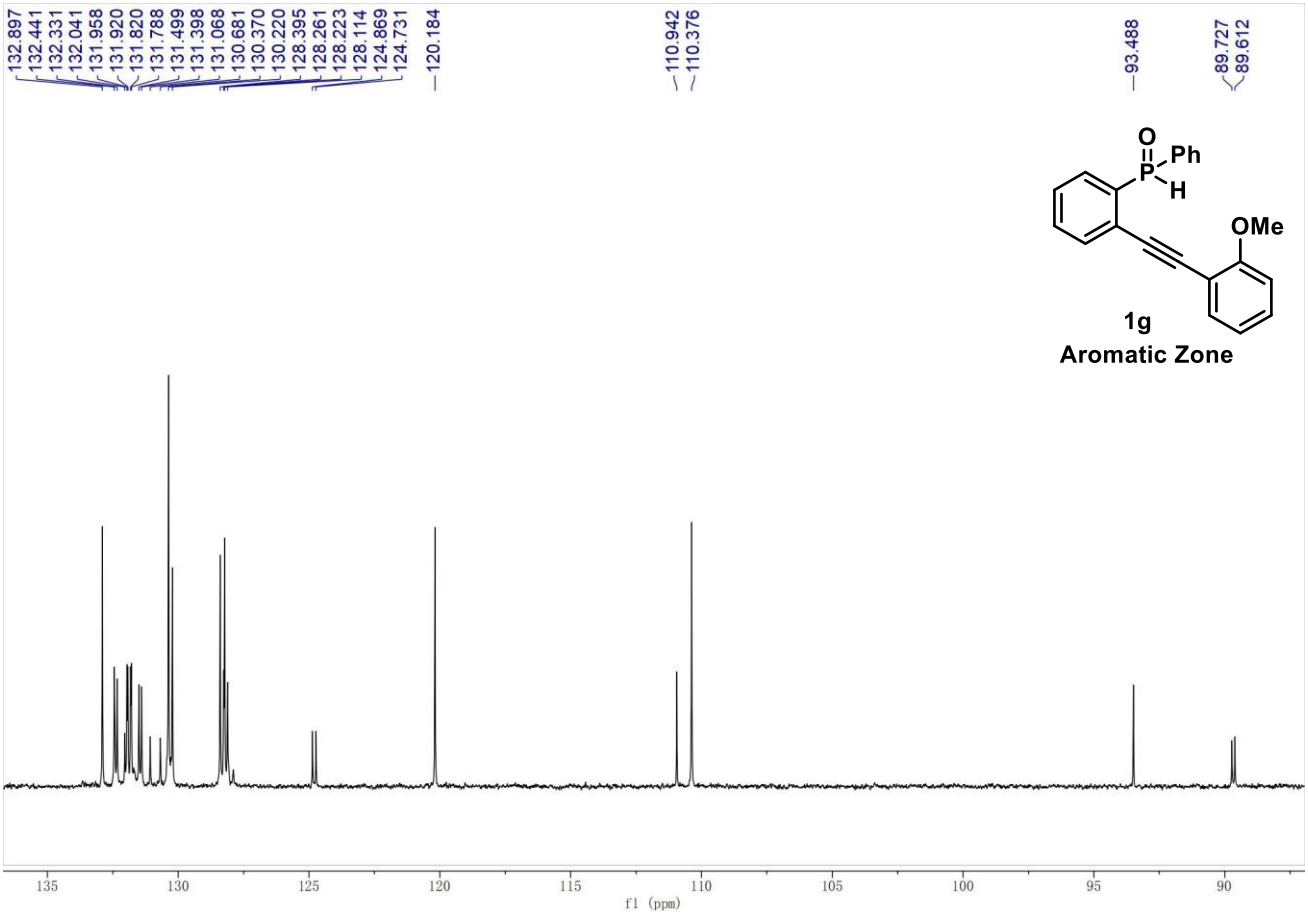


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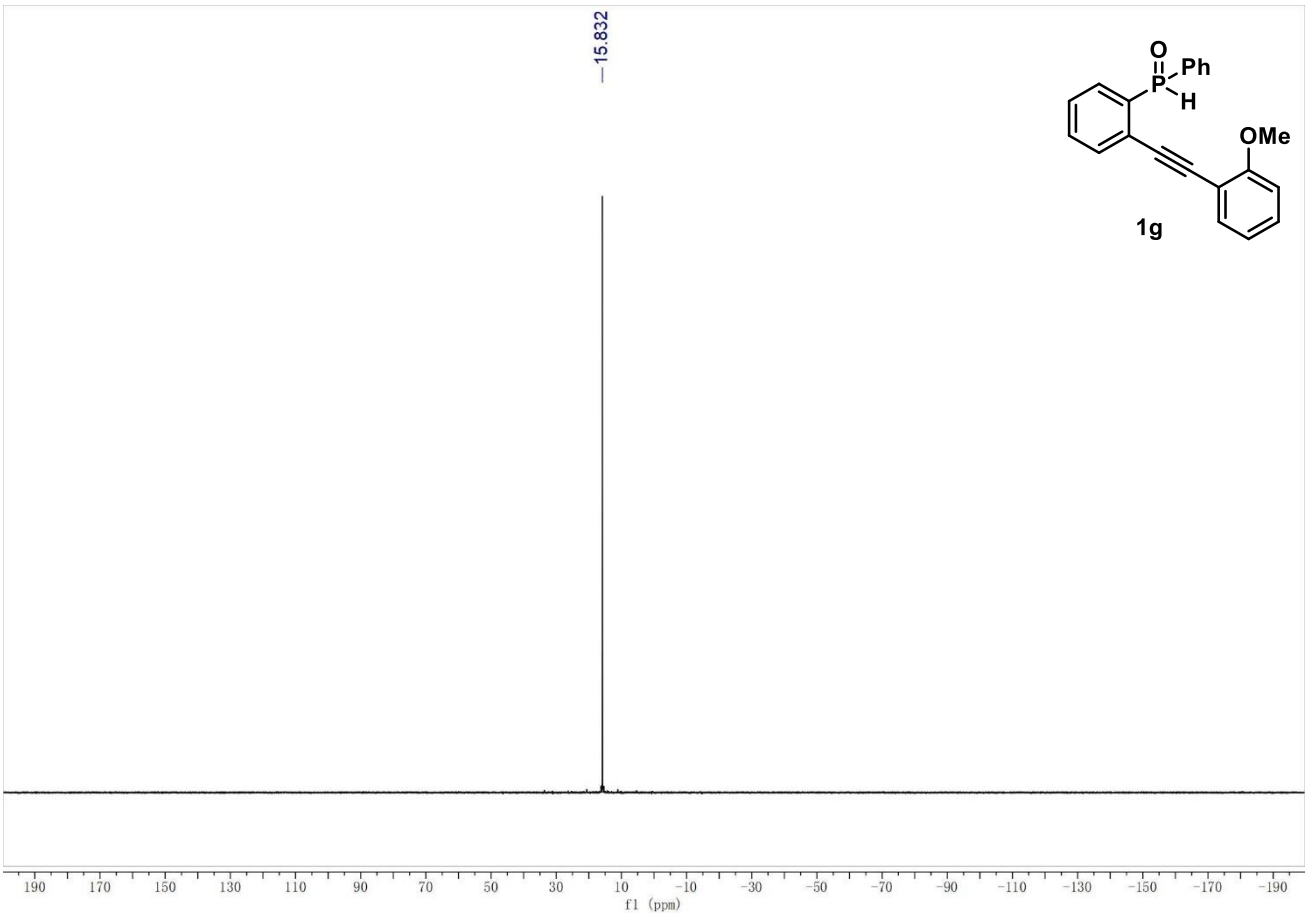

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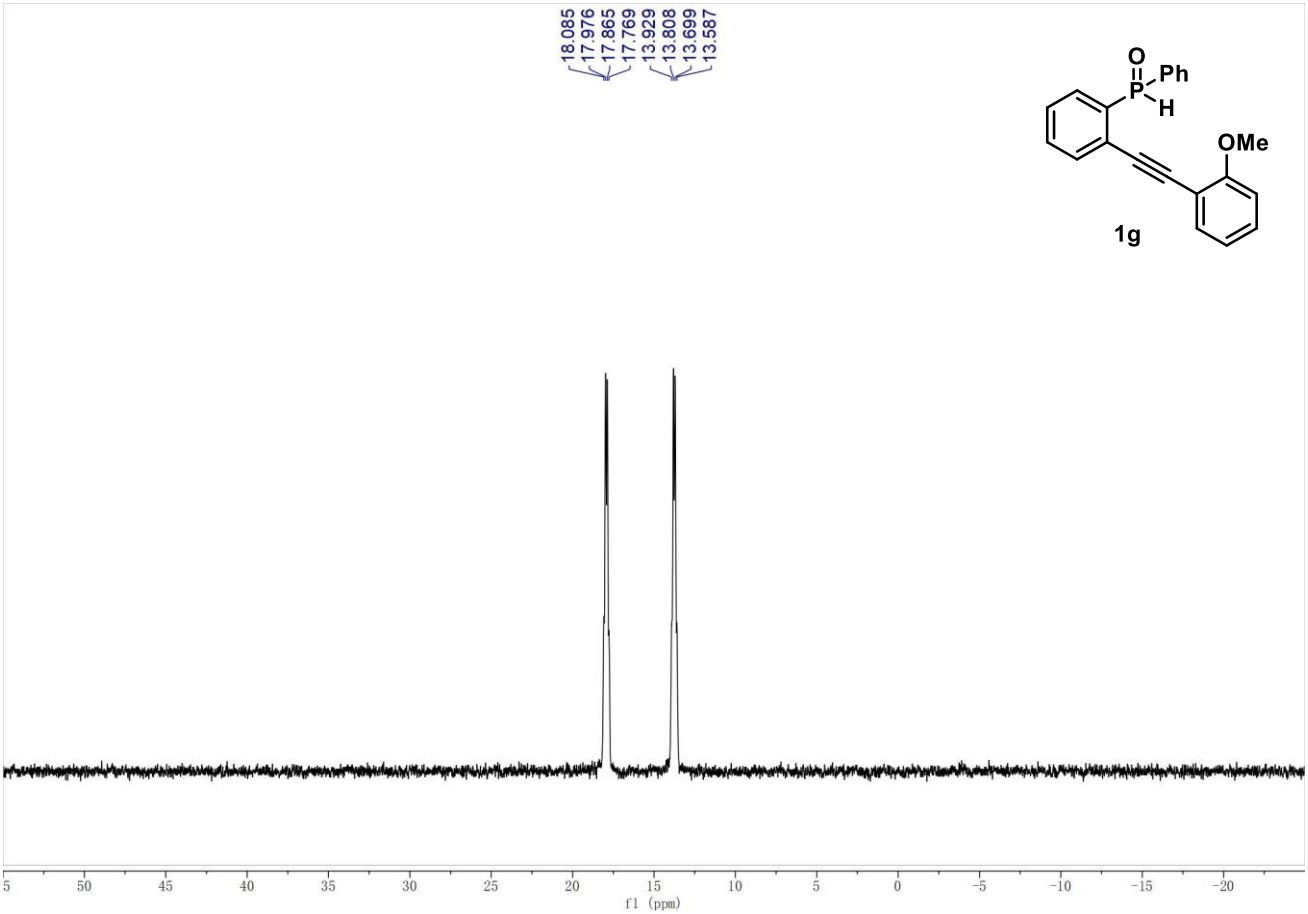


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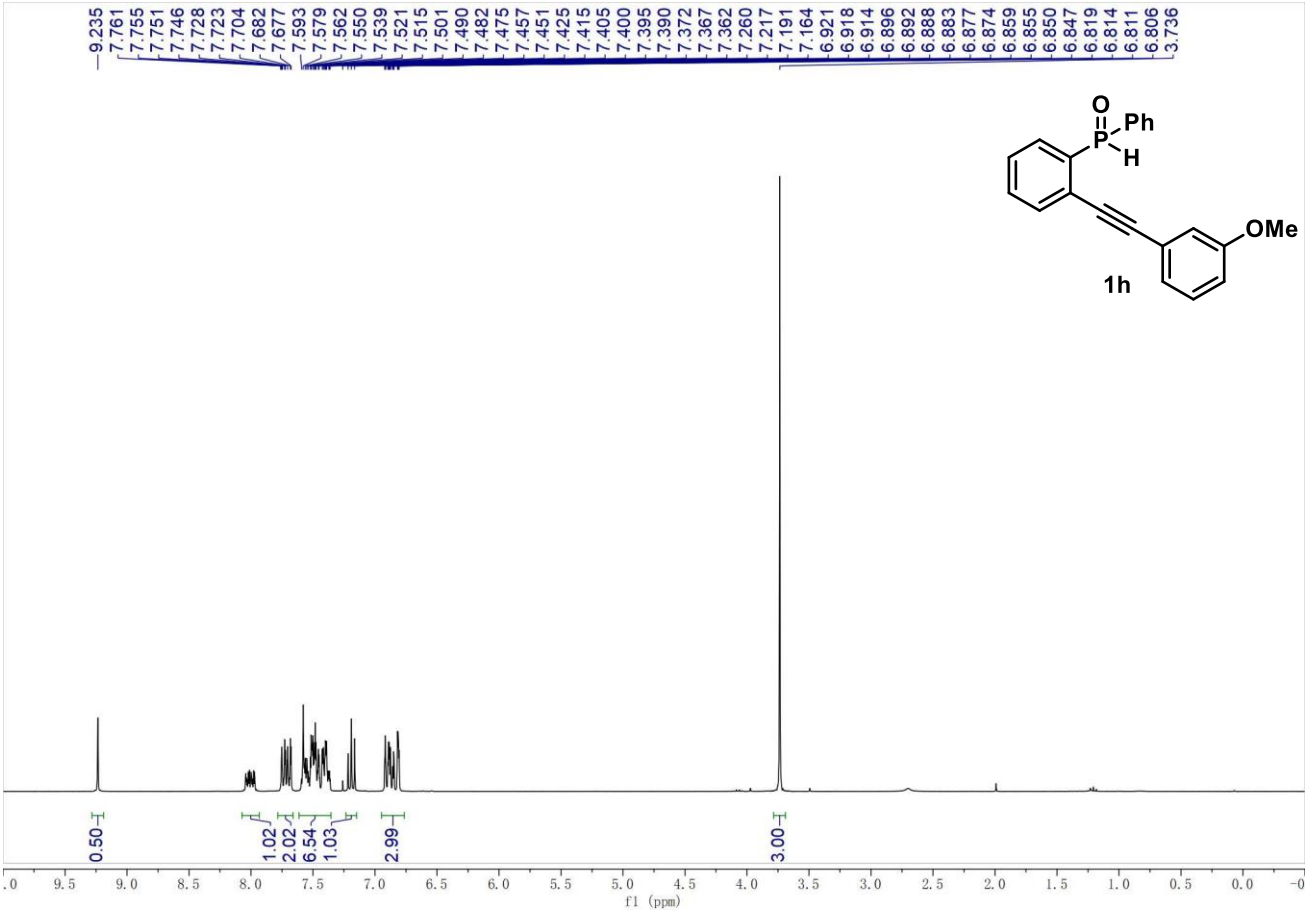
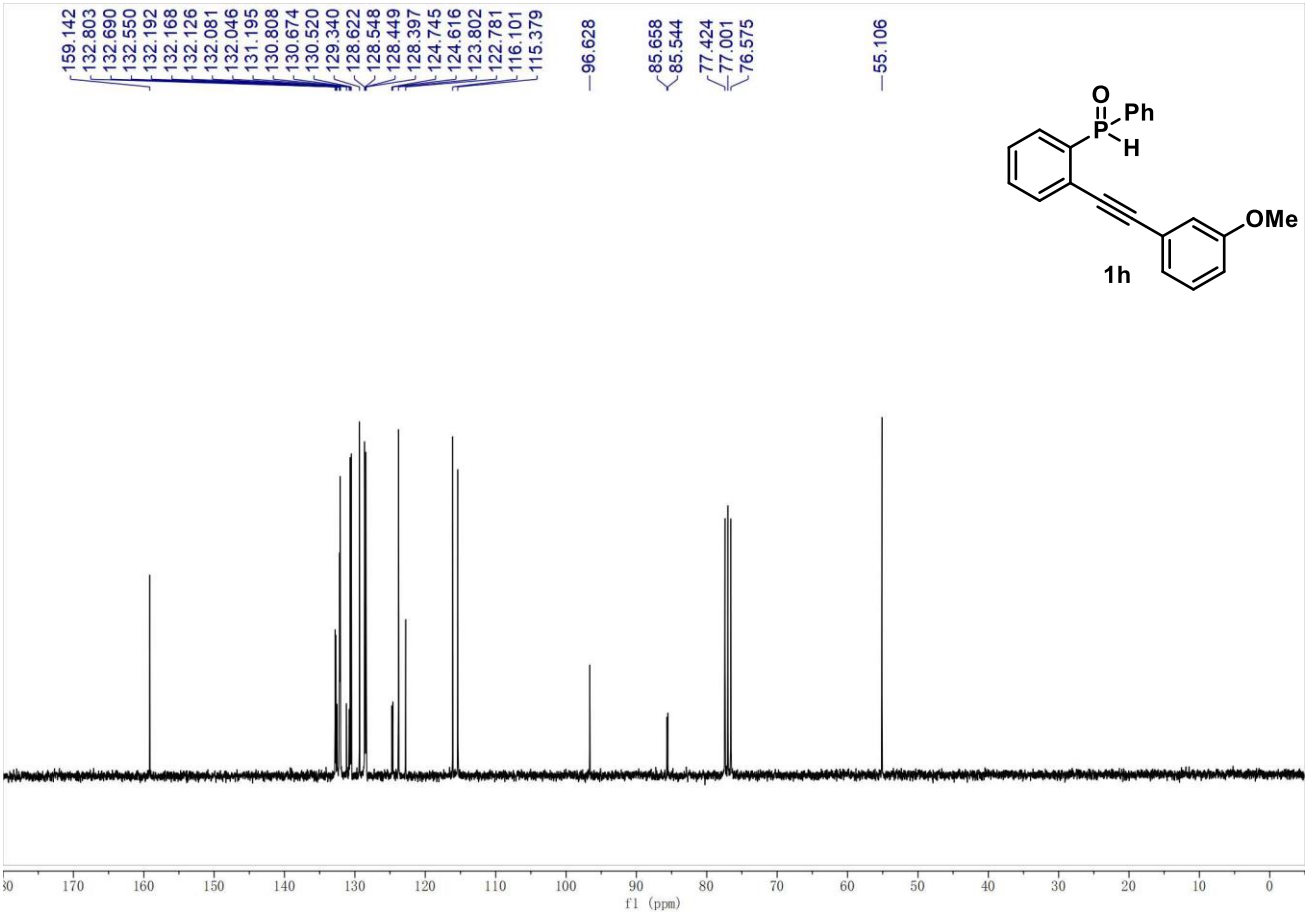
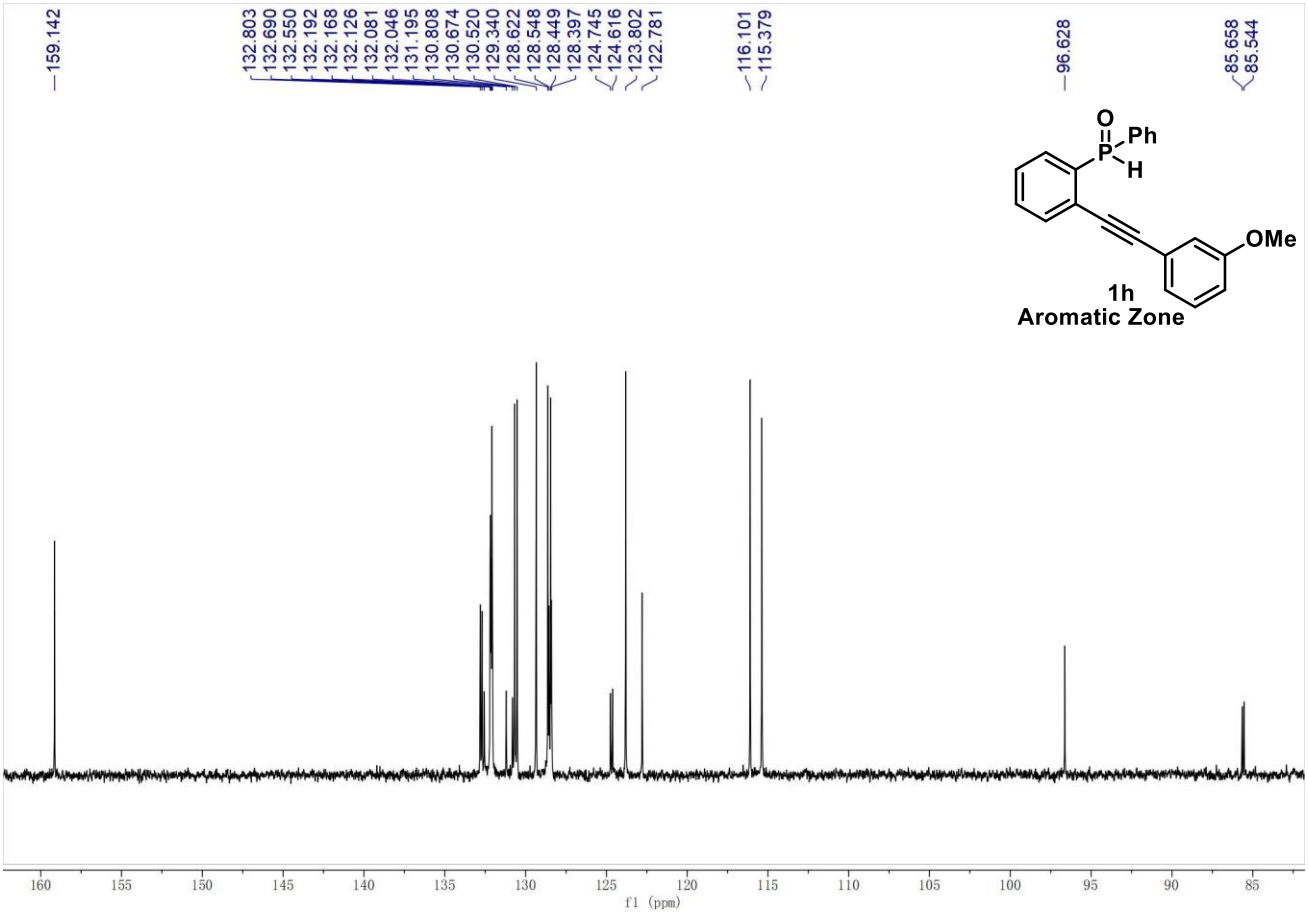
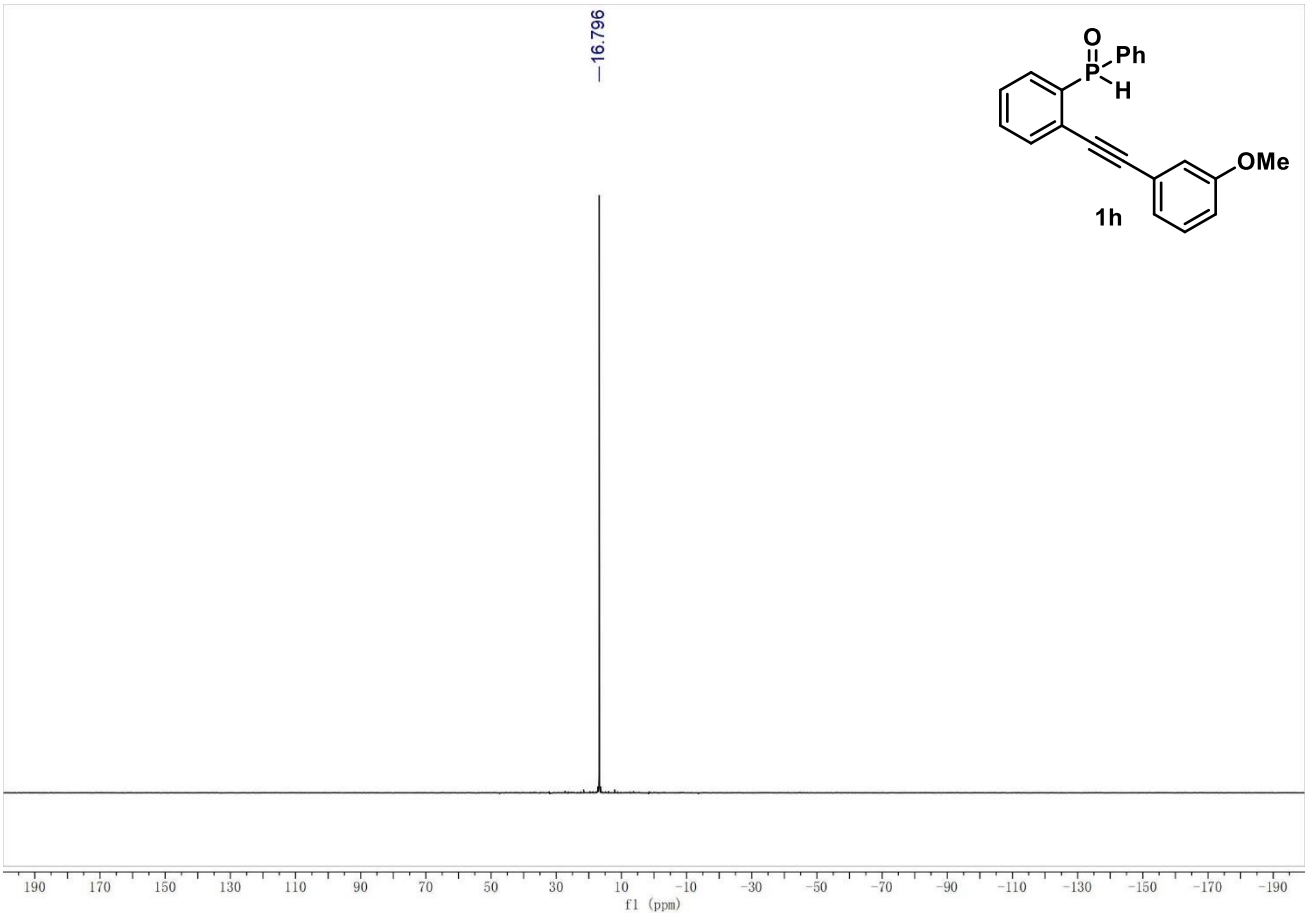


**$^{13}$C NMR spectrum of 1h (75 MHz, $CDCl_3$)**

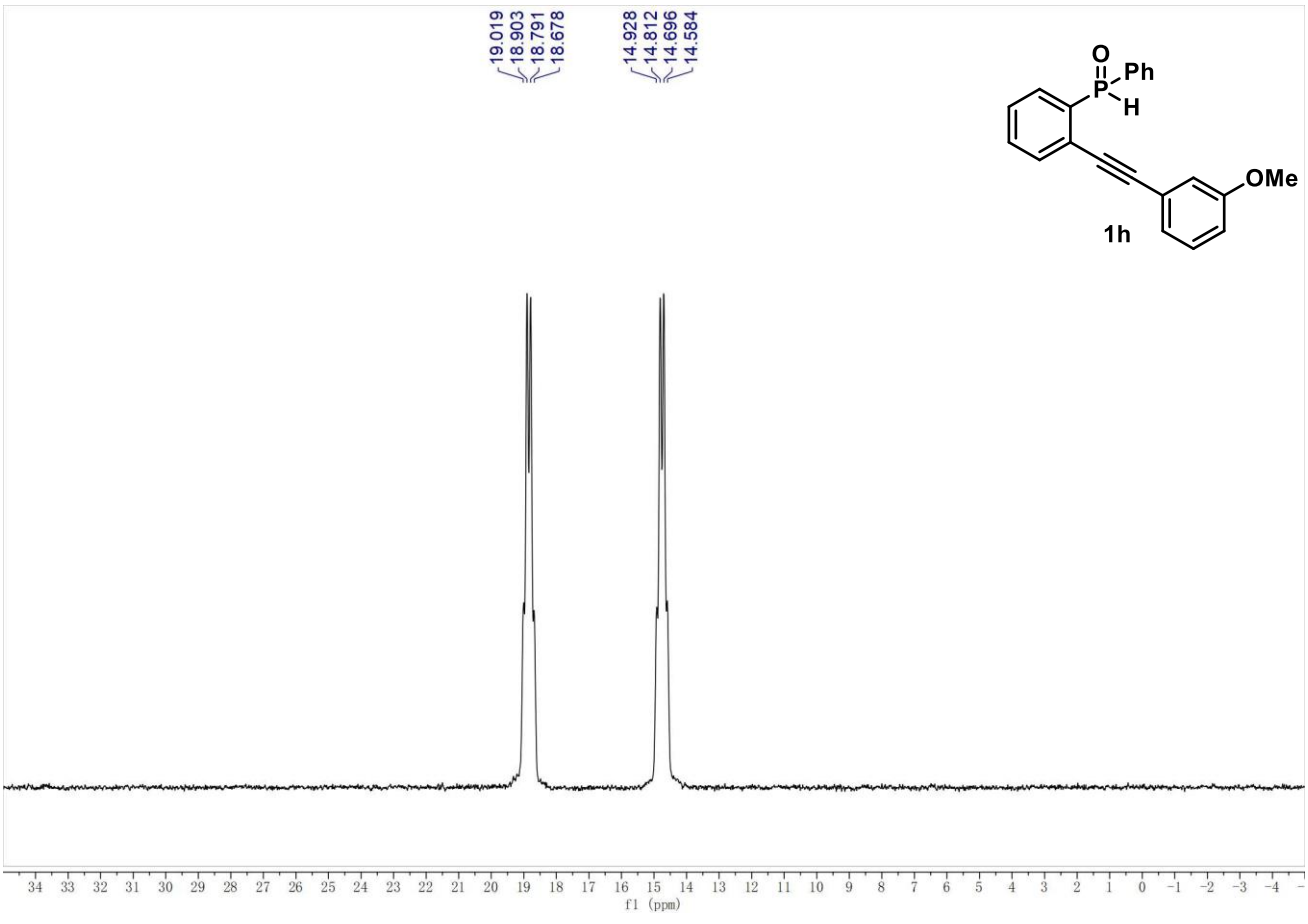


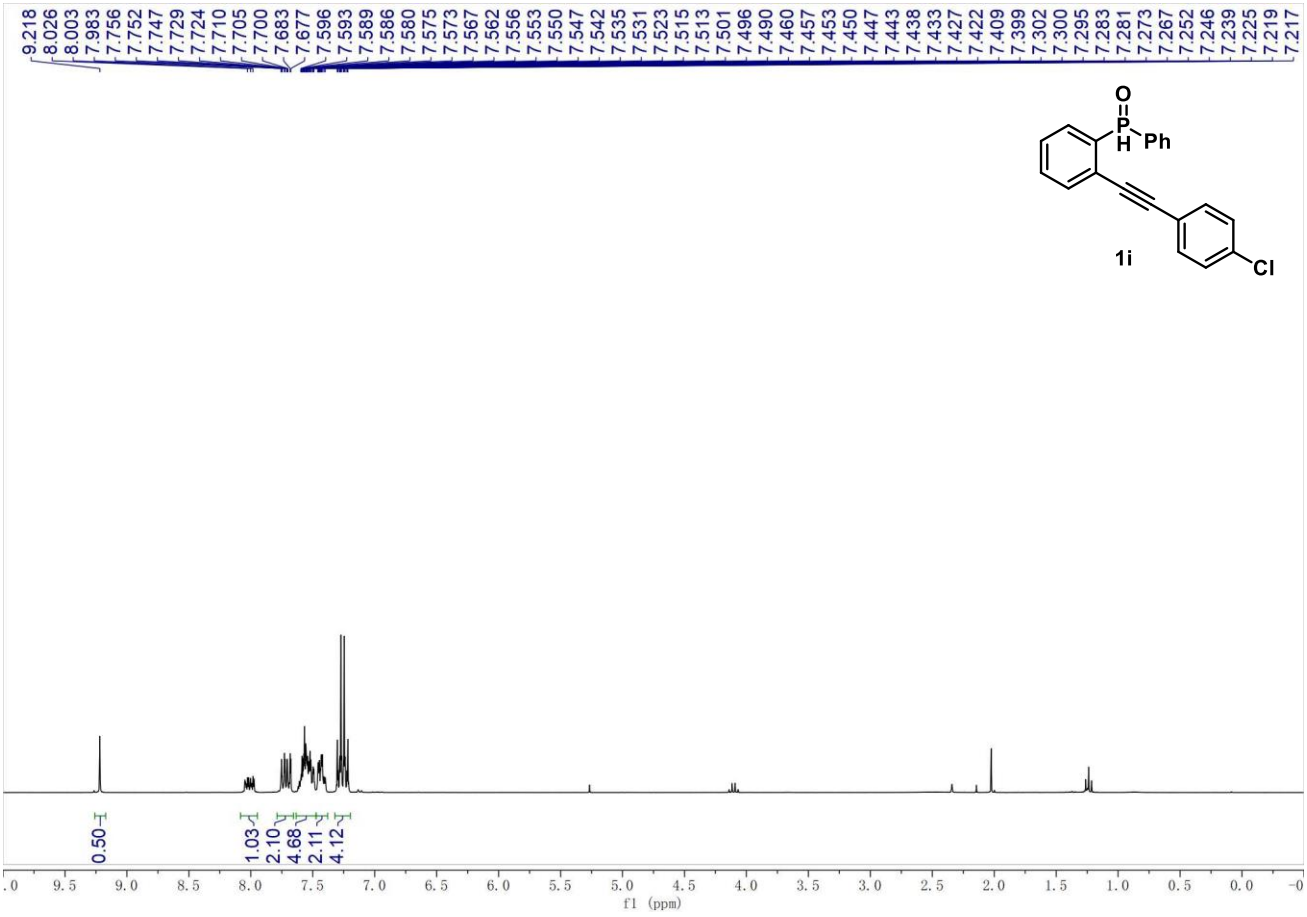
**$^{31}P\{^{1}H\}$ NMR spectrum of 1h (121 MHz, $CDCl_3$)**



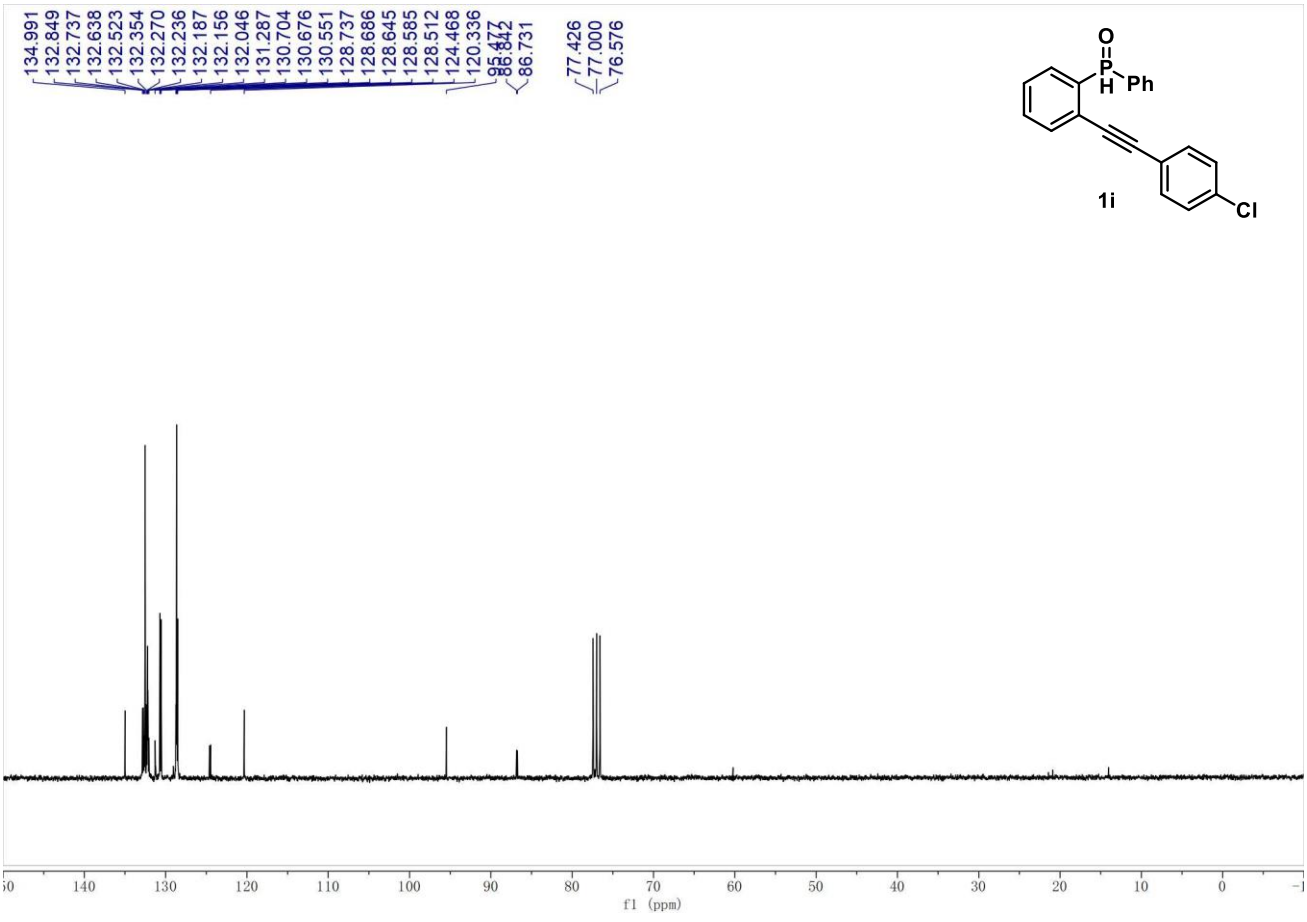

**$^{31}P$ NMR spectrum of 1h (121 MHz, $CDCl_3$)**

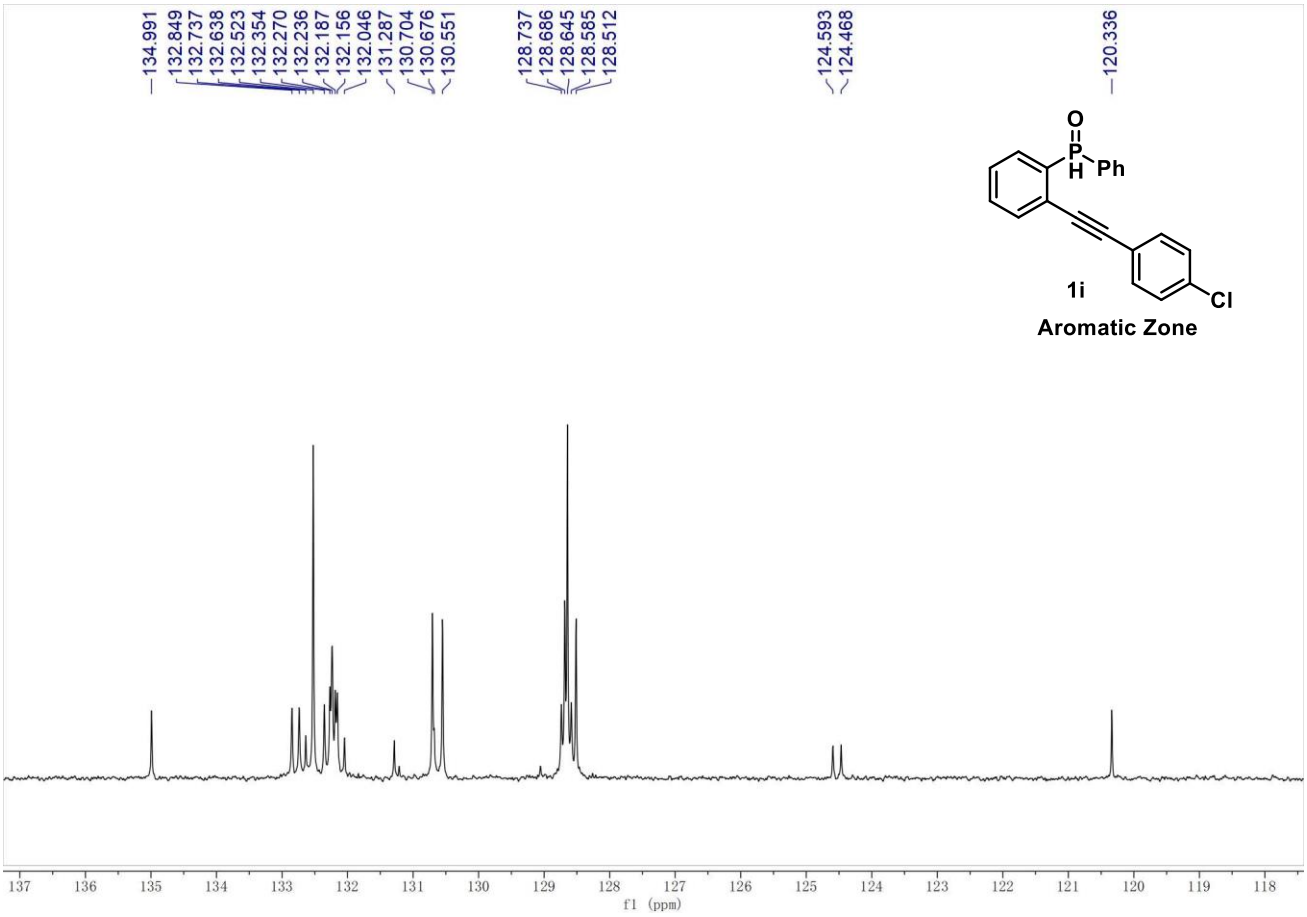


**$^{1}$H NMR spectrum of 1i (300 MHz, $CDCl_3$)**

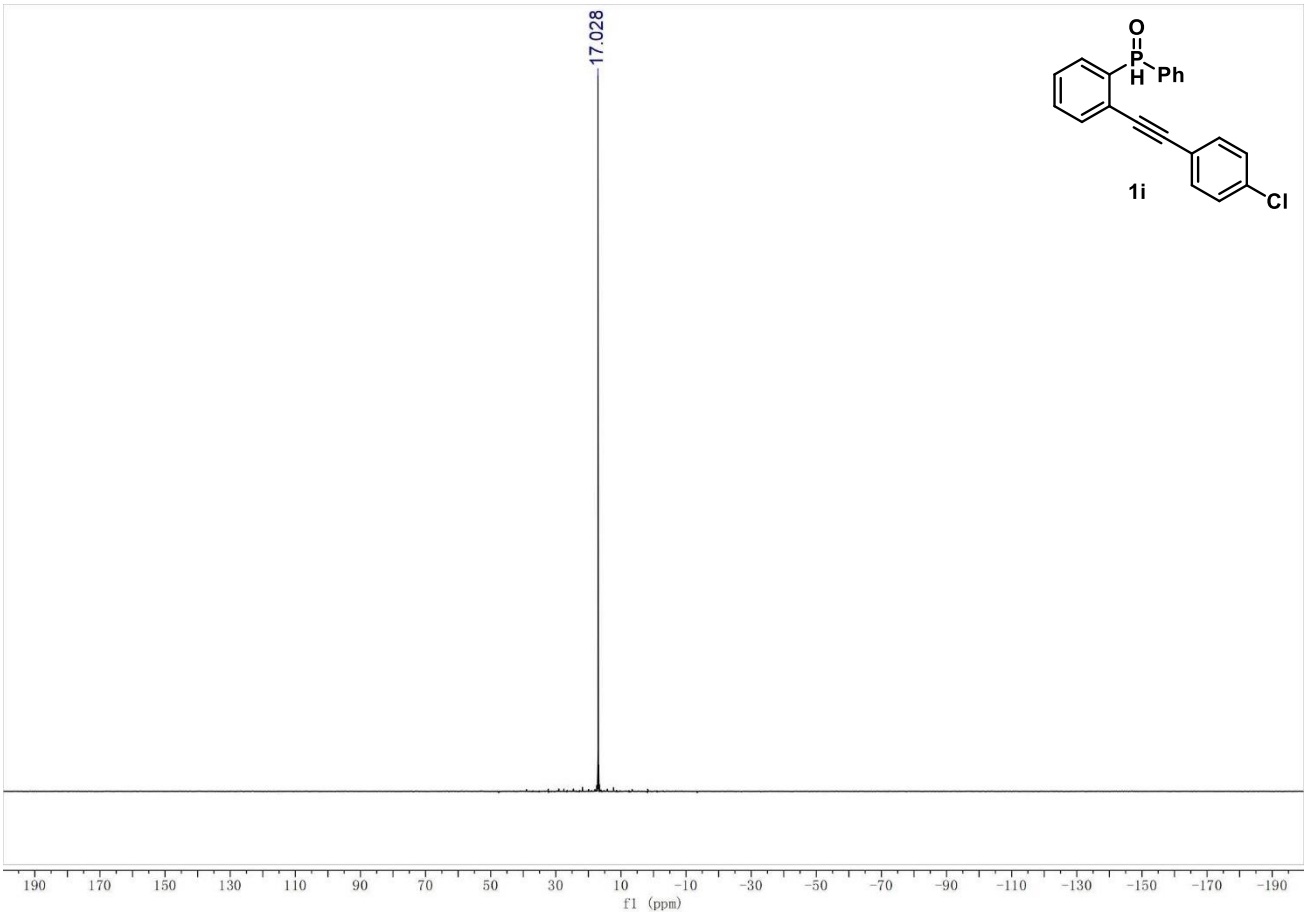



**$^{13}$C NMR spectrum of 1i (75 MHz, $CDCl_3$)**

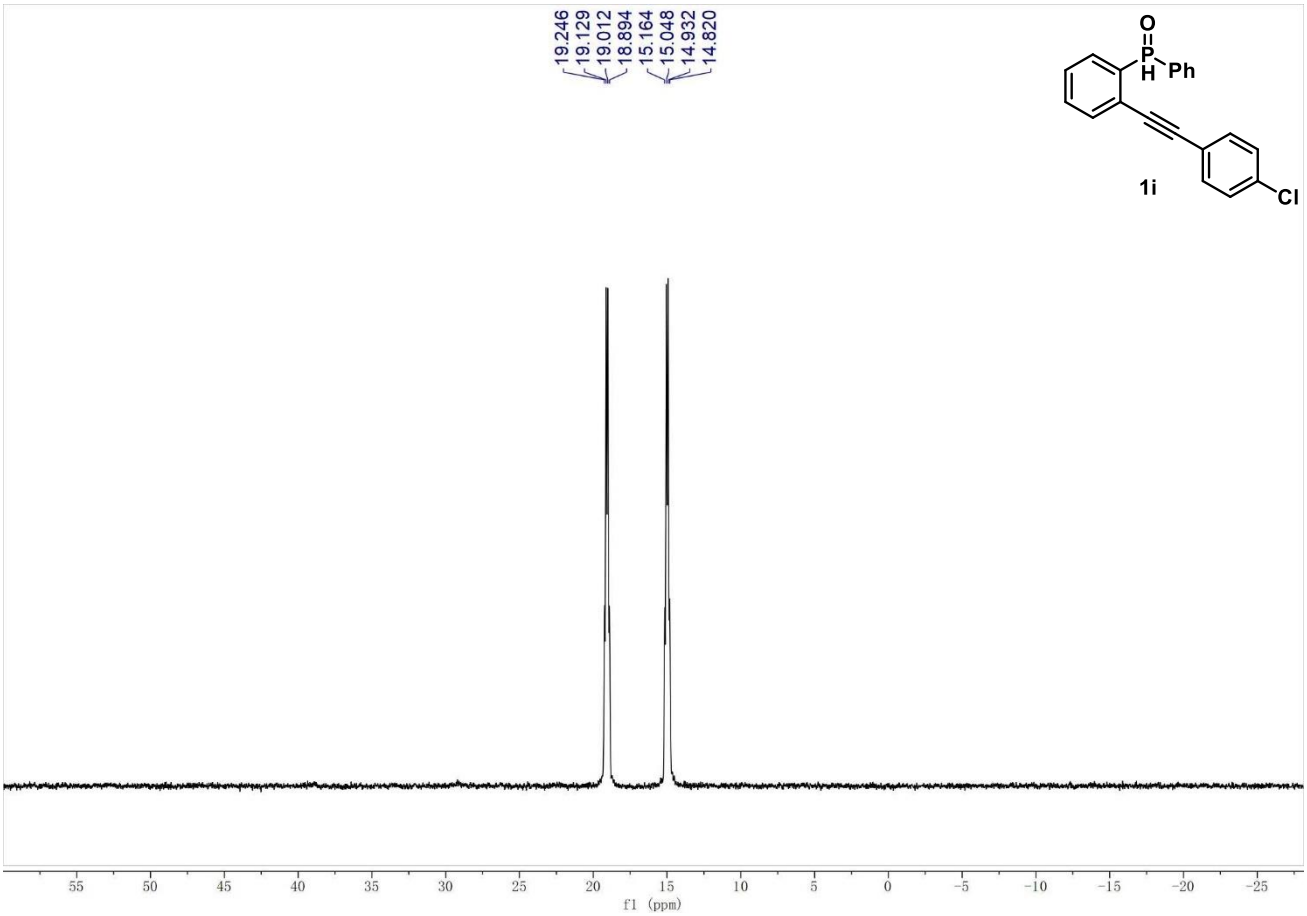




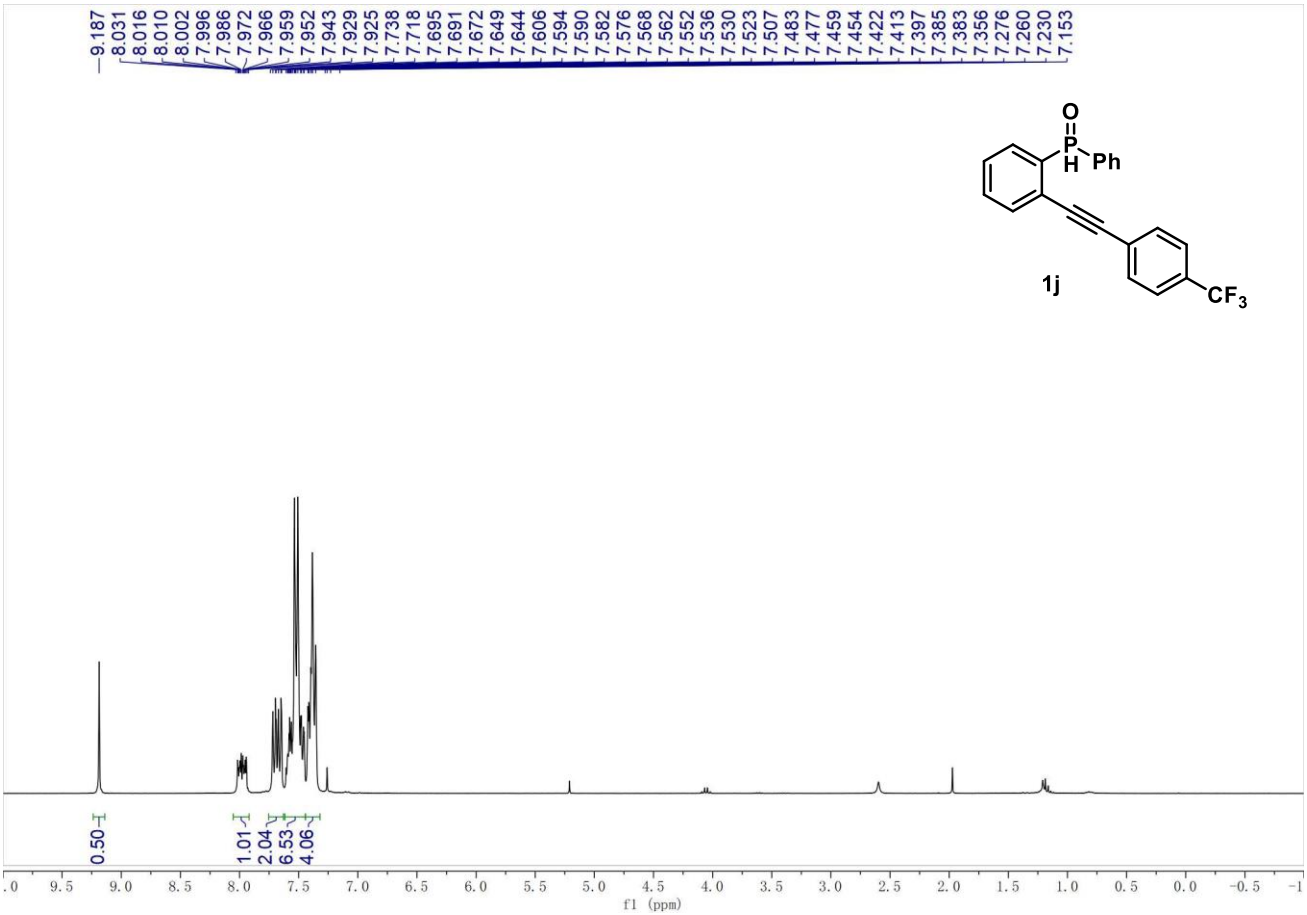

**$^{31}P\{^{1}H\}$ NMR spectrum of 1i (121 MHz, $CDCl_3$)**



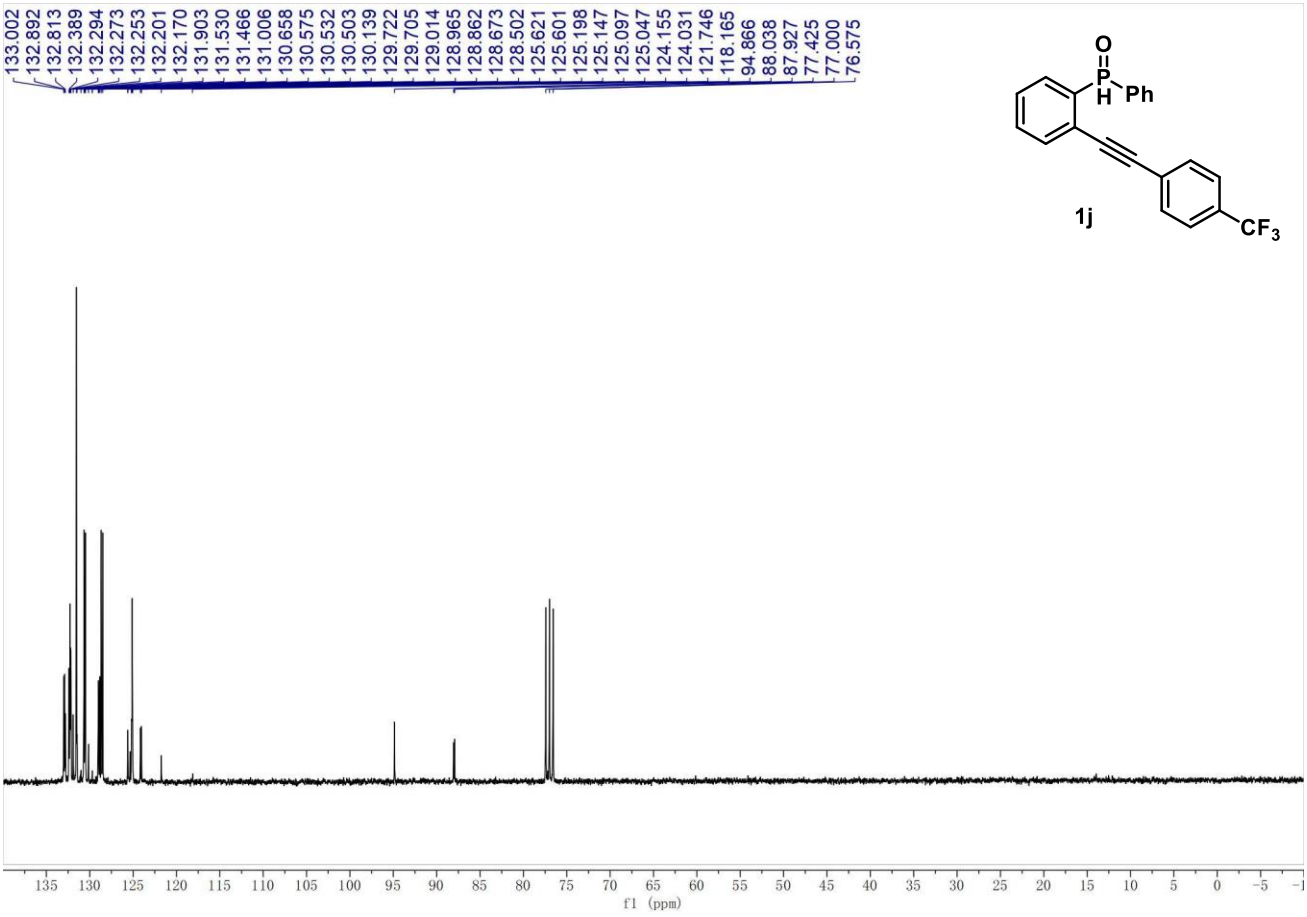
**$^{31}$P NMR spectrum of 1i (121 MHz, $CDCl_3$)**

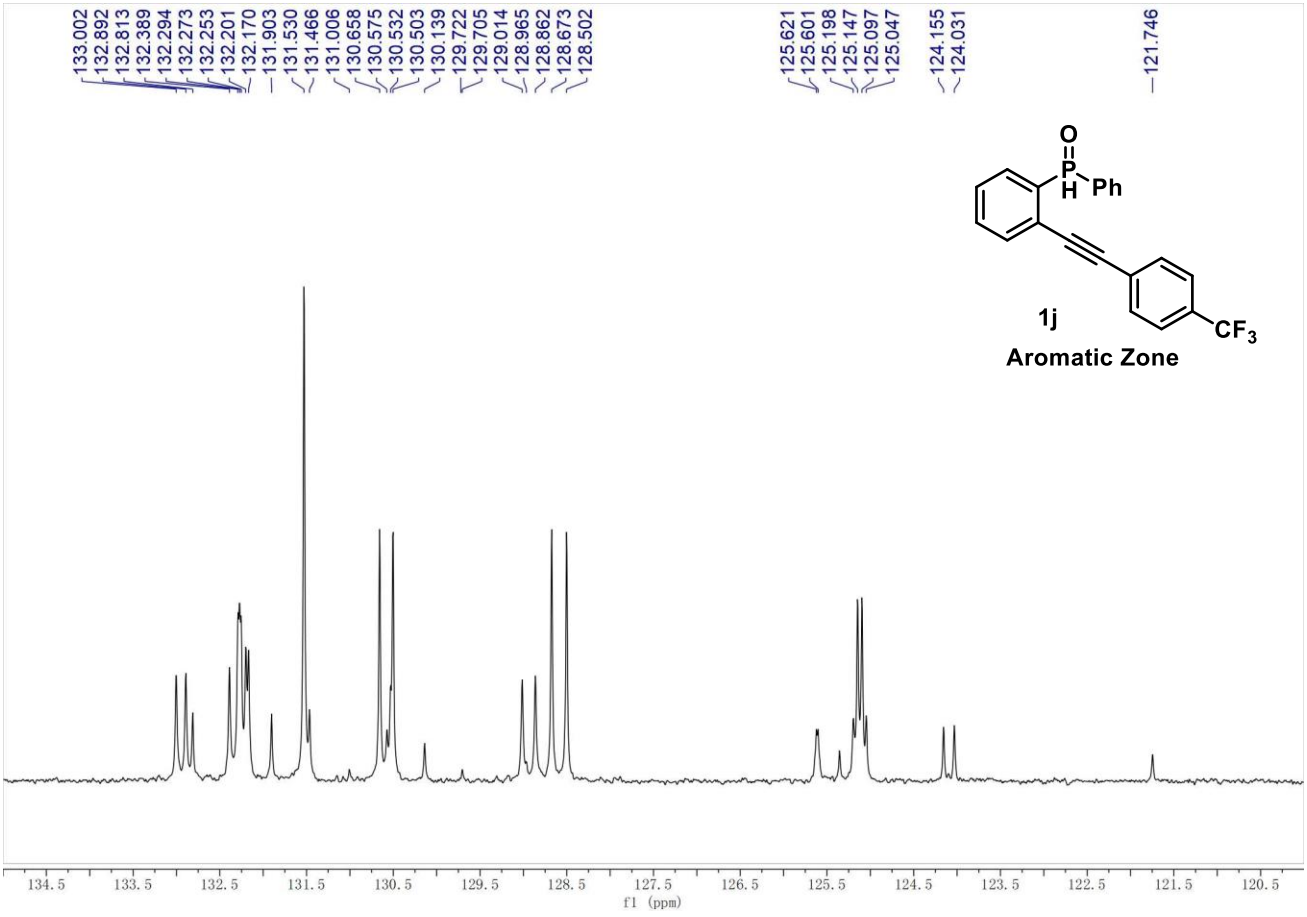



**$^{1}$H NMR spectrum of 1j (300 MHz, $CDCl_3$)**

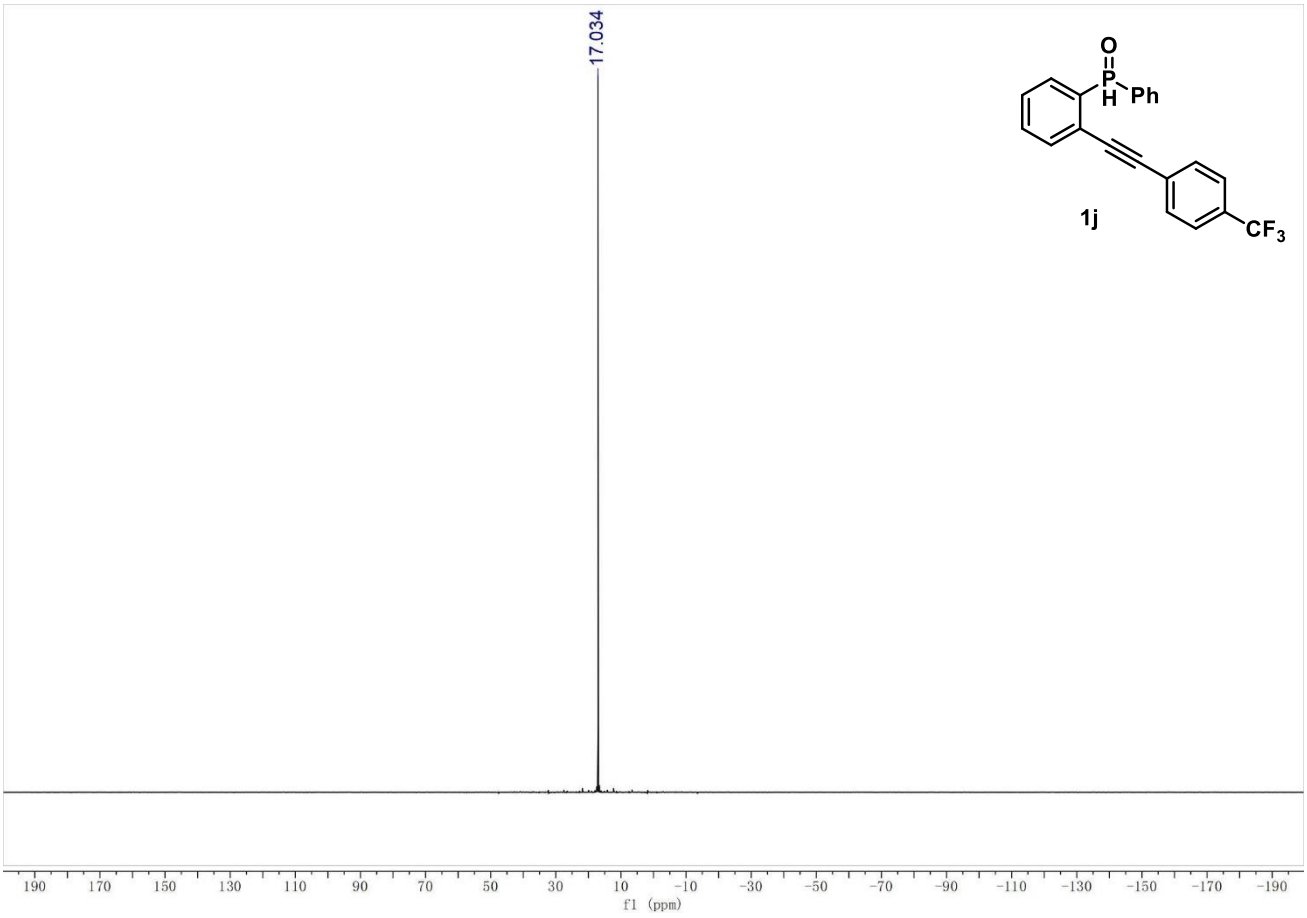


**$^{13}$C NMR spectrum of 1j (75 MHz, $CDCl_3$)**

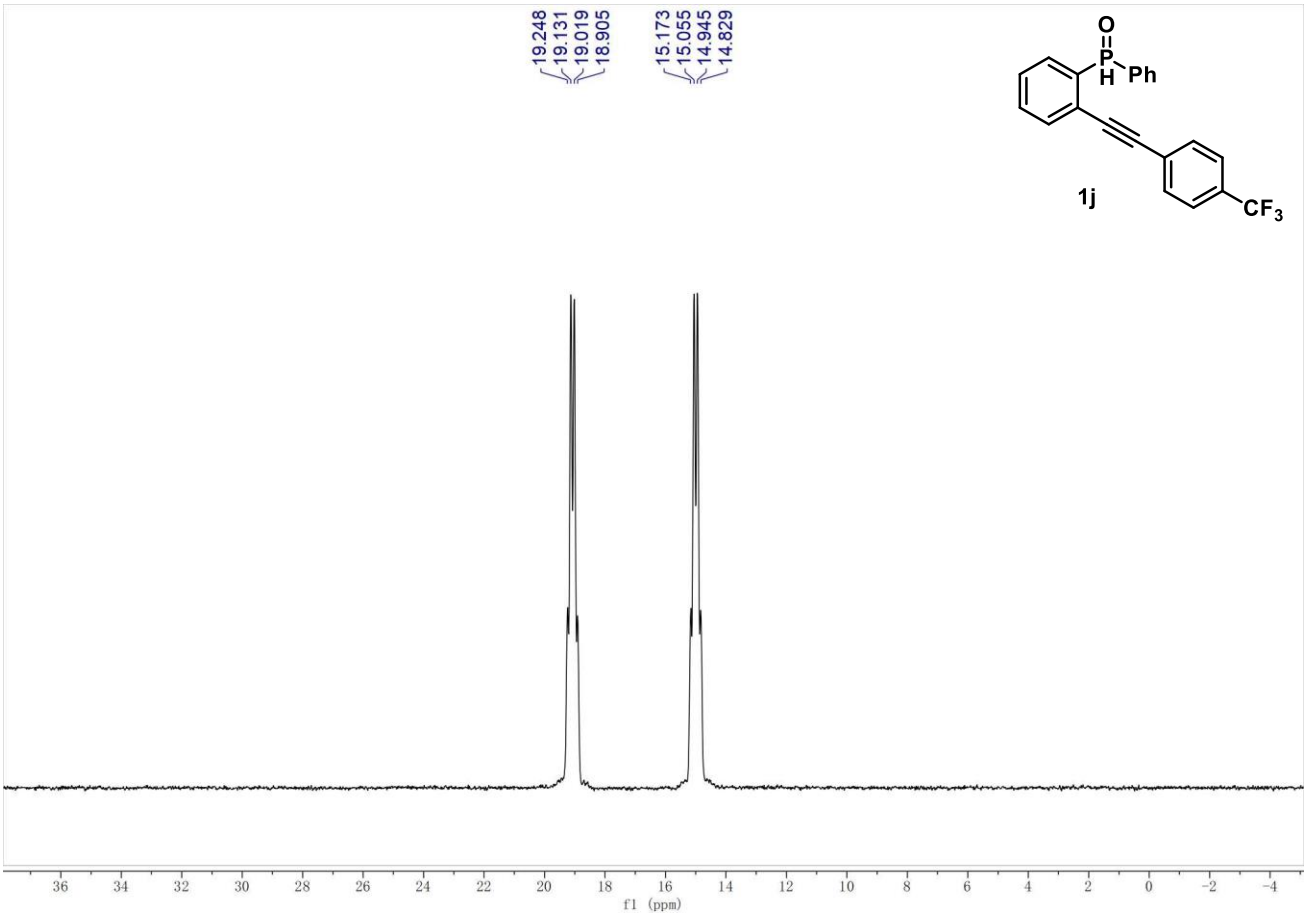


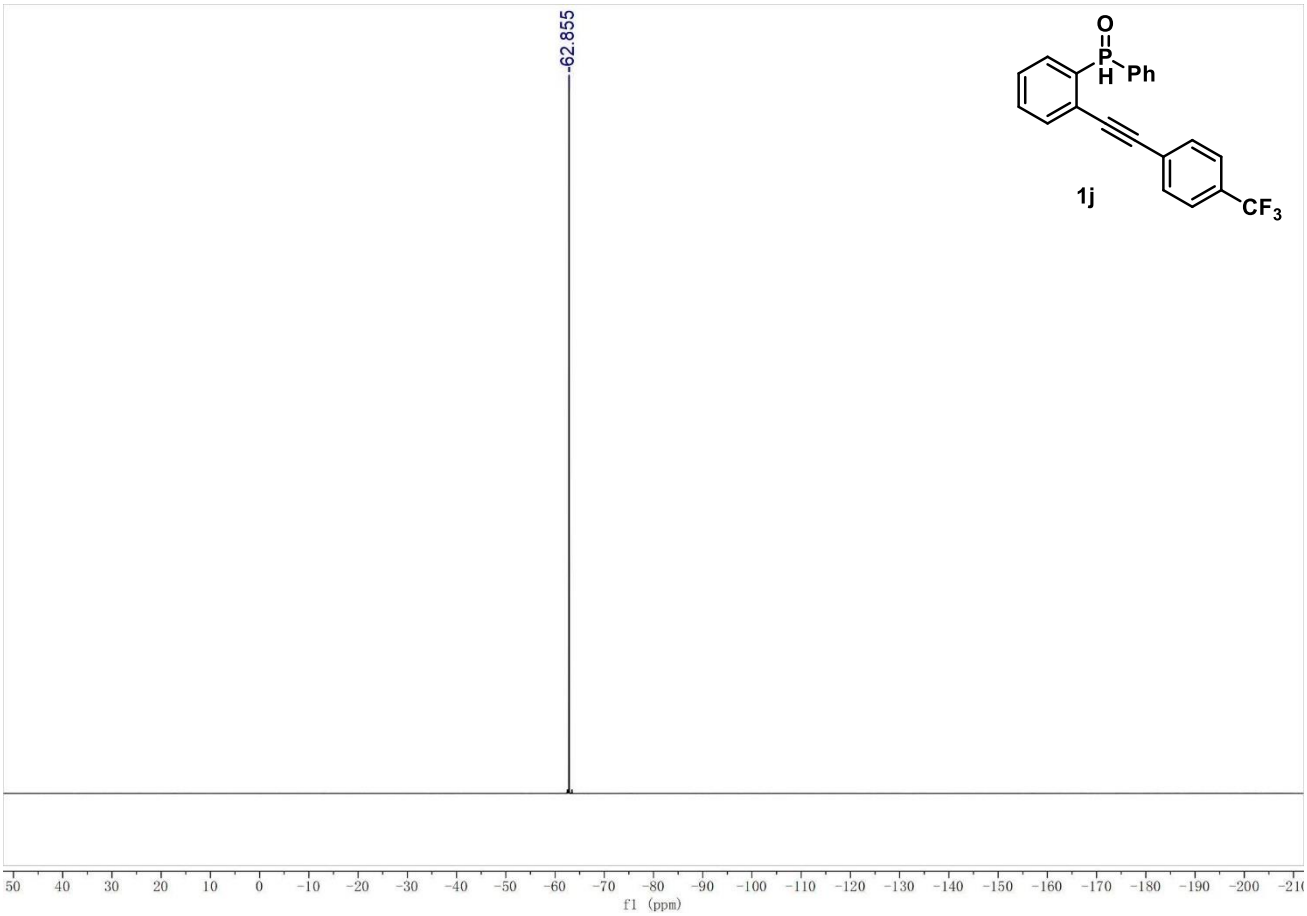
**$^{31}P\{^{1}H\}$ NMR spectrum of 1j (121 MHz, $CDCl_3$)**



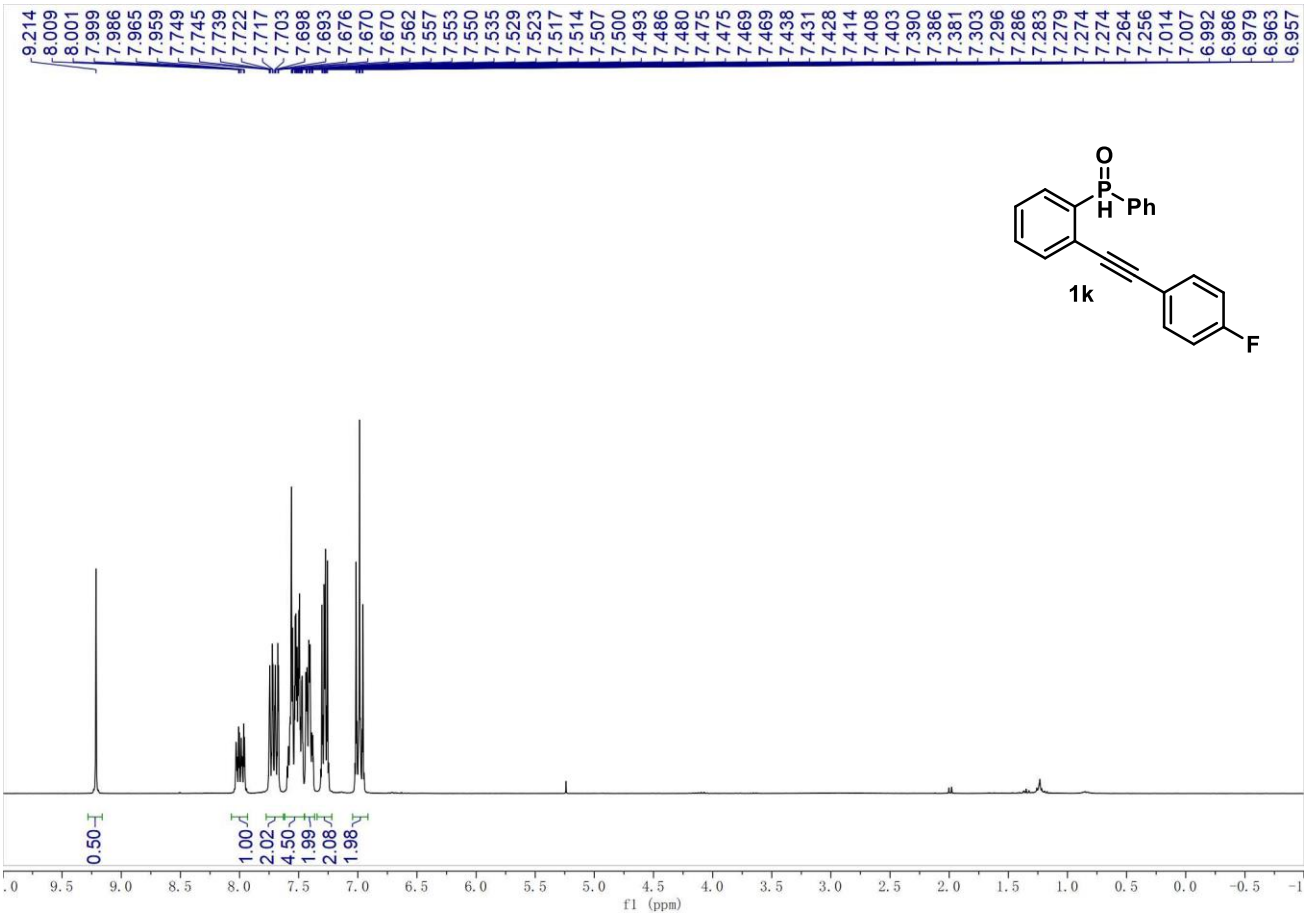

**$^{31}P$ NMR spectrum of 1j (121 MHz, $CDCl_3$)**



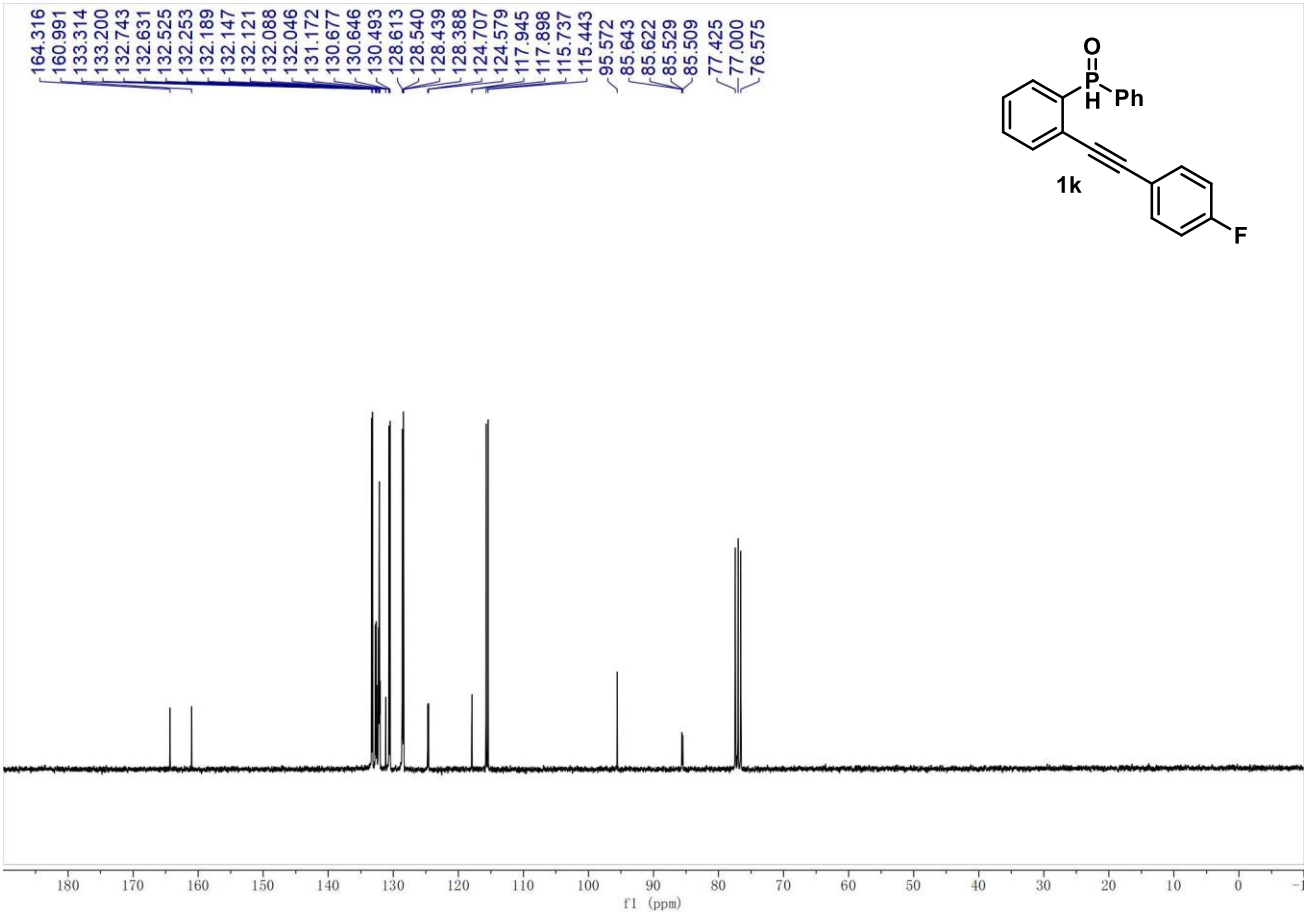
**$^{19}$F NMR spectrum of 1j (282 MHz, $CDCl_3$)**

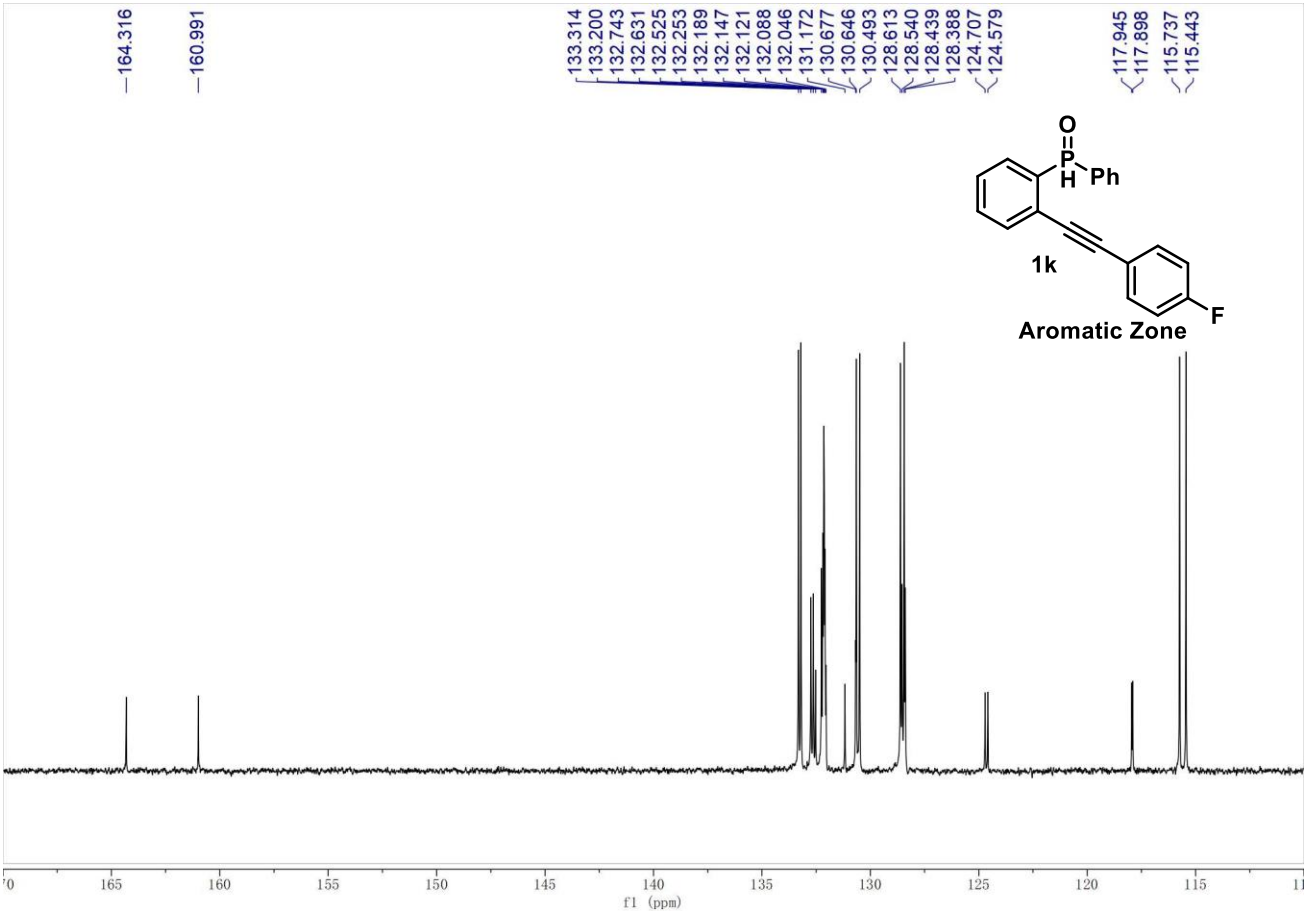



**$^{1}$H NMR spectrum of 1k (300 MHz, $CDCl_3$)**

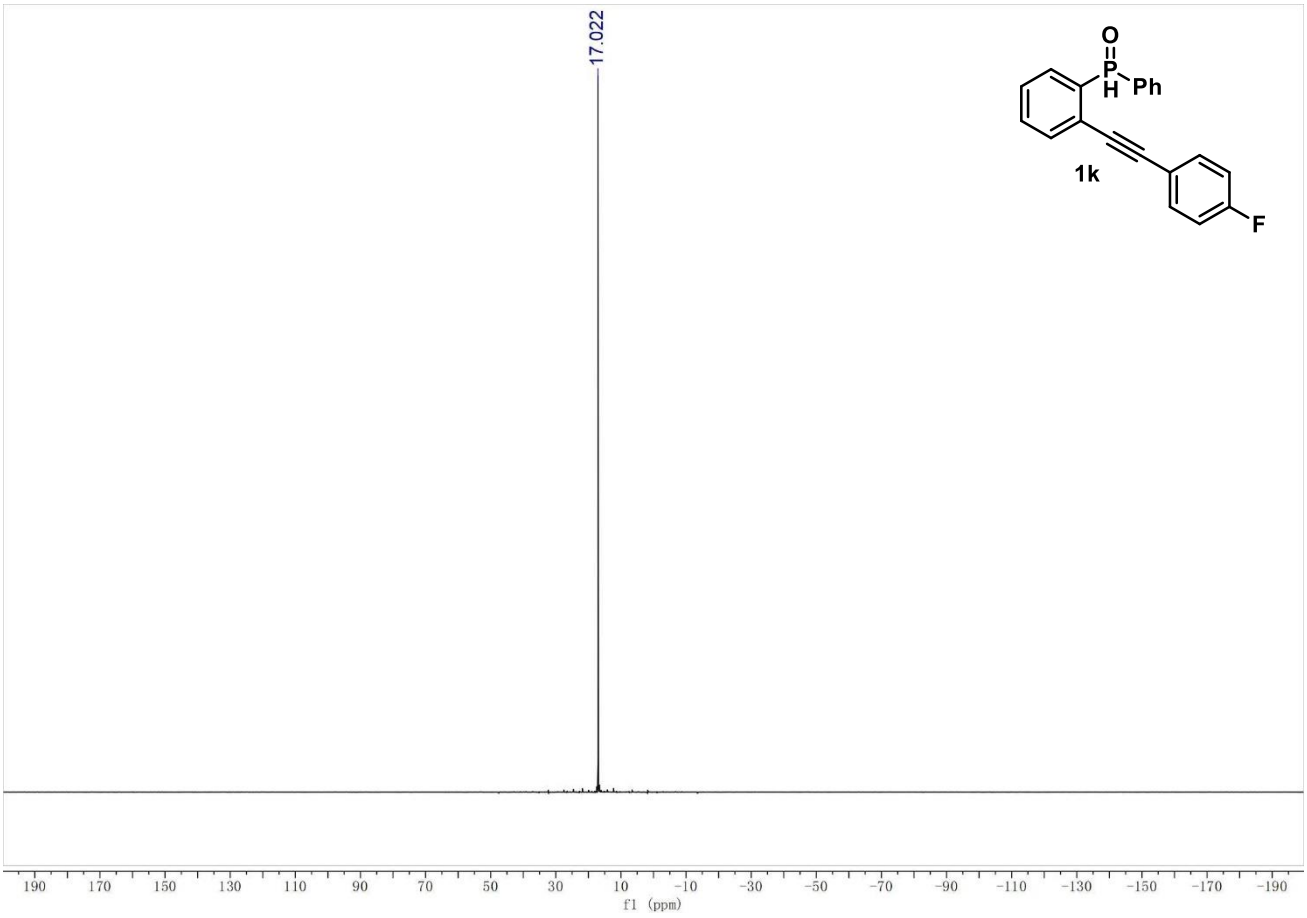


**$^{13}$C NMR spectrum of 1k (75 MHz, $CDCl_3$)**

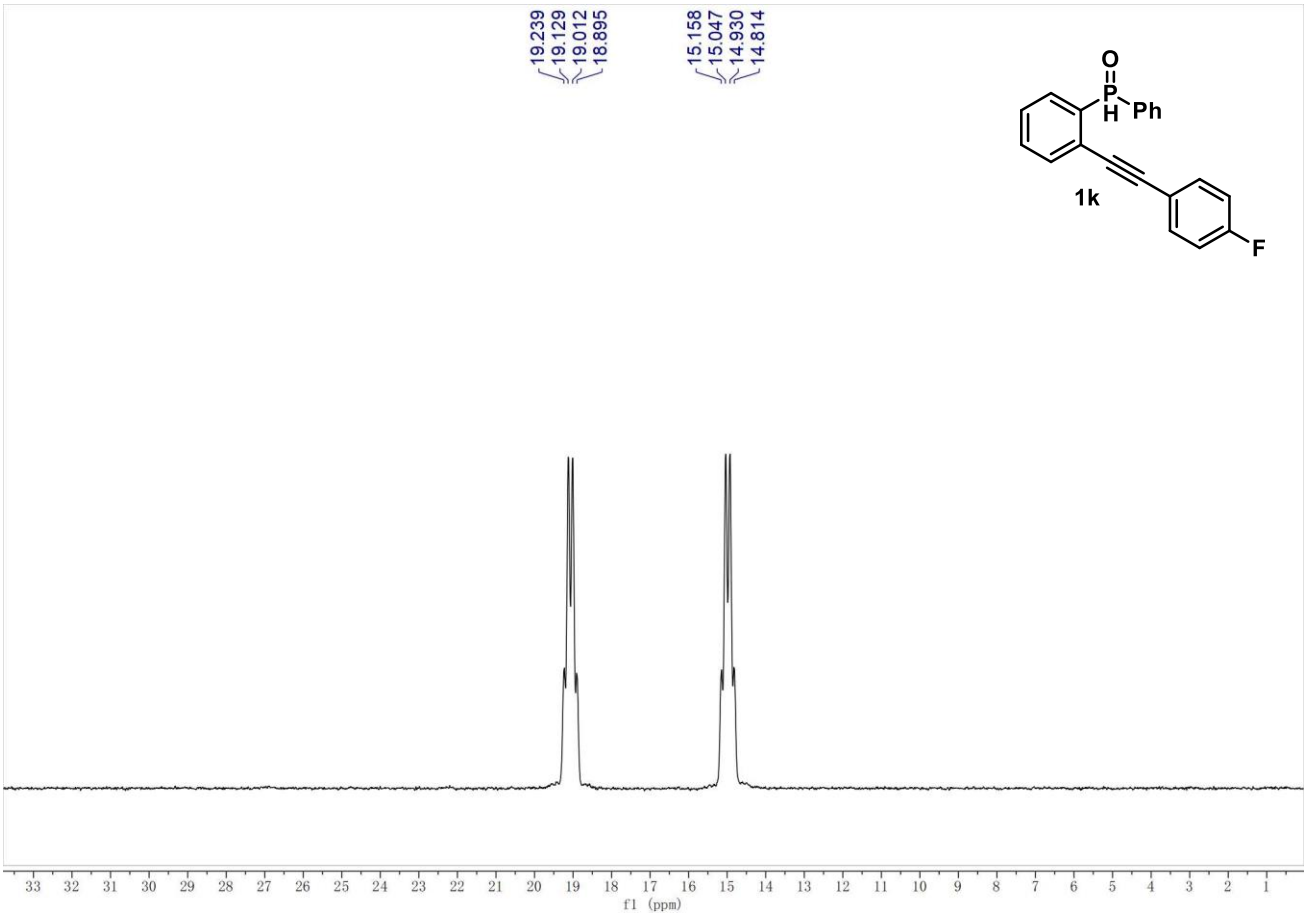


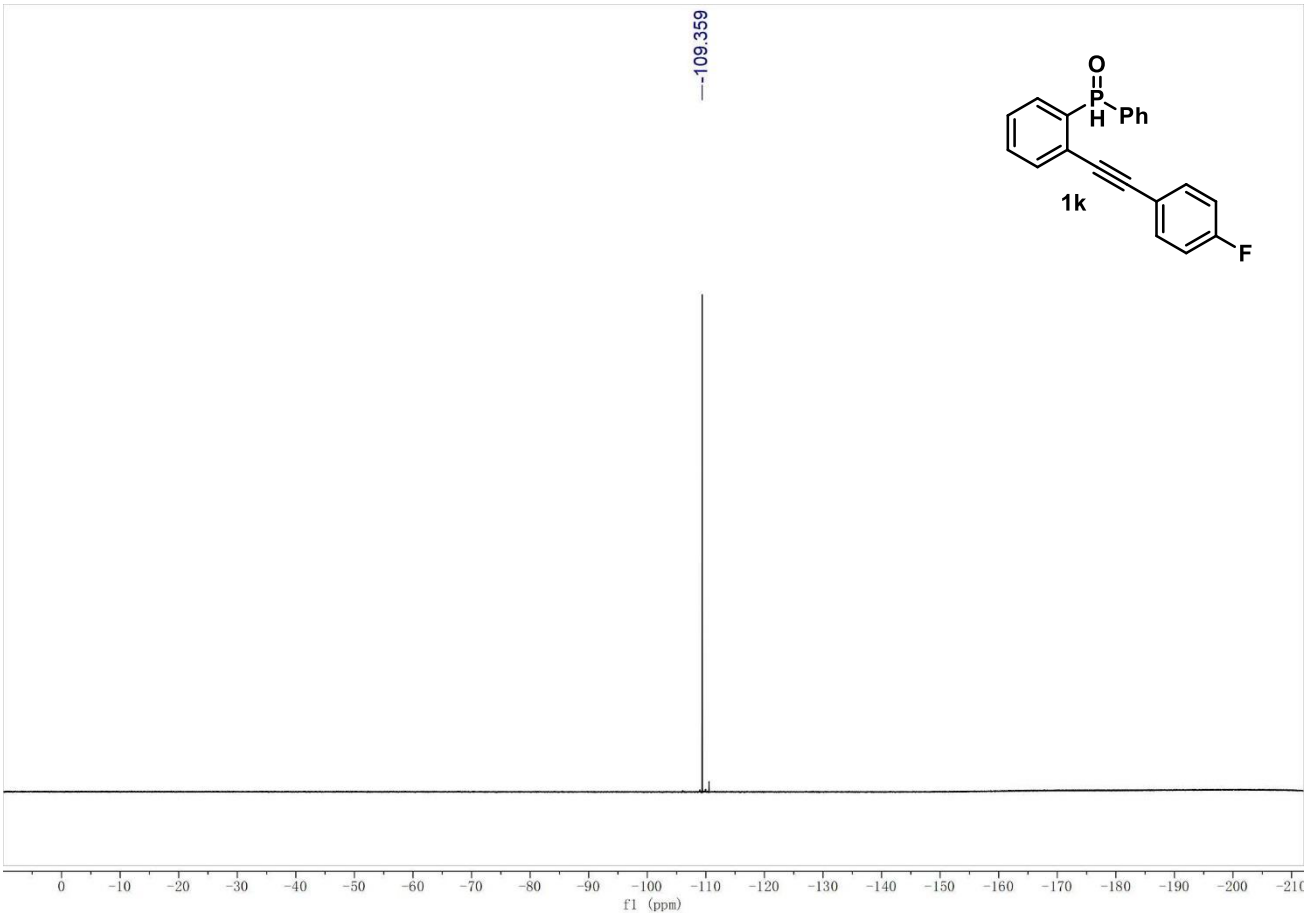
**$^{31}P\{^{1}H\}$ NMR spectrum of 1k (121 MHz, $CDCl_3$)**



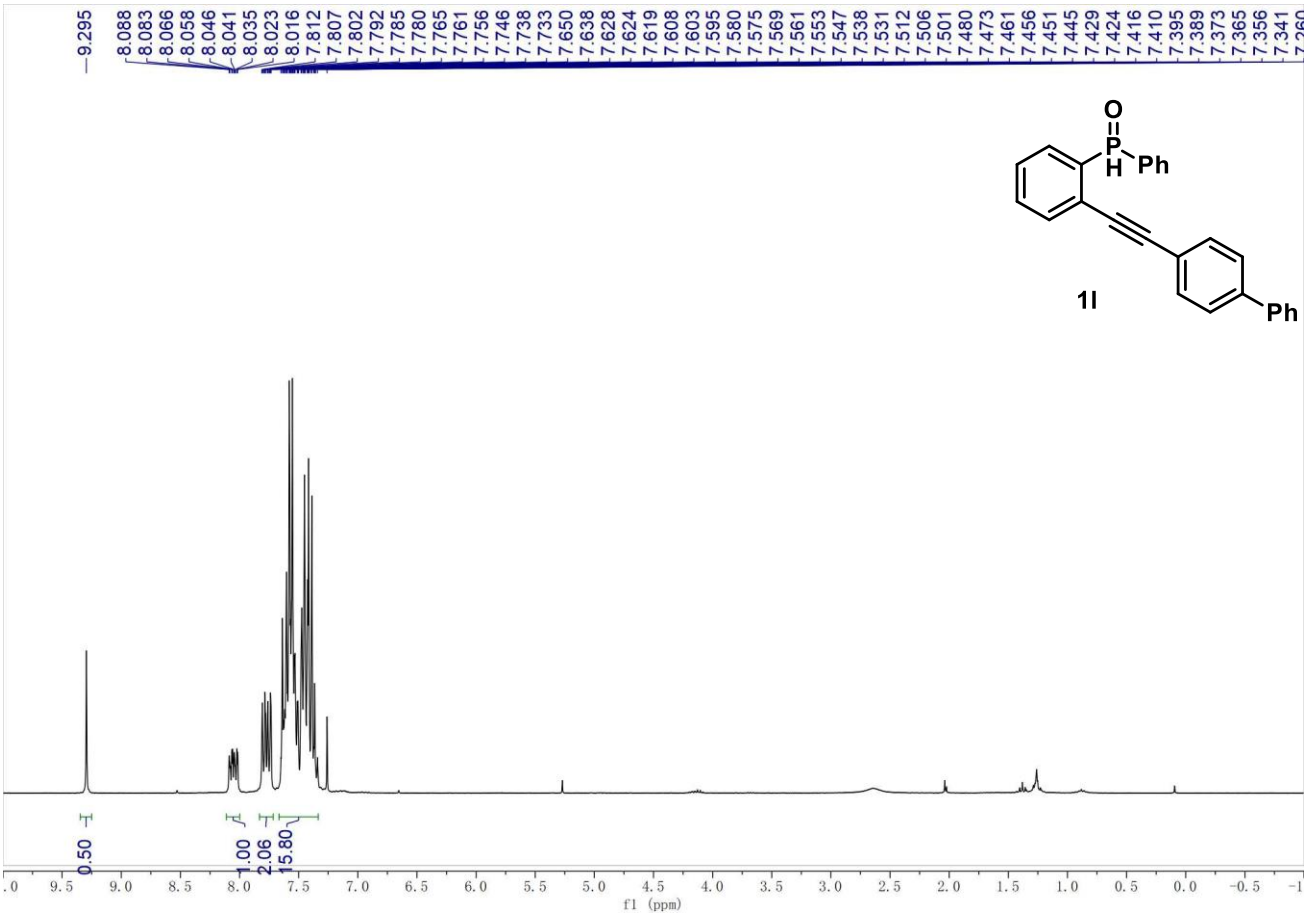

**$^{31}P$ NMR spectrum of 1k (121 MHz, $CDCl_3$)**



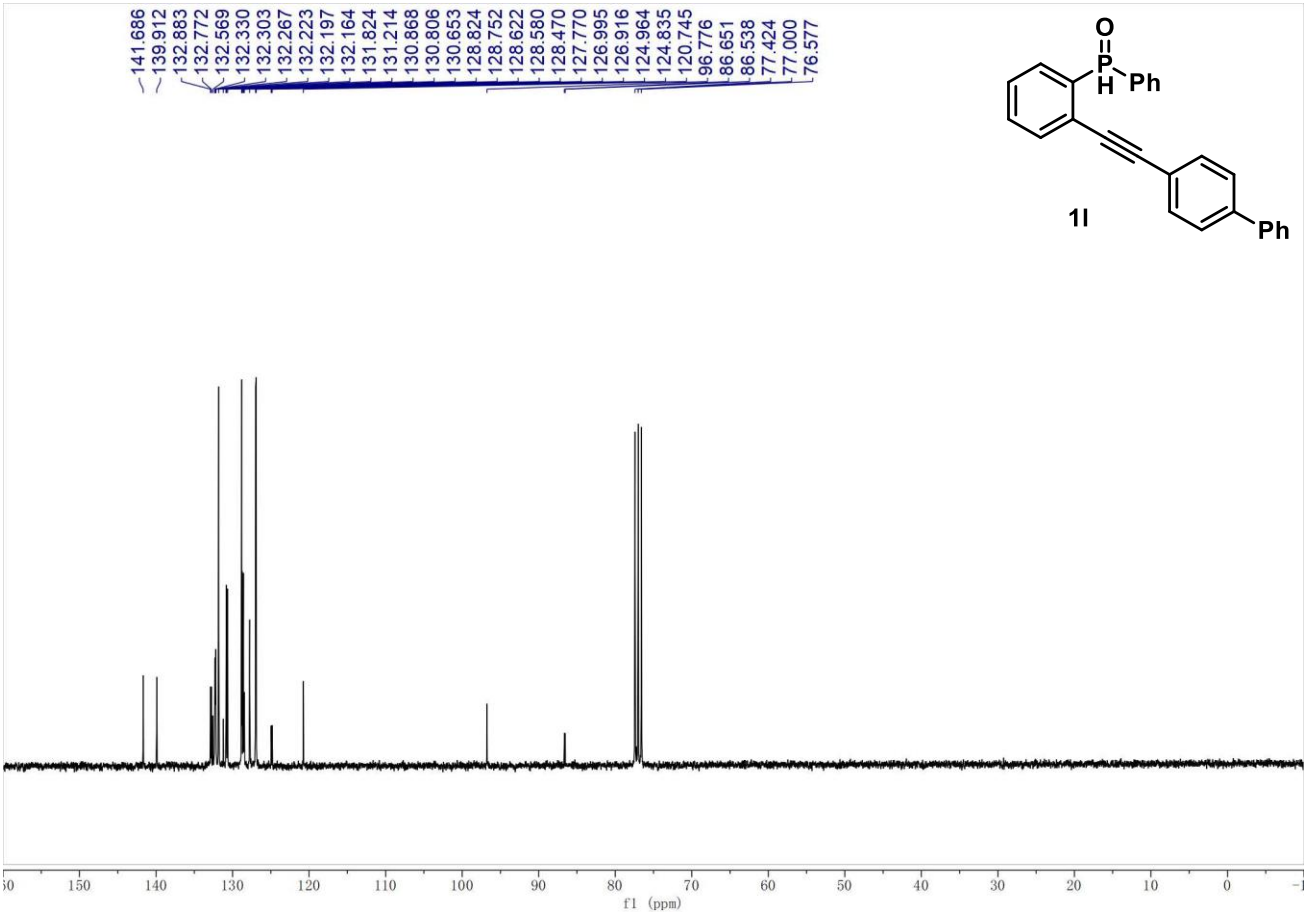
**$^{19}$F NMR spectrum of 1k (282 MHz, $CDCl_3$)**

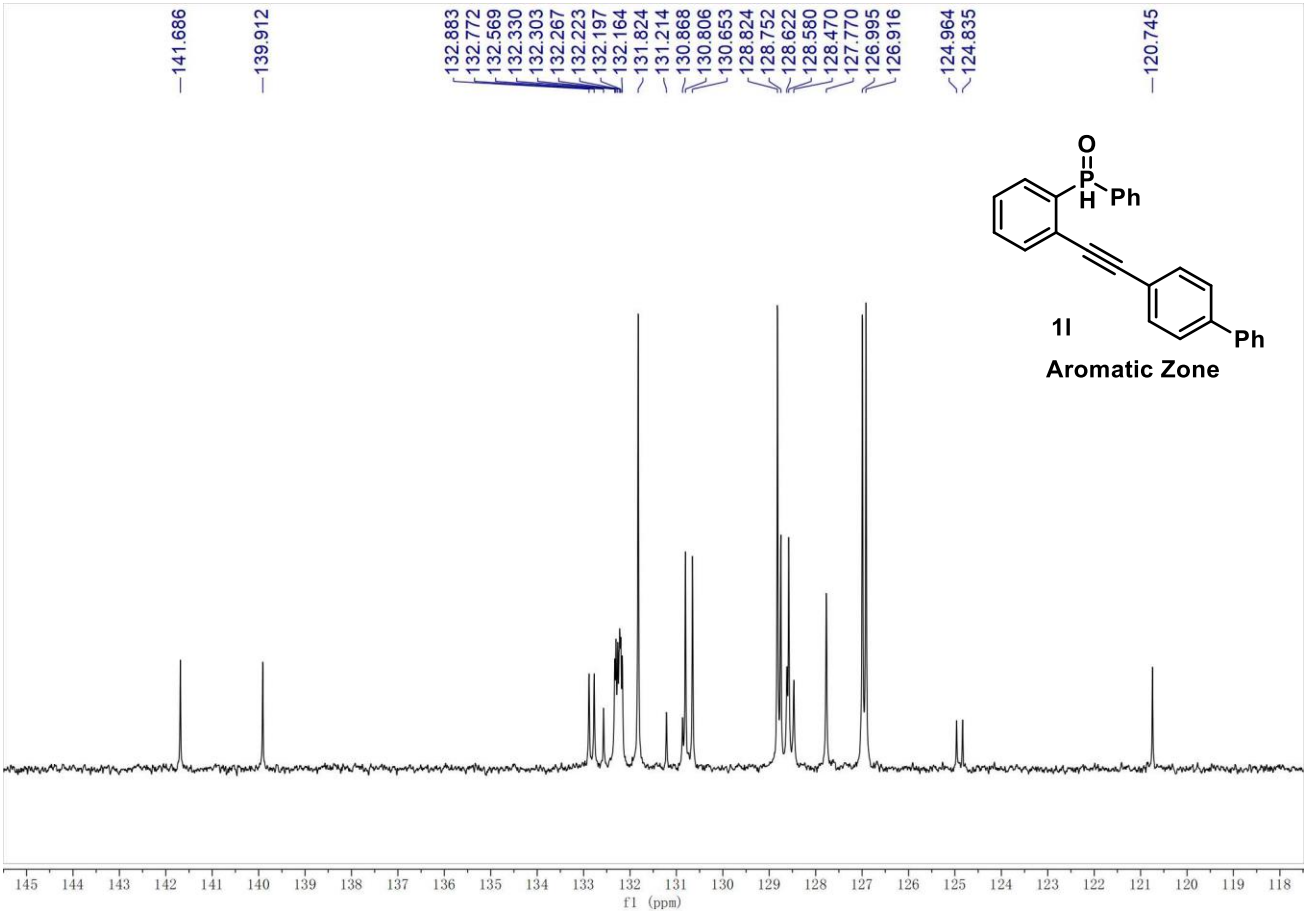



**$^{1}$H NMR spectrum of 1l (300 MHz, $CDCl_3$)**

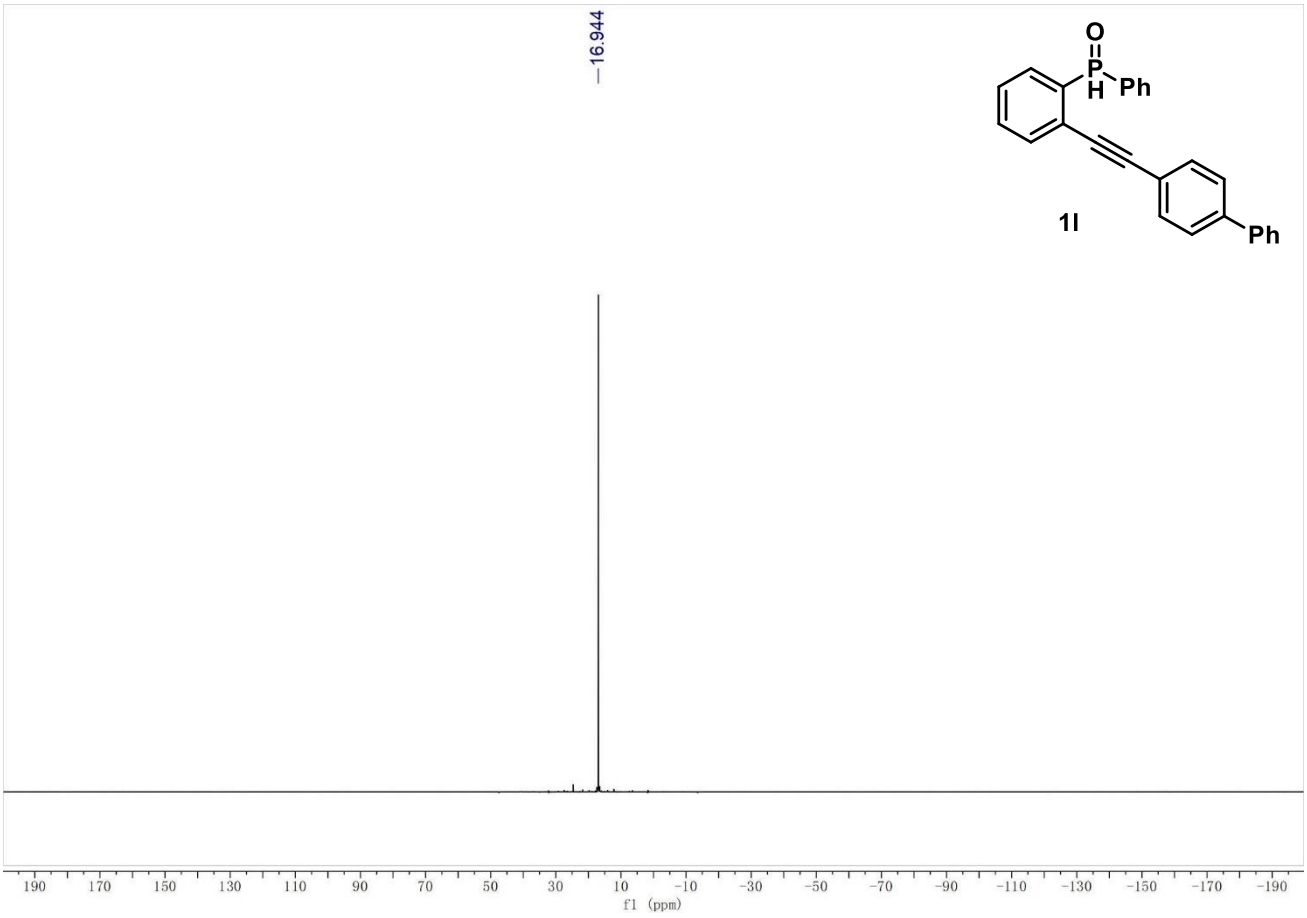


**$^{13}$C NMR spectrum of 1l (75 MHz, $CDCl_3$)**

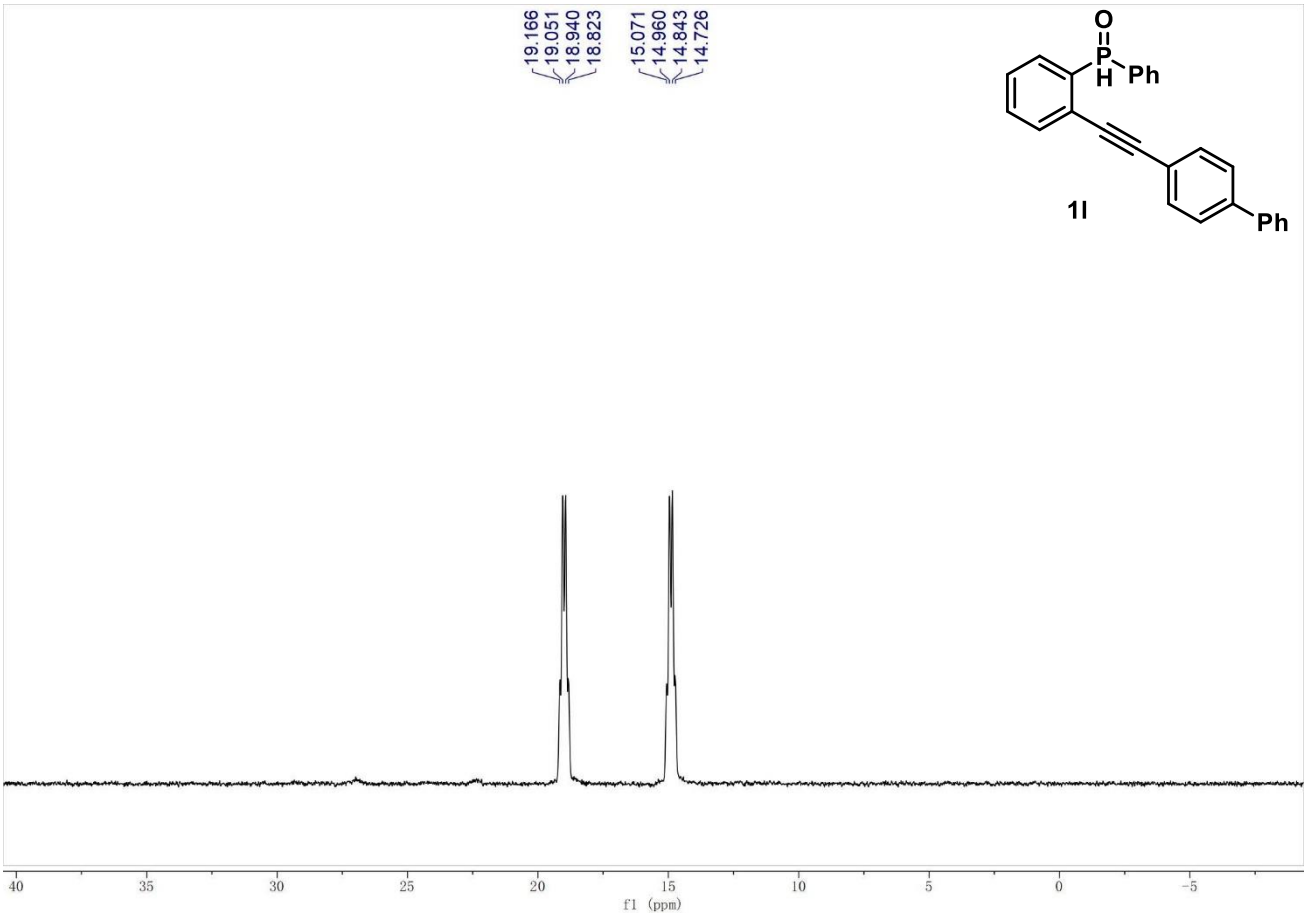


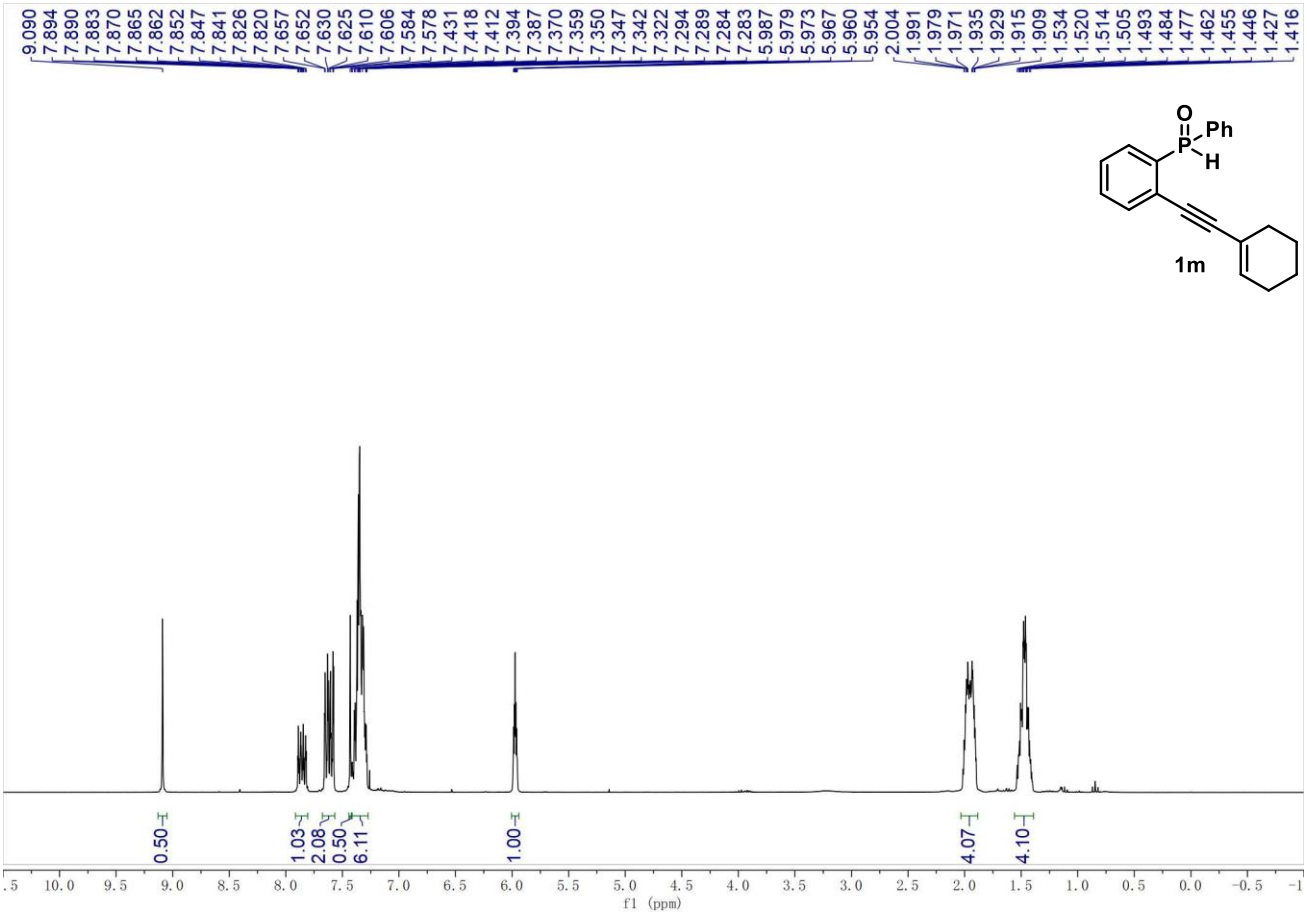
**$^{31}P\{^{1}H\}$ NMR spectrum of 1l (121 MHz, $CDCl_3$)**



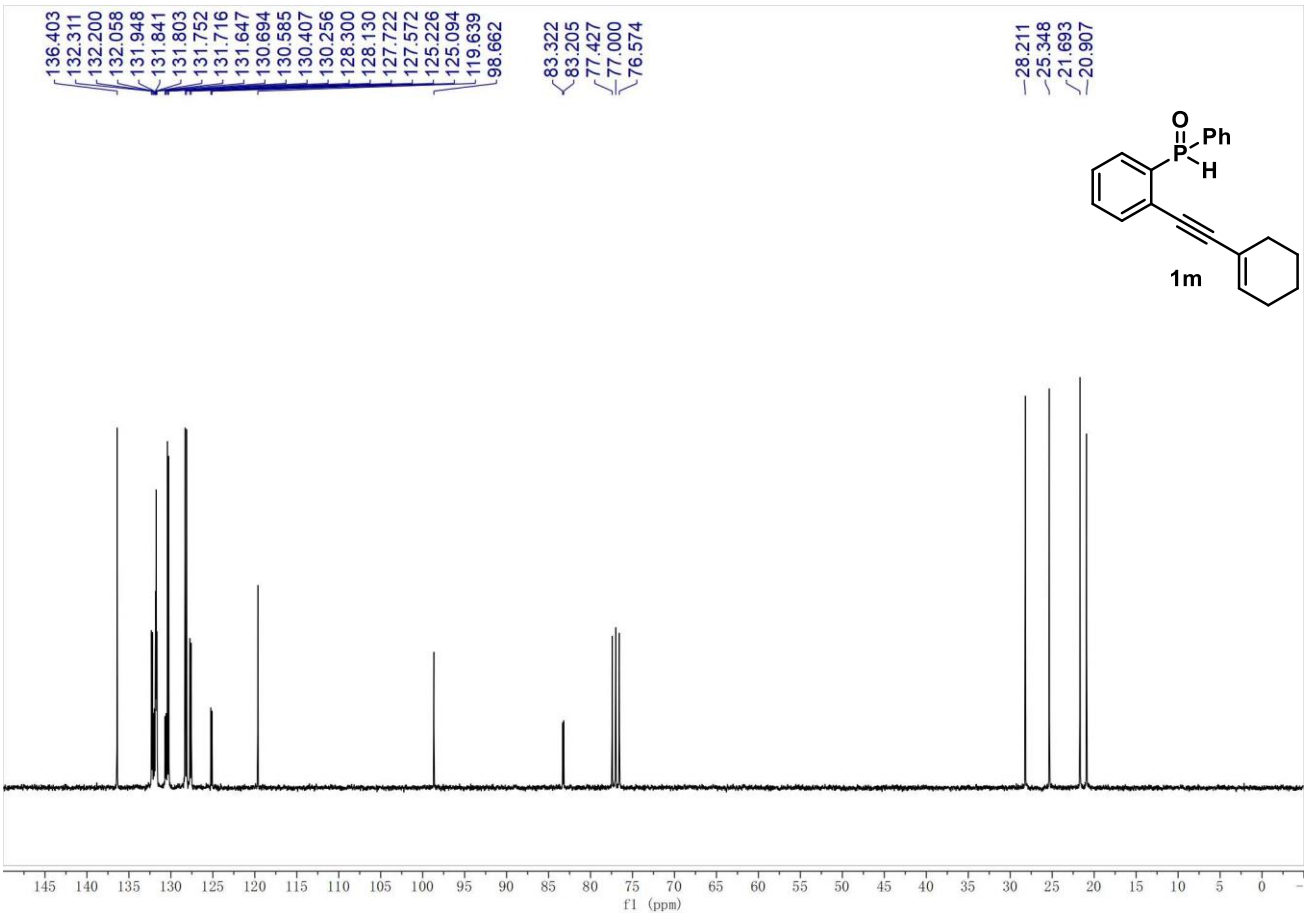

**$^{31}P$ NMR spectrum of 1l (121 MHz, $CDCl_3$)**

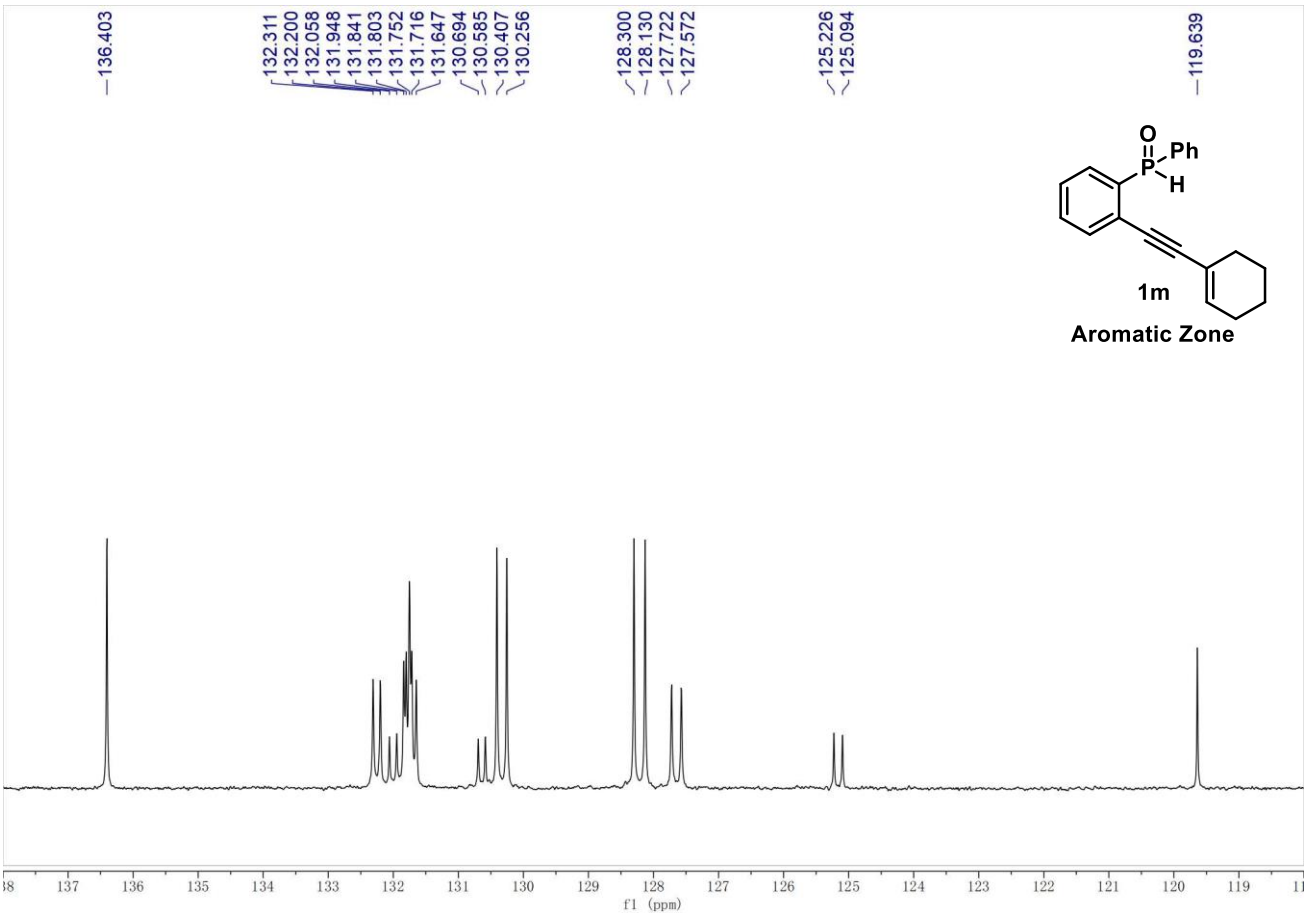


**$^{1}$H NMR spectrum of 1m (300 MHz, $CDCl_3$)**

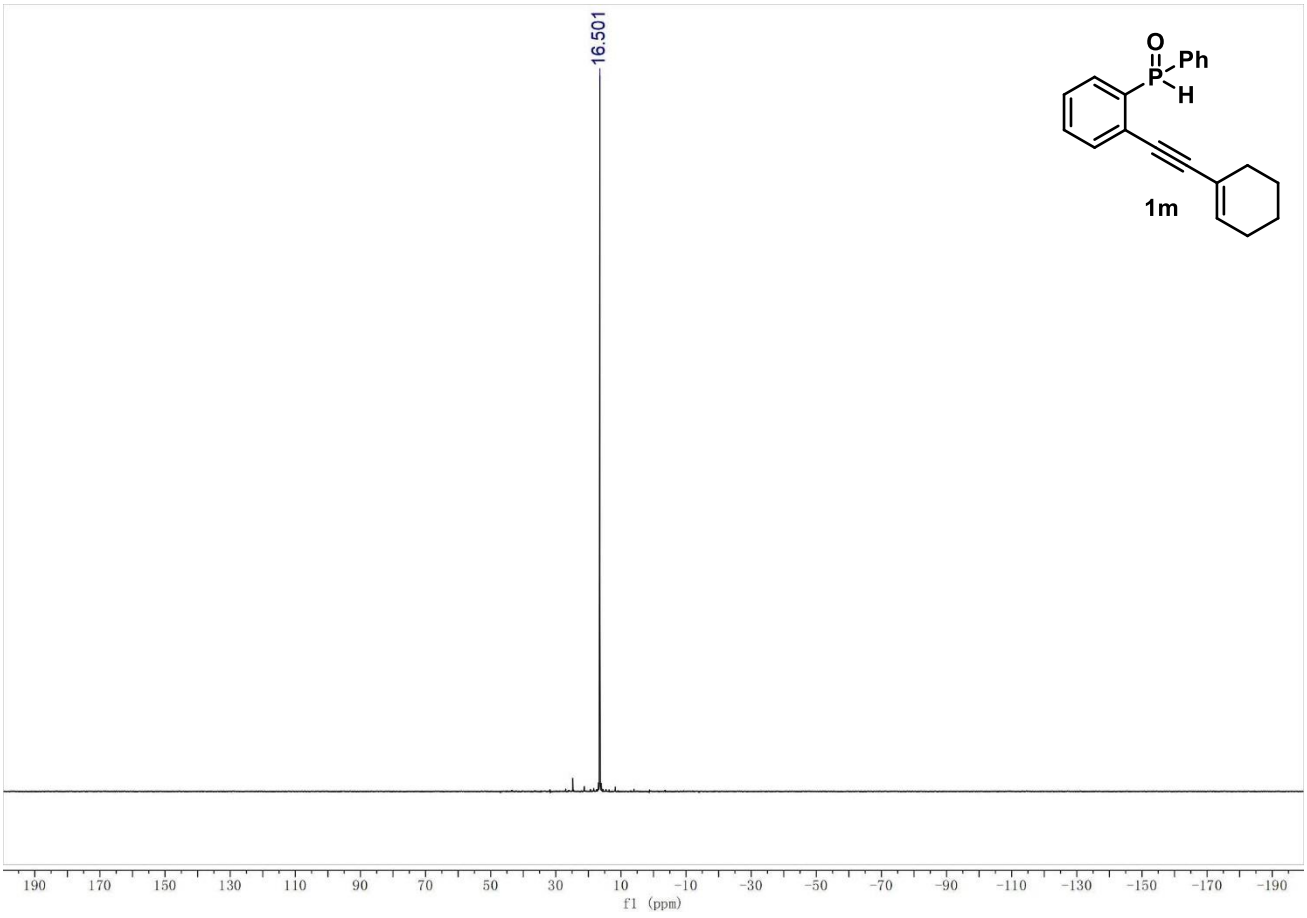



**$^{13}$C NMR spectrum of 1m (75 MHz, $CDCl_3$)**

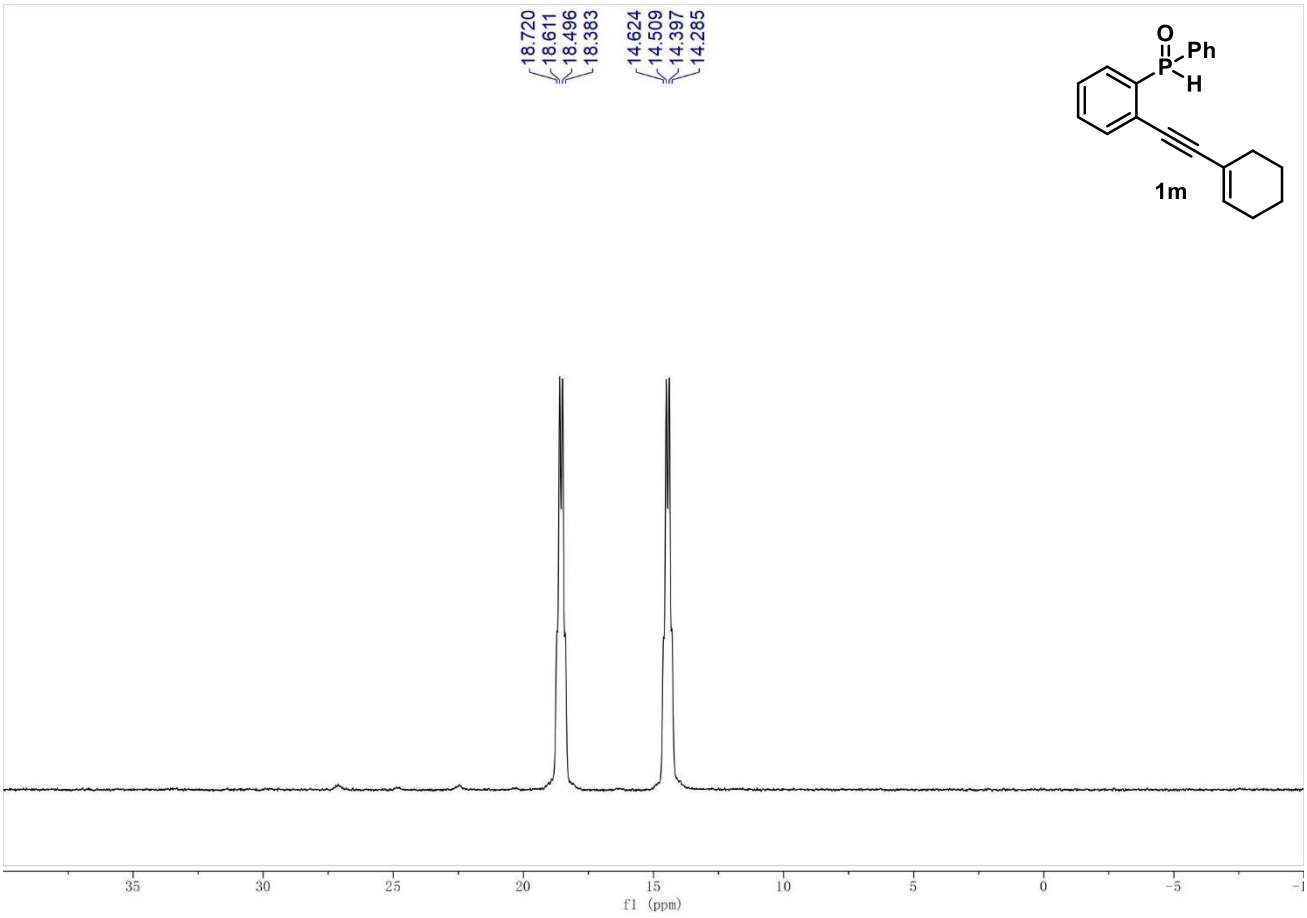




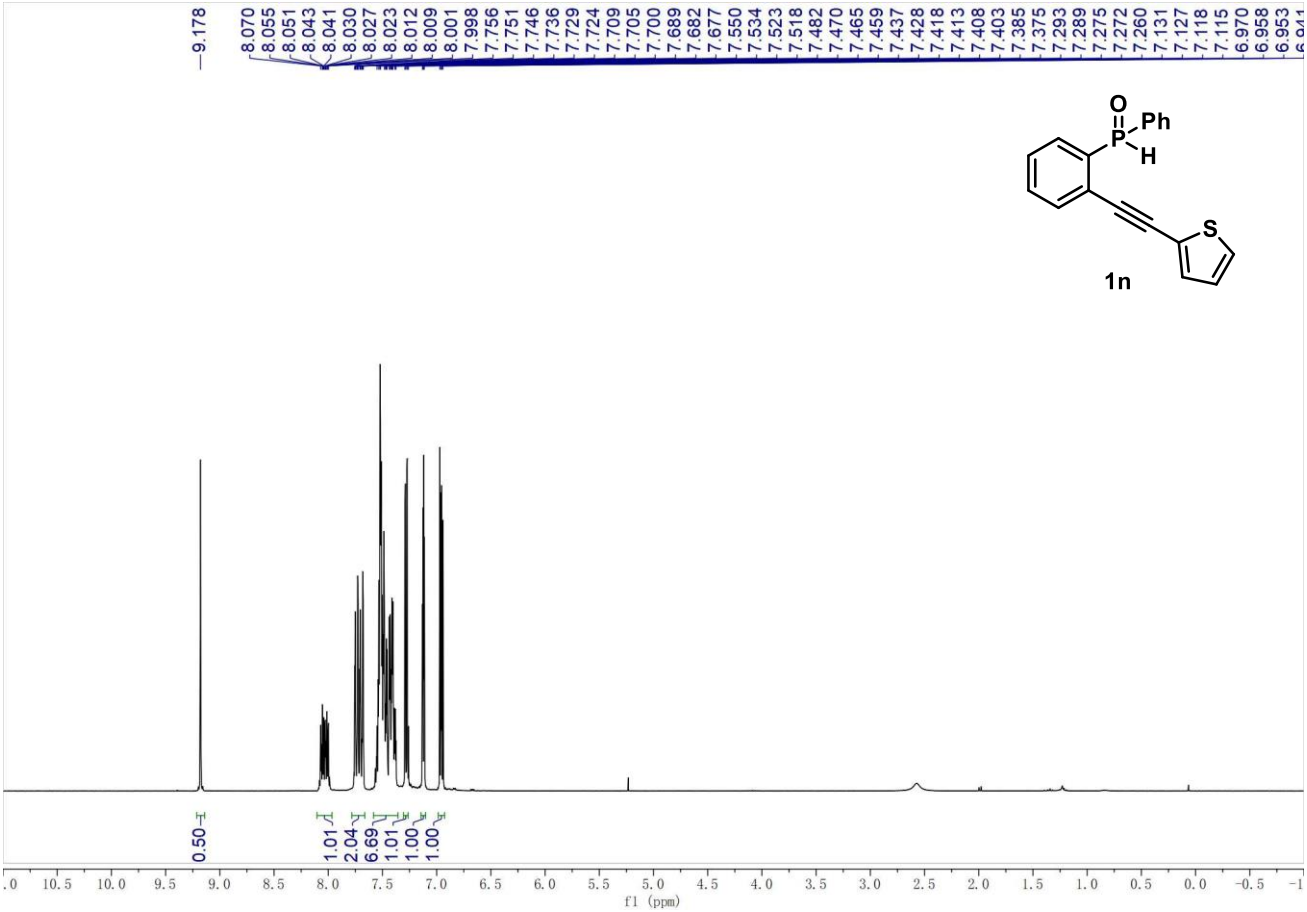

**$^{31}P\{^{1}H\}$ NMR spectrum of 1m (121 MHz, $CDCl_3$)**



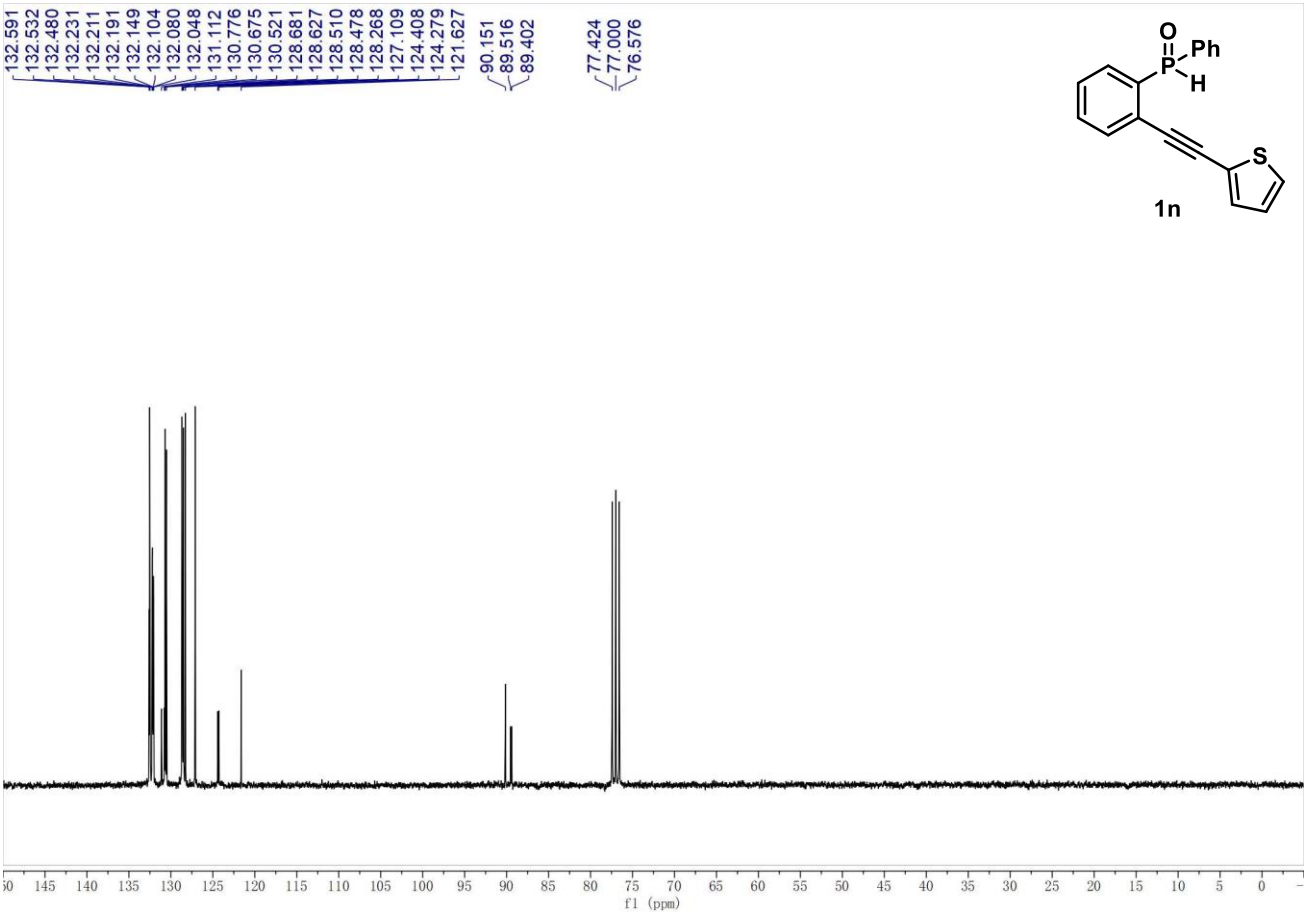
**$^{31}P$ NMR spectrum of 1m (121 MHz, $CDCl_3$)**

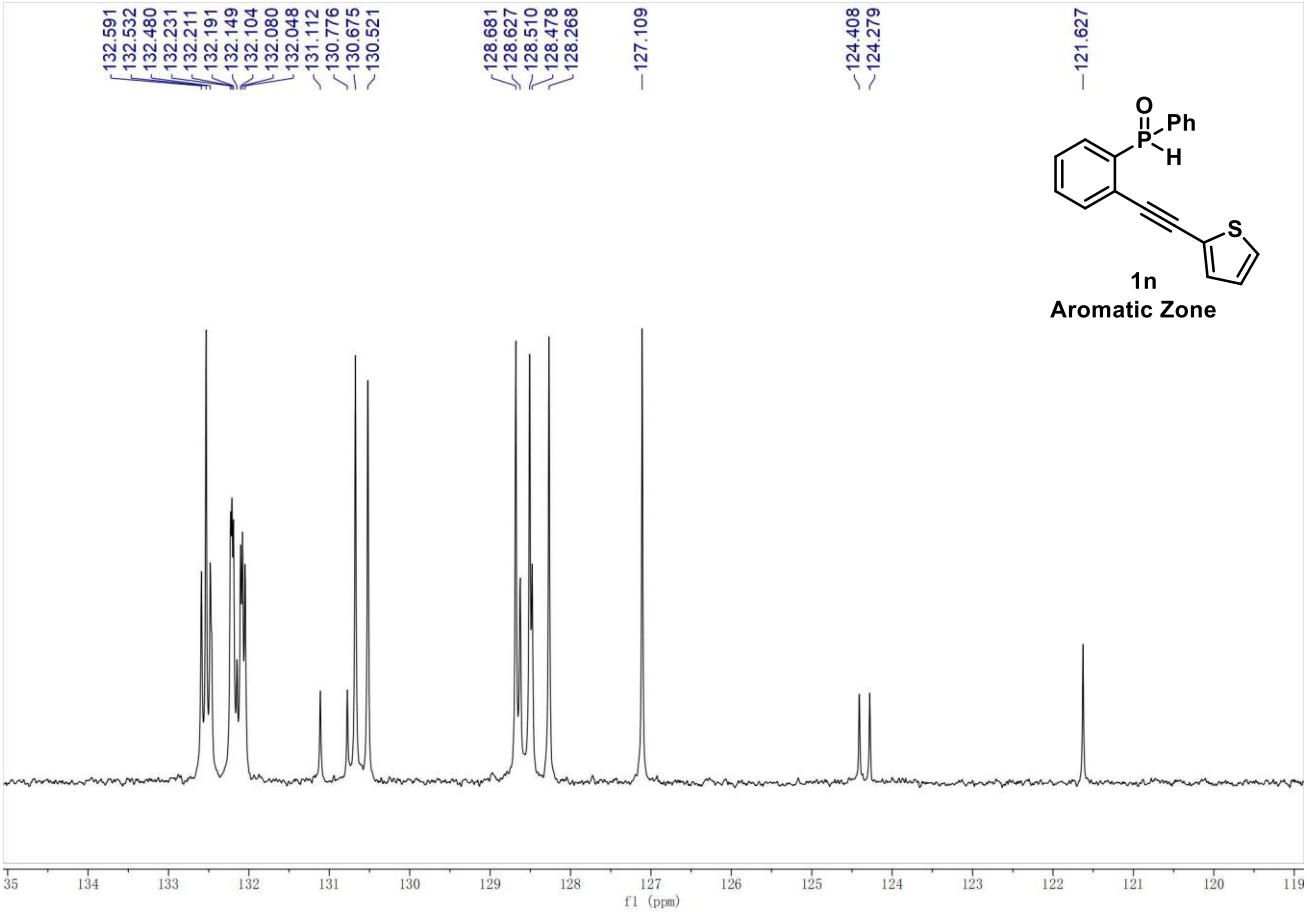



**$^{1}H$ NMR spectrum of 1n (300 MHz, $CDCl_3$)**

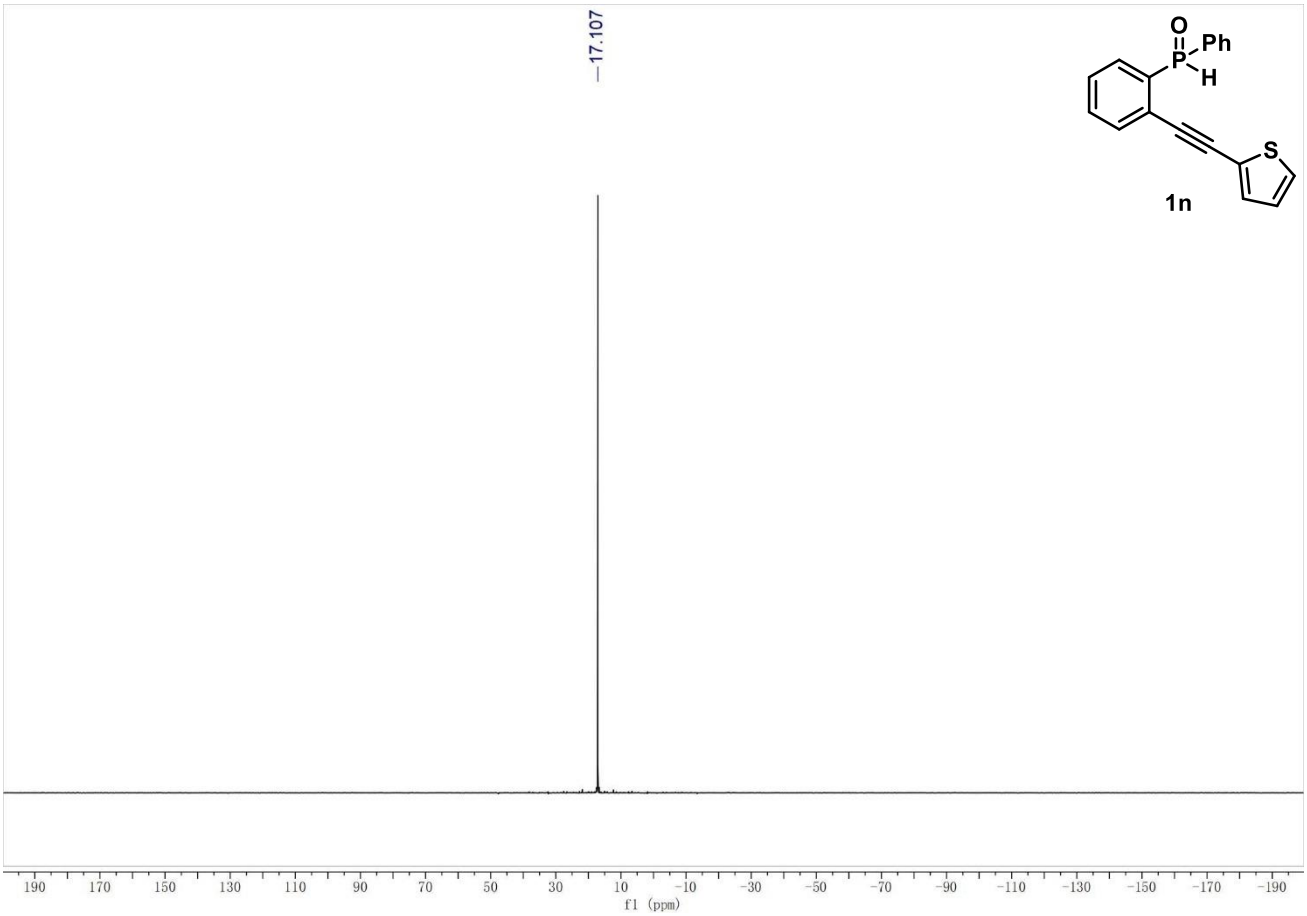


**$^{13}$C NMR spectrum of 1n (75 MHz, $CDCl_3$)**

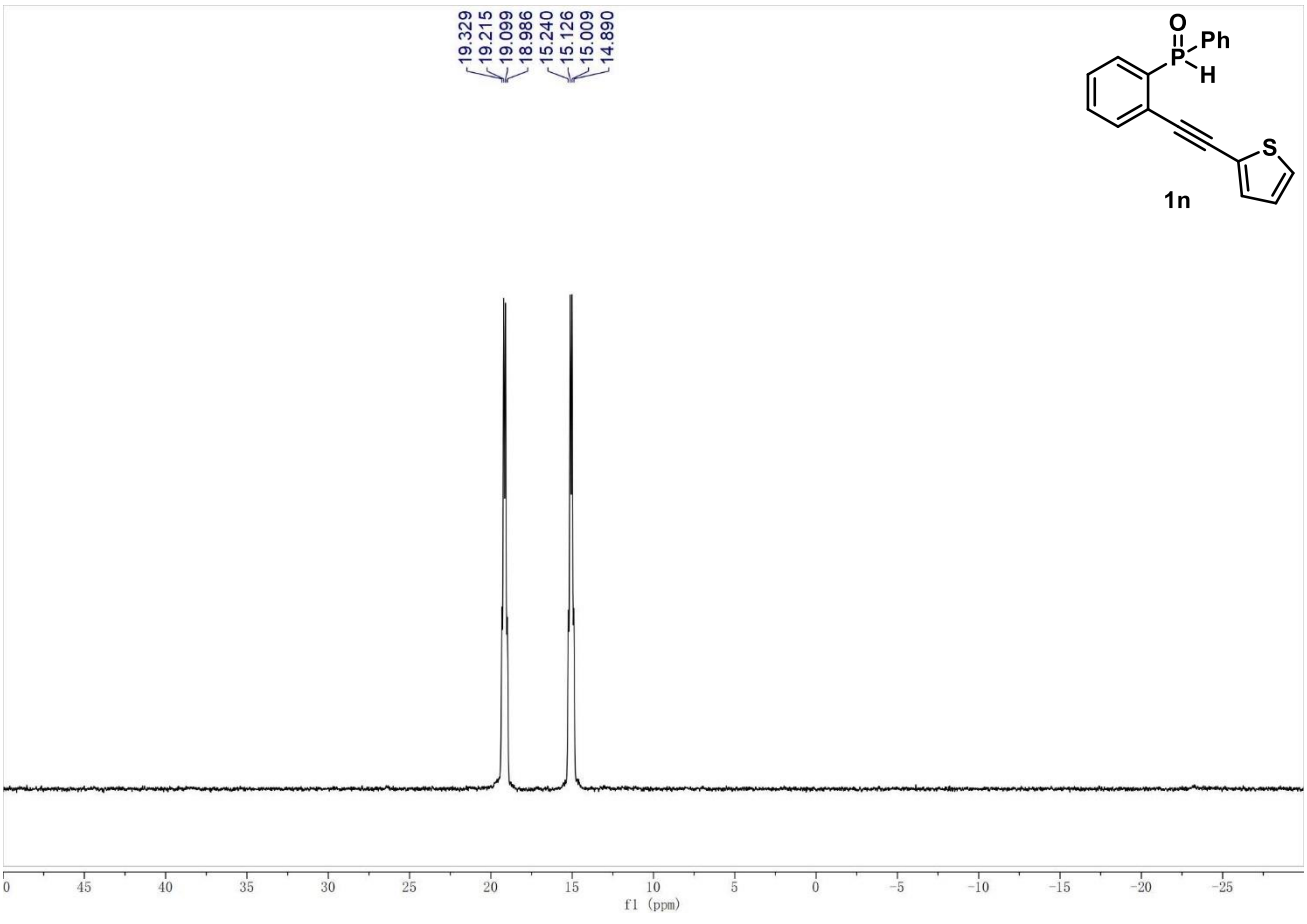


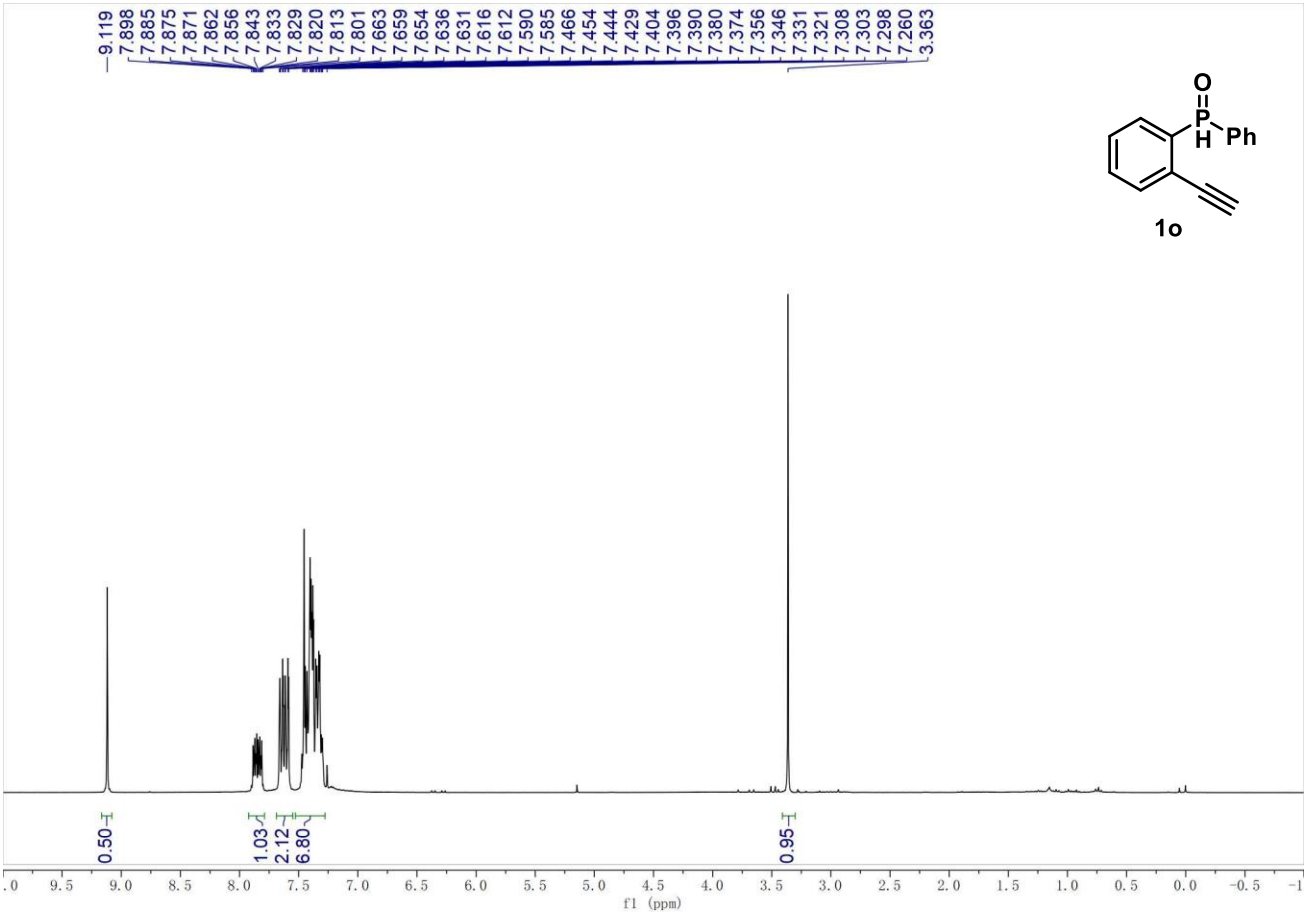
**$^{31}P\{^{1}H\}$ NMR spectrum of 1n (121 MHz, $CDCl_3$)**



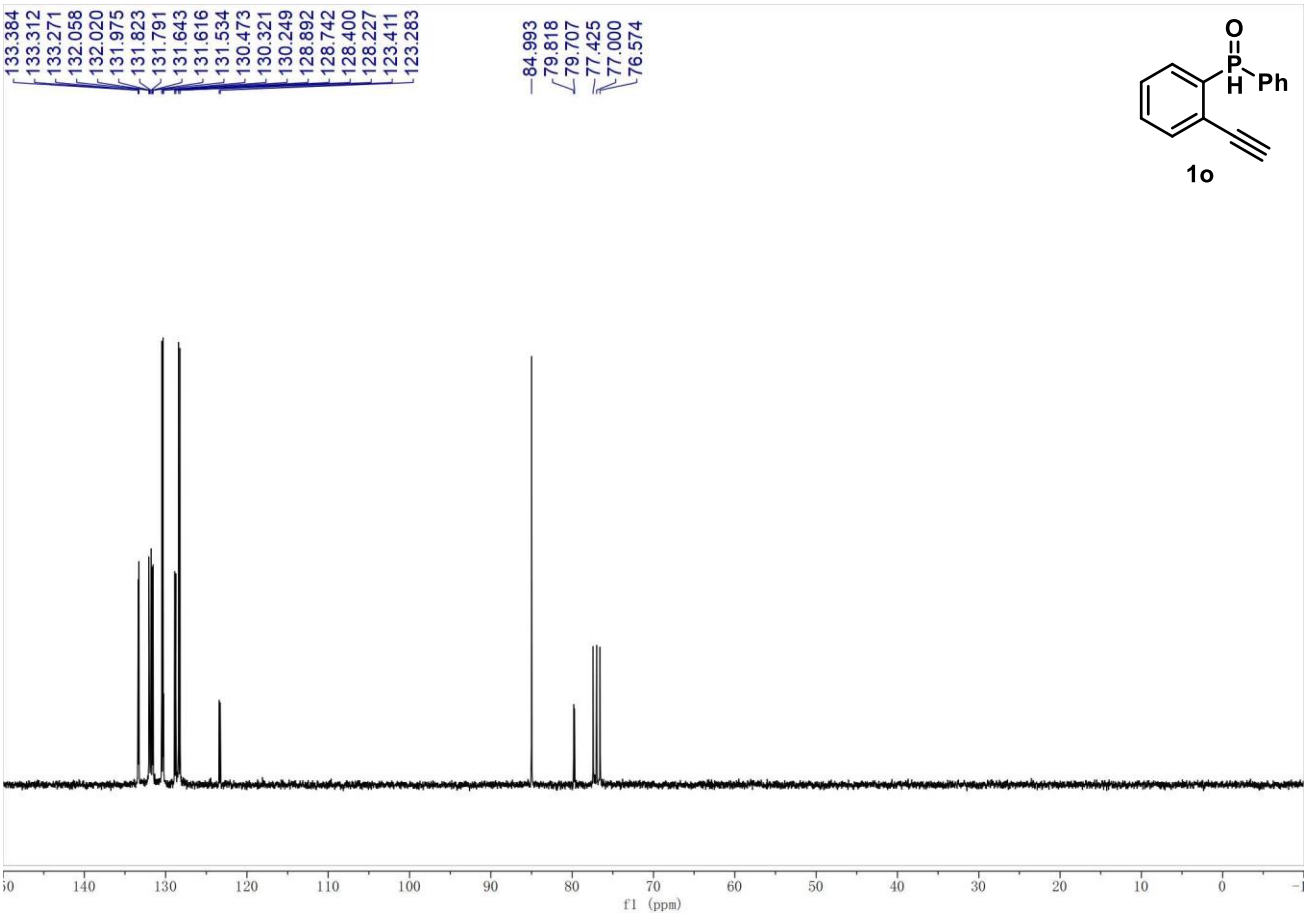

**$^{31}P$ NMR spectrum of 1n (121 MHz, $CDCl_3$)**

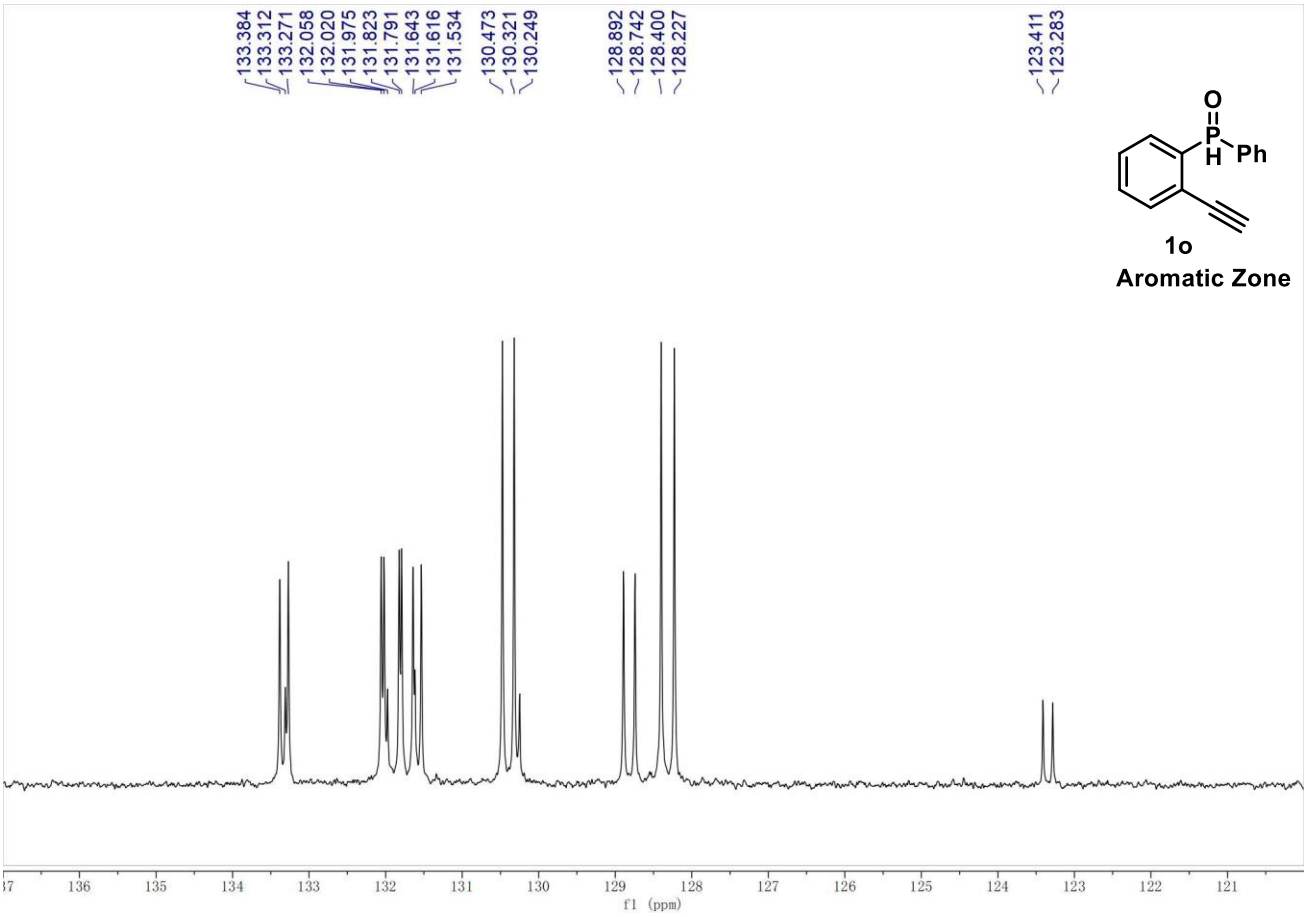


**$^{1}$H NMR spectrum of 1o (300 MHz, $CDCl_3$)**

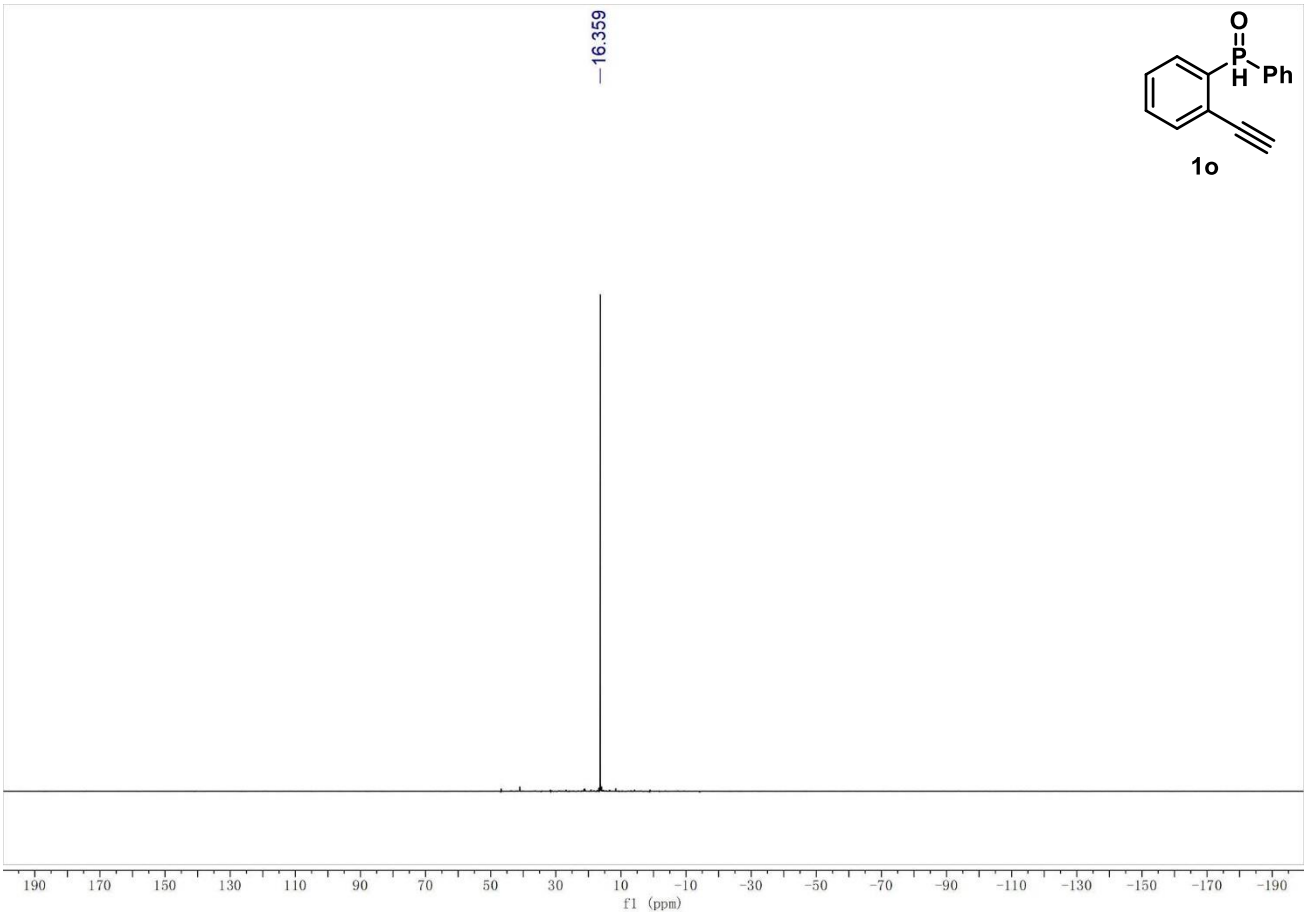



**$^{13}$C NMR spectrum of 1o (75 MHz, $CDCl_3$)**

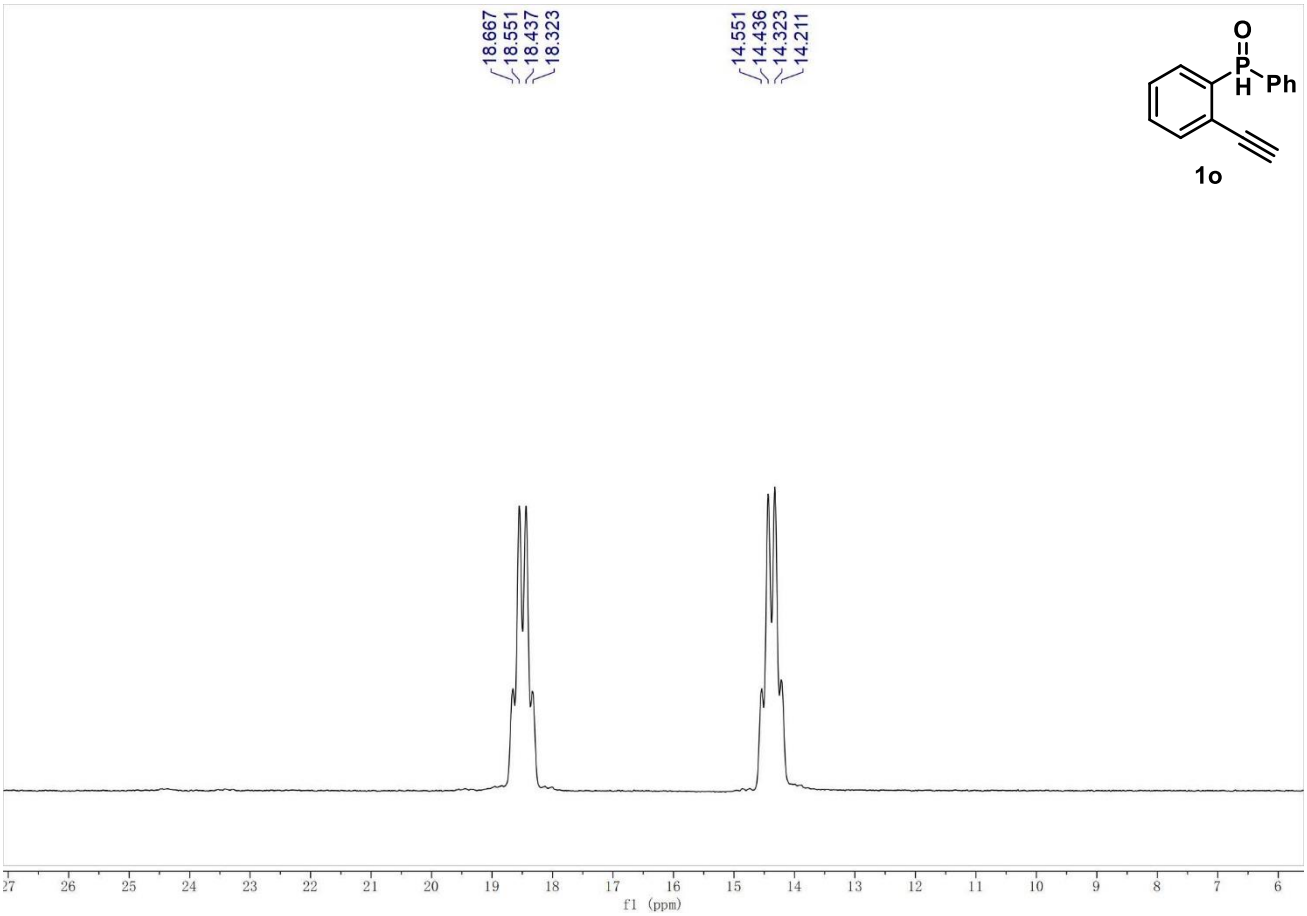




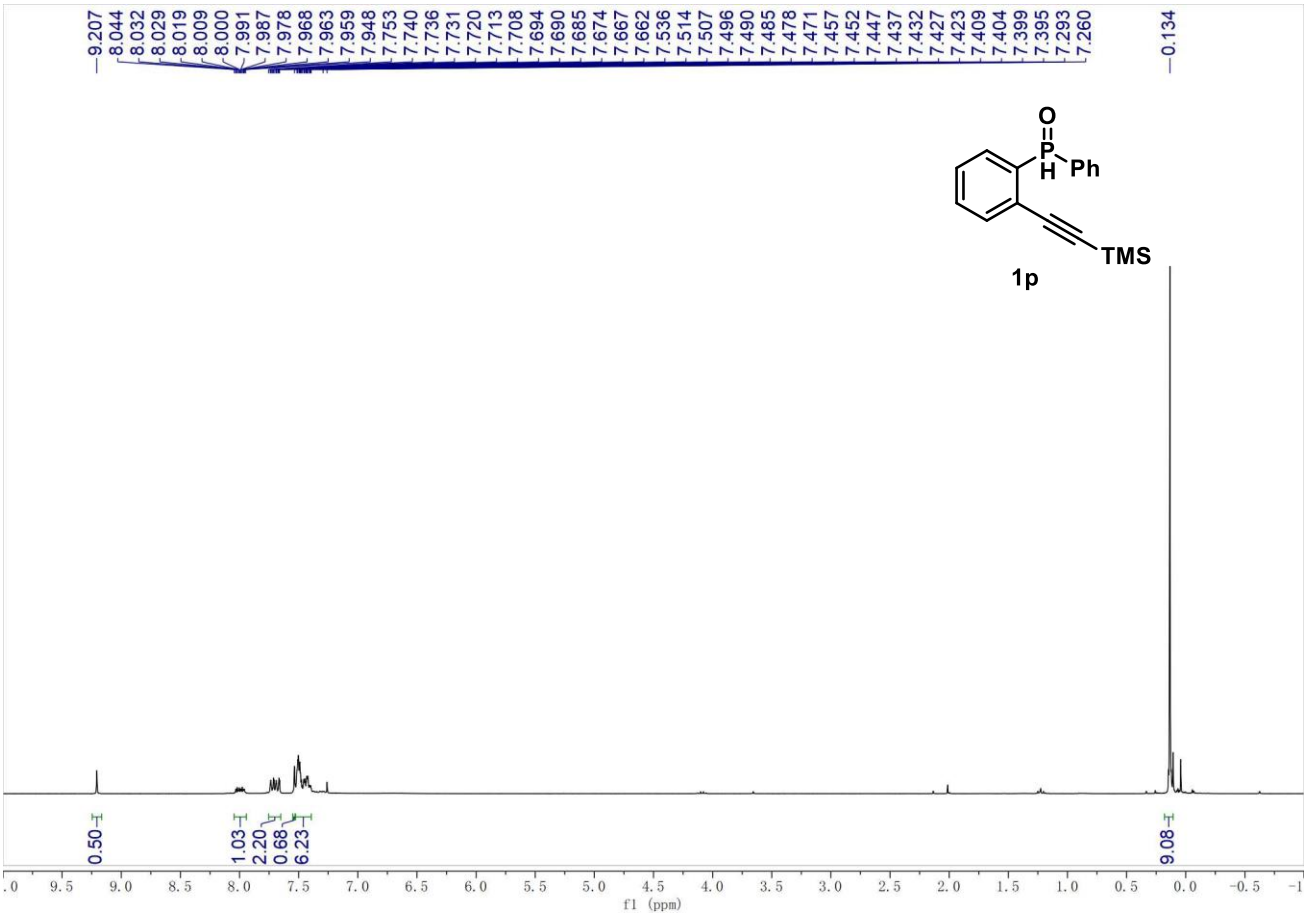

**$^{31}P\{^{1}H\}$ NMR spectrum of 1o (121 MHz, $CDCl_3$)**



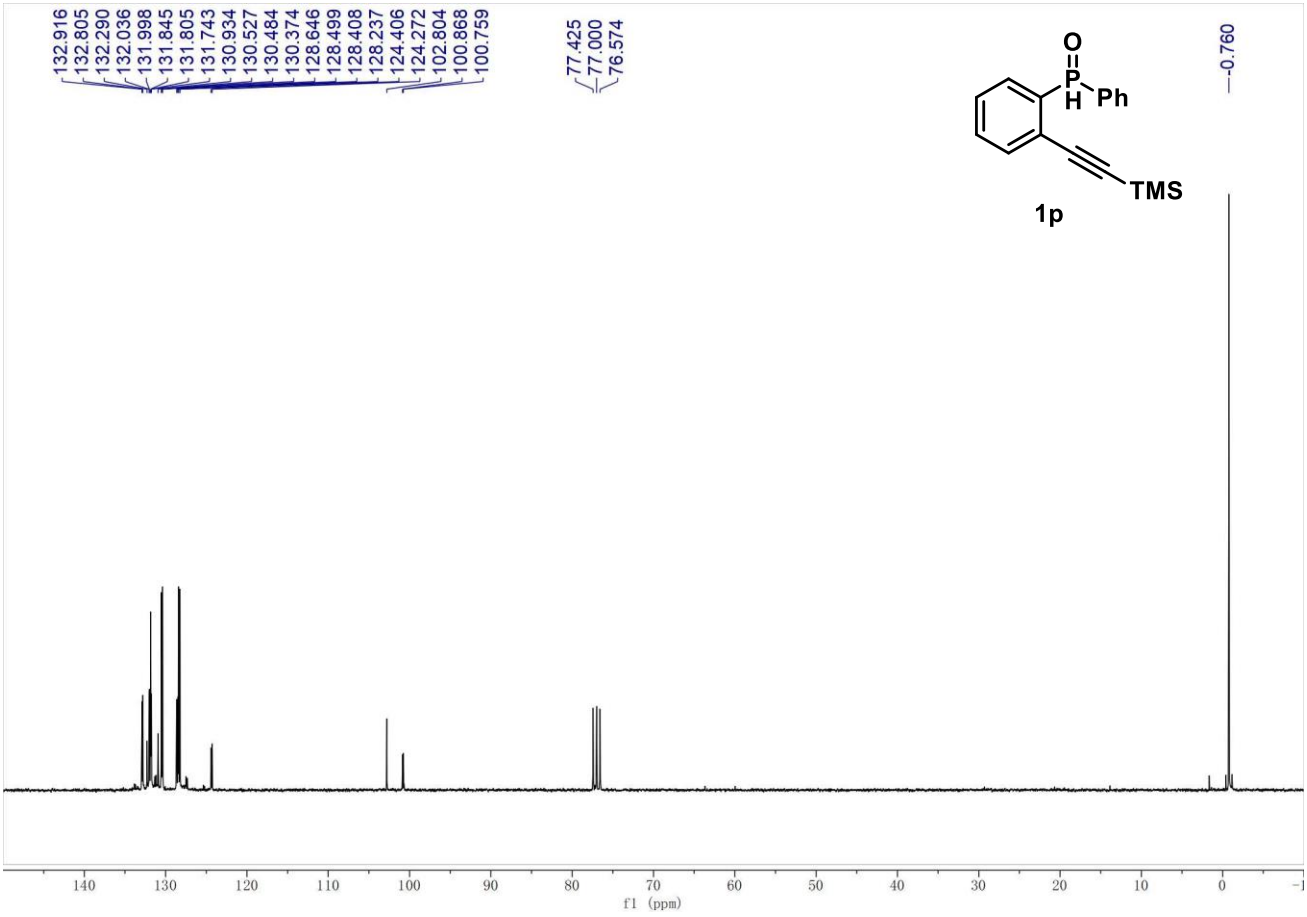
**$^{31}$P NMR spectrum of 1o (121 MHz, $CDCl_3$)**

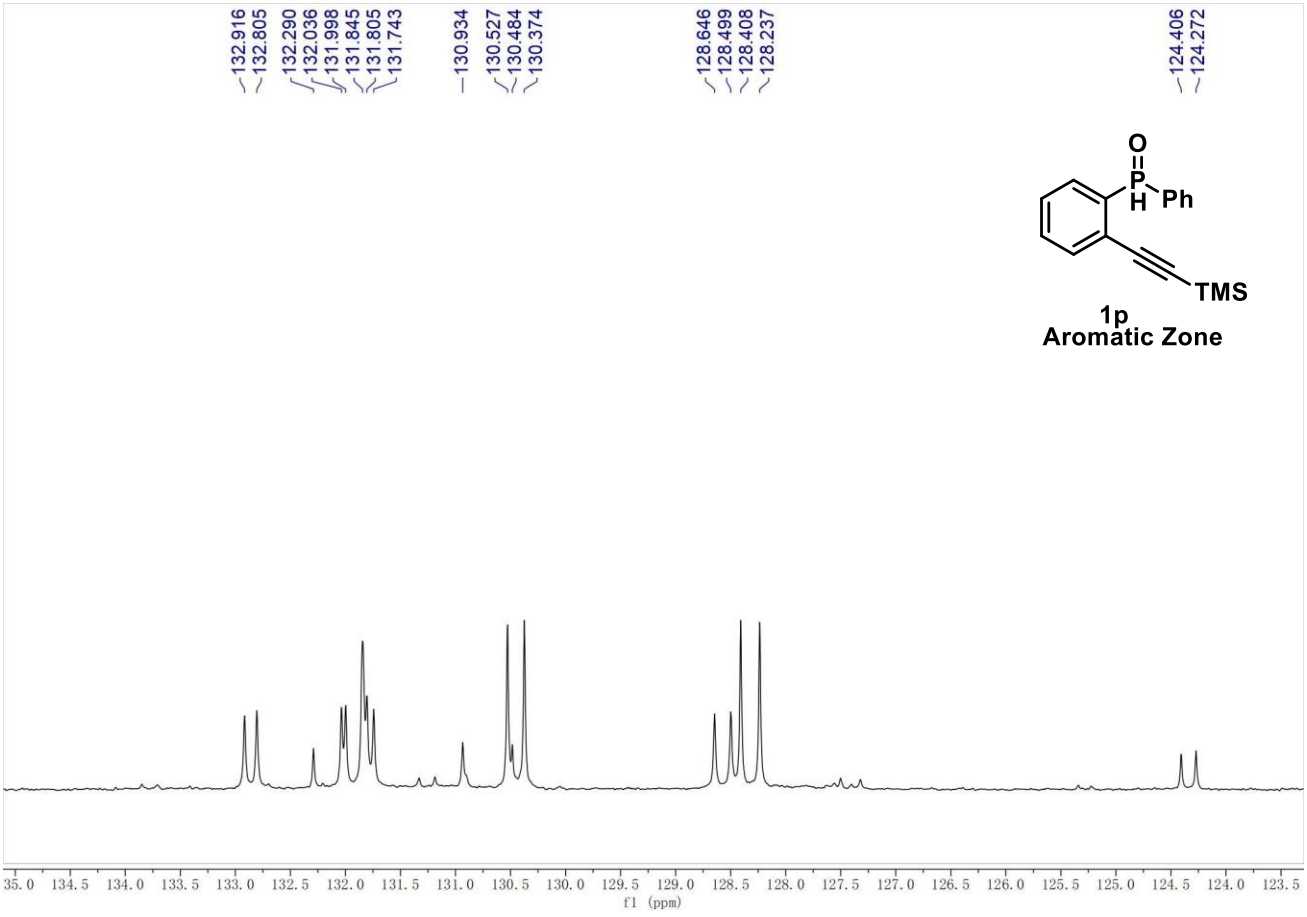



**$^{1}$H NMR spectrum of 1p (300 MHz, $CDCl_3$)**

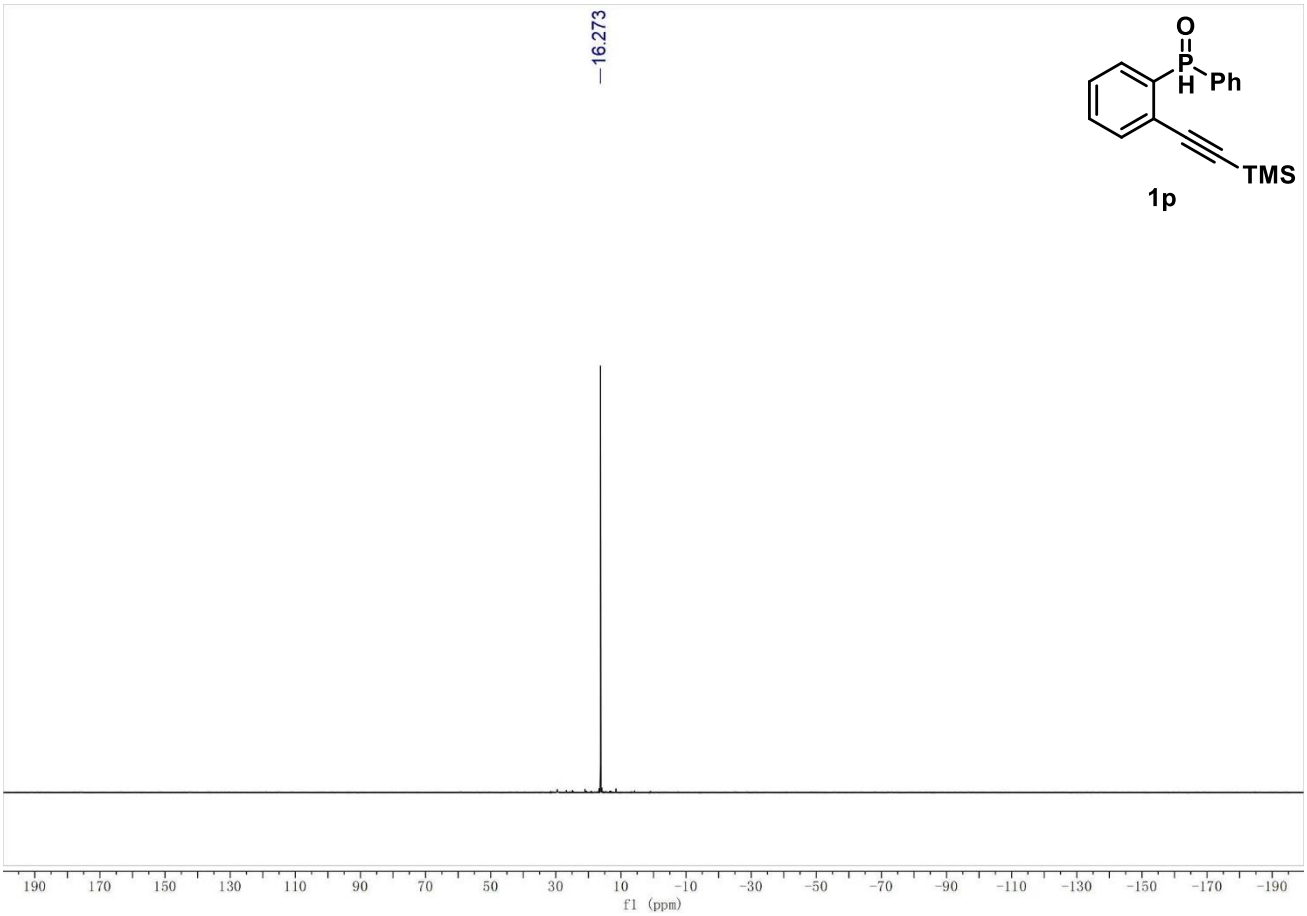


**$^{13}$C NMR spectrum of 1p (75 MHz, $CDCl_3$)**

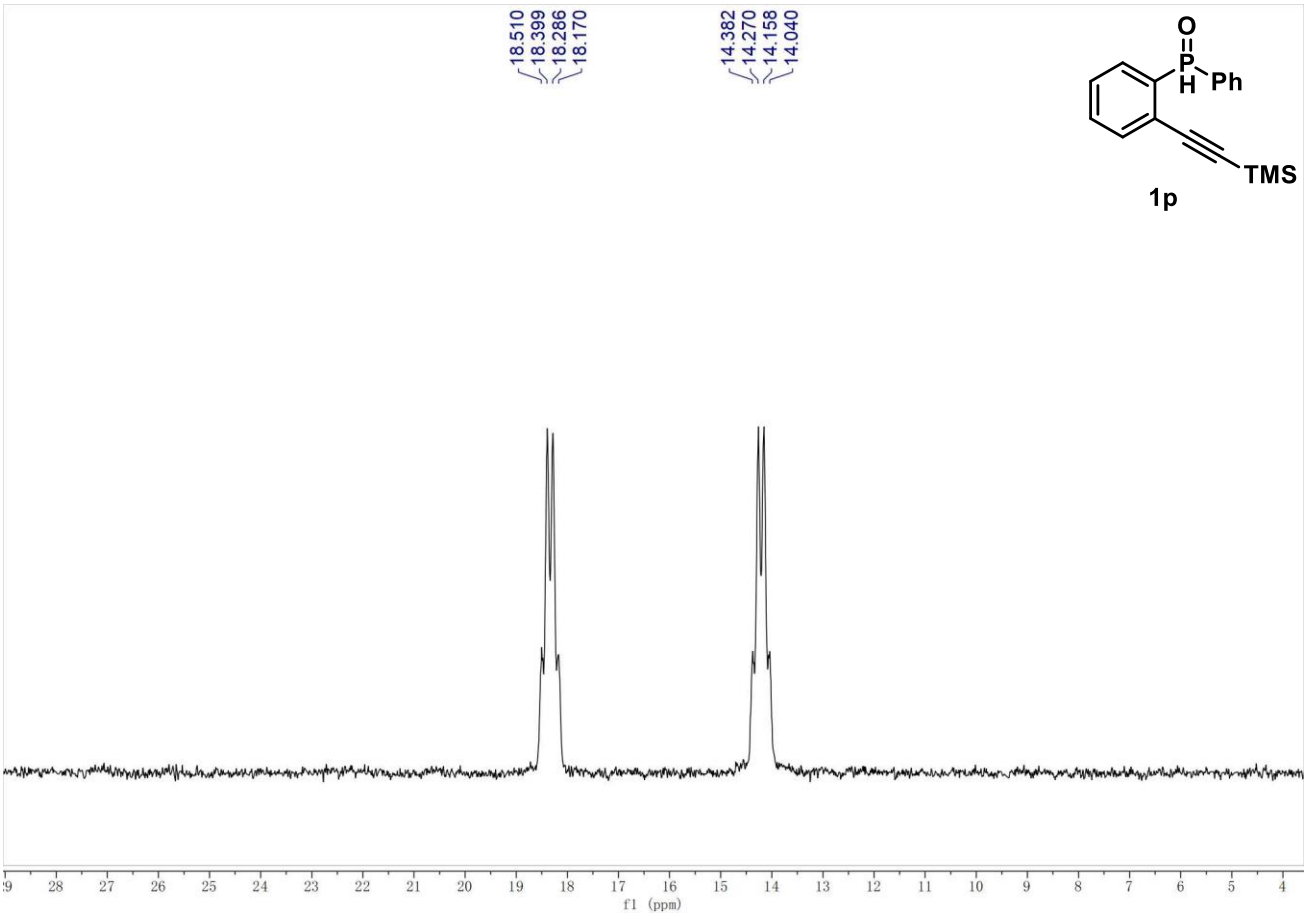


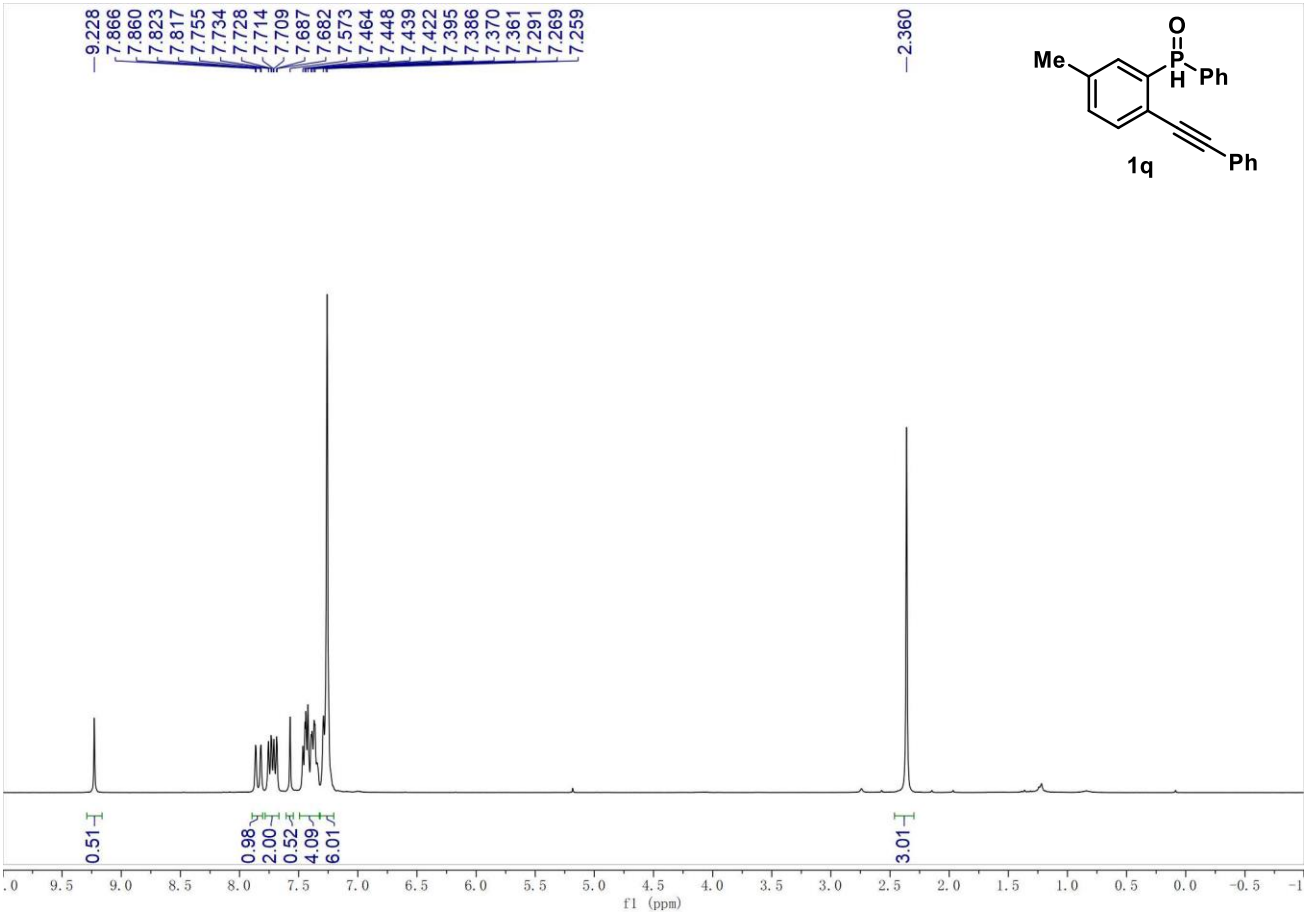
**$^{31}P\{^{1}H\}$ NMR spectrum of 1p (121 MHz, $CDCl_3$)**



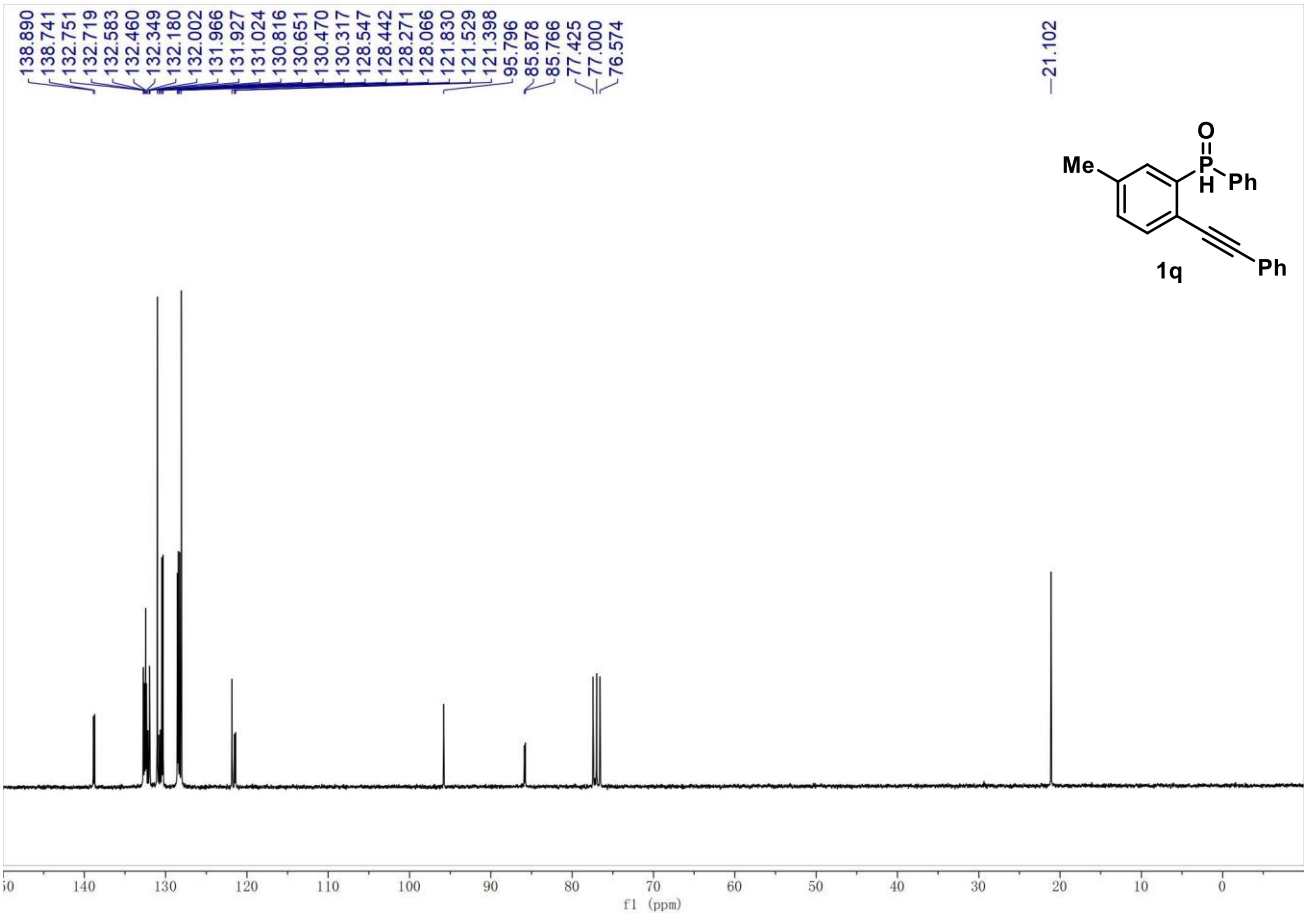

**$^{31}P$ NMR spectrum of 1p (121 MHz, $CDCl_3$**

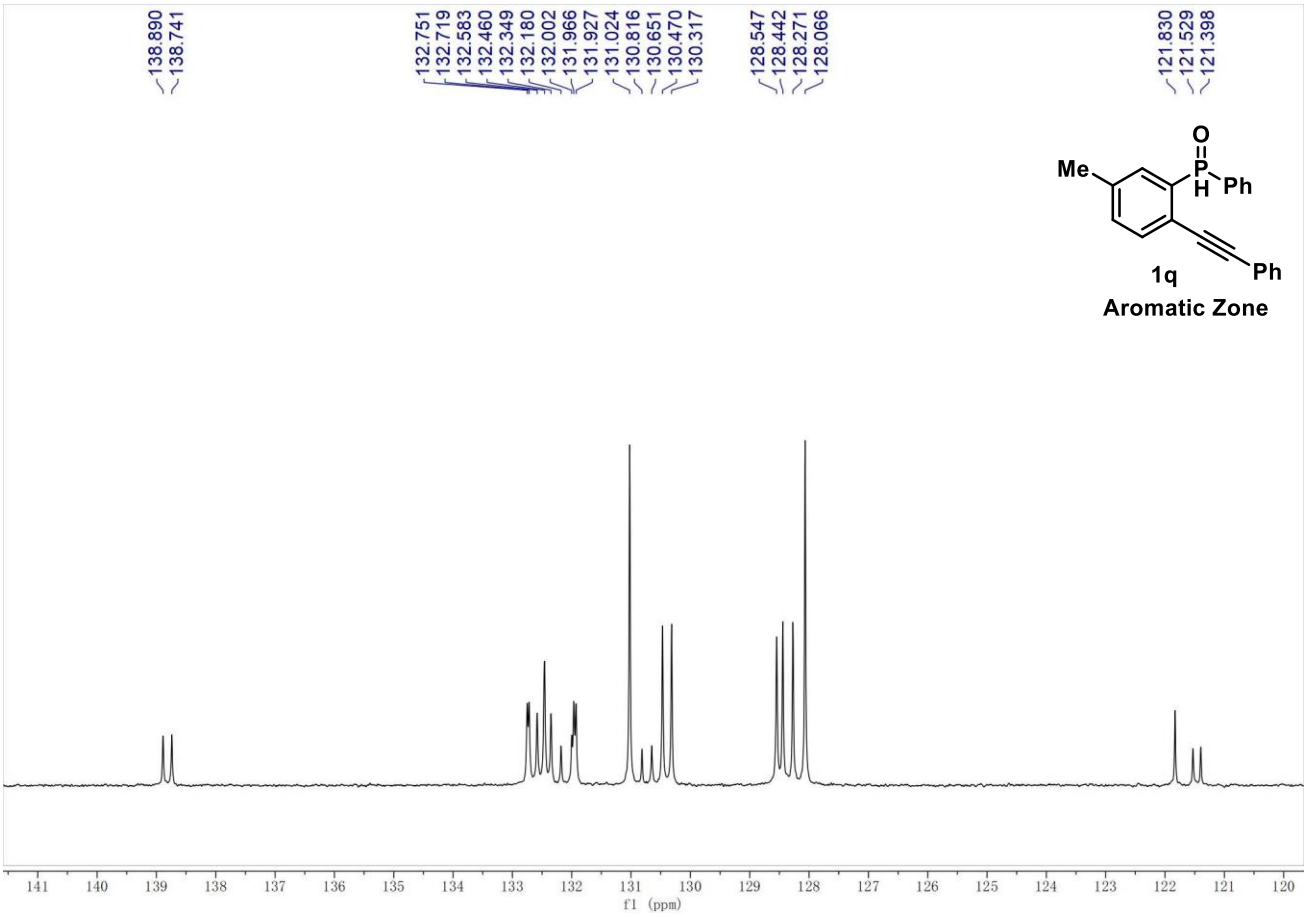


**$^{1}$H NMR spectrum of 1q (300 MHz, $CDCl_3$)**

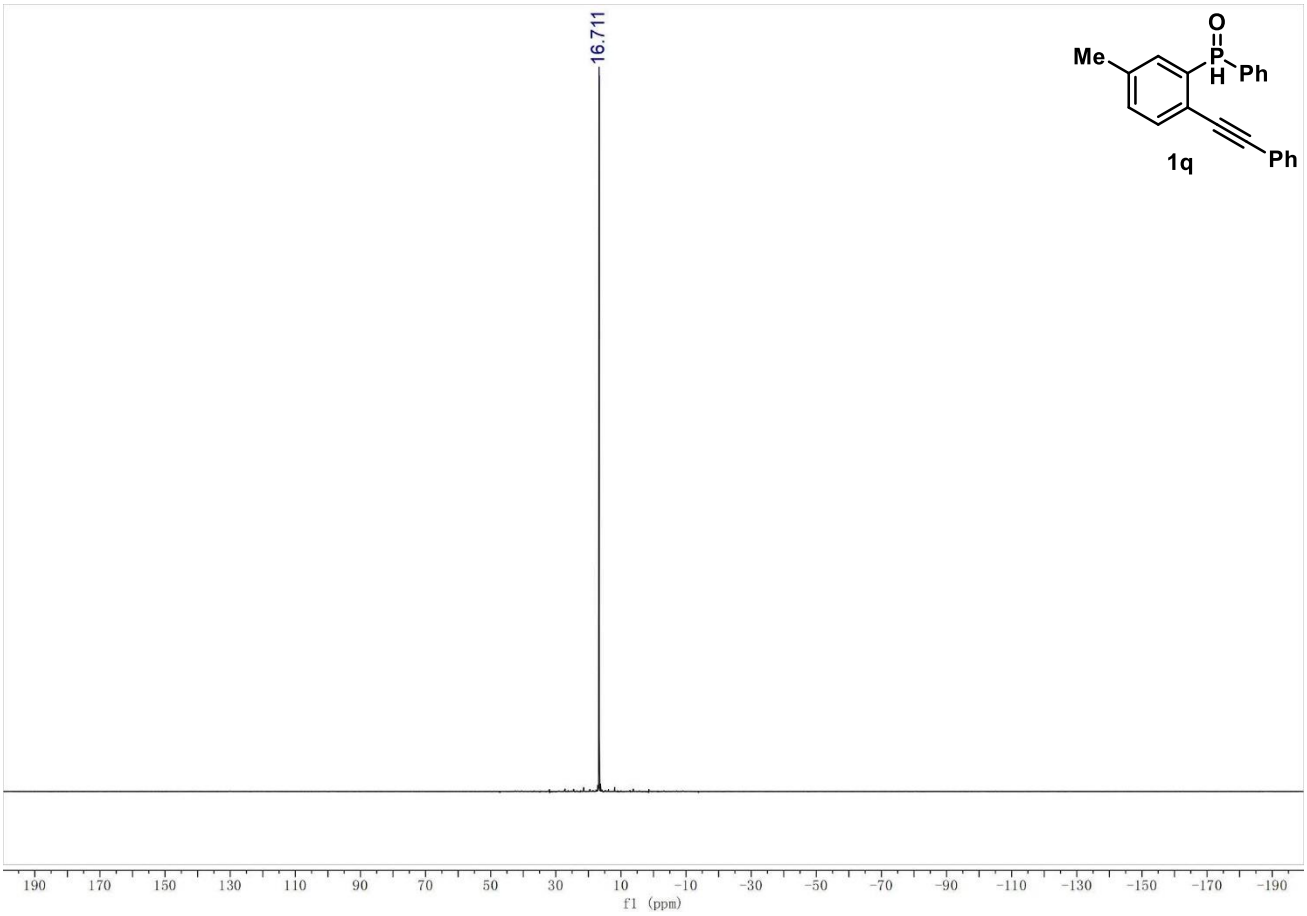



**$^{13}$C NMR spectrum of 1q (75 MHz, $CDCl_3$)**

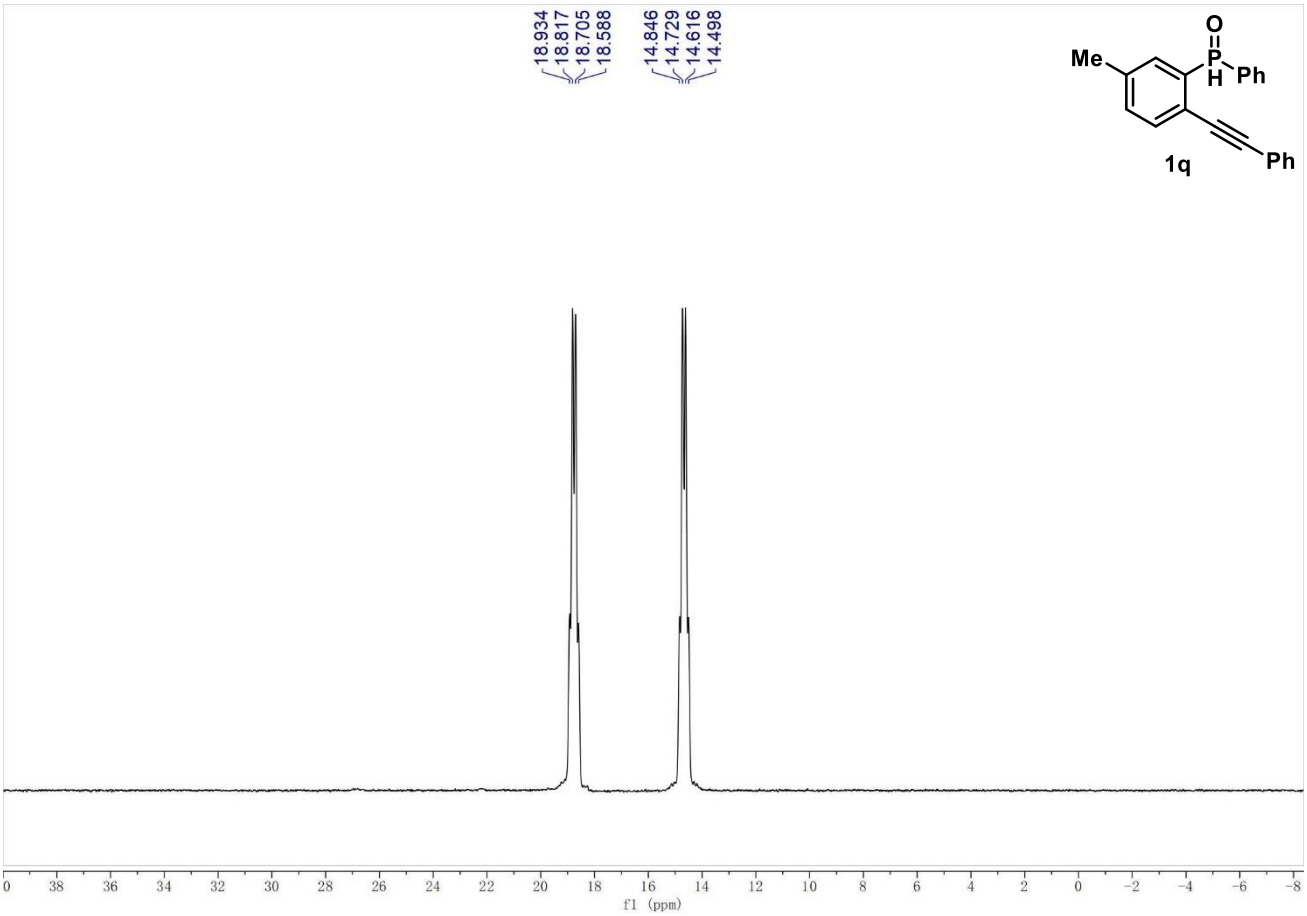




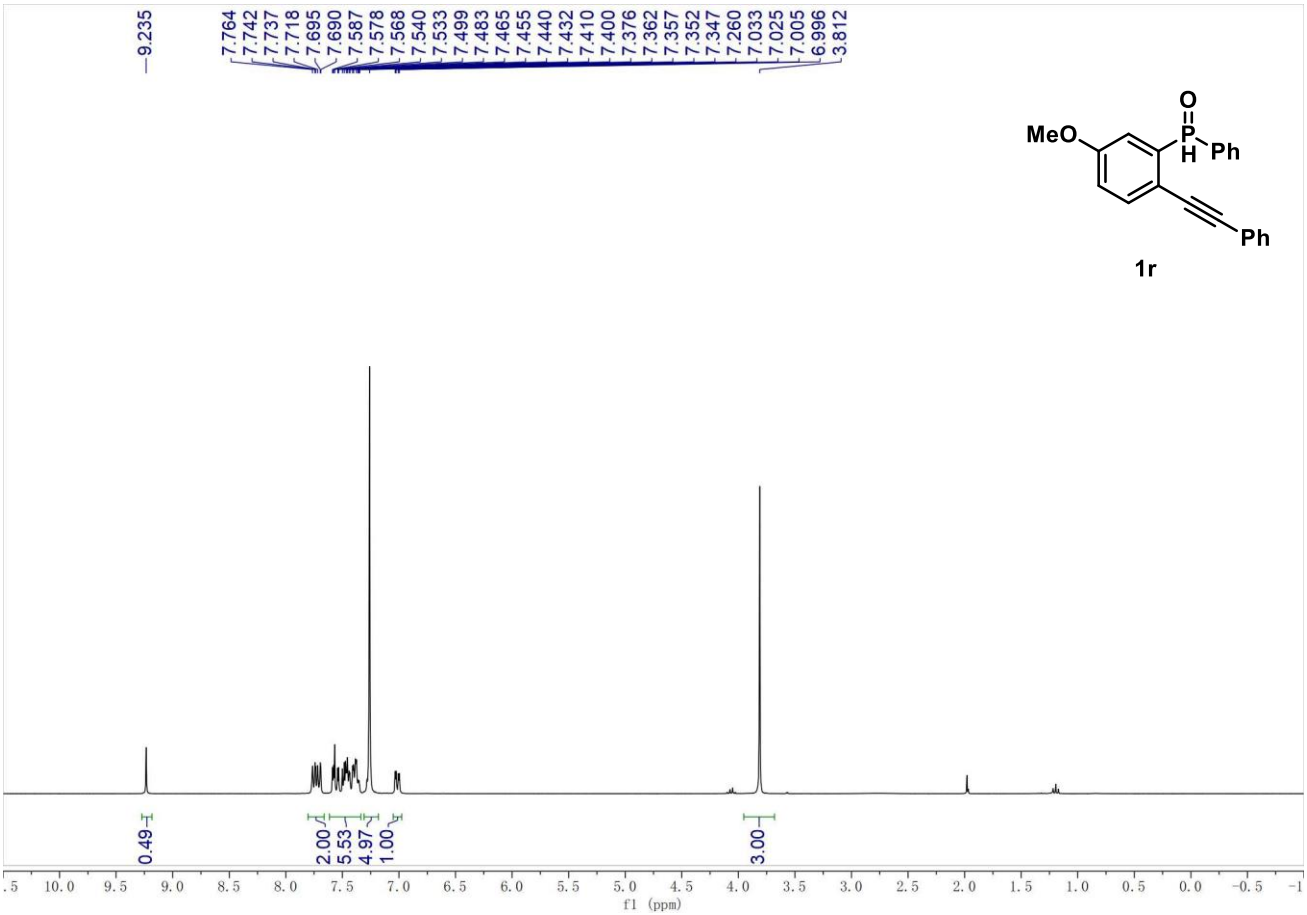

**$^{31}P\{^{1}H\}$ NMR spectrum of 1q (121 MHz, $CDCl_3$)**



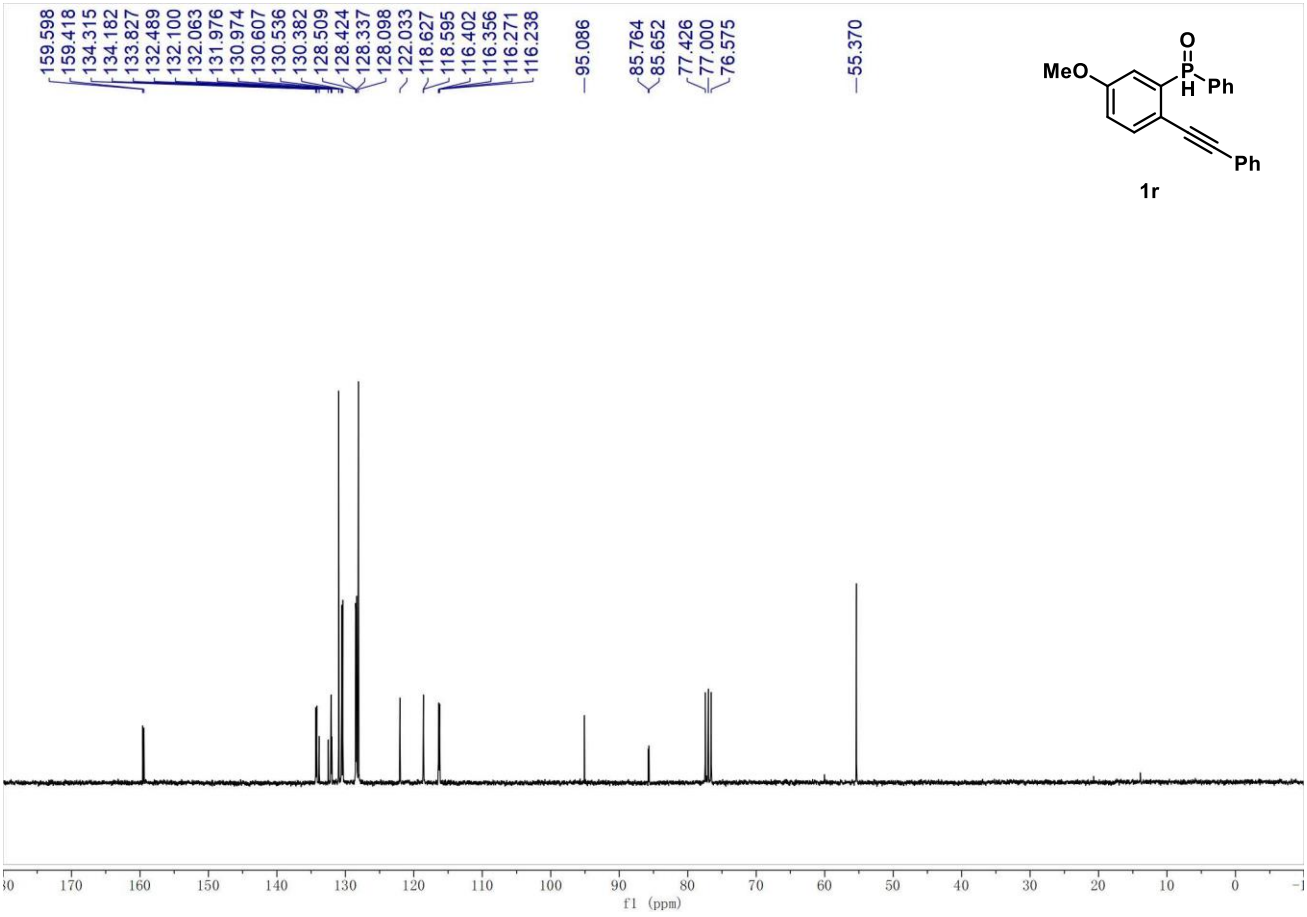
**$^{1}$P NMR spectrum of 1q (121 MHz, $CDCl_3$)**

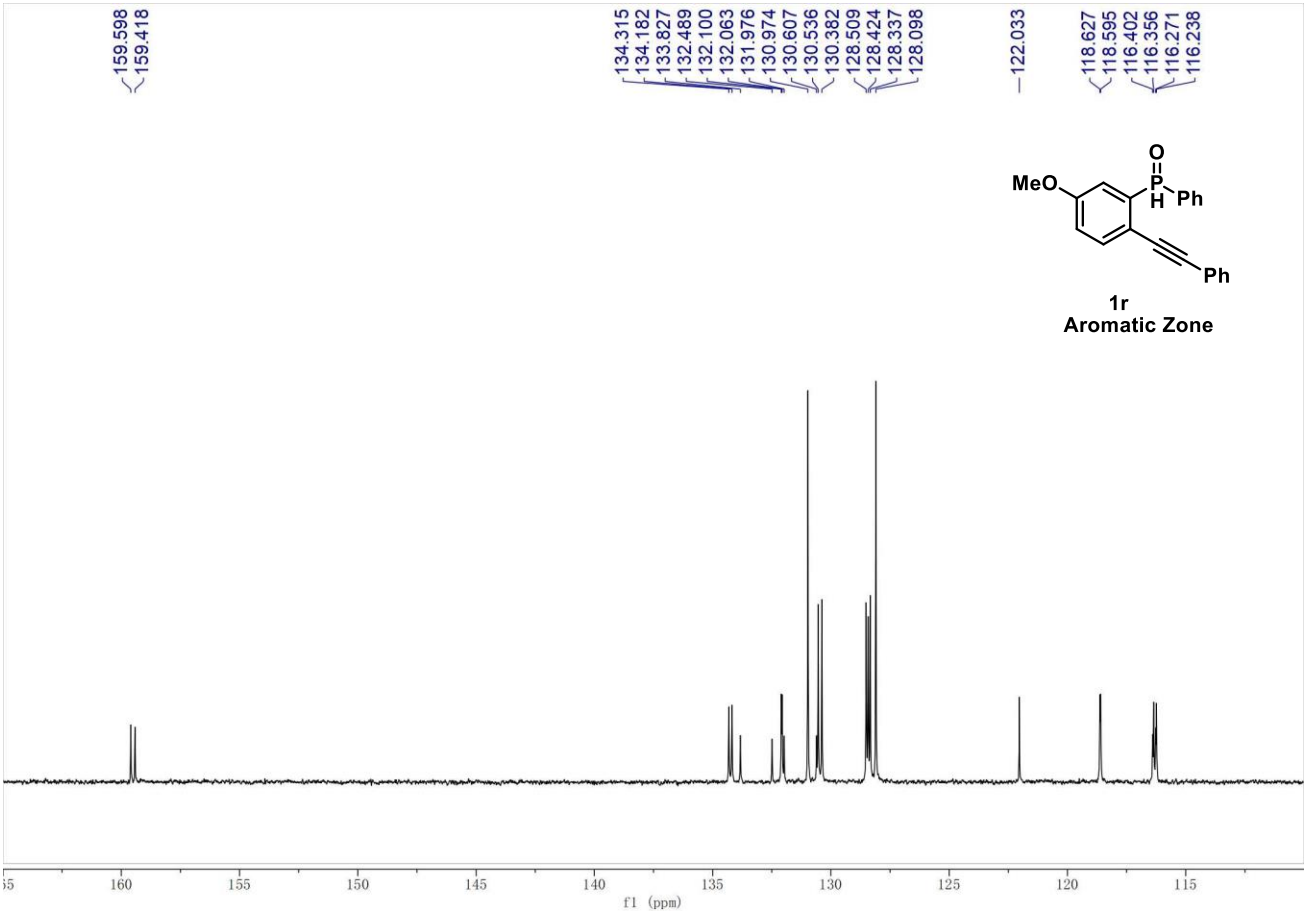



**$^{1}$H NMR spectrum of 1r (300 MHz, $CDCl_3$)**

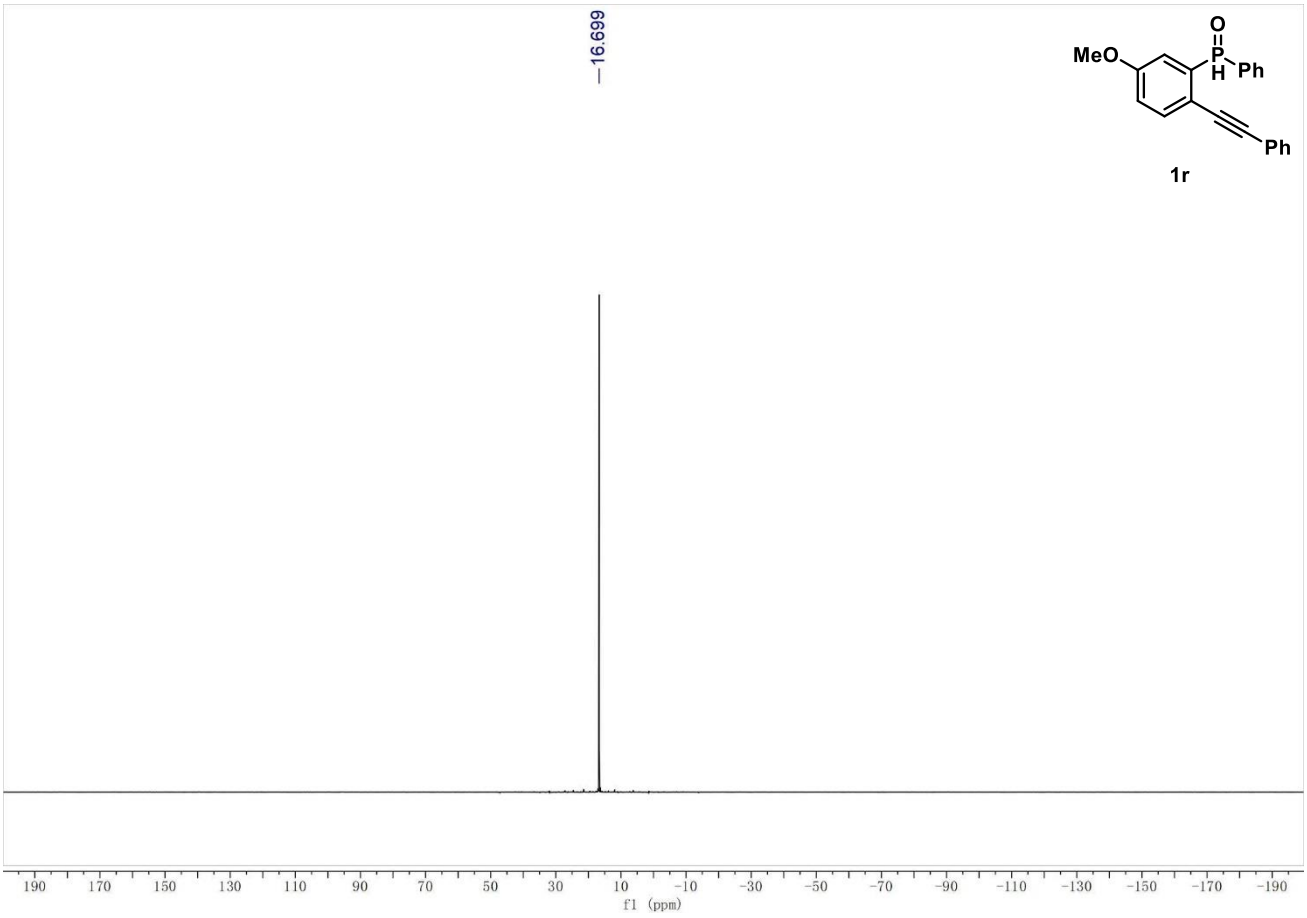


**$^{13}$C NMR spectrum of 1r (75 MHz, $CDCl_3$)**

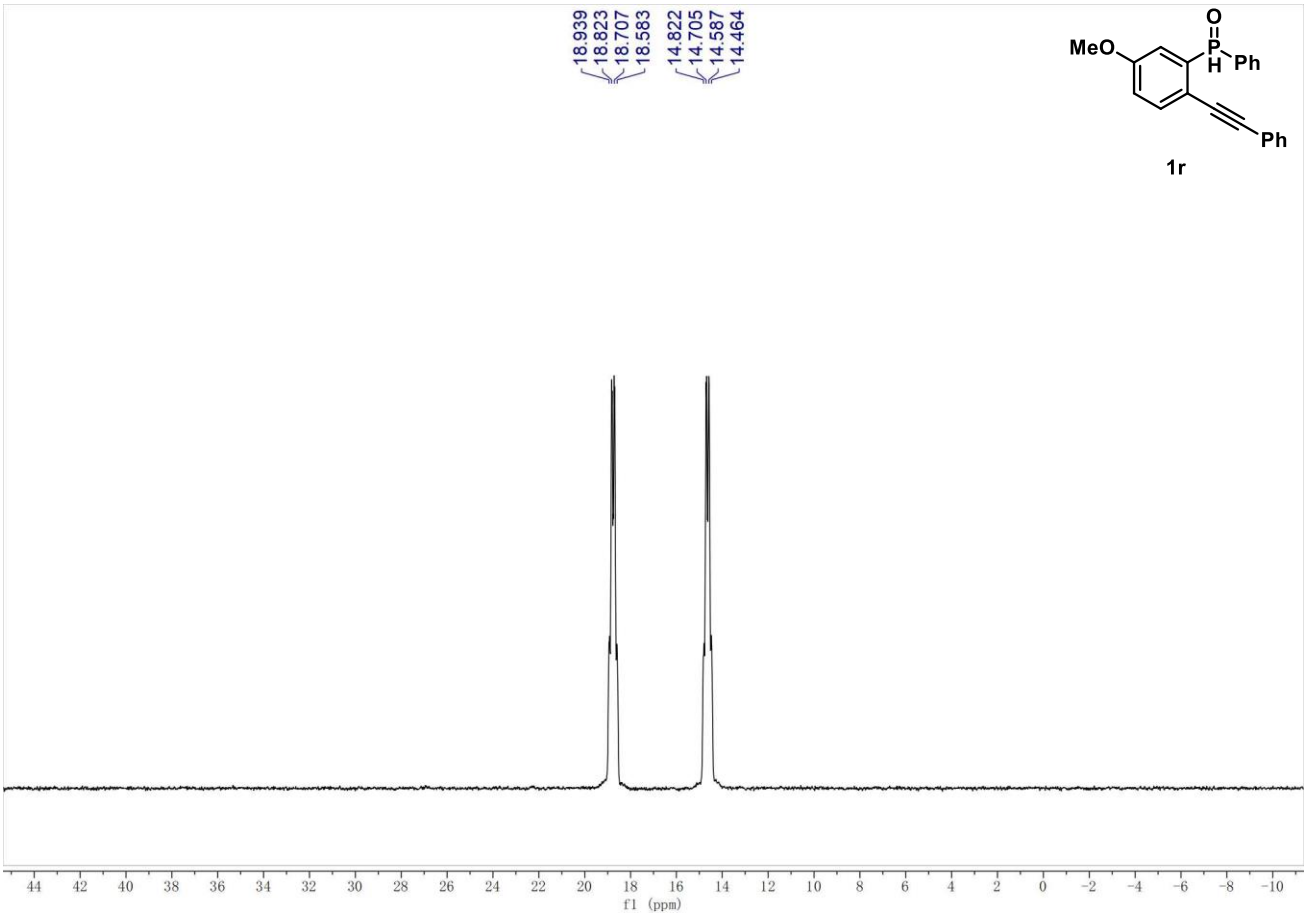


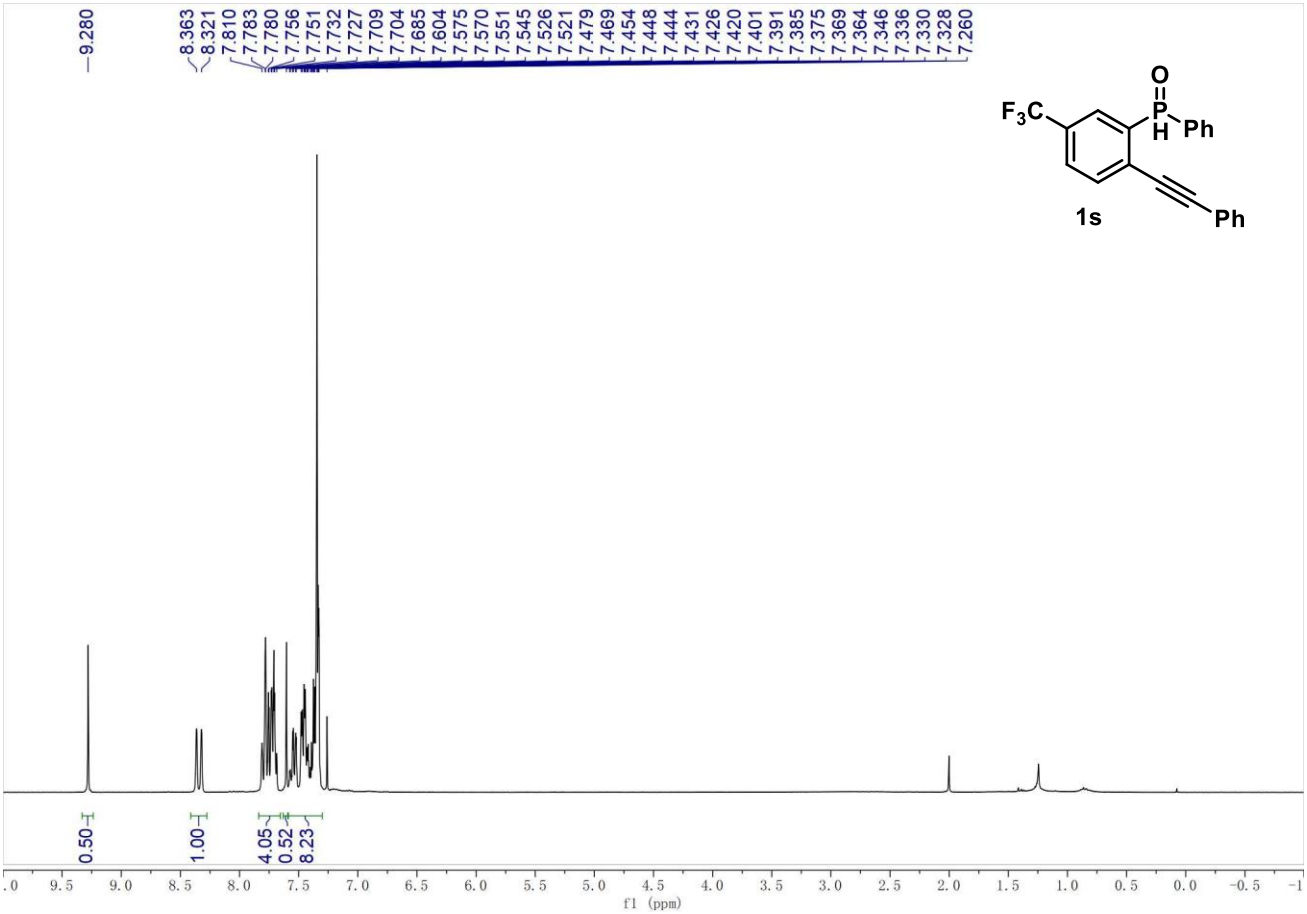
**$^{31}P\{^{1}H\}$ NMR spectrum of 1r (121 MHz, $CDCl_3$)**



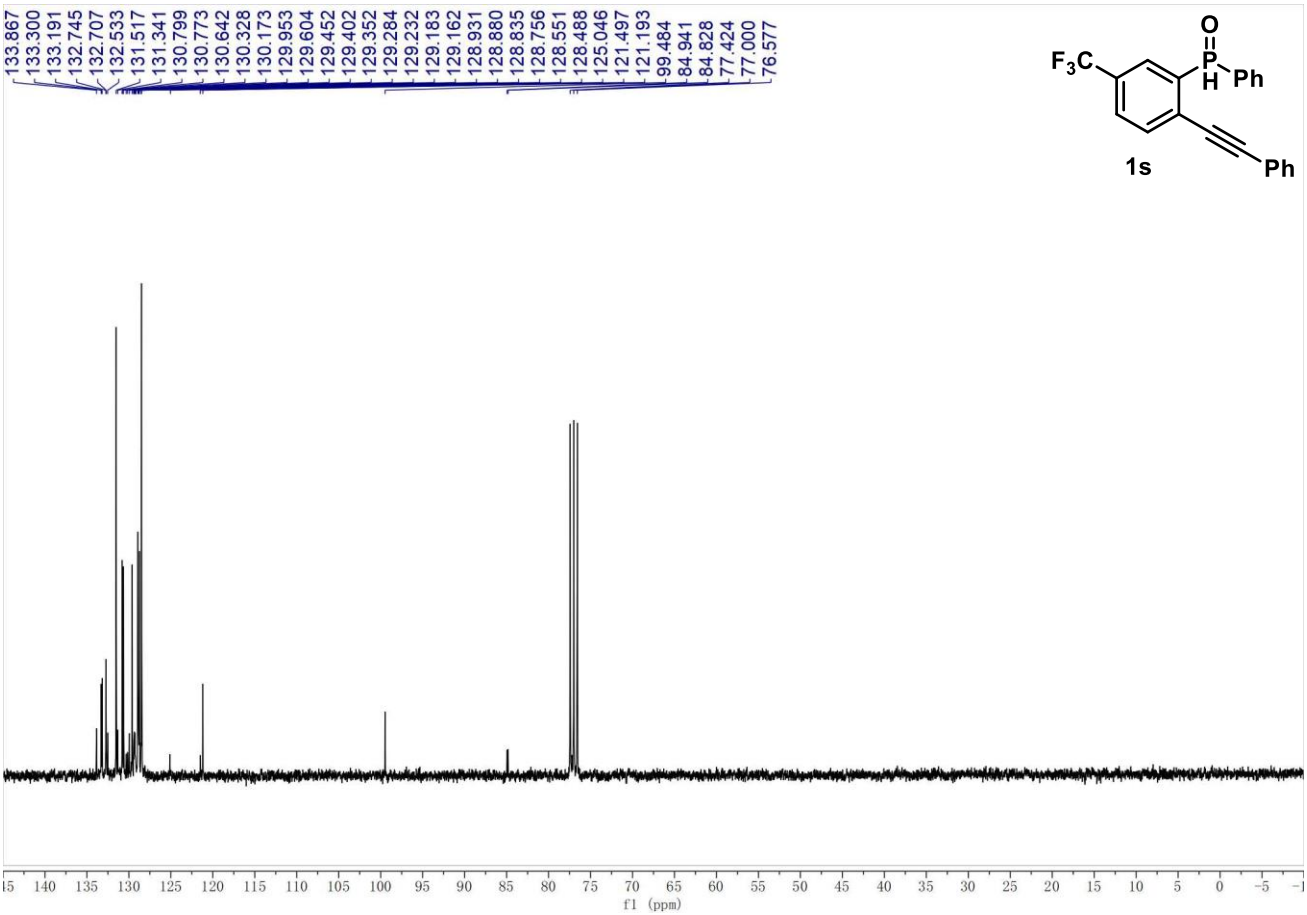

**$^{31}P$ NMR spectrum of 1r (121 MHz, $CDCl_3$)**

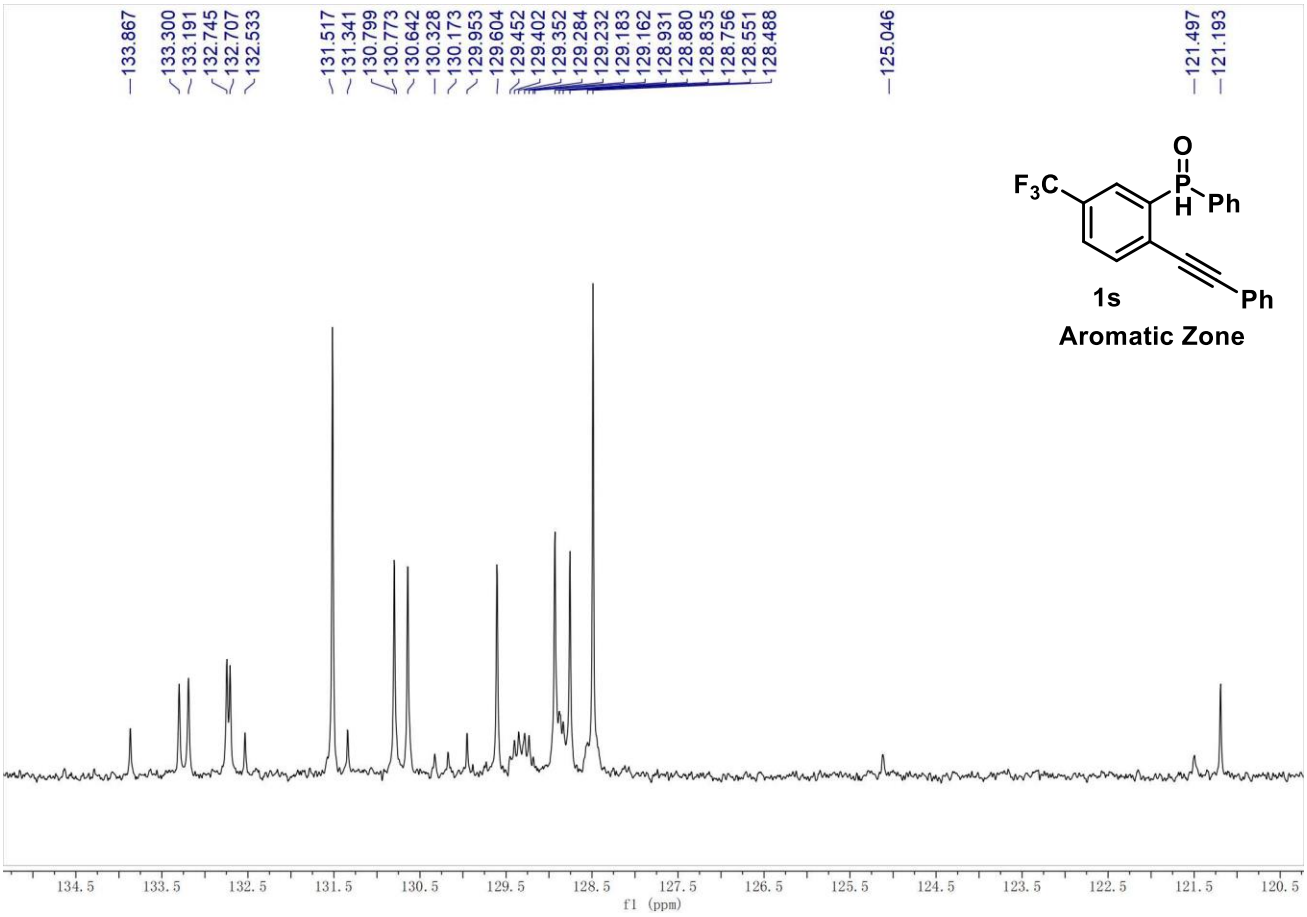


**$^{1}$H NMR spectrum of 1s (300 MHz, $CDCl_3$)**

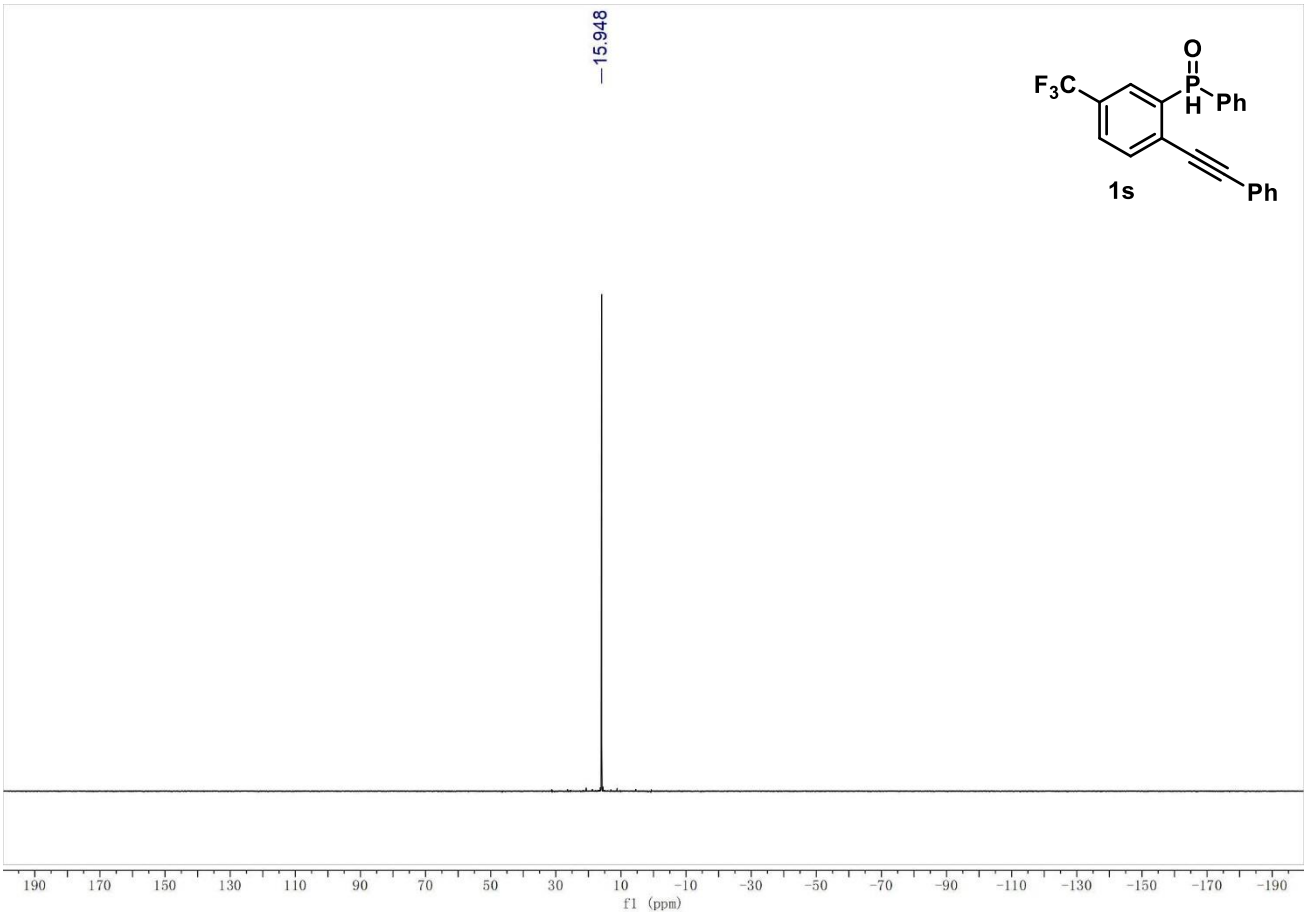



**$^{13}$C NMR spectrum of 1s (75 MHz, $CDCl_3$)**

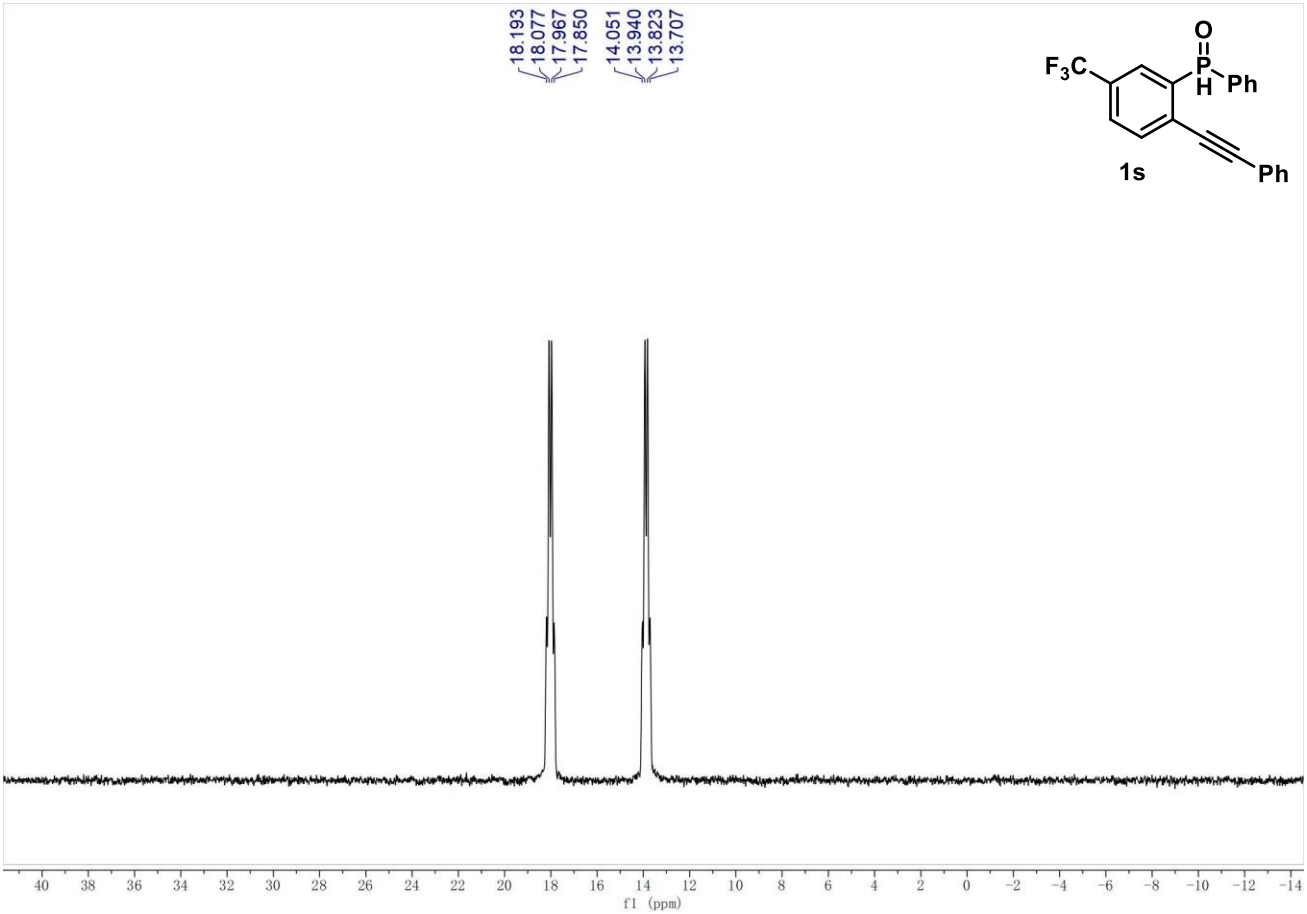




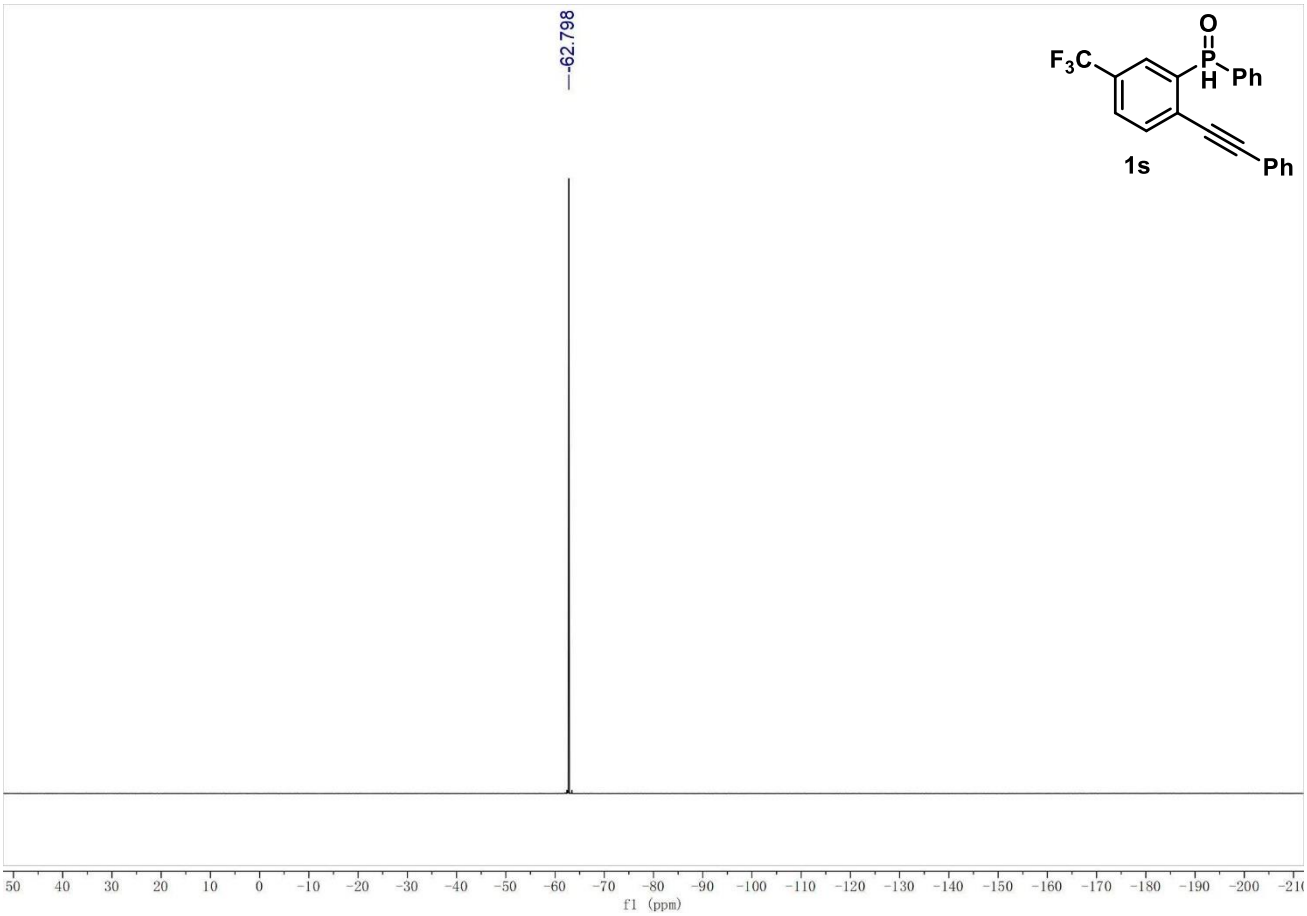

**$^{31}P\{^{1}H\}$ NMR spectrum of 1s (121 MHz, $CDCl_3$)**



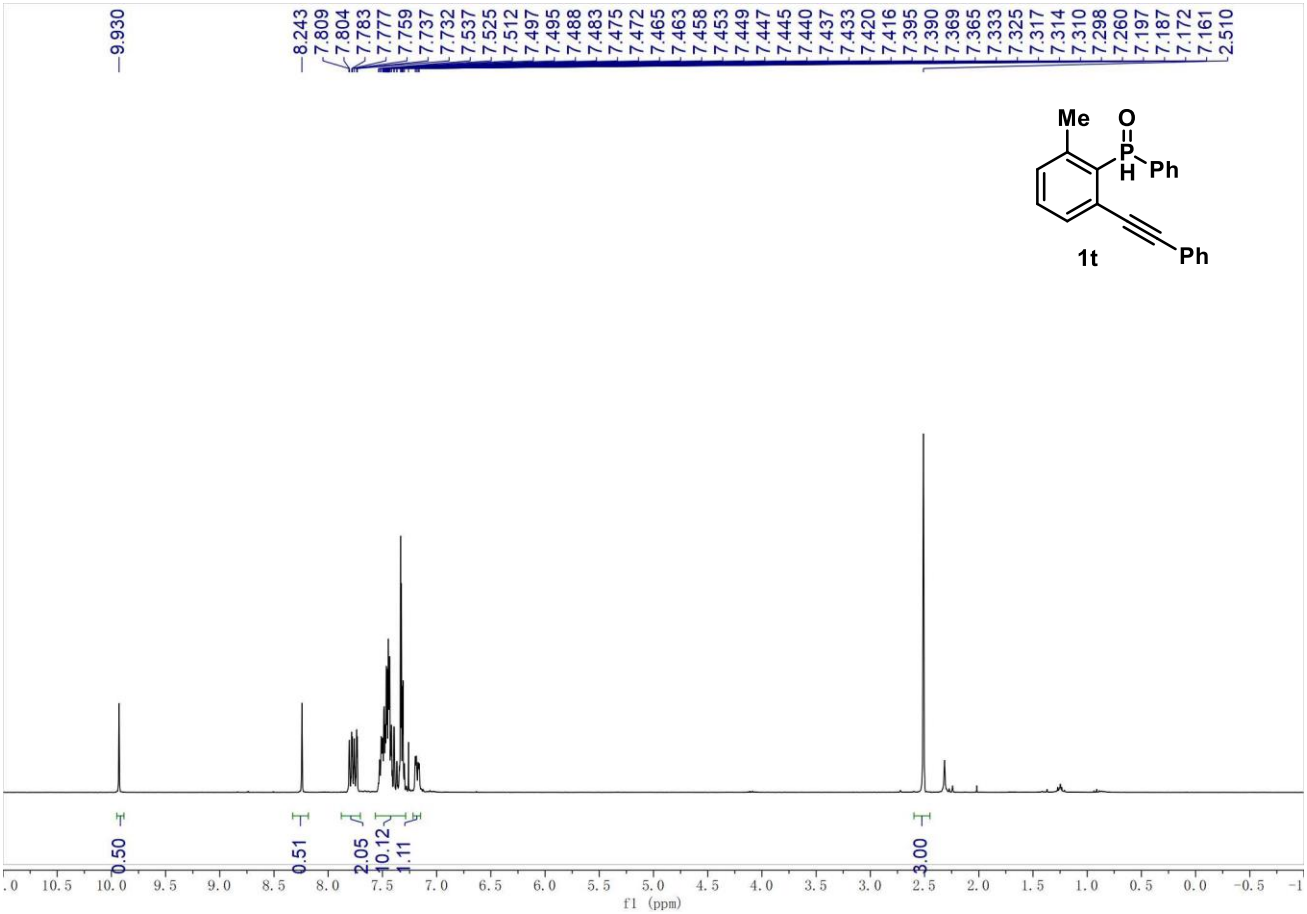
**$^{31}$P NMR spectrum of 1s (121 MHz, $CDCl_3$)**



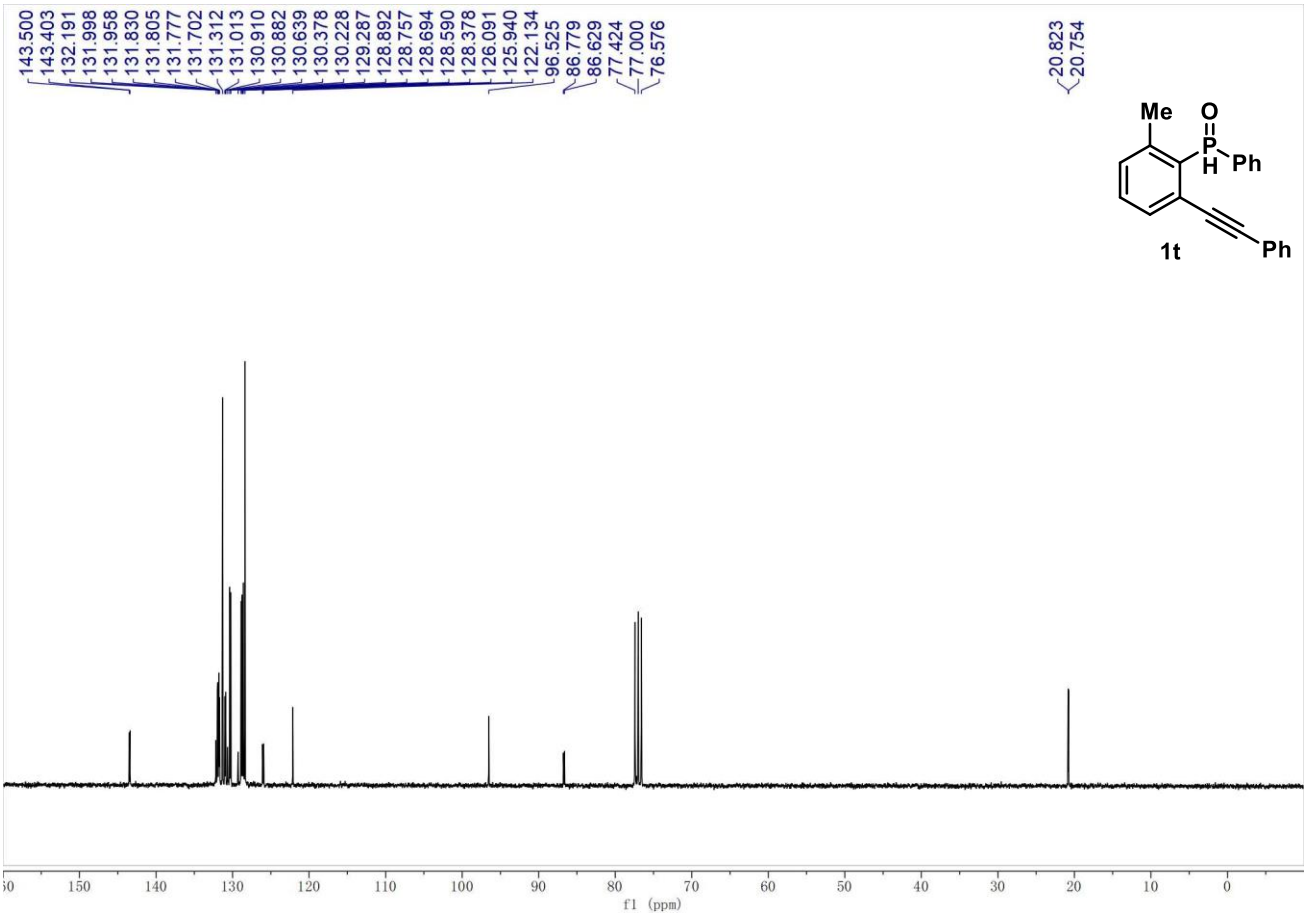

**$^{19}$F NMR spectrum of 1s (282 MHz, $CDCl_3$)**

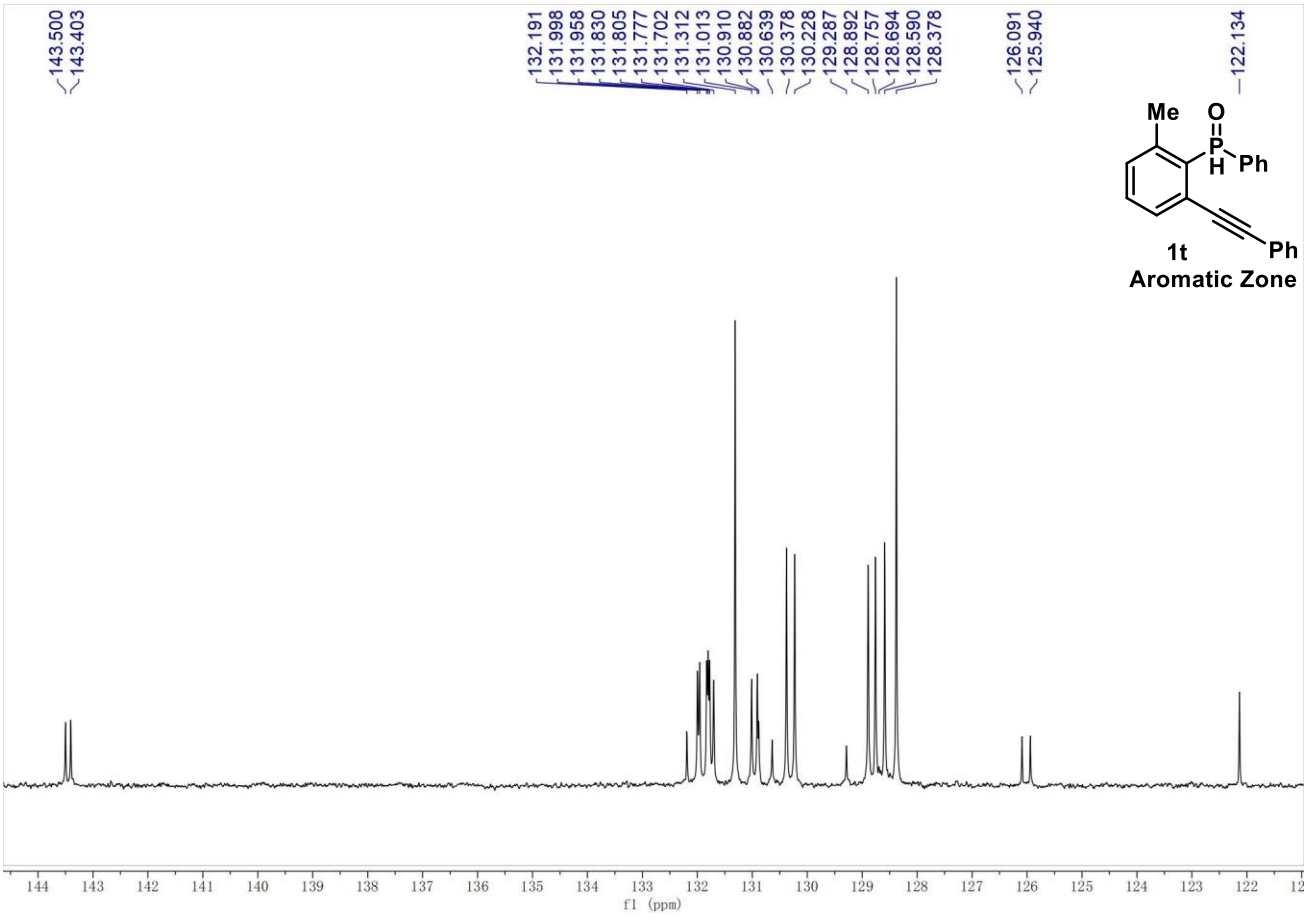


**$^{1}$H NMR spectrum of 1t (300 MHz, $CDCl_3$)**

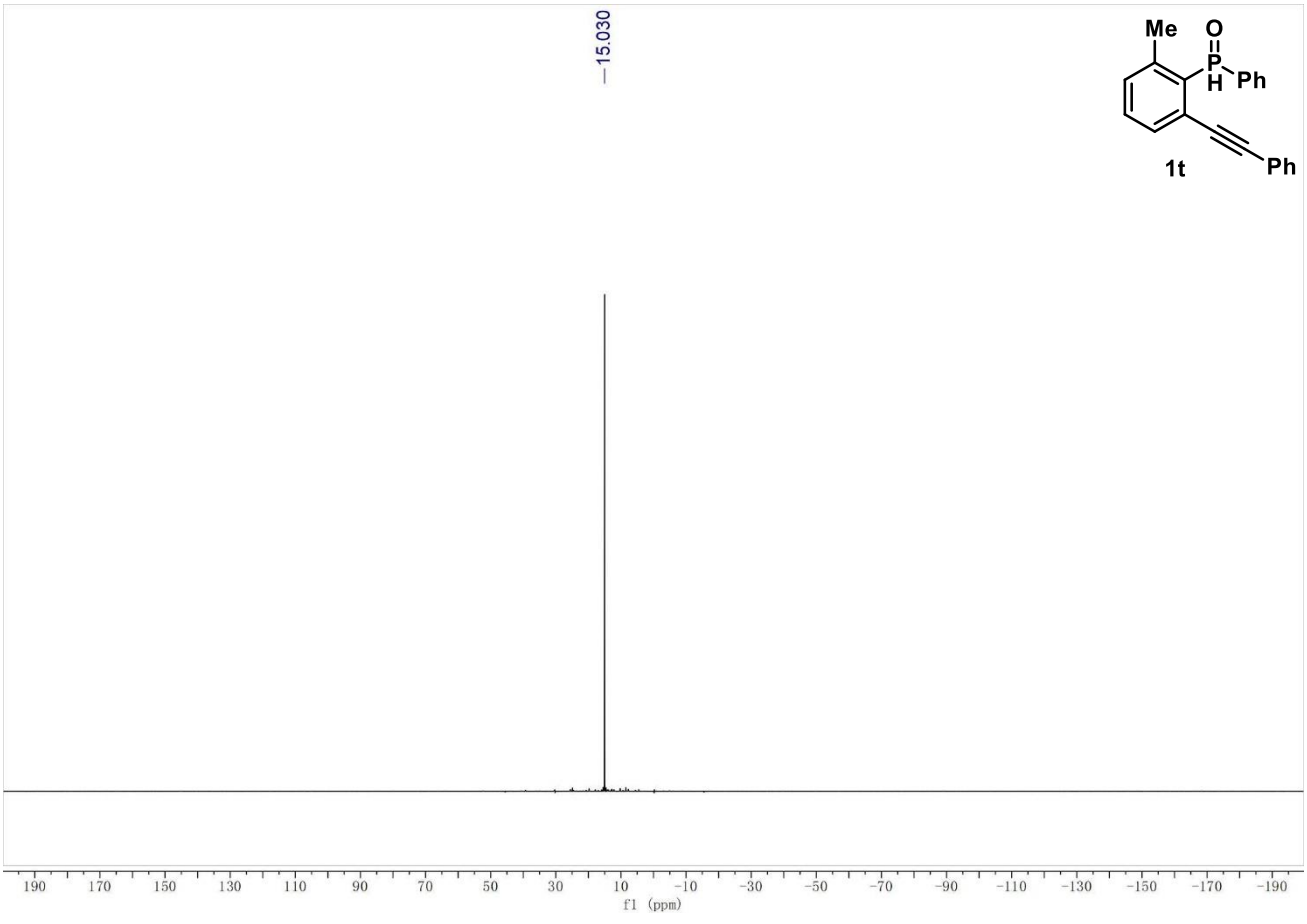



**$^{13}$C NMR spectrum of 1t (75 MHz, $CDCl_3$)**

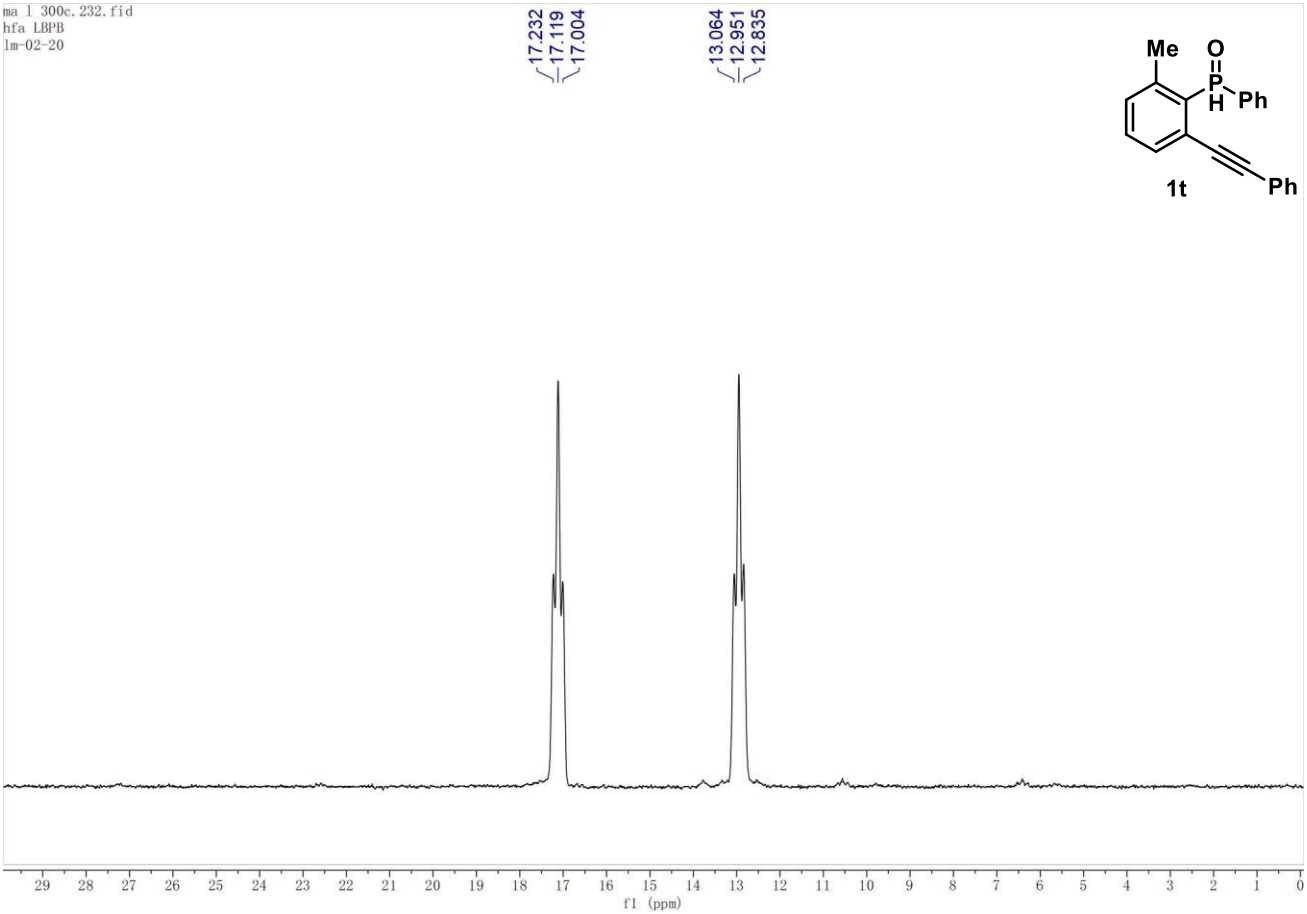




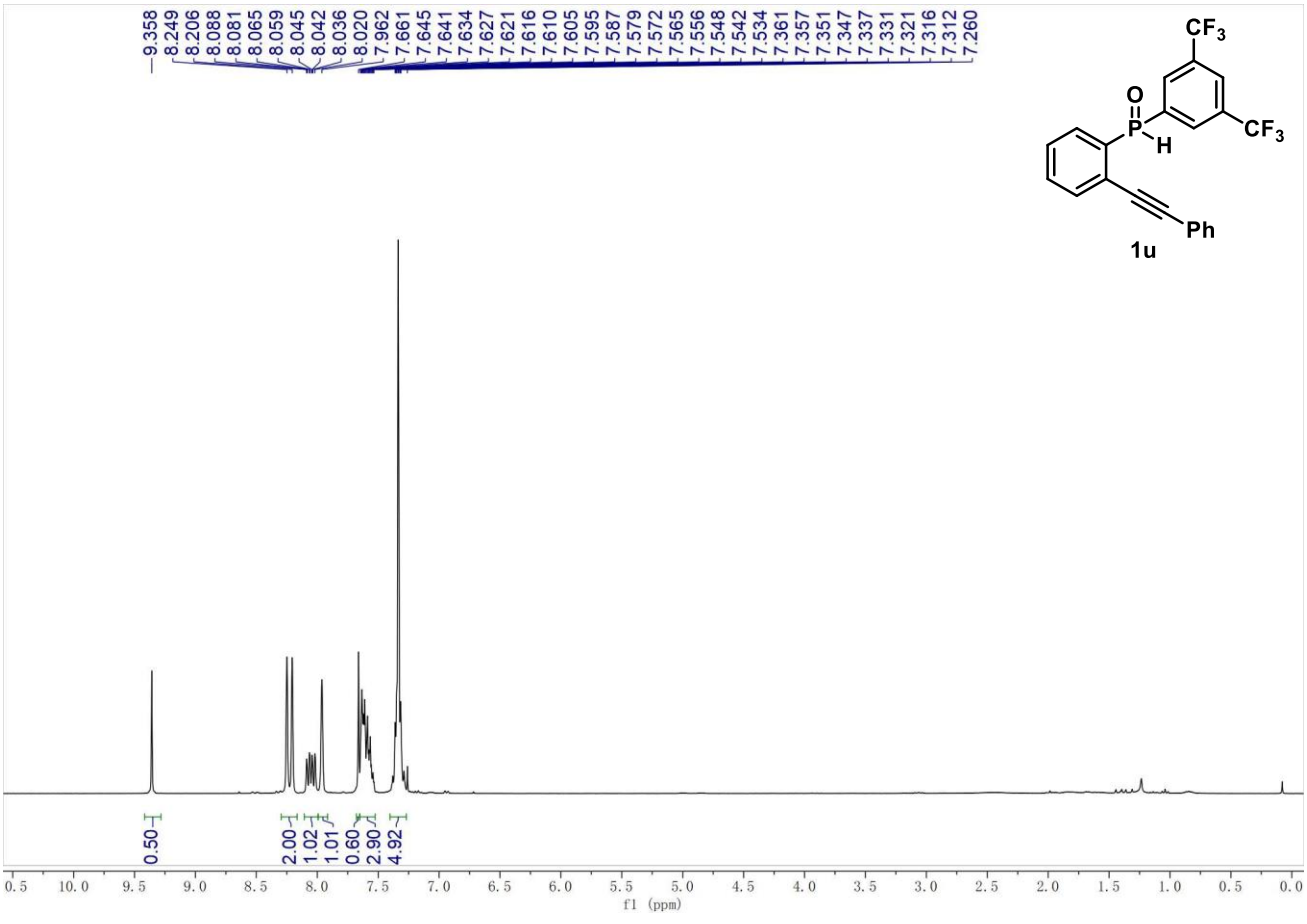

**$^{31}P\{^{1}H\}$ NMR spectrum of 1t (121 MHz, $CDCl_3$)**



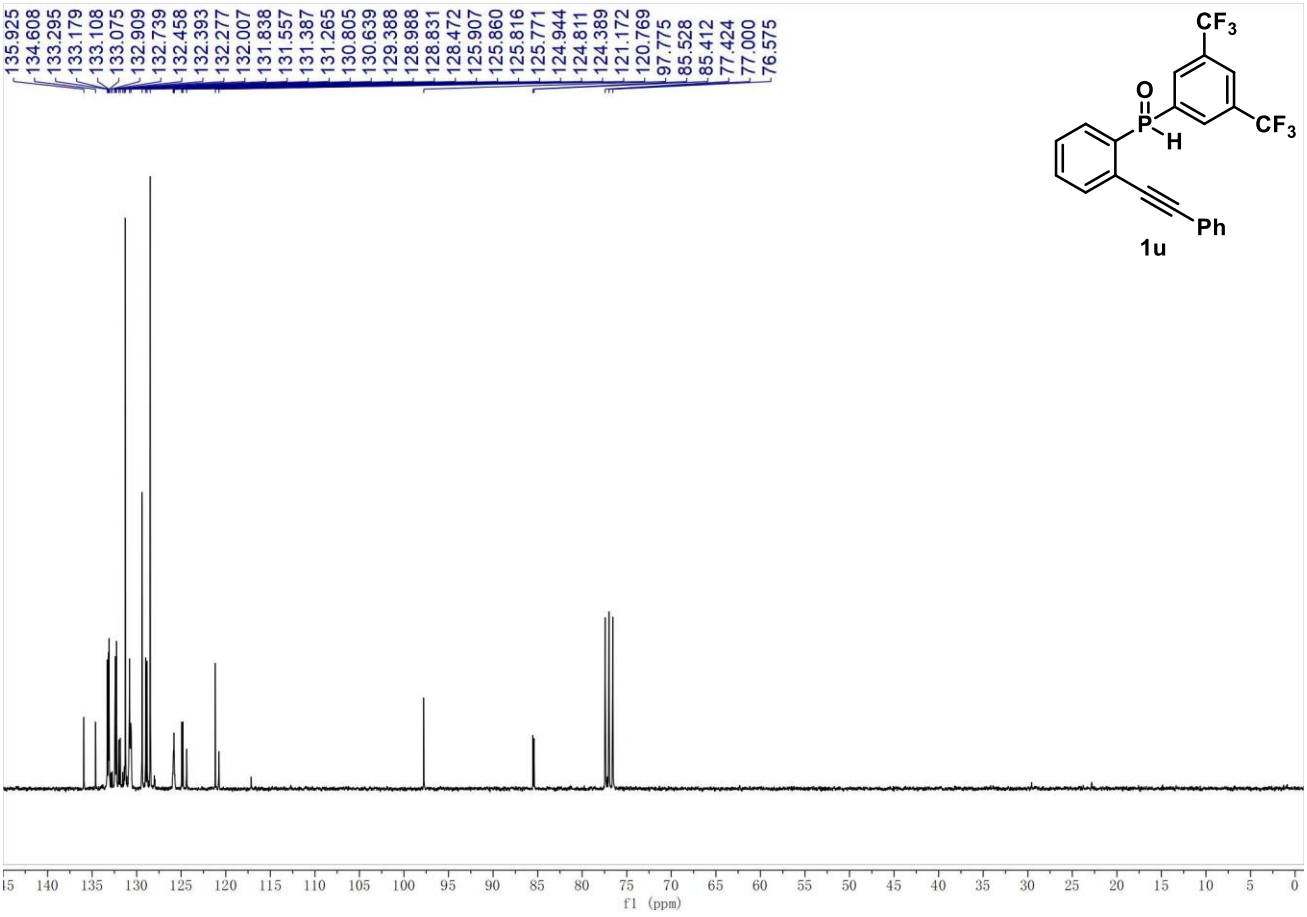
**$^{31}$P NMR spectrum of 1t (121 MHz, $CDCl_3$)**

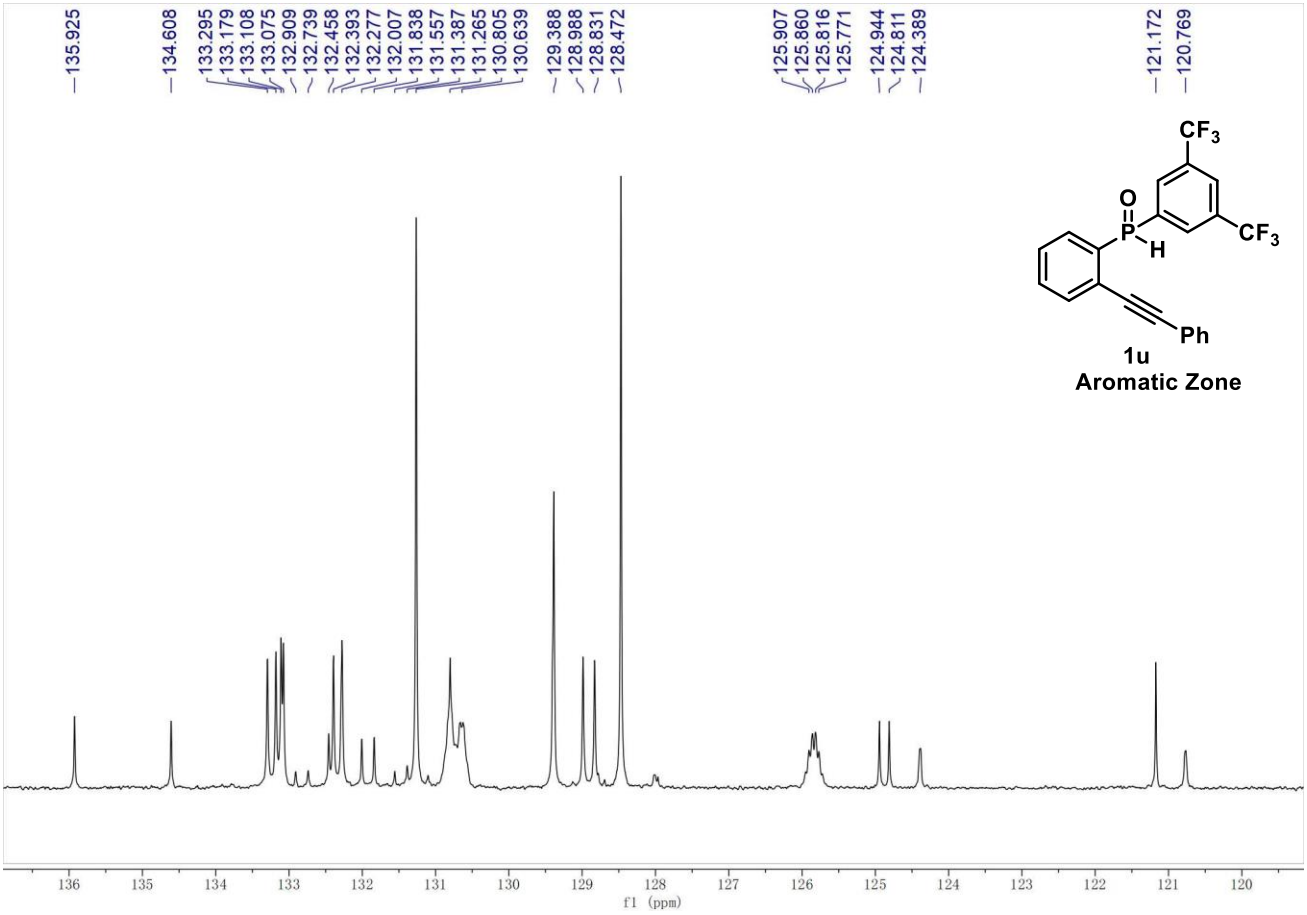



**$^{1}$H NMR spectrum of 1u (300 MHz, $CDCl_3$)**

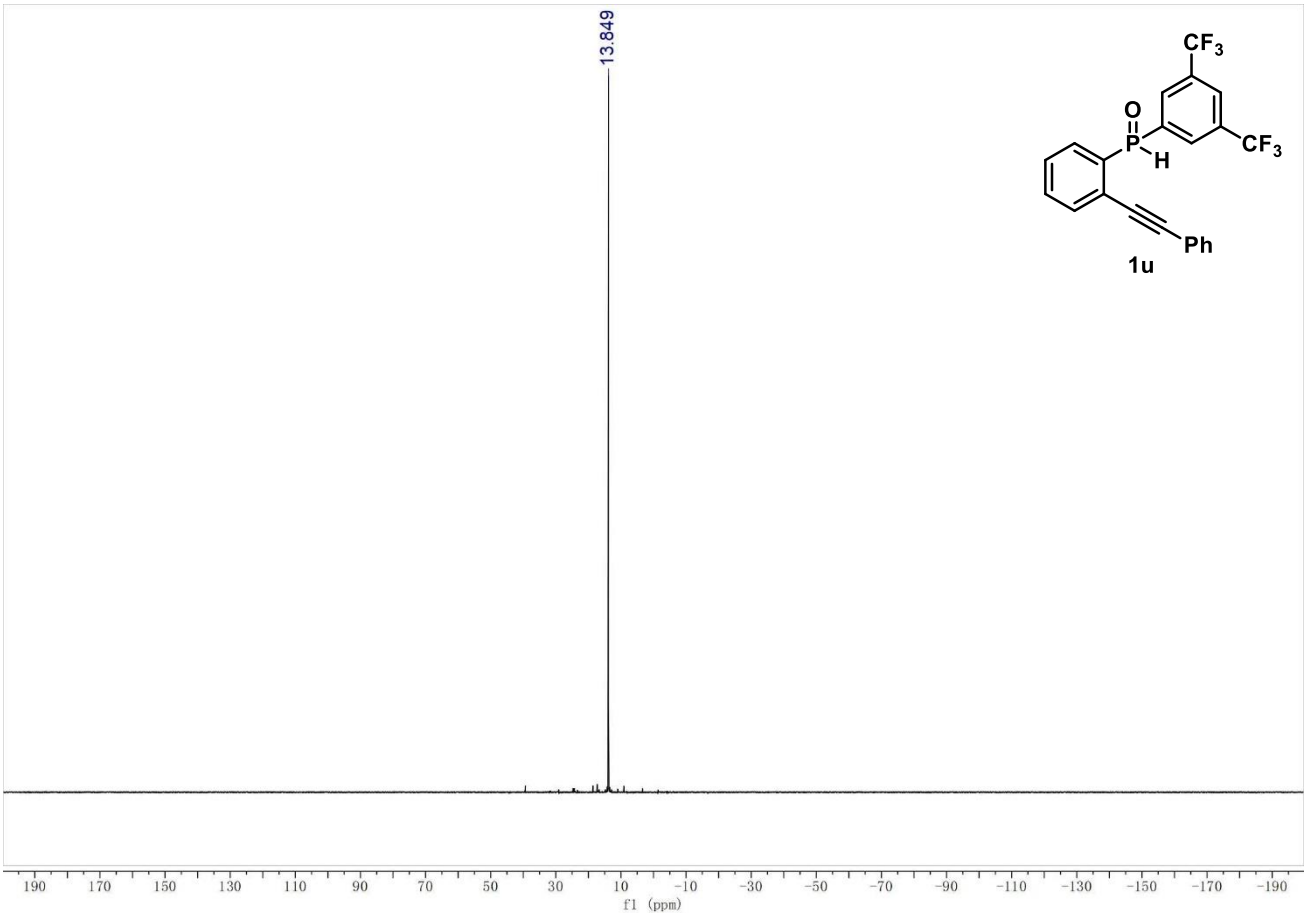


**$^{13}$C NMR spectrum of 1u (75 MHz, $CDCl_3$)**

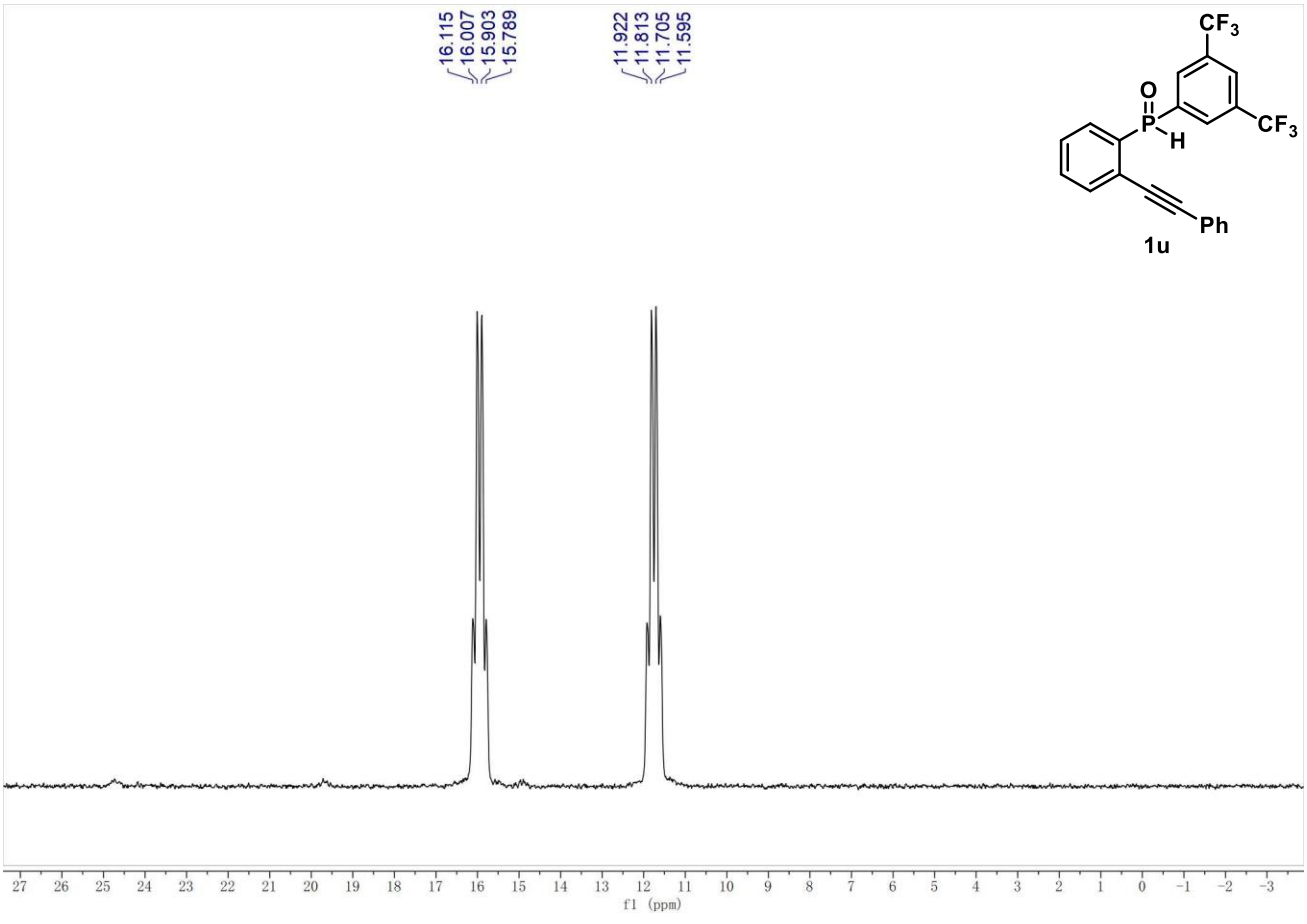


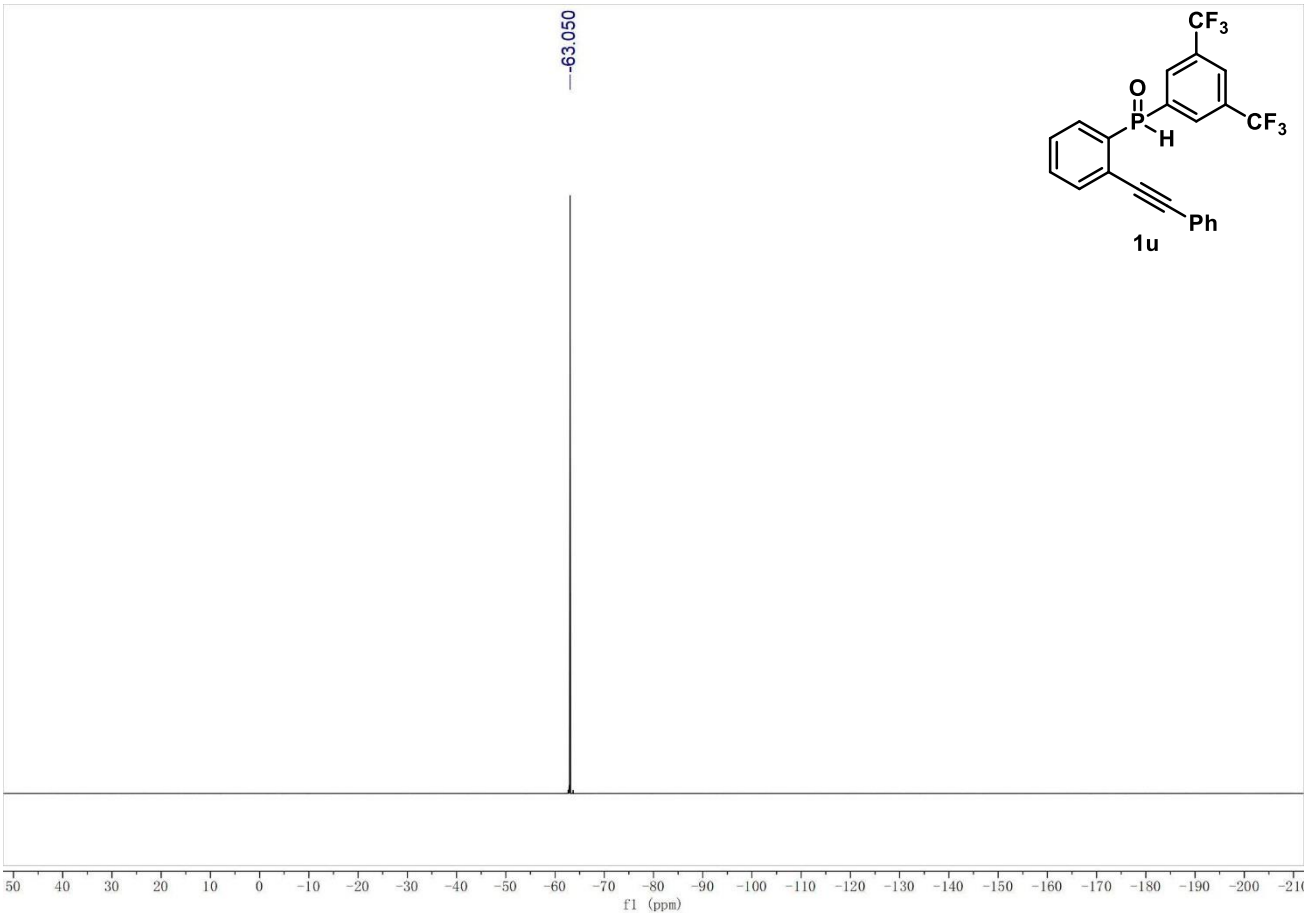
**$^{31}P\{^{1}H\}$ NMR spectrum of 1u (121 MHz, $CDCl_3$)**



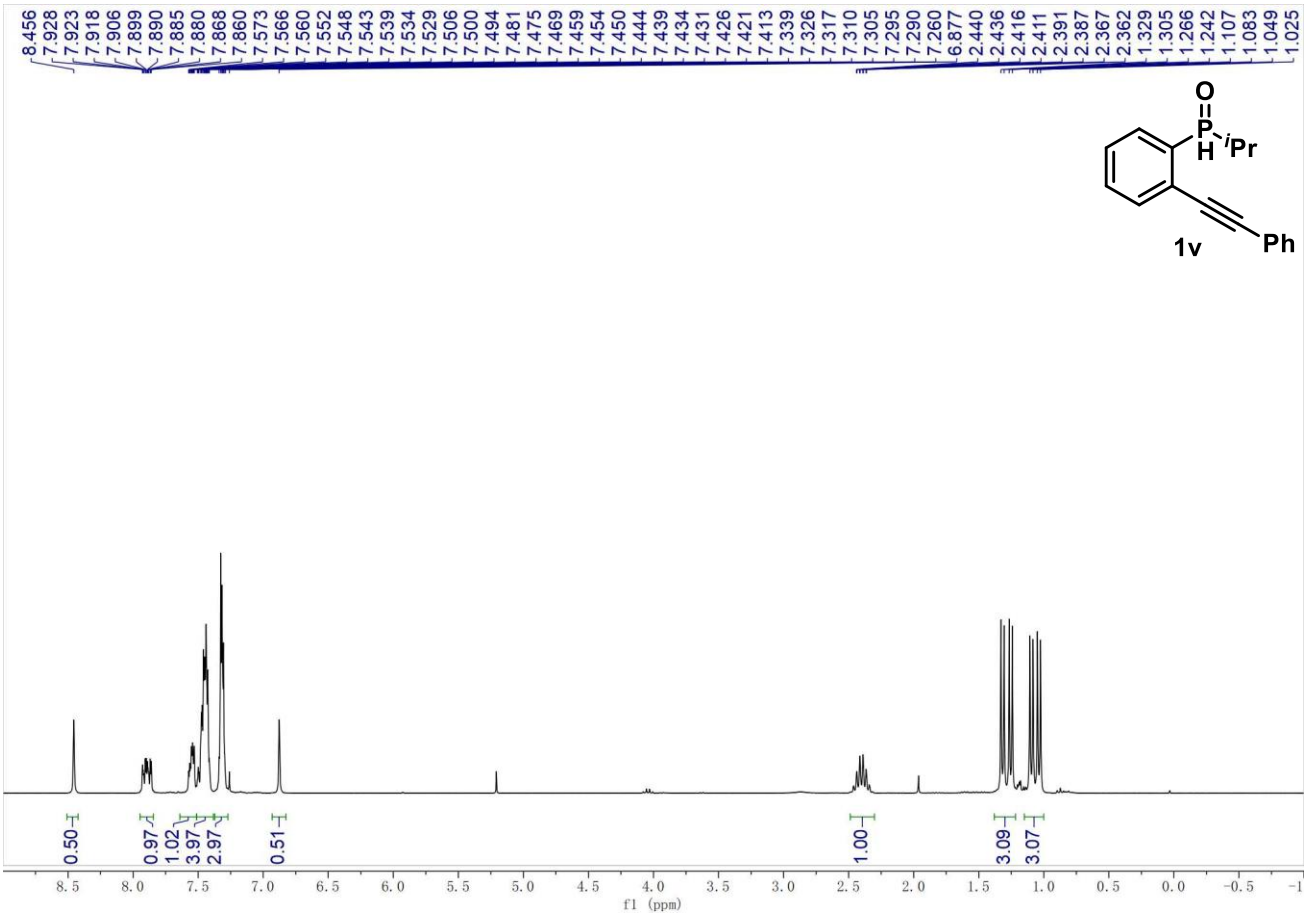

**$^{31}P$ NMR spectrum of 1u (121 MHz, $CDCl_3$)**



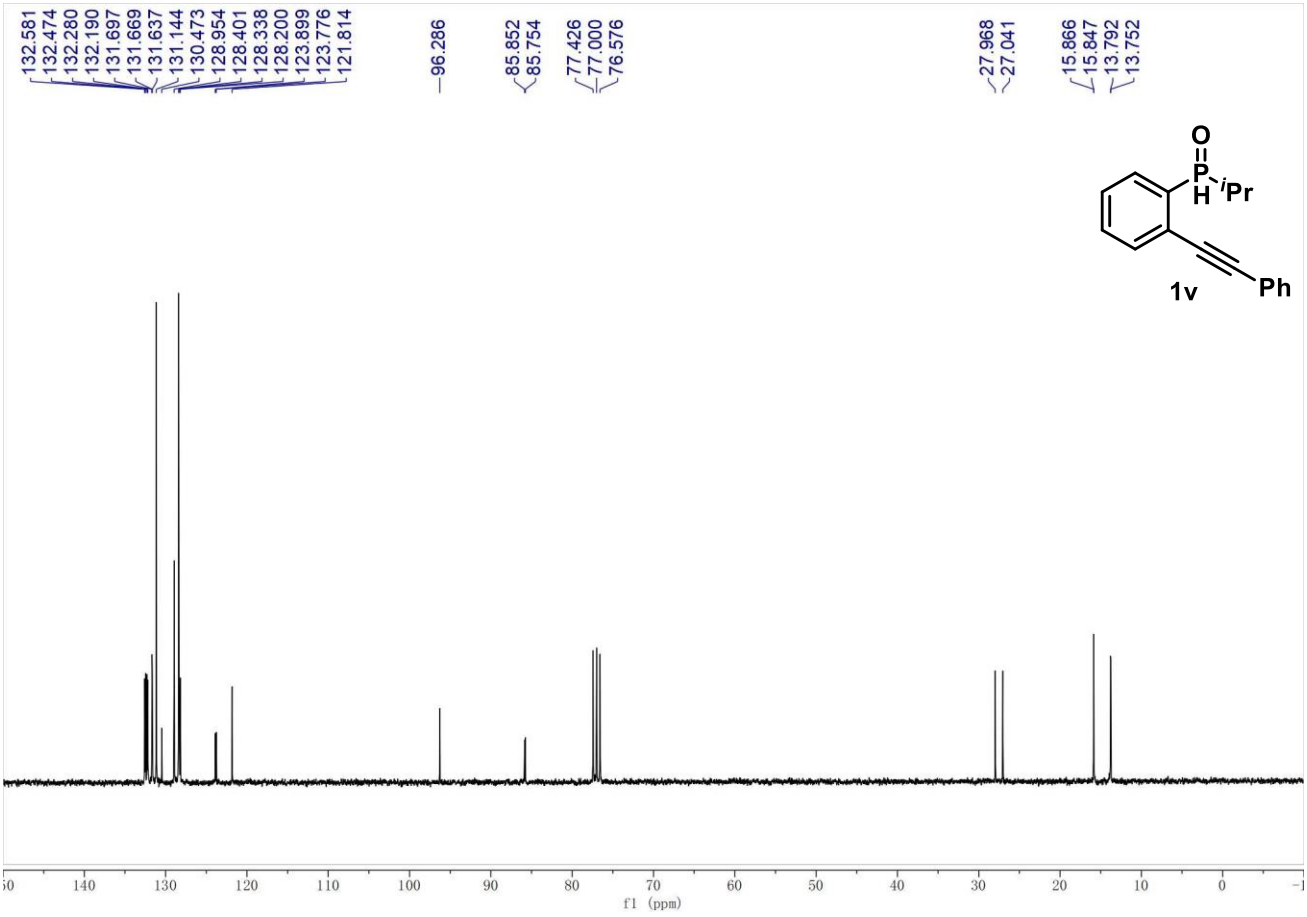
**$^{19}$F NMR spectrum of 1u (282 MHz, $CDCl_3$)**

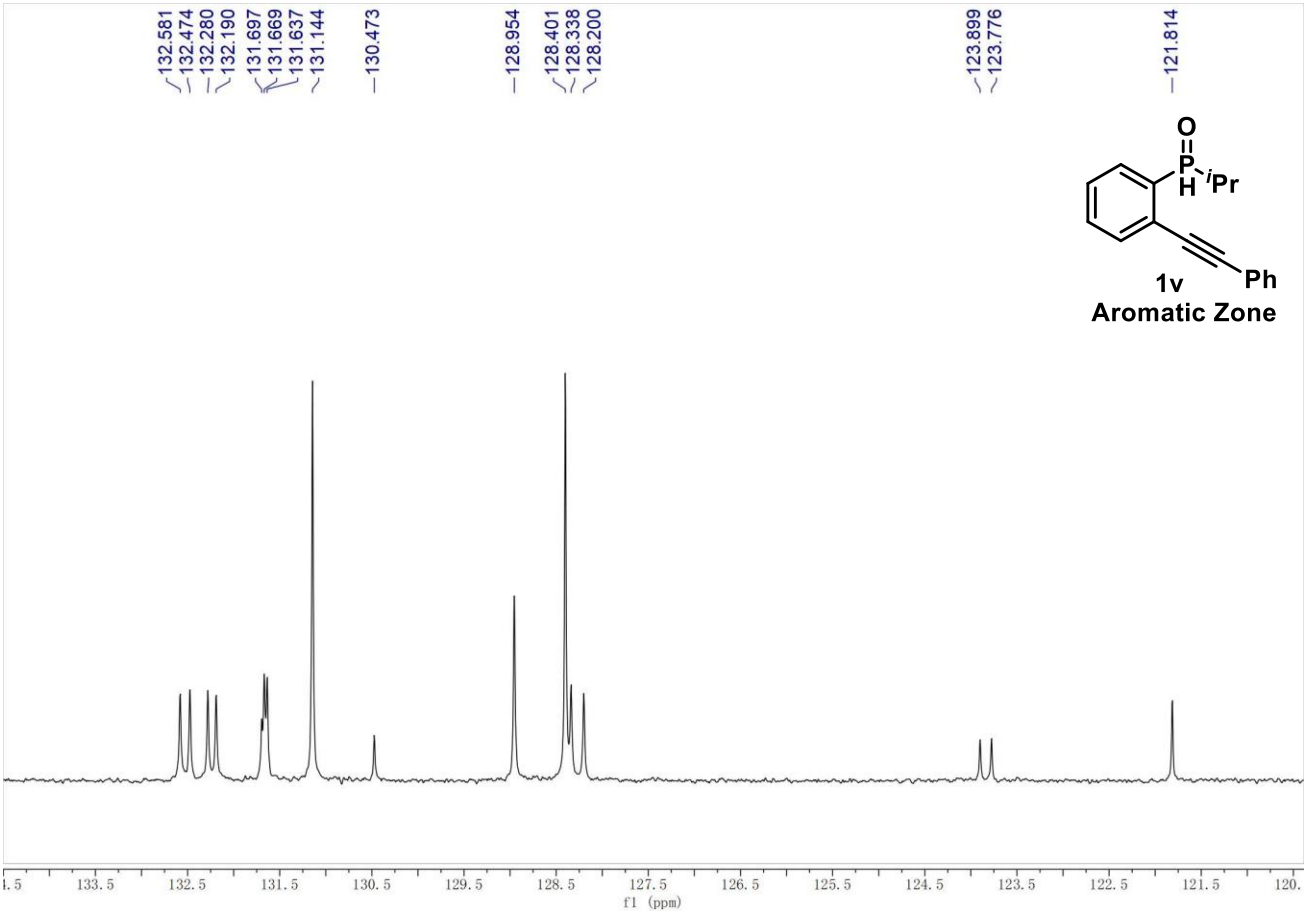



**$^{1}$H NMR spectrum of 1v (300 MHz, $CDCl_3$)**

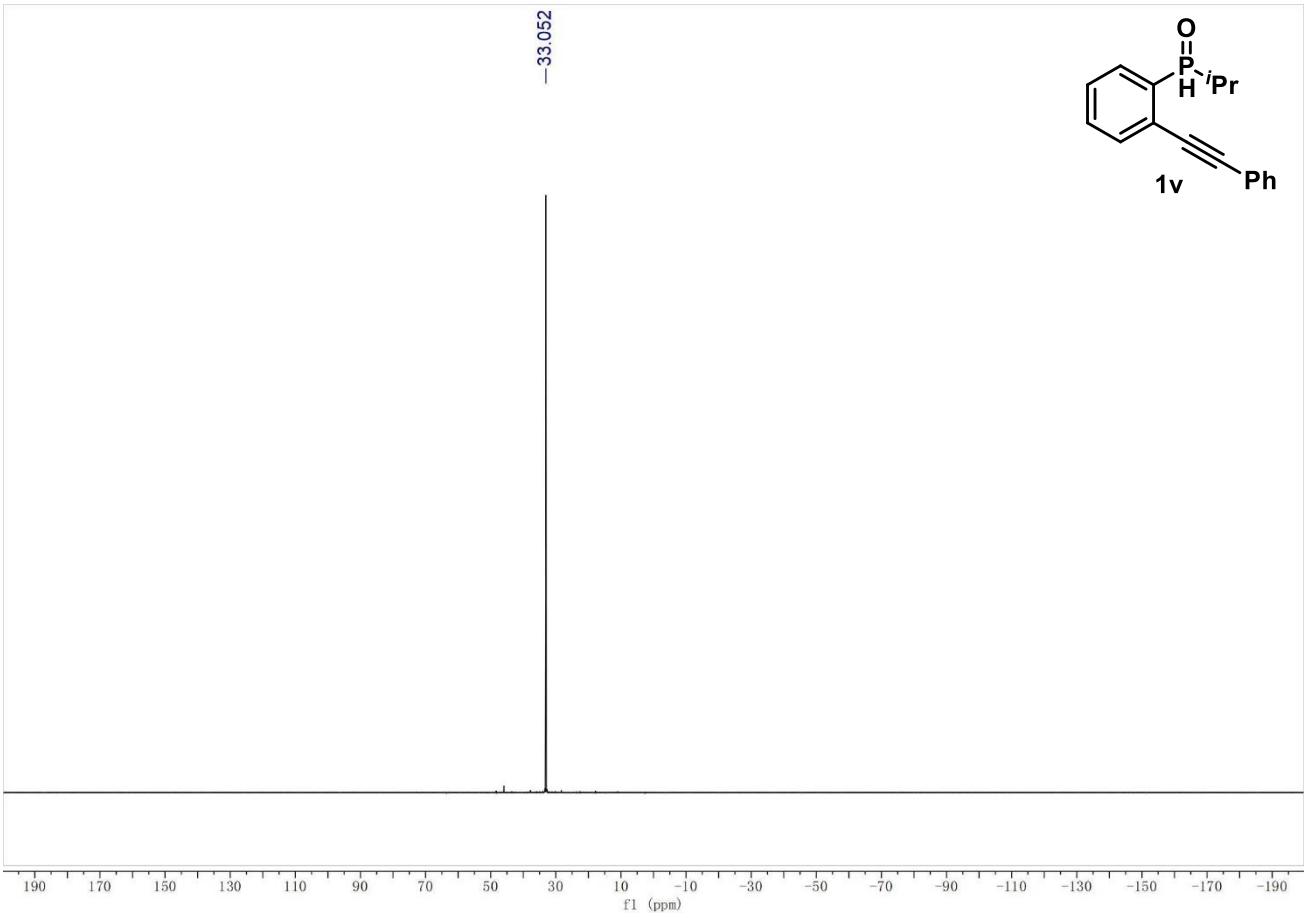


**$^{13}$C NMR spectrum of 1v (75 MHz, $CDCl_3$)**

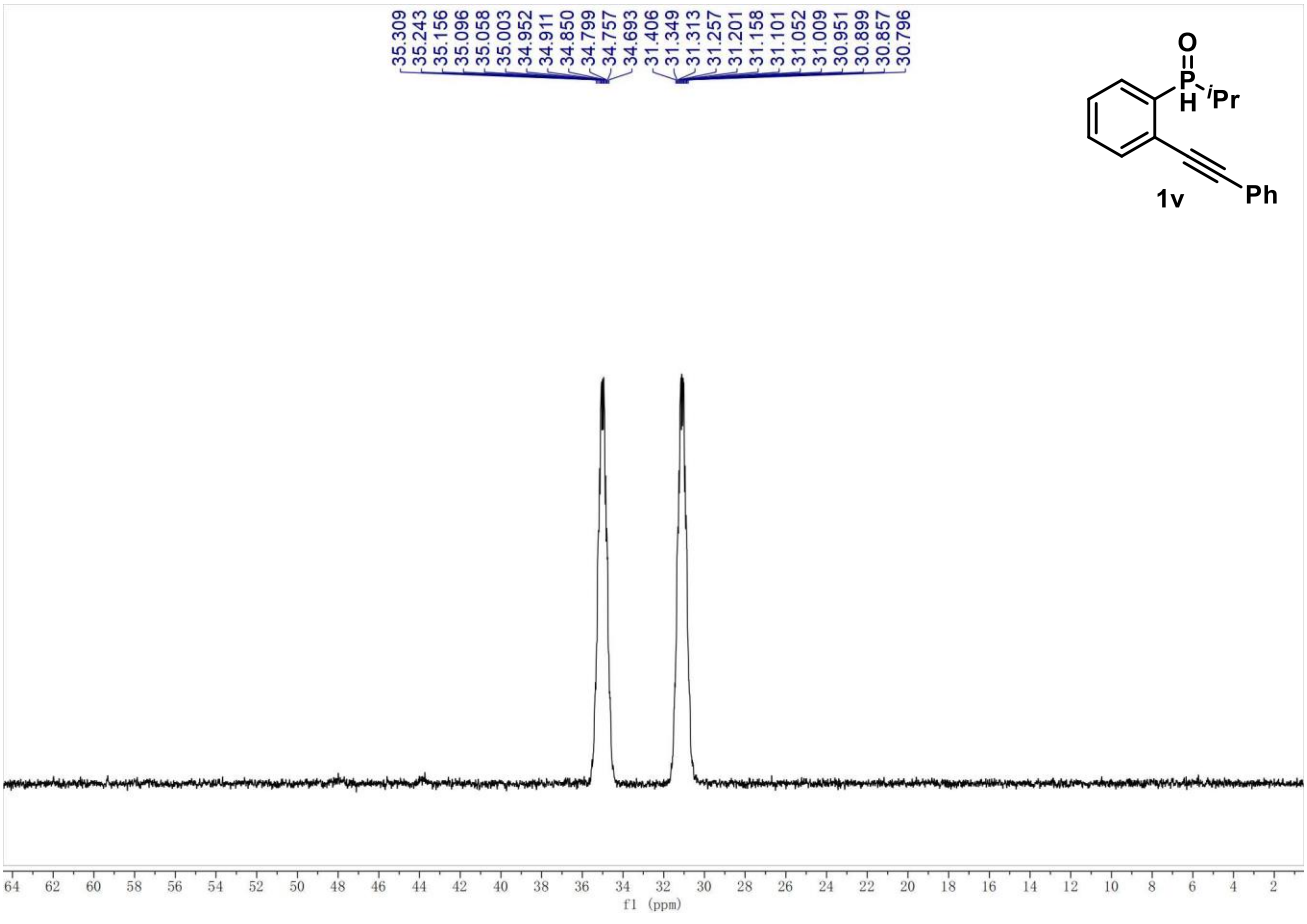


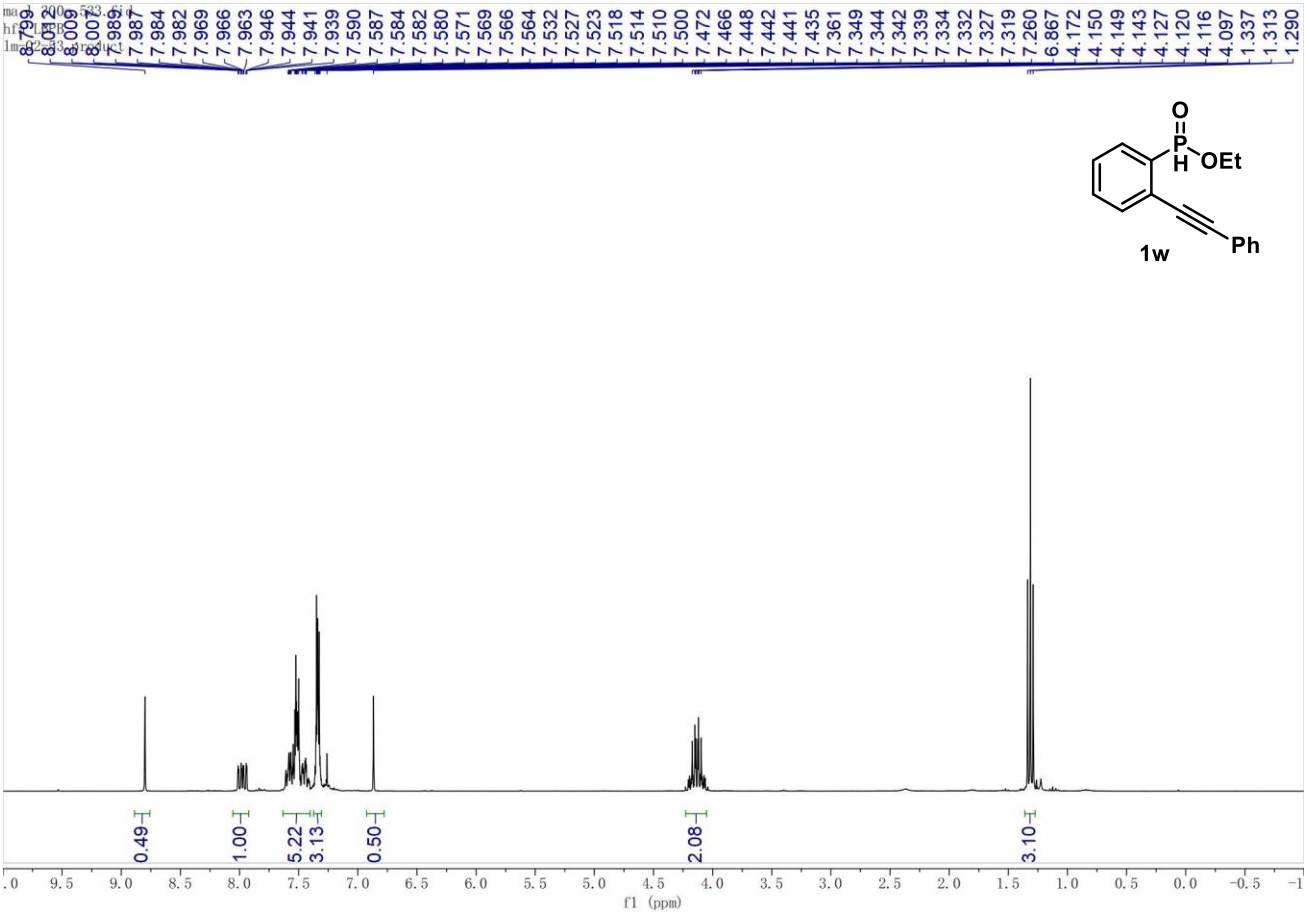
**$^{31}P\{^{1}H\}$ NMR spectrum of 1v (121 MHz, $CDCl_3$)**



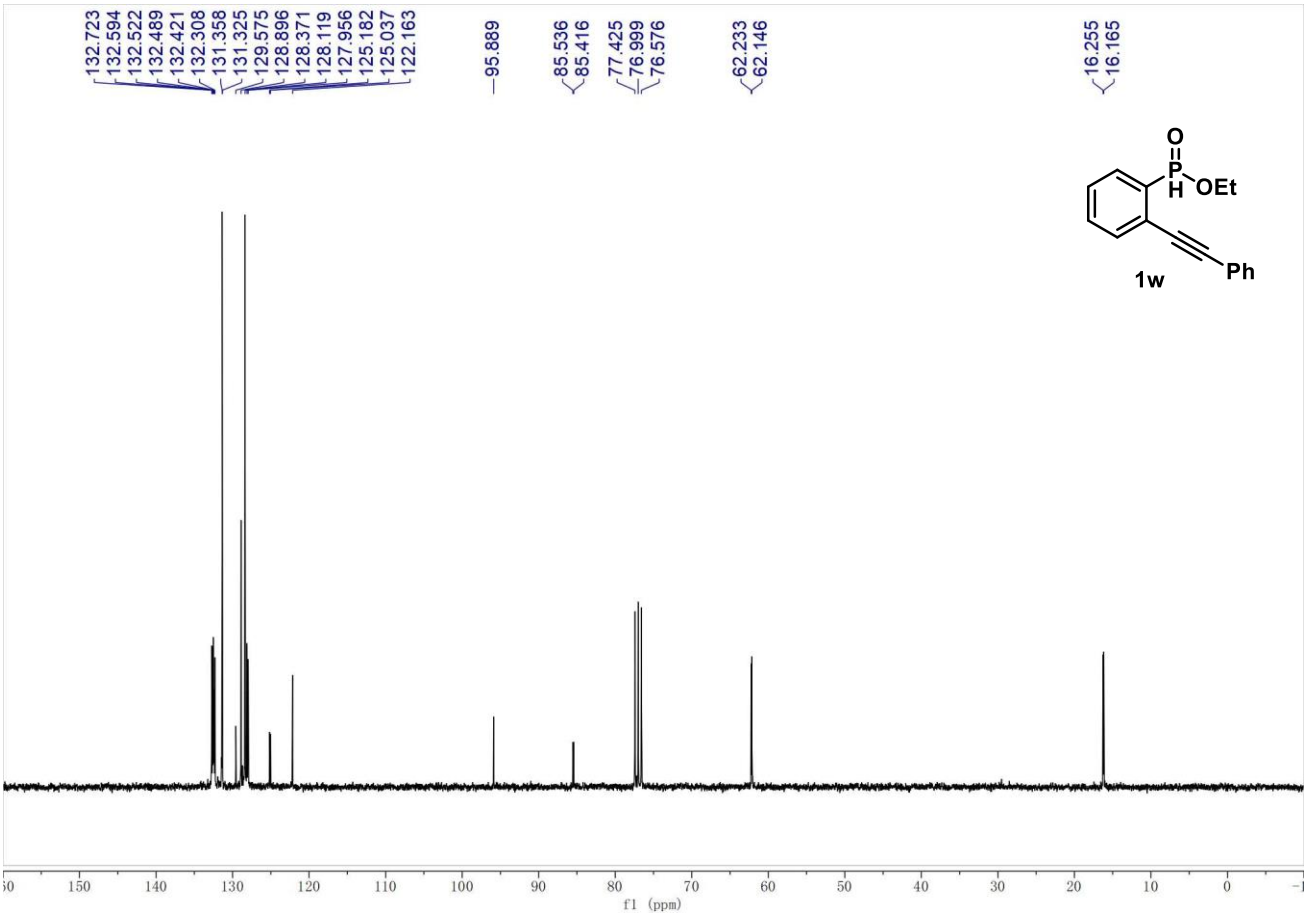

**$^{31}P$ NMR spectrum of 1v (121 MHz, $CDCl_3$)**

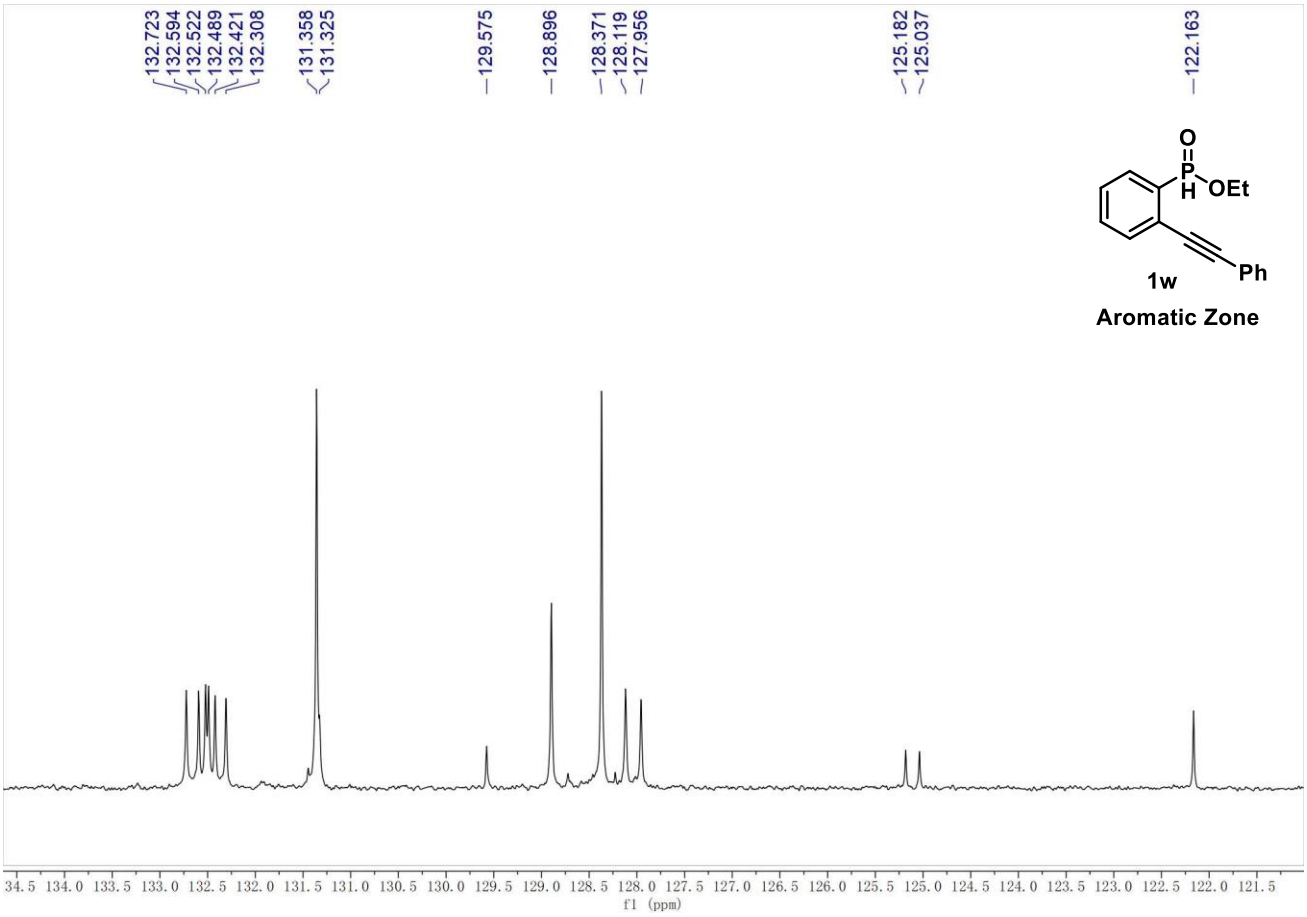


**$^{1}$H NMR spectrum of 1w (300 MHz, $CDCl_3$)**

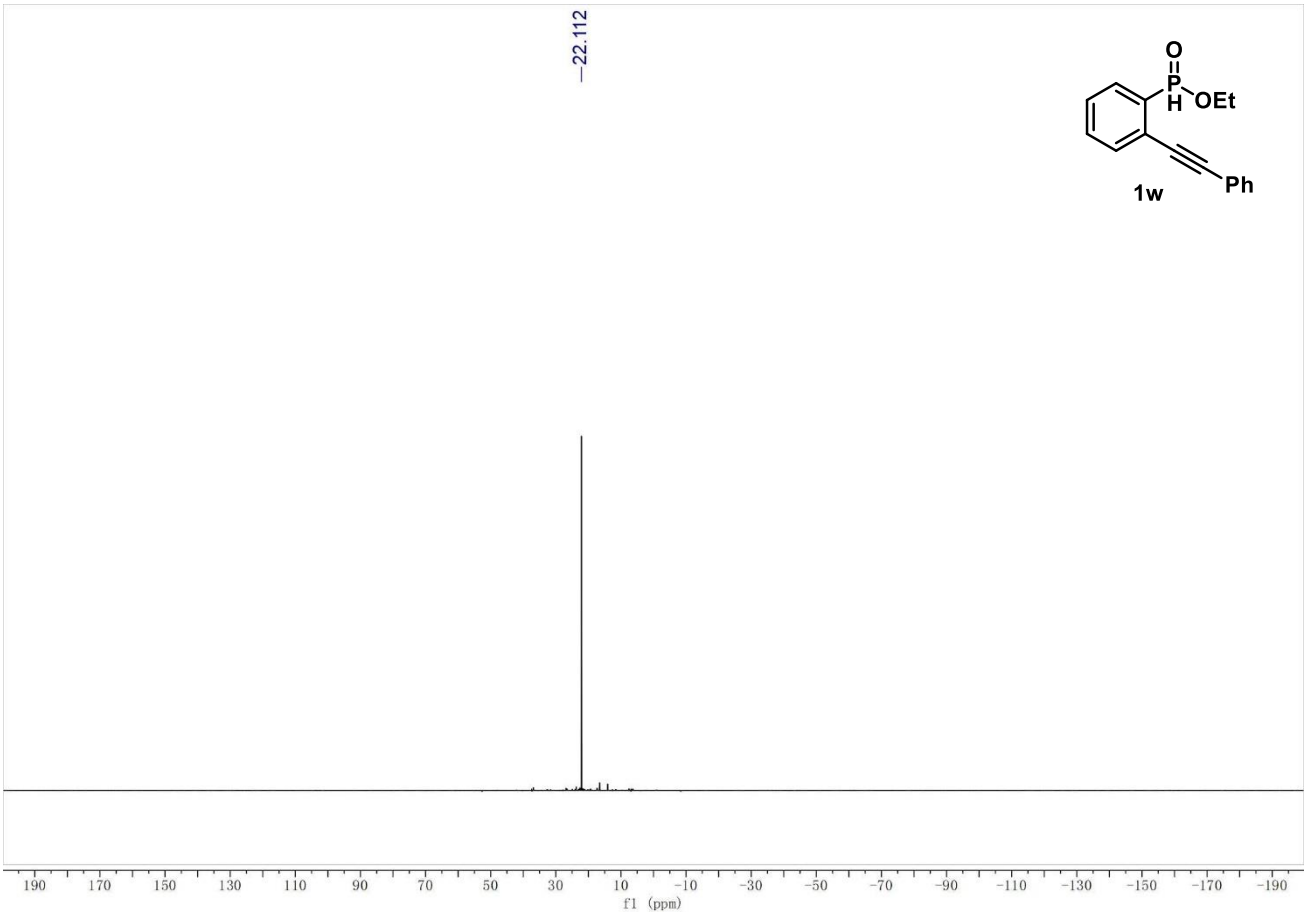



**$^{13}$C NMR spectrum of 1w (75 MHz, $CDCl_3$)**

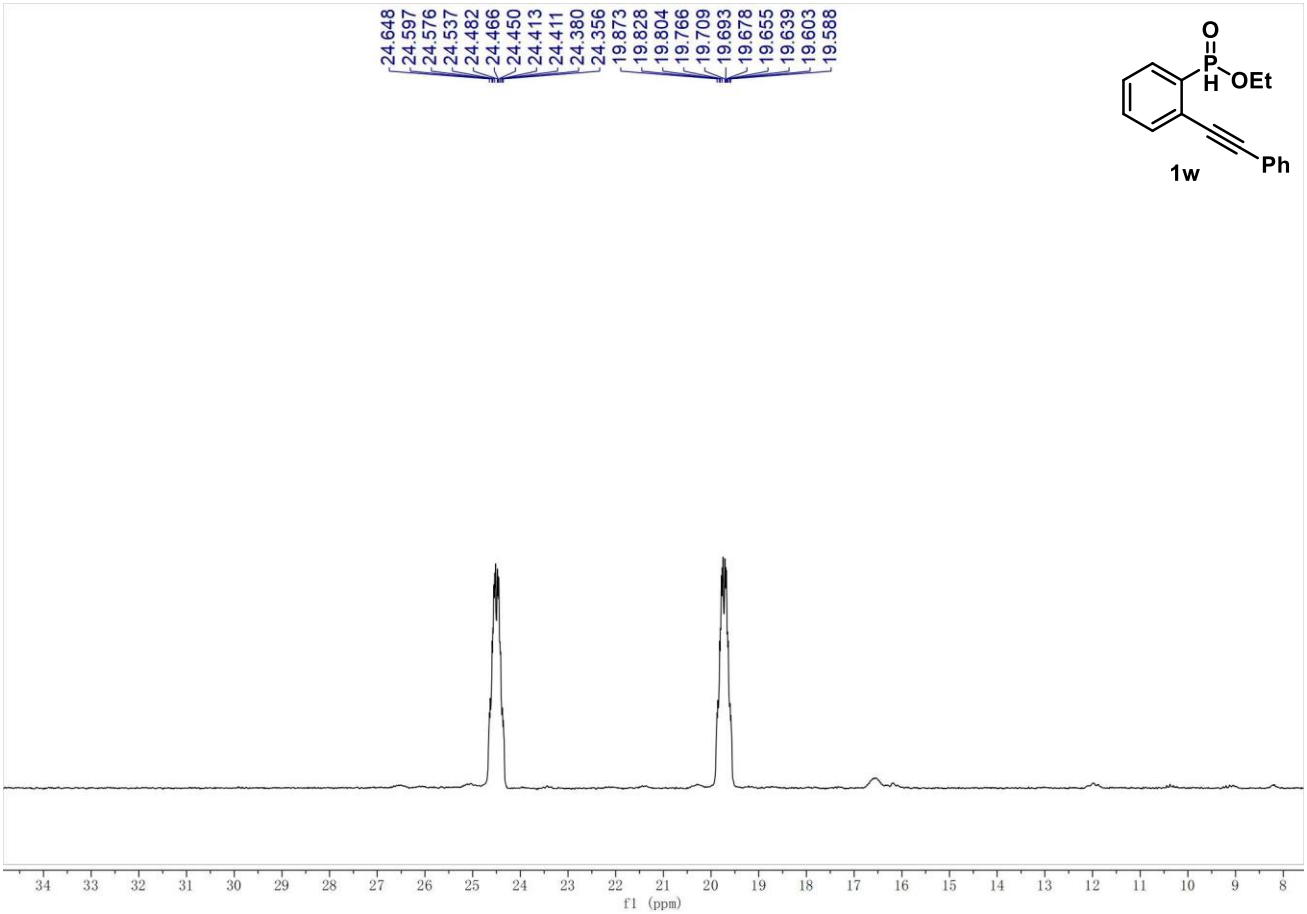




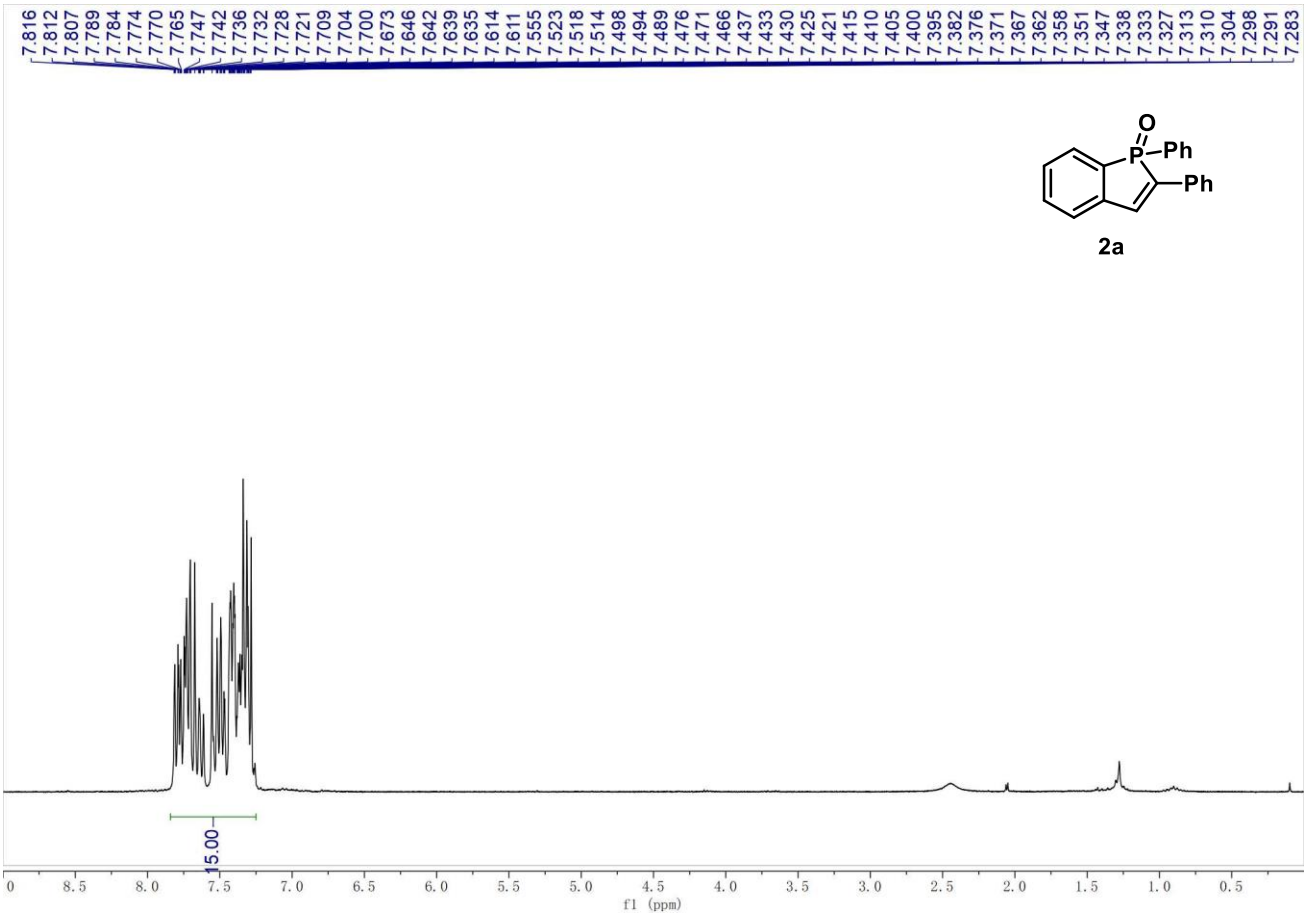

**$^{31}P\{^{1}H\}$ NMR spectrum of 1w (121 MHz, $CDCl_3$)**



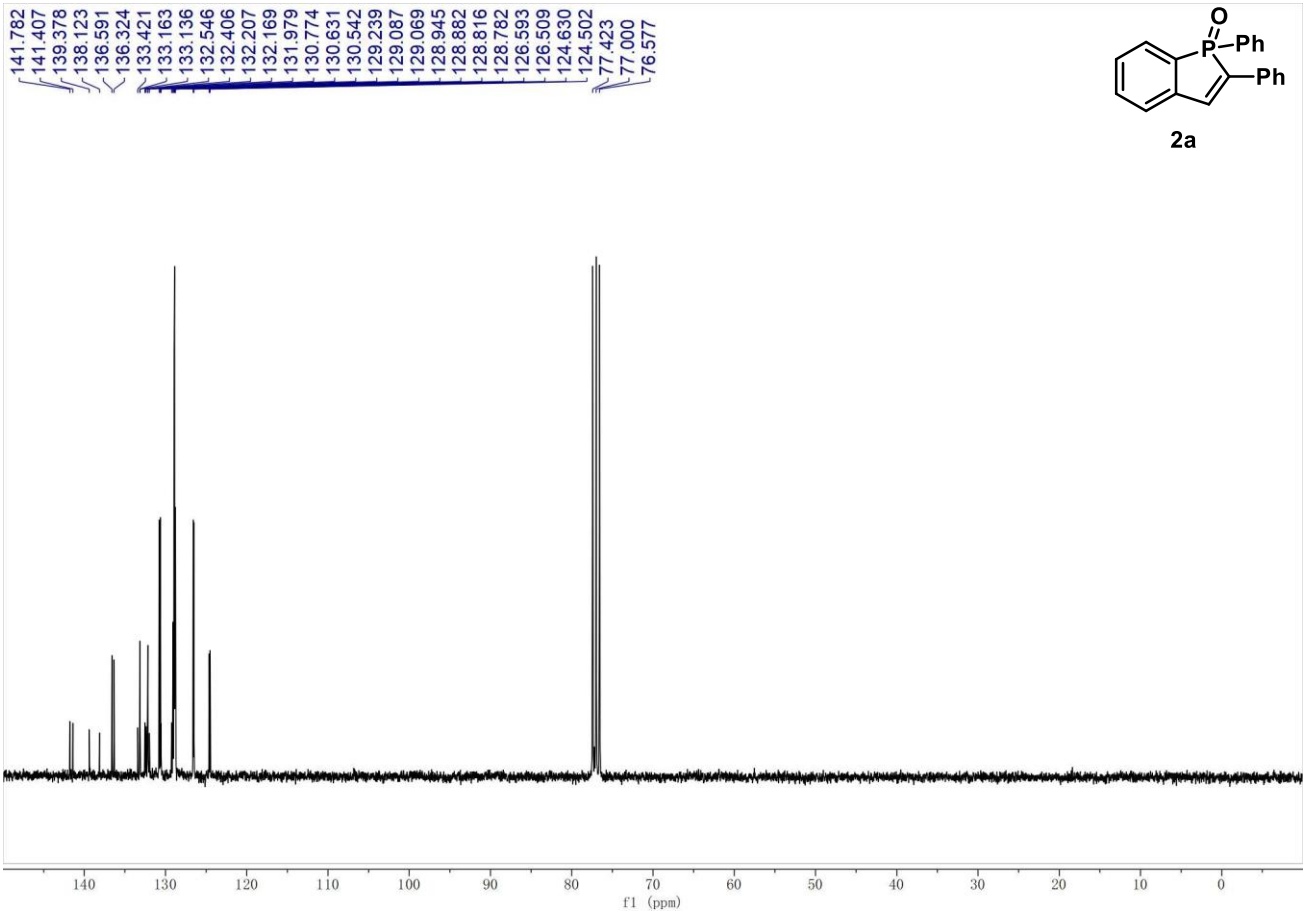
**$^{31}$P NMR spectrum of 1w (121 MHz, $CDCl_3$)**

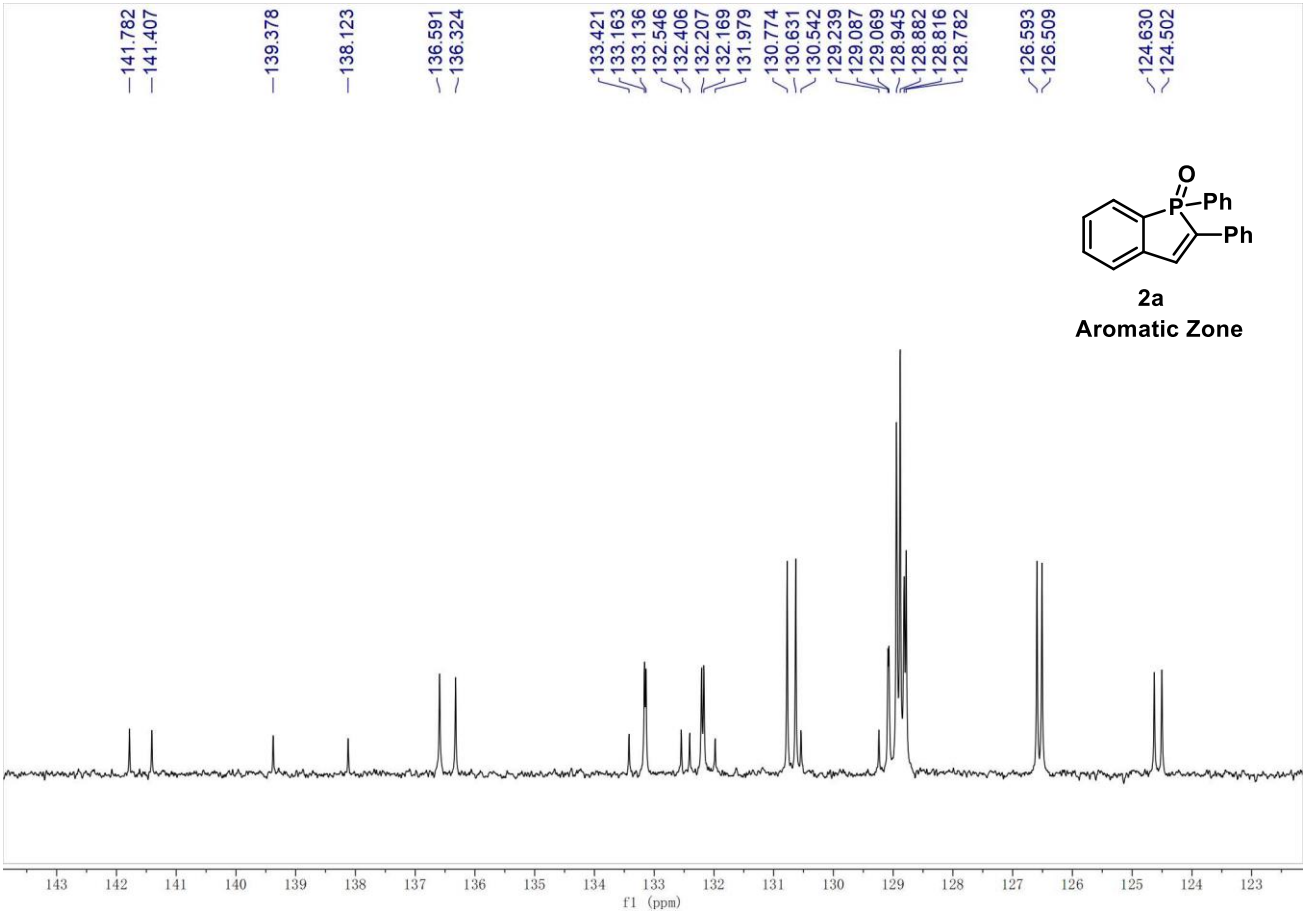



**$^{1}$H NMR spectrum of 2a (300 MHz, $CDCl_3$)**

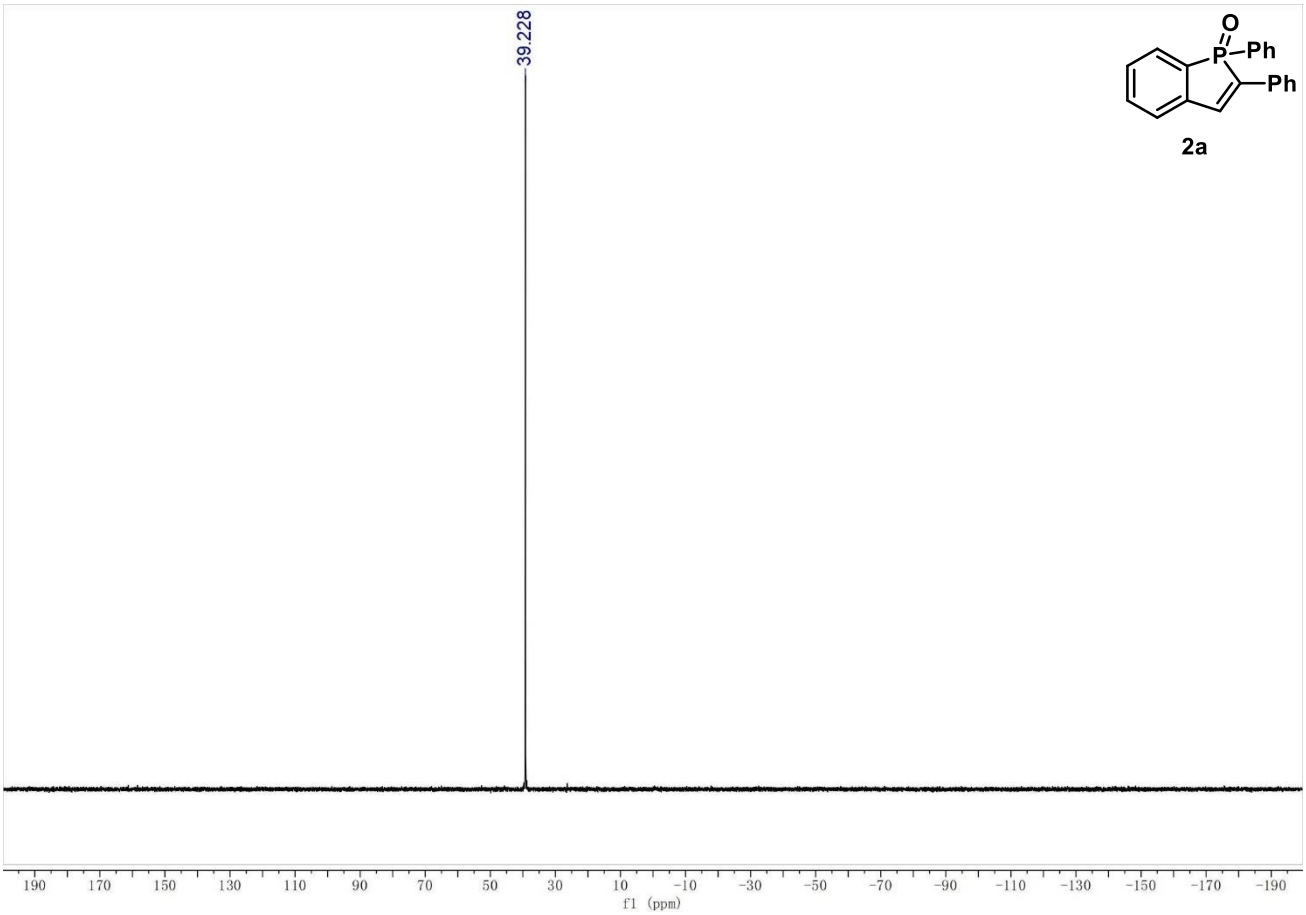


**$^{13}$C NMR spectrum of 2a (75 MHz, $CDCl_3$)**

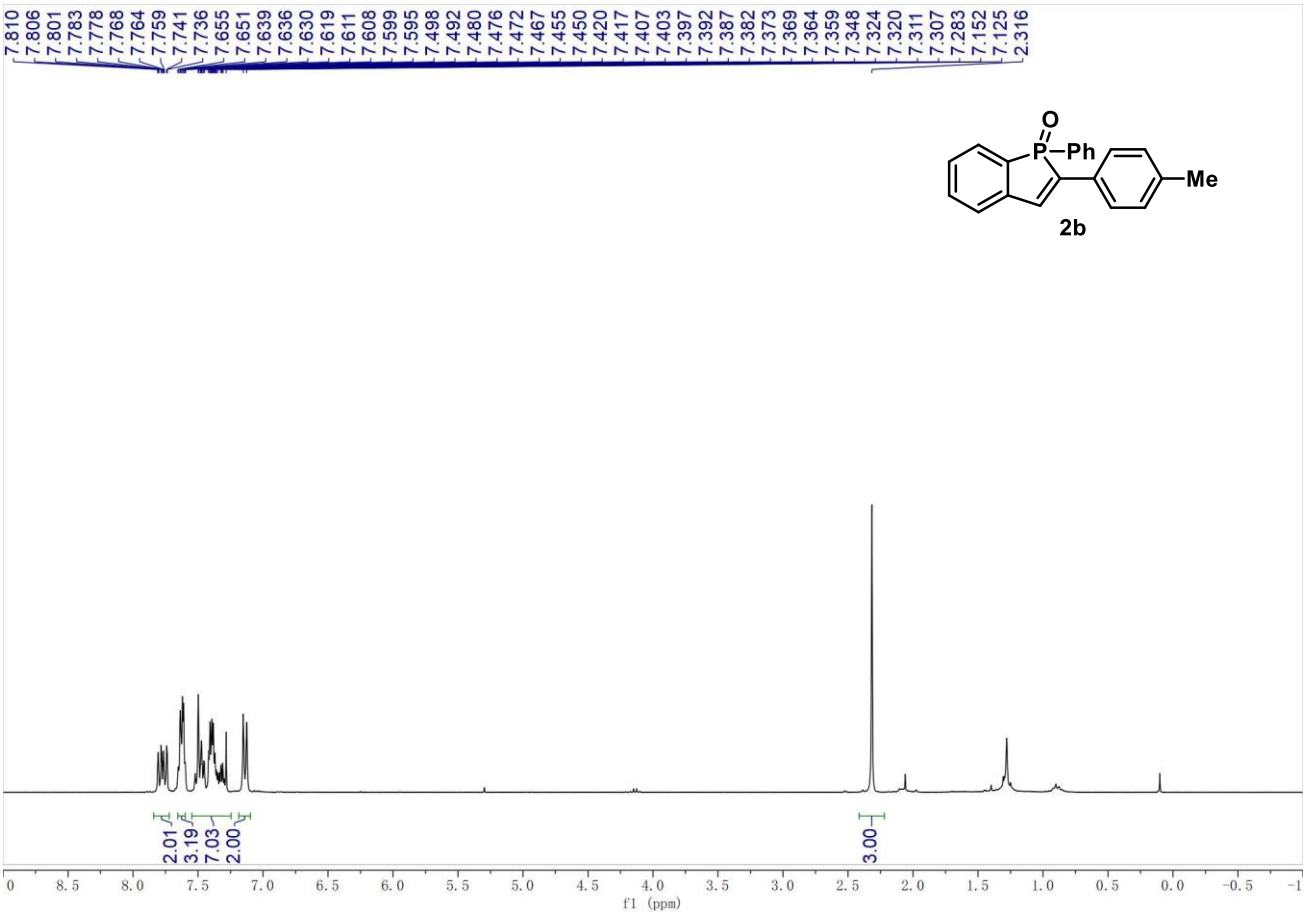


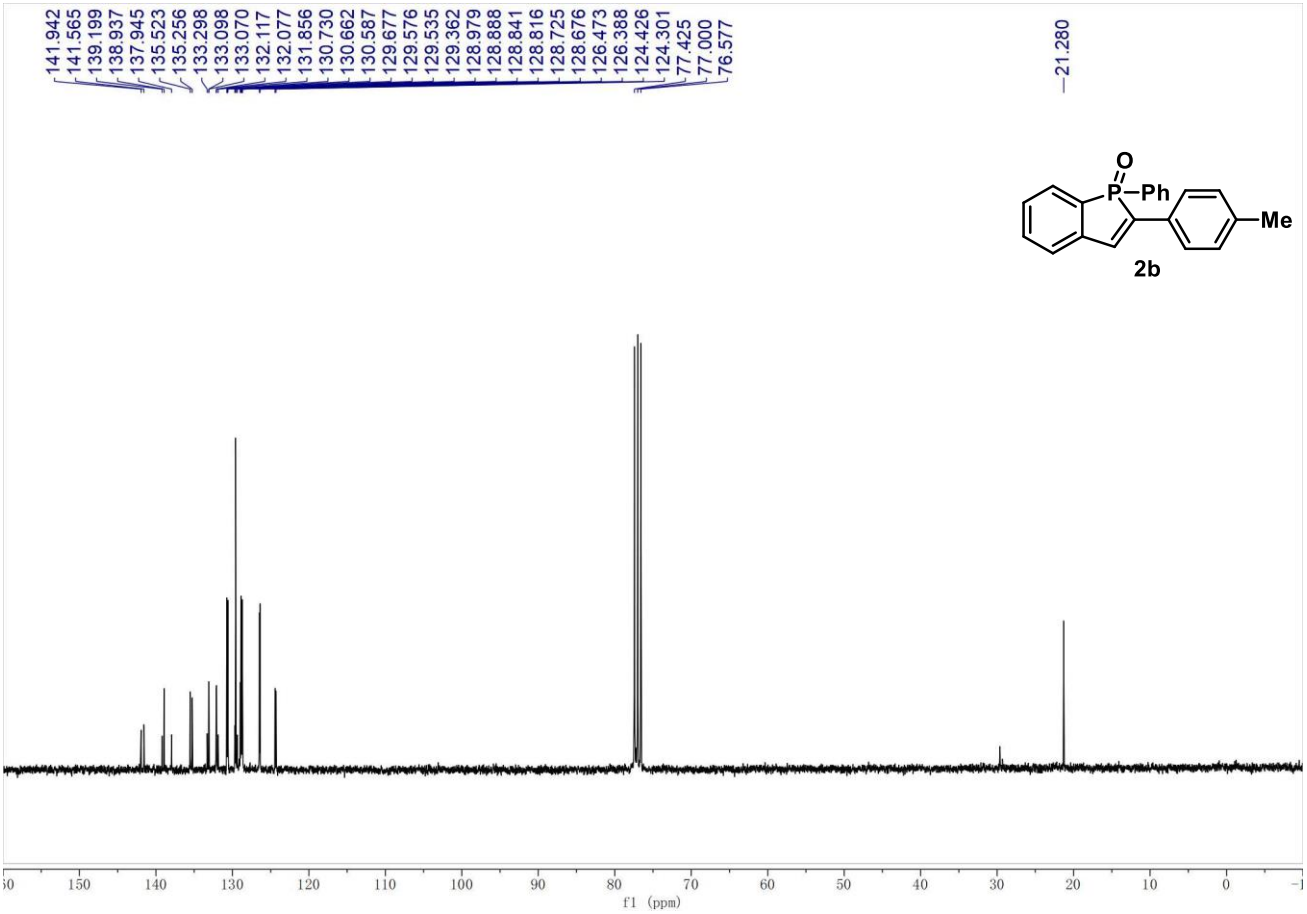
**$^{31}P\{^{1}H\}$ NMR spectrum of 2a (121 MHz, $CDCl_3$)**

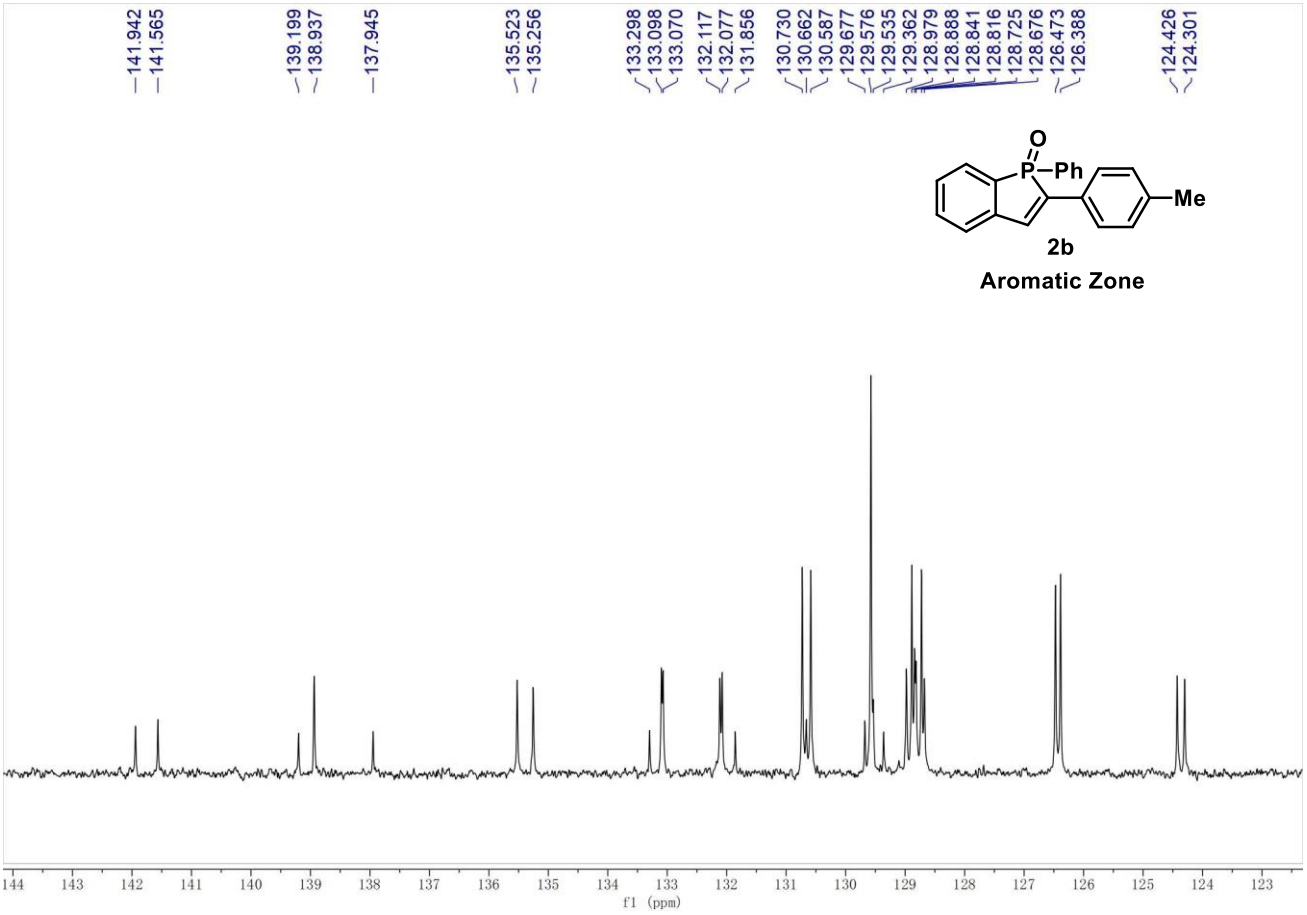



**$^{1}H$ NMR spectrum of 2b (300 MHz, $CDCl_3$)**

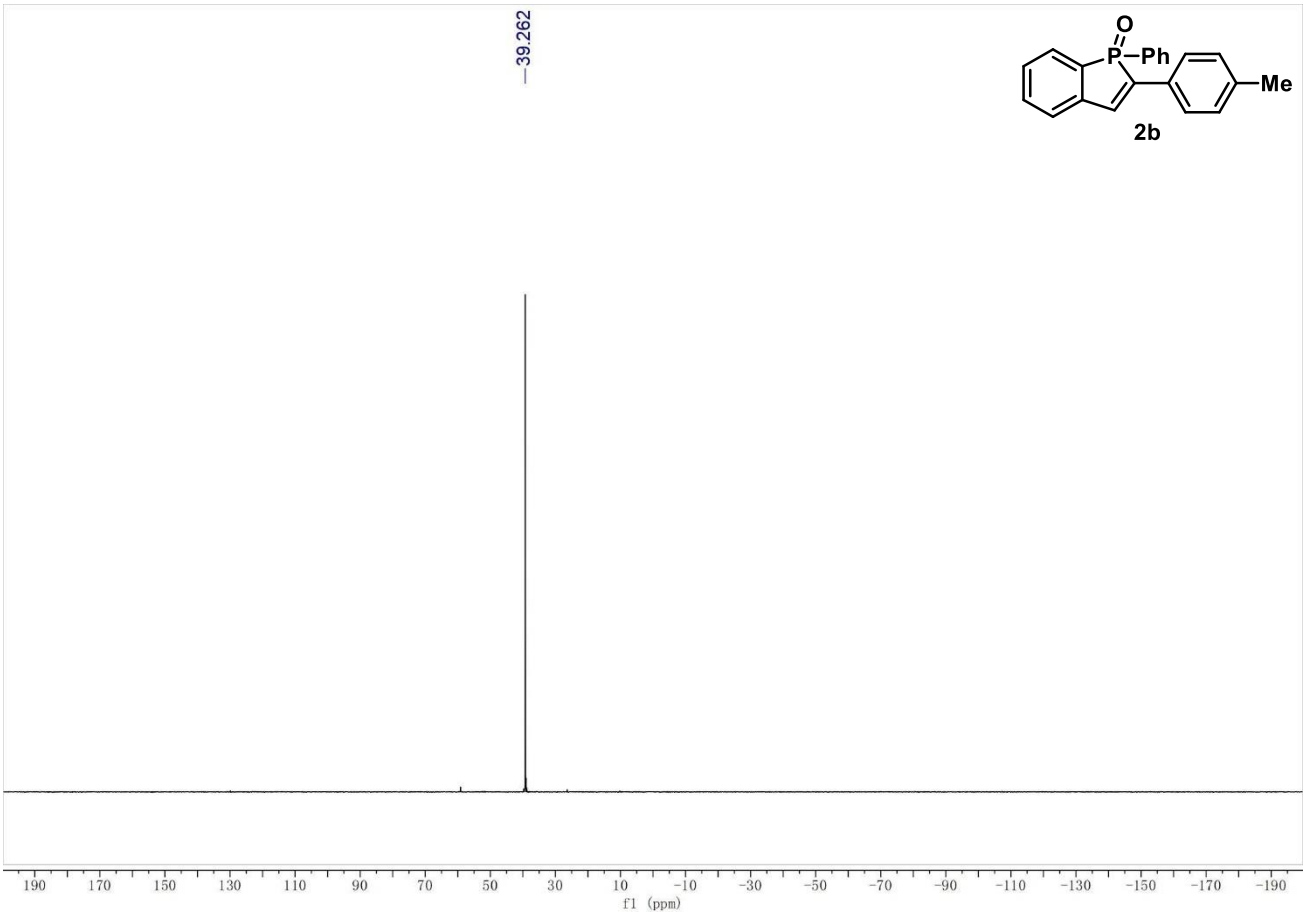


**$^{13}$C NMR spectrum of 2b (75 MHz, $CDCl_3$)**

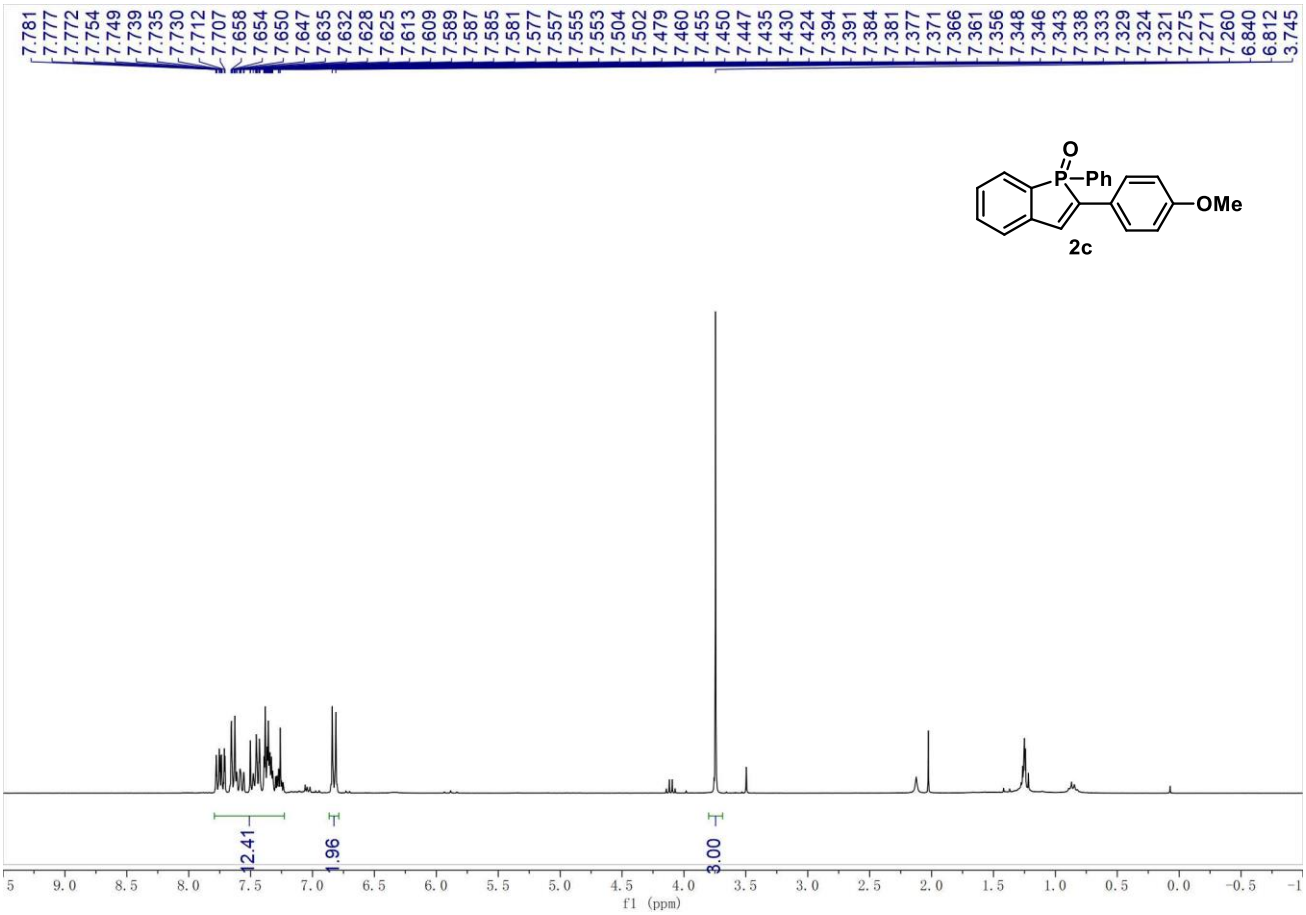


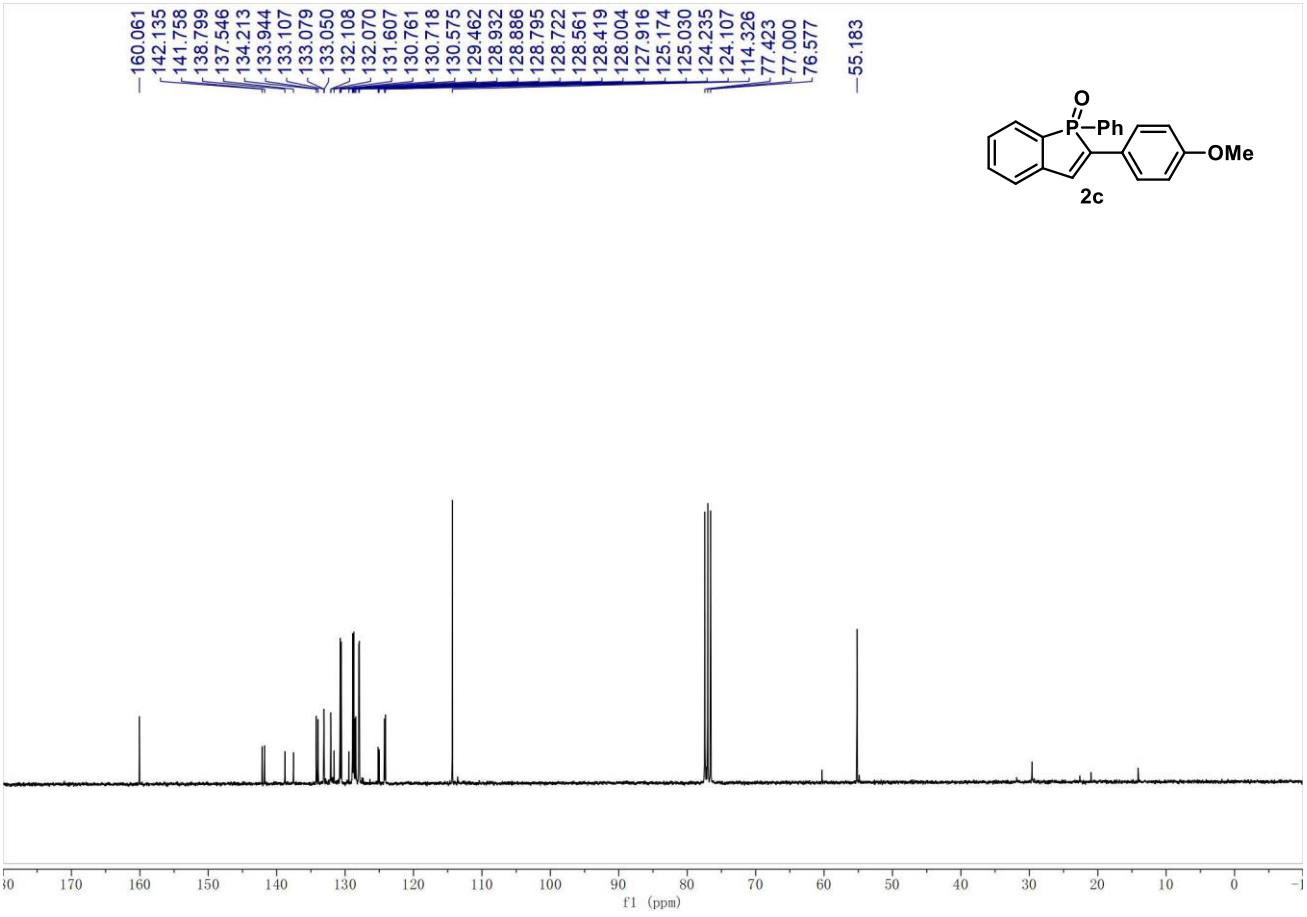
**$^{31}P\{^{1}H\}$ NMR spectrum of 2b (121 MHz, $CDCl_3$)**

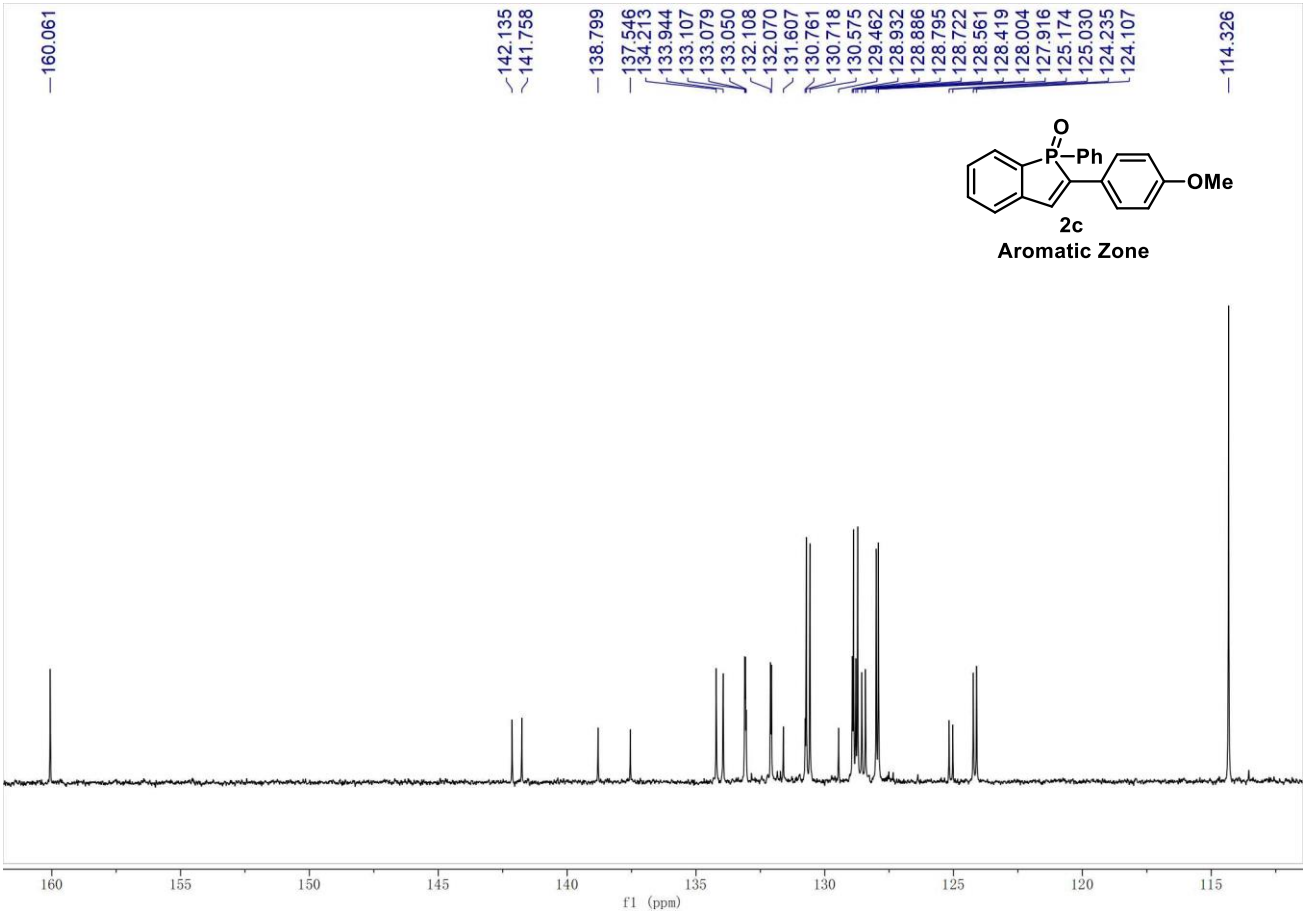



**$^{1}H$ NMR spectrum of 2c (300 MHz, $CDCl_3$)**

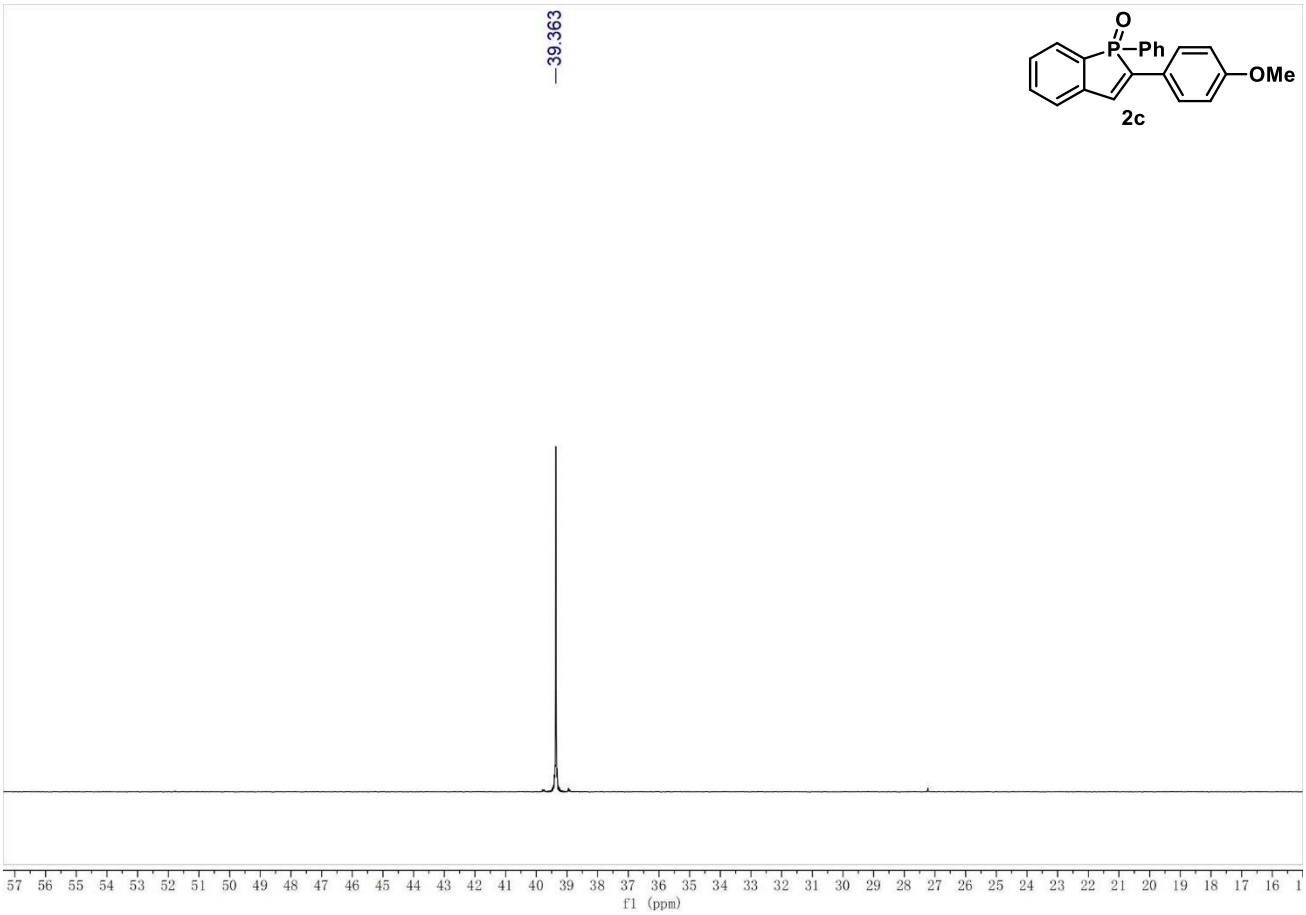


**$^{13}$C NMR spectrum of 2c (75 MHz, $CDCl_3$)**

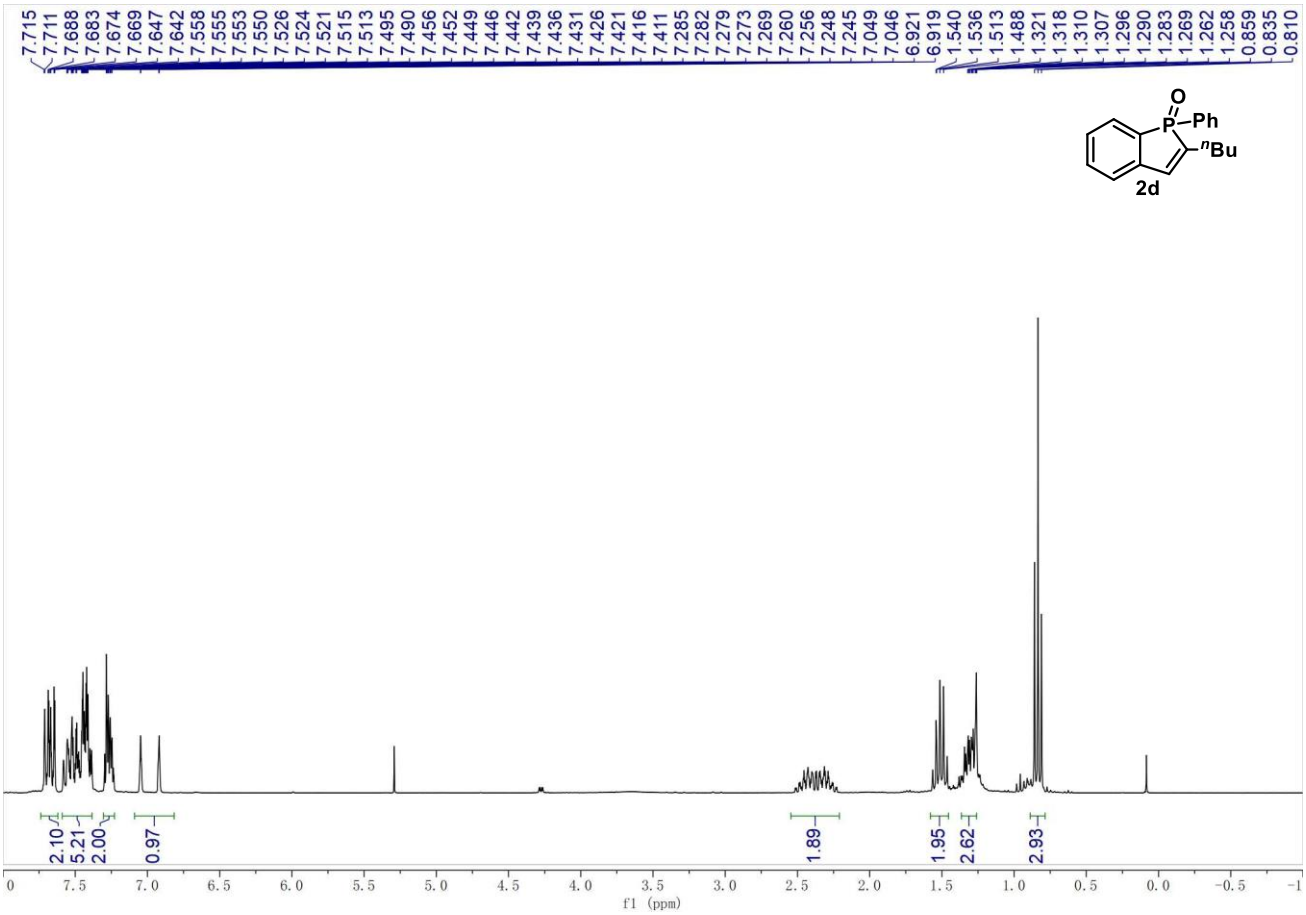


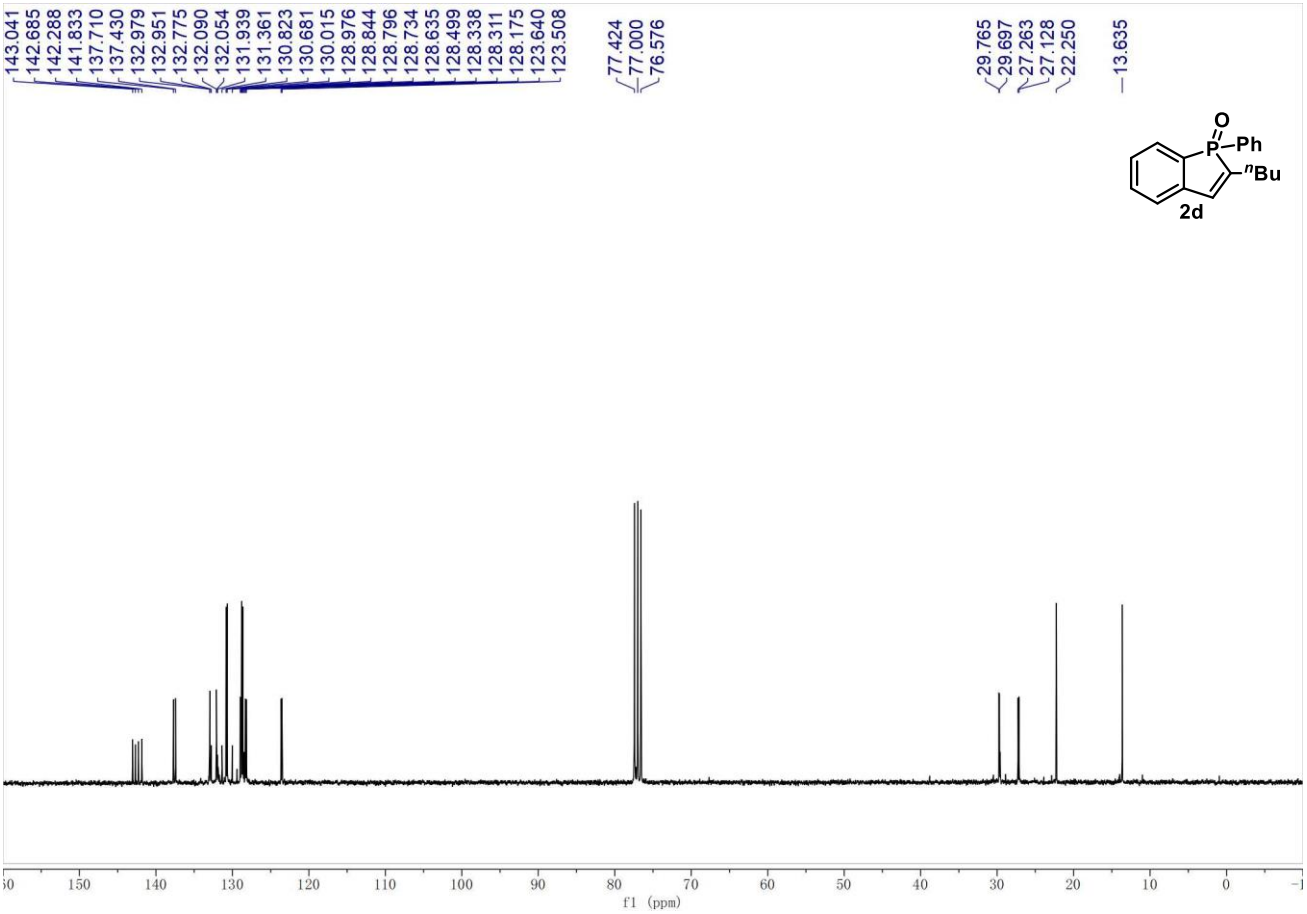
**$^{31}P\{^{1}H\}$ NMR spectrum of 2c (121 MHz, $CDCl_3$)**

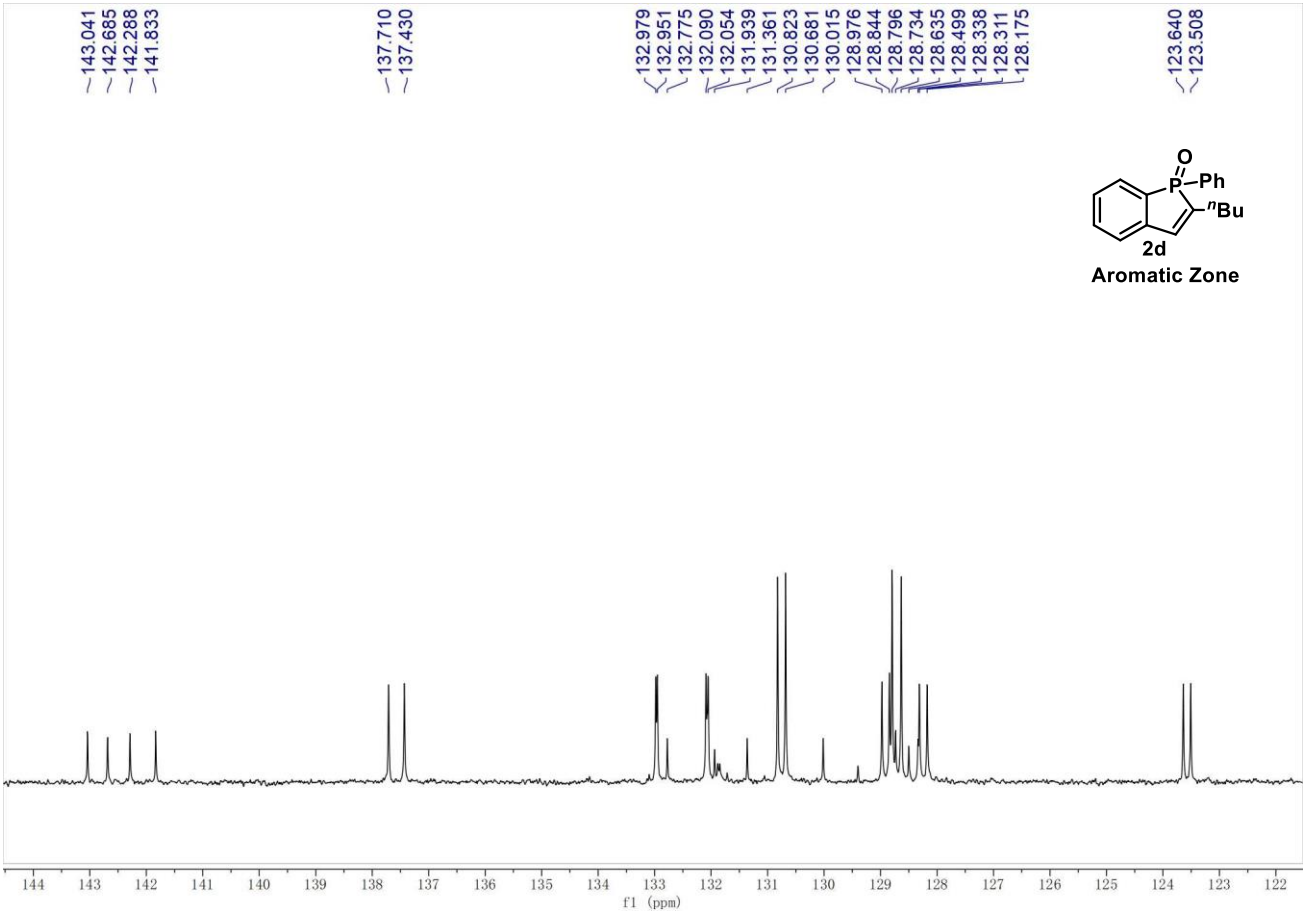



**$^{1}H$ NMR spectrum of 2d (300 MHz, $CDCl_3$)**

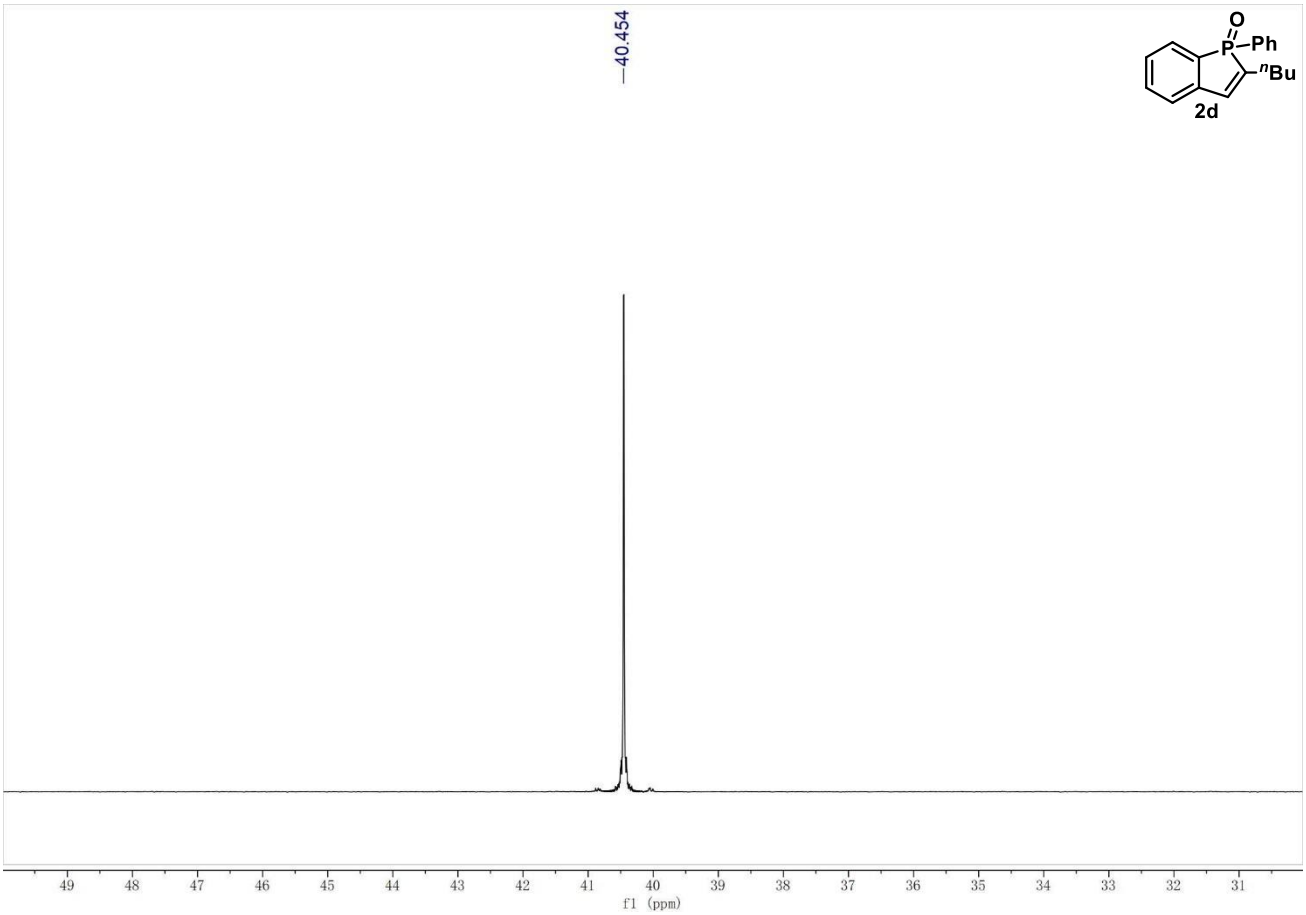


**$^{13}$C NMR spectrum of 2d (75 MHz, $CDCl_3$)**

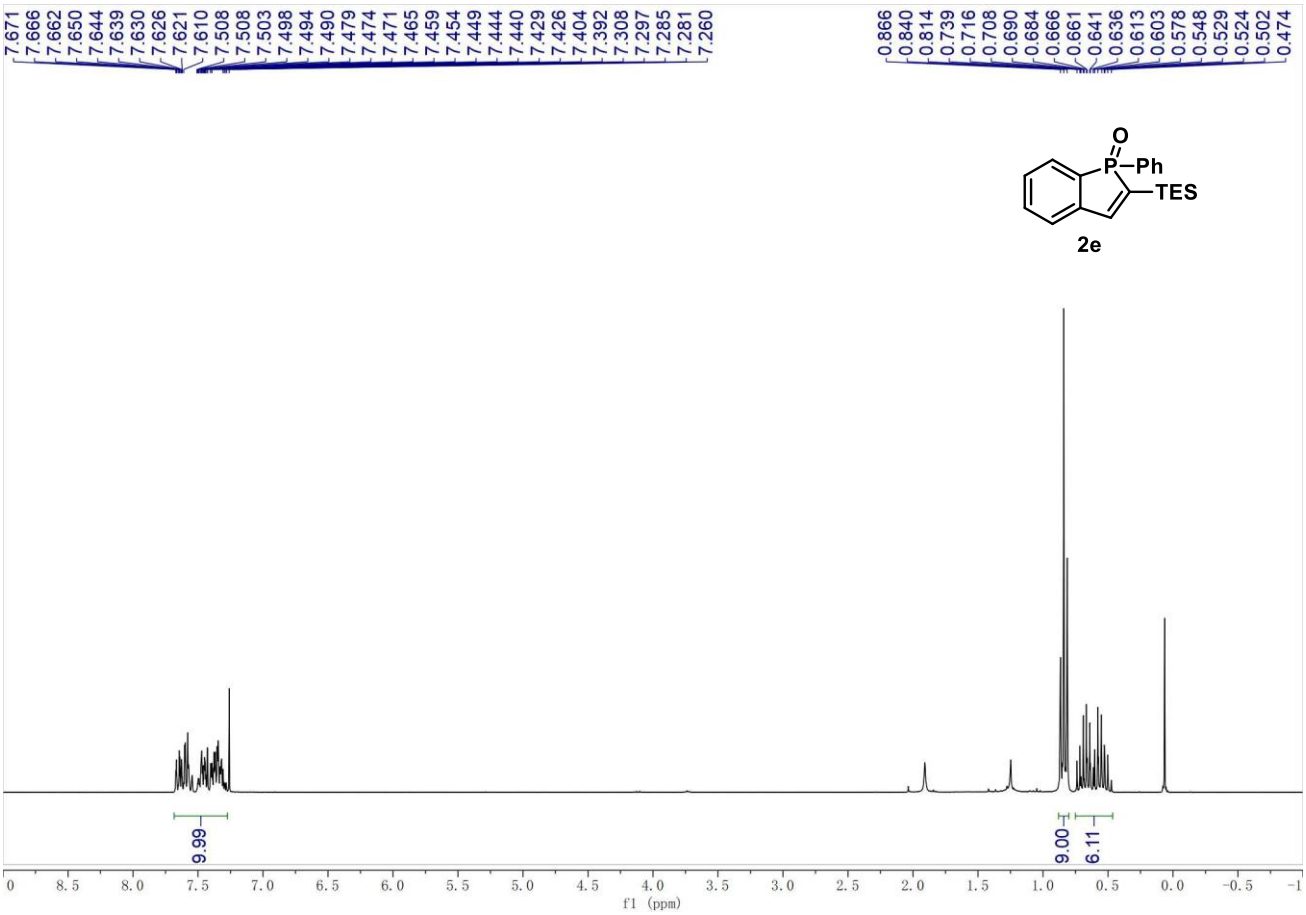


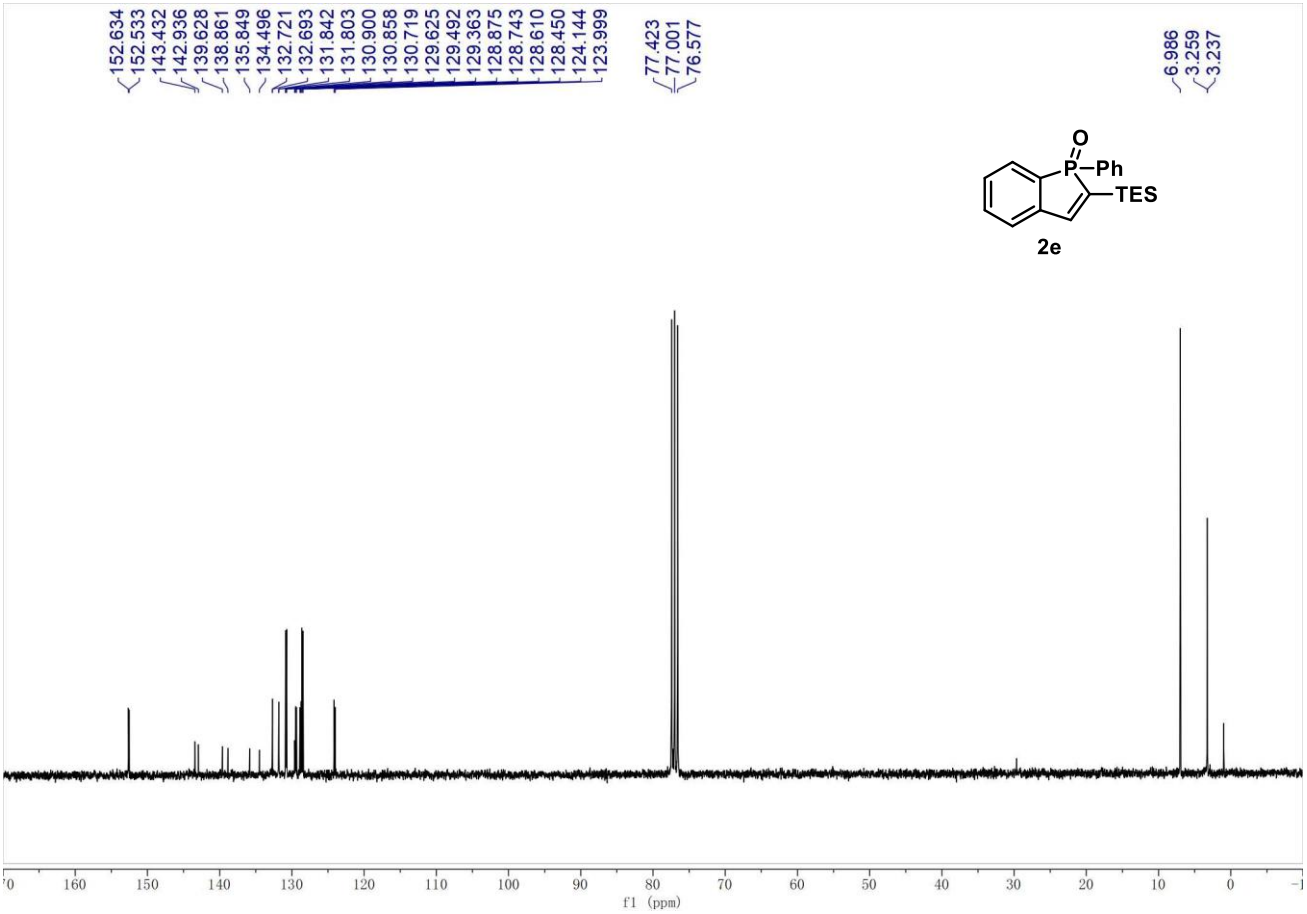
**$^{31}P\{^{1}H\}$ NMR spectrum of 2d (121 MHz, $CDCl_3$)**

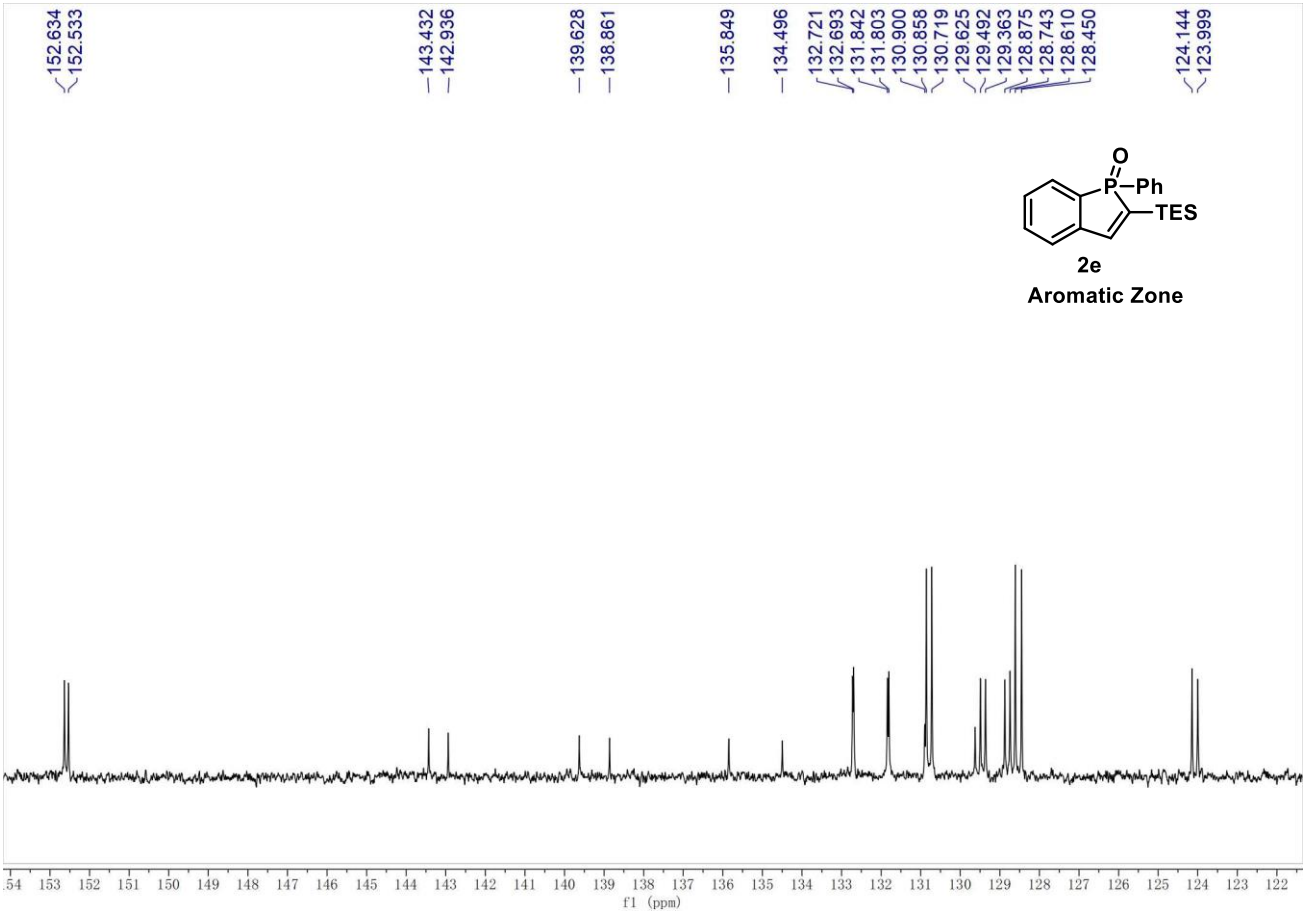



**$^{1}H$ NMR spectrum of 2e (300 MHz, $CDCl_3$)**

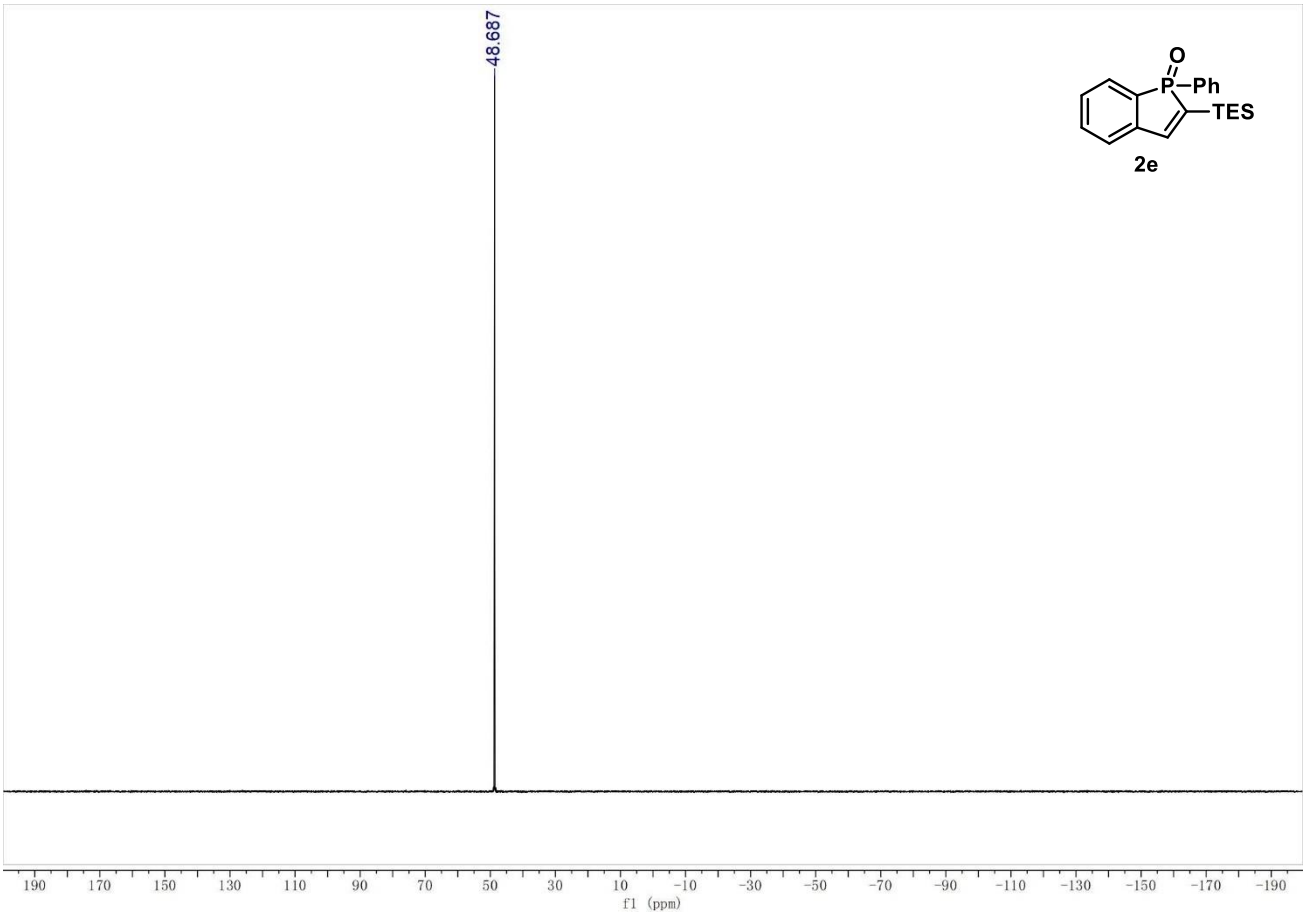


**$^{13}$C NMR spectrum of 2e (75 MHz, $CDCl_3$)**

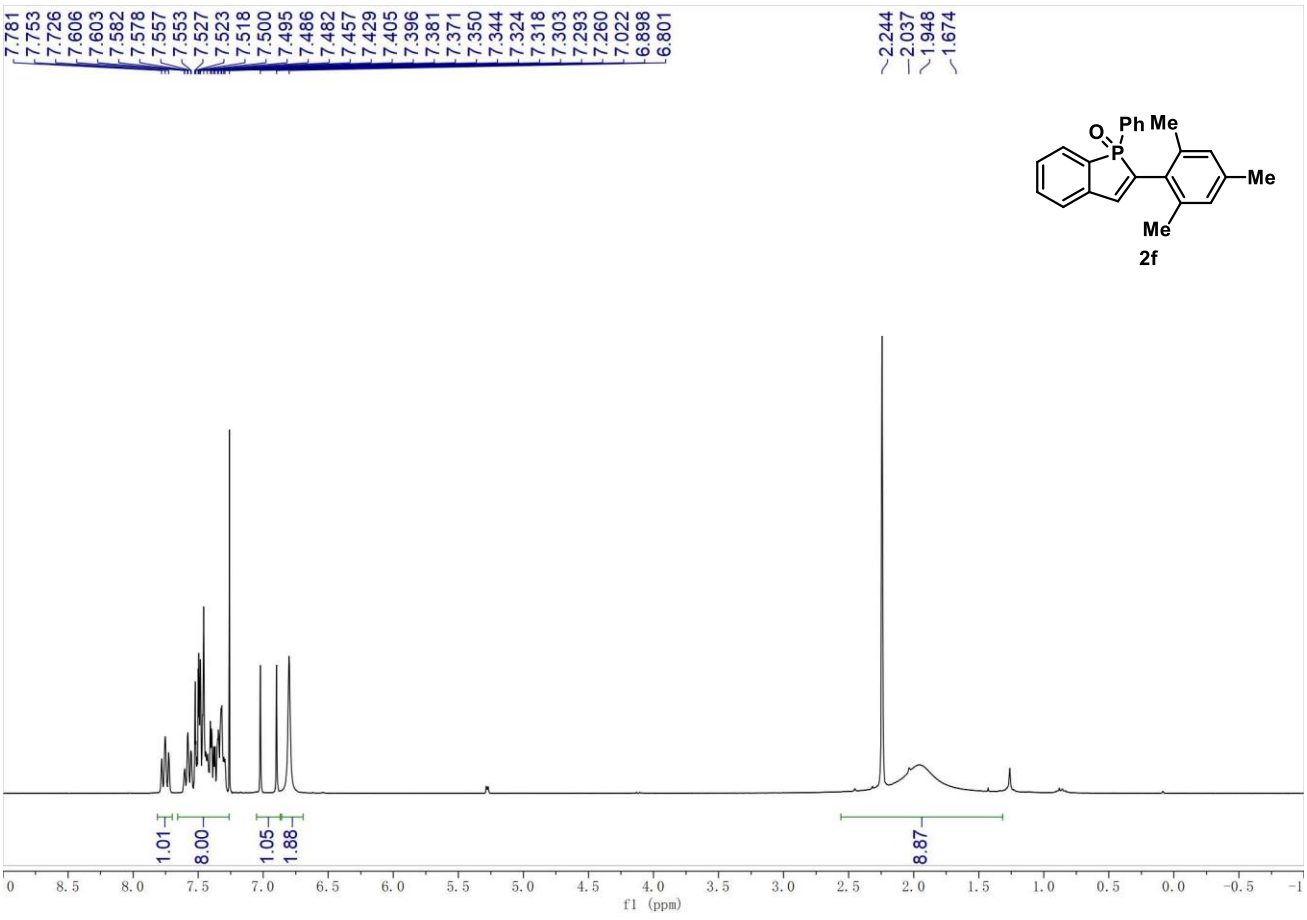


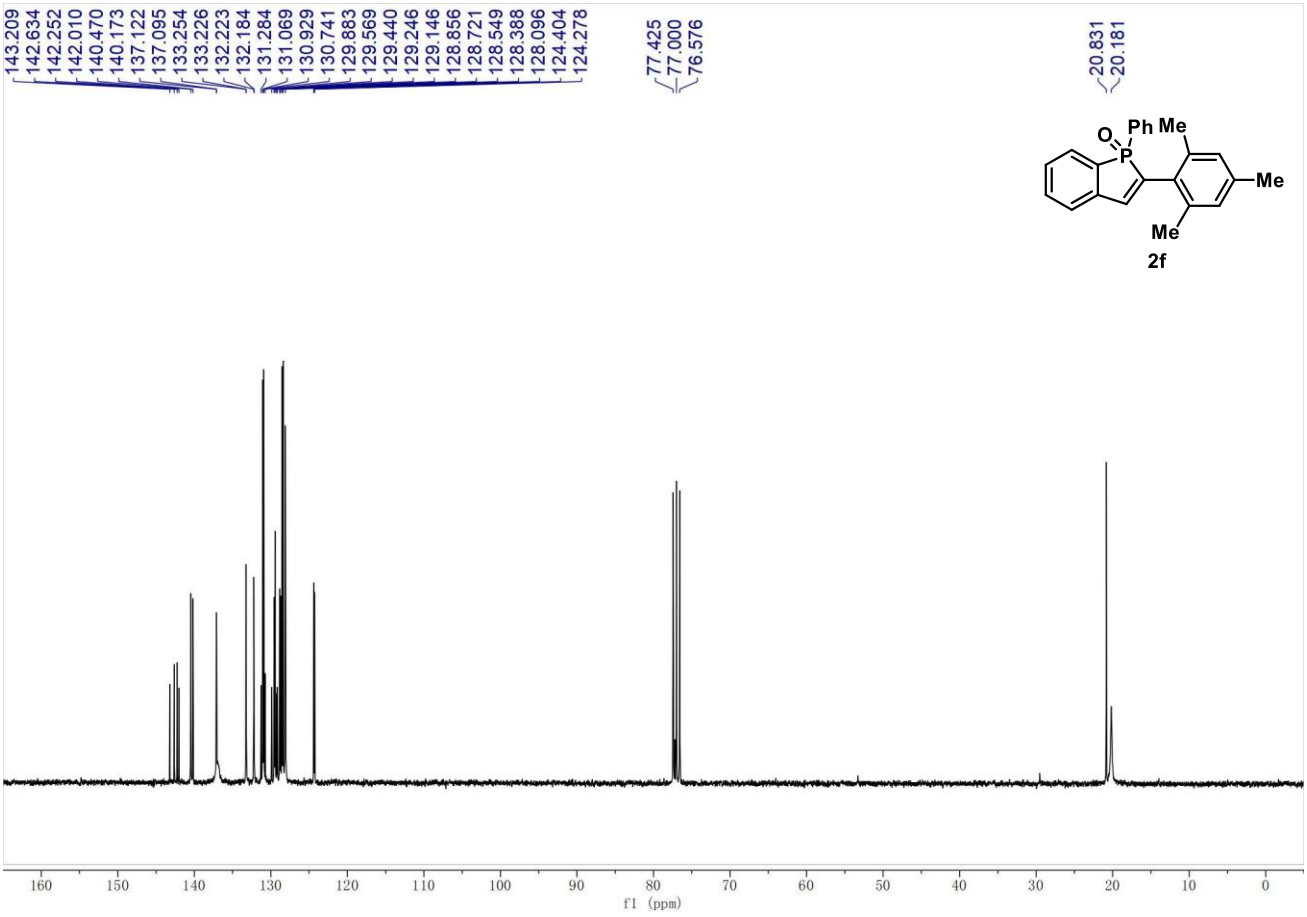
**$^{31}P\{^{1}H\}$ NMR spectrum of 2e (121 MHz, $CDCl_3$)**

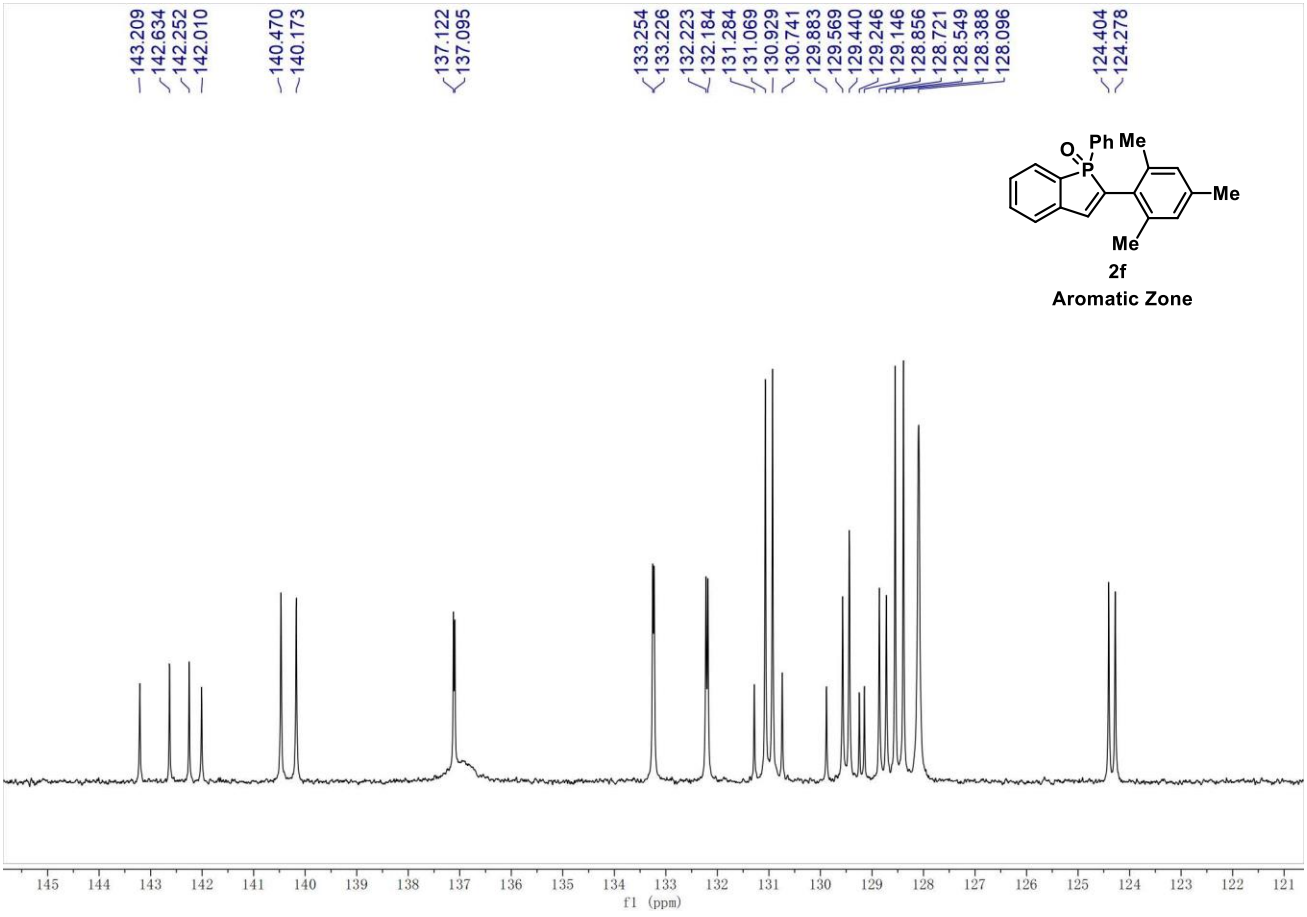



**$^{1}H$ NMR spectrum of 2f (300 MHz, $CDCl_3$)**

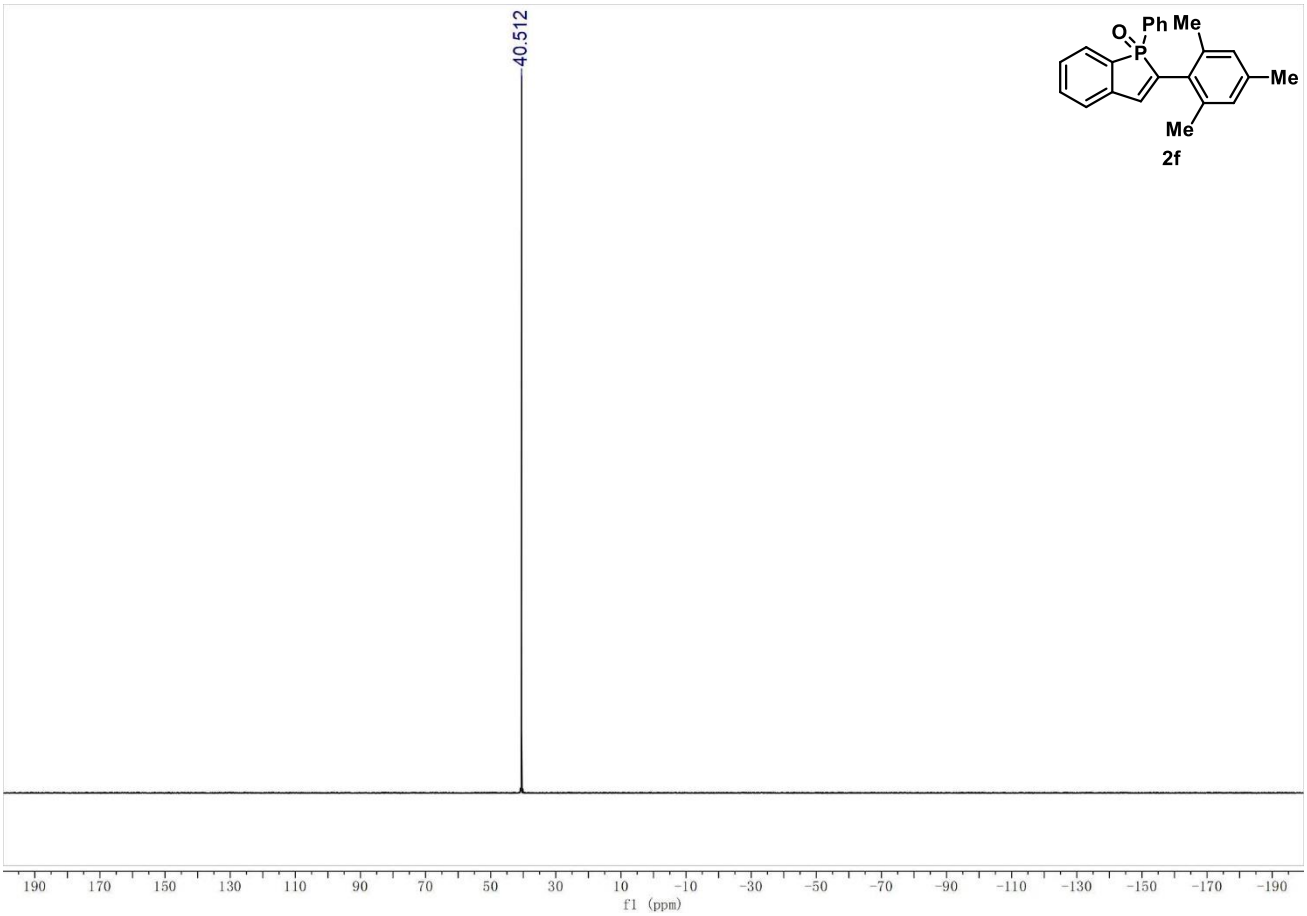


**$^{13}$C NMR spectrum of 2f (75 MHz, $CDCl_3$)**

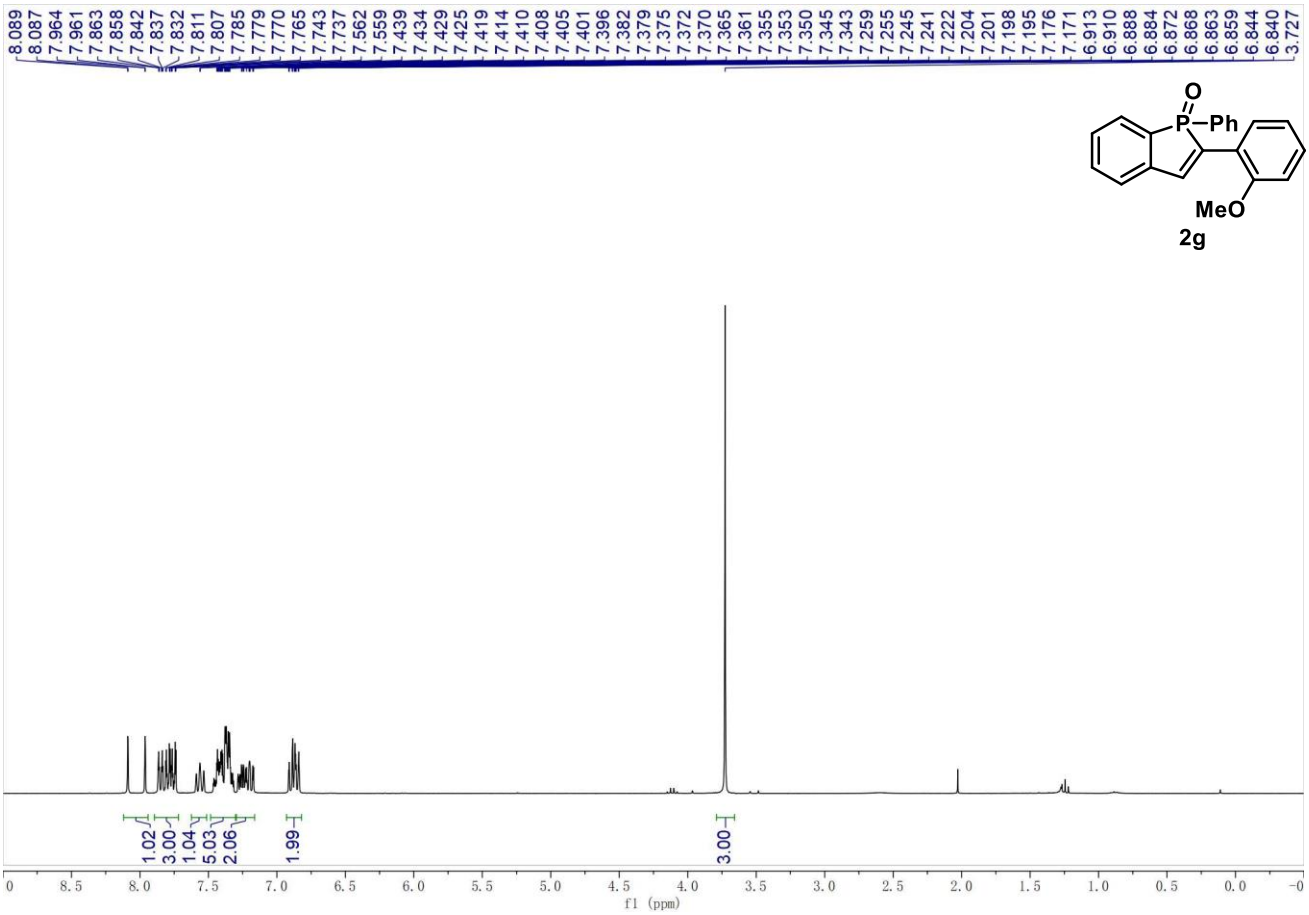


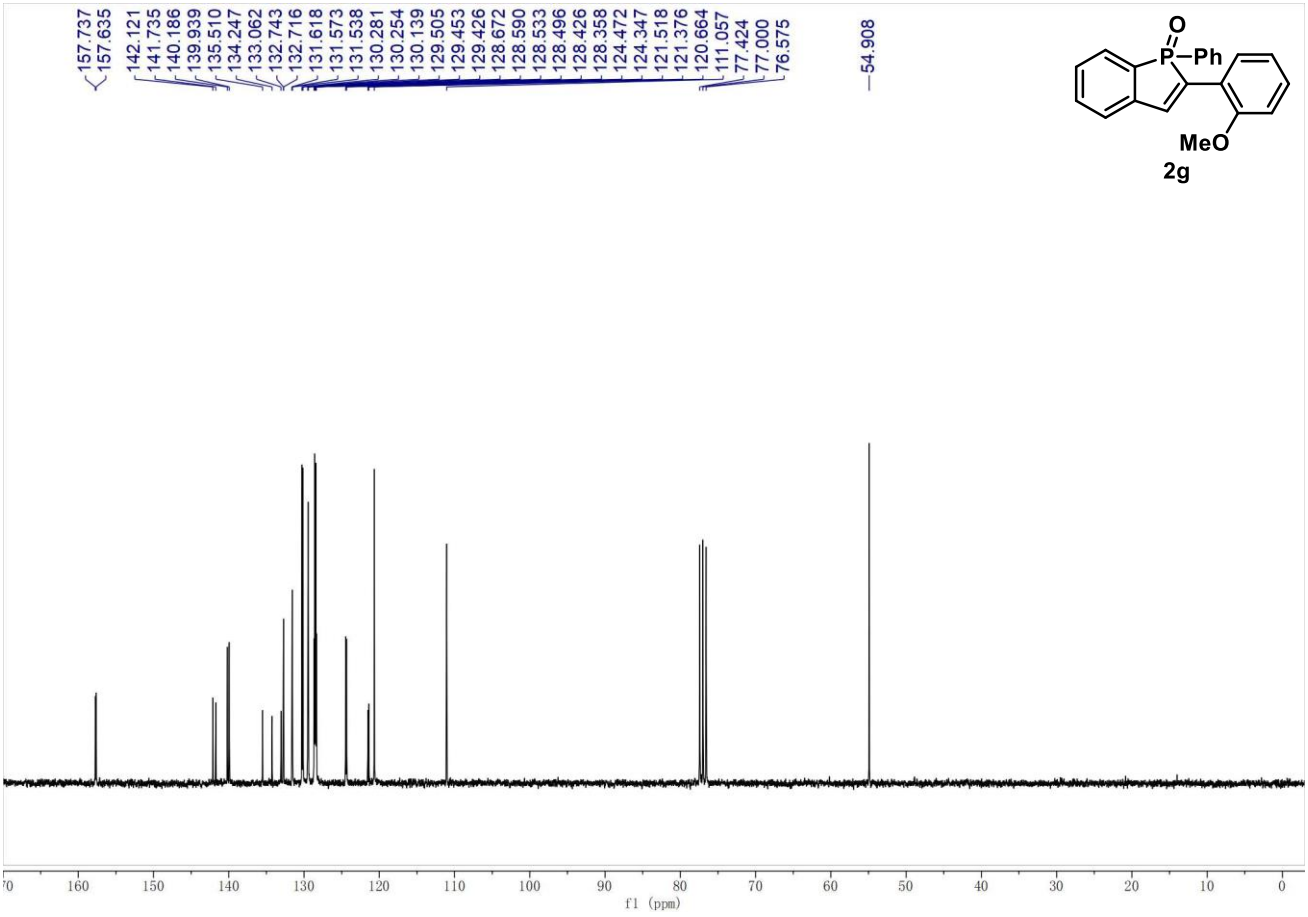
**$^{31}P\{^{1}H\}$ NMR spectrum of 2f (121 MHz, $CDCl_3$)**

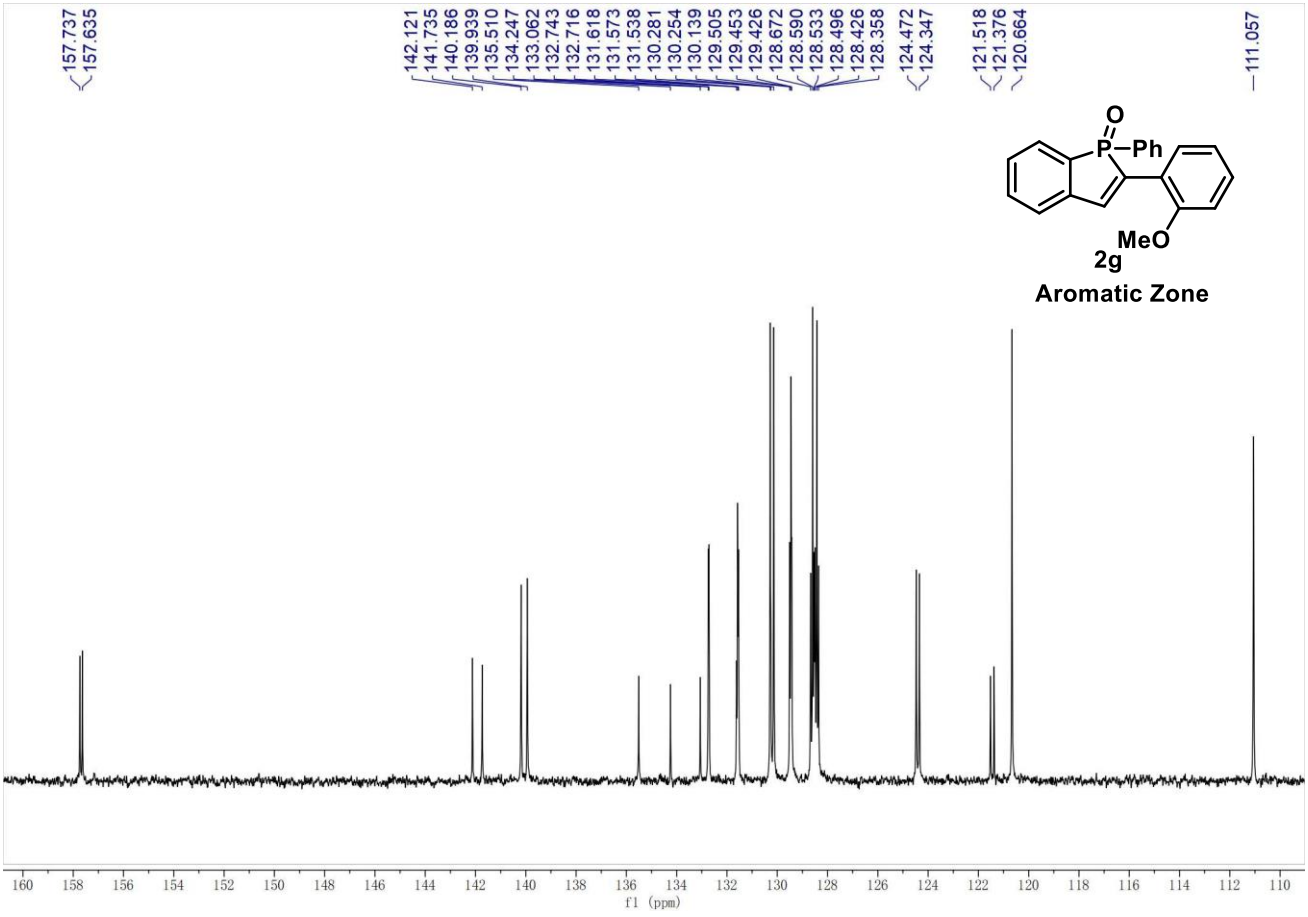



**$^{1}H$ NMR spectrum of 2g (300 MHz, $CDCl_3$)**

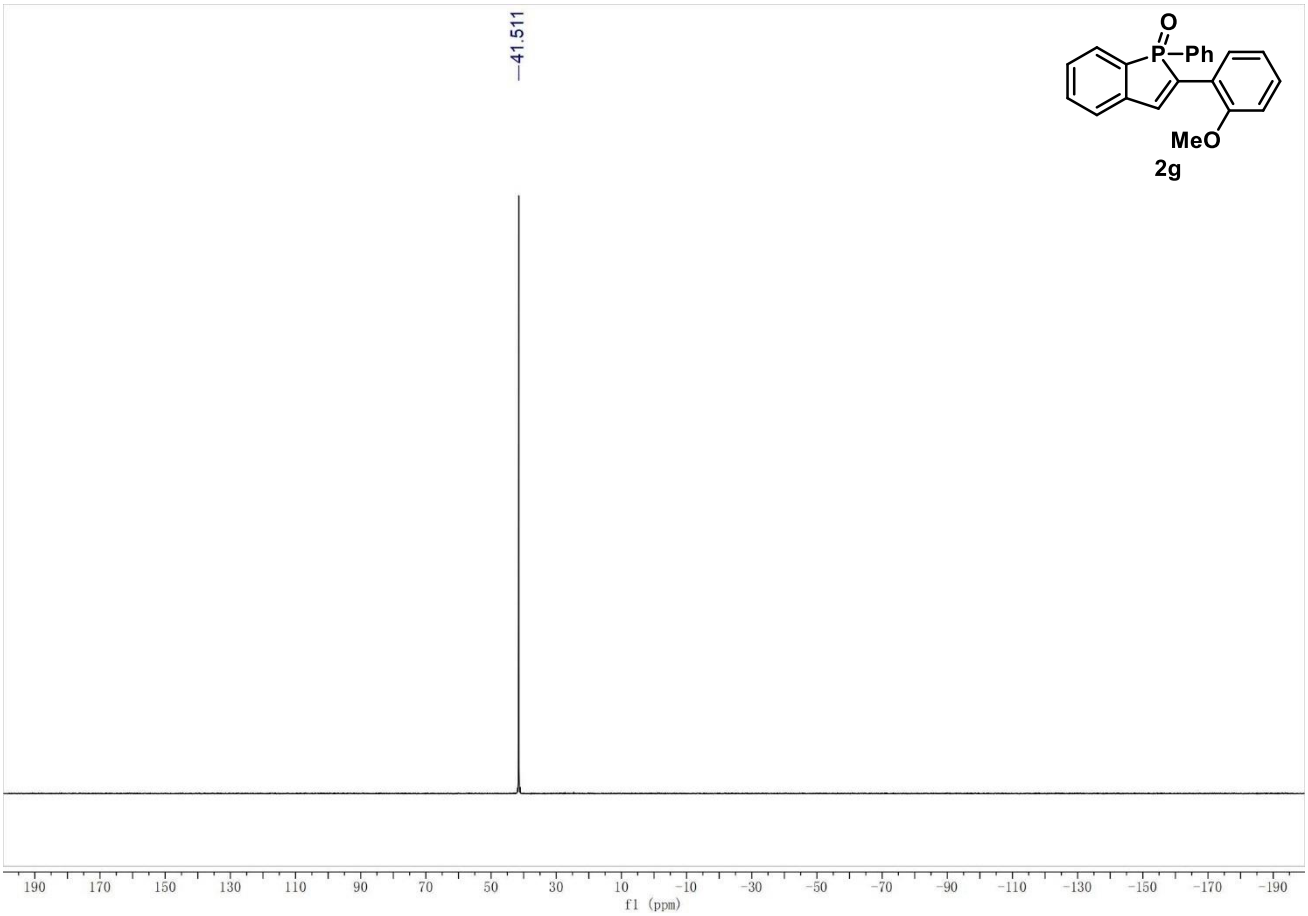


**$^{13}$C NMR spectrum of 2g (75 MHz, $CDCl_3$)**

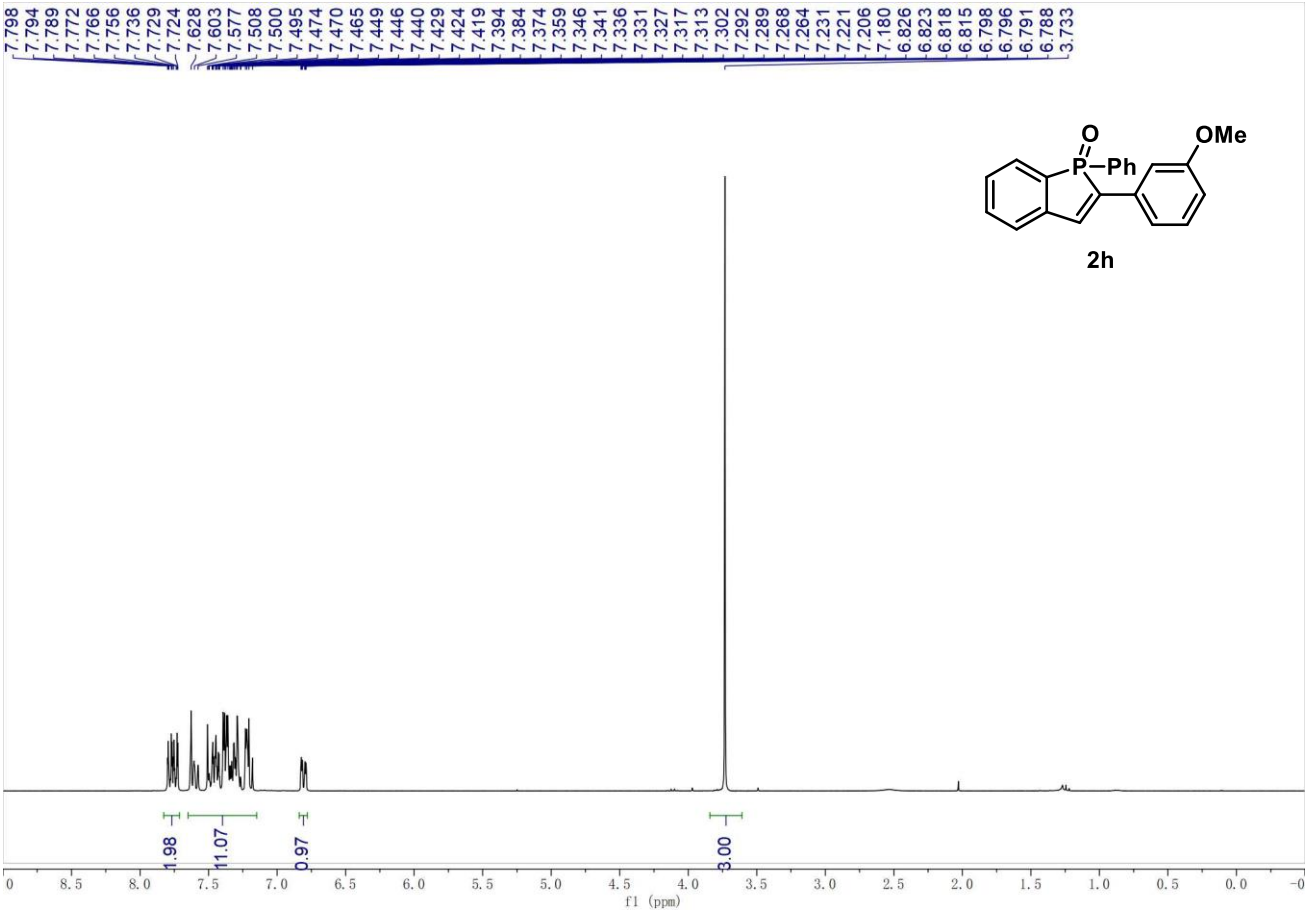


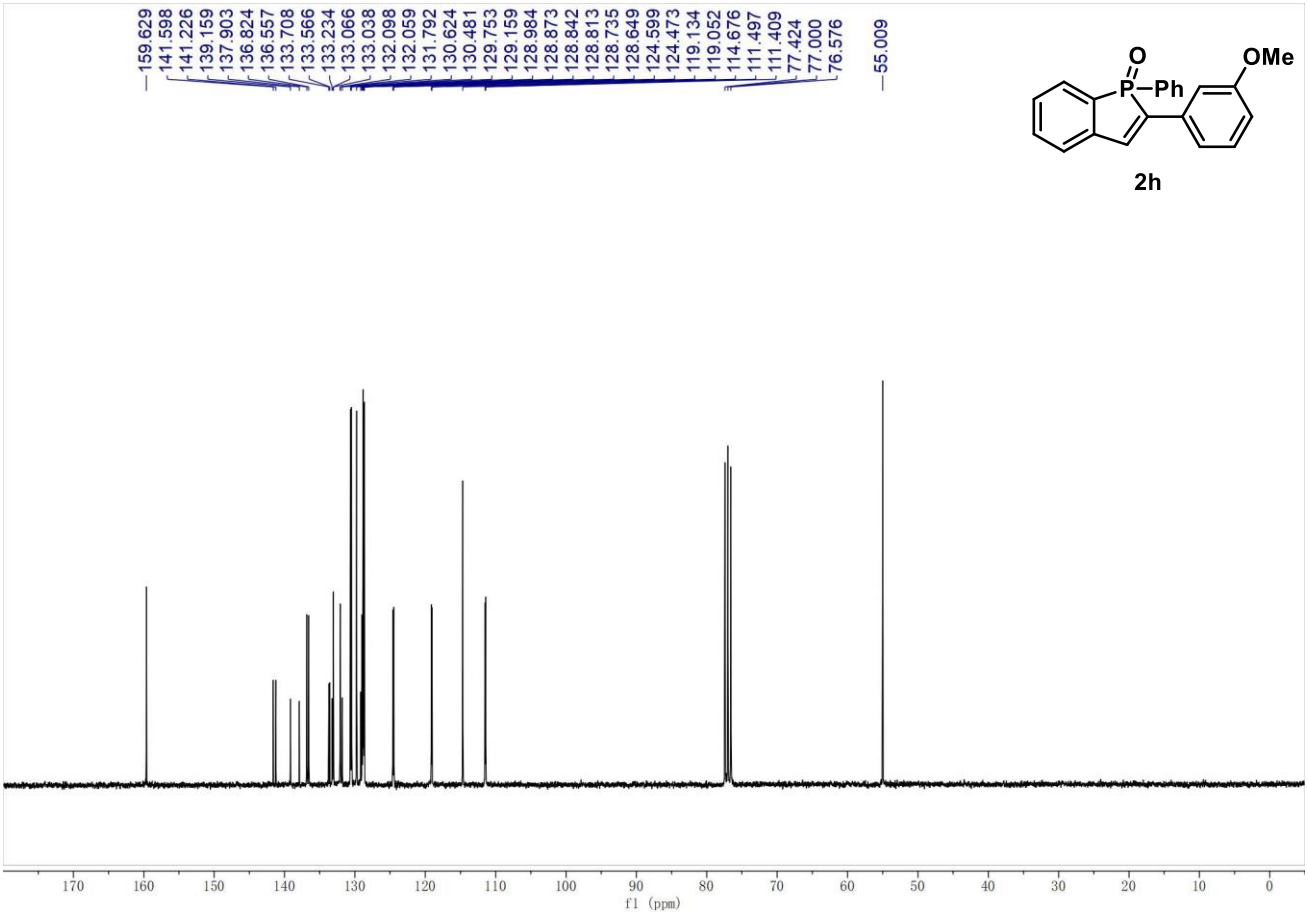
**$^{31}P\{^{1}H\}$ NMR spectrum of 2g (121 MHz, $CDCl_3$)**

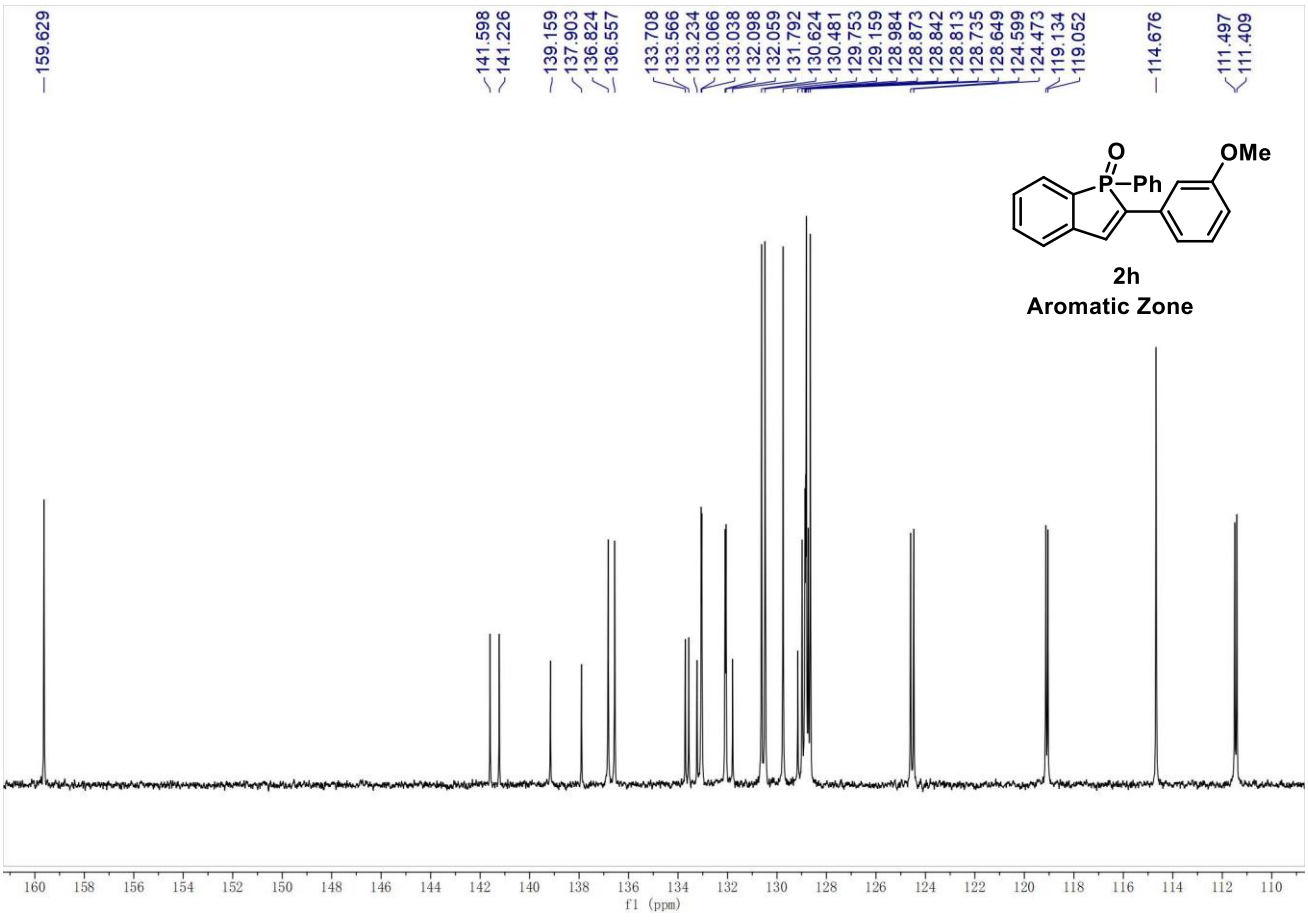



**$^{1}H$ NMR spectrum of 2h (300 MHz, $CDCl_3$)**

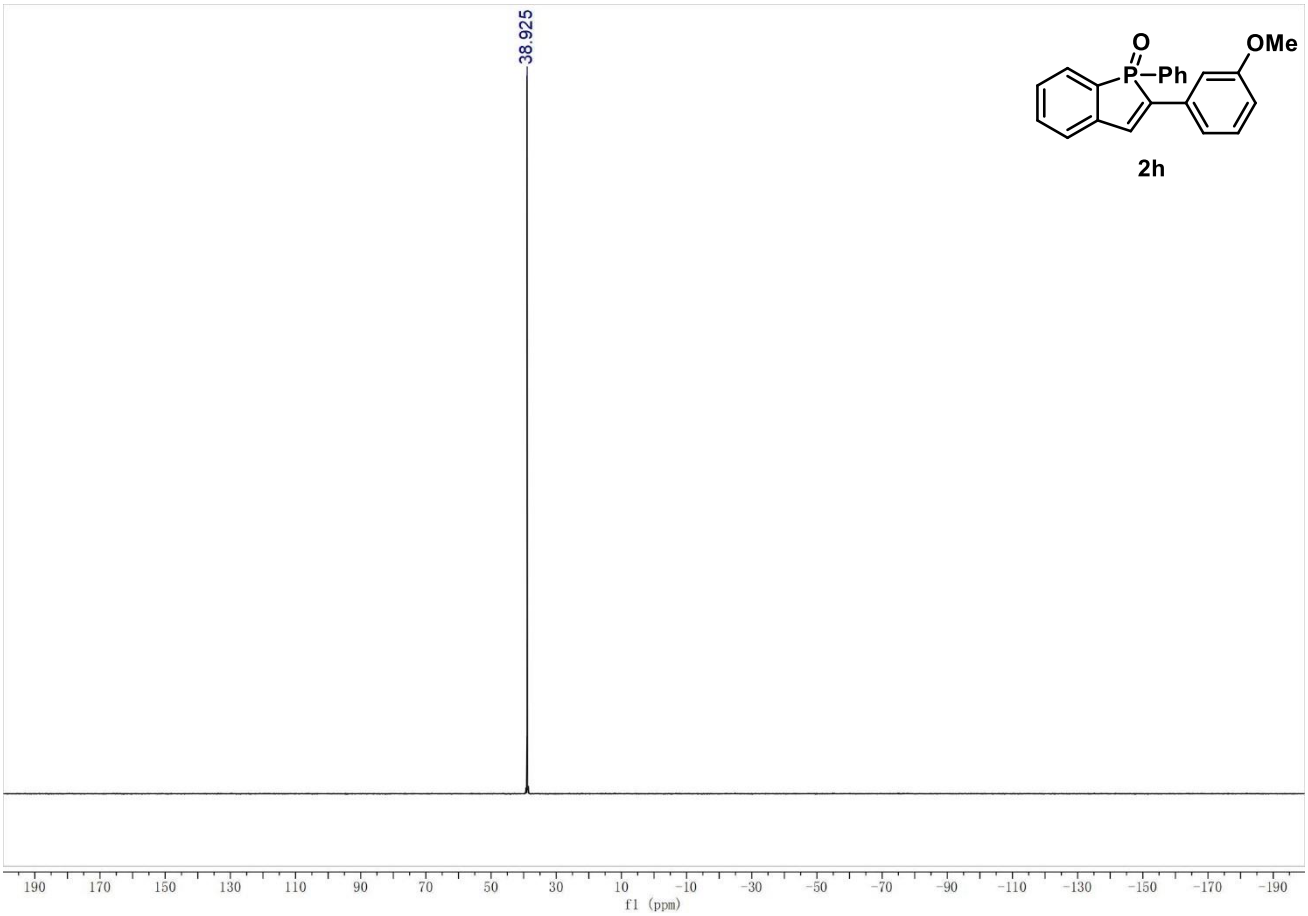


**$^{13}$C NMR spectrum of 2h (75 MHz, $CDCl_3$)**

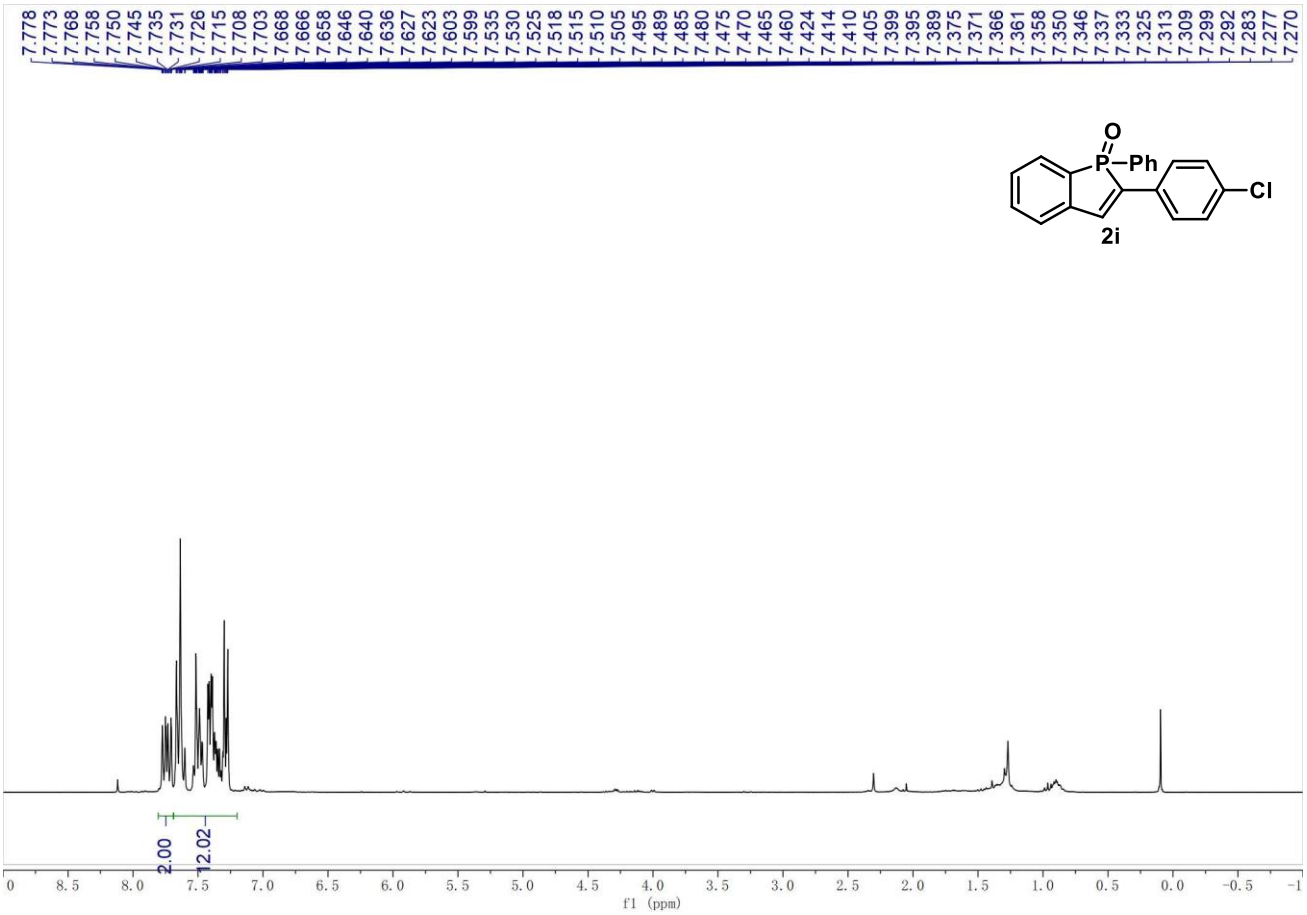


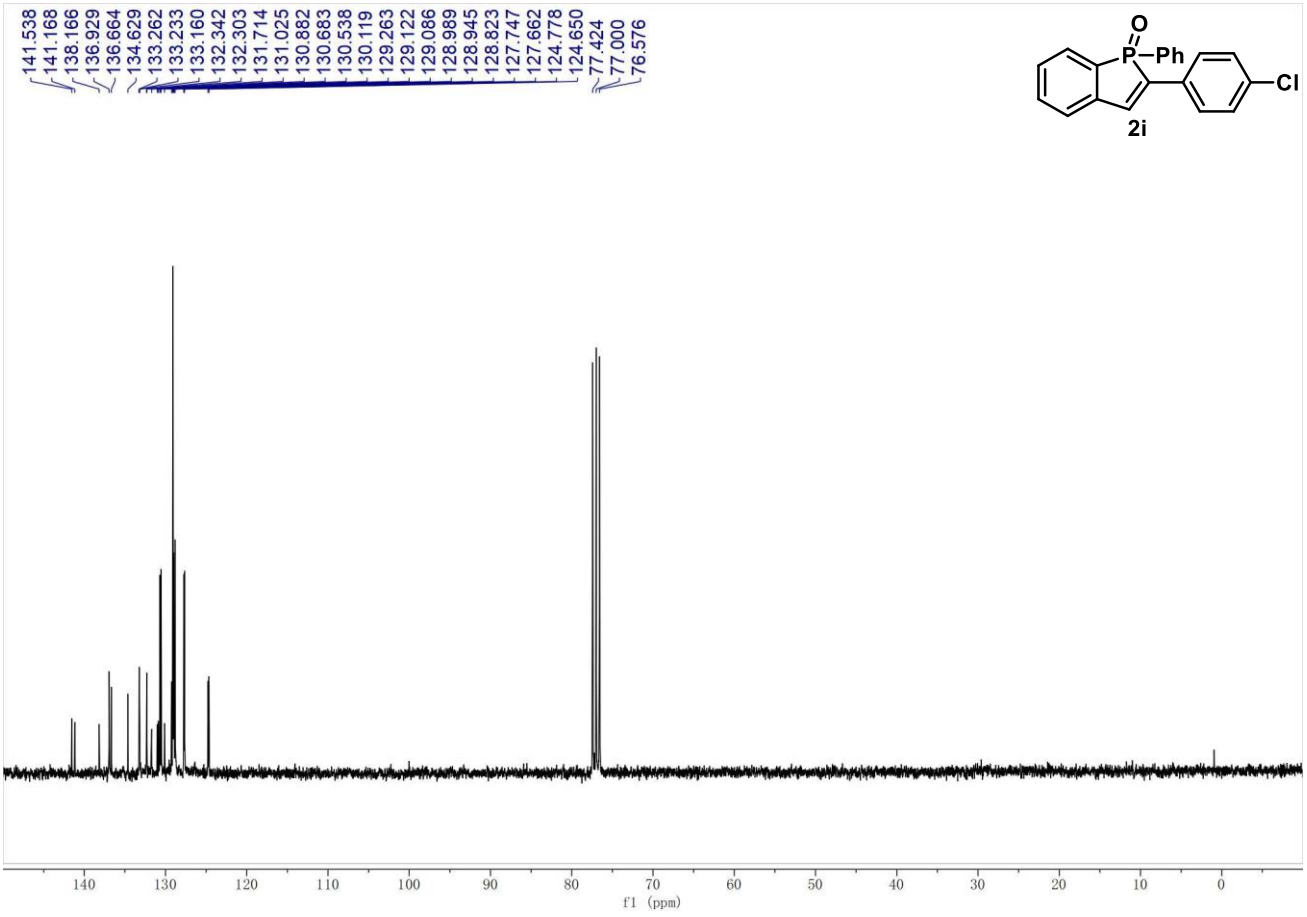
**$^{31}P\{^{1}H\}$ NMR spectrum of 2h (121 MHz, $CDCl_3$)**

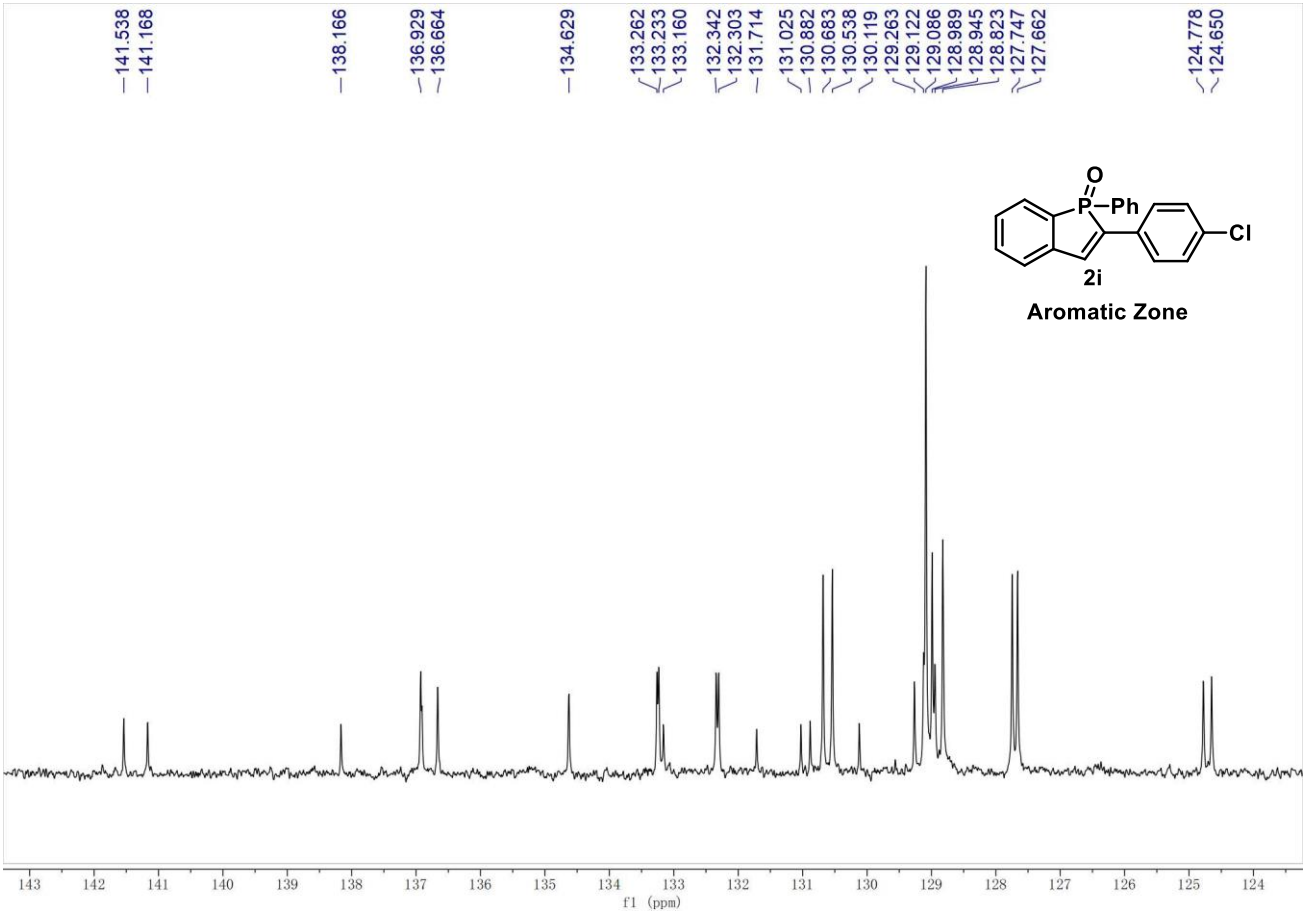



**$^{1}H$ NMR spectrum of 2i (300 MHz, $CDCl_3$)**

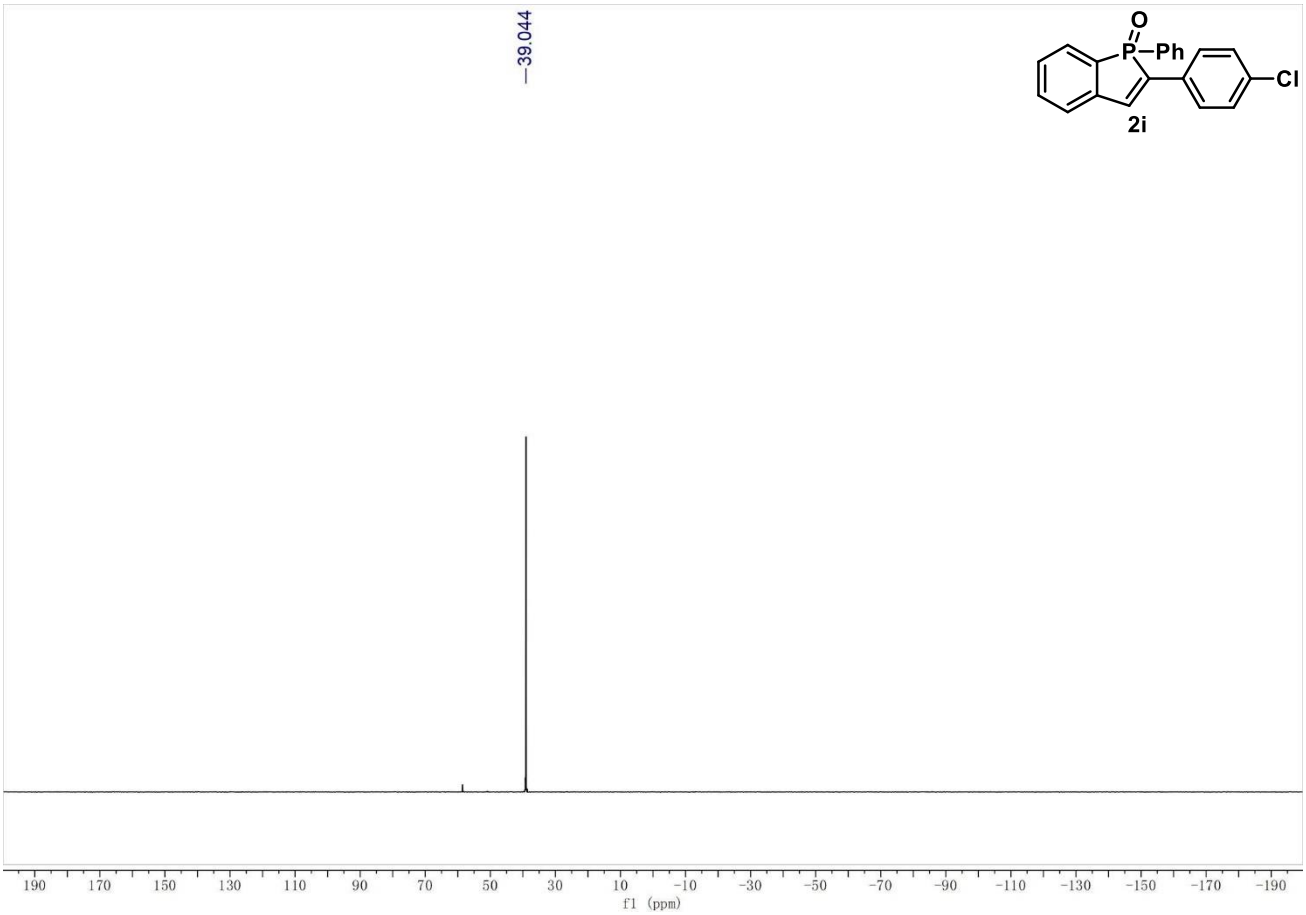


**$^{13}$C NMR spectrum of 2i (75 MHz, $CDCl_3$)**

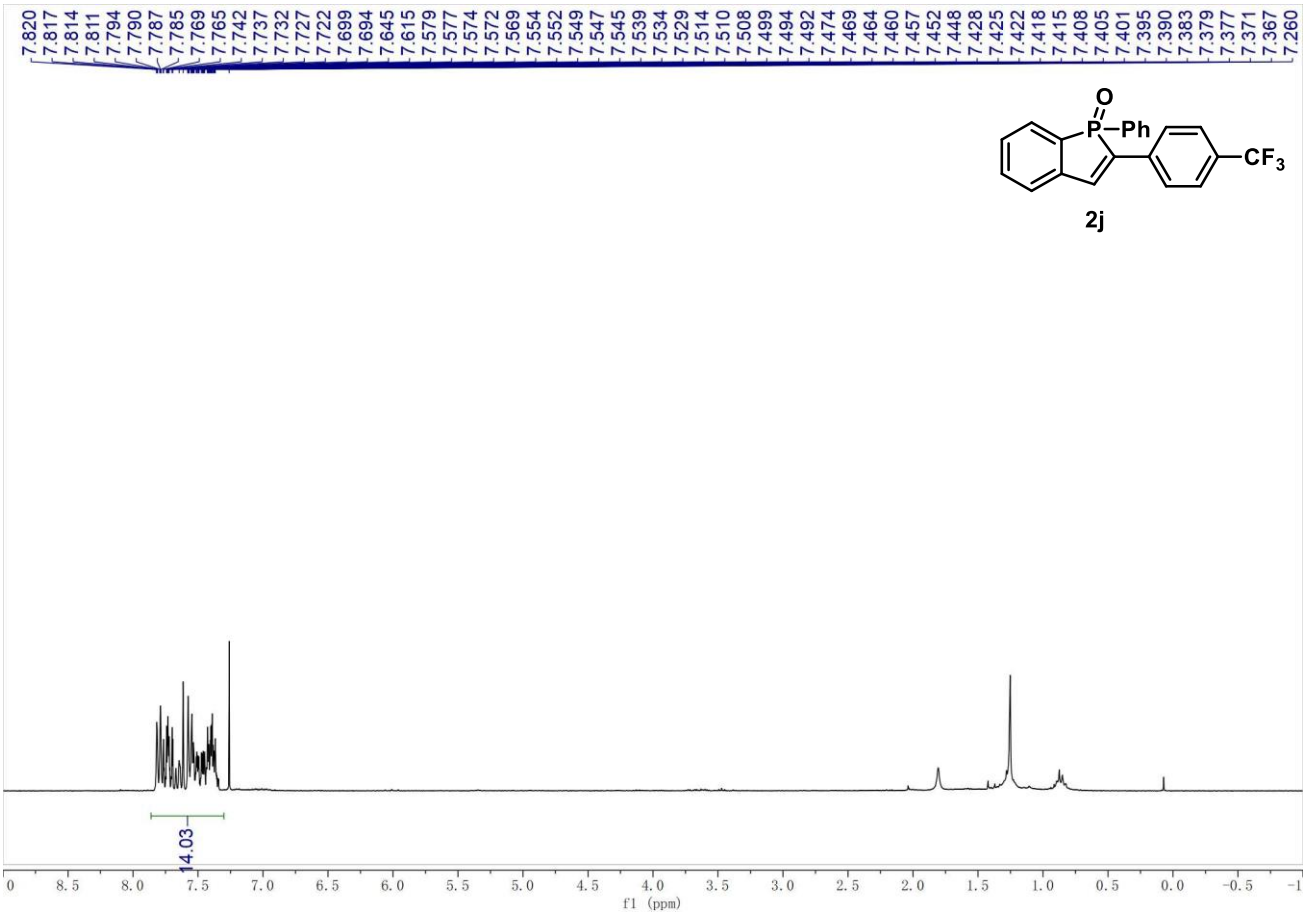


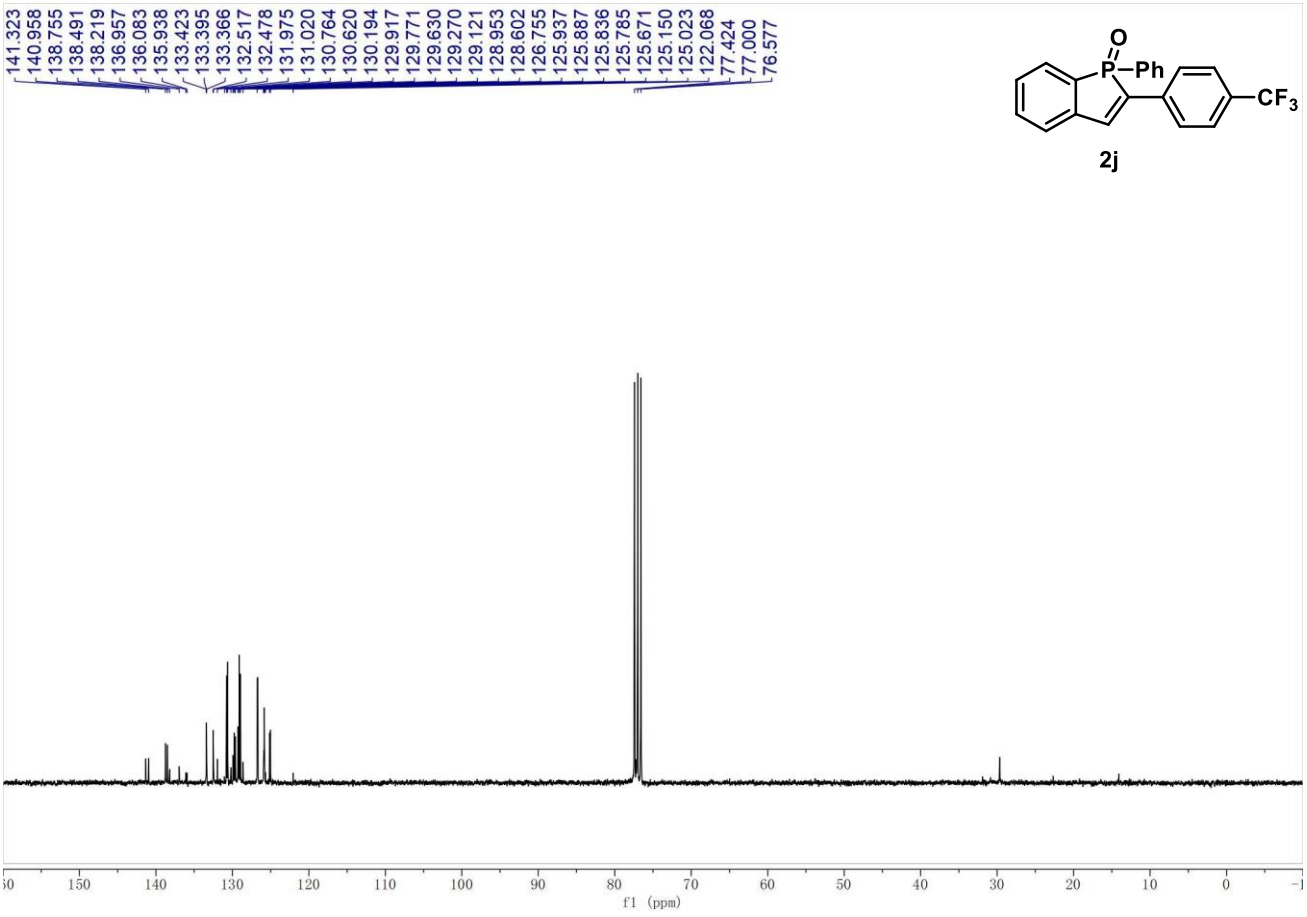
**$^{31}P\{^{1}H\}$ NMR spectrum of 2i (121 MHz, $CDCl_3$)**

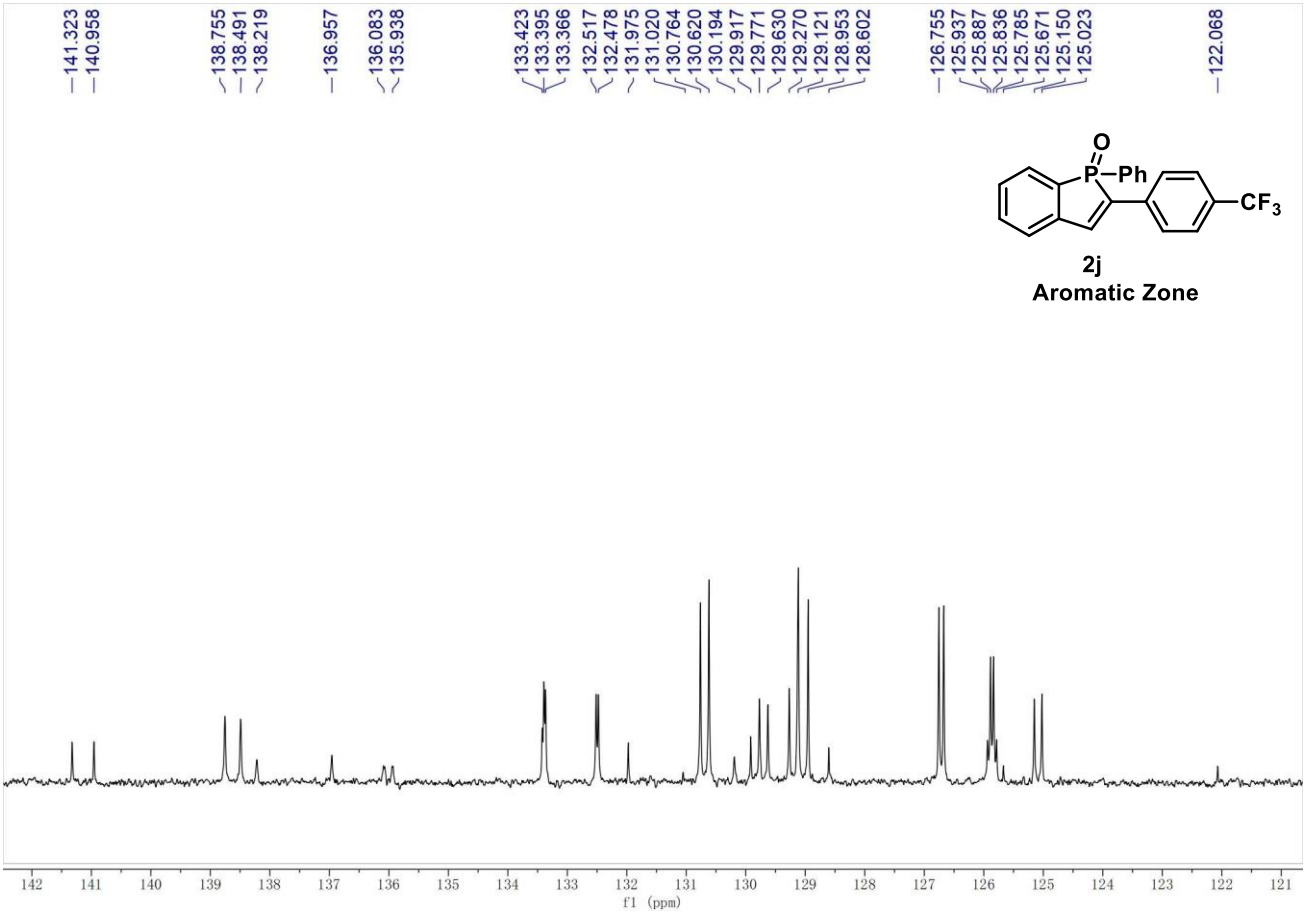



**$^{1}H$ NMR spectrum of 2j (300 MHz, $CDCl_3$)**

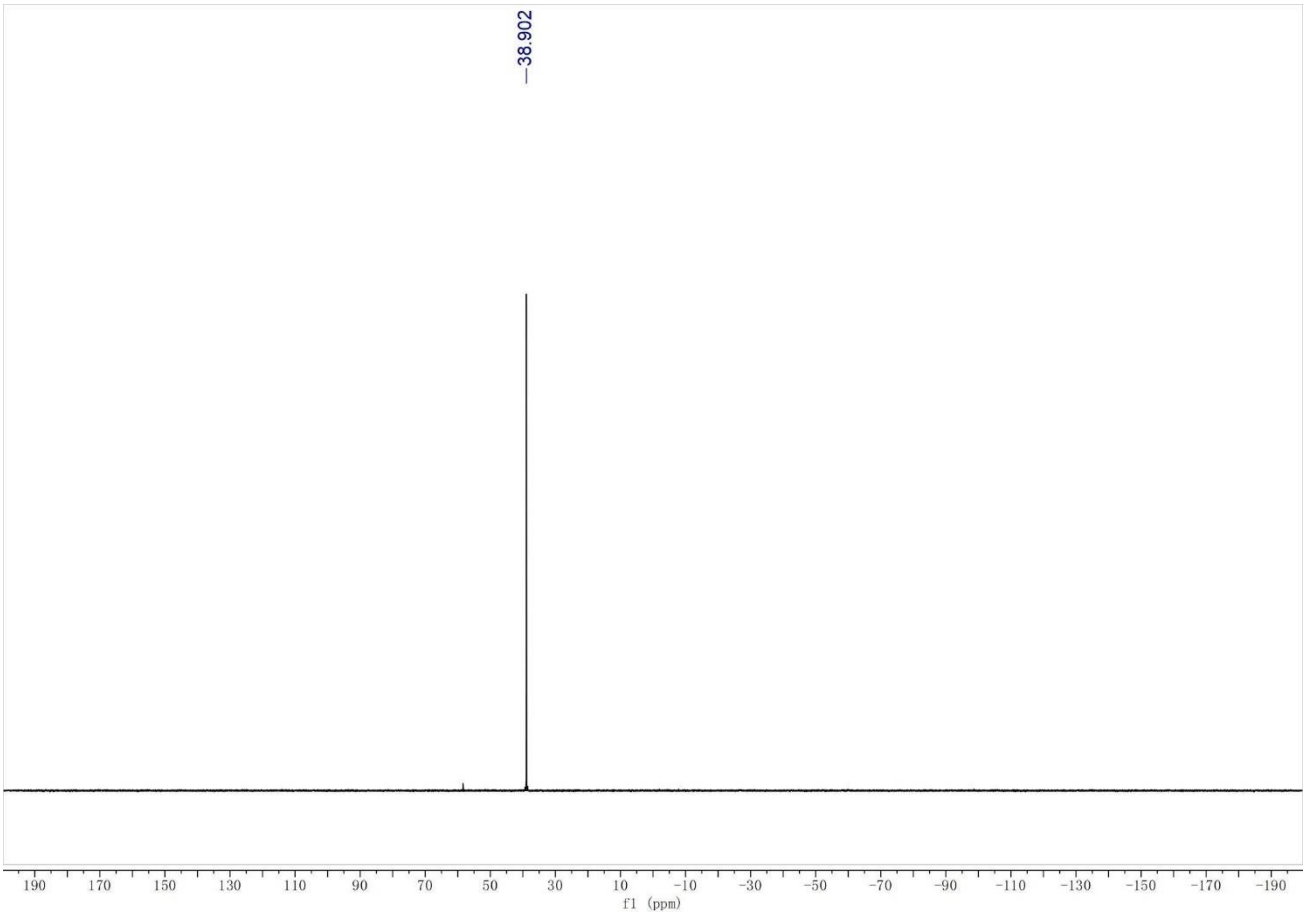


**$^{13}$C NMR spectrum of 2j (75 MHz, $CDCl_3$)**

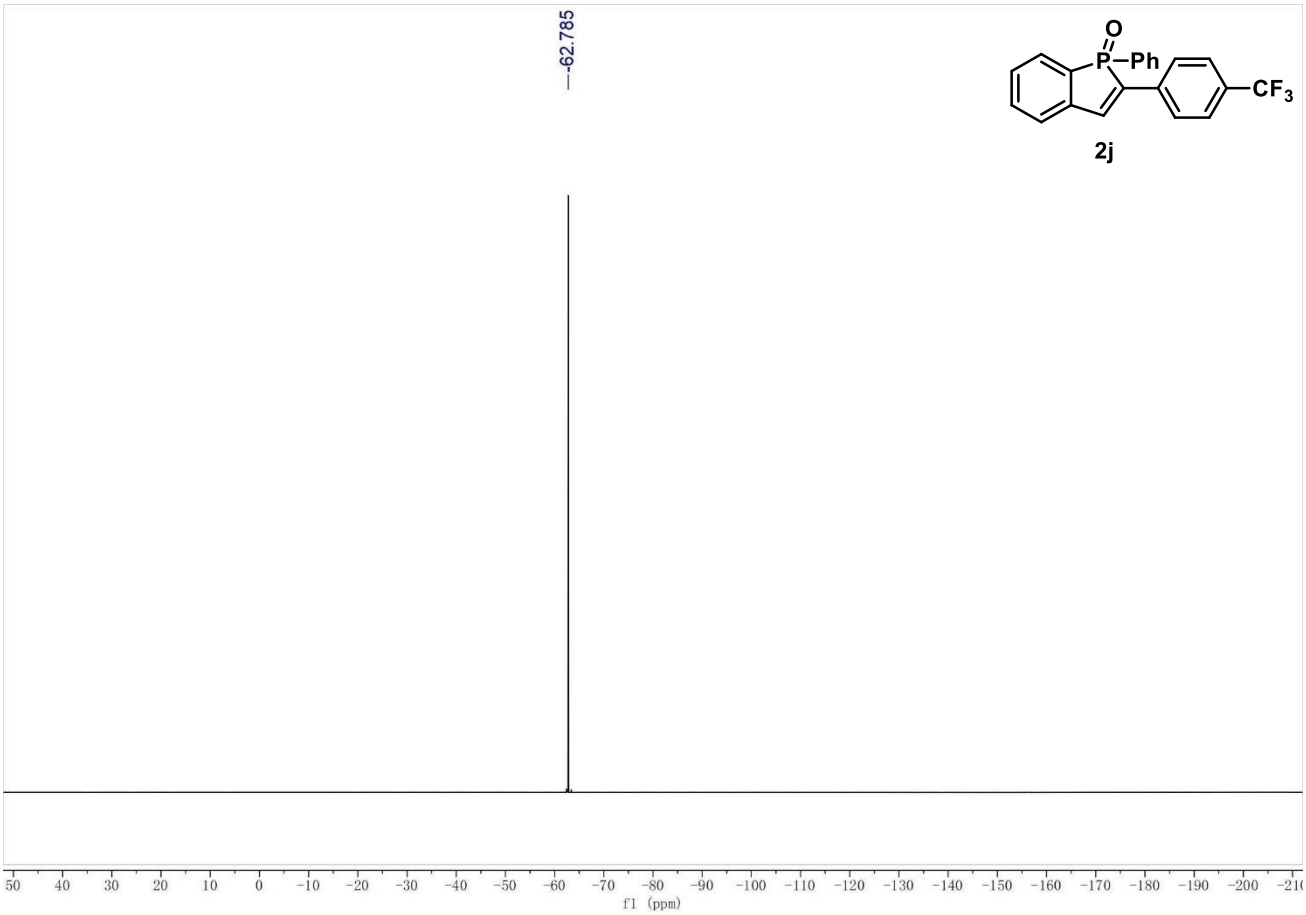


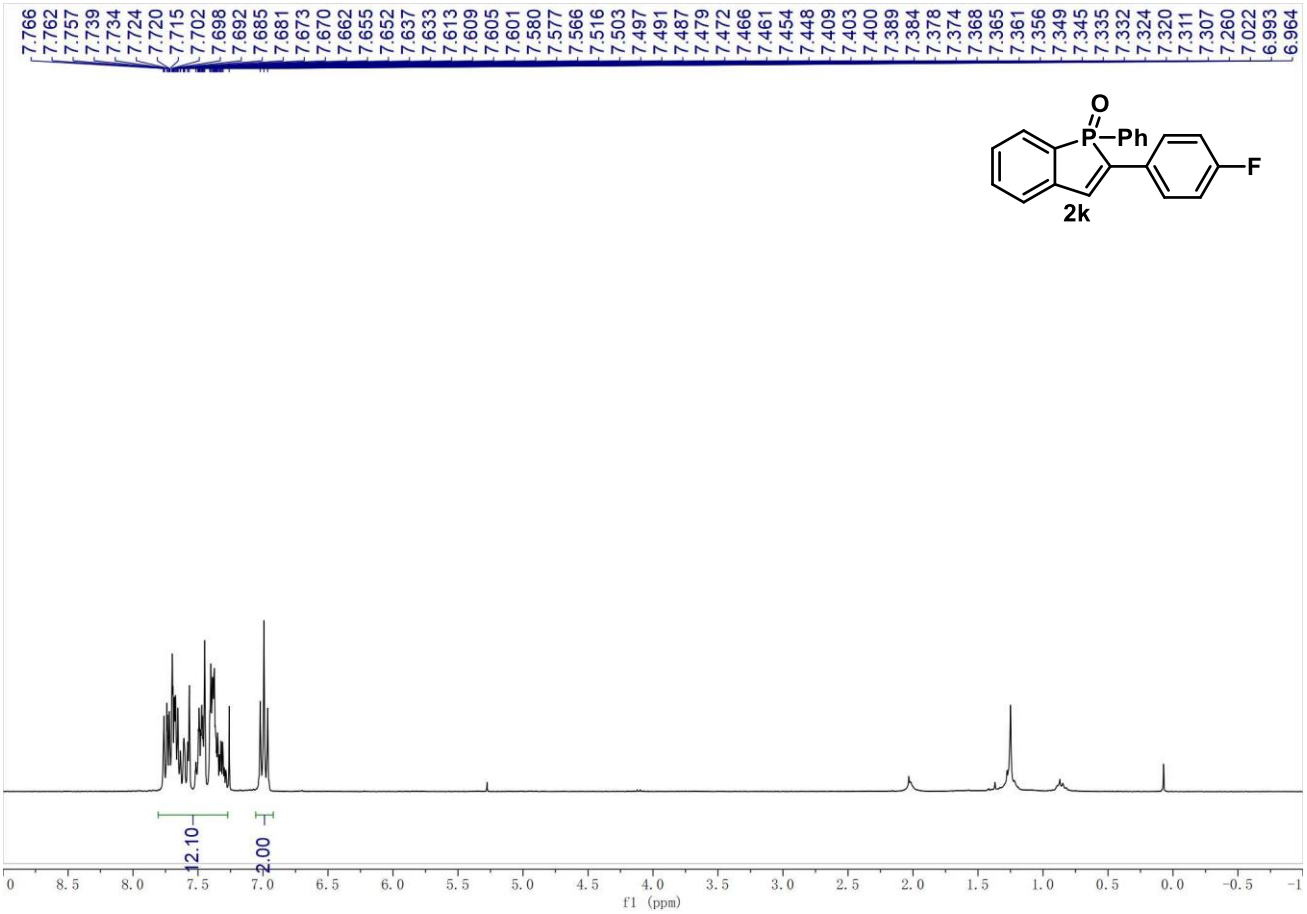
**$^{31}P\{^{1}H\}$ NMR spectrum of 2j (121 MHz, $CDCl_3$)**



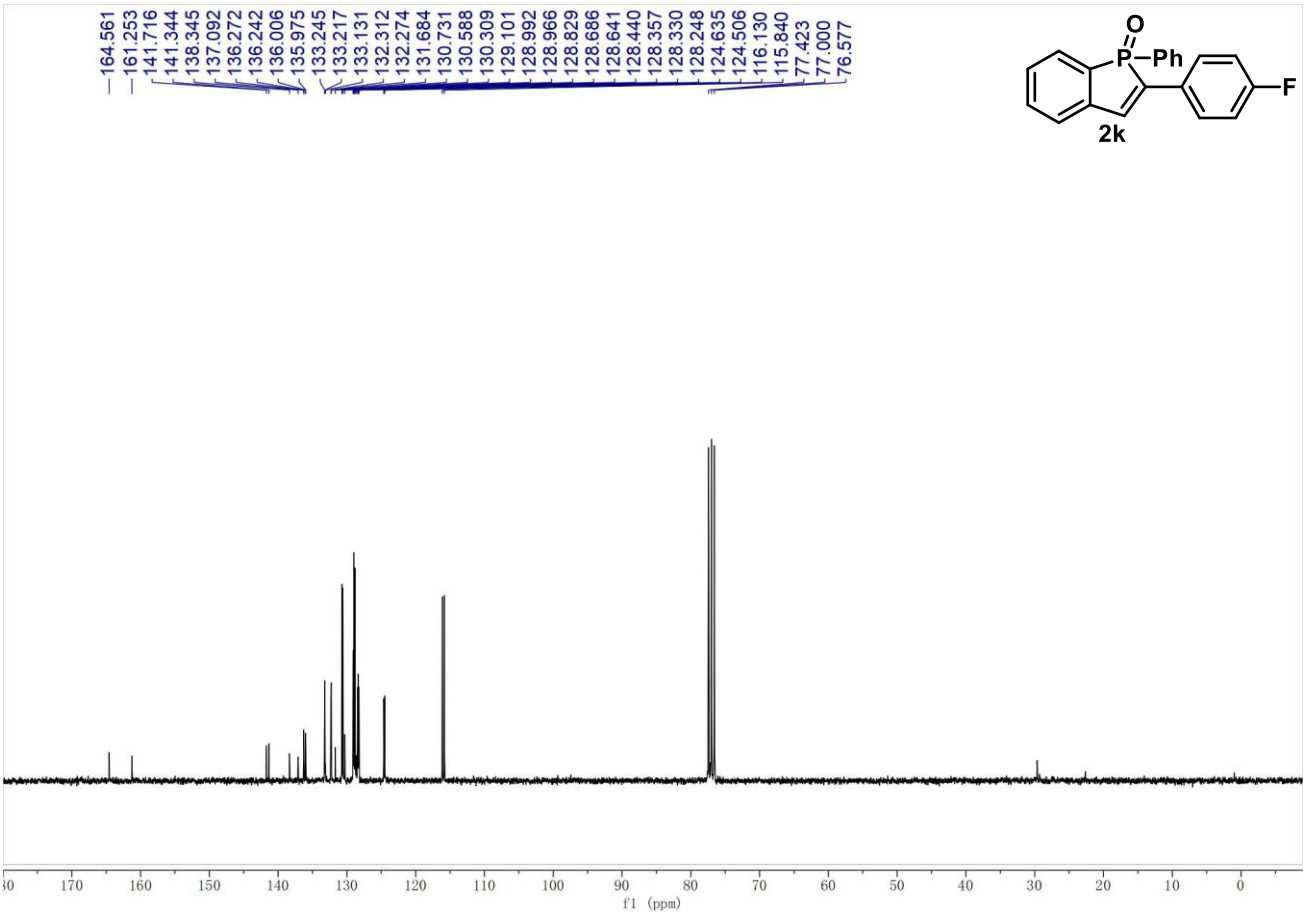

**$^{19}F$ NMR spectrum of 2j (282 MHz, $CDCl_3$)**

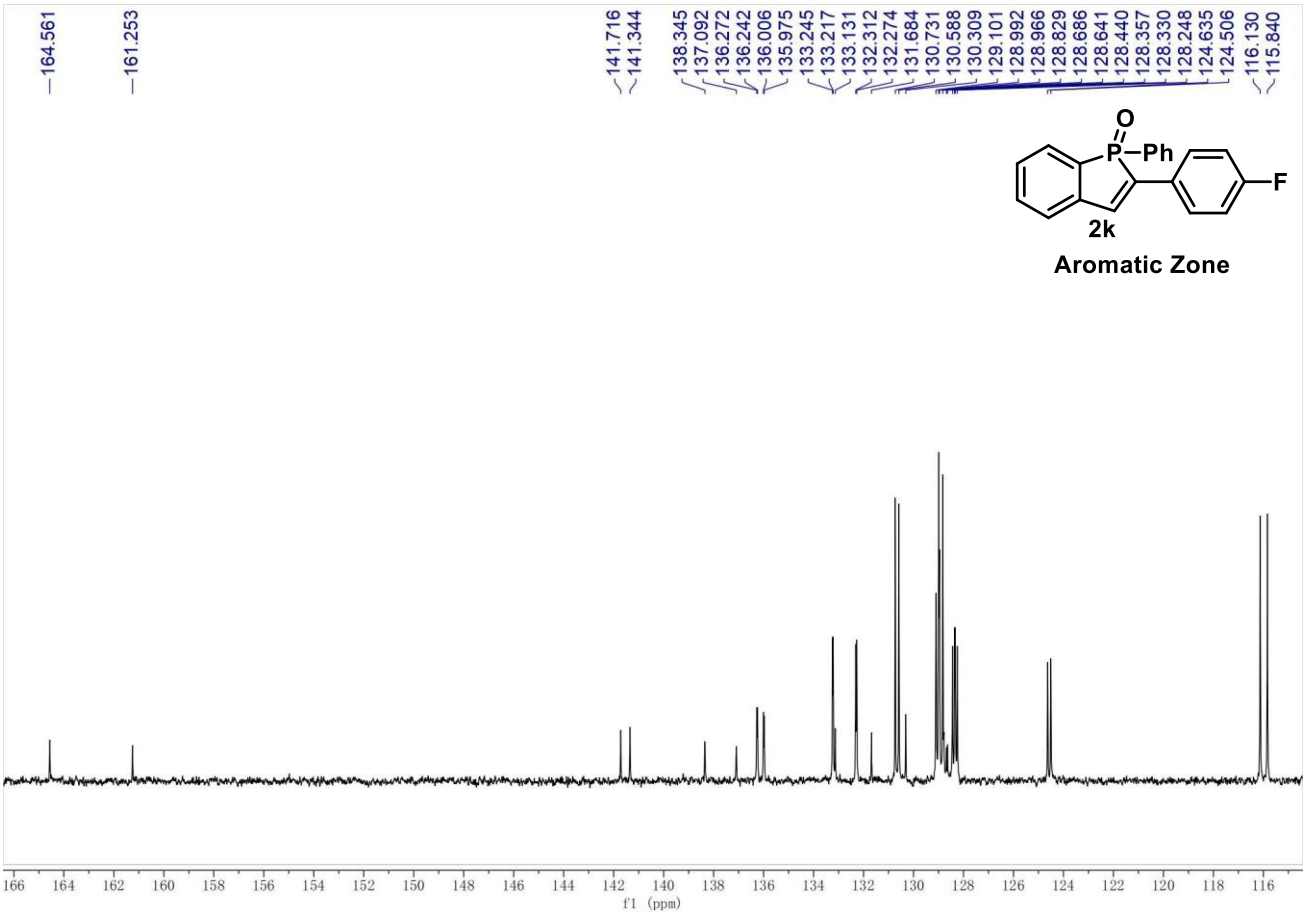


**$^{1}$H NMR spectrum of 2k (300 MHz, $CDCl_3$)**

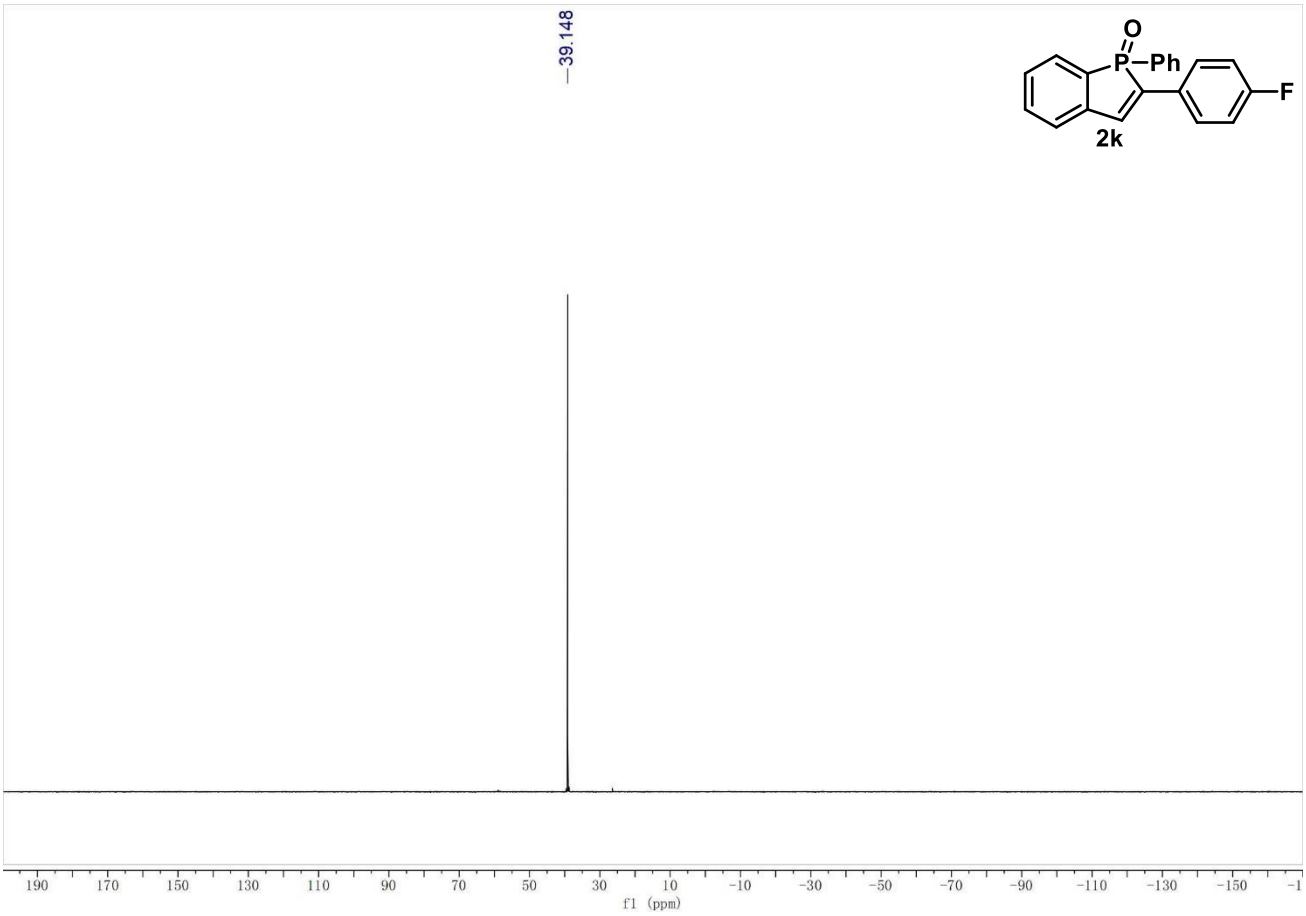



**$^{13}$C NMR spectrum of 2k (75 MHz, $CDCl_3$)**

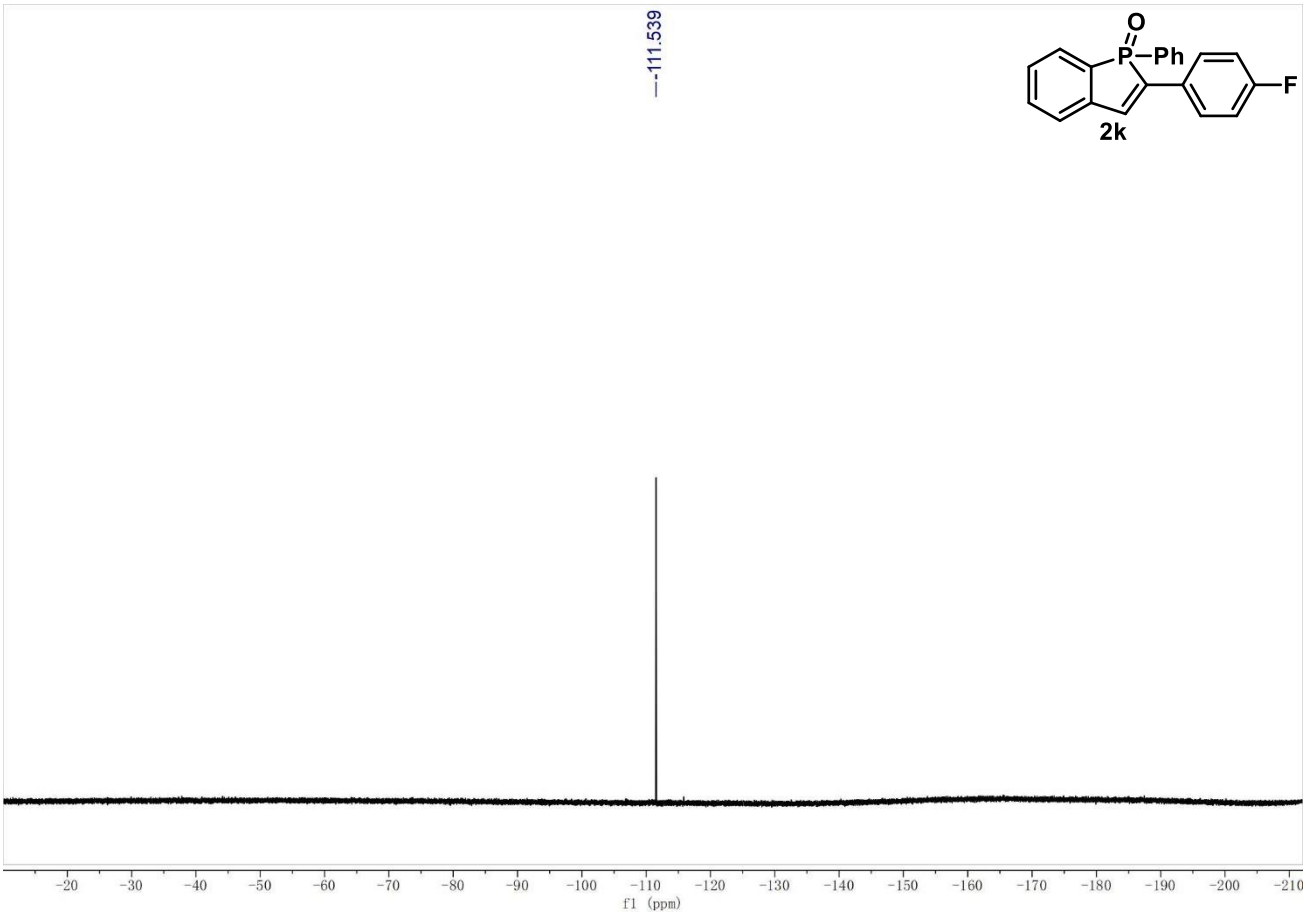




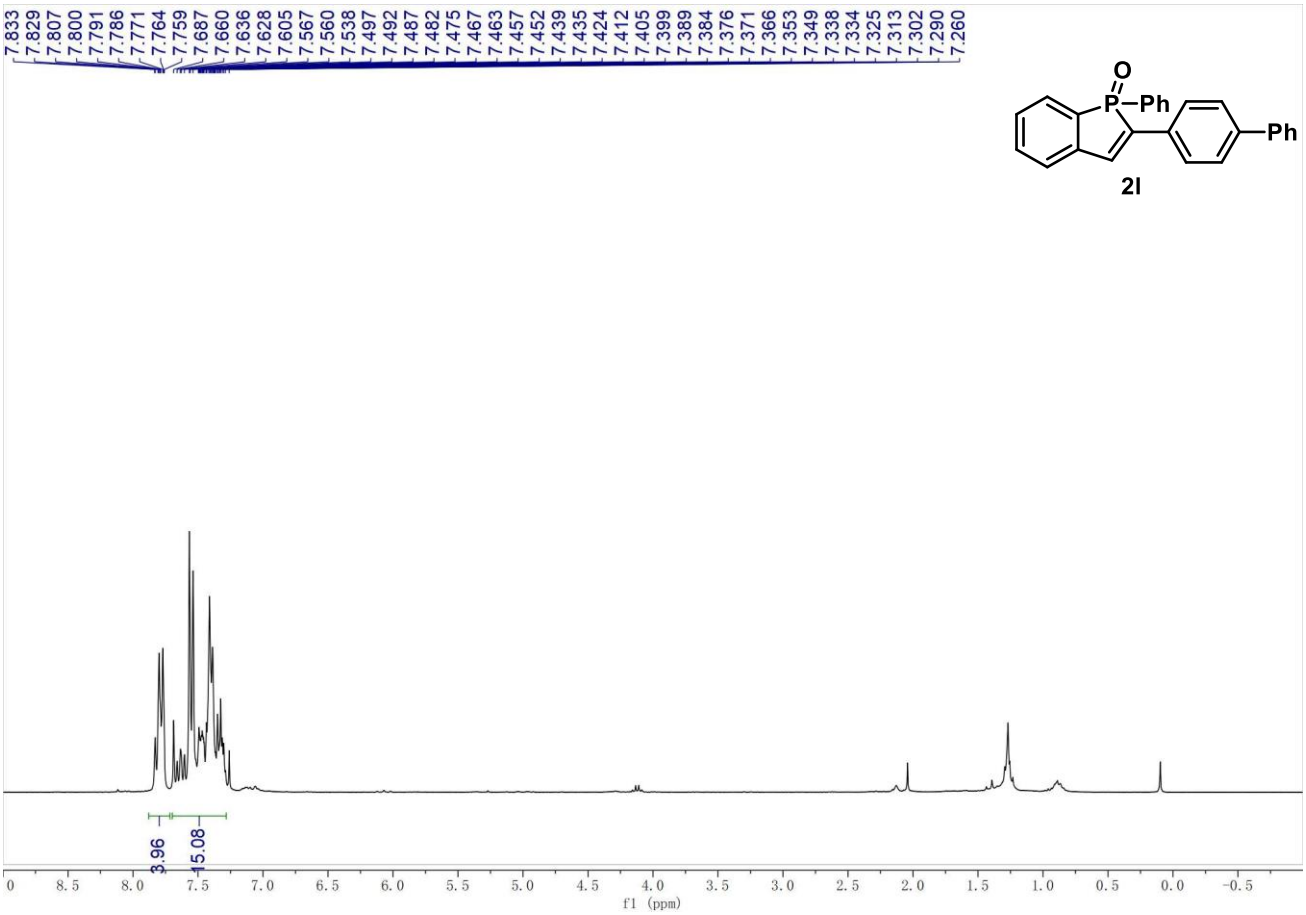

**$^{31}P\{^{1}H\}$ NMR spectrum of 2k (121 MHz, $CDCl_3$)**



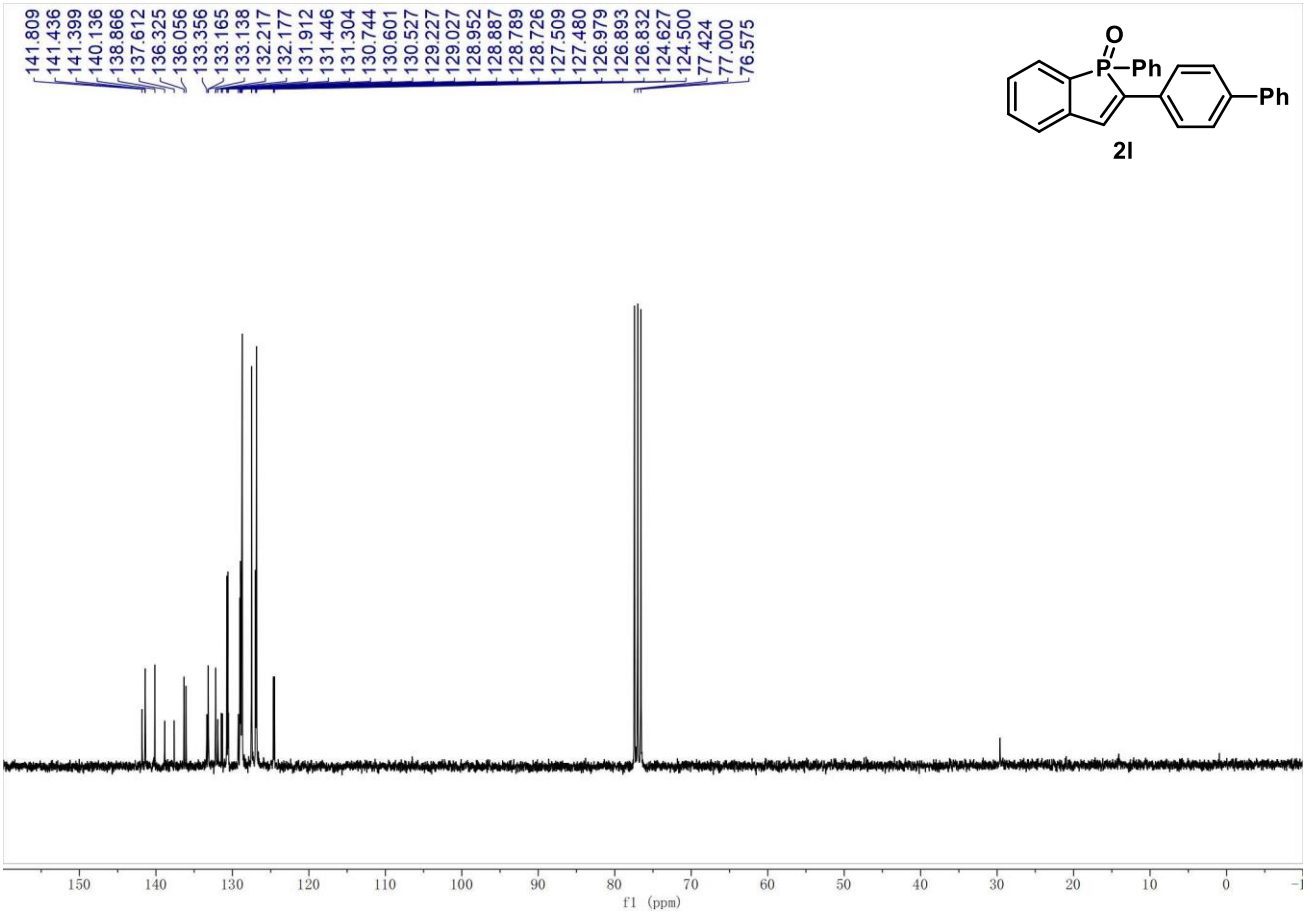
**$^{19}$F NMR spectrum of 2k (282 MHz, $CDCl_3$)**

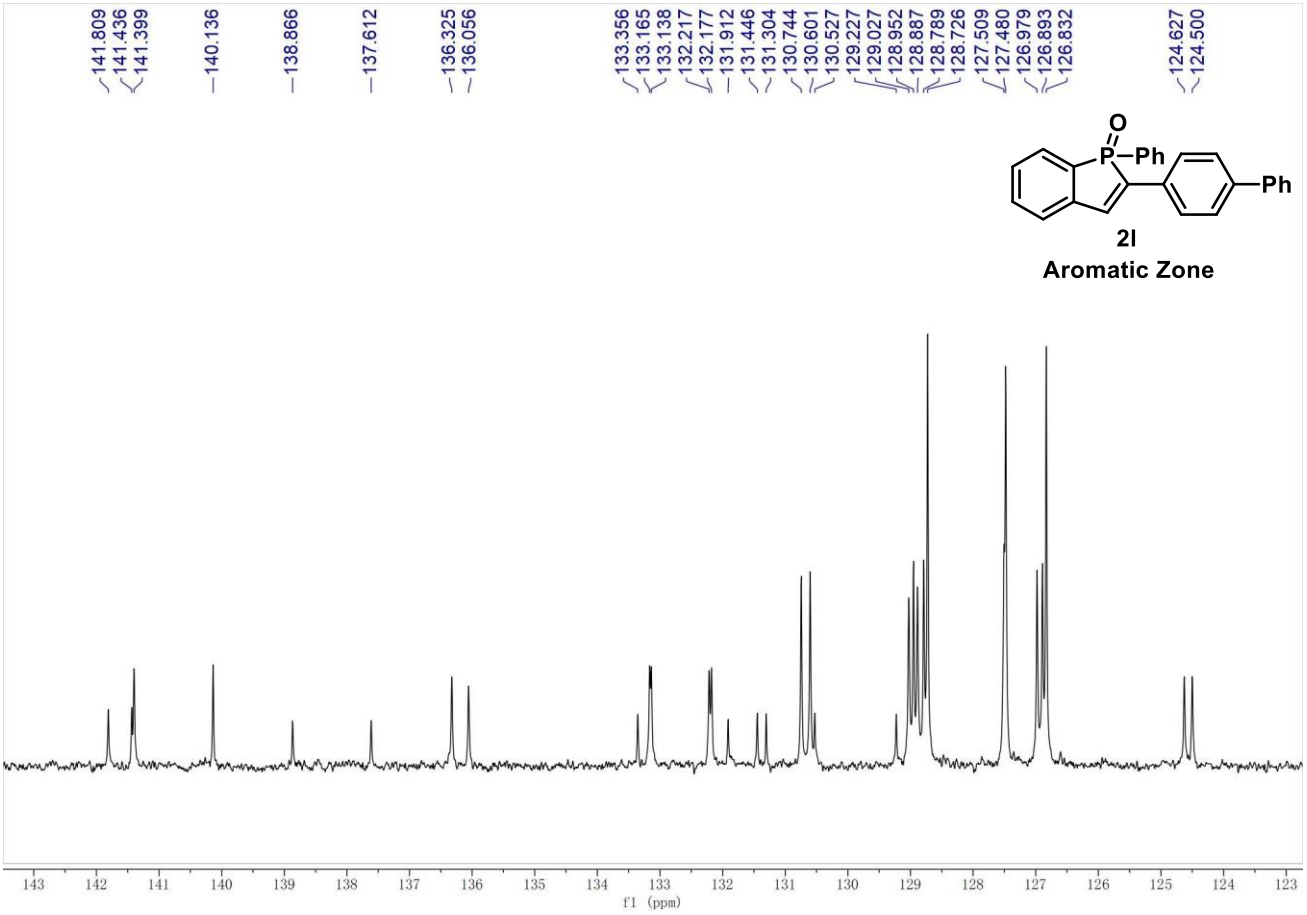



**$^{1}$H NMR spectrum of 2l (300 MHz, $CDCl_3$)**

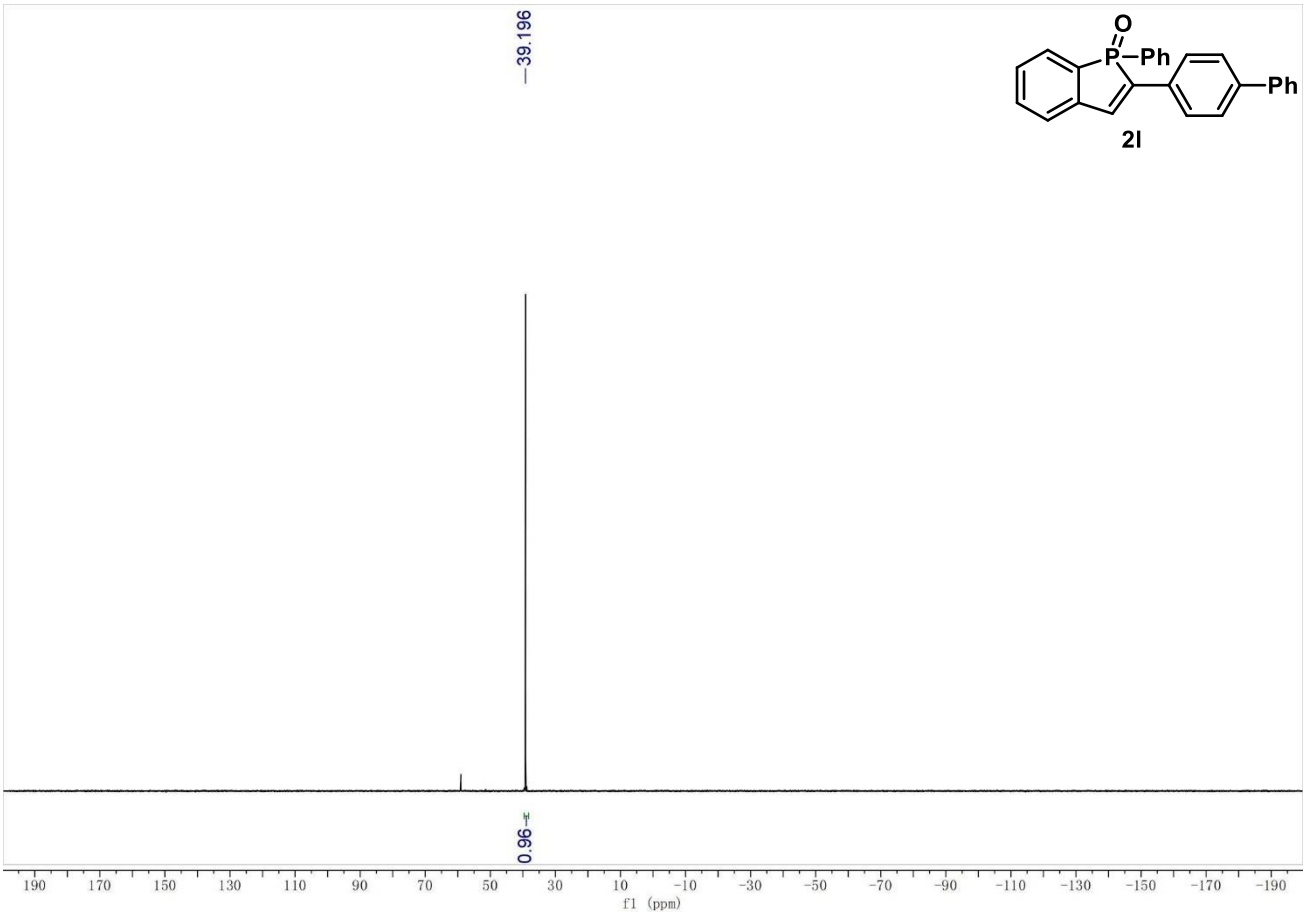


**$^{13}C$ NMR spectrum of 2l (75 MHz, $CDCl_3$)**

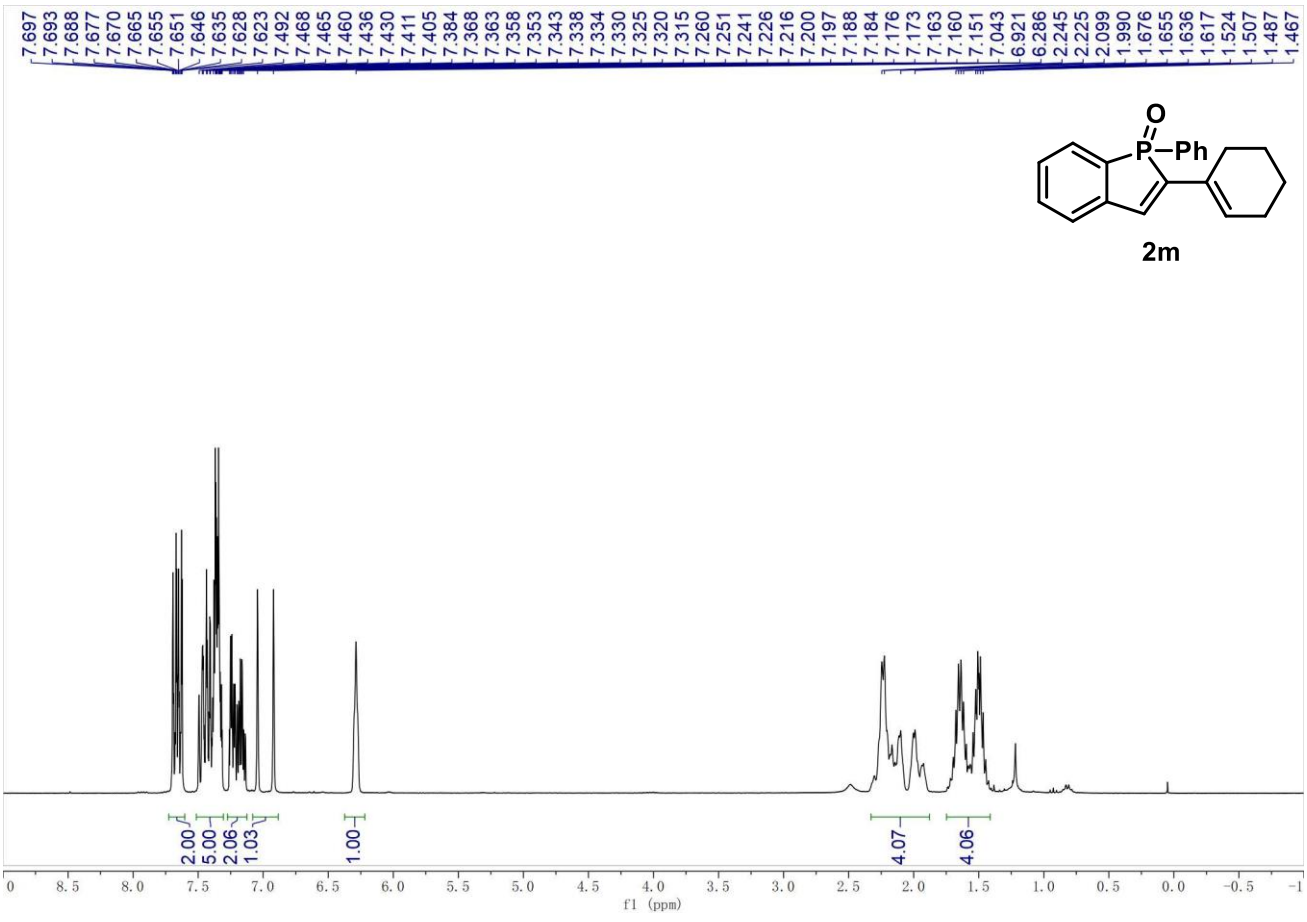


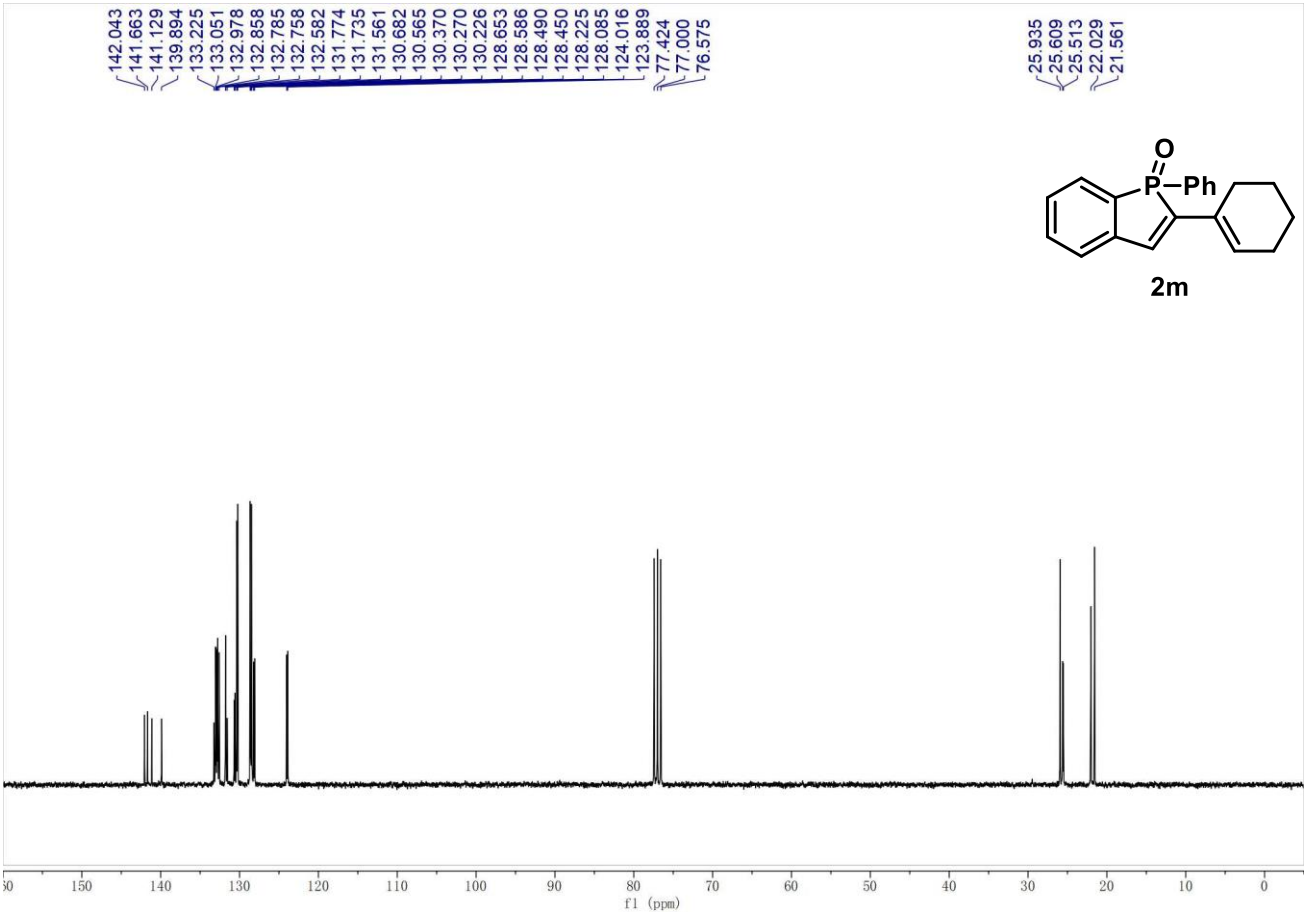
**$^{31}P\{^{1}H\}$ NMR spectrum of 2l (121 MHz, $CDCl_3$)**

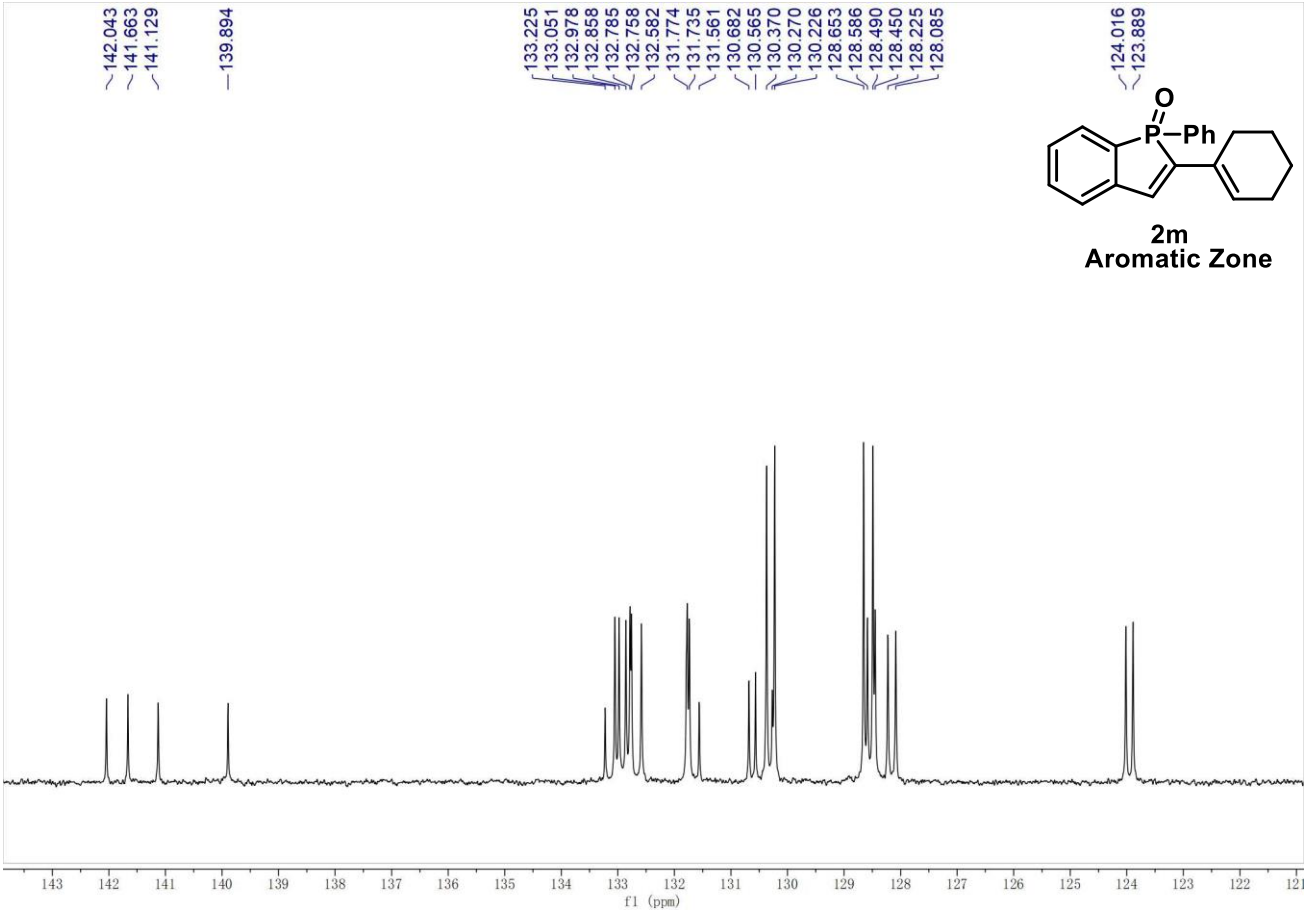



**$^{1}H$ NMR spectrum of 2m (300 MHz, $CDCl_3$)**

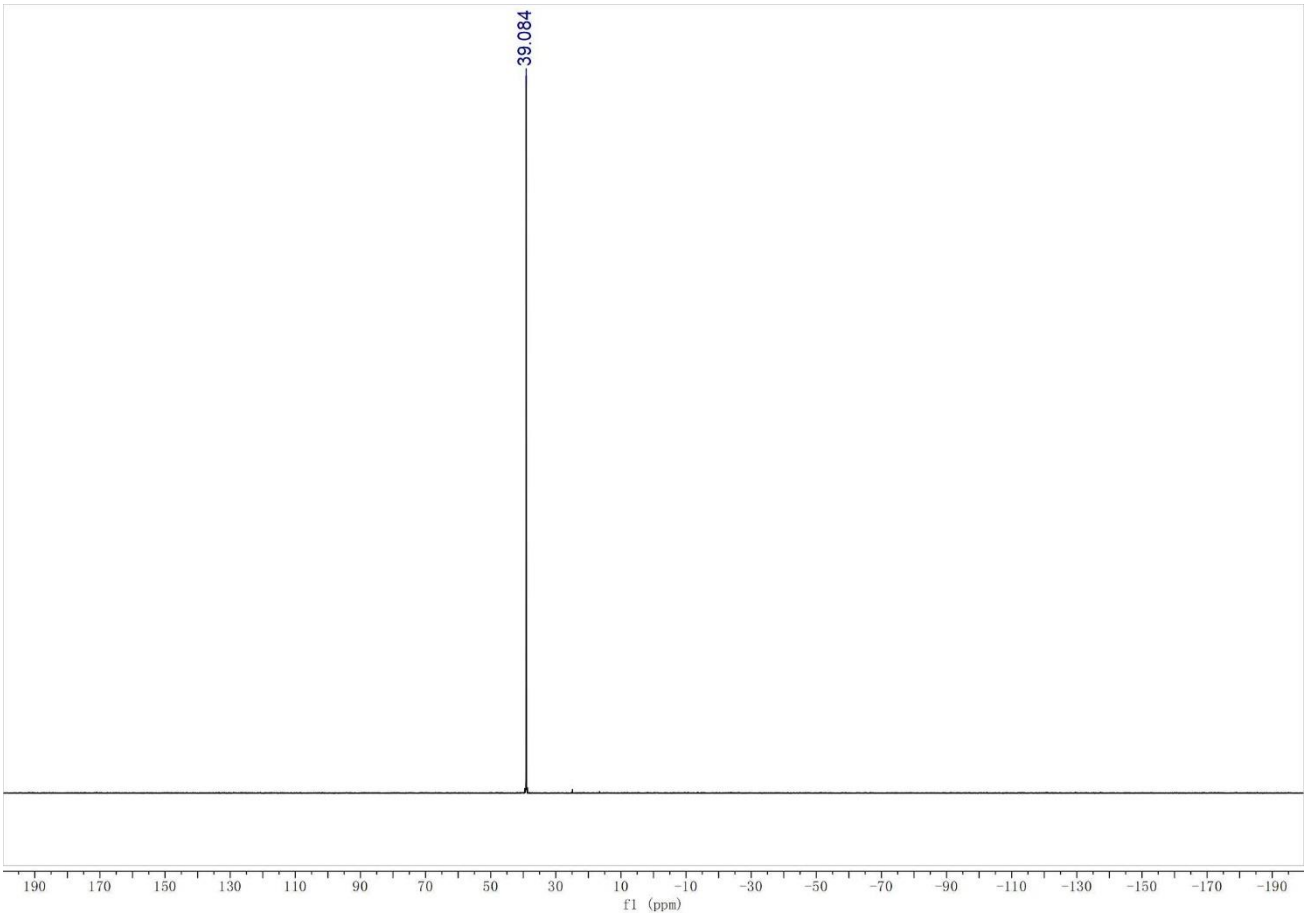


**$^{13}$C NMR spectrum of 2m (75 MHz, $CDCl_3$)**

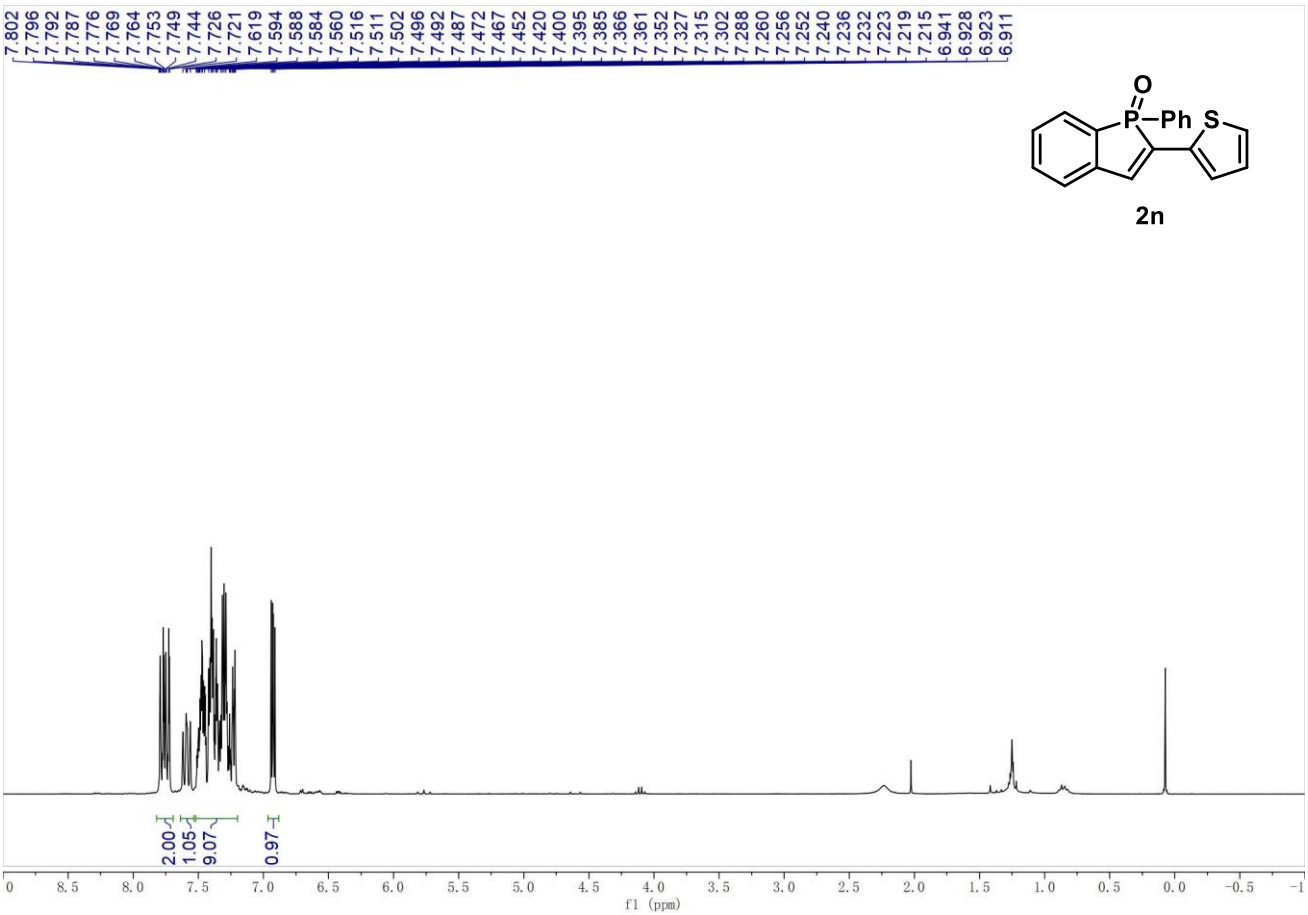


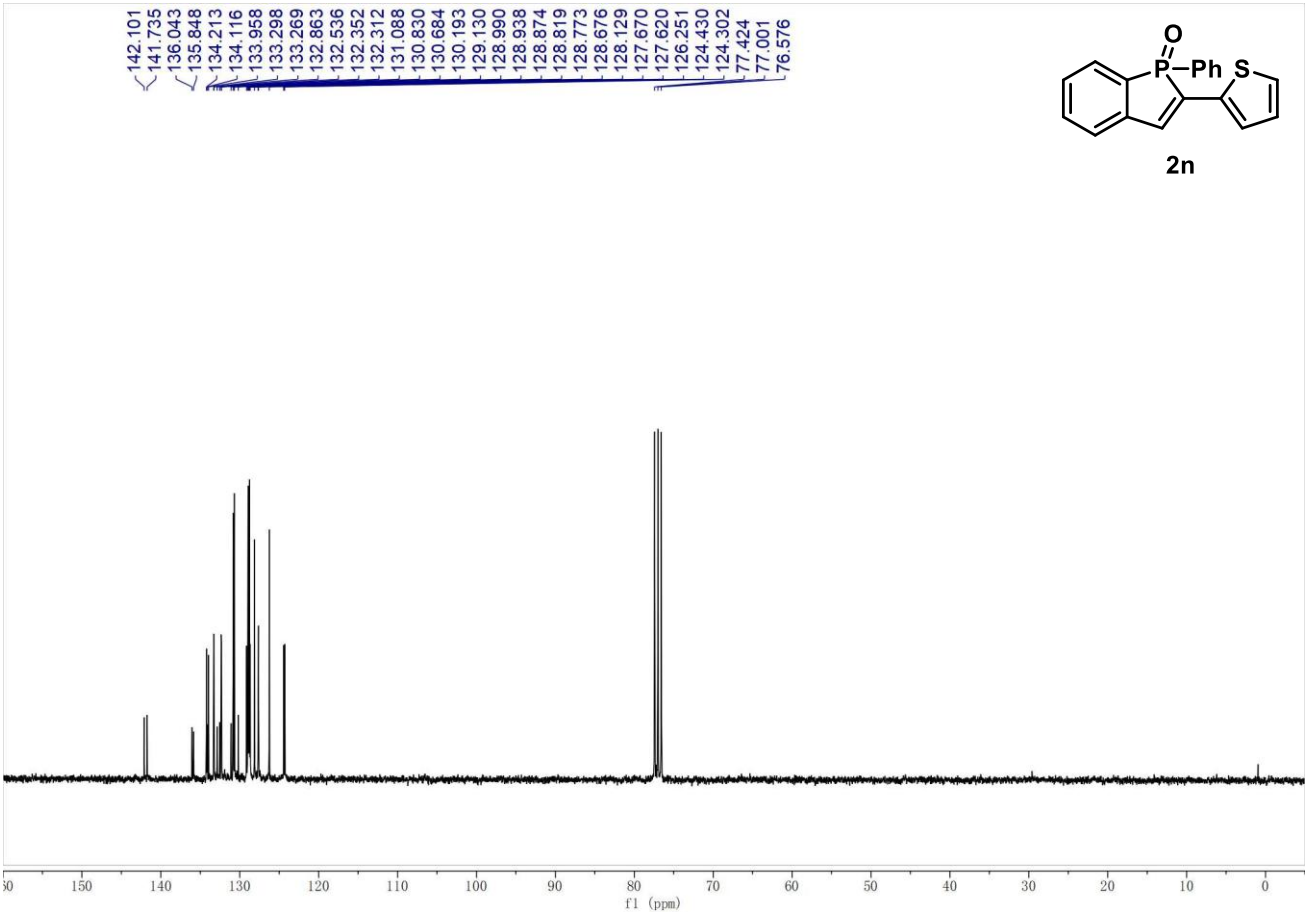
**$^{31}P\{^{1}H\}$ NMR spectrum of 2m (121 MHz, $CDCl_3$)**

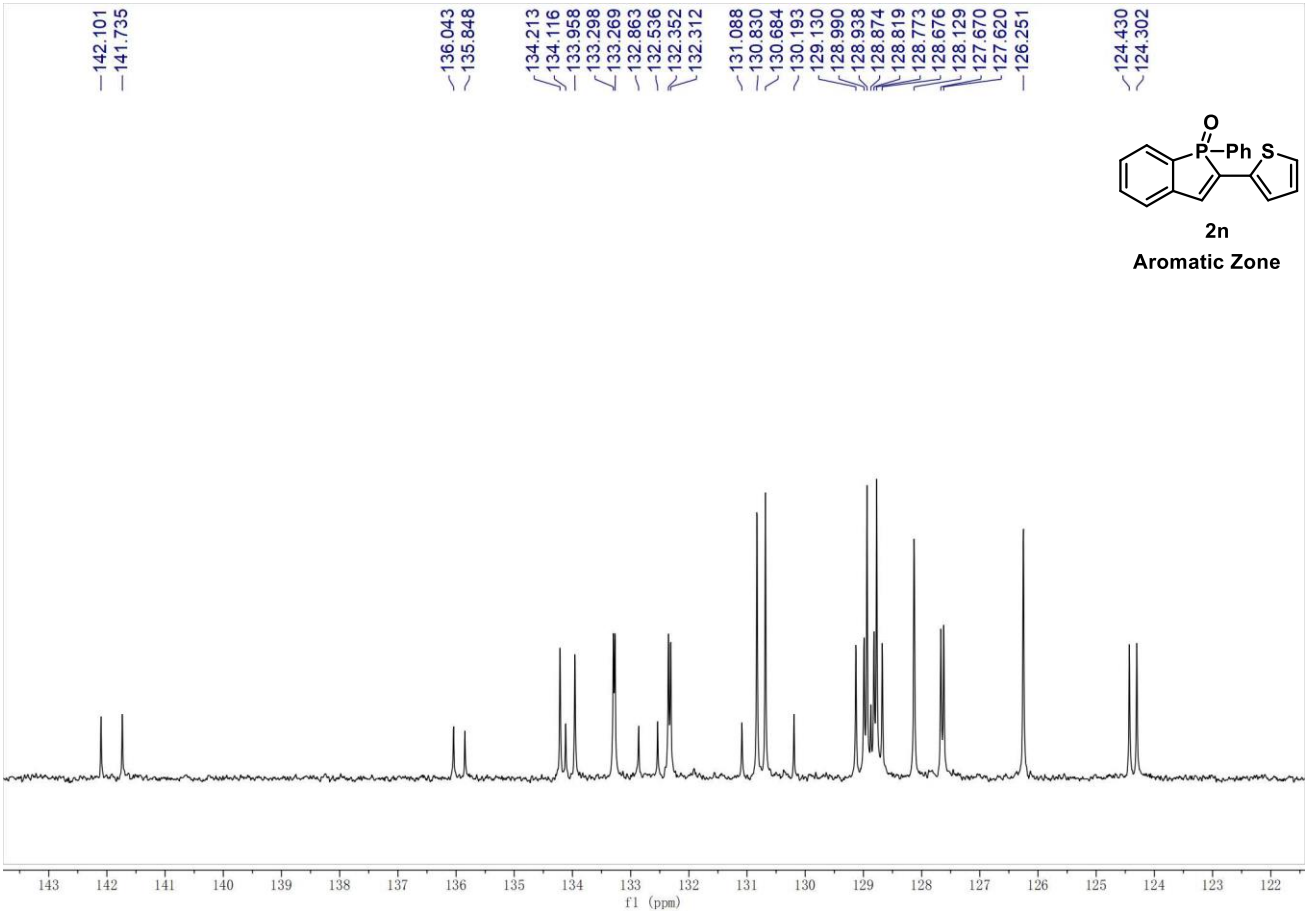



**$^{1}H$ NMR spectrum of 2n (300 MHz, $CDCl_3$)**

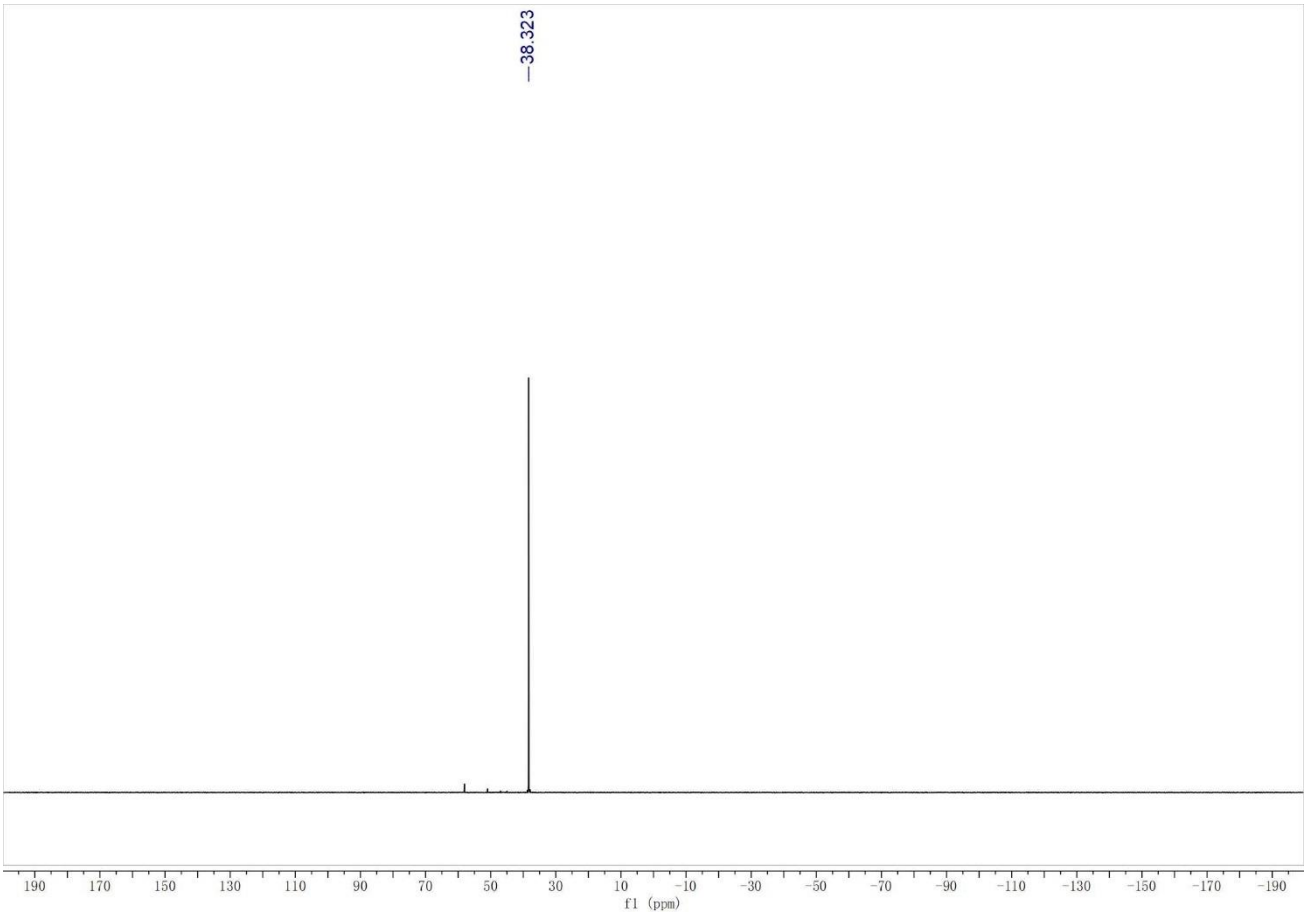


**$^{13}$C NMR spectrum of 2n (75 MHz, $CDCl_3$)**

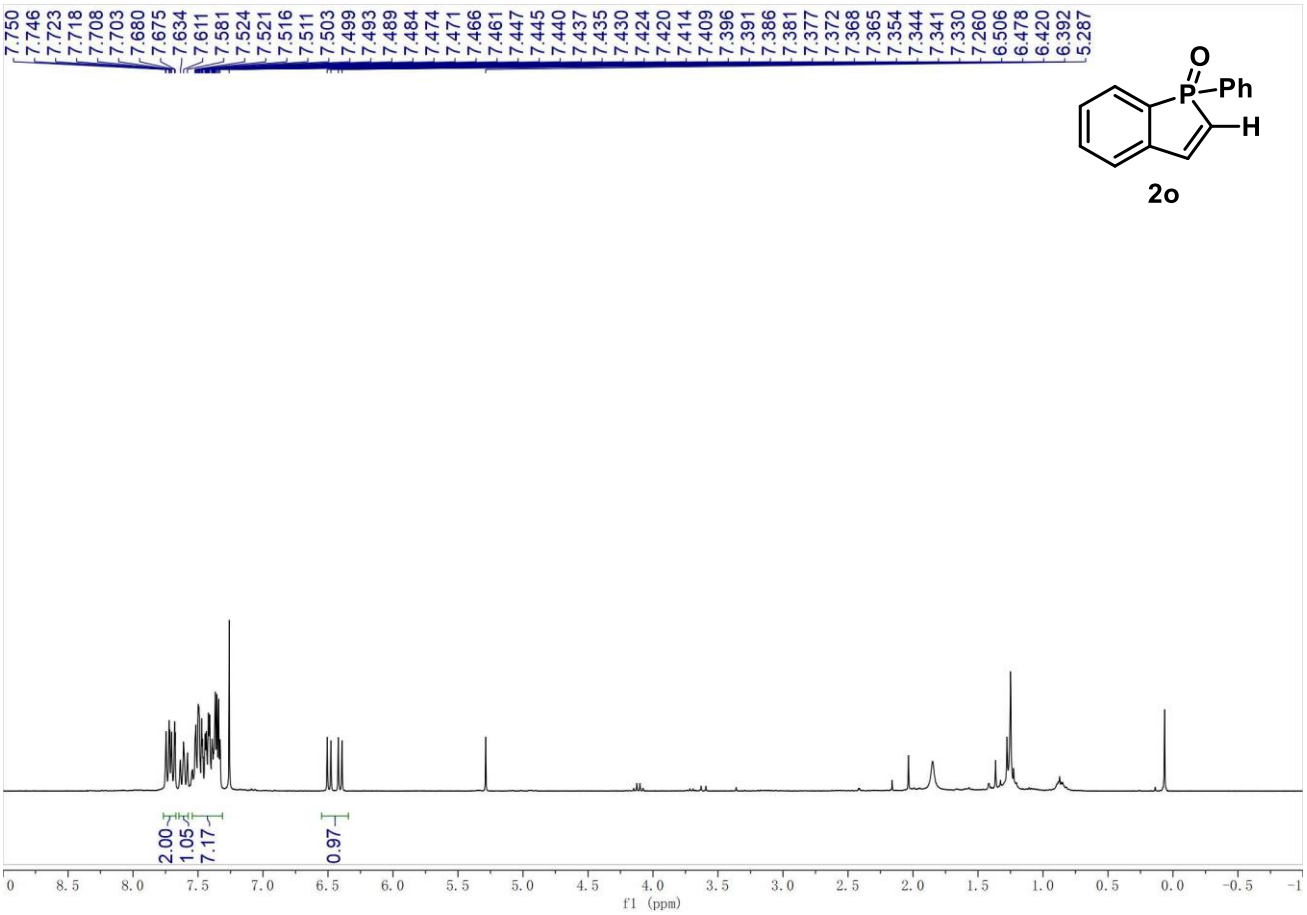


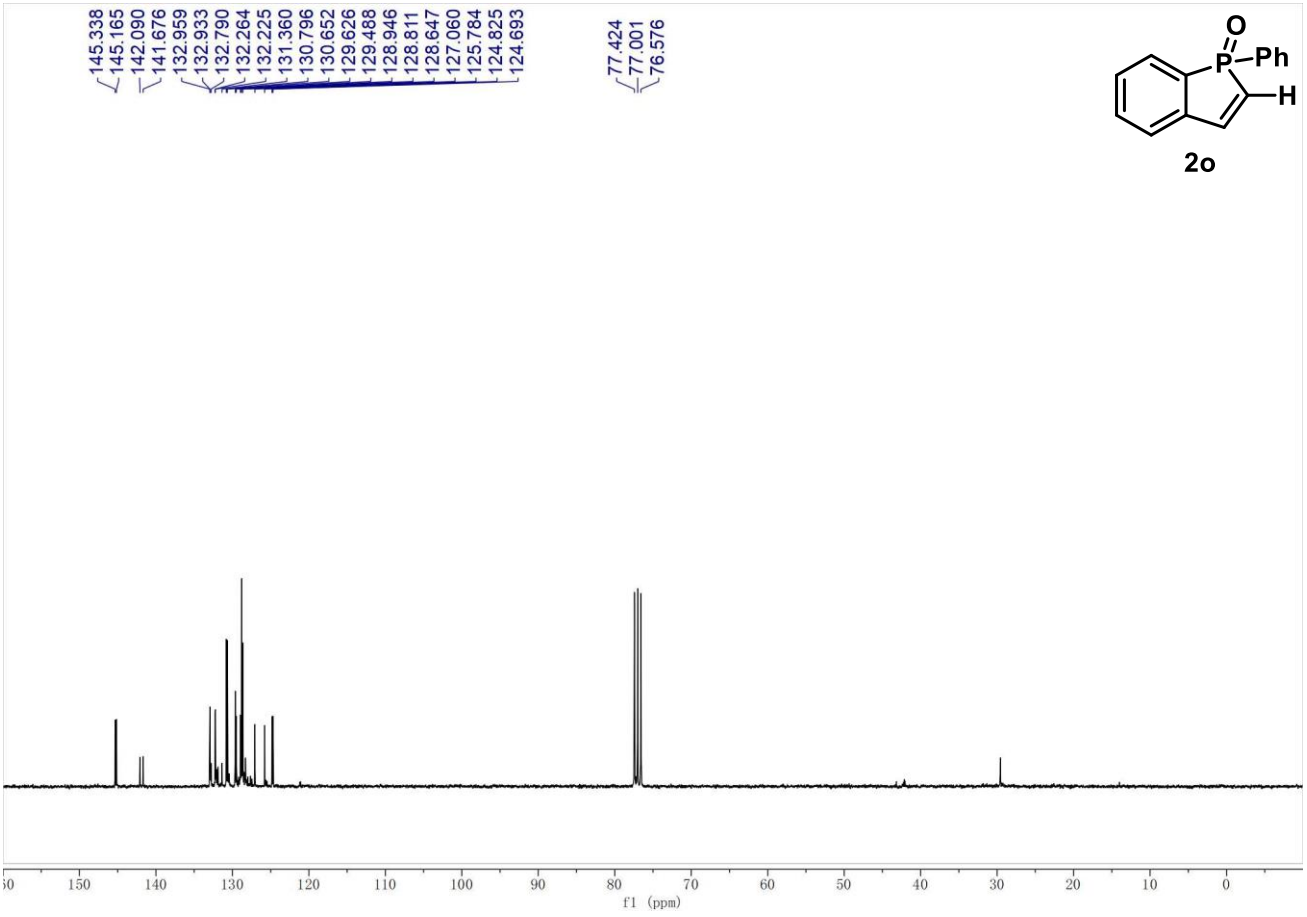
**$^{31}P\{^{1}H\}$ NMR spectrum of 2n (121 MHz, $CDCl_3$)**

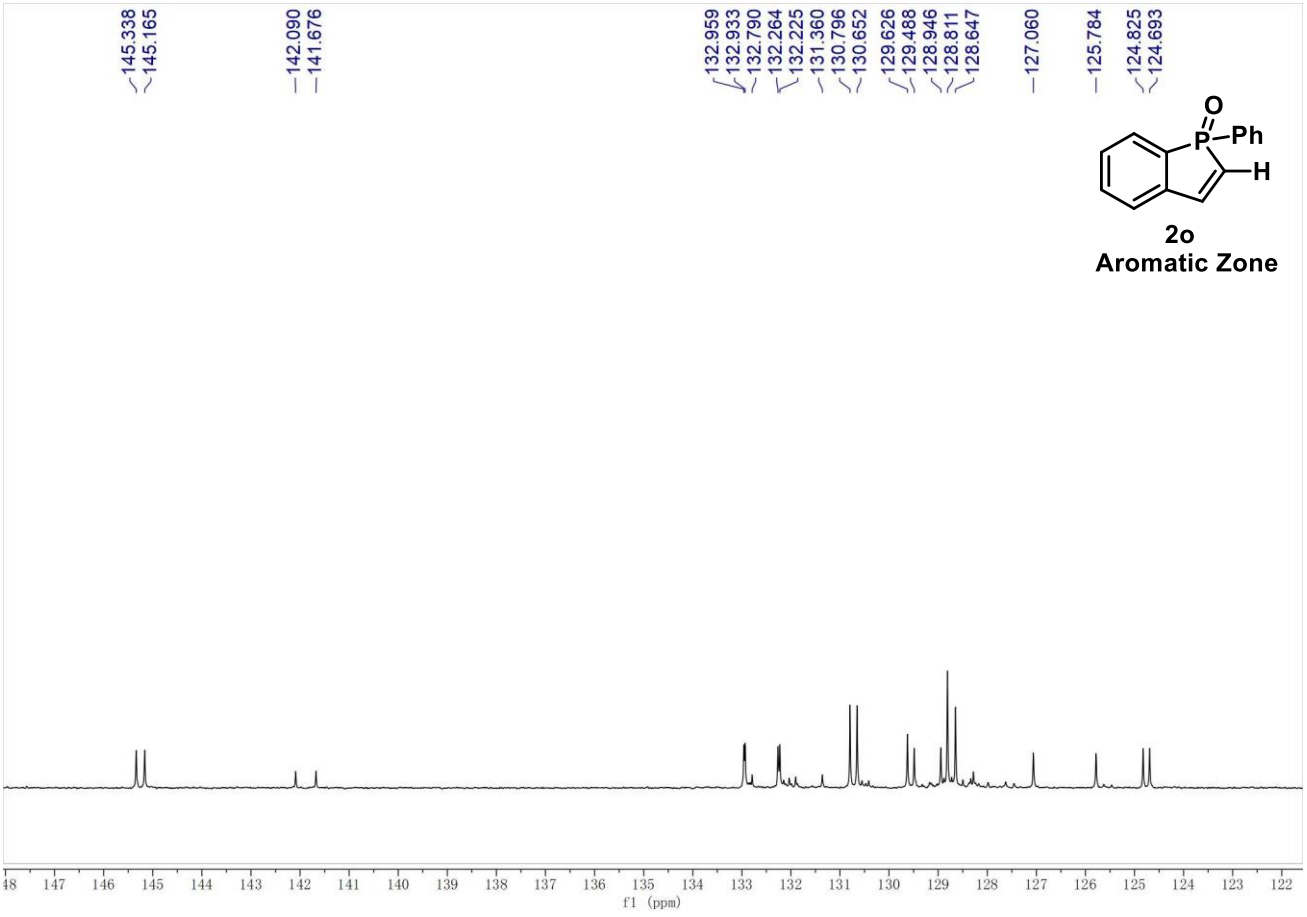



**$^{1}H$ NMR spectrum of 2o (300 MHz, $CDCl_3$)**

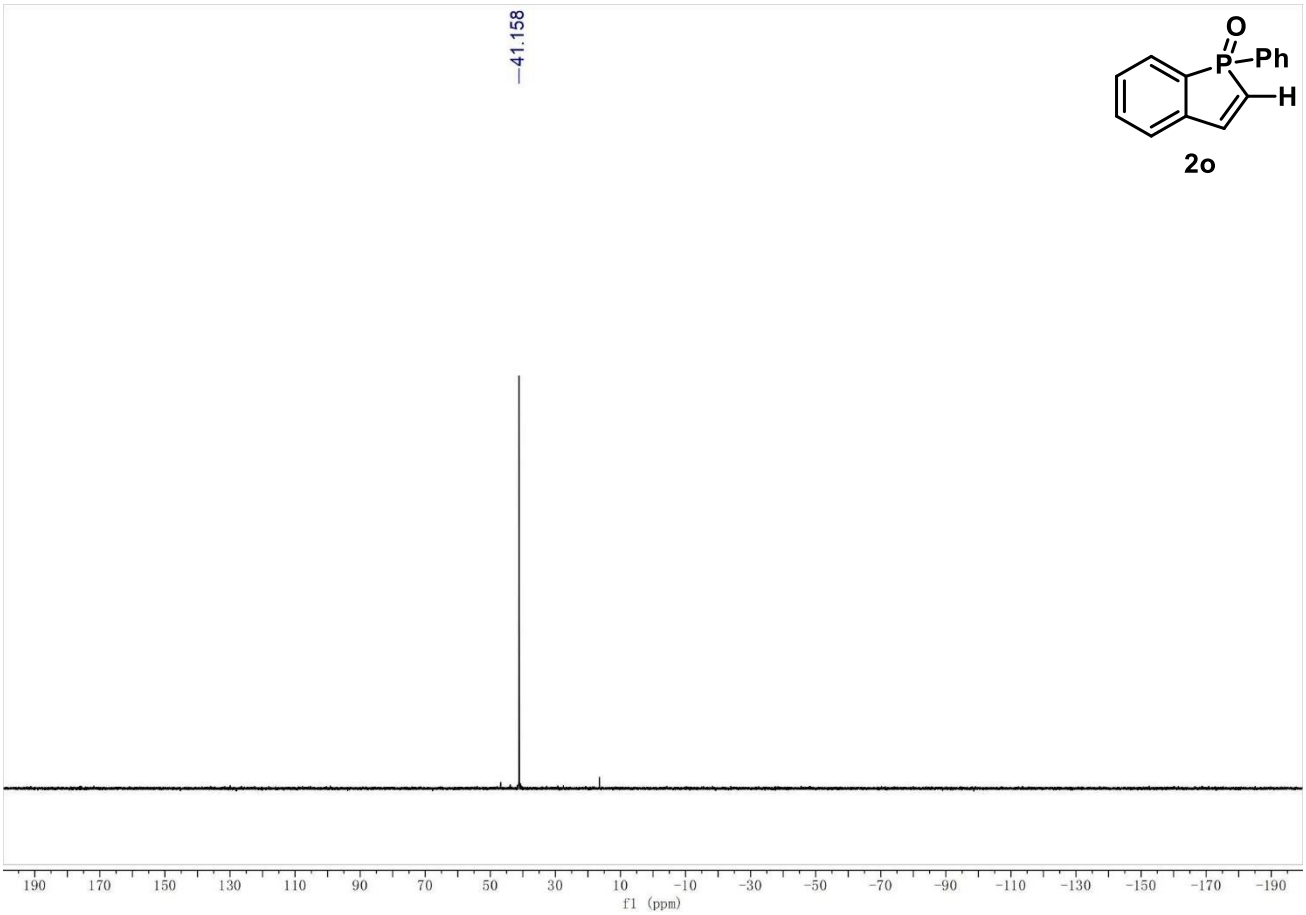


**$^{13}$C NMR spectrum of 2o (75 MHz, $CDCl_3$)**

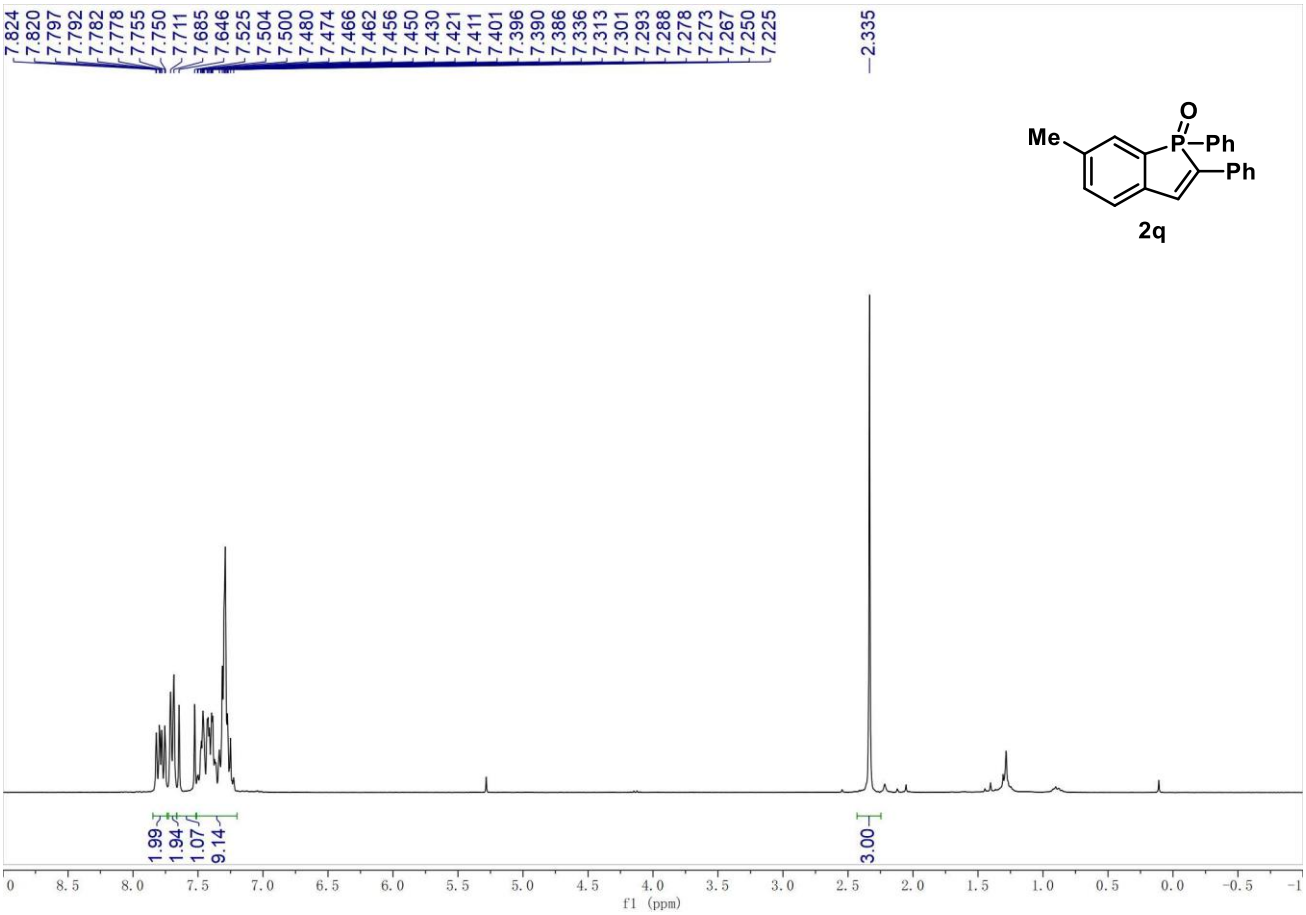


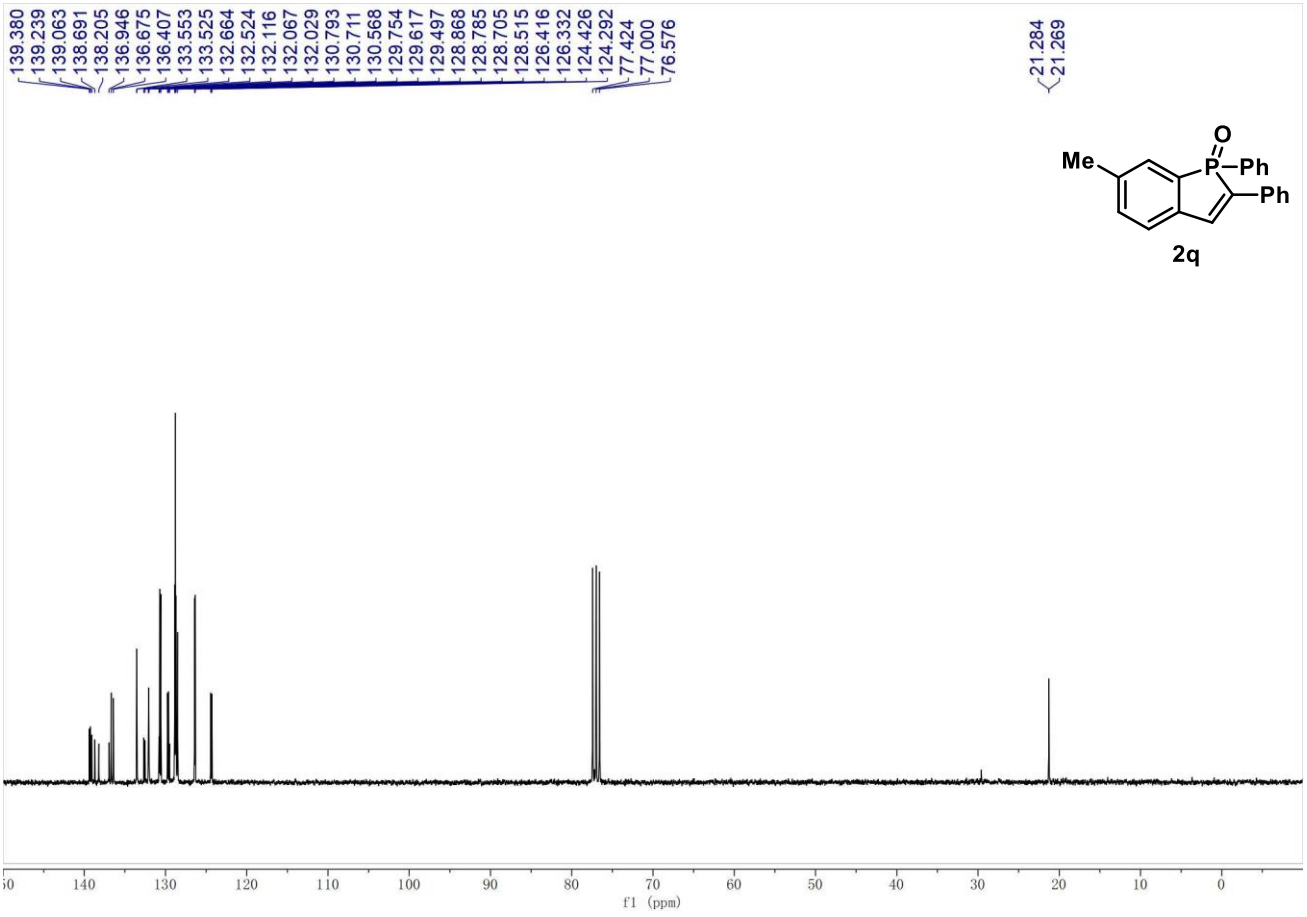
**$^{31}P\{^{1}H\}$ NMR spectrum of 2o (121 MHz, $CDCl_3$)**

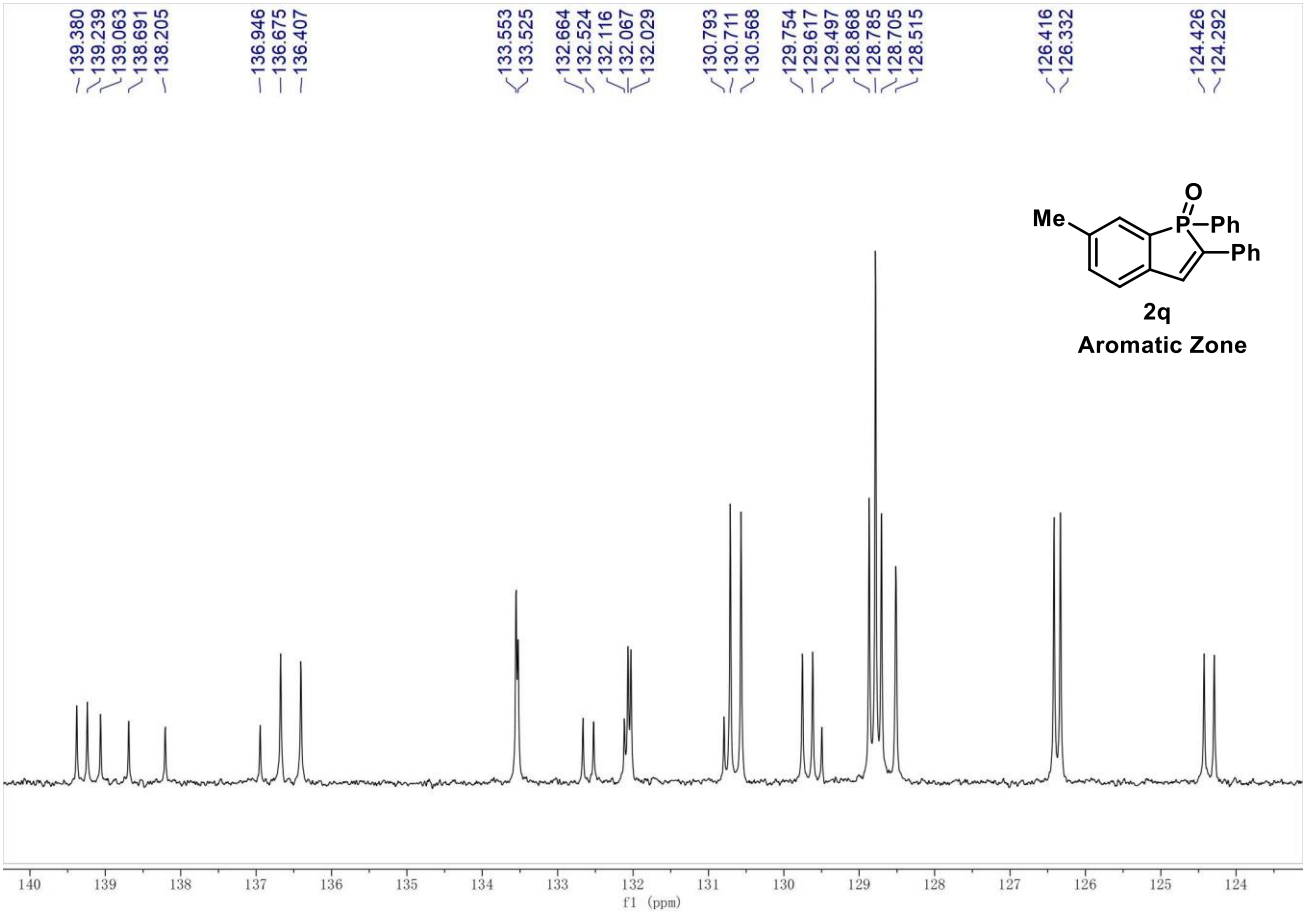



**$^{1}H$ NMR spectrum of 2q (300 MHz, $CDCl_3$)**

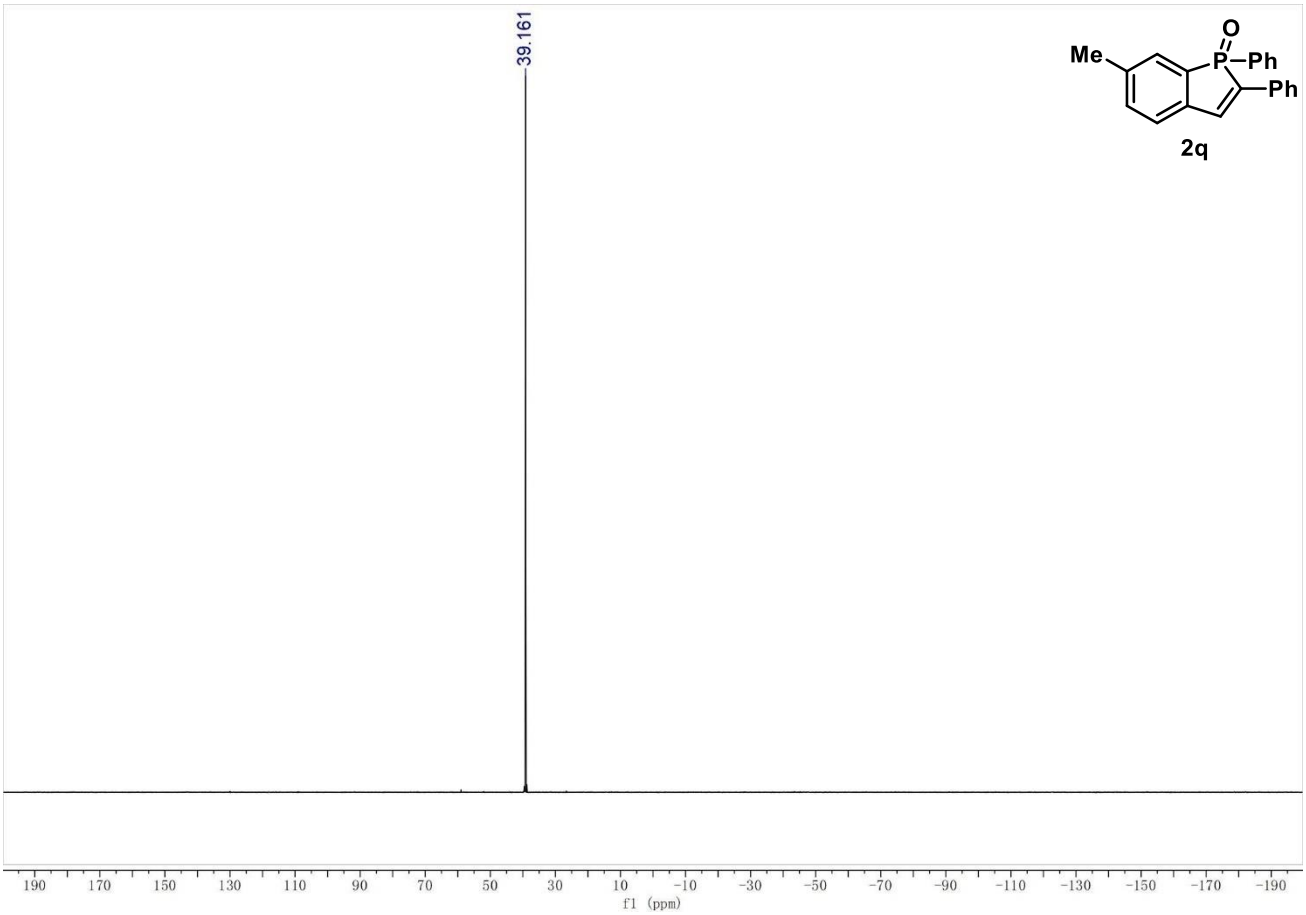


**$^{13}$C NMR spectrum of 2q (75 MHz, $CDCl_3$)**

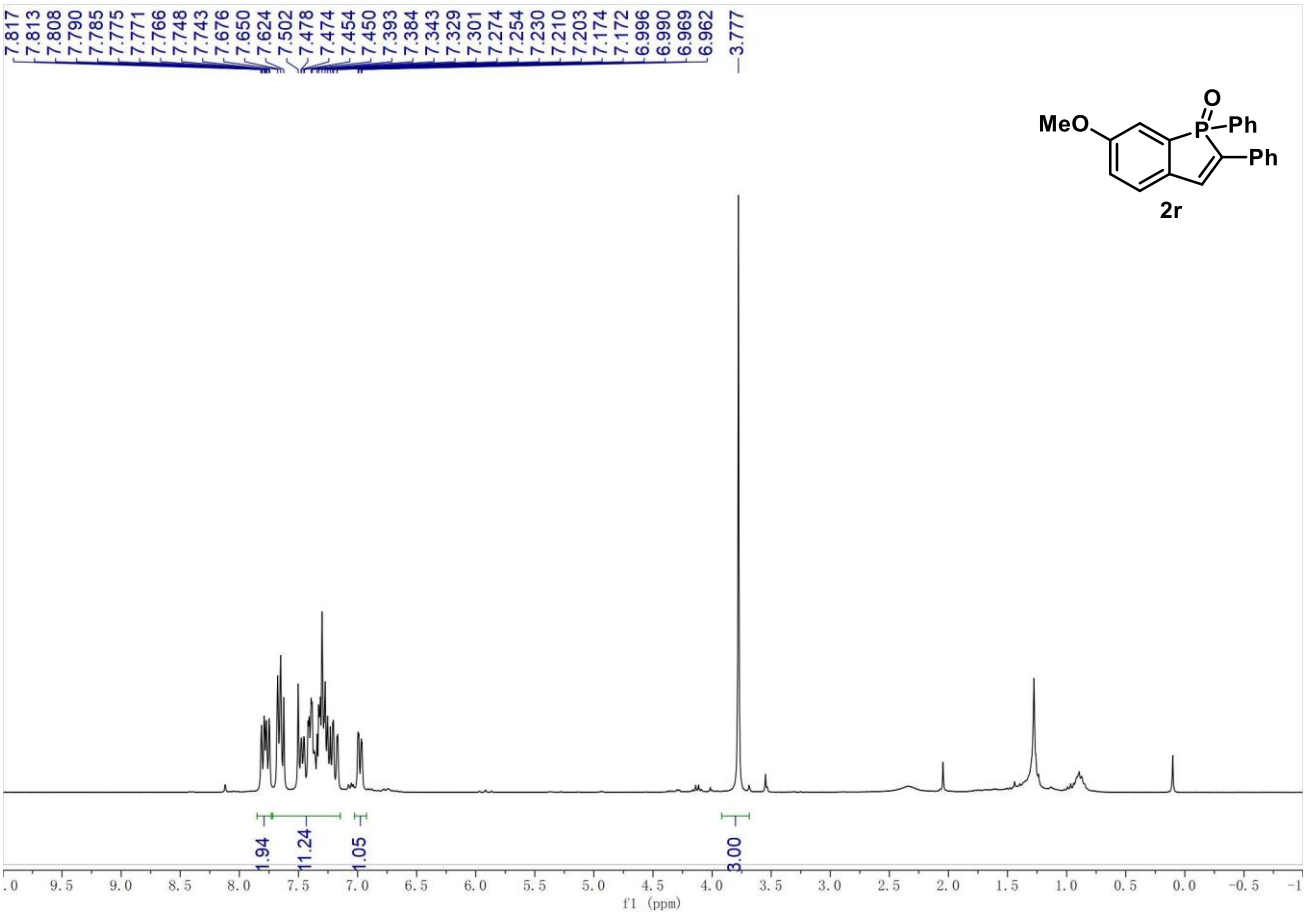


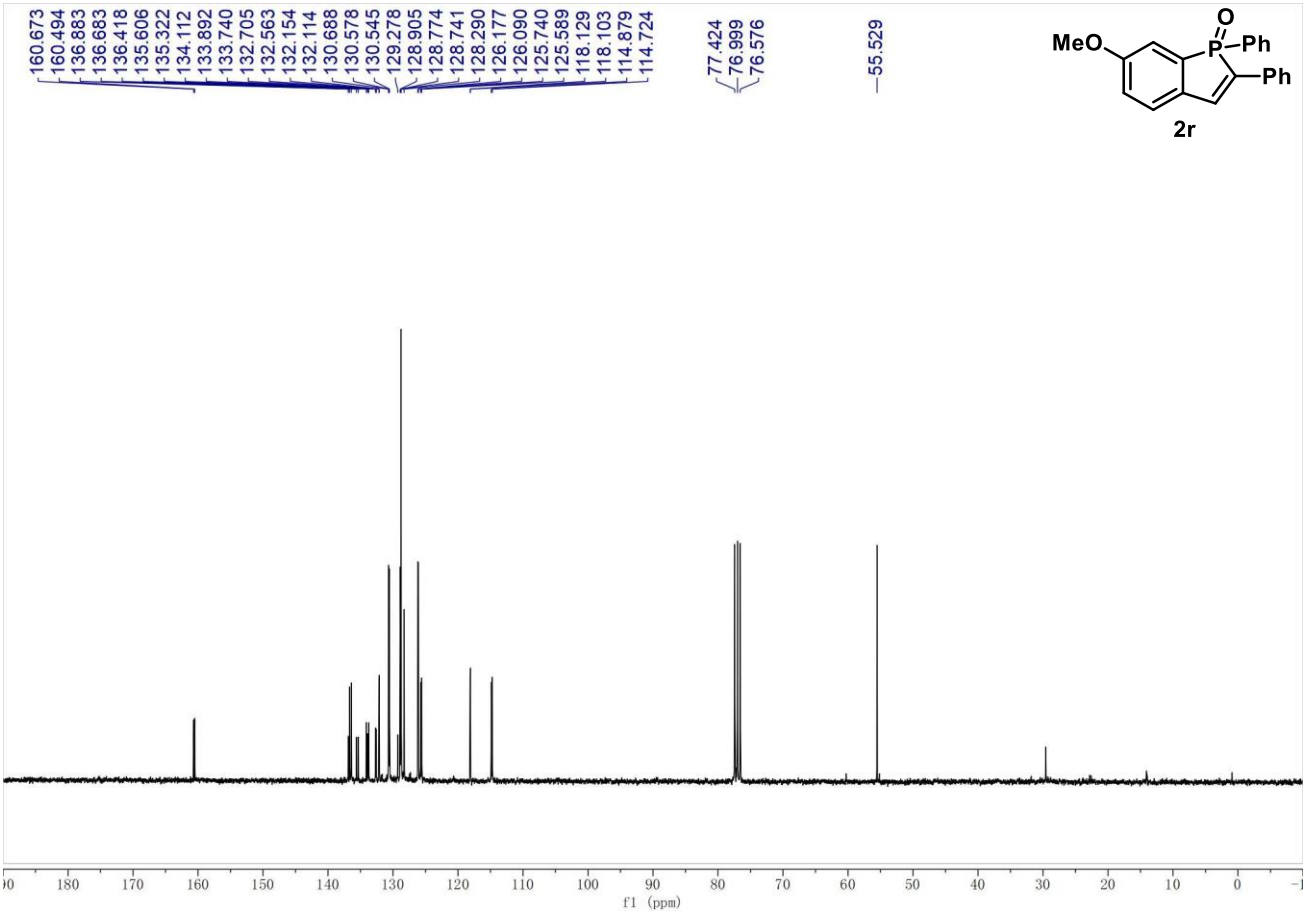
**$^{31}P\{^{1}H\}$ NMR spectrum of 2q (121 MHz, $CDCl_3$)**

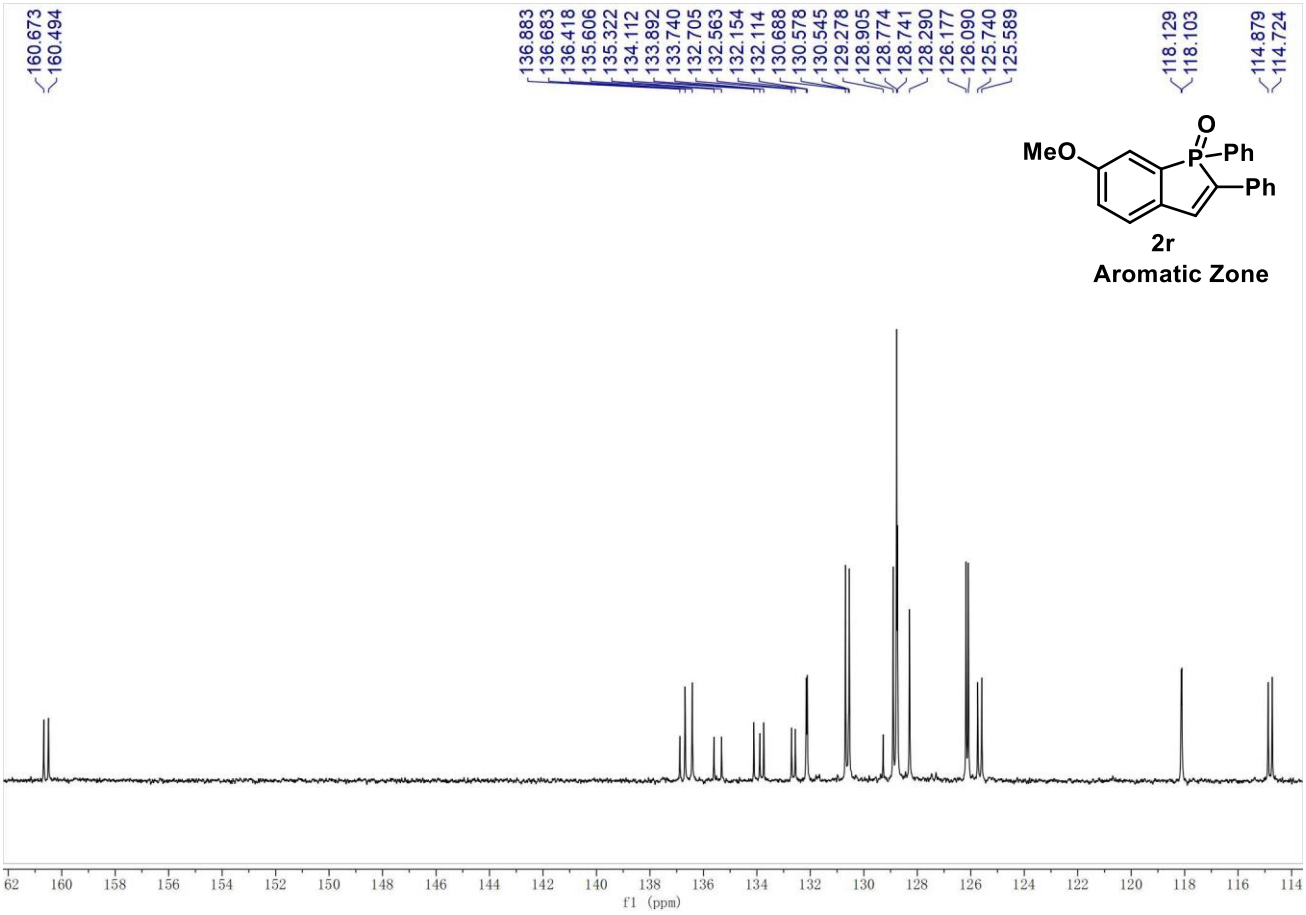



**$^{1}H$ NMR spectrum of 2r (300 MHz, $CDCl_3$)**

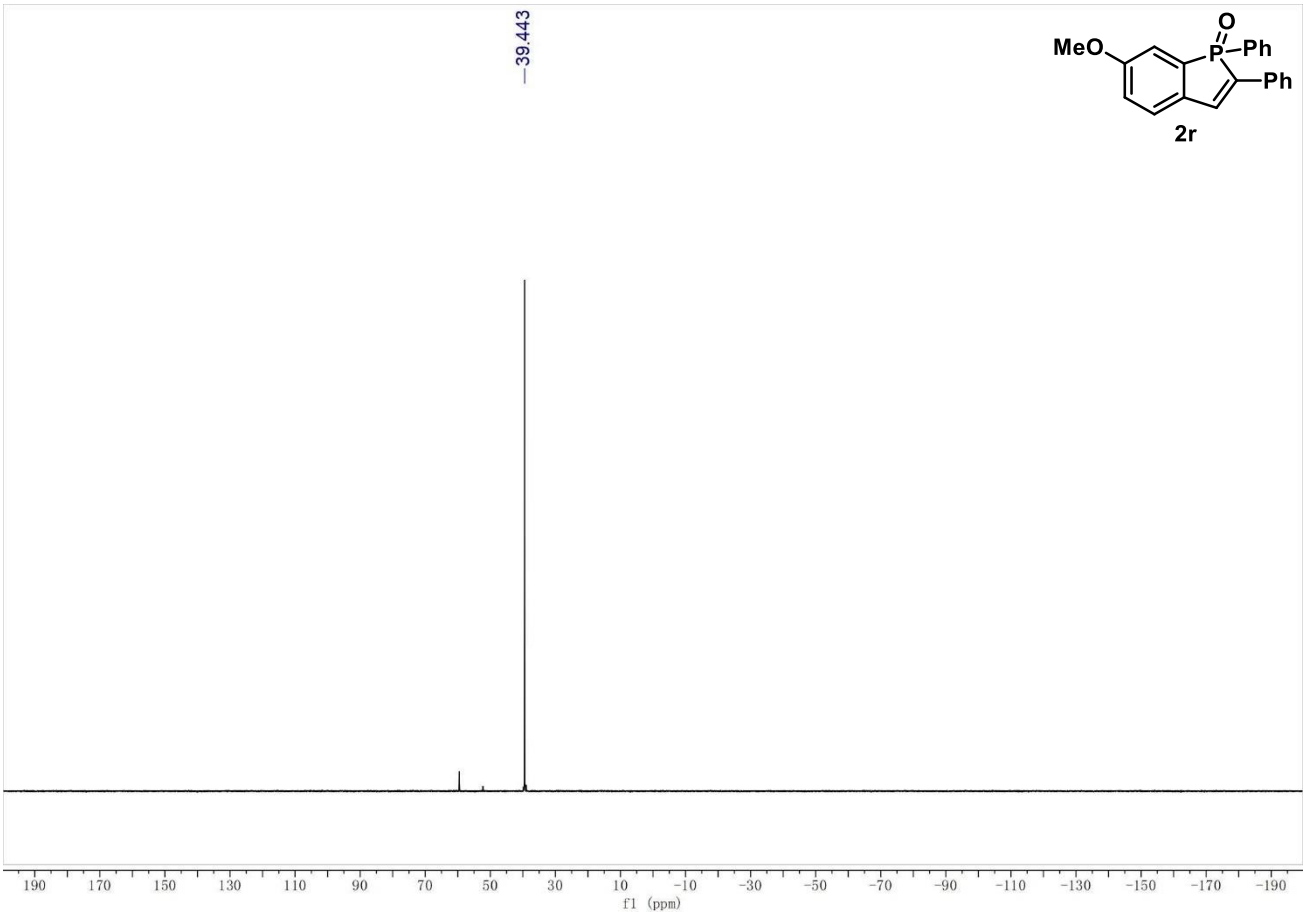


**$^{13}$C NMR spectrum of 2r (75 MHz, $CDCl_3$)**

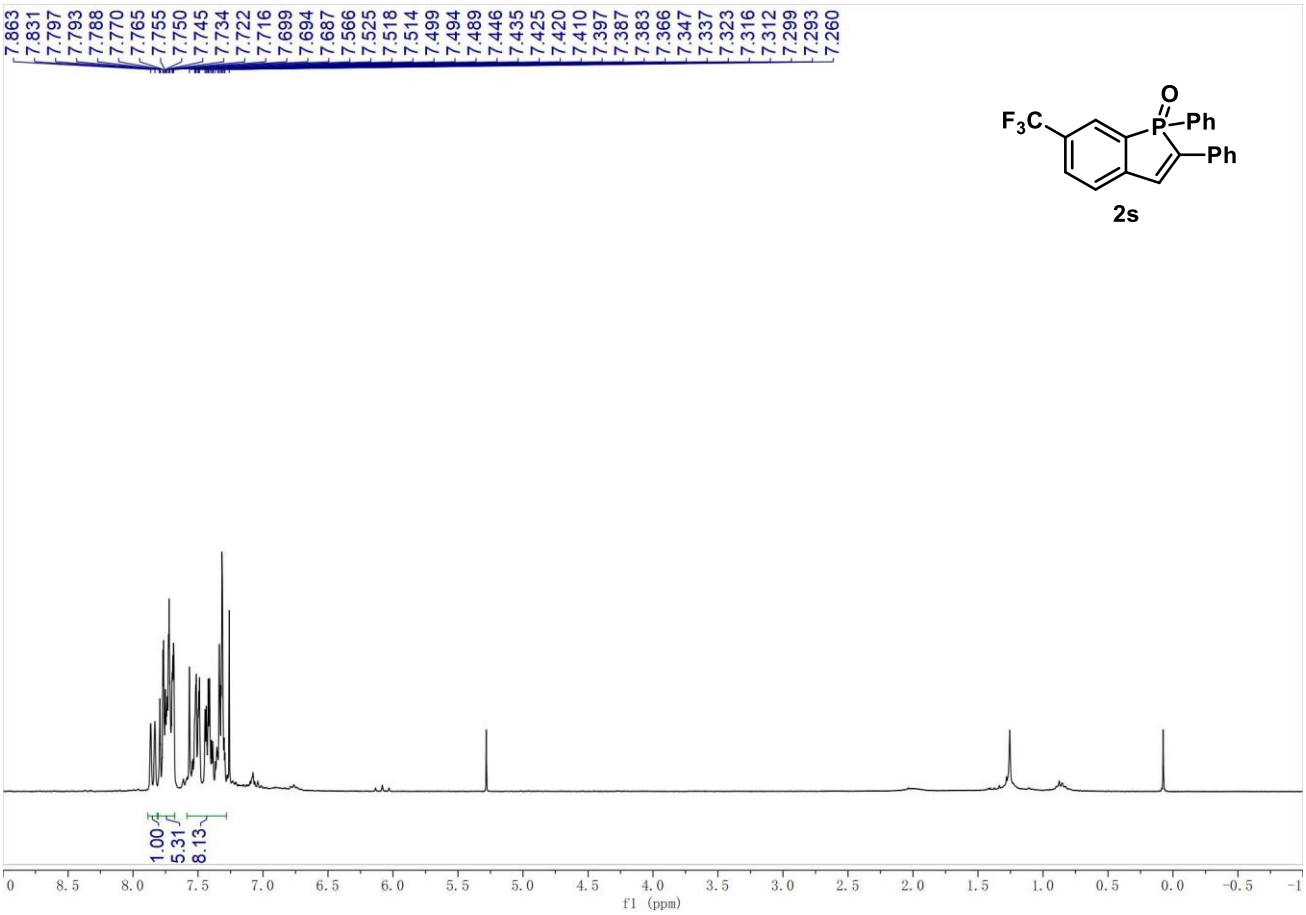


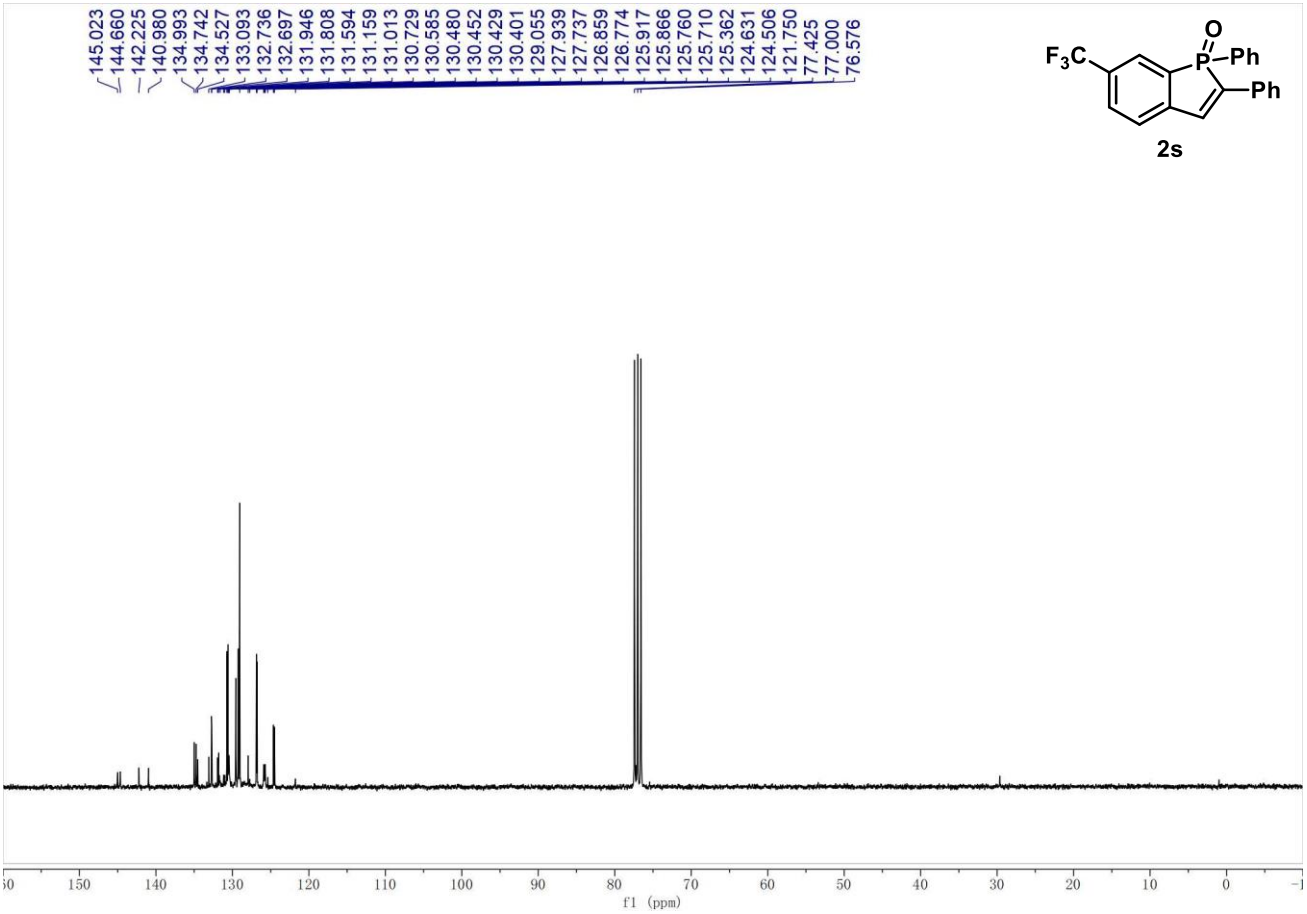
**$^{31}P\{^{1}H\}$ NMR spectrum of 2r (121 MHz, $CDCl_3$)**

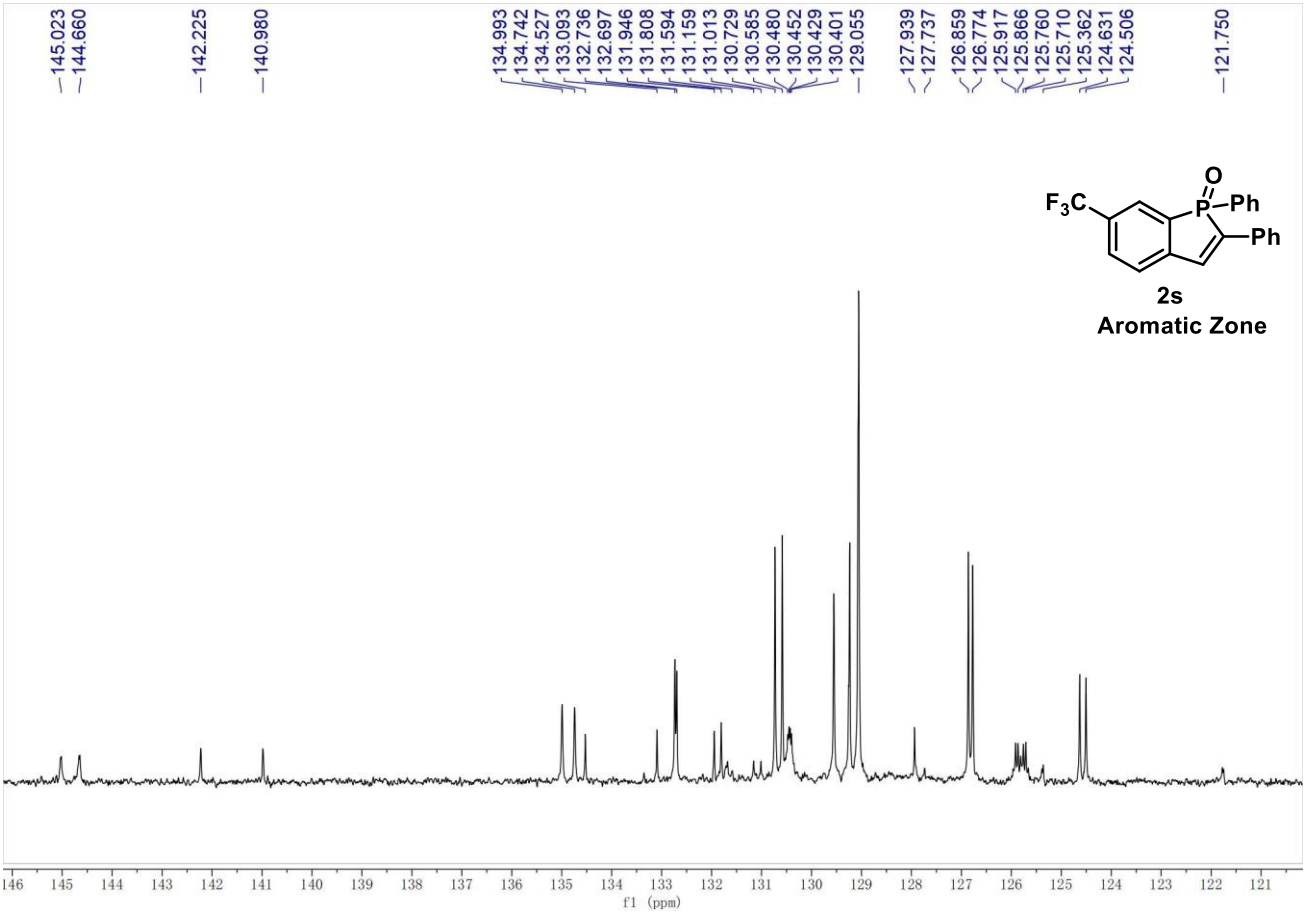



**$^{1}H$ NMR spectrum of 2s (300 MHz, $CDCl_3$)**

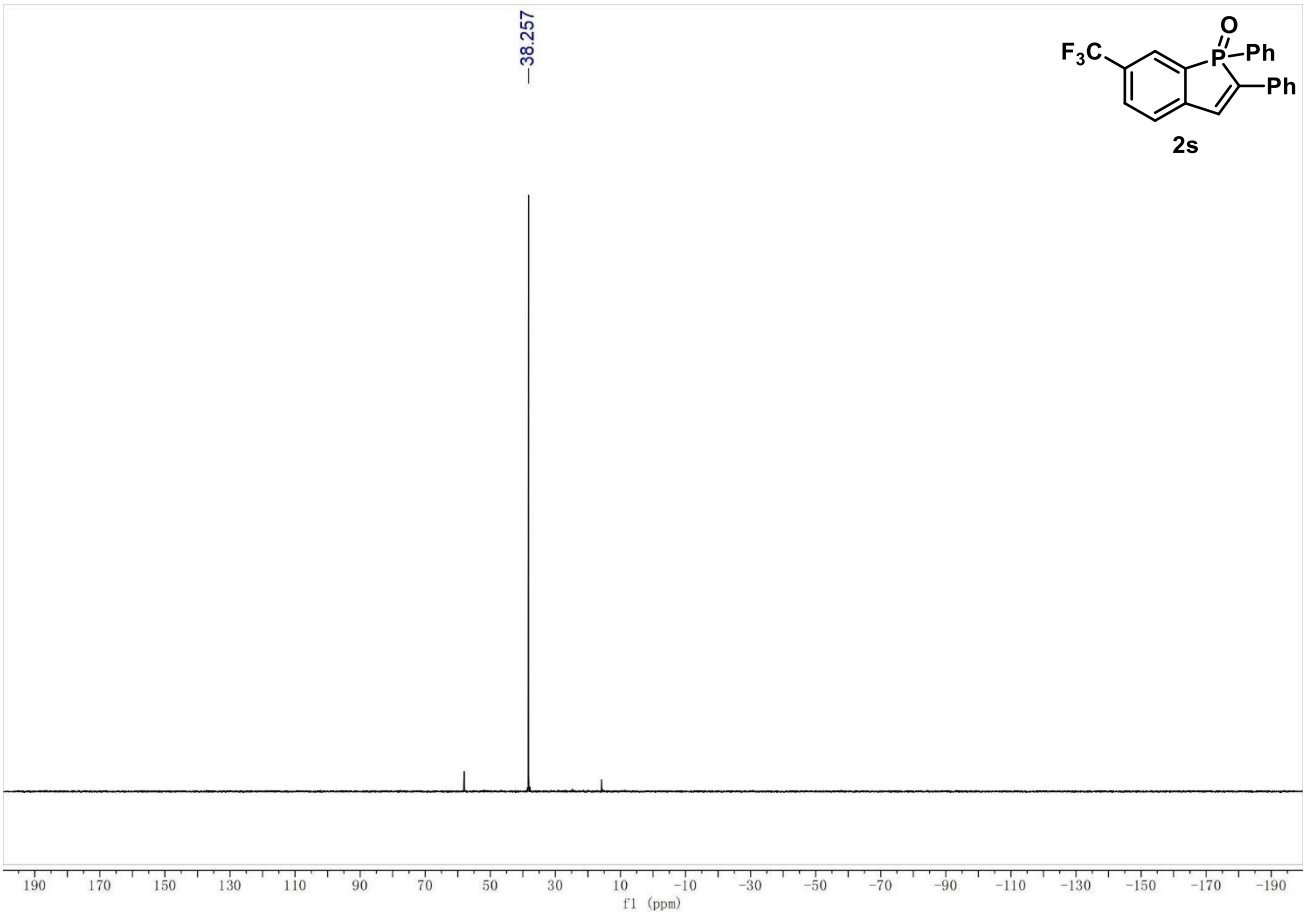


**$^{13}$C NMR spectrum of 2s (75 MHz, $CDCl_3$)**

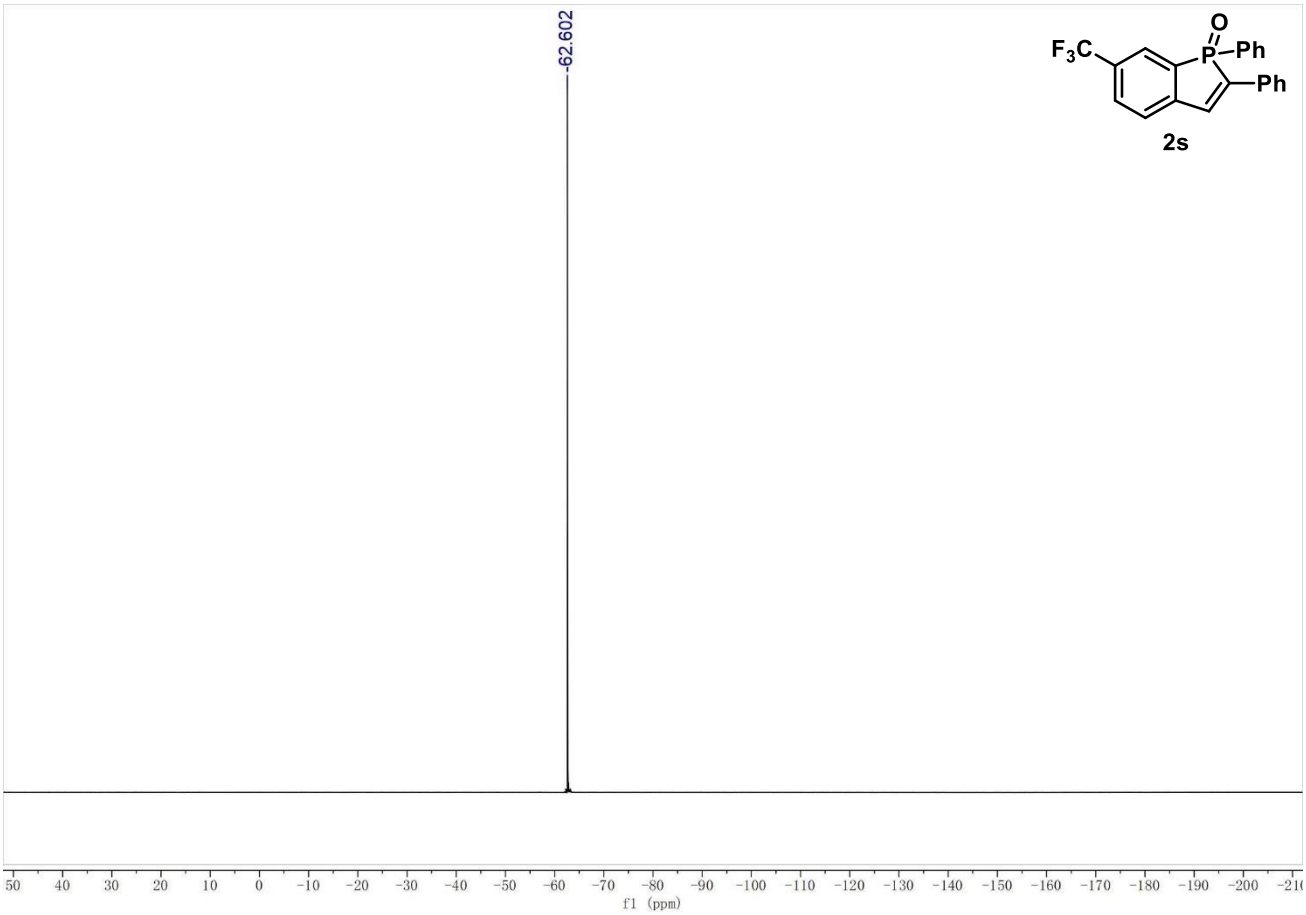


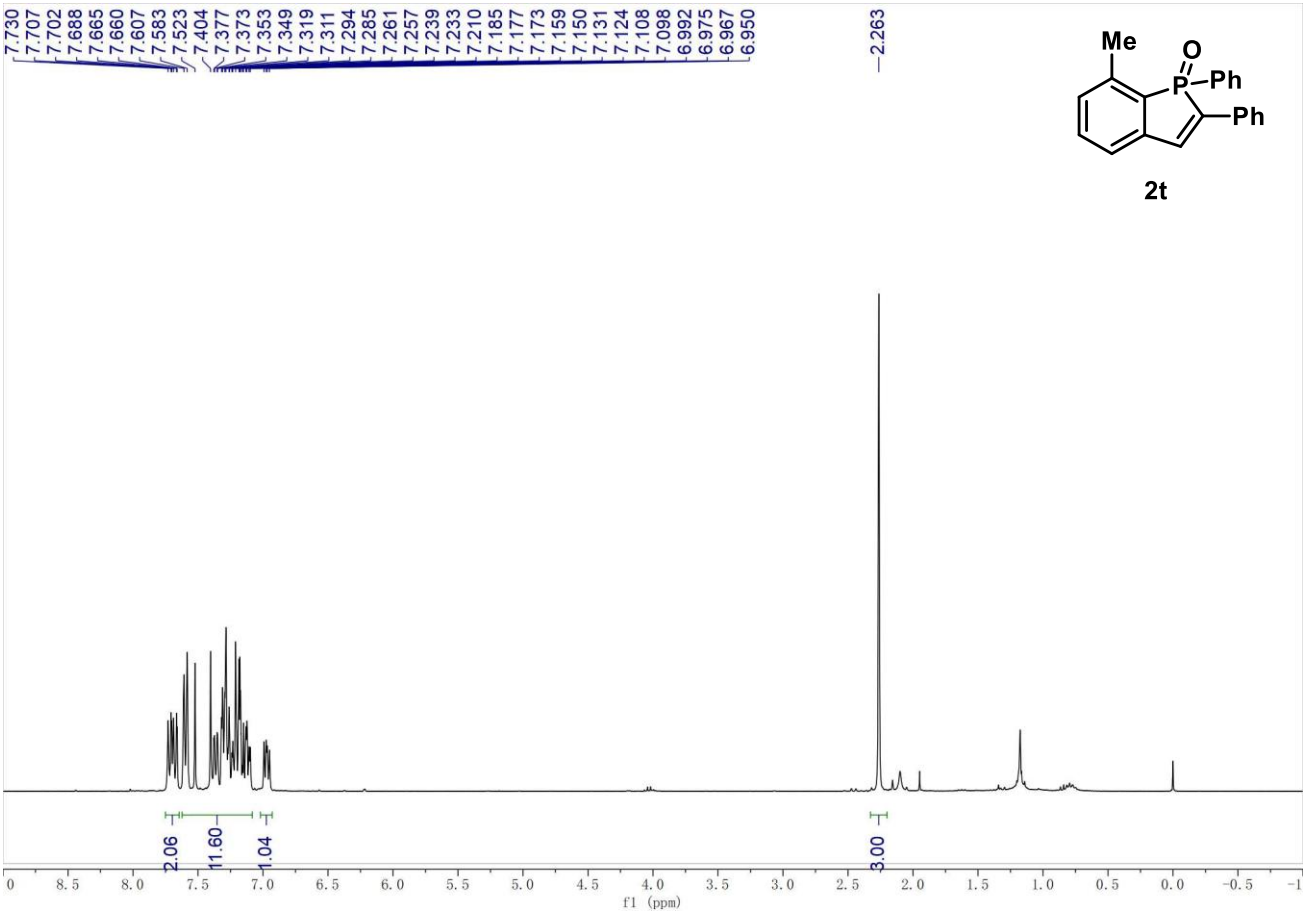
**$^{31}P\{^{1}H\}$ NMR spectrum of 2s (121 MHz, $CDCl_3$)**



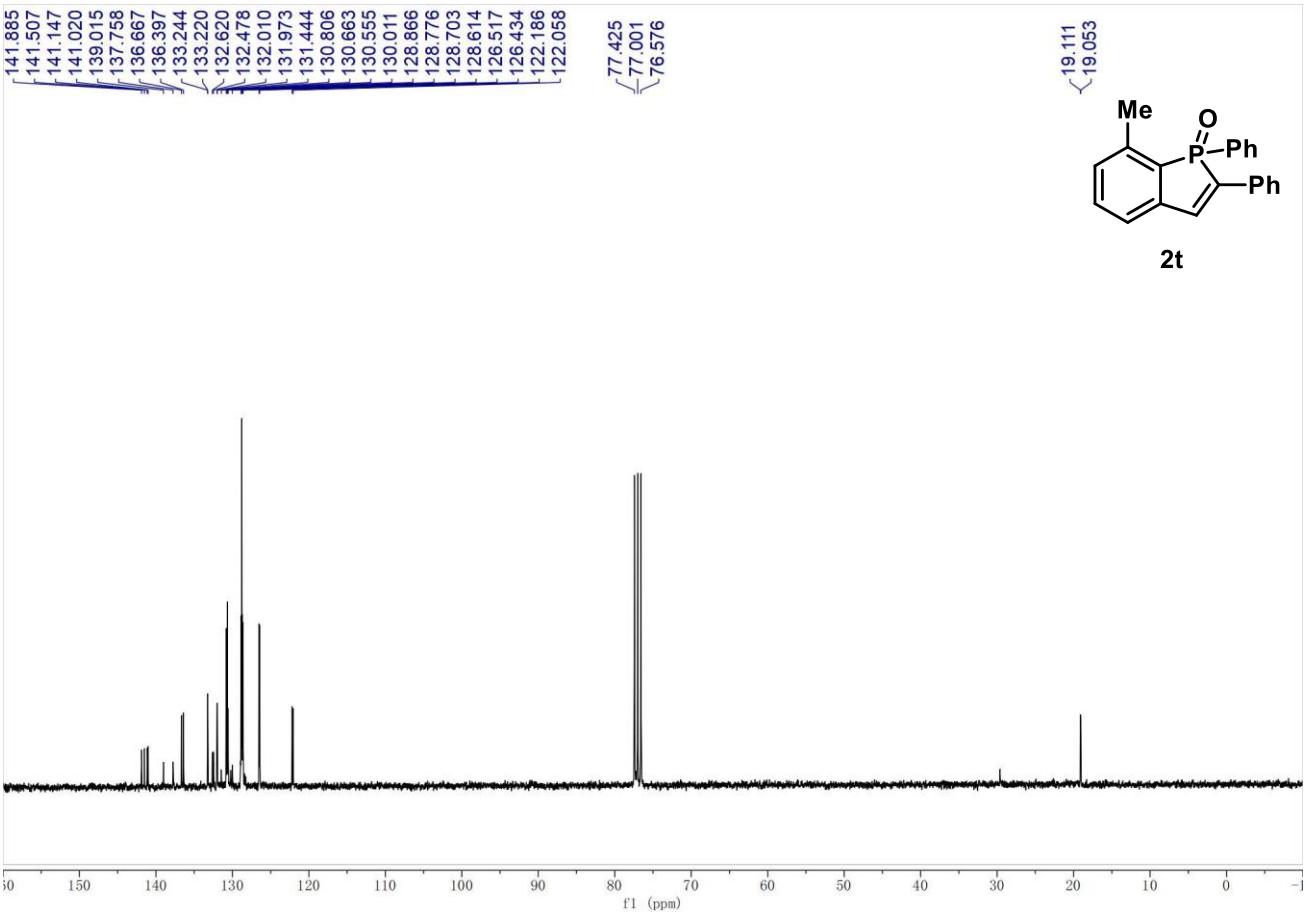

**$^{19}F$ NMR spectrum of 2s (282 MHz, $CDCl_3$)**

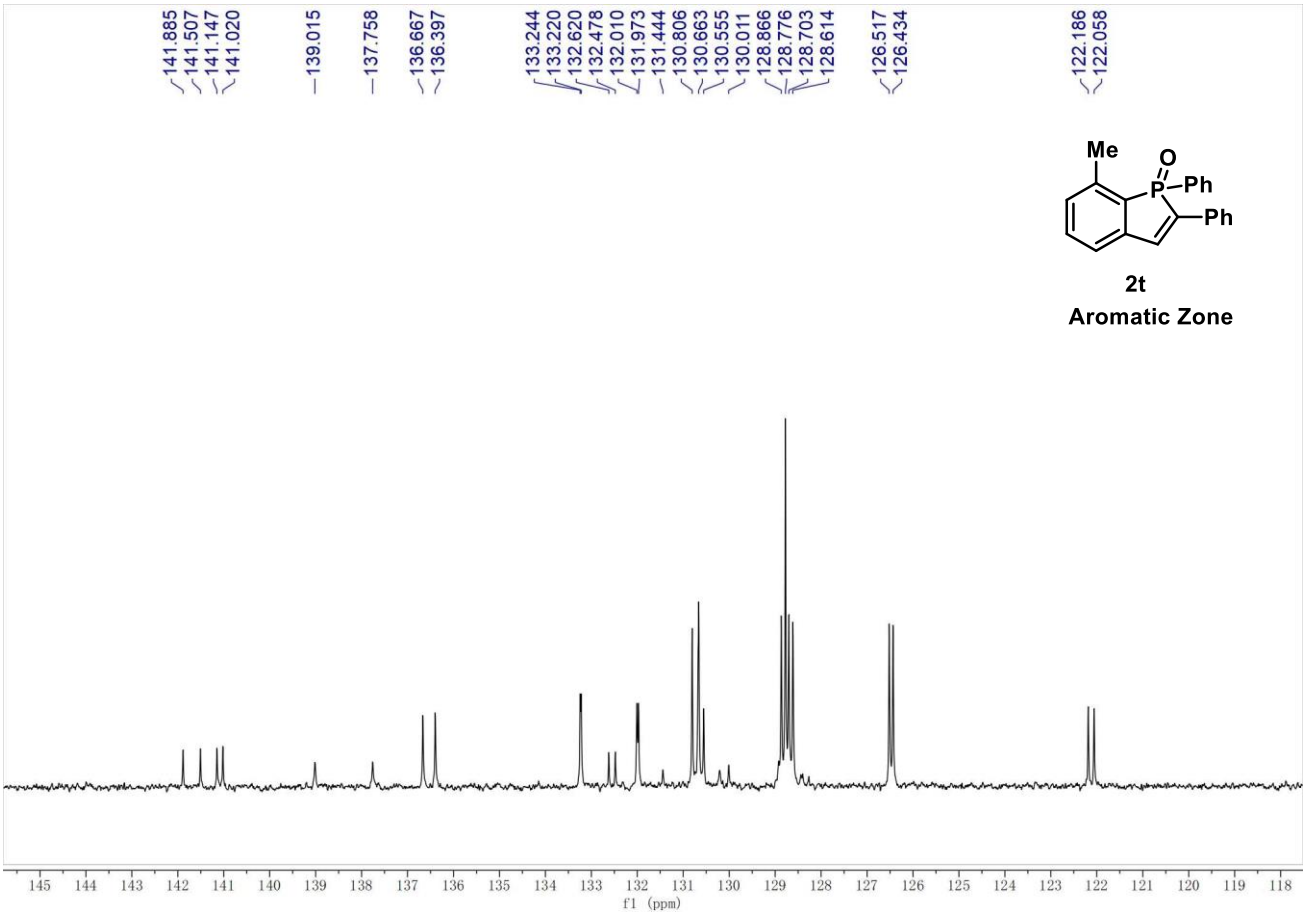


**$^{1}$H NMR spectrum of 2t (300 MHz, $CDCl_3$)**

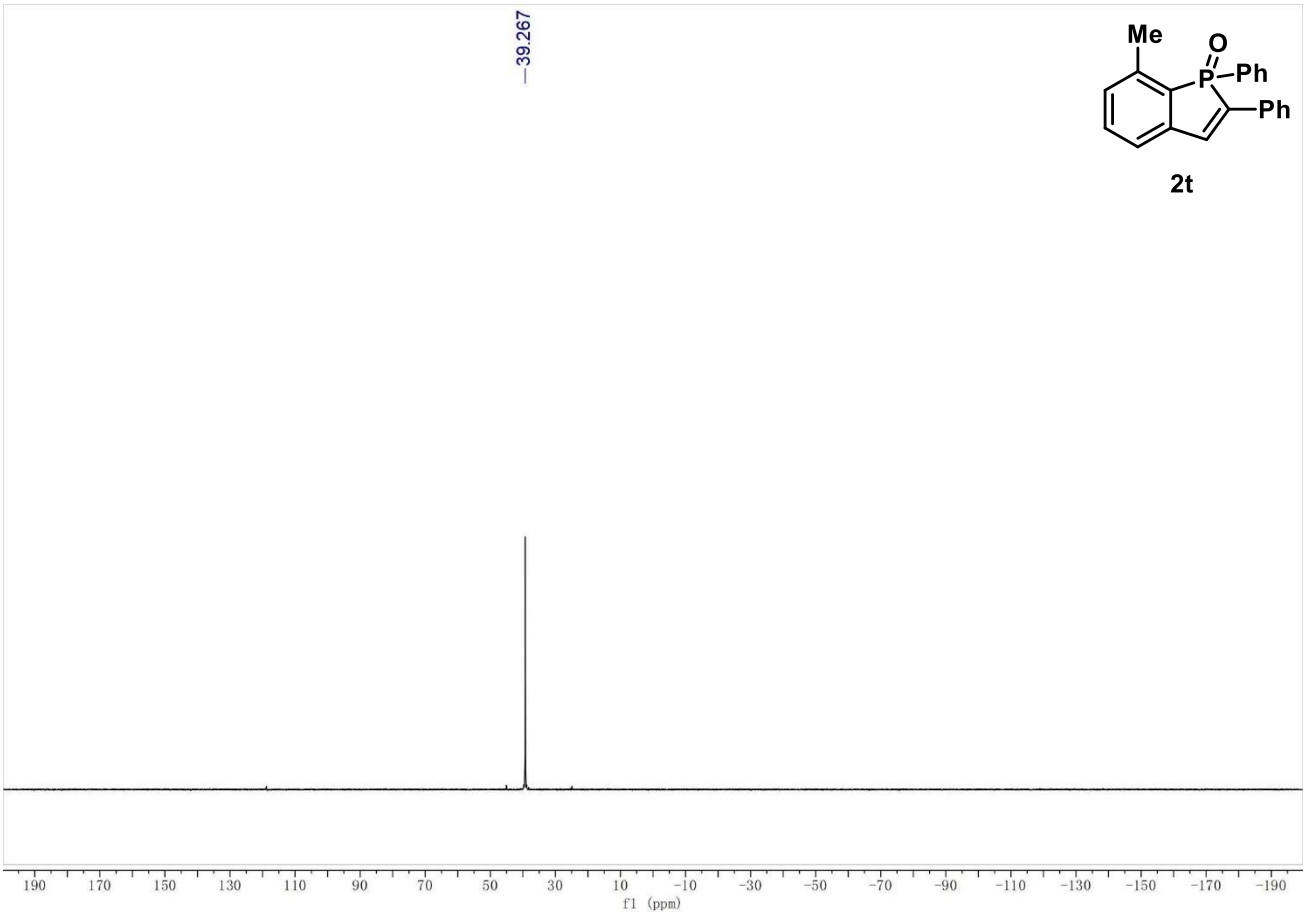



**$^{13}$C NMR spectrum of 2t (75 MHz, $CDCl_3$)**

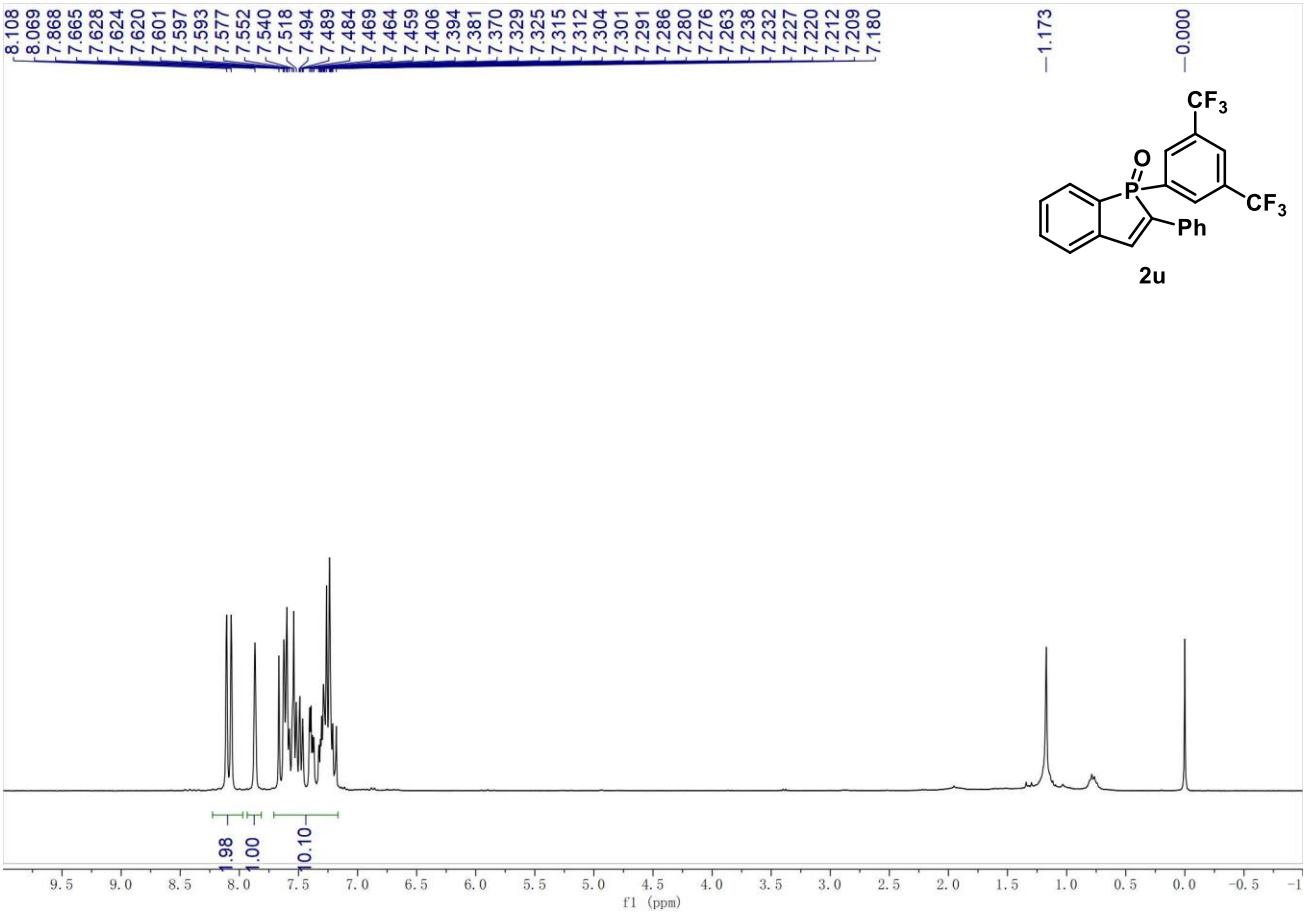





**$^{31}P\{^{1}H\}$ NMR spectrum of 2t (121 MHz, $CDCl_3$)**



**$^{1}$H NMR spectrum of 2u (300 MHz, $CDCl_3$)**

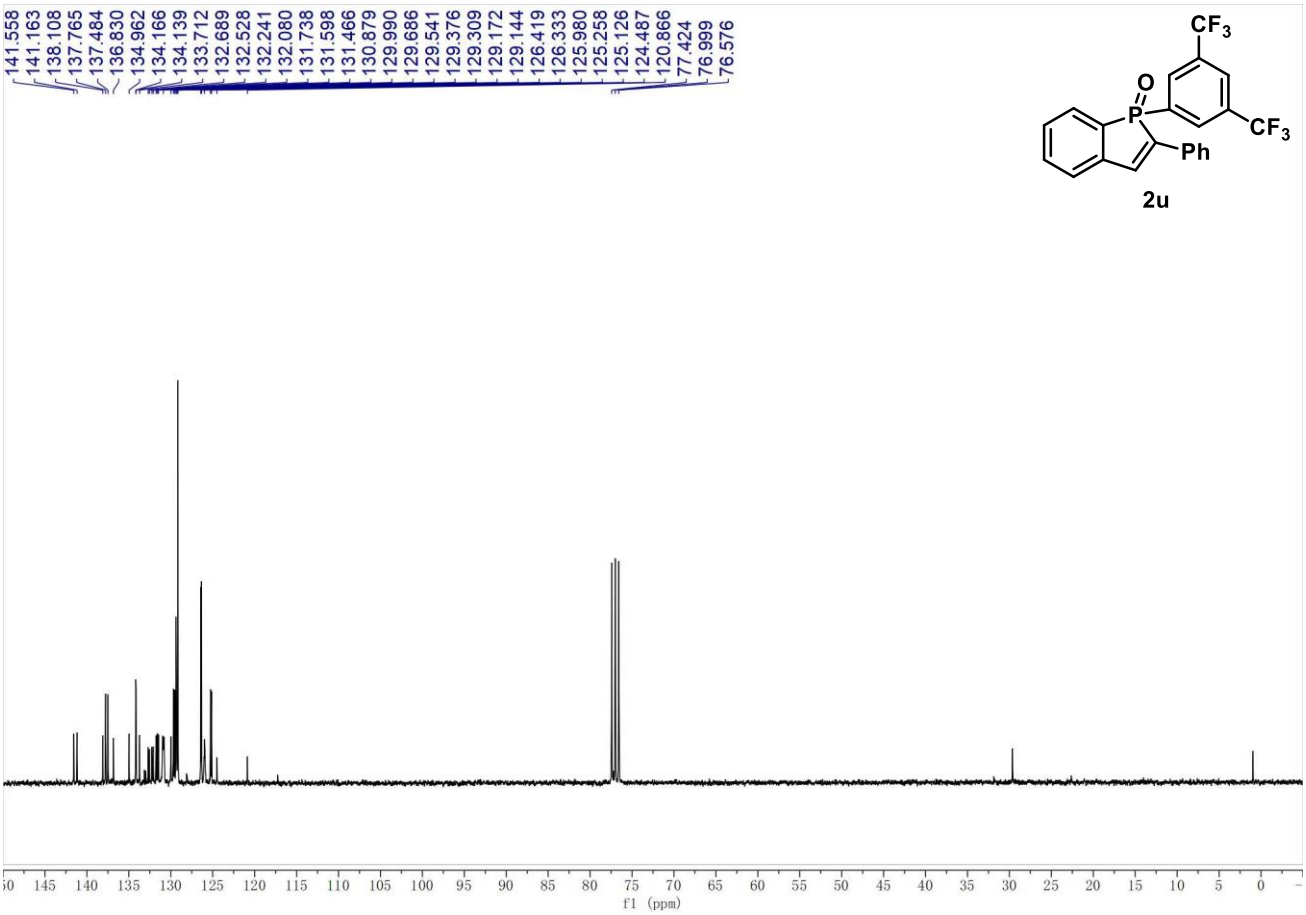






2u

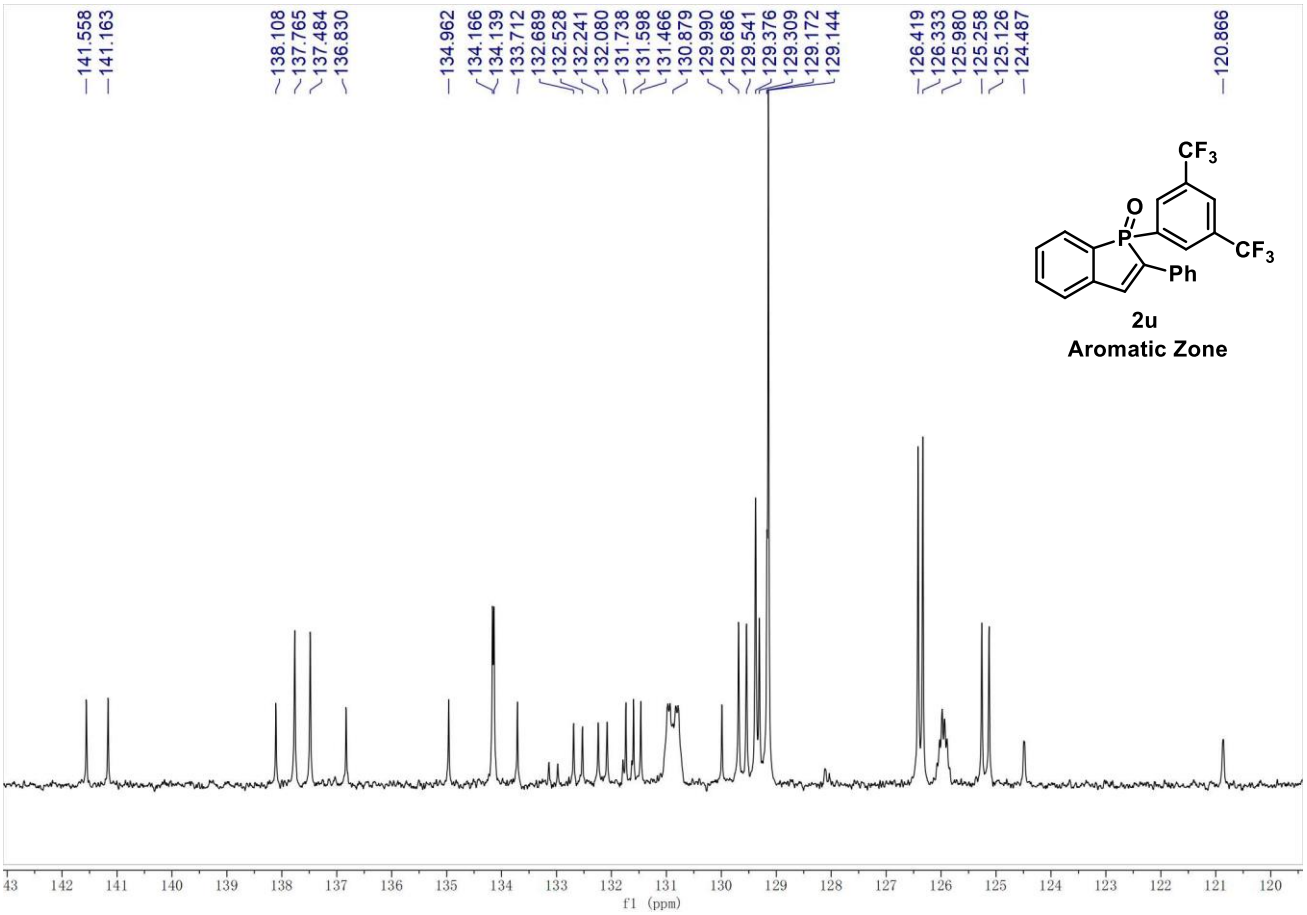
**$^{13}$C NMR spectrum of 2u (75 MHz, $CDCl_3$)**



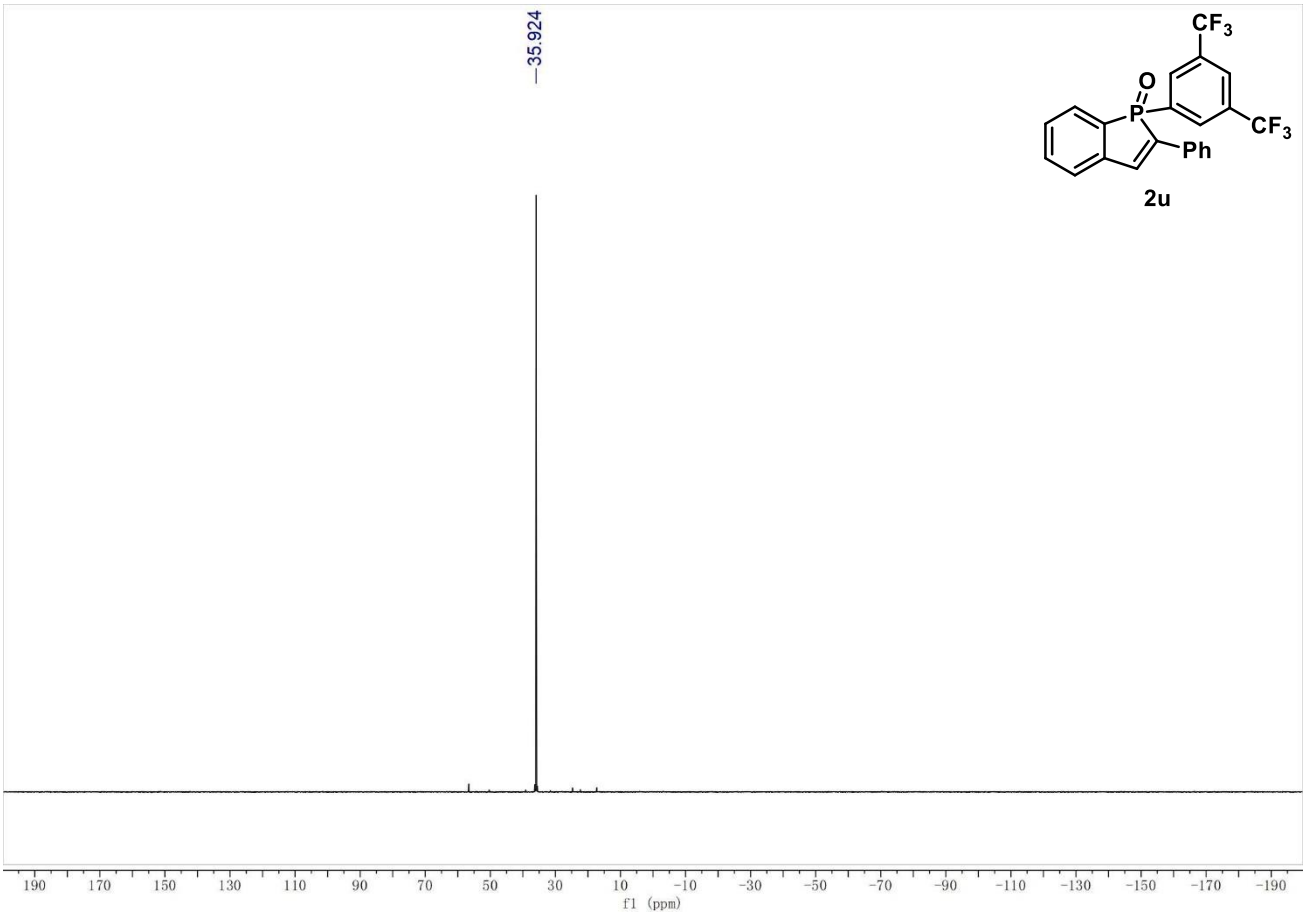




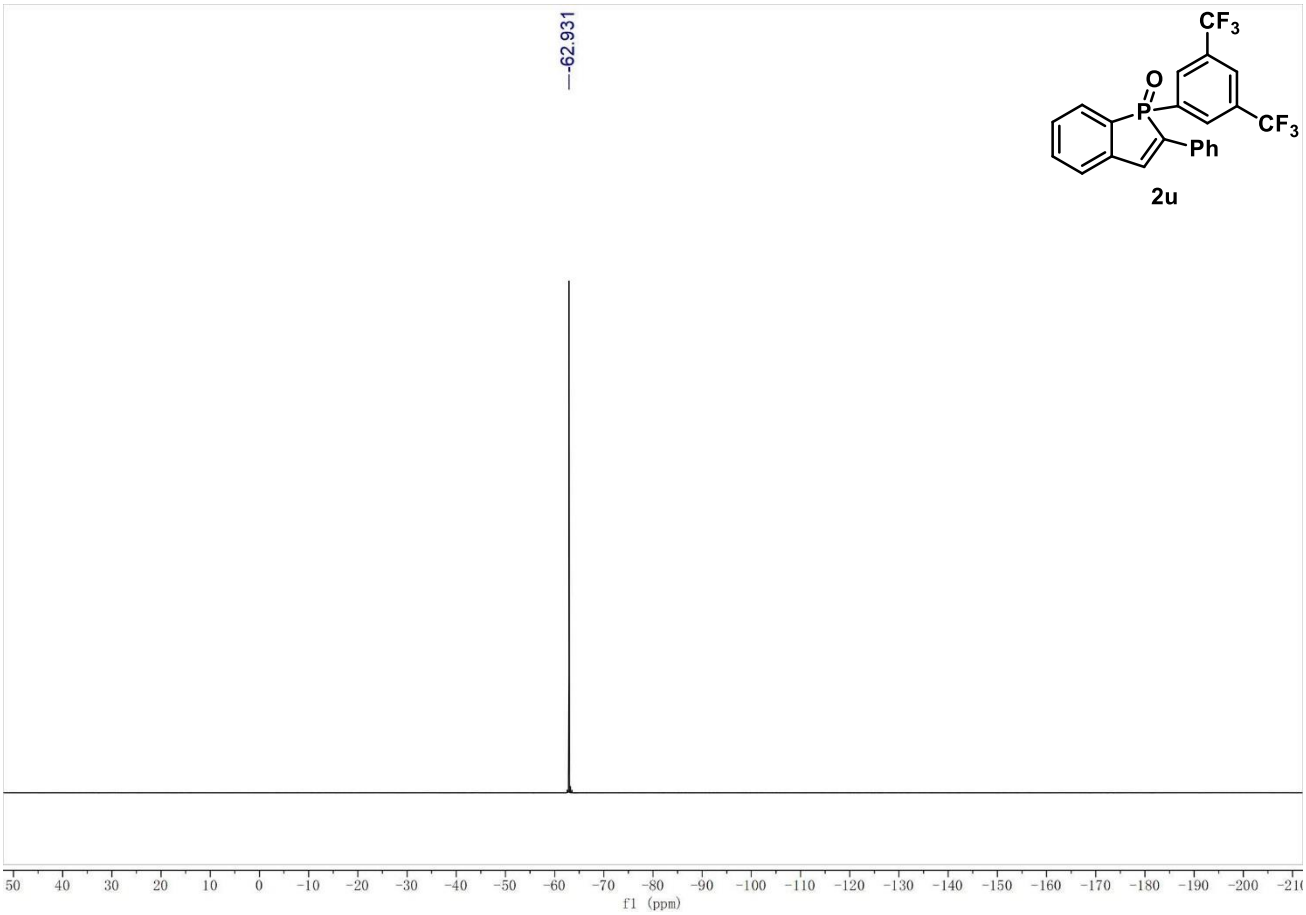
2u



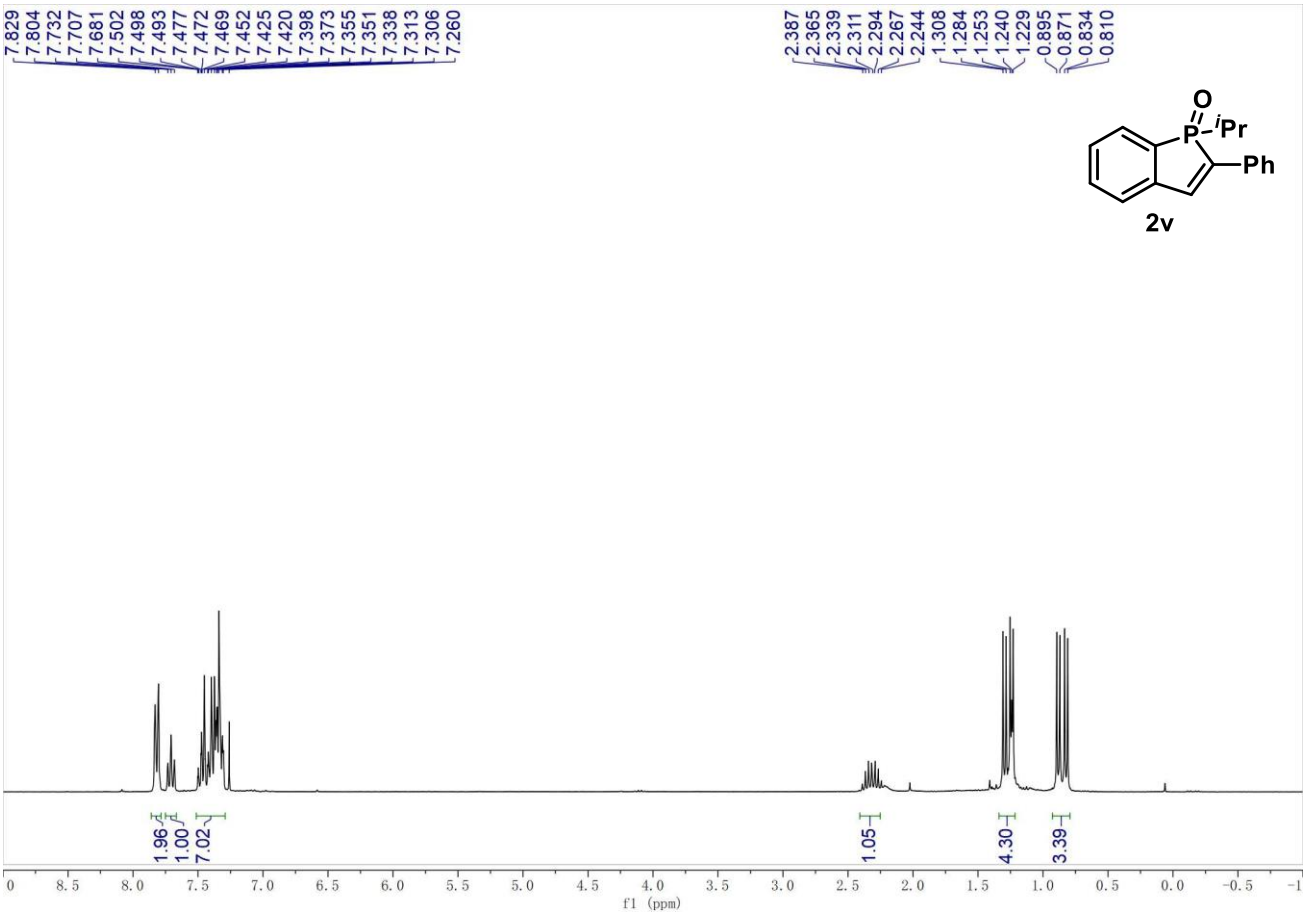

**$^{31}P\{^{1}H\}$ NMR spectrum of 2u (121 MHz, $CDCl_3$)**



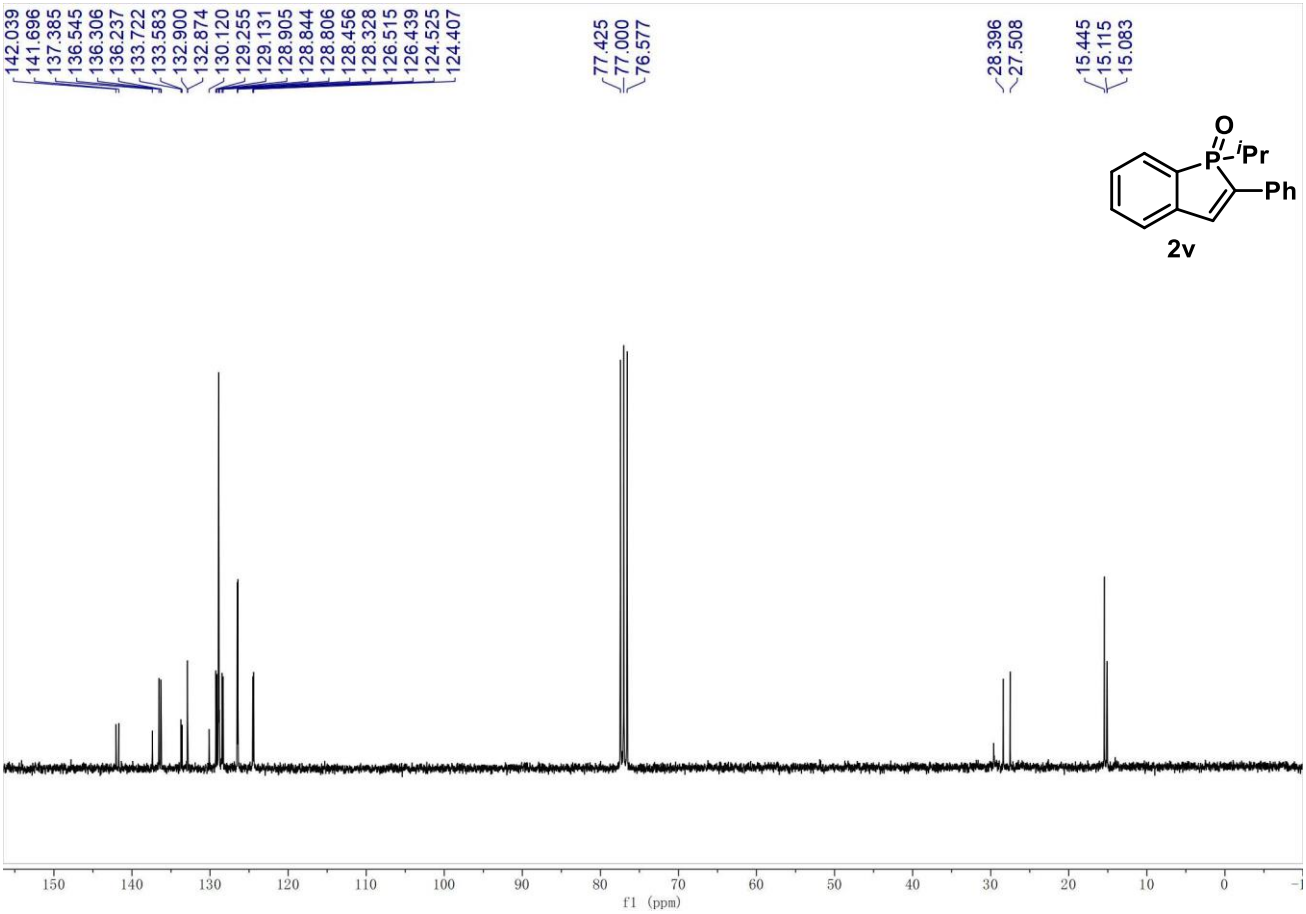
**$^{19}$F NMR spectrum of 2u (282 MHz, $CDCl_3$)**

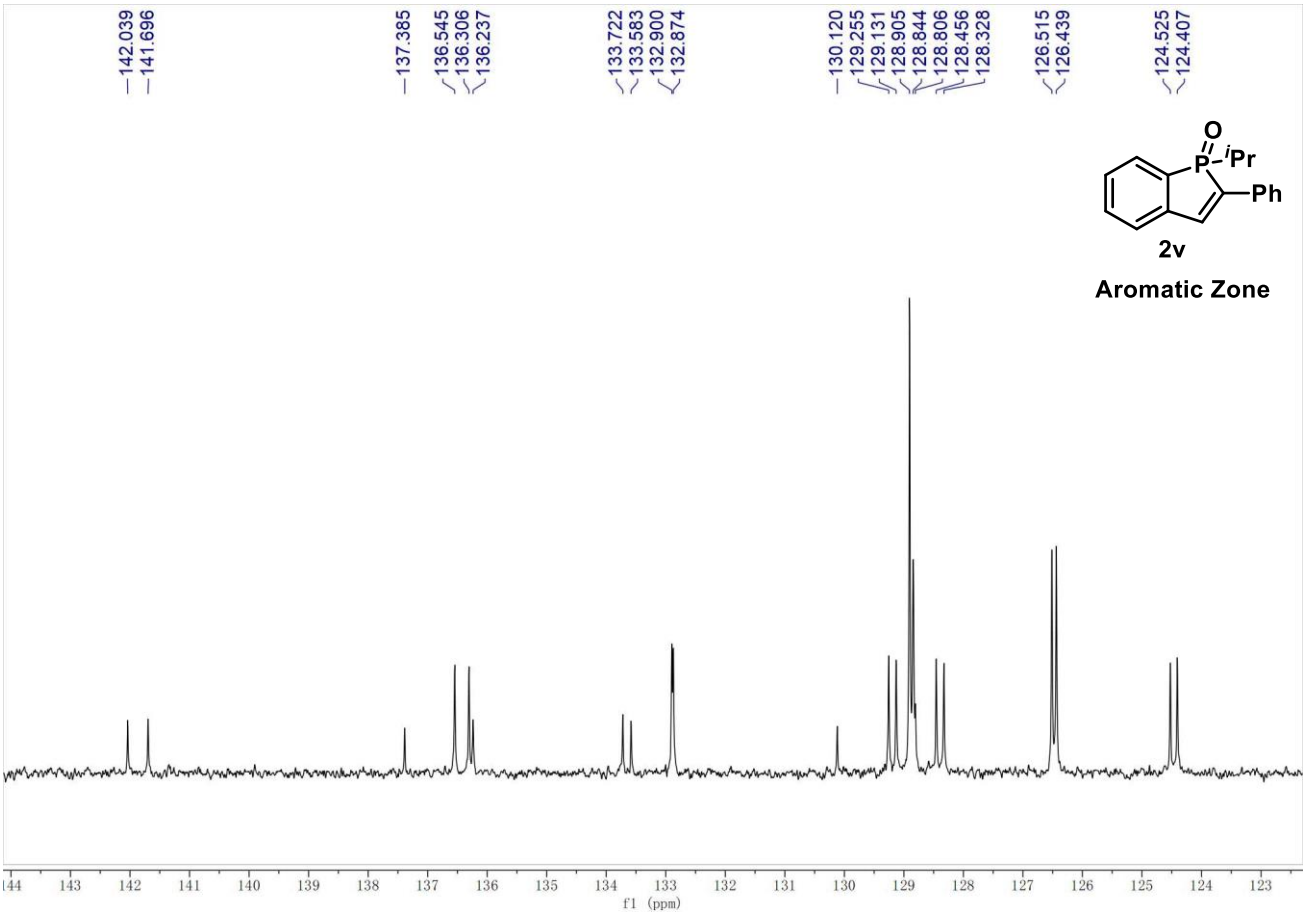



**$^{1}$H NMR spectrum of 2v (300 MHz, $CDCl_3$)**

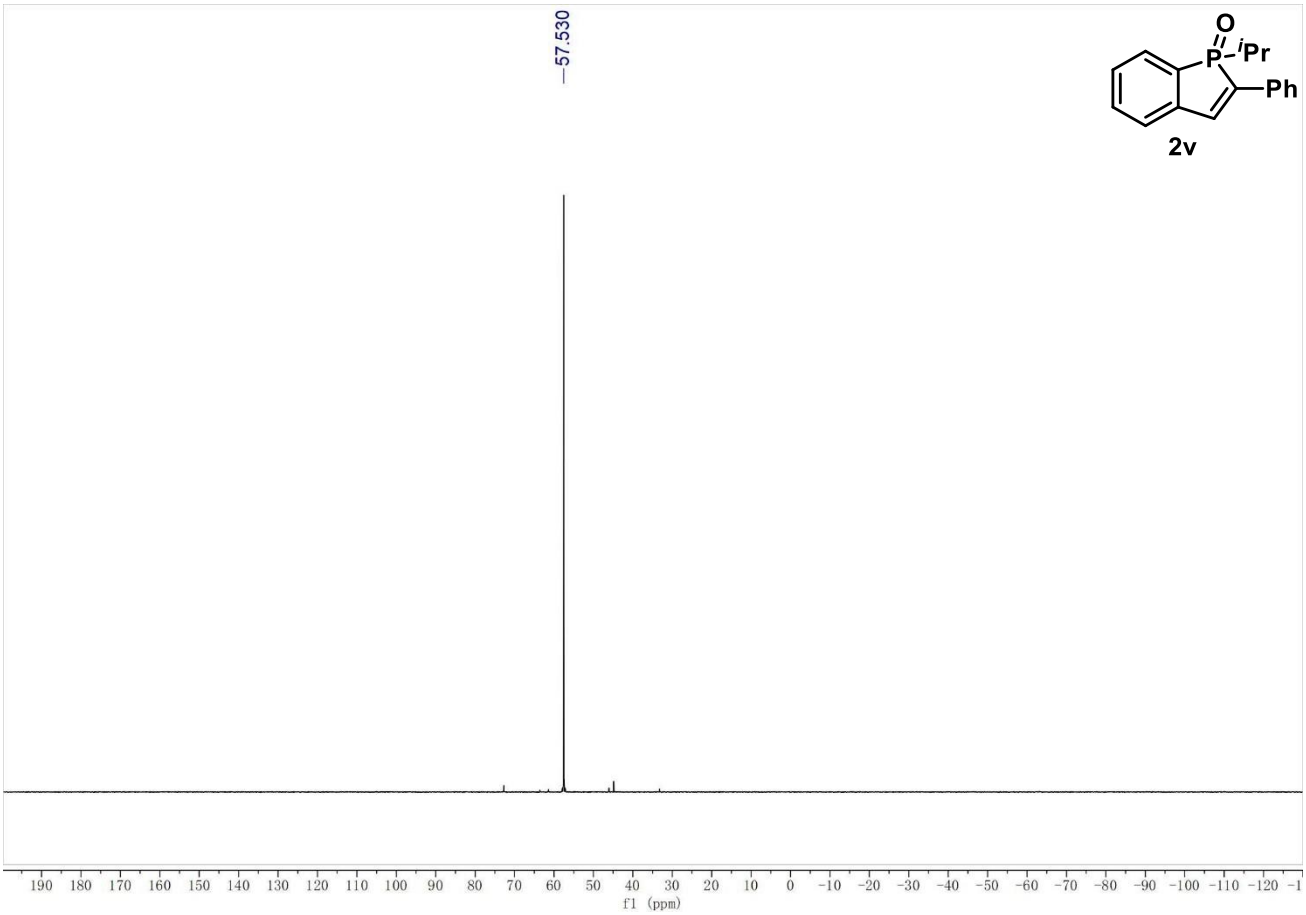


**$^{13}$C NMR spectrum of 2v (75 MHz, $CDCl_3$)**

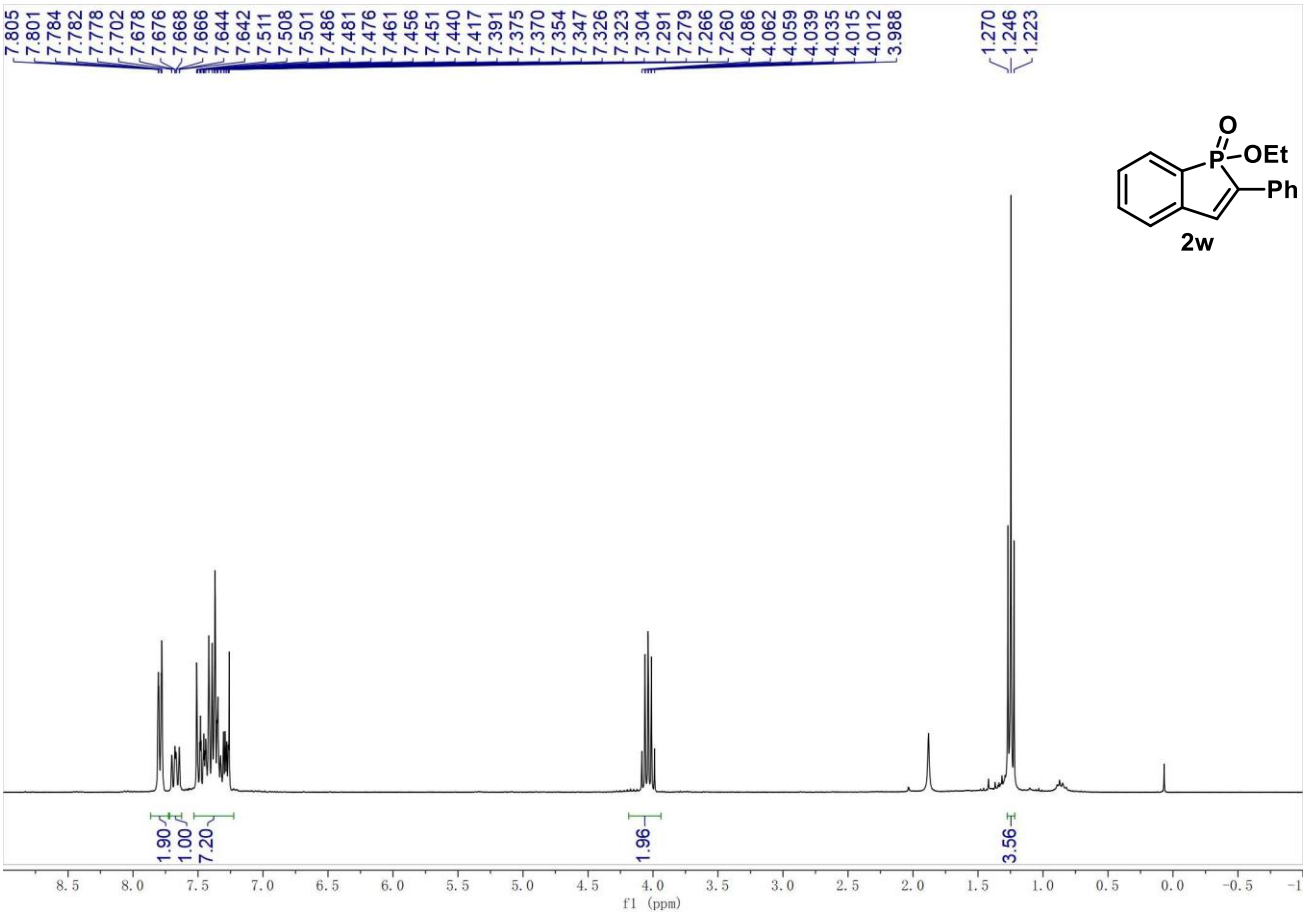


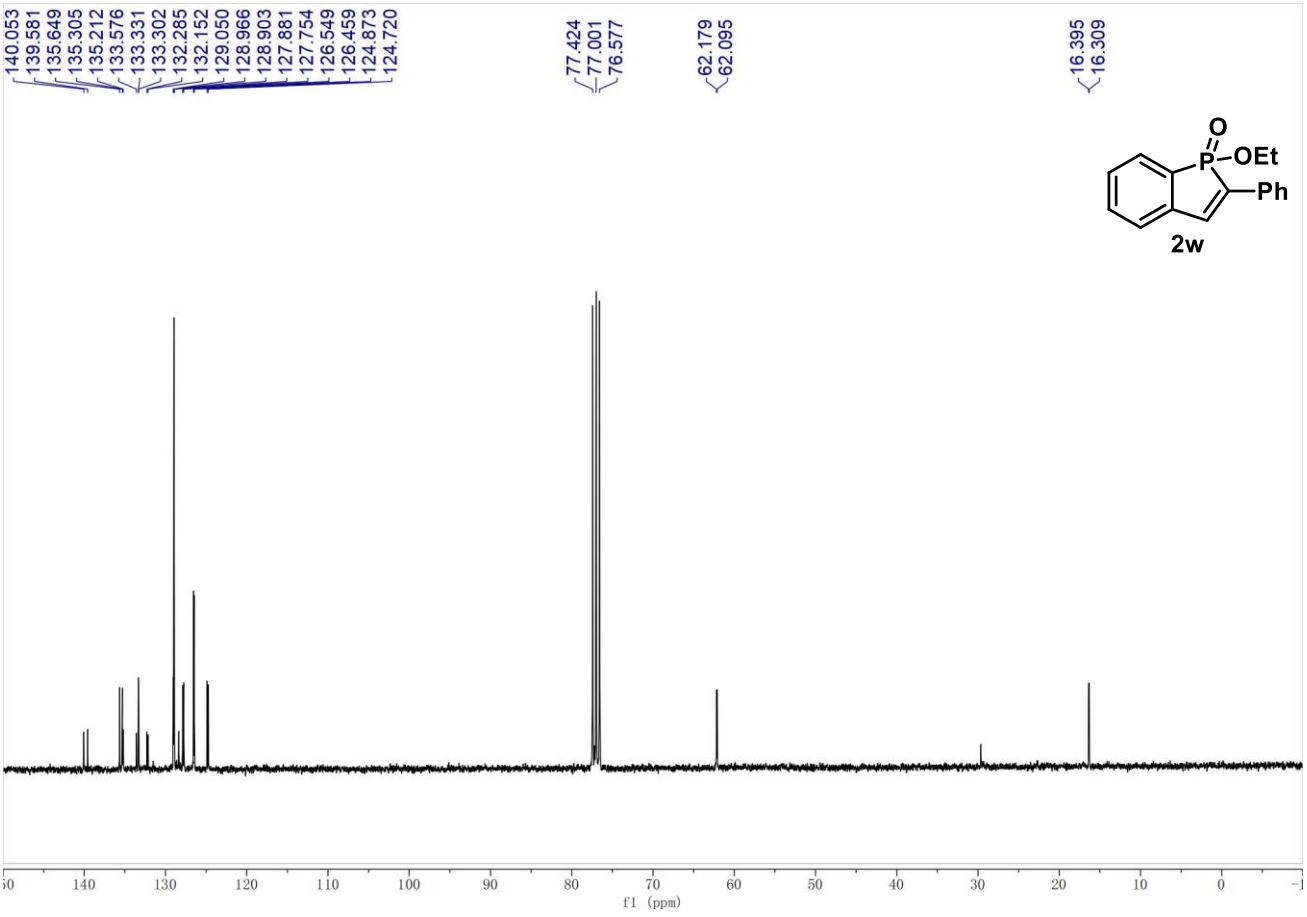
**$^{31}P\{^{1}H\}$ NMR spectrum of 2v (121 MHz, $CDCl_3$)**

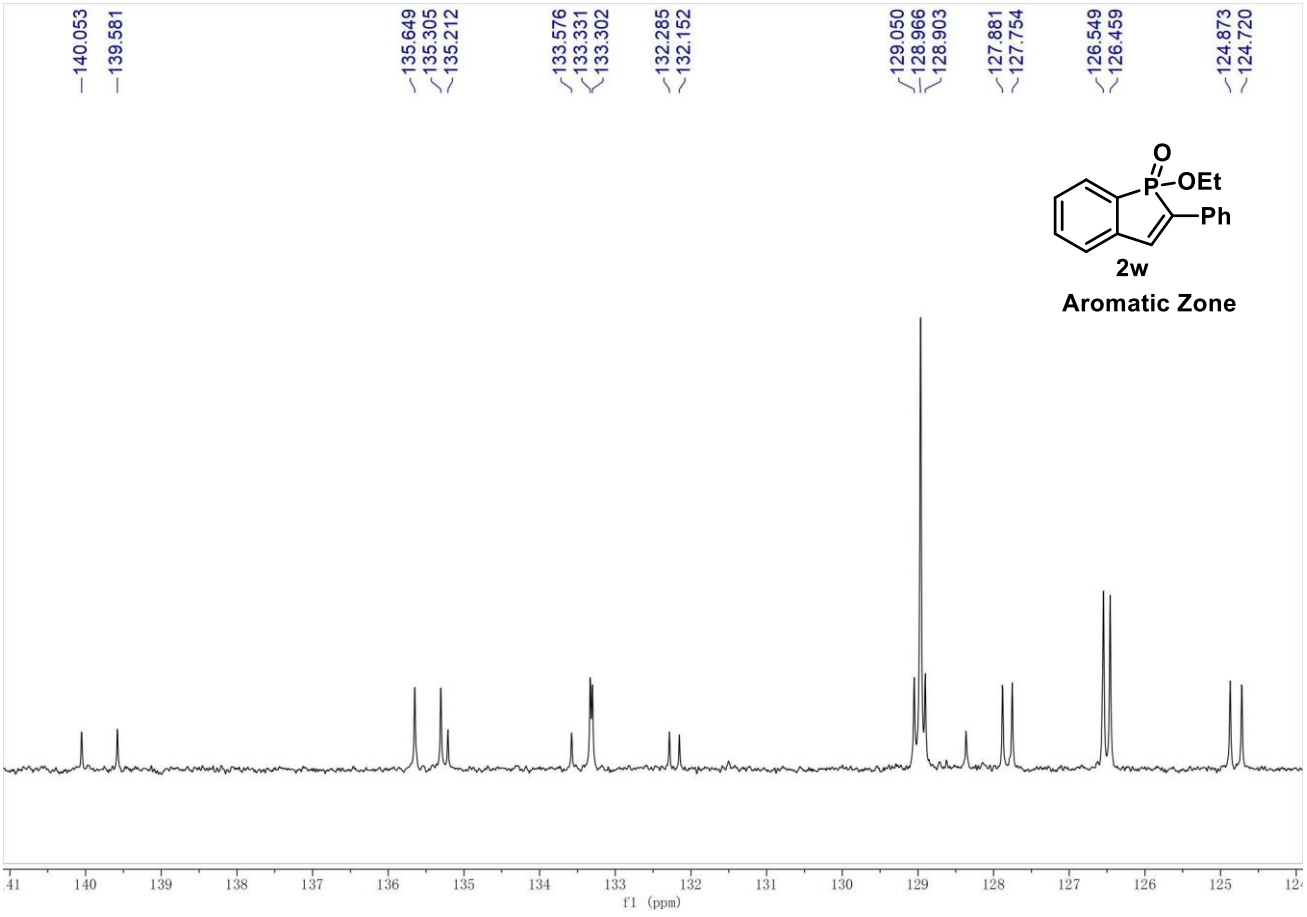



**$^{1}H$ NMR spectrum of 2w (300 MHz, $CDCl_3$)**

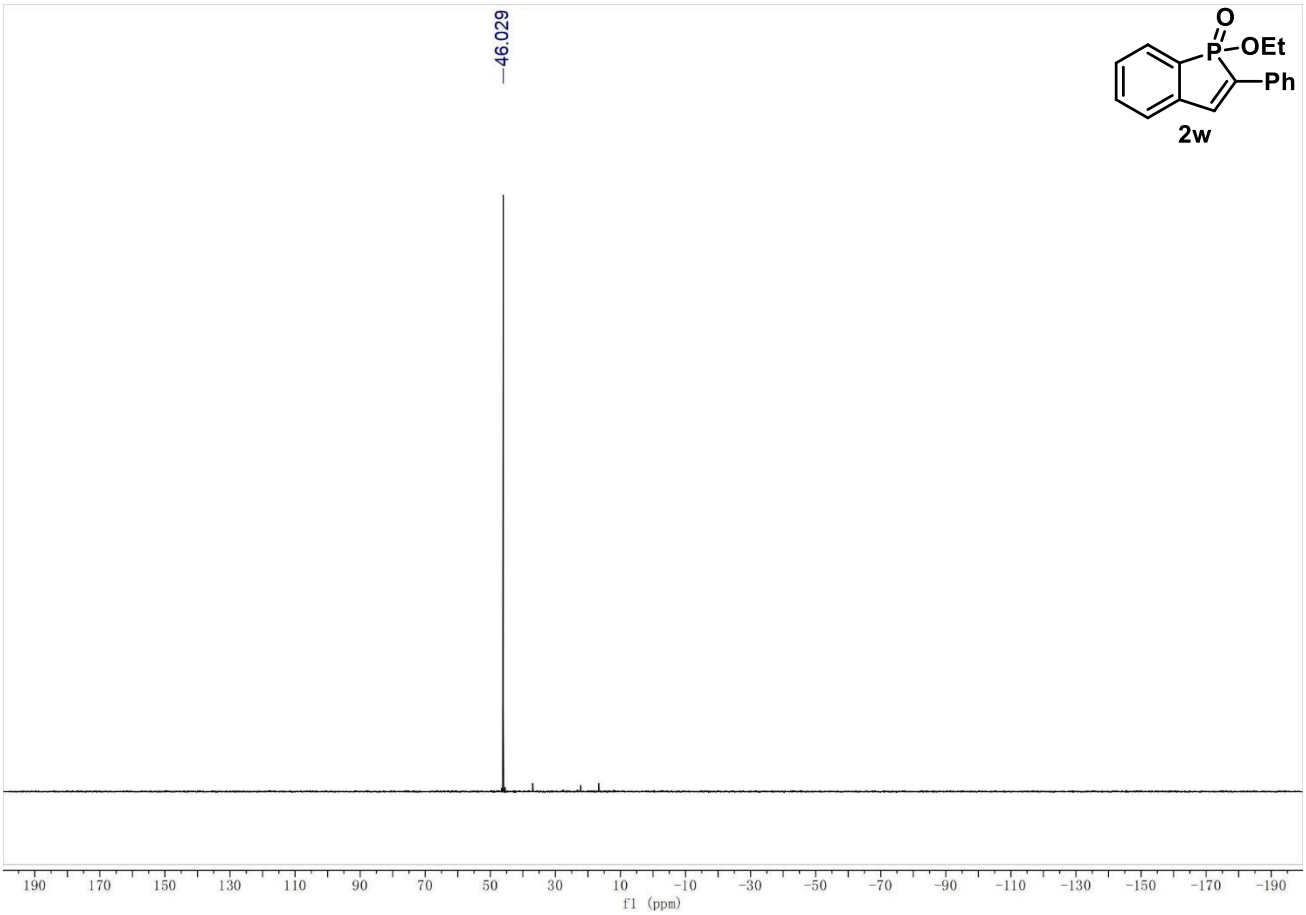


**$^{13}$C NMR spectrum of 2w (75 MHz, $CDCl_3$)**

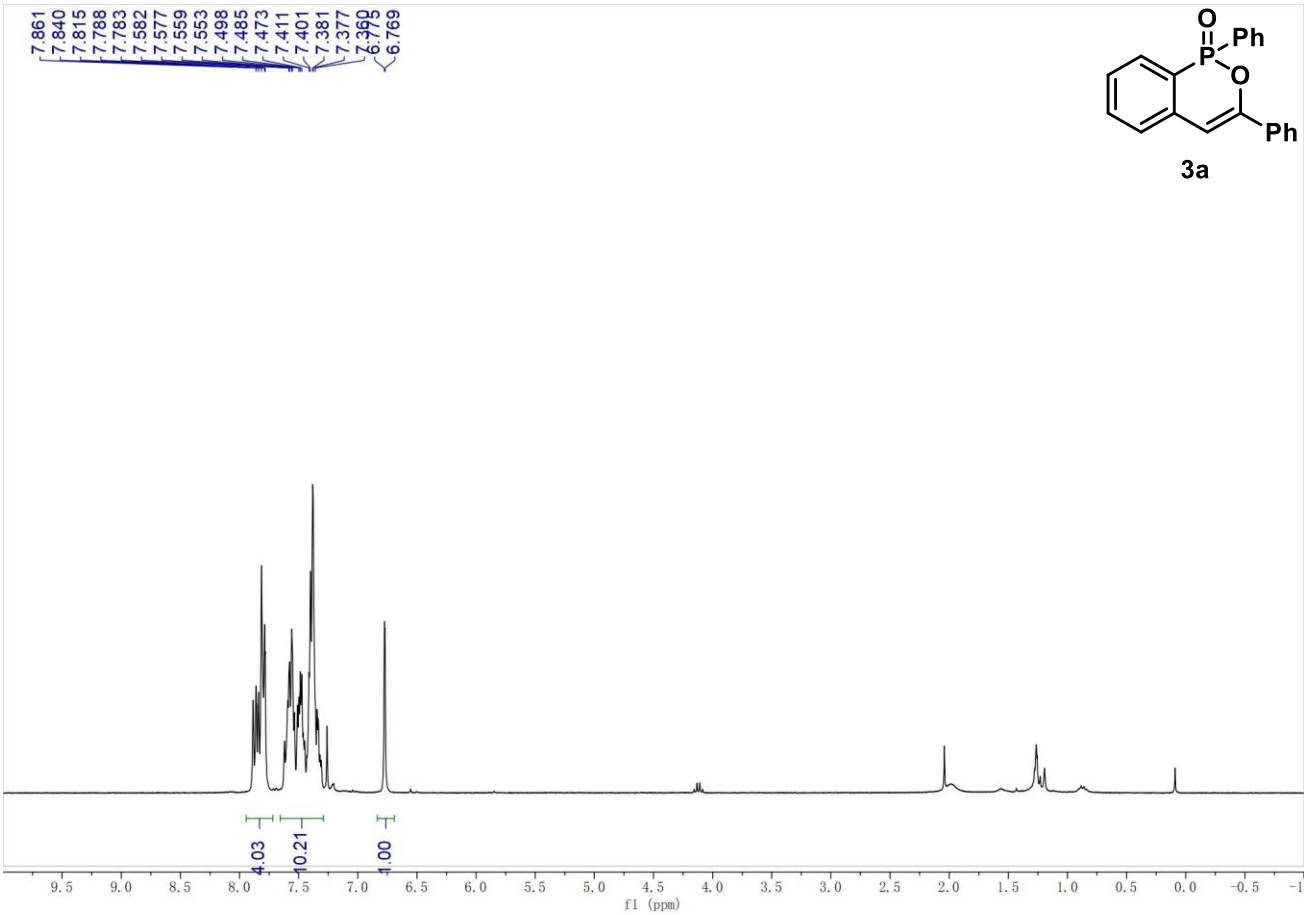


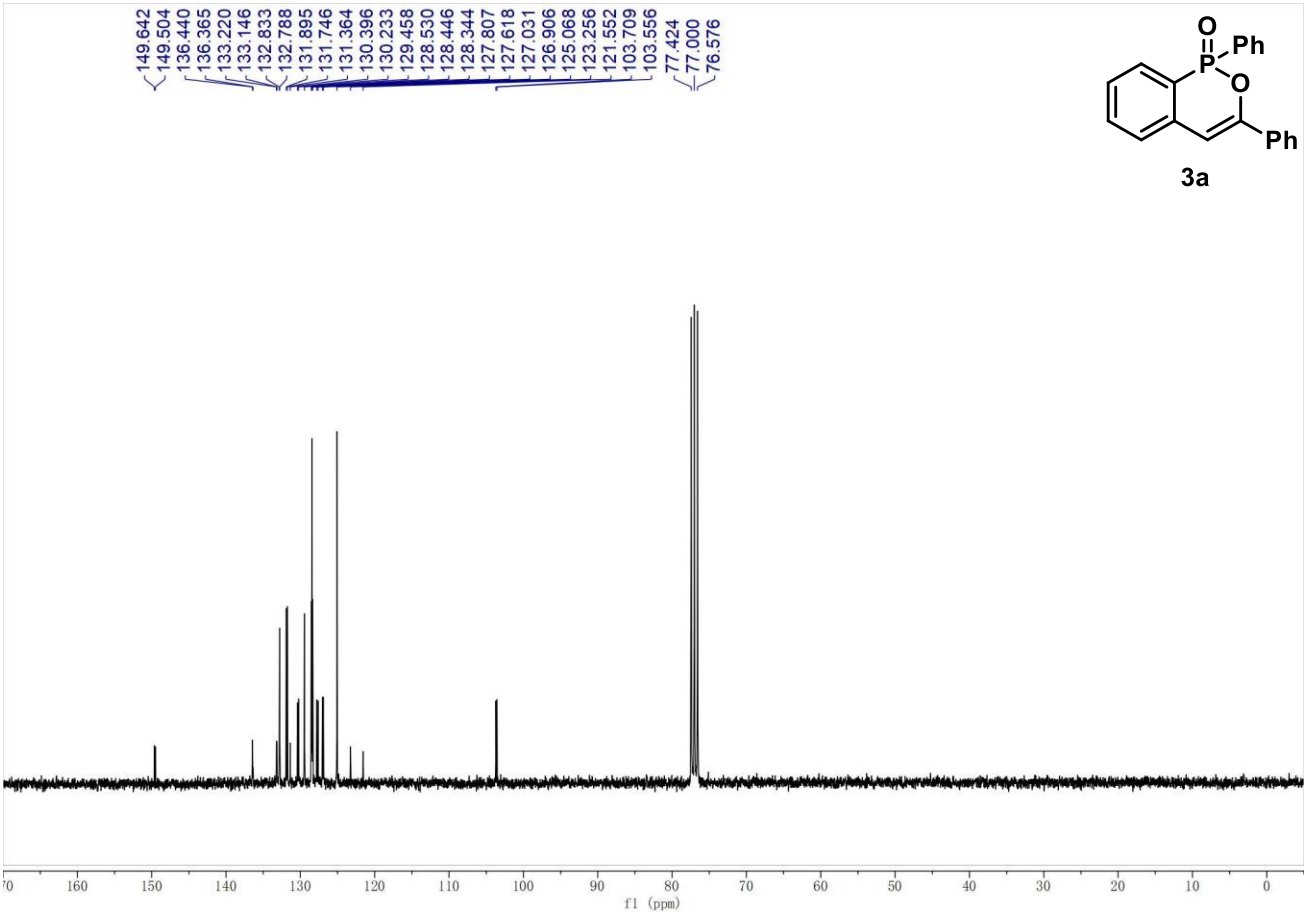
**$^{31}P\{^{1}H\}$ NMR spectrum of 2w (121 MHz, $CDCl_3$)**

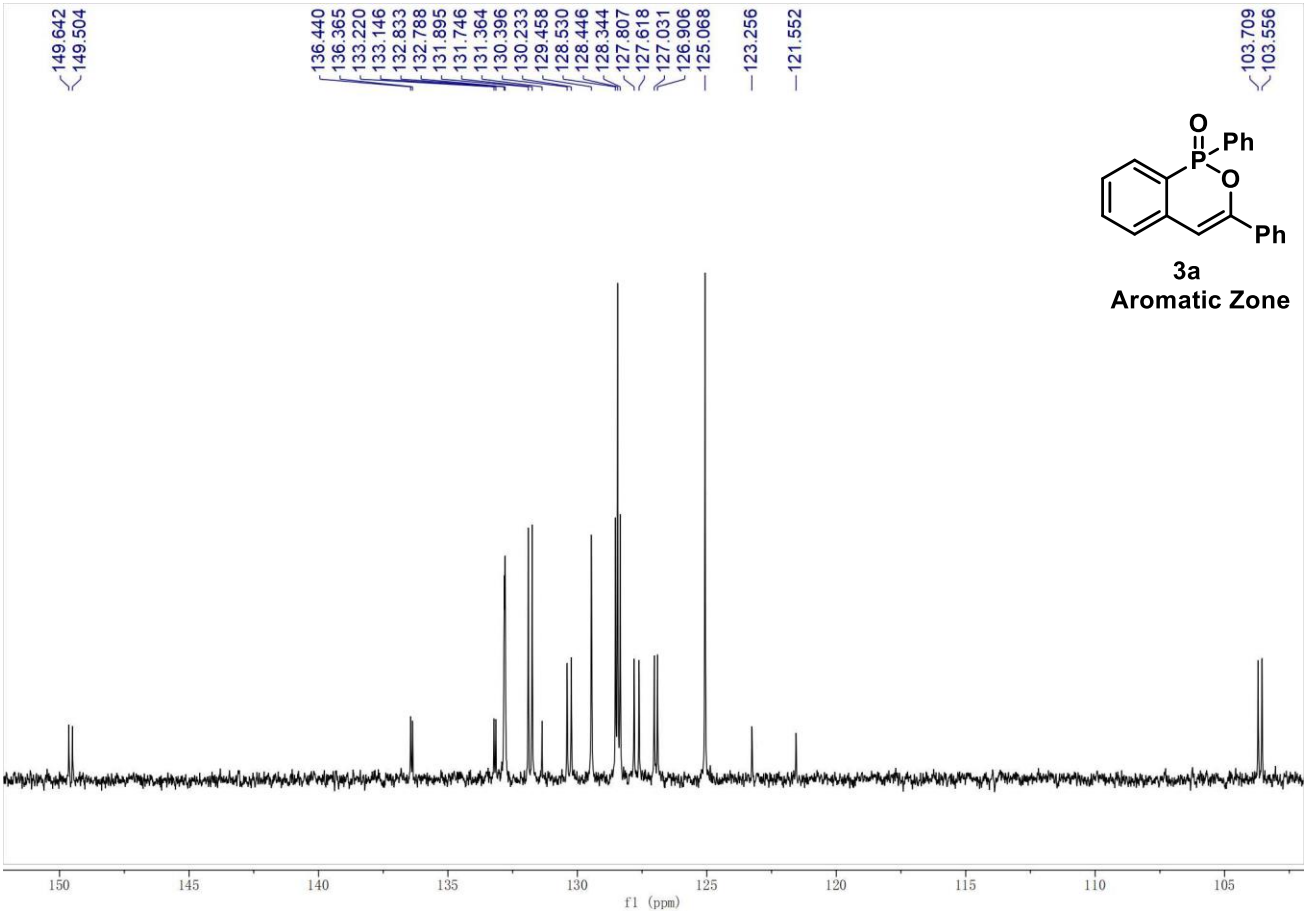



**$^{1}H$ NMR spectrum of 3a (300 MHz, $CDCl_3$)**

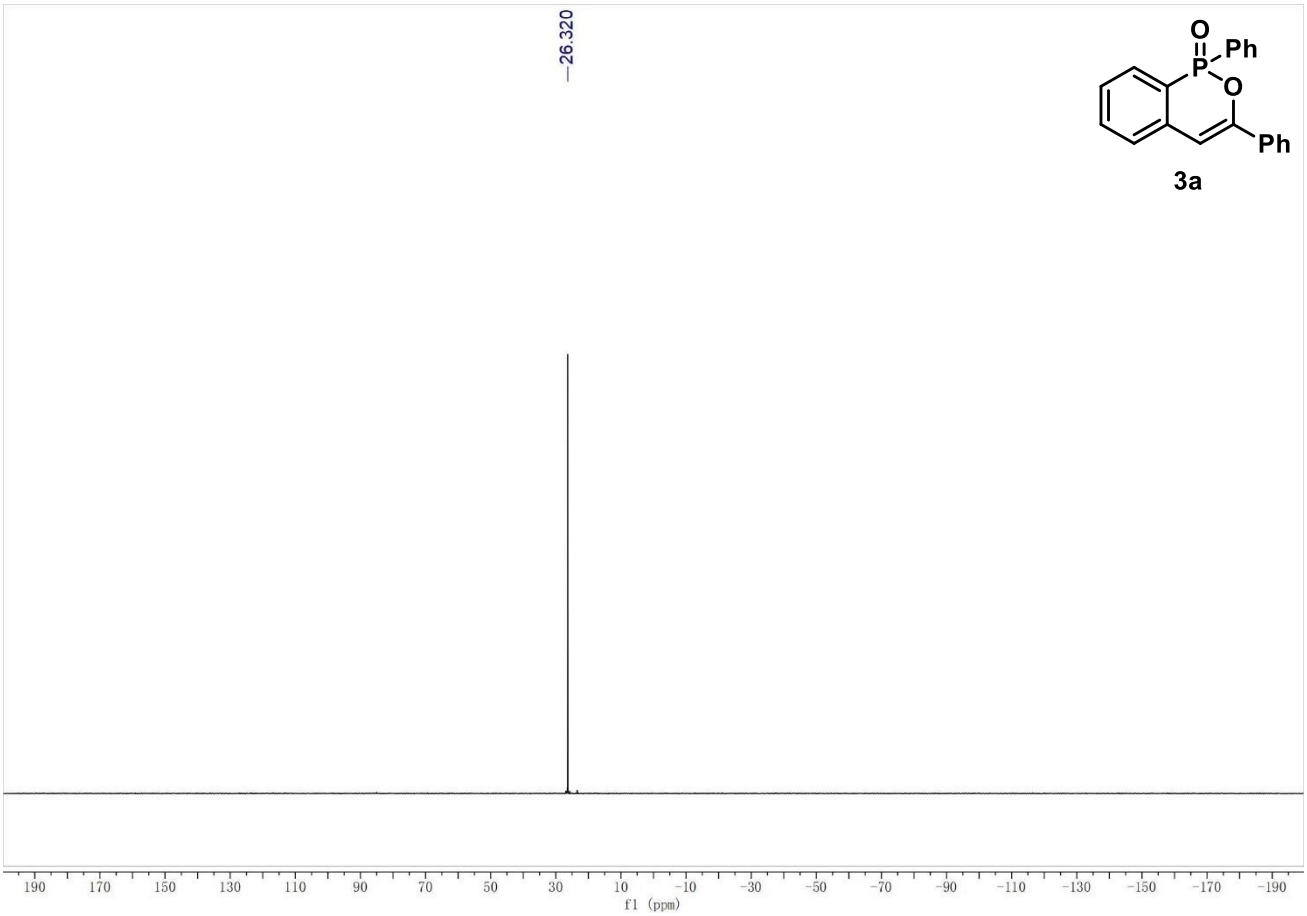


**$^{13}$C NMR spectrum of 3a (75 MHz, $CDCl_3$)**

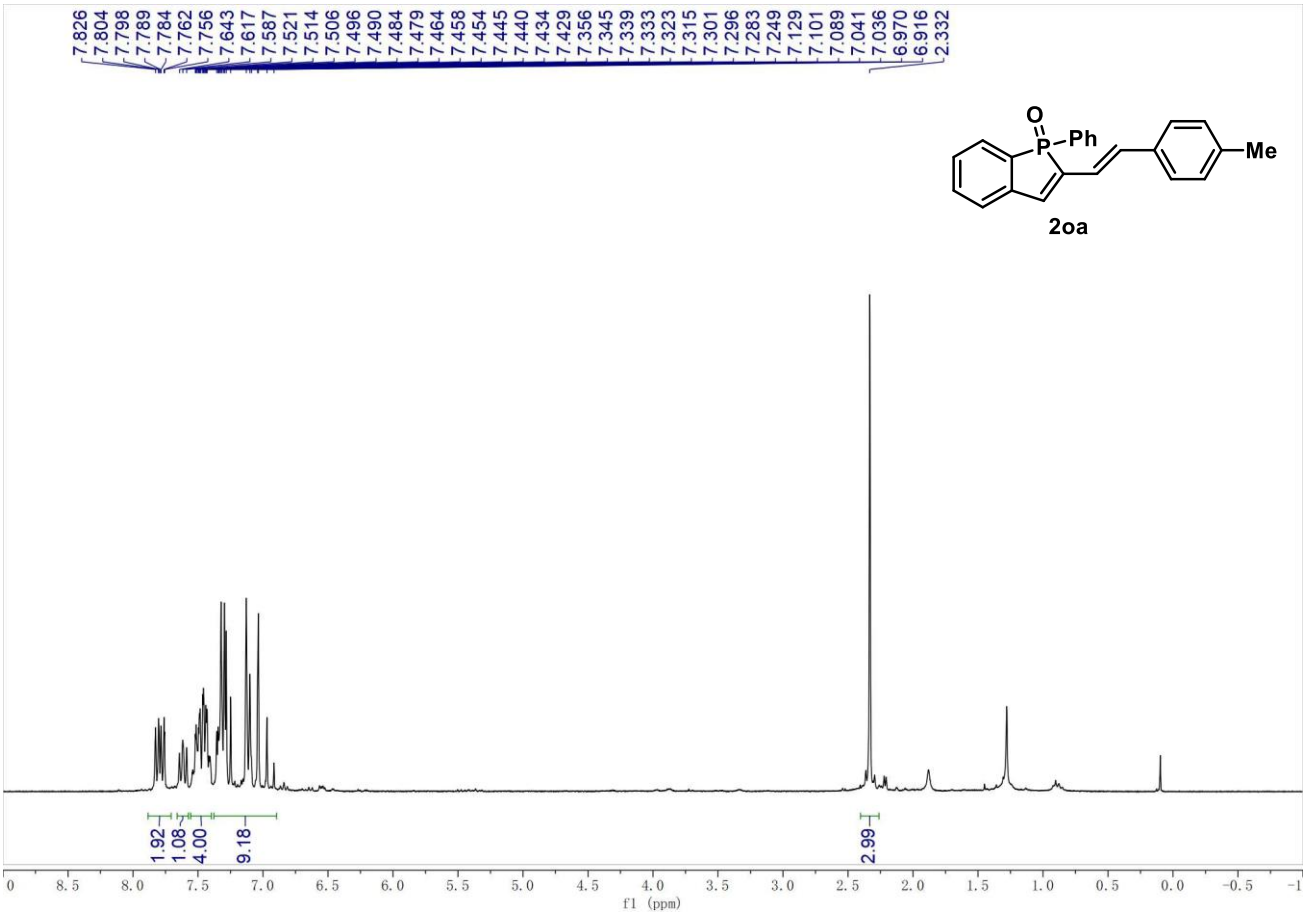


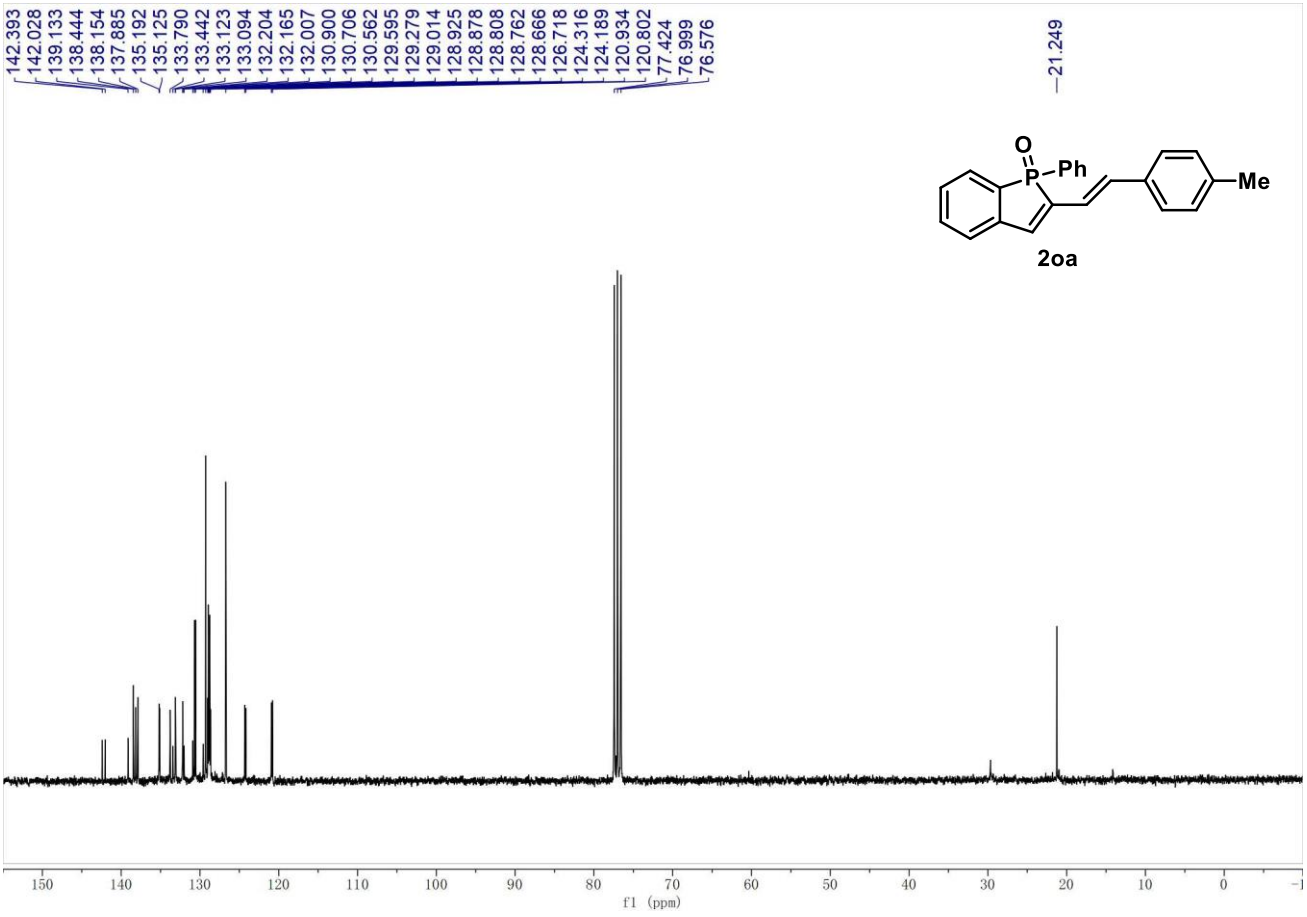
**$^{31}P\{^{1}H\}$ NMR spectrum of 3a (121 MHz, $CDCl_3$)**

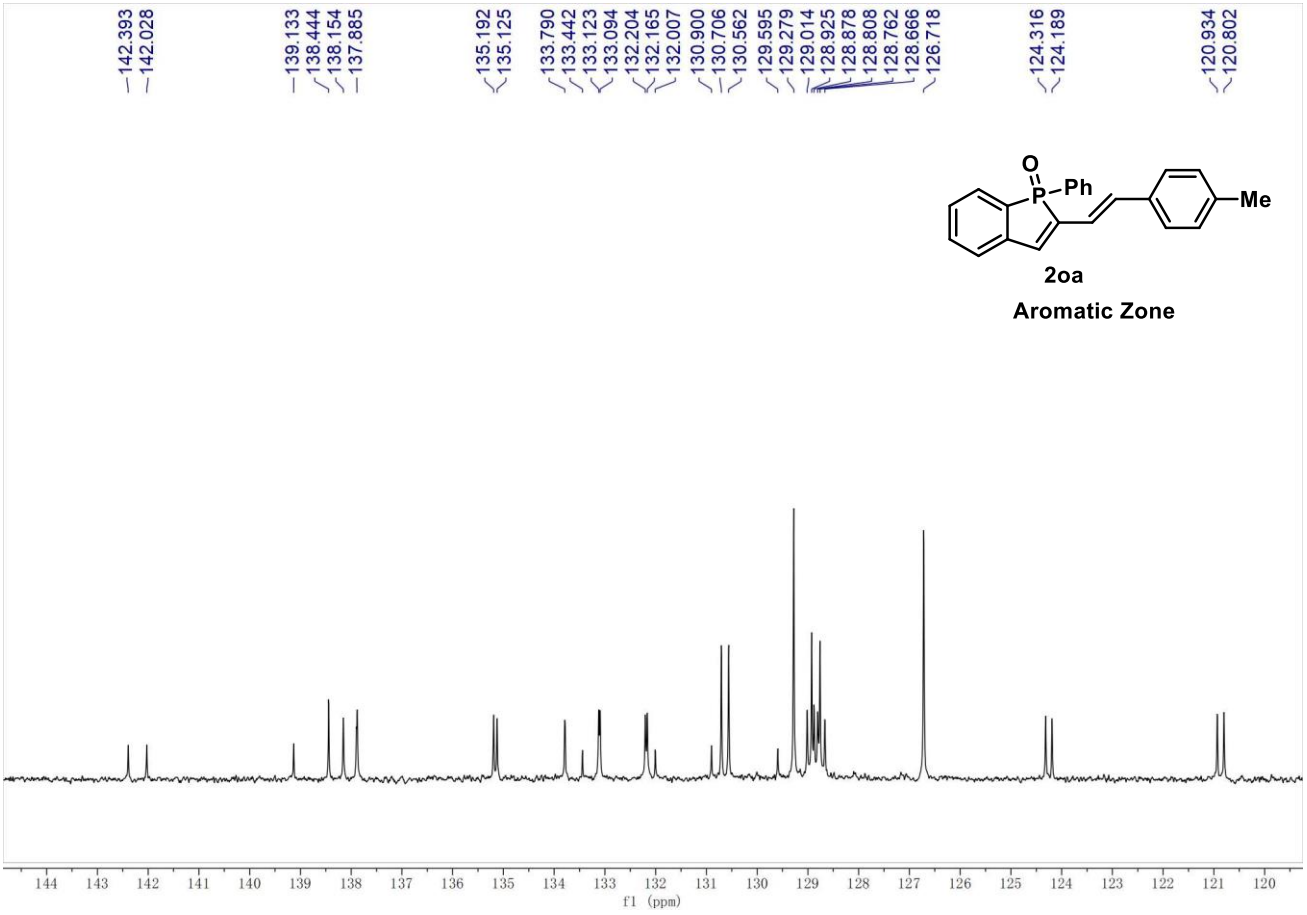



**$^{1}H$ NMR spectrum of 2oa (300 MHz, $CDCl_3$)**

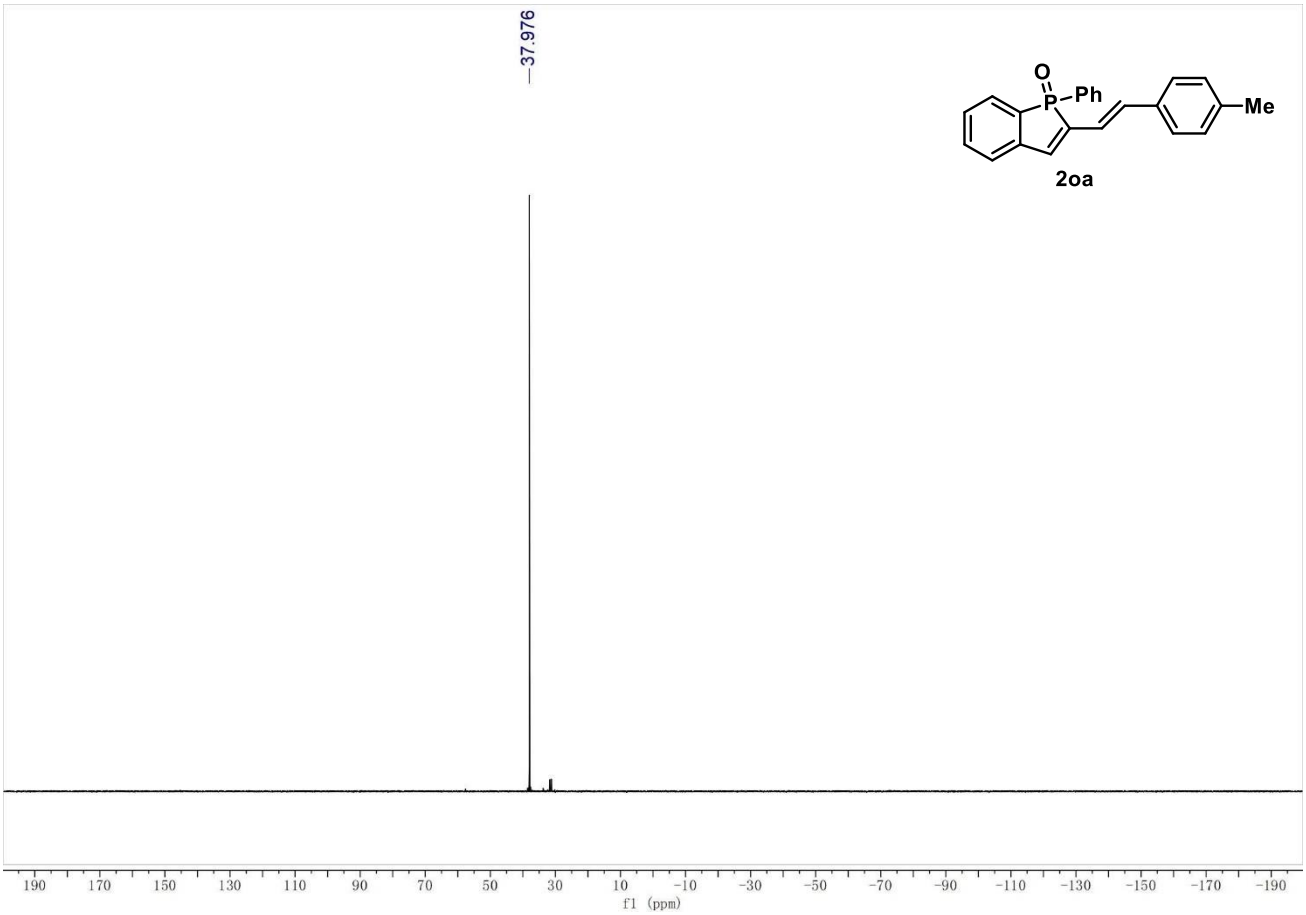


**$^{13}$C NMR spectrum of 2oa (75 MHz, $CDCl_3$)**

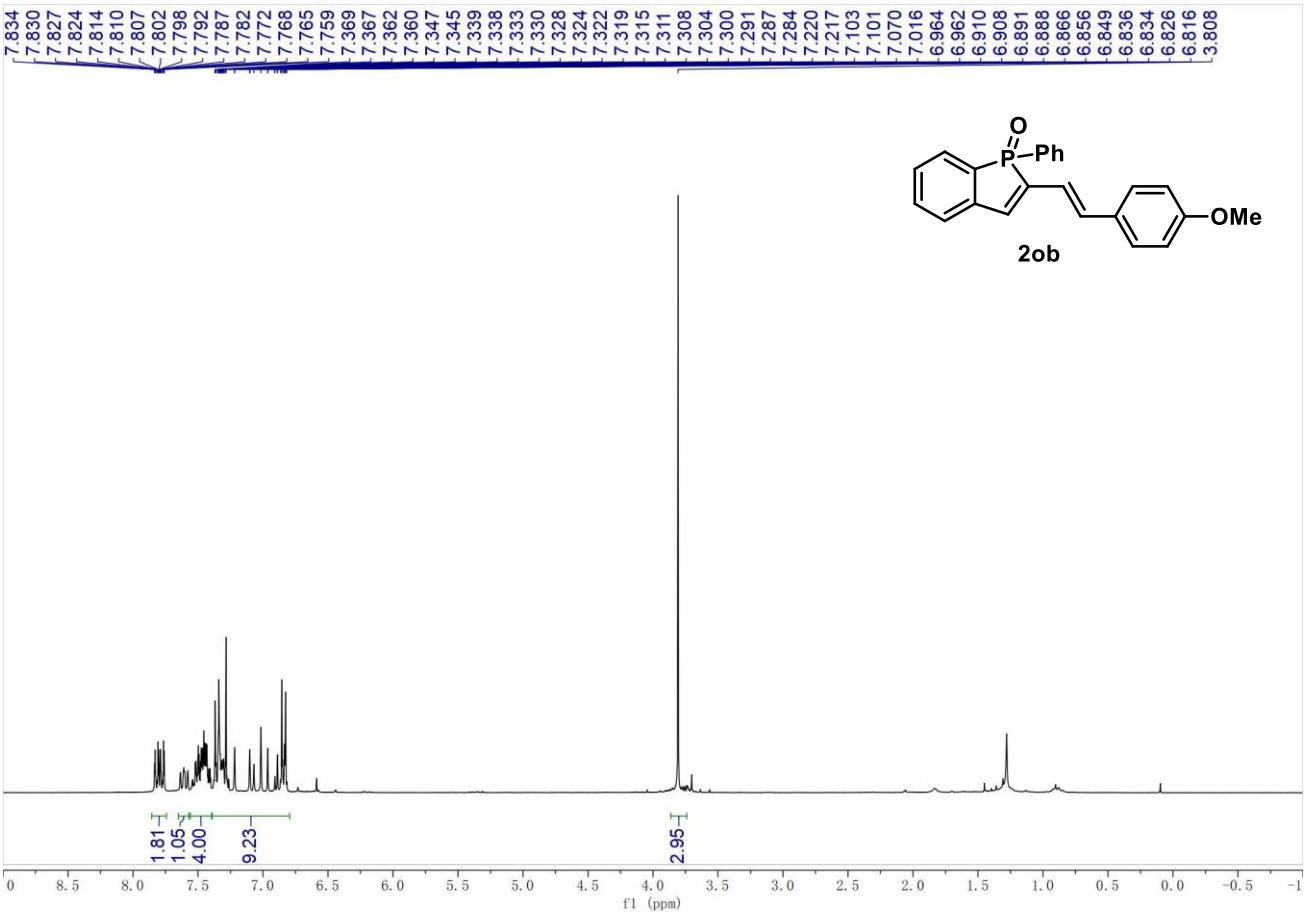


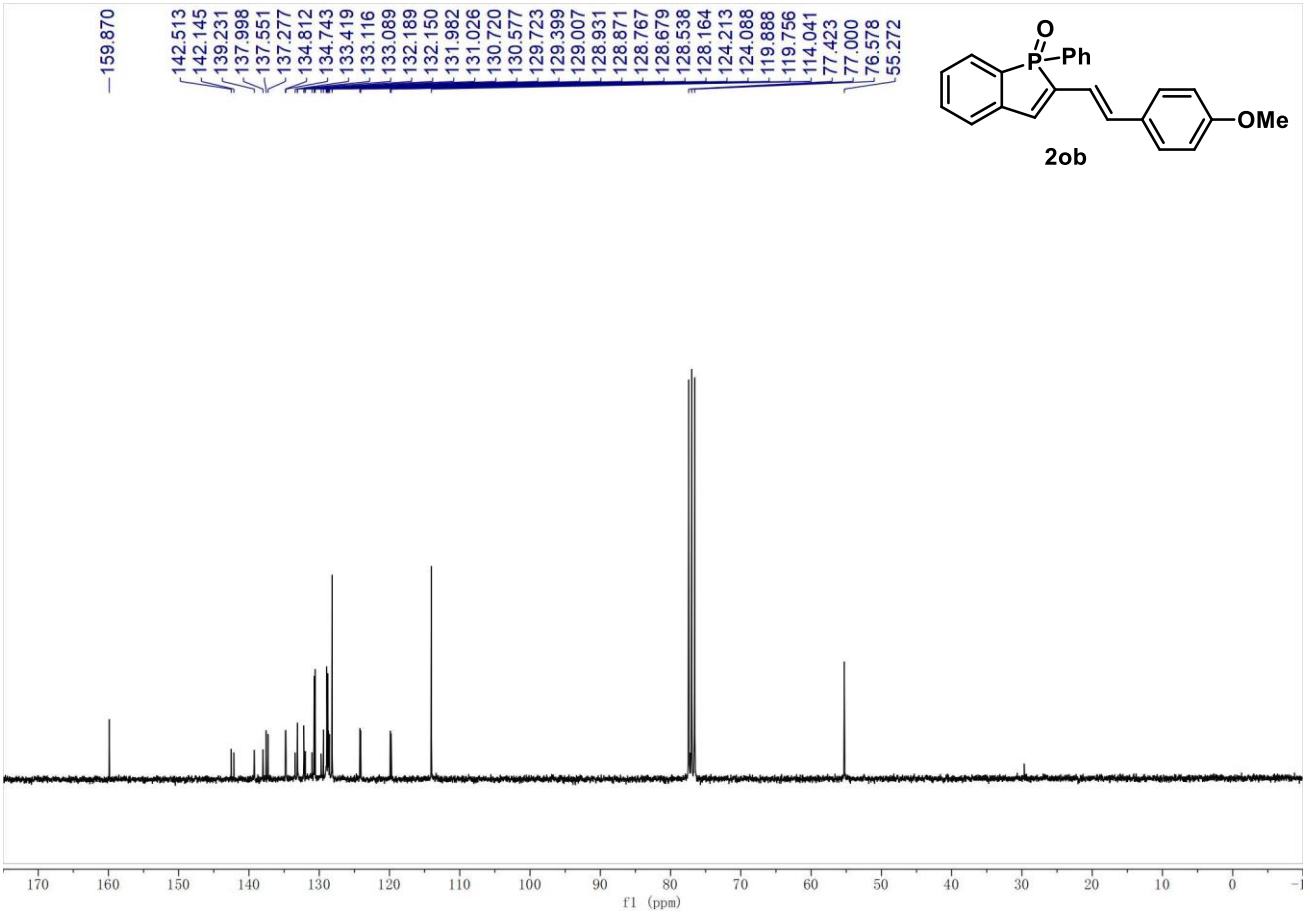
**$^{31}P\{^{1}H\}$ NMR spectrum of 2oa (121 MHz, $CDCl_3$)**

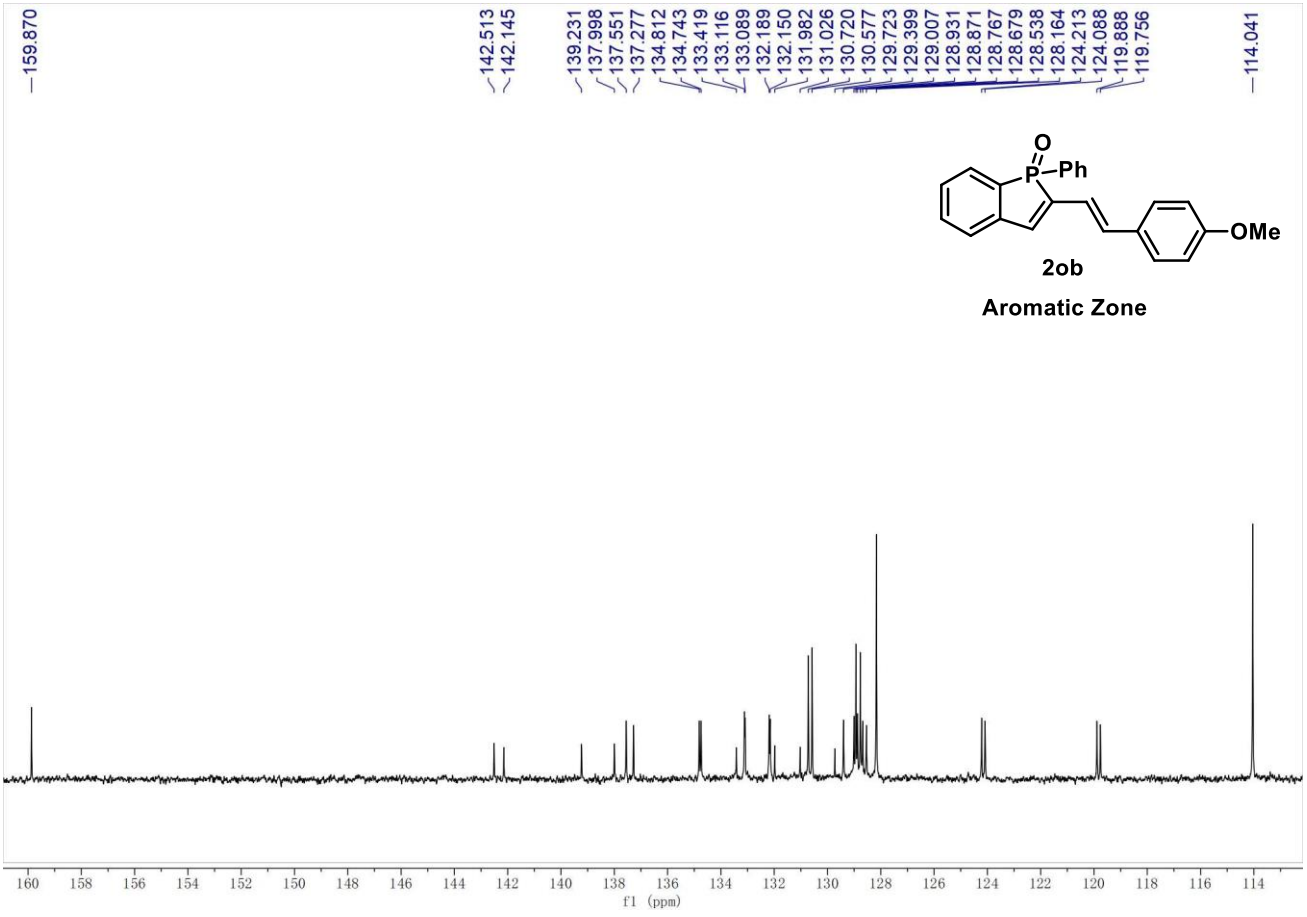



**$^{1}H$ NMR spectrum of 2ob (300 MHz, $CDCl_3$)**

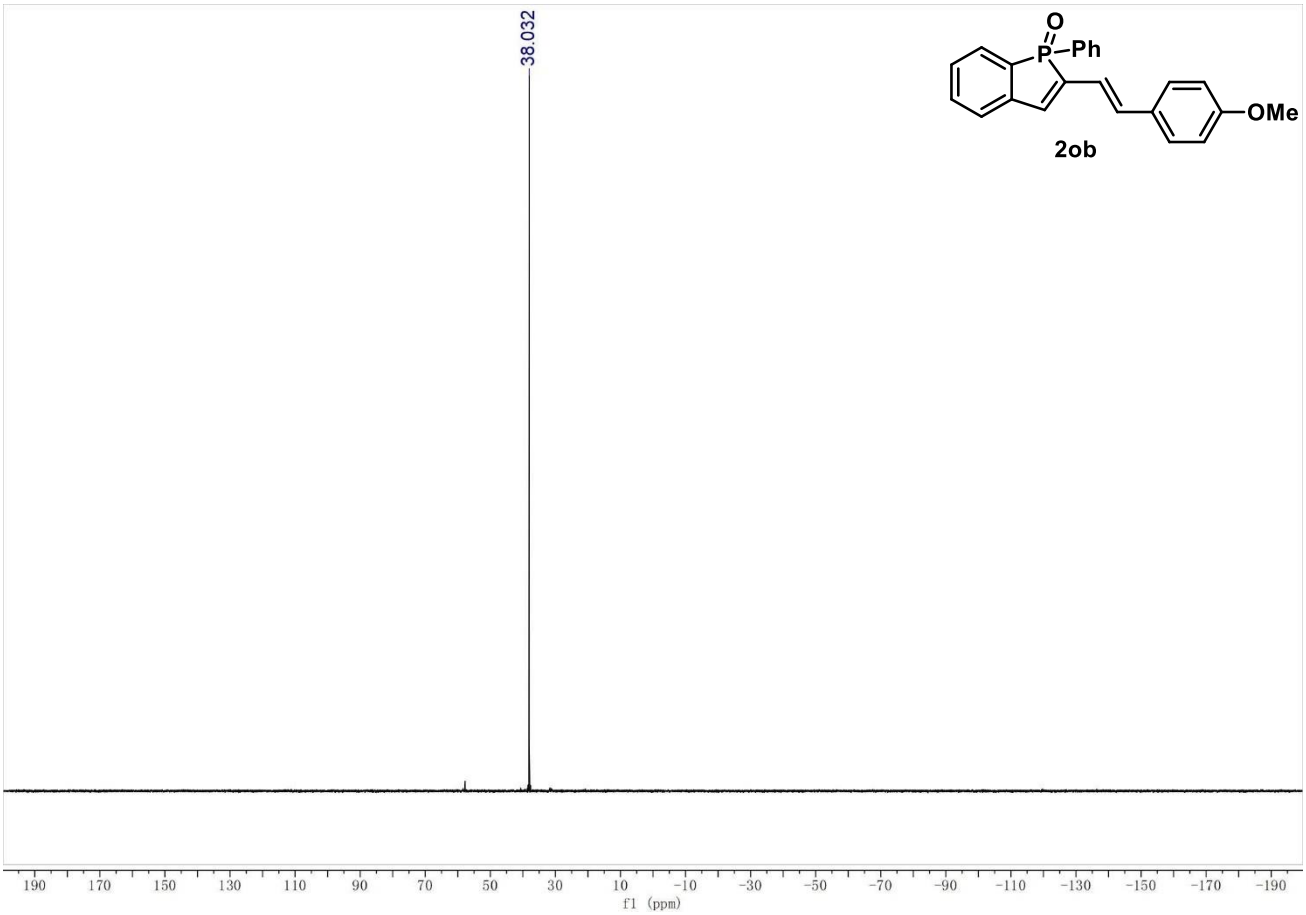


**$^{13}$C NMR spectrum of 2ob (75 MHz, $CDCl_3$)**

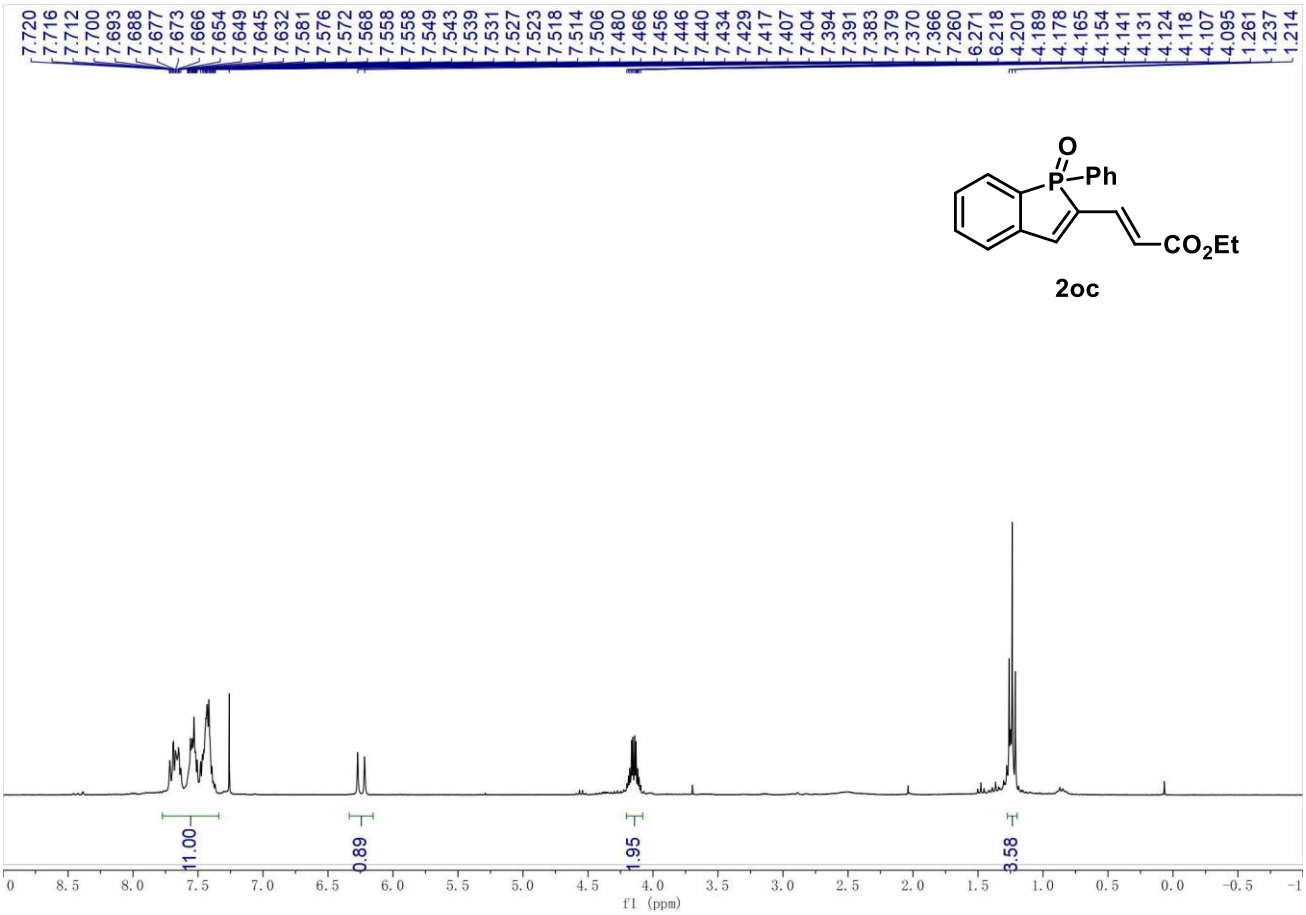


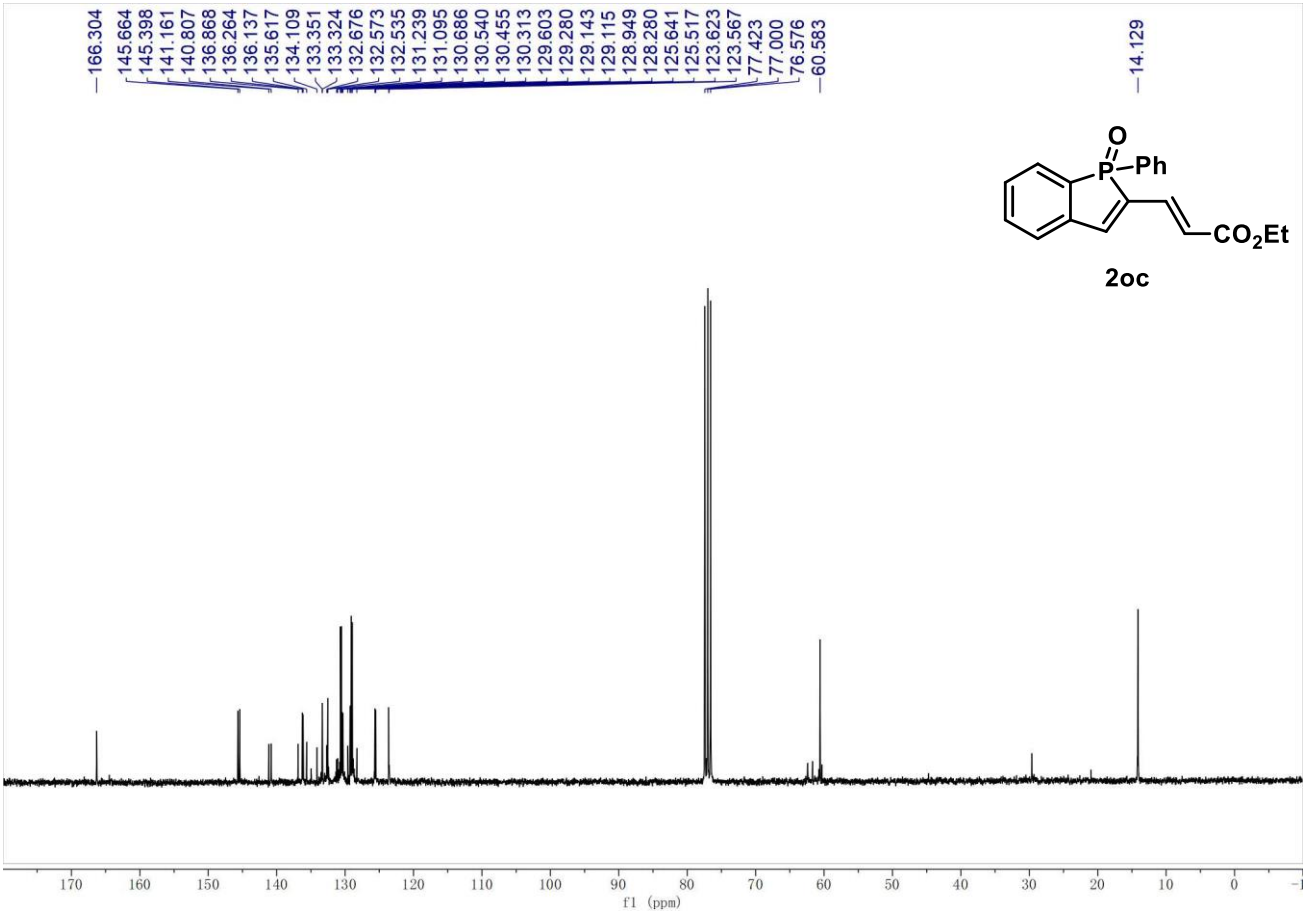
**$^{31}P\{^{1}H\}$ NMR spectrum of 2ob (121 MHz, $CDCl_3$)**

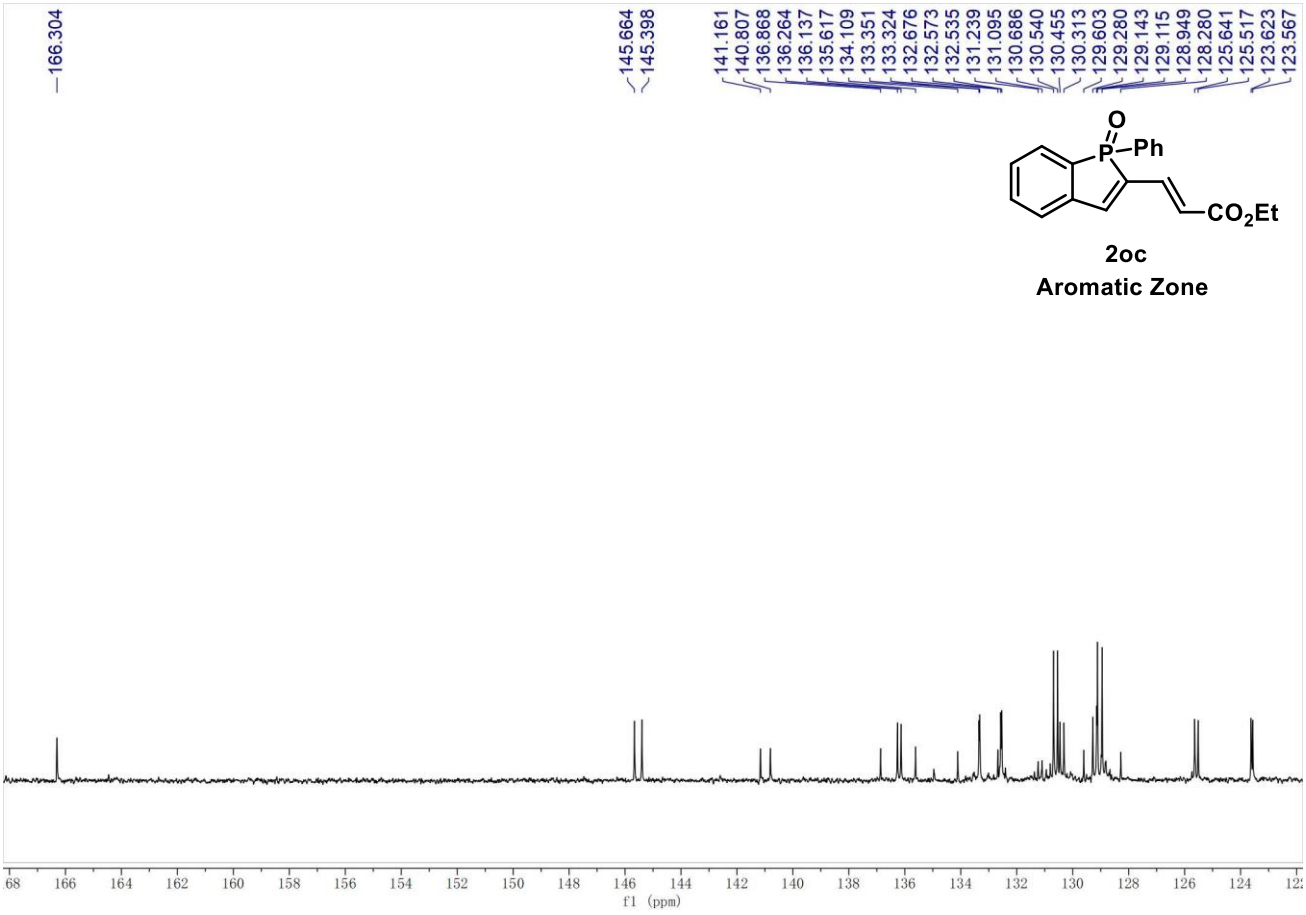



**$^{1}H$ NMR spectrum of 2oc (300 MHz, $CDCl_3$)**



**$^{13}$C NMR spectrum of 2oc (75 MHz, $CDCl_3$)**



**$^{31}P\{^{1}H\}$ NMR spectrum of 2oc (121 MHz, $CDCl_3$)**