Supplementary Information

Barium-Catalyzed C-OH/P-H Dehydrative Cross-coupling for C-P Bond Construction

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1. General Information

Unless otherwise noted, all commercially available compounds were used as received. All solvents were purified according to standard procedures. The ^{1}H NMR and spectra was recorded at 400MHz, ^{13}C NMR was recorded at 101MHz. ^{31}P NMR was recorded at 162 MHz. ^{1}H and ^{13}C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (*J*) are in Hertz (Hz). HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. The starting materials **2a** purchased from *J&K Chemical Ltd* (Shanghai), dibenzo[c,e][1,2]oxaphosphinine 6-oxide and additive KPF_6 were purchased from *Energy Chemical Ltd* (Shanghai). The catalyst $Ba(NTf_2)_2$ was purchased from *Tokyo Chemical Industry* (TCI) (Shanghai) CO., *Ltd*. Other phosphine oxides **2** [1] and allylic alcohols [2] were readily prepared according to the related literatures.

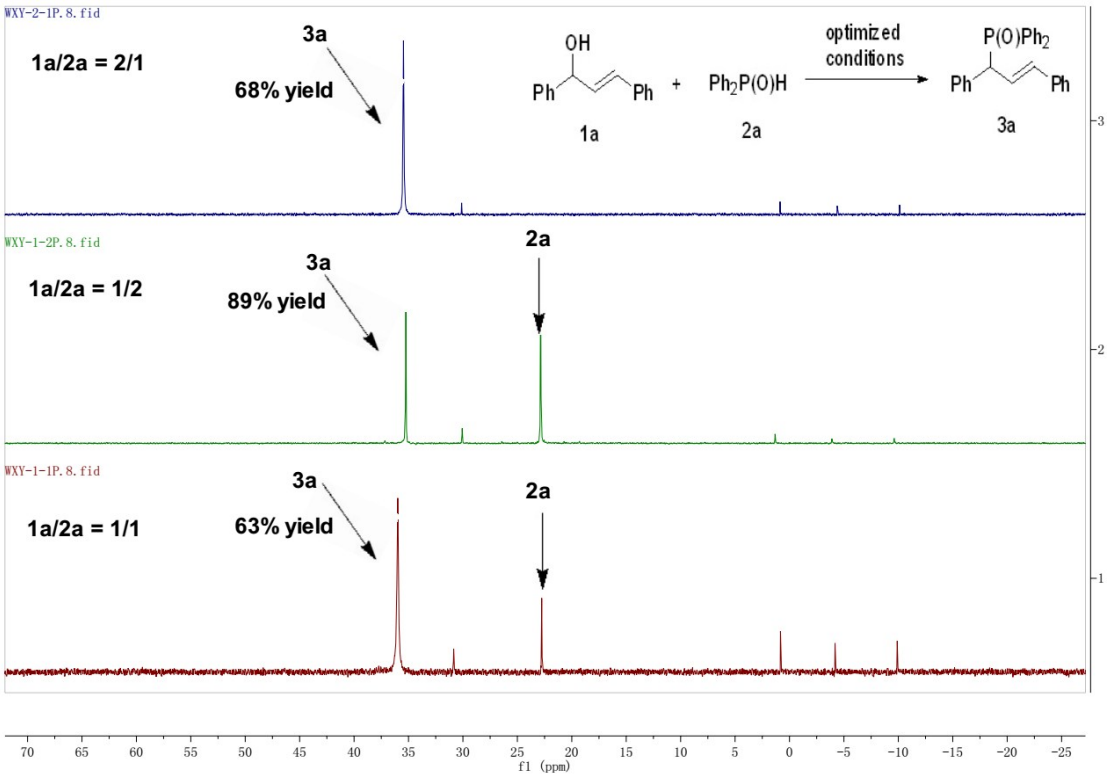
2. General Procedure for The C-OH/P-H Dehydrative Cross-Coupling

Phosphine oxide **2** (0.6 mmol) was added to allylic alcohol **1** (0.3 mmol), $Ba(NTf_2)_2$ (0.03 mmol) and KPF_6 (0.03 mmol) in acetonitrile (2 mL) in Schlenk tube (10 mL). The reaction was stirred at 100 ^{o}C (oil bath) or 30 ^{o}C for 12h. After complete conversion, the residue was purified *via* PTLC (Petroleum ether (bp: 60-90 ^{o}C)/ethyl acetate = 1:1) or column chromatography (Petroleum ether (bp: 60-90 ^{o}C)/ethyl acetate = 1:1) to afford the corresponding products **3a-3af**.

3. Addition Experiments

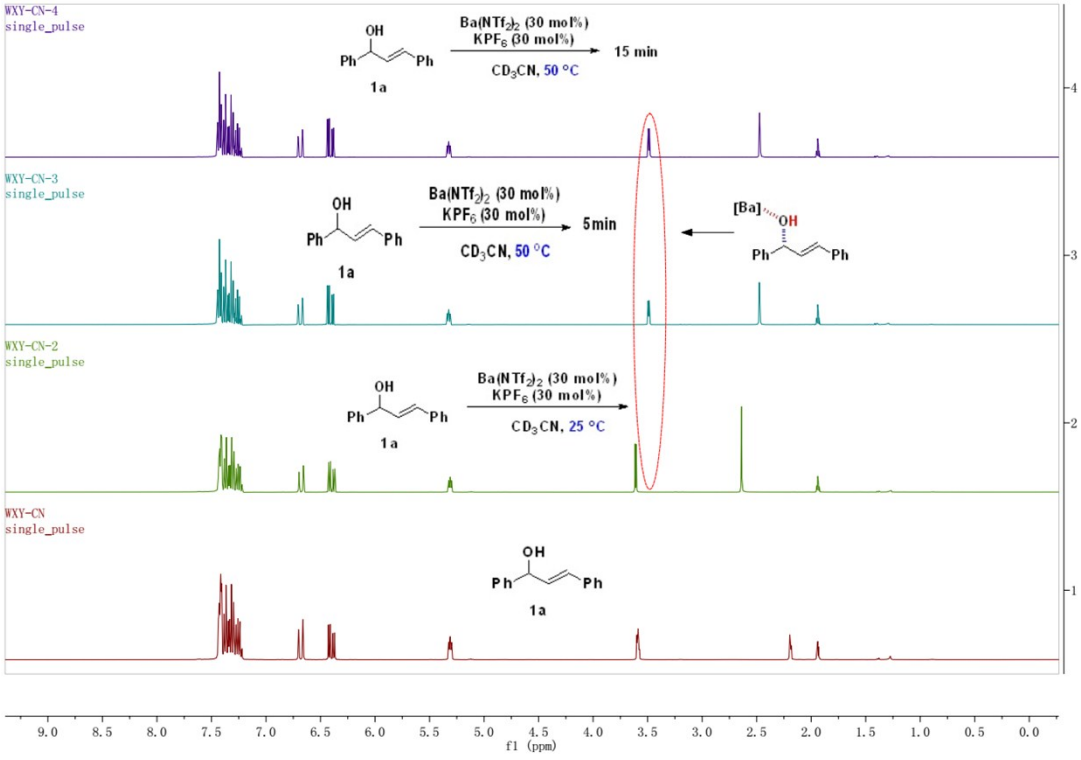
3.1 The role of phosphine oxide in this reaction.

We performed the reaction between **1a** and **2a** in 1/1, 2/1 and 1/2 ratio. The crude ^{31}P NMR was as shown follow. Judging from the crude NMR and TLC investigation, no by-product can be isolated. The ratio of 1a/2a was 1/2 give the best yield. Instead of involved into the reaction, the extra one equivalent of phosphine oxide **2a** still can be detected by NMR, which might be able to promote the reaction through equilibrium system in this reaction.



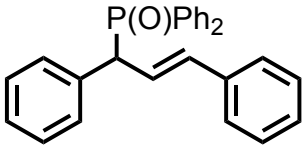
3.2 The interaction between catalyst and allylic alcohols.

we conducted the NMR study by measure the ^{1}H NMR spectra of the mixture of 1a, $Ba(NTf_2)_2$ and KPF_6 in CD_3CN. As is shown in the following picture, the interaction between catalyst and **1a** was obviously, especially at the higher temperature (50 ^oC).



4. Analytical Data for All New Compounds

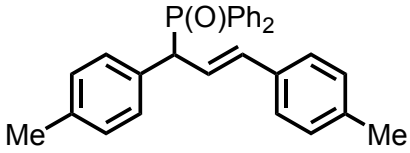
(*E*)-(1,3-diphenylallyl)diphenylphosphine oxide (3a)[3]



Following the general procedure, **3a** was isolated as white solid. Mp: 212-214 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.62 – 7.55 (m, 2H), 7.51 – 7.41 (m, 3H), 7.38 – 7.34 (m, 3H), 7.31 – 7.25 (m, 2H), 7.24 – 7.19 (m, 6H), 7.18 – 7.13 (m, 2H), 6.64 – 6.54 (m, 1H), 6.32 (dd, J = 15.8, 4.8 Hz, 1H), 4.39 (dd, J = 9.8, 9.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 136.81, 136.78, 136.03 (d, $J_{C\text{-}P}$ = 5.9 Hz), 134.55, 134.44, 132.23 (d, $J_{C\text{-}P}$ = 29.5 Hz), 131.89 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.84, 131.76, 131.62 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.46, 131.37, 131.27 (d, $J_{C\text{-}P}$ = 29.7 Hz) 129.59, 129.53, 128.68, 128.66, 128.61, 128.53, 128.50, 128.35, 128.23, 127.71, 127.23 (d, $J_{C\text{-}P}$ = 2.1 Hz), 126.48, 124.70 (d, $J_{C\text{-}P}$ = 7.2 Hz), 52.41 (d, $J_{C\text{-}P}$ = 65.0 Hz). IR (KBr): 3079.55, 3057.34, 3024.68, 1645.32, 1275.42, 764.22, 748.72, 721.94, 692,32. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{27}H_{24}OP$ 395.1565, found 395.1562.

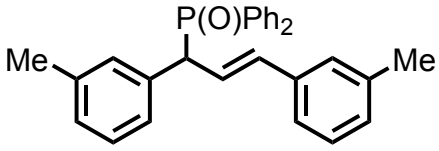
The Procedure for gram scale reaction (3a): Diphenylphosphine oxide (2.02g, 10 mmol) was added to (E)-1,3-diphenylprop-2-en-1-ol (1.05g, 5 mmol), $Ba(NTf_2)_2$ (0.35g, 0.5 mmol) and KPF_6 (0.09g, 0.5 mmol) in acetonitrile (15 ml). The reaction was stirred at 100 °C for 12h. Corresponding (E)-(1,3-diphenylallyl)diphenylphosphine oxide (**3a**) precipitated from the solvent (65% yield, the was purity over 98% by NMR). The solvent was removed under reduced pressure. The residue was purified by silica gel chromatography with Petroleum ether (bp: 60-90 °C)/ethyl acetate = 1:1 to give (E)-(1,3-diphenylallyl)diphenylphosphine oxide (**3a**) as white solid (1.68 g, 85% yield).

(*E*)-(1,3-di-p-tolylallyl)diphenylphosphine oxide (3b)[3]



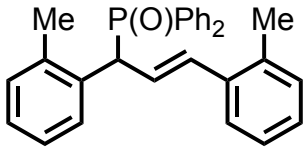
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3b** was isolated as white solid. Mp: 186-187 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.88 – 7.78 (m, 2H), 7.66 – 7.56 (m, 2H), 7.50 – 7.34 (m, 4H), 7.33 – 7.20 (m, 4H), 7.14 – 6.98 (m, 6H), 6.57 – 6.45 (m, 1H), 6.26 (dd, J = 15.7, 3.6 Hz, 1H), 4.34 (dd, J = 9.6, 9.6 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 137.38, 136.70 (d, $J_{C\text{-}P}$ = 2.4 Hz), 134.16, 134.05, 132.92, 132.86, 132.33 (d, $J_{C\text{-}P}$ = 29.4 Hz), 131.78, 131.70, 131.49, 131.44, 131.35, 131.22, 129.34, 129.30, 129.28, 129.12, 128.45, 128.34, 128.25, 128.14, 126.30, 123.68 (d, $J_{C\text{-}P}$ = 7.0 Hz), 51.87 (d, $J_{C\text{-}P}$ = 65.4 Hz) 21.21, 21.11. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.45. IR (KBr): 3005.80, 2989.46, 2921.39, 2853.46, 1632.32, 1275.43, 802.30, 822,85, 764.27, 749.80, 703.74. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{29}H_{28}OP$ 423.1878, found 423.1876.

(*E*)-(1,3-di-m-tolylallyl)diphenylphosphine oxide (3c)[3]



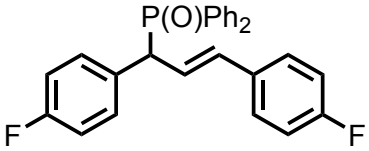
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3c** was isolated as white solid. Mp: 164-167 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.90 – 7.79 (m, 2H), 7.61 – 7.53 (m, 2H), 7.51 – 7.41 (m, 3H), 7.40 – 7.33 (m, 1H), 7.33 – 7.22 (m, 2H), 7.18 – 7.04 (m, 5H), 7.03 – 6.94 (m, 3H), 6.65 – 6.50 (m, 1H), 6.29 (dd, *J* = 15.8, 3.6 Hz, 1H), 4.33 (dd, *J* = 9.5, 9.5 Hz, 1H), 2.27 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 138.13, 137.98, 136.70 (d, $J_{C\text{-}P}$ = 2.2 Hz), 135.89 (d, $J_{C\text{-}P}$ = 5.9 Hz), 134.40, 134.29, 132.29 (d, $J_{C\text{-}P}$ = 33.6 Hz), 131.79, 131.71, 131.45, 131.36, 131.16, 130.17 (d, $J_{C\text{-}P}$ = 5.6 Hz), 128.47, 128.38, 128.30, 128.18, 128.07, 127.88, 127.86, 127.00, 126.48 (d, $J_{C\text{-}P}$ = 5.8 Hz), 124.48 (d, $J_{C\text{-}P}$ = 7.2 Hz), 123.68, 52.33 (d, $J_{C\text{-}P}$ = 65.2 Hz), 21.43, 21.34. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.40. IR (KBr): 3005.23, 2955.52, 2922.56, 1632.32, 1275.35, 764.19, 749.49, 723.82, 703.27. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{29}H_{28}OP$ 423.1878, found 423.1878.

(*E*)-(1,3-di-o-tolylallyl)diphenylphosphine oxide (3d)



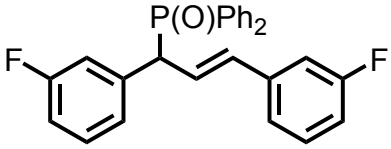
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3d** was isolated as white solid. Mp: 168-170 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.99 – 7.79 (m, 3H), 7.60 – 7.40 (m, 5H), 7.40 – 7.15 (m, 5H), 7.15 – 6.91 (m, 5H), 6.56 – 6.41 (m, 1H), 6.35 (dd, *J* = 15.7, 7.6 Hz, 1H), 4.64 (dd, *J* = 9.5, 9.5 Hz, 1H), 2.14 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 135.94, 135.82 (d, $J_{C\text{-}P}$ = 7.3 Hz), 135.15, 134.43 (d, $J_{C\text{-}P}$ = 5.2 Hz), 132.83, 132.48, 132.37, 131.97, 131.89, 131.83, 131.59, 131.16, 131.08, 130.95, 130.44, 129.98, 129.44 (d, $J_{C\text{-}P}$ = 4.8 Hz), 128.58, 128.46, 128.23, 128.11, 127.51, 127.13, 126.57, 126.01, 125.96, 47.77 (d, $J_{C\text{-}P}$ = 66.1 Hz) 19.79, 19.52. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.90. IR (KBr): 3005.97, 2955.24, 2923.15, 2868.71, 1645.32, 1275.43, 764.13, 748.82, 723.82, 695,97. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{29}H_{28}OP$ 423.1878, found 423.1880.

(*E*)-(1,3-bis(4-fluorophenyl)allyl)diphenylphosphine oxide (3e)[3]



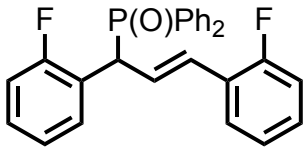
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3e** was isolated as white solid. Mp: 183-187 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.02 – 7.72 (m, 2H), 7.71 – 7.22 (m, 10H), 7.22 – 7.06 (m, 2H), 7.04 – 6.81 (m, 4H), 6.53 – 6.37 (m, 1H), 6.27 (dd, *J* = 15.7, 8Hz, 1H), 4.37 (dd, *J* = 9.2, 9.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 161.96 (d, $J_{C\text{-}F}$ = 246.1 Hz), 162.33 (d, $J_{C\text{-}F}$ = 247.2 Hz), 133.37, 133.26, 132.70, 131.92, 131.65, 131.56, 131.25, 131.16, 131.03, 130.97, 130.89, 128.59, 128.48, 128.37, 128.25, 127.94, 127.86, 124.13 (d, $J_{C\text{-}P}$ = 5.5 Hz), 115.60, 115.48, 115.40, 115.27, 51.24 (d, $J_{C\text{-}P}$ = 65.3 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.33. ^{19}F NMR (376 MHz, Chloroform-*d*) δ = -114.00, -115.03. IR (KBr): 3055.84, 2988.53, 2901.28, 1645.32, 1223.56, 1158.75, 843.19, 818.56, 752.09, 718.92, 705.68, 693.26. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{27}H_{22}F_2OP$ 431.1376, found 431.1376.

(*E*)-(1,3-bis(3-fluorophenyl)allyl)diphenylphosphine oxide (3f)[3]



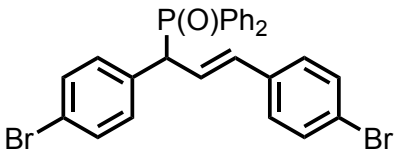
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3f** was isolated as white solid. Mp: 187-190 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.91 – 7.80 (m, 2H), 7.66 – 7.56 (m, 2H), 7.56 – 7.44 (m, 3H), 7.44 – 7.38 (m, 1H), 7.37 – 7.28 (m, 2H), 7.24 – 7.02 (m, 4H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.93 – 6.83 (m, 3H), 6.60 – 6.48 (m, 1H), 6.27 (dd, *J* = 15.8, 3.8 Hz, 1H), 4.36 (dd, *J* = 9.3, 9.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 162.92 (d, J_{C-F} = 245.5 Hz), 162.66 (d, J_{C-F} = 245.0 Hz), 138.75 (dd, *J* = 7.7, 2.4 Hz), 138.17 (dd, *J* = 7.3, 6.1 Hz), 133.59 (dd, *J* = 11.1, 2.6 Hz), 132.03, 131.80, 131.63, 131.54, 131.25, 131.17, 130.75 (d, J_{C-P} = 18.9 Hz), 130.04 (dd, J_{C-P} = 8.5, 1.6 Hz), 129.97, 129.88, 128.64, 128.53, 128.41, 128.29, 125.55 (d, J_{C-P} = 7.4 Hz), 125.14 (d, J_{C-P} = 5.9), 122.20, 116.40 (d, J_{C-P} = 22.3), 114.55 (d, J_{C-P} = 21.3 Hz), 114.23 (d, J_{C-P} = 21.0 Hz), 112.91 (d, J_{C-P} = 21.7 Hz), 51.91 (d, J_{C-P} = 64.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.09. ^{19}F NMR (376 MHz, Chloroform-*d*) δ = -112.26, -113.37. IR (KBr): 3059.11, 2914.73, 1643,43, 1275.42, 1144.02, 748.45, 729.76, 719.73, 700.28. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{27}H_{22}F_2OP$ 431.1376, found 431.1377.

(*E*)-(1,3-bis(2-fluorophenyl)allyl)diphenylphosphine oxide (3g)



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3g** was isolated as white solid. Mp: 193-195 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.06 – 7.78 (m, 3H), 7.74 – 7.28 (m, 9H), 7.21 – 7.06 (m, 3H), 7.06 – 6.80 (m, 3H), 6.69 – 6.56 (m, 1H), 6.51 (dd, *J* = 16.0, 7.9 Hz, 1H), 4.90 (dd, *J* = 7.9, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 159.88 (d, J_{C-F} = 248.0 Hz), 159.68 (d, J_{C-F} = 248.0 Hz), 131.94, 131.71, 131.55, 131.46, 130.95, 130.87, 130.69, 129.07 (d, J_{C-P} = 8.3 Hz), 128.75 (d, J_{C-P} = 8.4 Hz), 128.63, 128.51, 128.32, 128.20, 127.26, 125.83 (dd, $J_{C-F,C-P}$ = 7.3, 3.9 Hz), 124.57, 124.25 (d, J_{C-P} = 11.7 Hz), 124.02 (d, J_{C-P} = 3.4 Hz), 123.21 (dd, $J_{C-F,C-P}$ = 14.5, 4.9 Hz), 115.52 (d, J_{C-P} = 22.0 Hz), 115.11 (d, J_{C-P} = 22.8 Hz), 43.14 (d, J_{C-P} = 65.7 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.90. ^{19}F NMR (376 MHz, Chloroform-*d*) δ = -118.26, -118.48. IR (KBr): 2954.83, 2920.11, 1645.11, 1275.39, 763.46, 750.49, 721.37, 706.04, 695.57. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{27}H_{22}F_2OP$ 431.1376, found 431.1374.

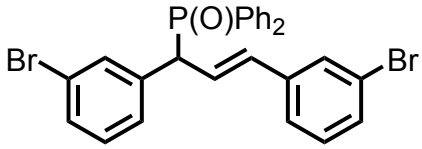
(*E*)-(1,3-bis(4-bromophenyl)allyl)diphenylphosphine oxide (3h)[3]



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3h** was isolated as white solid. Mp: 209-211 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.88 – 7.80 (m, 2H), 7.64 – 7.54 (m, 2H), 7.53 – 7.37 (m, 4H), 7.37 – 7.29 (m, 6H), 7.28 – 7.20 (m, 2H), 7.08 – 6.99 (m, 2H), 6.57 – 6.42 (m, 1H), 6.21 (dd, *J* = 15.8, 3.8 Hz, 1H), 4.33 (dd, *J* = 9.2, 9.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 135.36, 134.82 (d, J_{C-P} = 5.9 Hz), 133.55, 133.44, 132.01, 131.83, 131.80, 131.73, 131.58, 131.52, 131.24, 131.15, 131.10, 131.04, 130.76 (d, J_{C-P} = 13.5 Hz), 128.63, 128.51, 128.46, 128.35, 127.87, 124.90 (d, *J* = 7.3 Hz), 121.61, 121.36, 51.59 (d, J_{C-P} = 64.6 Hz). ^{31}P NMR (162 MHz,

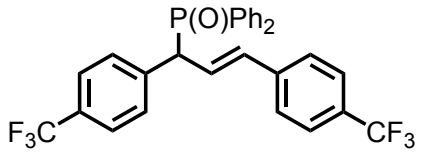
Chloroform-*d*) δ = 30.95. IR (KBr): 2955.24, 2923.37, 2851.80,, 1654.60, 1275.37, 816.03, 749.73, 722.77, 707,41, 546.22, 518.87. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{27}H_{22}Br_2OP$ 550.9775, found 550.9775.

(*E*)-(1,3-bis(3-bromophenyl)allyl)diphenylphosphine oxide (3i)



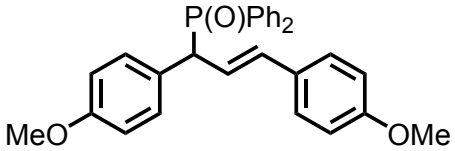
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3i** was isolated as white solid. Mp: 127-129 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.90 – 7.81 (m, 2H), 7.64 – 7.55 (m, 2H), 7.55 – 7.42 (m, 4H), 7.42 – 7.25 (m, 7H), 7.13 – 7.03 (m, 3H), 6.59 – 6.47 (m, 1H), 6.23 (dd, *J* = 15.8, 3.7 Hz, 1H), 4.34 (dd, *J* = 9.2, 9.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 137.44, 136.97 (d, $J_{C\text{-}P}$ = 5.8 Hz), 132.33, 132.22, 131.27, 131.02, 130.81, 130.55, 130.46, 130.20, 130.11, 129.56 (d, $J_{C\text{-}P}$ = 15.9 Hz), 129.57, 129.30 (d, $J_{C\text{-}P}$ = 2.3 Hz), 129.07 (d, $J_{C\text{-}P}$ = 1.9 Hz), 128.93, 128.20, 127.61, 127.49, 127.37, 127.26, 126.92 (d, $J_{C\text{-}P}$ = 5.5 Hz), 124.53 (d, $J_{C\text{-}P}$ = 7.2 Hz), 123.92, 121.59, 121.42, 50.79 (d, $J_{C\text{-}P}$ = 64.2 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.17. IR (KBr): 3053.50, 2919.32, 1642.18, 1275.47, 792.33, 749.04, 721.70, 700,74, 557.48, 513.78. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{27}H_{22}Br_2OP$ 550.9775, found 550.9777.

(*E*)-(1,3-bis(4-(trifluoromethyl)phenyl)allyl)diphenylphosphine oxide (3j)



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3j** was isolated as white solid. Mp: 188-189 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 2H), 7.65 – 7.55 (m, 2H), 7.55 – 7.45 (m, 9H), 7.45 – 7.38 (m, 1H), 7.38 – 7.21 (m, 4H), 6.74 – 6.58 (m, 1H), 6.35 (dd, *J* = 15.8, 3.7 Hz, 1H), 4.48 (dd, *J* = 9.2, 9.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 139.91, 139.79, 133.71 (d, $J_{C\text{-}P}$ = 10.9 Hz), 132.28 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.08 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.69, 131.61, 131.56, 131.43, 131.26, 131.18, 130.59, 130.45, 129.86, 129.80, 129.54, 128.83, 128.72, 128.63, 128.51, 126.73, 126.64, 126.63, 125.63, 125.55, 122.81, 52.27 (d, $J_{C\text{-}P}$ = 63.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.06. ^{19}F NMR (376 MHz, Chloroform-*d*) δ = -62.49. IR (KBr): 3062.97, 2914.48, 1614.36, 1330.53, 1225.68, 1066.33, 847.95, 832.39, 811.19, 720.08. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{29}H_{22}F_6OP$ 531.1312, found 531.1326.

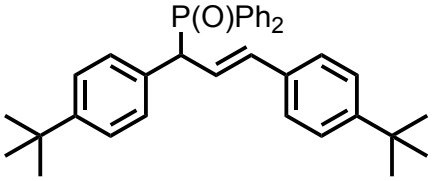
(*E*)-(1,3-bis(4-methoxyphenyl)allyl)diphenylphosphine oxide (3k)



Following the general procedure, the reaction was conducted at 30 °C for 12h. **3k** was isolated as white solid. Mp: 147-149 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.88 – 7.78 (m, 2H), 7.66 – 7.55 (m, 2H), 7.46 – 7.30 (m, 4H), 7.30 – 7.20 (m, 4H), 7.14 – 7.04 (m, 2H), 6.73 – 6.67 (m, 4H), 6.44 – 6.33 (m, 1H), 6.24 (dd, *J* = 15.8, 3.6 Hz, 1H), 4.34 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.71 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 159.14, 158.59 (d, $J_{C\text{-}P}$ = 2.2 Hz), 133.69 (d, $J_{C\text{-}P}$ = 11.4 Hz), 132.25 (d, $J_{C\text{-}P}$ = 30.7 Hz), 131.69, 131.60, 131.47, 131.33, 131.24, 131.14, 130.48, 130.43, 129.50,

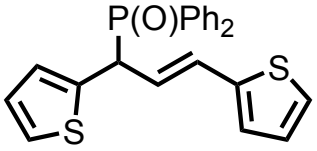
128.47, 128.36, 128.29, 128.17, 127.92 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.52, 122.28 (d, $J_{C\text{-}P}$ = 6.8 Hz), 114.02, 113.79, 55.24, 55.13, 51.13 (d, $J_{C\text{-}P}$ = 66.2 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.80. IR (KBr): 3055.44, 3031.68, 3002.49，2954.91, 2935.35, 1644.69, 1250.82, 829.28, 812.85, 732.68, 720.15. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{29}H_{28}O_3P$ 455.1776, found 455.1779.

(*E*)-(1,3-bis(4-(tert-butyl)phenyl)allyl)diphenylphosphine oxide (3l)



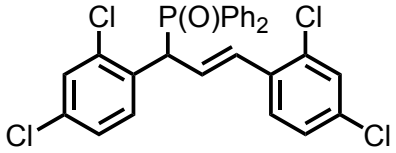
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3l** was isolated as white solid. Mp: 261-264 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.90 – 7.77 (m, 2H), 7.61 – 7.34 (m, 6H), 7.33 – 7.11 (m, 10H), 6.61 – 6.46 (m, 1H), 6.33 (dd, *J* =15.6, 7.8 Hz 1H), 4.35 (dd, *J* = 9.6, 9.6 Hz, 1H), 1.27 (s, 9H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 150.73, 150.02 (d, $J_{C\text{-}P}$ = 2.6 Hz), 134.16, 134.03, 132.86, 132.80, 132.67, 131.96, 131.88, 131.83 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.71, 131.52, 131.43, 131.05, 129.12 (d, $J_{C\text{-}P}$ = 5.7 Hz), 128.58, 128.47, 128.26, 128.14, 126.21, 125.55, 125.44, 124.00 (d, $J_{C\text{-}P}$ = 6.8 Hz), 51.92 (d, $J_{C\text{-}P}$ = 65.4 Hz), 34.66, 34.53, 31.42, 31.37. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.27. IR (KBr): 2962.57, 2929.36, 2906.16, 2866.40, 1646.67, 1266.14, 731.54, 717.99, 706.83. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{35}H_{40}OP$ 507.2817, found 507.2802.

(*E*)-(1,3-di(thiophen-2-yl)allyl)diphenylphosphine oxide (3m)



Following the general procedure, the reaction was conducted at 30 °C for 12h. **3m** was isolated as white solid. Mp: 204-207 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.76 (m, 2H), 7.74 – 7.65 (m, 2H), 7.55 – 7.41 (m, 4H), 7.40 – 7.33 (m, 2H), 7.11 (dd, *J* = 13.7, 5.0 Hz, 2H), 7.04 (s, 1H), 6.93 – 6.84 (m, 2H), 6.80 (d, *J* = 3.2 Hz, 1H), 6.48 (dd, *J* = 15.6, 3.8 Hz, 1H), 6.35 – 6.19 (m, 1H), 4.68 (dd, *J* = 12.3, 8.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 141.36 (d, $J_{C\text{-}P}$ = 3.1 Hz), 136.80 (d, $J_{C\text{-}P}$ = 6.0 Hz), 132.00 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.85 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.78, 131.70, 131.53, 131.44, 130.66 (d, $J_{C\text{-}P}$ = 30.4 Hz), 128.58, 128.46, 128.43, 128.31, 127.67 (d, $J_{C\text{-}P}$ = 10.9 Hz), 127.31, 127.23 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.11 (d, $J_{C\text{-}P}$ = 2.3 Hz), 125.93 (d, $J_{C\text{-}P}$ = 2.1 Hz), 124.97 (d, $J_{C\text{-}P}$ = 2.5 Hz), 124.66, 123.36 (d, $J_{C\text{-}P}$ = 6.7 Hz), 47.06 (d, *J* = 66.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 30.46. IR (KBr): 3104.06, 3054,70, 1636.36, 1275.40, 749.72, 722.10, 695.83. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{23}H_{20}OPS_2$ 407.0693, found 407.0695.

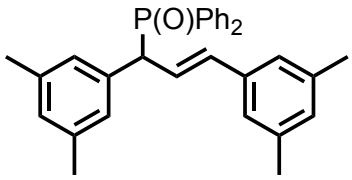
(*E*)-(1,3-bis(2,4-dichlorophenyl)allyl)diphenylphosphine oxide (3n)



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3n** was isolated as white solid. Mp: 160-164 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, J = 8.3, 1.8 Hz, 1H), 7.94 – 7.84 (m, 2H), 7.66 – 7.57 (m, 2H), 7.56 – 7.47 (m, 3H), 7.45 – 7.39 (m, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.22 (m, 3H), 7.12 (dd, J = 8.5, 2.1 Hz, 1H), 6.60 (dd, *J* = 15.7, 3.9 Hz, 1H), 6.42 – 6.30 (m, 1H),

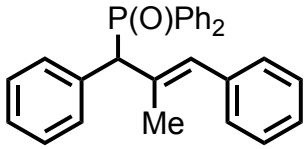
5.07 (dd, J_{H-P} = 8.8, 8.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 134.35, 134.27, 133.98, 133.79 (d, J_{C-P} = 2.4 Hz), 133.44 (d, J_{C-P} = 1.9 Hz), 133.16, 133.13, 132.48 (d, J_{C-P} = 4.2 Hz), 132.22 (d, J_{C-P} = 2.9 Hz), 132.06 (d, J_{C-P} = 2.9 Hz), 131.65, 131.60, 131.55, 131.46, 130.98, 130.66, 130.63, 130.55, 129.31, 128.88, 128.76, 128.57, 128.46, 127.89, 127.25, 126.61 (d, J_{C-P} = 7.4 Hz), 46.89 (d, J_{C-P} = 65.5 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.19. IR (KBr): 3094.36, 3075.78, 3052.29, 2921.75, 1632.75, 1258.72, 773.30, 749.19, 724.75, 699.44. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{27}H_{20}Cl_4OP$ 531.0006, found 531.0008.

(*E*)-(1,3-bis(3,5-dimethylphenyl)allyl)diphenylphosphine oxide (3o)



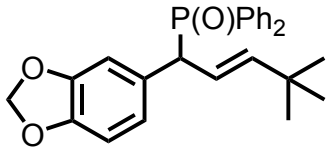
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3o** was isolated as white solid. Mp: 193-196 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.79 (m, 2H), 7.61 – 7.53 (m, 2H), 7.51 – 7.33 (m, 4H), 7.33 – 7.22 (m, 2H), 6.91 (s, 2H), 6.85 (s, 2H), 6.80 (d, J = 8.2 Hz, 2H), 6.65 – 6.50 (m, 1H), 6.25 (dd, *J* = 15.7, 3.8 Hz, 1H), 4.28 (dd, *J* = 9.5, 9.5 Hz, 1H), 2.23 (s, 6H), 2.19 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 137.90 (d, J_{C-P} = 1.8 Hz), 137.84, 136.71 (d, J_{C-P} = 2.4 Hz), 135.82 (d, J_{C-P} = 5.9 Hz), 134.30 (d, J_{C-P} = 11.5 Hz), 132.38 (d, J_{C-P} = 37.3 Hz), 131.82, 131.74, 131.68 (d, J_{C-P} = 2.8 Hz), 131.42 (d, J_{C-P} = 37.2 Hz), 131.51, 131.42, 129.28, 128.75 (d, J_{C-P} = 2.3 Hz), 128.44, 128.32, 128.12, 128.01, 127.23 (d, J_{C-P} = 5.8 Hz), 124.37, 124.30, 52.28 (d, J_{C-P} = 65.3 Hz), 21.30, 21.22. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.48. IR (KBr): 3054.01, 2955.16, 2922.20, 2850.71, 1645.52, 1264.48, 722.77, 703.77. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{31}H_{32}OP$ 451.2191, found 451.2189.

(*E*)-(2-methyl-1,3-diphenylallyl)diphenylphosphine oxide (3p)



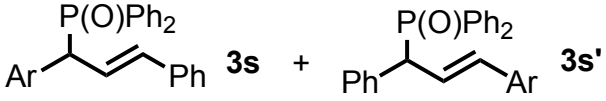
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3p** was isolated as white solid. Mp: 226-229 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.63 – 7.56 (m, 2H), 7.55 – 7.43 (m, 5H), 7.42 – 7.35 (m, 1H), 7.34 – 7.27 (m, 2H), 7.26 – 7.17 (m, 5H), 7.17 – 7.12 (m, 1H), 6.95 (d, *J* = 7.2 Hz, 2H), 6.68 (s, 1H), 4.22 (d, *J* = 8.8 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 137.70, 135.62 (d, J_{C-P} = 4.6 Hz), 134.54 (d, J_{C-P} = 5.8 Hz), 133.36 (d, J_{C-P} = 26.5 Hz), 132.39 (d, J_{C-P} = 24.8 Hz), 131.48 (d, J_{C-P} = 2.7 Hz), 131.34, 131.26, 131.19, 131.10, 130.79 (d, J_{C-P} = 9.2 Hz), 130.19, 130.12, 128.79, 128.42, 128.36, 128.30, 128.17, 127.89, 127.12, 126.33, 56.46 (d, J_{C-P} = 66.6 Hz), 18.07 (d, J_{C-P} = 4.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.46. IR (KBr): 3052.01, 3022.26, 2918.71, 2851.81, 1647.61, 1275.80, 741.66, 722.09, 700.11. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{28}H_{26}OP$ 409.1721, found 409.1712.

(*E*)-(1-(benzo[d][1,3]dioxol-5-yl)-4,4-dimethylpent-1-en-3-yl)diphenylphosphine oxide (3q)



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3q** was isolated as white solid. Mp: 246-248 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.78 (m, 2H), 7.65 – 7.58 (m, 2H), 7.52 – 7.38 (m, 4H), 7.36 – 7.30 (m, 2H), 6.90 (dd, J = 1.6, 1.6 Hz, 1H), 6.72 – 6.68 (m, 1H), 6.63 (d, J = 8.0 Hz, 1H), 5.88 (s, 2H), 5.71 – 5.59 (m, 1H), 5.34 (dd, J = 15.8, 4.3 Hz, 1H), 4.05 (dd, J = 9.3, 9.3 Hz, 1H), 0.79 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*D*) δ = 147.66, 147.00, 146.89, 146.57, 132.70, 132.28, 131.91, 131.82, 131.75, 131.56, 131.53, 131.50, 131.38, 131.32, 131.30, 130.18, 130.11, 128.35, 128.34, 128.24, 122.64, 122.58, 119.49, 119.43, 109.81, 109.75, 108.27, 108.25, 101.00, 52.08, 51.43, 33.28, 29.20, 29.18. ^{13}C NMR (101 MHz, Chloroform-*d*) δ147.65 (d, J = 1.9 Hz), 146.94 (d, $J_{C\text{-}P}$ = 11.0 Hz), 146.57, 132.49 (d, $J_{C\text{-}P}$ = 42.2 Hz), 122.61 (d, $J_{C\text{-}P}$ = 6.7 Hz), 119.46 (d, $J_{C\text{-}P}$ = 6.4 Hz), 109.78 (d, $J_{C\text{-}P}$ = 5.3 Hz), 108.26 (d, $J_{C\text{-}P}$ = 1.9 Hz), 51.76 (d, $J_{C\text{-}P}$ = 65.7 Hz), 29.19 (d, $J_{C\text{-}P}$ = 1.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.31. IR (KBr): 3055.14, 3024.02, 2958.16, 2924.47, 1607.12, 1250.39, 812.61, 752.18, 719.58. HRMS (ESI/[M+H]$^{+}$) Calcd. for:$C_{26}H_{28}O_3P$ 419.1776, found 419.1774.

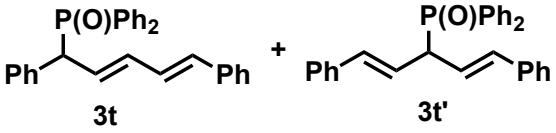
(*E*)-(1-(4-bromophenyl)-3-phenylallyl)diphenylphosphine oxide (3s) and (*E*)-(3-(4-bromophenyl)-1-phenylallyl)diphenylphosphine oxide (3s')



Ar = 4-BrC_6H_4

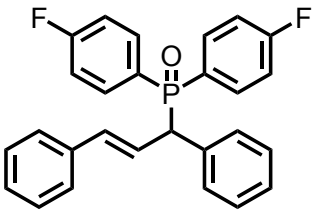
Following the general procedure, the reaction was conducted at 100 °C for 12h. A mixture of **3s** and **3s'** was isolated as white solid, Mp: 178-180 °C. (A trace amount of mixture **3s'/3s = 9/1** was isolated through PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 2:1) for five times, and **3s'** was selected as reference. Then we assign the pick for **3s** and **3s'** by combination of spectrum of DEPT-135 and **3s'** (**^{1}**H NMR, ^{13}C NMR and ^{31}P NMR)). ^{1}H NMR (400 MHz, Chloroform-*d,* mixture of **3s** and **3s'**) δ 7.90 – 7.80 (m, 2H (**3s**) + 2H (**3s'**)), 7.65 – 7.52 (m, 2H (**3s**) + 2H (**3s'**)), 7.52 – 7.40 (m, 2H (**3s**) + 4H (**3s'**)), 7.40 – 7.27 (m, 7H (**3s**) + 4H (**3s'**)), 7.26 – 7.13 (m, 4H (**3s**) + 7H (**3s'**)), 7.07 – 7.01 (m, 2H (**3s**)), 6.63 – 6.54 (m, 1H (**3s**)), 6.54 – 6.46 (m, 1H (**3s'**)), 6.31 (dd, *J* = 15.8, 3.7 Hz, 1H (**3s**)), 6.23 (dd, *J* = 15.8, 3.9 Hz, 1H (**3s'**)), 4.37 (d, *J* = 9.3, 1H (**3s**)), 4.37 (d, *J* = 9.3, 1H (**3s'**)). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 136.54 (d, *J* = 2.2 Hz (**3s'**)), 135.71 (d, *J* = 6.5 Hz (**3s**)), 135.66 (d, *J* = 2.2 Hz (**3s**)), 135.17 (d, *J* = 5.9 Hz (**3s'**)), 134.93 (**3s'**), 134.82 (**3s'**), 133.33 (**3s**), 133.22 (**3s**), 132.05 (**3s'**), 131.86 (**3s'**), 131.83 (**3s'**), 131.75 (**3s'** + **3s**), 131.70 (**3s'** + **3s**), 131.62 (**3s**), 131.42 (**3s**), 131.36 (**3s'**), 131.33 (**3s**), 131.27 (**3s'**), 131.22 (**3s**), 131.18 (**3s'**), 131.12 (**3s'**), 131.08 (d, *J* = 9.8 Hz (**3s**)), 130.87 (d, *J* = 24.6 Hz (**3s'**)), 129.53 (d, *J* = 5.8 Hz (**3s**)), 128.75 (**3s**), 128.70 (**3s'**), 128.66 (**3s**), 128.59 (**3s'**), 128.54 (**3s'**), 128.39 (**3s**), 128.27 (**3s**), 127.99 (d, *J* = 1.4 Hz (**3s**)), 127.89 (**3s'**), 127.35 (d, *J* = 2.1 Hz (**3s**)), 126.47 (d, *J* = 1.4 Hz (**3s** + **3s'**)), 125.55 (d, *J* = 7.5 Hz (**3s**)), 124.03 (d, *J* = 7.0 Hz (**3s'**)), 121.50 (**3s**), 121.32 (**3s'**), 52.38 (d, *J* = 64.6 Hz (**3s**)), 51.64 (d, *J* = 64.7 Hz (**3s'**)). ^{31}P NMR (162 MHz, Chloroform-*d,* mixture of **3s** and **3s'** (**3s**/**3s'** = 1/1)) δ = 32.18 (**3s**), 31.82 (**3s'**). HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{27}H_{23}$BrOP 473.0670, found 473.0674.

((2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)diphenylpiihosphine oxide (3t) and ((1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-yl)diphenylphosphine oxide (3t')



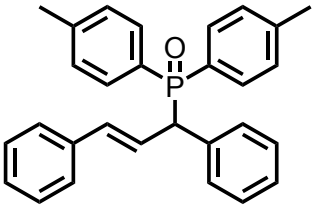
Following the general procedure, the reaction was conducted at 30 °C for 12h. A mixture of **3t** and **3t'** **(3t/3t' = 2/1)** was isolated as white solid. Mp: 181-183 °C. Then the two isomer can be further separated by carefully PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 2:1) for five times, 10 mg **3t'** and 12 mg pure **3t** was obtained to check the NMR. For **3t**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.80 (m, 2H), 7.57 – 7.43 (m, 5H), 7.40 – 7.33 (m, 1H), 7.32 – 7.24 (m, 8H), 7.23 – 7.13 (m, 4H), 6.68 (dd, *J* = 15.6, 9.7 Hz, 1H), 6.32 (dd, *J* = 15.6, 1.6 Hz, 1H), 6.24 – 6.03 (m, 2H), 4.30 (dd, *J* = 10.2, 8.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 137.11 (d, *J* = 1.4 Hz), 135.82 (d, *J* = 6.2 Hz), 134.99, 134.87, 132.51, 132.13 (d, *J* = 33.7 Hz), 131.94, 131.81, 131.73, 131.61, 131.32, 131.00, 129.57, 129.51, 128.66, 128.53, 128.36 (d, *J* = 3.6 Hz), 128.30, 128.22, 128.19, 127.66, 127.22 (d, *J* = 2.4 Hz), 126.40, 52.24 (d, *J* = 65.3 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.00. For **3t':** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 1H), 7.84 – 7.81 (m, 2H), 7.81 – 7.79 (m, 1H), 7.54 – 7.48 (m, 2H), 7.47 – 7.40 (m, 4H), 7.27 – 7.23 (m, 8H), 7.22 – 7.16 (m, 2H), 6.47 – 6.31 (m, 4H), 4.18 – 4.06 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 136.82 (d, *J* = 2.5 Hz), 134.69, 134.58, 132.02, 131.91, 131.76, 131.68, 130.95, 128.64, 128.53, 127.79, 126. 46, 123.15, 123.07, 49.90 (d, *J* = 66.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.28. HRMS (ESI/[M+H]$^+$) Calcd. for:$C_{29}H_{26}OP$ 427.1721, found 427.1721.

(*E*)-(1,3-diphenylallyl)bis(4-fluorophenyl)phosphine oxide (3u)



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3u** was isolated as white solid. Mp: 194-196 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.92 – 7.77 (m, 2H), 7.61 – 7.46 (m, 2H), 7.38 – 7.28 (m, 2H), 7.28 – 7.12 (m, 10H), 7.04 – 6.95 (m, 2H), 6.71 – 6.46 (m, 1H), 6.35 (dd, *J* = 15.8, 3.6 Hz, 1H), 4.33 (dd, *J* = 9.3, 9.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 164.99 (dd, $J_{C\text{-}P,C\text{-}F}$ = 253.6, 3.1 Hz), 164.76 (dd, $J_{C\text{-}P,C\text{-}F}$ = 253.5, 3.1 Hz), 136.44 (d, $J_{C\text{-}P}$ = 2.4 Hz), 135.56 (d, $J_{C\text{-}P}$ = 5.9 Hz), 134.77, 134.65, 134.23, 134.14, 134.05, 133.84, 133.74, 133.65, 129.36 (d, *J* = 5.8 Hz), 128.73, 128.71, 128.52, 127.90 (d, $J_{C\text{-}P}$ = 33.4 Hz), 127.83, 127.38 (d, $J_{C\text{-}P}$ = 2.2 Hz), 126.92 (d, $J_{C\text{-}P}$ = 31.1 Hz), 126.39, 124.07 (d, $J_{C\text{-}P}$ = 7.3 Hz), 116.00, 115.65, 52.60 (d, $J_{C\text{-}P}$ = 66.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 30.32. ^{19}F NMR (376 MHz, Chloroform-*d*) δ = -106.42, -106.67. IR (KBr): 3059.78, 3027.91, 3004.30, 2955.54, 2869.01, 1670.10, 1275.42, 748.44, 724.31. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{27}H_{22}F_2OP$ 431.1376, found 431.1374.

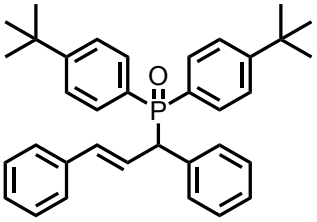
(*E*)-(1,3-diphenylallyl)di-p-tolylphosphine oxide (3v)



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3v** was isolated as white solid. Mp: 219-220 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.75 – 7.67 (m, 2H), 7.50 – 7.40 (m, 2H), 7.39 – 7.31 (m, 2H), 7.27 – 7.19 (m, 8H), 7.18 – 7.13 (m, 2H), 7.12 – 7.03 (m, 2H), 6.67 – 6.53 (m, 1H), 6.33 (dd, *J* = 15.8, 3.5 Hz, 1H), 4.34 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.35 (s, 3H), 2.27 (s, 3H).

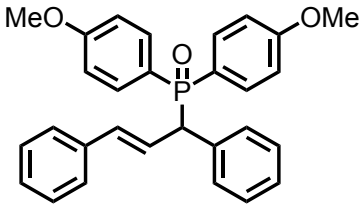
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 142.08 (d, J_{C-P} = 2.6 Hz), 141.80 (d, J_{C-P} = 2.6 Hz), 136.84 (d, J_{C-P} = 2.2 Hz), 136.25 (d, J_{C-P} = 5.8 Hz), 134.16 (d, J_{C-P} = 11.3 Hz), 131.76, 131.67, 131.39, 131.30, 129.52 (d, J_{C-P} = 5.6 Hz), 129.28, 129.24, 129.12, 128.98, 128.86, 128.52, 128.41, 127.90, 127.53, 127.02 (d, J_{C-P} = 2.1 Hz), 126.40, 125.00 (d, J_{C-P} = 7.0 Hz), 52.47 (d, J_{C-P} = 65.0 Hz), 21.62, 21.55. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.72. IR (KBr): 3080.97, 3057.63, 3025.30, 3004.65, 2988.95, 2919.17, 1656.75, 1275.53, 747.87, 721.95. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{29}H_{28}OP$ 423.1878, found 423.1878.

(*E*)-bis(4-(tert-butyl)phenyl)(1,3-diphenylallyl)phosphine oxide (3w)



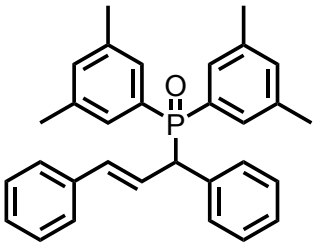
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3w** was isolated as white solid. Mp: 248-249 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.80 – 7.66 (m, 2H), 7.54 – 7.42 (m, 4H), 7.38 – 7.27 (m, 4H), 7.25 – 7.12 (m, 8H), 6.68 – 6.48 (m, 1H), 6.34 – 6.17 (m, 1H), 4.34 (dd, *J* = 9.4, 9.4 Hz, 1H), 1.30 (s, 9H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.02 (d, J_{C-P} = 2.8 Hz), 154.79 (d, J_{C-P} = 2.8 Hz), 136.92, 136.35 (d, J_{C-P} = 5.8 Hz), 134.15 (d, J_{C-P} = 11.2 Hz), 131.69, 131.60, 131.31, 131.22, 129.52 (d, J_{C-P} = 5.7 Hz), 129.13 (d, J_{C-P} = 34.2 Hz), 128.46, 128.38, 128.15 (d, J_{C-P} = 34.0 Hz), 127.48, 126.98, 126.37, 125.44, 125.32, 125.20, 125.15, 125.08, 52.59 (d, J_{C-P} = 64.9 Hz), 34.98, 34.88, 31.15, 31.08. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.66. IR (KBr): 3080.80, 3060.65, 3026.27, 2867.81, 1663.72, 1268.66, 825.48, 745.04, 699,51. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{35}H_{40}OP$ 507.2817 found 507.2817.

(*E*)-(1,3-diphenylallyl)bis(4-methoxyphenyl)phosphine oxide (3x)



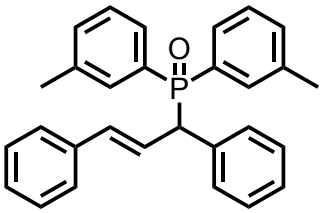
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3x** was isolated as white solid. Mp: 223-226 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.78 – 7.67 (m, 2H), 7.52 – 7.40 (m, 2H), 7.38 – 7.28 (m, 2H), 7.28 – 7.11 (m, 8H), 7.02 – 6.91 (m, 2H), 6.85 – 6.73 (m, 2H), 6.65 – 6.50 (m, 1H), 6.34 (dd, *J* = 3.8, 0.9 Hz, 1H), 4.29 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 162.21 (d, J_{C-P} = 2.9 Hz), 161.97 (d, J_{C-P} = 2.8 Hz), 136.83, 136.34 (d, J_{C-P} = 5.8 Hz), 134.08 (d, J_{C-P} = 11.3 Hz), 133.61, 133.51, 133.24, 133.14, 129.51, 129.45, 128.52, 128.42, 127.52, 127.02, 126.39, 126.38, 125.09 (d, J_{C-P} = 7.1 Hz), 123.61 (d, J_{C-P} = 56.5 Hz), 122.58 (d, J_{C-P} = 56.6 Hz), 114.01, 113.89, 113.76, 113.63, 55.30, 55.22, 52.89 (d, *J* = 65.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 31.43. IR (KBr): 3058.34, 3025.82, 2962.21, 2905.86, 1645.20, 1251.56, 825.00, 801.23, 726.66, 728.87. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{29}H_{28}O_3P$ 455.1776, found 455.1776.

(*E*)-bis(3,5-dimethylphenyl)(1,3-diphenylallyl)phosphine oxide (3y)



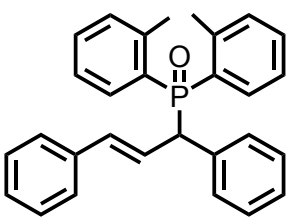
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3y** was isolated as white solid. Mp: 209-211 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.47 – 7.40 (m, 2H), 7.39 – 7.33 (m, 2H), 7.27 – 7.19 (m, 6H), 7.19 – 7.13 (m, 4H), 7.10 (s, 1H), 6.99 (s, 1H), 6.64 – 6.50 (m, 1H), 6.30 (dd, *J* = 15.8, 3.8 Hz, 1H), 4.33 (dd, *J* = 9.5, 9.5 Hz, 1H), 2.30 (s, 6H), 2.20 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 138.02, 137.90, 137.75, 137.62, 136.87 (d, J_{C-P} = 2.5 Hz), 136.26 (d, J_{C-P} = 6.0 Hz), 134.26, 134.15, 133.43 (d, J_{C-P} = 2.9 Hz), 133.17 (d, J_{C-P} = 2.9 Hz), 131.84 (d, J_{C-P} = 27.4 Hz), 130.89 (d, J_{C-P} = 27.6 Hz), 129.58, 129.53, 129.43, 129.34, 129.06, 128.98, 128.46, 128.37, 127.48, 126.99 (d, J_{C-P} = 2.4 Hz), 126.39, 125.03 (d, J_{C-P} = 7.1 Hz), 52.33 (d, J_{C-P} = 64.3 Hz), 21.37, 21.25. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.03. IR (KBr): 3057.14, 3024.09, 2954.84, 2920.54, 2853.57, 1645.20, 1274.09, 750.00, 727.98, 699,89. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{31}H_{32}OP$ 451.2191, found 451.2193.

(*E*)-(1,3-diphenylallyl)di-m-tolylphosphine oxide (3z)



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3z** was isolated as white solid. Mp: 171-173 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 11.4 Hz, 1H), 7.59 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.41 – 7.27 (m, 6H), 7.25 – 7.20 (m, 6H), 7.20 – 7.14 (m, 4H), 6.63 – 6.51 (m, 1H), 6.30 (dd, *J* = 15.7, 3.7 Hz, 1H), 4.34 (dd, *J* = 9.1, 9.1 Hz, 1H), 2.34 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 138.46, 138.35, 138.18, 138.07, 136.85 (d, J_{C-P} = 2.5 Hz), 136.13 (d, J_{C-P} = 5.9 Hz), 134.45, 134.34, 132.71, 132.63, 132.38, 132.28, 132.20, 131.96 (d, J_{C-P} = 31.9 Hz), 131.00 (d, J_{C-P} = 31.9 Hz), 129.61, 129.55, 128.59, 128.48, 128.35, 128.26, 128.17, 128.08, 127.95, 127.63, 127.15 (d, J_{C-P} = 2.4 Hz), 126.48, 124.84 (d, J_{C-P} = 7.3 Hz), 52.44 (d, J_{C-P} = 64.9 Hz), 21.52, 21.40. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.52. IR (KBr): 3024.29, 2917.75, 2850.05, 1645.20, 1275.85, 747.41, 732.91. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{29}H_{28}OP$ 423.1878, found 423.1862.

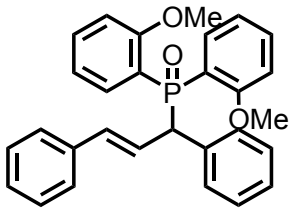
(*E*)-(1,3-diphenylallyl)di-o-tolylphosphine oxide (3aa)



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3aa** was isolated as white solid. Mp: 170-173 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.84 – 7.72 (m, 1H), 7.51 – 7.31 (m, 4H), 7.31 – 7.13 (m, 11H), 7.09 – 6.96 (m, 2H), 6.87 – 6.70 (m, 1H), 6.54 – 6.44 (m, 1H), 4.52 (dd,

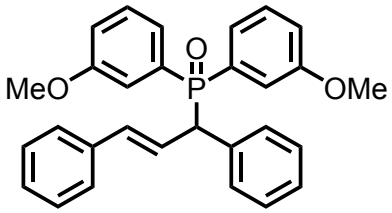
J = 8.6, 8.6 Hz, 1H), 2.37 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 143.15 (d, $J_{C\text{-}P}$ = 7.2 Hz), 142.65 (d, $J_{C\text{-}P}$ = 7.7 Hz), 137.09 (d, $J_{C\text{-}P}$ = 5.4 Hz), 136.96 (d, $J_{C\text{-}P}$ = 1.6 Hz), 134.31, 134.20, 132.16, 132.04, 132.01, 131.94, 131.70, 131.64, 131.61, 131.59, 131.41, 131.38, 130.88 (d, $J_{C\text{-}P}$ = 38.8 Hz), 129.74, 129.69, 128.55, 127.70, 127.09 (d, $J_{C\text{-}P}$ = 2.2 Hz), 126.51, 125.81 (d, $J_{C\text{-}P}$ = 6.3 Hz), 125.35 (d, $J_{C\text{-}P}$ = 11.8 Hz), 125.14 (d, $J_{C\text{-}P}$ = 12.1 Hz), 50.80 (d, $J_{C\text{-}P}$ = 65.7 Hz), 21.43 (d, $J_{C\text{-}P}$ = 3.8 Hz), 21.13 (d, $J_{C\text{-}P}$ = 3.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 35.66. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{29}H_{27}OP$ 423.1878, found 423.1865.

(*E*)-(1,3-diphenylallyl)bis(2-methoxyphenyl)phosphine oxide (3ab)



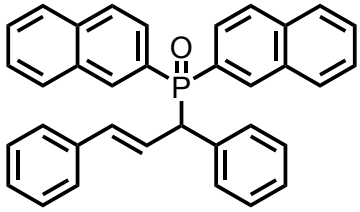
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3ab** was isolated as white solid. Mp: 181-182 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, J = 12.8, 7.6 Hz, 1H), 7.61 (dd, J = 13.0, 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.38 (dd, J = 8.4, 8.4 Hz, 1H), 7.32 – 7.03 (m, 9H), 6.97 (dd, J = 7.5, 7.5 Hz, 1H), 6.87 – 6.64 (m, 4H), 6.46 (dd, J = 15.8, 2.6 Hz, 1H), 4.97 (dd, $J_{H\text{-}P}$ = 10.6, 10.6 Hz, 1H), 3.69 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 160.35 (d, $J_{C\text{-}P}$ = 3.4 Hz), 159.95 (d, $J_{C\text{-}P}$ = 3.4 Hz), 138.09 (d, $J_{C\text{-}P}$ = 5.7 Hz), 137.45 (d, $J_{C\text{-}P}$ = 2.0 Hz), 134.62 (d, $J_{C\text{-}P}$ = 6.2 Hz), 134.30 (d, $J_{C\text{-}P}$ = 6.2 Hz), 133.35, 133.16, 132.77 (d, $J_{C\text{-}P}$ = 12.5 Hz), 129.46, 129.40, 128.46, 128.26, 127.32, 127.19 (d, $J_{C\text{-}P}$ = 6.7 Hz), 126.70, 126.68, 126.42, 126.41, 121.80 (d, J = 13.7 Hz), 120.83 (d, $J_{C\text{-}P}$ = 14.1 Hz), 120.76 (d, $J_{C\text{-}P}$ = 11.1 Hz), 120.45 (d, $J_{C\text{-}P}$ = 11.1 Hz), 110.98 (d, $J_{C\text{-}P}$ = 6.8 Hz), 110.51 (d, $J_{C\text{-}P}$ = 6.8 Hz), 55.51, 55.27, 51.09 (d, $J_{C\text{-}P}$ = 69.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 33.22. IR (KBr): 3060.19, 3024.40, 2966.46, 2937.53, 1645.32, 1274.32, 800.76, 749.01, 726.76. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{29}H_{28}O_3P$ 455.1776, found 455.1771.

(*E*)-(1,3-diphenylallyl)bis(3-methoxyphenyl)phosphine oxide (3ac)



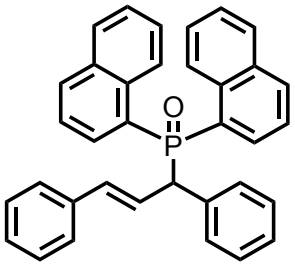
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3ac** was isolated as white solid. Mp: 173-175 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 5H), 7.26 – 7.15 (m, 9H), 7.14 – 7.00 (m, 3H), 6.95 – 6.88 (m, 1H), 6.66 – 6.55 (m, 1H), 6.34 (dd, J = 15.8, 3.8 Hz, 1H), 4.33 (dd, J = 9.4, 9.4 Hz, 1H), 3.74 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 159.63 (d, $J_{C\text{-}P}$ = 14.0 Hz), 159.32 (d, $J_{C\text{-}P}$ = 14.3 Hz), 136.78 (d, $J_{C\text{-}P}$ = 2.8 Hz), 136.11 (d, $J_{C\text{-}P}$ = 6.1 Hz), 134.54, 134.43, 133.45 (d, $J_{C\text{-}P}$ = 39.0 Hz), 132.49 (d, $J_{C\text{-}P}$ = 39.0 Hz), 129.74, 129.59, 129.46, 129.33, 128.70, 128.54, 127.74, 127.25 (d, $J_{C\text{-}P}$ = 2.7 Hz), 126.51, 124.68 (d, $J_{C\text{-}P}$ = 7.5 Hz), 123.72, 123.63, 123.47, 123.37, 118.41 (d, $J_{C\text{-}P}$ = 3.1 Hz), 118.33 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.72 (d, $J_{C\text{-}P}$ = 9.1 Hz), 116.05 (d, $J_{C\text{-}P}$ = 9.3 Hz), 55.49, 55.39, 52.51 (d, $J_{C\text{-}P}$ = 65.1 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.46. IR (KBr): 3057.44, 3021.59, 2959.12，2919.49, 1647.15, 1286.03, 749.08, 725.56. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{29}H_{28}O_3P$ 455.1776, found 455.1786.

(*E*)-(1,3-diphenylallyl)di(naphthalen-2-yl)phosphine oxide (3ad)



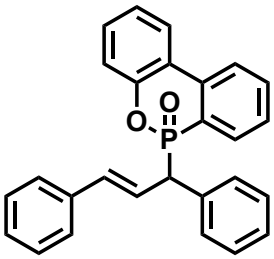
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3ad** was isolated as white solid. Mp: 217-218 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, J = 13.0 Hz, 1H), 8.22 (d, J = 13.3 Hz, 1H), 7.98 – 7.84 (m, 4H), 7.83 – 7.74 (m, 3H), 7.70 – 7.63 (m, 1H), 7.63 – 7.41 (m, 6H), 7.27 – 7.11 (m, 8H), 6.79 – 6.66 (m, 1H), 6.45 (dd, *J* = 15.7, 3.8 Hz, 1H), 4.67 (dd, *J* = 9.4, 9.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 136.75 (d, $J_{C\text{-}P}$ = 2.4 Hz), 136.08 (d, $J_{C\text{-}P}$ = 5.8 Hz), 134.74, 134.62, 134.54, 134.34, 134.27, 133.83, 133.75, 132.70 (d, $J_{C\text{-}P}$ = 12.5 Hz), 132.49 (d, $J_{C\text{-}P}$ = 12.6 Hz), 129.55 (d, $J_{C\text{-}P}$ = 35.0 Hz), 129.70, 129.65, 129.12, 129.01, 128.80, 128.59 (d, $J_{C\text{-}P}$ = 35.1 Hz), 128.53, 128.35, 128.24, 128.16, 128.10, 127.98, 127.92, 127.83, 127.74, 127.36 (d, $J_{C\text{-}P}$ = 2.5 Hz), 127.04, 126.87, 126.53, 126.44 (d, $J_{C\text{-}P}$ = 9.7 Hz), 126.23 (d, $J_{C\text{-}P}$ = 9.7 Hz), 124.75 (d, $J_{C\text{-}P}$ = 7.2 Hz), 52.37 (d, $J_{C\text{-}P}$ = 65.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 32.29. IR (KBr): 3054.09, 3022.17, 2913.91, 1624.80, 1271.41, 859.51, 819.83, 743.50, 710.17. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{35}H_{28}OP$ 495.1878, found 495.1877.

(*E*)-(1,3-diphenylallyl)di(naphthalen-1-yl)phosphine oxide (3ae)



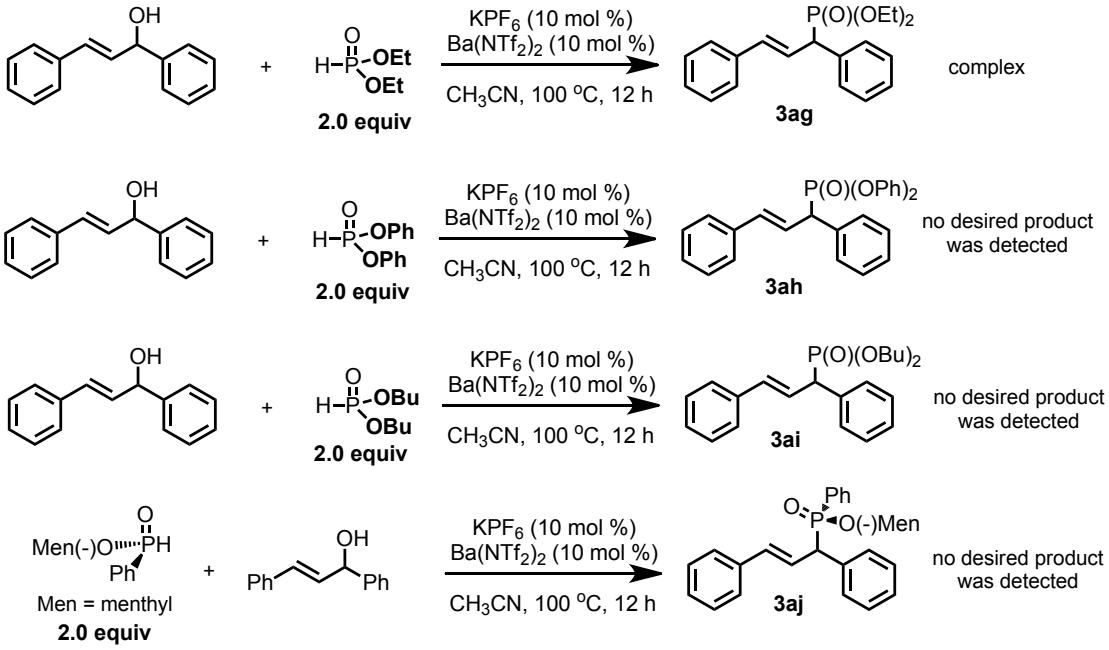
Following the general procedure, the reaction was conducted at 100 °C for 12h. **3ae** was isolated as white solid. Mp: 246-248 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 8.5 Hz, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.13 (dd, *J* = 14.3, 7.1 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.76 (m, 3H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.47 (dd, *J* = 6.8, 6.8 Hz, 1H), 7.41 – 7.25 (m, 7H), 7.25 – 7.02 (m, 8H), 6.83 – 6.72 (m, 1H), 6.38 (dd, *J* = 15.7, 3.8 Hz, 1H), 4.78 (dd, *J* = 9.0, 9.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 136.95 (d, $J_{C\text{-}P}$ = 5.7 Hz), 136.84 (d, $J_{C\text{-}P}$ = 2.4 Hz), 134.40, 134.26 (d, $J_{C\text{-}P}$ = 7.6 Hz), 134.03, 133.98 (d, $J_{C\text{-}P}$ = 9.0 Hz), 133.96 (d, $J_{C\text{-}P}$ = 7.8 Hz), 133.70, 133.61, 133.12 (d, $J_{C\text{-}P}$ = 3.4 Hz), 132.88 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.18 (d, $J_{C\text{-}P}$ = 2.4 Hz), 132.08 (d, $J_{C\text{-}P}$ = 2.4 Hz), 130.03 (d, $J_{C\text{-}P}$ = 22.7 Hz), 129.73, 129.68, 129.10 (d, $J_{C\text{-}P}$ = 23.2 Hz), 128.88, 128.70, 128.55, 128.43, 127.64, 127.30, 127.17, 127.08, 126.67 (d, $J_{C\text{-}P}$ = 4.8 Hz), 126.50, 126.48, 126.34, 126.16, 125.84 (d, $J_{C\text{-}P}$ = 6.6 Hz), 124.40 (d, $J_{C\text{-}P}$ = 13.5 Hz), 124.22 (d, $J_{C\text{-}P}$ = 13.6 Hz), 52.06 (d, $J_{C\text{-}P}$ = 66.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 36.68. IR (KBr): 3078.68, 3024.10, 2921.02, 2880.94, 1641.60, 1274.95, 831.53, 749.63, 699.15. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{35}H_{28}OP$ 495.1878, found 495.1880.

(*E*)-6-(1,3-diphenylallyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (3af) (diastereoisomers)



Following the general procedure, the reaction was conducted at 100 °C for 12h. **3af** was isolated as white solid. Mp: 163-166 °C. Then the two isomer can be further separated by carefully PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 2:1) for five times, one of the pure isomer was obtained in 6 mg and the NMR was checked and set as reference to assign picks of this two isomer. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.88 (m, 2H), 7.78 (dd, *J* = 11.8, 7.5 Hz, 1H), 7.73 – 7.64 (m, 1H), 7.40 (td, *J* = 7.5, 3.0 Hz, 1H), 7.35 – 7.20 (m, 10H), 7.19 – 7.16 (m, 2H), 6.98 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.47 (ddd, *J* = 16.3, 9.6, 7.2 Hz, 1H), 6.22 (dd, *J* = 15.7, 4.8 Hz, 1H), 4.01 (dd, *J* = 16.2, 9.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 150.06 (d, *J* = 8.2 Hz), 136.58, 136.31, 135.46, 135.32, 134.50, 133.74, 132.58 (d, *J* = 8.3 Hz), 130.89, 129.30, 128.91, 128.66, 128.27, 128.15, 128.04, 127.72, 126.57, 125.33, 124.72, 124.08, 123.88, 123.78, 122.67, 120.82 (d, *J* = 6.6 Hz), 51.77 (d, *J* = 86.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 33.42. Another diastereoisomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.83 (m, 2H), 7.71 – 7.58 (m, 1H), 7.49 – 7.35 (m, 2H), 7.31 – 7.25 (m, 7H), 7.23 – 7.19 (m, 6H), 6.64 – 6.51 (m, 1H), 6.46 – 6.35 (m, 1H), 4.01 (dd, *J* = 16.4, 9.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 149.87 (d, *J* = 3.1 Hz), 136.49, 136.20, 134.78, 134.66, 134.40, 133.58, 131.76 (d, *J* = 8.7 Hz), 130.82, 129.35, 128.80, 128.64, 128.18, 128.05, 127.96, 127.66, 124.71, 124.61, 123.94, 123.61, 123.51, 122.92, 122.68, 122.55, 122.49, 120.57 (d, *J* = 6.6 Hz), 51.74 (d, *J* = 86.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 34.06. IR (KBr): 3058.03, 3025.09, 2961.19, 2912.32, 1639.70, 1275.98, 753.85, 714.91. HRMS (ESI/[M+H]$^{+}$) Calcd. for: $C_{27}H_{22}O_2P$ 409.1357, found 409.1348.

With the attempt the get more information of this reaction, other P-H species (such as diethyl (dibutyl or phenyl) phosphite etc.) was investigated. Unfortunately, under the identity condition, no desired products can be isolated.



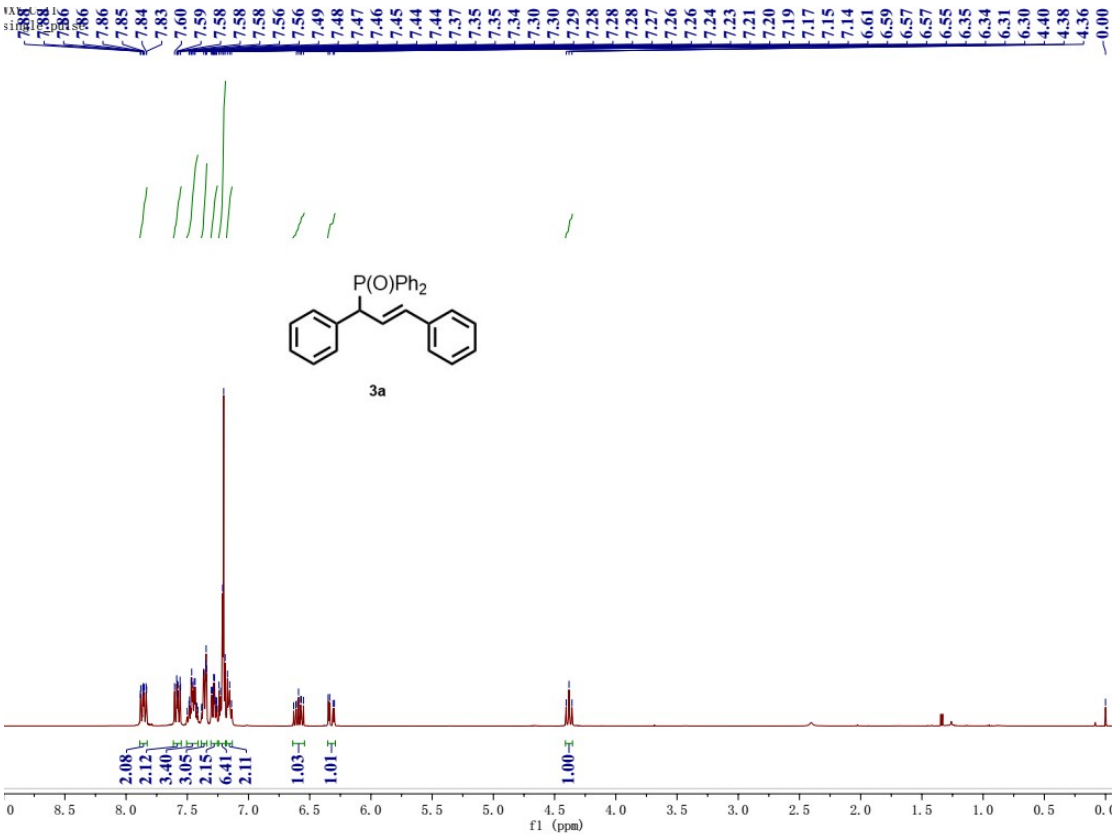
5. References

[1] C. C. Chen, J. Waser, *Chem.Commun.* **2014**, *50*, 12923.

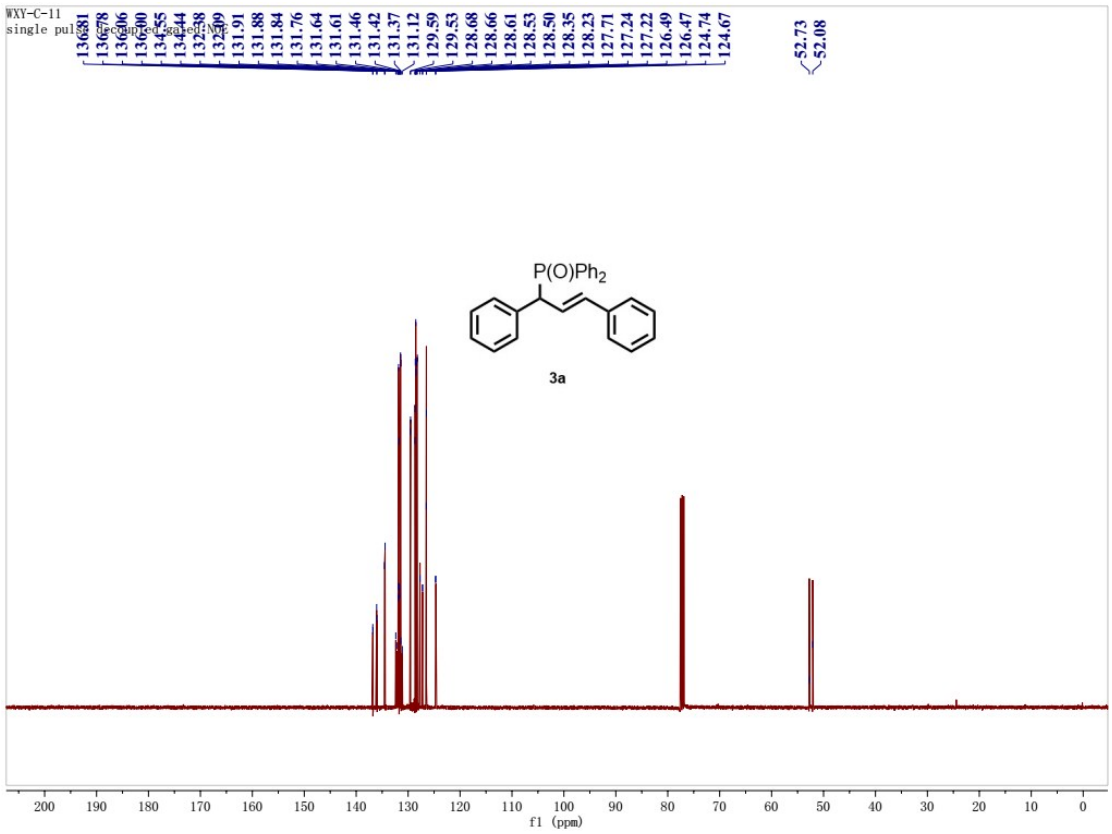
[2] a) Liu, S.; Liebeskind, L. S. *J. Am. Chem. Soc*. **2008**, *130*, 6918； b) Fukuzawa, S.; Fujinami, T.; Yamauchi, S.; Sakai, S. *J. Chem. Soc. Perkin. Trans.* **1986**, *1*, 1929.

[3] L. Zhang, W. Liu, X. Zhao, *Eur. J. Org. Chem.* **2014**, *31,* 6846-6849.

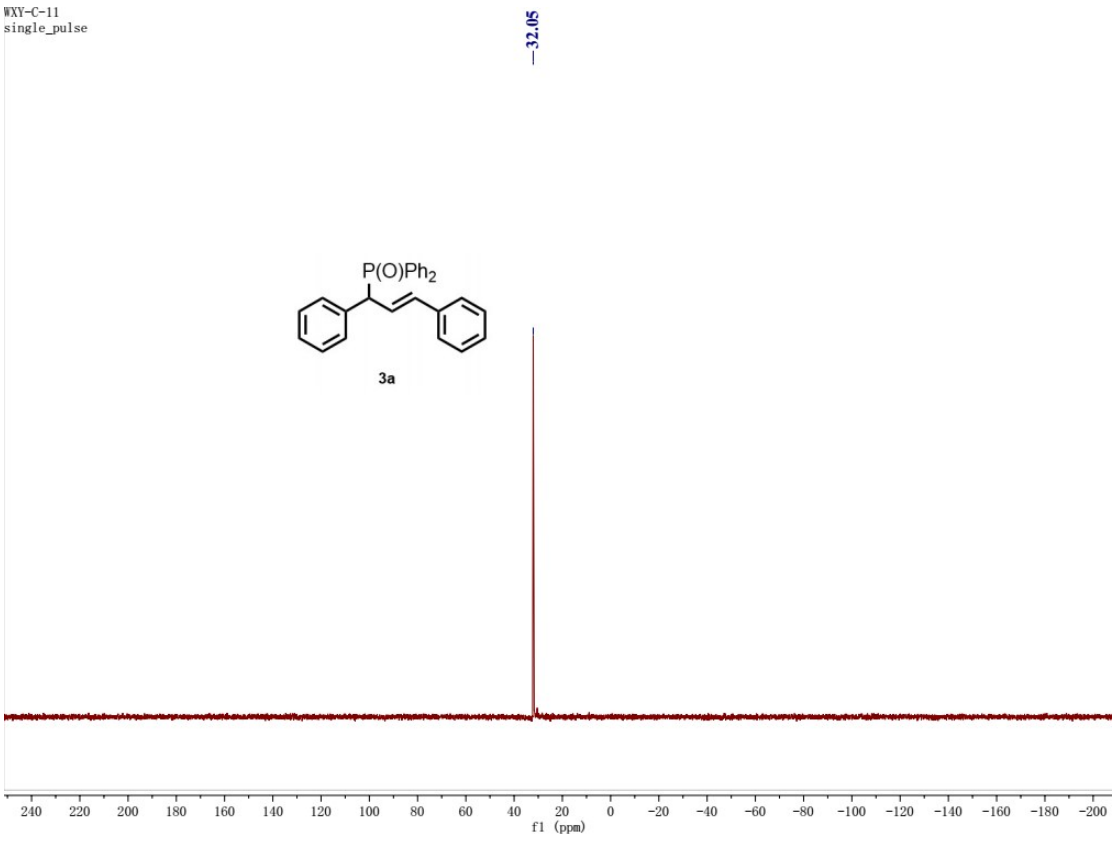
6.NMR Spectra for New Compounds



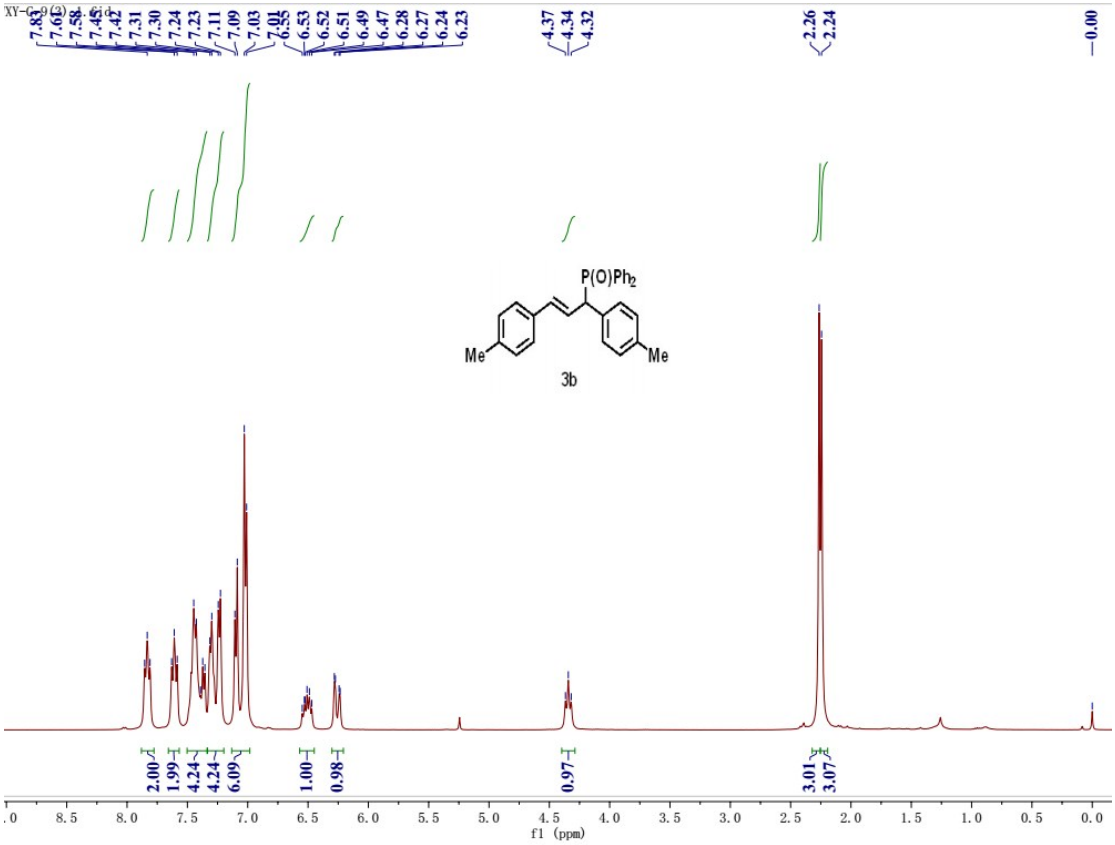
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3a.**



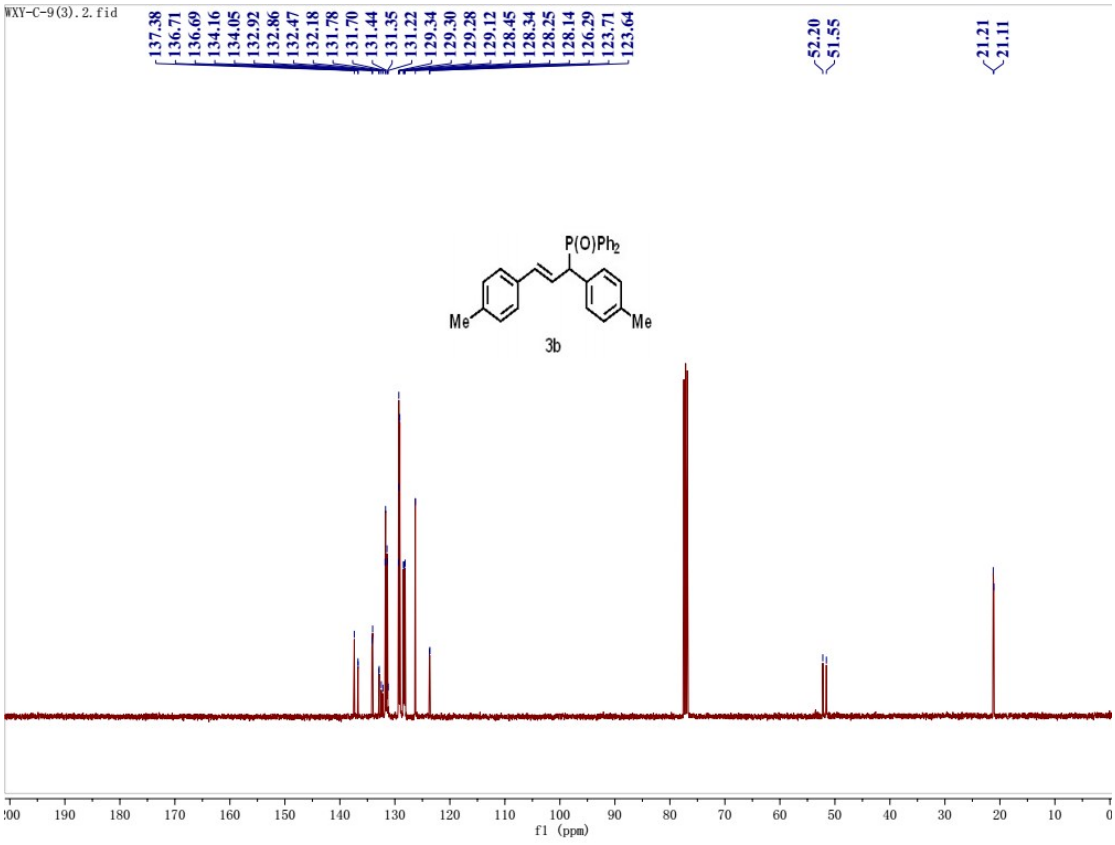
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3a.**



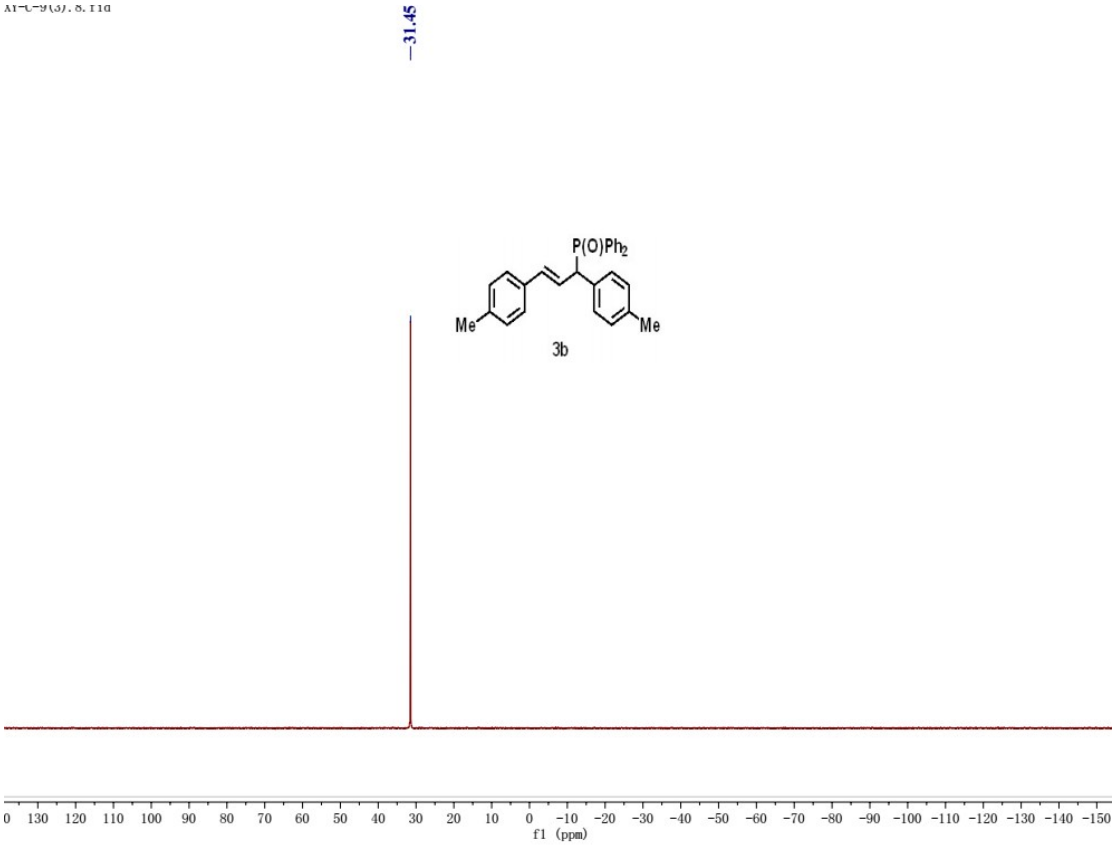
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3a.**



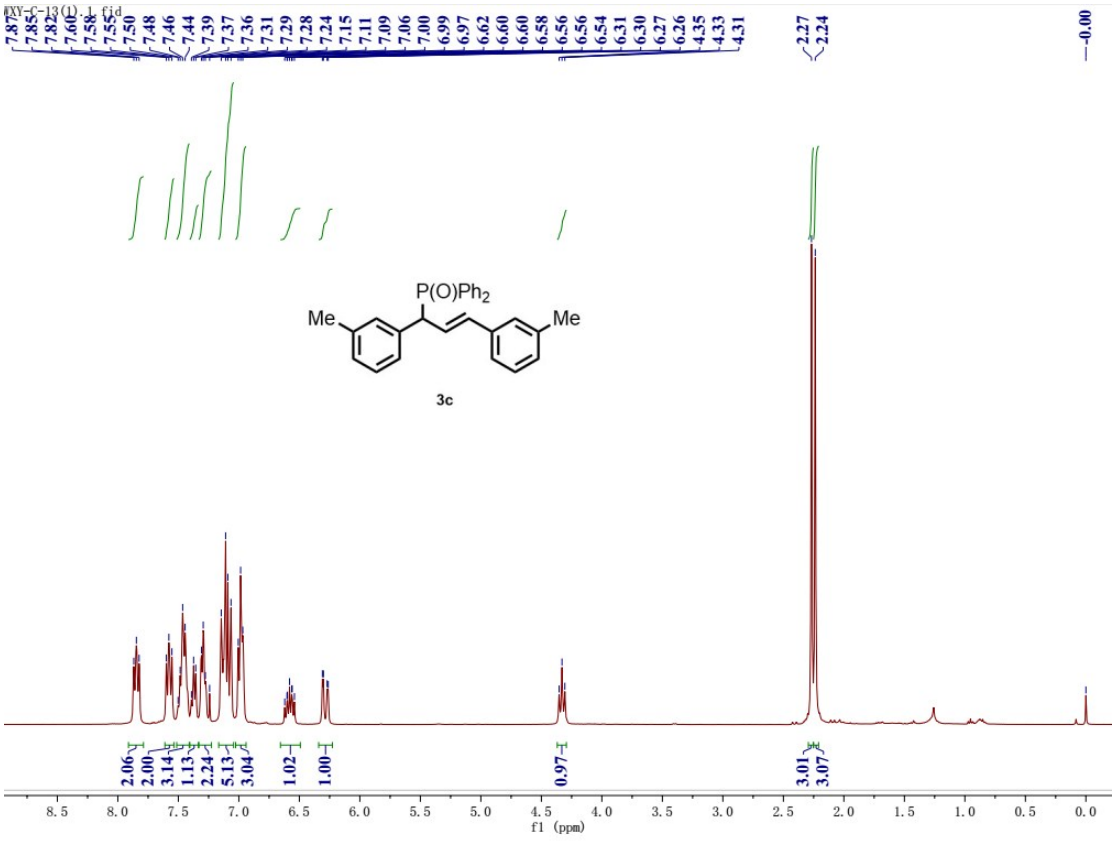
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3b.**



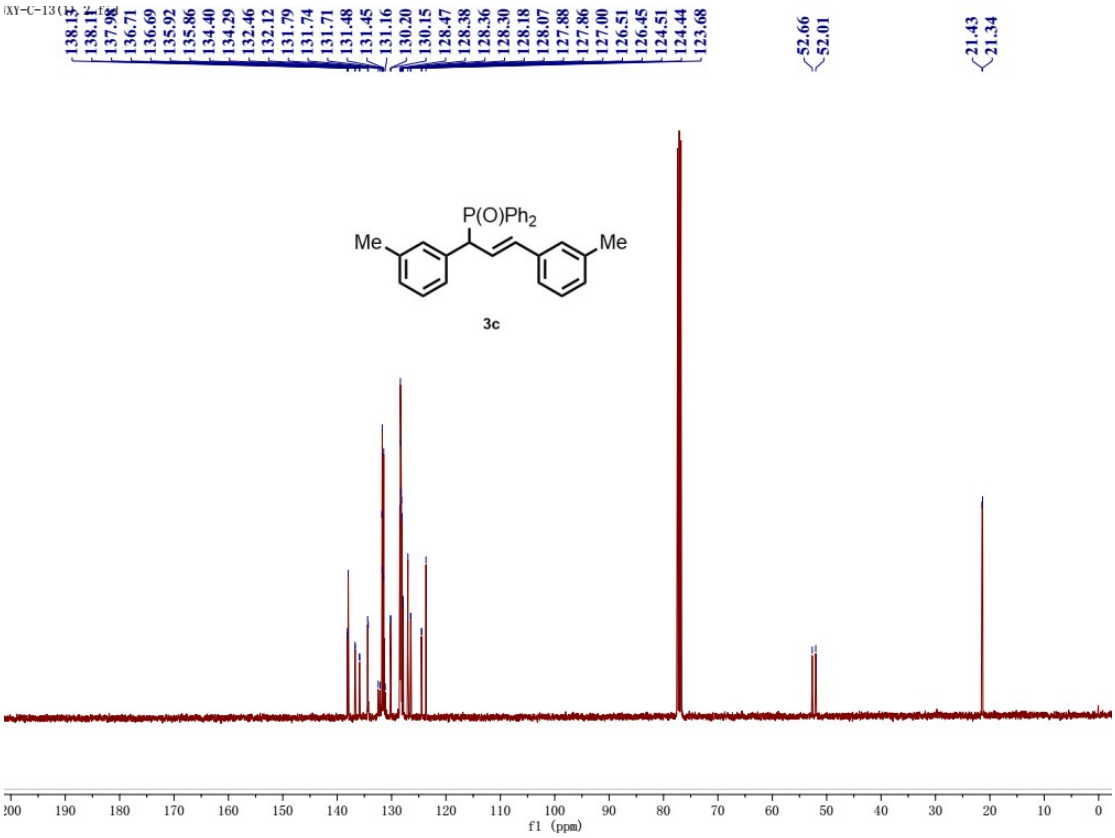
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3b.**



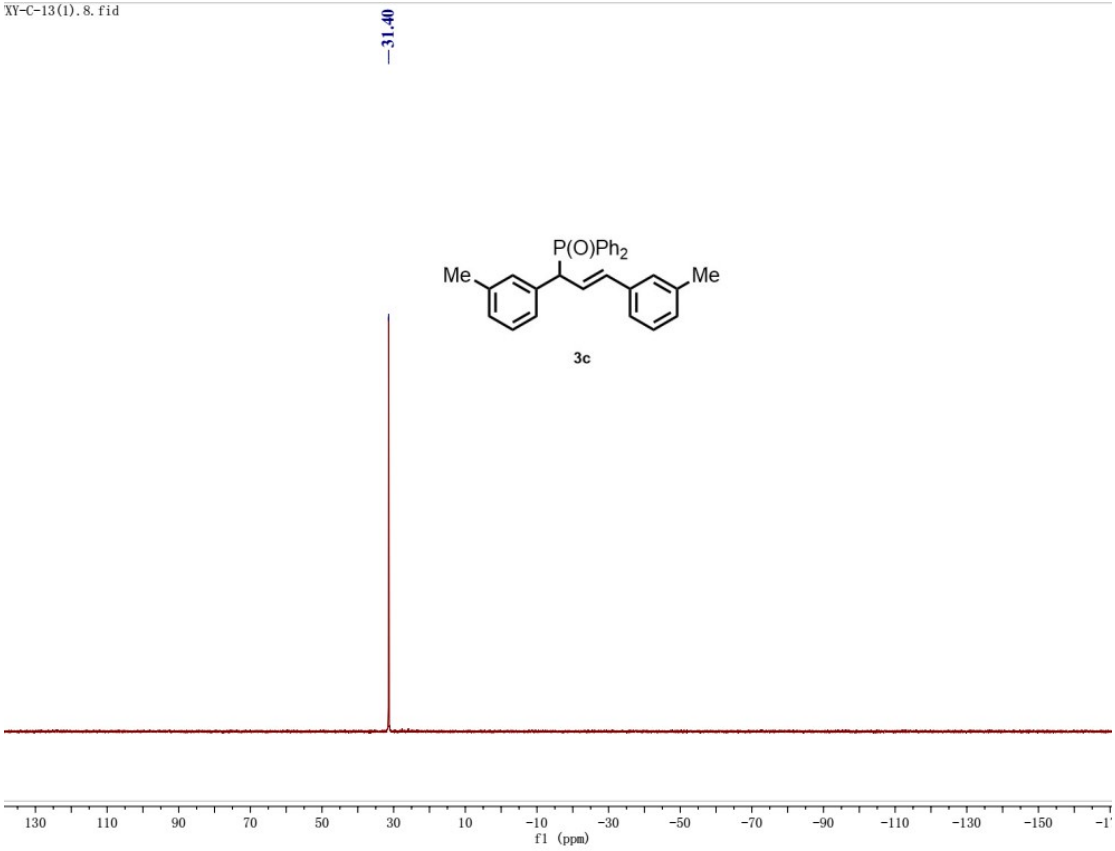
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3b.**



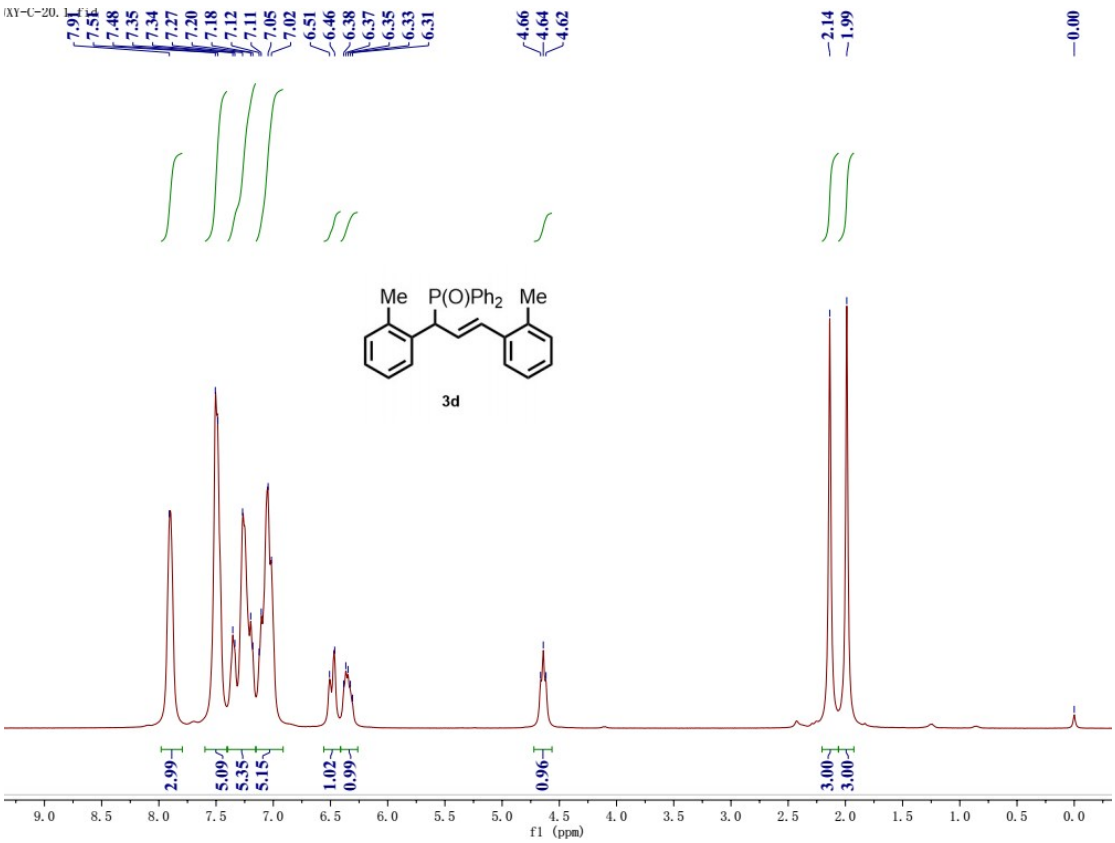
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3c.**



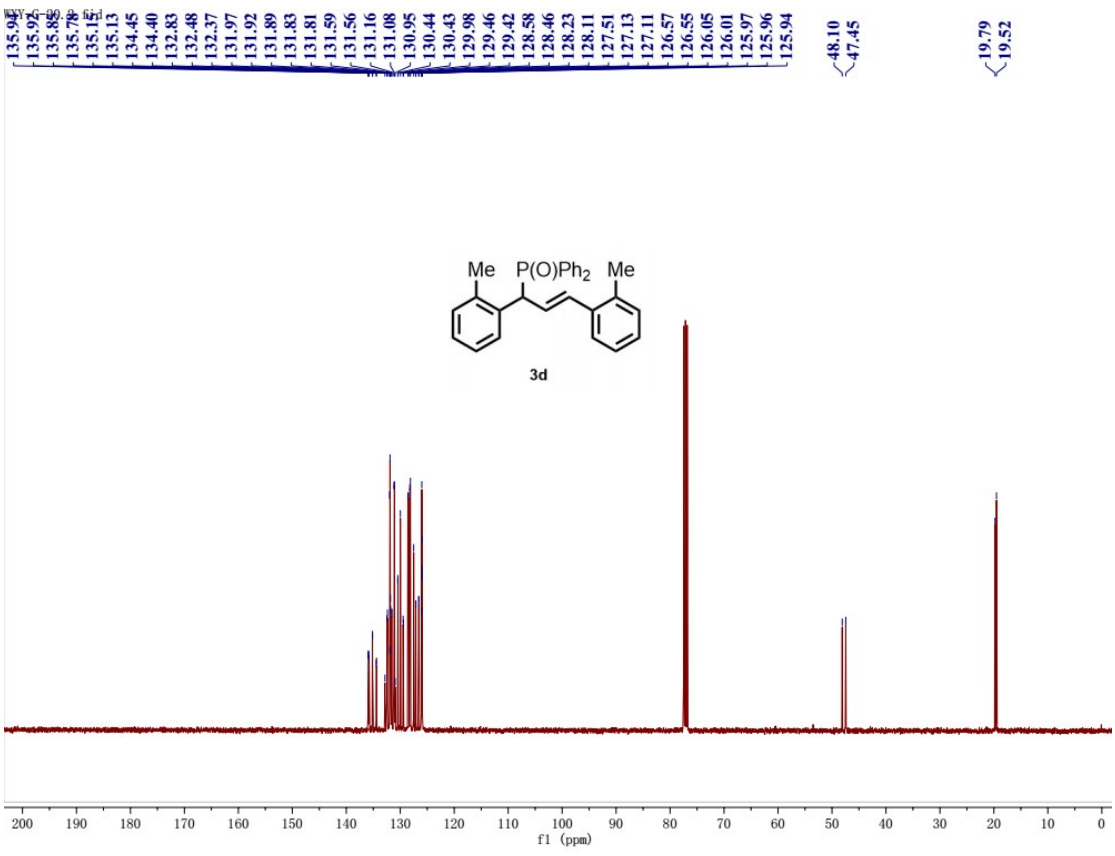
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3c.**



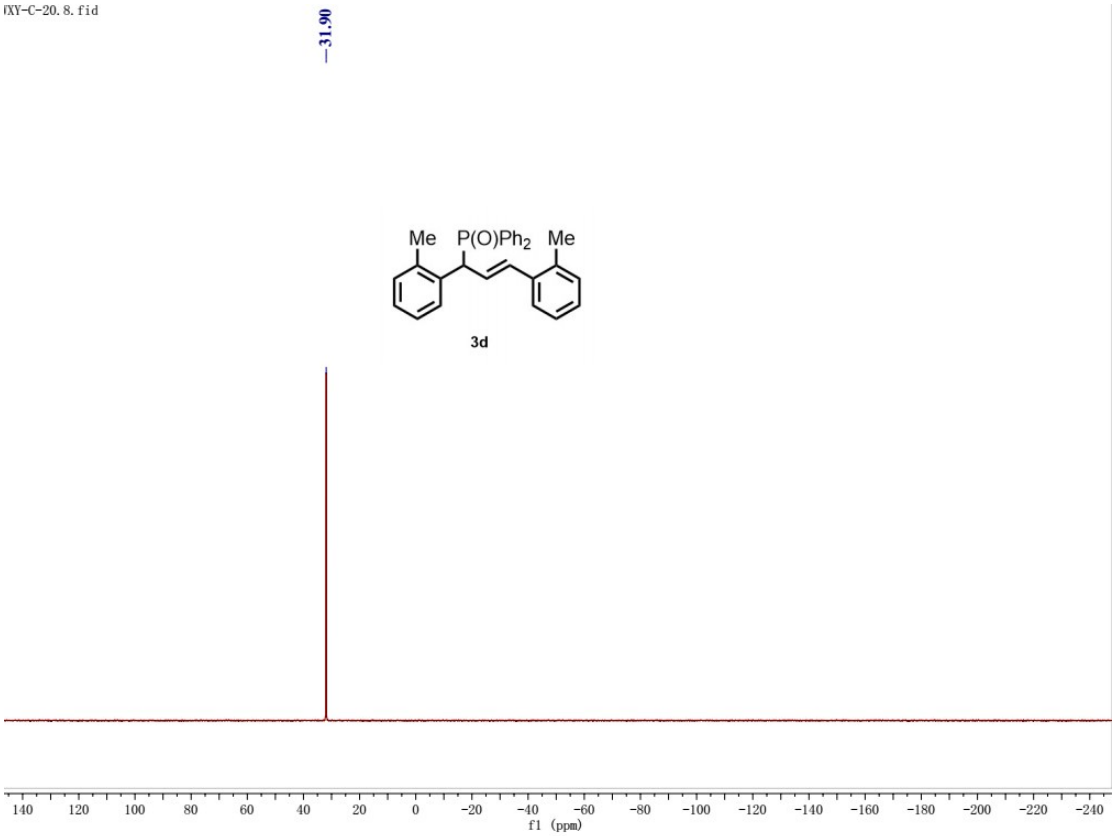
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3c.**



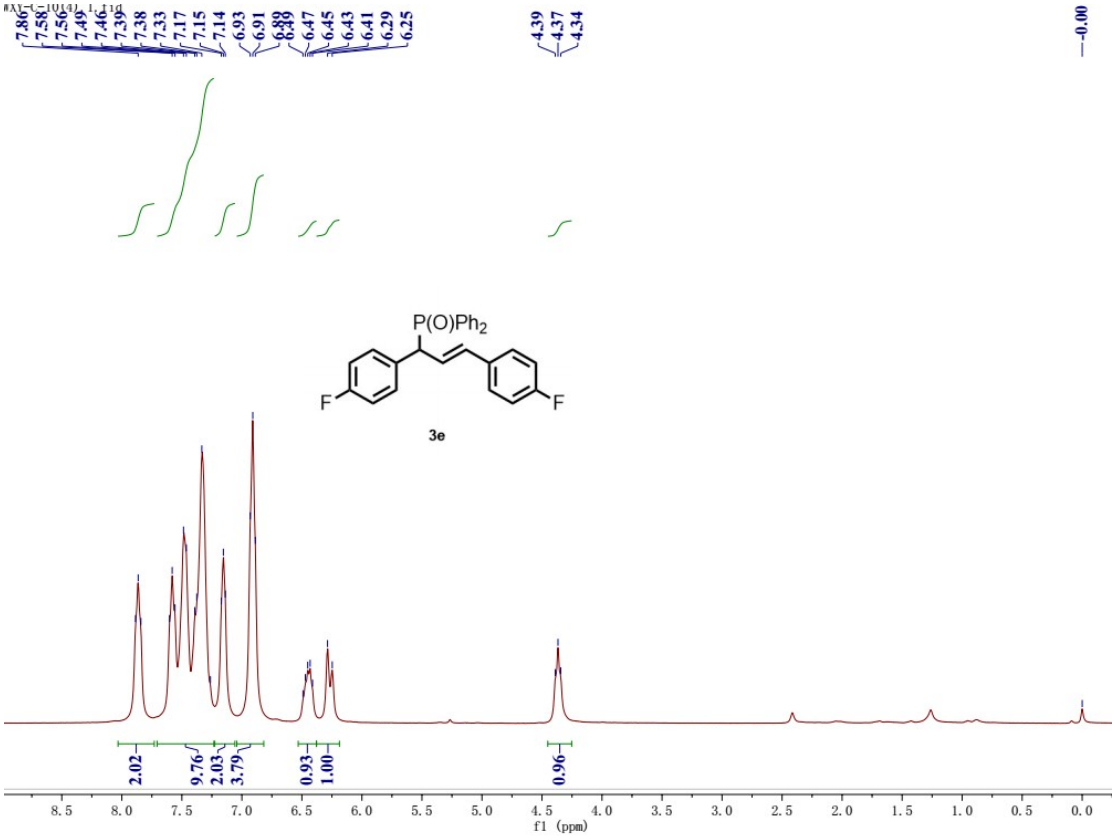
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3d.**



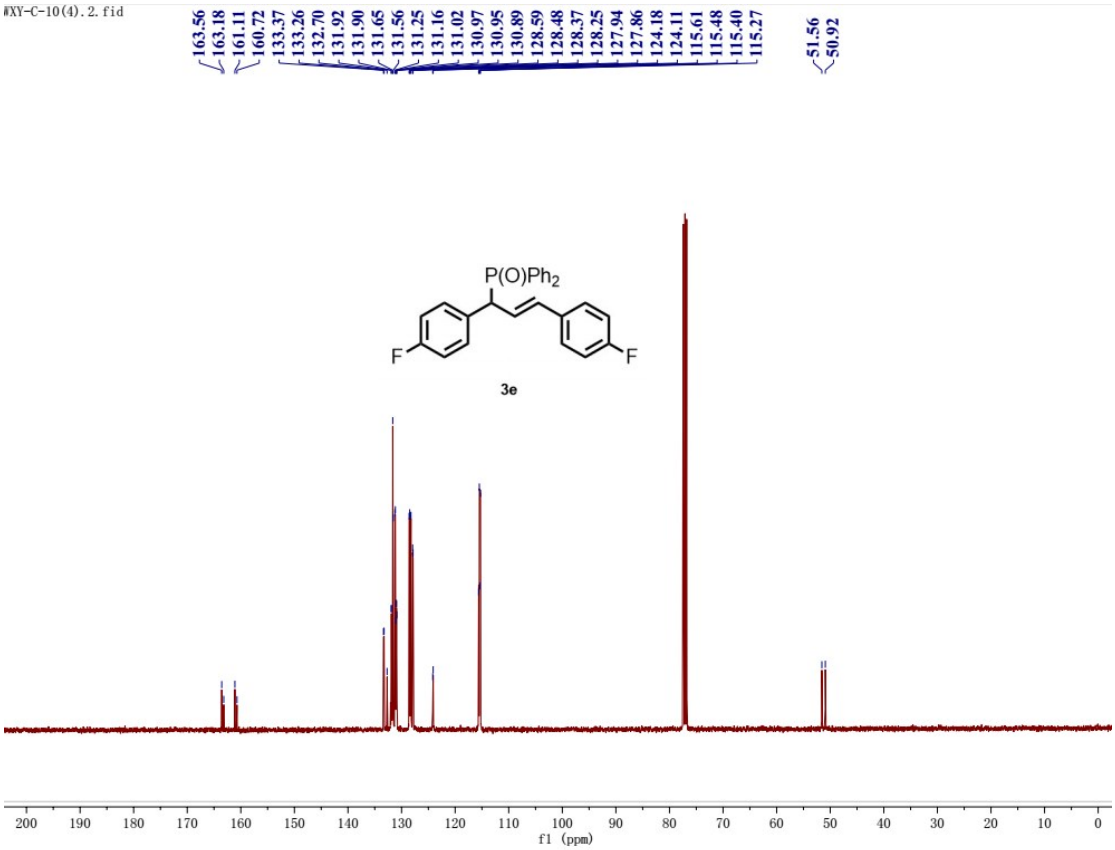
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3d.**



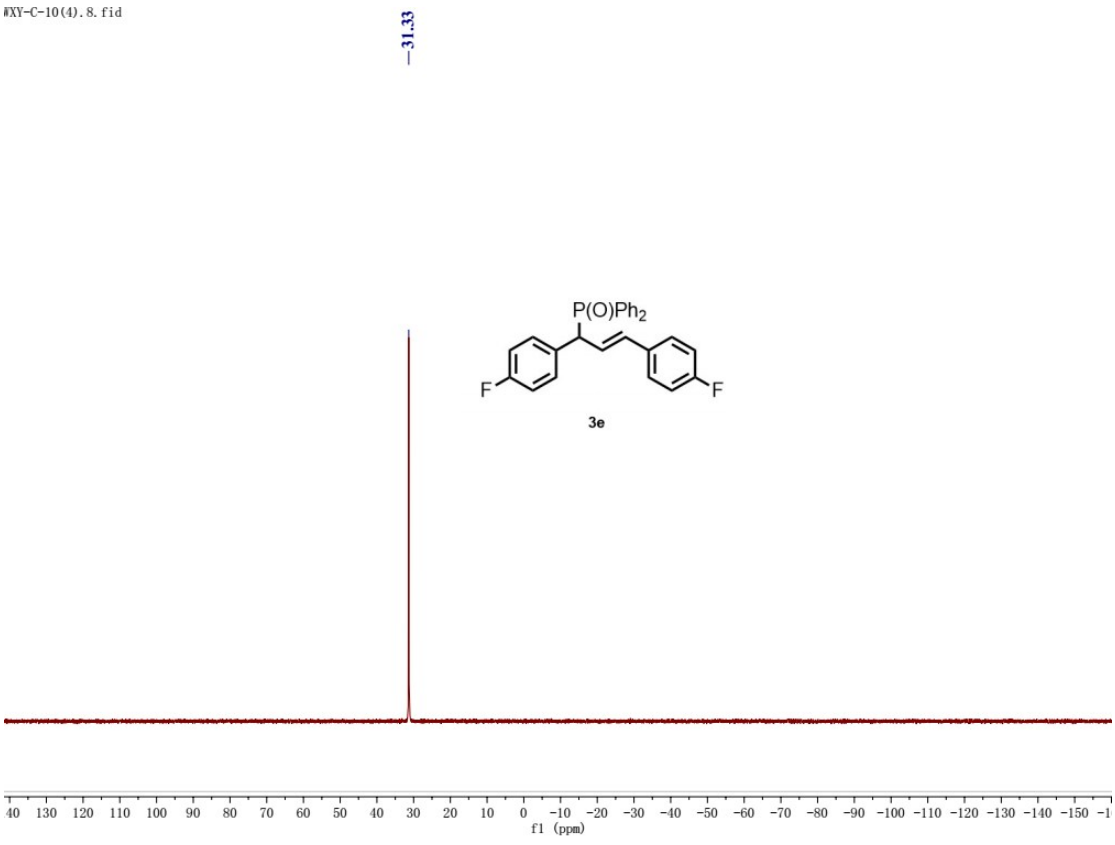
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3d.**



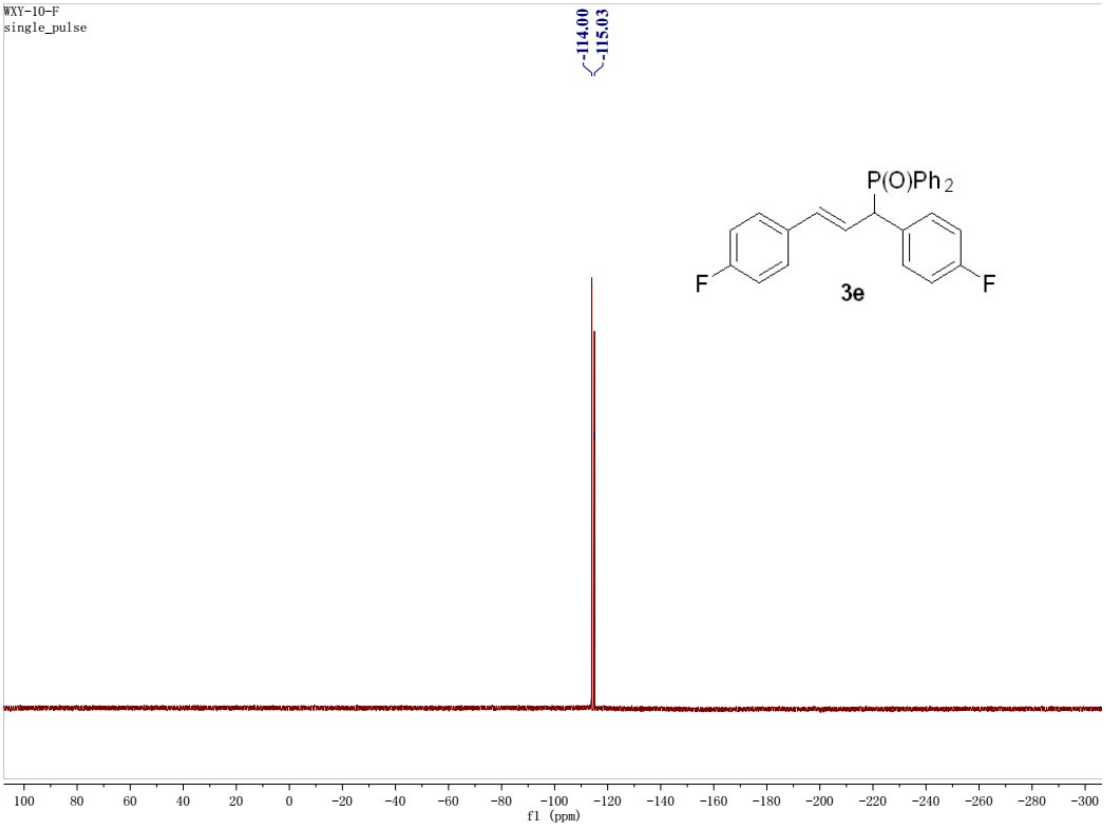
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3e.**



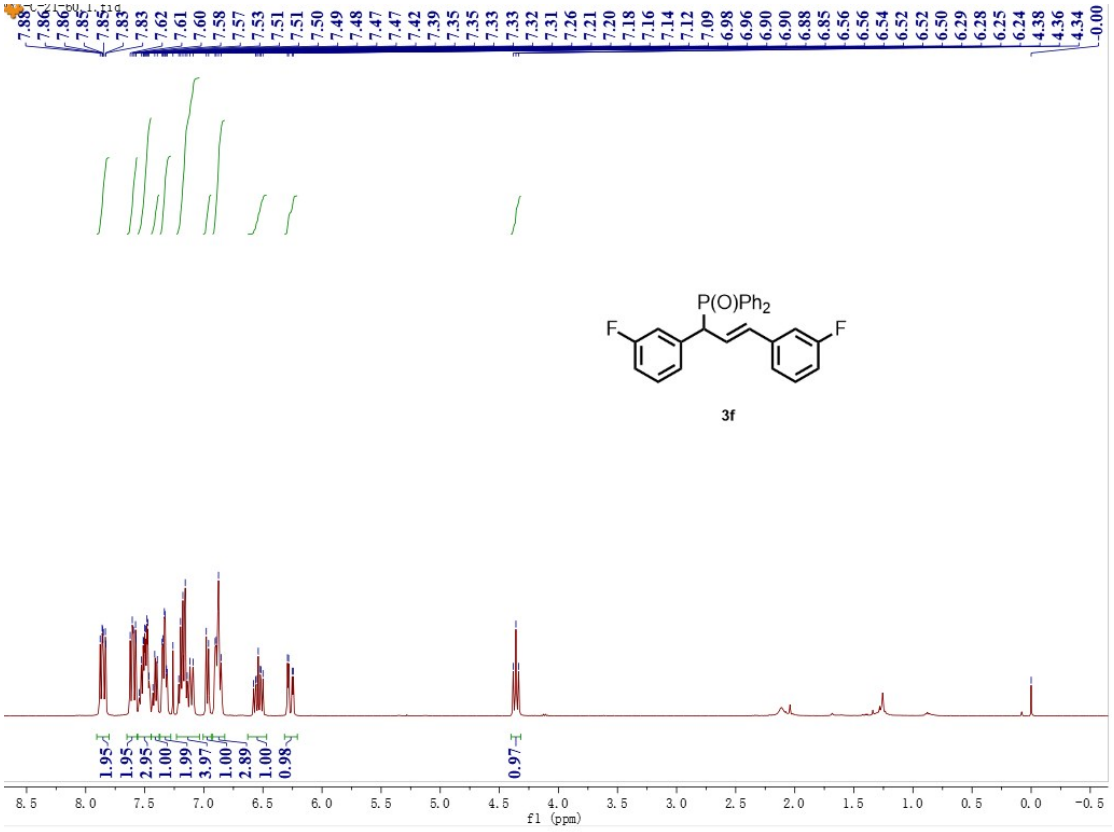
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3e.**



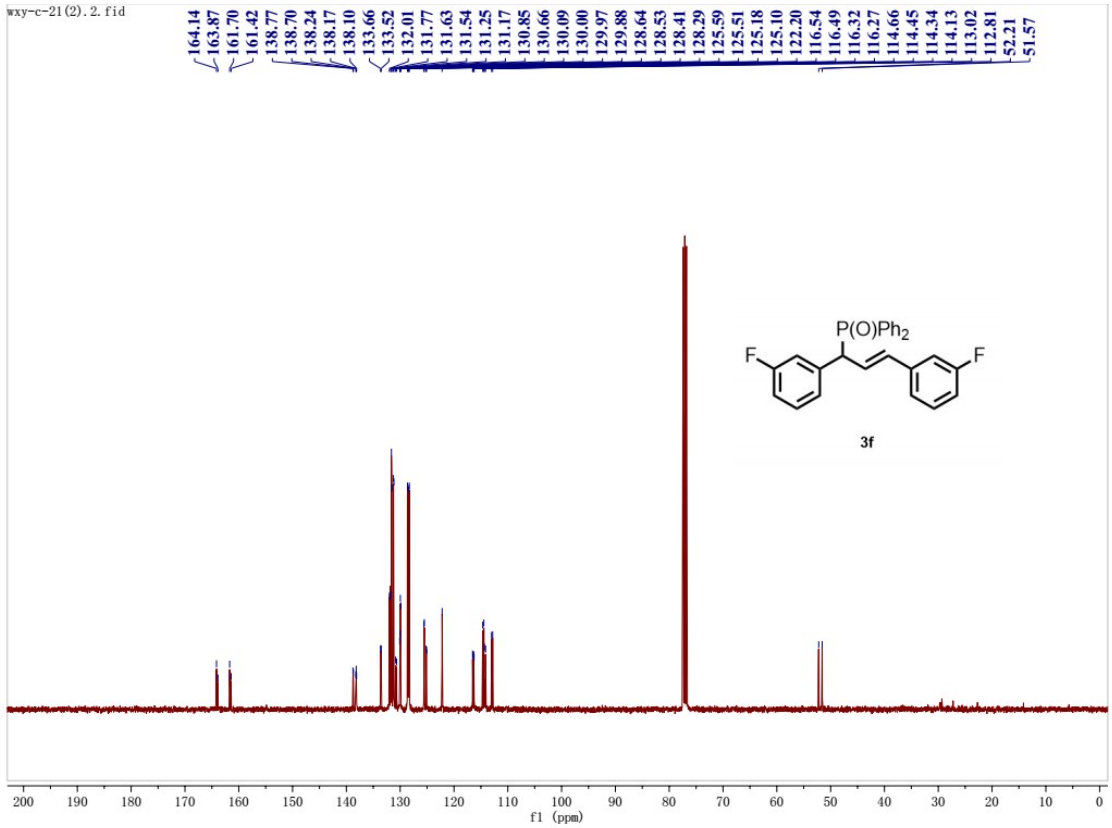
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3e.**



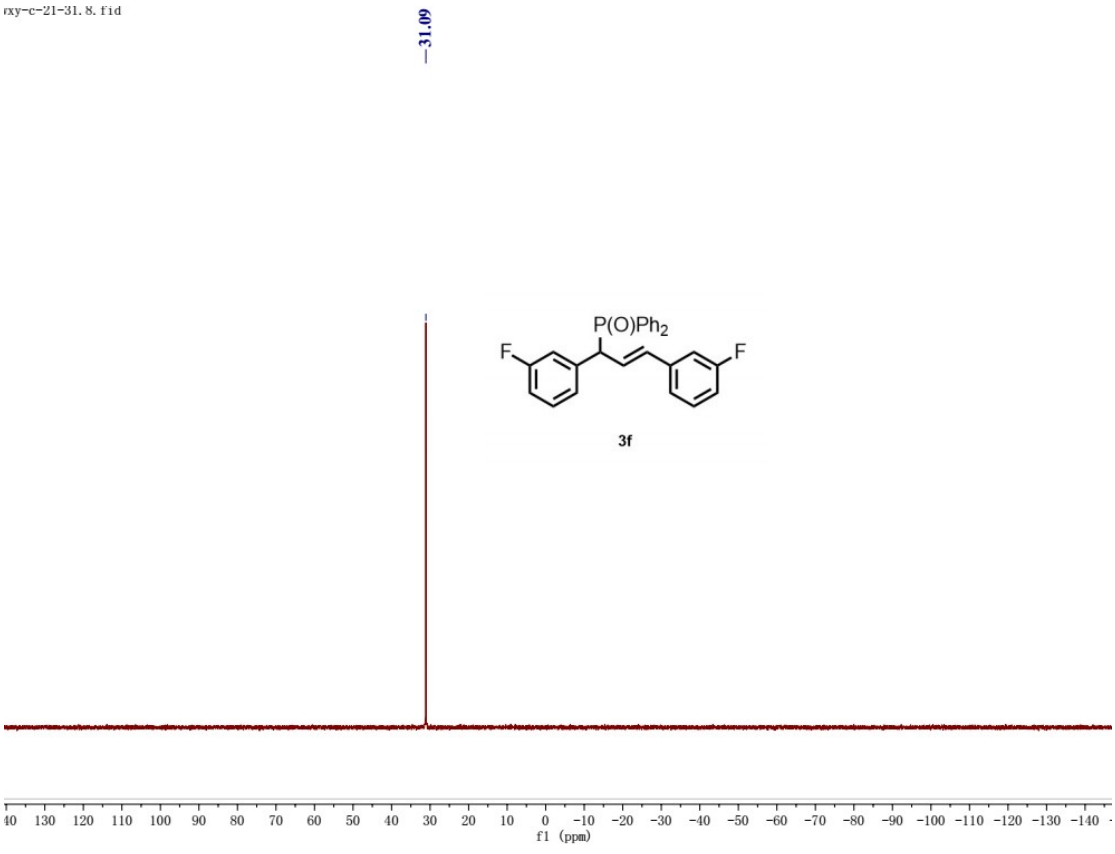
^{19}F NMR (376 MHz, Chloroform-d) spectra for compound **3e.**



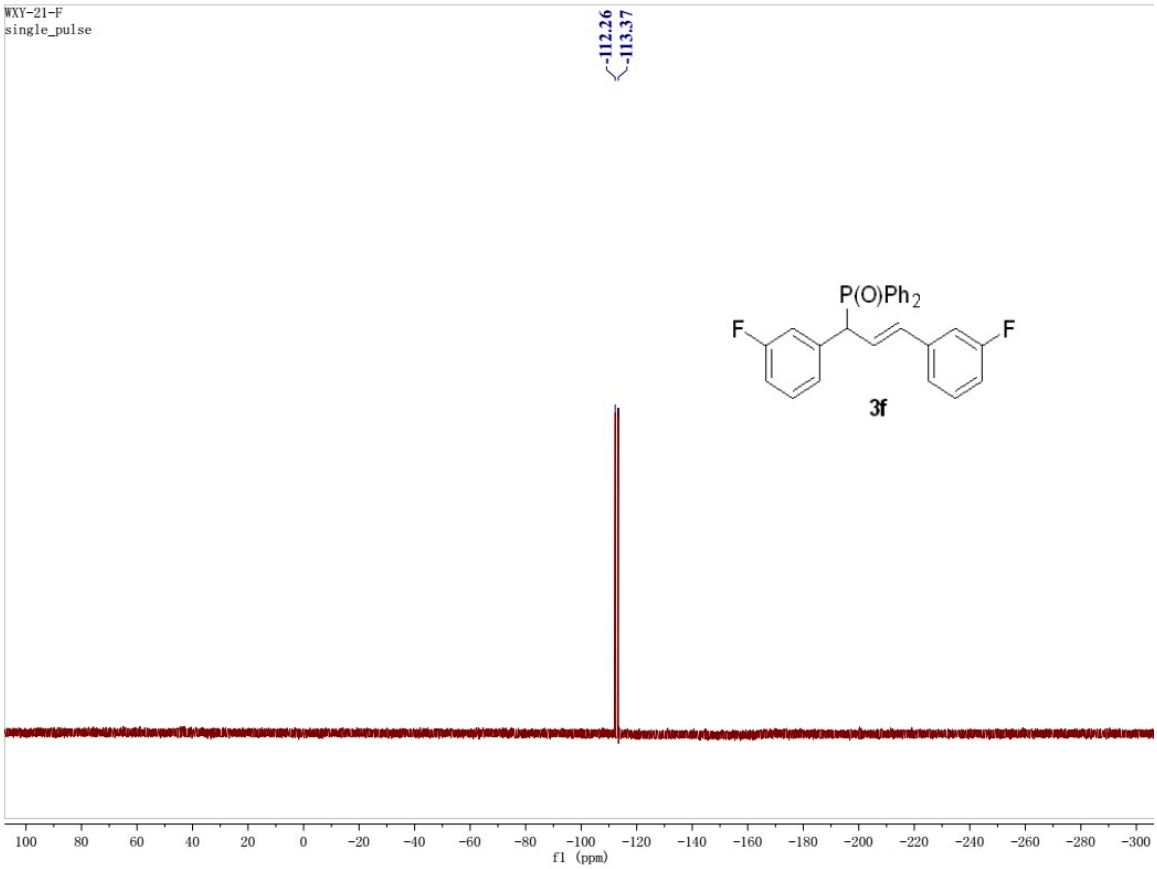
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3f.**



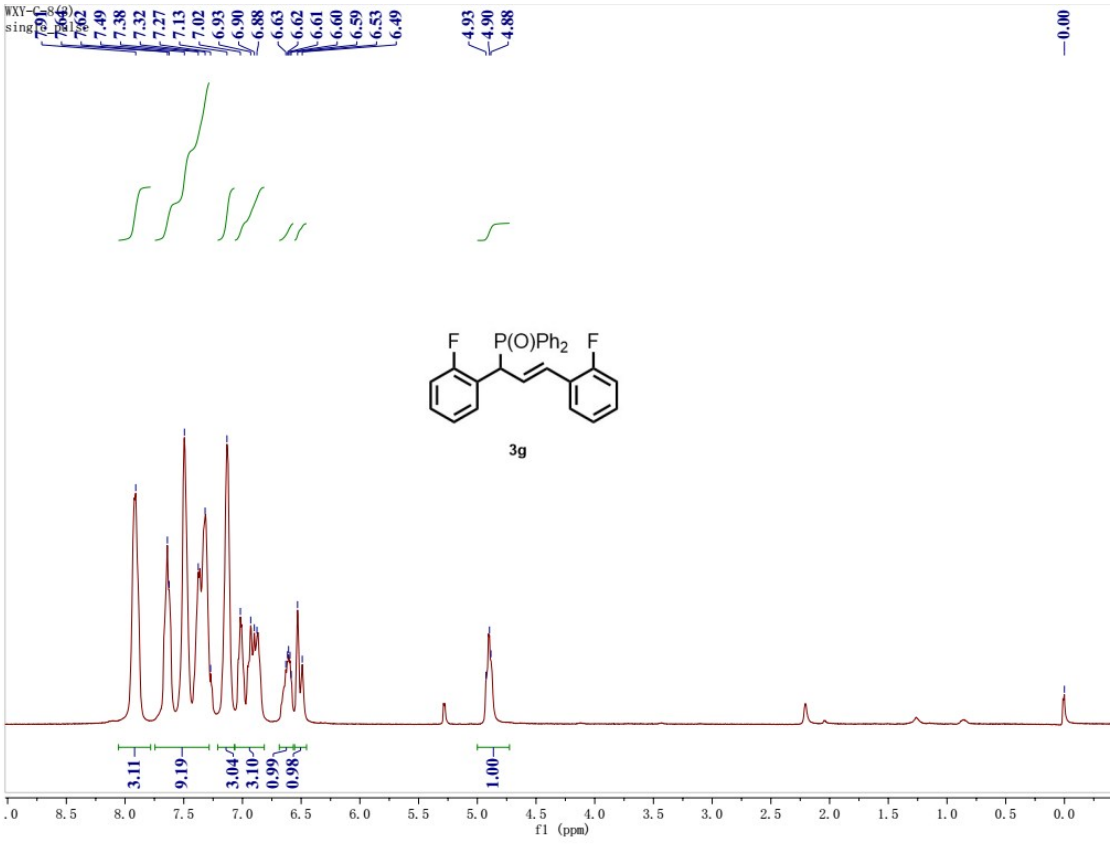
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3f.**



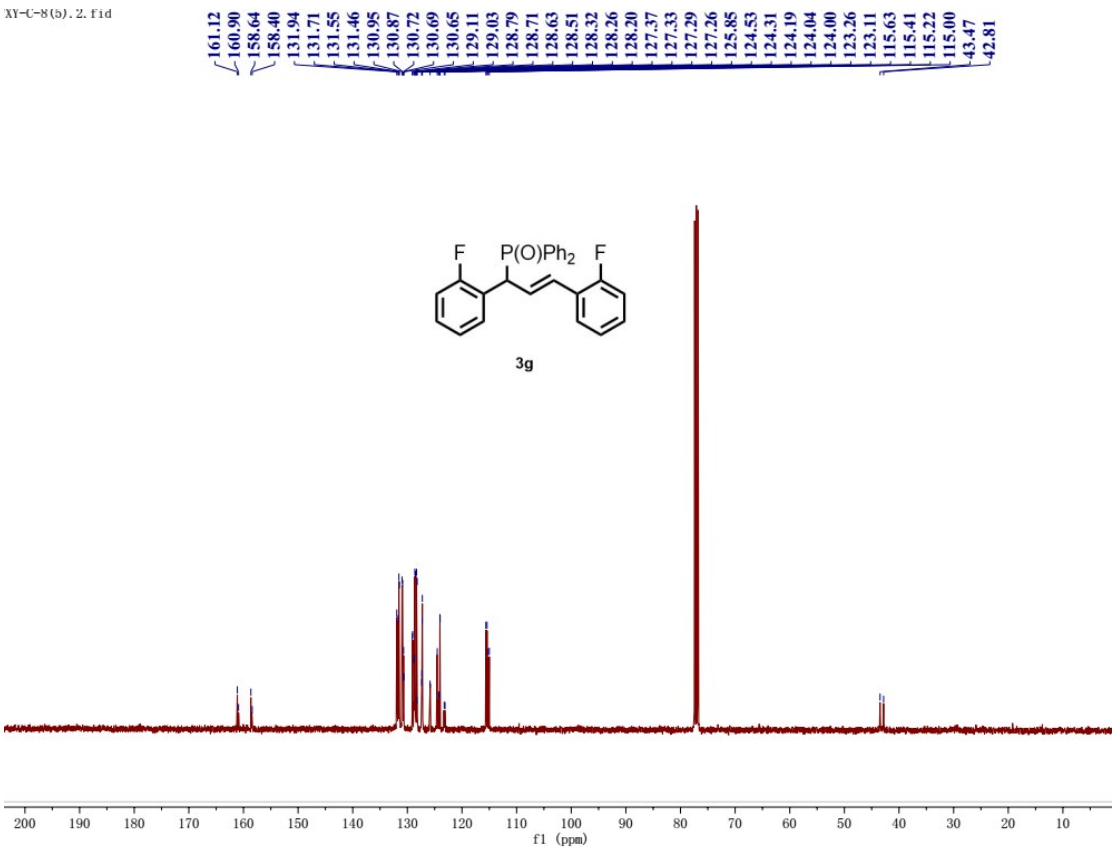
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3f.**



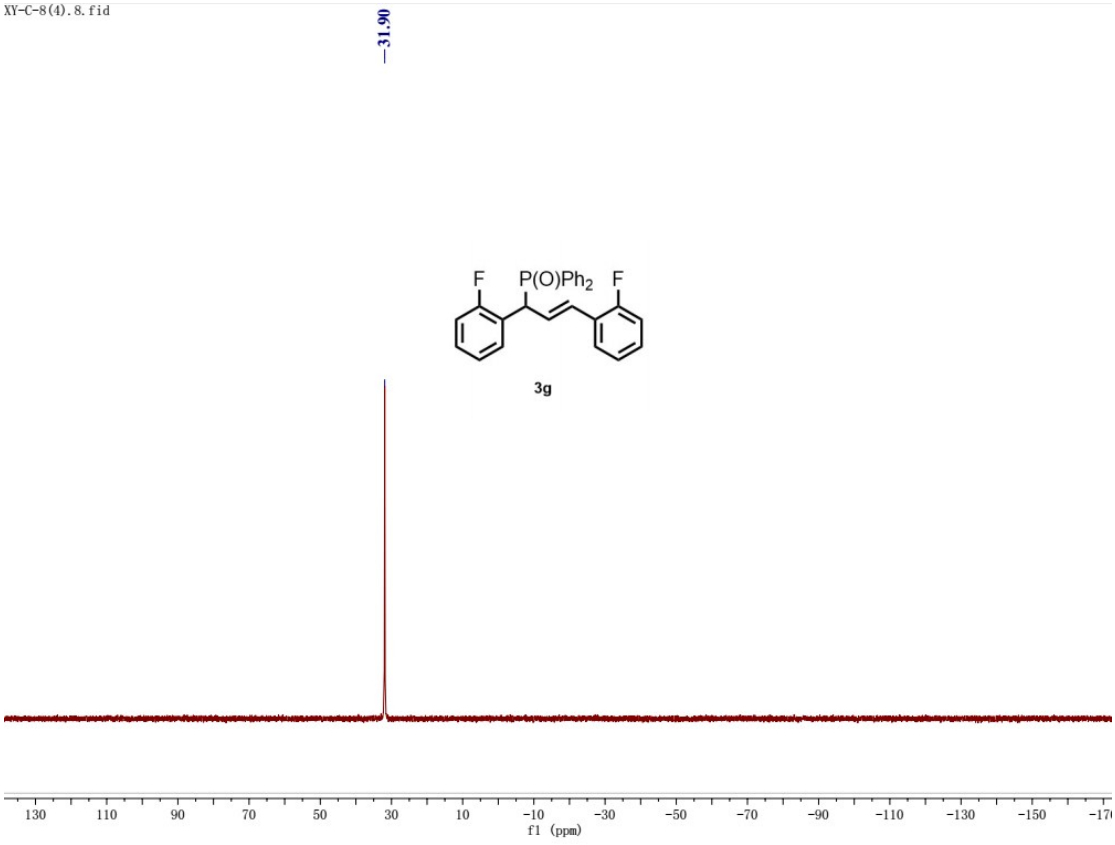
^{19}F NMR (376 MHz, Chloroform-d) spectra for compound **3f.**



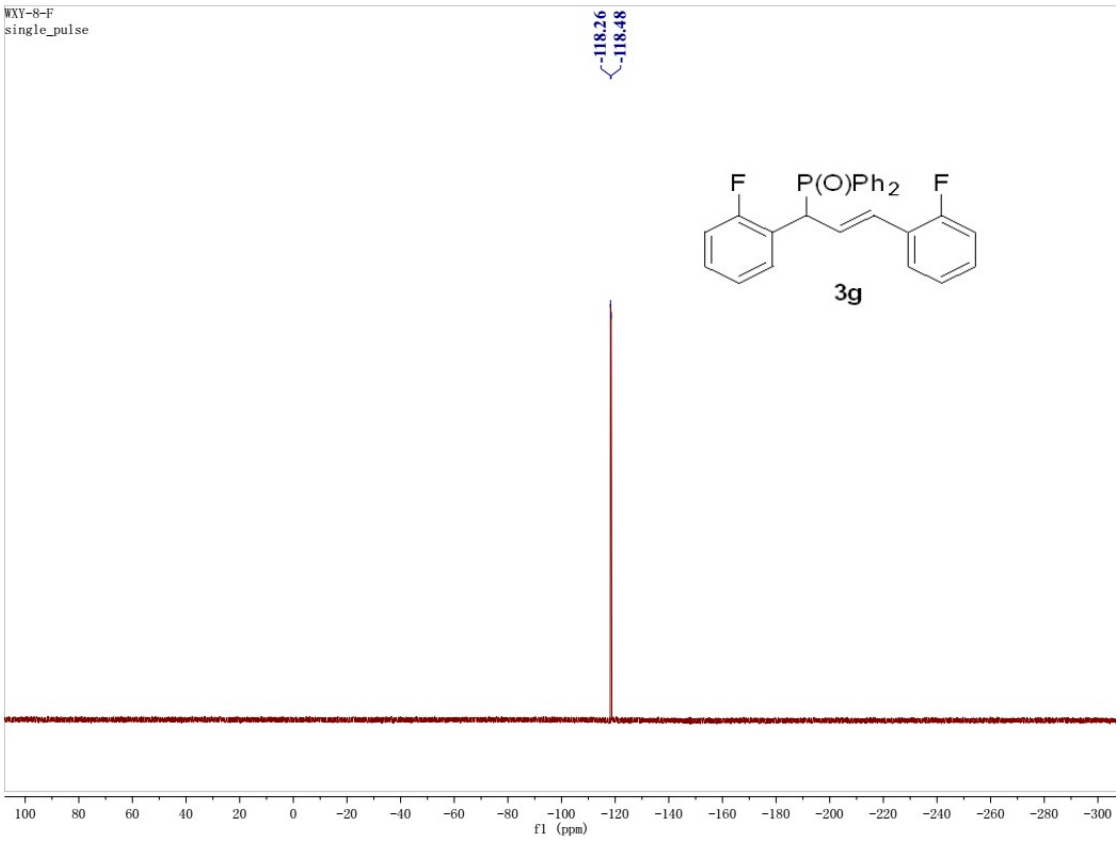
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3g.**



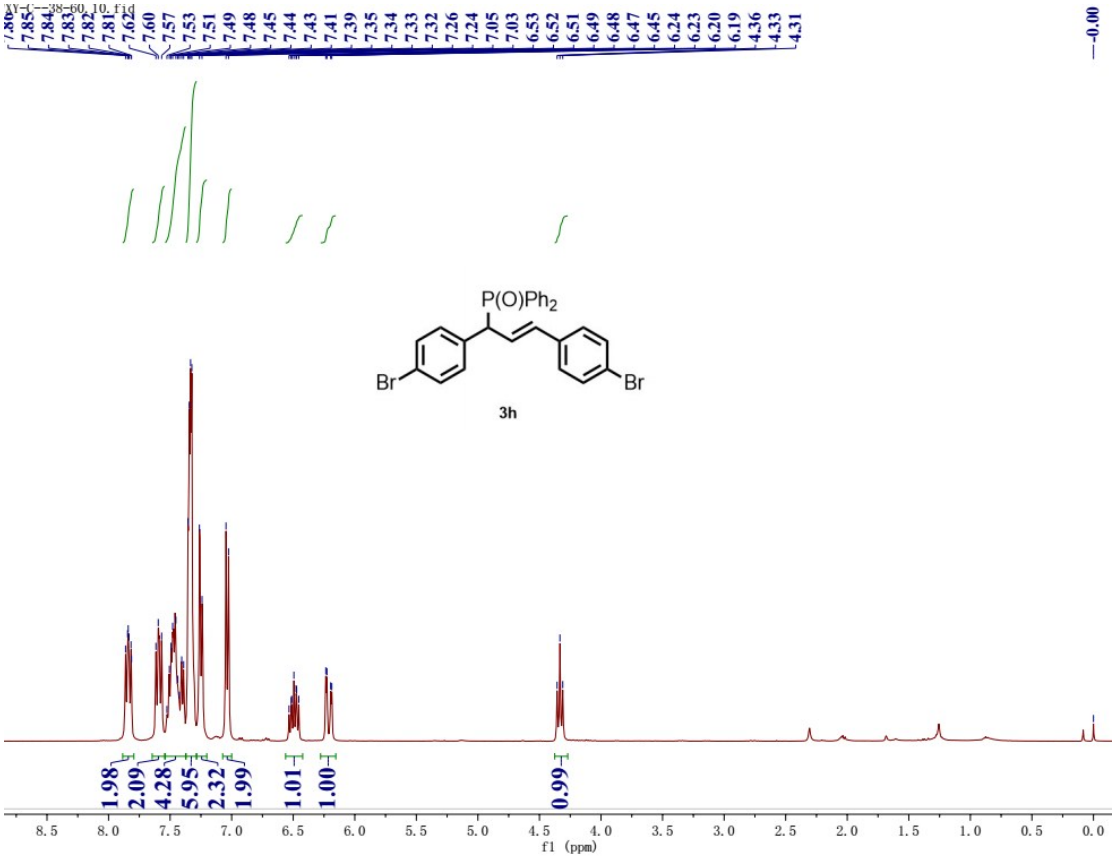
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3g.**



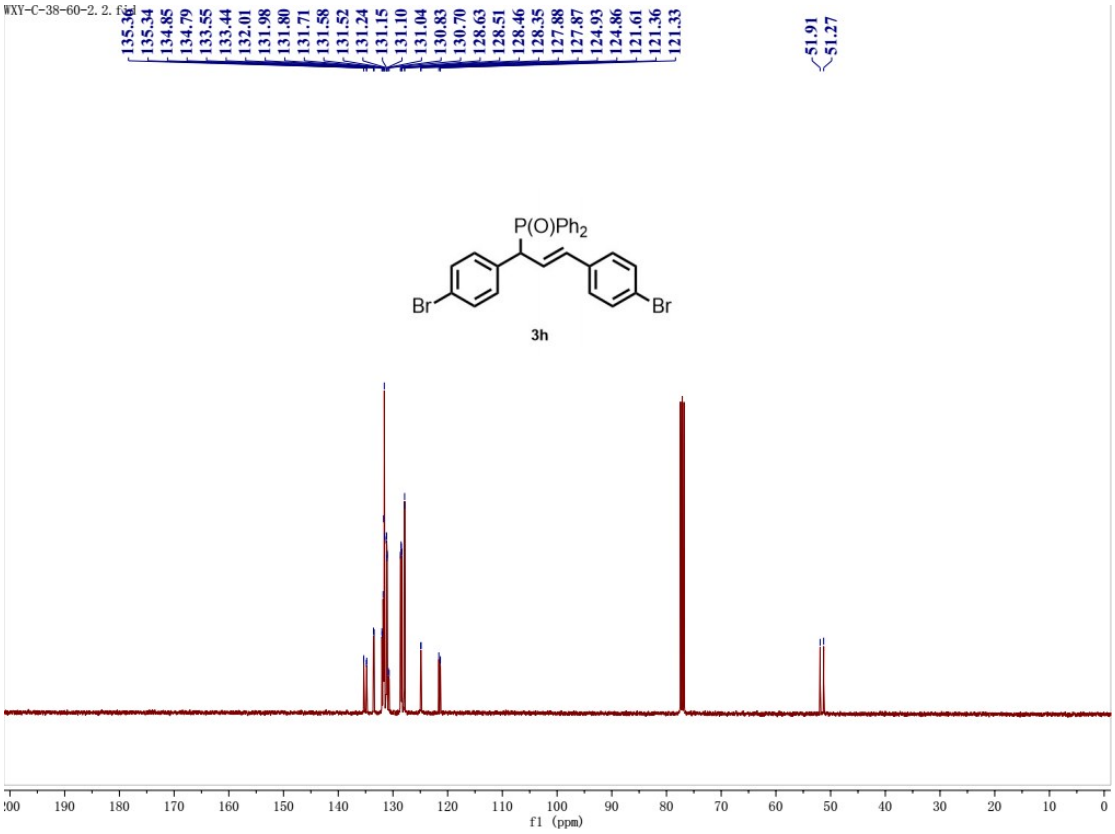
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3g.**



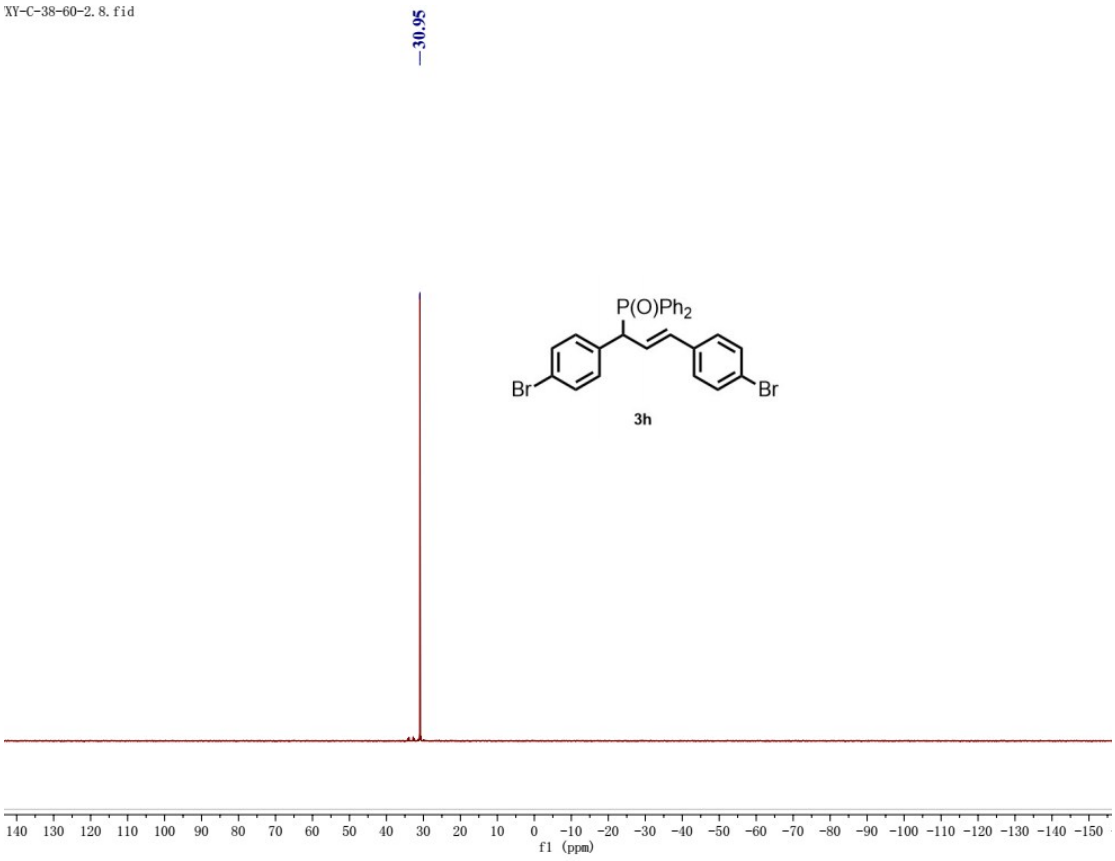
^{19}F NMR (376 MHz, Chloroform-d) spectra for compound **3g.**



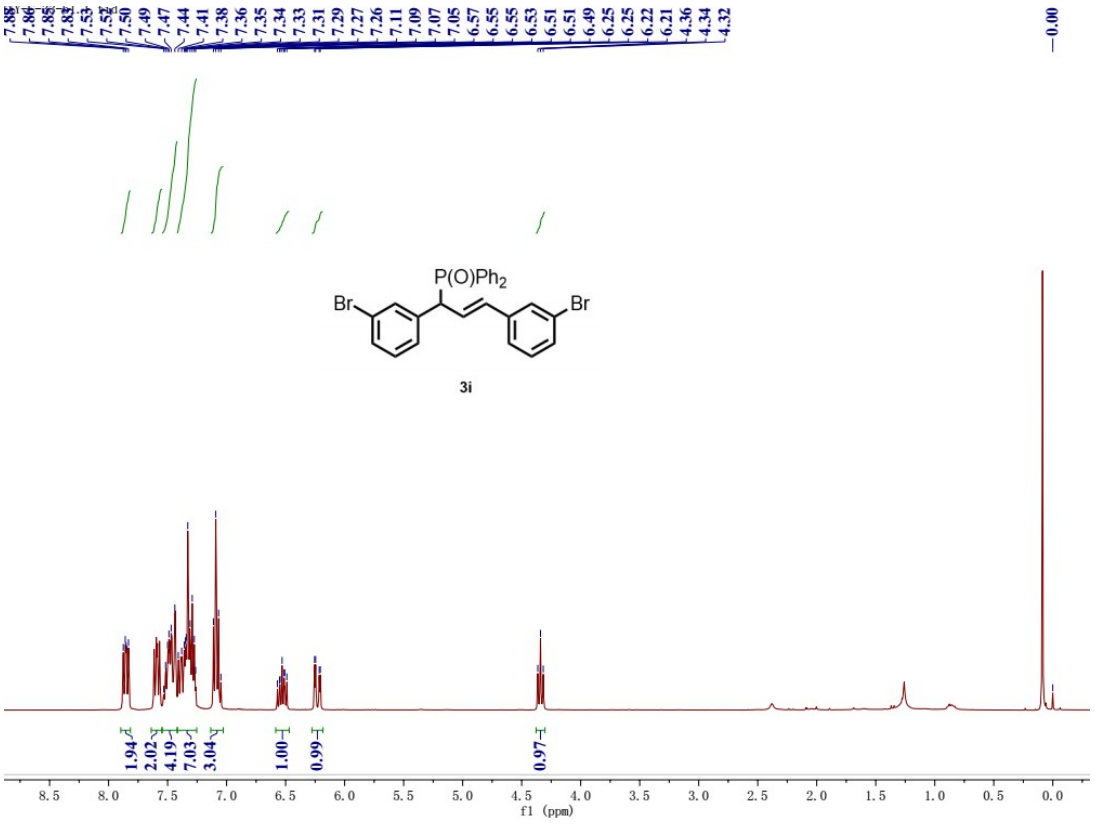
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3h.**



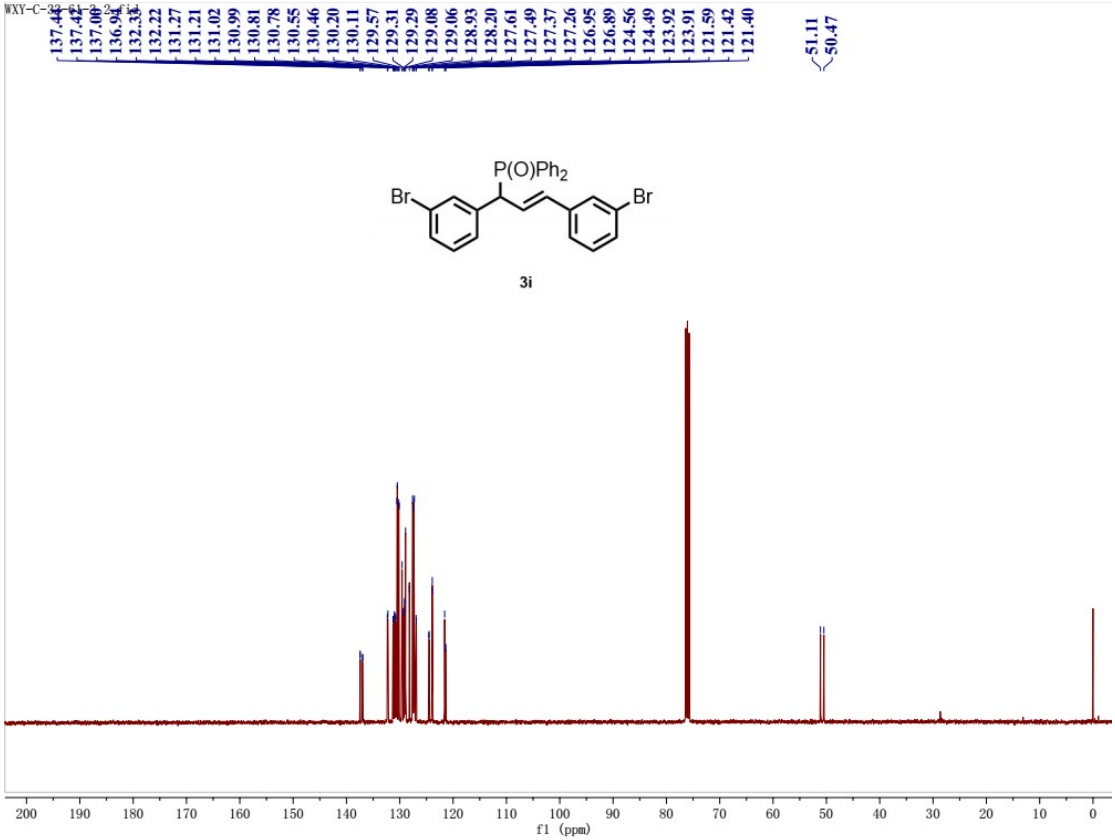
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3h.**



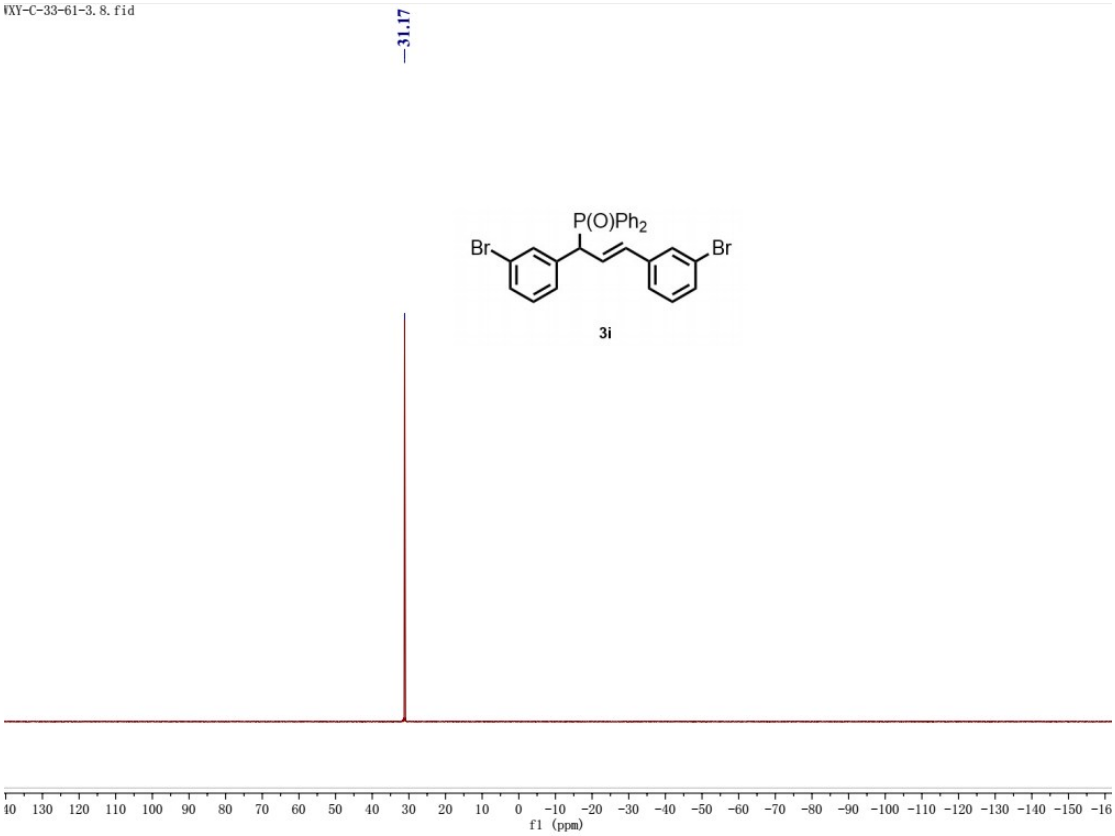
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3h.**



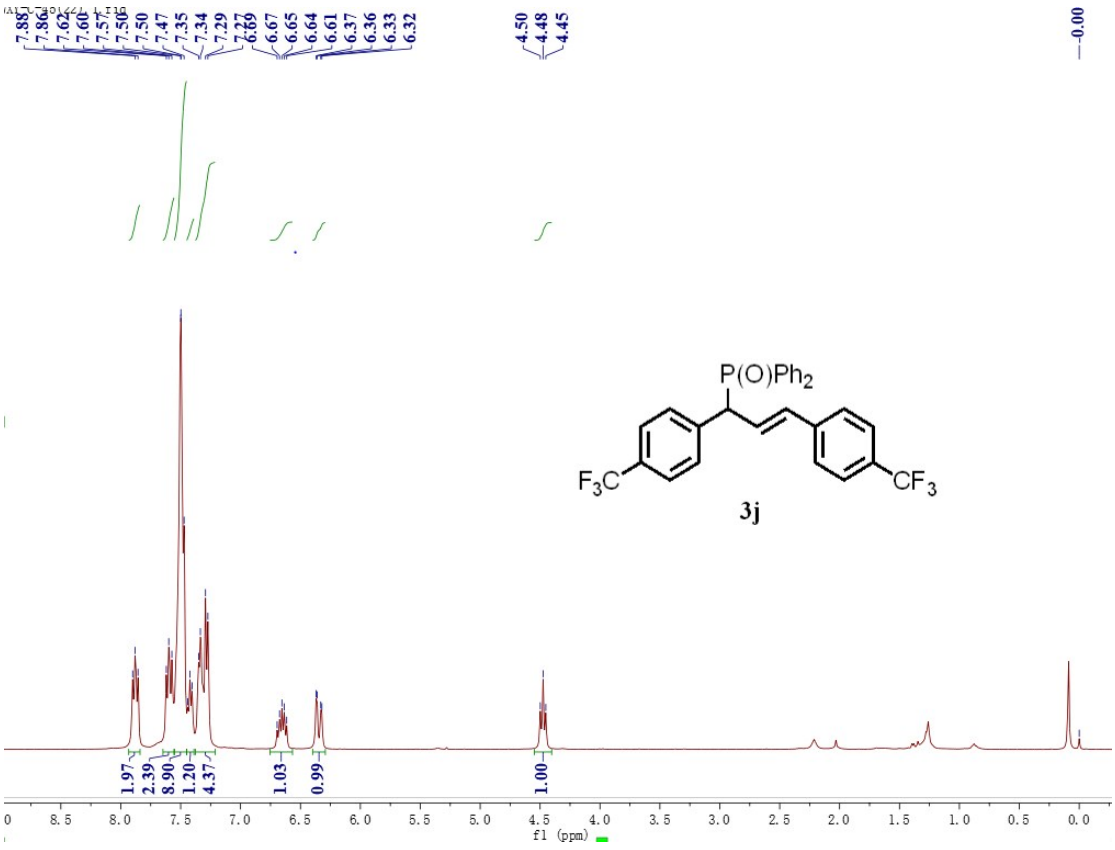
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3i.**



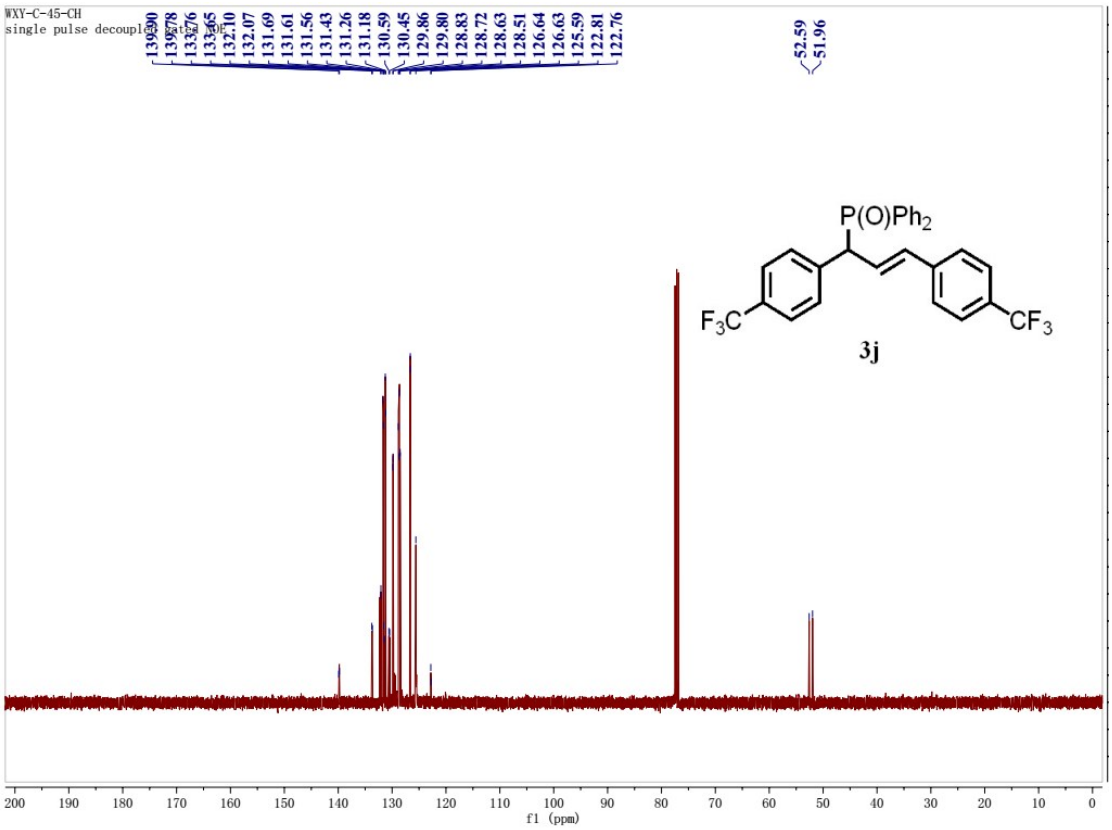
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3i.**



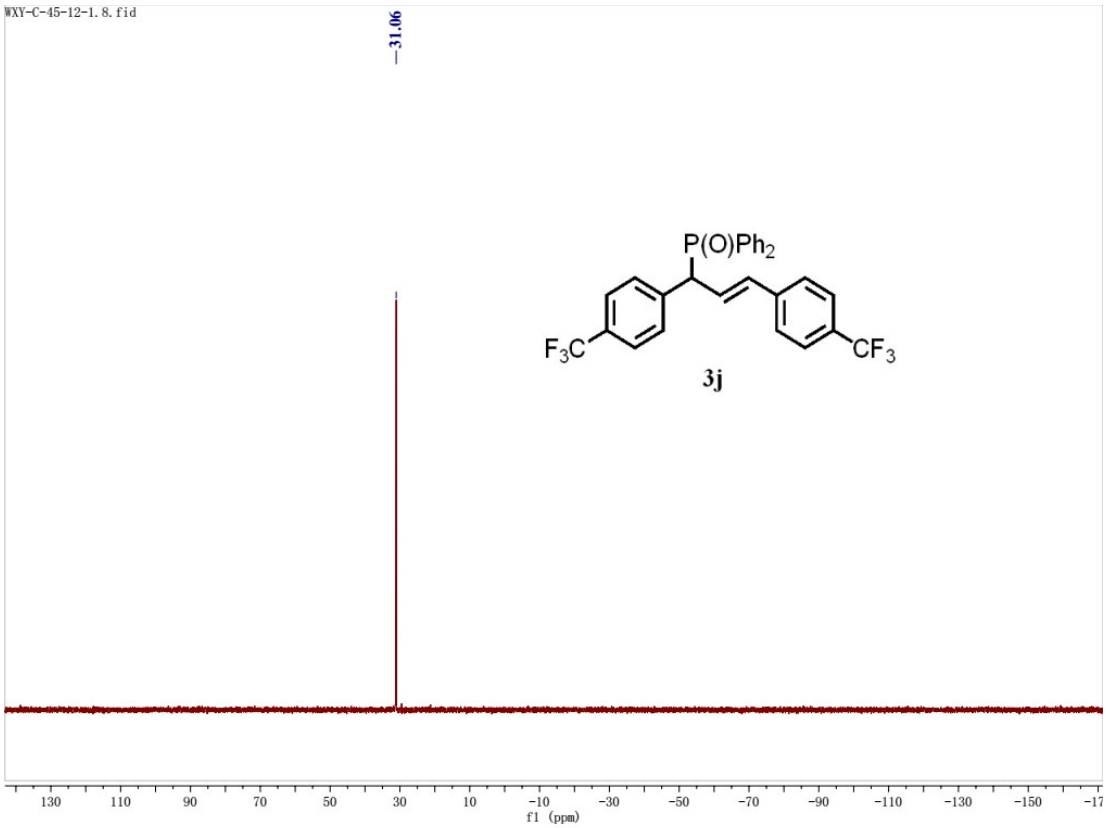
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3i.**



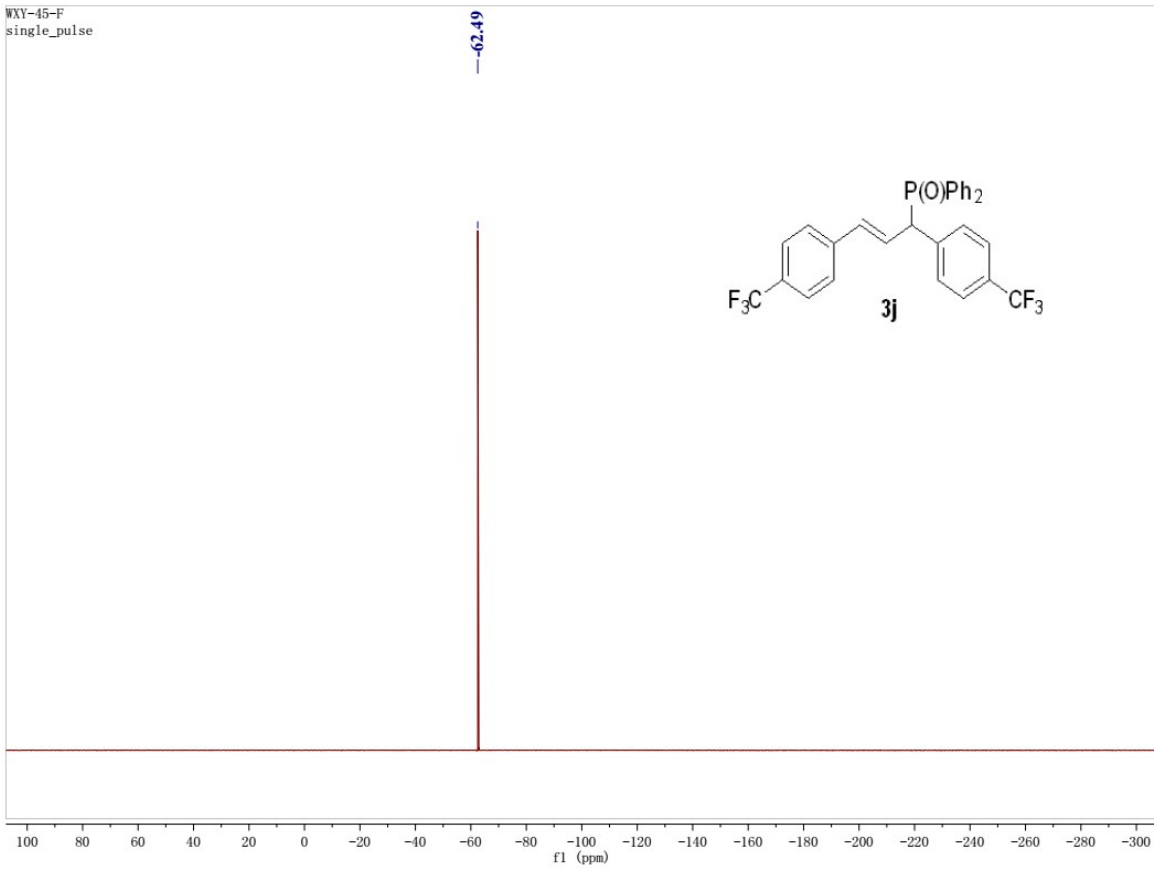
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3j.**



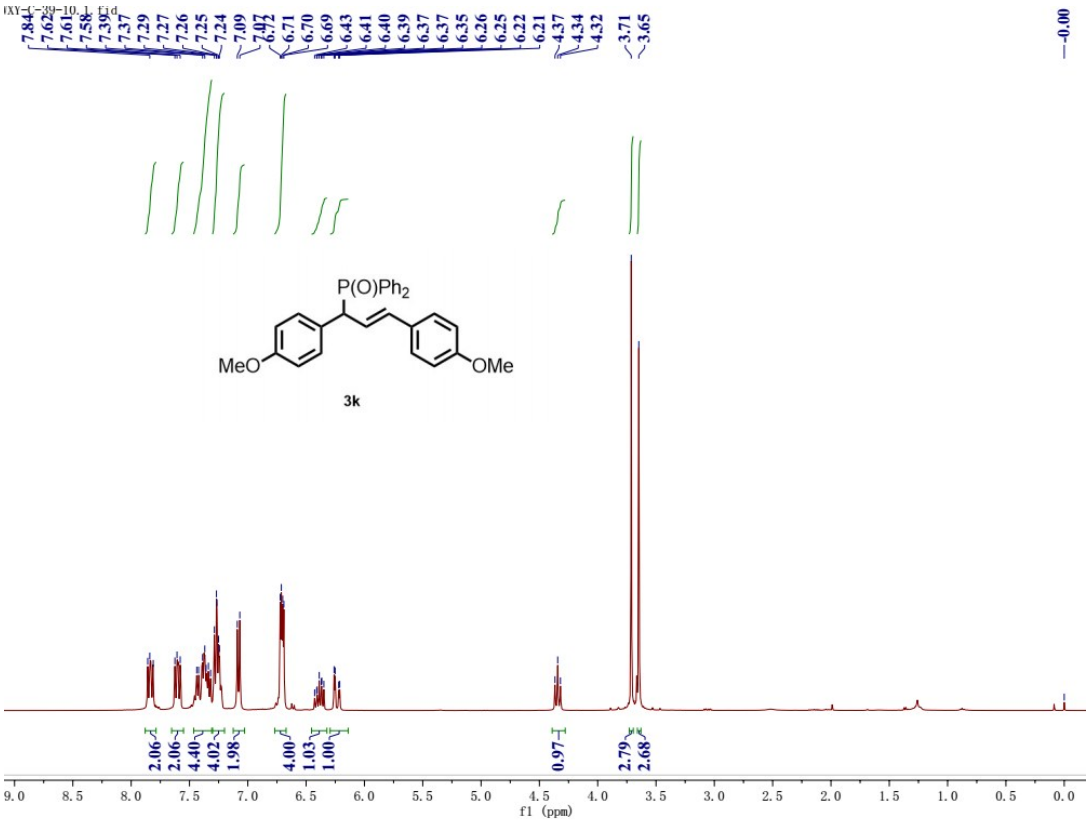
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3j.**



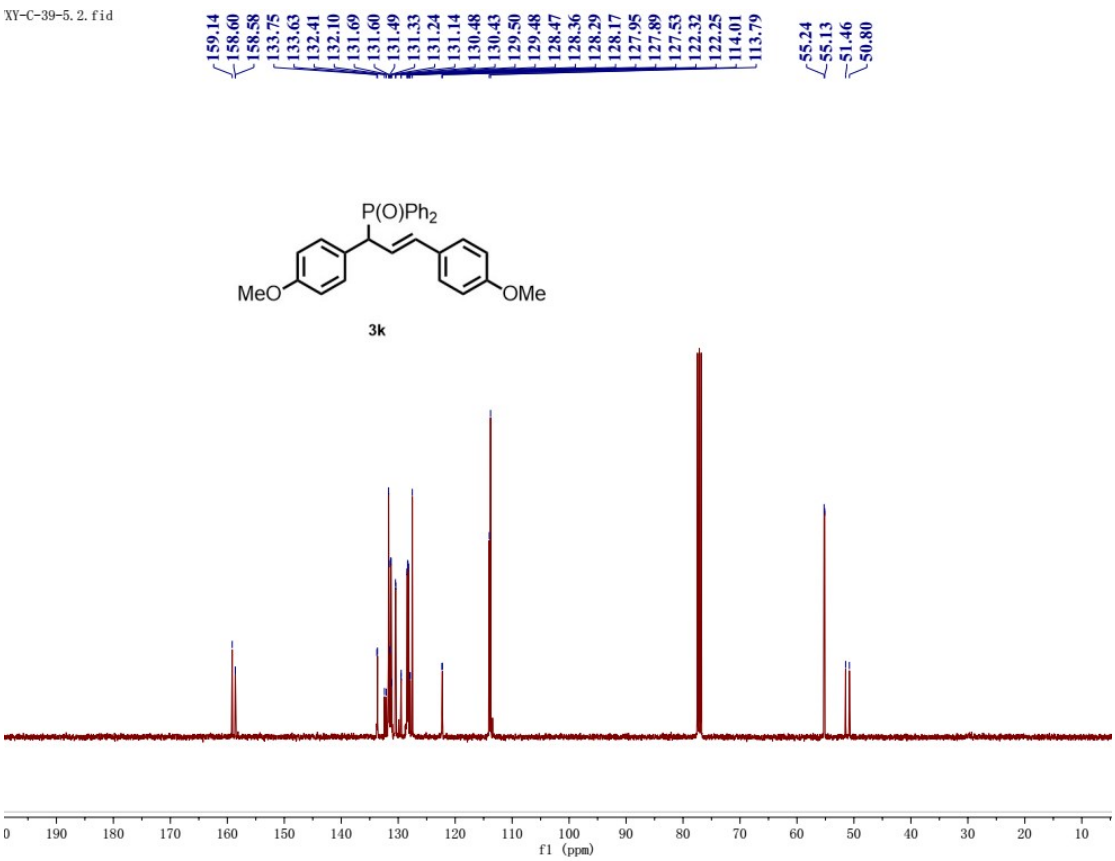
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3j.**



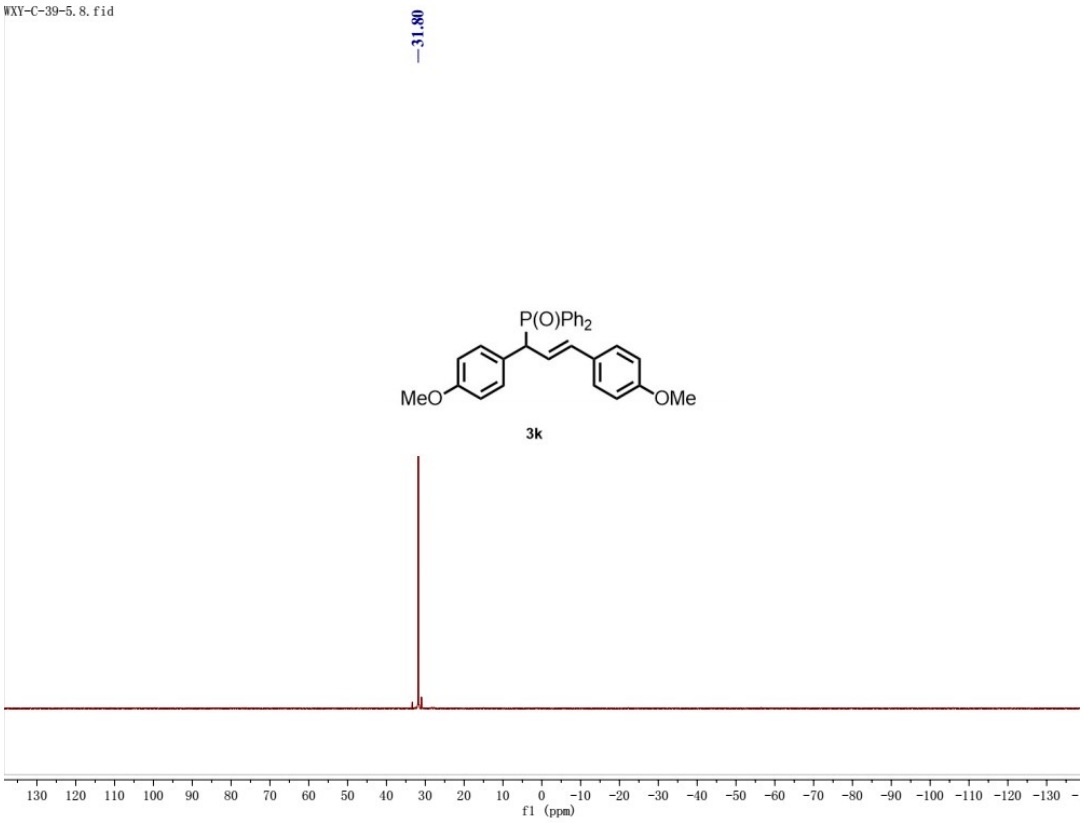
^{19}F NMR (376 MHz, Chloroform-d) spectra for compound **3j.**



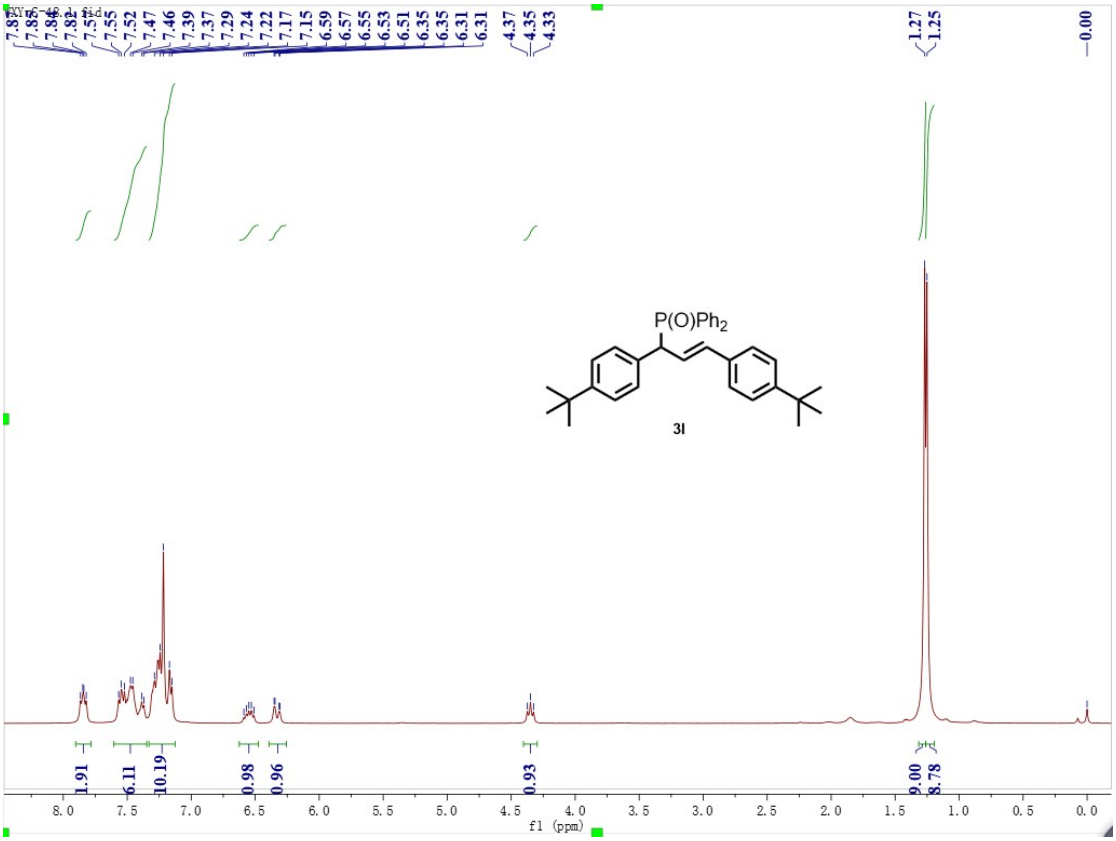
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3k.**



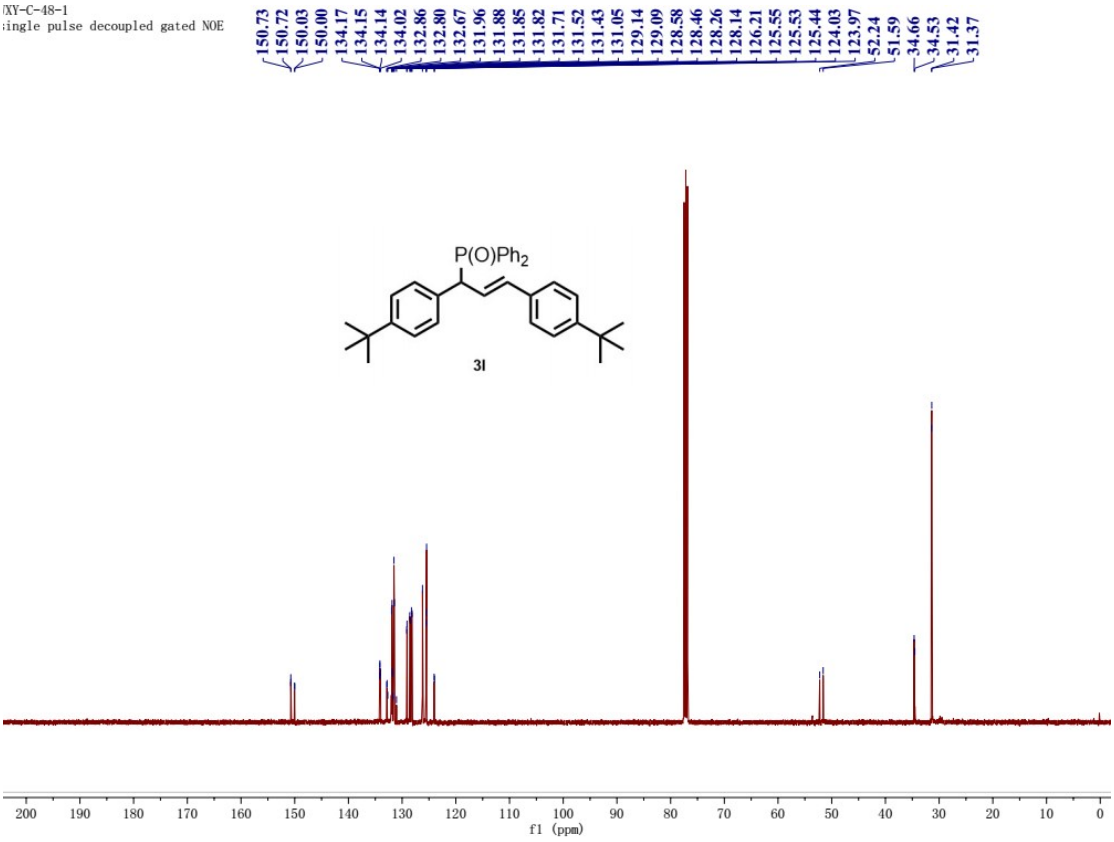
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3k.**



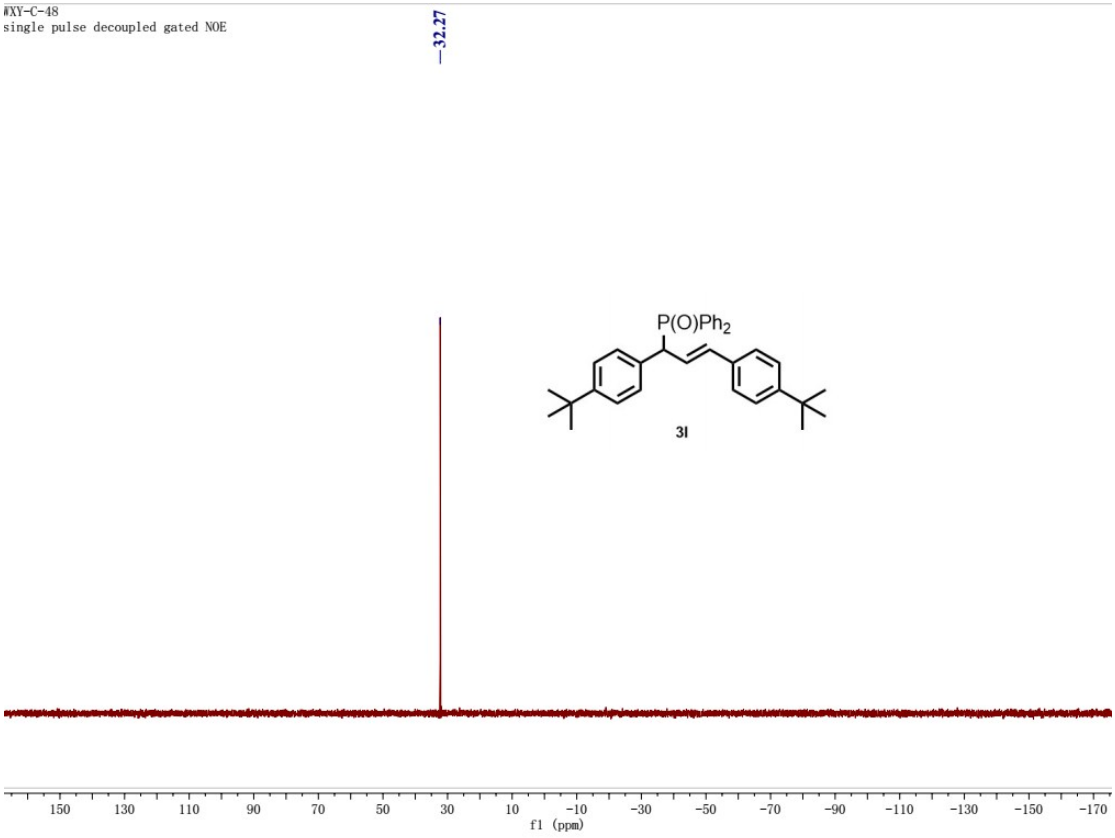
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3k.**



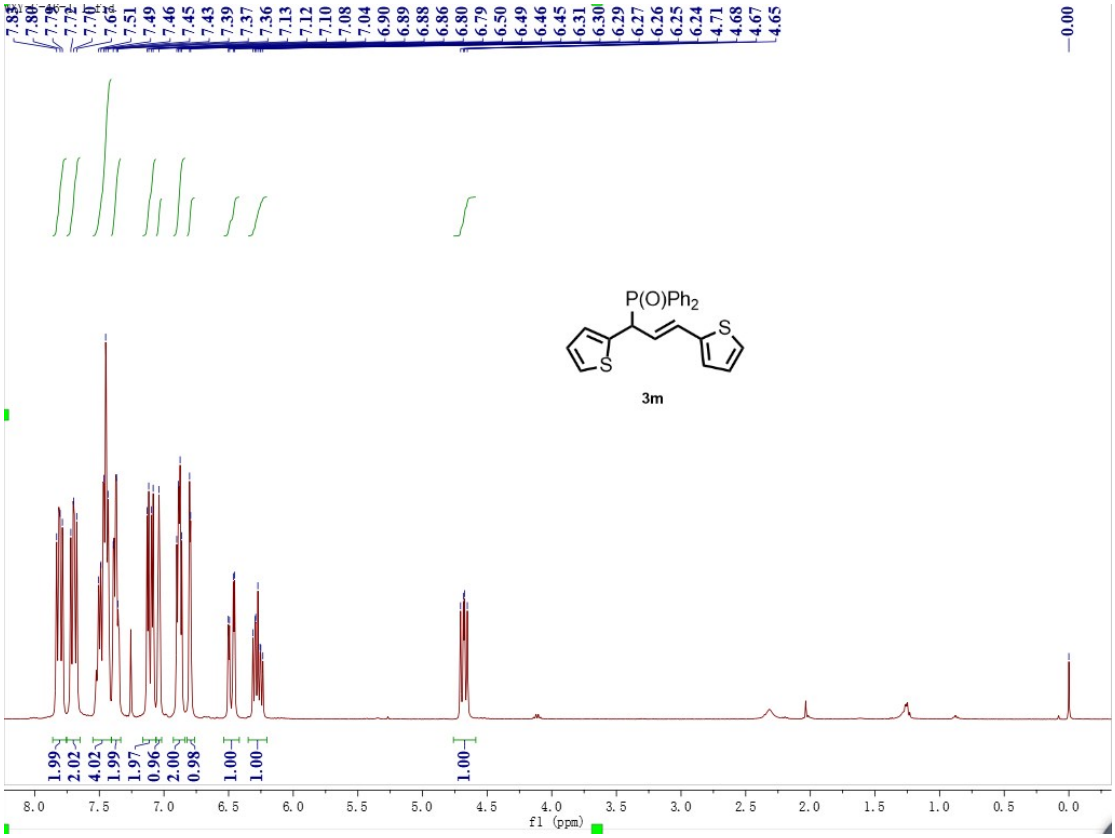
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3l.**



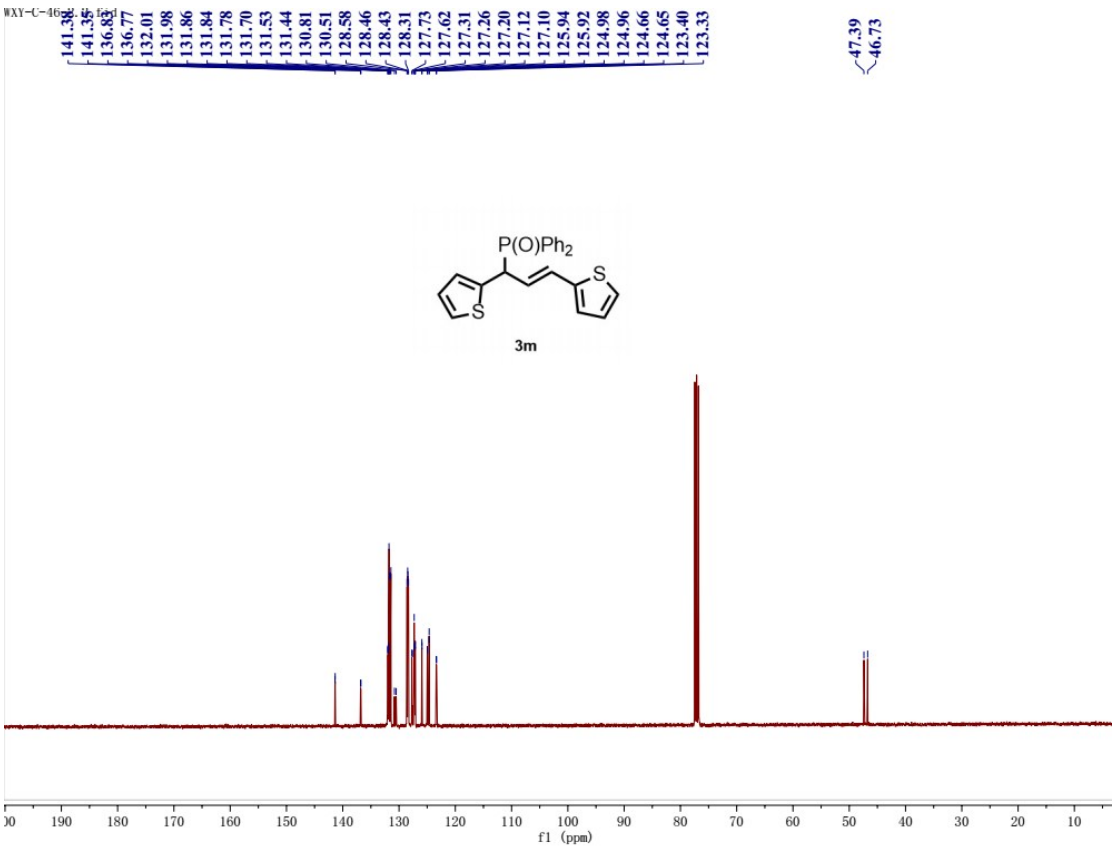
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3l.**



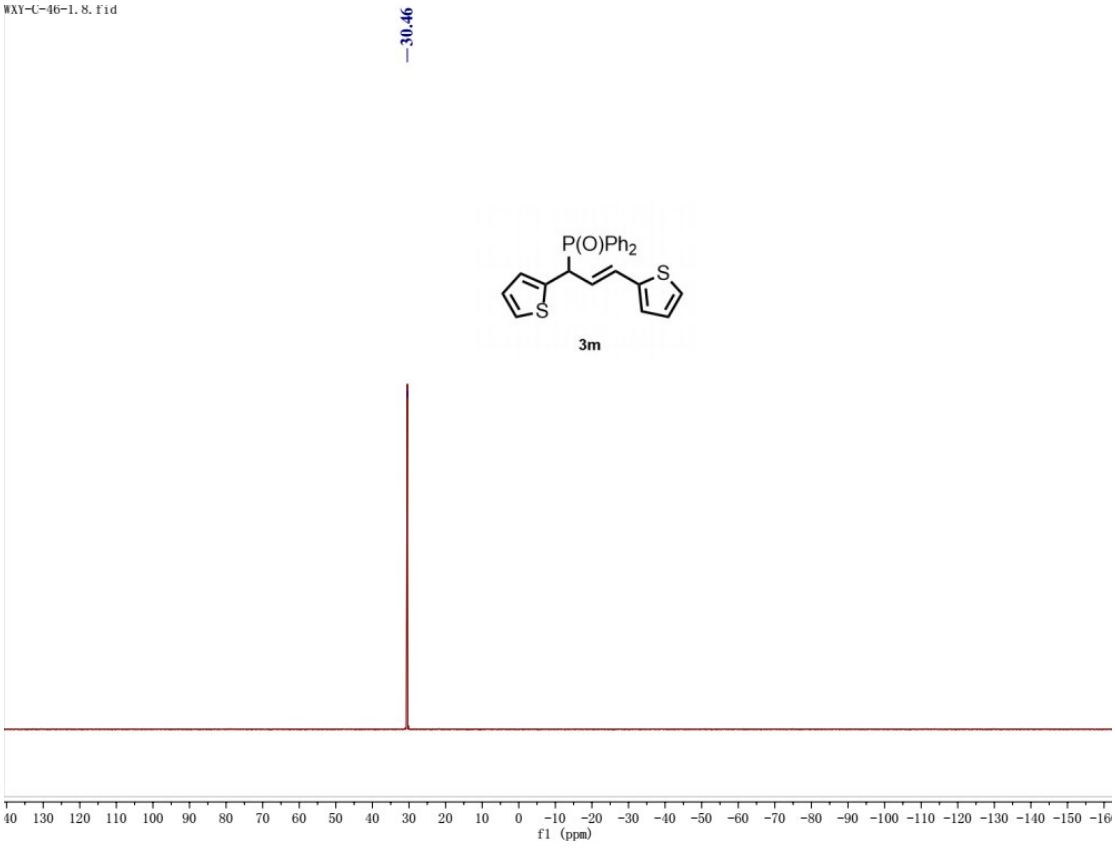
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3l.**



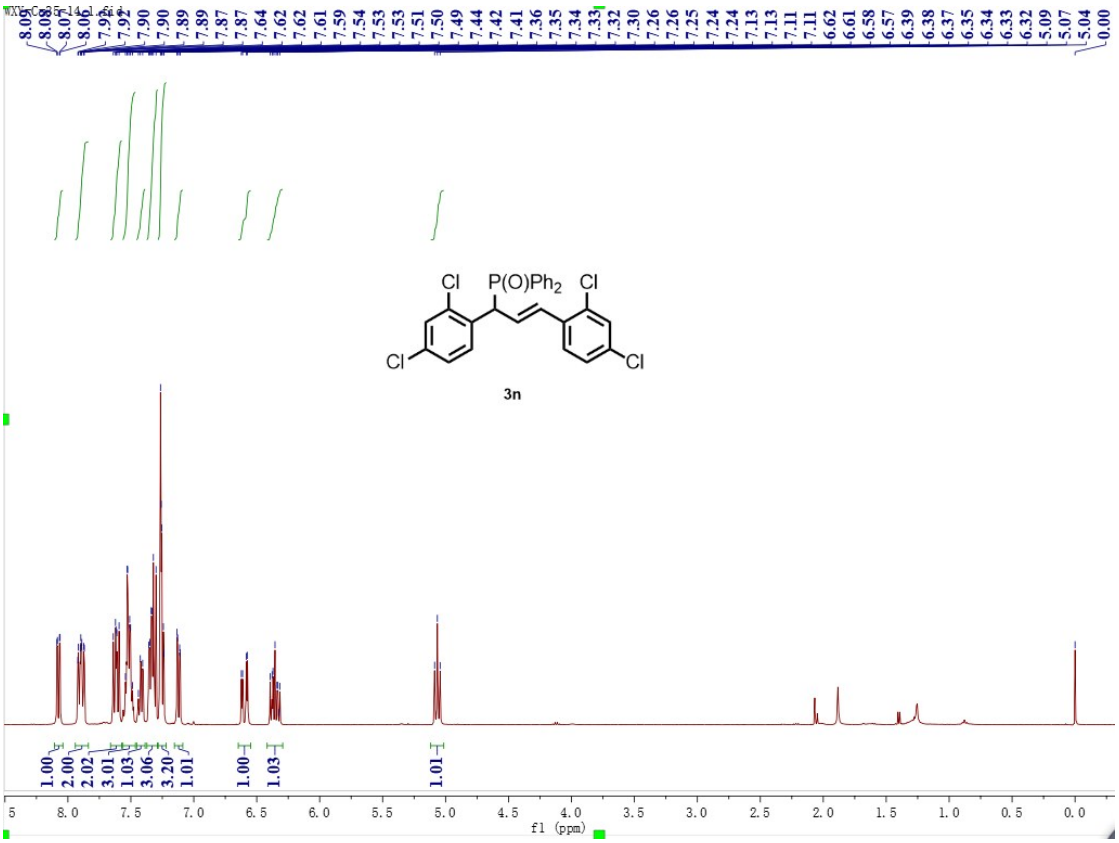
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3m.**



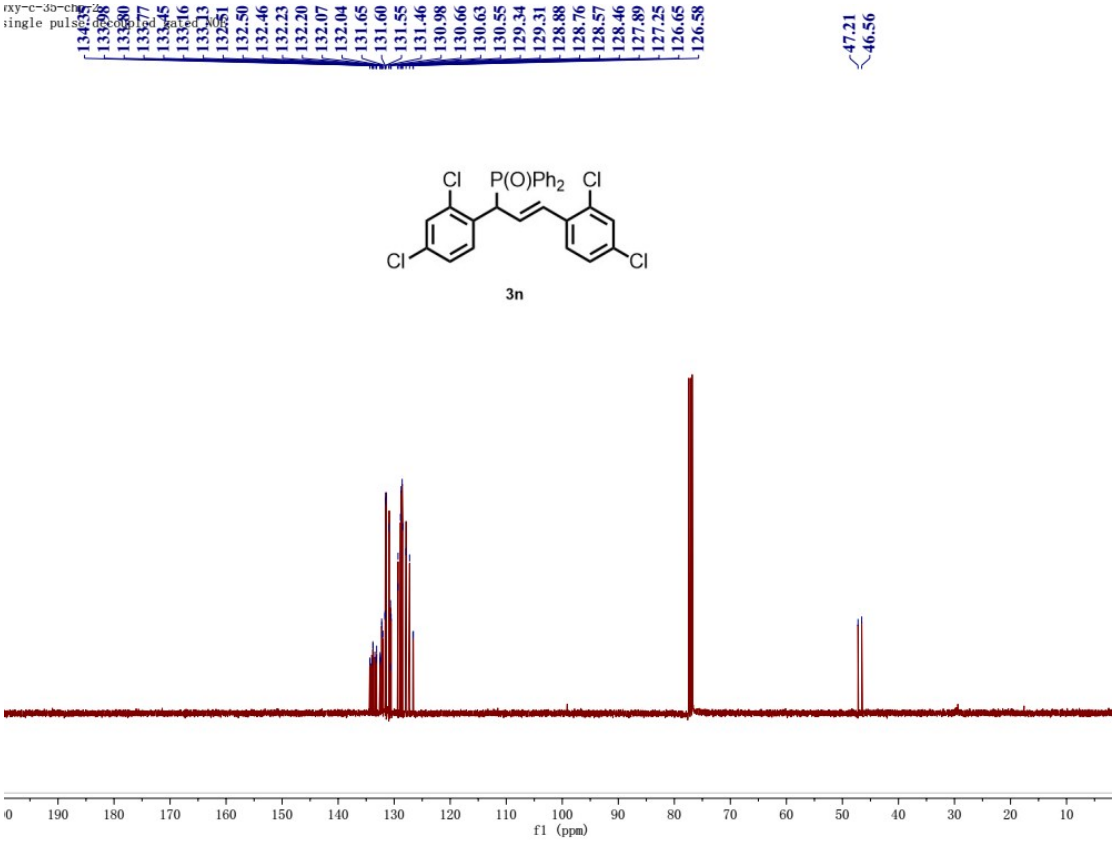
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3m.**



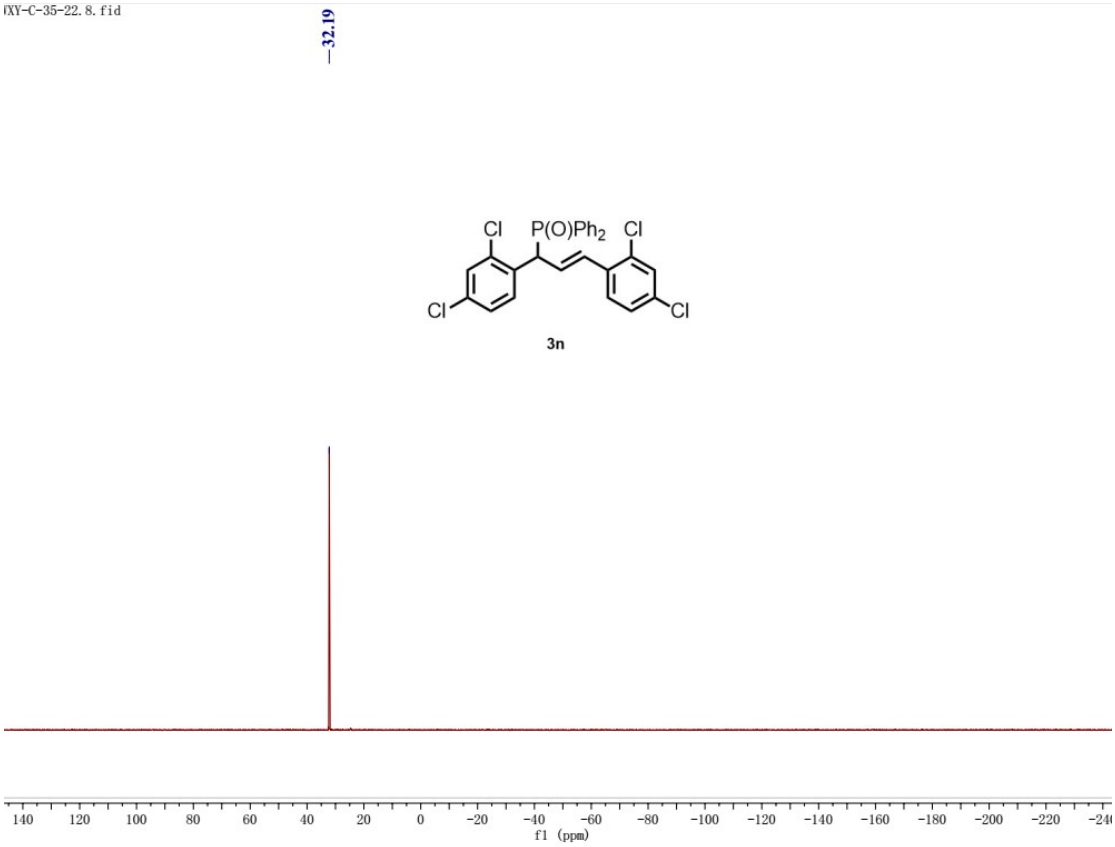
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3m.**



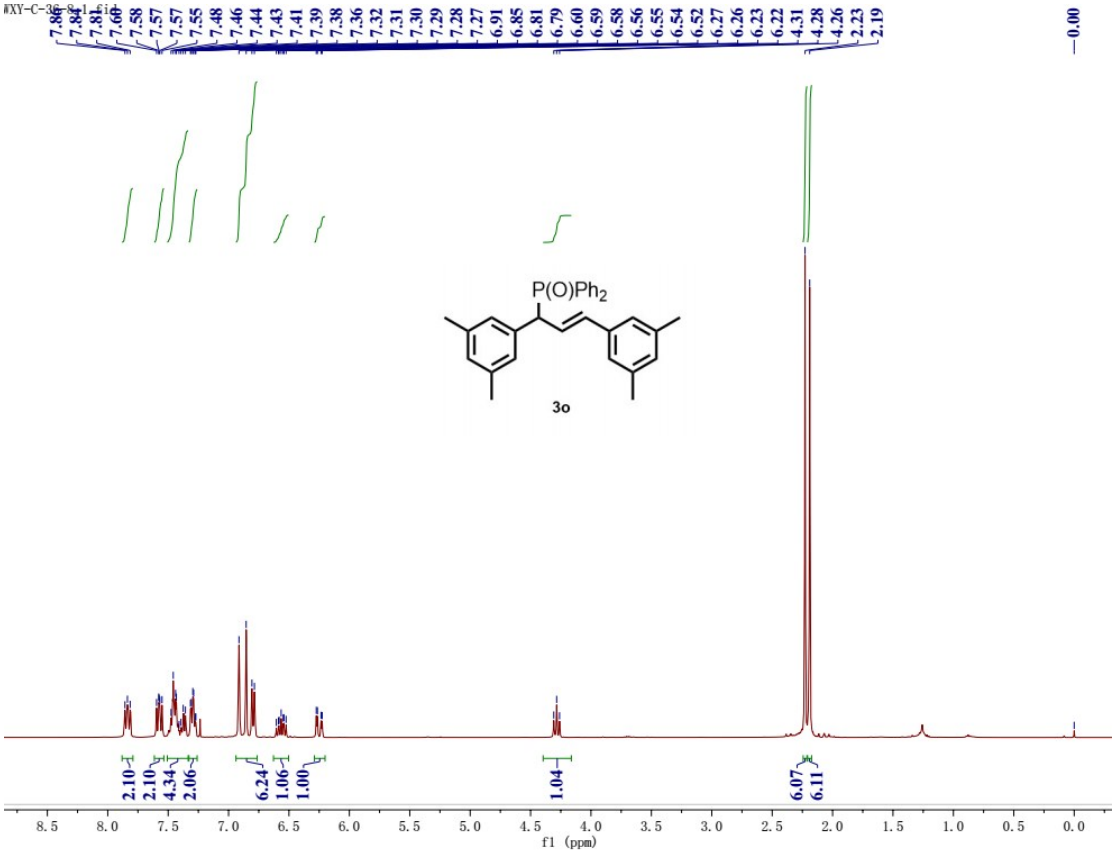
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3n.**



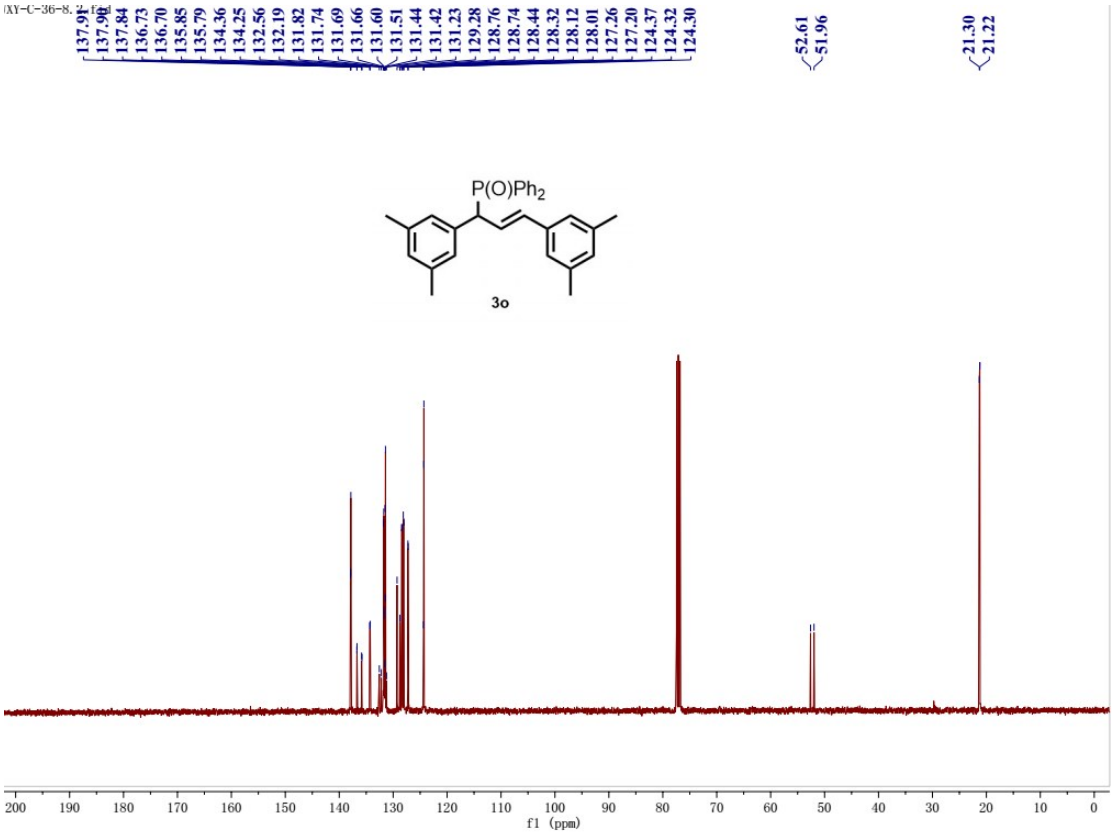
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3n.**



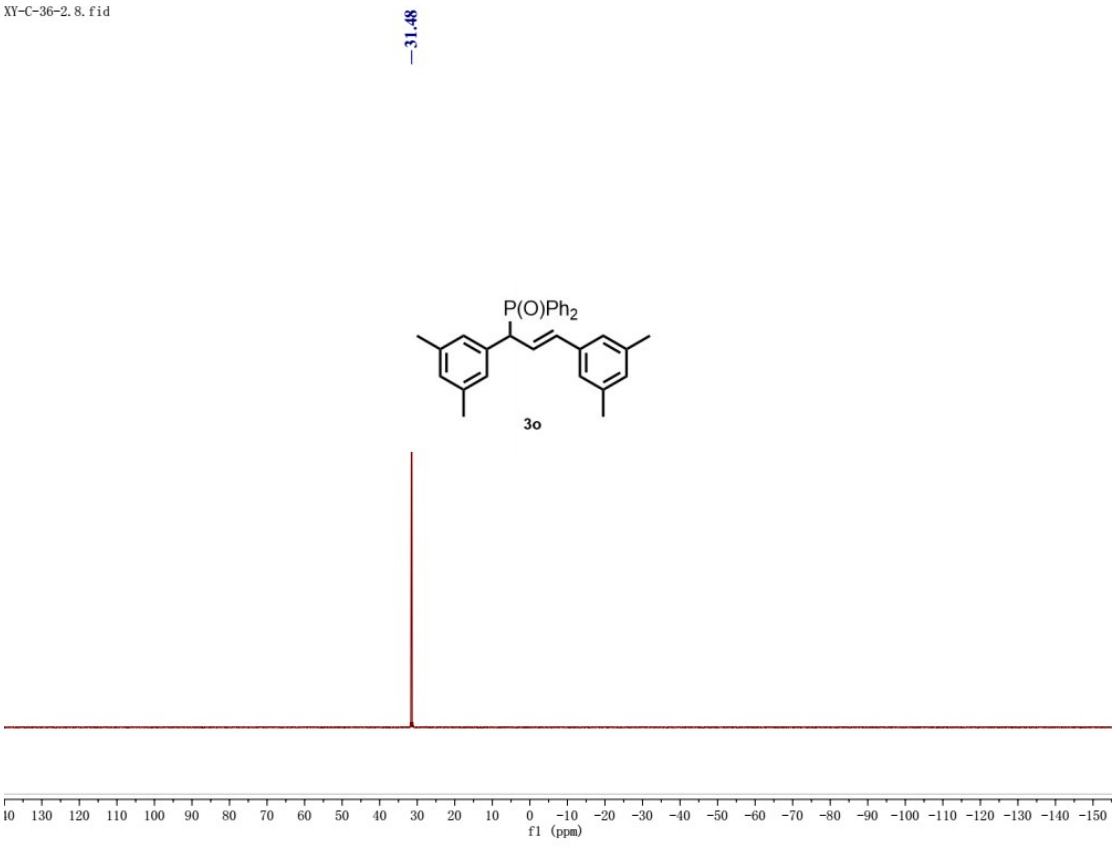
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3n.**



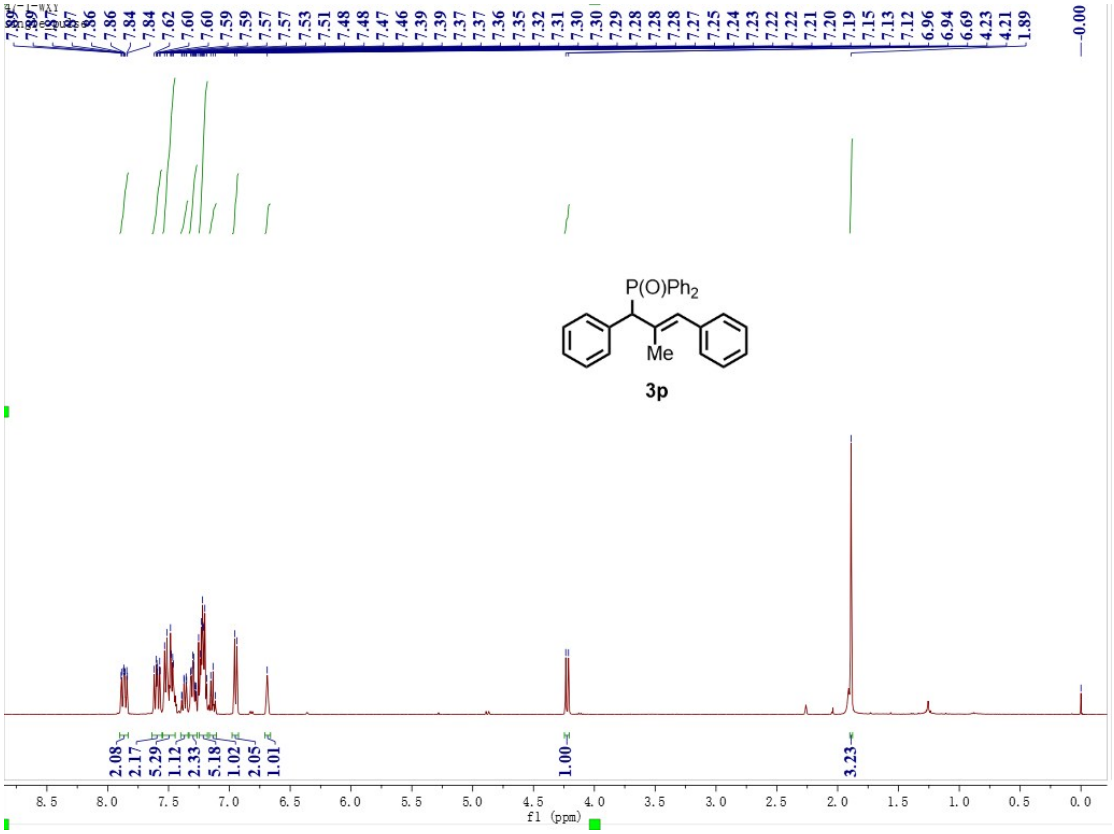
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3o.**



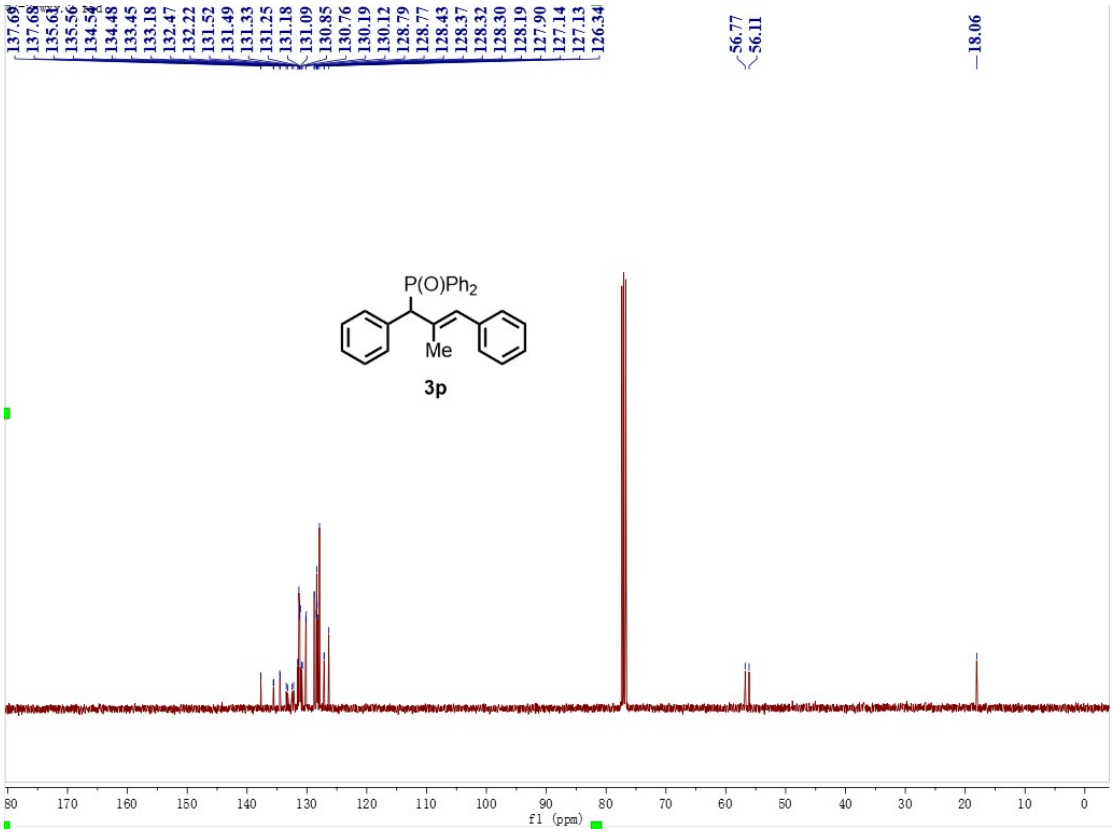
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3o.**



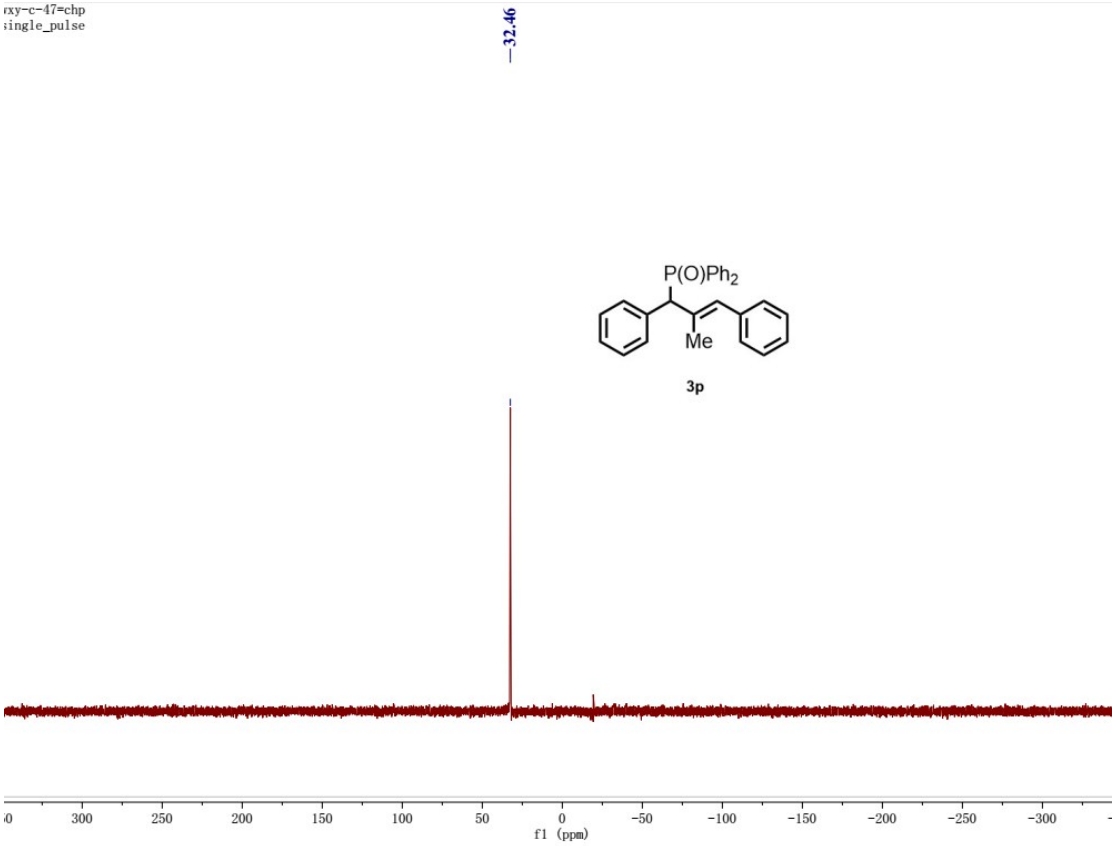
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3o.**



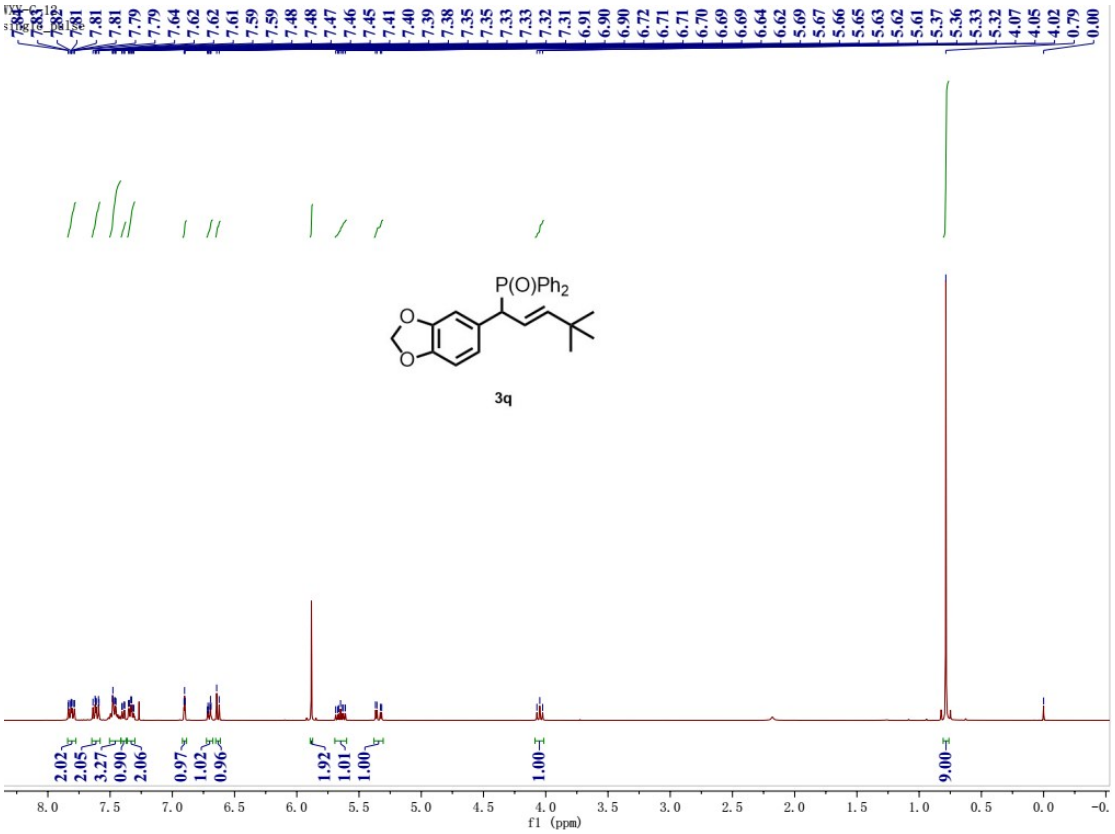
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3p.**



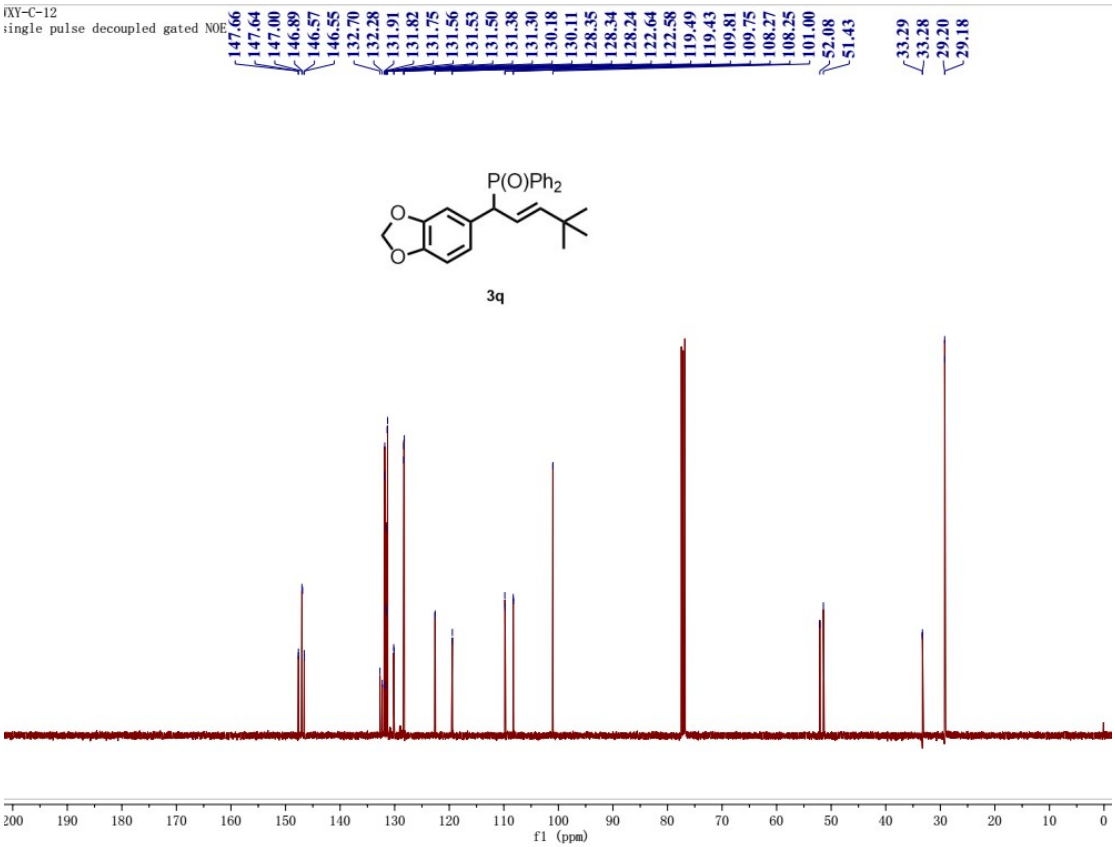
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3p.**



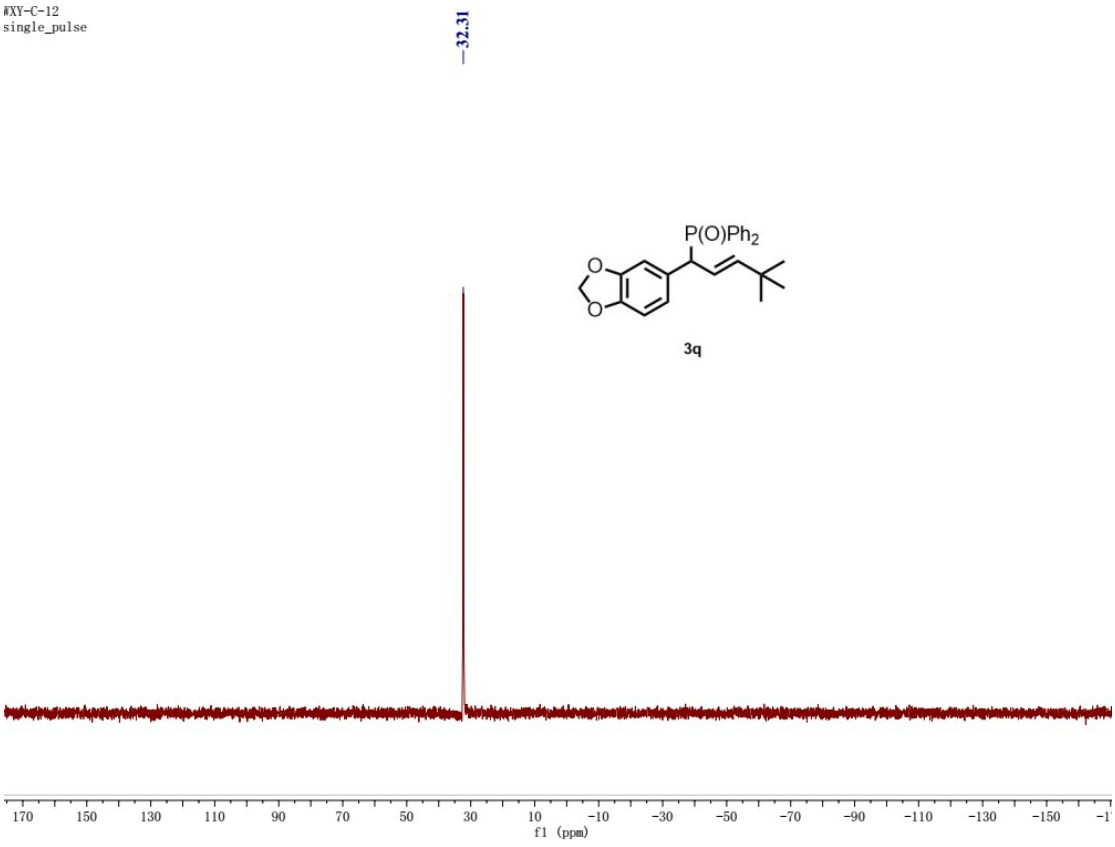
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3p.**



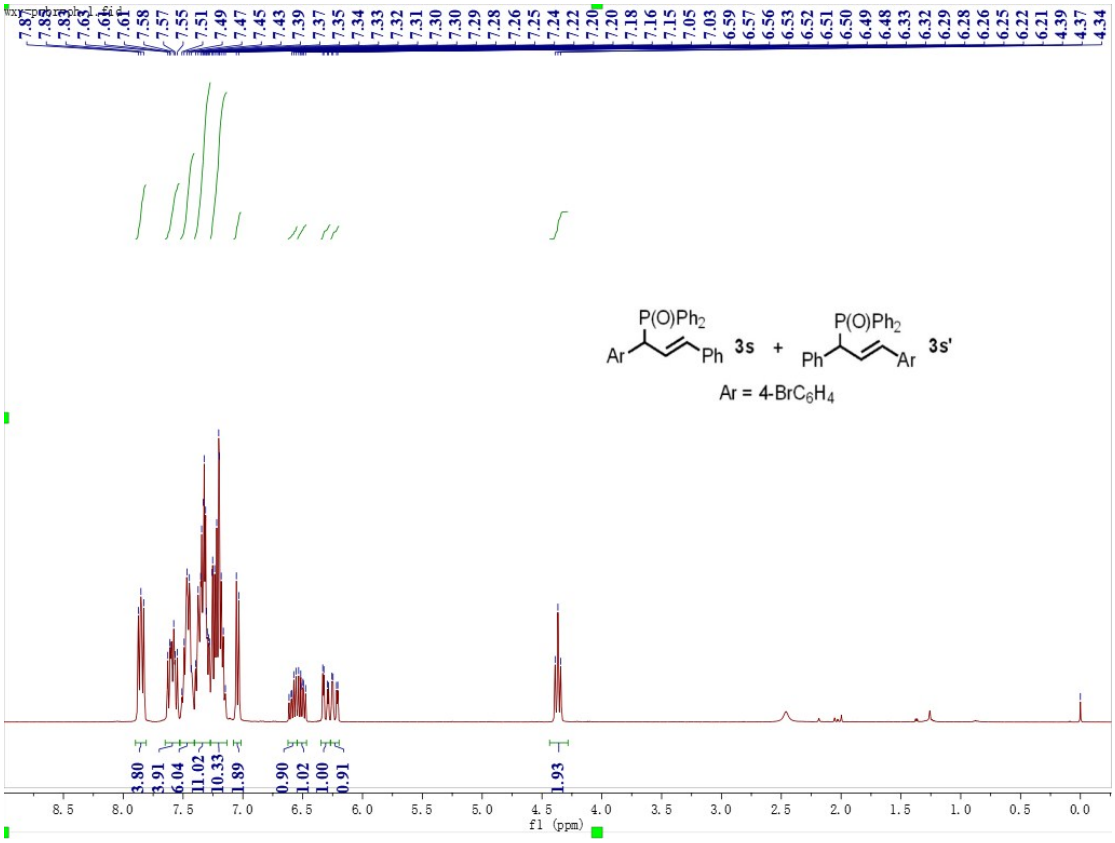
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3q.**



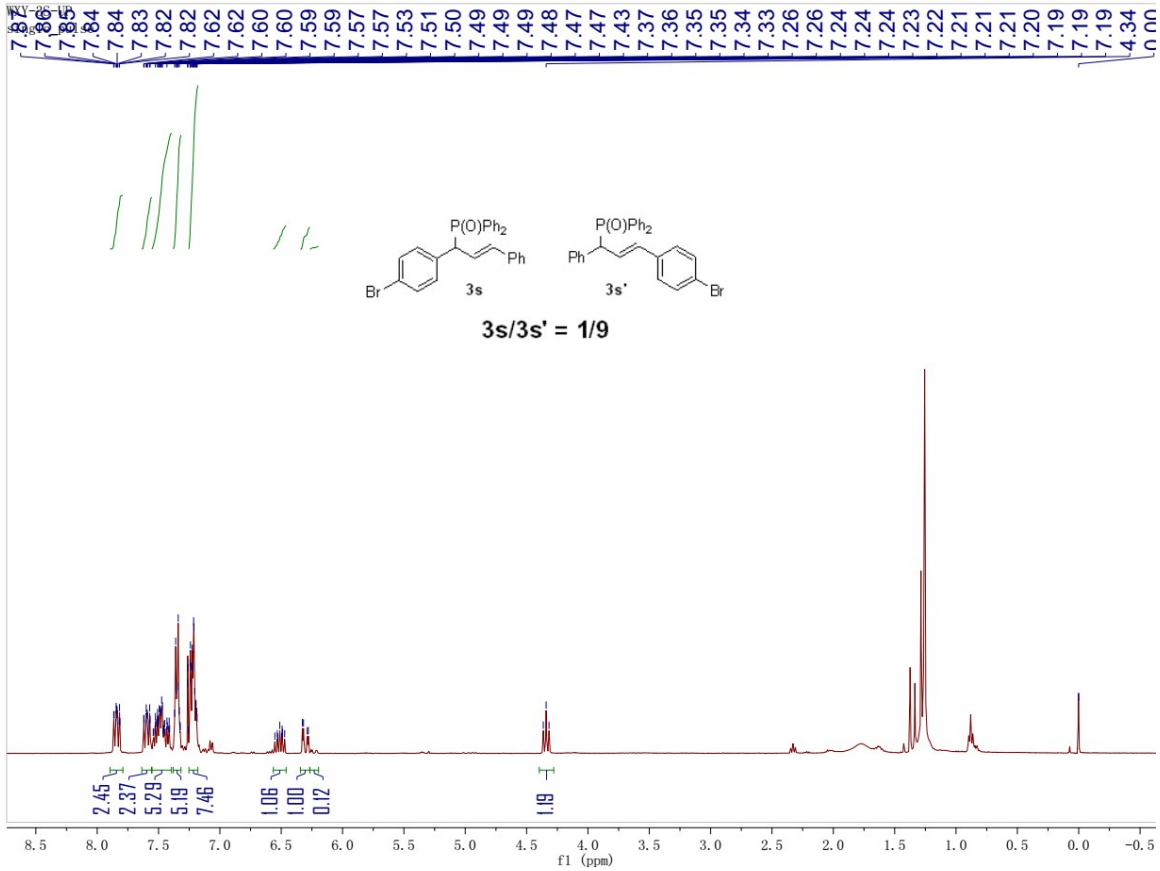
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3q.**



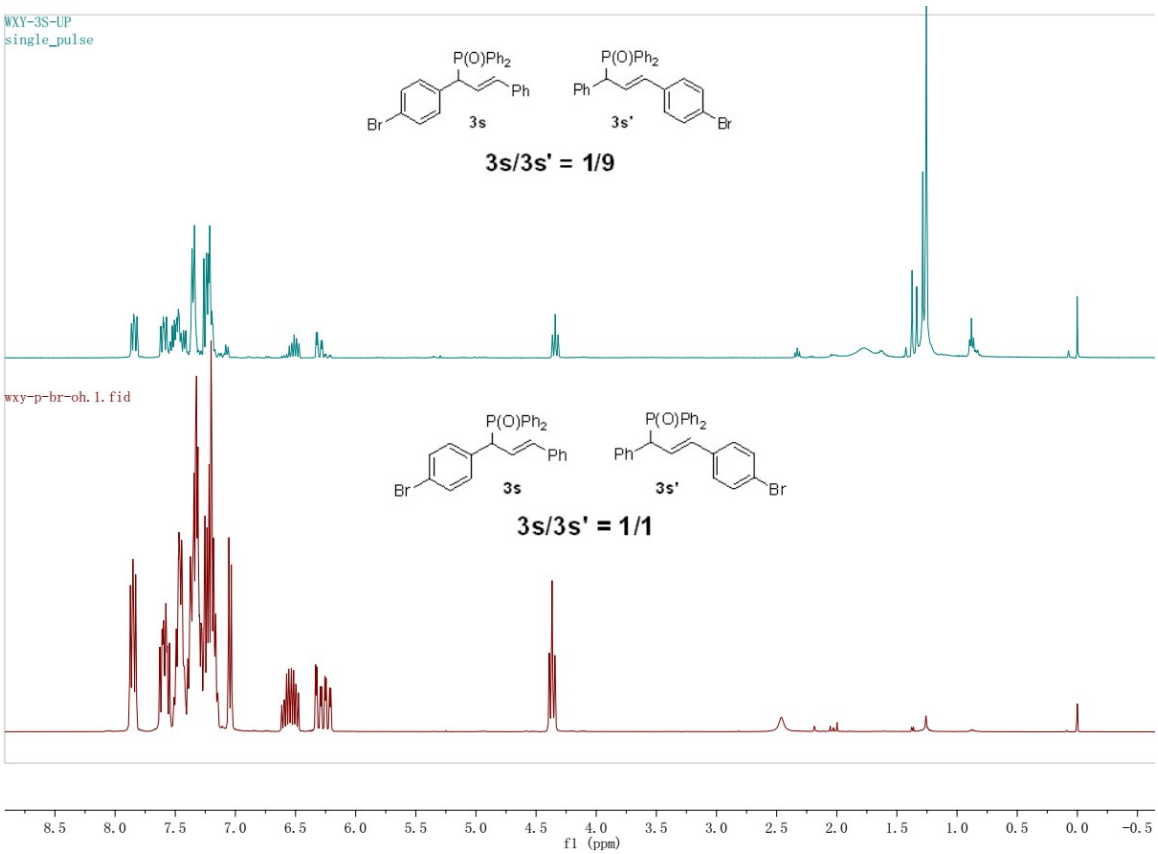
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3q.**



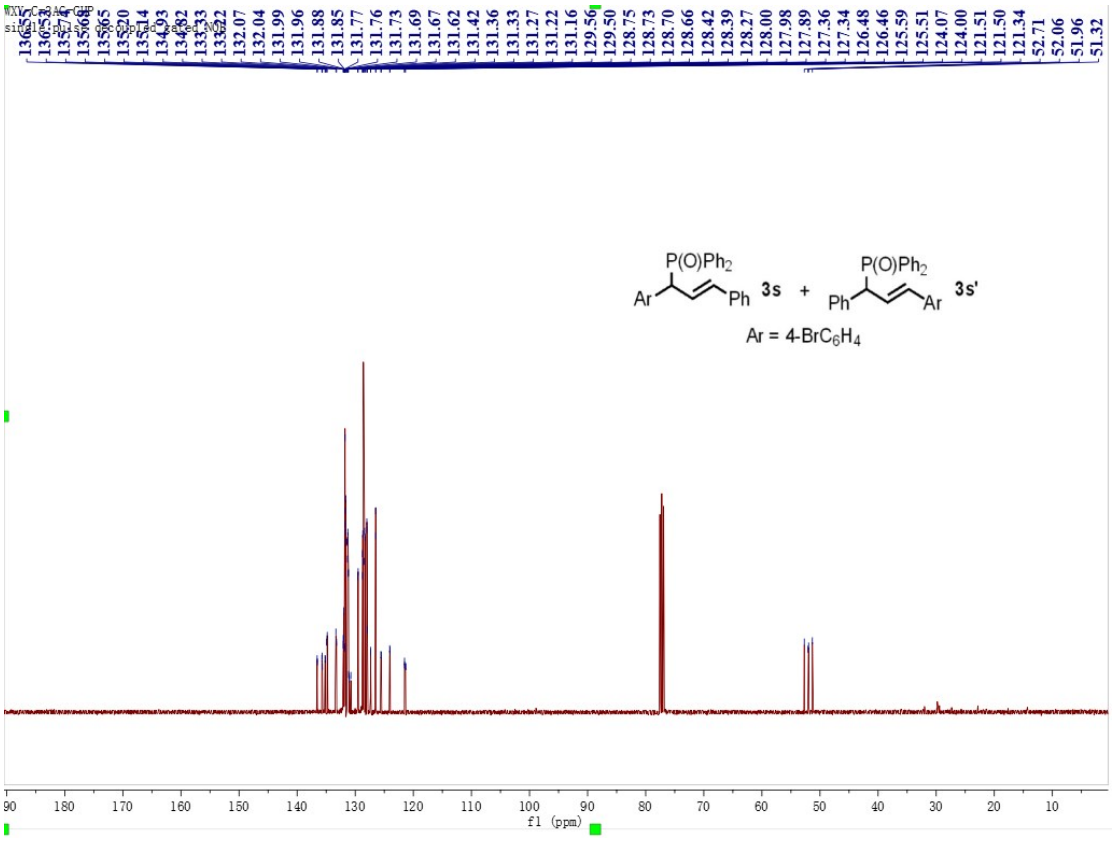
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3s** and **3s'(3s/3s' = 1/1).**



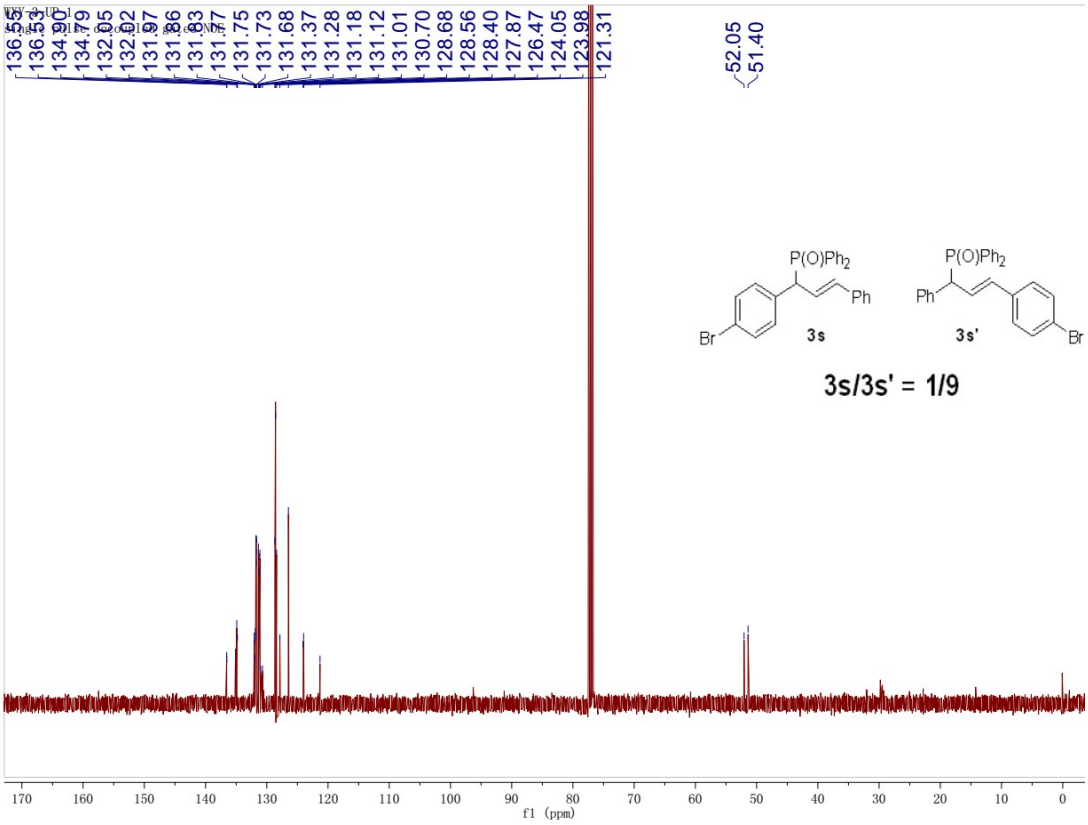
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3s** and **3s'(3s/3s' = 1/9).**



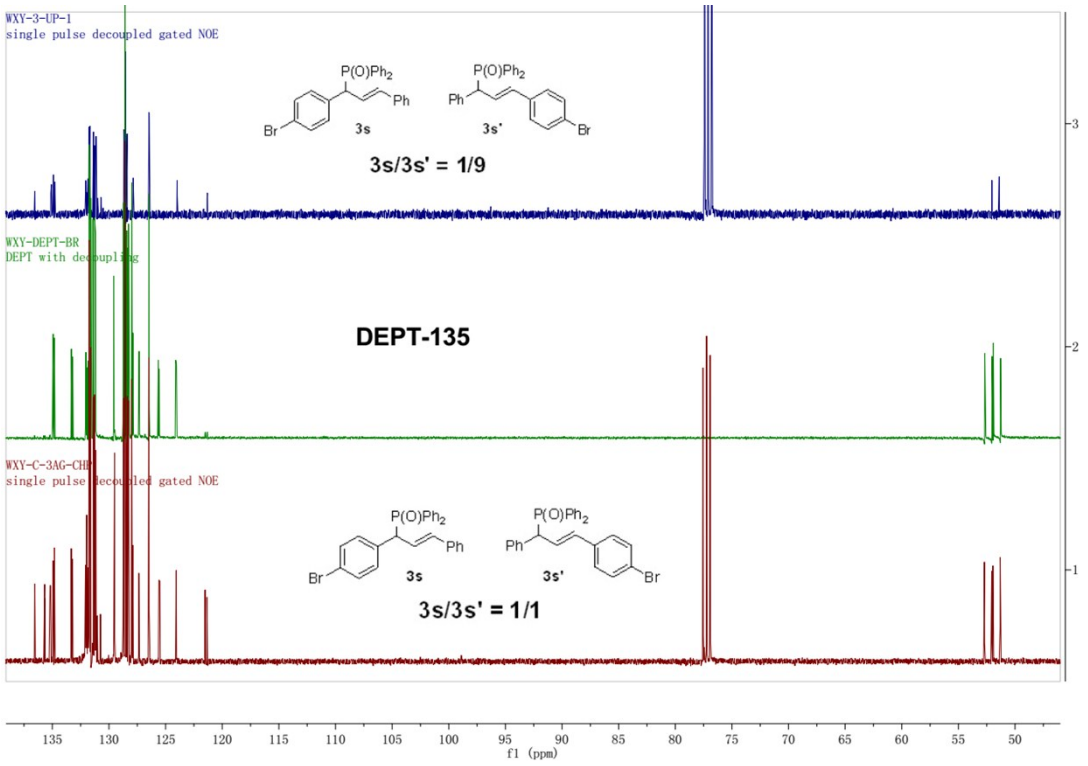
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3s** and **3s'(comparation).**



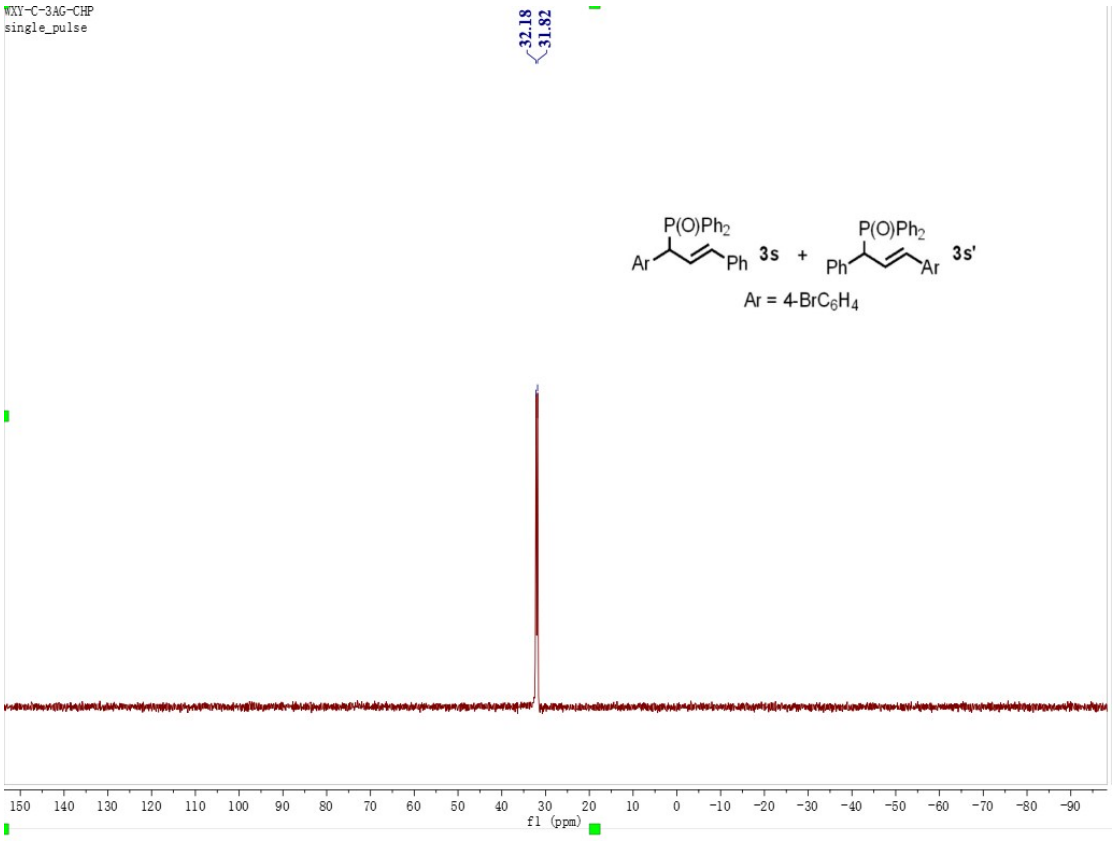
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3s** and **3s' (3s/3s' = 1/1).**



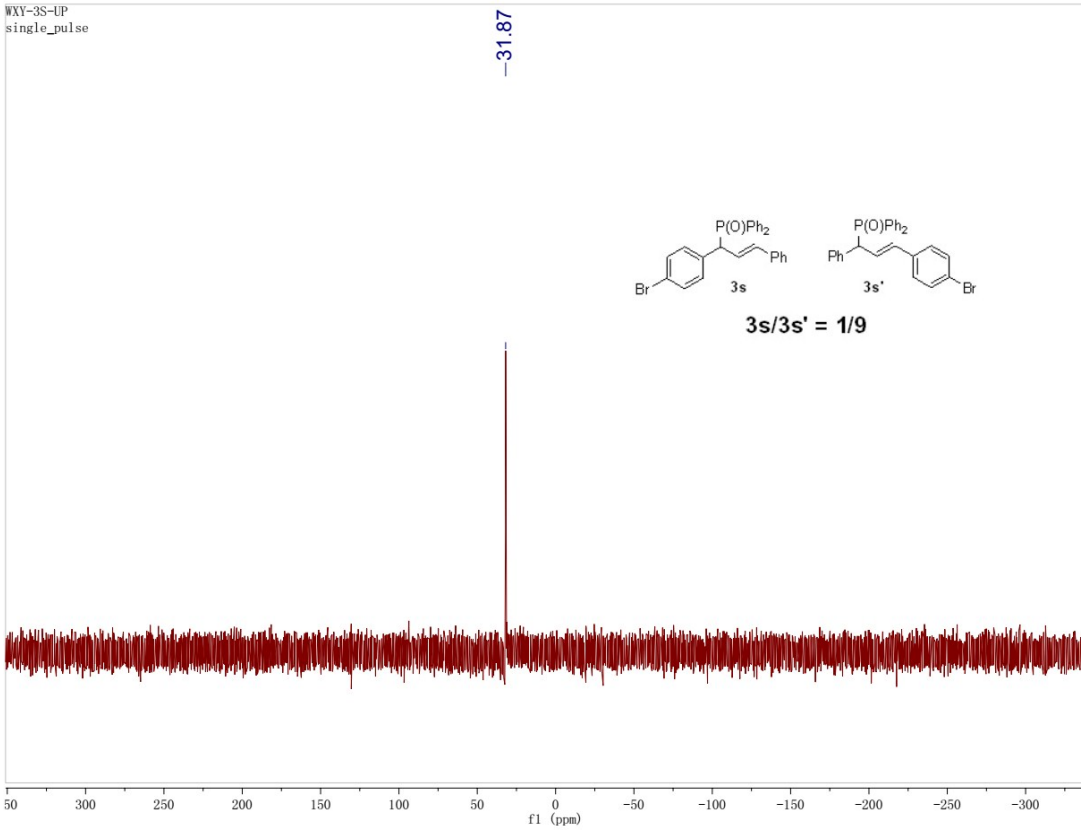
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3s** and **3s' (3s/3s' = 1/9).**



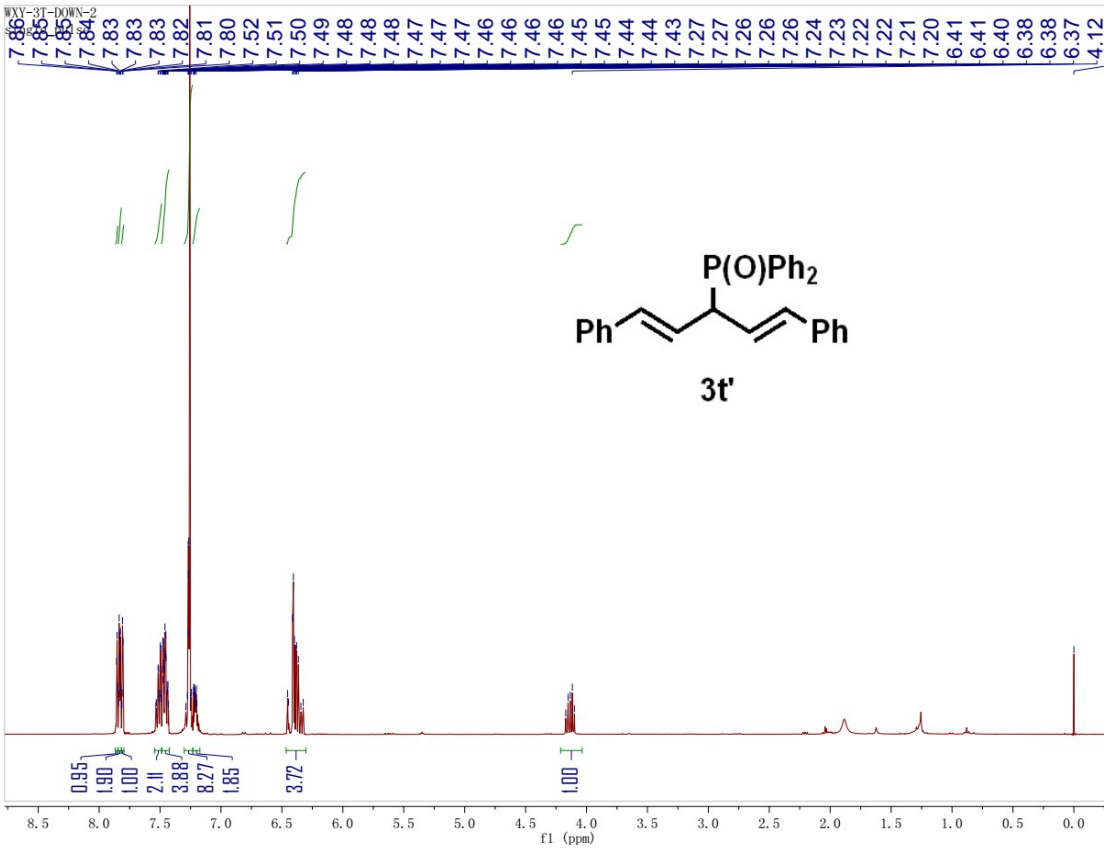
^{13}C NMR (101 MHz, Chloroform-d) spectra**.**



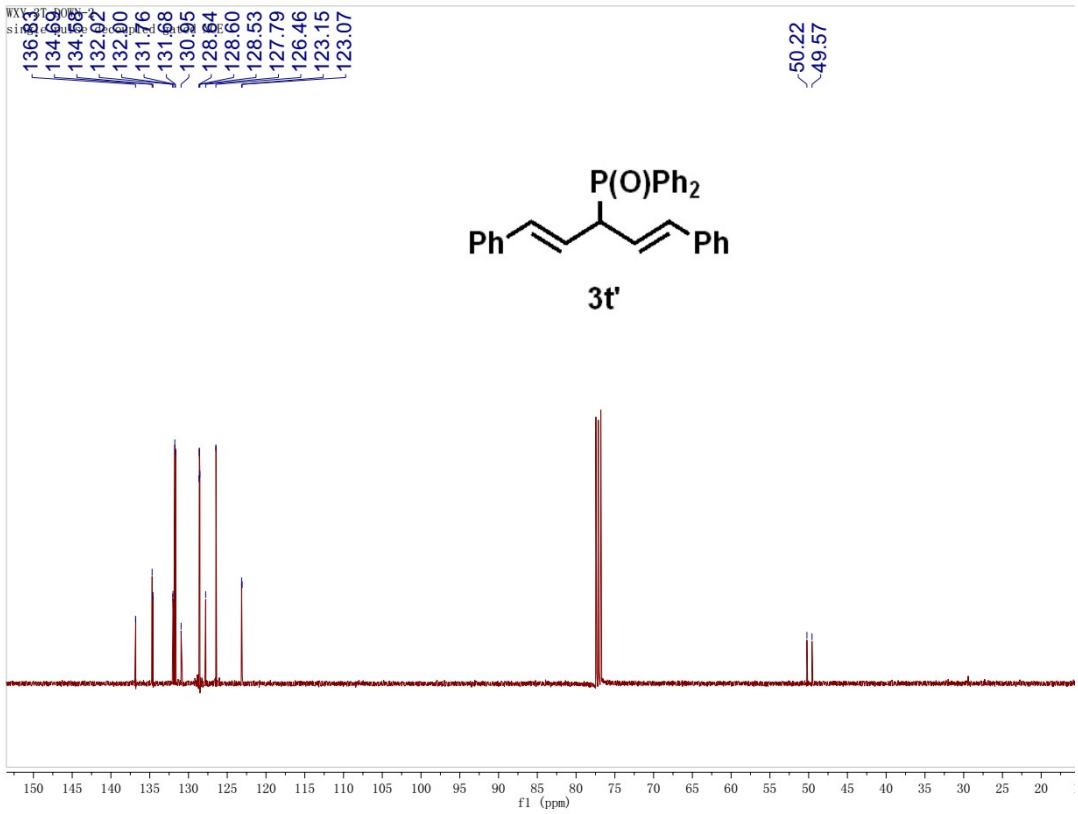
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3s** and **3s' (3s/3s' = 1/1).**



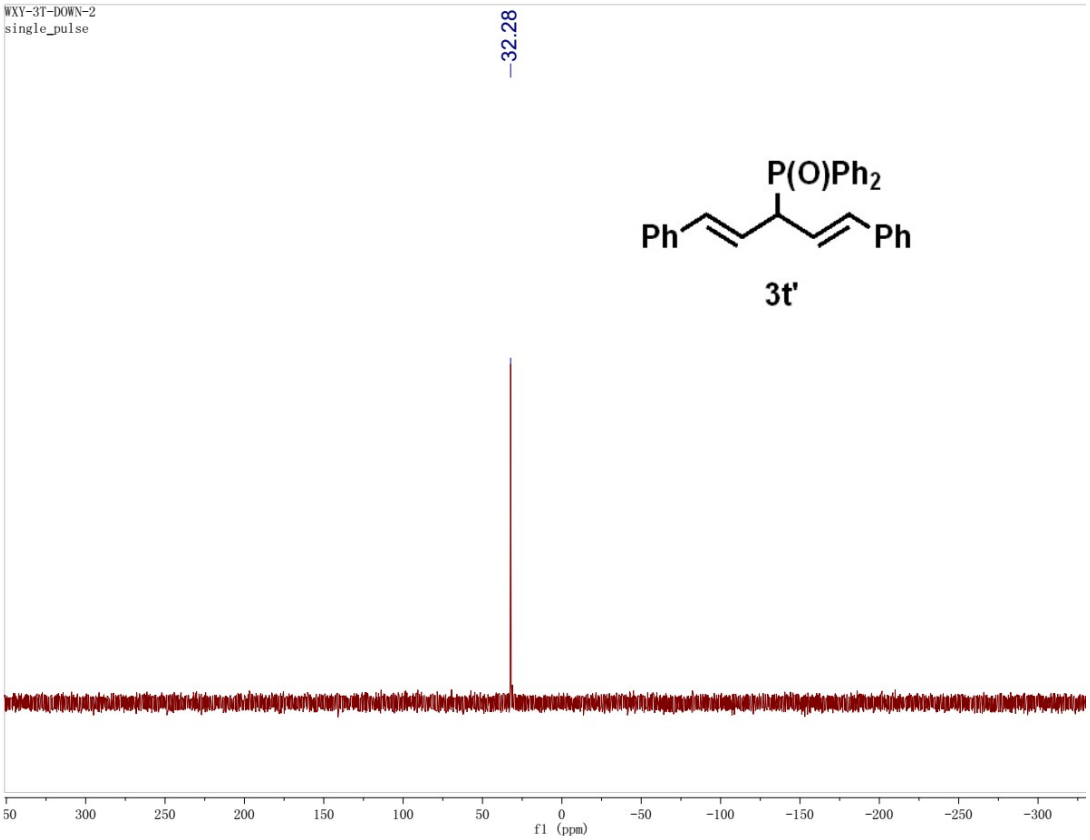
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3s** and **3s' (3s/3s' = 1/9).**



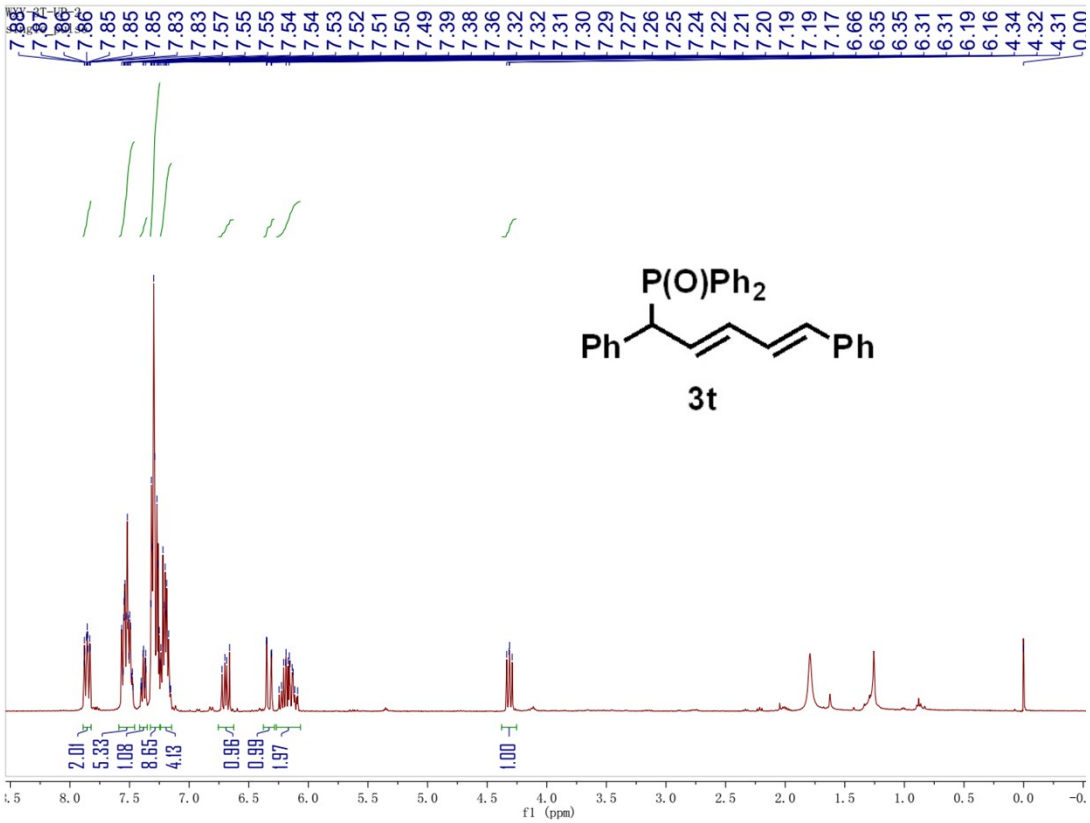
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3t'.**



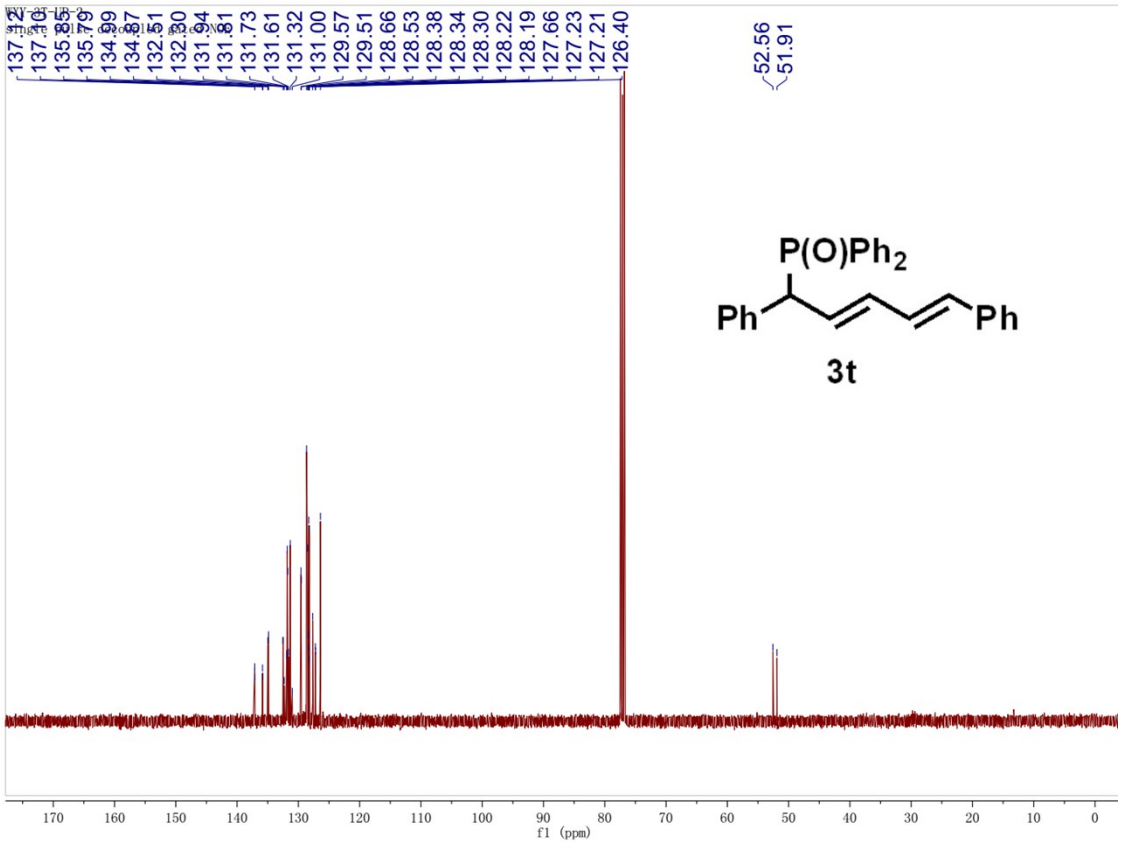
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3t'.**



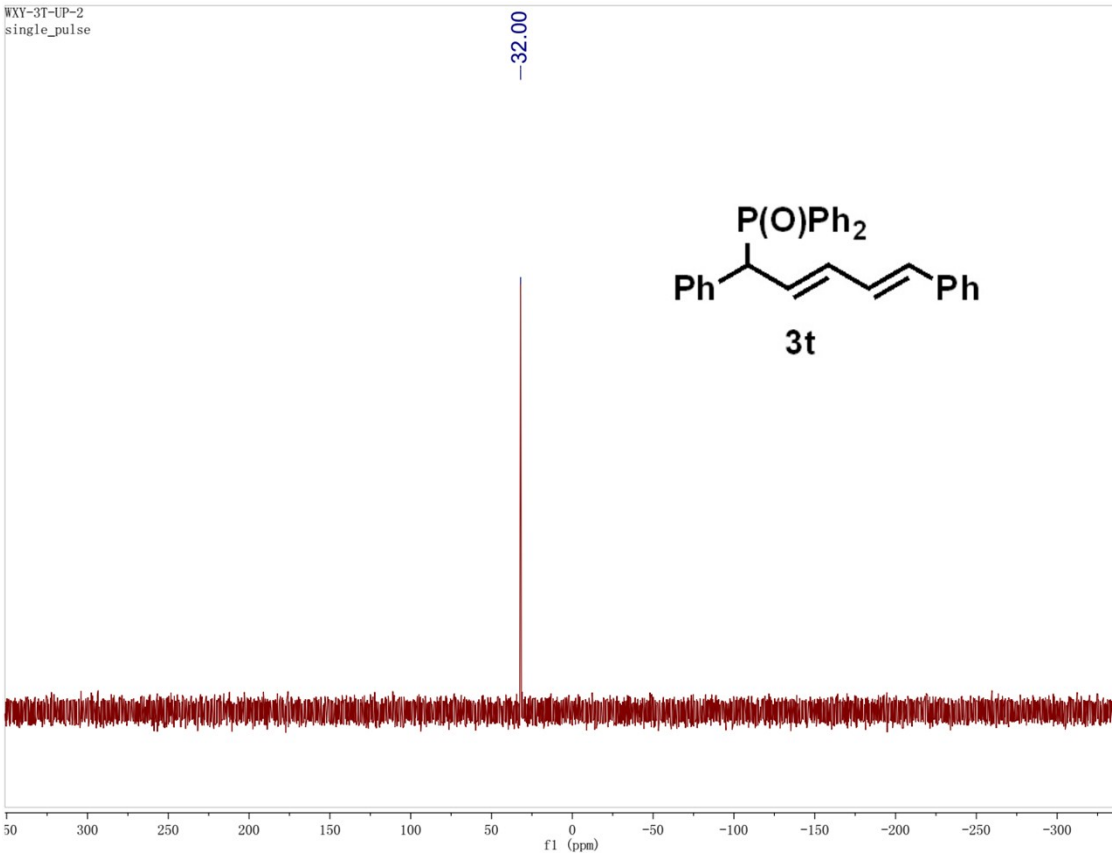
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3t'.**



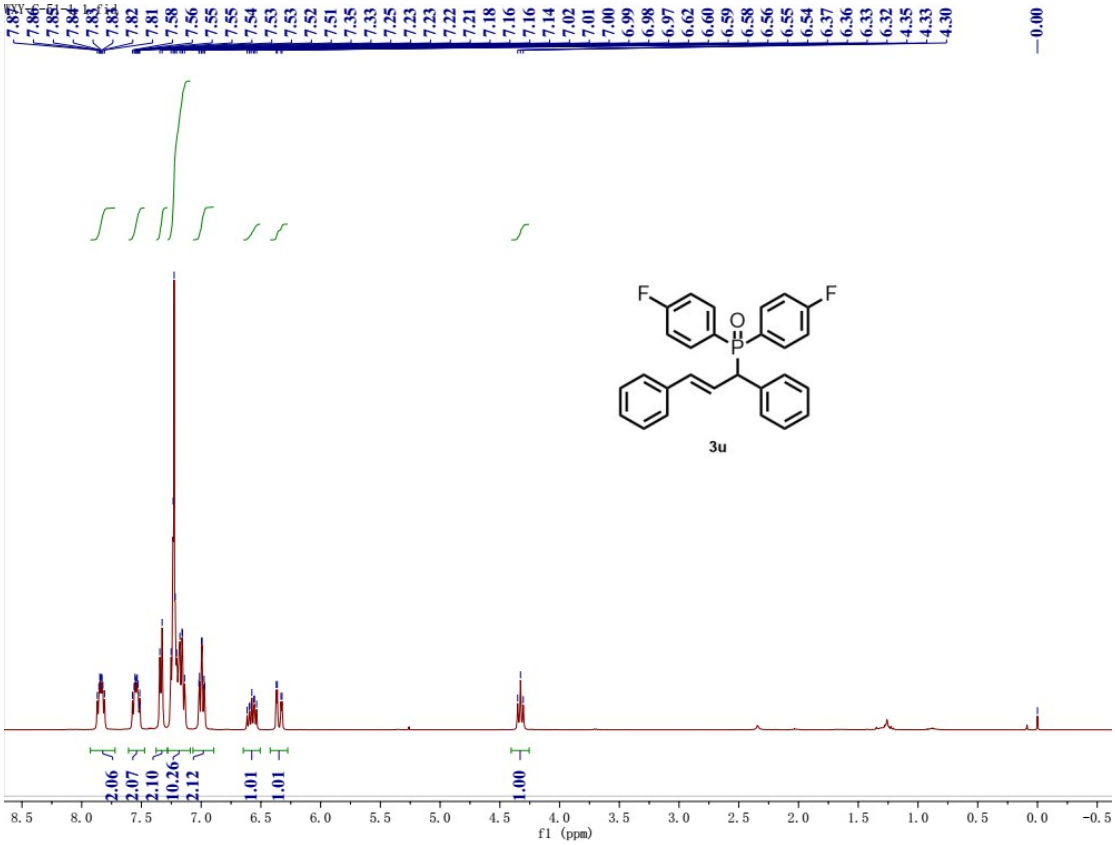
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3t.**



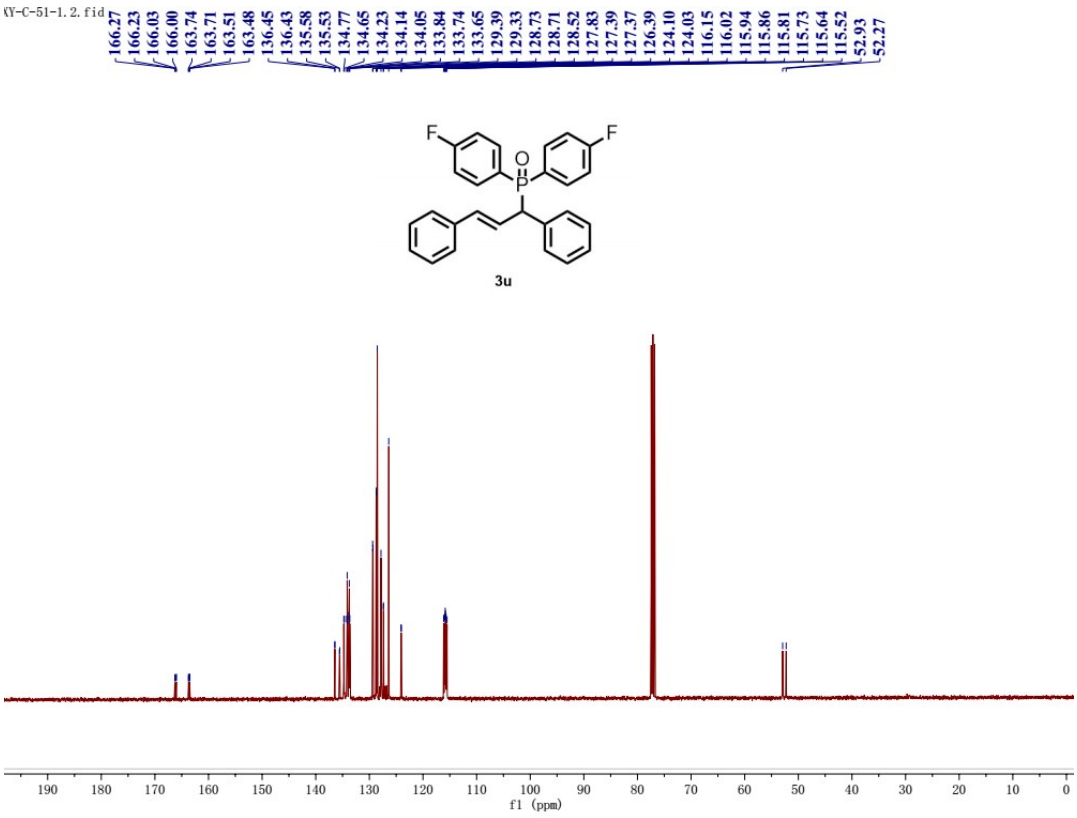
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3t.**



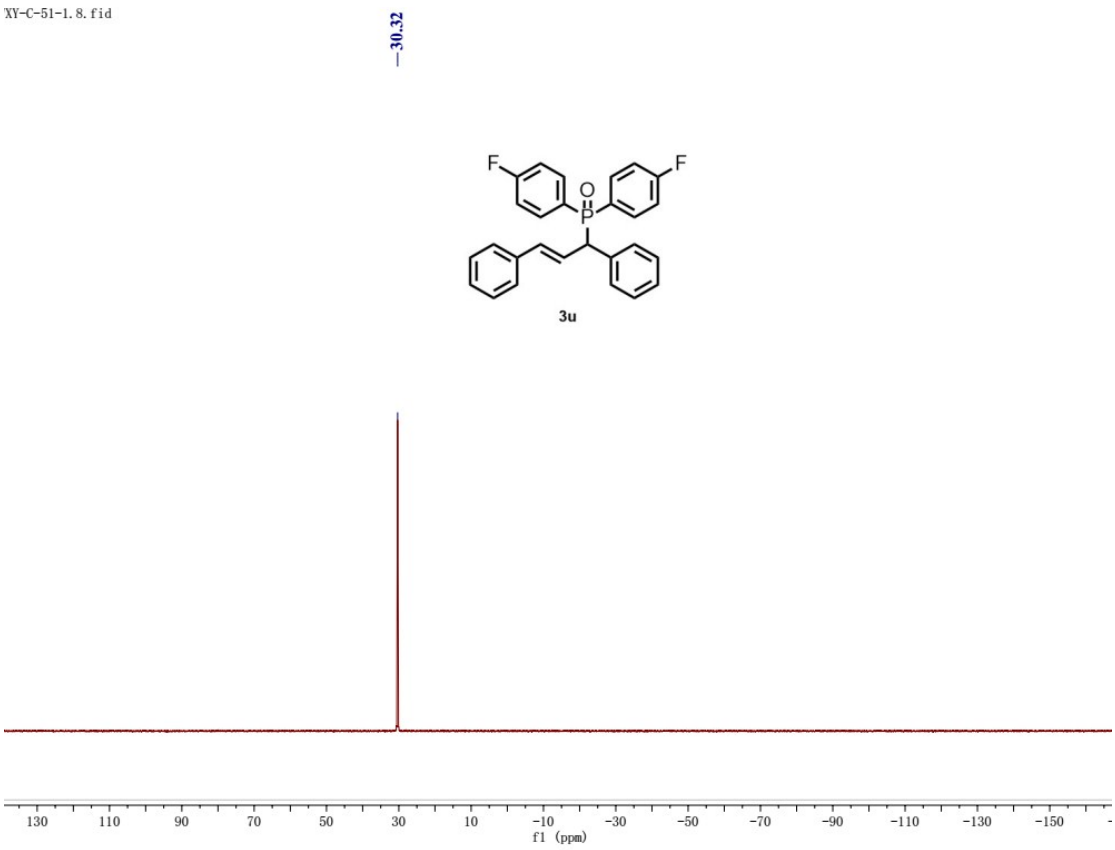
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3t'.**



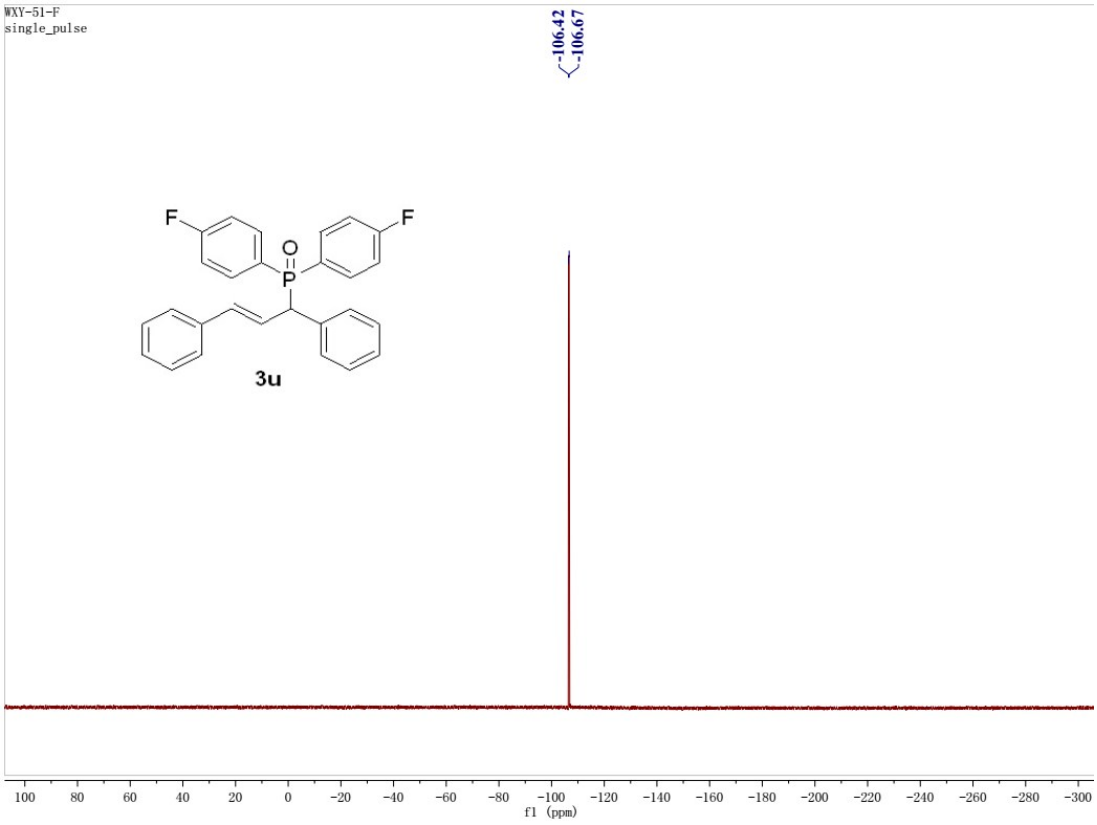
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3u.**



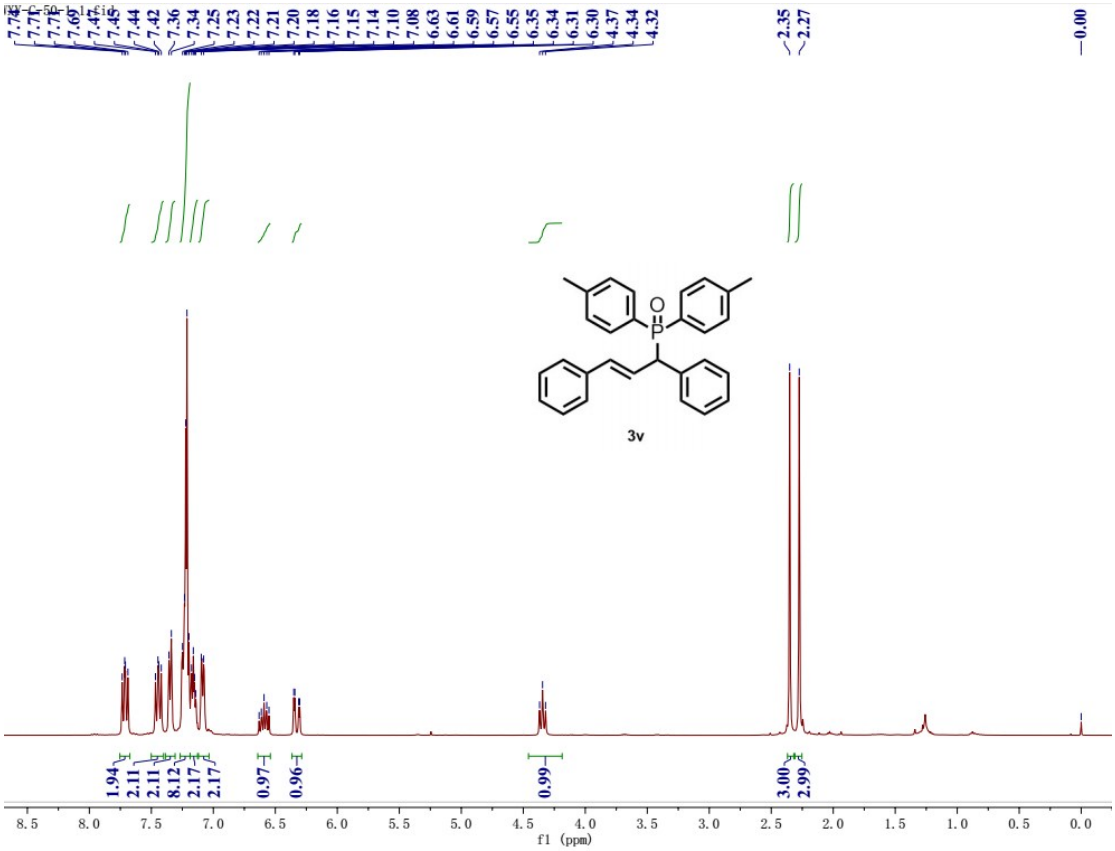
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3u.**



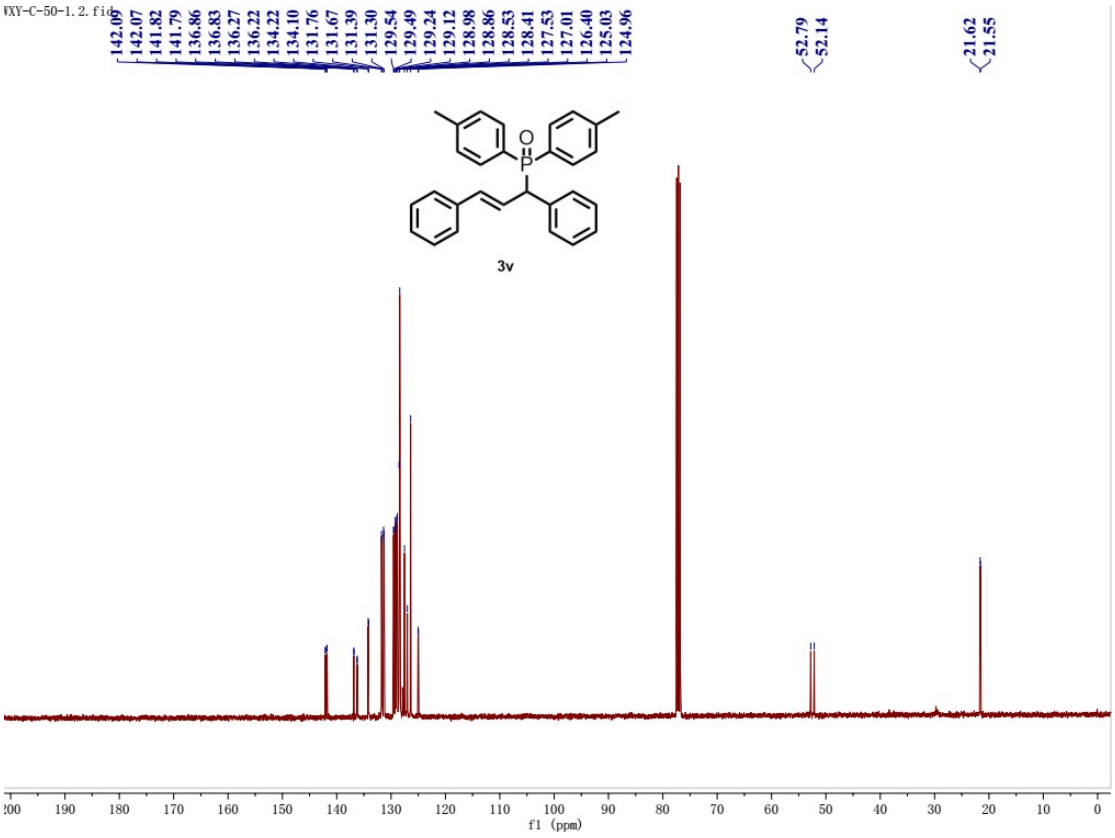
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3u.**



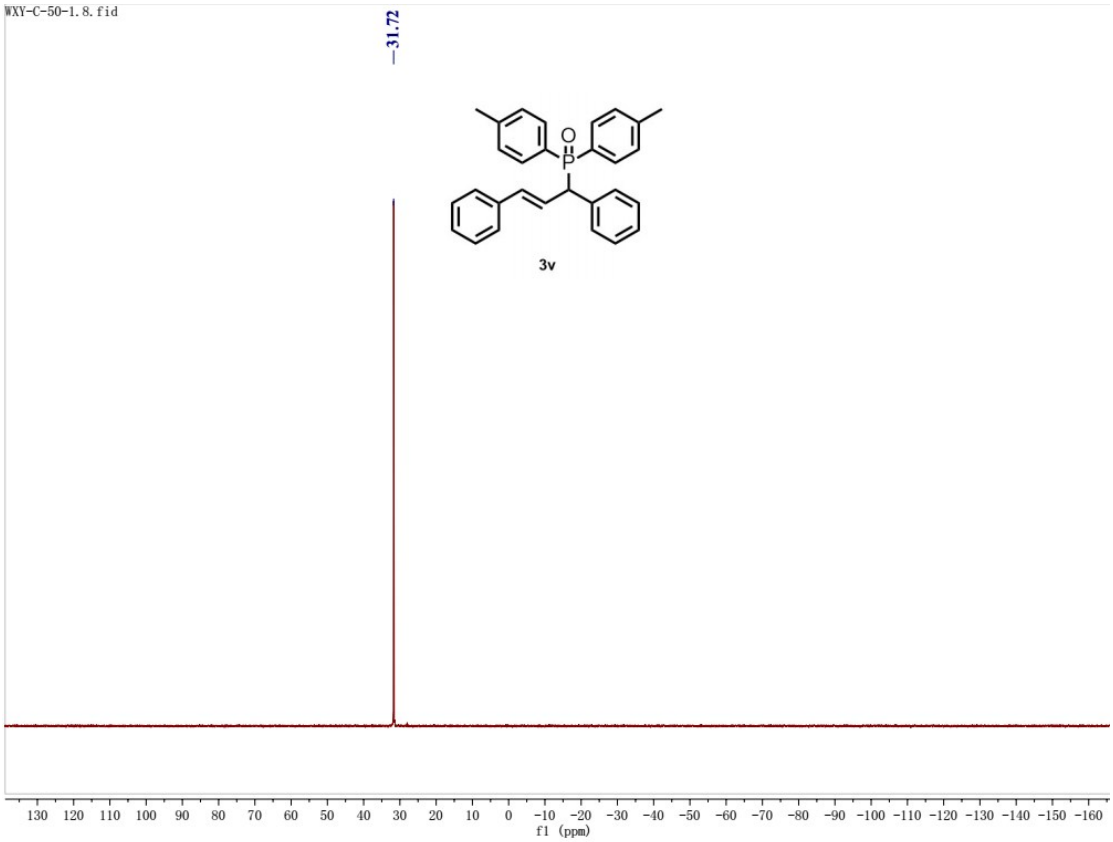
^{19}F NMR (376 MHz, Chloroform-d) spectra for compound **3u.**



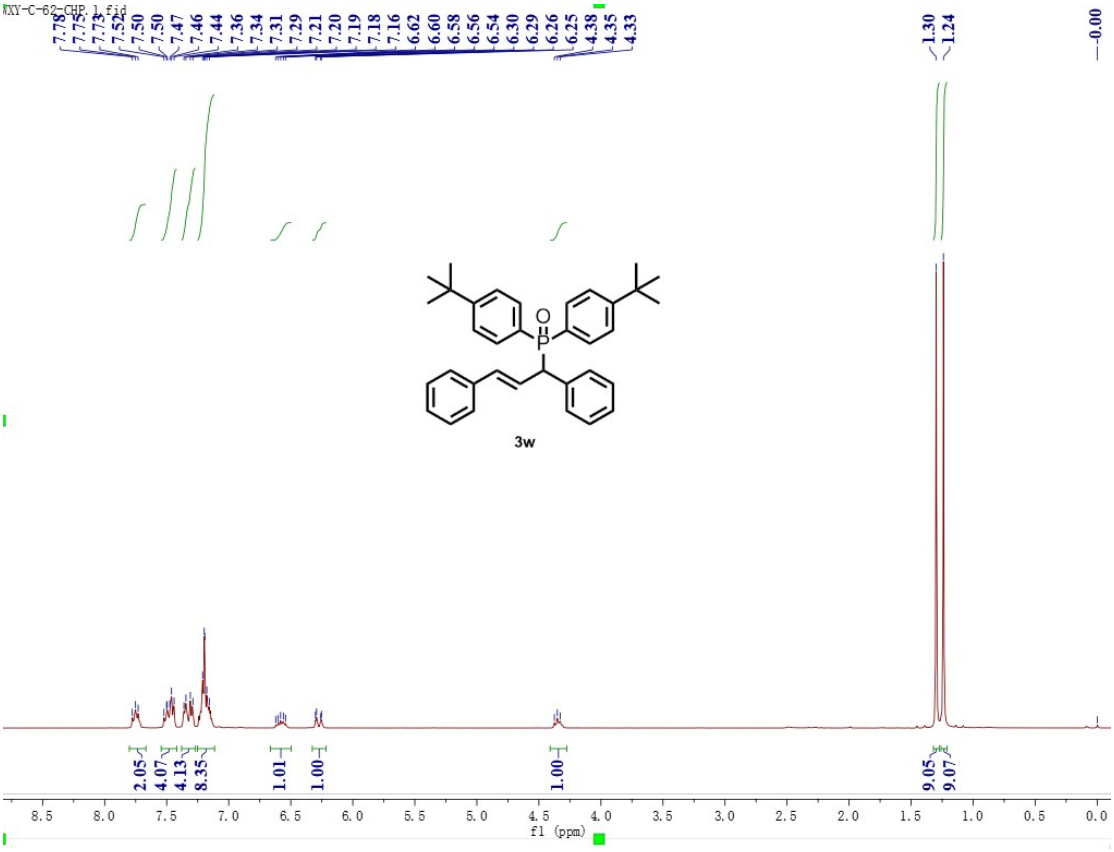
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3v.**



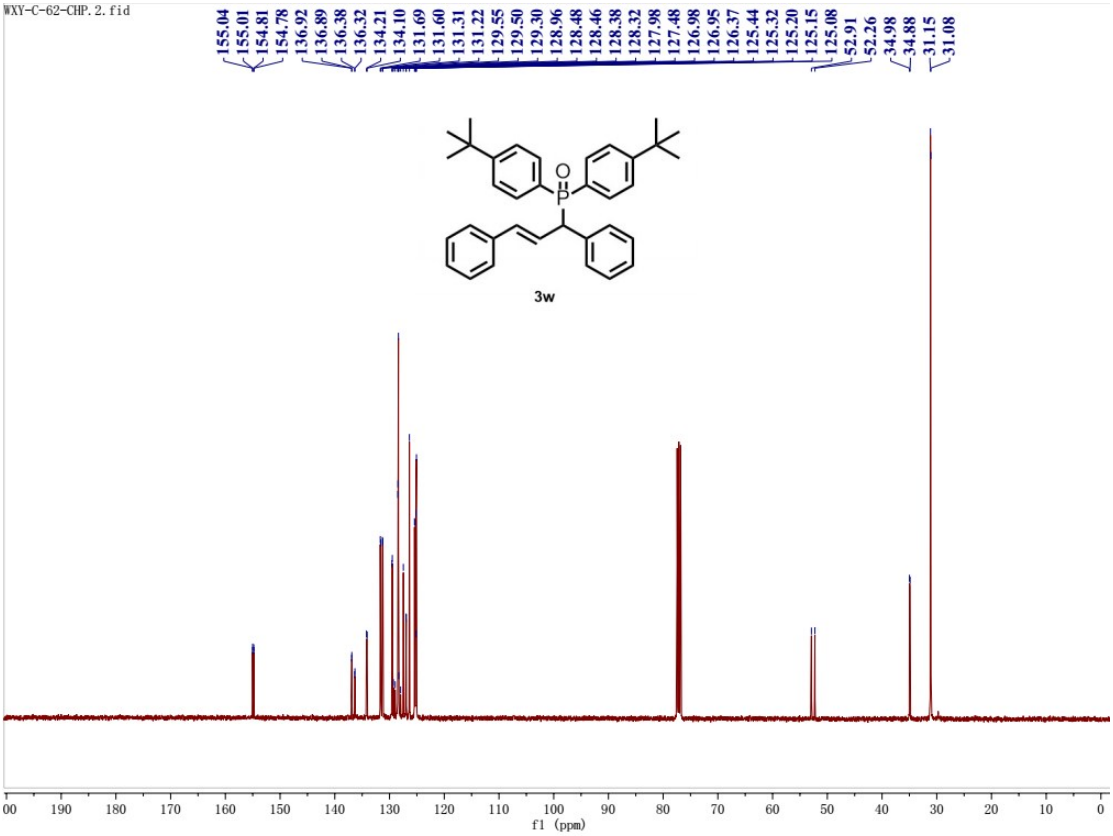
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3v.**



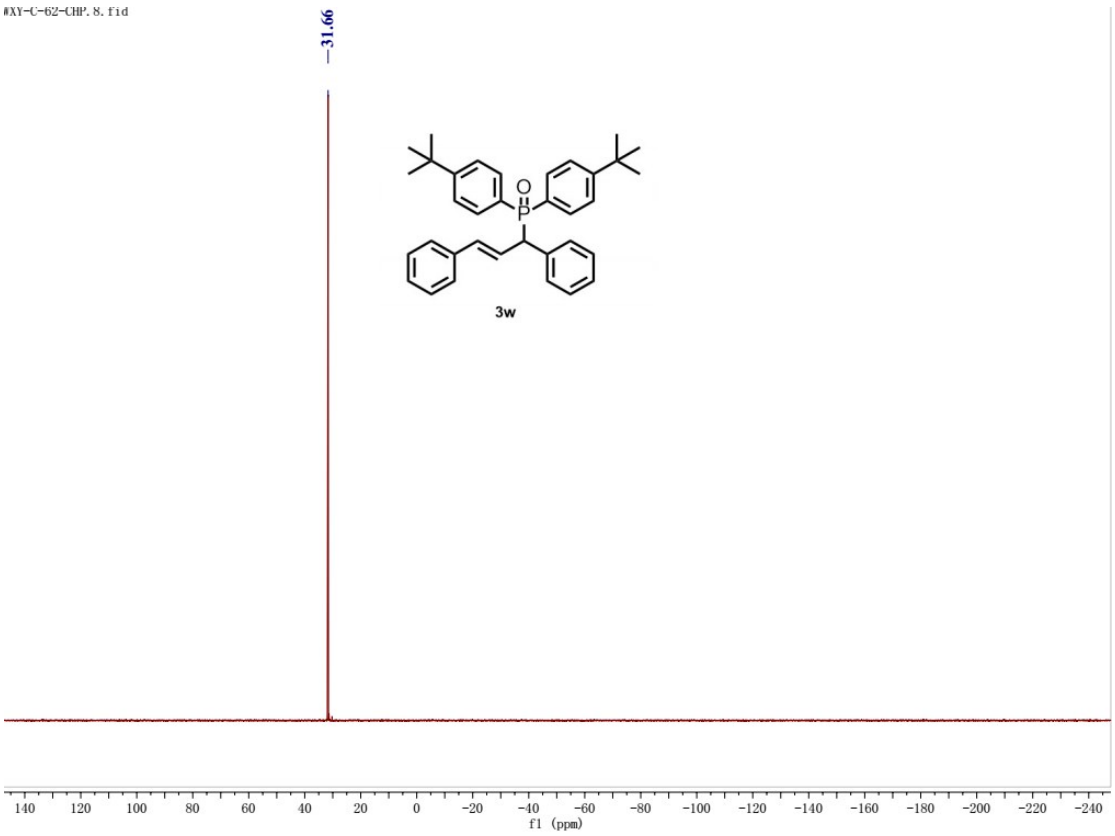
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3v.**



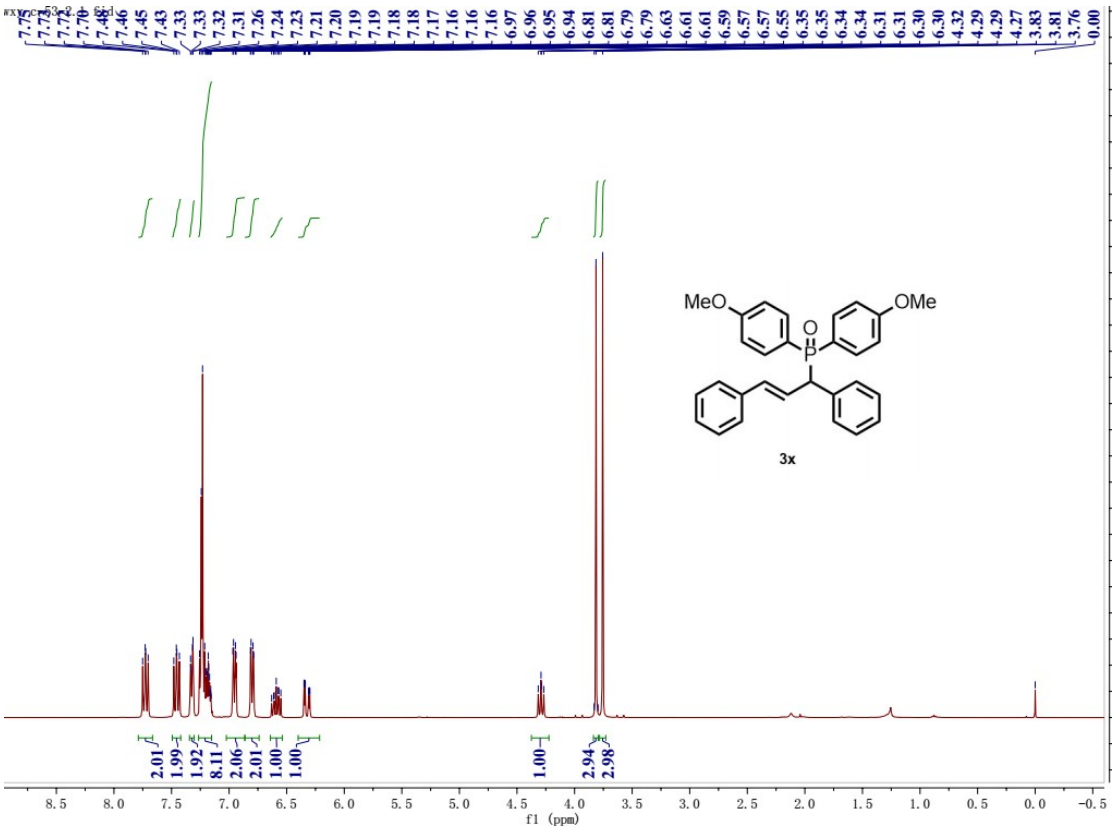
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3w.**



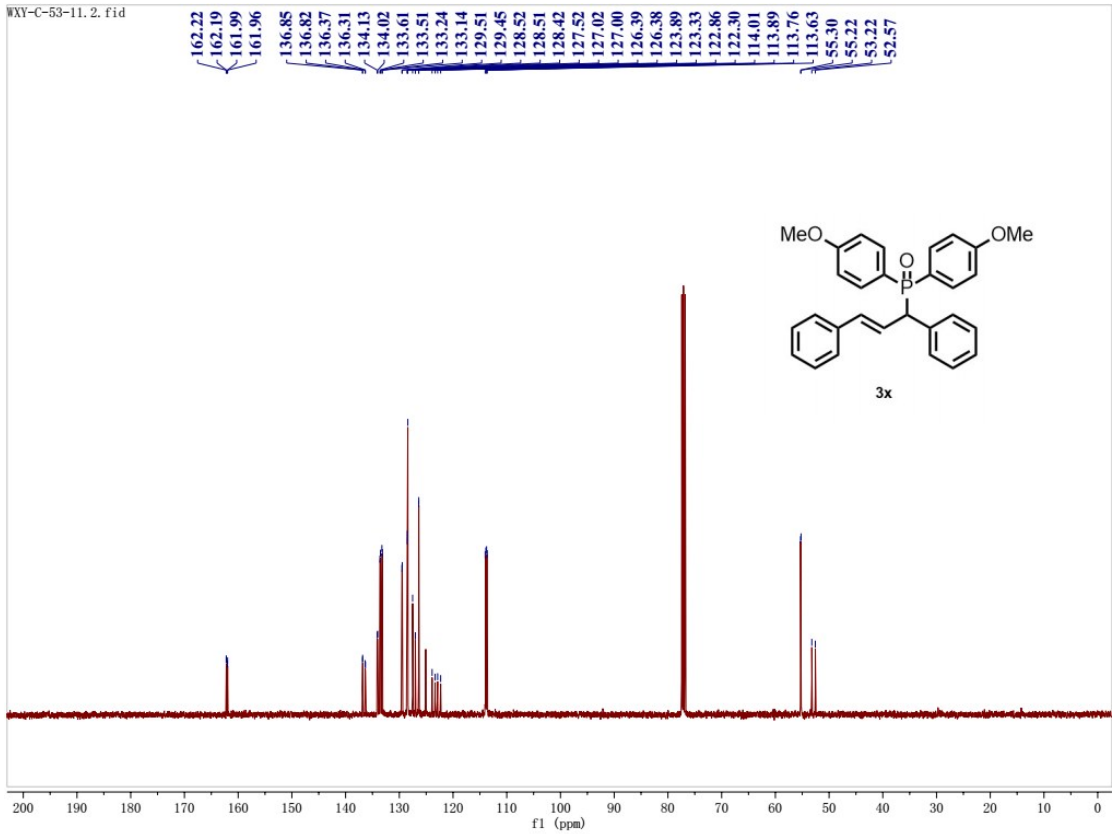
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3w.**



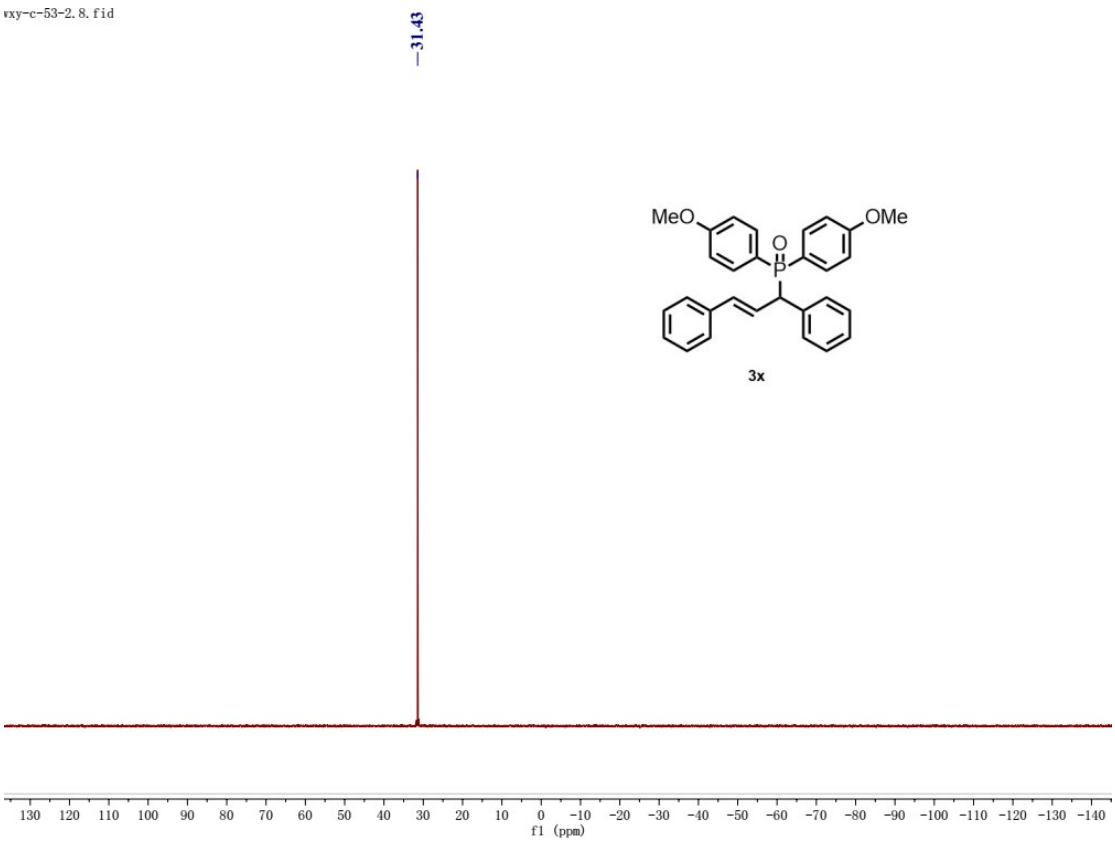
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3w.**



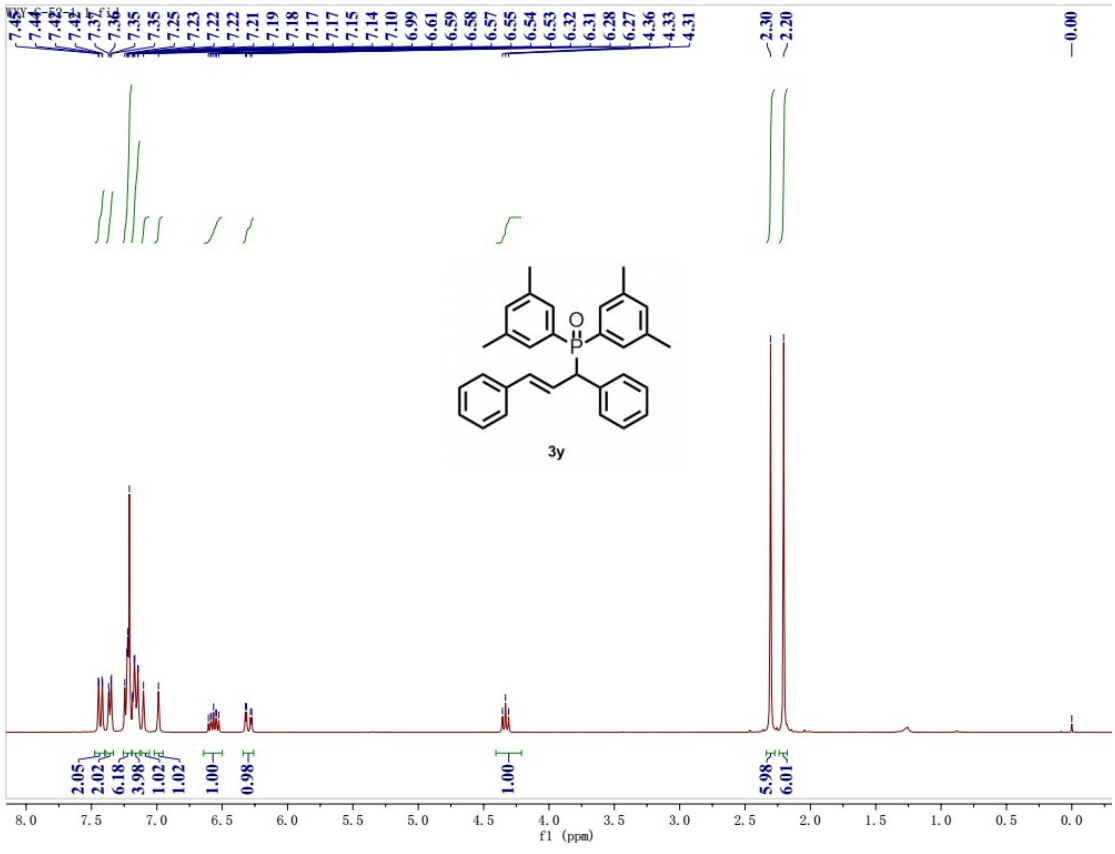
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3x.**



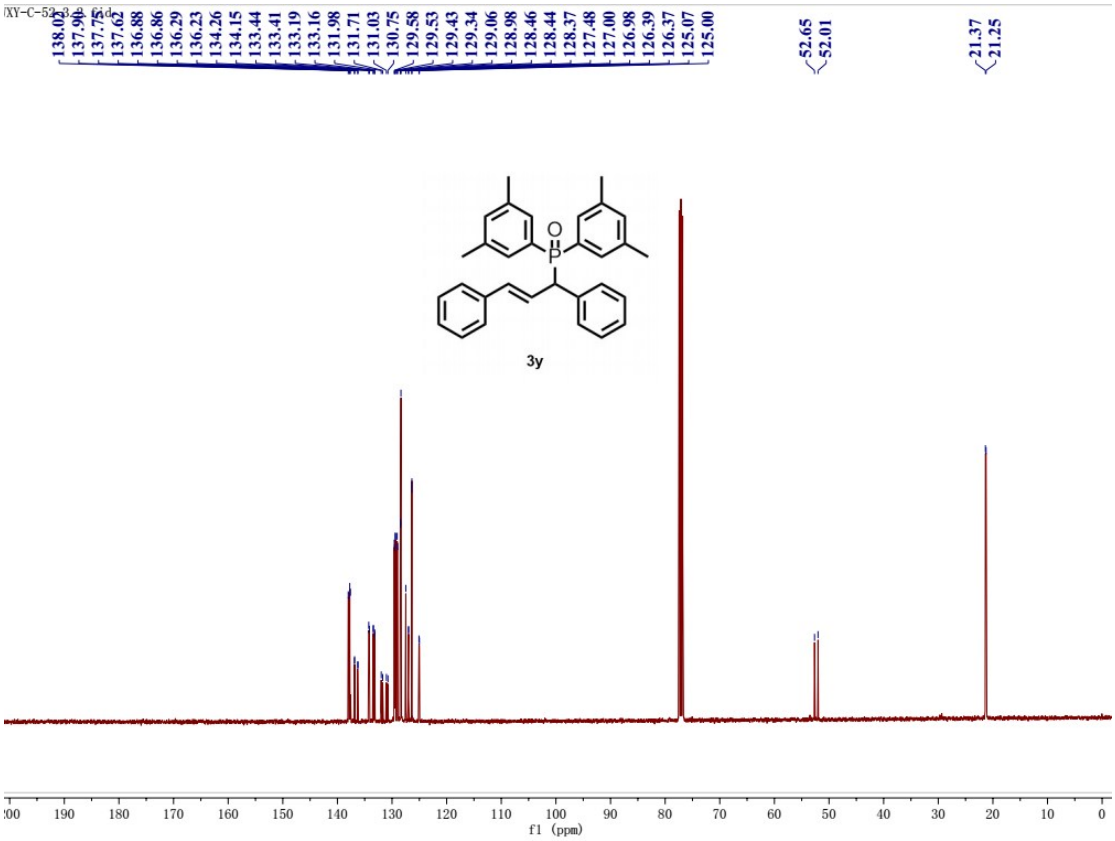
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3x.**



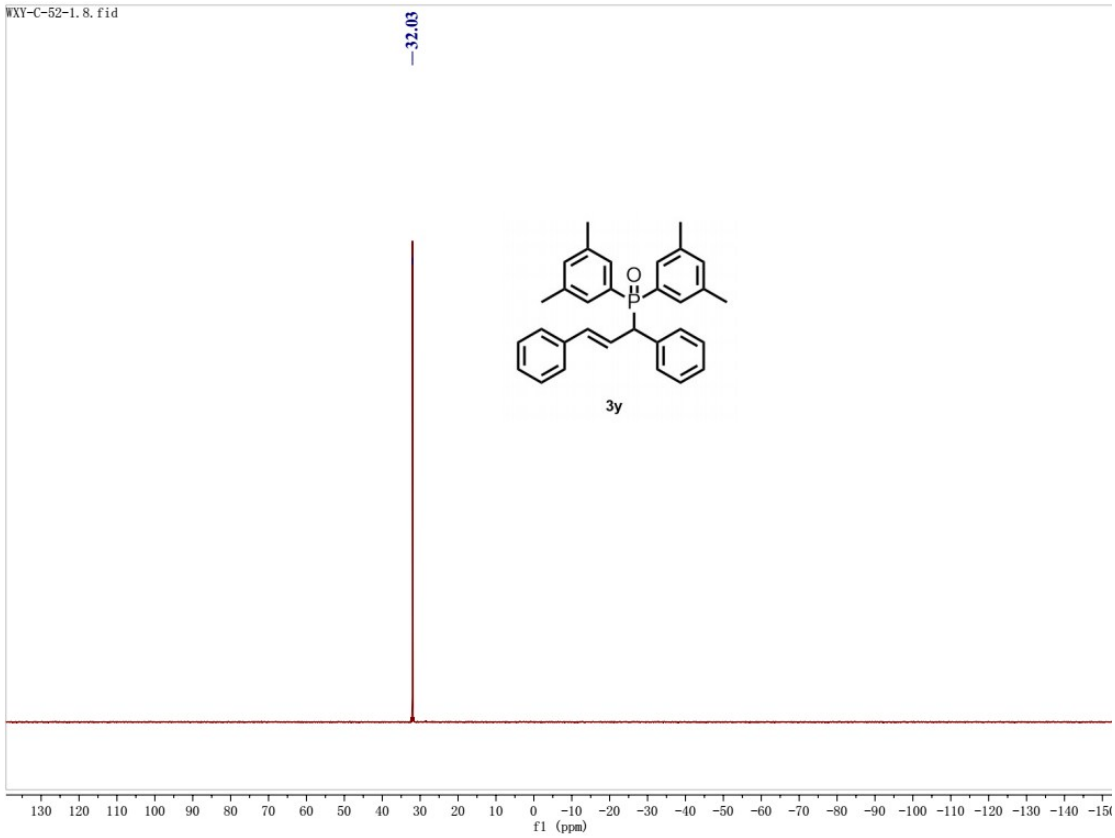
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3x.**



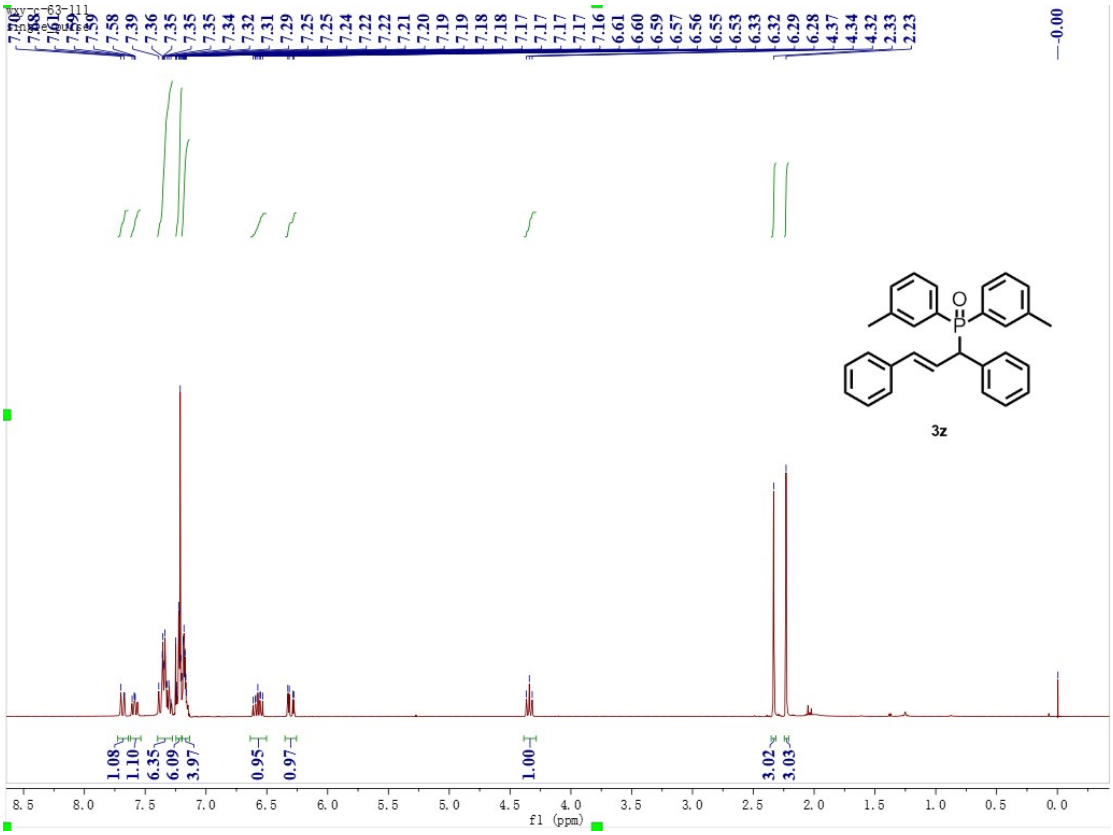
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3y.**



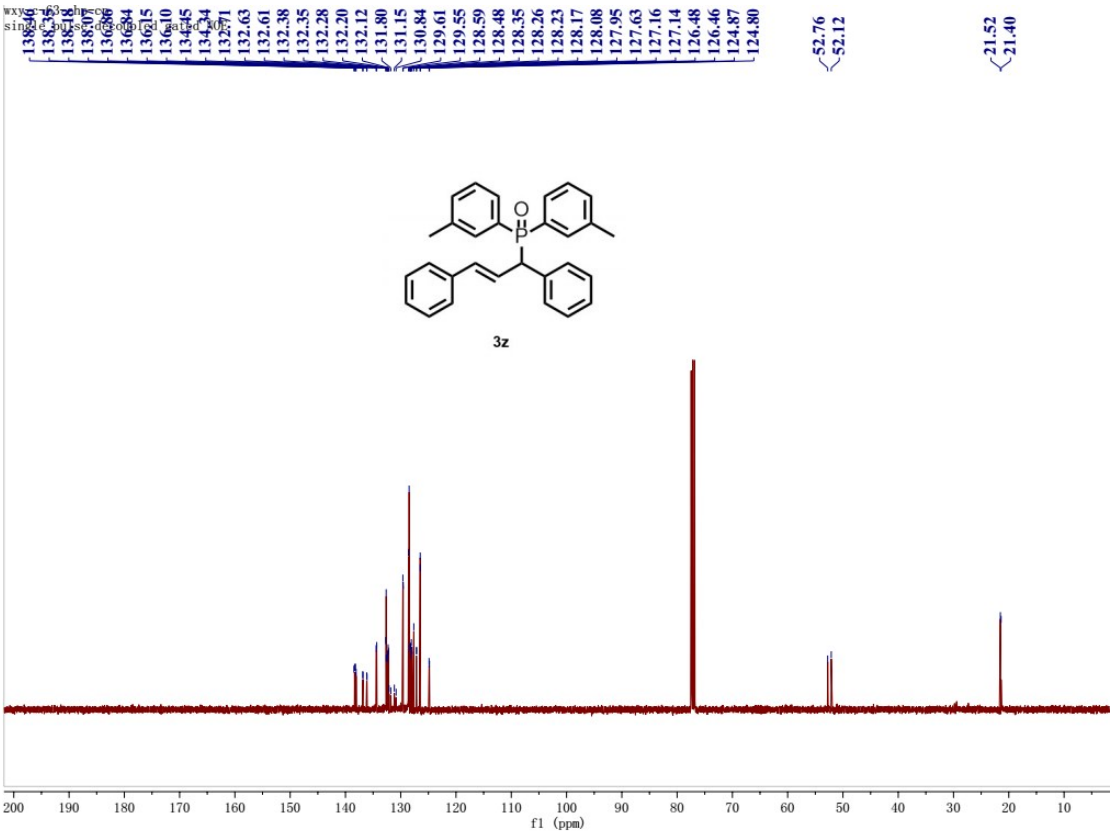
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3y.**



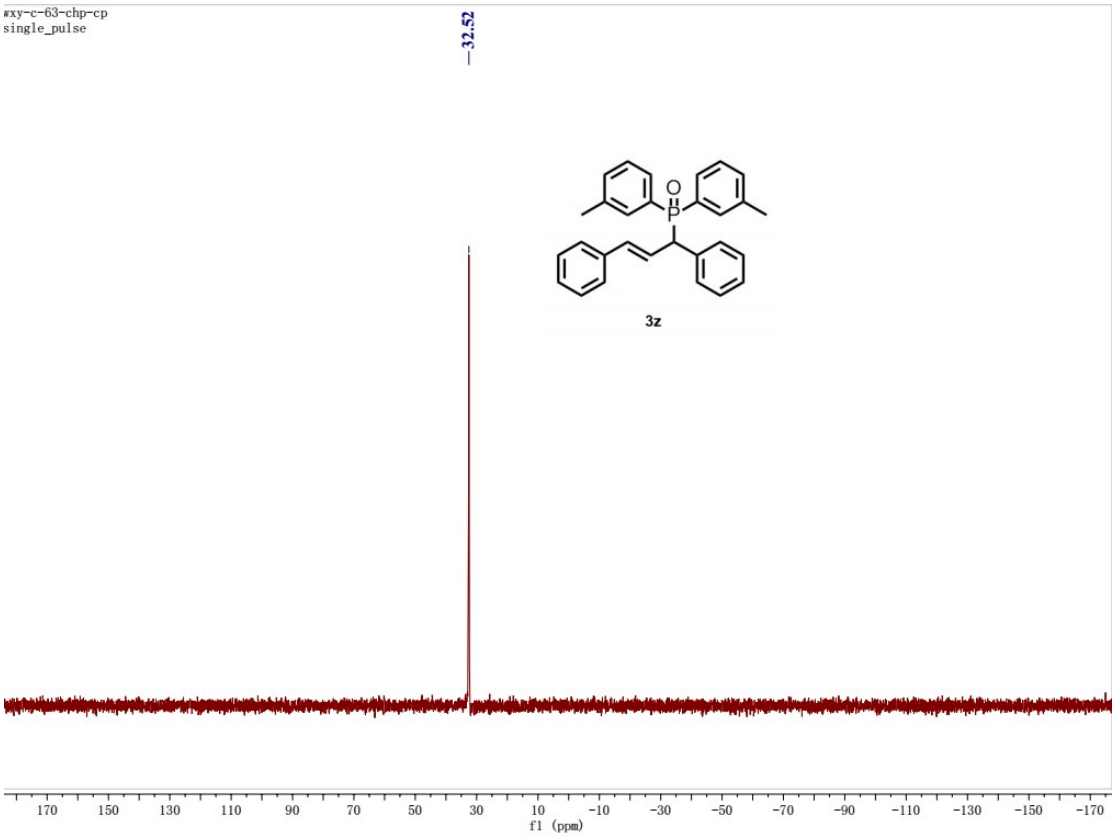
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3y.**



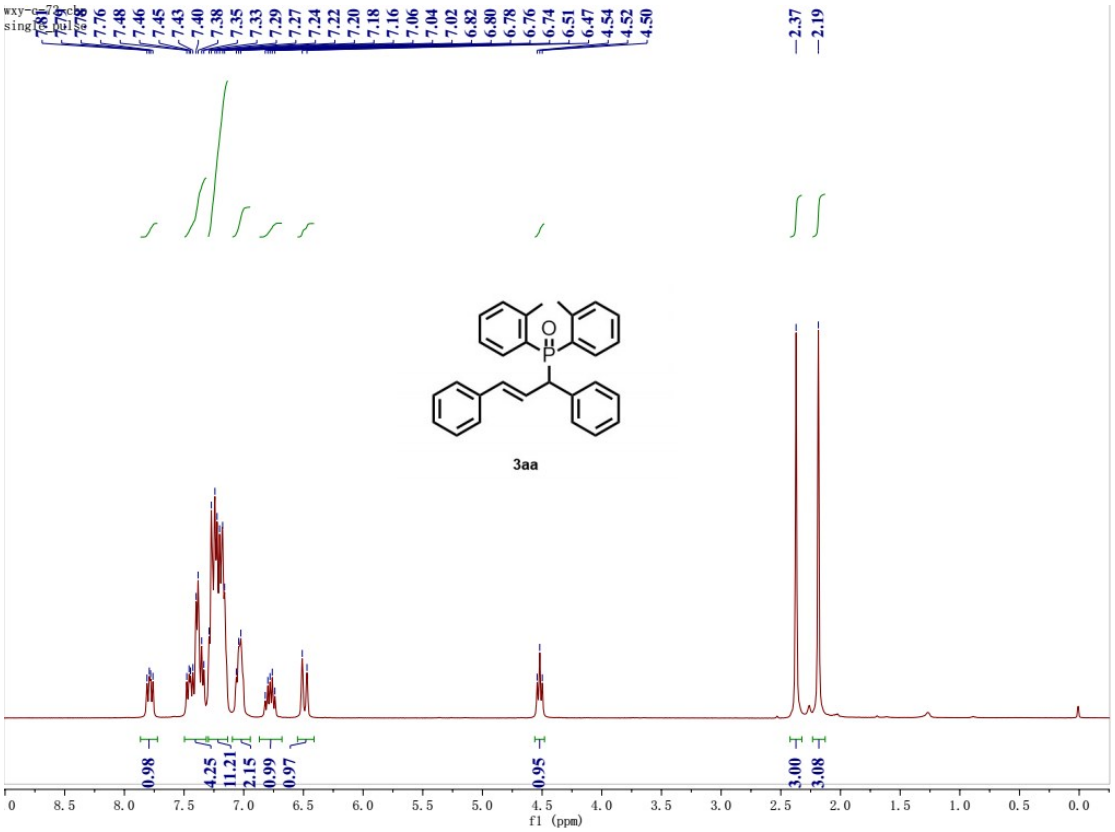
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3z.**



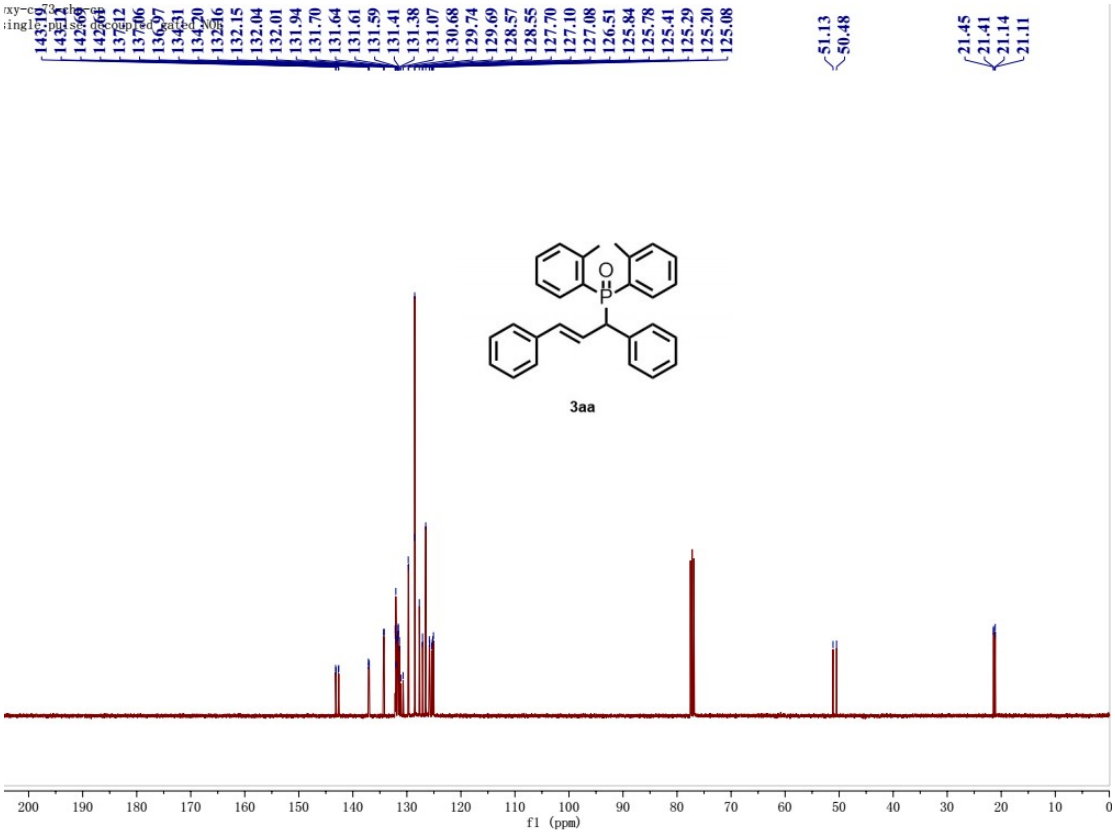
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3z.**



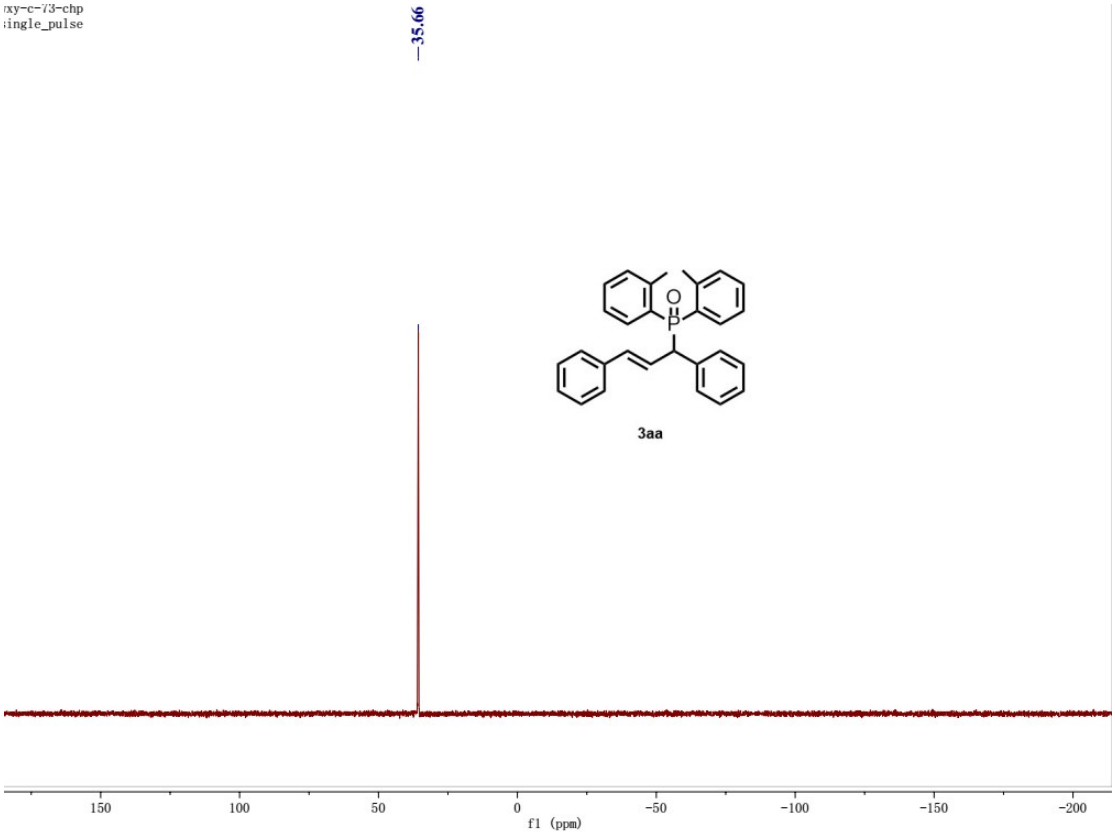
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3z.**



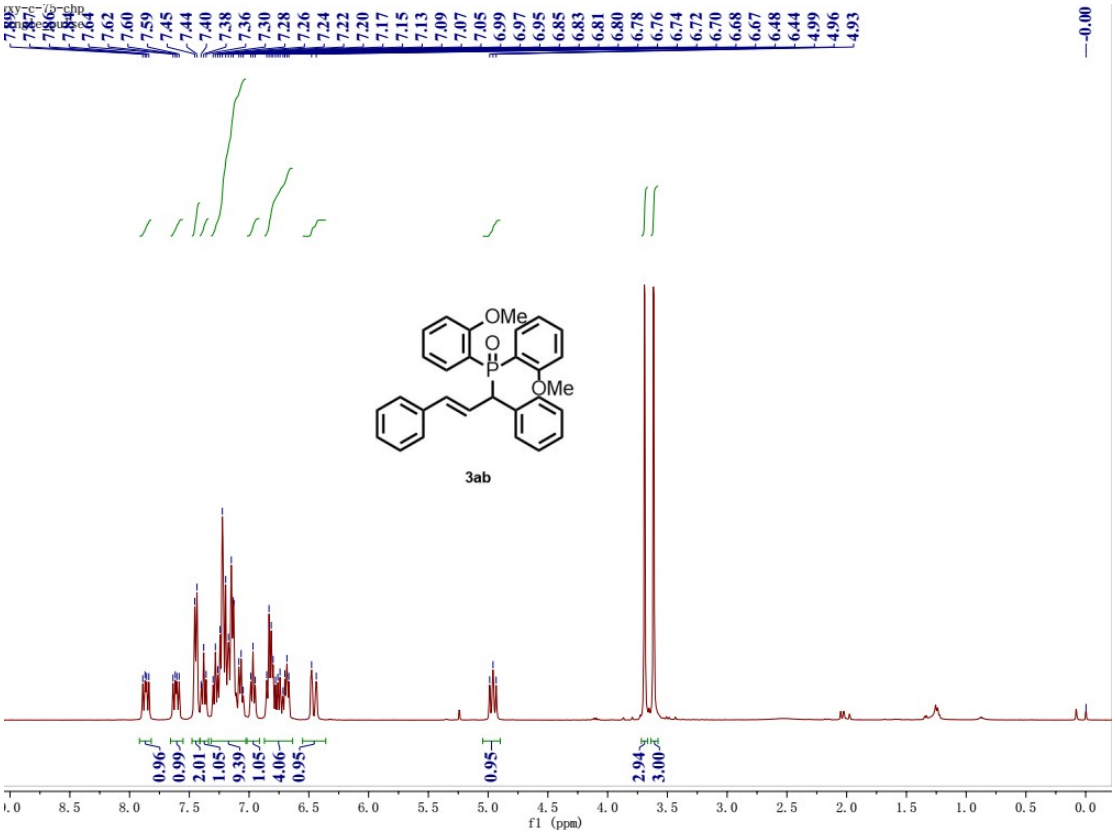
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3aa.**



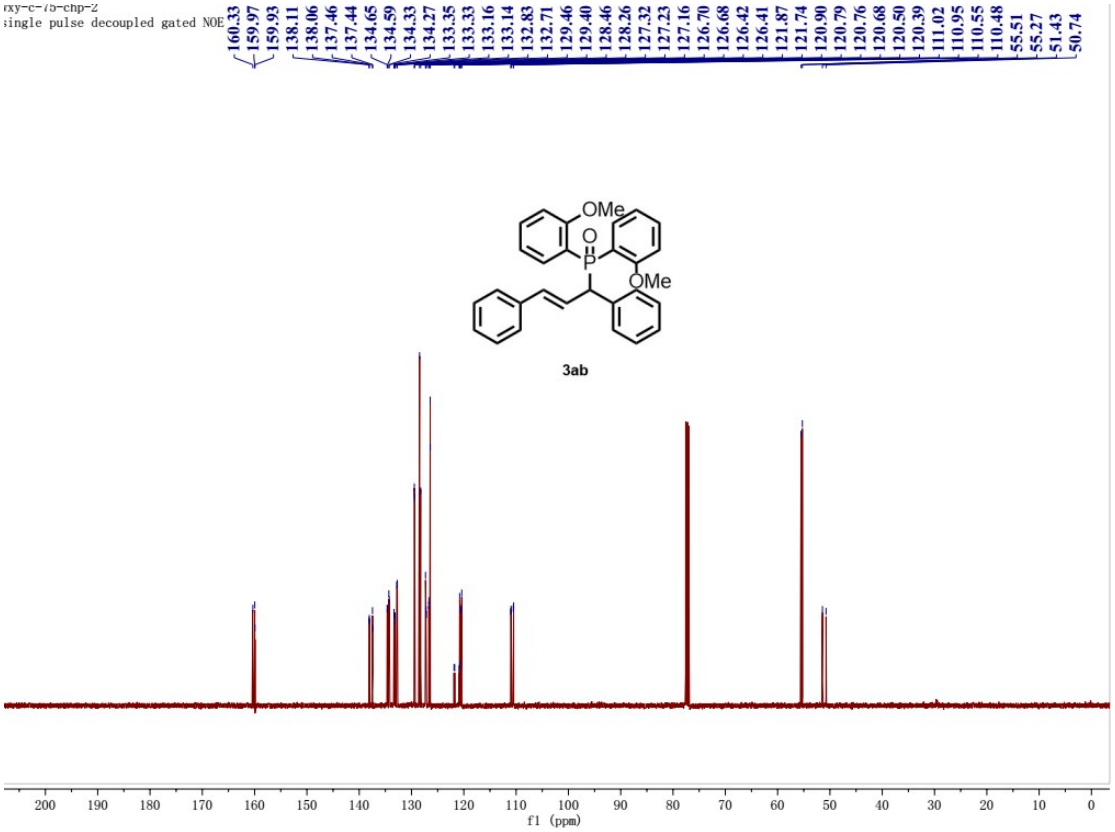
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3aa.**



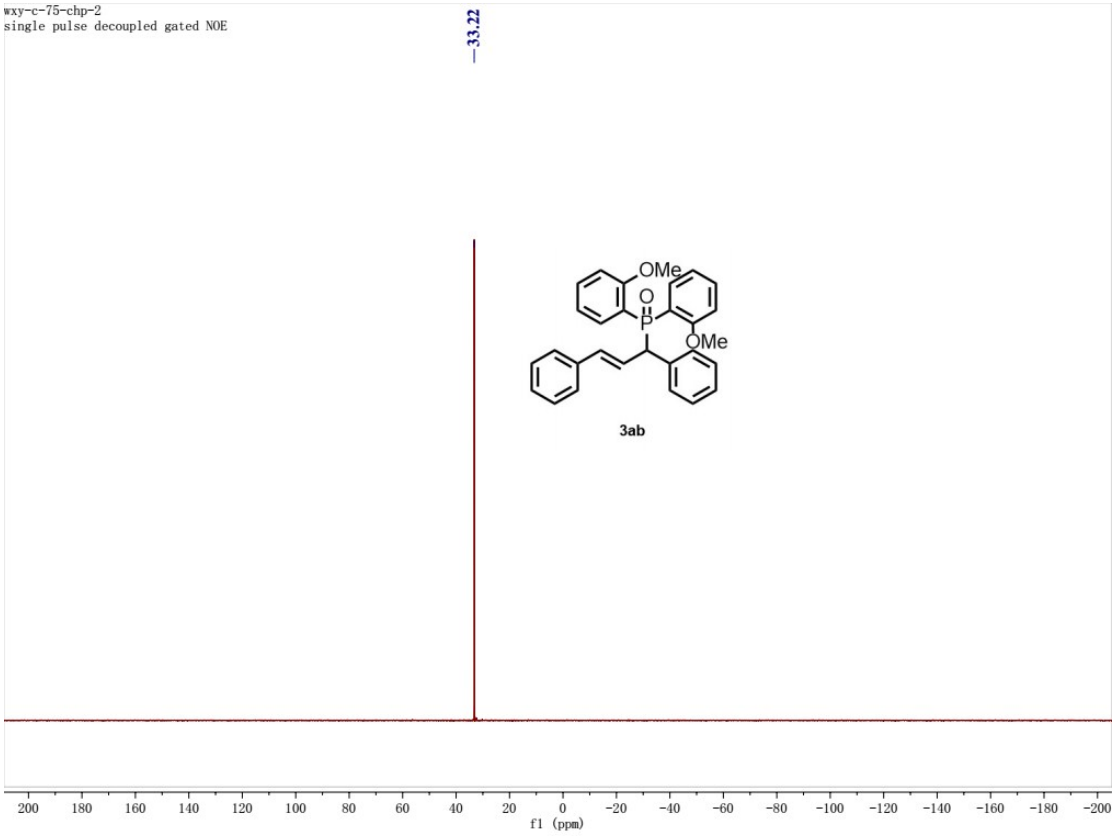
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3aa.**



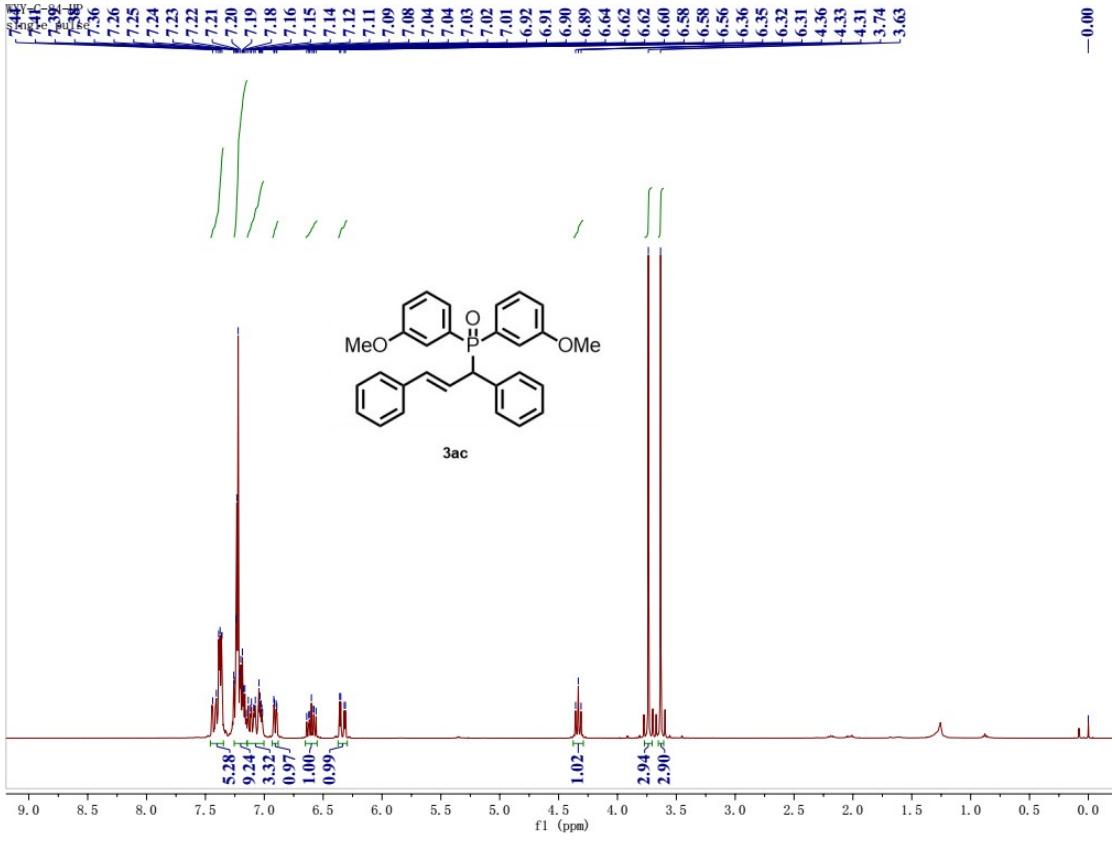
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3ab.**



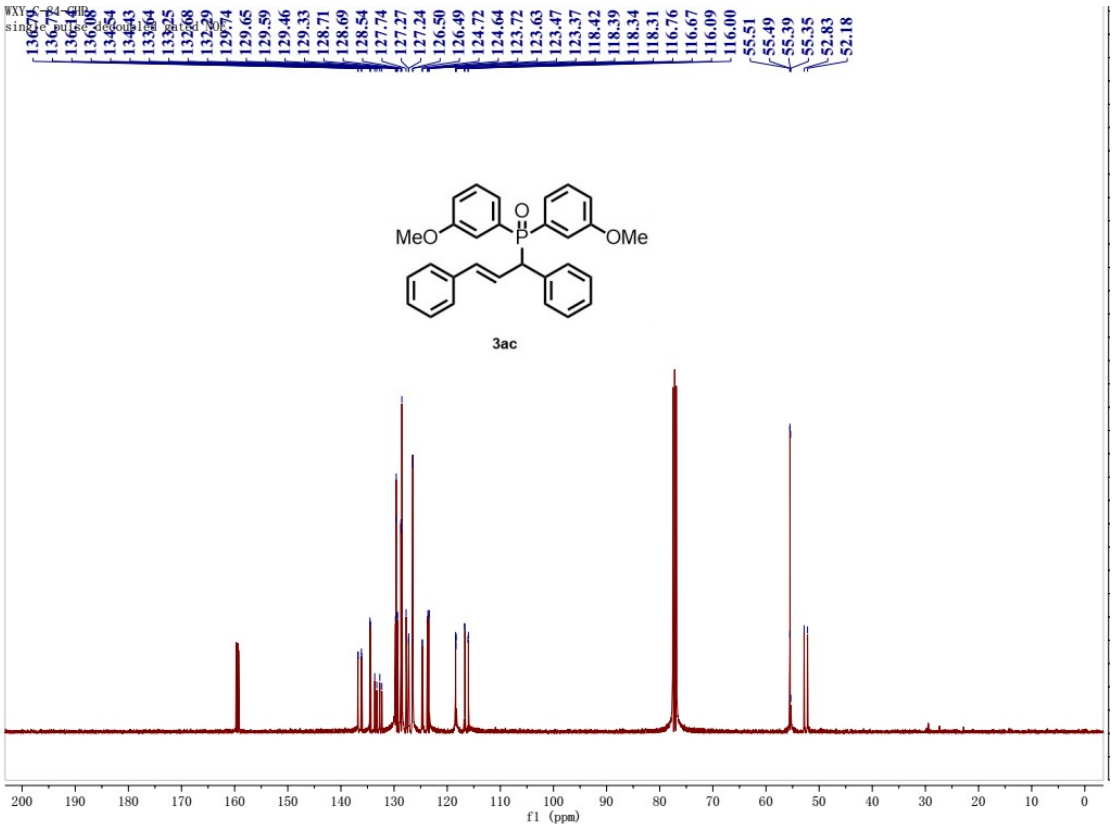
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3ab.**



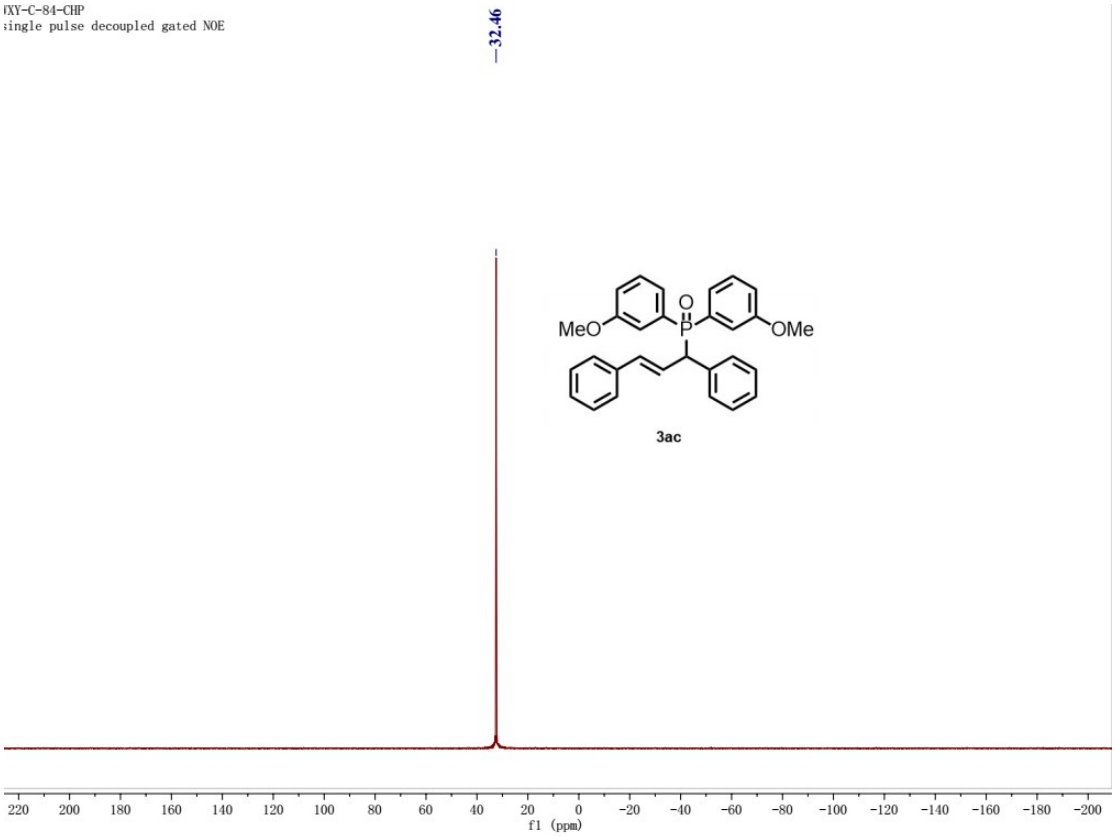
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3ab.**



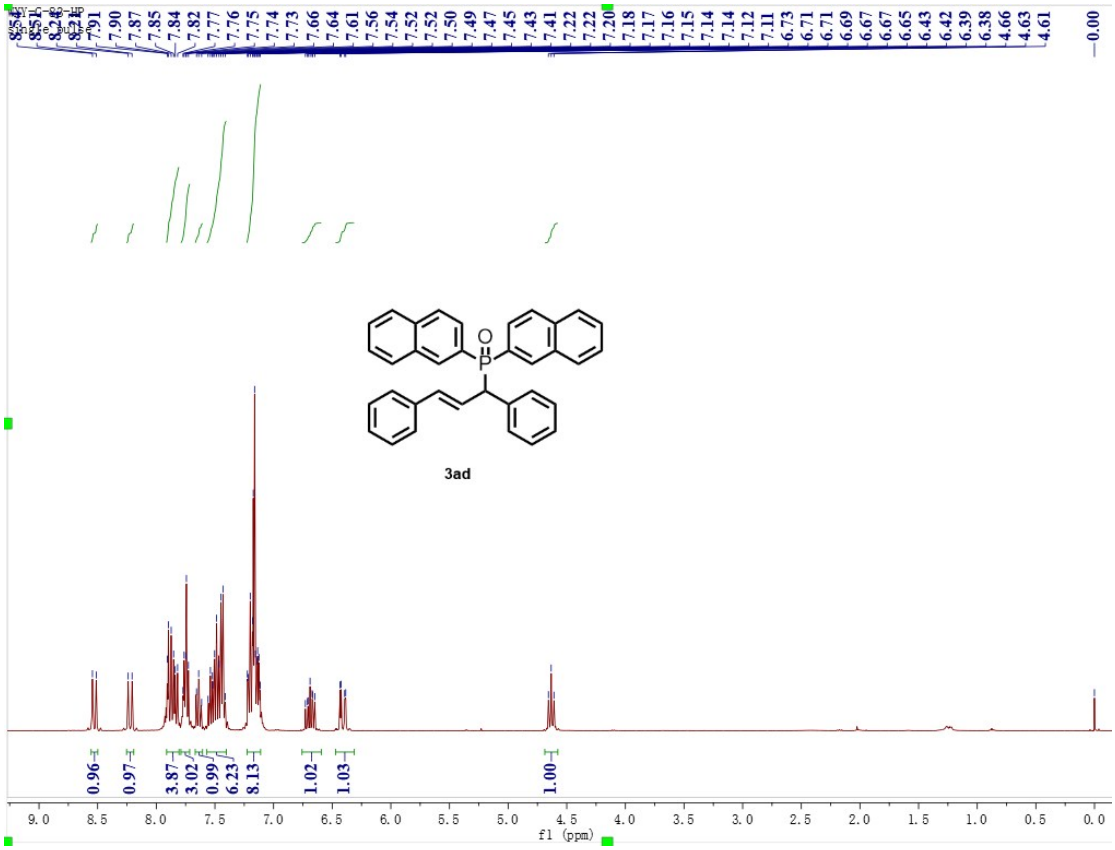
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3ac.**



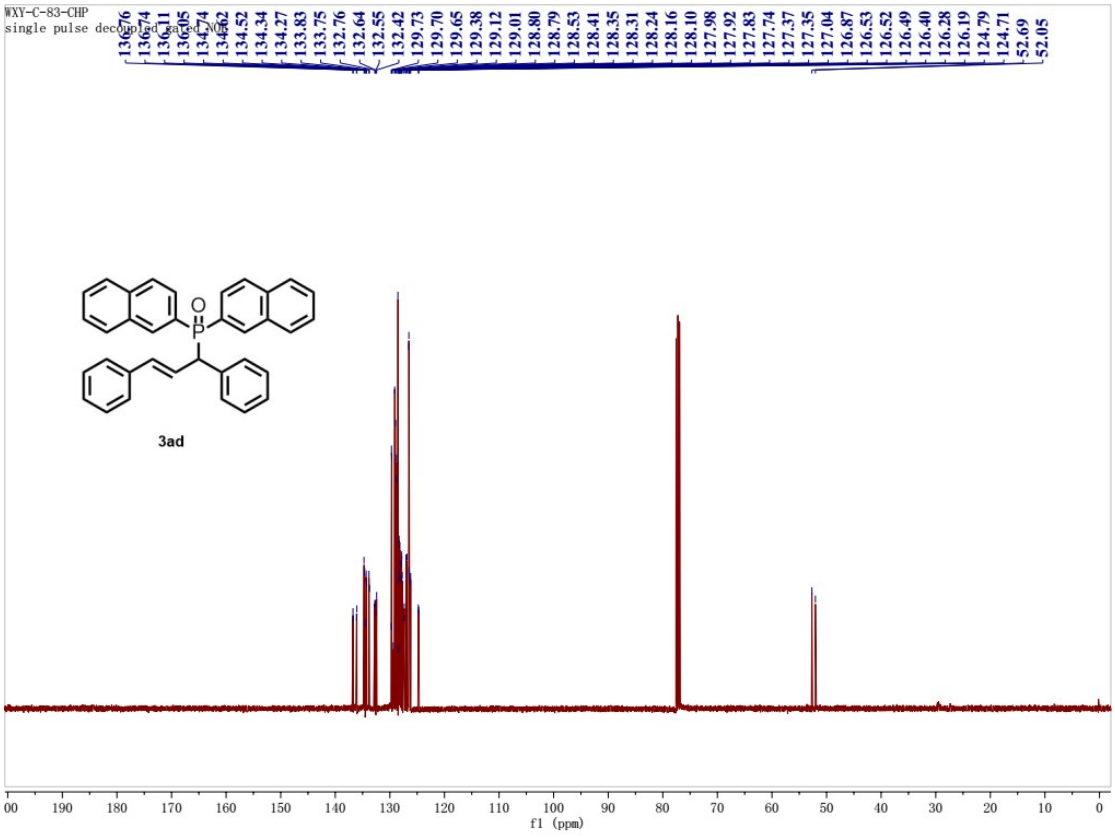
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3ac.**



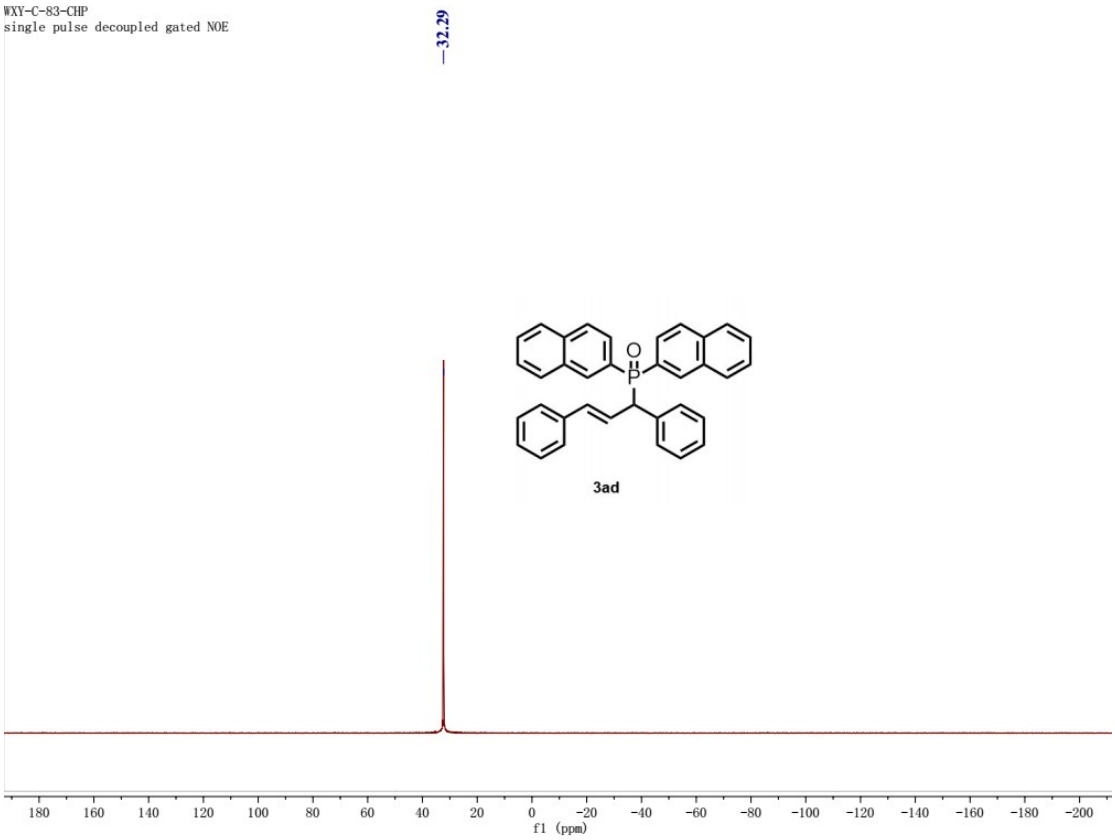
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3ac.**



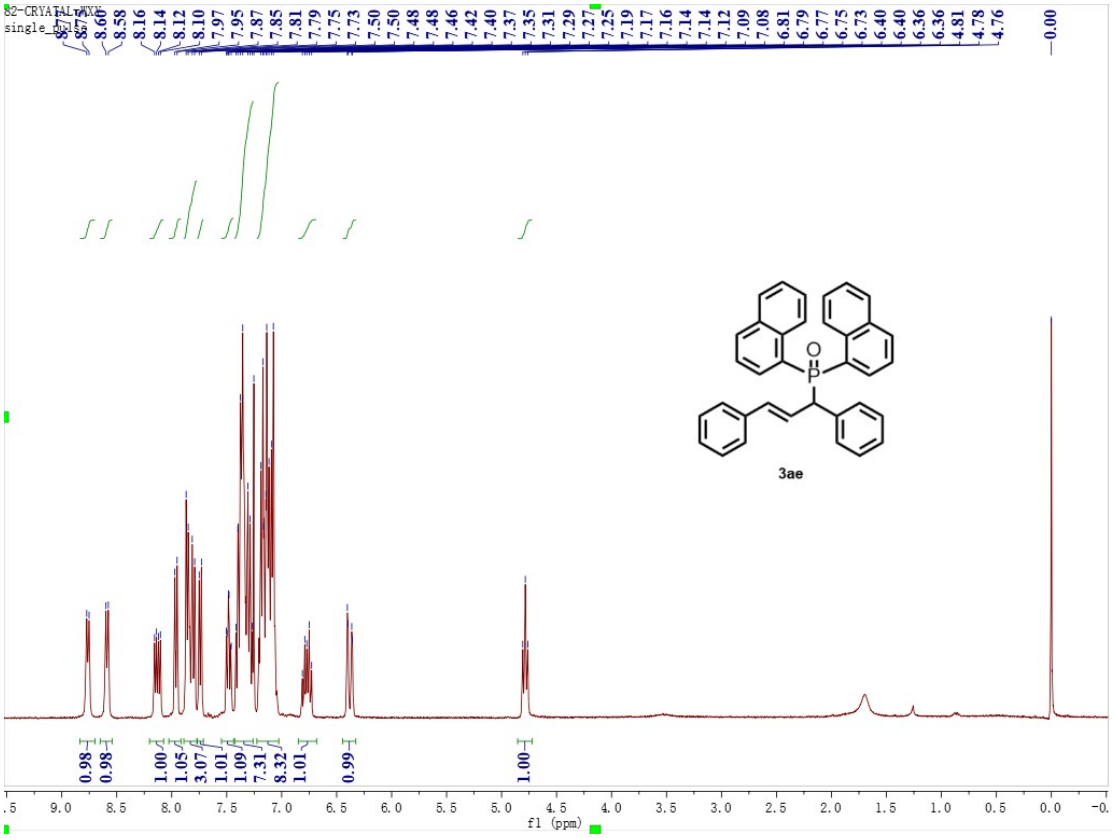
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3ad.**



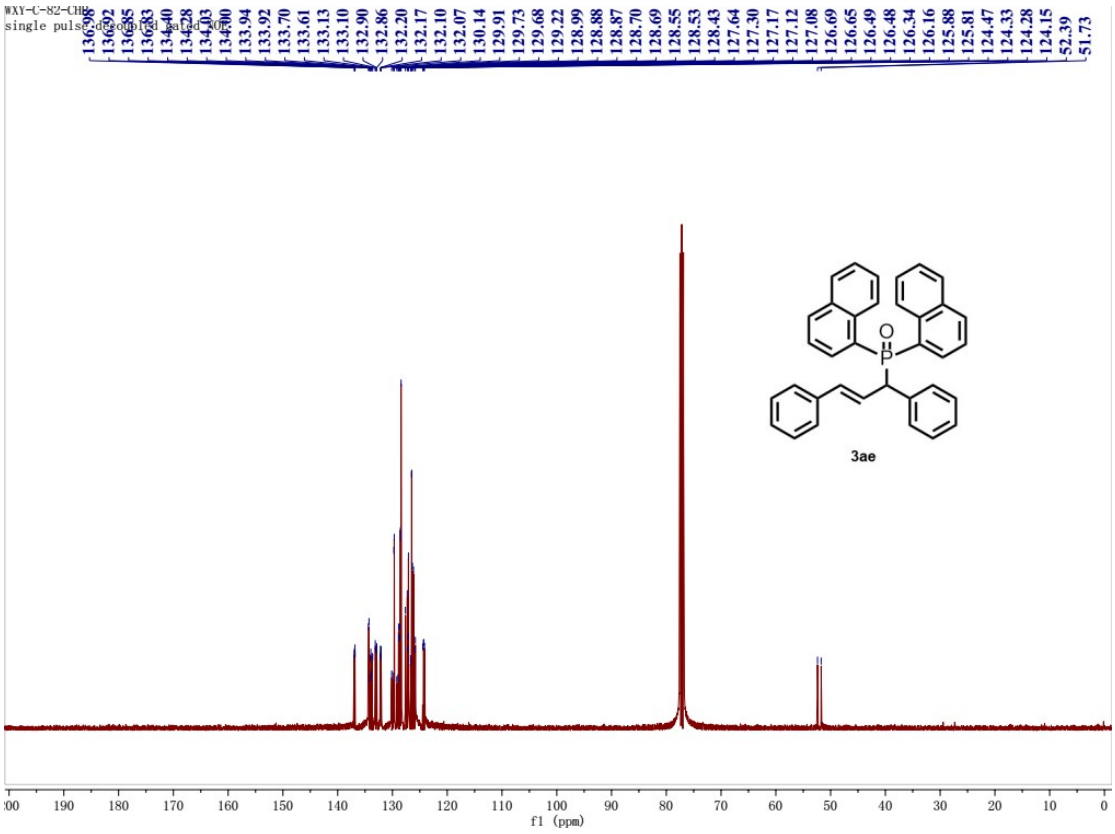
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3ad.**



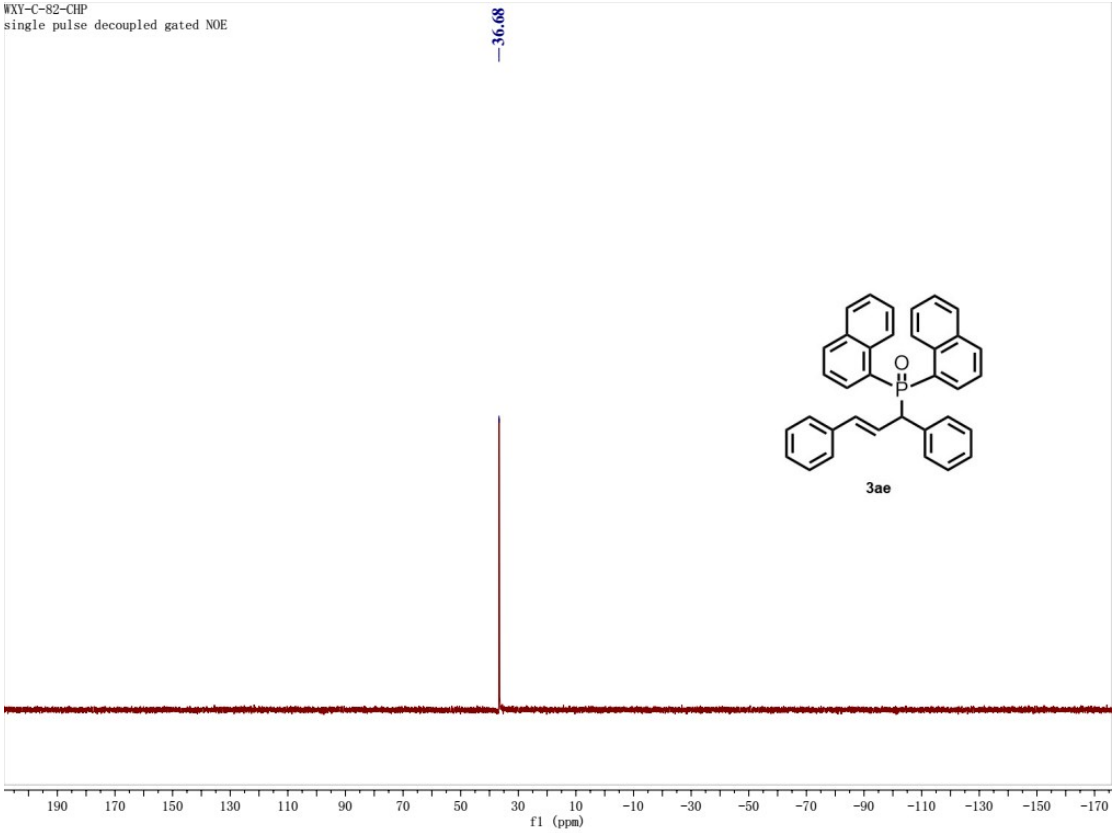
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3ad.**



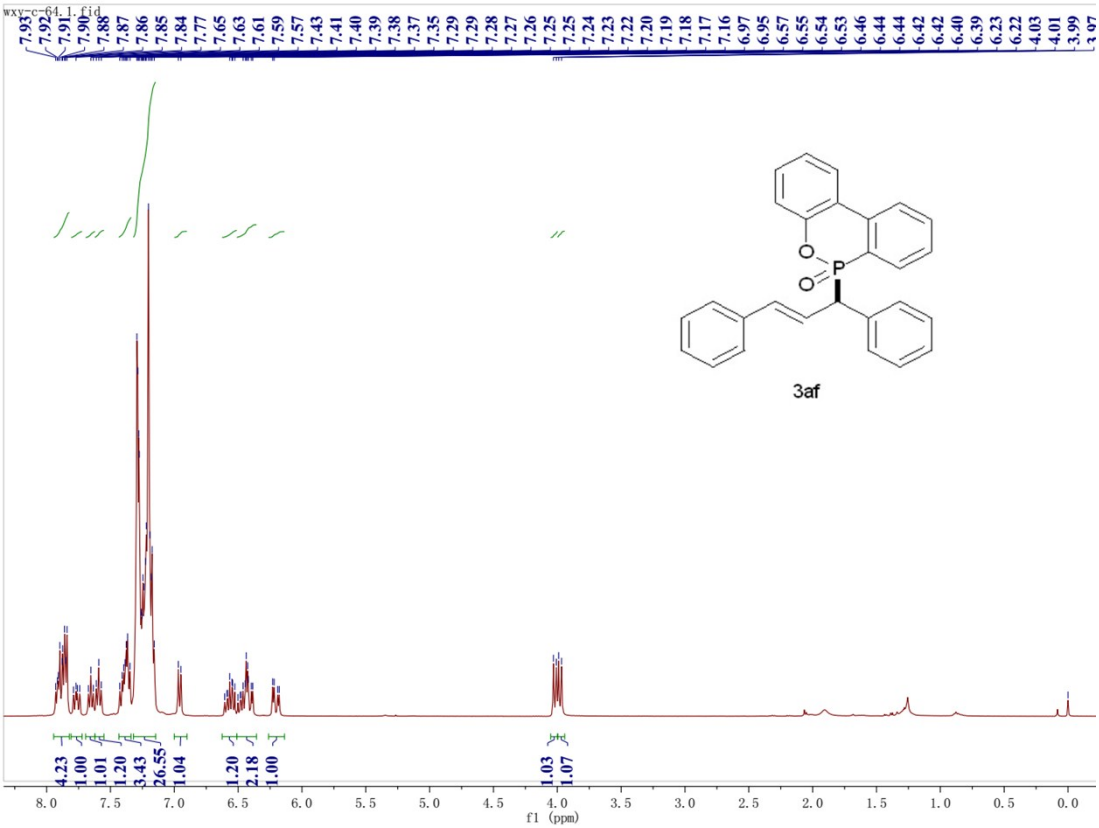
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3ae.**



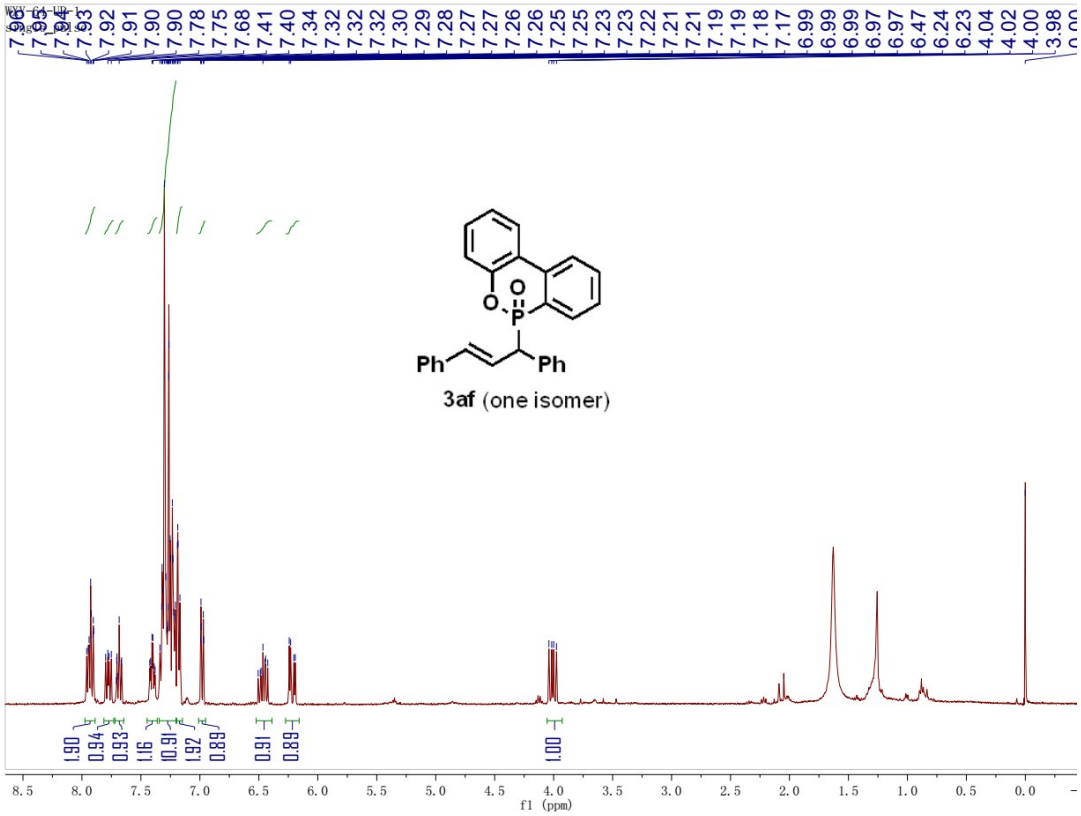
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3ae.**



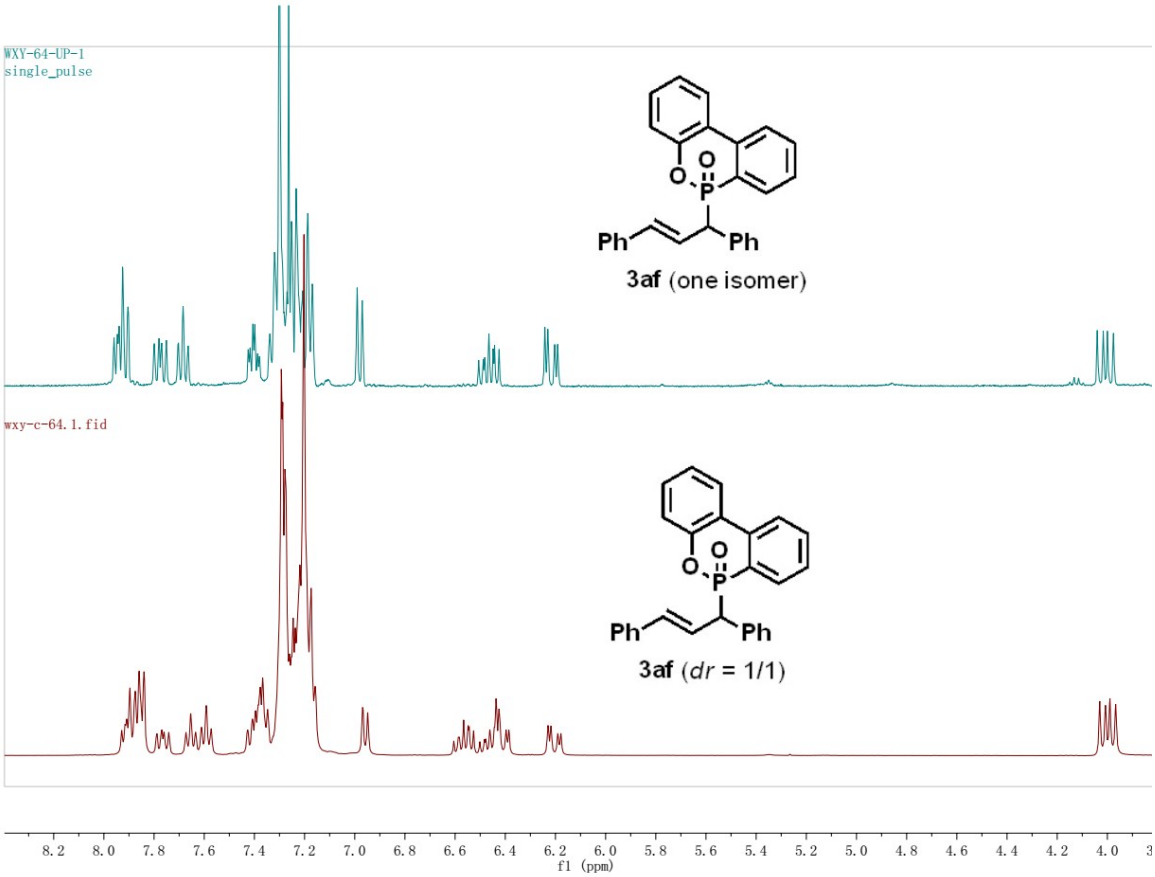
^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3ae.**



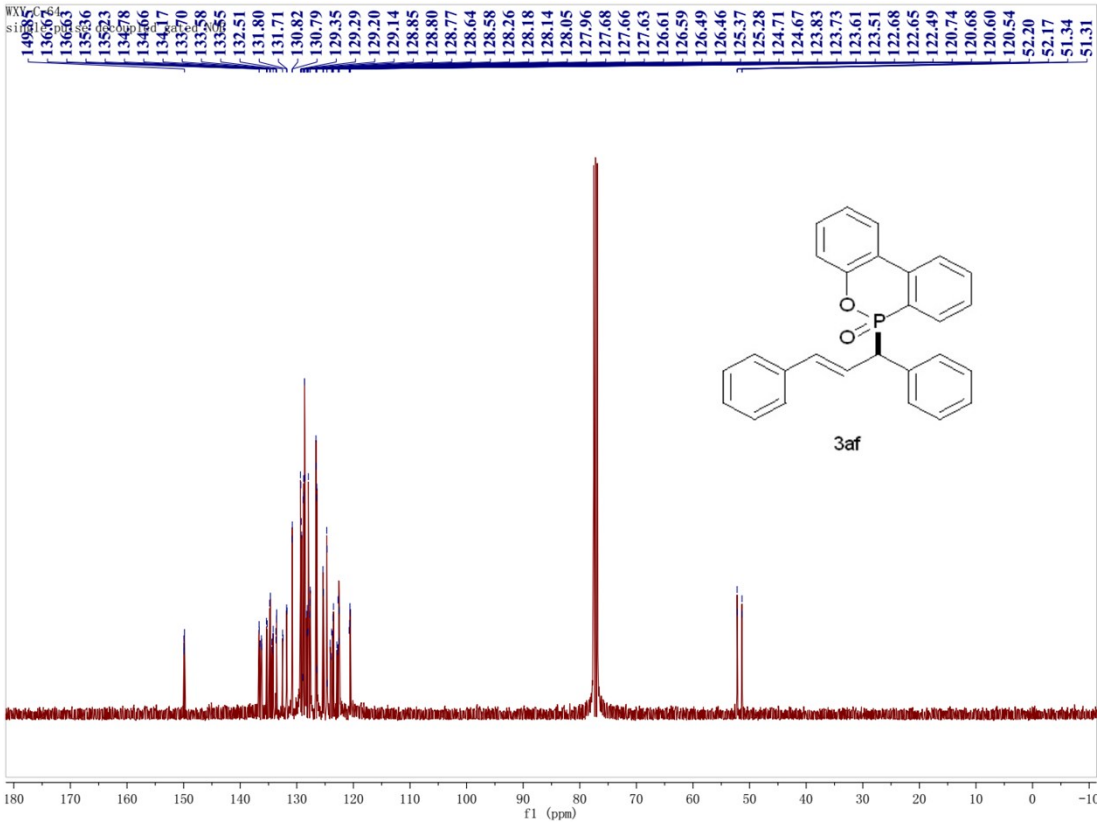
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3af** (dr = 1/1)**.**



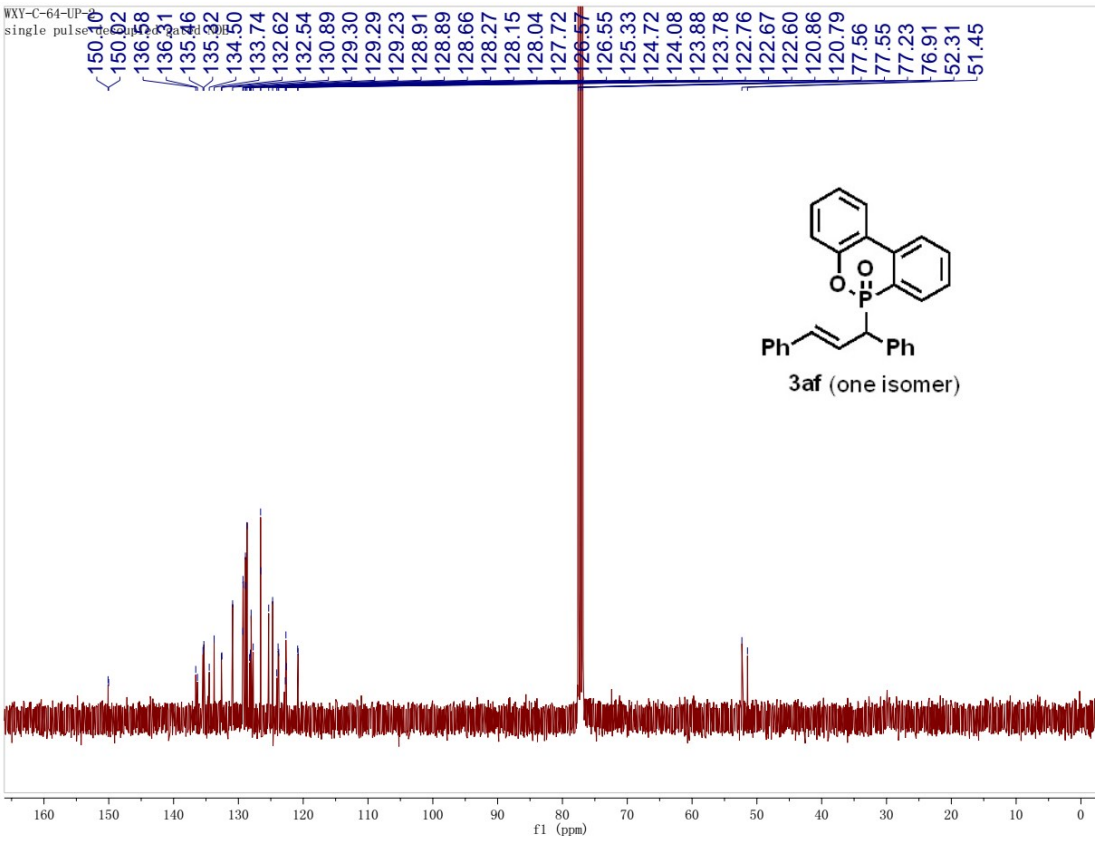
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3af** (one isomer)**.**



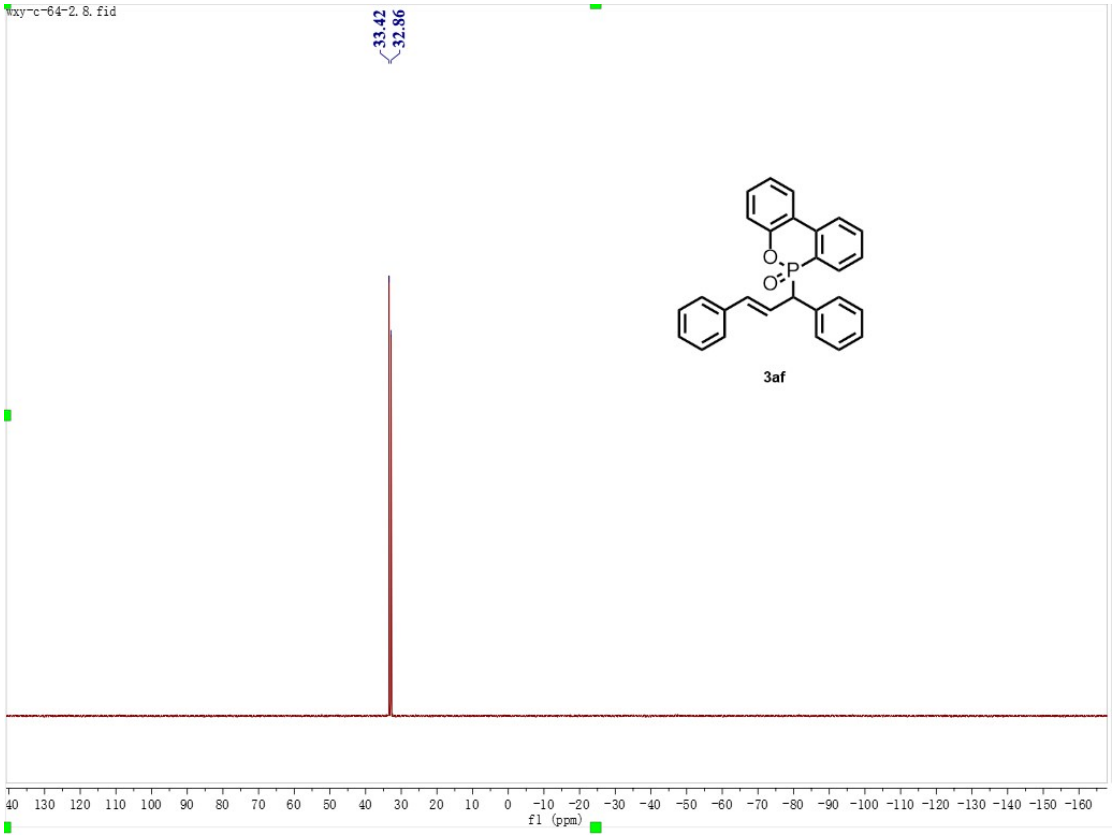
^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3af** (comparation)



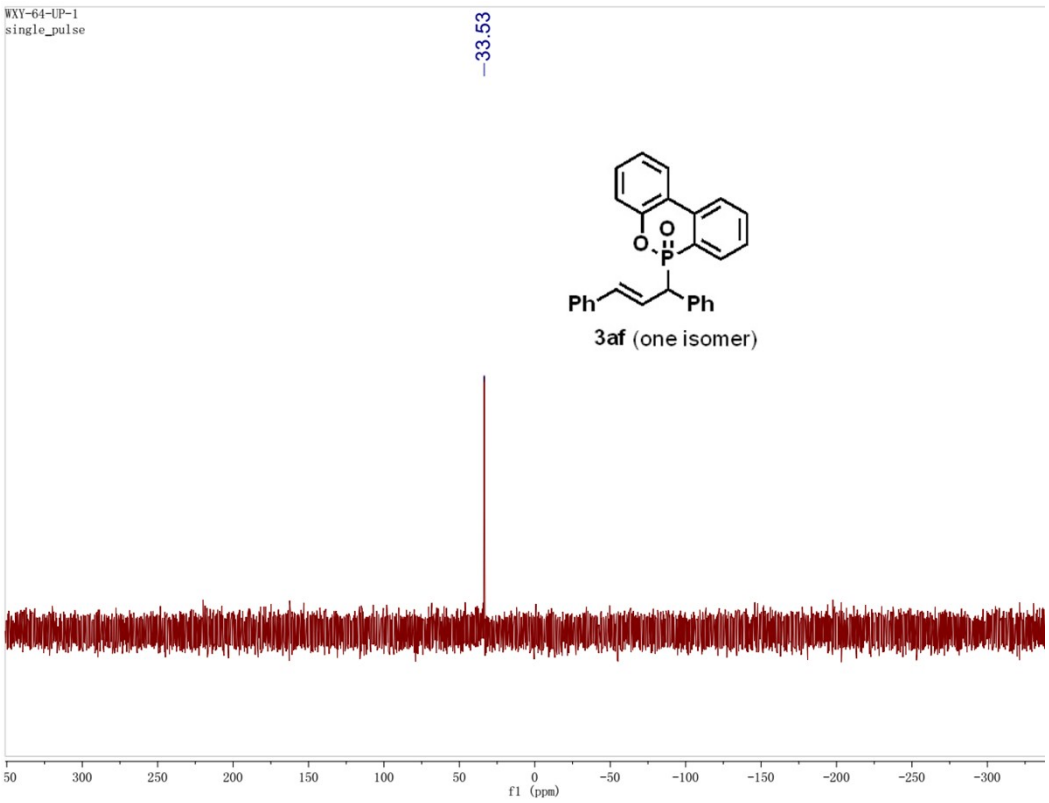
^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3af** (dr = 1/1)**.**



^{13}C NMR (101 MHz, Chloroform-d) spectra for compound **3af** (one isomer)**.**



^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3af** (dr = 1/1)**.**



^{31}P NMR (162 MHz, Chloroform-d) spectra for compound **3af** (one isomer)**.**