Supplemental Materials for

Copper-Catalyzed Allenynylative C–P Couplings of Diynylic Acetates with Hydrophosphoryl Compounds Leading to Phosphorylated Allenynes

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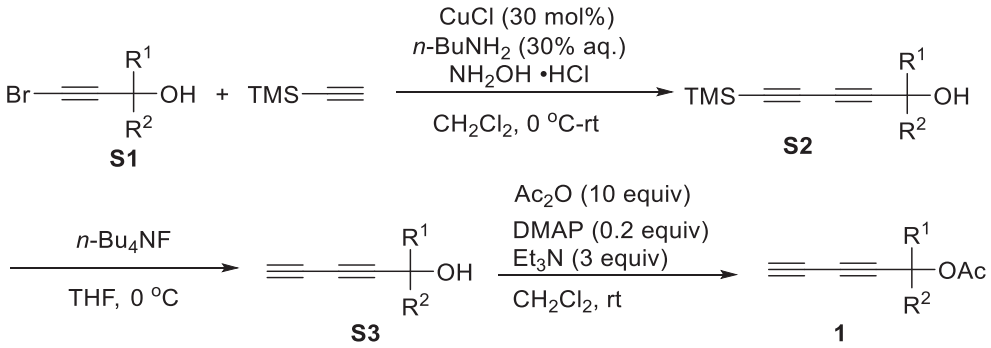
Contents

1. General Information

Unless otherwise specified, all reactions were performed in Schlenk flasks under dry N_2 atmosphere. All solvents were distilled prior to use using appropriate drying agents. Thin layer chromatography was performed on precoated glass-backed plates and visualized with UV light at 254 nm. Flash chromatography was performed on silica gel using petroleum ether and EtOAc as eluent. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Ascend^{TM} 400 spectrometer at 400 MHz. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Ascend^{TM} 400 spectrometer at 100 MHz. Phosphorus nuclear magnetic resonance (^{31}P NMR) spectra were recorded on a Bruker Ascend^{TM} 400 spectrometer at 160 MHz. Spectra were obtained in $CDCl_3$ or acetone-d6. Chemical shifts are expressed in ppm and *J* values are given in Hz. Proton chemical shifts are reported relative to internal tetramethylsilane (TMS, δ 0.0 ppm), or with the solvent reference relative to TMS employed as an internal standard ($CDCl_3$, δ 7.26 ppm). Carbon chemical shifts were reported in ppm relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm). Phosphorus chemical shifts were recorded using 85% phosphoric acid as the external standard. HRMS analysis was performed on an Agilent 6540 UHD accurate-mass quadrupole time-of-flight (Q-TOF) mass spectrometer in the electrospray ionization mode. Starting materials **1** were prepared following literature method and a general procedure was described as below.[1] Hydrophosphoryl compounds were purchased from commercial source, or prepared via literature methods.[2] Other chemicals were commercially available and used as received.

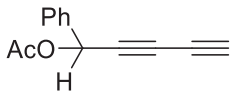
2. Starting materials 1



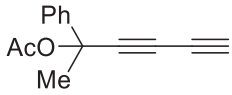
General procedure for the synthesis of diynylic acetates 1.[1] To a 100 mL Schlenk flask was added CuCl (2.7 mmol, 30 mol%) and aq. *n*-$BuNH_2$ (30%wt, 25 mL) under N_2. Several pinchs of NH_2OH•HCl was added until a blue color disappeared. The mixture was cooled to 0 °C. Then, trimethylsilylacetylene (10.8 mmol, 1.2 equiv) and alkynyl bromide **S1** (9 mmol) in CH_2Cl_2 (15 mL) were successively added dropwise. Approximately

every 2 minutes pinchs of NH_2OH•HCl was added, or when the solution developed a blue color. After the reaction was complete (monitored by TLC), the resulting suspension was filtered through Celite, and washed with DCM. The aqueous mixture was extracted with DCM (3 × 20 mL); the combined organic phases were washed with brine and dried over $MgSO_4$. After filtration and concentration, the crude oil was dissolved in THF (10 mL) at 0 ºC. Then, a solution of tetrabutylammonium fluoride trihydrate dissolved in THF (10 mL) was added dropwise. After stirring for 1.5 h, the reaction mixture was quenched with water (10 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water and brine, and dried over $MgSO_4$. A brown oil (**S3**) was obtained after filtration and concentration. The crude **S3** was used without further purification. To the above crude **S3** dissolved in CH_2Cl_2 (20 mL) was added triethylamine (3 equiv, 27 mmol) and 4-dimethylaminopyridine (DMAP, 0.2 equiv, 1.8 mmol) at 0 ºC under N_2. Acetic anhydride (10 equiv) was added dropwise. The reaction was stirred overnight. The reaction was carefully quenched with aq. $NaHCO_3$ to be neutral, and the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water, brine, and dried with $MgSO_4$. After filtration and concentration, the crude material was purified by column chromatography to afford diynylic acetates **1** as brown oil in moderate to good yields (52%~65%), which were stored below -30 ºC under dark.

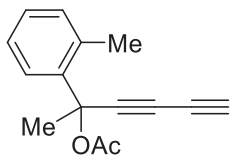
Characterization data of 1.



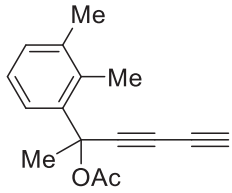
1-phenylpenta-2,4-diyn-1-yl acetate (1a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.51–7.48 (m, 2H), 7.41–7.38 (m, 3H), 6.47 (s, 1H), 2.25 (*d*, *J* = 0.8 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.5, 135.8, 129.3, 128.8, 127.7, 72.4, 71.1, 69.5, 67.2, 65.5, 20.9. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{10}O_2Na^+$ 221.0573, found 221.0580.



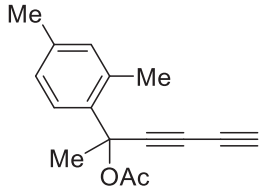
2-phenylhexa-3,5-diyn-2-yl acetate (1a'): [1] ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.55–7.52 (m, 2H), 7.39–7.35 (m, 2H), 7.32–7.28 (m, 1H), 2.31 (s, 1H), 2.08 (s, 3H), 1.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.5, 141.6, 128.5, 128.1, 124.7, 75.3, 74.9, 71.5, 69.8, 67.4, 31.6, 21.5.



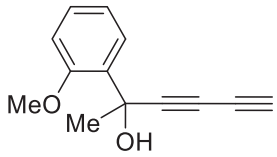
2-(o-tolyl)hexa-3,5-diyn-2-yl acetate (1b): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64–7.62 (m, 1H), 7.23–7.21 (m, 2H), 7.18–7.15 (m, 1H), 2.50 (s, 3H), 2.30 (s, 1H), 2.10 (s, 3H), 2.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.4, 138.2, 134.7, 132.6, 128.3, 126.3, 126.0, 76.4, 75.4, 71.2, 70.0, 67.4, 28.5, 21.4, 21.0. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{14}O_2Na^+$ 249.0886, found 249.0891.



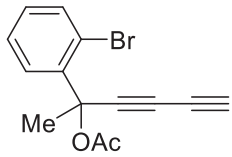
2-(2,3-dimethylphenyl)hexa-3,5-diyn-2-yl acetate (1c): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53–7.50 (m, 1H), 7.15–7.09 (m, 2H), 2.39 (s, 3H), 2.29 (s, 1H), 2.28 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.4, 138.7, 138.0, 133.6, 130.2, 125.4, 124.3, 76.5, 75.7, 71.0, 69.9, 67.5, 28.5, 21.4, 20.9, 16.8. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}O_2Na^+$ 263.1043, found 263.1050.



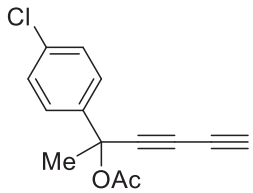
2-(2,4-dimethylphenyl)hexa-3,5-diyn-2-yl acetate (1d): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50 (d, J = 8.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 2.47 (s, 3H), 2.30 (s, 3H), 2.29 (s, 1H), 2.08 (s, 3H), 2.03 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.4, 138.0, 135.2, 134.6, 133.4, 126.6, 126.3, 76.2, 75.5, 71.0, 69.8, 67.5, 28.3, 21.4, 20.8. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}O_2Na^+$ 263.1043, found 263.1050.



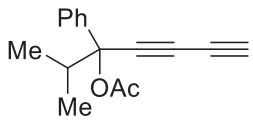
2-(2-methoxyphenyl)hexa-3,5-diyn-2-ol (1e'): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.43 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.34–7.29 (m, 1H), 7.01–6.96 (m, 2H), 4.52 (s, 1H), 3.96 (s, 3H), 2.19 (s, 1H), 1.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 156.9, 131.2, 129.5, 125.9, 121.1, 111.8, 79.5, 68.5, 67.8, 67.0, 55.8, 28.6. HRMS (ESI/Q-TOF) m/z: $[M-H]^-$ calcd for $C_{13}H_{11}O_2^-$ 199.0765, found 199.0759.



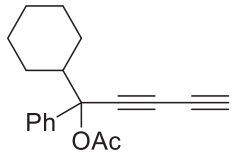
2-(2-bromophenyl)hexa-3,5-diyn-2-yl acetate (1f): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.57 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.36–7.32 (m, 1H), 7.17–7.13 (m, 1H), 2.32 (s, 1H), 2.13 (s, 3H), 2.06 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.5, 138.5, 135.5, 129.6, 129.2, 127.5, 119.0, 76.1, 74.5, 71.8, 70.2, 67.3, 28.3, 21.1. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{11}O_2BrNa^+$ 312.9835, found 312.9844.



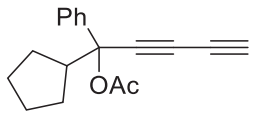
2-(4-chlorophenyl)hexa-3,5-diyn-2-yl acetate (1g): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.47 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.32 (s, 1H), 2.07 (s, 3H), 1.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.4, 140.2, 134.0, 128.6, 126.3, 74.7, 74.3, 71.7, 70.1, 67.1, 31.4, 21.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{11}O_2ClNa^+$ 269.0340, found 269.0345.



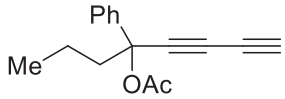
2-methyl-3-phenylhepta-4,6-diyn-3-yl acetate (1h): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.45 (d, J = 7.2 Hz, 2H), 7.35–7.27 (m, 3H), 2.30–2.23 (m, 2H), 2.06 (s, 3H), 1.17 (d, J = 6.8 Hz, 3H), 0.74 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.3, 140.0, 128.1, 127.9, 125.5, 82.6, 72.8, 72.8, 69.0, 67.5, 40.5, 21.5, 17.8, 17.0. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}O_2Na^+$ 263.1043, found 263.1048.



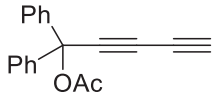
1-cyclohexyl-1-phenylpenta-2,4-diyn-1-yl acetate (1i): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.44–7.42 (m, 2H), 7.34–7.24 (m, 3H), 2.27 (s, 1H), 2.12–2.09 (m, 1H), 2.06 (s, 3H), 1.91–1.78 (m, 2H), 1.64–1.62 (m, 2H), 1.35–1.06 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.3, 139.9, 128.1, 127.8, 125.5, 82.1, 73.3, 72.8, 69.1, 67.6, 49.9, 27.8, 26.8, 26.04, 26.00, 25.98, 21.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{20}O_2Na^+$ 303.1356, found 303.1366.



1-cyclopentyl-1-phenylpenta-2,4-diyn-1-yl acetate (1j): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.47 (d, *J* = 7.6 Hz, 2H), 7.35–7.31 (m, 2H), 7.28–7.24 (m, 1H), 2.55–2.46 (m, 1H), 2.26 (s, 1H), 2.06 (s, 3H), 1.90–1.22 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.4, 140.9, 128.36, 127.9, 125.2, 82.1, 73.5, 72.3, 69.0, 67.6, 52.3, 28.6, 27.8, 25.7, 25.4, 21.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}O_2Na^+$ 289.1199, found 289.1206.

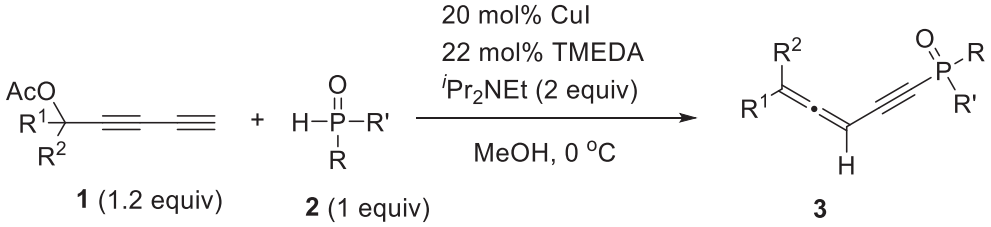


4-phenylocta-5,7-diyn-4-yl acetate (1k): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.47 (d, *J* = 7.6 Hz, 2H), 7.36–7.25 (m, 3H), 2.29 (s, 1H), 2.16–2.09 (m, 1H), 2.07 (s, 3H), 1.98–1.90 (m, 1H), 1.58–1.48 (m, 1H), 1.32–1.24 (m, 1H), 0.89 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.4, 140.8, 128.4, 128.0, 125.0, 78.8, 74.3, 72.2, 69.5, 67.5, 46.3, 21.5, 17.5, 13.8. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}O_2Na^+$ 263.1043, found 263.1048.



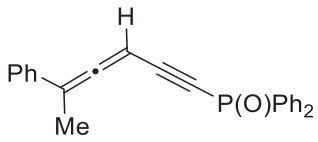
1,1-diphenylpenta-2,4-diyn-1-yl acetate (1l):[1] ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.47 (d, *J* = 7.6 Hz, 4H), 7.34–7.26 (m, 6H), 2.33 (s, 1H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.0, 141.4, 128.4, 128.2, 126.2, 79.0, 74.0, 73.8, 70.6, 67.4, 21.6.

3. Experimental prcedures and characterization data for the products 3-7

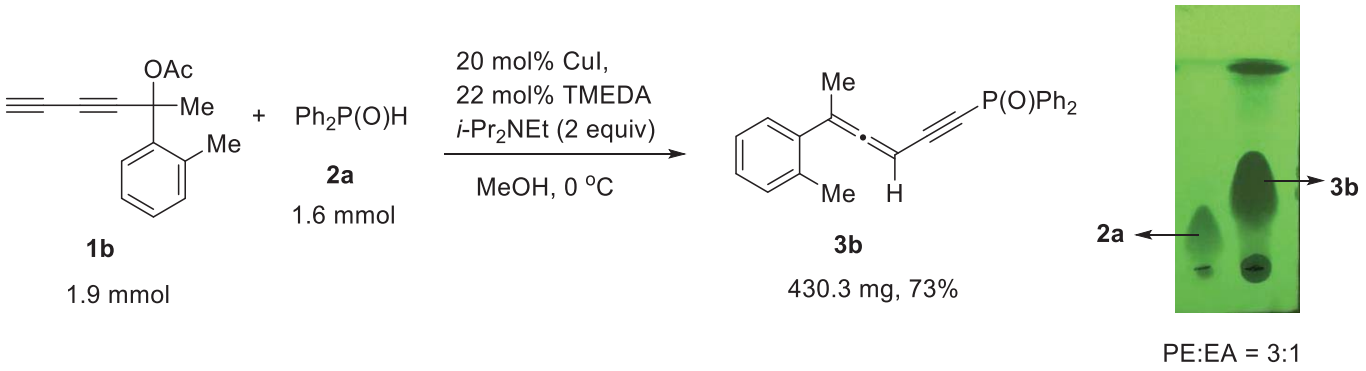


General procedure for the copper-catalyzed reactions of diynylic acetates with hydrophosphoryl compounds. To an oven-dried Schlenk tube (10 mL) with Teflon plug valves were added CuI (0.04 mmol). The Schlenk tube was then evacuated and back-filled with N_2 (3 cycles). Degassed dry MeOH (0.5 mL), and TMEDA (0.044 mmol) was sequentially injected under N_2 atmosphere at room temperature. The solution was stirred for 15 min and then cooled to 0 °C. *i*-Pr_2NEt (0.4 mmol) was added. Hydrophosphoryl compound **2** (0.2

mmol) and diynylic acetates **1** (1.2 equiv) in MeOH (1.5 mL) were then injected with stirring. The tube was sealed and the resulting mixture was stirred at 0 °C for 15-60 min (monitored by TLC). The reaction mixture was filtrated over celite and the the filtrate was concentrated to dryness with silica gel. The powder residue was purified by column chromatography on silica gel (PE/EtOAc 10/1 to 1/1) to afford phosphorylated allenynes **3**. **Note: the obtained products 3 were generally not very stable, and should be storred below -30 °C under dark or used immediately for synthetic purpose.**

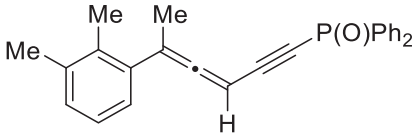


Diphenyl(5-phenylhexa-3,4-dien-1-yn-1-yl)phosphine oxide (3a): 0.2 mmol scale. Yield: 53.8 mg, 76%. Yellow slurry gum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86–7.81 (m, 4H), 7.53–7.44 (m, 6H), 7.37–7.35 (m, 4H), 7.29–7.27 (m, 1H), 5.86 (dq, $J_{P\text{-}H} = J_{H\text{-}H} = 2.8$ Hz, 1H), 2.17 (d, $J = 2.8$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 216.3 (d, $J_{C\text{-}P} = 2.9$ Hz), 134.1, 133.0 (d, $J_{C\text{-}P} = 121.5$ Hz), 132.2 (d, $J_{C\text{-}P} = 3.2$ Hz), 131.0 (d, $J_{C\text{-}P} = 11.0$ Hz), 128.7, 128.6 (d, $J_{C\text{-}P} = 10.2$ Hz), 128.0, 126.4, 104.9, 99.3 (d, $J_{C\text{-}P} = 29.6$ Hz), 83.0 (d, $J_{C\text{-}P} = 169.6$ Hz), 76.1 (d, $J_{C\text{-}P} = 4.7$ Hz), 16.4. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 8.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{20}OP^+$ 355.1246, found 355.1252.

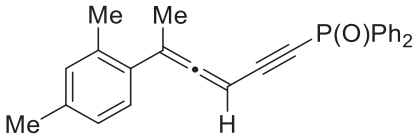


Diphenyl(5-(o-tolyl)hexa-3,4-dien-1-yn-1-yl)phosphine oxide (3b): 1.6 mmol scale reaction. To an oven-dried Schlenk tube (10 mL) with Teflon plug valves were added CuI (0.32 mmol, 60.8 mg). The Schlenk tube was then evacuated and back-filled with N_2 (3 cycles). Degassed dry MeOH (1 mL), and TMEDA (0.35 mmol, 52 μL) was sequentially injected under N_2 atmosphere at room temperature. The solution was stirred for 15 min and then cooled to 0 °C. *i*-Pr$_2$NEt (3.2 mmol, 640 μL) was injected. Diphenylphosphine oxide **2a** (1.6 mmol, 323.2 mg) and diynylic acetates **1b** (1.92 mmol, 434.5 mg) in degassed MeOH (3 mL) were then injected under nitrogen with vigorous stirring. The tube was sealed and the resulting mixture was stirred at 0 °C for 60 min (monitored by TLC, see figure above). After filtration over celite, the filtrate was concentrated to dryness with silica gel powder. The powder residue was purified by column chromatography on silica gel (PE/EtOAc

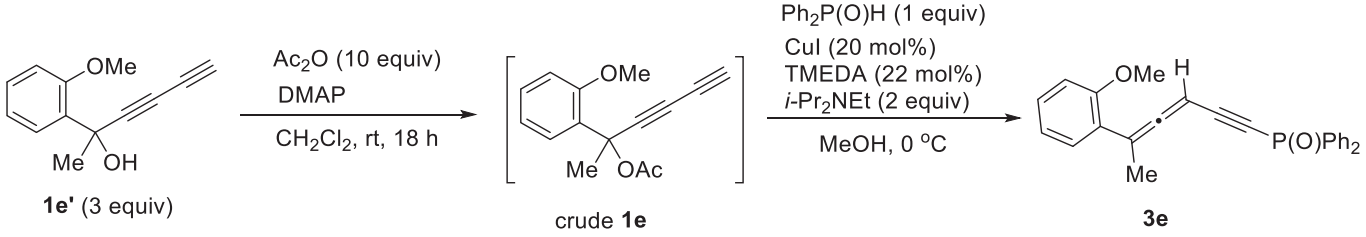
10/1 to 3/1) to afford 430.3 mg of **3b** (73% yield). Yellow slurry gum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87–7.81 (m, 4H), 7.54–7.45 (m, 6H), 7.22–7.19 (m, 4H), 5.58 (dq, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 3.2 Hz, 1H), 2.33 (s, 3H), 2.12 (d, J = 3.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 214.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 135.9, 135.0, 133.10 (d, $J_{C\text{-}P}$ = 121.4 Hz), 133.08 (d, $J_{C\text{-}P}$ = 121.4 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 11.2 Hz), 130.8, 128.6 (d, $J_{C\text{-}P}$ = 12.6 Hz), 127.9, 127.4, 126.2, 103.7, 99.8 (d, $J_{C\text{-}P}$ = 29.9 Hz), 83.5 (d, $J_{C\text{-}P}$ = 170.6 Hz), 73.6 (d, $J_{C\text{-}P}$ = 4.7 Hz), 20.6, 20.0. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 8.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}OP^+$ 369.1403, found 369.1408.



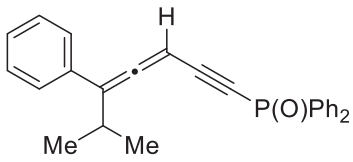
(5-(2,3-dimethylphenyl)hexa-3,4-dien-1-yn-1-yl)diphenylphosphine oxide (3c): 0.4 mmol scale. Yield: 123.8 mg, 81%. Yellow slurry gum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87–7.82 (m, 4H), 7.54–7.46 (m, 6H), 7.11–7.06 (m, 3H), 5.54 (dq, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 3.2 Hz, 1H), 2.28 (s, 3H), 2.23 (s, 3H), 2.09 (d, J = 2.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 137.5, 135.7, 134.0, 133.0 (d, $J_{C\text{-}P}$ = 121.4 Hz), 132.9 (d, $J_{C\text{-}P}$ = 121.4 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.85 (d, $J_{C\text{-}P}$ = 11.3 Hz), 130.84 (d, $J_{C\text{-}P}$ = 11.1 Hz), 129.3, 128.4 (d, $J_{C\text{-}P}$ = 13.3 Hz), 125.9, 125.3, 104.3, 99.9 (d, $J_{C\text{-}P}$ = 30.0 Hz), 83.1 (d, $J_{C\text{-}P}$ = 171.0 Hz), 73.0 (d, $J_{C\text{-}P}$ = 4.8 Hz), 20.6, 20.2, 16.4. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 8.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{24}OP^+$ 383.1559, found 383.1566.



(5-(2,4-dimethylphenyl)hexa-3,4-dien-1-yn-1-yl)diphenylphosphine oxide (3d): 0.4 mmol scale. Yield: 121.9 mg, 80%. Yellow slurry gum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86–7.81 (m, 4H), 7.55–7.45 (m, 6H), 7.11–7.06 (m, 3H), 5.56 (dq, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 3.2 Hz, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.10 (d, J = 3.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 214.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 137.7, 135.8, 133.05 (d, $J_{C\text{-}P}$ = 121.7 Hz), 133.04 (d, $J_{C\text{-}P}$ = 121.4 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.0, 131.5, 131.0 (d, $J_{C\text{-}P}$ = 10.9 Hz), 128.5 (d, $J_{C\text{-}P}$ = 13.4 Hz), 127.2, 126.8, 103.5, 100.0 (d, $J_{C\text{-}P}$ = 29.9 Hz), 83.2 (d, $J_{C\text{-}P}$ = 171.3 Hz), 73.4 (d, $J_{C\text{-}P}$ = 4.6 Hz), 21.0, 20.6, 20.0. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 8.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{24}OP^+$ 383.1559, found 383.1568.

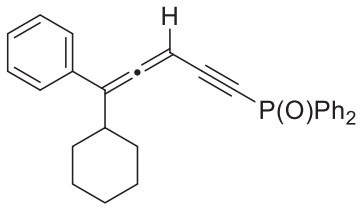


(5-(2-methoxyphenyl)hexa-3,4-dien-1-yn-1-yl)diphenylphosphine oxide (3e): To a solution of **1e'** (1.2 mmol, 240.0 mg) in CH_2Cl_2 (5 mL) was added triethylamine (0.5 mL, 3.6 mmol, 3 equiv) and 4-dimethylaminopyridine (DMAP, 29.8 mg, 0.2 equiv, 0.24 mmol) at 0 °C under N_2. Acetic anhydride (12 mmol, 1.2 mL, 10 equiv) was added dropwise. The result solution was naturally warmed to room temperature and stirred overnight (18 h). The reaction was carefully quenched with aq. $NaHCO_3$ to be neutral, and the organic layer was separated. The aqueous phase was quenched with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with water, brine, and dried with $MgSO_4$. After filtration and concentration, the crude **1e** was obtained and used directly (Noted: **1e** is easily hydrolyzed upon purification by column chromatography on silica gel using elutent with Et_3N. Pleasingly, the copper-catalyzed reaction proceeded well with the crude **1e** without further purification.*)*. To an oven-dried Schlenk tube (10 mL) with Teflon plug valves were added CuI (0.08 mmol, 15.5 mg). The Schlenk tube was then evacuated and back-filled with N_2 (3 cycles). MeOH (1 mL) and TMEDA (0.09 mmol, 13 μL) was sequentially injected under N_2 atmosphere at room temperature. The solution was stirred for 15 min and then cooled to 0 °C. *i*-Pr_2NEt (0.8 mmol, 160 μL) was injected. Diphenylphosphine oxide **2a** (0.4 mmol, 80.8 mg) and the above crude **1e** in degassed MeOH (2 mL) were then injected under nitrogen with vigorous stirring. The tube was sealed and the resulting mixture was stirred at 0 °C for 15 min (monitored by TLC). After filtration over celite, the filtrate was concentrated to dryness with silica gel powder. The powder residue was purified by column chromatography on silica gel (PE/EtOAc 5/1 to 1/1) to afford 121.5 mg of **3e** (79% yield). Yellow slurry gum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88–7.83 (m, 4H), 7.54–7.45 (m, 6H), 7.29–7.27 (m, 1H), 7.21 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 6.96 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.88 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 5.61 (dq, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 2.8 Hz, 1H), 3.79 (s, 3H), 2.15 (d, J = 3.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 216.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 156.9, 133.13 (d, $J_{C\text{-}P}$ = 121.6 Hz), 133.11 (d, $J_{C\text{-}P}$ = 121.1 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 130.8 (d, $J_{C\text{-}P}$ = 11.0 Hz), 129.1, 128.4 (d, $J_{C\text{-}P}$ = 13.3 Hz), 128.2, 123.8, 120.5, 111.1, 100.9, 100.6 (d, $J_{C\text{-}P}$ = 30.4 Hz), 82.3 (d, $J_{C\text{-}P}$ = 172.1 Hz), 72.4 (d, $J_{C\text{-}P}$ = 5.0 Hz), 55.4, 18.4. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 8.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}O_2P^+$ 385.1352, found 385.1360.

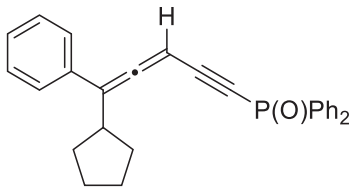


(6-methyl-5-phenylhepta-3,4-dien-1-yn-1-yl)diphenylphosphine oxide (3h): 0.2 mmol scale. Yield: 58.9 mg, 76%. Yellow slurry gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.81 (m, 4H), 7.55–7.44 (m, 6H), 7.36–7.33 (m, 4H), 7.30–7.27 (m, 1H), 5.90 (dd, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 2.8 Hz, 1H), 2.93–2.86 (m, 1H), 1.17 (d, J = 6.8 Hz, 3H), 1.15 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 215.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.9, 132.1 (d, $J_{C\text{-}P}$ = 121.5 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 11.2 Hz), 128.7, 128.6 (d, $J_{C\text{-}P}$ = 13.3 Hz), 127.9, 127.1, 117.3, 99.8 (d, $J_{C\text{-}P}$ = 30.0 Hz), 83.2 (d, $J_{C\text{-}P}$ = 170.8 Hz), 77.8 (d, $J_{C\text{-}P}$ = 4.8 Hz), 29.1, 21.9, 21.8.

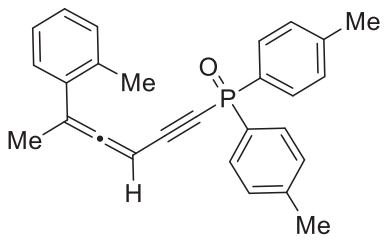
^{31}P NMR (160 MHz, $CDCl_3$): δ = 8.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{24}OP^+$ 383.1559, found 383.1566.



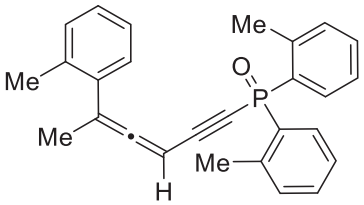
(5-cyclohexyl-5-phenylpenta-3,4-dien-1-yn-1-yl)diphenylphosphine oxide (3i): 0.2 mmol scale. Yield: 59.1 mg, 70%. Yellow slurry gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.82 (m, 4H), 7.55–7.45 (m, 6H), 7.37–7.32 (m, 4H), 7.29–7.26 (m, 1H), 5.87 (dd, $J_{P-H} = J_{H-H} = 2.8$ Hz, 1H), 2.55–2.49 (m, 1H), 1.94–1.70 (m, 4H), 1.41–1.28 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 215.7 (d, $J_{C-P} = 2.8$ Hz), 133.9, 132.2 (d, $J_{C-P} = 121.4$ Hz), 132.1 (d, $J_{C-P} = 2.9$ Hz), 131.0 (d, $J_{C-P} = 11.2$ Hz), 128.7, 128.6 (d, $J_{C-P} = 13.3$ Hz), 127.9, 127.1, 116.2, 99.9 (d, $J_{C-P} = 29.8$ Hz), 82.7 (d, $J_{C-P} = 170.9$ Hz), 77.6 (d, $J_{C-P} = 4.7$ Hz), 38.6, 32.4, 32.3, 26.39, 26.37, 26.1. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 8.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{28}OP^+$ 423.1872, found 423.1876.



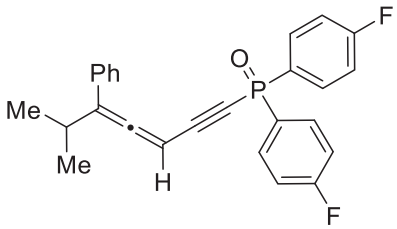
(5-cyclopentyl-5-phenylpenta-3,4-dien-1-yn-1-yl)diphenylphosphine oxide (3j): 0.2 mmol scale. Yield: 53.9 mg, 66%. Yellow slurry gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.81 (m, 4H), 7.54–7.45 (m, 6H), 7.37–7.35 (m, 4H), 7.29–7.27 (m, 1H), 5.89 (dd, $J_{P-H} = J_{H-H} = 2.8$ Hz, 1H), 3.07–3.01 (m, 1H), 1.99–1.93 (m, 2H), 1.72–1.60 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 215.1 (d, $J_{C-P} = 2.9$ Hz), 134.3, 133.1 (d, $J_{C-P} = 121.4$ Hz), 132.1 (d, $J_{C-P} = 2.9$ Hz), 130.9 (d, $J_{C-P} = 11.1$ Hz), 128.6, 128.5 (d, $J_{C-P} = 12.4$ Hz), 127.8, 127.1, 115.1, 99.6 (d, $J_{C-P} = 29.8$ Hz), 82.8 (d, $J_{C-P} = 170.3$ Hz), 77.8 (d, $J_{C-P} = 4.8$ Hz), 39.7, 32.3, 32.0, 24.9, 24.8. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 8.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{26}OP^+$ 409.1716, found 409.1723.



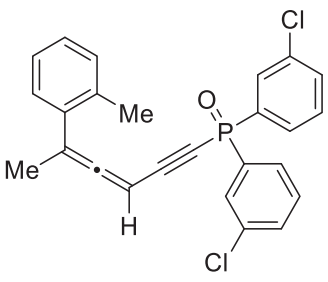
Di-*p*-tolyl(5-(*o*-tolyl)hexa-3,4-dien-1-yn-1-yl)phosphine oxide (3l): 0.2 mmol scale. Yield: 56.2 mg, 71%. Yellow slurry gum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.21–7.19 (m, 4H), 5.56 (dq, $J_{P-H} = J_{H-H} = 2.8$ Hz, 1H). 2.39 (s, 6H), 2.34 (s, 3H), 2.11 (d, $J = 2.8$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.8 (d, $J_{C-P} = 2.7$ Hz), 142.6 (d, $J_{C-P} = 3.0$ Hz), 135.9, 135.0, 130.9 (d, $J_{C-P} = 11.6$ Hz), 130.7, 130.0 (d, $J_{C-P} = 123.8$ Hz), 129.2 (d, $J_{C-P} = 13.9$ Hz), 127.8, 127.3, 126.1, 103.4, 99.1 (d, $J_{C-P} = 29.7$ Hz), 83.9 (d, $J_{C-P} = 169.1$ Hz), 73.1 (d, $J_{C-P} = 4.6$ Hz), 21.59, 21.57, 20.6, 19.9. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 8.6. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{26}OP^+$ 397.1716, found 397.1721.



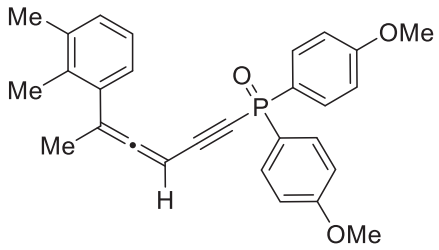
di-o-tolyl(5-(o-tolyl)hexa-3,4-dien-1-yn-1-yl)phosphine oxide (3m): 0.2 mmol scale. Yield: 54.9 mg, 69%. Yellow slurry gum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.01–7.95 (m, 2H), 7.46–7.42 (m, 2H), 7.34–7.31 (m, 2H), 7.23–7.19 (m, 6H), 5.58 (dq, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 2.8 Hz, 1H), 2.37 (s, 6H), 2.32 (s, 3H), 2.11 (d, J = 2.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 141.6 (d, $J_{C\text{-}P}$ = 10.6 Hz), 141.5 (d, $J_{C\text{-}P}$ = 10.6 Hz), 135.9, 135.1, 132.8 (d, $J_{C\text{-}P}$ = 11.9 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 11.7 Hz), 130.7 (d, $J_{C\text{-}P}$ = 118.5 Hz), 130.67 (d, $J_{C\text{-}P}$ = 118.2 Hz), 130.71, 127.8, 127.4, 126.1, 125.7 (d, $J_{C\text{-}P}$ = 13.2 Hz), 103.5, 99.3 (d, $J_{C\text{-}P}$ = 29.1 Hz), 83.7 (d, $J_{C\text{-}P}$ = 168.1 Hz), 73.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 21.14, 21.09, 20.5, 20.0. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 8.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{26}OP^+$ 397.1716, found 397.1721.



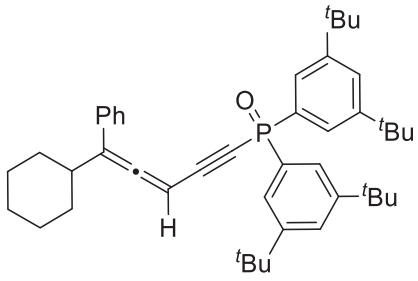
bis(4-fluorophenyl)(6-methyl-5-phenylhepta-3,4-dien-1-yn-1-yl)phosphine oxide (3n): 0.2 mmol scale. Yield: 48.0 mg, 57%. Yellow slurry gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.78 (m, 4H), 7.42–7.28 (m, 5H), 7.23–7.14 (m, 4H), 5. 89 (dd, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 2.8 Hz, 1H), 2.94–2.87 (m, 1H), 1.17 (d, J = 6.4 Hz, 3H), 1.15 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 215.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 165.3 (dd, $J_{C\text{-}F}$ = 252.5 Hz, $J_{C\text{-}P}$ = 3.5 Hz), 133.8, 133.5 (dd, $J_{C\text{-}P}$ = 12.8 Hz, $J_{C\text{-}F}$ = 8.8 Hz), 128.96 (d, $J_{C\text{-}P}$ = 125.2 Hz), 128.93 (d, $J_{C\text{-}P}$ = 125.7 Hz), 128.8, 128.0, 127.1, 117.5, 116.1 (dd, $J_{C\text{-}F}$ = 21.5 Hz, $J_{C\text{-}P}$ = 14.8 Hz), 100.5 (d, $J_{C\text{-}P}$ = 30.8 Hz), 82.3 (d, $J_{C\text{-}P}$ = 174.0 Hz), 77.6 (d, $J_{C\text{-}P}$ = 4.8 Hz), 29.1, 21.9, 21.8. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 6.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{22}OPF_2^+$ 419.1371, found 419.1376.



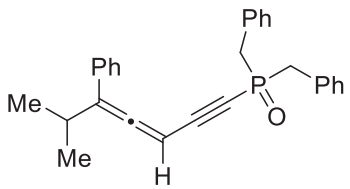
bis(3-chlorophenyl)(5-(o-tolyl)hexa-3,4-dien-1-yn-1-yl)phosphine oxide (3o): 0.2 mmol scale. Yield: 58.9 mg, 68%. Yellow slurry gum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79 (d, J = 6.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.21–7.19 (m, 4H), 5.56 (dq, $J_{P\text{-}H}$ = $J_{H\text{-}H}$ = 2.8 Hz, 1H). 2.35 (s, 3H), 2.14 (d, J = 3.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.8 (d, J = 2.7 Hz), 135.9, 135.2 (d, $J_{C\text{-}P}$ = 17.9 Hz), 134.90 (d, J = 120.8 Hz), 134.87 (d, J = 120.9 Hz), 134.81, 132.6 (d, J = 2.7 Hz), 130.8, 130.7, 130.2 (d, $J_{C\text{-}P}$ = 14.6 Hz), 129.0 (d, $J_{C\text{-}P}$ = 10.7 Hz), 128.0, 127.4, 126.2, 104.1, 101.4 (d, $J_{C\text{-}P}$ = 31.3 Hz), 82.1 (d, $J_{C\text{-}P}$ = 176.9 Hz), 73.3 (d, $J_{C\text{-}P}$ = 4.9 Hz), 20.6, 19.9. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 8.6. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{20}OPCl_2^+$ 437.0623, found 437.0631.



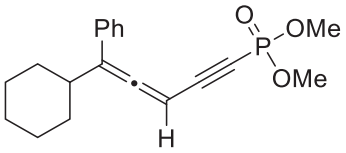
(5-(2,3-dimethylphenyl)hexa-3,4-dien-1-yn-1-yl)bis(4-methoxyphenyl)phosphine oxide (3p): 0.2 mmol scale. Yield: 39.0 mg, 45%. Yellow slurry gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7. 76 (d, J = 8.0 Hz, 2H), 7. 72 (d, J = 8.0 Hz, 2H), 7.11–7.05 (m, 3H), 6. 96 (d, J = 8.8 Hz, 4H), 5.52 (dq, $J_{P\text{-}H} = J_{H\text{-}H}$ = 3.2 Hz, 1H), 3.84 (s, 6H), 2.28 (s, 3H), 2.23 (s, 3H), 2.08 (d, J = 3.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.2 (d, J = 2.8 Hz), 162.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 137.6, 136.0, 134.2, 133.0, 132.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 129.4, 125.6 (d, $J_{C\text{-}P}$ = 24.2 Hz), 124.8 (d, $J_{C\text{-}P}$ = 128.9 Hz), 114.1 (d, $J_{C\text{-}P}$ = 14.5 Hz), 104.3, 99.2 (d, $J_{C\text{-}P}$ = 30.1 Hz), 84.0 (d, $J_{C\text{-}P}$ = 169.9 Hz), 73.2 (d, $J_{C\text{-}P}$ = 4.9 Hz), 55.4, 20.7, 20.4, 16.6. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 7.98. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{28}O_3P^+$ 443.1771, found 433.1782.



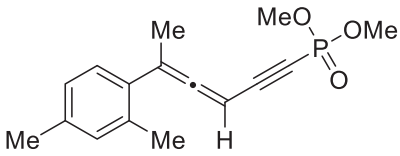
(5-cyclohexyl-5-phenylpenta-3,4-dien-1-yn-1-yl)bis(3,5-di-*tert*-butylphenyl)phosphine oxide (3q): 0.2 mmol scale. Yield: 78.2 mg, 61%. Yellow slurry gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7. 71–7.70 (m, 2H), 7. 67–7.66 (m, 2H), 7. 57 (s, 2H), 7. 33 (s, 2H), 7. 32 (s, 2H), 7.27–7.23 (m, 1H), 5.87 (dd, $J_{P\text{-}H} = J_{H\text{-}H}$ = 2.8 Hz, 1H), 2.54–2.47 (m, 1H), 1.95–1.88 (m, 2H), 1.95–1.69 (m, 3H), 1.32–1.18 (m, 5H), 1.29 (d, J = 0.8 Hz, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 215.4 (d, J = 2.8 Hz), 151.0 (d, $J_{C\text{-}P}$ = 13.1 Hz), 133.9, 132.2 (d, $J_{C\text{-}P}$ = 120.2 Hz), 128.7, 127.8, 127.1, 126.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 125.3 (d, $J_{C\text{-}P}$ = 11.8 Hz), 115.9, 98.7 (d, $J_{C\text{-}P}$ = 28.5 Hz), 83.9 (d, $J_{C\text{-}P}$ = 165.6 Hz), 77.9 (d, $J_{C\text{-}P}$ = 4.6 Hz), 38.5, 35.1, 32.5, 32.4, 31.3, 26.4, 26.1. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 10.7. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{45}H_{60}OP^+$ 647.4376, found 647.4391.



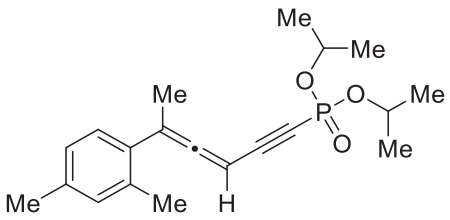
dibenzyl(6-methyl-5-phenylhepta-3,4-dien-1-yn-1-yl)phosphine oxide (3r): 0.4 mmol scale. Yield: 87.2 mg, 53%. Yellow slurry gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.24 (m, 15H), 5.73 (dd, $J_{P\text{-}H} = J_{H\text{-}H}$ = 2.8 Hz, 1H), 3.27 (d, J = 2.4 Hz, 2H), 3.23 (d, J = 2.0 Hz, 2H), 2.93–2.86 (m, 1H), 1.16 (d, J = 3.2 Hz, 3H), 1.14 (d, J = 3.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 214.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 133.9, 131.7 (d, $J_{C\text{-}P}$ = 7.0 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.0 Hz), 130.0 (d, $J_{C\text{-}P}$ = 5.6 Hz), 129.8 (d, $J_{C\text{-}P}$ = 5.1 Hz), 128.8 (d, $J_{C\text{-}P}$ = 2.4 Hz), 128.7, 128.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.9, 127.1 (d, $J_{C\text{-}P}$ = 3.4 Hz), 127.0, 126.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 117.0, 99.0 (d, $J_{C\text{-}P}$ = 25.4 Hz), 82.0 (d, $J_{C\text{-}P}$ = 155.7 Hz), 77.7 (d, $J_{C\text{-}P}$ = 4.3 Hz), 38.5 (d, $J_{C\text{-}P}$ = 75.6 Hz), 35.4 (d, $J_{C\text{-}P}$ = 60.9 Hz), 28.8, 21.9, 21.7. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 20.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{28}OP^+$ 411.1872, found 411.1878.



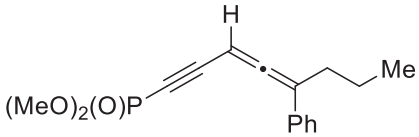
dimethyl (5-cyclohexyl-5-phenylpenta-3,4-dien-1-yn-1-yl)phosphonate (3t): 0.4 mmol scale. Yield: 82.5 mg, 63%. Yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.37–7.28 (m, 5H), 5.81 (t, $J_{P-H} = J_{H-H}$ = 2.8 Hz, 1H), 3.82 (d, J = 3.0 Hz, 3H), 3.79 (d, J = 3.0 Hz, 3H), 3.07–3.02 (m, 1H), 1.99–1.91 (m, 2H), 1.73–1.48 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 215.3 (d, J_{C-P} = 3.7 Hz), 134.2, 128.7, 127.9, 127.1, 115.3, 94.2 (d, J_{C-P} = 53.0 Hz), 76.3 (d, J_{C-P} = 302.5 Hz), 77.1 (d, J_{C-P} = 6.1 Hz), 53.4 (d, J_{C-P} = 5.5 Hz), 39.7, 32.2, 32.1, 24.93, 24.89. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -2.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{24}O_3P^+$ 331.1458, found 331.1464.



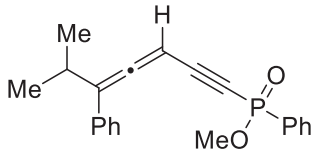
dimethyl (5-(2,4-dimethylphenyl)hexa-3,4-dien-1-yn-1-yl)phosphonate (3u): 0.3 mmol scale. Yield: 69.7 mg, 80%. Yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.11 (d, J = 8.0 Hz, 1H), 7.04–7.02 (m, 2H), 5.48 (dq, J_{P-H} = J_{H-H} = 3.2 Hz, 1H), 3.80 (d, J = 3.0 Hz, 6H), 2.33 (s, 3H), 2.31 (s, 3H), 2.10 (d, J = 2.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 214.5 (d, J_{C-P} = 3.6 Hz), 137.7, 135.7, 131.7, 131.5, 127.2, 126.8, 103.7, 94.6 (d, J_{C-P} = 53.0 Hz), 77.1 (d, J_{C-P} = 302.7 Hz), 72.7 (d, J_{C-P} = 6.6 Hz), 53.3 (d, J_{C-P} = 5.5 Hz), 21.0, 20.5, 19.8. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -2.7. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}O_3P^+$ 291.1145, found 291.1150.



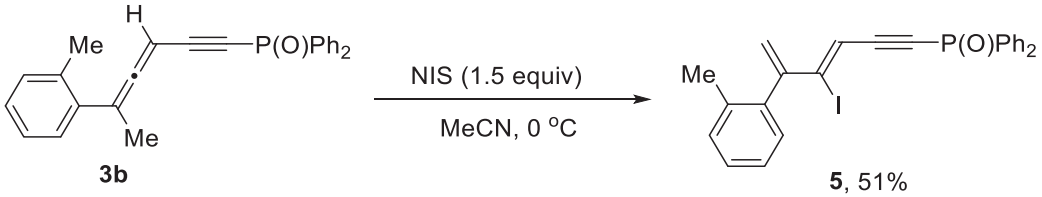
diisopropyl (5-(2,4-dimethylphenyl)hexa-3,4-dien-1-yn-1-yl)phosphonate (3v): 0.3 mmol scale. Yield: 49.8 mg, 48%. Yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.11–7.09 (m, 1H), 7.03–7.01 (m, 2H), 5.45 (t, J = 3.2 Hz, 1H), 4.80–4.68 (m, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 2.09 (d, J = 3.2 Hz, 3H), 1.36 (d, J = 6.4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 214.2 (d, J_{C-P} = 3.5 Hz), 137.7, 135.8, 132.0, 131.6, 127.3, 126.8, 103.4, 92.7 (d, J_{C-P} = 52.5 Hz), 80.2 (d, J_{C-P} = 298.6 Hz), 73.1 (d, J_{C-P} = 6.6 Hz), 72.2 (d, J_{C-P} = 5.4 Hz), 23.9 (d, J_{C-P} = 4.6 Hz), 23.6 (d, J_{C-P} = 4.8 Hz), 21.0, 20.6, 19.9. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -8.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{28}O_3P^+$ 347.1771, found 347.1778.



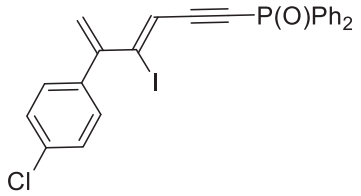
dimethyl (5-phenylocta-3,4-dien-1-yn-1-yl)phosphonate (3w): Yield: 43.0 mg, 70%. Yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36–7.35 (m, 4H), 7.30–7.28 (m, 1H), 5.80 (dt, J_{P-H} = J_{H-H} = 3.2 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.52–2.46 (m, 2H), 1.61–1.55 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 216.3 (d, J_{C-P} = 3.6 Hz), 133.7, 128.6, 128.0, 126.5, 110.0, 94.0 (d, J_{C-P} = 52.9 Hz), 76.9 (d, J_{C-P} = 302.2 Hz), 76.4 (d, J_{C-P} = 6.5 Hz), 53.3 (d, J_{C-P} = 5.5 Hz), 31.8, 20.3, 13.7. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -2.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}O_3P^+$ 291.1145, found 291.1150.



methyl (6-methyl-5-phenylhepta-3,4-dien-1-yn-1-yl)(phenyl)phosphinate (3x): 0.2 mmol scale. Yield: 36.4 mg, 54%. Yellow slurry solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.87 (m, 2H), 7.59–7.56 (m, 1H), 7.52–7.48 (m, 2H), 7.37–7.28 (m, 5H), 5.82 (t, *J* = 2.8 Hz, 1H), 3.85 (d, *J* = 12.4 Hz, 3H), 2.93–2.85 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.13 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 215.0 (d, J_{C-P} = 3.0 Hz), 133.8, 132.7 (d, J_{C-P} = 3.0 Hz), 131.0 (d, J_{C-P} = 11.2 Hz), 130.5 (d, J_{C-P} = 164.4 Hz), 128.6, 128.5 (d, J_{C-P} = 14.9 Hz), 127.8, 127.0, 117.1, 96.2 (d, J_{C-P} = 39.4 Hz), 80.9 (d, J_{C-P} = 217.5 Hz), 77.4 (d, J_{C-P} = 5.3 Hz), 52.2 (d, J_{C-P} = 6.5 Hz), 28.91, 28.89, 21.8, 21.7. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 11.82, 11.80. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}O_2P^+$ 337.1352, found 337.1360.

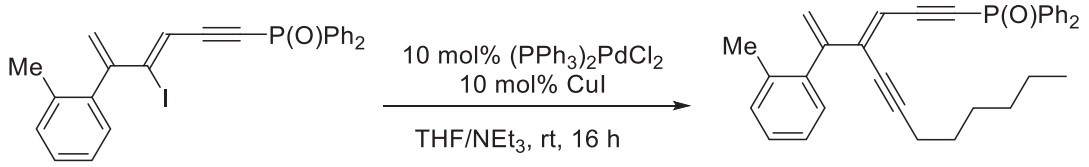


(Z)-(4-iodo-5-(o-tolyl)hexa-3,5-dien-1-yn-1-yl)diphenylphosphine oxide (5): An oven-dried flask was charged with **3b** (88.2 mg, 0.24 mmol) and MeCN (2 mL). The solution was cooled with an ice bath. N-iodosuccinimide (0.36 mmol, 82.1 mg) was added slowly. The reaction mixture was stirred for 1 hour. After removing the solvent in vacuo, the residues were purified with flash chromatography on silica (petroleum ether/ethyl acetate: 5/1-3:1 v/v) to afford **5** as a yellow slurry solid. Yield: 63.6 mg, 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.86 (m, 4H), 7.56–7.54 (m, 2H), 7.49–7.46 (m, 4H), 7.27–7.16 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.06 (d, *J* = 2.8 Hz, 1H), 5.99 (s, 1H), 5.52 (s, 1H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148. 8, 137.2, 136.0, 132.5 (d, J_{C-P} = 2.9 Hz), 131.9 (d, J_{C-P} = 131.1 Hz), 131.2 (d, J_{C-P} = 11.6 Hz), 130.4, 129.6, 129.3, 128.7 (d, J_{C-P} = 13.7 Hz), 128.5, 126.0, 123.2 (d, J_{C-P} = 3.6 Hz), 119.1 (d, J_{C-P} = 4.6 Hz), 106.5 (d, J_{C-P} = 30.5 Hz), 90.7 (d, J_{C-P} = 168.5 Hz), 19. 6. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 8.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}OPI^+$ 495.0369, found 495.0375.



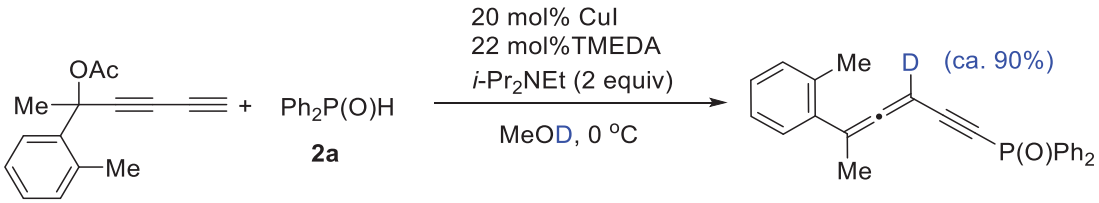
(Z)-(5-(4-chlorophenyl)-4-iodohexa-3,5-dien-1-yn-1-yl)diphenylphosphine oxide (4): this compound was obtained following a similar procedure. 33.1 mg, ca. 25%. Yellow slurry gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.88 (m, 4H), 7.56–7.54 (m, 2H), 7.51–7.48 (m, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 2.8 Hz, 1H), 5.75 (s, 1H), 5.53 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.2,

136.0, 134.6, 132.6 (d, $J_{C\text{-}P}$ = 121.7 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 11.3 Hz), 129.7, 128.8, 128.7 (d, $J_{C\text{-}P}$ = 13.5 Hz), 124.3, 121.4 (d, $J_{C\text{-}P}$ = 3.6 Hz), 120.0 (d, $J_{C\text{-}P}$ = 4.8 Hz), 105.0 (d, $J_{C\text{-}P}$ = 29.1 Hz), 91.4 (d, $J_{C\text{-}P}$ = 164.2 Hz). ^{31}P NMR (160 MHz, $CDCl_3$): δ = 8.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{18}OPClI^+$ 514.9823, found 514.9834.



5 **6**, 54%

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with $PdCl_2(Ph_3P)_2$ (8.5 mg, 10 mol %) and CuI (2.3 mg, 10 mol %). The Schlenk tube was sealed and then evacuated and backfilled with N2 (3 cycles). A solution of **5** (62.5 mg, 0.12 mmol) in 2 mL of THF, 1-octyne (27 μL, 0.18 mmol) and 0.5 mL of Et_3N was subsequently injected to the Schlenk tube. The reaction mixture was stirred at room temperature overnight. After removing the solvent in vacuo, the residues were purified with flash chromatography on silica(petroleum ether/ethyl acetate: 5/1-3:1 v/v) to afford **6** as a yellow slurry solid. Yield: 30.6 mg, 54%. Yellow slurry gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.84 (m, 4H), 7.52–7.50 (m, 2H), 7.47–7.42 (m, 4H), 7.24–7.17 (m, 3H), 7.04 (d, J = 7.6 Hz, 1H), 6.12 (s, 1H), 5.39 (d, J = 3.2 Hz, 1H), 5.32 (s, 1H), 2.38 (d, J = 6.8 Hz, 2H), 2.16 (s, 3H), 1.58–1.50 (m, 2H), 1.42–1.26 (m, 6H), 0.89 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.5, 140.3 (d, $J_{C\text{-}P}$ = 3.1 Hz), 138.1, 136.1, 133.3 (d, $J_{C\text{-}P}$ = 121.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 11.1 Hz), 130.1, 129.7, 128.5 (d, $J_{C\text{-}P}$ = 13.4 Hz), 128.1, 125.8, 122.3, 112.2 (d, $J_{C\text{-}P}$ = 4.9 Hz), 104.4 (d, $J_{C\text{-}P}$ = 30.4 Hz), 102.4, 90.4 (d, $J_{C\text{-}P}$ = 170.6 Hz), 76.4, 31.3, 28.7, 28.5, 22.5, 19.8, 19.5, 14.1. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 7.9. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{33}H_{34}OP^+$ 477.2342, found 477.2351.



1b **3b-D**

To an oven-dried Schlenk tube (10 mL) with Teflon plug valves were added CuI (0.03 mmol, 6.0 mg). The Schlenk tube was then evacuated and back-filled with N_2 (3 cycles). MeOD (0.2 mL) and TMEDA (0.036 mmol, 6 μL) were sequentially injected under N_2 atmosphere at room temperature. The solution was stirred for 15 min and then cooled to 0 °C. *i*-Pr2NEt (0.3 mmol, 60 μL) was added. Diphenylphosphine oxide **2a** (0.15 mmol, 30.5 mg) and diynylic acetate **1b** (0.18 mmol, 40.9 mg) in MeOD (0.4 mL) were then injected under

nitrogen with vigorous stirring. The tube was sealed and the resulting mixture was stirred at 0 °C. After the reaction was complete (ca. 15 min, monitored by TLC), the reaction mixture was concentrated to dryness with silica gel. The powder residue was purified by column chromatography on silica gel (PE/EtOAc 3/1) to afford **3b-D**. 40.2 mg, 72%. Yellow slurry gum. Identity of the product and deuterium content was determined by NMR. For ^{1}H and ^{13}C NMR spectra of **3b-D**, see Figures S1 and S2. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87–7.81 (m, 4H), 7.54–7.45 (m, 6H), 7.22–7.19 (m, 4H), 5.58 (t, J = 3.2 Hz, 0.09H), 2.34 (s, 3H), 2.12 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 214.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 135.9, 135.0, 133.10 (d, $J_{C\text{-}P}$ = 121.4 Hz), 133.08 (d, $J_{C\text{-}P}$ = 121.4 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 11.2 Hz), 130.8, 128.6 (d, $J_{C\text{-}P}$ = 12.6 Hz), 127.9, 127.4, 126.2, 103.7, 99.8 (d, $J_{C\text{-}P}$ = 29.9 Hz), 83.5 (d, $J_{C\text{-}P}$ = 170.6 Hz), 19.6, 18.9. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 8.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}DOP^+$ 370.1466, found 370.1471.

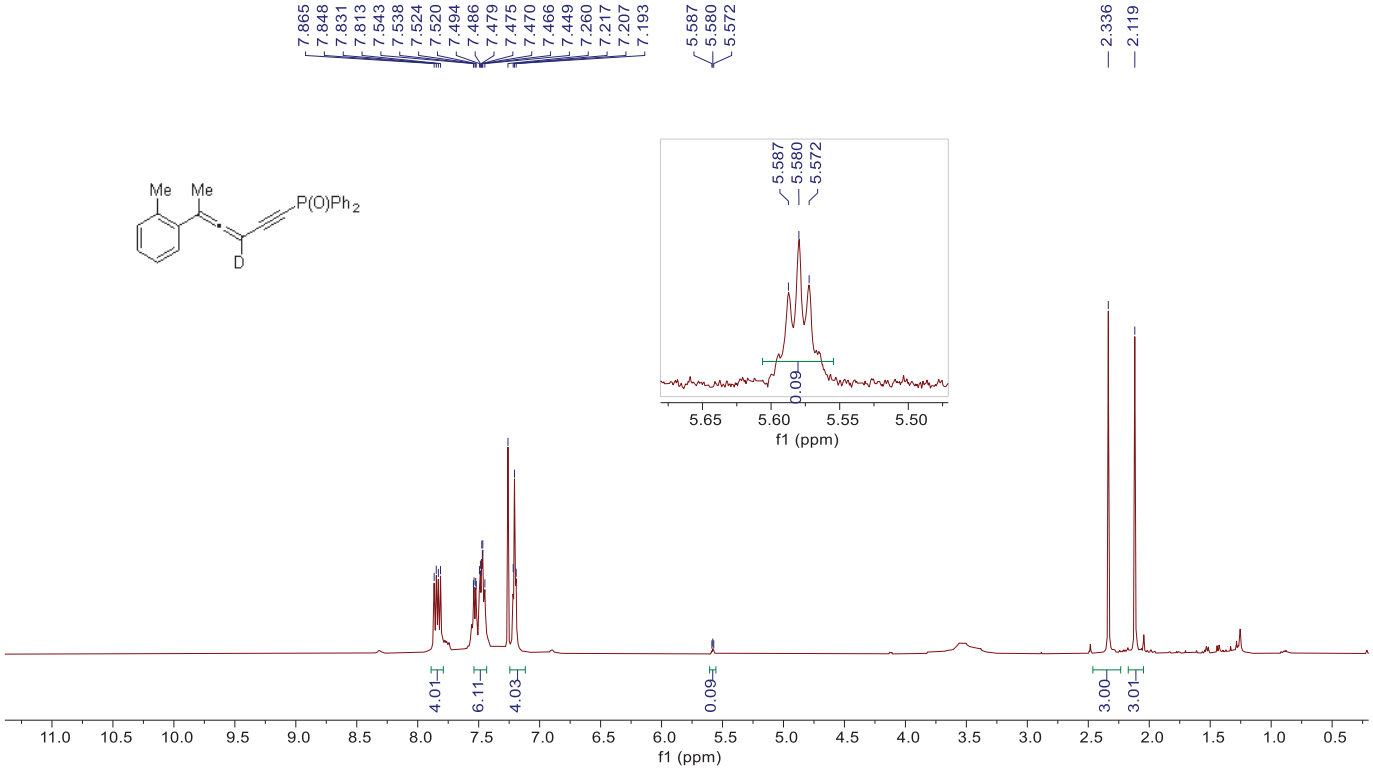


Figure S1. ^{1}H NMR of **3b-D**

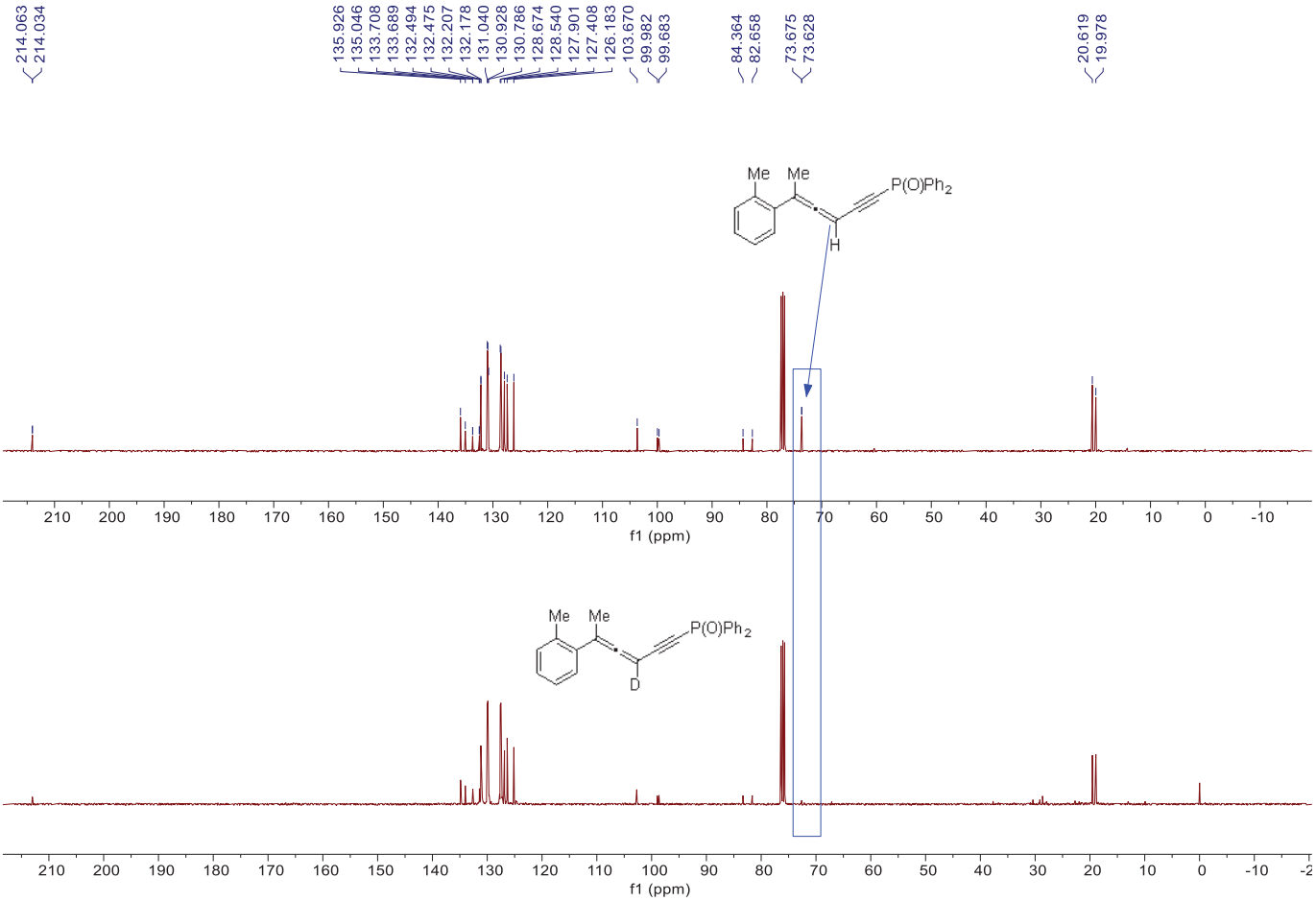
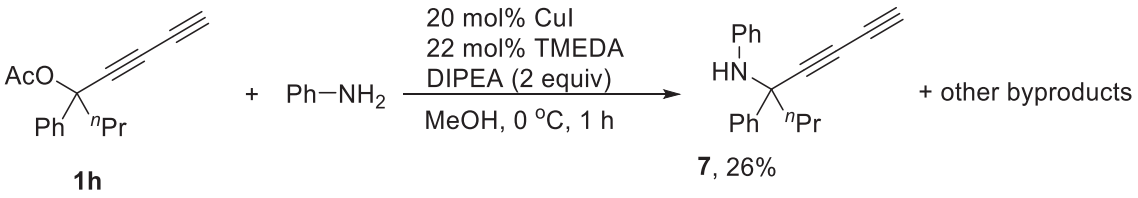


Figure S2. Comparison on ^{13}C NMR spectra between **3b** and **3b-D**



To an oven-dried Schlenk tube (10 mL) with Teflon plug valves were added CuI (0.04 mmol, 7.6 mg). The Schlenk tube was then evacuated and back-filled with N_2 (3 cycles). MeOH (0.5 mL) and TMEDA (0.044 mmol, 7 μL) were sequentially injected under N_2 atmosphere at room temperature. The solution was stirred for 15 min and then cooled to 0 °C. *i*-Pr$_2$NEt (0.4 mmol, 80 μL) was added. Aniline **2a** (0.3 mmol, 27.9 mg) and diynylic acetate **1h** (0.2 mmol, 48.1 mg) in MeOH (1.5 mL) were then injected under nitrogen with vigorous stirring. The tube was sealed and the resulting mixture was stirred at 0 °C for 1 hour. After the reaction was complete, the reaction mixture was concentrated to dryness. The powder residue was purified by column

chromatography on silica gel (PE with 0.5% Et_3N) to afford pure product **7** (14.3 mg, 26%). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (d, *J* = 7.6 Hz, 2H), 7.35–7.25 (m, 3H), 7.06–7.02 (m, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 2H), 4.28 (s, 1H), 2.12 (s, 3H), 2.02–1.86 (m, 2H), 1.57–1.48 (m, 1H), 137–1.26 (m, 1H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.57, 141.96, 128.58, 128.48, 127.48, 126.02, 118.48, 115.63, 78.38, 69.26, 67.89, 67.45, 59.66, 49.21, 17.72, 13.86. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}N^+$ 274.1590, found 274.1595.

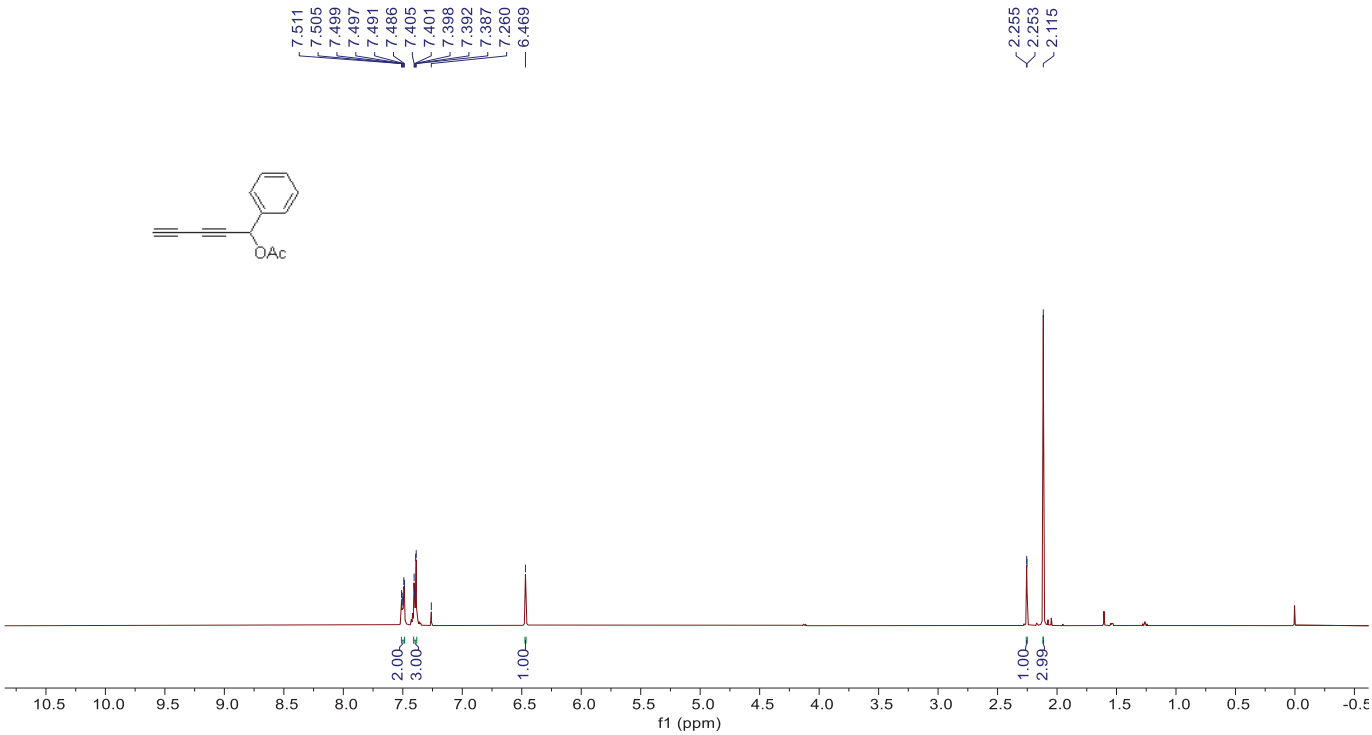
4. References

[1] S. Ghorai, D. Lee, *Org. Lett.* **2021**, *23*, 697–701.

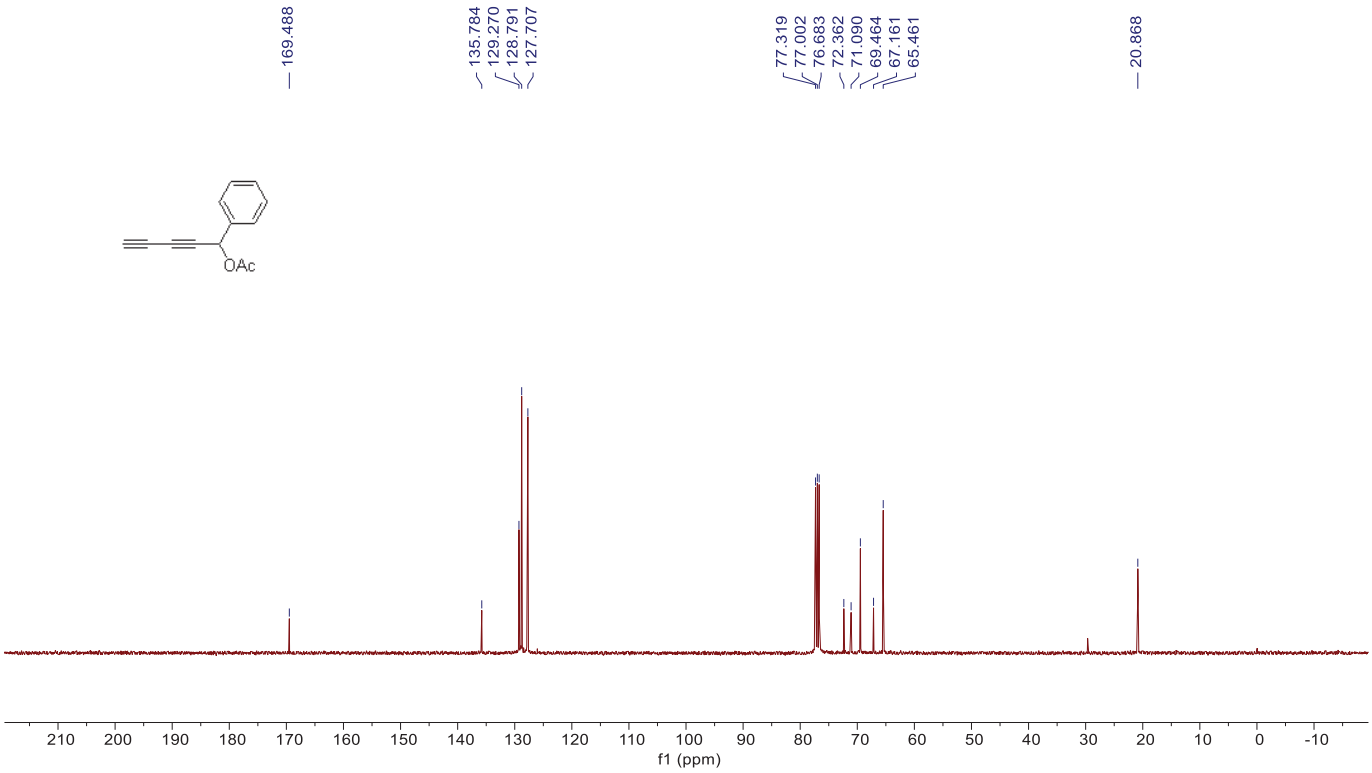
[2] (a) H. R. Hays, *J. Org. Chem.* **1968**, *33*, 3690. (b) C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett*. **2005**, *7*, 4277.

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

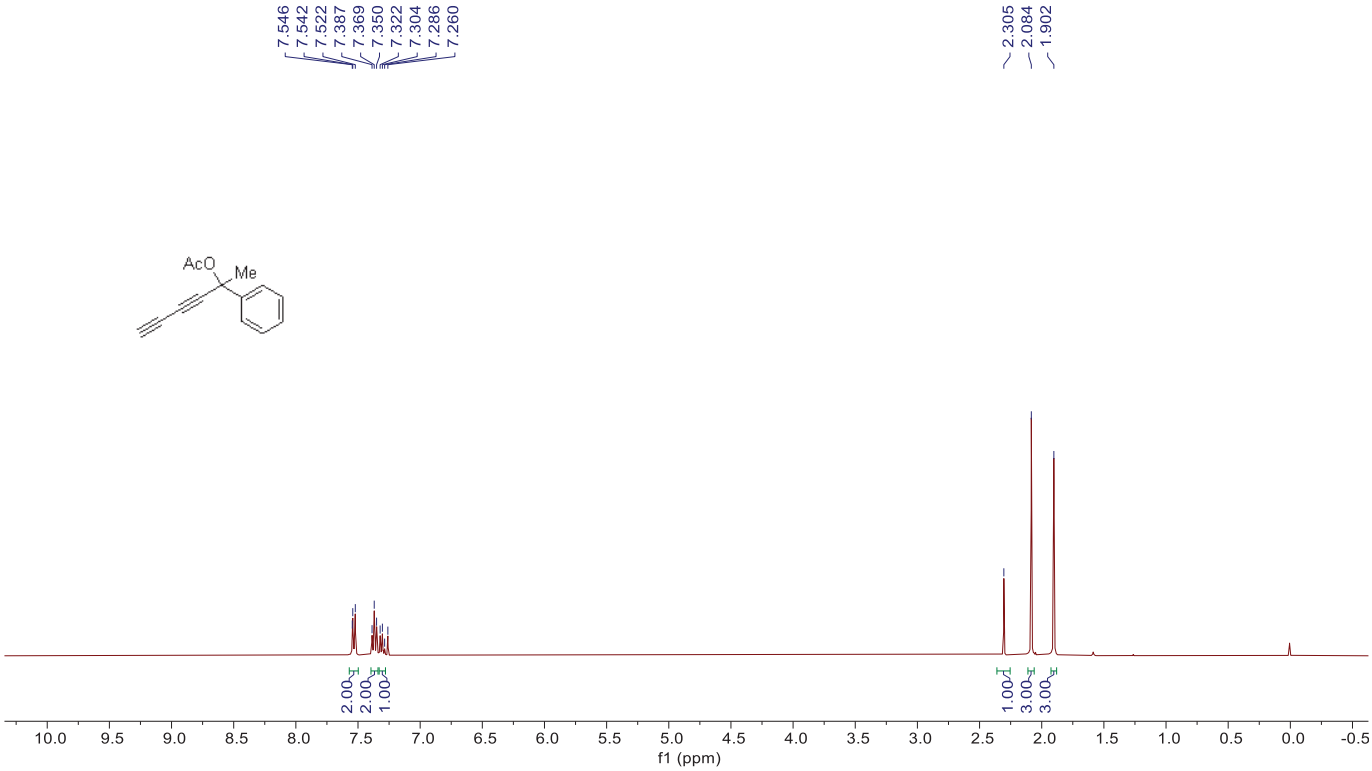
^{1}H NMR of **1a** ($CDCl_3$, 400 MHz)



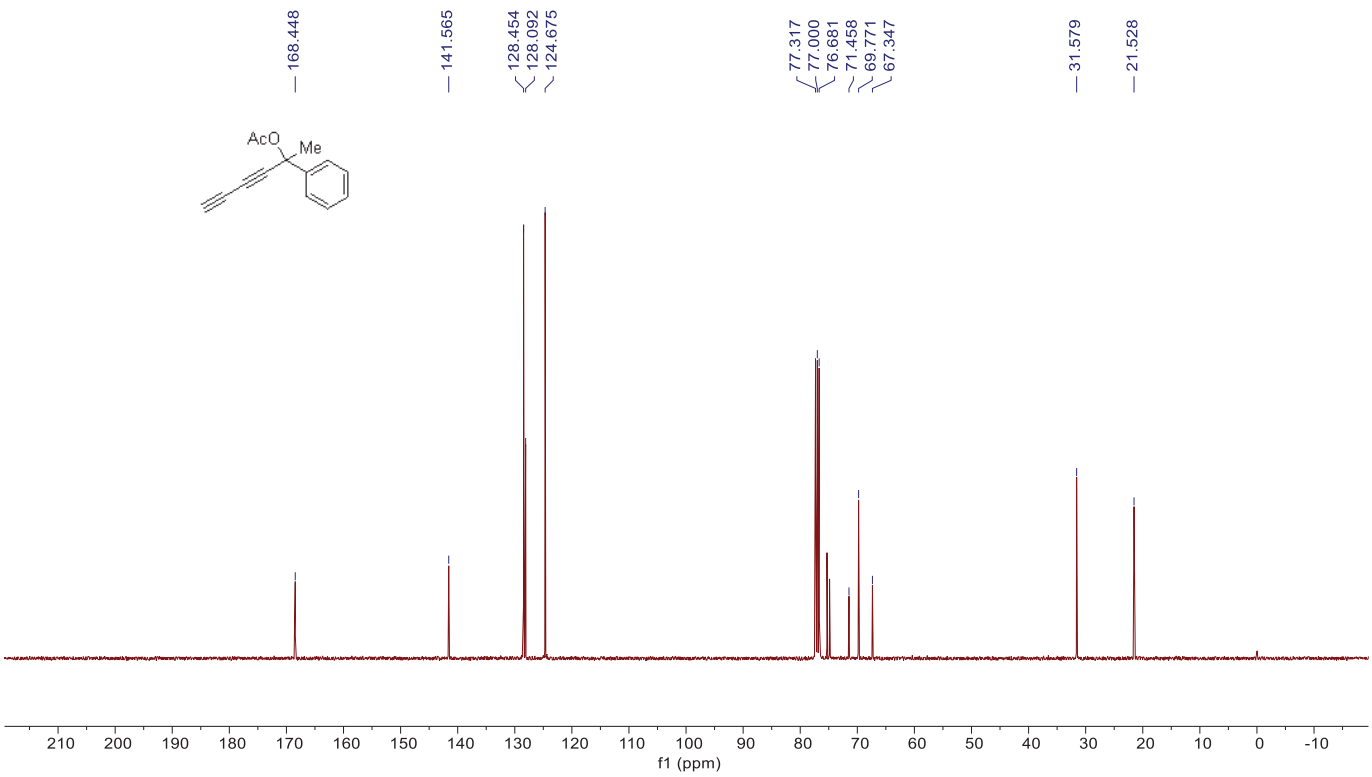
^{13}C NMR of **1a** ($CDCl_3$, 100 MHz)



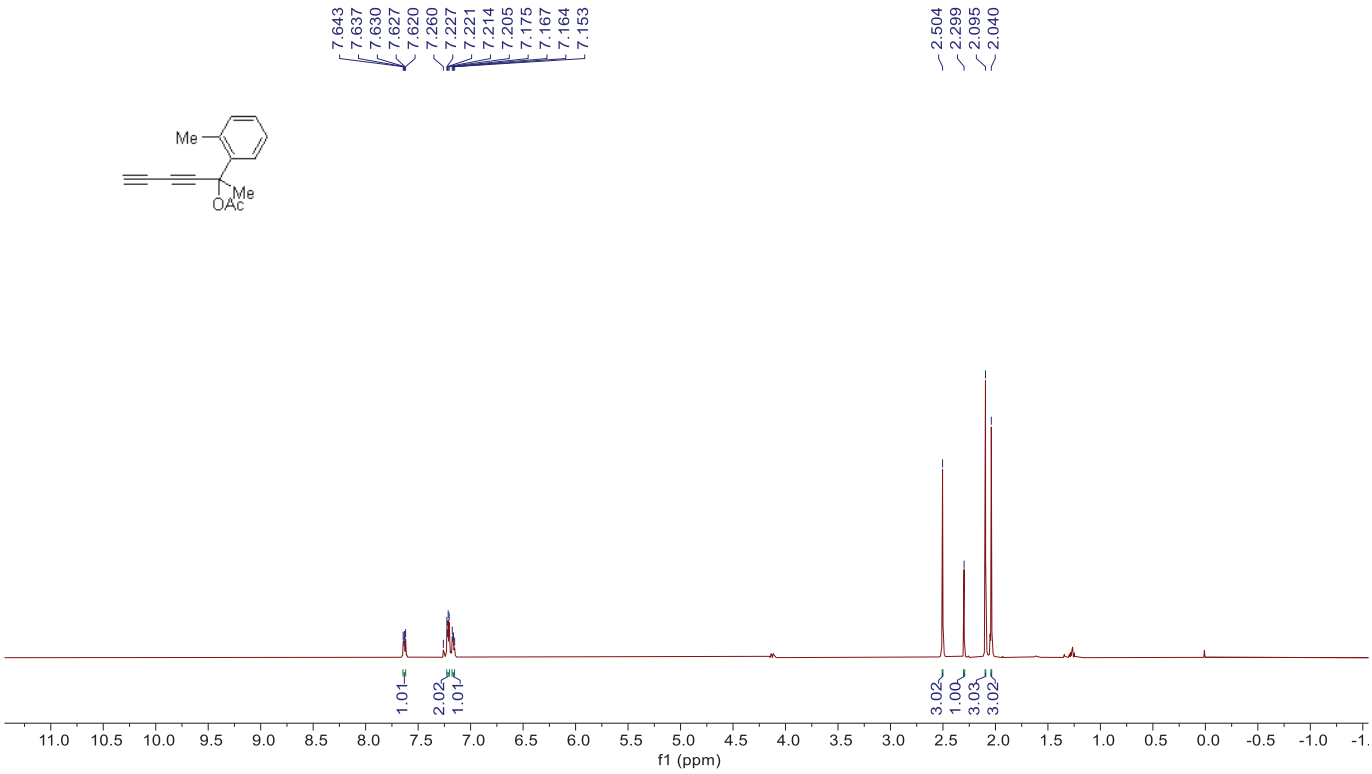
^{1}H NMR of **1a'** ($CDCl_3$, 400 MHz)



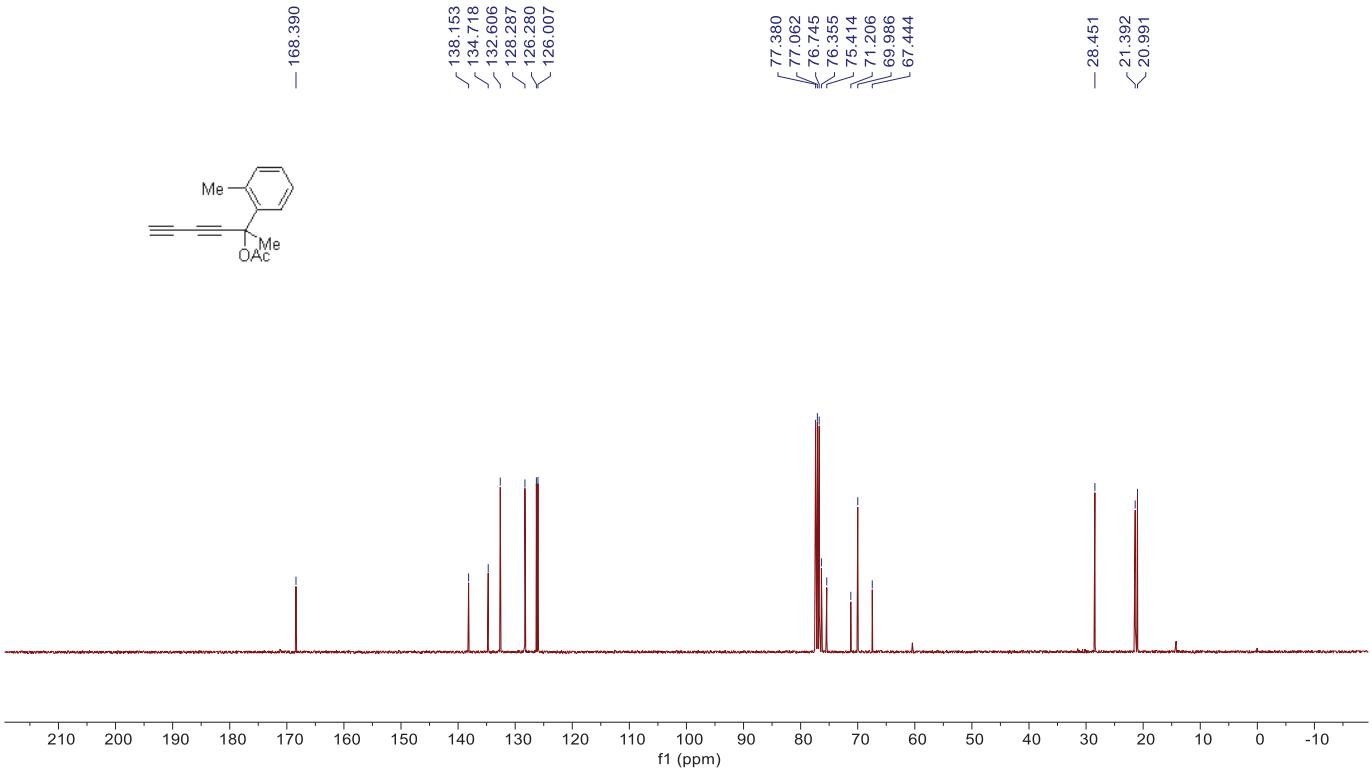
^{13}C NMR of **1a'** ($CDCl_3$, 100 MHz)



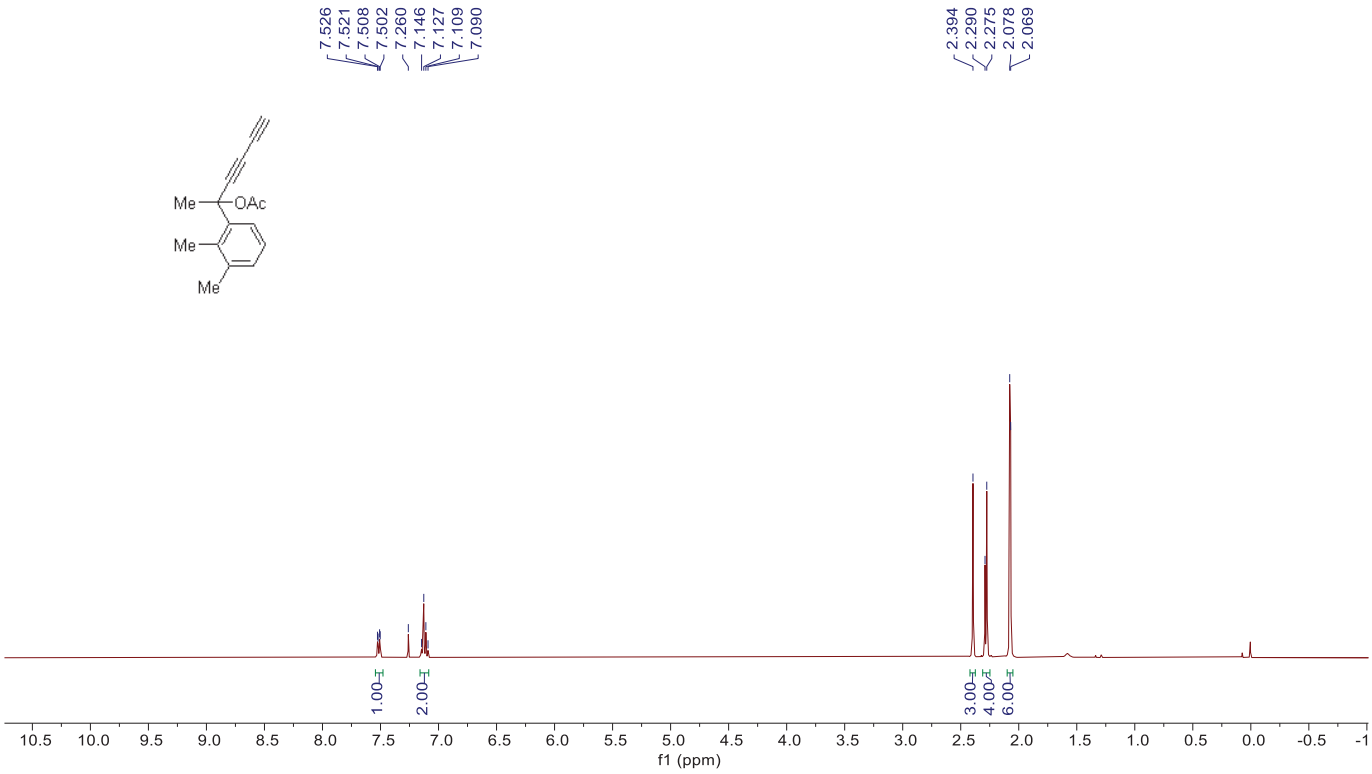
^{1}H NMR of **1b** ($CDCl_3$, 400 MHz)



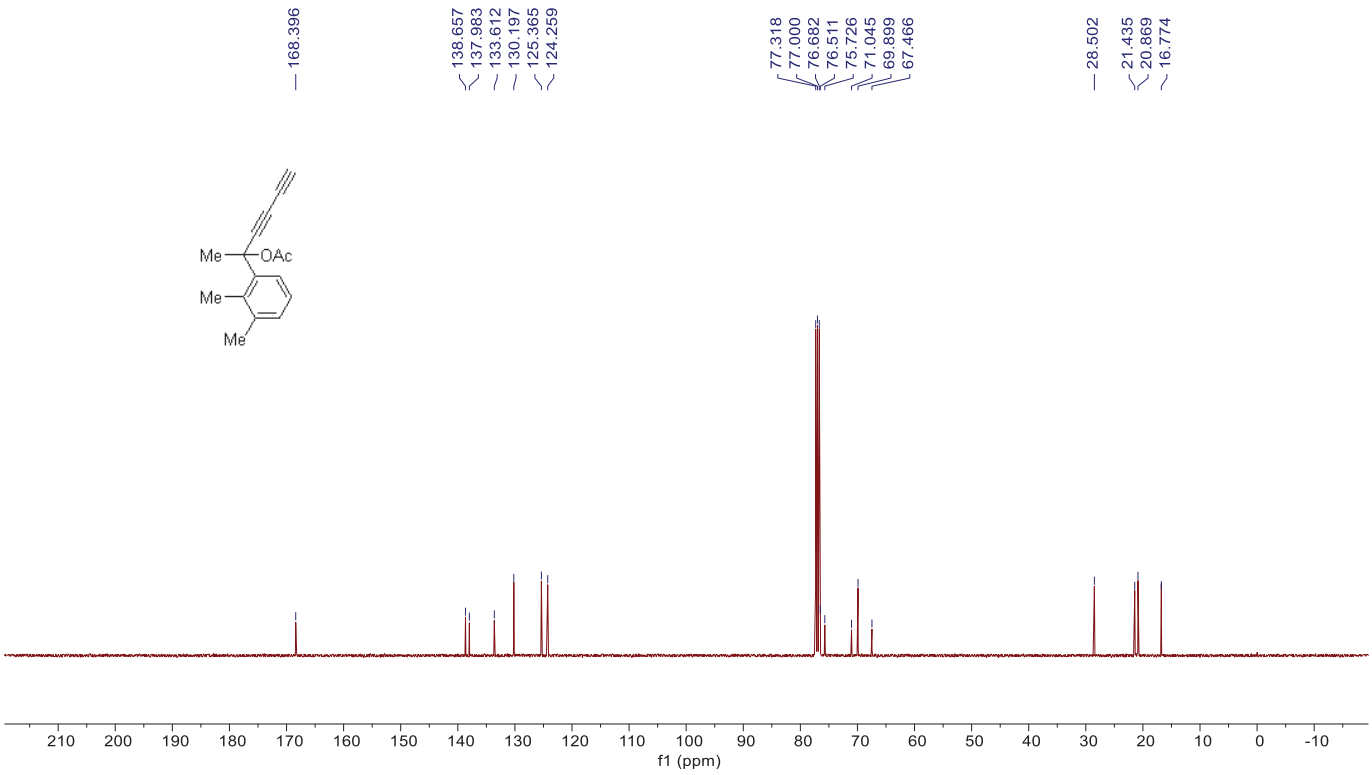
^{13}C NMR of **1b** ($CDCl_3$, 100 MHz)



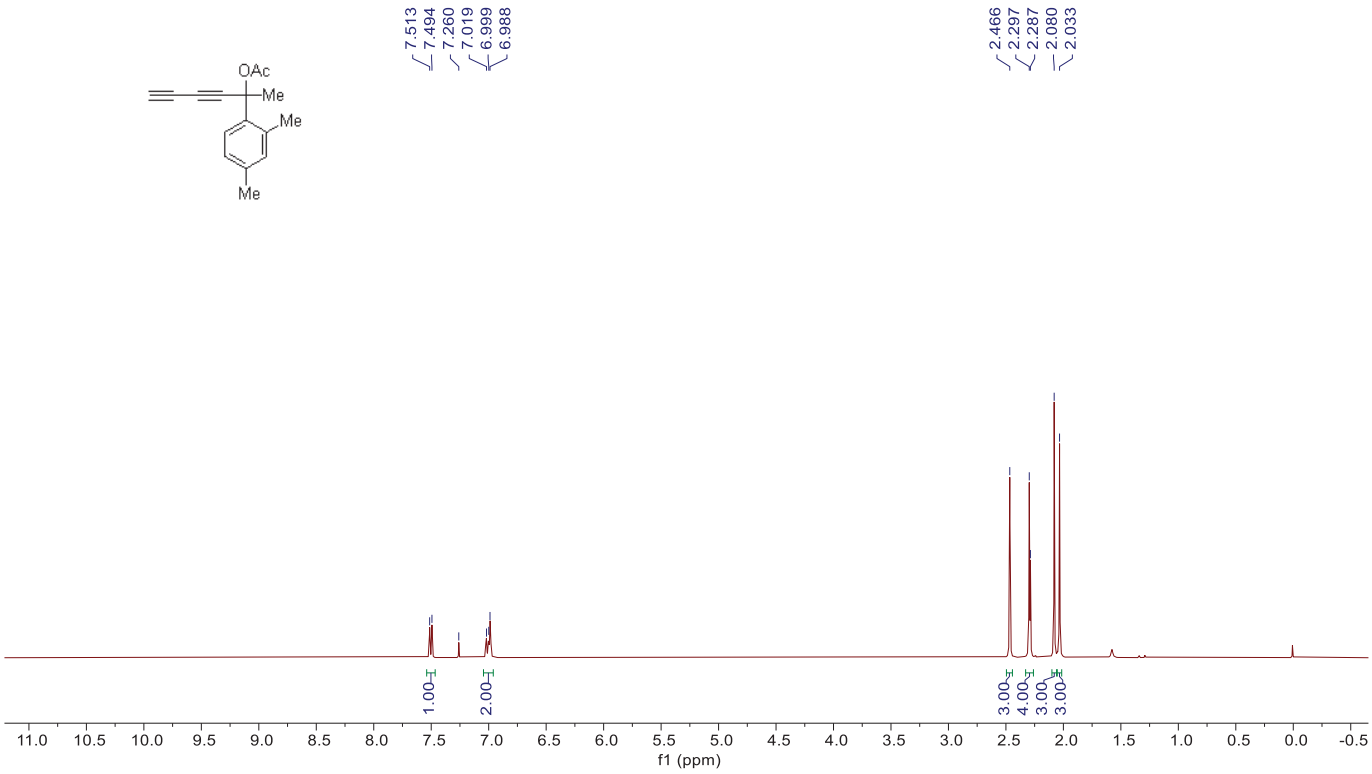
^{1}H NMR of **1c** ($CDCl_3$, 400 MHz)



^{13}C NMR of **1c** ($CDCl_3$, 100 MHz)



^{1}H NMR of **1d** ($CDCl_3$, 400 MHz)



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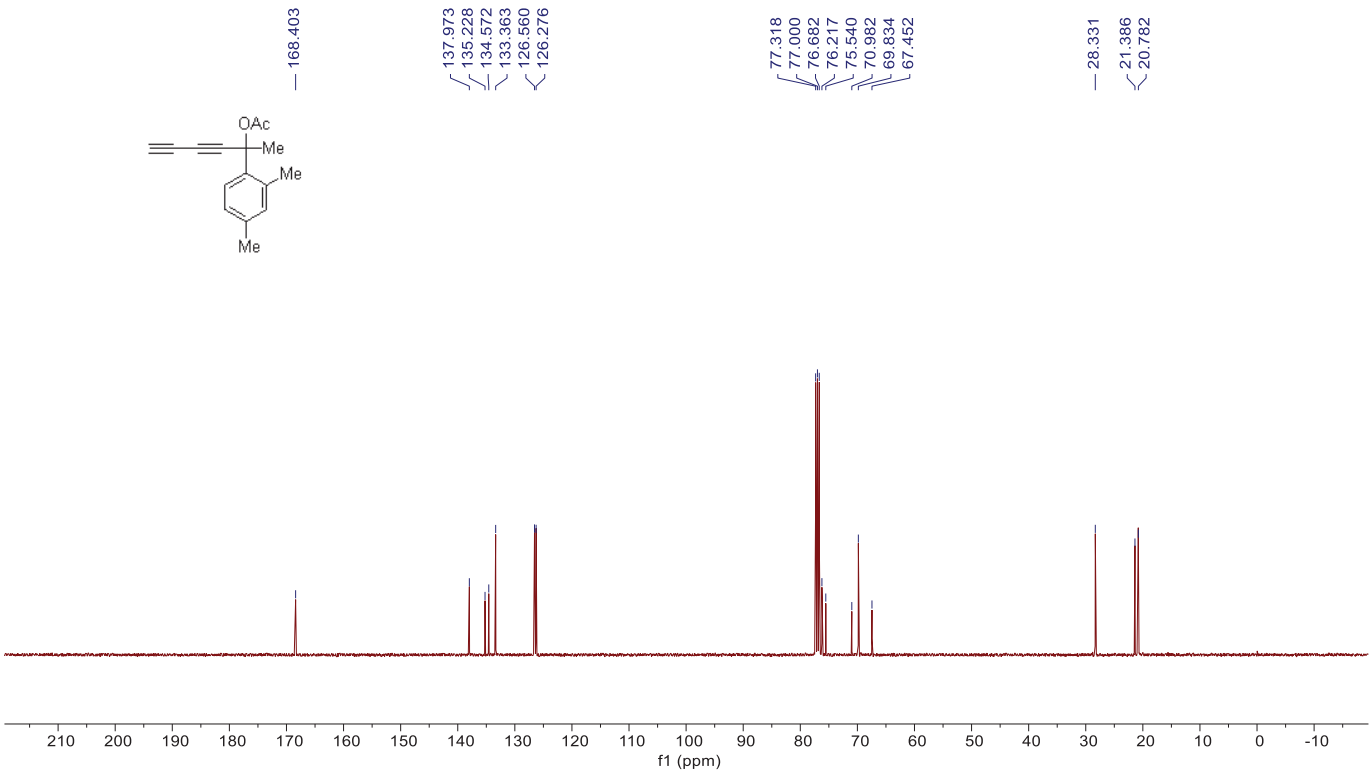
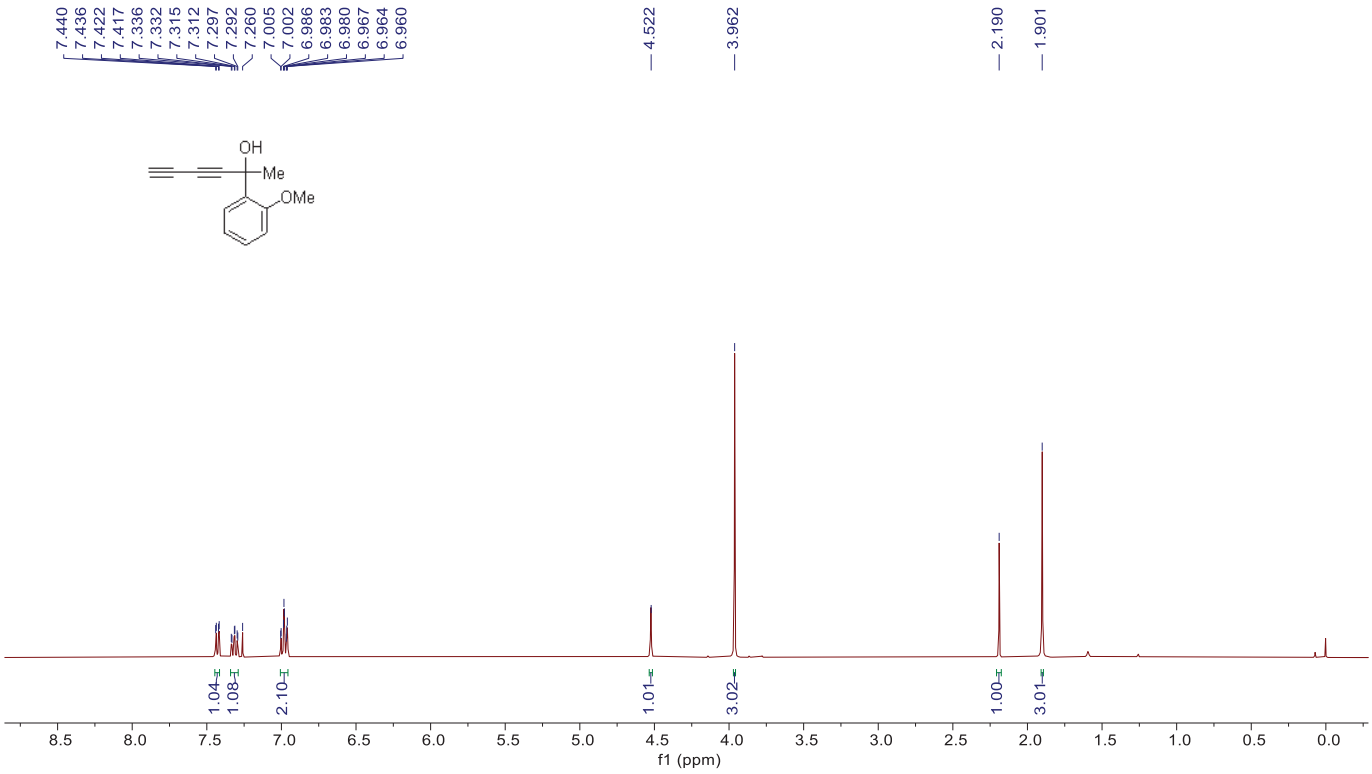
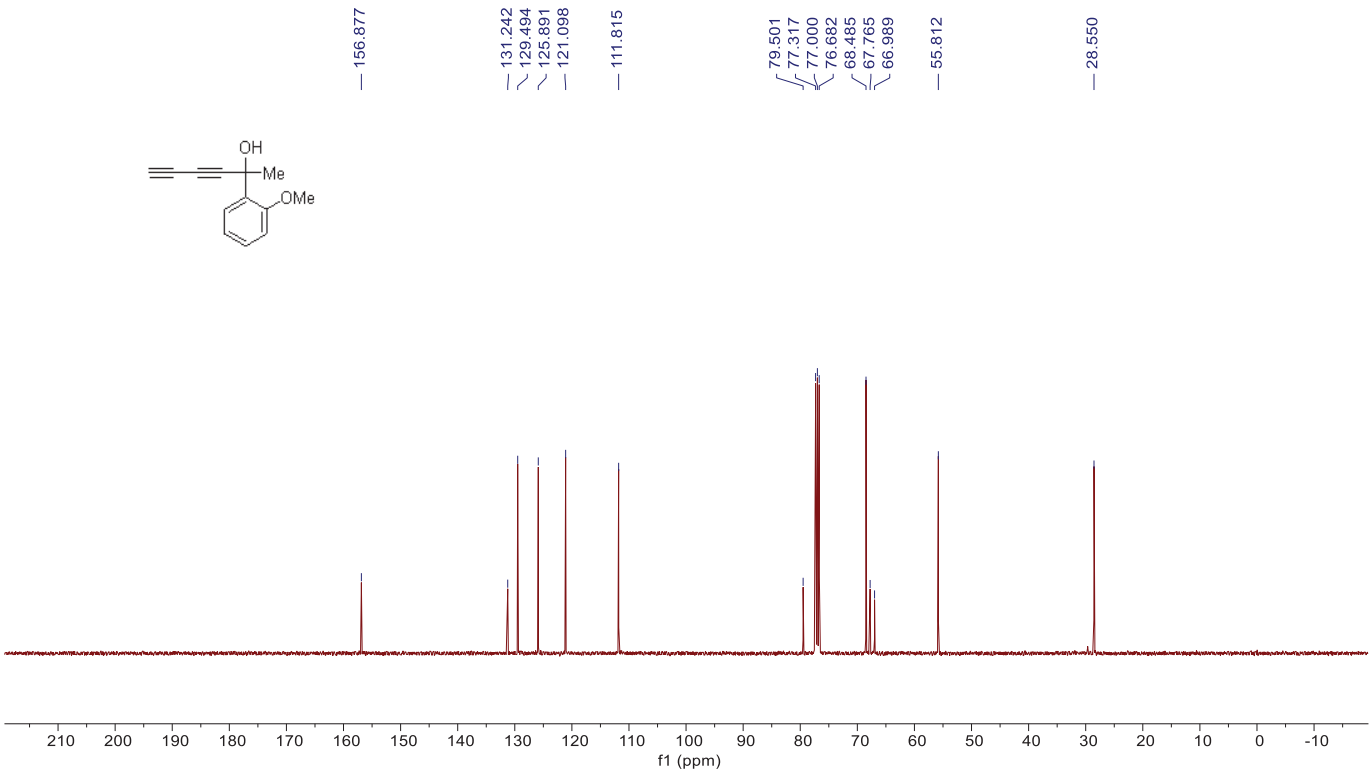


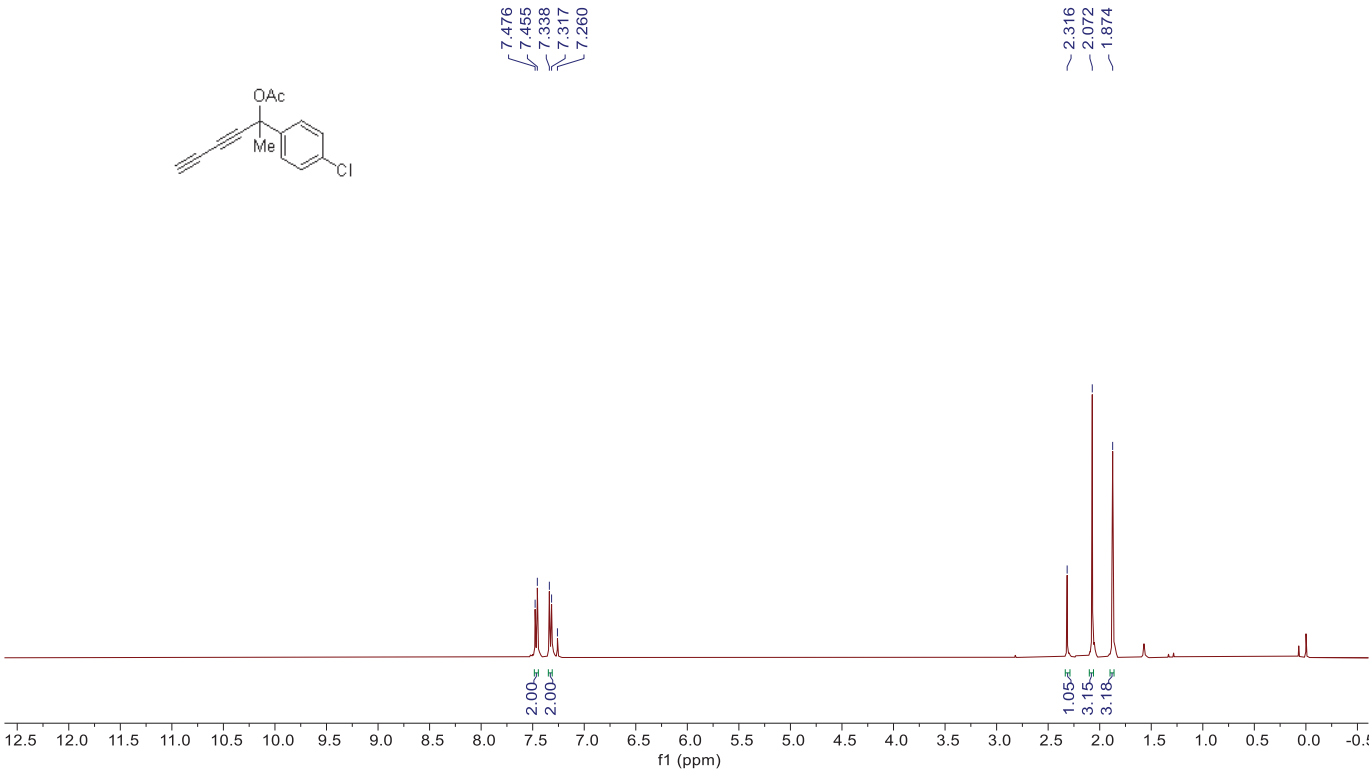
^{1}H NMR of **1e** ($CDCl_3$, 400 MHz)



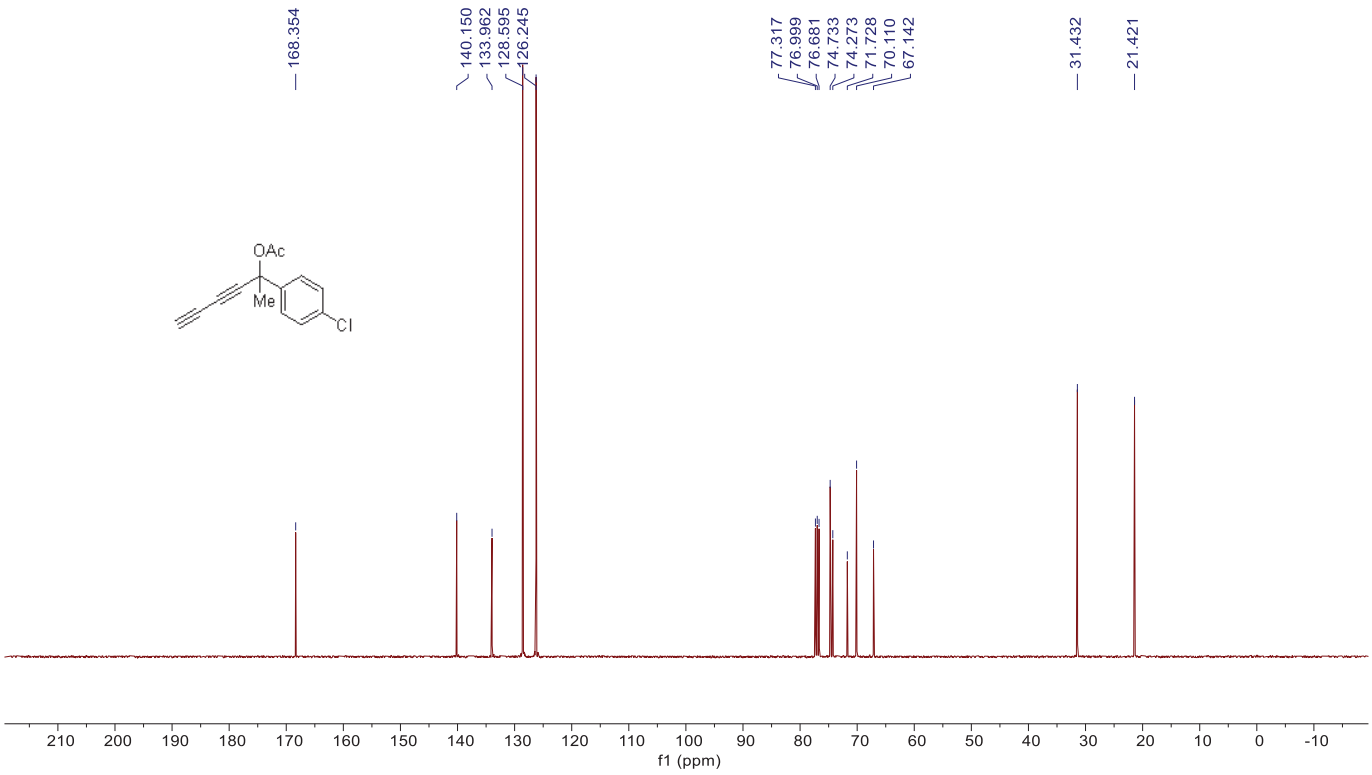
^{13}C NMR of **1e** ($CDCl_3$, 100 MHz)



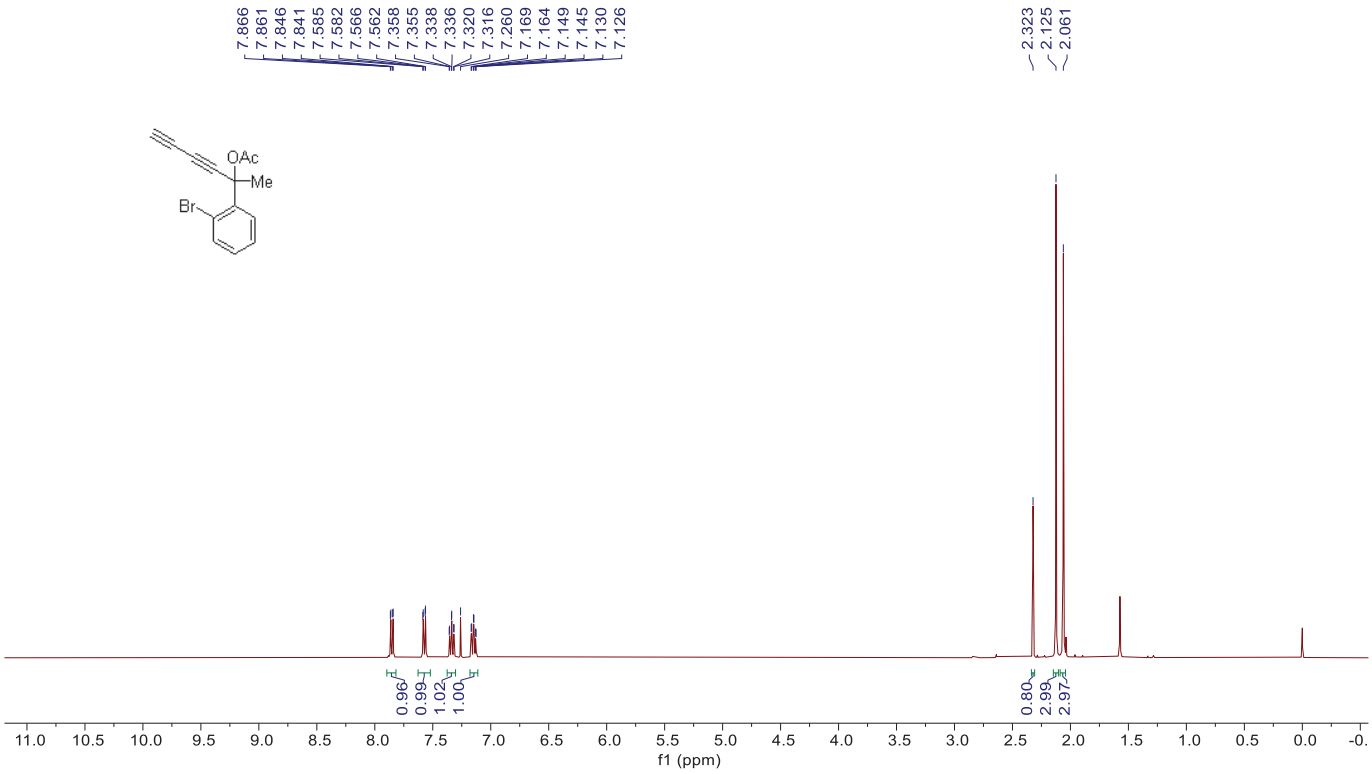
^{1}H NMR of **1f** ($CDCl_3$, 400 MHz)



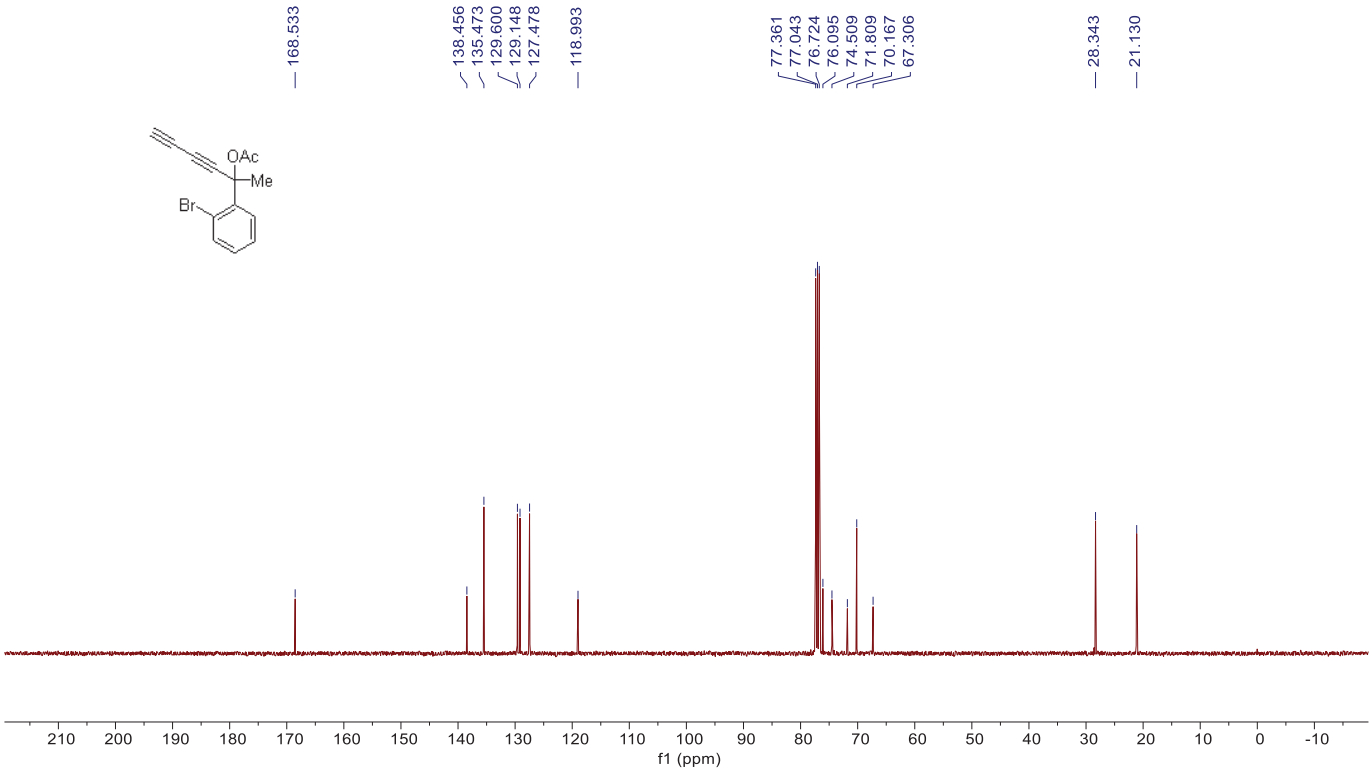
^{13}C NMR of **1f** ($CDCl_3$, 100 MHz)



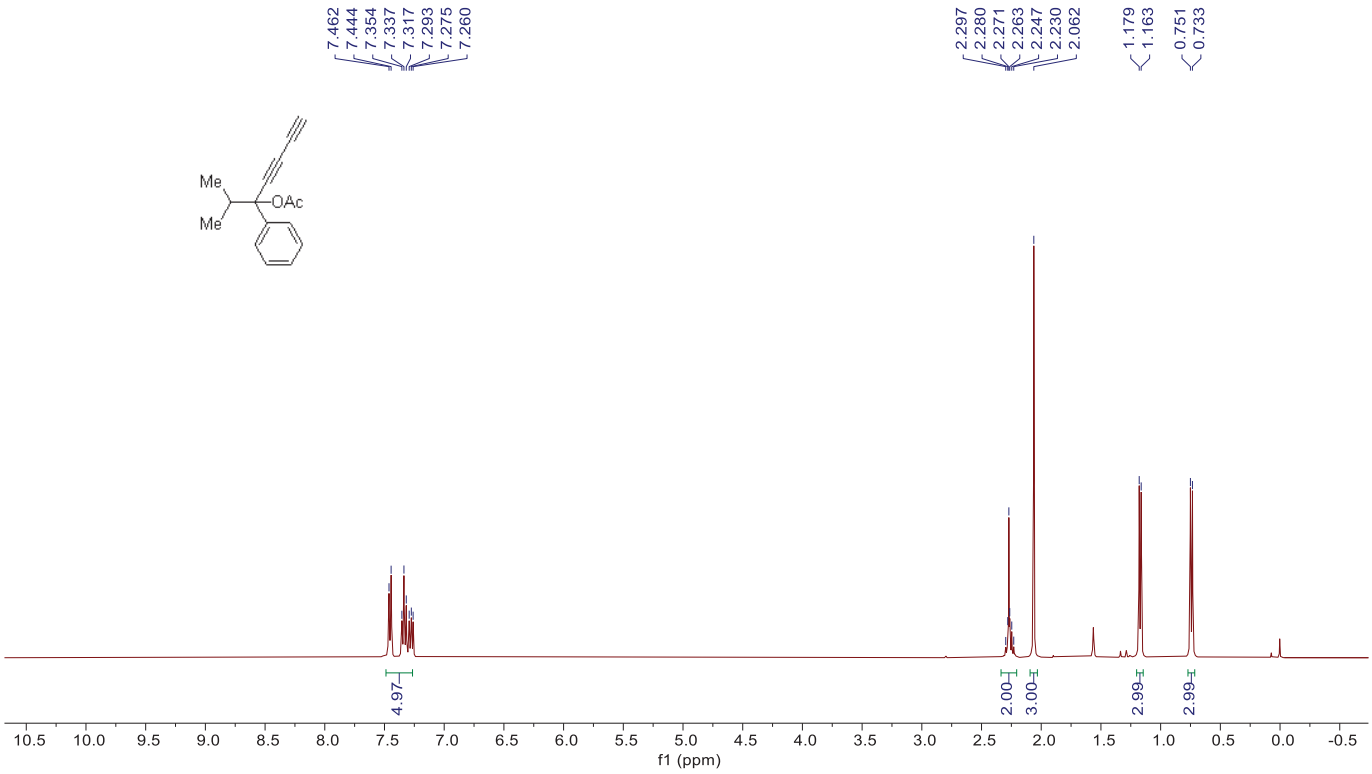
^{1}H NMR of **1g** ($CDCl_3$, 400 MHz)



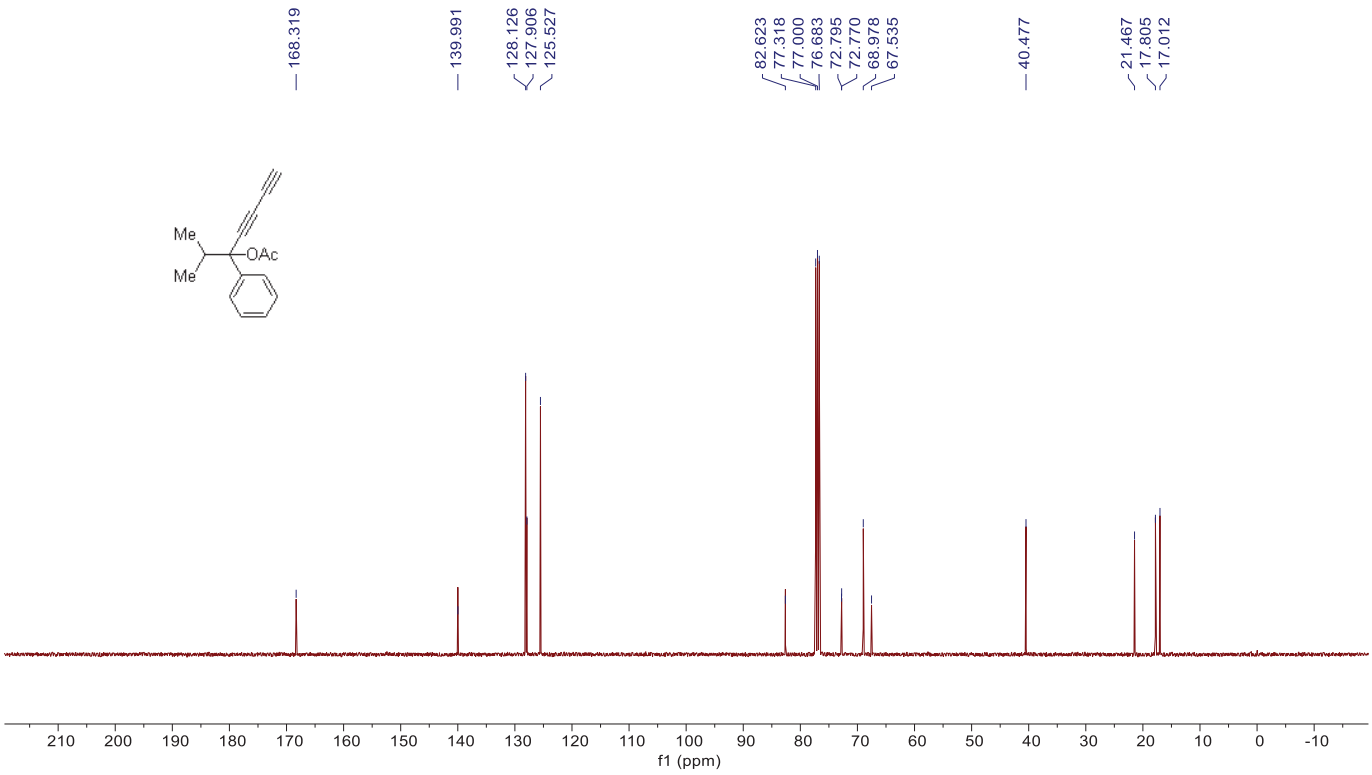
^{13}C NMR of **1g** ($CDCl_3$, 100 MHz)



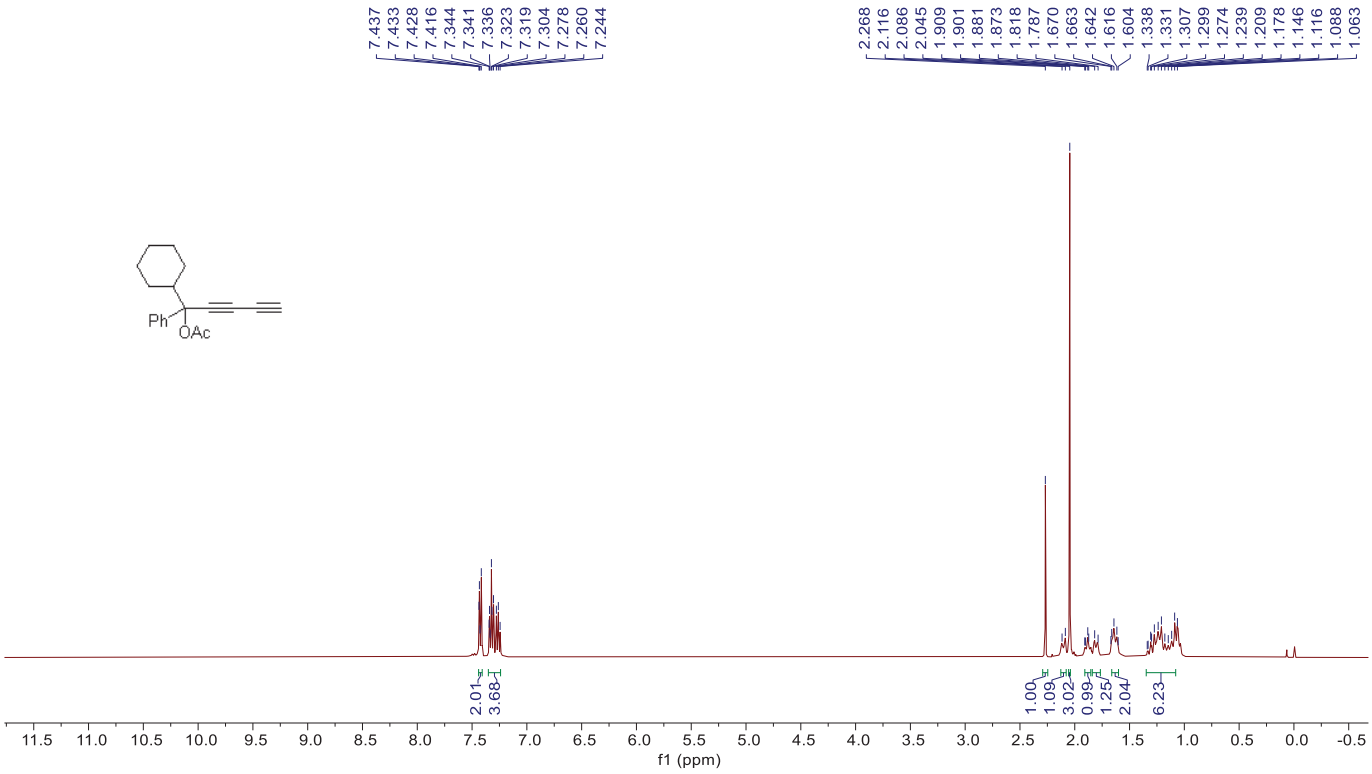
^{1}H NMR of **1h** ($CDCl_3$, 400 MHz)



^{13}C NMR of **1h** ($CDCl_3$, 100 MHz)



^{1}H NMR of **1i** ($CDCl_3$, 400 MHz)



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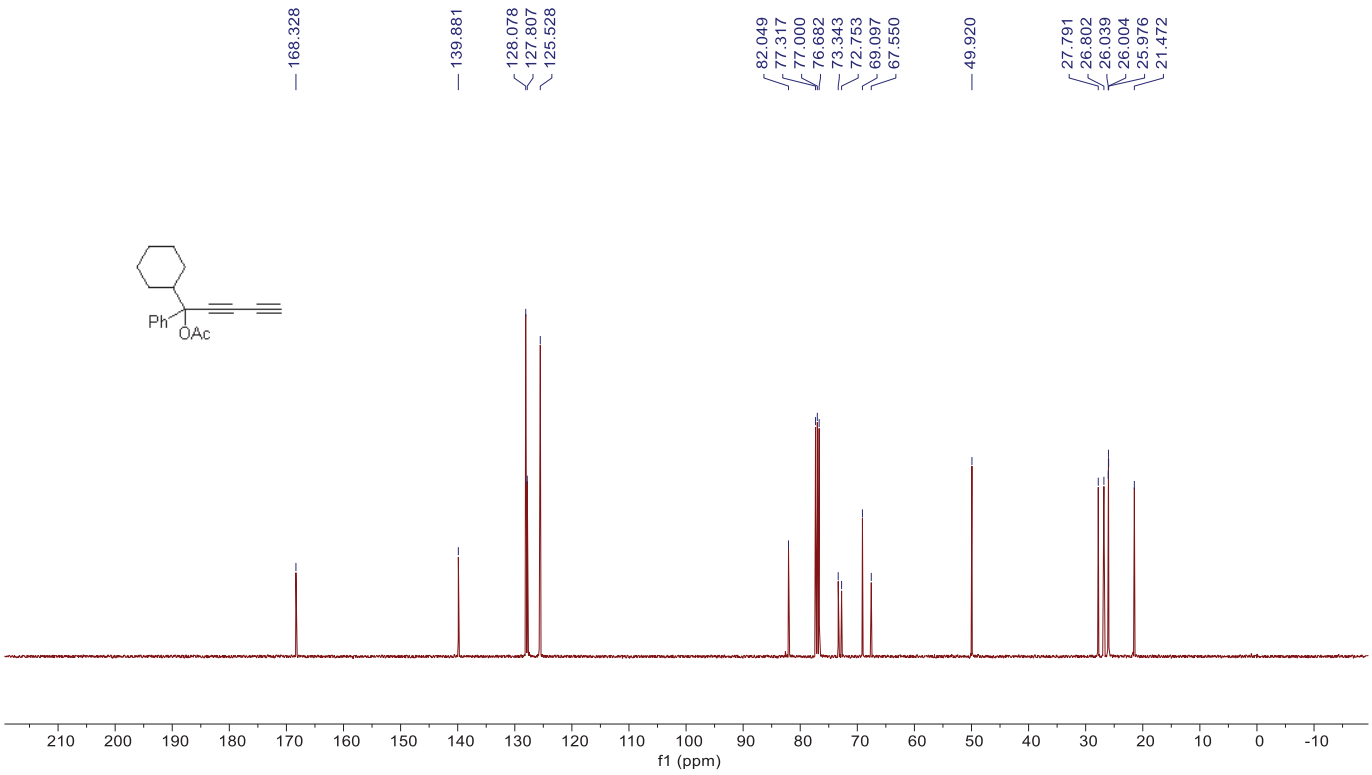
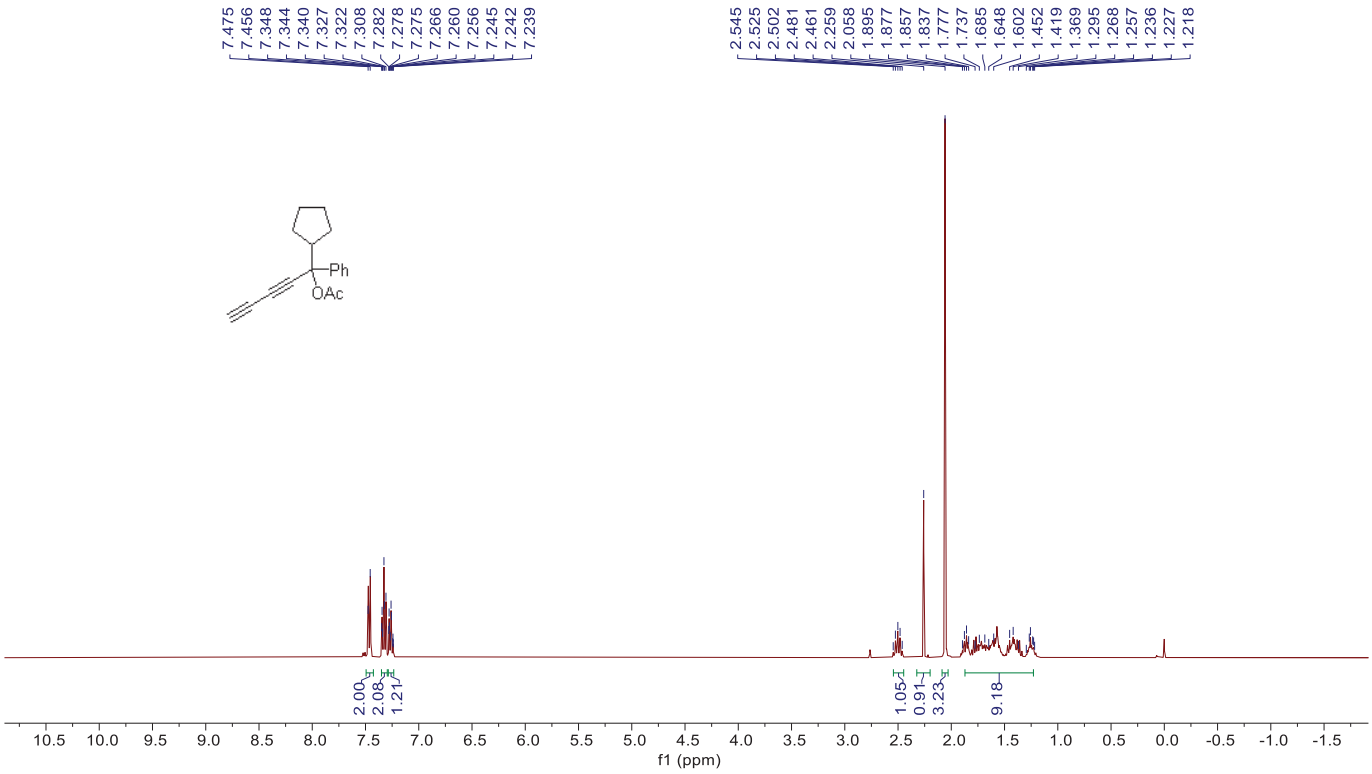


^{1}H NMR of **1j** ($CDCl_3$, 400 MHz)



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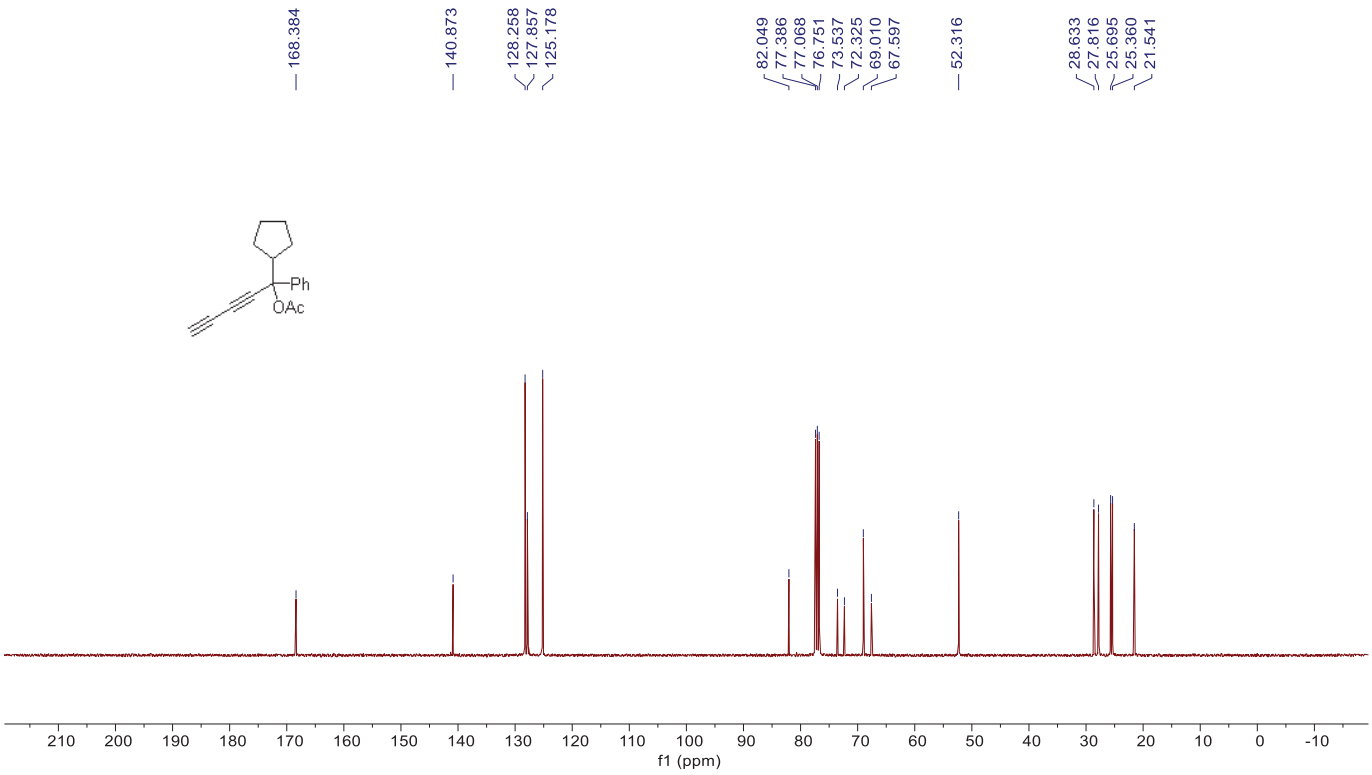

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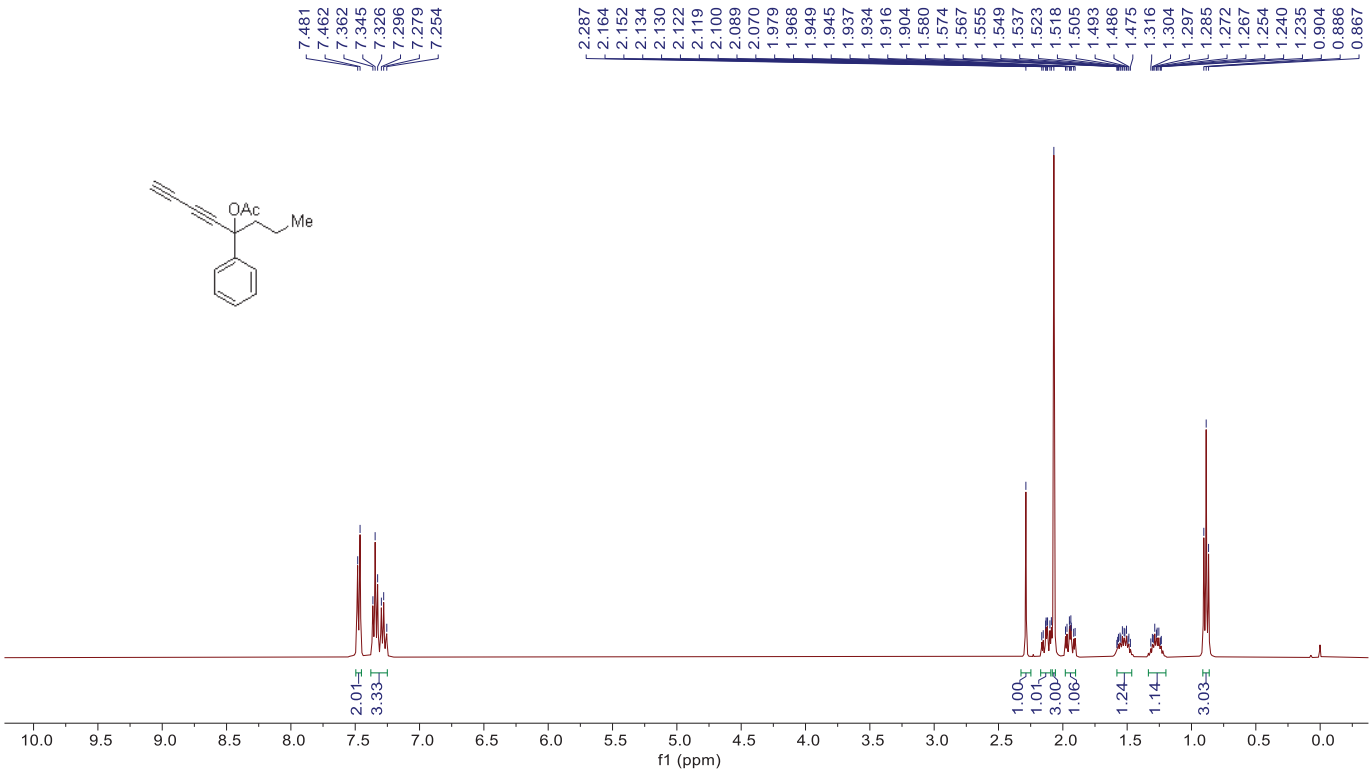

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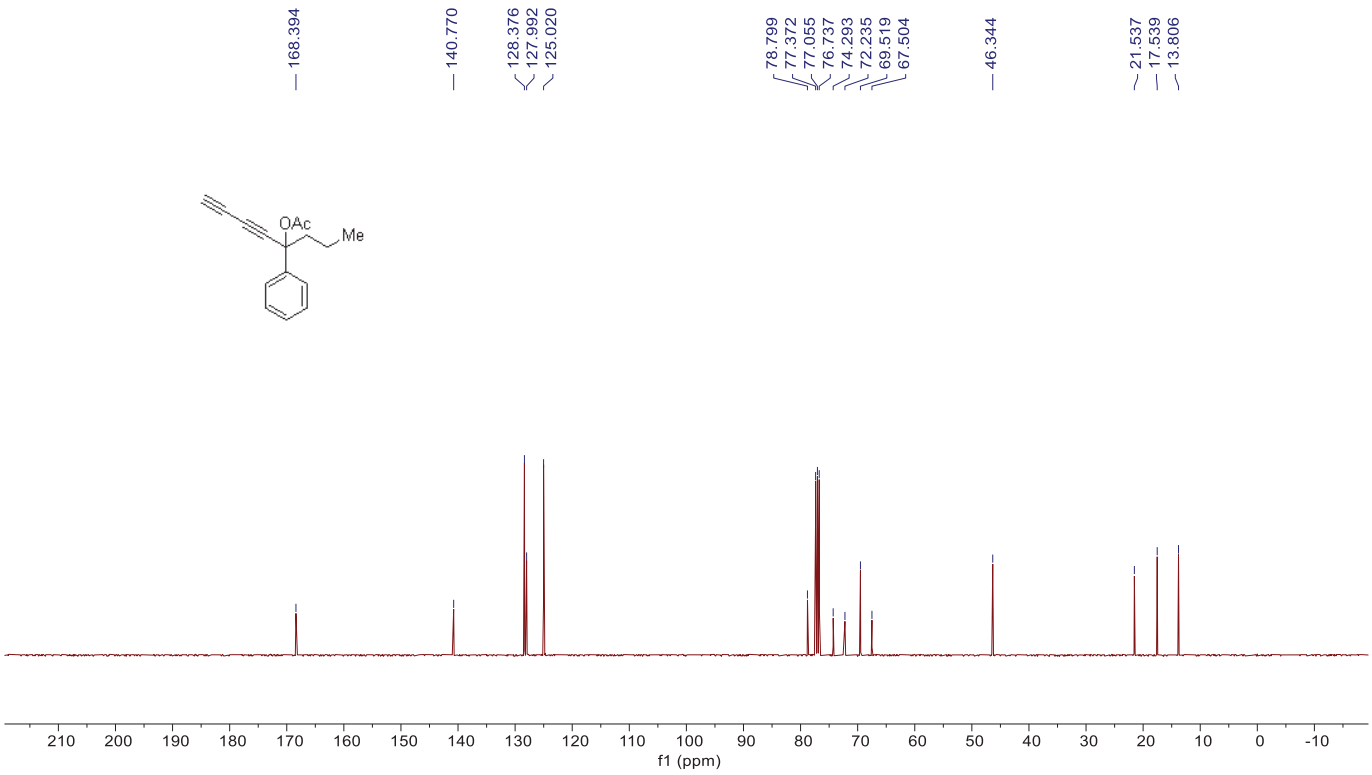

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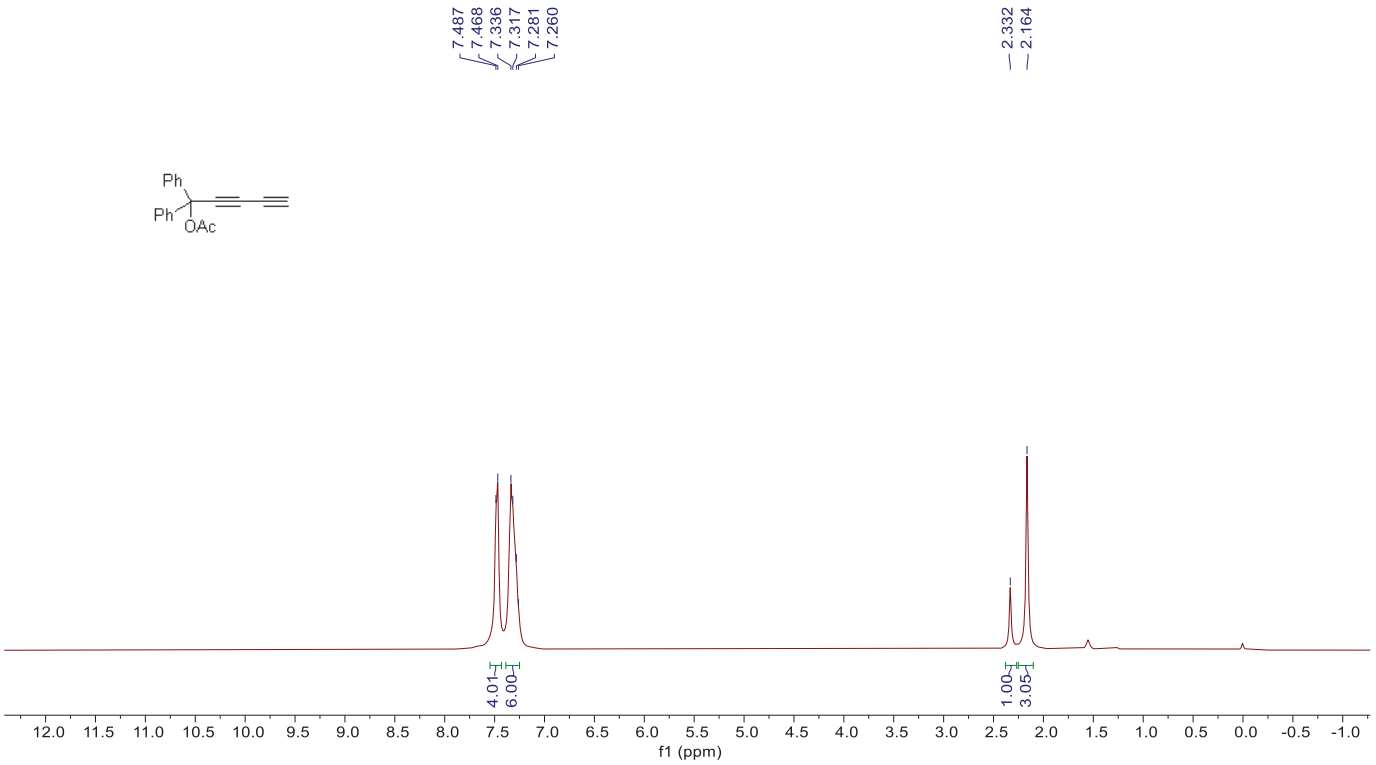

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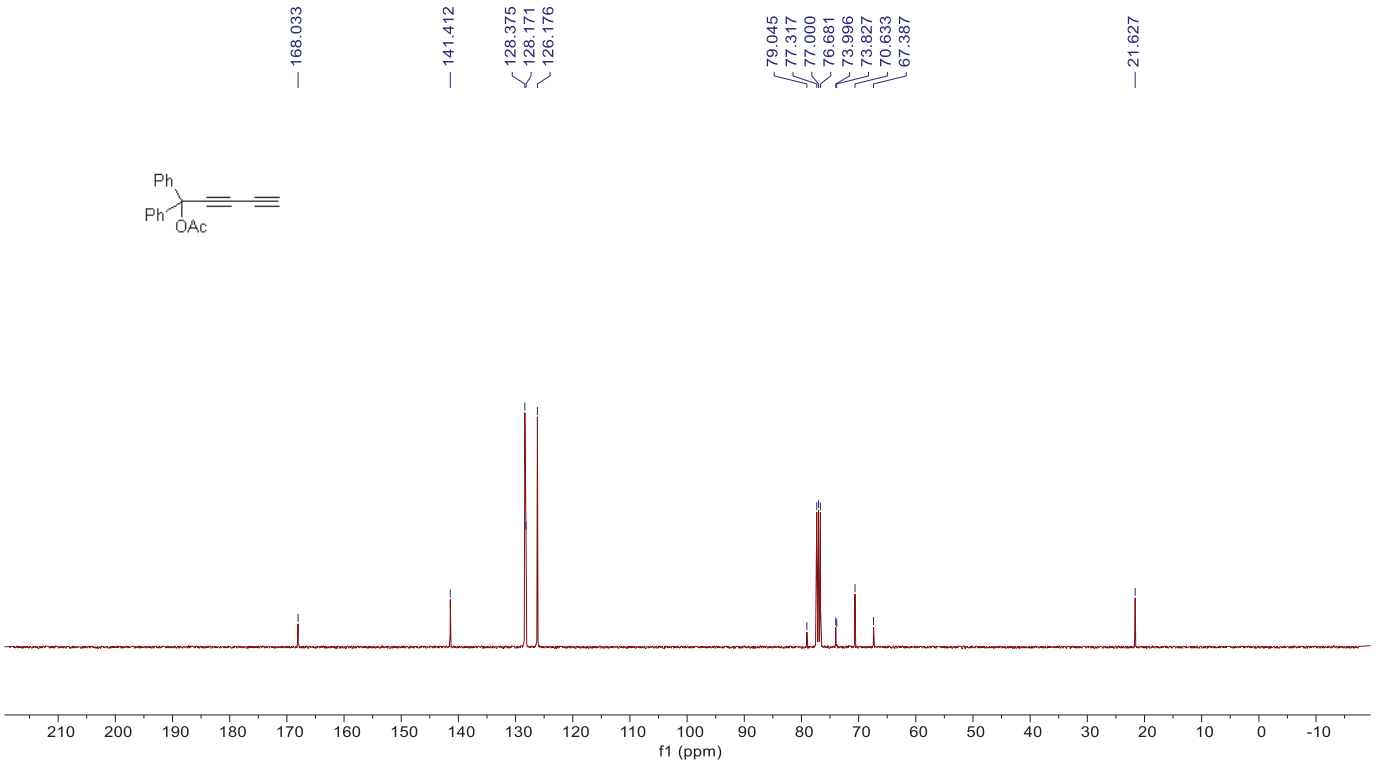
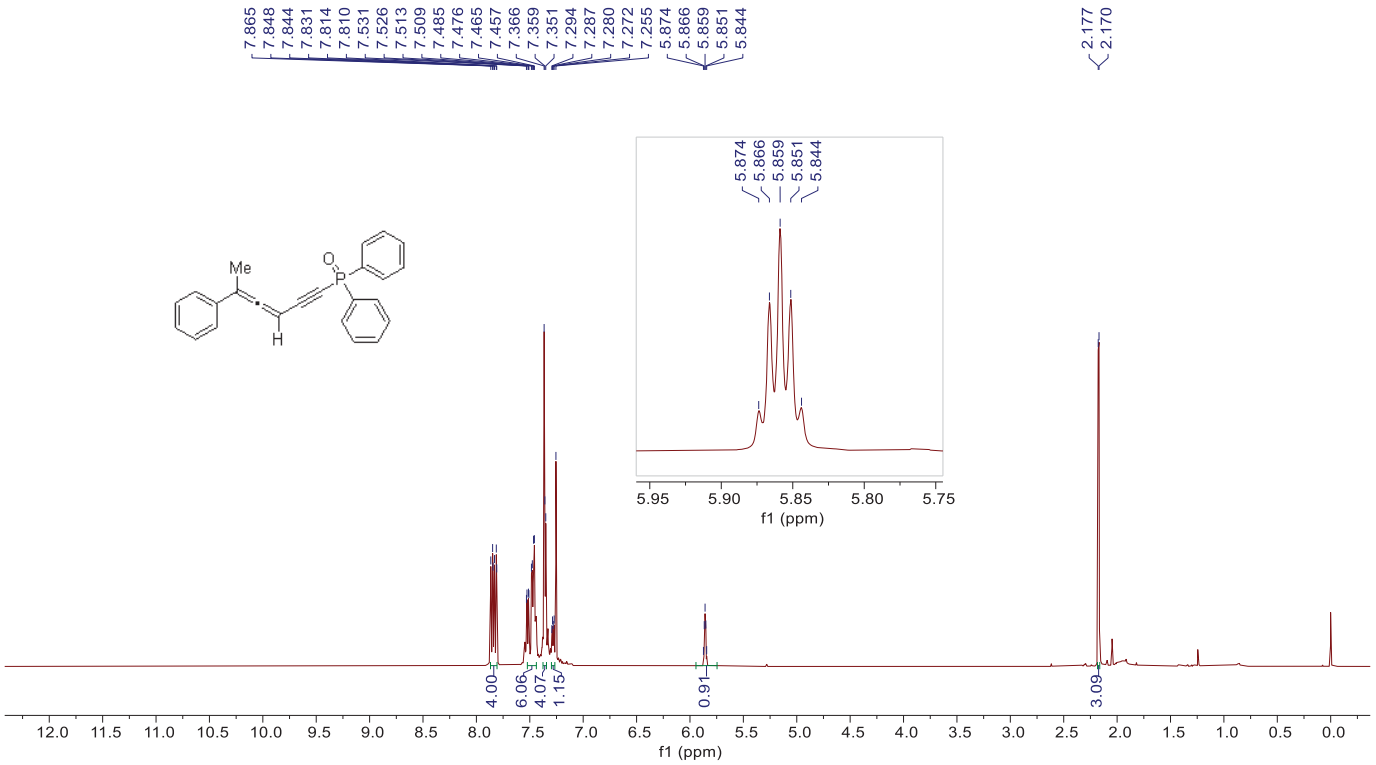
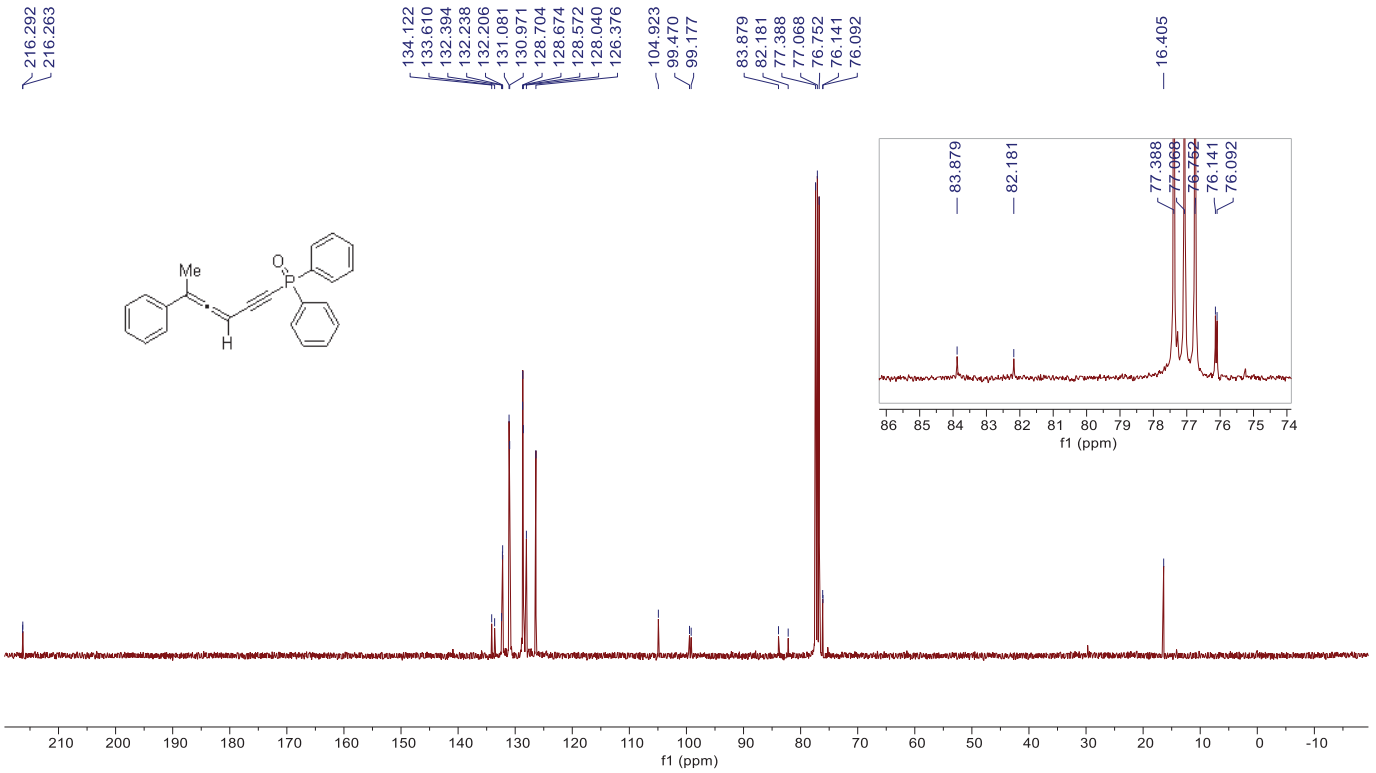


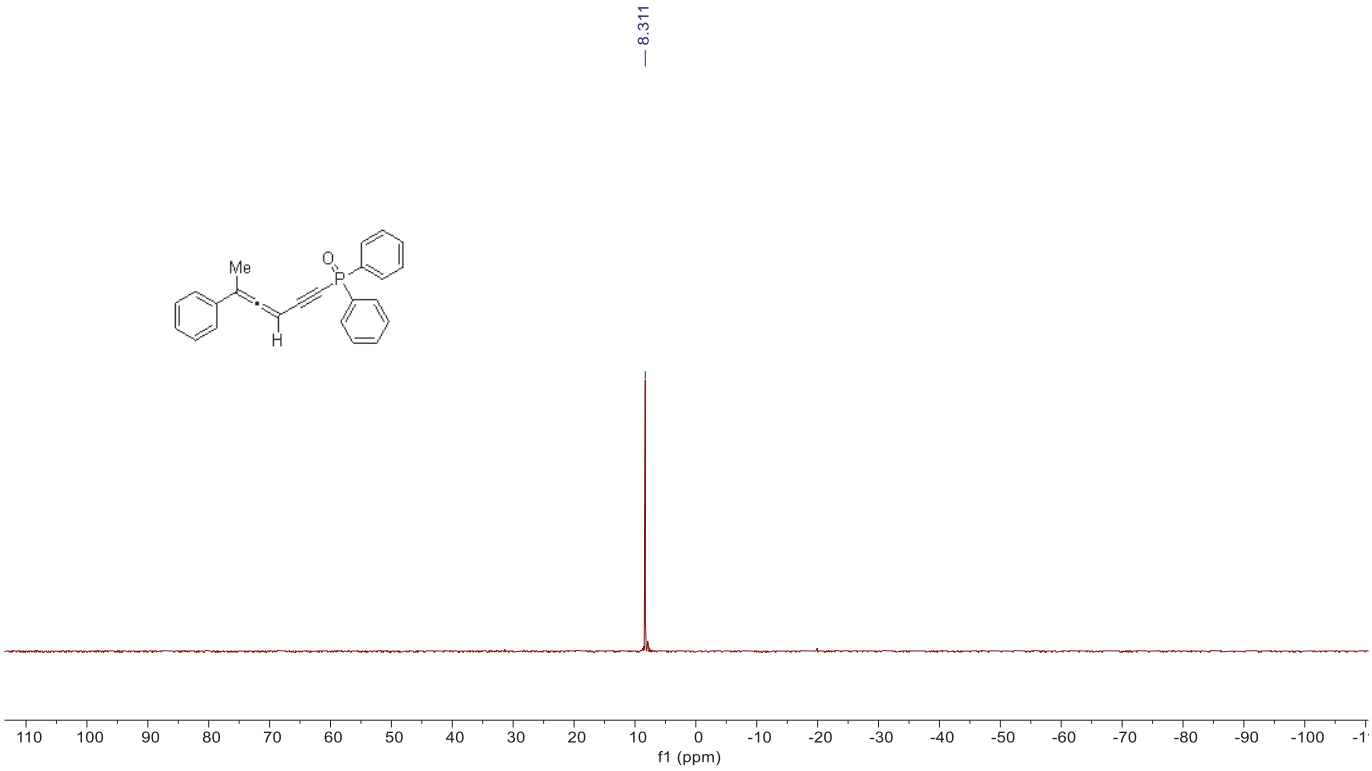
^{1}H NMR of **3a** ($CDCl_3$, 400 MHz)



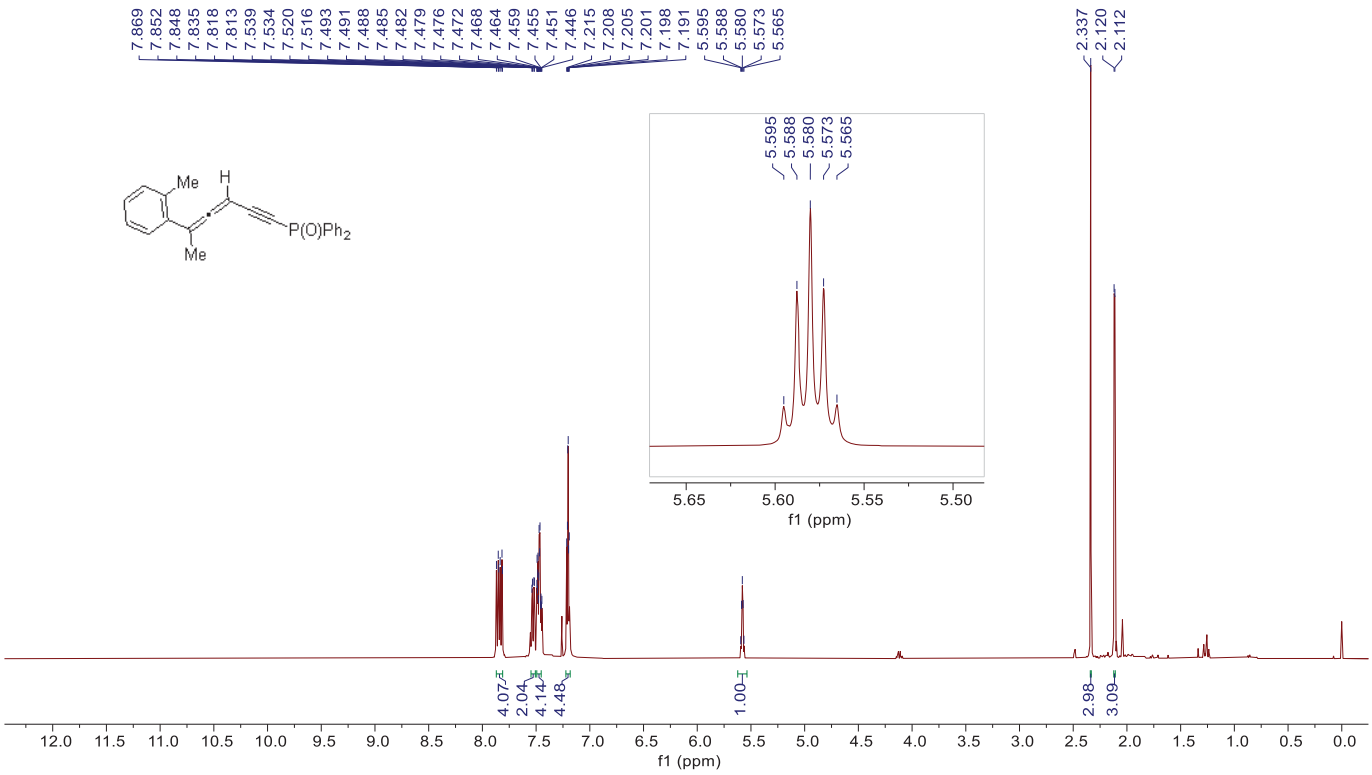
^{13}C NMR of **3a** ($CDCl_3$, 100 MHz)



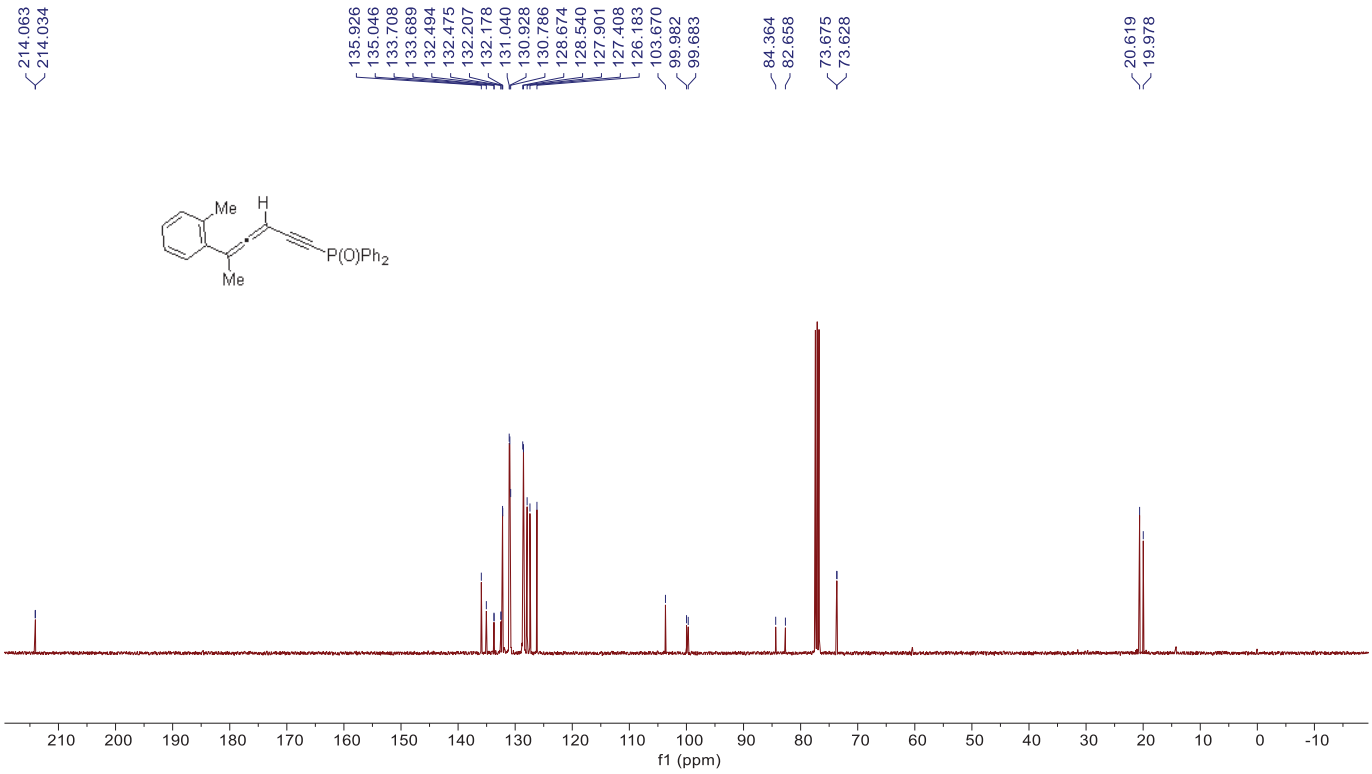
^{31}P NMR of **3a** ($CDCl_3$, 160 MHz)



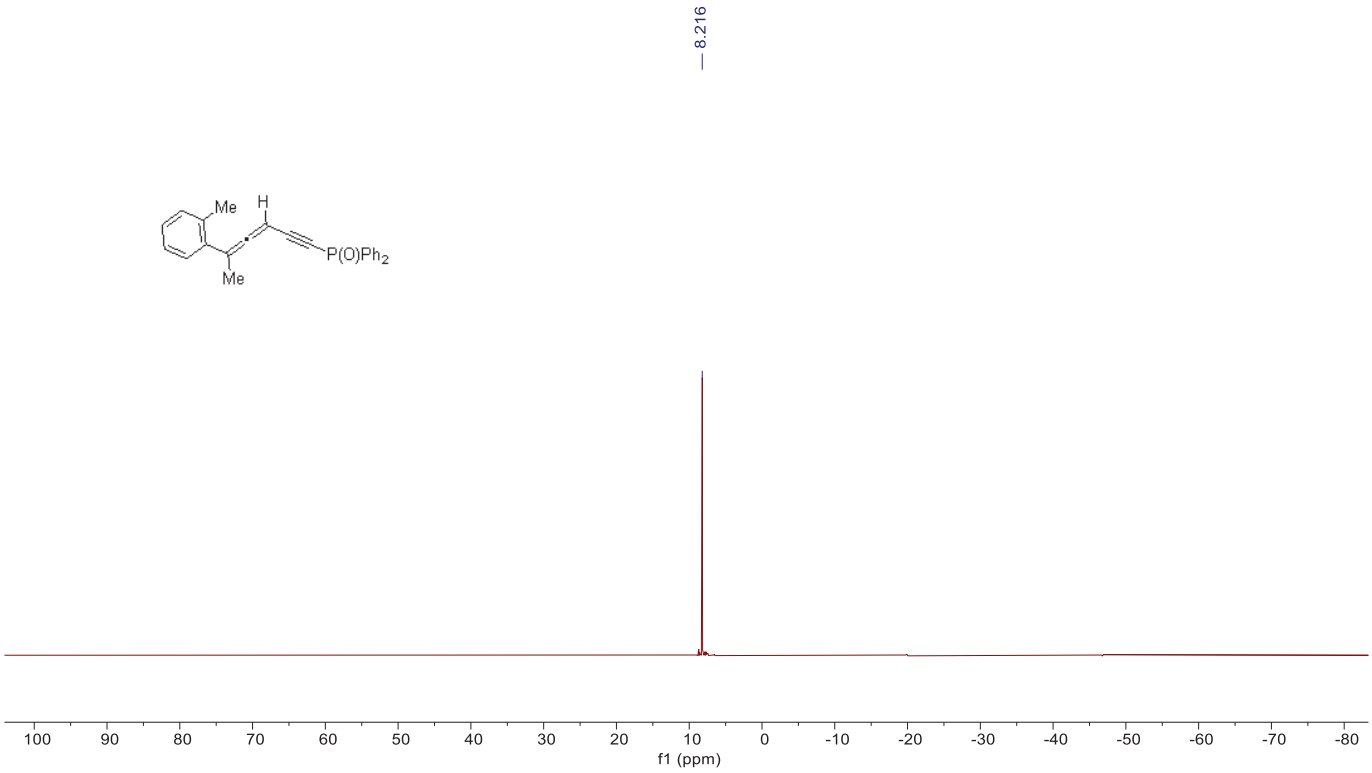
^{1}H NMR of **3b** ($CDCl_3$, 400 MHz)



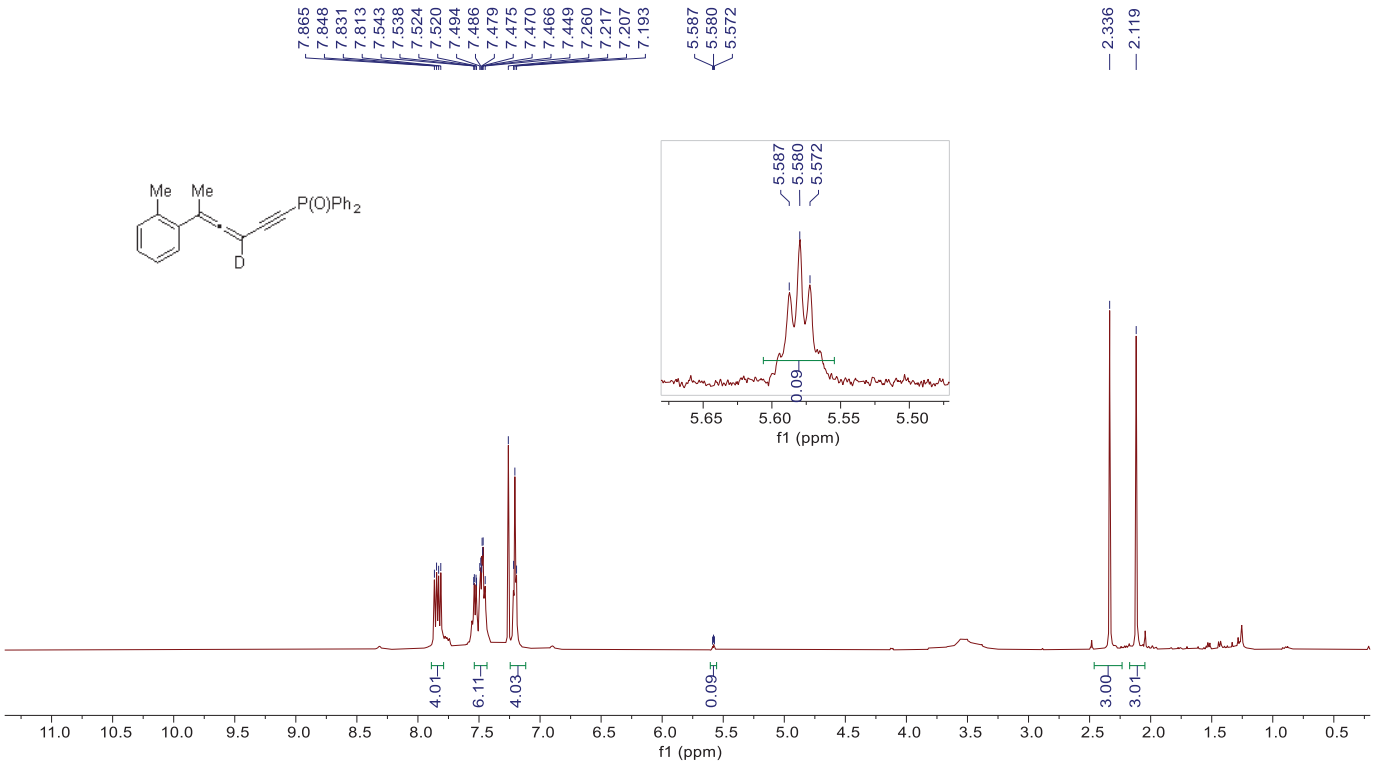
^{13}C NMR of **3b** ($CDCl_3$, 100 MHz)



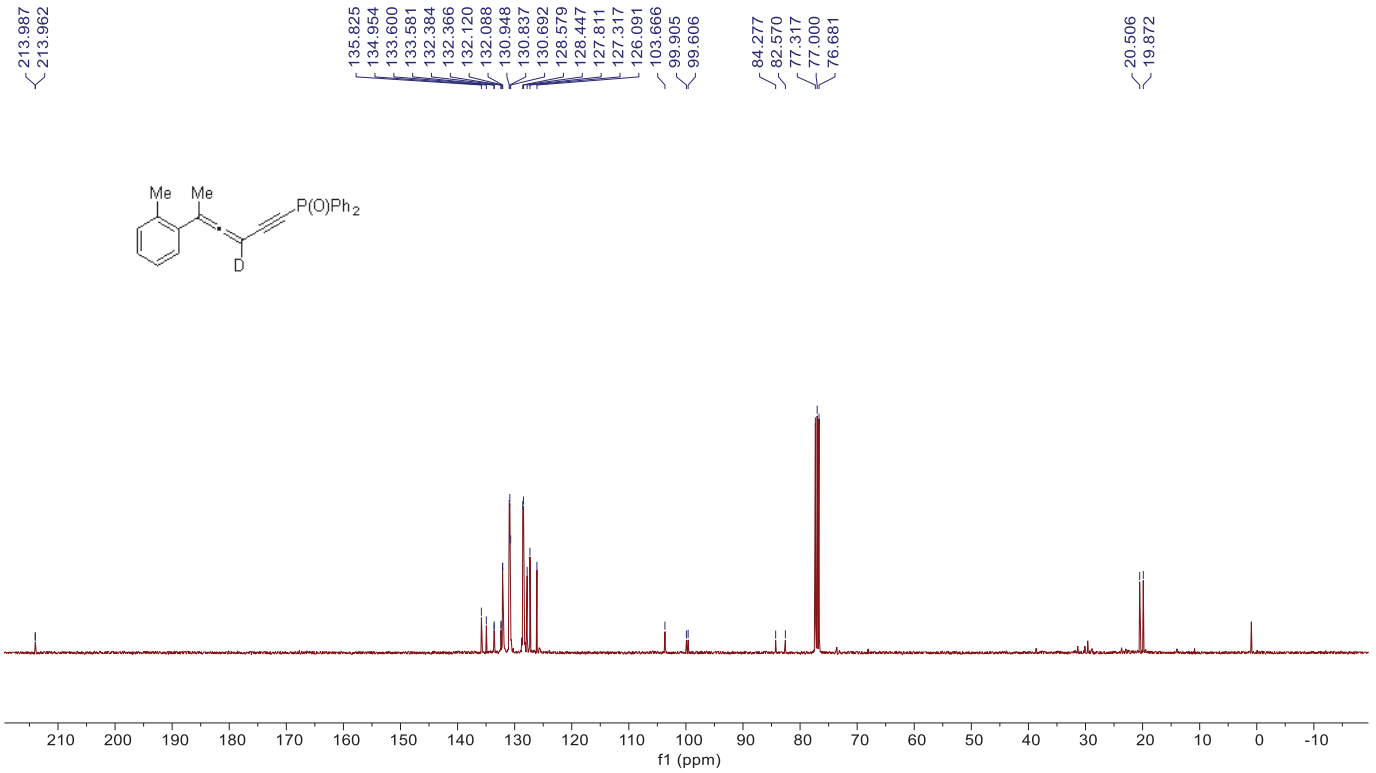
^{31}P NMR of **3b** ($CDCl_3$, 160 MHz)



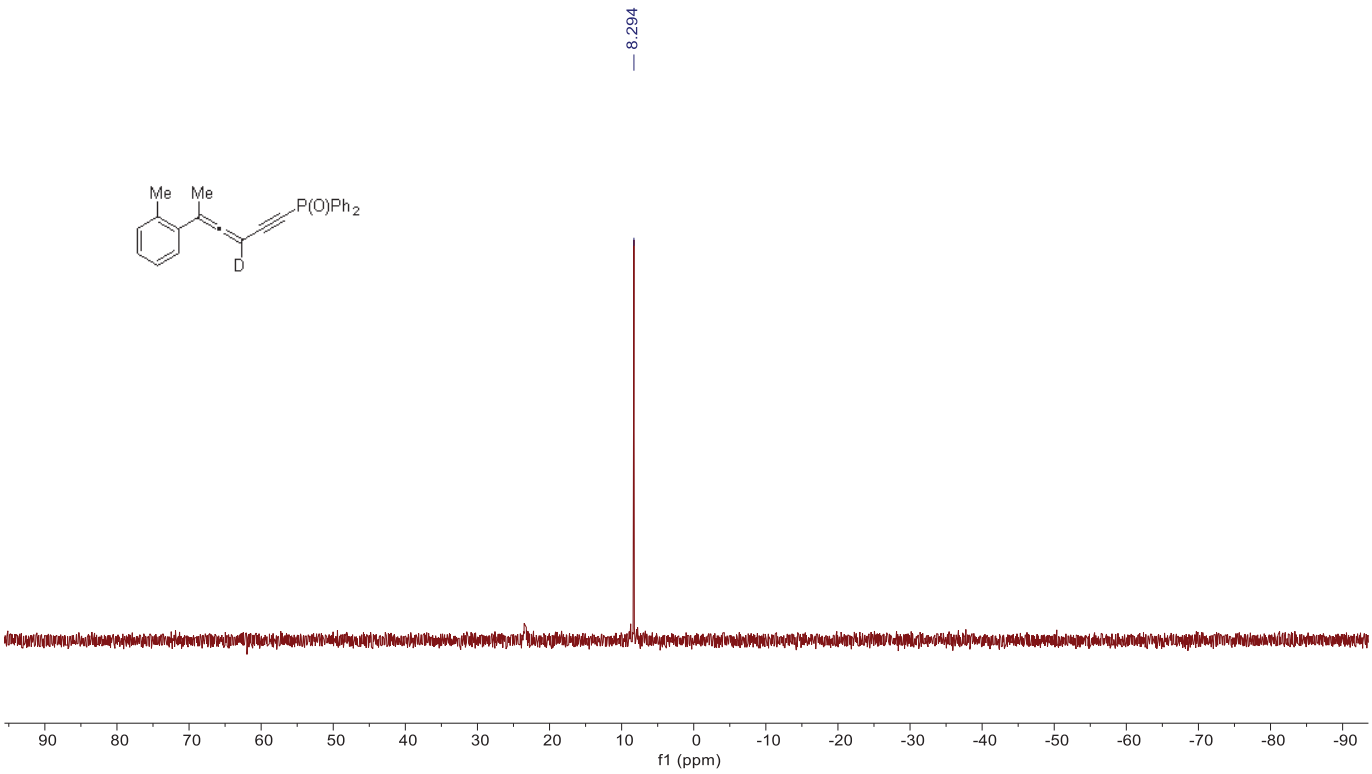
^{1}H NMR of **3b-D** ($CDCl_3$, 400 MHz)



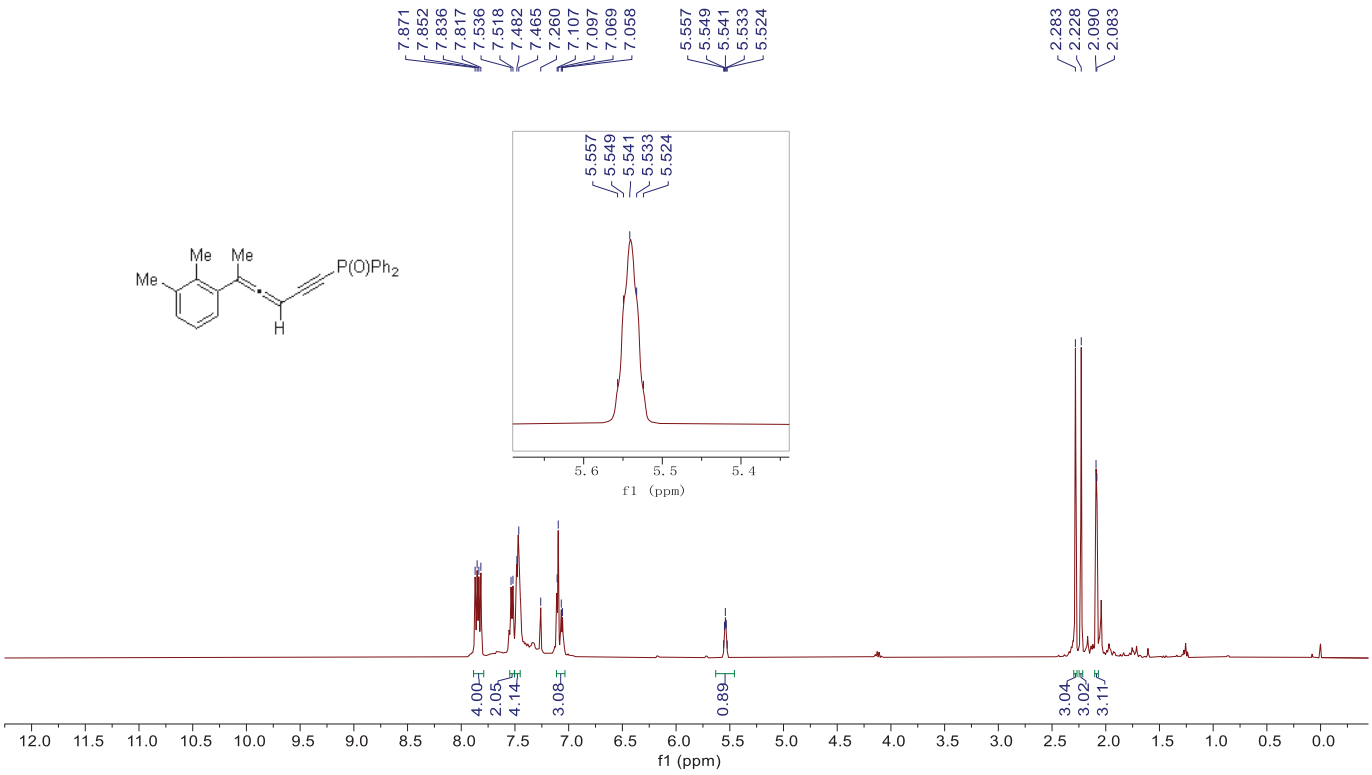
^{13}C NMR of **3b-D** ($CDCl_3$, 100 MHz)



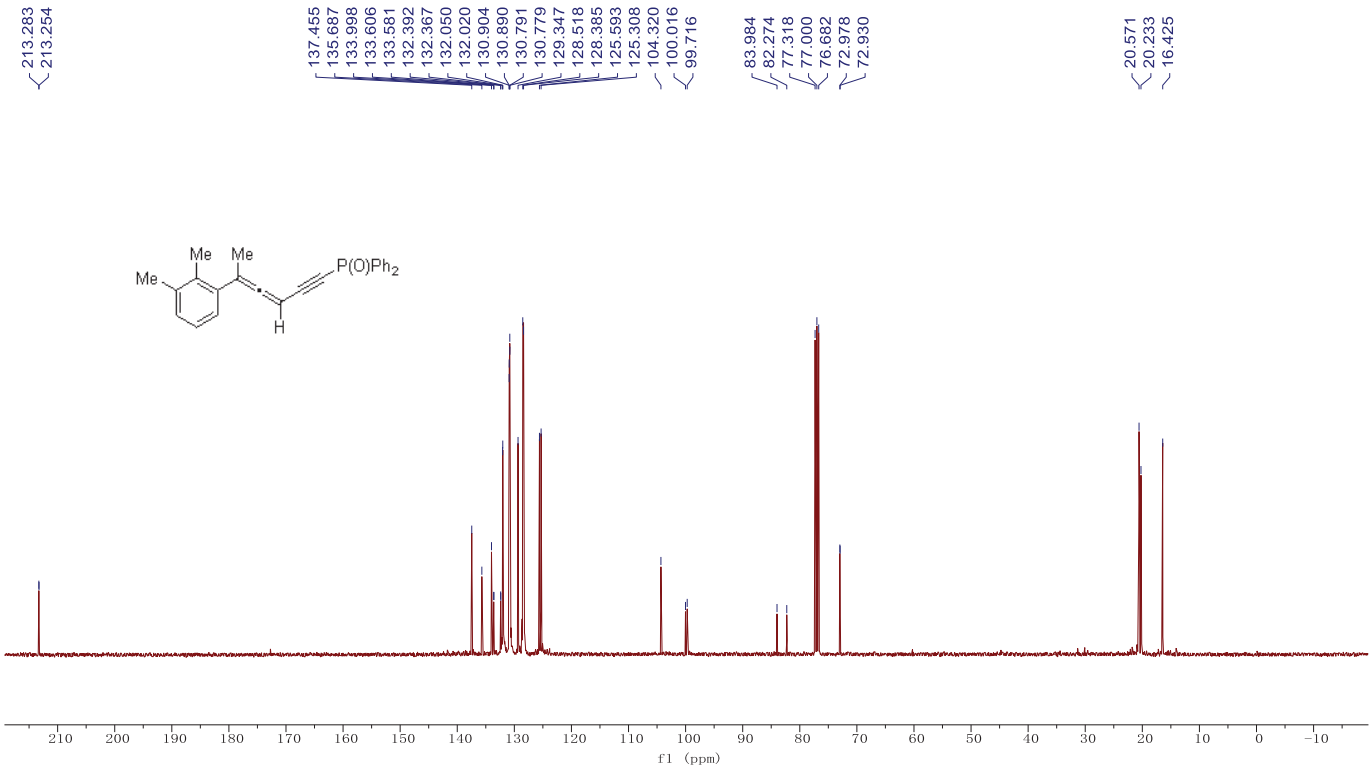
^{31}P NMR of **3b-D** ($CDCl_3$, 160 MHz)



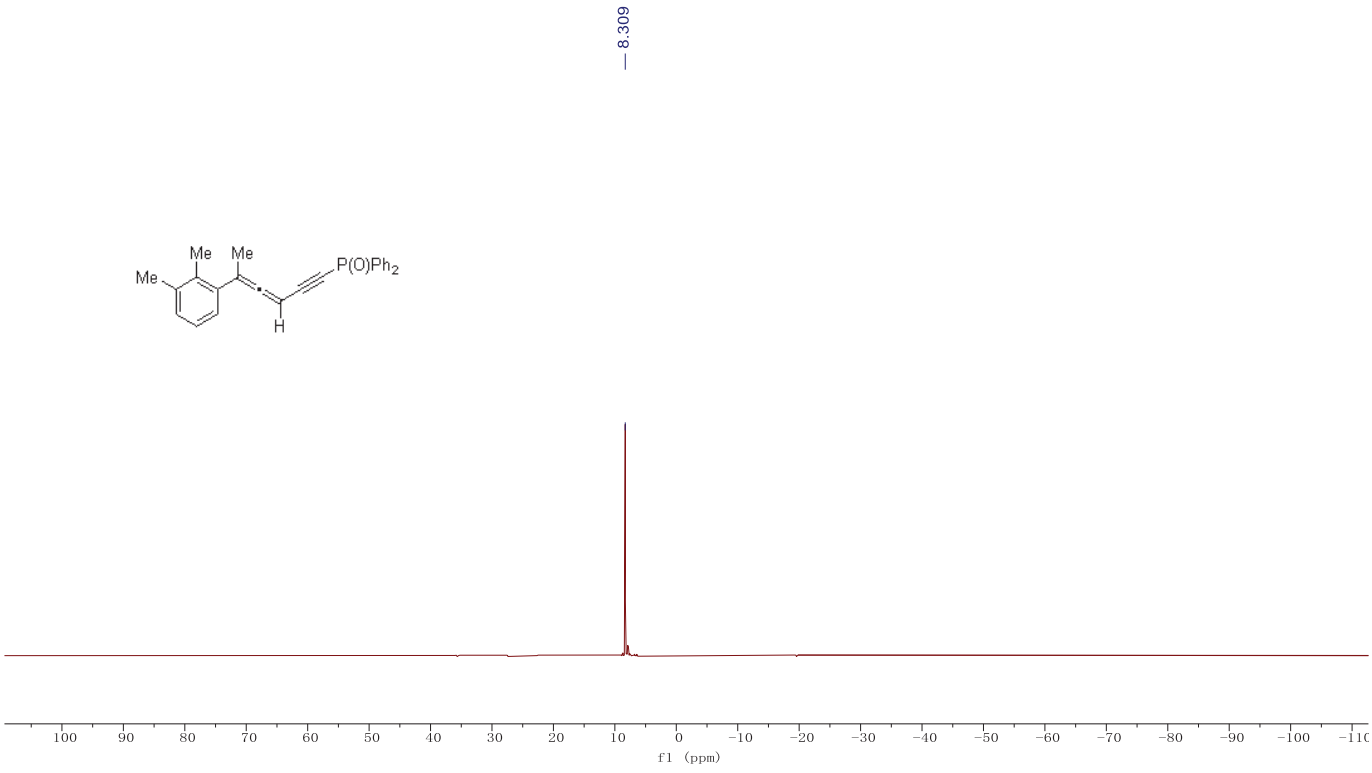
^{1}H NMR of **3c** ($CDCl_3$, 400 MHz)



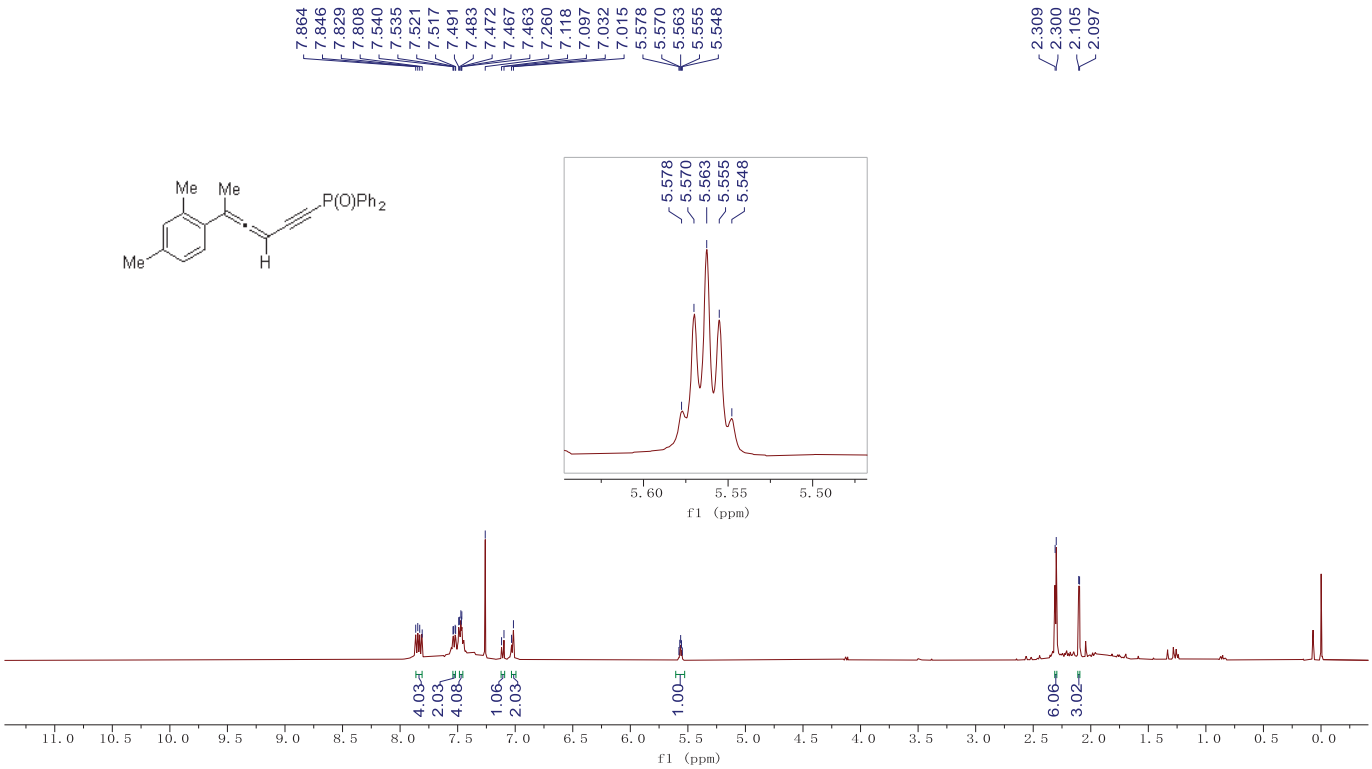
^{13}C NMR of **3c** ($CDCl_3$, 100 MHz)



^{31}P NMR of **3c** ($CDCl_3$, 160 MHz)



^{1}H NMR of **3d** ($CDCl_3$, 400 MHz)



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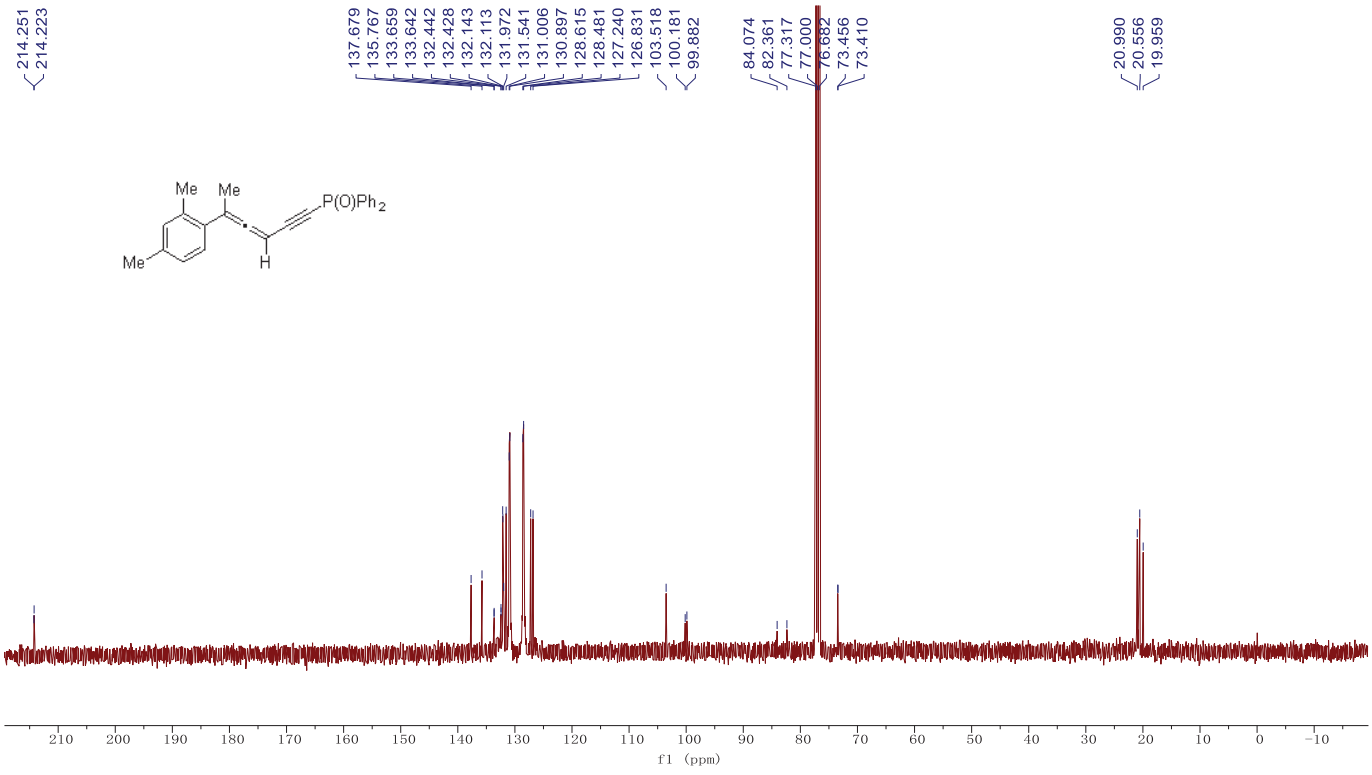
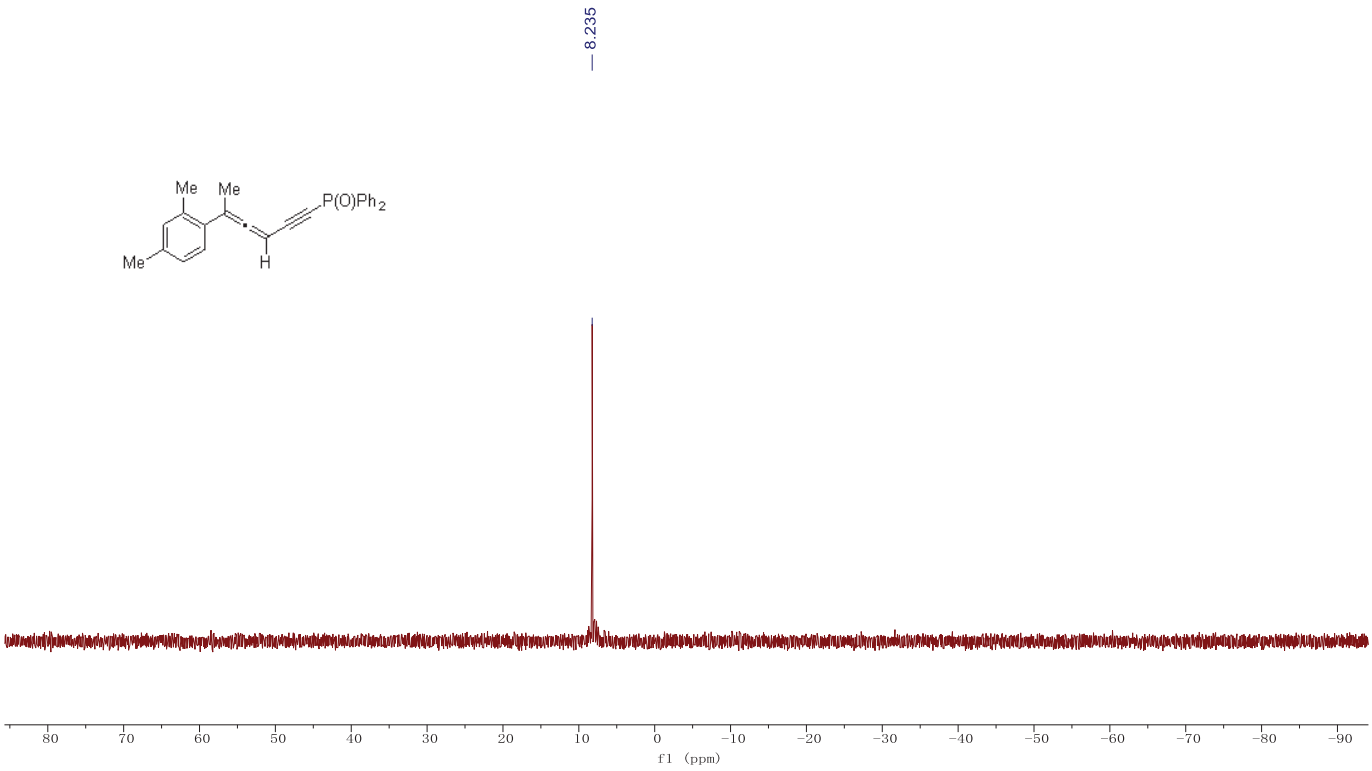
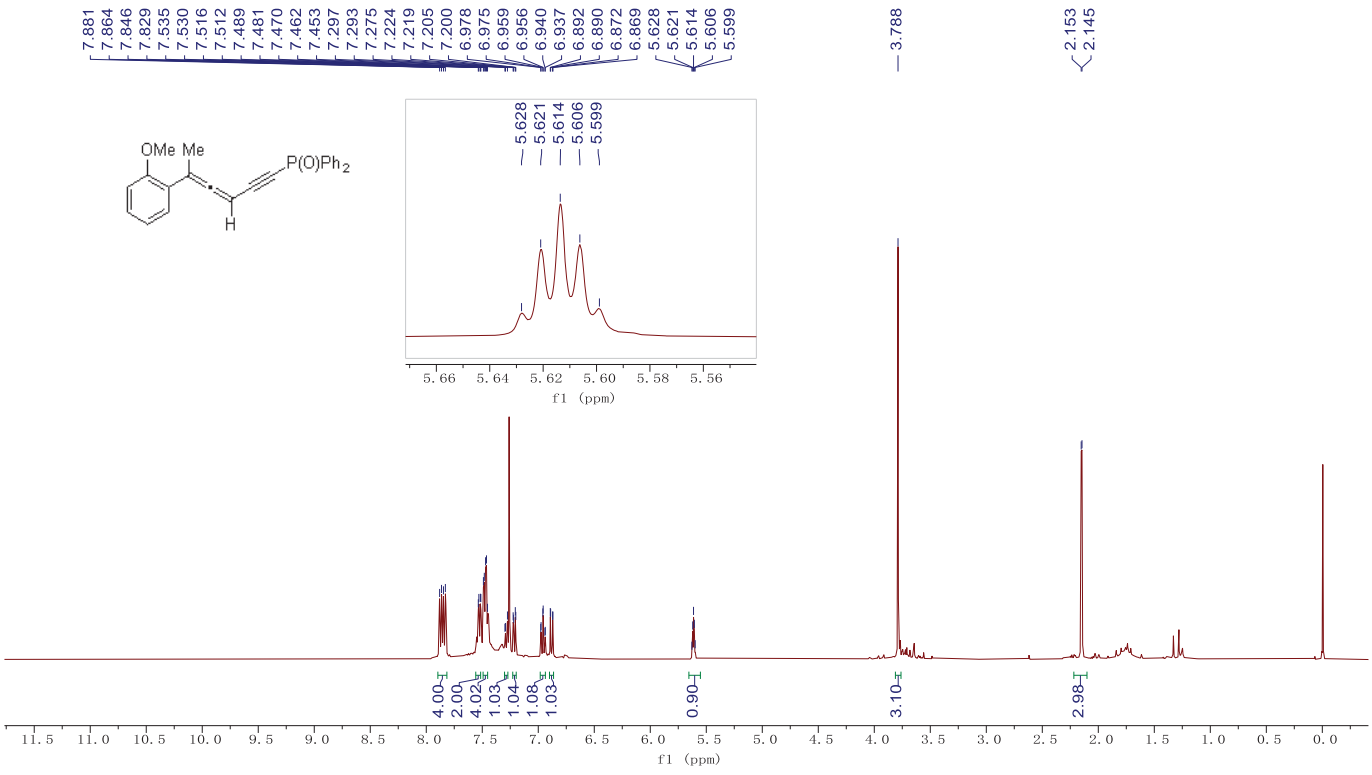


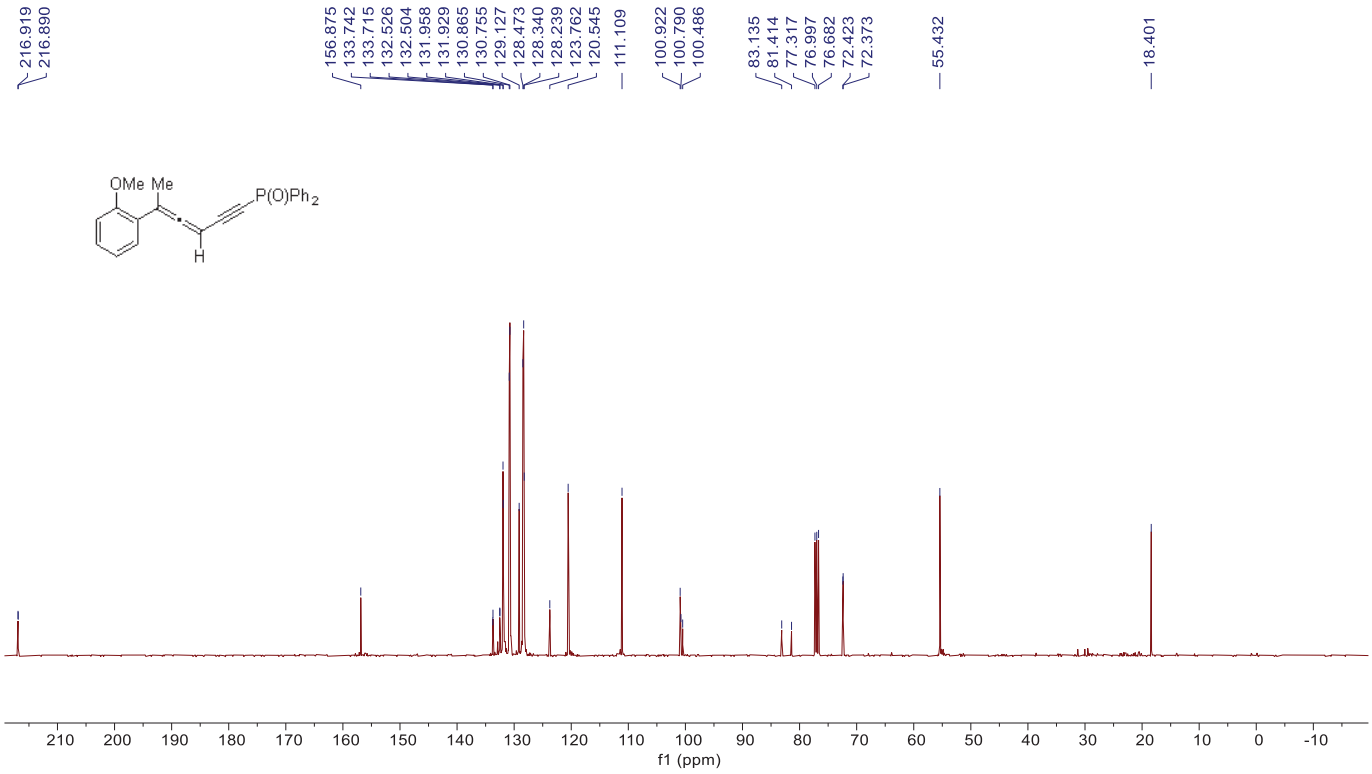
^{31}P NMR of **3d** ($CDCl_3$, 160 MHz)



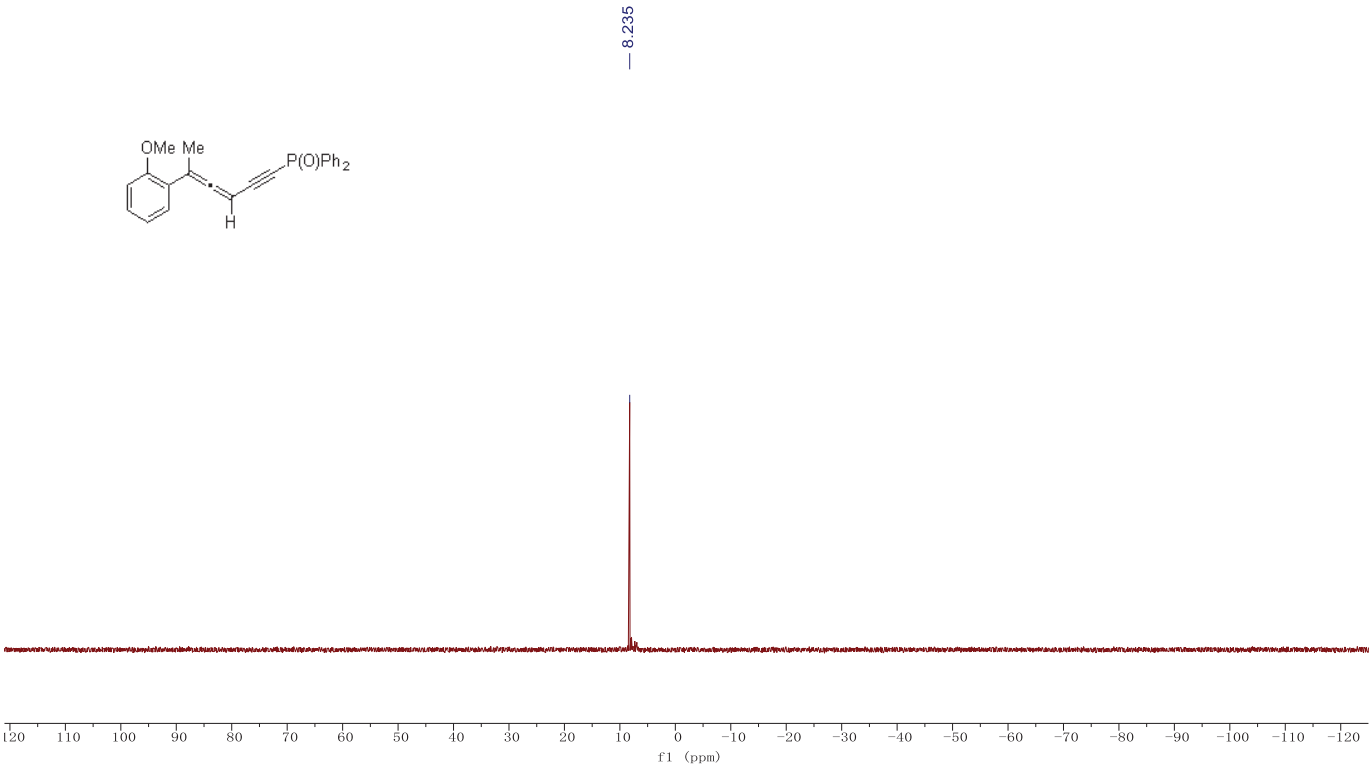
^{1}H NMR of **3e** ($CDCl_3$, 400 MHz)



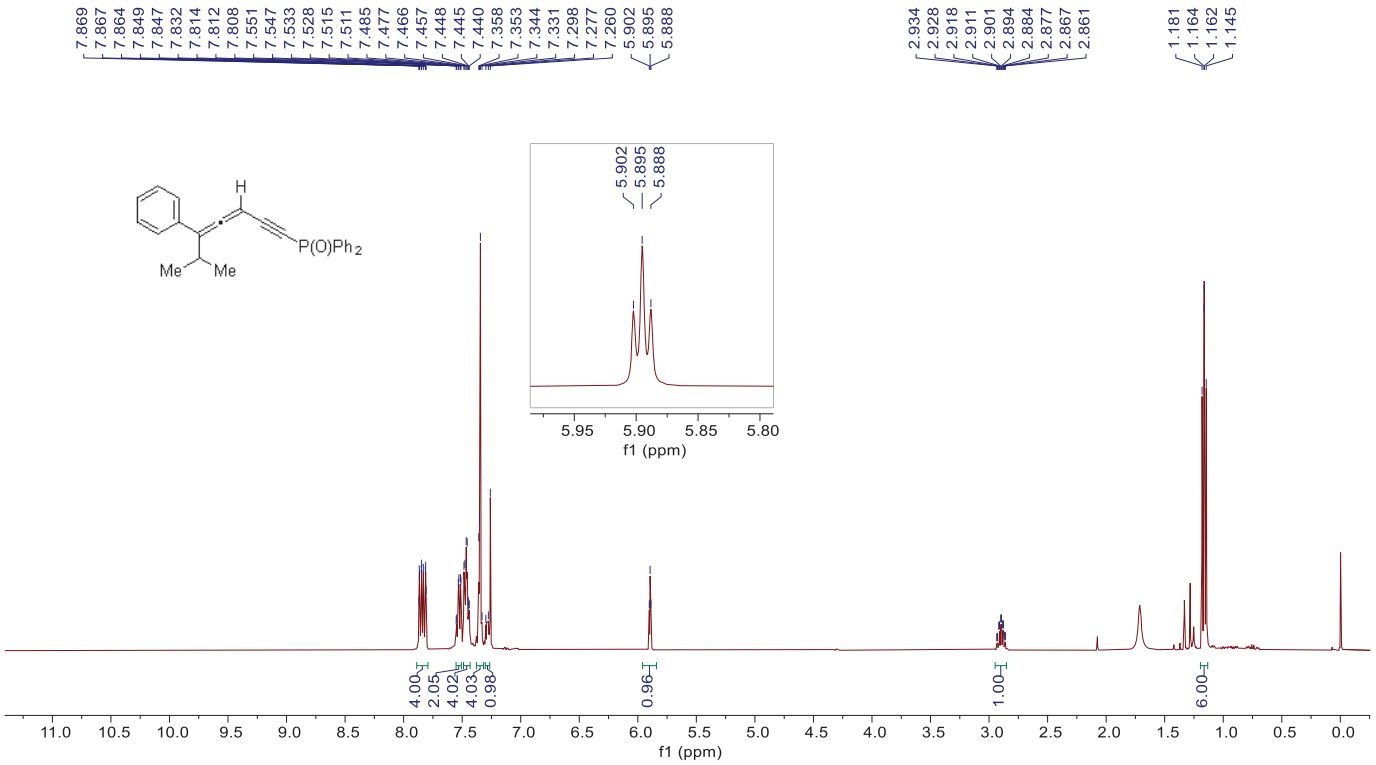
^{13}C NMR of **3e** ($CDCl_3$, 100 MHz)



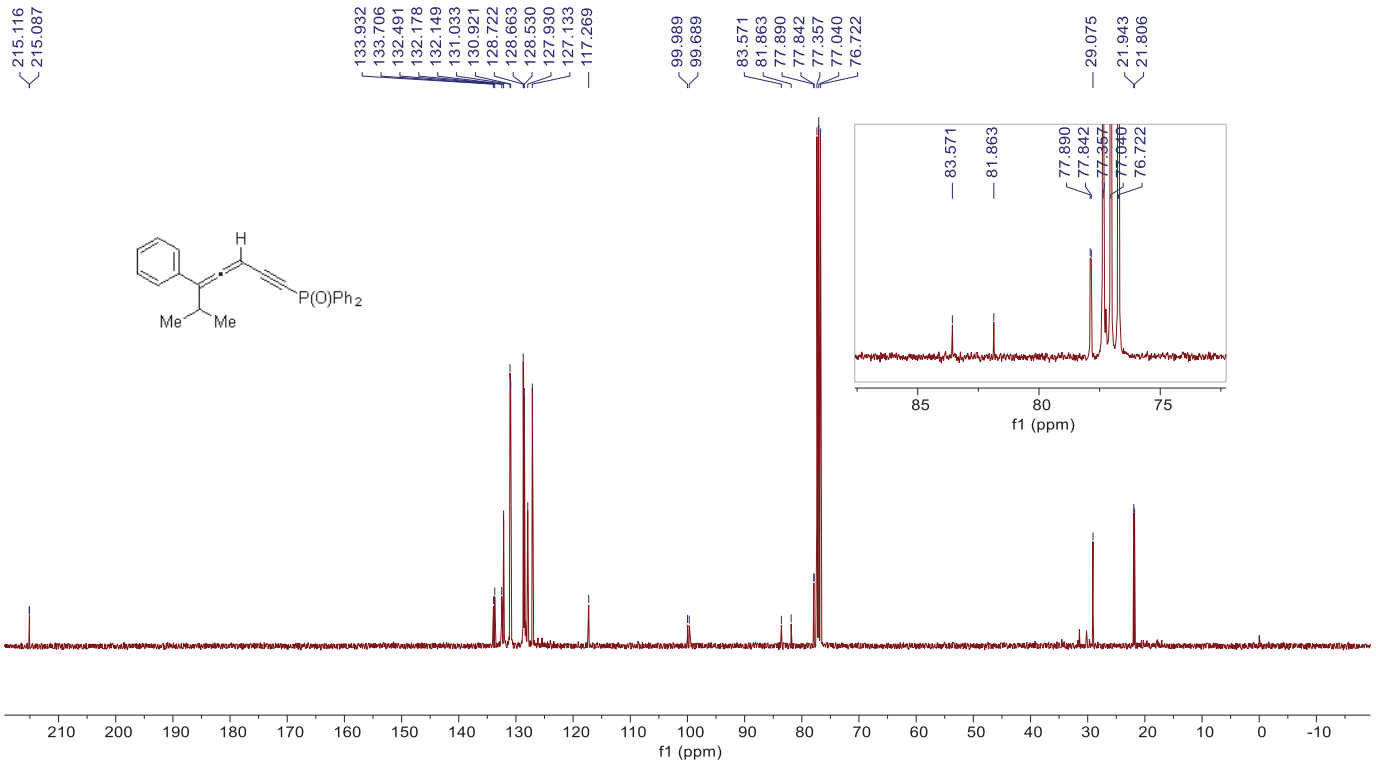
^{31}P NMR of **3e** ($CDCl_3$, 160 MHz)



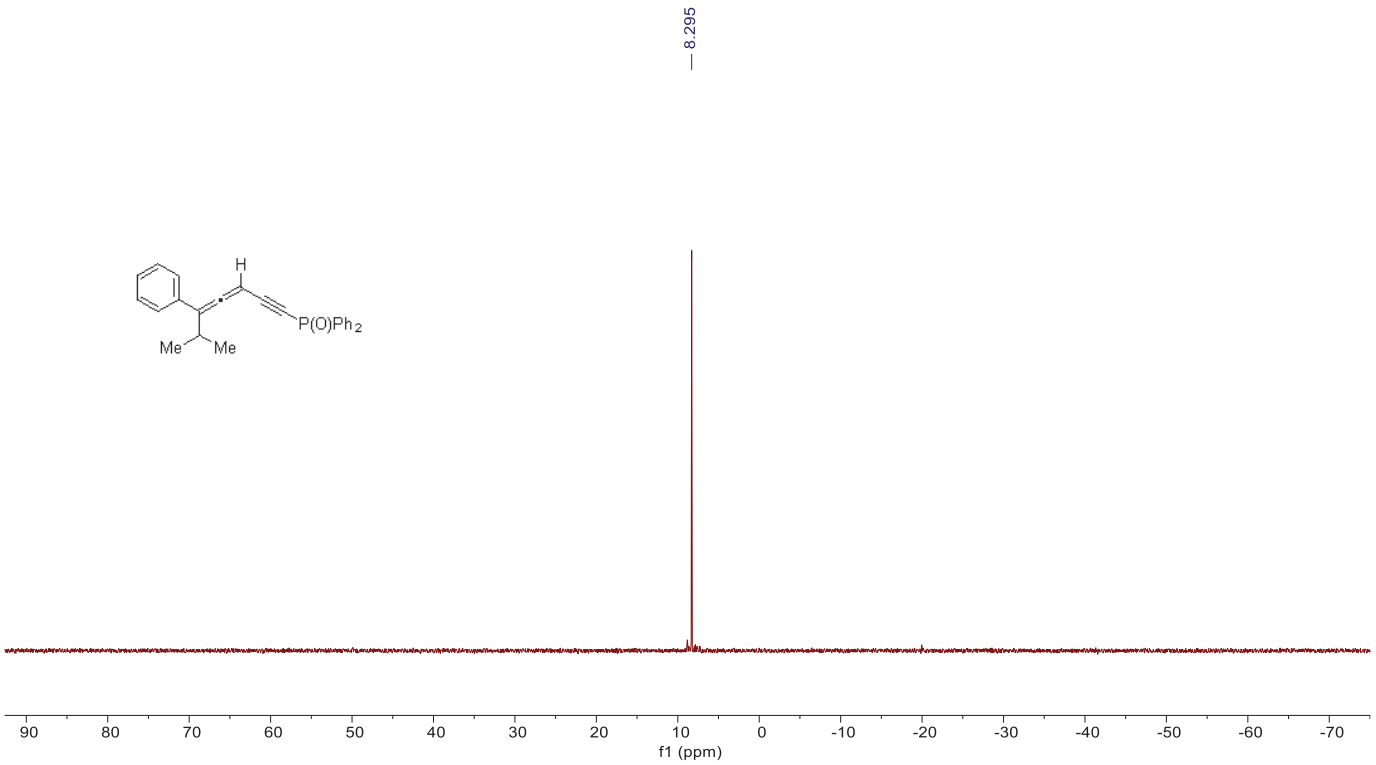
^{1}H NMR of **3h** ($CDCl_3$, 400 MHz)



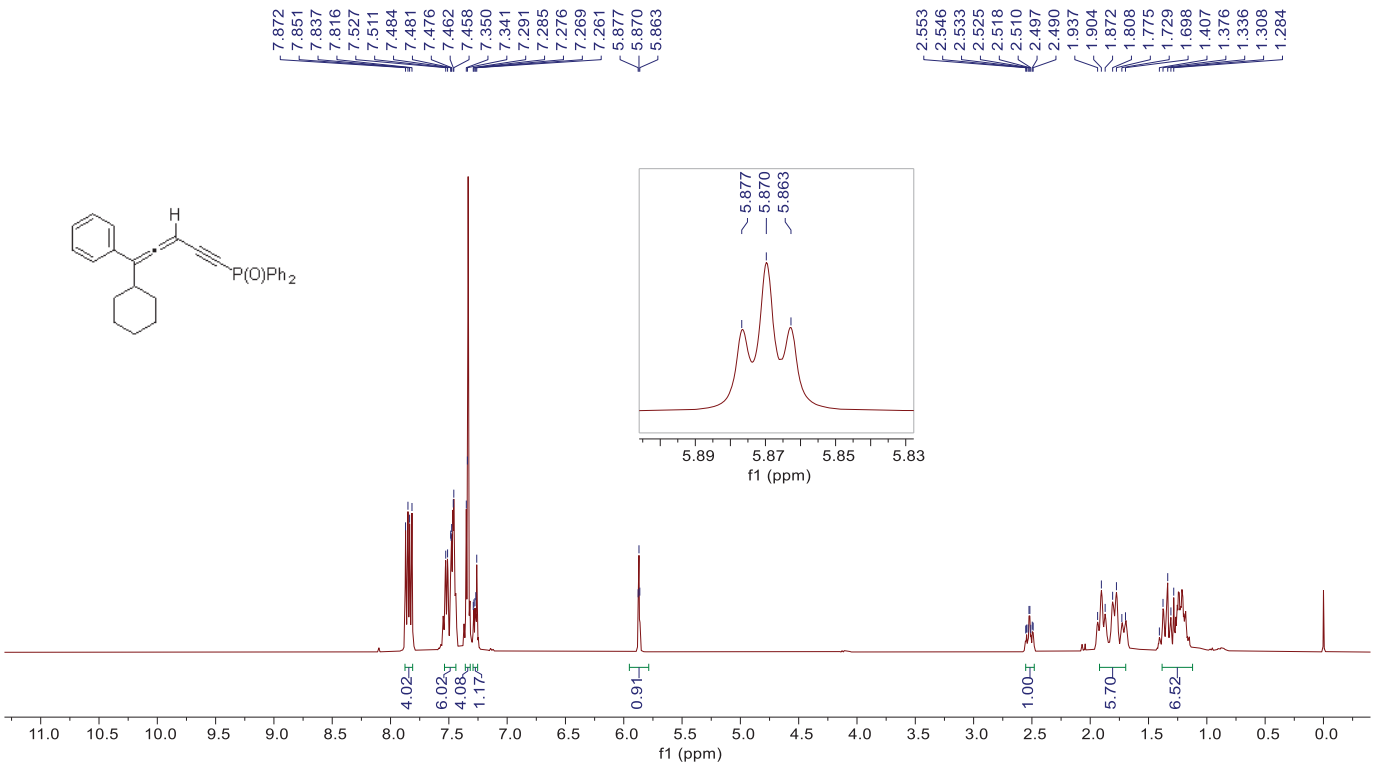
^{13}C NMR of **3h** ($CDCl_3$, 100 MHz)



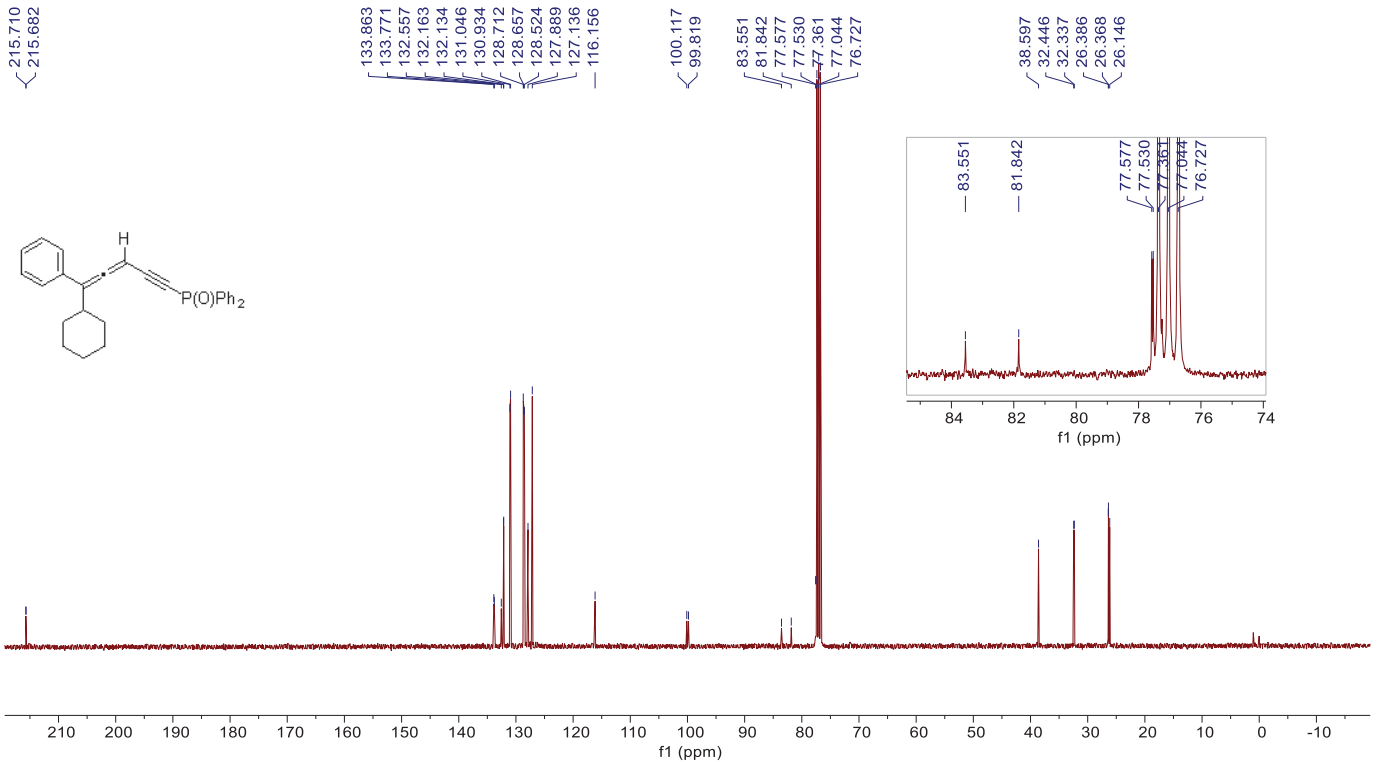
^{31}P NMR of **3h** ($CDCl_3$, 160 MHz)



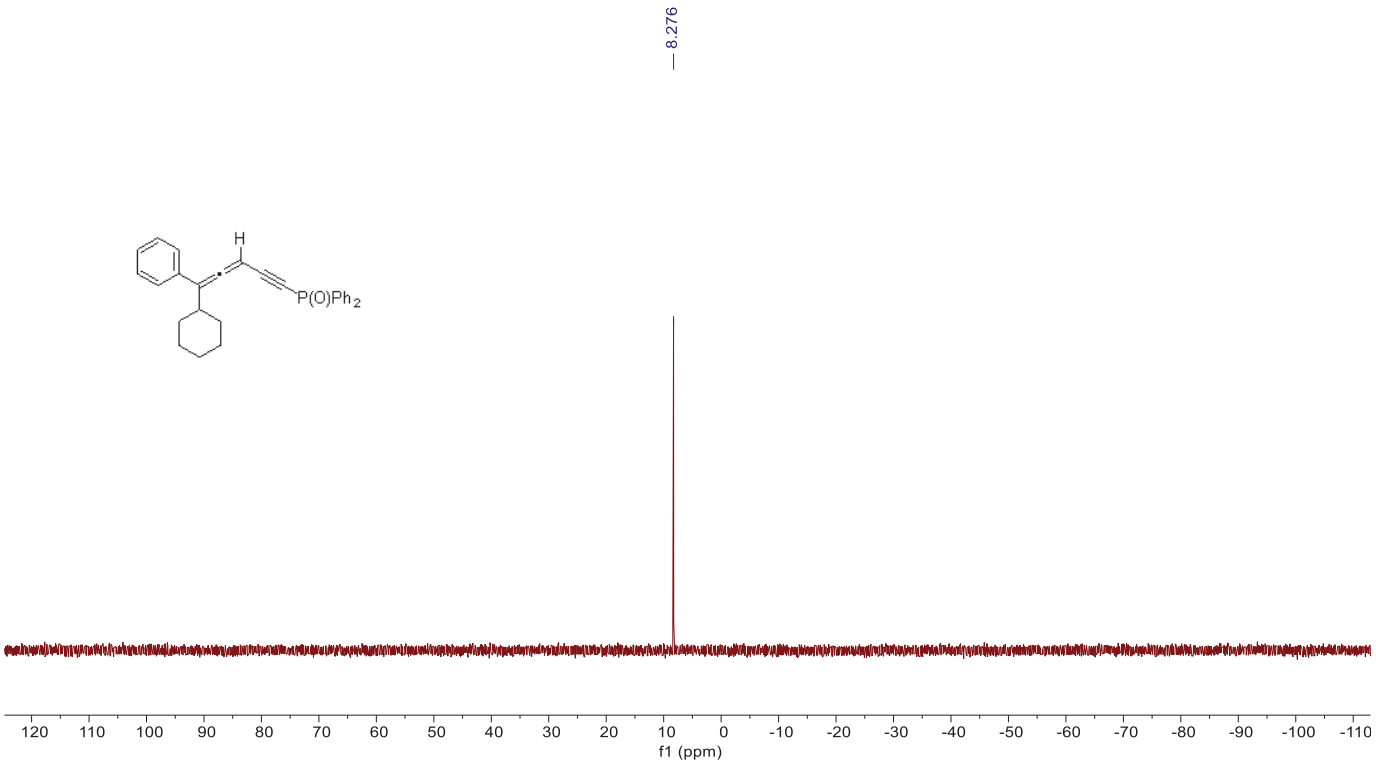
^{1}H NMR of **1i** ($CDCl_3$, 400 MHz)



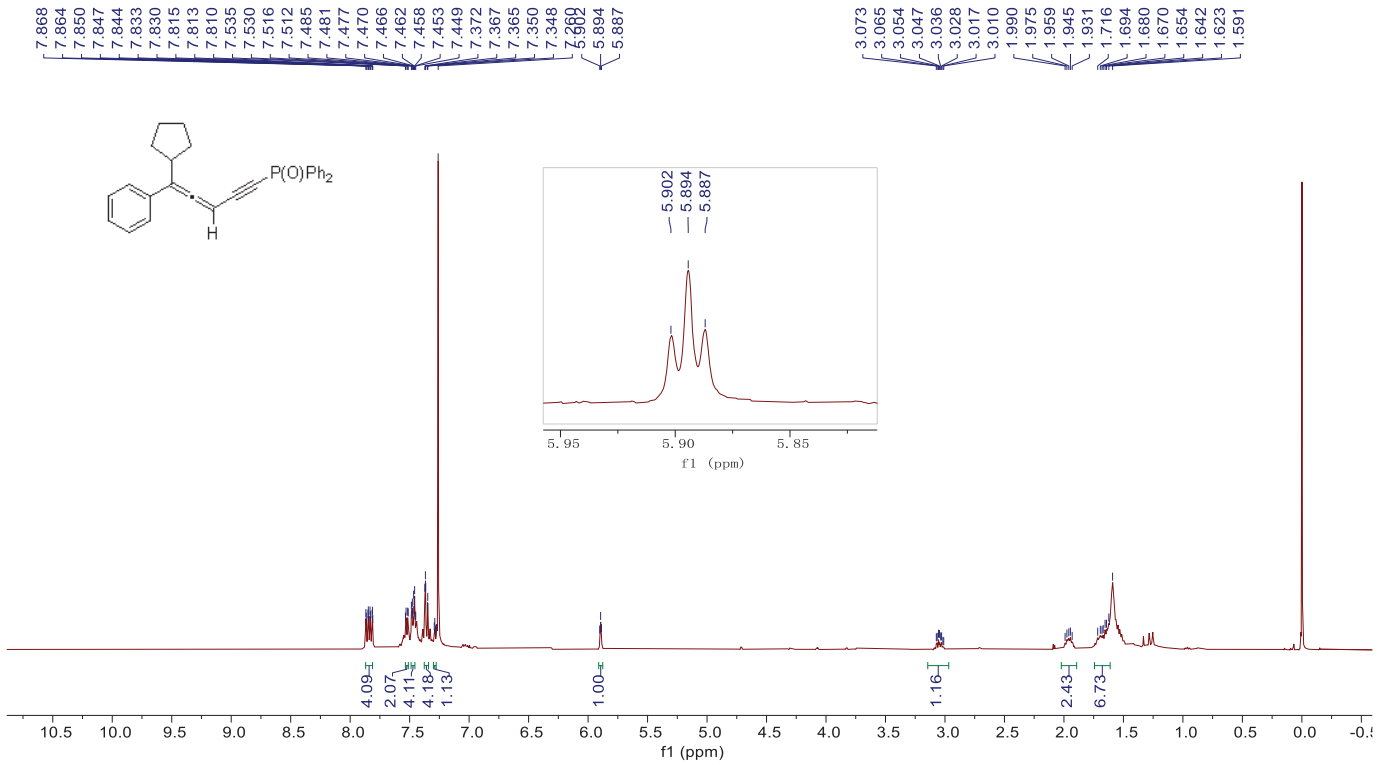
^{13}C NMR of **1i** ($CDCl_3$, 100 MHz)



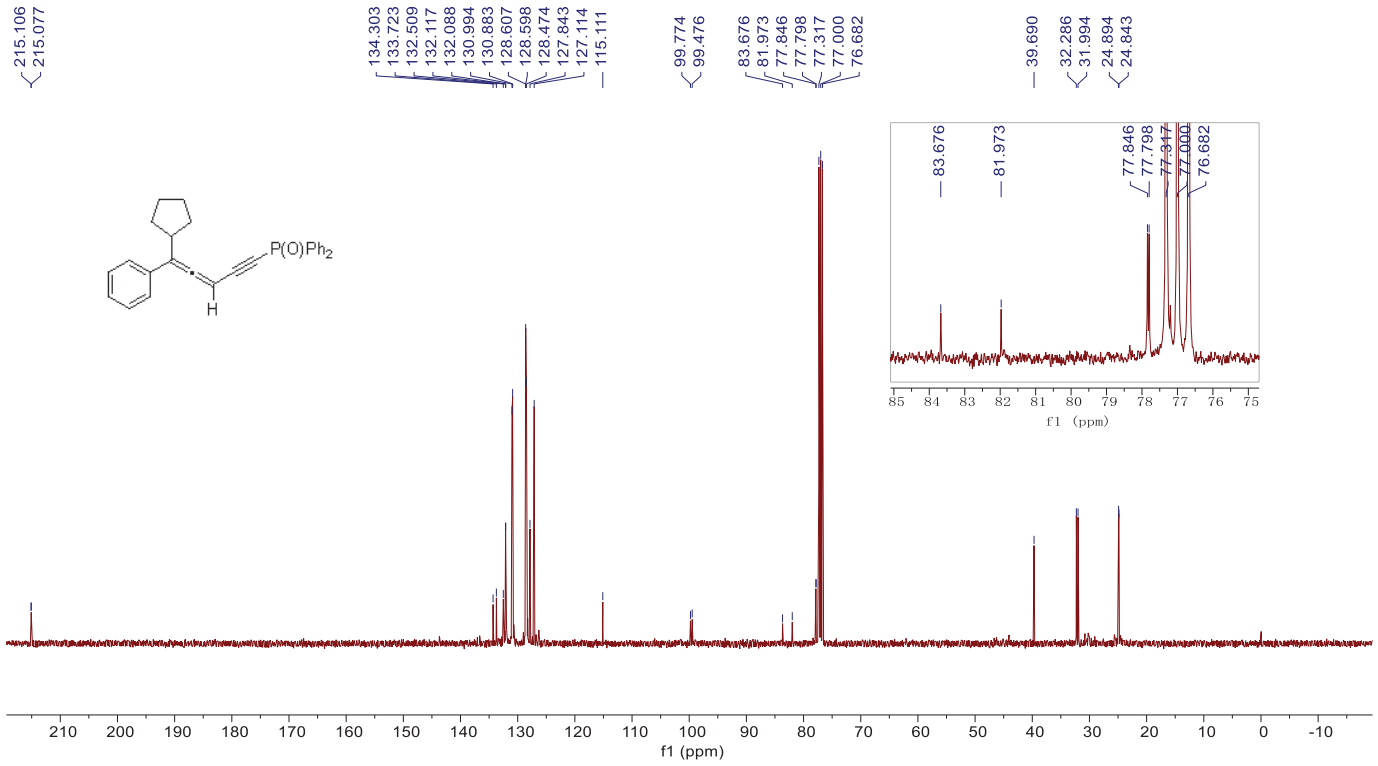
^{31}P NMR of **3i** ($CDCl_3$, 160 MHz)



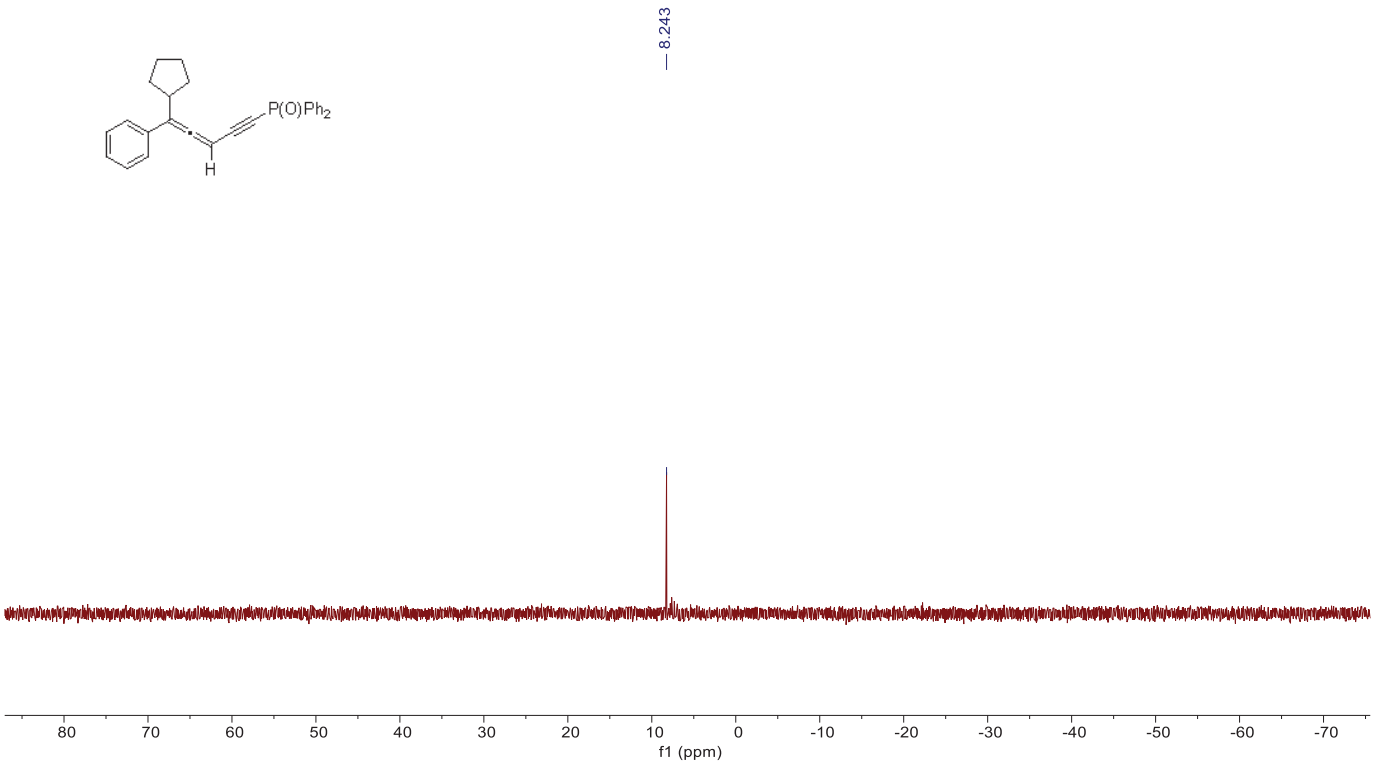
^{1}H NMR of **3j** ($CDCl_3$, 400 MHz)



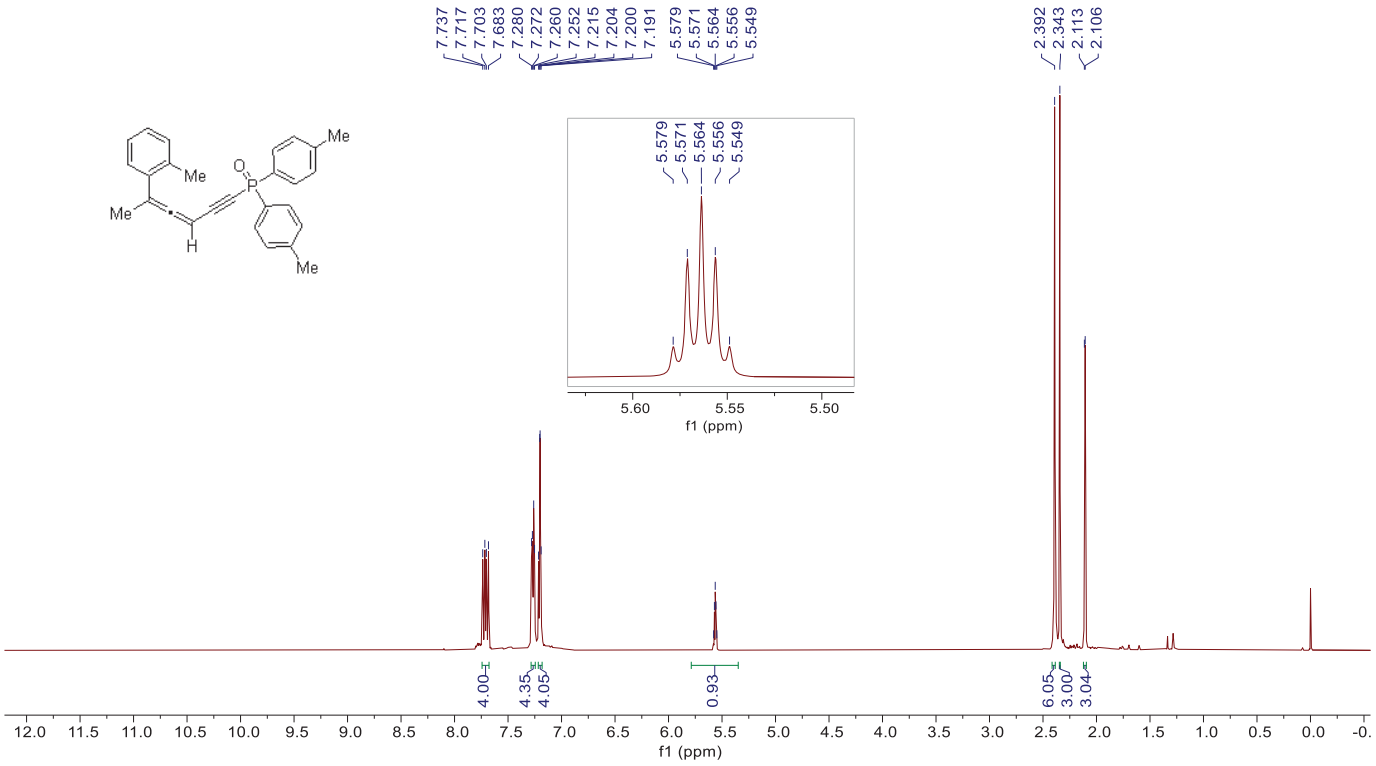
^{13}C NMR of **3j** ($CDCl_3$, 100 MHz)



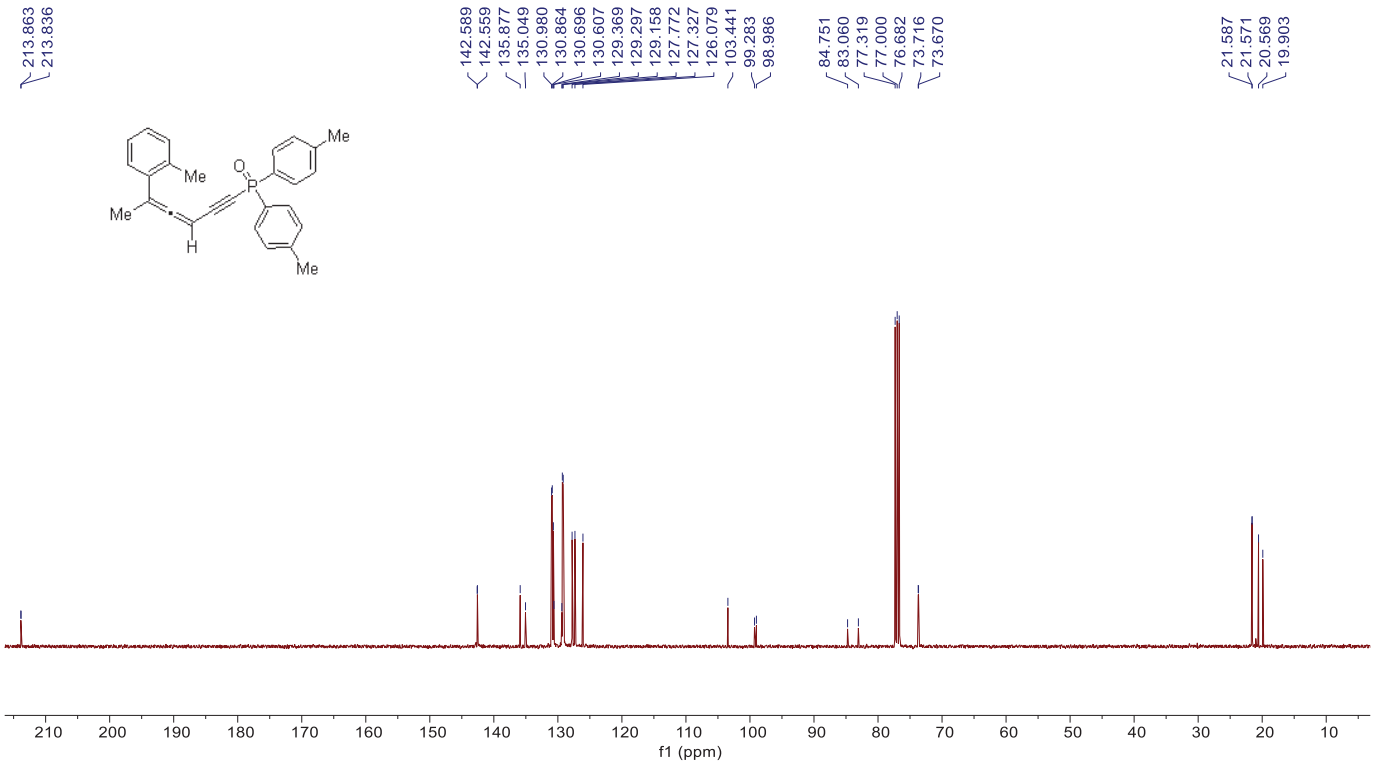
^{31}P NMR of **3j** ($CDCl_3$, 160 MHz)



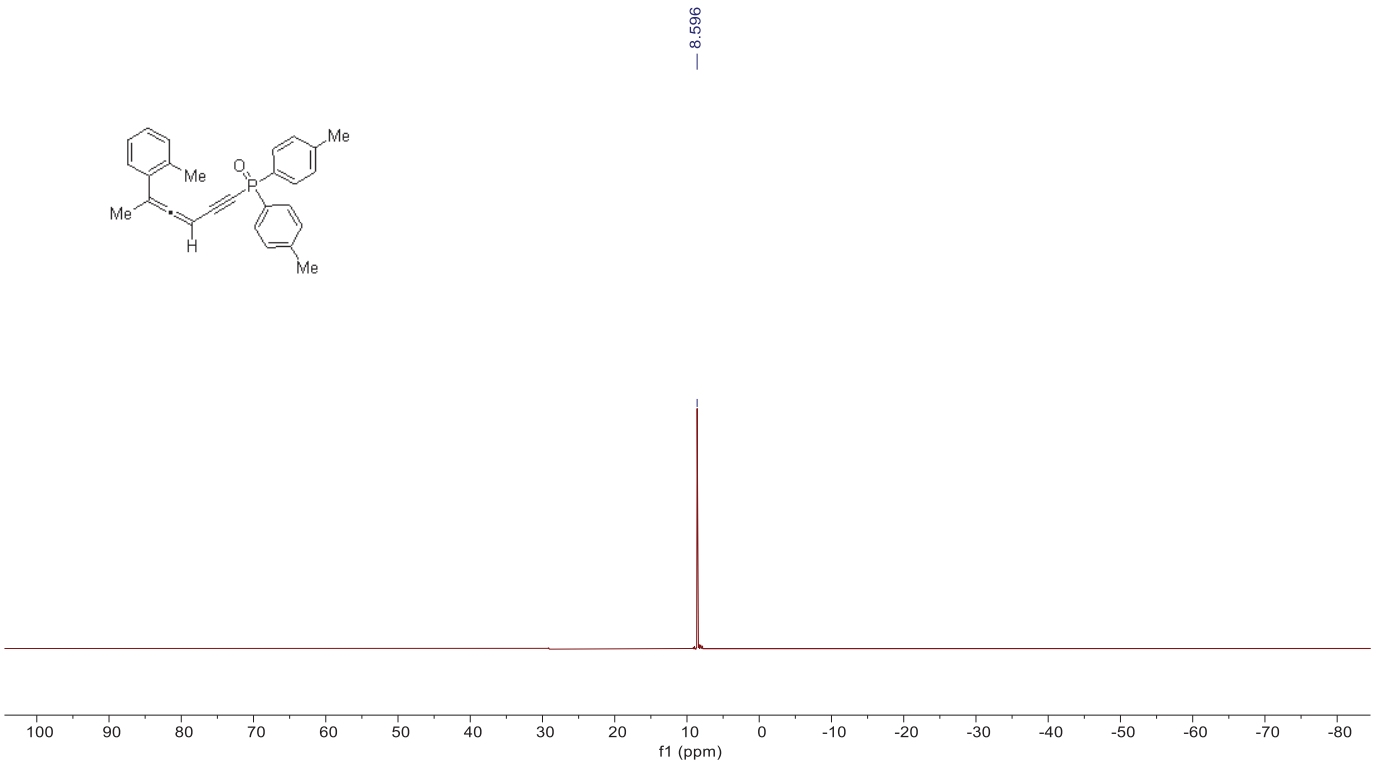
^{1}H NMR of **3l** ($CDCl_3$, 400 MHz)



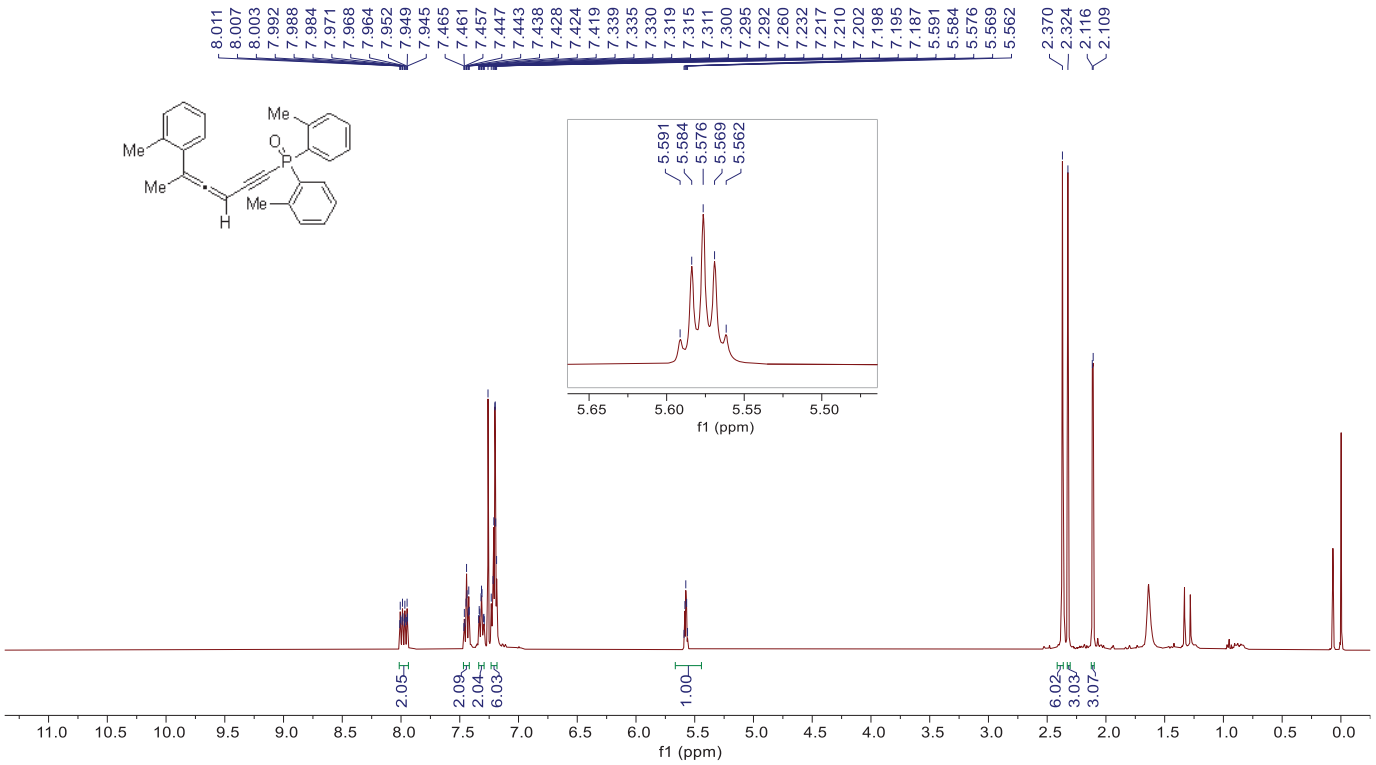
^{13}C NMR of **3l** ($CDCl_3$, 100 MHz)



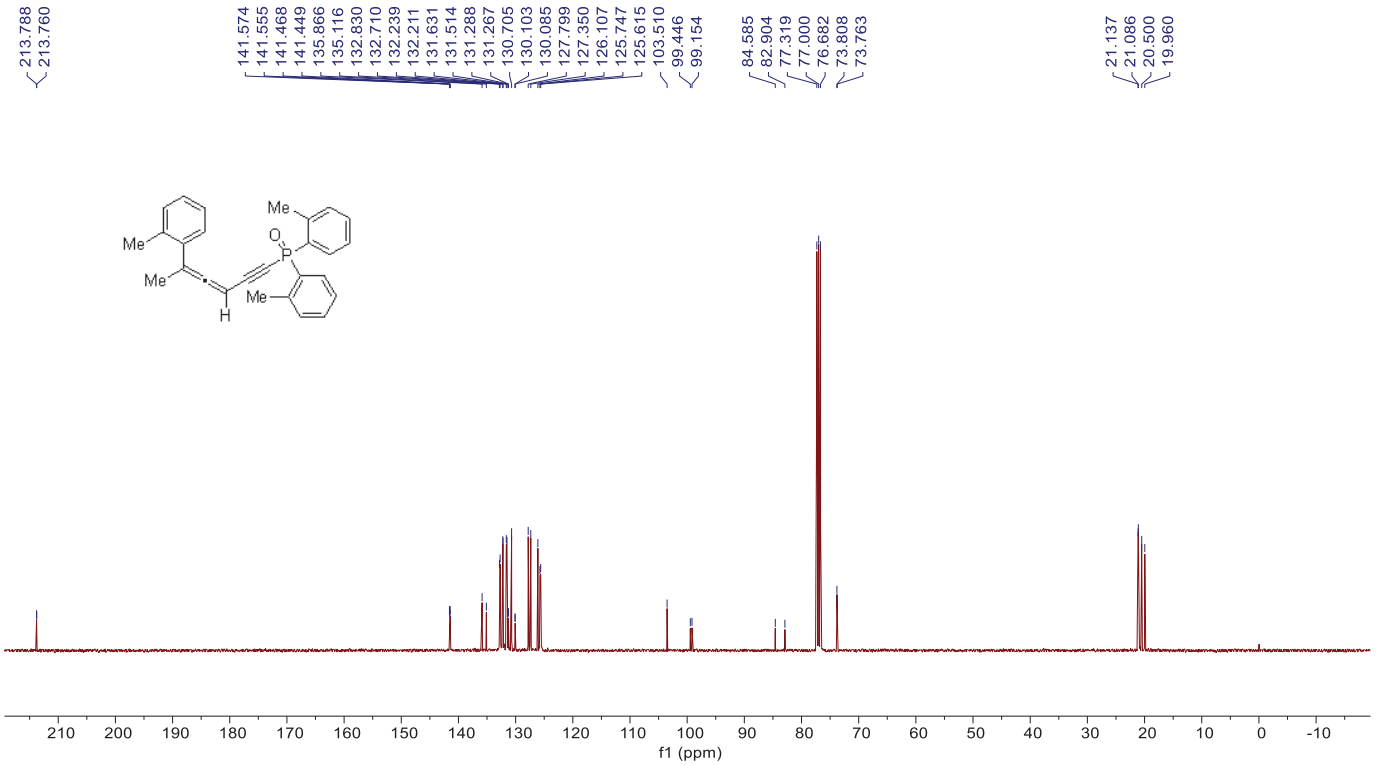
^{31}P NMR of **3l** ($CDCl_3$, 160 MHz)



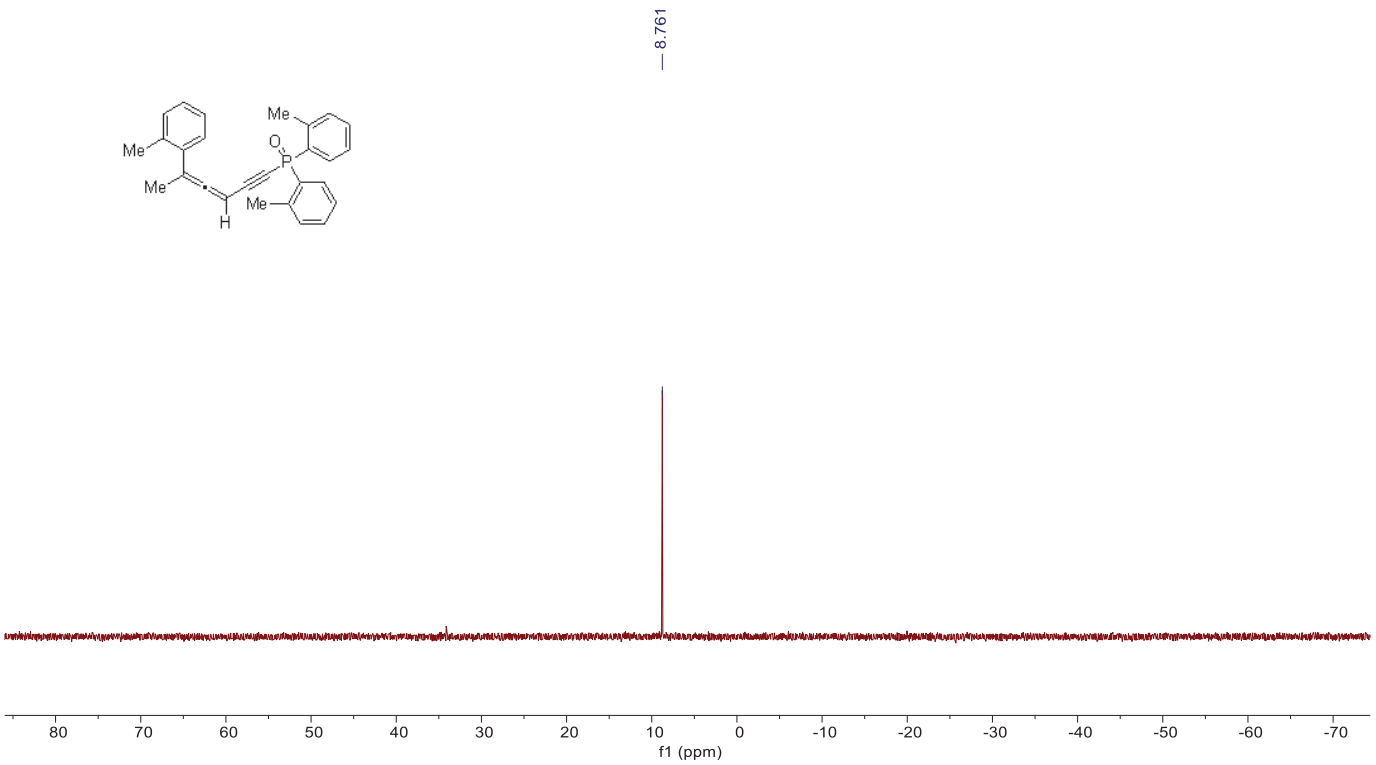
^{1}H NMR of **3m** ($CDCl_3$, 400 MHz)



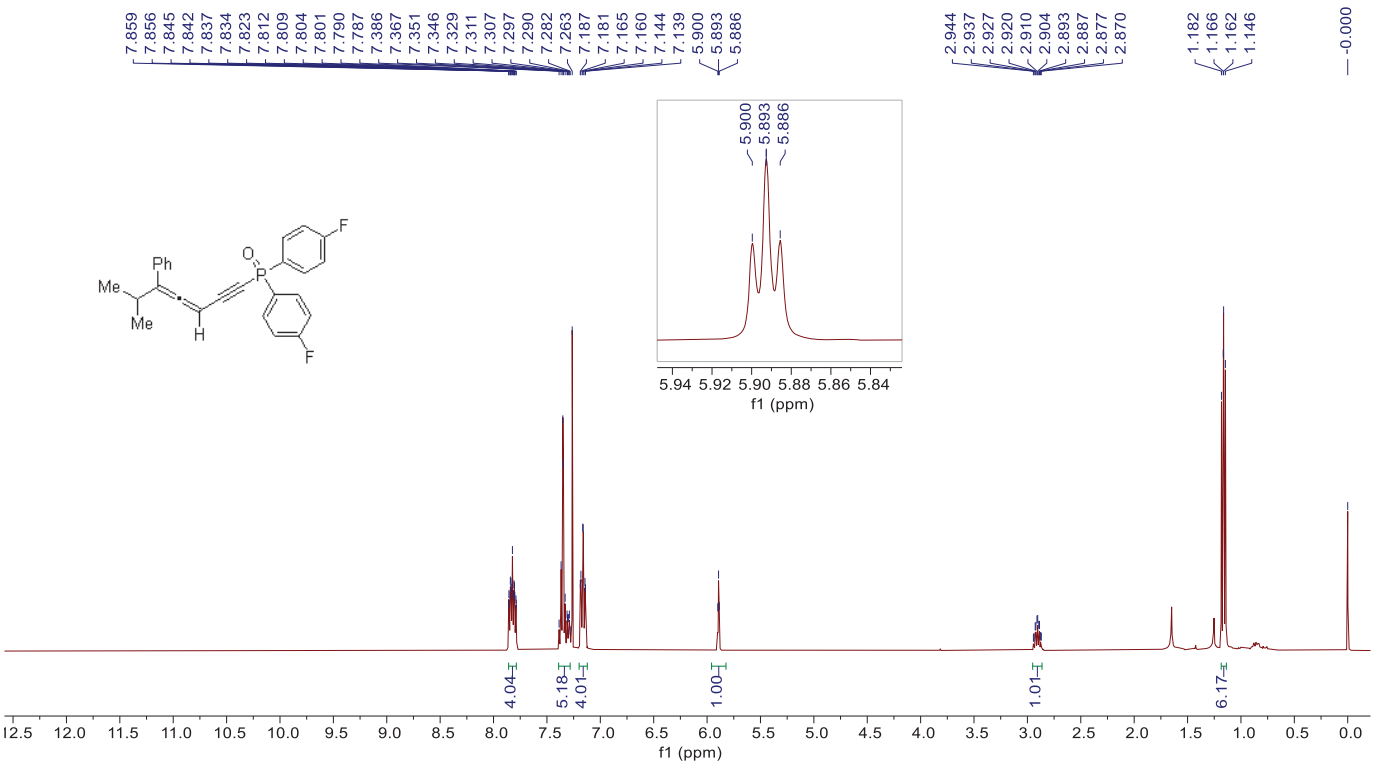
^{13}C NMR of **3m** ($CDCl_3$, 100 MHz)



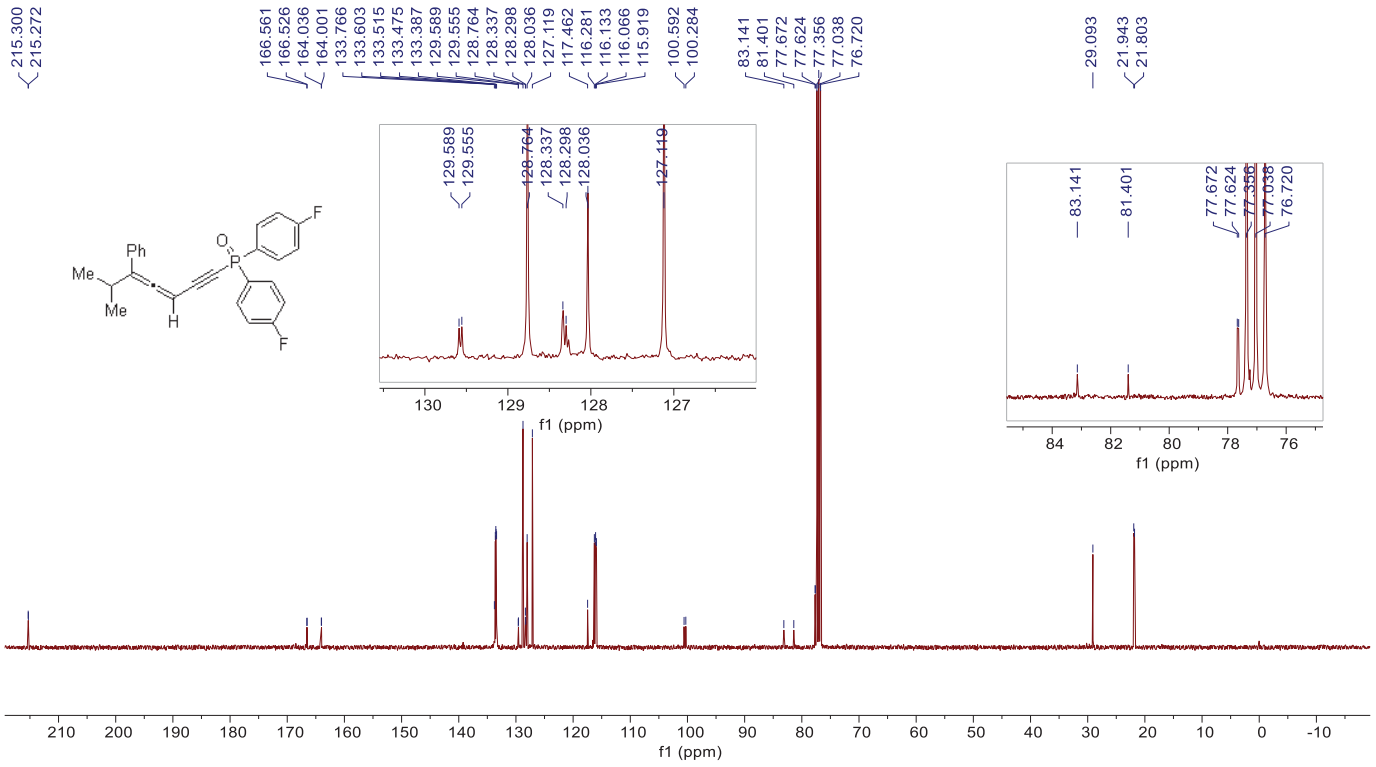
^{31}P NMR of **3m** ($CDCl_3$, 160 MHz)



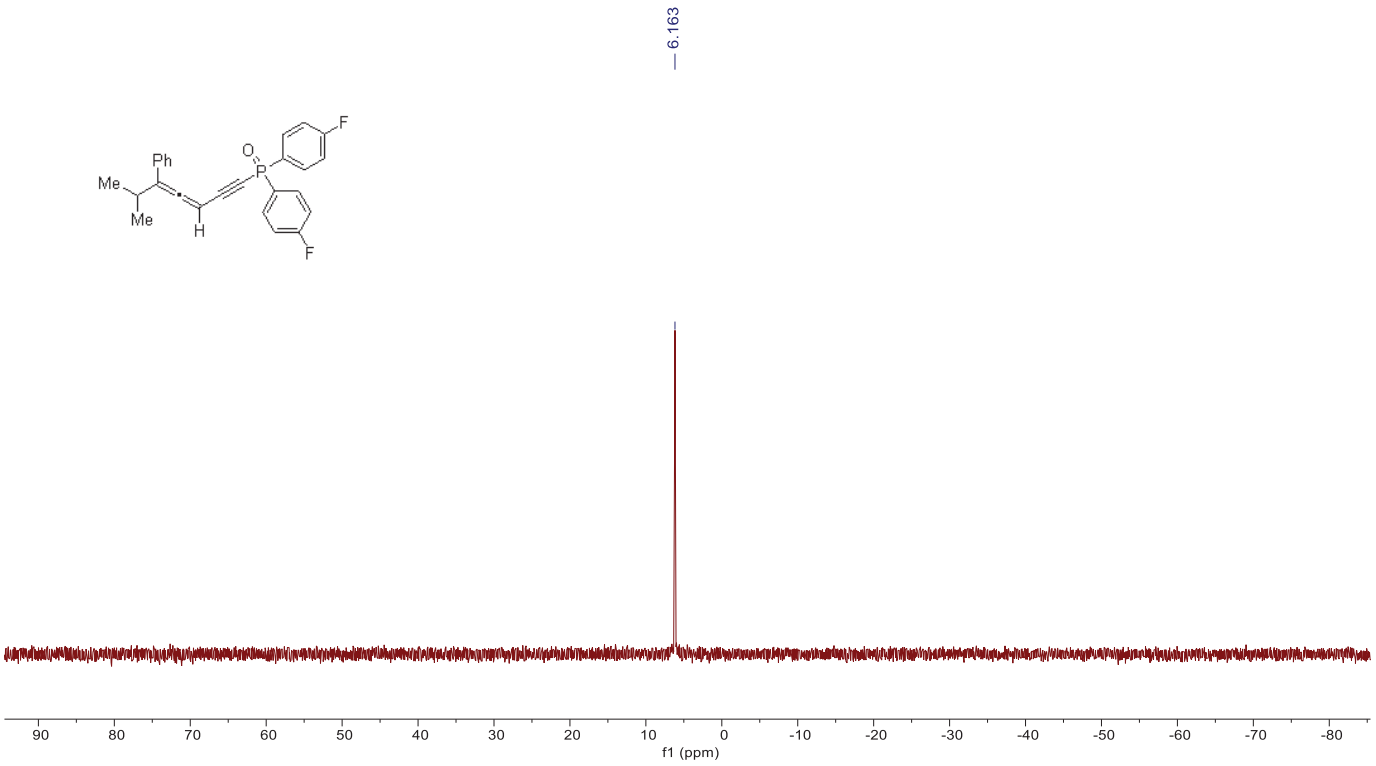
^{1}H NMR of **3n** ($CDCl_3$, 400 MHz)



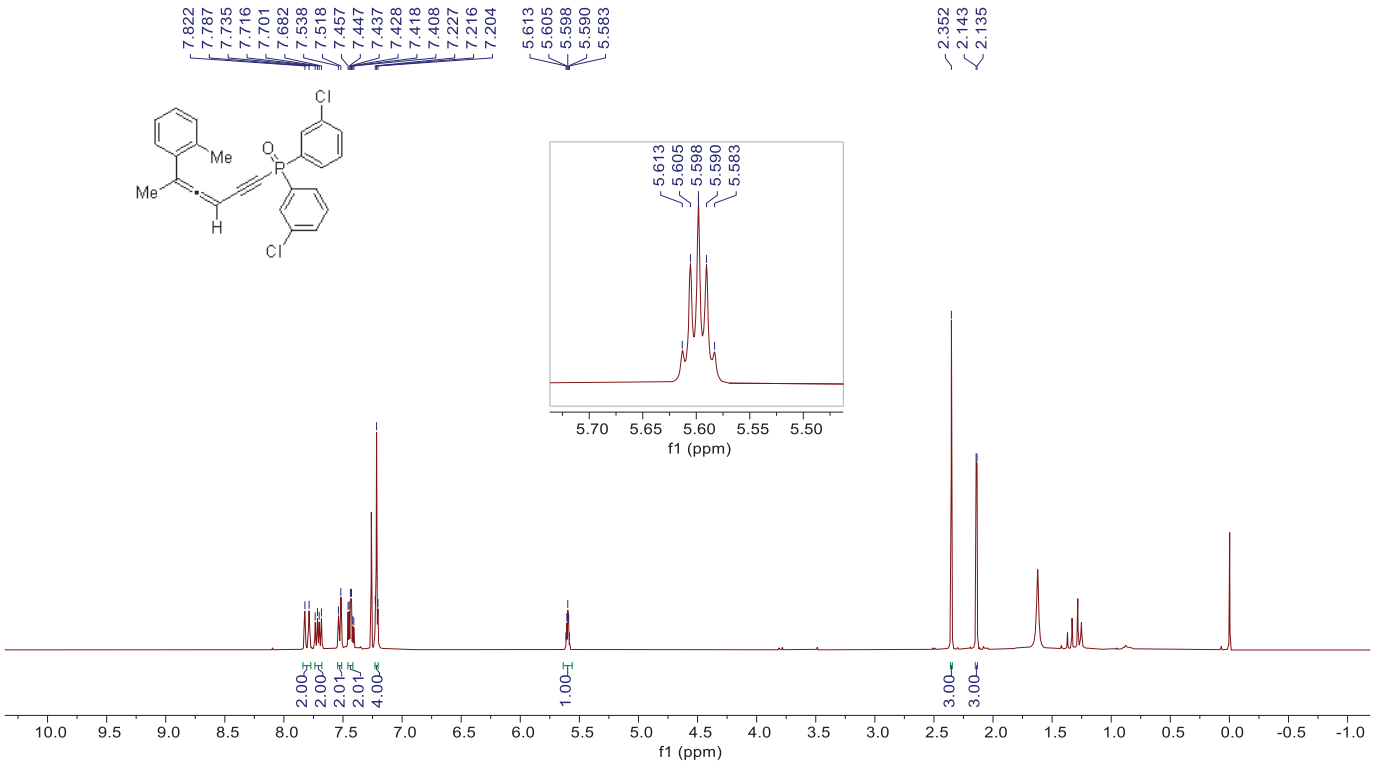
^{13}C NMR of **3n** ($CDCl_3$, 100 MHz)



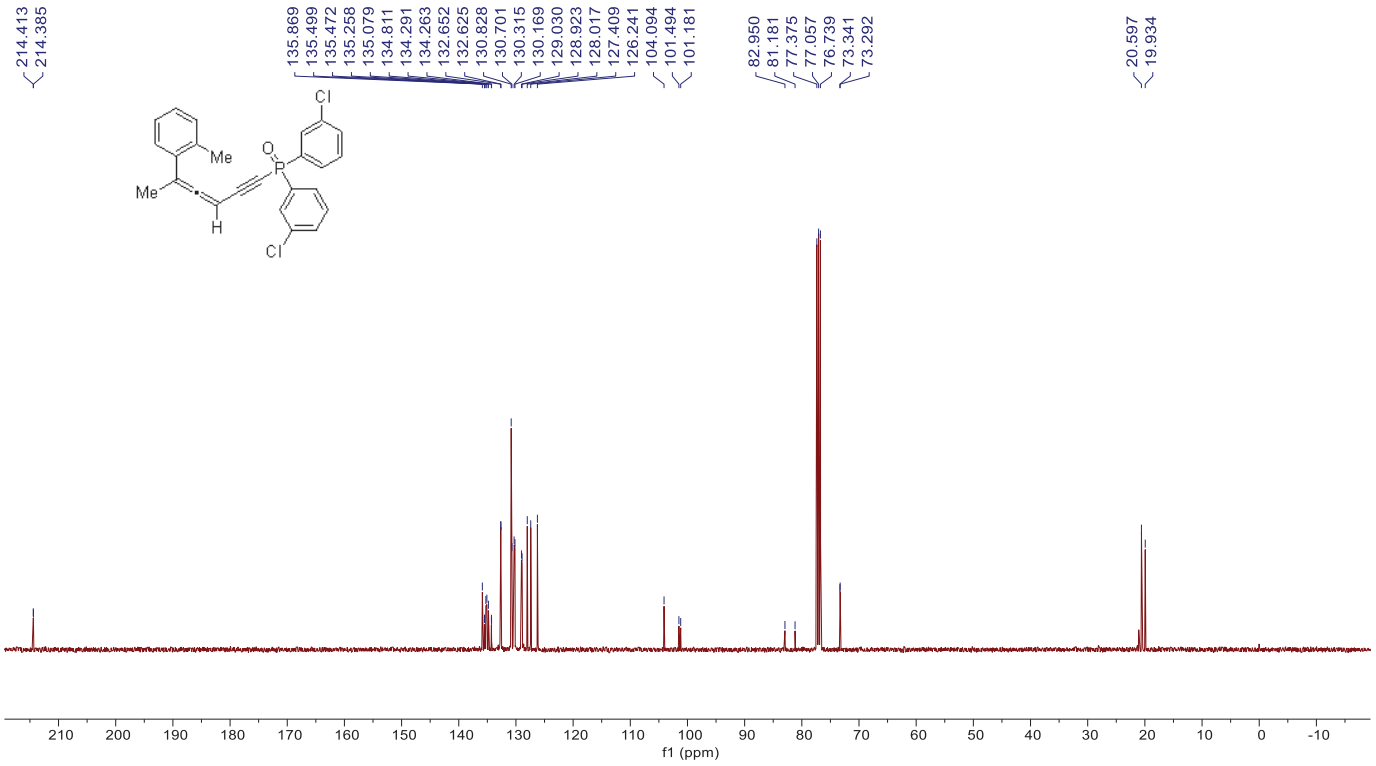
^{31}P NMR of **3n** ($CDCl_3$, 160 MHz)



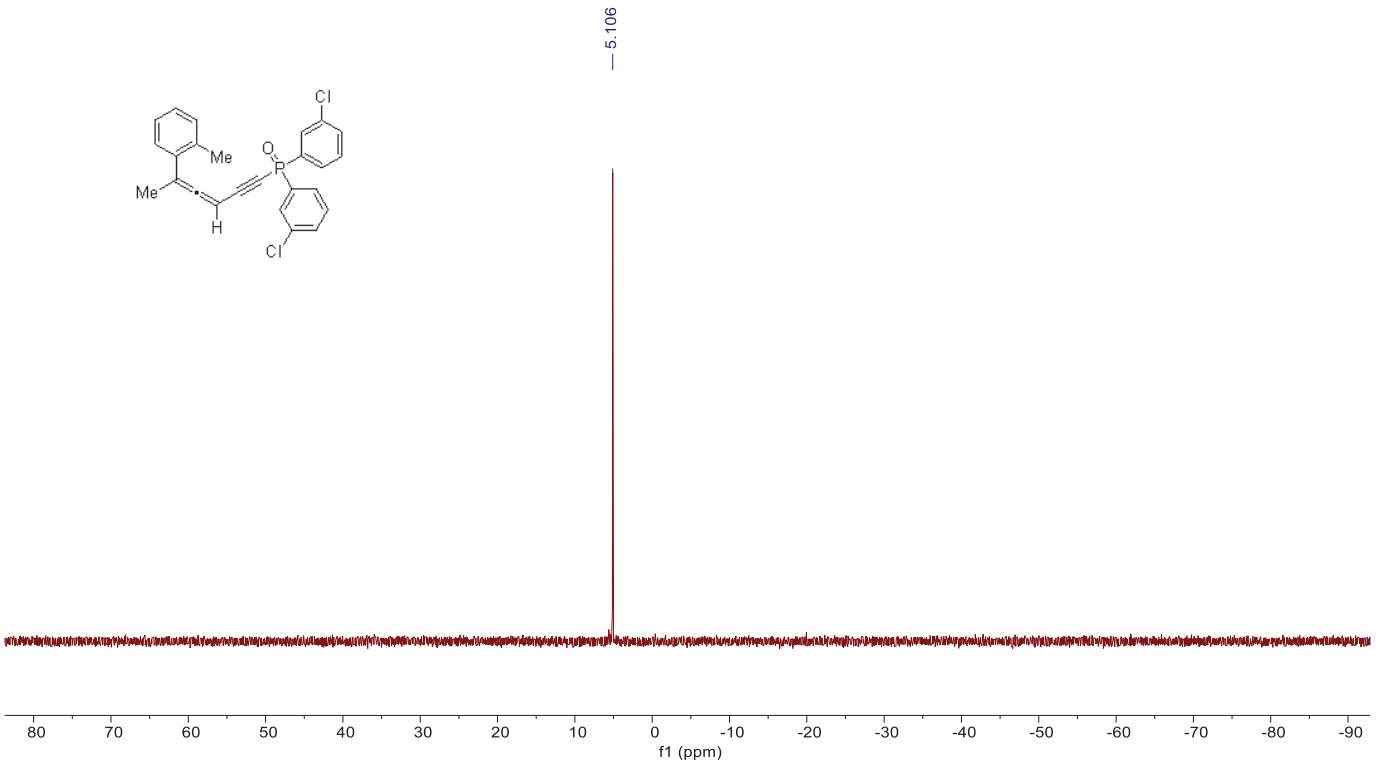
^{1}H NMR of **3o** ($CDCl_3$, 400 MHz)



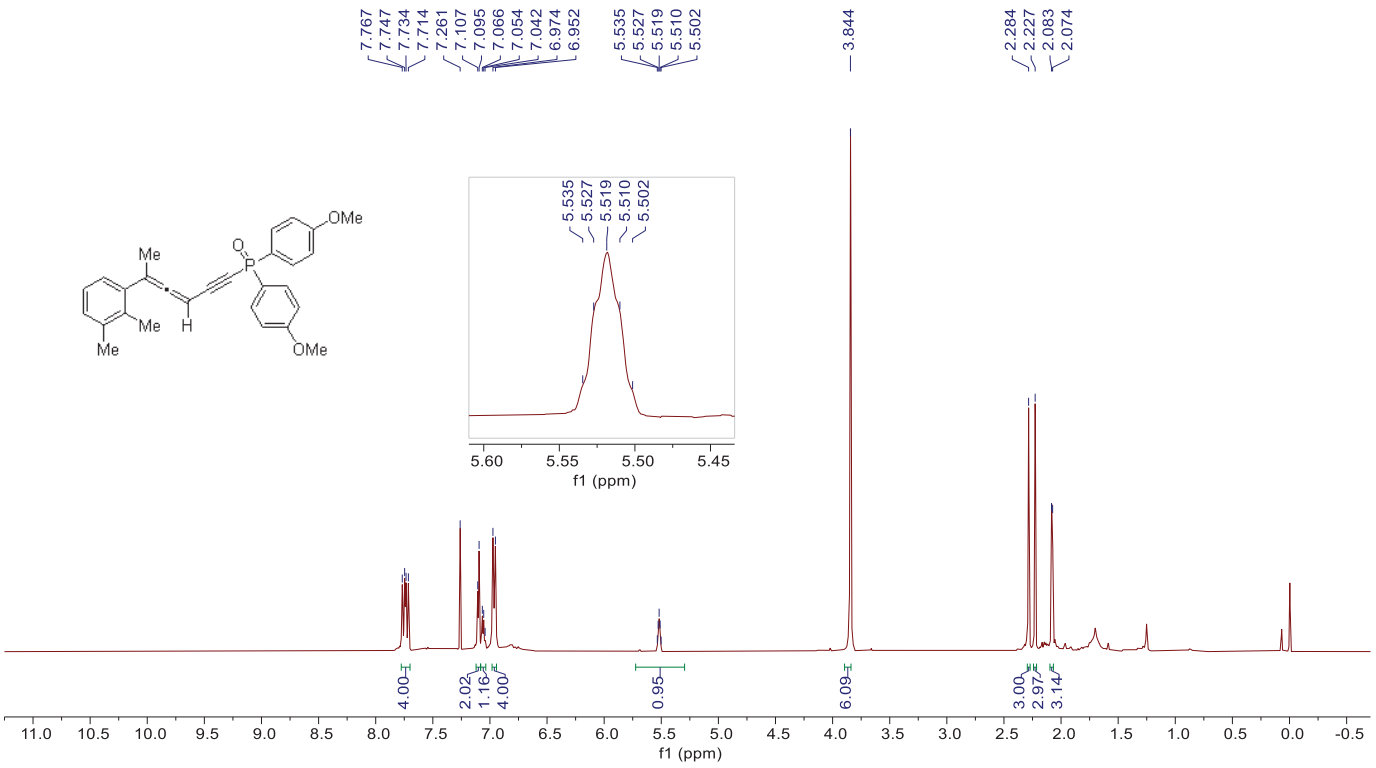
^{13}C NMR of **3o** ($CDCl_3$, 100 MHz)



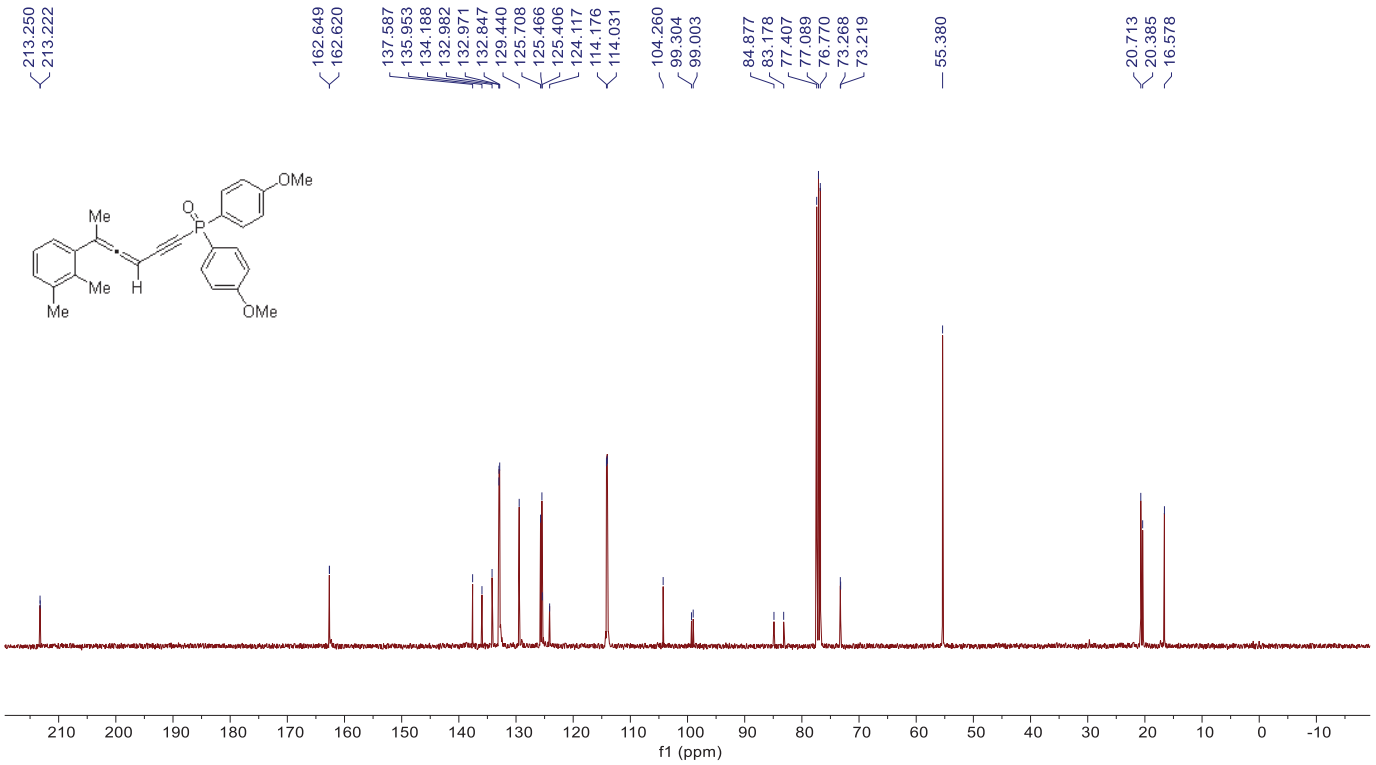
^{31}P NMR of **3o** ($CDCl_3$, 160 MHz)



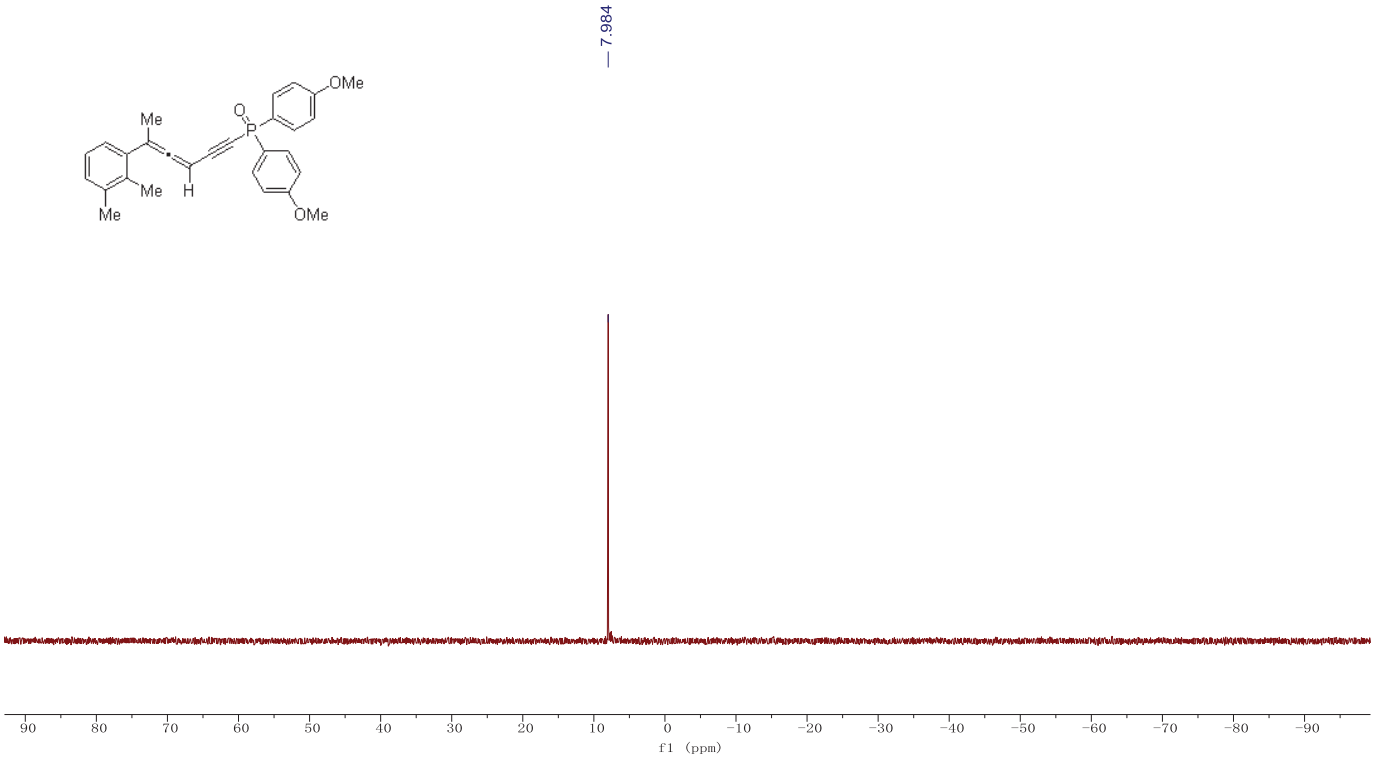
^{1}H NMR of **3p** ($CDCl_3$, 400 MHz)



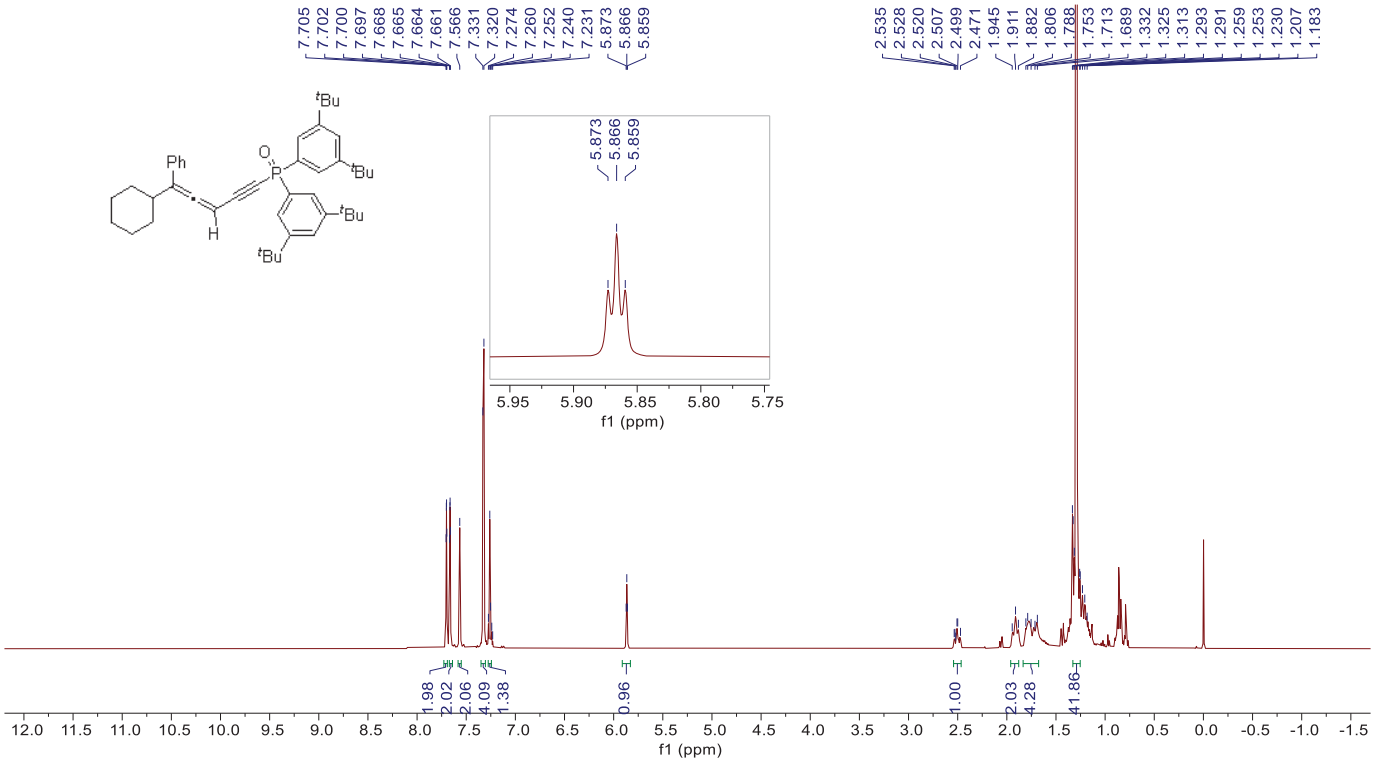
^{13}C NMR of **3p** ($CDCl_3$, 100 MHz)



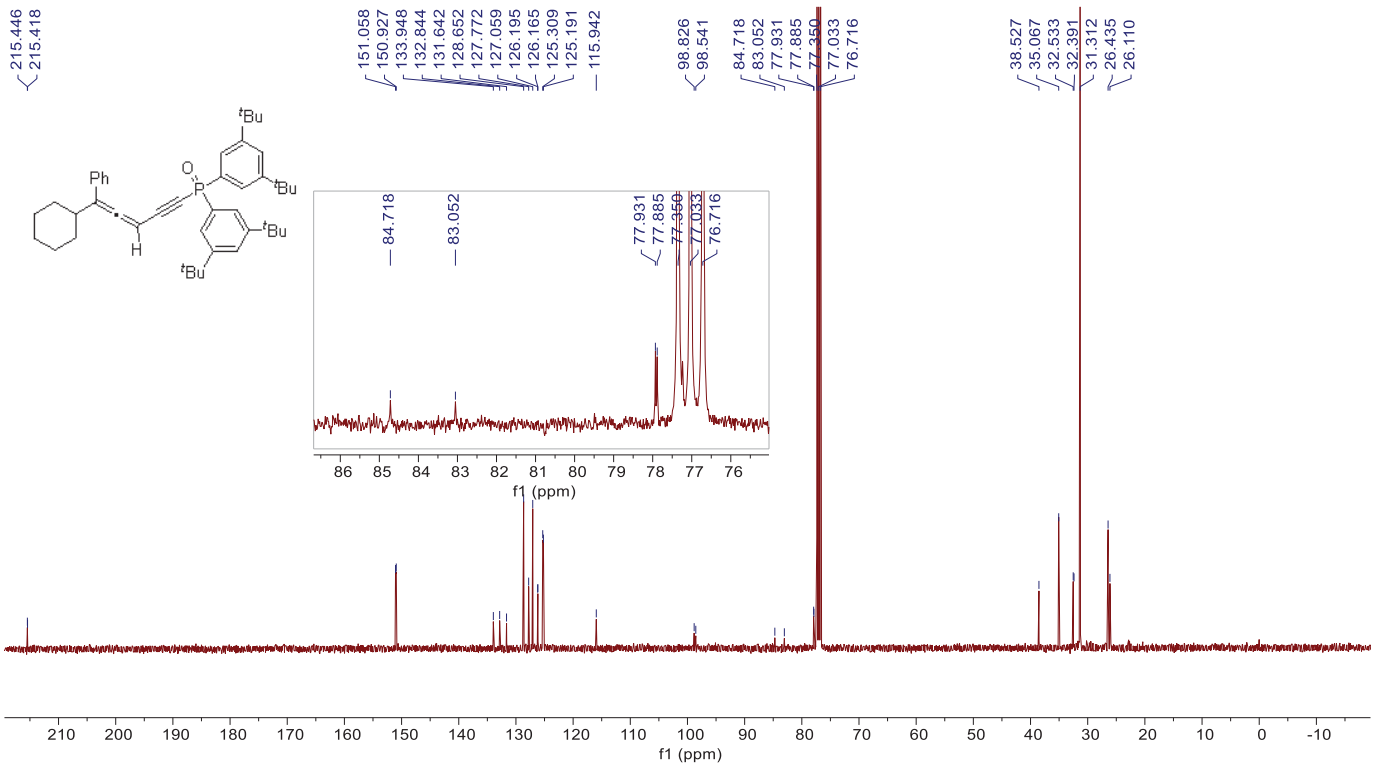
^{31}P NMR of **3p** ($CDCl_3$, 160 MHz)



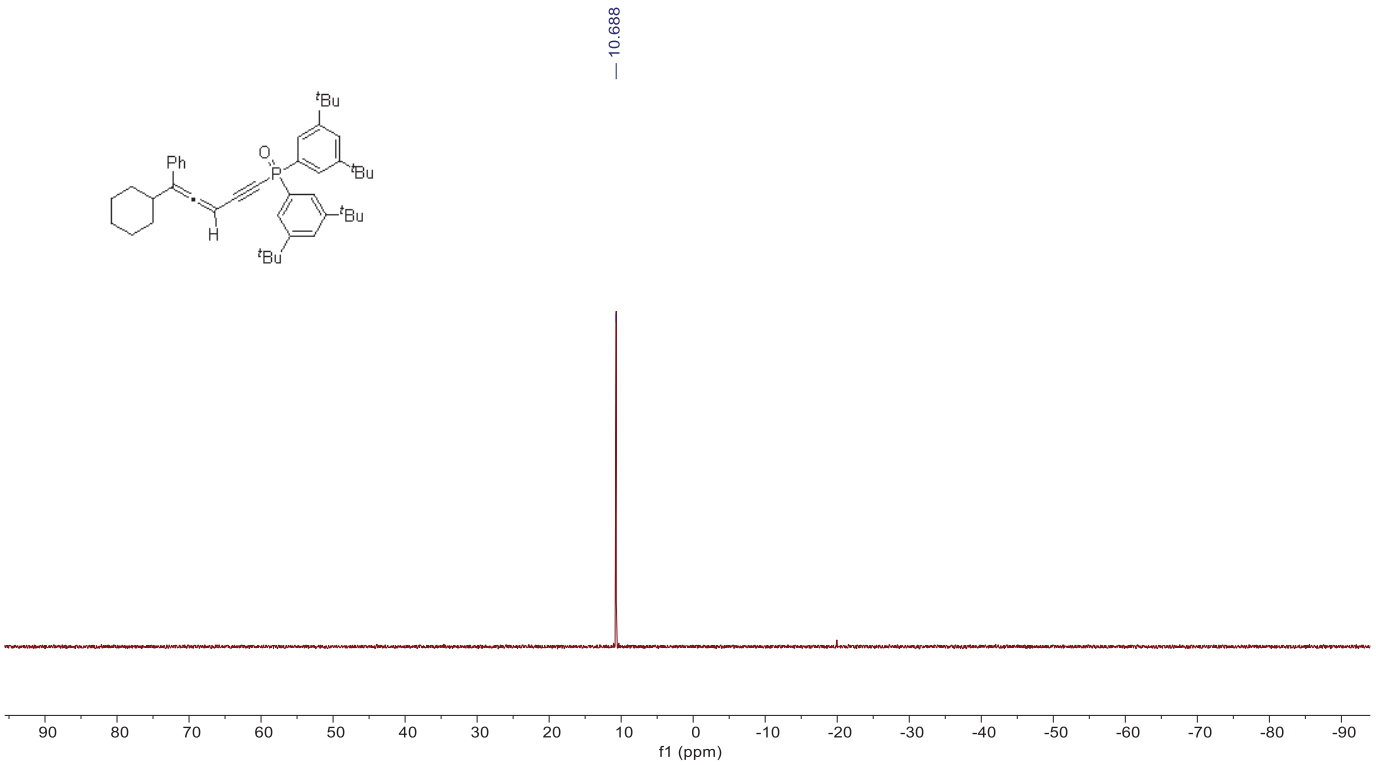
^{1}H NMR of **3q** ($CDCl_3$, 400 MHz)



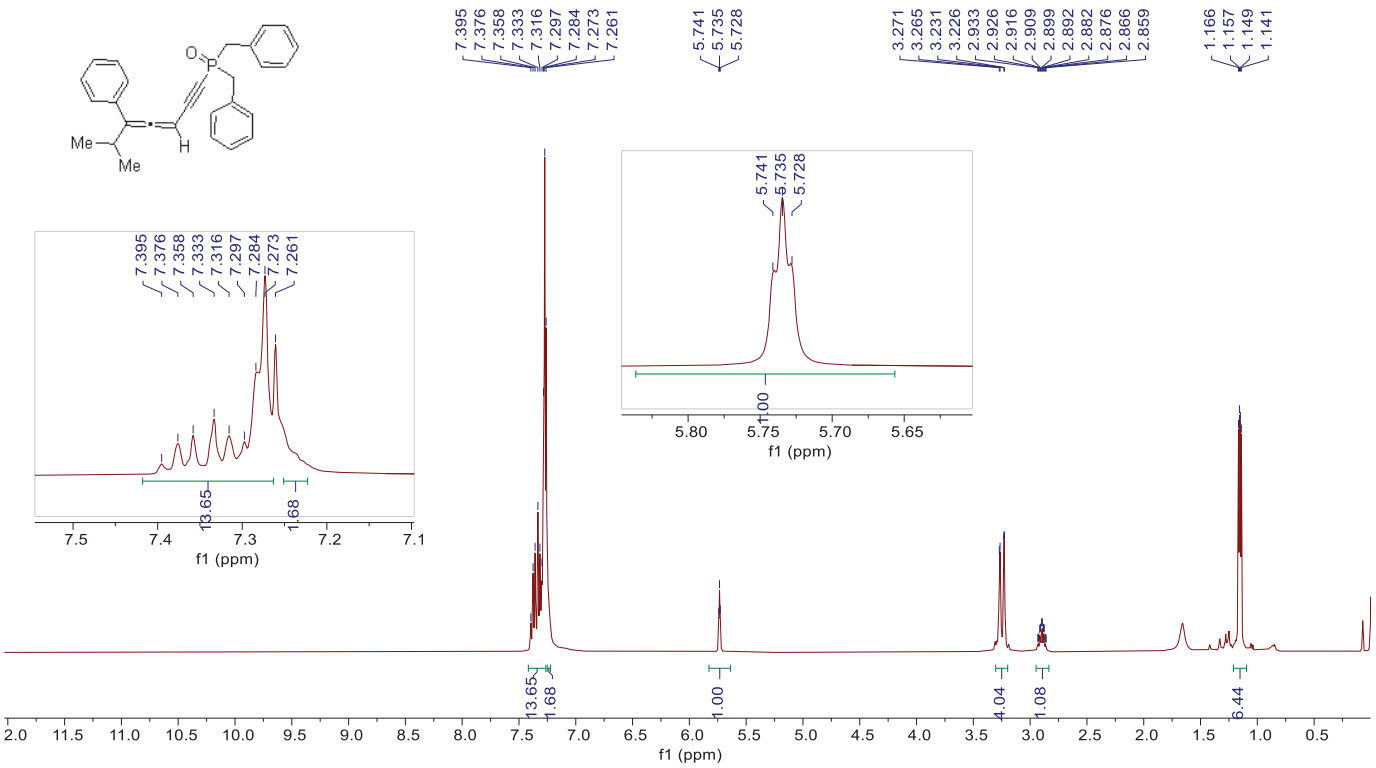
^{13}C NMR of **3q** ($CDCl_3$, 100 MHz)



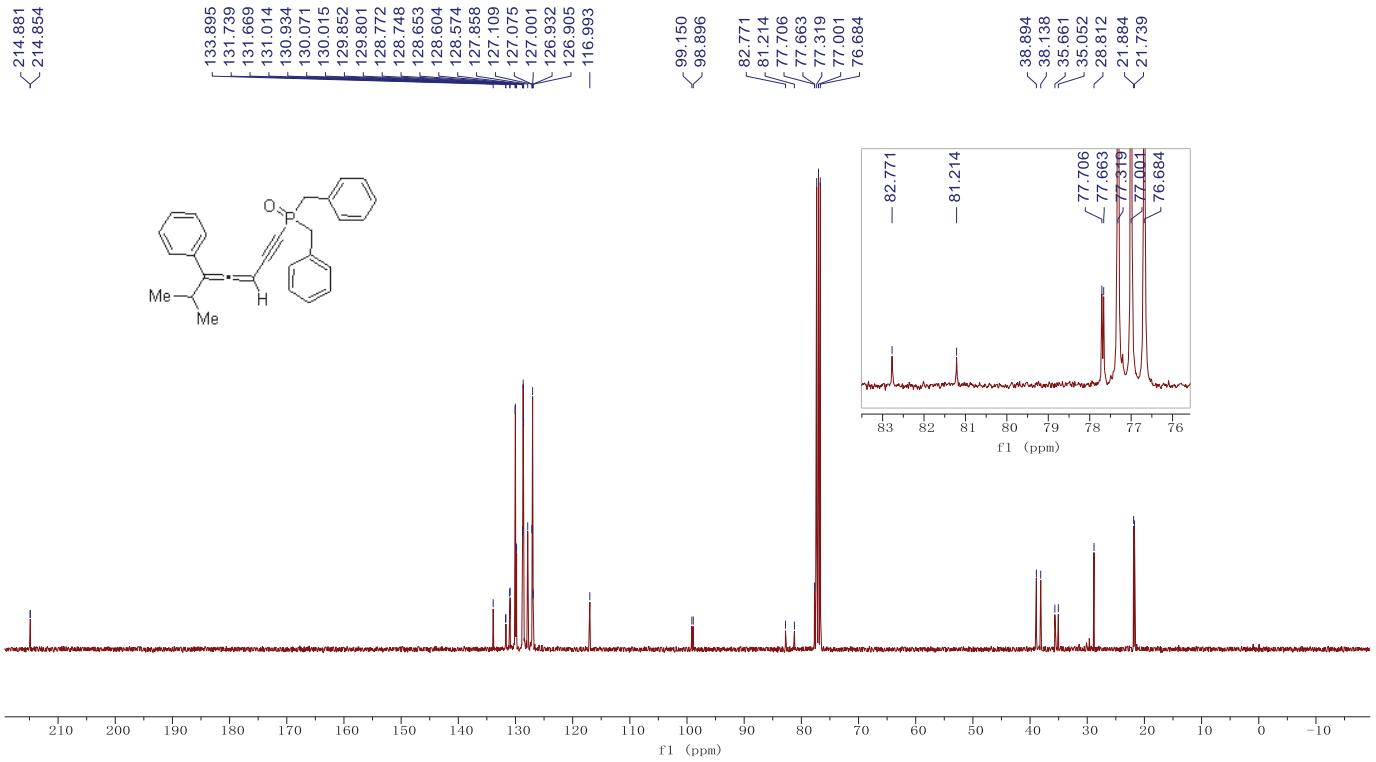
^{31}P NMR of **3q** ($CDCl_3$, 160 MHz)



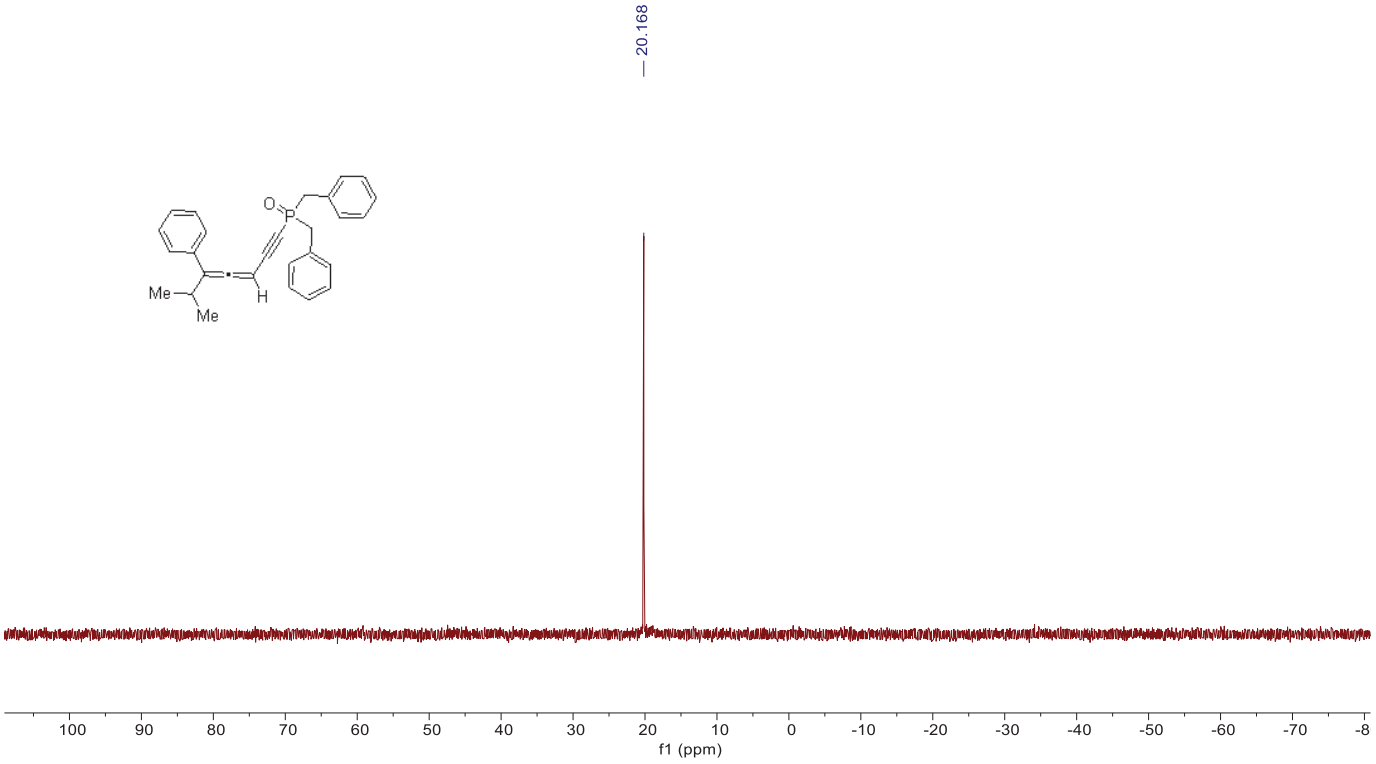
^{1}H NMR of **3r** ($CDCl_3$, 400 MHz)



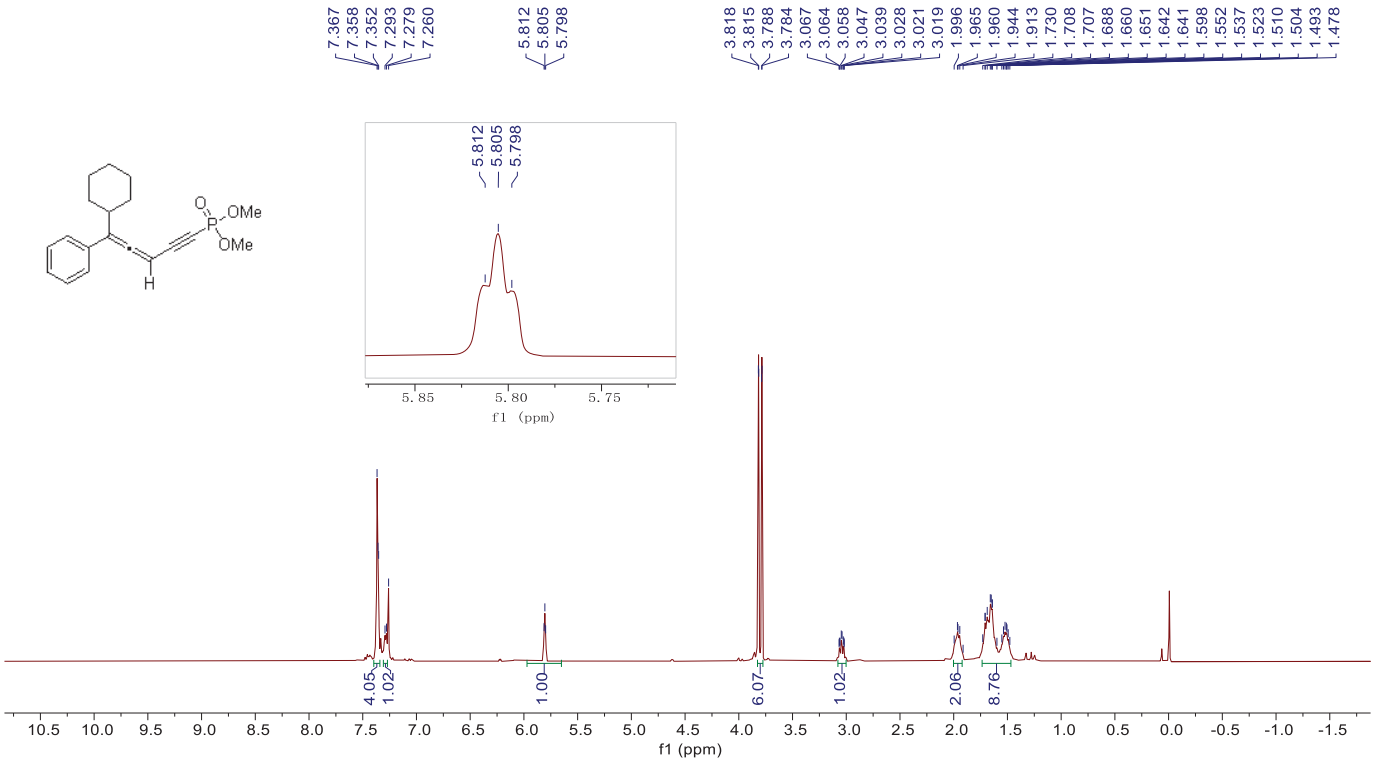
^{13}C NMR of **3r** ($CDCl_3$, 100 MHz)



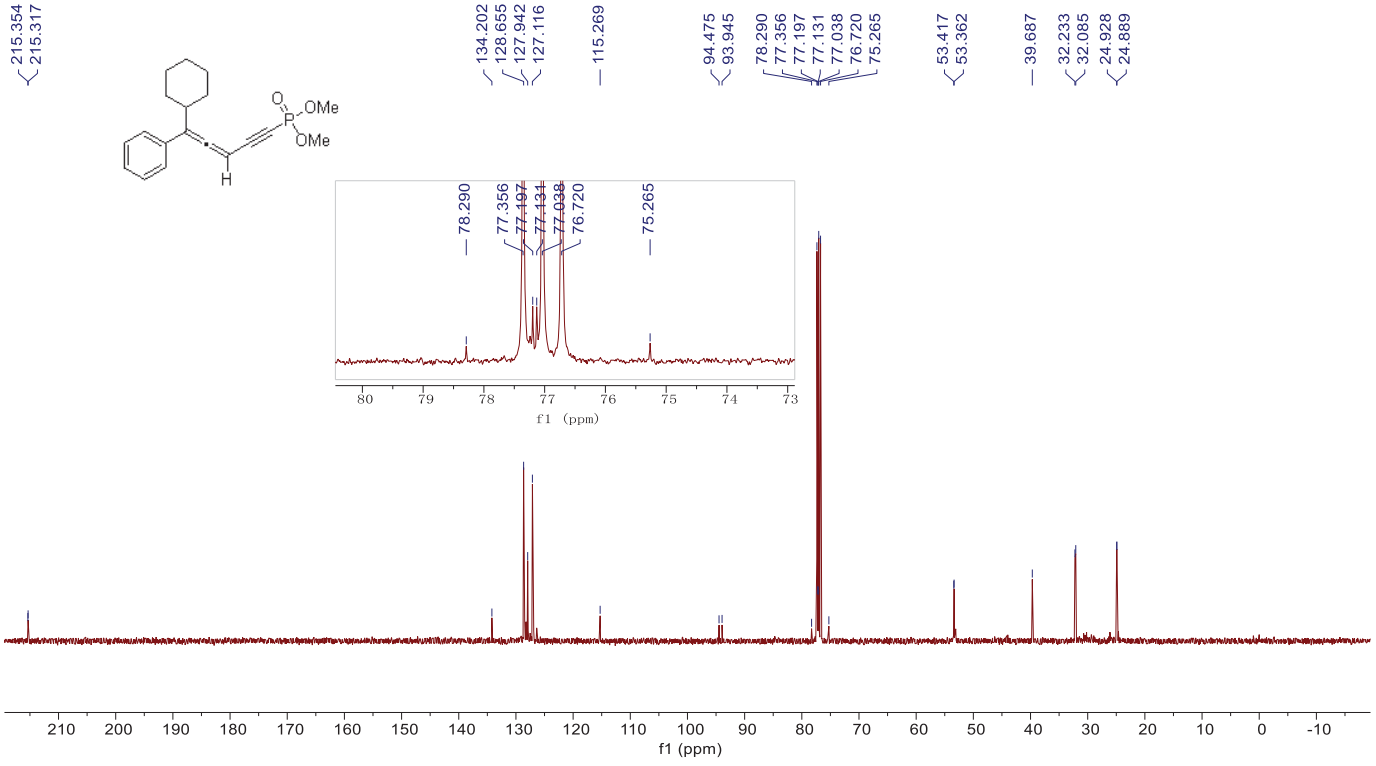
^{31}P NMR of **3r** ($CDCl_3$, 160 MHz)



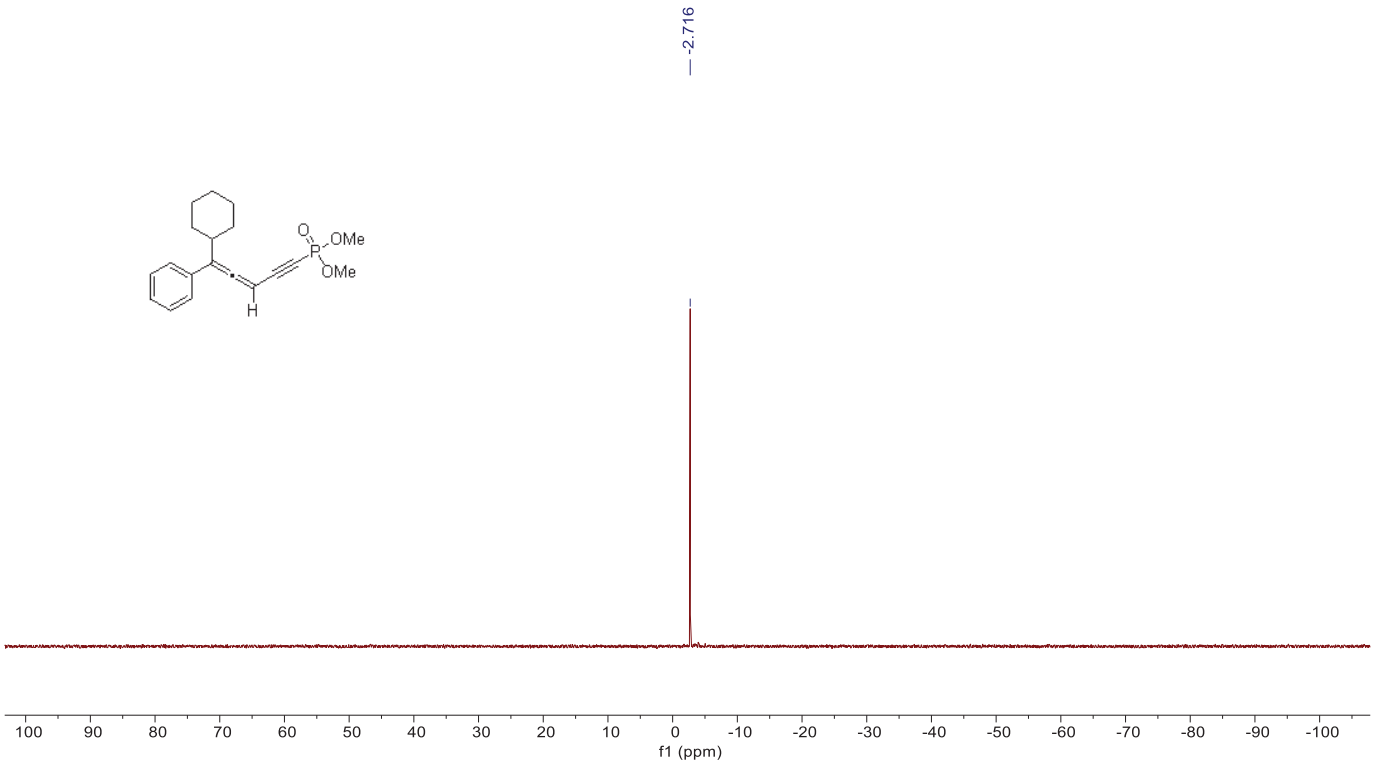
^{1}H NMR of **3t** ($CDCl_3$, 400 MHz)



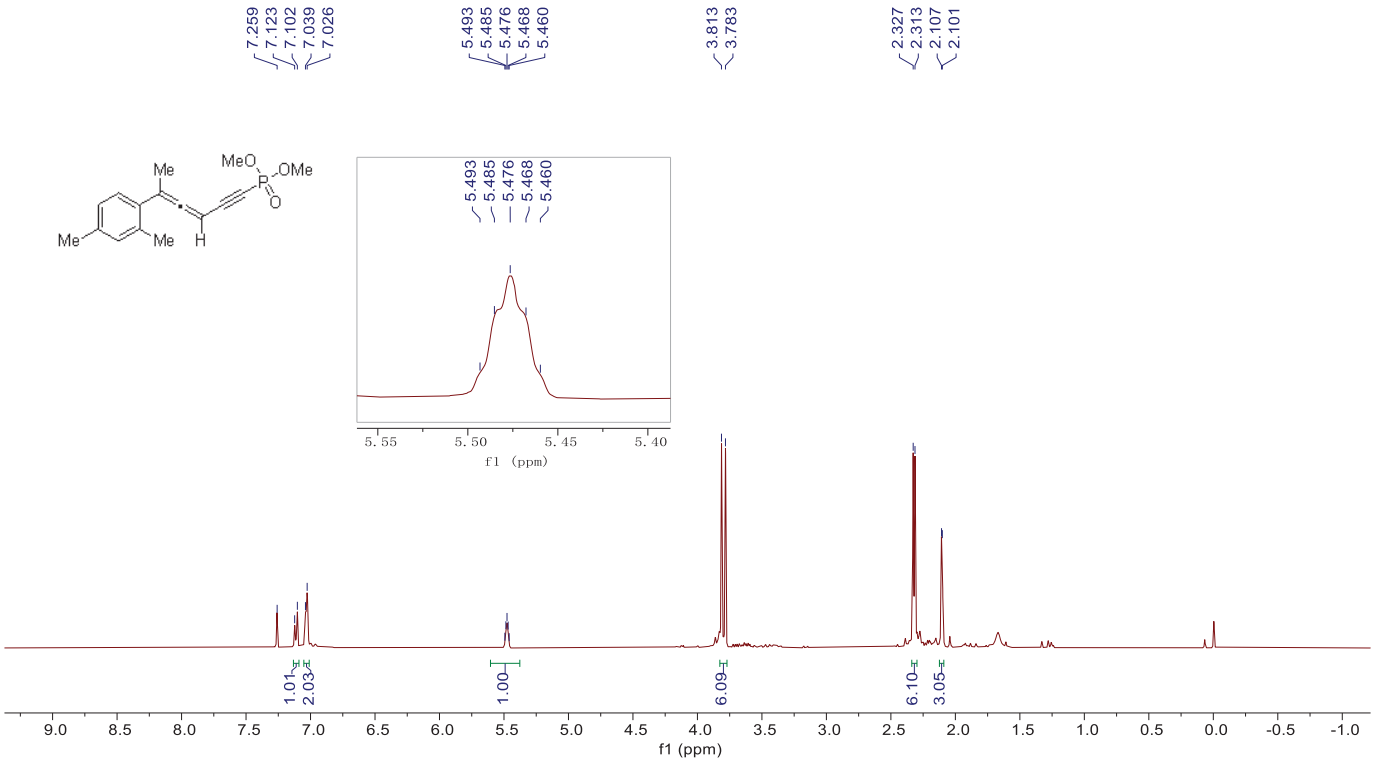
^{13}C NMR of **3t** ($CDCl_3$, 100 MHz)



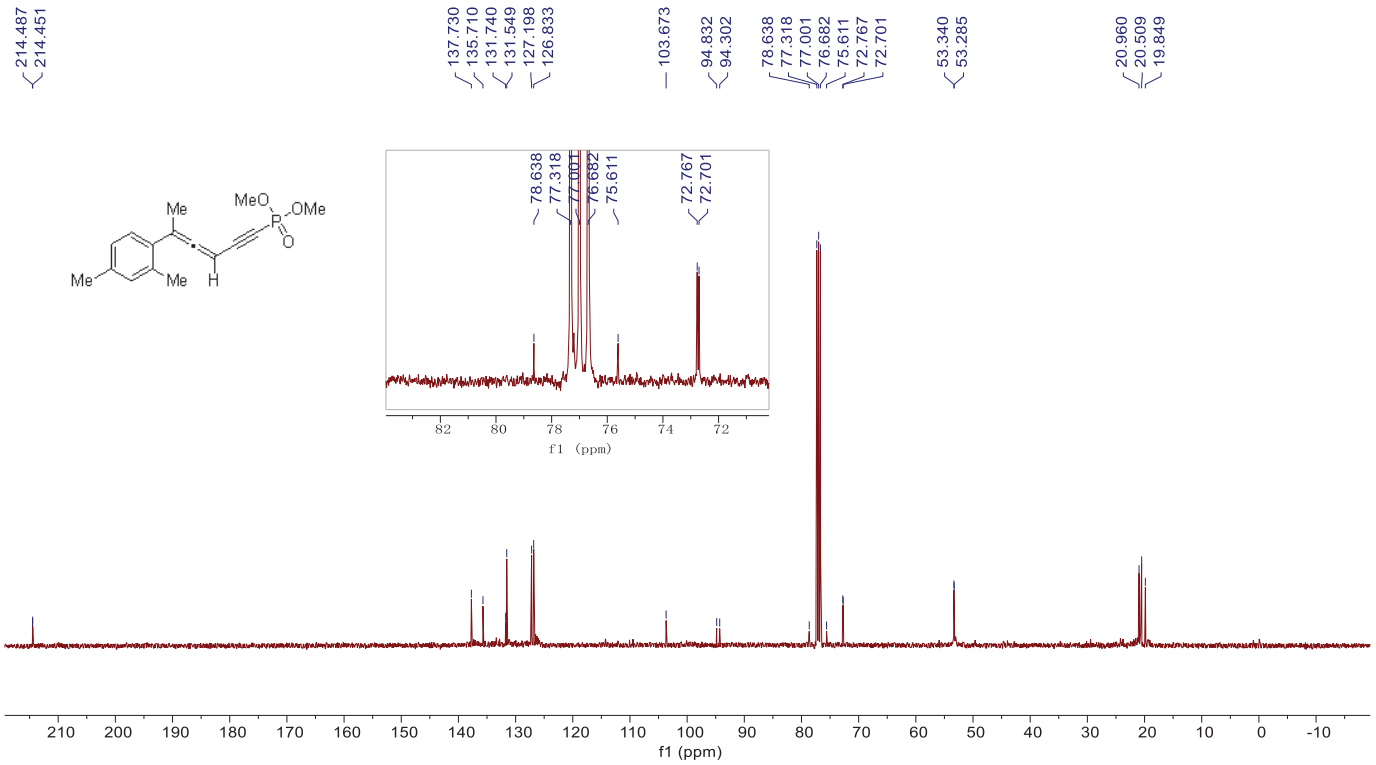
^{31}P NMR of **3t** ($CDCl_3$, 160 MHz)



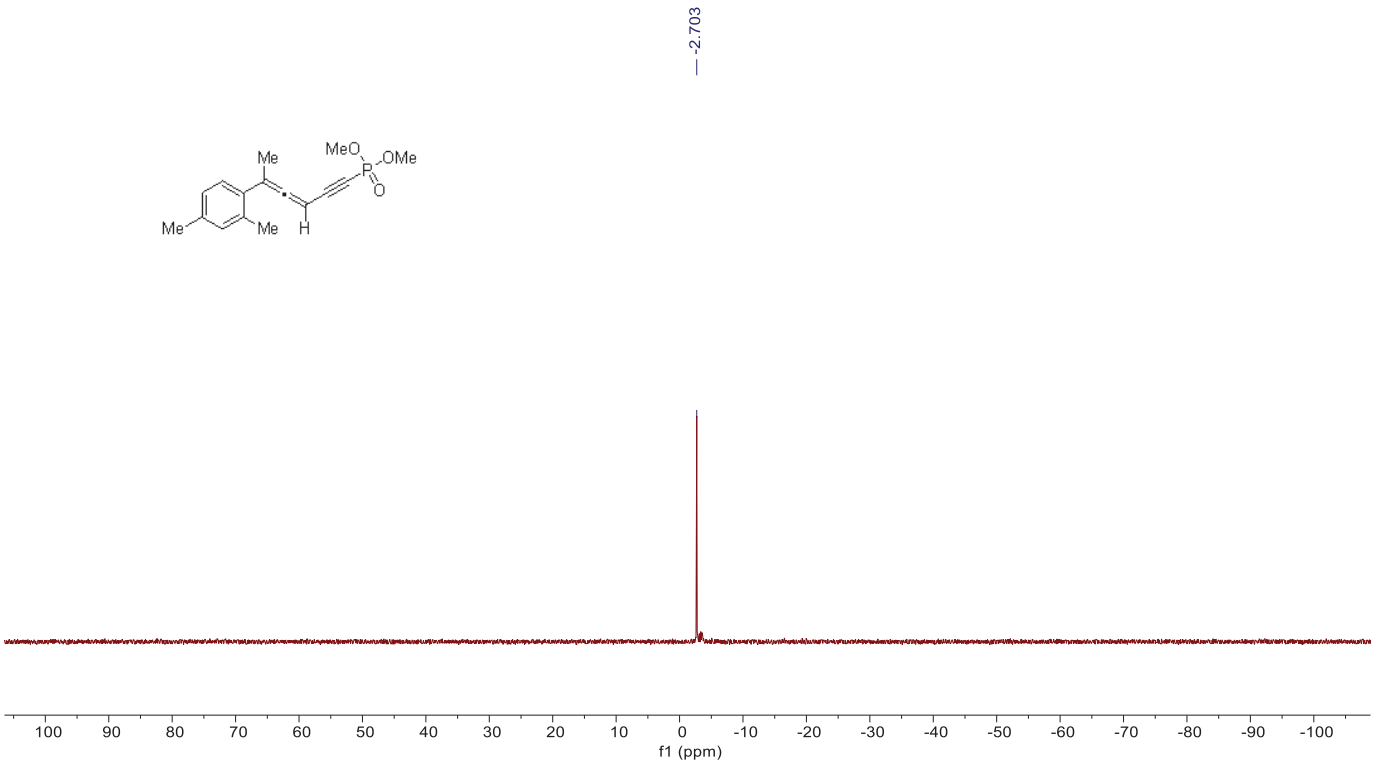
^{1}H NMR of **3u** ($CDCl_3$, 400 MHz)



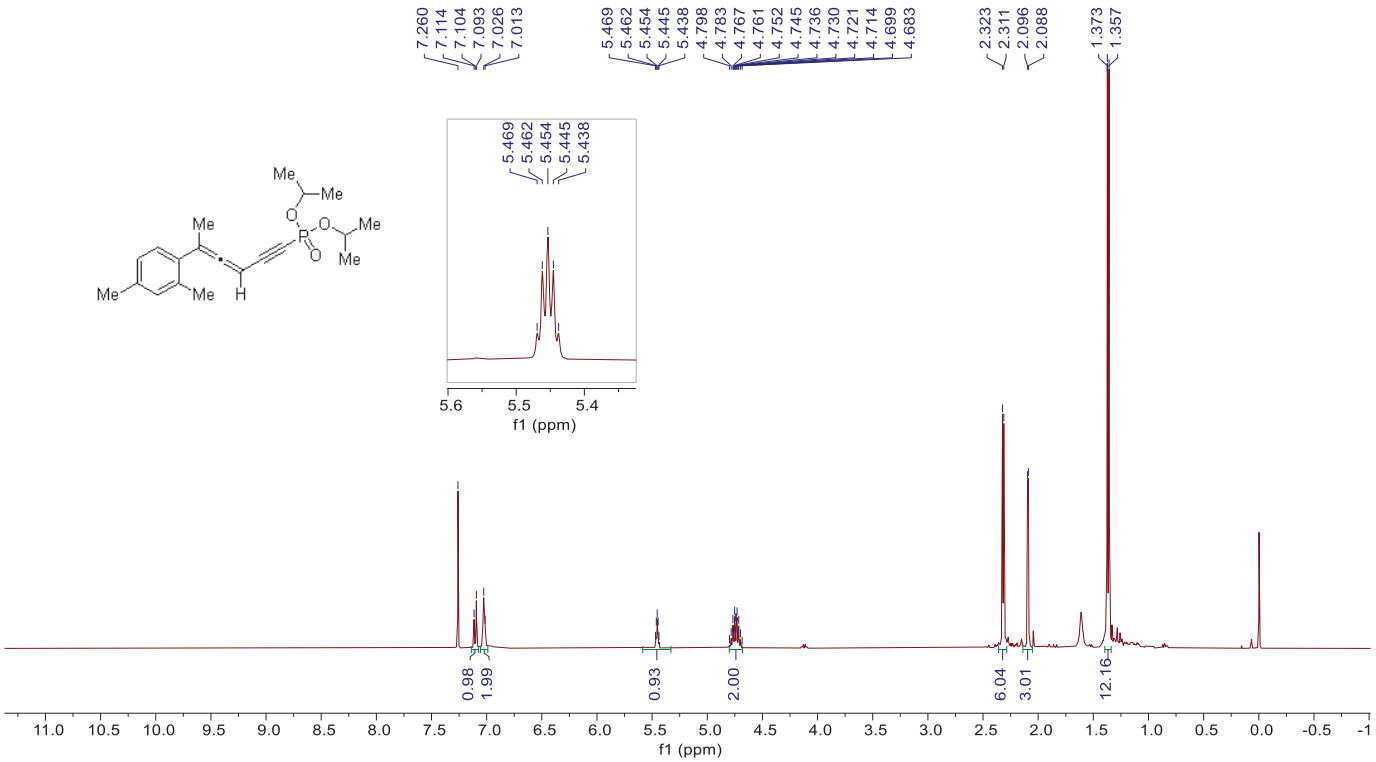
^{13}C NMR of **3u** ($CDCl_3$, 100 MHz)



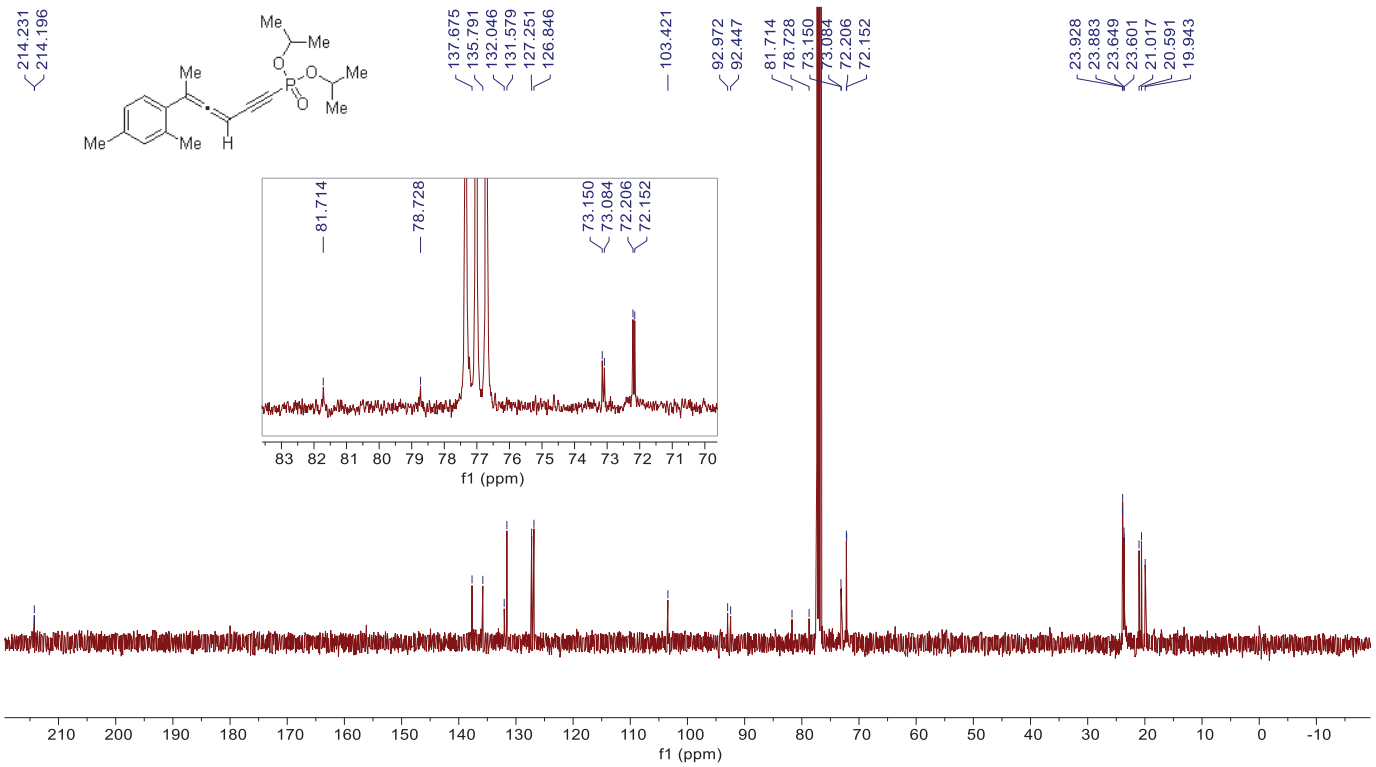
^{31}P NMR of **3u** ($CDCl_3$, 160 MHz)



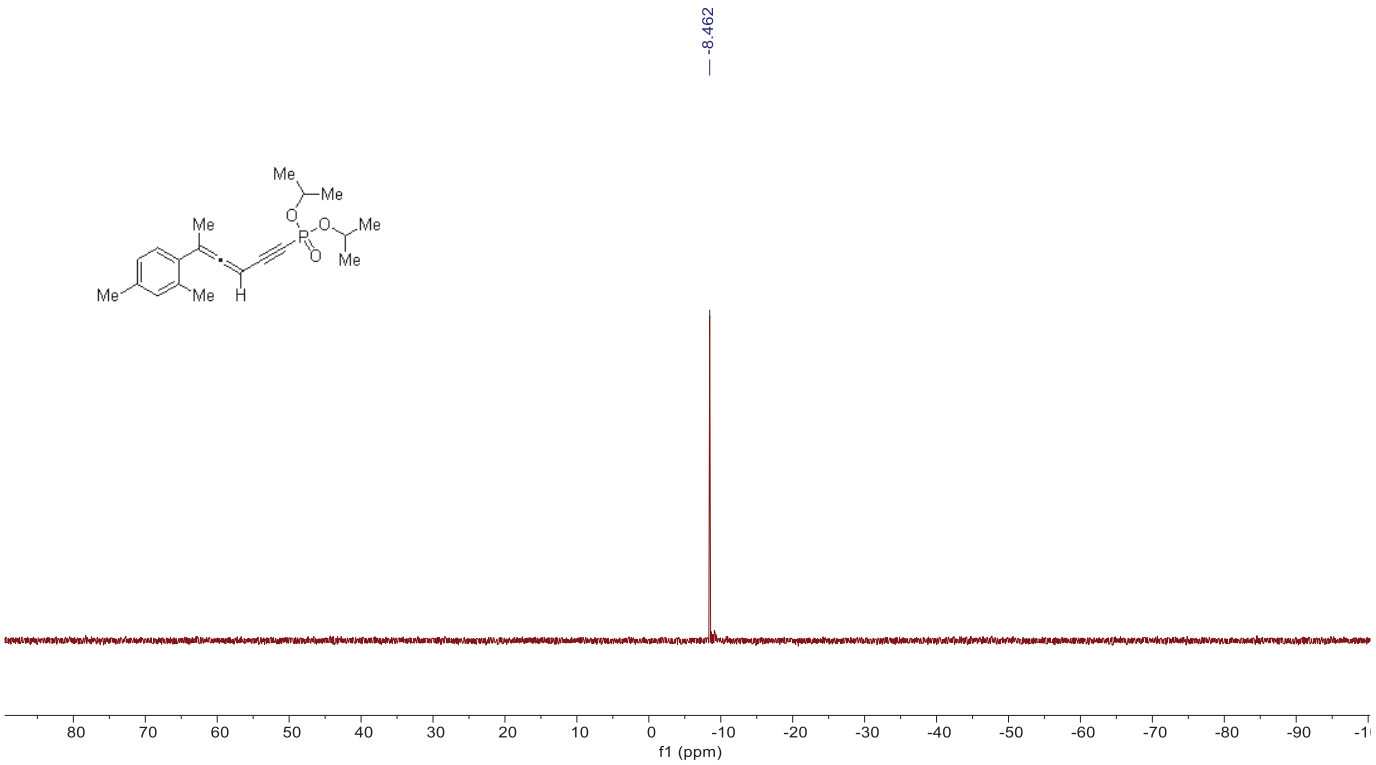
^{1}H NMR of **3v** ($CDCl_3$, 400 MHz)



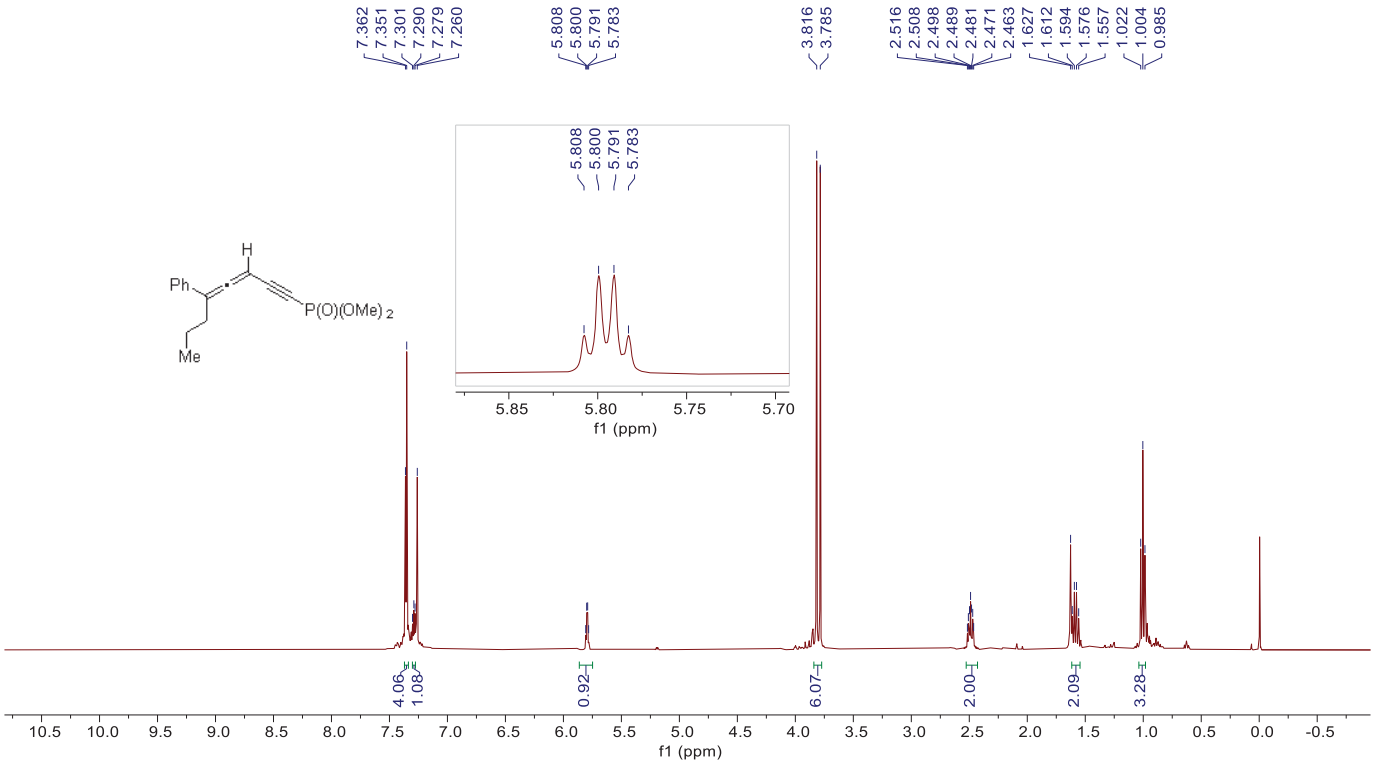
^{13}C NMR of **3v** ($CDCl_3$, 100 MHz)



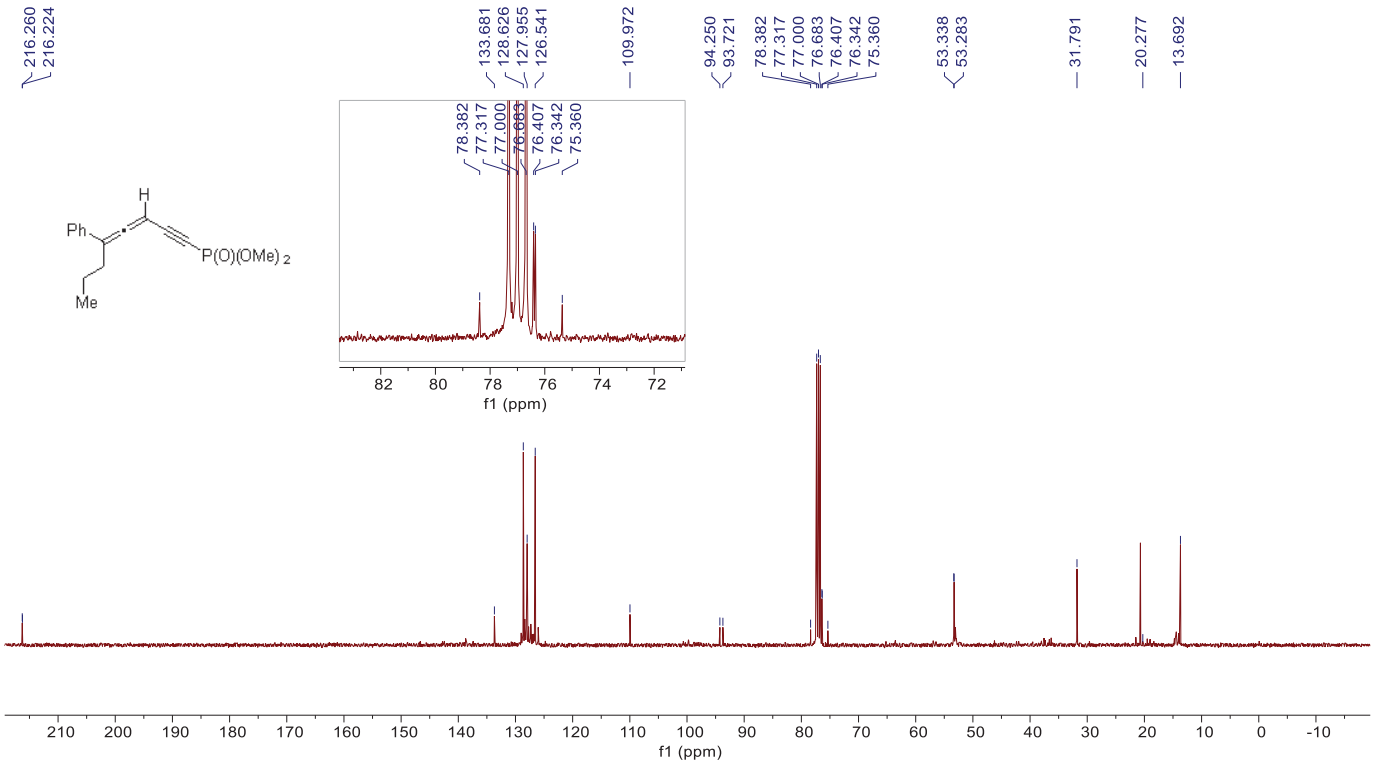
^{31}P NMR of **3v** ($CDCl_3$, 160 MHz)



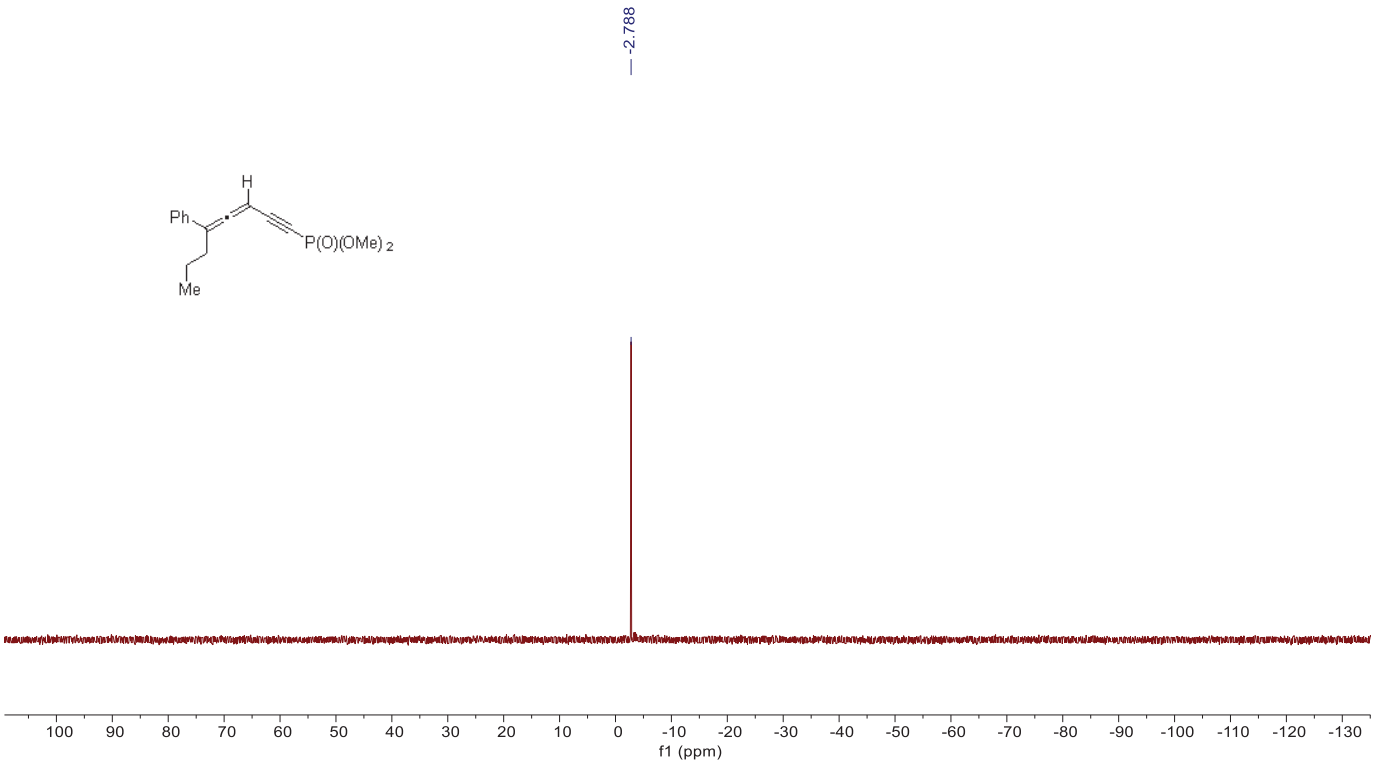
^{1}H NMR of **3w** ($CDCl_3$, 400 MHz)



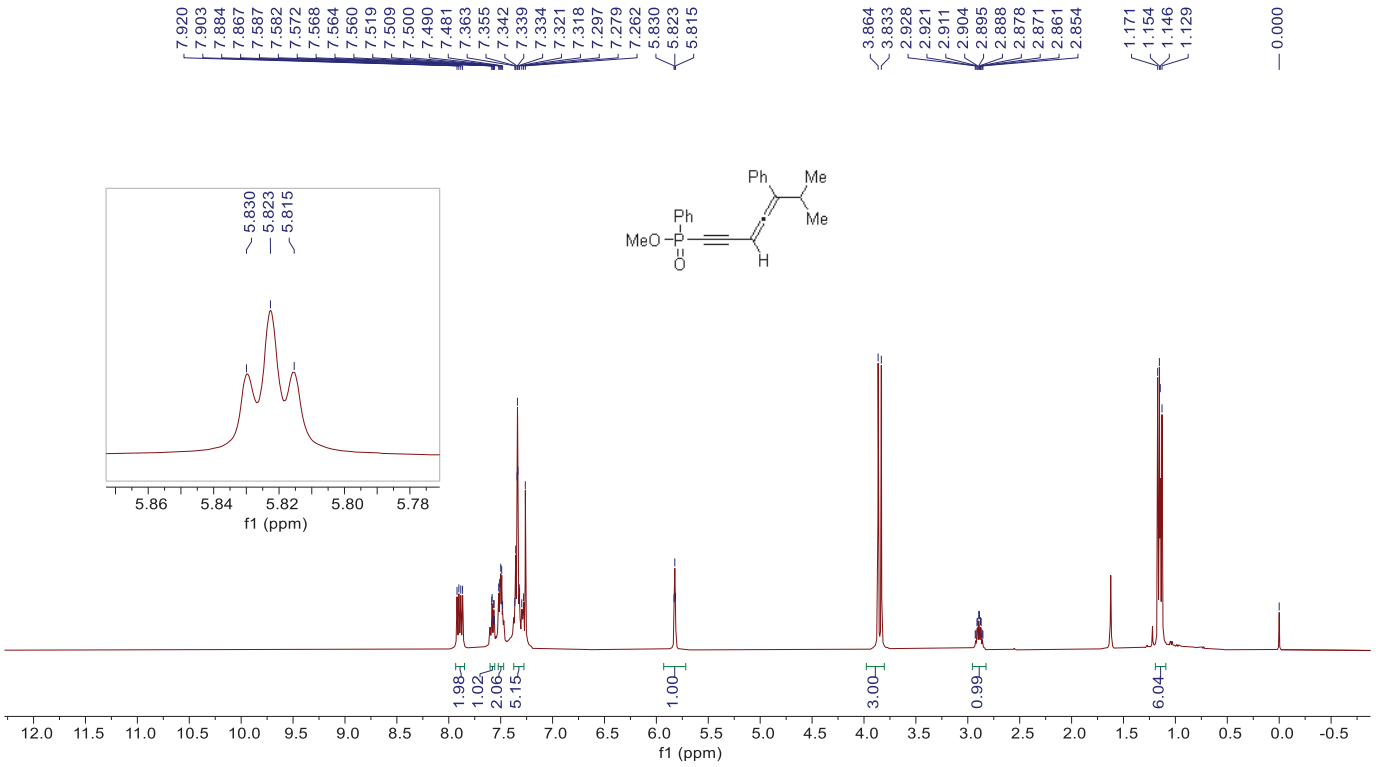
^{13}C NMR of **3w** ($CDCl_3$, 100 MHz)



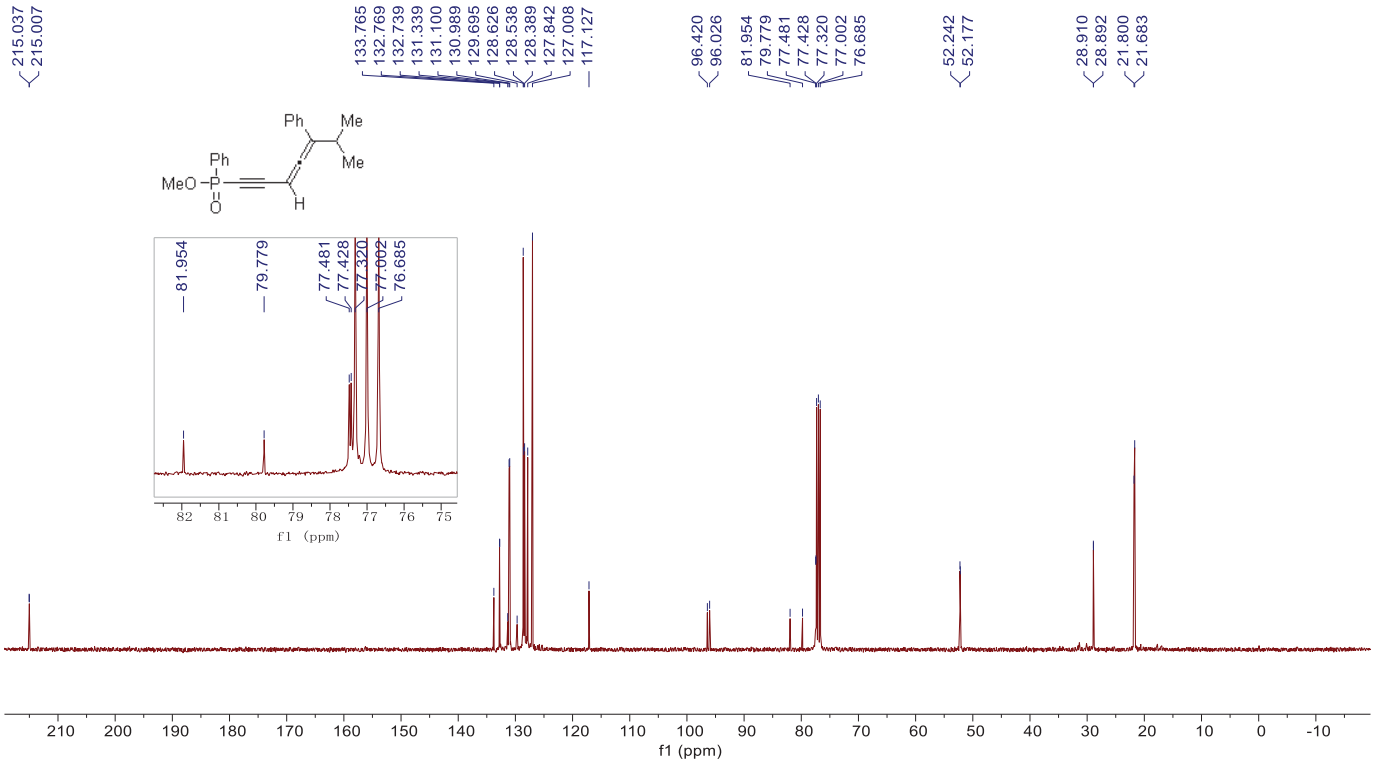
^{31}P NMR of **3w** ($CDCl_3$, 160 MHz)



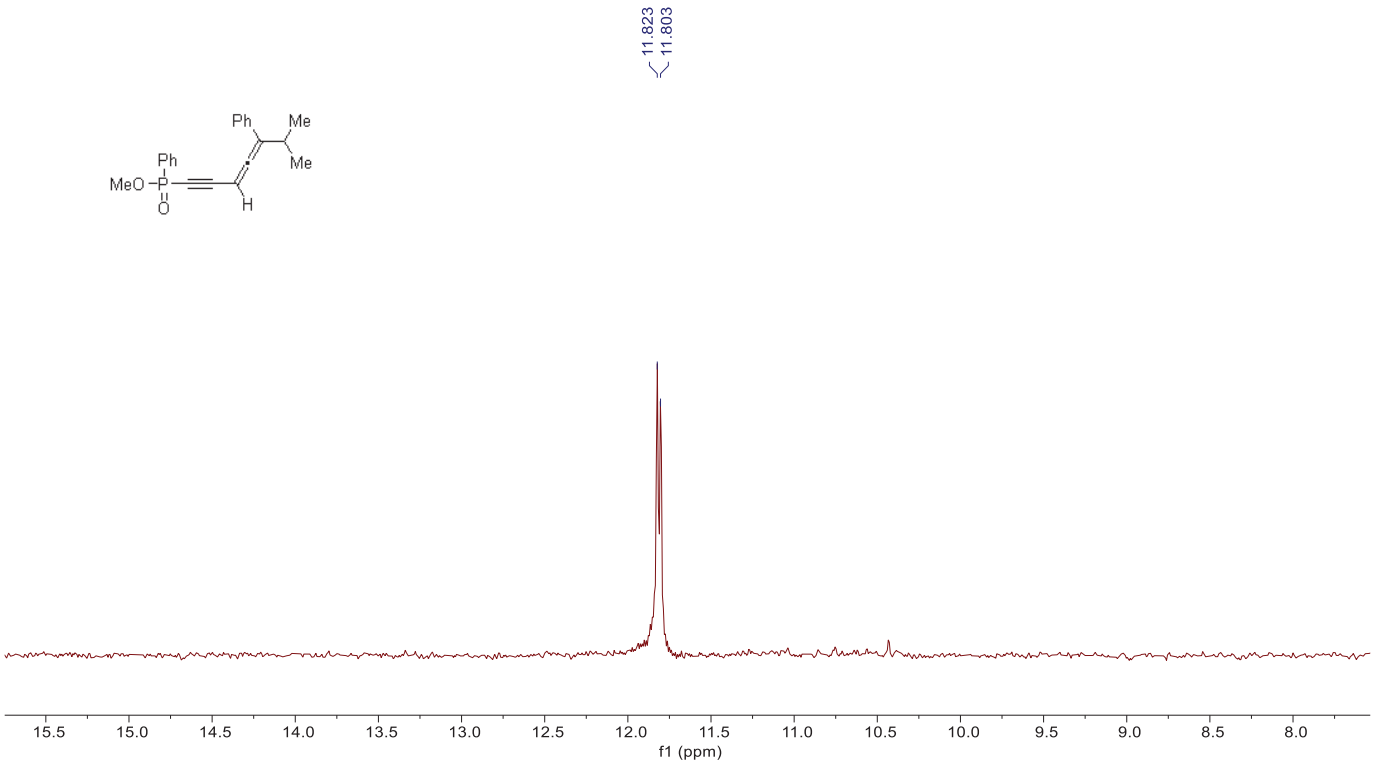
^{1}H NMR of **3x** ($CDCl_3$, 400 MHz)



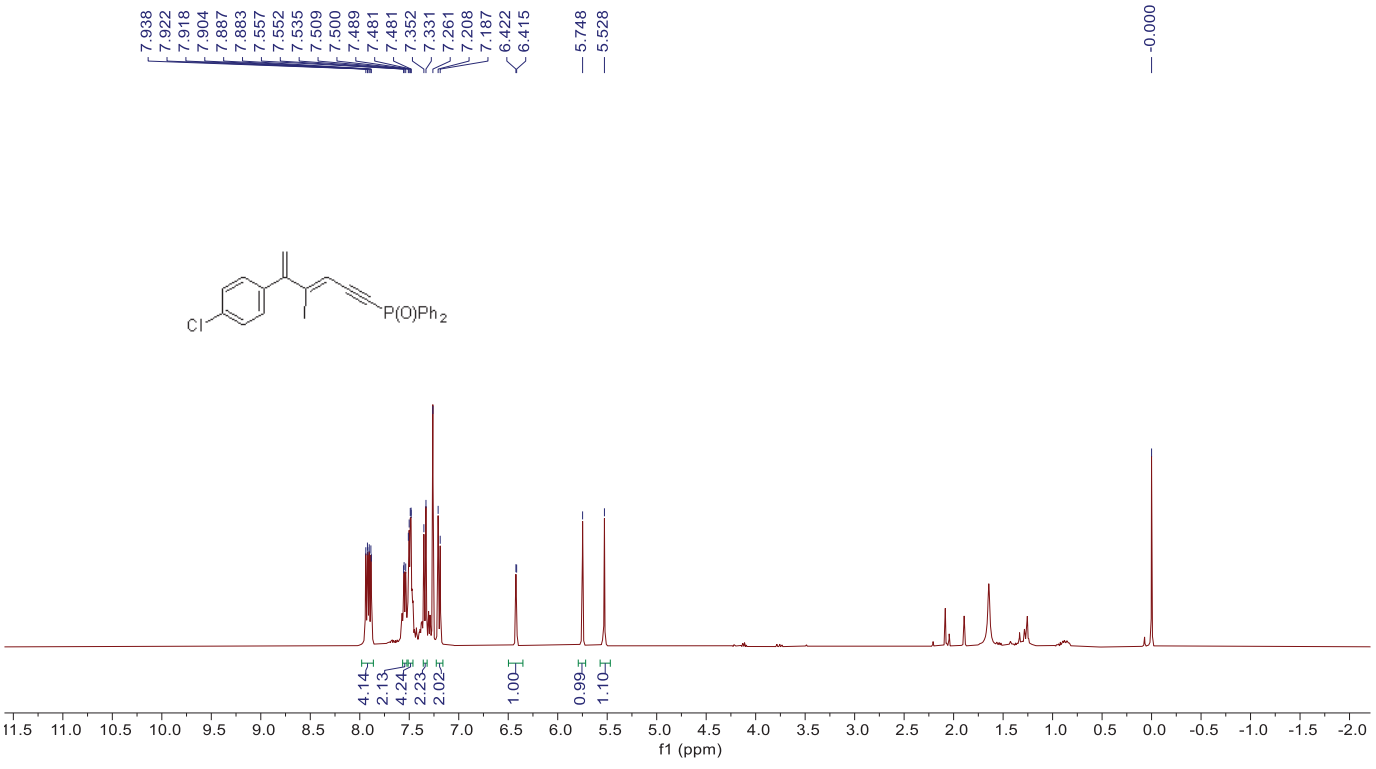
^{13}C NMR of **3x** ($CDCl_3$, 100 MHz)



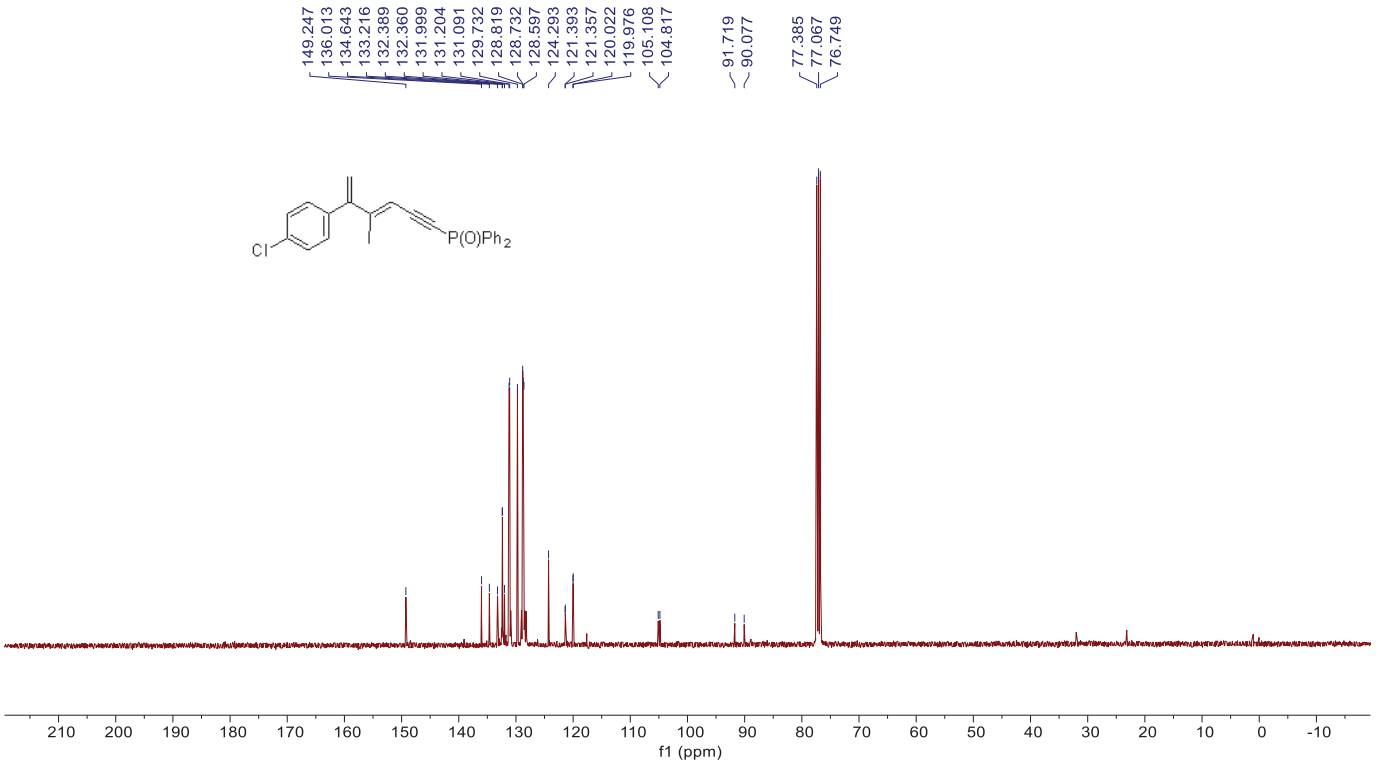
^{31}P NMR of **3x** ($CDCl_3$, 160 MHz)



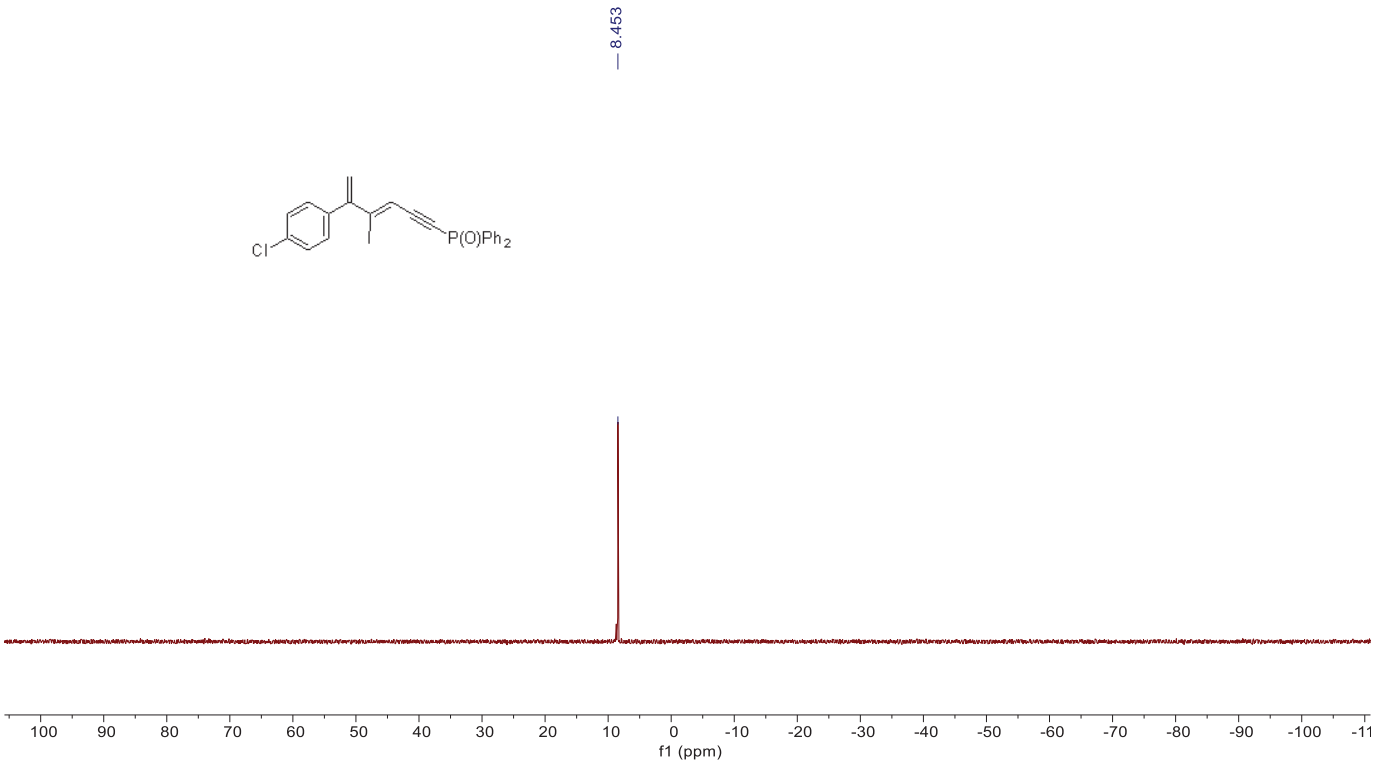
^{1}H NMR of **4** ($CDCl_3$, 400 MHz)



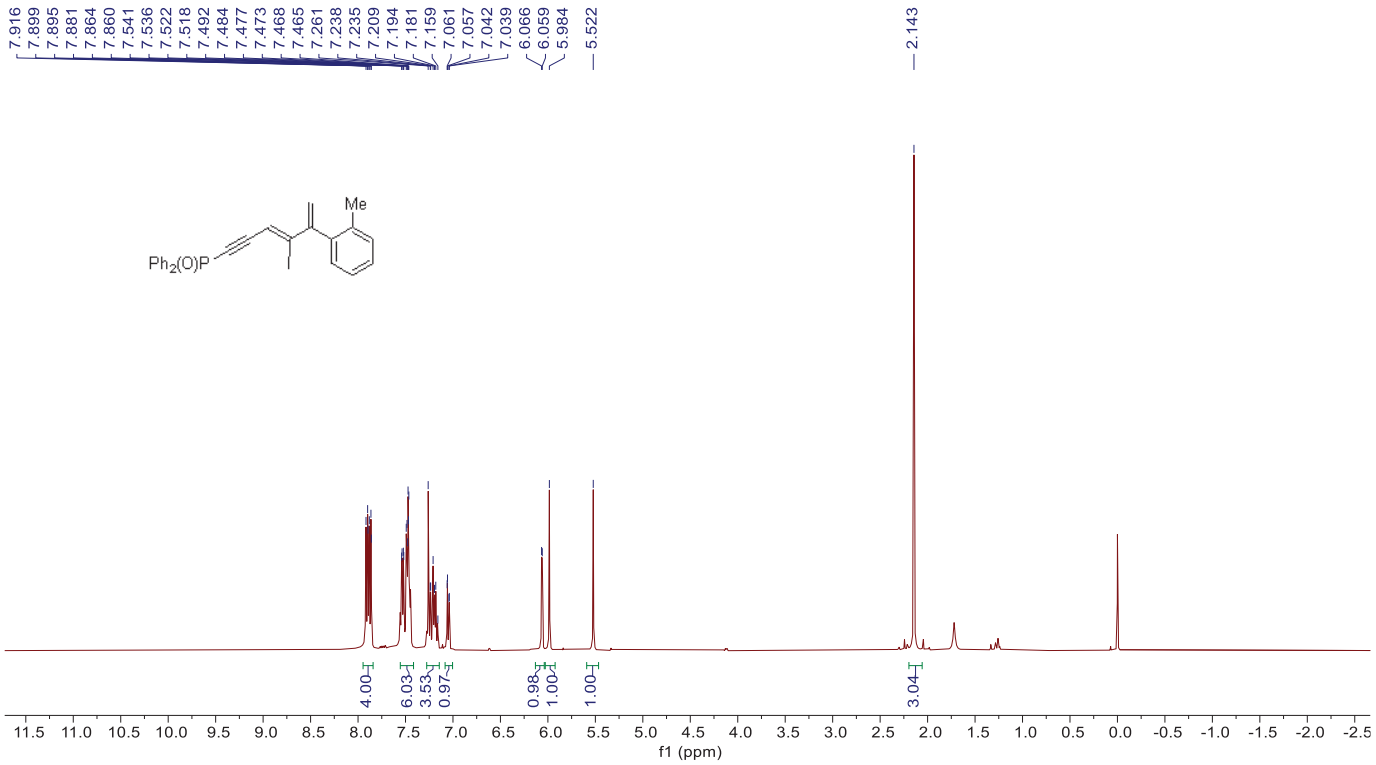
^{13}C NMR of **4** ($CDCl_3$, 100 MHz)



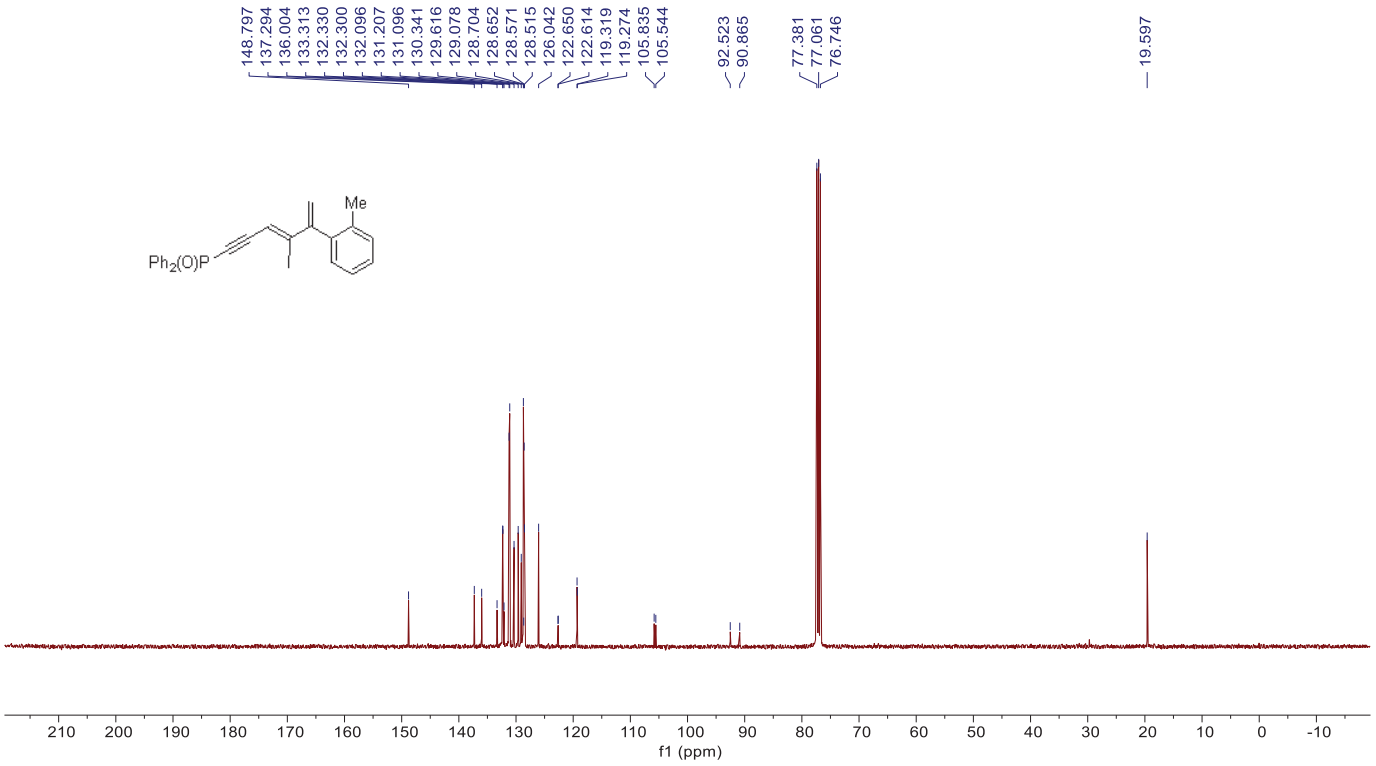
^{31}P NMR of **4** ($CDCl_3$, 160 MHz)



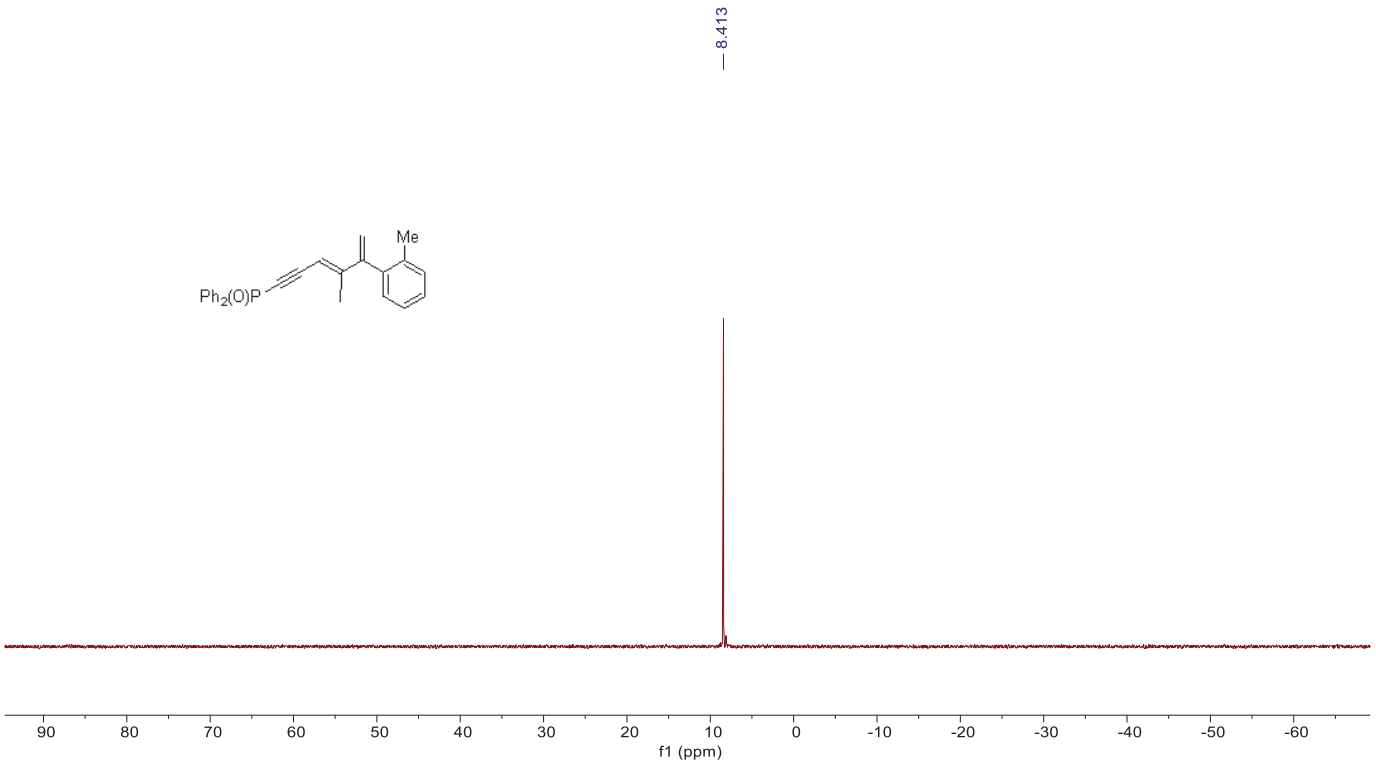
^{1}H NMR of **5** ($CDCl_3$, 400 MHz)



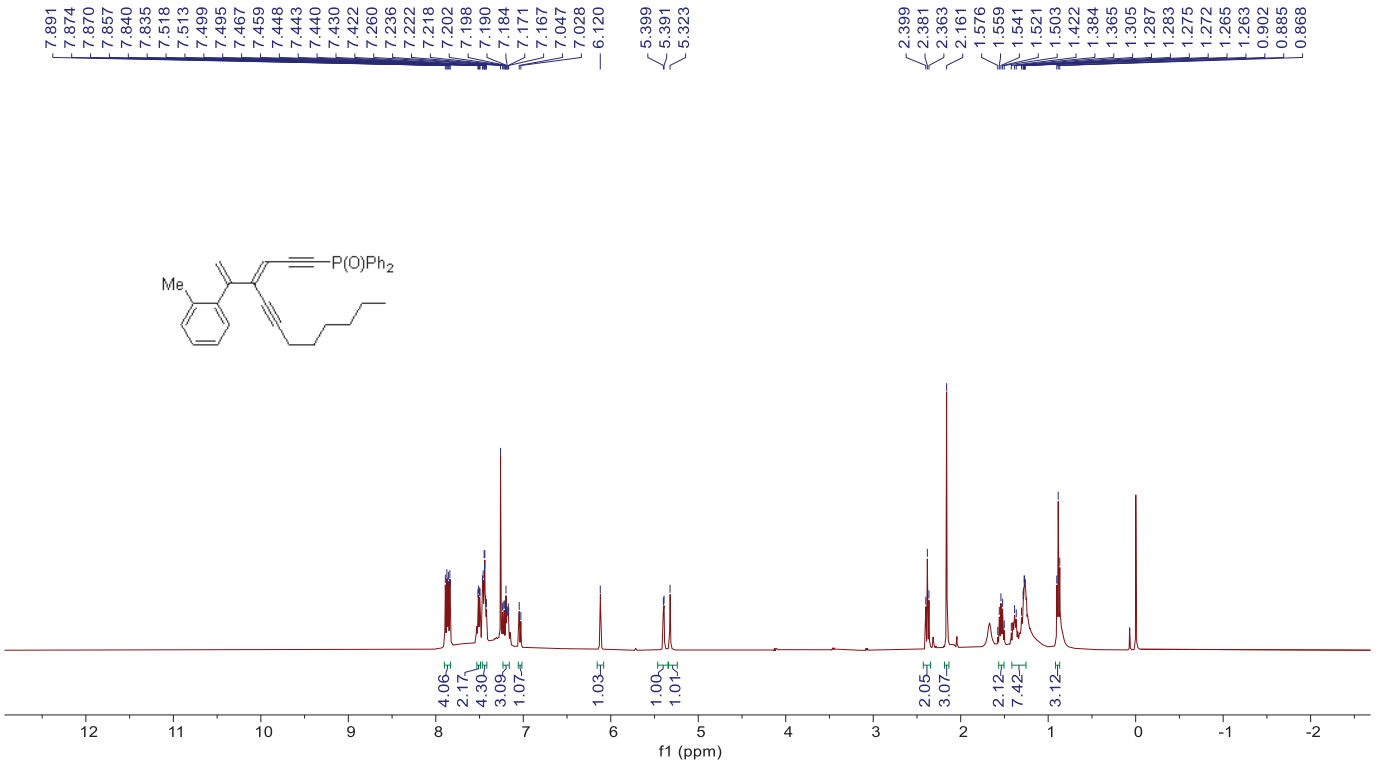
^{13}C NMR of **5** ($CDCl_3$, 100 MHz)



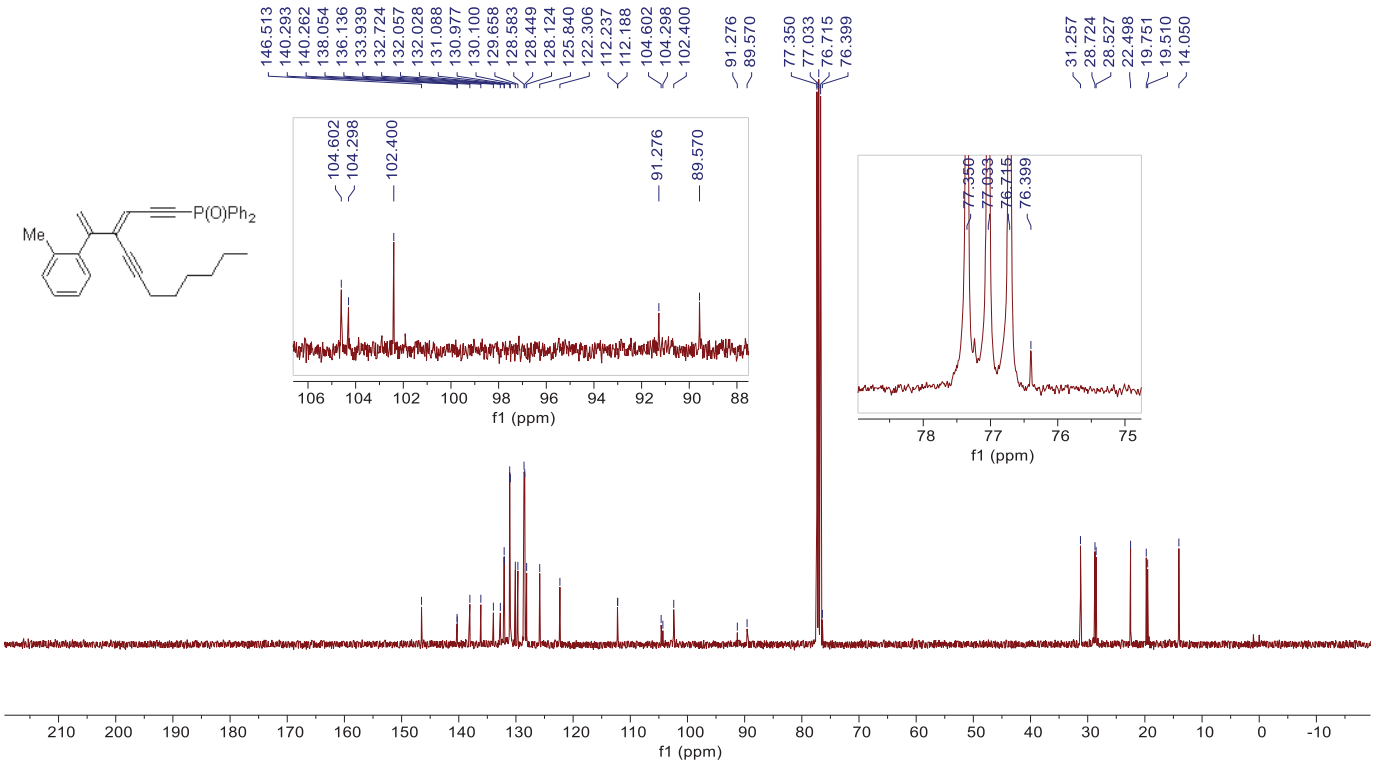
^{31}P NMR of **5** ($CDCl_3$, 160 MHz)



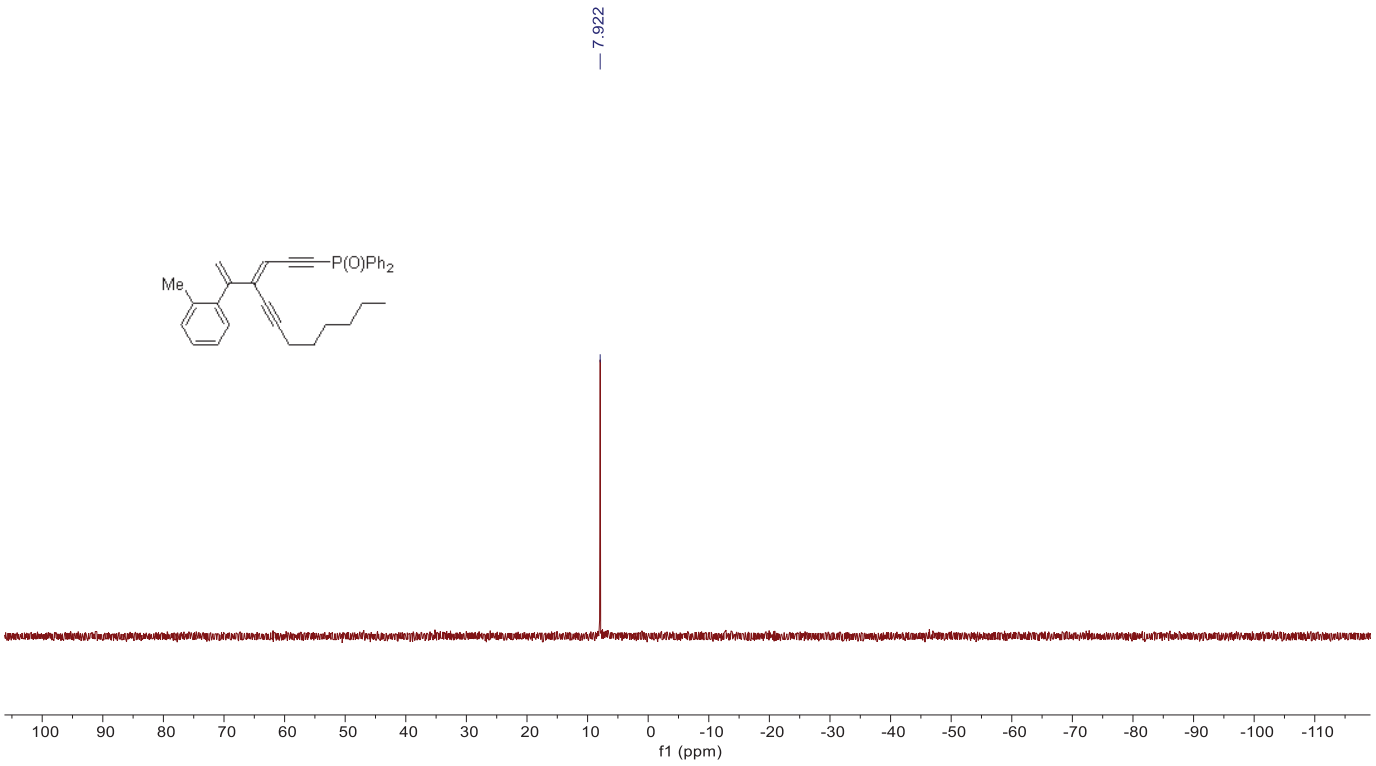
^{1}H NMR of **6** ($CDCl_3$, 400 MHz)



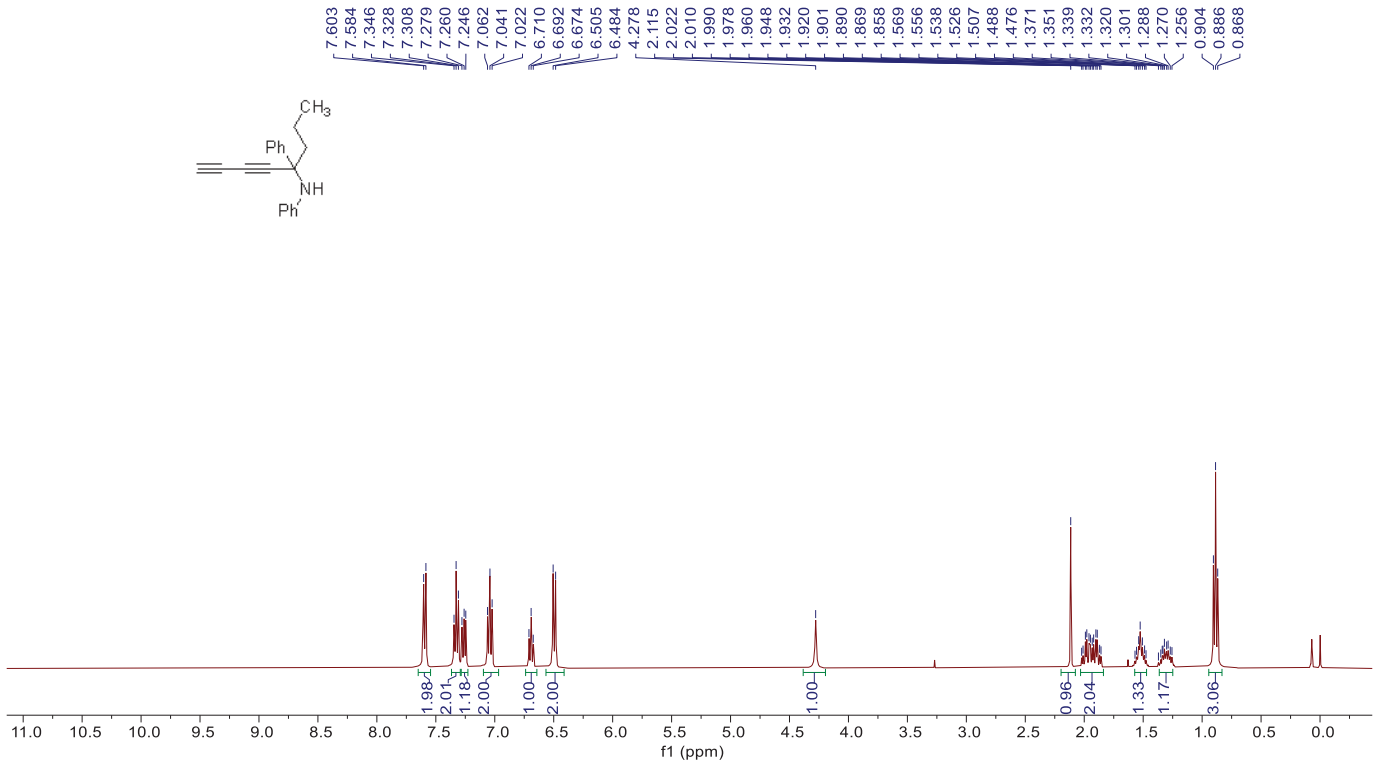
^{13}C NMR of **6**($CDCl_3$, 100 MHz)



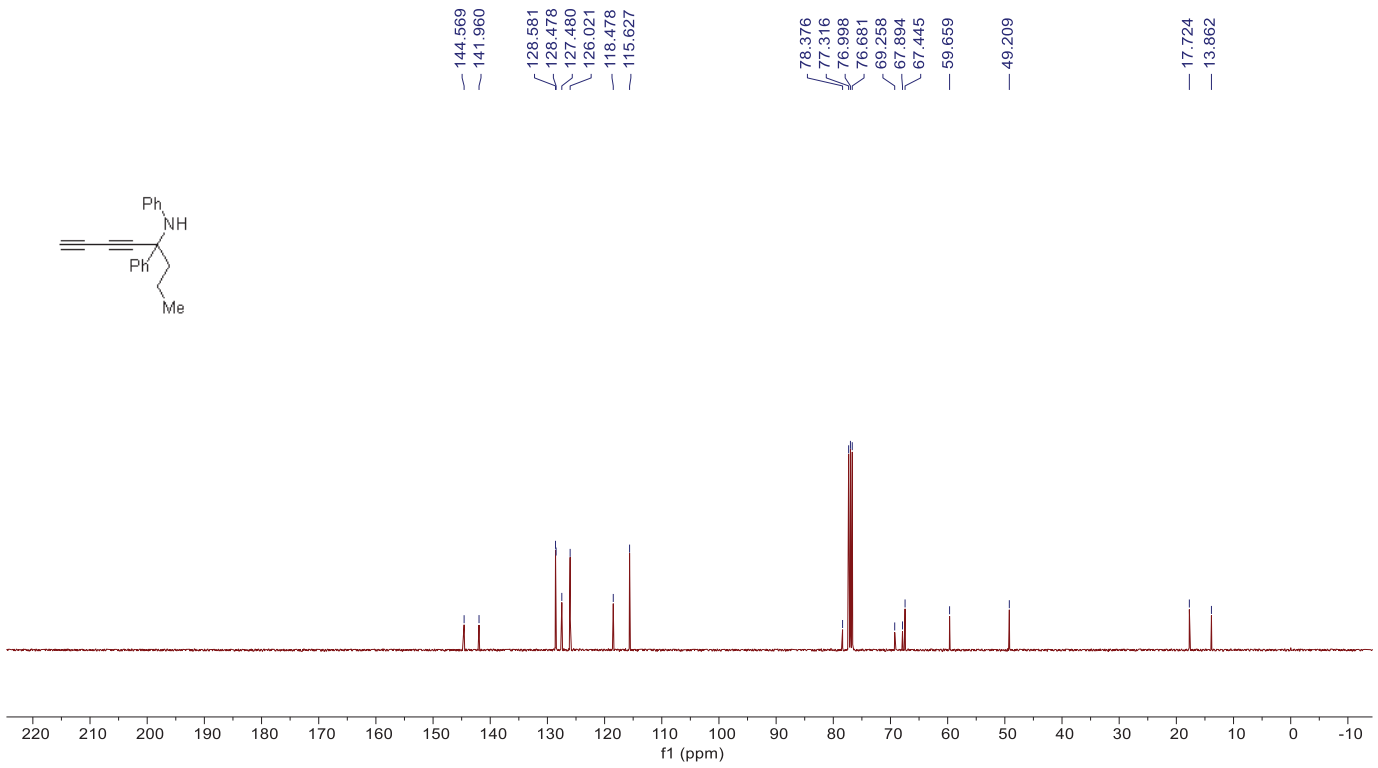
^{31}P NMR of **6** ($CDCl_3$, 160 MHz)



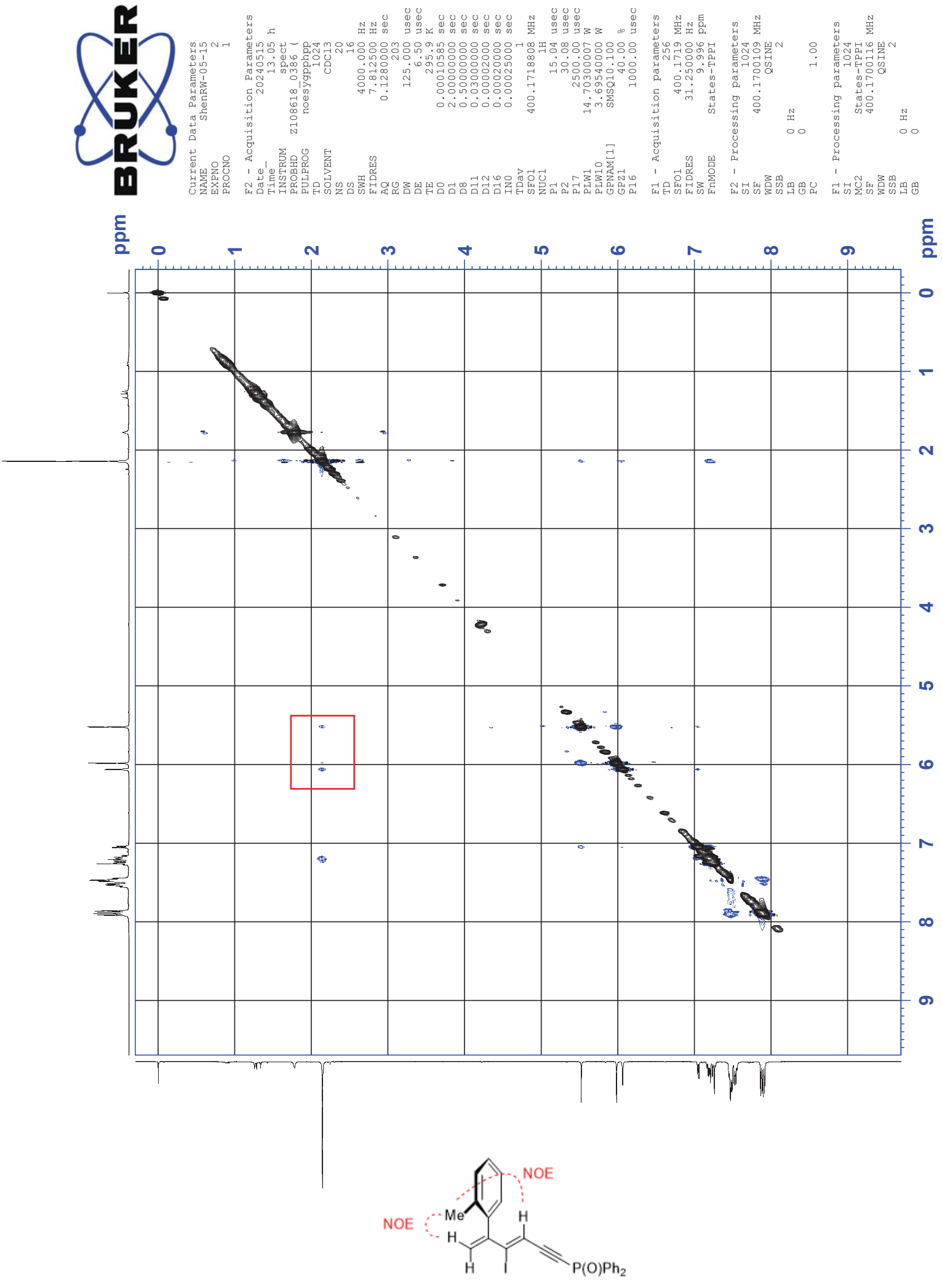
^{1}H NMR of **7** ($CDCl_3$, 400 MHz)

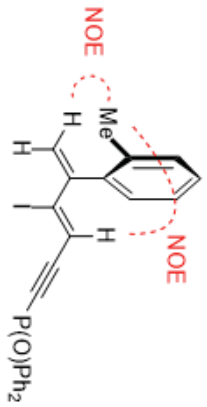


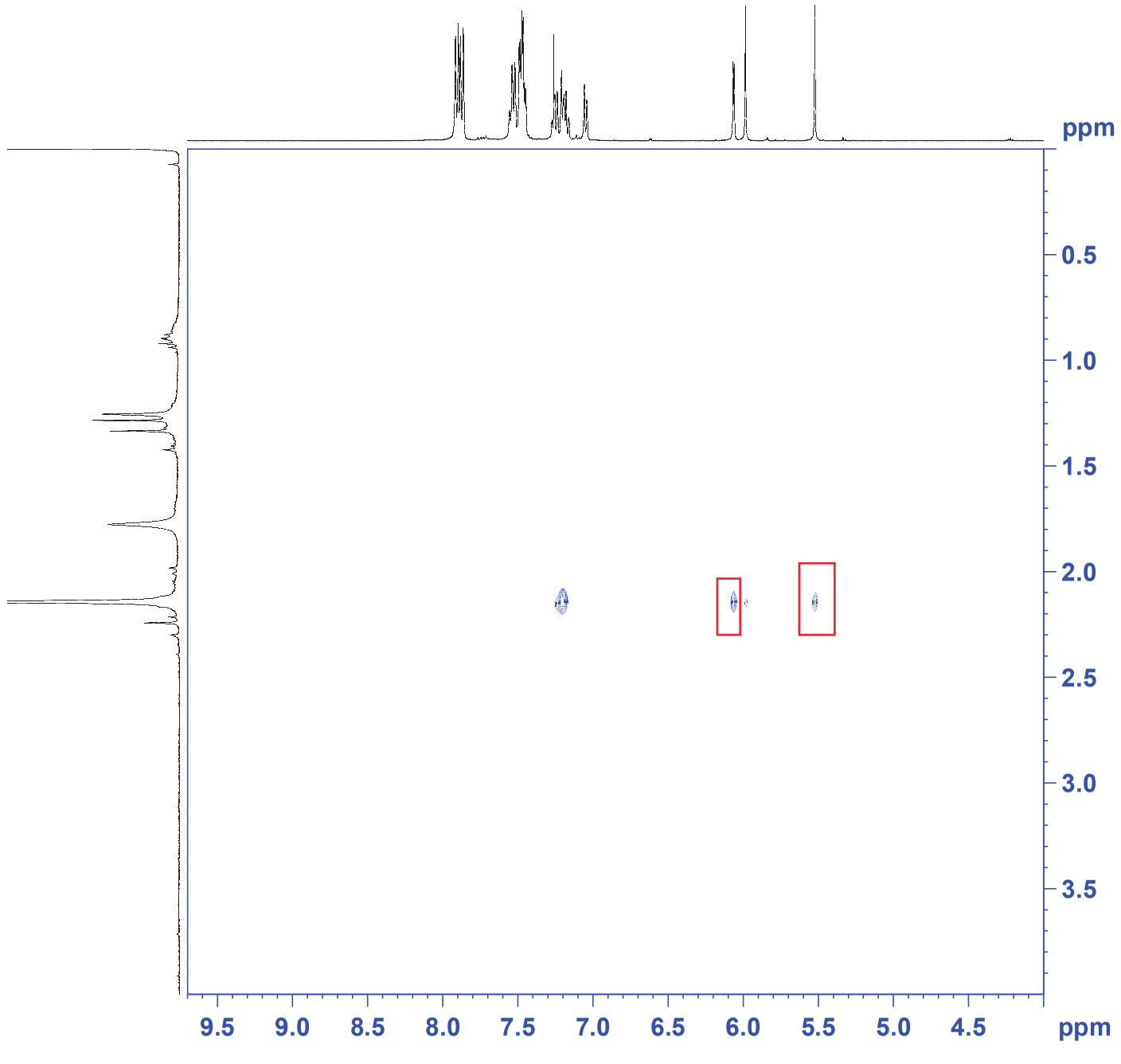
^{13}C NMR of **7** ($CDCl_3$, 100 MHz)



6. NOESY Spectra of 5







BRUKER

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Current Data Parameters
NAME        ShenRW-05-15
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240515
Time              13.05 h
INSTRUM             spect
PROBHD   Z108618_0386 (
PULPROG     noesygpphpp
TD                  1024
SOLVENT             CDC13
NS                    20
DS                    16
SWH           4000.000 Hz
FIDRES           7.812500 Hz
AQ            0.1280000 sec
RG                   203
DW             125.000 usec
DE               6.50 usec
TE              295.9 K
D0            0.00010585 sec
D1            2.00000000 sec
D8            0.50000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D16           0.00020000 sec
IN0           0.00025000 sec
TDav                   1
SFO1         400.1718808 MHz
NUC1                1H
P1               15.04 usec
P2               30.08 usec
P17            2500.00 usec
PLW1         14.70300007 W
PLW10         3.69540000 W
GPNAM[1]      SMSQ10.100
GPZ1             40.00 %
P16            1000.00 usec

F1 - Acquisition parameters
TD                   256
SFO1           400.1719 MHz
FIDRES        31.250000 Hz
SW                9.996 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                  1024
SF           400.1700109 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                 1.00

F1 - Processing parameters
SI                  1024
MC2          States-TPPI
SF           400.1700116 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```