

Supporting Information

Palladium-Catalyzed Dehydrogenative Coupling of Terminal Alkynes with Secondary Phosphine Oxides

Jia Yang,^a Tieqiao Chen,^{*a} Yongbo Zhou,^a Shuang-Feng Yin^a and Li-Biao Han^{*ab}

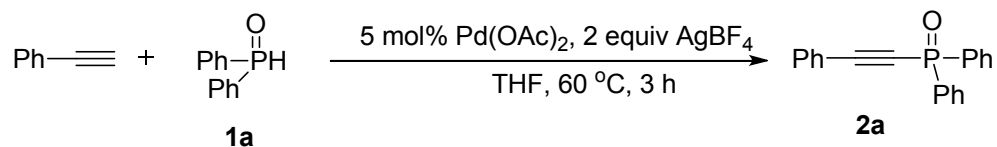
^aState Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China, and ^bNational Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

chentieqiao@hnu.edu.cn; libiao-han@aist.go.jp

General information

Reactions for the synthesis of metal intermediates were conducted in a glove box ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). All other reactions were carried out in oven-dried Schlenk tubes under N_2 atmosphere. Dry solvents were obtained by purification according to standard methods. Reagents were used as received unless otherwise noted. 1H NMR, ^{13}C NMR and ^{31}P NMR data were obtained on a Bruker-400 spectrometer (400 MHz for 1H , 100 MHz for ^{13}C , and 162 MHz for ^{31}P NMR spectroscopy). Mass spectra were measured on a Shimadzu GCMS-QP2010 Plus spectrometer (EI). HRMS were conducted in the Analytical Center at Hunan University, China.

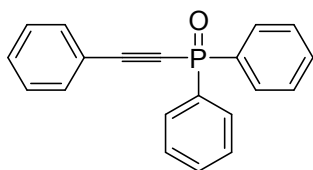
General procedure



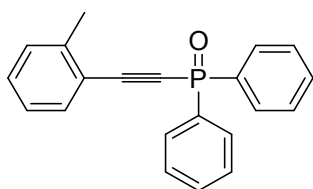
Under N_2 atmosphere, 0.2 mmol diphenylphosphine oxide, 0.2 mmol phenylacetylene, 5 mol% Pd(OAc)_2 , 0.4 mmol AgBF_4 and 0.5 mL THF were charged into a 10 mL schlenck tube, and the mixture was stirred at 60 $^\circ\text{C}$ for 3 h. Then 1 mL Et_3N was added. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm , pether/ethyl acetate as eluent) to afford analytically pure

alkynylphosphorus compounds **2**.

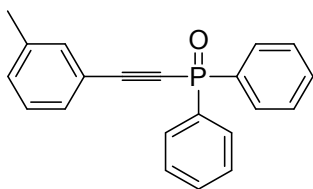
Characterization data of **2**



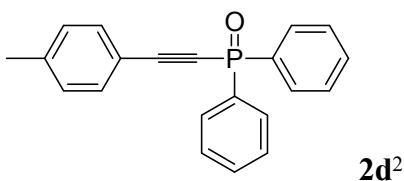
Following general procedure (60 °C, 3 h), **2a** was isolated as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.88–7.94 (m, 4H), 7.43–7.61 (m, 9H), 7.38 (t, 2H, *J* = 7.2 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 8.34; ¹³C NMR (100 MHz, CDCl₃) δ 133.06 (d, *J*_{P-C} = 121.4 Hz), 132.56 (d, *J*_{P-C} = 1.7 Hz), 132.28 (d, *J*_{P-C} = 2.7 Hz), 131.00 (d, *J*_{P-C} = 11.2 Hz), 130.74, 128.69 (d, *J*_{P-C} = 13.4 Hz), 128.60, 119.96 (d, *J*_{P-C} = 3.9 Hz), 105.47 (d, *J*_{P-C} = 29.8 Hz), 82.88 (d, *J*_{P-C} = 169.4 Hz). MS (EI): 302.



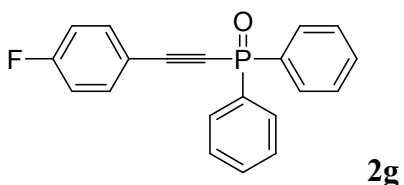
Following general procedure (60 °C, 6 h), **2b** was isolated as a white solid. m.p.: 92–93 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.89–7.95 (m, 4H), 7.48–7.57 (m, 7H), 7.34 (t, 1H, *J* = 7.2 Hz), 7.17–7.27 (m, 2H), 2.47 (s, 3H); ³¹P NMR (162 MHz, CDCl₃) δ 8.26; ¹³C NMR (100 MHz, CDCl₃) δ 141.89 (d, *J*_{P-C} = 1.6 Hz), 133.26 (d, *J*_{P-C} = 121.3 Hz), 133.03 (d, *J*_{P-C} = 1.9 Hz), 132.22 (d, *J*_{P-C} = 2.9 Hz), 130.97 (d, *J*_{P-C} = 11.1 Hz), 130.72, 129.82, 128.66 (d, *J*_{P-C} = 13.4 Hz), 125.84, 119.83 (d, *J*_{P-C} = 3.9 Hz), 104.71 (d, *J*_{P-C} = 30.0 Hz), 86.60 (d, *J*_{P-C} = 169.5 Hz), 20.73. HRMS: Cal.316.1017, Found 316.1011.



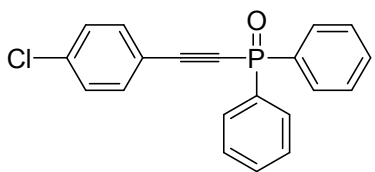
Following general procedure (60 °C, 6 h), **2c** was isolated as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.88–7.93 (m, 4H), 7.47–7.57 (m, 6H), 7.39–7.42 (m, 2H), 7.26–7.27 (m, 2H), 2.35 (s, 3H); ³¹P NMR (162 MHz, CDCl₃) δ 8.28; ¹³C NMR (100 MHz, CDCl₃) δ 138.44, 133.19 (d, *J*_{P-C} = 121.4 Hz), 132.98 (d, *J*_{P-C} = 1.9 Hz), 132.20 (d, *J*_{P-C} = 2.9 Hz), 131.64, 130.99 (d, *J*_{P-C} = 11.1 Hz), 129.69 (d, *J*_{P-C} = 1.9 Hz), 128.65 (d, *J*_{P-C} = 13.4 Hz), 128.49, 119.78 (d, *J*_{P-C} = 4.0 Hz), 105.82 (d, *J*_{P-C} = 30.0 Hz), 82.51 (d, *J*_{P-C} = 169.5 Hz), 21.16. MS (EI): 316.



Following general procedure (60 °C, 6 h), **2d** was isolated as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.88–7.93 (m, 4H), 7.47–7.57 (m, 8H), 7.18 (d, 2H, *J* = 8.0 Hz), 2.38 (s, 3H); ³¹P NMR (162 MHz, CDCl₃) δ 8.18; ¹³C NMR (100 MHz, CDCl₃) δ 141.40, 133.17 (d, *J*_{P-C} = 121.4 Hz), 132.50 (d, *J*_{P-C} = 1.9 Hz), 132.22 (d, *J*_{P-C} = 2.9 Hz), 131.00 (d, *J*_{P-C} = 11.1 Hz), 129.37, 128.66 (d, *J*_{P-C} = 13.4 Hz), 116.84 (d, *J*_{P-C} = 4.1 Hz), 106.04 (d, *J*_{P-C} = 30.3 Hz), 82.21 (d, *J*_{P-C} = 170.7 Hz), 21.78. MS (EI): 316.

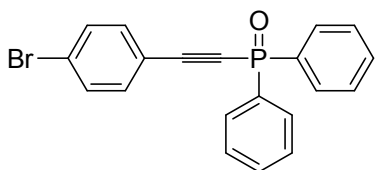


Following general procedure (60 °C, 6 h), **2g** was isolated as a white solid. m.p.: 126–127 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87–7.93 (m, 4H), 7.48–7.61 (m, 8H), 7.07 (t, 2H, *J* = 8.4 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 8.34; ¹³C NMR (100 MHz, CDCl₃) δ 163.88 (d, *J*_{F-C} = 252.2 Hz), 134.82 (dd, *J*_{P-C} = 1.9 Hz, *J*_{F-C} = 8.9 Hz), 132.89 (d, *J*_{P-C} = 121.4 Hz), 132.35 (d, *J*_{P-C} = 2.9 Hz), 130.97 (d, *J*_{P-C} = 11.1 Hz), 128.72 (d, *J*_{P-C} = 13.5 Hz), 116.15 (d, *J*_{F-C} = 22.3 Hz), 104.31 (d, *J*_{P-C} = 29.8 Hz), 82.84 (d, *J*_{P-C} = 168.9 Hz). HRMS: Cal. 320.0766, Found 320.0752.



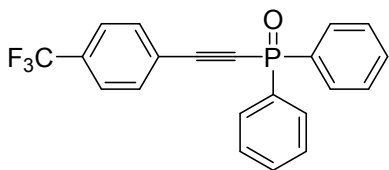
2h

Following general procedure (60 °C, 18 h), **2h** was isolated as a white solid. m.p.: 158–159 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.87–7.92 (m, 4H), 7.48–7.58 (m, 8H), 7.35 (d, 2H, $J = 8.4$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 8.34; ^{13}C NMR (100 MHz, CDCl_3) δ 137.12, 133.76 (d, $J_{\text{P-C}} = 1.8$ Hz), 132.80 (d, $J_{\text{P-C}} = 121.6$ Hz), 132.37 (d, $J_{\text{P-C}} = 2.9$ Hz), 130.99 (d, $J_{\text{P-C}} = 11.2$ Hz), 129.07, 128.73 (d, $J_{\text{P-C}} = 13.4$ Hz), 118.43 (d, $J_{\text{P-C}} = 4.0$ Hz), 104.05 (d, $J_{\text{P-C}} = 24.4$ Hz), 83.98 (d, $J_{\text{P-C}} = 166.5$ Hz). HRMS: Cal. 336.0471, Found 336.0454.



2i³

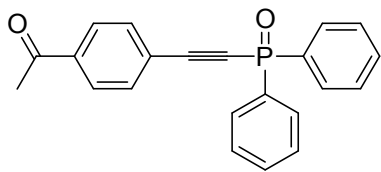
Following general procedure (60 °C, 24 h), **2i** was isolated as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.87–7.92 (m, 4H), 7.44–7.58 (m, 10H); ^{31}P NMR (162 MHz, CDCl_3) δ 8.35; ^{13}C NMR (100 MHz, CDCl_3) δ 133.86 (d, $J_{\text{P-C}} = 1.9$ Hz), 132.73 (d, $J_{\text{P-C}} = 121.4$ Hz), 132.42 (d, $J_{\text{P-C}} = 2.9$ Hz), 132.00, 130.98 (d, $J_{\text{P-C}} = 11.2$ Hz), 128.75 (d, $J_{\text{P-C}} = 13.4$ Hz), 125.51, 118.84 (d, $J_{\text{P-C}} = 4.0$ Hz), 104.09 (d, $J_{\text{P-C}} = 29.2$ Hz), 84.13 (d, $J_{\text{P-C}} = 166.3$ Hz). MS (EI): 380.



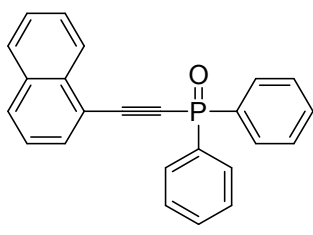
2j³

Following general procedure (60 °C, 6 h), **2j** was isolated as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.87–7.92 (m, 4H), 7.64–7.73 (m, 4H), 7.50–7.66 (m, 6H); ^{31}P NMR (162 MHz, CDCl_3) δ 8.45; ^{13}C NMR (100 MHz, CDCl_3) δ 132.87 (d, $J_{\text{P-C}} = 1.8$ Hz), 132.53 (d, $J_{\text{P-C}} = 2.9$ Hz), 132.49 (d, $J_{\text{P-C}} = 121.7$ Hz), 132.30 (q, $J_{\text{F-C}} = 33.1$ Hz), 131.00 (d, $J_{\text{P-C}} = 11.1$ Hz), 128.79 (d, $J_{\text{P-C}} = 13.5$ Hz), 125.57 (q, $J_{\text{F-C}} = 3.7$ Hz), 123.73 (d, $J_{\text{P-C}} = 4.0$ Hz), 123.49 (q, $J_{\text{F-C}} = 269.3$ Hz), 103.14 (d, $J_{\text{P-C}} = 29.1$ Hz), 85.27 (d, $J_{\text{P-C}}$

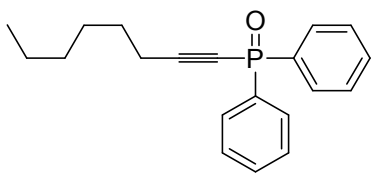
= 163.5 Hz). MS (EI): 370.



Following general procedure (60 °C, 18 h), **2k** was isolated as a white solid. m.p.: 151–152 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, 2H, *J* = 8.4 Hz), 7.88–7.93 (m, 4H), 7.69 (d, 2H, *J* = 8.4 Hz), 7.49–7.60 (m, 6H), 2.62 (s, 3H); ³¹P NMR (162 MHz, CDCl₃) δ 8.47; ¹³C NMR (100 MHz, CDCl₃) δ 196.98, 138.12, 132.75 (d, *J*_{P-C} = 1.8 Hz), 132.62 (d, *J*_{P-C} = 121.6 Hz), 132.46 (d, *J*_{P-C} = 2.9 Hz), 131.00 (d, *J*_{P-C} = 11.2 Hz), 128.76 (d, *J*_{P-C} = 13.5 Hz), 128.31, 124.47 (d, *J*_{P-C} = 3.9 Hz), 103.80 (d, *J*_{P-C} = 28.7 Hz), 85.82 (d, *J*_{P-C} = 163.9 Hz), 26.70. HRMS: Cal.344.0966, Found 344.0950.

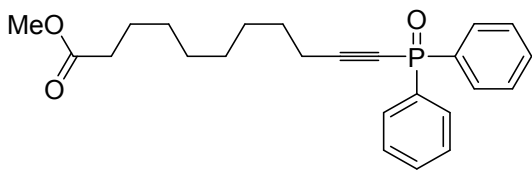


Following general procedure (60 °C, 24 h), **2l** was isolated as an oil. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, 1H, *J* = 8.0 Hz), 7.92–8.01 (m, 5H), 7.85 (d, 2H, *J* = 6.4 Hz), 7.51–7.59 (m, 8H), 7.45 (t, 1H, *J* = 8.0 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 8.50; ¹³C NMR (100 MHz, CDCl₃) δ 133.36 (d, *J*_{P-C} = 1.3 Hz), 133.13 (d, *J*_{P-C} = 121.4 Hz), 132.98, 132.63 (d, *J*_{P-C} = 2.1 Hz), 132.37 (d, *J*_{P-C} = 2.9 Hz), 131.43, 131.05 (d, *J*_{P-C} = 11.2 Hz), 128.78 (d, *J*_{P-C} = 13.5 Hz), 128.61, 127.78, 126.98, 125.67, 125.09, 117.43 (d, *J*_{P-C} = 4.0 Hz), 104.09 (d, *J*_{P-C} = 29.8 Hz), 87.59 (d, *J*_{P-C} = 168.0 Hz). MS (EI): 352.

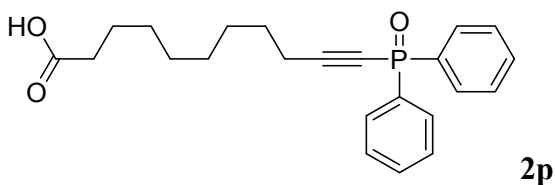


Following general procedure (60 °C, 6 h), **2n** was isolated as a oil. ¹H NMR (400 MHz,

CDCl₃) δ 7.81–7.87 (m, 4H), 7.43–7.52 (m, 6H), 2.41–2.46 (m, 2H), 1.58–1.65 (m, 2H), 1.38–1.45 (m, 2H), 1.27–1.29 (m, 4H), 0.87 (t, 3H, $J = 6.4$ Hz); ³¹P NMR (162 MHz, CDCl₃) δ 7.56; ¹³C NMR (100 MHz, CDCl₃) δ 133.38 (d, $J_{\text{P-C}} = 121.1$ Hz), 132.03 (d, $J_{\text{P-C}} = 2.9$ Hz), 130.81 (d, $J_{\text{P-C}} = 11.2$ Hz), 128.51 (d, $J_{\text{P-C}} = 13.3$ Hz), 109.85 (d, $J_{\text{P-C}} = 30.3$ Hz), 74.84 (d, $J_{\text{P-C}} = 174.2$ Hz), 31.11, 28.47, 27.47 (d, $J_{\text{P-C}} = 1.6$ Hz), 22.43, 19.74 (d, $J_{\text{P-C}} = 3.1$ Hz), 13.99. HRMS: Cal. 310.1487, Found 310.1475.

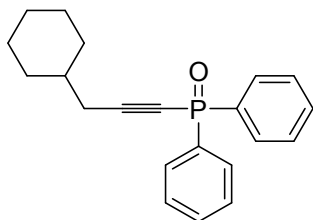


Following general procedure (60 °C, 18 h), **2o** was isolated as a white solid. m.p.: 143–145 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80–7.85 (m, 4H), 7.44–7.55 (m, 6H), 3.66 (s, 3H), 2.45 (dt, 2H, $J = 6.8$ Hz, $J_{\text{P-H}} = 3.6$ Hz), 2.29 (t, 2H, $J = 7.6$ Hz), 1.57–1.66 (m, 4H), 1.38–1.43 (m, 2H), 1.26–1.31 (m, 6H); ³¹P NMR (162 MHz, CDCl₃) δ 7.54; ¹³C NMR (100 MHz, CDCl₃) δ 174.27, 133.47 (d, $J_{\text{P-C}} = 121.1$ Hz), 132.03 (d, $J_{\text{P-C}} = 2.9$ Hz), 130.88 (d, $J_{\text{P-C}} = 11.1$ Hz), 128.53 (d, $J_{\text{P-C}} = 13.4$ Hz), 109.72 (d, $J_{\text{P-C}} = 30.3$ Hz), 74.97 (d, $J_{\text{P-C}} = 173.8$ Hz), 51.47, 34.05, 29.71, 29.04 (d, $J_{\text{P-C}} = 2.1$ Hz), 28.79 (d, $J_{\text{P-C}} = 0.5$ Hz), 27.54 (d, $J_{\text{P-C}} = 1.6$ Hz), 24.88, 19.78 (d, $J_{\text{P-C}} = 3.1$ Hz). HRMS: Cal. 396.1854, Found 396.1864.



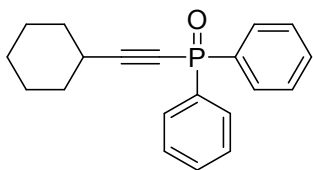
Following general procedure (60 °C, 24 h), **2p** was isolated as a white solid. m.p.: 242–244 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81–7.86 (m, 4H), 7.47–7.54 (m, 6H), 2.47 (b, 2H), 2.34 (t, 2H, $J = 6.8$ Hz), 1.63 (b, 3H), 1.26–1.45 (m, 10H); ³¹P NMR (162 MHz, CDCl₃) δ 8.50; ¹³C NMR (100 MHz, CDCl₃) δ 177.27, 132.85 (d, $J_{\text{P-C}} = 123.3$ Hz), 132.22 (d, $J_{\text{P-C}} = 2.9$ Hz), 130.95 (d, $J_{\text{P-C}} = 11.3$ Hz), 128.61 (d, $J_{\text{P-C}} = 13.4$ Hz), 110.24 (d, $J_{\text{P-C}} = 30.9$ Hz), 74.63 (d, $J_{\text{P-C}} = 175.6$ Hz), 34.18, 28.29, 28.04, 28.00, 27.92, 27.20 (d, $J_{\text{P-C}} = 1.3$ Hz), 24.51, 19.82 (d, $J_{\text{P-C}} = 3.0$ Hz). HRMS: Cal. 382.1698, Found

382.1687.



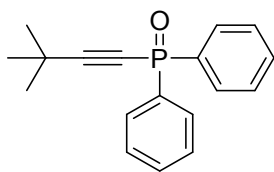
2q

Following general procedure (60 °C, 24 h), **2q** was isolated as a white solid. m.p.: 81–82 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73–7.79 (m, 4H), 7.39–7.47 (m, 6H), 2.28 (b, 2H), 1.75(d, 2H, *J* = 4.4 Hz), 1.56–1.66 (m, 3H), 0.95–1.22 (m, 6H); ³¹P NMR (162 MHz, CDCl₃) δ 7.58; ¹³C NMR (100 MHz, CDCl₃) δ 133.52 (d, *J*_{P-C} = 121.0 Hz), 132.02 (d, *J*_{P-C} = 2.8 Hz), 130.87 (d, *J*_{P-C} = 11.1 Hz), 128.54 (d, *J*_{P-C} = 23.4 Hz), 108.92 (d, *J*_{P-C} = 30.5 Hz), 75.73 (d, *J*_{P-C} = 174.3 Hz), 36.77, 32.73, 27.52 (d, *J*_{P-C} = 3.0 Hz), 26.02, 25.96. HRMS: Cal. 322.1487, Found 322.1471.



2r

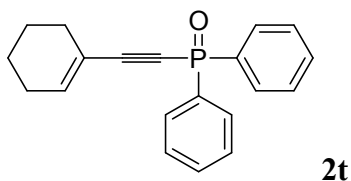
Following general procedure (100 °C, 18 h), **2r** was isolated as an oil. ¹H NMR (400 MHz, CDCl₃) δ 7.73–7.78 (m, 4H), 7.36–7.46 (m, 6H), 2.54–2.59 (m, 1H), 1.78–1.82 (m, 2H), 1.61–1.66 (m, 2H), 1.45–1.55 (m, 3H), 1.24–1.28 (m, 3H); ³¹P NMR (162 MHz, CDCl₃) δ 7.67; ¹³C NMR (100 MHz, CDCl₃) δ 133.56 (d, *J*_{P-C} = 121.0 Hz), 131.99 (d, *J*_{P-C} = 2.9 Hz), 130.84 (d, *J*_{P-C} = 11.1 Hz), 128.53 (d, *J*_{P-C} = 13.3 Hz), 113.23 (d, *J*_{P-C} = 29.6 Hz), 74.55 (d, *J*_{P-C} = 174.2 Hz), 31.45 (d, *J*_{P-C} = 1.3 Hz), 29.82 (d, *J*_{P-C} = 3.0 Hz), 25.56, 24.59. HRMS: Cal. 308.1330, Found 308.1314.



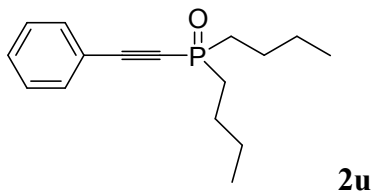
2s

Following general procedure (100 °C, 18 h), **2s** was isolated as a white solid. m.p.: 130–

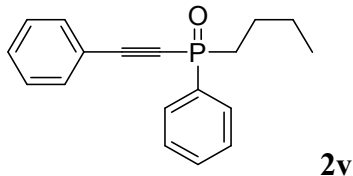
131 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.79–7.85 (m, 4H), 7.44–7.54 (m, 6H), 1.34 (s, 9H); ^{31}P NMR (162 MHz, CDCl_3) δ 7.64; ^{13}C NMR (100 MHz, CDCl_3) δ 133.60 (d, $J_{\text{P-C}} = 121.0$ Hz), 131.97 (d, $J_{\text{P-C}} = 2.9$ Hz), 130.83 (d, $J_{\text{P-C}} = 11.1$ Hz), 128.53 (d, $J_{\text{P-C}} = 13.3$ Hz), 116.79 (d, $J_{\text{P-C}} = 28.7$ Hz), 73.08 (d, $J_{\text{P-C}} = 173.8$ Hz), 29.98 (d, $J_{\text{P-C}} = 1.5$ Hz), 28.51 (d, $J_{\text{P-C}} = 2.8$ Hz). HRMS: Cal. 282.1174, Found 282.1157.



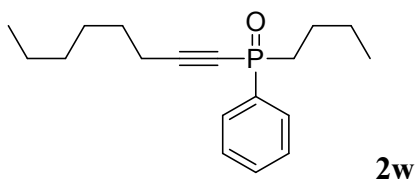
Following general procedure (60 °C, 24 h), **2t** was isolated as a white solid. m.p.: 110–111 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.85 (b, 4H), 7.46–7.54 (m, 6H), 6.48 (b, 1H), 2.16–2.20 (m, 4H), 1.59–1.67 (m, 4H); ^{31}P NMR (162 MHz, CDCl_3) δ 8.13; ^{13}C NMR (100 MHz, CDCl_3) δ 140.70 (d, $J_{\text{P-C}} = 12.6$ Hz), 132.49 (d, $J_{\text{P-C}} = 121.2$ Hz), 130.94 (d, $J_{\text{P-C}} = 2.9$ Hz), 129.90 (d, $J_{\text{P-C}} = 11.1$ Hz), 127.53 (d, $J_{\text{P-C}} = 14.3$ Hz), 117.88 (d, $J_{\text{P-C}} = 4.2$ Hz), 106.81 (d, $J_{\text{P-C}} = 30.2$ Hz), 79.08 (d, $J_{\text{P-C}} = 173.2$ Hz), 26.98 (d, $J_{\text{P-C}} = 1.0$ Hz), 24.88, 20.82, 20.05. HRMS: Cal. 306.1174, Found 306.1166.



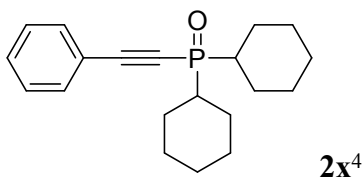
Following general procedure (60 °C, 24 h), **2u** was isolated as an oil. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, 2H, $J = 7.6$ Hz), 7.35–7.46 (m, 3H), 1.89–2.01 (m, 4H), 1.69–1.77 (m, 4H), 1.45–1.54 (m, 4H), 0.97 (t, 6H, $J = 7.2$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 26.13; ^{13}C NMR (100 MHz, CDCl_3) δ 132.38 (d, $J_{\text{P-C}} = 1.7$ Hz), 130.34, 128.54, 120.24 (d, $J_{\text{P-C}} = 3.6$ Hz), 102.42 (d, $J_{\text{P-C}} = 25.1$ Hz), 82.94 (d, $J_{\text{P-C}} = 143.7$ Hz), 31.12 (d, $J_{\text{P-C}} = 79.6$ Hz), 24.03 (d, $J_{\text{P-C}} = 4.1$ Hz), 23.95 (d, $J_{\text{P-C}} = 15.8$ Hz), 13.66. HRMS: Cal. 262.1487, Found 262.1472.



Following general procedure (60 °C, 24 h), **2v** was isolated as an oil. ¹H NMR (400 MHz, CDCl₃) δ 7.81–7.86 (m, 2H), 7.29–7.51 (m, 8H), 2.02–2.11 (m, 2H), 1.55–1.65 (m, 2H), 1.33–1.42 (m, 2H), 0.84 (t, 3H, *J* = 8.0 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 17.01; ¹³C NMR (100 MHz, CDCl₃) δ 132.49 (d, *J*_{P-C} = 1.7 Hz), 132.27 (d, *J*_{P-C} = 114.5 Hz), 132.19 (d, *J*_{P-C} = 2.8 Hz), 130.53 (d, *J*_{P-C} = 5.5 Hz), 130.40, 128.70 (d, *J*_{P-C} = 12.8 Hz), 128.58, 120.07 (d, *J*_{P-C} = 3.8 Hz), 103.75 (d, *J*_{P-C} = 27.5 Hz), 82.86 (d, *J*_{P-C} = 156.0 Hz), 33.67 (d, *J*_{P-C} = 83.7 Hz), 23.90 (d, *J*_{P-C} = 2.1 Hz), 23.84 (d, *J*_{P-C} = 24.9 Hz), 13.62. HRMS: Cal. 282.1174, Found 282.1157.

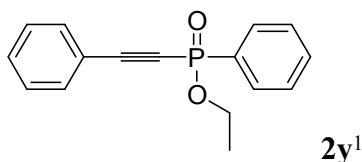


Following general procedure (60 °C, 24 h), **2w** was isolated as an oil. ¹H NMR (400 MHz, CDCl₃) δ 7.81–7.86 (m, 2H), 7.49–7.57 (m, 3H), 2.40 (t, 2H, *J* = 7.2 Hz), 1.97–2.05 (m, 2H), 1.57–1.62 (m, 4H), 1.38–1.43 (m, 4H), 1.30 (b, 4H), 0.89 (t, 6H, *J* = 6.8 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 16.38; ¹³C NMR (100 MHz, CDCl₃) δ 132.59 (d, *J*_{P-C} = 114.3 Hz), 131.88 (d, *J*_{P-C} = 2.8 Hz), 130.30 (d, *J*_{P-C} = 10.5 Hz), 128.47 (d, *J*_{P-C} = 12.7 Hz), 107.83 (d, *J*_{P-C} = 28.1 Hz), 74.69 (d, *J*_{P-C} = 161.9 Hz), 33.67 (d, *J*_{P-C} = 84.0 Hz), 31.10, 28.43, 27.48, 23.85 (d, *J*_{P-C} = 9.5 Hz), 23.73 (d, *J*_{P-C} = 22.4 Hz), 22.41, 19.54 (d, *J*_{P-C} = 2.9 Hz), 13.94, 13.53. HRMS: Cal. 290.1800, Found 290.1782.

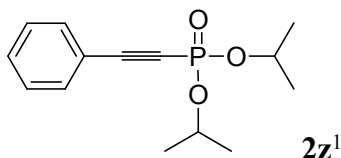


Following general procedure (60 °C, 12 h), **2x** was isolated as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.54–7.56 (m, 2H), 7.35–7.46 (m, 3H), 2.05–2.08 (m, 2H), 1.86–

1.99 (m, 8H), 1.68–1.76 (m, 2H), 1.49–1.61 (m, 4H), 1.21–1.41 (m, 6H); ^{31}P NMR (162 MHz, CDCl_3) δ 35.75; ^{13}C NMR (100 MHz, CDCl_3) δ 132.44 (d, $J_{\text{P-C}} = 1.6$ Hz), 130.29, 128.52, 120.31 (d, $J_{\text{P-C}} = 3.5$ Hz), 103.41 (d, $J_{\text{P-C}} = 21.8$ Hz), 81.02 (d, $J_{\text{P-C}} = 137.0$ Hz), 36.69 (d, $J_{\text{P-C}} = 78.3$ Hz), 26.29 (d, $J_{\text{P-C}} = 9.5$ Hz), 26.15 (d, $J_{\text{P-C}} = 9.2$ Hz), 25.82 (d, $J_{\text{P-C}} = 1.3$ Hz), 25.74 (d, $J_{\text{P-C}} = 3.2$ Hz), 24.66 (d, $J_{\text{P-C}} = 3.3$ Hz). MS (EI): 314.



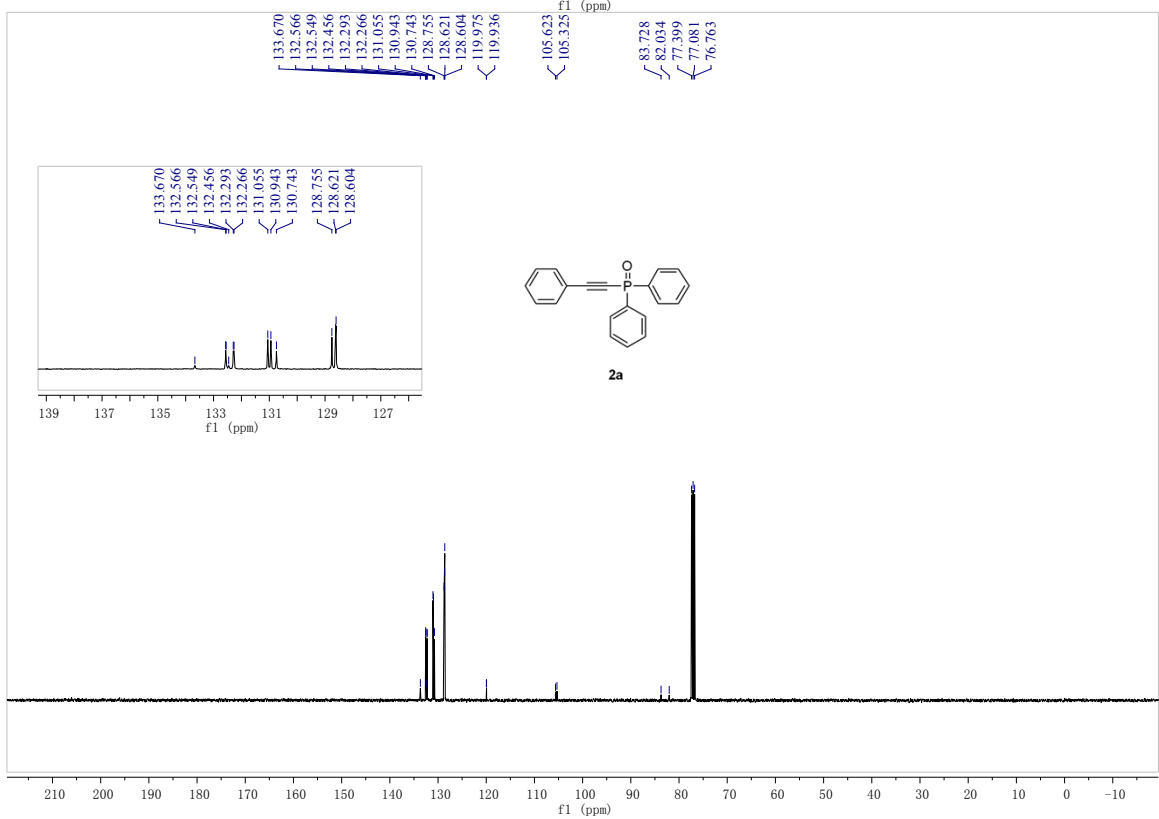
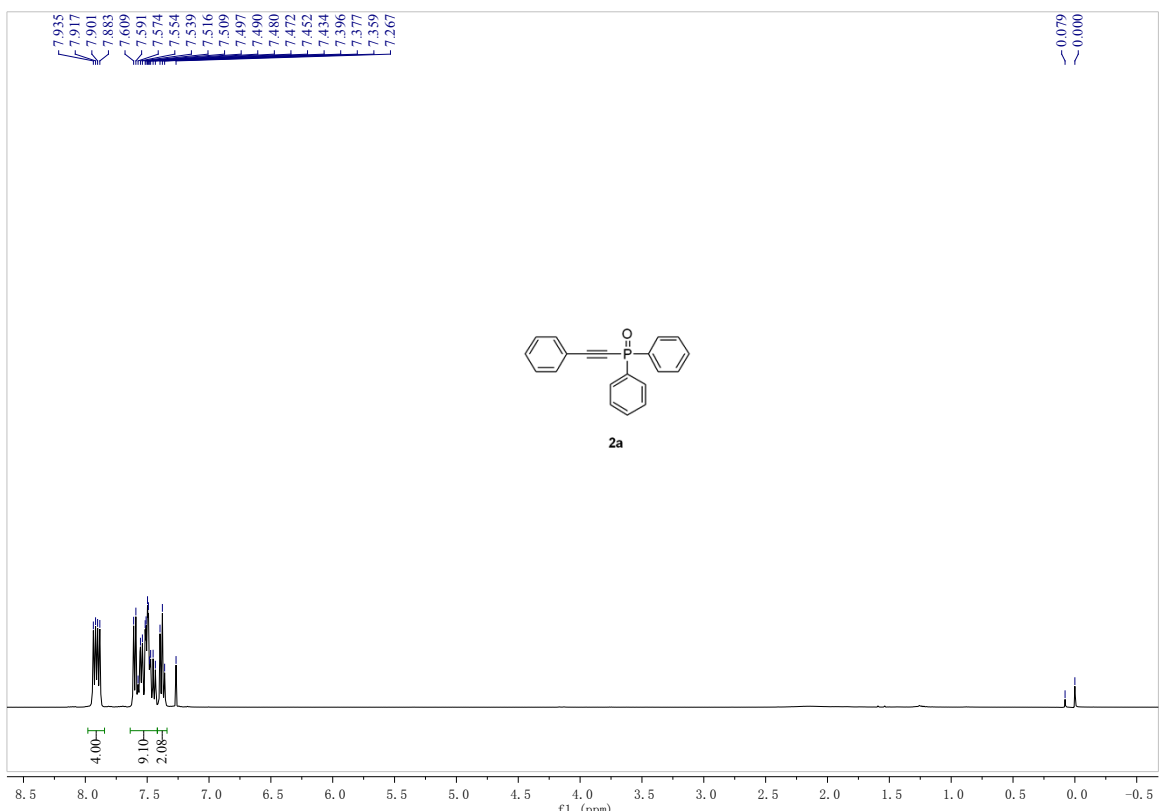
Under N_2 atmosphere, 0.2 mmol $\text{Ph}(\text{EtO})\text{P}(\text{O})\text{H}$ **1e**, 0.2 mmol phenylacetylene, 5 mol% $\text{Pd}(\text{OAc})_2$, 0.4 mmol AgBF_4 , 0.4 mmol triethylamine and 1 mL THF were charged into a 10 mL schlenck tube, the mixture was stirred at 100 °C for 16 hours. **2y** was isolated as an oil. ^1H NMR (400 MHz, CDCl_3) δ 7.93–7.80 (m, 2H), 7.51–7.56 (m, 5H), 7.42–7.46 (m, 1H), 7.34–7.38 (m, 2H), 4.26–4.35 (m, 2H), 1.44 (t, 3H, $J = 11.2$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 9.74; ^{13}C NMR (100 MHz, CDCl_3) δ 132.84 (d, $J_{\text{P-C}} = 2.9$ Hz), 132.59 (d, $J_{\text{P-C}} = 1.6$ Hz), 131.14 (d, $J_{\text{P-C}} = 11.2$ Hz), 131.07 (d, $J_{\text{P-C}} = 164.6$ Hz), 130.68, 128.60 (d, $J_{\text{P-C}} = 14.8$ Hz), 128.56, 119.74 (d, $J_{\text{P-C}} = 4.3$ Hz), 101.59 (d, $J_{\text{P-C}} = 39.3$ Hz), 81.66 (d, $J_{\text{P-C}} = 214.7$ Hz), 62.34 (d, $J_{\text{P-C}} = 6.3$ Hz), 16.40 (d, $J_{\text{P-C}} = 7.1$ Hz). MS (EI): 270.

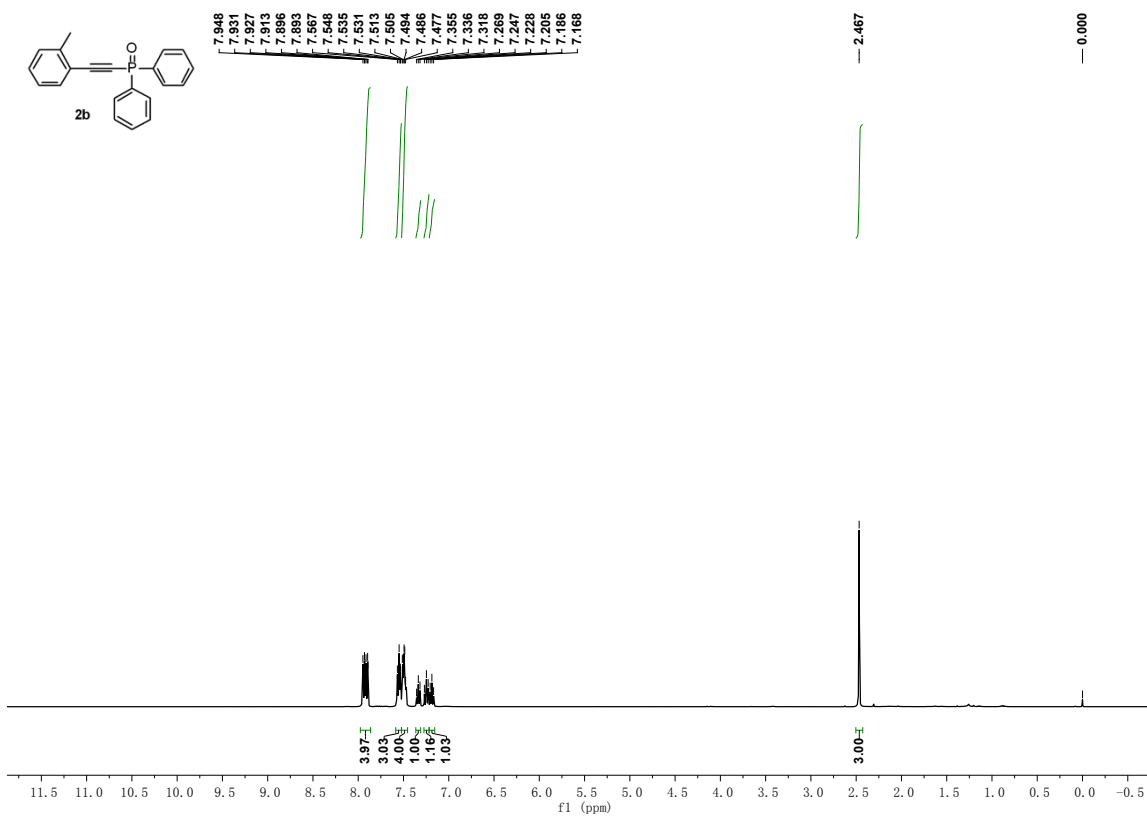
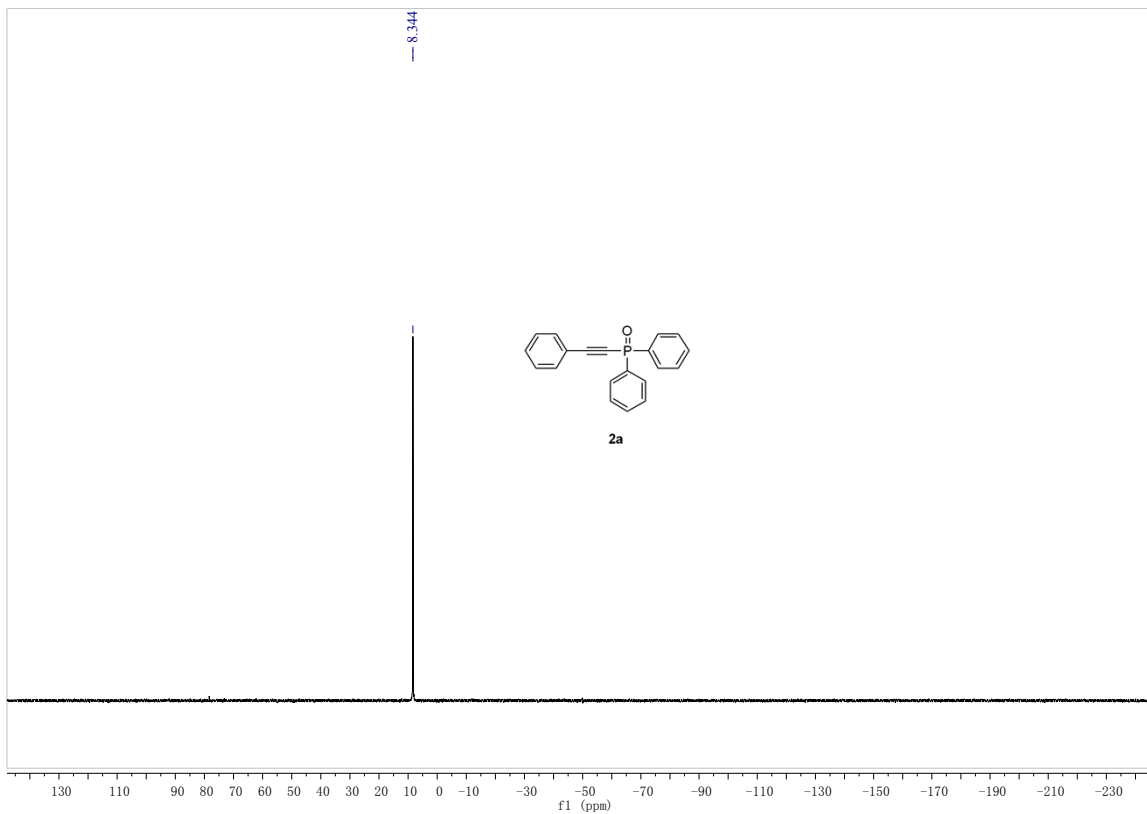


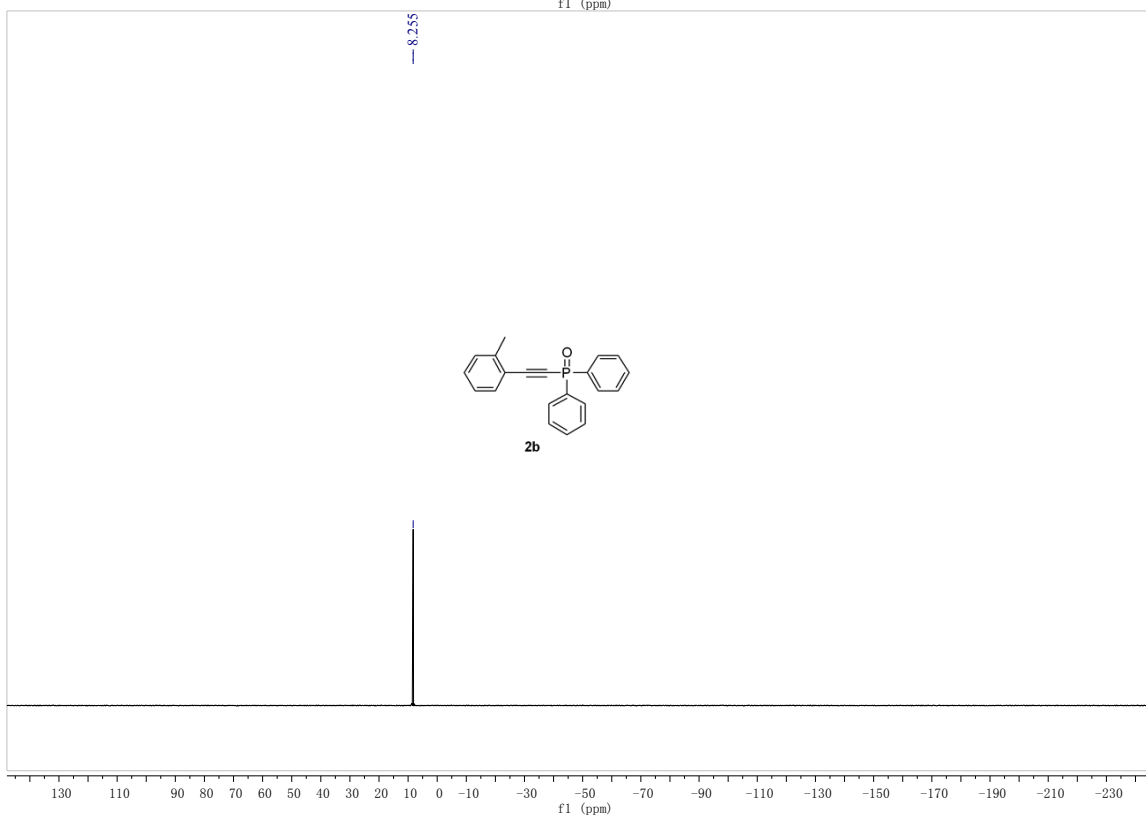
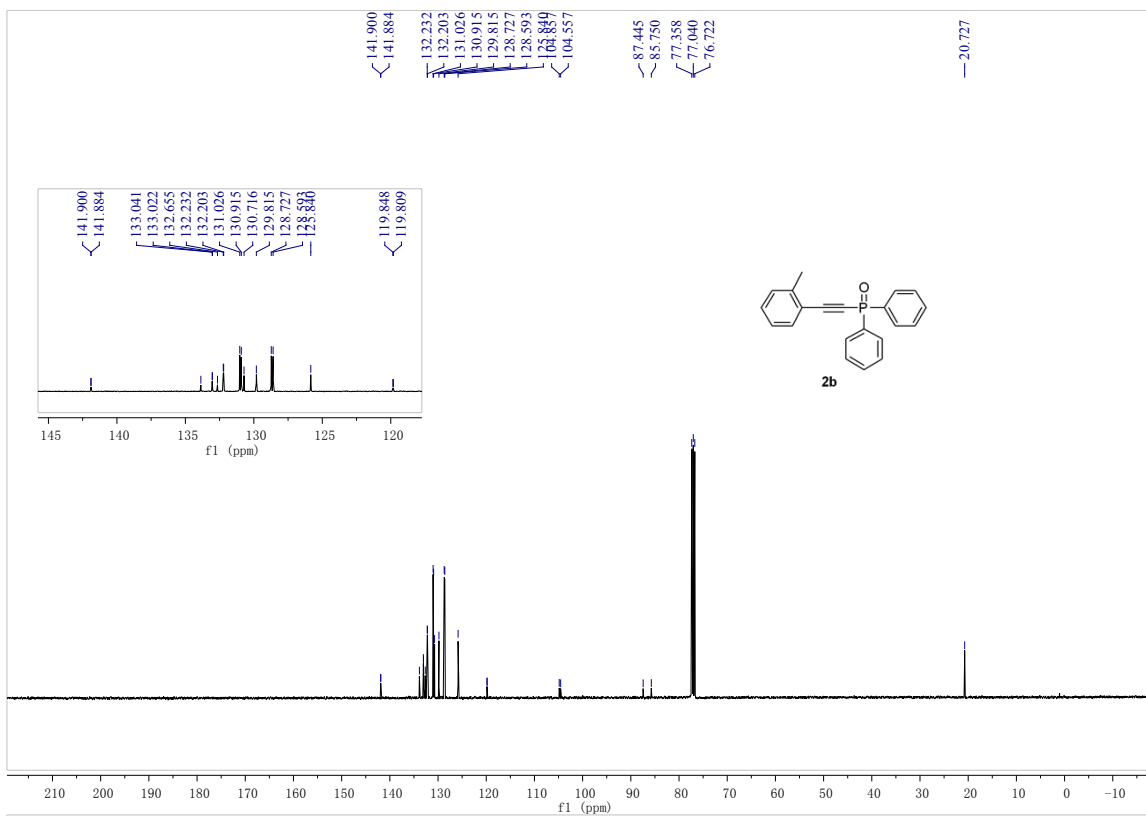
Under N_2 atmosphere, 0.2 mmol diisopropylphoshite **1f**, 0.4 mmol phenylacetylene, 5 mol% $\text{Pd}(\text{OAc})_2$, 0.4 mmol AgBF_4 , 0.4 mmol Et_3N and 1 mL THF were charged into a 10 mL schlenck tube, the mixture was stirred at 100 °C for 16 hours. **2z** was isolated as an oil. ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, 2H, $J = 6.8$ Hz), 7.45 (t, 1H, $J = 6.8$ Hz), 7.38 (t, 2H, $J = 7.2$ Hz), 4.80–4.84 (m, 2H), 1.42 (d, 12H, $J = 4.2$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ -8.52; ^{13}C NMR (100 MHz, CDCl_3) δ 132.46 (d, $J_{\text{P-C}} = 1.3$ Hz), 130.50, 128.51, 119.74 (d, $J_{\text{P-C}} = 5.5$ Hz), 98.11 (d, $J_{\text{P-C}} = 52.6$ Hz), 79.74 (d, $J_{\text{P-C}} = 297.1$ Hz), 72.33 (d, $J_{\text{P-C}} = 5.4$ Hz), 23.89 (d, $J_{\text{P-C}} = 4.5$ Hz), 23.61 (d, $J_{\text{P-C}} = 4.7$ Hz). MS (EI): 266.

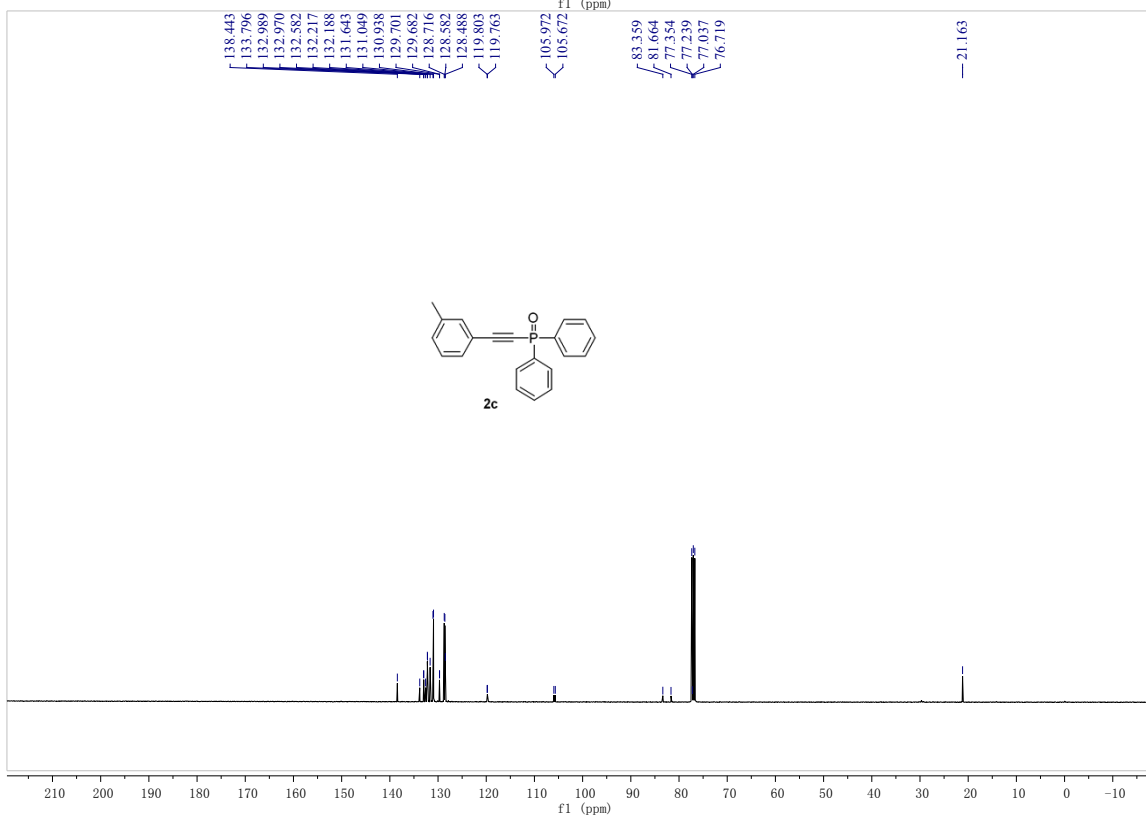
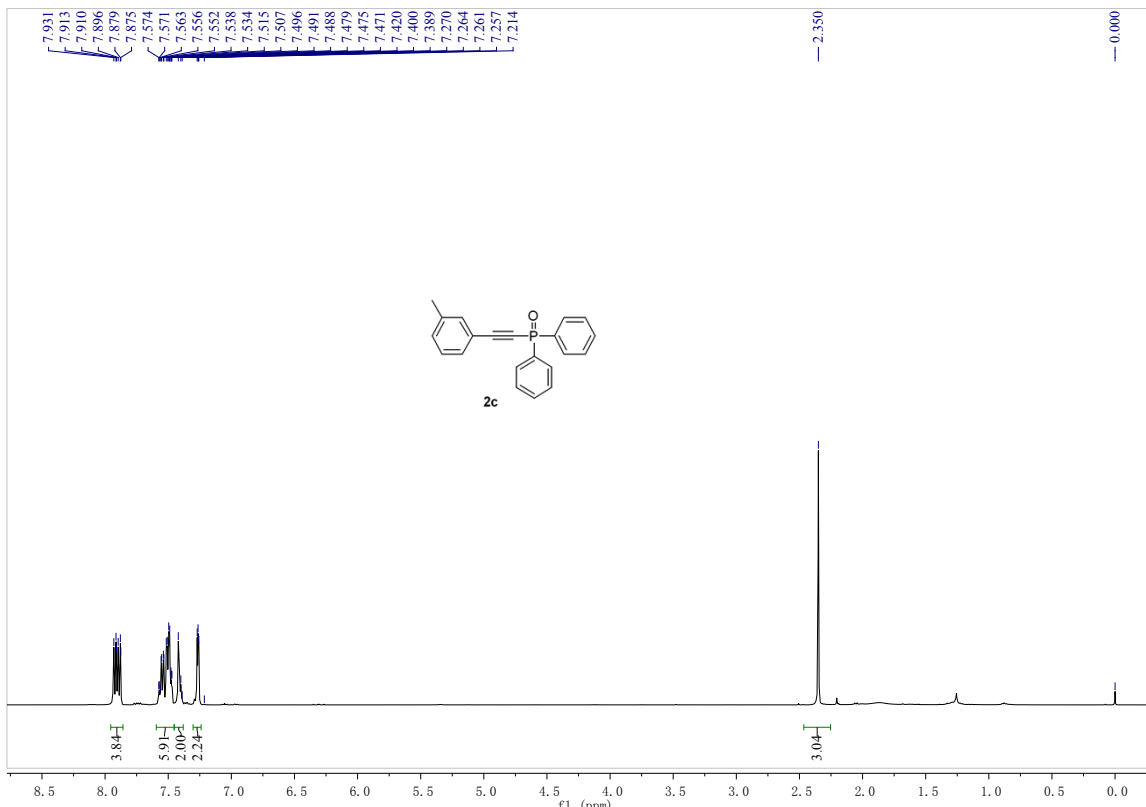
- (1) Y. Wang, J. Gan, L. Liu, H. Yuan, Y. Gao, Y. Liu and Y. Zhao, *J. Org. Chem.*, 2014, **79**, 3678.
- (2) J. Hu, N. Zhao, B. Yang, G. Wang, L.-N. Guo, Y.-M. Liang and S.-D. Yang, *Chem. Eur. J.*, 2011, **17**, 5516.
- (3) X. Yang, D. Matsuo, Y. Suzuma, J.-K. Fang, F. Xu, A. Orita, J. Otera, S. Kajiyama, N. Koumura and K. Hara, *Synlett.*, 2011, **16**, 2402.
- (4) S. Doherty, J. G. Knight, C. H. Smyth and G. A. Jorgenson, *Adv. Synth. Catal.*, 2008, **350**, 1808.

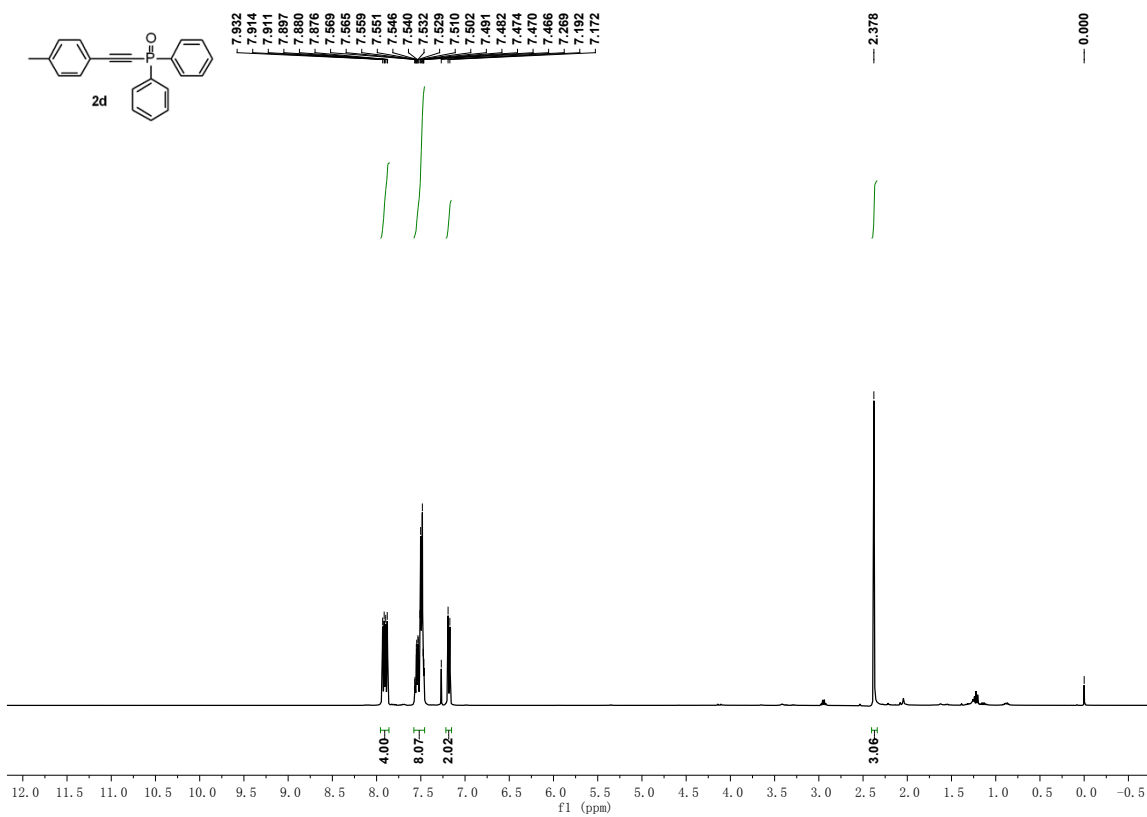
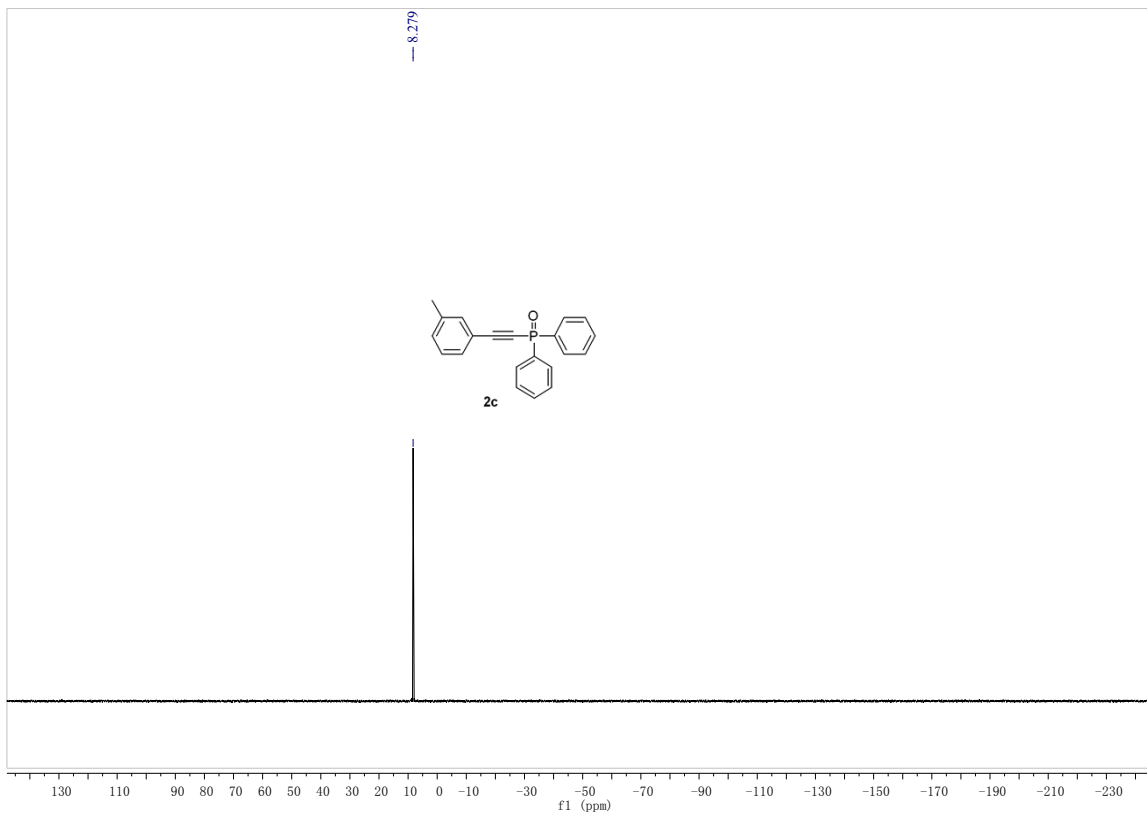
Copies of ^1H NMR, ^{31}P NMR and ^{13}C NMR spectra

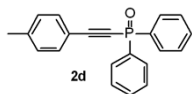




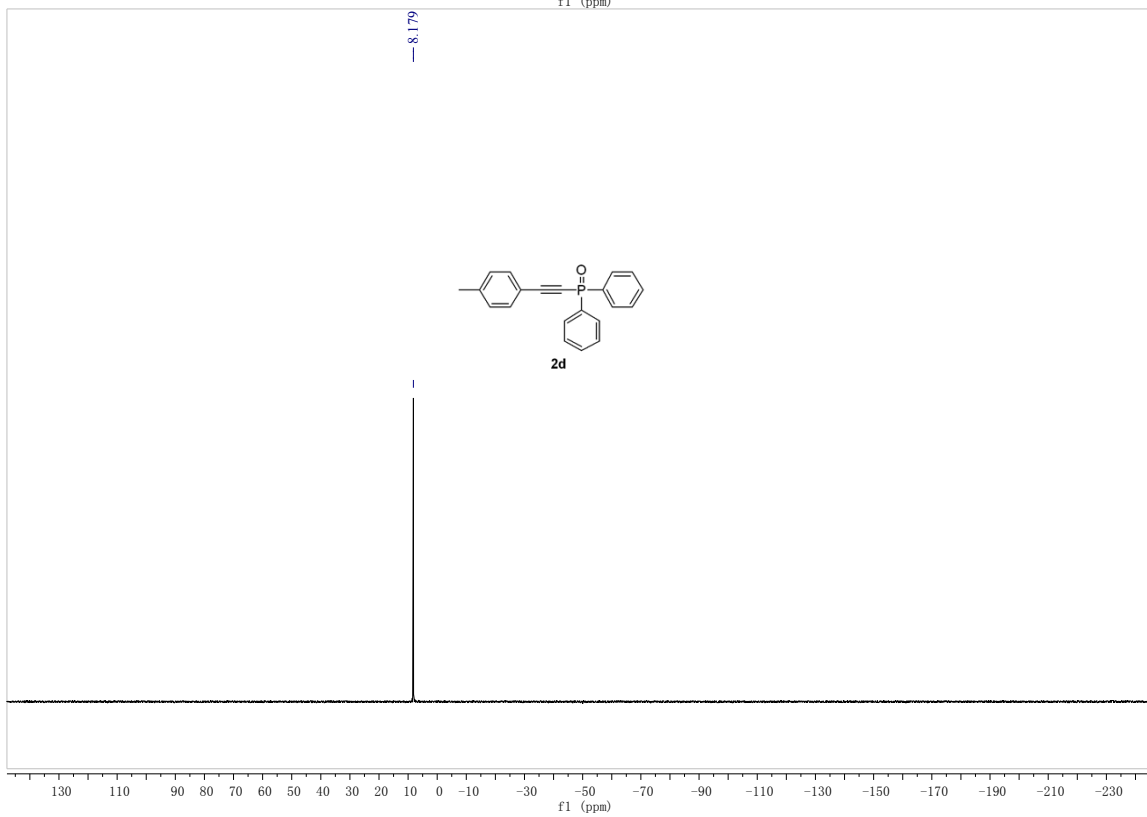
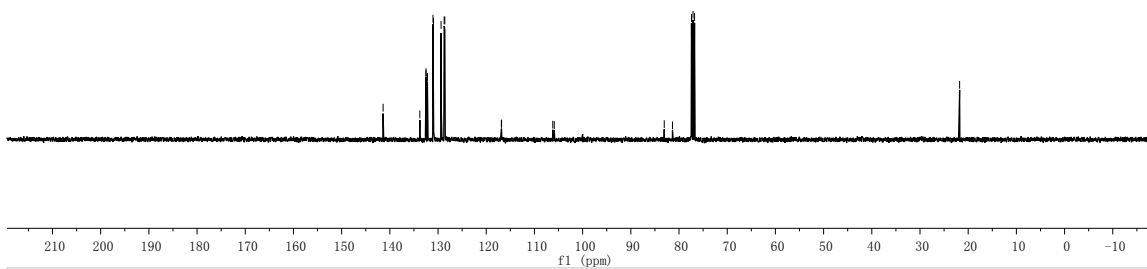


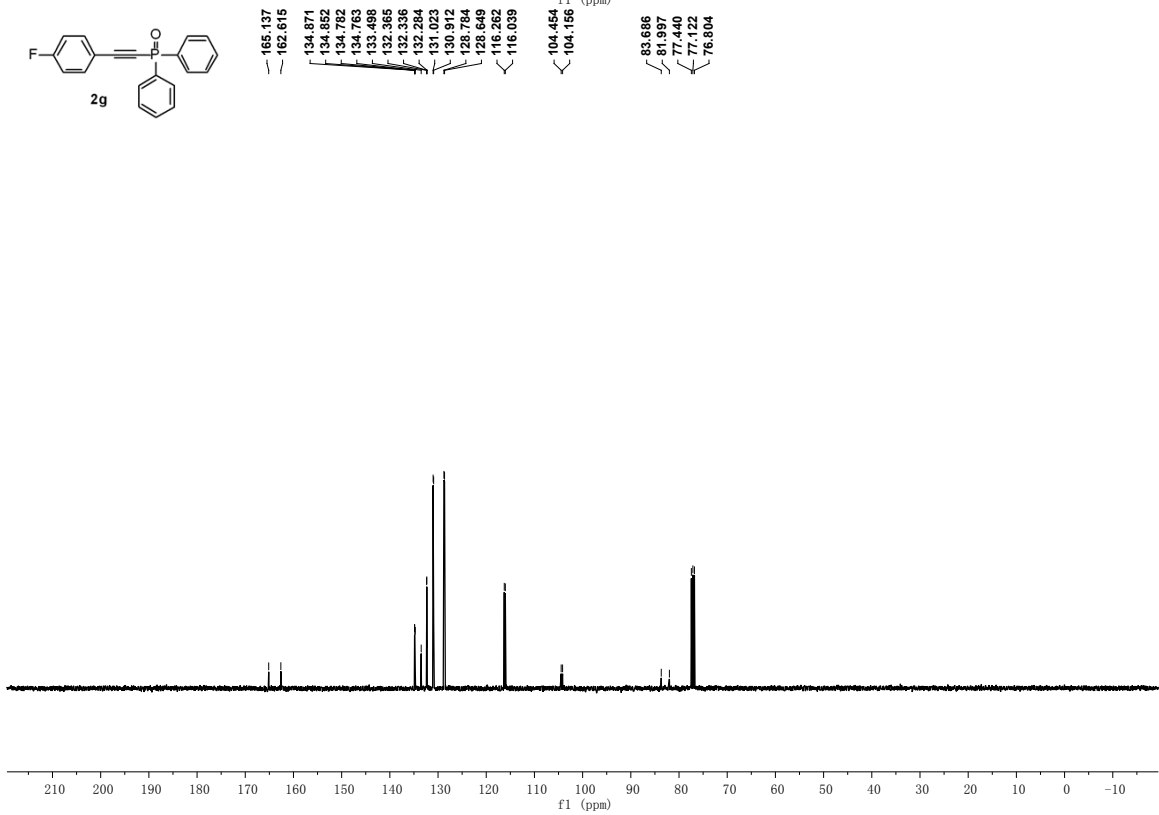
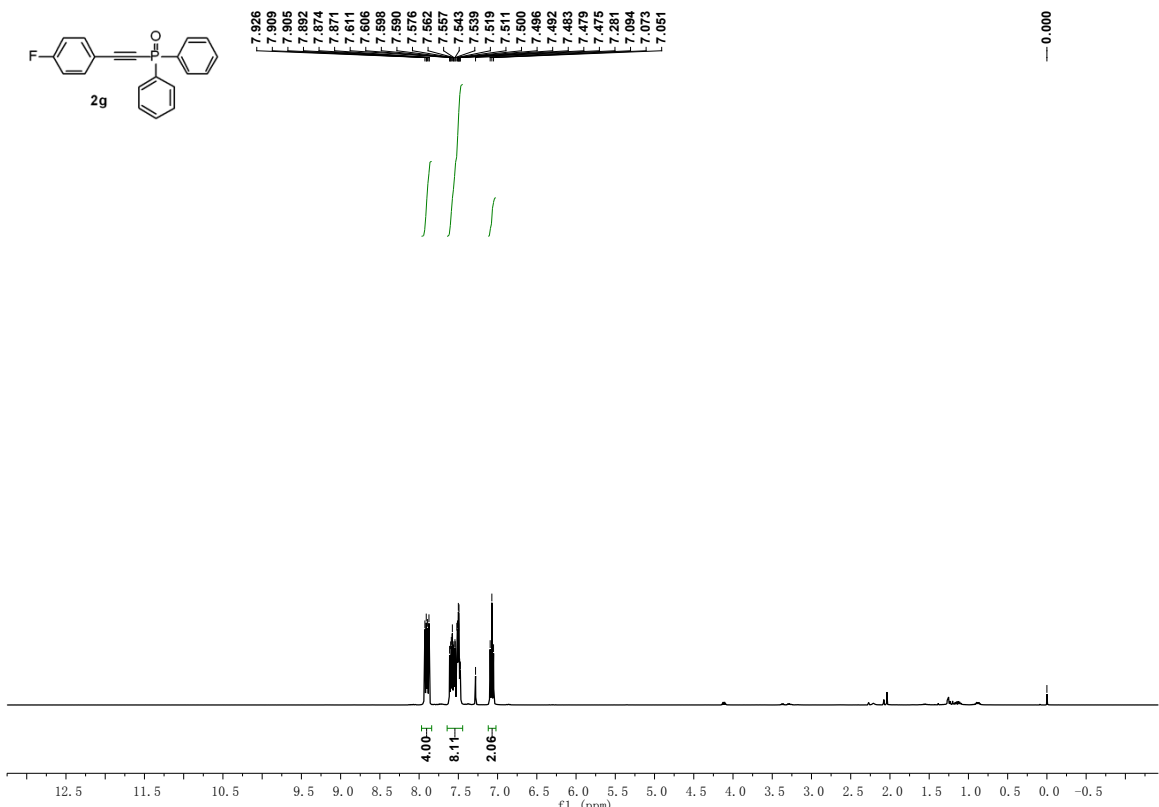


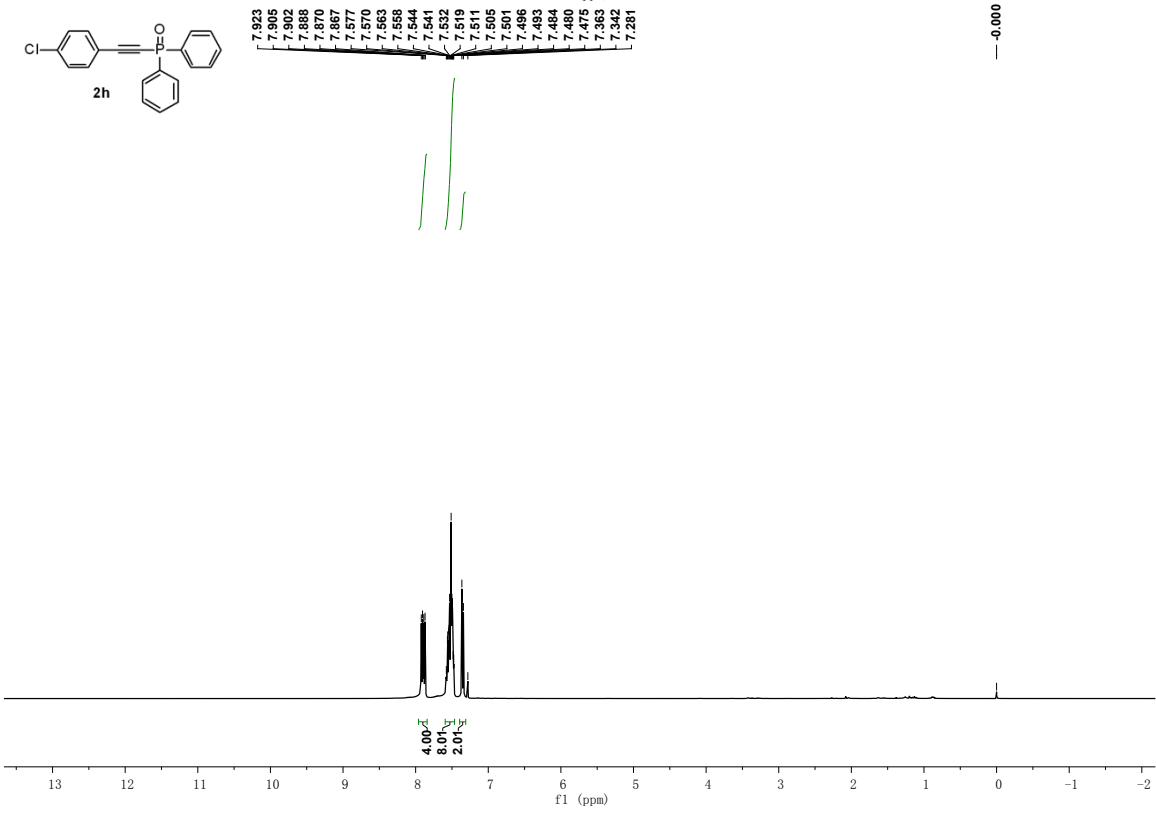
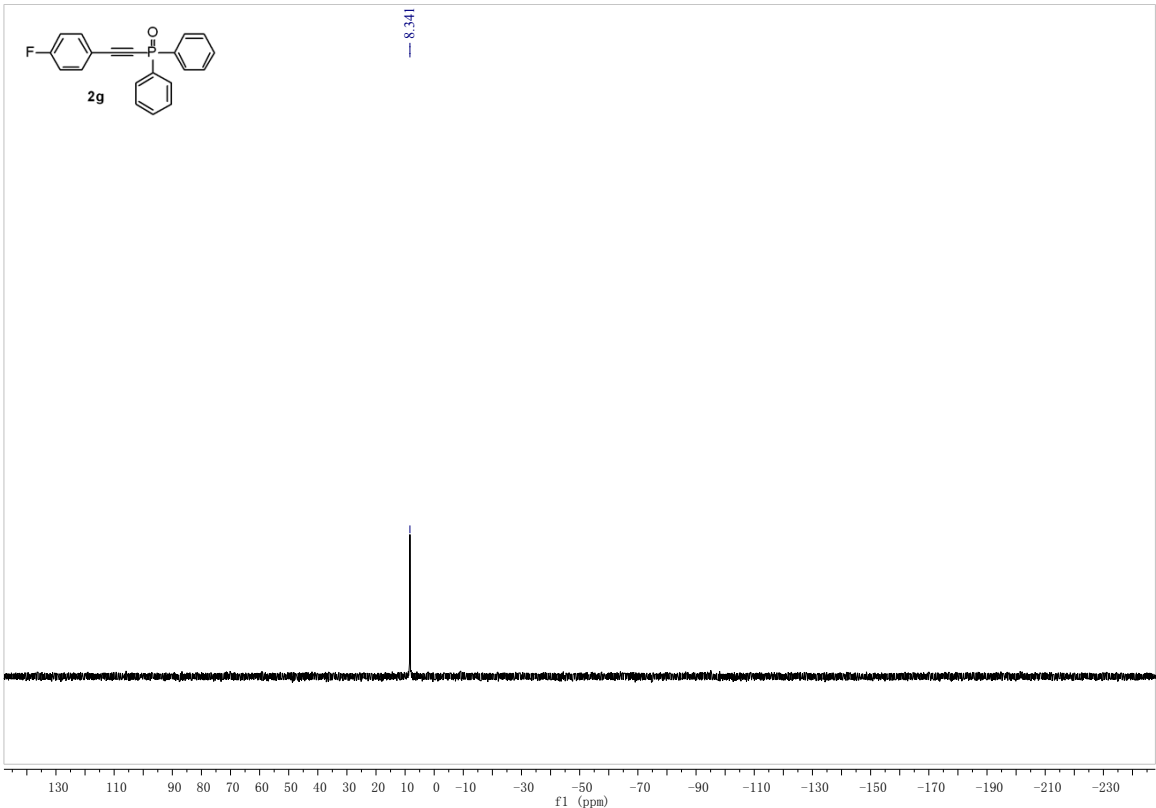


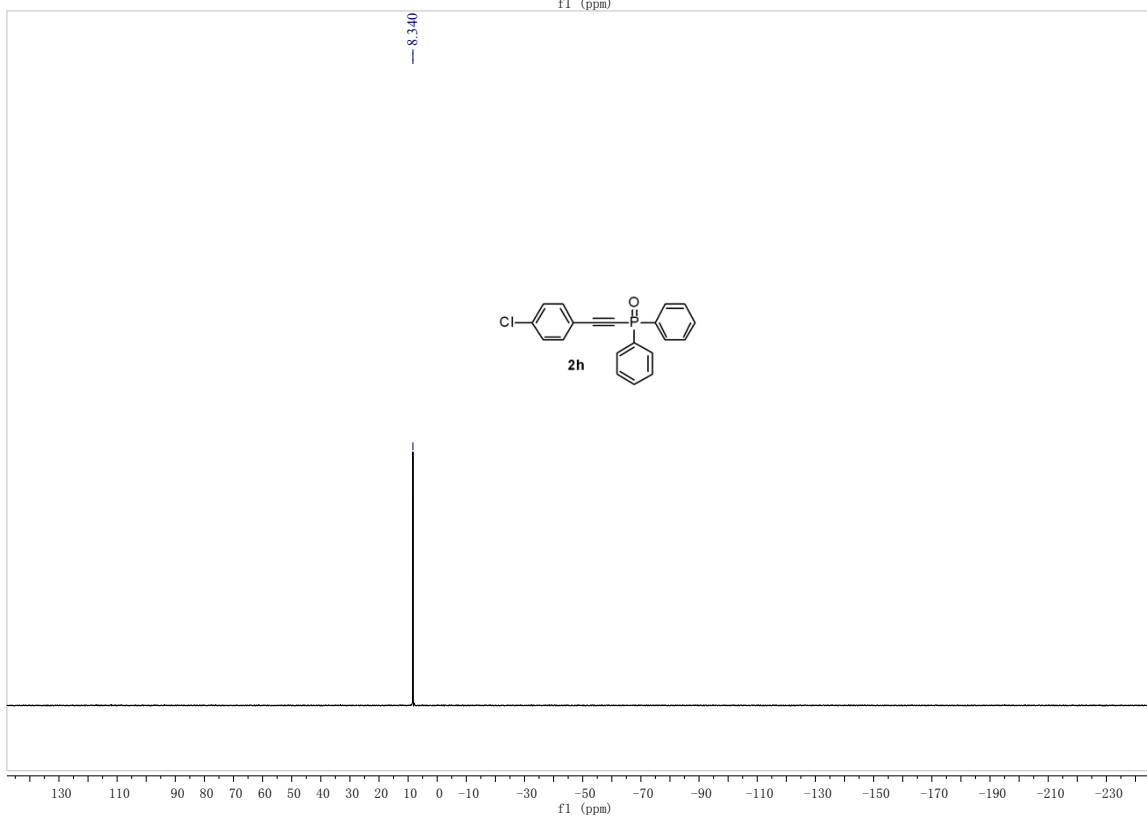
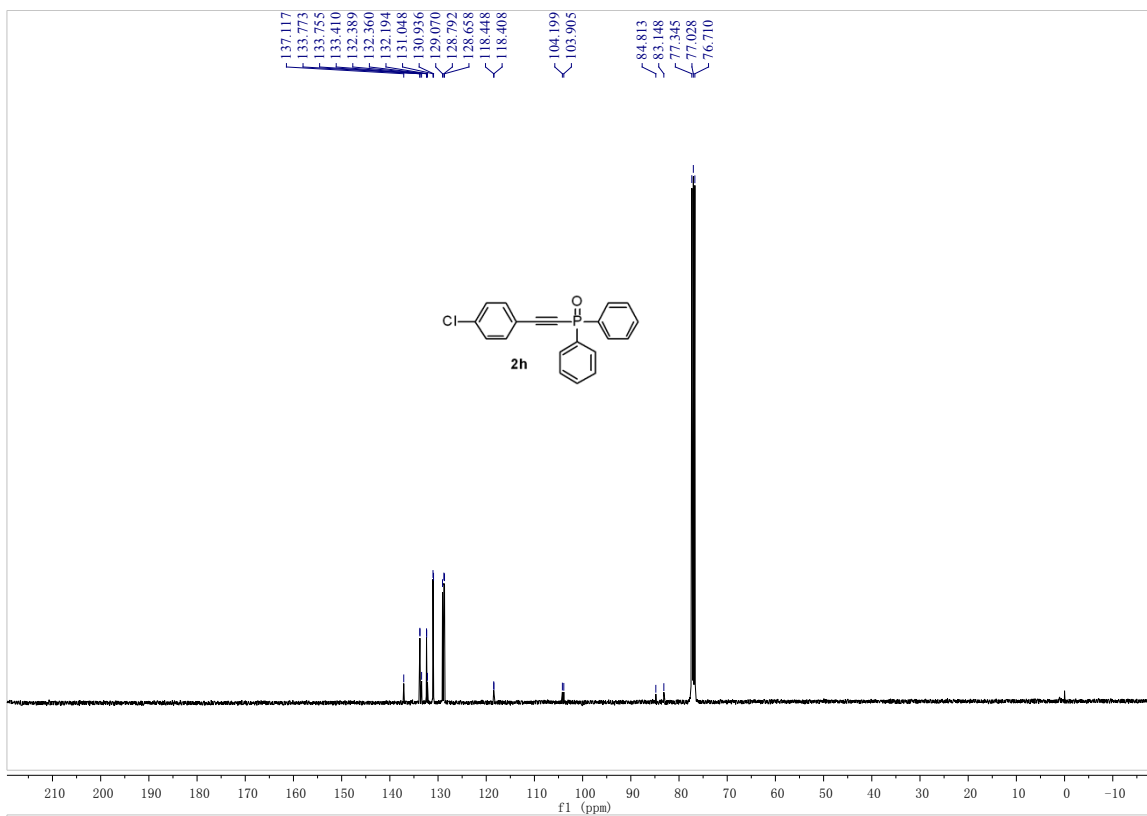


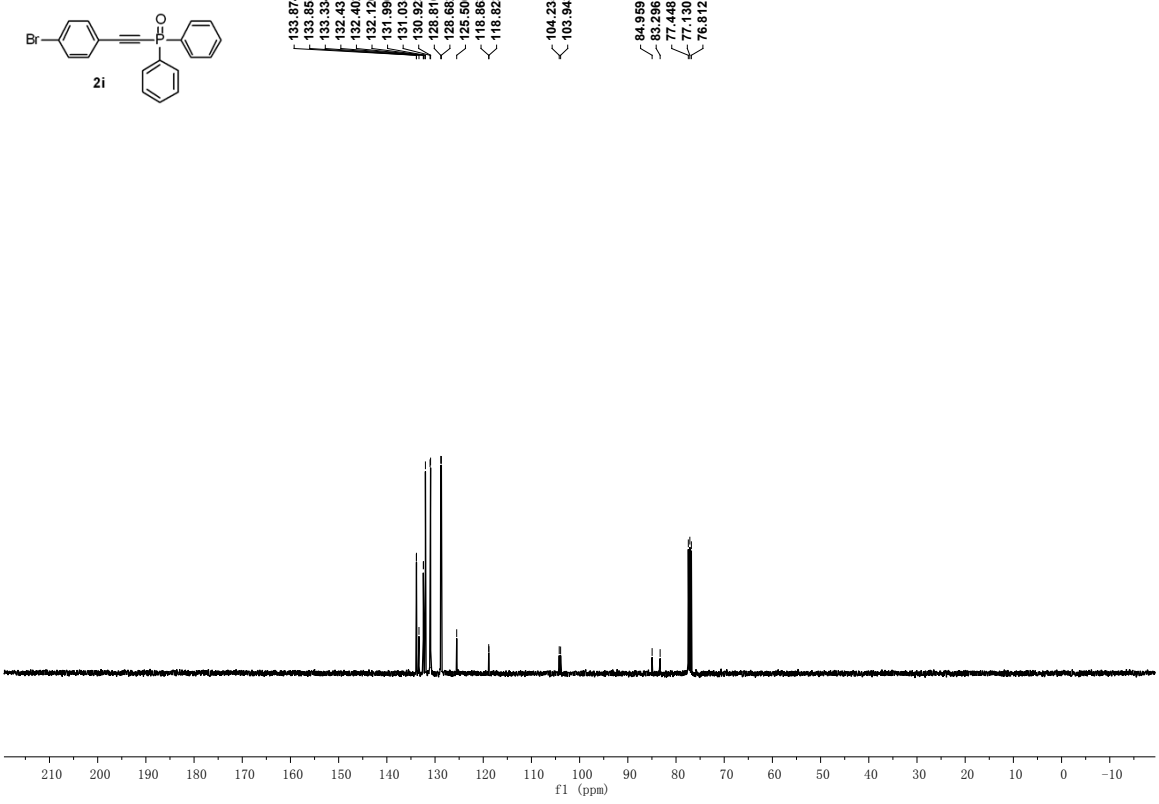
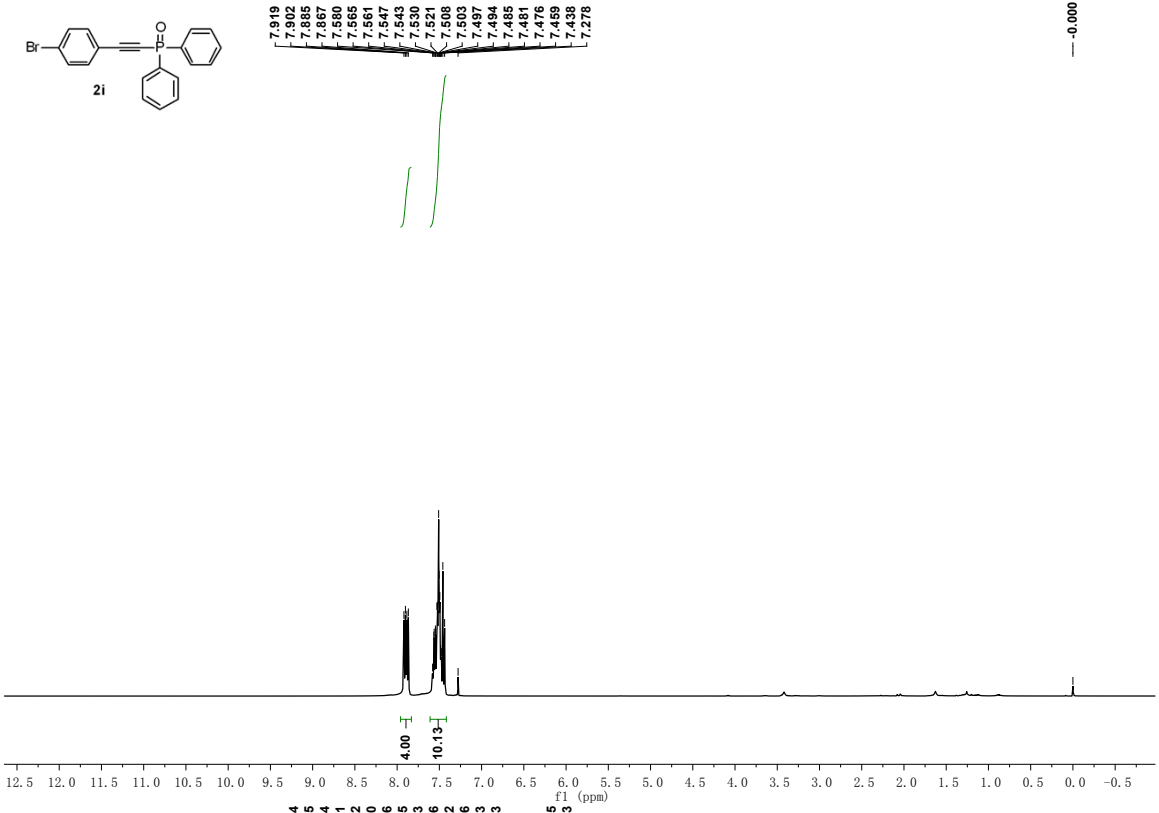
— 141.396
 / 132.485
 / 131.052
 / 130.944
 / 129.373
 / 128.730
 / 118.588
 / 116.522
 / 106.192
 / 105.889
 / 83.064
 / 77.344
 / 77.096
 / 76.778
 — 21.777

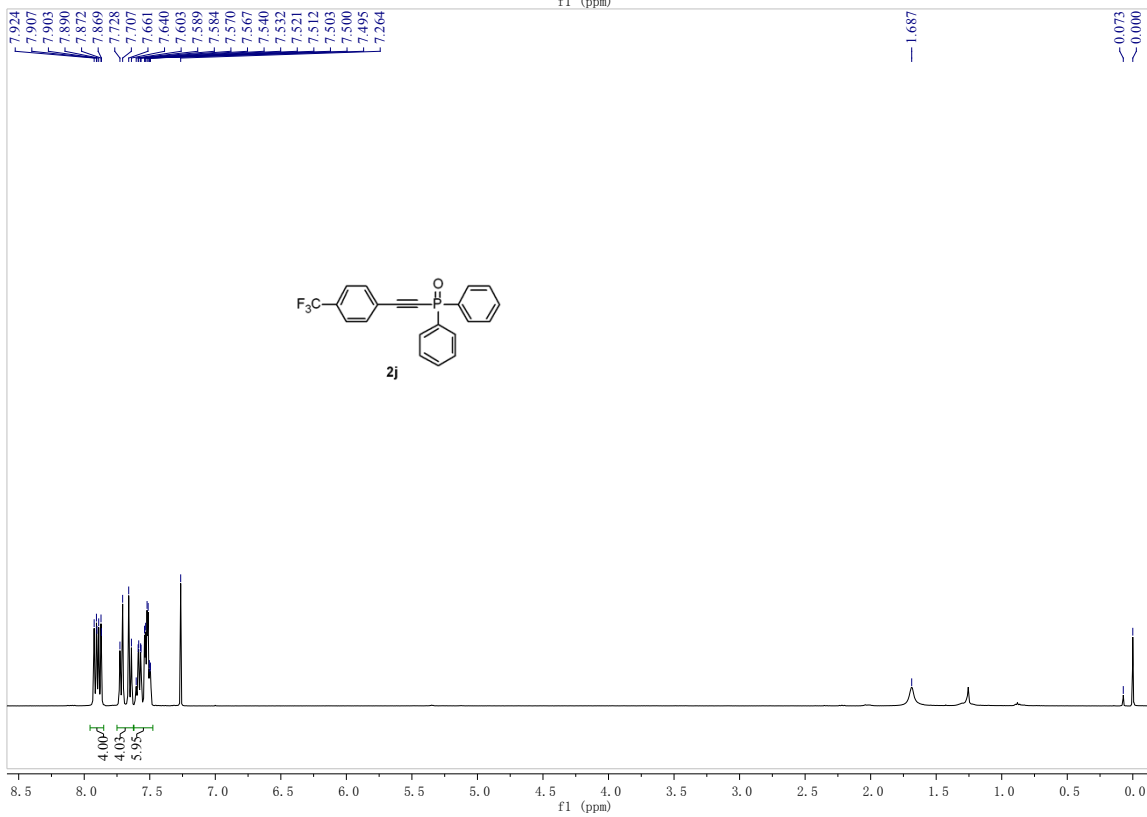
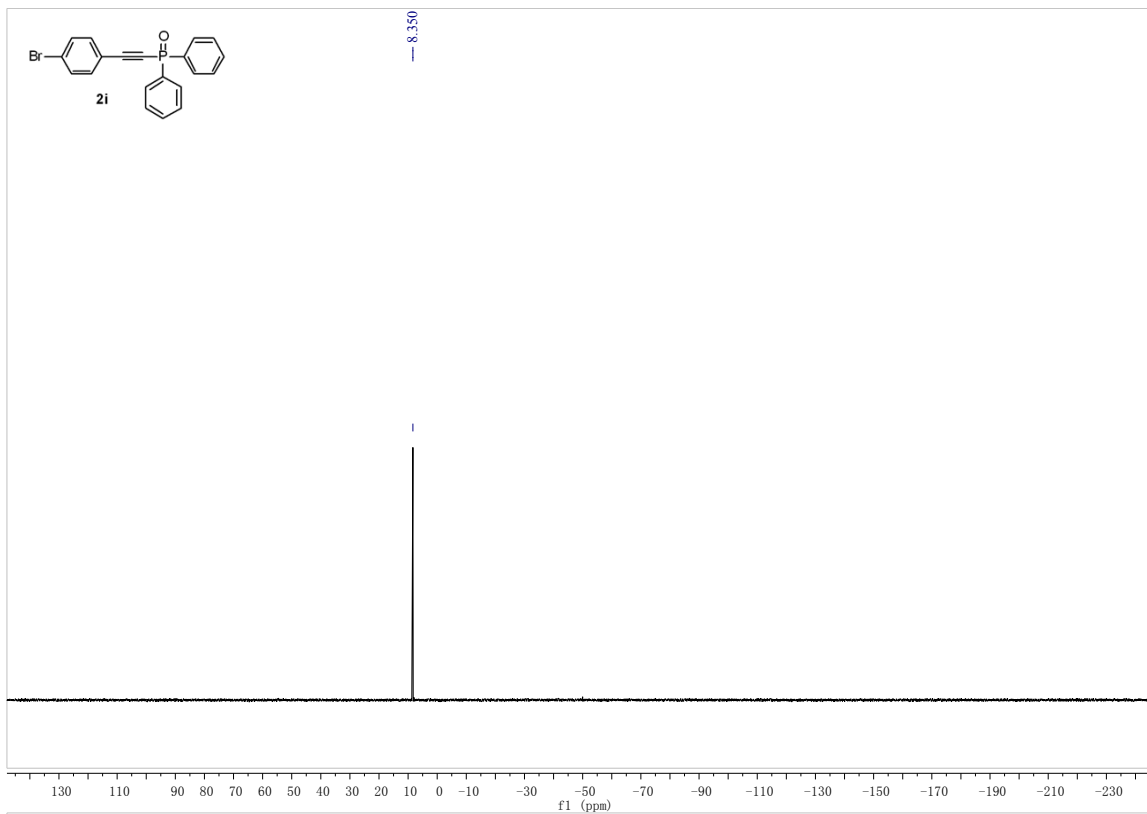


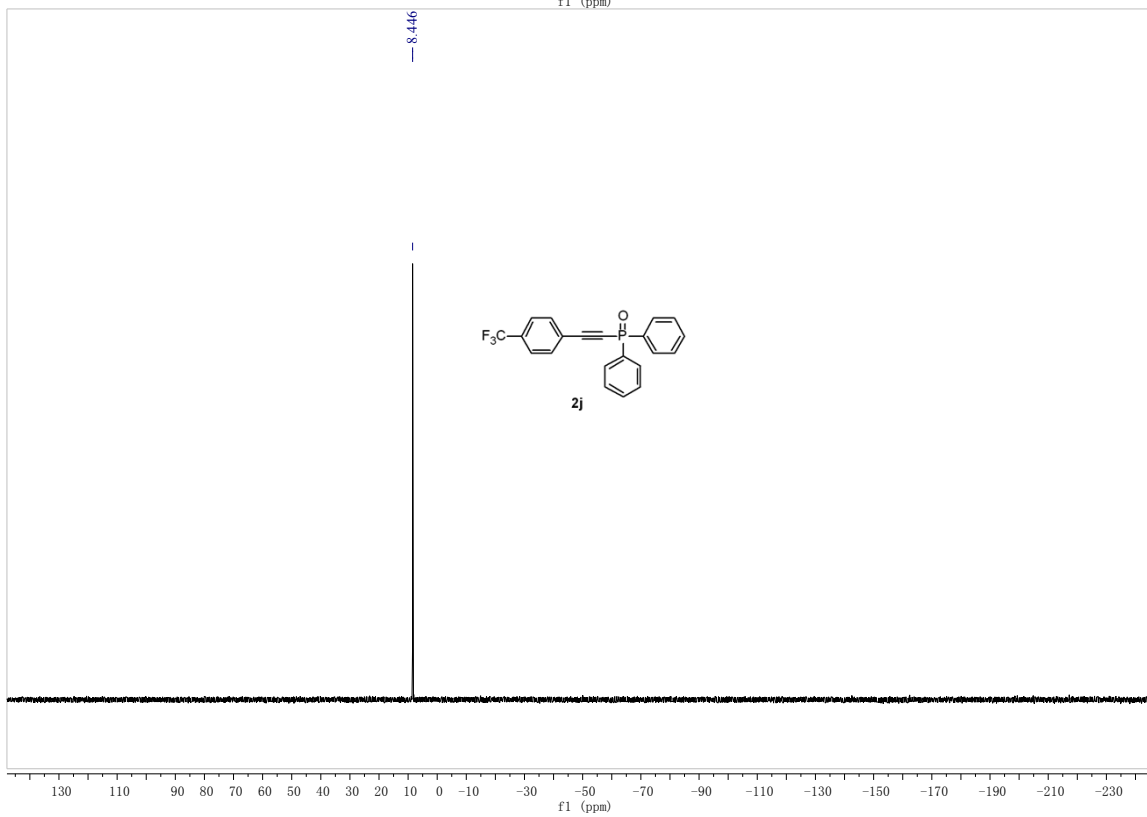
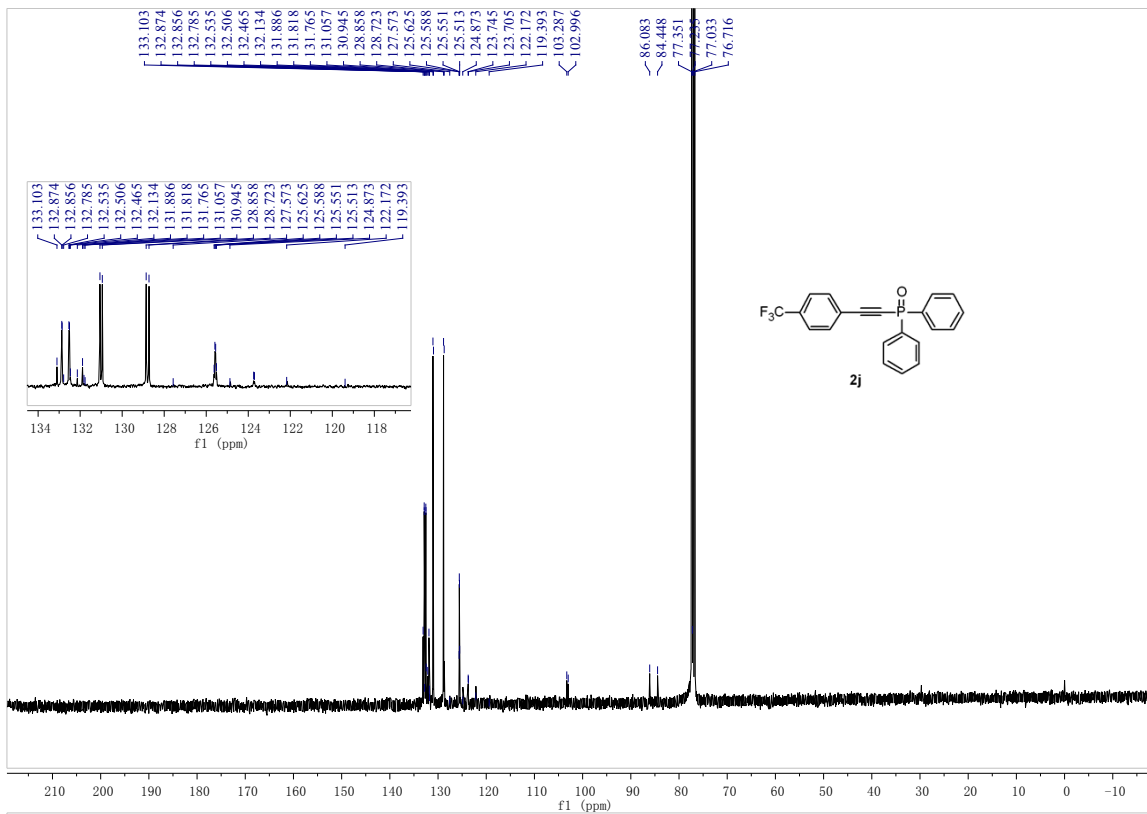


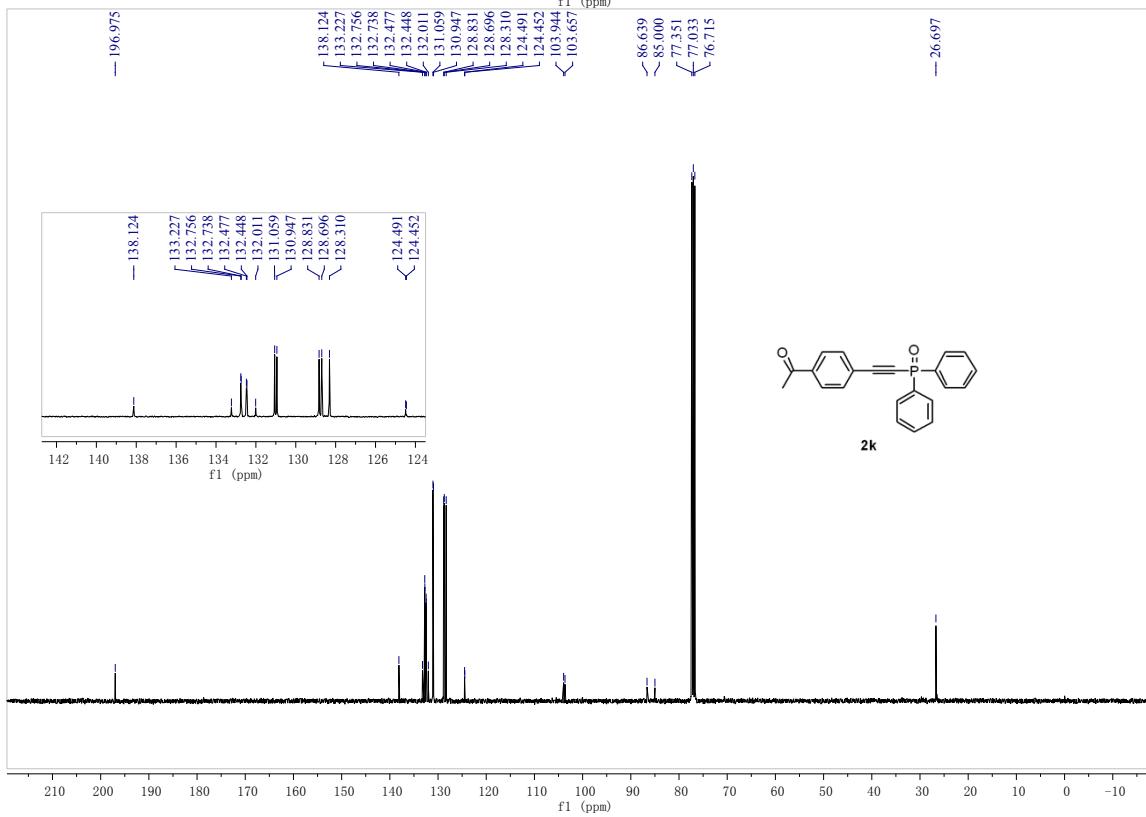
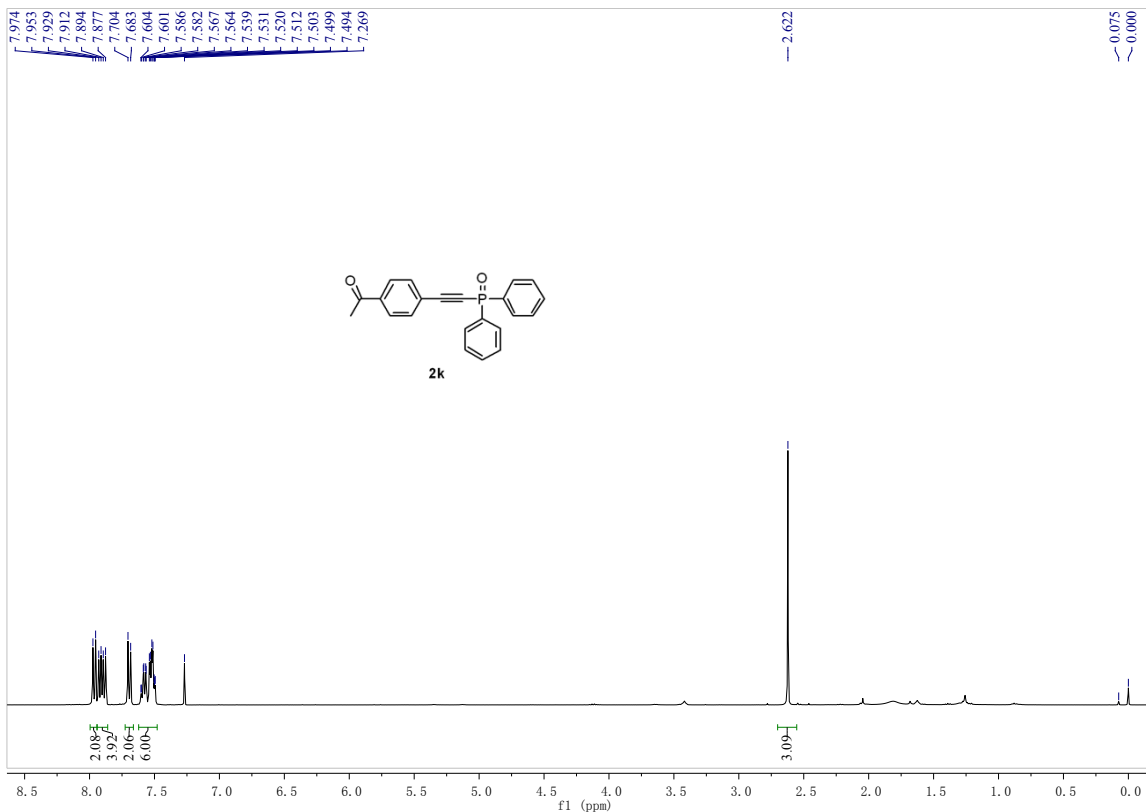


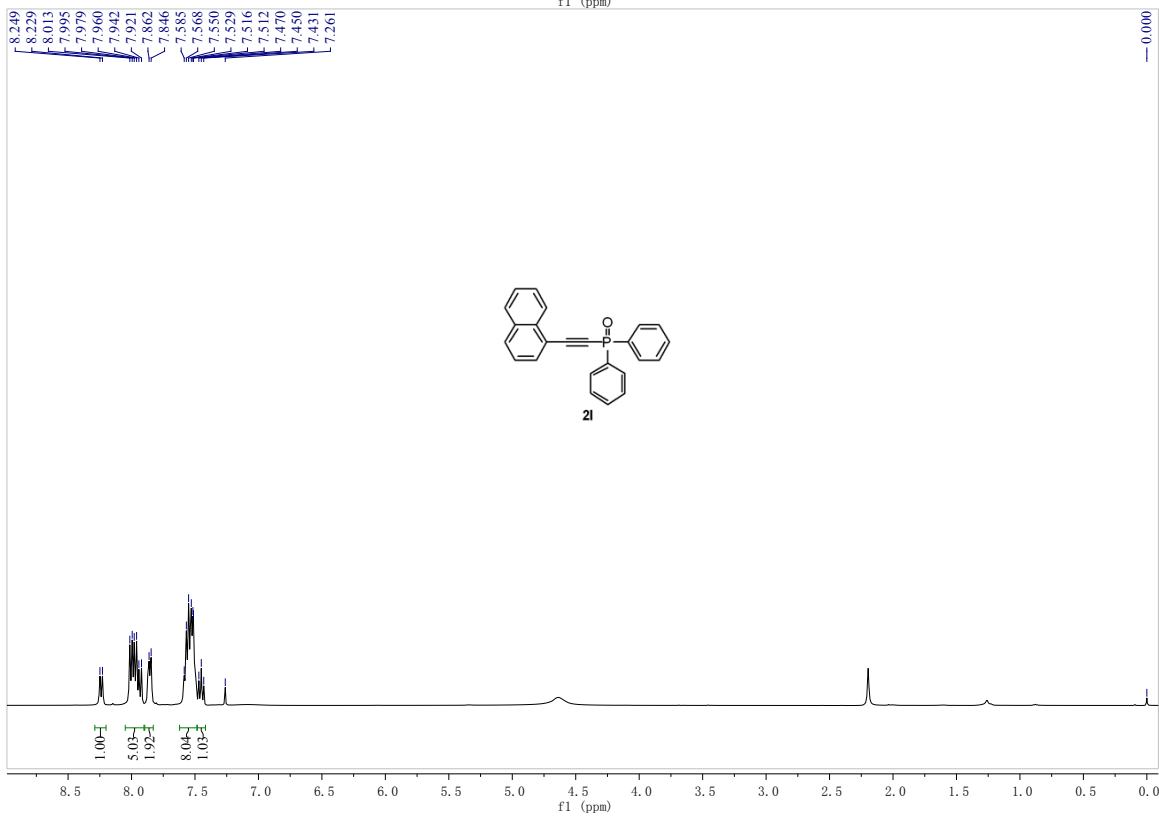
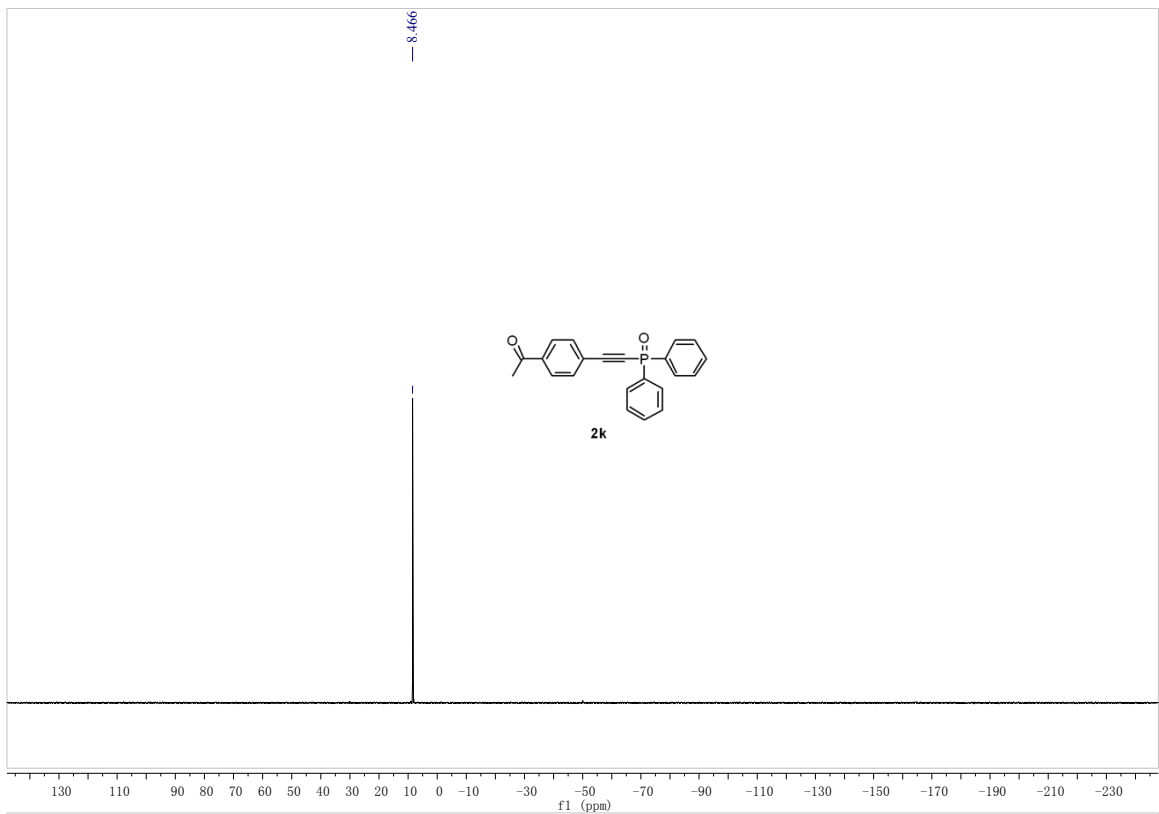


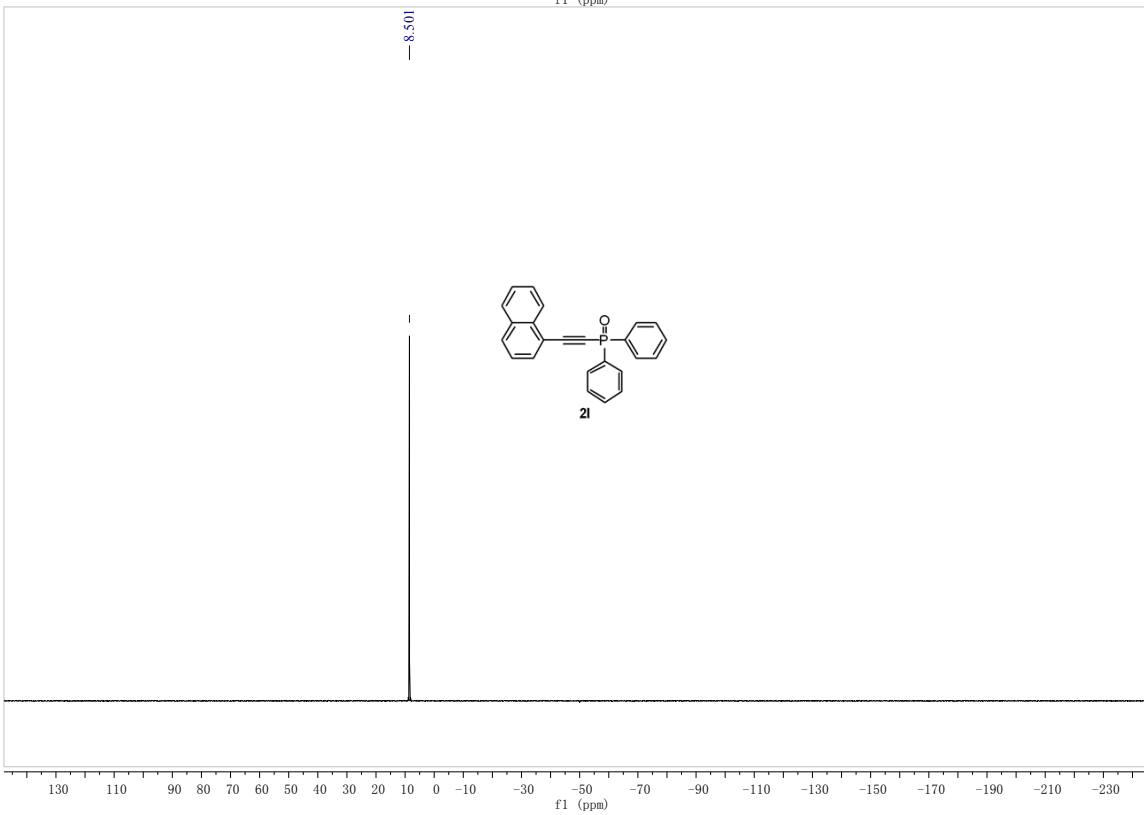
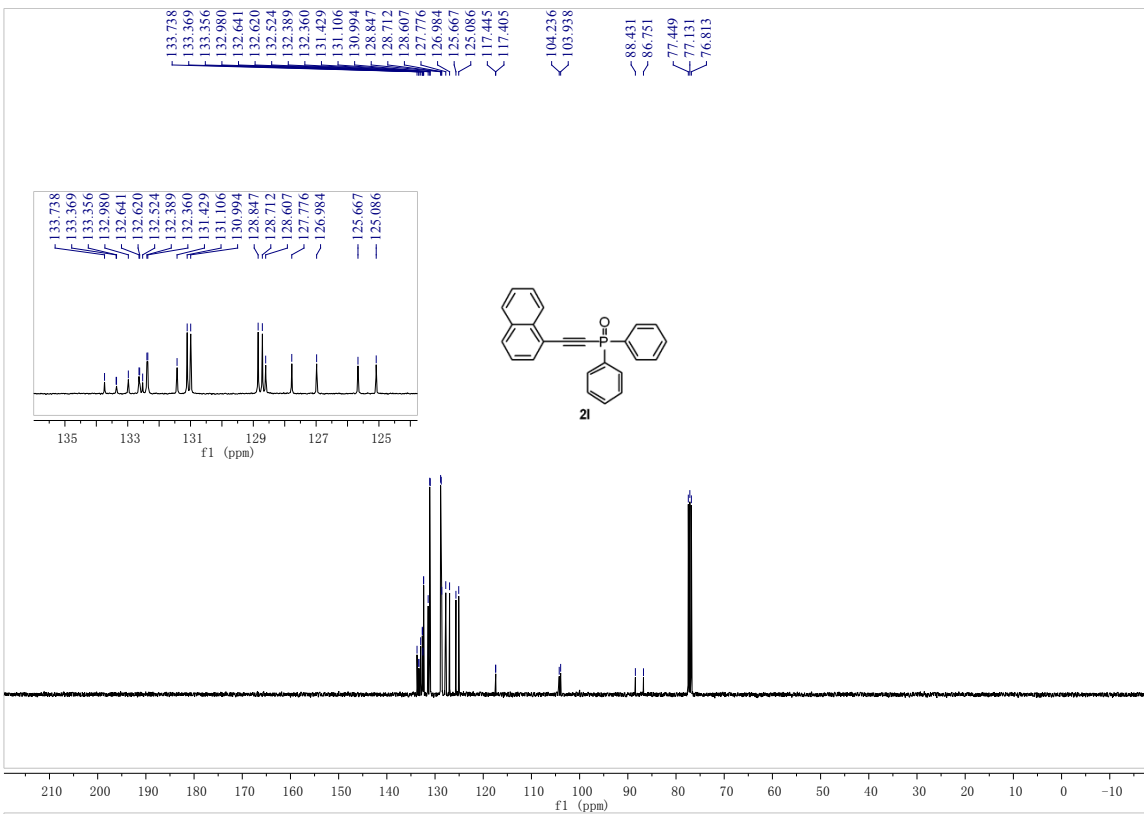


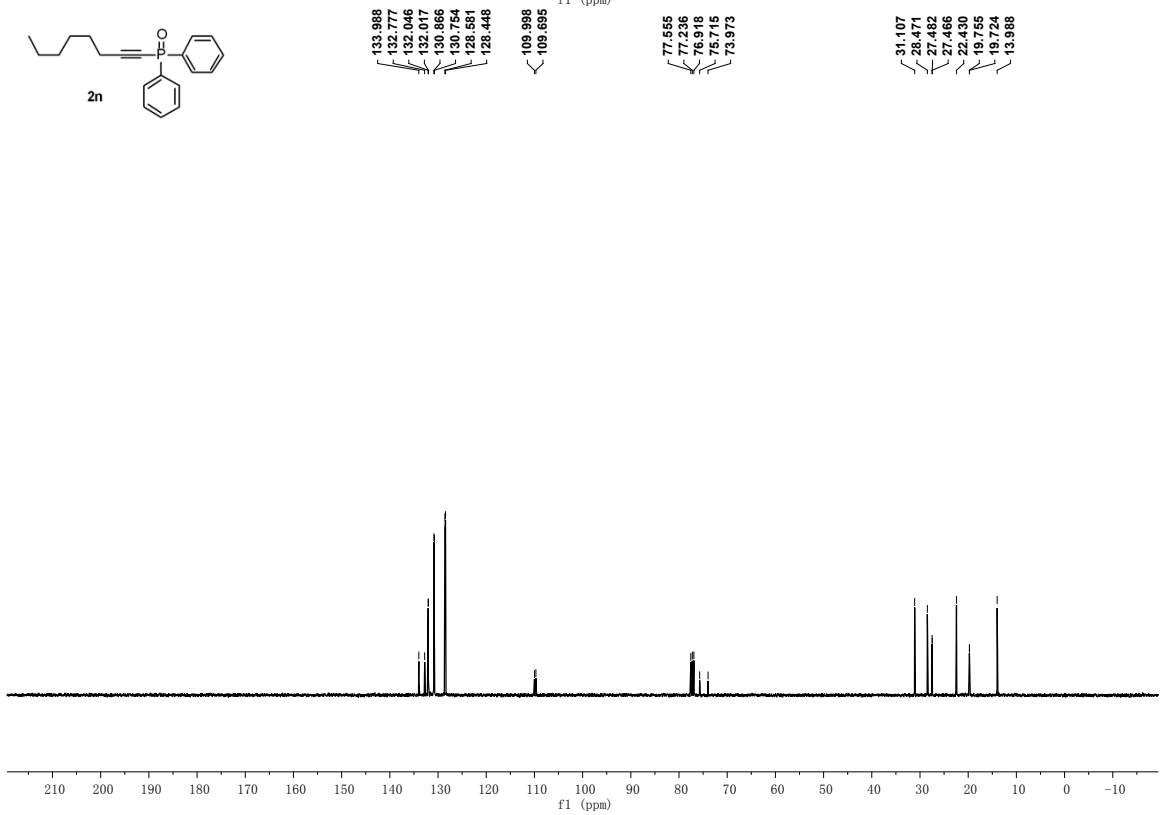
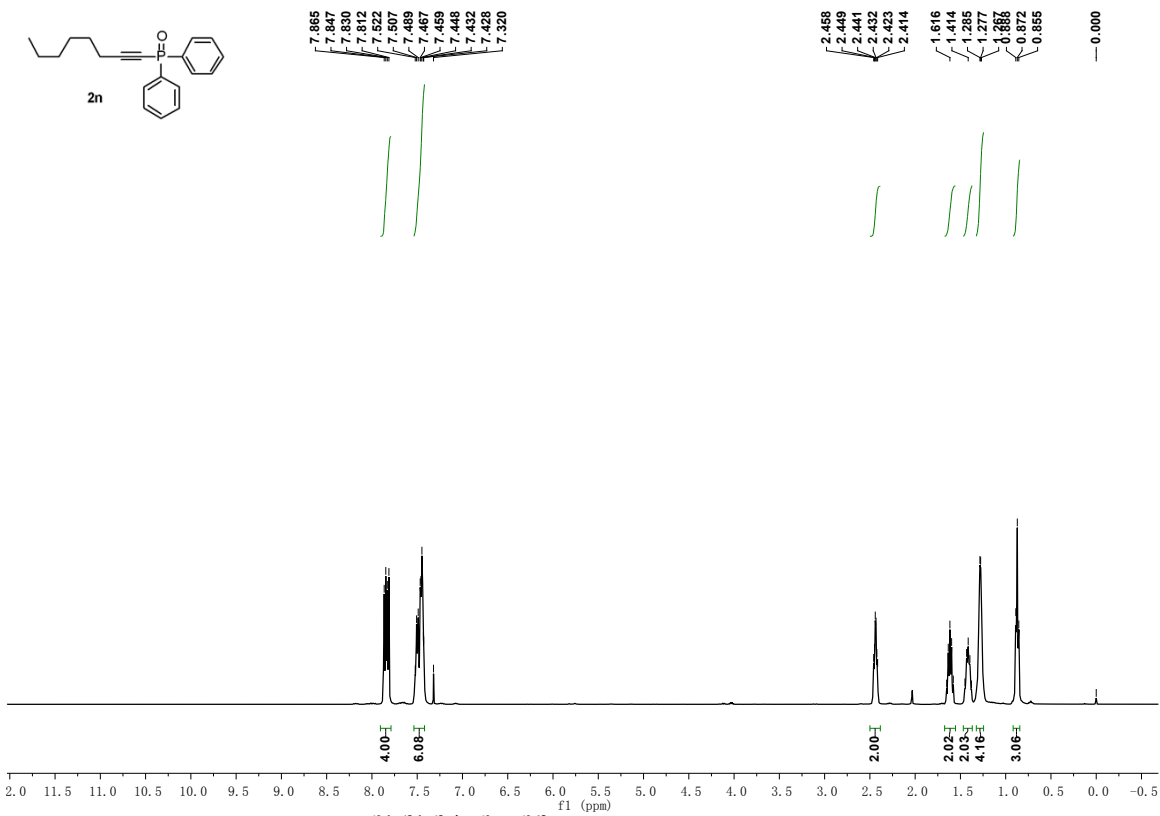


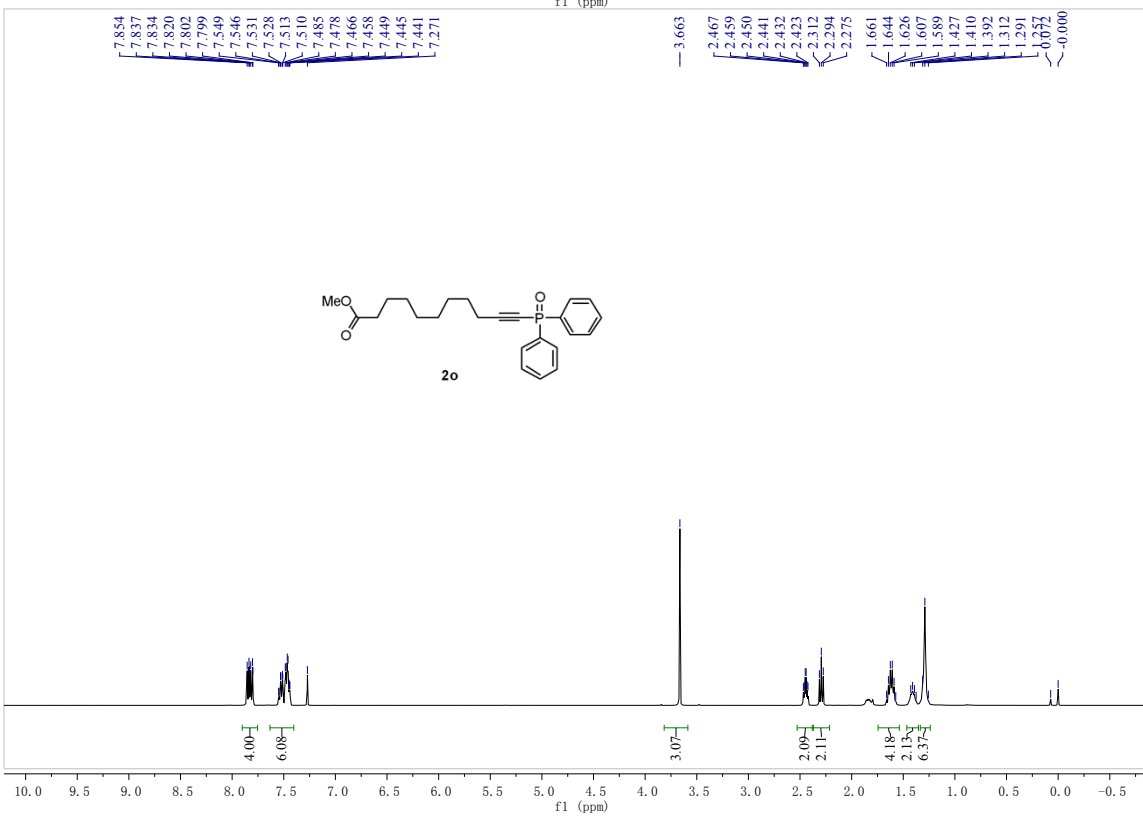
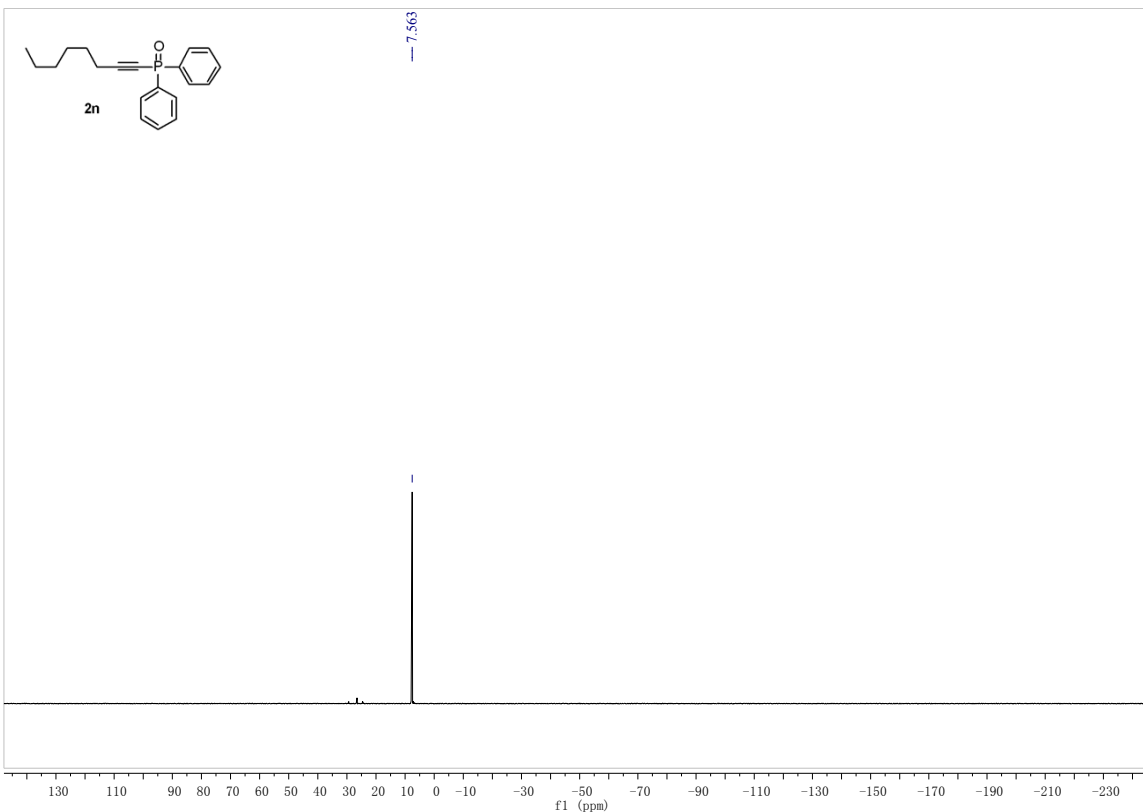


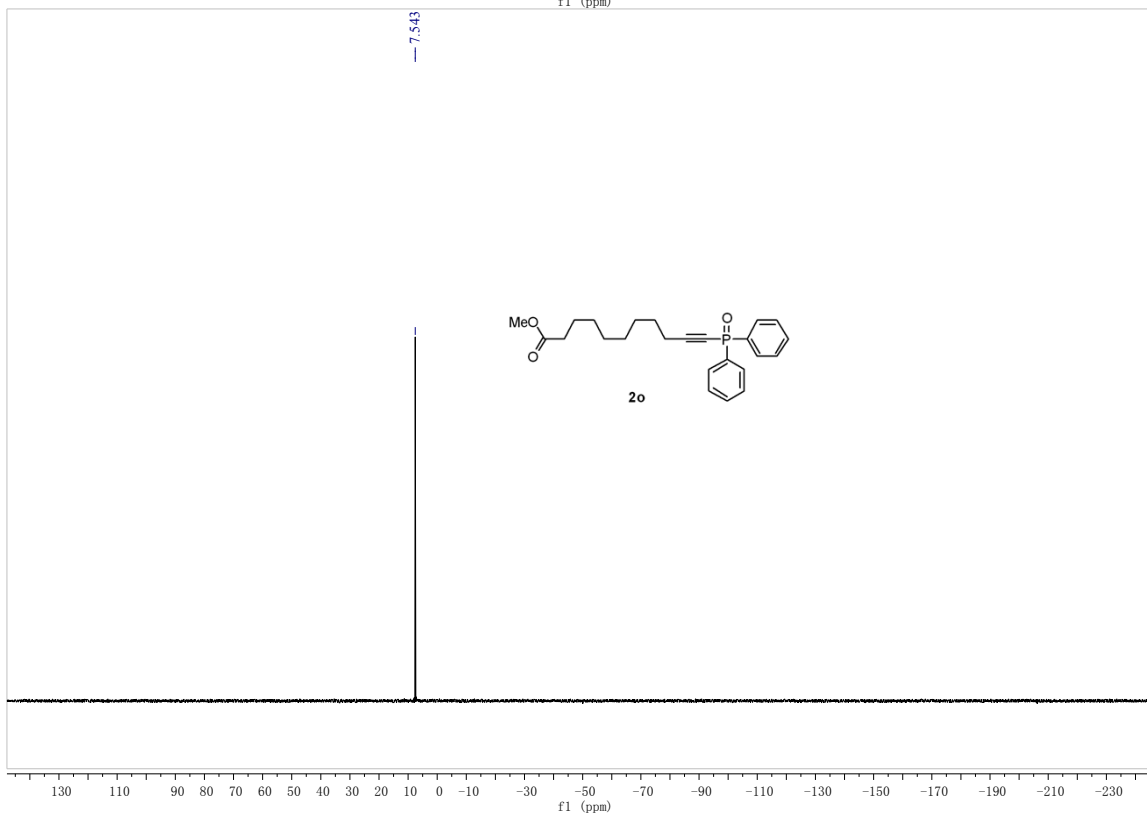
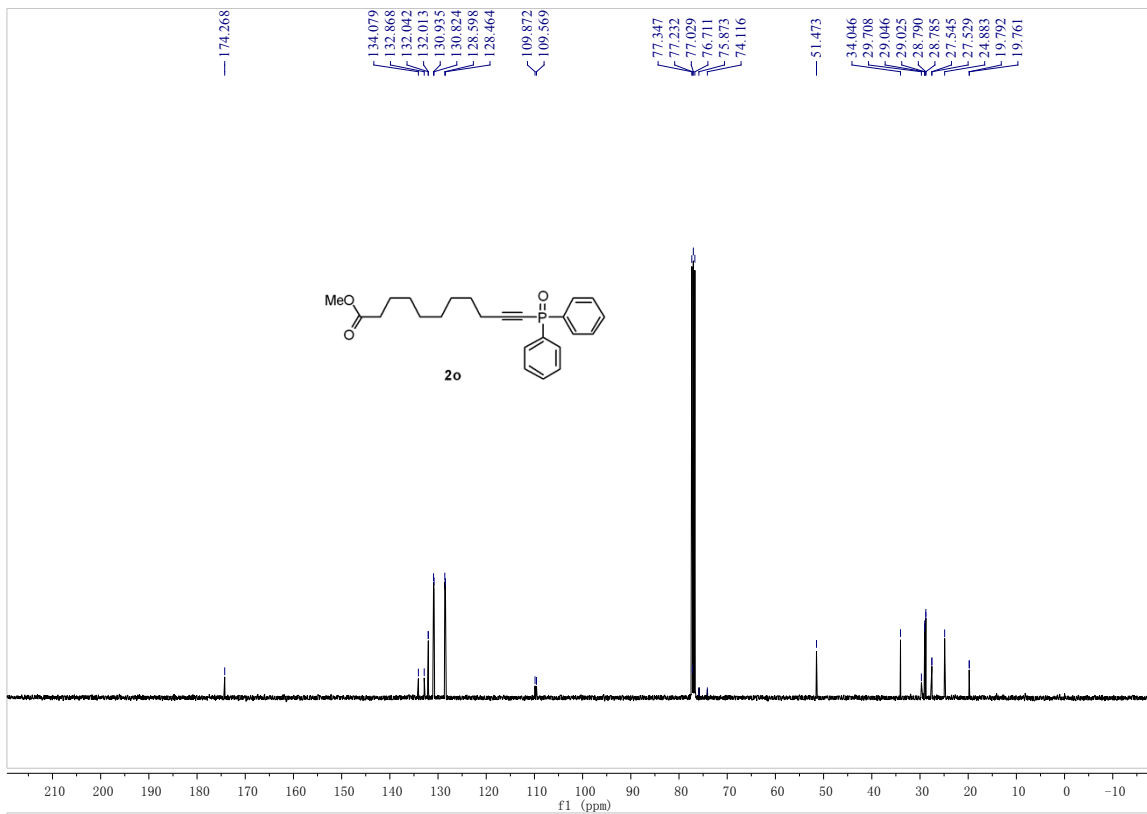


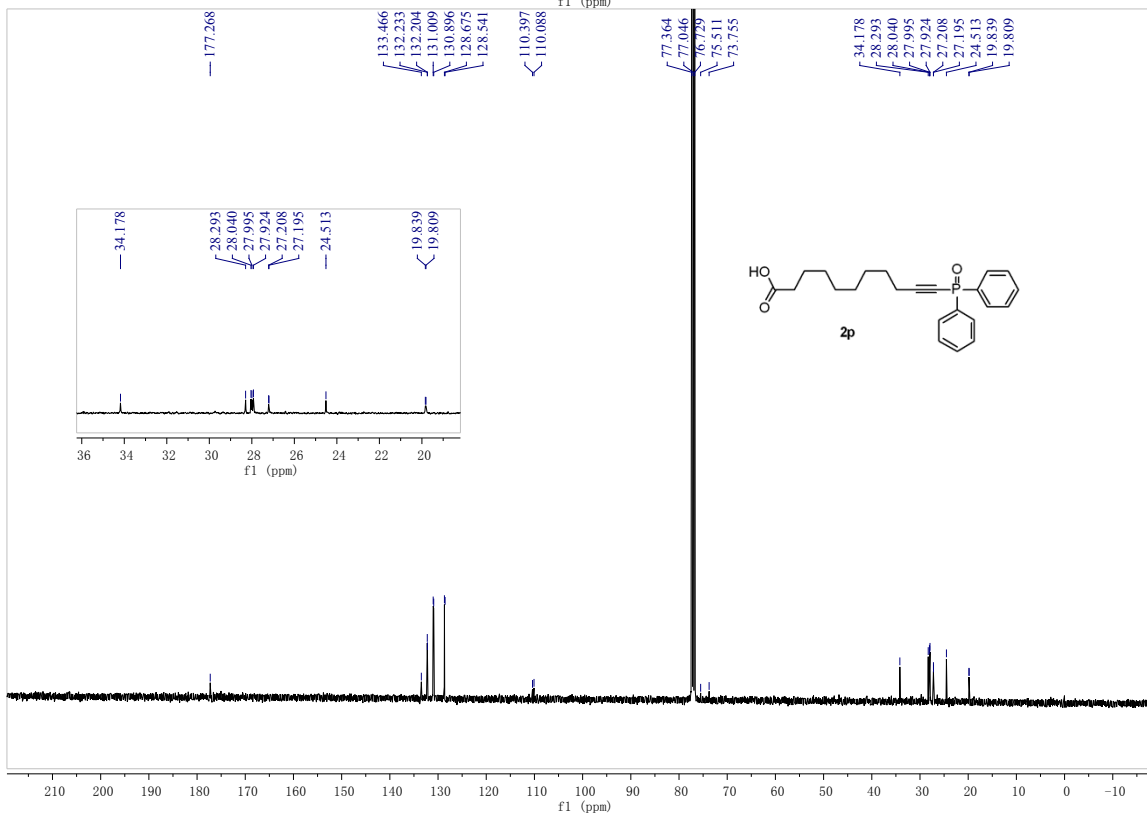
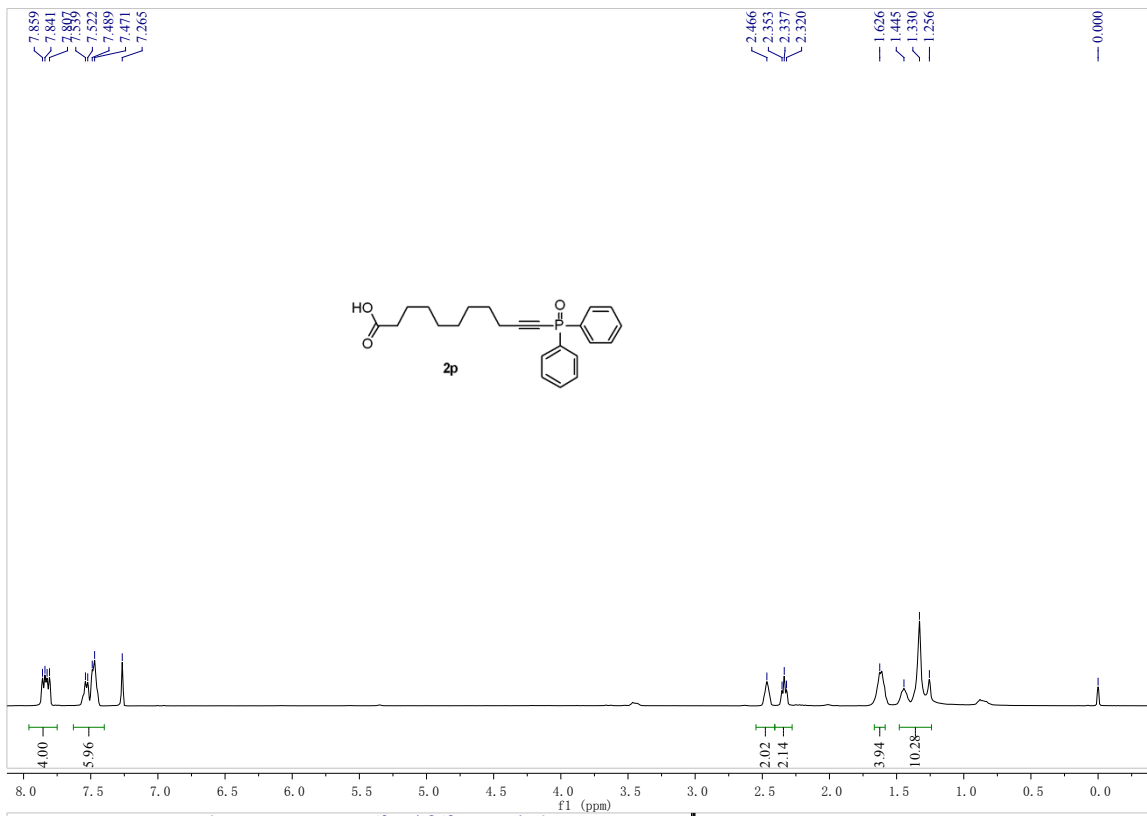


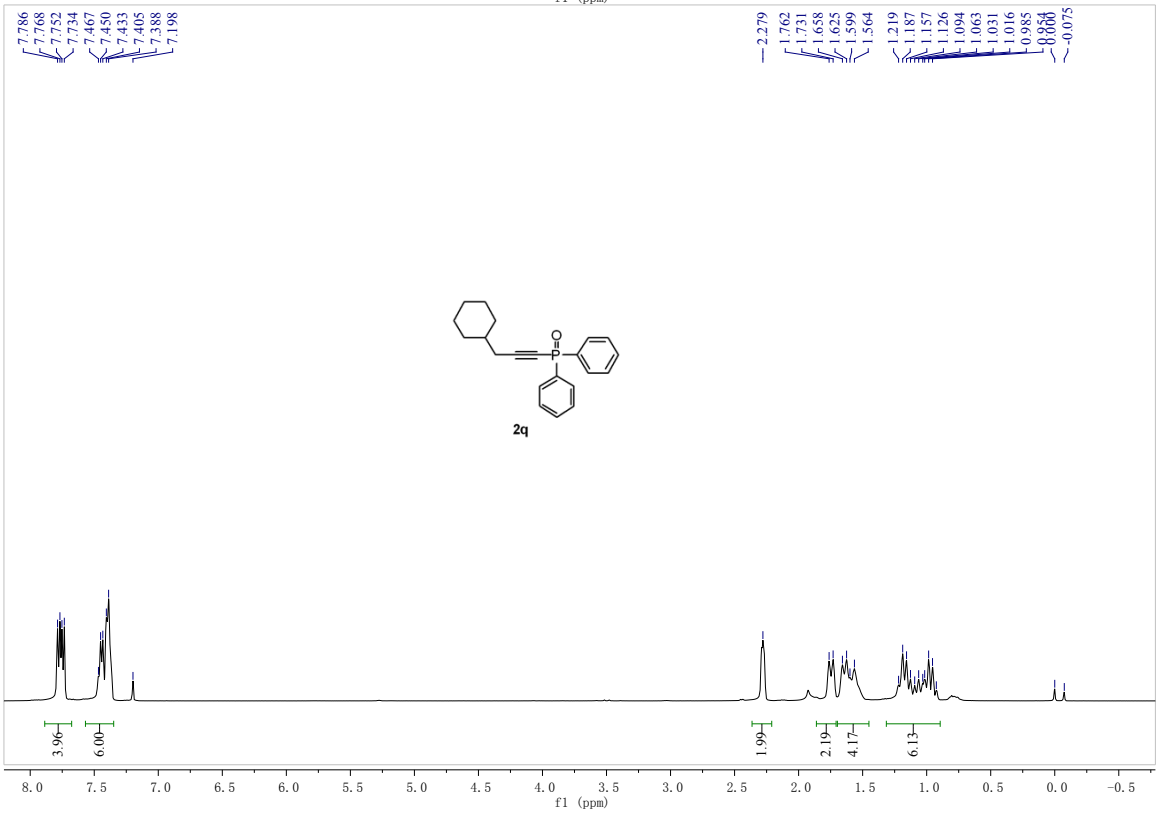
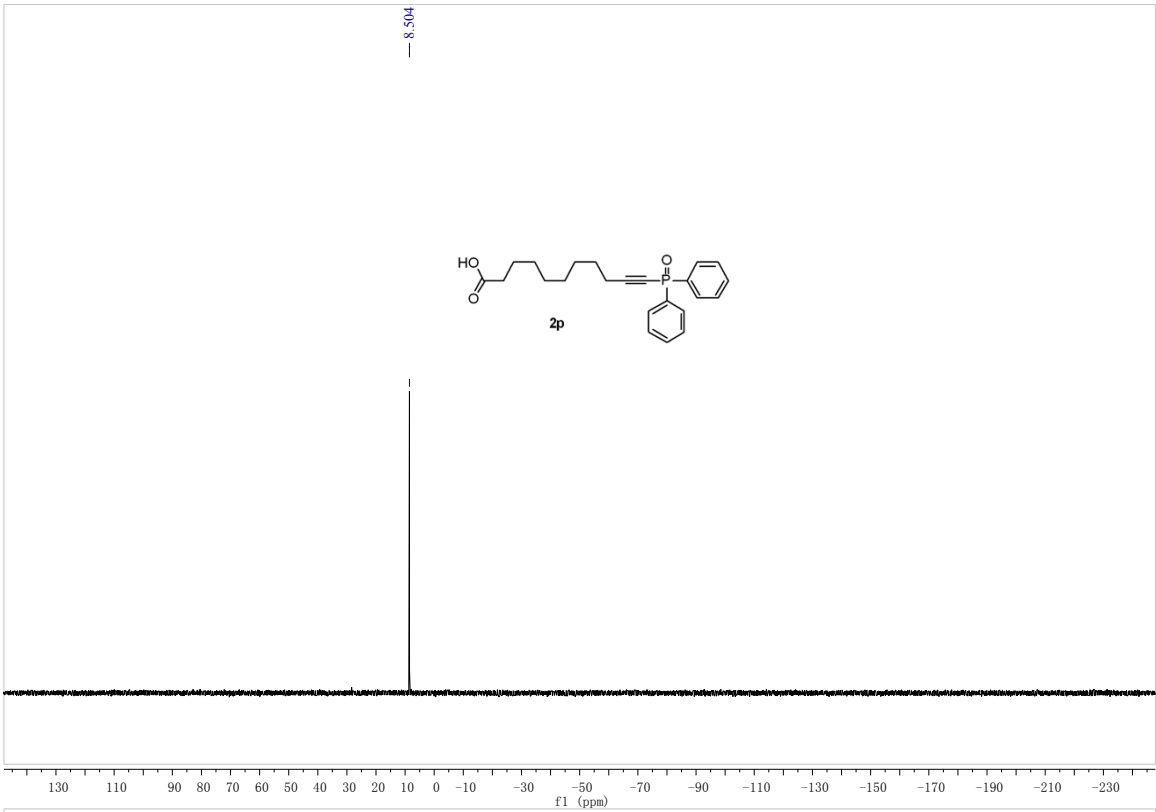


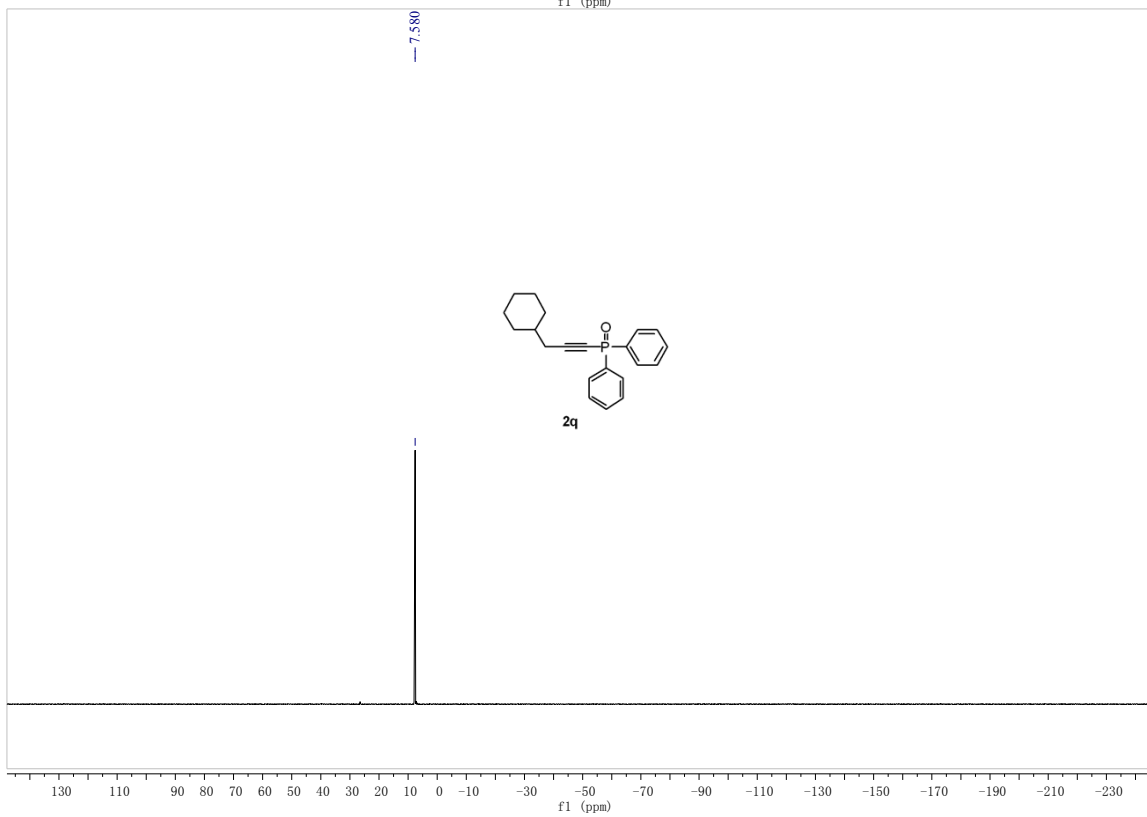
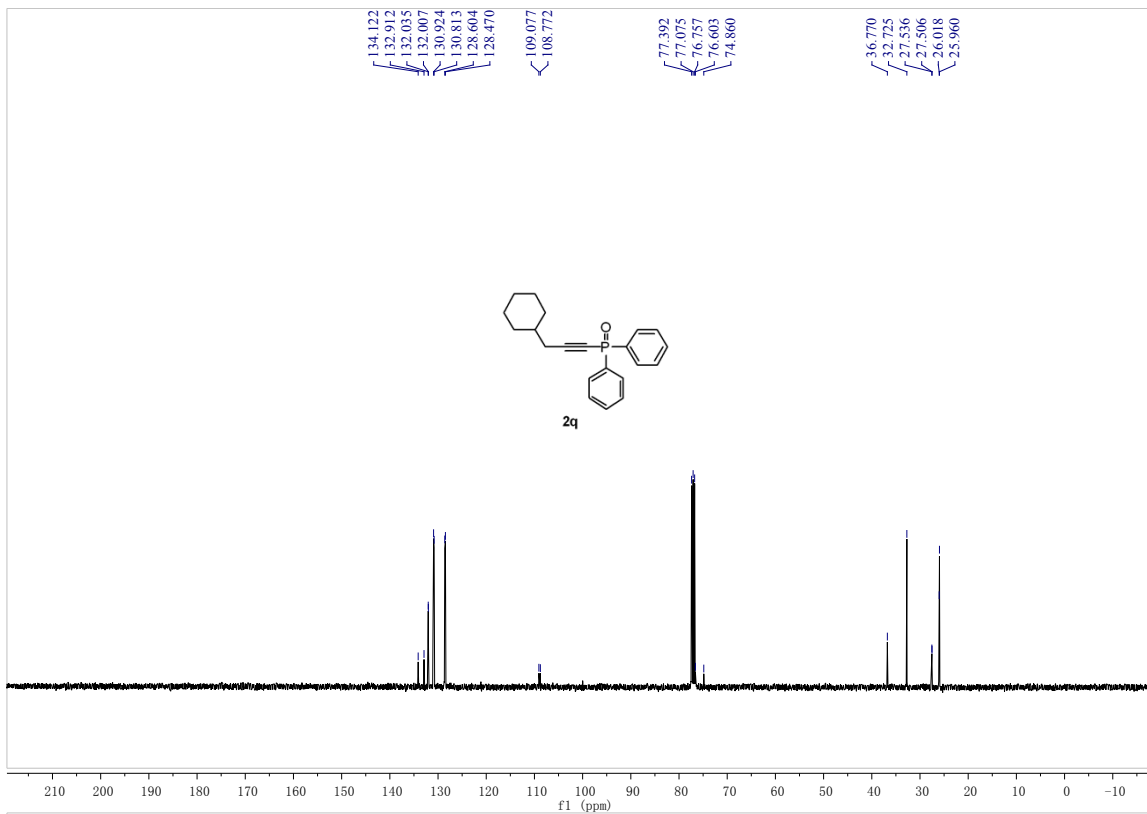


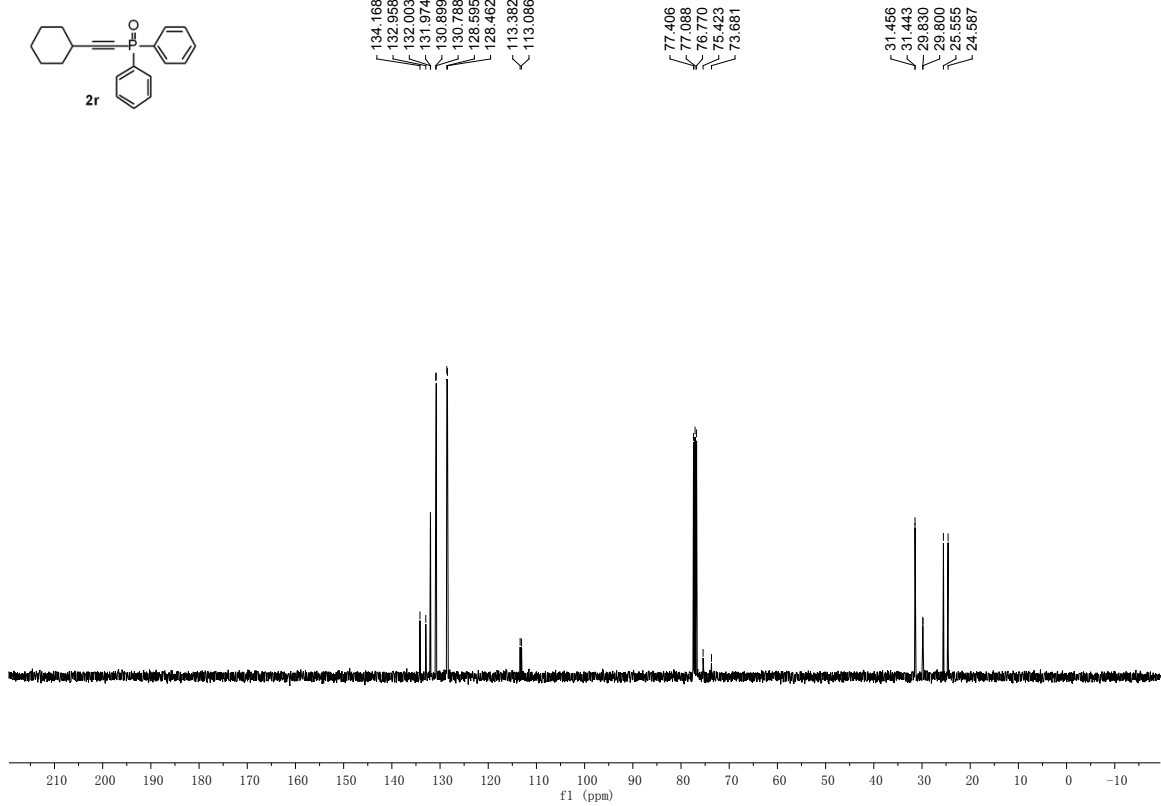
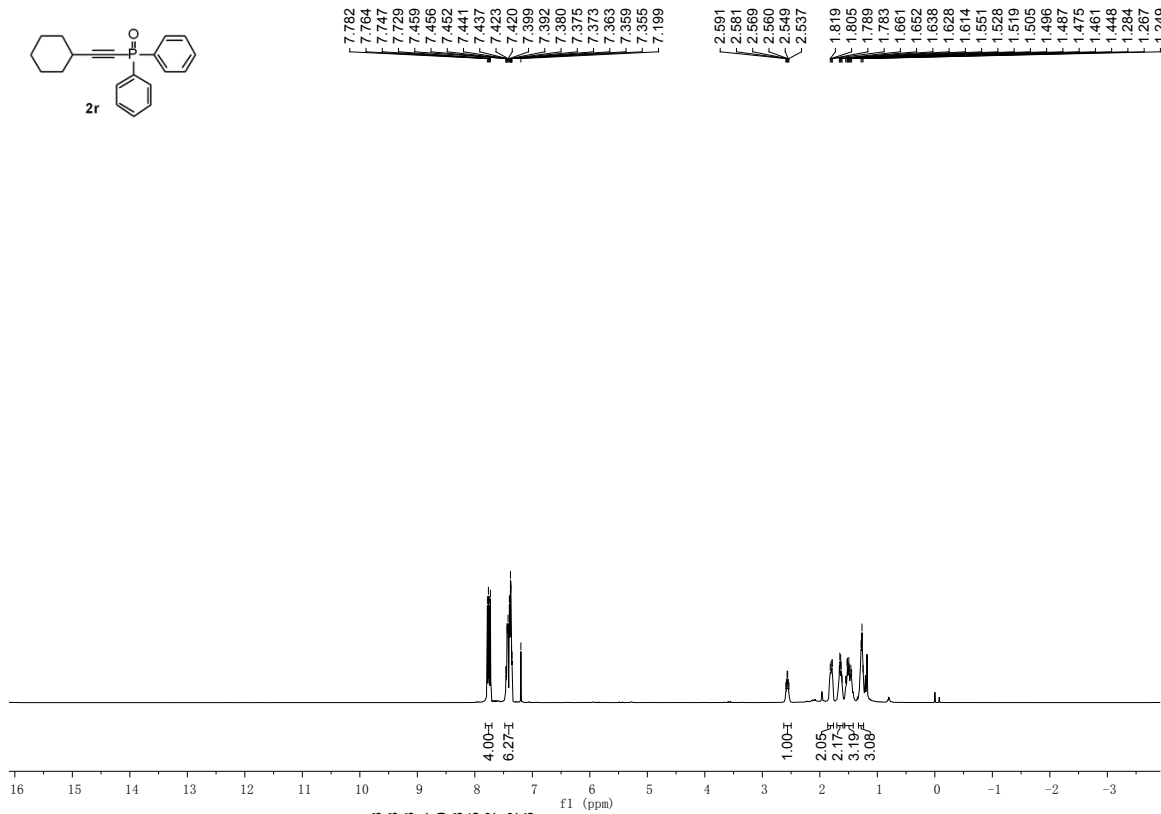
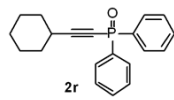


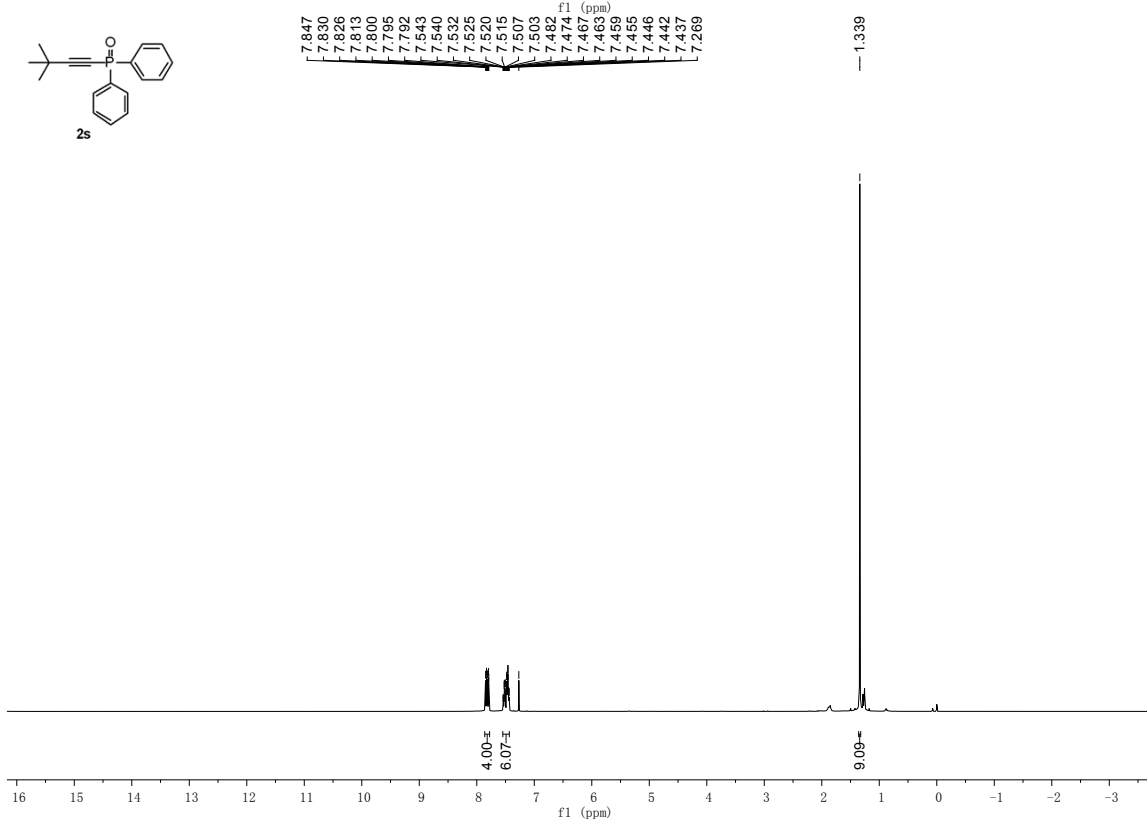
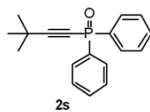
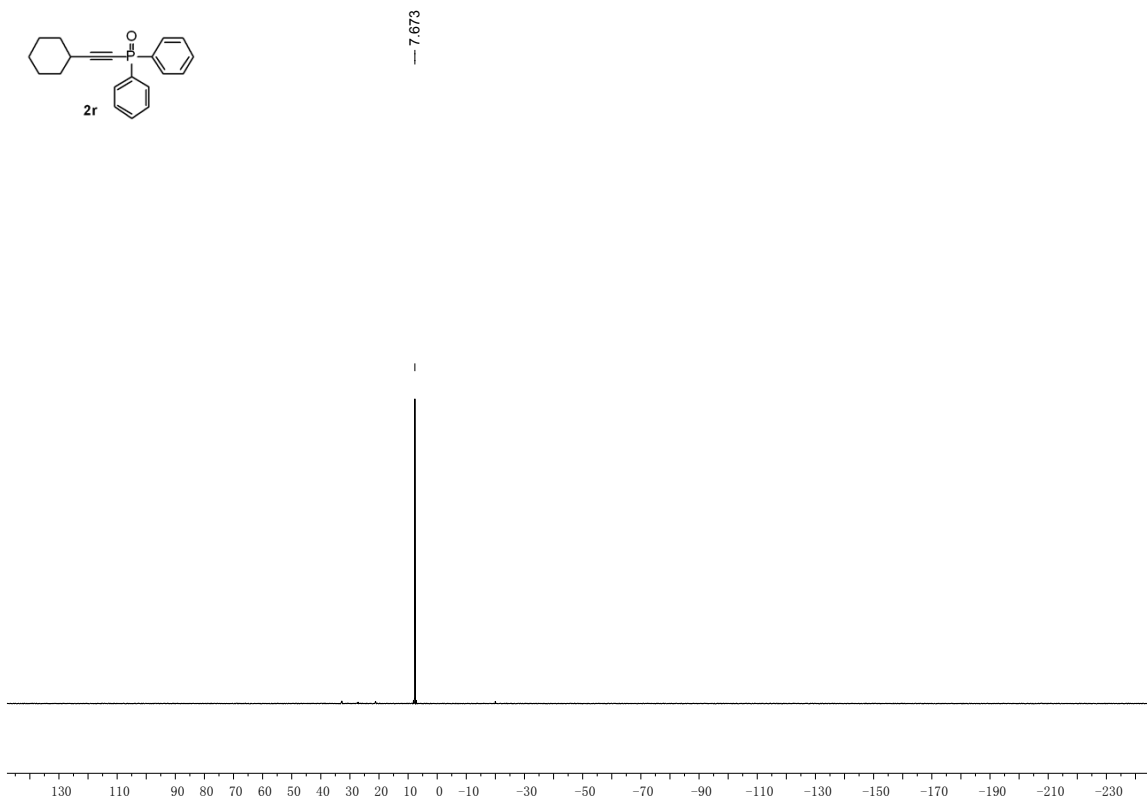
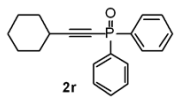


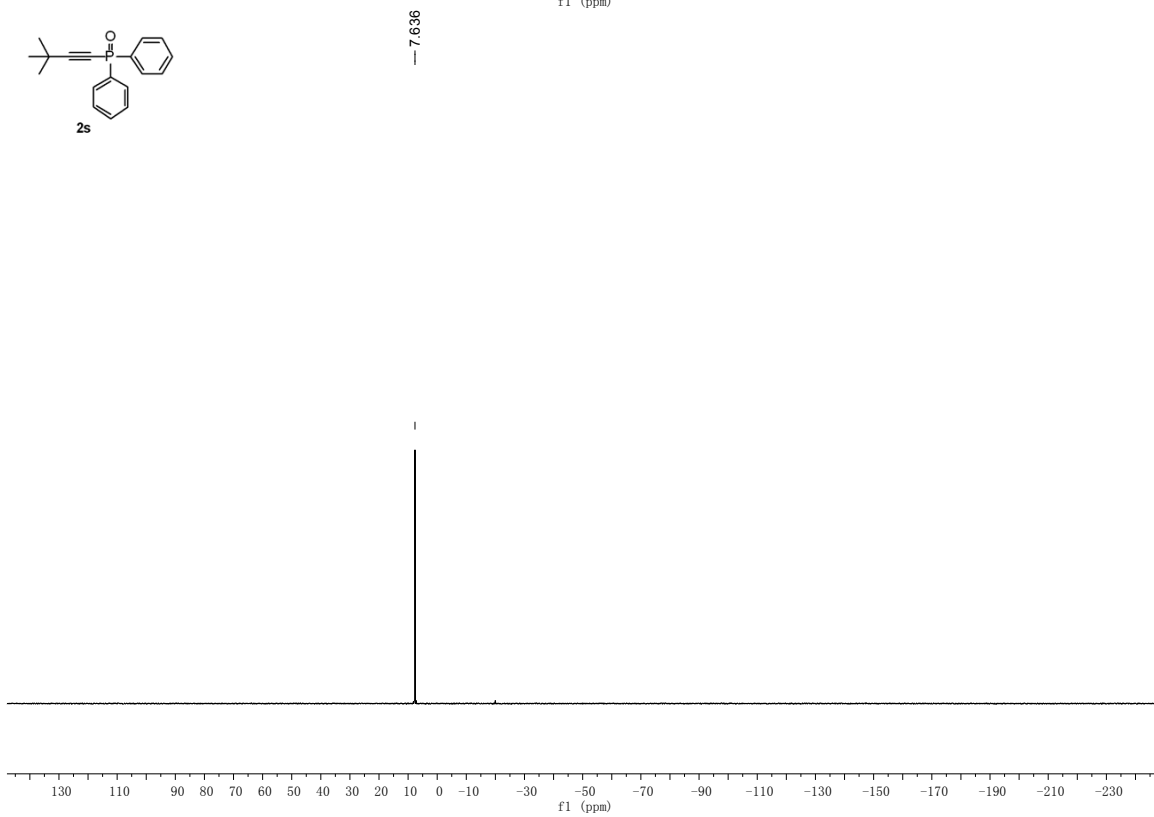
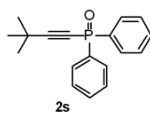
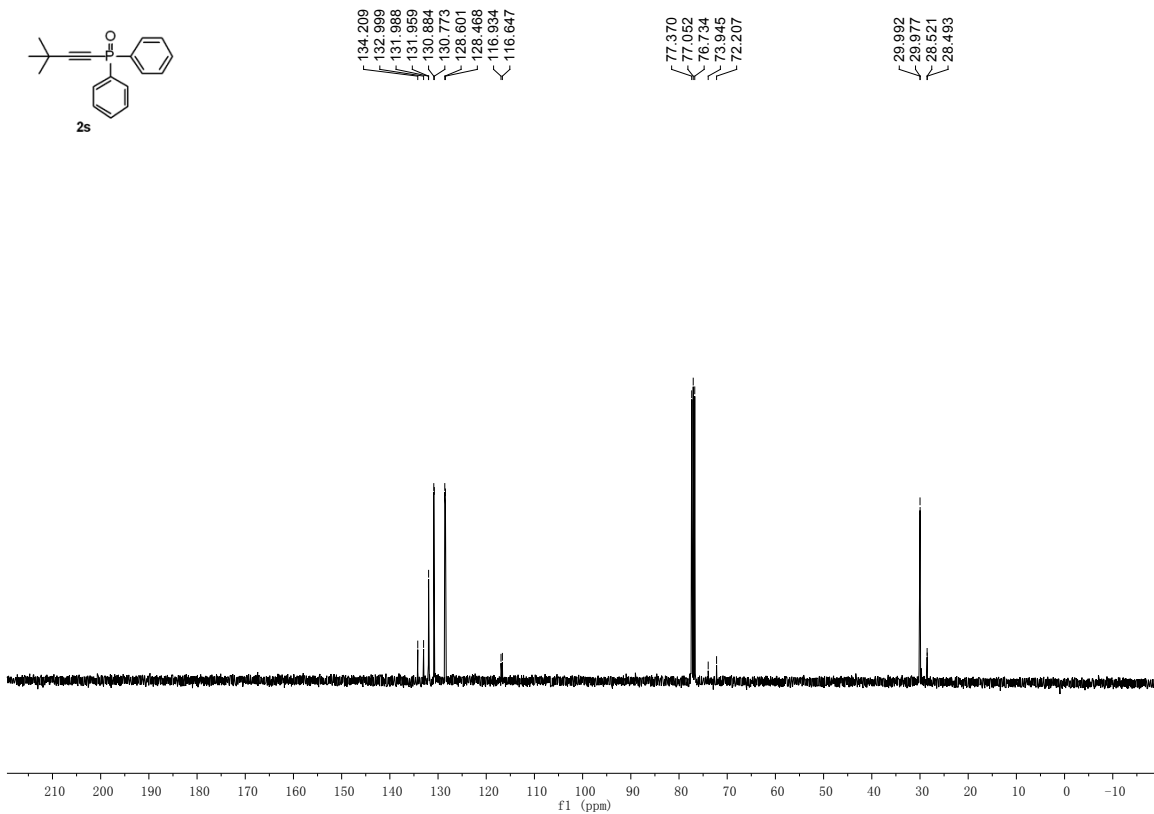
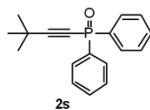


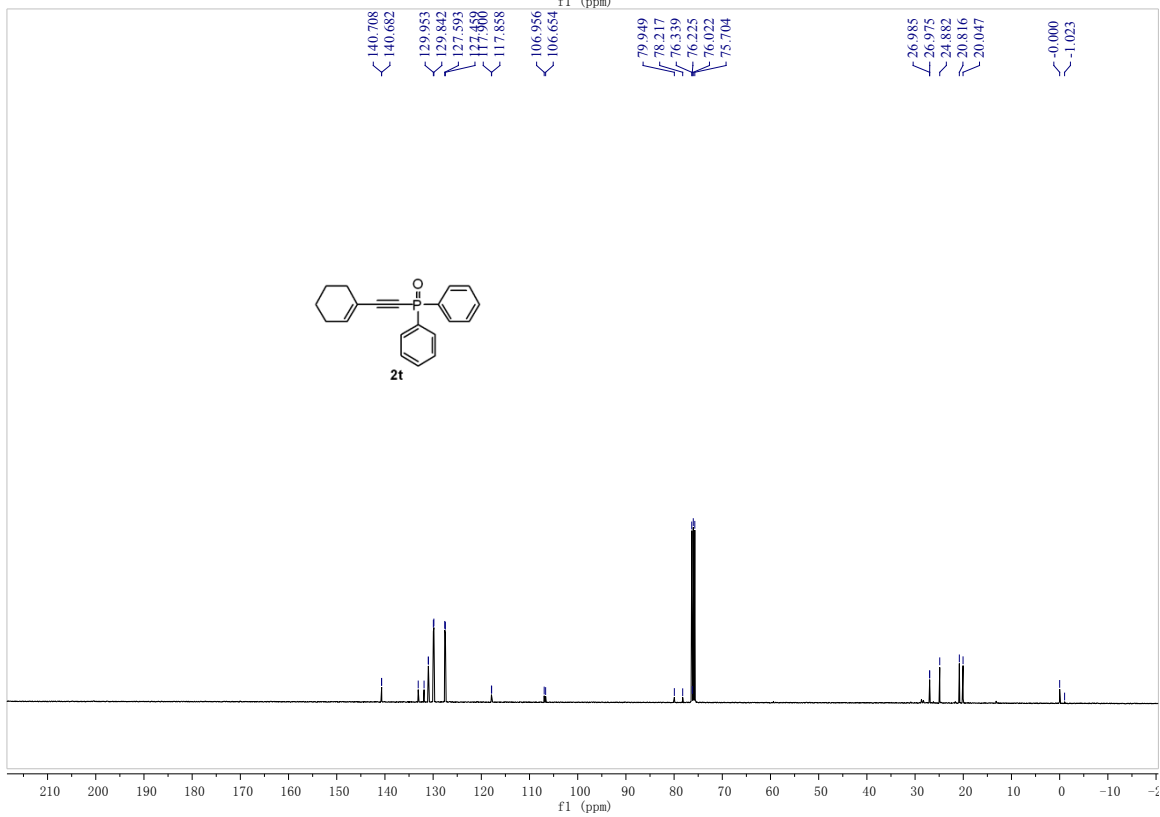
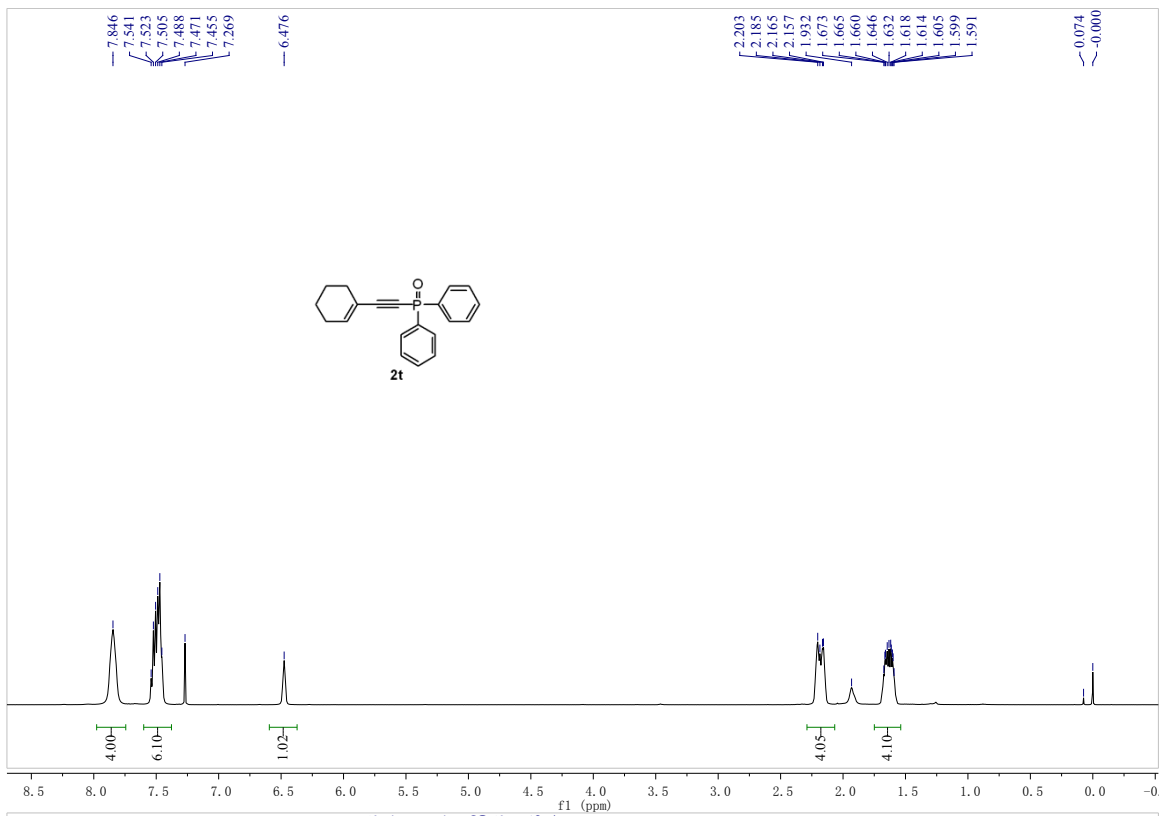


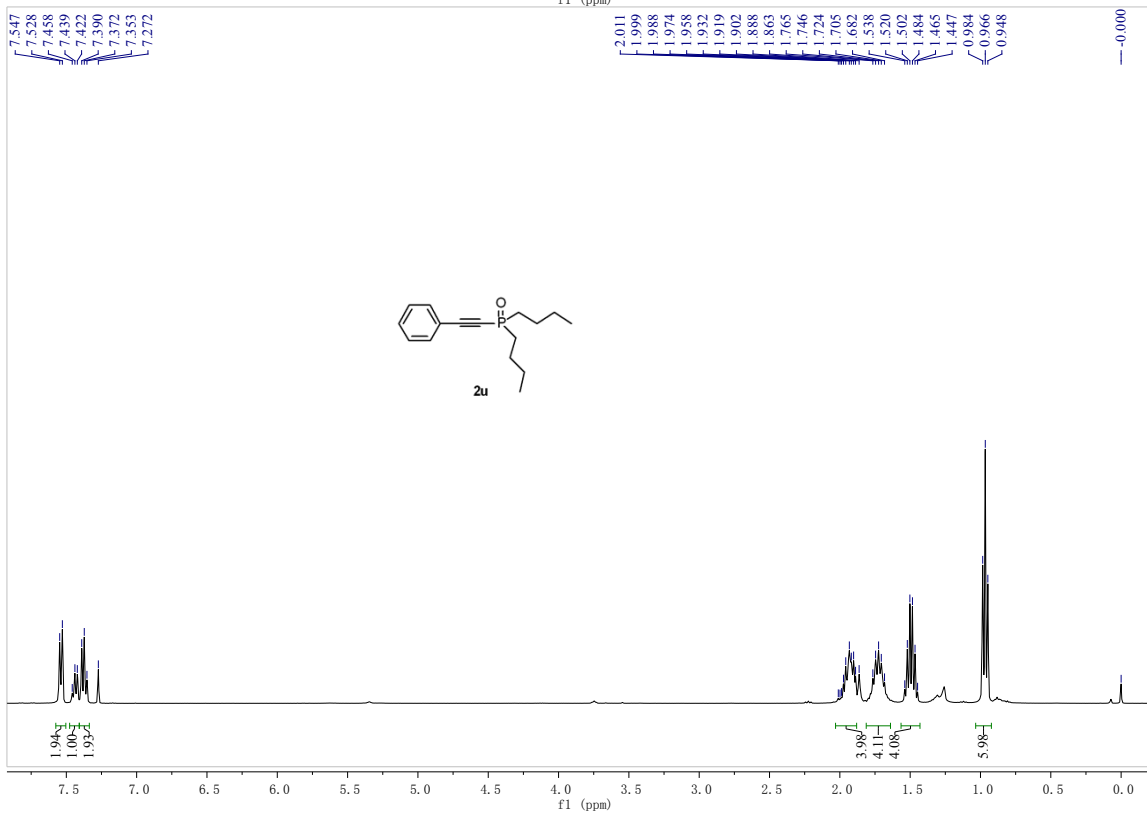
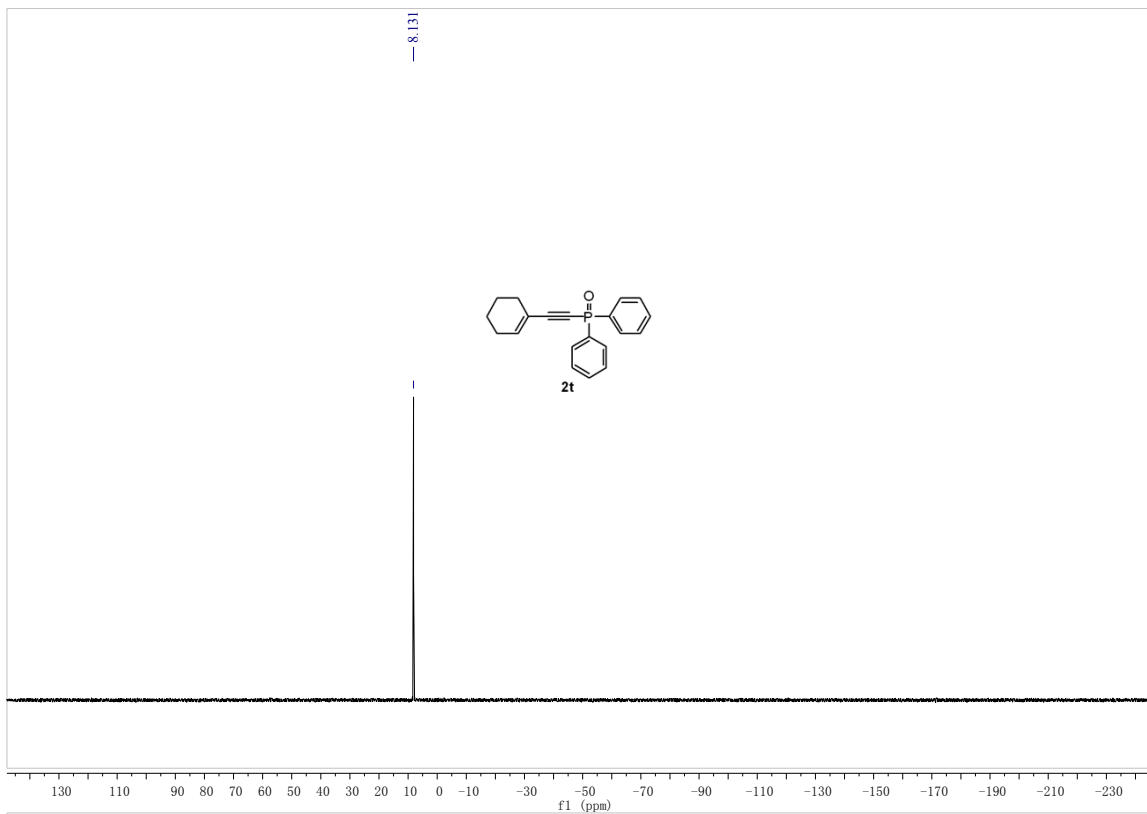


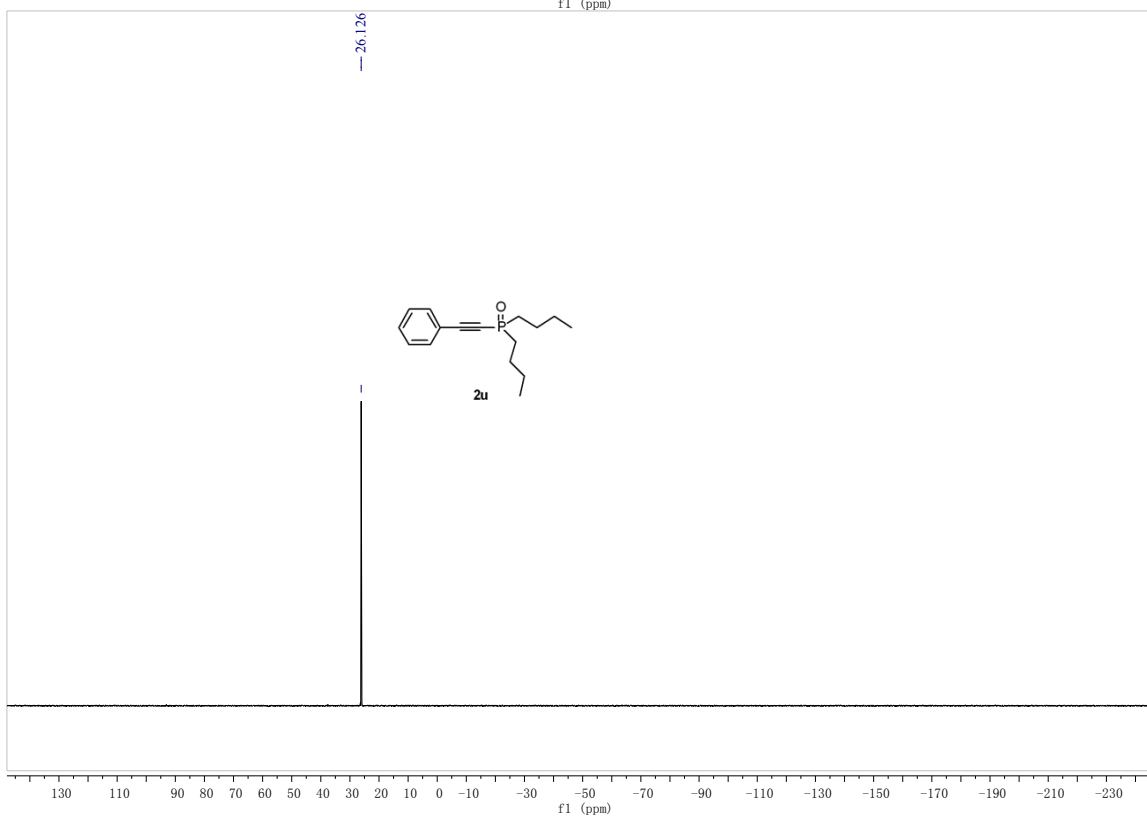
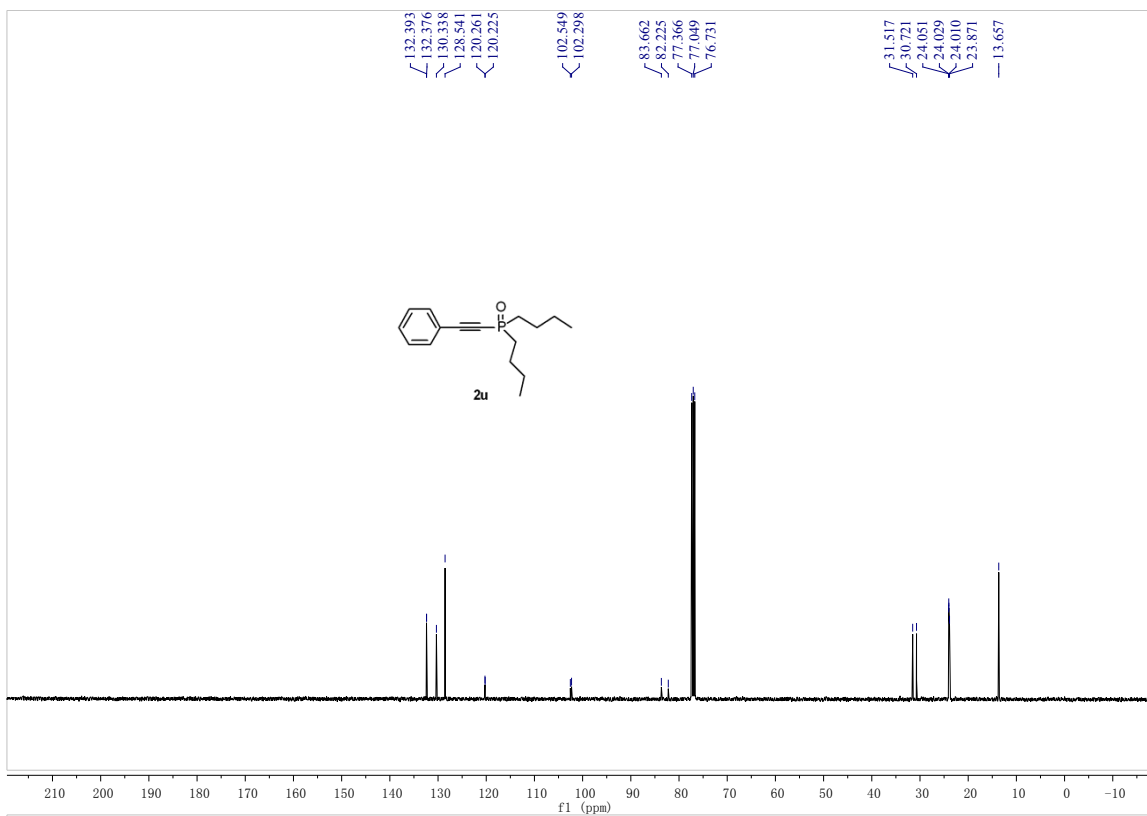


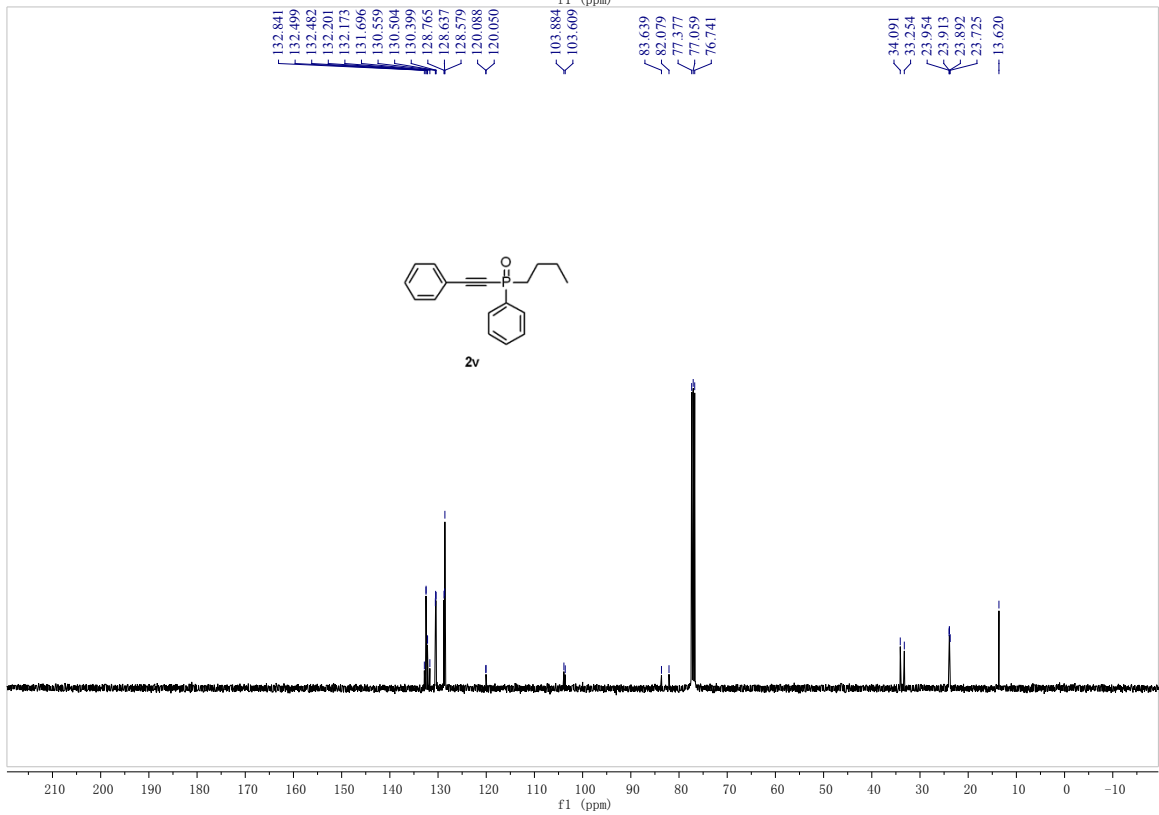
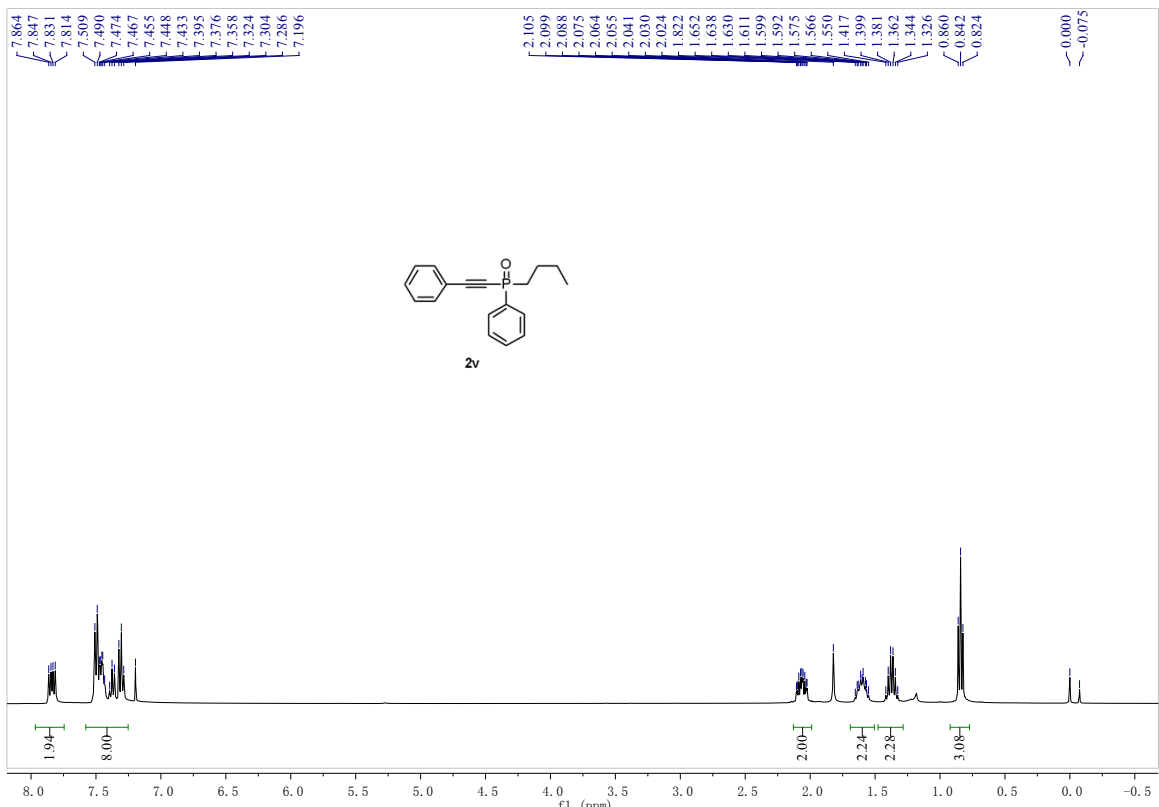


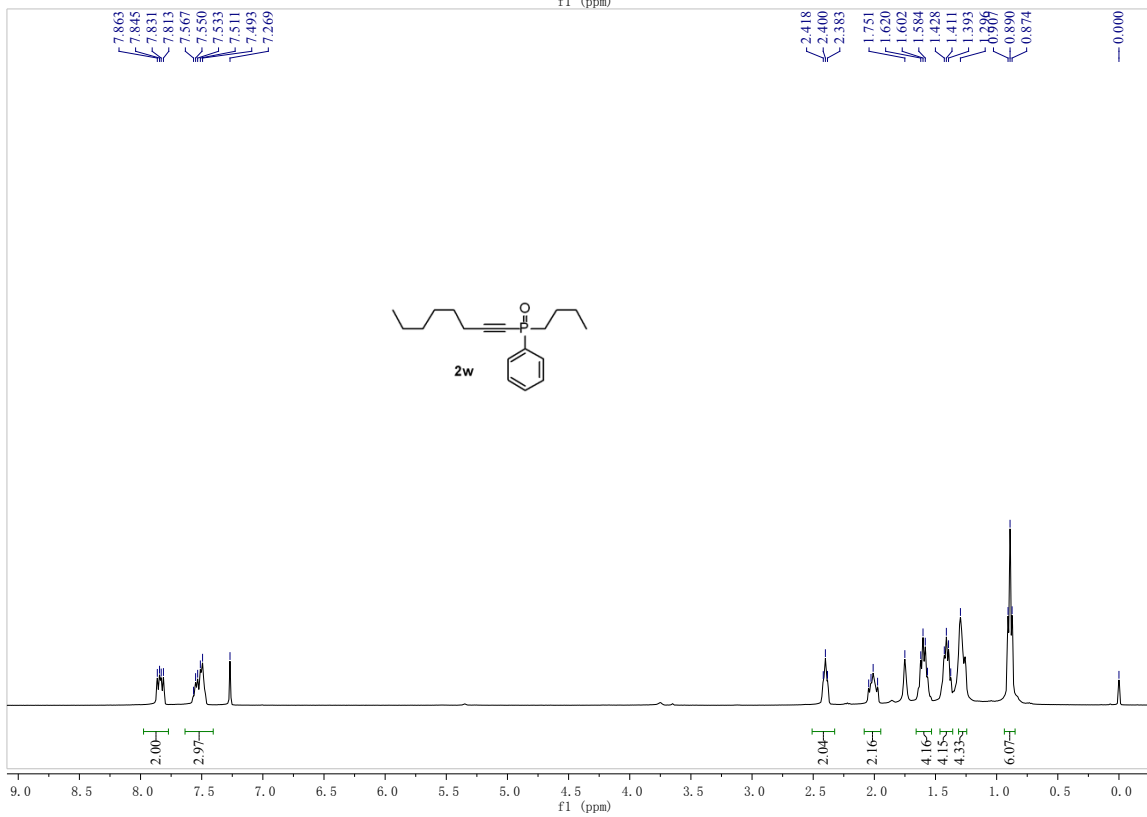
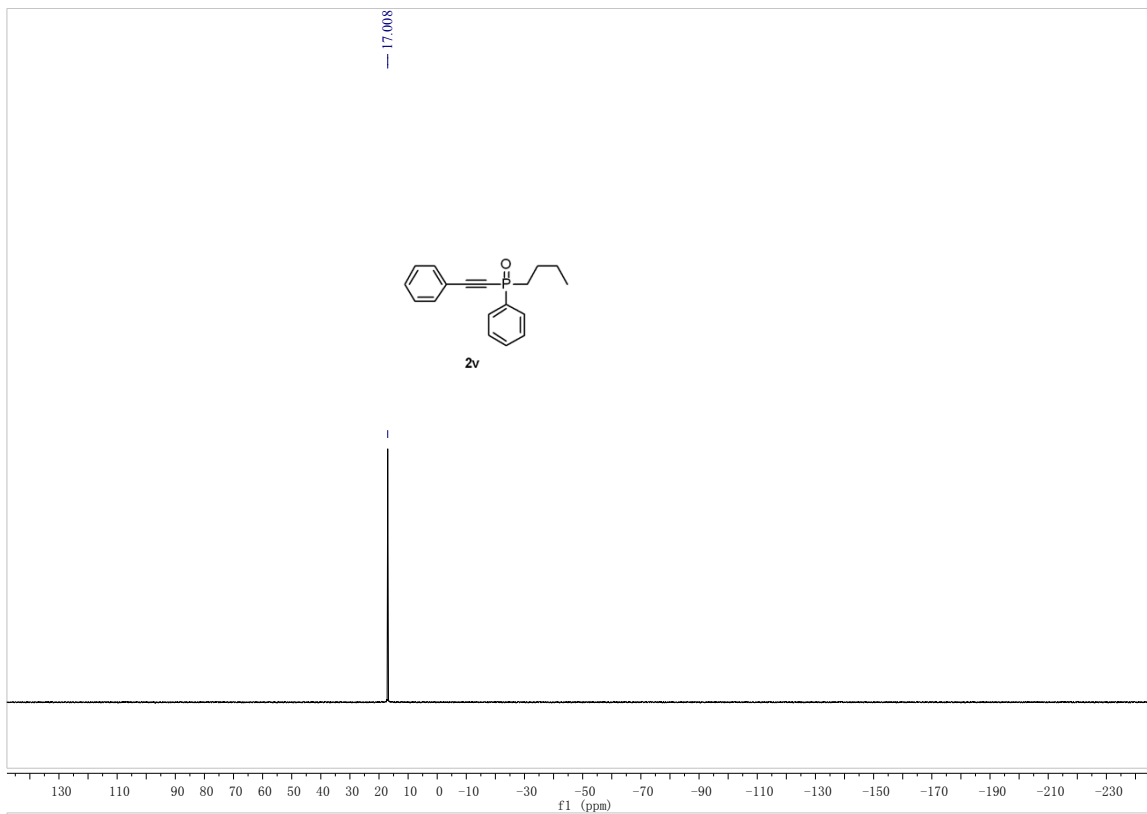


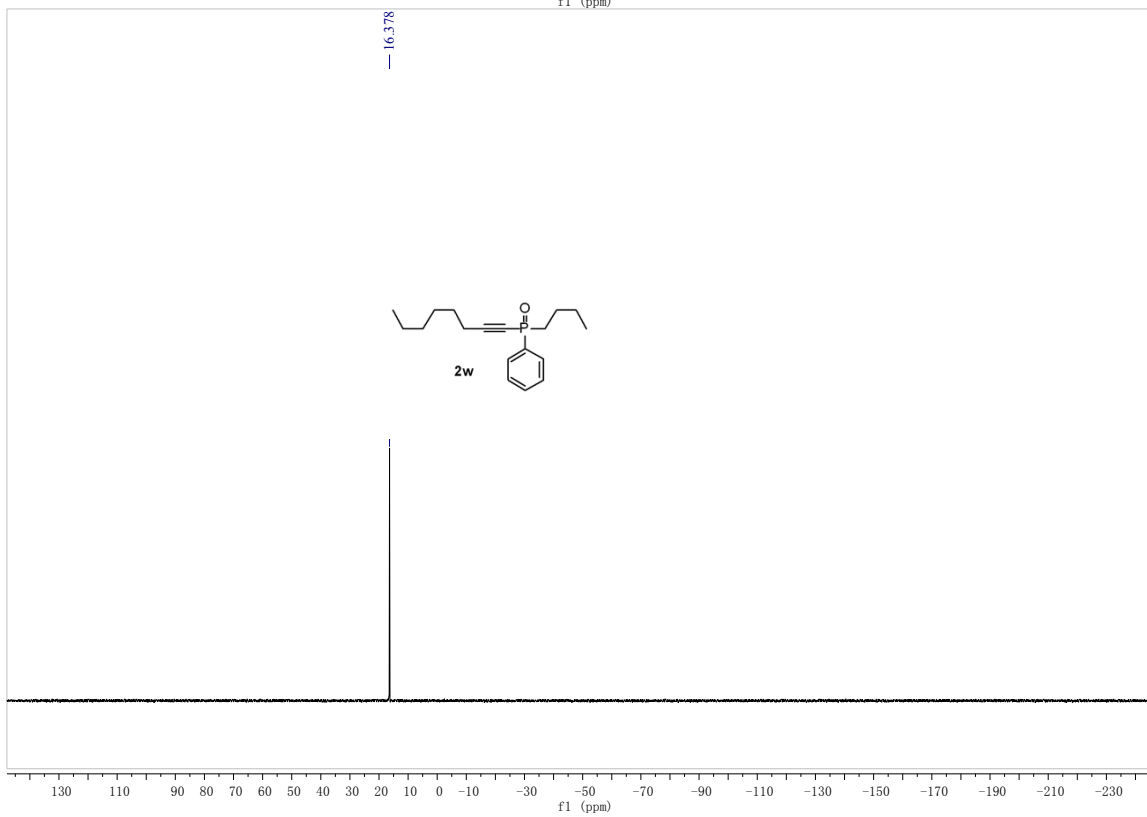
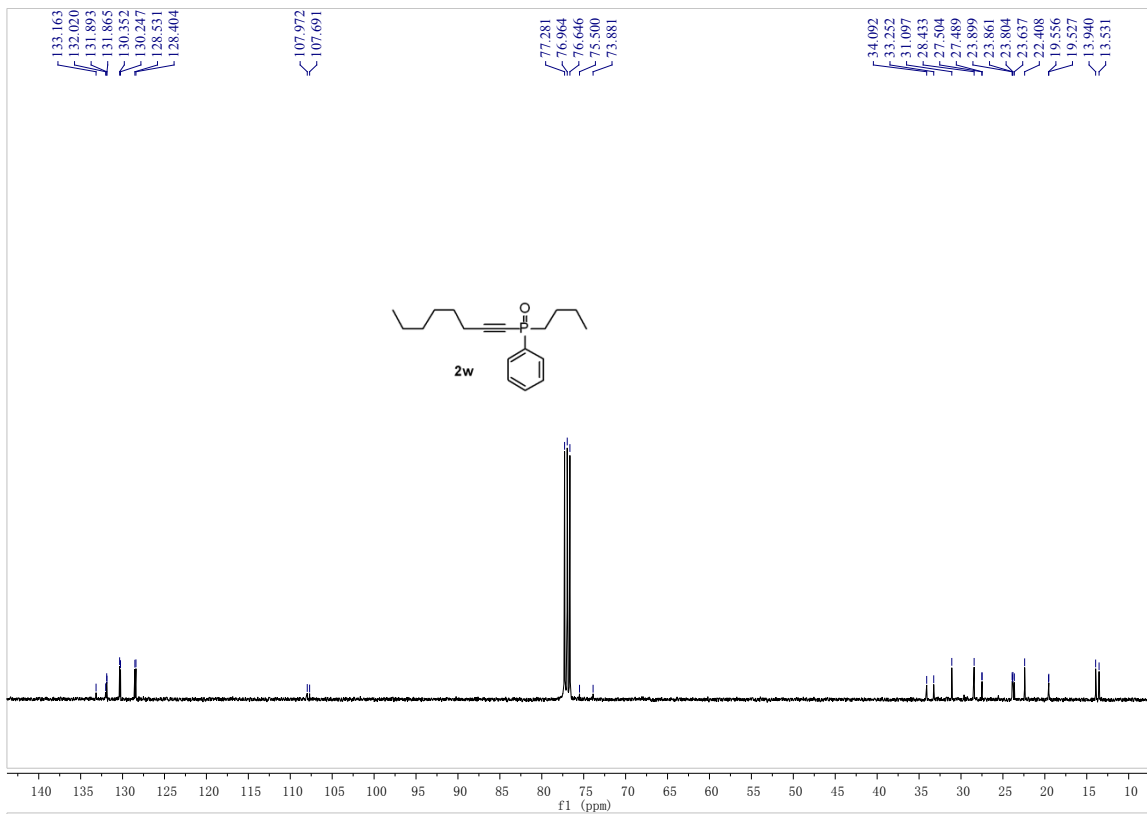


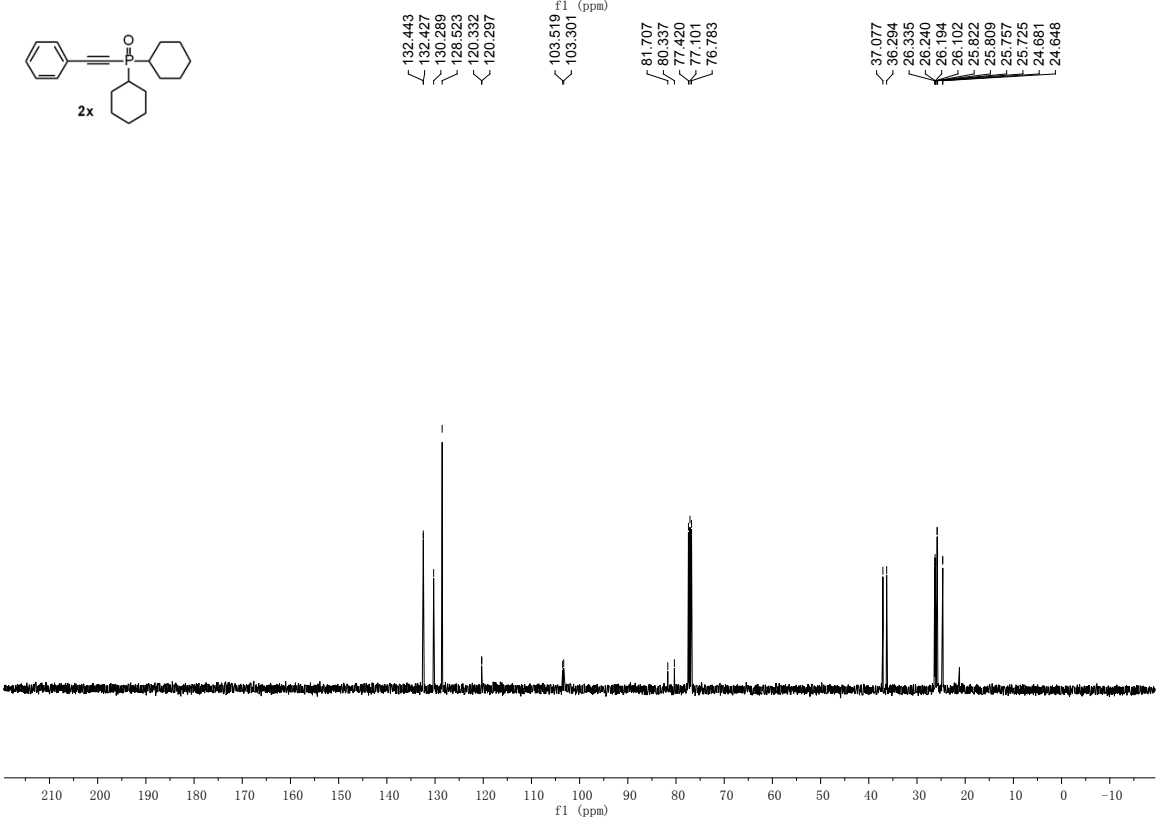
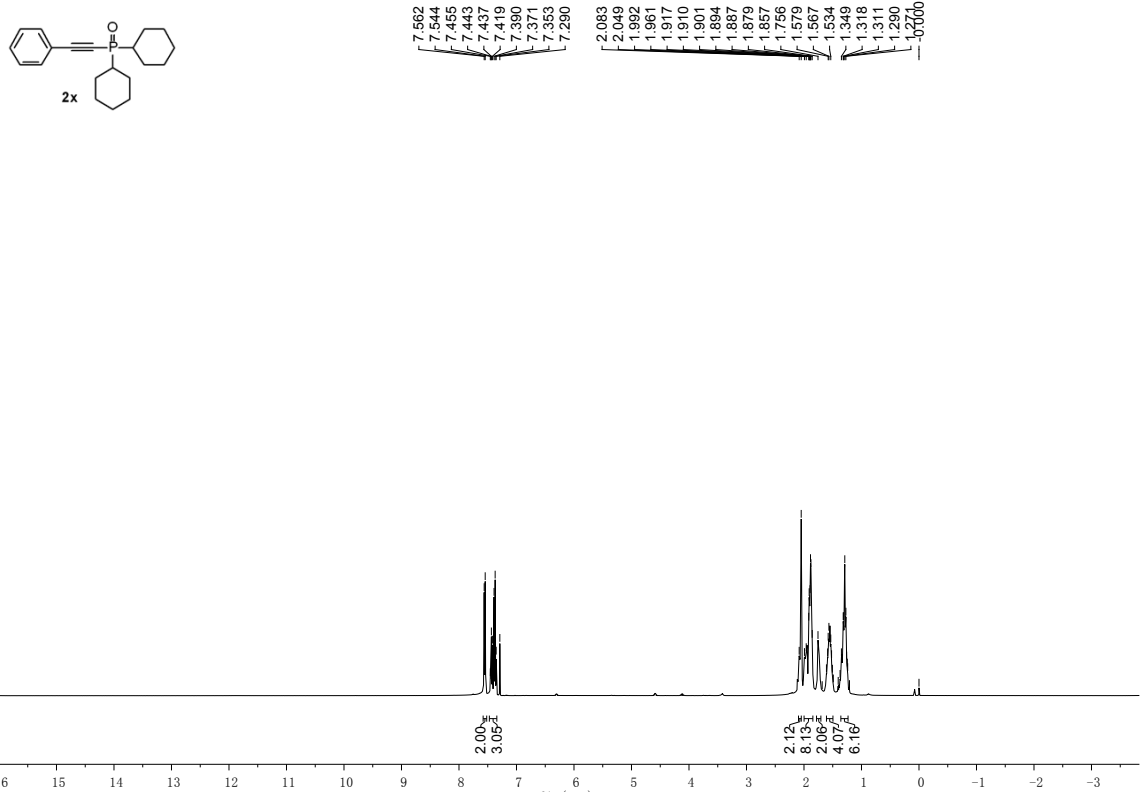


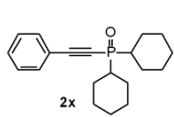










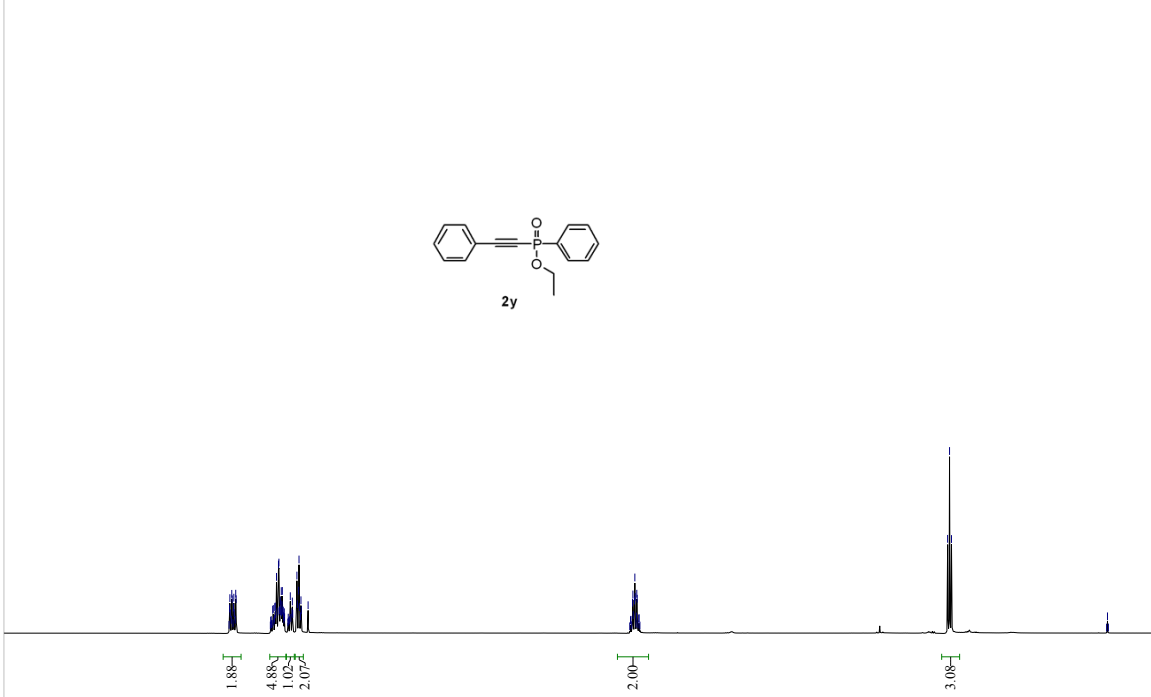
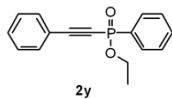


— 35.745



130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

7.992 7.988 7.985 7.976 7.971 7.967 7.956 7.953 7.949 7.940 7.935 7.932 7.913 7.613 7.598 7.594 7.583 7.579 7.576 7.572 7.564 7.551 7.546 7.542 7.537 7.530 7.527 7.525 7.521 7.517 7.514 7.511 7.507 7.503 7.500 7.497 7.493 7.491 7.487 7.445 7.439 7.433 7.423 7.420 7.417 7.378 7.375 7.363 7.359 7.356 7.345 7.341 7.339 7.339 7.276 4.338 4.324 4.320 4.317 4.310 4.306 4.302 4.299 4.288 4.285 4.282 4.267 4.264 1.456 1.438 1.420 0.000



0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

