

Stereoselective synthesis of vinylphosphonates and phosphine oxides via silver-catalyzed phosphorylation of styrenes

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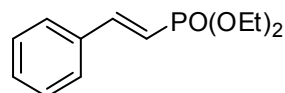
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General Remarks:

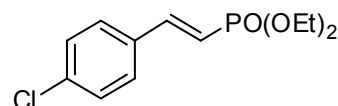
All the solvents and commercially available reagents were purchased from commercial sources and used directly. Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on 400 MHz in CDCl_3 and ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 using TMS as internal standard. ^{31}P NMR spectra was recorded on the same instrument.

Typical procedure for the preparation of alkenylphosphine oxides.

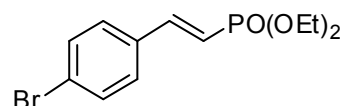
Dialkylphosphonate (0.45 mmol), styrene (0.3 mmol), potassium persulfate (0.6 mmol), TEMPO (0.12 mmol), AgNO_3 (0.015 mmol) and dry toluene (2.0 ml) were added to a 25-ml Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was next sealed under air and stirred at 100 °C for 6 hours. After the completion of the reaction, The brownish suspension was cooled to rt, filtered over a plug of silica gel (washed with EtOAc), and concentrated. The crude residue was purified by flash chromatography over silica gel.

(*E*)-diethyl styrylphosphonate (2a**)¹**

IR(KBr)/ cm^{-1} : 2956, 2924, 2850, 1604, 1511, 1461, 1257, 1173, 1025, 961. ^1H NMR (400 MHz, CDCl_3): δ 7.57-7.27 (m, 6H), 6.27 (t, J = 20 Hz, 1H), 4.16-4.14 (m, 4H), 1.36 (t, J = 8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.8 (d, $J_{\text{C-P}}$ = 6 Hz), 134.8 (d, $J_{\text{C-P}}$ = 25 Hz), 130.2, 128.8, 127.7, 113.9 (d, $J_{\text{C-P}}$ = 190 Hz), 61.8 (d, $J_{\text{C-P}}$ = 5 Hz), 16.3 (d, $J_{\text{C-P}}$ = 6 Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 19.6. MS: m/z 240.1 (M^+).

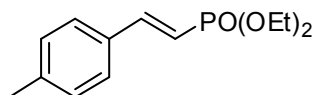
(*E*)-diethyl 4-chlorostyrylphosphonate (2b**)¹**

IR(KBr)/ cm^{-1} : 2988, 2930, 2860, 1600, 1511, 1460, 899. ^1H NMR (400 MHz, CDCl_3): δ 7.45-7.41 (m, 3H), 7.32 (d, J = 8 Hz, 2H), 6.24 (t, J = 20 Hz, 1H), 4.17-4.10 (m, 4H), 1.36 (t, J = 8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.2 (d, $J_{\text{C-P}}$ = 7 Hz), 136.1, 133.3 (d, $J_{\text{C-P}}$ = 25 Hz), 129.1, 128.9, 114.8 (d, $J_{\text{C-P}}$ = 190 Hz), 61.9 (d, $J_{\text{C-P}}$ = 6 Hz), 16.4 (d, $J_{\text{C-P}}$ = 6 Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 19.0. MS: m/z 274.1 (M^+).

(*E*)-diethyl 4-bromostyrylphosphonate (2c**)¹**

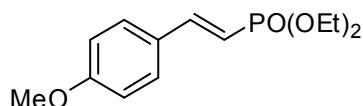
IR(KBr)/ cm^{-1} : 2980, 2930, 1970, 1620, 1510, 1230, 1112, 975. ^1H NMR (400 MHz, CDCl_3): δ 7.53-7.45 (m, 3H), 7.37 (d, J = 8 Hz, 2H), 6.27 (t, J = 16 Hz, 1H), 4.26-4.02 (m, 4H), 1.36 (t, J = 4 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.3 (d, $J_{\text{C-P}}$ = 6 Hz), 133.6 (d, $J_{\text{C-P}}$ = 3 Hz), 132.1, 128.5, 124.5, 114.8 (d, $J_{\text{C-P}}$ = 194 Hz), 61.9 (d, $J_{\text{C-P}}$ = 5 Hz), 16.4 (d, $J_{\text{C-P}}$ = 6 Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 19.1. MS: m/z 318.0 (M^+).

(*E*)-diethyl 4-methylstyrylphosphonate (2d**)³**



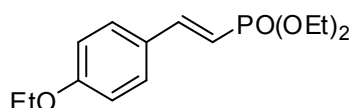
IR(KBr)/cm⁻¹: 2960, 2934, 2856, 1614, 1521, 1462, 1260, 1175, 1030, 961. ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 20 Hz, 1H), 7.42 (d, *J* = 12 Hz, 2H), 7.19 (d, *J* = 8 Hz, 2H), 6.20 (t, *J* = 20 Hz, 1H), 4.22-4.07 (m, 4H), 2.37 (s, 3H), 1.35 (t, *J* = 8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 148.8 (d, *J*_{C-P} = 6 Hz), 140.6, 132.1 (d, *J*_{C-P} = 23 Hz), 129.5, 127.7, 112.4 (d, *J*_{C-P} = 191 Hz), 61.7 (d, *J*_{C-P} = 6 Hz), 21.4, 16.3 (d, *J*_{C-P} = 6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 20.1. MS:m/z 254.1 (M⁺).

(*E*)-diethyl 4-methoxystyrylphosphonate (**2e**)¹



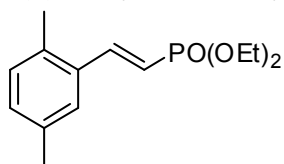
IR(KBr)/cm⁻¹: 2956, 2924, 2850, 1604, 1511, 1461, 1257, 1025, 751. ¹H NMR (400 MHz, CDCl₃): δ 7.50-7.40 (m, 3H), 6.90 (d, *J* = 8 Hz, 2H), 6.08 (t, *J* = 20 Hz, 1H), 4.15-4.08 (m, 4H), 3.84 (s, 3H), 1.35 (t, *J* = 8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 161.3, 148.5 (d, *J*_{C-P} = 7 Hz), 129.3, 127.5 (d, *J*_{C-P} = 23 Hz), 114.2, 110.6 (d, *J*_{C-P} = 192 Hz), 61.7 (d, *J*_{C-P} = 5 Hz), 55.4, 16.3 (d, *J*_{C-P} = 6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 20.5. MS:m/z 270.1 (M⁺).

(*E*)-diethyl 4-ethoxystyrylphosphonate (**2f**)¹



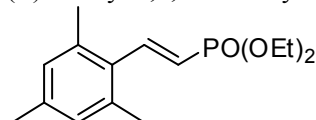
IR(KBr)/cm⁻¹: 2955, 2924, 2851, 1610, 1465, 1260, 1030, 788. ¹H NMR (400 MHz, CDCl₃): δ 7.50-7.40 (m, 3H), 6.89 (d, *J* = 8 Hz, 2H), 6.08 (t, *J* = 16 Hz, 1H), 4.18-4.10 (m, 4H), 4.09-4.04 (m, 2H), 1.43 (t, *J* = 8 Hz, 3H), 1.35 (t, *J* = 8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 160.7, 148.5 (d, *J*_{C-P} = 7 Hz), 129.3, 127.4 (d, *J*_{C-P} = 23 Hz), 114.7, 110.5 (d, *J*_{C-P} = 192 Hz), 63.6, 61.7 (d, *J*_{C-P} = 5 Hz), 16.4 (d, *J*_{C-P} = 7 Hz), 14.7; ³¹P NMR (162 MHz, CDCl₃): δ 20.6. MS:m/z 284.1 (M⁺).

(*E*)-diethyl 2,5-dimethylstyrylphosphonate (**2g**)



IR(KBr)/cm⁻¹: 2963, 2935, 2860, 1614, 1520, 1455, 1256, 1160, 1031, 955. ¹H NMR (400 MHz, CDCl₃): δ 7.80-7.70 (m, 1H), 7.35 (s, 1H), 7.09 (s, 2H), 6.18 (t, *J* = 20 Hz, 1H), 4.17-4.10 (m, 4H), 2.39 (s, 3H), 2.33 (s, 3H), 1.36 (t, *J* = 8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 146.5 (d, *J*_{C-P} = 7 Hz), 135.7, 134.2, 133.6 (d, *J*_{C-P} = 22 Hz), 130.7, 130.6, 136.5, 114.6 (d, *J*_{C-P} = 189 Hz), 61.7 (d, *J*_{C-P} = 6 Hz), 20.9, 19.2, 16.4 (d, *J*_{C-P} = 7 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 19.7. HRMS (EI, m/z): calcd for C₁₄H₂₁O₃P⁺ [M⁺]: 268.1228; Found: 268.1231.

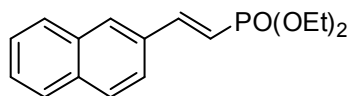
(*E*)-diethyl 2,4,6-trimethylstyrylphosphonate (**2h**)⁴



IR(KBr)/cm⁻¹: 2979, 2924, 1615, 1447, 1247, 1025, 963. ¹H NMR (400 MHz, CDCl₃): δ 7.65-7.55 (m, 1H), 6.88 (d, *J* = 8 Hz, 2H), 5.87 (d, *J* = 20 Hz, 1H), 4.19-4.12 (m, 4H), 2.31 (s, 6H), 2.28 (s,

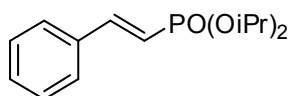
3H), 1.37 (t, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.5 (d, $J_{\text{C-P}} = 6$ Hz), 138.1, 136.0, 129.5 (d, $J_{\text{C-P}} = 6$ Hz), 129.0, 119.8 (d, $J_{\text{C-P}} = 184$ Hz), 61.7 (d, $J_{\text{C-P}} = 5$ Hz), 20.9, 20.8, 16.3 (d, $J_{\text{C-P}} = 7$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 18.8. MS: m/z 282.2 (M^+).

(*E*)-diethyl (2-(naphthalen-2-yl)vinyl)phosphonate (**2i**)¹



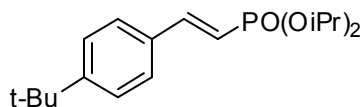
IR(KBr)/ cm^{-1} : 2956, 2924, 2853, 1460, 1376, 1259, 1050, 1024, 668. ^1H NMR (400 MHz, CDCl_3): δ 7.95-7.79 (m, 5H), 7.51 (d, $J = 8$ Hz, 3H), 6.37 (t, $J = 20$ Hz, 1H), 4.25-4.10 (m, 4H), 1.37 (t, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.7 (d, $J_{\text{C-P}} = 7$ Hz), 134.1, 133.1, 132.2 (d, $J_{\text{C-P}} = 23$ Hz), 129.4, 128.6, 128.5, 127.7, 127.2, 126.7, 123.1, 113.8 (d, $J_{\text{C-P}} = 191$ Hz), 61.8 (d, $J_{\text{C-P}} = 6$ Hz), 16.3 (d, $J_{\text{C-P}} = 6$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 19.7. MS: m/z 290.1 (M^+).

(*E*)-diisopropyl styrylphosphonate (**2j**)⁵



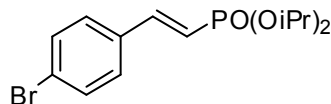
IR(KBr)/ cm^{-1} : 3401, 2978, 1616, 1105, 984, 744. ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.44 (m, 3H), 7.38 (d, $J = 4$ Hz, 3H), 6.27 (t, $J = 16$ Hz, 1H), 4.76-4.68 (m, 2H), 1.37 (d, $J = 8$ Hz, 6H), 1.32 (d, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.9 (d, $J_{\text{C-P}} = 7$ Hz), 134.9 (d, $J_{\text{C-P}} = 23$ Hz), 130.0, 128.8, 127.6, 115.3 (d, $J_{\text{C-P}} = 191$ Hz), 70.5 (d, $J_{\text{C-P}} = 6$ Hz), 24.0 (d, $J_{\text{C-P}} = 5$ Hz), 23.9 (d, $J_{\text{C-P}} = 4$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 17.4. MS: m/z 268.1 (M^+).

(*E*)-diisopropyl 4-(tert-butyl)styrylphosphonate (**2k**)



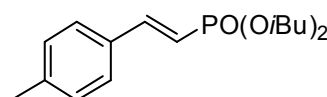
IR(KBr)/ cm^{-1} : 2975, 2930, 2865, 2160, 1710, 1470, 1175, 975. ^1H NMR (400 MHz, CDCl_3): δ 7.48-7.40 (m, 5H), 6.22 (t, $J = 5$ Hz, 1H), 4.74-4.68 (m, 2H), 1.37 (d, $J = 4$ Hz, 6H), 1.31 (d, $J = 8$ Hz, 15H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.5, 117.7 (d, $J_{\text{C-P}} = 6$ Hz), 132.2 (d, $J_{\text{C-P}} = 23$ Hz), 127.44, 125.7, 114.4 (d, $J_{\text{C-P}} = 191$ Hz), 70.3 (d, $J_{\text{C-P}} = 5$ Hz), 34.8, 31.1, 24.1 (d, $J_{\text{C-P}} = 4$ Hz), 23.9 (d, $J_{\text{C-P}} = 4$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 19.0. HRMS (EI, m/z): calcd for $\text{C}_{18}\text{H}_{29}\text{O}_3\text{P}^+$ [M^+]: 324.1854; Found: 324.1855.

(*E*)-diisopropyl 4-bromostyrylphosphonate (**2l**)



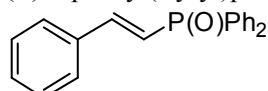
IR(KBr)/ cm^{-1} : 3325, 2958, 2768, 1616, 1116, 988, 786. ^1H NMR (400 MHz, CDCl_3): δ 7.53-7.27 (m, 5H), 6.26 (t, $J = 20$ Hz, 1H), 4.76-4.69 (m, 2H), 1.37 (d, $J = 8$ Hz, 6H), 1.33 (d, $J = 4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.4 (d, $J_{\text{C-P}} = 7$ Hz), 133.9 (d, $J_{\text{C-P}} = 24$ Hz), 132.0, 129.1, 124.3, 116.3 (d, $J_{\text{C-P}} = 191$ Hz), 70.6 (d, $J_{\text{C-P}} = 6$ Hz), 24.1 (d, $J_{\text{C-P}} = 4$ Hz), 24.0 (d, $J_{\text{C-P}} = 5$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 16.8. HRMS (EI, m/z): calcd for $\text{C}_{14}\text{H}_{20}\text{BrO}_3\text{P}^+$ [M^+]: 346.0333; Found: 346.0335.

(*E*)-diisobutyl 4-methylstyrylphosphonate (**2m**)



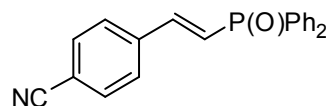
IR(KBr)/cm⁻¹: 2955, 2923, 2856, 1614, 1456, 1251, 1024, 966, 740. ¹H NMR (400 MHz, CDCl₃): δ 7.58-7.48 (m, 3H), 7.45-7.39 (m, 2H), 6.27 (t, *J* = 16 Hz, 1H), 3.94-3.74 (m, 4H), 1.97 (t, *J* = 8 Hz, 2H), 0.96 (d, *J* = 8 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 148.8, 134.8 (d, *J*_{C-P} = 17 Hz), 132.2, 130.2 (d, *J*_{C-P} = 195 Hz), 128.1 (d, *J*_{C-P} = 113 Hz), 113.5 (d, *J*_{C-P} = 192 Hz), 71.8 (d, *J*_{C-P} = 6 Hz), 29.1 (t, *J*_{C-P} = 4 Hz), 18.7 (d, *J*_{C-P} = 2 Hz), 18.6 (d, *J*_{C-P} = 2 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 19.6. HRMS (EI, *m/z*): calcd for C₁₇H₂₇O₃P⁺ [*M*⁺]: 310.1698; Found: 310.1700.

(*E*)-diphenyl(styryl)phosphine oxide (**2n**)²



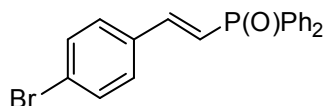
IR(KBr)/cm⁻¹: 3424, 1609, 1183, 1114, 745. ¹H NMR (400 MHz, CDCl₃): δ 7.83-7.74 (m, 4H), 7.53-7.45 (m, 9H), 7.38 (d, *J* = 16 Hz, 3H), 6.85 (d, *J* = 20 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 147.4 (d, *J*_{C-P} = 3 Hz), 134.9 (d, *J*_{C-P} = 18 Hz), 133.4 (d, *J*_{C-P} = 23 Hz), 132.1 (t, *J*_{C-P} = 14 Hz), 131.8 (d, *J*_{C-P} = 2 Hz), 131.3 (d, *J*_{C-P} = 10 Hz), 131.0 (d, *J*_{C-P} = 10 Hz), 119.0 (d, *J*_{C-P} = 104 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 24.5. MS:*m/z* 304.1 (*M*⁺).

(*E*)-4-(2-(diphenylphosphoryl)vinyl)benzonitrile (**2o**)²



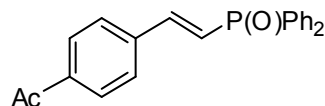
IR(KBr)/cm⁻¹: 3396, 2925, 1605, 1436, 1121, 1026, 726, 526. ¹H NMR (400 MHz, CDCl₃): δ 7.75 (t, *J* = 8 Hz, 4H), 7.69-7.61 (m, 4H), 7.58-7.46 (m, 7H), 6.99 (t, *J* = 16 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 145.2, 139.1 (d, *J*_{C-P} = 18 Hz), 132.6, 132.5, 132.2 (d, *J*_{C-P} = 2 Hz), 131.3 (d, *J*_{C-P} = 10 Hz), 128.8 (d, *J*_{C-P} = 12 Hz), 128.2, 123.5 (d, *J*_{C-P} = 100 Hz), 118.3, 113.2; ³¹P NMR (162 MHz, CDCl₃): δ 24.2. MS:*m/z* 329.1 (*M*⁺).

(*E*)-(4-bromostyryl)diphenylphosphine oxide (**2p**)⁶



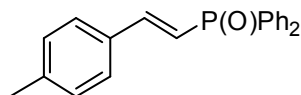
IR(KBr)/cm⁻¹: 3435, 3055, 1603, 1510, 1183, 1119, 510. ¹H NMR (400 MHz, CDCl₃): δ 7.75 (t, *J* = 8 Hz, 4H), 7.56-7.45 (m, 9H), 7.38 (d, *J* = 8 Hz, 2H), 6.84 (t, *J* = 20 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 146.1 (d, *J*_{C-P} = 4 Hz), 133.9 (d, *J*_{C-P} = 18 Hz), 133.0, 132.0, 131.9, 131.3 (d, *J*_{C-P} = 10 Hz), 129.2, 128.6 (d, *J*_{C-P} = 12 Hz), 124.3, 119.8 (d, *J*_{C-P} = 103 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 24.6. MS:*m/z* 382.0 (*M*⁺).

(*E*)-1-(4-(2-(diphenylphosphoryl)vinyl)phenyl)ethanone (**2q**)⁶



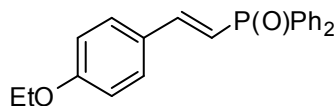
IR(KBr)/cm⁻¹: 3422, 2926, 1603, 1510, 1258, 1177, 517. ¹H NMR (400 MHz, CDCl₃): δ 7.75 (t, *J* = 8 Hz, 4H), 7.54 (d, *J* = 8 Hz, 4H), 7.47 (t, *J* = 8 Hz, 5H), 7.12 (t, *J* = 8 Hz, 2H), 6.81 (t, *J* = 20 Hz, 1H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 169.0, 151.8, 146.3 (d, *J*_{C-P} = 4 Hz), 131.8 (d, *J*_{C-P} = 3 Hz), 131.2 (d, *J*_{C-P} = 10 Hz), 130.8 (t, *J*_{C-P} = 4 Hz), 128.8, 128.5 (d, *J*_{C-P} = 12 Hz), 121.9, 121.6, 119.0 (d, *J*_{C-P} = 104 Hz), 21.0; ³¹P NMR (162 MHz, CDCl₃): δ 25.0. MS:*m/z* 346.1 (*M*⁺).

(*E*)-(4-methylstyryl)diphenylphosphine oxide (**2r**)²



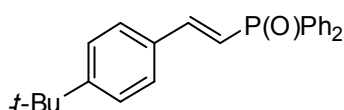
IR(KBr)/cm⁻¹: 3402, 2960, 1602, 1431, 1064, 768, 538. ¹H NMR (400 MHz, CDCl₃): δ 7.76 (t, *J* = 8 Hz, 4H), 7.52-7.41 (m, 9H), 7.19 (t, *J* = 8 Hz, 2H), 6.78 (t, *J* = 20 Hz, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.4 (d, *J*_{C-P} = 3 Hz), 140.4, 133.3 (d, *J*_{C-P} = 105 Hz), 132.2 (d, *J*_{C-P} = 18 Hz), 131.7 (d, *J*_{C-P} = 3 Hz), 131.3 (d, *J*_{C-P} = 9 Hz), 131.0 (q, *J*_{C-P} = 82 Hz), 128.5 (d, *J*_{C-P} = 12 Hz), 118.0 (d, *J*_{C-P} = 104 Hz), 21.3; ³¹P NMR (162 MHz, CDCl₃): δ 25.1. MS:m/z 318.1 (M⁺).

(*E*)-(4-ethoxystyryl)diphenylphosphine oxide (**2s**)



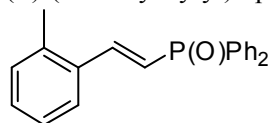
IR(KBr)/cm⁻¹: 3402, 2895, 1622, 1425, 1065, 775, 538. ¹H NMR (400 MHz, CDCl₃): δ 7.76 (t, *J* = 8 Hz, 4H), 7.53-7.38 (m, 9H), 6.88 (d, *J* = 8 Hz, 2H), 6.66 (t, *J* = 20 Hz, 1H), 4.07-4.02 (m, 2H), 1.41 (t, *J* = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 160.5, 147.1 (d, *J*_{C-P} = 4 Hz), 133.0 (d, *J*_{C-P} = 105 Hz), 131.7 (d, *J*_{C-P} = 2 Hz), 131.3 (d, *J*_{C-P} = 10 Hz), 129.3, 128.5 (d, *J*_{C-P} = 12 Hz), 127.6 (d, *J*_{C-P} = 18 Hz), 115.6 (d, *J*_{C-P} = 106 Hz), 114.6, 63.5, 14.6; ³¹P NMR (162 MHz, CDCl₃): δ 25.1. HRMS (EI, m/z): calcd for C₂₂H₂₁O₂P⁺ [M⁺]: 348.1279; Found: 348.1280.

(*E*)-(4-(tert-butyl)styryl)diphenylphosphine oxide (**2t**)



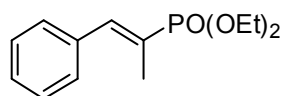
IR(KBr)/cm⁻¹: 3389, 2895, 2768, 1650, 1410, 1064, 778, 540. ¹H NMR (400 MHz, CDCl₃): δ 4.76 (t, *J* = 8 Hz, 4H), 7.55-7.38 (m, 11H), 6.80 (t, *J* = 20 Hz, 1H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 153.6, 147.5 (d, *J*_{C-P} = 3 Hz), 132.8 (d, *J*_{C-P} = 106 Hz), 131.9 (d, *J*_{C-P} = 2 Hz), 131.4 (d, *J*_{C-P} = 10 Hz), 131.2 (d, *J*_{C-P} = 9 Hz), 128.6 (d, *J*_{C-P} = 12 Hz), 127.7, 125.8, 117.8 (d, *J*_{C-P} = 104 Hz), 34.9, 31.2; ³¹P NMR (162 MHz, CDCl₃): δ 25.3. HRMS (EI, m/z): calcd for C₂₄H₂₅OP⁺ [M⁺]: 360.1643; Found: 360.1640.

(*E*)-(2-methylstyryl)diphenylphosphine oxide (**2u**)²



IR(KBr)/cm⁻¹: 3405, 2863, 2754, 1645, 1260, 1006, 886. ¹H NMR (400 MHz, CDCl₃): δ 7.79 (t, *J* = 8 Hz, 3H), 7.48-7.36 (m, 9H), 6.40 (d, *J* = 24 Hz, 1H), 2.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.3 (d, *J*_{C-P} = 2 Hz), 141.8 (d, *J*_{C-P} = 17 Hz), 131.4 (d, *J*_{C-P} = 3 Hz), 130.8 (d, *J*_{C-P} = 10 Hz), 129.1, 128.6, 128.5, 128.4, 118.0 (d, *J*_{C-P} = 104 Hz), 19.6 (d, *J*_{C-P} = 8 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 22.0. MS:m/z 318.1 (M⁺).

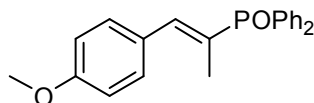
(*E*)-diethyl (1-phenylprop-1-en-2-yl)phosphonate (**2v**)⁷



IR(KBr)/cm⁻¹: 2955, 2924, 2853, 1681, 1256, 1051, 1024, 677. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.28 (m, 6H), 4.16-4.08 (m, 4H), 2.08 (d, *J* = 16 Hz, 3H), 1.33 (t, *J* = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.6 (d, *J*_{C-P} = 11 Hz), 135.5 (d, *J*_{C-P} = 23 Hz), 133.3 (d, *J*_{C-P} = 196 Hz),

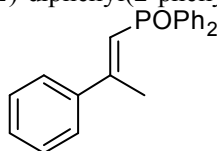
129.4, 128.3, 61.7 (d, J_{C-P} = 6 Hz), 16.3 (t, J_{C-P} = 6 Hz), 14.2 (d, J_{C-P} = 9 Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 22.2. MS:m/z 254.1 (M^+).

(*E*)-(1-(4-methoxyphenyl)prop-1-en-2-yl)diphenylphosphine oxide (**2w**)



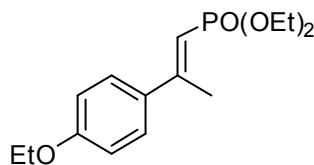
IR(KBr)/ cm^{-1} : 3405, 2858, 2825, 1645, 1260, 1026, 796. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (t, J = 8 Hz, 2H), 7.86 (d, J = 8 Hz, 2H), 7.74 (t, J = 8 Hz, 2H), 7.50 (d, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 3H), 7.39 (d, J = 8 Hz, 2H), 6.82 (d, J = 8 Hz, 2H), 3.83 (s, 3H), 1.55 (dd, J = 16 Hz, J = 4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.6, 132.0 (d, J_{C-P} = 2 Hz), 131.8 (d, J_{C-P} = 9 Hz), 131.5 (d, J_{C-P} = 9 Hz), 130.5 (d, J_{C-P} = 16 Hz), 130.3 (d, J_{C-P} = 49 Hz), 128.5 (d, J_{C-P} = 5 Hz), 128.3 (d, J_{C-P} = 5 Hz), 55.5, 45.4 (d, J_{C-P} = 60 Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 31.9. HRMS (EI, m/z): calcd for $\text{C}_{22}\text{H}_{21}\text{O}_2\text{P}^+$ [M^+]: 348.1279; Found: 348.1281.

(*E*)-diphenyl(2-phenylprop-1-en-1-yl)phosphine oxide (**2x**)⁸



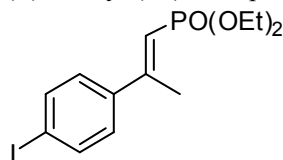
IR(KBr)/ cm^{-1} : 3415, 2798, 1655, 1255, 1026, 776. ^1H NMR (400 MHz, CDCl_3): δ 7.79 (t, J = 8 Hz, 4H), 7.59-7.36 (m, 11H), 6.40 (d, J = 24 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.3, 141.8 (d, J_{C-P} = 17 Hz), 134.4 (d, J_{C-P} = 104 Hz), 131.4 (d, J_{C-P} = 2 Hz), 130.8 (d, J_{C-P} = 10 Hz), 129.1, 128.6, 128.4 (d, J_{C-P} = 7 Hz), 125.8, 118.3 (d, J_{C-P} = 104 Hz), 19.6 (d, J_{C-P} = 8 Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 22.0. MS:m/z 318.1 (M^+).

(*E*)-diethyl (2-(4-ethoxyphenyl)prop-1-en-1-yl)phosphonate (**2y**)



IR(KBr)/ cm^{-1} : 2956, 2924, 2850, 1610, 1465, 1260, 788. ^1H NMR (400 MHz, CDCl_3): δ 7.45-7.43 (d, J = 8 Hz, 2H), 6.88 (d, J = 8 Hz, 2H), 5.85 (d, J = 16 Hz, 1H), 4.15-4.08 (m, 4H), 4.06-4.01 (m, 2H), 2.48 (s, 3H), 1.43 (t, J = 8 Hz, 3H), 1.35 (t, J = 8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 156.4 (d, J_{C-P} = 8 Hz), 132.5 (d, J_{C-P} = 24 Hz), 136.3, 113.2, 119.9 (d, J_{C-P} = 191 Hz), 62.52, 60.4 (d, J_{C-P} = 6 Hz), 18.0 (d, J_{C-P} = 8 Hz), 15.4 (d, J_{C-P} = 7 Hz), 13.7; ^{31}P NMR (162 MHz, CDCl_3): δ 19.1. HRMS (EI, m/z): calcd for $\text{C}_{15}\text{H}_{23}\text{O}_4\text{P}^+$ [M^+]: 298.1334; Found: 298.1337.

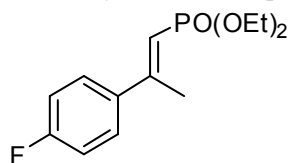
(*E*)-diethyl (2-(4-iodophenyl)prop-1-en-1-yl)phosphonate (**2z**)



IR(KBr)/ cm^{-1} : 2957, 2925, 2854, 1251, 1051, 1027, 961, 803. ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 5.90 (d, J = 16 Hz, 1H), 4.16-4.09 (m, 4H), 3.47 (s, 3H), 1.36 (t, J = 8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.8 (d, J_{C-P} = 9 Hz), 141.1 (d, J_{C-P} = 23 Hz), 137.6, 137.1 (d, J_{C-P} = 12 Hz), 127.7, 114.5 (d, J_{C-P} = 189 Hz), 61.6 (d, J_{C-P} = 5 Hz), 19.0 (d, J_{C-P} = 7 Hz), 16.4 (d, J_{C-P} = 7 Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 17.7. HRMS (EI, m/z): calcd

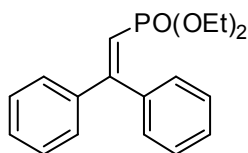
for $C_{13}H_{18}O_3IP^+[M^+]$: 380.0038; Found: 380.0041.

(E)-diethyl (2-(4-fluorophenyl)prop-1-en-1-yl)phosphonate (**2aa**)⁸



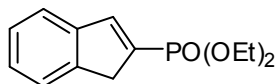
IR(KBr)/ cm^{-1} : 2960, 2914, 2846, 1620, 1465, 1258, 768. 1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.44 (m, 2H), 7.06 (t, $J = 8$ Hz, 2H), 5.86 (d, $J = 16$ Hz, 1H), 4.17-4.10 (m, 4H), 2.49 (d, $J = 4$ Hz, 3H), 1.36 (t, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 162.0, 156.8 (d, $J_{C-P} = 9$ Hz), 127.8 (d, $J_{C-P} = 8$ Hz), 115.49, 115.28, 113.4 (d, $J_{C-P} = 190$ Hz), 61.5 (d, $J_{C-P} = 6$ Hz), 19.3 (d, $J_{C-P} = 7$ Hz), 16.4 (d, $J_{C-P} = 6$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.1. MS:m/z 336.1 (M^+).

diethyl (2,2-diphenylvinyl)phosphonate (**2ab**)⁸



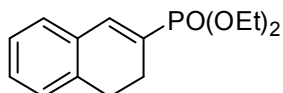
IR(KBr)/ cm^{-1} : 2958, 2914, 2846, 1626, 1462, 1258, 1056, 998, 865, 706. 1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.27 (m, 10H), 6.19 (d, $J = 16$ Hz, 1H), 3.95-3.79 (m, 4H), 1.13 (t, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (d, $J_{C-P} = 6$ Hz), 141.5 (d, $J_{C-P} = 22$ Hz), 138.8 (d, $J_{C-P} = 7$ Hz), 129.7 (d, $J_{C-P} = 2$ Hz), 129.3, 128.6, 128.2, 127.9 (d, $J_{C-P} = 28$ Hz), 125.6, 114.7 (d, $J_{C-P} = 192$ Hz), 61.4 (d, $J_{C-P} = 6$ Hz), 16.1 (d, $J_{C-P} = 7$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.7. MS:m/z 316.1 (M^+).

diethyl 1H-inden-2-ylphosphonate (**2ac**)⁹



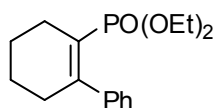
IR(KBr)/ cm^{-1} : 2960, 2925, 2867, 1444, 1242, 1051, 1025, 864, 794, 697. 1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, $J = 12$ Hz, 1H), 7.52 (d, $J = 8$ Hz, 2H), 7.34-7.28 (m, 2H), 4.19-4.10 (m, 4H), 3.65 (s, 2H), 1.35 (t, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 145.3 (d, $J_{C-P} = 3$ Hz), 142.5 (d, $J_{C-P} = 20$ Hz), 133.3 (d, $J_{C-P} = 189$ Hz), 127.2, 126.8, 124.0 (d, $J_{C-P} = 2$ Hz), 122.8, 61.9 (d, $J_{C-P} = 5$ Hz), 40.0 (d, $J_{C-P} = 14$ Hz), 16.3 (d, $J_{C-P} = 6$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.2. MS:m/z 252.1 (M^+).

diethyl (3,4-dihydronaphthalen-2-yl)phosphonate (**2ad**)



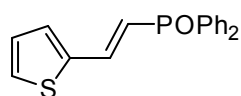
IR(KBr)/ cm^{-1} : 2956, 2924, 1253, 1055, 1023, 968, 762. 1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, $J = 20$ Hz, 1H), 7.26-7.14 (m, 4H), 4.15-4.09 (m, 4H), 2.86 (t, $J = 8$ Hz, 2H), 2.47 (t, $J = 8$ Hz, 2H), 1.35 (t, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4 (d, $J_{C-P} = 10$ Hz), 136.2 (d, $J_{C-P} = 2$ Hz), 132.0 (d, $J_{C-P} = 19$ Hz), 129.9 (d, $J_{C-P} = 43$ Hz), 128.3 (d, $J_{C-P} = 50$ Hz), 128.0, 127.3 (d, $J_{C-P} = 63$ Hz), 126.3 (d, $J_{C-P} = 88$ Hz), 61.8 (d, $J_{C-P} = 6$ Hz), 27.2 (d, $J_{C-P} = 9$ Hz), 22.7 (d, $J_{C-P} = 9$ Hz), 16.4 (d, $J_{C-P} = 6$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.9. HRMS (EI, m/z): calcd for $C_{14}H_{19}O_3P^+[M^+]$: 266.1072; Found: 266.1073.

diethyl (3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)phosphonate (**2ae**)



IR(KBr)/cm⁻¹: 2954, 2924, 2842, 1454, 1222, 1024, 745. ¹H NMR (400 MHz, CDCl₃): δ 7.30 (d, *J* = 8 Hz, 3H), 7.21 (t, *J* = 8 Hz, 2H), 3.95-3.86 (m, 4H), 3.84-3.74 (m, 2H), 3.56-3.46 (m, 2H), 3.27 (d, *J* = 24 Hz, 2H), 2.14-2.04 (m, 2H), 1.13 (t, *J* = 8 Hz, 6H), 0.94 (t, *J* = 8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 142.7, 133.2 (d, *J*_{C-P} = 9 Hz), 130.7 (d, *J*_{C-P} = 12 Hz), 128.0, 126.7, 126.5, 61.5 (d, *J*_{C-P} = 7 Hz), 61.3 (d, *J*_{C-P} = 7 Hz), 36.4, 35.0, 25.4 (d, *J*_{C-P} = 4 Hz), 23.8 (d, *J*_{C-P} = 4 Hz), 18.5 (d, *J*_{C-P} = 2 Hz), 16.1 (d, *J*_{C-P} = 6 Hz), 16.0 (d, *J*_{C-P} = 6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 29.2. HRMS (EI, *m/z*): calcd for C₁₆H₂₃O₃P⁺ [*M*⁺]: 294.1385; Found: 294.1387.

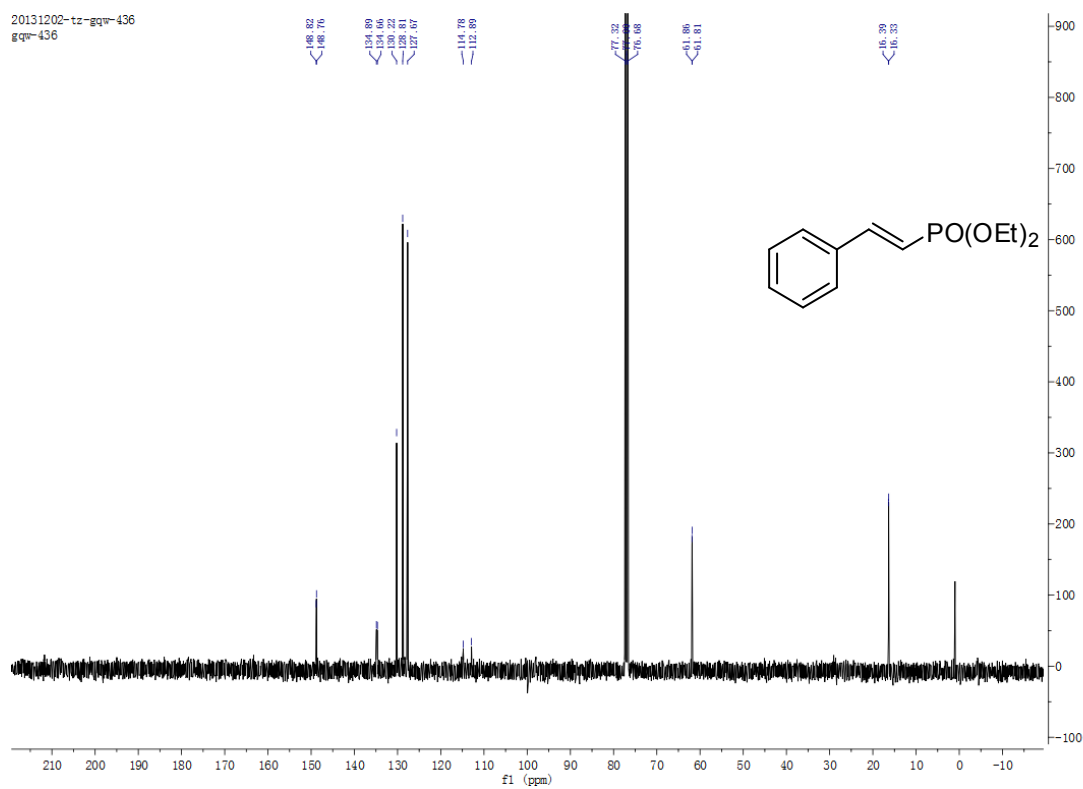
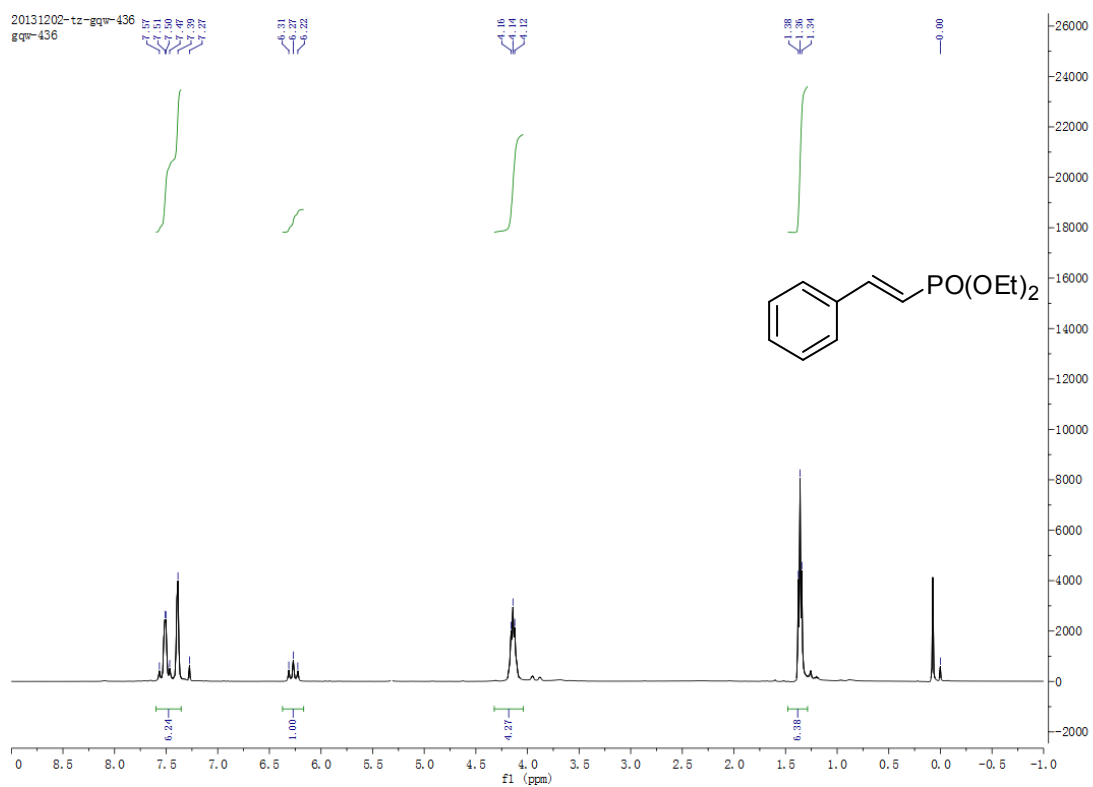
(*E*)-(2-(thiophen-2-yl)vinyl) diphenylphosphine oxide (**2af**)⁵

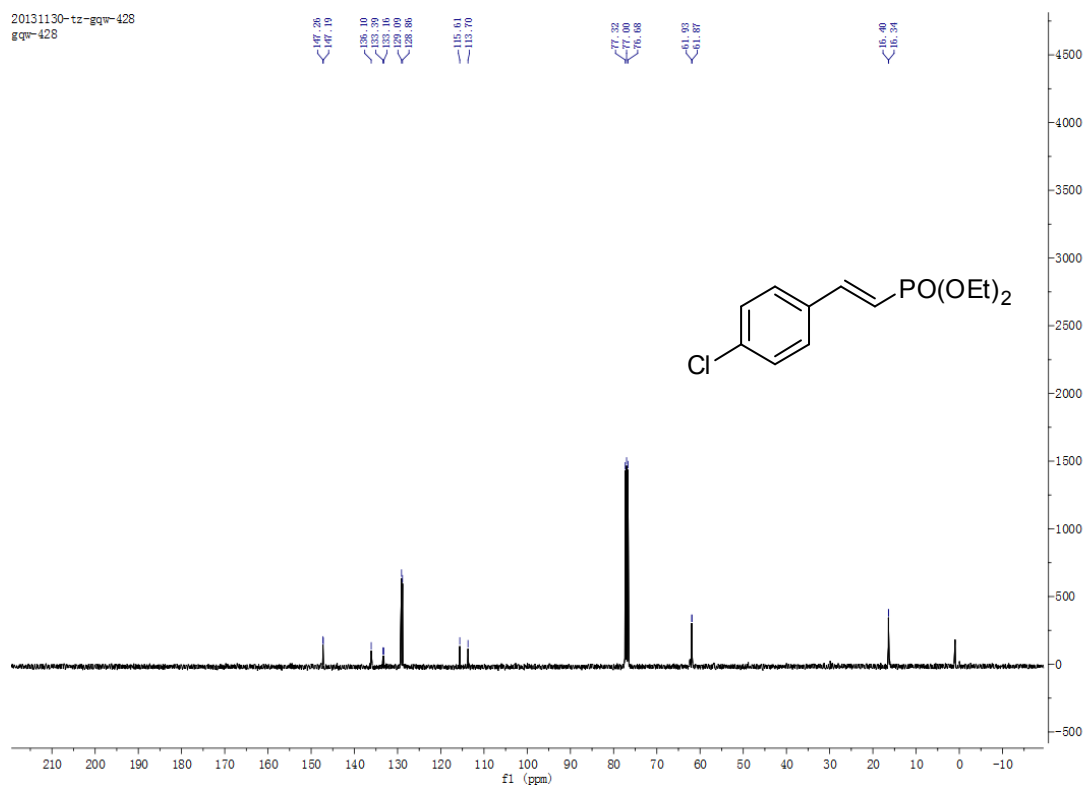
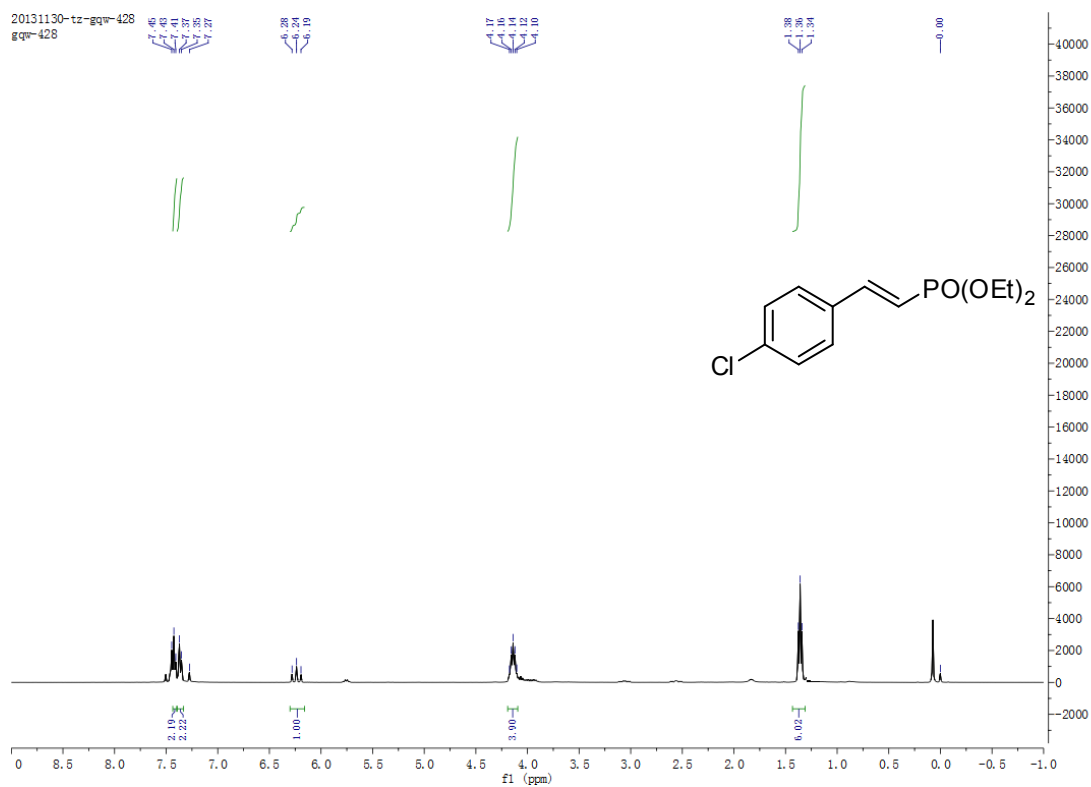


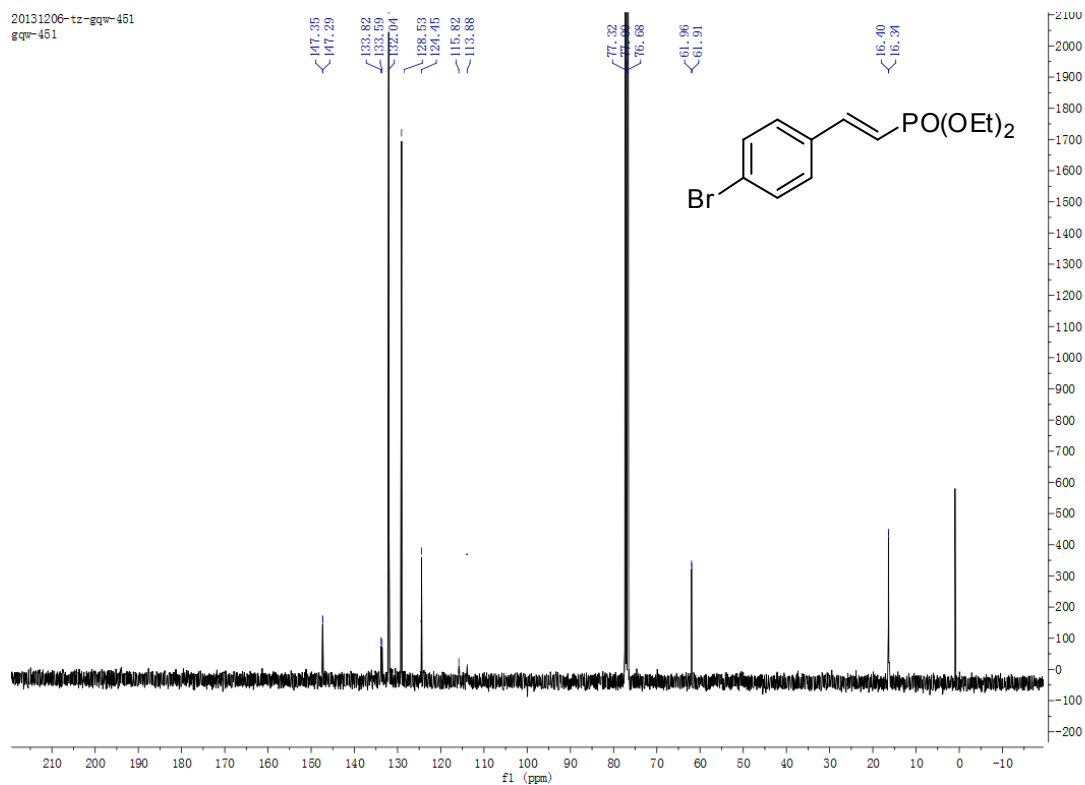
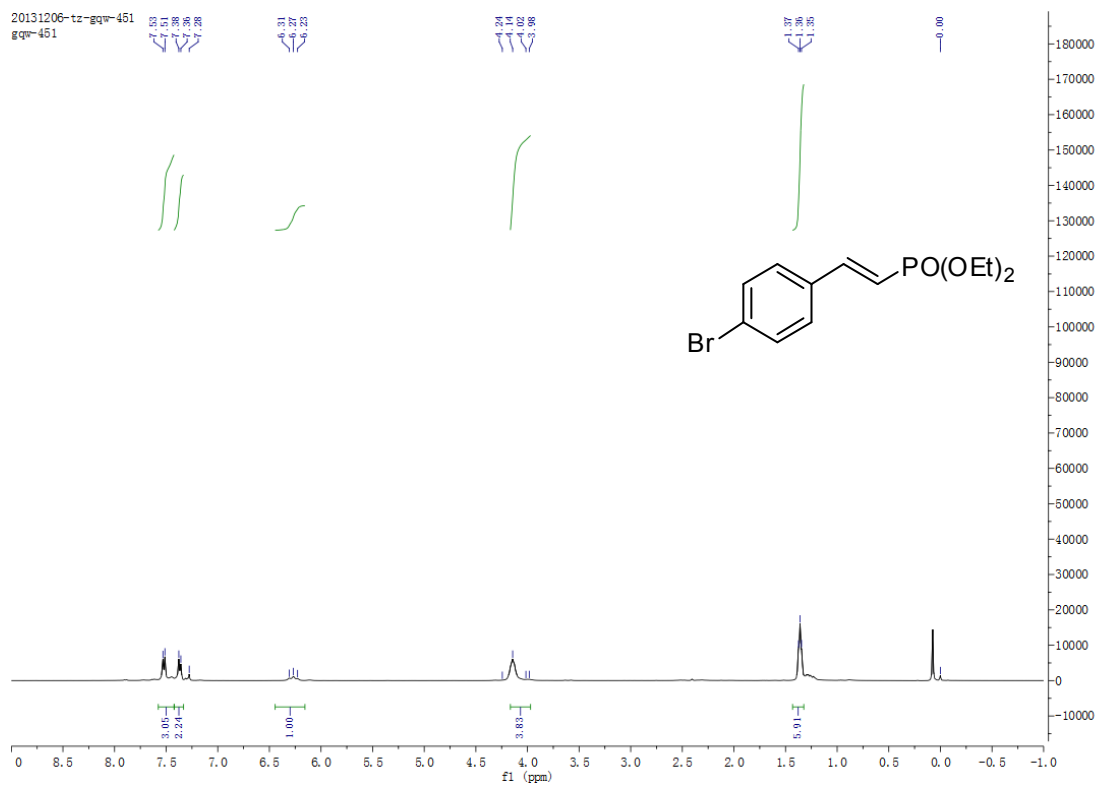
IR(KBr)/cm⁻¹: 3451, 2820, 1616, 1206, 1125, 864, 755. ¹H NMR (400 MHz, CDCl₃): δ 7.77-7.72 (m, 4 H), 7.60-7.48 (m, 7 H), 7.35 (d, *J* = 4 Hz, 1 H), 7.19 (d, *J* = 4 Hz, 1 H), 7.03 (d, *J* = 4 Hz, 1 H), 6.58 (dd, *J* = 20 Hz, *J* = 16 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 140.9, 140.6, 140.0 (d, *J*_{C-P} = 4 Hz), 133.2 (d, *J*_{C-P} = 106 Hz), 131.8 (d, *J*_{C-P} = 2 Hz), 131.3 (d, *J*_{C-P} = 10 Hz), 130.1, 128.6 (d, *J*_{C-P} = 12 Hz), 128.0 (d, *J*_{C-P} = 4 Hz), 118.0 (d, *J*_{C-P} = 106 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 22.4. MS:*m/z* 310.1 (*M*⁺).

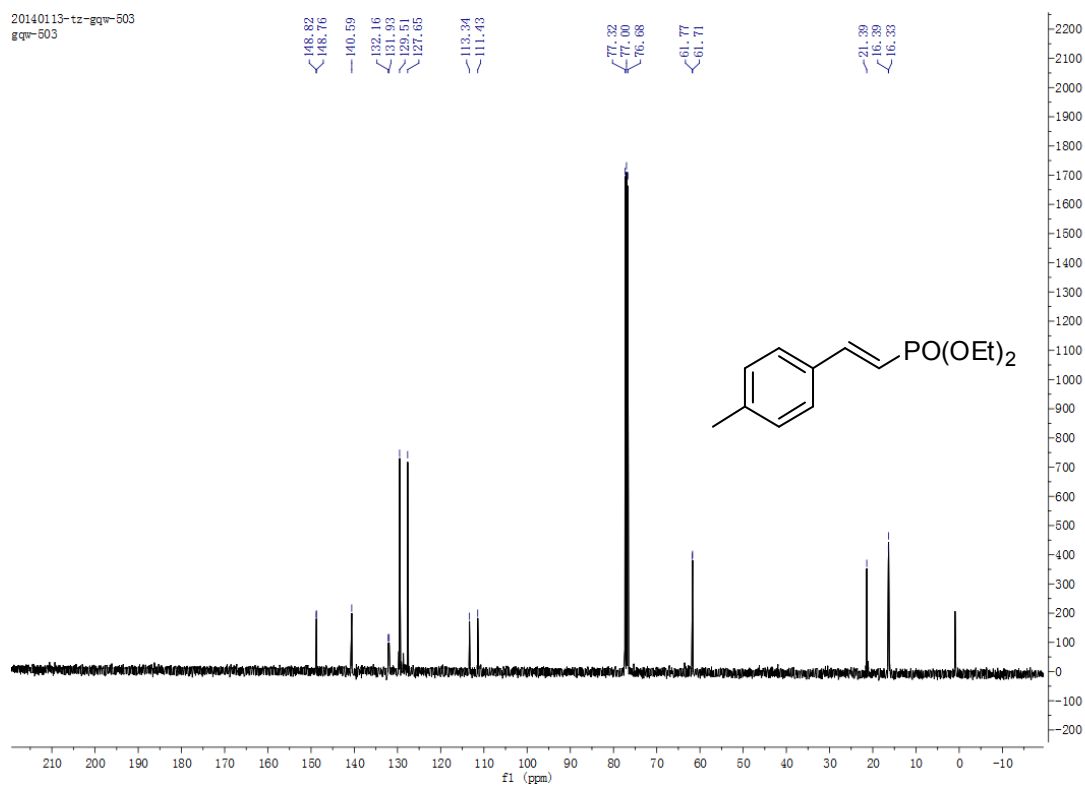
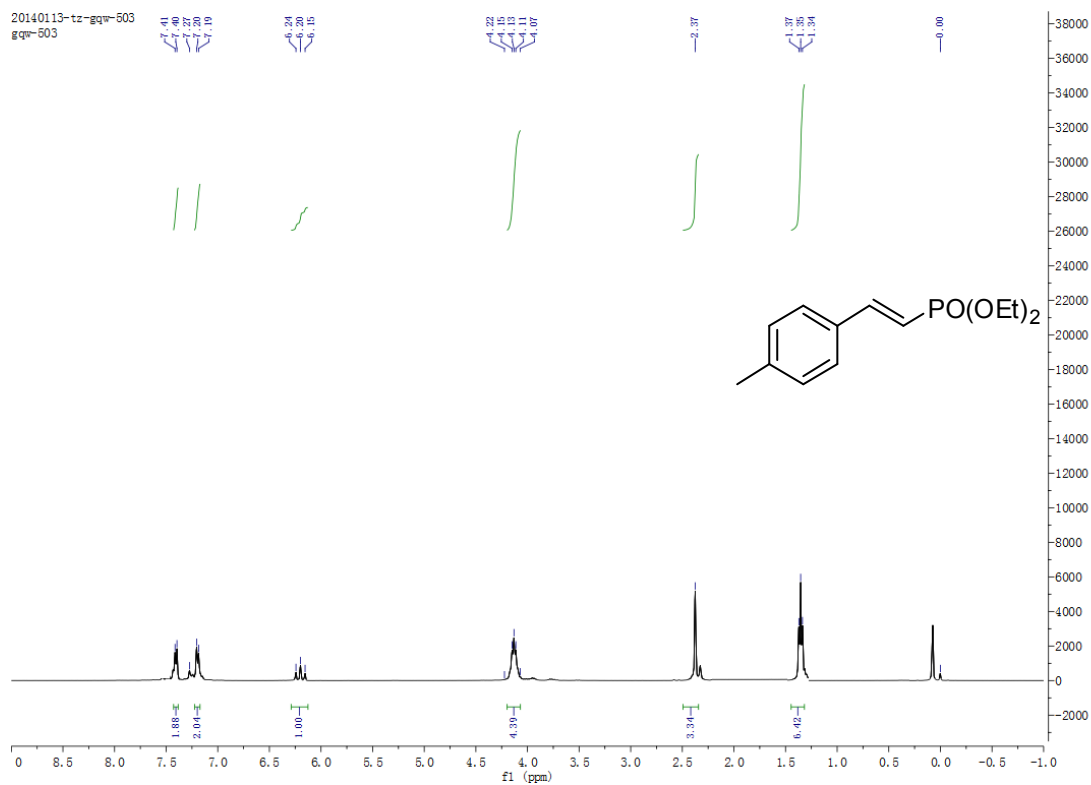
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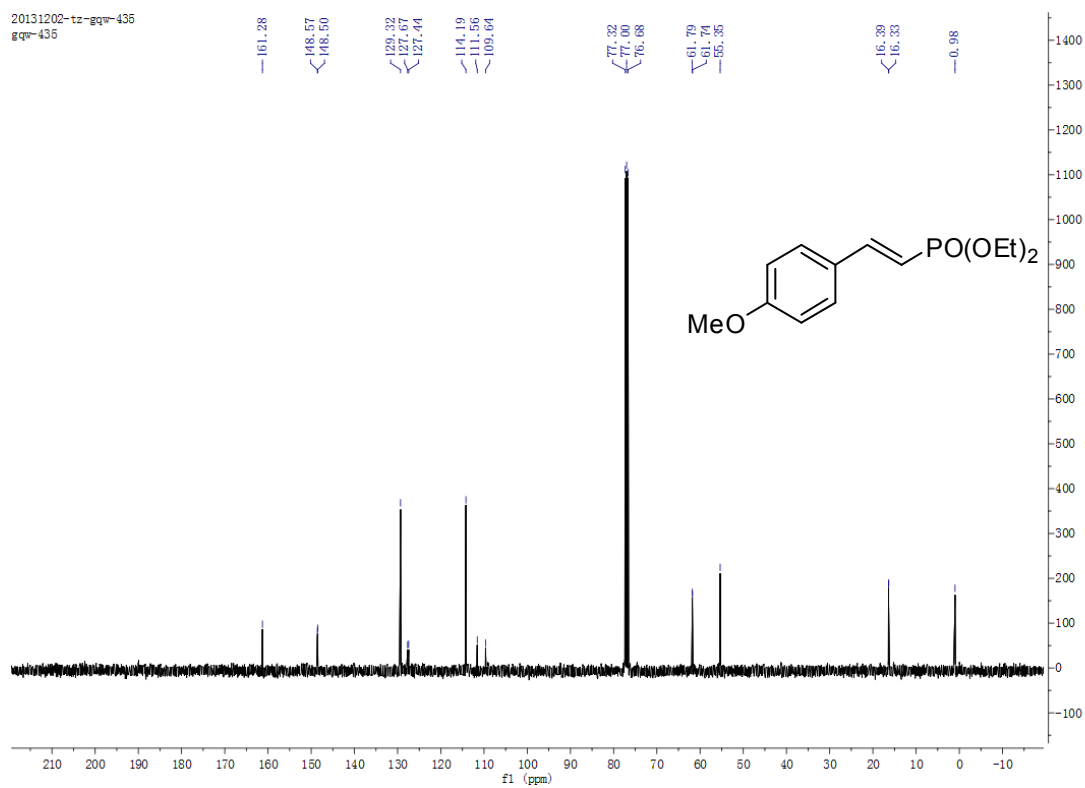
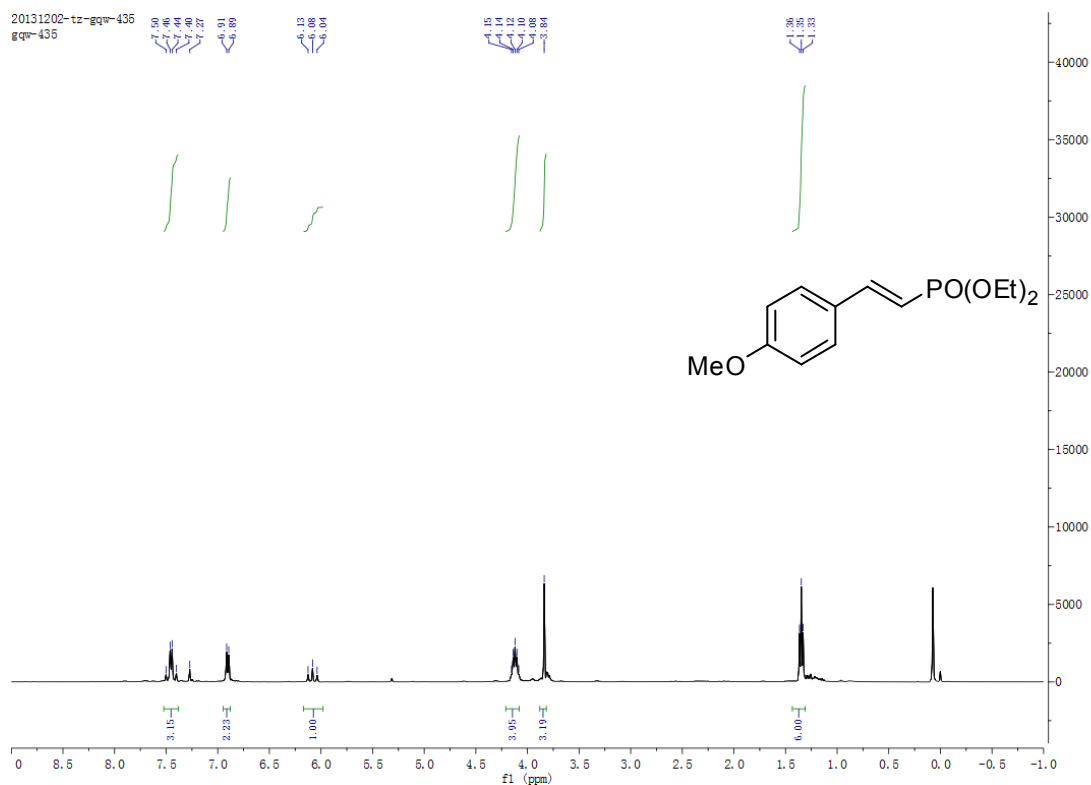
1. W. Al-Maksoud, J. Mesnager, F. Jaber, C. Pinel, L. Djakovitch, *J. Organomet. Chem.* 2009, **694**, 3222.
2. J. Hu, N. Zhao, B. Yang, G. Wang, L.-N. Guo, Y.-M. Liang, S.-D. Yang, *Chem. Eur. J.* 2011, **17**, 5516.
3. C. Wang, Y. Pan, D. Yang, *J. Organomet. Chem.* 2005, **690**, 1705.
4. H. Lahrache, S. Robin, G. Rousseau, *Tetrahedron L.* 2005, **46**, 1635.
5. Y. Wu, L. Liu, K. Yan, P. Xu, Y. Gao, Y. Zhao, *J. Org. Chem.* 2014, **79**, 8118.
6. G. Hu, Y. Gao, Y. Zhao, *Org. Lett.* 2014, **16**, 4464.
7. G. W. Kabalka, S. K. Guchhait, *Org. Lett.* 2003, **5**, 729.
8. Z.-C. Duan, X.-P. Hu, D.-Y. Wang, J.-D. Huang, S.-B. Yu, J. Deng, Z. Zheng, *Adv. Synth. Catal.* 2008, **350**, 1979.
9. D. N. Kazulkin, A. N. Ryabov, V. V. Izmer, A. V. Churakov, I. P. Beletskaya, C. J. Burns, A. Z. Voskoboinikov, *Organometallics* 2005, **24**, 3024.

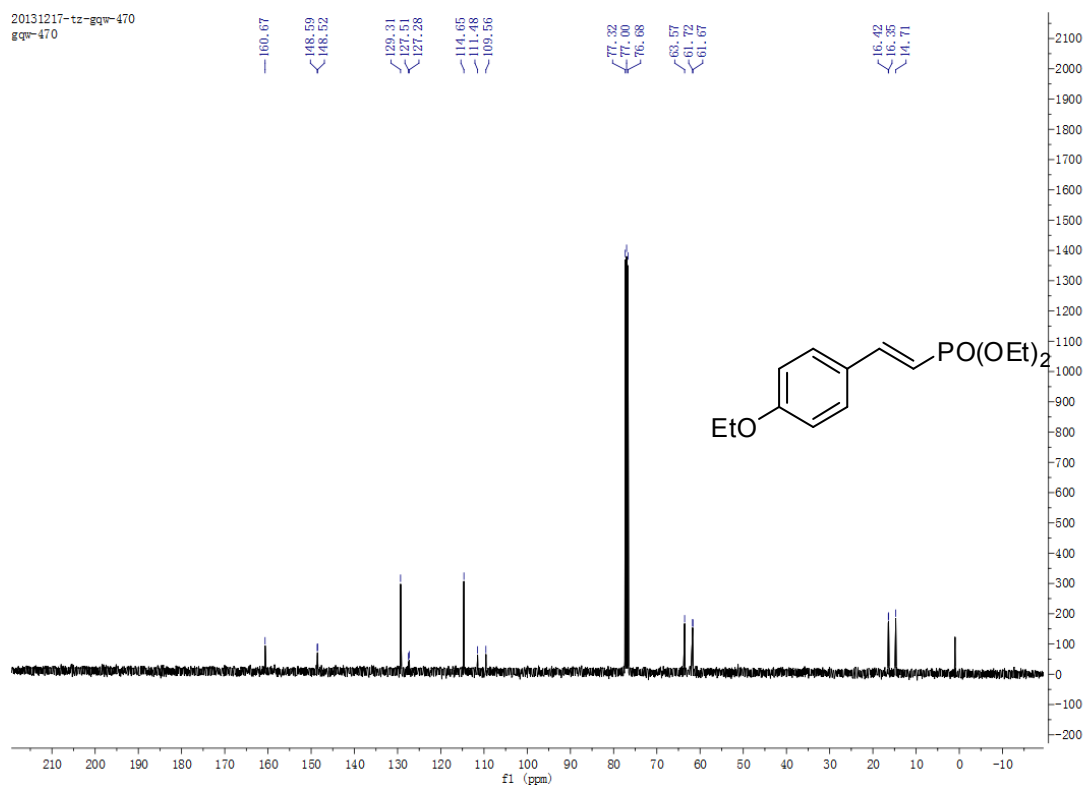
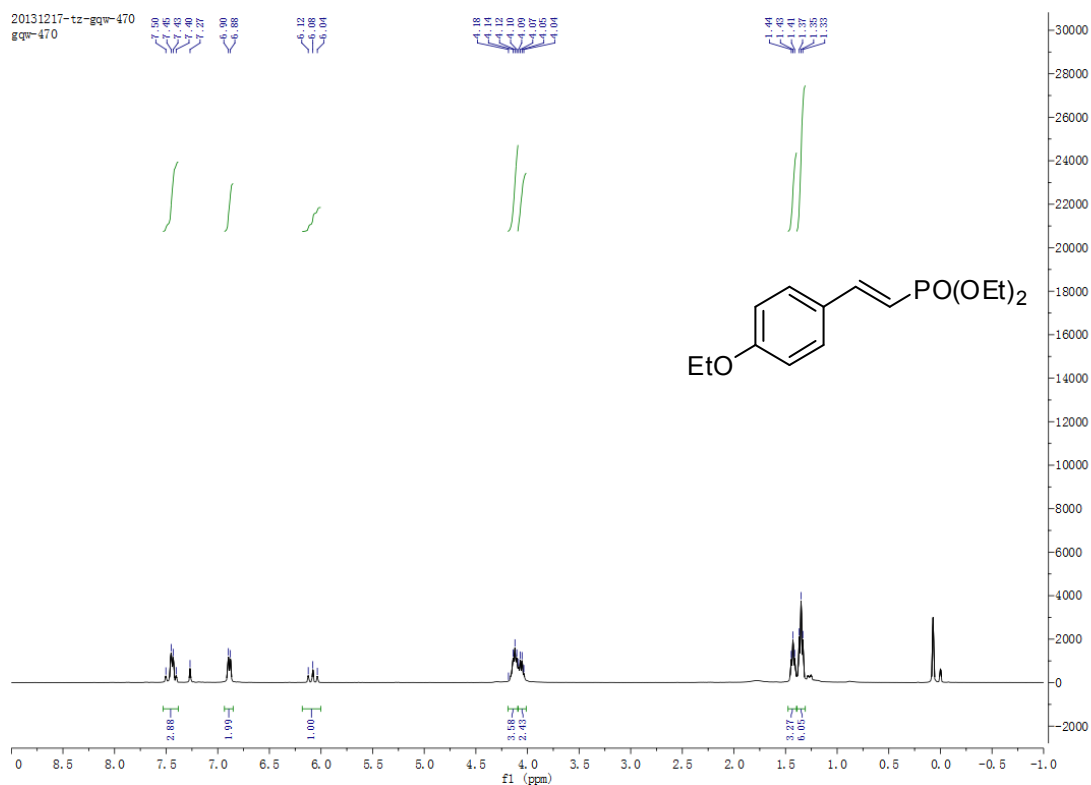


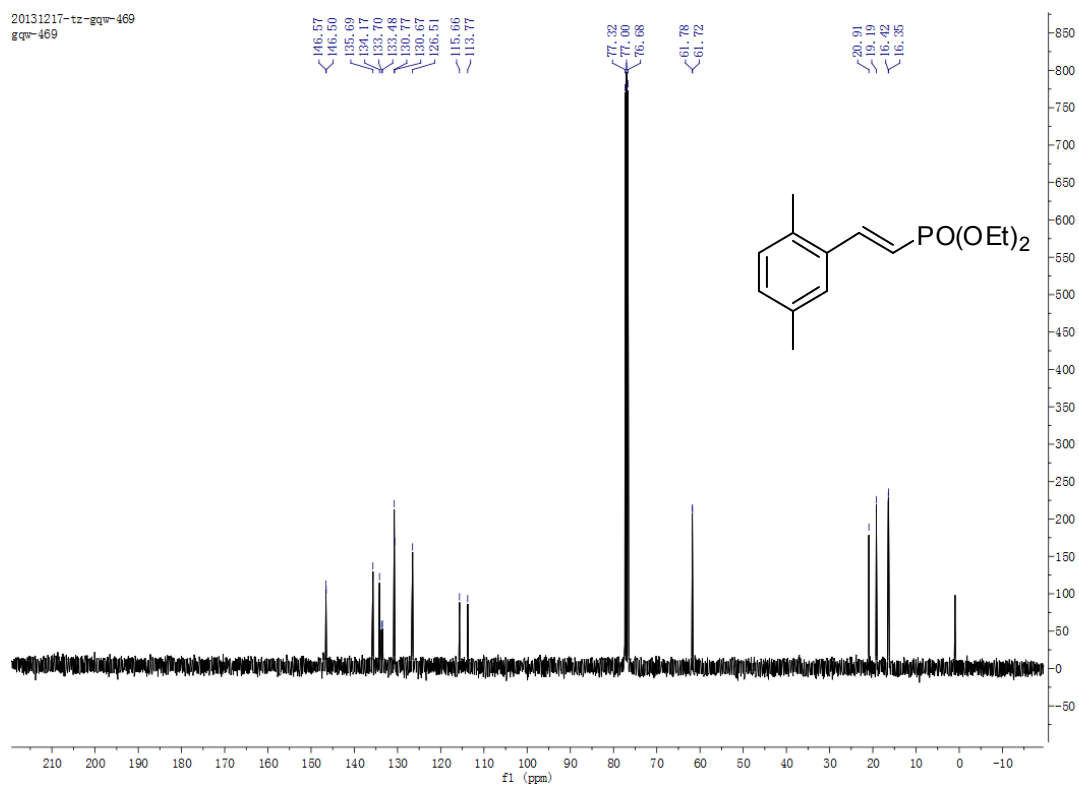
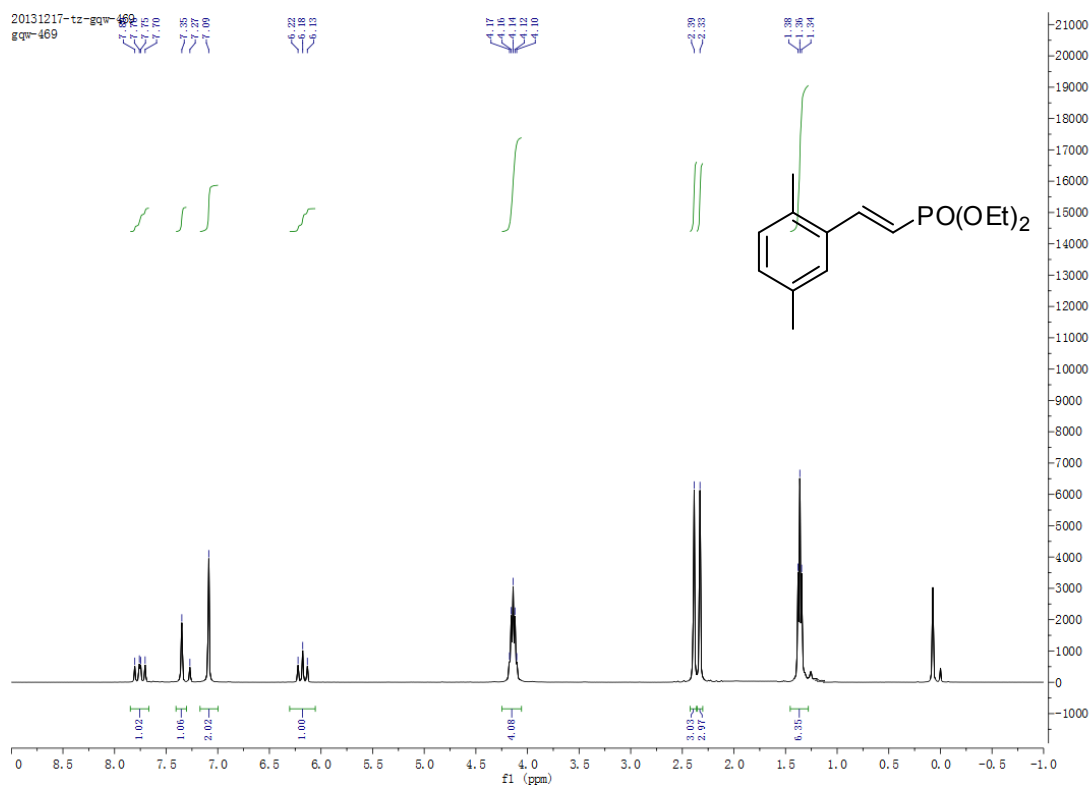


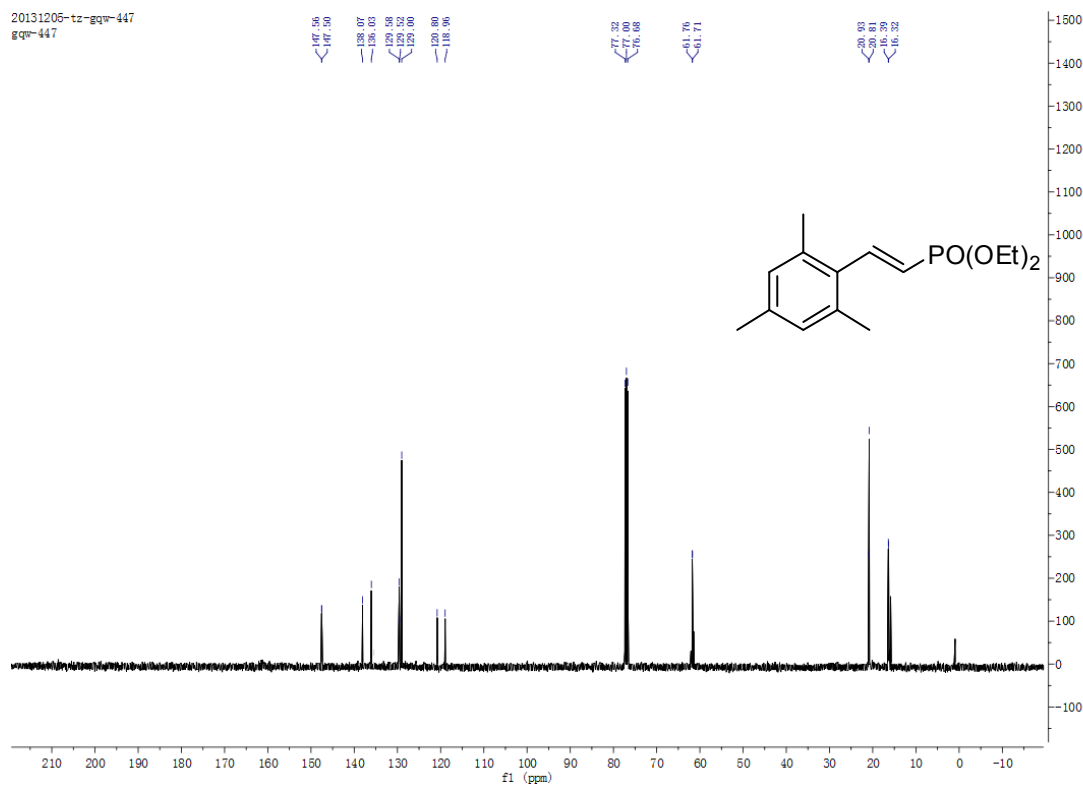
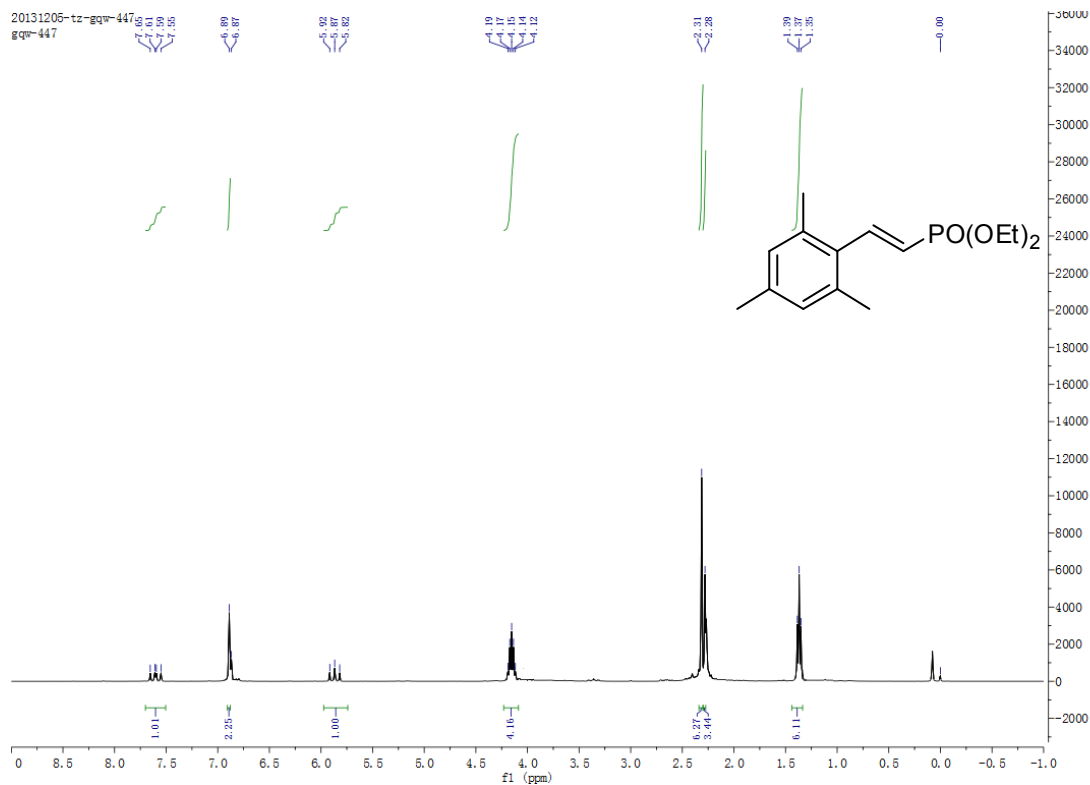


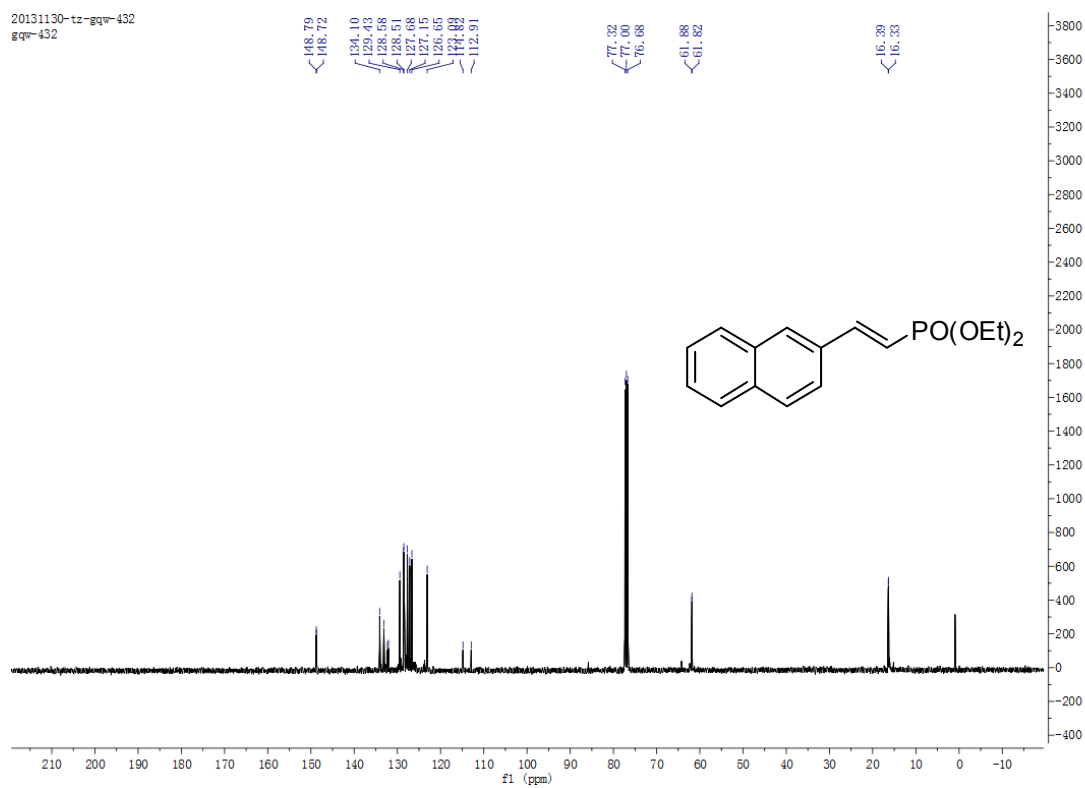
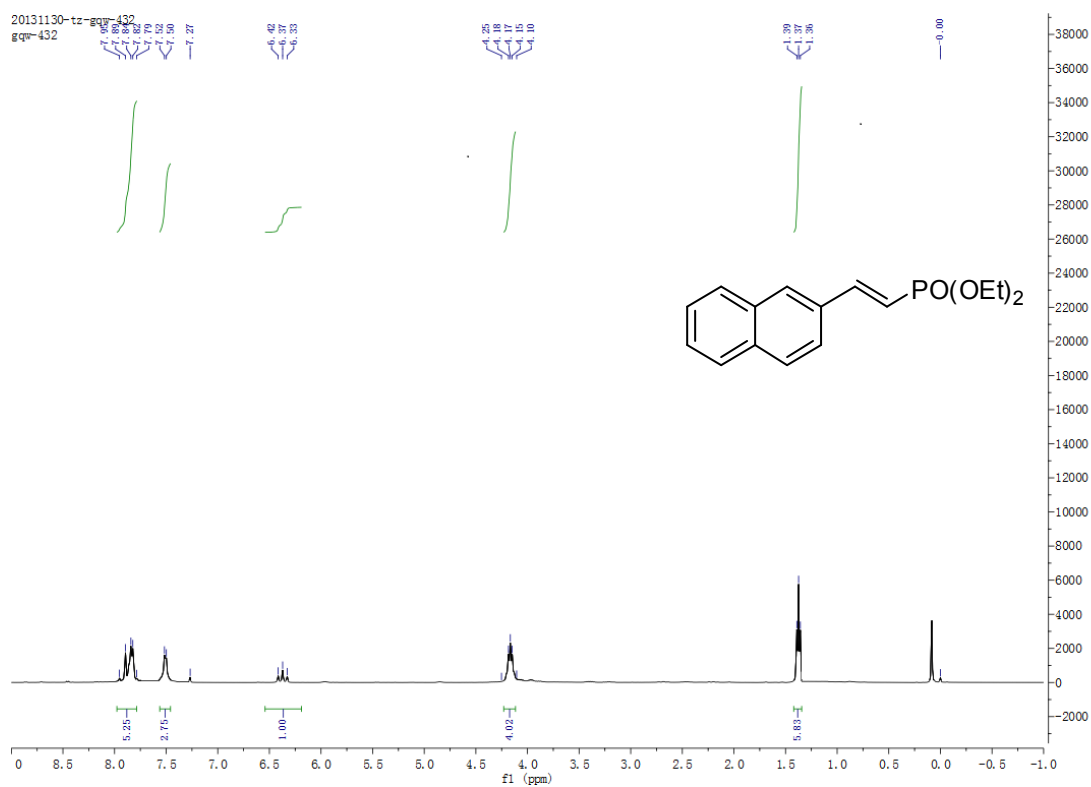




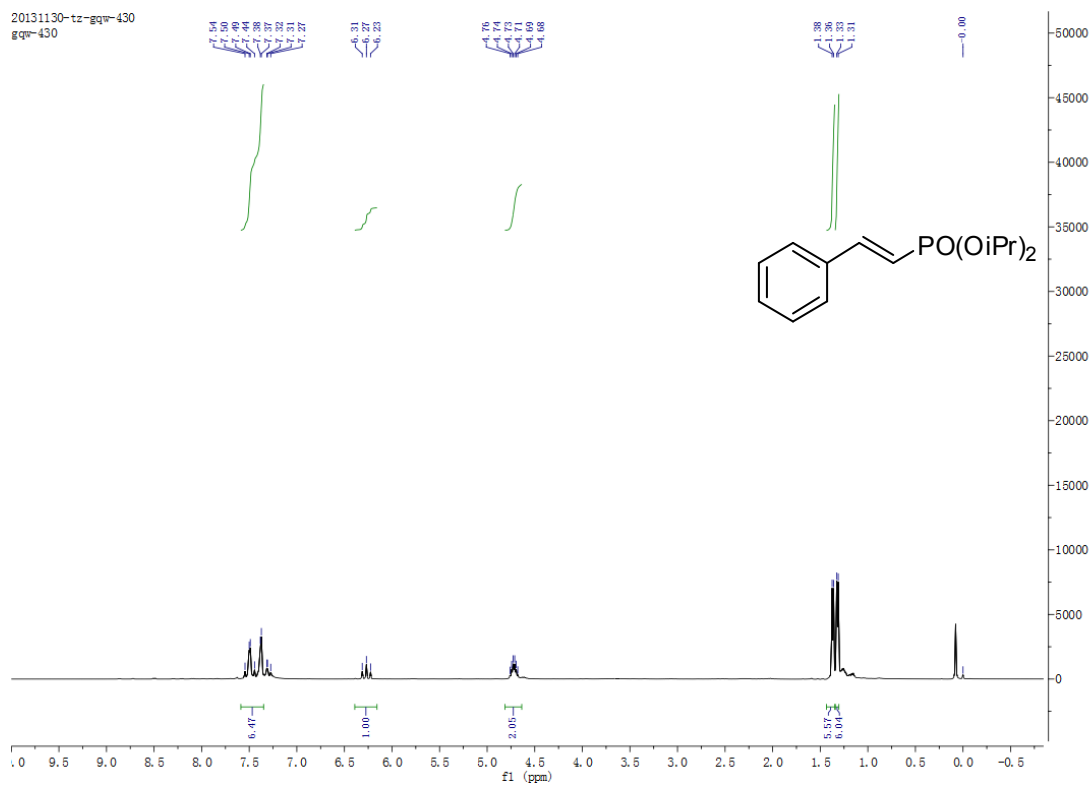




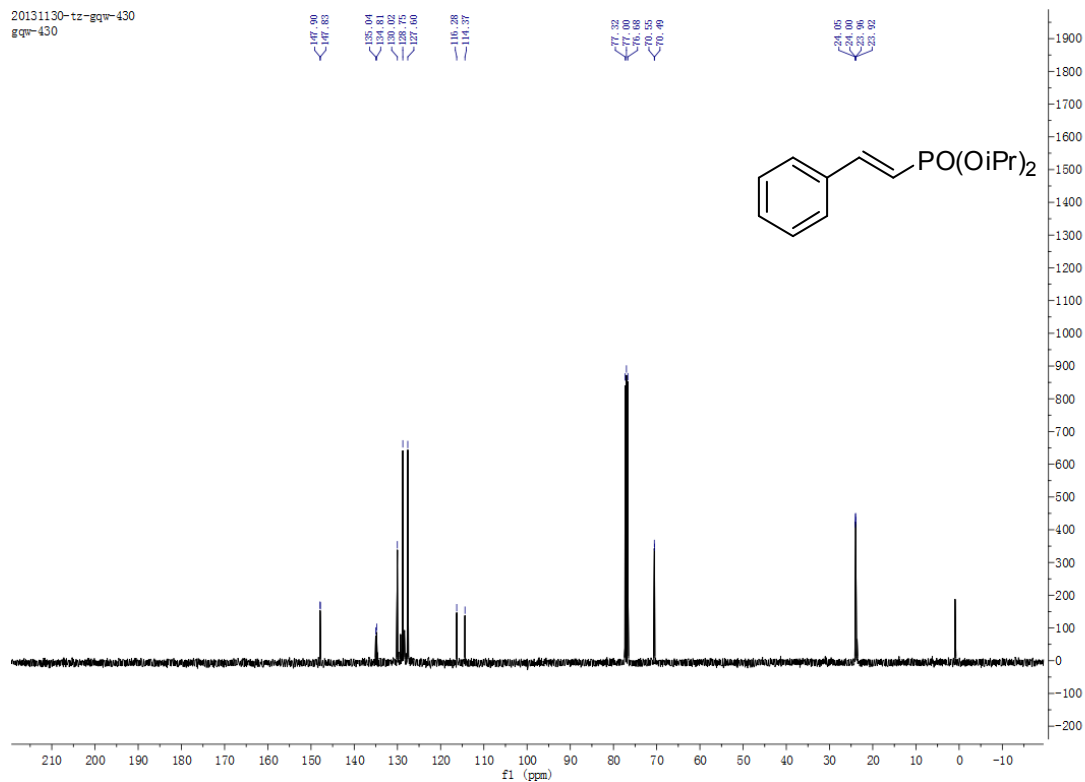


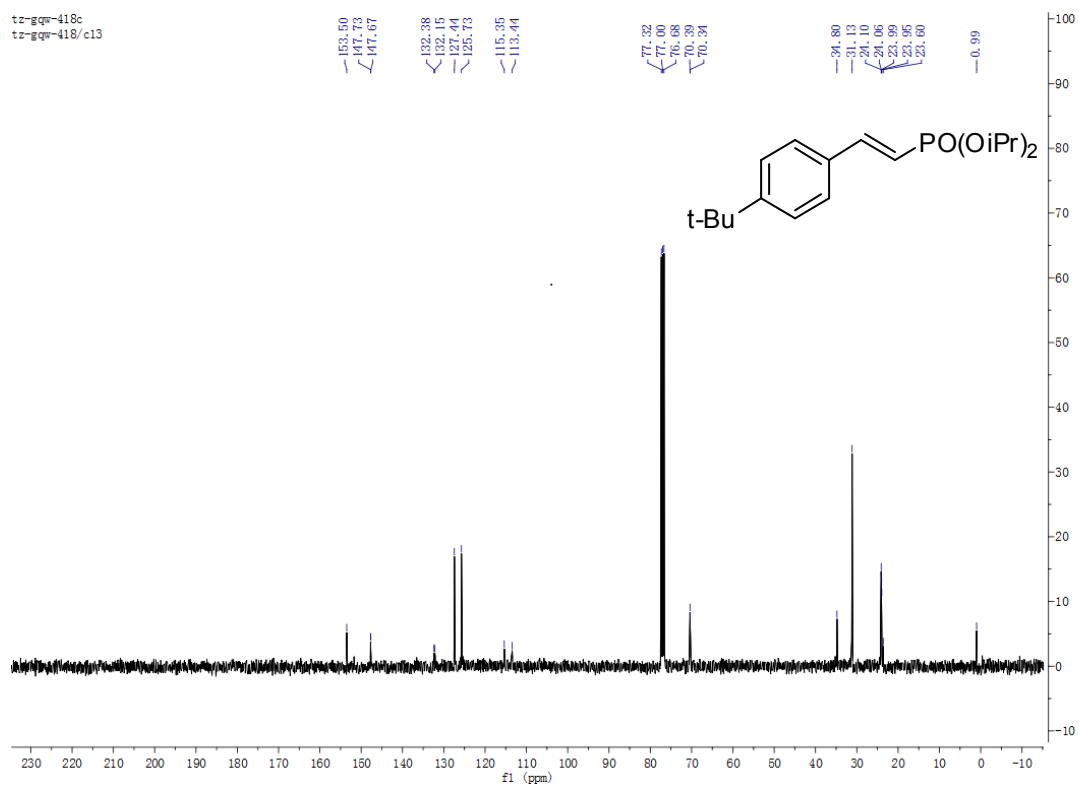
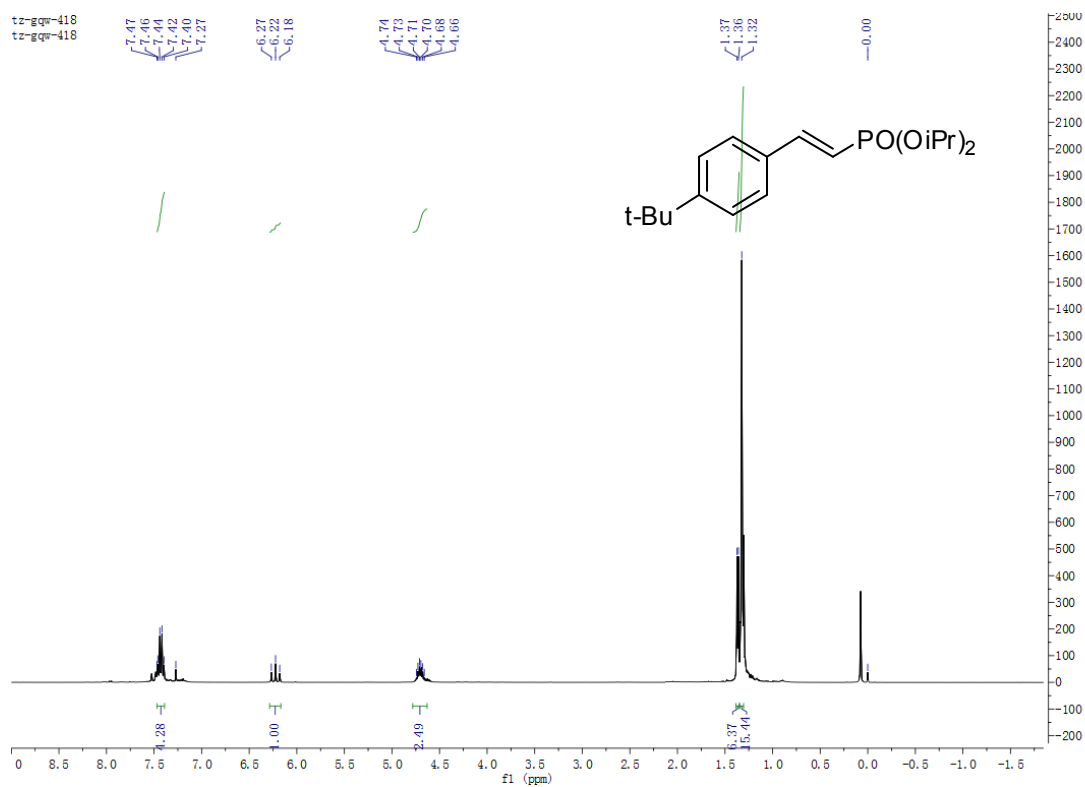


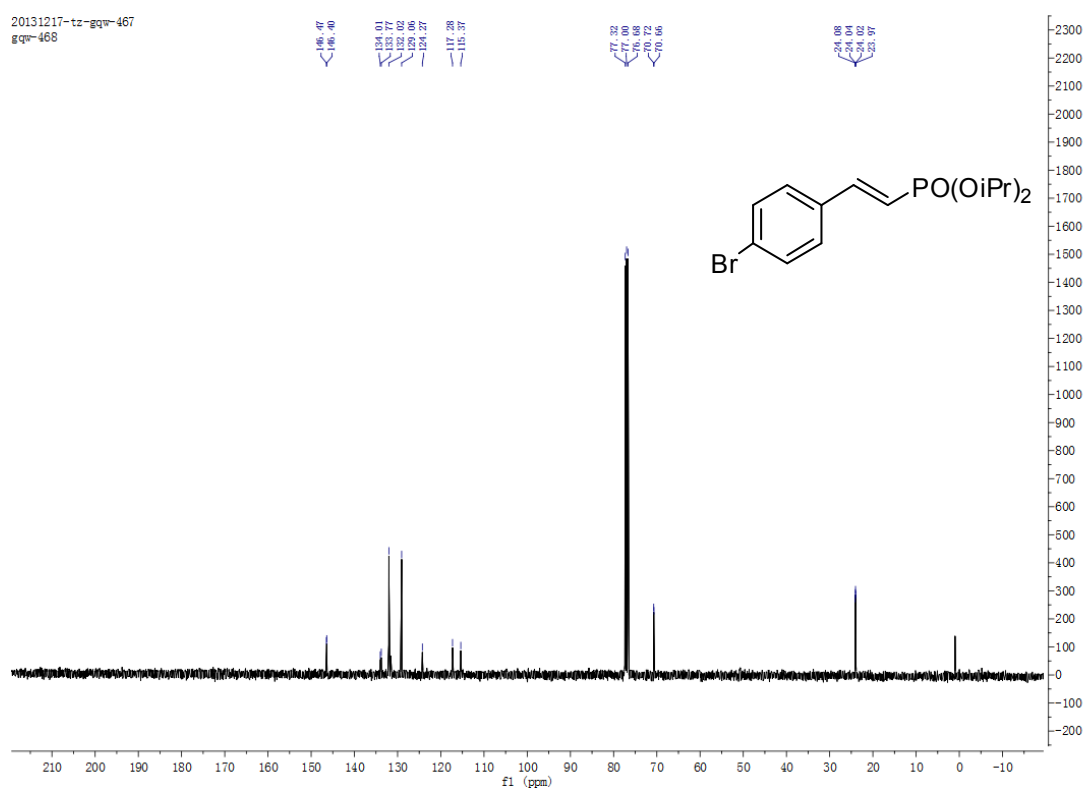
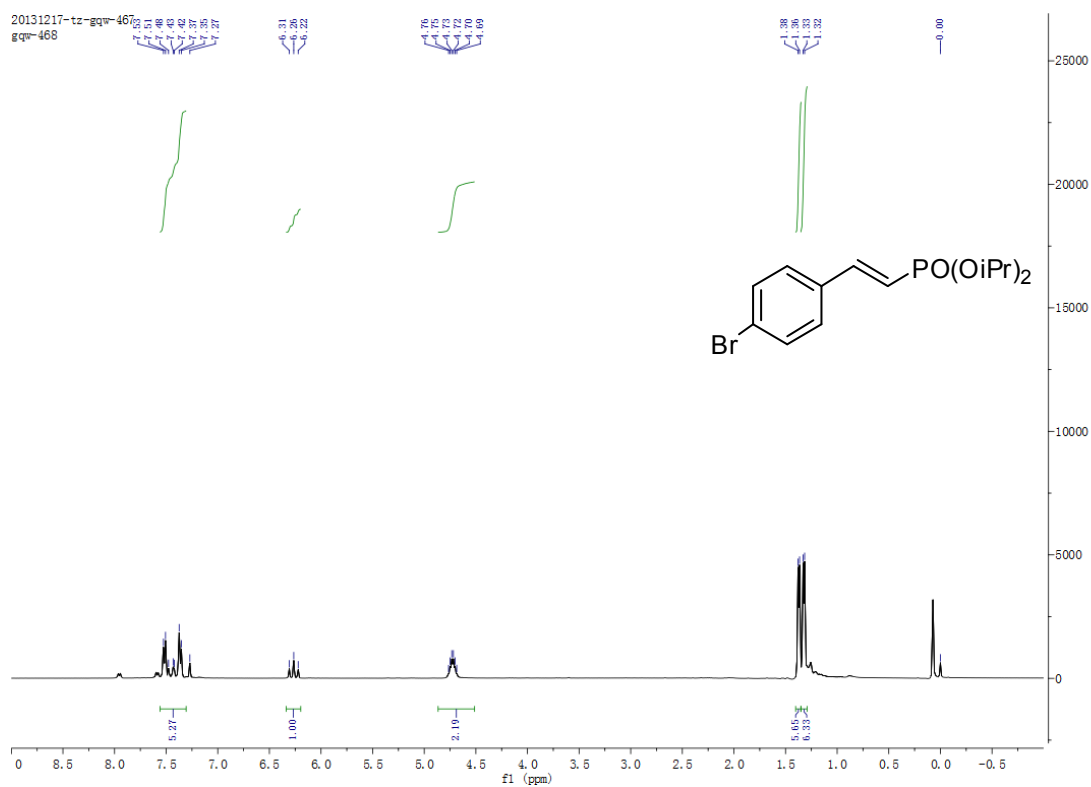
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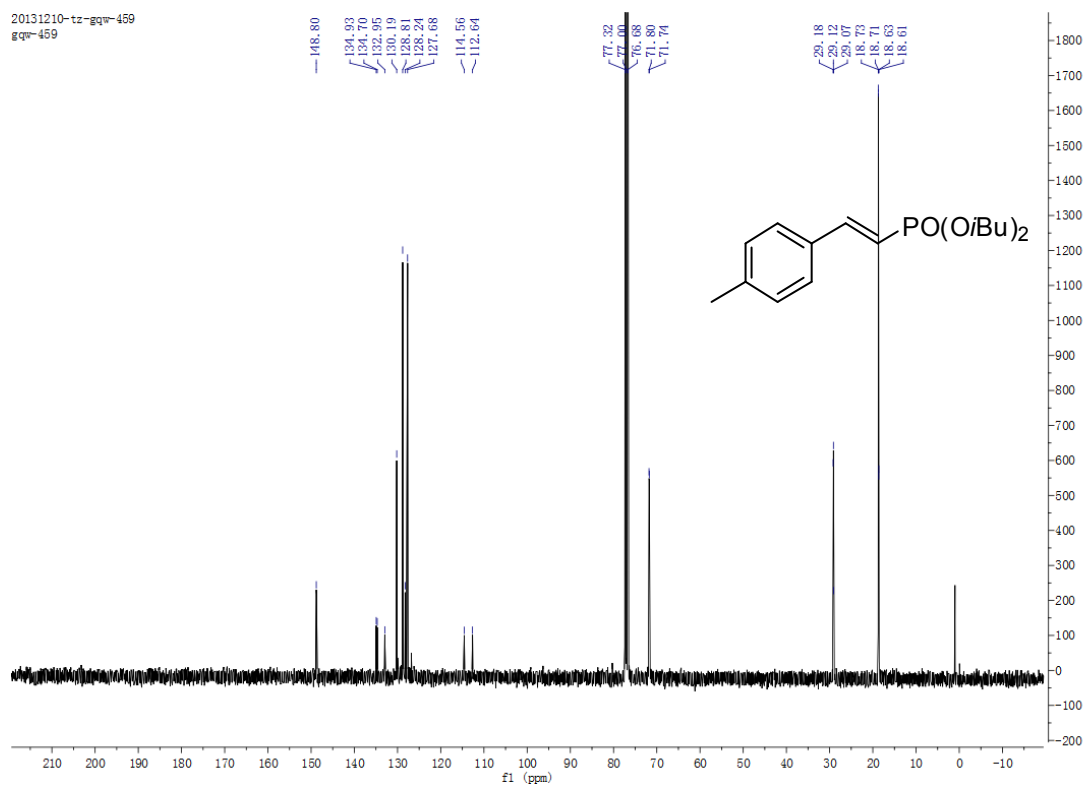
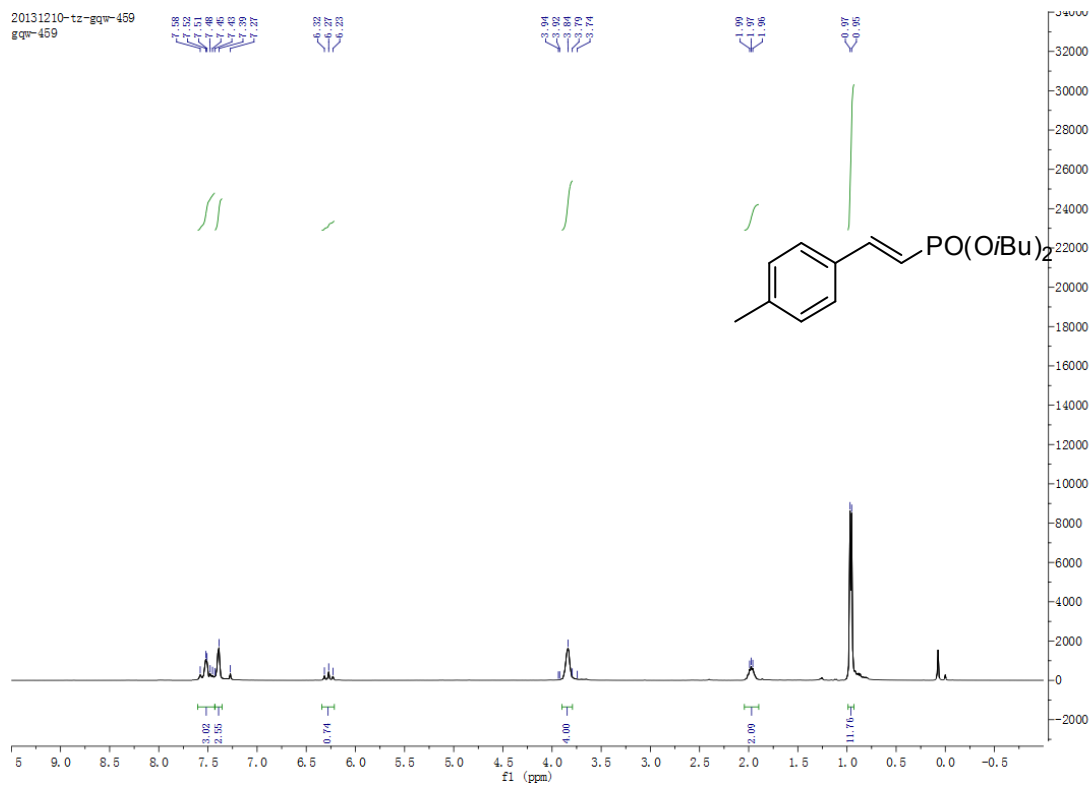


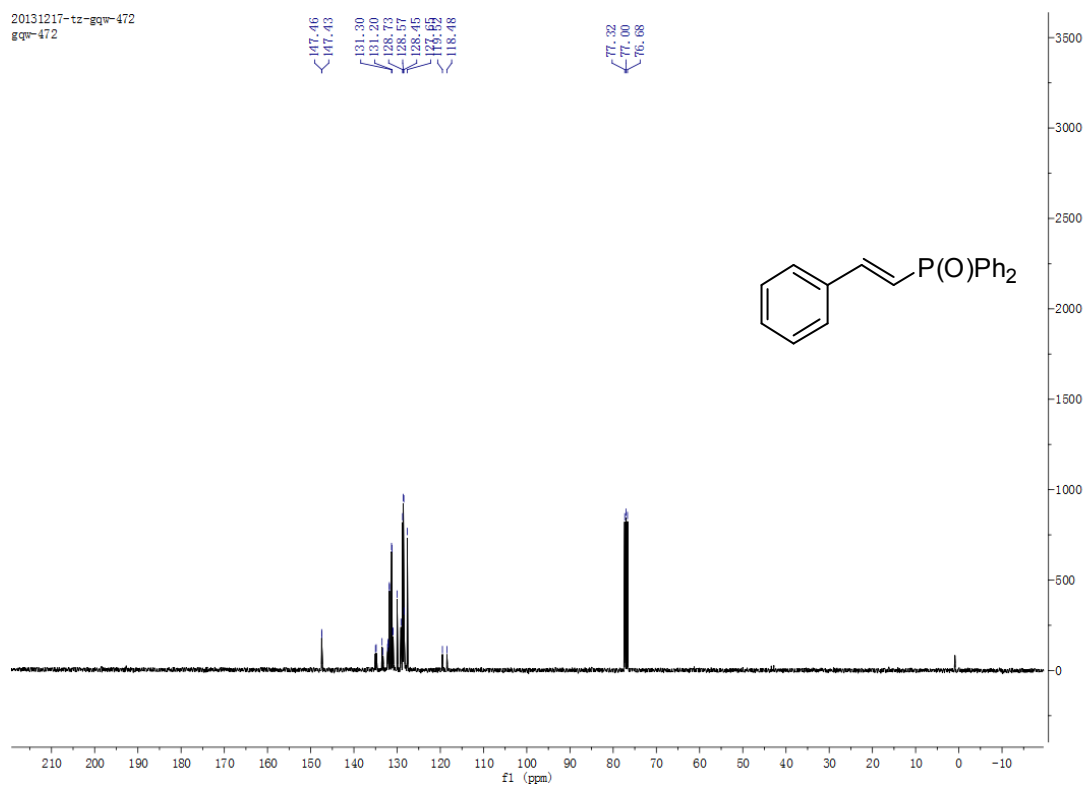
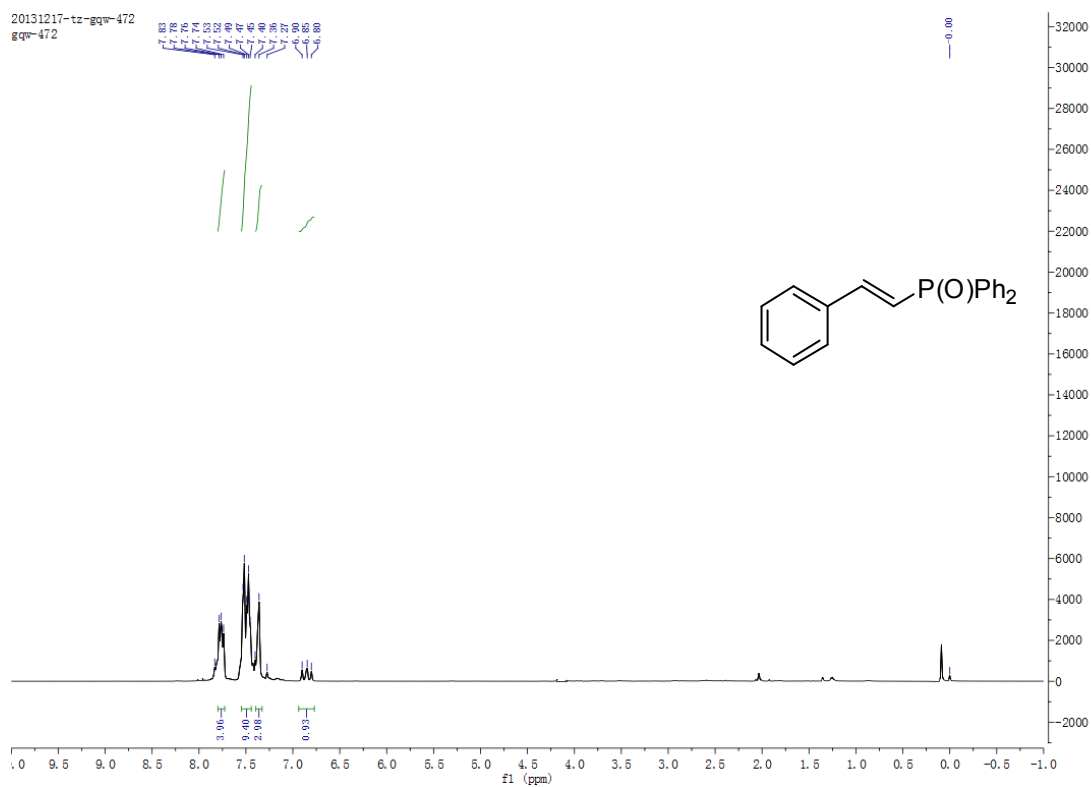
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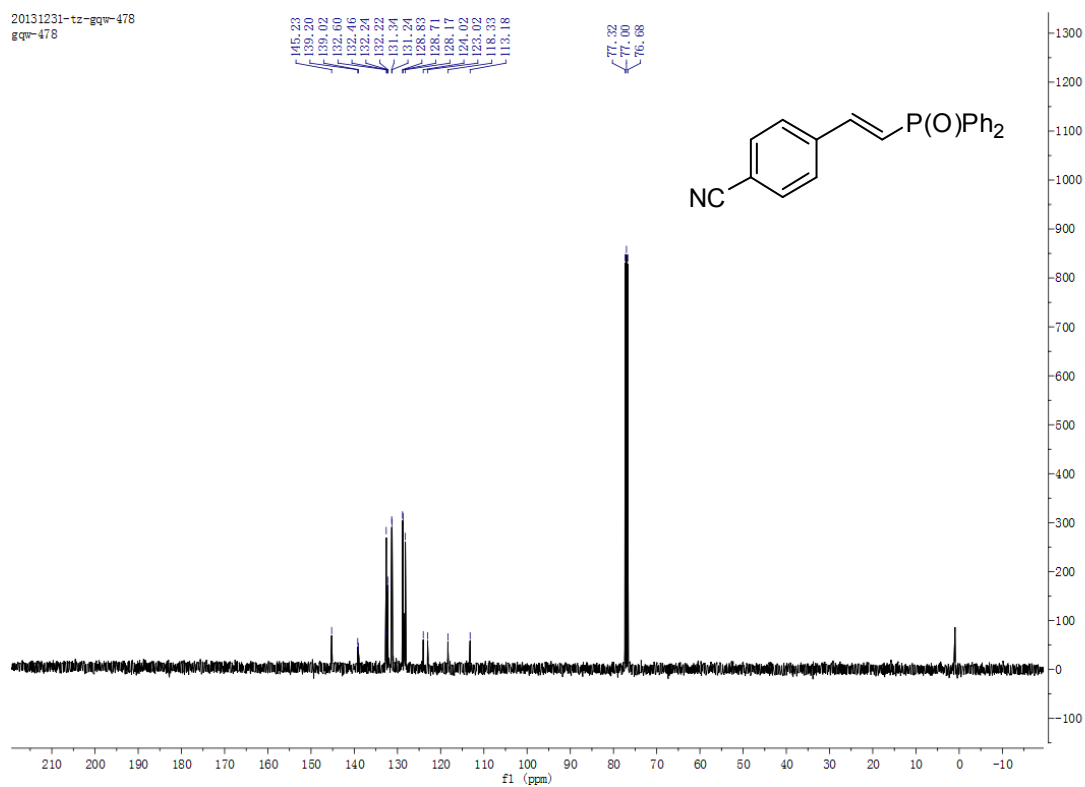
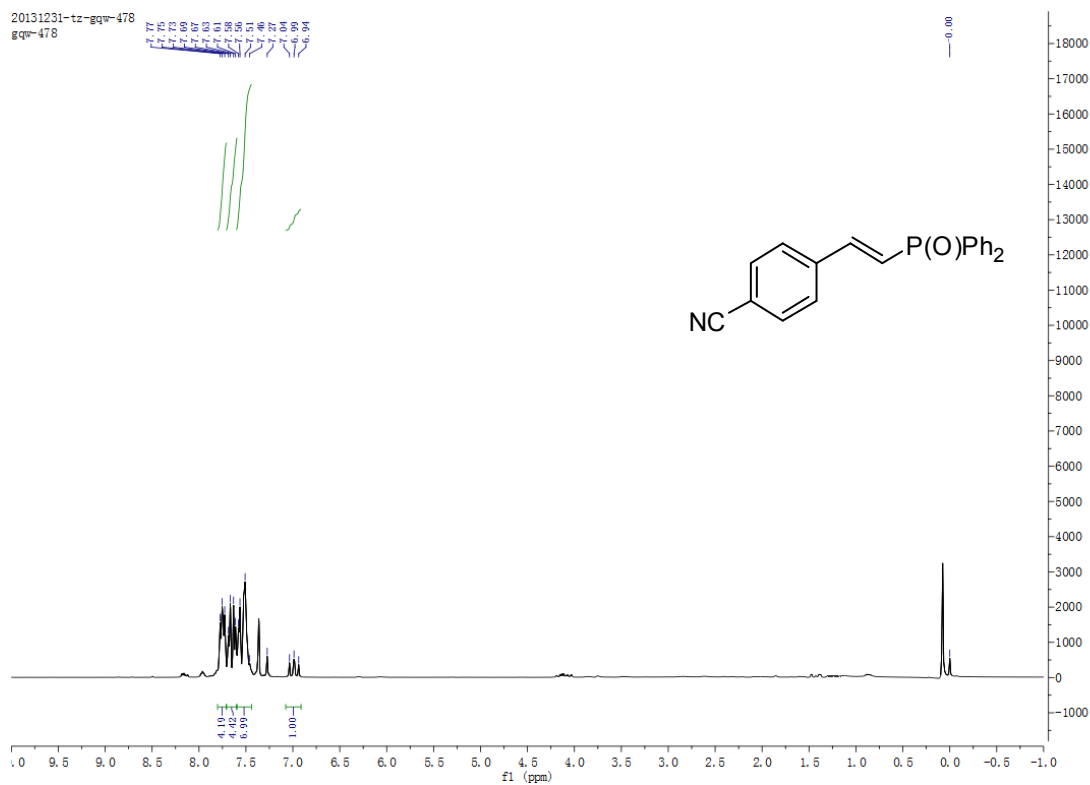


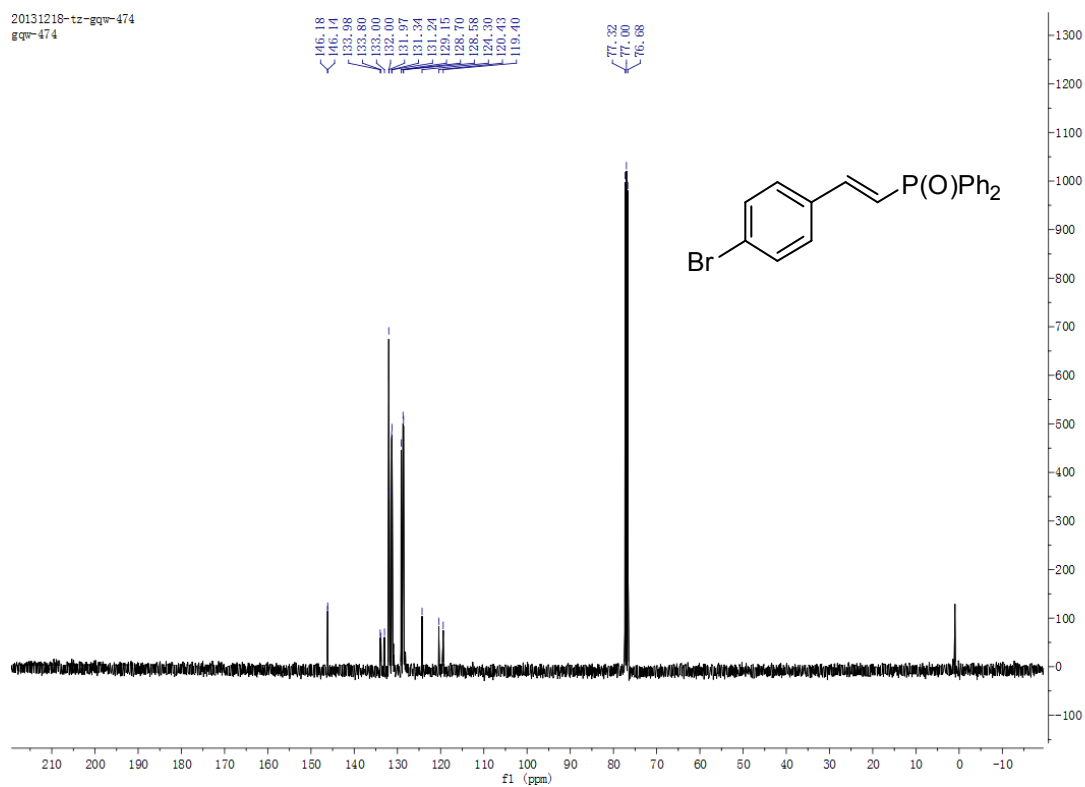
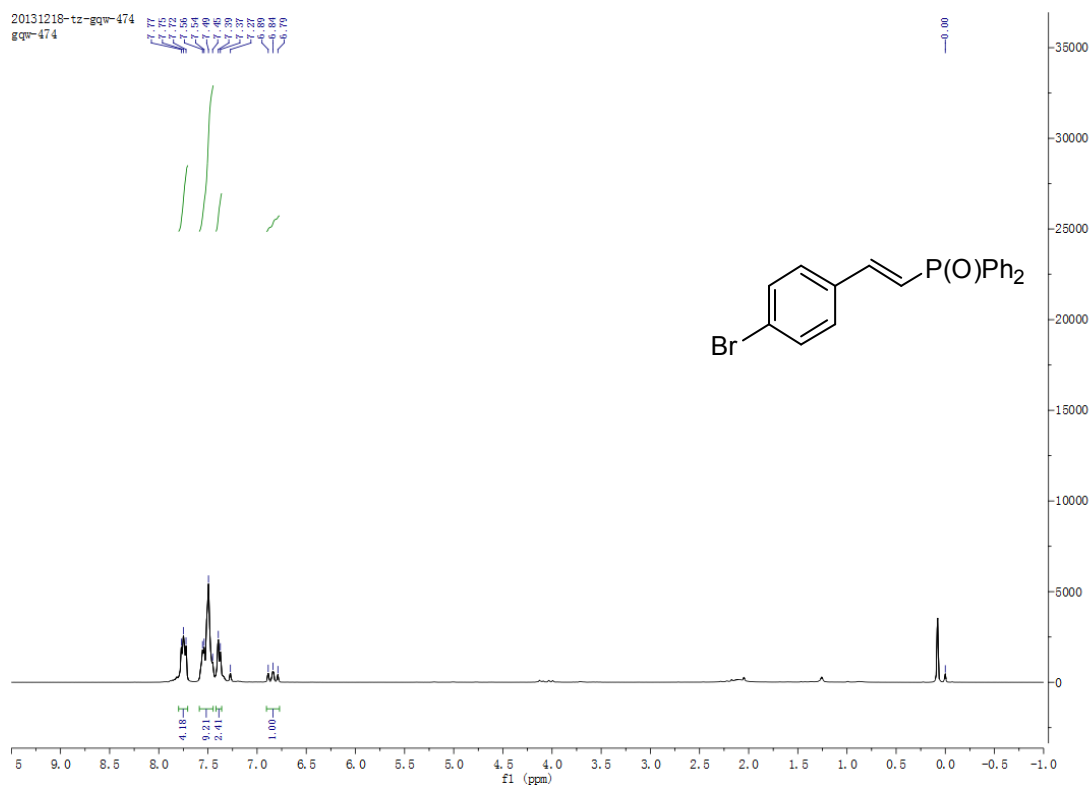


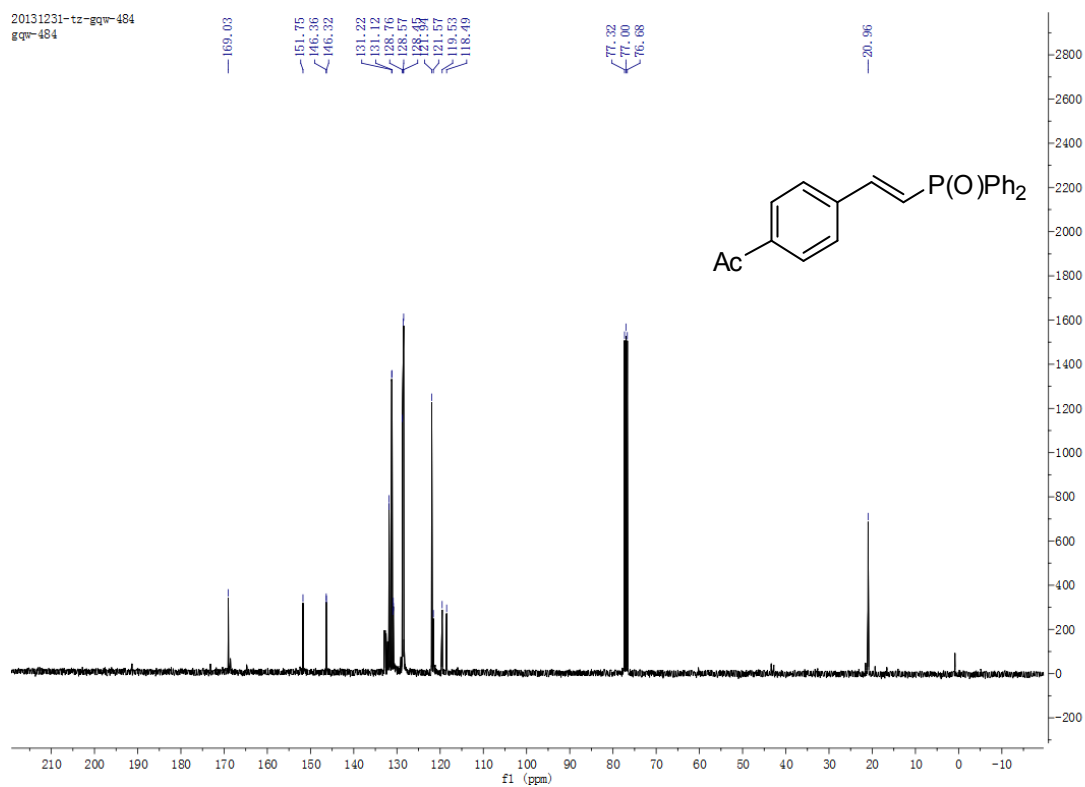
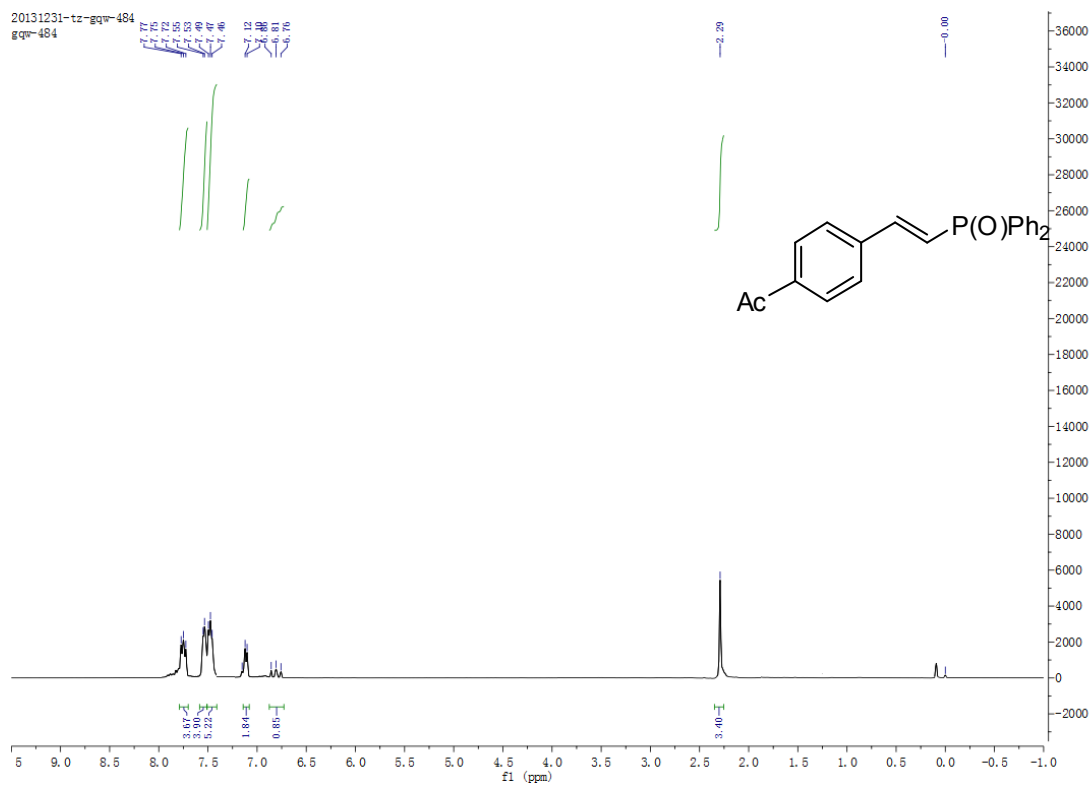


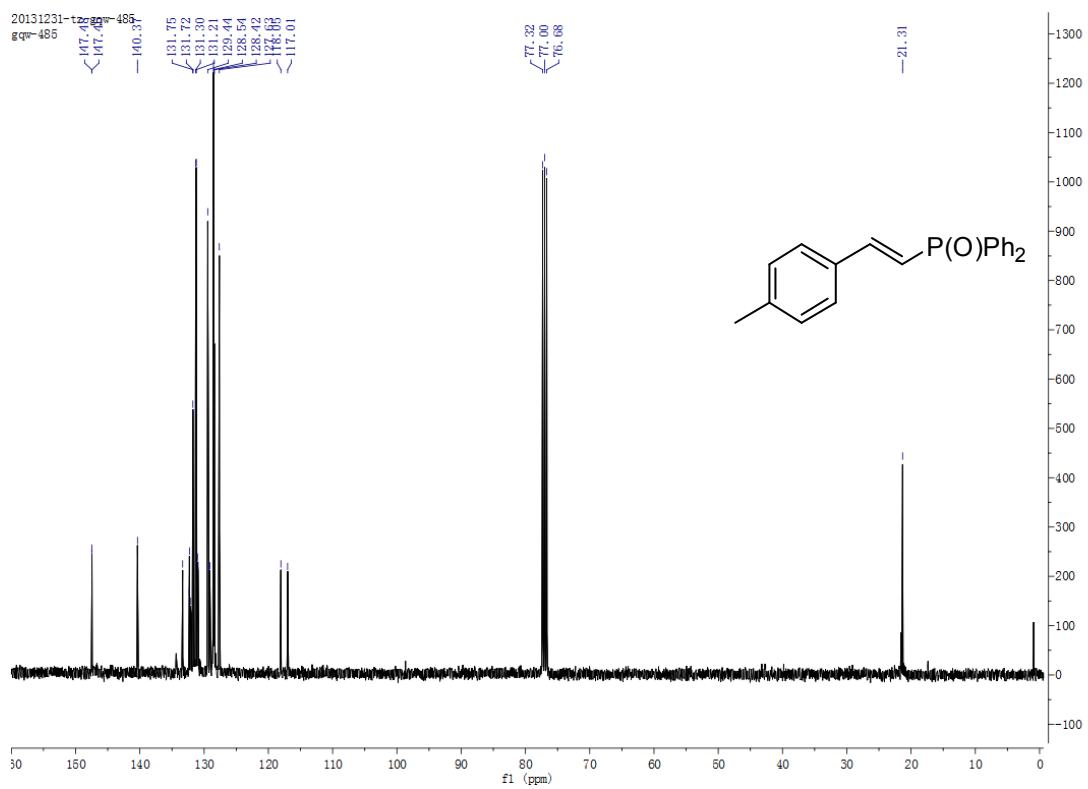
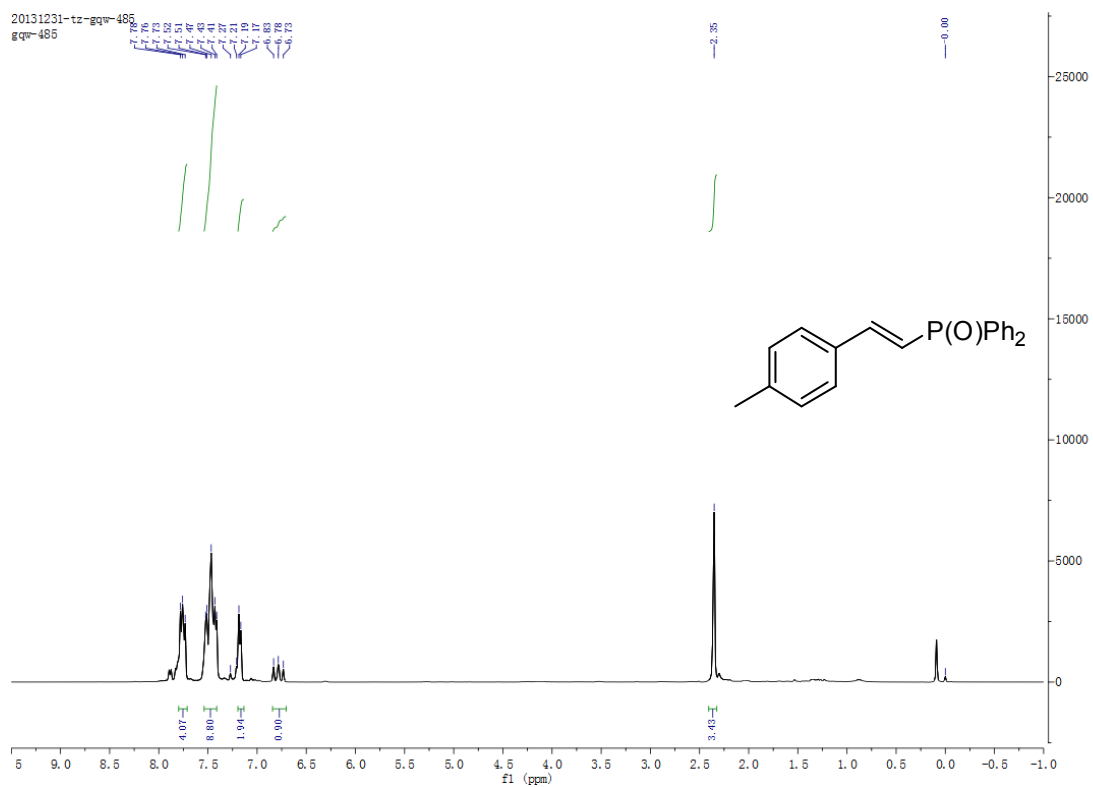


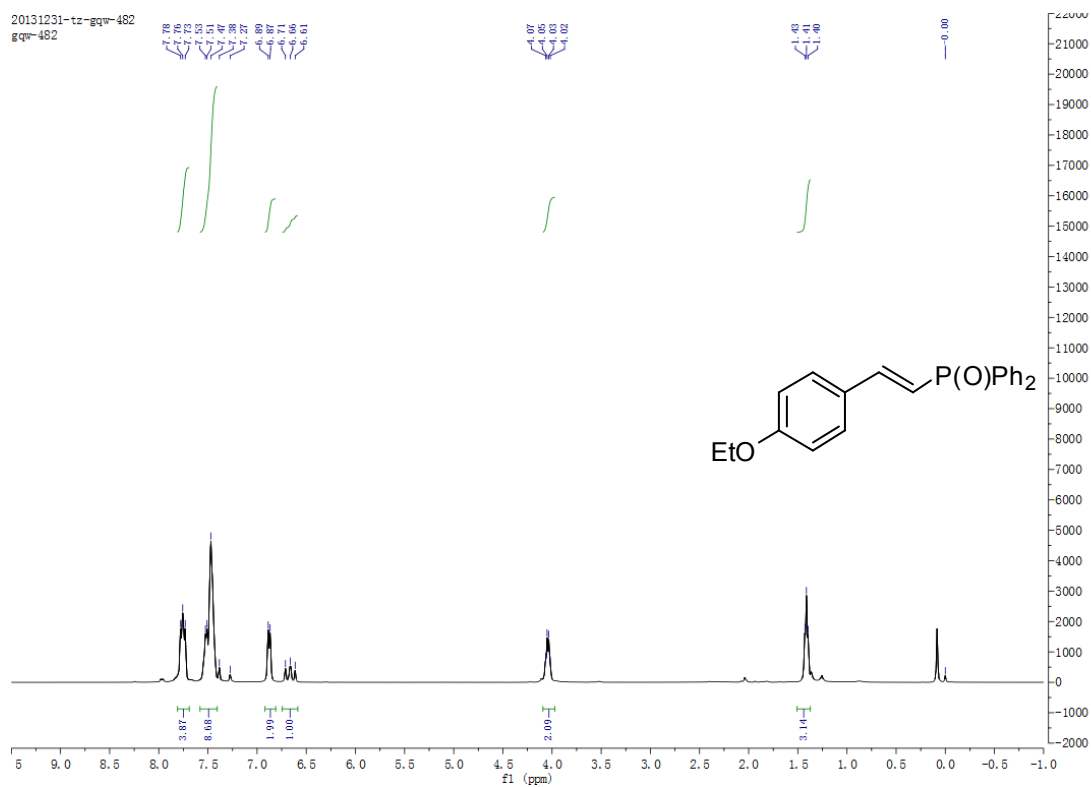


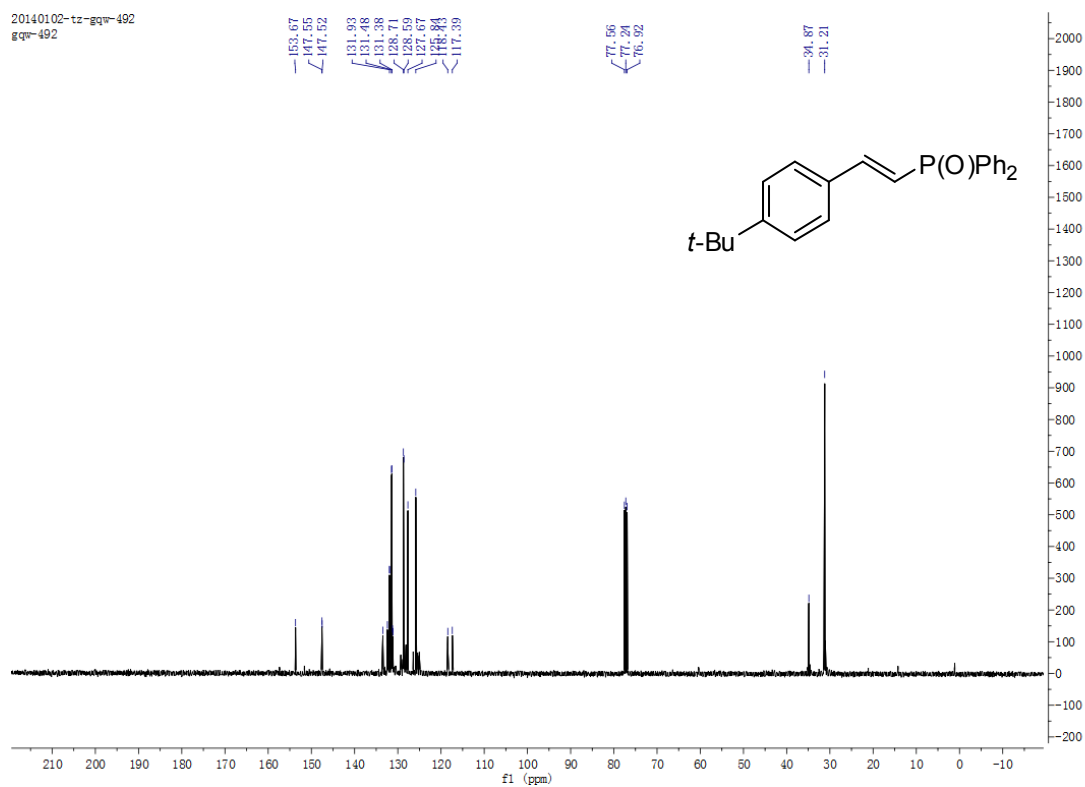
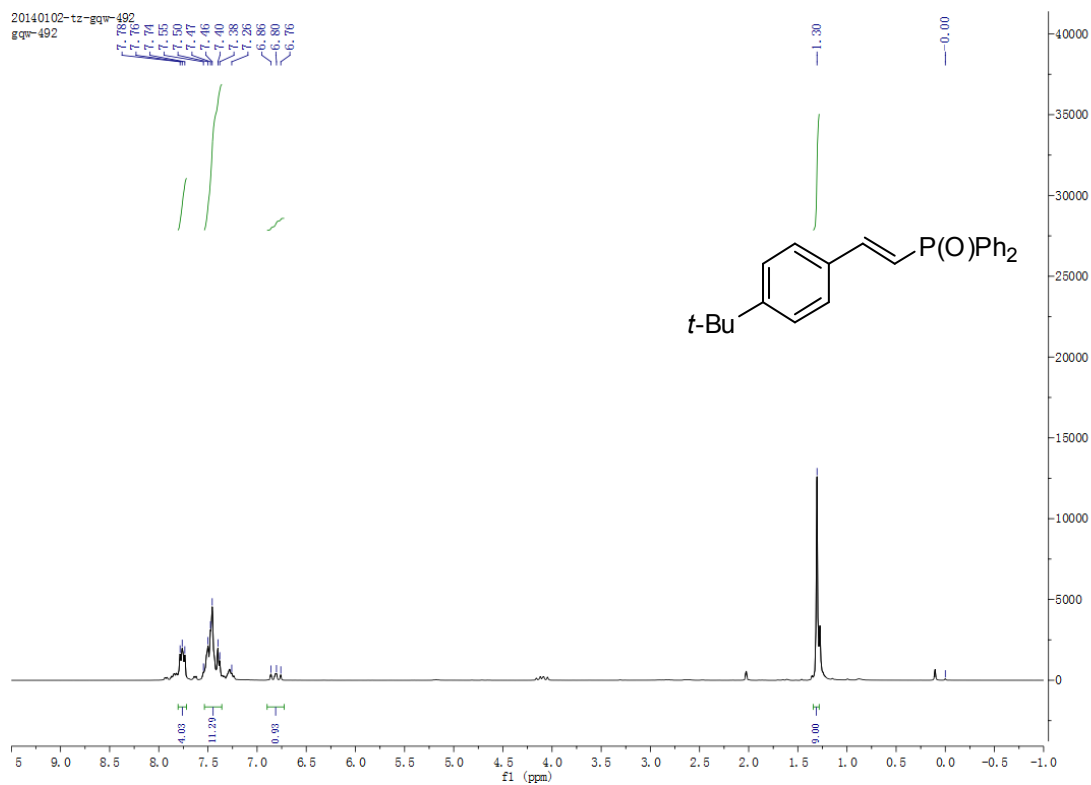


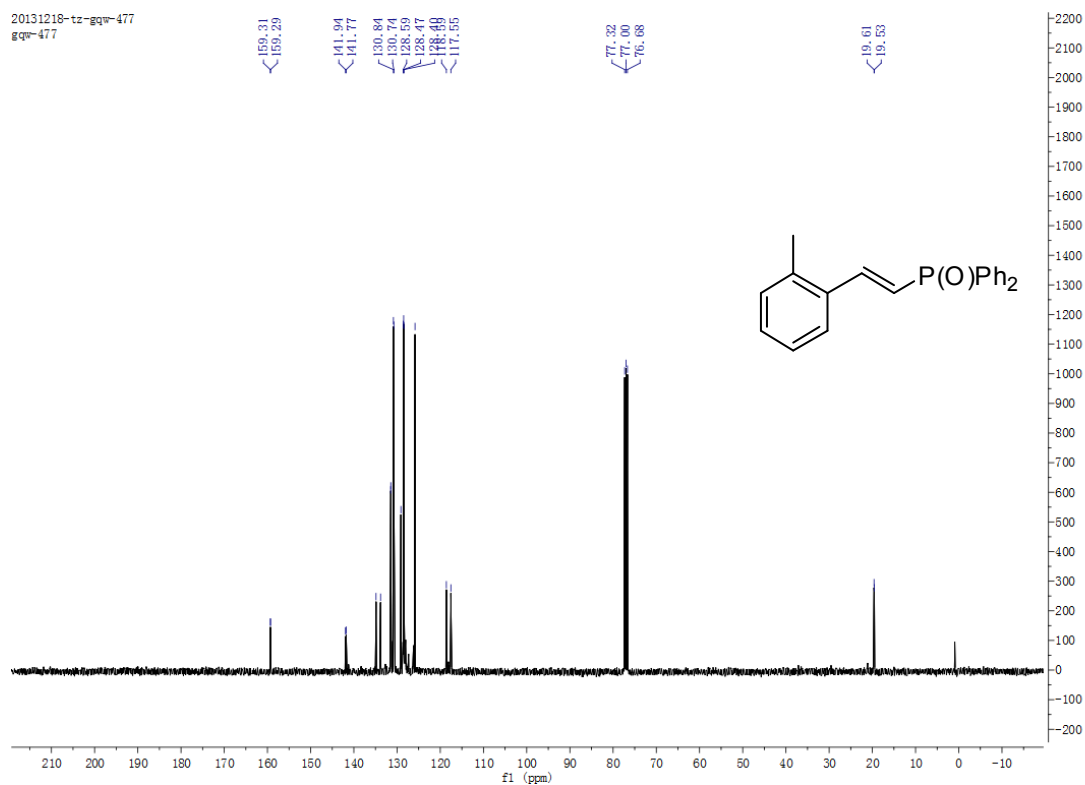
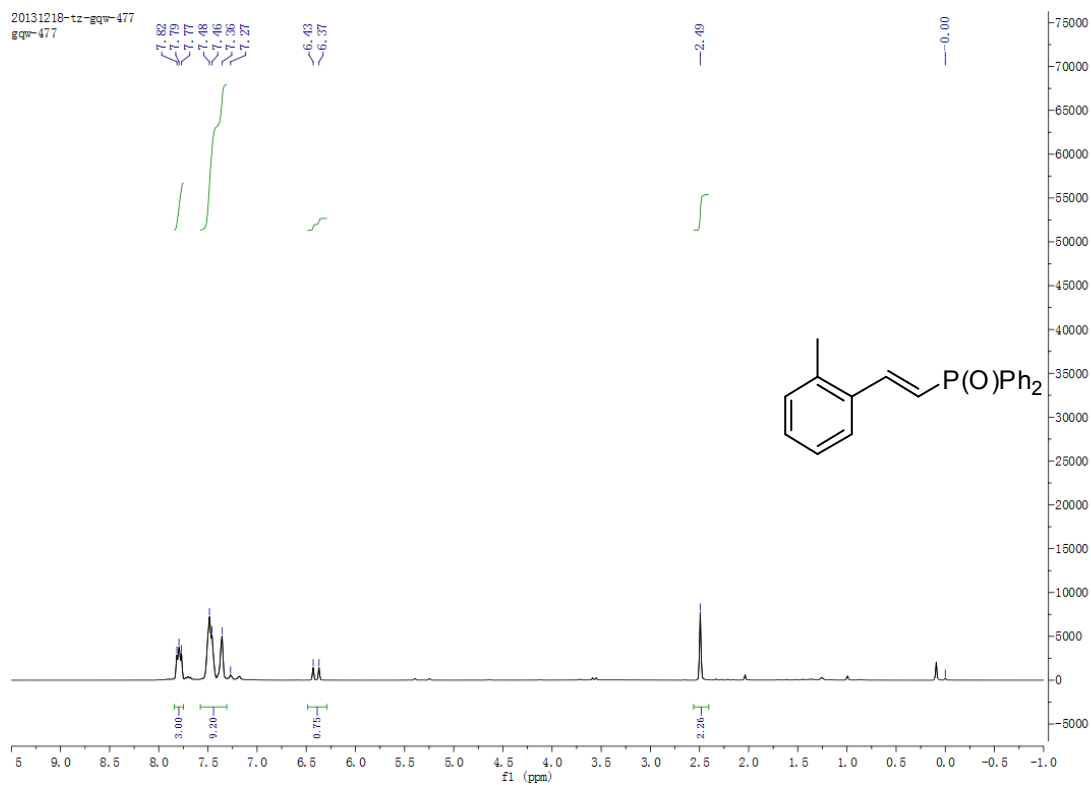




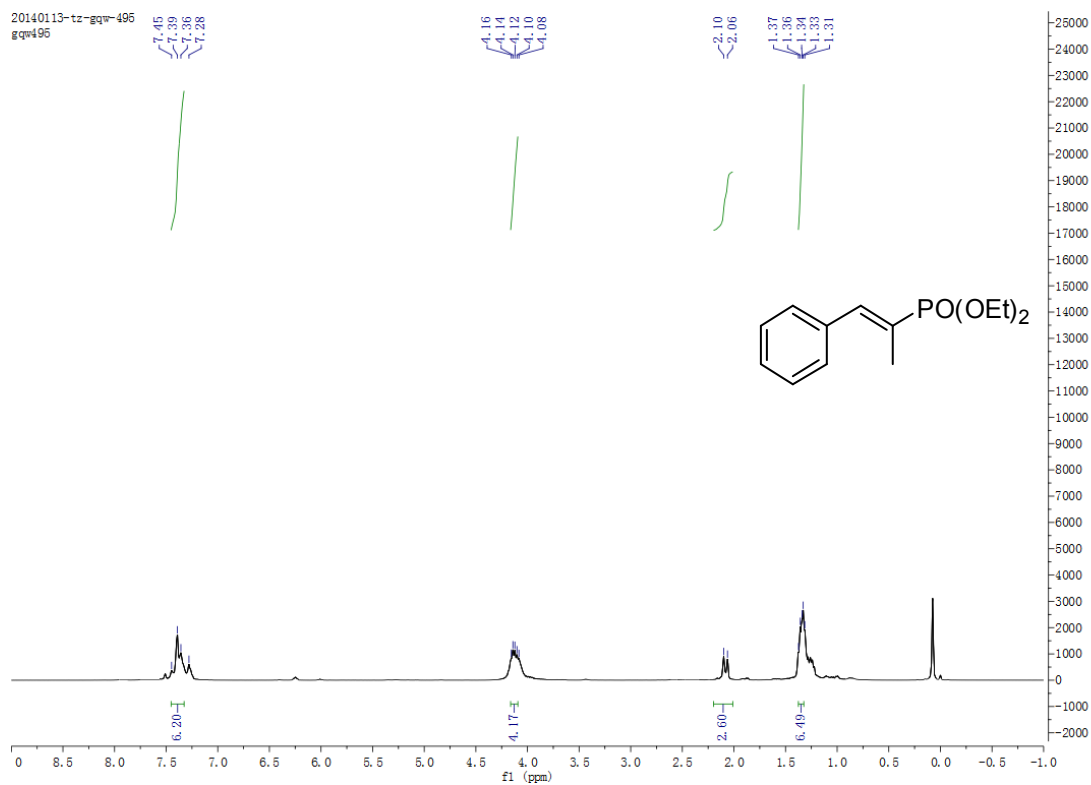




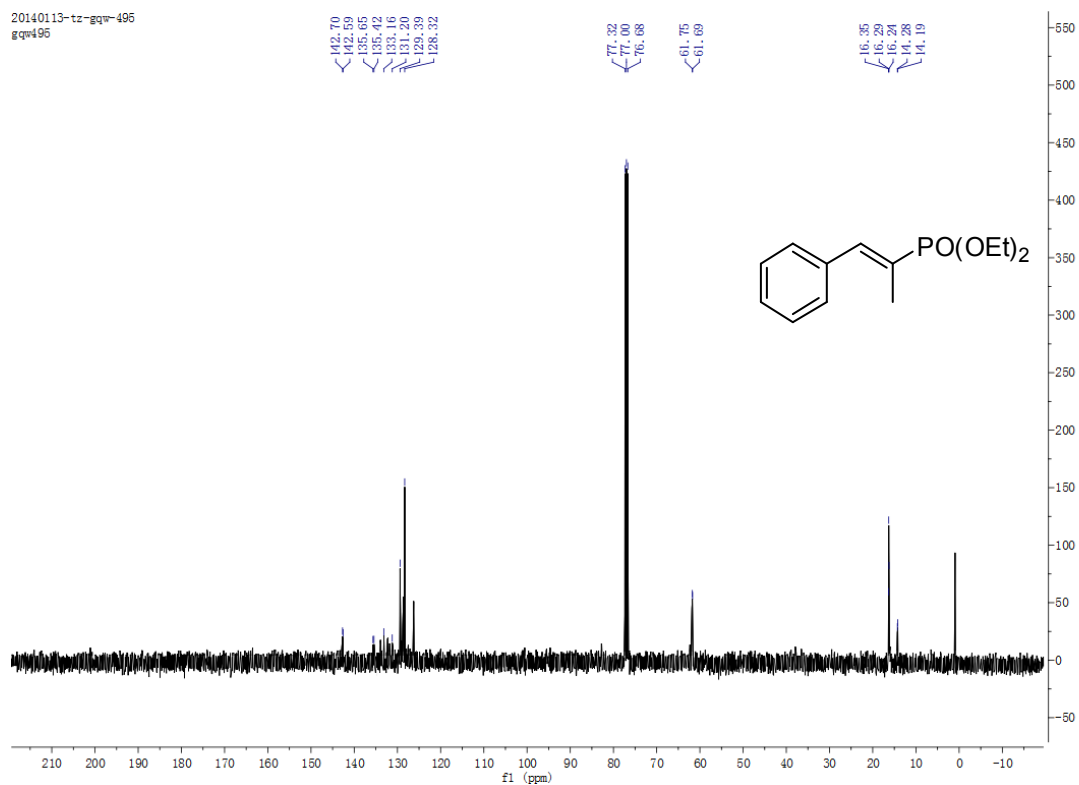


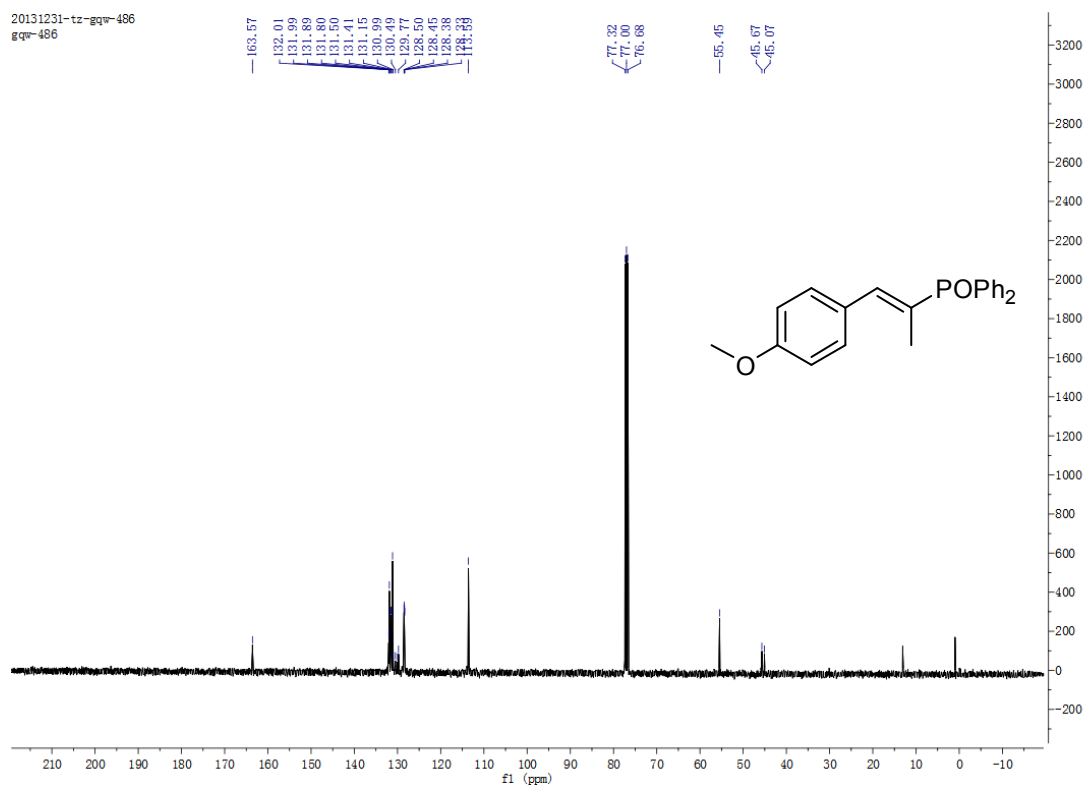
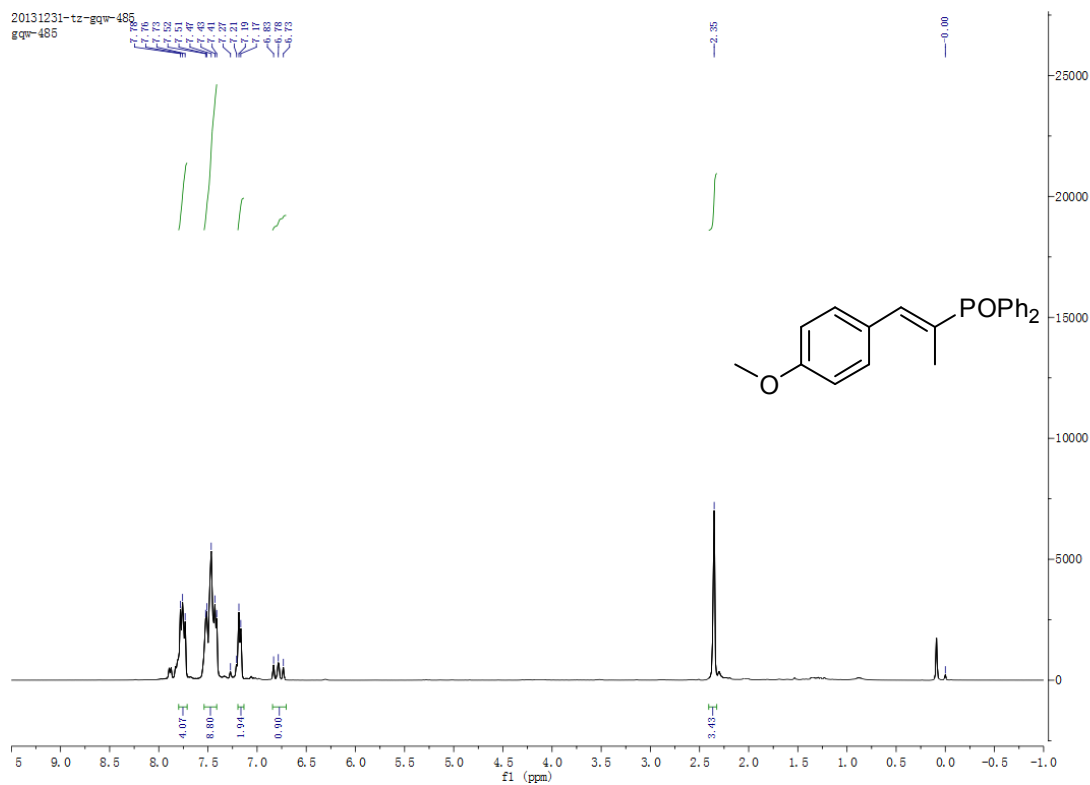


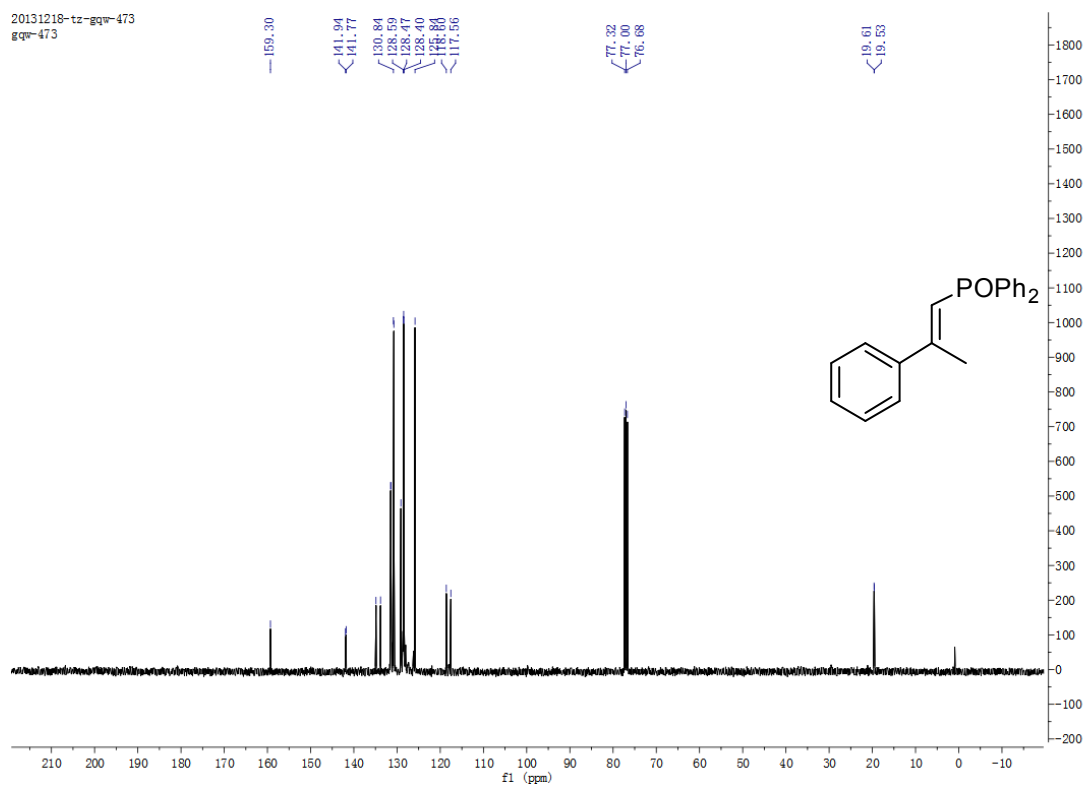
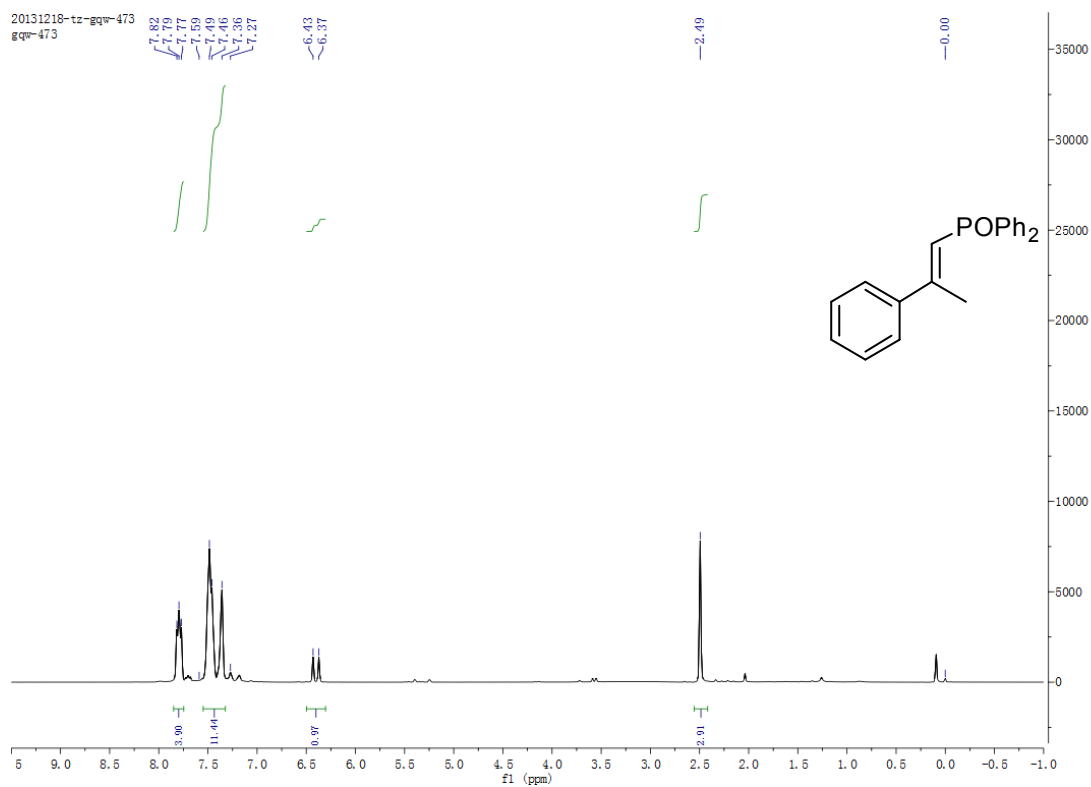
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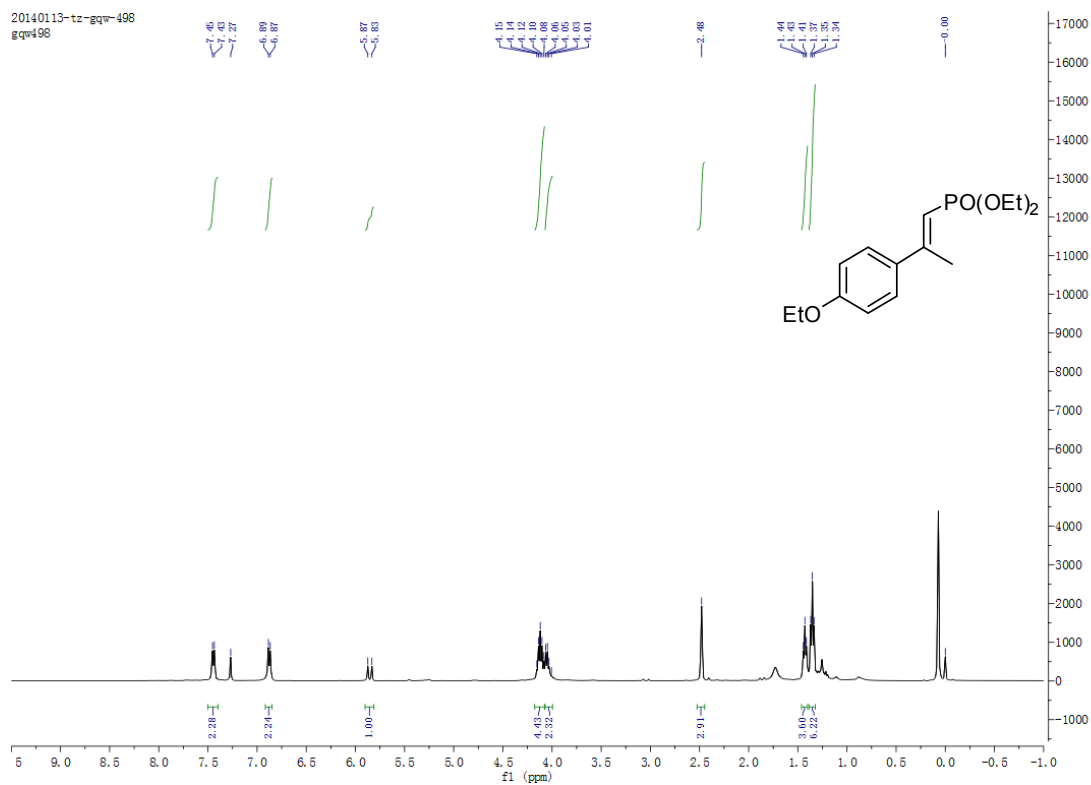
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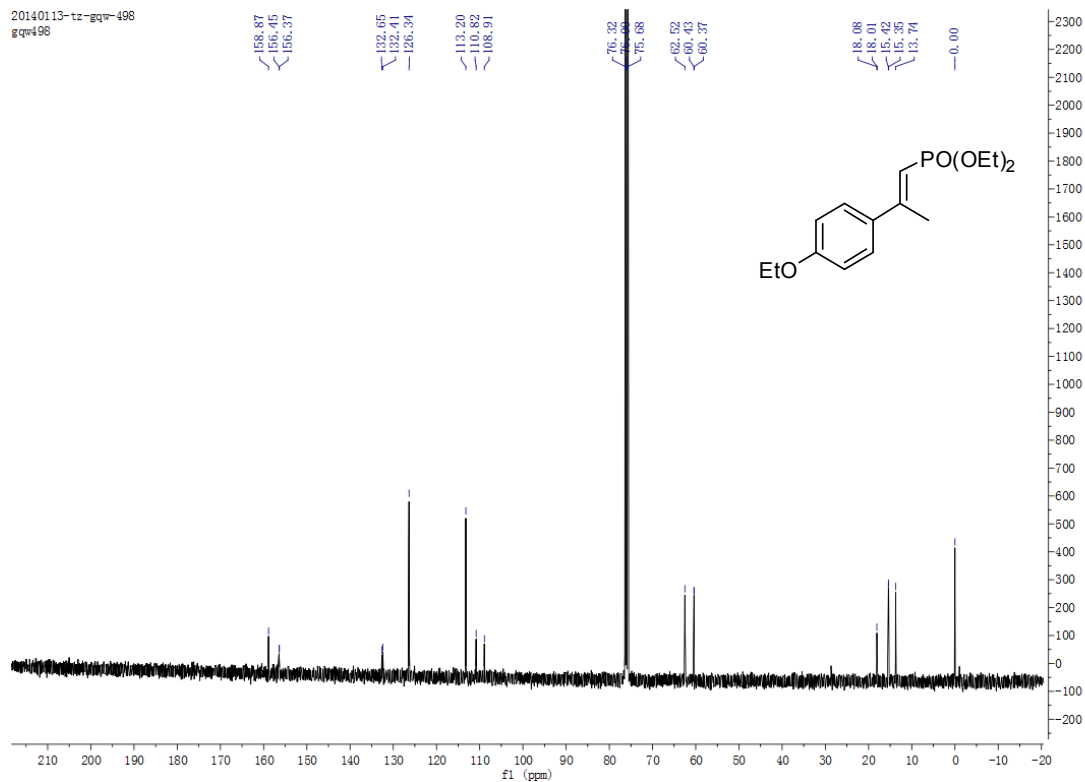


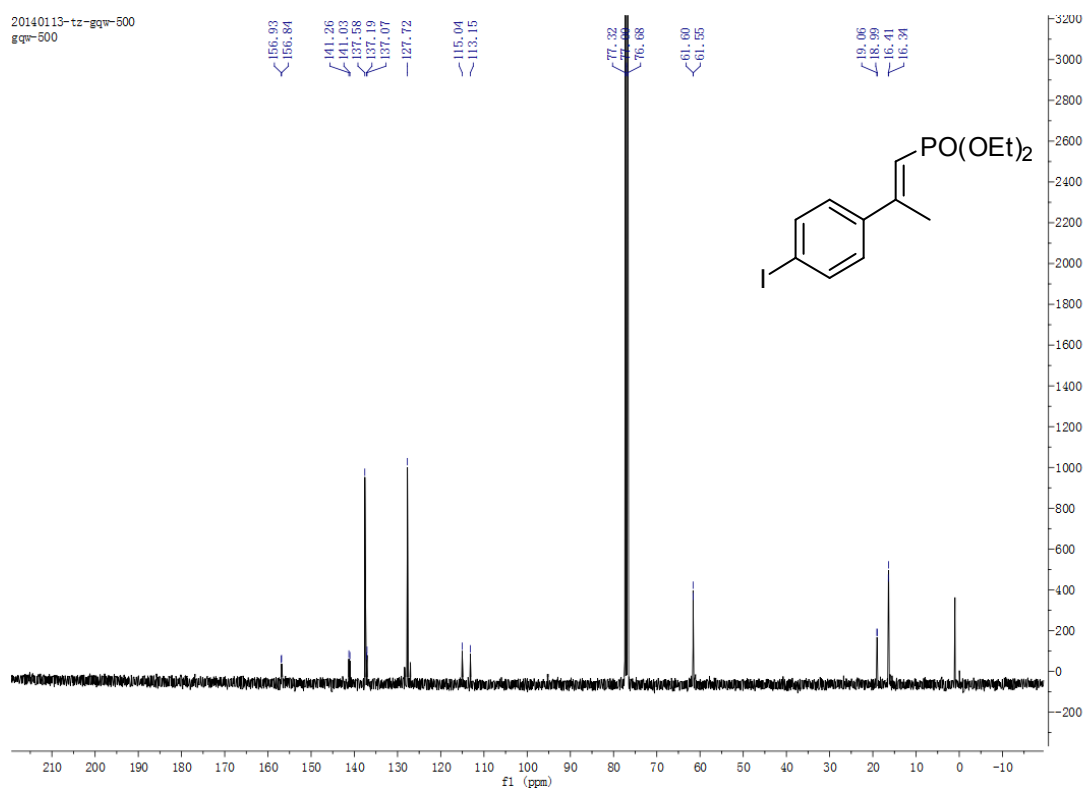
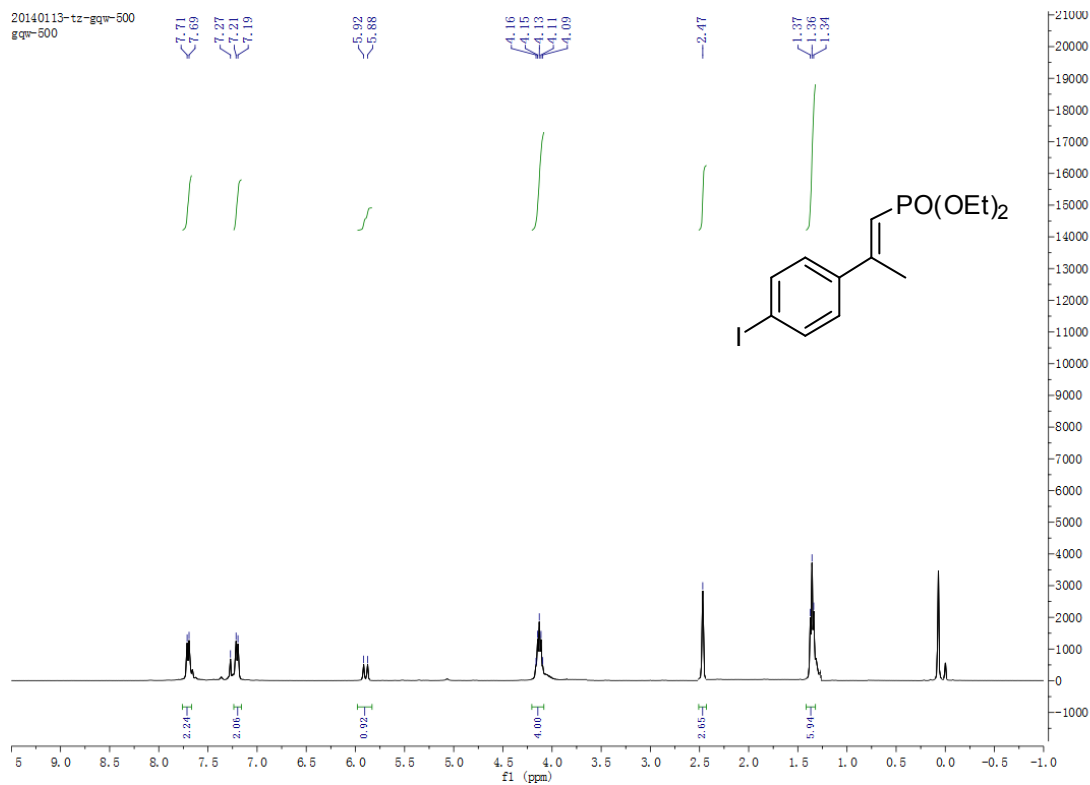


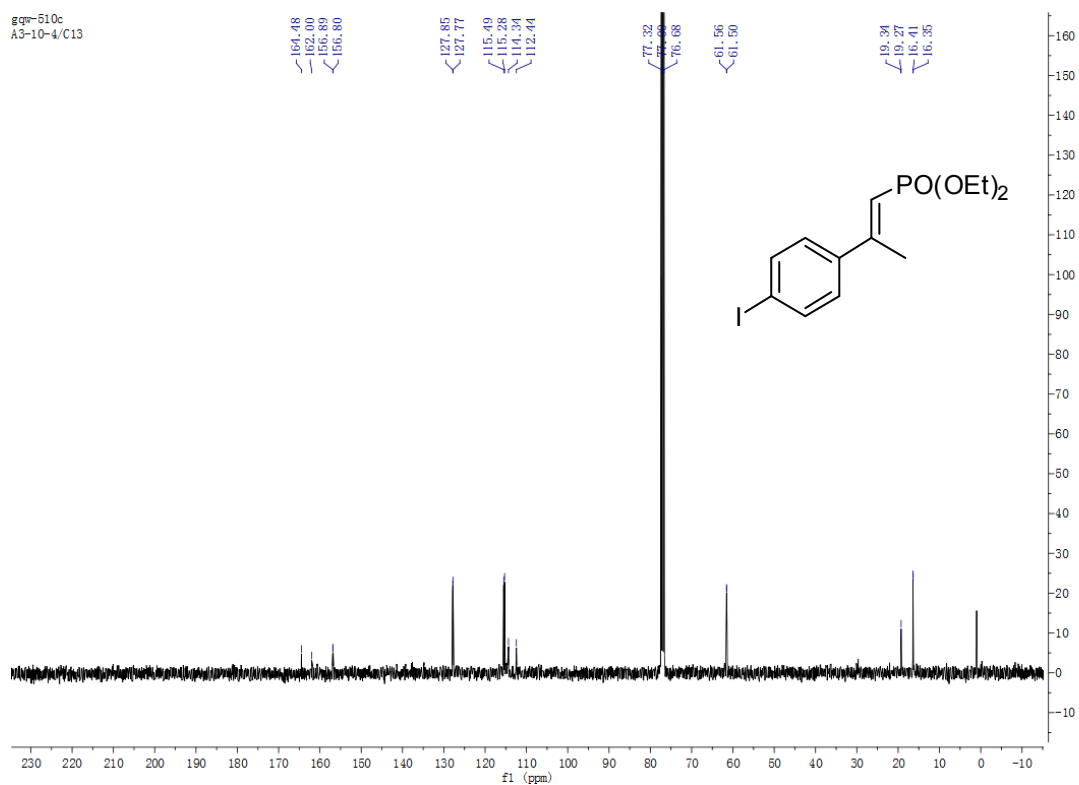
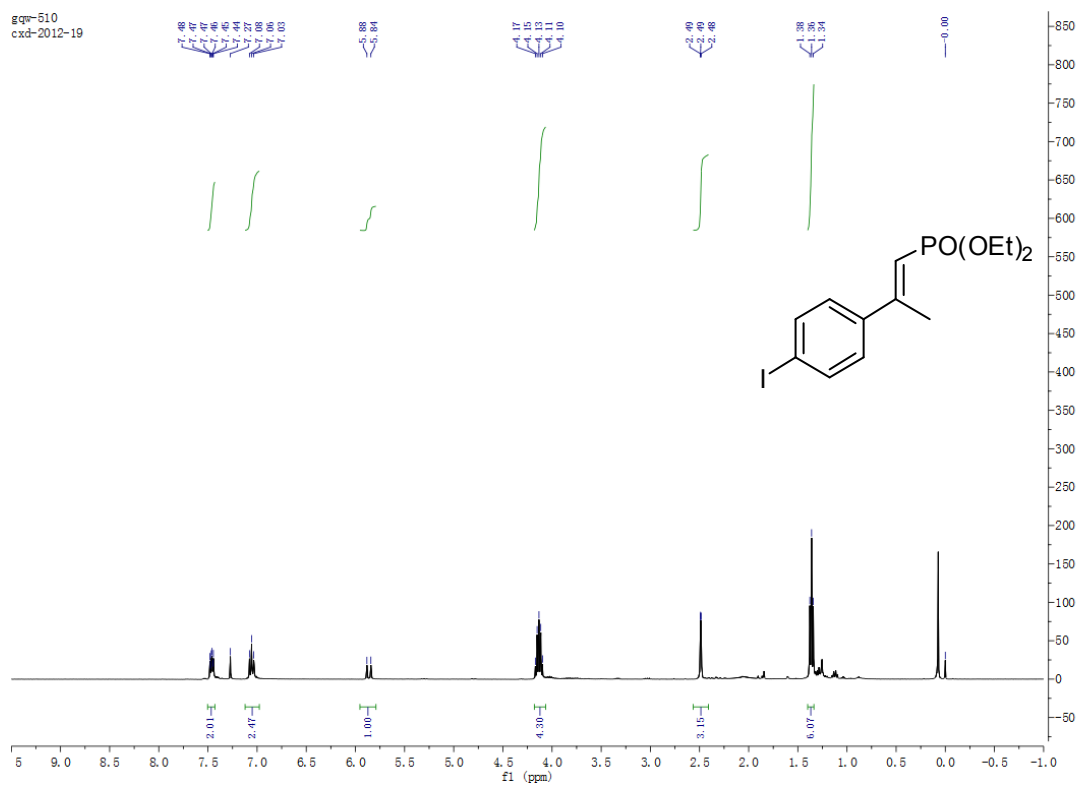
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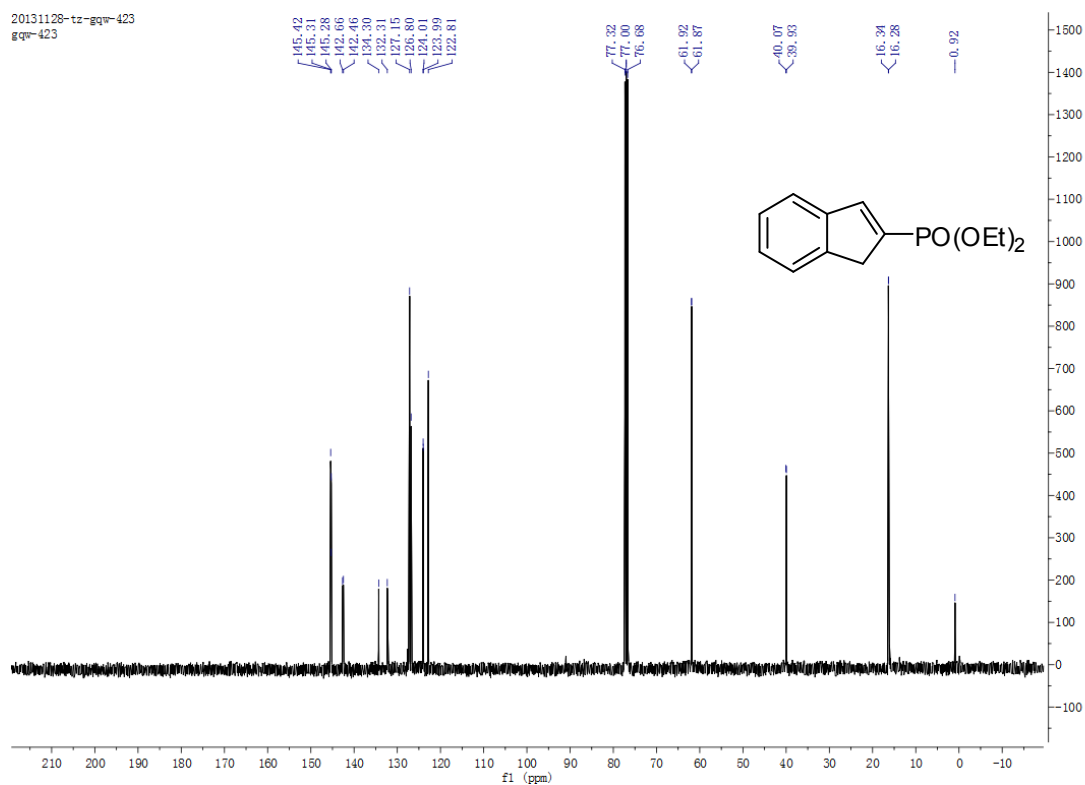
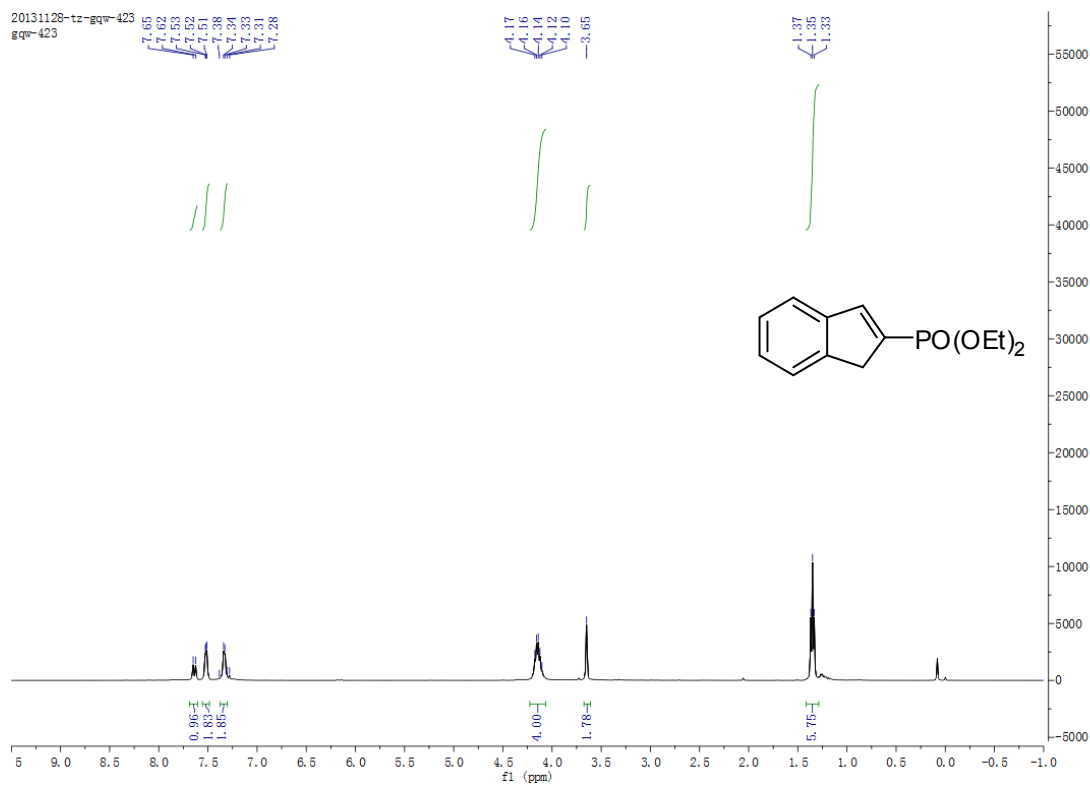


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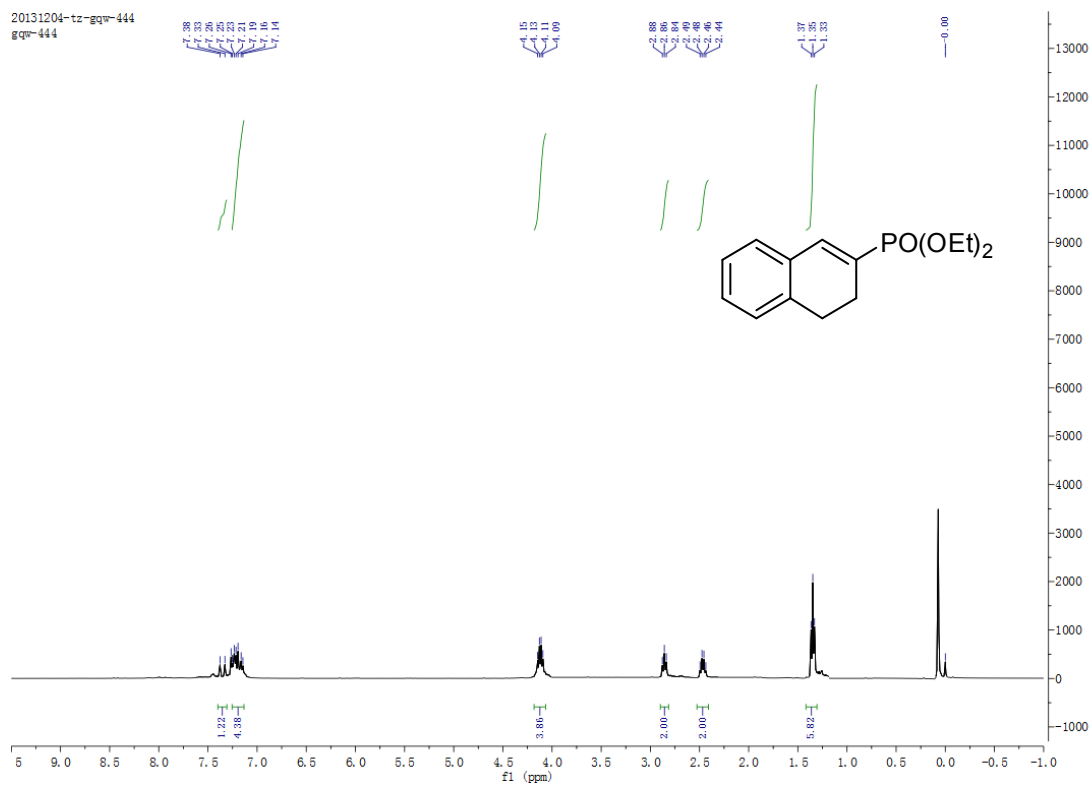








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