Supporting Information

Substituents-dependent [4+2] or [2+2] cycloadditions of phenylallenyl phosphine oxides with arynes

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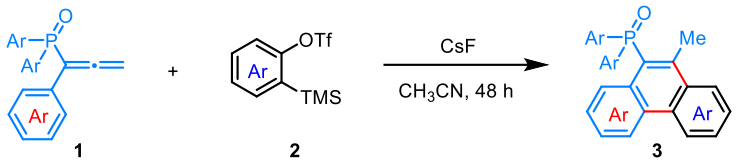
Table of Contents

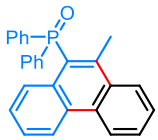
1. General methods

NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz (Bruker Avance). ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). ^{19}F NMR spectra were recorded at 375 MHz (Bruker Avance). ^{31}P NMR spectra were recorded at 162 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. IR spectra were recorded on a Thermo Fisher Nicolet Avatar 360 FTIR spectrometer on a KBr beam splitter. All the solvents were used directly without any purification.

2. Experimental data for the formation of 3

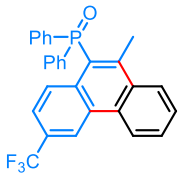


General procedure: To a 5.0 mL vial were successively added allenylphosphine oxides **1** (0.30 mmol), CsF (91.1 mg, 0.60 mmol) and 1.0 mL of CH_3CN. And then, aryne precursors **2** (0.60 mmol) were added by syringe. The resulting mixture was stirred at 25 or 80 °C for 48 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **3**. Compounds **3i**, **3i'**, **3j**, **3j'**, **3k**, **3k'**, **3l**, **3l'**, **3m** and **3s-3u** were obtained at 80 °C. Other products were obtained at 25 °C. Notably, when 3-methoxy substituted benzyne precursor was used, the desired [4+2] cycloadduct was not obtained at all. Instead, benzo[*b*][1,4]oxaphosphinin-4-ium **4a** was produced in 58% yield. The use of 4,5-difluoro-substituted benzyne afforded both the [4+2] cycloadduct **3r** and benzo[*b*][1,4]oxaphosphonin-4-ium **4b** in 22% and 23% yields, respectively.



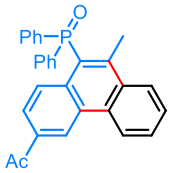
(10-Methylphenanthren-9-yl)diphenylphosphine oxide (**3a**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 66.3 mg, 56% yield; reaction time = 48 h; mp 200.5-200.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.78-7.63 (m, 6H), 7.52-7.46 (m, 3H), 7.42-7.38 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 1H), 2.61 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2 (d, *J* = 8.0 Hz, 1C), 136.8, 135.8, 131.9 (d, *J* = 2.0 Hz, 1C), 131.8, 131.7, 131.6, 131.2 (d, *J* = 3.0 Hz, 1C), 131.1 (d, *J* = 10.0 Hz, 1C), 129.7 (d, *J* = 9.0 Hz, 1C), 128.7, 128.6, 128.6, 127.1, 126.0 (d, *J* = 25.0 Hz, 1C), 125.2, 124.8, 122.8 (d, *J* = 29.0 Hz, 1C), 21.4 (d, *J* = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.99. IR (KBr) ν 1436, 1170, 1109, 750 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{22}OP$ $[M+H]^+$: 393.1408, found: 393.1412.



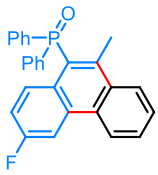
(10-Methyl-6-(trifluoromethyl)phenanthren-9-yl)diphenylphosphine oxide (**3b**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1 to 3:1); 54.7 mg, 40% yield; reaction time = 48 h; mp 196.9-197.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.75 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 12.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.84-7.80 (m, 1H), 7.74-7.69 (m, 5H), 7.53-7.41 (m, 7H), 2.59 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3 (d, *J* = 8.0 Hz, 1C), 136.0, 135.0, 133.8 (d, *J* = 10.0 Hz, 1C), 131.8 (d, *J* = 12.0 Hz, 1C), 131.6 (d, *J* = 3.0 Hz, 1C), 131.4 (d, *J* = 2.0 Hz, 1C), 131.0 (d, *J* = 10.0 Hz, 1C), 129.4 (d, *J* = 9.0 Hz, 1C), 129.2 (d, *J* = 5.0 Hz, 1C), 128.8 (d, *J* = 12.0 Hz, 1C), 128.0, 127.6 (d, *J* = 32.0 Hz, 1C), 125.5 (d, *J* = 10.0 Hz, 1C), 125.4, 124.5, 123.0, 121.8 (q, *J* = 3.0 Hz, 1C), 120.0 (q, *J* = 3.0 Hz, 1C), 21.7 (d, *J* = 8.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.14; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.26. IR (KBr) ν 1621, 1480, 1361, 1114, 758 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{20}ONaPF_3$ $[M+Na]^+$: 483.1102, found: 483.1106.



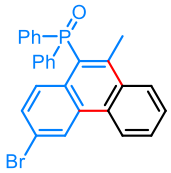
1-(10-(Diphenylphosphoryl)-9-methylphenanthren-3-yl)ethan-1-one (**3c**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 56.7 mg, 44% yield; reaction time = 48 h; mp 255.9-256.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.83 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.76 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.70 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 5H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.44-7.39 (m, 4H), 2.69 (s, 3H), 2.61 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 146.0, 136.4, 135.3, 135.0, 133.9, 132.1, 132.0, 131.6 (d, *J* = 3.0 Hz, 1C), 131.0 (d, *J* = 10.0 Hz, 1C), 129.5 (d, *J* = 9.0 Hz, 1C), 129.3, 129.0, 128.8, 127.8, 125.5, 124.8, 123.5, 123.2, 26.9, 21.8 (d, *J* = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.79. IR (KBr) ν 1679, 1250, 1188, 759 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{23}O_2NaP$ $[M+Na]^+$: 457.1333, found: 457.1335.



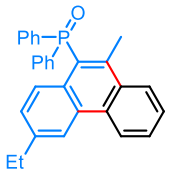
(6-Fluoro-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3d**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 71.0 mg, 58% yield; reaction time = 48 h; mp 183.9-184.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.0 Hz, 1H), 8.54 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.78-7.66 (m, 6H), 7.51-7.47 (m, 2H), 7.44-7.40 (m, 4H), 7.05-7.00 (m, 1H), 2.53 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 159.6, 141.8 (d, *J* = 6.0 Hz, 1C), 136.4, 135.4, 131.8 (d, *J* = 12.0 Hz, 1C), 131.4 (d, *J* = 3.0 Hz, 1C), 131.0 (d, *J* = 10.0 Hz, 1C), 130.9 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1C), 128.7 (d, *J* = 12.0 Hz, 1C), 128.5 (dd, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1C), 127.7, 125.4, 125.3, 124.4, 123.1, 114.8 (d, *J* = 23.0 Hz, 1C), 107.7 (d, *J* = 23.0 Hz, 1C), 21.4 (d, *J* = 8.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.07; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.54. IR (KBr) ν 1614, 1493, 1437, 1187, 754 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}ONaPF$ $[M+Na]^+$: 433.1133, found: 433.1136.



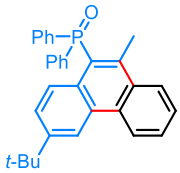
(6-Bromo-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3e**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 66.5 mg, 47% yield; reaction time = 48 h; mp 232.0-232.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 12.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.72-7.65 (m, 5H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.43-7.40 (m, 4H), 7.34 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3 (d, *J* = 8.0 Hz, 1C), 136.3, 135.3, 131.8 (d, *J* = 12.0 Hz, 1C), 131.5 (q, *J* = 2.0 Hz, 1C), 131.1, 131.0, 130.7 (d, *J* = 2.0 Hz, 1C), 130.4 (d, *J* = 10.0 Hz, 1C), 130.1 (d, *J* = 6.0 Hz, 1C), 128.9, 128.9, 128.7, 127.8, 125.3 (d, *J* = 13.0 Hz, 1C), 124.5, 123.0, 120.6, 21.5 (d, *J* = 7.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.09. IR (KBr) ν 1514, 1482, 1191, 1106, 759 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{21}OPBr$ $[M+H]^+$: 471.0513, found: 471.0517.



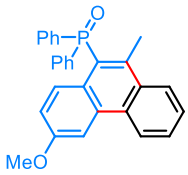
(6-Ethyl-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3f**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1 to 3:1); 69.9 mg, 56% yield; reaction time = 48 h; mp 167.5-167.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.0 Hz, 1H), 8.46 (s, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.77-7.69 (m, 5H), 7.66-7.62 (m, 1H), 7.50-7.46 (m, 2H), 7.43-7.38 (m, 4H), 7.12 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.81 (q, *J* = 8.0 Hz, 2H), 2.59 (d, *J* = 4.0 Hz, 3H), 1.31 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0 (d, *J* = 9.0 Hz, 1C), 141.9, 136.8, 135.8, 131.8 (d, *J* = 2.0 Hz, 1C), 131.7, 131.2 (d, *J* = 3.0 Hz, 1C), 131.1 (d, *J* = 10.0 Hz, 1C), 129.9 (dd, dd, J_1 = 10.0 Hz, J_2 = 8.0 Hz, 1C), 128.6 (d, *J* = 12.0 Hz, 1C), 128.5 (d, *J* = 6.0 Hz, 1C), 128.4, 126.9, 126.4, 125.2, 124.6, 122.9, 121.2, 29.0, 21.2 (d, *J* = 7.0 Hz, 1C), 15.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.48. IR (KBr) ν 1434, 1190, 1103, 756 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{26}OP$ $[M+H]^+$: 421.1721, found: 421.1726.



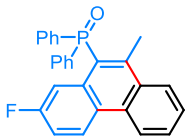
(6-(*tert*-Butyl)-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3g**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 91.8 mg, 68% yield; reaction time = 48 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.0 Hz, 1H), 8.65 (s, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.78-7.71 (m, 5H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.51-7.48 (m, 2H), 7.44-7.40 (m, 4H), 7.36 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.56 (d, *J* = 4.0 Hz, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 141.8 (d, *J* = 9.0 Hz, 1C), 136.6, 135.6, 132.1 (d, *J* = 2.0 Hz, 1C), 131.7 (d, *J* = 13.0 Hz, 1C), 131.3 (d, *J* = 3.0 Hz, 1C), 131.1 (d, *J* = 10.0 Hz, 1C), 129.7 (d, *J* = 10.0 Hz, 1C), 129.4 (d, *J* = 9.0 Hz, 1C), 128.6 (d, *J* = 12.0 Hz, 1C), 128.4, 128.2 (d, *J* = 5.0 Hz, 1C), 126.8, 125.2, 124.3, 122.8, 118.2, 34.9, 31.3, 21.3 (d, *J* = 7.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.02. IR (KBr) ν 1470, 1180, 1109, 754 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{29}ONaP$ $[M+Na]^+$: 471.1854, found: 471.1858.



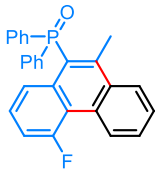
(6-Methoxy-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3h**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1 to 2:1); 79.8 mg, 63% yield; reaction time = 48 h; mp 200.5-200.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 12.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.76-7.69 (m, 5H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.49-7.45 (m, 2H), 7.42-7.38 (m, 4H), 6.90 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 3.94 (s, 3H), 2.54 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 140.2 (d, *J* = 8.0 Hz, 1C), 136.8, 135.8, 131.9 (d, *J* = 12.0 Hz, 1C), 131.4 (d, *J* = 8.0 Hz, 1C), 131.2 (d, *J* = 2.0 Hz, 1C), 131.1 (d, *J* = 10.0 Hz, 1C), 130.1 (d, *J* = 6.0 Hz, 1C), 128.7 (d, *J* = 13.0 Hz, 1C), 128.2, 127.1, 126.4 (d, *J* = 10.0 Hz, 1C), 125.3, 124.4, 123.0, 115.2, 104.4, 55.3, 21.1 (d, *J* = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.41. IR (KBr) ν 1614, 1439, 1233, 1110, 757 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{23}O_2NaP$ $[M+Na]^+$: 445.1333, found: 445.1338.



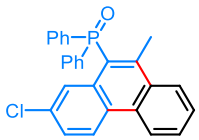
(7-Fluoro-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3i**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 4:1); 30.0 mg, 24% yield; reaction time = 48 h; mp 198.2-198.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (t, *J* = 8.0 Hz, 2H), 8.24 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.78-7.70 (m, 5H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.45-7.42 (m, 4H), 7.29-7.26 (m, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 159.3, 144.2 (d, *J* = 8.0 Hz, 1C), 136.1, 135.1, 133.5, 131.6, 131.1 (d, *J* = 9.0 Hz, 1C), 129.0, 128.8 (d, *J* = 12.0 Hz, 1C), 126.9, 126.4, 125.4, 124.7 (d, *J* = 9.0 Hz, 1C), 122.8, 115.0 (d, *J* = 23.0 Hz, 1C), 113.7 (d, *J* = 7.0 Hz, 1C), 113.4 (d, *J* = 6.0 Hz, 1C), 21.6 (d, *J* = 8.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.16; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.68. IR (KBr) ν 1615, 1485, 1177, 1110, 756 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}OFNaP$ $[M+Na]^+$: 433.1133, found: 433.1137.



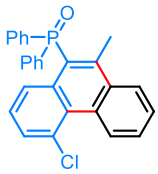
(5-Fluoro-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3i'**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 4:1); 27.3 mg, 22% yield; reaction time = 48 h; mp 219.1-219.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.71-7.66 (m, 5H), 7.49-7.46 (m, 2H), 7.42-7.38 (m, 4H), 7.25-7.15 (m, 2H), 2.54 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 159.6, 144.5 (d, *J* = 8.0 Hz, 1C), 136.6, 135.6, 134.1 (d, *J* = 8.0 Hz, 1C), 132.1 (d, *J* = 12.0 Hz, 1C), 131.3 (d, *J* = 2.0 Hz, 1C), 131.0 (d, *J* = 8.0 Hz, 1C), 128.9 (d, *J* = 2.0 Hz, 1C), 128.7 (d, *J* = 12.0 Hz, 1C), 128.0, 127.8, 127.3, 125.9 (d, *J* = 10.0 Hz, 1C), 124.8, 119.2, 113.1 (d, *J* = 25.0 Hz, 1C), 21.9 (d, *J* = 8.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.13 (d, *J* = 3.7 Hz, 1F); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.55. IR (KBr) ν 1437, 1166, 1107, 758 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{21}OFP$ $[M+H]^+$: 411.1314, found: 411.1313.



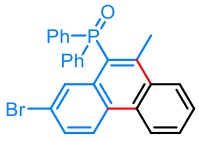
(7-Chloro-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3j**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 28.3 mg, 22% yield; reaction time = 48 h; mp 189.6-189.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.0 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.38 (d, *J* = 4.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.79-7.65 (m, 6H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.47-7.41 (m, 5H), 2.63 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (d, *J* = 8.0 Hz, 1C), 136.2, 135.2, 132.8 (d, *J* = 10.0 Hz, 1C), 132.1, 131.5 (d, *J* = 3.0 Hz, 1C), 131.4 (t, *J* = 3.0 Hz, 1C), 131.1 (d, *J* = 10.0 Hz, 1C), 129.0, 128.8 (d, *J* = 12.0 Hz, 1C), 128.1 (d, *J* = 9.0 Hz, 1C), 127.8 (d, *J* = 6.0 Hz, 1C), 127.4, 126.6, 125.4, 125.0, 124.1, 122.9, 21.5 (d, *J* = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.98. IR (KBr) ν 1598, 1438, 1173, 1110, 768 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{21}OPCl$ $[M+H]^+$: 427.1019, found: 427.1022.



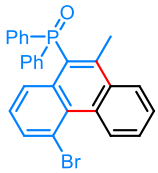
(5-Chloro-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3j'**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 34.0 mg, 27% yield; reaction time = 48 h; mp 203.8-204.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 3H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.42-7.37 (m, 4H), 7.14 (t, *J* = 8.0 Hz, 1H), 2.46 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4 (d, *J* = 8.0 Hz, 1C), 136.5, 135.5, 134.5 (d, *J* = 10.0 Hz, 1C), 133.0 (d, *J* = 13.0 Hz, 1C), 131.3 (d, *J* = 3.0 Hz, 1C), 131.1 (d, *J* = 2.0 Hz, 1C), 130.9 (d, *J* = 9.0 Hz, 1C), 130.2 (d, *J* = 2.0 Hz, 1C), 129.9, 128.7 (d, *J* = 12.0 Hz, 1C), 127.9, 127.5, 127.2 (dd, J_1 = 9.0 Hz, J_2 = 4.0 Hz, 1C), 127.2, 125.9, 125.3, 124.1, 21.9 (d, *J* = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.96. IR (KBr) ν 1431, 1183, 1107, 756 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}ONaPCl$ $[M+Na]^+$: 449.0838, found: 449.0840.



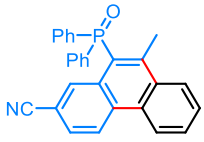
(7-Bromo-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3k**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 4:1); 27.9 mg, 20% yield; reaction time = 48 h; mp 192.0-192.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 12.0 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.78-7.65 (m, 6H), 7.58 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.53-7.49 (m, 2H), 7.46-7.41 (m, 4H), 2.66 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7 (d, *J* = 8.0 Hz, 1C), 136.2, 135.2, 133.1 (d, *J* = 10.0 Hz, 1C), 131.5 (d, *J* = 3.0 Hz, 1C), 131.4 (d, *J* = 5.0 Hz, 1C), 131.0 (d, *J* = 10.0 Hz, 1C), 130.9 (d, *J* = 5.0 Hz, 1C), 129.2, 129.0, 128.8 (d, *J* = 12.0 Hz, 1C), 128.3 (d, *J* = 8.0 Hz, 1C), 127.5, 125.4, 124.2, 124.0, 122.8, 120.4, 21.5 (d, *J* = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.64. IR (KBr) ν 1590, 1437, 1170, 1112, 761 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}ONaPBr$ $[M+Na]^+$: 493.0333, found: 493.0337.



(5-Bromo-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3k'**)

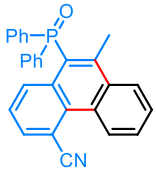
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 4:1); 33.5 mg, 24% yield; reaction time = 48 h; mp 188.8-189.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.74-7.64 (m, 6H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 4H), 7.06 (t, *J* = 8.0 Hz, 1H), 2.45 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3 (d, *J* = 8.0 Hz, 1C), 136.5, 135.4, 134.4 (d, *J* = 10.0 Hz, 1C), 133.8, 133.0 (d, *J* = 13.0 Hz, 1C), 131.3 (d, *J* = 2.0 Hz, 1C), 131.0 (d, *J* = 10.0 Hz, 1C), 130.5 (d, *J* = 2.0 Hz, 1C), 128.7 (d, *J* = 12.0 Hz, 1C), 128.5 (d, *J* = 9.0 Hz, 1C), 127.7 (d, *J* = 11.0 Hz, 1C), 127.7, 126.6, 126.3, 125.2, 123.9, 119.4 (d, *J* = 2.0 Hz, 1C), 21.8 (d, *J* = 7.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.04. IR (KBr) ν 1431, 1183, 1106, 755 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{21}OPBr$ $[M+H]^+$: 471.0513, found: 471.0516.



10-(Diphenylphosphoryl)-9-methylphenanthrene-2-carbonitrile (**3l**)

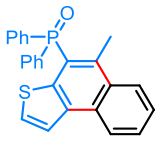
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 4:1); 18.5 mg, 15% yield; reaction time = 48 h; mp 229.7-229.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s,

1H), 8.72 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.78-7.69 (m, 6H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.49-7.44 (m, 4H), 2.60 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (d, *J* = 8.0 Hz, 1C), 135.6, 134.6, 133.4 (d, *J* = 5.0 Hz, 1C), 132.5 (d, *J* = 2.0 Hz, 1C), 132.4, 131.9 (d, *J* = 3.0 Hz, 1C), 131.5 (d, *J* = 10.0 Hz, 1C), 131.1 (d, *J* = 10.0 Hz, 1C), 130.7 (d, *J* = 2.0 Hz, 1C), 129.4, 129.0 (d, *J* = 12.0 Hz, 1C), 128.8, 127.6, 125.5, 123.7, 123.5, 118.8, 109.4, 21.6 (d, *J* = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.38. IR (KBr) ν 2224, 1437, 1176, 1104, 753 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{20}NONaP$ $[M+Na]^+$: 440.1180, found: 440.1184.



10-(Diphenylphosphoryl)-9-methylphenanthrene-4-carbonitrile (**3l'**)

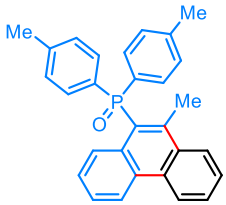
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 4:1); 27.7 mg, 22% yield; reaction time = 48 h; mp 233.4-233.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 8.0 Hz, 1H), 8.81 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.45-7.40 (m, 4H), 7.33 (t, *J* = 8.0 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7 (d, *J* = 8.0 Hz, 1C), 136.0, 135.4, 135.0, 133.3 (d, *J* = 6.0 Hz, 1C), 132.8 (dd, J_1 = 26.0 Hz, J_2 = 10.0 Hz, 1C), 131.6 (d, *J* = 3.0 Hz, 1C), 131.0 (d, *J* = 10.0 Hz, 1C), 129.9 (d, *J* = 10.0 Hz, 1C), 129.7 (d, *J* = 2.0 Hz, 1C), 128.9 (d, *J* = 12.0 Hz, 1C), 128.8, 126.1, 125.5, 125.2, 125.1, 124.9, 121.5, 107.5, 22.0 (d, *J* = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.54. IR (KBr) ν 2217, 1436, 1183, 1107, 748 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{20}NONaP$ $[M+Na]^+$: 440.1180, found: 440.1184.



(5-Methylnaphtho[2,1-*b*]thiophen-4-yl)diphenylphosphine oxide (**3m**)

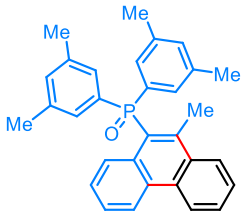
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 49.2 mg, 41% yield; reaction time = 48 h; mp 213.9-214.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.98 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.81-7.76 (m, 4H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.60-7.54 (m, 4H), 7.49-7.44 (m, 4H), 2.64 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1 (d, *J* = 8.0 Hz, 1C), 137.3 (d, *J* = 8.0 Hz, 1C), 136.3 (d, *J* = 9.0 Hz, 1C),

133.9, 132.8, 132.0 (d, J = 10.0 Hz, 1C), 132.0 (d, J = 2.0 Hz, 1C), 130.6 (dd, J_1 = 8.0 Hz, J_2 = 6.0 Hz, 1C), 128.7 (d, J = 12.0 Hz, 1C), 128.3 (d, J = 29.0 Hz, 1C), 125.8, 125.2, 124.2, 122.8, 121.8, 120.1, 20.2 (d, J = 7.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.59. IR (KBr) ν 1432, 1177, 1109, 698 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{19}ONaPS$ $[M+Na]^+$: 421.0792, found: 421.0793.



(10-Methylphenanthren-9-yl)di-p-tolylphosphine oxide (**3n**)

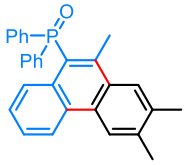
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1 to 1:1); 52.9 mg, 36% yield; reaction time = 48 h; mp 78.6-79.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 10.0 Hz, 1H), 8.64 (d, J = 5.0 Hz, 1H), 8.40 (d, J = 5.0 Hz, 1H), 8.13 (d, J = 5.0 Hz, 1H), 7.75 (t, J = 10.0 Hz, 1H), 7.64 (t, J = 10.0 Hz, 1H), 7.60 (d, J = 5.0 Hz, 2H), 7.57 (d, J = 10.0 Hz, 2H), 7.50 (t, J = 10.0 Hz, 1H), 7.25 (t, J = 10.0 Hz, 1H), 7.21-7.20 (m, 4H), 2.61 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9 (d, J = 7.5 Hz, 1C), 141.6 (d, J = 2.5 Hz, 1C), 133.5, 132.7, 131.9 (d, J = 6.3 Hz, 1C), 131.8, 131.6 (d, J = 12.5 Hz, 1C), 131.1 (d, J = 9.0 Hz, 1C), 129.6 (d, J = 8.8 Hz, 1C), 129.4 (d, J = 12.5 Hz, 1C), 129.0, 128.6 (d, J = 6.3 Hz, 1C), 128.5, 127.0, 125.9 (d, J = 20.0 Hz, 1C), 125.2 (d, J = 4.0 Hz, 1C), 122.9, 122.6, 21.5, 21.3 (d, J = 8.0 Hz, 1C); ^{31}P NMR (202 MHz, $CDCl_3$) δ 30.52. IR (KBr) ν 1494, 1176, 1107, 756 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{25}ONaP$ $[M+Na]^+$: 443.1541, found: 443.1543.



Bis(3,5-dimethylphenyl)(10-methylphenanthren-9-yl)phosphine oxide (**3o**)

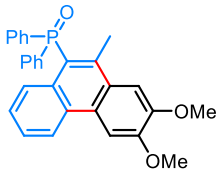
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1 to 0:1); 49.7 mg, 55% yield; reaction time = 48 h; mp 183.1-183.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, J = 10.0 Hz, 1H), 8.64 (d, J = 10.0 Hz, 1H), 8.44 (d, J = 5.0 Hz, 1H), 8.13 (d, J = 10.0 Hz, 1H), 7.75 (t, J = 10.0 Hz, 1H), 7.64 (t, J = 10.0 Hz, 1H), 7.50 (d, J = 10.0 Hz, 1H), 7.30 (s, 2H), 7.28 (s, 2H), 7.24 (s, 1H), 7.08 (s, 2H), 2.59 (s, 3H), 2.25 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7 (d, J =

7.5 Hz, 1C), 138.2 (d, *J* = 12.5 Hz, 1C), 136.3, 135.5, 133.1 (d, *J* = 2.5 Hz, 1C), 132.1 (d, *J* = 10.0 Hz, 1C), 131.9, 131.7 (d, *J* = 13.8 Hz, 1C), 129.7 (d, *J* = 8.8 Hz, 1C), 128.7 (d, *J* = 8.8 Hz, 1C), 128.4, 127.0, 126.2, 126.0, 125.8, 125.3, 122.9, 122.5, 21.4 (d, *J* = 7.5 Hz, 1C), 21.3; ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.55. IR (KBr) ν 2922, 1451, 1178, 759 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{30}OP$ $[M+H]^+$: 449.2034, found: 449.2030.



Diphenyl(2,3,10-trimethylphenanthren-9-yl)phosphine oxide (**3p**)

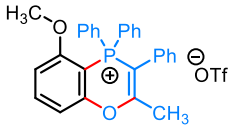
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 79.1 mg, 63% yield; reaction time = 48 h; mp 209.3-209.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 12.0 Hz, 1H), 8.47 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 3H), 7.41-7.38 (m, 4H), 7.19 (t, *J* = 8.0 Hz, 1H), 2.56 (s, 6H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9 (d, *J* = 8.0 Hz, 1C), 138.3, 137.1, 136.4, 136.1, 131.5 (d, *J* = 10.0 Hz, 1C), 131.1 (d, *J* = 10.0 Hz, 1C), 131.1, 130.3 (d, *J* = 2.0 Hz, 1C), 130.1 (d, *J* = 13.0 Hz, 1C), 129.4 (d, *J* = 9.0 Hz, 1C), 128.6 (d, *J* = 12.0 Hz, 1C), 128.5, 125.8, 125.5, 125.3, 123.3, 122.4, 21.4 (d, *J* = 8.0 Hz, 1C), 20.5, 20.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.90. IR (KBr) ν 1439, 1180, 1100, 755 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{26}OP$ $[M+H]^+$: 421.1721, found: 421.1725.



(2,3-Dimethoxy-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3q**)

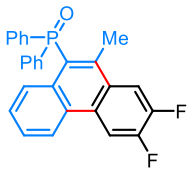
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 45.9 mg, 34% yield; reaction time = 48 h; mp 177.3-177.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 12.0 Hz, 1H), 8.31 (d, *J* = 12.0 Hz, 1H), 8.04 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 3H), 7.42-7.39 (m, 5H), 7.18 (t, *J* = 8.0 Hz, 1H), 4.16 (s, 3H), 4.02 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 149.4, 142.1 (d, *J* = 8.0 Hz, 1C), 137.1, 136.1, 131.4 (d, *J* = 10.0 Hz, 1C), 131.2 (d, *J* = 10.0 Hz, 1C), 129.1 (d, *J* = 9.0 Hz, 1C), 128.6 (d, *J* = 12.0 Hz, 1C), 127.3 (d, *J* = 2.0 Hz, 1C), 126.7 (d, *J* = 12.0 Hz, 1C), 125.7, 124.9, 123.6, 122.6,

122.2, 105.4, 103.3, 56.0, 55.9, 21.5 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.26. IR (KBr) ν 1514, 1436, 1261, 1198, 755 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{25}O_3NaP$ [M+Na]$^+$: 475.1439, found: 475.1442.



5-Methoxy-2-methyl-3,4,4-triphenyl-4*H*-benzo[*b*][1,4]oxaphosphinin-4-ium trifluoromethanesulfonate (**4a**)

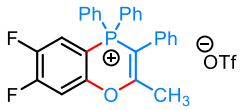
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 0:1); 98.8 mg, 58% yield; reaction time = 48 h; mp 182.1-182.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (t, J = 8.0 Hz, 1H), 7.84-7.81 (m, 2H), 7.69-7.64 (m, 8H), 7.36-7.31 (m, 2H), 7.26 (t, J = 8.0 Hz, 2H), 7.14 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H), 3.63 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.0, 160.4, 155.2, 138.7, 134.6 (d, J = 3.0 Hz, 1C), 133.8 (d, J = 12.0 Hz, 1C), 131.4 (d, J = 4.0 Hz, 1C), 130.0 (d, J = 4.0 Hz, 1C), 129.6 (d, J = 14.0 Hz, 1C), 129.2 (d, J = 2.0 Hz, 1C), 128.9 (d, J = 2.0 Hz, 1C), 119.0 (d, J = 98.0 Hz, 1C), 111.5 (d, J = 5.0 Hz, 1C), 108.5 (d, J = 5.0 Hz, 1C), 91.5 (d, J = 89.0 Hz, 1C), 88.9 (d, J = 91.0 Hz, 1C), 56.8, 20.7 (d, J = 7.0 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.73; ^{31}P NMR (162 MHz, DMSO-d_6) δ -9.74. IR (KBr) ν 1619, 1439, 1149, 750 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{24}O_2P$ [M-OTf]$^+$: 423.1514, found: 423.1498.



(2,3-Difluoro-10-methylphenanthren-9-yl)diphenylphosphine oxide (**3r**)

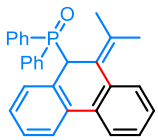
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1 to 0:1); 27.8 mg, 22% yield; reaction time = 48 h; mp 223.5-224.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45-8.41 (m, 2H), 8.33 (d, J = 5.0 Hz, 1H), 7.88 (dd, J_1 = 10.0 Hz, J_2 = 5.0 Hz, 1H), 7.70 (dd, J_1 = 10.0 Hz, J_2 = 5.0 Hz, 4H), 7.51 (dd, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 3H), 7.44-7.41 (m, 4H), 7.25 (d, J = 10.0 Hz, 1H), 2.55 (d, J = 5.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2 (d, J = 15.0 Hz, 1C), 151.0, 150.2, 141.8, 136.2, 135.4, 131.8 (d, J = 2.5 Hz, 1C), 131.7 (d, J = 2.5 Hz, 1C), 131.5 (d, J = 2.5 Hz, 1C), 131.1 (d, J = 9.0 Hz, 1C), 129.7, 128.8 (d, J = 12.5 Hz, 1C), 128.2 (d, J = 12.5 Hz, 1C),

126.5, 126.3, 122.7, 112.9 (d, J = 20.0 Hz, 1C), 110.6 (d, J = 17.5 Hz, 1C), 21.4 (d, J = 7.5 Hz, 1C); ^{19}F NMR (470 MHz, $CDCl_3$) δ -133.96, -136.14; ^{31}P NMR (202 MHz, $CDCl_3$) δ 30.24. IR (KBr) ν 2924, 1505, 1441, 1175, 1113, 757 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}OPF_2$ $[M+H]^+$: 429.1220, found: 429.1223.



6,7-Difluoro-2-methyl-3,4,4-triphenyl-4*H*-benzo[*b*][1,4]oxaphosphinin-4-ium trifluoromethanesulfonate (**4b**)

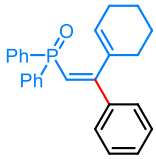
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1 to 0:1); 39.9 mg, 23% yield; reaction time = 48 h; mp 93.4-93.7 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (t, J = 10.0 Hz, 2H), 7.68-7.61 (m, 8H), 7.46-7.42 (m, 1H), 7.32-7.21 (m, 4H), 6.91 (d, J = 5.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 152.6 (d, J = 11.3 Hz, 1C), 135.6 (d, J = 2.5 Hz, 1C), 134.0 (d, J = 11.3 Hz, 1C), 131.3 (d, J = 4.0 Hz, 1C), 130.5, 130.4, 129.6 (d, J = 2.5 Hz, 1C), 129.4 (d, J = 1.3 Hz, 1C), 129.0 (d, J = 5.0 Hz, 1C), 122.2, 119.6, 119.0, 118.5 (dd, J_1 = 19.0 Hz, J_2 = 7.5 Hz, 1C), 110.2 (dd, J_1 = 21.3 Hz, J_2 = 7.5 Hz, 1C), 96.1 (d, J = 90.0 Hz, 1C), 90.7 (d, J = 90.0 Hz, 1C), 20.9 (d, J = 7.5 Hz, 1C); ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.20, -119.91 to -119.99 (m, 1F), -134.10 to -134.19 (m, 1F); ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.95. IR (KBr) ν 1615, 1505, 1273, 1157, 1034, 756 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{20}OF_2P$ $[M-OTf]^+$: 429.1220, found: 429.1221.



Diphenyl(10-(propan-2-ylidene)-9,10-dihydrophenanthren-9-yl)phosphine oxide (**3s**)

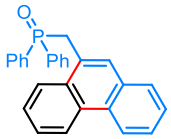
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 22.4 mg, 18% yield; reaction time = 48 h; mp 185.9-186.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 3H), 7.42 (t, J = 8.0 Hz, 1H), 7.32-7.22 (m, 8H), 7.20-7.11 (m, 5H), 7.01 (t, J = 8.0 Hz, 1H), 4.95 (d, J = 20.0 Hz, 1H), 1.94 (d, J = 8.0 Hz, 3H), 1.75 (d, J = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6 (d, J = 4.0 Hz, 1C), 134.9 (d, J = 2.0 Hz, 1C), 133.9 (d, J = 3.0 Hz, 1C), 133.2 (d, J = 12.0 Hz, 1C), 132.1 (q, J = 9.0 Hz, 1C), 131.4 (d, J = 3.0 Hz, 1C), 131.1 (d, J = 9.0 Hz, 1C), 129.7 (d, J = 5.0 Hz, 1C), 129.6 (d, J = 1.0 Hz, 1C), 128.8, 127.8 (d, J = 3.0 Hz, 1C), 127.6 (d, J = 12.0 Hz, 1C), 127.5, 127.2 (d, J = 3.0 Hz, 1C), 126.6, 124.3 (d, J = 7.0 Hz, 1C), 123.7, 123.6, 49.5 (d, J

= 60.0 Hz, 1C), 22.8 (d, *J* = 2.0 Hz, 1C), 21.4 (d, *J* = 3.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.79. IR (KBr) ν 1440, 1189, 1106, 753 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{25}ONaP$ $[M+Na]^+$: 443.1541, found: 443.1544.



(*E*)-(2-(Cyclohex-1-en-1-yl)-2-phenylvinyl)diphenylphosphine oxide (**3t**)

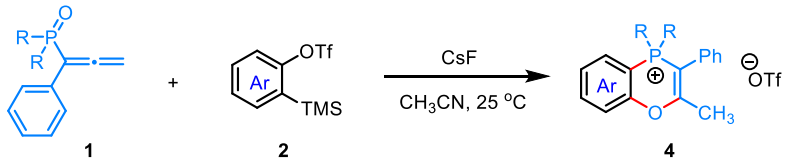
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1 to 2:1); 23.3 mg, 20% yield; reaction time = 48 h; mp 148.5-149.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 4H), 7.47-7.39 (m, 8H), 7.36-7.34 (m, 3H), 6.39 (d, *J* = 20.0 Hz, 1H), 6.30 (s, 1H), 1.92 (d, *J* = 4.0 Hz, 2H), 1.50 (s, 2H), 1.18-1.13 (m, 2H), 1.08-1.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (d, *J* = 4.0 Hz, 1C), 139.7 (d, *J* = 16.0 Hz, 1C), 135.8, 135.4 (d, *J* = 7.0 Hz, 1C), 134.8, 133.4, 130.9 (dd, J_1 = 14.0 Hz, J_2 = 3.0 Hz, 1C), 129.2, 128.4, 128.2 (d, *J* = 12.0 Hz, 1C), 127.5, 119.4 (d, *J* = 106.0 Hz, 1C), 27.3, 25.1, 21.7, 21.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.16. IR (KBr) ν 2375, 1574, 1433, 1176, 1109, 751 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{25}ONaP$ $[M+Na]^+$: 407.1541, found: 407.1543.



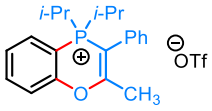
(Phenanthren-9-ylmethyl)diphenylphosphine oxide (**3u**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 44.9 mg, 38% yield; reaction time = 48 h; mp 217.2-217.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.75-7.71 (m, 4H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.53-7.46 (m, 5H), 7.41-7.36 (m, 4H), 4.14 (d, *J* = 16.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 131.9, 131.7 (d, *J* = 2.0 Hz, 1C), 131.2, 131.2 (d, *J* = 2.0 Hz, 1C), 131.1, 130.5 (d, *J* = 1.0 Hz, 1C), 129.8 (d, *J* = 2.0 Hz, 1C), 129.4 (d, *J* = 7.0 Hz, 1C), 128.4 (d, *J* = 12.0 Hz, 1C), 128.2 (d, *J* = 1.0 Hz, 1C), 126.5, 126.4, 126.3 (d, *J* = 8.0 Hz, 1C), 126.2, 125.0, 122.8, 122.3 (d, *J* = 1.0 Hz, 1C), 35.1 (d, *J* = 66.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.53. IR (KBr) ν 1438, 1185, 1109, 727 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{22}OP$ $[M+H]^+$: 393.1408, found: 393.1412.

3. Experimental data for the formation of 4

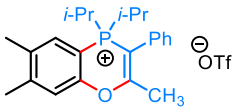


General procedure: To a 5.0 mL vial were successively added allenylphosphine oxides **1** (0.30 mmol), CsF (91.1 mg, 0.60 mmol) and 1.0 mL of CH_3CN. And then, benzyne precursors **2** (0.60 mmol) were added by syringe. The resulting mixture was stirred at 25 °C for 48 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether / ethyl acetate = 1:1 to pure ethyl acetate) to afford the corresponding products **4**.



4,4-Diisopropyl-2-methyl-3-phenyl-4*H*-benzo[*b*][1,4]oxaphosphinin-4-ium trifluoromethanesulfonate (**4c**)

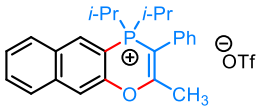
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 0:1); 86.9 mg, 61% yield; reaction time = 48 h; mp 169.4-169.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.55-7.47 (m, 3H), 7.40 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.24-3.11 (m, 2H), 2.17 (s, 3H), 1.32 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 6H), 0.97 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 155.8, 136.5, 131.4 (d, *J* = 6.0 Hz, 1C), 130.9 (d, *J* = 6.0 Hz, 1C), 130.2 (d, *J* = 3.0 Hz, 1C), 130.2, 130.0 (d, *J* = 2.0 Hz, 1C), 127.3 (d, *J* = 10.0 Hz, 1C), 122.4, 119.2 (d, *J* = 5.0 Hz, 1C), 95.6 (d, *J* = 77.0 Hz, 1C), 88.2 (d, *J* = 76.0 Hz, 1C), 23.2 (d, *J* = 47.0 Hz, 1C), 20.5 (d, *J* = 6.0 Hz, 1C), 15.3 (dd, J_1 = 5.0 Hz, J_2 = 2.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.23; ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.88. IR (KBr) ν 1613, 1273, 1151, 766 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{26}OP$ [M-OTf]$^+$: 325.1721, found: 325.1724.



4,4-Diisopropyl-2,6,7-trimethyl-3-phenyl-4*H*-benzo[*b*][1,4]oxaphosphinin-4-ium trifluoromethanesulfonate (**4d**)

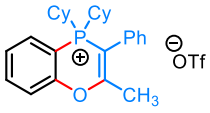
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 0:1); 26.2

mg, 17% yield; reaction time = 48 h; mp 184.3-184.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 12.0 Hz, 1H), 7.55-7.47 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 4.0 Hz, 1H), 3.22-3.09 (m, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 2.14 (s, 3H), 1.32 (dd, J_1 = 20.0 Hz, J_2 = 8.0 Hz, 6H), 0.97 (dd, J_1 = 20.0 Hz, J_2 = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 154.2, 147.3, 137.3 (d, *J* = 11.0 Hz, 1C), 131.3 (d, *J* = 5.0 Hz, 1C), 130.6 (d, *J* = 6.0 Hz, 1C), 130.3 (d, *J* = 3.0 Hz, 1C), 130.1 (d, *J* = 1.0 Hz, 1C), 129.9 (d, *J* = 2.0 Hz, 1C), 122.5, 119.5 (d, *J* = 6.0 Hz, 1C), 92.0 (d, *J* = 80.0 Hz, 1C), 88.1 (d, *J* = 76.0 Hz, 1C), 23.2 (d, *J* = 48.0 Hz, 1C), 20.5, 19.0, 15.5 (d, *J* = 2.0 Hz, 1C), 15.3 (d, *J* = 3.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.21; ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.61. IR (KBr) ν 1607, 1271, 1152, 1031, 764 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{30}OP$ [M-OTf]$^{+}$: 353.2034, found: 353.2037.



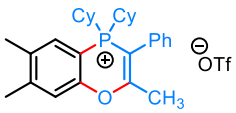
4,4-Diisopropyl-2-methyl-3-phenyl-4*H*-naphtho[2,3-*b*][1,4]oxaphosphinin-4-ium trifluoromethanesulfonate (**4e**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 0:1); 21.6 mg, 14% yield; reaction time = 48 h; mp 222.7-222.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 12.0 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 4.0 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.57-7.50 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.44-3.35 (m, 2H), 2.22 (s, 3H), 1.37 (dd, J_1 = 20.0 Hz, J_2 = 8.0 Hz, 6H), 1.00 (dd, J_1 = 20.0 Hz, J_2 = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 150.4, 136.6, 135.5 (d, *J* = 5.0 Hz, 1C), 131.4 (d, *J* = 5.0 Hz, 1C), 131.2 (d, *J* = 12.0 Hz, 1C), 130.8, 130.4 (d, *J* = 3.0 Hz, 1C), 130.2, 130.1 (d, *J* = 4.0 Hz, 1C), 130.0 (d, *J* = 2.0 Hz, 1C), 127.4, 127.0, 122.6, 115.2 (d, *J* = 5.0 Hz, 1C), 95.8 (d, *J* = 77.0 Hz, 1C), 87.8 (d, *J* = 76.0 Hz, 1C), 23.4 (d, *J* = 48.0 Hz, 1C), 20.7 (d, *J* = 7.0 Hz, 1C), 15.4 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.21; ^{31}P NMR (162 MHz, $CDCl_3$) δ 12.38. IR (KBr) ν 1605, 1266, 1154, 1031, 760 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{28}OP$ [M-OTf]$^{+}$: 375.1878, found: 375.1879.



4,4-Dicyclohexyl-2-methyl-3-phenyl-4*H*-benzo[*b*][1,4]oxaphosphinin-4-ium trifluoromethanesulfonate (**4f**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 0:1); 79.6 mg, 48% yield; reaction time = 48 h; mp 211.3-212.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (t, *J* = 8.0 Hz, 1H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.56-7.49 (m, 3H), 7.38 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.77 (q, *J* = 8.0 Hz, 2H), 2.15 (s, 3H), 1.85-1.65 (m, 10H), 1.44-1.36 (m, 6H), 1.00-0.90 (m, 2H), 0.61-0.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 155.6, 136.3, 131.4 (d, *J* = 6.0 Hz, 1C), 131.2 (d, *J* = 6.0 Hz, 1C), 130.3 (d, *J* = 3.0 Hz, 1C), 130.1, 130.0 (d, *J* = 2.0 Hz, 1C), 127.3 (d, *J* = 10.0 Hz, 1C), 122.5, 119.2 (d, *J* = 5.0 Hz, 1C), 95.6 (d, *J* = 78.0 Hz, 1C), 87.7 (d, *J* = 77.0 Hz, 1C), 31.6 (d, *J* = 46.0 Hz, 1C), 25.6 (t, *J* = 12.0 Hz, 1C), 25.2 (dd, J_1 = 17.0 Hz, J_2 = 3.0 Hz, 1C), 25.0 (d, *J* = 1.0 Hz, 1C), 20.5 (d, *J* = 6.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.12; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.34. IR (KBr) ν 2936, 1612, 1269, 1150, 770 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{34}OP$ [M-OTf]$^{+}$: 405.2347, found: 405.2348.

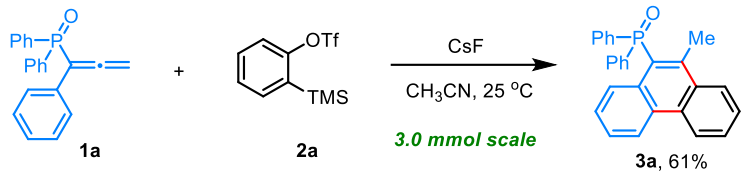


4,4-Dicyclohexyl-2,6,7-trimethyl-3-phenyl-4*H*-benzo[*b*][1,4]oxaphosphinin-4-ium trifluoromethanesulfonate (**4g**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1 to 0:1); 63.2 mg, 36% yield; reaction time = 48 h; mp 210.5-211.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 12.0 Hz, 1H), 7.55-7.50 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 4.0 Hz, 1H), 2.79-2.71 (m, 2H), 2.42 (s, 3H), 2.38 (s, 3H), 2.12 (s, 3H), 1.87-1.85 (m, 4H), 1.70-1.67 (m, 6H), 1.48-1.35 (m, 6H), 1.03-0.94 (m, 2H), 0.63-0.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 154.1, 147.2, 137.2 (d, *J* = 10.0 Hz, 1C), 131.6 (d, *J* = 5.0 Hz, 1C), 130.5 (d, *J* = 3.0 Hz, 1C), 130.4 (d, *J* = 7.0 Hz, 1C), 130.0, 129.9, 122.5, 119.6 (d, *J* = 6.0 Hz, 1C), 92.2 (d, *J* = 80.0 Hz, 1C), 87.5 (d, *J* = 77.0 Hz, 1C), 31.7 (d, *J* = 47.0 Hz, 1C), 25.7 (dd, J_1 = 13.0 Hz, J_2 = 5.0 Hz, 1C), 25.4 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1C), 25.2, 20.5 (d, *J* = 6.0 Hz, 1C), 20.4, 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.16; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.15. IR (KBr) ν 1613, 1269, 1154, 757 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{38}OP$ [M-OTf]$^{+}$: 433.2660, found: 433.2663.

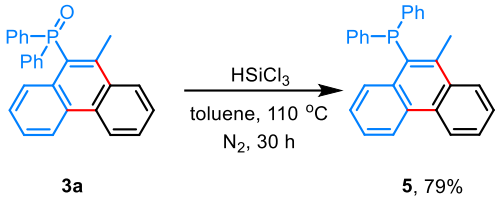
4. Methodology application

4.1 Scalable preparation of 3a

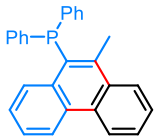


General procedure: To a 5.0 mL vial were successively added allenylphosphine oxide **1a** (3.0 mmol), CsF (0.91 g, 6.0 mmol) and 10.0 mL of CH_3CN. And then, benzyne precursor **2a** (6.0 mmol) were added by syringe. The resulting mixture was stirred at 25 °C for 48 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether / ethyl acetate = 5:1 to 3:1) to afford the corresponding product **3a** (288.8 mg, 61%).

4.2 Chemical conversion of 3a



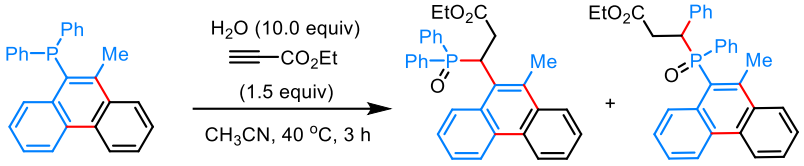
General procedure: To a solution of **3a** (78.9 mg, 0.2 mmol) in tuluene (2.0 mL) was added $HSiCl_3$ (812.7 mg, 6.0 mmol). After being stirred at 110 °C for 30 h, water was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography (petroleum ether / ethyl acetate = 250:1 to 100:1) to obtain **5** in 79% yield.



(10-Methylphenanthren-9-yl)diphenylphosphane (**5**)

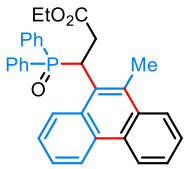
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 250:1 to 100:1); 59.8 mg, 79% yield; reaction time = 30 h; mp 169.1-169.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.0 Hz, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 8.45 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 4H), 7.31 (q, *J* = 8.0 Hz, 7H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1 (d, *J* = 20.0 Hz, 1C), 136.7 (d, *J* = 15.0 Hz, 1C), 133.4 (d, *J* = 10.0 Hz, 1C), 131.9 (d, *J* = 5.0 Hz, 1C), 131.5, 131.4, 131.2, 130.1 (d, *J* = 3.0 Hz, 1C), 129.6 (d, *J* = 18.0 Hz, 1C), 129.0 (d, *J* = 17.0 Hz, 1C), 128.4 (d, *J* = 5.0 Hz, 1C), 127.7, 127.4, 126.8, 126.0, 125.7 (d, *J* = 2.0 Hz, 1C), 125.7, 122.7

(d, J = 19.0 Hz, 1C), 21.0 (d, J = 29.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ -17.58. IR (KBr) ν 3057, 1480, 1433, 747 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{22}P$ $[M+H]^+$: 377.1459, found: 377.1461.



5 **6**, 34% **6'**, 24%

General procedure: To a 5.0 mL vial were successively added organic phosphine **5** (154.1 mg, 0.4 mmol), ethyl propiolate (58.8 mg, 0.6 mmol), H_2O (72.0 μL, 4.0 mmol) and 2.0 mL of CH_3CN. The resulting mixture was stirred at 40 °C for 3 h. And then, the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 to 4:1) to afford the corresponding products **6** and its regio-isomer **6'** (Due to the difficulty in separating these two isomers, we only the pure spectrum of **6**).



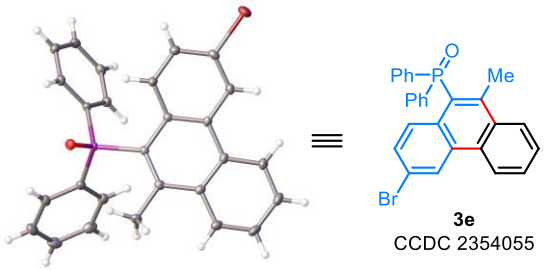
Ethyl 3-(diphenylphosphoryl)-3-(10-methylphenanthren-9-yl)propanoate (**6**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 4:1); 66.4 mg, 34% yield; reaction time = 3 h; mp 149.1-149.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60-8.52 (m, 3H), 8.07 (d, J = 12.0 Hz, 1H), 7.82 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.65 (t, J = 8.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.52-7.39 (m, 5H), 7.09 (d, J = 4.0 Hz, 2H), 6.82 (d, J = 8.0 Hz, 3H), 4.78-4.72 (m, 1H), 4.07-3.99 (m, 2H), 3.56-3.50 (m, 1H), 3.49-3.35 (m, 1H), 2.91 (s, 3H), 1.09 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (d, J = 16.0 Hz, 1C), 144.1 (d, J = 9.0 Hz, 1C), 137.1, 136.0 (d, J = 5.0 Hz, 1C), 131.6, 131.4-131.3 (m, 1C), 130.3 (d, J = 9.0 Hz, 1C), 129.2 (d, J = 9.0 Hz, 1C), 128.9 (d, J = 11.0 Hz, 1C), 128.7 (d, J = 6.0 Hz, 1C), 128.3, 127.6 (d, J = 2.0 Hz, 1C), 127.1 (d, J = 5.0 Hz, 1C), 126.9 (d, J = 2.0 Hz, 1C), 126.8, 125.8 (d, J = 13.0 Hz, 1C), 125.1, 123.7, 122.6 (d, J = 7.0 Hz, 1C), 60.8, 43.4 (d, J = 66.0 Hz, 1C), 36.4, 18.7 (d, J = 6.0 Hz, 1C), 14.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.91. IR (KBr) ν 3452, 1738, 1437, 1200, 1167, 750 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{22}P$ $[M+H]^+$: 377.1459, found: 377.1461.

5. Crystal structures

5.1 Crystal structure of 3e

Preparation of the single crystals of **3e**: 20.0 mg of pure compound **3e** was dissolved in the combined solvents of dichloromethane, petroleum ether and ethyl acetate (8.0 mL, v/v/v = 2:5:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at 2-8 ºC. After about seven days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **3e**. The data were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 149.99(10) K during data collection.



3e
CCDC 2354055

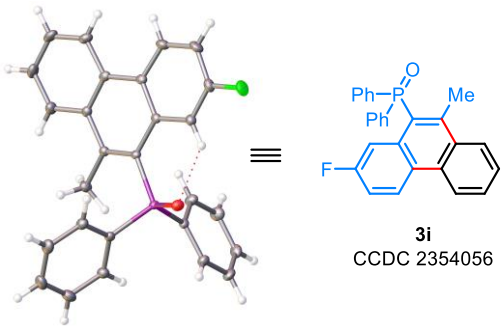
Table S1 Crystal data and structure refinement for **3e**.

Identification code	**3e**
Empirical formula	$C_{27}H_{20}BrOP$
Formula weight	471.31
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.9801(3)
b/Å	17.8286(8)
c/Å	15.0481(7)
α/°	90
β/°	102.601(4)
γ/°	90
Volume/Å^3	2089.38(16)
Z	4

ρ_{calc}g/cm^3	1.498
μ/mm^{-1}	3.527
F(000)	960.0
Crystal size/mm^3	0.16 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.8 to 147.226
Index ranges	-9 ≤ h ≤ 6, -21 ≤ k ≤ 21, -17 ≤ l ≤ 18
Reflections collected	7911
Independent reflections	4099 [R_{int} = 0.0366, R_{sigma} = 0.0455]
Data/restraints/parameters	4099/0/272
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0497, wR_2 = 0.1321
Final R indexes [all data]	R_1 = 0.0553, wR_2 = 0.1378

5.2 Crystal structure of 3i

Preparation of the single crystals of **3i**: 10.0 mg of pure compound **3i** was dissolved in the combined solvents of dichloromethane and petroleum ether (6.0 mL, v/v = 1:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at 15 ºC. After about two days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **3i**. The data were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 169.99(10) K during data collection.



3i
CCDC 2354056

Table S2 Crystal data and structure refinement for **3i**.

Identification code	**3i**
Empirical formula	$C_{27}H_{20}FOP$
Formula weight	410.40
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.1019(2)
b/Å	13.6934(3)
c/Å	12.1992(2)
α/°	90
β/°	91.695(2)
γ/°	90
Volume/Å^3	2020.72(6)
Z	4
ρ_{calc}g/cm^3	1.349
μ/mm^{-1}	1.410
F(000)	856.0
Crystal size/mm^3	0.16 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.712 to 147.066
Index ranges	$-10 \leq h \leq 14$, $-16 \leq k \leq 16$, $-15 \leq l \leq 13$
Reflections collected	7847
Independent reflections	3965 [R_{int} = 0.0337, R_{sigma} = 0.0410]
Data/restraints/parameters	3965/0/272
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0512, wR_2 = 0.1342
Final R indexes [all data]	R_1 = 0.0547, wR_2 = 0.1402

Largest diff. peak/hole / e Å^{-3} 0.48/-0.52

5.3 Crystal structure of 3s

Preparation of the single crystals of **3s**: 20.0 mg of pure compound **3s** was dissolved in the combined solvents of dichloromethane and petroleum ether (6.0 mL, v/v = 1:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at 20 °C. After about two days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **3s**. The data were collected on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 120.00(10) K during data collection.

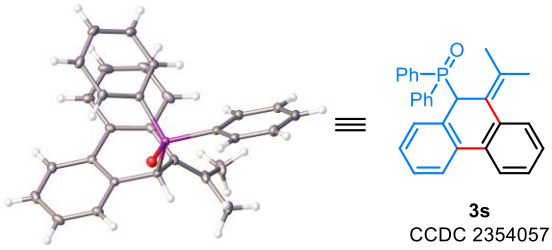


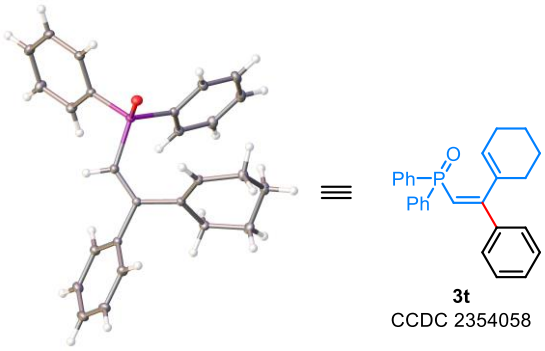
Table S3 Crystal data and structure refinement for **3s**.

Identification code	**3s**
Empirical formula	$C_{29}H_{25}OP$
Formula weight	420.46
Temperature/K	120.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.16530(10)
b/Å	15.5130(2)
c/Å	13.4254(2)
α/°	90
β/°	109.7320(10)
γ/°	90
Volume/Å^3	2188.84(5)

Z	4
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	1.244
F(000)	888.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.944 to 152.86
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -16 ≤ l ≤ 13
Reflections collected	16480
Independent reflections	4430 [R_{int} = 0.0196, R_{sigma} = 0.0164]
Data/restraints/parameters	4430/0/282
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.0955
Final R indexes [all data]	R_1 = 0.0405, wR_2 = 0.0963
Largest diff. peak/hole / e Å^{-3}	0.34/-0.37

5.4 Crystal structure of 3t

Preparation of the single crystals of **3t**: 20.0 mg of pure compound **3t** was dissolved in the combined solvents of dichloromethane and petroleum ether (2.0 mL, v/v = 1:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at 16 ºC. After about two days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure and relative configuration of **3t**. The data were collected on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 153.15 K during data collection.



3t
CCDC 2354058

Table S4 Crystal data and structure refinement for **3t**.

Identification code	**3t**
Empirical formula	$C_{26}H_{25}OP$
Formula weight	384.43
Temperature/K	153.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.0883(6)
b/Å	6.3238(2)
c/Å	21.6180(8)
α/°	90
β/°	109.454(4)
γ/°	90
Volume/Å^3	2073.83(14)
Z	4
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	1.261
F(000)	816.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.826 to 153.534
Index ranges	$-20 \le h \le 20$, $-3 \le k \le 7$, $-27 \le l \le 27$

Reflections collected	13907
Independent reflections	4158 [R_{int} = 0.0460, R_{sigma} = 0.0389]
Data/restraints/parameters	4158/0/253
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0607, wR_2 = 0.1649
Final R indexes [all data]	R_1 = 0.0726, wR_2 = 0.1727
Largest diff. peak/hole / e $Å^{-3}$	0.41/-0.40

5.5 Crystal structure of 4a

Preparation of the single crystals of **4a**: 20.0 mg of pure compound **4a** was dissolved in the combined solvents of dichloromethane and ethyl acetate (3.0 mL, v/v = 2:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After about two days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **4a**. The data were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 150.00 K during data collection.

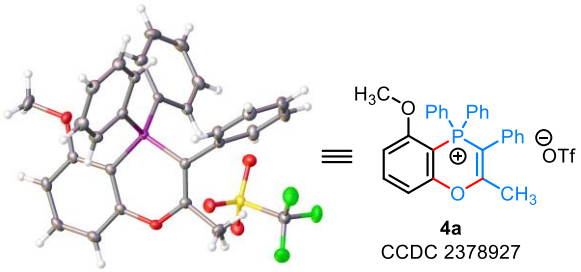


Table S5 Crystal data and structure refinement for **4a**.

Identification code	**4a**
Empirical formula	$C_{29}H_{24}F_3O_5PS$
Formula weight	572.51
Temperature/K	150.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.5096(6)

b/Å	15.4521(8)
c/Å	16.5422(9)
α/°	90
β/°	90.04(4)
γ/°	90
Volume/Å^3	2686.4(3)
Z	4
ρ_{calc}g/cm^3	1.416
μ/mm^{-1}	2.157
F(000)	1184.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.83 to 136.558
Index ranges	-12 ≤ h ≤ 11, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	29596
Independent reflections	4817 [R_{int} = 0.0483, R_{sigma} = 0.0358]
Data/restraints/parameters	4817/0/354
Goodness-of-fit on F^2	1.118
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.1039
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.1045
Largest diff. peak/hole / e Å^{-3}	0.26/-0.45

5.6 Crystal structure of 4c

Preparation of the single crystals of **4c**: 20.0 mg of pure compound **4c** was dissolved in the combined solvents of dichloromethane and petroleum ether (2.0 mL, v/v = 1:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at 16 °C. After about two days, several small particles were observed at

the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **4c**. The data were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 169.99(10) K during data collection.

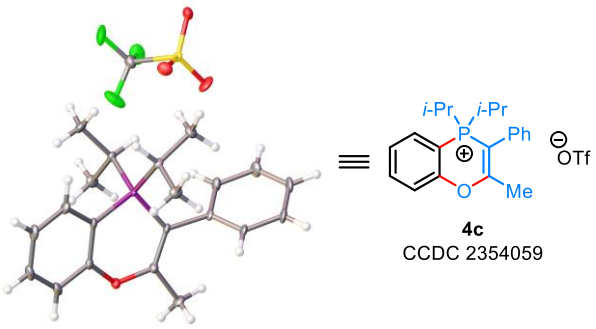


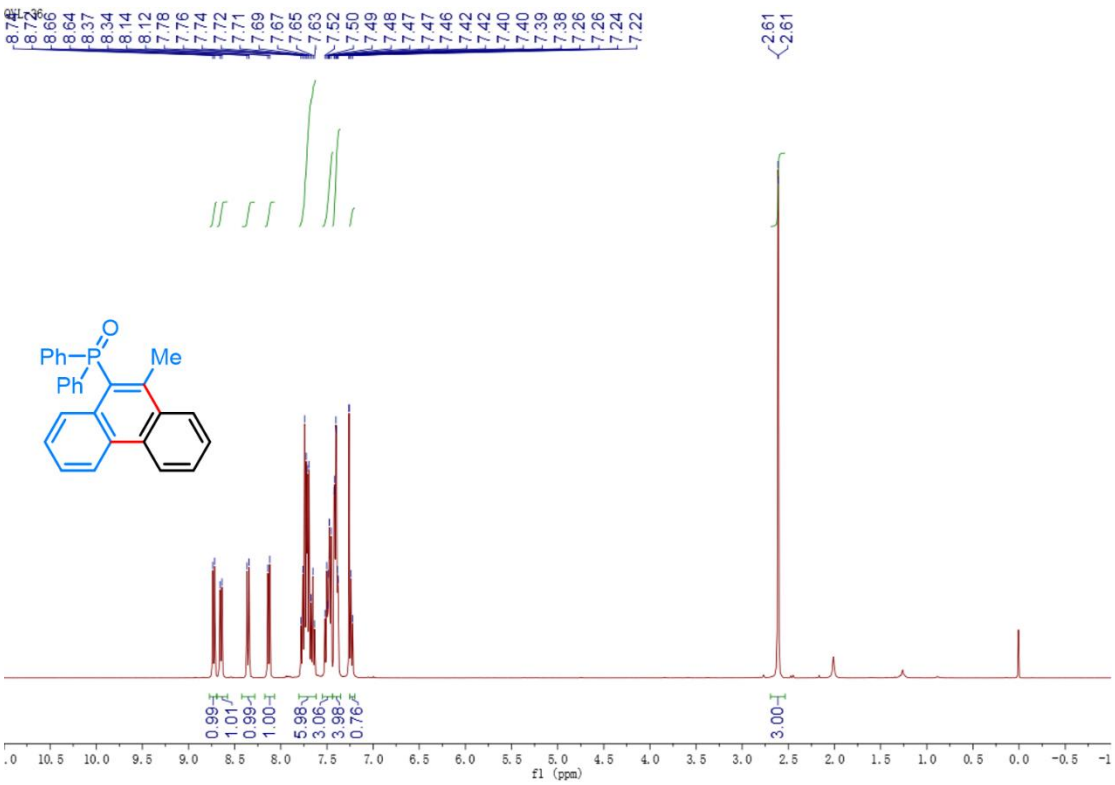
Table S6 Crystal data and structure refinement for **4c**.

Identification code	**4c**
Empirical formula	$C_{23}H_{27}Cl_3F_3O_4PS$
Formula weight	593.82
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.2309(2)
b/Å	22.3914(4)
c/Å	12.3597(2)
α/°	90
β/°	106.861(2)
γ/°	90
Volume/Å^3	2709.69(9)
Z	4
ρ_{calc}g/cm^3	1.456
μ/mm^{-1}	4.778
F(000)	1224.0

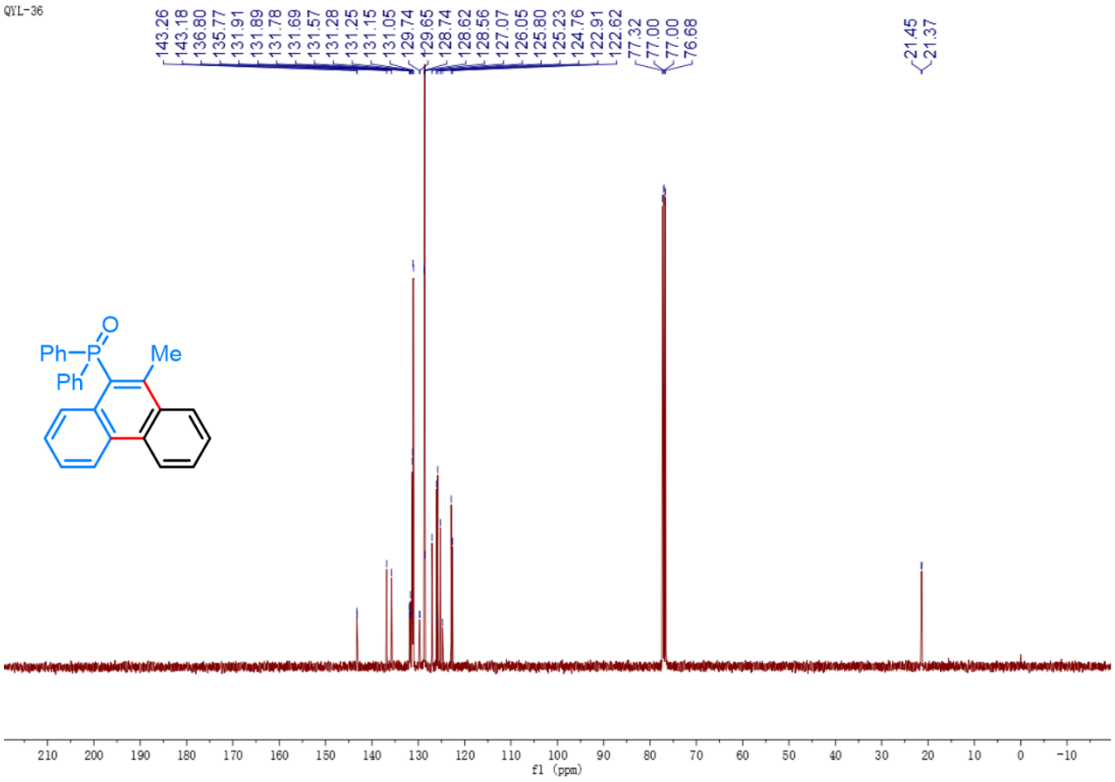
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.896 to 147.642
Index ranges	$-12 \leq h \leq 11$, $-27 \leq k \leq 26$, $-15 \leq l \leq 13$
Reflections collected	11093
Independent reflections	5355 [R_{int} = 0.0494, R_{sigma} = 0.0557]
Data/restraints/parameters	5355/7/322
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0658, wR_2 = 0.1762
Final R indexes [all data]	R_1 = 0.0711, wR_2 = 0.1840
Largest diff. peak/hole / e $Å^{-3}$	0.96/-0.85

6. NMR spectra

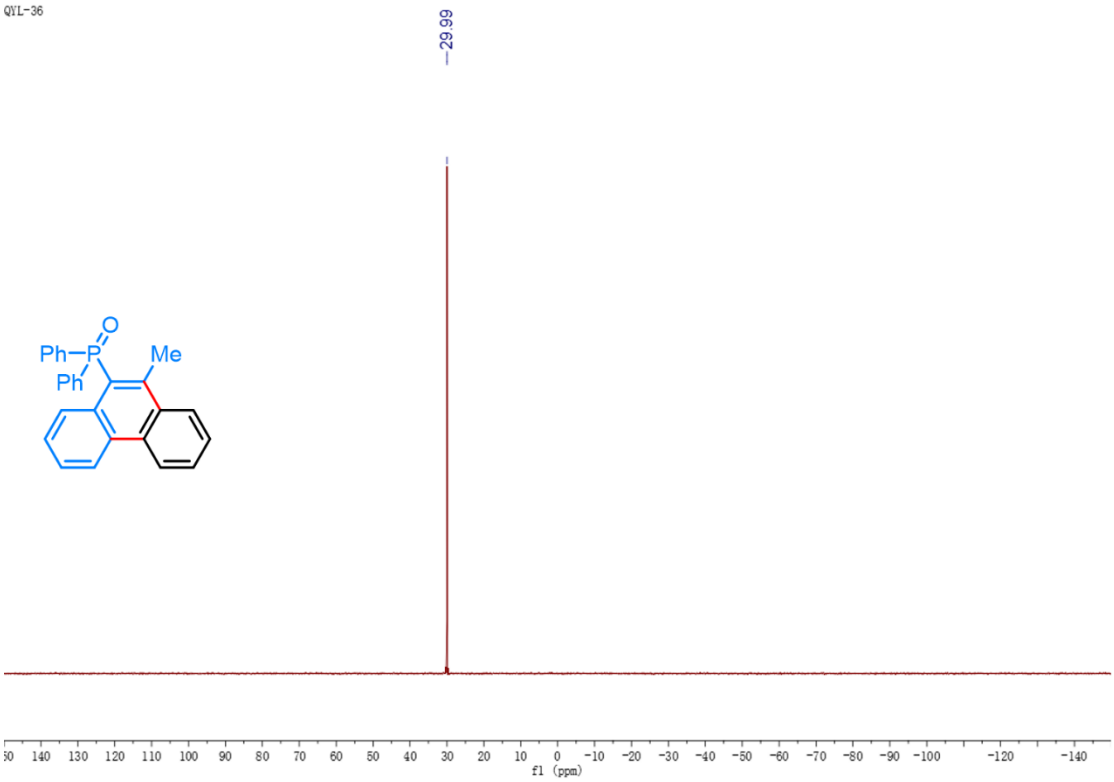
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



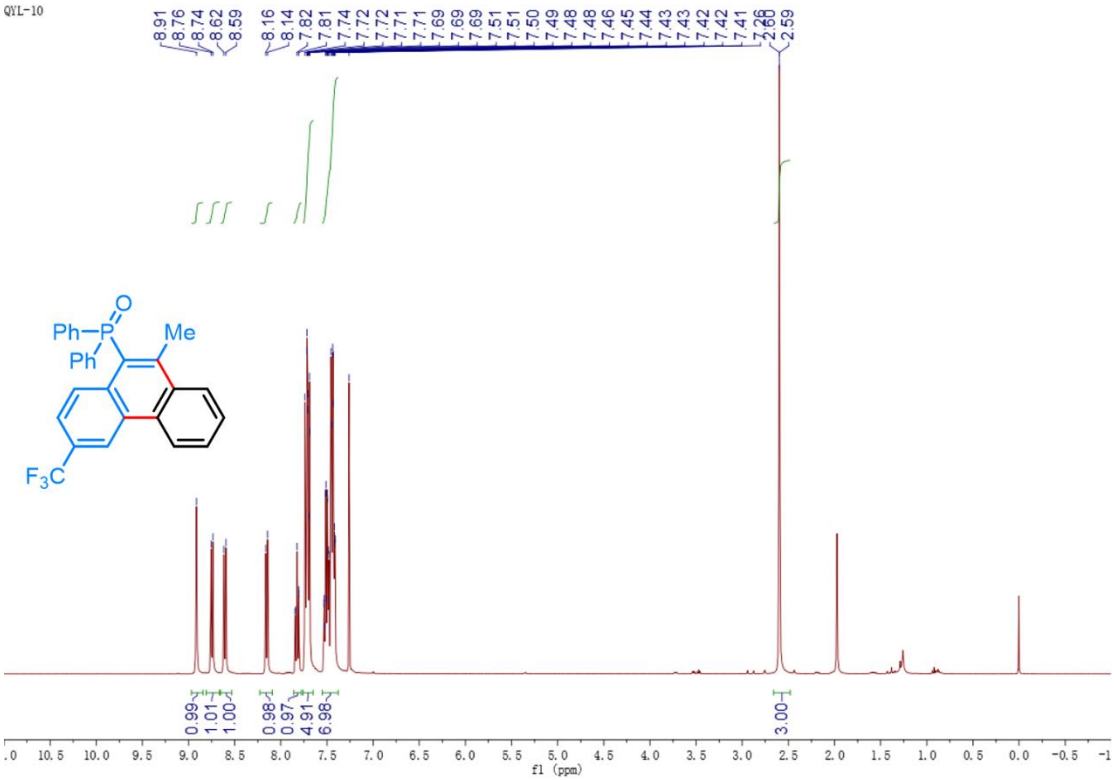
^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)



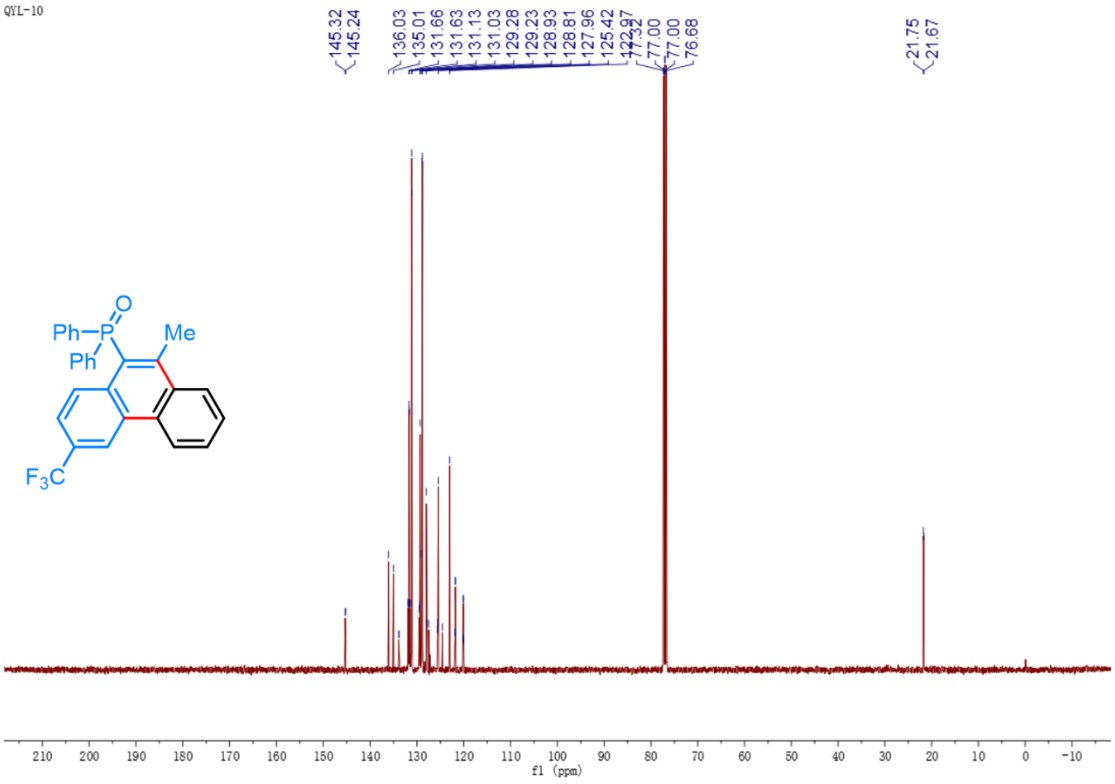
^{31}P NMR spectrum of **3a** (162 MHz, $CDCl_3$)



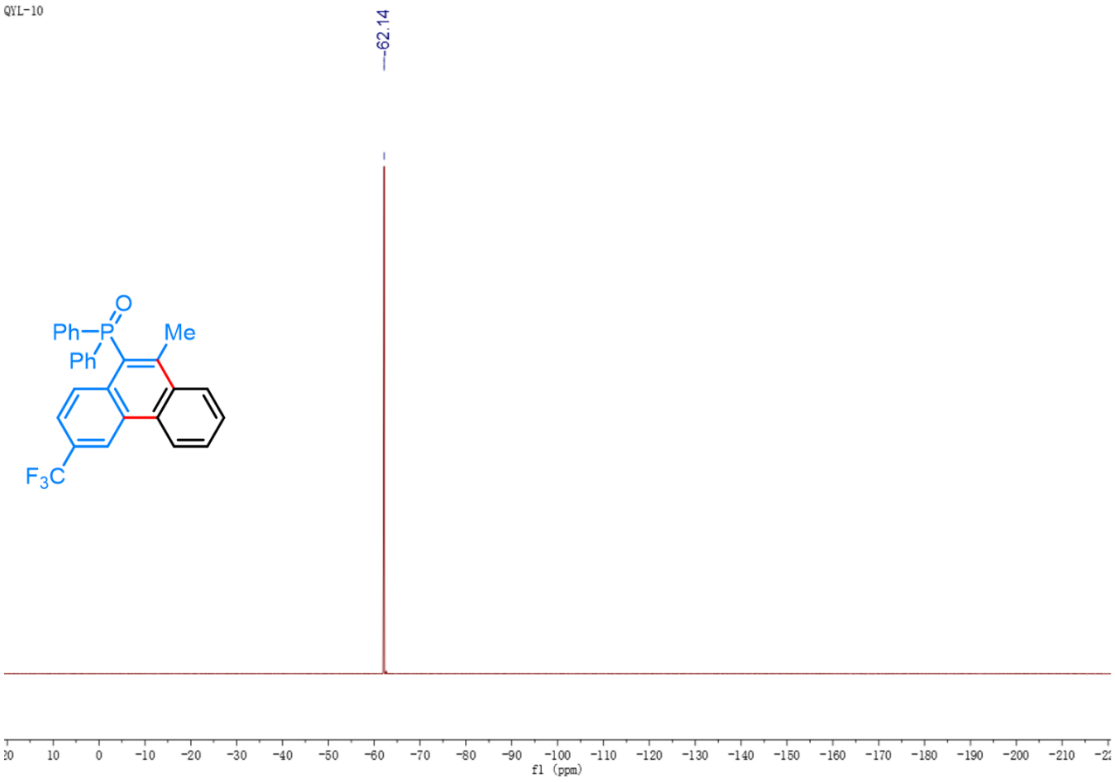
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



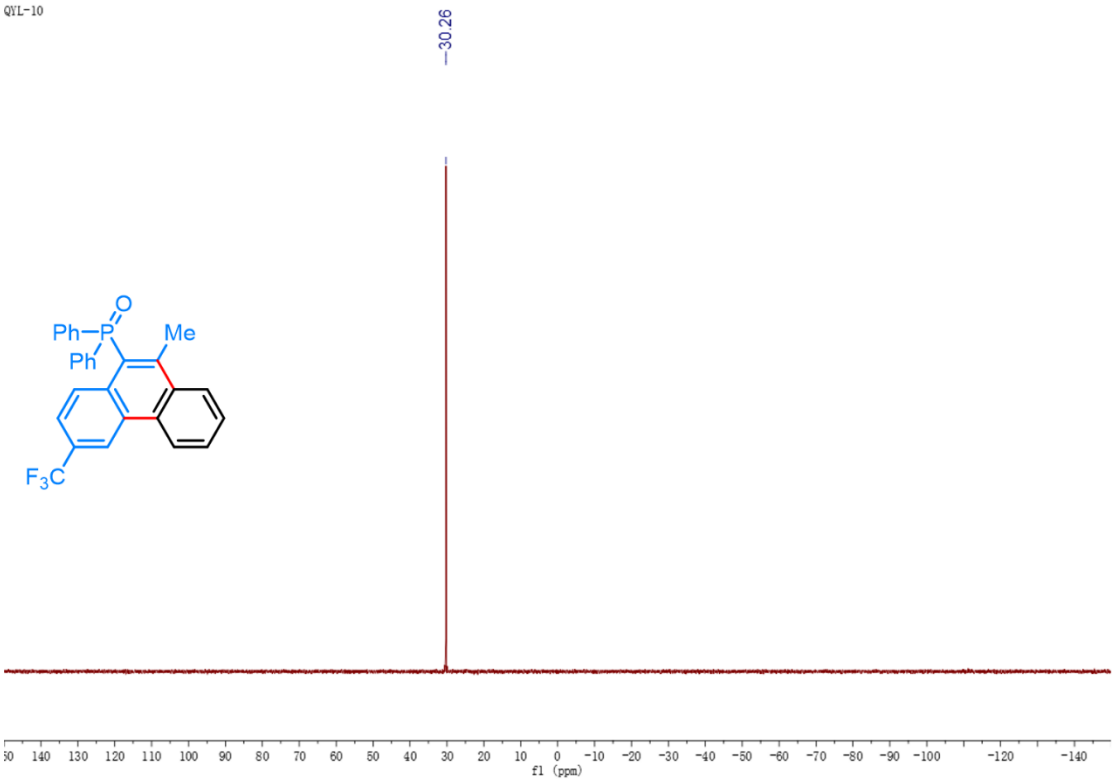
^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)



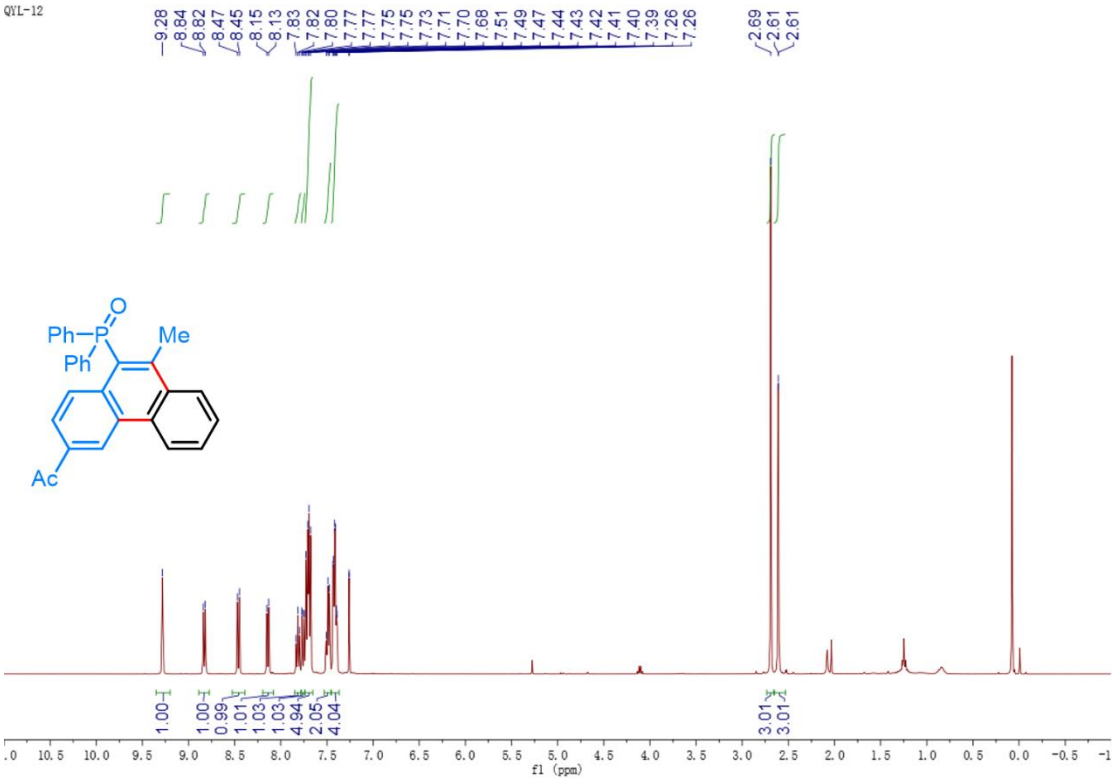
^{19}F NMR spectrum of **3b** (376 MHz, $CDCl_3$)



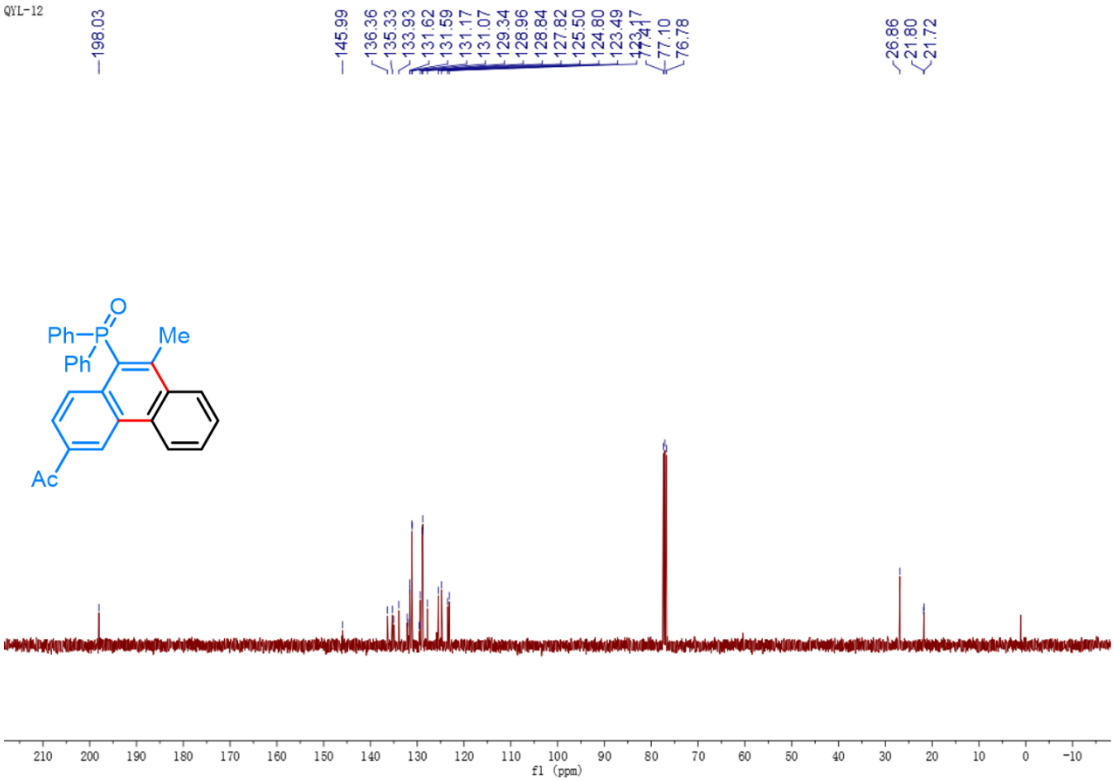
^{31}P NMR spectrum of **3b** (162 MHz, $CDCl_3$)



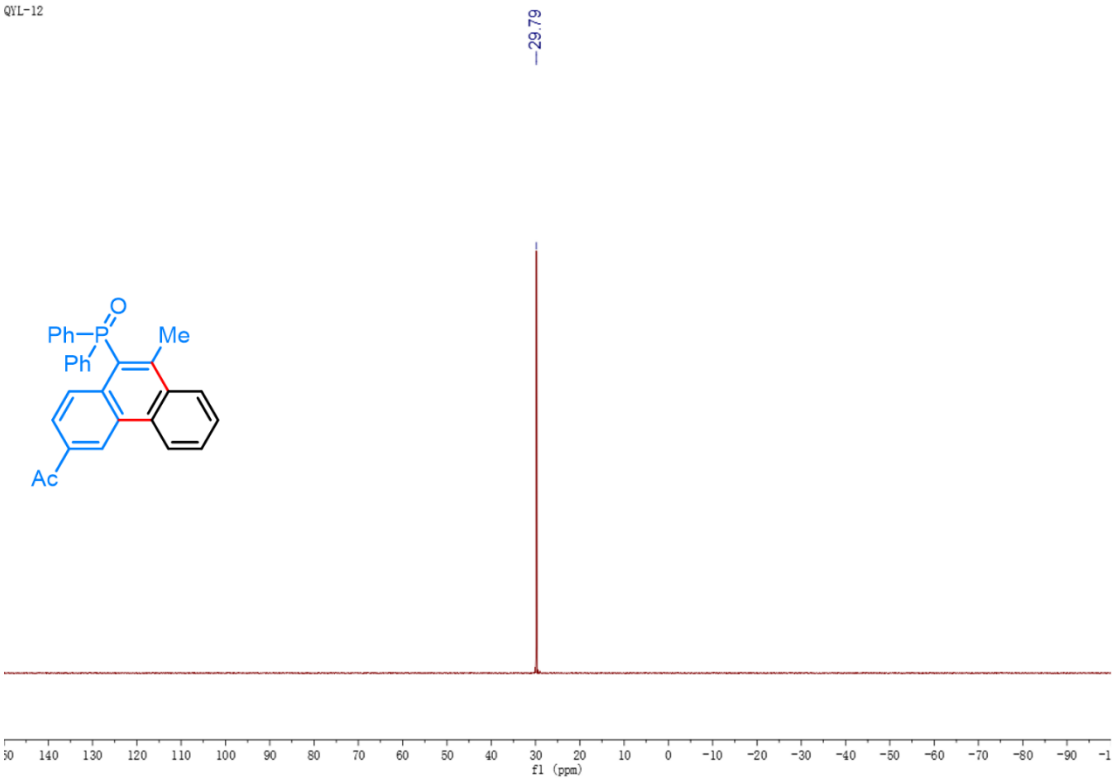
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)



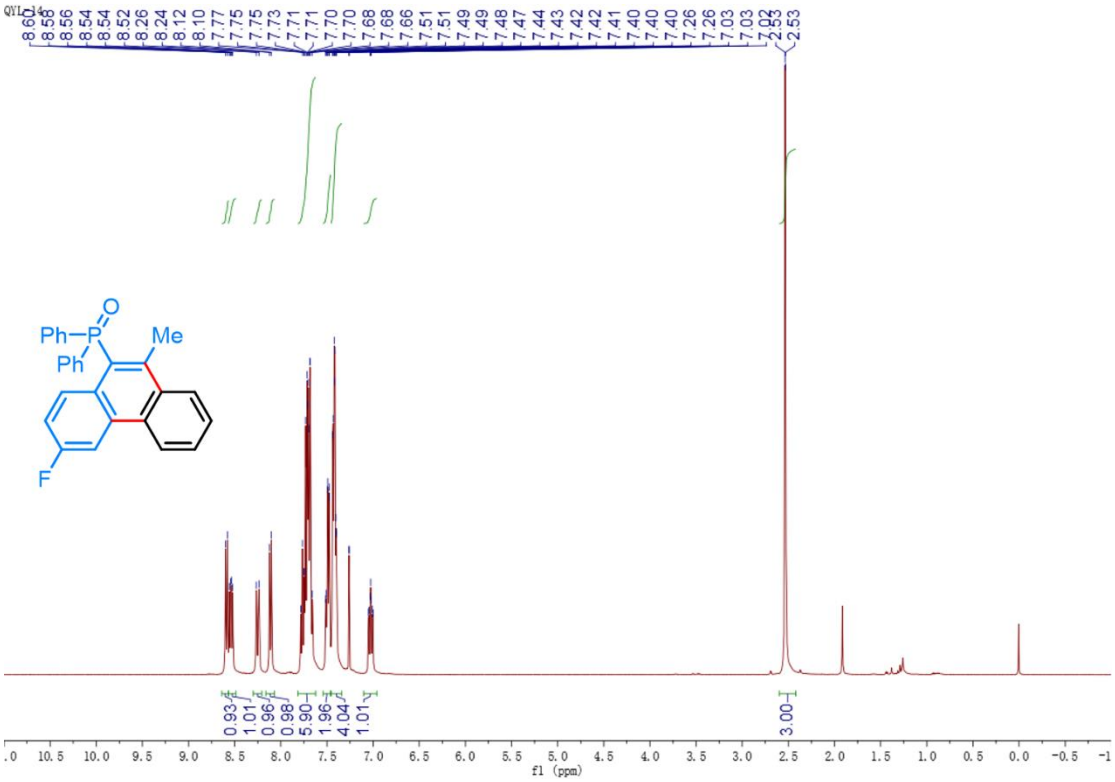
^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$)



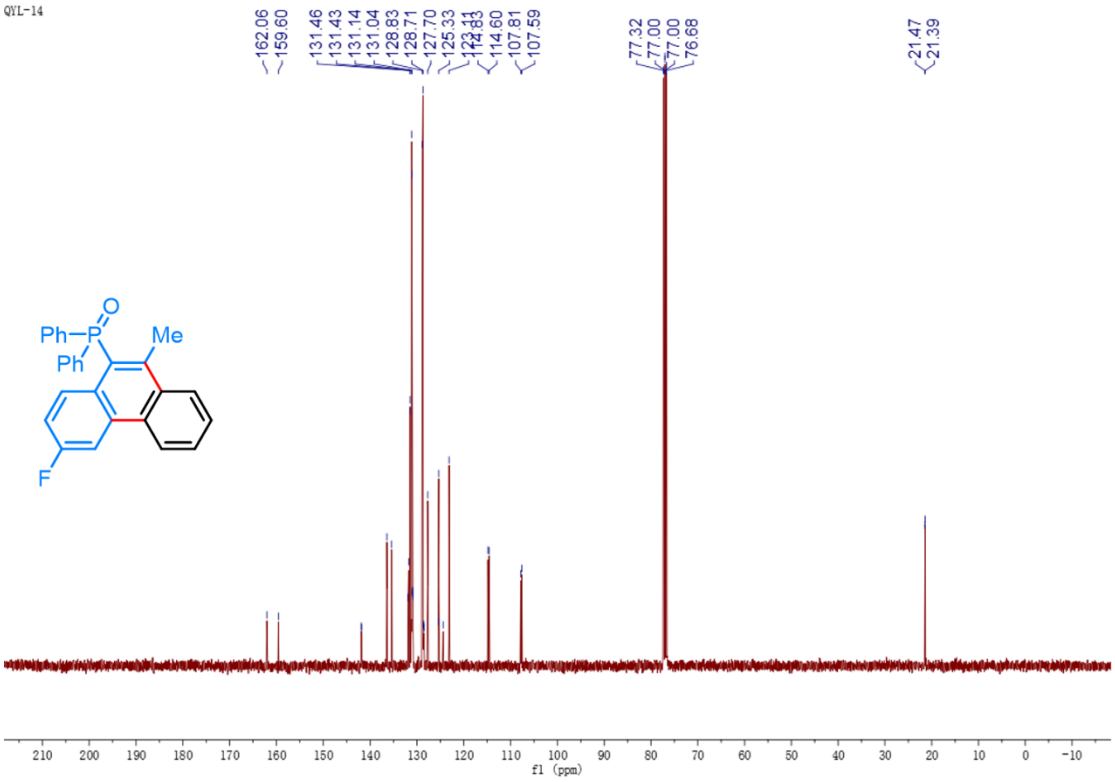
^{31}P NMR spectrum of **3c** (162 MHz, $CDCl_3$)



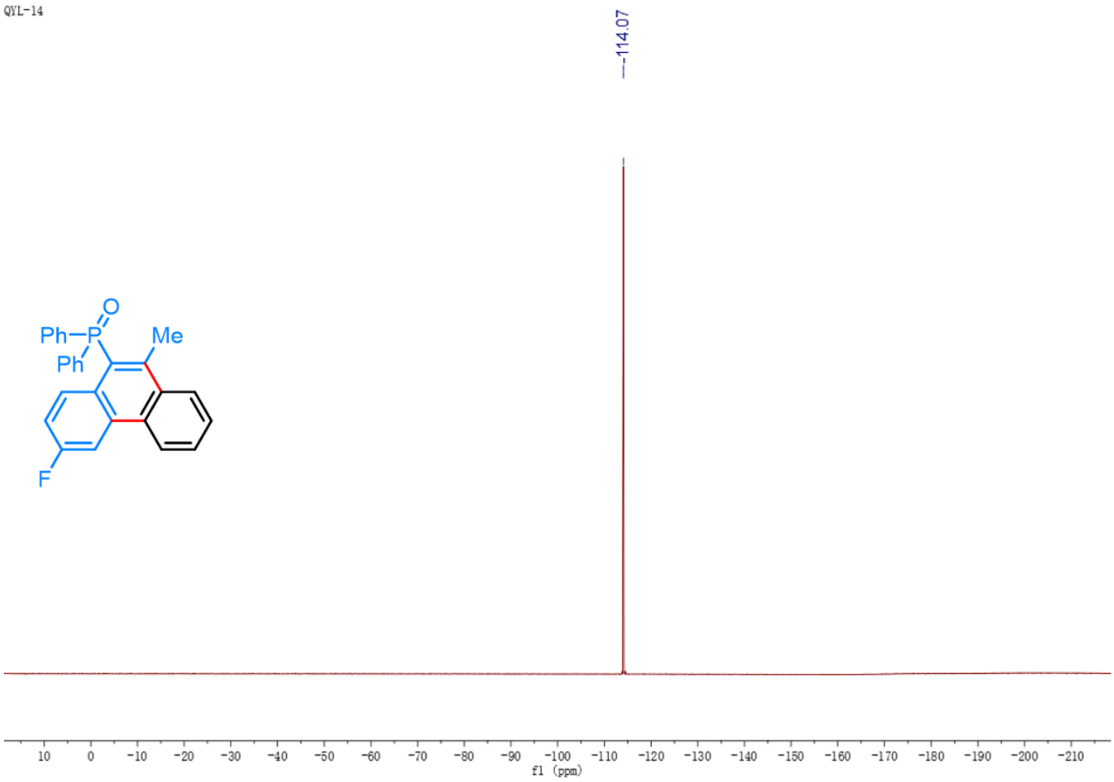
^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)



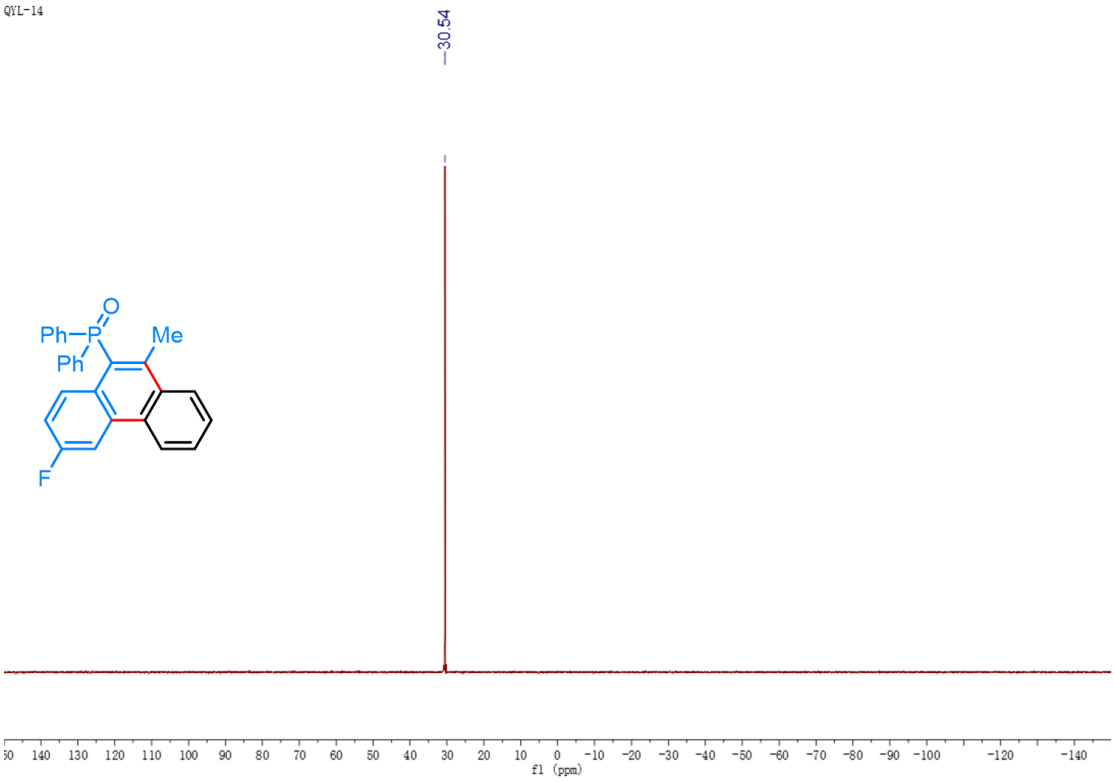
^{13}C NMR spectrum of **3d** (100 MHz, $CDCl_3$)



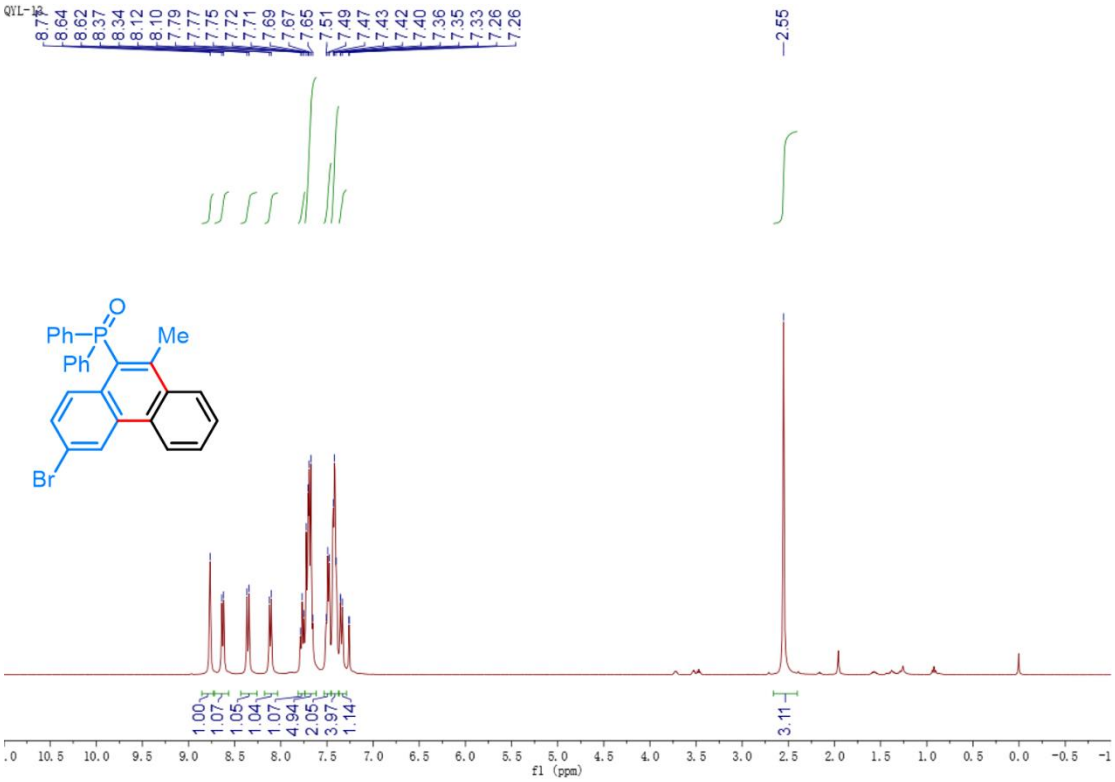
^{19}F NMR spectrum of **3d** (376 MHz, $CDCl_3$)



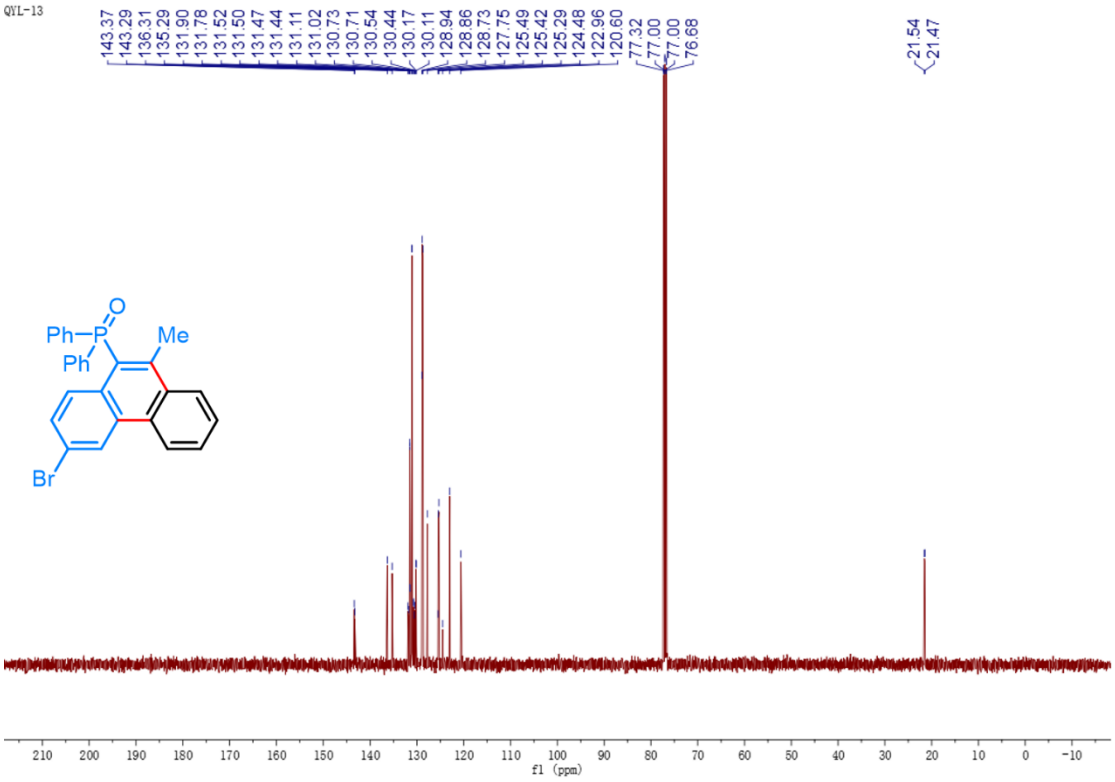
^{31}P NMR spectrum of **3d** (162 MHz, $CDCl_3$)



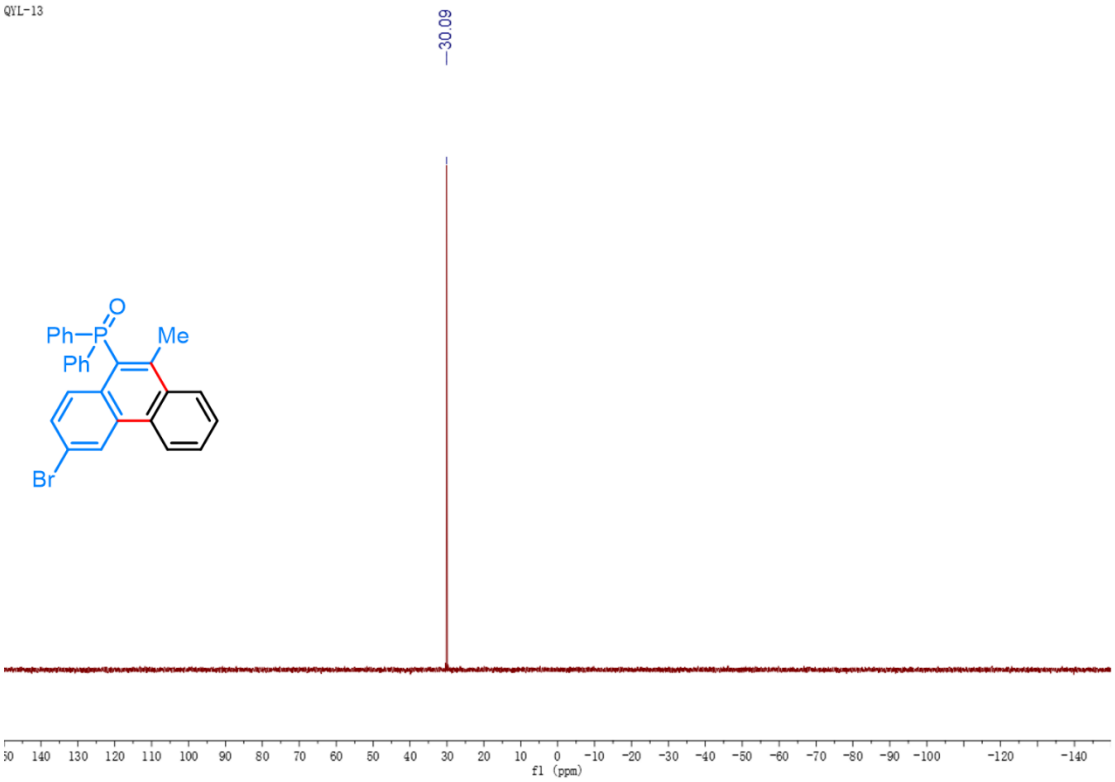
^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



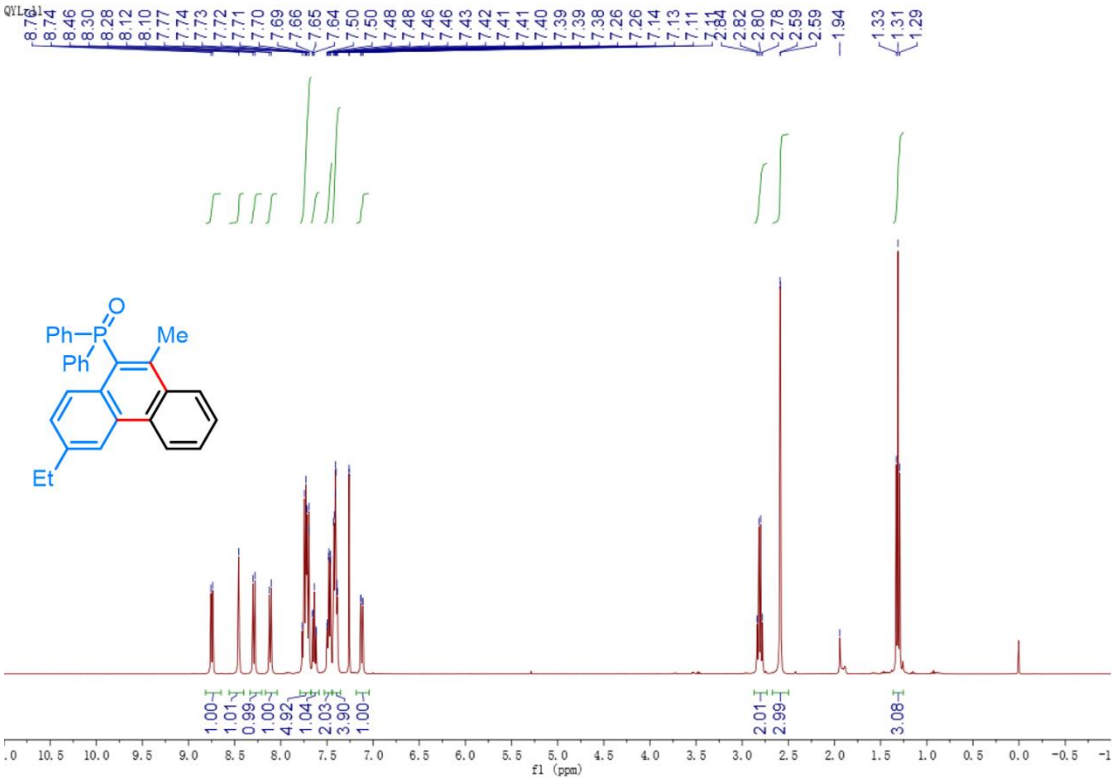
^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$)



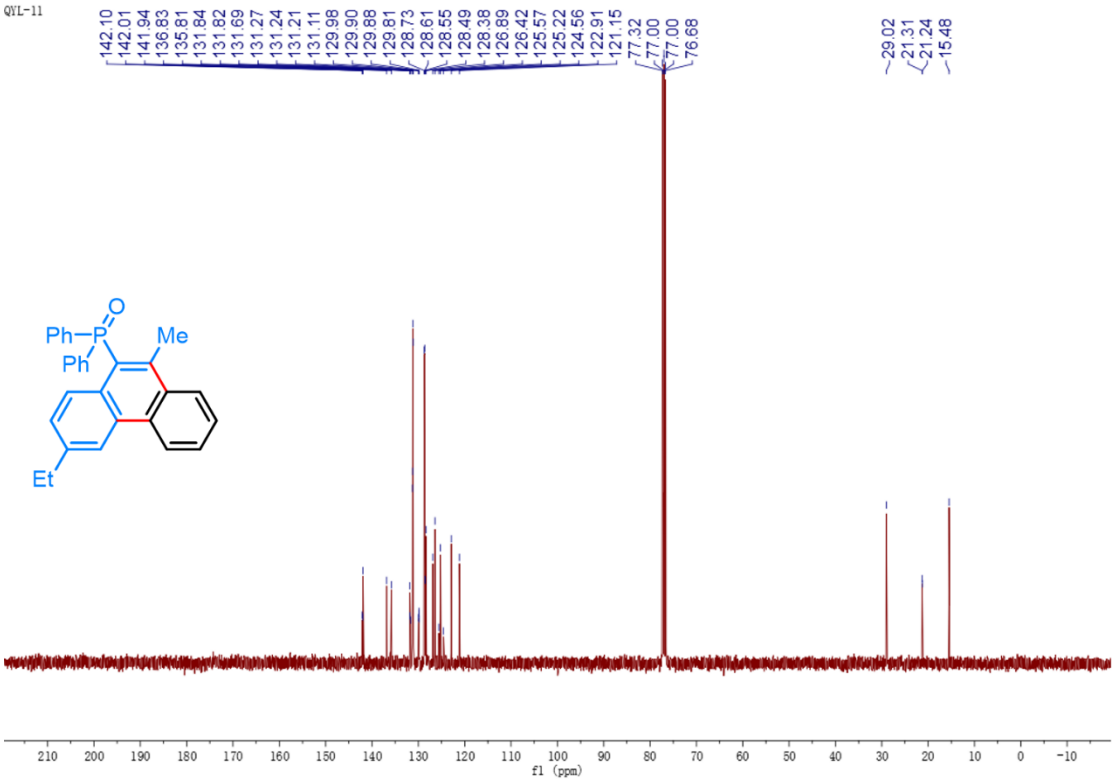
^{31}P NMR spectrum of **3e** (162 MHz, $CDCl_3$)



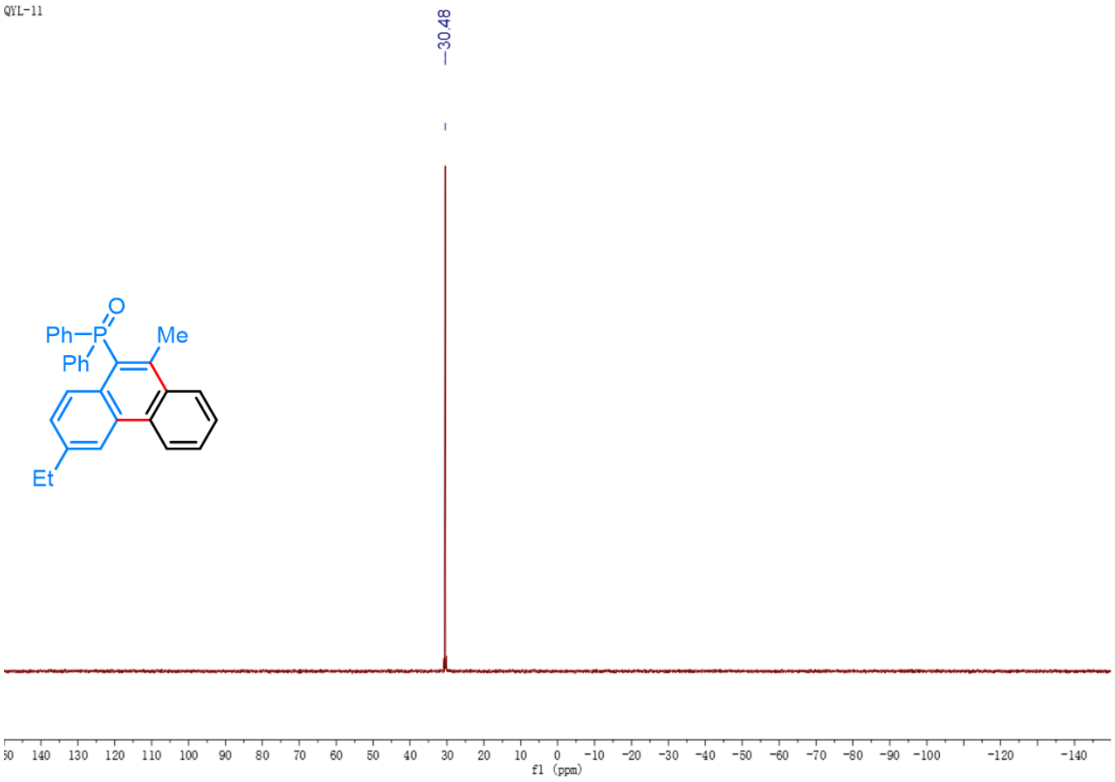
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



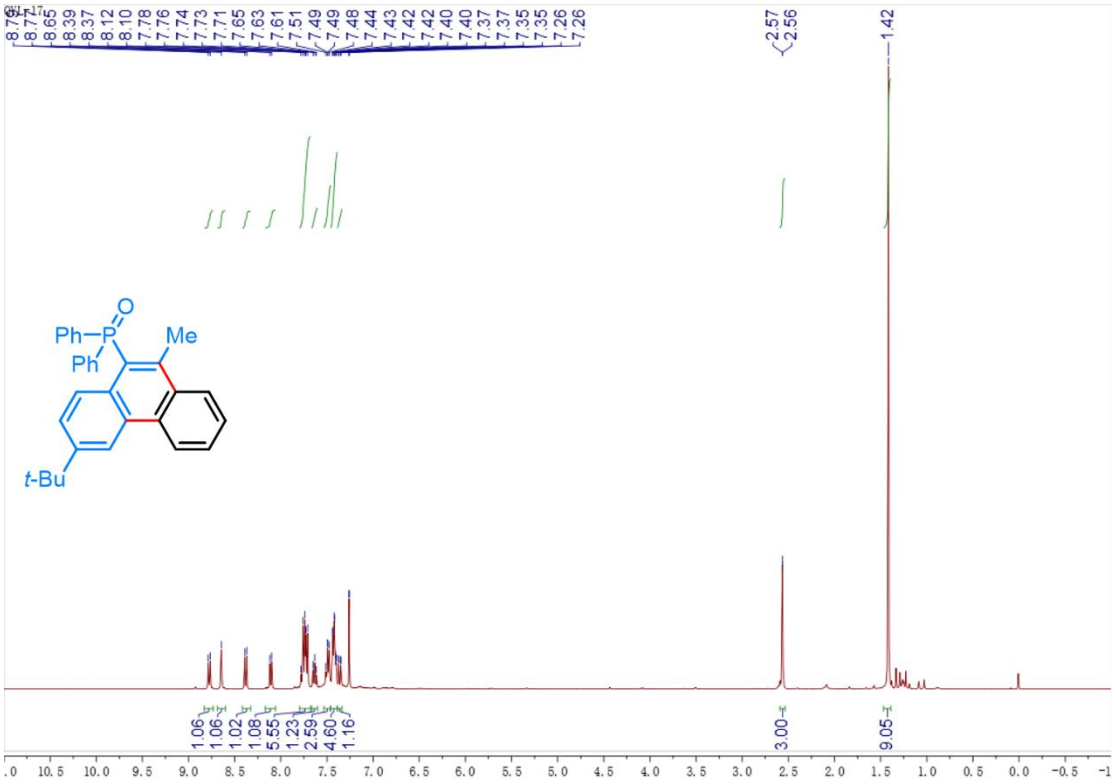
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



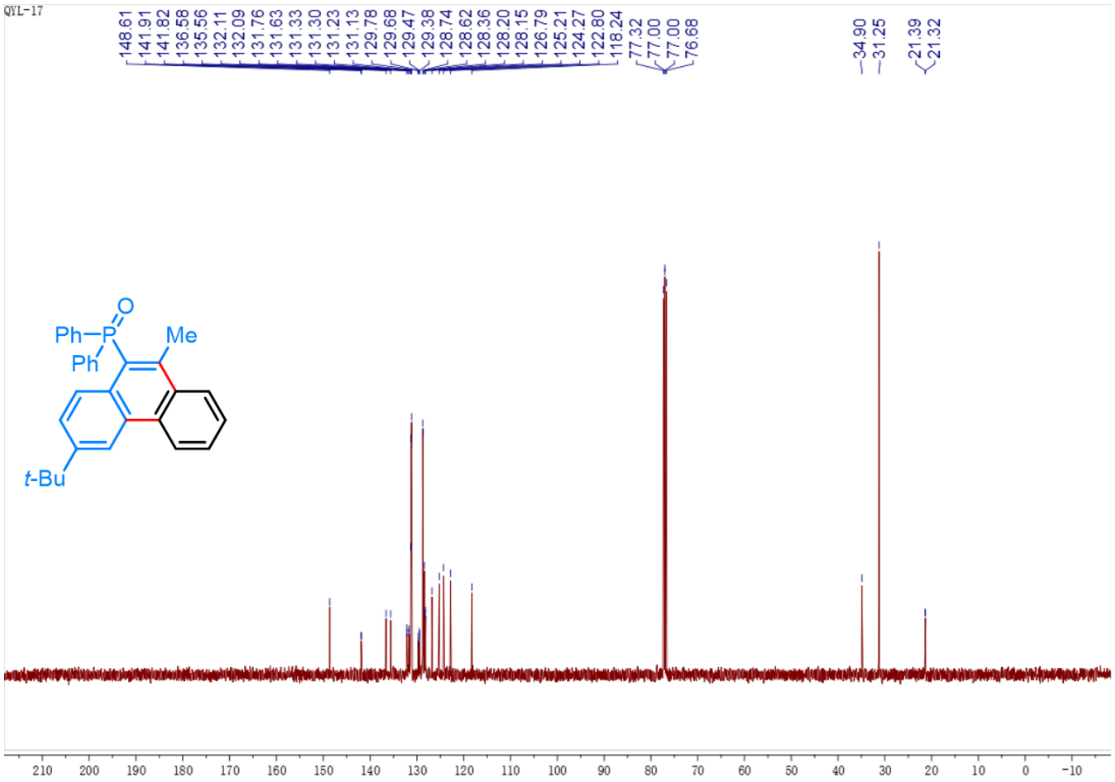
^{31}P NMR spectrum of **3f** (162 MHz, $CDCl_3$)



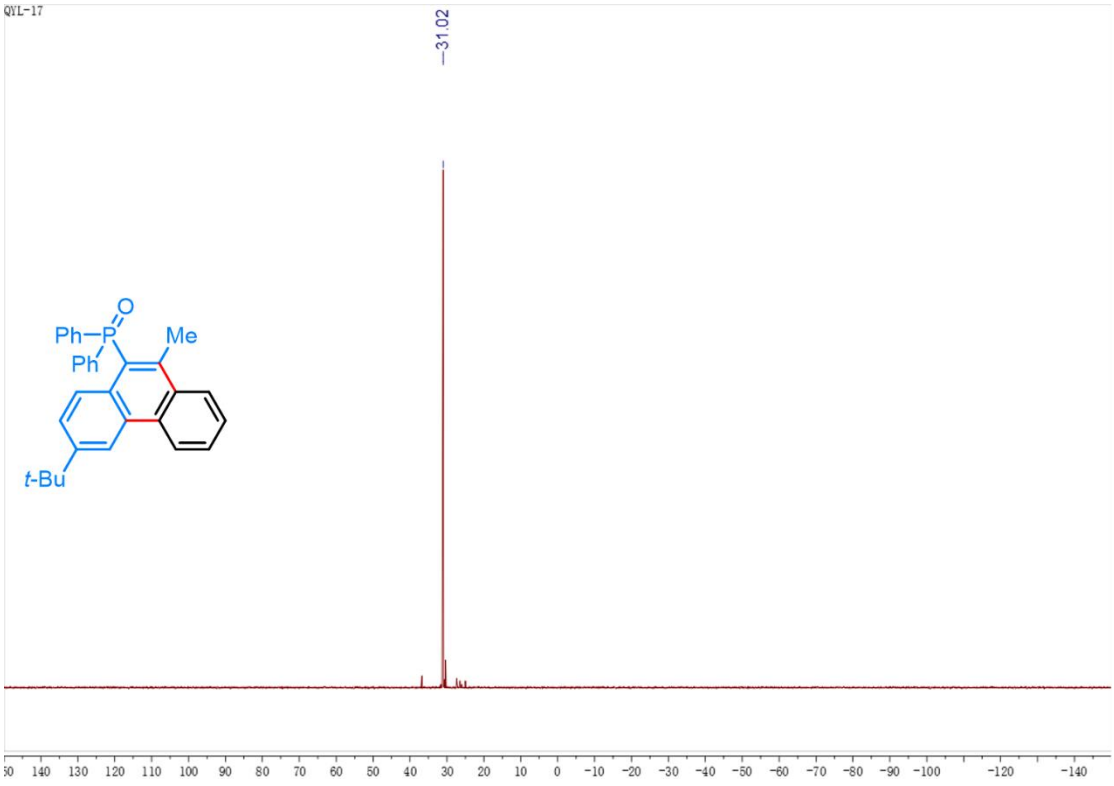
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



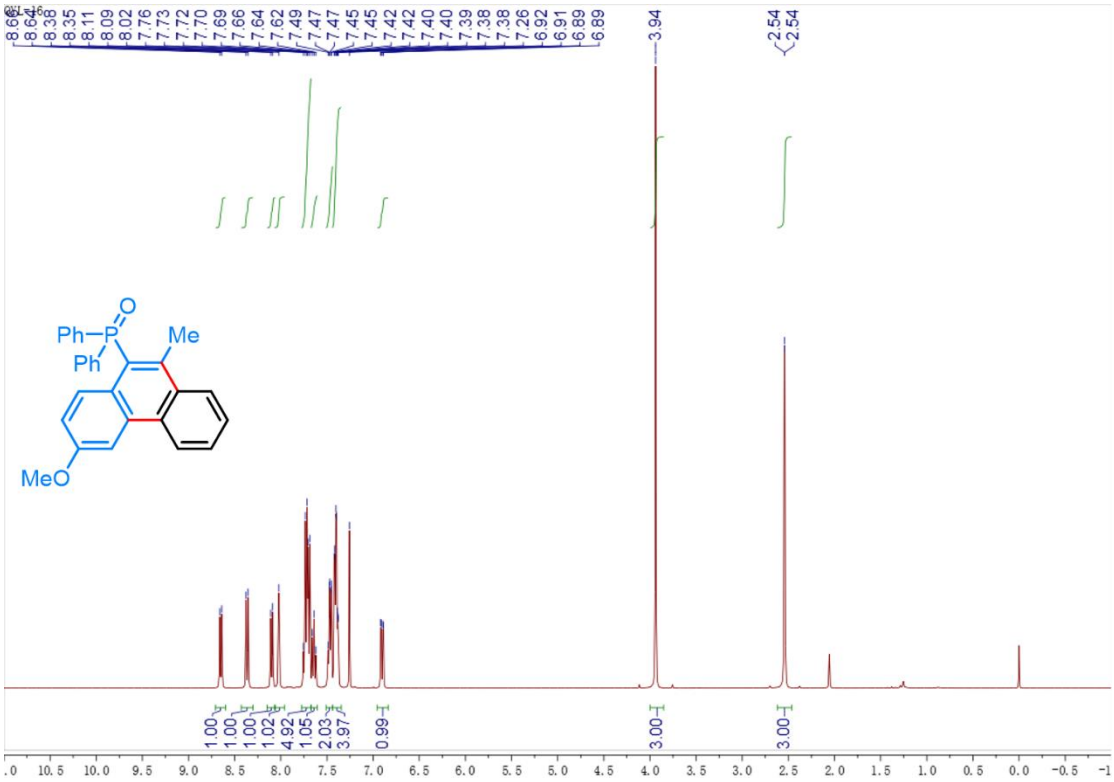
^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$)



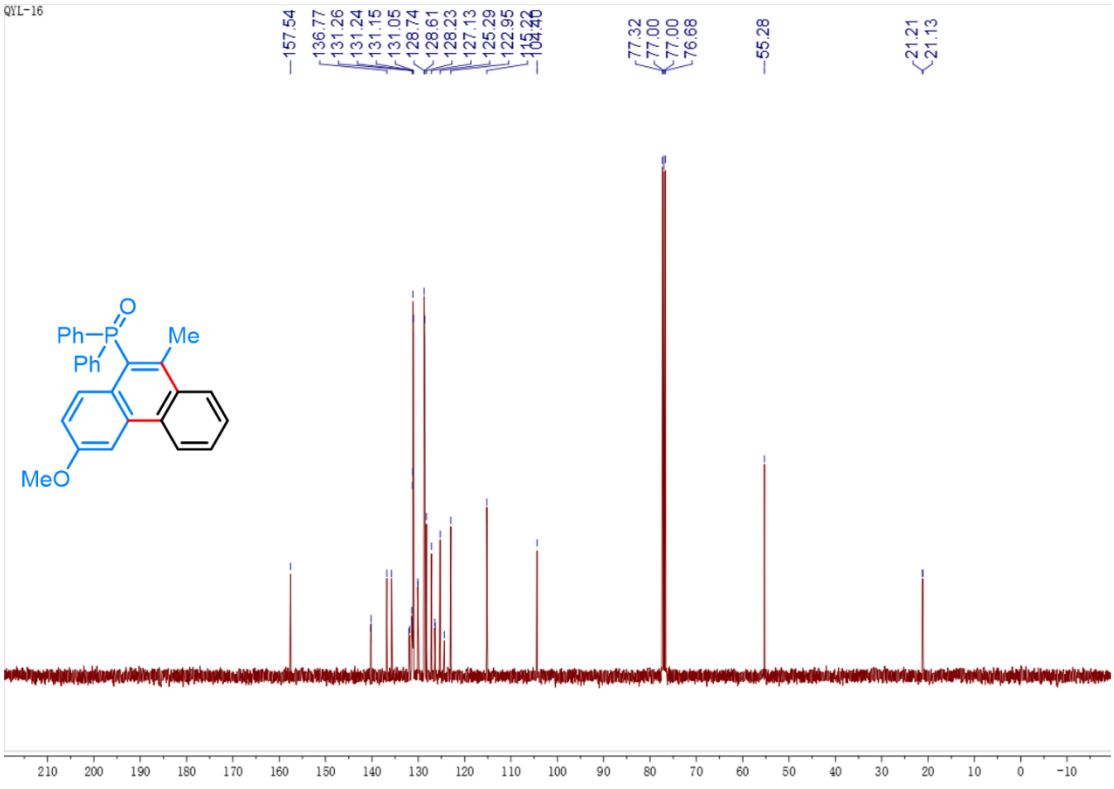
^{31}P NMR spectrum of **3g** (162 MHz, $CDCl_3$)



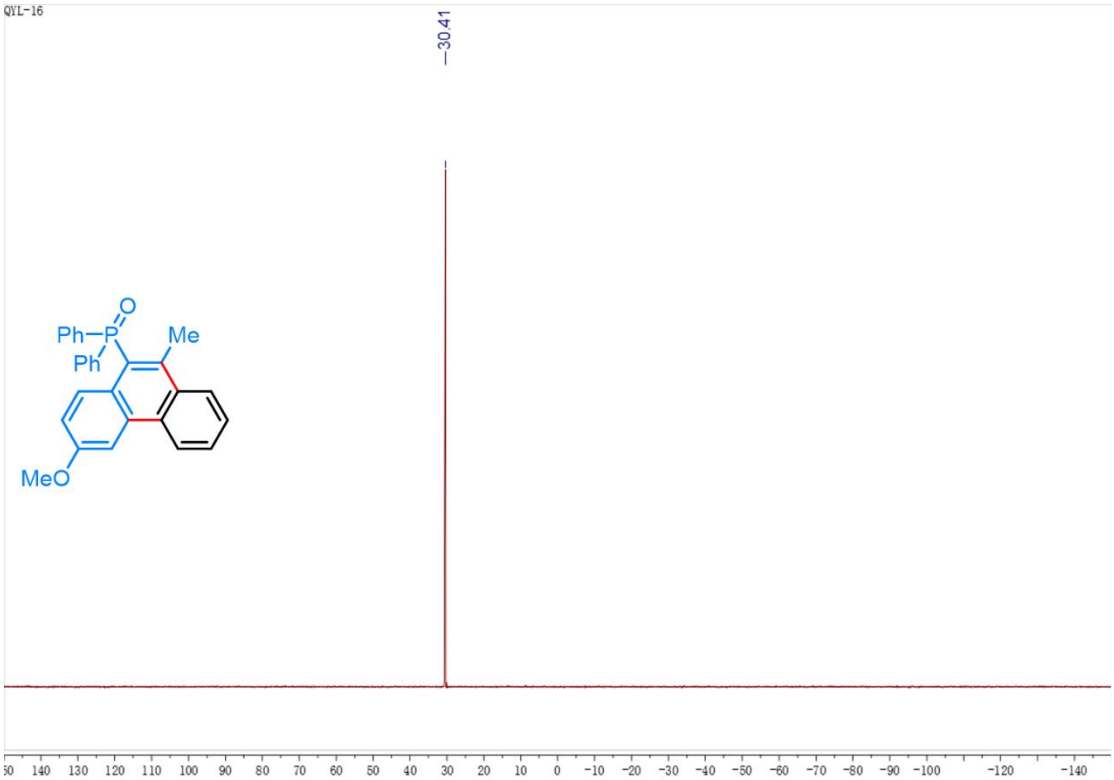
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



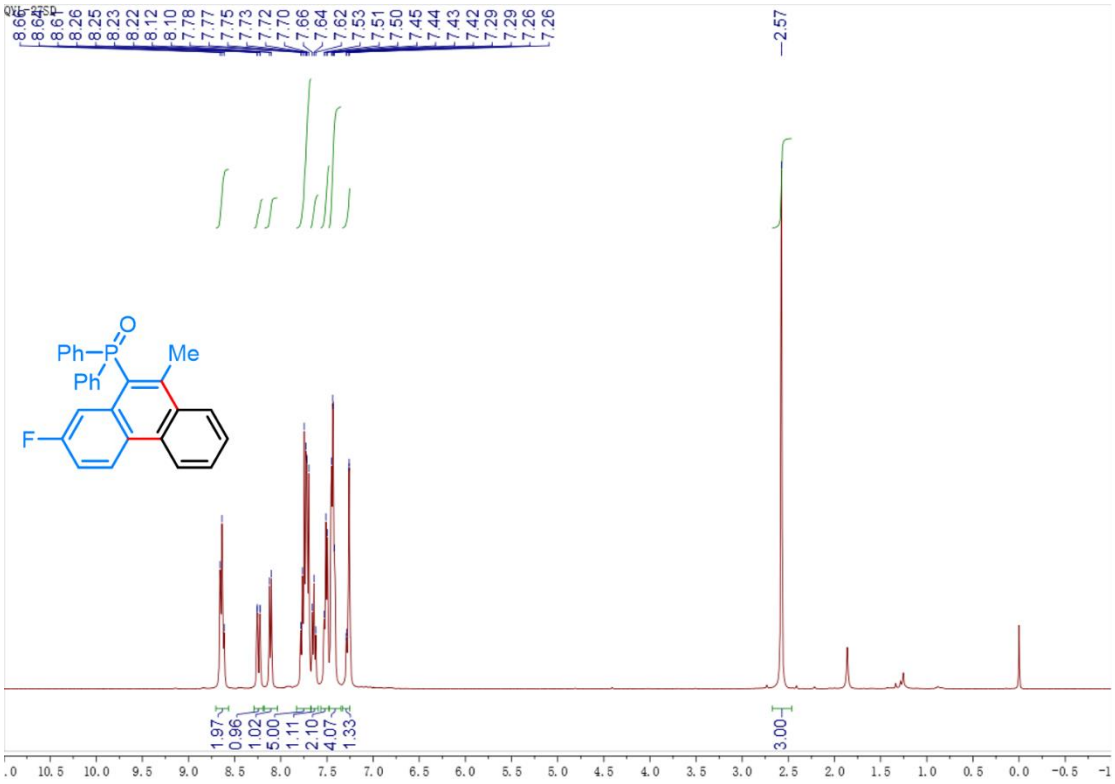
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



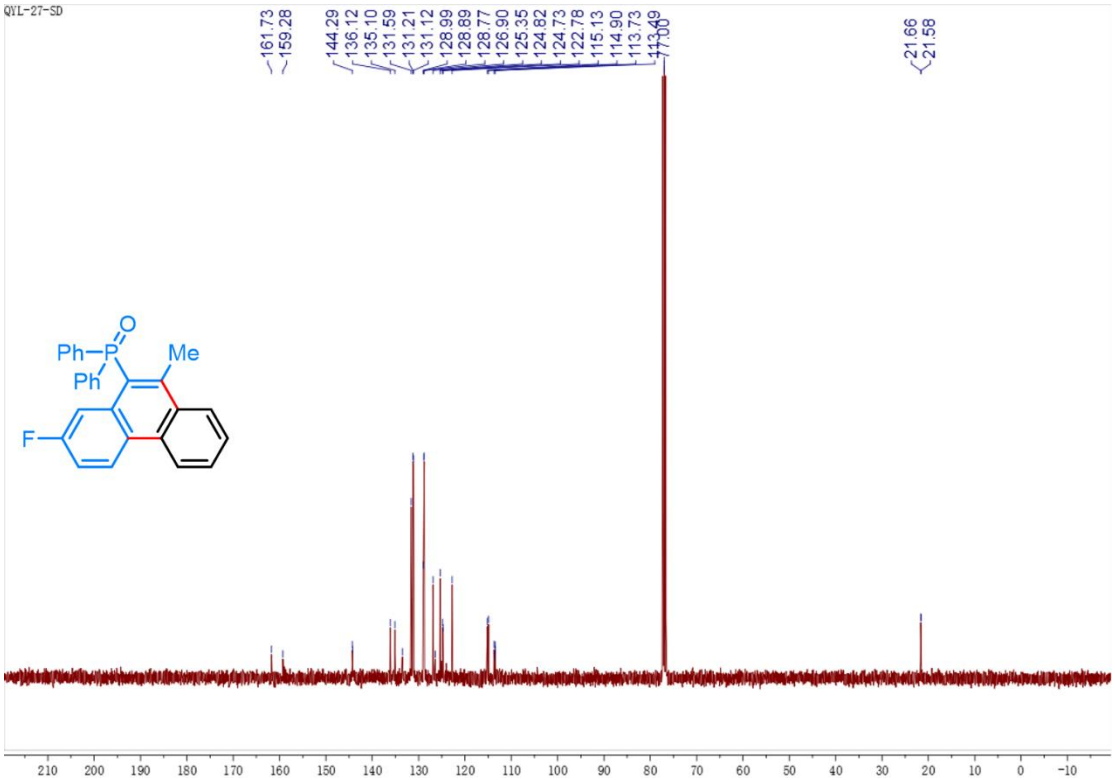
^{31}P NMR spectrum of **3h** (162 MHz, $CDCl_3$)



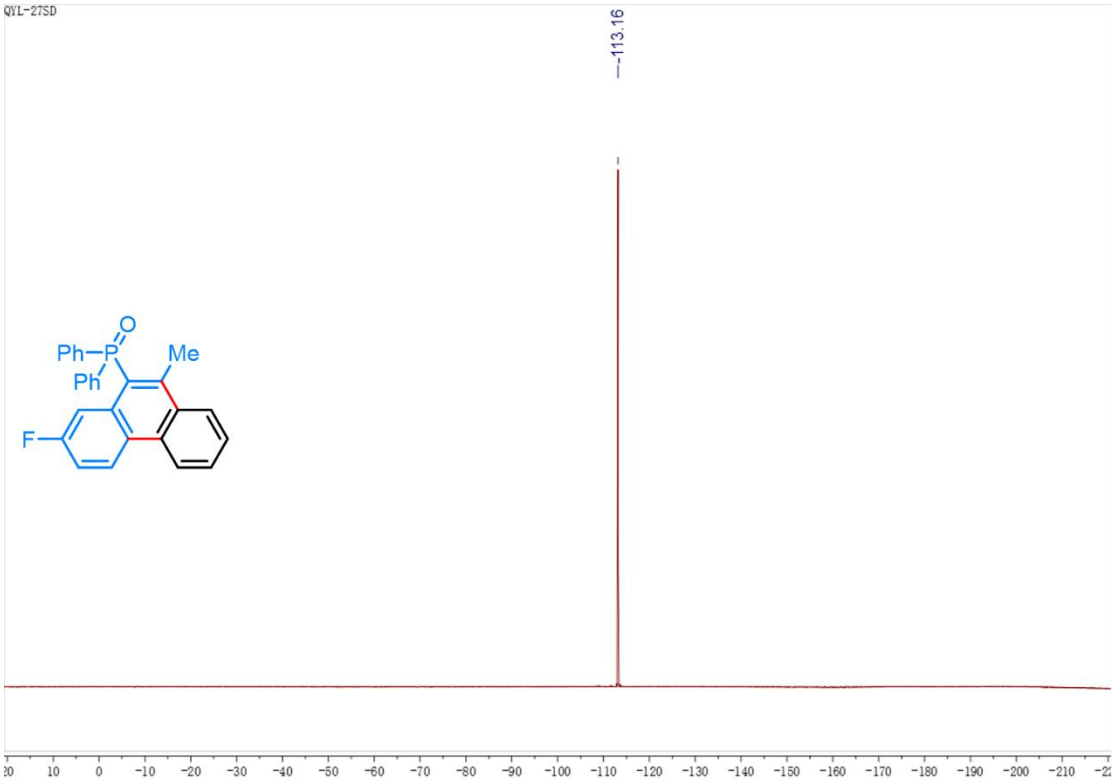
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)



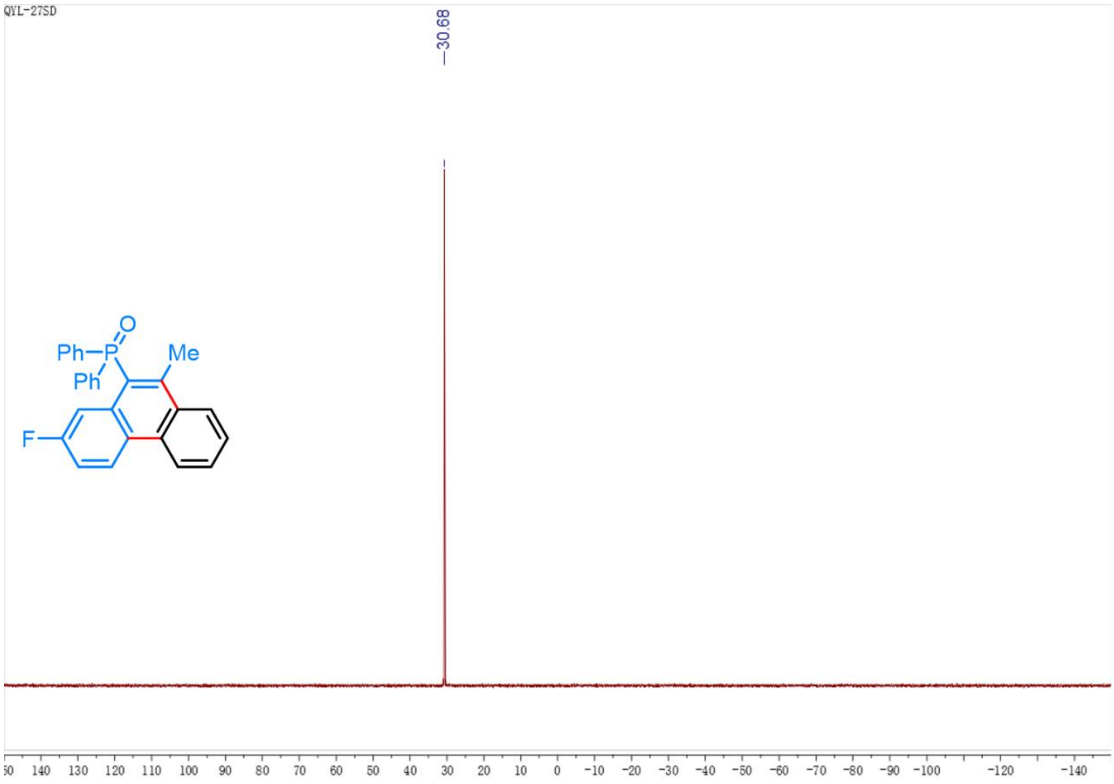
^{13}C NMR spectrum of **3i** (100 MHz, $CDCl_3$)



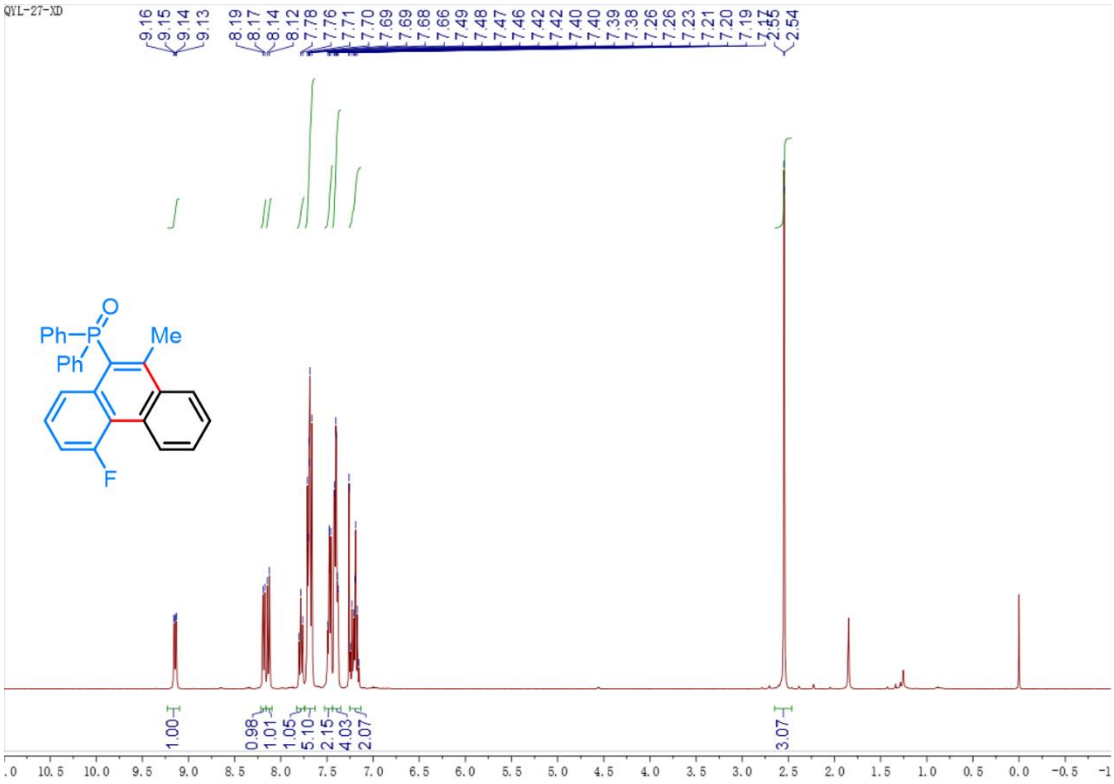
^{19}F NMR spectrum of **3i** (376 MHz, $CDCl_3$)



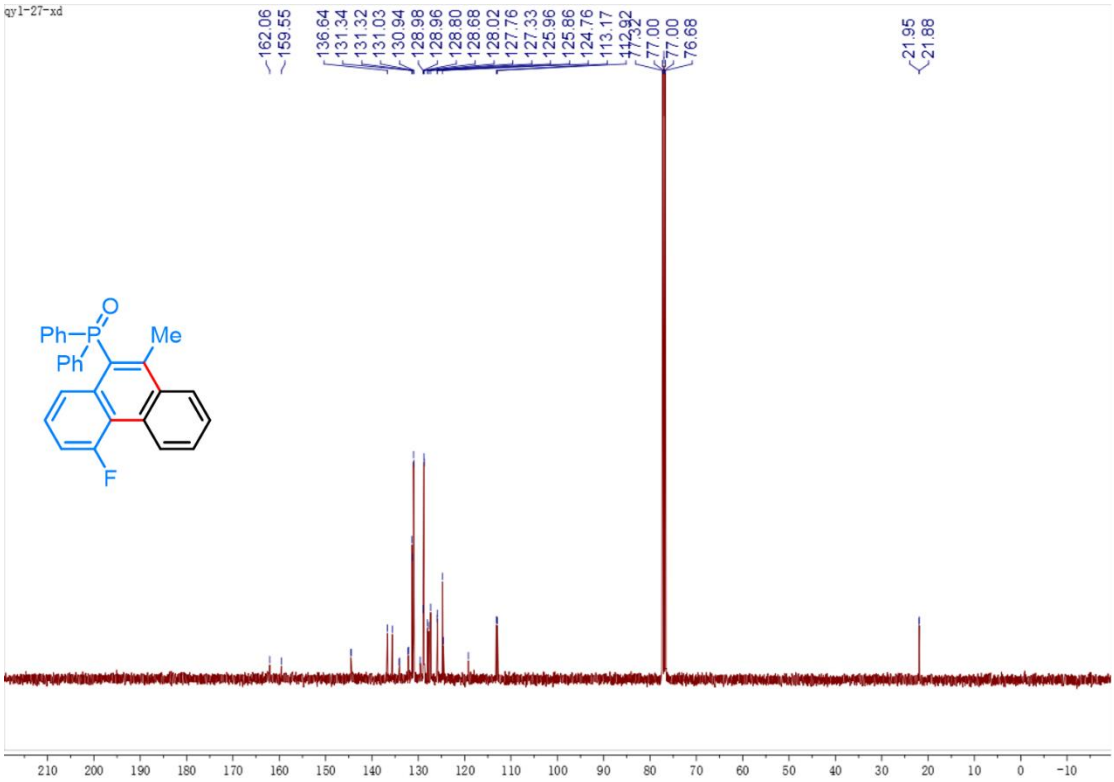
^{31}P NMR spectrum of **3i** (162 MHz, $CDCl_3$)



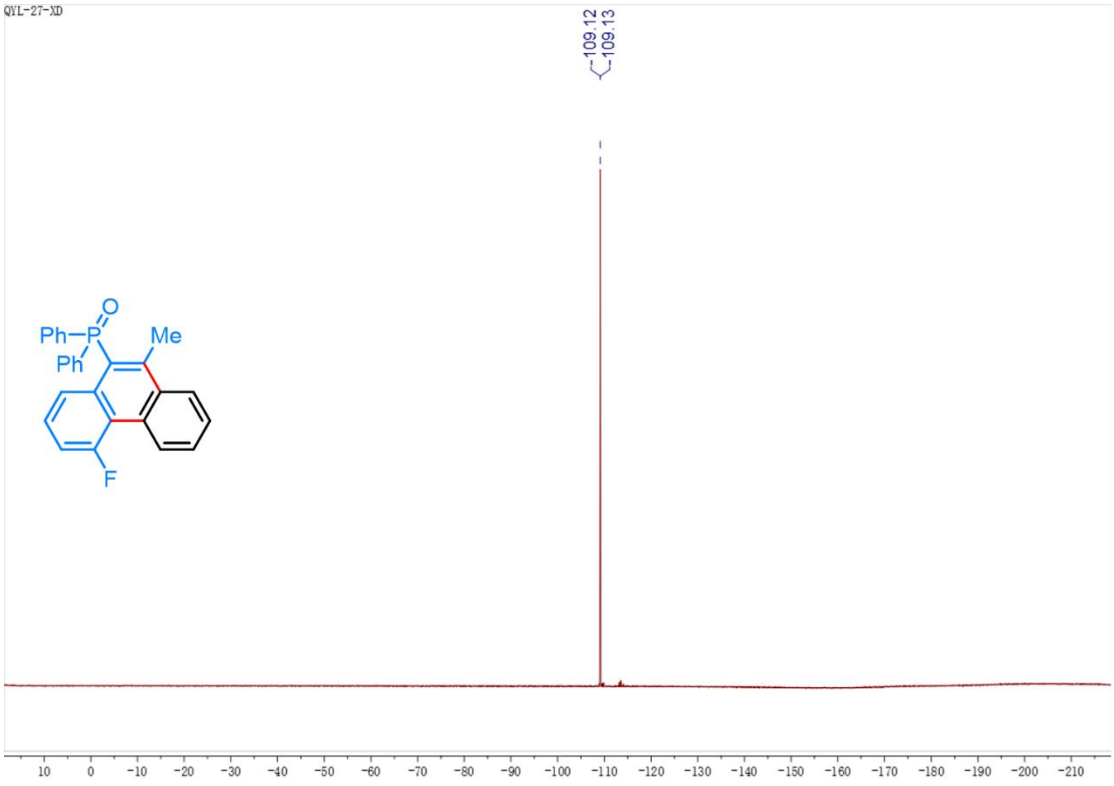
^{1}H NMR spectrum of **3i'** (400 MHz, $CDCl_3$)



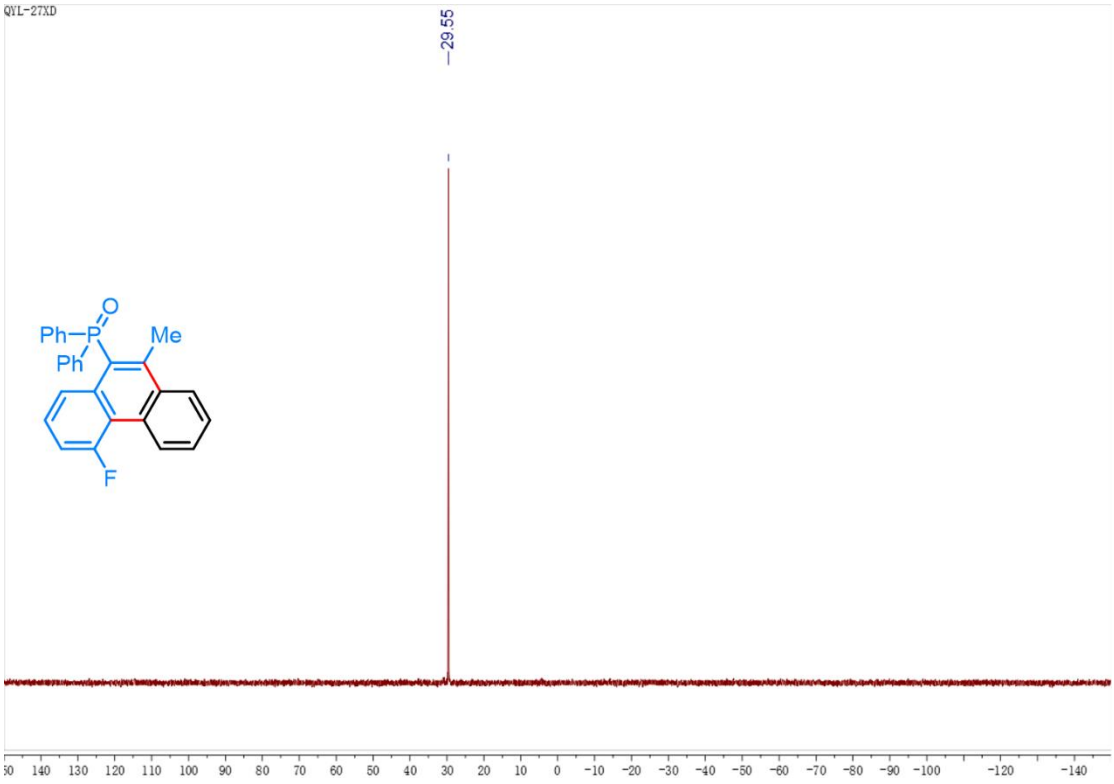
^{13}C NMR spectrum of **3i'** (100 MHz, $CDCl_3$)



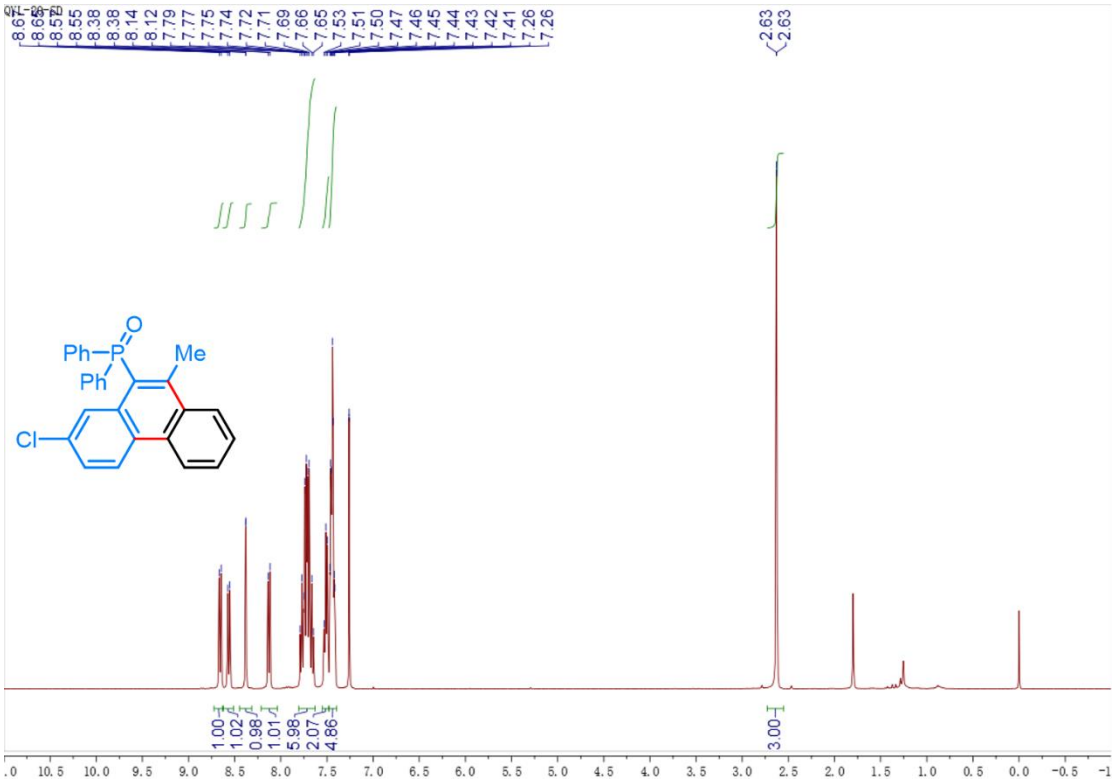
^{19}F NMR spectrum of **3i'** (376 MHz, $CDCl_3$)



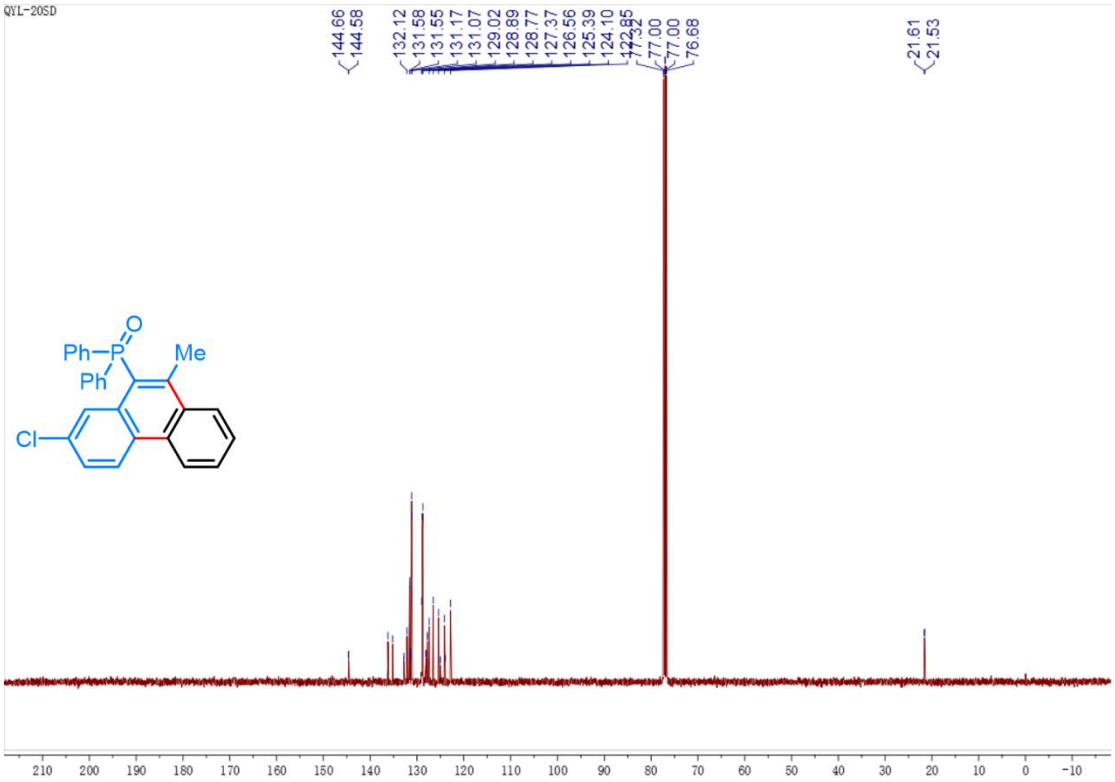
^{31}P NMR spectrum of **3i'** (162 MHz, $CDCl_3$)



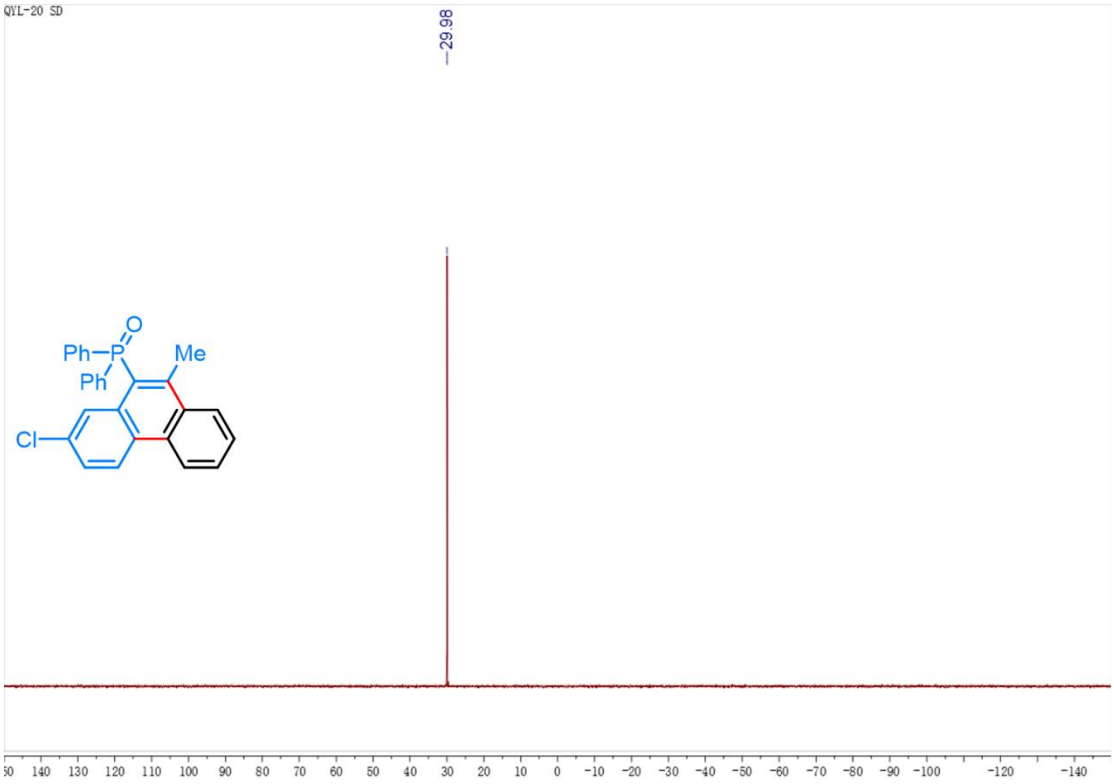
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



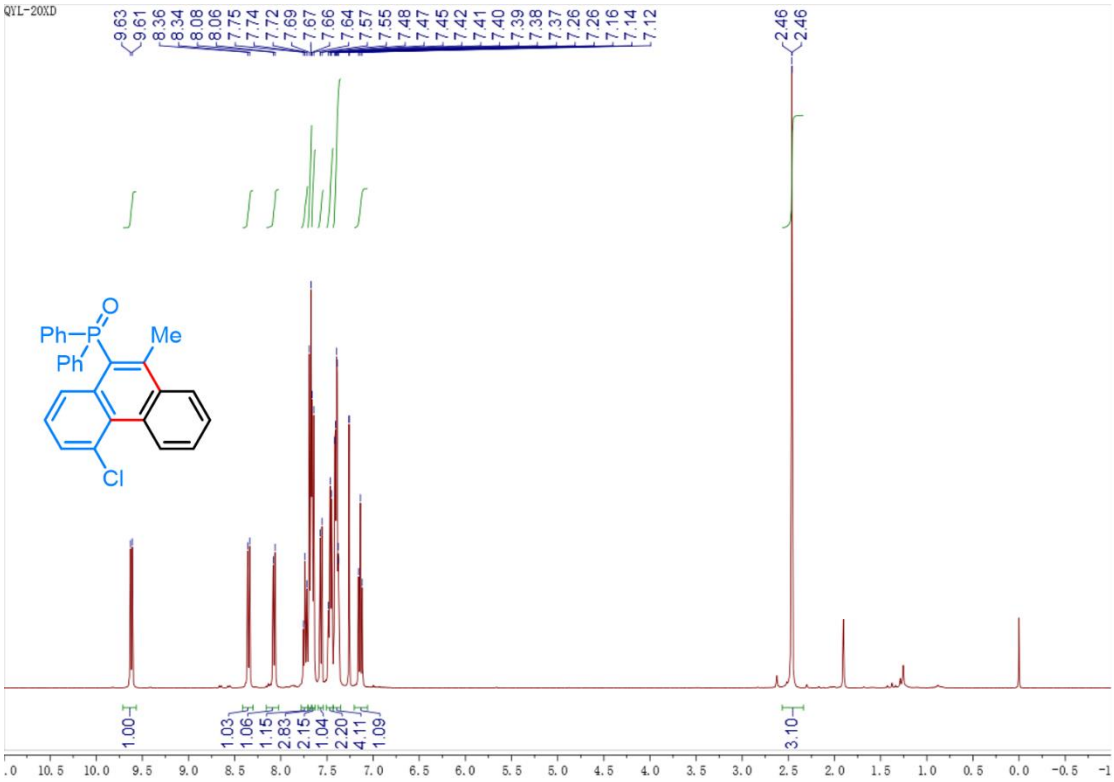
^{13}C NMR spectrum of **3j** (100 MHz, $CDCl_3$)



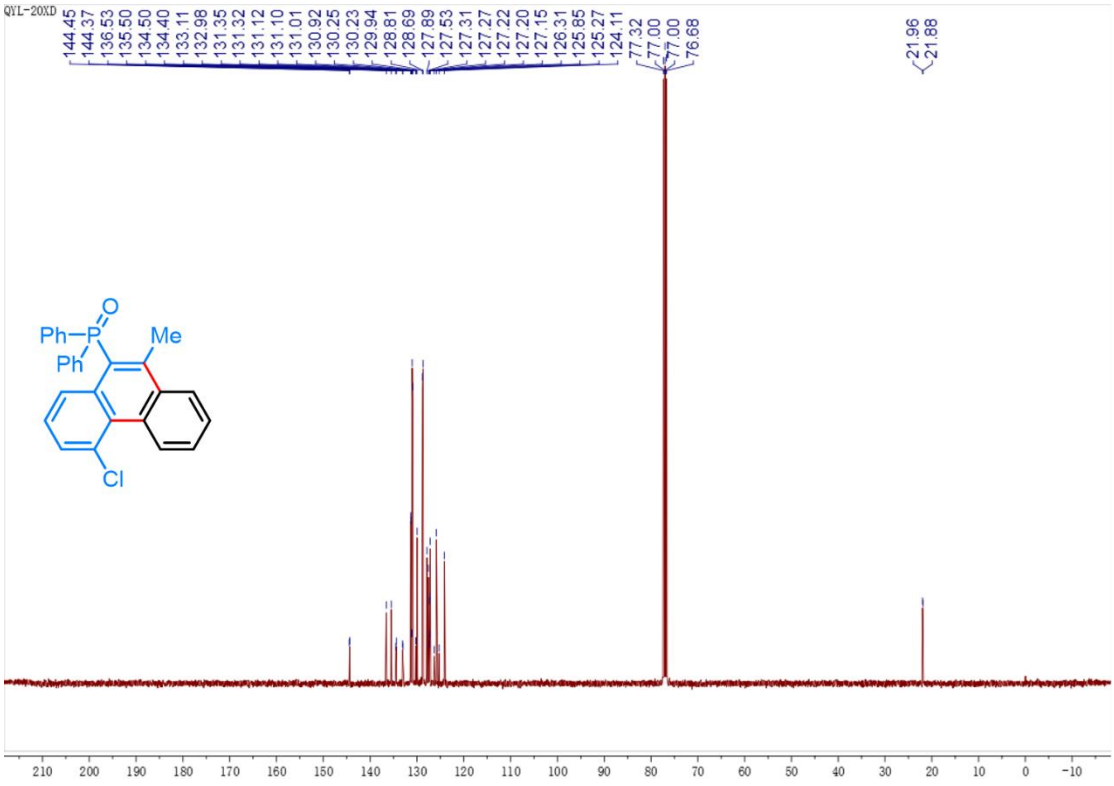
^{31}P NMR spectrum of **3j** (162 MHz, $CDCl_3$)



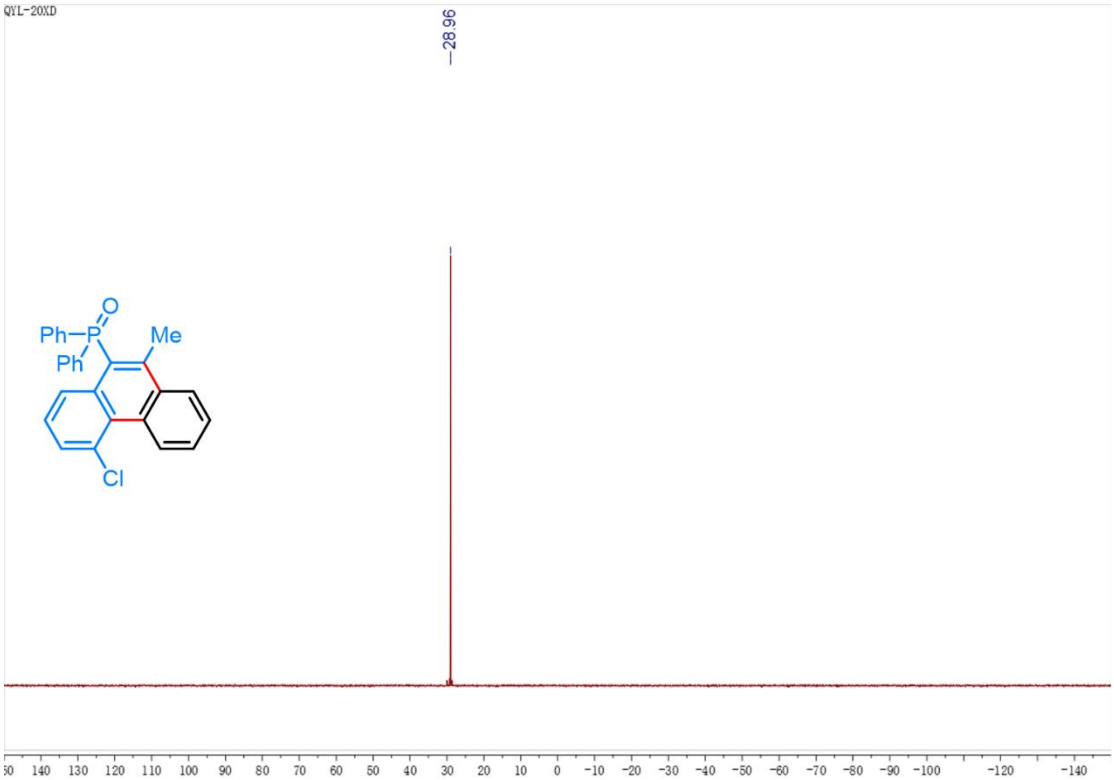
^{1}H NMR spectrum of **3j'** (400 MHz, $CDCl_3$)



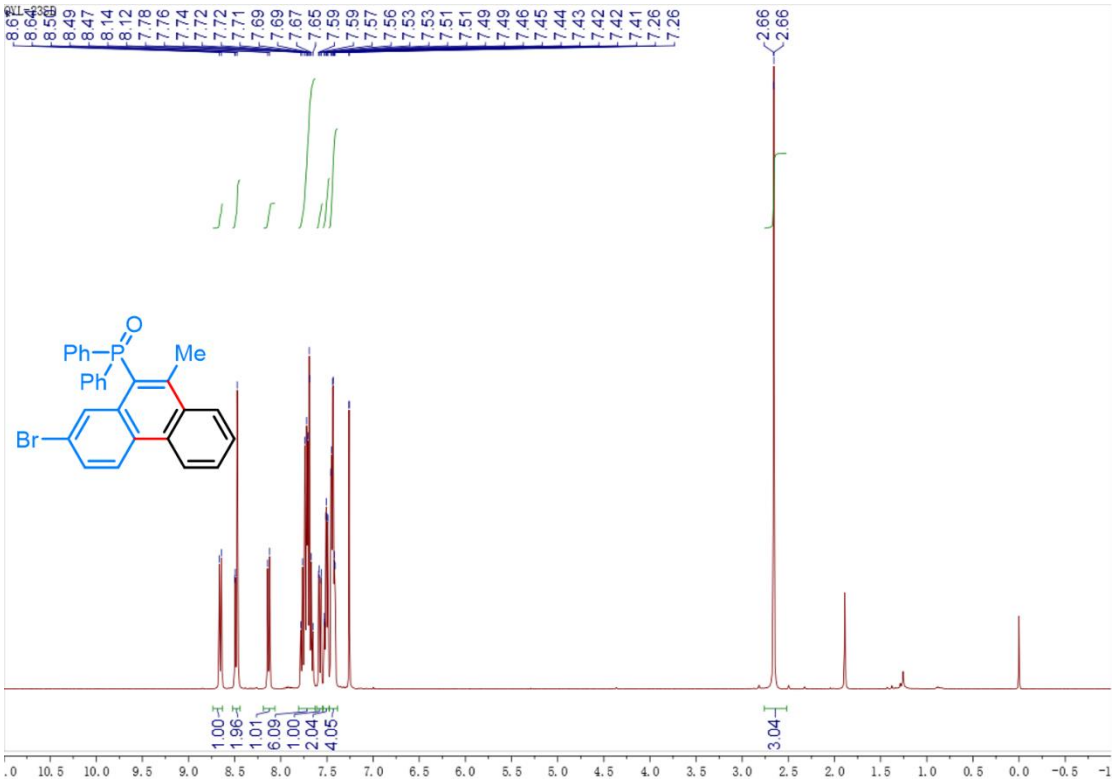
^{13}C NMR spectrum of **3j'** (100 MHz, $CDCl_3$)



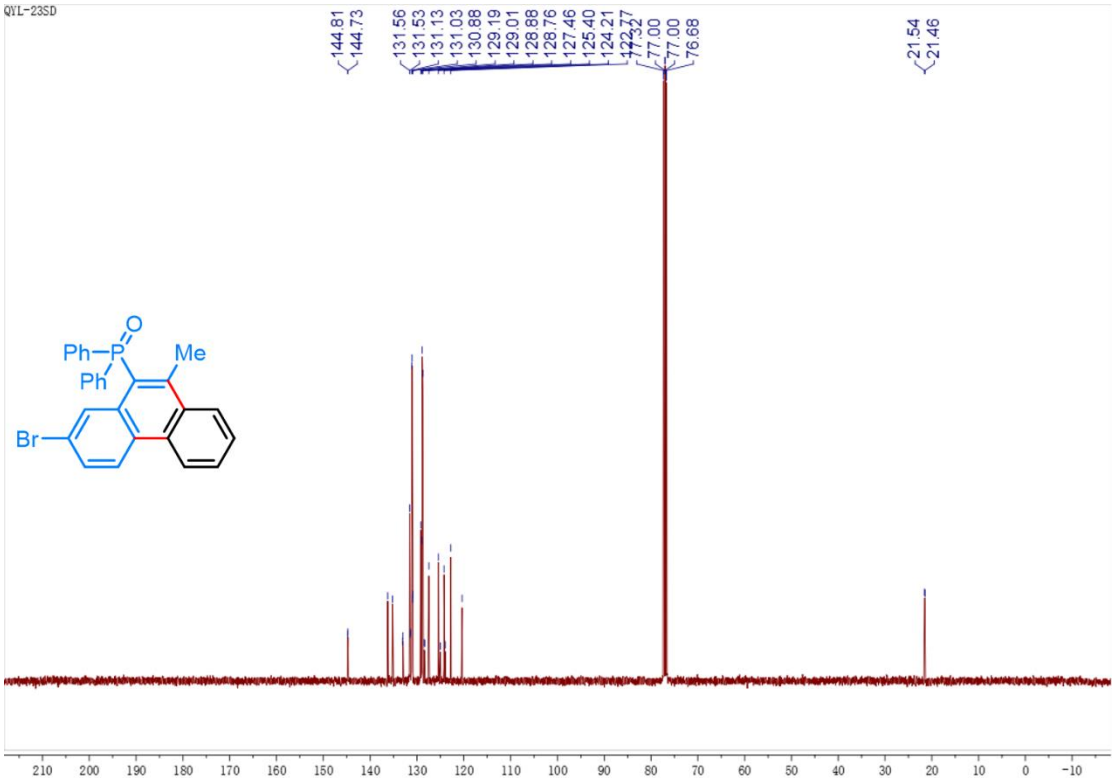
^{31}P NMR spectrum of **3j'** (162 MHz, $CDCl_3$)



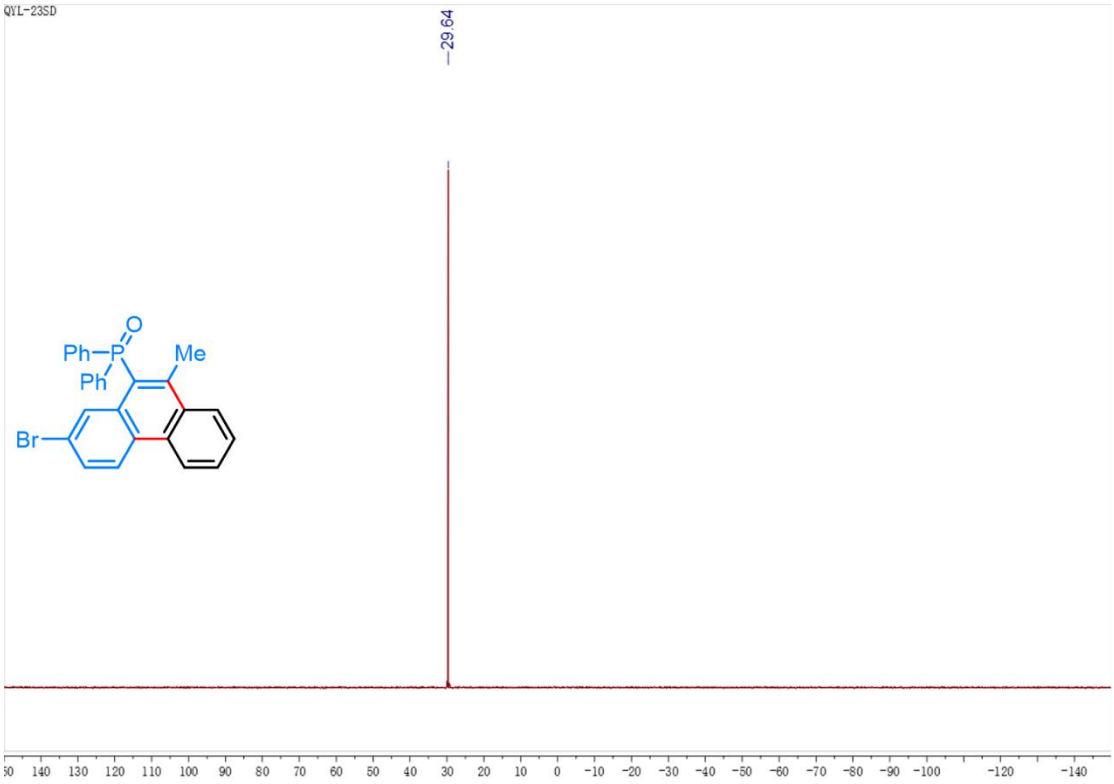
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



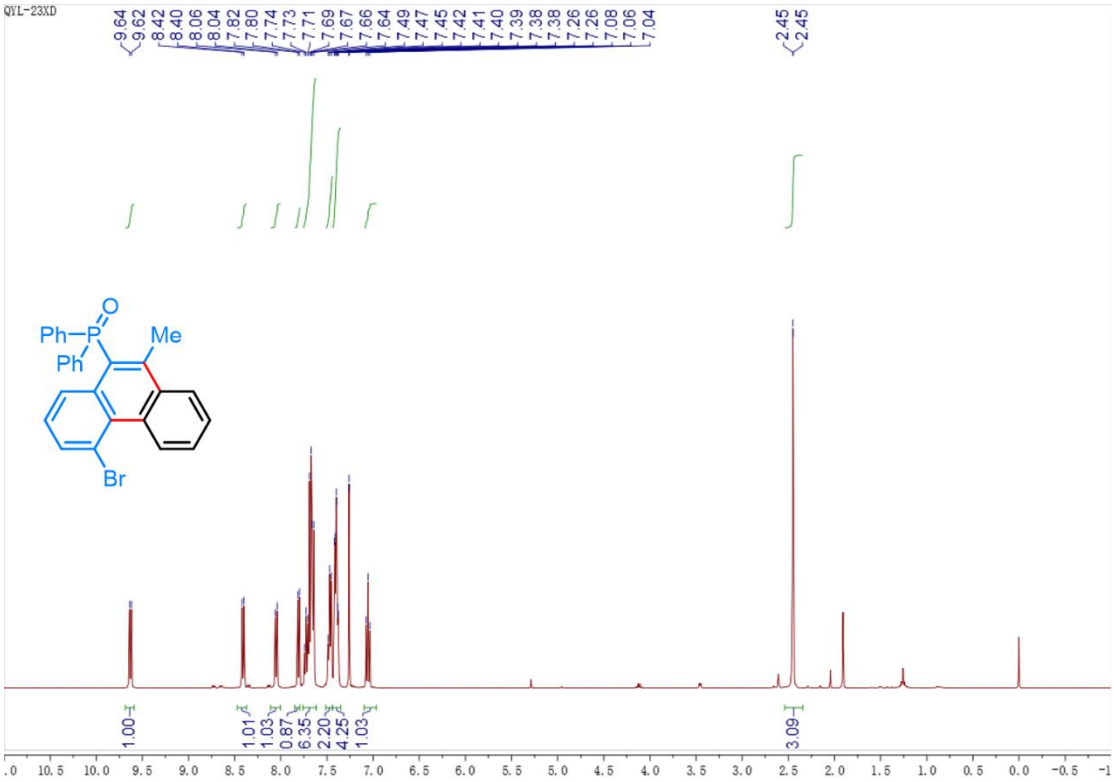
^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$)



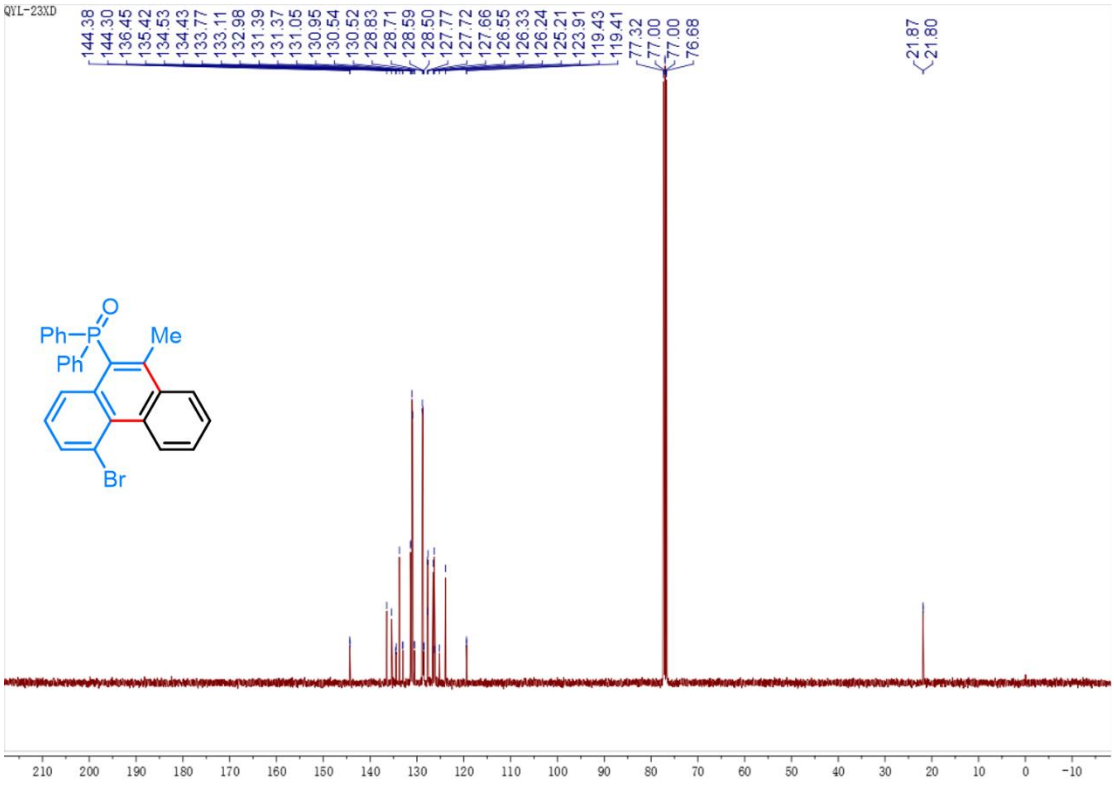
^{31}P NMR spectrum of **3k** (162 MHz, $CDCl_3$)



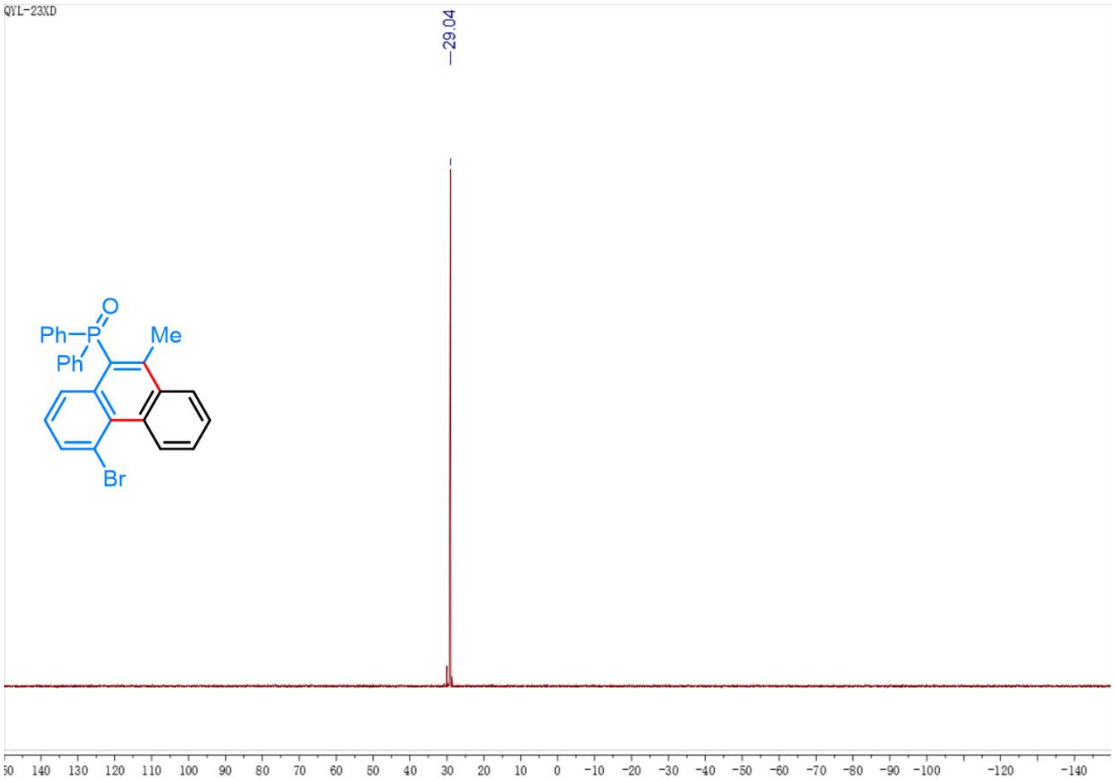
^{1}H NMR spectrum of **3k'** (400 MHz, $CDCl_3$)



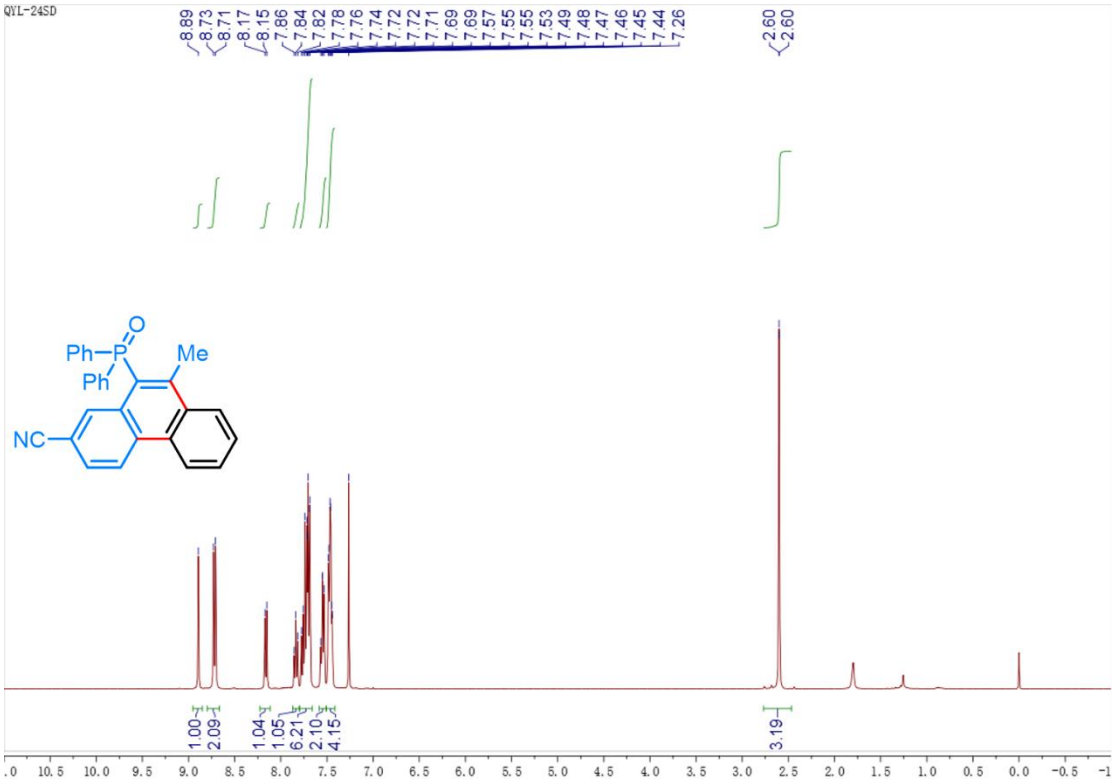
^{13}C NMR spectrum of **3k'** (100 MHz, $CDCl_3$)



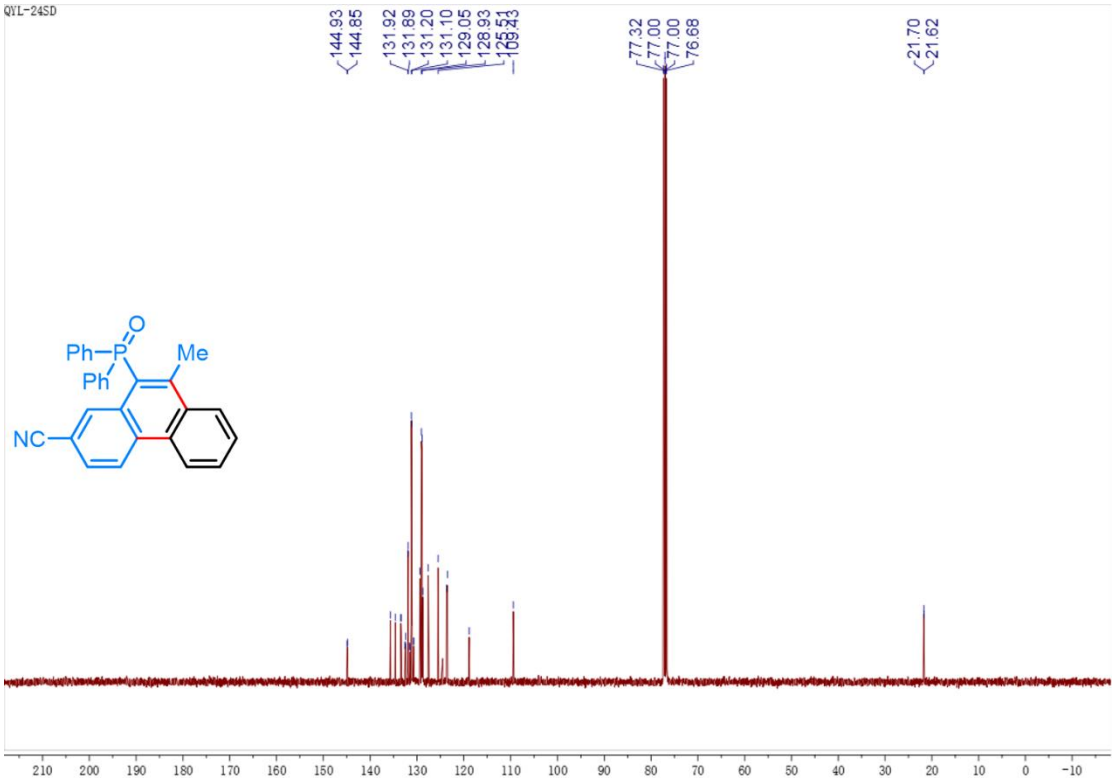
^{31}P NMR spectrum of **3k'** (162 MHz, $CDCl_3$)



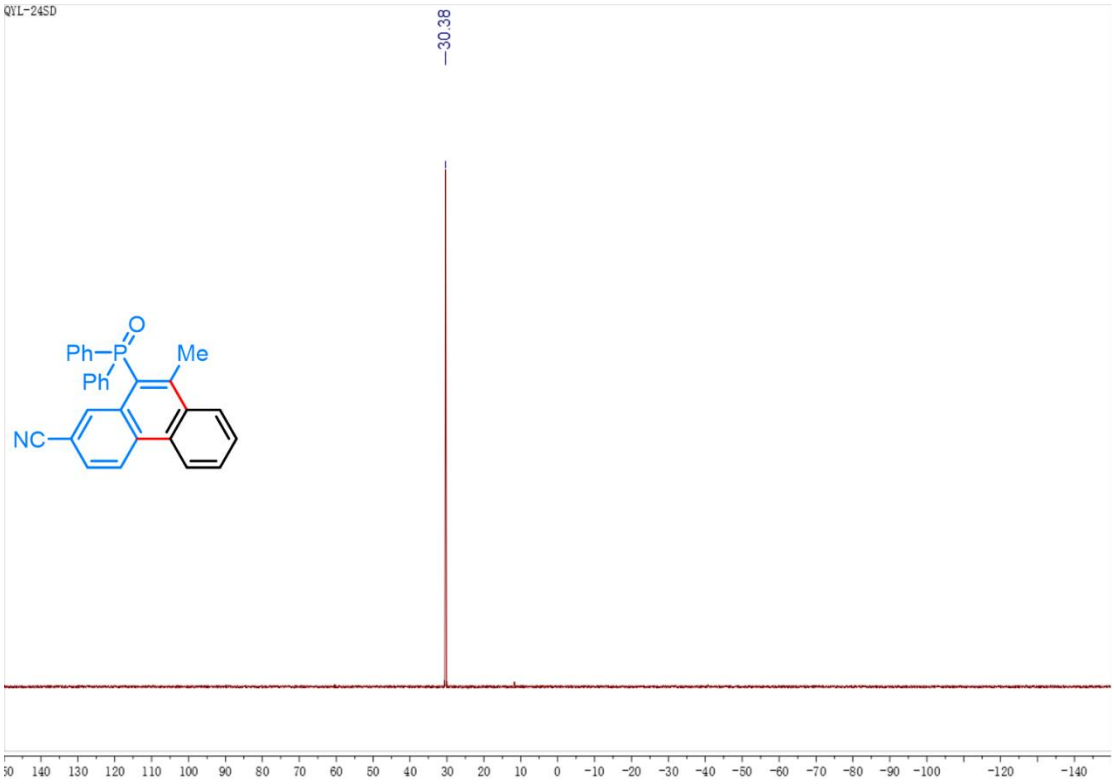
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



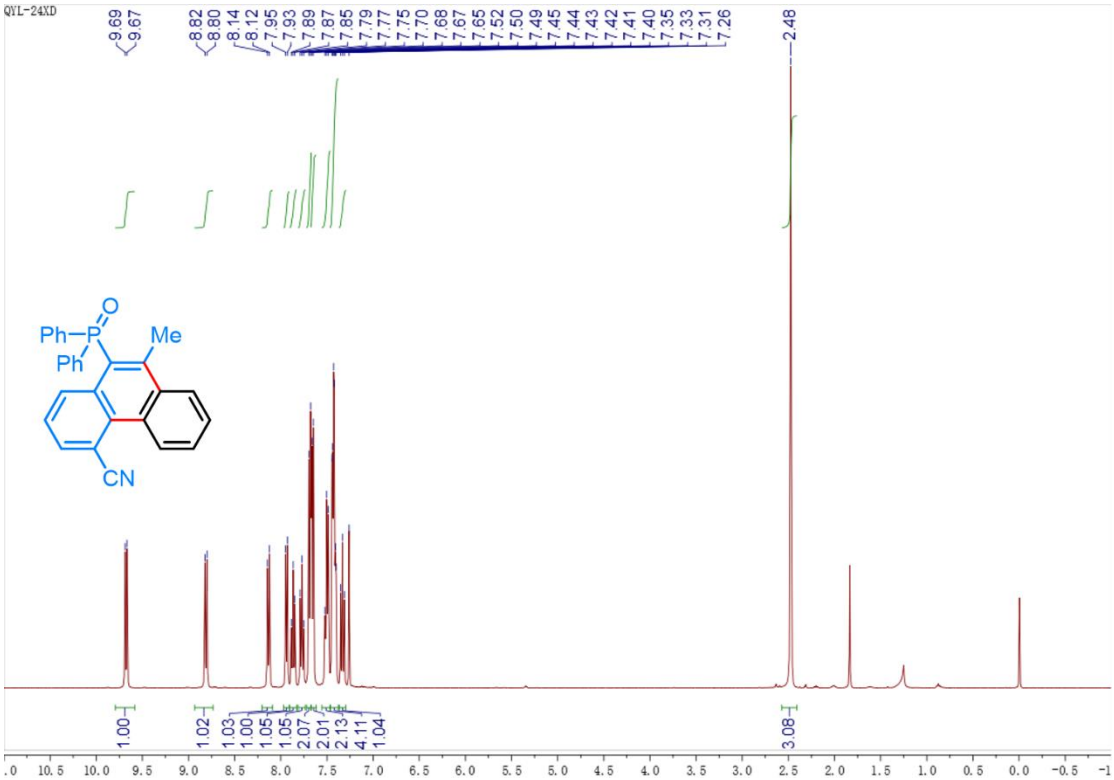
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



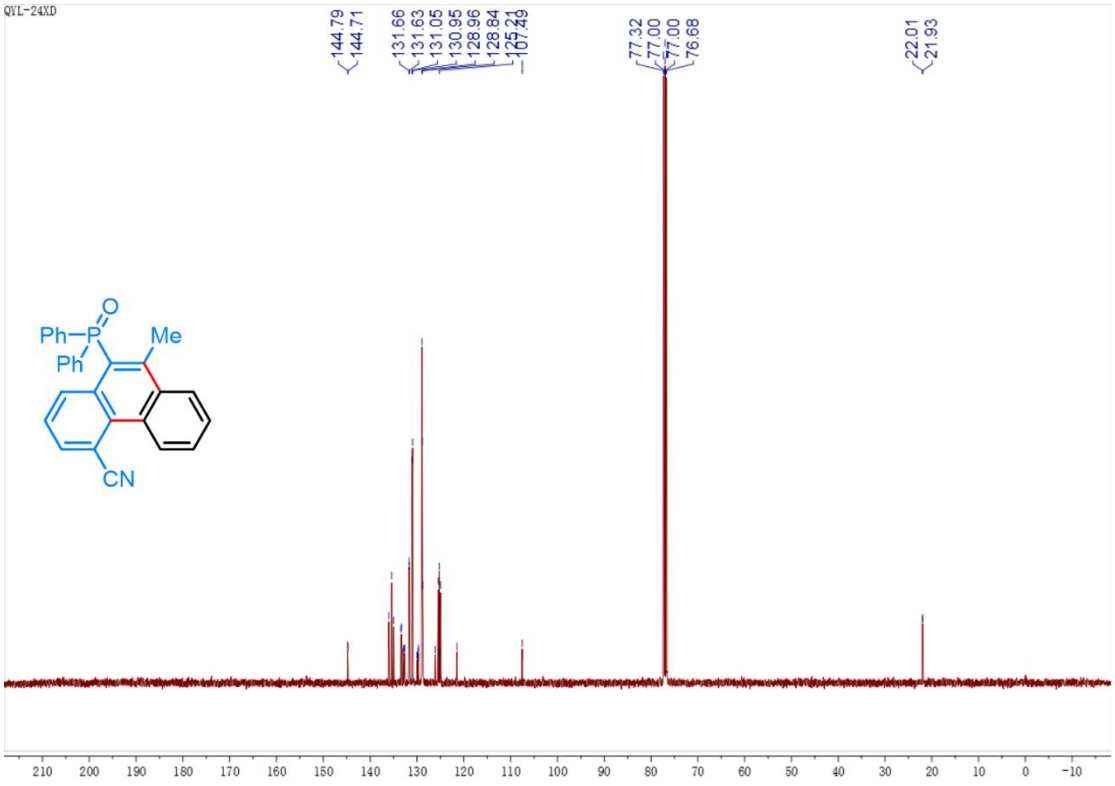
^{31}P NMR spectrum of **3l** (162 MHz, $CDCl_3$)



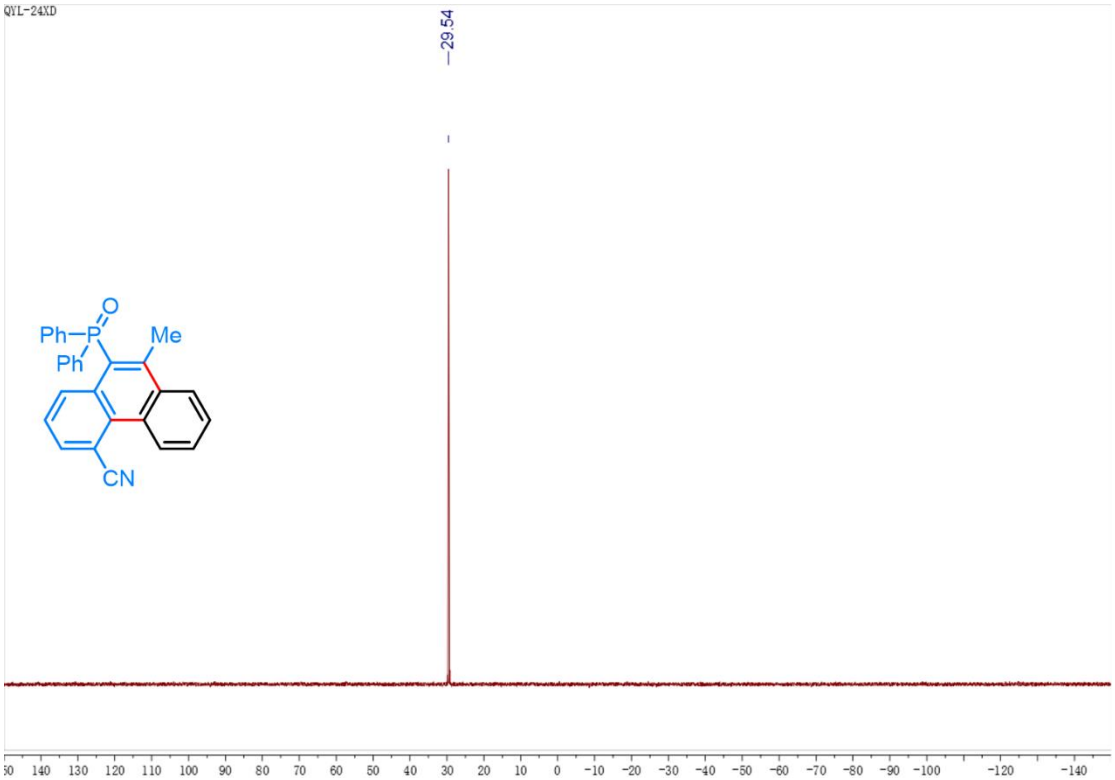
^{1}H NMR spectrum of **3l'** (400 MHz, $CDCl_3$)



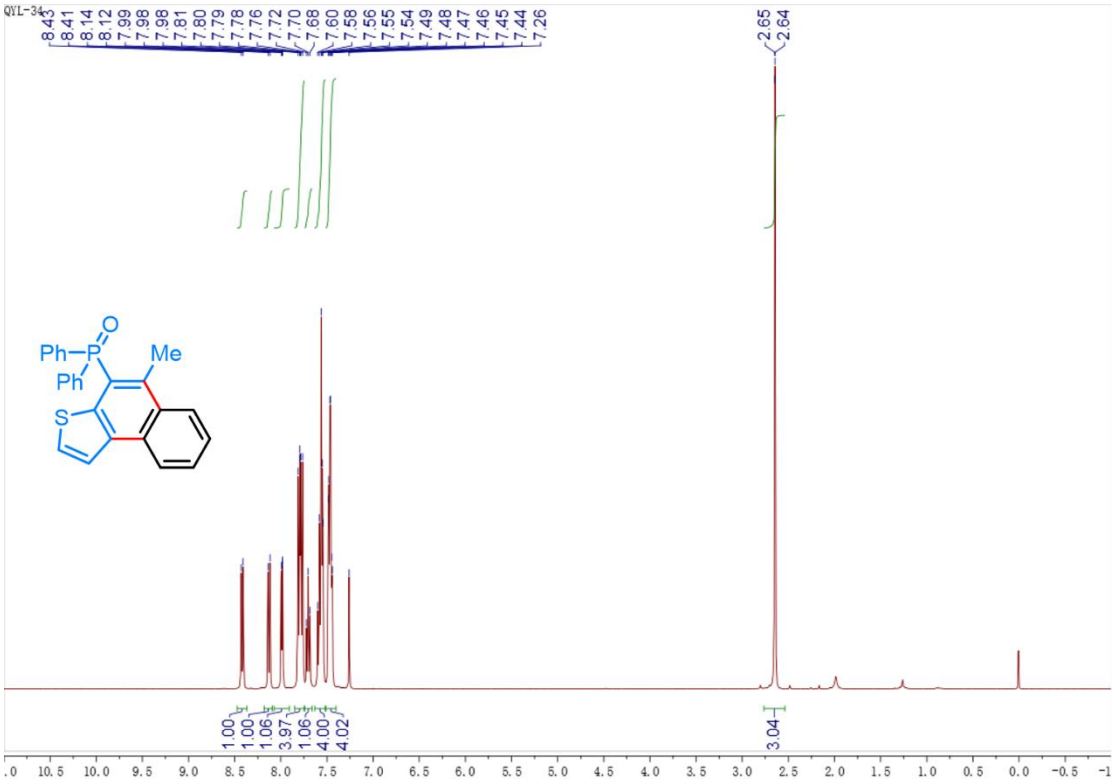
^{13}C NMR spectrum of **3l'** (100 MHz, $CDCl_3$)



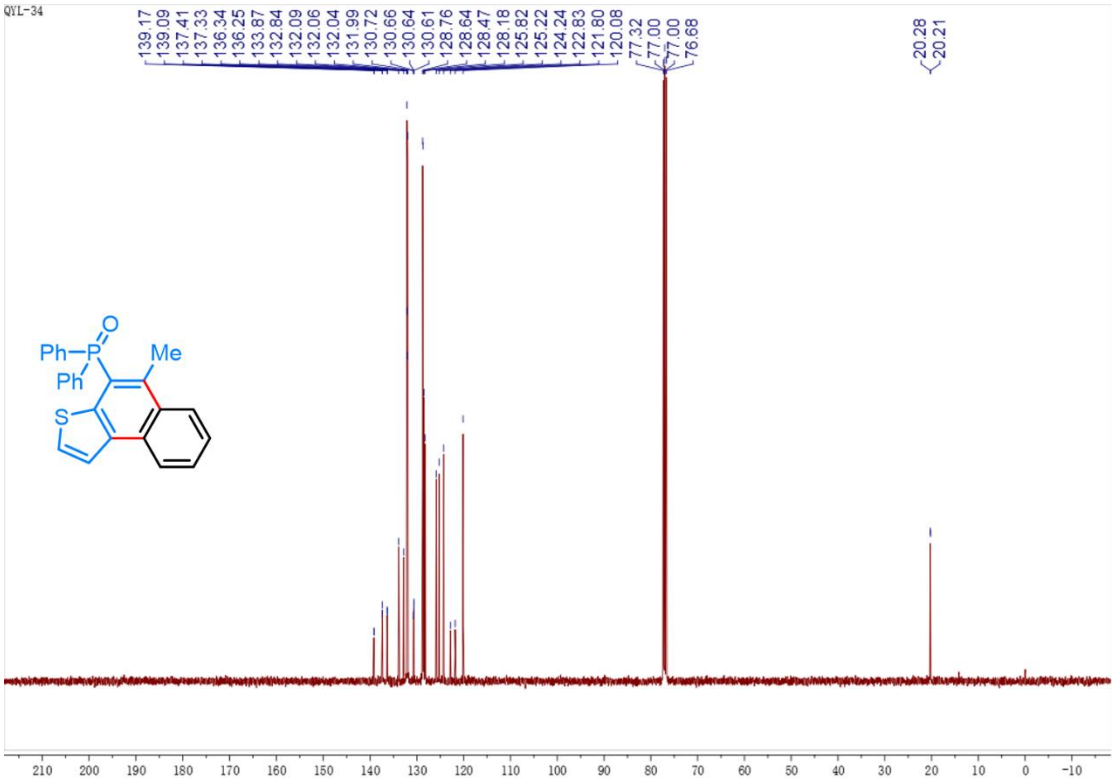
^{31}P NMR spectrum of **3l'** (162 MHz, $CDCl_3$)



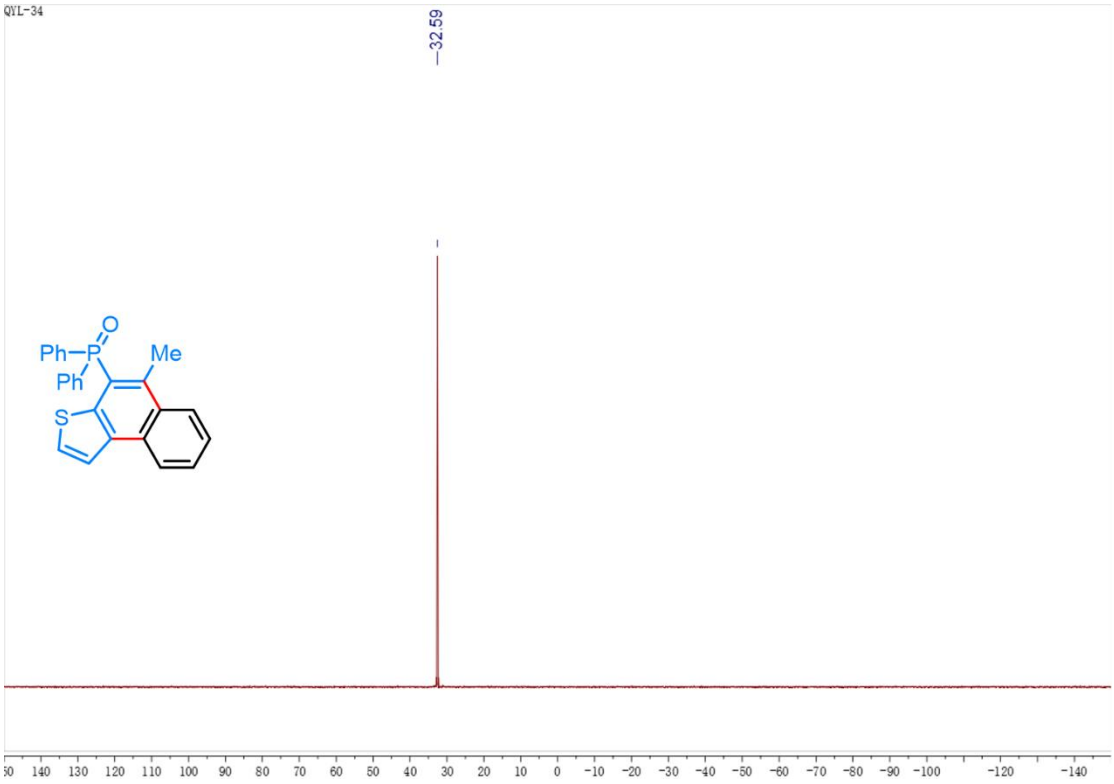
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



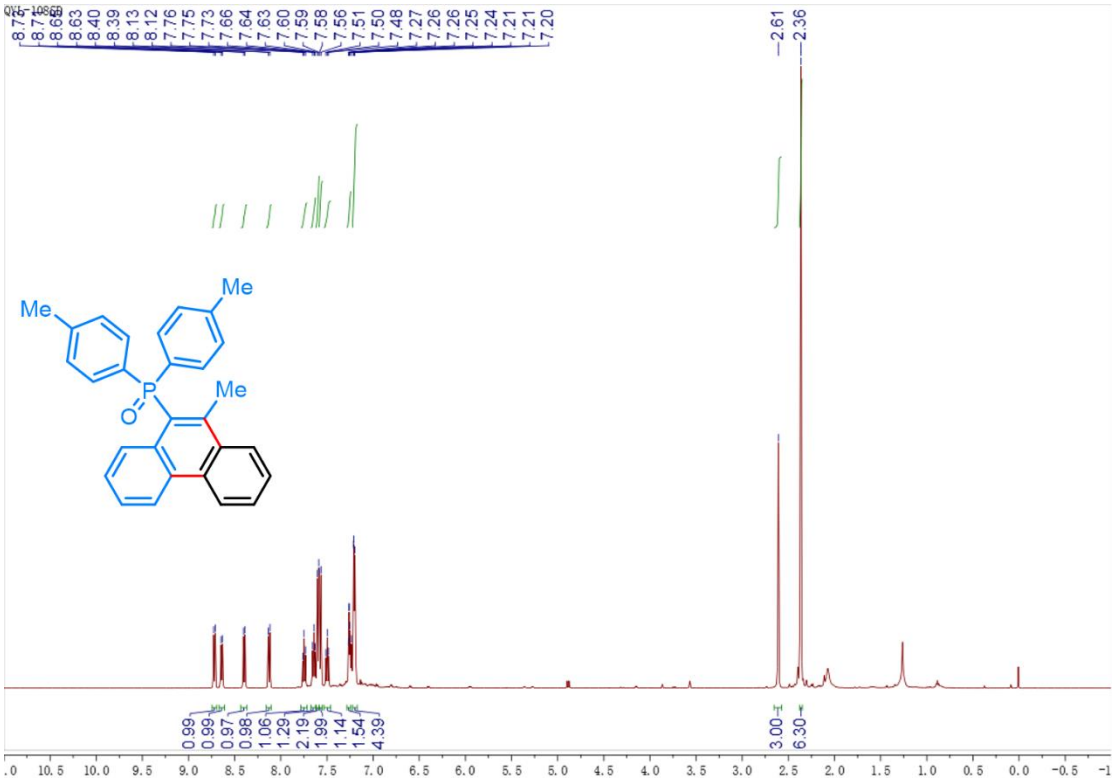
^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)



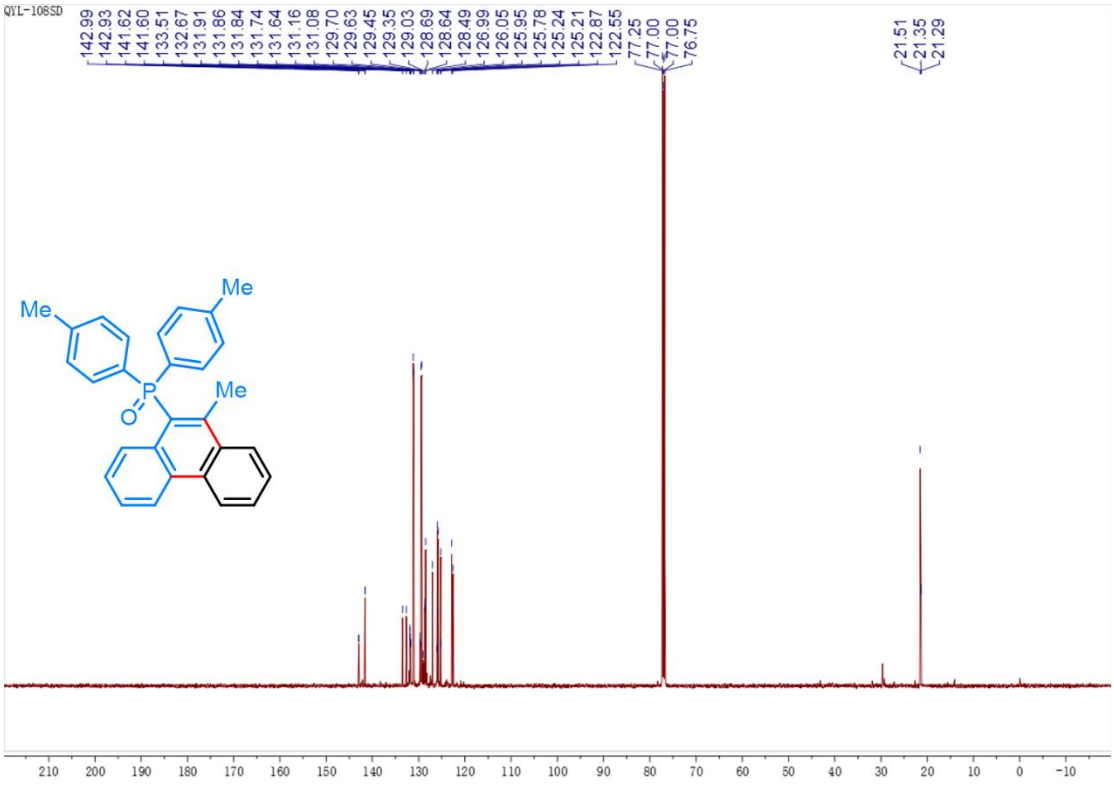
^{31}P NMR spectrum of **3m** (162 MHz, $CDCl_3$)



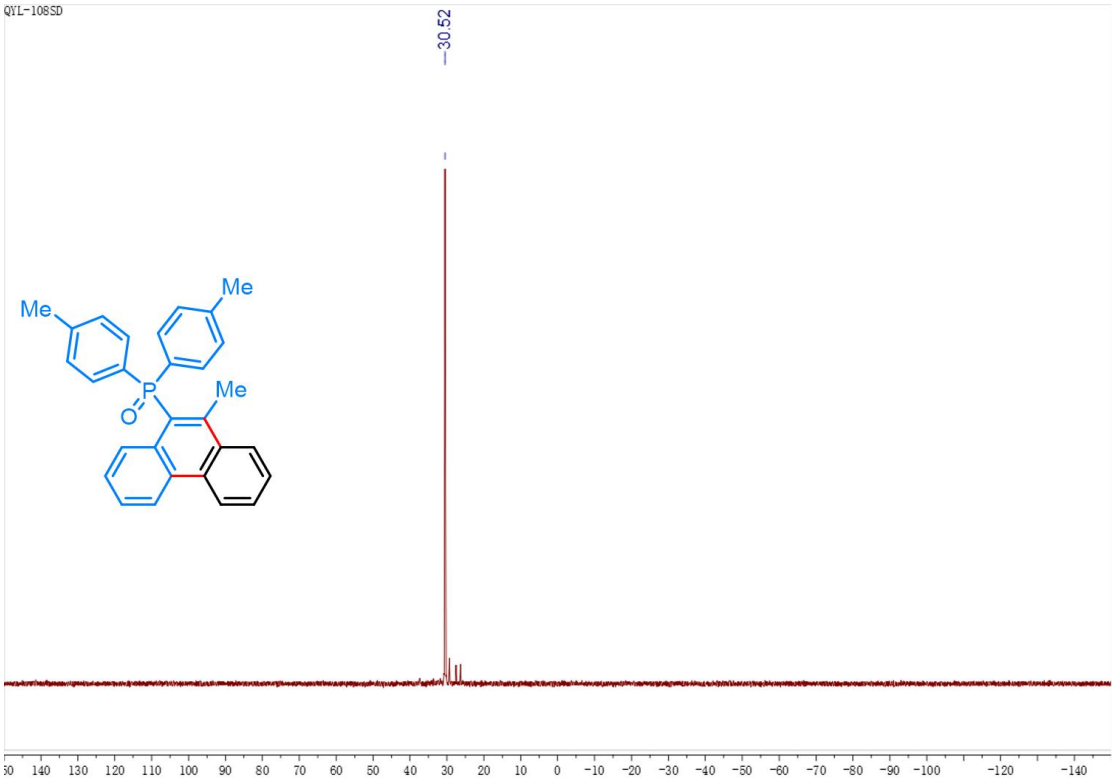
^{1}H NMR spectrum of **3n** (500 MHz, $CDCl_3$)



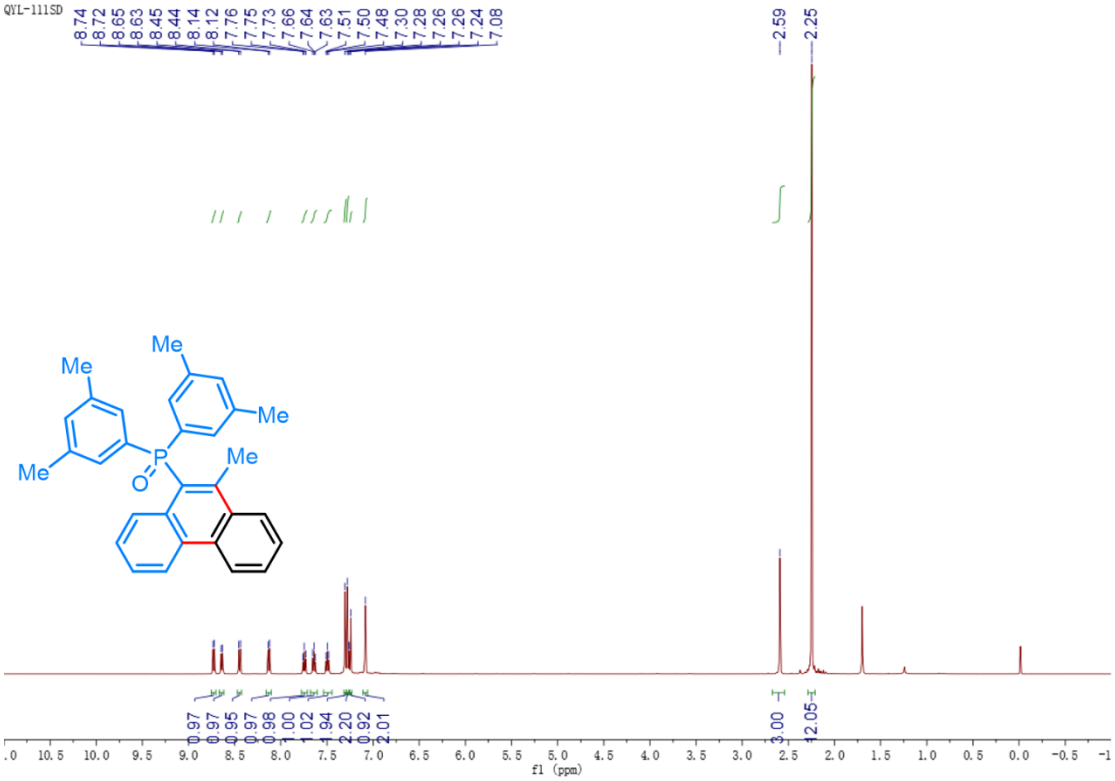
^{13}C NMR spectrum of **3n** (125 MHz, $CDCl_3$)



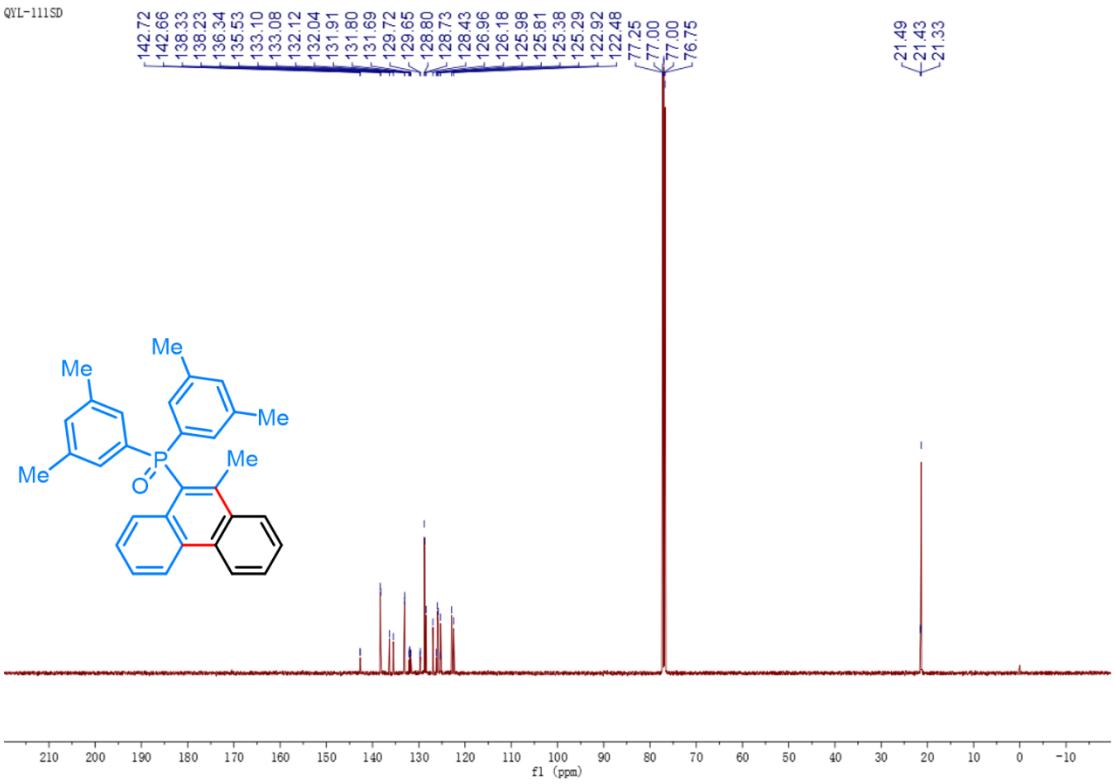
^{31}P NMR spectrum of **3n** (202 MHz, $CDCl_3$)



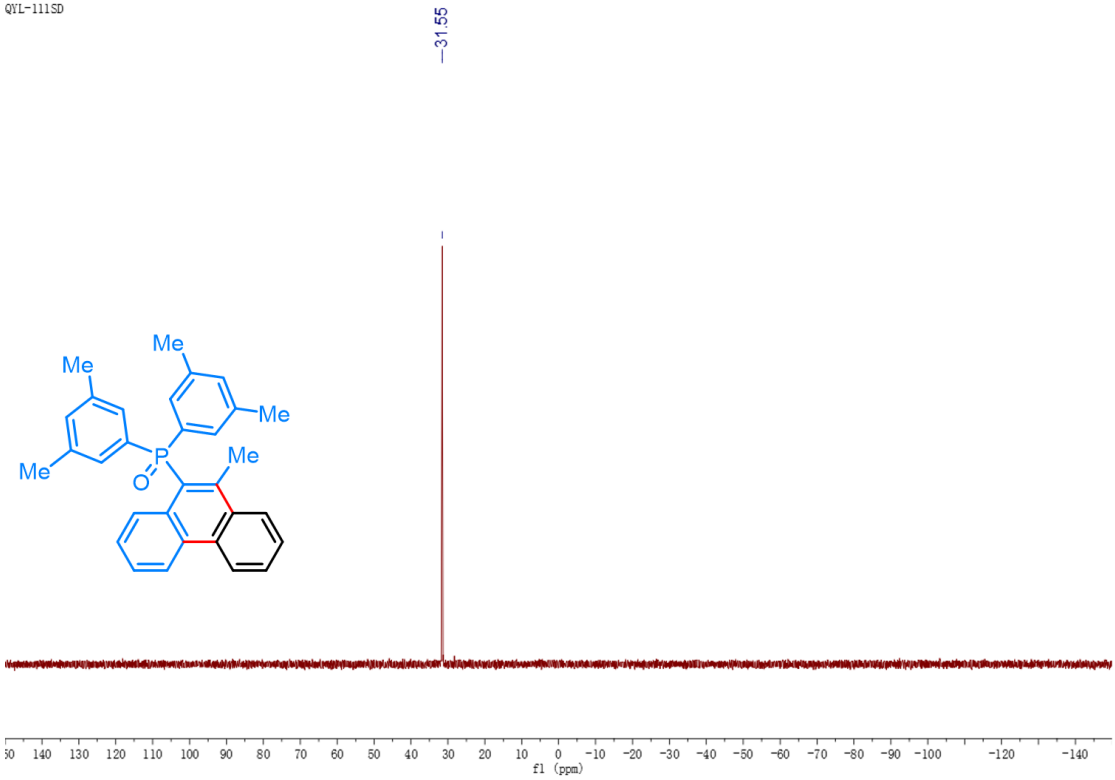
^{1}H NMR spectrum of **3o** (500 MHz, $CDCl_3$)



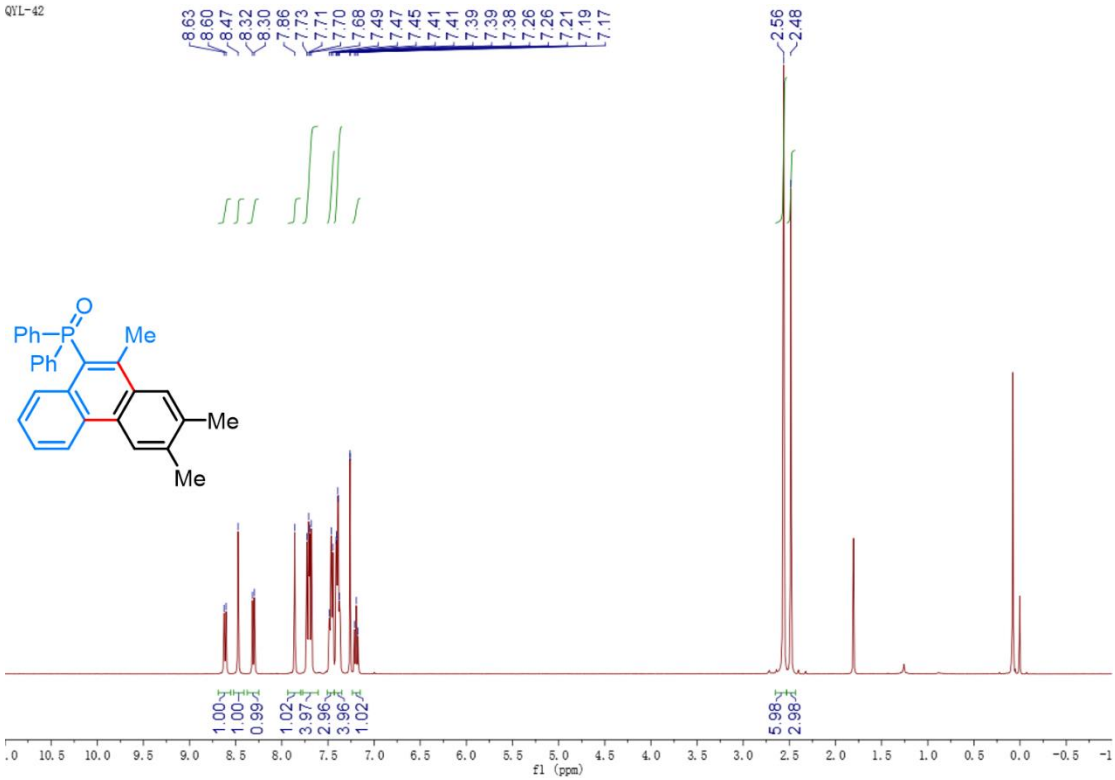
^{13}C NMR spectrum of **3o** (125 MHz, $CDCl_3$)



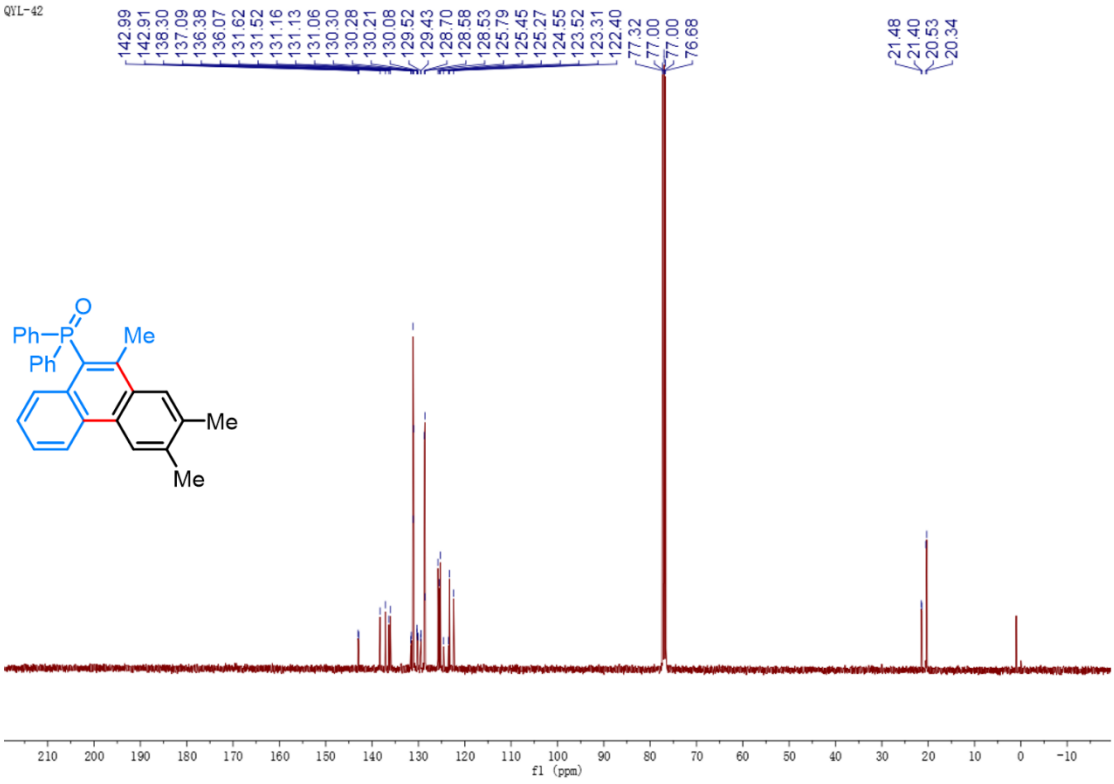
^{31}P NMR spectrum of **3o** (202 MHz, $CDCl_3$)



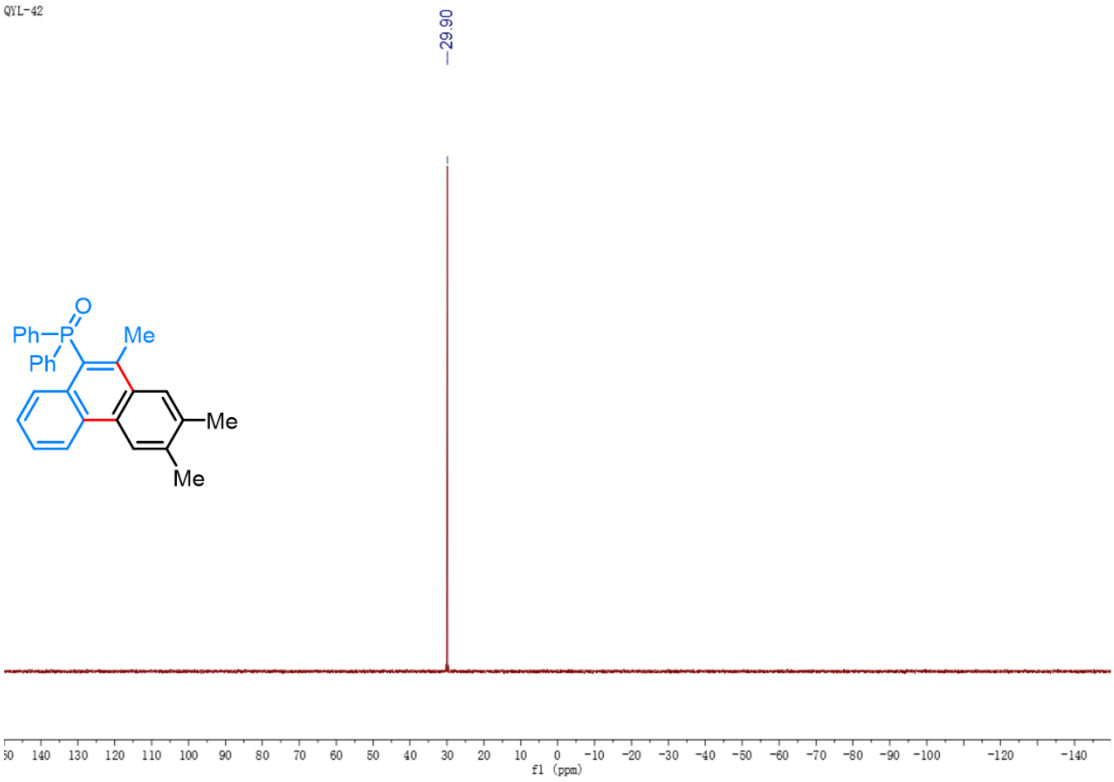
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)



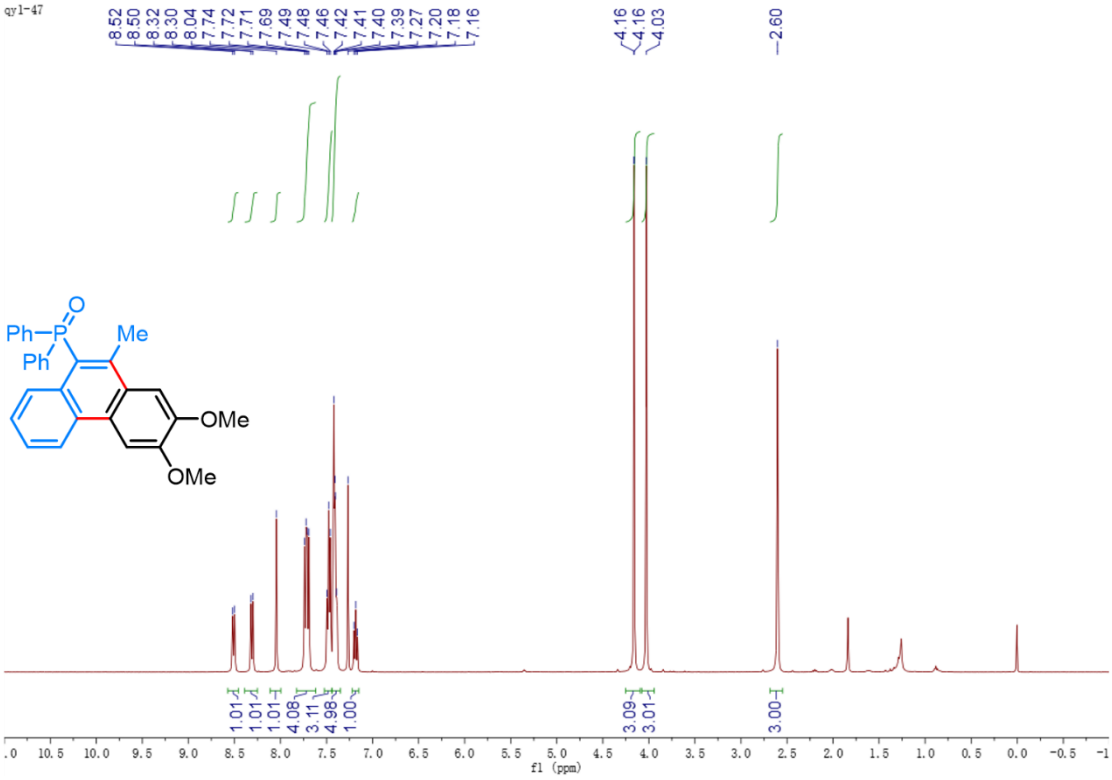
^{13}C NMR spectrum of **3p** (100 MHz, $CDCl_3$)



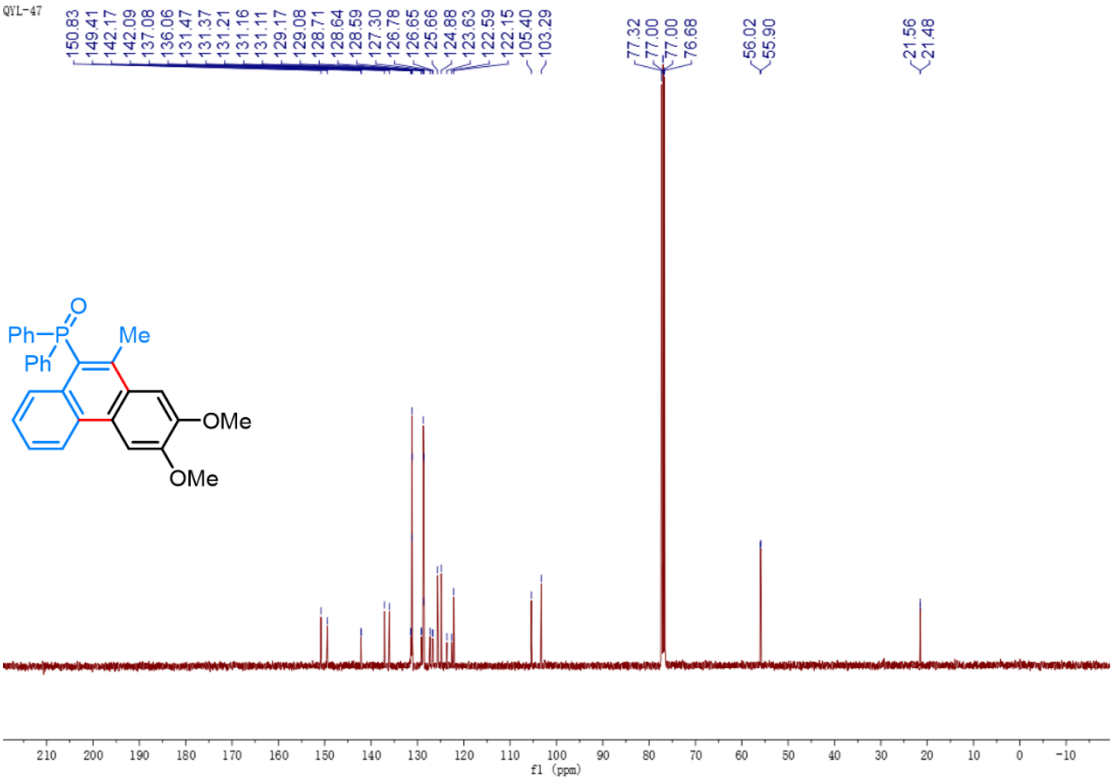
^{31}P NMR spectrum of **3p** (162 MHz, $CDCl_3$)



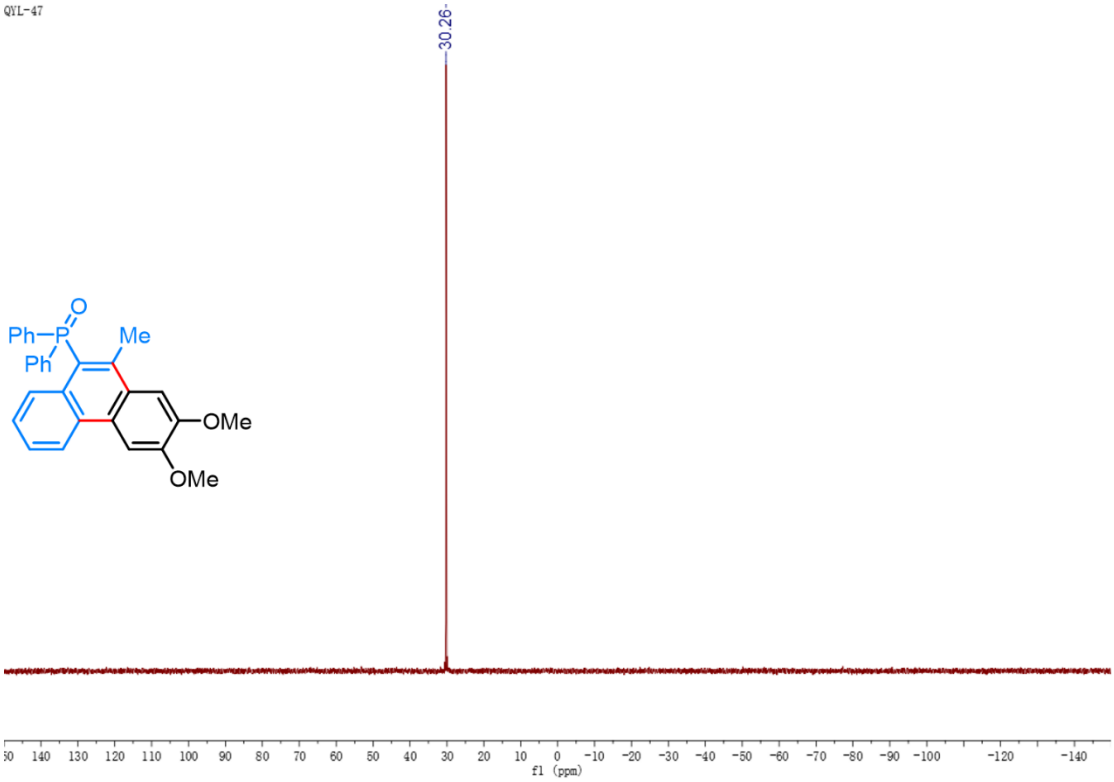
^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)



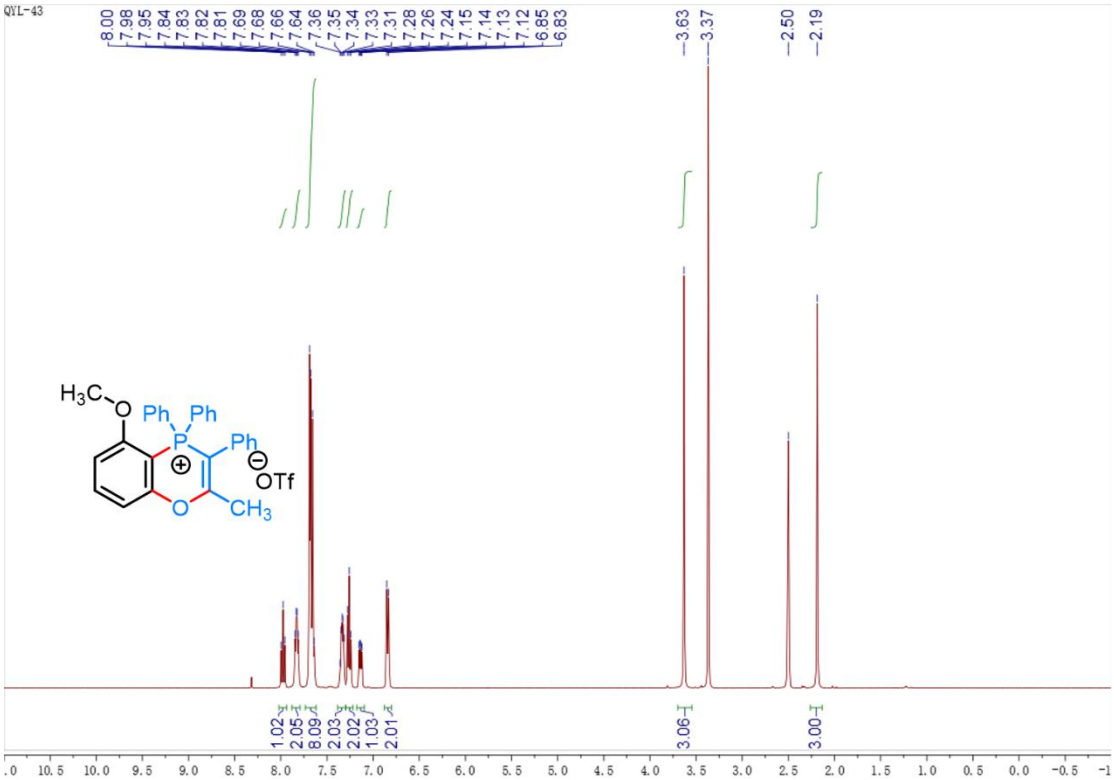
^{13}C NMR spectrum of **3q** (100 MHz, $CDCl_3$)



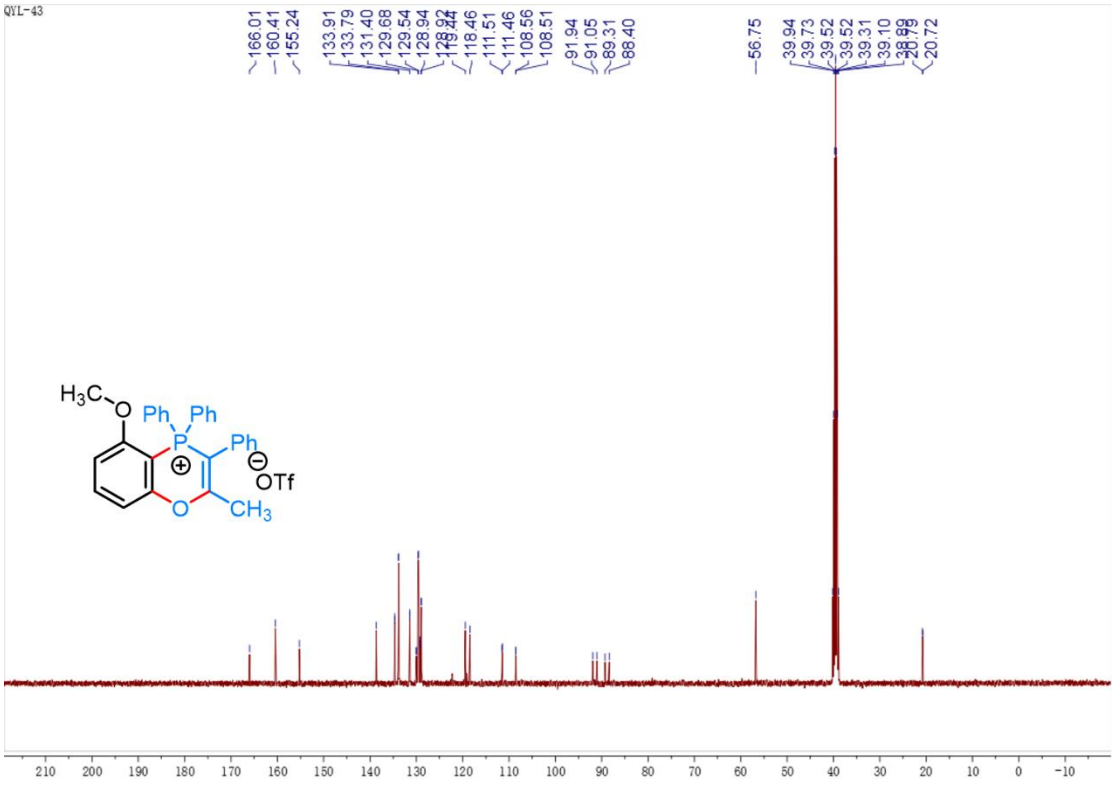
^{31}P NMR spectrum of **3q** (162 MHz, $CDCl_3$)



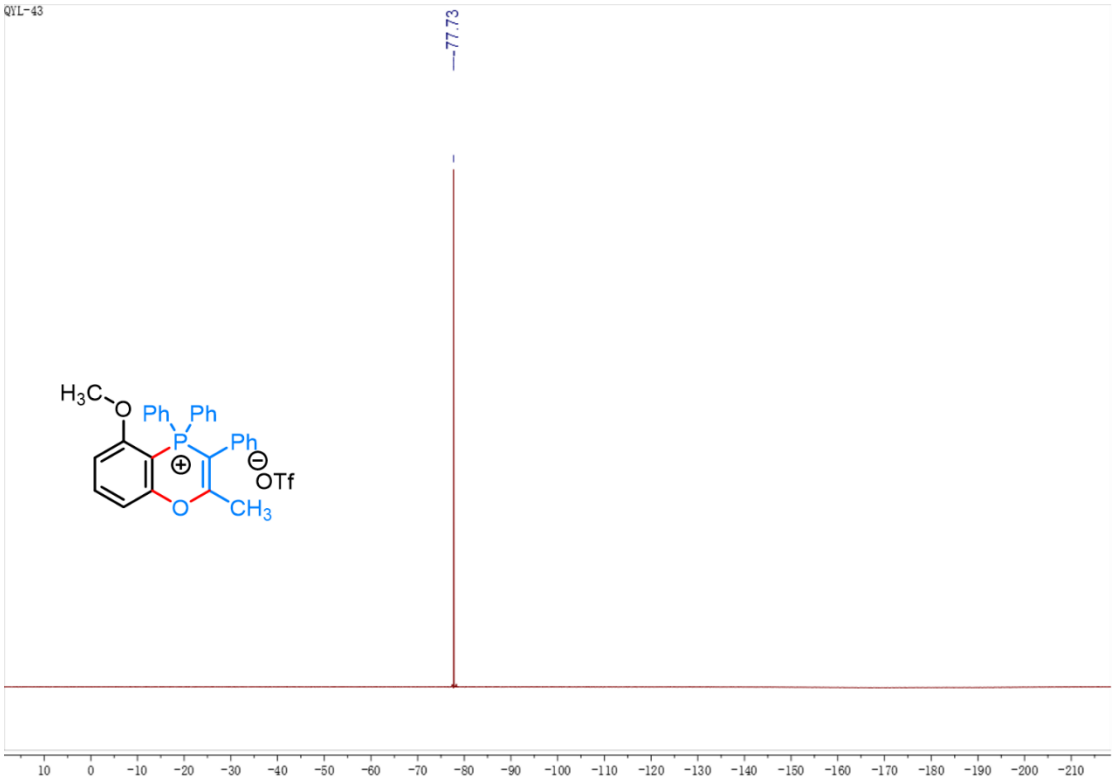
^{1}H NMR spectrum of **4a** (400 MHz, DMSO-d_6)



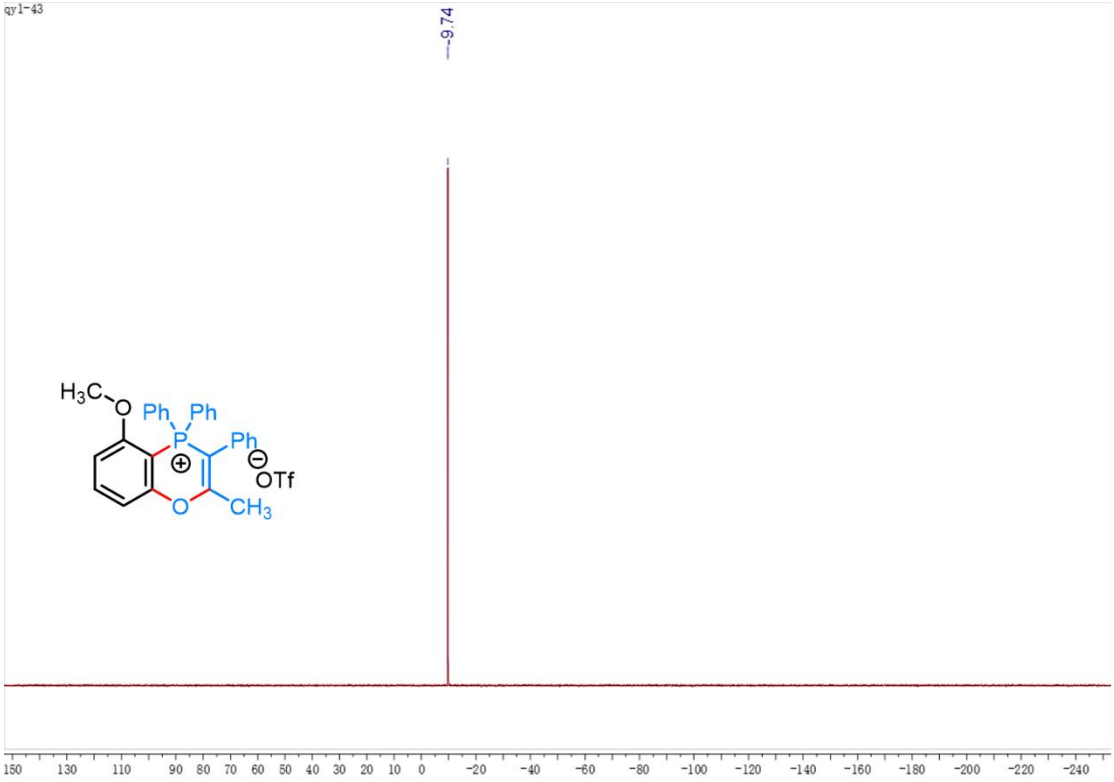
^{13}C NMR spectrum of **4a** (100 MHz, DMSO-d_6)



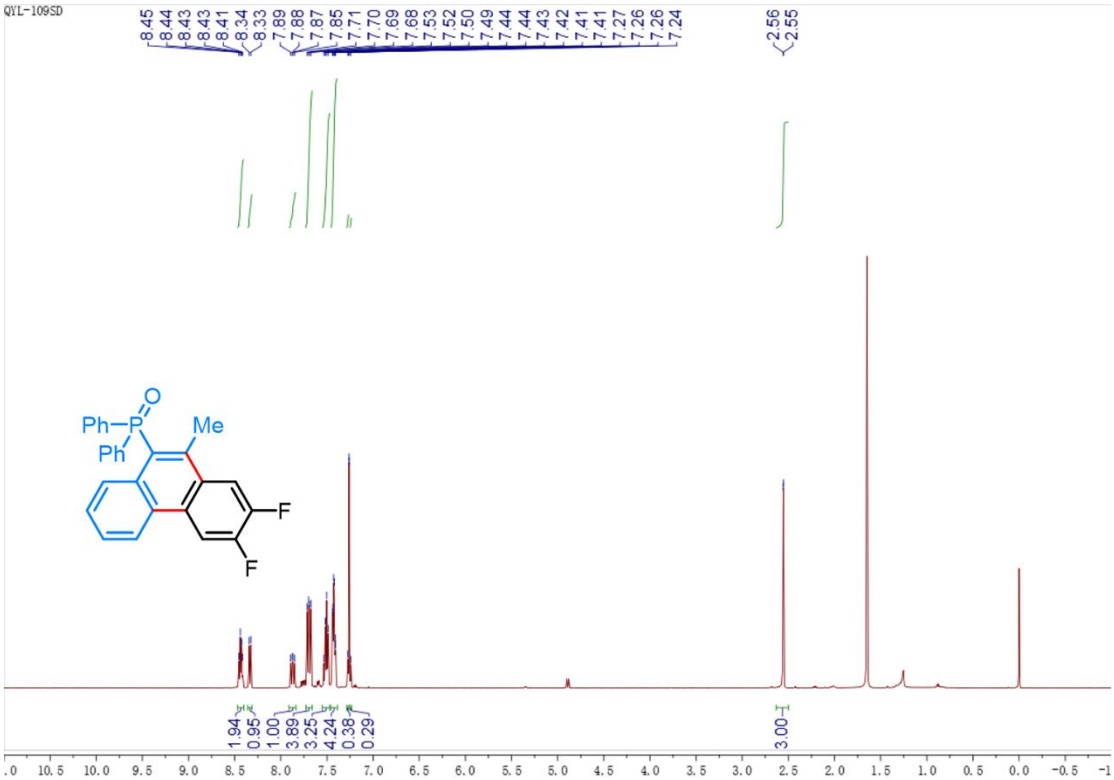
^{19}F NMR spectra of **4a** (376 MHz, DMSO-d_6)



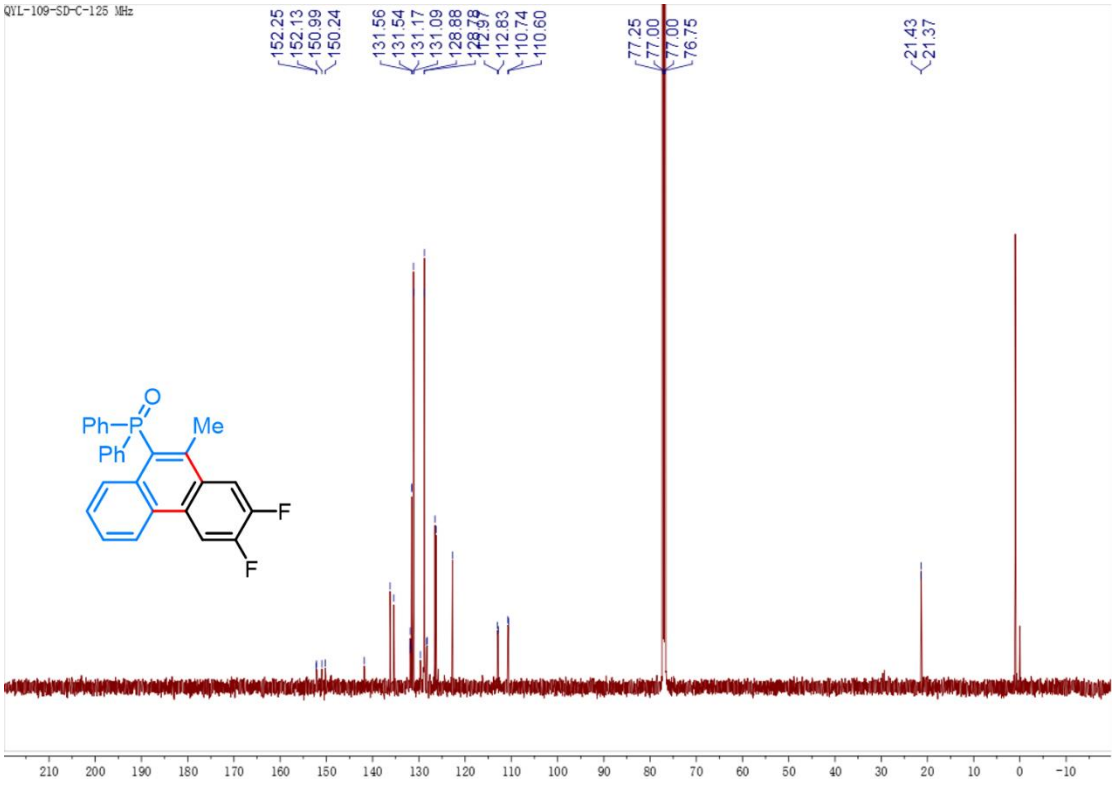
^{31}P NMR spectrum of **4a** (162 MHz, DMSO-d_6)



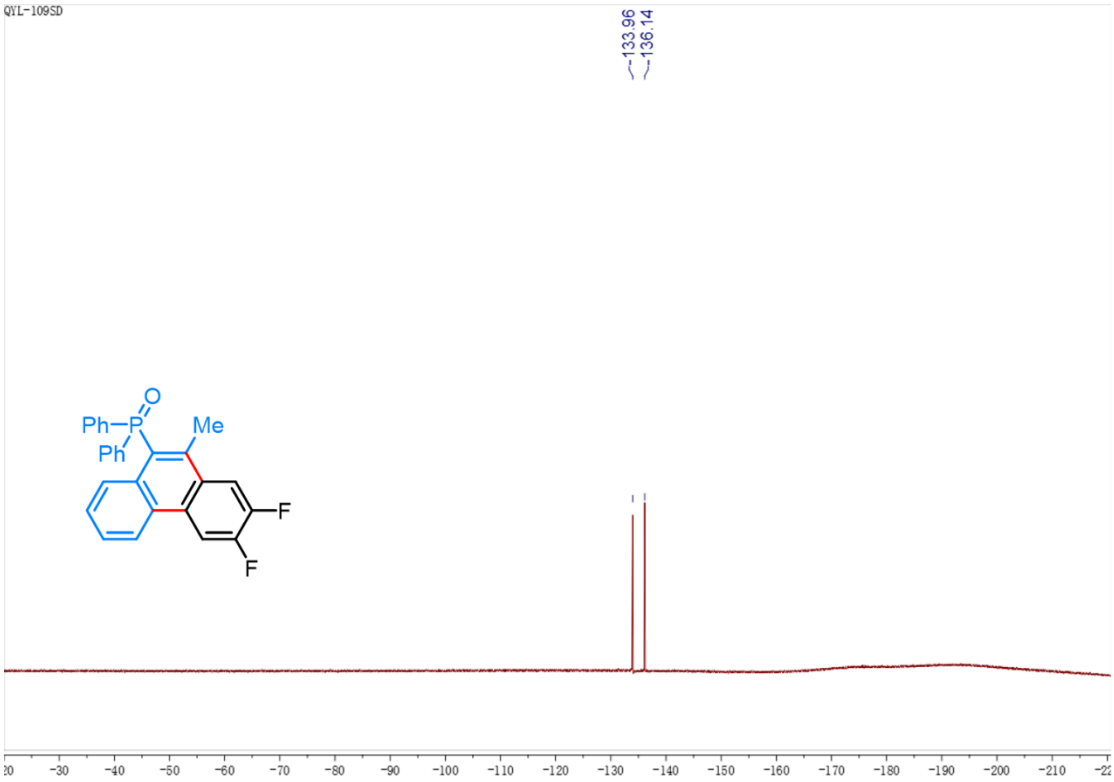
^{1}H NMR spectrum of **3r** (500 MHz, $CDCl_3$)



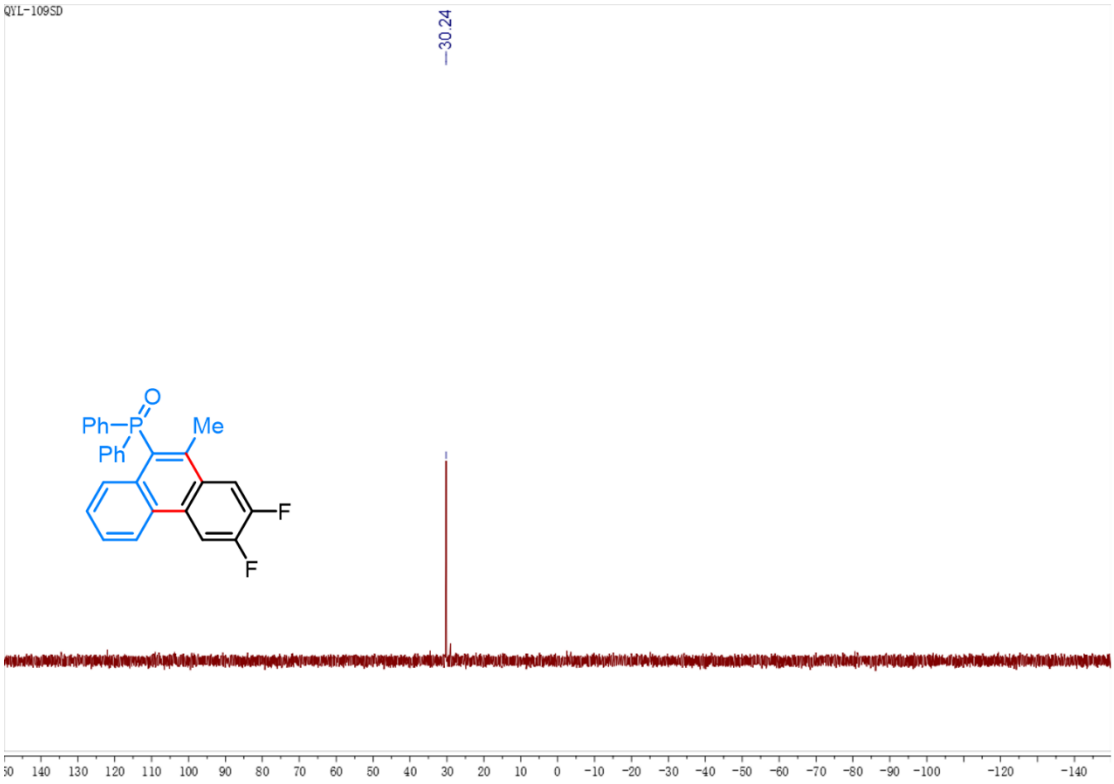
^{13}C NMR spectrum of **3r** (125 MHz, $CDCl_3$)



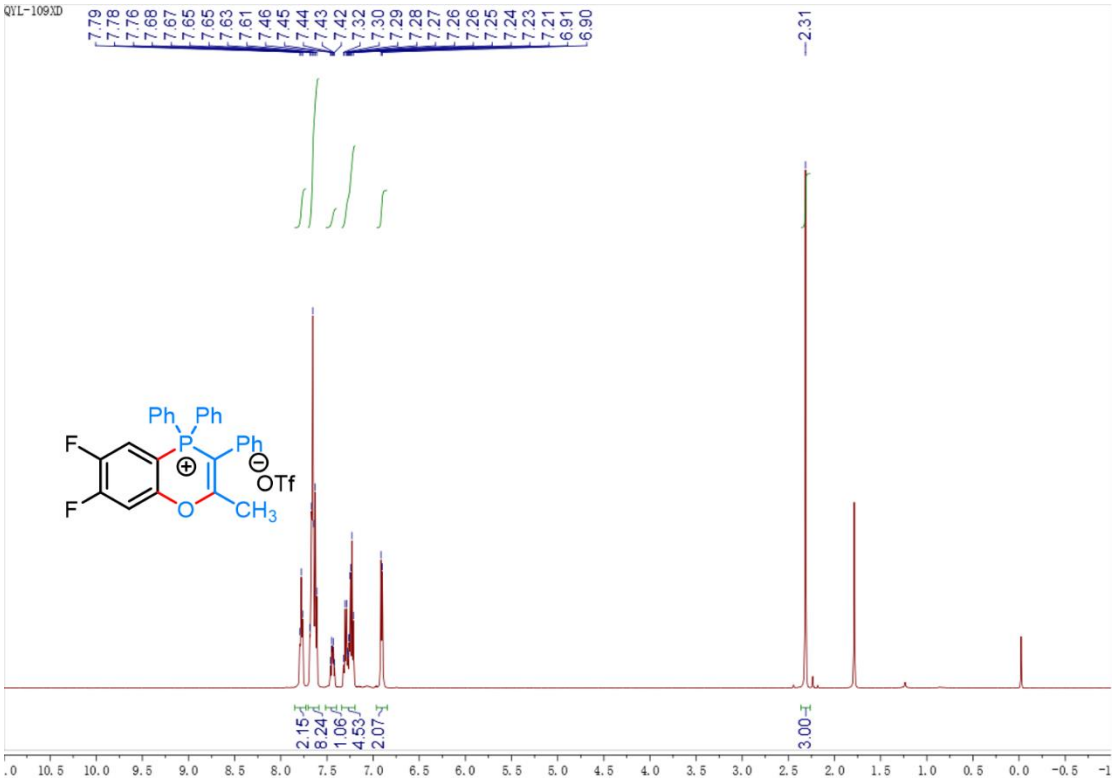
^{19}F NMR spectra of **3r** (470 MHz, $CDCl_3$)



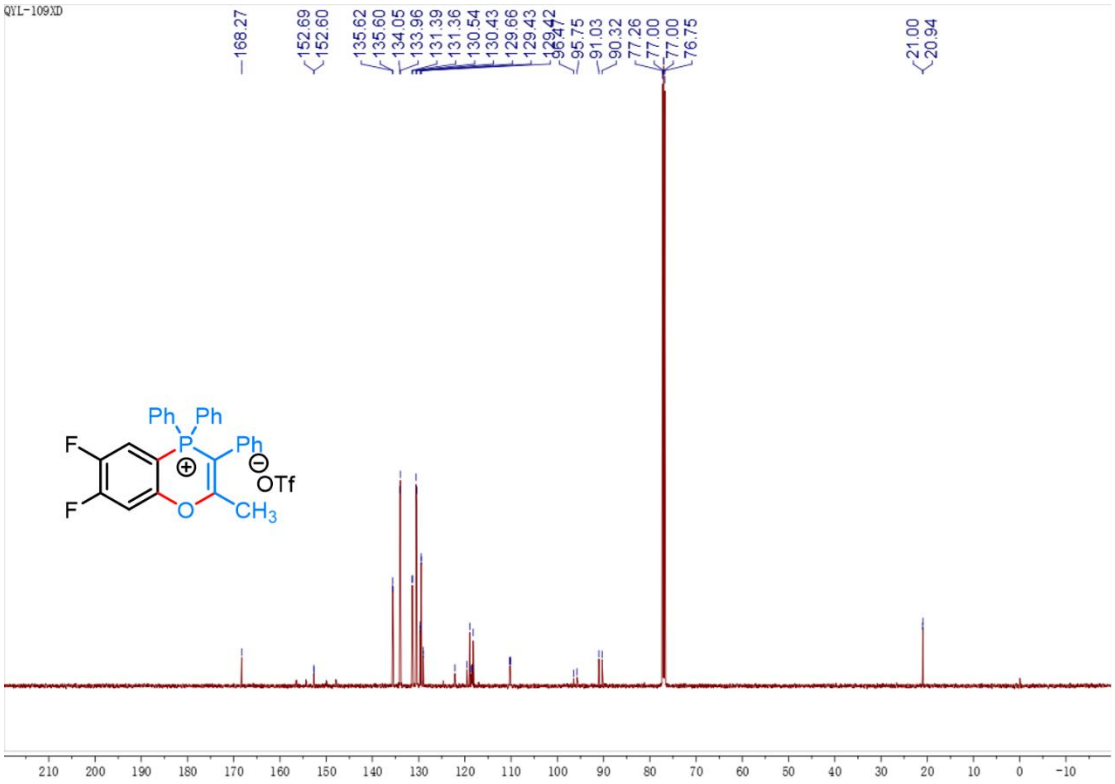
^{31}P NMR spectrum of **3r** (202 MHz, $CDCl_3$)



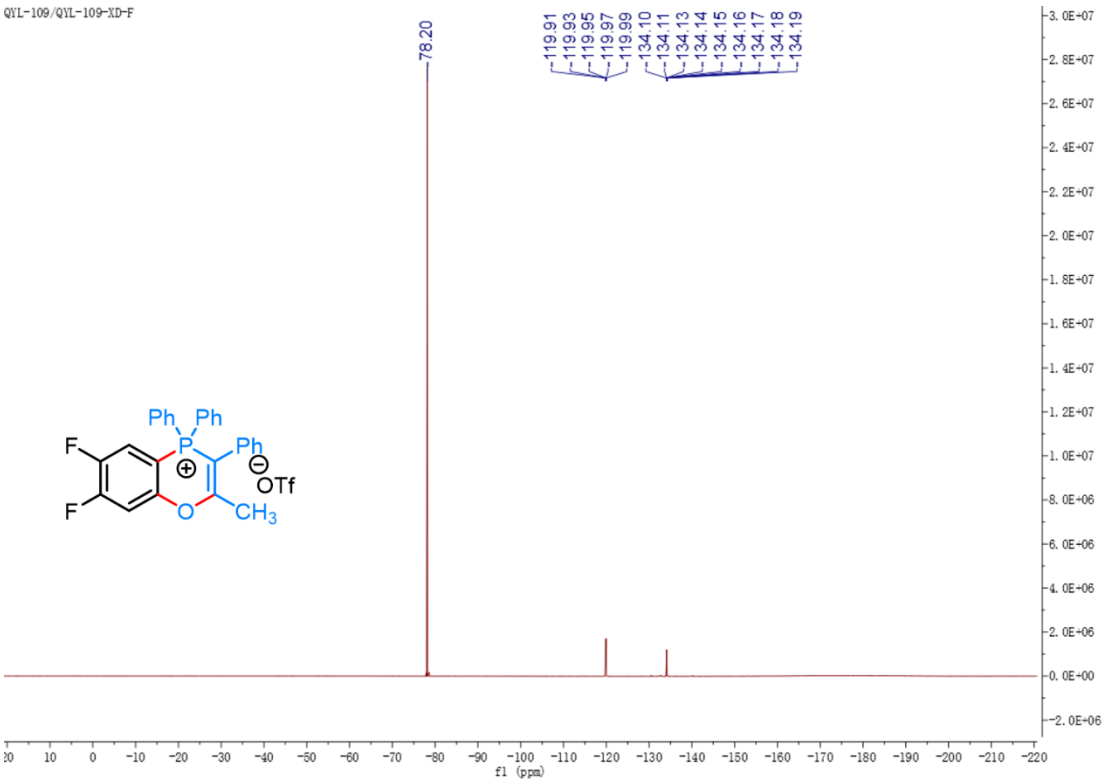
^{1}H NMR spectrum of **4b** (500 MHz, $CDCl_3$)



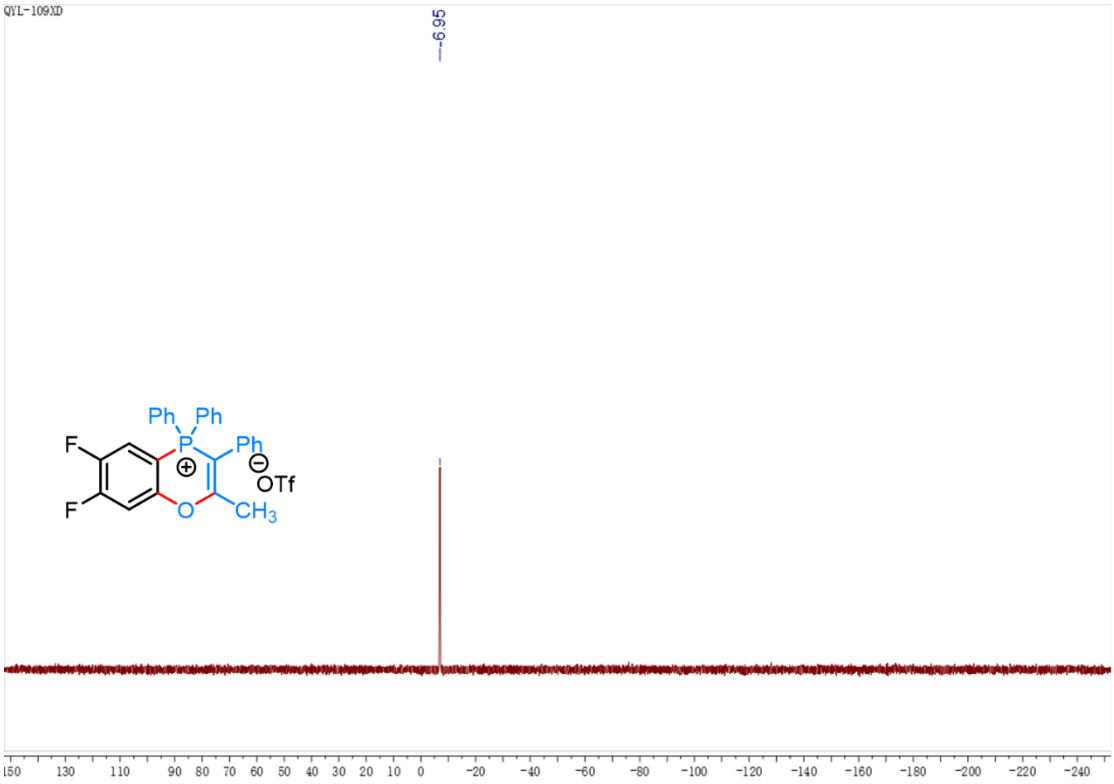
^{13}C NMR spectrum of **4b** (125 MHz, $CDCl_3$)



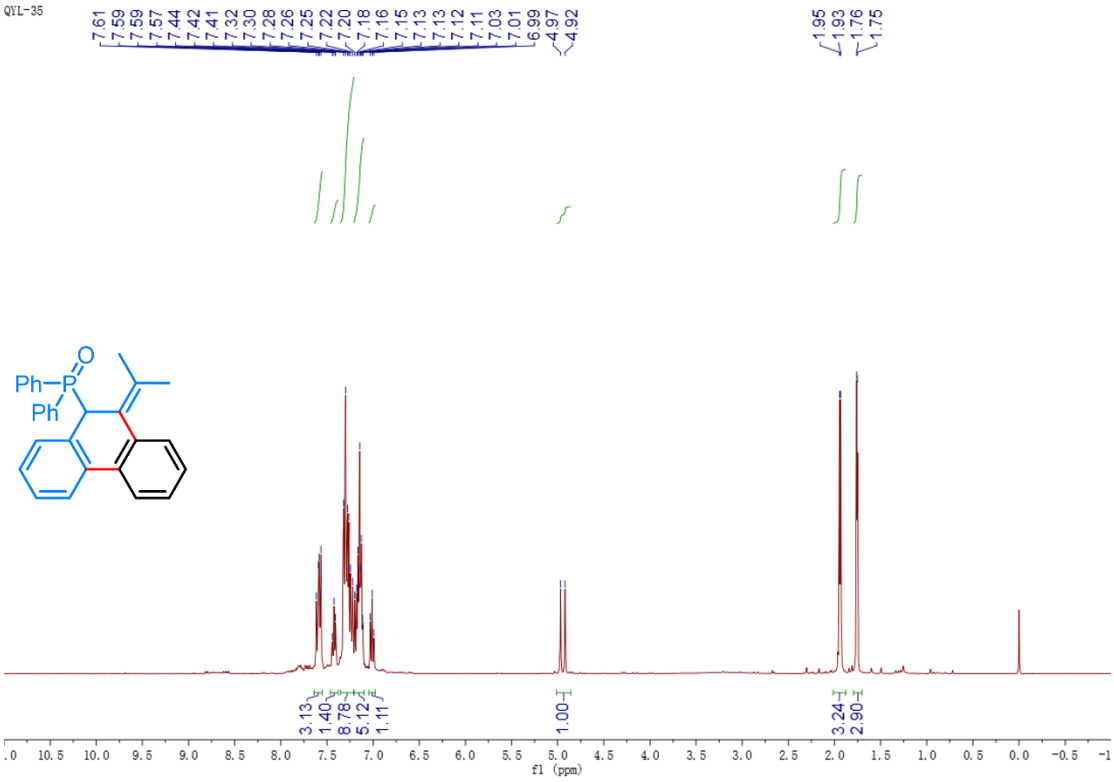
^{19}F NMR spectra of **4b** (470 MHz, $CDCl_3$)



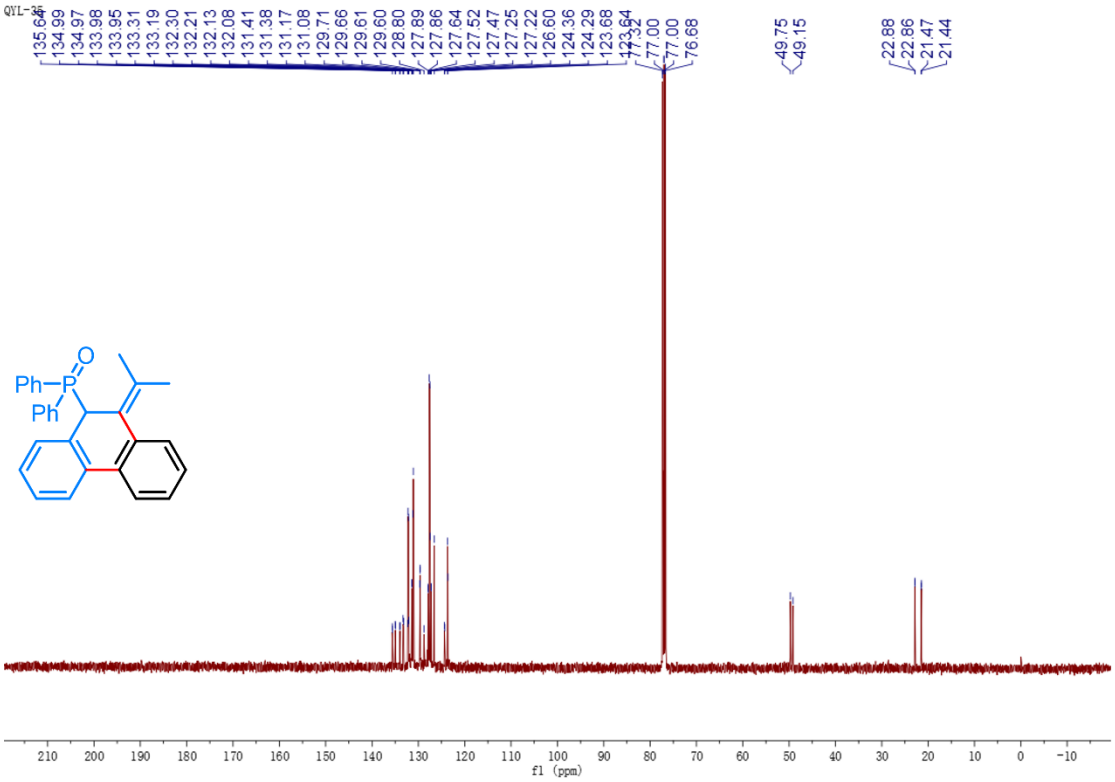
^{31}P NMR spectrum of **4b** (202 MHz, $CDCl_3$)



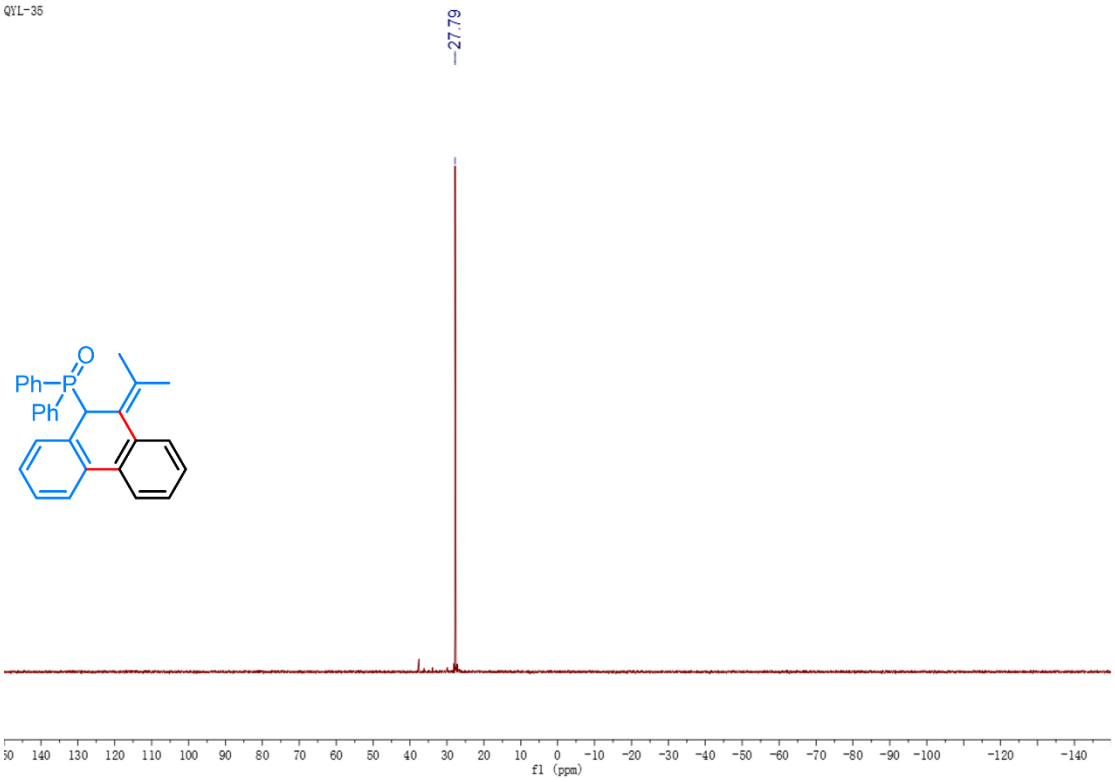
^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$)



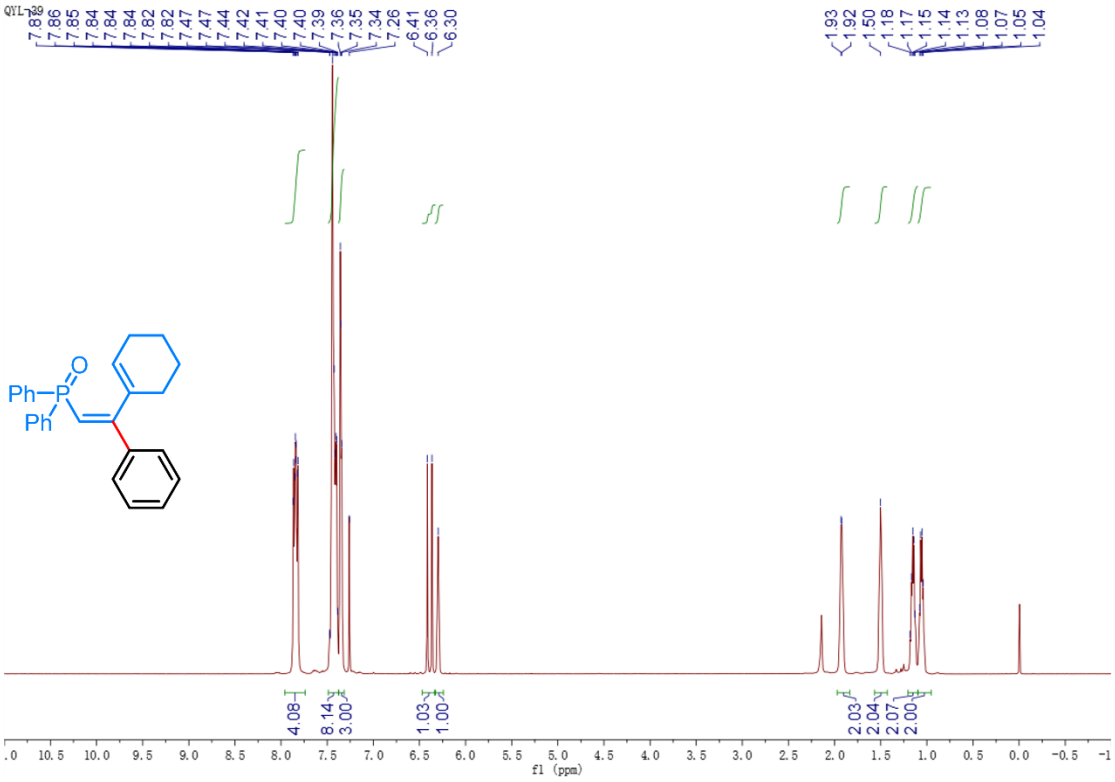
^{13}C NMR spectrum of **3s** (100 MHz, $CDCl_3$)



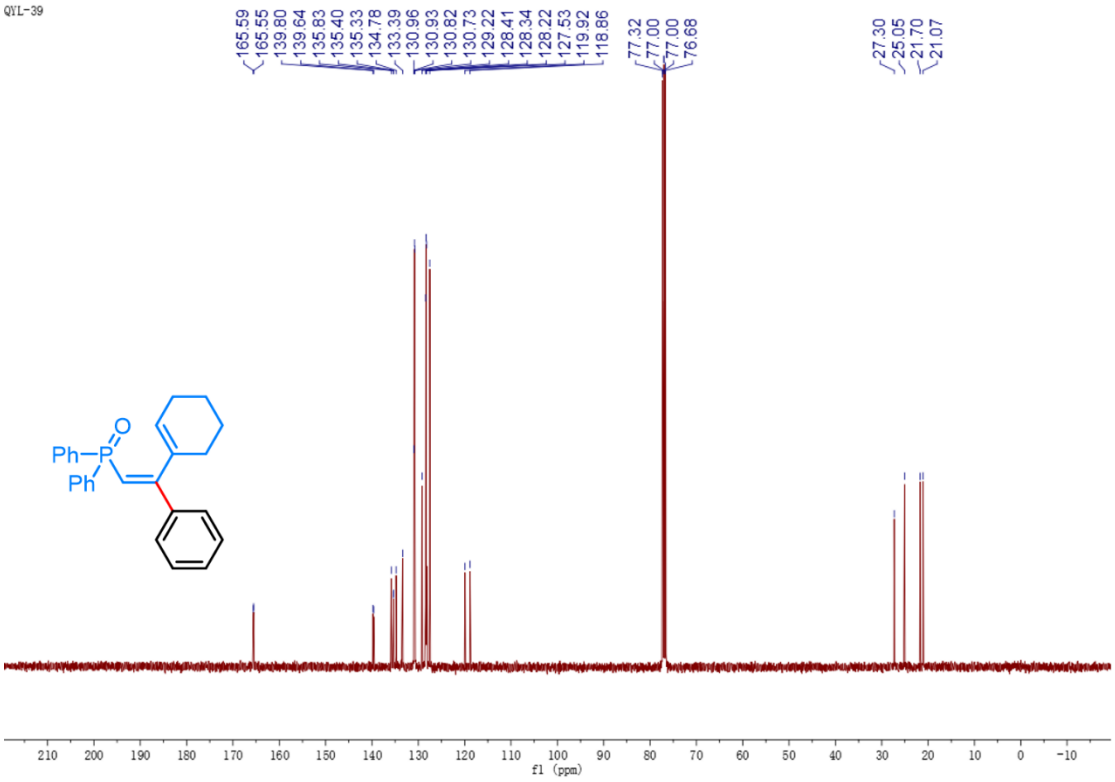
^{31}P NMR spectrum of **3s** (162 MHz, $CDCl_3$)



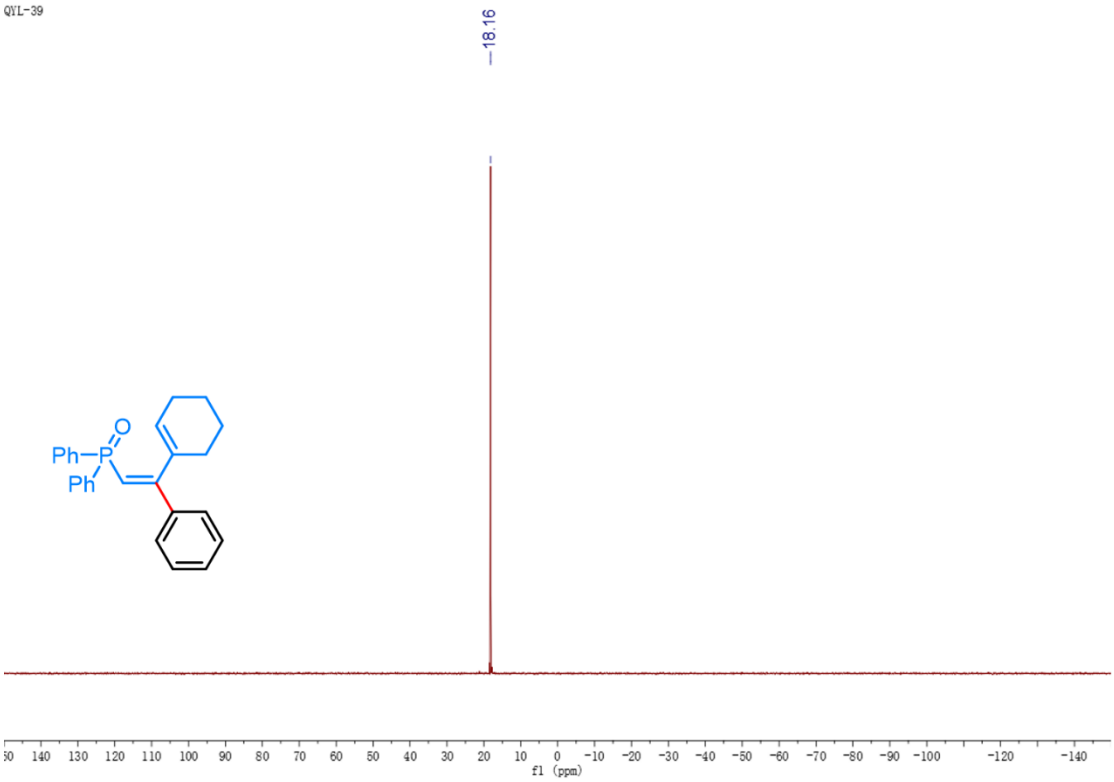
^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$)



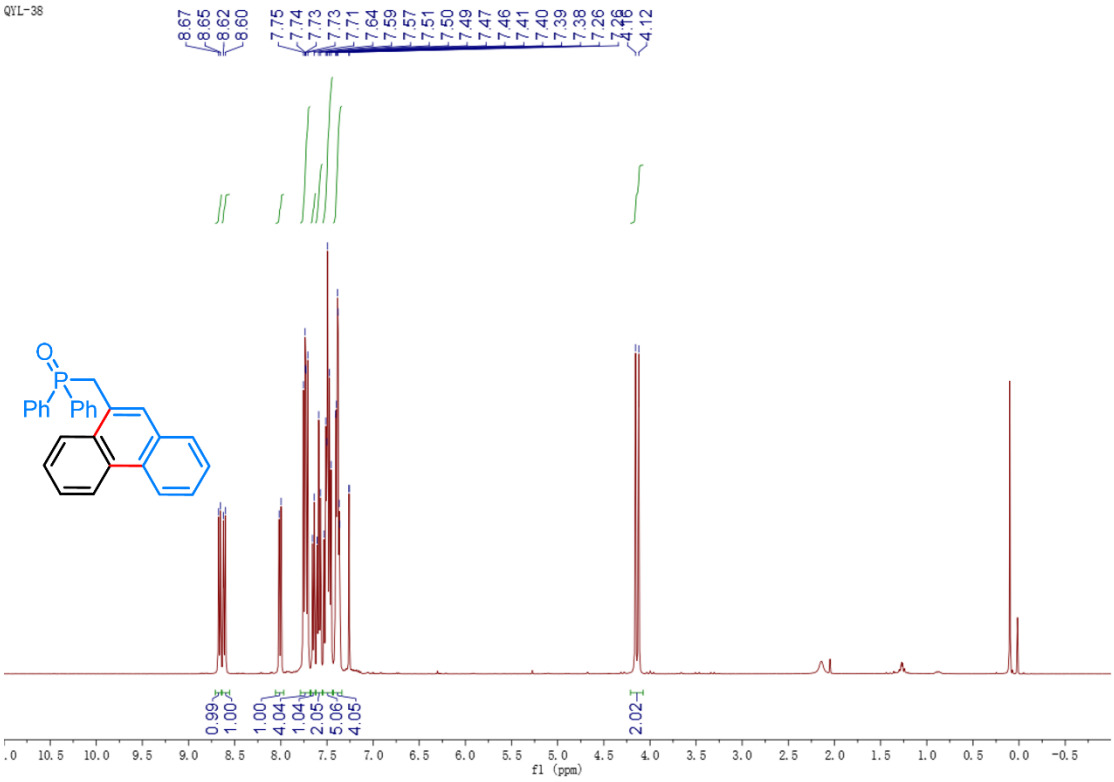
^{13}C NMR spectrum of **3t** (100 MHz, $CDCl_3$)



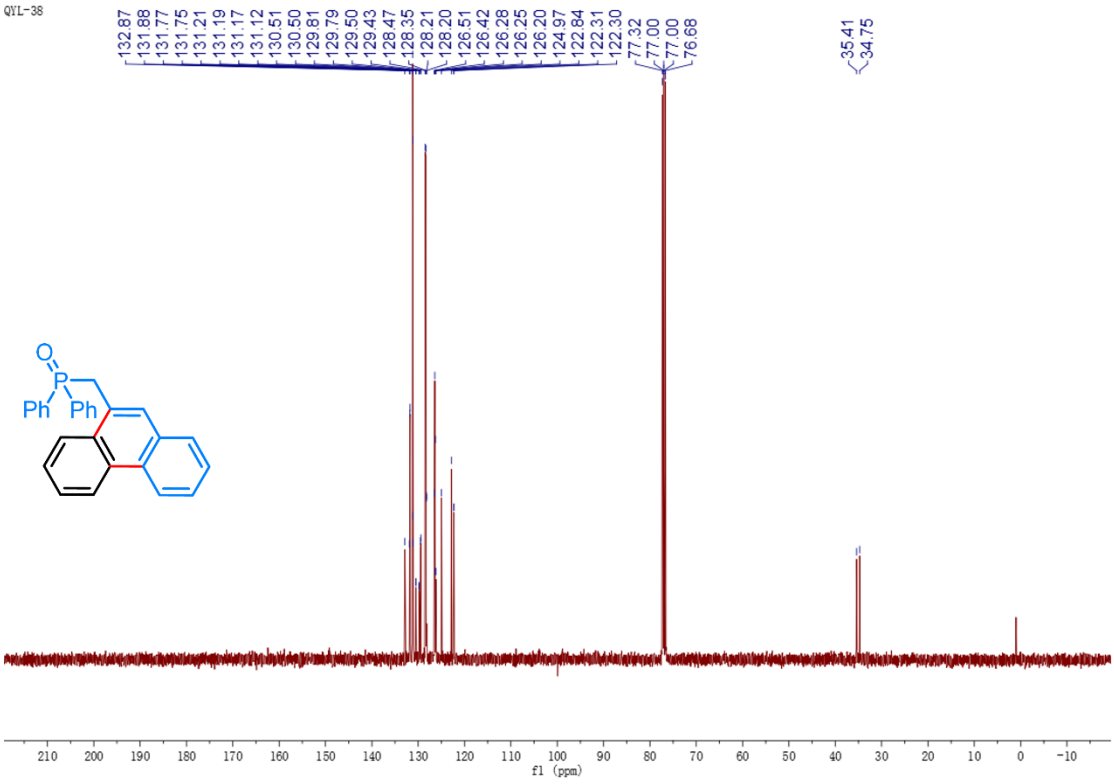
^{31}P NMR spectrum of **3t** (162 MHz, $CDCl_3$)



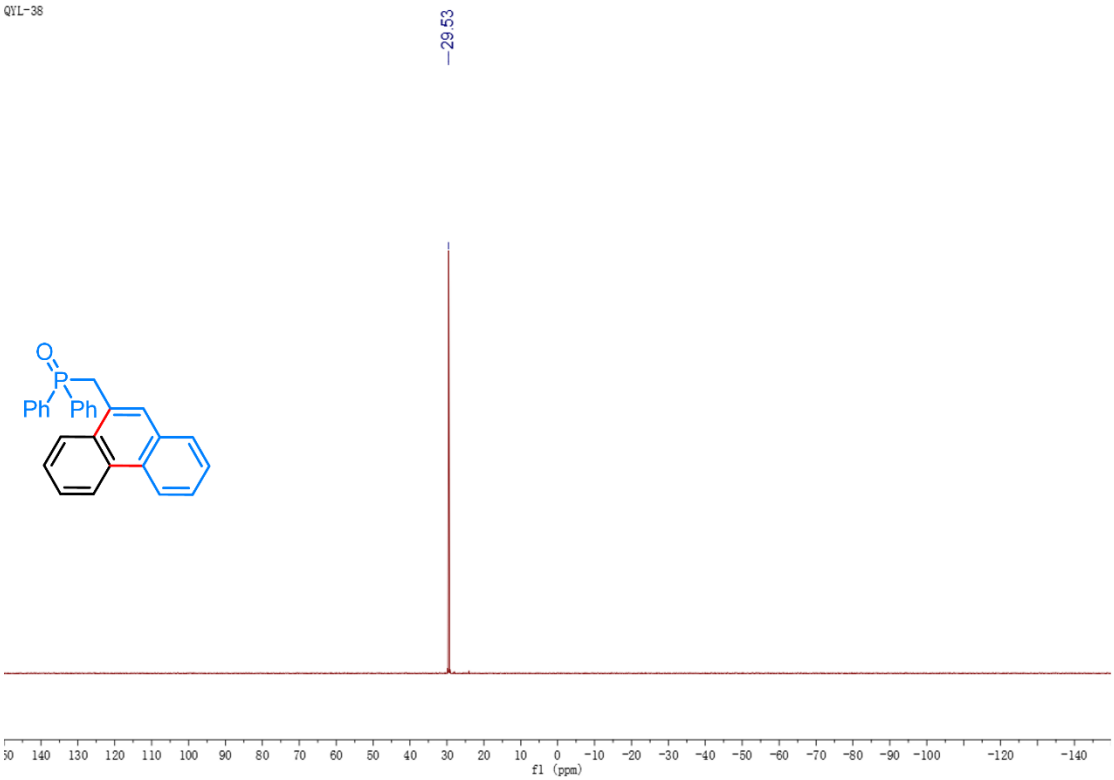
^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$)



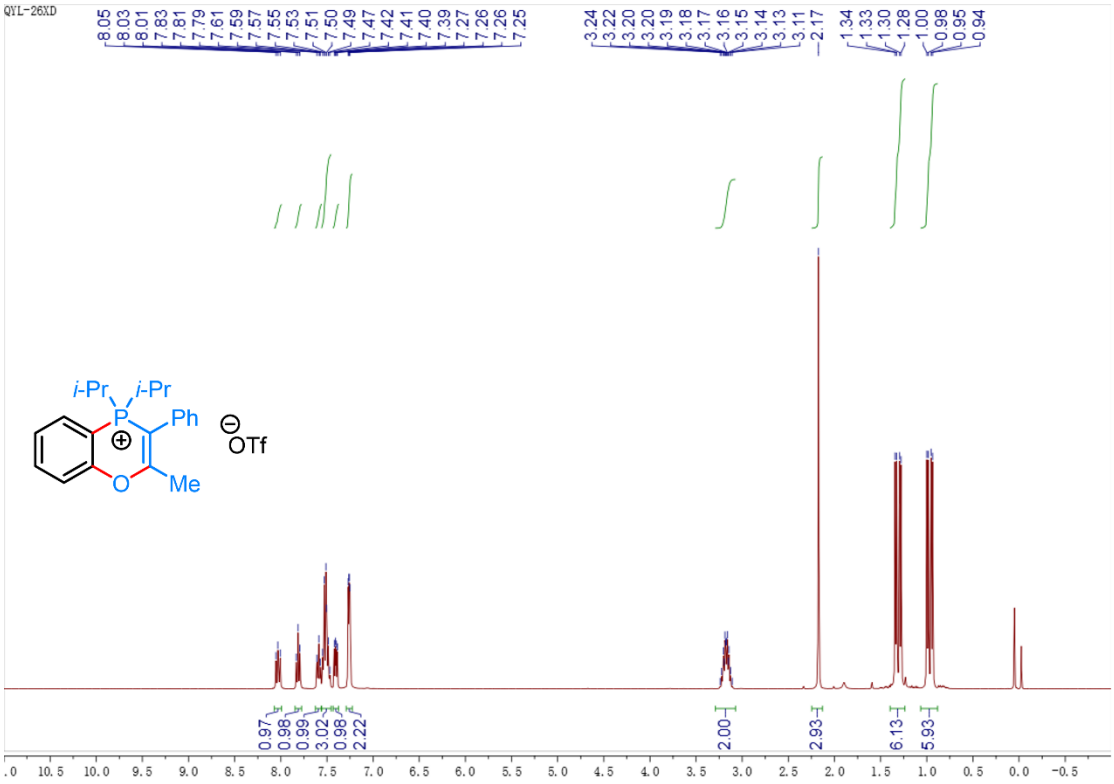
^{13}C NMR spectrum of **3u** (100 MHz, $CDCl_3$)



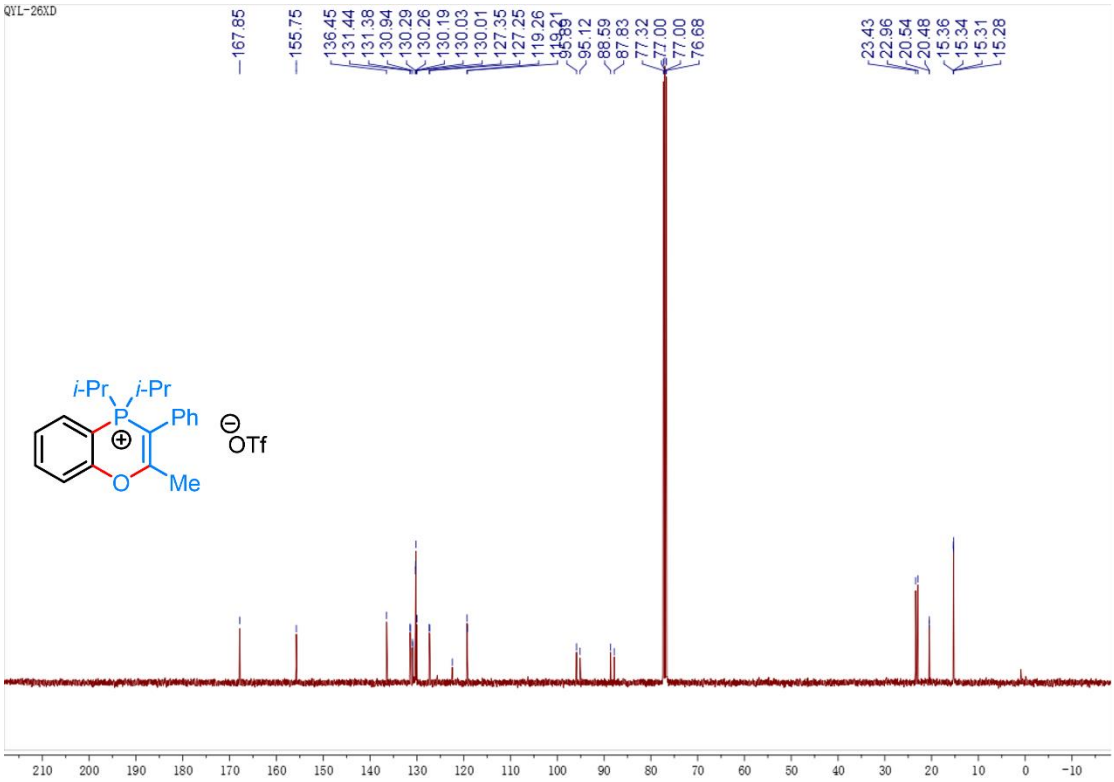
^{31}P NMR spectrum of **3u** (162 MHz, $CDCl_3$)



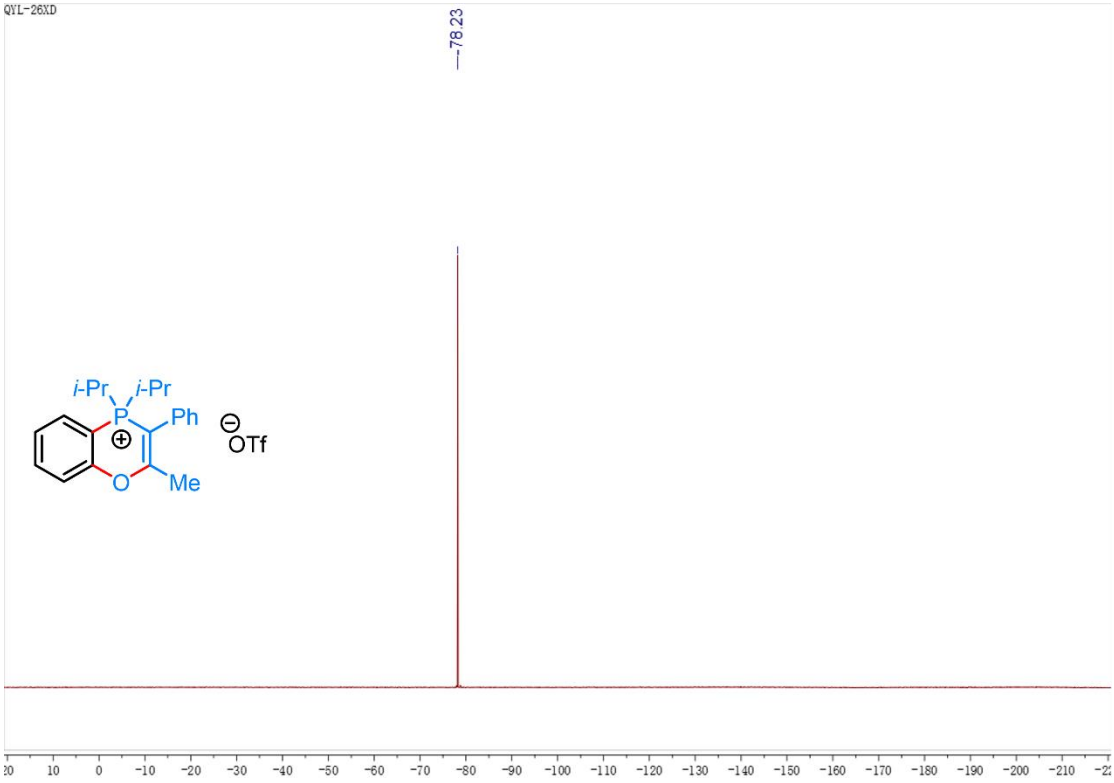
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)



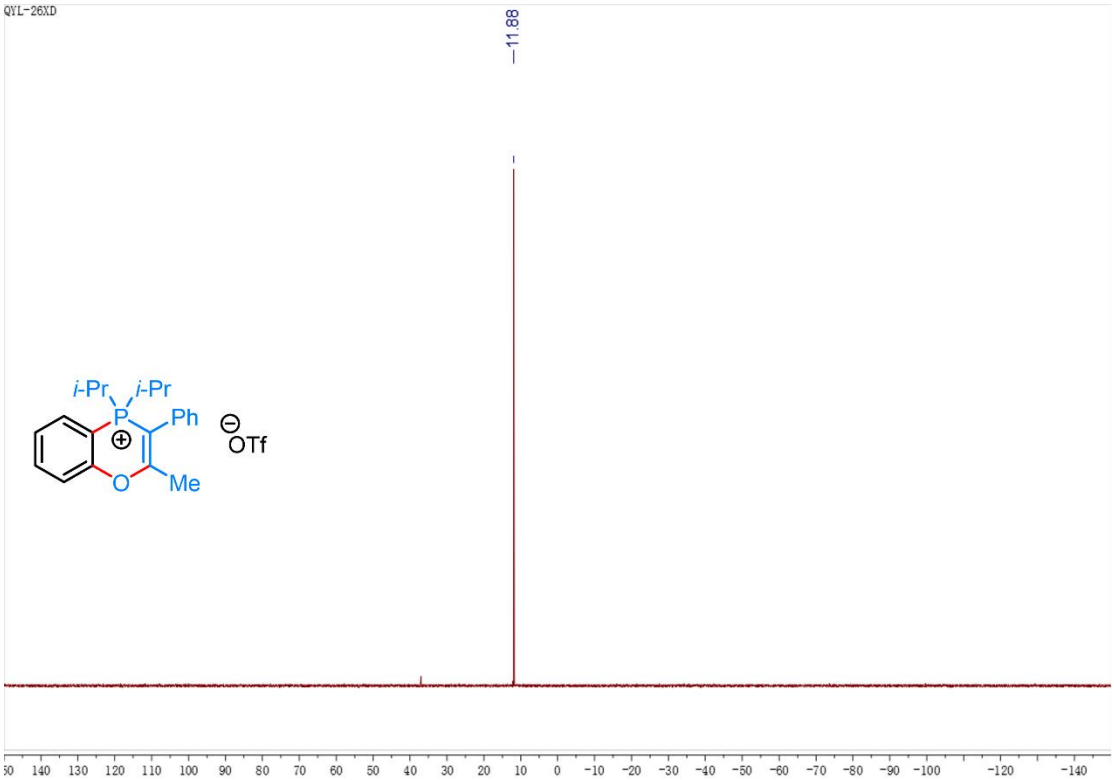
^{13}C NMR spectrum of **4c** (100 MHz, $CDCl_3$)



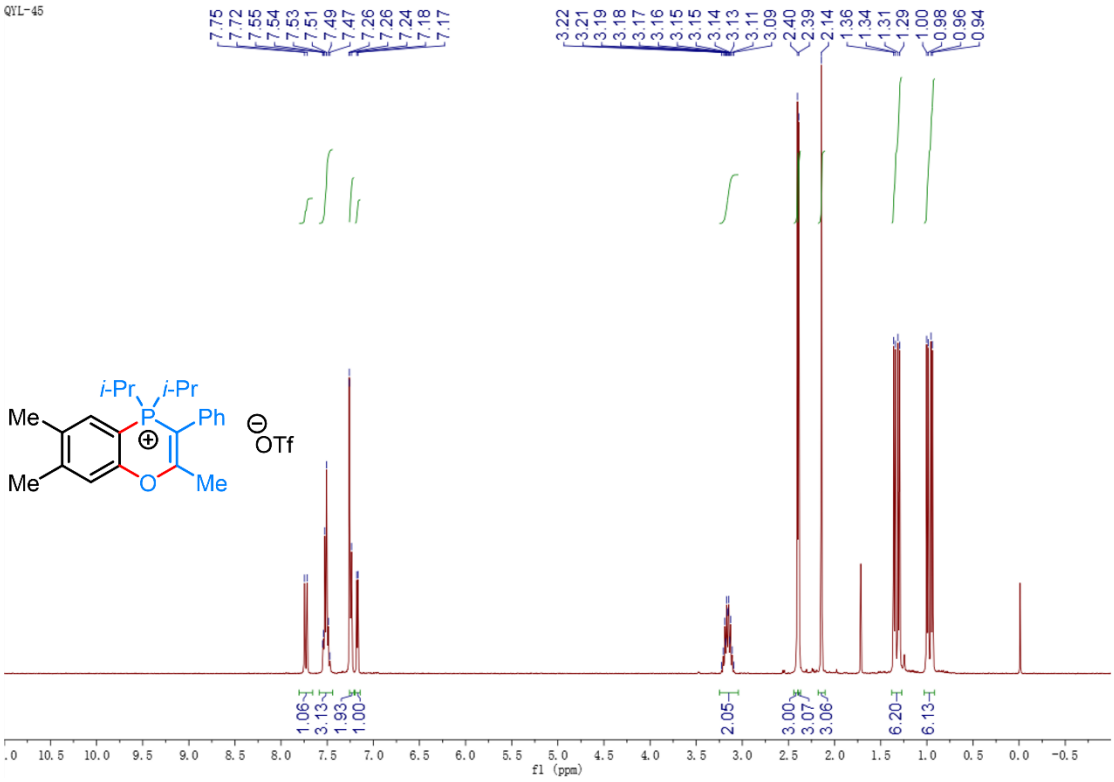
^{19}F NMR spectrum of **4c** (376 MHz, $CDCl_3$)



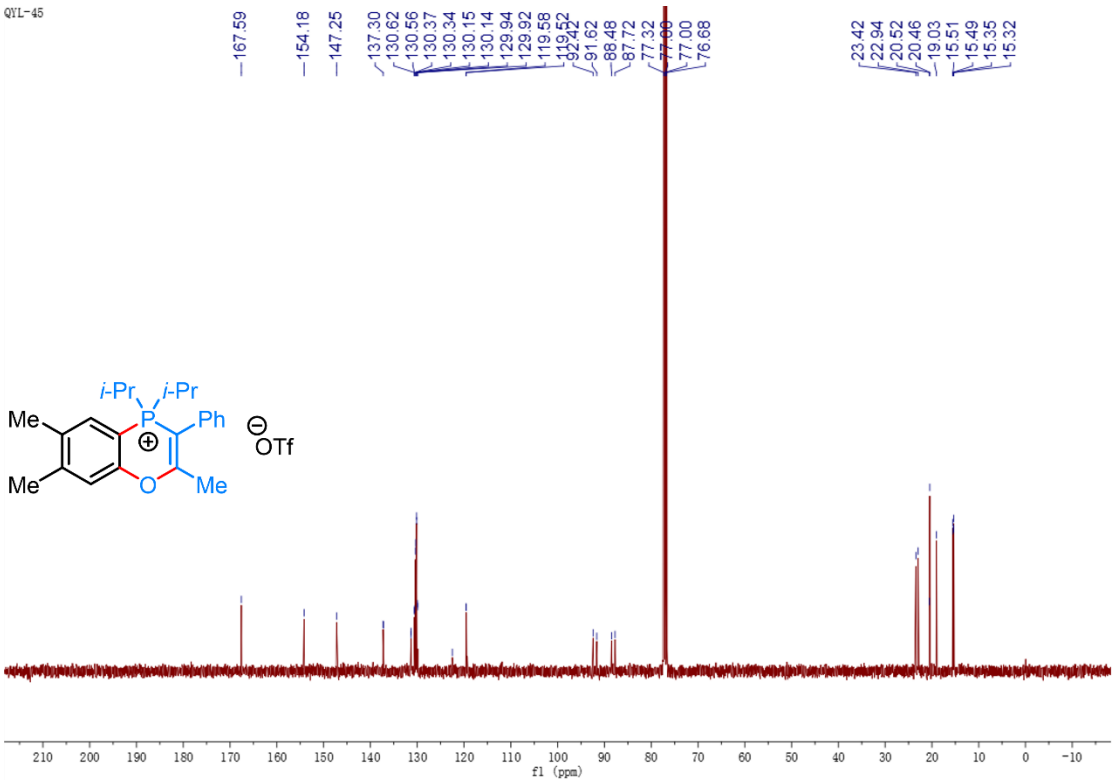
^{31}P NMR spectrum of **4c** (162 MHz, $CDCl_3$)



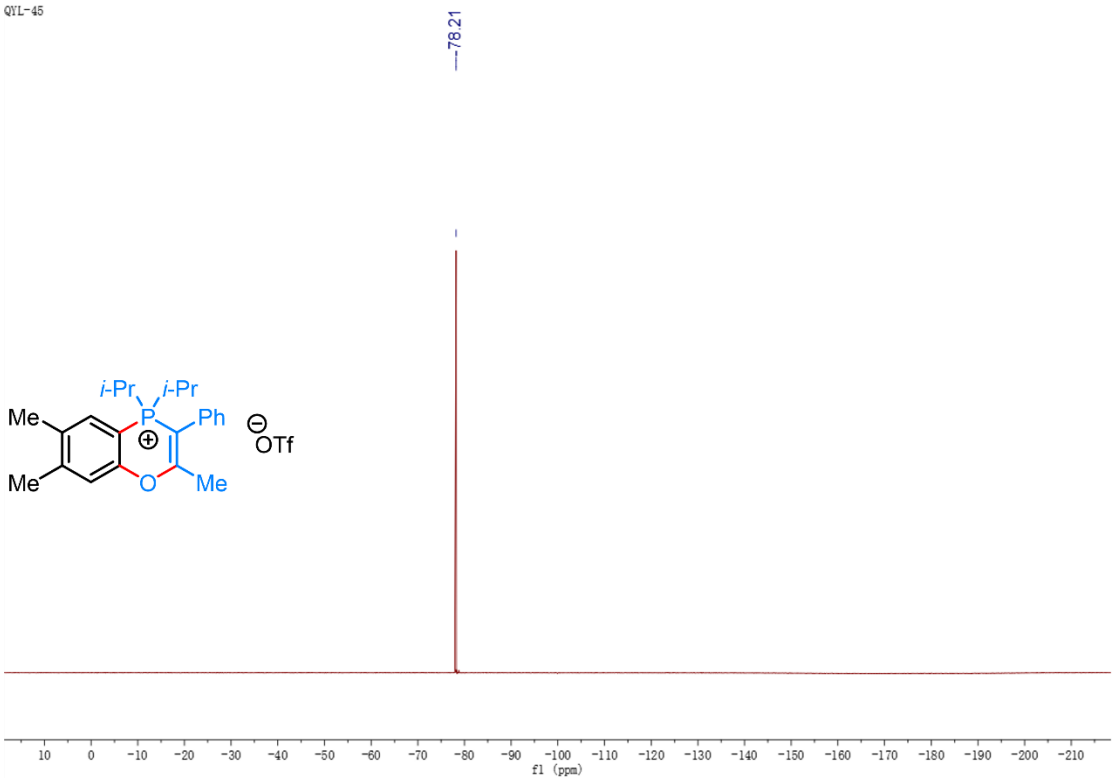
^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$)



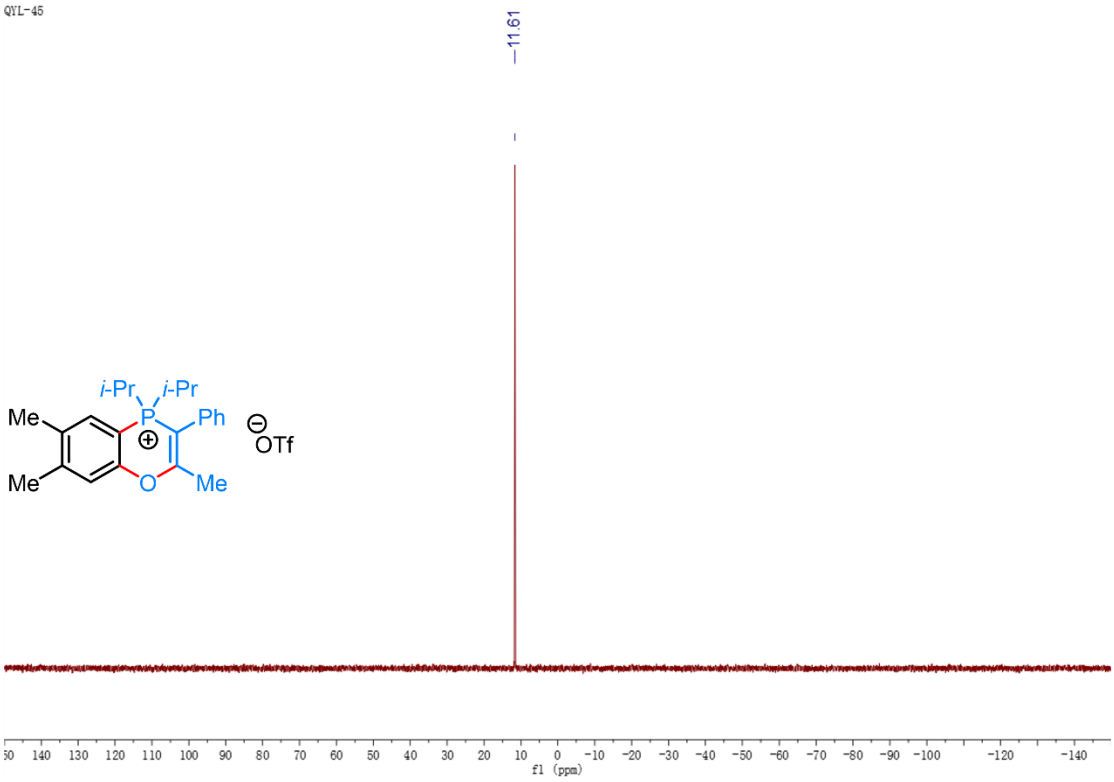
^{13}C NMR spectrum of **4d** (100 MHz, $CDCl_3$)



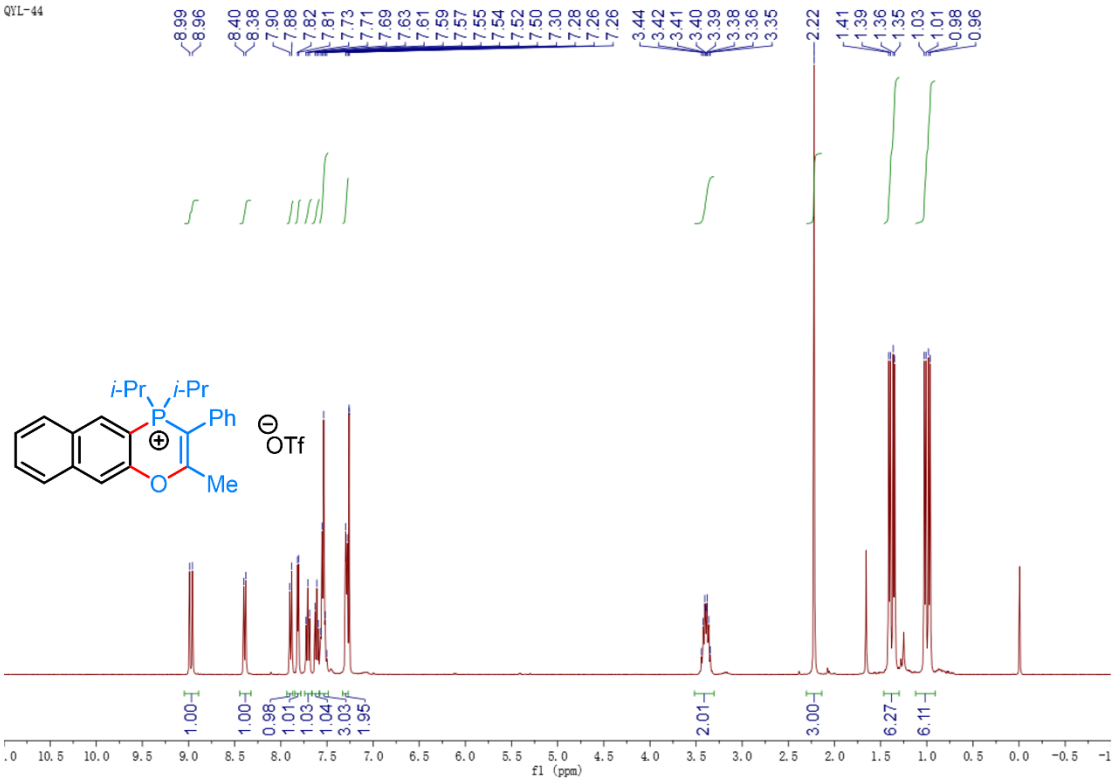
^{19}F NMR spectrum of **4d** (376 MHz, $CDCl_3$)



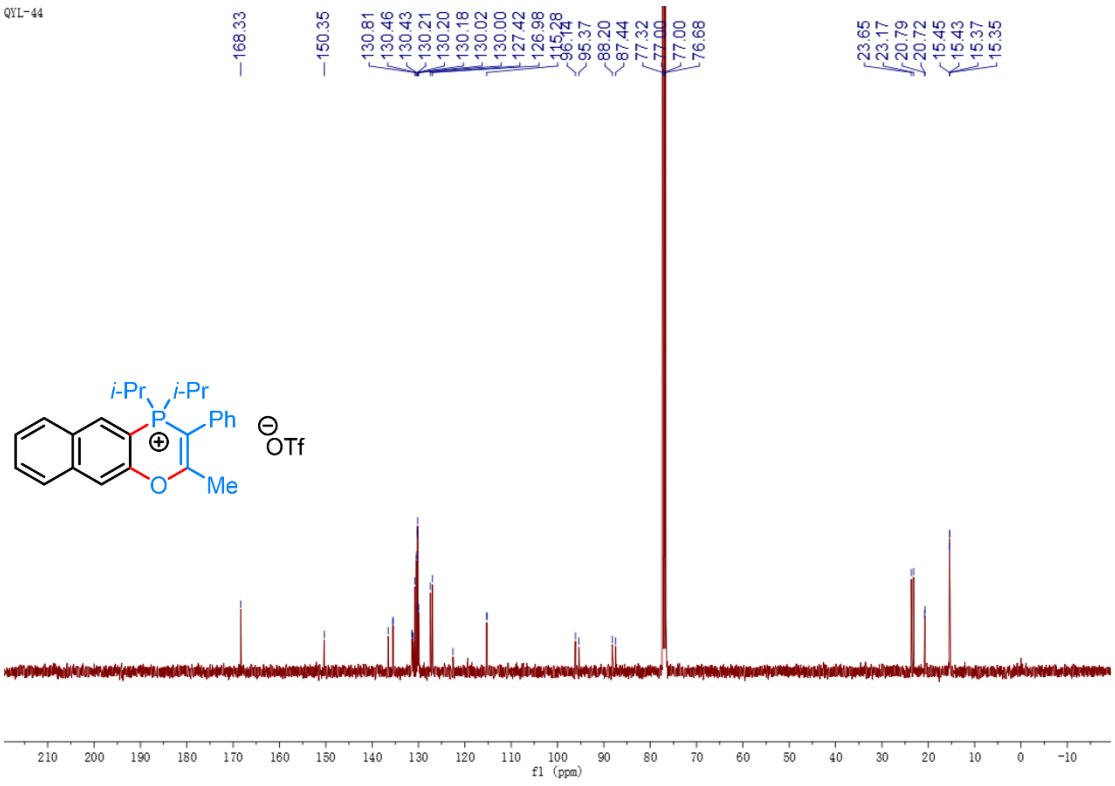
^{31}P NMR spectrum of **4d** (162 MHz, $CDCl_3$)



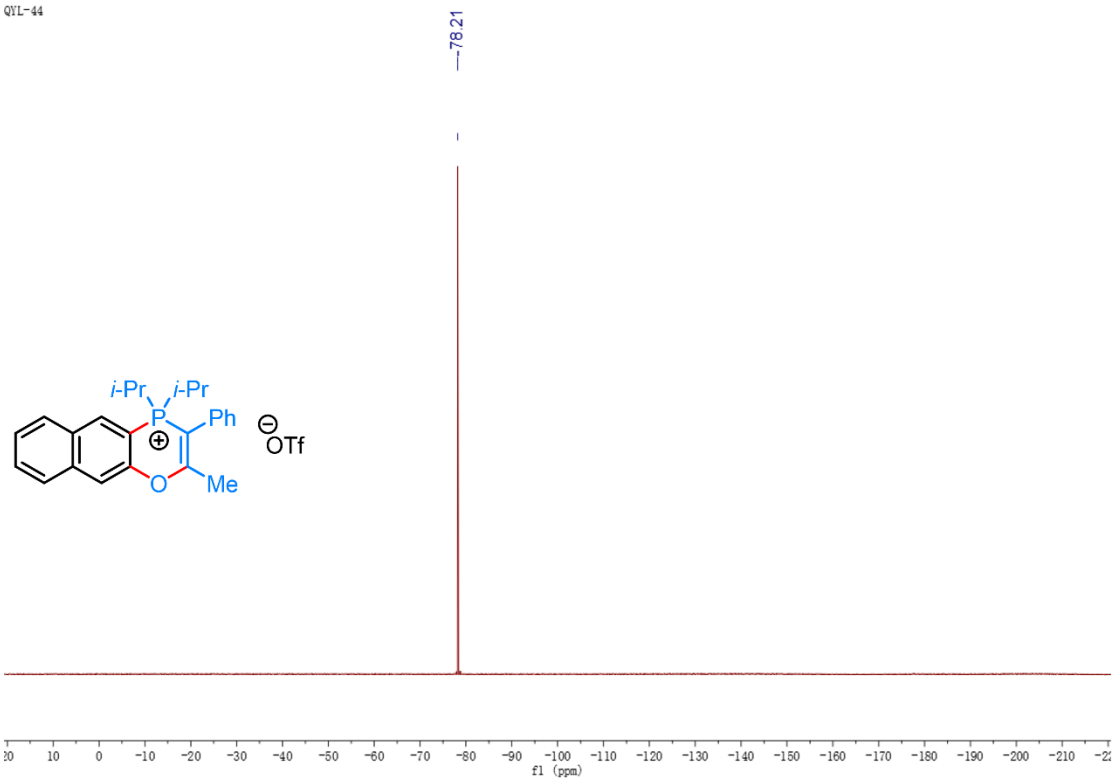
^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$)



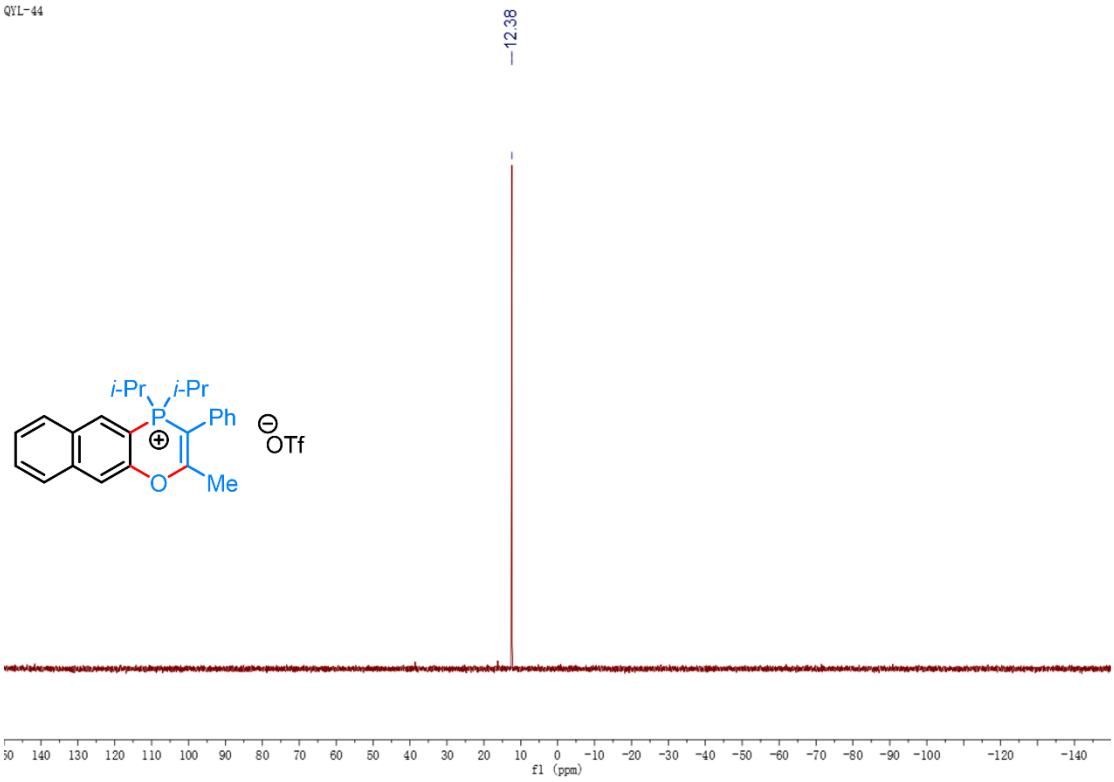
^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$)



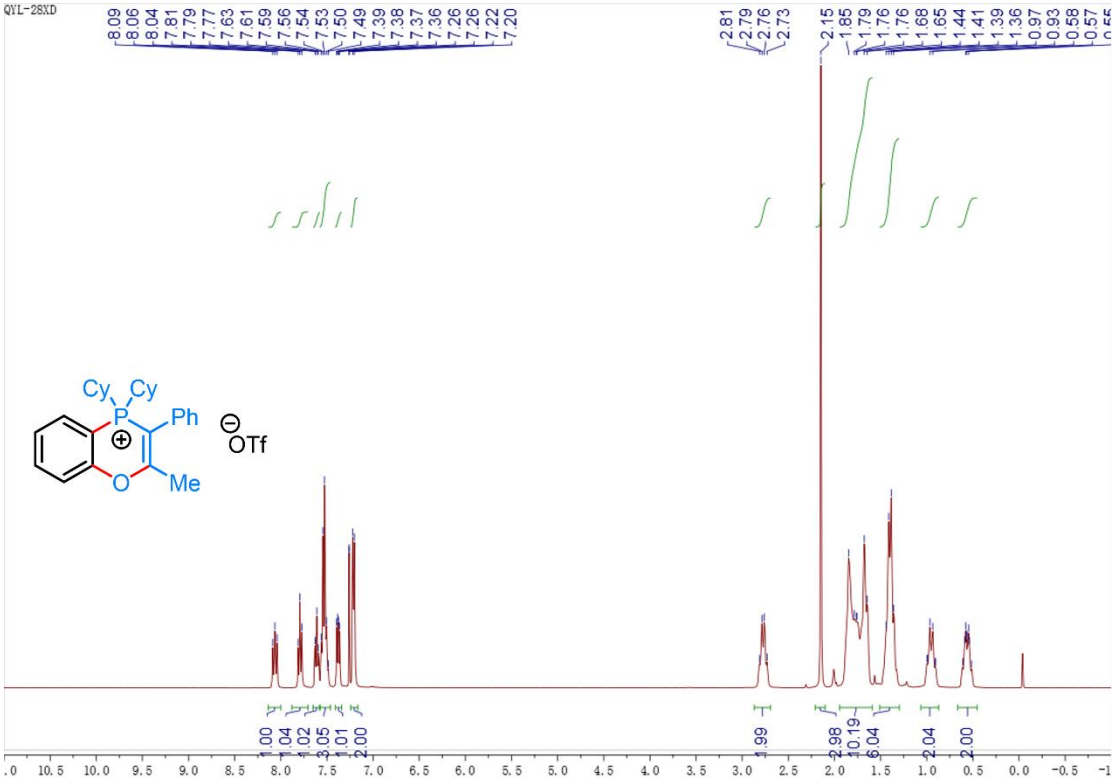
^{19}F NMR spectrum of **4e** (376 MHz, $CDCl_3$)



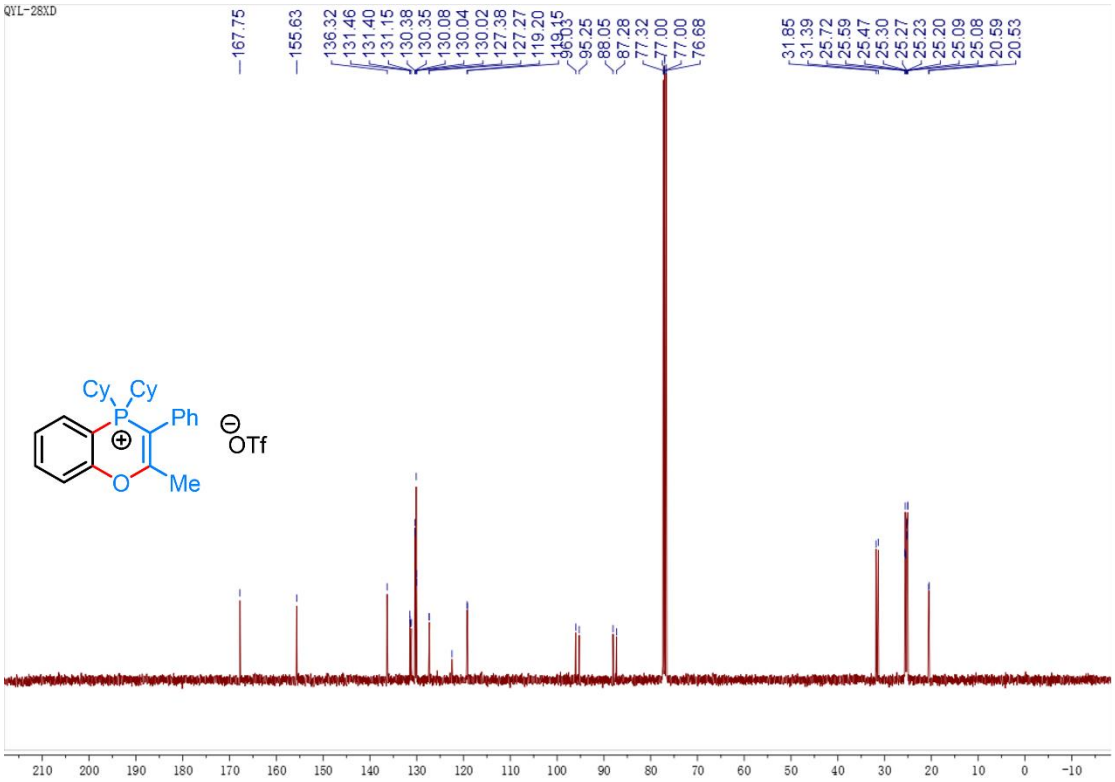
^{31}P NMR spectrum of **4e** (162 MHz, $CDCl_3$)



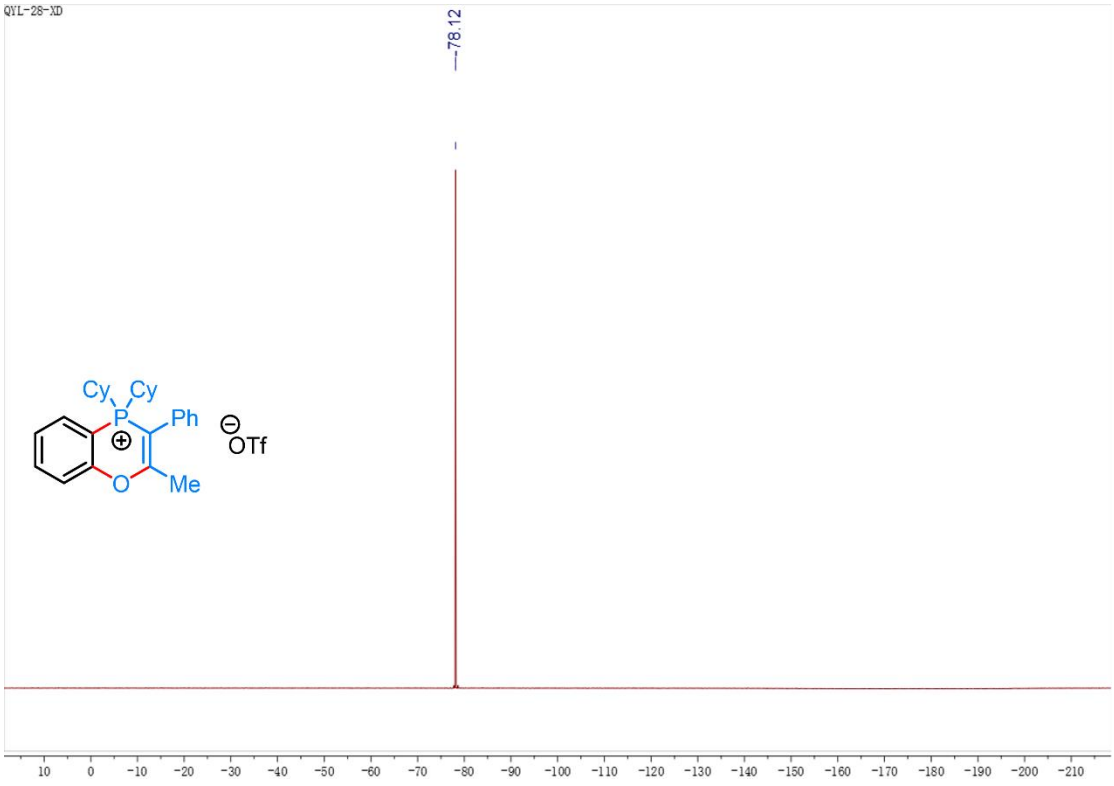
^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$)



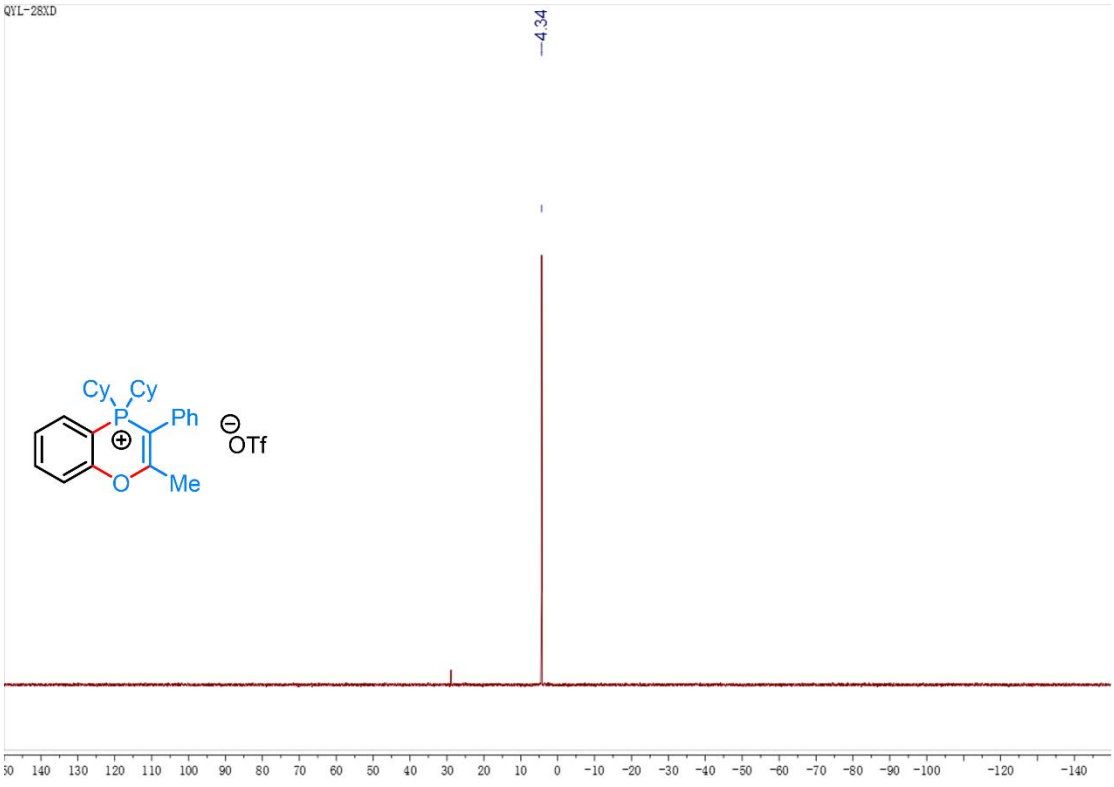
^{13}C NMR spectrum of **4f** (100 MHz, $CDCl_3$)



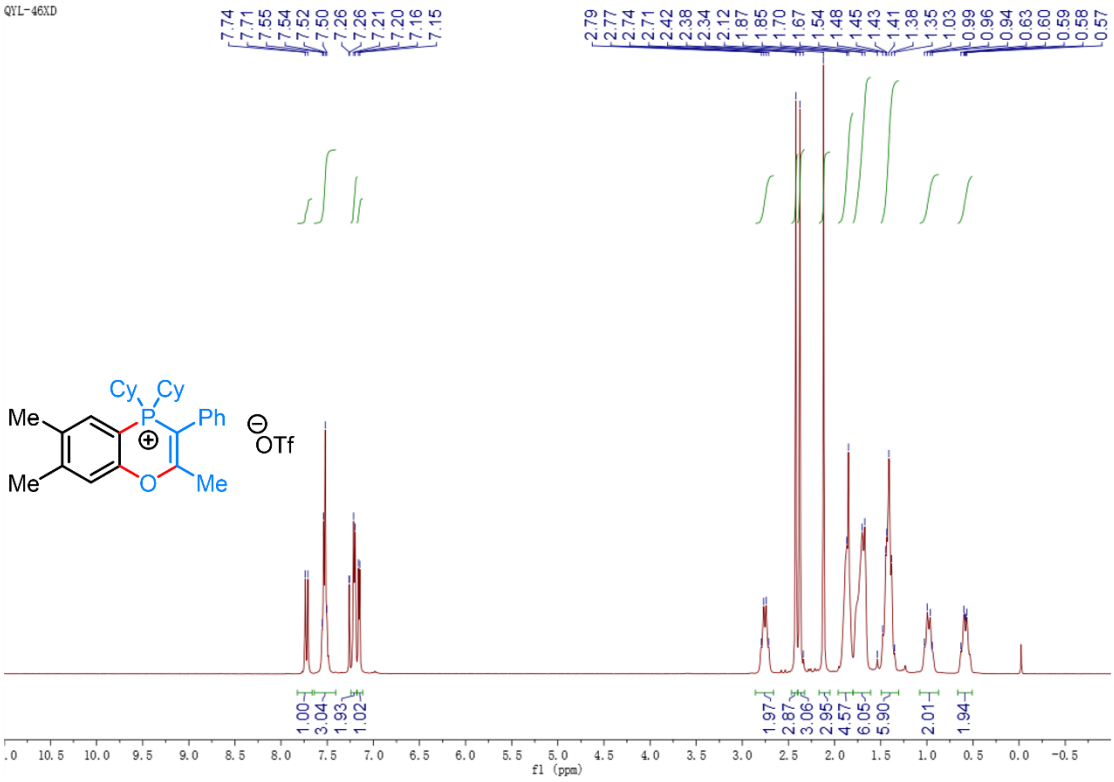
^{19}F NMR spectrum of **4f** (376 MHz, $CDCl_3$)



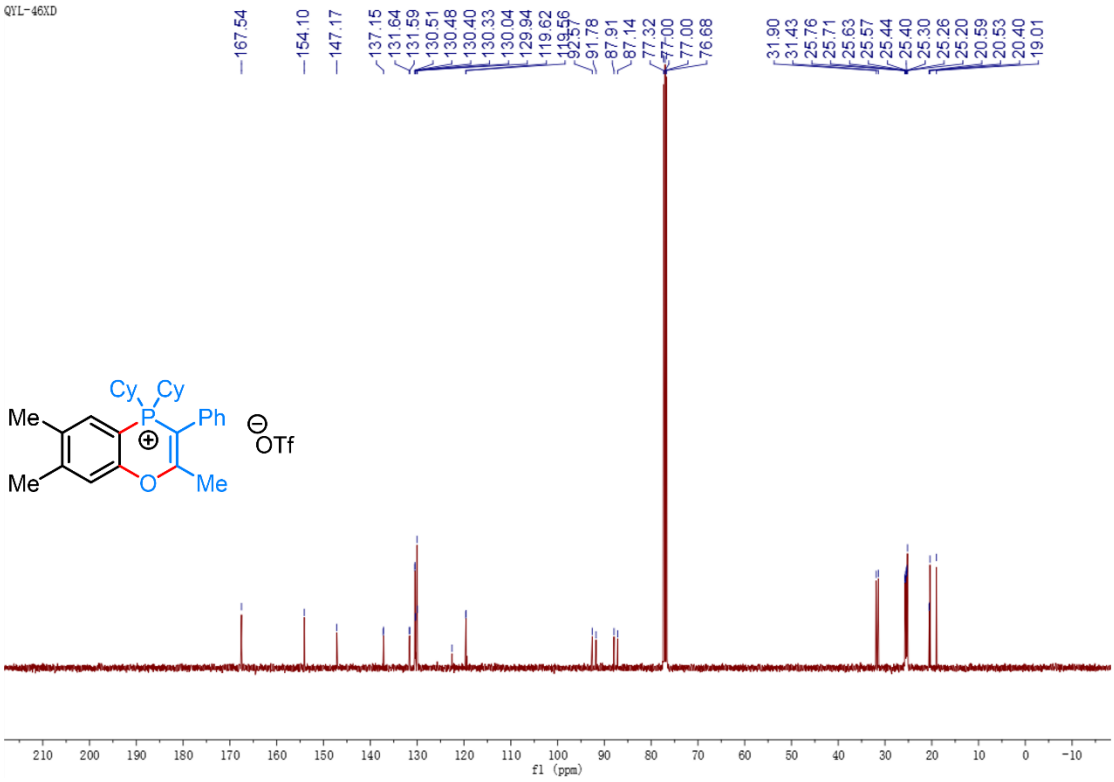
^{31}P NMR spectrum of **4f** (162 MHz, $CDCl_3$)



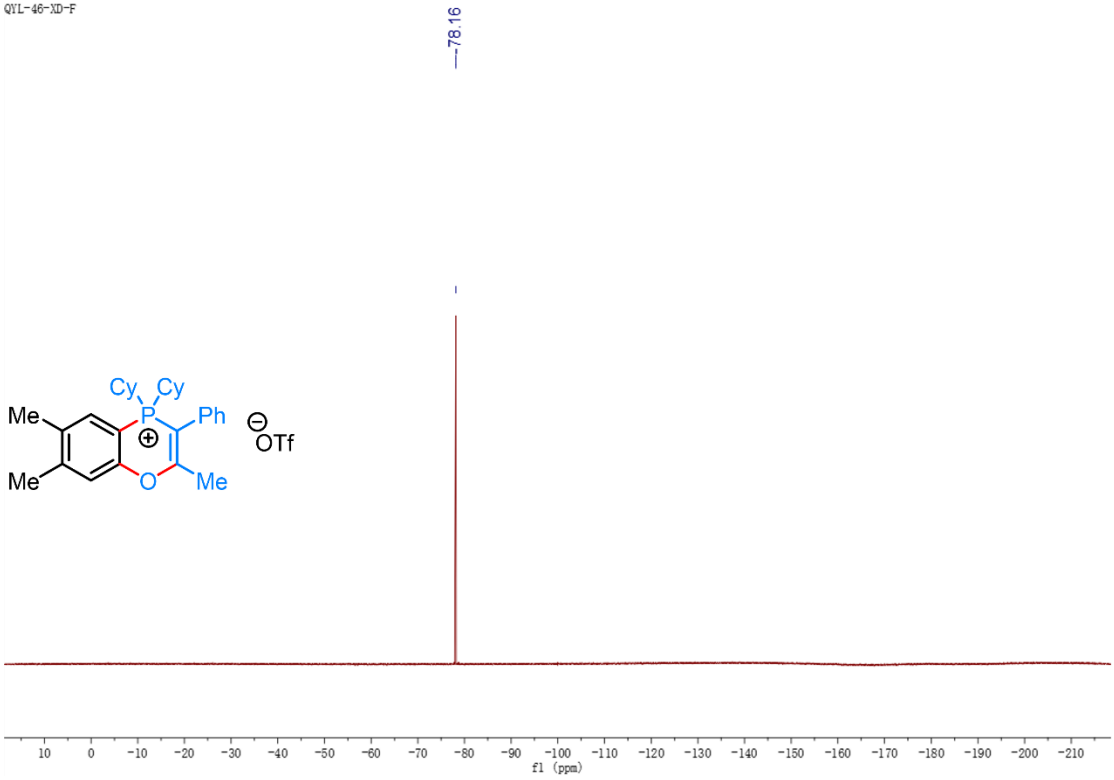
^{1}H NMR spectrum of **4g** (400 MHz, $CDCl_3$)



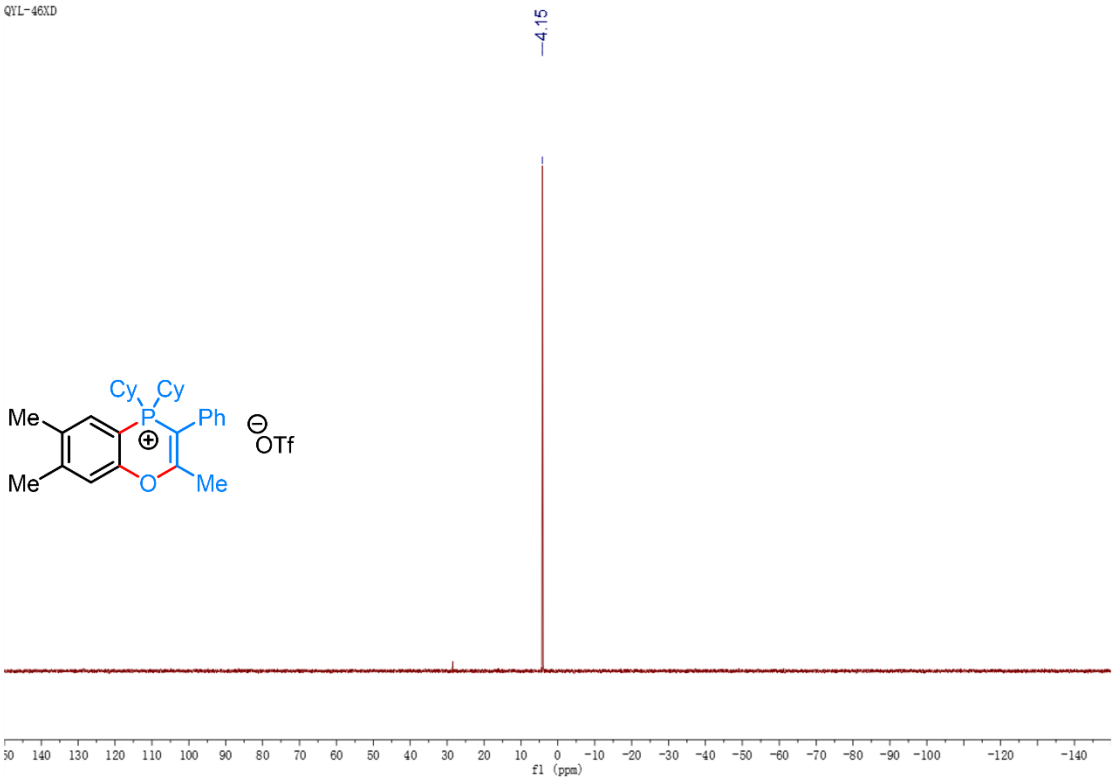
^{13}C NMR spectrum of **4g** (100 MHz, $CDCl_3$)



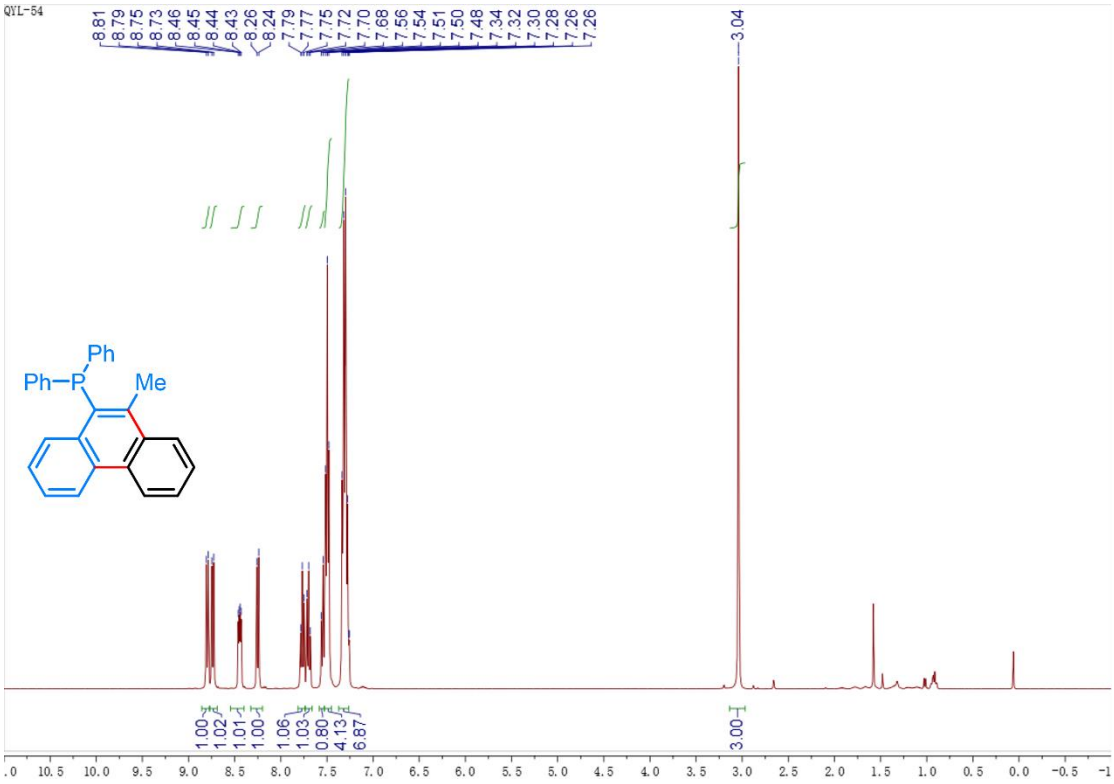
^{19}F NMR spectrum of **4g** (376 MHz, $CDCl_3$)



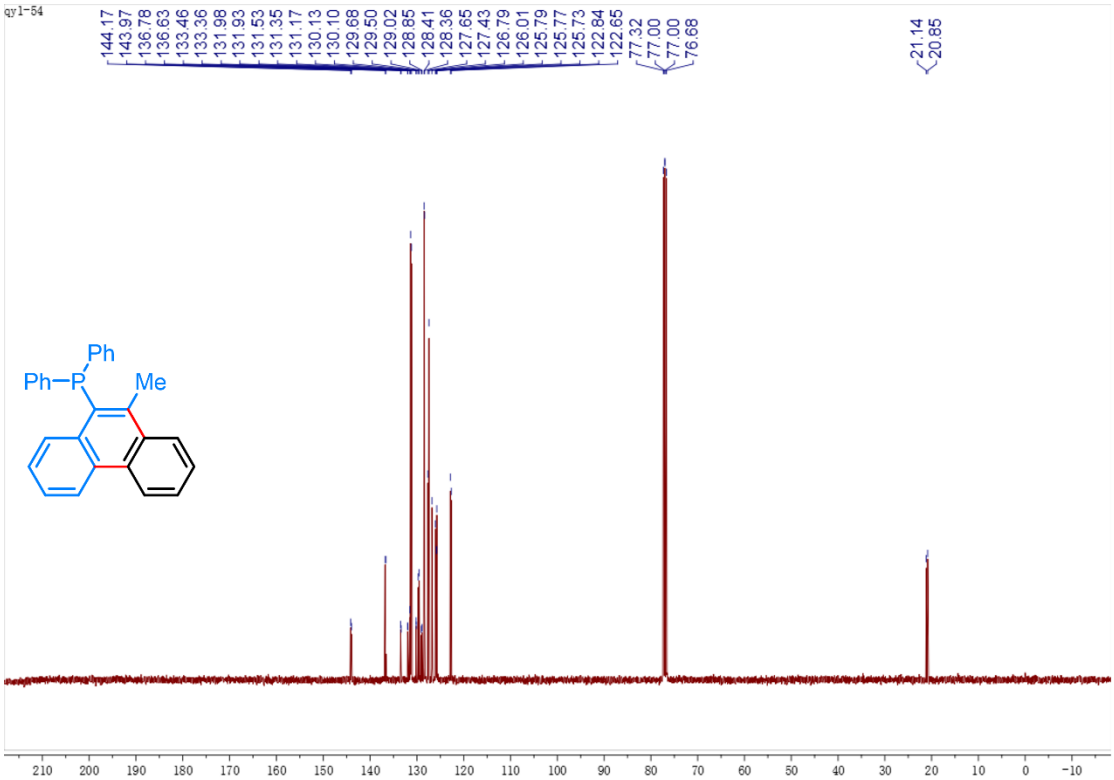
^{31}P NMR spectrum of **4g** (162 MHz, $CDCl_3$)



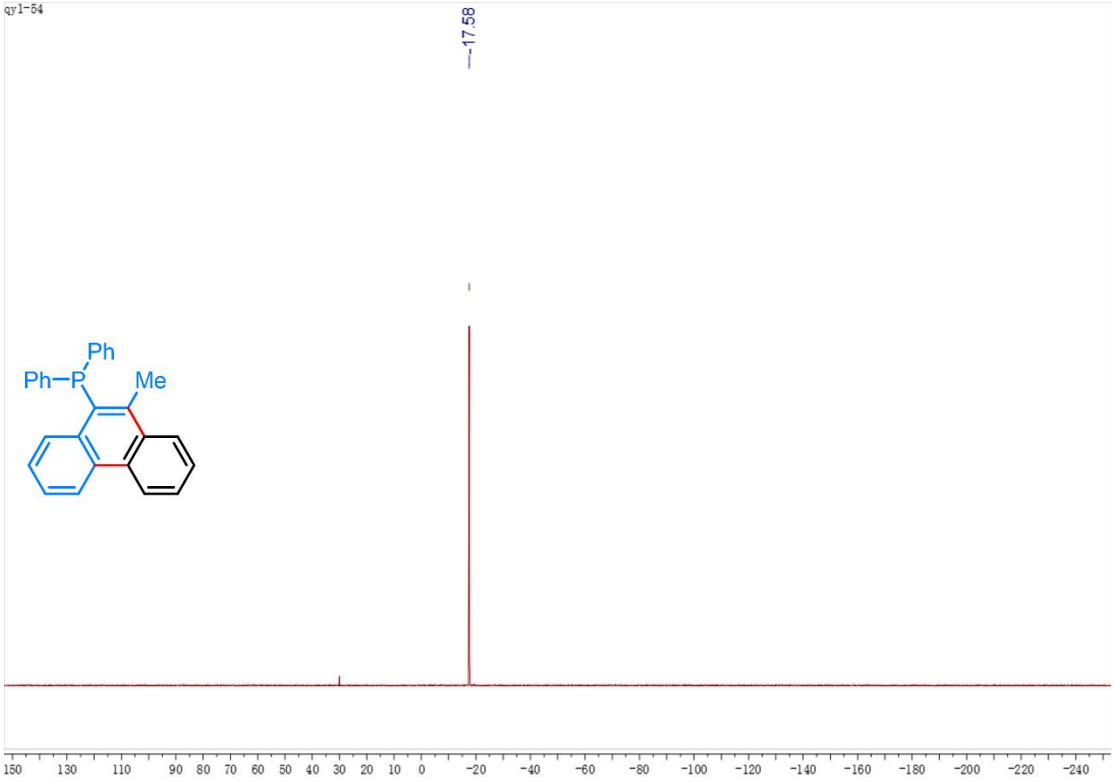
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)



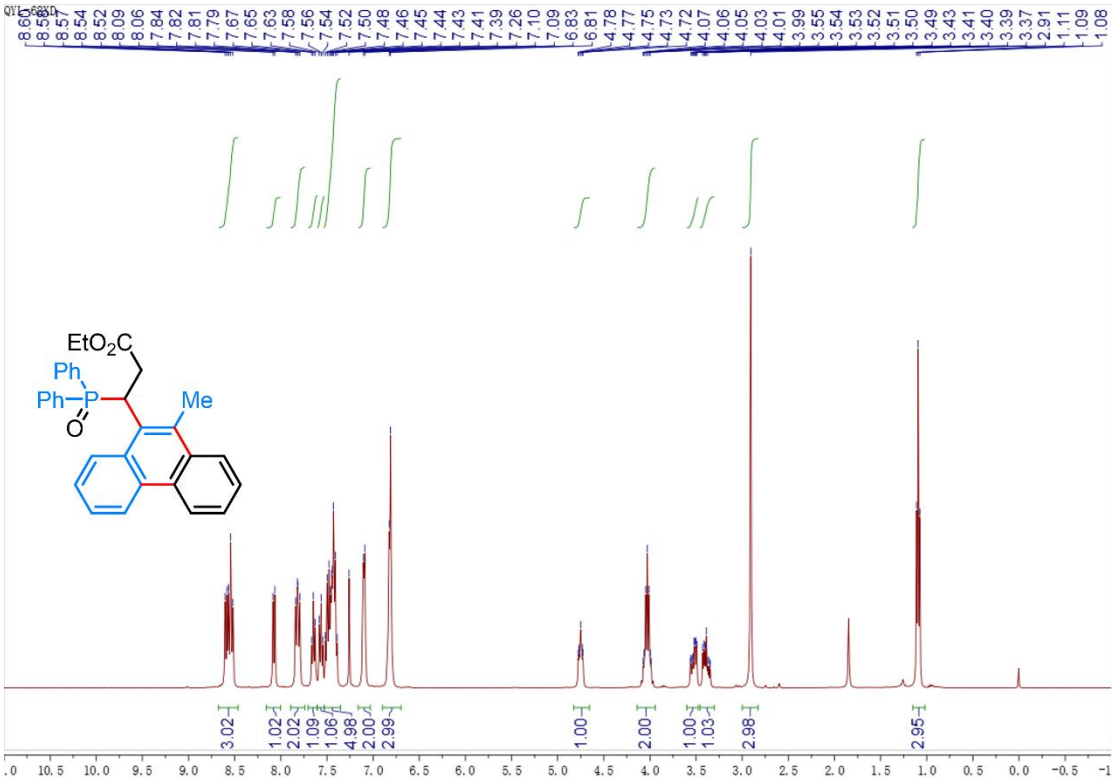
^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$)



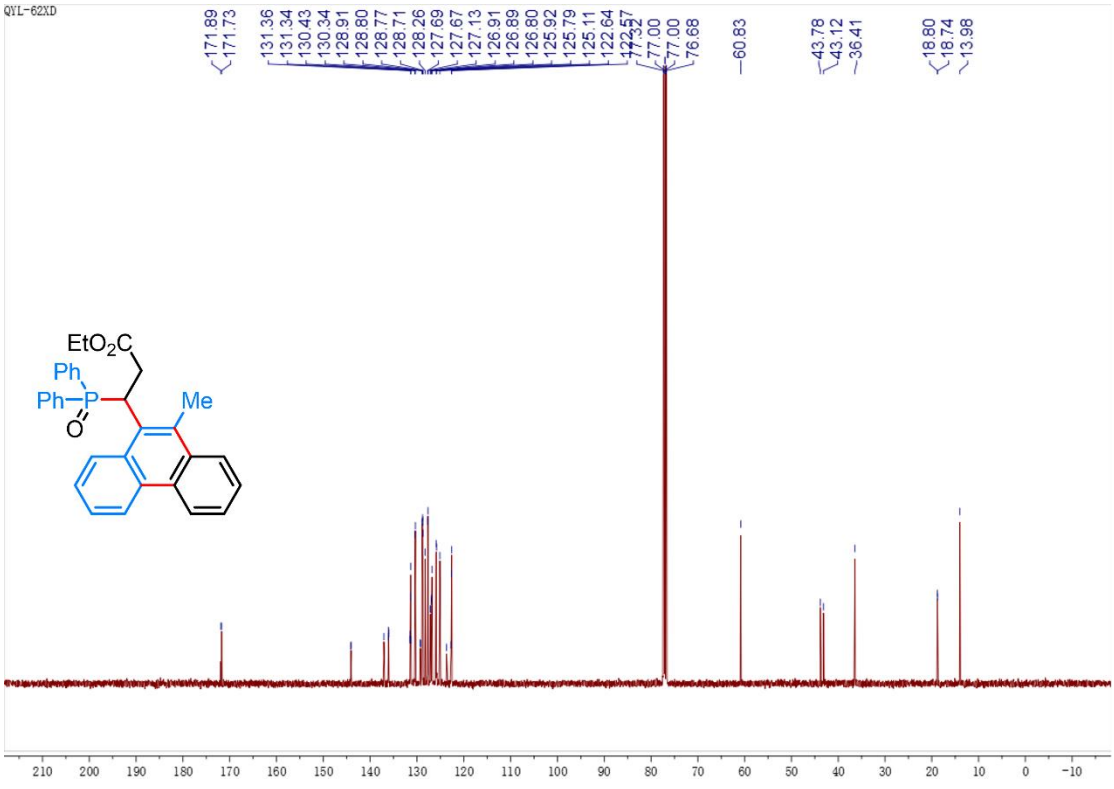
^{31}P NMR spectrum of **5** (162 MHz, $CDCl_3$)



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



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



^{31}P NMR spectrum of **6** (162 MHz, $CDCl_3$)