Supporting Information

Cu-catalyzed tandem cross-coupling/cyclization of aryl diazophosphonates with phenylacetylene derivatives

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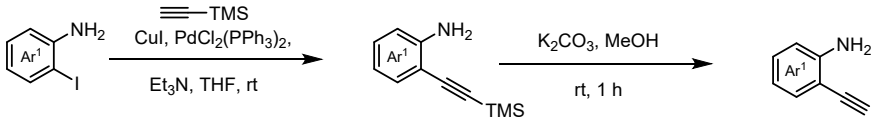
1. General information

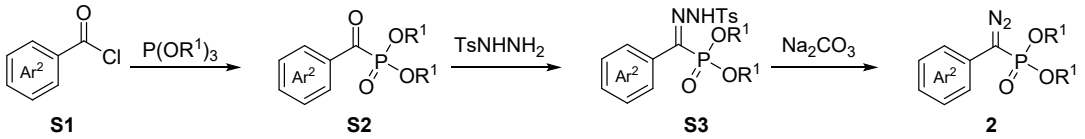
All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents used in the reactions were distilled from appropriate drying agents prior to use. If not noted, catalysts and other chemicals were commercially available and used without further purification.

^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively. ^{31}P NMR and ^{19}F NMR spectra were recorded at 162 MHz and 376 MHz respectively. Chemical shifts are reported in (ppm) with the internal TMS signal at 0.0 ppm or chloroform signal at 7.26 ppm as a standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets). Flash column chromatography was performed using 200 – 300 mesh silica gel. Single-crystal X-ray Diffraction was performed on Bruker D8 VENTURE X-ray single crystal diffractometer. High resolution mass spectra were obtained on Bruker Daltonics micrOTOF-Q II spectrometer in ESI mode. Melting points (Mp) were recorded on an Electrothermal X-5 melting point apparatus and uncorrected.

2. Synthesis of starting materials

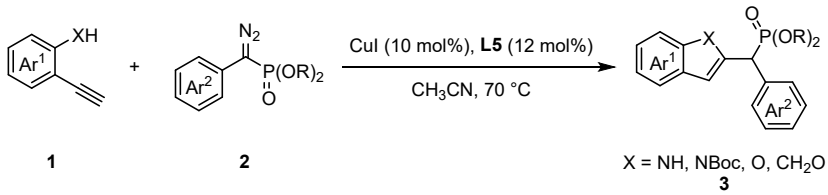


The related ethynylanilines derivatives were synthesized according to literature procedures.[1-3]



To a flame-dried 50 mL flask was added acid chloride **S1** (10 mmol, 1.0 equiv) at 0 °C. Then phosphite $P(OR_1)_3$ (10 mmol, 1.0 equiv) was added dropwise and the mixture was stirred at room temperature for 4 h to afford **S2** that was used in the next step without further purification. A solution of $TsNHNH_2$ (1.86 g, 10 mmol, 1.0 equiv) in THF (10 mL) in a 25 mL flask was chilled to 0 °C and then concentrated HCl (0.42 mL, 5 mmol, 0.5 equiv) was added. The resulting solution was stirred at 0 °C while the resulting yellow oil **S2** was added dropwise. Upon completion, the mixture was allowed to warm to room temperature and stirred for 12 h. The organic layers were concentrated under reduced pressure to yield the crude product **S3** (the corresponding *N*-tosylhydrazone). Under an ambient atmosphere, Na_2CO_3 (2.4 g, 22 mmol, 2.2 equiv) was added to a solution of the corresponding *N*-tosylhydrazone **S3** in Et_2O. Then water (25 mL) and Et_2O (5 mL) were added and the mixture was stirred at room temperature for 24 h. Upon completion, the mixture was extracted with Et_2O for three times, washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by chromatography (silica gel, PE/EtOAc/Et_3N = 100/50/6, v/v/v) to give the desired product **2**.

3. Typical procedures

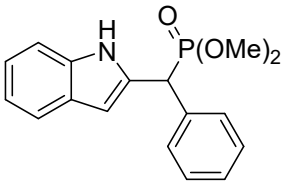


Procedure for products **3aa–3xx** (condition A): In an argon atmosphere, **2a** (68 mg, 0.30 mmol, 1.5 equiv) was added to a suspention of **1a** (0.20 mmol, 1.0 equiv), CuI (4 mg, 0.02 mmol, 0.1 equiv) and (±)-MonoPhos (8.6 mg, 0.024 mmol, 0.12 equiv) in CH_3CN (2 mL). The reaction was stirred at 70 °C and monitored by TLC. Upon completion, the resulting mixture was filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give products **3aa–3xx**.

Procedure for products **3yy–3an** (condition B): In an argon atmosphere, **2a** (68 mg, 0.30 mmol, 1.5 equiv) was added to a solution of **1a** (0.20 mmol, 1.0 equiv), CuI (4 mg, 0.02 mmol, 0.1 equiv), (±)-MonoPhos (8.6 mg, 0.024 mmol, 0.12 equiv) and $^{i}Pr_2NH$ (12.4 mg, 0.12 mmol, 1.2 equiv) in CH_3CN (2 mL). The reaction was stirred at 70 °C and monitored by TLC. Upon completion, the resulting mixture was filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give products **3yy–3an**.

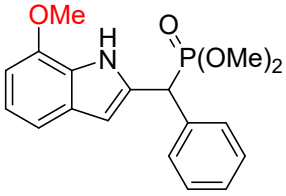
4. Characterization data for the products of 3aa–3an

dimethyl ((1H-indol-2-yl)(phenyl)methyl)phosphonate (3aa)



White solid, 56.7 mg, 90% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 185.5 – 186.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.27 (s, 1H), 7.50 (dd, J = 12.7, 7.8 Hz, 3H), 7.41 – 7.29 (m, 4H), 7.16 (t, J = 7.7 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.34 (s, 1H), 4.71 (d, J = 25.6 Hz, 1H), 3.63 (d, J = 10.8 Hz, 3H), 3.55 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.3, 134.8 (d, *J* = 6.5 Hz), 132.9, 129.2 (d, *J* = 6.6 Hz), 128.8, 128.1, 127.7 (d, *J* = 2.6 Hz), 121.9, 120.2, 119.9, 111.1, 102.7, 102.6, 77.8 – 76.1 (m), 53.9 (d, *J* = 6.8 Hz), 45.1, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.93 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{18}NO_3PH^{\oplus}$ 316.1097, found 316.1104.

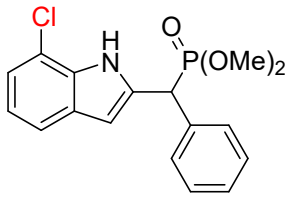
dimethyl ((7-methoxy-1H-indol-2-yl)(phenyl)methyl)phosphonate (3bb)



White solid, 62.1 mg, 90% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 134.2 – 135.2 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.23 (s, 1H), 7.49 (d, J = 7.8 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.13 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 6.61 (d, J = 7.7 Hz, 1H), 6.36 (d, J = 0.8 Hz, 1H), 4.69 (d, J = 25.6 Hz, 1H), 3.95 (s, 3H), 3.64 (d, J = 10.8 Hz, 3H), 3.55 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.01, 134.90 (d, *J* = 6.0 Hz), 132.39 (d, *J*

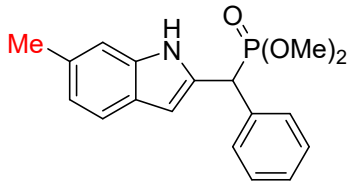
= 7.3 Hz), 129.28 (d, *J* = 6.7 Hz), 128.77, 127.67 (d, *J* = 3.2 Hz), 126.80, 120.24, 112.96, 103.06 (d, *J* = 9.8 Hz), 77.39 – 76.55 (m), 55.21, 53.92 (d, *J* = 6.7 Hz), 53.51 (d, *J* = 7.3 Hz), 45.13, 43.76. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.91 (s). **HRMS (ESI)**: $[M+Na]^{\oplus}$ calcd. for $C_{18}H_{20}NO_4PNa^{\oplus}$ 368.1022, found 368.1021.

dimethyl((7-chloro-1H-indol-2- yl)(phenyl)methyl)phosphonate (3cc)



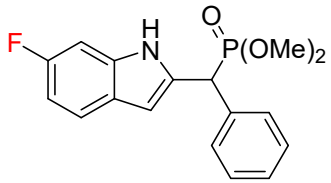
White solid, 68.3 mg, 98% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 152.5 – 153.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.33 (s, 1H), 7.51 – 7.47 (m, 2H), 7.43 – 7.31 (m, 4H), 7.16 (d, J = 7.6 Hz, 1H), 7.01 (t, J = 7.8 Hz, 1H), 6.41 (s, 1H), 4.70 (d, J = 25.8 Hz, 1H), 3.68 (d, J = 10.9 Hz, 3H), 3.55 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.3 (d, *J* = 7.0 Hz), 133.9 (d, *J* = 7.5 Hz), 133.5, 129.5, 129.3 (d, *J* = 6.6 Hz), 128.9, 127.9 (d, *J* = 2.8 Hz), 121.3, 120.6, 118.8, 116.4, 103.7 (d, *J* = 9.6 Hz), 77.9 – 76.2 (m), 54.1 (d, *J* = 6.7 Hz), 53.5 (d, *J* = 7.1 Hz), 45.1, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.58 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{17}ClNO_3PH^{\oplus}$ 350.0707, found 350.0716.

dimethyl ((6-methyl-1H-indol-2-yl)(phenyl)methyl)phosphonate (3dd)



White solid, 53.9 mg, 82% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 200.3 – 201.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.12 (s, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.28 (m, 4H), 7.19 (d, *J* = 0.8 Hz, 1H), 6.91 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.27 (s, 1H), 4.68 (d, *J* = 25.6 Hz, 1H), 3.62 (d, *J* = 10.8 Hz, 3H), 3.55 (d, *J* = 10.6 Hz, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 136.8, 135.0 (d, *J* = 6.5 Hz), 132.2 (d, *J* = 7.9 Hz), 131.9, 129.4 (d, *J* = 6.7 Hz), 128.9 (d, *J* = 2.2 Hz), 127.8 (d, *J* = 2.6 Hz), 126.0, 121.7, 120.0, 111.2, 102.5 (d, *J* = 10.5 Hz), 53.9 (dd, *J* = 45.1, 7.0 Hz), 45.2, 43.8, 21.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.91 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{20}NO_3PH^{\oplus}$ 330.1254, found 330.1261.

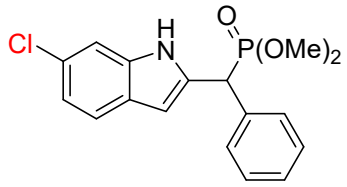
dimethyl ((6-fluoro-1H-indol-2-yl)(phenyl)methyl)phosphonate (3ee)



White solid, 49.9 mg, 75% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 170.4 – 171.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.29 (s, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.28 (m, 4H), 7.07 (dd, J = 9.4, 2.3 Hz, 1H), 6.83 (ddd, J = 9.7, 8.6, 2.3 Hz, 1H), 6.29 (d, J = 1.4 Hz, 1H), 4.67 (d, J = 25.6 Hz, 1H), 3.64 (d, J = 10.8 Hz, 3H), 3.55 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 156.8, 134.8 (d, *J* = 8.0 Hz), 134.6 (d, *J* = 6.8 Hz), 132.7, 129.2 (d, *J*

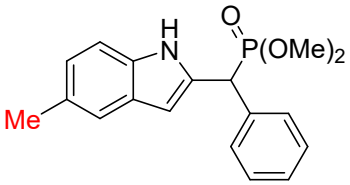
= 6.9 Hz), 128.8, 128.4 (d, *J* = 10.0 Hz), 127.8 (d, *J* = 2.3 Hz), 111.7 (d, *J* = 9.6 Hz), 110.1, 105.0 (d, *J* = 23.4 Hz), 102.7 (dd, *J* = 10.5, 4.9 Hz), 77.7 – 76.1 (m), 54.1 (d, *J* = 7.3 Hz), 53.4 (d, *J* = 7.3 Hz), 45.1, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.60 (s). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -124.65 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{17}FNO_3PH^{\oplus}$ 334.1003, found 334.1011.

dimethyl ((6-chloro-1H-indol-2-yl)(phenyl)methyl)phosphonate (3ff)



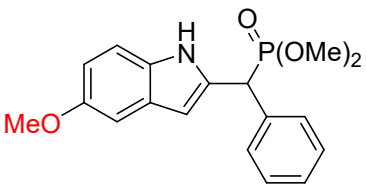
White solid, 68.4 mg, 98% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 183.7 – 185.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.34 (s, 1H), 7.49 (d, J = 7.4 Hz, 2H), 7.33 (dt, J = 13.9, 7.0 Hz, 3H), 7.09 (t, J = 7.9 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.50 (d, J = 7.6 Hz, 1H), 6.43 (t, J = 2.5 Hz, 1H), 4.70 (d, J = 25.6 Hz, 1H), 3.91 (s, 3H), 3.62 (d, J = 10.9 Hz, 3H), 3.56 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.6, 134.5 (d, *J* = 6.6 Hz), 133.8 (d, *J* = 7.9 Hz), 129.2 (d, *J* = 6.6 Hz), 128.8 (d, *J* = 2.1 Hz), 127.8 (d, *J* = 2.8 Hz), 127.6, 126.6, 121.1, 120.5, 111.1, 102.6 (d, *J* = 10.3 Hz), 77.5 – 76.1 (m), 54.1 (d, *J* = 6.7 Hz), 53.6 (d, *J* = 7.3 Hz), 45.1, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.68 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{17}ClNO_3PH^{\oplus}$ 350.0707, found 350.0713.

dimethyl ((5-methyl-1H-indol-2-yl)(phenyl)methyl)phosphonate (3gg)



White solid, 61.2 mg, 93% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 180.3 – 181.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.16 (s, 1H), 7.51 – 7.43 (m, 2H), 7.38 – 7.26 (m, 5H), 6.99 (d, J = 6.4 Hz, 1H), 6.26 (s,1H), 4.69 (d, J = 25.6 Hz, 1H), 3.62 (d, J = 10.8 Hz, 3H), 3.55 (d, J = 10.7 Hz, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.9 (d, *J* = 6.5 Hz), 134.5, 132.8 (d, *J* = 7.9 Hz), 129.2 (d, *J* = 6.6 Hz), 129.1, 128.7, 128.3 (d, *J* = 10.5 Hz), 127.7 (d, *J* = 2.8 Hz), 119.9, 110.8, 102.1 (d, *J* = 10.3 Hz), 77.9 – 75.8 (m), 53.9 (d, *J* = 7.2 Hz), 53.5 (d, *J* = 7.1 Hz), 45.1, 43.7, 21.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.97 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{20}NO_3PH^{\oplus}$ 330.1254, found 330.1263.

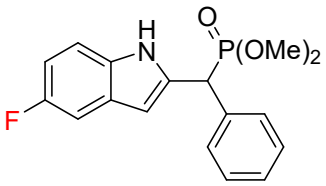
dimethyl ((5-methoxy-1H-indol-2-yl)(phenyl)methyl)phosphonate (3hh)



White solid, 59.3 mg, 86% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 180.2 – 181.4 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.18 (s, 1H), 7.50 – 7.44 (m, 2H), 7.40

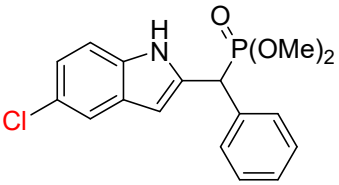
– 7.24 (m, 4H), 6.98 (d, J = 2.4 Hz, 1H), 6.83 (dd, J = 8.8, 2.5 Hz, 1H), 6.27 (s, 1H), 4.68 (d, J = 25.6 Hz, 1H), 3.82 (s, 3H), 3.63 (d, J = 10.9 Hz, 3H), 3.54 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.2, 134.8 (d, *J* = 6.5 Hz), 133.5 (d, *J* = 7.5 Hz), 131.4, 129.2 (d, *J* = 7.0 Hz), 128.8, 128.5, 127.7 (d, *J* = 2.8 Hz), 111.9 (d, *J* = 27.7 Hz), 102.4 (d, *J* = 10.7 Hz), 102.1, 77.6 – 75.9 (m), 55.8, 54.0 (d, *J* = 7.2 Hz), 53.5 (d, *J* = 7.3 Hz), 45.1, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.94 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{20}NO_4PH^{\oplus}$ 346.1203, found 346.1205.

dimethyl ((5-fluoro-1H-indol-2-yl)(phenyl)methyl)phosphonate (3ii)



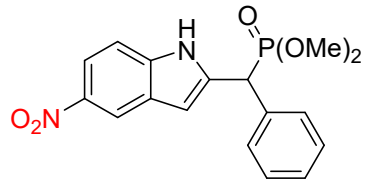
White solid, 61.9 mg, 93% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 169.1 – 170.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.39 (s, 1H), 7.47 (d, J = 2.6 Hz, 3H), 7.40 – 7.27 (m, 4H), 7.11 (dd, J = 8.7, 2.1 Hz, 1H), 6.27 (s, 1H), 4.68 (d, J = 25.6 Hz, 1H), 3.63 (d, J = 10.9 Hz, 3H), 3.54 (d, J = 10.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 156.8, 134.8 (d, *J* = 8.0 Hz), 134.6 (d, *J* = 6.8 Hz), 132.7, 129.2 (d, *J* = 6.9 Hz), 128.8, 128.4 (d, *J* = 10.0 Hz), 127.8 (d, *J* = 2.3 Hz), 111.7 (d, *J* = 9.6 Hz), 110.1, 105.0 (d, *J* = 23.4 Hz), 102.7 (dd, *J* = 10.5, 4.9 Hz), 77.7 – 76.1 (m), 54.1 (d, *J* = 7.3 Hz), 53.4 (d, *J* = 7.3 Hz), 45.1, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.69 (s). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -124.71 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{17}FNO_3PH^{\oplus}$ 334.1003, found 334.0997.

dimethyl ((5-chloro-1H-indol-2-yl)(phenyl)methyl)phosphonate (3jj)



White solid, 65.6mg, 94% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 195.7 – 196.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.39 (s, 1H), 7.47 (d, J = 2.6 Hz, 3H), 7.39 – 7.27 (m, 4H), 7.11 (dd, J = 8.7, 2.1 Hz, 1H), 6.27 (s, 1H), 4.68 (d, J = 25.6 Hz, 1H), 3.63 (d, J = 10.9 Hz, 3H), 3.54 (d, J = 10.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.7 – 134.3 (m), 129.2 (d, *J* = 6.7 Hz), 128.8, 127.8 (d, *J* = 2.8 Hz), 125.5, 122.2, 119.6, 112.1, 102.2 (d, *J* = 10.3 Hz), 77.5 – 76.1 (m), 54.1 (d, *J* = 7.3 Hz), 53.5 (d, *J* = 7.3 Hz), 45.1, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.66 (s)**. HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{17}ClNO_3PH^{\oplus}$ 350.0707, found 350.0711.

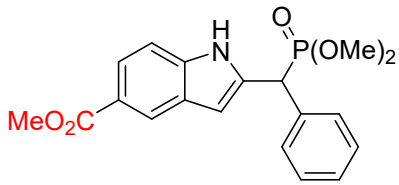
dimethyl ((5-nitro-1H-indol-2-yl)(phenyl)methyl)phosphonate (3kk)



White solid, 63.3 mg, 88% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 190.2 – 191.7 °C. **^{1}H NMR** (400 MHz,

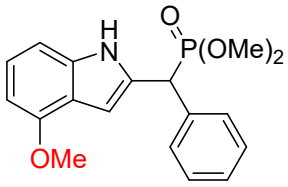
$CDCl_3$) δ (ppm) 9.83 (s, 1H), 8.47 (d, J = 2.2 Hz, 1H), 8.08 (dd, J = 8.9, 2.2 Hz, 1H), 7.51 – 7.30 (m, 6H), 6.47 (s, 1H), 4.71 (d, J = 25.8 Hz, 1H), 3.67 (d, J = 10.9 Hz, 3H), 3.56 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.1, 139.2, 136.7 (d, *J* = 8.0 Hz), 133.9 (d, *J* = 6.7 Hz), 129.2 (d, *J* = 6.6 Hz), 129.1, 128.2 (d, *J* = 2.8 Hz), 127.4, 117.6, 117.3, 111.1, 104.6 (d, *J* = 10.9 Hz), 77.6 – 75.9 (m), 54.3 (d, *J* = 6.7 Hz), 53.5 (d, *J* = 7.3 Hz), 45.0, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.26 (s). **HRMS (ESI)**: $[M+Na]^{\oplus}$ calcd. for $C_{17}H_{17}N_2O_5PNa^{\oplus}$ 383.0767, found 383.0763.

methyl 2-((dimethoxyphosphoryl)(phenyl)methyl)-1H-indole-5-carboxylate (3ll)



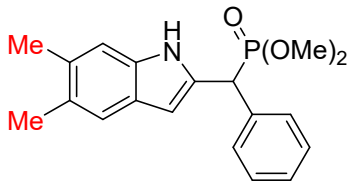
White solid, 55.9 mg, 75% yield. R_f = 0.30 (PE/EtOAc = 1/1). Mp 194.5 – 195.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.58 (s, 1H), 8.28 (d, J = 1.6 Hz, 1H), 7.48 (d, J = 8.3 Hz, 2H), 7.42 – 7.27 (m, 4H), 6.42 (s, 1H), 4.71 (d, J = 25.6 Hz, 1H), 3.90 (s, 3H), 3.64 (d, J = 10.8 Hz, 3H), 3.54 (d, J = 10.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 138.8, 134.5 (d, *J* = 7.9 Hz), 134.4 (d, *J* = 6.6 Hz), 129.3 (d, *J* = 6.6 Hz), 128.9, 127.9 (d, *J* = 2.5 Hz), 127.6, 123.2, 121.9, 110.8, 103.7, 77.5 – 76.6 (m), 54.2 (d, *J* = 7.1 Hz), 53.6 (d, *J* = 7.2 Hz), 51.8, 45.0, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.25 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{19}H_{20}NO_5PH^{\oplus}$ 374.1152, found 374.1155.

dimethyl ((4-methoxy-1H-indol-2-yl)(phenyl)methyl)phosphonate (3mm)



White solid, 65.5 mg, 95% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 162.3 – 163.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.34 (s, 1H), 7.49 (d, J = 7.4 Hz, 2H), 7.33 (dt, J = 13.9, 7.0 Hz, 3H), 7.09 (t, J = 7.9 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.50 (d, J = 7.6 Hz, 1H), 6.43 (t, J = 2.5 Hz, 1H), 4.70 (d, J = 25.6 Hz, 1H), 3.91 (s, 3H), 3.62 (d, J = 10.9 Hz, 3H), 3.56 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.9, 137.6, 134.8 (d, *J* = 6.5 Hz), 131.4 (d, *J* = 8.0 Hz), 129.3 (d, *J* = 7.1 Hz), 128.8 (d, *J* = 1.9 Hz), 127.6 (d, *J* = 2.8 Hz), 122.7, 118.7, 104.6, 100.2 – 99.2 (m), 77.9 – 76.1 (m), 55.2, 53.9 (d, *J* = 7.2 Hz), 53.5 (d, *J* = 7.2 Hz), 45.0, 43.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.97 (s). **HRMS (ESI)**: $[M+Na]^{\oplus}$ calcd. for $C_{18}H_{20}NO_4PNa^{\oplus}$ 368.1022, found 368.1016.

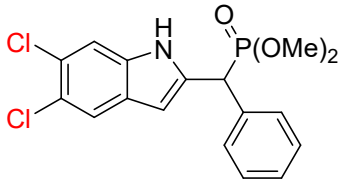
dimethyl ((5,6-dimethyl-1H-indol-2-yl)(phenyl)methyl)phosphonate (3nn)



White solid, 56.4 mg, 82% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 209.5 – 210.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$)

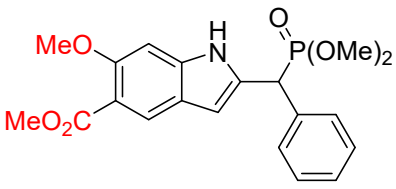
δ (ppm) 9.08 (s, 1H), 7.50 – 7.42 (m, 2H), 7.38 – 7.24 (m, 4H), 6.23 (s, 1H), 4.68 (d, J = 25.6 Hz, 1H), 3.61 (d, J = 10.8 Hz, 3H), 3.55 (d, J = 10.7 Hz, 3H), 2.33 (d, J = 13.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.2, 135.0 (d, *J* = 6.5 Hz), 131.8 (d, *J* = 8.0 Hz), 130.9, 129.2 (d, *J* = 6.6 Hz), 128.7, 128.5, 127.6 (d, *J* = 2.8 Hz), 120.3, 111.5, 102.0 (d, *J* = 10.7 Hz), 77.8 – 76.3 (m), 53.9 (d, *J* = 7.2 Hz), 53.5 (d, *J* = 6.7 Hz), 45.1, 43.7, 20.0. **^{31}P NMR** (162 MHz, CDCl3) δ 26.21 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{19}H_{22}NO_3PNa^{\oplus}$ 366.1230, found 366.1230.

dimethyl ((5,6-dichloro-1H-indol-2-yl)(phenyl)methyl)phosphonate (3oo)



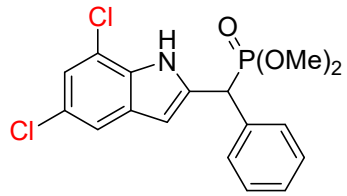
White solid, 67.4 mg, 88% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 178.2 – 179.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.55 (s, 1H), 7.56 (s, 1H), 7.46 (d, J = 5.8 Hz, 3H), 7.38 – 7.28 (m, 3H), 6.25 (s, 1H), 4.67 (d, J = 25.7 Hz, 1H), 3.64 (d, J = 10.8 Hz, 3H), 3.55 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.3 (d, *J* = 8.0 Hz), 135.1, 134.2 (d, *J* = 6.6 Hz), 129.2 (d, *J* = 6.9 Hz), 128.9, 128.0 (d, *J* = 2.8 Hz), 125.6, 123.8, 121.1, 112.6, 102.1 (d, *J* = 10.5 Hz), 77.9 – 76.43 (m), 54.2 (d, *J* = 7.1 Hz), 53.5 (d, *J* = 7.2 Hz), 45.0, 43.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.37 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{16}Cl_2NO_3PH^{\oplus}$ 384.0318, found 384.0318.

methyl2-((dimethoxyphosphoryl)(phenyl)methyl)-6-methoxy-1H-indole-5-carboxylate (3pp)



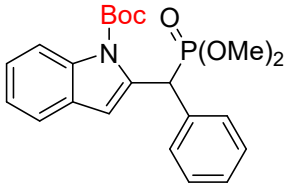
Yellow oil, 50.7 mg, 63% yield. R_f = 0.30 (PE/EtOAc = 1/1). Mp 174.5 – 175.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.36 (s, 1H), 8.03 (s, 1H), 7.51 – 7.43 (m, 2H), 7.42 – 7.27 (m, 3H), 6.92 (s, 1H), 6.29 (s, 1H), 4.66 (d, *J* = 25.6 Hz, 1H), 3.89 (d, *J* = 14.0 Hz, 6H), 3.63 (d, *J* = 10.8 Hz, 3H), 3.55 (d, *J* = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 167.5, 156.4, 139.5, 134.7 (d, *J* = 6.7 Hz), 133.4 (d, *J* = 8.3 Hz), 129.4 (d, *J* = 6.6 Hz), 129.0 (d, *J* = 1.8 Hz), 128.0 (d, *J* = 2.5 Hz), 125.0, 121.6, 114.1, 103.5 (d, *J* = 10.8 Hz), 94.4, 56.5, 54.0 (dd, *J* = 54.0, 7.1 Hz), 51.9, 45.1, 43.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.10 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{20}H_{22}NO_6PH^{\oplus}$ 404.1258, found 404.1253.

dimethyl ((5,7-dichloro-1H-indol-2-yl)(phenyl)methyl)phosphonate (3qq)



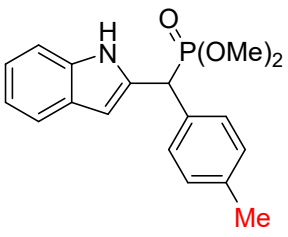
White solid, 75.8 mg, 99% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 181.3 – 182.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.44 (s, 1H), 7.51 – 7.43 (m, 2H), 7.42 – 7.28 (m, 4H), 7.16 (d, J = 1.8 Hz, 1H), 6.35 (d, J = 0.8 Hz, 1H), 4.69 (d, J = 25.8 Hz, 1H), 3.68 (d, J = 10.9 Hz, 3H), 3.55 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.4 (d, *J* = 7.2 Hz), 134.1 (d, *J* = 7.2 Hz), 132.1, 129.9, 129.3 (d, *J* = 6.5 Hz), 128.9 (d, *J* = 2.5 Hz), 128.1 (d, *J* = 2.8 Hz), 125.5, 121.4, 118.4, 116.8, 103.3 (d, *J* = 9.7 Hz), 77.75 – 76.12 (m), 54.2 (d, *J* = 7.2 Hz), 53.5 (d, *J* = 7.2 Hz), 45.0, 43.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.40 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{16}Cl_2NO_3PH^{\oplus}$ 384.0318, found 384.0309.

tert-butyl2-((dimethoxyphosphoryl)(phenyl)methyl)-1H-indole-1-carboxylate (3rr)



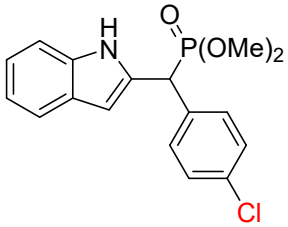
White solid, 82.6 mg, 99% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 111.5 – 112.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.97 – 7.87 (m, 1H), 7.62 – 7.50 (m, 1H), 7.49 – 7.42 (m, 2H), 7.32 – 7.27 (m, 3H), 7.25 – 7.17 (m, 3H), 5.88 (d, *J* = 26.0 Hz, 1H), 3.70 (d, *J* = 10.8 Hz, 3H), 3.51 (d, *J* = 10.7 Hz, 3H), 1.58 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 150.4, 136.4, 135.3 (d, *J* = 3.3 Hz), 134.8 (d, *J* = 6.7 Hz), 130.1 (d, *J* = 6.3 Hz), 128.9 (d, *J* = 1.7 Hz), 128.4 (d, *J* = 2.4 Hz), 127.5 (d, *J* = 2.9 Hz), 124.3, 122.9, 120.9, 115.6, 111.3 (d, *J* = 4.7 Hz), 84.4, 53.7 (dd, *J* = 20.0, 7.1 Hz), 43.5, 42.1, 28.2. **^{31}P NMR** (162 MHz, CDCl3) δ 25.40 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{22}H_{26}NO_5PH^{\oplus}$ 416.1621, found 416.1629.

dimethyl ((1H-indol-2-yl)(p-tolyl)methyl)phosphonate (3ss)



White solid, 42.7 mg, 65% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 164.5 – 165.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.23 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.32 (m, 3H), 7.19 – 7.11 (m, 3H), 7.10 – 7.02 (m, 1H), 6.32 (s, 1H), 4.66 (d, *J* = 25.6 Hz, 1H), 3.62 (d, *J* = 10.8 Hz, 3H), 3.56 (d, *J* = 10.6 Hz, 3H), 2.33 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 137.6 (d, *J* = 2.8 Hz), 136.4, 133.3 (d, *J* = 7.7 Hz), 131.9 (d, *J* = 6.8 Hz), 129.7 (d, *J* = 2.1 Hz), 129.3 (d, *J* = 6.7 Hz), 128.3, 122.0, 120.4, 120.0, 111.2, 102.7 (d, *J* = 10.4 Hz), 53.9 (dd, *J* = 49.7, 7.1 Hz), 44.8, 43.4, 21.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.14 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{20}NO_3PH^{\oplus}$ 330.1254, found 330.1262.

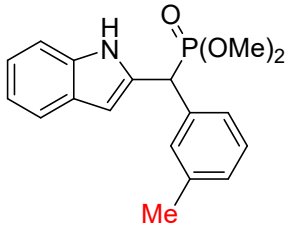
dimethyl ((4-chlorophenyl)(1H-indol-2-yl)methyl)phosphonate (3tt)



White solid, 50.9 mg, 73% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 153.5 – 154.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm)

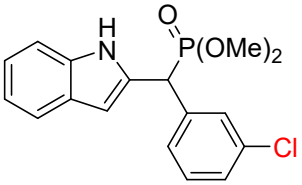
9.28 (s, 1H), 7.53 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 – 7.29 (m, 5H), 7.18 (t, *J* = 6.9 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 4.68 (d, *J* = 25.6 Hz, 1H), 3.61 (dd, *J* = 17.8, 10.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 136.4, 133.9 (d, *J* = 3.3 Hz), 133.6 (d, *J* = 6.6 Hz), 132.5 (d, *J* = 8.0 Hz), 130.7 (d, *J* = 6.6 Hz), 129.1 (d, *J* = 2.1 Hz), 128.2, 122.3, 120.5, 120.1, 111.3, 103.0 (d, *J* = 10.3 Hz), 54.0 (dd, *J* = 38.8, 7.1 Hz), 44.5, 43.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.35 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{17}ClNO_3PH^{\oplus}$ 350.0707, found 350.0697**.**

dimethyl ((1H-indol-2-yl)(m-tolyl)methyl)phosphonate (3uu)



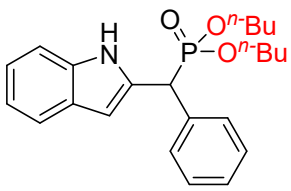
White solid, 38.2 mg, 58% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 280.5 – 281.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.26 (s, 1H), 7.52 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.39 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.32 – 7.22 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.34 (s, 1H), 4.67 (d, *J* = 25.5 Hz, 1H), 3.63 (d, *J* = 10.8 Hz, 3H), 3.55 (d, *J* = 10.7 Hz, 3H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 138.7 (d, *J* = 2.1 Hz), 136.4, 134.8 (d, *J* = 6.4 Hz), 133.2 (d, *J* = 8.0 Hz), 130.0 (d, *J* = 6.9 Hz), 128.7 (dd, *J* = 12.8, 2.4 Hz), 128.3, 126.4 (d, *J* = 6.6 Hz), 122.0, 120.4, 120.0, 111.3, 102.7 (d, *J* = 10.5 Hz), 53.9 (dd, *J* = 52.7, 7.1 Hz), 45.1, 43.8, 21.6. **^{31}P NMR** (162 MHz, CDCl3) δ 25.95 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{20}NO_3PH^{\oplus}$ 330.1254, found 330.1247.

dimethyl ((4-chlorophenyl)(1H-indol-2-yl)methyl)phosphonate (3vv)



White solid, 50.9 mg, 73% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 153.5 – 154.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.28 (s, 1H), 7.53 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 – 7.29 (m, 5H), 7.18 (t, *J* = 6.9 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 4.68 (d, *J* = 25.6 Hz, 1H), 3.61 (dd, *J* = 17.8, 10.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 136.4, 133.9 (d, *J* = 3.3 Hz), 133.6 (d, *J* = 6.6 Hz), 132.5 (d, *J* = 8.0 Hz), 130.7 (d, *J* = 6.6 Hz), 129.1 (d, *J* = 2.1 Hz), 128.2, 122.3, 120.5, 120.1, 111.3, 103.0 (d, *J* = 10.3 Hz), 54.0 (dd, *J* = 38.8, 7.1 Hz), 44.5, 43.2. **^{31}P NMR** (162 MHz, CDCl3) δ 26.18 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{17}ClNO_3PH^{\oplus}$ 350.0707, found 350.0697.

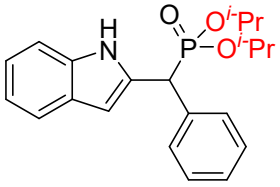
dipropyl ((1H-indol-2-yl)(phenyl)methyl)phosphonate (3ww)



White solid, 40.8 mg, 55% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 124.5 – 125.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.36 (s, 1H), 7.58 – 7.44 (m, 3H), 7.42 – 7.27 (m,4H), 7.15 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.06 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.31 (s, 1H), 4.68 (d, *J* = 25.5 Hz, 1H), 4.02 – 3.82 (m, 3H),

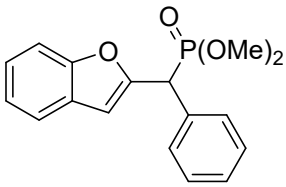
3.77 – 3.65 (m, 1H), 1.54 – 1.34 (m, 4H), 1.30 – 1.15 (m, 4H), 0.80 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 136.3, 135.4, 133.5 (d, *J* = 7.9 Hz), 129.5 (d, *J* = 6.7 Hz), 128.8 (d, *J* = 1.8 Hz), 128.3, 127.7 (d, *J* = 2.6 Hz), 121.9, 120.3, 119.9, 111.2, 102.6, 67.0 (dd, *J* = 41.6, 7.4 Hz), 45.7, 44.3, 32.5 (d, *J* = 5.8 Hz), 18.7 (d, *J* = 1.3 Hz), 13.6 (d, *J* = 1.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.08 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{21}H_{26}NO_3PH^{\oplus}$ 372.1723, found 372.1723.

diisopropyl ((1H-indol-2-yl)(phenyl)methyl)phosphonate (3xx)



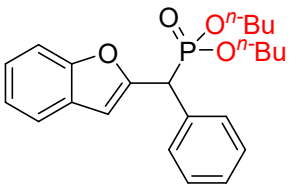
White solid, 52.7 mg, 71% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 191.5 – 192.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.38 (s, 1H), 7.53 – 7.44 (m, 3H), 7.43 – 7.22 (m, 1H), 7.14 (t, *J* = 6.9 Hz, 3H), 7.05 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.28 (s, 1H), 4.66 – 4.44 (m, 3H), 1.24 (dd, *J* = 13.6, 6.2 Hz, 6H), 1.07 (d, *J* = 6.2 Hz, 3H), 0.89 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 136.3, 135.7 (d, *J* = 6.4 Hz), 133.9 (d, *J* = 8.0 Hz), 129.6 (d, *J* = 6.6 Hz), 128.7 (d, *J* = 2.0 Hz), 128.3, 127.6 (d, *J* = 2.6 Hz), 121.8, 120.3, 119.8, 111.2, 102.7 (d, *J* = 10.6 Hz), 72.2 (dd, *J* = 60.2, 7.4 Hz), 46.4, 45.0, 24.4 (d, *J* = 3.2 Hz), 24.2 (d, *J* = 3.6 Hz), 23.8 (d, *J* = 5.2 Hz), 23.3 (d, *J* = 5.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.10 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{21}H_{26}NO_3PH^{\oplus}$ 372.1723, found 372.1712.

dimethyl (benzofuran-2-yl(phenyl)methyl)phosphonate (3yy)



Yellow oil, 25.3 mg, 40% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.56 – 7.46 (m, 3H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.25 – 7.18 (m, 2H), 6.94 (d, *J* = 2.3 Hz, 1H), 4.69 (d, *J* = 25.8 Hz, 1H), 3.72 (d, *J* = 10.9 Hz, 3H), 3.56 (d, *J* = 10.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 154.9, 152.7 (d, *J* = 1.7 Hz), 133.7 (d, *J* = 6.9 Hz), 129.6 (d, *J* = 6.4 Hz), 128.9 (d, *J* = 2.4 Hz), 128.6 (d, *J* = 1.8 Hz), 128.0 (d, *J* = 2.8 Hz), 124.3, 123.0, 121.1, 111.3, 106.0 (d, *J* = 5.2 Hz), 53.9 (dd, *J* = 17.8, 7.0 Hz), 46.1, 44.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.55 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{17}H_{17}O_4PH^{\oplus}$ 317.0937, found 317.0946.

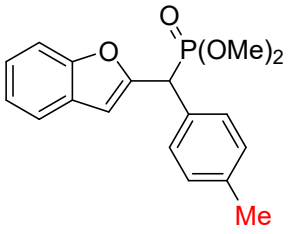
dipropyl (benzofuran-2-yl(phenyl)methyl)phosphonate (3zz)



Yellow oil, 33.5 mg, 45% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.57 – 7.47 (m, 3H), 7.44 – 7.15 (m, 6H), 6.94 (d, *J* = 2.4 Hz, 1H), 4.66 (d, *J* =

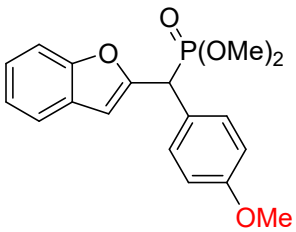
25.6 Hz, 1H), 4.11 – 3.86 (m, 3H), 3.74 (dd, *J* = 10.1, 7.6 Hz, 1H), 1.62 – 1.39 (m, 4H), 1.26 (dq, *J* = 27.1, 7.4 Hz, 5H), 0.83 (q, *J* = 7.5 Hz, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 154.9, 153.1 (d, *J* = 1.5 Hz), 134.1, 129.7 (d, *J* = 6.4 Hz), 128.7 (d, *J* = 1.8 Hz), 127.8 (d, *J* = 2.8 Hz), 124.1, 122.9, 121.0, 111.2, 105.9 (d, *J* = 5.1 Hz), 66.9 (dd, *J* = 11.5, 7.3 Hz), 46.5, 45.1, 32.6 (dd, *J* = 8.3, 5.9 Hz), 18.7 (d, *J* = 6.5 Hz), 13.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.39 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{21}H_{25}O_4PH^{\oplus}$ 373.1563, found 373.1556.

dimethyl (benzofuran-2-yl(p-tolyl)methyl)phosphonate (3ab)



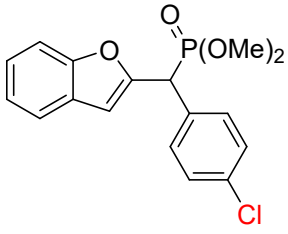
Yellow oil, 33 mg, 50% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.53 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 – 7.35 (m, 3H), 7.35 – 7.15 (m, 4H), 6.94 – 6.88 (m, 1H), 4.66 (d, *J* = 25.8 Hz, 1H), 3.72 (d, *J* = 10.9 Hz, 3H), 3.58 (d, *J* = 10.8 Hz, 3H), 2.33 (d, *J* = 1.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 154.9, 152.9 (d, *J* = 1.6 Hz), 137.8 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 6.9 Hz), 129.6 (d, *J* = 2.3 Hz), 129.4 (d, *J* = 6.4 Hz), 128.6 (d, *J* = 1.9 Hz), 124.2, 122.9, 121.1, 111.2, 105.9 (d, *J* = 5.2 Hz), 53.8 (dd, *J* = 19.4, 7.1 Hz), 45.6, 44.2, 21.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.36 (s). **(ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{19}O_4PH^{\oplus}$ 331.1094, found 331.1094.

dimethyl (benzofuran-2-yl(4-methoxyphenyl)methyl)phosphonate (3ac)



Yellow oil, 45.7 mg, 66% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.53 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.42 (ddd, *J* = 8.1, 6.3, 1.7 Hz, 3H), 7.23 – 7.13 (m, 2H), 6.94 – 6.82 (m, 3H), 4.63 (d, *J* = 25.8 Hz, 1H), 3.78 (s, 3H), 3.71 (d, *J* = 10.8 Hz, 3H), 3.57 (d, *J* = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 159.4 (d, *J* = 2.7 Hz), 154.9, 153.0, 130.7 (d, *J* = 6.4 Hz), 128.6 (d, *J* = 1.8 Hz), 125.5 (d, *J* = 7.1 Hz), 124.2, 122.9, 121.1, 114.3 (d, *J* = 2.2 Hz), 111.2, 105.8 (d, *J* = 5.1 Hz), 55.4, 53.8 (dd, *J* = 22.3, 7.0 Hz), 45.2, 43.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.29 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{19}O_5PH^{\oplus}$ 347.1043, found 347.1049.

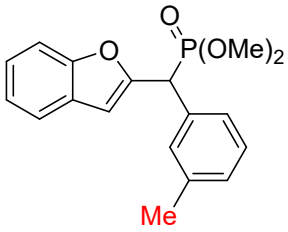
dimethyl (benzofuran-2-yl(4- chlorophenyl)methyl)phosphonate (3ad)



Yellow oil, 23.7 mg, 33% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 1H), 7.48 – 7.38 (m, 4H), 7.35 – 7.29 (m, 3H), 7.23 – 7.17 (m, 1H), 6.91 (dt, *J* = 2.6, 0.9 Hz, 1H), 4.66 (d, *J* = 25.8 Hz, 1H), 3.72 (d, *J* = 10.9 Hz, 3H), 3.60 (d, *J* = 10.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 154.9, 152.9 (d, *J* = 1.6 Hz), 137.8 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 6.9 Hz), 129.6 (d, *J* = 2.3 Hz),

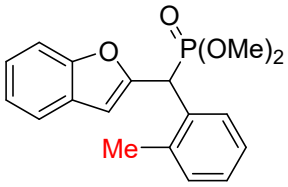
129.4 (d, J = 6.4 Hz), 128.6 (d, J = 1.9 Hz), 124.2, 122.9, 121.1, 111.2, 105.9 (d, J = 5.2 Hz), 53.8 (dd, J = 19.4, 7.1 Hz), 45.6, 44.2, 21.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.34 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{16}O_3PH^{\oplus}$ 350.1094, found 350.1094.

dimethyl (benzofuran-2-yl(m-tolyl)methyl)phosphonate (3ae)



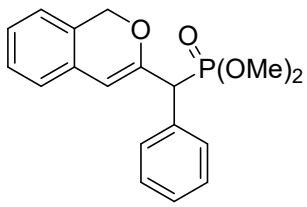
Yellow oil, 30 mg, 46% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 6.9 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.24 (d, J = 8.3 Hz, 3H), 7.20 – 7.13 (m, 3H), 7.03 (d, J = 7.6 Hz, 1H), 6.86 (d, J = 2.5 Hz, 1H), 4.57 (d, J = 25.8 Hz, 1H), 3.67 – 3.62 (m, 3H), 3.49 (d, J = 10.8 Hz, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 151.7, 137.4 (d, J = 5.0 Hz), 132.3 (d, J = 6.6 Hz), 129.4, 129.1 (d, J = 6.4 Hz), 128.7 (d, J = 3.8 Hz), 127.8 – 127.3 (m), 125.4 (d, J = 6.3 Hz), 123.4, 120.7, 119.9, 110.1, 104.8 (d, J = 5.1 Hz), 54.3 – 51.7 (m), 43.4, 28.6, 21.4 – 19.8 (m). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.45 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{19}O_4PH^{\oplus}$ 331.1094, found 331.1097.

dimethyl (benzofuran-2-yl(o-tolyl)methyl)phosphonate (3af)



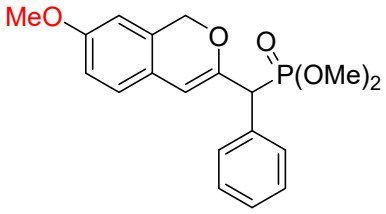
Yellow oil, 25 mg, 38% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 1H), 7.67 – 7.60 (m, 1H), 7.46 (dd, J = 7.2, 1.7 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.15 – 7.12 (m, 3H), 6.85 (d, J = 2.5 Hz, 1H), 4.89 (d, J = 26.3 Hz, 1H), 3.67 (d, J = 10.9 Hz, 3H), 3.45 (d, J = 10.7 Hz, 3H), 2.41 (d, J = 1.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 138.2, 136.5 (d, J = 8.6 Hz), 132.9, 131.9 (d, J = 6.4 Hz), 129.8 – 129.3 (m), 127.7 (dd, J = 8.9, 3.0 Hz), 126.8 – 126.1 (m), 124.1, 122.8, 120.9, 111.1, 105.9 (d, J = 5.0 Hz), 53.8 (dd, J = 19.6, 12.5 Hz), 41.3, 39.9, 21.1, 19.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.75 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{19}O_4PH^{\oplus}$ 331.1094, found 331.1094.

dimethyl ((1H-isochromen-3-yl)(phenyl)methyl)phosphonate (3ag)



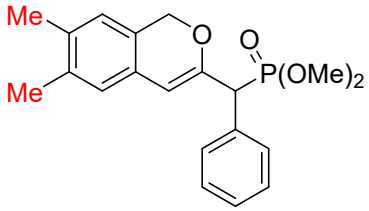
Yellow oil, 29.7 mg, 45% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.57 – 7.49 (m, 2H), 7.39 – 7.27 (m, 3H), 7.23 – 7.08 (m, 2H), 7.02 – 6.93 (m, 2H), 6.12 (d, J = 2.6 Hz, 1H), 5.10 (s, 2H), 4.01 (d, J = 25.4 Hz, 1H), 3.76 (d, J = 10.9 Hz, 3H), 3.57 (d, J = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 152.8 (d, J = 4.9 Hz), 134.3, 131.2, 129.6 (d, J = 6.8 Hz), 128.8 (d, J = 2.0 Hz), 128.3, 127.8 (d, J = 2.7 Hz), 127.5, 126.8, 123.8, 123.5, 105.1 (d, J = 7.8 Hz), 69.5, 53.7 (dd, J = 7.0, 4.7 Hz), 50.5, 49.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.02 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{19}O_4PH^{\oplus}$ 331.1094, found 331.1084.

dimethyl ((7-methoxy-1H-isochromen-3-yl)(phenyl)methyl)phosphonate (3ah)



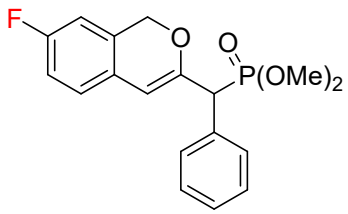
Yellow oil, 26.6 mg, 37% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.56 – 7.48 (m, 2H), 7.39 – 7.22 (m, 3H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.73 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 6.08 (d, *J* = 2.7 Hz, 1H), 5.05 (s, 2H), 3.99 (d, *J* = 25.4 Hz, 1H), 3.82 – 3.71 (m, 6H), 3.56 (d, *J* = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 158.9, 150.6 (d, *J* = 5.0 Hz), 134.4 (d, *J* = 6.4 Hz), 129.6 (d, *J* = 6.6 Hz), 129.2, 128.7 (d, *J* = 2.1 Hz), 127.8 (d, *J* = 2.7 Hz), 124.7, 124.1, 113.1, 110.2, 104.8 (d, *J* = 7.9 Hz), 69.4, 55.5, 53.7 (dd, *J* = 6.9, 2.6 Hz), 50.4, 49.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.10 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{19}H_{21}O_5PH^{\oplus}$ 361.1199, found 361.1197.

dimethyl ((6,7-dimethyl-1H-isochromen-3-yl)(phenyl)methyl)phosphonate (3ai)



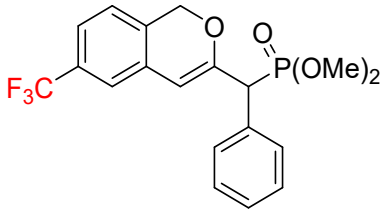
Yellow oil, 35.2 mg, 49% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.56 – 7.48 (m, 2H), 7.40 – 7.22 (m, 3H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.06 (d, *J* = 2.6 Hz, 1H), 5.04 (s, 2H), 4.00 (d, *J* = 25.4 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 3H), 3.56 (d, *J* = 10.7 Hz, 3H), 2.20 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 151.8 (d, *J* = 5.0 Hz), 136.3, 135.1, 134.4 (d, *J* = 6.2 Hz), 129.6 (d, *J* = 6.7 Hz), 128.7 (d, *J* = 2.0 Hz), 127.7 (d, *J* = 2.7 Hz), 125.1, 124.8, 105.0 (d, *J* = 8.0 Hz), 69.2, 53.7 (dd, *J* = 7.0, 5.6 Hz), 50.5, 49.1, 19.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.60 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{20}H_{23}O_4PH^{\oplus}$ 359.1407, found 359.1400.

dimethyl ((7-fluoro-1H-isochromen-3-yl)(phenyl)methyl)phosphonate (3aj)



Yellow oil, 34.8 mg, 50% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.57 – 7.47 (m, 2H), 7.39 – 7.24 (m, 3H), 6.97 – 6.81 (m, 1H), 6.70 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.10 (d, *J* = 2.6 Hz, 1H), 5.05 (s, 1H), 4.00 (d, *J* = 25.4 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 3H), 3.55 (d, *J* = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 163.0, 160.5, 152.0, 134.1 (d, *J* = 6.4 Hz), 129.6 (d, *J* = 6.7 Hz), 128.8 (d, *J* = 2.0 Hz), 127.9 (d, *J* = 2.7 Hz), 127.3 (d, *J* = 3.0 Hz), 124.9 (d, *J* = 7.9 Hz), 114.8 (d, *J* = 21.6 Hz), 111.3 (d, *J* = 22.9 Hz), 69.0 (d, *J* = 2.2 Hz), 53.7 (dd, *J* = 16.6, 7.0 Hz), 50.3, 48.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.68 (s). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.03 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{18}FO_4PH^{\oplus}$ 349.1000, found 349.0990.

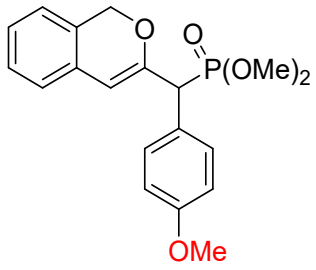
dimethyl(phenyl(6-(trifluoromethyl)-1H-isochromen-3-yl)methyl)phosphonat (3ak)



Yellow oil, 36.6 mg, 46% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.55 – 7.47 (m, 2H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.22 (s, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.17 (d, *J* = 2.5 Hz, 1H), 5.14 (s, 2H), 4.02 (d, *J* = 25.3 Hz, 1H), 3.76 (d, *J* = 10.9 Hz, 3H), 3.56 (d, *J* = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 155.2 (d, *J* = 4.7 Hz), 134.7, 133.7 (d, *J* = 6.6 Hz), 129.6 (d, *J* = 6.8 Hz), 128.9 (d, *J* = 2.0 Hz), 128.0 (d, *J* = 2.5 Hz), 127.6, 125.4 (d, *J* = 3.7 Hz), 123.4, 120.9 (d, *J* = 3.9 Hz), 104.3 (d, *J* = 7.6 Hz), 69.1, 53.8 (dd, *J* = 24.8, 7.0 Hz), 50.5, 49.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.49 (s). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.10 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{19}H_{18}F_3O_4PH^{\oplus}$ 399.0968, found 399.0974.

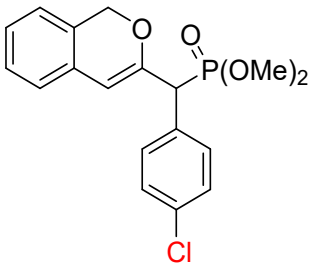
dimethyl ((1H-isochromen-3-yl)(4-methoxyphenyl)methyl)phosphonate (3al)

Yellow oil, 48.9 mg, 68% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.44 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.18 (td, *J* = 7.5, 1.4 Hz, 1H), 7.12 (td, *J* = 7.4, 1.4 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.09 (d, *J* = 2.5 Hz, 1H), 5.09 (s, 2H), 3.96 (d, *J* = 25.4 Hz, 1H), 3.79 (s, 3H), 3.75 (d, *J* = 10.8 Hz, 3H), 3.57 (d, *J* = 10.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 159.2 (d, *J* = 2.5 Hz), 153.0 (d, *J* = 4.4 Hz), 131.2 (d, *J* = 1.4 Hz), 130.7 (d, *J* = 6.8 Hz), 128.3, 127.4, 126.7, 126.0 (d, *J* = 6.5 Hz), 123.8, 123.4, 114.2 (d, *J* = 2.0 Hz), 104.9 (d, *J* = 7.9 Hz), 69.4, 55.4, 53.7 (dd, *J* = 8.9, 7.0 Hz), 49.5, 48.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.56 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{19}H_{21}O_5PH^{\oplus}$ 361.1199, found 361.1205.

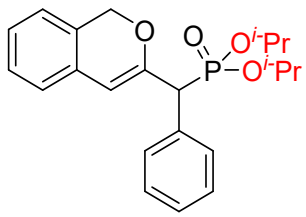


dimethyl ((4-chlorophenyl)(1H-isochromen-3-yl)methyl)phosphonate (3am)

Yellow oil, 30.6 mg, 42% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.52 (dt, *J* = 8.0, 1.8 Hz, 2H), 7.44 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.22 (s, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.17 (d, *J* = 2.5 Hz, 2H), 5.13 (s, 1H), 4.02 (d, *J* = 25.3 Hz, 1H), 3.76 (d, *J* = 10.9 Hz, 3H), 3.55 (d, *J* = 10.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 152.1 (d, *J* = 5.2 Hz), 133.7 (d, *J* = 3.2 Hz), 132.7 (d, *J* = 6.4 Hz), 130.8 (d, *J* = 6.7 Hz), 128.8 (d, *J* = 2.1 Hz), 128.3, 127.3, 126.8, 123.8, 123.4, 105.2 (d, *J* = 7.8 Hz), 69.4, 53.7 (t, *J* = 7.3 Hz), 53.5, 49.7, 48.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.45 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{18}H_{18}ClO_4PH^{\oplus}$ 365.0704, found 365.0714.

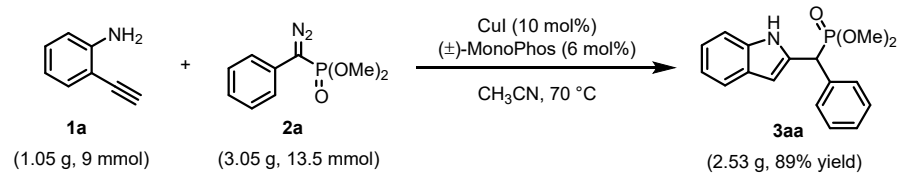


diisopropyl ((1H-isochromen-3-yl)(phenyl)methyl)phosphonate (3an)



Yellow oil, 63.3 mg, 80% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.66 – 7.48 (m, 2H), 7.38 – 7.25 (m, 3H), 7.18 (td, *J* = 7.6, 1.4 Hz, 1H), 7.10 (td, *J* = 7.4, 1.3 Hz, 1H), 6.96 (td, *J* = 5.8, 3.0 Hz, 2H), 6.20 (d, *J* = 2.4 Hz, 1H), 5.06 (s, 2H), 4.72 (dp, *J* = 7.6, 6.1 Hz, 1H), 4.48 (dp, *J* = 7.5, 6.1 Hz, 1H), 3.90 (d, *J* = 25.4 Hz, 1H), 1.31 (d, *J* = 6.2 Hz, 3H), 1.23 (dd, *J* = 6.2, 4.4 Hz, 6H), 0.91 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 153.5 (d, *J* = 3.5 Hz), 134.8 (d, *J* = 6.1 Hz), 131.4, 129.8 (d, *J* = 6.8 Hz), 128.5 (d, *J* = 2.1 Hz), 128.2, 127.5 - 127.4 (m), 126.5, 123.7, 123.3, 104.8 (d, *J* = 7.2 Hz), 71.4 (dd, *J* = 26.6, 7.1 Hz), 69.3, 51.4, 50.0, 24.4 (dd, *J* = 12.4, 2.9 Hz), 23.9 (d, *J* = 5.6 Hz), 23.3 (d, *J* = 6.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 23.64 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{22}H_{27}O_4PH^{\oplus}$387.1720, found 387.1730.

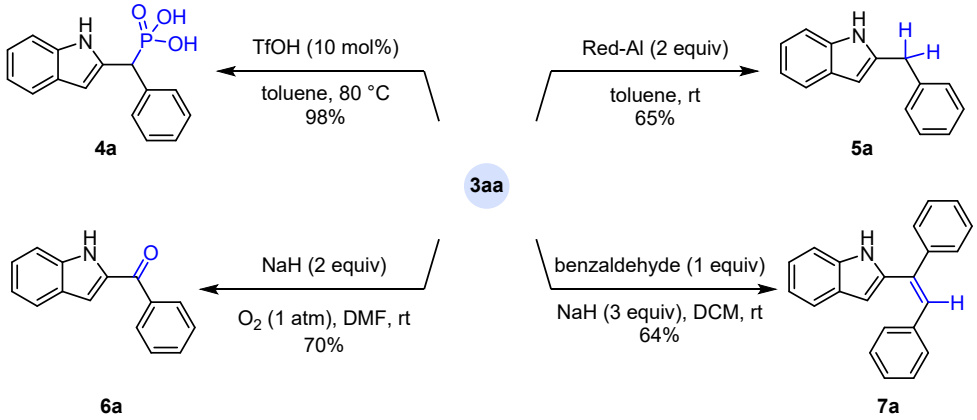
5. Gram-scale reaction



1a (1.05 g, 9 mmol) + **2a** (3.05 g, 13.5 mmol) → **3aa** (2.53 g, 89% yield)

In an argon atmosphere, **2a** (13.5 mmol, 1.5 equiv) was added to a solution of **1a** (9.0 mmol, 1.0 equiv), CuI (0.45 mmol, 0.05 equiv), (±)-MonoPhos ligand (0.54 mmol, 0.06 equiv) in CH_3CN (40 mL). After the reaction was stirred at 70 °C for 12 h, the resulting mixture was filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **3aa** (2.53g) in a yield of 89%.

6. Synthetic transformations



4a **5a**

6a **7a**

4a) In an argon atmosphere, **3aa** (0.1mmol, 1.0 equiv) was added to a solution of TfOH (0.3 mmol, 3.0 equiv) in toluene (2 mL). After the reaction was stirred at 80 °C for 6 h, the resulting mixture was filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **4a**. White solid, 56.3 mg, 98% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 189.5 – 180.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 10.81 (s, 1H), 7.51 – 7.38 (m, 3H), 7.38 – 7.24 (m, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.04 – 6.86 (m, 2H), 6.52 (s, 1H), 4.49 (d, *J* = 24.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 136.2 (d, *J* = 5.9 Hz), 134.5 (d, *J* = 3.8 Hz), 133.9, 127.5 (d, *J* = 6.2 Hz), 126.2, 126.1 (d, *J* = 1.9 Hz), 124.5 (d, *J* = 2.6 Hz), 118.6, 117.6, 116.9, 109.2, 98.7 (d, *J* = 5.7 Hz), 44.0 (d, *J* = 134.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.39 (s). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{15}H_{14}NO_3PH^{\oplus}$ 288.0784, found 288.0791.

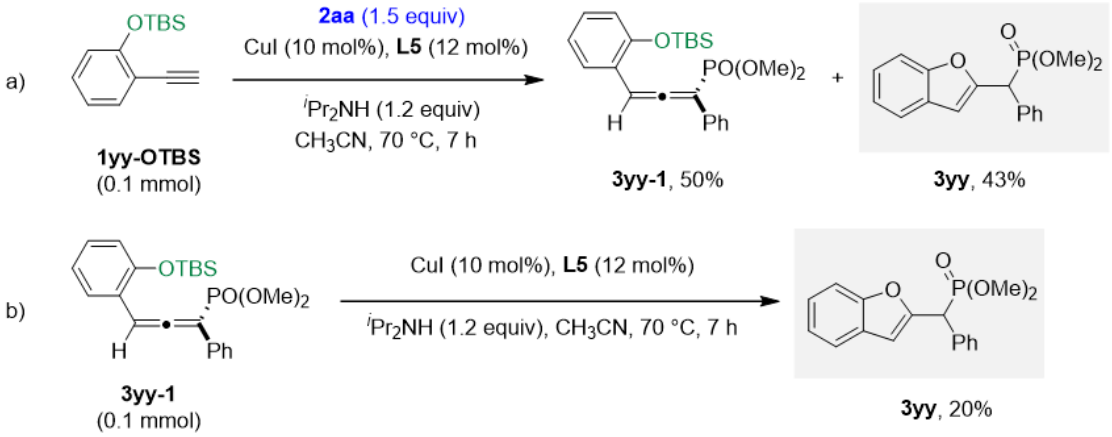
5a) In an argon atmosphere, **3aa** (0.1mmol, 1.0 equiv) was added to a solution of

Red-Al (0.2 mmol, 0.2 equiv) in toluene (2 mL). After the TLC monitoring reaction was completed, the resulting mixture was filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **5a**. White solid, 26.9 mg, 65% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 79.5 – 80.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.76 (s, 1H), 7.57 – 7.51 (m, 1H), 7.32 (ddd, *J* = 6.3, 4.9, 2.9 Hz, 2H), 7.28 – 7.21 (m, 4H), 7.09 (dtd, *J* = 16.1, 7.1, 1.3 Hz, 2H), 6.32 (d, *J* = 2.1 Hz, 1H), 4.12 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 138.6, 137.9, 136.3, 129.0, 128.8, 128.7, 126.8, 121.4, 120.1, 119.8, 110.6, 101.2, 34.8. **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{15}H_{13}NH^{\oplus}$ 208.1121, found 208.1111.

6a) Sodium hydride (0.2 mmol, 0.2 equiv) was added to a solution of **3aa** (0.1 mmol, 1.0 equiv) in DMF (2 mL). Then, the reaction tube was equipped with an oxygen balloon and stirred at room temperature for 4 h. The resulting mixture was filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **6a**. White solid, 30.8 mg, 70% yield. R_f = 0.30 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.05 – 7.97 (m, 2H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.58 – 7.47 (m, 3H), 7.38 (ddd, *J* = 8.3, 6.9, 1.1 Hz, 1H), 7.21 – 7.14 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.26, 138.03, 137.59, 134.37, 132.40, 129.26, 128.51, 127.76, 126.56, 123.27, 121.07, 112.87, 112.24, 77.57 – 76.59 (m). **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{15}H_{11}NOH^{\oplus}$ 222.0841, found 222.0846.

7a) Sodium hydride (0.2 mmol, 0.2 equiv) was added to a solution of **3aa** (0.1 mmol, 1.0 equiv) and benzaldehyde (0.1 mmol, 1.0 equiv) in DCM (2 mL). After the reaction was stirred at room temperature for 6 h, the resulting mixture was filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **7a.** White solid, 36.8 mg, 64% yield. R_f = 0.30 (PE/EtOAc = 2/1). Mp 79.5 – 80.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.91 (s, 1H), 7.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.42 – 7.32 (m, 3H), 7.24 (m, 6H), 7.17 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.11 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1H), 6.92 (s, 1H), 6.41 (dd, *J* = 2.2, 0.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 142.4, 137.0, 136.0 (d, *J* = 12.2 Hz), 134.0, 129.5, 129.3, 128.5 (d, *J* = 3.9 Hz), 128.4, 128.3, 128.1, 127.6, 122.4, 120.8, 119.9, 110.9, 105.5. **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd. for $C_{22}H_{17}NH^{\oplus}$ 296.1434, found 296.1437.

7. Control experiments

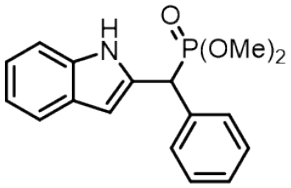


a) In an argon atmosphere, **1yy-OTBS** (0.1 mmol, 1.0 equiv) was added to a suspension of **2aa** (0.15 mmol, 1.5 equiv, CuI (0.01 mmol, 10 mol%), **L5** (0.012 mmol, 12 mol%), $^{i}Pr_2NH$ (0.12 mmol, 1.2 equiv) in CH_3CN (2 mL). Then the reaction was stirred at 70°C for 7 h to give **3yy-1** and **3yy** with yields of 50% and 43% respectively, which was determined by crude ^1H NMR using CH_2Br_2 (0.1 mmol) as internal standard. Characterization data for **3yy-1**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.40 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.31 – 7.24 (m, 2H), 7.18 – 7.10 (m, 2H), 6.92 (td, *J* = 7.5, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.80 (t, *J* = 11.6 Hz, 6H), 1.04 (s, 9H), 0.27 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.1, 152.5, 131.5 (d, *J* = 8.2 Hz), 129.1, 128.8, 128.2 (d, *J* = 2.6 Hz), 128.0, 127.6 (d, *J* = 5.9 Hz), 122.2 (d, *J* = 8.0 Hz), 121.8, 119.6, 101.4, 99.5, 92.9, 77.3, 53.5, 25.8, 18.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.36 (s). **^{1}HRMS (ESI)**: $[M+Na]^{\oplus}$ calcd. for $C_{23}H_{31}O_4PSiNa^{\oplus}$ 453.1621, found 453.1629.

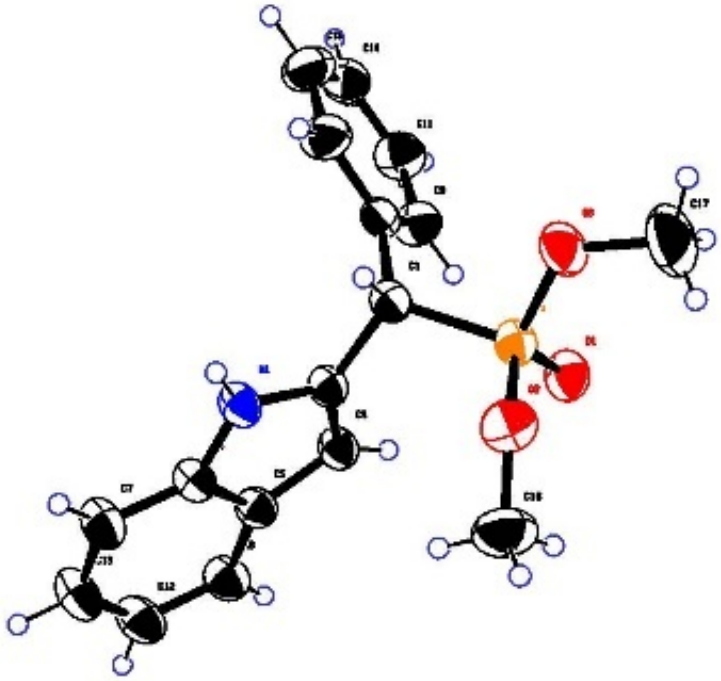
b) In an argon atmosphere, **3yy-1** (0.1 mmol, 1.0 equiv) was added to a suspension of CuI (0.01 mmol, 10 mol%), **L5** (0.012 mmol, 12 mol%), $^{i}Pr_2NH$ (0.12 mmol, 1.2 equiv) in CH_3CN (2 mL). Then the reaction was stirred at 70°C for 7 h to give **3yy** with a yield of 20%, which was determined by crude ^1H NMR using CH_2Br_2 (0.1 mmol) as internal standard.

8. X-ray crystallographic data of 3aa

The structure of **3aa** were determined by the X-ray diffraction analysis of single crystal, which recrystallized from a mixed solution of CH_2Cl_2 and *n*-hexane. CCDC 2426517 (**3aa**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



3aa



Identification code	exp_4767_auto
CCDC Deposit number	2426517
Empirical formula	$C_{17}H_{17}NO_3P$
Formula weight	314.28
Temperature/K	297.32
Crystal system	monoclinic

Space group	C2/c
a/Å	21.4243(4)
b/Å	13.8932(2)
c/Å	11.1722(2)
α/°	90
β/°	98.625(2)
γ/°	90
Volume/Å^3	3287.82(10)
Z	8
ρ_{calc}g/cm$_3$	1.270
μ/mm^{-1}	0.697
F(000)	1.583
Crystal size/mm^3	0.2 × 0.18 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.61 to 153.114
Index ranges	-26 ≤ h ≤ 26, -15 ≤ k ≤ 17, -14 ≤ l ≤ 12
Reflections collected	10997
Independent reflections	3289 [R_{int} = 0.0237, R_{sigma} = 0.0239]
Data/restraints/parameters	3289/0/202
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0. 1071
Final R indexes [all data]	R_1 = 0.0420, wR_2 = 0. 1111
Largest diff. peak/hole / e Å^{-3}	0.18/-0.26

9. References

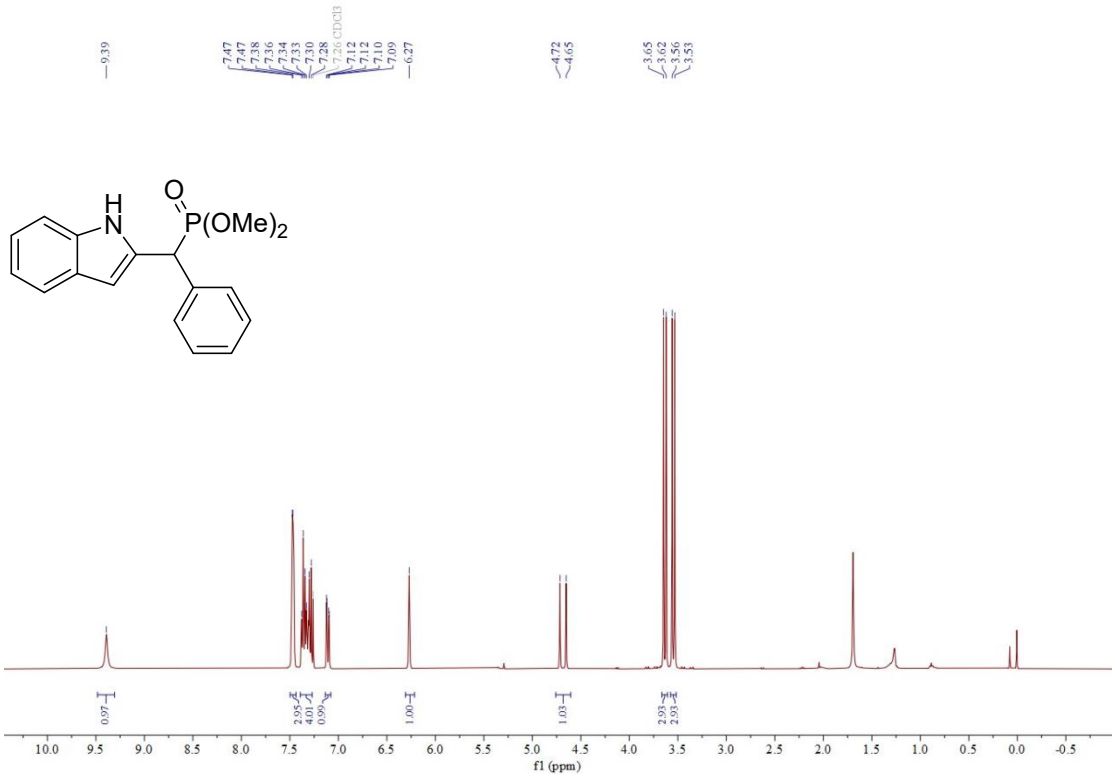
[1] H. Kusama, J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2002, **124**, 11592–11593.

[2] S.-Y. Yuan, Q.-Q. Yan, D. Wang, T.-T. Dan, L. He, C.-Y. He, W.-D. Chu and Q.-Z. Liu, *Org. Lett.*, 2021, **23**, 4823–4827.

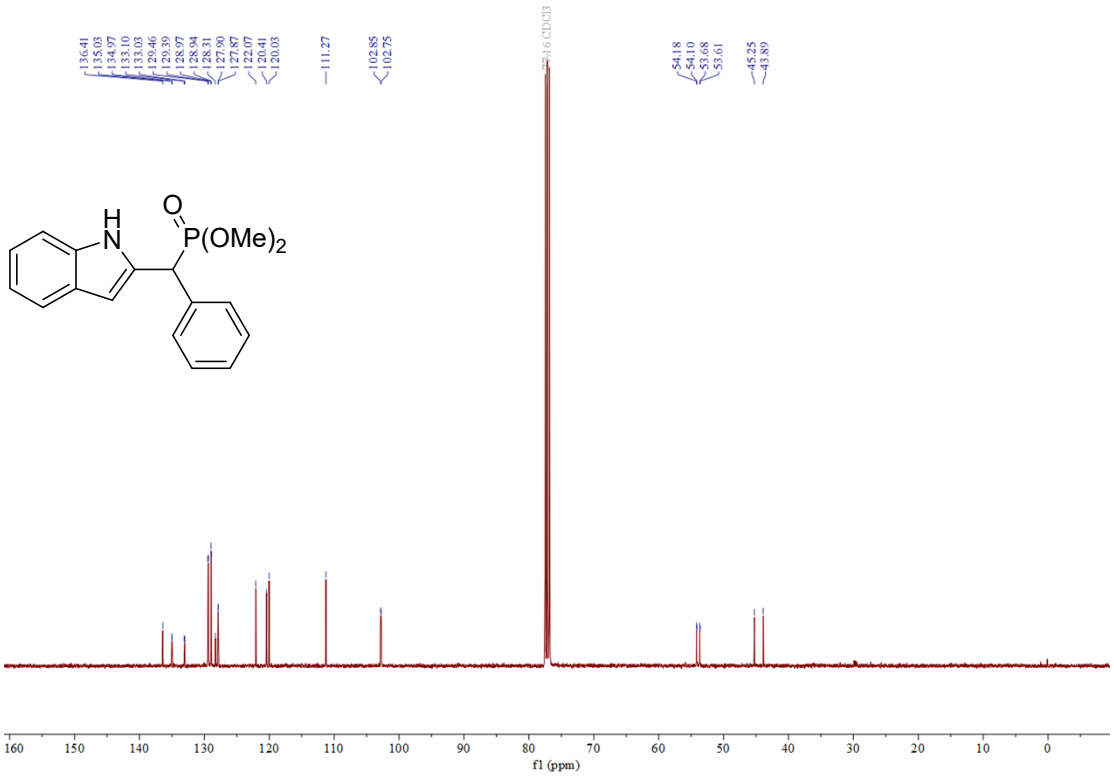
[3] Q.-Q. Yan, C.-K. Ruan, Y.-Q. Deng, Y.-C. Pu, W.-D. Chu, C.-Y. He and Q.-Z. Liu, *Org. Chem. Front.*, 2023, **10**, 4935–4940.

10. Copies of NMR spectra of products

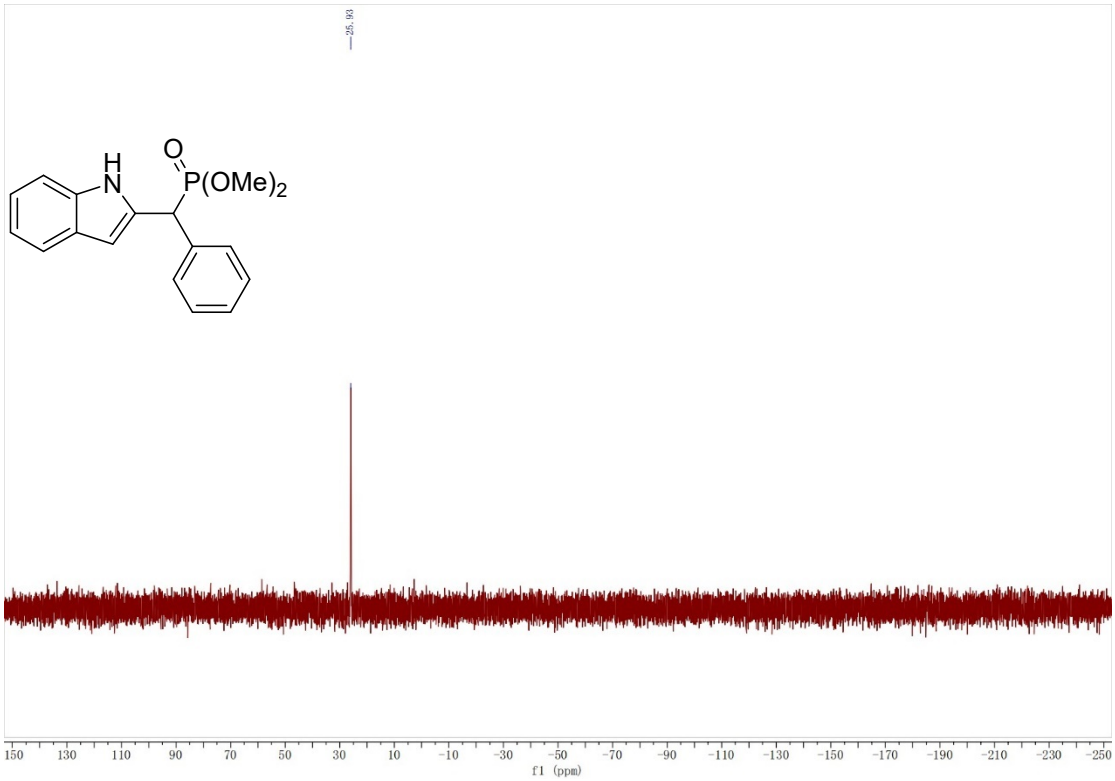
^{1}H NMR Spectra of **3aa** (400 MHz, $CDCl_3$)



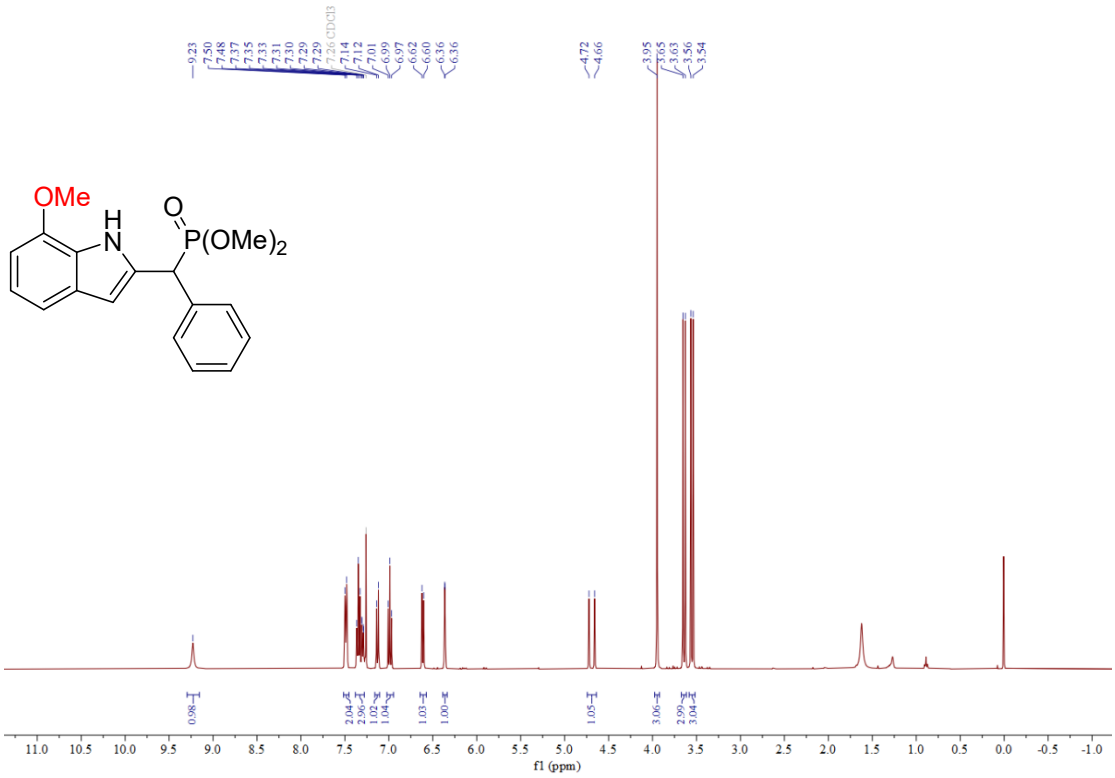
^{13}C NMR Spectra of **3aa** (100 MHz, $CDCl_3$)



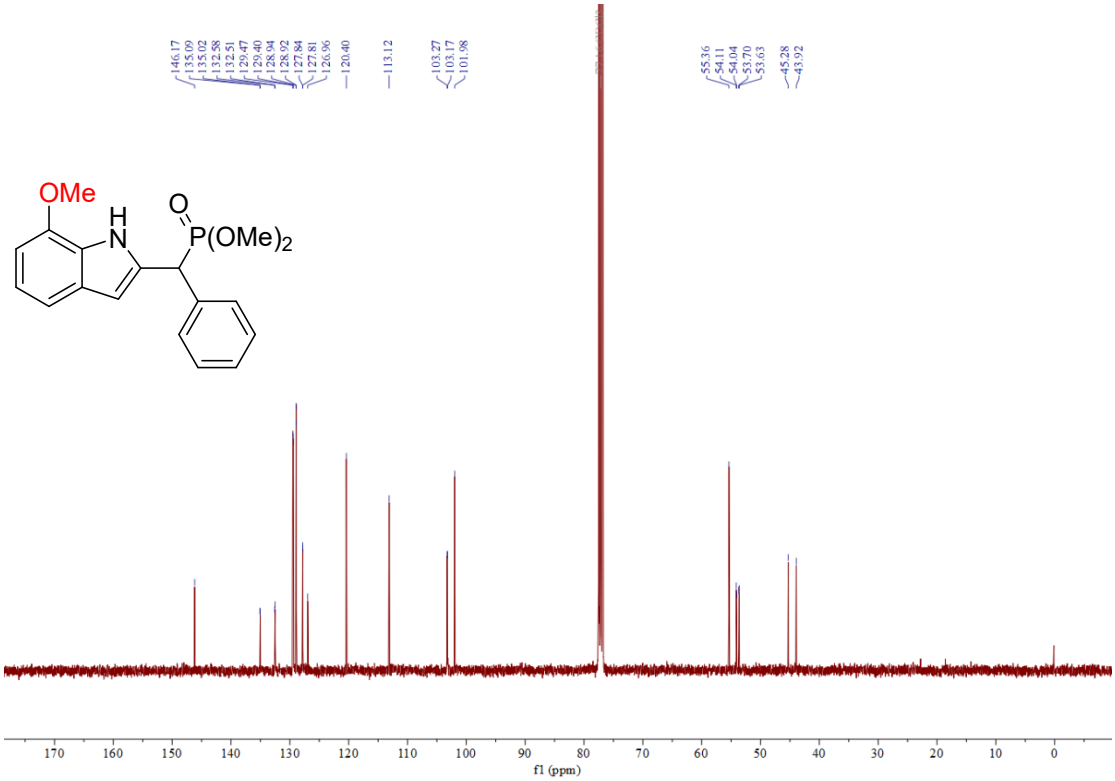
^{31}P NMR Spectra of **3aa** (162 MHz, $CDCl_3$)



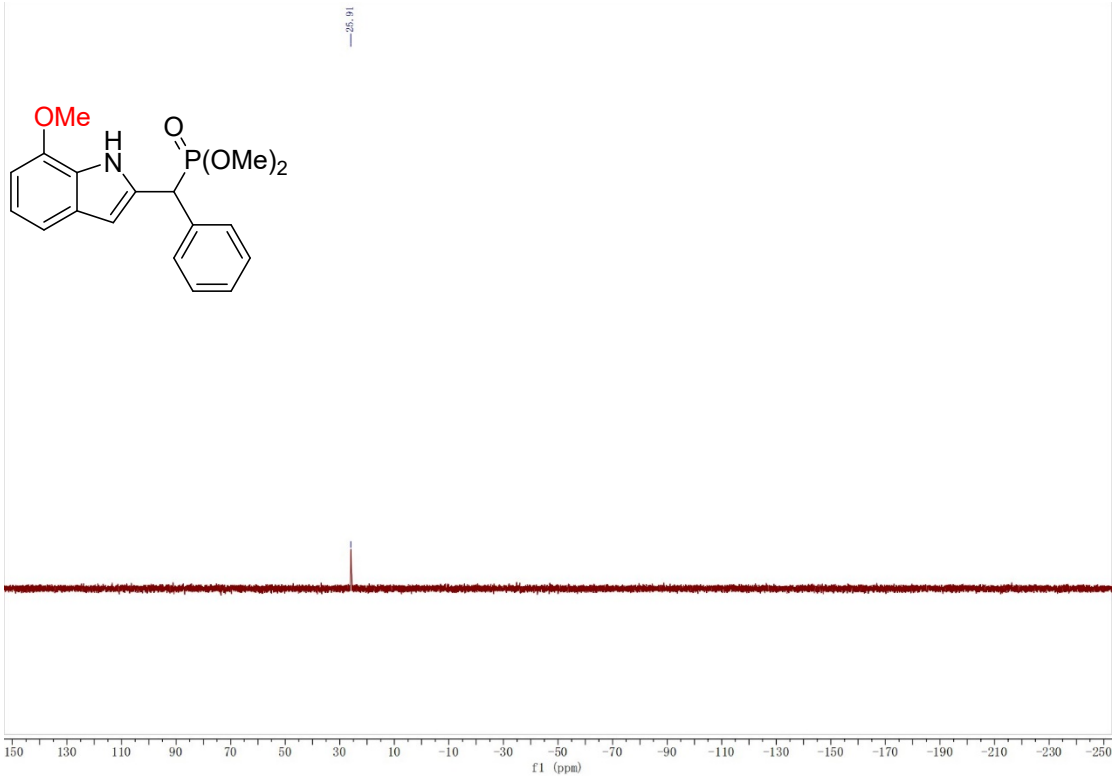
^{1}H NMR Spectra of **3bb** (400 MHz, $CDCl_3$)



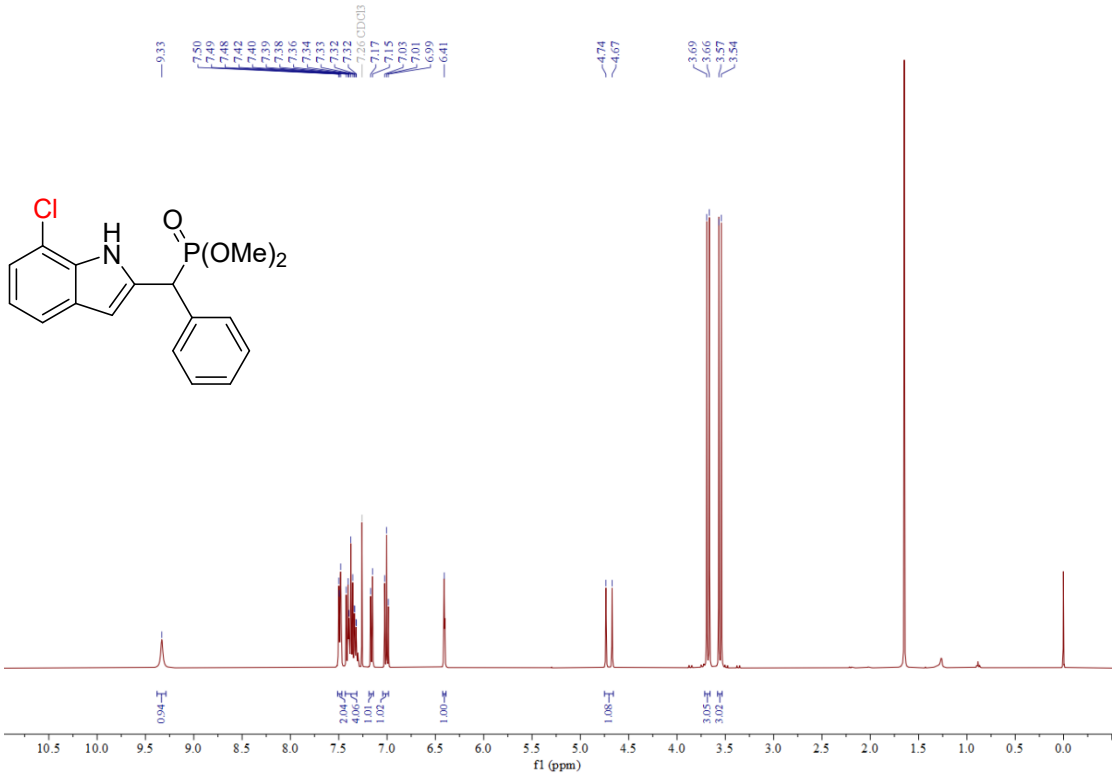
^{13}C NMR Spectra of **3bb** (100 MHz, $CDCl_3$)



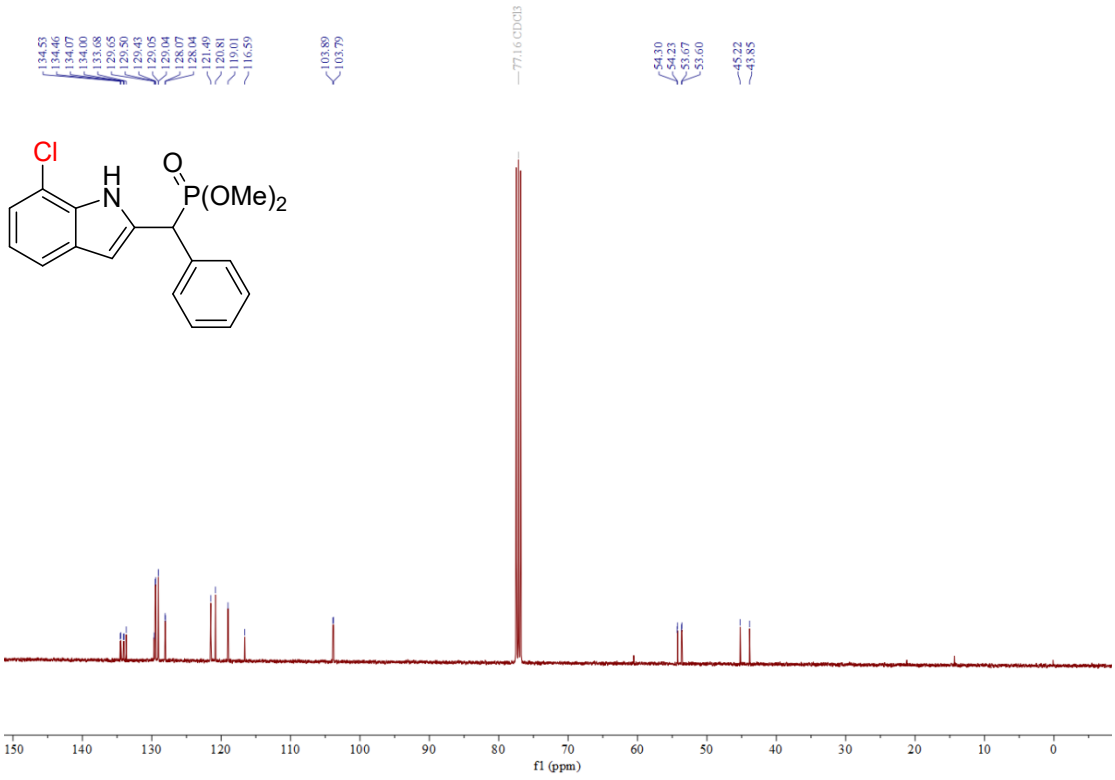
^{31}P NMR Spectra of **3bb** (162 MHz, $CDCl_3$)



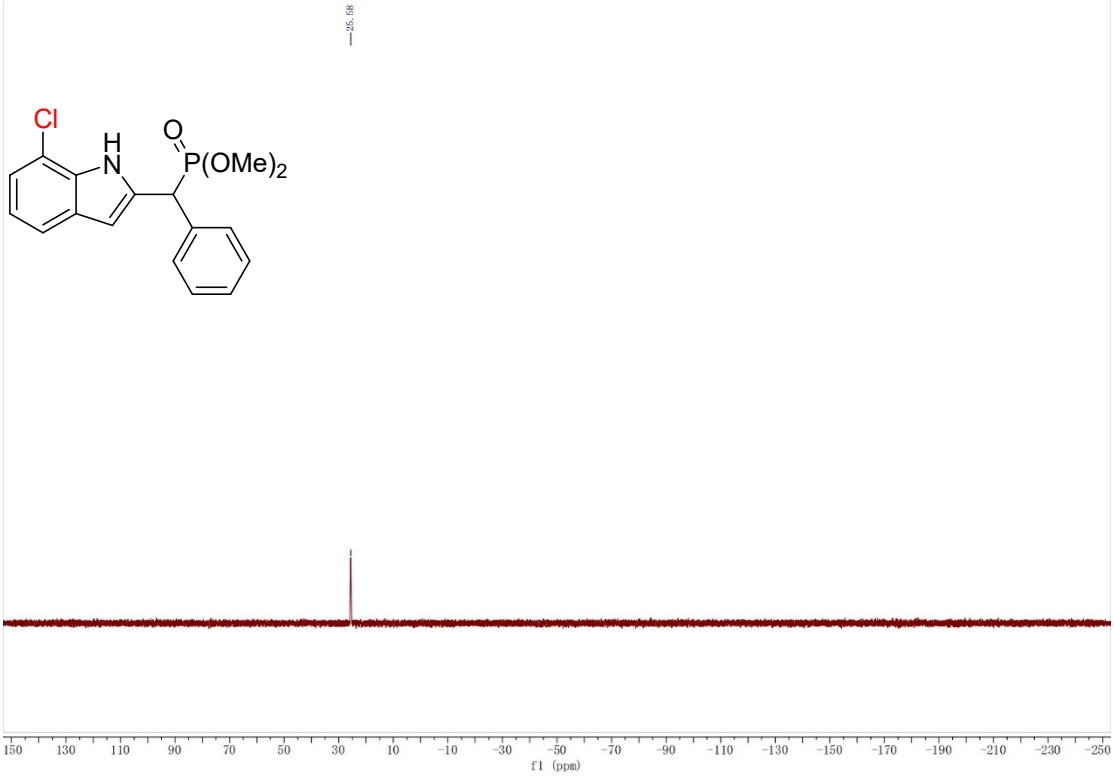
^{1}H NMR Spectra of **3cc** (400 MHz, $CDCl_3$)



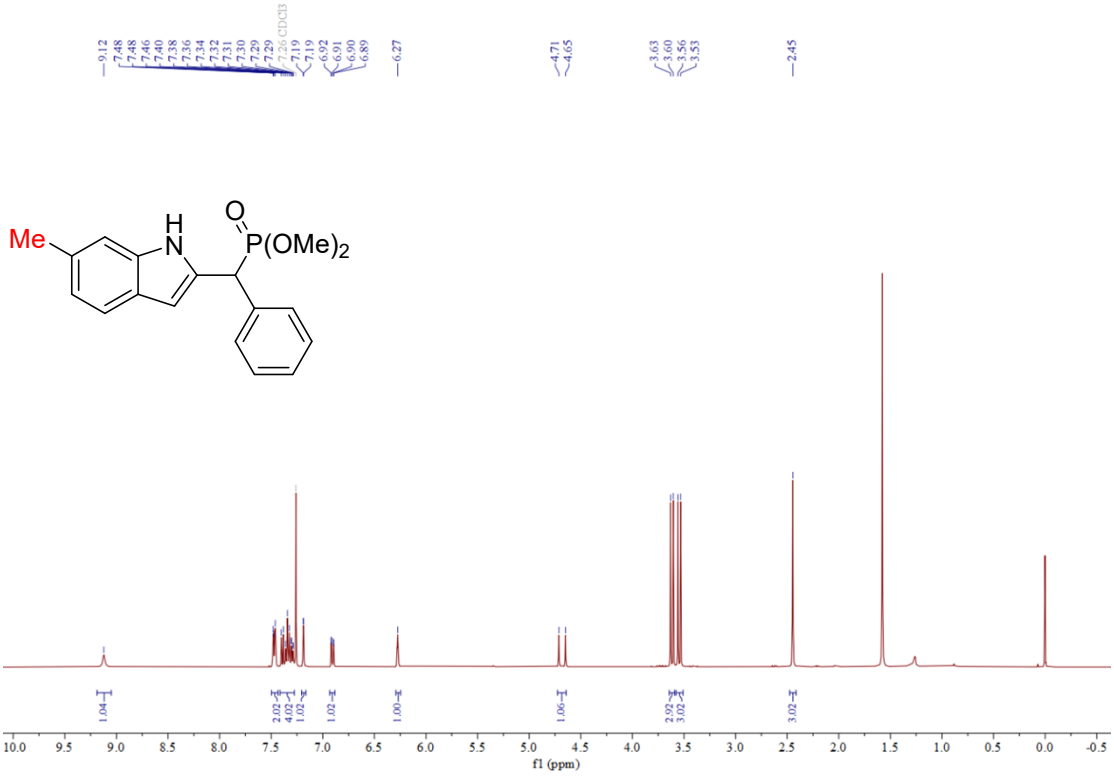
^{13}C NMR Spectra of **3cc** (100 MHz, $CDCl_3$)



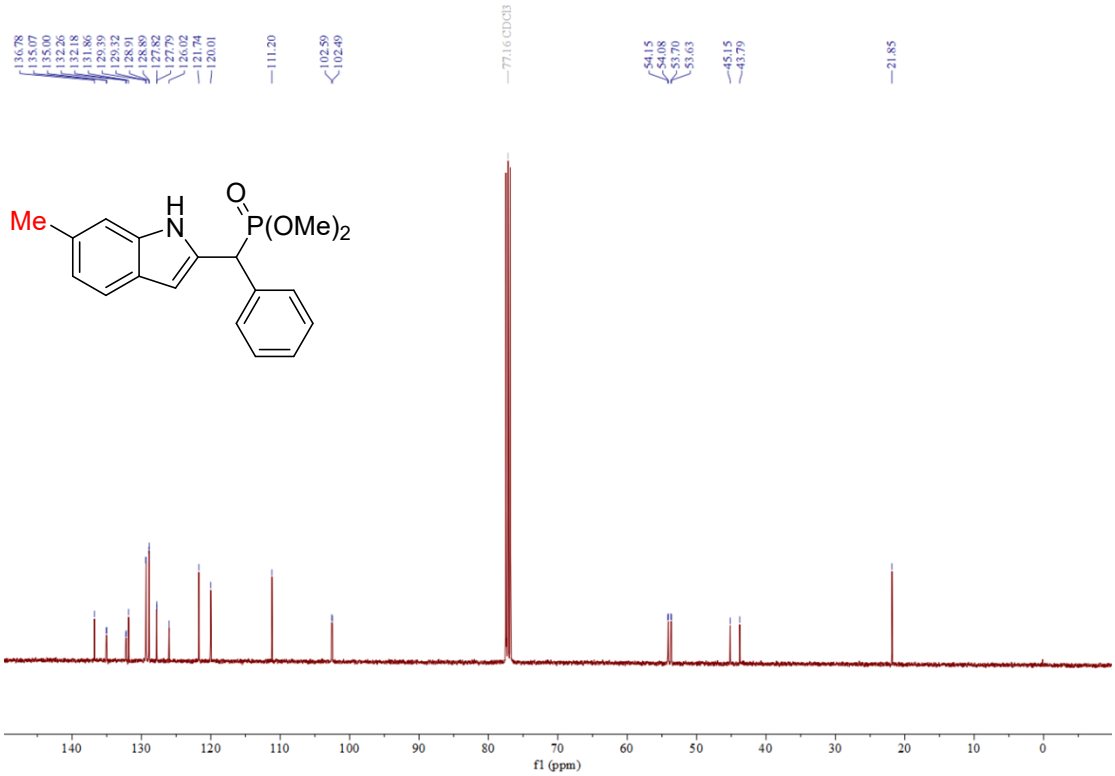
^{31}P NMR Spectra of **3cc** (162 MHz, $CDCl_3$)



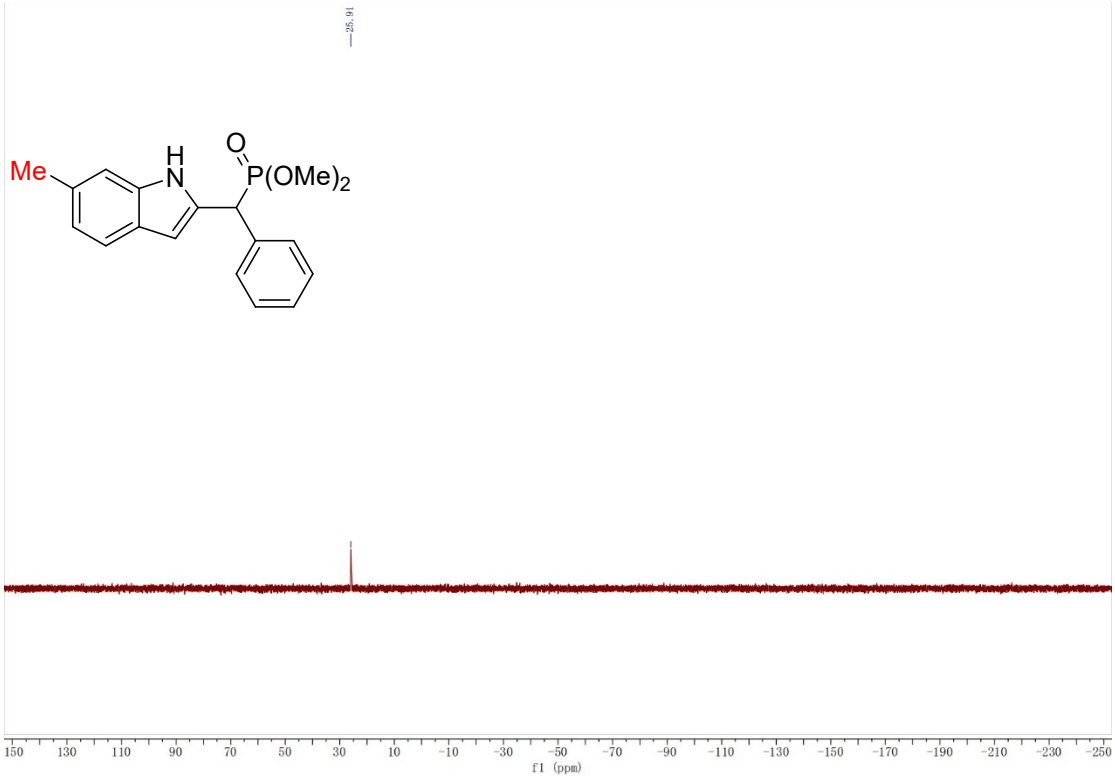
^{1}H NMR Spectra of **3dd** (400 MHz, $CDCl_3$)



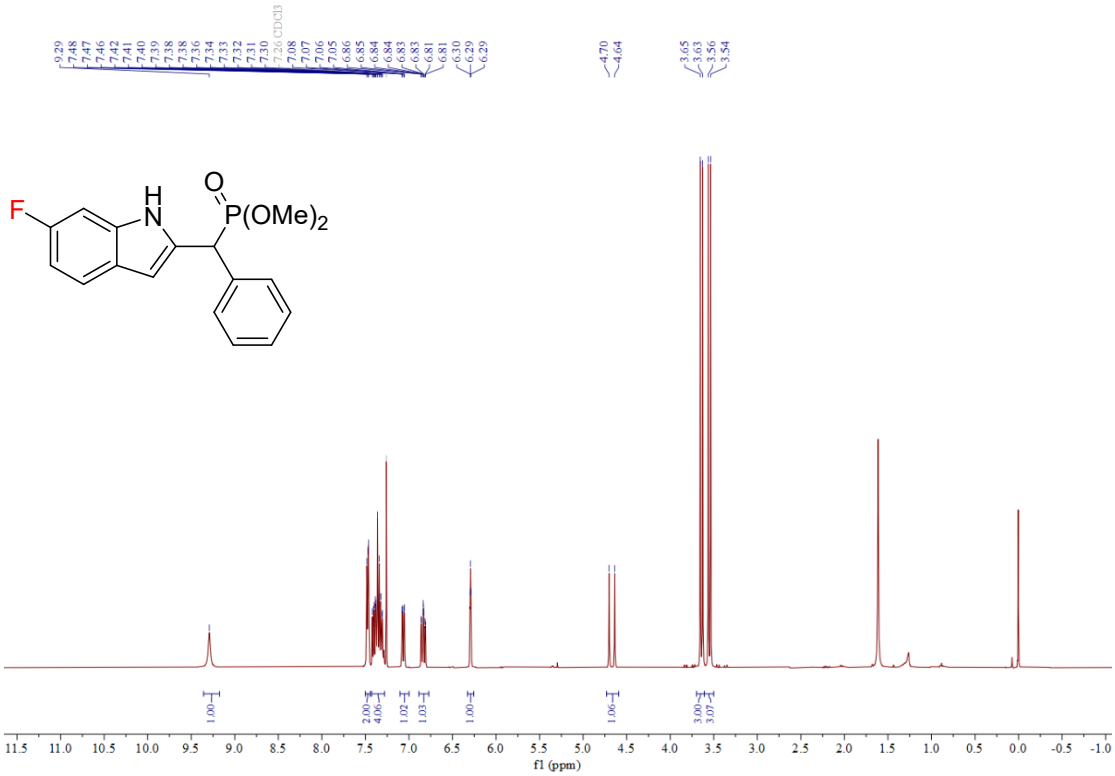
^{13}C NMR Spectra of **3dd** (100 MHz, $CDCl_3$)



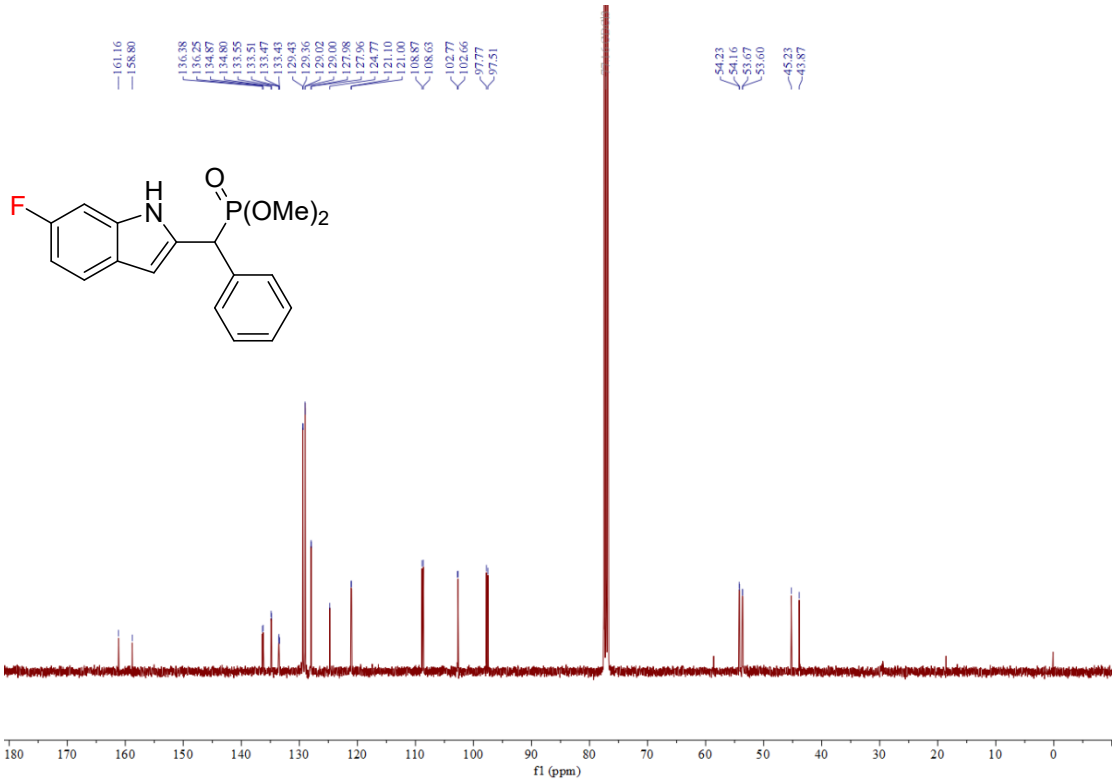
^{31}P NMR Spectra of **3dd** (162 MHz, $CDCl_3$)



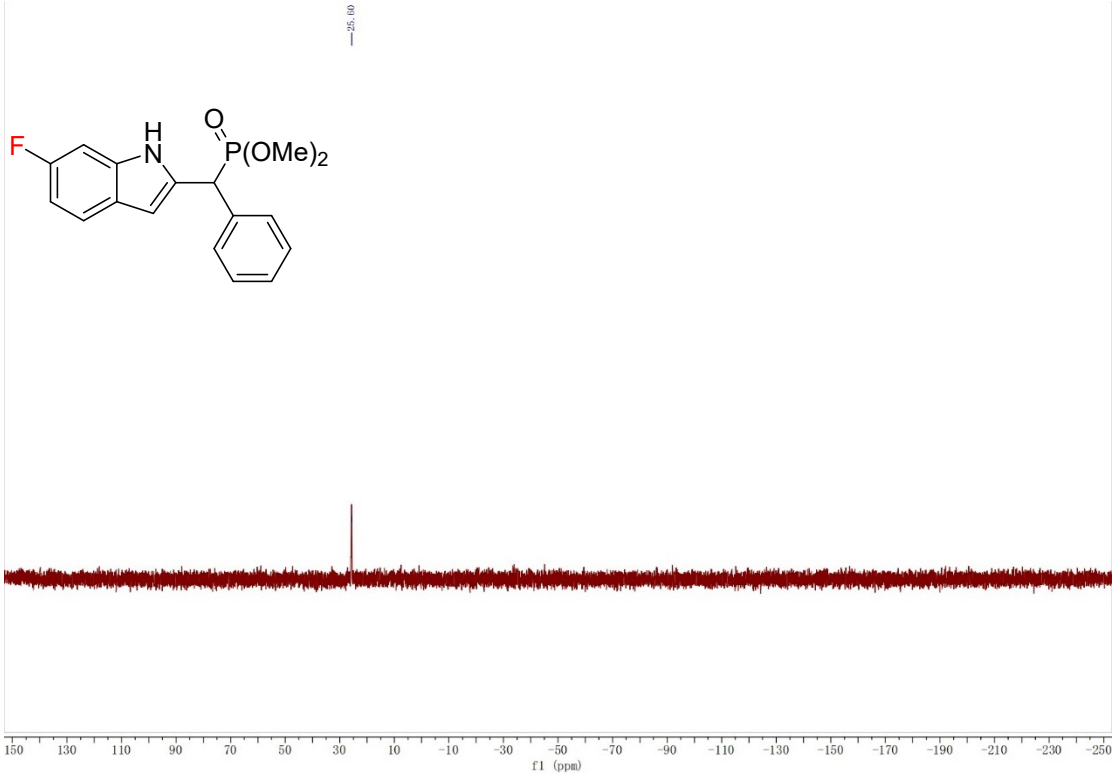
^{1}H NMR Spectra of **3ee** (400 MHz, $CDCl_3$)



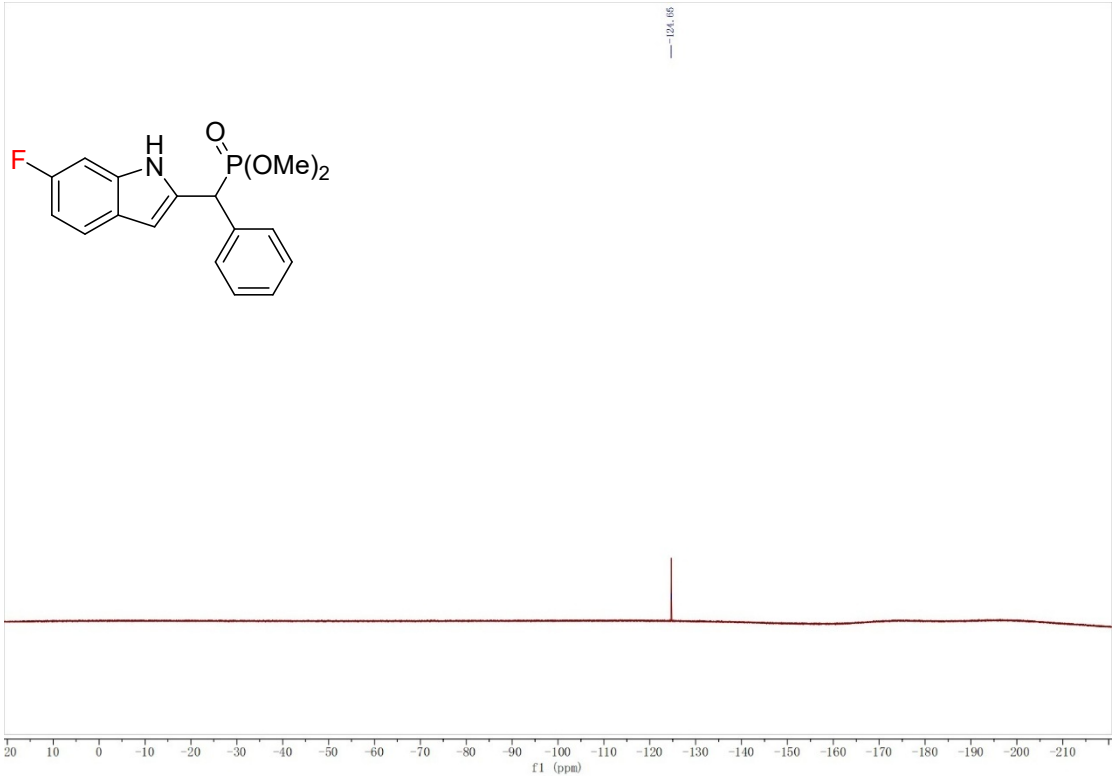
^{13}C NMR Spectra of **3ee** (100 MHz, $CDCl_3$)



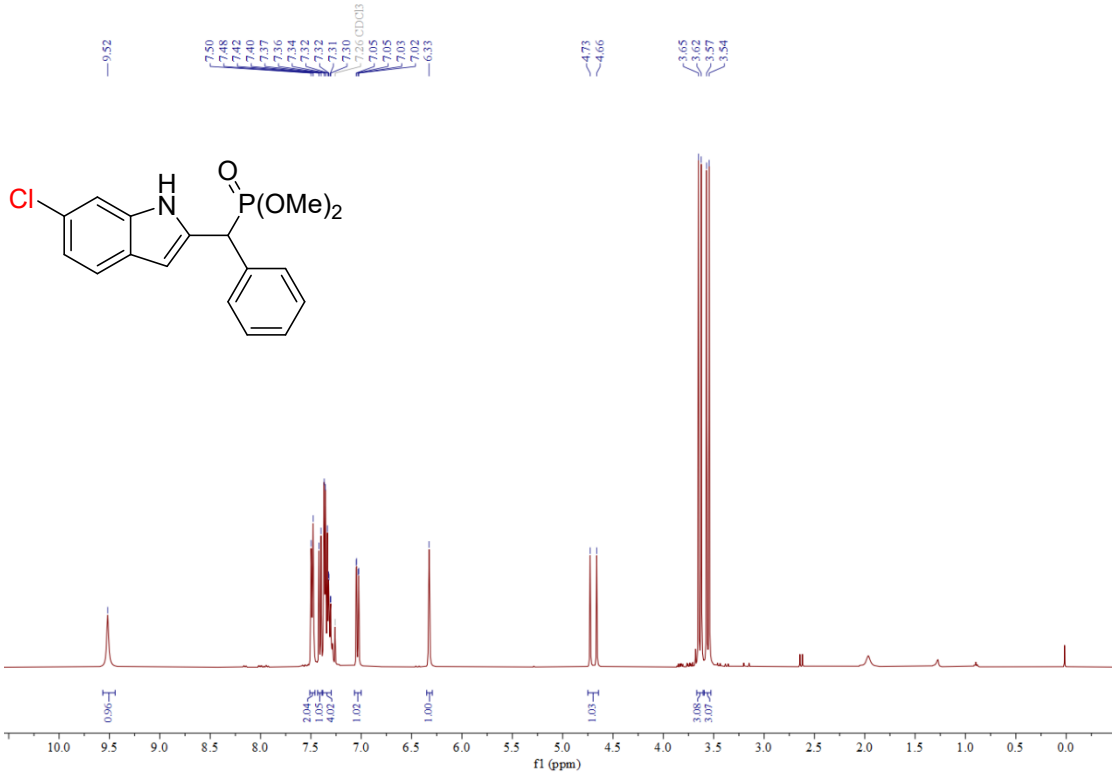
^{31}P NMR Spectra of **3ee** (162 MHz, $CDCl_3$)



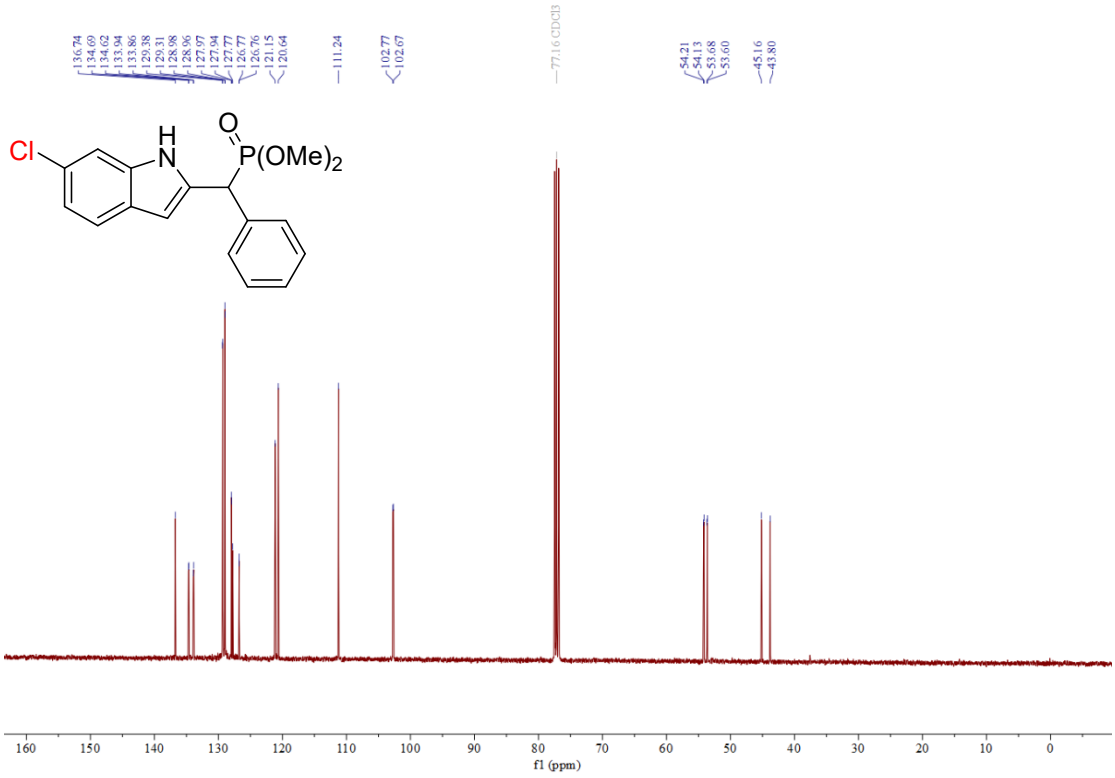
^{19}F NMR Spectra of **3ee** (376 MHz, $CDCl_3$)



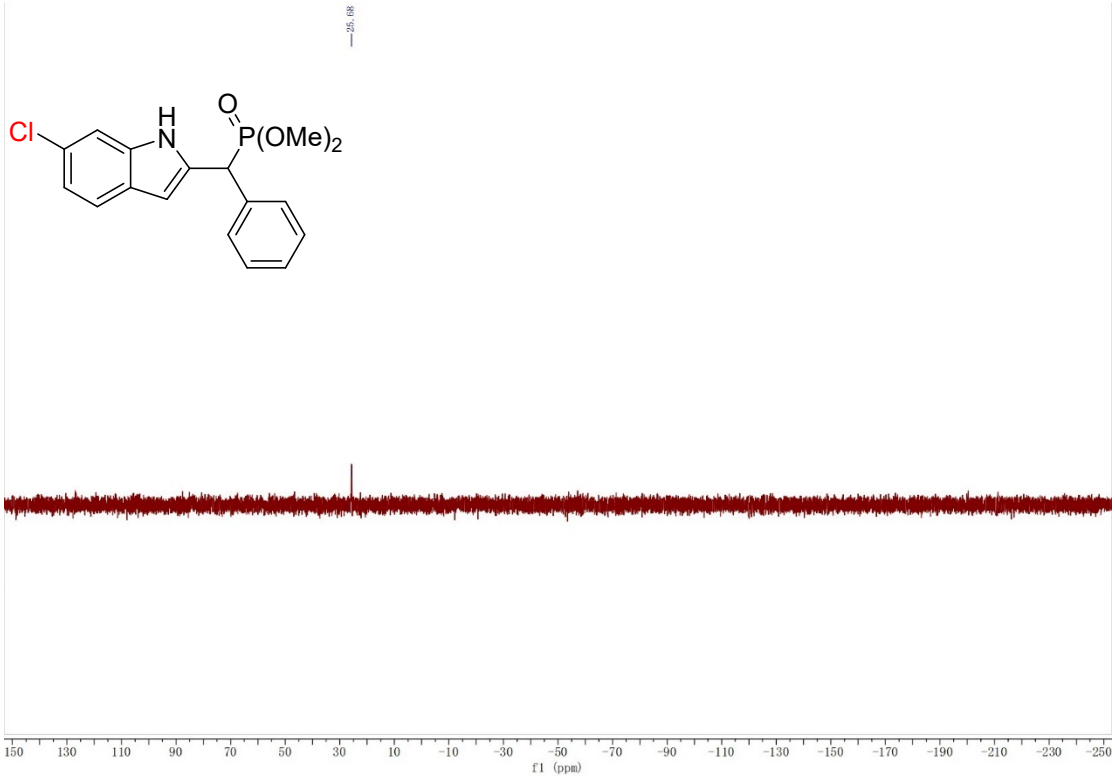
^{1}H NMR Spectra of **3ff** (400 MHz, $CDCl_3$)



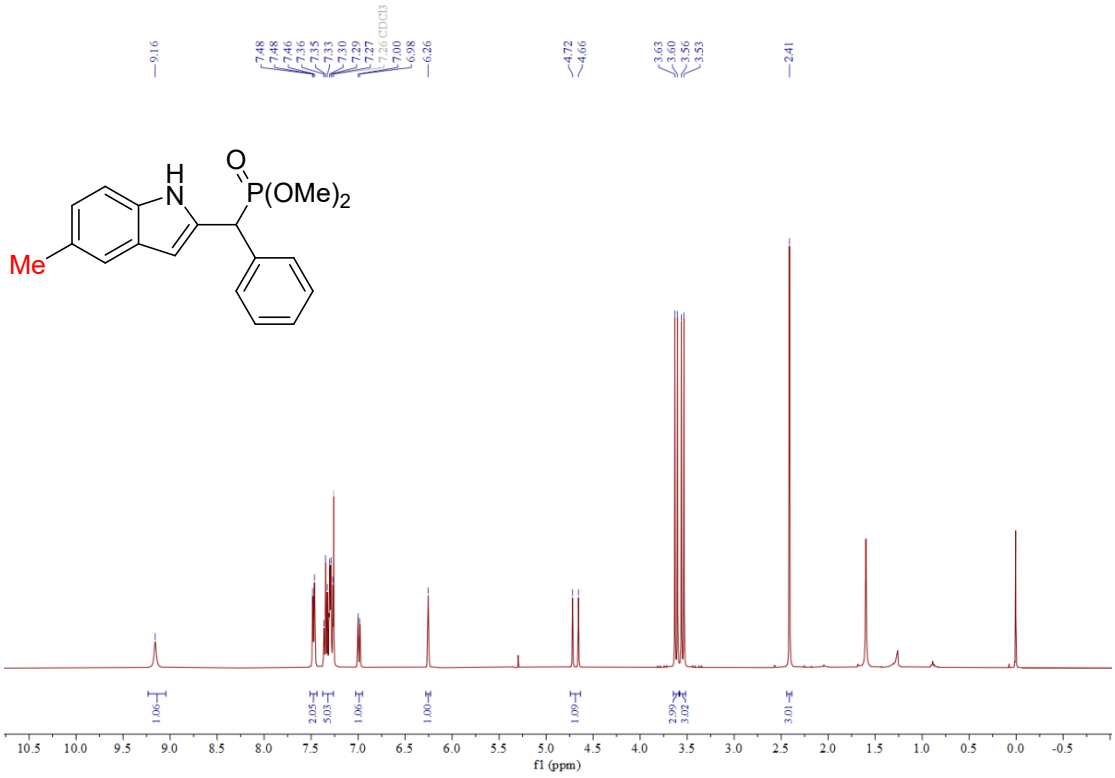
^{13}C NMR Spectra of **3ff** (100 MHz, $CDCl_3$)



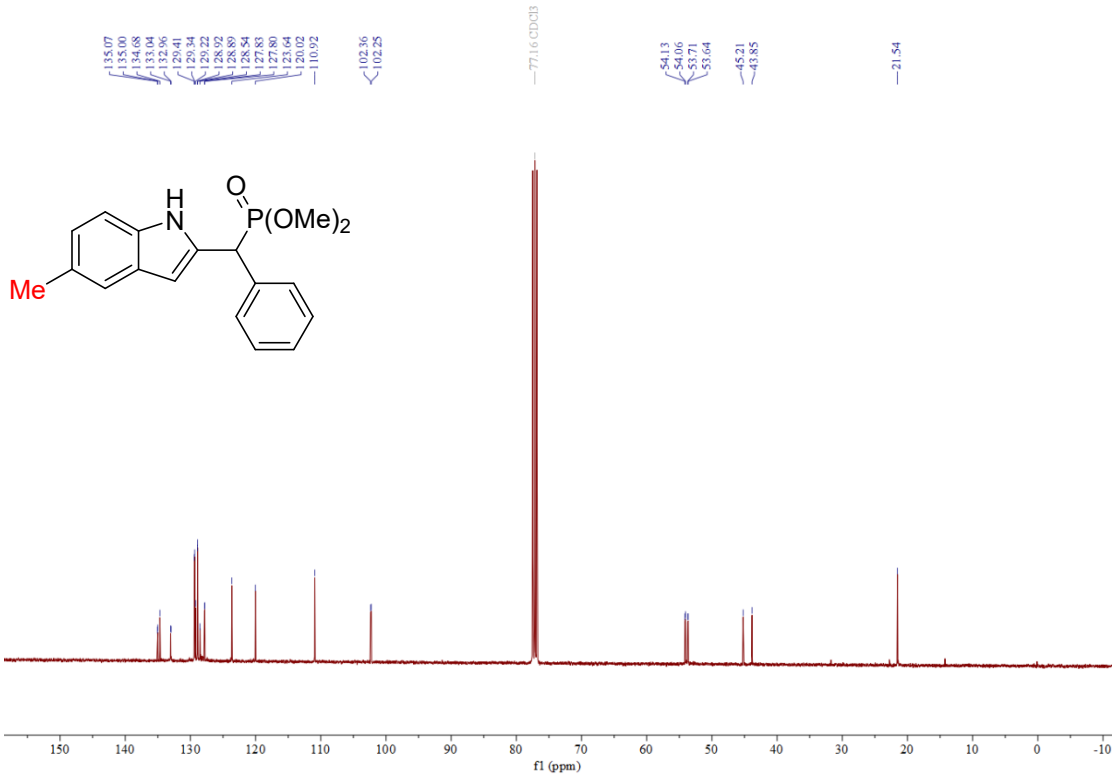
^{31}P NMR Spectra of **3ff** (162 MHz, $CDCl_3$)



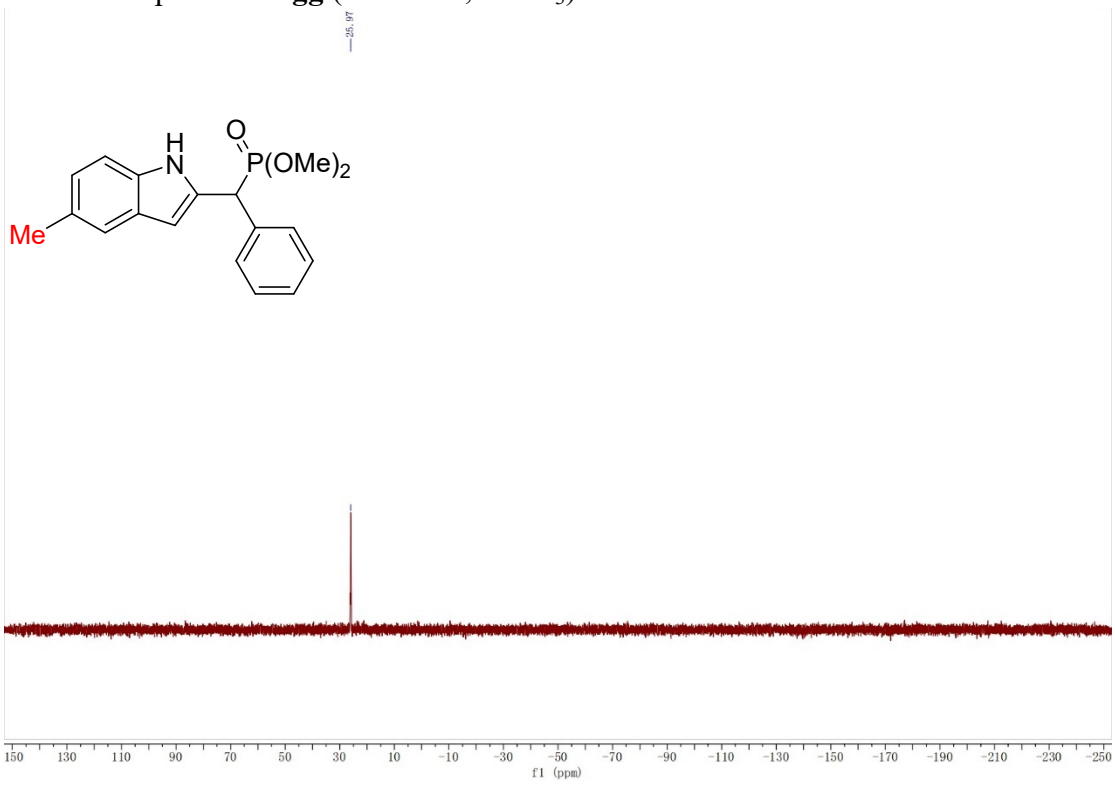
^{1}H NMR Spectra of **3gg** (400 MHz, $CDCl_3$)



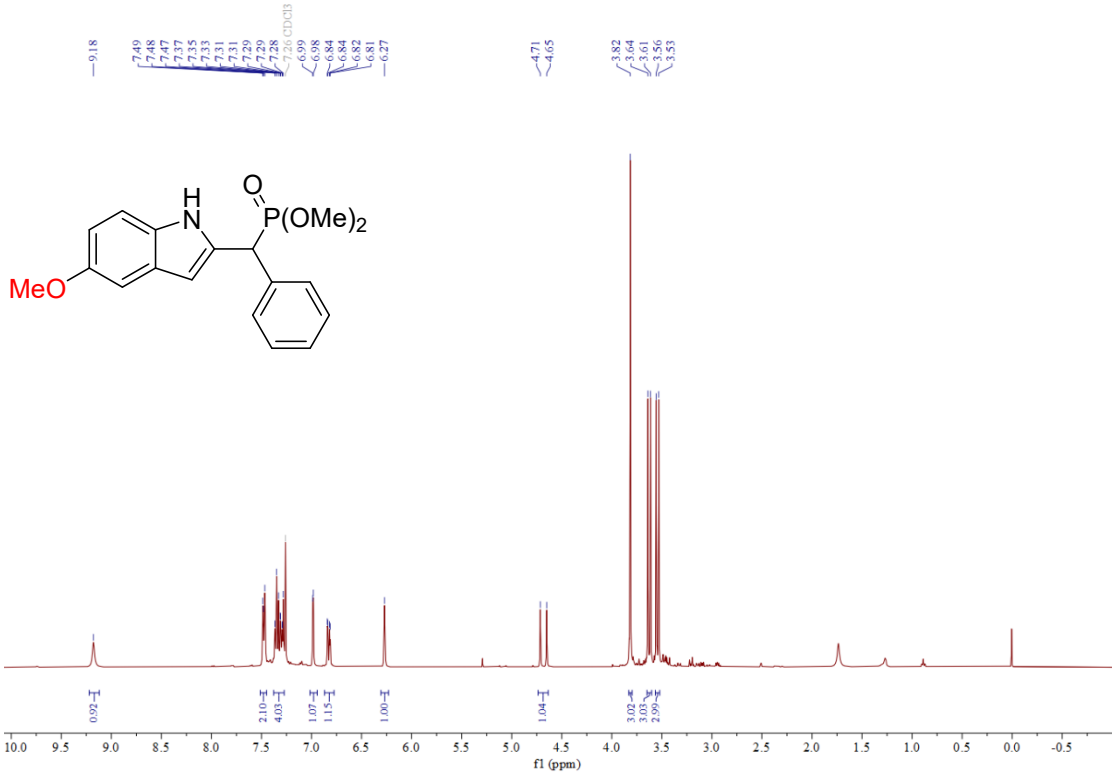
^{13}C NMR Spectra of **3gg** (100 MHz, $CDCl_3$)



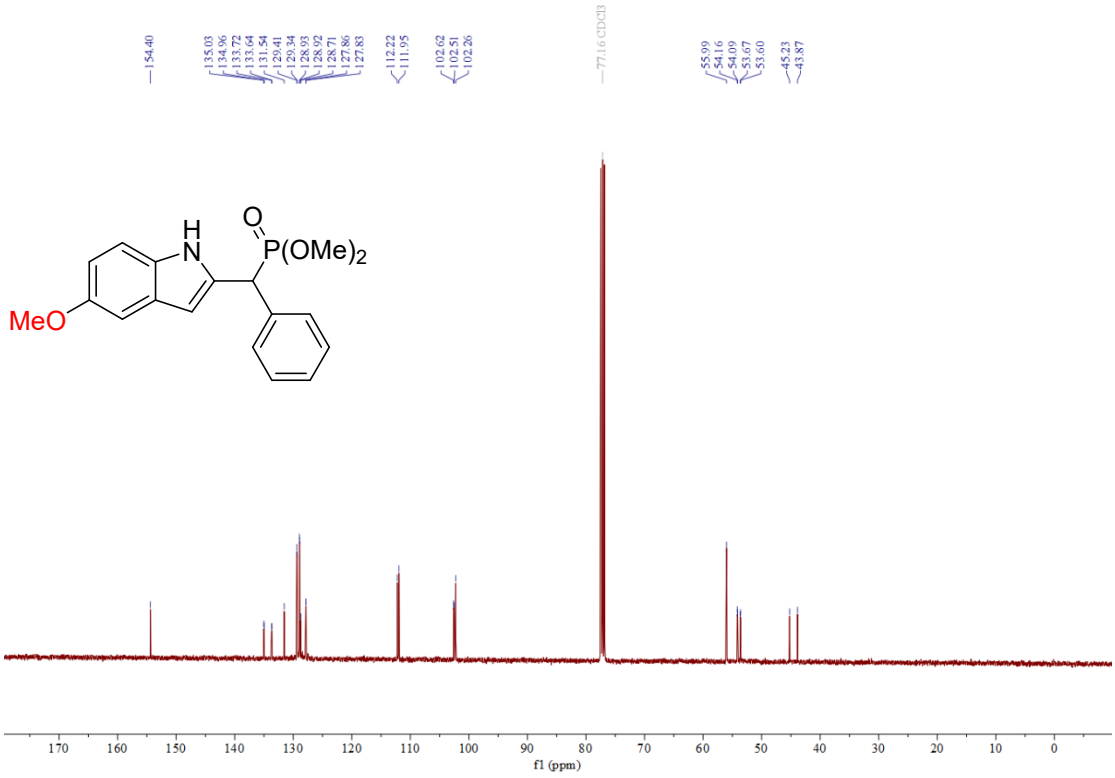
^{31}P NMR Spectra of **3gg** (162 MHz, $CDCl_3$)



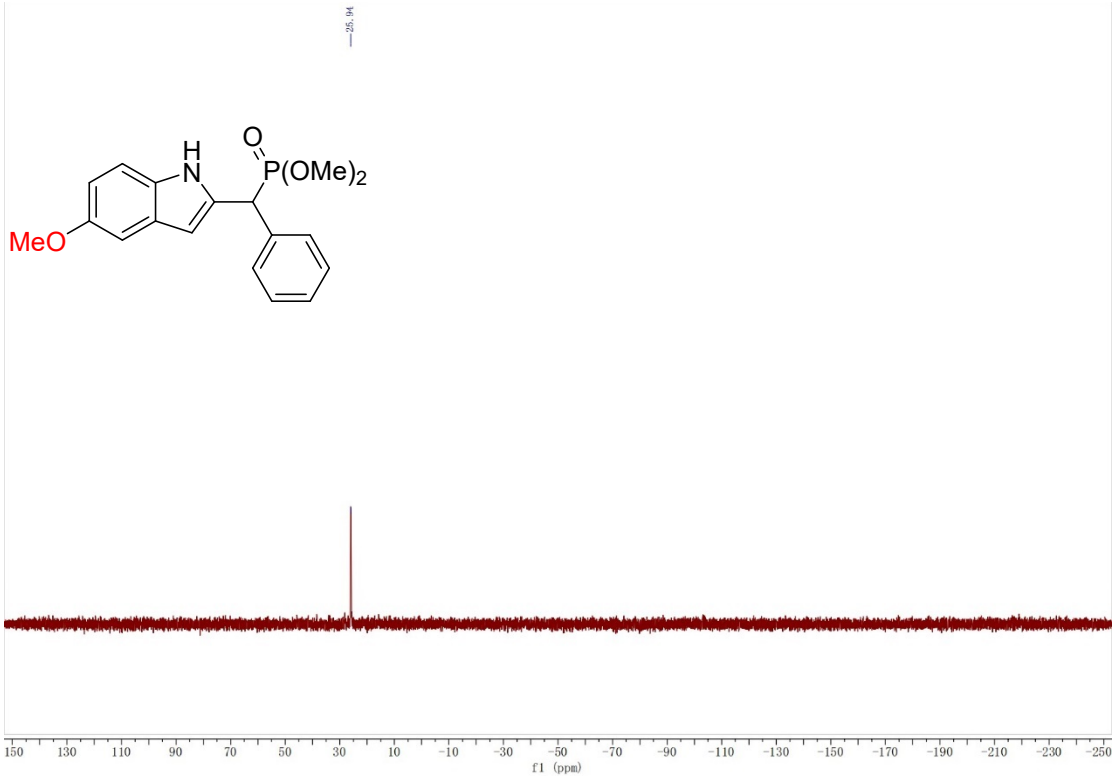
^{1}H NMR Spectra of **3hh** (400 MHz, $CDCl_3$)



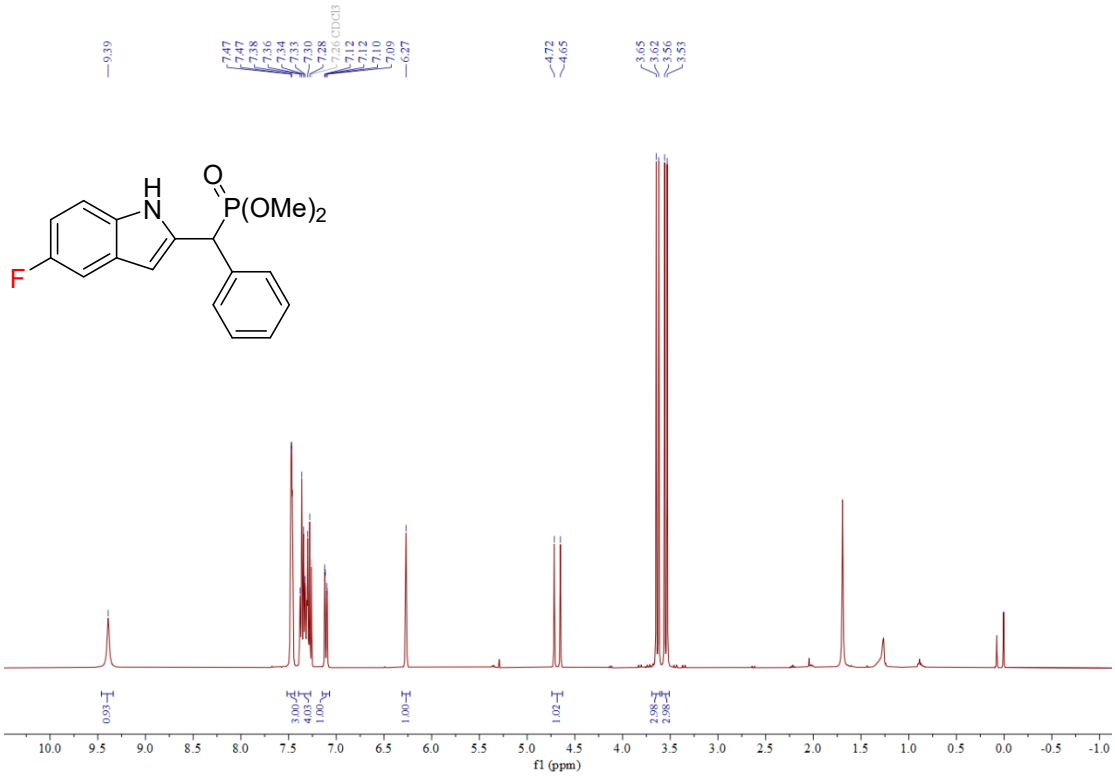
^{13}C NMR Spectra of **3hh** (100 MHz, $CDCl_3$)



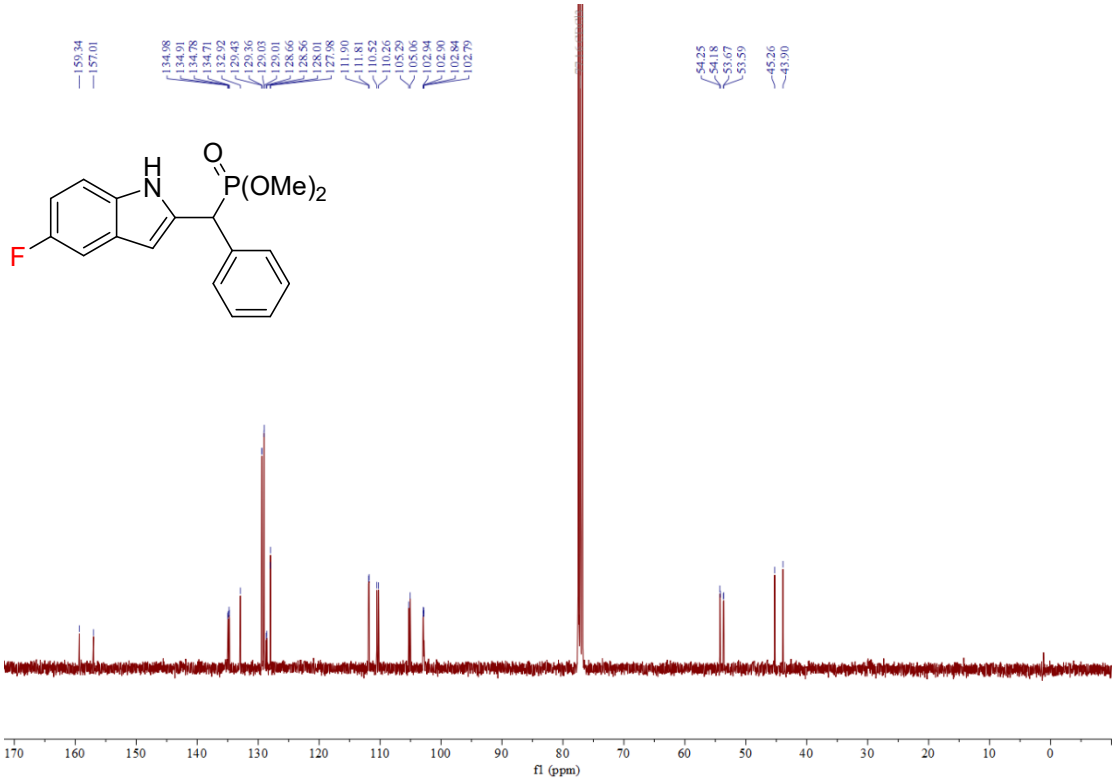
^{31}P NMR Spectra of **3hh** (162 MHz, $CDCl_3$)



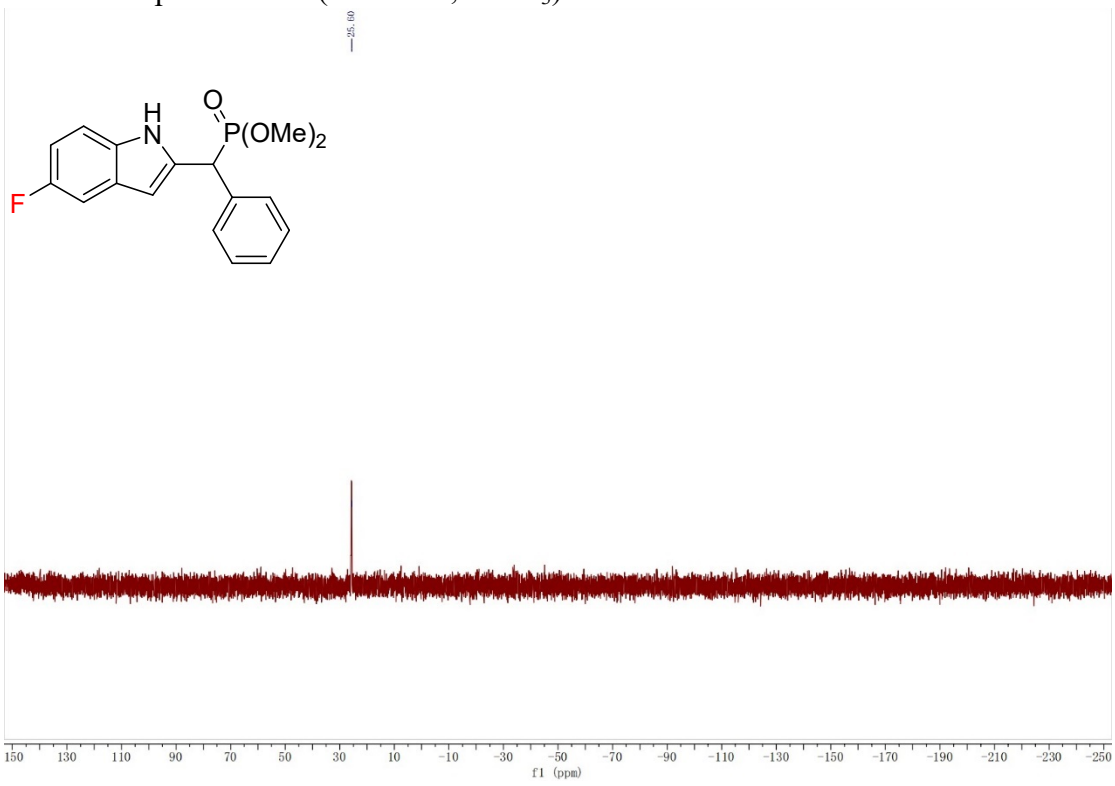
^{1}H NMR Spectra of **3ii** (400 MHz, $CDCl_3$)



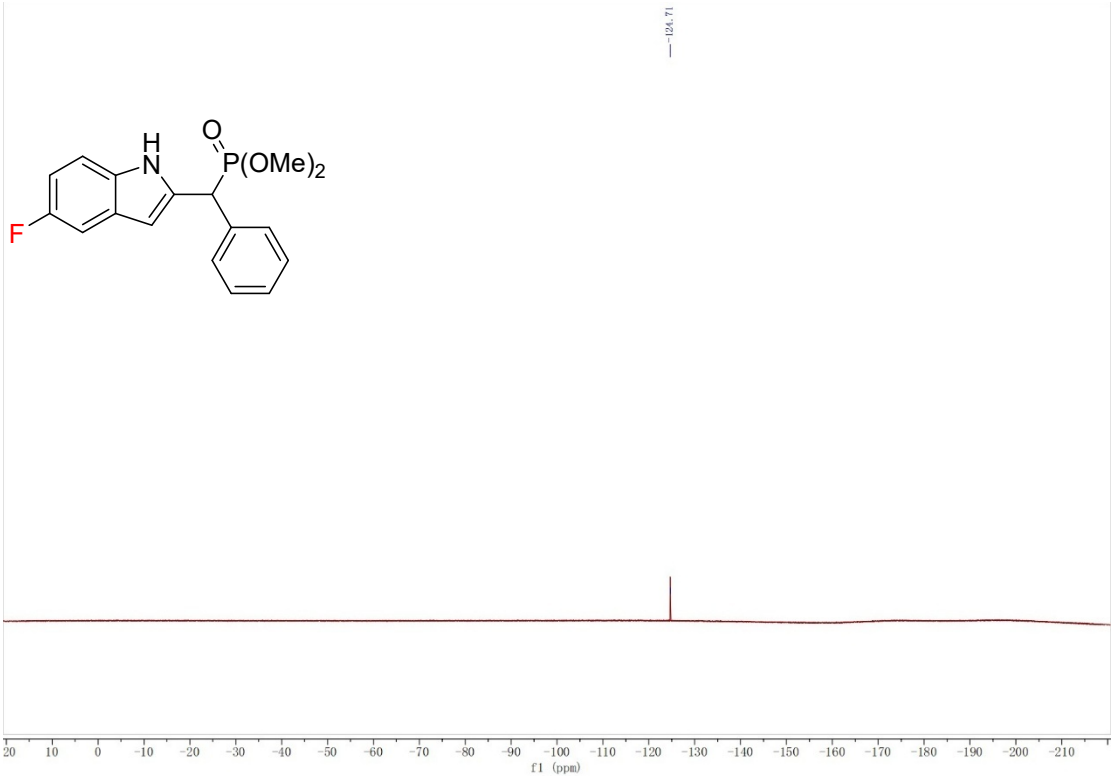
^{13}C NMR Spectra of **3ii** (100 MHz, $CDCl_3$)



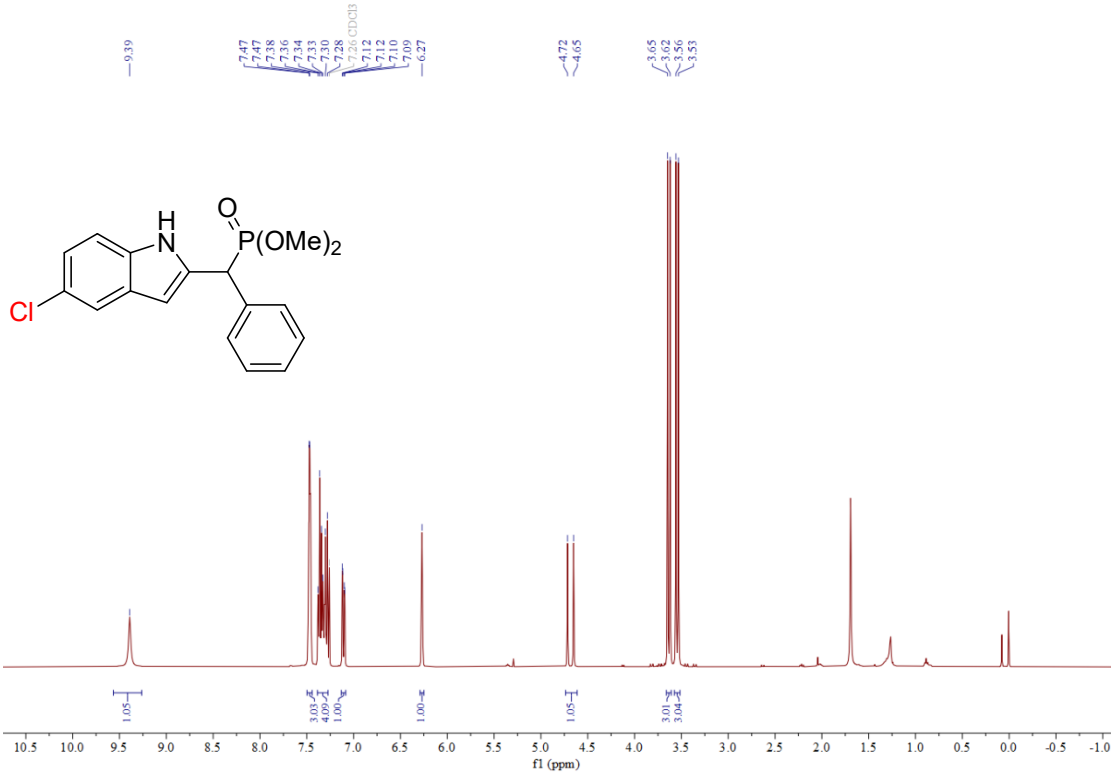
^{31}P NMR Spectra of **3ii** (162 MHz, $CDCl_3$)



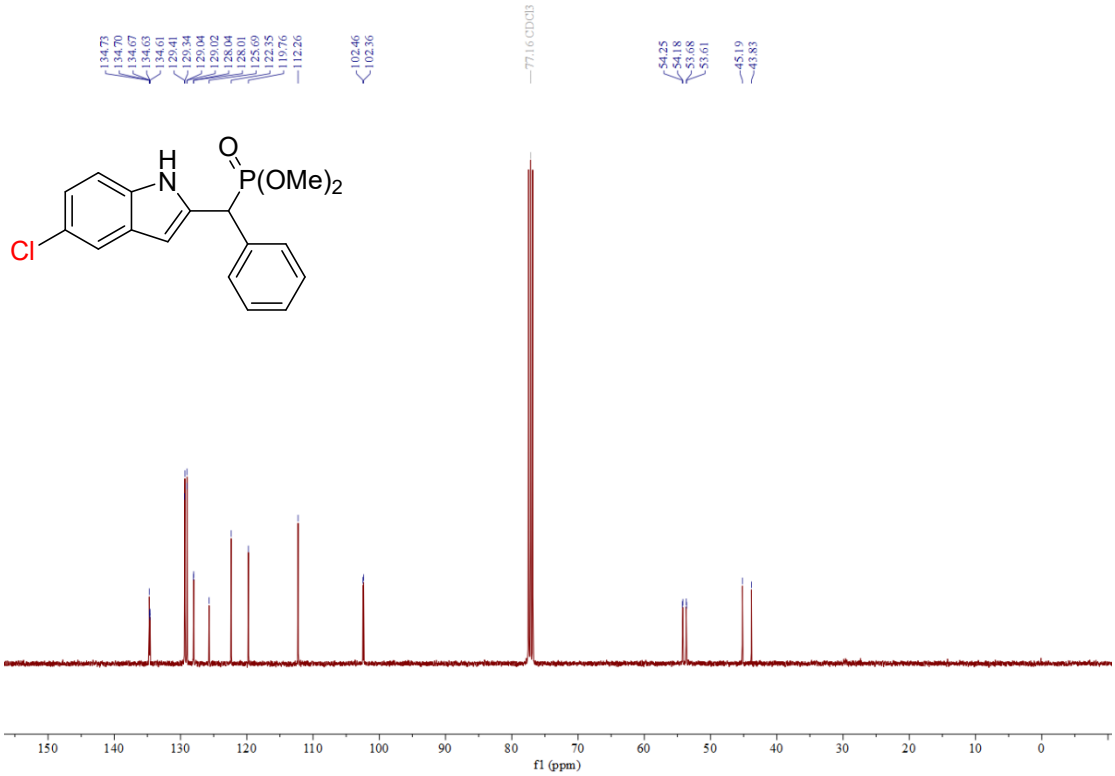
^{19}F NMR Spectra of **3ii** (376 MHz, $CDCl_3$)



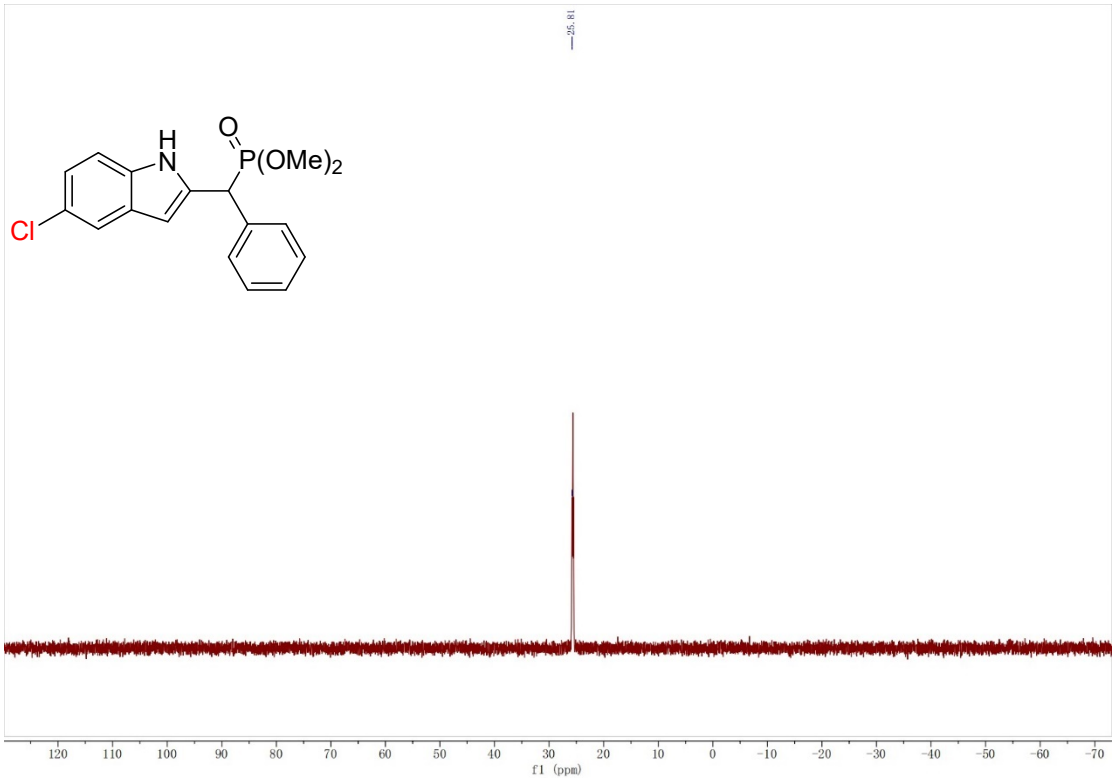
^{1}H NMR Spectra of **3jj** (400 MHz, $CDCl_3$)



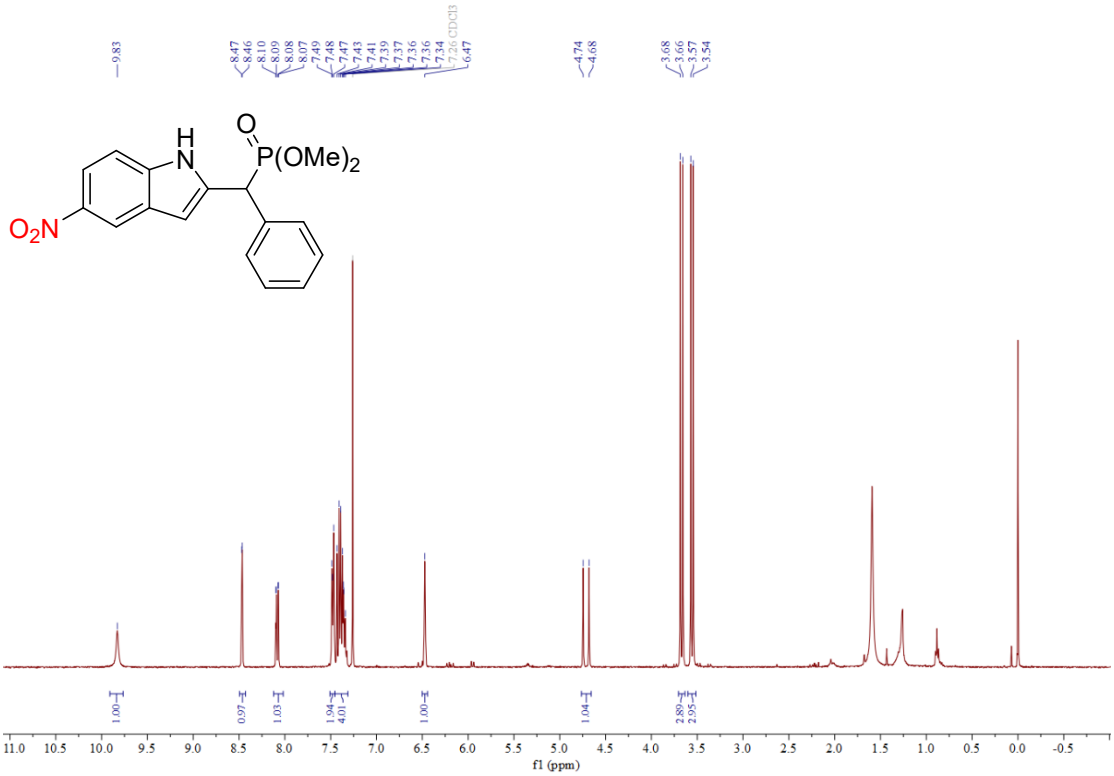
^{13}C NMR Spectra of **3jj** (100 MHz, $CDCl_3$)



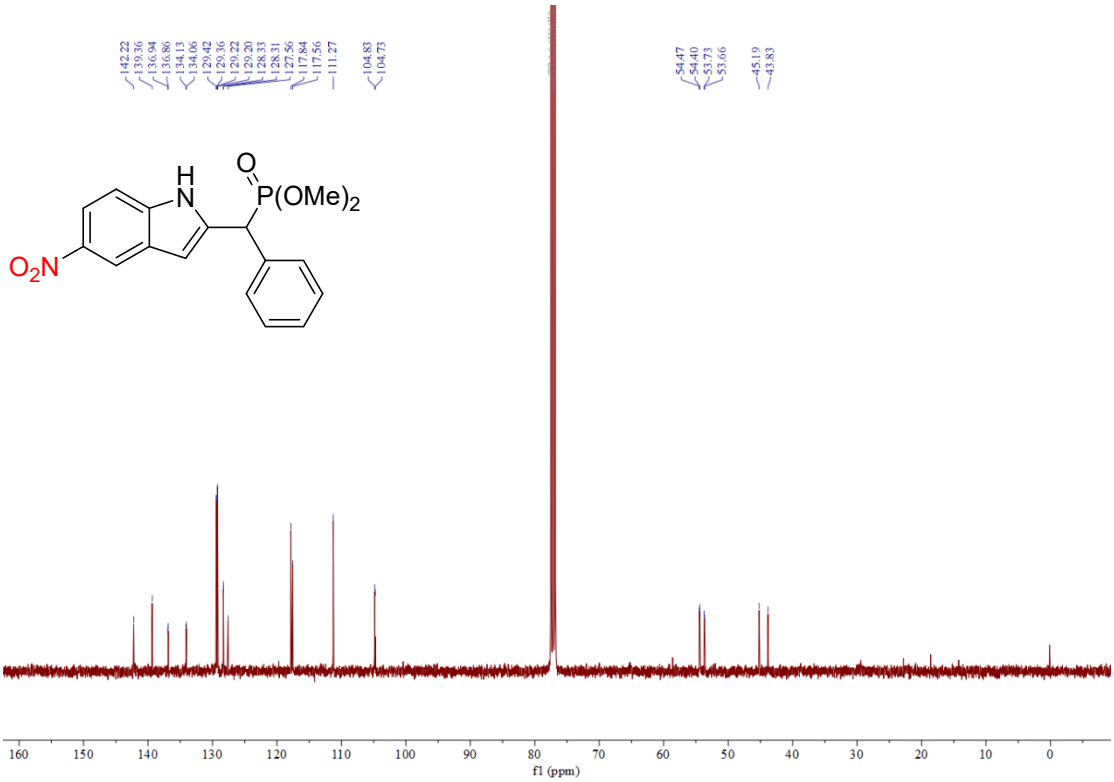
^{31}P NMR Spectra of **3jj** (162 MHz, $CDCl_3$)



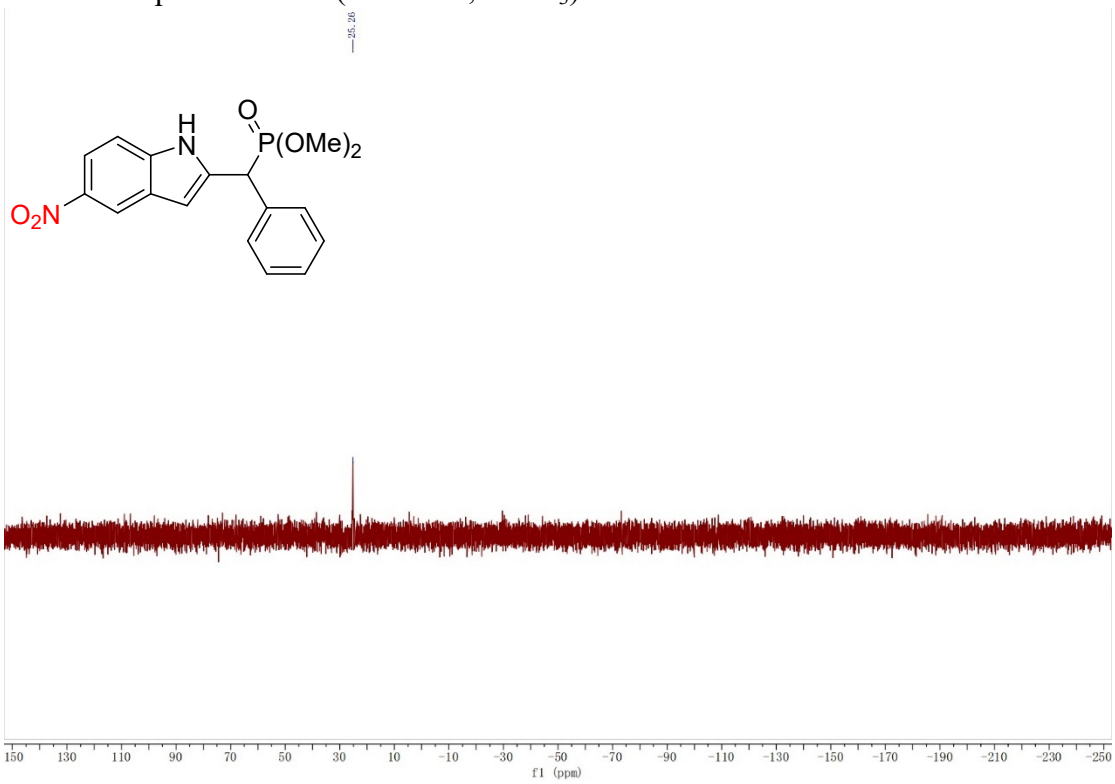
^{1}H NMR Spectra of **3kk** (400 MHz, $CDCl_3$)



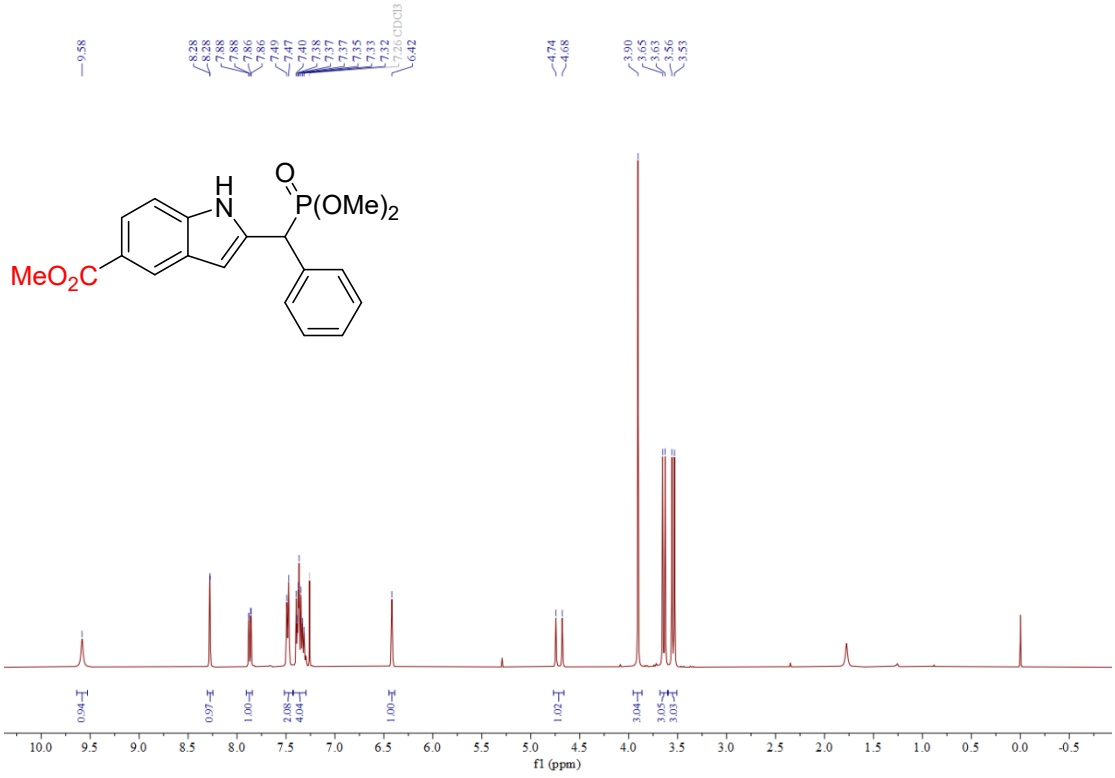
^{13}C NMR Spectra of **3kk** (100 MHz, $CDCl_3$)



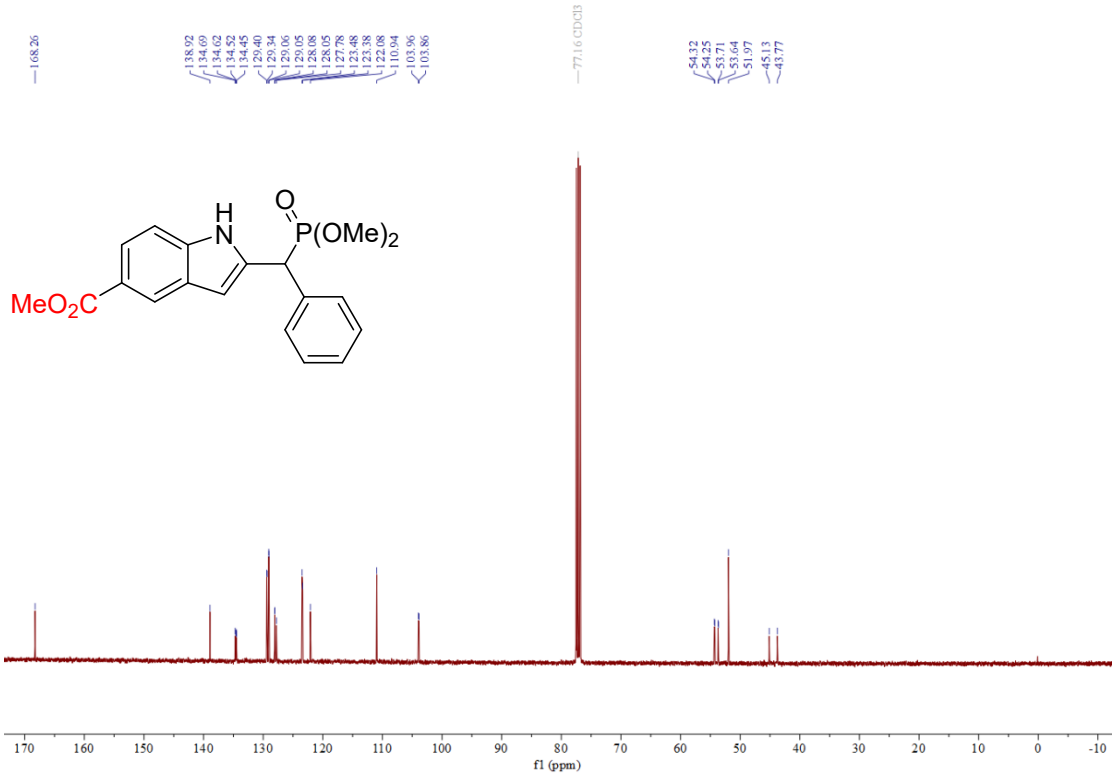
^{31}P NMR Spectra of **3kk** (162 MHz, $CDCl_3$)



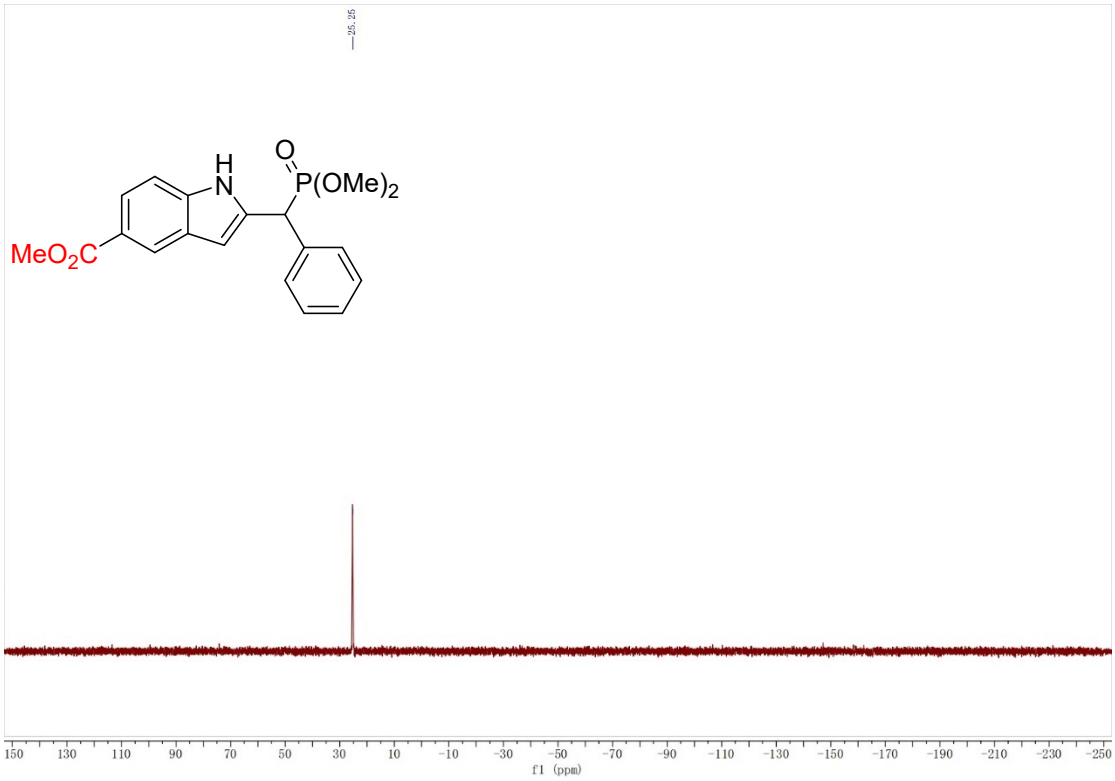
^{1}H NMR Spectra of **3ll** (400 MHz, $CDCl_3$)



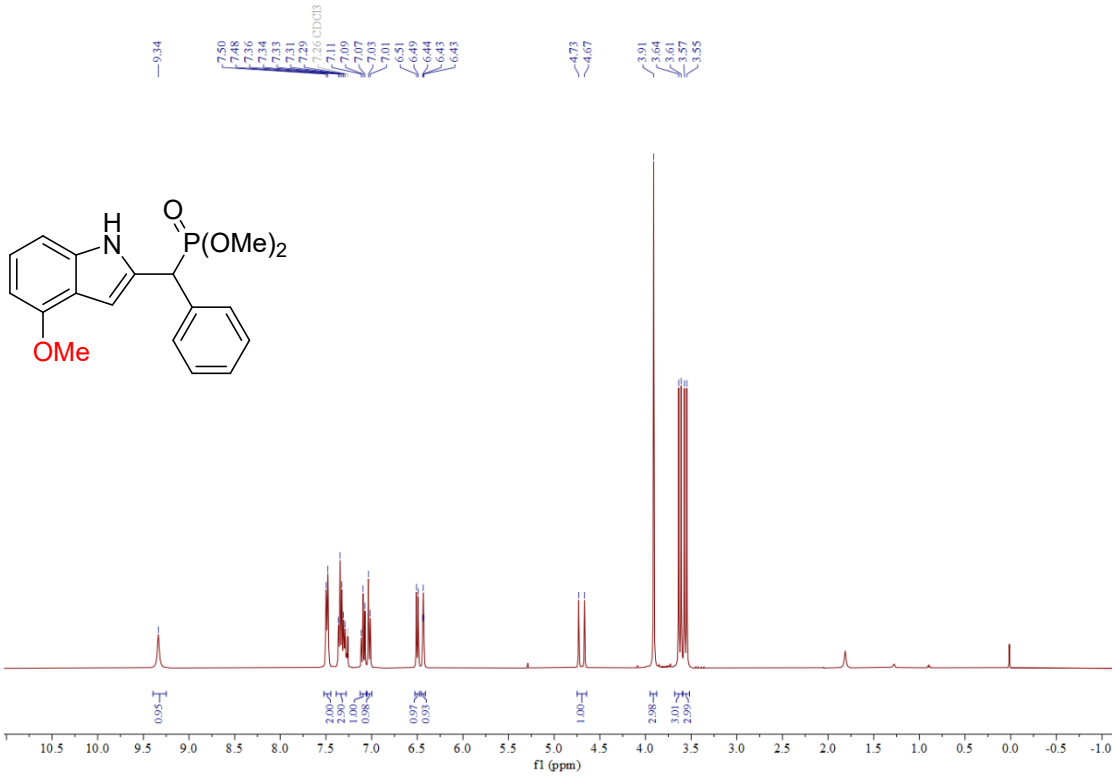
^{13}C NMR Spectra of **3ll** (100 MHz, $CDCl_3$)



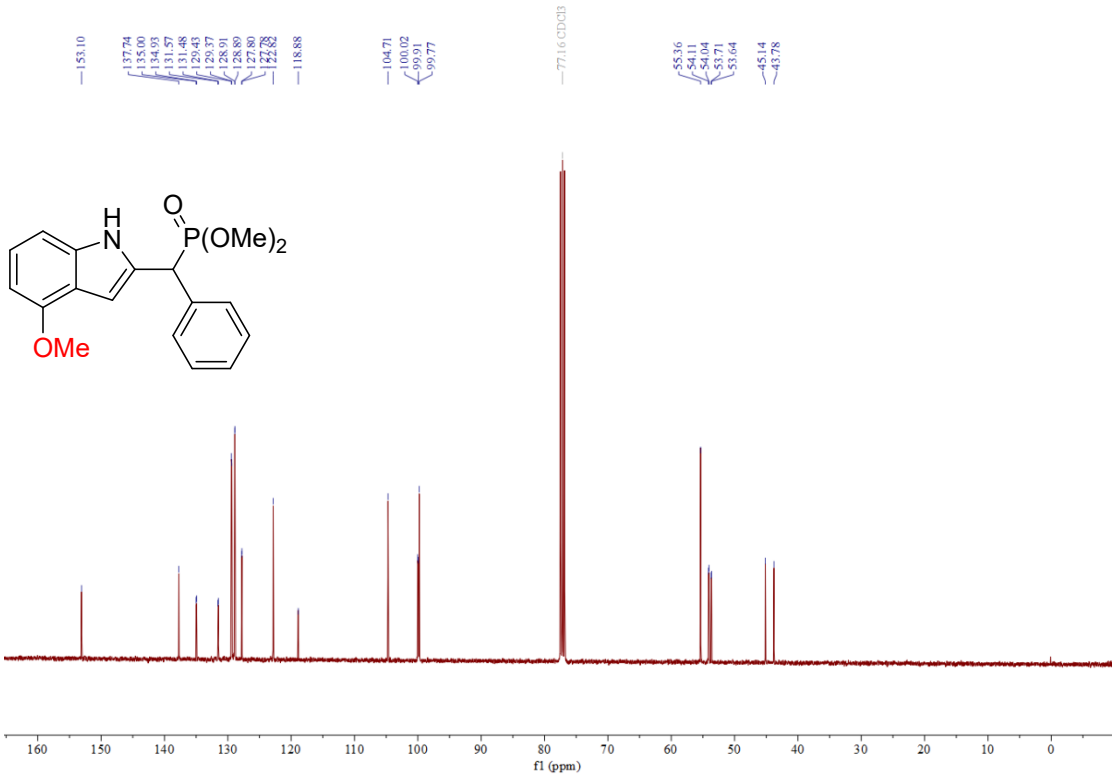
^{31}P NMR Spectra of **3ll** (162 MHz, $CDCl_3$)



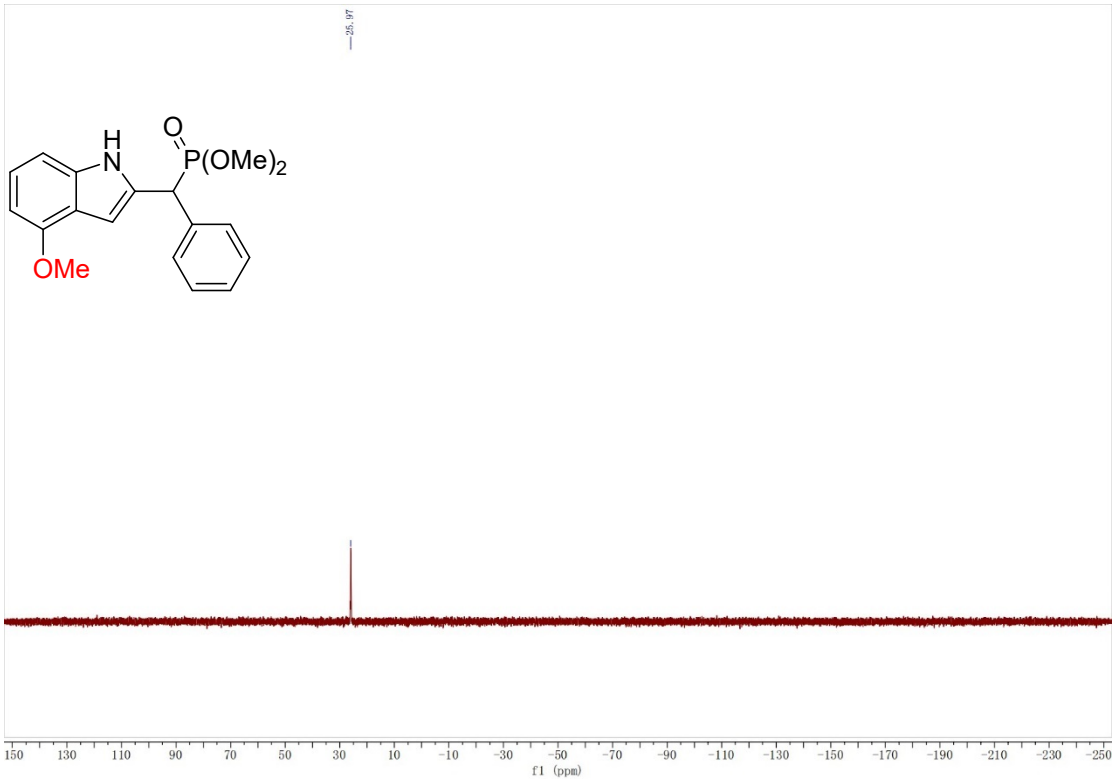
^{1}H NMR Spectra of **3mm** (400 MHz, $CDCl_3$)



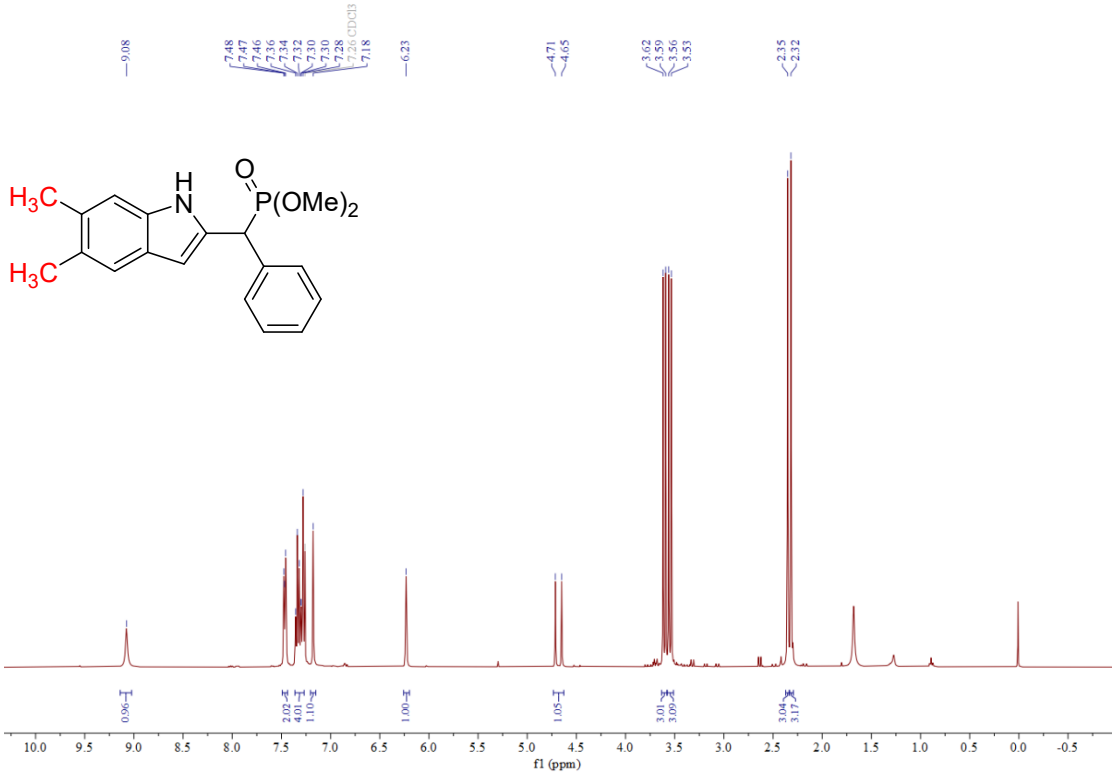
^{13}C NMR Spectra of **3mm** (100 MHz, $CDCl_3$)



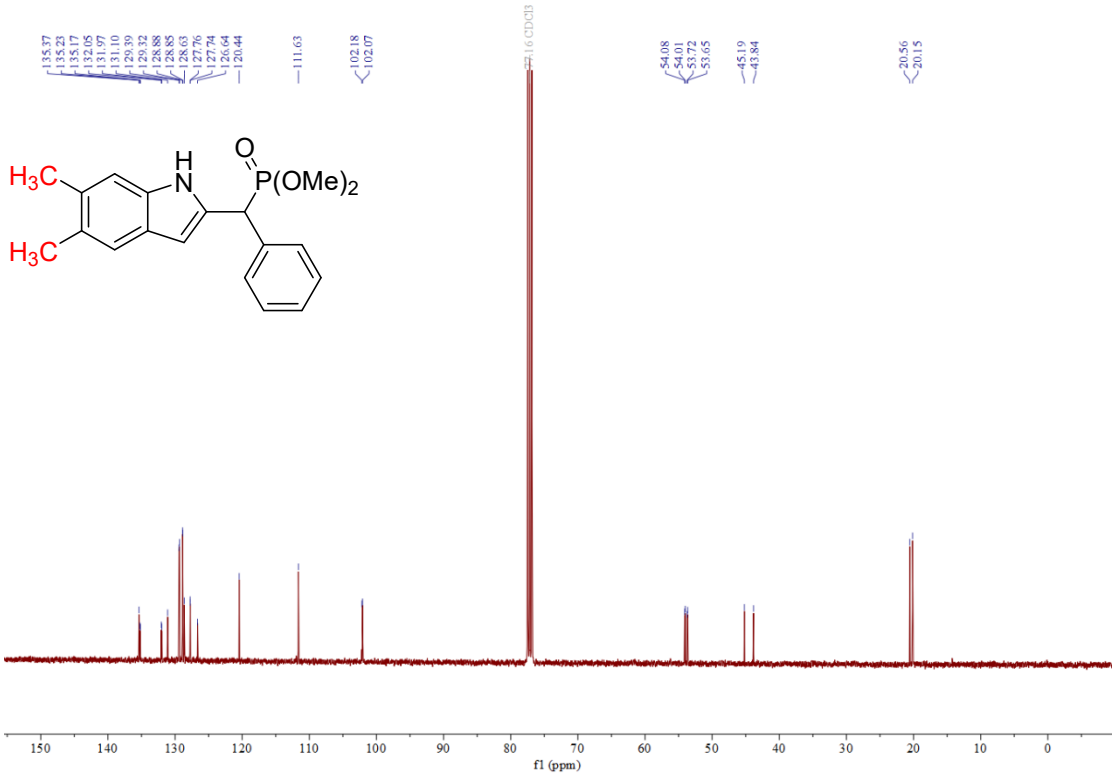
^{31}P NMR Spectra of **3mm** (162 MHz, $CDCl_3$)



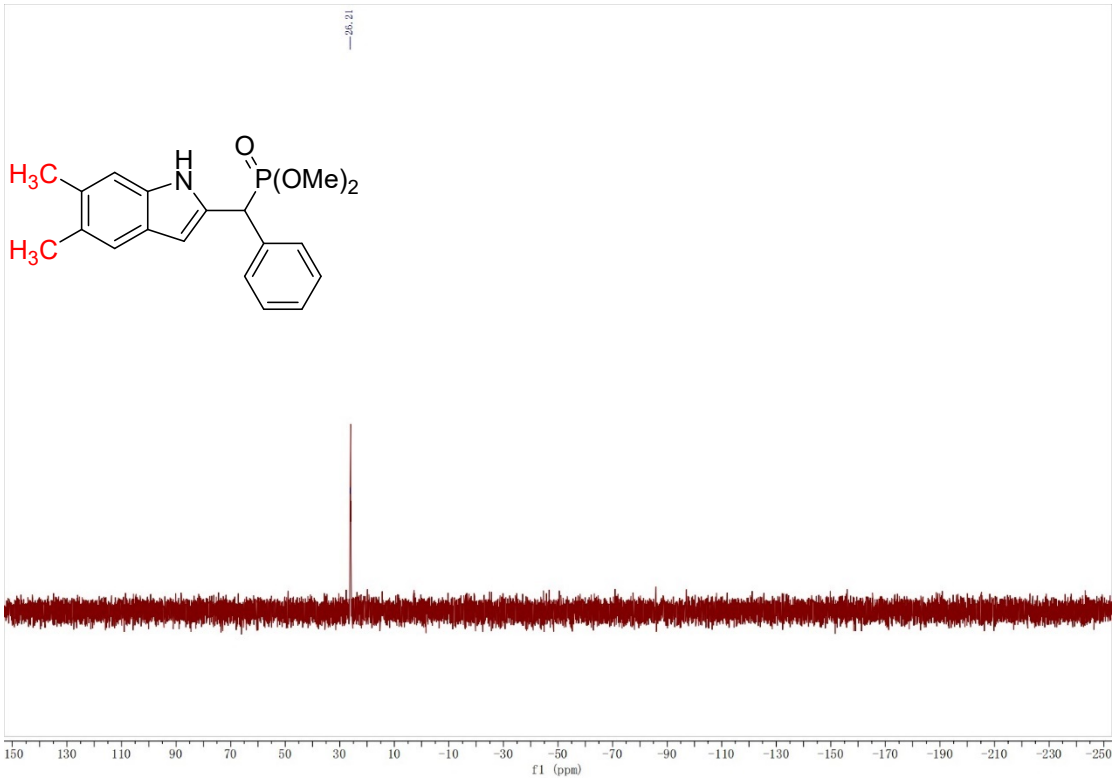
^{1}H NMR Spectra of **3nn** (400 MHz, $CDCl_3$)



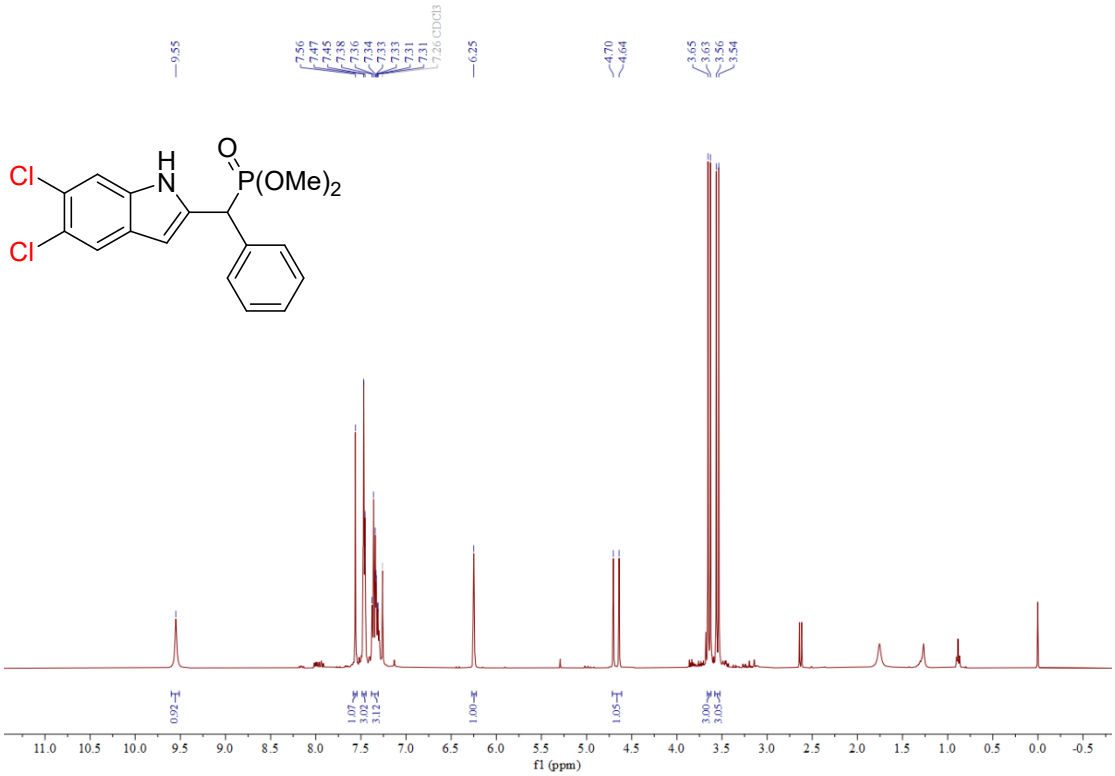
^{13}C NMR Spectra of **3nn** (100 MHz, $CDCl_3$)



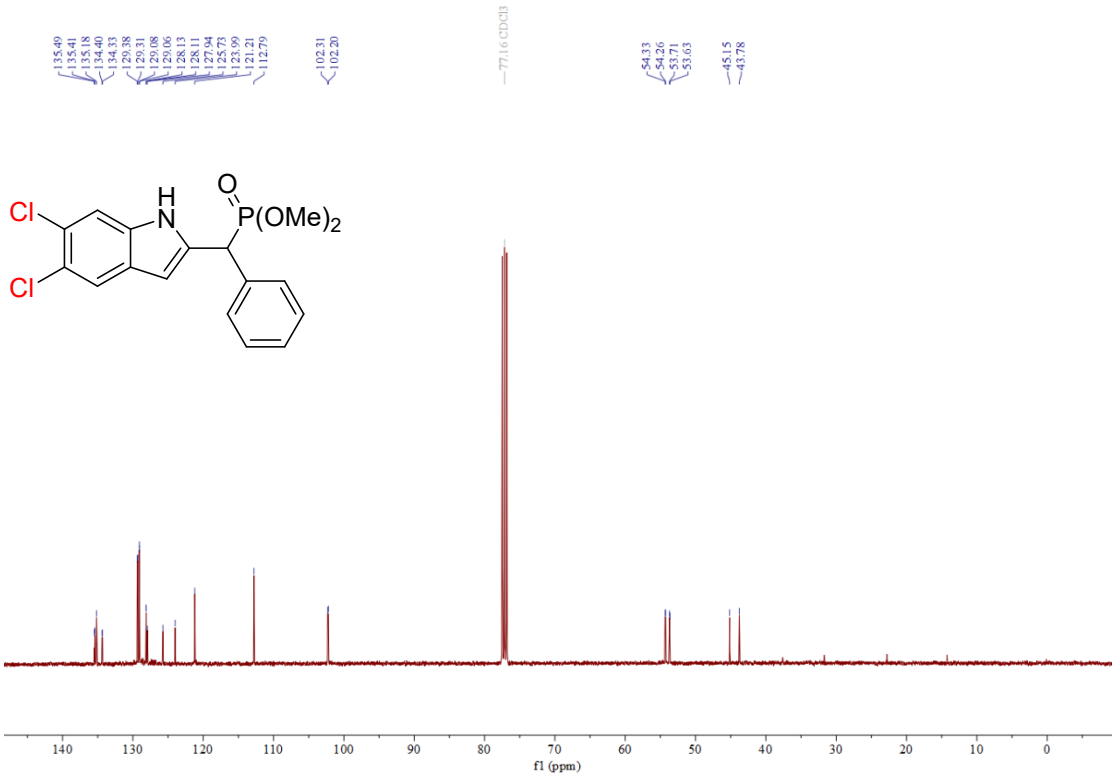
^{31}P NMR Spectra of **3nn** (162 MHz, $CDCl_3$)



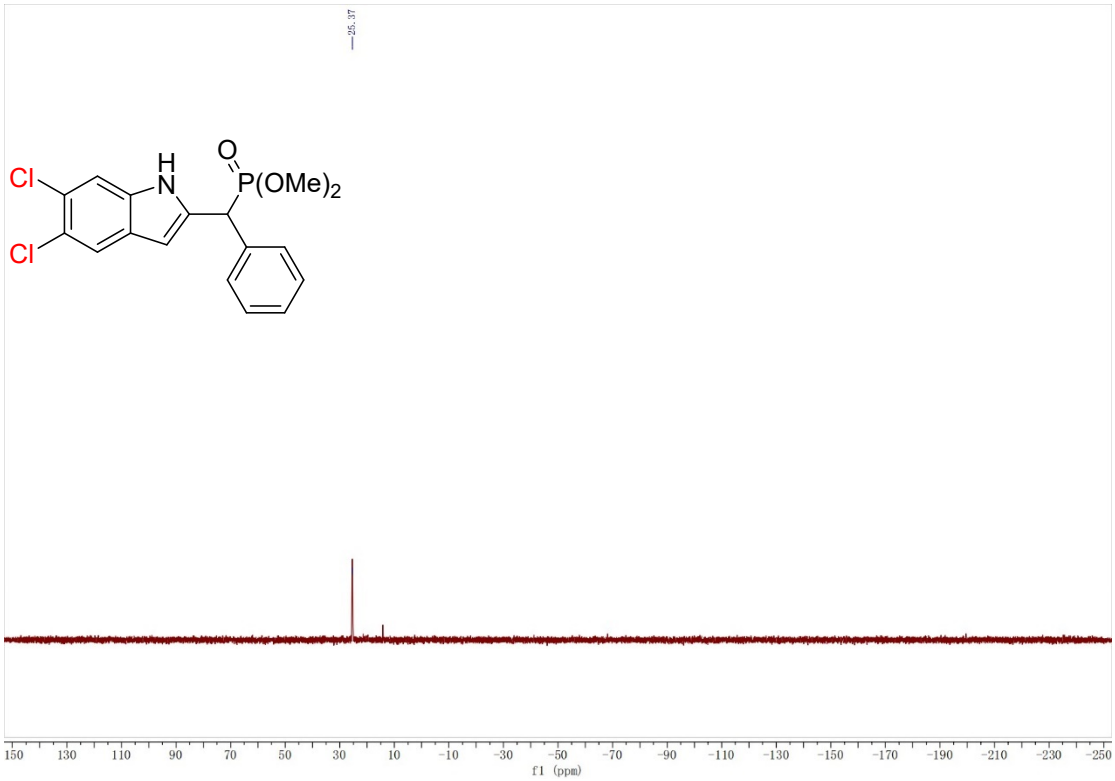
^{1}H NMR Spectra of **3oo** (400 MHz, $CDCl_3$)



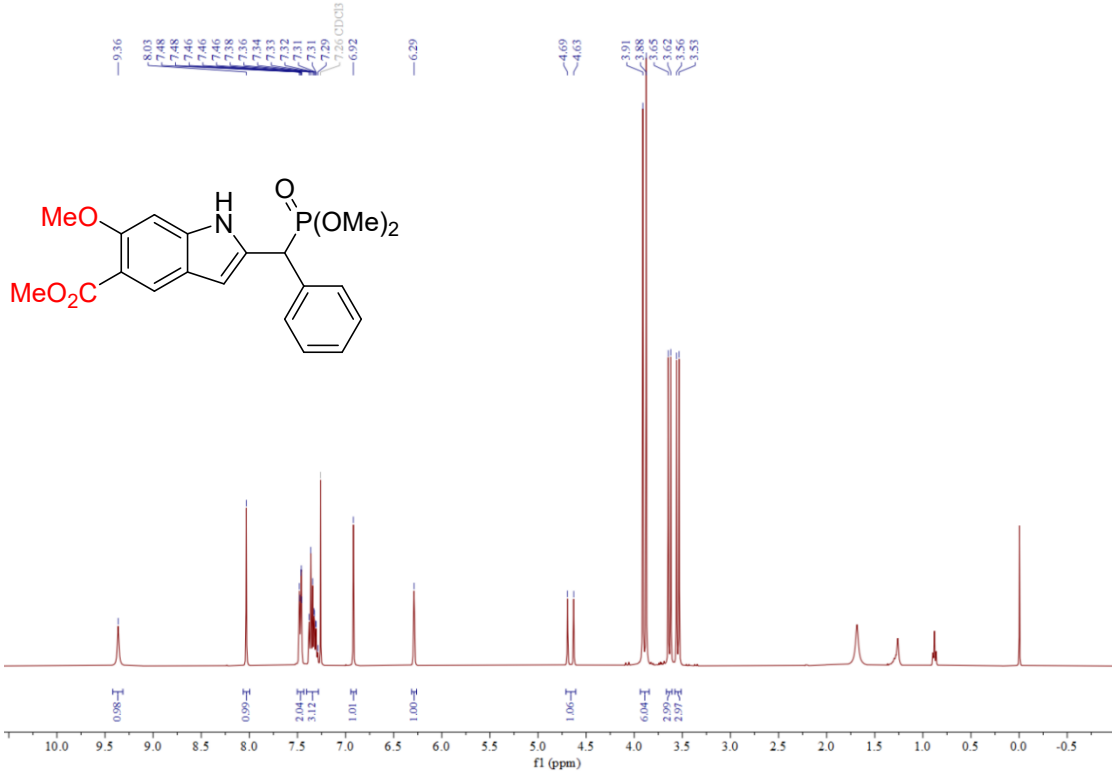
^{13}C NMR Spectra of **3oo** (100 MHz, $CDCl_3$)



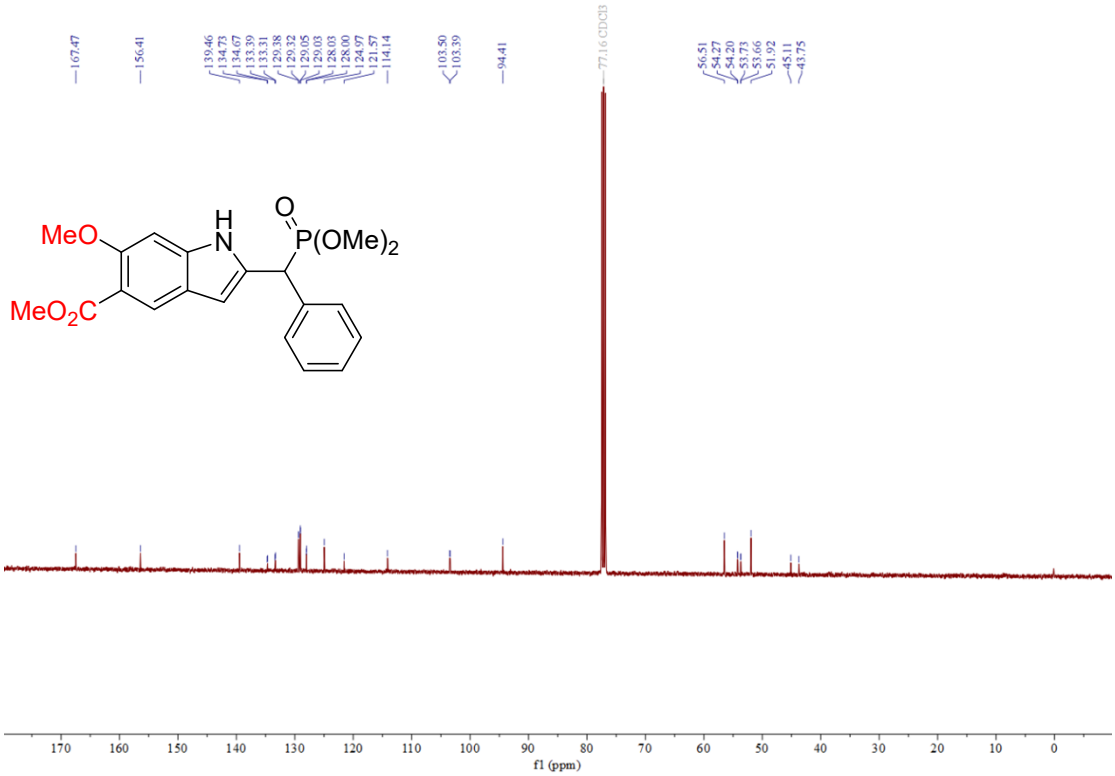
^{31}P NMR Spectra of **3oo** (162 MHz, $CDCl_3$)



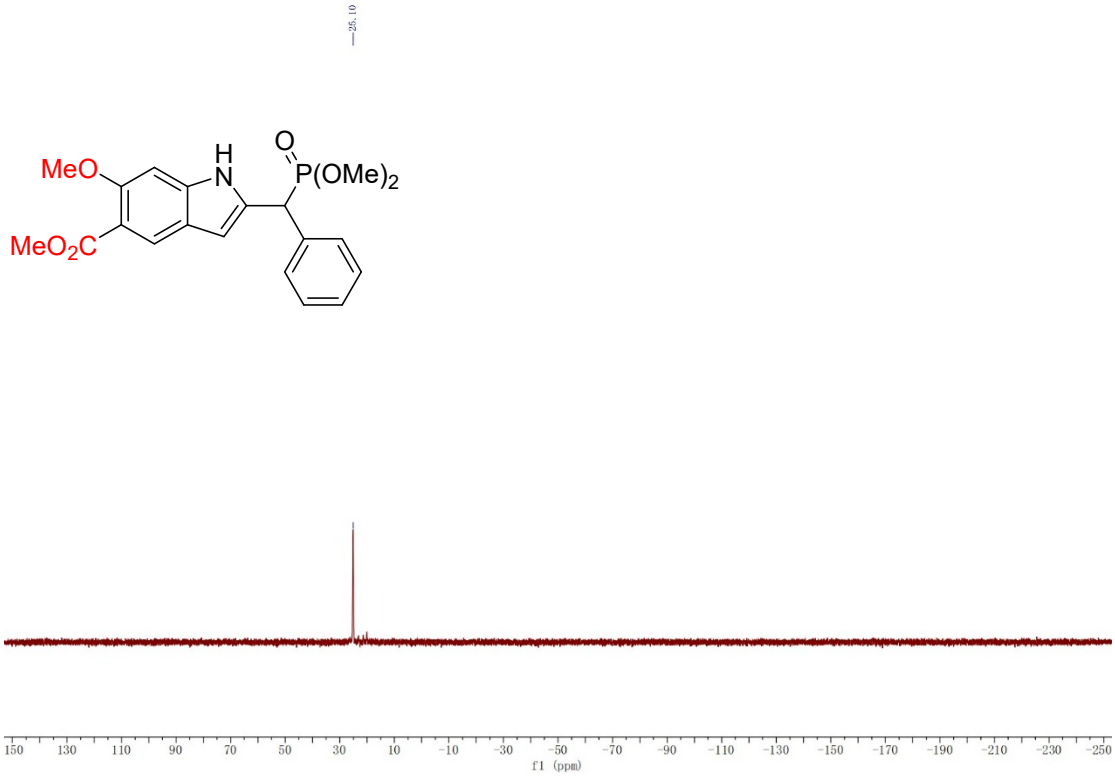
^{1}H NMR Spectra of **3pp** (400 MHz, $CDCl_3$)



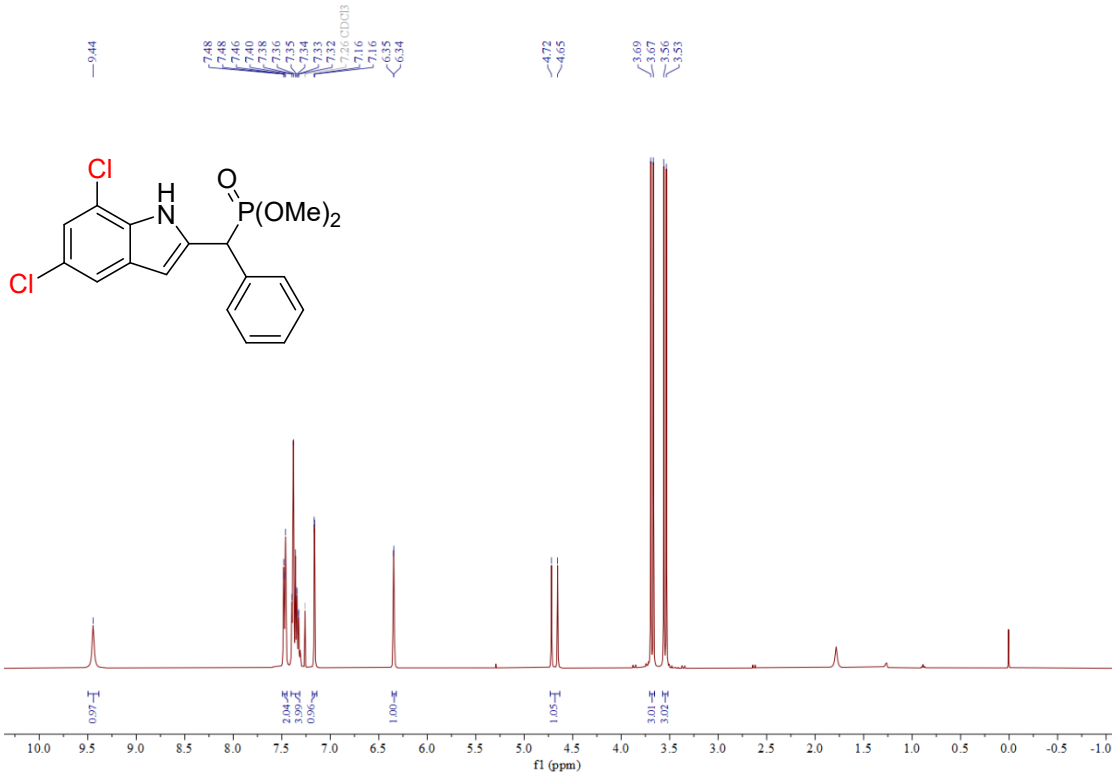
^{13}C NMR Spectra of **3pp** (100 MHz, $CDCl_3$)



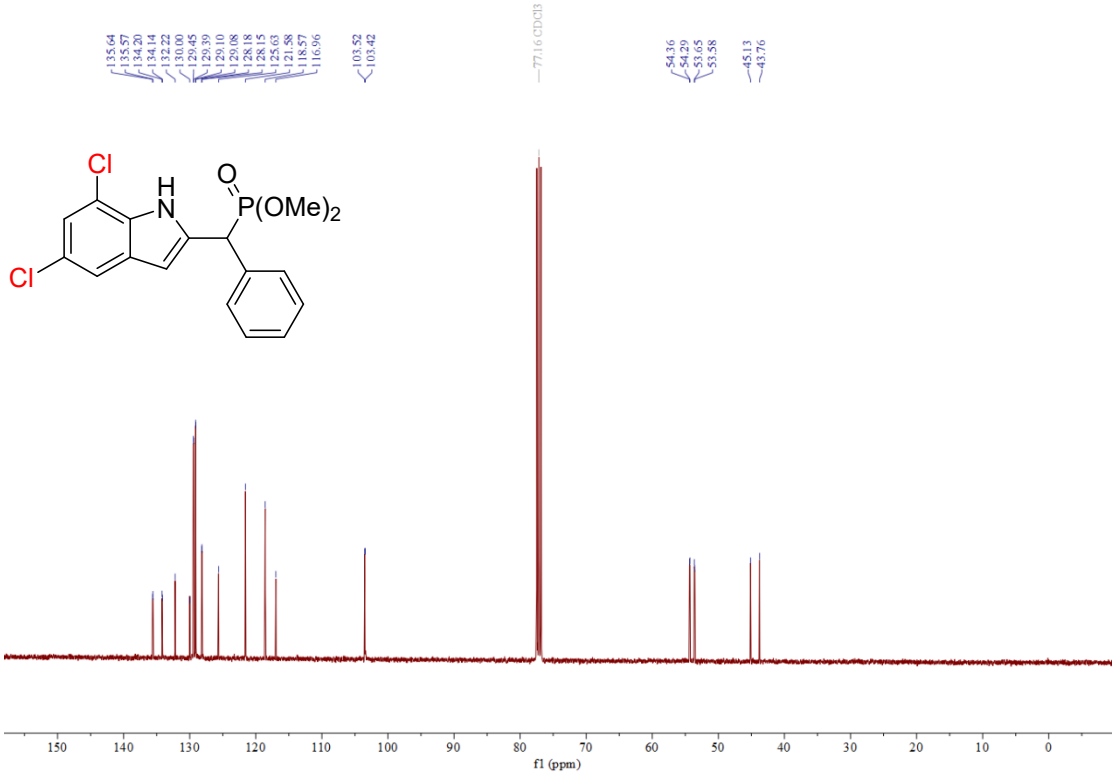
^{31}P NMR Spectra of **3pp** (162 MHz, $CDCl_3$)



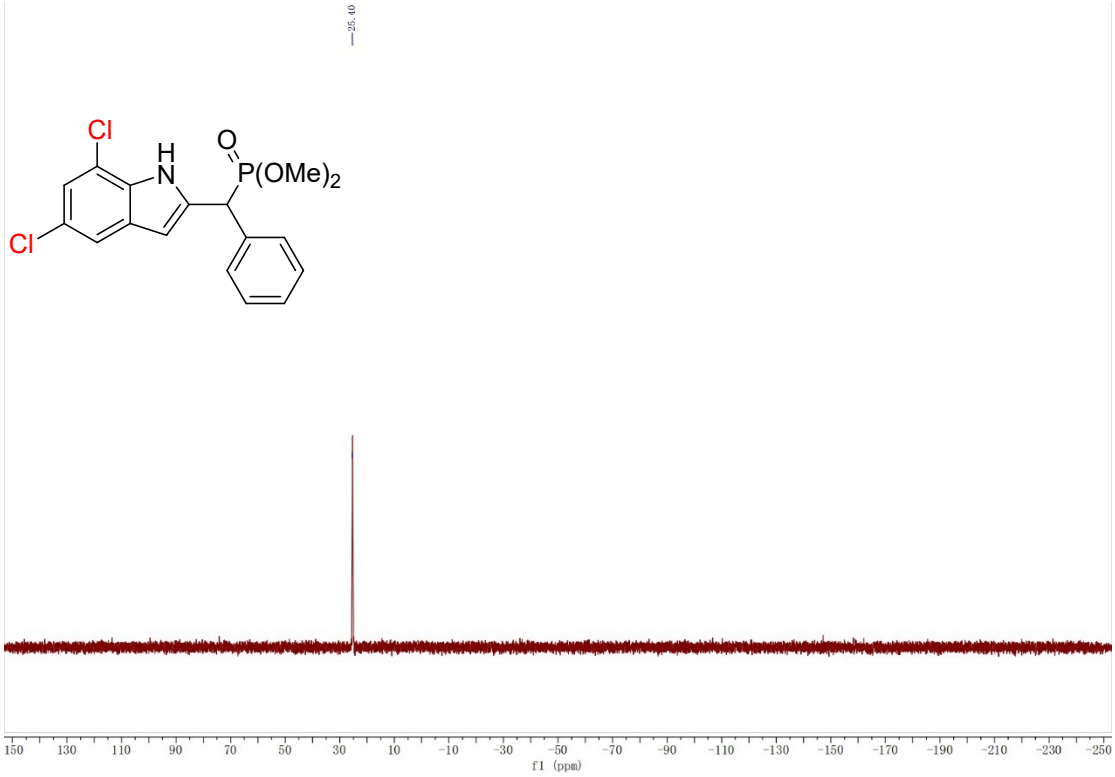
^{1}H NMR Spectra of **3qq** (400 MHz, $CDCl_3$)



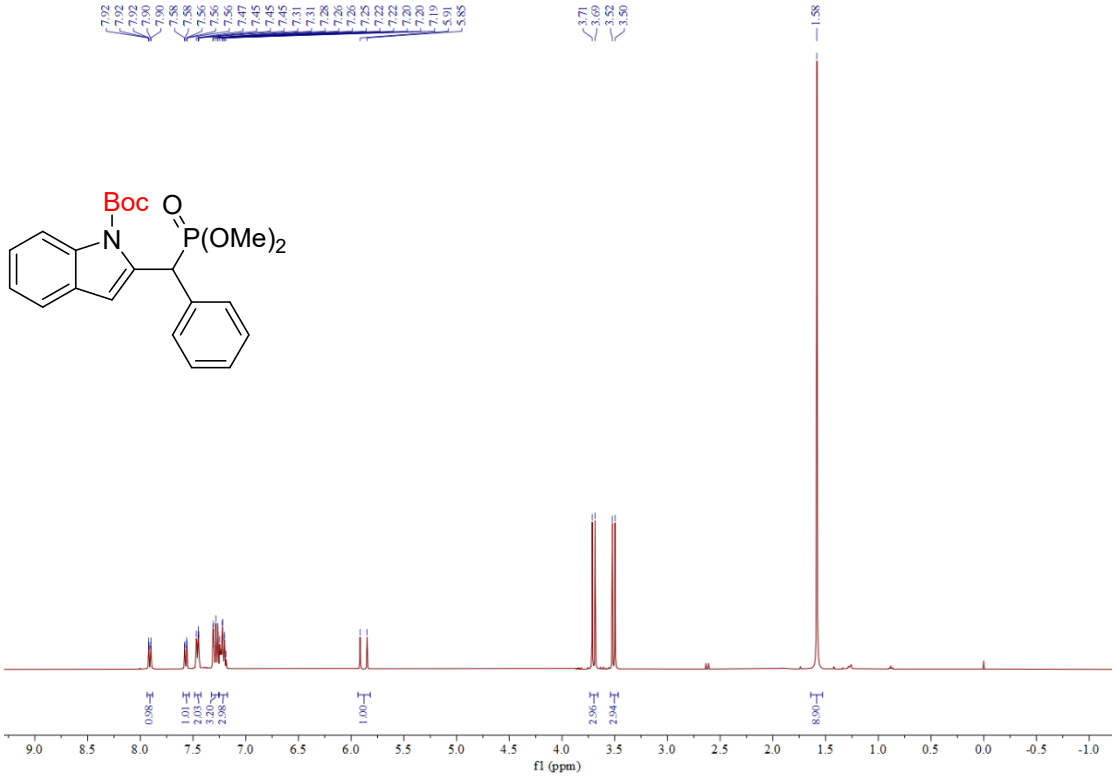
^{13}C NMR Spectra of **3qq** (100 MHz, $CDCl_3$)



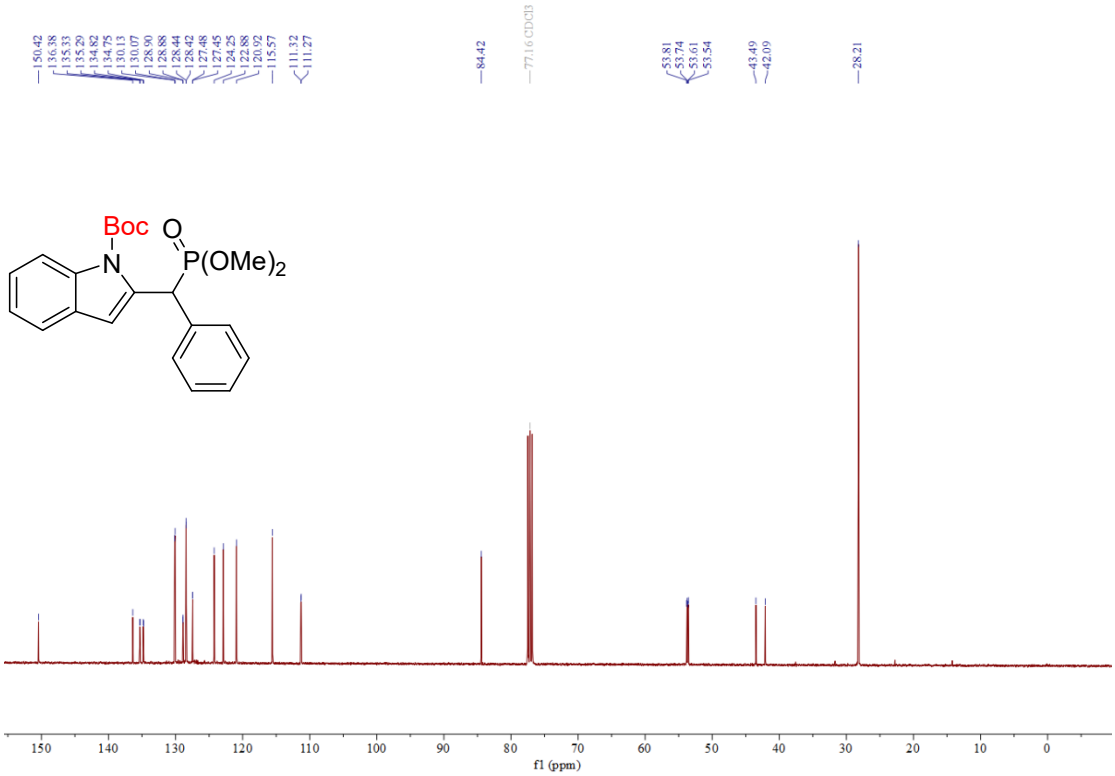
^{31}P NMR Spectra of **3qq** (162 MHz, $CDCl_3$)



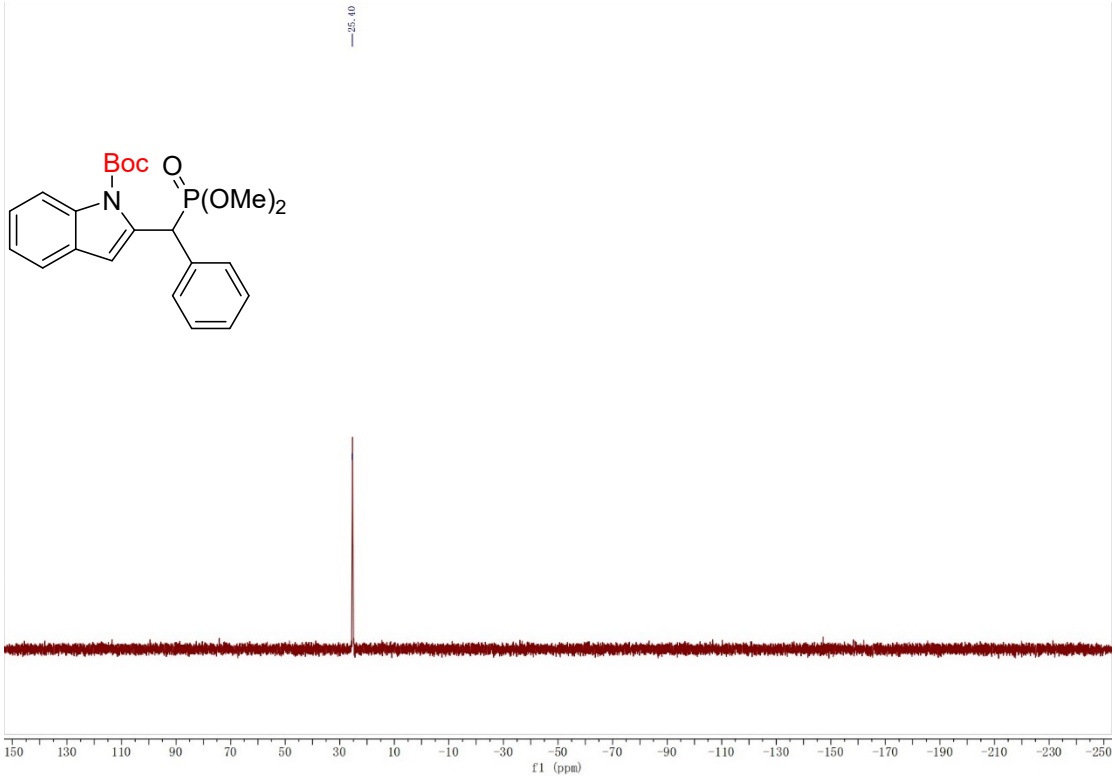
^{1}H NMR Spectra of **3rr** (400 MHz, $CDCl_3$)



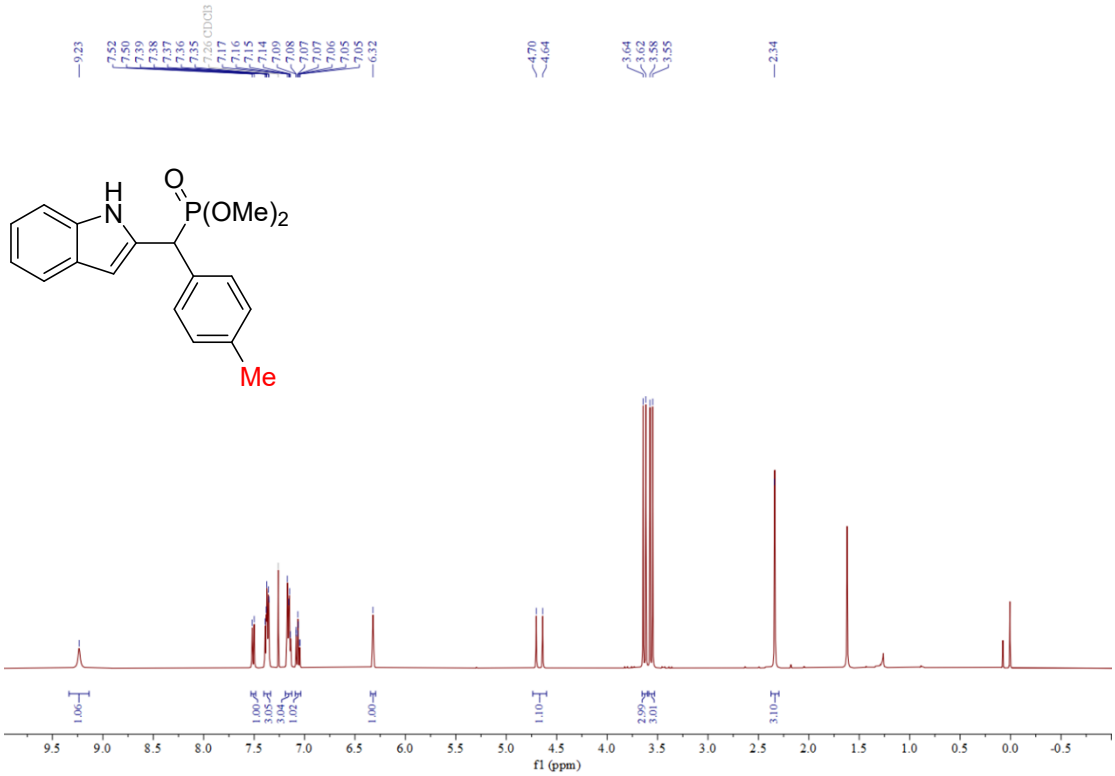
^{13}C NMR Spectra of **3rr** (100 MHz, $CDCl_3$)



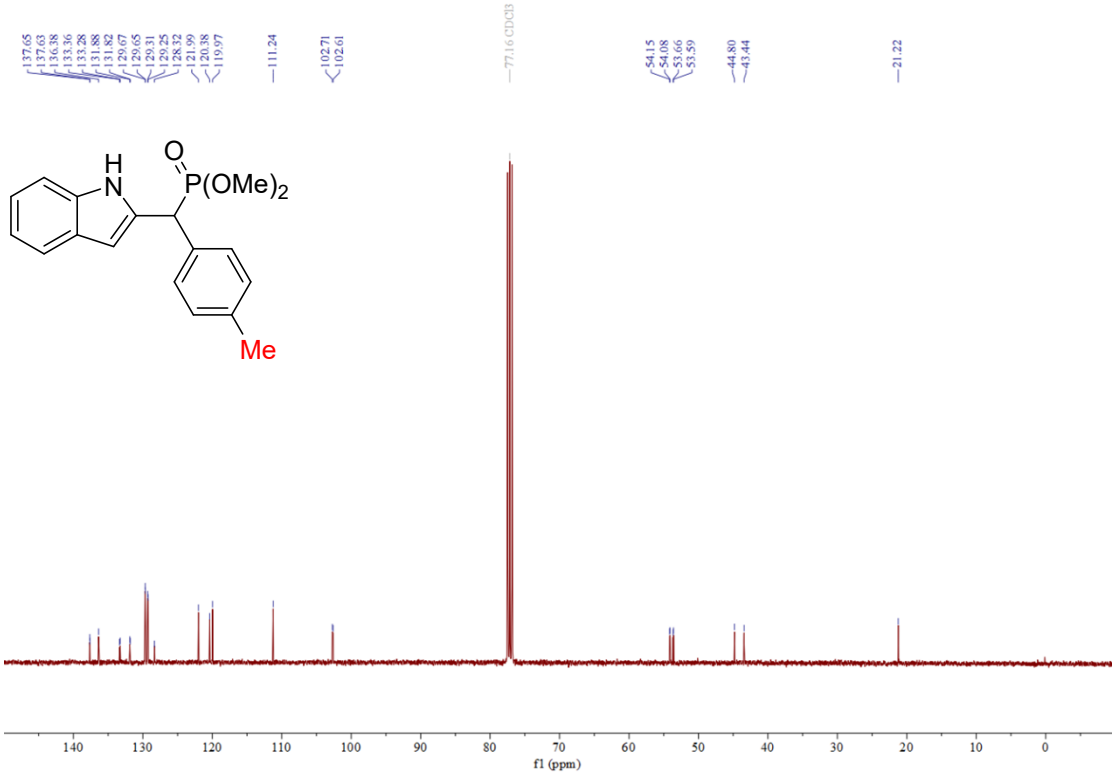
^{31}P NMR Spectra of **3rr** (162 MHz, $CDCl_3$)



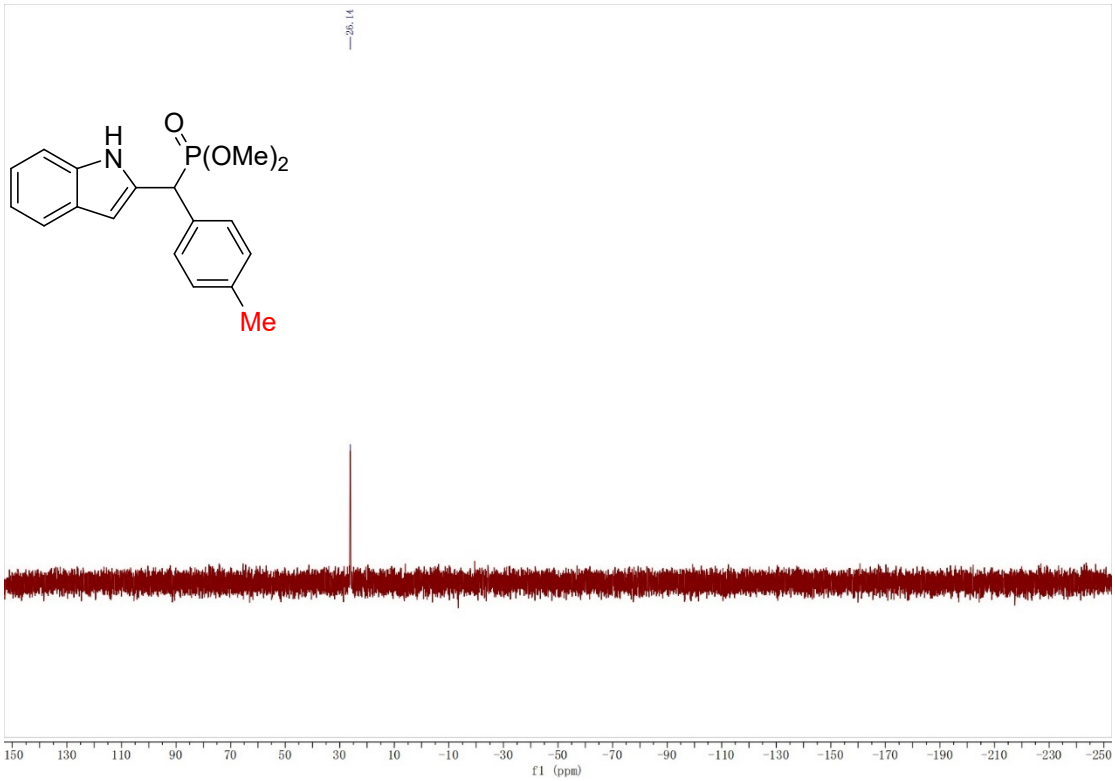
^{1}H NMR Spectra of **3ss** (400 MHz, $CDCl_3$)



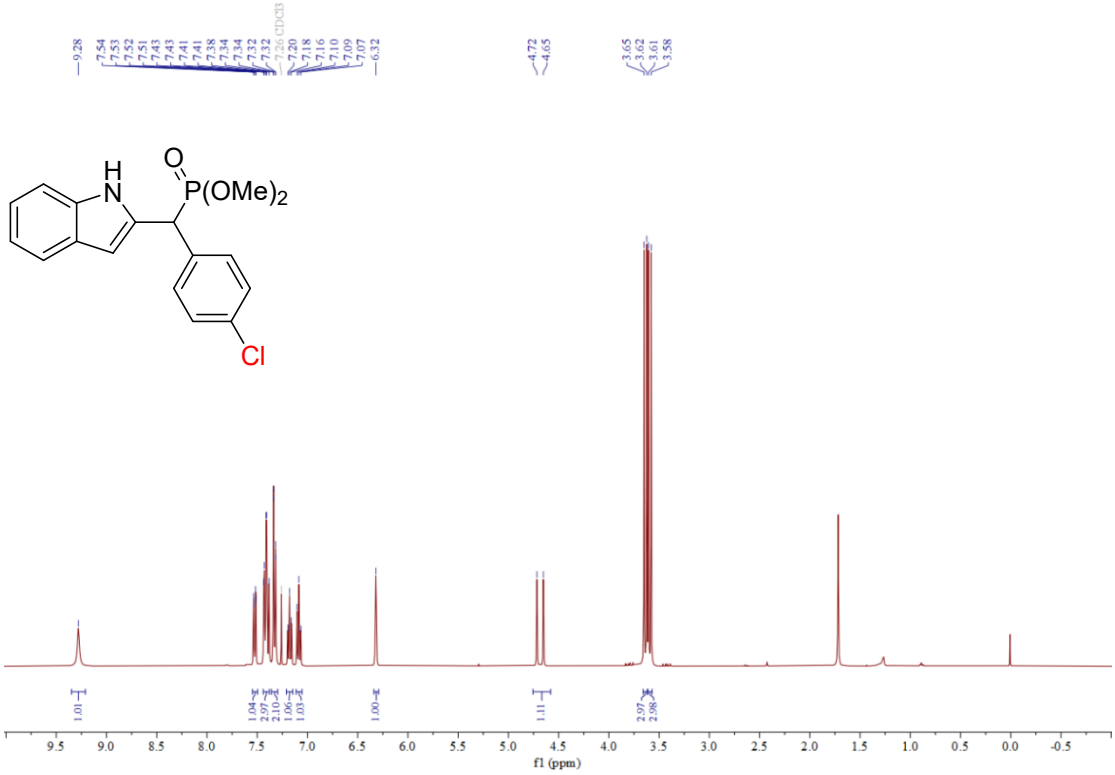
^{13}C NMR Spectra of **3ss** (100 MHz, $CDCl_3$)



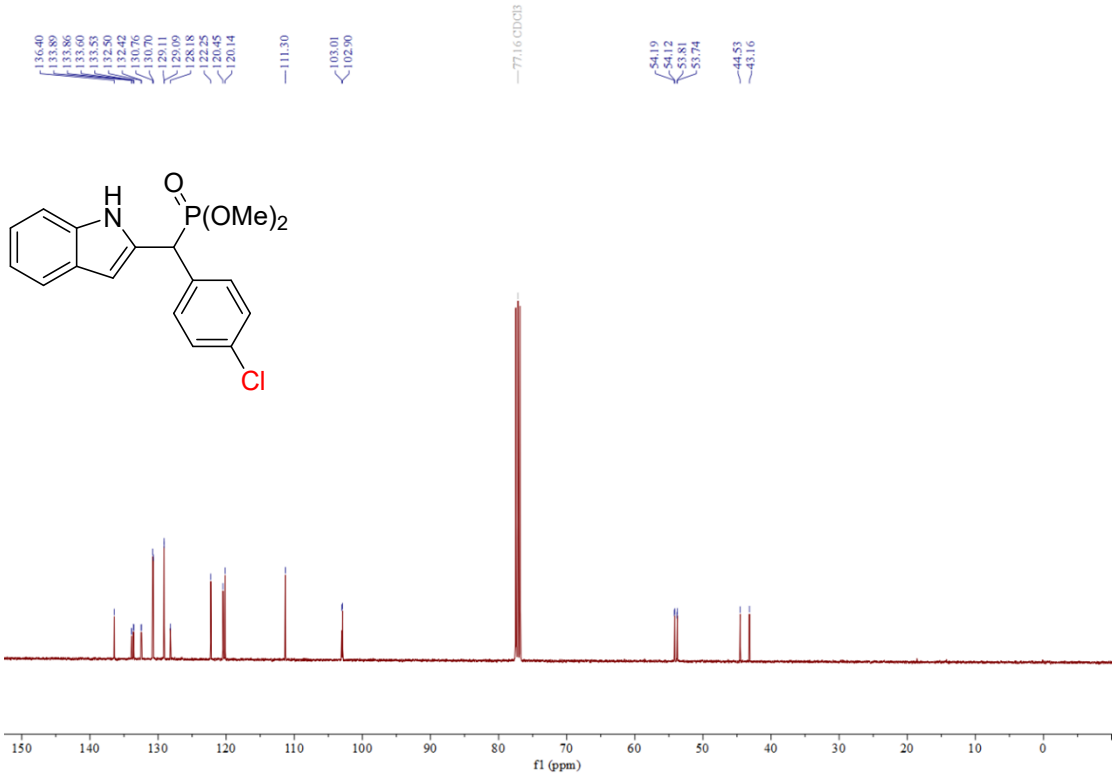
^{31}P NMR Spectra of **3ss** (162 MHz, $CDCl_3$)



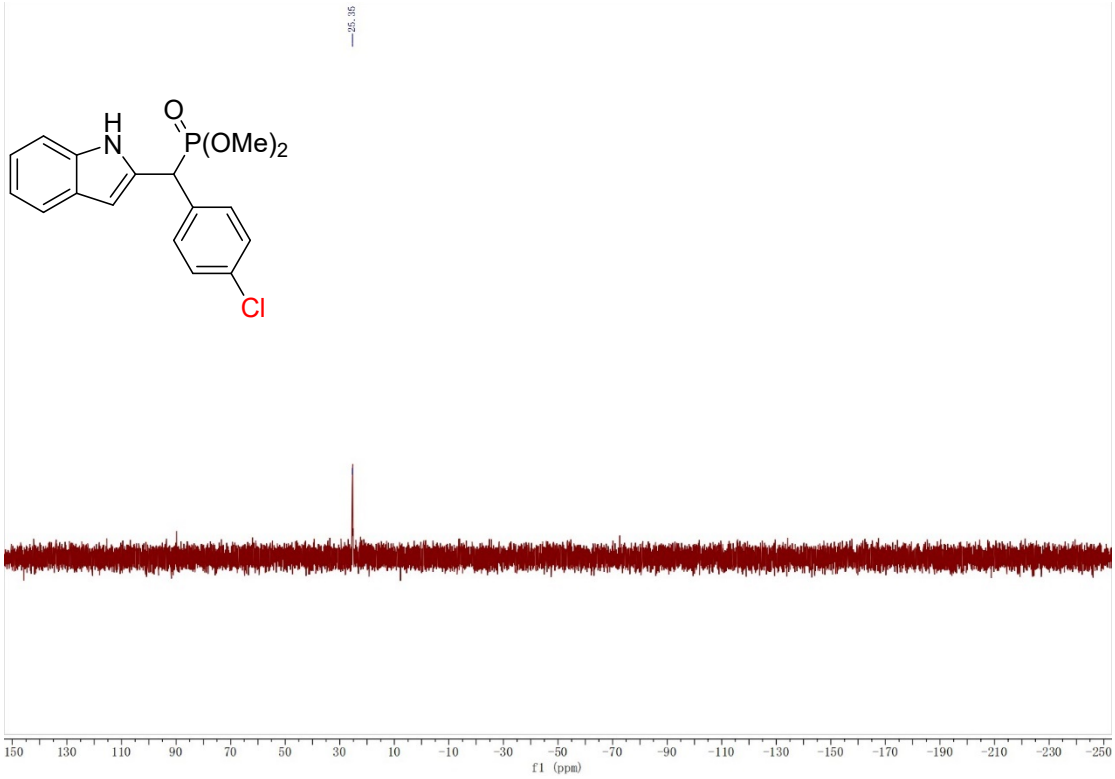
^{1}H NMR Spectra of **3tt** (400 MHz, $CDCl_3$)



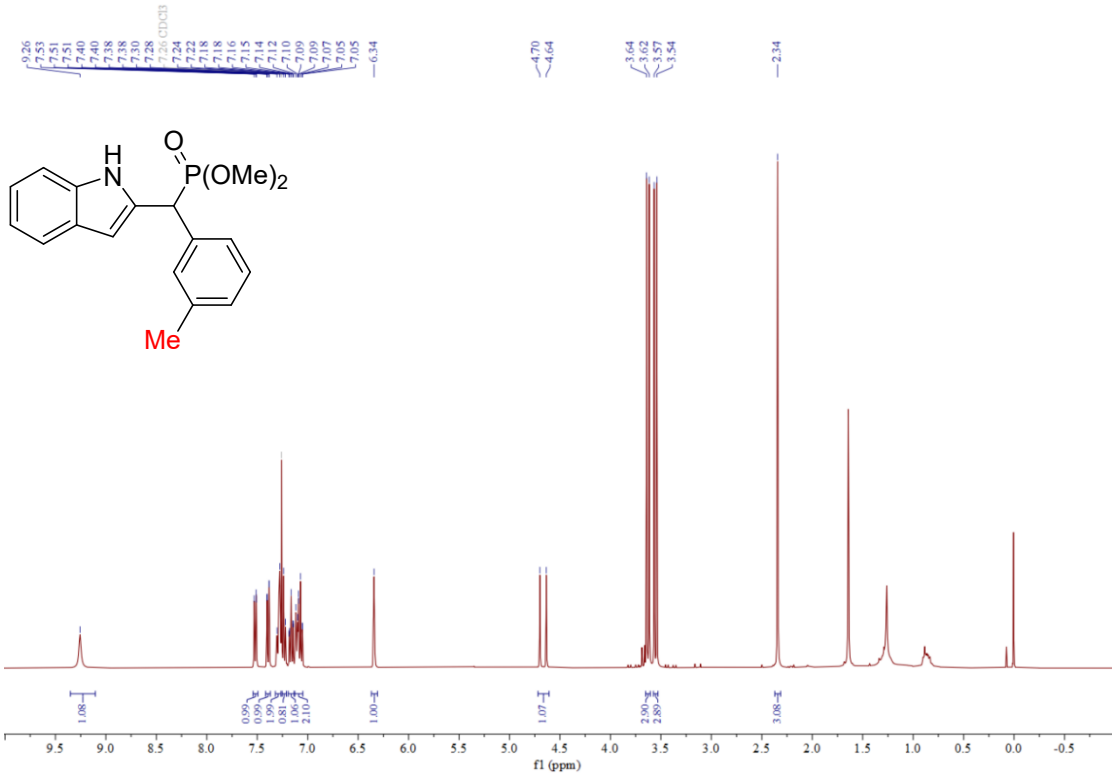
^{13}C NMR Spectra of **3tt** (100 MHz, $CDCl_3$)



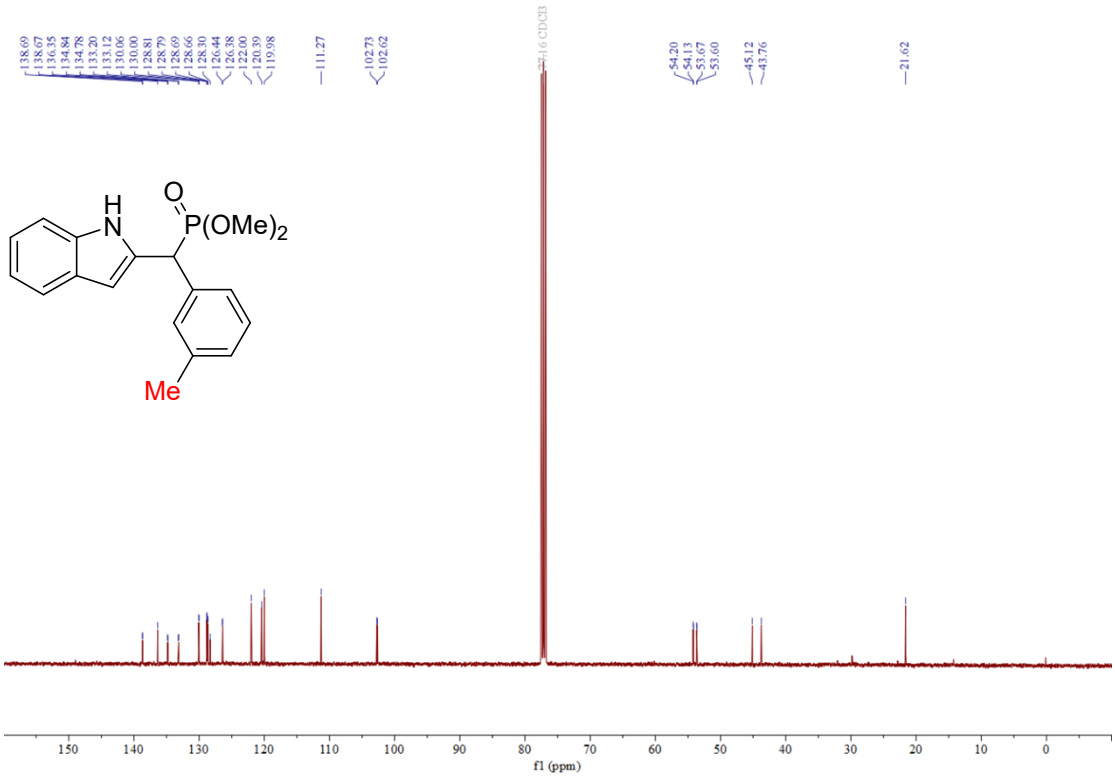
^{31}P NMR Spectra of **3tt** (162 MHz, $CDCl_3$)



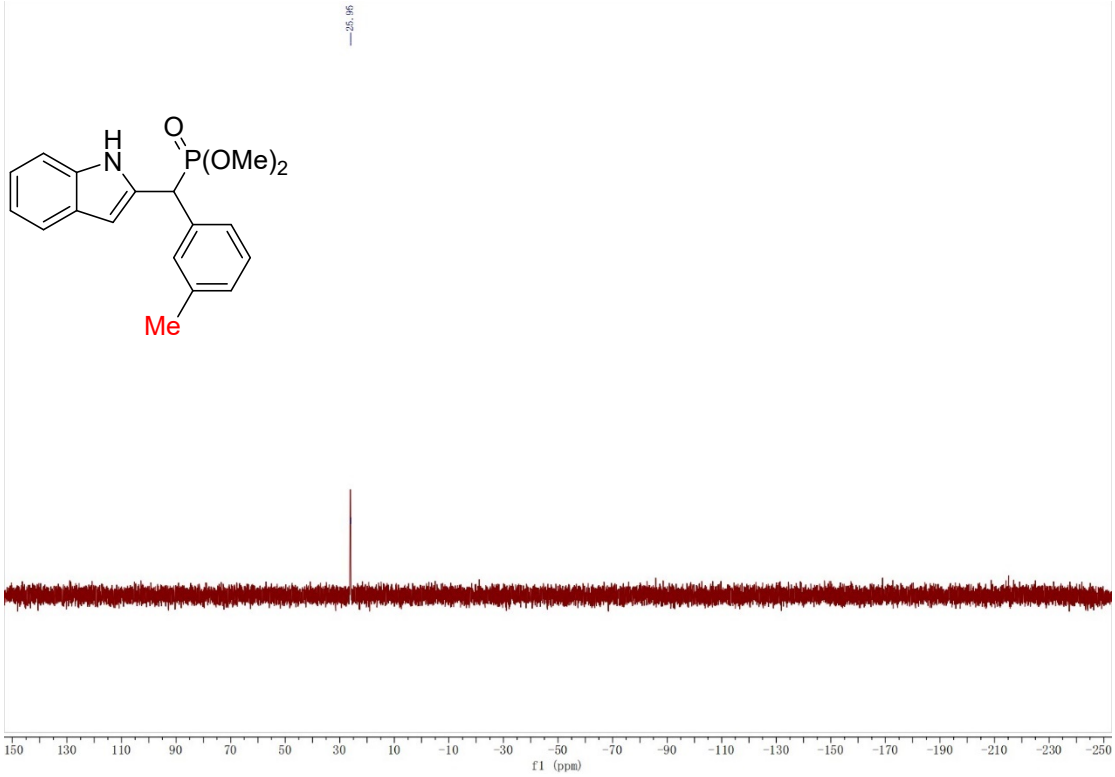
^{1}H NMR Spectra of **3uu** (400 MHz, $CDCl_3$)



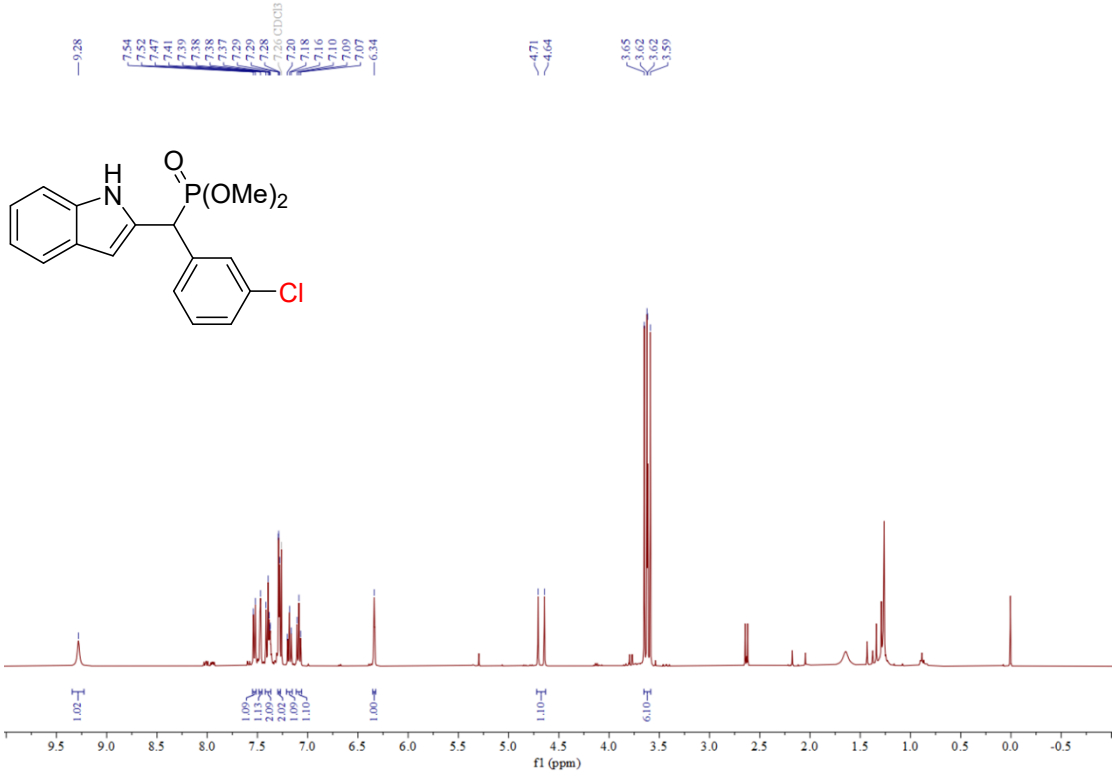
^{13}C NMR Spectra of **3uu** (100 MHz, $CDCl_3$)



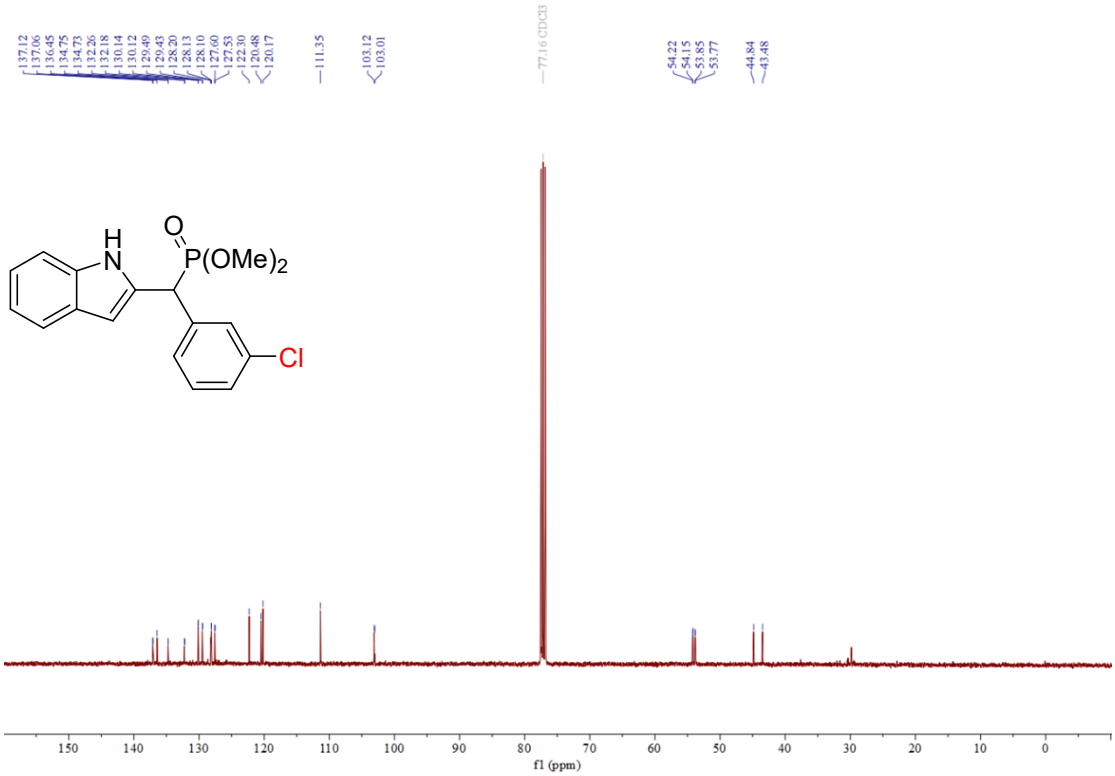
^{31}P NMR Spectra of **3uu** (162 MHz, $CDCl_3$)



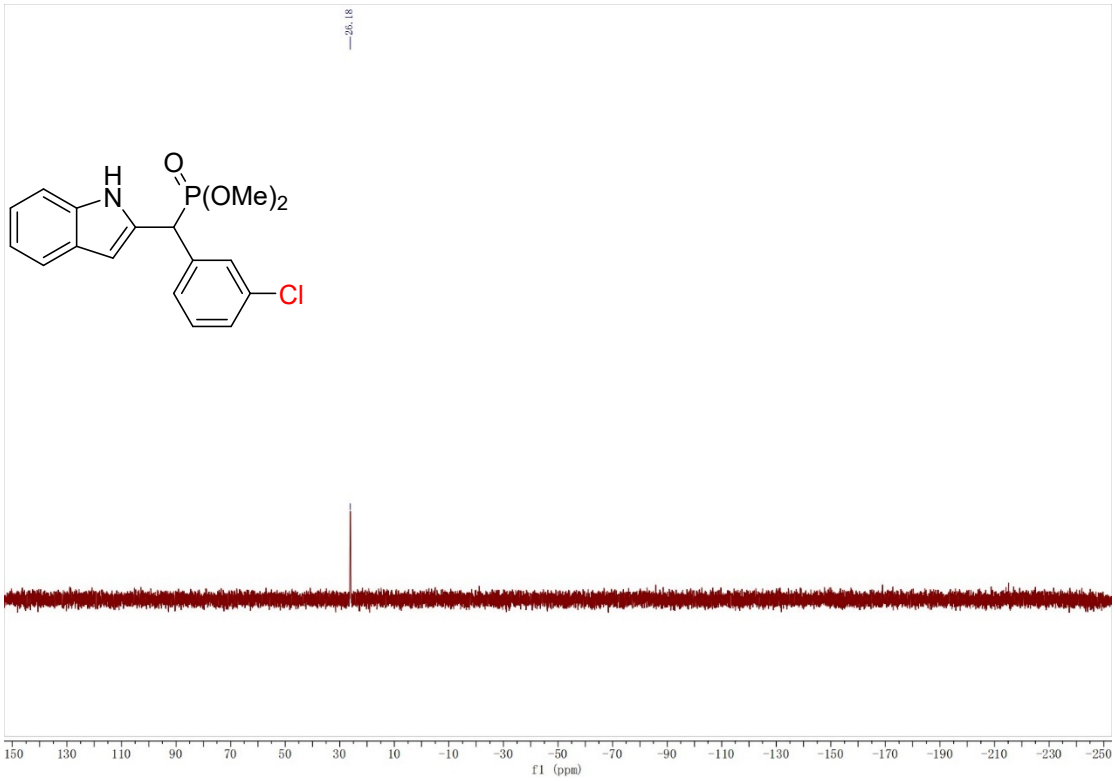
^{1}H NMR Spectra of **3vv** (400 MHz, $CDCl_3$)



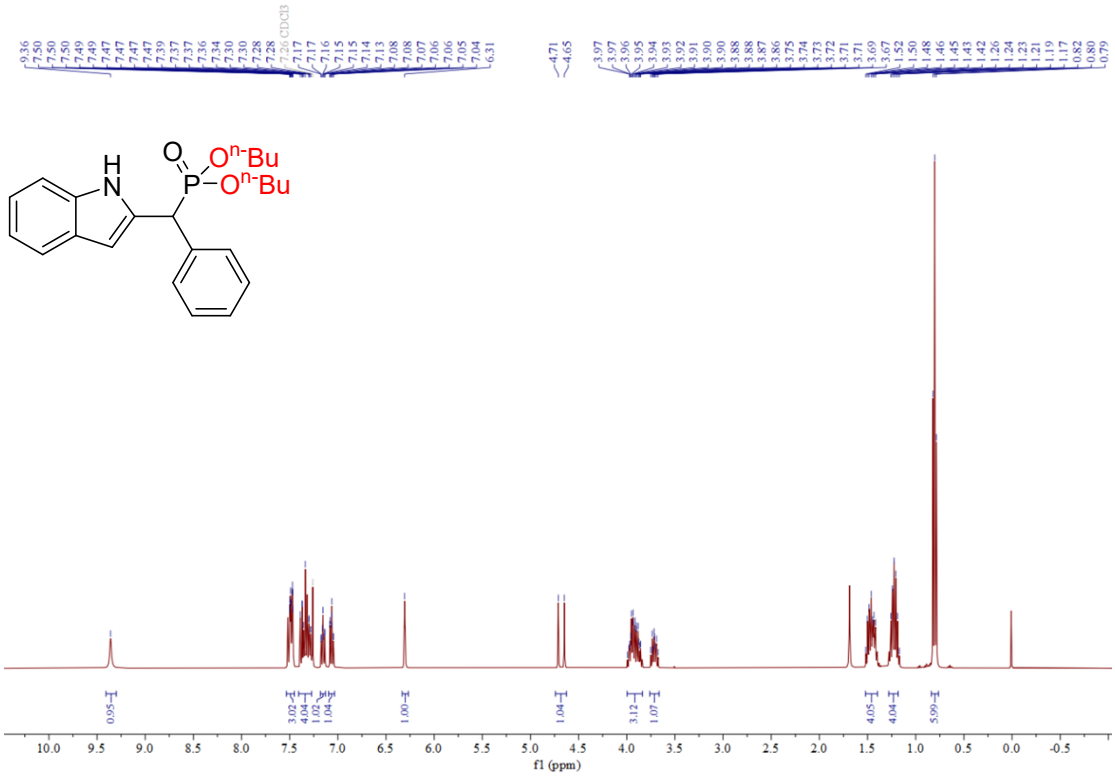
^{13}C NMR Spectra of **3vv** (100 MHz, $CDCl_3$)



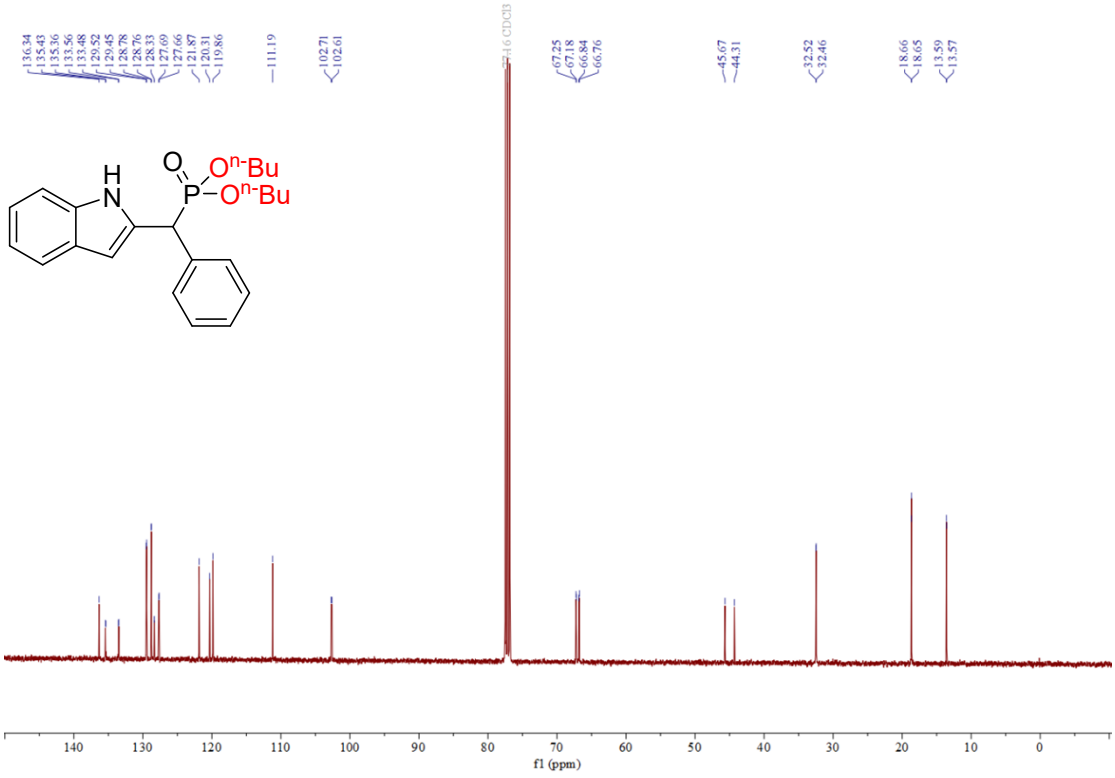
^{31}P NMR Spectra of **3vv** (162 MHz, $CDCl_3$)



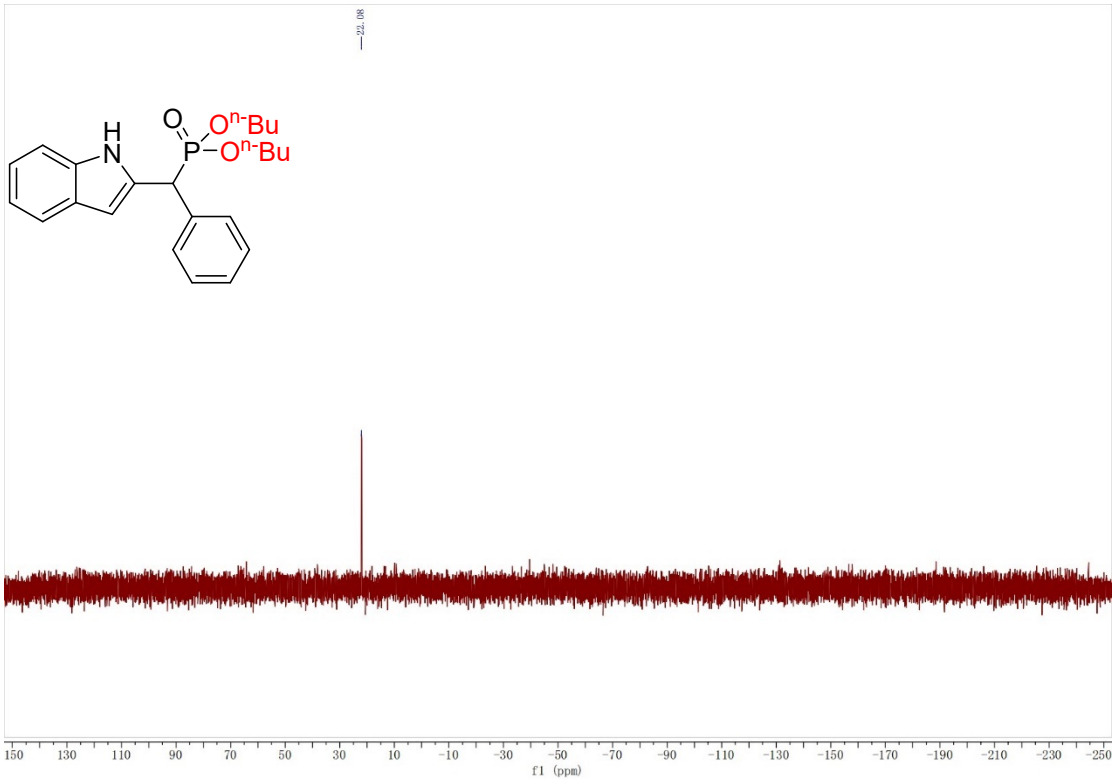
^{1}H NMR Spectra of **3ww** (400 MHz, $CDCl_3$)



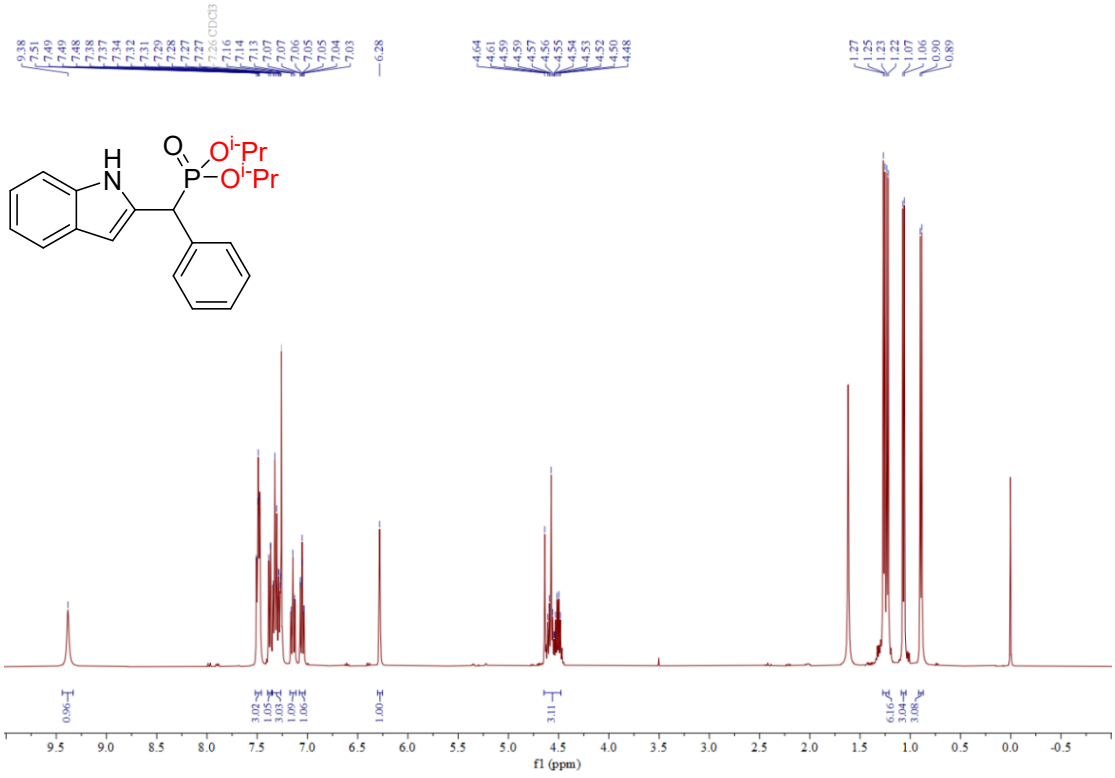
^{13}C NMR Spectra of **3ww** (100 MHz, $CDCl_3$)



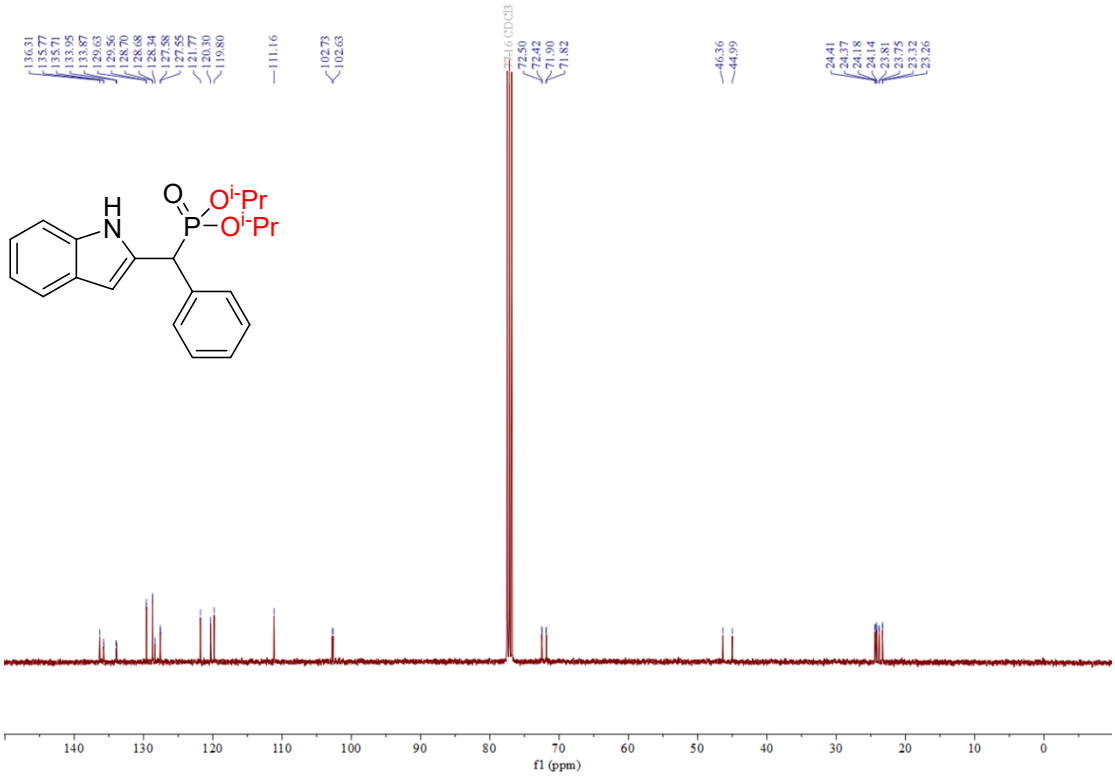
^{31}P NMR Spectra of **3ww** (162 MHz, $CDCl_3$)



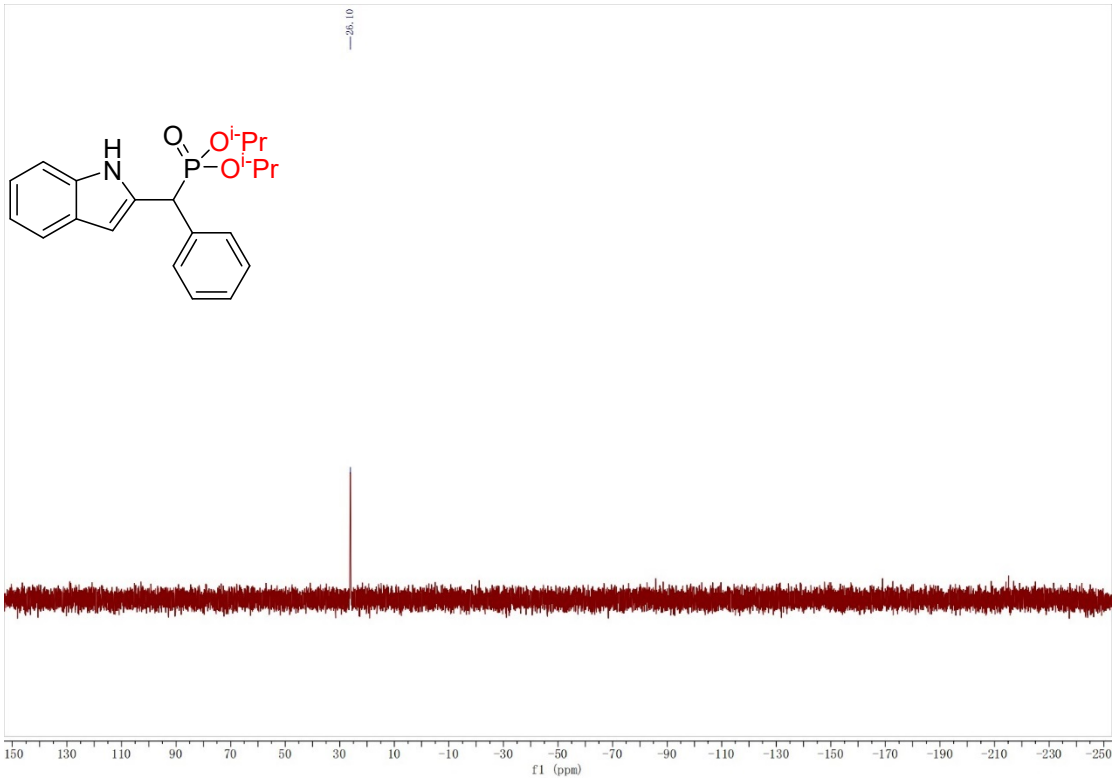
^{1}H NMR Spectra of **3xx** (400 MHz, $CDCl_3$)



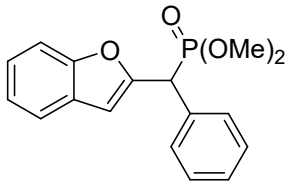
^{13}C NMR Spectra of **3xx** (100 MHz, $CDCl_3$)

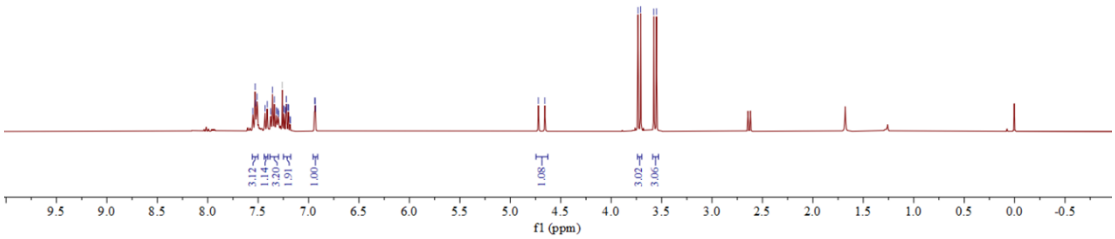


^{31}P NMR Spectra of **3xx** (162 MHz, $CDCl_3$)

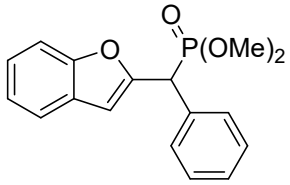


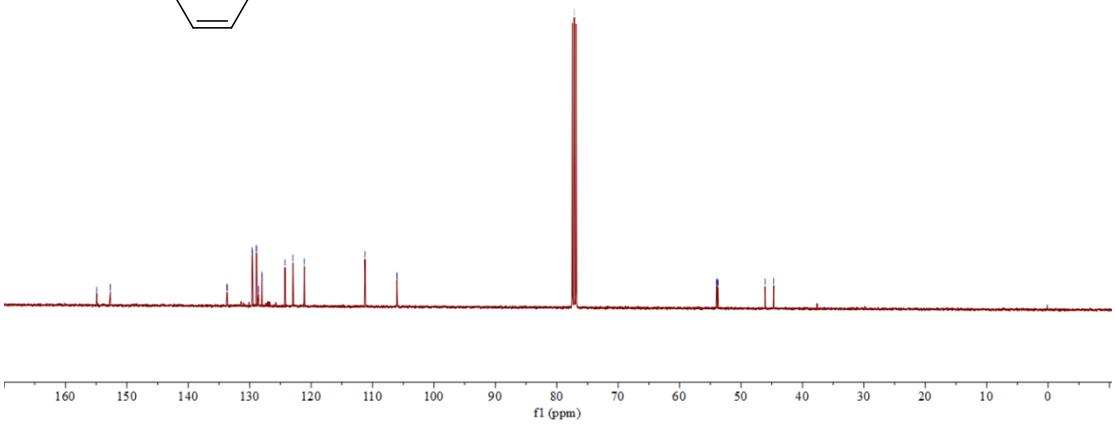
^{1}H NMR Spectra of **3yy** (400 MHz, $CDCl_3$)



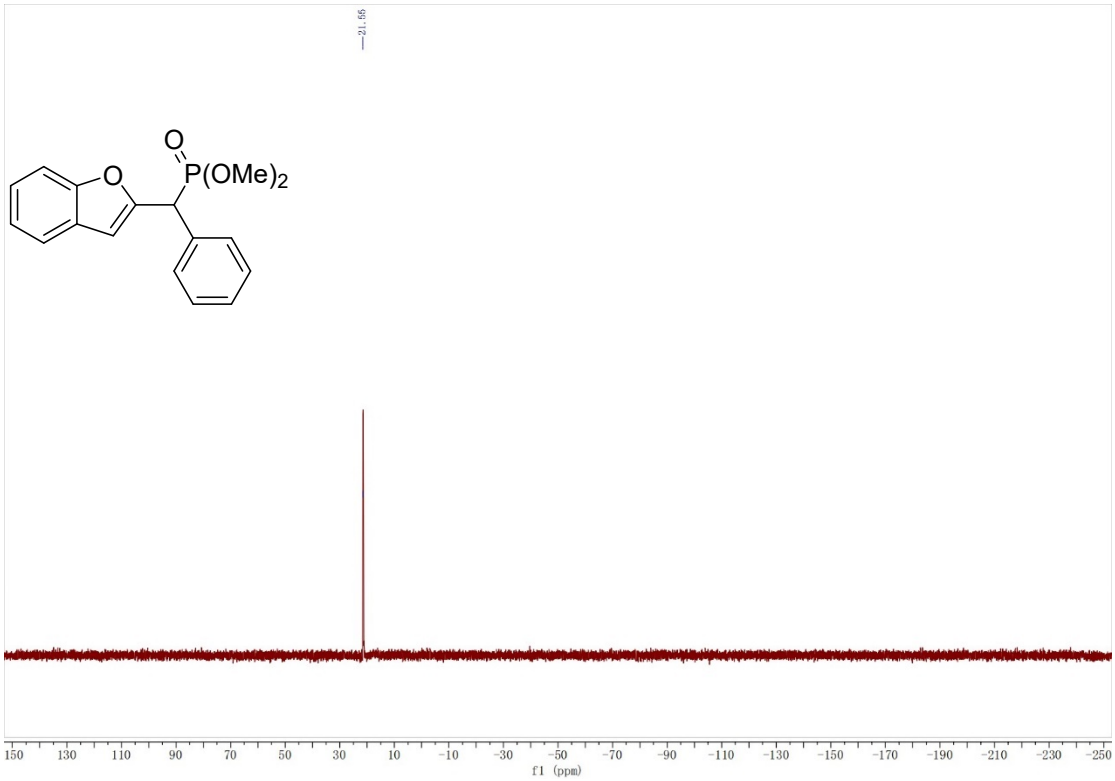


^{13}C NMR Spectra of **3yy** (100 MHz, $CDCl_3$)

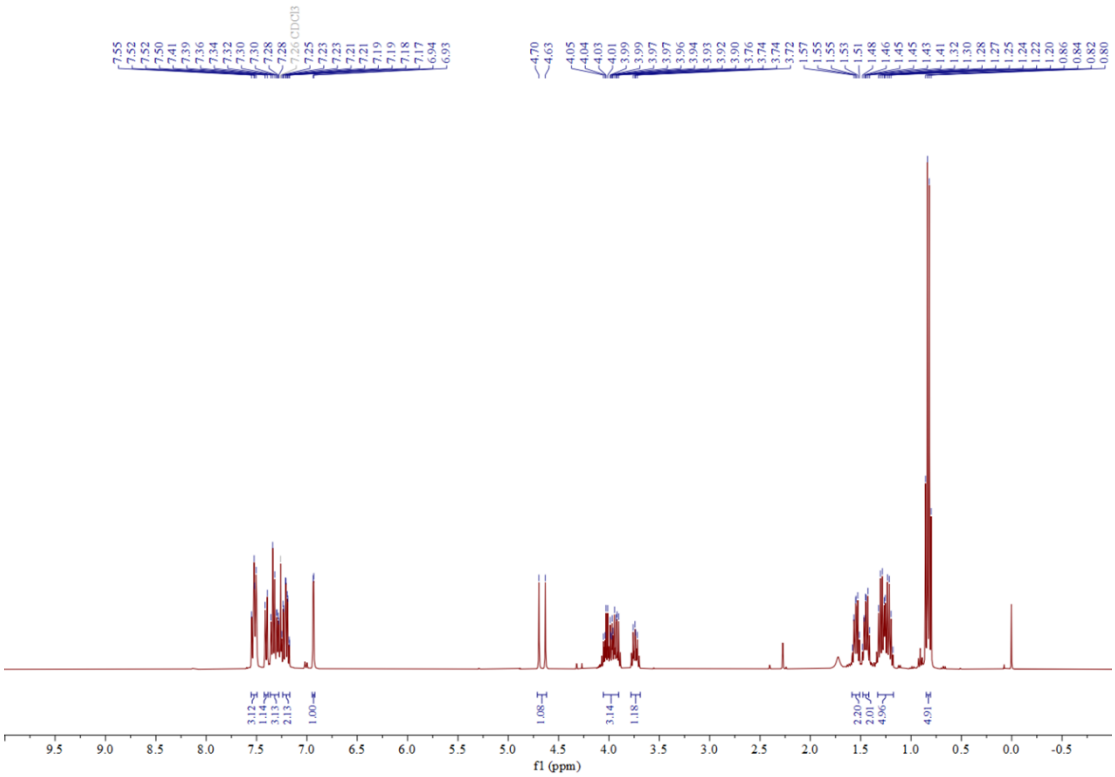




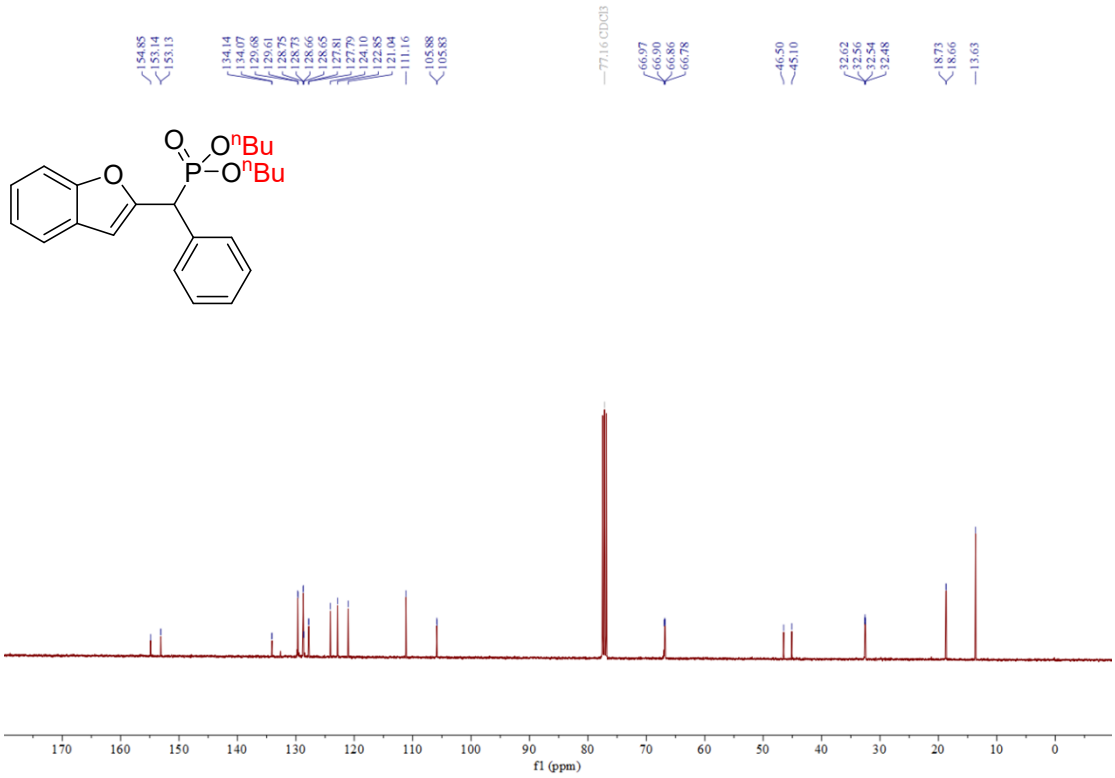
^{31}P NMR Spectra of **3yy** (162 MHz, $CDCl_3$)



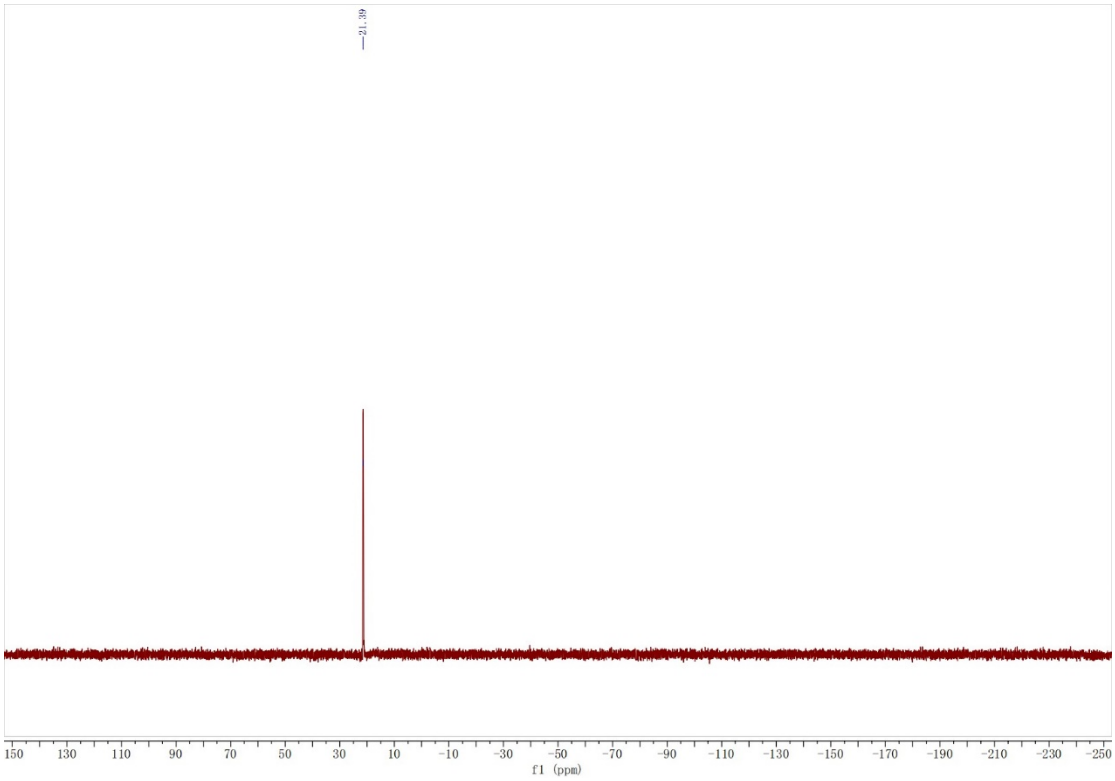
^{1}H NMR Spectra of **3zz** (400 MHz, $CDCl_3$)



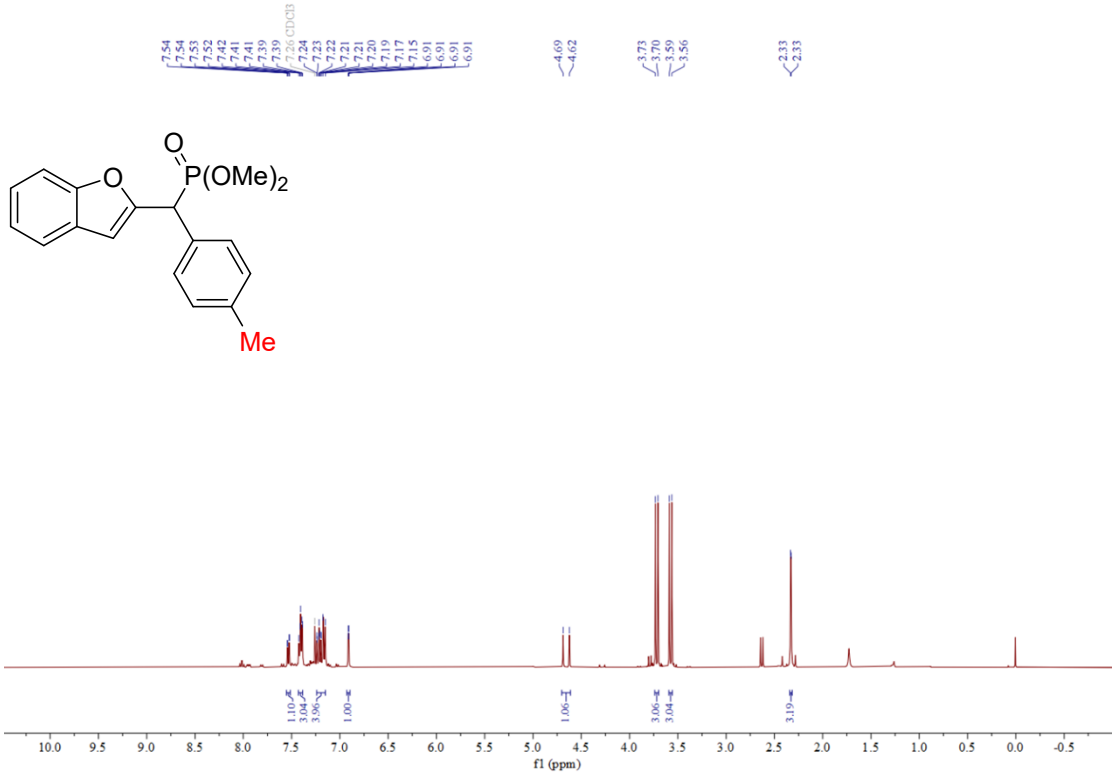
^{13}C NMR Spectra of **3zz** (100 MHz, $CDCl_3$)



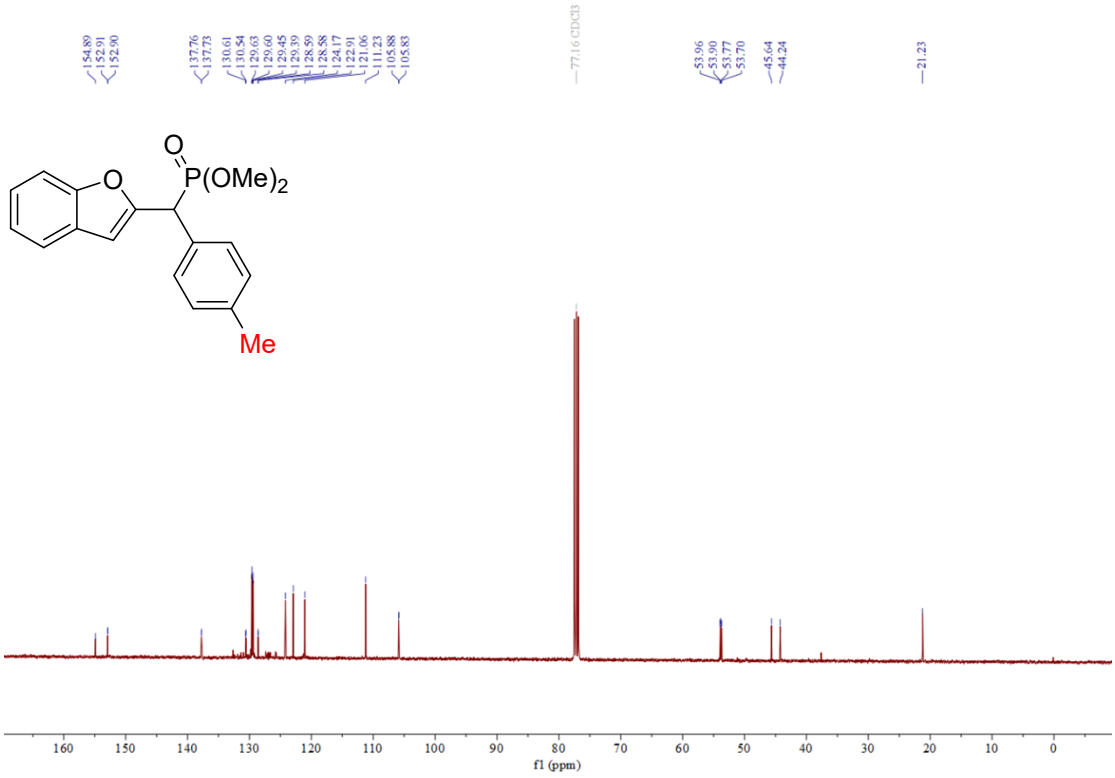
^{31}P NMR Spectra of **3zz** (162 MHz, $CDCl_3$)



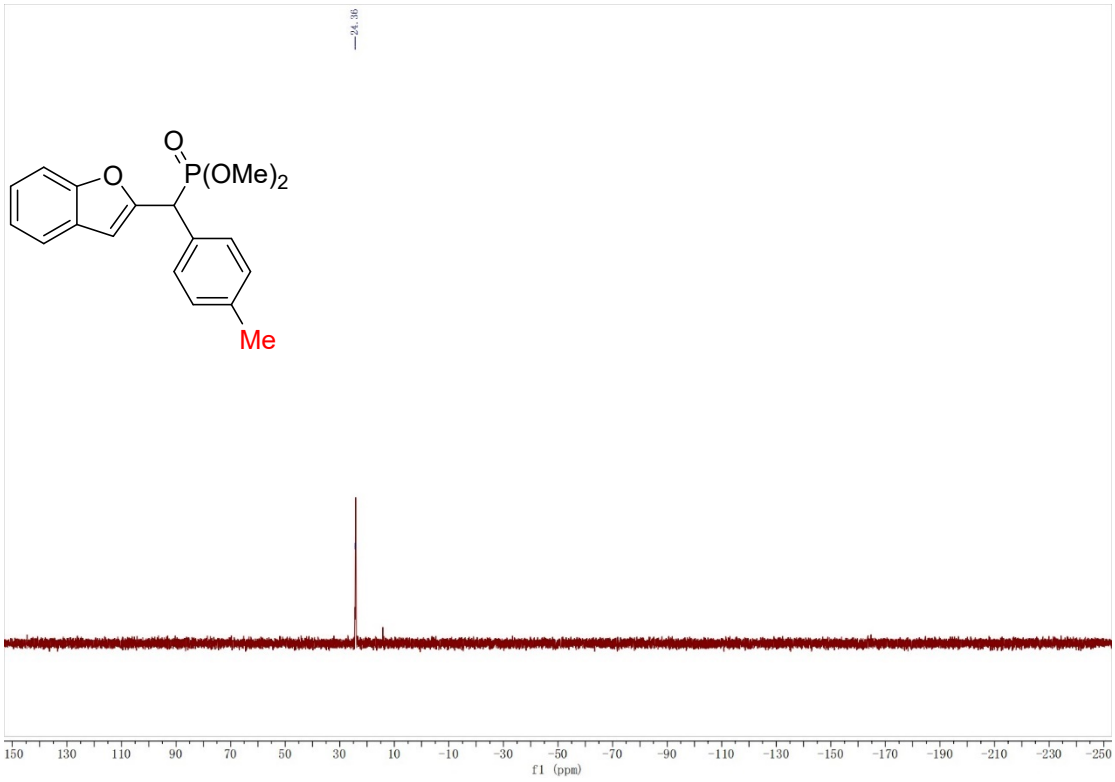
^{1}H NMR Spectra of **3ab** (400 MHz, $CDCl_3$)



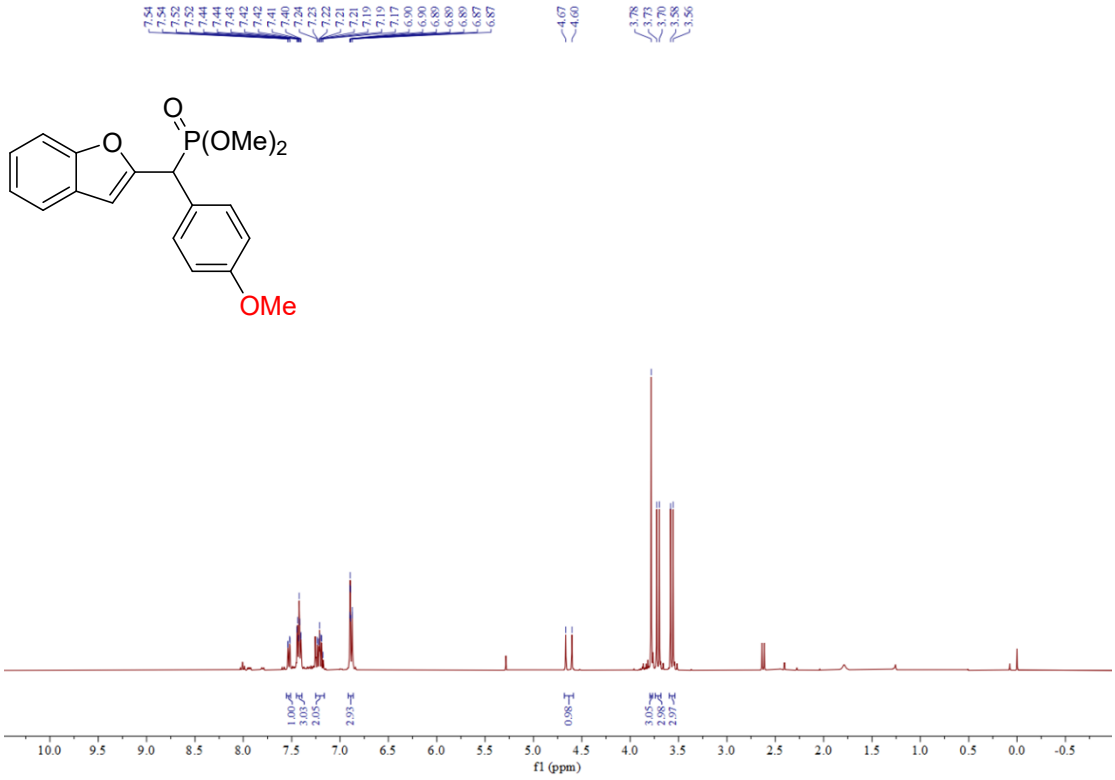
^{13}C NMR Spectra of **3ab** (100 MHz, $CDCl_3$)



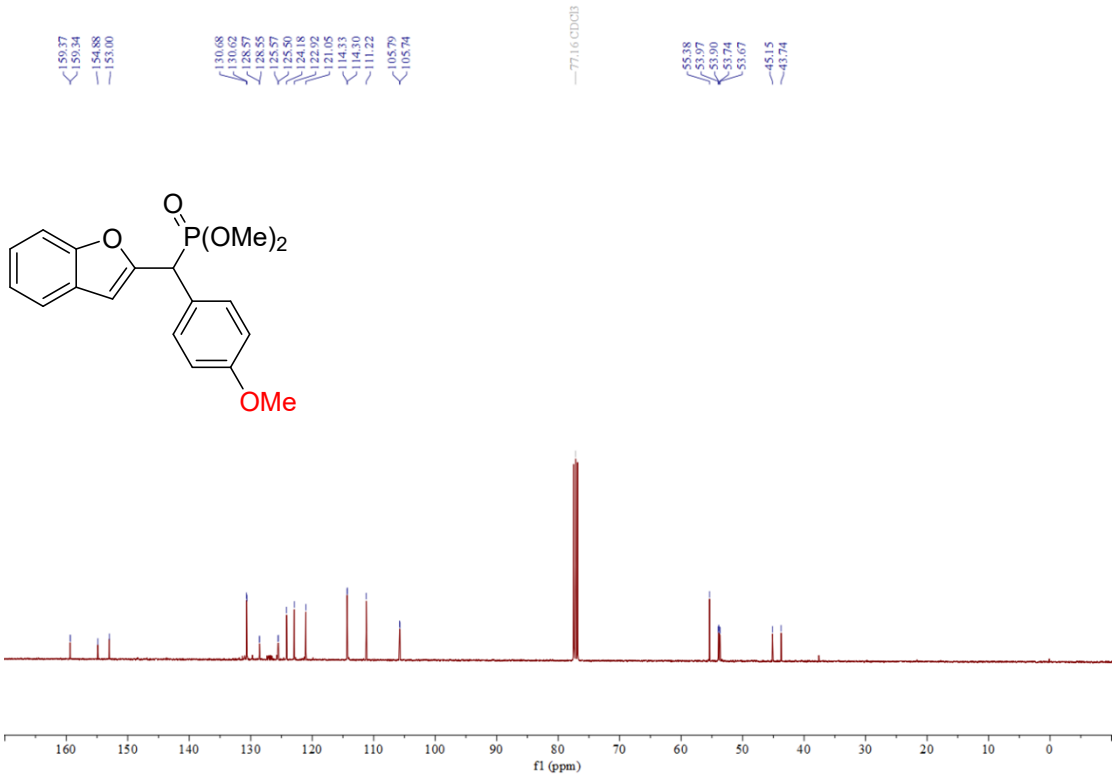
^{31}P NMR Spectra of **3ab** (162 MHz, $CDCl_3$)



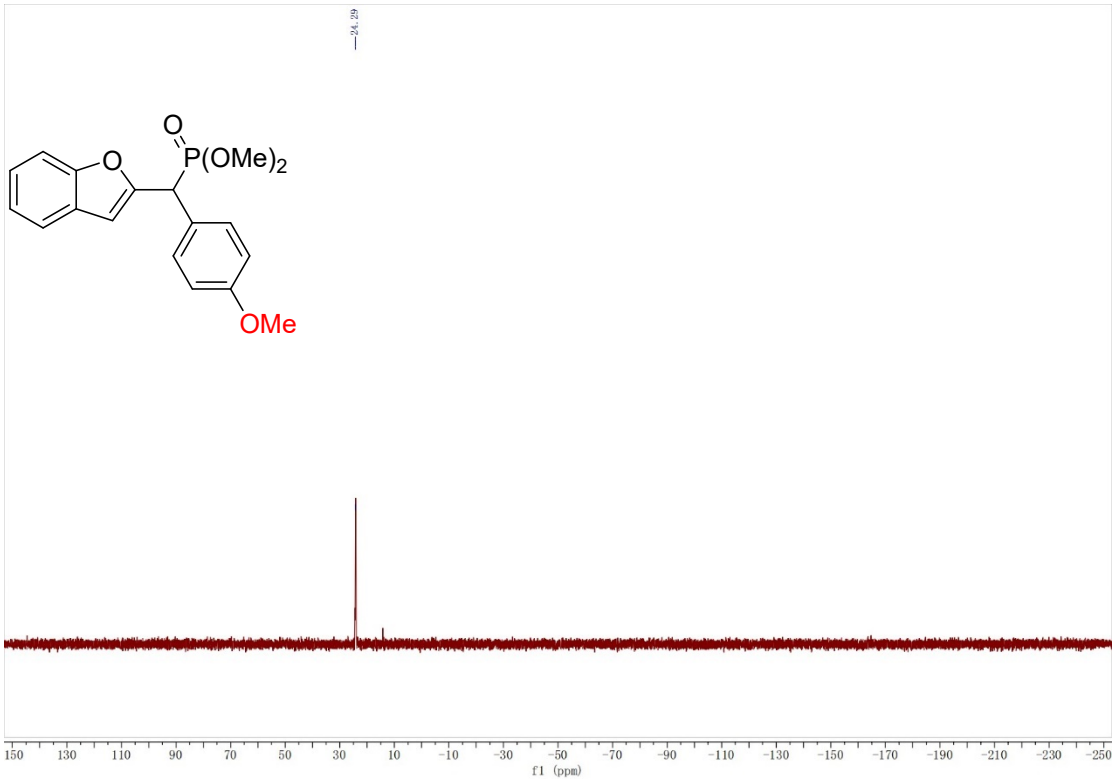
^{1}H NMR Spectra of **3ac** (400 MHz, $CDCl_3$)



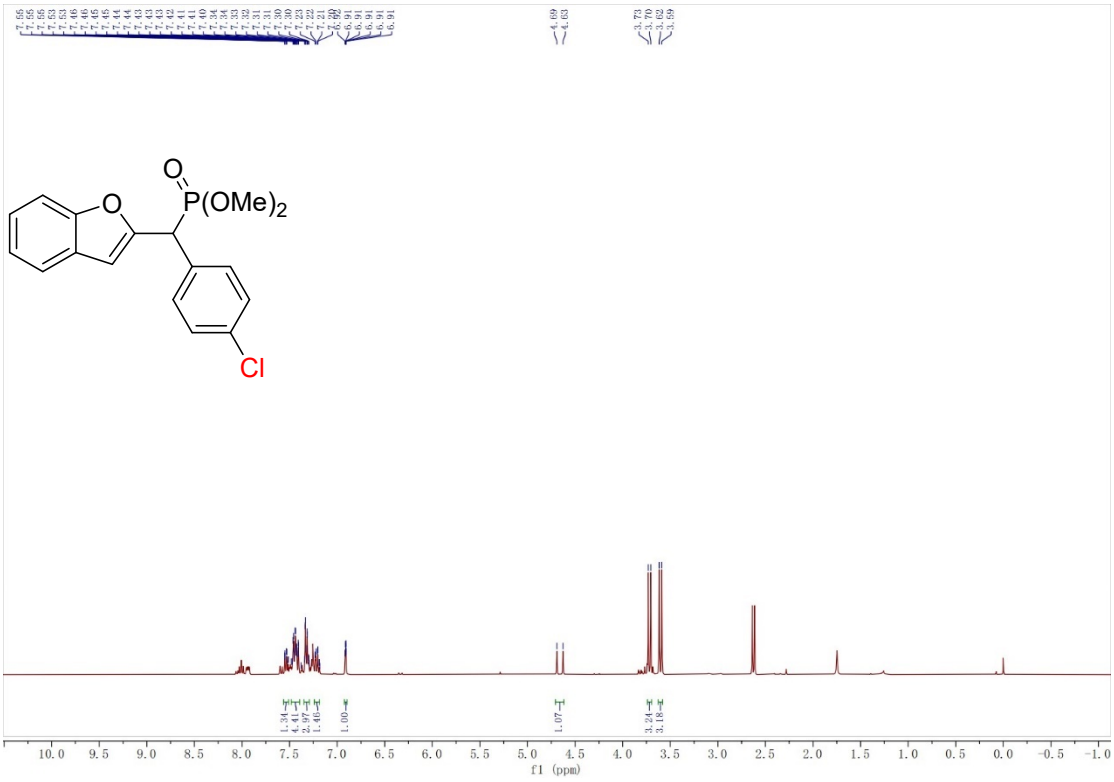
^{13}C NMR Spectra of **3ac** (100 MHz, $CDCl_3$)



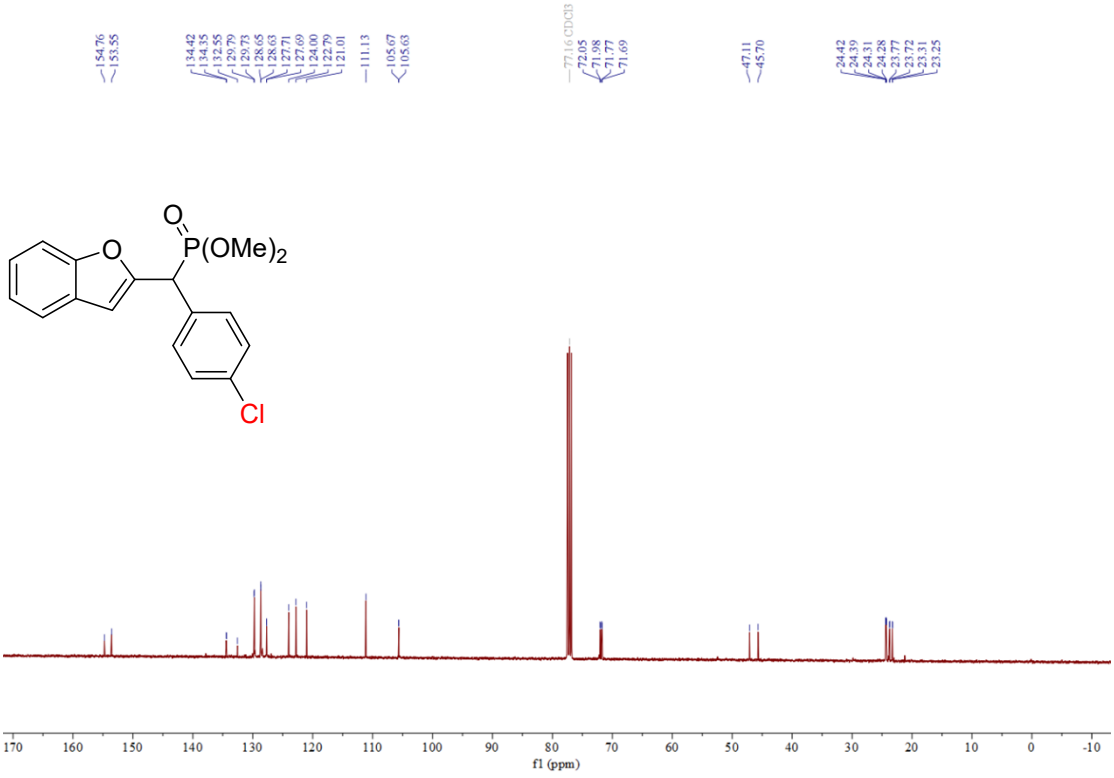
^{31}P NMR Spectra of **3ac** (162 MHz, $CDCl_3$)



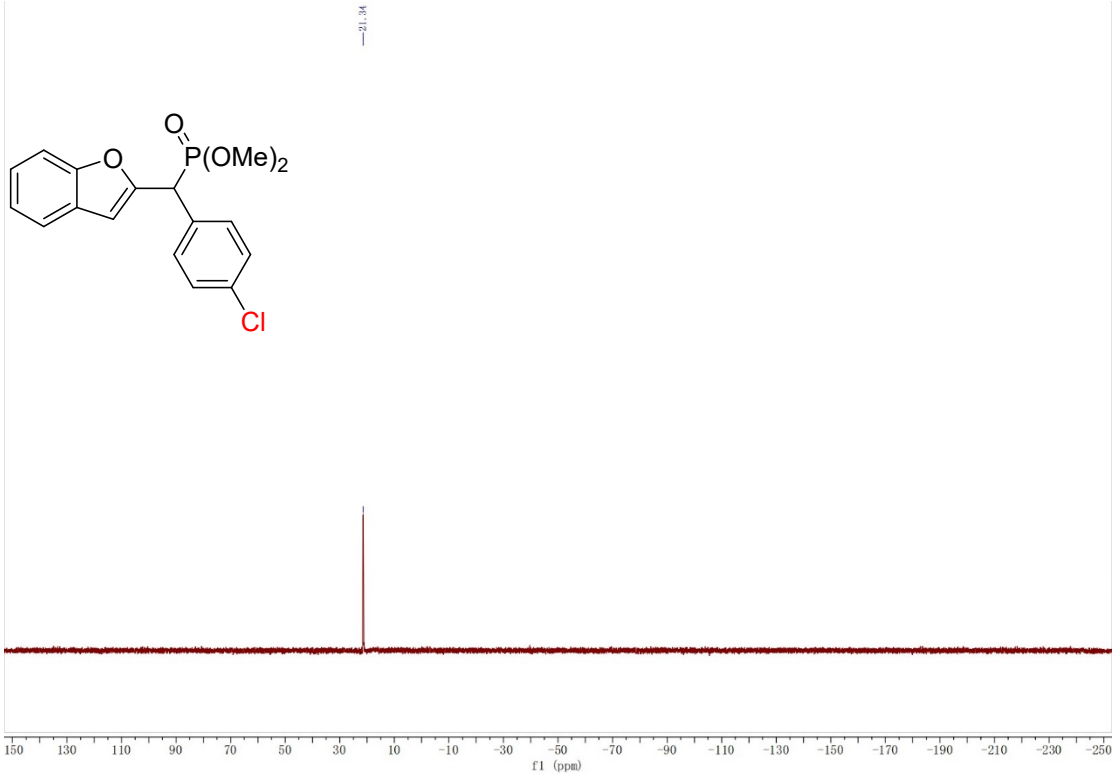
^{1}H NMR Spectra of **3ad** (400 MHz, $CDCl_3$)



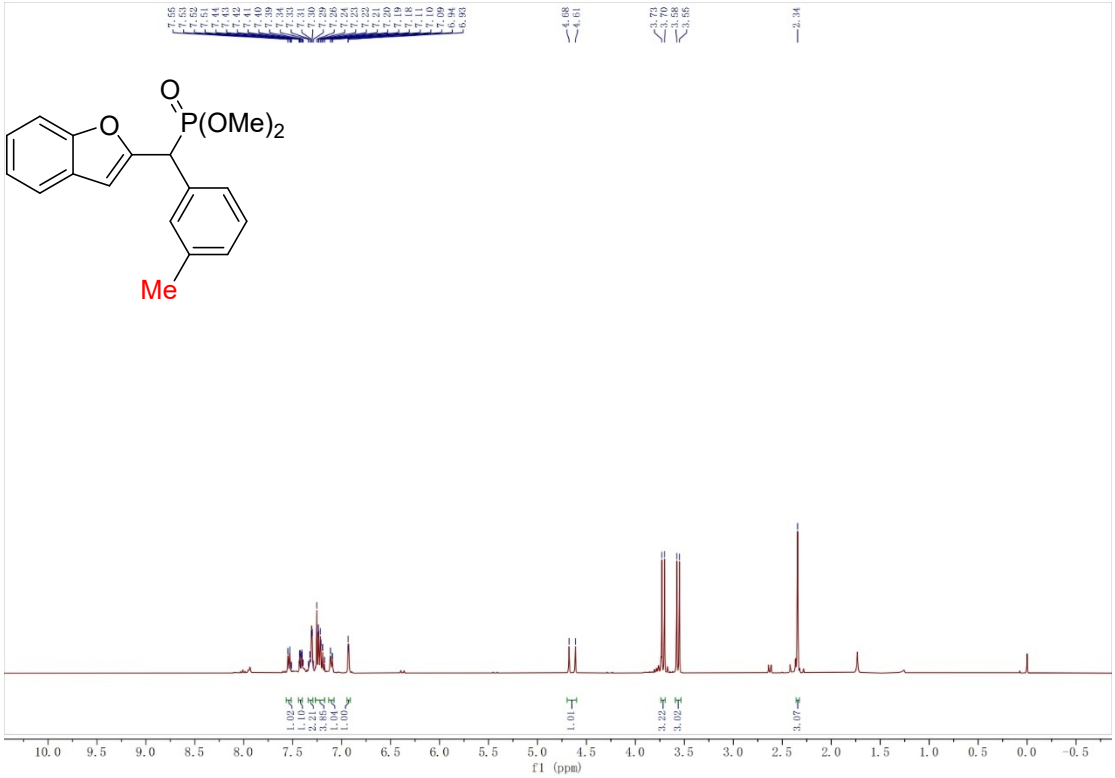
^{13}C NMR Spectra of **3ad** (100 MHz, $CDCl_3$)



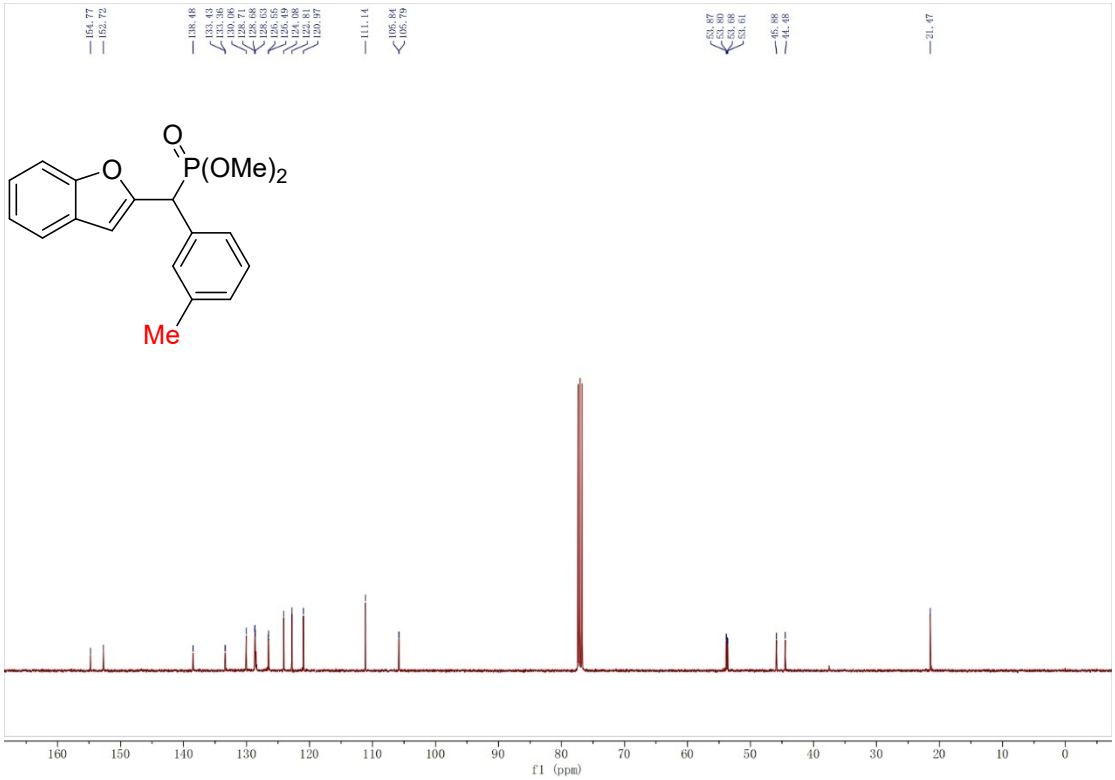
^{31}P NMR Spectra of **3ad** (162 MHz, $CDCl_3$)



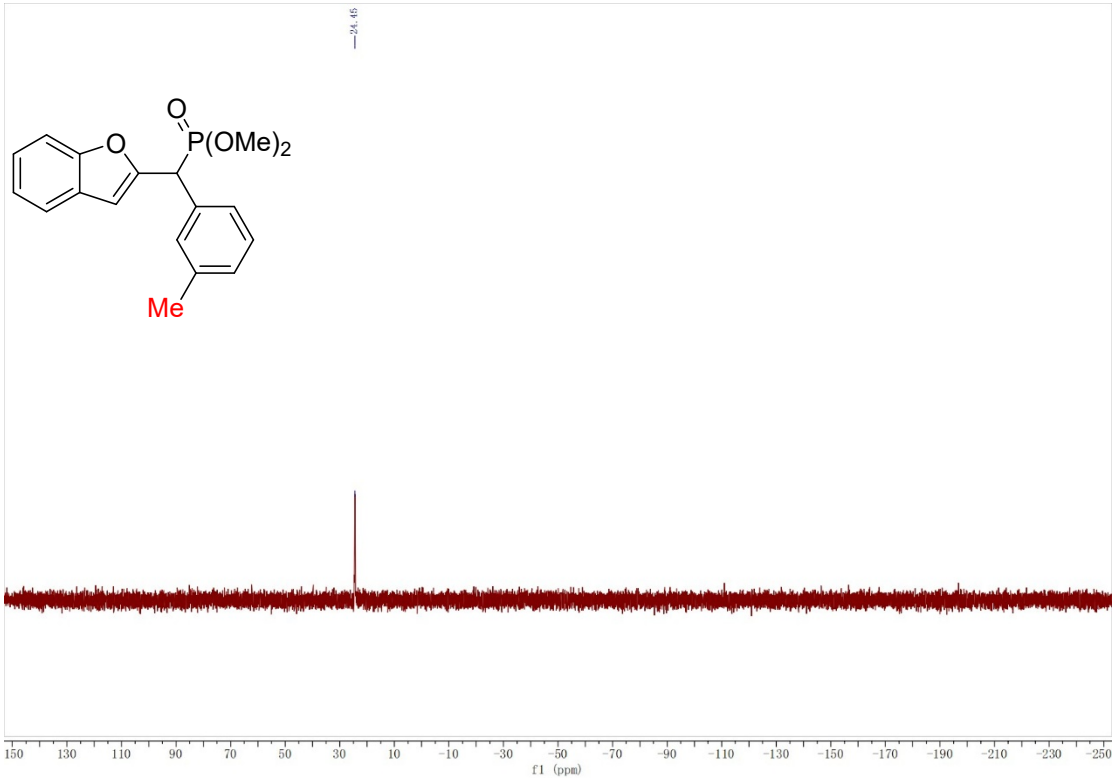
^{1}H NMR Spectra of **3ae** (400 MHz, $CDCl_3$)



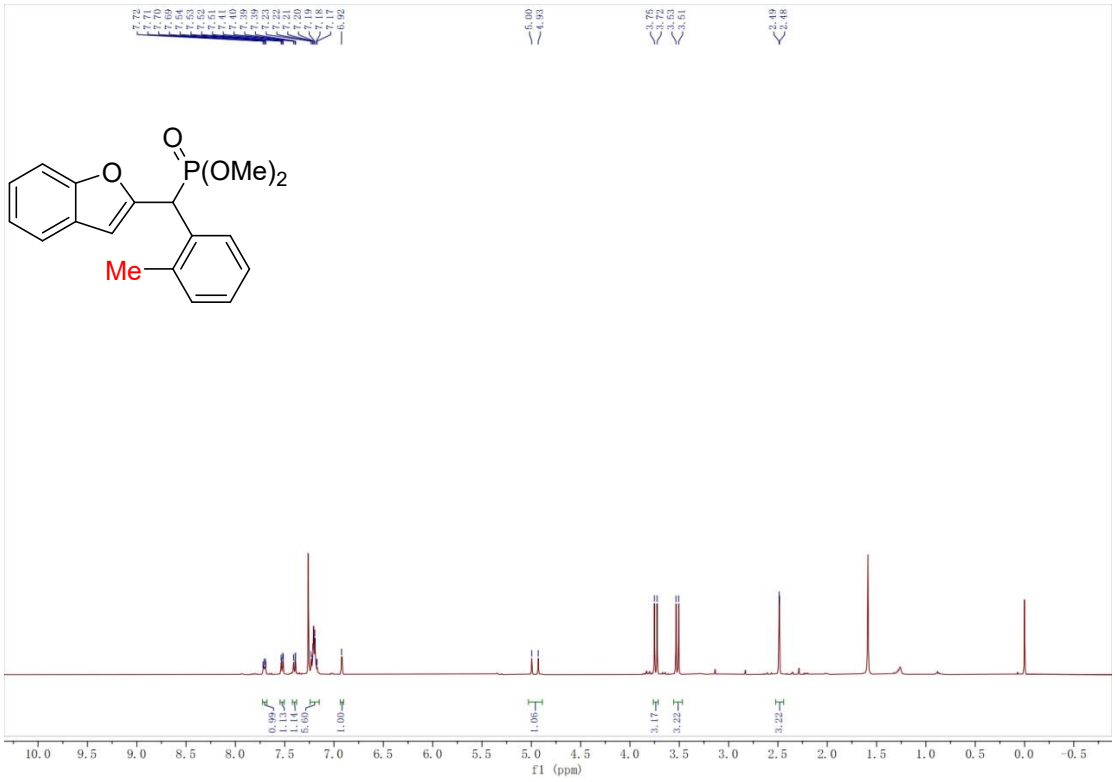
^{13}C NMR Spectra of **3ae** (100 MHz, $CDCl_3$)



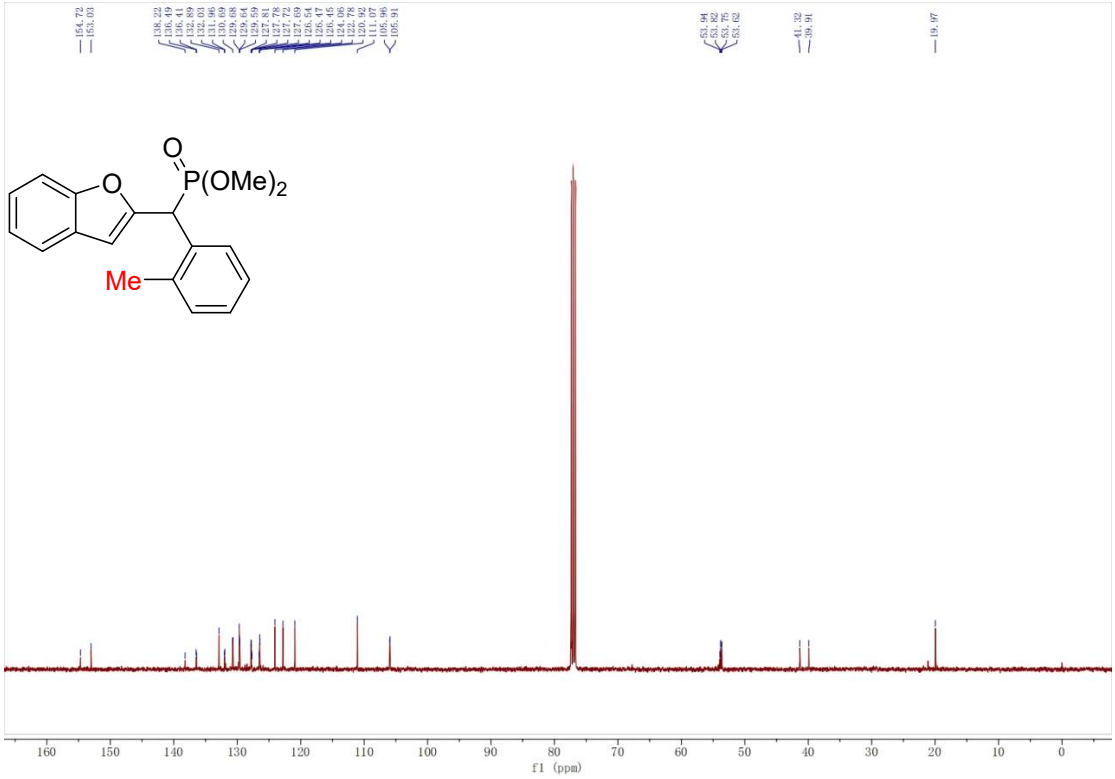
^{31}P NMR Spectra of **3ae** (162 MHz, $CDCl_3$)



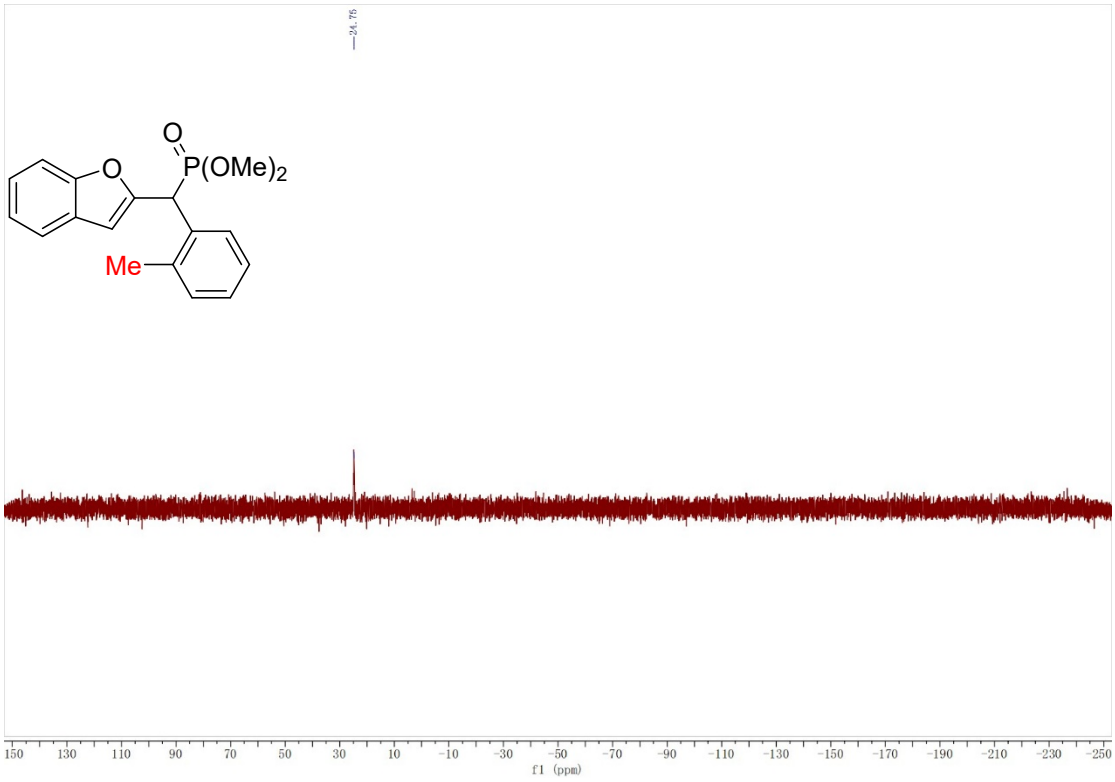
^{1}H NMR Spectra of **3af** (400 MHz, $CDCl_3$)



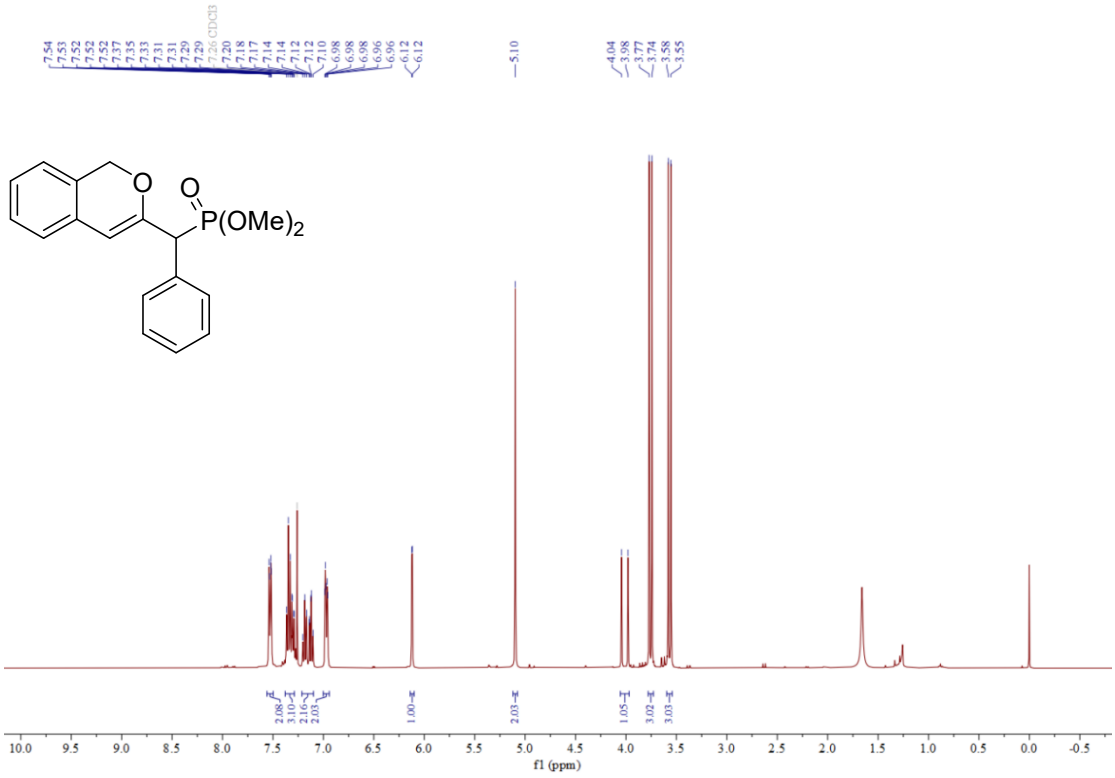
^{13}C NMR Spectra of **3af** (100 MHz, $CDCl_3$)



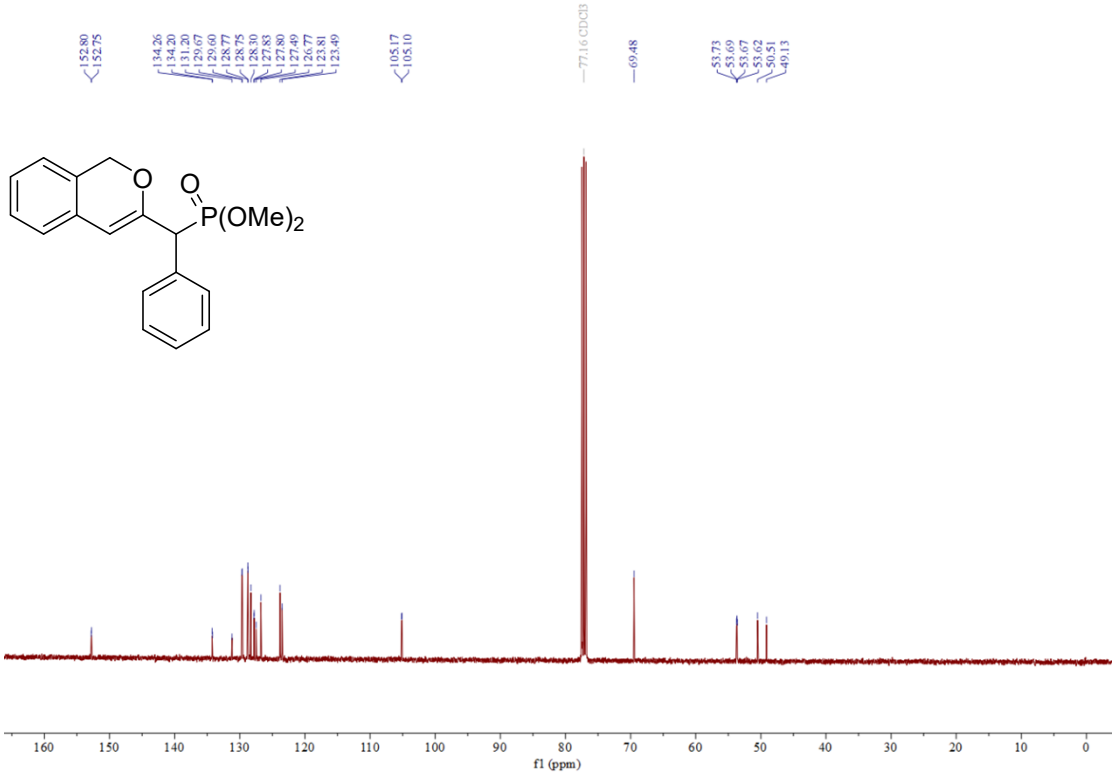
^{31}P NMR Spectra of **3af** (162 MHz, $CDCl_3$)



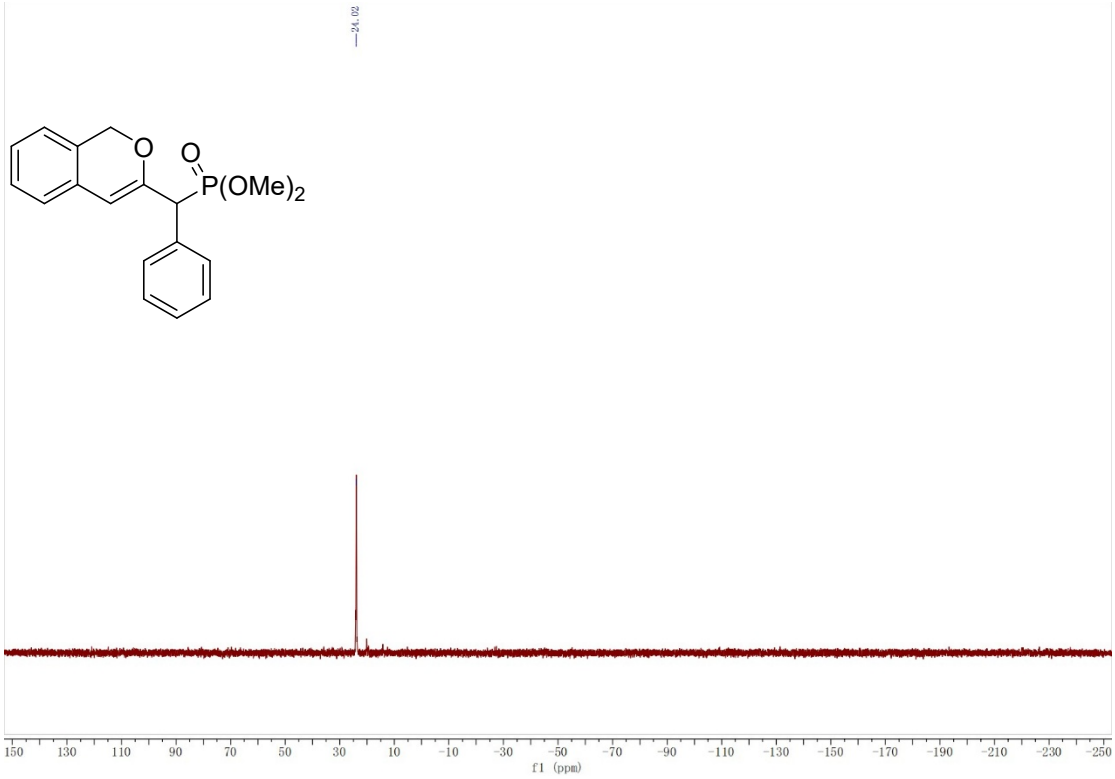
^{1}H NMR Spectra of **3ag** (400 MHz, $CDCl_3$)



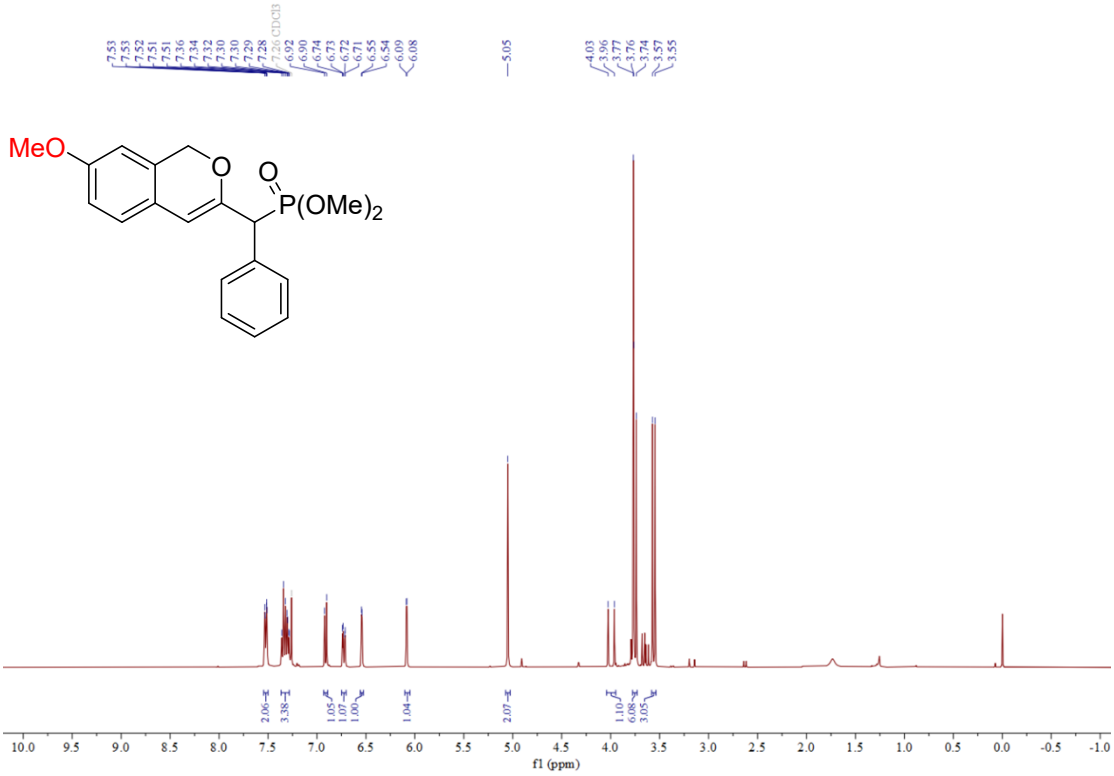
^{13}C NMR Spectra of **3ag** (100 MHz, $CDCl_3$)



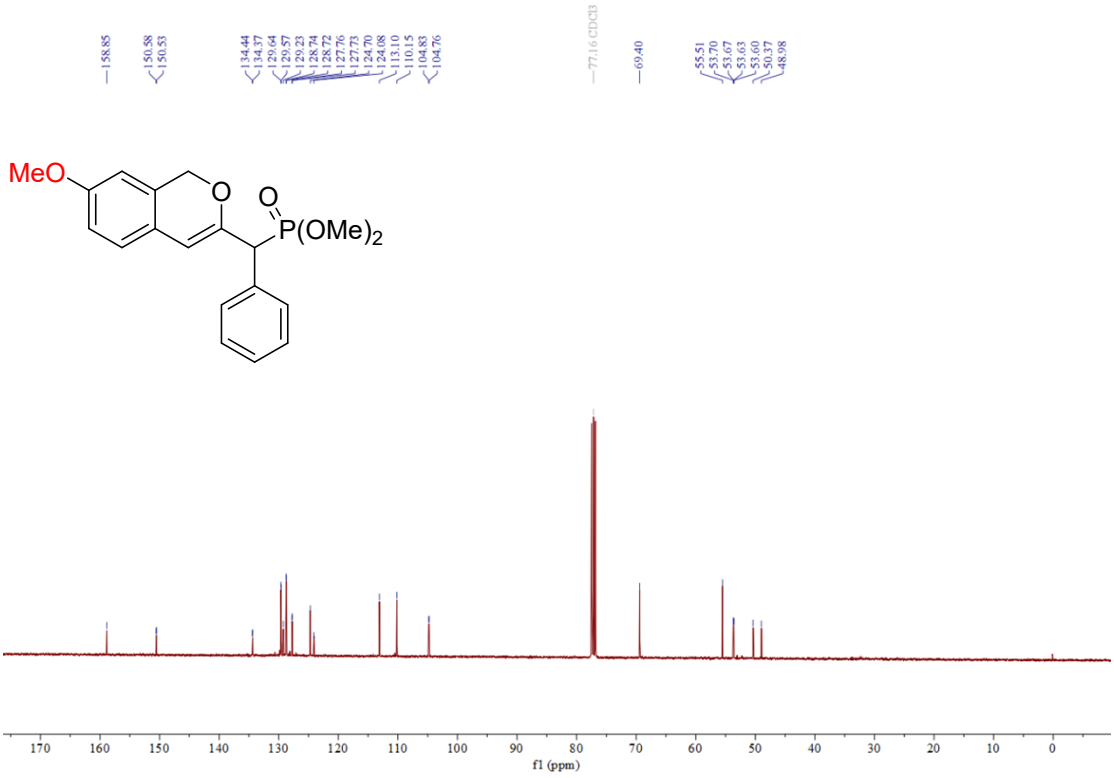
^{31}P NMR Spectra of **3ag** (162 MHz, $CDCl_3$)



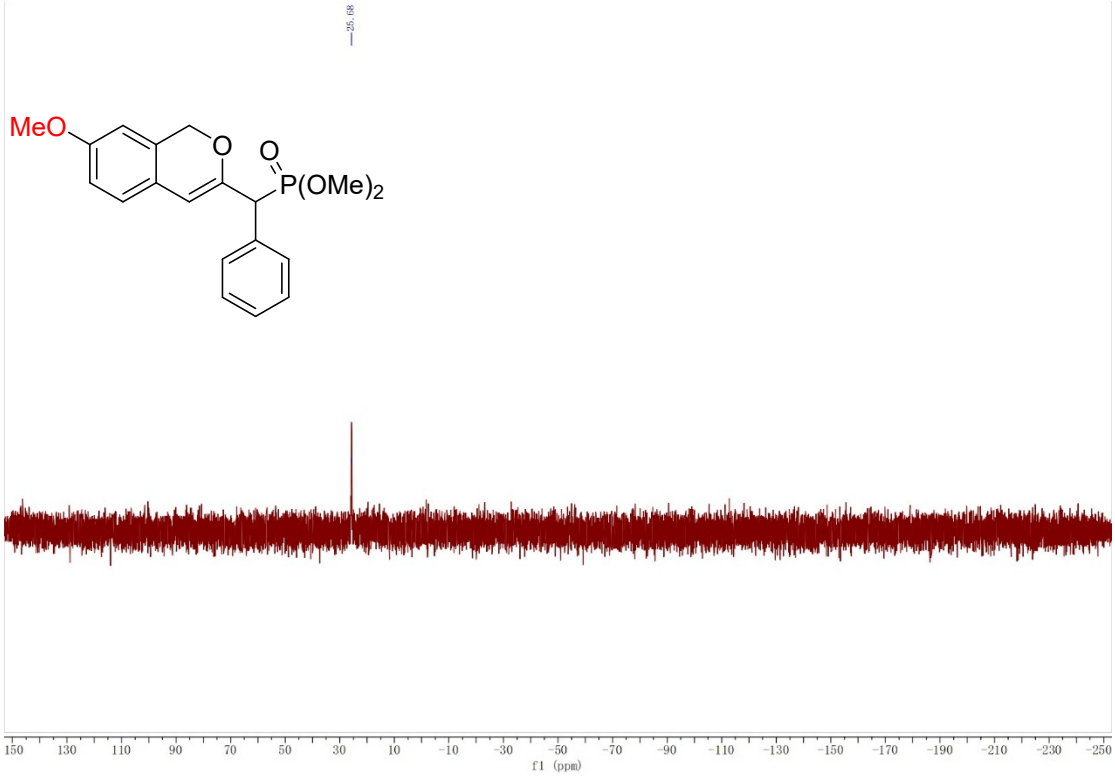
^{1}H NMR Spectra of **3ah** (400 MHz, $CDCl_3$)



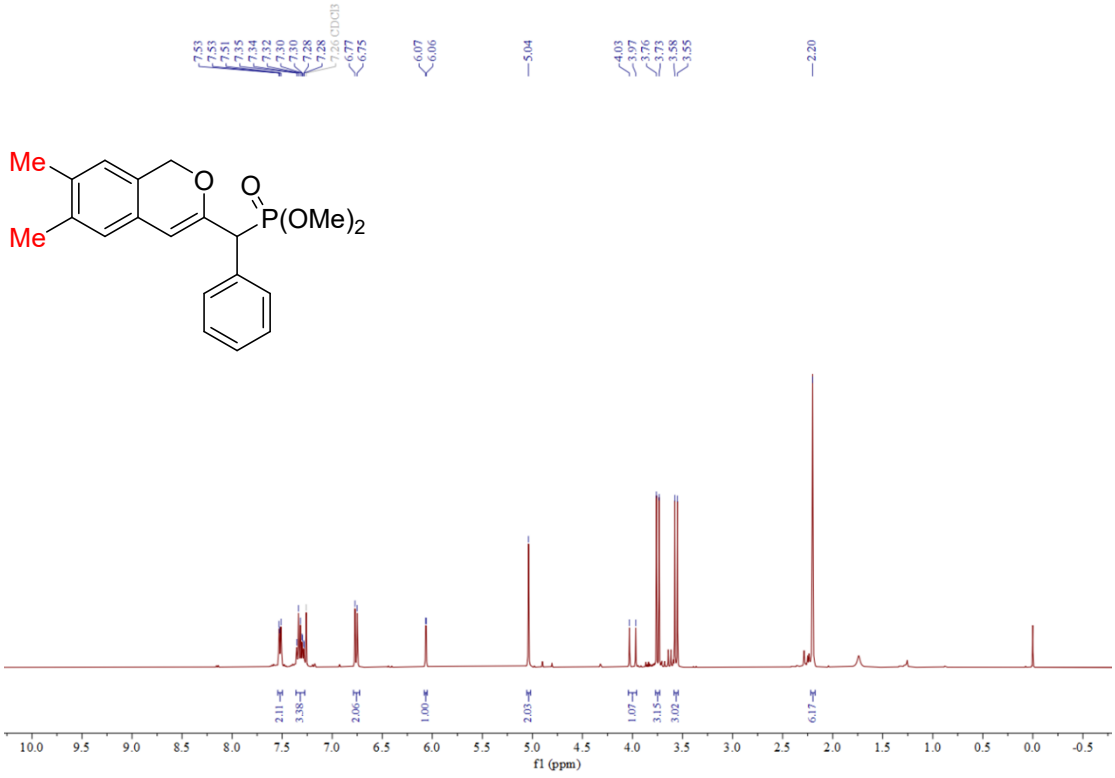
^{13}C NMR Spectra of **3ah** (100 MHz, $CDCl_3$)



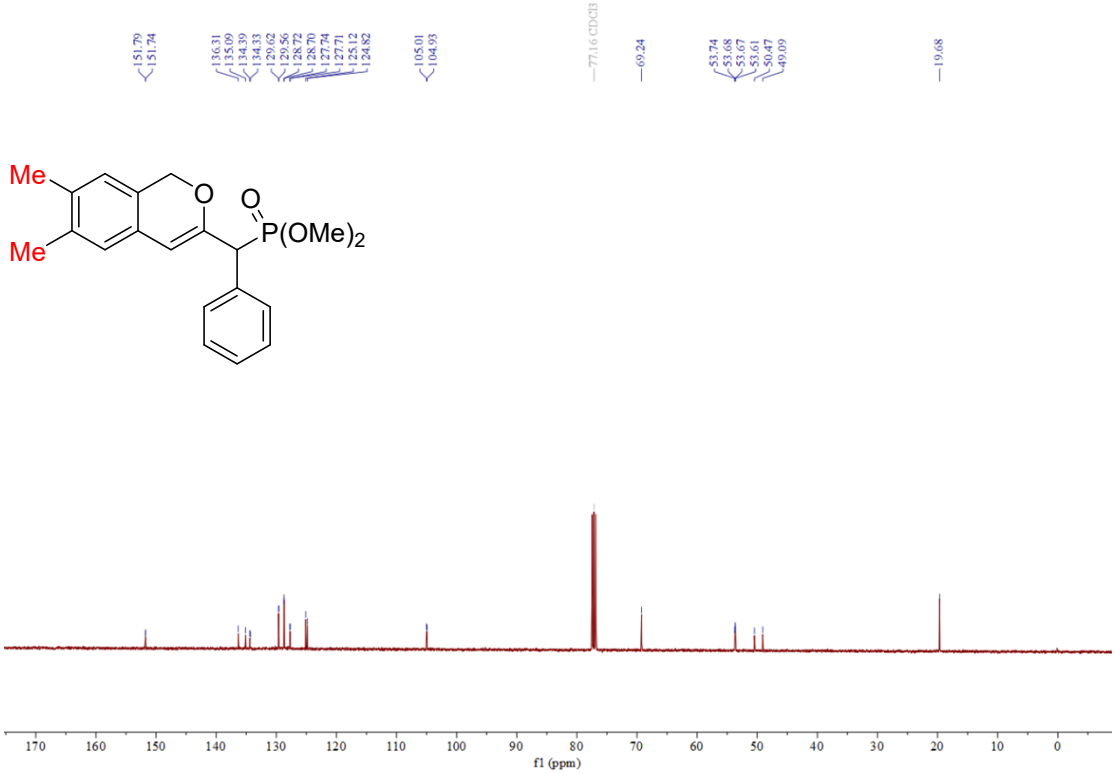
^{31}P NMR Spectra of **3ah** (162 MHz, $CDCl_3$)



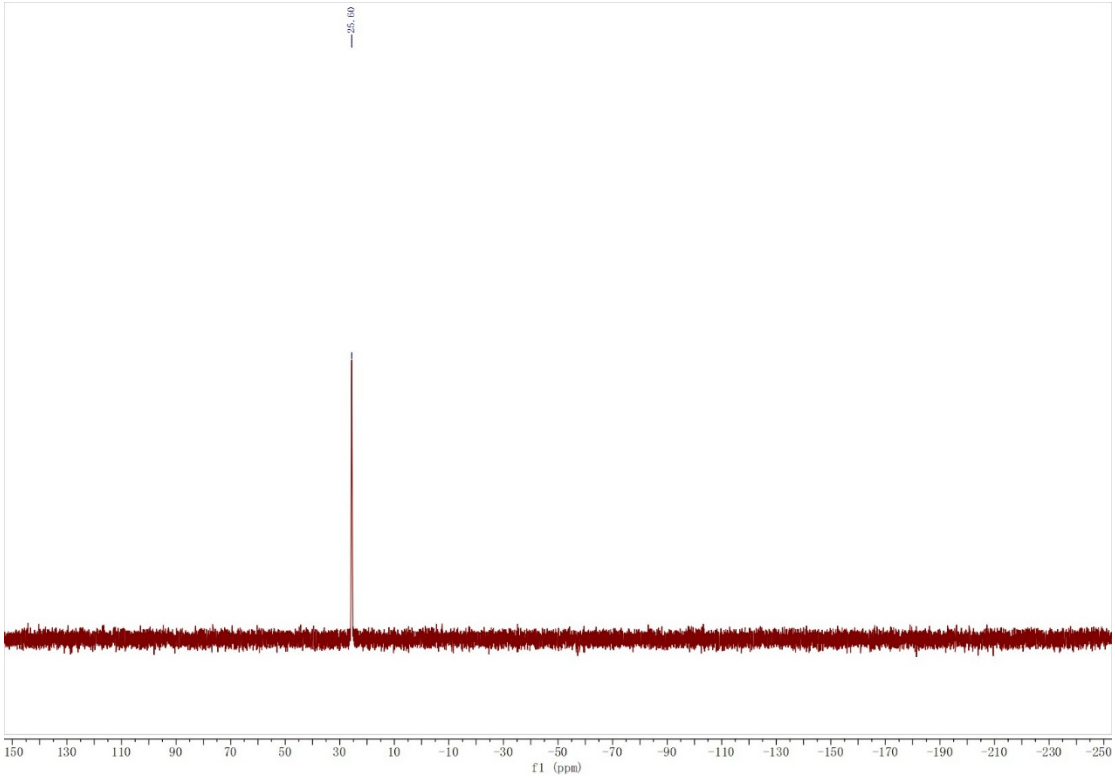
^{1}H NMR Spectra of **3ai** (400 MHz, $CDCl_3$)



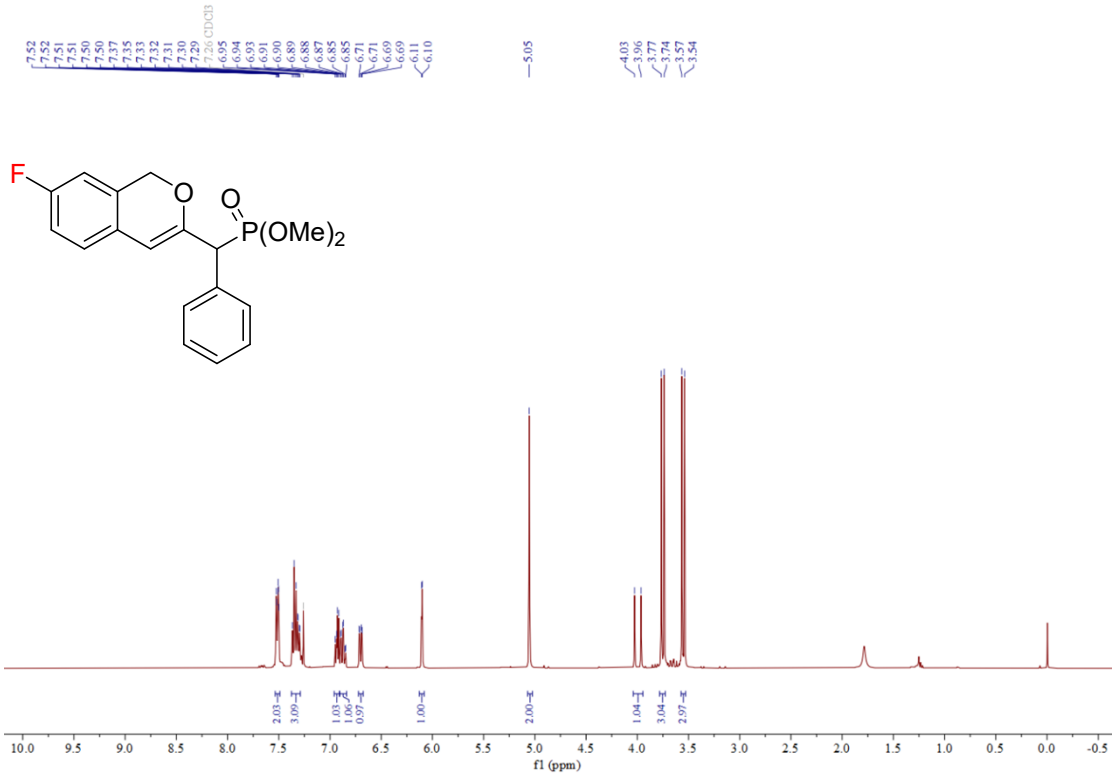
^{13}C NMR Spectra of **3ai** (100 MHz, $CDCl_3$)



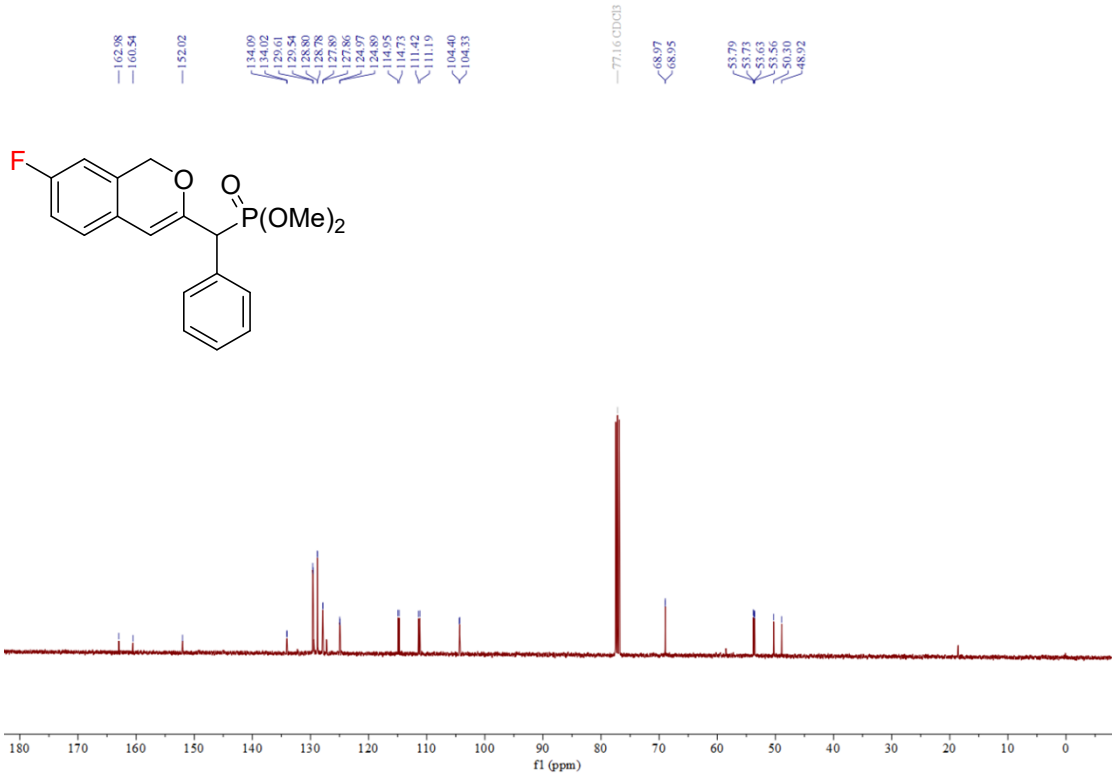
^{31}P NMR Spectra of **3ai** (162 MHz, $CDCl_3$)



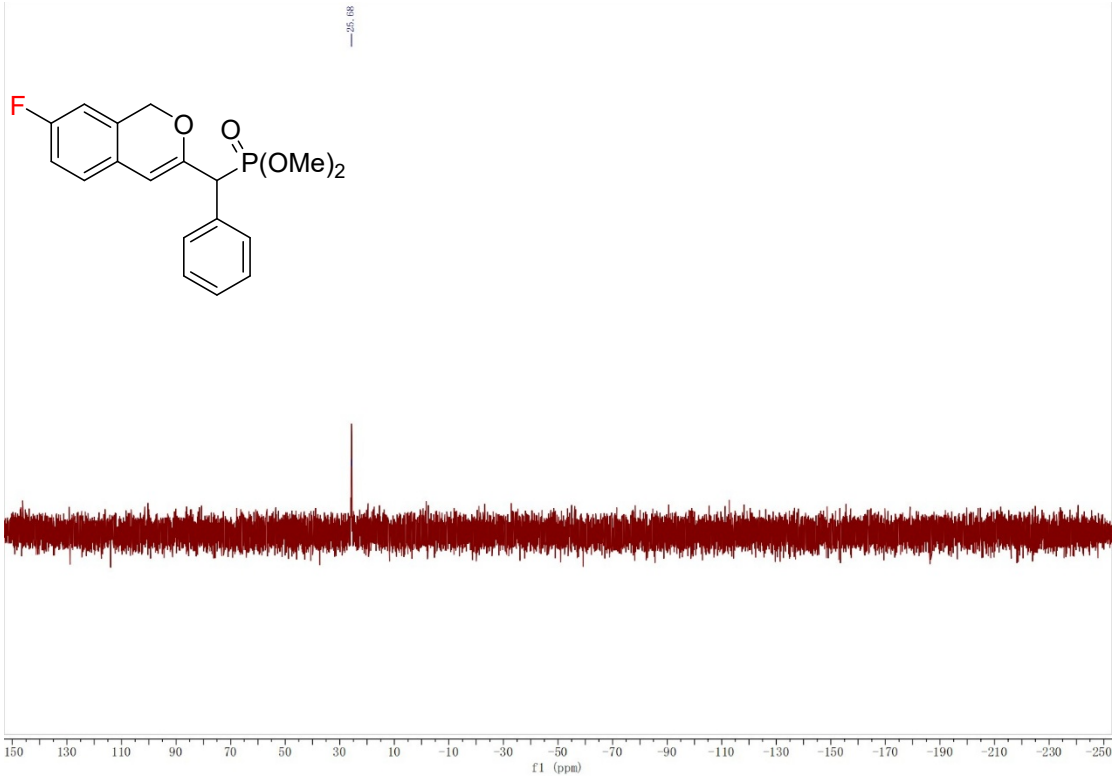
^{1}H NMR Spectra of **3aj** (400 MHz, $CDCl_3$)



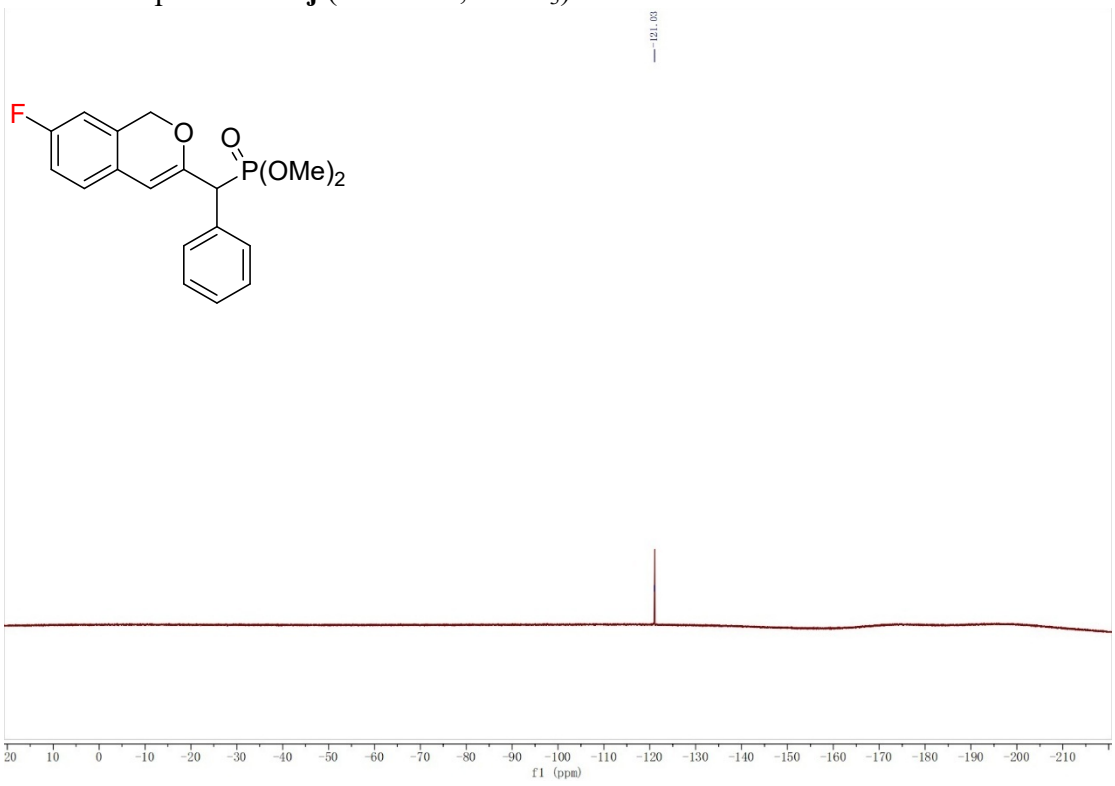
^{13}C NMR Spectra of **3aj** (100 MHz, $CDCl_3$)



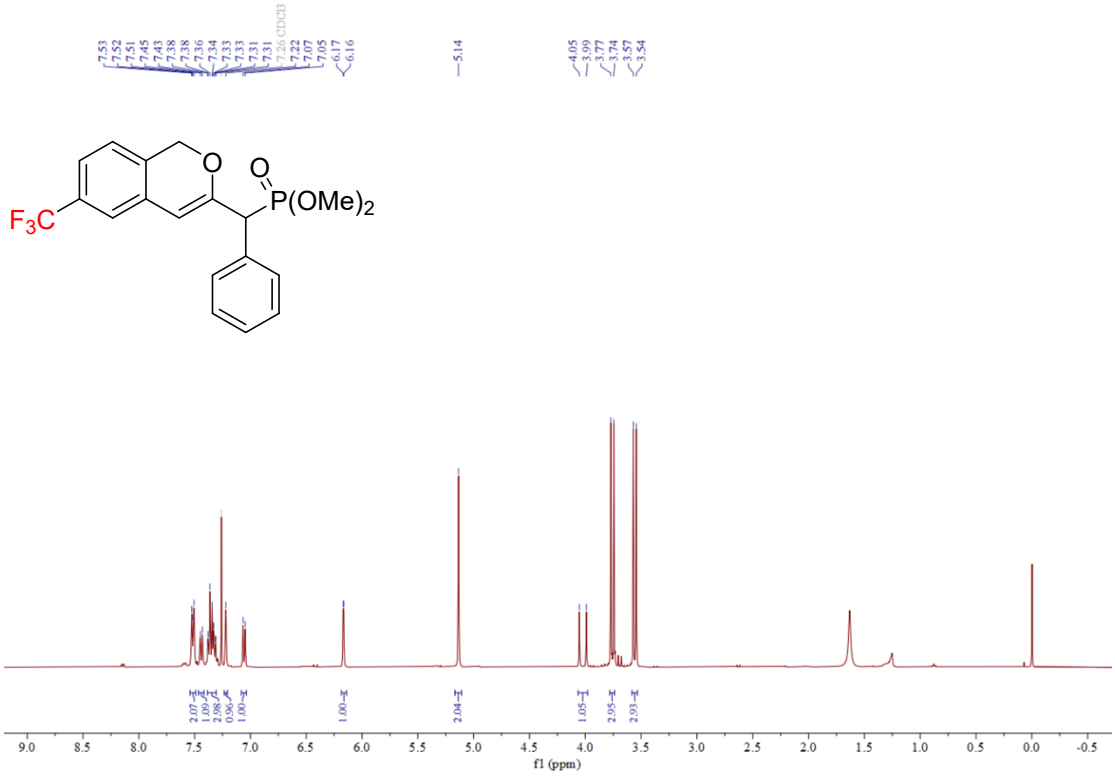
^{31}P NMR Spectra of **3aj** (162 MHz, $CDCl_3$)



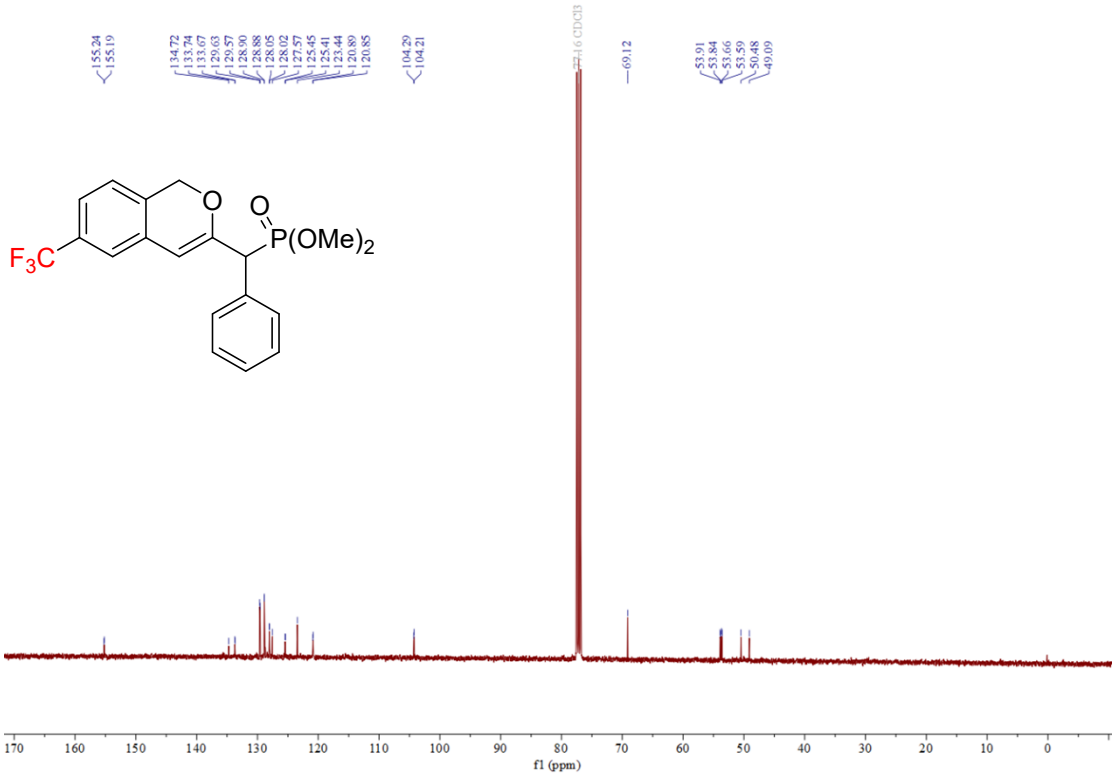
^{19}F NMR Spectra of **3aj** (376 MHz, $CDCl_3$)



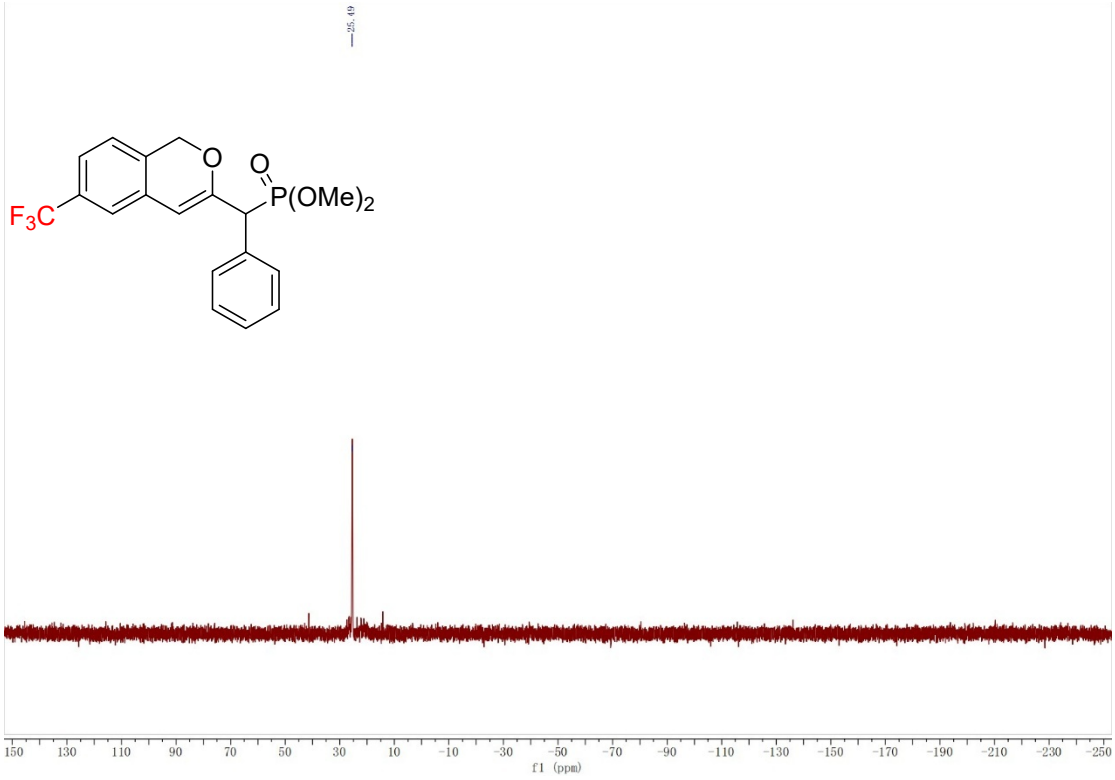
^{1}H NMR Spectra of **3ak** (400 MHz, $CDCl_3$)



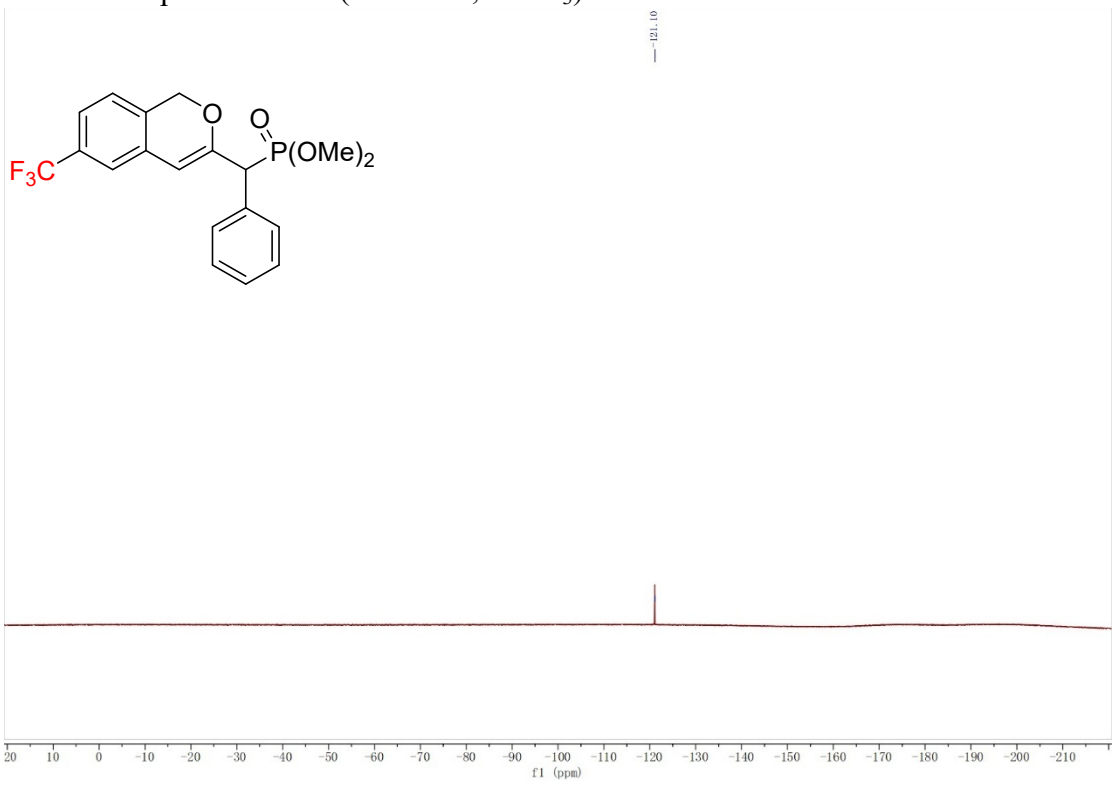
^{13}C NMR Spectra of **3ak** (100 MHz, $CDCl_3$)



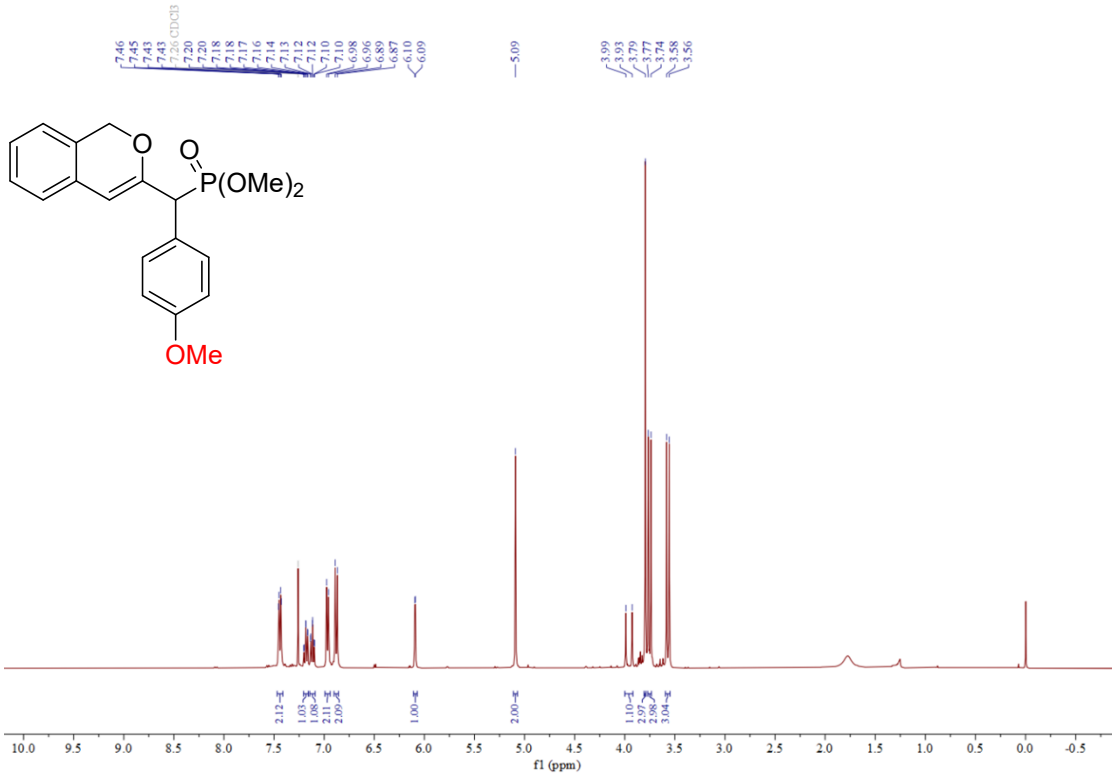
^{31}P NMR Spectra of **3ak** (162 MHz, $CDCl_3$)



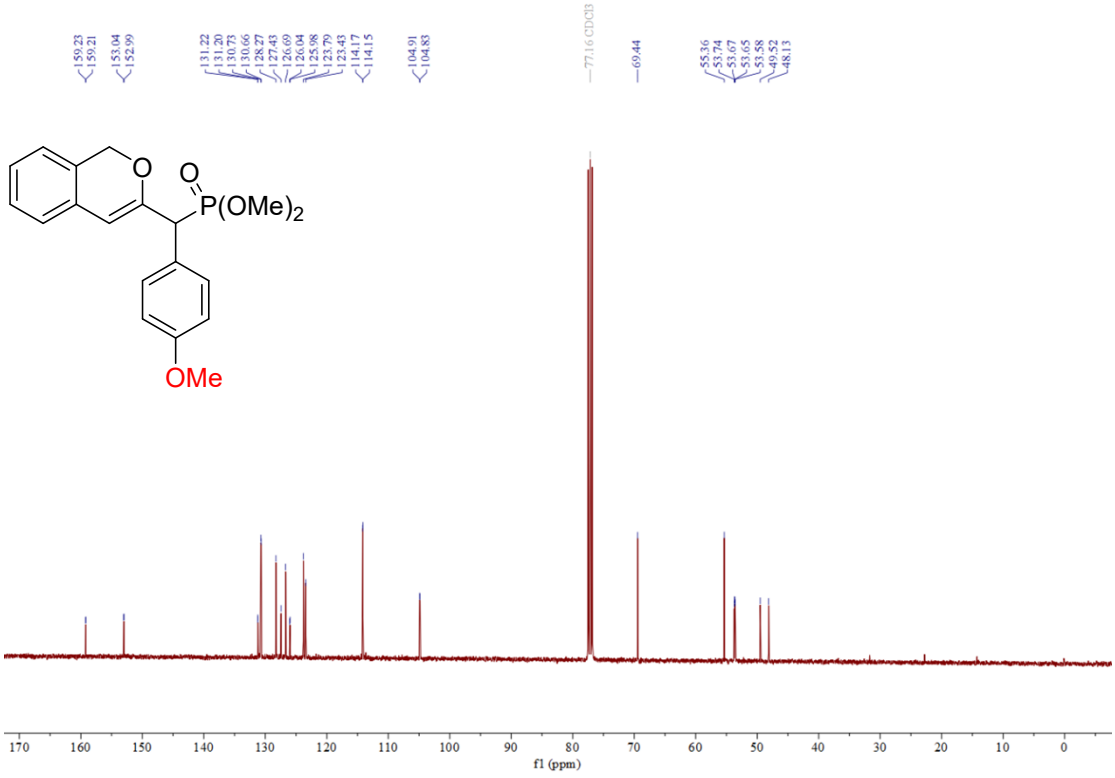
^{19}F NMR Spectra of **3ak** (376 MHz, $CDCl_3$)



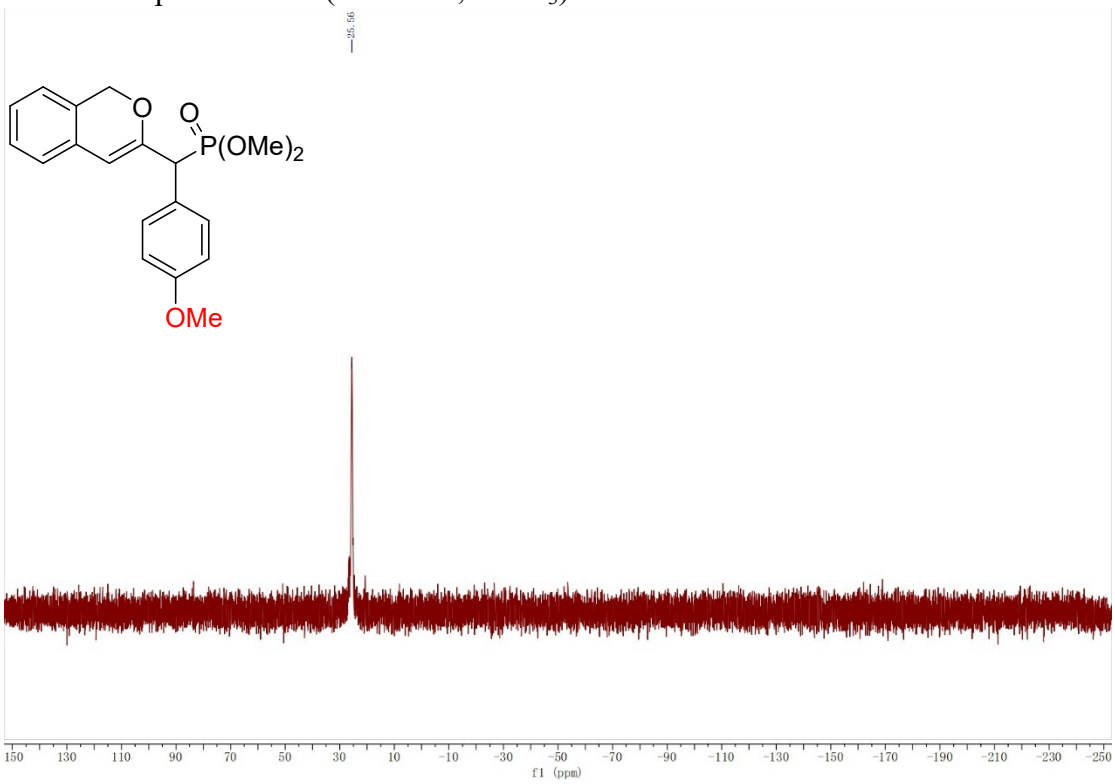
^{1}H NMR Spectra of **3al** (400 MHz, $CDCl_3$)



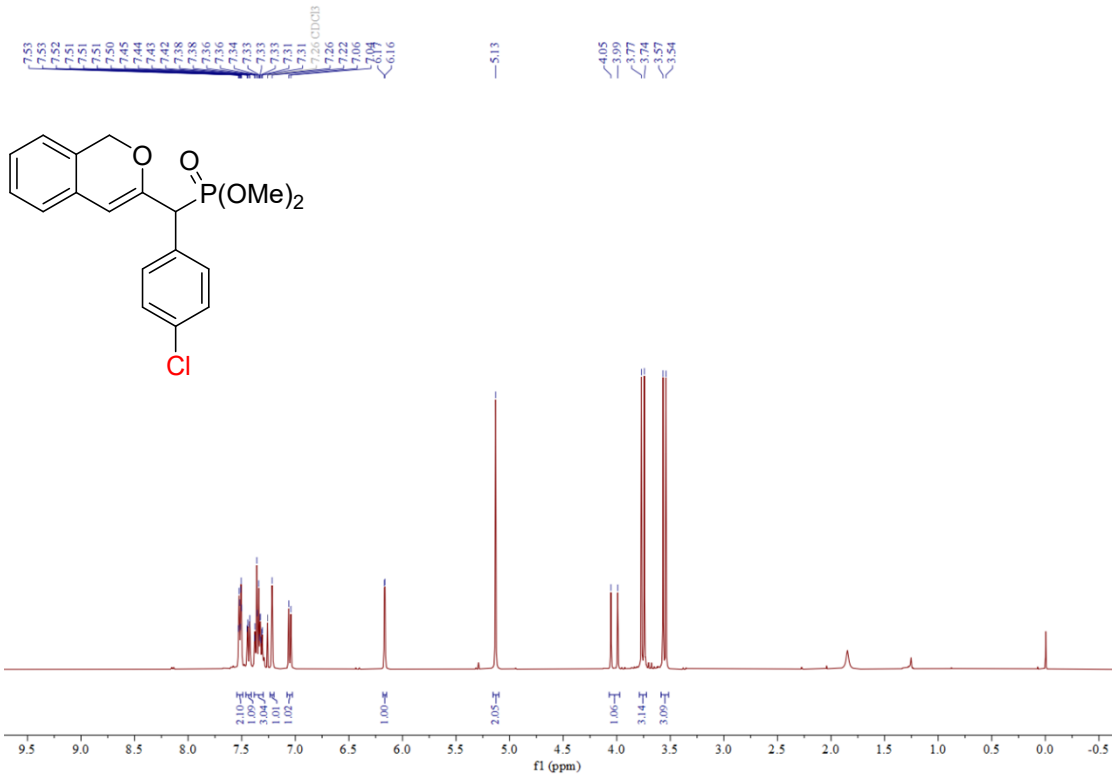
^{13}C NMR Spectra of **3al** (100 MHz, $CDCl_3$)



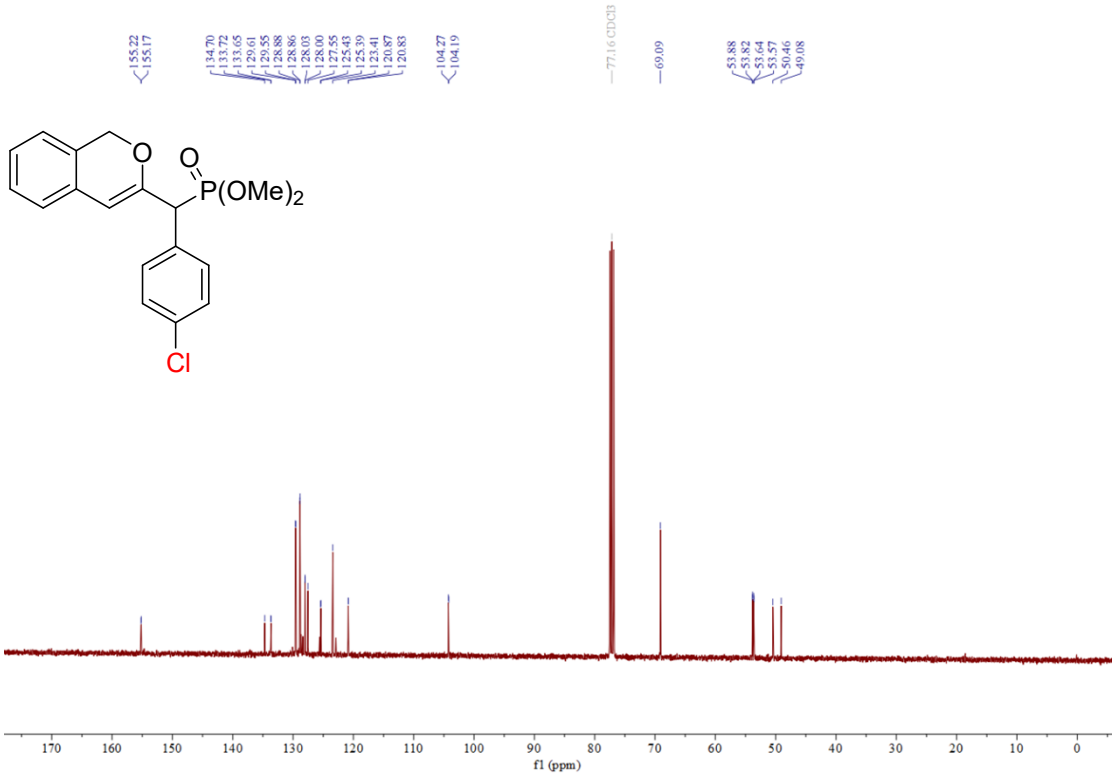
^{31}P NMR Spectra of **3al** (162 MHz, $CDCl_3$)



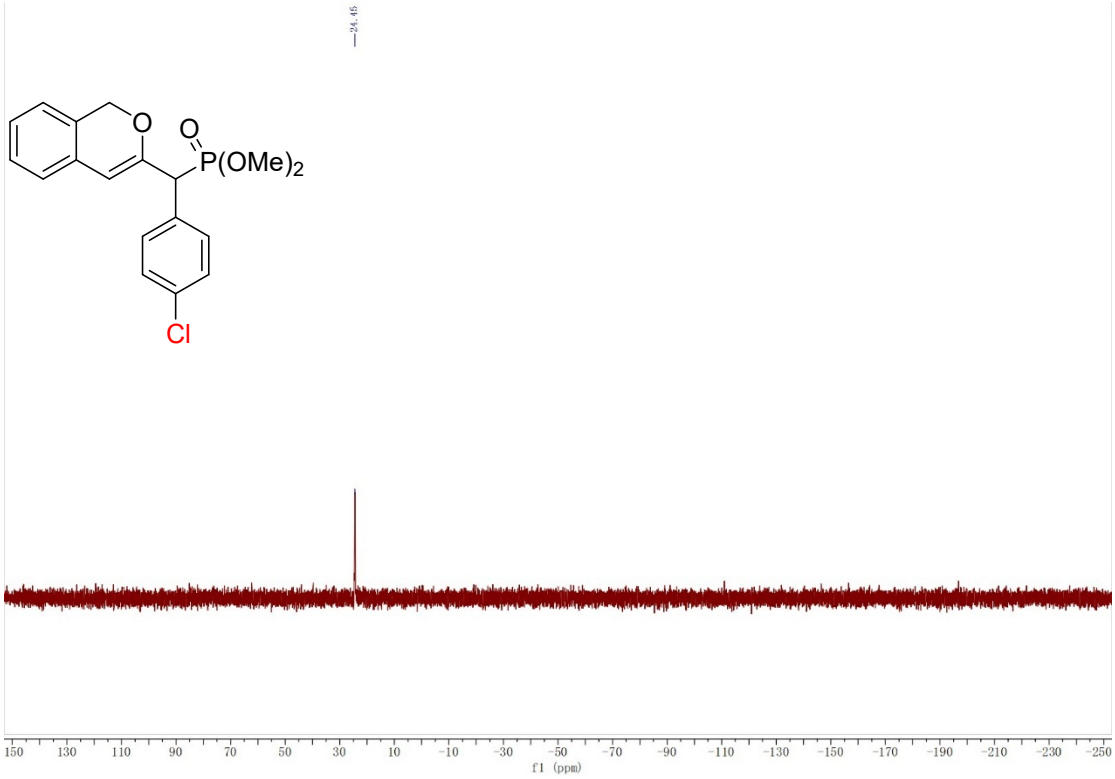
^{1}H NMR Spectra of **3am** (400 MHz, $CDCl_3$)



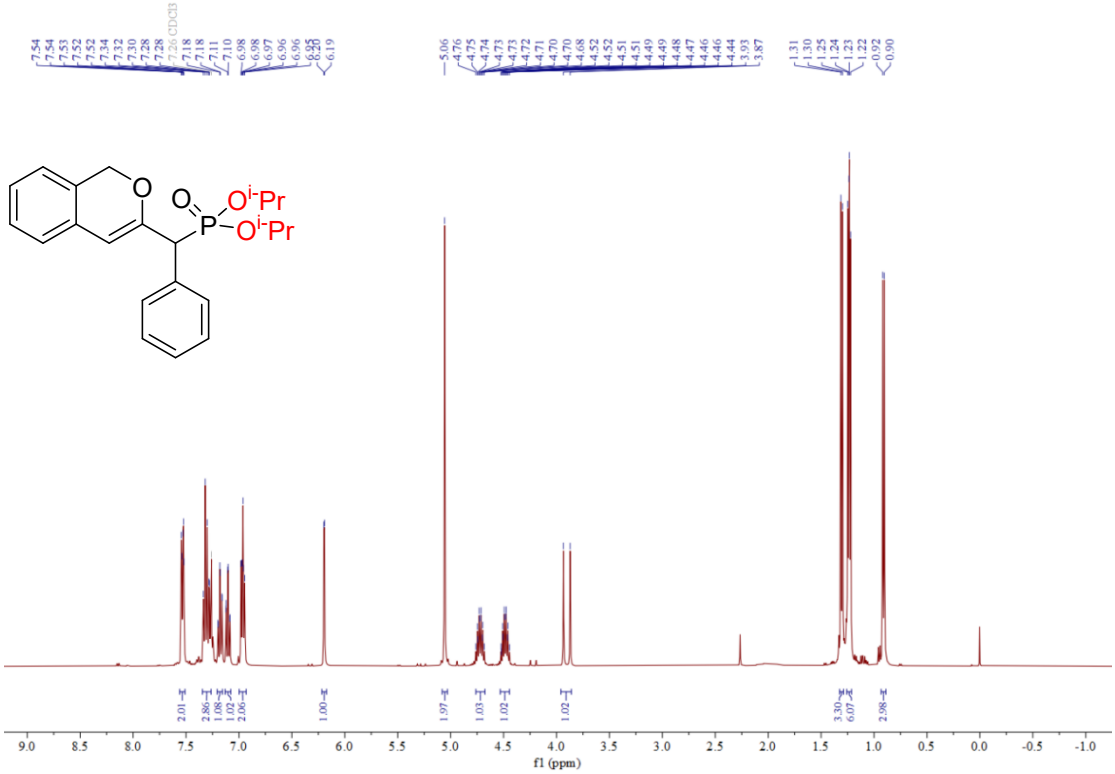
^{13}C NMR Spectra of **3am** (100 MHz, $CDCl_3$)



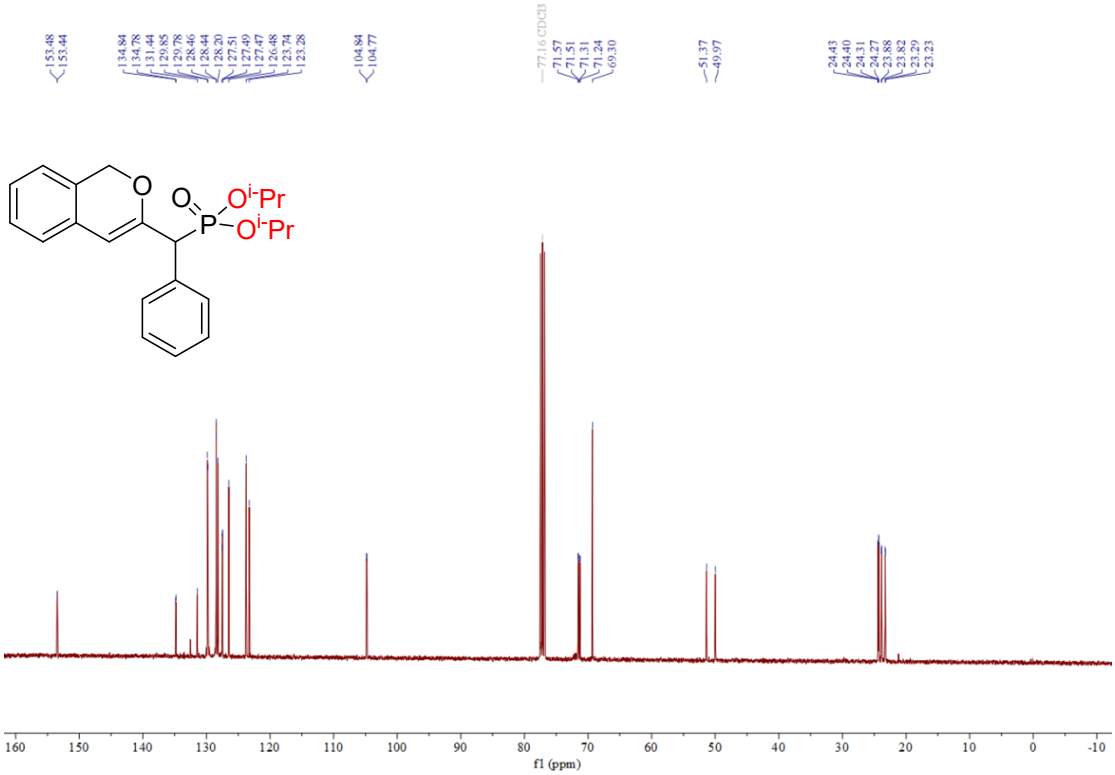
^{31}P NMR Spectra of **3am** (162 MHz, $CDCl_3$)



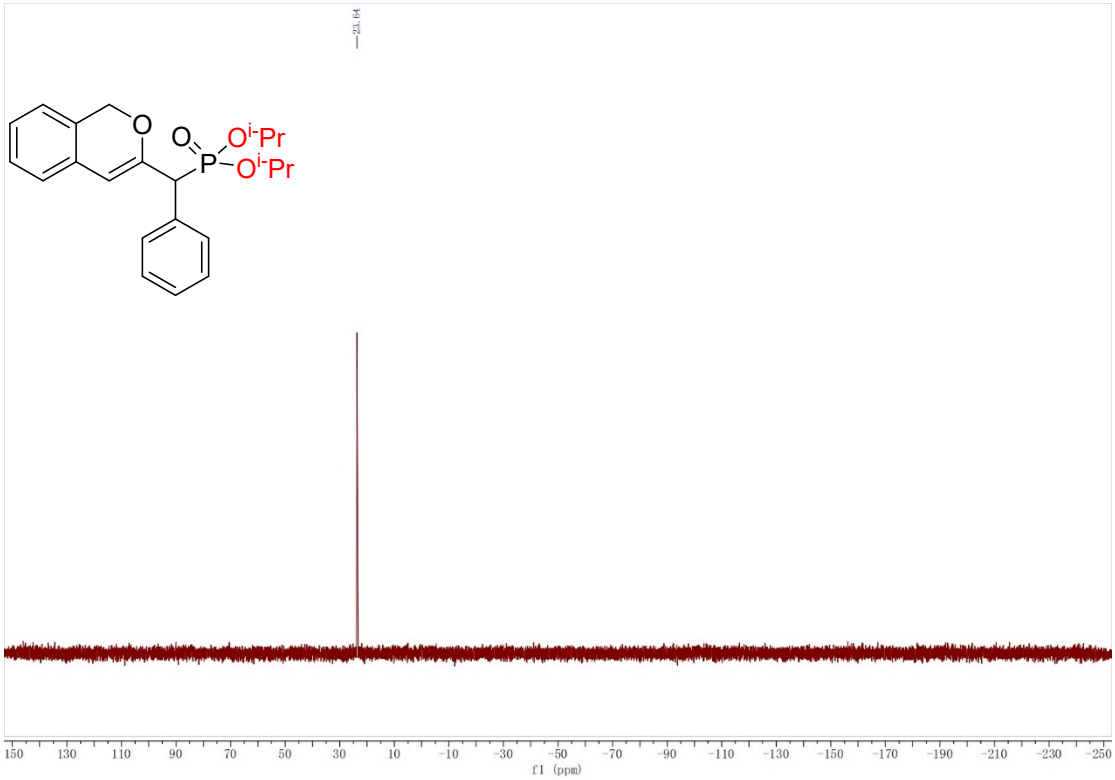
^{1}H NMR Spectra of **3an** (400 MHz, $CDCl_3$)



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

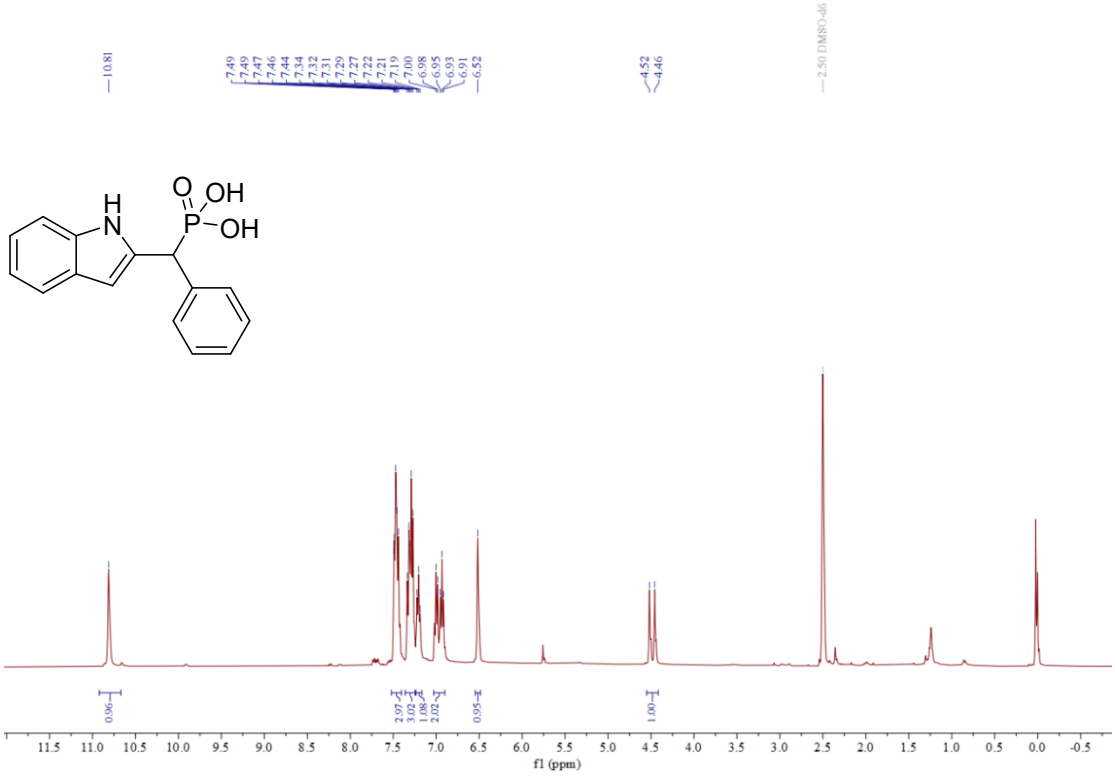


^{31}P NMR Spectra of **3an** (162 MHz, $CDCl_3$)

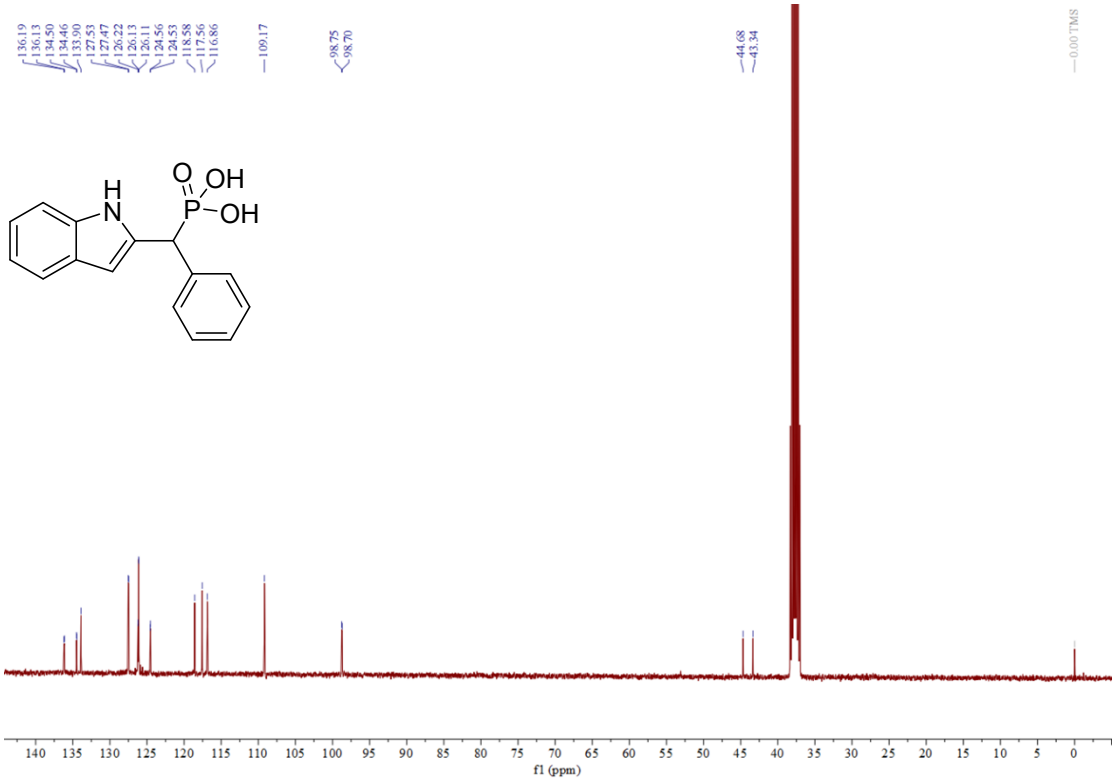


NMR Spectra of Products 4a–7a, 3yy-1:

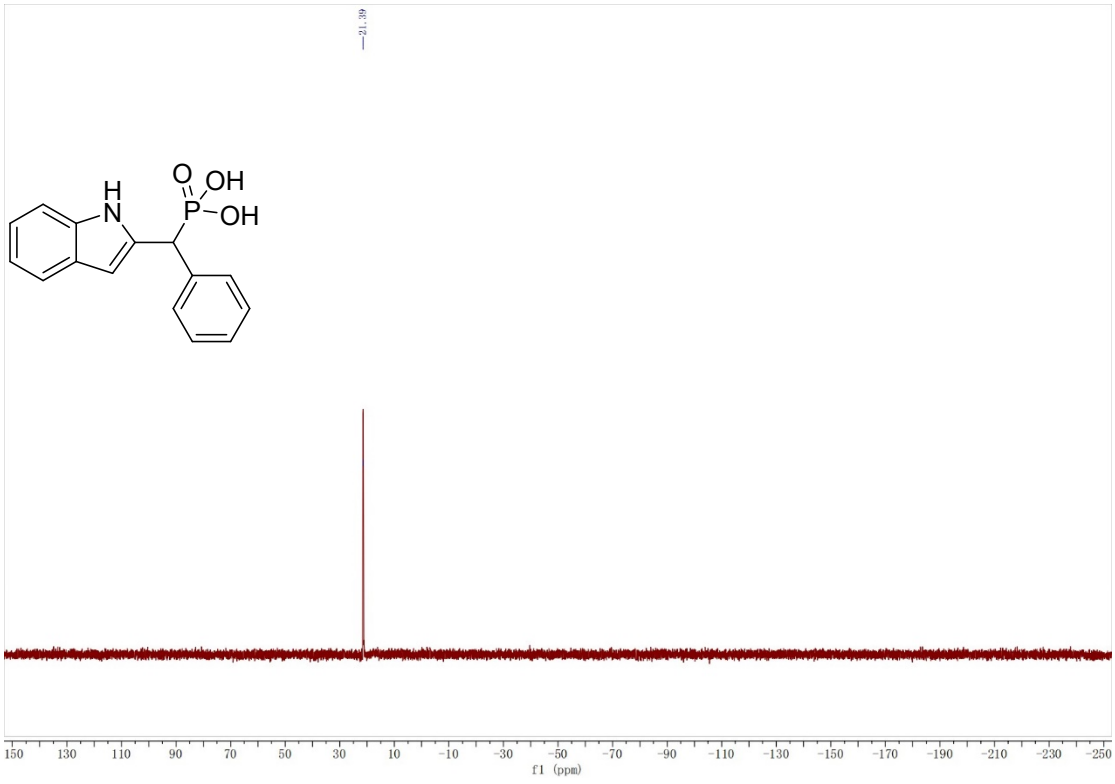
^{1}H NMR Spectra of **4a** (400 MHz, DMSO)



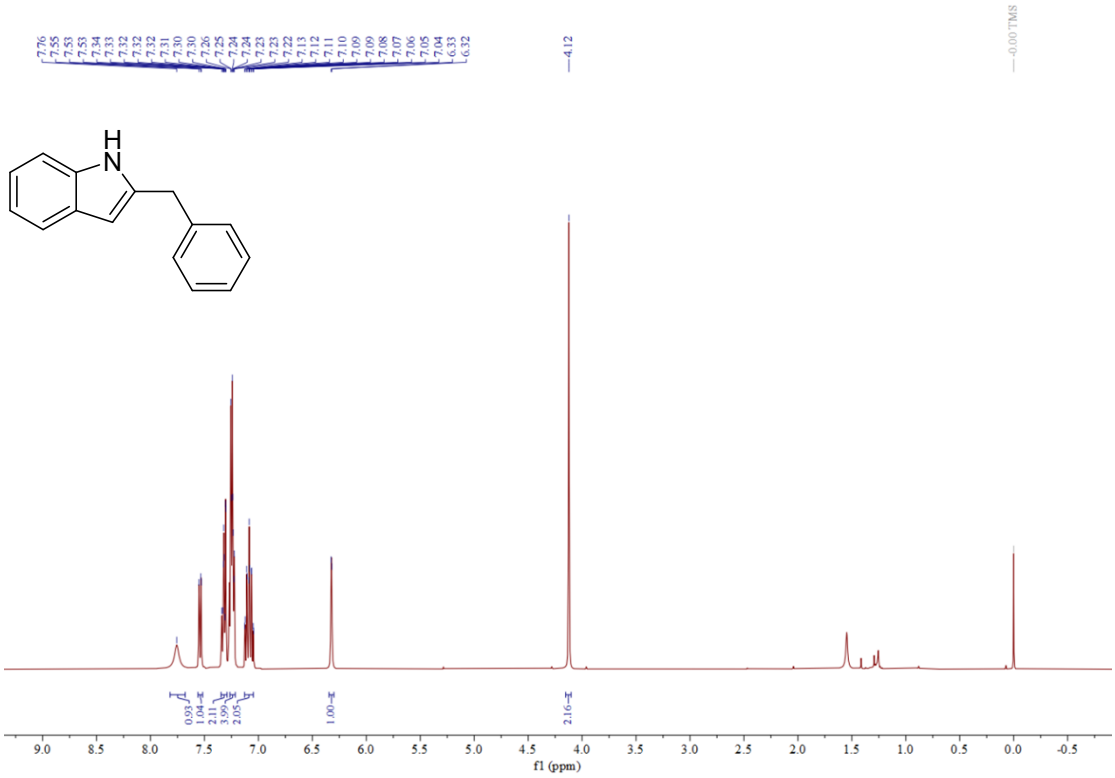
^{13}C NMR Spectra of **4a** (100 MHz, DMSO)



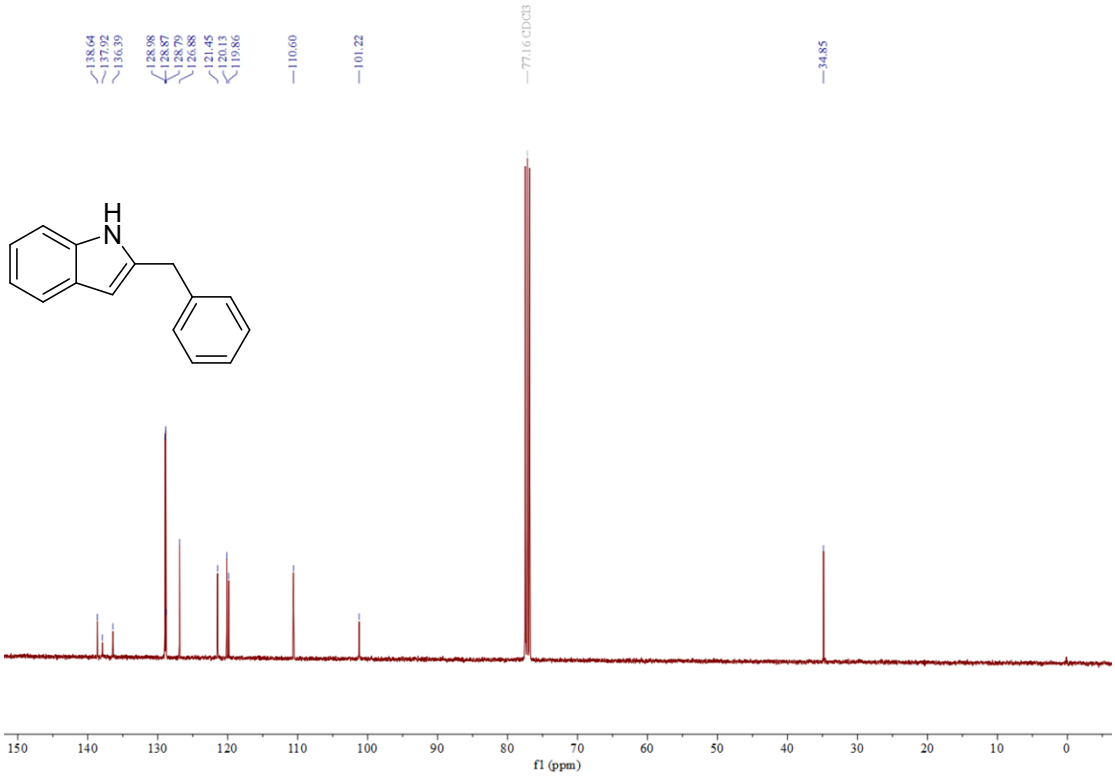
^{31}P NMR Spectra of **4a** (162 MHz, DMSO)



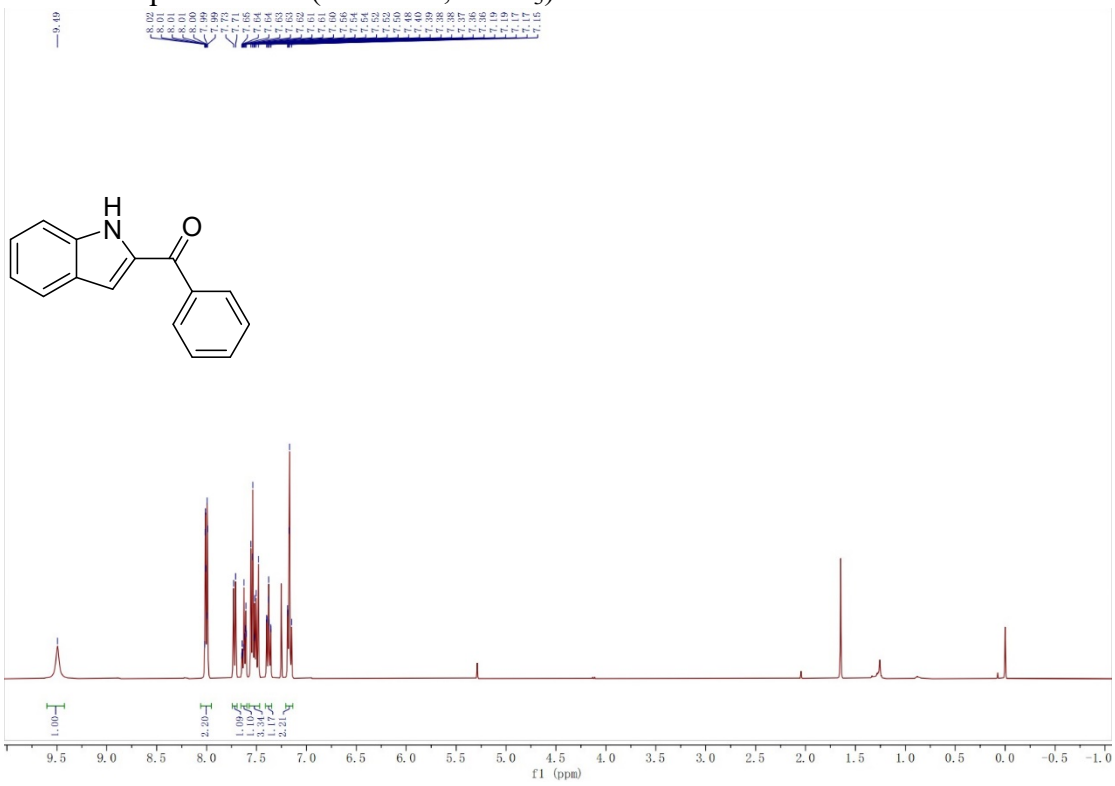
^{1}H NMR Spectra of **5a** (400 MHz, $CDCl_3$)



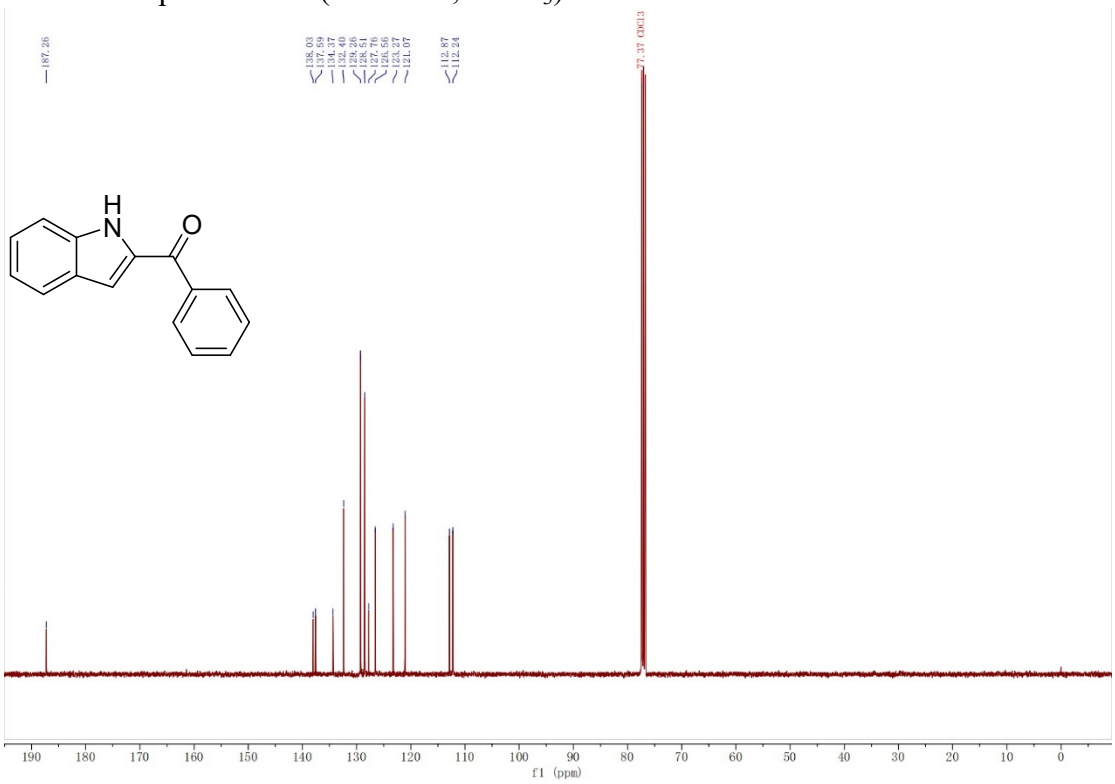
^{13}C NMR Spectra of **5a** (100 MHz, $CDCl_3$)



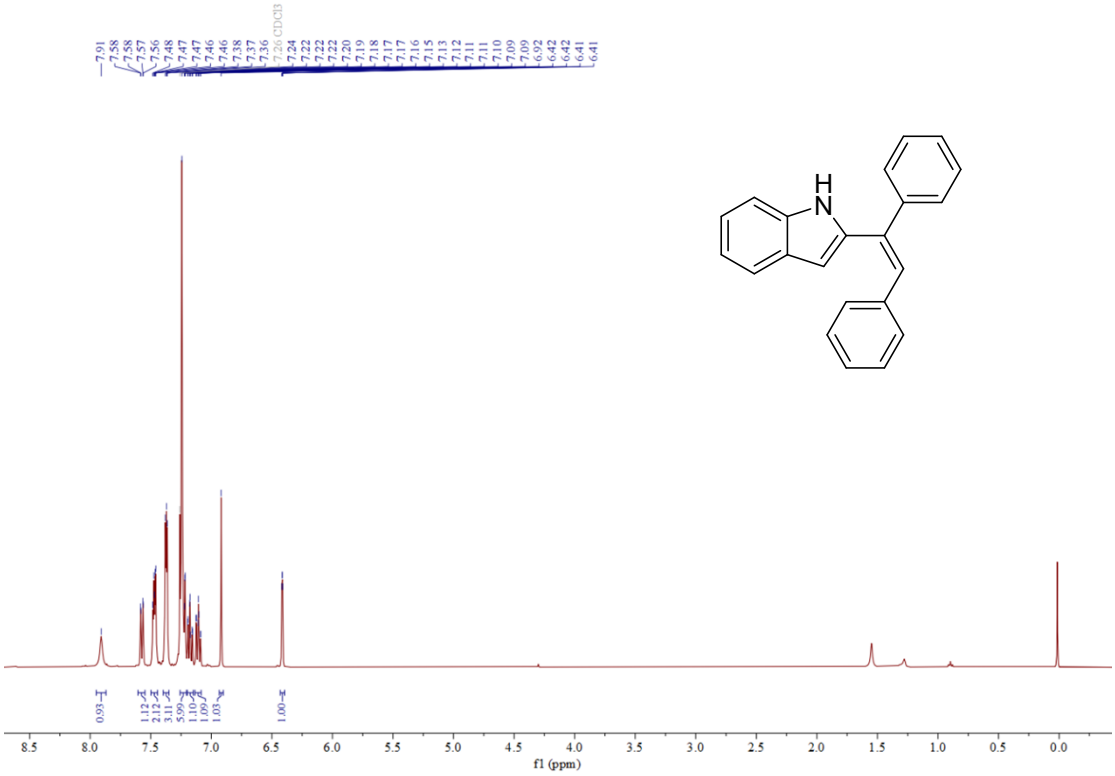
^{1}H NMR Spectra of **6a** (400 MHz, $CDCl_3$)



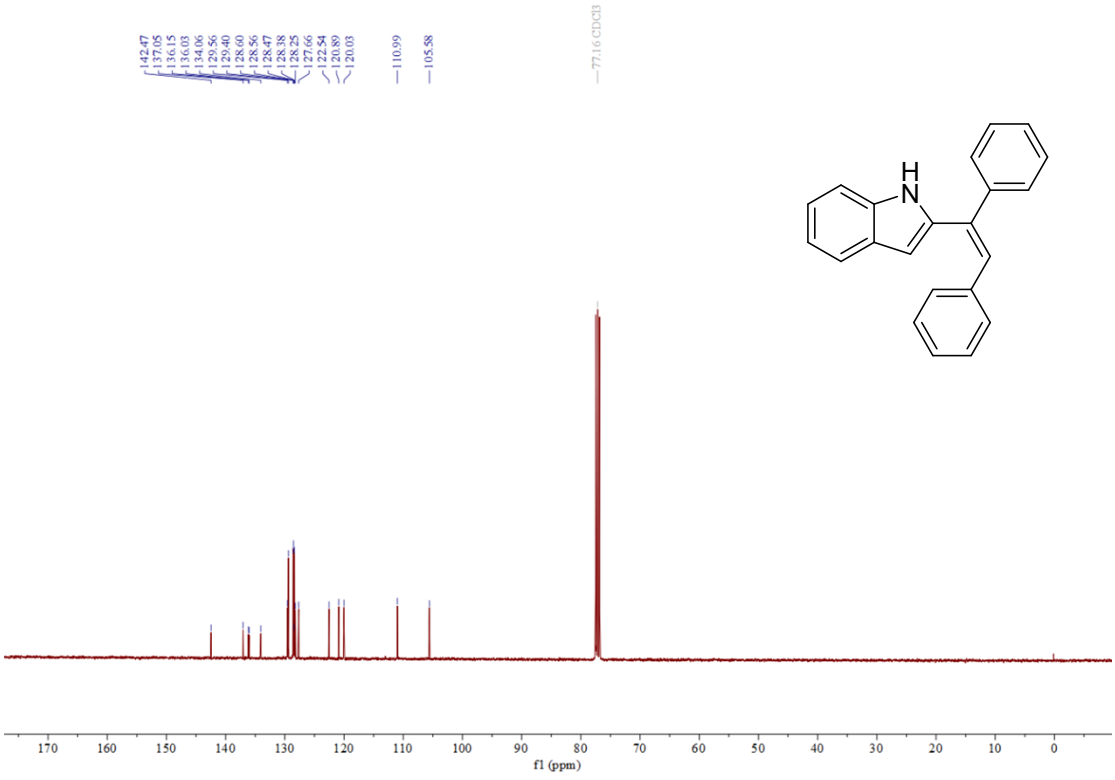
^{13}C NMR Spectra of **6a** (100 MHz, $CDCl_3$)



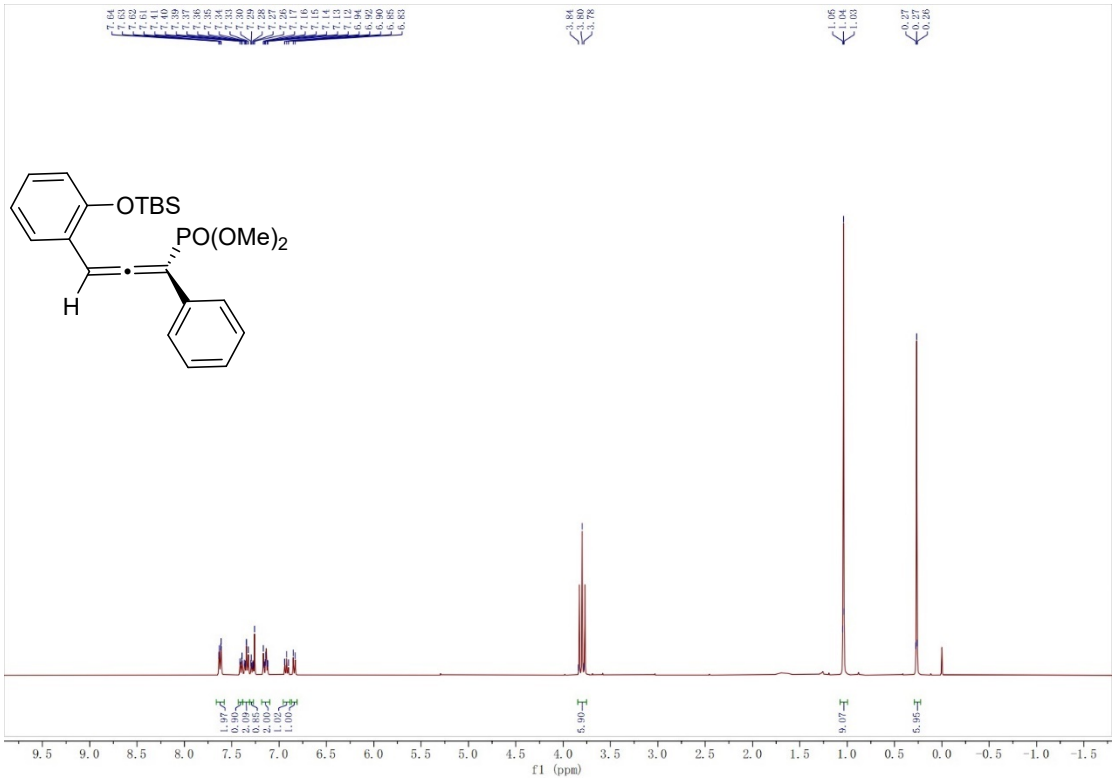
^{1}H NMR Spectra of **7a** (400 MHz, $CDCl_3$)



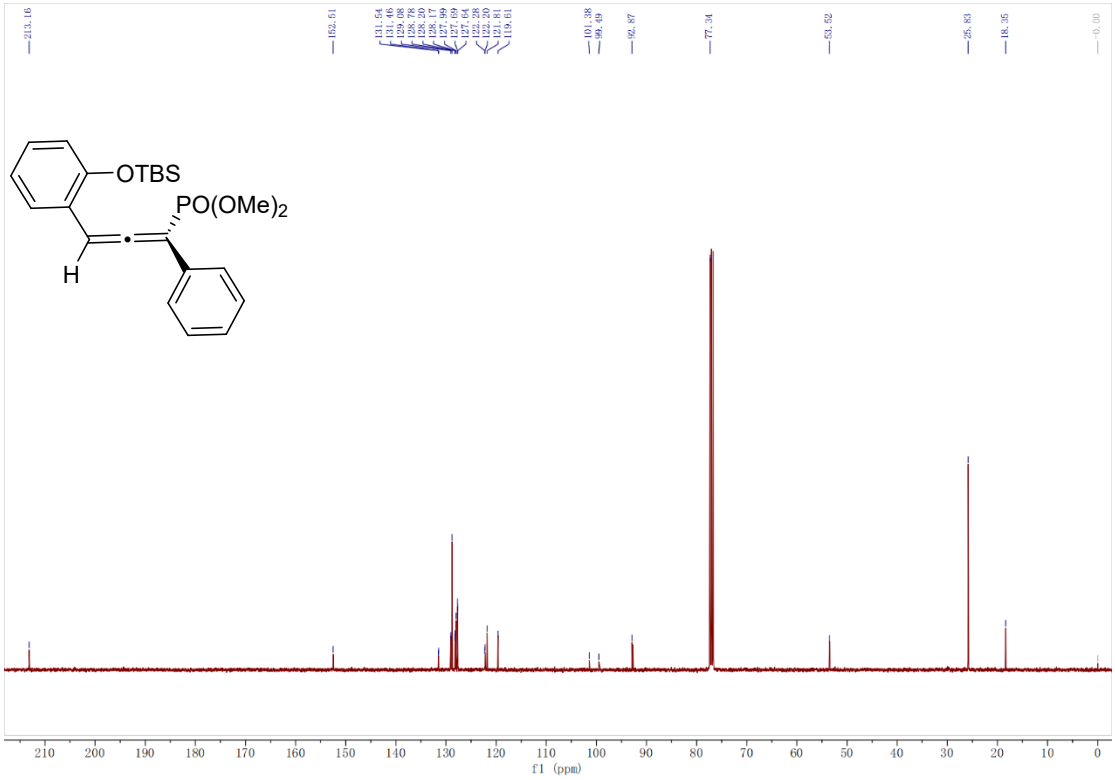
^{13}C NMR Spectra of **7a** (100 MHz, $CDCl_3$)



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



^{13}C NMR Spectra of **3yy-1** (100 MHz, $CDCl_3$)



^{31}P NMR Spectra of **3yy-1** (162 MHz, $CDCl_3$)