Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Silver-Catalyzed P-centered anion nucleophilic addition to isocyanide: Access to 2-phosphinoyl indoles/indol-3-ols

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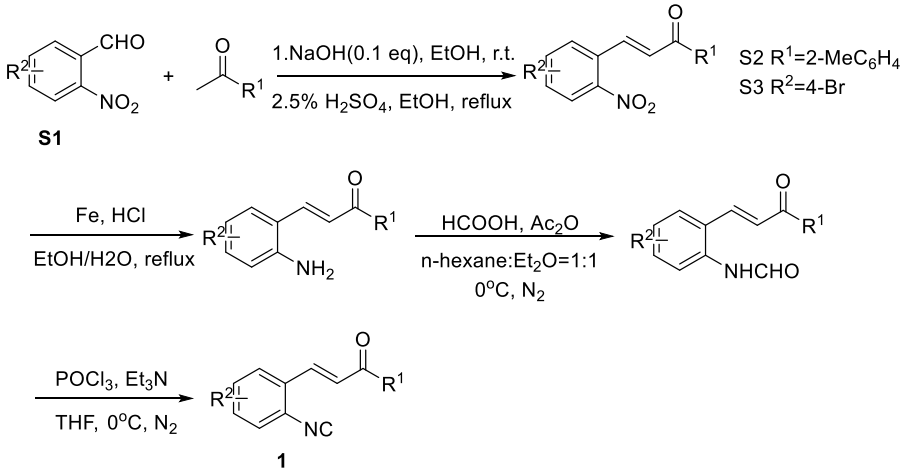
I. General information

All reagents were commercially available and used without further purification, unless otherwise indicated. Chromatography was carried out on flash silica gel (300−400 mesh). All reactions were monitored by TLC, performed on glass plates with precoated silica gel 60 (F254). ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra were measured on a 400 MHz Bruker instrument, with TMS as the internal standard. All chemical shifts are reported in ppm scale. High-resolution mass spectra (HRMS) were acquired using a Bruker microTOF II focusing spectrometer (ESI).

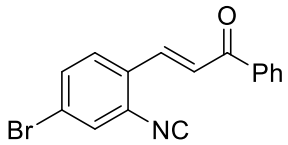
II. Preparation and analytical data of isocyanides 1 and 5

Isonitriles **1** was prepared according to previous literature report.[1]

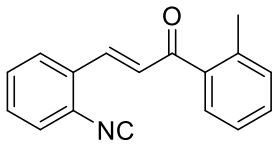


Ketones **S2** and **S3** were prepared from **S1** according to literature procedures. 2-nitrobenzaldehyde and acetophenone are commercially available. Isonitriles **1** were prepared according to the literature procedures by the typical formylation and dehydration procedure.

Analytical data of 3 (3d, 3j)

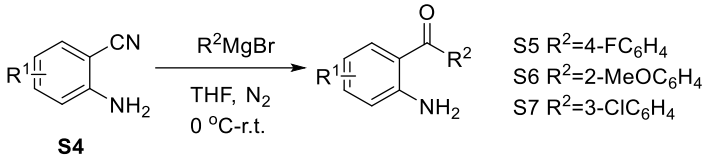


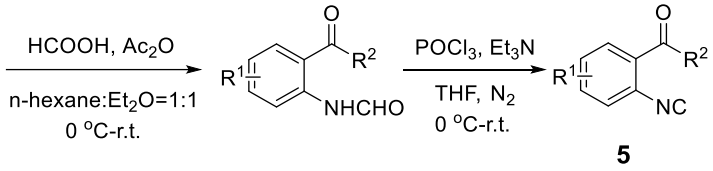
(E)-3-(4-Bromo-2-isocyanophenyl)-1-phenylprop-2-en-1-one (3d). Eluent: PE/EA (20:1), yellow solid (1.38g, 88%), **m.p.:** 120-123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.95 (d, *J* = 15.6 Hz, 1H), 7.67 – 7.58 (m, 5H), 7.52 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.7, 170.9, 137.5, 136.8, 133.4, 133.1, 130.8, 130.4, 128.8, 128.7, 128.7, 126.5, 124.2. **HRMS (ESI)** m/z: $[M+H]^+$ called for $C_{16}H_{11}BrNO^+$ 312.0019; found 312.0012.



(E)-3-(2-Isocyanophenyl)-1-(o-tolyl)prop-2-en-1-one(3g). Eluent: PE/EA(20:1)，yellow solid (1.0g, 83%), **m.p.:** 78-81 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.50-7.35 (m, 4H), 7.31 (s, 2H), 7.23 (d, *J* = 16 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.5, 169.0, 138.7, 138.2, 137.5, 131.6, 131.2, 131.1, 130.9, 130.2, 129.7, 128.5, 127.8, 127.2, 125.6, 20.5. **HRMS (ESI)** m/z: $[M+H]^+$ called for $C_{17}H_{14}NO^+$ 248.1070; found 248.1060.

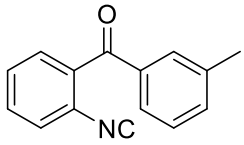
o-Carbonyl arylisonitrile **5** was prepared according to previous literature report.[2]



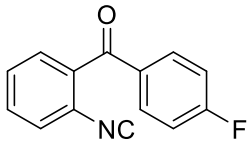


Ketones **S5**, **S6** and **S7** were prepared from **S4** according to literature procedures. (2-Aminophenyl)(phenyl)methanone and 2-aminophenyl ethenone are commercially available. Isocyanides **5** were prepared according to the literature procedures by the typical formylation and dehydration procedure.

Analytical data of 5 (5i, 5j, 5k, 5l)

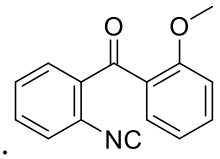


(2-Isocyanophenyl)(m-tolyl)methanone (5i). Eluent: PE/EA (20:1), yellow oli (0.59 mg, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.60 – 7.48 (m, 5H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.9, 138.7, 136.4, 136.2, 134.9, 131.4, 130.4, 129.4, 129.2, 128.6, 127.9, 127.6, 21.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NO^+$ 222.0913; found.222.0915.

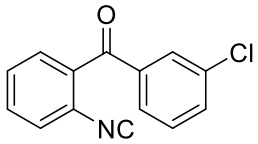


(4-Fluorophenyl)(2-isocyanophenyl)methanone (5j). Eluent: PE/EA (20:1), yellow solid (0.83g, 92%). **m.p.:** 51-53 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.60 – 7.55 (m**,** 1H**),** 7.54 – 7.45 (m, 3H), 7.17 (t, *J* = 8.8 Hz, 2H). **^{13} C**

NMR (101 MHz, $CDCl_3$) δ 192.1, 169.1, 166.3(d, *J* = 257.8 Hz), 135.9, 132.8(d,*J* = 9.7 Hz) , 132.6(d, *J* = 3.0 Hz) , 131.6, 129.3(d, *J* = 5.5 Hz), 127.9, 116.2, 116.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.050. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{14}H_9FON^+$ 226.0663; found 226.0647.



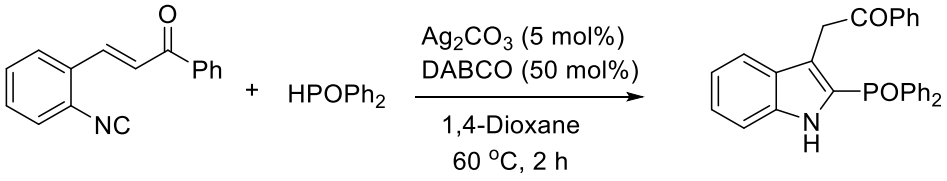
(2-Isocyanophenyl)(2-methoxyphenyl)methanone (5k). Eluent: PE/EA (20:1) , yellow solid (0.75g, 79%). **m.p.:** 56-58 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.58–7.39 (m, 5H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.63 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.2, 168.4, 156.0, 137.6, 134.6, 131.5, 131.1, 129.5, 129.2, 127.6, 127.3, 121.0, 111.7, 55.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NO_2^+$ 238.0863; found 238.0858.



(3-Chlorophenyl)(2-isocyanophenyl)methanone (5l). Eluent: PE/EA (20:1), yellow oil (0.78g, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (t, *J* = 2.0 Hz, 1H), 7.67 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.62–7.58 (m, 2H), 7.55–7.49 (m, 3H), 7.44 (t, *J* = 8.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.4, 169.4, 137.8, 135.4, 135.1, 133.9, 131.9, 130.1, 129.8, 129.5, 129.4, 128.3, 128.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{14}H_9ClNO^+$ 242.0367; found 242.0354.

III. Preparation and analytical data of 2-phosphinoyl indoles

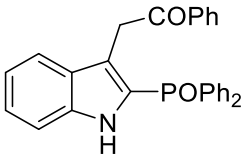
Typical synthetic procedure (with **3a** as an example)



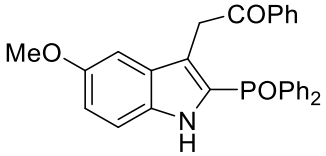
1a **2a** **3a**

(E)-3-(2-Isocyanophenyl)-1-phenylprop-2-en-1-one **1a** (0.3 mmol, 1.5 equiv, 70 mg), diphenylphosphine **2a** (0.2 mmol, 40 mg), Ag_2CO_3 (5 mol%, 2.8 mg) and DABCO (50 mol%, 11.2 mg) were dissolved in 1,4-dioxane (2.0 mL) in a pressure tube, it was placed in a metal bath and heated at 60 ºC for 2 h, until the complete consumption of **2a** as monitored by TLC. Then, the mixture was cooled to room temperature, diluted with water (20 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 1 : 1) to give product **3a** (59 mg, 68 % yield).

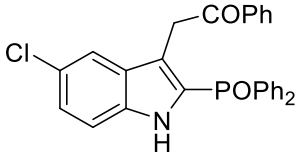
Analytical data of 2-phosphinoyl indoles 3



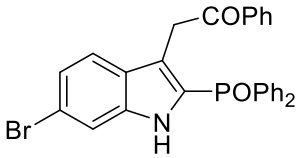
2-(2-(Diphenylphosphoryl)-1H-indol-3-yl)-1-phenylethan-1-one (3a). Eluent: PE/EA (1:1), yellow solid (59mg, 68%), **m.p.:** 228-230 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.70(d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.50−7.43 (m, 4H), 7.40–7.30 (m, 7H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 4.38 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.7, 138.1(d, *J* = 9.4 Hz), 136.6, 132.9, 132.5, 132.4, 132.1(d, *J* = 109.0 Hz), 132.0 (d, *J* = 10.7 Hz), 128.8(d, *J* = 12.6 Hz), 128.3 (d, *J* = 7.7 Hz), 124.8, 124.6(d, *J* = 123.2 Hz), 120.4 (d, *J* = 12.9 Hz), 119.6 (d, *J* = 12.8 Hz), 112.1, 35.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{23}NO_2P^+$ 436.1461; found 436.1454.



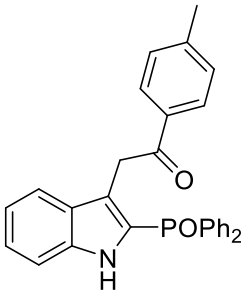
2-(2-(Diphenylphosphoryl)-5-methoxy-1H-indol-3-yl)-1-phenylethan-1-one (3b). Eluent: PE/EA (1:1), yellow solid (87 mg, 93%), **m.p.:** 241-243 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.73 – 7.64 (m, 4H), 7.47 (s, 3H), 7.42-7.30 (m, 6H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.95 – 6.83 (m, 2H), 4.38 (s, 2H), 3.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 154.7, 136.6, 133.3(d, *J* = 9.5 Hz), 132.9, 132.4, 132.3, 132.1(d, *J* = 108.9 Hz), 131.9(d, *J* = 10.6 Hz), 129.2(d, *J* = 11.3 Hz), 128.8(d, *J* = 12.5 Hz), 128.4(d, *J* = 2.1 Hz), 124.9(d, *J* = 123.4 Hz), 119.2(d, *J* = 12.9 Hz), 116.2, 112.9, 100.8, 55.8, 35.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{29}H_{25}NO_3P^+$ 466.1567; found 466.1588.



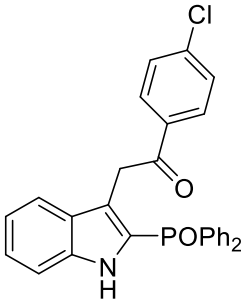
2-(5-Chloro-2-(diphenylphosphoryl)-1H-indol-3-yl)-1-phenylethan-1-one (3c). Eluent: PE/EA (1:1), yellow solid (53 mg, 56%), **m.p.:** 262-265 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.55-7.45 (m, 3H), 7.43 (s, 1H), 7.41 – 7.30 (m, 7H), 7.20 (d, *J* = 8.0 Hz, 1H), 4.25 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.2, 136.4 (d, *J* = 9.4 Hz), 136.3, 133.1, 132.6, 132.5, 131.9(d, *J* = 10.7 Hz), 131.6 (d, *J* = 109.5 Hz), 129.8 (d, *J* = 11.4 Hz), 128.9 (d, *J* = 12.6 Hz), 128.3 (d, *J* = 24.3 Hz), 126.4 (d, *J* = 121.5 Hz), 126.2, 125.2, 119.6, 118.6 (d, *J* = 12.9 Hz), 113.3, 35.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.4. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{21}ClNNaO_2P^+$ 492.0891; found 492.0871.



2-(6-Bromo-2-(diphenylphosphoryl)-1H-indol-3-yl)-1-phenylethan-1-one (3d). Eluent: PE/EA (1:1), yellow solid(74.5mg, 73%), **m.p.:** 140-142 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.70 – 7.59 (m, 4H), 7.55 (s, 1H), 7.51-7.41 (m, 3H), 7.38–7.24 (m, 7H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.21 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.4, 138.9 (d, *J* = 9.0 Hz), 136.4, 133.1, 132.5, 132.0, 131.9, 131.7 (d, *J* = 109.9 Hz), 128.9 (d, *J* = 12.1 Hz), 128.3 (d, *J* = 23.4 Hz), 127.6 (d, *J* = 11.1 Hz), 125.5 (d, *J* = 122.2 Hz), 123.7, 121.4, 119.0 (d, *J* = 12.5 Hz), 118.4, 115.3, 35.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.7. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{21}BrNNaO_2P^+$ 536.0385; found 536.0355.

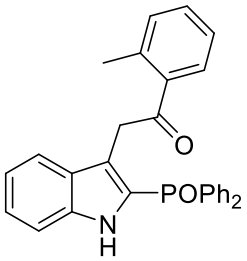


2-(2-(Diphenylphosphoryl)-1H-indol-3-yl)-1-(p-tolyl)ethan-1-one (3e). Eluent: PE/EA(1:1), yellow solid (62mg, 69%), **m.p.:** 216-218 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.77–7.64 (m, 6H), 7.52−7.45 (m, 3H), 7.42–7.32 (m, 5H), 7.22 (d, *J* = 8 Hz, 1H), 7.14 (d, *J* = 8 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 4.34 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 143.7, 138.0 (d, *J* = 9.3 Hz), 134.1, 132.4, 132.3, 132.1 (d, *J* = 109.0 Hz), 132.0 (d, *J* = 10.7 Hz), 129.0 (d, *J* = 15.6 Hz), 128.8, 128.4, 124.8, 124.5 (d, *J* = 123.1 Hz), 120.5, 120.4, 119.8 (d, *J* = 12.7 Hz), 112.0, 35.3, 21.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{29}H_{25}NO_2P^+$ 450.1617; found 450.1599.

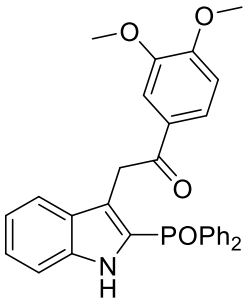


1-(4-Chlorophenyl)-2-(2-(diphenylphosphoryl)-1H-indol-3-yl)ethan-1-one (3f). Eluent: PE/EA (1:1), yellow solid (60.4mg, 65%), **m.p.:** 212-215 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.56-7.46 (m, 3H), 7.46−7.37 (m, 4H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.30-7.22 (m, 3H), 7.16 – 7.07 (m, 1H), 4.44 (s, 2H).**^{13} C NMR** (101 MHz, $CDCl_3$) δ 195.8, 139.3, 137.9 (d, *J* = 9.2 Hz), 134.8, 132.6, 132.5, 131.9 (d, *J* = 10.6 Hz), 131.5, 129.9,

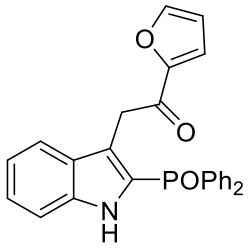
128.9 (d, *J* = 12.5 Hz), 128.8 (d, *J* = 11.2 Hz), 128.6, 124.9, 124.5 (d, *J* = 122.7 Hz), 120.6 (d, *J* = 25.6 Hz), 119.8 (d, *J* = 11.0 Hz), 120.0, 35.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{22}ClNO_2P^+$ 470.1071; found 470.1054.



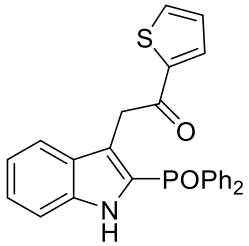
2-(2-(Diphenylphosphoryl)-1H-indol-3-yl)-1-(o-tolyl)ethan-1-one (3g). Eluent: PE/EA (1:1), yellow solid (56 mg, 64%), **m.p.:** 210-212 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.69 (dd, *J* = 11.6, 6.0 Hz, 4H), 7.49 (s, 4H), 7.39 (s, 5H), 7.34 –7.20 (m, 3H), 7.18-7.06 (m, *J* = 3 H), 4.34 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 138.2, 138.0 (d, *J* = 9.2 Hz), 137.5, 132.5, 132.4, 132.2 (d, *J* = 109.0 Hz), 131.9 (d, *J* = 10.7 Hz), 131.8, 131.2, 128.8 (d, *J* = 12.7 Hz), 128.6, 125.5, 124.8, 124.6 (d, *J* = 123.0 Hz), 120.4 (d, *J* = 32.5 Hz), 119.8 (d, *J* = 12.8 Hz), 112.1, 38.1, 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{29}H_{25}NO_2P^+$ 450.1617; found 450.1604.



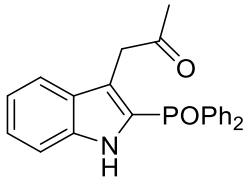
1-(3,4-Dimethoxyphenyl)-2-(2-(diphenylphosphoryl)-1H-indol-3-yl)ethan-1-one (3h). Eluent: PE/EA (1:1), yellow solid (63 mg, 64%), **m.p.:** 250-253 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.70(d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.51-7.46 (m, 2H), 7.44 (s, 1H), 7.42–7.36 (m, 4H), 7.33(d, *J* = 8.4 Hz, 1H), 7.25-7.20 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 4.41 (s, 2H), 3.87 (d, *J* = 8.4 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.5, 153.1, 148.8, 138.0 (d, *J* = 9.3 Hz), 132.4, 132.3, 132.1 (d, *J* = 108.9 Hz), 131.9 (d, *J* = 10.6 Hz), 129.8, 128.9, 128.8, 124.8, 124.3 (d, *J* = 123.0 Hz), 123.3, 120.7, 120.5, 120.4, 112.0, 110.5, 109.9, 56.0(d, *J* = 3.0 Hz), 35.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{30}H_{27}NO_4P^+$ 496.1672; found 496.1653.



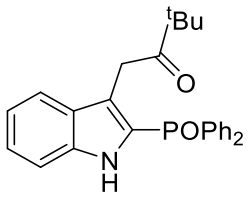
2-(2-(Diphenylphosphoryl)-1H-indol-3-yl)-1-(furan-2-yl)ethan-1-one (3i). Eluent: PE/EA (1:1)，yellow solid (64 mg, 75%), **m.p.:** 259-262 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.76 – 7.67 (m, 4H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.43 (s, 5H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.29−7.19 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.41 (s, 1H), 4.26 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.5, 153.1, 148.8, 138.0 (d, *J* = 9.2 Hz), 132.4, 132.3, 132.1 (d, *J* = 108.8 Hz), 131.9 (d, *J* = 10.6 Hz), 129.8, 128.8 (d, *J* = 12.2 Hz), 124.3 (d, *J* = 123.2 Hz), 124.0 (d, *J* = 152.5 Hz), 120.6 (d, *J* = 13.3 Hz), 120.4, 112.0, 110.2 (d, *J* = 62.0 Hz), 56.0 (d, *J* = 3.9 Hz), 35.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{21}NO_3P^+$ 426.1254; found 426.1245.



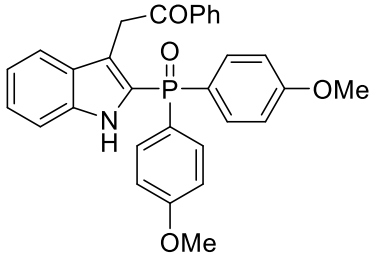
2-(2-(Diphenylphosphoryl)-1H-indol-3-yl)-1-(thiophen-2-yl)ethan-1-one (3j). Eluent: PE/EA (1:1)，yellow solid (59 mg, 67%), **m.p.:** 242-245 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.75−7.66 (m, 5H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.55−7.49 (m, 3H), 7.47−7.40 (m, 4H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.29–7.24 (m, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.01–6.96 (m, 1H), 4.39 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.7, 143.7, 137.9 (d, *J* = 9.3 Hz), 133.6, 132.8, 132.5, 132.4, 132.0 (d, *J* = 108.9 Hz), 128.9 (d, *J* = 12.5 Hz), 128.8, 128.7, 128.0, 124.8, 124.6 (d, *J* = 122.6 Hz), 120.7 (d, *J* = 3.8 Hz), 119.5 (d, *J* = 12.6 Hz), 112.0, 35.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{21}NO_2PS^+$ 442.1025; found 442.1016.



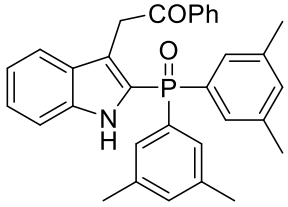
1-(2-(Diphenylphosphoryl)-1H-indol-3-yl)propan-2-one (3k). Eluent: PE/EA (1:1), yellow solid (24 mg, 32%), **m.p.:** 199-202 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.73 (d, *J* = 7.2 Hz, 4H), 7.70 (d, *J* = 7.6 Hz, 4H), 7.62-7.57 (m, 2H), 7.54 – 7.46 (m, 5H), 7.37 (d, *J* = 8.0 Hz,1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 3.83 (s, 2H), 1.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.0, 137.7 (d, *J* = 9.2 Hz), 132.7, 132.6, 131.9 (d, *J* = 109.0 Hz), 131.8 (d, *J* = 10.7 Hz), 129.0 (d, *J* = 12.5 Hz), 128.5 (d, *J* = 11.1 Hz), 125.0, 124.8 (d, *J* = 122.1 Hz), 120.4 (d, *J* = 65.4 Hz), 119.3 (d, *J* = 12.6 Hz), 112.0, 40.3, 29.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{21}NO_2P^+$ 374.1304; found 374.1296.



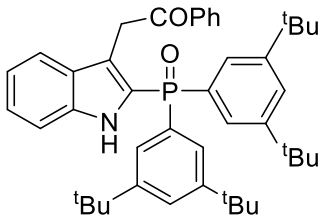
1-(2-(Diphenylphosphoryl)-1H-indol-3-yl)-3,3-dimethylbutan-2-one (3l). Eluent: PE/EA (1:1), yellow solid (22.4 mg, 27%), **m.p.:** 226-228 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.79−7.65 (m, 4H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.51−7.42 (m, 4H), 7.37−7.30 (m, 2H), 7.28–7.22 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 3.92 (s, 2H), 1.04 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.5, 138.0 (d, *J* = 8.8 Hz), 132.4, 132.2 (d, *J* = 108.0 Hz), 132.0 (d, *J* = 10.4 Hz), 128.8 (d, *J* = 12.5 Hz), 128.6, 124.9 (d, *J* = 123.9 Hz), 124.6, 124.3, 120.1 (d, *J* = 32.5 Hz), 119.8, 112.1, 44.2, 33.2, 26.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{27}NO_2P^+$ 416.1774; found 416.1765.



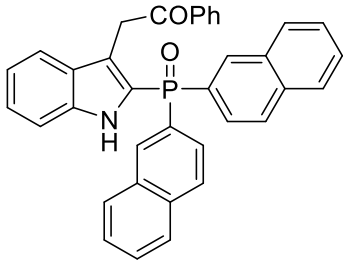
2-(2-(Bis(4-methoxyphenyl)phosphoryl)-1H-indol-3-yl)-1-phenylethan-1-one (3o). Eluent: PE/EA (1:1), yellow solid (56 mg, 56%), **m.p.:** 252-255 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.40−7.33 (m, 3H), 7.27 (t, *J* = 8.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 6.4 Hz, 4H), 4.38 (s, 2H), 3.76 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.7, 162.7 (d, *J* = 2.8 Hz), 137.8 (d, *J* = 9.3 Hz), 136.7, 133.8 (d, *J* = 12.1 Hz), 132.9, 128.9 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 10.3 Hz), 126.3, 125.1, 124.6, 124.0, 122.9, 120.3 (d, *J* = 11.7 Hz), 118.8 (d, *J* = 12.7 Hz), 114.4 (d, *J* = 13.6 Hz), 112.0, 55.3, 35.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{30}H_{27}NO_4P^+$ 496.1672; found 496.1657.



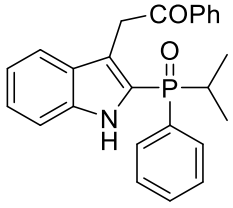
2-(2-(Bis(3,5-dimethylphenyl)phosphoryl)-1H-indol-3-yl)-1-phenylethan-1-one (3p). Eluent: PE/EA (1:1), yellow solid (73.1 mg, 74%), **m.p.:** 257-260 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.52−7.46 (m, 2H), 7.40 – 7.24 (m, 9H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (s, 2H), 4.37 (s, 2H), 2.23 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 138.7, 138.6, 137.6 (d, *J* = 9.1 Hz), 136.4, 134.3, 134.2, 132.9, 131.7 (d, *J* = 108.0 Hz), 129.4 (d, *J* = 10.6 Hz), 129.1 (d, *J* = 10.9 Hz), 128.3 (d, *J* = 8.9 Hz), 125.4 (d, *J* = 121.1 Hz), 124.6, 120.5, 119.1 (d, *J* = 12.4 Hz), 111.9, 35.3, 21.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{32}H_{31}NO_2P^+$ 492.2087; found 492.2070.



2-(2-(Bis(3,5-di-tert-butylphenyl)phosphoryl)-1H-indol-3-yl)-1-phenylethan-1-on-e (3q). Eluent: PE/EA (1:1), yellow solid (69.1 mg, 53%), **m.p.:** 248-250 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.59 (s, 2H), 7.56 (s, 4H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 4.26 (s, 2H), 1.22 (s, 36H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.7, 151.5 (d, *J* = 12.3 Hz), 137.8 (d, *J* = 8.9 Hz), 136.5, 132.9, 131.2 (d, *J* = 108.3 Hz), 129.0 (d, *J* = 11.2Hz), 128.3 (d, *J* = 15.6 Hz), 126.6, 126.5, 126.1 (d, *J* = 11.3 Hz), 125.4, 124.5, 120.6, 120.4, 118.6 (d, *J* = 12.5 Hz), 111.7, 35.3, 35.1, 31.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{44}H_{55}NO_2P^+$ 660.3965; found 660.3951.



2-(2-(Di(naphthalen-2-yl)phosphoryl)-1H-indol-3-yl)-1-phenylethan-1-one (3r). Eluent: PE/EA (1:1), yellow solid (65.2 mg, 61%), **m.p.:** 265-268 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.33 (s, 1H), 8.29 (s, 1H), 7.92–7.71 (m, 8H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.61-7.48 (m, 5H), 7.39-7.27 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 3H), 4.43 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 138.0 (d, *J* = 9.4 Hz), 136.2, 134.8, 134.7, 134.0 (d, *J* = 10.5 Hz), 132.6, 132.4 (d, *J* = 13.8 Hz), 129.1 (d, *J* = 109.6 Hz), 129.0, 128.9 (d, *J* = 11.4 Hz), 128.7 (d, *J* = 12.2 Hz), 128.4, 128.1, 127.9, 127.7, 126.9, 126.4 (d, *J* = 11.0 Hz), 124.7, 124.6 (d, *J* = 123.6 Hz), 120.4 (d, *J* = 11.2 Hz), 119.6 (d, *J* = 12.8 Hz), 112.1, 35.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{36}H_{27}NO_2P^+$ 536.1774; found 536.1758.

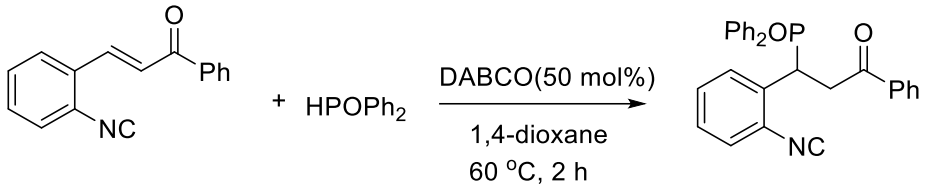


2-(2-(Isopropyl(phenyl)phosphoryl)-1H-indol-3-yl)-1-phenylethan-1-one (3s). Eluent: PE/EA (1:1), yellow solid (32 mg, 40%), **m.p.:** 133- 135 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.90−7.80 (m, 2H), 7.53–7.42 (m, 3H), 7.40-7.30 (m, 5H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 4.74 (d, *J* = 17.2 Hz, 1H), 4.56 (d, *J* = 17.2 Hz, 1H), 2.85 – 2.71 (m, 1H), 1.30-1.15 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 138.0 (d, *J* = 8.6 Hz), 136.7, 132.1, 132.0, 131.7 (d, *J* = 98.5 Hz), 130.9 (d, *J* = 9.3 Hz), 128.9 (d, *J* = 11.6 Hz), 128.8, 128.7 (d, *J* = 11.1 Hz), 128.6, 128.5 (d, *J* = 6.3 Hz), 124.5 (d, *J* = 112.3 Hz), 124.4, 120.2 (d, *J* = 15.5 Hz), 118.7 (d, *J* = 11.4 Hz), 112.0, 35.5, 27.7 (d, *J* = 75.6 Hz), 15.5 (d, *J* = 2.8 Hz), 14.9 (d, *J* = 2.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{25}H_{25}NO_2P^+$ 402.1617; found 402.1609.

Synthetic procedure of 4a and analytical data

Typical synthetic procedure 4a

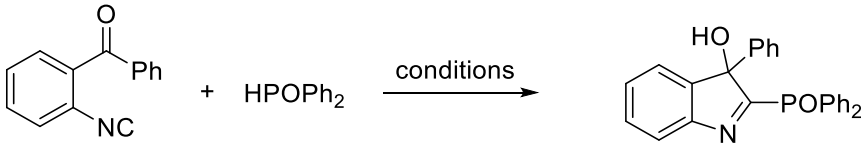


1a **2a** **4a**

(*E*)-3-(2-Isocyanophenyl)-1-phenylprop-2-en-1-one **1a** (0.3 mmol, 1.5 equiv, 70 mg), diphenylphosphine **2a** (0.2 mmol, 40 mg) and DABCO (50 mol%, 11.2 mg) were dissolved in 1,4-dioxane (2.0 mL) in a 15 mL pressure tube. It was placed in a metal bath and heated at 60 °C for 2 h, until the complete consumption of **2a** as monitored by TLC. Then, the mixture was cooled to room temperature, diluted with water (10 mL) and extracted with EtOAc (3 × 10mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 1 : 1) to give the prodcut **4a** (65 mg, 75 % yield). Eluent: PE/EA (1:1), yellow solid, **m.p.:** 194-196 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16–8.03(m, 2H), 7.85 (t, *J* = 7.6 Hz, 3H), 7.60 (s, 3H), 7.54−7.42 (m, 3H), 7.41−7.31 (m, 4H), 7.28−7.20 (m, 2H), 7.12 (q, *J* = 8.0 Hz, 2H), 4.96–4.86 (m, 1H), 4.16−4.00 (m, 1H), 3.50–3.37 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.7 (d, *J* = 13.5 Hz), 166.9, 136.0, 133.5, 133.2 (d, *J* = 5.2 Hz), 132.5 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 8.7 Hz), 131.0 (d, *J* = 53.2 Hz), 130.8 (d, *J* = 9.4 Hz), 130.0 (d, *J* = 47.7 Hz), 129.5 (d, *J* = 2.5 Hz), 129.2 (d, *J* = 11.4 Hz), 129.0 (d, *J* = 4.0 Hz), 128.4 (d, *J* = 52.9 Hz), 128.2 (d, *J* = 11.9 Hz), 127.8 (d, *J* = 2.6 Hz), 126.7 (d, *J* = 2.0 Hz), 38.8, 36.5 (d, *J* = 67.7 Hz).**^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.7.**HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{23}NO_2P^+$ 436.1461; found 436.1454.

IV. Optimization of reaction conditions for 2-phosphinoyl indol-3-ol

Optimization of reaction conditions[a]

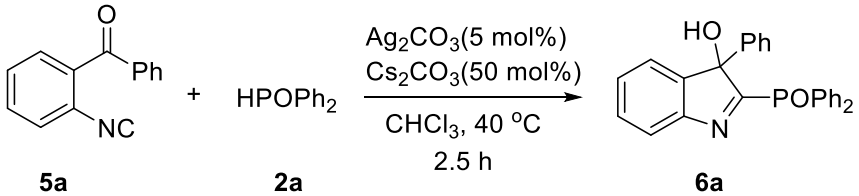


5 **2** **6**

Entry	5:2	Cata. (5 mol%)	Base.	Temp. (°C)	Sol.	Time. (h)	Yield (%)[b]
1	1.5:1	Ag_2CO_3	DABCO (50 mol%)	60	1,4-dioxane	2	38
2	1:1.5	Ag_2CO_3	Cs_2CO_3 (50 mol%)	60	$CHCl_3$	2.5	84
3	**1:1.5**	**Ag_2CO_3**	**Cs_2CO_3 (50 mol%)**	**40**	**$CHCl_3$**	**2.5**	**92**
4	1:1.5	Ag_2CO_3	Cs_2CO_3 (50 mol%)	r.t.	$CHCl_3$	2.5	72
5	1:1.5	Ag_2CO_3	Cs_2CO_3 (30 mol%)	40	$CHCl_3$	2.5	60
6	1:1.5	Ag_2CO_3	Cs_2CO_3 (100 mol%)	40	$CHCl_3$	2.5	83
7	1:1.5	Ag_2CO_3	Cs_2CO_3 (50 mol%)	40	DCM	2.5	78
8	1:1.5	Ag_2CO_3	Cs_2CO_3 (50 mol%)	40	DCE	2.5	84
9	1:1.8	Ag_2CO_3	Cs_2CO_3 (50 mol%)	40	$CHCl_3$	2.5	83

a) Reaction conditions: **5** (0.2 mmol), **2** (1.5 eq, 0.3 mmol), Ag_2CO_3 (5 mol%), Base and solvent (2 mL) were reacted in a pressure tube at different temperature for 2.5 h. b) Isolated yield.

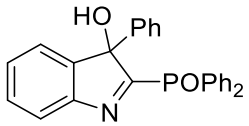
Typical synthetic procedure (with **6a** as an example)



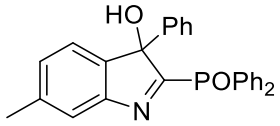
5a **2a** **6a**

(2-Isocyanophenyl)(phenyl)methanone **5a** (0.2 mmol, 41 mg), diphenylphosphine **2a** (0.3 mmol, 61 mg), Ag_2CO_3 (5 mol%, 2.8 mg), Cs_2CO_3 (50 mol%, 33 mg) and $CHCl_3$ (2.0 mL) were successively added to a pressure tube (15 mL). It was placed in a metal bath and heated at 40 °C for 2.5 h, until the complete consumption of **5a** as monitored by TLC. Then, the mixture was cooled to room temperature, diluted with water (10 mL) and extracted with DCM (3 × 10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 2 : 1) to give (3-hydroxy-3-phenyl-3H-indol-2-yl) diphenylphosphine oxide **6a** (75 mg, 75 %).

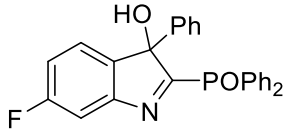
Analytical data of 2-phosphinoyl indoles-3-ols



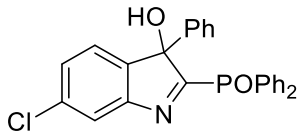
(3-Hydroxy-3-phenyl-3H-indol-2-yl)diphenylphosphine oxide (6a). Eluent: PE/EA (2:1), white solid (75.2 mg, 92%), **m.p.:** 206-208 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 6.8 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.54−7.46 (m, 4H), 7.45-7.35 (m, 2H), 7.31–7.22 (m, 4H), 7.10–6.96 (m, 5H), 5.71(s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.6 (d, *J* = 112.7 Hz), 154.1 (d, *J* = 25.0 Hz), 143.1 (d, *J* = 2.1 Hz), 137.1, 132.8 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 10.4 Hz), 131.1 (d, *J* = 10.4 Hz), 131.0 (d, *J* = 107.6 Hz), 129.7, 129.2 (d, *J* = 104.5 Hz), 129.1, 128.7 (d, *J* = 12.9 Hz), 128.3 (d, *J* = 12.7 Hz), 128.2, 127.8, 124.8, 123.6, 122.7, 92.0 (d, *J* = 19.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{21}NO_2P^+$ 410.1304; found 410.1301.



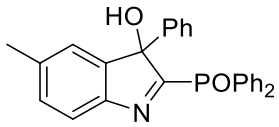
(3-Hydroxy-6-methyl-3-phenyl-3H-indol-2-yl) diphenylphosphine oxide (6b). Eluent: PE/EA (2:1), white solid (57 mg, 67%), **m.p.:** 180-182 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.60–7.46 (m, 6H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.31–7.21 (m, 2H), 7.13–6.95 (m, 7H), 5.65 (s, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.7 (d, *J* = 112.7 Hz), 154.4 (d, *J* = 25.1 Hz), 140.3 (d, *J* = 2.6 Hz), 139.9 (d, *J* = 2.6 Hz), 139.8, 137.4, 132.7 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 2.4 Hz), 132.0 (d, *J* = 10.1 Hz), 131.0 (d, *J* = 10.5 Hz), 131.1 (d, *J* = 107.3 Hz), 129.6, 129.4 (d, *J* = 104.6 Hz), 128.6 (d, *J* = 12.8 Hz), 128.2, 128.0 (d, *J* = 70.0 Hz), 124.9, 123.4, 123.2, 91.8 (d, *J* = 19.4 Hz), 21.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{23}NO_2P^+$ 424.1461; found 424.1465.



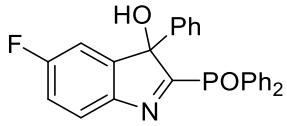
(6-Fluoro-3-hydroxy-3-phenyl-3H-indol-2-yl)diphenylphosphine oxide (6c). Eluent: PE/EA (2:1), white solid (56.4 mg, 66%), **m.p.:** 159−161 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96−7.81 (m, 2H), 7.60−7.35 (m, 7H), 7.32−7.22 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.1–6.89 (m, 6H), 5.75 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.0 (d, *J* = 120.0 Hz), 163.7 (d, *J* = 248.4 Hz), 155.4 (d, *J* = 25.3 Hz), 138.9, 136.7, 132.9 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 10.3 Hz), 131.0 (d, *J* = 10.4 Hz), 130.7 (d, *J* = 107.9 Hz), 129.5, 128.7 (d, *J* = 12.9 Hz), 128.4 (d, *J* = 12.8 Hz), 128.3, 127.9, 124.9, 124.4 (d, *J* = 9.7 Hz), 115.5 (d, *J* = 23.1 Hz), 110.5 (d, *J* = 24.6 Hz), 91.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{20}FNO_2P^+$ 428.1210; found 428.1209.



(6-Chloro-3-hydroxy-3-phenyl-3H-indol-2-yl)diphenylphosphine oxide (6d). Eluent: PE/EA (2:1), white solid (84.3 mg, 95%), **m.p.:** 179−182 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.69 (s, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54–7.46 (m, 4H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.32–7.23 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10-6.96 (m, 5H), 5.73 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.7 (d, *J* = 111.0 Hz), 155.2 (d, *J* = 25.1 Hz), 141.6, 136.5, 135.3, 132.9 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 10.0 Hz), 131.1 (d, *J* = 10.6 Hz), 130.7 (d, *J* = 107.9 Hz), 129.0 (d, *J* = 104.9 Hz), 128.8 (d, *J* = 10.7 Hz), 128.6, 128.4 (d, *J* = 12.8 Hz), 128.3, 128.0, 124.9, 124.4, 123.2, 91.7 (d, *J* = 19.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{20}ClNO_2P^+$ 444.0915; found 444.0905.

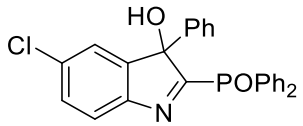


(3-Hydroxy-5-methyl-3-phenyl-3H-indol-2-yl)diphenylphosphine oxide (6e). Eluent: PE/EA (2:1), white solid (54 mg, 64%), **m.p.:** 221−224 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.8 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.63–7.58 (m, 2H), 7.57–7.49 (m, 4H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.34–7.26 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.13–6.99 (m, 6H), 5.69 (s, 1H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.7 (d, *J* = 111.0 Hz), 155.2 (d, *J* = 25.1 Hz), 143.4, 139.5, 137.4, 132.7 (d, *J* = 2.8 Hz), 132.1, 132.0 (d, *J* = 10.3 Hz), 131.2 (d, *J* = 107.7 Hz), 131.1 (d, *J* = 10.4 Hz), 130.1, 129.4 (d, *J* = 104.9 Hz), 128.6 (d, *J* = 12.8 Hz), 128.3 (d, *J* = 12.0 Hz), 128.2, 127.7, 125.0, 124.4, 122.3, 91.8 (d, *J* = 19.1 Hz), 21.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{23}NO_2P^+$ 424.1461; found 424.1461.

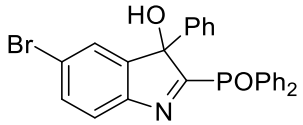


(5-Fluoro-3-hydroxy-3-phenyl-3H-indol-2-yl)diphenylphosphine oxide (6f). Eluent: PE/EA (2:1), white solid (75.3 mg, 88%), **m.p.:** 166−168 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.68−7.62 (m, 1H), 7.61–7.46 (m, 5H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32–7.22 (m, 2H), 7.11–6.97 (m, 6H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.80 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.7(d, *J* = 108.7, 4.3 Hz), 163.3 (d, *J* = 251.5 Hz), 150.0 (d, *J* = 24.4 Hz), 145.5 (d, *J* = 7.9 Hz), 136.6, 132.8 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 10.3 Hz), 131.1 (d, *J* = 10.5 Hz), 130.8 (d, *J* = 107.8 Hz), 129.2 (d, *J* = 104.9 Hz), 128.7 (d, *J* = 7.7 Hz), 128.4, 128.3 (d, *J* = 13.0 Hz), 128.0, 124.9, 123.7 (d, *J* = 9.2 Hz), 116.3 (d, *J* = 23.9 Hz), 111.8 (d, *J* = 25.3 Hz), 92.1 (d, *J* = 19.7 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.1. **^{19}F NMR** (376

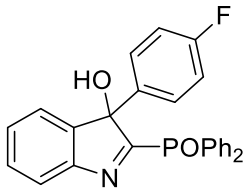
MHz, $CDCl_3$) δ -111.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{20}FNO_2P^+$ 428.1210; found 428.1213.



(5-Chloro-3-hydroxy-3-phenyl-3H-indol-2-yl)diphenylphosphine oxide (6g). Eluent: PE/EA (2:1), white solid (61.6 mg, 70%), **m.p.:** 222−224 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.66–7.38 (m, 7H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.31−7.24 (m, 2H), 7.20 (s, 1H), 7.11-6.96 (m, 5H), 5.76 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.1 (d, *J* = 112.0 Hz), 152.5 (d, *J* = 25.2 Hz), 144.9 (d, *J* = 2.7 Hz), 136.4, 135.1, 132.9 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 10.3 Hz), 131.0 (d, *J* = 10.4 Hz), 130.8 (d, *J* = 107.8 Hz), 129.8, 129.0 (d, *J* = 104.9 Hz), 128.6 (d, *J* = 10.7 Hz), 128.4, 128.3 (d, *J* = 12.9 Hz), 128.0, 124.9, 124.4, 123.5, 92.1 (d, *J* =19.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{20}ClNO_2P^+$ 444.0915; found 444.0904.

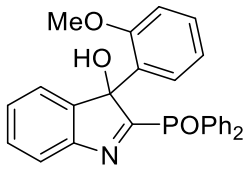


(5-Bromo-3-hydroxy-3-phenyl-3H-indol-2-yl)diphenylphosphine oxide (6h). Eluent: PE/EA (2:1), white solid (72.1 mg, 74%), **m.p.:** 221−223 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.61–7.46 (m, 7H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.36 (s, 1H), 7.31–7.24 (m, 2H), 7.11–6.96 (m, 5H), 5.77 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.1 (d, *J* = 111.9 Hz), 153.0 (d, *J* = 25.2 Hz), 145.1 (d, *J* =2.6 Hz), 136.3, 132.9 (d, J = 2.9 Hz), 132.8, 132.3 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 10.4 Hz), 131.0 (d, *J* = 10.5 Hz), 130.7 (d, *J* = 107.8 Hz), 128.9 (d, *J* = 96.8 Hz), 128.7 (d, *J* = 12.8 Hz), 128.4, 128.3 (d, *J* = 12.8), 128.0, 127.2, 124.9, 123.9, 123.2, 92.1 (d, *J* = 19.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{20}BrNO_2P^+$ 488.0410; found 488.0404.

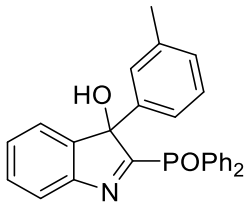


(3-(4-Fluorophenyl)-3-hydroxy-3H-indol-2-yl)diphenylphosphine oxide (6i). Eluent: PE/EA (2:1), white solid (62.8 mg, 74%), **m.p.:** 159−162 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.62–7.42 (m, 6H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.35–7.25 (m, 3H), 7.22 (d, *J* = 6.8 Hz, 1H), 7.07-6.98 (m, 2H), 6.65 (t, *J* = 8.8 Hz, 2H), 5.76 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.3 (d, *J* = 112.5 Hz), 162.3 (d, *J* = 247.3 Hz), 154.0 (d, *J* = 24.9 Hz), 142.7 (d, *J* = 2.5 Hz), 132.9 (d, *J* =2.9 Hz), 132.8 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 10.4 Hz), 131.0 (d, *J* = 10.4 Hz), 130.8 (d, *J* =107.8 Hz), 130.3 (d, *J* =104.9 Hz), 129.8, 129.2, 128.7 (d, *J* = 12.9 Hz), 128.4 (d, *J* = 12.8 Hz), 127.0 (d, *J* = 8.4 Hz), 123.6,

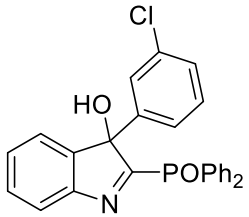
122.8, 115.1 (d, *J* = 21.9Hz), 91.6 (d, *J* = 19.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.8. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{26}H_{19}FNNaO_2P^+$ 450.1030; found 450.1026.



(3-Hydroxy-3-(2-methoxyphenyl)-3H-indol-2-yl)diphenylphosphine oxide (6j). Eluent: PE/EA (2:1), white solid (60.1 mg, 68%), **m.p.:** 140−143 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.6 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.60−7.46 (m, 5H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.36−7.25(m, 4H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.14−7.02 (m, 3H), 6.15 (d, *J* = 7.6 Hz, 1H), 5.23 (s, 1H), 2.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.3 (d, *J* = 115.3Hz), 155.4, 155.1, 141.6 (d, *J* = 2.9 Hz), 132.7 (d, *J* = 3.0 Hz), 132.2 (d, *J* = 10.3 Hz), 131.9 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 10.5 Hz), 131.2 (d, *J* = 106.9 Hz), 129.2, 129.1, 128.9 (d, *J* = 104.6 Hz), 128.6 (d, *J* = 12.7 Hz), 128.3, 128.0 (d, *J* = 12.6Hz), 127.2, 126.8, 122.6, 122.1, 120.8, 109.7, 88.8 (d, *J* = 20.5 Hz), 53.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{23}NO_3P^+$ 440.1410; found 440.1397.

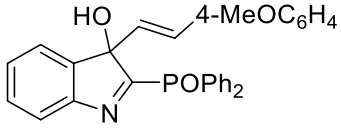


(3-Hydroxy-3-(m-tolyl)-3H-indol-2-yl)diphenylphosphine oxide (6k). Eluent: PE/EA (2:1), white solid (57.3 mg, 68%), **m.p.:** 78−80 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.61–7.49 (m, 5H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.41−7.35 (m,1H), 7.34–7.28 (m, 2H), 7.25 (d, *J* = 5.2 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 1.9 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.6 (d, *J* = 112.9 Hz), 154.0 (d, *J* = 25.3 Hz), 143.1 (d, *J* = 2.6 Hz), 137.8, 137.0, 132.7 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 10.7 Hz), 131.1 (d, *J* = 10.3 Hz), 131.0 (d, *J* = 107.4 Hz), 129.6, 129.4 (d, *J* = 104.3 Hz), 129.0, 128.7, 128.6, 128.3 (d, *J* = 8.3 Hz), 128.2, 125.5, 123.6, 122.7, 122.0, 92.0 (d, *J* = 19.2 Hz), 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{23}NO_2P^+$ 424.1461; found 424.1468.

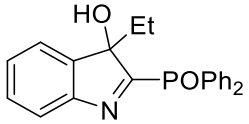


(3-(3-Chlorophenyl)-3-hydroxy-3H-indol-2-yl) diphenylphosphine oxide (6l). Eluent: PE/EA (2:1), white solid (70.1 mg, 79%), **m.p.:** 164−167 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.6 Hz,

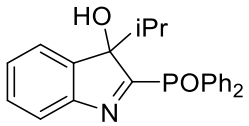
1H), 7.61–7.19 (m, 11H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.02–6.86 (m, 2H), 5.79 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.8 (d, *J* = 112.6Hz), 154.0 (d, *J* = 24.7Hz), 142.5 (d, *J* = 2.3Hz), 139.7, 134.2, 132.9 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 10.5 Hz), 131.0 (d, *J* = 15.4 Hz), 130.6 (d, *J* = 107.9 Hz), 129.9, 129.6, 129.3, 129.2, 128.9 (d, *J* = 104.5 Hz,), 128.7 (d, *J* = 12.9 Hz), 128.5 (d, *J* = 12.1 Hz), 128.0, 125.3, 123.6, 122.9, 91.5 (d, *J* = 19.3Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{26}H_{19}ClNNaO_3P^+$ 466.0734; found 466.0719.



(*E*)-(3-Hydroxy-3-(4-methoxystyryl)-3H-indol-2-yl)diphenylphosphine oxide (6m). Eluent: PE/EA (2:1), white solid (64 mg, 69%), **m.p.:** 129−132 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95-7.83 (m, 4H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.54−7.47 (m, 3H), 7.46–7.33 (m, 5H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.72 (t, *J* = 8.4 Hz, 3H), 5.78 (d, *J* = 15.6 Hz, 1H), 5.20 (s, 1H), 3.78 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 183.8 (d, *J* = 109.0 Hz), 159.6, 153.4 (d, *J* = 25.7 Hz), 141.6, 133.0 (d, *J* = 25.7 Hz), 132.7, 132.5, 132.1, 132.0 (d, *J* = 9.9 Hz), 131.8 (d, *J* = 9.7 Hz), 129.8, 129.6 (d, *J* = 100.6 Hz), 129.1, 129.1, 129.0 (d, *J* = 4.4 Hz), 128.9 (d, *J* = 2.6 Hz), 128.2, 124.5, 122.9, 114.4, 90.8 (d, *J* = 19.5 Hz), 55.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{29}H_{25}NO_3P^+$ 466.1567; found 466.1568.

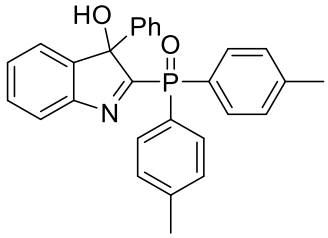


(3-Ethyl-3-hydroxy-3H-indol-2-yl)diphenylphosphine oxide (6n). Eluent: PE/EA (2:1), white solid (38.8 mg, 54%), **m.p.:** 35−38 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.58–7.52 (m, 3H), 7.50–7.41 (m, 3H), 7.40−7.30 (m, 2H), 4.48 (s, 1H), 2.30−2.20 (m, 1H), 2.17−2.07 (m, 1H), 0.37 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.3 (d, *J* = 111.3 Hz), 154.0 (d, *J* = 25.8 Hz), 139.7 (d, *J* = 2.9 Hz), 132.7 (d, *J* = 2.9 Hz), 132.6 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 107.2 Hz), 131.8 (d, *J* = 10.4 Hz), 131.5 (d, *J* = 10.0 Hz), 129.6 (d, *J* = 103.2 Hz), 129.5, 128.6 (d, *J* = 12.5 Hz), 128.7 (d, *J* = 12.8 Hz), 128.4, 123.0, 122.6, 92.4 (d, *J* = 19.2 Hz), 30.6, 7.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 23.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd d for $C_{22}H_{21}NO_2P^+$ 362.1304; found 362.1298.

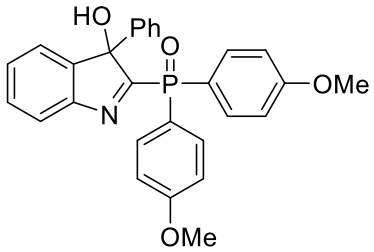


(3-Hydroxy-3-isopropyl-3H-indol-2-yl)diphenylphosphine oxide (6o). Eluent: PE/EA (2:1), white solid (50 mg, 67%), **m.p.:** 70−73 ℃.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.4 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.56–7.44 (m, 5H), 7.41−7.35 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.24–

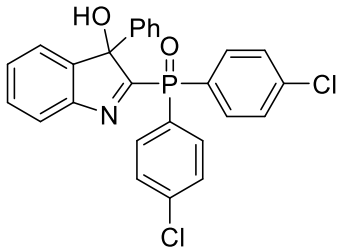
7.18 (m, 1H), 4.34 (s, 1H), 2.68−2.60 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 3H), 0.01 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.0 (d, *J* = 110.9 Hz), 154.6 (d, *J* = 26.2 Hz), 138.1 (d, *J* = 2.9 Hz), 132.6 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 107.3 Hz), 131.8 (d, *J* = 10.5 Hz), 131.6 (d, *J* = 9.8 Hz), 129.5, 129.3 (d, *J* = 103.1 Hz), 128.9 (d, *J* = 12.5 Hz), 128.7 (d, *J* = 12.8 Hz), 127.9, 124.3, 122.6, 95.1 (d, *J* = 18.9 Hz), 33.8, 16.3, 16.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 23.0 **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{23}NO_2P^+$ 376.1461; found 376.1443.



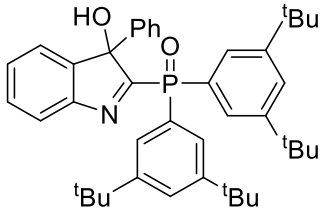
(3-Hydroxy-3-phenyl-3H-indol-2-yl)di-p-tolylphosphine oxide (6p). Eluent: PE/EA (2:1), white solid (61.9 mg, 71%), **m.p.:** 177−180 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.42–7.33 (m, 3H), 7.31–7.21 (m, 4H), 7.10−7.03 (m, 5H), 6.99 (t, *J* = 7.6 Hz, 2H), 5.79 (s, 1H), 2.39 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.1 (d, *J* = 112.5 Hz), 154.2 (d, *J* = 25.0 Hz), 143.4 (d, *J* = 2.7 Hz), 143.3 (d, *J* = 2.5 Hz), 142.7 (d, *J* = 2.9 Hz), 137.5, 132.1 (d, *J* = 10.8 Hz), 131.2 (d, *J* = 10.8 Hz), 129.6, 129.4 (d, *J* = 13.3 Hz), 129.1 (d, *J* = 13.3 Hz), 128.9, 128.2, 128.0 (d, *J* = 110.1 Hz), 127.6, 126.0 (d, *J* = 107.3 Hz), 125.0, 123.6, 122.6, 92.0 (d, *J* = 19.3 Hz), 21.7 (d, *J* = 1.5 Hz), 21.6 (d, *J* = 1.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{25}NO_2P^+$ 438.1617; found 438.1607.



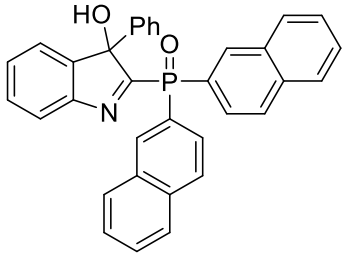
(3-Hydroxy-3-phenyl-3H-indol-2-yl)bis(4-methoxyphenyl)phosphine oxide (6q). Eluent: PE/EA (2:1), white solid (90 mg, 96%), **m.p.:** 69−71 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.42−7.34 (m, 3H), 7.29−7.20 (m, 3H), 7.10–6.96 (m, 7H), 6.76 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H), 3.80 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.3 (d, *J* = 113.5 Hz), 163.1 (d, *J* = 2.8 Hz), 162.6 (d, *J* = 2.9 Hz), 154.1 (d, *J* = 25.0 Hz), 143.3 (d, *J* = 2.7 Hz), 137.6, 134.1 (d, *J* = 12.1 Hz), 133.1 (d, *J* = 11.9 Hz), 129.6, 128.9, 128.2, 127.6, 125.0, 123.6, 122.6, 122.4 (d, *J* = 114.6 Hz), 120.3 (d, *J* = 112.0 Hz), 114.1 (d, *J* = 13.9 Hz), 113.9 (d, *J* = 13.8 Hz), 91.9 (d, *J* = 19.3 Hz), 55.4, 55.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{25}NO_4P^+$ 470.1516; found 470.1501.



bis(4-chlorophenyl)(3-hydroxy-3-phenyl-3H-indol-2-yl)phosphine oxide (6r). Eluent: PE/EA (2:1), white solid (63.7 mg, 67%), **m.p.:** 101−104 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.4 (d, *J* = 7.6 Hz, 2H), 7.43−7.35 (m, 3H), 7.31−7.20 (m, 4H), 7.12−6.99 (m, 5H), 5.47(s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.0 (d, *J* = 114.3 Hz), 153.9 (d, *J* = 25.5 Hz), 143.0 (d, *J* = 2.5 Hz), 139.7 (d, *J* = 3.5 Hz), 139.1 (d, *J* = 3.6 Hz), 136.8, 133.4 (d, *J* = 11.1 Hz), 132.4 (d, *J* = 11.3 Hz), 129.8, 129.4, 129.1 (d, *J* = 13.5 Hz), 129.0 (d, *J* = 109.9 Hz), 128.8 (d, *J* =13.5 Hz), 128.4, 128.0, 127.7 (d, *J* = 106.5 Hz), 125.0, 123.7, 122.8, 92.0 (d, *J* = 19.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{19}Cl_2NO_2P^+$ 478.0525; found 478.0512.

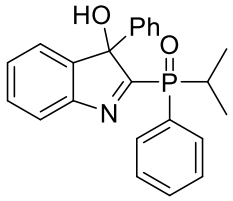


Bis(3,5-di-tert-butylphenyl)(3-hydroxy-3-phenyl-3H-indol-2-yl)phosphine oxide (6s). Eluent: PE/EA (2:1), white solid (85.7 mg, 68%), **m.p.:** 211-213 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79–7.69 (m, 3H), 7.62 (s, 1H), 7.46−7.40 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.28–7.18 (m, 2H), 7.07-7.02 (m, 2H), 6.99–6.88 (m, 3H), 5.97 (s, 1H), 1.30 (s, 18H), 1.23 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.3 (d, *J* = 110.5 Hz), 154.3 (d, *J* = 24.6 Hz), 150.9 (d, *J* = 12.5 Hz), 150.7 (d, *J* = 12.5 Hz), 143.5 (d, *J* = 2.4 Hz), 137.3, 130.0 (d, *J* = 106.4 Hz), 129.5, 128.8, 128.2 (d, *J* = 103.5 Hz), 128.0, 127.5, 126.9 (d, *J* = 2.9 Hz), 126.4 (d, *J* = 11.0 Hz), 126.2 (d, *J* = 3.0 Hz), 125.1 (d, *J* = 11.0 Hz), 125.0, 123.5, 122.5, 92.0 (d, *J* = 19.2 Hz), 35.1, 34.9, 31.3, 31.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{42}H_{53}NO_2P^+$ 634.3808; found 634.3803.



(3-Hydroxy-3-phenyl-3H-indol-2-yl)di(naphthalen-2-yl)phosphine oxide (6t). Eluent: PE/EA (2:1), white solid (77.9 mg, 76%), **m.p.:** 184−186 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 14.4 Hz, 1H), 8.08 (d, *J* = 14.4 Hz, 1H), 7.94 (d, *J* = 6.0

Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.77−7.69 (m, 3H), 7.64–7.45 (m, 5H), 7.41−7.34 (m, 1H), 7.29−7.22 (m, 2H), 7.15–7.04 (m, 2H), 6.83 (d, *J* = 6.4 Hz, 3H), 5.83 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.7 (d, *J* = 112.9 Hz), 154.2 (d, *J* = 25.3 Hz), 143.2, 137.3, 135.2 (d, *J* = 2.5 Hz), 134.8 (d, *J* = 2.4 Hz), 134.3 (d, *J* = 10.4 Hz), 134.0 (d, *J* = 9.3 Hz), 132.4 (d, *J* = 12.0 Hz), 132.3 (d, *J* = 11.8 Hz), 129.7, 129.2, 129.1, 129.0, 128.6 (d, *J* = 12.2 Hz), 128.5 (d, *J* = 14.4 Hz), 128.3, 128.2, 128.1, 128.0 (d, *J* = 108.4 Hz), 127.9, 127.8, 126.9 (d, *J* = 12.9 Hz), 126.7 (d, *J* = 10.8 Hz), 126.4 (d, *J* = 105.2 Hz), 125.4 (d, *J* = 12.0 Hz), 125.0, 123.7, 122.8, 92.1 (d, *J* = 19.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{34}H_{25}NO_2P^+$ 510.1617; found 510.1605.



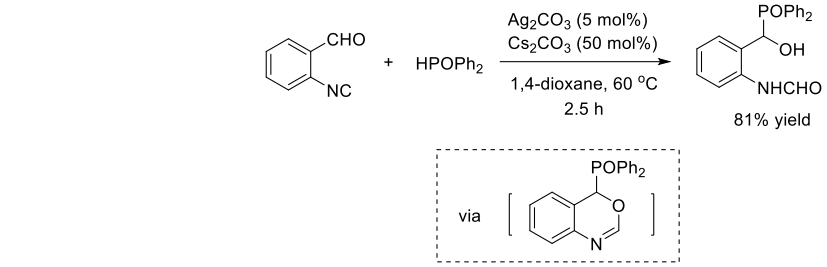
(3-Hydroxy-3-phenyl-3H-indol-2-yl)(isopropyl)(phenyl)phosphine oxide 6u/6u' The diastereomers **6u** and **6u'** can be isolated by column chromatography by using PE/EA (2:1) as eluent. A combined 51% yield in a ratio of 1:1 dr was determined by ^{1}H NMR of the crude products (using CH_2Br_2 as an internal standard).

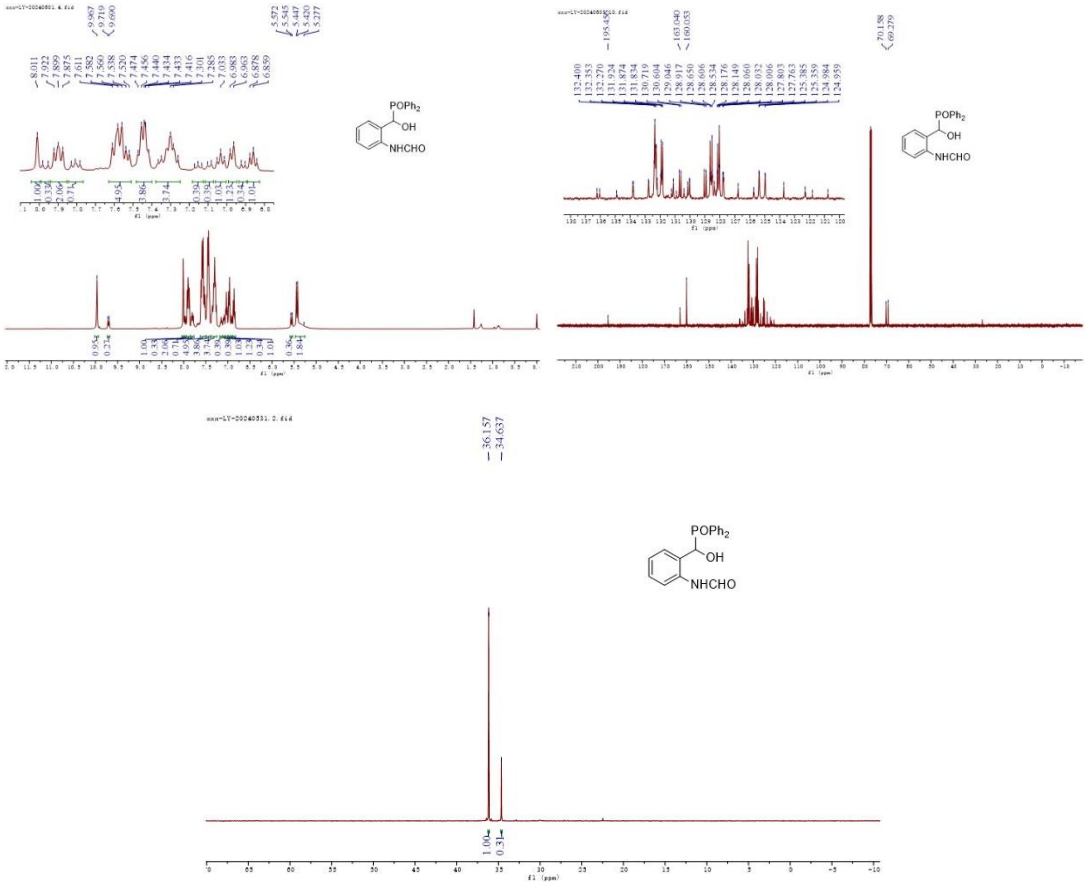
6u: m.p.: >300 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.46–7.34 (m, 4H), 7.29−7.22 (m, 3H), 7.20 (d, *J* = 6.8 Hz, 1H), 7.01–6.87 (m, 5H), 5.54 (s, 1H), 2.83−2.73 (m, 1H), 1.43 (dd, *J* = 17.2, 6.8 Hz, 3H), 1.05 (dd, *J* = 18.0, 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.6 (d, *J* = 101.8 Hz), 154.1 (d, *J* = 23.3 Hz), 143.1 (d, *J* = 2.2 Hz), 137.0, 131.8 (d, *J* = 2.8 Hz), 130.2, 130.1 (d, *J* = 9.6 Hz), 130.0 (d, *J* = 50.9 Hz), 129.6, 128.9, 128.5 (d, *J* = 57.6 Hz), 128.4 (d, *J* = 12.1 Hz), 128.1, 127.6, 124.8, 123.6, 122.4, 91.5 (d, *J* = 16.6 Hz), 27.4 (d, *J* = 72.4 Hz), 15.0 (d, *J* = 3.8 Hz), 13.7 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 38.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{23}NO_2P^+$ 376.1461; found 376.1481.
6u': m.p.: 91−93 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10–8.01 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.59–7.48 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.34–7.25 (m, 6H), 7.23 (d, *J* = 7.2 Hz, 1H), 1.99-1.87 (m, 1H), 0.96−0.81 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.5 (d, *J* = 101.8 Hz), 154.3 (d, *J* = 23.4 Hz), 143.3, 137.4, 132.2 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 8.4 Hz), 129.7, 129.0 (d, *J* = 95.2 Hz), 128.9, 128.5, 128.4, 128.1, 125.3, 123.6, 122.4, 92.6 (d, *J* = 17.7 Hz), 29.5 (d, *J* = 69.6 Hz), 14.6, 14.2 (d, *J* = 2.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 37.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{23}NO_2P^+$ 376.1461; found 376.1483.

The reaction of 2-isocyanobenzaldehyde with diphenyl phosphine oxide 2a

When 2-isocyanobenzaldehyde was treated with diphenyl phosphine oxide under the standard conditions, α-hydroxyphosphine oxide was obtained in 81% yield, probably via the phosphorus nucleophilic addition to the aldehyde group to form a benzo[d][1,3]oxazine intermediate, which hydrolyzed to give the final product N-(2-

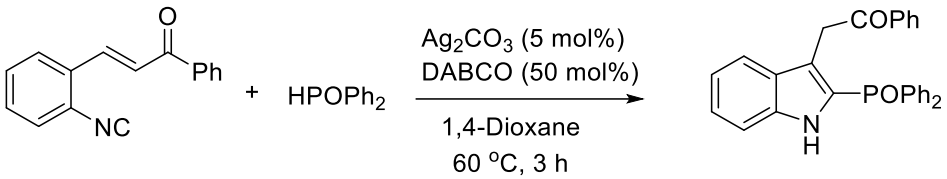
((diphenylphosphoryl)(hydroxy)methyl)phenyl)formamide.





V. Scale-up experiment

Scale-up experiment of 2-phosphinoyl indoles

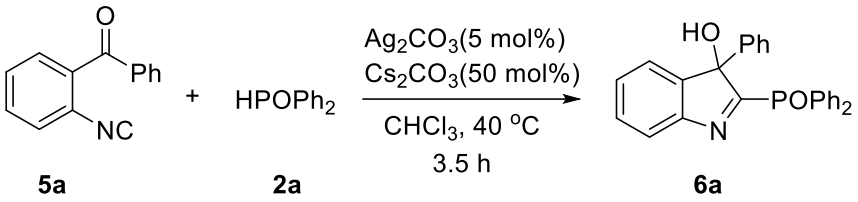


1a **2a** **3a**

(*E*)-3-(2-isocyanophenyl)-1-phenylprop-2-en-1-one **1a** (4.8 mmol, 1.5 eq, 1.12 g) , diphenylphosphine oxide **2a** (3.2 mmol, 0.65 g), Ag_2CO_3 (5 mol%, 44.12 mg), DABCO (50 mol%, 179.49 mg) and 1,4-dioxane (32 mL) were successively added to a round bottom flask (100 mL). The flask was placed in a metal bath and heated at 60 °C for 2 h, until the complete consumption of **2a** as monitored by TLC. Then, the

mixture was cooled to room temperature, diluted with water (100 mL) and extracted with EtOAc (3 × 50 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 1 : 1) to give 2-(2-(diphenylphosphoryl)-1H-indol-3-yl)-1-phenylethan-1-one **3a** (1.00 g, 72 %).

Scale-up experiment of 2-phosphinoyl indoles-3-ol

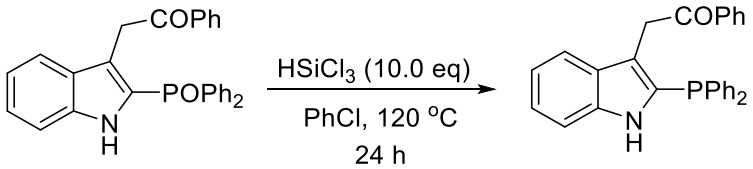


5a **2a** **6a**

(2-isocyanophenyl)(phenyl)methanone **1a** (3 mmol, 0.62 g), diphenylphosphine oxide **2a** (4.5 mmol, 0.91 g), Ag_2CO_3 (5 mol%, 41.36 mg), Cs_2CO_3(50 mol%, 488.73 mg) and $CHCl_3$(25 mL) were successively added to a round bottom flask (100 mL). The flask was placed in a metal bath and heated at 40 °C for 3.5 h, until the complete consumption of **5a** as monitored by TLC. Then, the mixture was diluted with water (100 mL) and extracted with DCM (3 × 30 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 2 : 1) to give (3-hydroxy-3-phenyl-3H-indol-2-yl)diphenylphosphine oxide **3a** (0.96 g, 78 %).

VI. Synthetic utility of 2-phosphinoyl indoles

Reduction reaction of 2-phosphinoyl indoles[3]

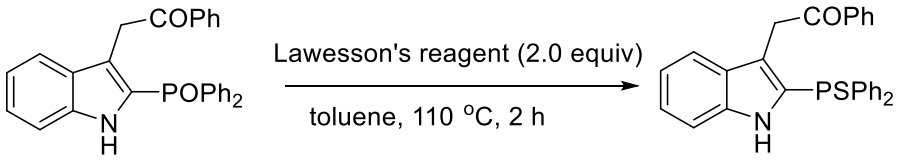


3a **8**

To a 25 mL round bottom flask was added 2-(2-(diphenylphosphoryl)-1H-indol -3-yl)-1-phenylethan-1-one **3a** (0.2 mmol, 87.10 mg), $HSiCl_3$ (10.0 eq, 270.90 mg) and PhCl (2 mL). The flask was placed in a metal bath and heated at 120 °C for 24 h, until the complete consumption of **3a** as monitored by TLC. the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (petroleum ether / ethyl acetate = 20 : 1) to give the 2-(2-(diphenylphosphanyl)-1H-indol-3-yl)- 1-phenylethan- 1-one **8** (70.50 mg, 84 %).Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.71 (s, 1H), 7.62(d, *J* = 8.0 Hz, 1H), 7.47–7.41 (m, 2H), 7.35−7.27 (m, 11H), 7.20−7.11 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 4.68 (s,

2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 140.0 (d, *J* = 51.3 Hz), 138.4, 136.6, 135.7 (d, *J* = 7.8 Hz), 133.0 (d, *J* = 18.7 Hz), 132.9, 129.5 (d, *J* = 66.2 Hz), 129.0, 128.9 (d, *J* = 6.7 Hz), 128.8 (d, *J* = 2.1 Hz), 128.7 (d, *J* = 9.0 Hz), 128.5 (d, *J* = 6.2 Hz), 128.4, 123.6, 120.1 (d, *J* = 9.6 Hz), 119.9, 111.2, 36.5 (d, *J* = 12.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -34.7(s, 1P). **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{23}NOP^+$ 420.1512; found 420.1500.

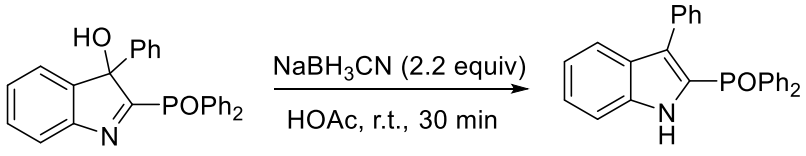
Thioreaction of 2-phosphinoyl indoles[4]



3a **9**

To a 15 mL pressure tubing was added 2-(2-(diphenylphosphoryl)-1H-indol-3- yl)-1-phenylethan-1-one **3a** (0.15 mmol, 65.2 mg), Lawesson's reagent (2.0 eq, 121.34 mg) and toluene (2 mL). Then the reaction mixture was stirred for 2 hour at 110 °C. Upon completion, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give the 2-(2-((diphenyl-l4-sulfanylidene)- phosphanyl)-1H-indol-3-yl)-1- phenylethane-1-one **9** (33.8 mg, 50 %). White solid, **m.p.** 82-84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.73 (t, *J* = 8.4 Hz, 4H), 7.51 (t, *J* = 10.2 Hz, 1H), 7.39 (m, 10H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 4.19 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.9, 137.3 (d, *J* = 9.4 Hz), 136.4, 133.0, 132.1 (d, *J* = 89.4 Hz), 132.0, 131.9, 131.6, 129.6 (d, *J* = 10.9 Hz), 128.9 (d, *J* = 13.0 Hz), 128.2 (d, *J* = 31.7 Hz), 124.9, 123.2 (d, *J* = 103.8 Hz), 120.7, 120.3, 118.2 (d, *J* = 11.2 Hz), 112.0, 35.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{23}NOPS^+$ 452.1232; found 452.1217.

Synthesis of 3-phenyl-2-phosphoroyl-indole 10[5]

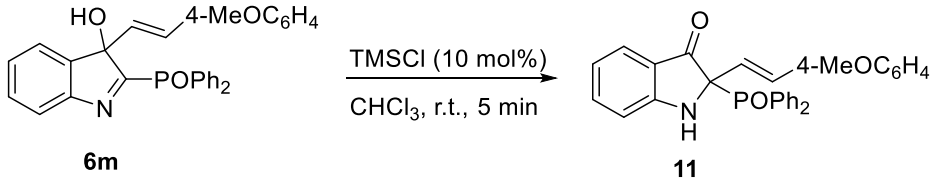


5a **10**

$NaBH_3CN$ (2.2 equiv) was added in batches to a 25 ml round bottom flask containing (3-hydroxy-3-phenyl-3H-indol-2-yl)diphenylphosphine oxide **5a** (0.2 mmol, 88.8 mg) and HOAc (1.5 ml) at 0 °C, and the mixture was stirred at room temperature for another 30 minutes. After the reaction is completed, the reaction is quenched with a saturated Na_2CO_3 solution, and the organic phase is extracted and collected with DCM (3 × 10 mL). It is dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ethyl

acetate=2/1) to obtain diphenyl (3-phenyl-1H-indole-2-yl) phosphine oxide **10** (60.6 mg, 77%). White solid, **m.p.** 228−230 ℃.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.63–7.47 (m, 6H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.32−7.24 (s, 5H), 7.15−7.00 (m, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.5 (d, *J* = 51.3 Hz), 133.5, 132.6, 132.1, 131.9, 131.5, 130.5, 128.6 (d, *J* = 11.3 Hz), 128.4 (d, *J* = 12.7 Hz), 127.8, 126.8, 126.6 (d, *J* = 13.5 Hz), 124.7, 123.4, 120.6 (d, *J* = 14.9 Hz), 112.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{21}NOP^+$ 394.1355; found 394.1350.

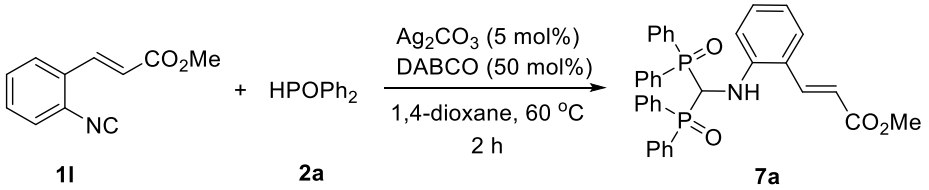
Synthesis of (*E*)-2-(diphenylphosphoryl)-2-(4-methoxystyryl)indolin-3-one 11



In a 15 mL pressure tubing was added (*E*)-(3-hydroxy-3- (4-methoxystyryl)-3H -indol-2-yl)diphenylphosphine oxide **6m** (0.1 mmol, 46.5 mg), TMSCl (10 mol%) and $CHCl_3$ (1 ml)， then the pressure tubing was stirred at room temperature for 5 min. After the reaction is finished, concentrate under reduced pressure to obtain the (*E*)-2-(diphenylphosphoryl) -2 -(4-methoxystyryl)indolin-3-one **11** (44.6 mg, 98 %). Yellow solid, **m.p.** 213-215 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.6 Hz, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.65–7.53 (m, 3H), 7.41 (s, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.28–7.25 (m, 1H), 7.24–7.17 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.90−6.85 (m, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.35 (dd, *J* = 16.0, 4.4 Hz, 1H), 3.74 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 160.3 (d, *J* = 3.2 Hz), 159.4, 137.3, 132.8 (d, *J* = 9.5 Hz), 132.6 (d, *J* = 3.0 Hz), 132.4 (d, *J* = 9.1 Hz), 132.2 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 9.4 Hz), 129.7 (d, *J* = 20.9 Hz), 129.1 (d, *J* = 3.3 Hz), 128.8, 128.6 (d, *J* = 12.1 Hz), 128.1 (d, *J* = 10.2 Hz), 128.0, 124.7, 120.6, 120.1 (d, *J* = 3.8 Hz), 119.0, 113.8, 112.4, 75.4 (d, *J* = 62.6 Hz), 55.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{29}H_{25}NO_3P^+$ 466.1567; found 466.1553.

VII. Mechanistic investigation

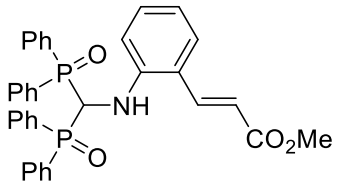
Mechanism verification experiment (with 7a as an example)



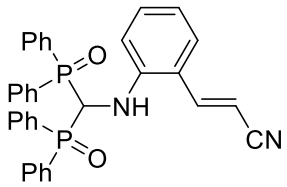
(*E*)-3-(2-isocyanophenyl) methyl acrylate **1l** (0.2 mmol, 37.413 mg), diphenylphosphine oxide **2a** (0.4 mmol, 80.9 mg), Ag_2CO_3 (5 mol%, 2.8 mg), DABCO (50 mol%, 11.2 mg) and 1.4-dioxane（2 ml）were successively added to a pressure tube,

tighten the stopper, heated and stirred in a 60 °C metal bath for 2 hours (monitor the complete consumption of **1l** by TLC). The reaction mixture was cooled to room temperature, diluted with water (10 mL) and extract the mixture with EtOAc (3 × 10 mL). The organic layers were combined, dry over anhydrous Na_2SO_4 and concentrate under reduced pressure. The crude product was purified by column chromatography (dichloromethane/methanol=30/1) to obtain **7a** (65 mg, 50%) of (*E*) -3- (2- (bis (diphenylphosphoryl) methyl) amino) phenyl) methyl acrylate.

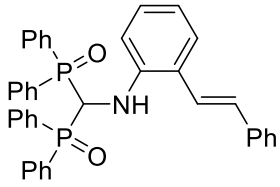
Analytical data of 7a, 7b and 7c.



Methyl (*E*)-3-(2-((bis(diphenylphosphoryl)methyl)amino)phenyl)acrylate (7a). Eluent: CH_2Cl_2/MeOH (30:1), green solid (64.7 mg, 55%), **m.p.:** 168−171 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.81 (m, 4H), 7.80–7.73 (m, 4H), 7.47–7.24 (m, 13H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 8.4 Hz, 1H), 6.06 (d, *J* = 16.0 Hz, 1H), 5.32 (q, *J* = 12.4 Hz, 1H), 4.83 (s, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 144.0 (t, *J* = 2.5 Hz), 139.5, 132.1, 131.6 (t, *J* = 4.7 Hz), 131.0 (d, *J* = 2.8 Hz), 130.9 (d, *J* = 103.7 Hz), 130.8, 130.0 (d, *J* = 2.8 Hz), 128.4 (m, 1C), 121.6, 119.5, 119.1, 112.7, 57.0 (t, *J* = 63.8 Hz), 51.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{35}H_{32}NO_4P_2^+$ 592.1801; found 592.1776.

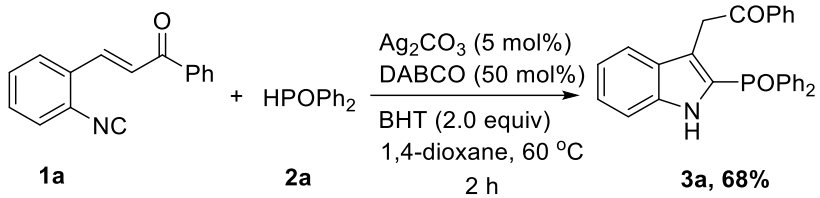


(*E*)-3-(2-((Bis(diphenylphosphoryl)methyl)amino)phenyl)acrylonitrilemethyl (7b). Eluent: CH_2Cl_2/MeOH (30:1), yellow solid (101.3 mg, 91%), **m.p.:** 161-163 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92−7.82 (m, 4H), 7.80−7.68 (m, 4H), 7.57−7.17 (m, 12H), 7.06–6.97 (m, 2H), 6.91 (d, *J* = 4.1 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 5.47 (d, *J* = 4.1 Hz, 1H), 5.33−5.20 (m, 1H), 4.67–4.56 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 144.0 (t, *J* = 2.5 Hz), 132.3, 131.9, 131.5 (m, 1C), 130.4，130.1 (d, *J* = 100.7 Hz), 128.5 (m, 1C), 127.4, 121.1, 119.5, 118.1, 113.7, 97.2, 57.8 (d, *J* = 62.9 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{34}H_{29}N_2O_2P_2^+$ 559.1699; found 559.1665.



(*E*)-(((2-Styrylphenyl)amino)methylene)bis(diphenylphosphine oxide)methyl (7c). Eluent: CH_2Cl_2/MeOH (30:1), yellow solid (100.6 mg, 83%), **m.p.:** 159−161 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92−7.80 (m, 4H), 7.80−7.69 (m, 4H), 7.48–7.17 (m, 17H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.77−6.64 (m, 2H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 1H), 5.36 (s, 1H), 4.73 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9 (t, *J* = 2.6 Hz), 137.2, 132.0 (d, *J* = 3.7 Hz), 131.7 (t, *J* = 5.0 Hz), 131.6 (t, *J* = 4.3 Hz), 31.3 (d, *J* = 2.8 Hz), 130.9 (d, *J* = 103.5 Hz), 130.3 (d, *J* = 2.8 Hz), 128.7, 128.5 (t, *J* = 6.1 Hz), 128.3 (t, *J* = 6.2 Hz), 127.8, 127.3, 126.6, 125.1, 123.2, 119.1, 112.3, 56.9 (t, *J* = 64.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{39}H_{34}NO_2P_2^+$ 610.2059; found 610.2029

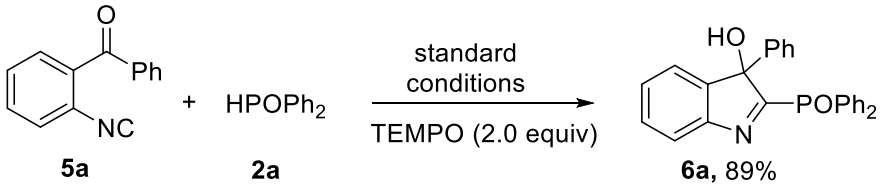
Radical trapping experiment of 3a



1a **2a** **3a, 68%**

(*E*) -3- (3- (2-isocyanophenol) -1-phenylpropane-2-en-1-one **1a** (0.3 mmol, 1.5 equiv, 70 mg), diphenylphosphine oxide **2a** (0.2 mmol, 40.4 mg), Ag_2CO_3 (5 mol%, 2.8 mg), DABCO (50 mol%, 11.2 mg), BHT (0.4 mmol, 2.0 equiv, 88.1 mg) and 1.4-dioxane (2.0 mL) were successively added to a pressure resistant tube. After tightening the stopper, heated at 60 °C for 2 hours. TLC indicated that substrate **1a** was consumed. The reaction mixture was work up as before and product **3a** was obtained in 68% yield.

Radical trapping experiment of 5a



5a **2a** **6a,** 89%

(2-isocyanophenyl) (phenyl) ketone **5a** (0.2 mmol, 41.4 mg), diphenylphosphine oxide **2a** (0.3 mmol, 1.5 equiv, 60.7 mg), Ag_2CO_3 (5 mol%, 2.8 mg), Cs_2CO_3 (50 mol%, 32.6 mg), TEMPO (2.0 equiv) and $CHCl_3$ (2 ml) were successively added to a 15 mL pressure tube, tighten the stopper, heated in a 40 ℃ metal bath for 2.5 hours, and monitor the complete consumption of **5a** through TLC. The reaction mixture was work up as before, and product **6a** was obtained in 89% yield.

References

1. Z. Hu, H. Yuan, Y. Men, Q. Liu, J. Zhang and X. Xu, *Angew. Chem. Int. Ed.* 2016, **55**, 7077–7080.
2. Y. Gue, Z. Hu, J Dong, Q. Liu and X. Xu, *Org. Lett.* 2017, **19**, 5292−5295.
3. C. Chen, J. Ding, L. Liu, Y. Huang and B. Zhu, *Adv. Synth. Catal*. 2022, **364**, 200–205.
4. Y, Liu. P, Xie. J. Li, W. Bai and J. Jiang, *Org. Lett.* 2019, **21**, 4944–4949.
5. X. Guo, J. Dong, Y. Zhu, L. Bao, Z. Hu and X. Xu, *Chin. Chem. Lett*. 2023, **34**, 107608.

VIII. X-ray Crystallographic Data of compound 3a, 6m and 11

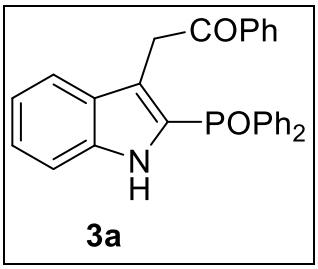
X-ray Crystallographic Data of compound 3a

Sample preparation

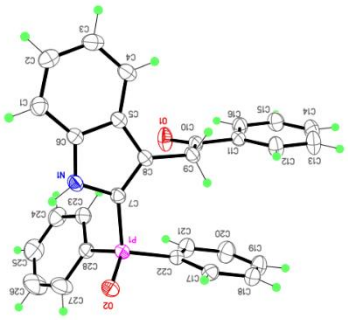
30 mg of **3a** was dissolved in EtOAc and petroleum ether (500 μL / 3 mL) and the solvent was evaporated slowly at room atmosphere.

Crystal measurement for compound 3a

Suitable single crystals of complex **3a** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 293K on an Agilent SuperNova CCD-based diffractometer (Cu Kα radiation λ = 1.54184 Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT. Corrections for incident and diffracted beam absorption effects were applied using SADABS. None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F2 by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2Ueq of the attached atom.



3a



3a CCDC 2334871, displacement ellipsoids are drawn at the 30% probability level. Crystal data and structure refinement for 3a

Empirical formula	$C_{28}H_{22}NO_2P$
Formula weight	435.44
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.2305(5)
b/Å	9.3886(6)
c/Å	15.0613(6)
α/°	83.016(4)
β/°	81.790(4)
γ/°	62.191(6)
Volume/Å^3	1140.40(11)
Z	2
ρ_{calc}mg/mm^3	1.268
m/mm^{-1}	1.261

F(000)	456.0
Crystal size/mm^3	0.25 × 0.2 × 0.15
2Θ range for data collection	10.68 to 140.74°
Index ranges	-11 ≤ h ≤ 10, -11 ≤ k ≤ 11, -12 ≤ l ≤ 18
Reflections collected	8124
Independent reflections	4282[R(int) = 0.0209]
Data/restraints/parameters	4282/0/289
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.1035
Final R indexes [all data]	R_1 = 0.0514, wR_2 = 0.1106
Largest diff. peak/hole / e Å^{-3}	0.25/-0.31

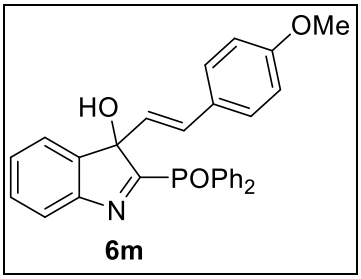
X-ray Crystallographic Data of compound 6m and 11

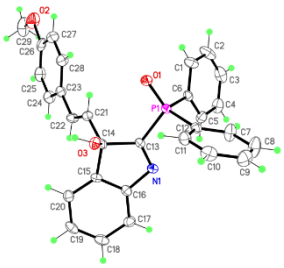
Crystal measurement for compound 6m and 11

Suitable single crystals of complex **6m** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 113.15 K on an Agilent SuperNova CCD-based diffractometer (Cu Kα radiation λ = 1.54184 Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT. Corrections for incident and diffracted beam absorption effects were applied using SADABS. None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F2 by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2Ueq of the attached atom.

Sample preparation

25 mg of **6m** was dissolved in EtOAc and petroleum ether (500 μL / 3 mL) and the solvent was evaporated slowly at room atmosphere.





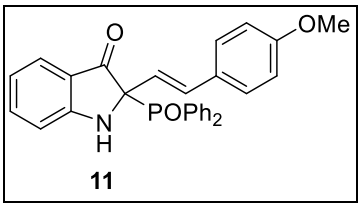
6m CCDC 2334872, displacement ellipsoids are drawn at the 30% Probability level. Crystal data and structure refinement for 6m

Empirical formula	$C_{29}H_{24}NO_3P$
Formula weight	465.46
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.1021(9)
b/Å	10.6285(9)
c/Å	12.0861(10)
α/°	95.272(7)

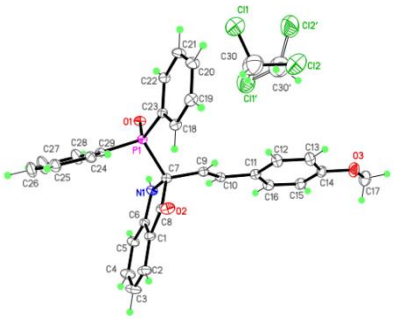
β/°	112.661(8)
γ/°	92.657(7)
Volume/Å^3	1187.71(17)
Z	2
ρ_{calc}mg/mm^3	1.302
m/mm^{-1}	1.278
F(000)	488.0
Crystal size/mm^3	0.08 × 0.06 × 0.02
2Θ range for data collection	7.98 to 134.08°
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	8165
Independent reflections	4223[R(int) = 0.0488]
Data/restraints/parameters	4223/0/309
Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, wR_2 = 0.1101
Final R indexes [all data]	R_1 = 0.0751, wR_2 = 0.1253
Largest diff. peak/hole / e Å^{-3}	0.32/-0.38

Sample preparation

25 mg of **11** was dissolved in EtOAc and petroleum ether (500 μL / 3 mL) and the solvent was evaporated slowly at room atmosphere.



11



11 CCDC 2334873, displacement ellipsoids are drawn at the 25% Probability level.

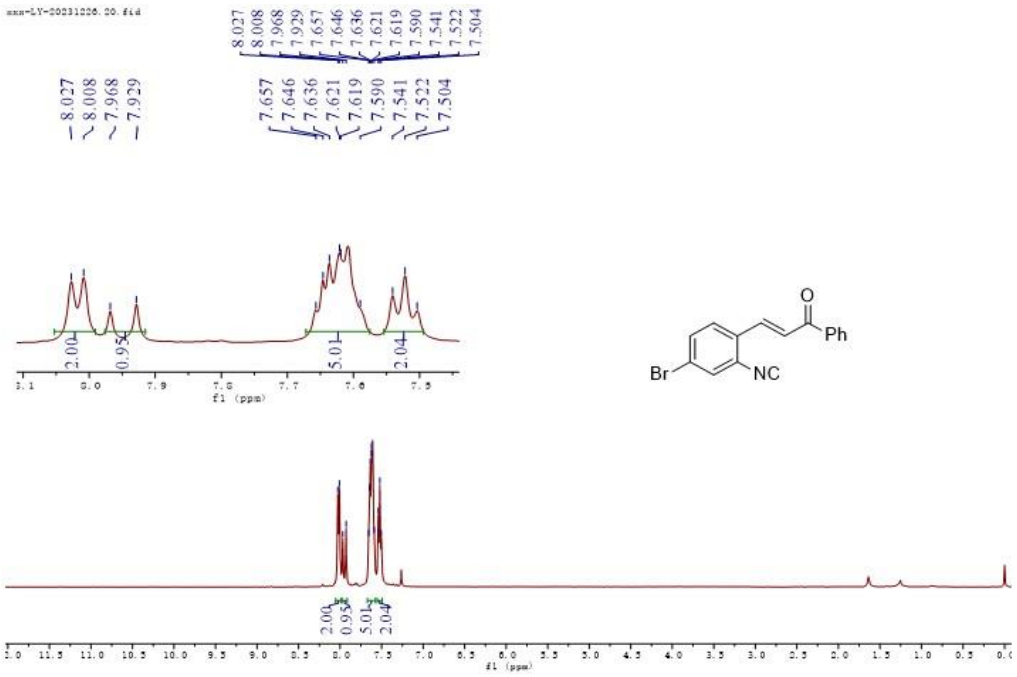
Crystal data and structure refinement for 11

Empirical formula	$C_{29.6}H_{25.2}Cl_{1.2}NO_3P$
Formula weight	516.42
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.9338(7)
b/Å	11.4115(6)
c/Å	13.4261(9)
α/°	91.104(5)
β/°	99.247(6)
γ/°	107.898(5)
Volume/Å^3	1425.67(16)
Z	2
ρ_{calc}mg/mm^3	1.203
m/mm^{-1}	2.123

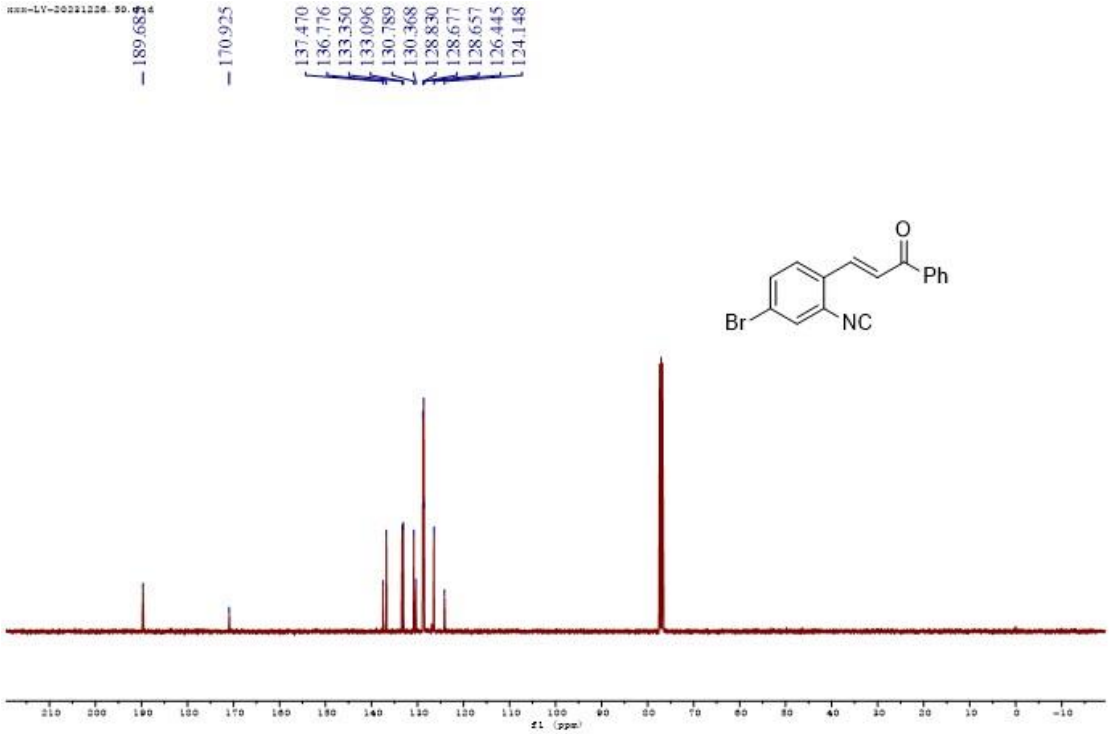
F(000)	538.0
Crystal size/mm^3	0.16 × 0.11 × 0.07
2Θ range for data collection	9.5 to 134.16°
Index ranges	$-11 \leq h \leq 11$, $-13 \leq k \leq 11$, $-15 \leq l \leq 16$
Reflections collected	10015
Independent reflections	5070[R(int) = 0.0320]
Data/restraints/parameters	5070/23/350
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0677, wR_2 = 0.1921
Final R indexes [all data]	R_1 = 0.0815, wR_2 = 0.2079
Largest diff. peak/hole / e $Å^{-3}$	0.91/-0.50

IX. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra of compounds 1, 3, 4, 5, 6, 7, 8, 9, 10 and 11

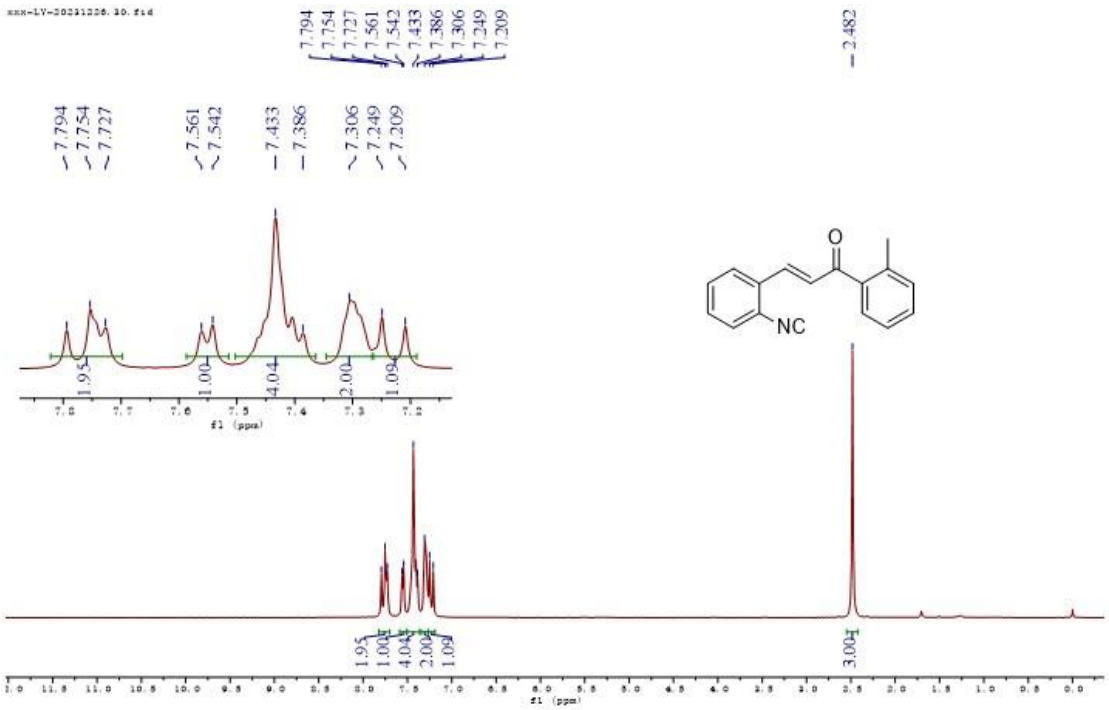
^{1}H NMR (400 MHz, $CDCl_3$) for **1d**



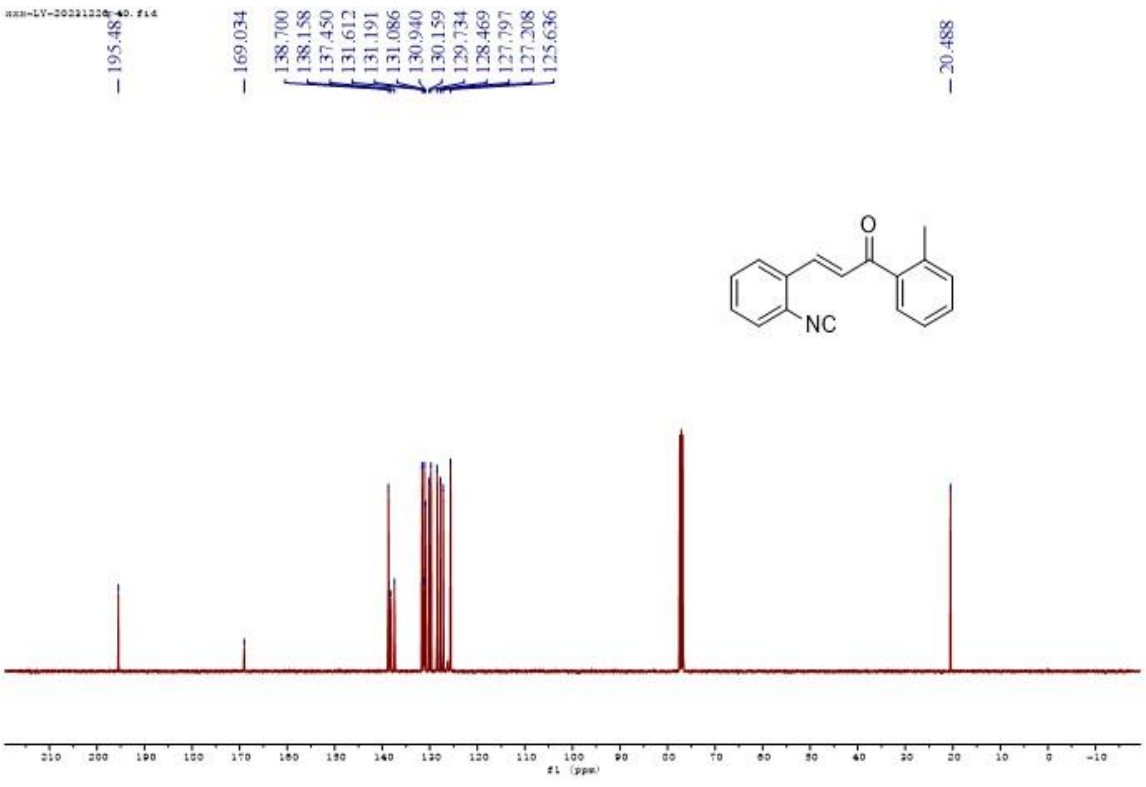
^{13}C NMR (100 MHz, $CDCl_3$) for **1d**



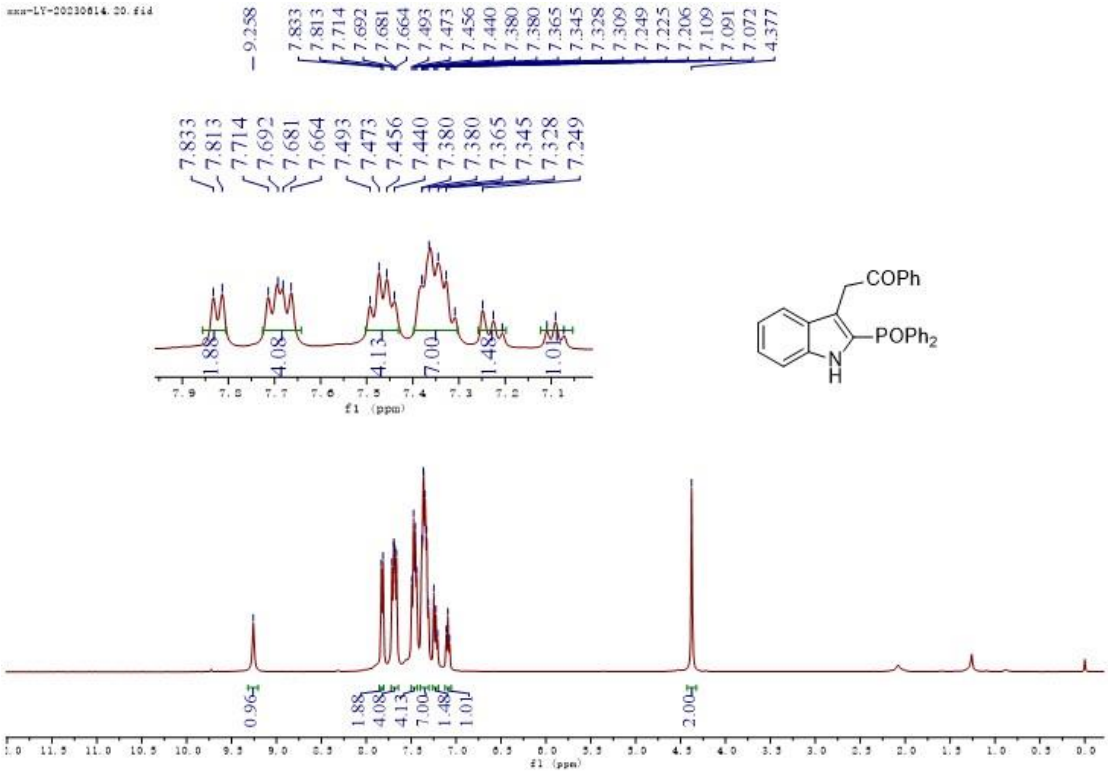
^{1}H NMR (400 MHz, $CDCl_3$) for **1g**



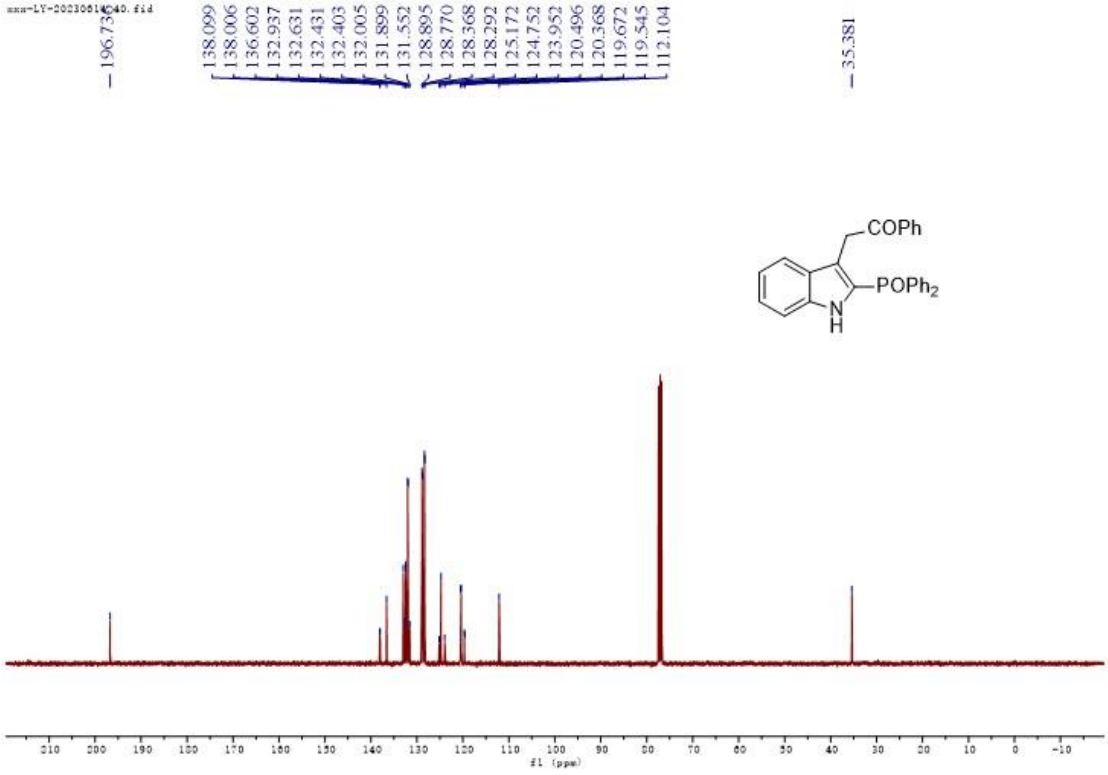
^{13}C NMR (100 MHz, $CDCl_3$) for **1g**



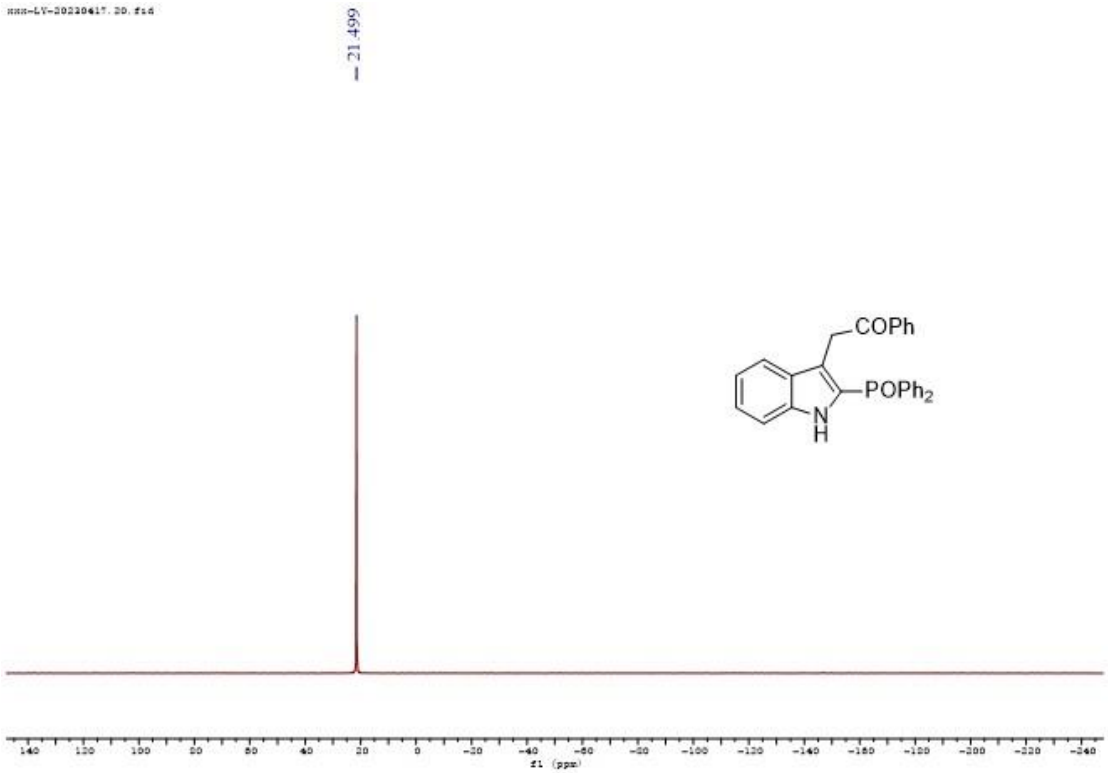
^{1}H NMR (400 MHz, $CDCl_3$) for **3a**



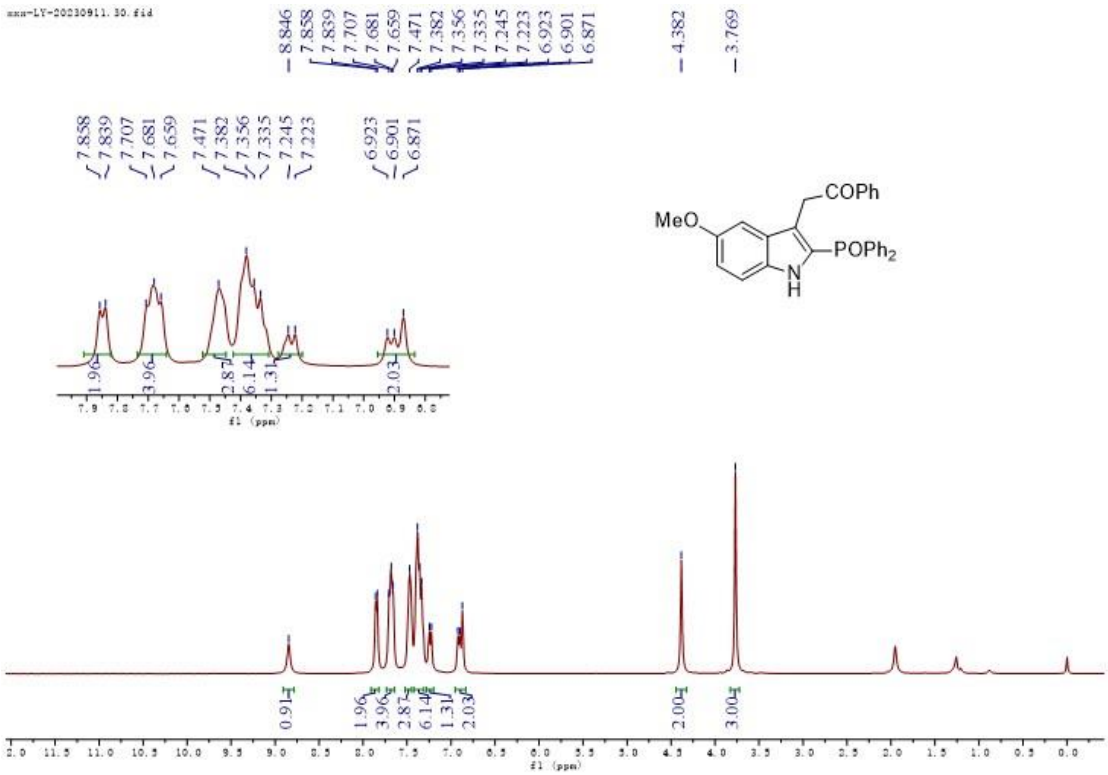
^{13}C NMR (101 MHz, $CDCl_3$) for **3a**



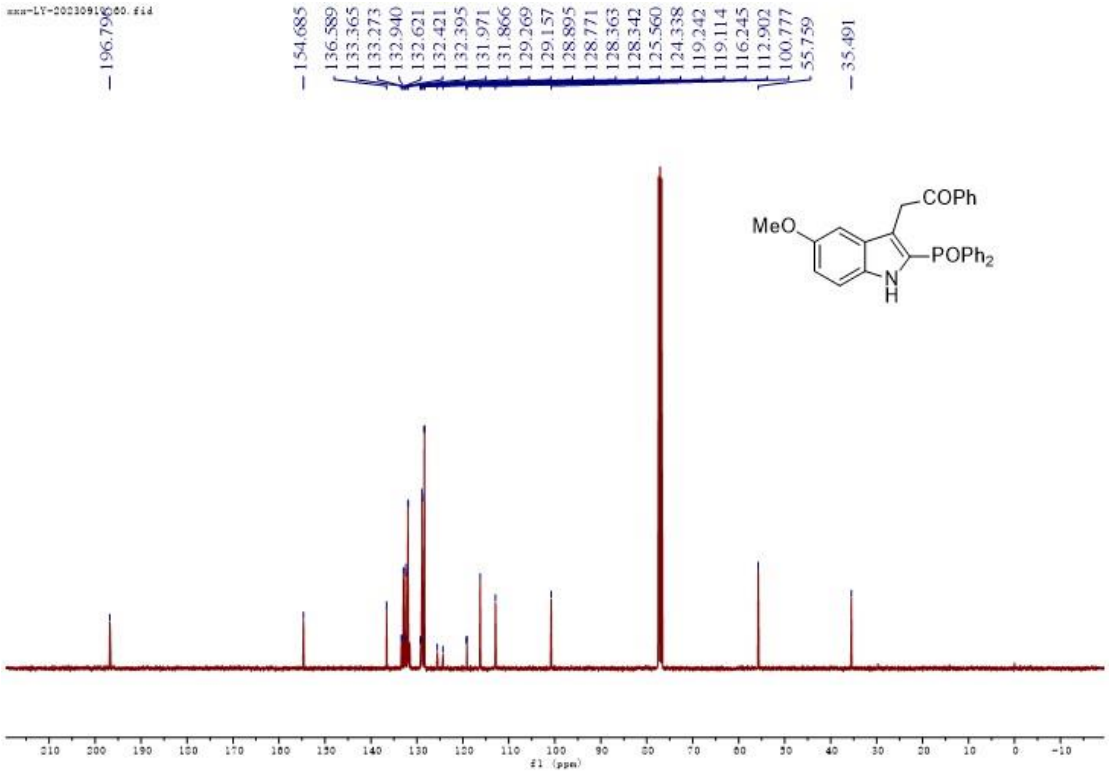
^{31}P NMR (162 MHz, $CDCl_3$) for **3a**



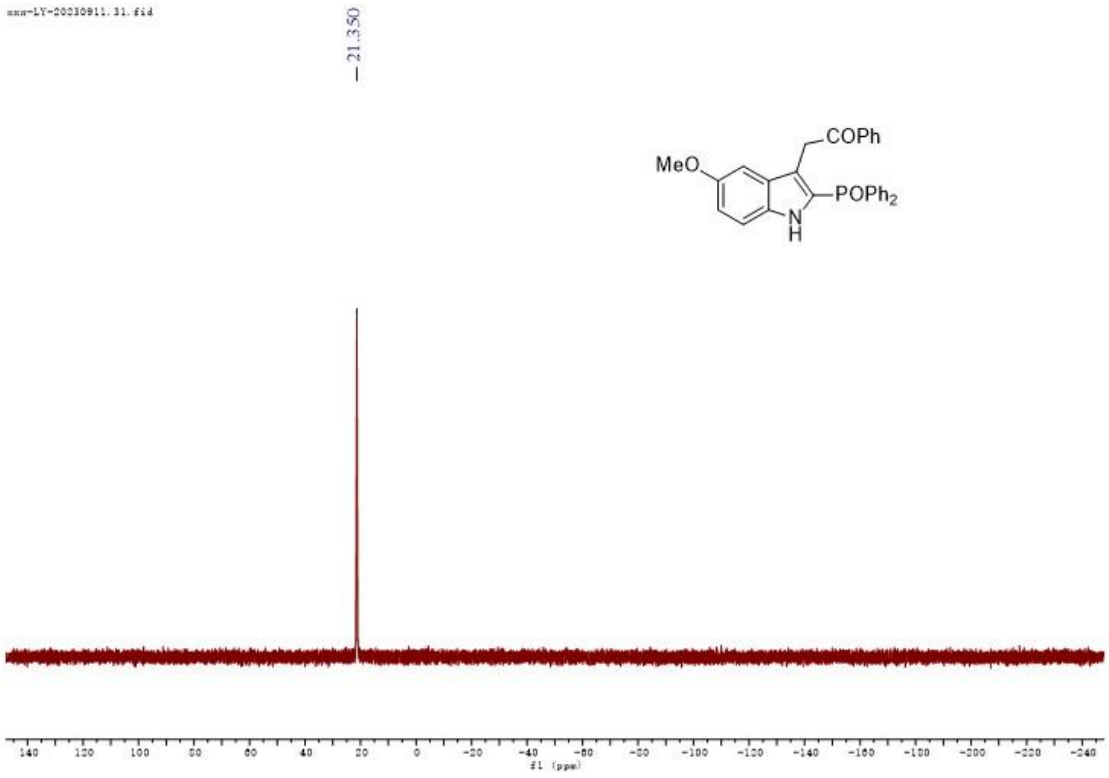
^{1}H NMR (101 MHz, $CDCl_3$) for **3b**



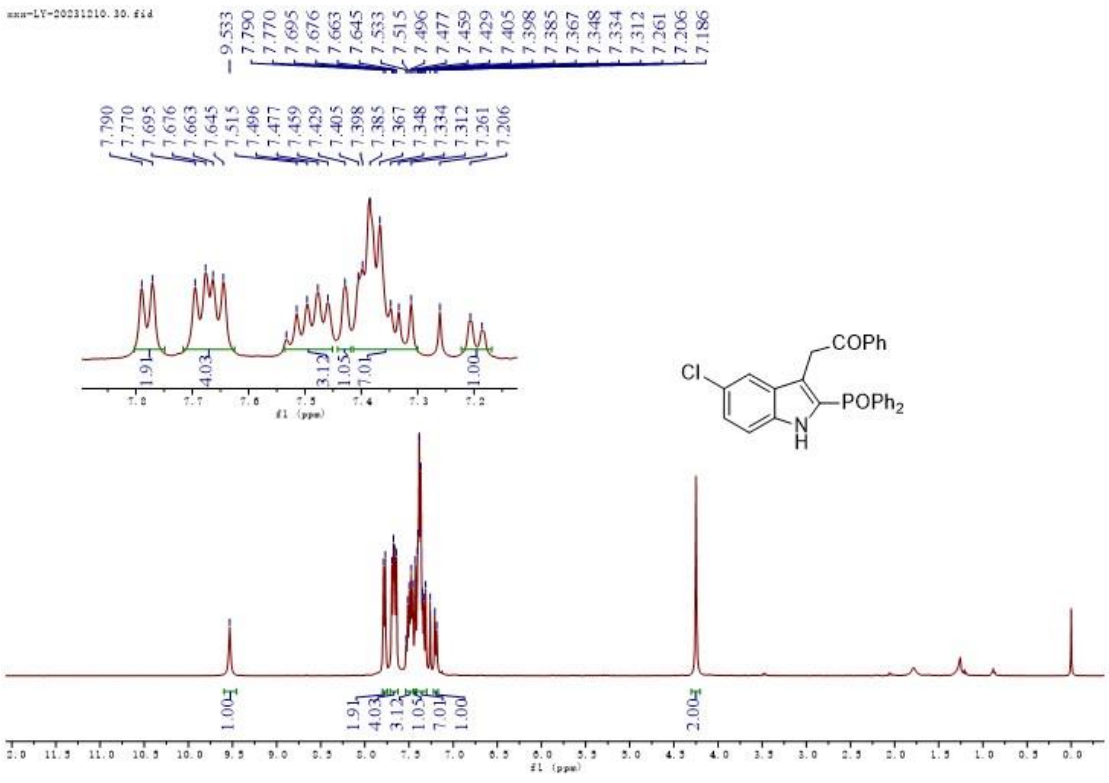
^{13}C NMR (400 MHz, $CDCl_3$) for **3b**



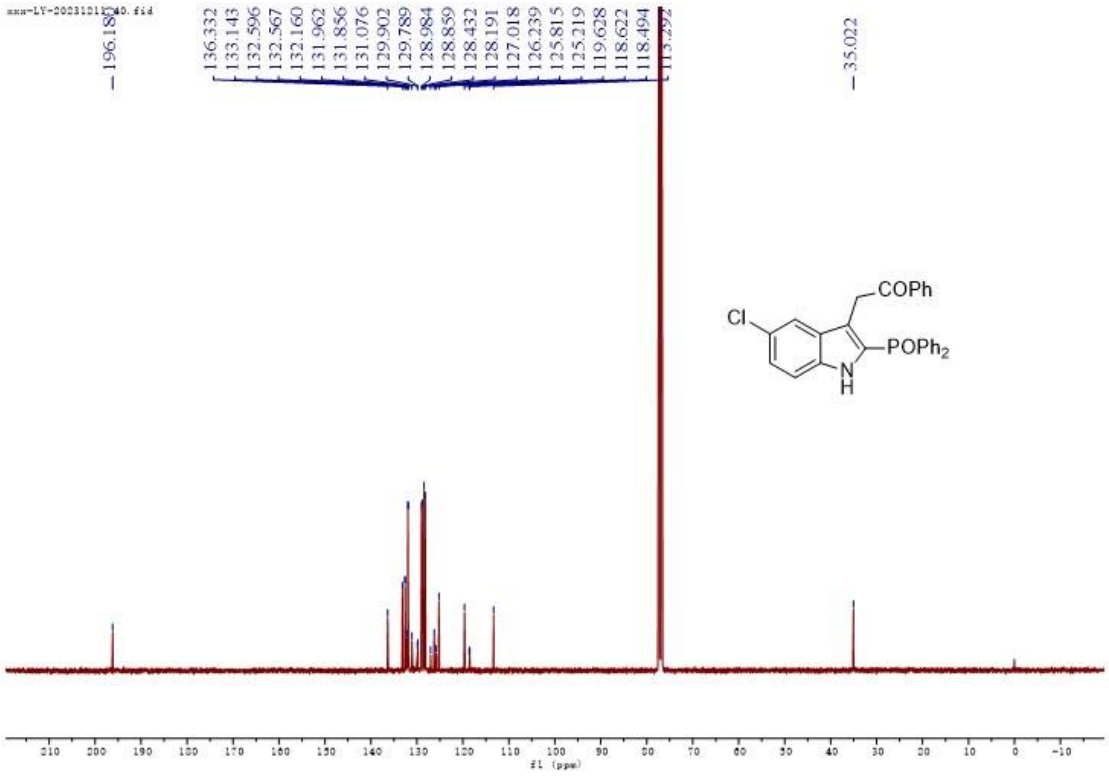
^{31}P NMR (162 MHz, $CDCl_3$) for **3b**



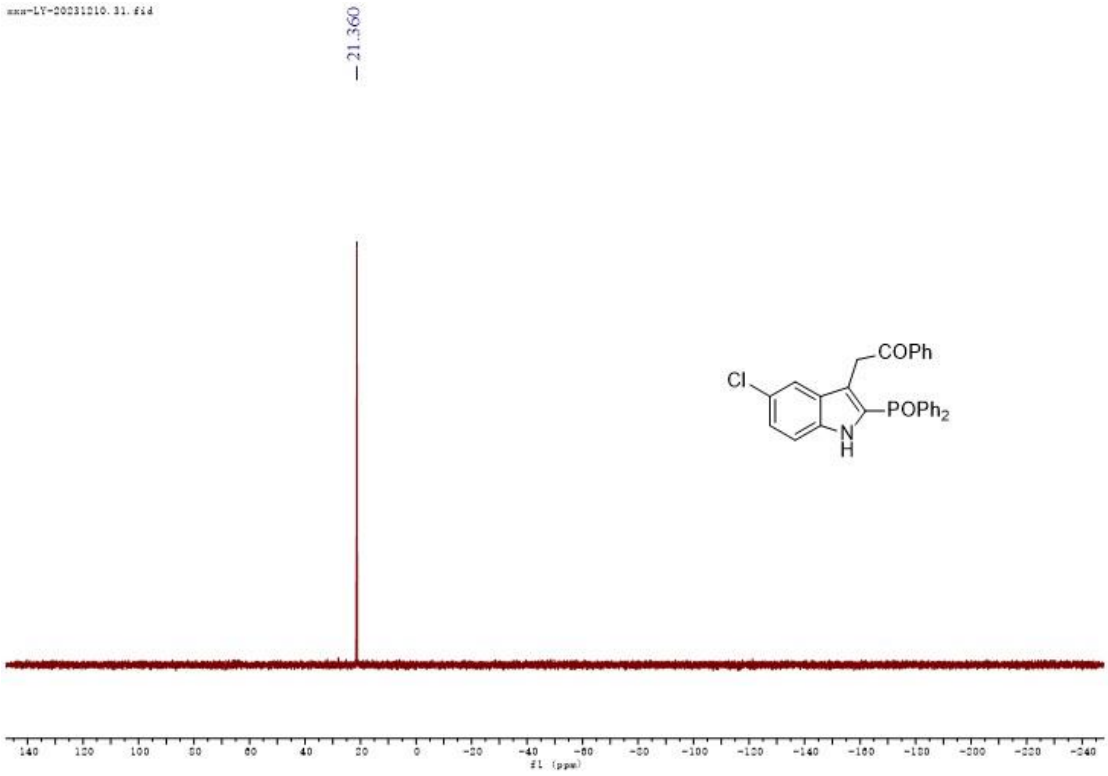
^{1}H NMR (400 MHz, $CDCl_3$) for **3c**



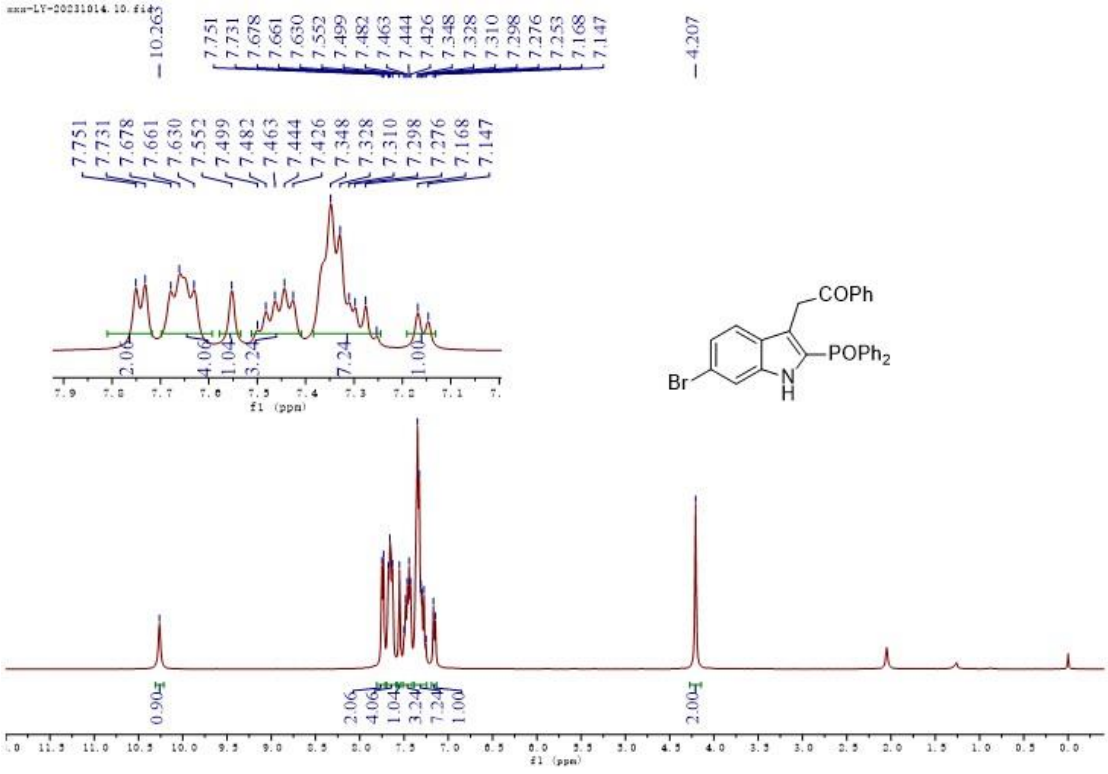
^{13}C NMR (101 MHz, $CDCl_3$) for **3c**



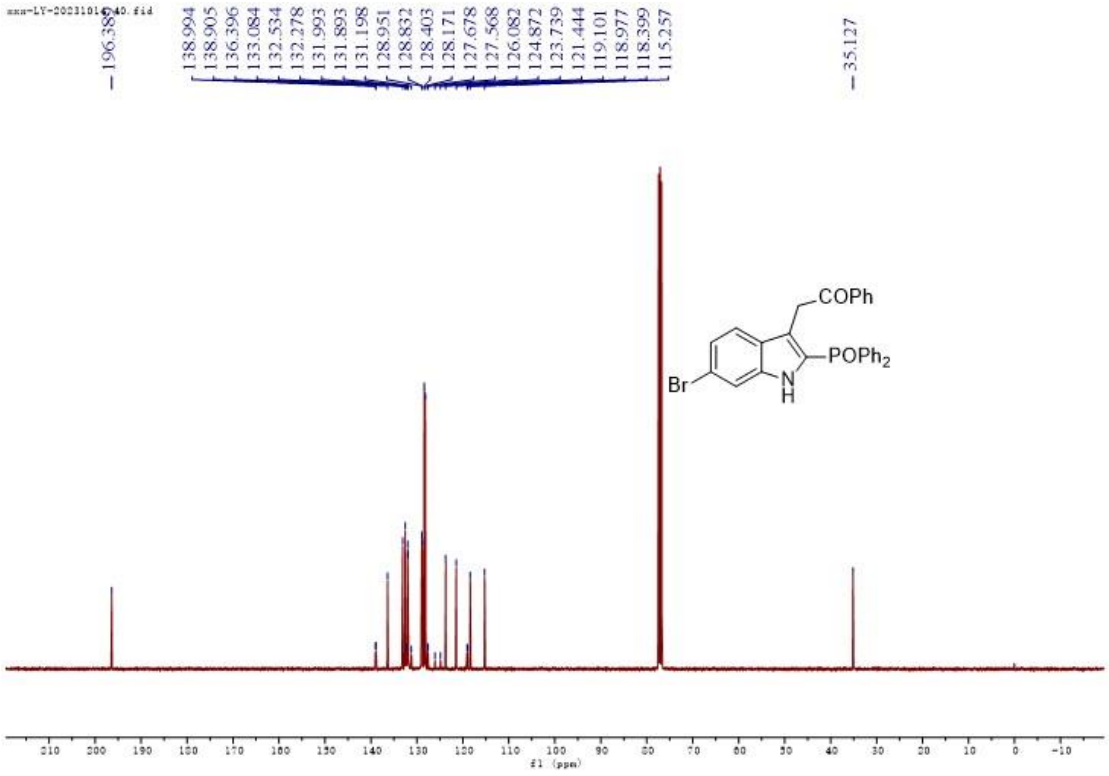
^{31}P NMR (162 MHz, $CDCl_3$) for **3c**



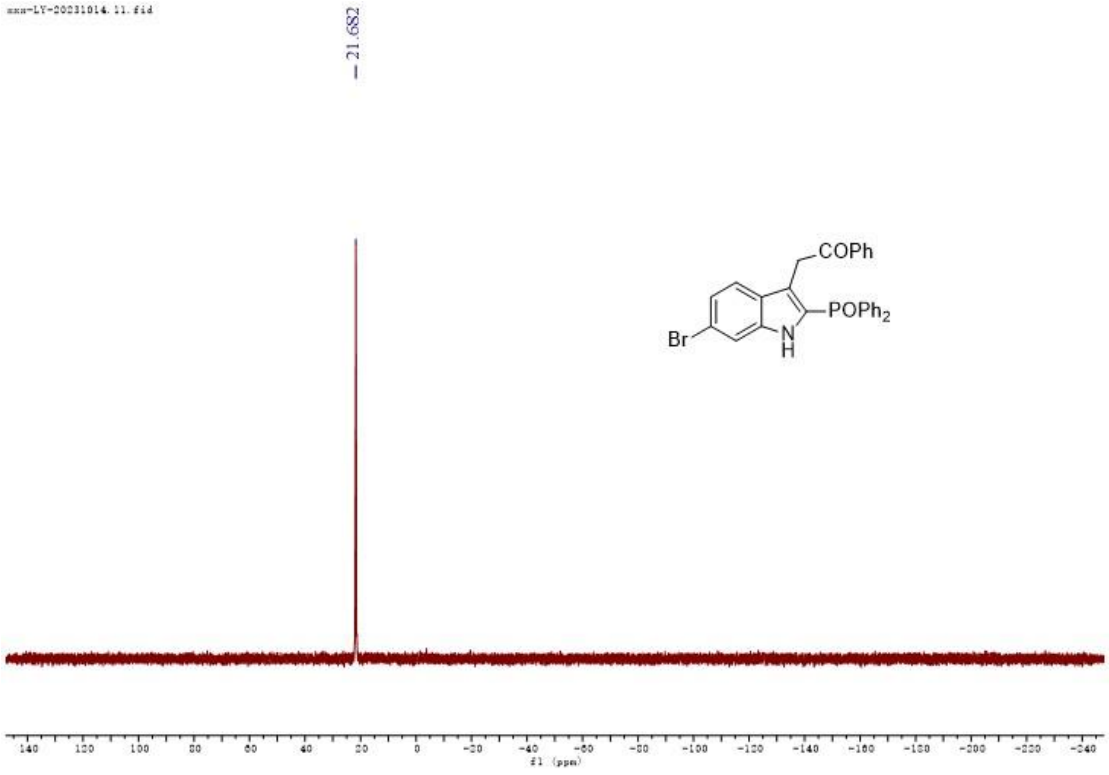
^{1}H NMR (400 MHz, $CDCl_3$) for **3d**



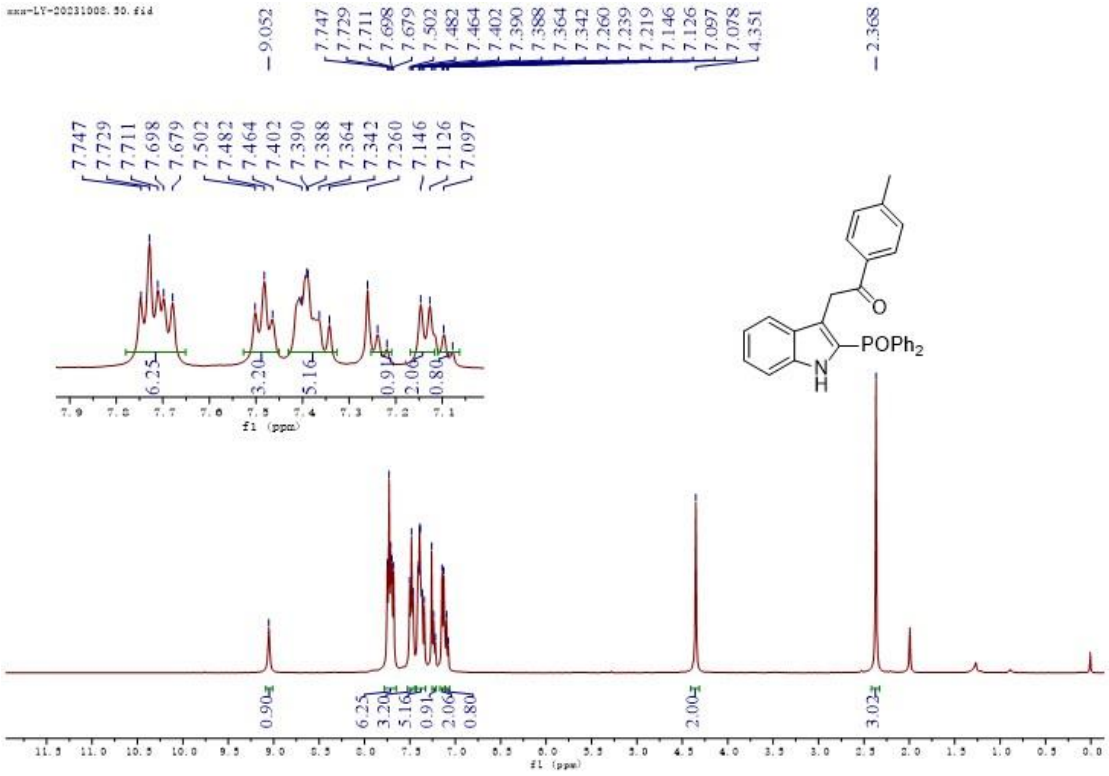
^{13}C NMR (101 MHz, $CDCl_3$) for **3d**



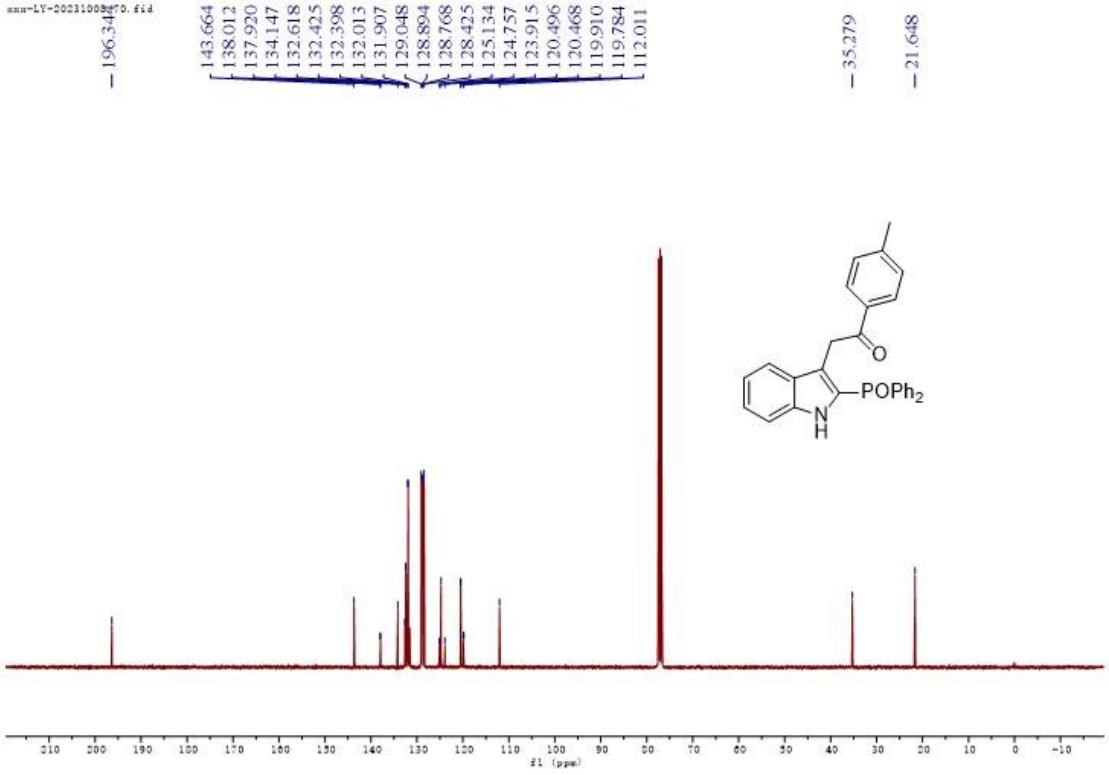
^{31}P NMR (162 MHz, $CDCl_3$) for **3d**



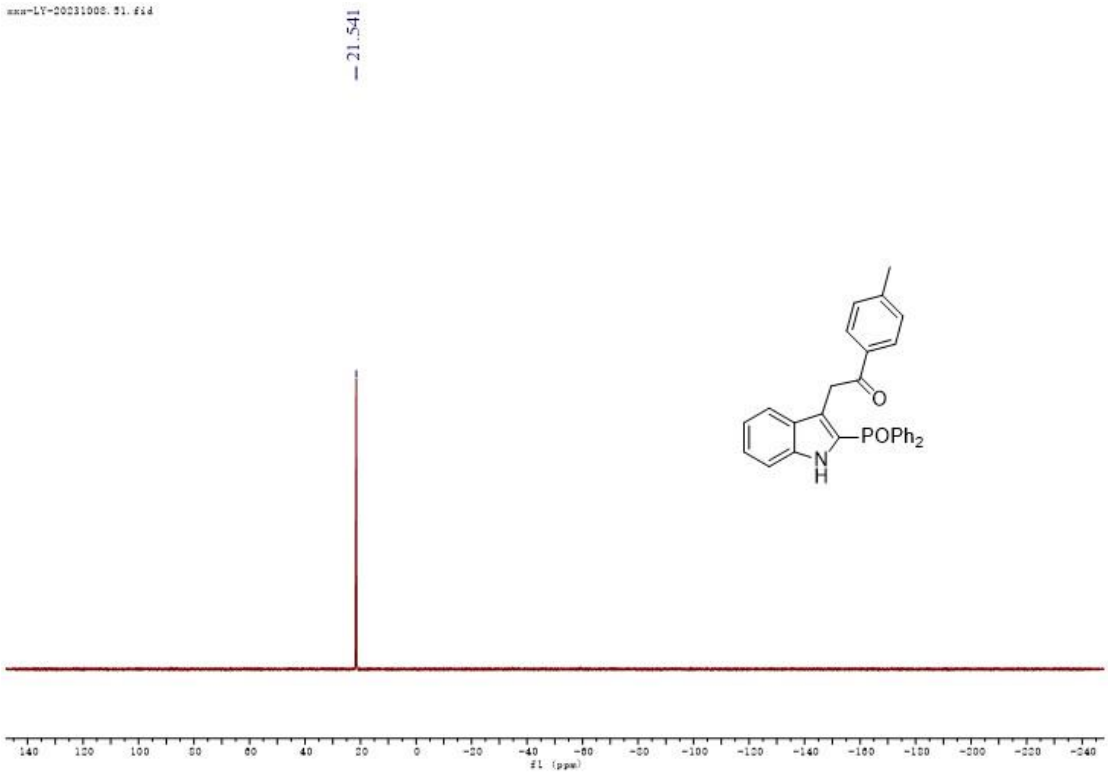
^{1}H NMR (400 MHz, $CDCl_3$) for **3e**



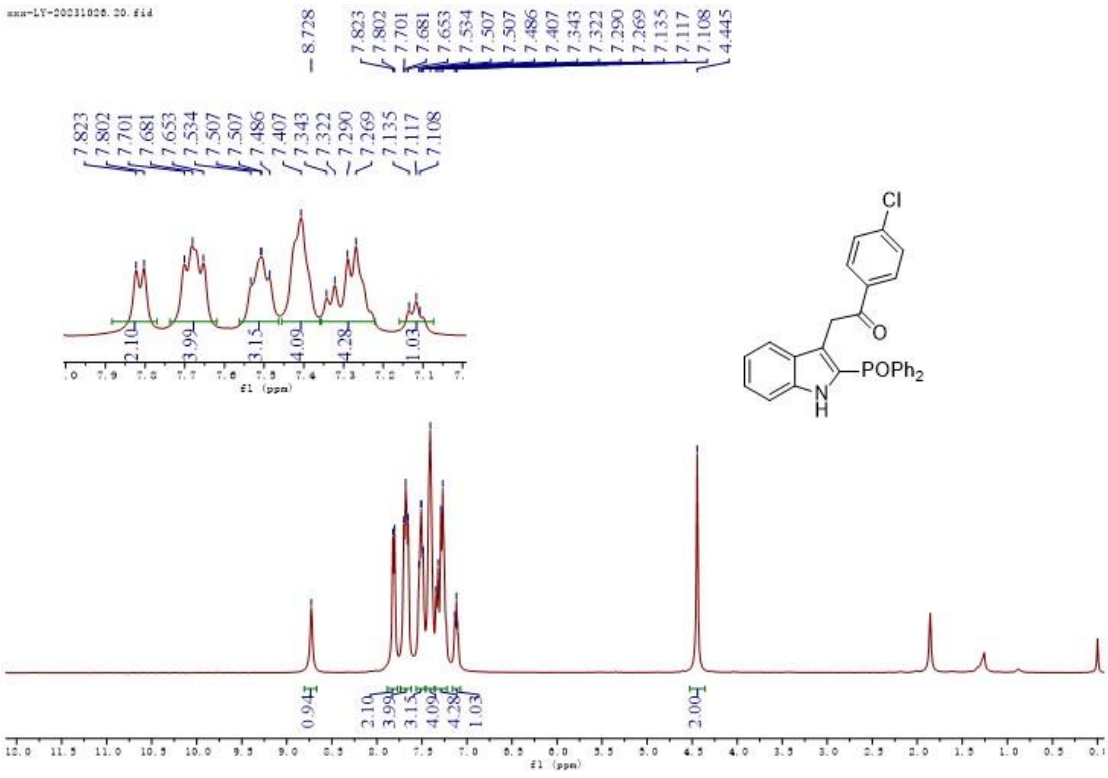
^{13}C NMR (101 MHz, $CDCl_3$) for **3e**



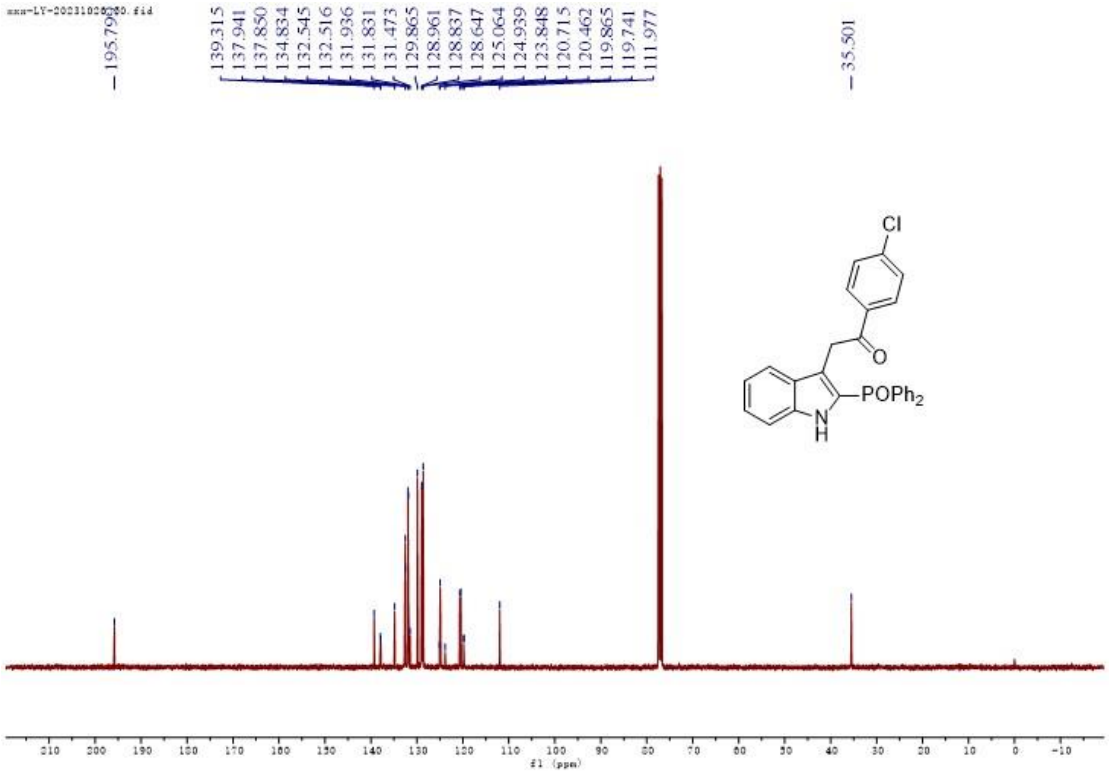
^{31}P NMR (162 MHz, $CDCl_3$) for **3e**



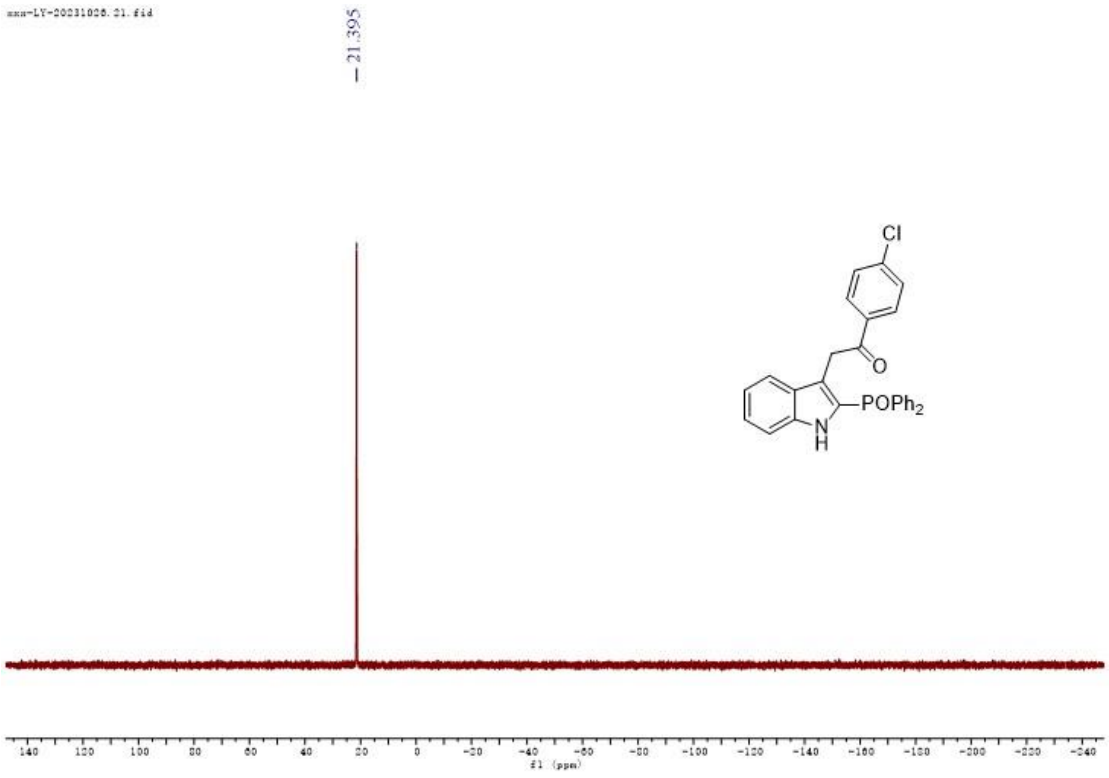
^{13}H NMR (400 MHz, $CDCl_3$) for **3f**



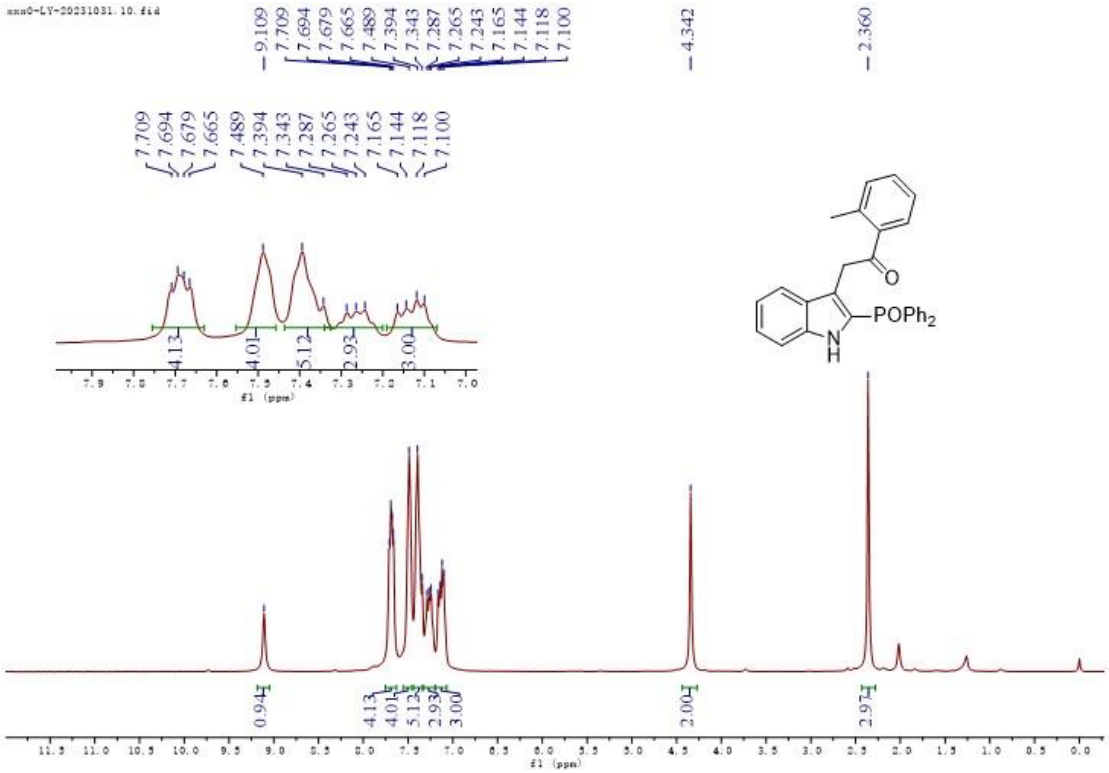
^{13}C NMR (101 MHz, $CDCl_3$) for **3f**



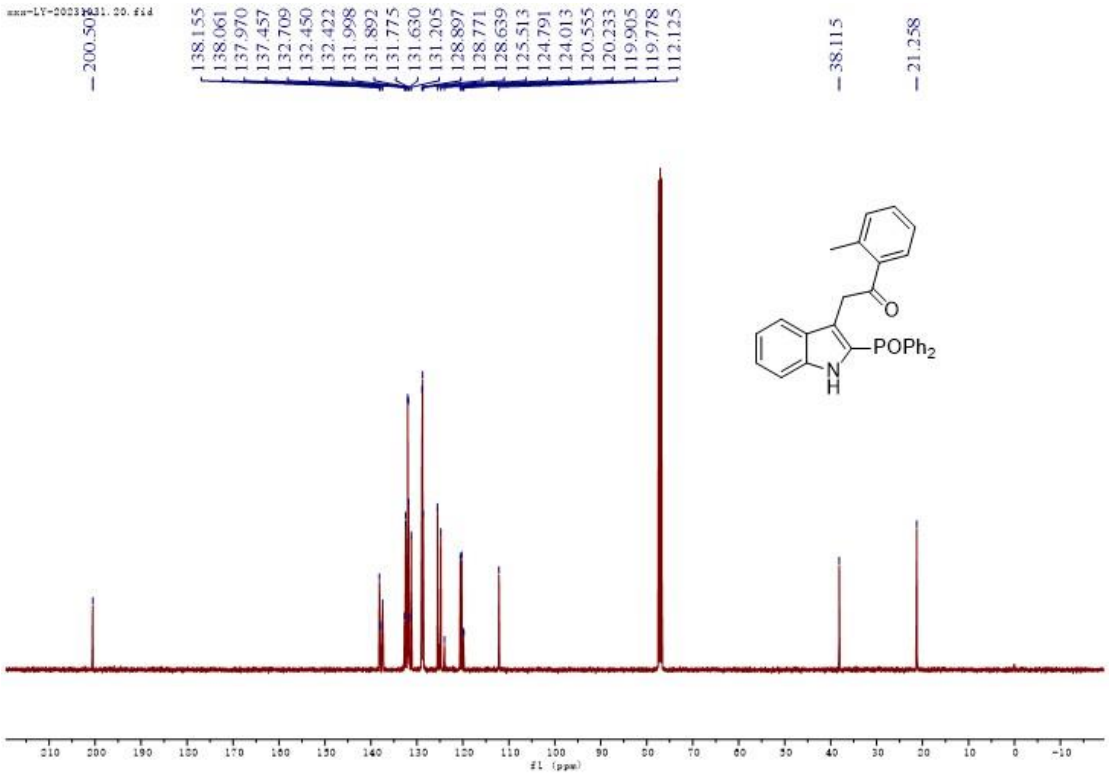
^{31}P NMR (162 MHz, $CDCl_3$) for **3f**



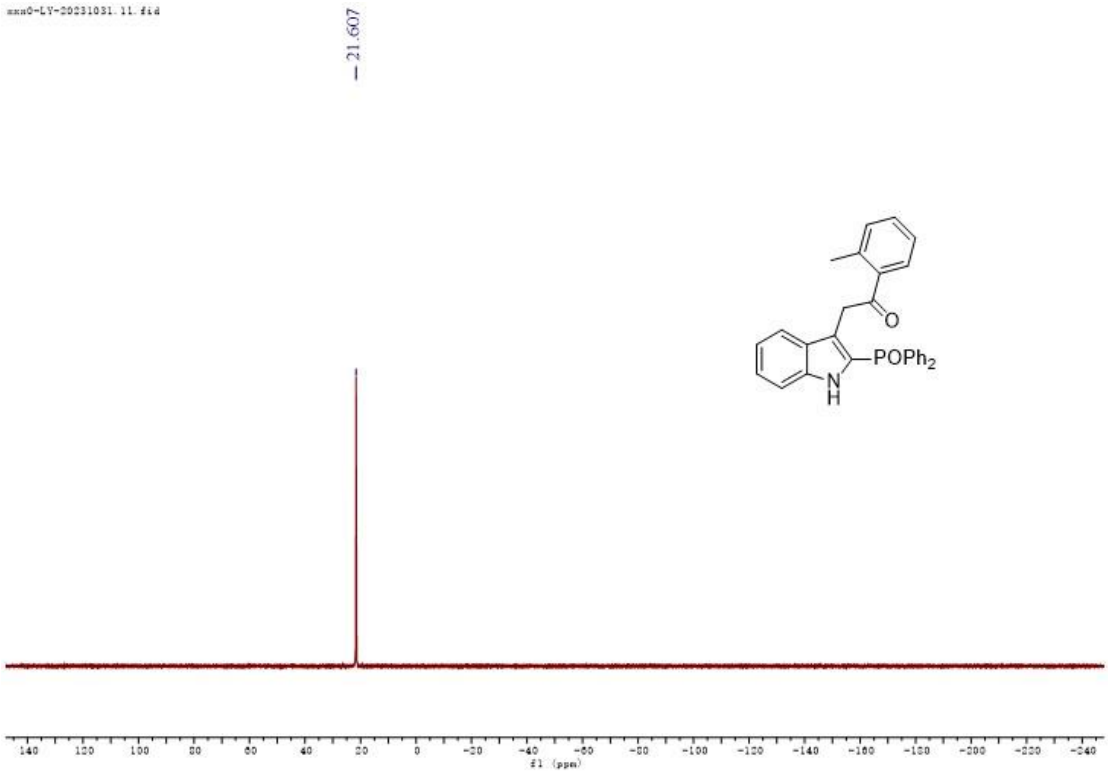
^{1}H NMR (400 MHz, $CDCl_3$) for **3g**



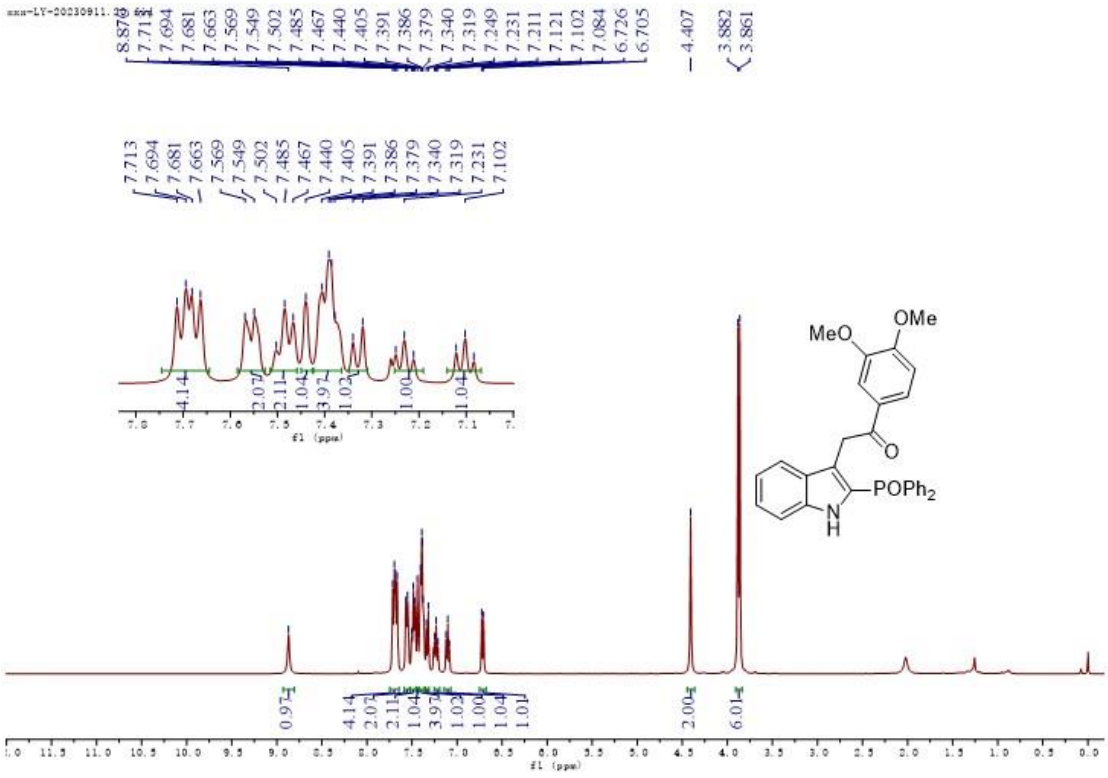
^{13}C NMR (101 MHz, $CDCl_3$) for **3g**



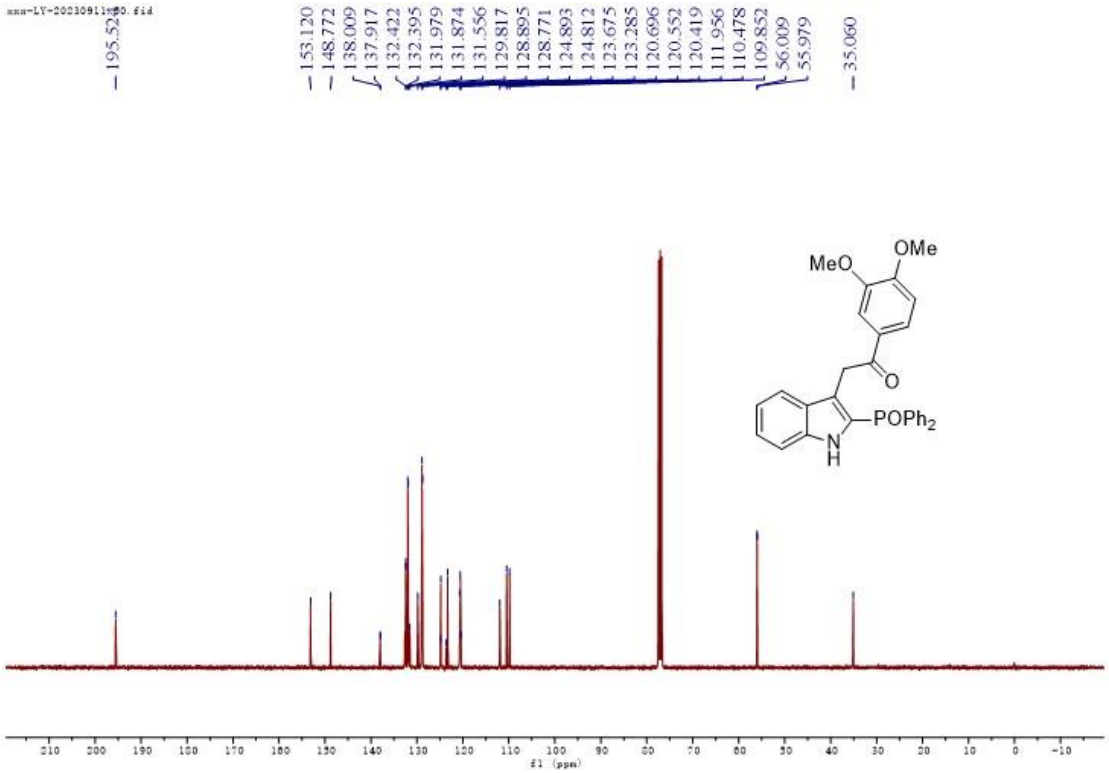
^{31}P NMR (162 MHz, $CDCl_3$) for **3g**



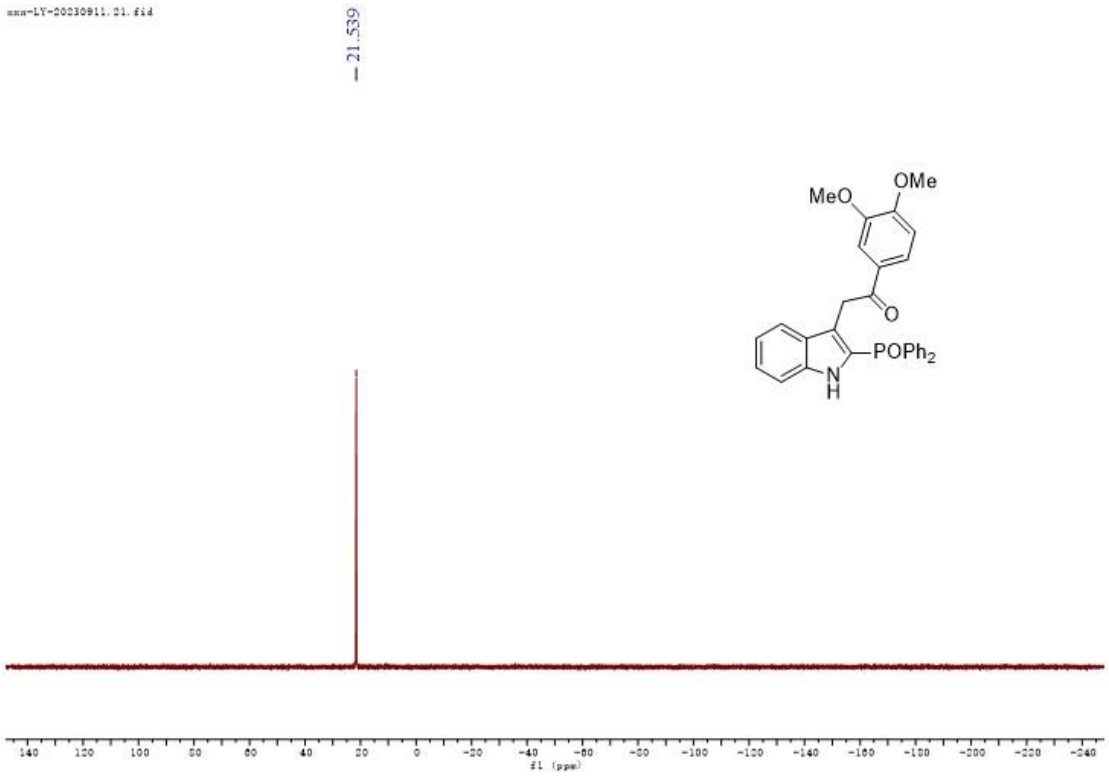
^{1}H NMR (400 MHz, $CDCl_3$) for **3h**



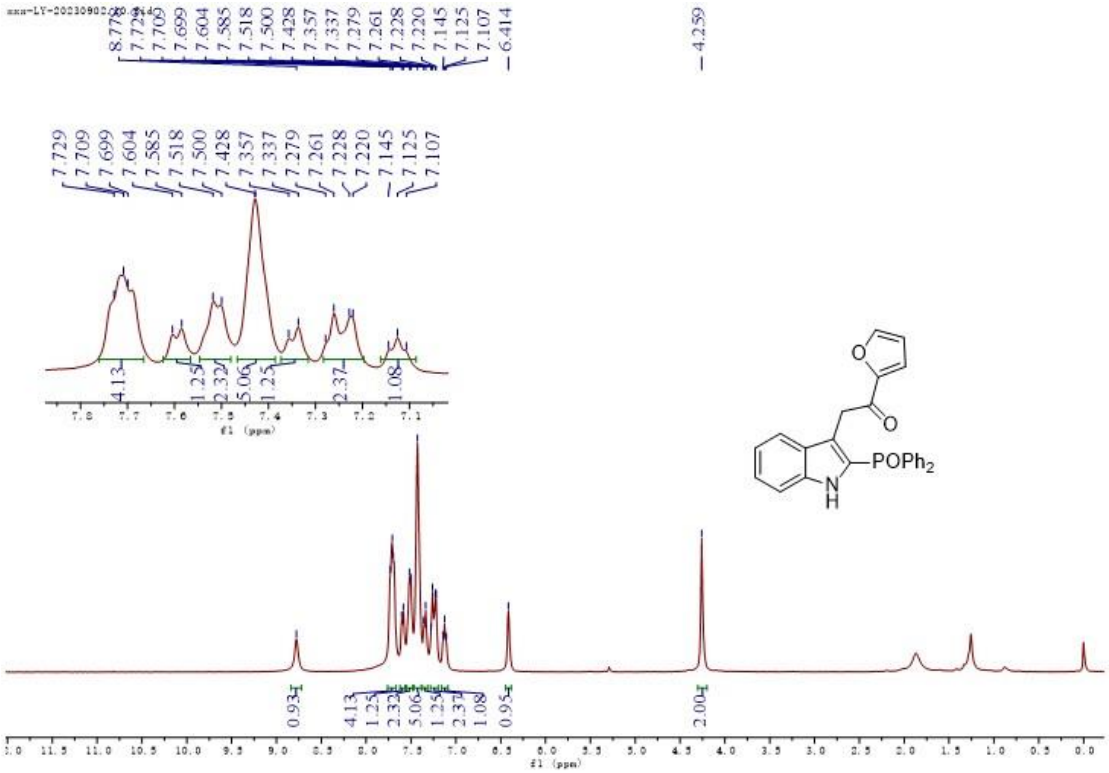
^{13}C NMR (101 MHz, $CDCl_3$) for **3h**



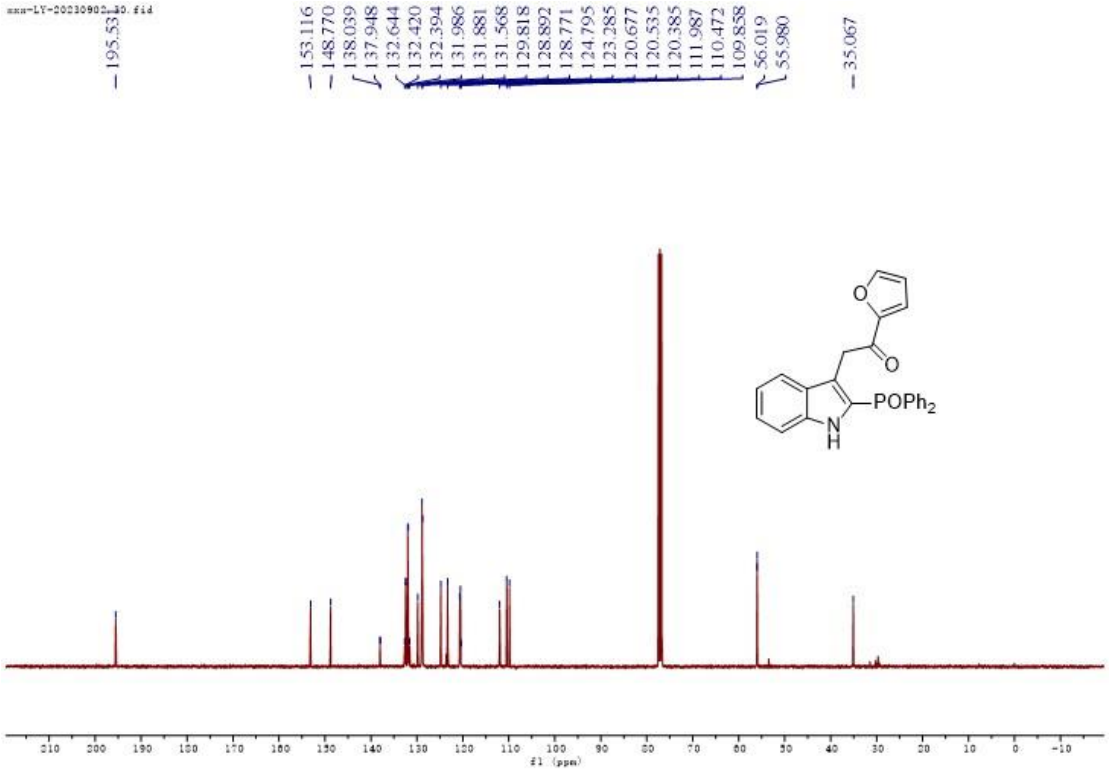
^{31}P NMR (162 MHz, $CDCl_3$) for **3h**



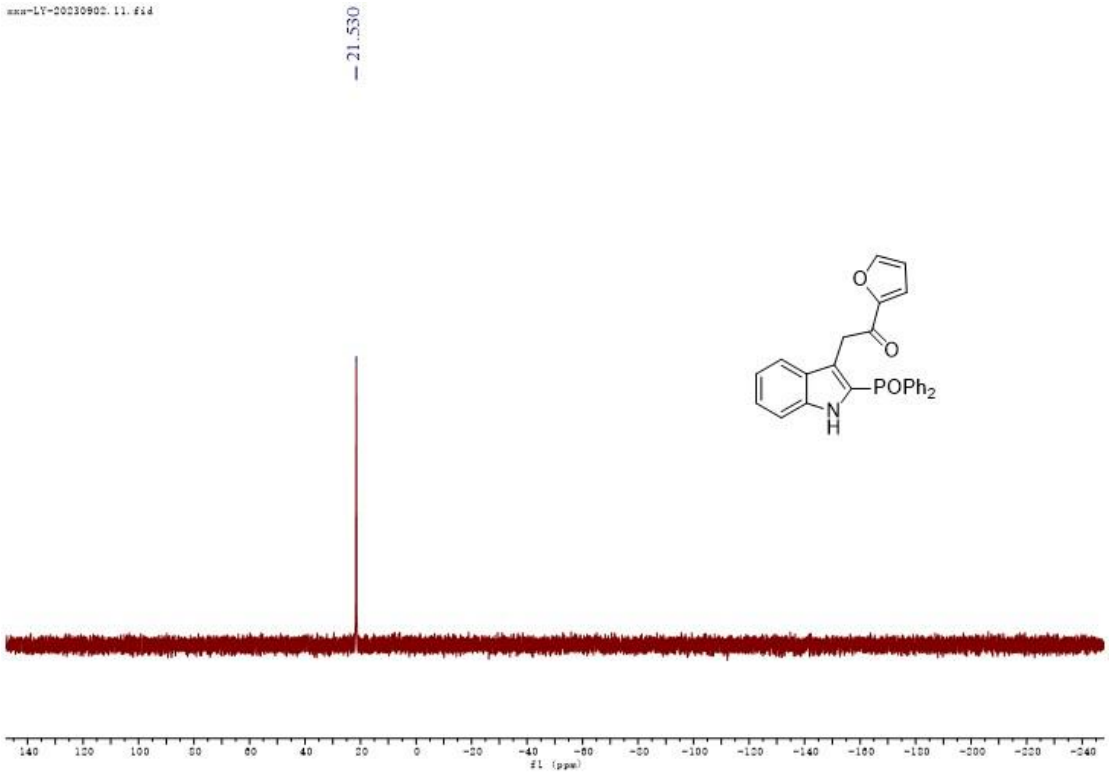
^{1}H NMR (400 MHz, $CDCl_3$) for **3i**



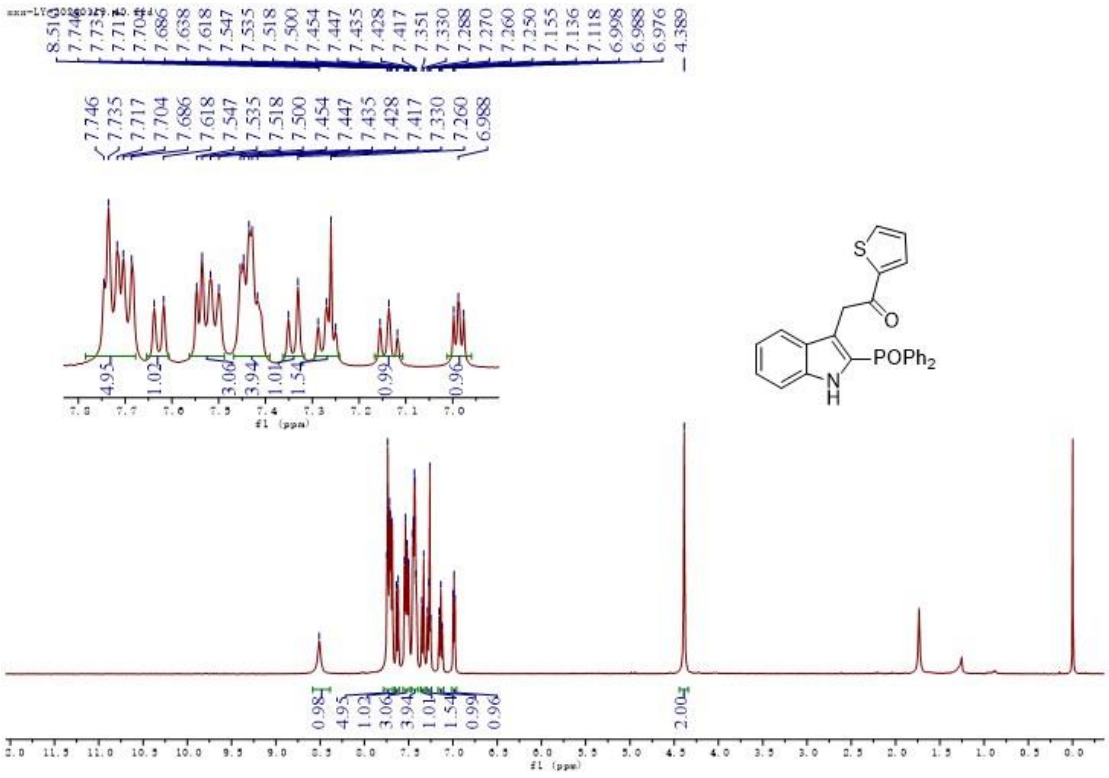
^{13}C NMR (101 MHz, $CDCl_3$) for **3i**



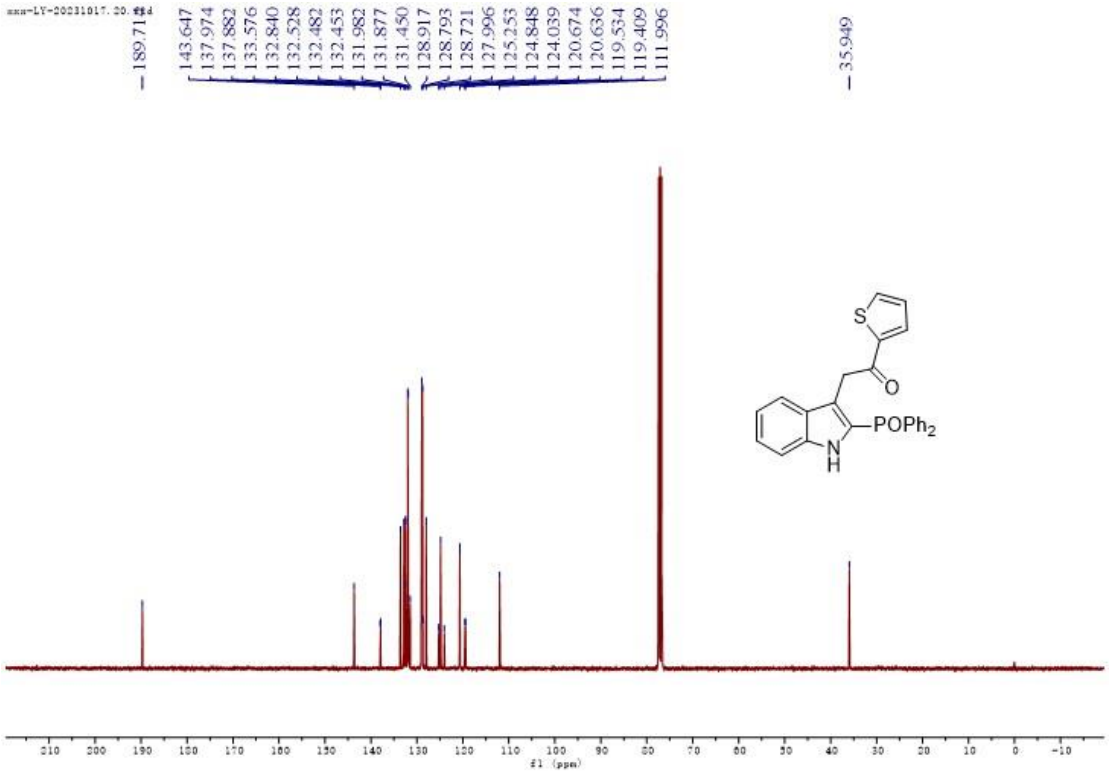
^{31}P NMR (162 MHz, $CDCl_3$) for **3i**



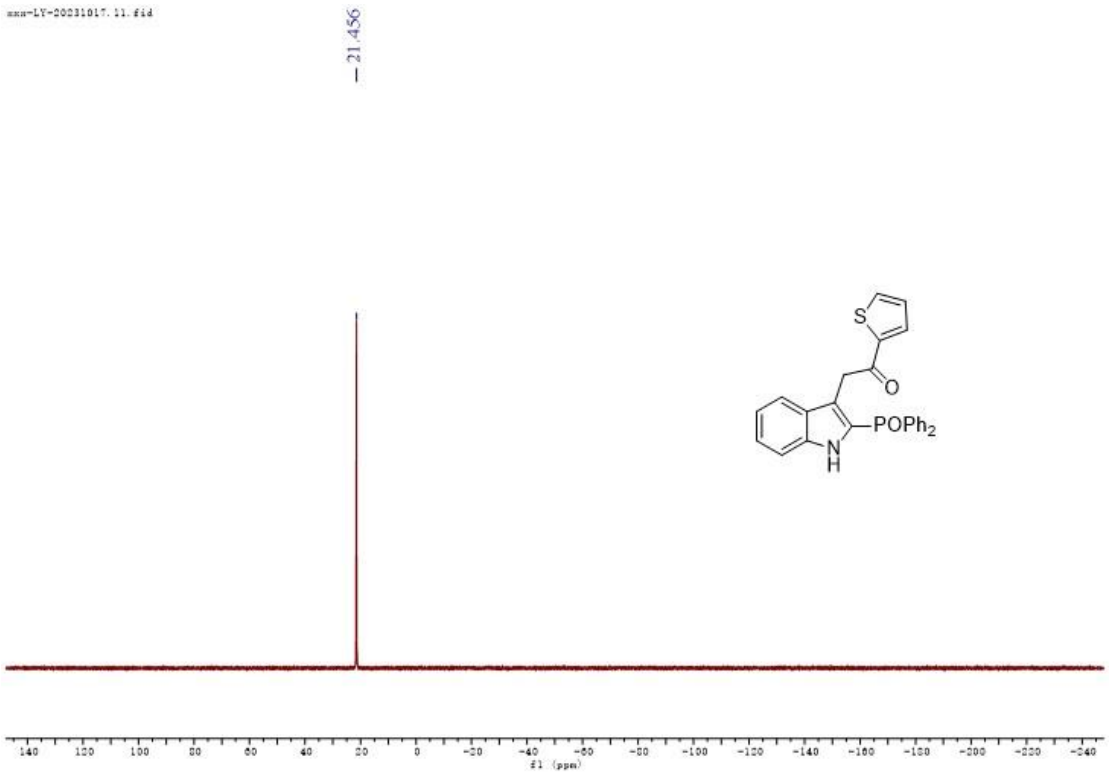
^{1}H NMR (400 MHz, $CDCl_3$) for **3j**



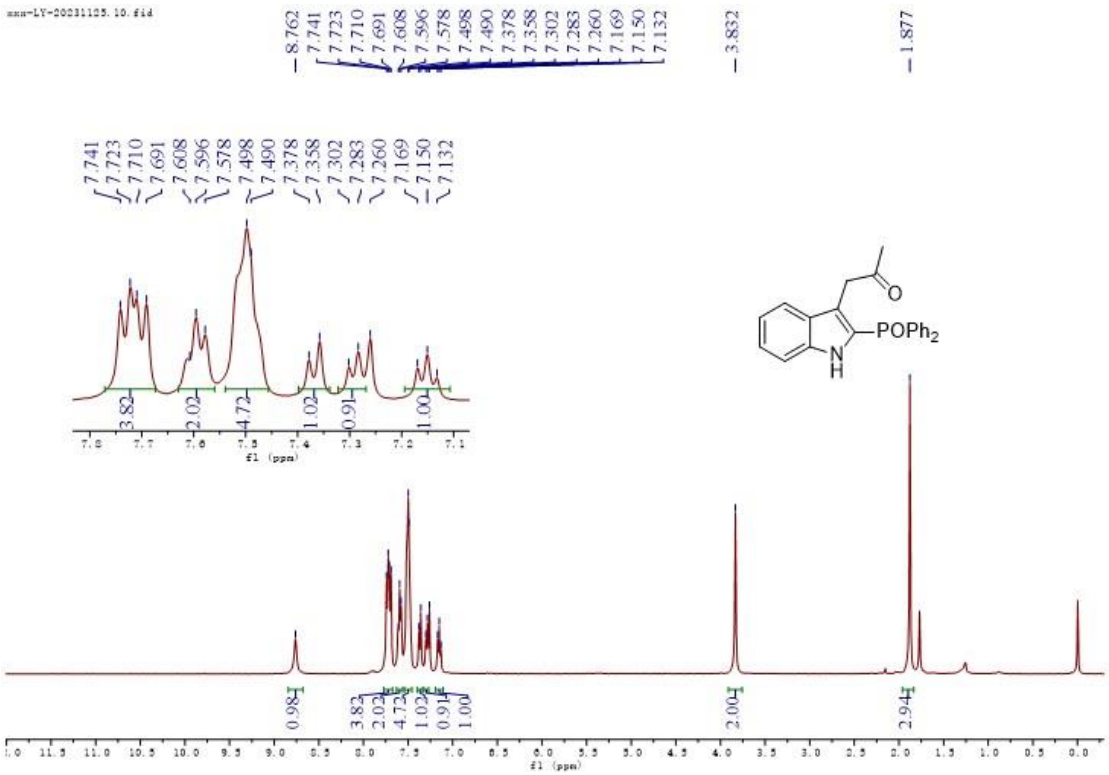
^{31}H NMR (101 MHz, $CDCl_3$) for **3j**



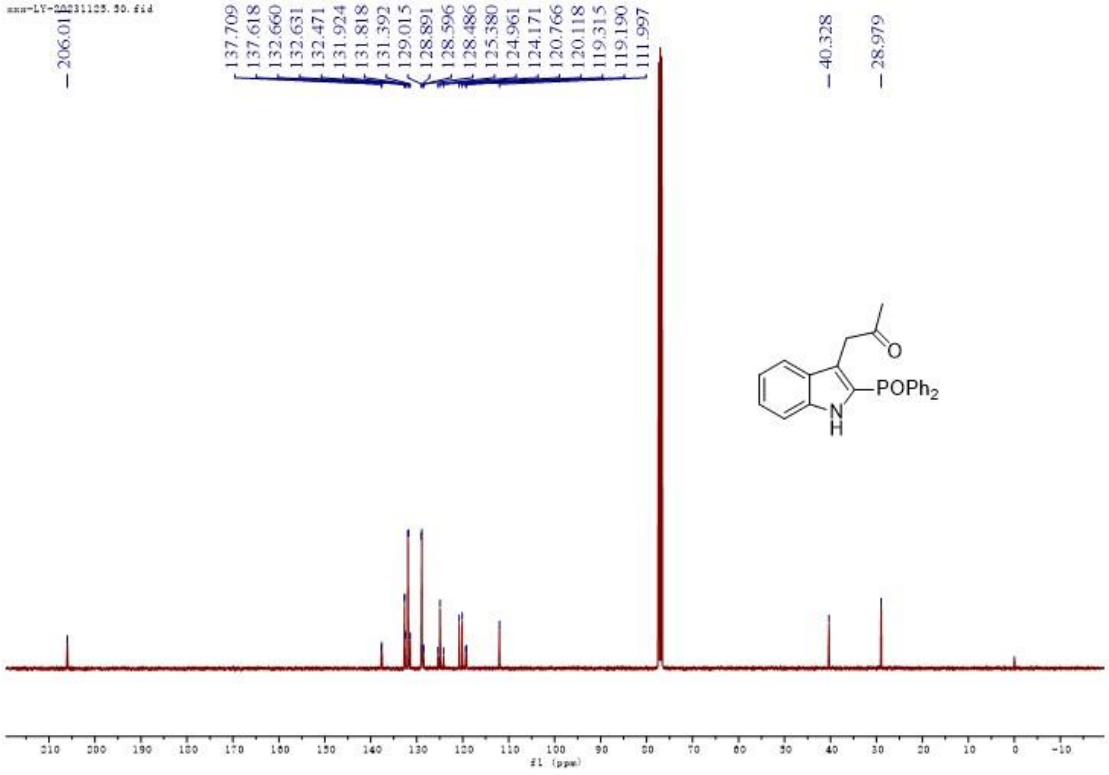
^{31}P NMR (162 MHz, $CDCl_3$) for **3j**



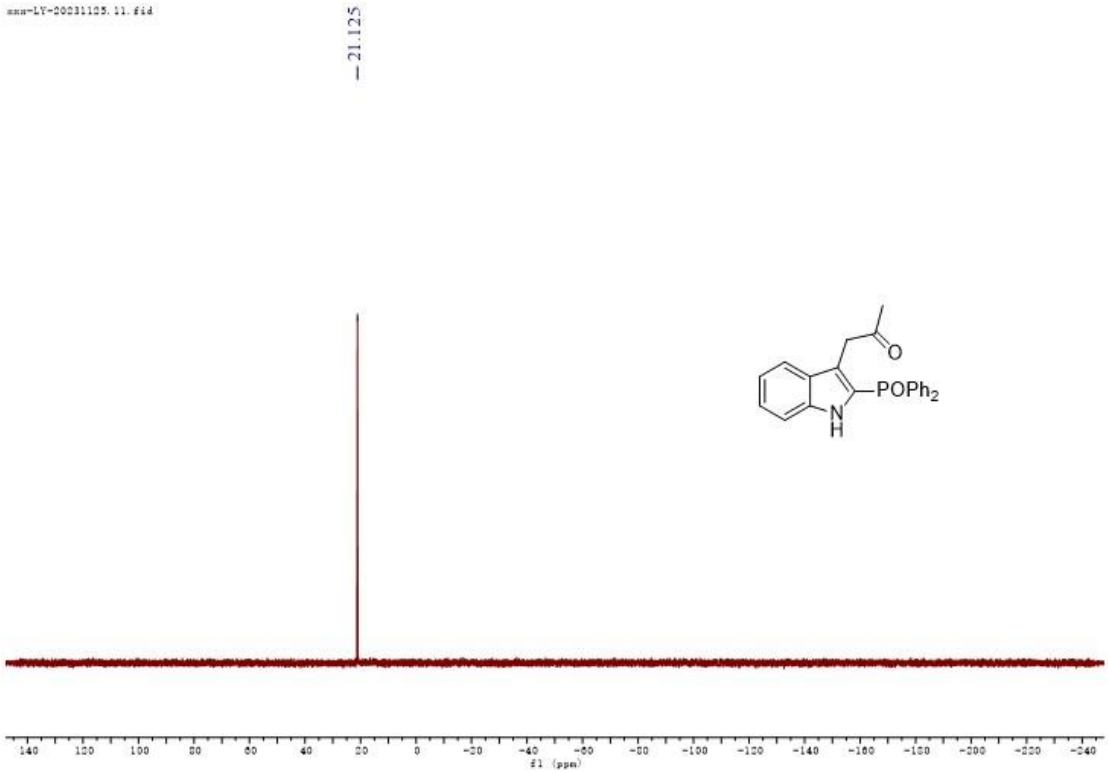
^{1}H NMR (400 MHz, $CDCl_3$) for **3k**



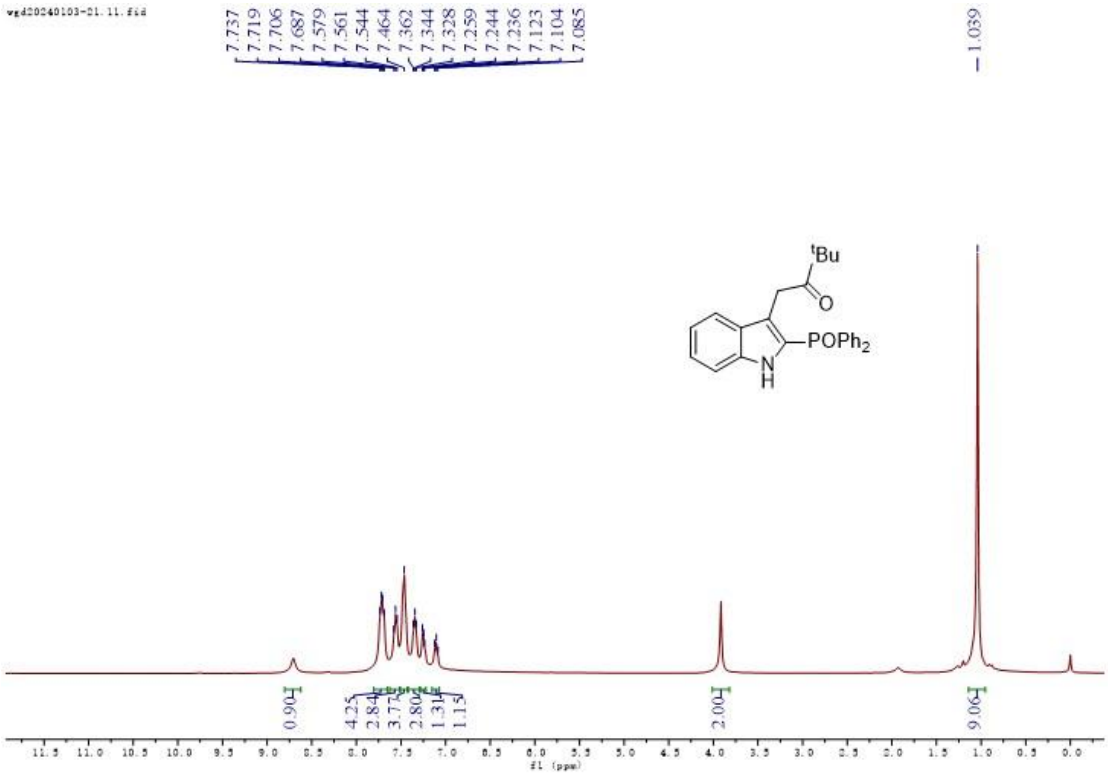
^{13}C NMR (101 MHz, $CDCl_3$) for **3k**



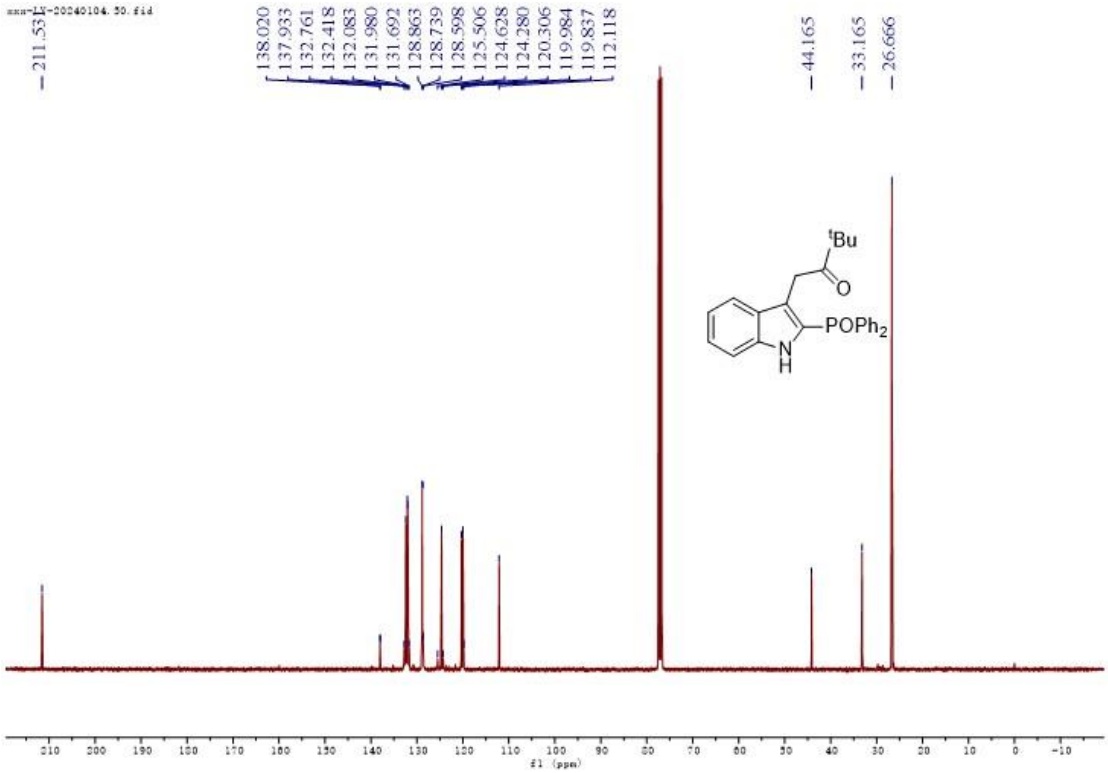
^{31}P NMR (162 MHz, $CDCl_3$) for **3k**



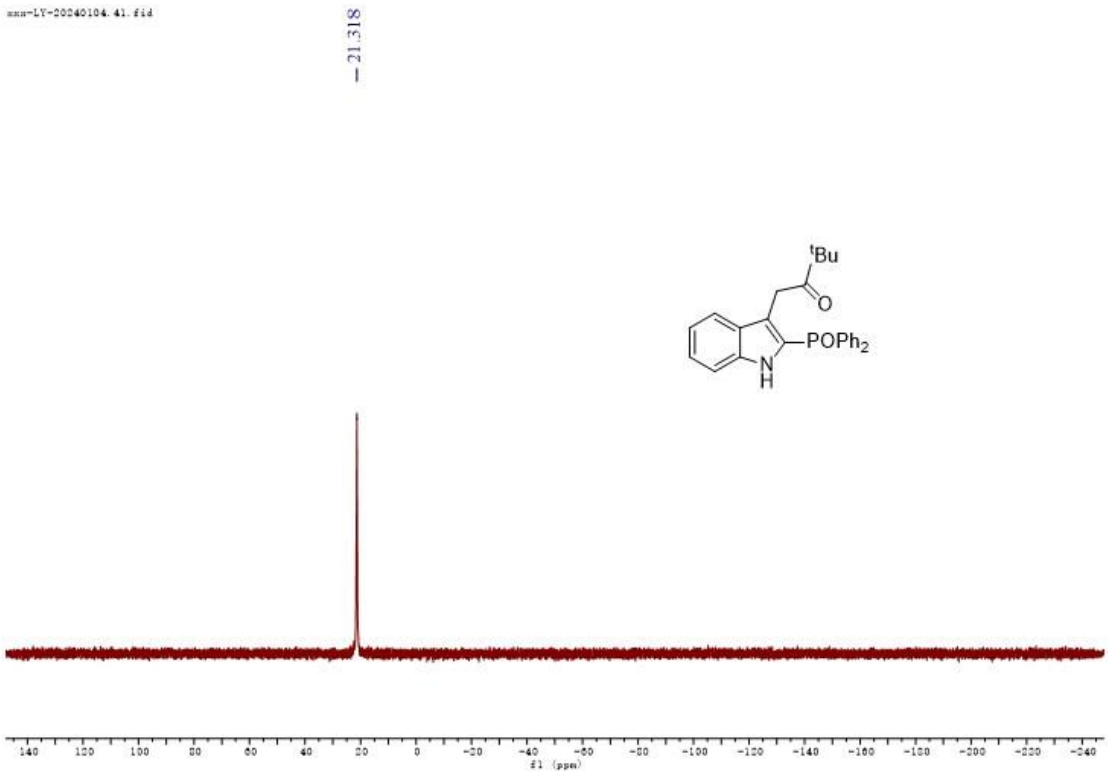
^{1}H NMR (400 MHz, $CDCl_3$) for **3l**



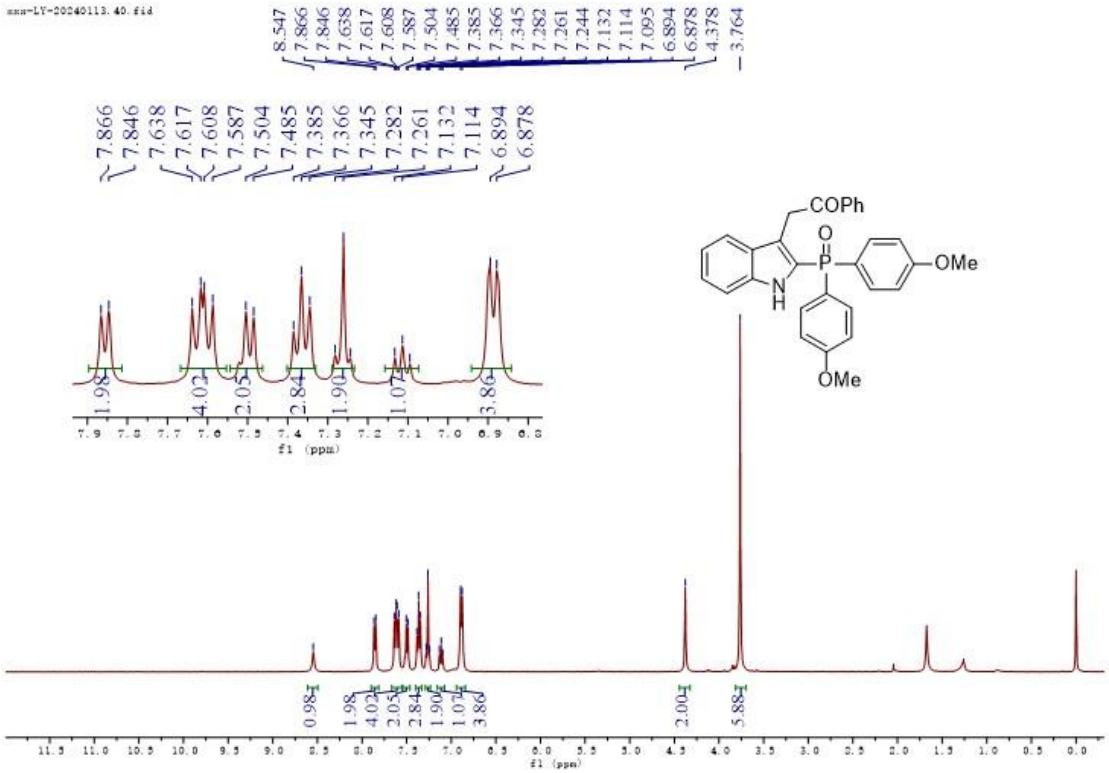
^{13}C NMR (101 MHz, $CDCl_3$) for **3l**



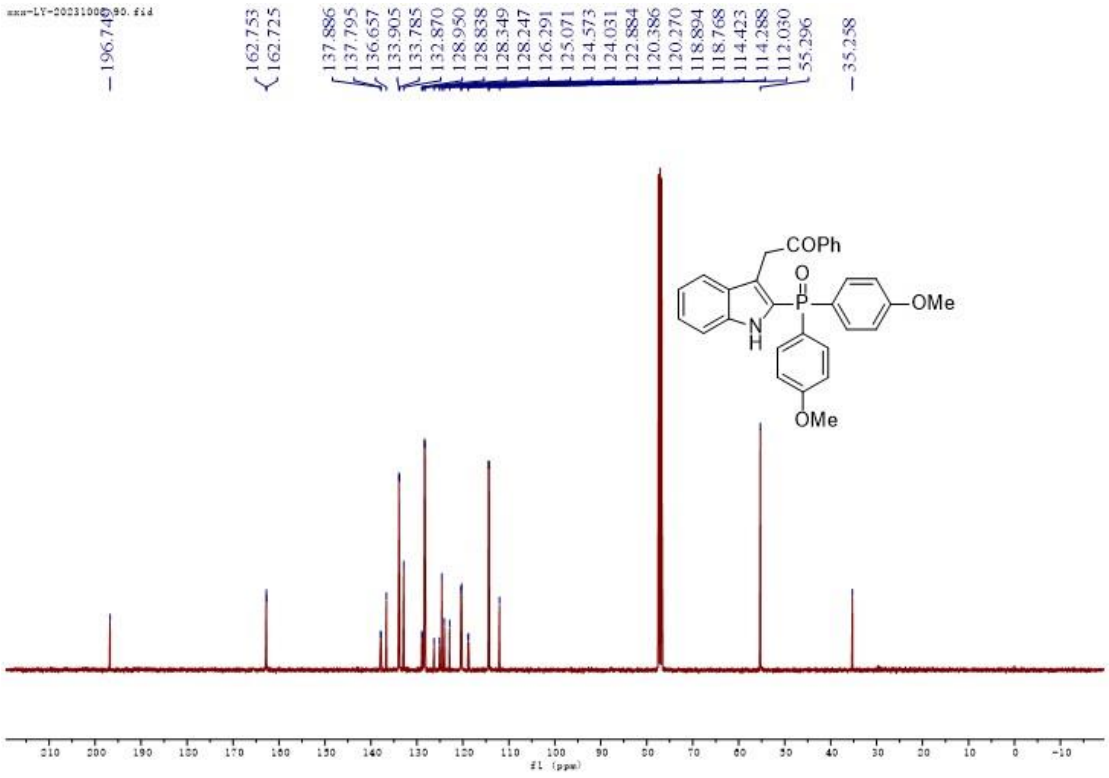
^{31}P NMR (162 MHz, $CDCl_3$) for **3l**



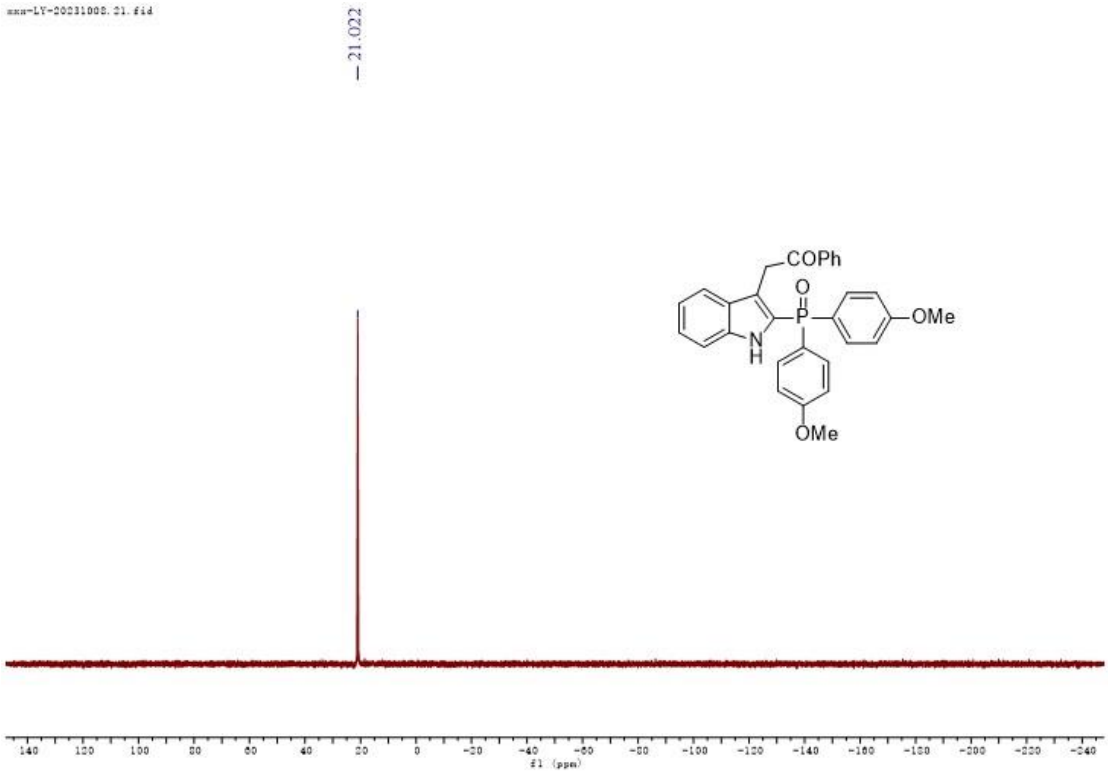
^{1}H NMR (400 MHz, $CDCl_3$) for **3o**



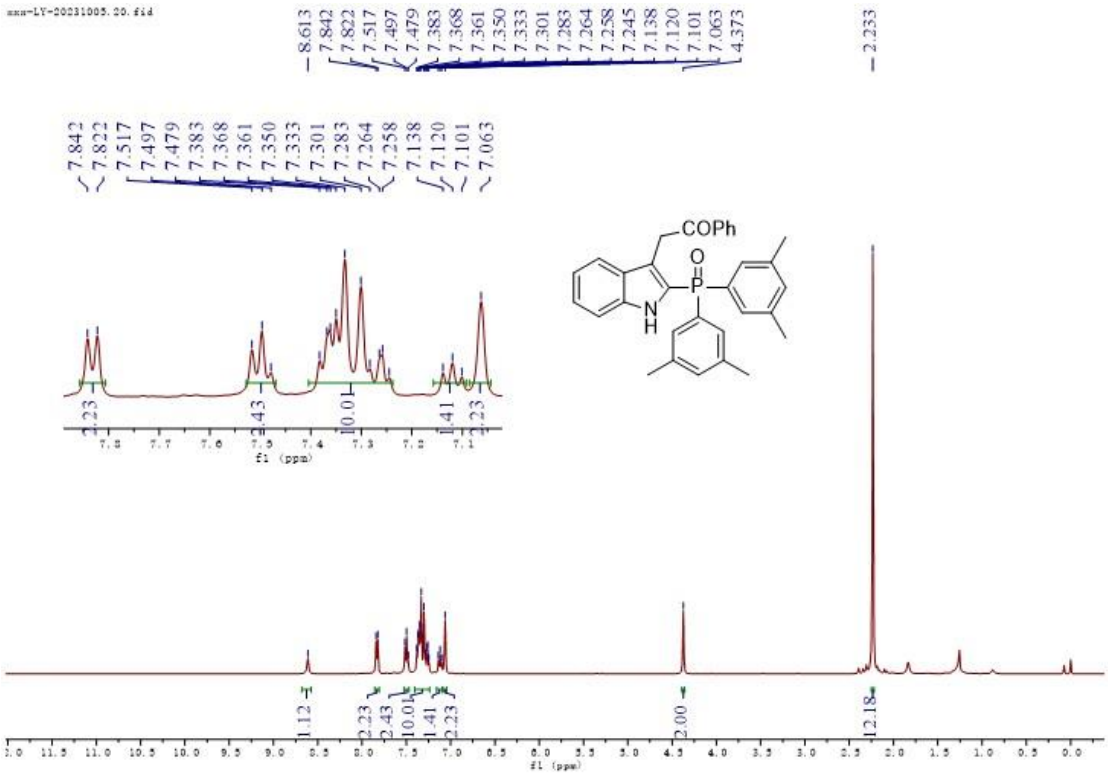
^{13}C NMR (101 MHz, $CDCl_3$) for **3o**



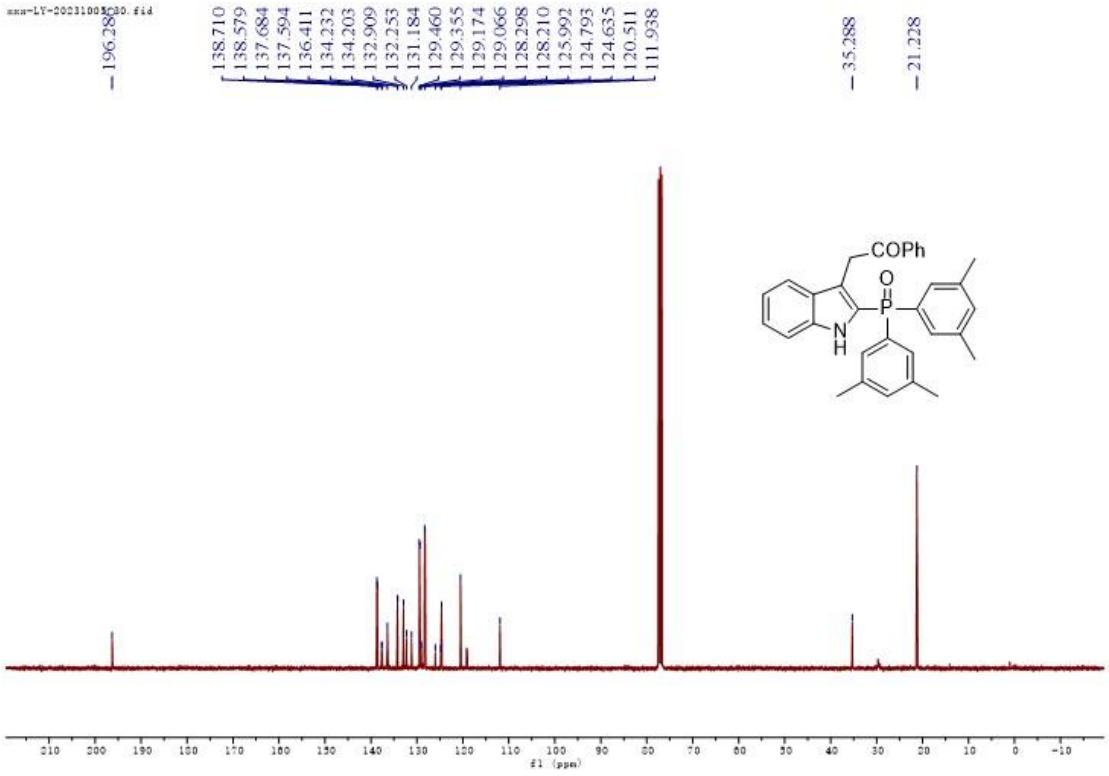
^{31}P NMR (162 MHz, $CDCl_3$) for **3o**



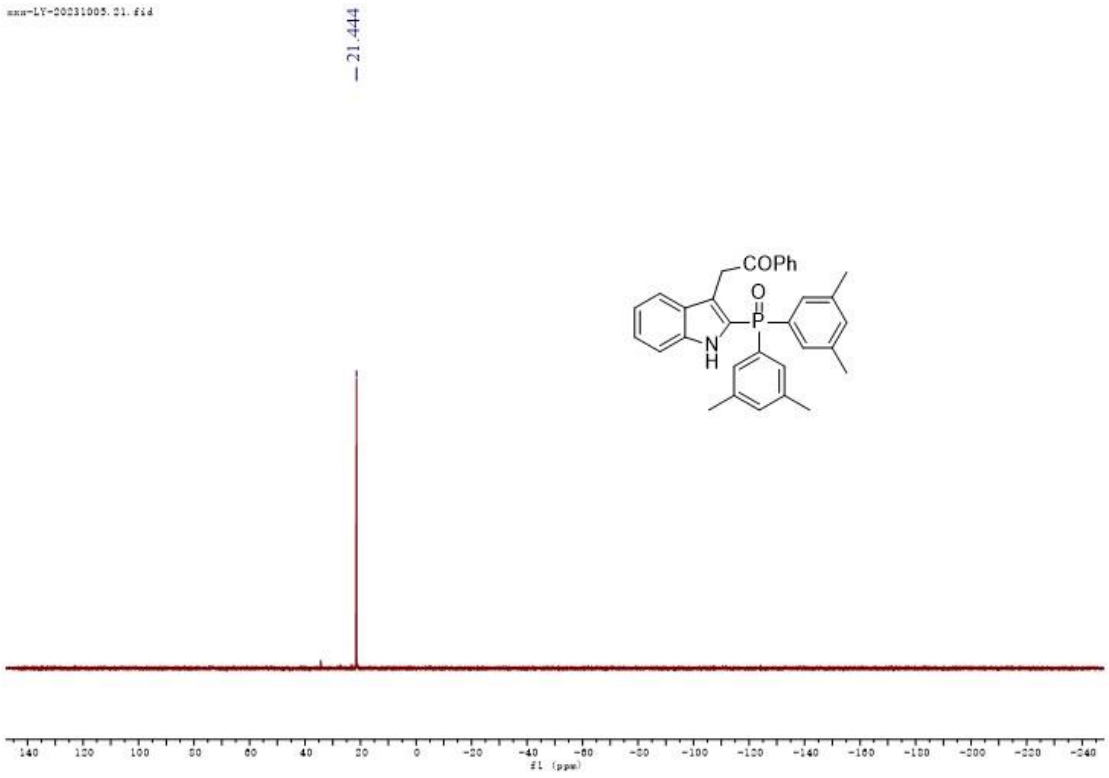
^{1}H NMR (400 MHz, $CDCl_3$) for **3p**



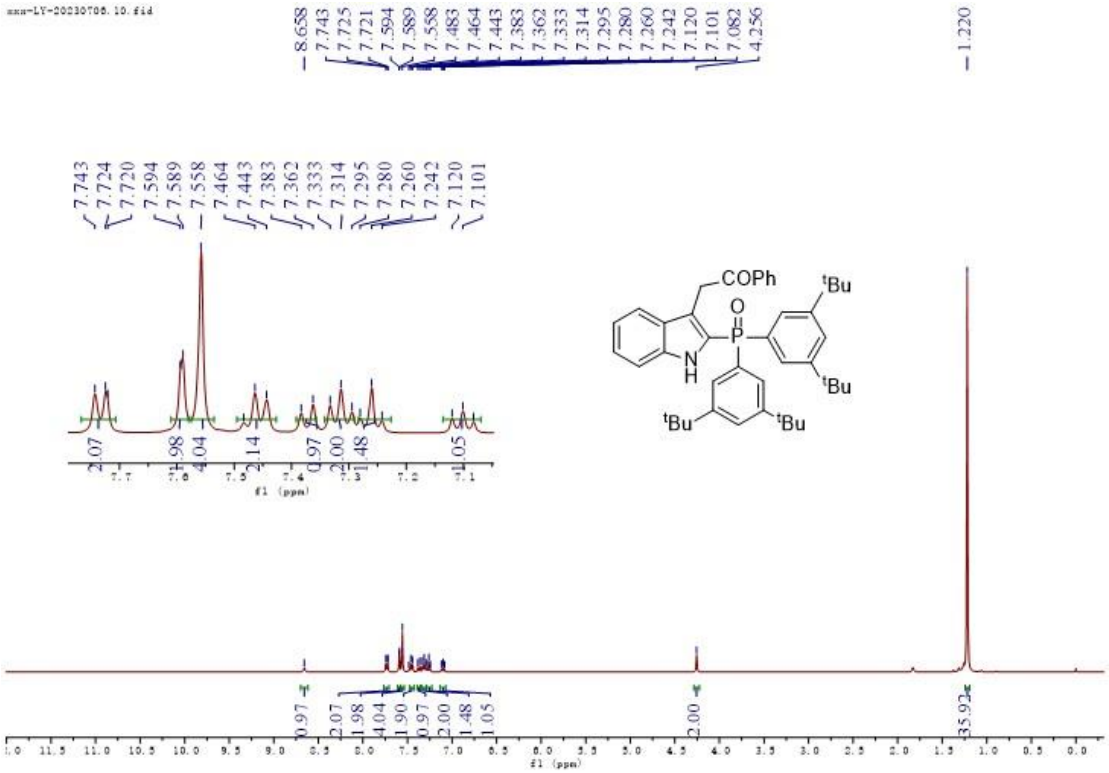
^{13}C NMR (101 MHz, $CDCl_3$) for **3p**



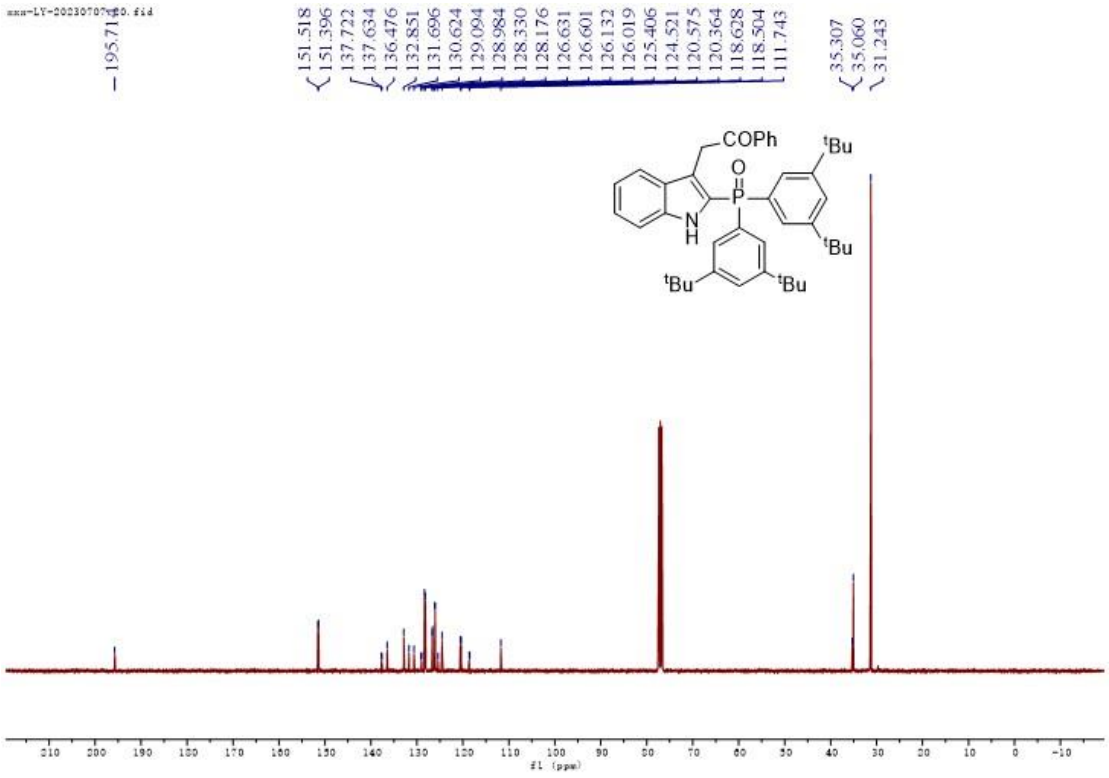
^{31}P NMR (162 MHz, $CDCl_3$) for **3p**



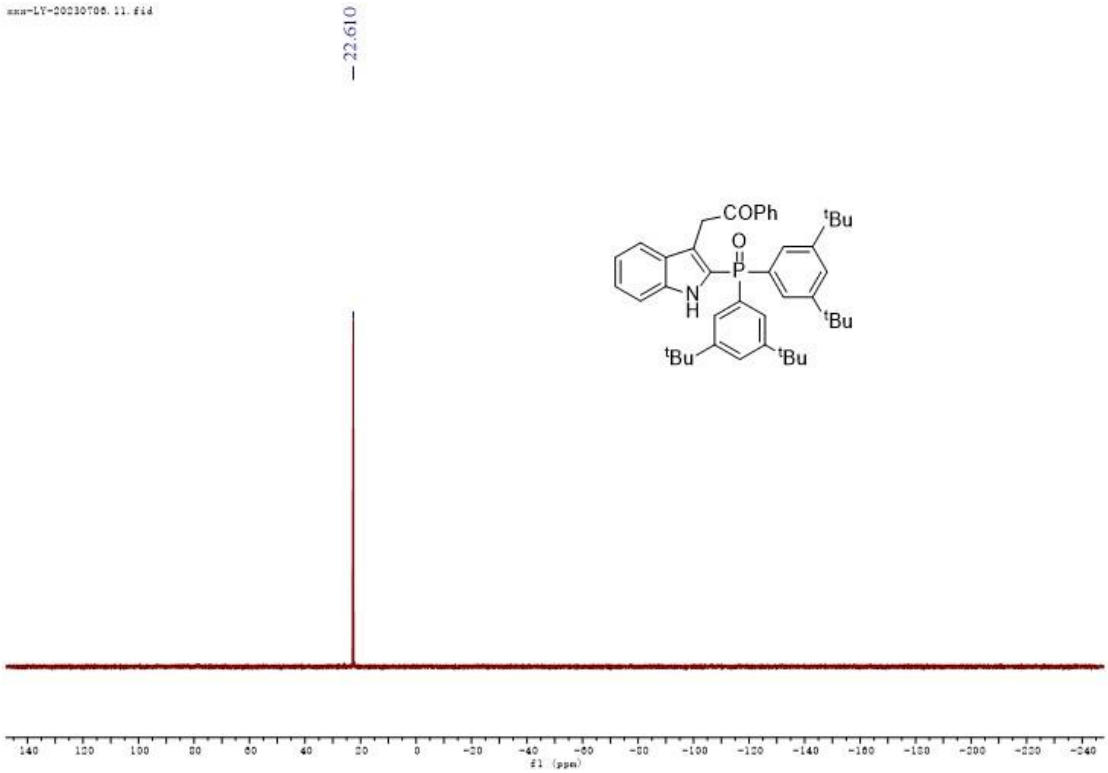
^{1}H NMR (400 MHz, $CDCl_3$) for **3q**



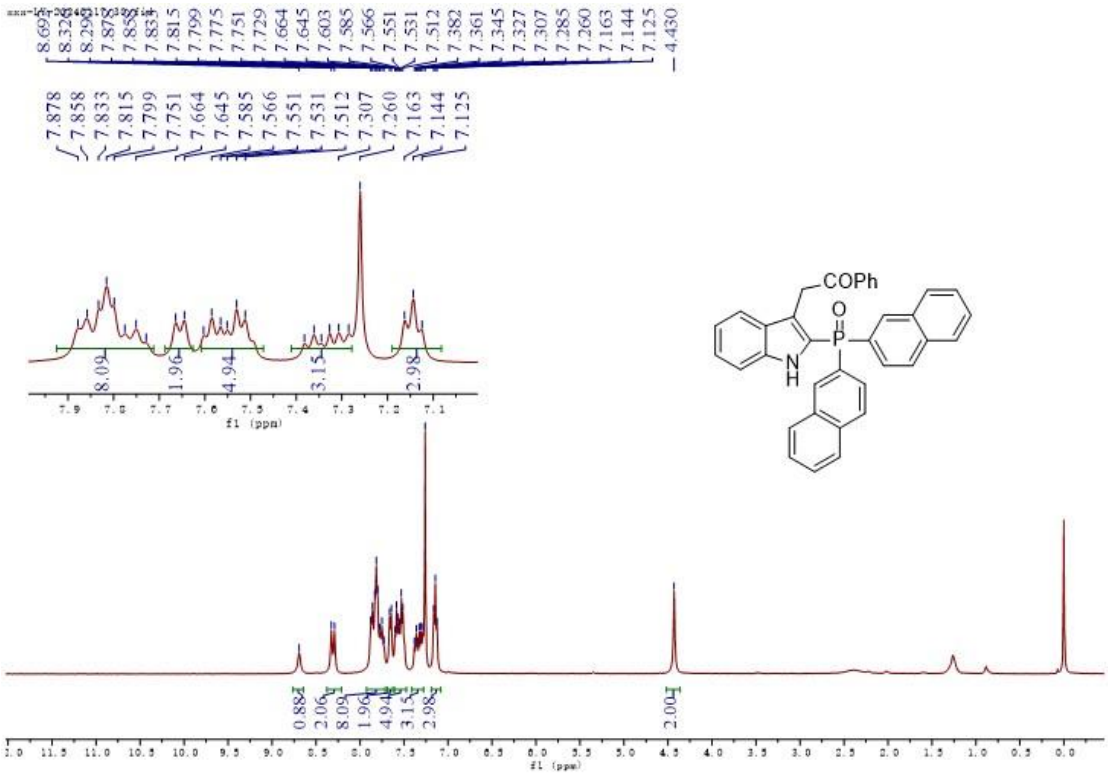
^{13}C NMR (101 MHz, $CDCl_3$) for **3q**



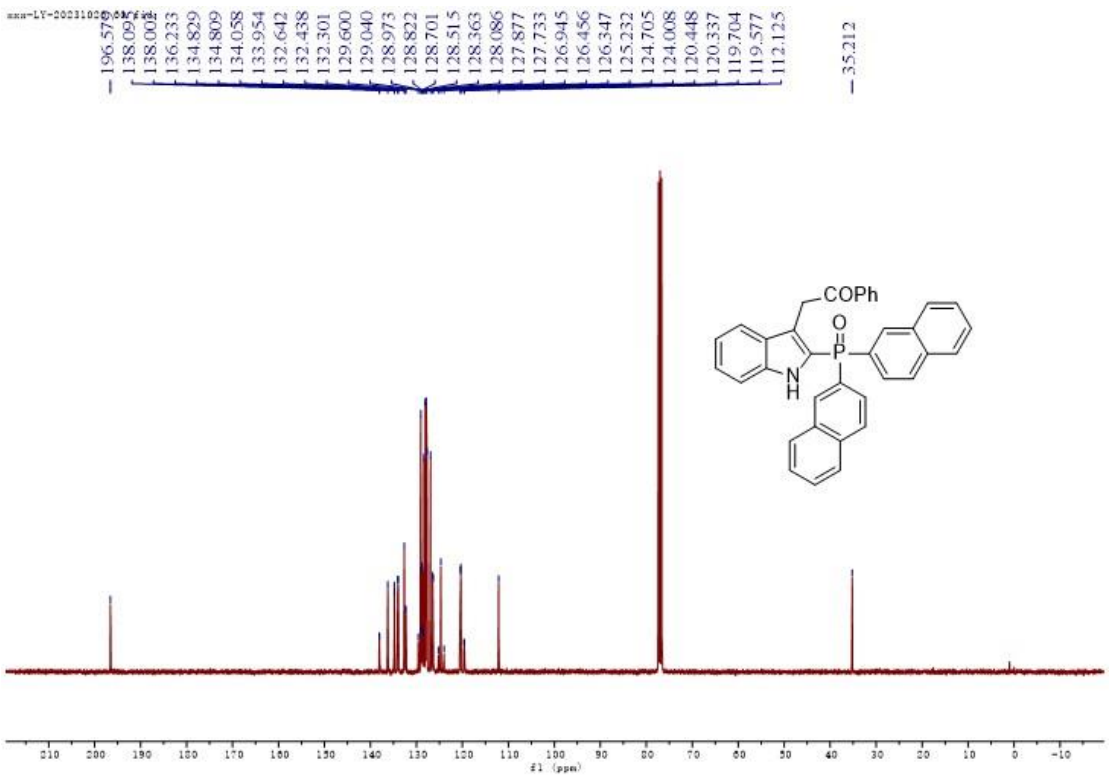
^{31}P NMR (162 MHz, $CDCl_3$) for **3q**



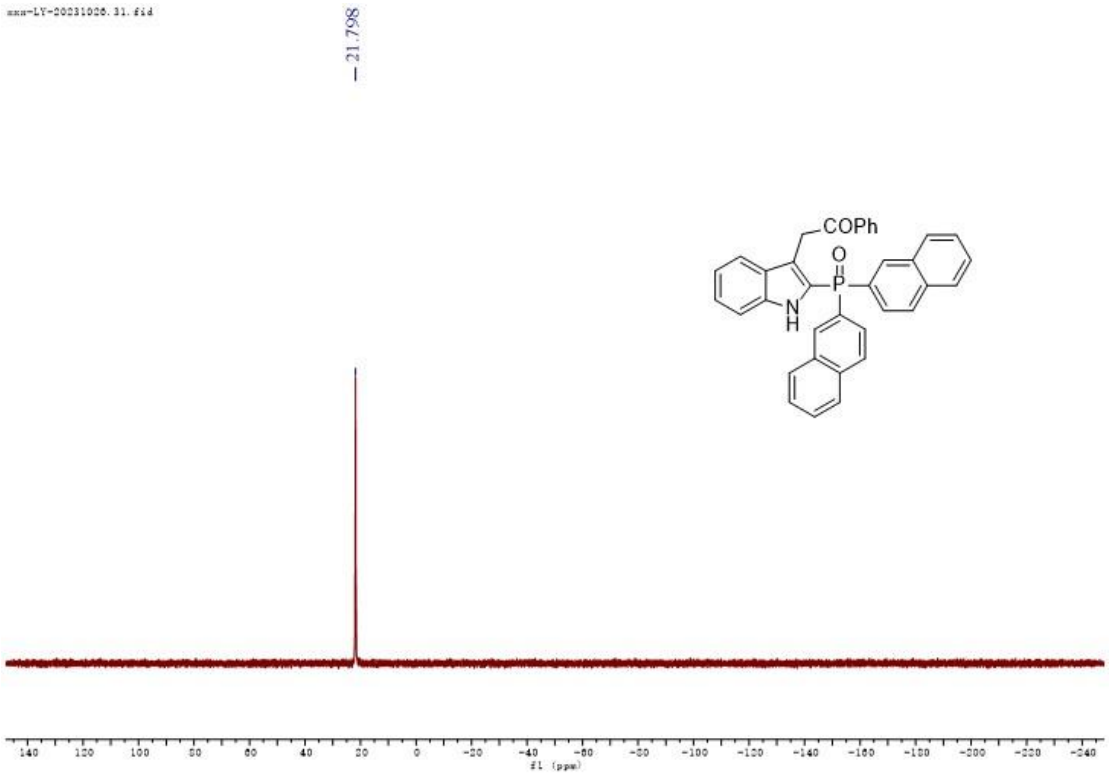
^{1}H NMR (400 MHz, $CDCl_3$) for **3r**



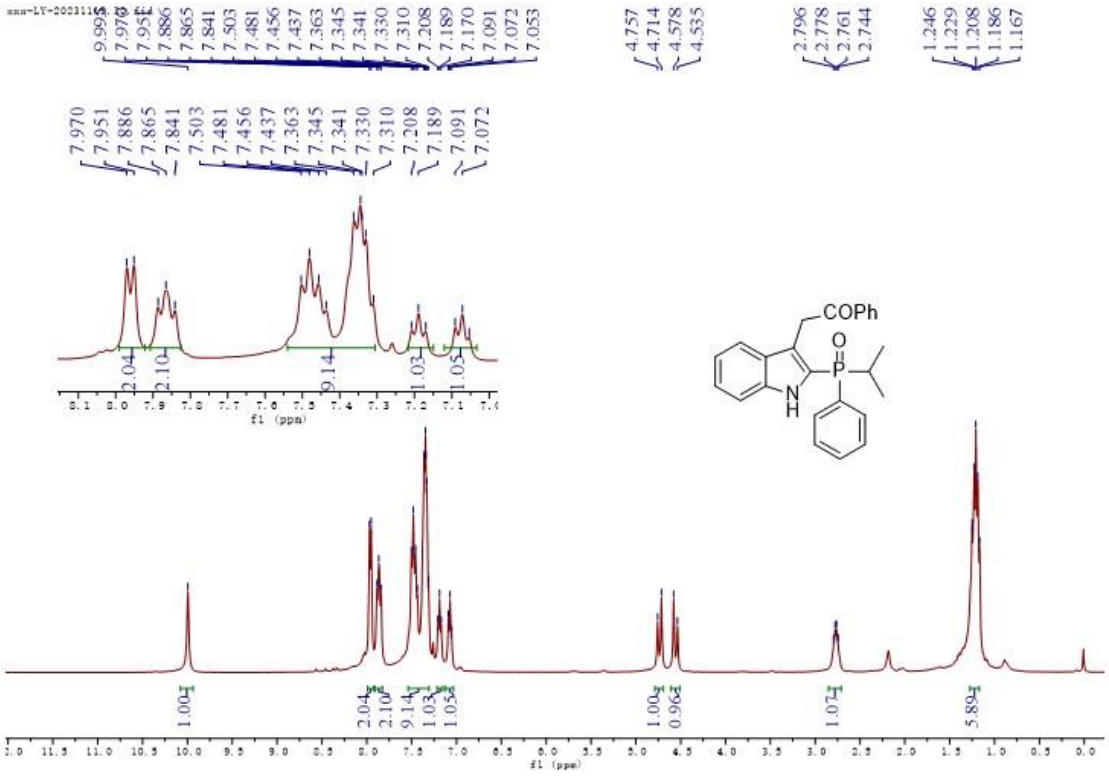
^{13}C NMR (101 MHz, $CDCl_3$) for **3r**



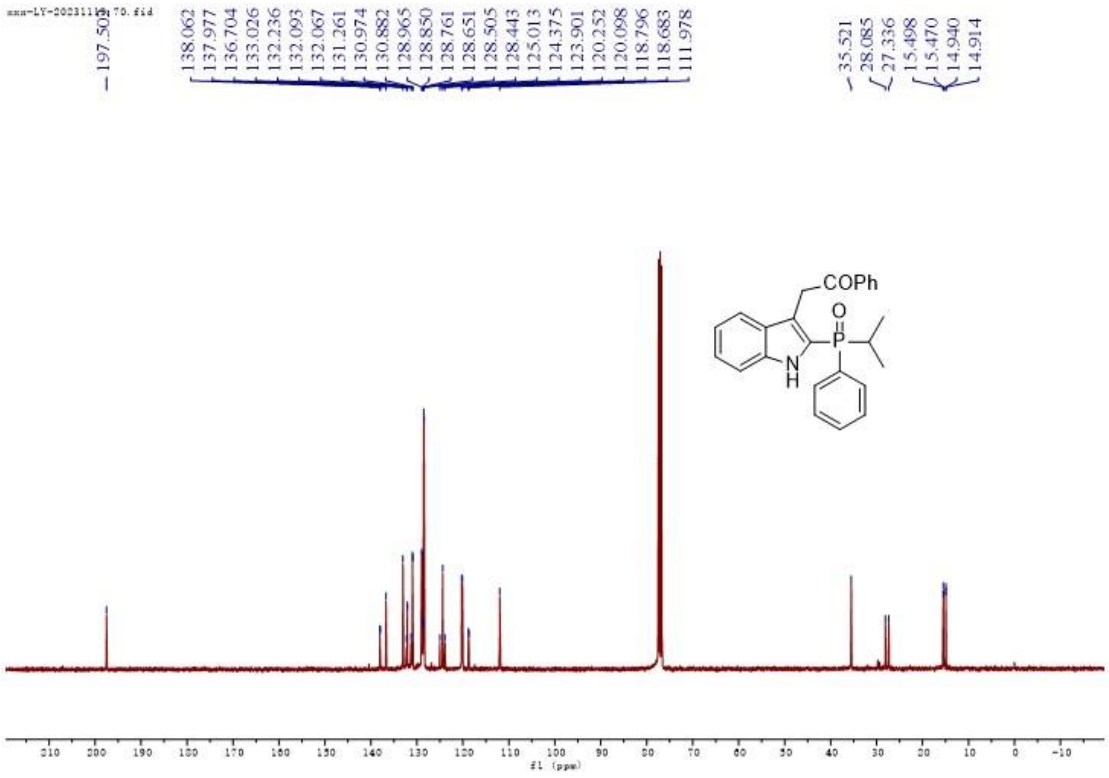
^{31}P NMR (162MHz, $CDCl_3$) for **3r**



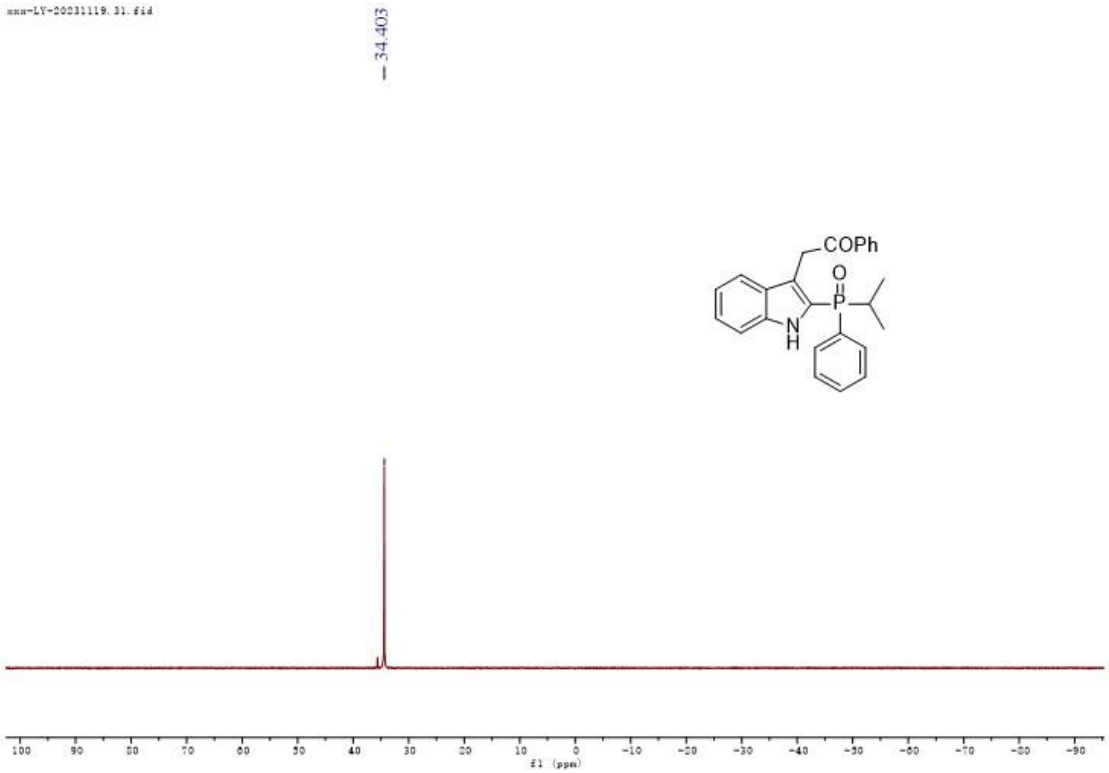
^{1}H NMR (400 MHz, $CDCl_3$) for **3s**



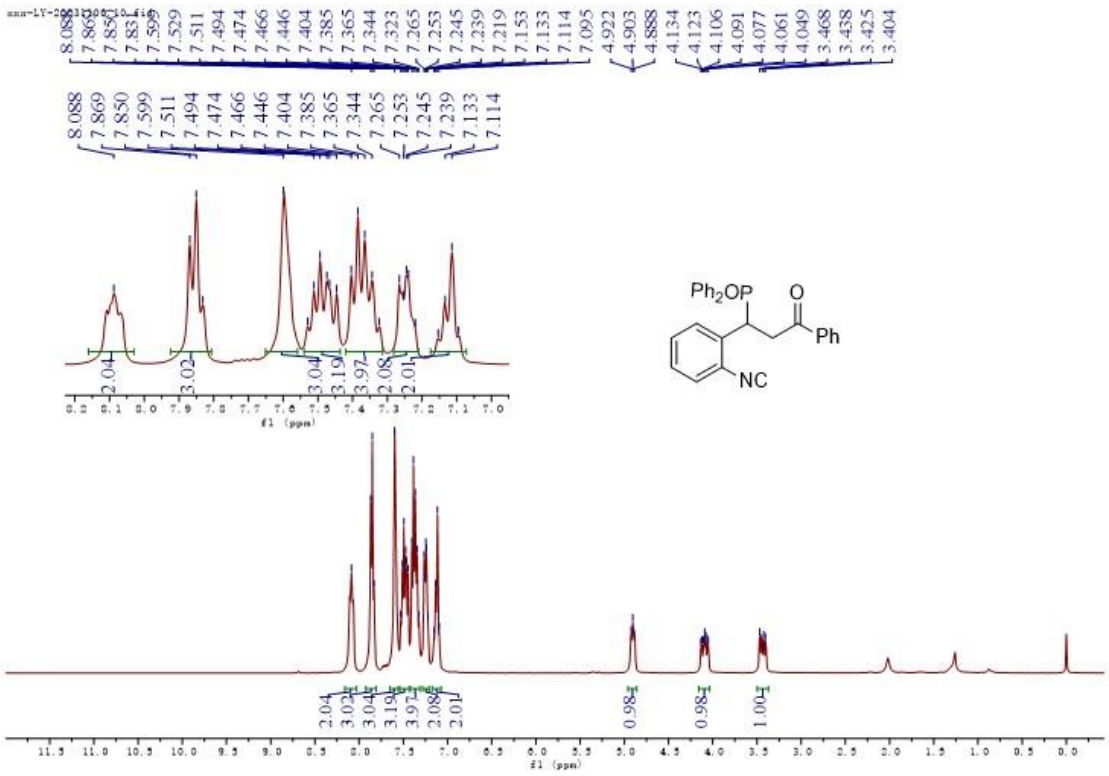
^{13}C NMR (101 MHz, $CDCl_3$) for **3t**



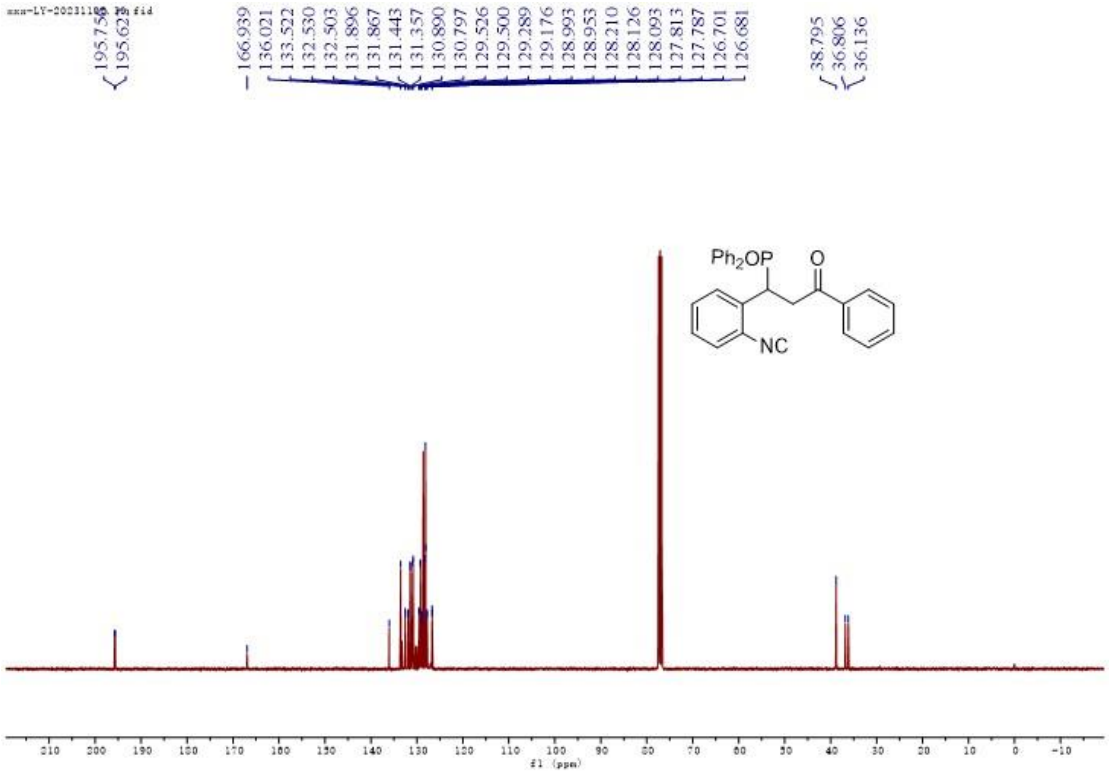
^{31}P NMR (162 MHz, $CDCl_3$) for **3s**



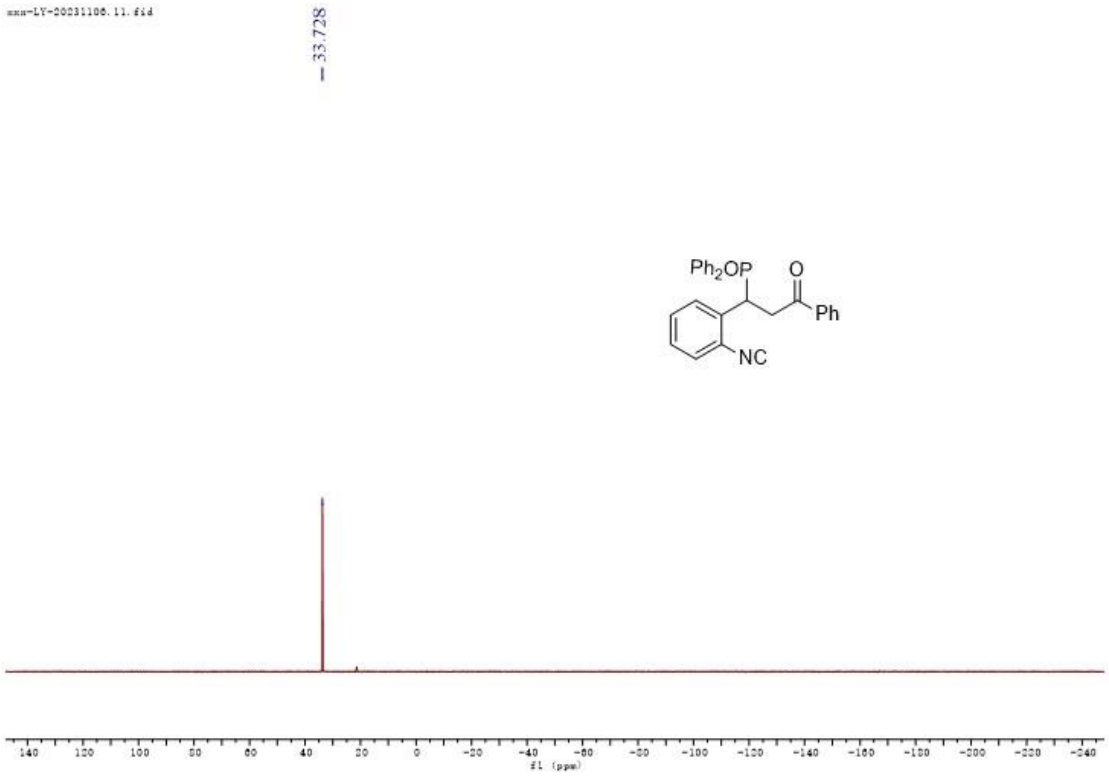
^{1}H NMR (400 MHz, $CDCl_3$) for **4a**



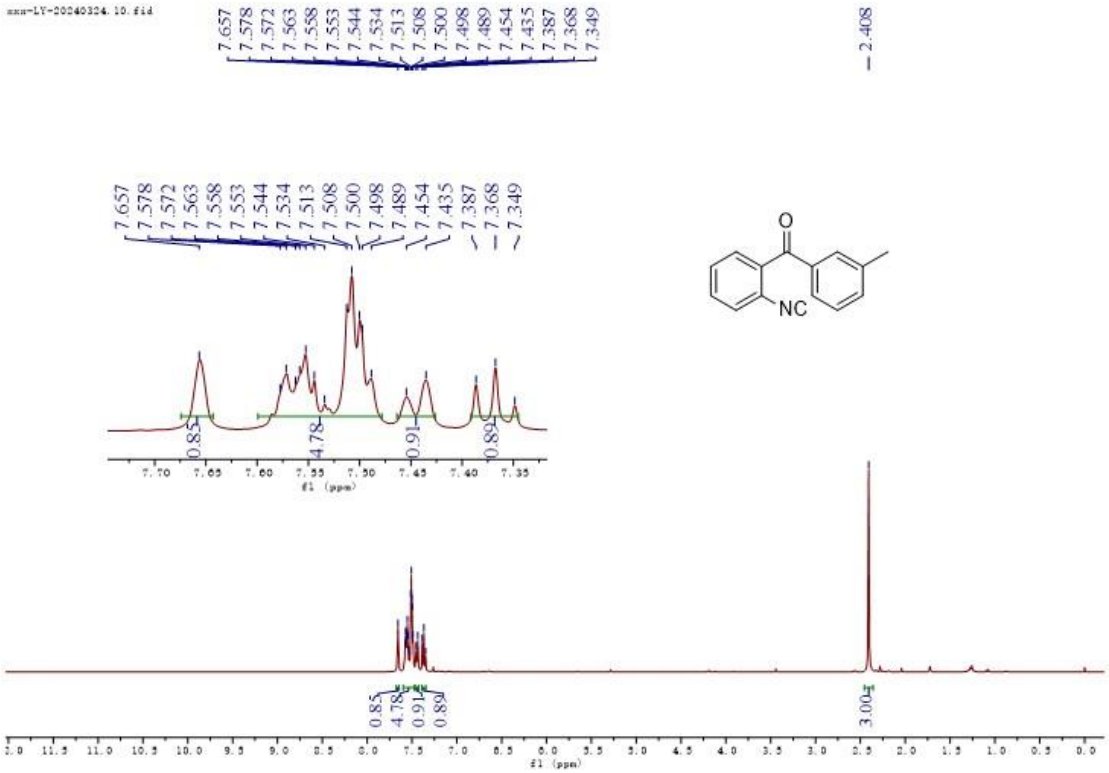
^{13}C NMR (101 MHz, $CDCl_3$) for **4a**



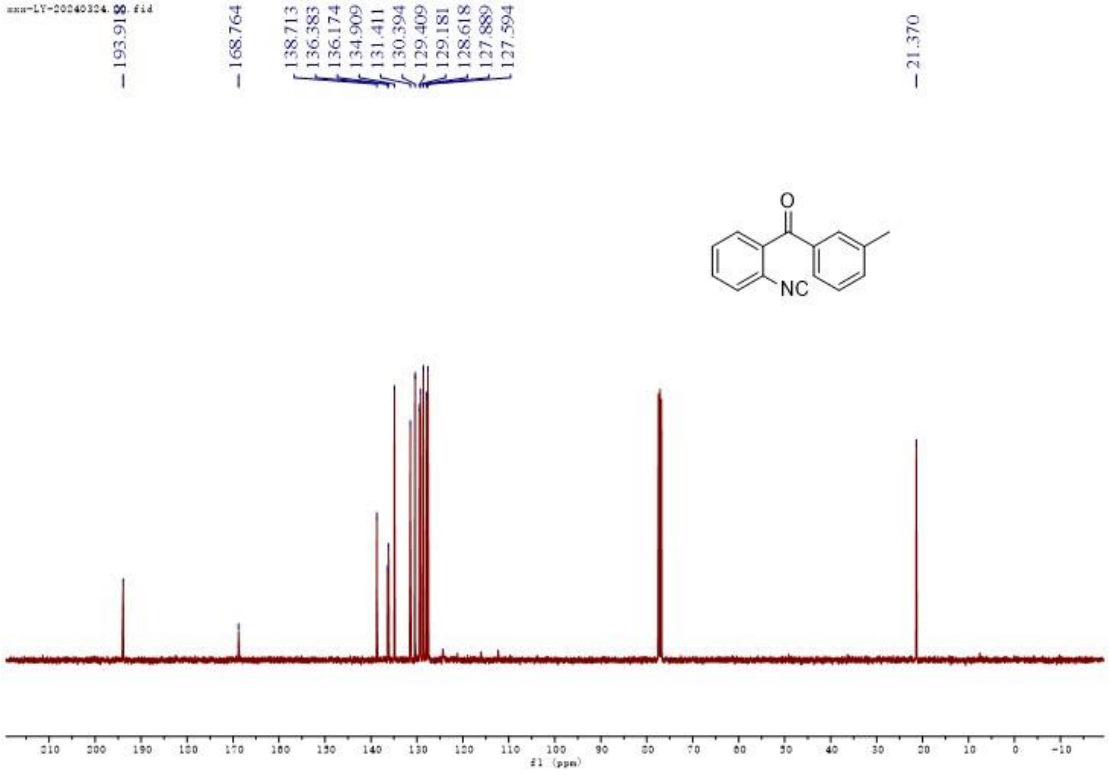
^{31}P NMR (162 MHz, $CDCl_3$) for **4a**



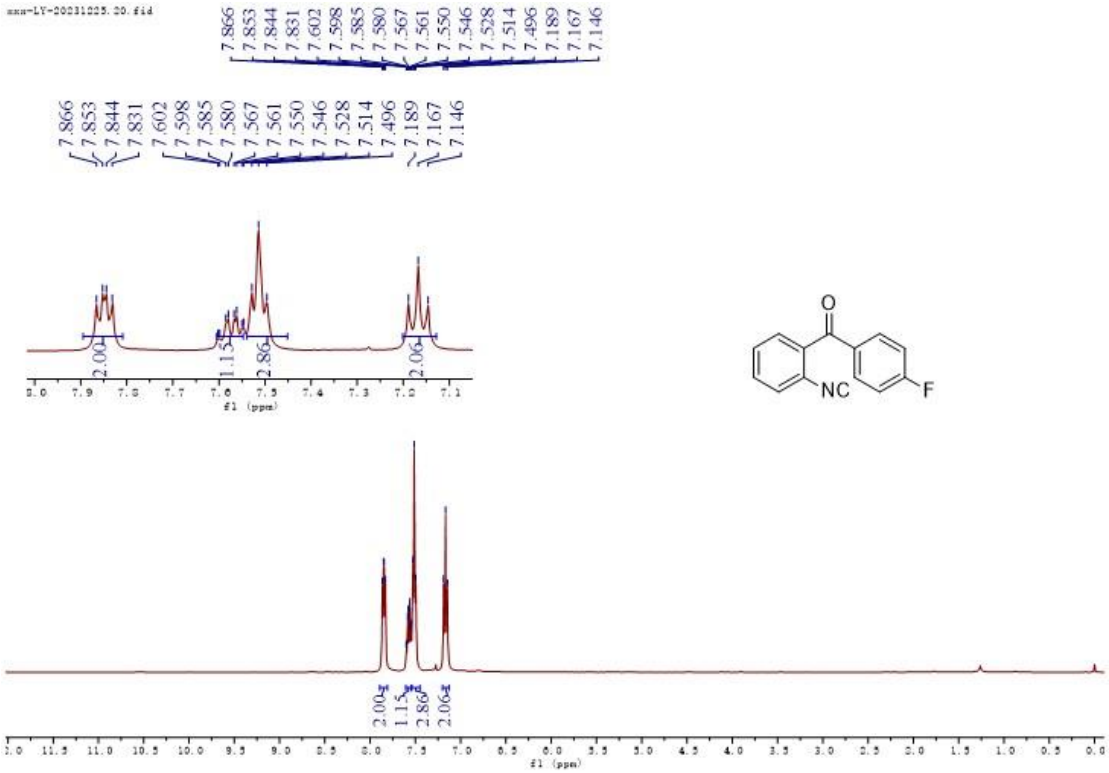
^{1}H NMR (400 MHz, $CDCl_3$) for **5i**



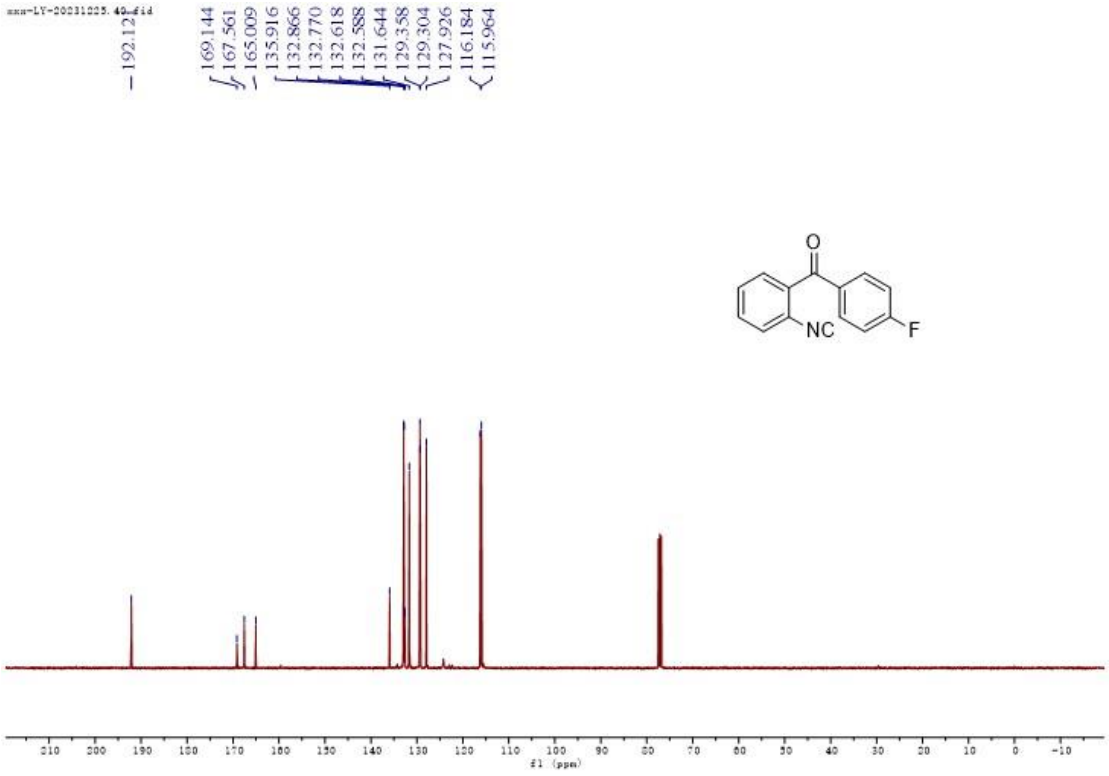
^{13}C NMR (101 MHz, $CDCl_3$) for **5i**



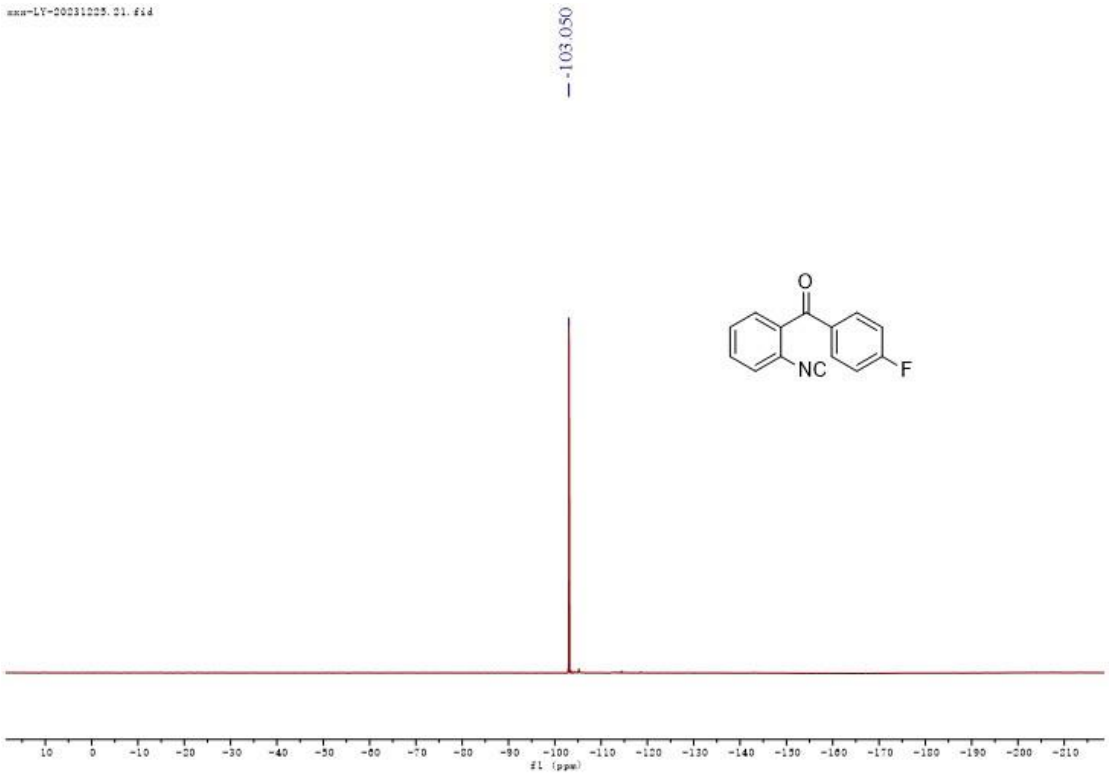
^{1}H NMR (400 MHz, $CDCl_3$) for **5j**



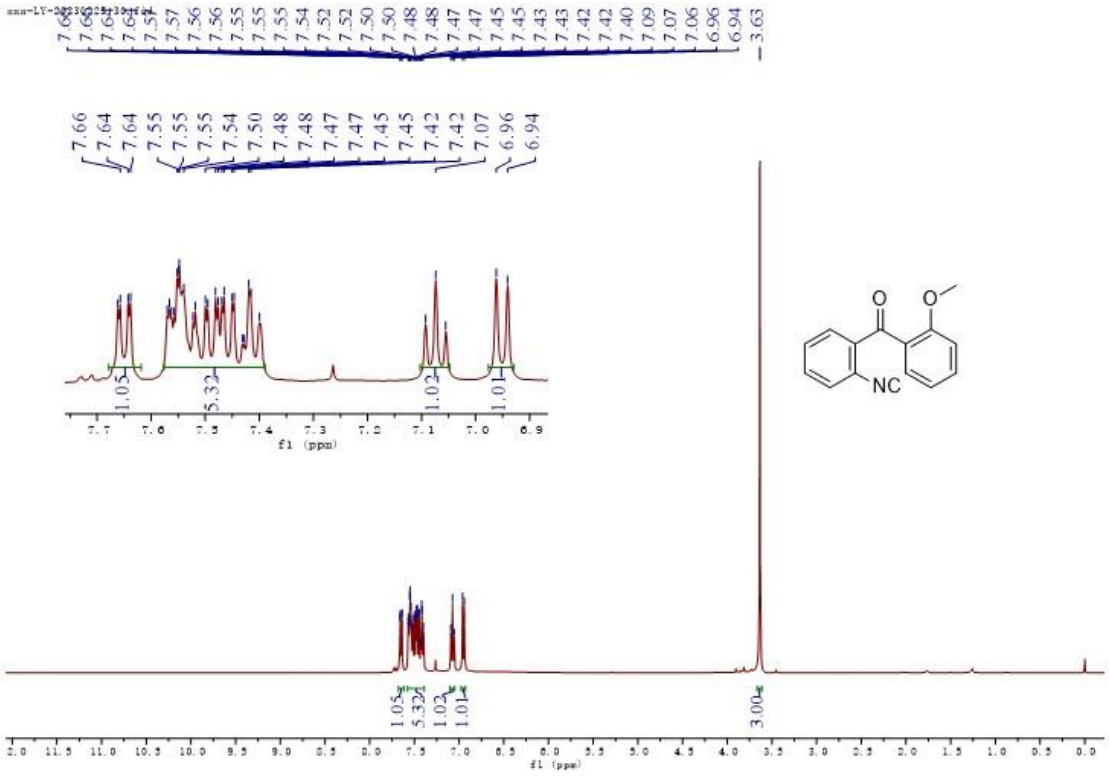
^{13}C NMR (101 MHz, $CDCl_3$) for **5j**



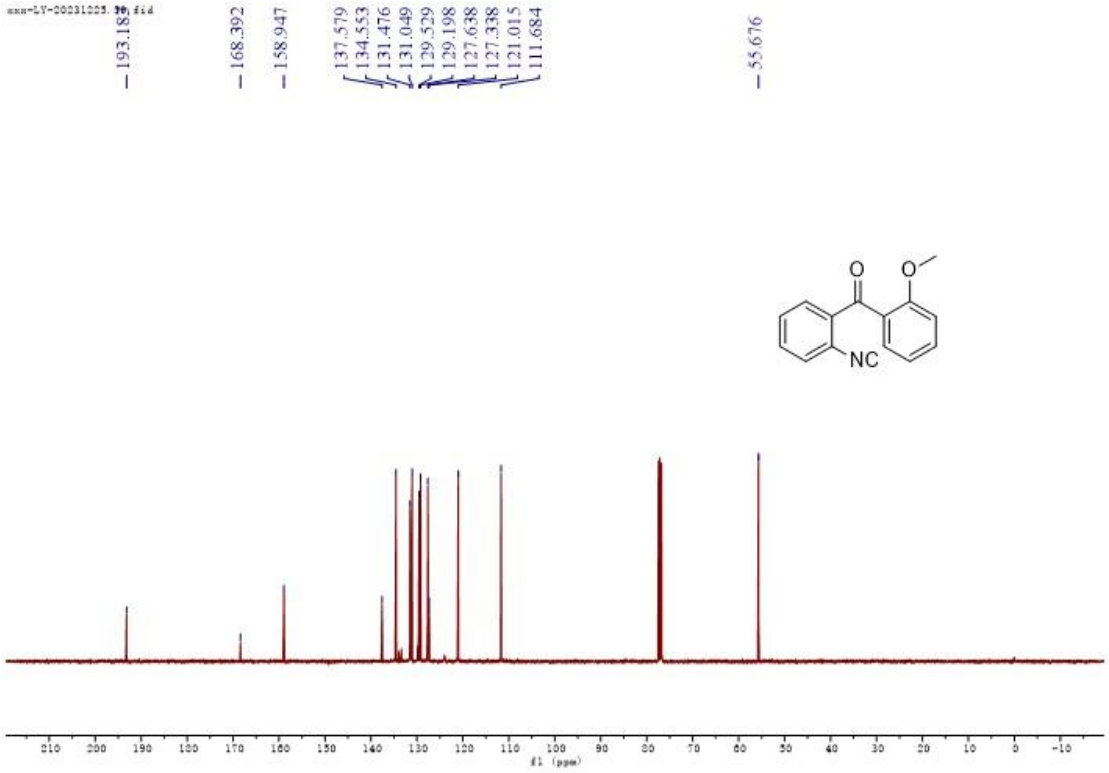
^{19}F NMR (376 MHz, $CDCl_3$) for **5j**



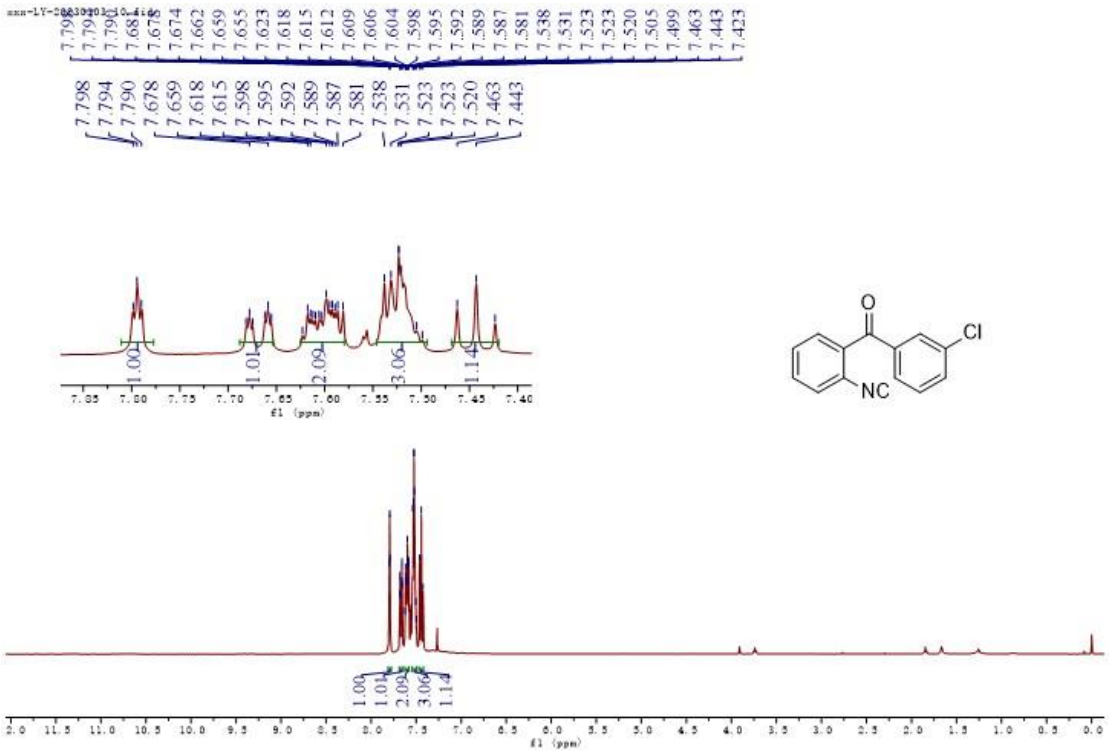
^{1}H NMR (400 MHz, $CDCl_3$) for **5k**



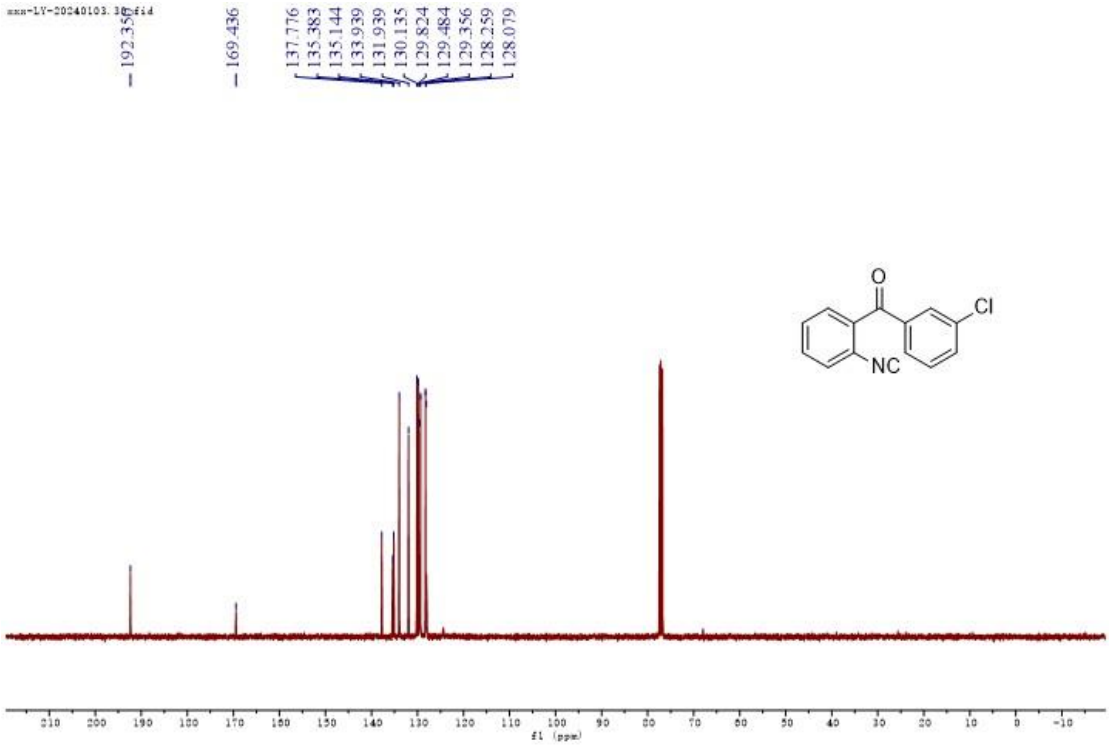
^{13}C NMR (101 MHz, $CDCl_3$) for **5k**



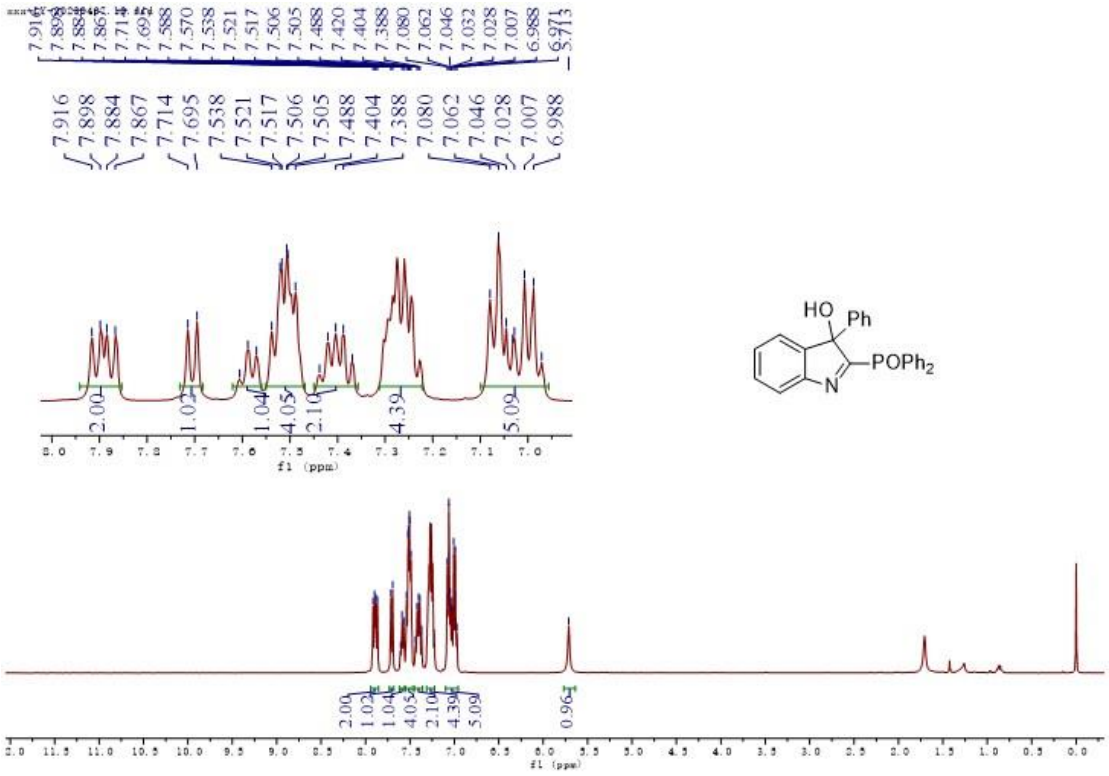
^{1}H NMR (400 MHz, $CDCl_3$) for **5l**



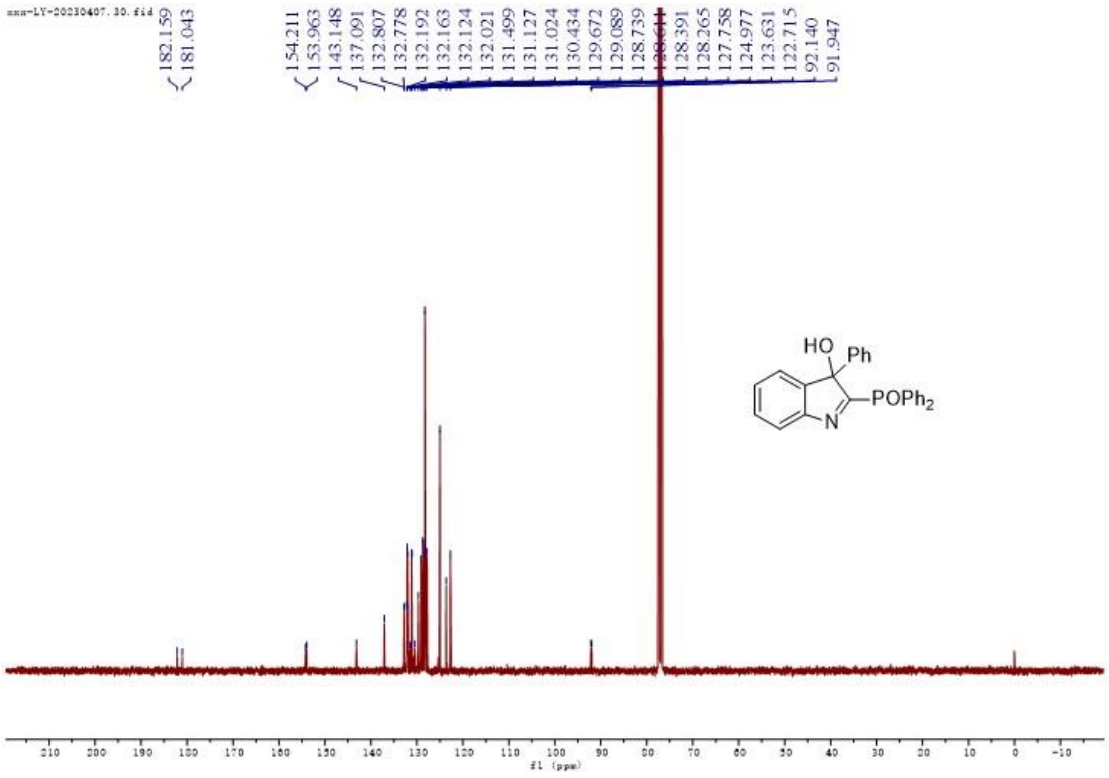
^{13}C NMR (101 MHz, $CDCl_3$) for **5l**



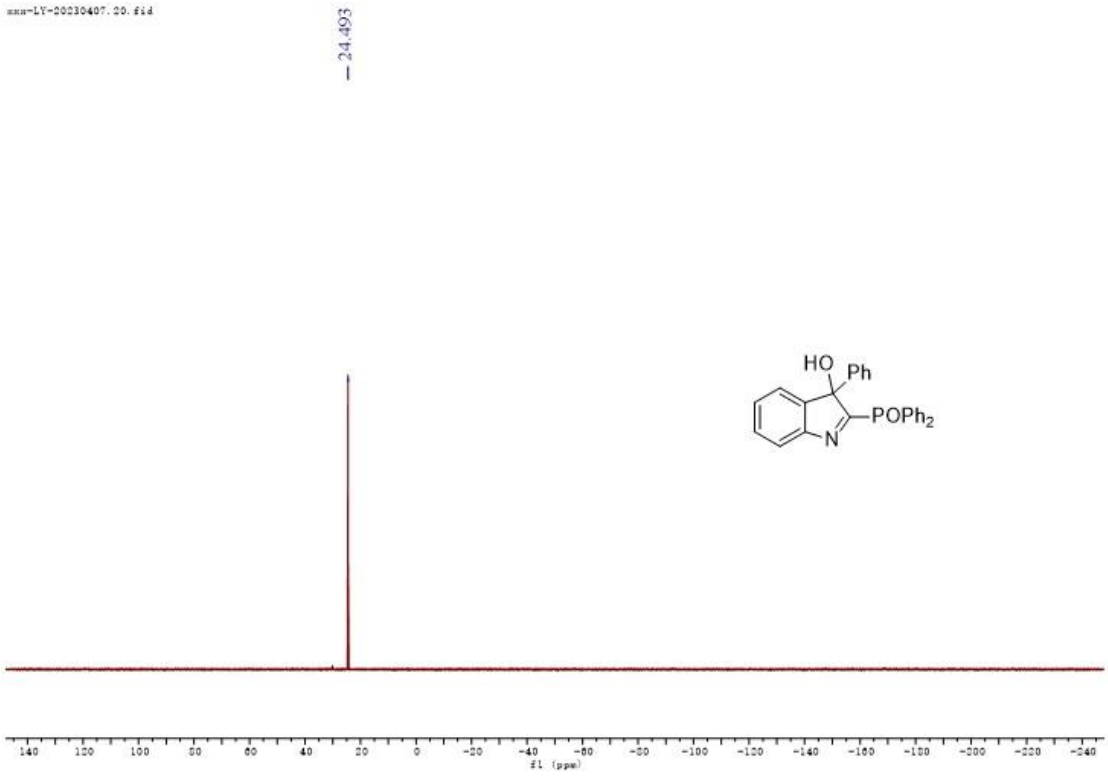
^{1}H NMR (400 MHz, $CDCl_3$) for **6a**



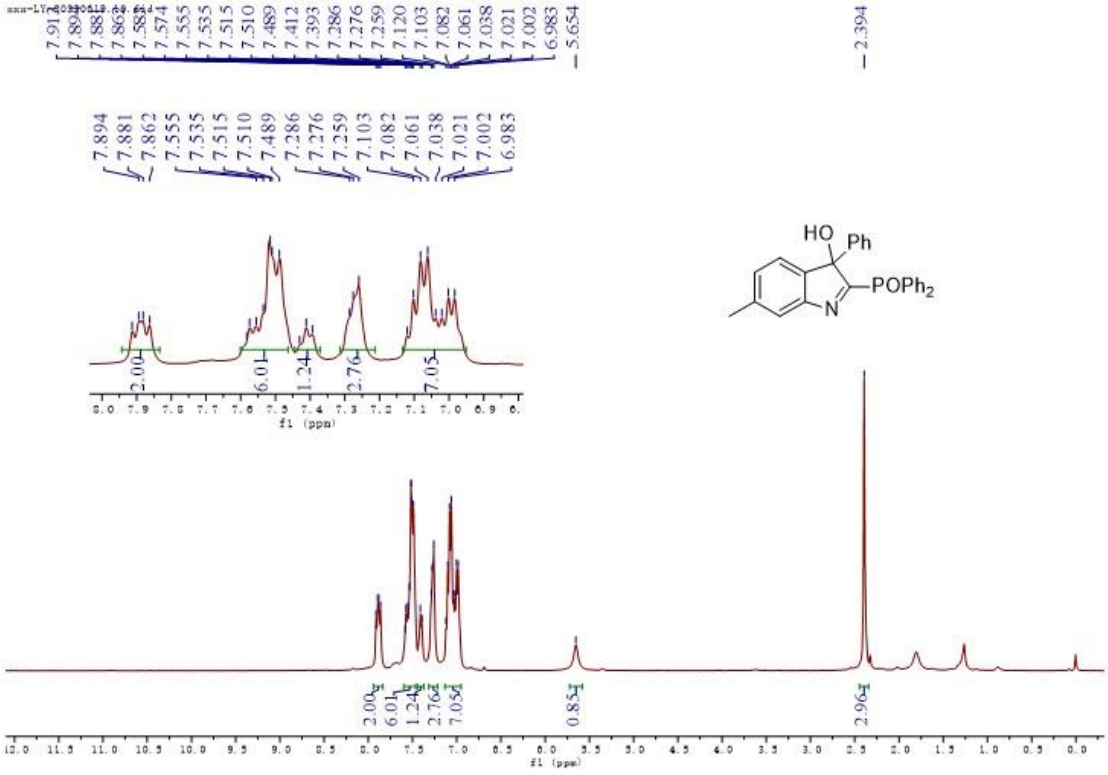
^{13}C NMR (101 MHz, $CDCl_3$) for **6a**



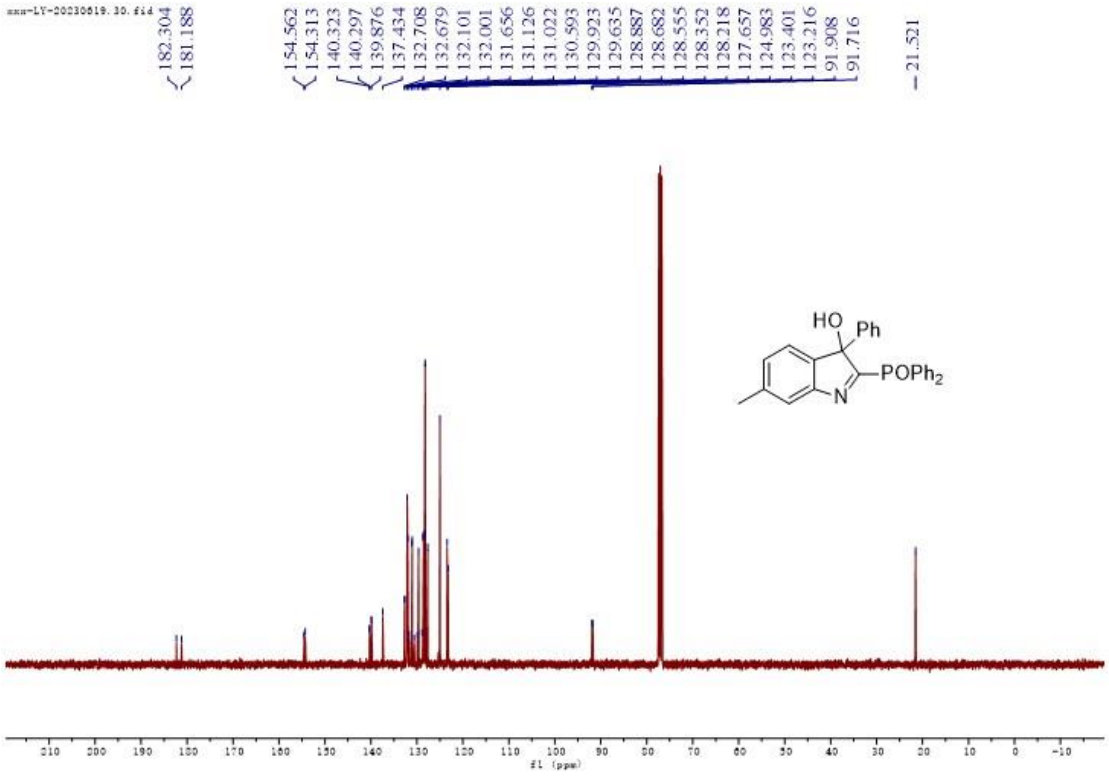
^{31}P NMR (162 MHz, $CDCl_3$) for **6a**



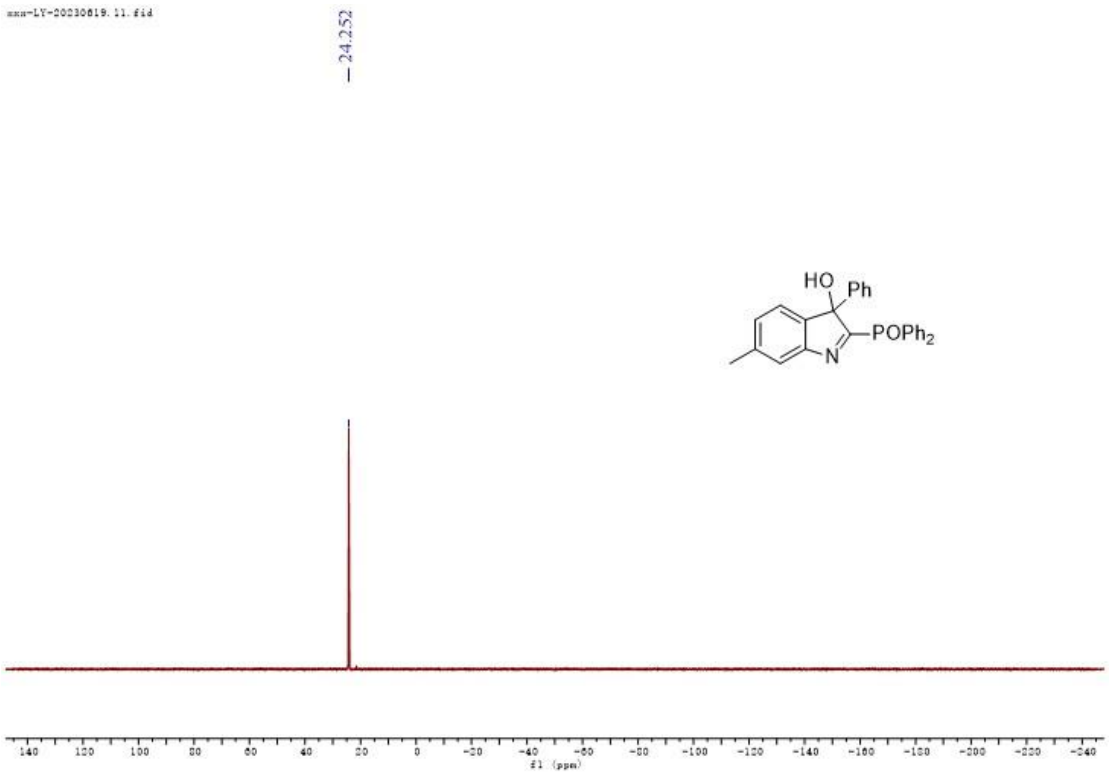
^{1}H NMR (400 MHz, $CDCl_3$) for **6b**



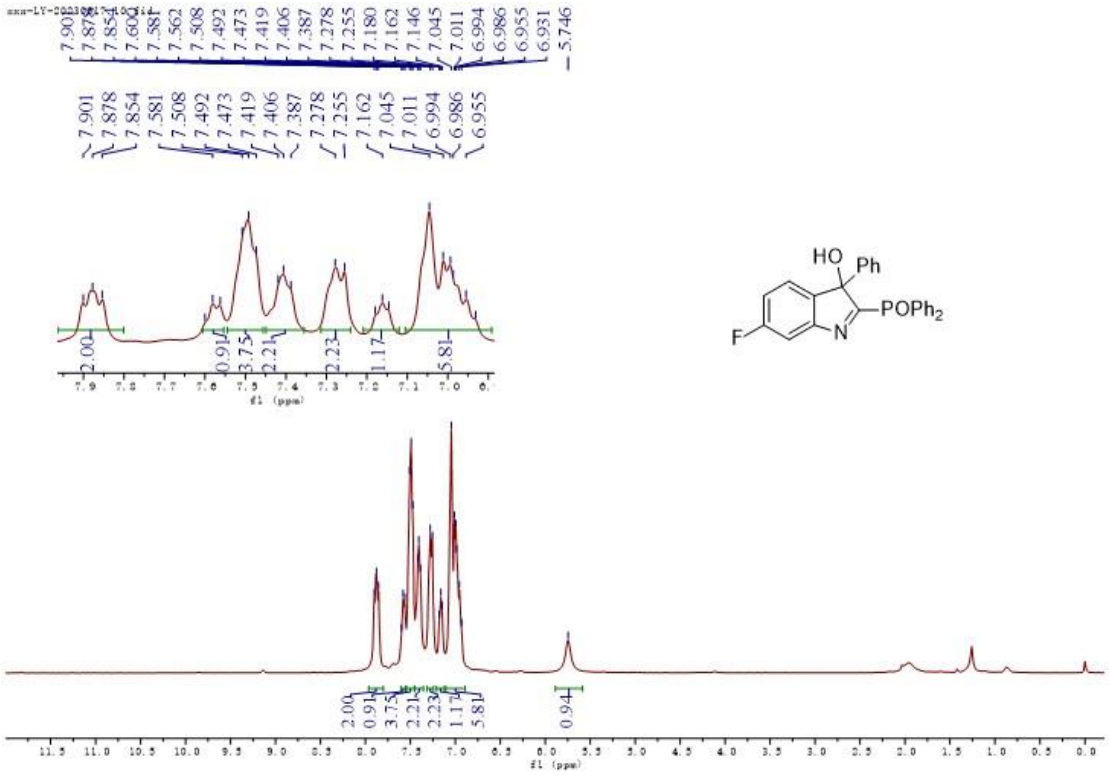
^{13}C NMR (101 MHz, $CDCl_3$) for **6b**



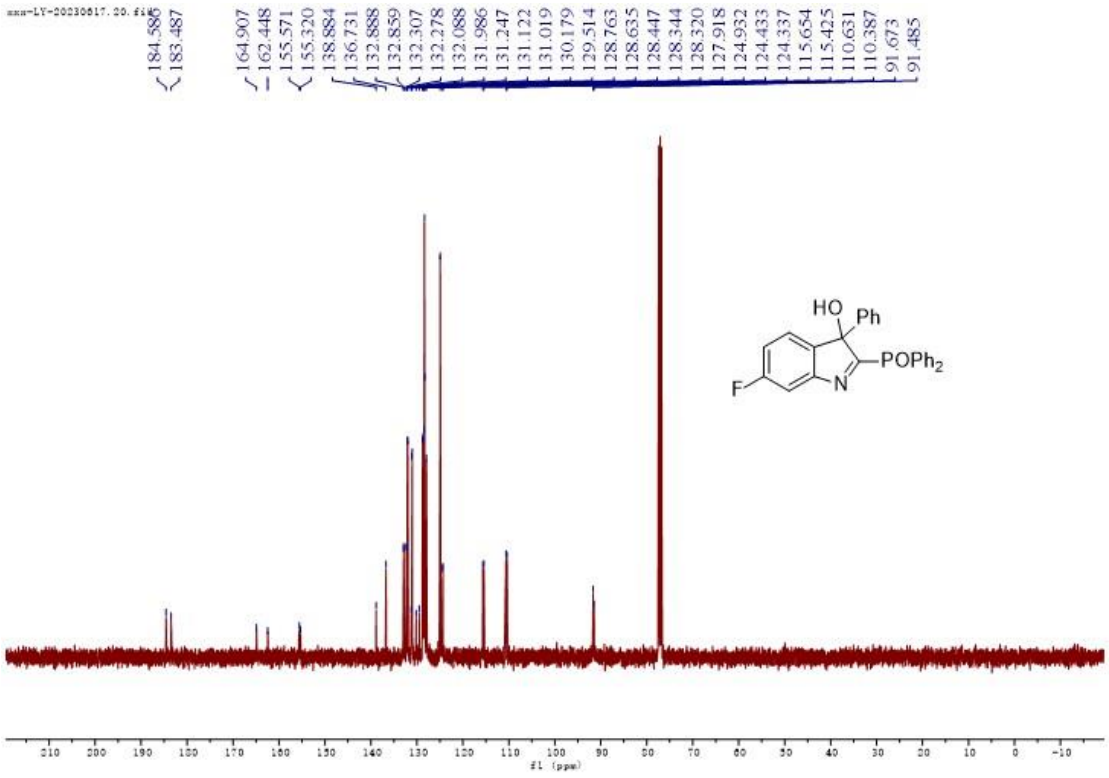
^{31}P NMR (162 MHz, $CDCl_3$) for **6b**



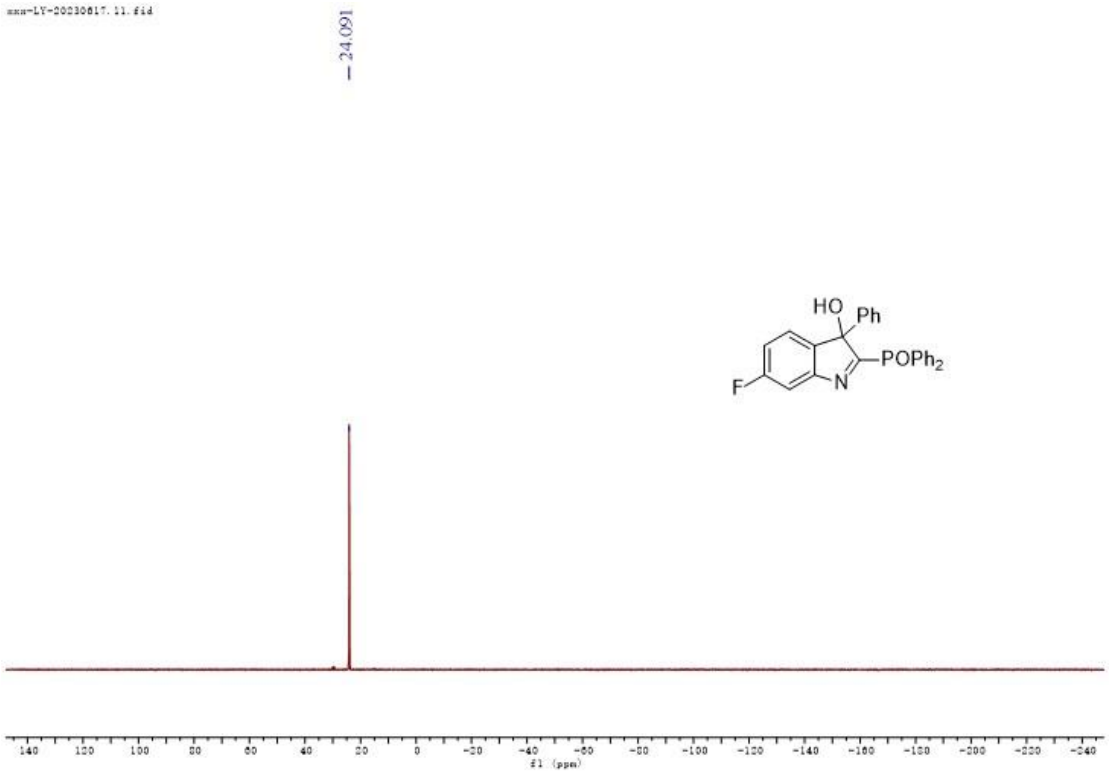
^{1}H NMR (400 MHz, $CDCl_3$) for **6c**



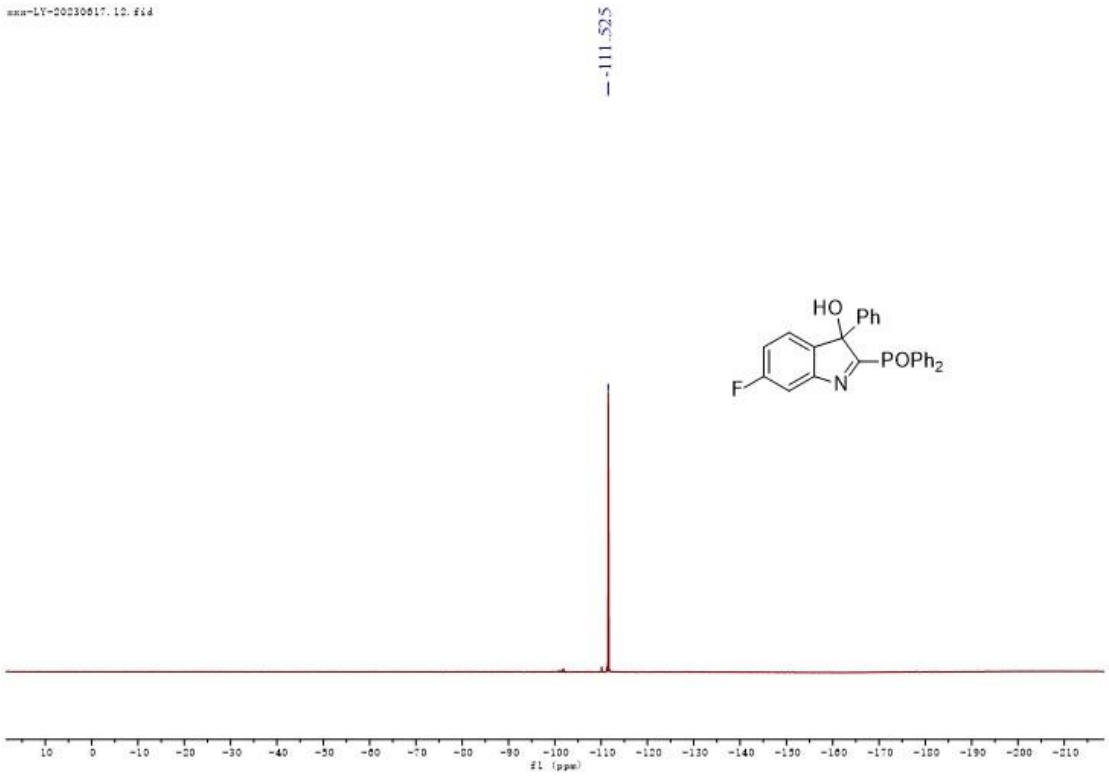
^{13}C NMR (101 MHz, $CDCl_3$) for **6c**



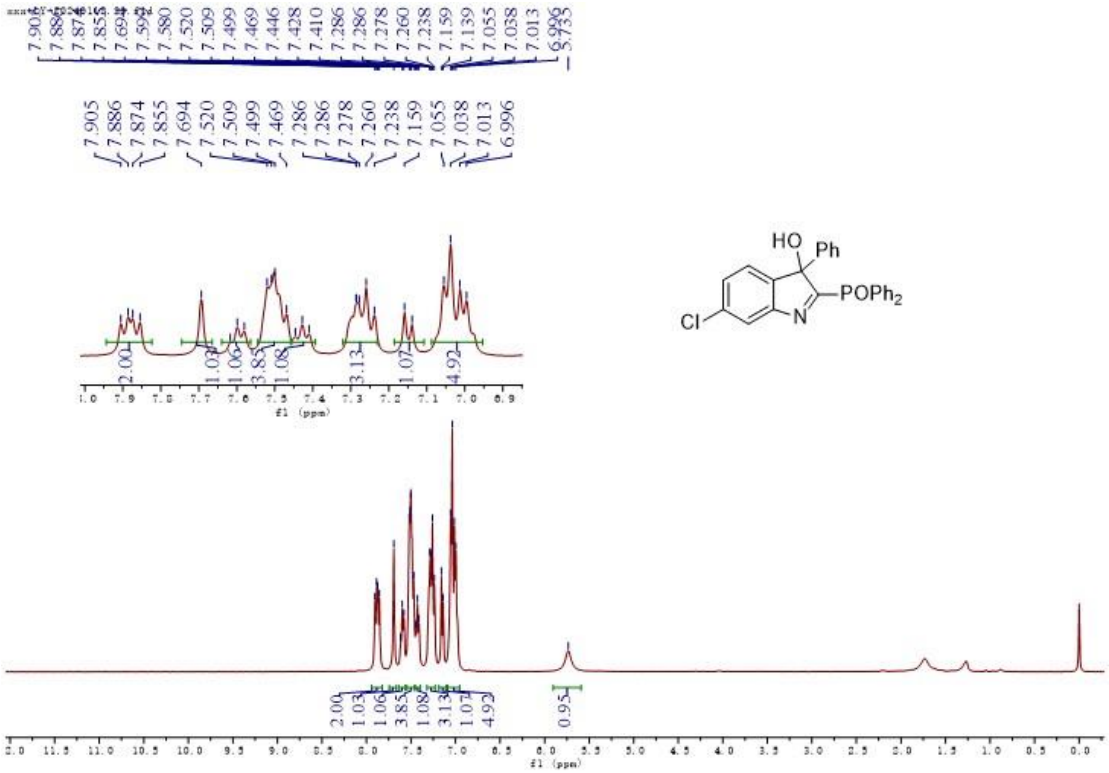
^{31}P NMR (162 MHz, $CDCl_3$) for **6c**



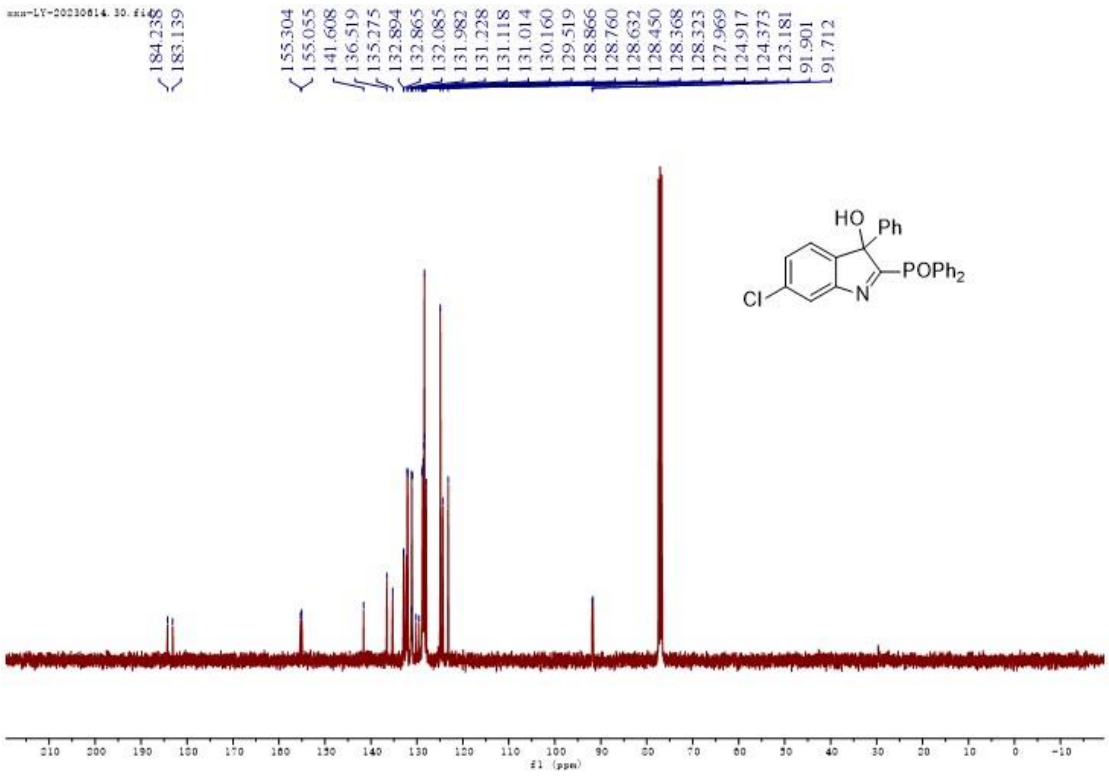
^{19}F NMR (376 MHz, $CDCl_3$) for **6c**



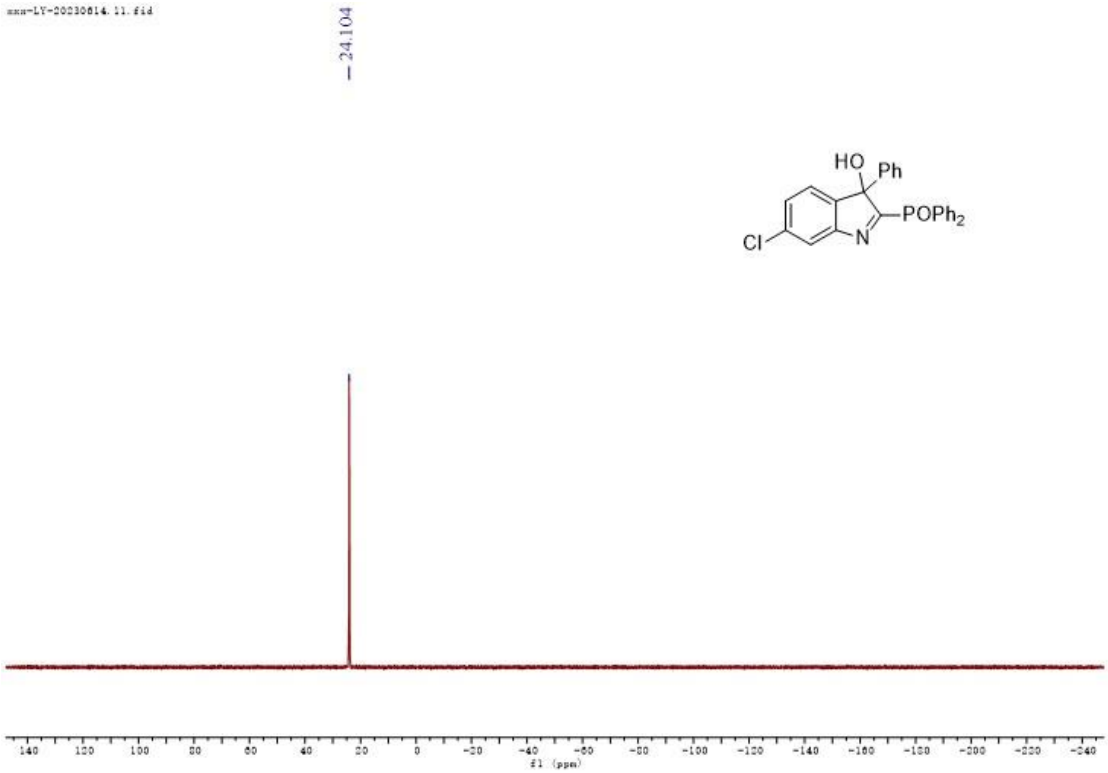
^{1}H NMR (400 MHz, $CDCl_3$) for **6d**



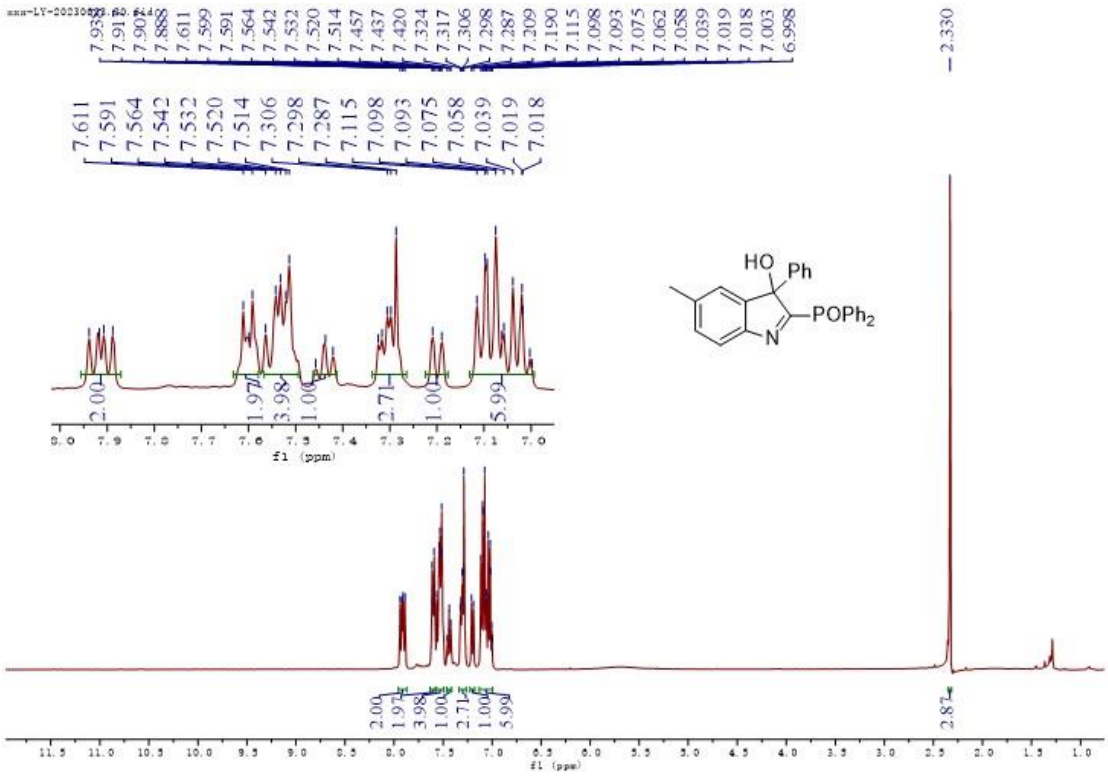
^{13}C NMR (101 MHz, $CDCl_3$) for **6d**



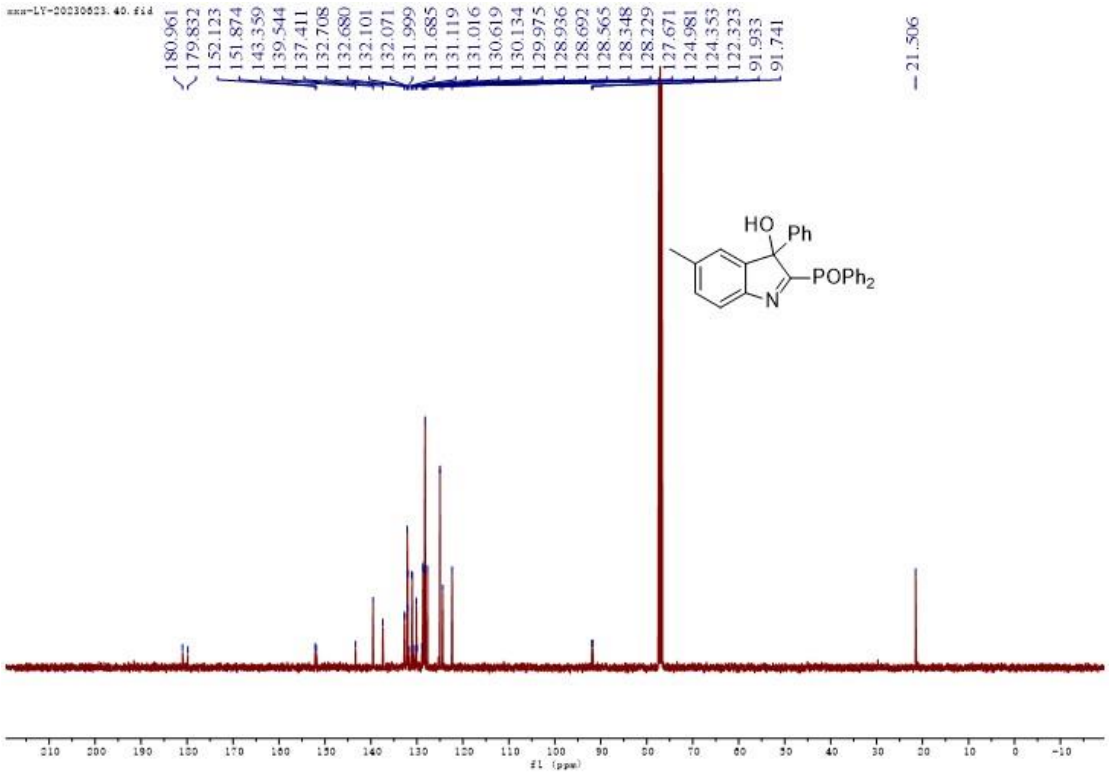
^{31}P NMR (162 MHz, $CDCl_3$) for **6d**



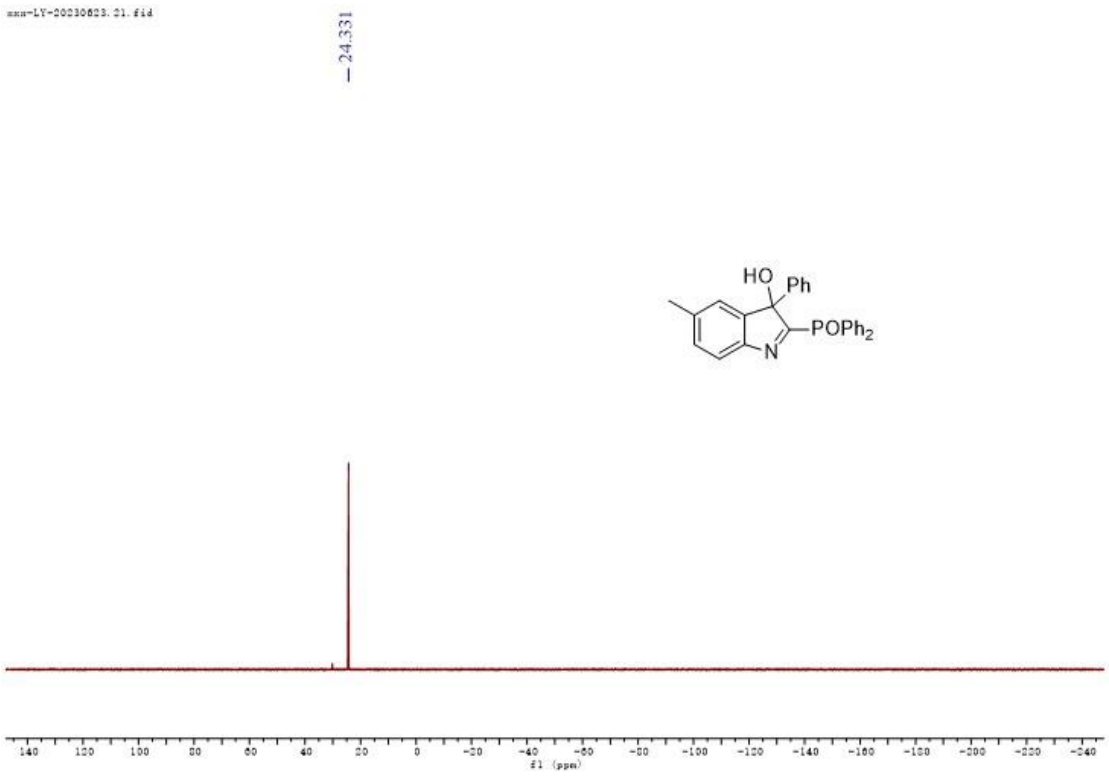
^{1}H NMR (400 MHz, $CDCl_3$) for **6e**



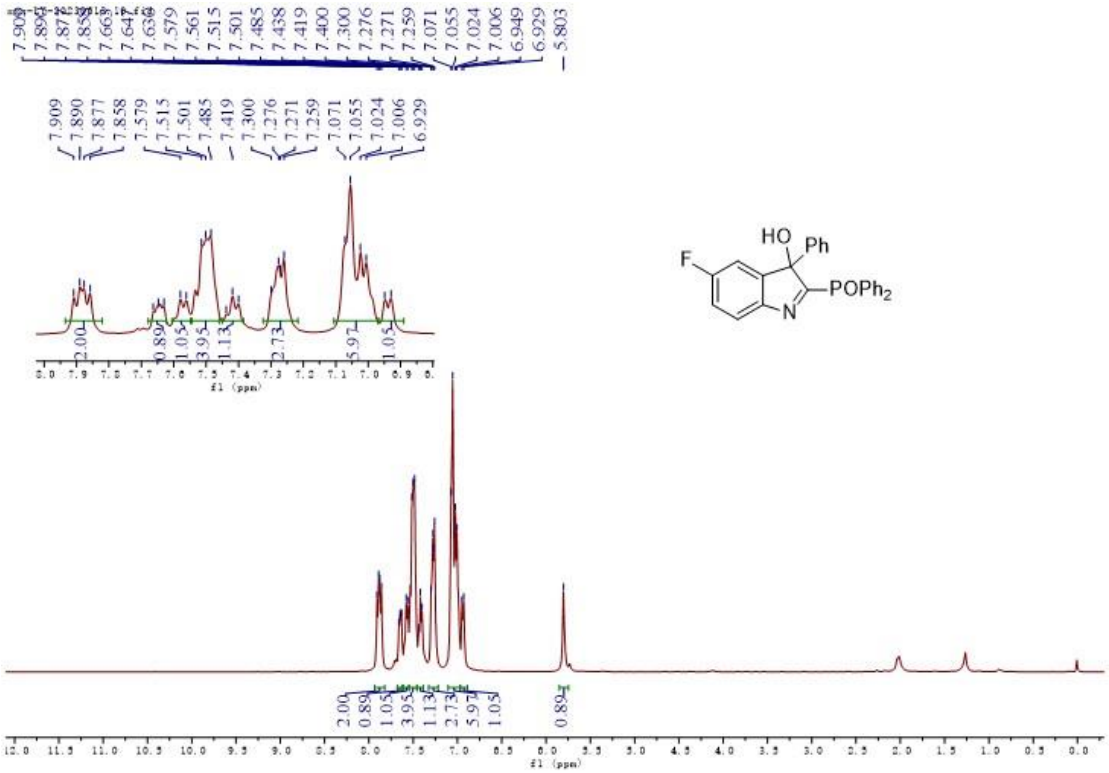
^{13}C NMR (101 MHz, $CDCl_3$) for **6e**



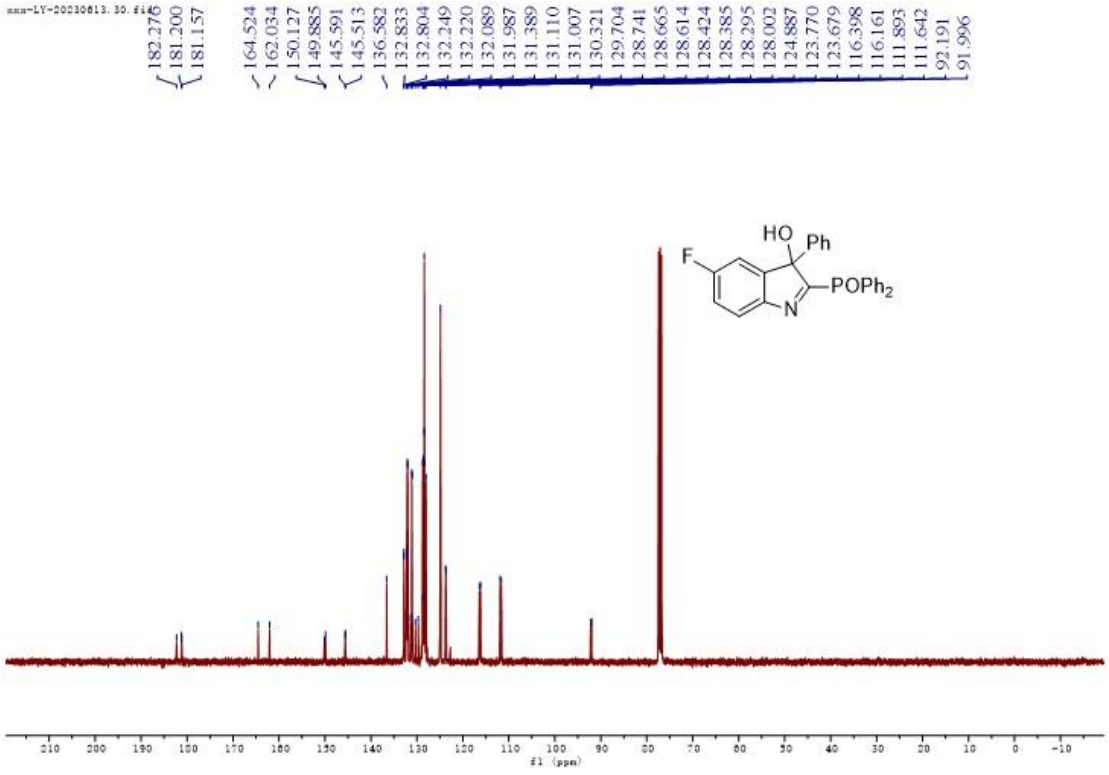
^{31}P NMR (162 MHz, $CDCl_3$) for **6e**



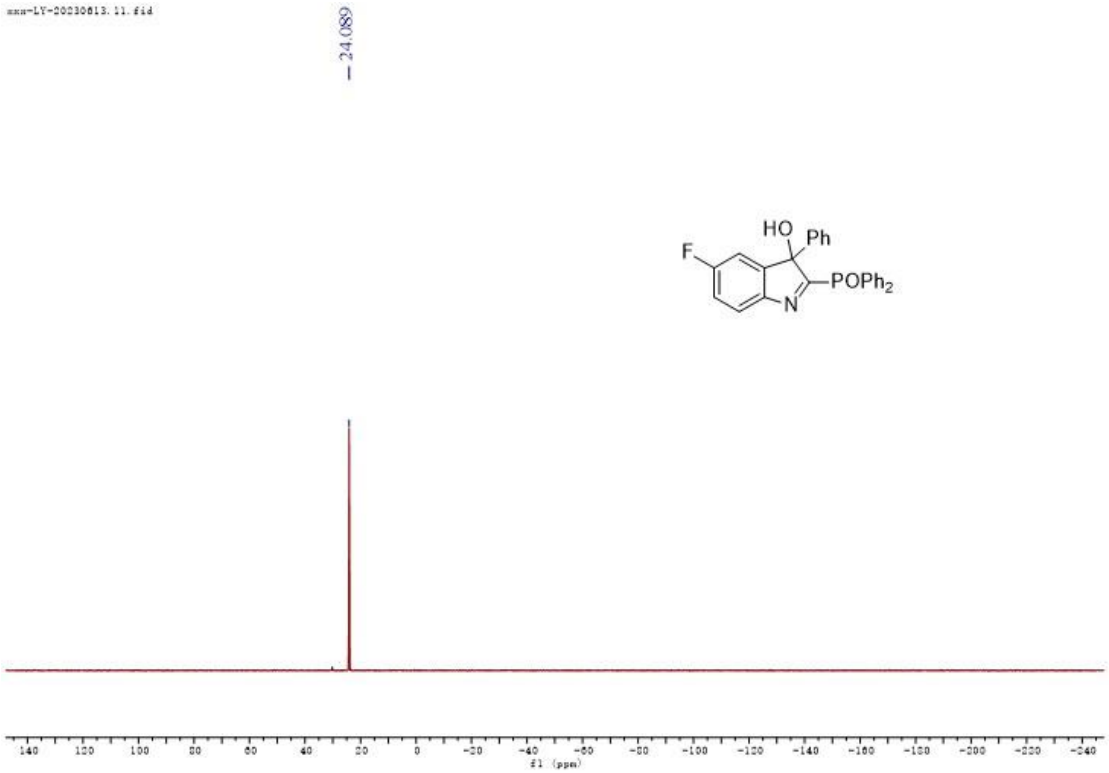
^{1}H NMR (400 MHz, $CDCl_3$) for **6f**



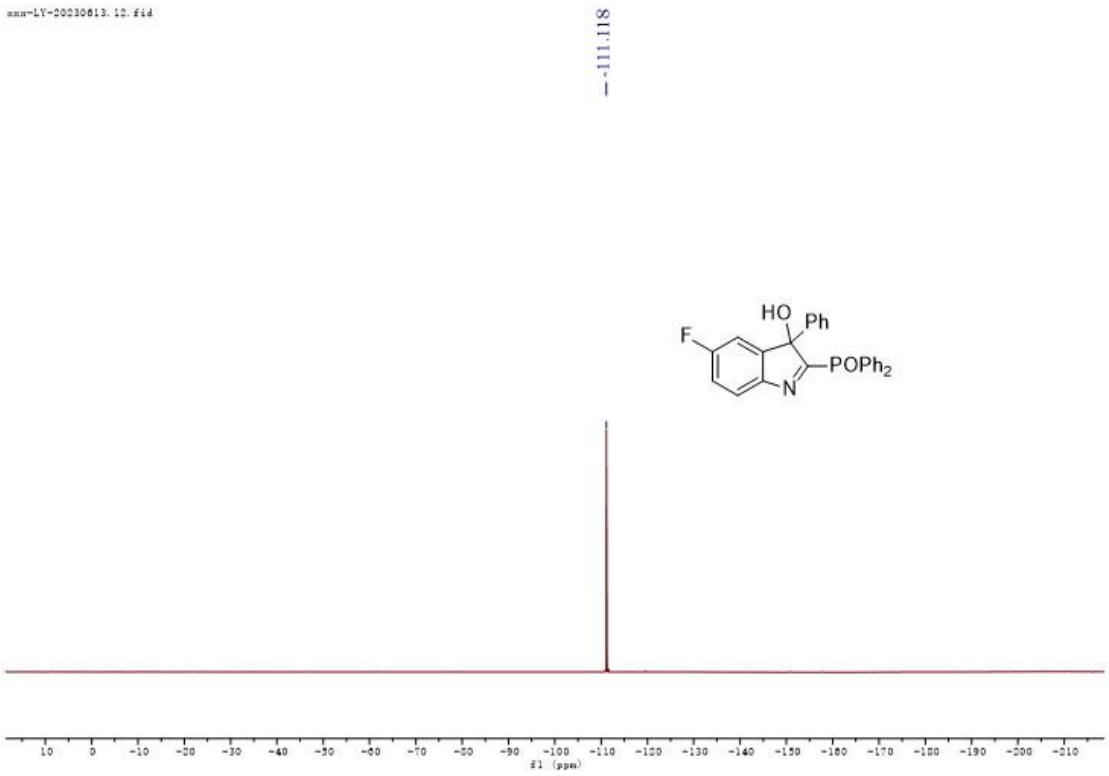
^{13}C NMR (101 MHz, $CDCl_3$) for **6f**



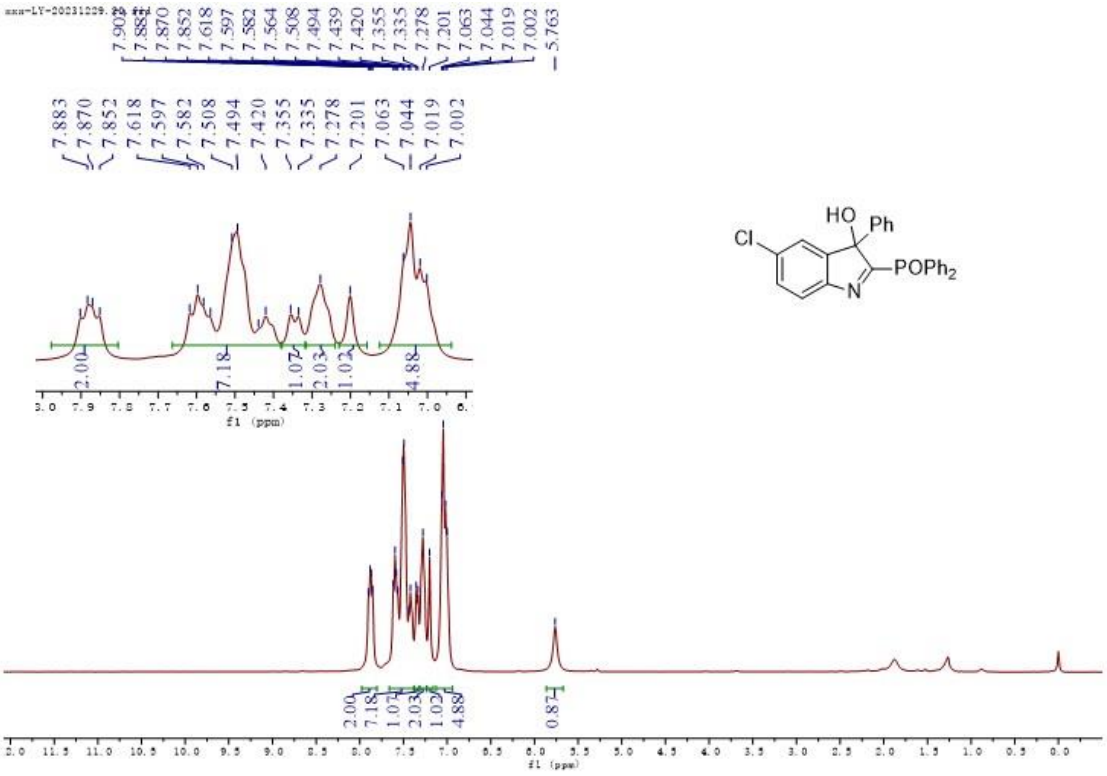
^{31}P NMR (162 MHz, $CDCl_3$) for **6f**



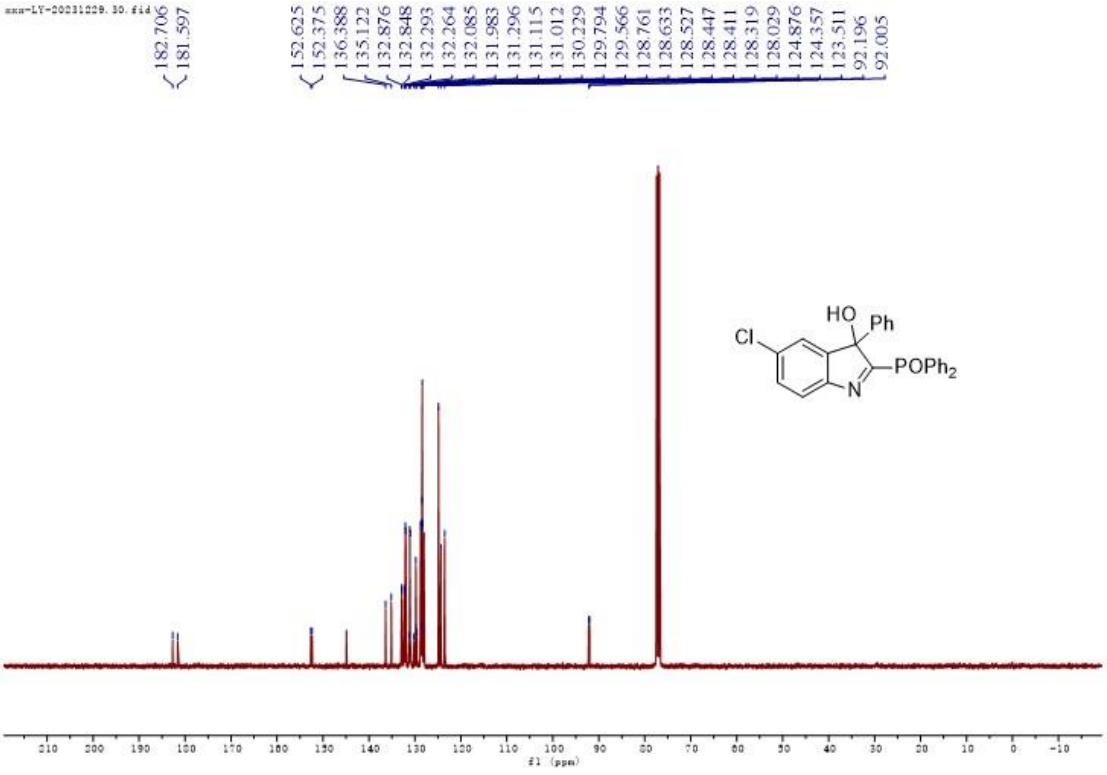
^{19}F NMR (376 MHz, $CDCl_3$) for **6f**



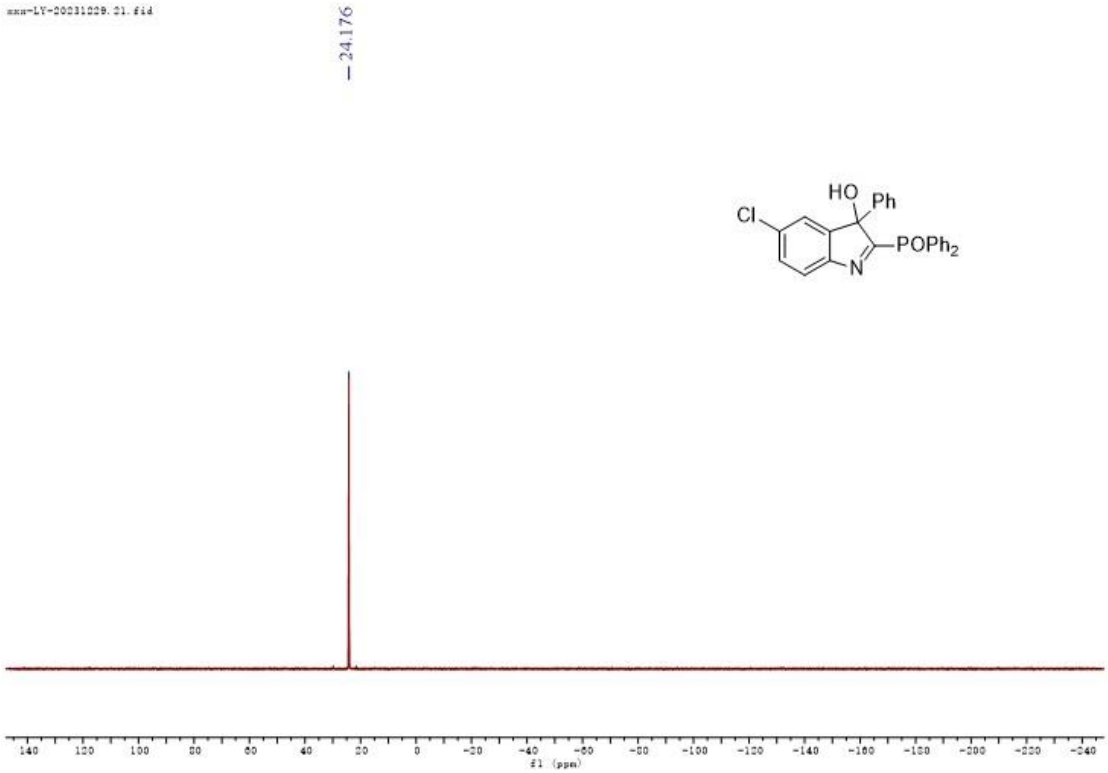
^{1}H NMR (400 MHz, $CDCl_3$) for **6g**



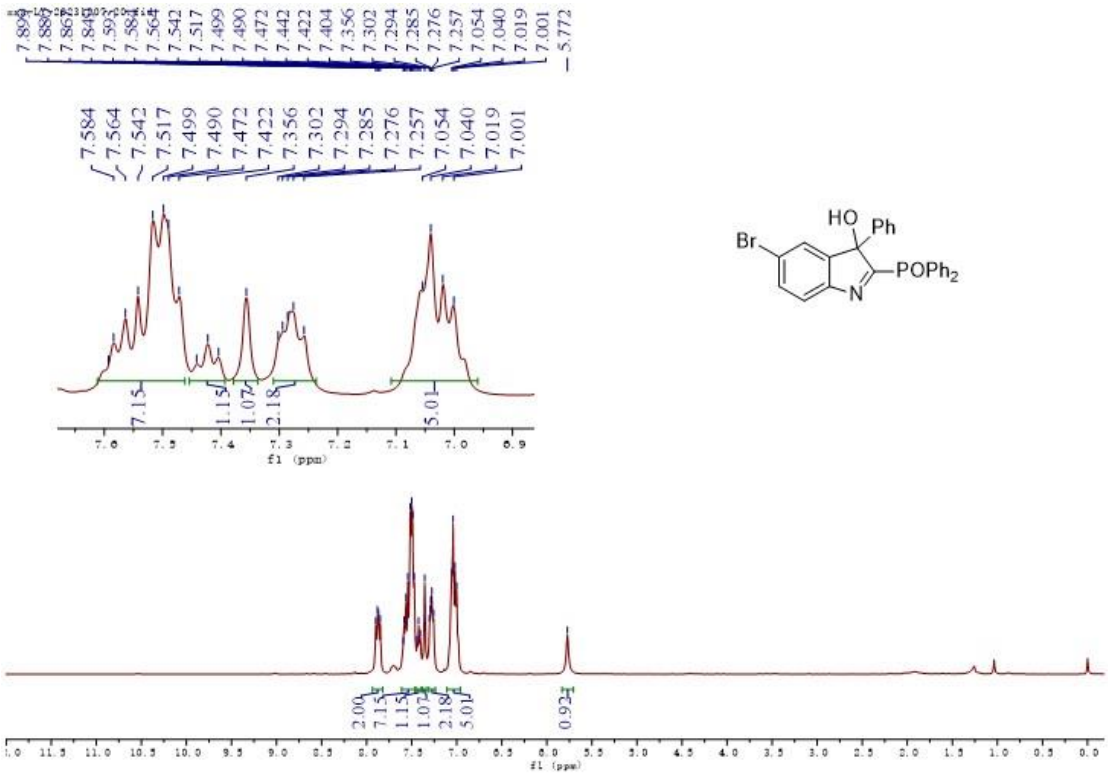
^{13}C NMR (101 MHz, $CDCl_3$) for **6g**



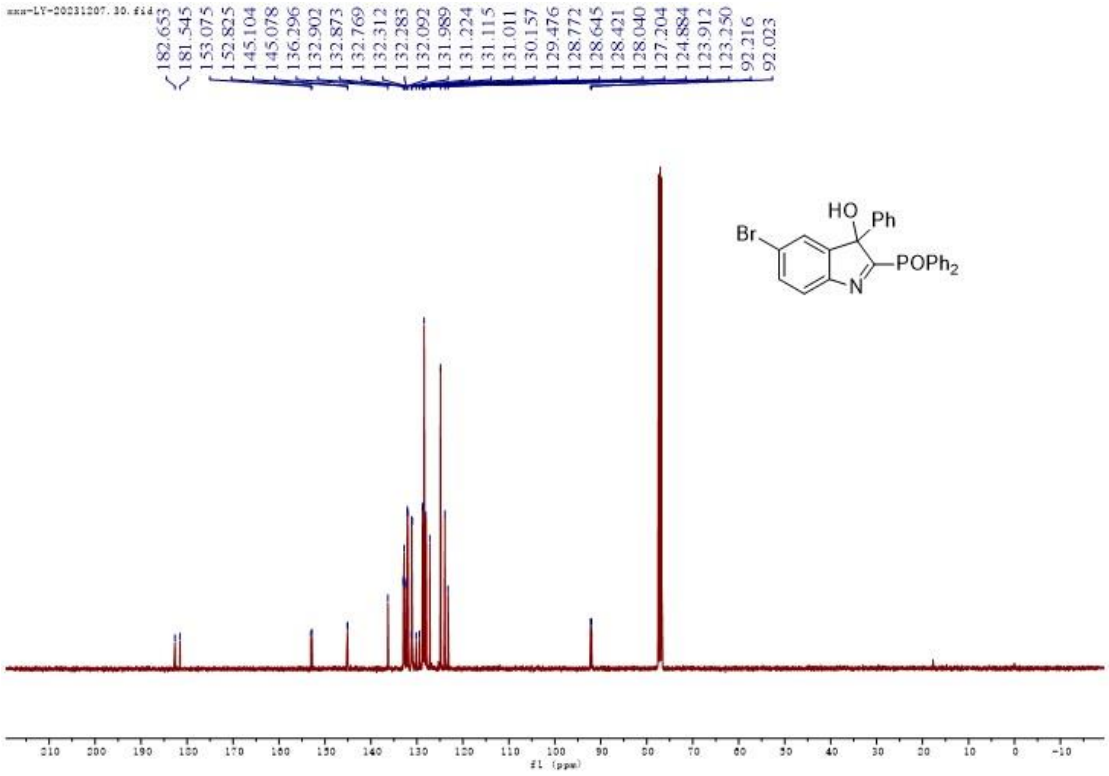
^{31}P NMR (162 MHz, $CDCl_3$) for **6g**



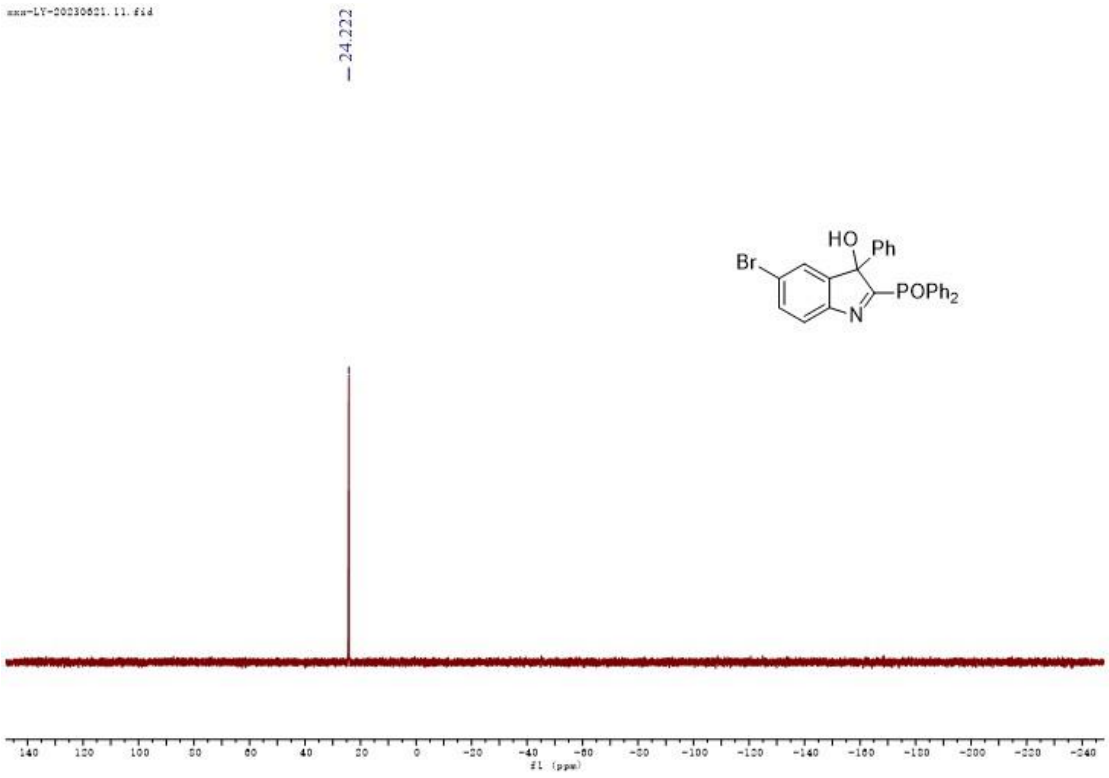
^{1}H NMR (400 MHz, $CDCl_3$) for **6h**



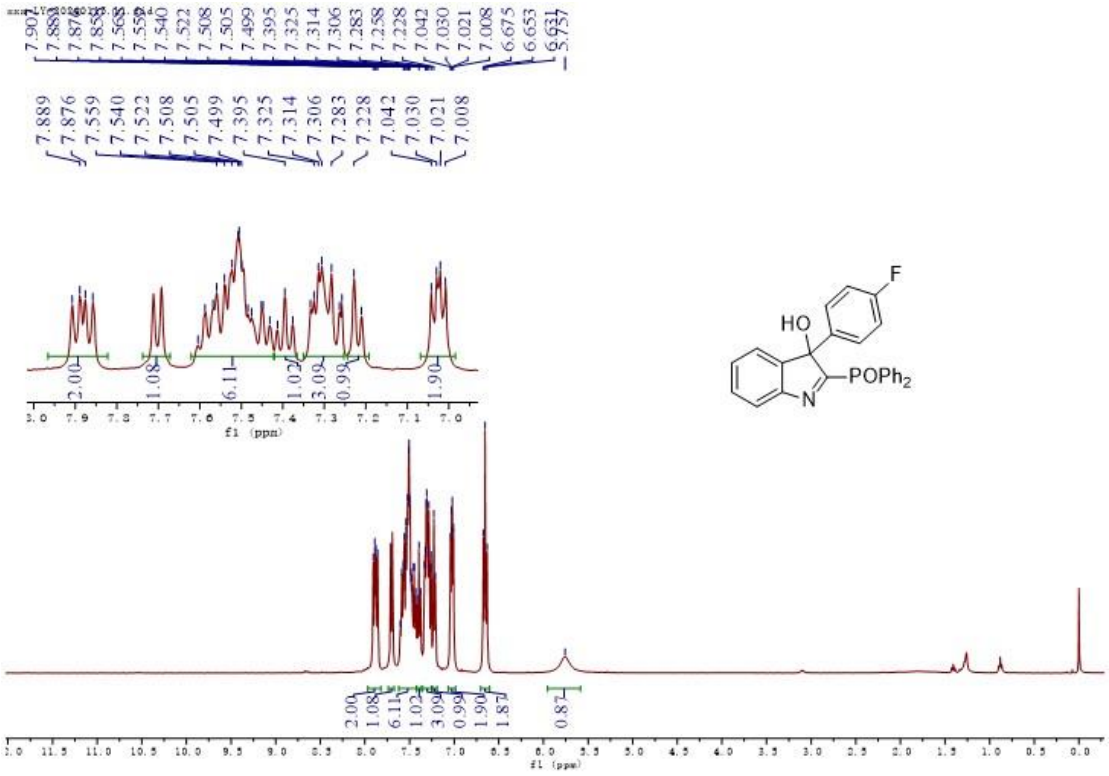
^{13}C NMR (101 MHz, $CDCl_3$) for **6h**



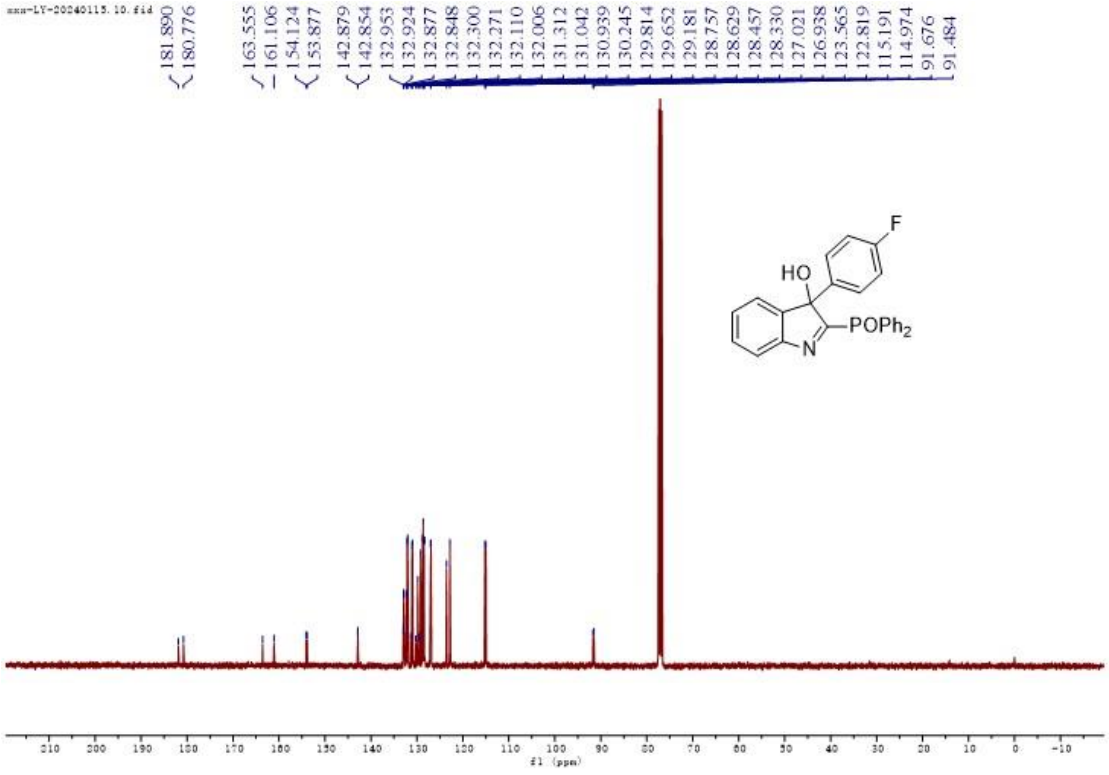
^{31}P NMR (162 MHz, $CDCl_3$) for **6h**



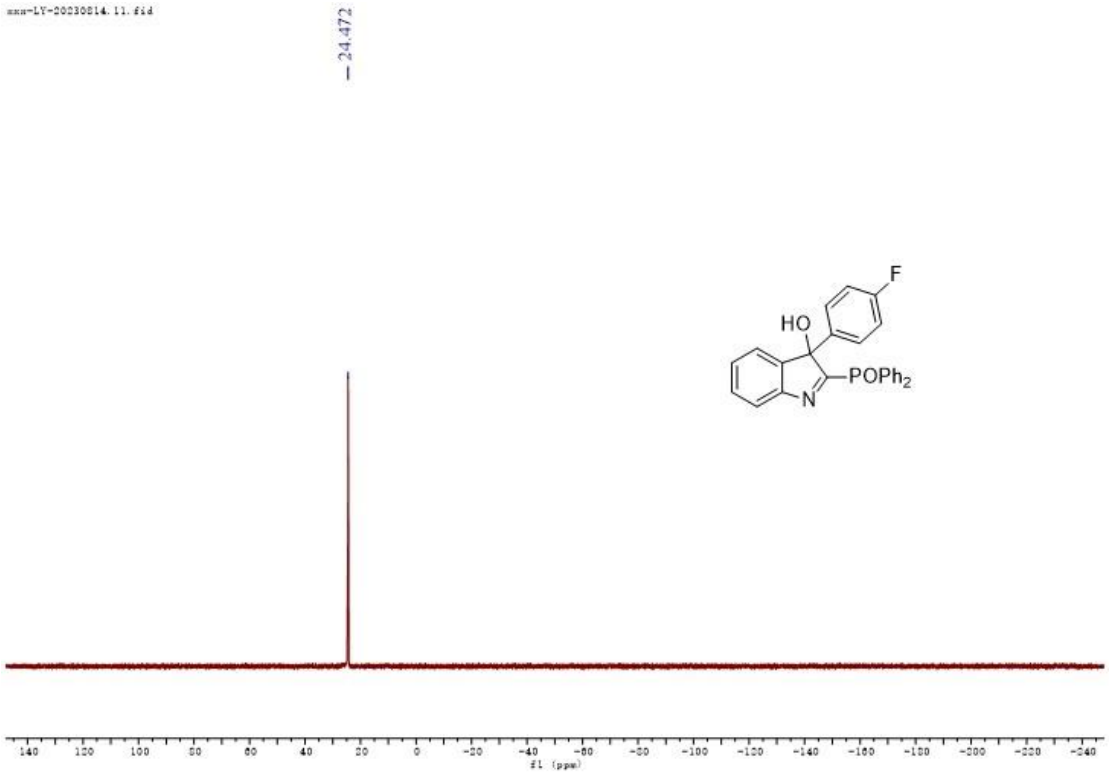
^{1}H NMR (400 MHz, $CDCl_3$) for **6i**



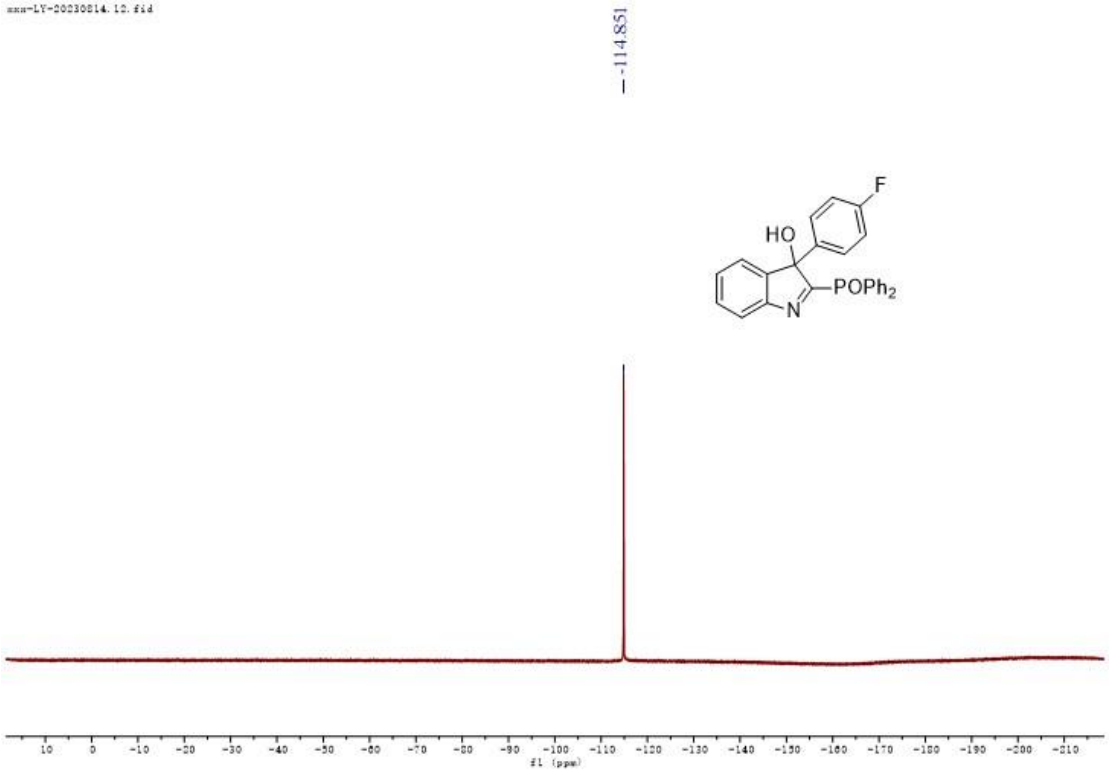
^{13}C NMR (101 MHz, $CDCl_3$) for **6i**



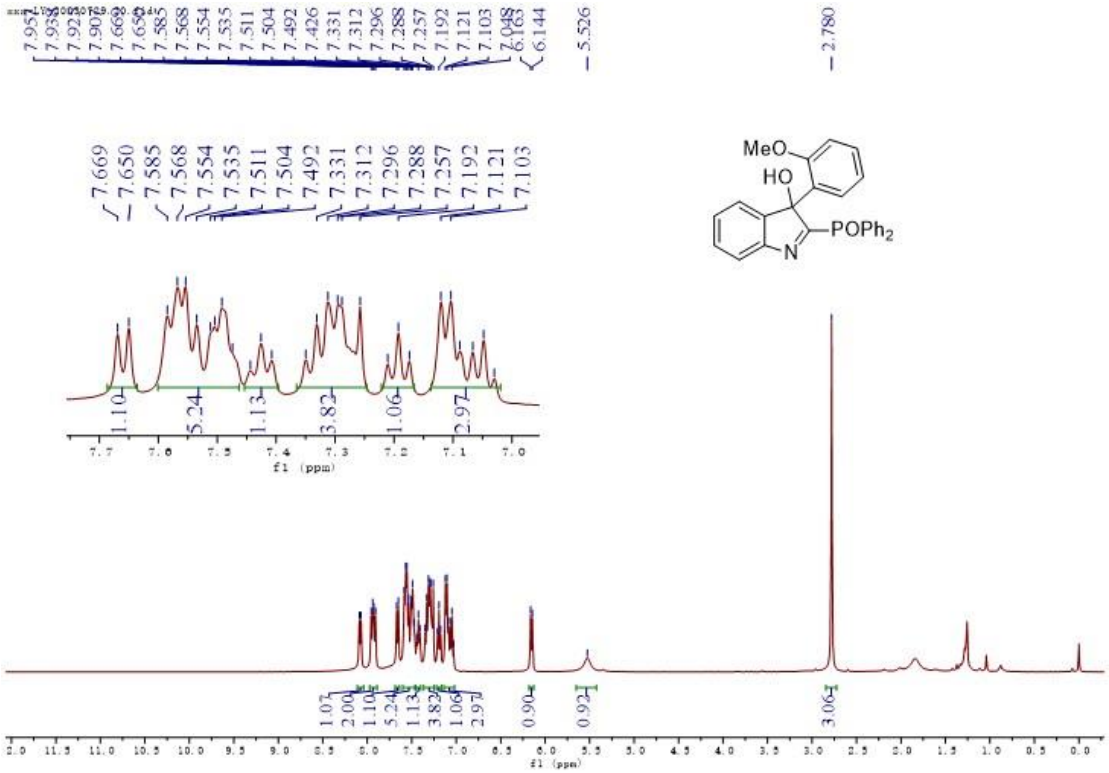
^{31}P NMR (162 MHz, $CDCl_3$) for **6i**



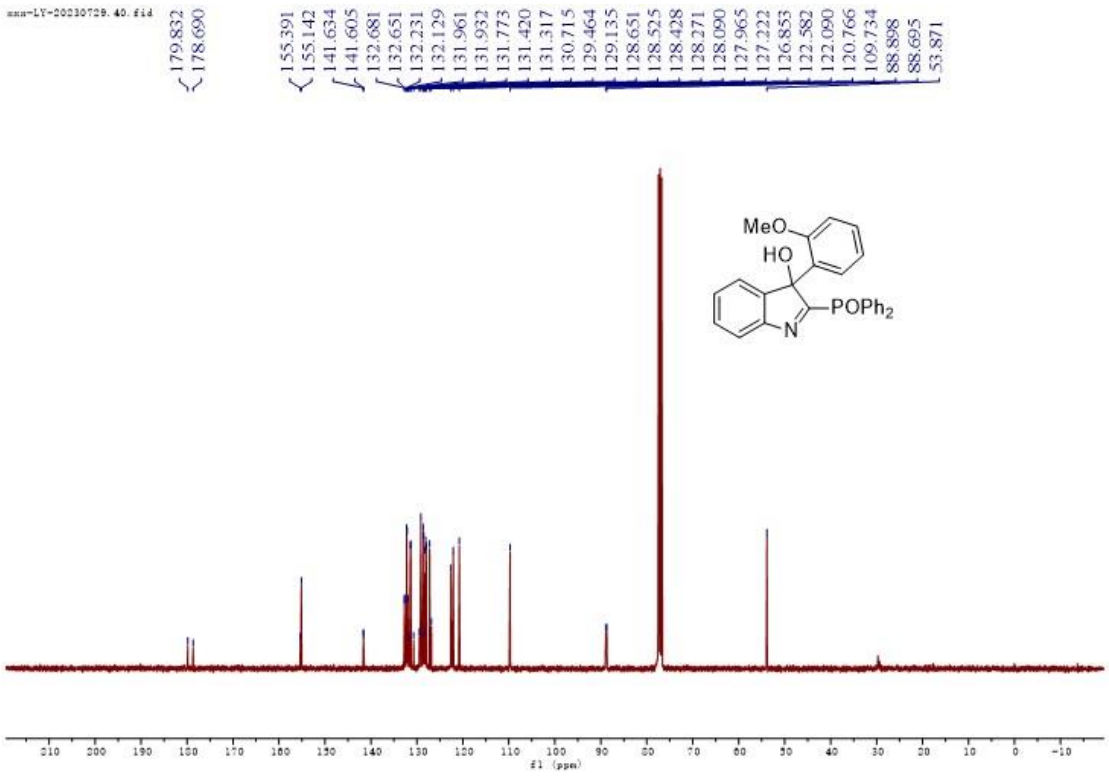
^{19}F NMR (376 MHz, $CDCl_3$) for **6i**



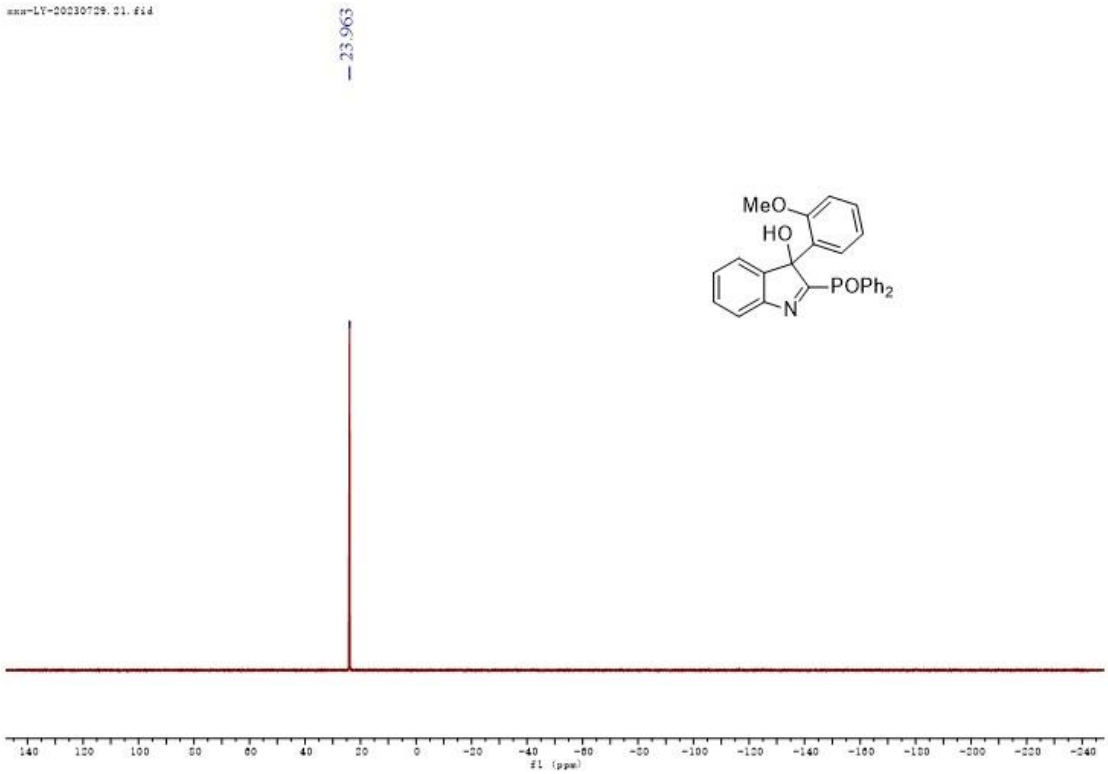
^{1}H NMR (400 MHz, $CDCl_3$) for **6j**



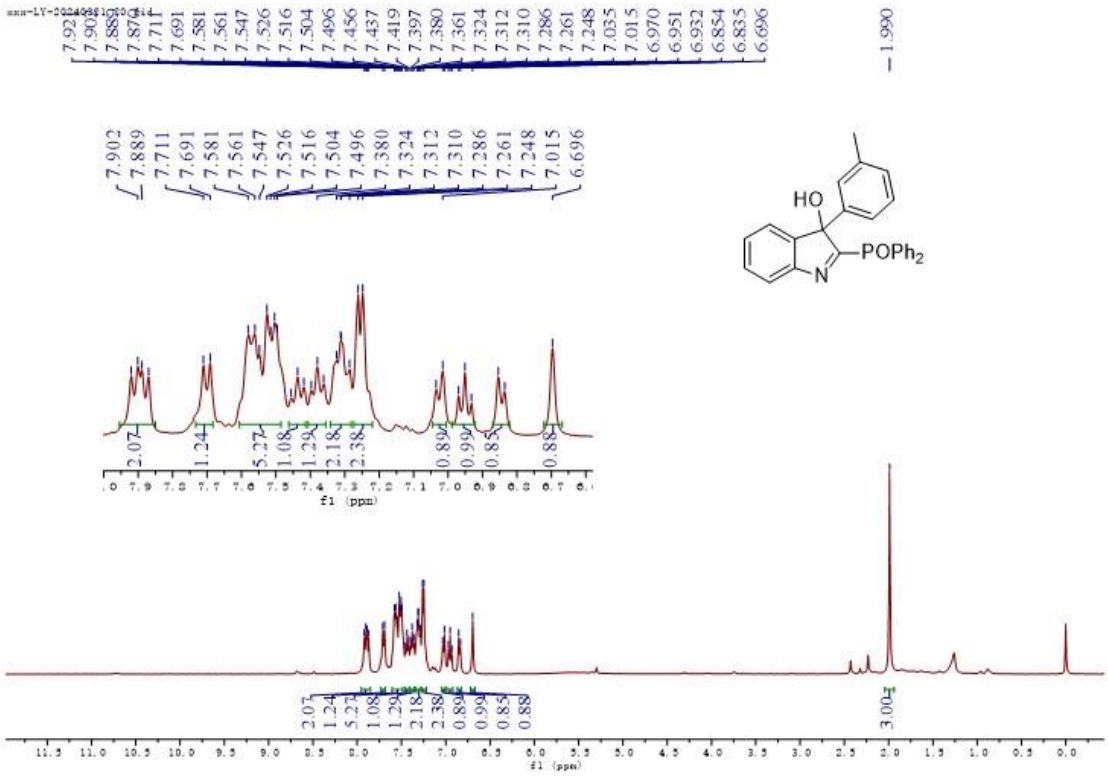
^{13}C NMR (101 MHz, $CDCl_3$) for **6j**



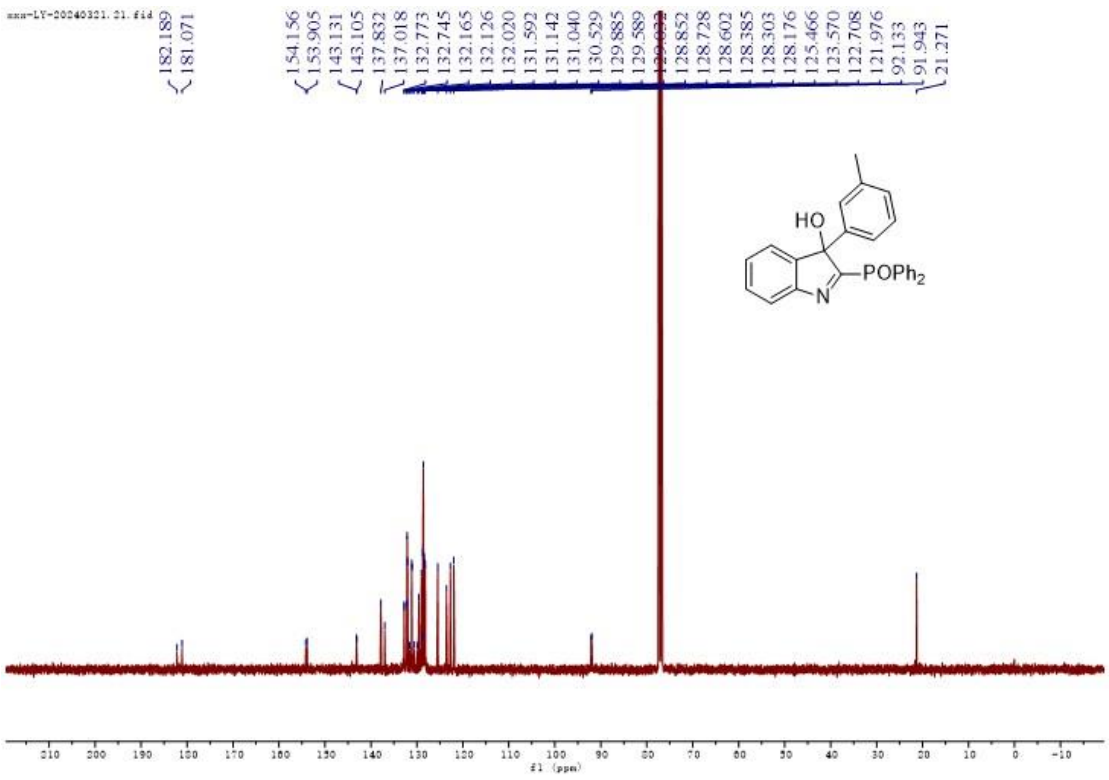
^{31}P NMR (162 MHz, $CDCl_3$) for **6j**



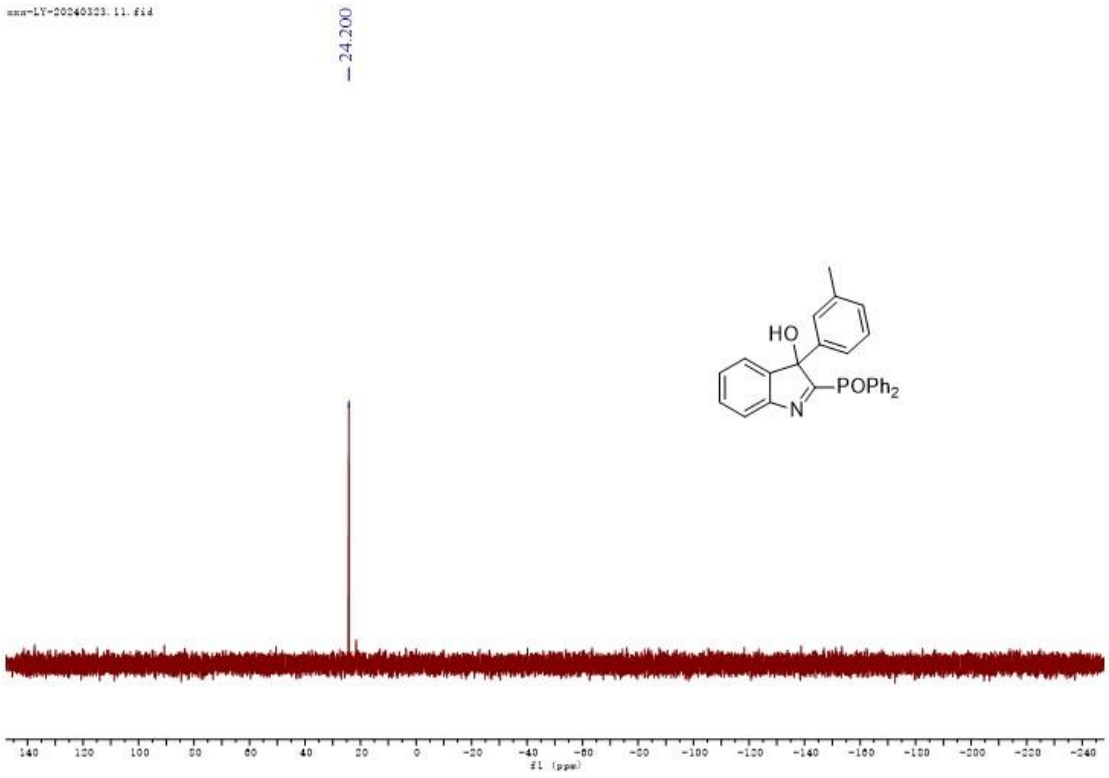
^{1}H NMR (400 MHz, $CDCl_3$) for **6k**



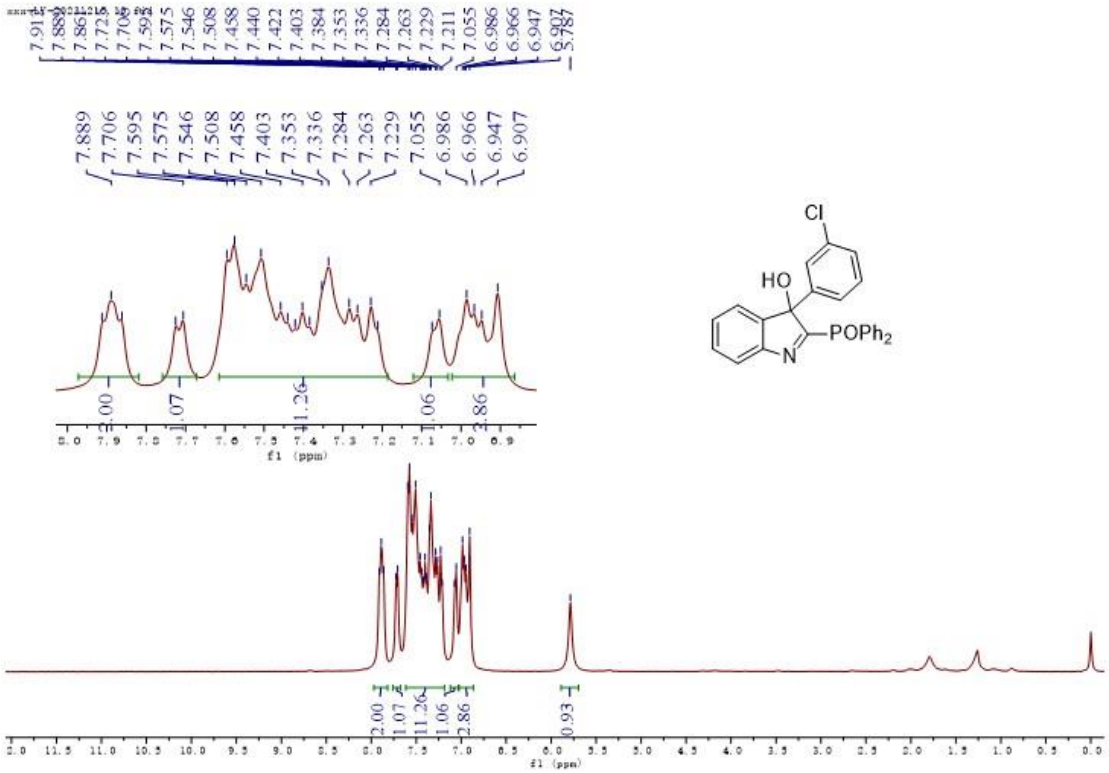
^{13}C NMR (101 MHz, $CDCl_3$) for **6k**



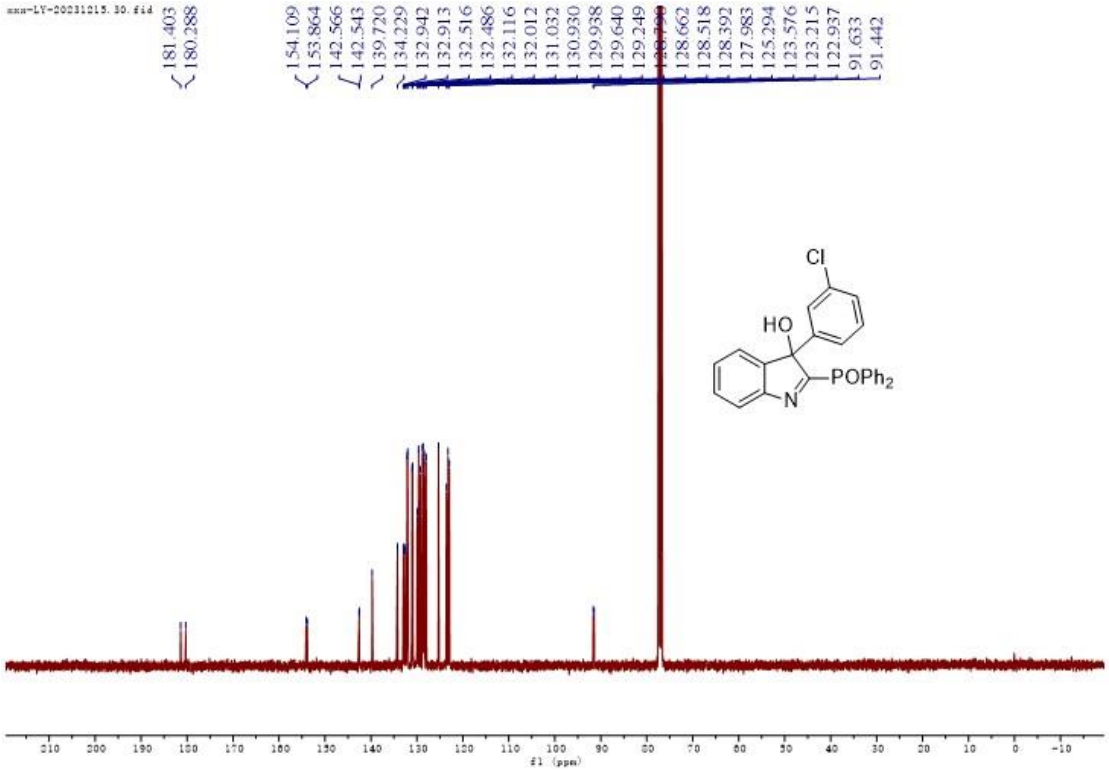
^{31}P NMR (162 MHz, $CDCl_3$) for **6k**



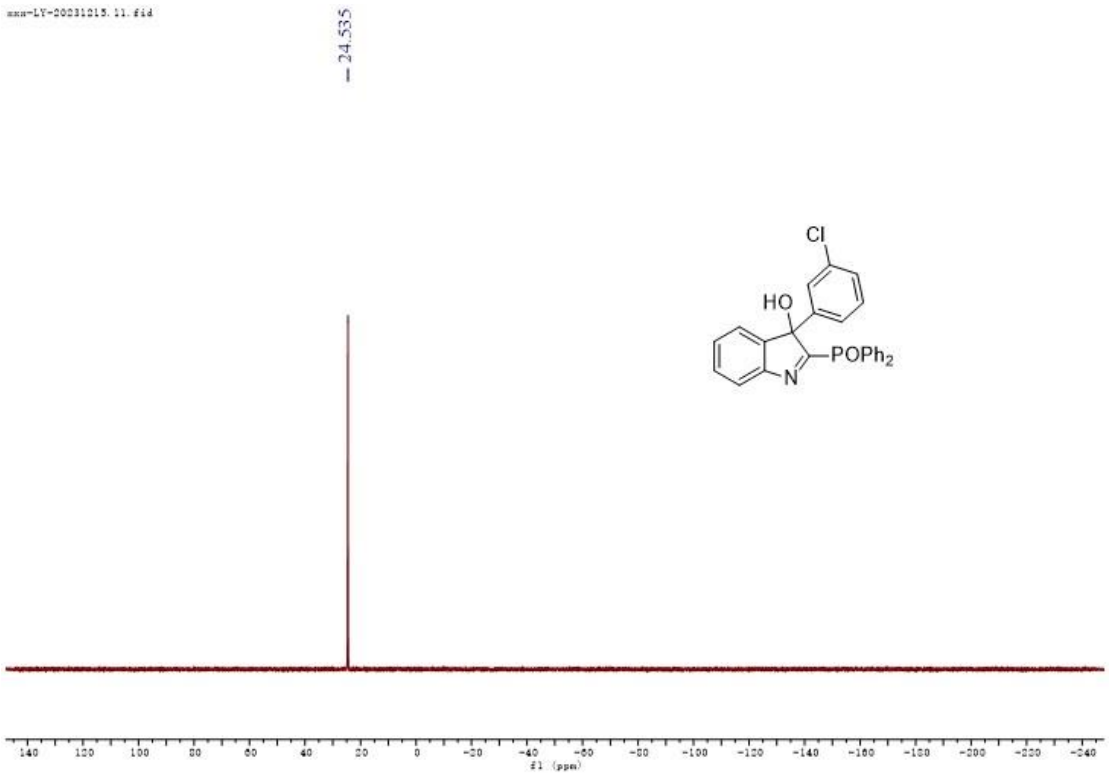
^{1}H NMR (400 MHz, $CDCl_3$) for **6l**



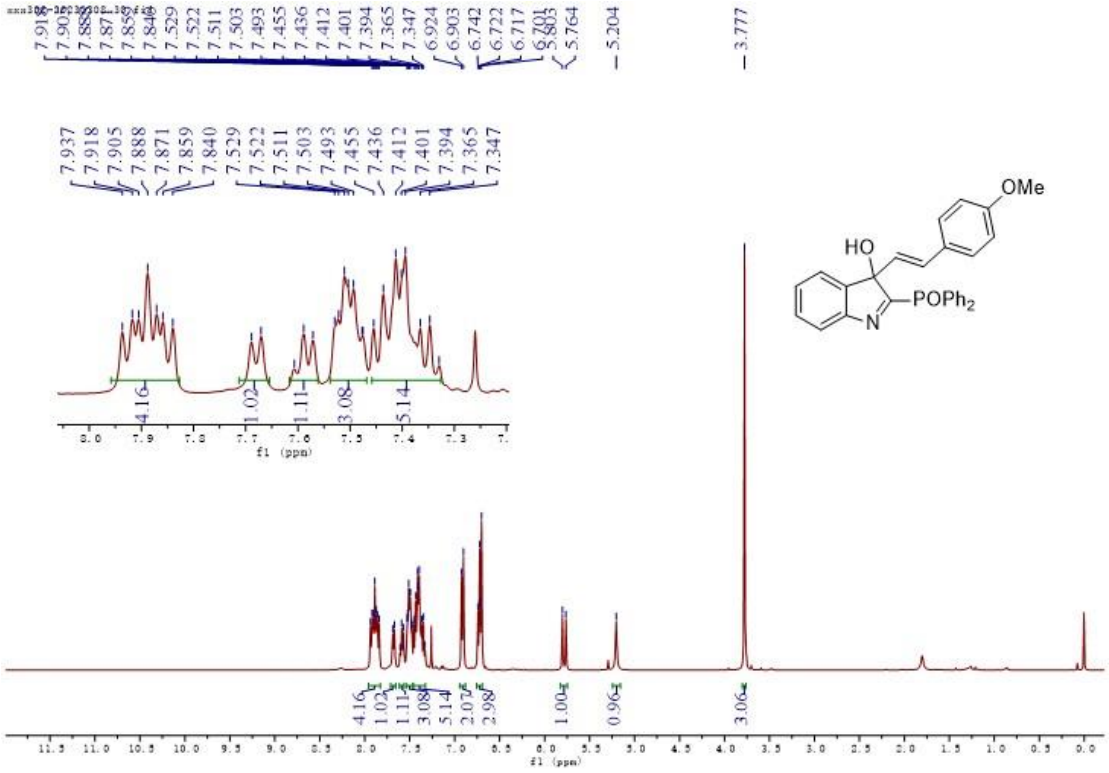
^{13}C NMR (101 MHz, $CDCl_3$) for **6l**



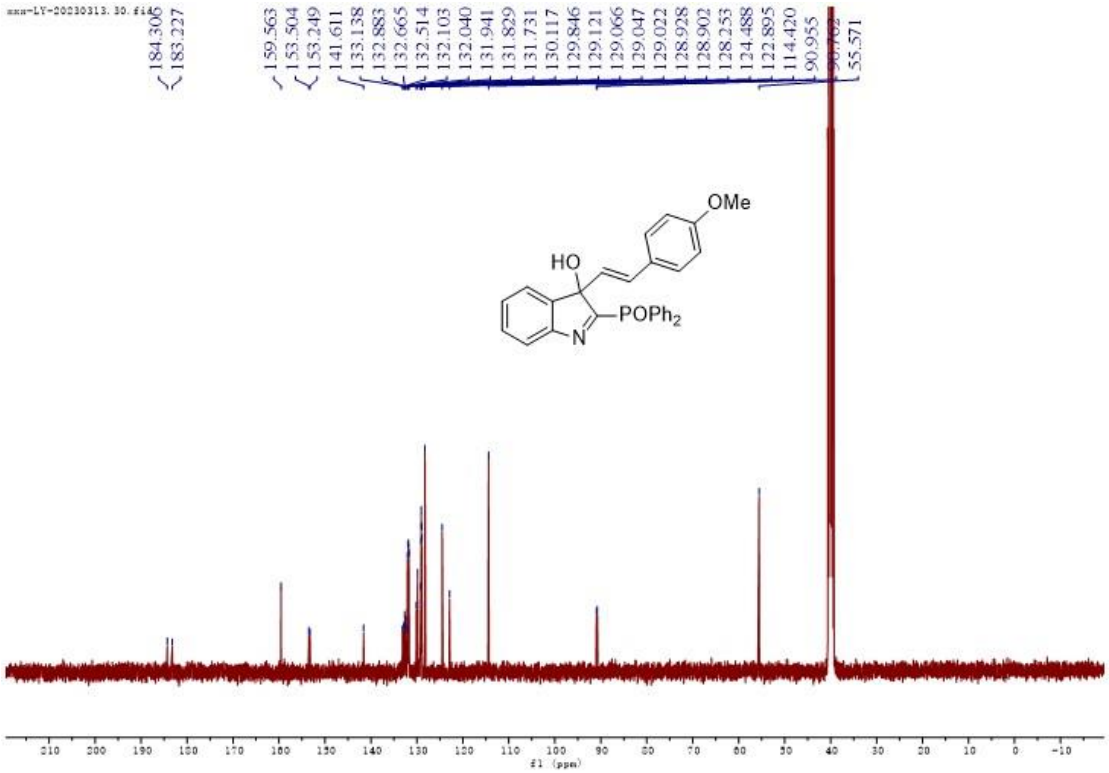
^{31}P NMR (162 MHz, $CDCl_3$) for **6l**



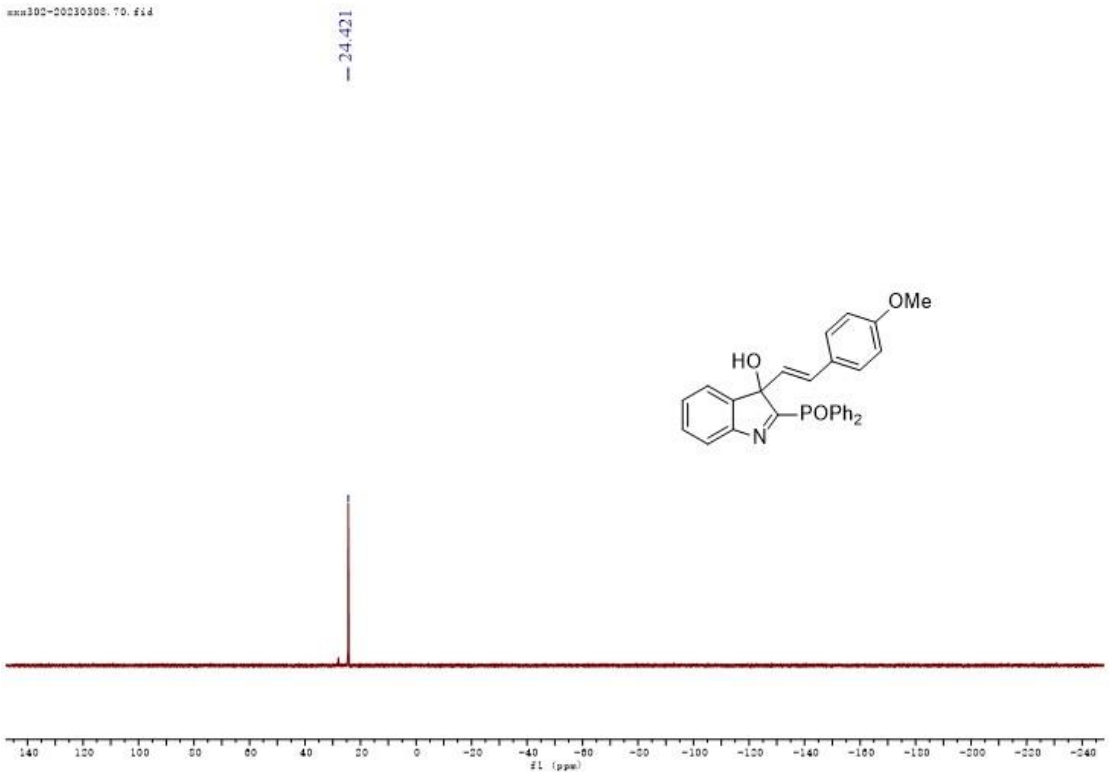
^{1}H NMR (400 MHz, $CDCl_3$) for **6m**



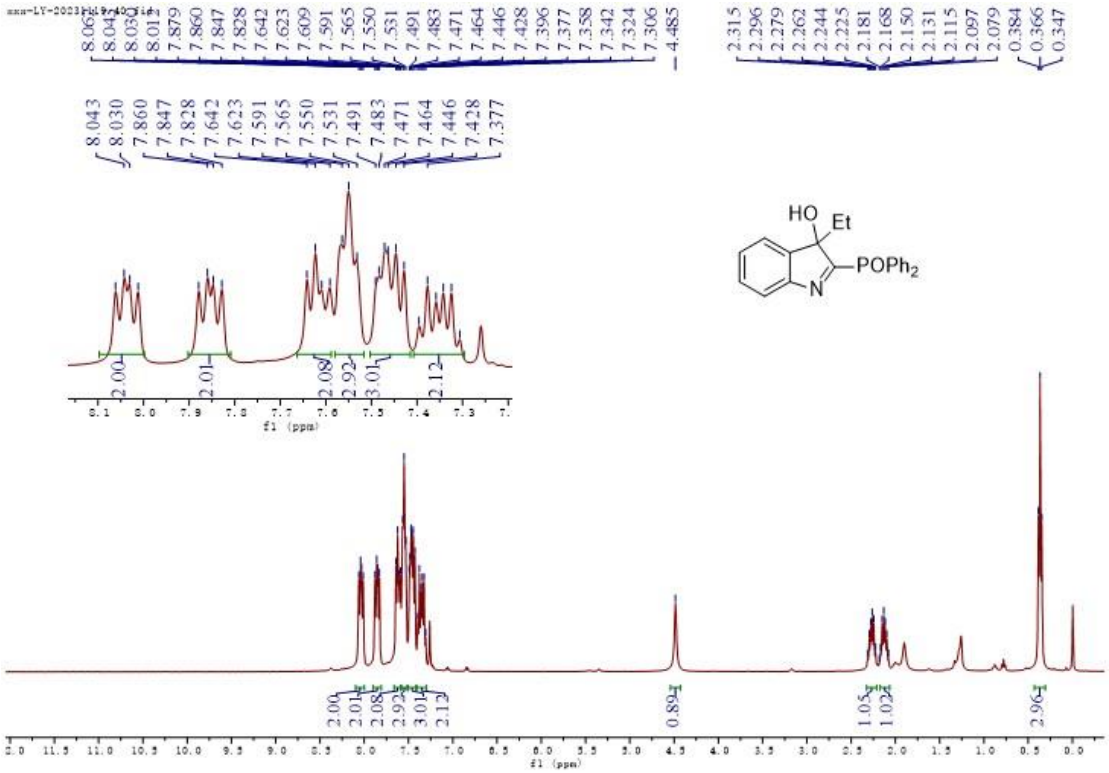
^{13}C NMR (101 MHz, DMSO-d_6) for **6m**



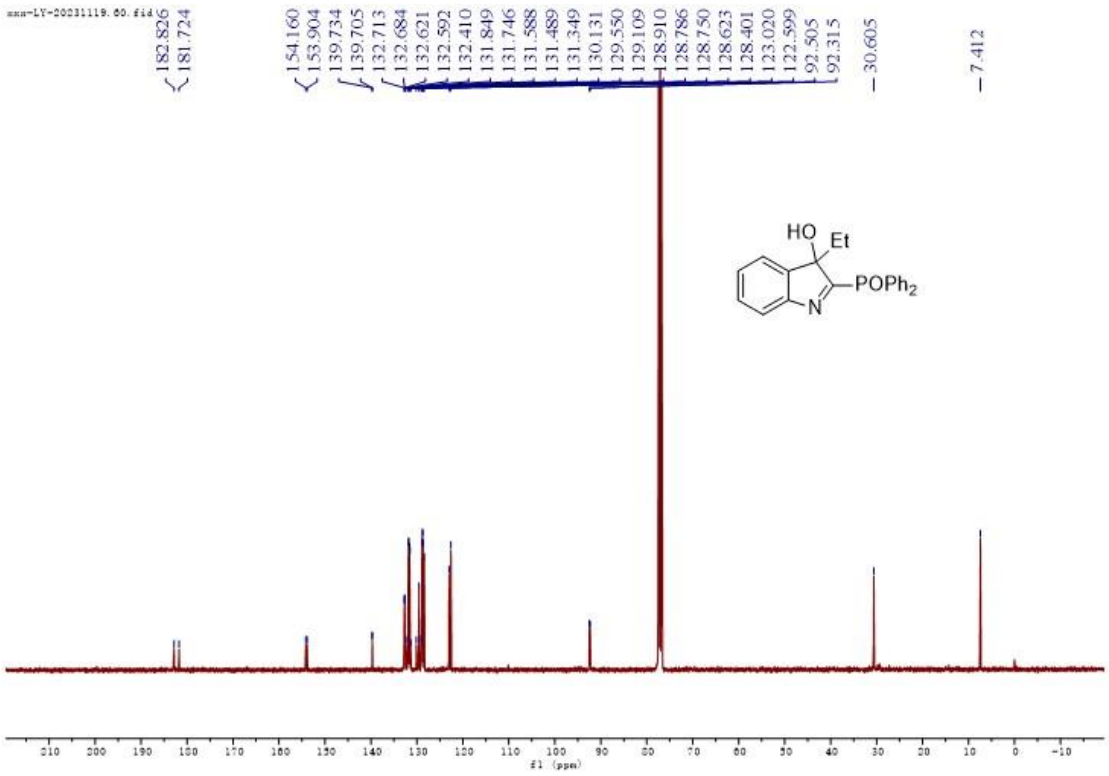
^{31}P NMR (162 MHz, $CDCl_3$) for **6m**



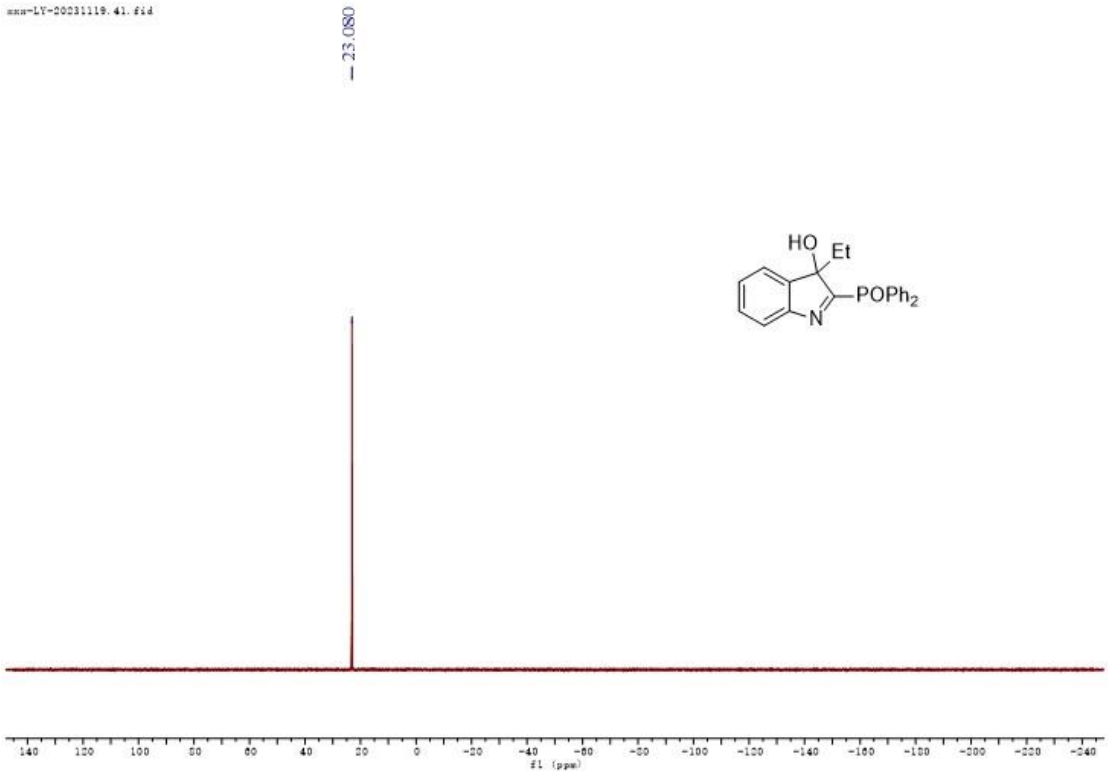
^{1}H NMR (400 MHz, $CDCl_3$) for **6n**



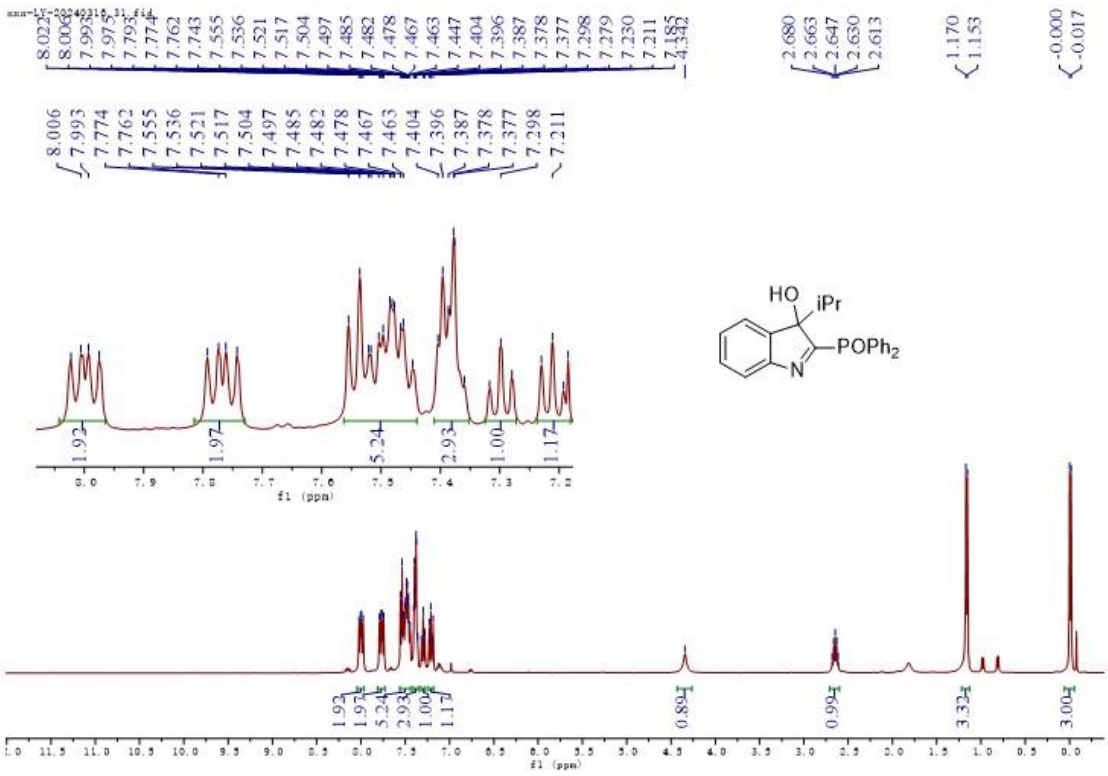
^{13}C NMR (101 MHz, $CDCl_3$) for **6n**



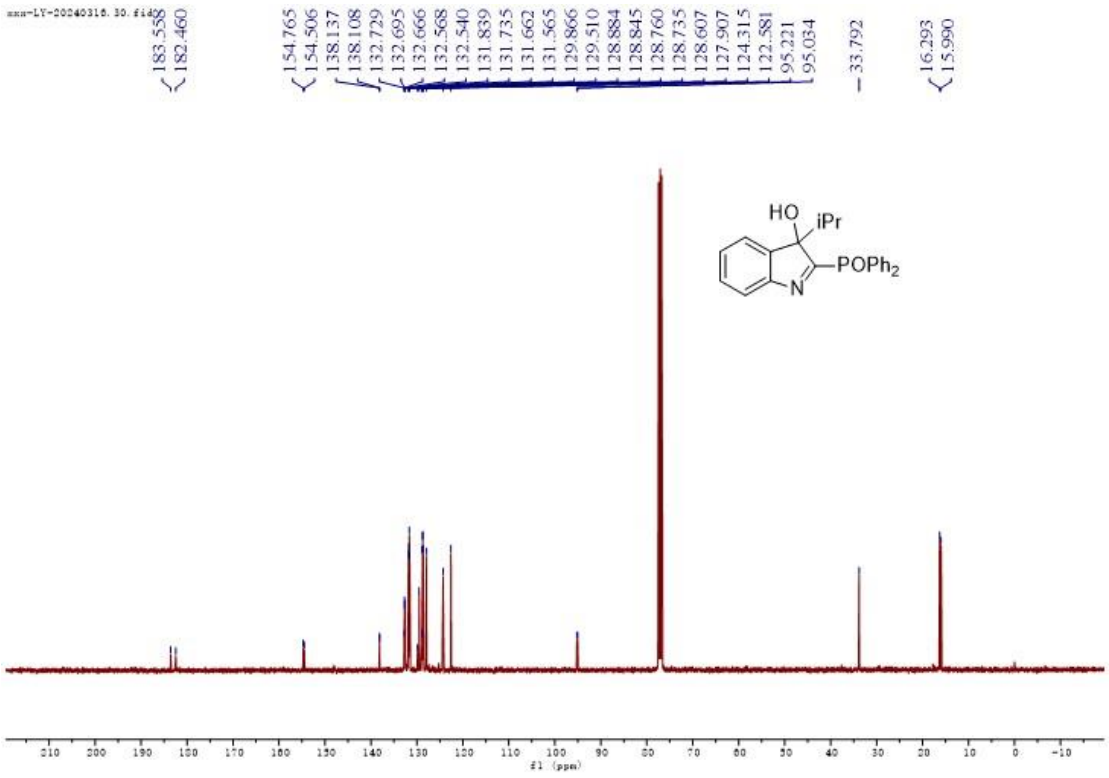
^{31}P NMR (162 MHz, $CDCl_3$) for **6n**



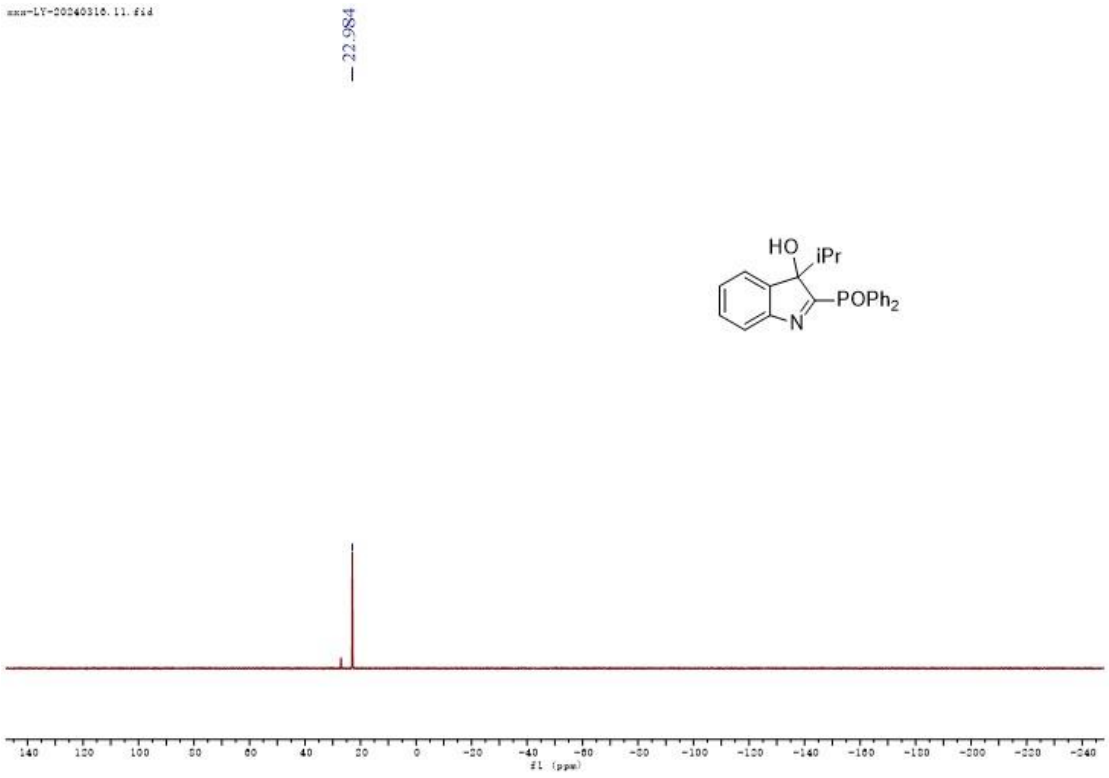
^{1}H NMR (400 MHz, $CDCl_3$) for **6o**



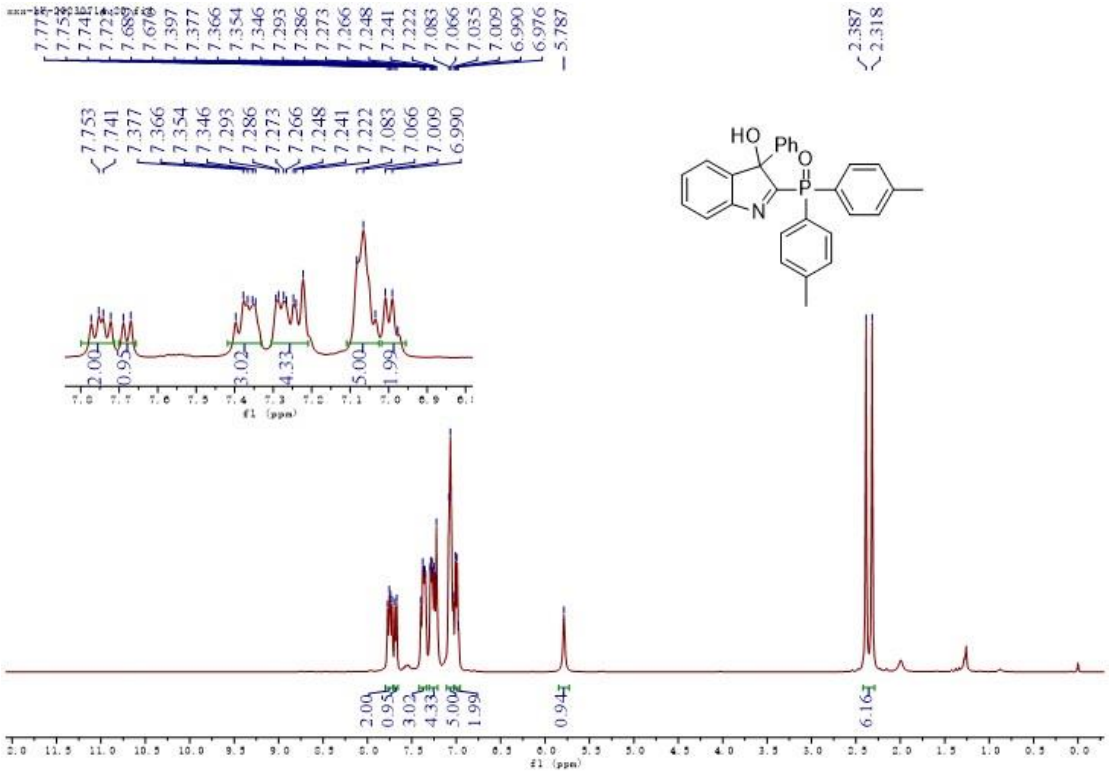
^{13}C NMR (101 MHz, $CDCl_3$) for **6o**



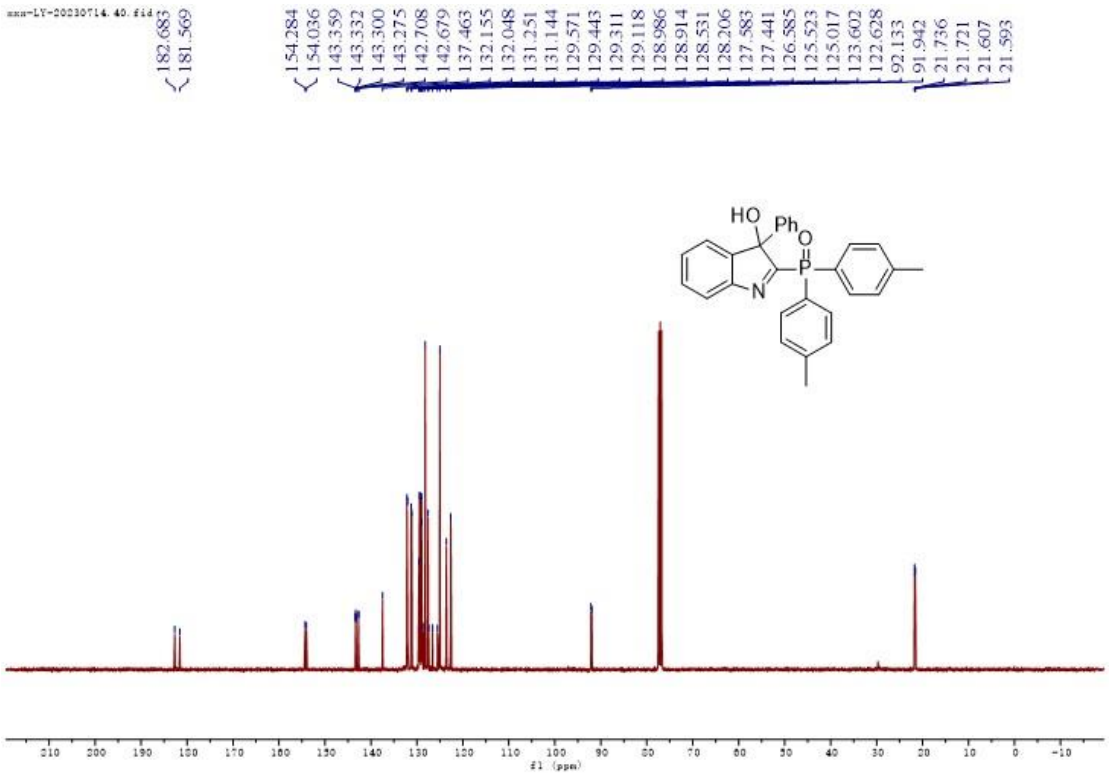
^{31}P NMR (162 MHz, $CDCl_3$) for **6o**



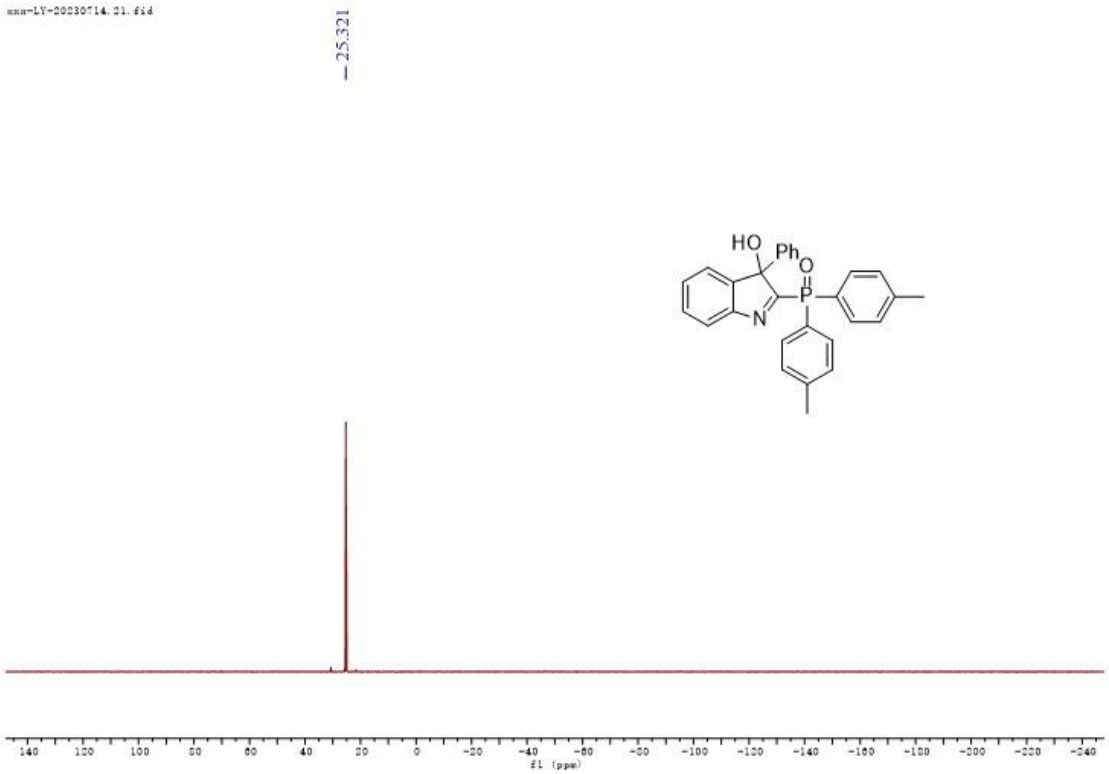
^{1}H NMR (400 MHz, $CDCl_3$) for **6p**



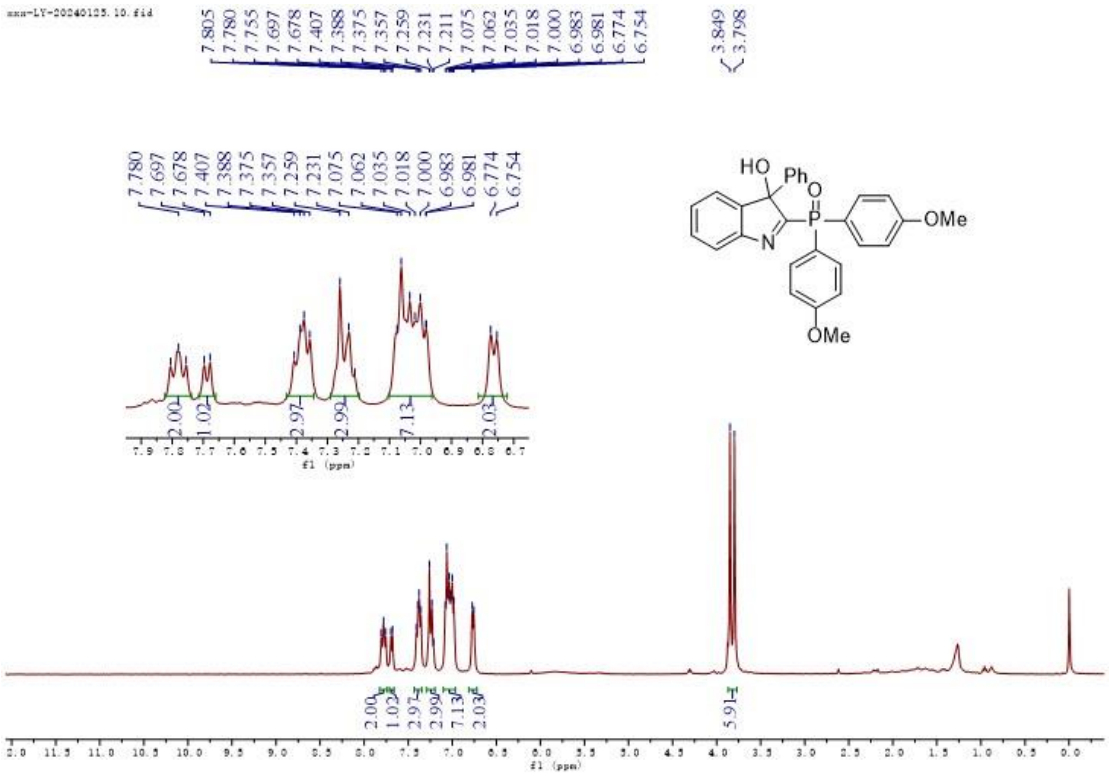
^{13}C NMR (101 MHz, $CDCl_3$) for **6p**



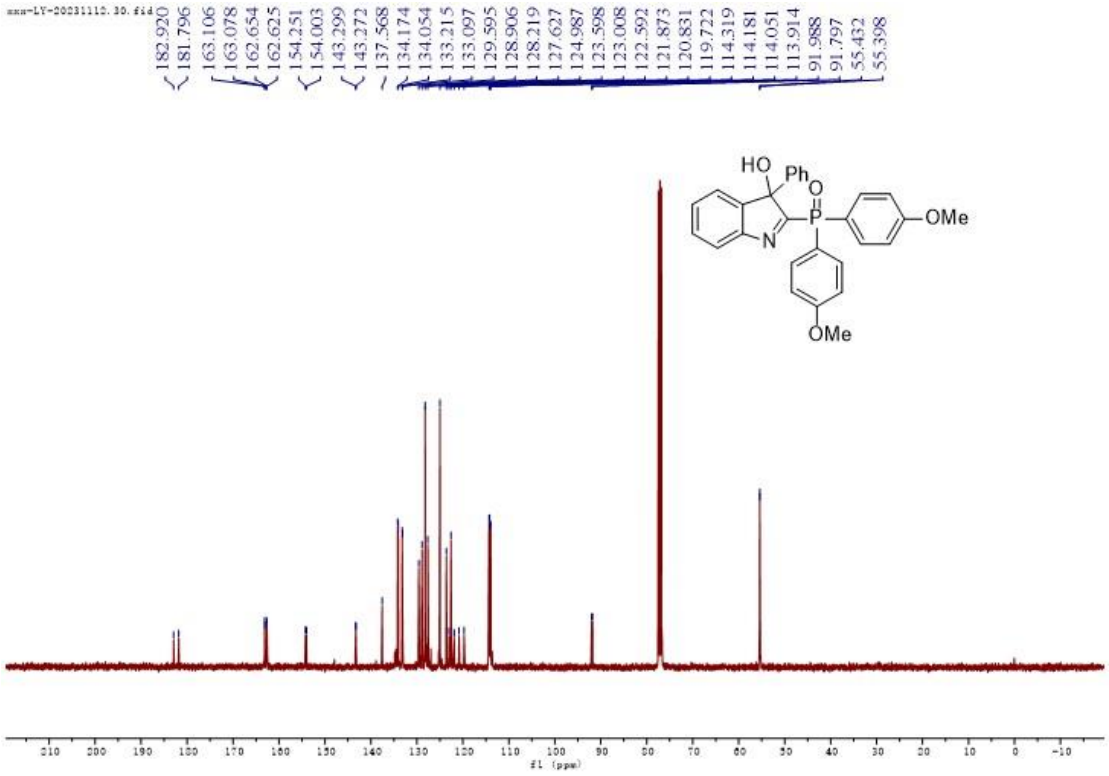
^{31}P NMR (162 MHz, $CDCl_3$) for **6p**



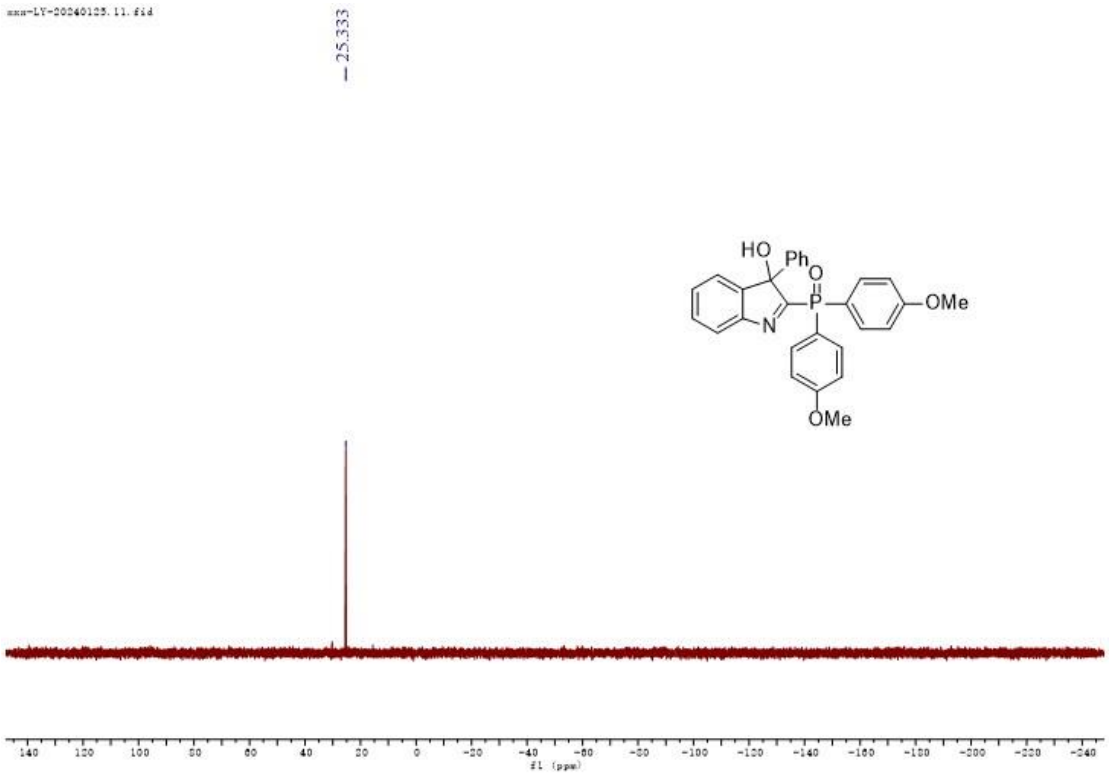
^{1}H NMR (400 MHz, $CDCl_3$) for **6q**



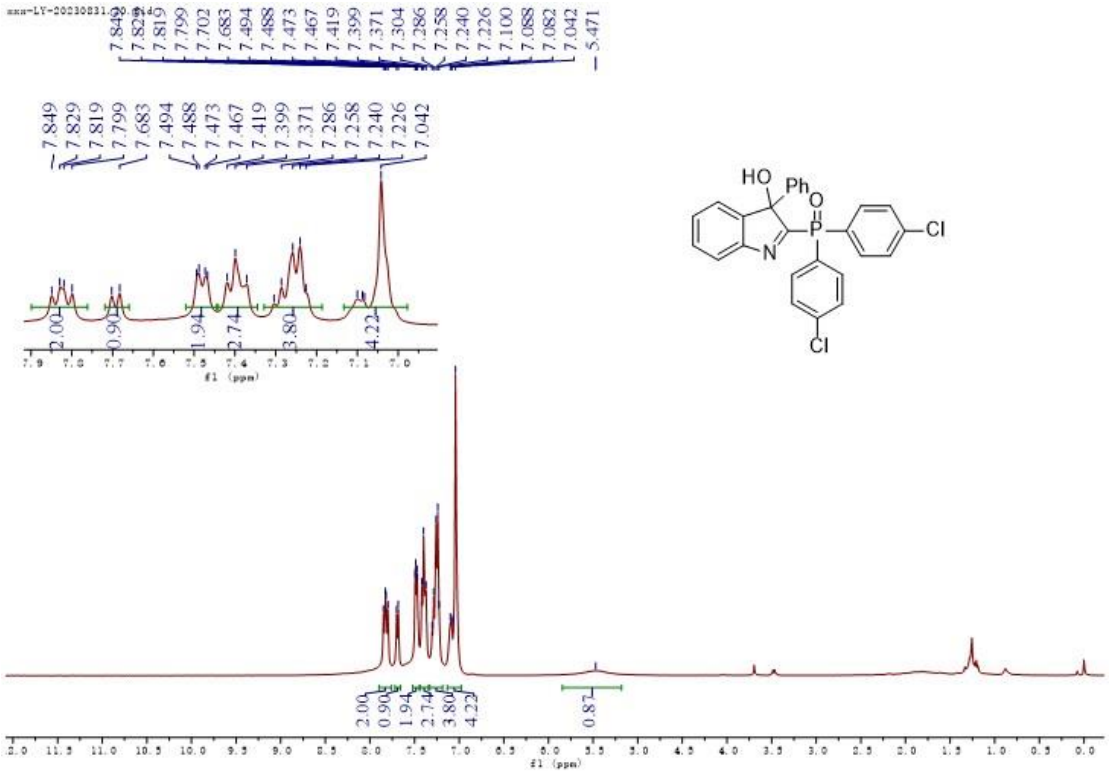
^{13}C NMR (101 MHz, $CDCl_3$) for **6q**



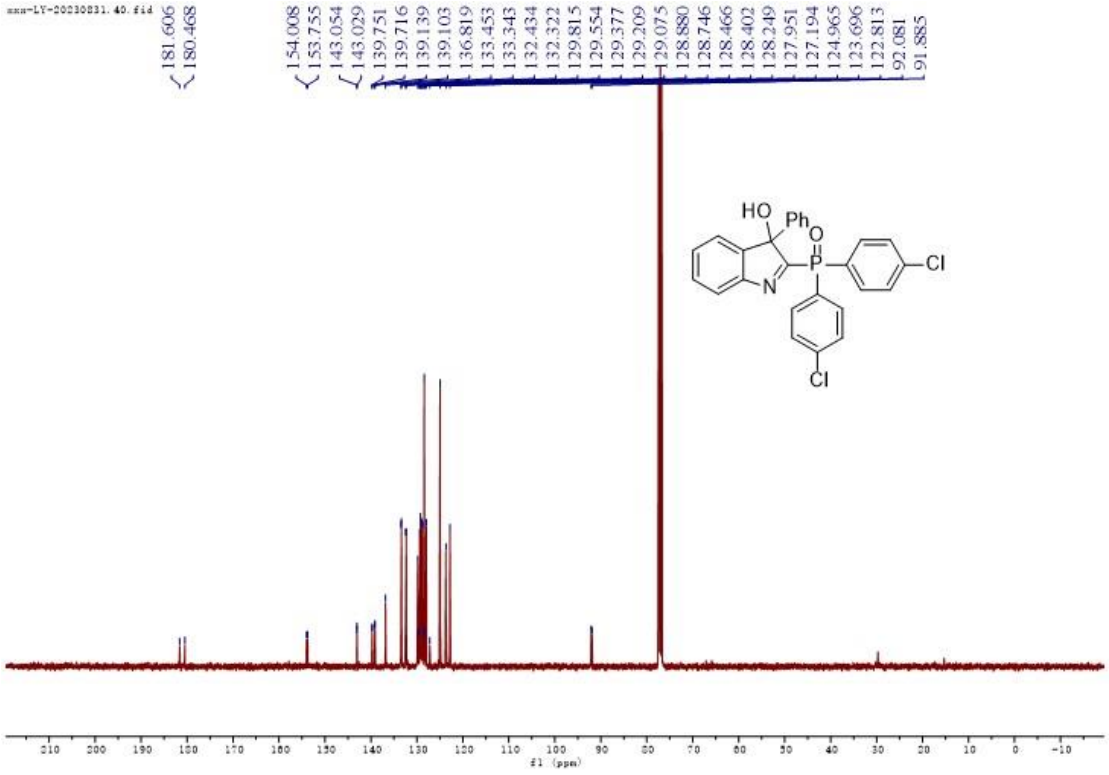
^{31}P NMR (162 MHz, $CDCl_3$) for **6q**



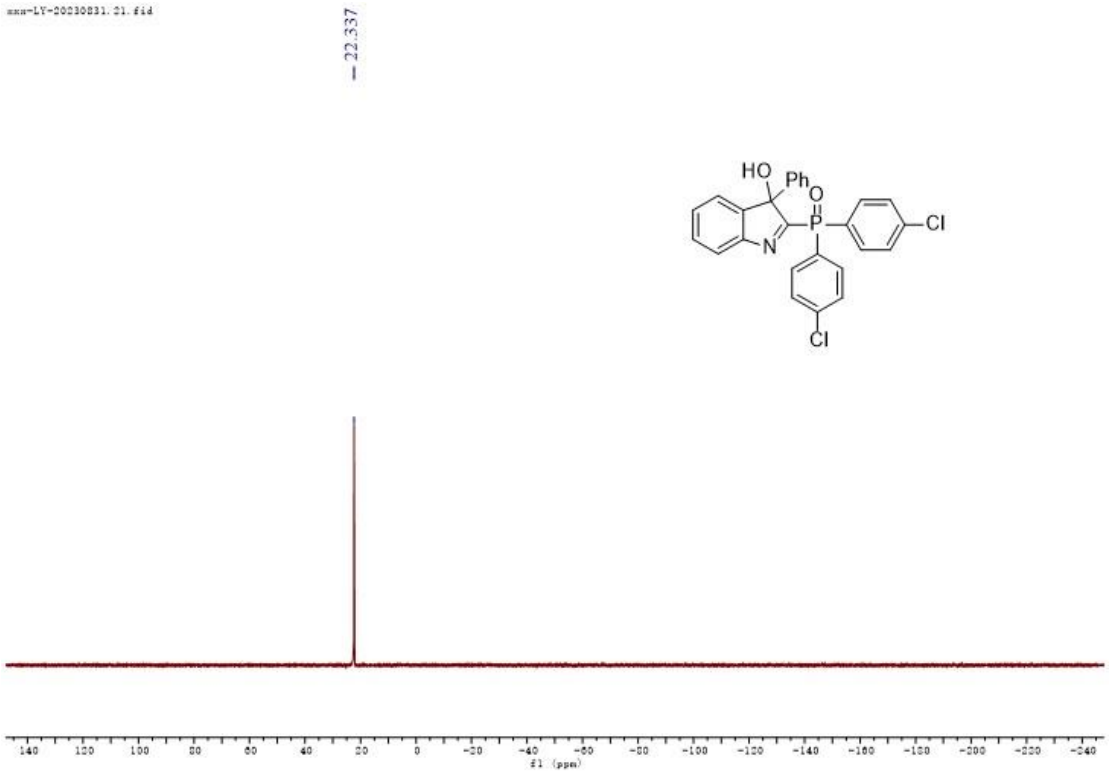
^{1}H NMR (400 MHz, $CDCl_3$) for **6q**



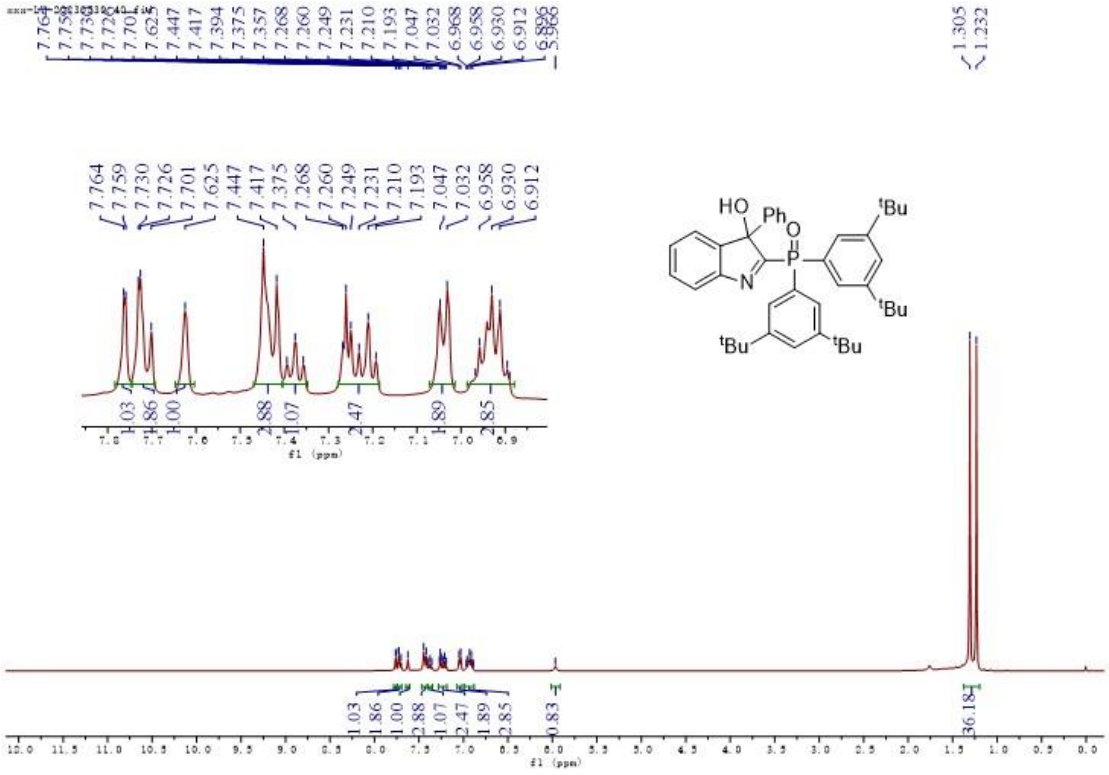
^{13}C NMR (101 MHz, $CDCl_3$) for **6r**



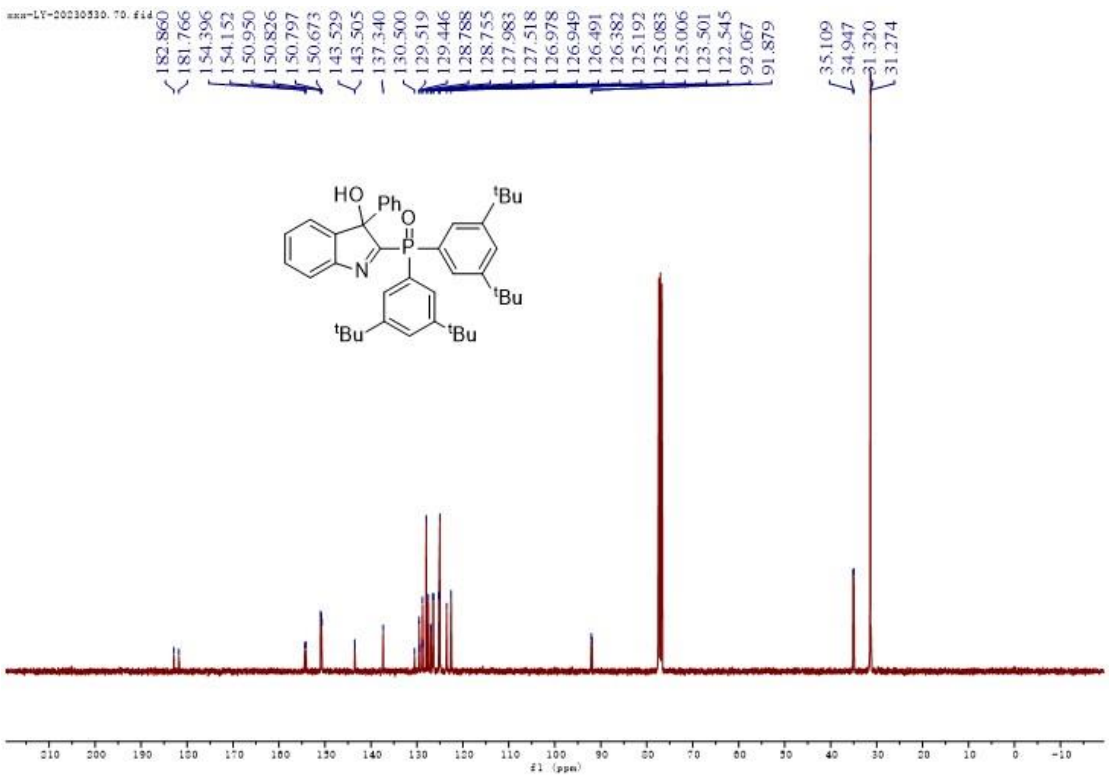
^{31}P NMR (162 MHz, $CDCl_3$) for **6r**



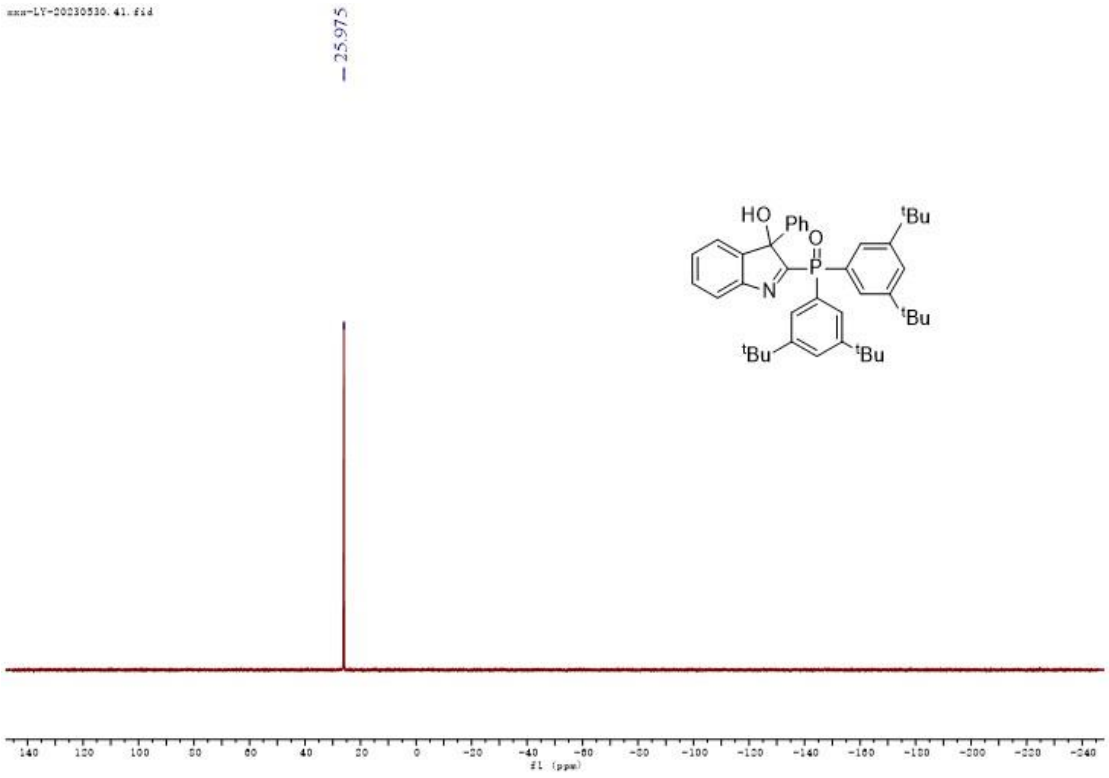
^{1}H NMR (400 MHz, $CDCl_3$) for **6s**



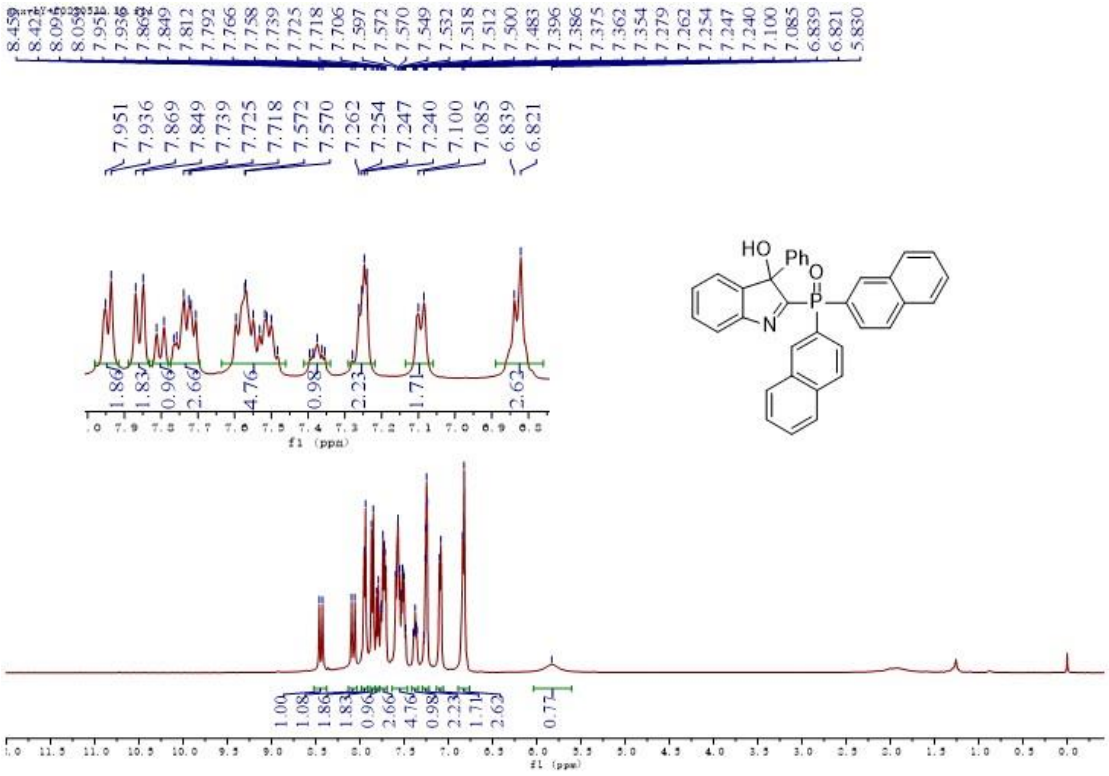
^{13}C NMR (101 MHz, $CDCl_3$) for **6s**



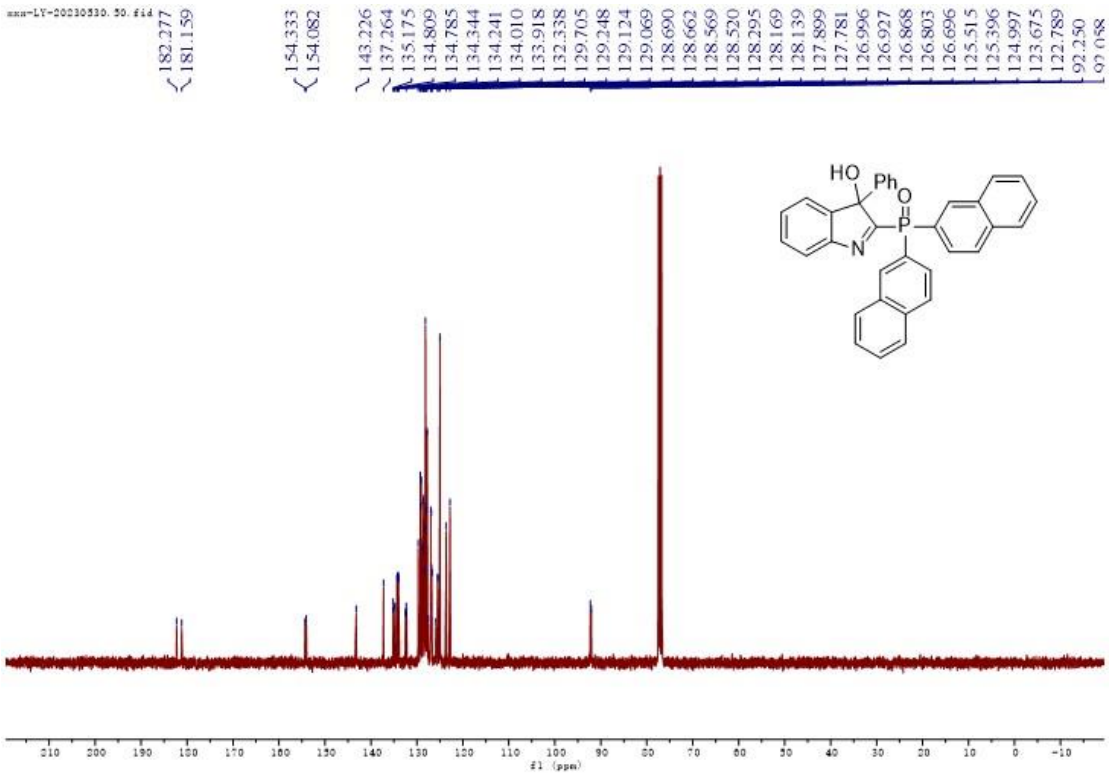
^{31}P NMR (162 MHz, $CDCl_3$) for **6s**



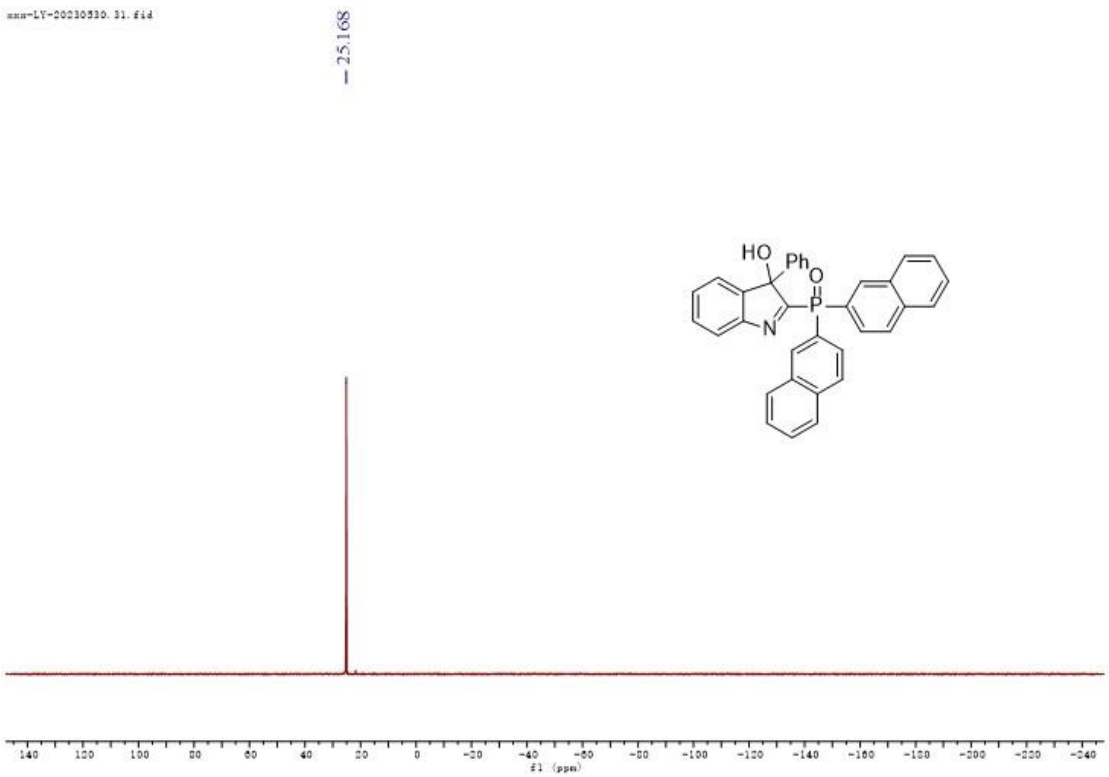
^{1}H NMR (400 MHz, $CDCl_3$) for **6t**



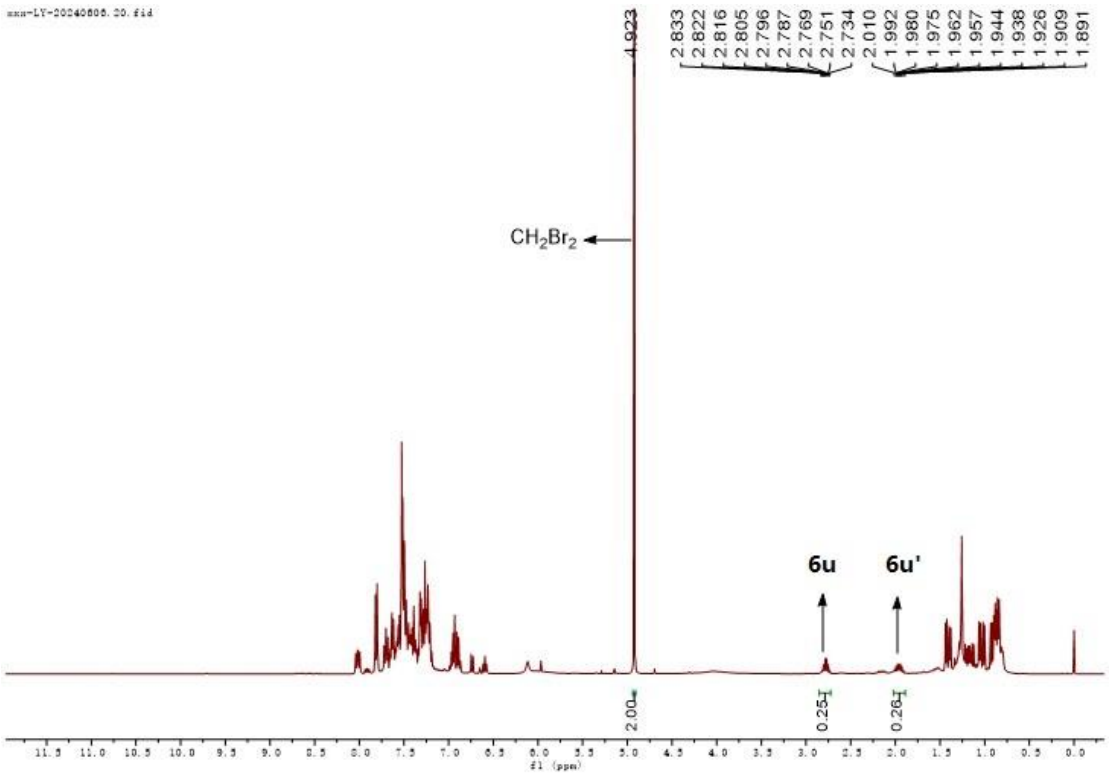
^{13}C NMR (101 MHz, $CDCl_3$) for **6t**



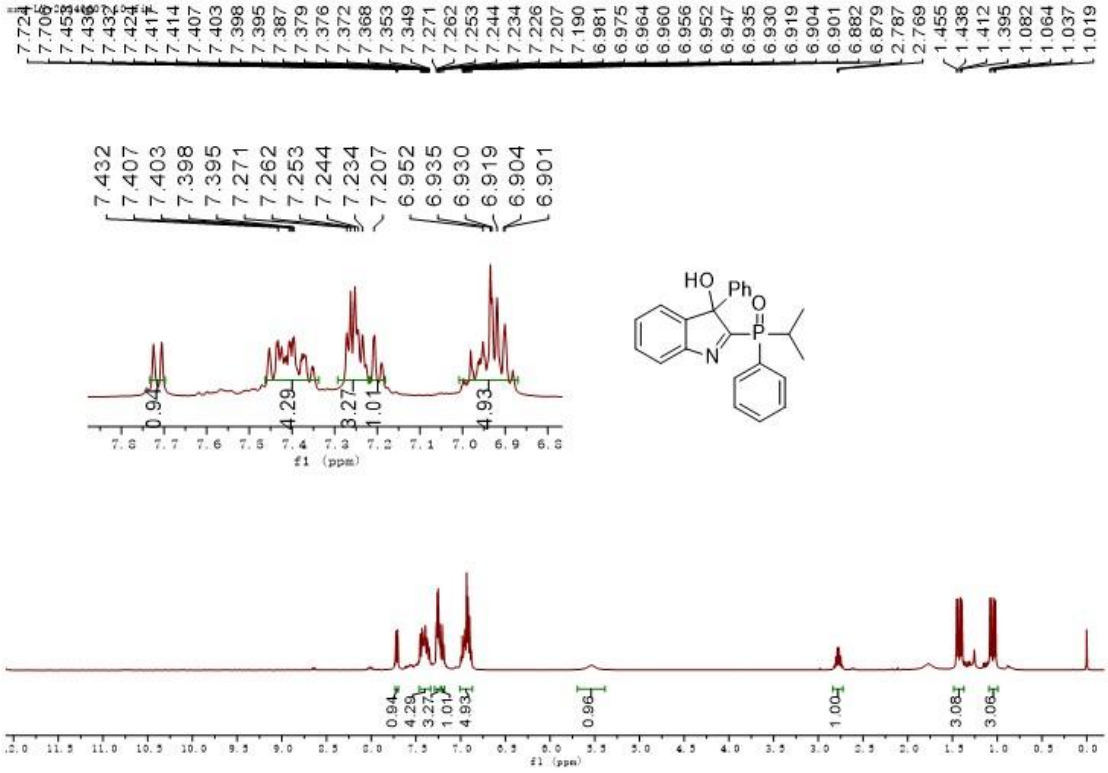
^{31}P NMR (162 MHz, $CDCl_3$) for **6t**



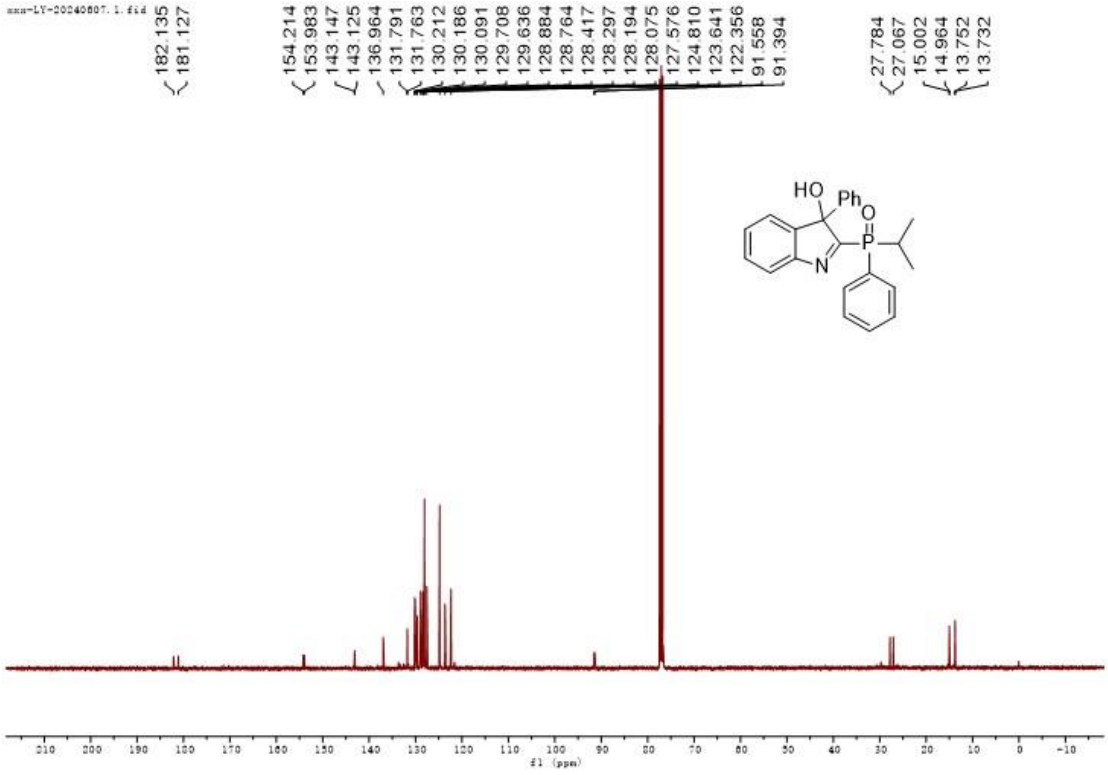
^{1}H NMR (400 MHz, $CDCl_3$) for the crude products of **6u** and **6u'**



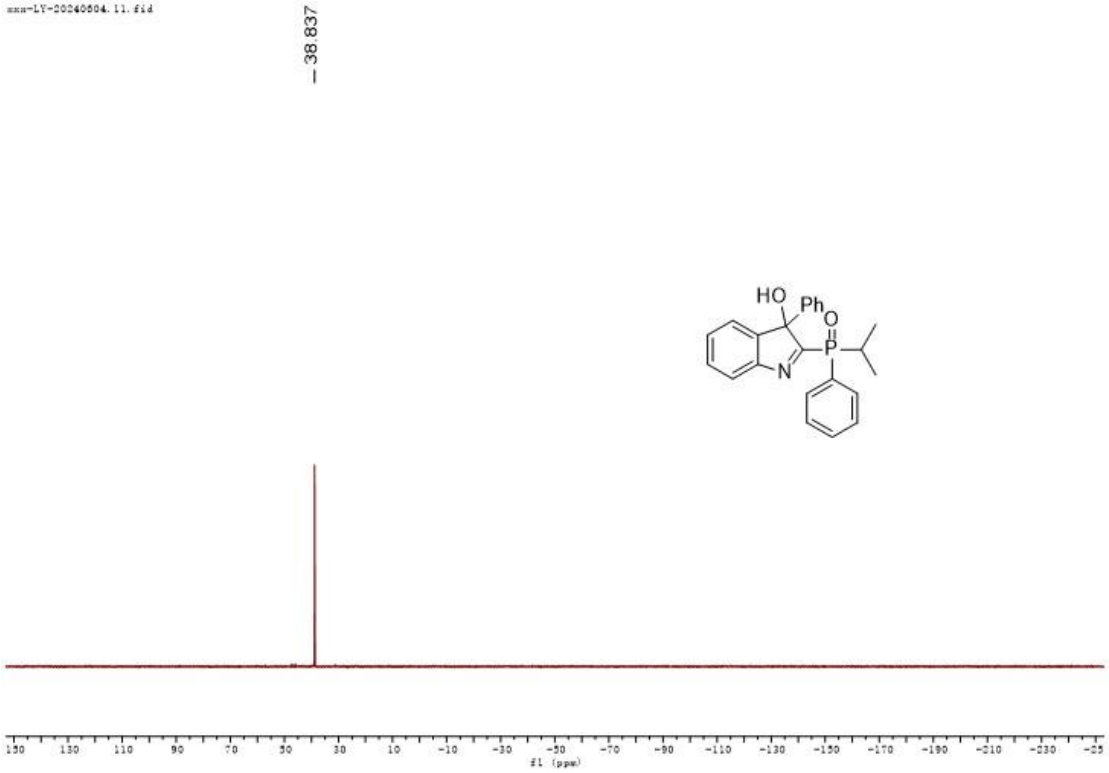
^{1}H NMR (400 MHz, $CDCl_3$) for **6u**



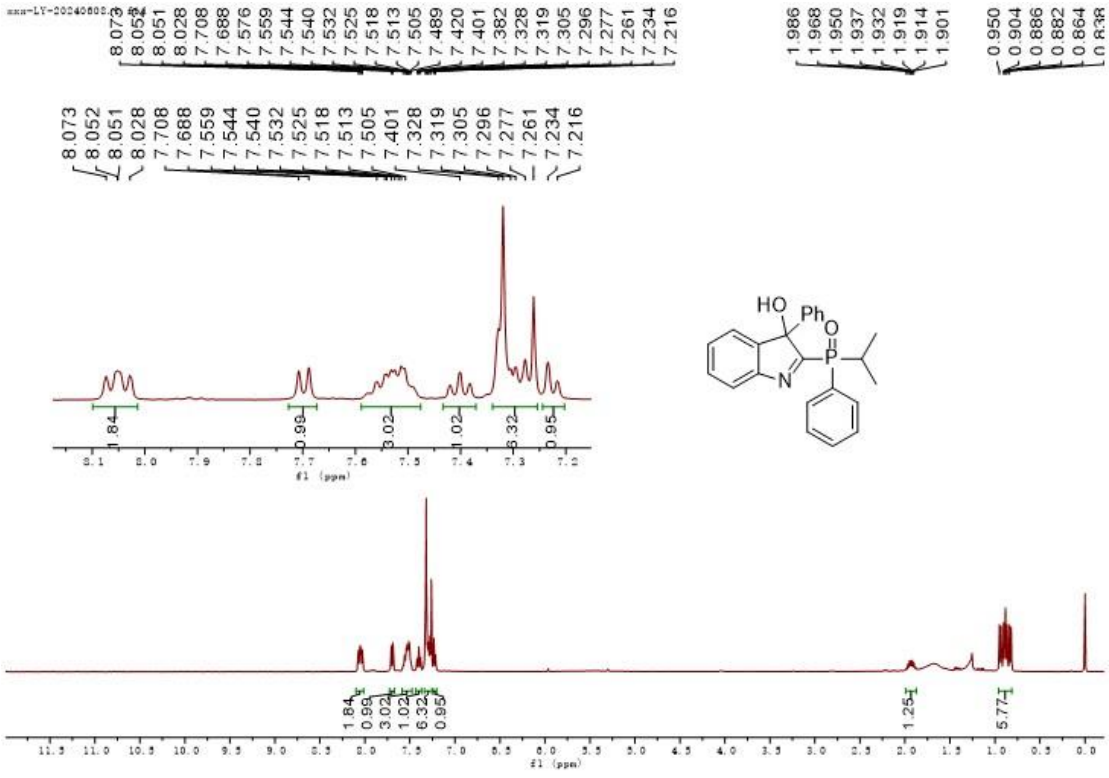
^{13}C NMR (101 MHz, $CDCl_3$) for **6t**



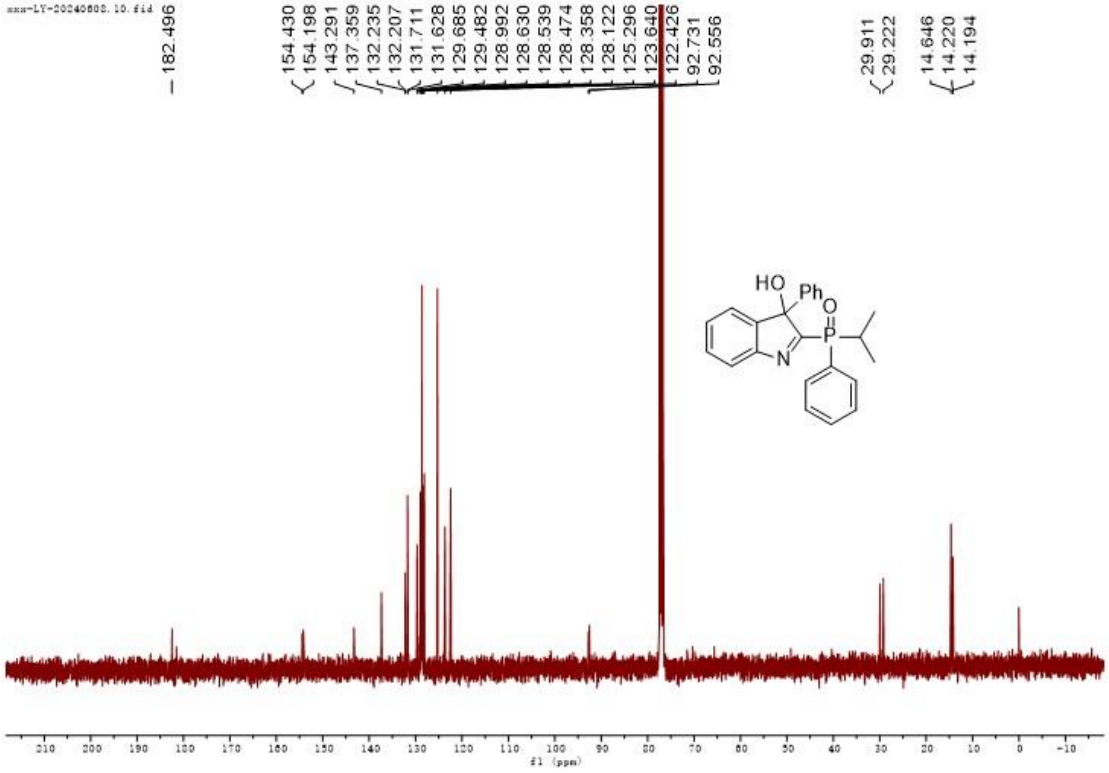
^{31}P NMR (162 MHz, $CDCl_3$) for **6u**



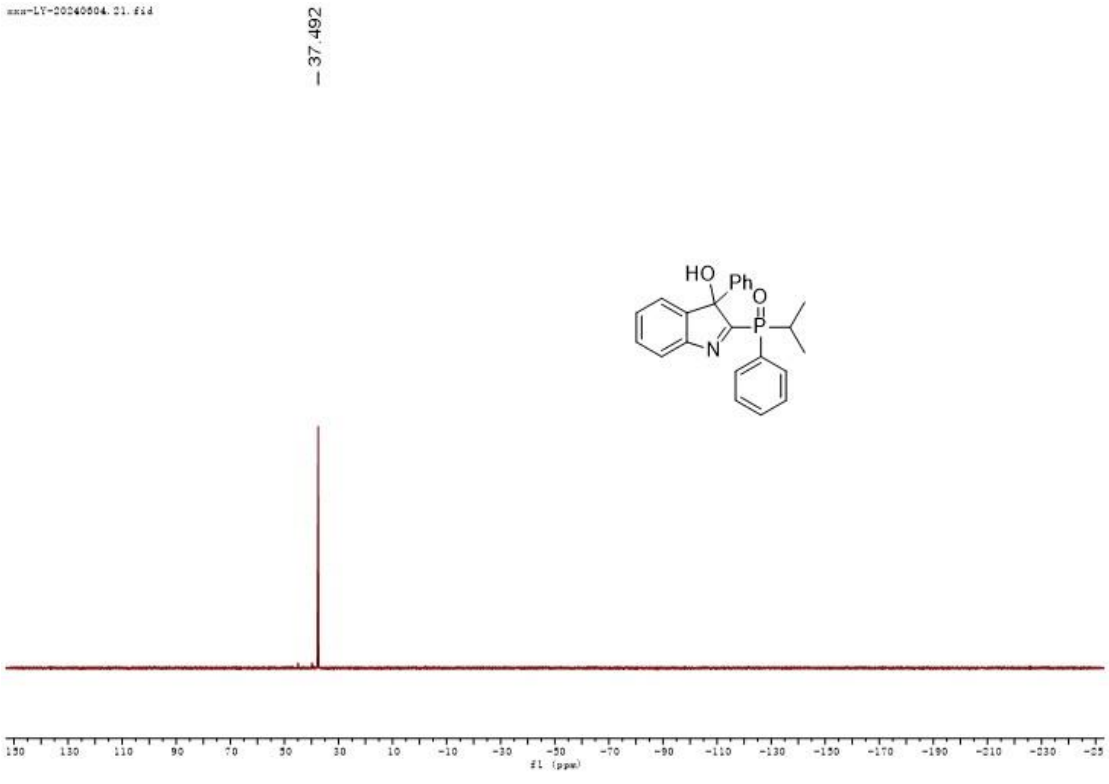
^{1}H NMR (400 MHz, $CDCl_3$) for **6u'**



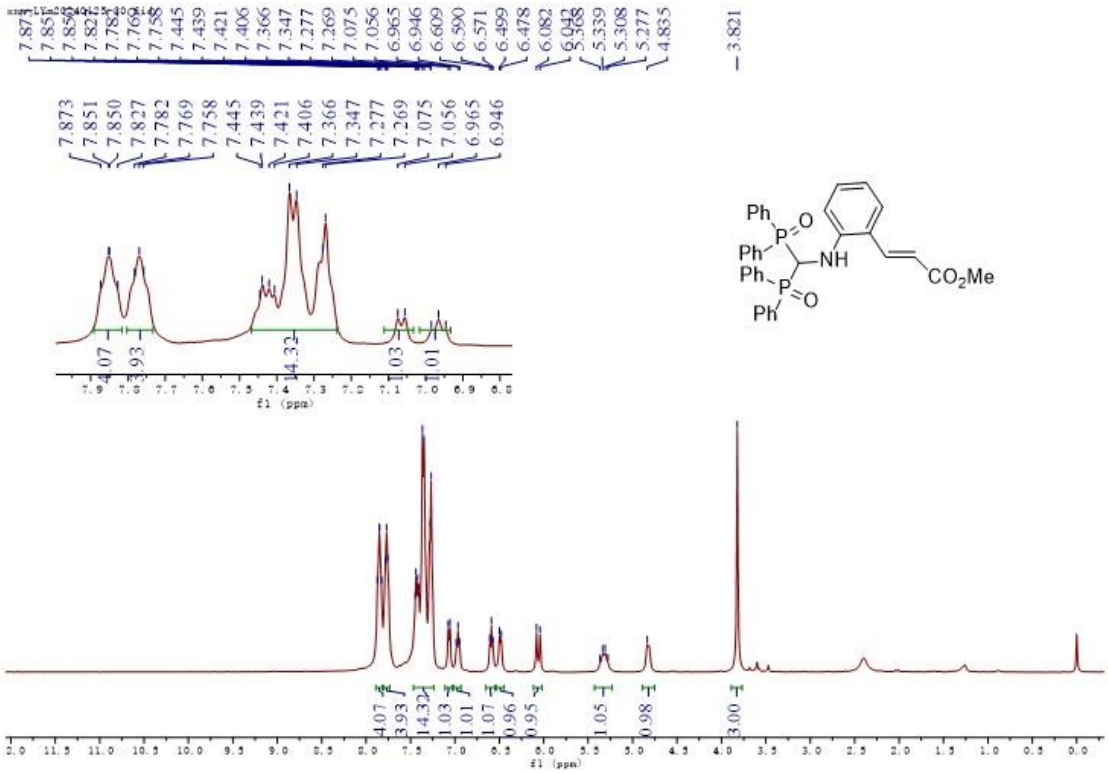
^{13}C NMR (101 MHz, $CDCl_3$) for **6t**



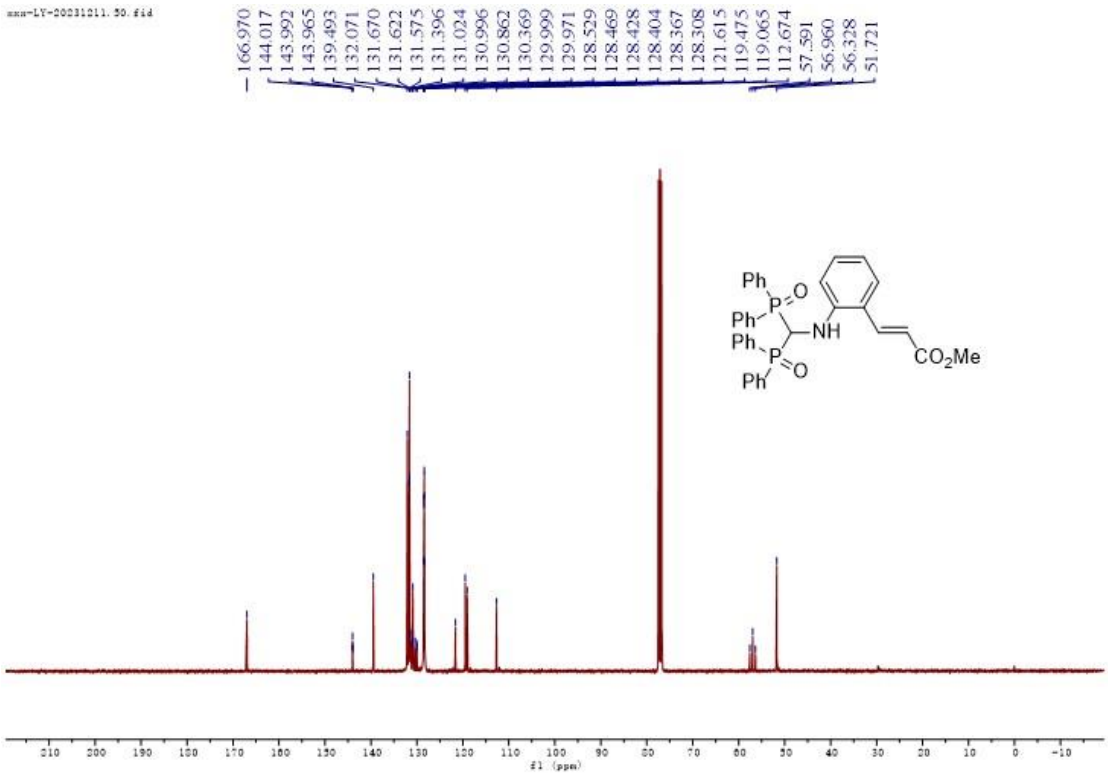
^{31}P NMR (162 MHz, $CDCl_3$) for **6u'**



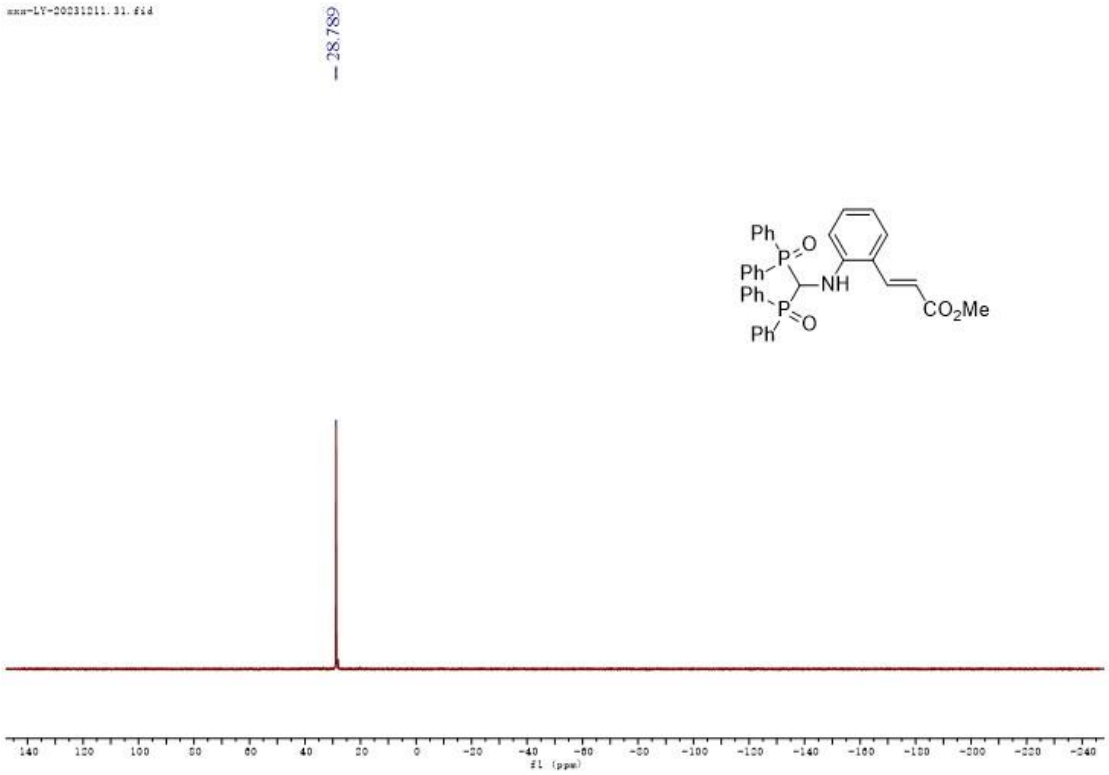
^{1}H NMR (400 MHz, $CDCl_3$) for **7a**



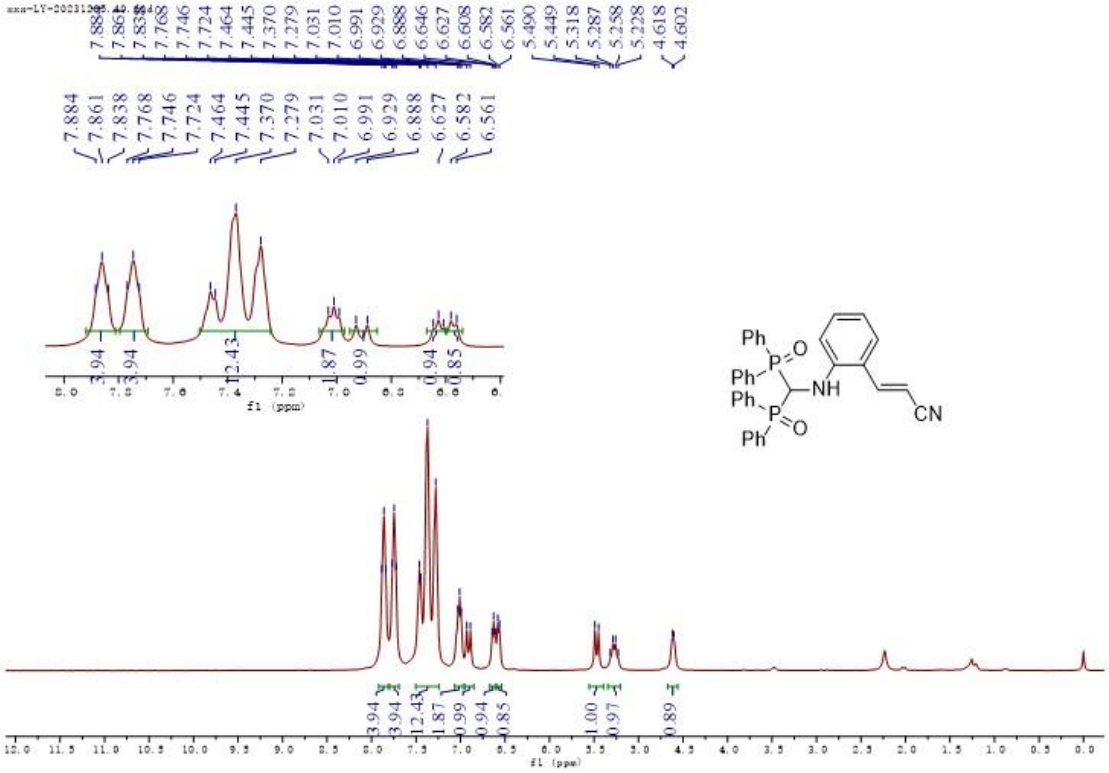
^{13}C NMR (101 MHz, $CDCl_3$) for **7a**



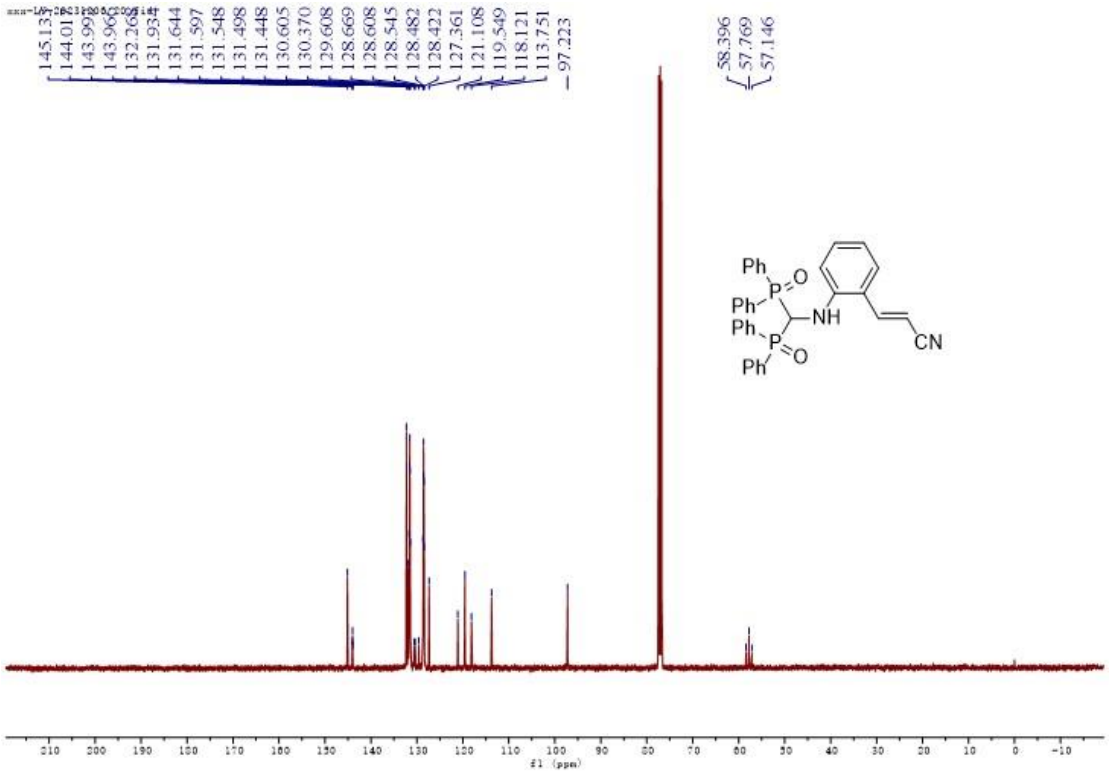
^{31}P NMR (162 MHz, $CDCl_3$) for **7a**



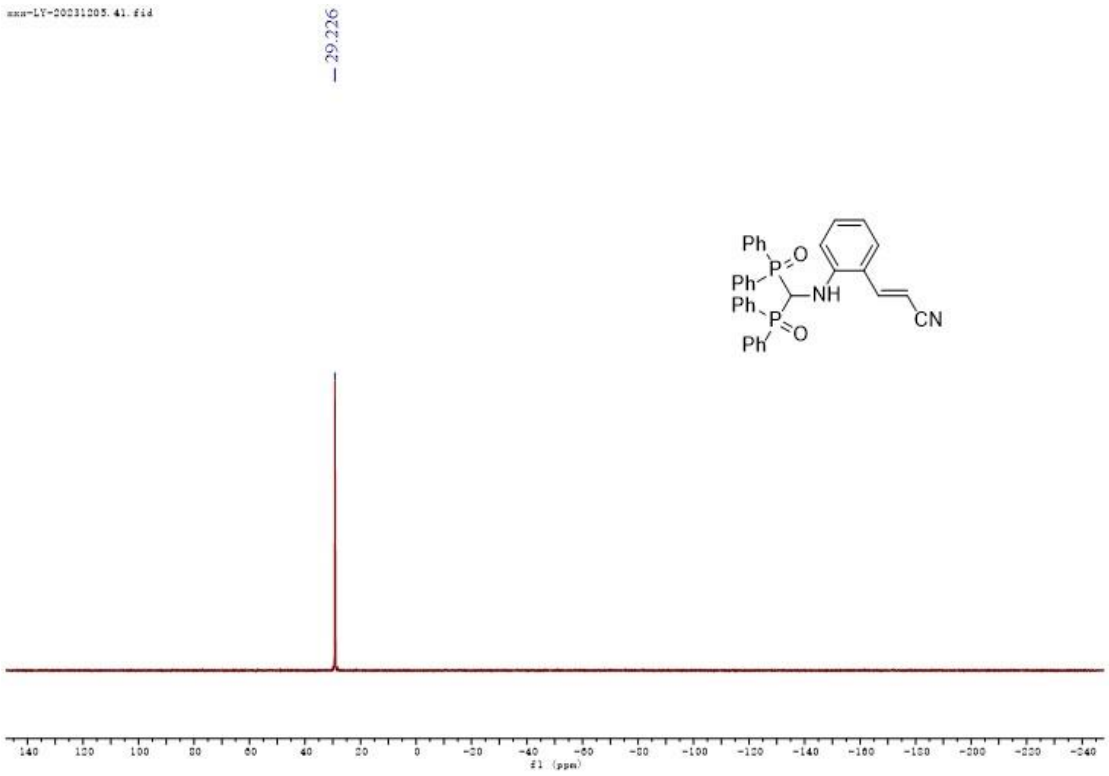
^{1}H NMR (400 MHz, $CDCl_3$) for **7b**



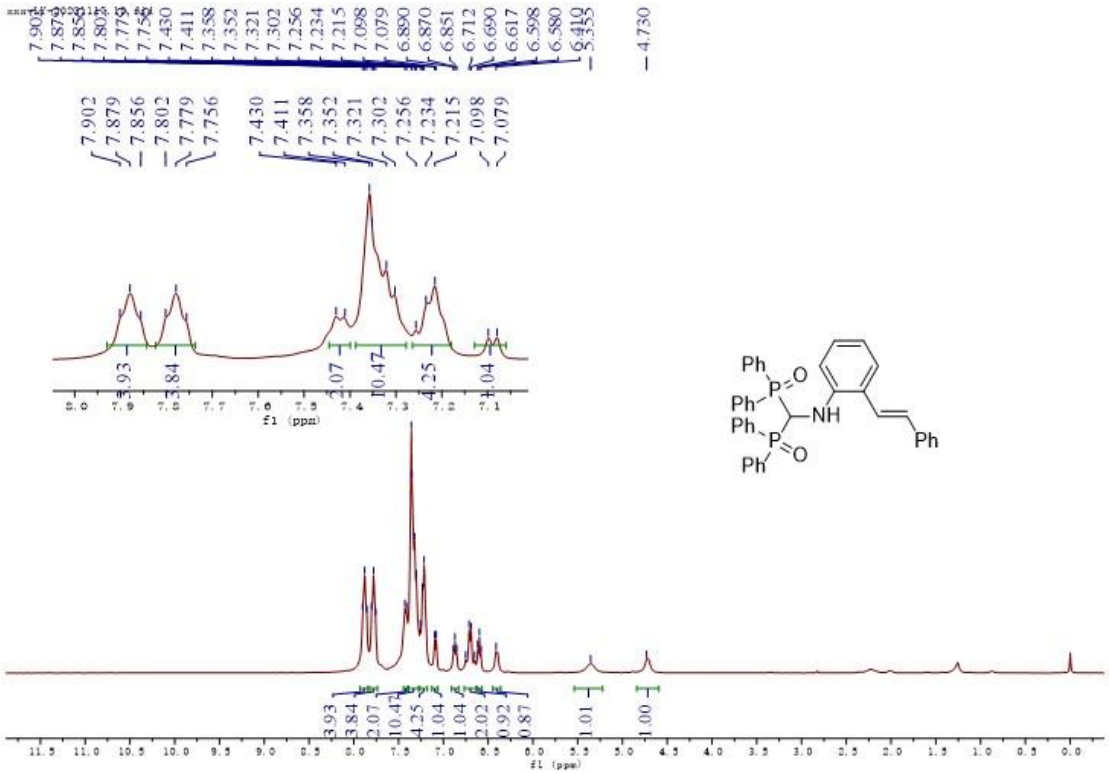
^{13}C NMR (101 MHz, $CDCl_3$) for **7b**



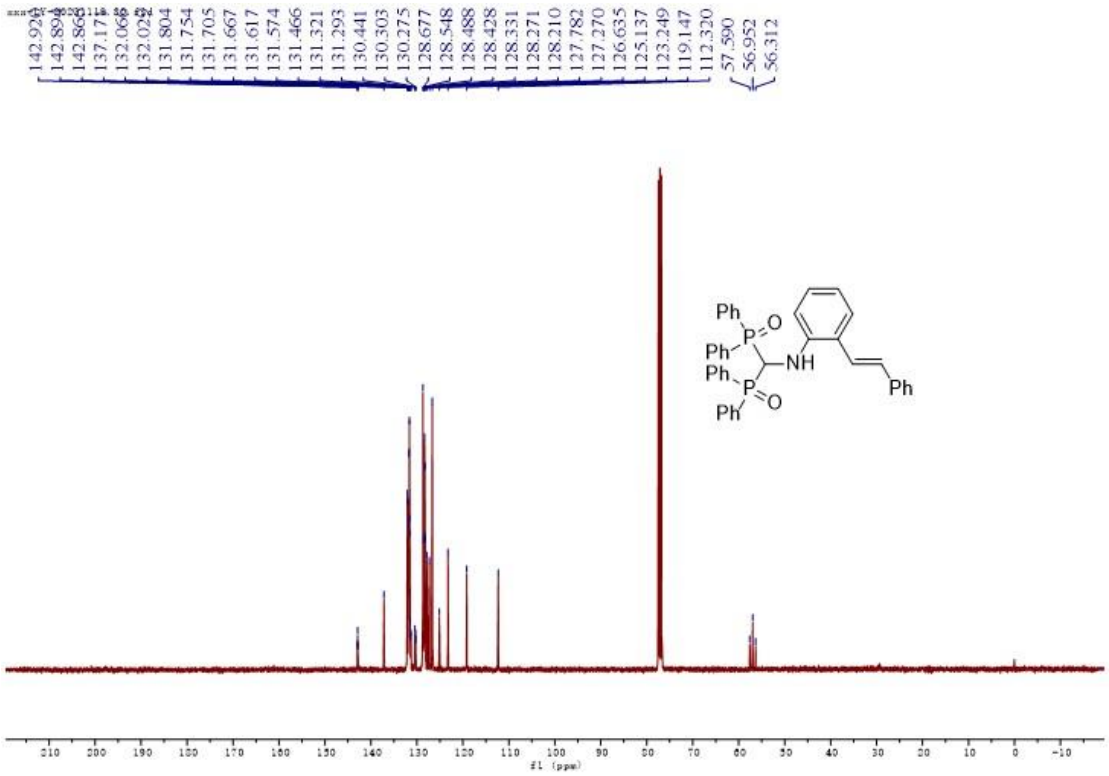
^{31}P NMR (162 MHz, $CDCl_3$) for **7b**



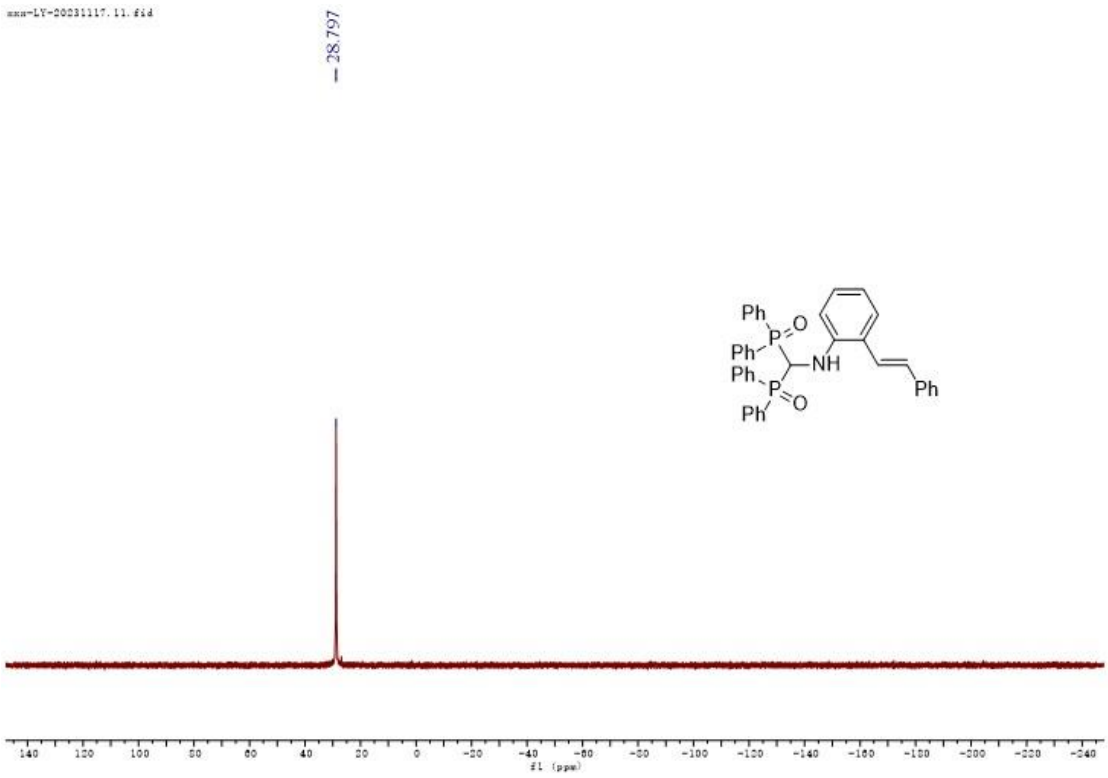
^{1}H NMR (400 MHz, $CDCl_3$) for **7c**



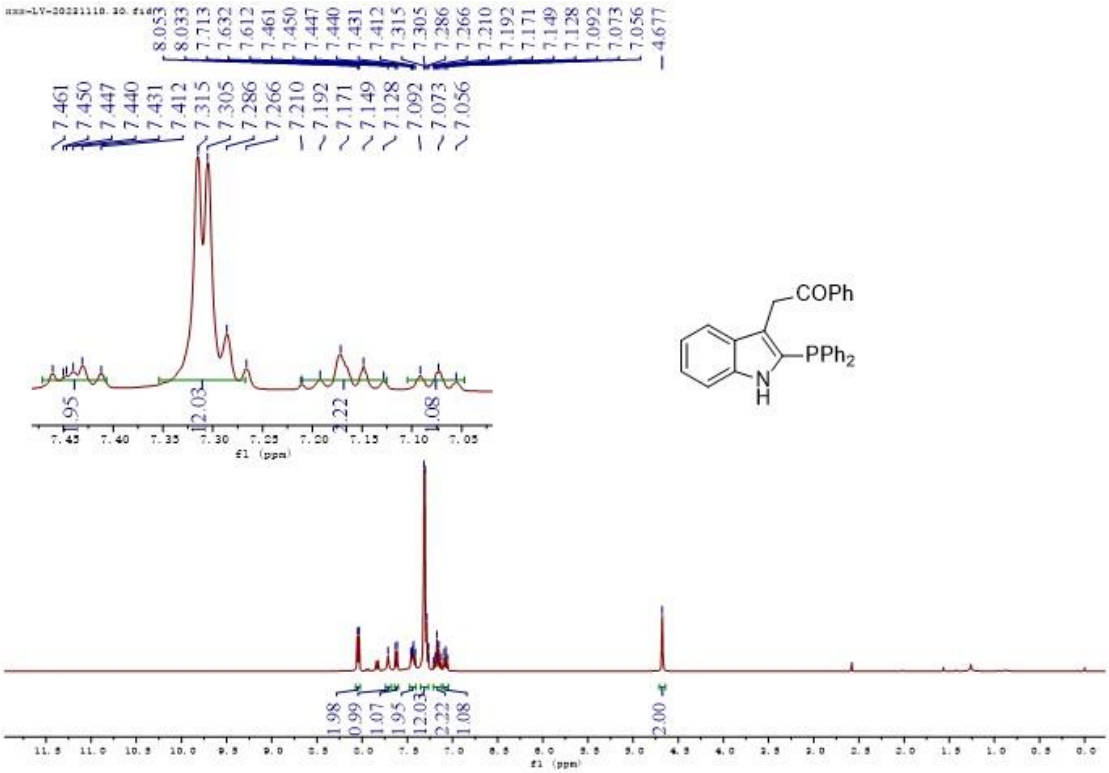
^{13}C NMR (101 MHz, $CDCl_3$) for **7c**



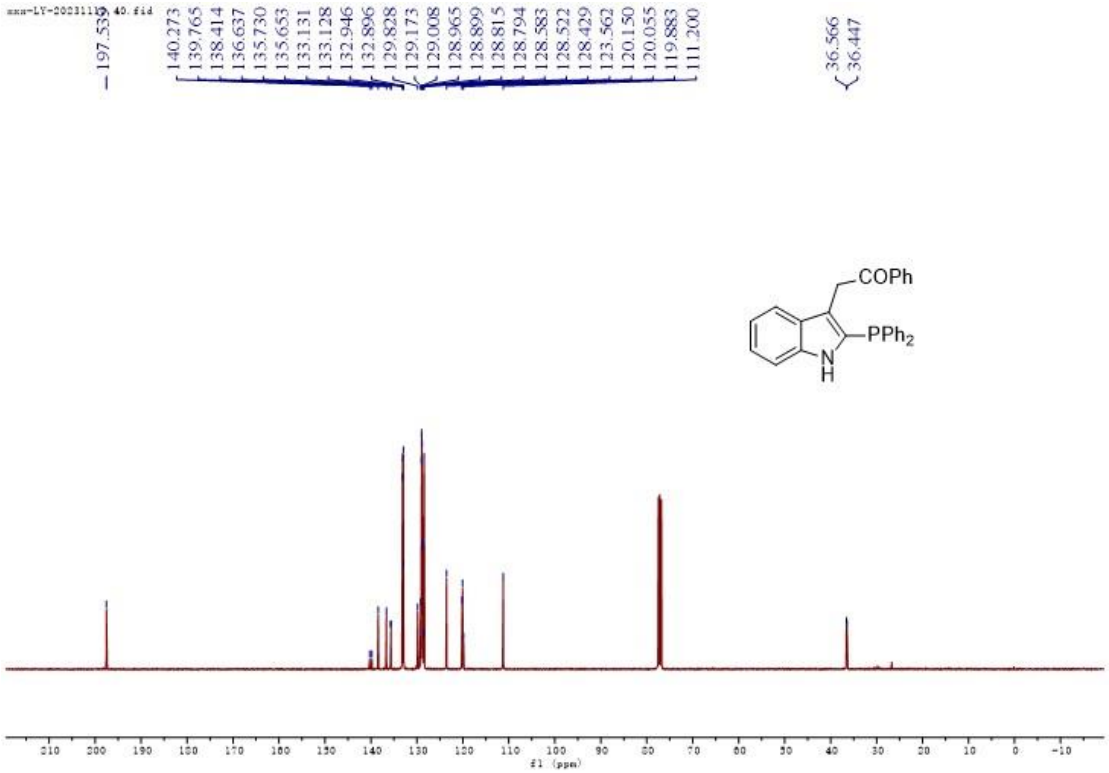
^{31}P NMR (162MHz, $CDCl_3$) for **7c**



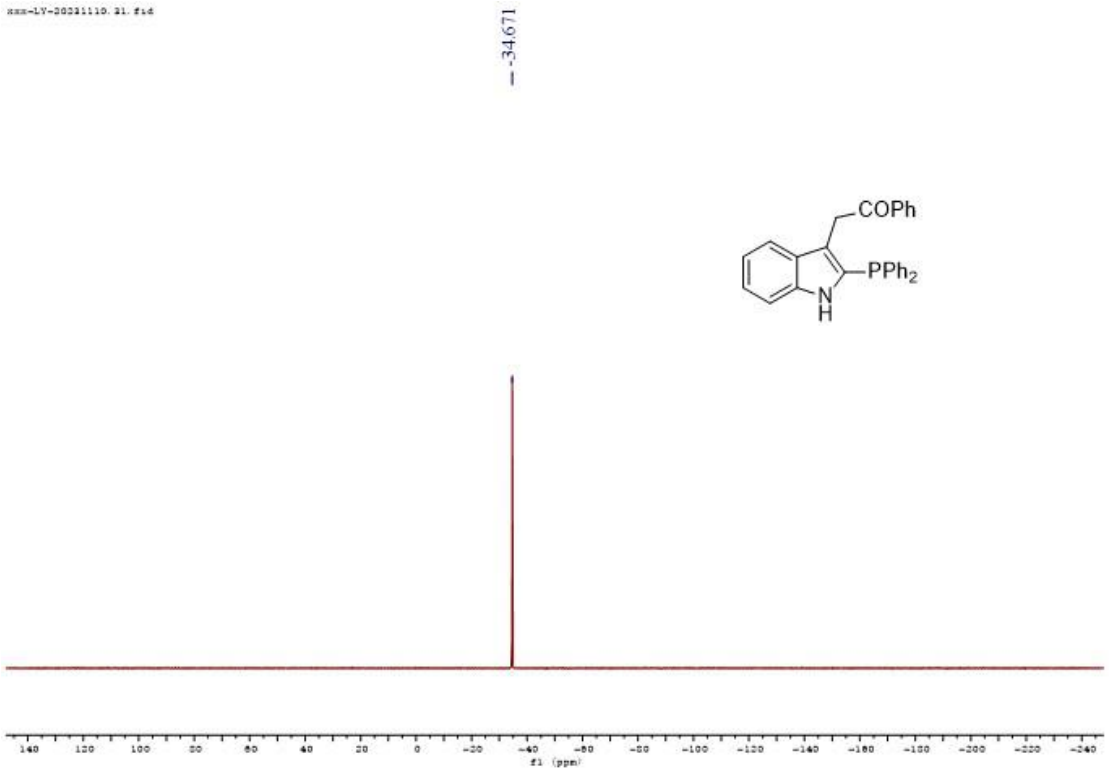
^{1}H NMR (400 MHz, $CDCl_3$) for **8**



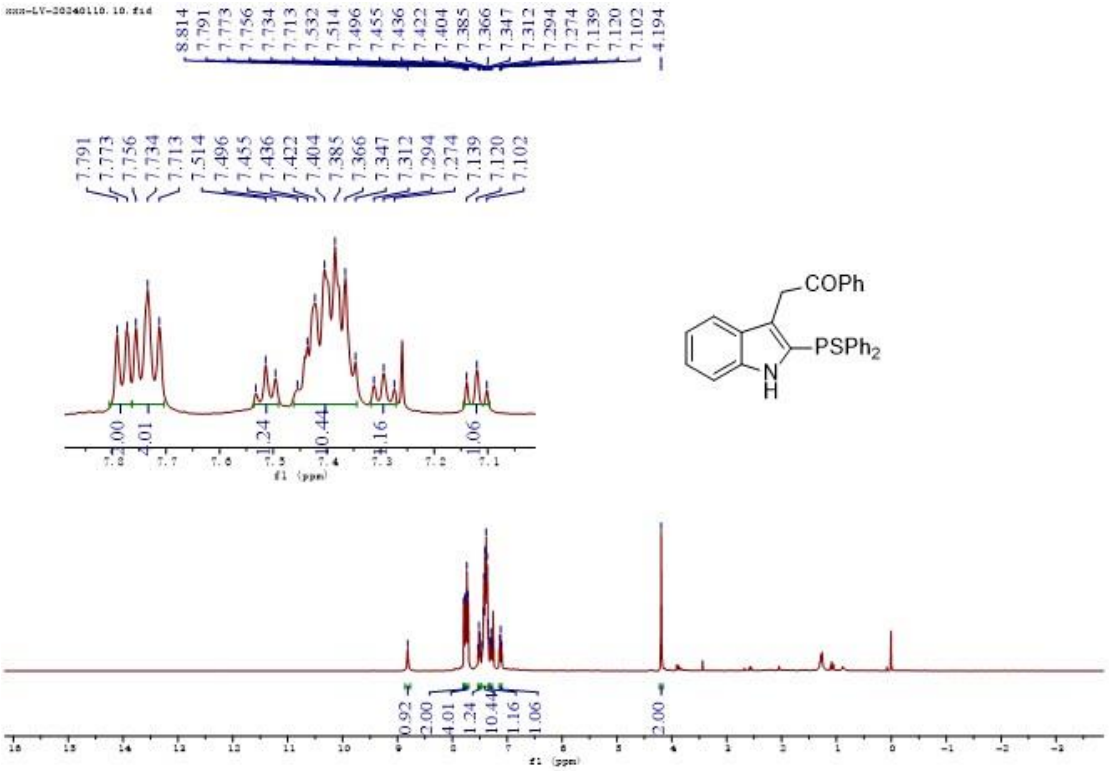
^{13}C NMR (101 MHz, $CDCl_3$) for **8**



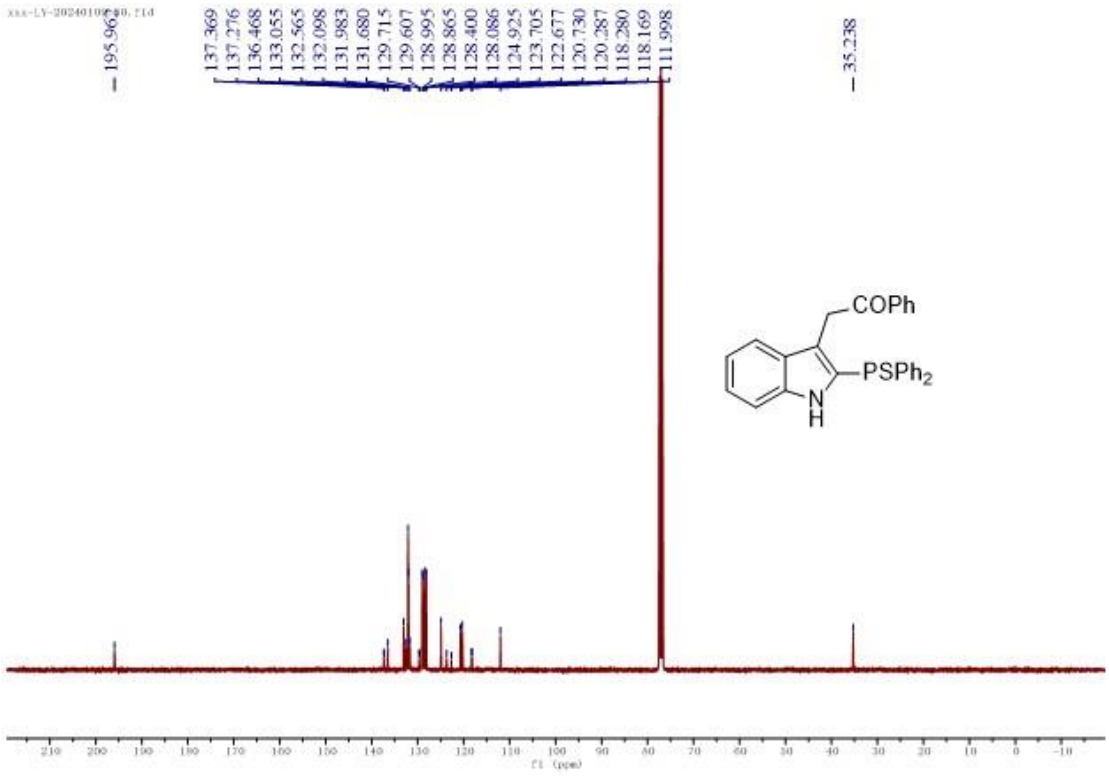
^{31}P NMR (162 MHz, $CDCl_3$) for **8**



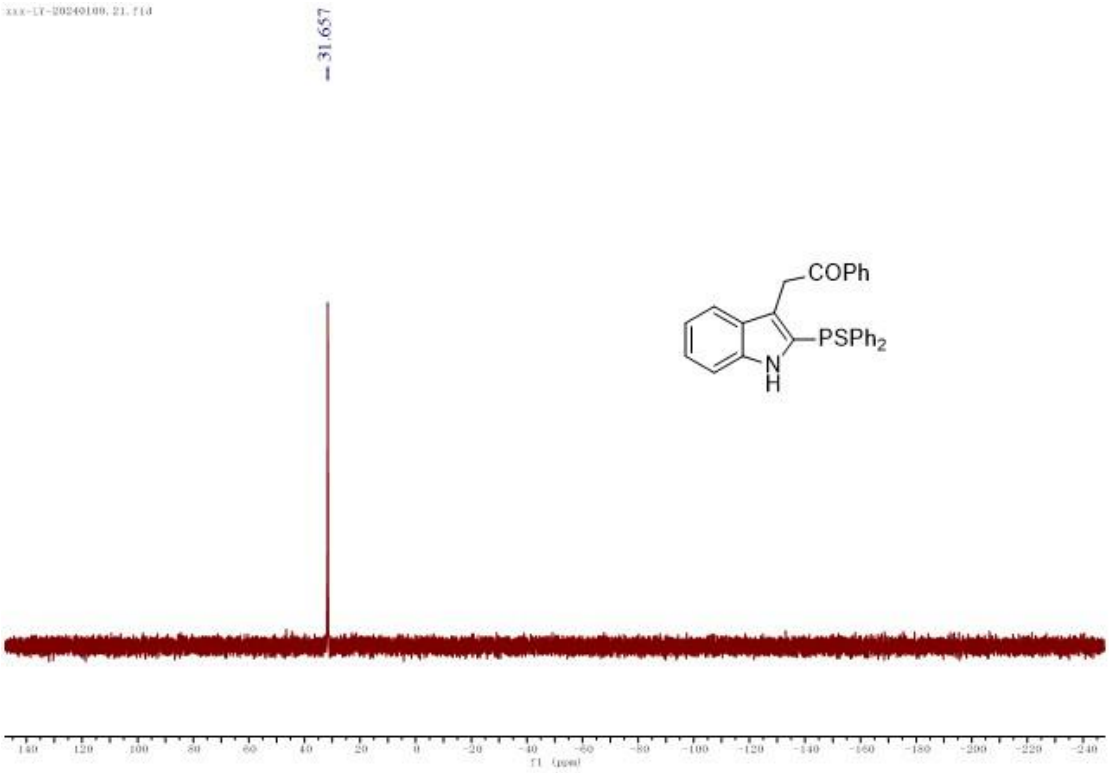
^{1}H NMR (400 MHz, $CDCl_3$) for **9**



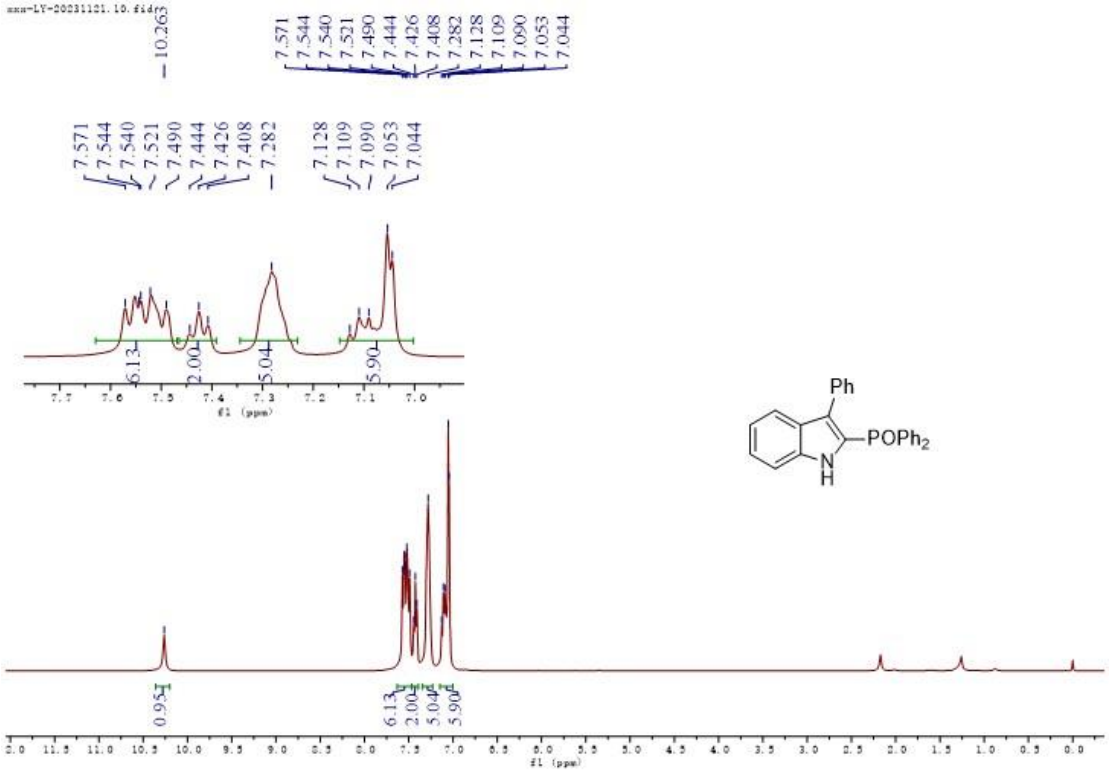
^{13}C NMR (101 MHz, $CDCl_3$) for **9**



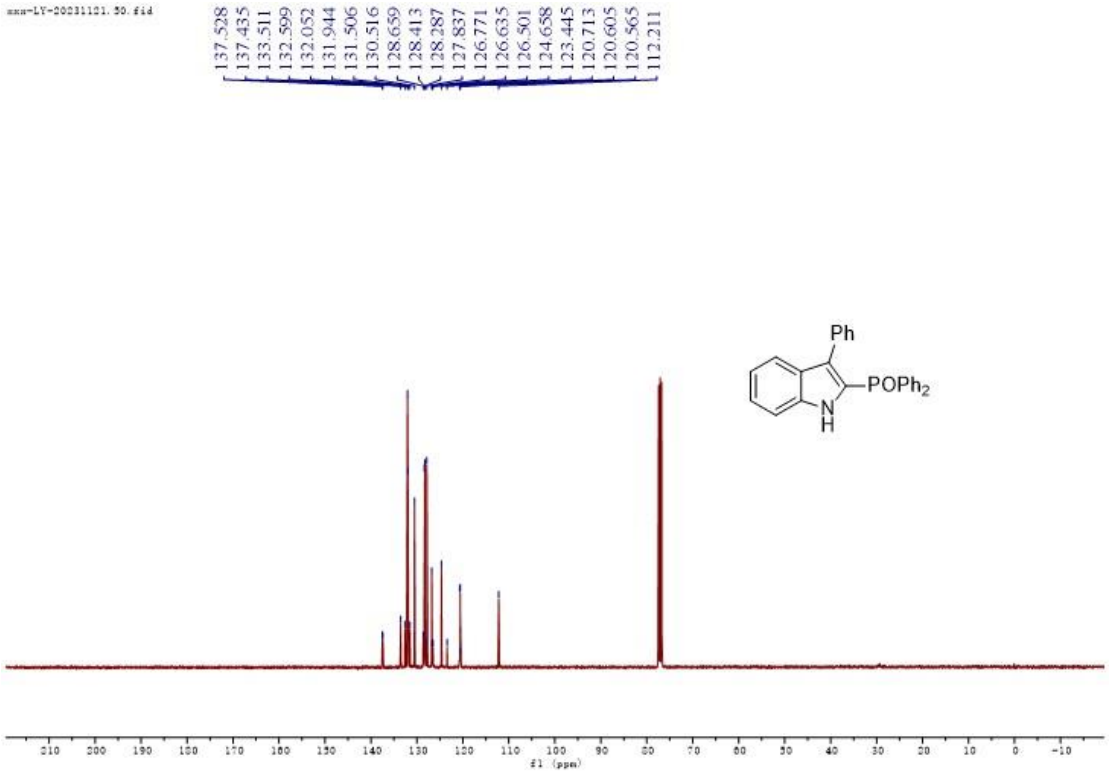
^{31}P NMR (162 MHz, $CDCl_3$) for **9**



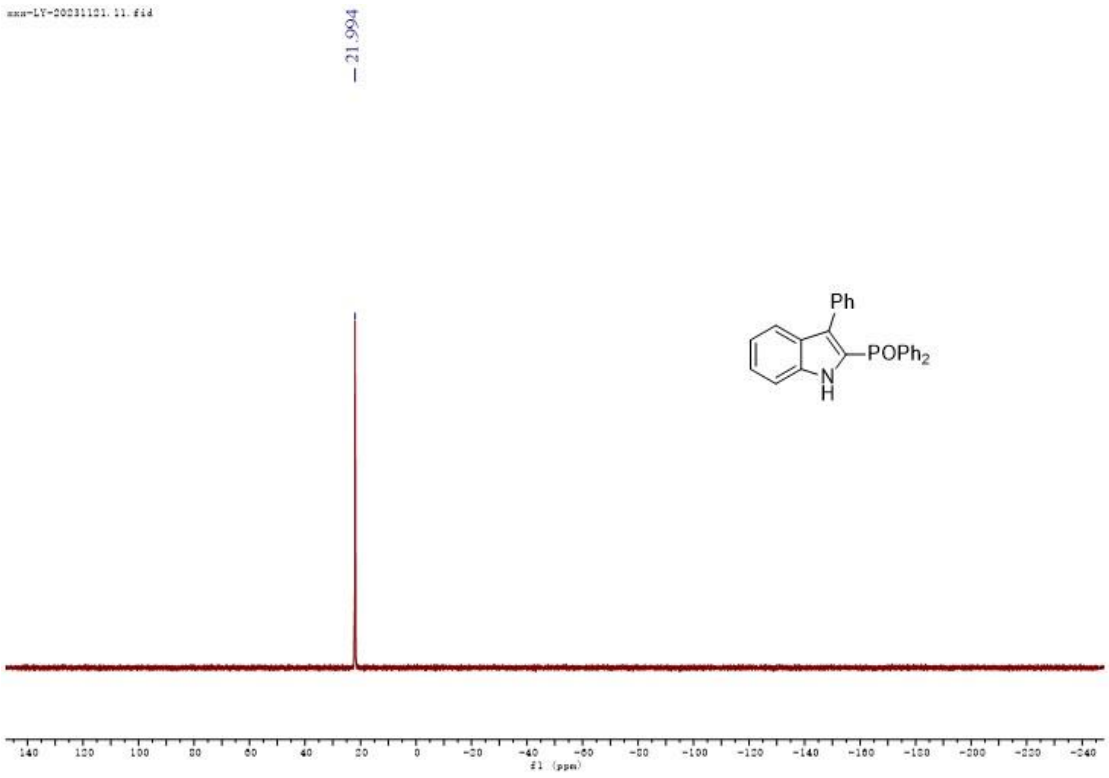
^{1}H NMR (400 MHz, $CDCl_3$) for **10**



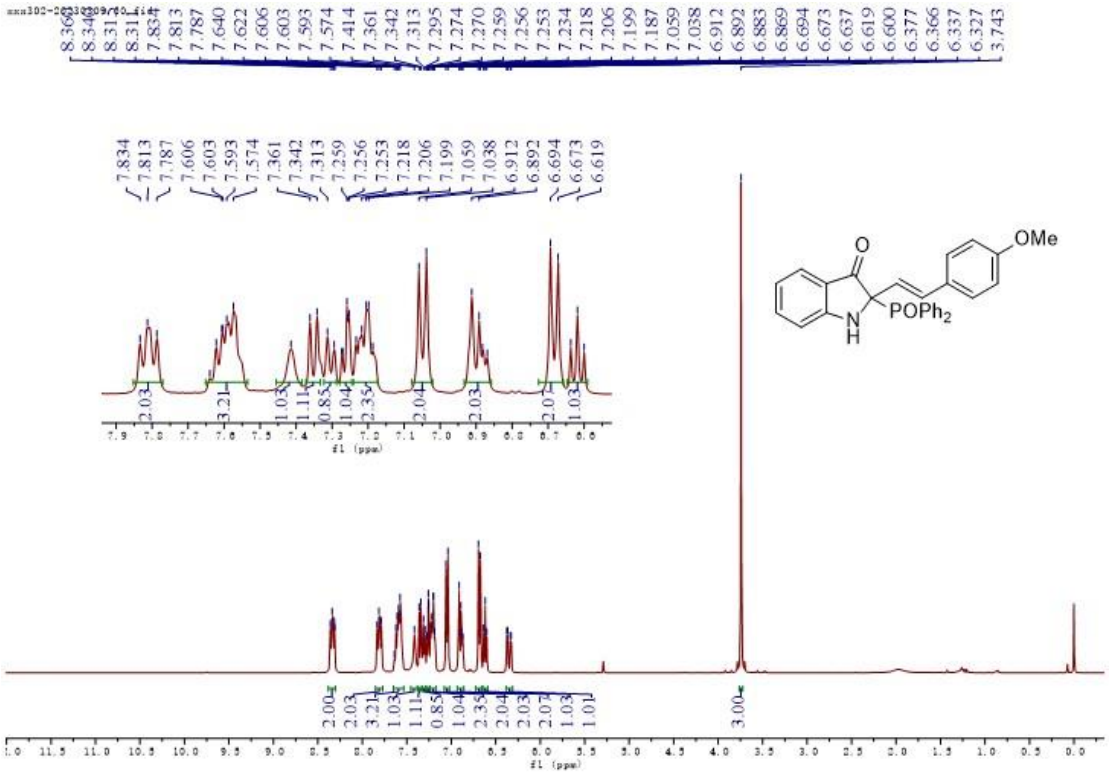
^{13}C NMR (101 MHz, $CDCl_3$) for **10**



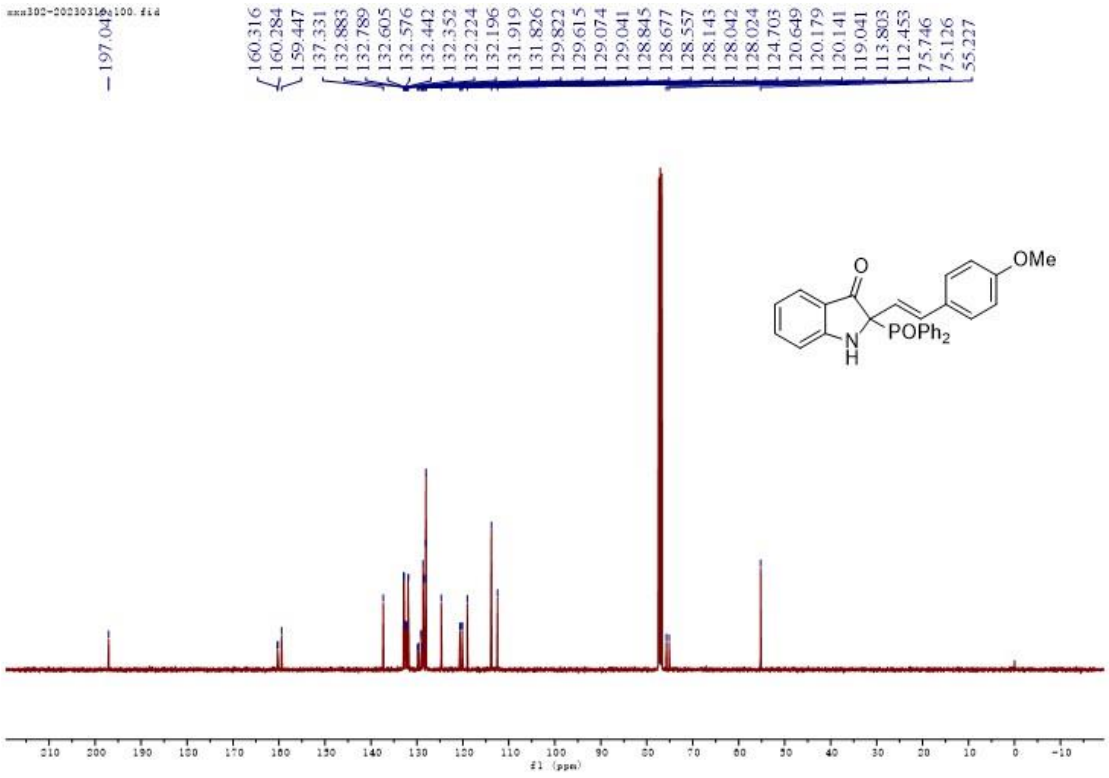
^{31}P NMR (162 MHz, $CDCl_3$) for **10**



^{1}H NMR (400 MHz, $CDCl_3$) for **11**



^{13}C NMR (101 MHz, $CDCl_3$) for **11**



^{31}P NMR (162 MHz, $CDCl_3$) for **11**