Palladium Metallaphotoredox-Catalyzed 3-Acylation of Indole Derivatives

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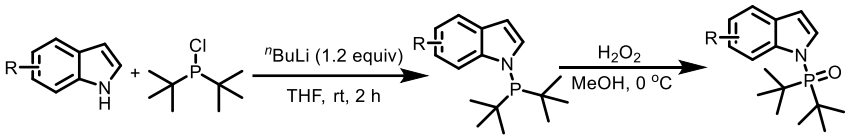
Supporting Information

Content

1. General information

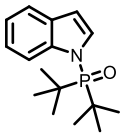
Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. ^{19}F NMR spectra were recorded on a Varian 400 instrument spectrometer. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T, ESI/ Quadrupole Mass Analyzer, ESI-QMA). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). When heating is needed for reaction, we use heating mantle as heat source.

2. Preparation of starting materials



To a two-neck flask contained indole (3.0 mmol, 1.0 equiv) was added anhydrous THF (8 mL) under nitrogen. The reaction vessel was fitted with a rubber stopper and a three-way valve with nitrogen balloon, and was evacuated and back-filled with nitrogen. Subsequently, a solution of nBuLi (solution in hexanes, 3.6 mmol, 1.2 equiv) was added dropwise. After stirring for 15 min, chloro-dialkyl phosphine (3.6 mmol, 1.2 equiv) was added dropwise. The mixture was allowed to stir and warm to room temperature until complete by TLC analysis. Then, 1.2 mL of MeOH was added and most of the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of MeOH (some DCM could be added to help dissolve) and cooled to 0 °C. Slow addition of excess H_2O_2 (0.6 mL of 30% solution, approx. 6 mmol) caused the completion of oxidation process. After adding 4.8 mL of Na_2SO_3 (2 M solution) dropwise, the solution was stirred for 2 h, allowed to warm to room temperature, treated with 7.2 mL of HCl (10% solution), and stirred for another hour. Most of MeOH was removed under reduced pressure, and the remaining residue was poured into 30 mL of H2O and extracted with DCM (3 × 25 mL). The combined organics were dried over Na_2SO_4 and evaporated to give the crude product. Further purification was carried out by recrystallization or column chromatography (silica gel, petroleum ether /EtOAc /DCM).

Di-*tert*-butyl(1*H*-indol-1-yl)phosphine oxide(1a)



665 mg, 80 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)

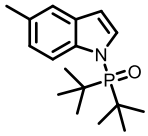
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.68 (s, 1H), 1.34 (d, *J* = 14.7 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 129.2 (d, *J C-P*= 5.3 Hz), 126.4 (d, *J C-P* = 5.0 Hz), 123.4, 121.5, 120.1, 116.3, 107.1 (d, *J C-P* = 5.0 Hz), 38.6 (d, *J C-P* = 69.1 Hz), 26.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 62.86.

The data is consist with previous literature.[1]

Di-*tert*-butyl(5-methyl-1*H*-indol-1-yl)phosphine oxide(1b)



715 mg, 82 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)

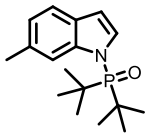
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.37 (s, 1H), 7.20 (s, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 1.7 Hz, 1H), 2.43 (s, 3H), 1.33 (d, *J* = 14.6 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 129.5 (d, *J* = 5.5 Hz), 126.5 (d, *J* = 4.7 Hz), 125.1, 120.02, 115.9, 106.8 (d, *J* = 8.7 Hz), 38.6 (d, *J* = 69.4 Hz), 26.7, 21.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 62.36.

The data is consist with previous literature.[1]

Di-*tert*-butyl(6-methyl-1*H*-indol-1-yl)phosphine oxide(1c)



742 mg, 85 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)

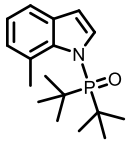
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 3.2, 1.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.66 – 6.60 (m, 1H), 2.45 (s, 3H), 1.34 (d, *J* = 14.6 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 133.3, 126.9 (d, *J* = 5.6 Hz), 125.7 (d, *J* = 5.1 Hz), 123.2, 119.7, 116.1, 110.0, 106.9 (d, *J* = 5.0 Hz), 38.6 (d, *J* = 69.3 Hz), 26.7, 22.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 62.46.

The data is consist with previous literature.[1]

Di-*tert*-butyl(7-methyl-1*H*-indol-1-yl)phosphine oxide(1d)



620 mg, 71 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)

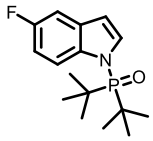
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 1H), 7.36 – 7.29 (m, 1H), 7.11 (d, *J* = 4.7 Hz, 2H), 6.71 (d, *J* = 2.1 Hz, 1H), 2.88 (s, 3H), 1.34 (d, *J* = 14.6 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 131.4 (d, *J* = 4.4 Hz), 127.9 (d, *J* = 3.1 Hz), 127.6, 126.5, 122.0, 118.2 (d, *J* = 3.6 Hz), 107.9 (d, *J* = 4.2 Hz), 39.6 (d, *J* = 68.5 Hz), 27.3, 24.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 61.69.

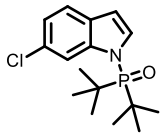
The data is consist with previous literature.[1]

Di-*tert*-butyl(5-fluoro-1*H*-indol-1-yl)phosphine oxide(1e)



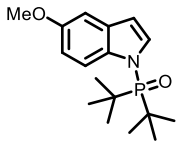
769 mg, 87 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 9.0, 4.7 Hz, 1H), 7.26 (s, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.94 (td, *J* = 9.0, 1.9 Hz, 1H), 6.62 (s, 1H), 1.31 (d, *J* = 14.8 Hz, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8 (d, *J* = 237.0 Hz), 138.0, 129.9, 128.0 (d, *J* = 4.6 Hz), 117.2 (d, *J* = 9.0 Hz), 111.6 (d, *J* = 25.2 Hz), 107.1 (t, *J* = 4.5 Hz), 105.1 (d, *J* = 23.4 Hz), 38.6 (d, *J* = 69.0 Hz), 26.7.
^{31}P NMR (162 MHz, $CDCl_3$) δ 63.34.
The data is consist with previous literature.[1]

Di-*tert*-butyl(6-chloro-1H-indol-1-yl)phosphine oxide(1f)



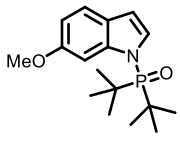
839 mg, 90 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 2.3 Hz, 1H), 7.14 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.65 (s, 1H), 1.33 (d, *J* = 14.8 Hz, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 129.3, 127.7, 127.0 (d, *J* = 4.7 Hz), 122.3, 120.8, 116.2, 107.0 (d, *J* = 4.8 Hz), 38.6 (d, *J* = 68.6 Hz), 26.6.
^{31}P NMR (162 MHz, $CDCl_3$) δ 63.79.
The data is consist with previous literature.[1]

Di-*tert*-butyl(5-methoxy-1*H*-indol-1-yl)phosphine oxide(1g)



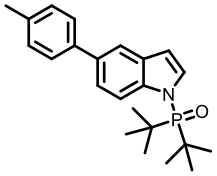
746 mg, 81 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 9.2 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 1.9 Hz, 1H), 6.86 (dd, *J* = 9.2, 2.5 Hz, 1H), 6.61 (d, *J* = 2.2 Hz, 1H), 3.82 (s, 3H), 1.32 (d, *J* = 14.7 Hz, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 136.5, 129.8, 126.9 (d, *J* = 4.8 Hz), 117.0, 112.9, 106.9 (d, *J* = 5.1 Hz), 102.0, 55.6, 38.5 (d, *J* = 69.4 Hz), 26.7.
^{31}P NMR (162 MHz, $CDCl_3$) δ 62.46.
The data is consist with previous literature.[1]

Di-*tert*-butyl(6-methoxy-1*H*-indol-1-yl)phosphine oxide(1h)



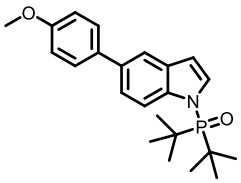
773 mg, 84 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 2.7 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.60 (s, 1H), 3.86 (s, 3H), 1.35 (d, *J* = 14.7 Hz, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 142.6, 125.1 (d, *J* = 4.8 Hz), 123.1 (d, *J* = 5.6 Hz), 120.4, 112.1, 106.9 (d, *J* = 15.3 Hz), 98.9 (d, *J* = 8.6 Hz), 55.5, 38.6 (d, *J* = 69.2 Hz), 26.7.
^{31}P NMR (162 MHz, $CDCl_3$) δ 63.05.
The data is consist with previous literature.[1]

Di-*tert*-butyl(5-(p-tolyl)-1*H*-indol-1-yl)phosphine oxide(1i)



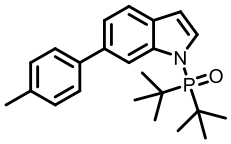
880 mg, 80 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.8 Hz, 1H), 7.77 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.47 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 6.77 – 6.68 (m, 1H), 2.40 (s, 1H), 1.36 (d, *J* = 14.7 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 139.1, 136.1, 134.8, 129.7 (d, *J* = 5.4 Hz), 129.3, 127.1, 126.9 (d, *J* = 4.8 Hz), 123.1, 118.3, 116.4, 107.4 (d, *J* = 5.0 Hz), 38.6 (d, *J* = 69.1 Hz), 26.7, 21.1.
^{31}P NMR (162 MHz, $CDCl_3$) δ 62.87.
The data is consist with previous literature.[1]

Di-*tert*-butyl(5-(4-methoxyphenyl)-1H-indol-1-yl)phosphine oxide(1j)



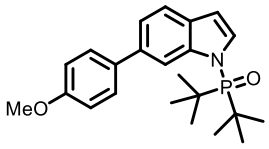
930 mg, 81 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.8 Hz, 1H), 7.73 (s, 1H), 7.60 – 7.50 (m, 2H), 7.44 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.02 – 6.92 (m, 2H), 6.76 – 6.67 (m, 1H), 3.85 (s, 3H), 1.36 (d, *J* = 14.7 Hz, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 140.8, 134.6 (d, *J* = 9.2 Hz), 129.7 (d, *J* = 5.5 Hz), 128.3, 126.9 (d, *J* = 4.5 Hz), 122.9, 118.0, 116.4, 114.1, 107.3 (d, *J* = 5.0 Hz), 55.3, 38.6 (d, *J* = 69.3 Hz), 26.7.
^{31}P NMR (162 MHz, $CDCl_3$) δ 62.83.
The data is consist with previous literature.[1]

Di-*tert*-butyl(6-(p-tolyl)-1H-indol-1-yl)phosphine oxide(1k)



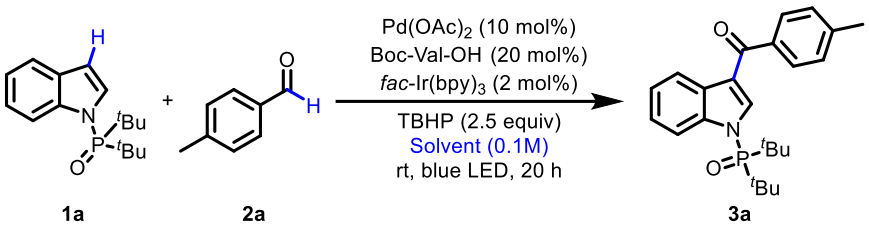
836 mg, 76 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.65 (dd, *J* = 8.2, 1.9 Hz, 3H), 7.50 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.28 (dd, *J* = 3.5, 1.5 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.76 – 6.66 (m, 1H), 2.41 (s, 3H), 1.39 (d, *J* = 14.8 Hz, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 139.0, 136.5, 136.3, 129.3, 128.3 (d, *J* = 5.3 Hz), 127.3, 126.8 (d, *J* = 4.7 Hz), 120.9, 120.2, 114.5, 106.9 (d, *J* = 5.1 Hz), 38.7 (d, *J* = 69.0 Hz), 26.7, 21.1.
^{31}P NMR (162 MHz, $CDCl_3$) δ 62.97.
The data is consist with previous literature.[1]

Di-*tert*-butyl(6-(4-methoxyphenyl)-1H-indol-1-yl)phosphine oxide (1l)



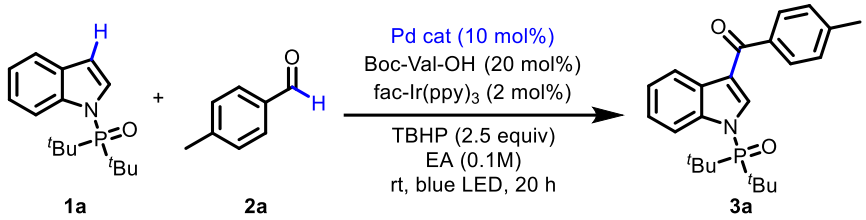
869 mg, 78 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). (known compound)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 – 8.71 (m, 1H), 7.67 – 7.63 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.43 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.24 (dd, *J* = 3.5, 1.4 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.78 – 6.59 (m, 1H), 3.84 (s, 3H), 1.36 (d, *J* = 14.7 Hz, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 142.4, 136.2, 134.6, 128.5, 128.1 (d, *J* = 5.2 Hz), 126.7 (d, *J* = 5.0 Hz), 120.8, 120.2, 114.2, 114.0, 106.9 (d, *J* = 4.6 Hz), 55.4, 38.6 (d, *J* = 69.0 Hz), 26.7.
^{31}P NMR (162 MHz, $CDCl_3$) δ 63.10.
The data is consist with previous literature.[1]

3. Additional data for optimization of conditions



Entry	Slovent	Yield %
1	MeCN	21%
2	DMSO	NR
3	THF	NR
4	DCE	<10%
5	EtOH	<10%
6	Toluene	NR
7	Actone	NR
8	DMF	NR
9	**Ethyl acetate**	**37%**

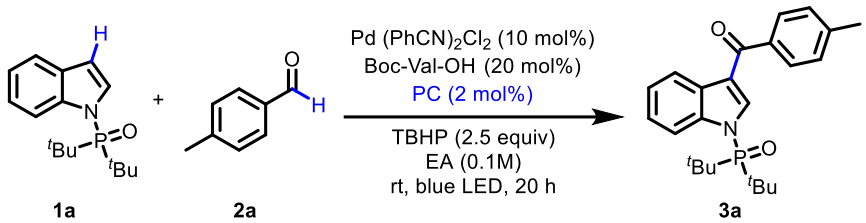
Condition: 1a (0.1 mmol, 1 equiv), **2a** (0.25 mmol, 2.5 equiv), Pd $(PhCN)_2Cl_2$ (10 mol%), *fac*-$Ir(ppy)_3$ (0.002 mmol, 0.02 equiv), Boc-Val-OH (0.1 mmol, 1 equiv), TBHP (50 µL, 2.5M in decane)solvent (1 mL), rt, Ar, 24 h 30 W blue LED. Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard. NR = no reaction.



1a 2a 3a

Entry	Pd cat	Yield %
1	$Pd(TFA)_2$	28%
2	$PdCl_2$	39%
3	$PdBr_2$	20%
4	$Pd(MeCN)Cl_2$	<10%
5	**Bis(benzonitrile)$PdCl_2$**	**49%**
6	$[(Cinnamyl)PdCl]_2$	NR

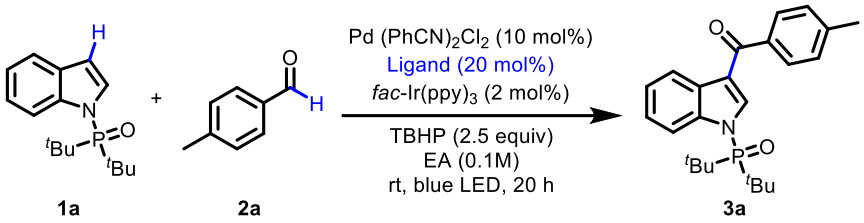
Condition: 1a (0.1 mmol, 1 equiv), **2a** (0.25 mmol, 2.5 equiv), Pd catalyst (10 mol%), *fac*-$Ir(ppy)_3$ (0.002 mmol, 0.02 equiv), Boc-Val-OH (0.02 mmol, 0.2 equiv), TBHP (50 µL, 2.5M in decane), ethyl acetate (1 mL), rt, Ar, 24 h 30 W blue LED. Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard. NR = no reaction.



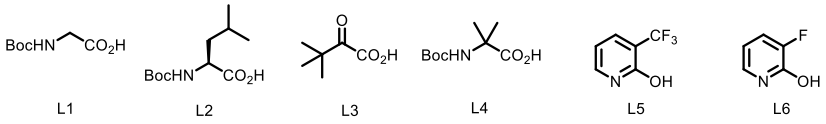
1a 2a 3a

Entry	PC	Yield %
7	$Ru(bpy)_3PF_6$	<20%
8	$[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$	trace
9	$Ir[(bpy)_2(dtbpy)]PF_6$	<20%

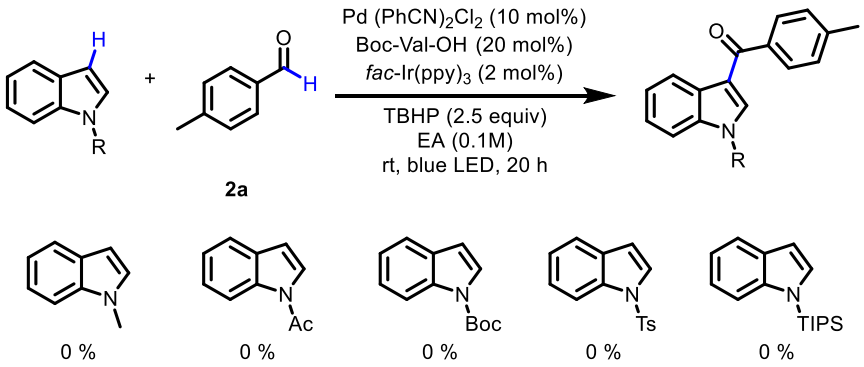
Condition: 1a (0.1 mmol, 1 equiv), **2a** (0.25 mmol, 2.5 equiv), Pd $(PhCN)_2Cl_2$ (10 mol%), photo catalyst (0.002 mmol, 0.02 equiv), Boc-Val-OH (0.02 mmol, 0.2 equiv), TBHP (50 µL, 2.5M in decane), ethyl acetate (1 mL), rt, Ar, 24 h 30 W blue LED. Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard. NR = no reaction.



Entry	Ligand	Yield %
1	L1	NR
2	L2	NR
3	**L3**	**70%**
4	**L4**	**80%**
5	L5	NR
6	L6	NR



Condition: 1a (0.1 mmol, 1 equiv), **2a** (0.25 mmol, 2.5 equiv), Pd $(PhCN)_2Cl_2$ (10 mol%), *fac*-$Ir(ppy)_3$ (0.002 mmol, 0.02 equiv), ligand (0.02 mmol, 0.2 equiv), TBHP (50 µL, 2.5M in decane), ethyl acetate (1 mL), rt, Ar, 24 h 30 W blue LED. Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard. NR = no reaction.

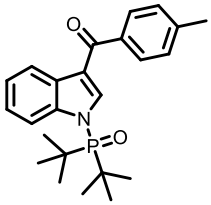


4. General procedure for the synthesis of 3a-3dd

A mixture of *di-tert-butylphosphine oxide indole derivatives* (0.1 mmol), $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 0.1 equiv), *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002 mmol, 0.02 equiv), Boc-Aib-OH (3.7 mg, 0.02 mmol, 0.2 equiv), dry ethyl acetate (1.0 mL), TBHP (50 µL, 0.25 mmol, 2.5 equiv) and benzaldehyde derivatives (0.25 mmol, 2.5 equiv) in a 4 mL vial, then the vial was purged with Ar for 1 min under stirring. The vial was sealed with PTFE cap. The reaction was stirred and irradiated with a 30 W Blue LEDs (approximately 1 cm away from the light source) at room

temperature for 24 h. The reaction mixture was diluted with 5.0 mL of ethyl acetate and filtered through a plug of celite, followed by washing with 15 mL of ethyl acetate. The combined residue was concentrated under reduced pressure, and then the resulting crude product was purified by column chromatography (eluent: *n*-hexane/Acetone) to provide the product **3a-3dd**.

(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)(p-tolyl)methanone (3a)



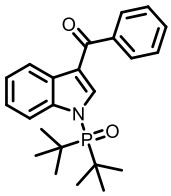
28.5 mg, 73 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 119-121 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.41 (m, 1H), 8.18 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.28 – 7.21 (m, 4H), 7.18 (s, 1H), 2.38 (s, 3H), 1.28 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 142.7, 142.3, 137.3, 134.3 (d, *J* = 4.4 Hz), 129.2, 129.0, 127.2 (d, *J* = 4.4 Hz), 125.1, 123.6, 121.7, 120.2 (d, *J* = 4.1 Hz), 116.4, 38.8 (d, *J* = 67.4 Hz), 26.7, 21.6.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{31}NO_2P$ 396.2087; Found 396.2090.

(1-(di-tert-butylphosphoryl)-1*H*-indol-3-yl)(phenyl)methanone (3b)



18.0 mg, 47 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 83-85 ^{o}C

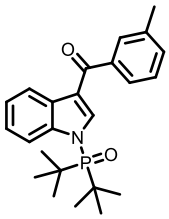
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.51 (m, 1H), 8.32 – 8.24 (m, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.32 (m, 2H), 1.36 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 142.4, 140.0, 134.7 (d, *J* = 4.4 Hz), 131.9, 128.8, 128.5, 127.1 (d, *J* = 4.5 Hz), 125.2, 123.7, 121.7, 120.1 (d, *J* = 3.7 Hz), 116.4, 38.8 (d, *J* = 67.4 Hz), 26.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.29.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{23}H_{29}NO_2P$ 382.1930; Found 382.1927.

(1-(di-tert-butylphosphoryl)-1*H*-indol-3-yl)(*m*-tolyl)methanone (3c)



28.4 mg, 72 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 110-112 ^{o}C

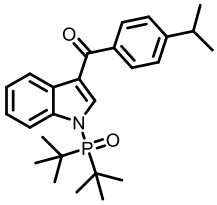
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.47 (m, 1H), 8.35 – 8.20 (m, 1H), 7.67 (d, *J* = 2.0 Hz, 2H), 7.62 (d, *J* = 6.3 Hz, 1H), 7.39 (d, *J* = 6.2 Hz, 2H), 7.37 – 7.31 (m, 2H), 2.43 (s, 3H), 1.35 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 142.3, 139.9, 138.3, 134.7 (d, *J* = 4.9 Hz), 132.7, 129.6, 128.3, 127.2 (d, *J* = 4.3 Hz), 126.0, 125.1, 123.7, 121.7, 120.1 (d, *J* = 4.1 Hz), 116.4, 38.8 (d, *J* = 67.4 Hz), 26.7, 21.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.31.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{31}NO_2P$ 396.2087; Found 396.2087.

(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)(4-isopropylphenyl)methanone (3d)



32.1 mg, 76 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 105-107 ^{o}C

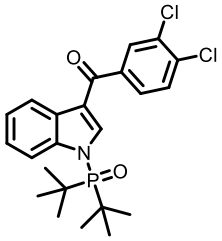
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 – 8.49 (m, 1H), 8.34 – 8.21 (m, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 1.7 Hz, 1H), 7.38 (s, 1H), 7.36 – 7.30 (m, 3H), 3.14 – 2.89 (m, 1H), 1.37 (d, *J* = 15.0 Hz, 18H), 1.31 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 153.5, 142.3, 137.5, 134.2 (d, *J* = 4.4 Hz), 129.2, 127.3 (d, *J* = 4.3 Hz), 126.6, 125.0, 123.6, 121.7, 120.1 (d, *J* = 4.1 Hz), 116.4, 38.8 (d, *J* = 67.3 Hz), 34.2, 26.7, 23.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.20.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{26}H_{35}NO_2P$ 424.2400; Found 424.2401.

(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)(3,4-dichlorophenyl)methanone (3e)



28.3 mg, 63 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 99-101 ^{o}C

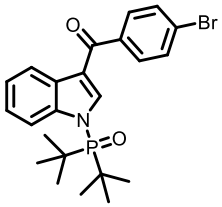
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.53 (m, 1H), 8.27 – 8.22 (m, 1H), 7.93 (d, *J* = 1.9 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.34 (m, 2H), 1.37 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 142.5, 139.6, 136.6, 134.8 (d, *J* = 4.1 Hz), 133.1, 131.1, 130.8, 128.0, 126.9 (d, *J* = 4.3 Hz), 125.6, 124.1, 121.6, 119.5 (d, *J* = 3.9 Hz), 116.7, 39.0 (d, *J* = 67.1 Hz), 26.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.70.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{23}H_{27}Cl_2NO_2P$ 450.1151; Found 450.1153.

(4-bromophenyl)(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)methanone(3f)



18.8 mg, 41 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 176-178 °C

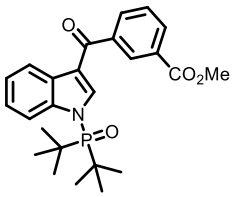
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.53 (m, 1H), 8.26 – 8.20 (m, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 3H), 7.37 – 7.32 (m, 2H), 1.36 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 142.4, 138.7, 134.5 (d, *J* = 4.1 Hz), 131.8, 130.4, 126.9 (d, *J* = 4.2 Hz), 126.8, 125.3, 123.8, 121.6, 119.8 (d, *J* = 4.2 Hz), 116.5, 38.8 (d, *J* = 67.2 Hz), 26.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.48.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}BrNO_2P$ 460.1036; Found 460.1037.

methyl 3-(1-(di-tert-butylphosphoryl)-1H-indole-3-carbonyl)benzoate (3g)



30.2 mg, 69 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 117-119 °C

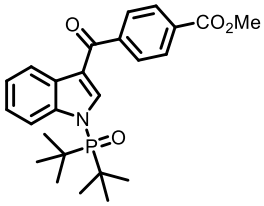
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.9 Hz, 1H), 8.30 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.82 (t, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 1.3 Hz, 1H), 7.33 – 7.24 (m, 2H), 3.96 (s, 3H), 1.40 (d, *J* = 14.8 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 151.1, 142.6, 134.7, 132.5, 130.9, 129.0, 128.9, 128.0, 127.4 (d, *J* = 4.7 Hz), 124.2, 123.8 (d, *J* = 4.8 Hz), 122.3, 121.6 (d, *J* = 4.8 Hz), 119.1, 116.7, 52.4, 38.8 (d, *J* = 68.6 Hz), 26.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 64.02.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{25}H_{31}BrNO_4P$ 440.1985; Found 440.1986.

methyl 4-(1-(di-tert-butylphosphoryl)-1H-indole-3-carbonyl)benzoate (3h)



28.0 mg, 64 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 122-124 °C

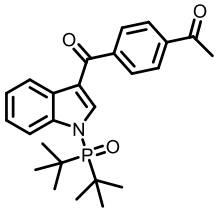
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.47 (m, 1H), 8.32 – 8.22 (m, 1H), 8.18 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.41 – 7.31 (m, 2H), 3.98 (s, 3H), 1.35 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 166.4, 143.7, 142.4, 135.0 (d, *J* = 4.3 Hz), 132.9, 129.7, 128.6, 126.8 (d, *J* = 4.2 Hz), 125.4, 124.0, 121.7, 119.9 (d, *J* = 4.2 Hz), 116.5, 52.5, 38.8 (d, *J* = 66.8 Hz), 26.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.89.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{25}H_{31}BrNO_4P$ 440.1985; Found 440.1988.

1-(4-(1-(di-tert-butylphosphoryl)-1H-indole-3-carbonyl)phenyl)ethan-1-one(3i)



27.4 mg, 65 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 195-197 ^{o}C

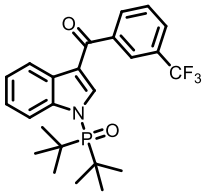
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 1.2 Hz, 1H), 7.33 – 7.23 (m, 2H), 2.65 (s, 3H), 1.39 (d, *J* = 14.8 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 197.4, 142.7, 139.5, 135.4, 129.1, 127.7, 126.9 (d, *J* = 5.0 Hz), 124.4 (d, *J* = 4.5 Hz), 124.2, 122.4, 121.2 (d, *J* = 4.9 Hz), 119.0, 116.8, 38.7 (d, *J* = 68.6 Hz), 26.8, 26.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 63.79.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{25}H_{31}NO_3P$ 424.2036; Found 424.2038.

(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)(3-(trifluoromethyl)phenyl) methanone (3j)



23.3 mg, 52 % yellow oil. Rf = 0.5 (Hexane: Acetone = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.55 (m, 1H), 8.33 – 8.29 (m, 1H), 8.08 (d, *J* = 6.5 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.41 – 7.34 (m, 2H), 1.38 (s, 9H), 1.34 (s, 9H).

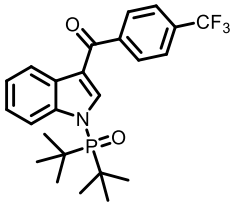
^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 142.4, 140.5, 134.9 (d, *J* = 4.3 Hz), 132.1, 130.7 (q, *J* = 33.1 Hz), 129.5, 128.4 (q, *J* = 3.3 Hz), 126.9 (d, *J* = 4.3 Hz), 125.7 (q, *J* = 3.4 Hz), 125.5, 124.0, 123.5 (q, *J* = 228.8 Hz), 121.6, 119.4 (d, *J* = 3.9 Hz), 116.5, 38.8 (d, *J* = 66.9 Hz), 26.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.76.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.68.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{28}F_3NO_2P$ 450.1804; Found 450.1809.

(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)(4-(trifluoromethyl)phenyl) methanone (3k)



25.5 mg, 57 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 149-151 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.53 (m, 1H), 8.25 – 8.20 (m, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 2.1 Hz, 1H), 7.34 (dd, *J* = 6.2, 3.3 Hz, 1H), 1.34 (d, *J* = 15.0

Hz, 18H).

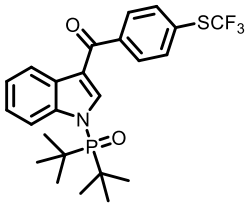
^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 143.2, 142.6, 135.0 (d, *J* = 4.3 Hz), 133.5 (d, *J* = 32.7 Hz), 129.1, 126.9 (q, *J* = 4.3 Hz), 125.7 (q, *J* = 7.2, 3.5 Hz), 125.6, 124.1, 123.8 (q, *J* = 272.8 Hz), 121.7, 119.8 (d, *J* = 4.1 Hz), 116.7, 38.9 (d, *J* = 67.0 Hz), 26.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.66.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.83.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{28}F_3NO_2P$ 450.1804; Found 450.1806.

(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)(4-((trifluoromethyl)thio)phenyl) methanone (3l)



35.1 mg, 73 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 108-110 ^oC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.52 (m, 1H), 8.28 – 8.21 (m, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 2.1 Hz, 1H), 7.38 – 7.33 (m, 2H), 1.35 (d, *J* = 15.0 Hz, 18H).

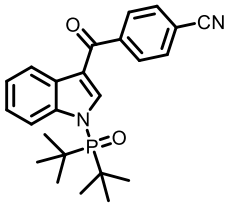
^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 142.4, 141.9, 135.9, 135.8, 134.9 (d, *J* = 4.2 Hz), 129.7 (q, *J* = 234.1 Hz), 126.8 (d, *J* = 4.2 Hz), 126.4, 125.5, 124.0, 121.6, 119.8 (d, *J* = 4.0 Hz), 116.5, 38.8 (d, *J* = 67.0 Hz), 26.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.71.

^{19}F NMR (376 MHz, $CDCl_3$) δ -41.91.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{28}F_3NO_2PS$ 482.1525; Found 482.1526.

4-(1-(di-tert-butylphosphoryl)-1H-indole-3-carbonyl)benzonitrile (3m)



16.6 mg, 41 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 109-111 ^oC

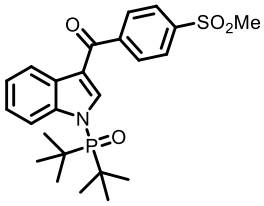
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.55 (m, 1H), 8.26 – 8.18 (m, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.36 (dd, *J* = 6.2, 3.2 Hz, 2H), 1.35 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 142.7, 139.4, 132.7, 128.1, 126.7 (d, *J* = 4.5 Hz), 124.6 (d, *J* = 4.5 Hz), 124.4, 122.53, 120.6 (d, *J* = 4.4 Hz), 119.0, 118.7, 116.9, 110.2, 38.8 (d, *J* = 68.5 Hz), 26.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 64.00.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{28}N_2O_2P$ 407.1883; Found 407.1886.

(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)(4-(methylsulfonyl)phenyl)methanone (3n)



18.4 mg, 40 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 196-198 °C

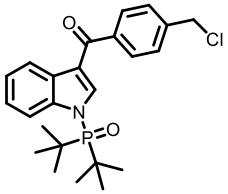
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.55 (m, 1H), 8.29 – 8.23 (m, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.37 (dd, *J* = 6.1, 3.3 Hz, 2H), 3.13 (s, 3H), 1.35 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 144.7, 143.2, 142.5, 135.1 (d, *J* = 4.3 Hz), 129.4, 127.7, 126.6 (d, *J* = 4.3 Hz), 125.6, 124.2, 121.6, 119.6 (d, *J* = 3.9 Hz), 116.7, 44.4, 38.9 (d, *J* = 66.9 Hz), 26.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.97.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{31}NO_4PS$ 460.1706; Found 460.1708.

(4-(chloromethyl)phenyl)(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)methanone (3o)



25.3 mg, 59 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 108-110 °C

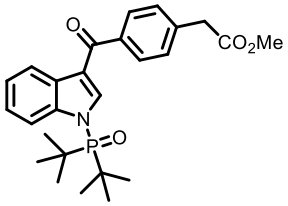
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.54 (m, 1H), 8.29 – 8.21 (m, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.31 (m, 2H), 4.66 (s, 2H), 1.36 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 142.3, 141.3, 139.8, 134.6 (d, *J* = 4.3 Hz), 129.3, 128.6, 127.0 (d, *J* = 4.4 Hz), 125.3, 123.8, 121.7, 119.9 (d, *J* = 4.0 Hz), 116.5, 45.5, 38.8 (d, *J* = 67.2 Hz), 26.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.67.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}ClNO_2P$ 430.1697; Found 430.1697.

Methyl 2-(4-(1-(di-tert-butylphosphoryl)-1H-indole-3-carbonyl)phenyl)acetate (3p)



24.0 mg, 53 % yellow oil. Rf = 0.4 (Hexane: Acetone = 3:1).

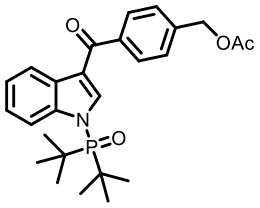
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.51 (m, 1H), 8.27 – 8.22 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.28 (m, 2H), 3.71 (s, 3H), 3.70 – 3.66 (m, 2H), 1.33 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 171.4, 142.3, 138.7, 138.2, 134.4 (d, *J* = 4.4 Hz), 134.4, 129.5, 129.2, 127.2 (d, *J* = 4.2 Hz), 125.2, 123.7, 121.7, 120.0 (d, *J* = 4.2 Hz), 116.4, 52.2, 41.0, 38.8 (d, *J* = 67.3 Hz), 26.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.50.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{26}H_{33}NO_4P$ 454.2142; Found 454.2141.

4-(1-(di-tert-butylphosphoryl)-1H-indole-3-carbonyl)benzyl acetate (3q)



28.1 mg, 62 % yellow oil. Rf = 0.5 (Hexane: Acetone = 3:1).

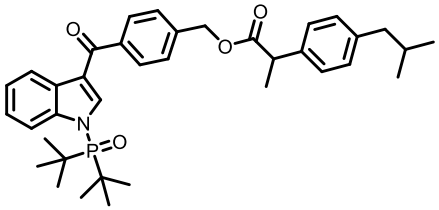
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 1.4 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.26 – 7.22 (m, 1H), 5.17 (s, 2H), 2.13 (s, 3H), 1.39 (d, *J* = 14.8 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 168.3, 142.6, 134.7, 134.6, 129.1, 128.2, 127.5 (d, *J* = 5.0 Hz), 124.1, 123.8 (d, J = 4.7 Hz), 122.2, 121.9 (d, J = 4.8 Hz), 119.2, 116.7, 66.3, 38.8 (d, *J* = 68.8 Hz), 26.8, 21.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 63.67.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{26}H_{33}NO_4P$ 454.2142; Found 454.2148.

4-(1-(di-tert-butylphosphoryl)-1H-indole-3-carbonyl)benzyl 2-(4-isobutylphenyl) propanoate (3r)



25.8 mg, 43 % yellow oil. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 149-152 °C

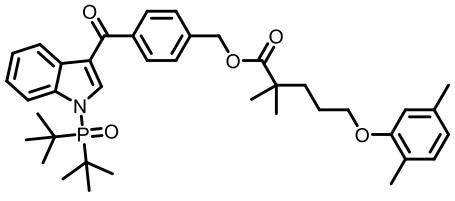
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.53 (m, 1H), 8.30 – 8.22 (m, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 2H), 3.80 (q, *J* = 7.1 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.90 – 1.78 (m, 1H), 1.54 (d, *J* = 7.2 Hz, 3H), 1.36 (d, *J* = 15.0 Hz, 18H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 174.5, 142.4, 140.8, 140.3, 139.5, 137.4, 134.5 (d, *J* = 4.3 Hz), 129.4, 129.0, 127.3, 127.2, 127.1 (d, *J* = 4.2 Hz), 125.2, 123.8, 121.6, 120.1 (d, *J* = 3.8 Hz), 116.4, 65.5, 45.2, 45.0, 38.8 (d, *J* = 67.3 Hz), 30.2, 28.3, 26.7, 22.4, 18.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.55.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{37}H_{47}NO_4P$ 600.3237; Found 600.3242.

4-(1-(di-tert-butylphosphoryl)-1H-indole-3-carbonyl)benzyl 5-(2,5-dimethylphen oxy) -2,2-dimethylpentanoate (3s)



25.0 mg, 39 % yellow oil. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 149-152 °C

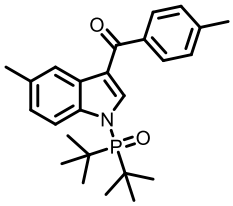
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.56 (m, 1H), 8.31 – 8.25 (m, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.69 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.62 (s, 1H), 5.24 (s, 2H), 3.94 (d, *J* = 5.7 Hz, 2H), 2.32 (s, 3H), 2.18 (s, 3H), 1.80 (s, 4H), 1.37 (d, *J* = 15.0 Hz, 18H), 1.30 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 177.6, 157.0, 142.5, 140.6, 139.7, 136.63 134.7 (d, *J* = 4.3 Hz), 130.5, 129.2, 127.6, 127.2 (d, *J* = 4.0 Hz), 125.3, 123.9, 123.6, 121.8, 120.9, 120.2 (d, *J* = 4.0 Hz), 116.6, 112.1, 67.9, 65.5, 42.4, 38.9 (d, *J* = 67.2 Hz), 37.2, 26.8, 25.3, 21.5, 15.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.38.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{39}H_{51}NO_5P$ 644.3499; Found 644.3499.

(1-(di-tert-butylphosphoryl)-5-methyl-1H-indol-3-yl)(p-tolyl)methanone (3t)



27.4 mg, 67 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 134-136 °C

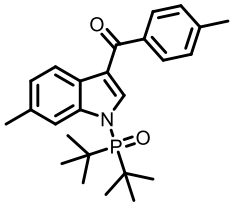
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.7 Hz, 1H), 8.10 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 3H), 2.45 (s, 3H), 1.35 (d, *J* = 14.9 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 142.6, 140.5, 137.6, 134.4 (d, *J* = 4.7 Hz), 133.3, 129.1, 129.0, 127.4 (d, *J* = 4.5 Hz), 126.6, 121.4, 119.8 (d, *J* = 3.9 Hz), 115.9, 38.8 (d, *J* = 67.5 Hz), 26.7, 21.6, 21.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 64.90.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}NO_2P$ 410.2243; Found 410.2242.

(1-(di-tert-butylphosphoryl)-6-methyl-1H-indol-3-yl)(p-tolyl)methanone (3u)



29.8 mg, 73 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 199-201 °C

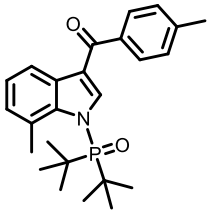
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.16 (dd, *J* = 8.1, 0.9 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H), 1.35 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 142.7, 142.6, 137.3, 135.1, 133.8 (d, *J* = 4.6 Hz), 129.1, 129.0, 125.3, 124.9 (d, *J* = 4.4 Hz), 121.2, 120.2 (d, *J* = 4.1 Hz), 116.1, 38.8 (d, *J* = 67.5 Hz), 26.7, 22.0, 21.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.26.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}NO_2P$ 410.2243; Found 410.2244.

(1-(di-tert-butylphosphoryl)-7-methyl-1H-indol-3-yl)(p-tolyl)methanone (3v)



18.8 mg, 46 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 168-170 ^{o}C

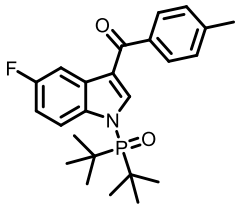
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 3.6 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.27 (s, 1H), 7.22 (d, *J* = 7.0 Hz, 1H), 2.90 (s, 3H), 2.45 (s, 3H), 1.33 (d, *J* = 14.9 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 142.6, 141.3, 137.3, 136.5 (d, *J* = 6.7 Hz), 130.2, 129.2, 129.1, 128.9, 126.4, 123.9, 119.9 (d, *J* = 5.4 Hz), 119.6, 39.8 (d, *J* = 66.5 Hz), 27.2, 24.0, 21.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 64.16.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}NO_2P$ 410.2243; Found 410.2241.

(1-(di-tert-butylphosphoryl)-5-fluoro-1H-indol-3-yl)(p-tolyl)methanone (3w)



21 mg, 51 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 187-189 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 9.2, 4.7 Hz, 1H), 7.94 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.77 – 7.69 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 2.7 Hz, 1H), 7.04 (dd, *J* = 9.1, 2.6 Hz, 1H), 2.44 (s, 3H), 1.34 (d, *J* = 15.1 Hz, 18H).

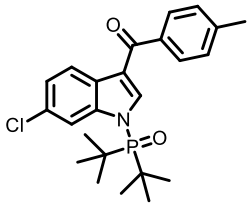
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 159.9 (d, *J* = 239.9 Hz), 142.9, 138.5, 136.9, 135.4 (d, *J* = 4.2 Hz), 129.3, 128.9, 128.2 (dd, *J* = 11.1, 4.5 Hz), 119.9 (t, *J* = 4.0 Hz), 117.4 (d, *J* = 9.0 Hz), 113.3 (d, *J* = 25.2 Hz), 107.1 (d, *J* = 25.0 Hz), 38.8 (d, *J* = 66.9 Hz), 26.6, 21.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 66.02.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.57 – -124.52 (m).

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}FNO_2P$ 414.1993; Found 414.1990.

(6-chloro-1-(di-tert-butylphosphoryl)-1H-indol-3-yl)(p-tolyl)methanone (3x)



15.9 mg, 37 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 211-213 ^{o}C

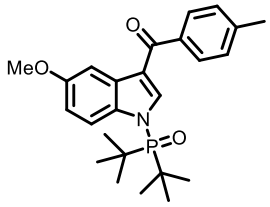
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 3H), 2.46 (s, 3H), 1.36 (d, *J* = 15.1 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 142.9, 142.5, 136.9, 134.5 (d, *J* = 4.1 Hz), 130.9, 129.2, 129.0, 125.8 (d, *J* = 3.9 Hz), 124.4, 122.5, 119.9 (d, *J* = 3.4 Hz), 116.3, 38.8 (d, *J* = 66.8 Hz), 26.6, 21.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 66.15.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}ClNO_2P$ 430.1697; Found 430.1699.

(1-(di-tert-butylphosphoryl)-5-methoxy-1H-indol-3-yl)(p-tolyl)methanone (3y)



23.0 mg, 54 % yellow oil. Rf = 0.5 (Hexane: Acetone = 3:1).

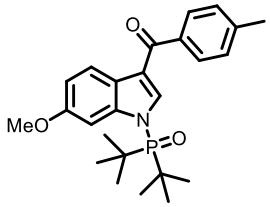
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 9.2 Hz, 1H), 7.80 (d, *J* = 2.5 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.96 (dd, *J* = 9.2, 2.7 Hz, 1H), 3.88 (s, 3H), 2.46 (s, 3H), 1.35 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 156.8, 142.6, 137.3, 136.9, 134.7 (d, *J* = 4.4 Hz), 130.2, 129.2, 128.9, 128.1 (d, *J* = 4.4 Hz), 117.2, 115.2, 102.9, 55.7, 38.8 (d, *J* = 67.5 Hz), 26.7, 21.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.10.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}NO_3P$ 426.2193; Found 426.2195.

(1-(di-tert-butylphosphoryl)-6-methoxy-1H-indol-3-yl)(p-tolyl)methanone (3z)



26.7 mg, 63 % white solid. Rf = 0.5 (Hexane: Acetone = 3:1). M. P. = 131-133 ^{o}C

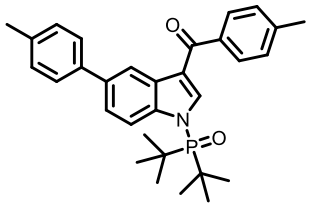
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.2 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 6.96 (dd, *J* = 8.8, 2.3 Hz, 1H), 3.85 (s, 3H), 2.43 (s, 3H), 1.35 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 157.9, 143.4, 142.6, 137.3, 133.1 (d, *J* = 4.4 Hz), 130.1, 129.1, 129.0, 122.0, 121.0 (d, *J* = 4.3 Hz), 113.9, 99.0, 55.5, 38.8 (d, *J* = 67.4 Hz), 26.7, 21.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.48.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}NO_3P$ 426.2193; Found 426.2193.

(1-(di-tert-butylphosphoryl)-5-(p-tolyl)-1H-indol-3-yl)(p-tolyl)methanone (3aa)



30.7 mg, 63 % white solid. Rf = 0.4 (Hexane: Acetone = 3:1). M. P. = 193-195 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.8 Hz, 1H), 8.51 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 2H),

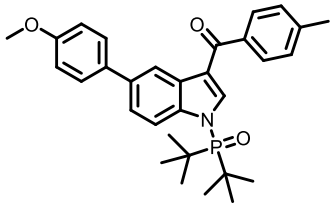
7.69 (s, 1H), 7.59 (d, *J* = 6.7 Hz, 3H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 3H), 2.46 (s, 3H), 2.40 (s, 3H), 1.38 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 142.7, 141.6, 138.6, 137.3, 136.9, 136.5, 134.7 (d, *J* = 4.1 Hz), 129.4, 129.2, 129.1, 127.8 (d, *J* = 4.3 Hz), 127.3, 124.6, 120.3 (d, *J* = 3.7 Hz), 119.7, 116.5, 38.8 (d, *J* = 67.2 Hz), 26.7, 21.6, 21.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.34.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{31}H_{37}NO_2P$ 486.2556; Found 486.2556.

(1-(di-tert-butylphosphoryl)-5-(4-methoxyphenyl)-1H-indol-3-yl)(p-tolyl) methanone (3bb)



28.5 mg, 57 % white solid. Rf = 0.4 (Hexane: Acetone = 3:1). M. P. = 188-190 ^oC

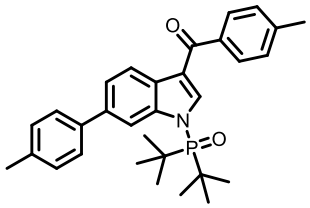
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.8 Hz, 1H), 8.48 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.55 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H), 2.46 (s, 3H), 1.38 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 158.8, 142.7, 141.4, 137.3, 136.7, 134.7 (d, *J* = 4.2 Hz), 134.2, 129.2, 129.1, 128.5, 127.8 (d, *J* = 4.3 Hz), 124.4, 120.3 (d, *J* = 3.9 Hz), 119.42, 116.5, 114.1, 55.3, 38.8 (d, *J* = 67.4 Hz), 26.7, 21.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.25.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{31}H_{37}NO_3P$ 502.2506; Found 502.2504.

(1-(di-tert-butylphosphoryl)-6-(p-tolyl)-1H-indol-3-yl)(p-tolyl)methanone (3cc)



29.6 mg, 61 % white solid. Rf = 0.4 (Hexane: Acetone = 3:1). M. P. = 225-227 ^oC

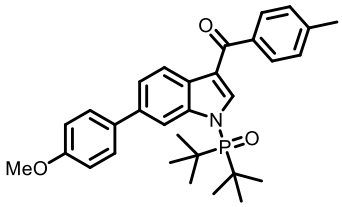
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 1.0 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.66 – 7.60 (m, 3H), 7.32 (d, *J* = 7.9 Hz, 3H), 7.23 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H), 2.39 (s, 3H), 1.39 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 143.1, 142.7, 138.5, 138.2, 137.2, 136.7, 134.6, 134.6, 130.1, 129.4, 129.2, 129.0, 127.4, 126.3, 126.3, 122.9, 121.8, 120.1, 120.1, 114.4, 39.2, 38.5, 26.7, 21.6, 21.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.59.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{31}H_{37}NO_2P$ 486.2556; Found 486.2557.

(1-(di-tert-butylphosphoryl)-6-(4-methoxyphenyl)-1H-indol-3-yl)(p-tolyl) methanone (3dd)



34.1 mg, 68 % white solid. Rf = 0.4 (Hexane: Acetone = 3:1). M. P. = 210-212 °C

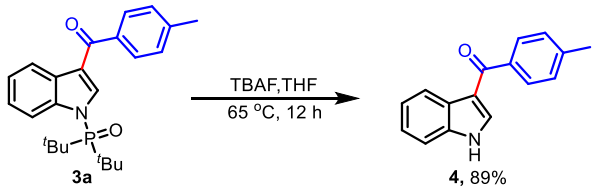
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 1.1 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.67 (dd, *J* = 4.1, 2.0 Hz, 2H), 7.66 – 7.64 (m, 1H), 7.59 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.46 (s, 3H), 1.38 (d, *J* = 15.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 159.0, 143.1, 142.7, 137.8, 137.3, 134.5 (d, *J* = 4.7 Hz), 134.0, 129.1, 129.1, 128.5, 126.0 (d, *J* = 4.4 Hz), 122.8, 121.7, 120.1 (d, *J* = 4.1 Hz), 114.1, 55.4, 38.8 (d, *J* = 67.5 Hz), 26.7, 21.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 65.41.

HRMS(ESI-QMA) m/z: $[M+H]^+$ Calcd for $C_{31}H_{37}NO_3P$ 502.2506; Found 502.2508.

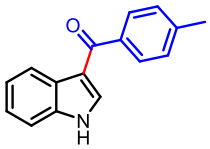
5. Synthetic applications



3a **4**, 89%

A mixture of **3a** (0.1 mmol, 39.5 mg, 1 equiv), TBAF (1 M in THF, 0.2 mL) and THF (3.0 mL) were added in a tube under air atmosphere. After this, the mixture was stirred at 65 °C for 12 h. After the reaction was completed. the resulting mixture was extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **4** was obtained in 89% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 20/1).

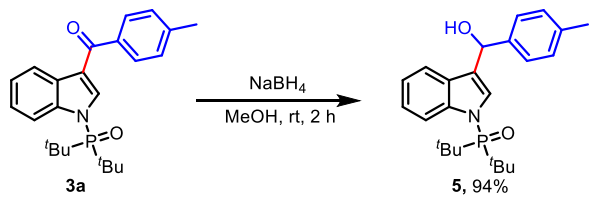
(1H-indol-3-yl)(p-tolyl)methanone (4)



20.8 mg, 89 % white solid. Rf = 0.5 (hexane: ethyl acetate = 5:1).(known coumpound)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.43 – 8.33 (m, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 2.9 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.32 – 7.27 (m, 3H), 7.24 (d, *J* = 2.4 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 141.9, 138.0, 136.5, 133.8, 129.1, 126.5, 124.0, 122.8, 122.5, 117.2, 111.60, 21.7.

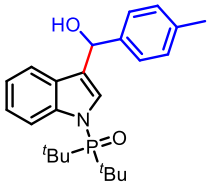


3a **5**, 94%

A mixture of **3a** (0.1 mmol, 39.5 mg, 1 equiv), MeOH (2.0 mL) and $NaBH_4$ (0.25 mmol, 10

mg, 2.5 equiv) were added in a tube under air atmosphere. After this, the mixture was stirred at room temperature for 2 h. After the reaction was completed. the resulting mixture was extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **5** was obtained in 94% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ Acetone (v/v = 5/1).

di-tert-butyl(3-(hydroxy(p-tolyl)methyl)-1H-indol-1-yl)phosphine oxide (5)



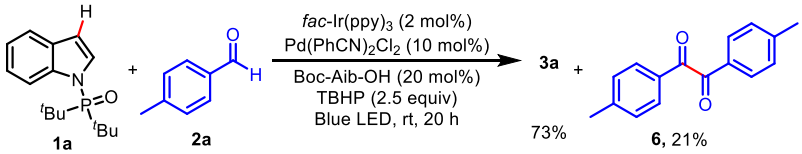
37.6 mg, 94 % white solid. Rf = 0.5 (hexane: ethyl acetate = 5:1) M. P. = 149-152 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.17 (m, 3H), 7.11 (dj, *J* = 5.4 Hz, 2H), 6.12 (s, 1H), 3.52 (s, 1H), 2.37 (s, 3H), 1.33 (dd, *J* = 14.7, 8.2 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.2, 137.5, 129.2, 127.4 (d, *J* = 5.2 Hz), 126.7, 124.2 (d, *J* = 5.1 Hz), 124.0 (d, *J* = 4.6 Hz), 123.7, 121.5, 119.3, 116.4, 70.3, 38.6 (d, *J* = 69.0 Hz), 26.7, 21.2.

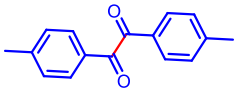
^{31}P NMR (162 MHz, $CDCl_3$) δ 63.08.

6 Mechanism experiments



A mixture of ***1a*** (27.7 mg, 0.1 mmol, 1equiv), $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01mmol, 0.1 equiv), *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002 mmol, 0.02 equiv), Boc-Aib-OH (3.7 mg, 0.02 mmol, 0.2 equiv), dry ethyl acetate (1.0 mL), TBHP (50 μL, 0.25 mmol, 2.5 equiv) and **2a** (0.25 mmol, 2.5 equiv) in a 4 mL vial, then the vial was purged with Ar for 1 min under stirring. The vial was sealed with PTFE cap. The reaction was stirred and irradiated with a 30 W Blue LEDs (approximately 1 cm away from the light source) at room temperature for 20 h. The desired product 6 was obtained in 21% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ ethyl acetate (v/v = 20/1).

1,2-di-p-tolylethane-1,2-dione (6)

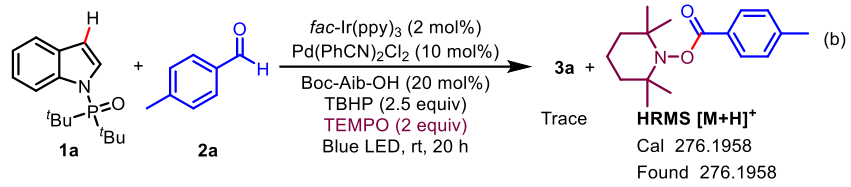


12.4 mg, 21 % white solid. Rf = 0.5 (hexane: ethyl acetate = 20:1). (known coumpound).

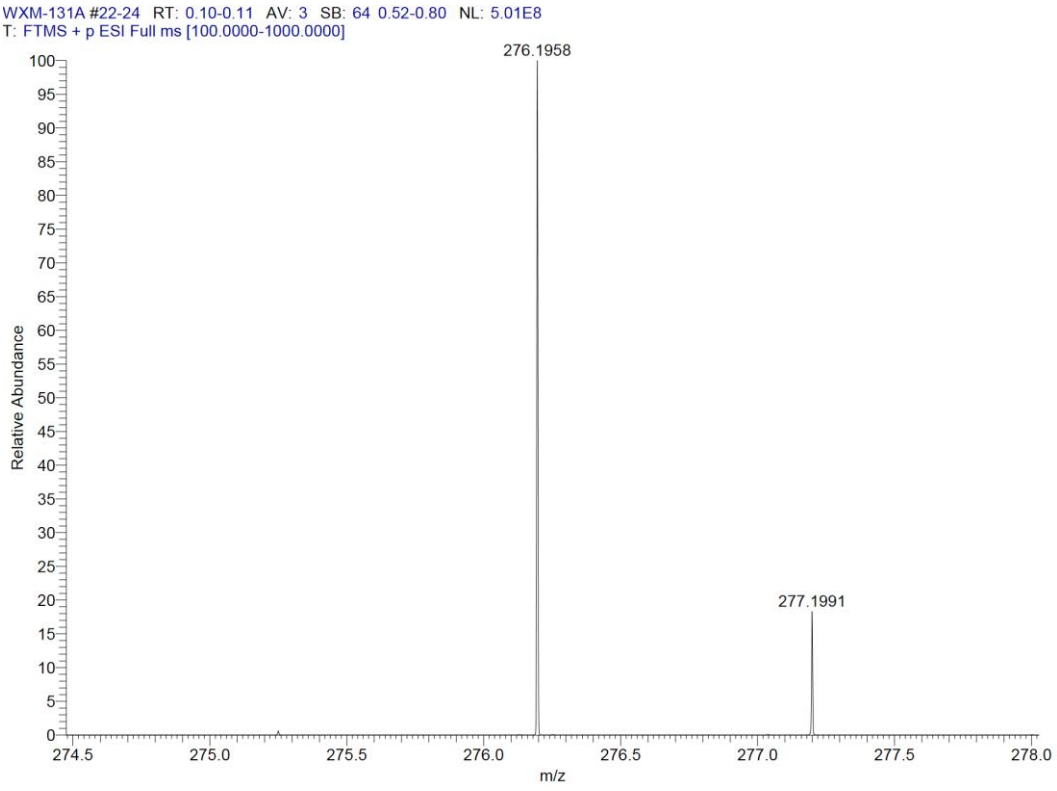
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 4H), 2.44 (s, 6H).

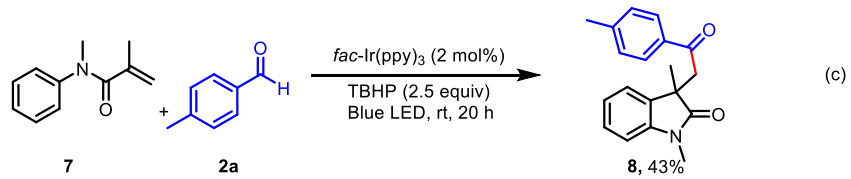
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 144.8, 130.4, 129.4, 126.7, 21.9.

The data is consisted with previous literature.[2]



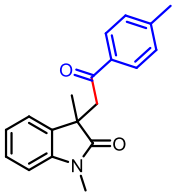
A mixture of ***1a*** (27.7 mg, 0.1 mmol, 1equiv), $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01mmol, 0.1 equiv), *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002 mmol, 0.02 equiv), Boc-Aib-OH (3.7 mg, 0.02 mmol, 0.2 equiv), dry ethyl acetate (1.0 mL), TBHP (50 µL, 0.25 mmol, 2.5 equiv), TEMPO (2 equiv) and **2a** (0.25 mmol, 2.5 equiv) in a 4 mL vial, then the vial was purged with Ar for 1 min under stirring. The vial was sealed with PTFE cap. The reaction was stirred and irradiated with a 30 W Blue LEDs (approximately 1 cm away from the light source) at room temperature for 20 h. No desired product 3a was detected. And the coupling product of Acyl radical and TEMPO was detected by HRMS





A mixture of ***7*** (17.5 mg, 0.1 mmol, 1equiv), *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002 mmol, 0.02 equiv), dry ethyl acetate (1.0 mL), TBHP (50 µL, 0.25 mmol, 2.5 equiv) and **2a** (0.25 mmol, 2.5 equiv) in a 4 mL vial, then the vial was purged with Ar for 1 min under stirring. The vial was sealed with PTFE cap. The reaction was stirred and irradiated with a 30 W Blue LEDs (approximately 1 cm away from the light source) at room temperature for 20 h. The desired product 8 was obtained in 43% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ ethyl acetate (v/v = 10/1).

1,3-dimethyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one(8)

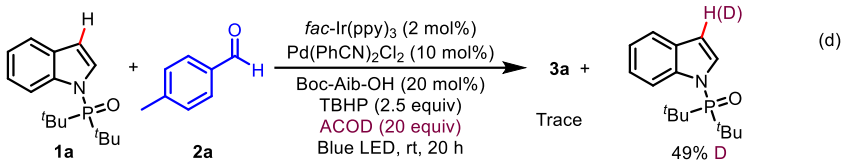


16.0 mg, 43 % white solid. Rf = 0.3 (Hexane: ethyl acetate = 4:1), (known compound).

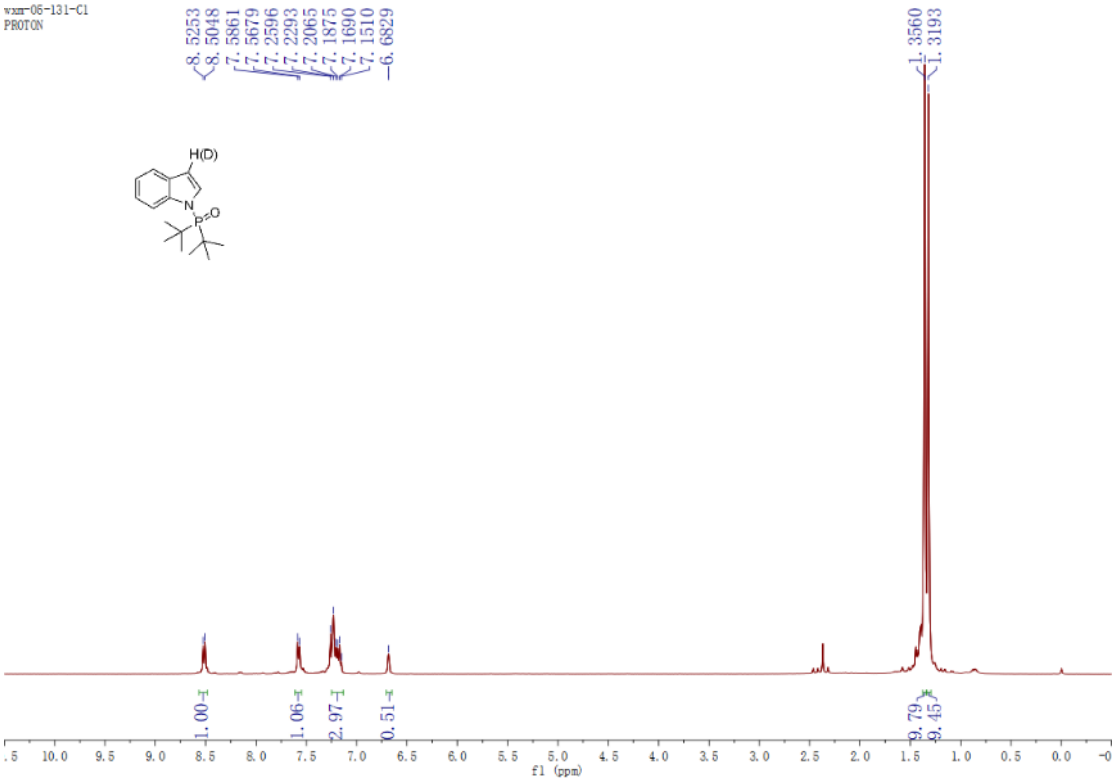
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.3 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.66 (q, *J* = 17.9 Hz, 2H), 3.31 (s, 3H), 2.37 (s, 3H), 1.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 180.6, 143.8, 134.0, 133.8, 129.1, 128.1, 127.8, 122.1, 121.8, 108.1, 45.9, 45.3, 26.4, 24.9, 21.6.

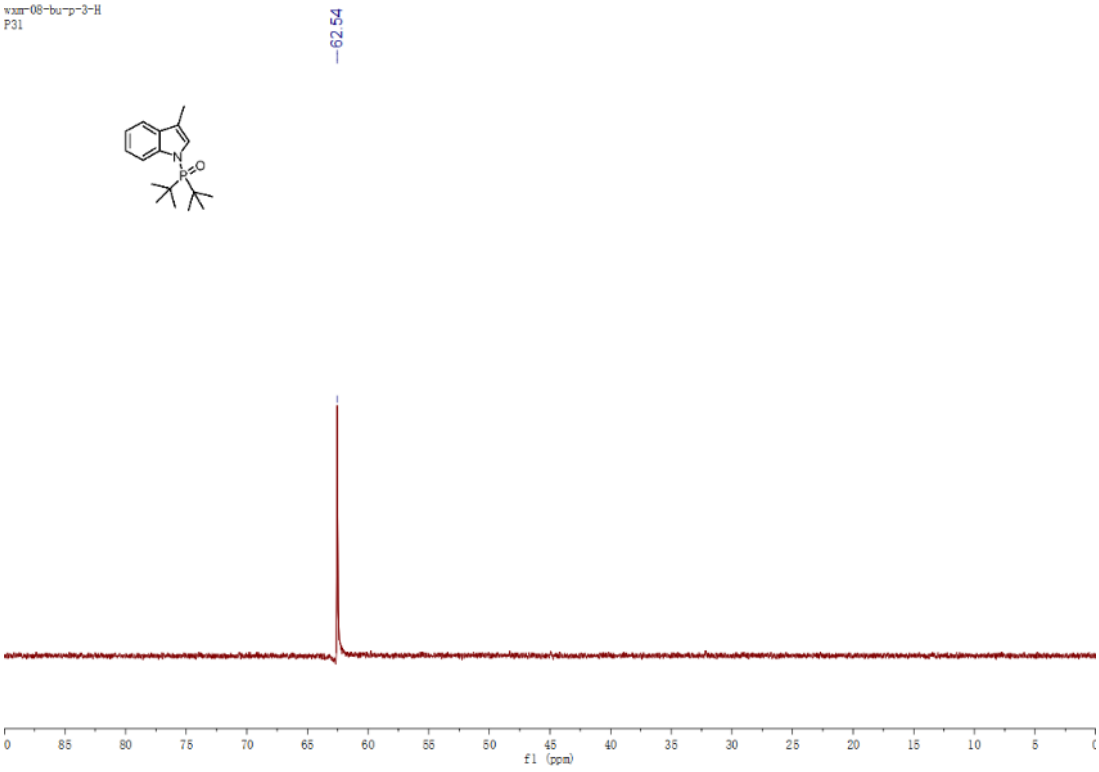
The data is consisted with previous literature.[3]

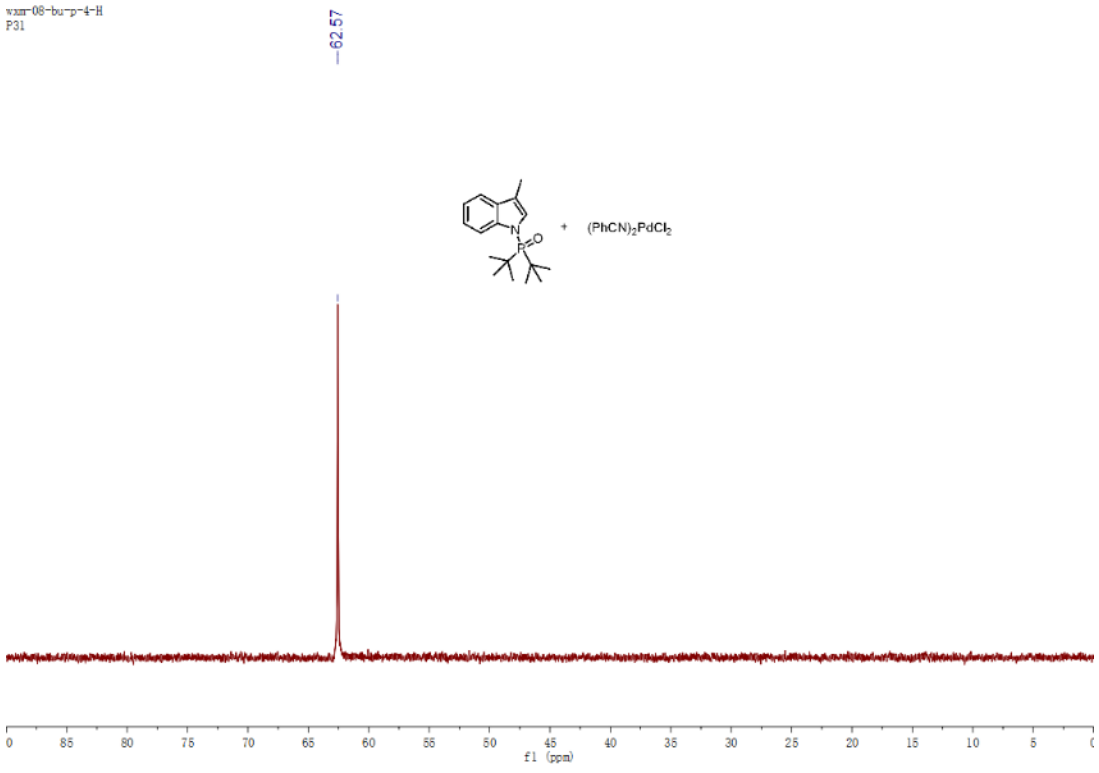


A mixture of ***1a*** (27.7 mg, 0.1 mmol, 1equiv), $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01mmol, 0.1 equiv), *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002 mmol, 0.02 equiv), Boc-Aib-OH (3.7 mg, 0.02 mmol, 0.2 equiv), dry ethyl acetate (1.0 mL), TBHP (50 µL, 0.25 mmol, 2.5 equiv), deuterated acetic acid (20 equiv) and **2a** (0.25 mmol, 2.5 equiv) in a 4 mL vial, then the vial was purged with Ar for 1 min under stirring. The vial was sealed with PTFE cap. The reaction was stirred and irradiated with a 30 W Blue LEDs (approximately 1 cm away from the light source) at room temperature for 20 h. No desired product **3a** was detected. We isolated the starting material **1a**.

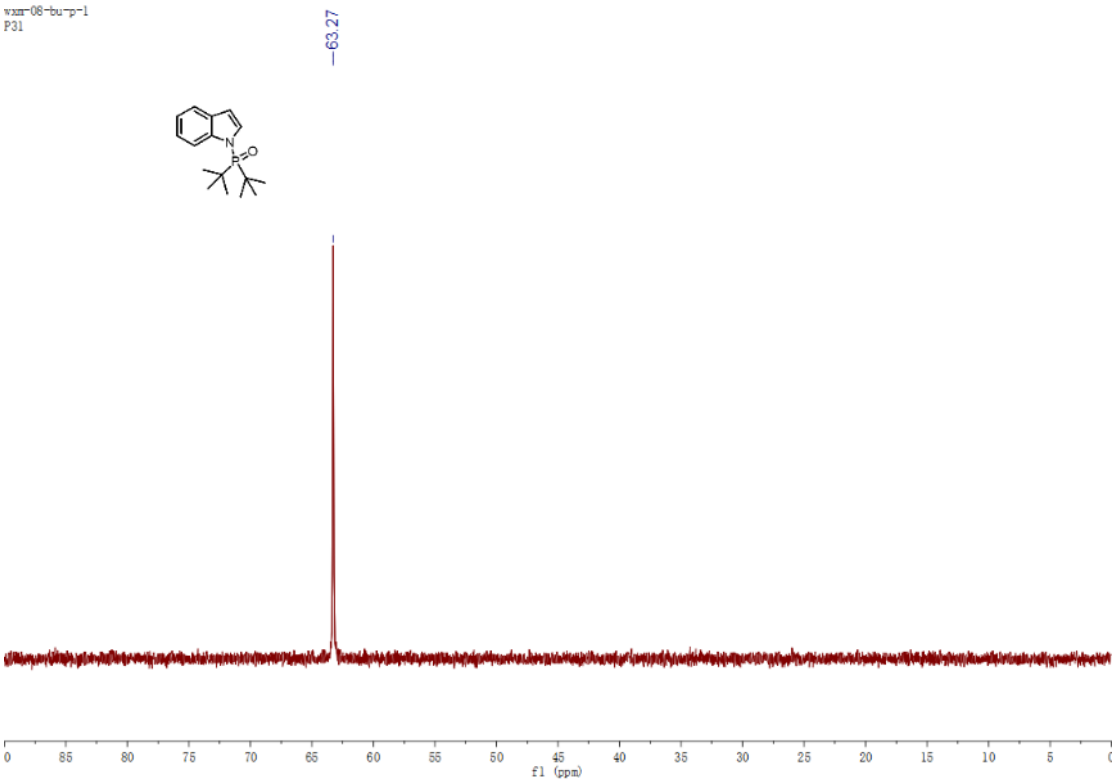


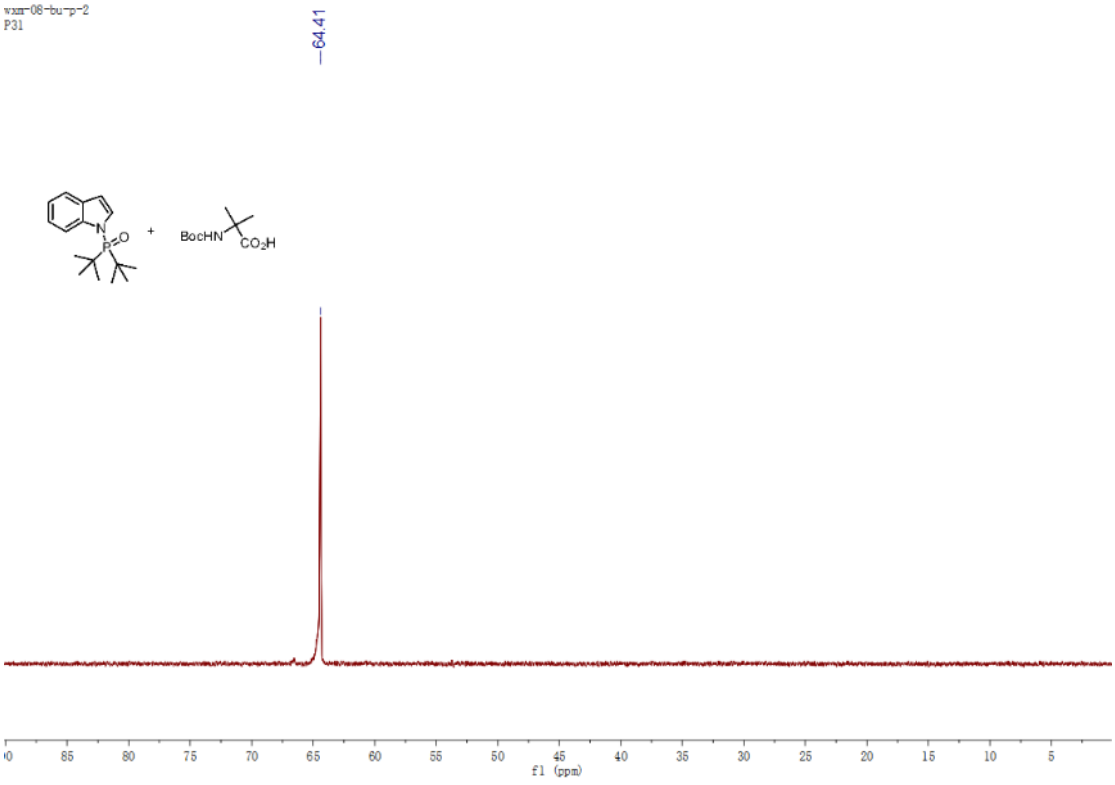
In order to provide that there is no coordination between the Pd catalyst and phosphine oxide, we prepared phosphine oxide protected 3-methyl-indole. When we test the ^{31}P NMR of phosphine oxide protected 3-methyl-indole and the combination of phosphine oxide protected 3-methyl-indole and Pd catalyst, we did not see a change of phosphine spectrum.





While when we test the ^{31}P NMR of phosphine oxide protected 3-methyl-indole and the combination of phosphine oxide protected 3-methyl-indole and amino acid ligand, there is an obvious change (63.27 ppm to 64.41 ppm). We guess that the ligand could interact with phosphine oxide via hydrogen bond, which could be helpful with the stabilization of organic palladium intermediates.





7 X-ray structure of 3a

Crystals **3a** were grown in slow diffusion with Acetone/Hexanes = 1:1 mL for two days as clusters of yellow prisms. The crystallographic data of **3a** were collected on a Rigaku Saturn70 (4x4 bin mode) diffractometer at 113(2) K with Mo-Kα radiation (λ = 0.710747 Å) by ω scan mode. The program Crystal Clear was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL8 package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied using SADABS program). Displacement ellipsoids are scaled to the 50% probability level.

Bond precision: C-C = 0.0018 A Wavelength=0.71073

Cell: a=16.6702(8) b=8.6322(3) c=16.6363(7)
alpha=90 beta=116.458(6) gamma=90

Temperature: 113 K

	Calculated	Reported
Volume	2143.23(19)	2143.23(19)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C24 H30 N O2 P	C24 H30 N O2 P
Sum formula	C24 H30 N O2 P	C24 H30 N O2 P
Mr	395.46	395.46
Dx,g cm-3	1.226	1.226
Z	4	4
Mu (mm-1)	0.147	0.147
F000	848.0	848.0
F000'	848.72	
h,k,lmax	25,13,25	25,12,25
Nref	7983	7447
Tmin,Tmax	0.968,0.975	0.756,1.000
Tmin'	0.968	

Correction method= # Reported T Limits: Tmin=0.756 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.933 Theta(max)= 32.836

R(reflections)= 0.0479(5814) wR2(reflections)= 0.1296(7447)

S = 1.034 Npar= 260

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

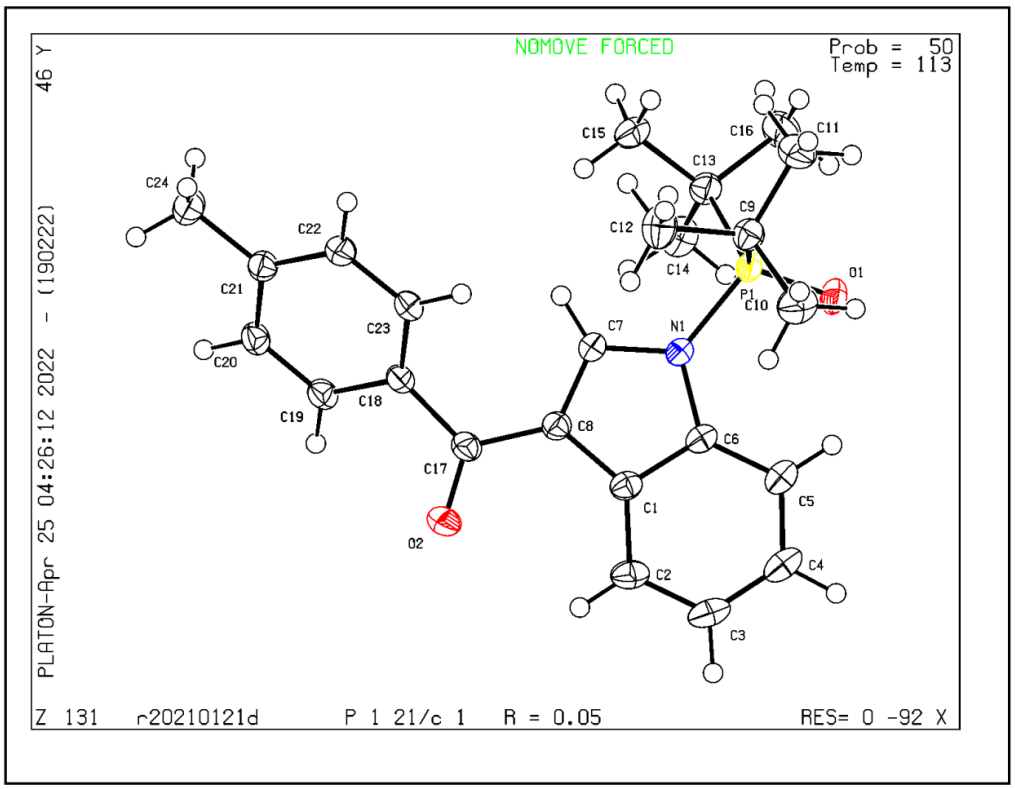
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 3.383 Check

Alert level G

PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 510 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF .... 1 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..... 4.2 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 17 Info

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
5 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check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Temp = 113
46 Y
PLATON-Apr 25 04:26:12 2022 - (190222)
C24
C22
C21
C23
C20
C18
C19
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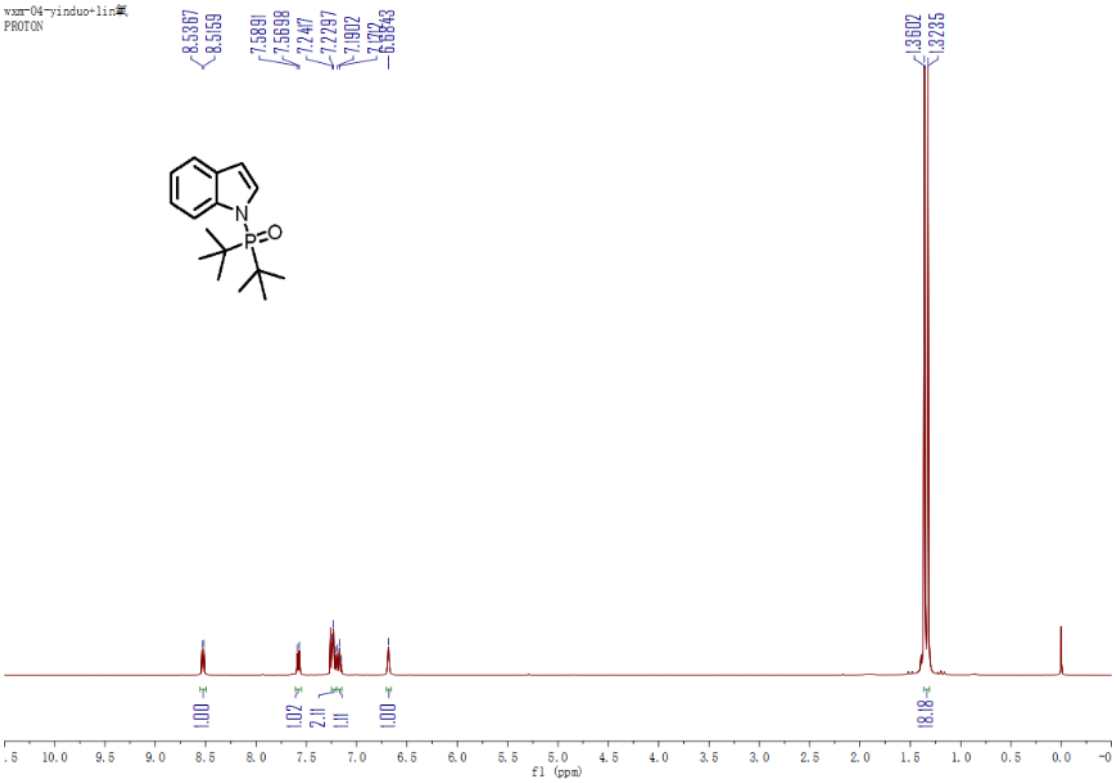
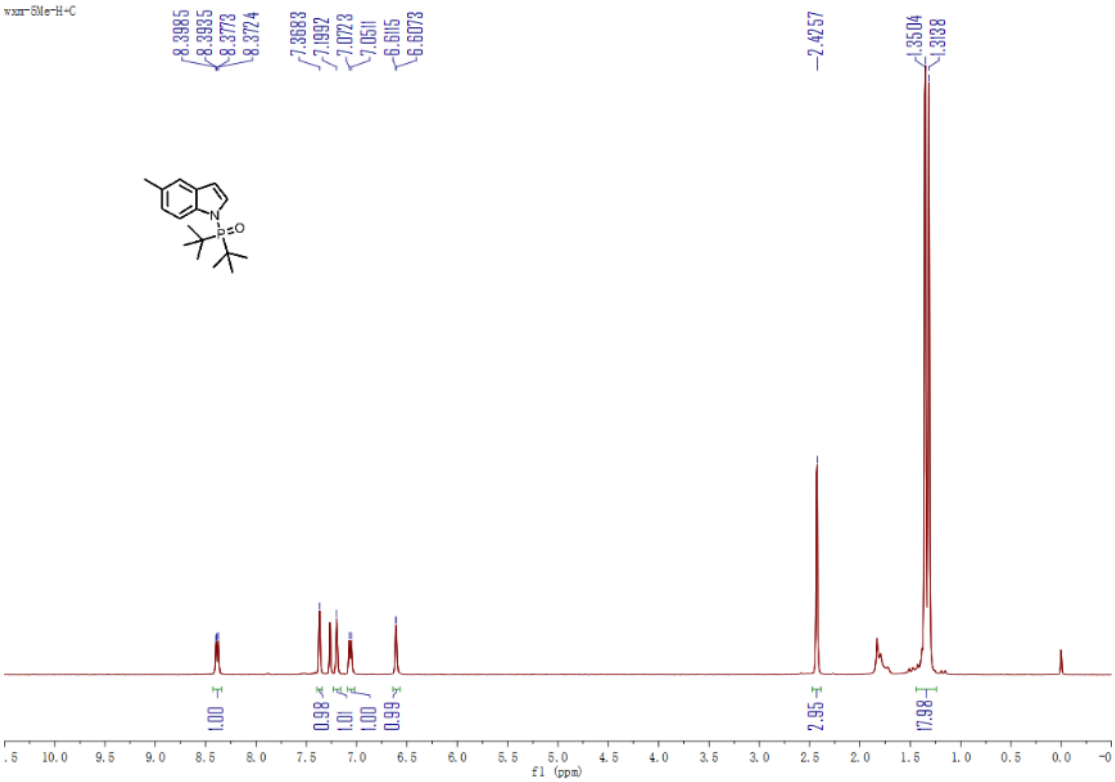
O2
C15
C16
C11
C13
C9
C12
C14
P1
O1
C10
C7
N1
C8
C6
C1
C5
C2
C4
C3
Z 131 r20210121d P 1 21/c 1 R = 0.05
RES= 0 -92 X

8. NMR spectrum

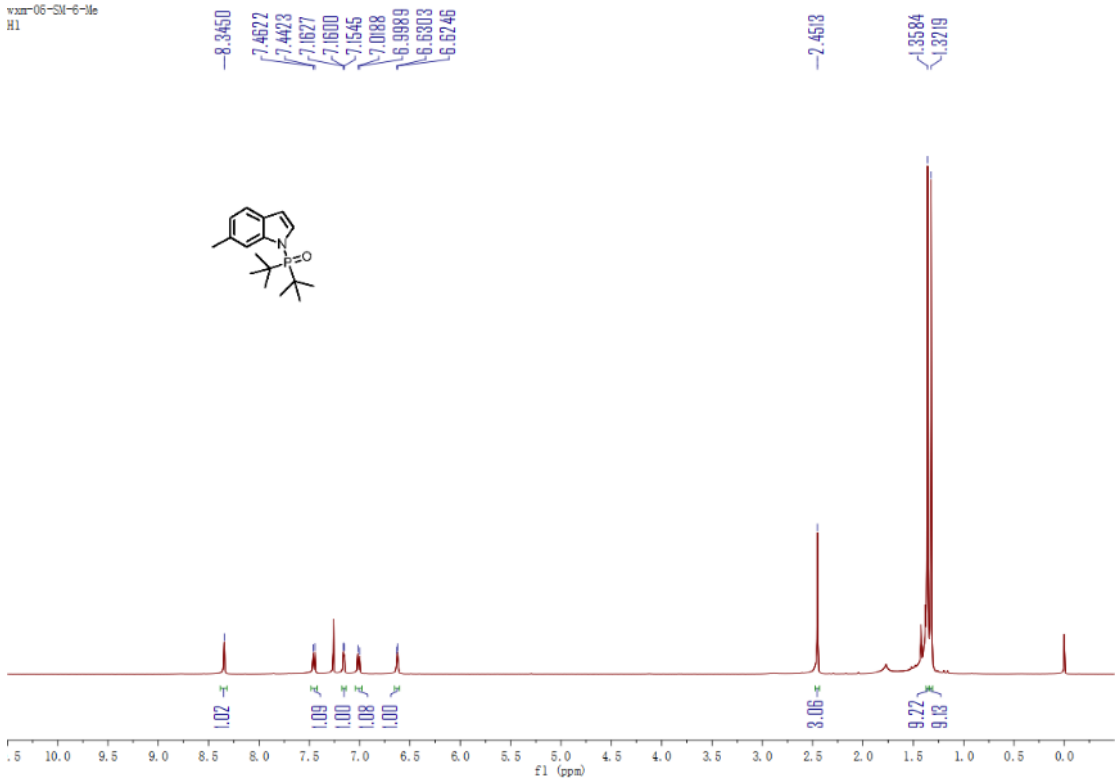
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1a**



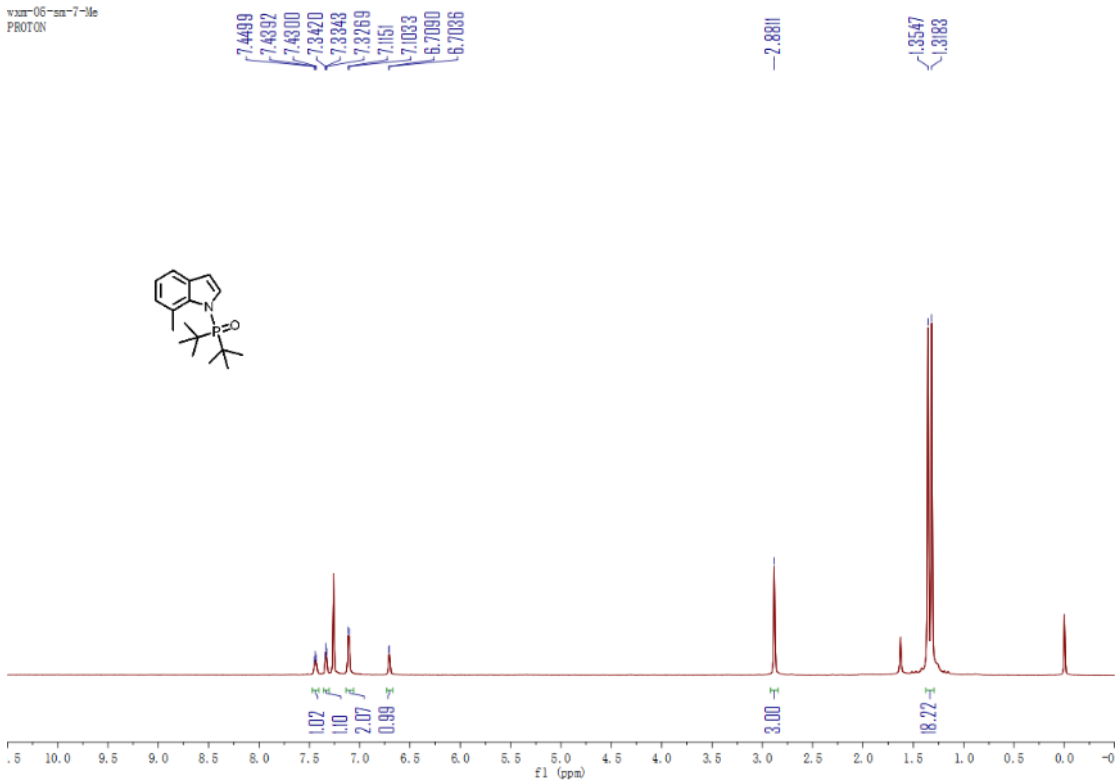
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1b**



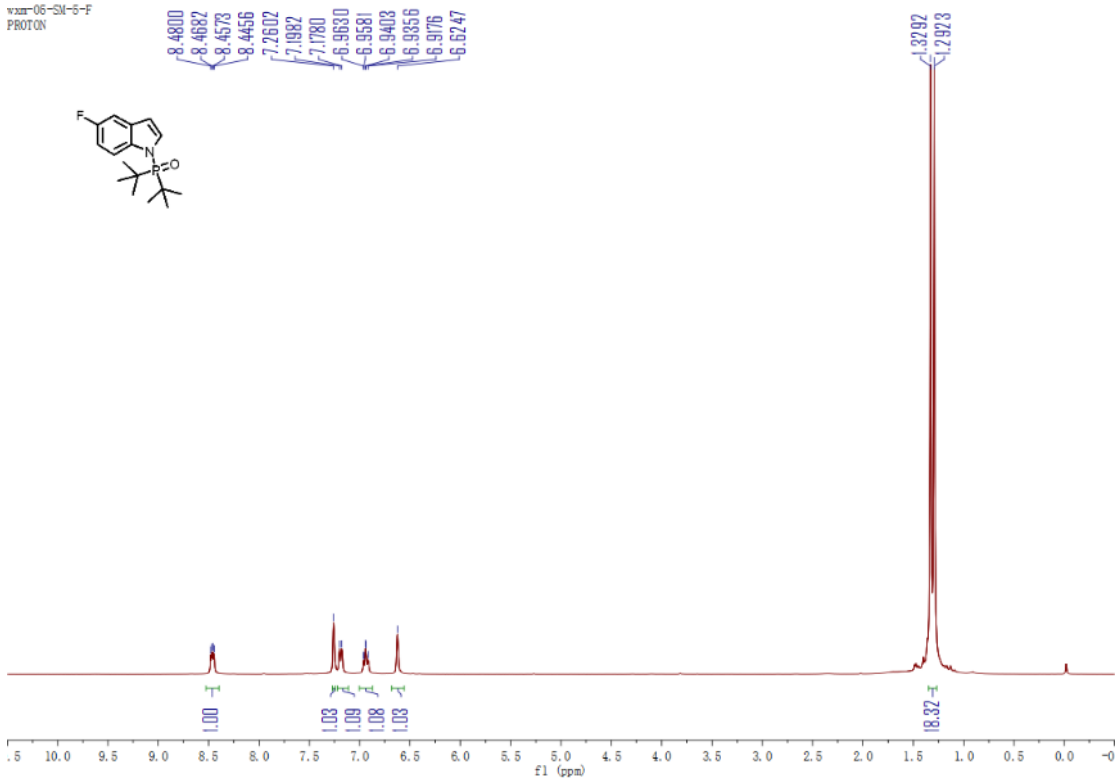
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1c**



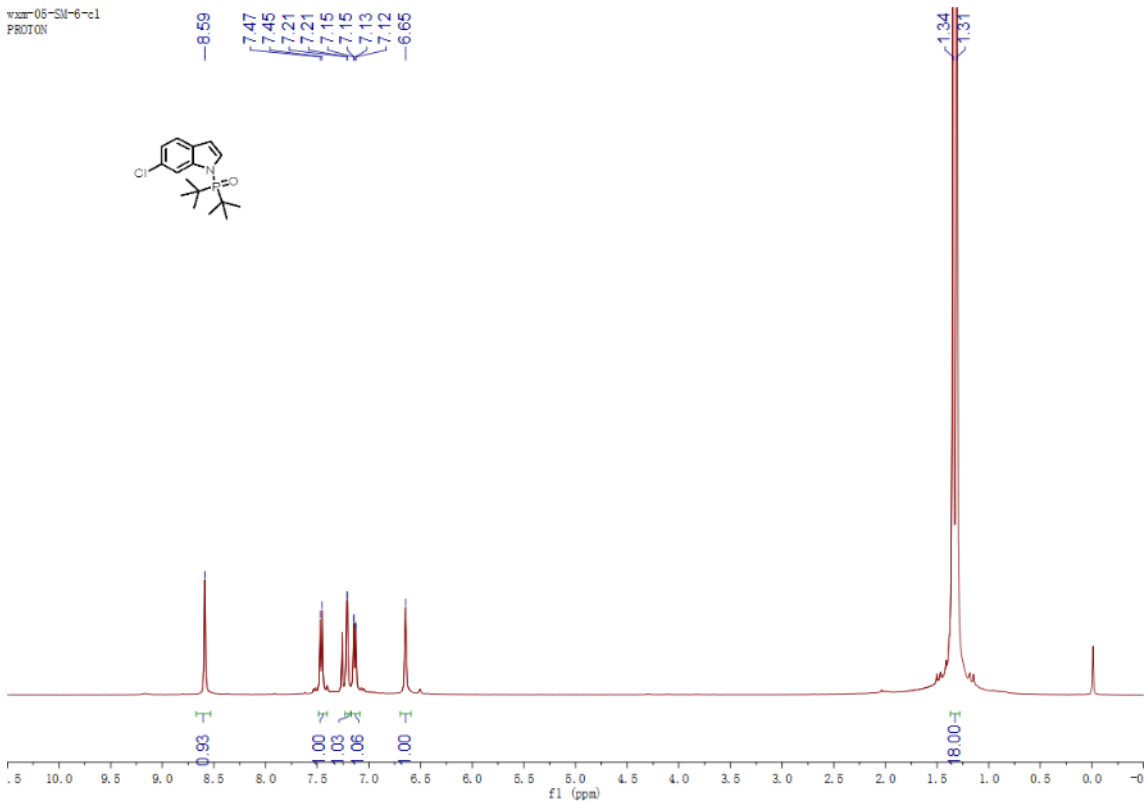
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1d**



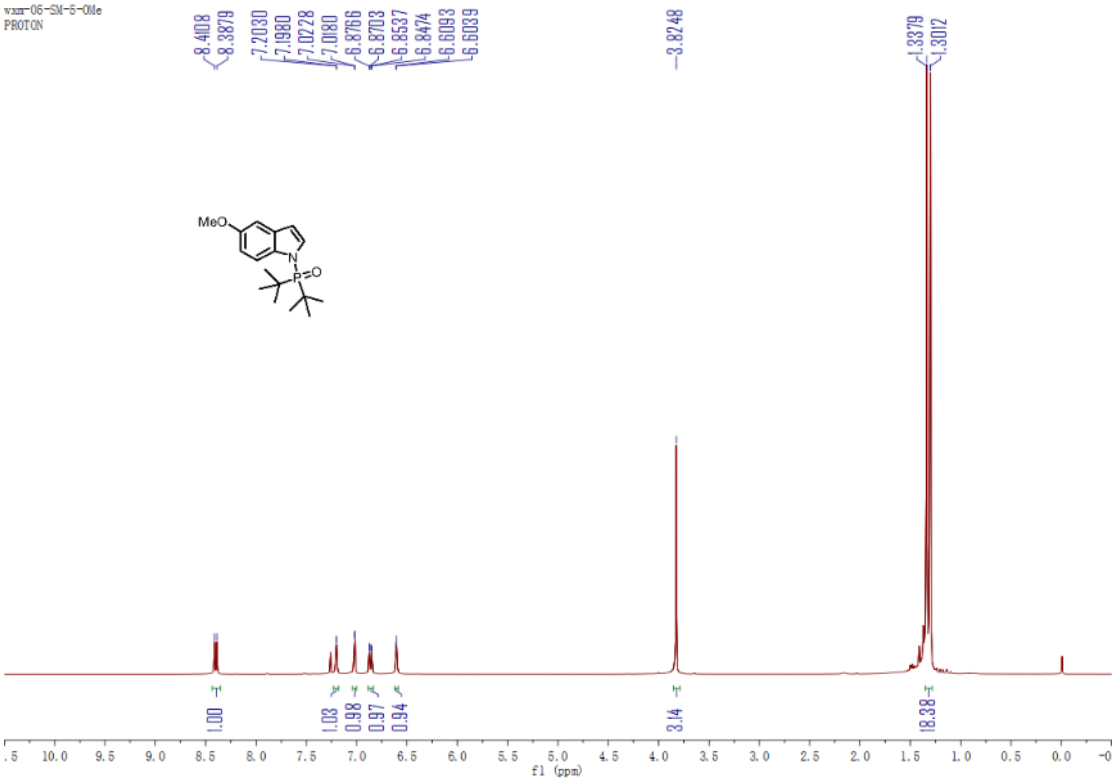
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1e**



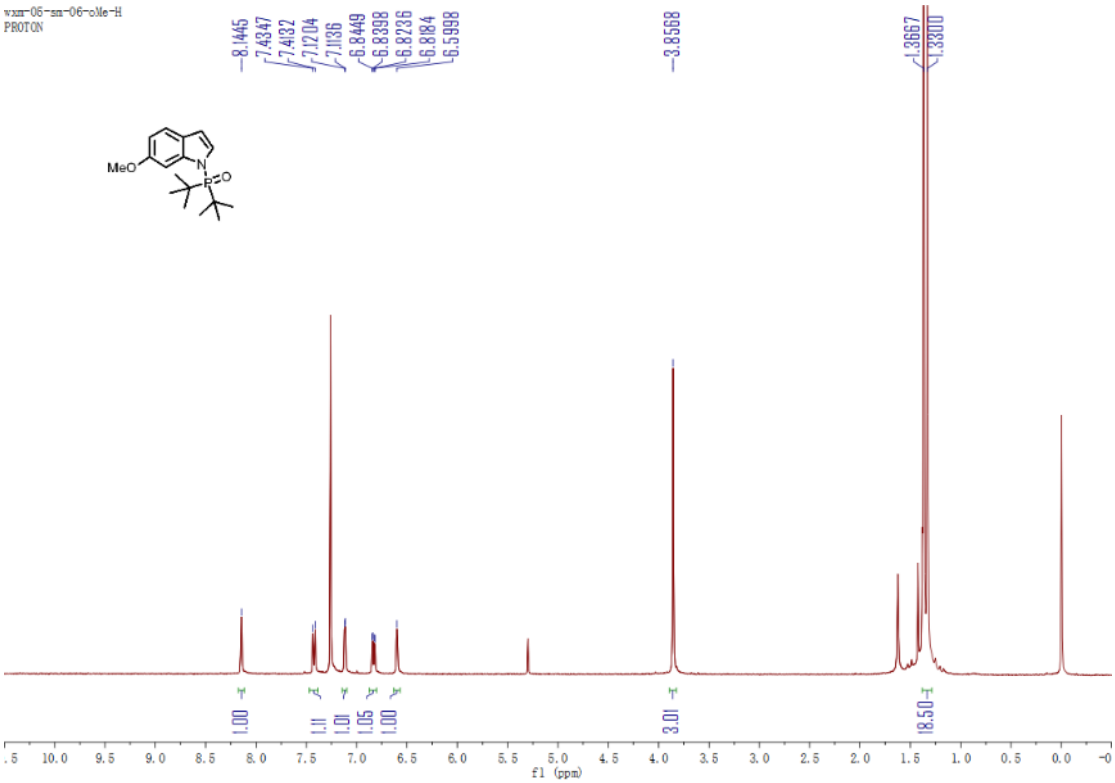
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1f**



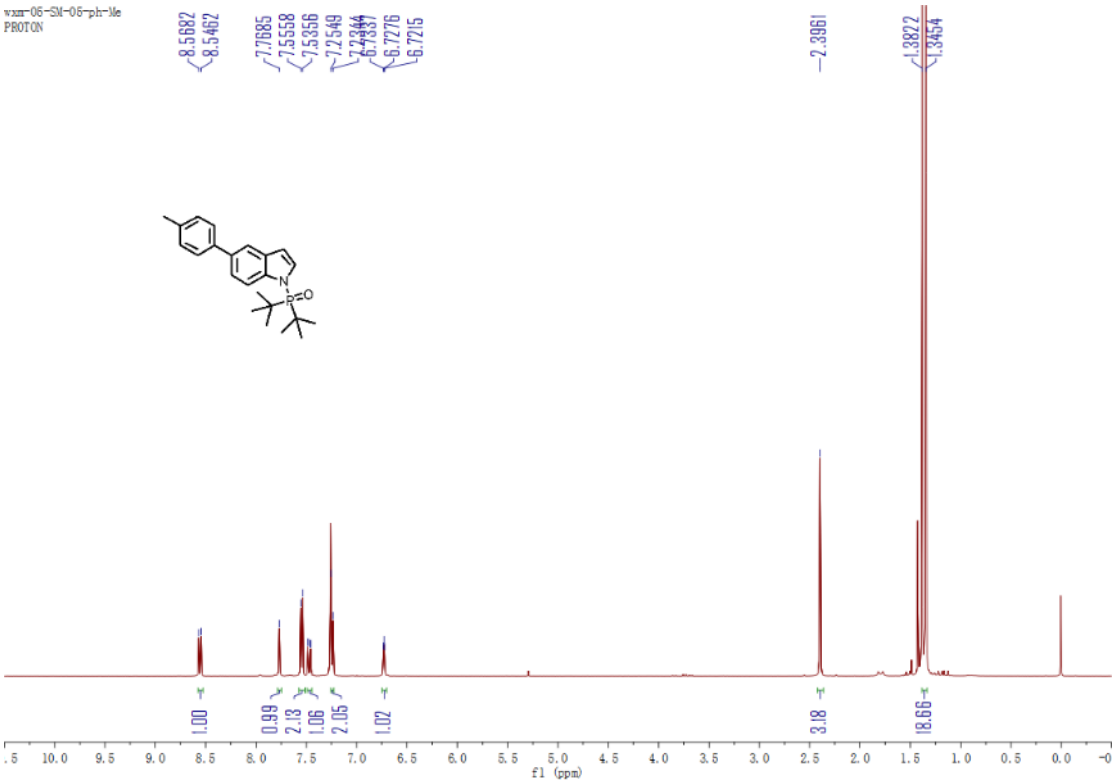
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1g**



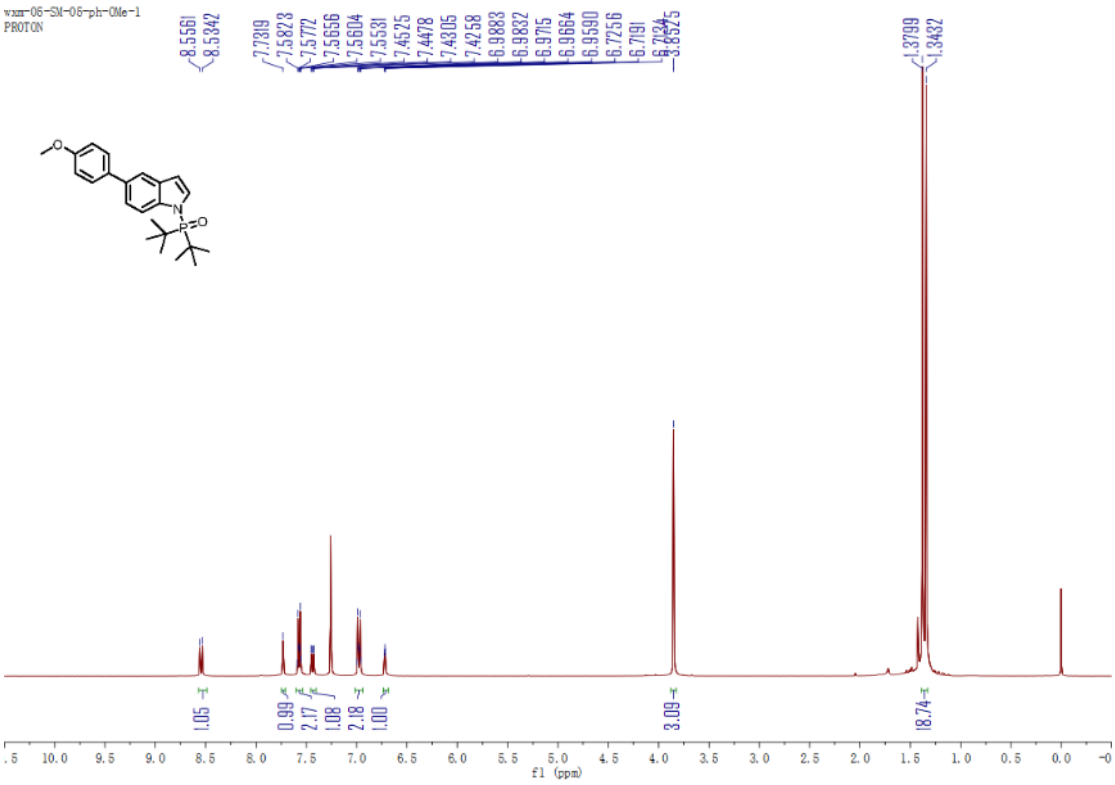
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1h**



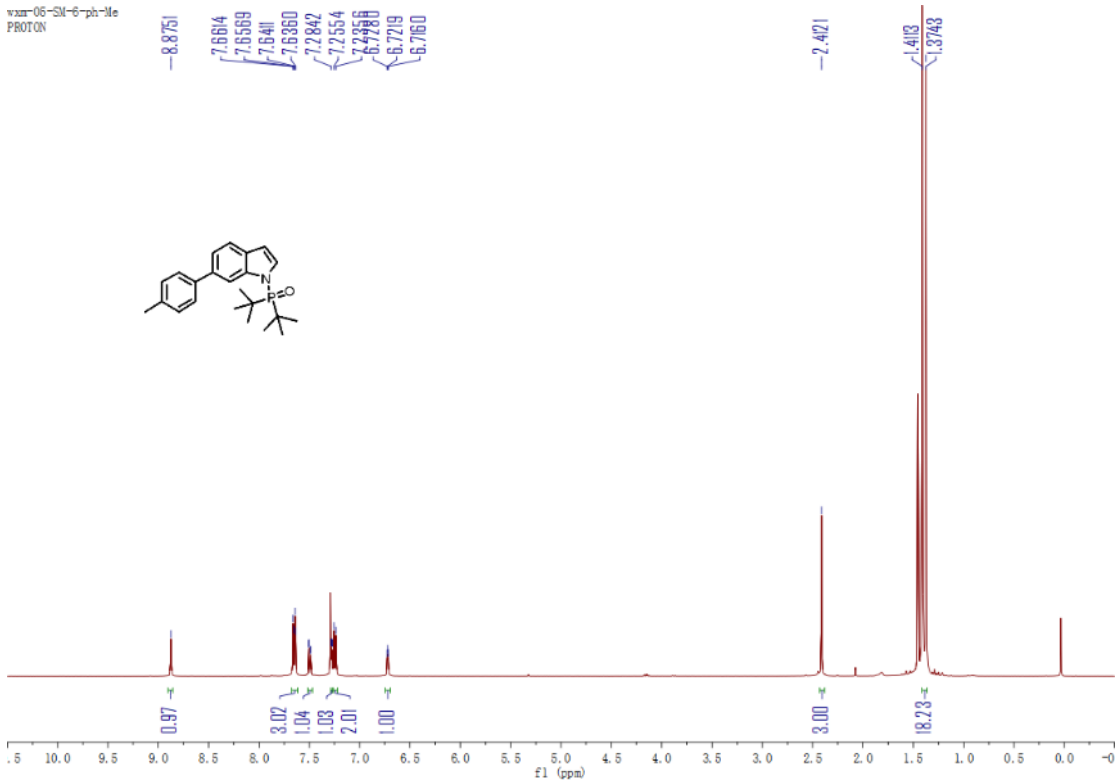
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1i**



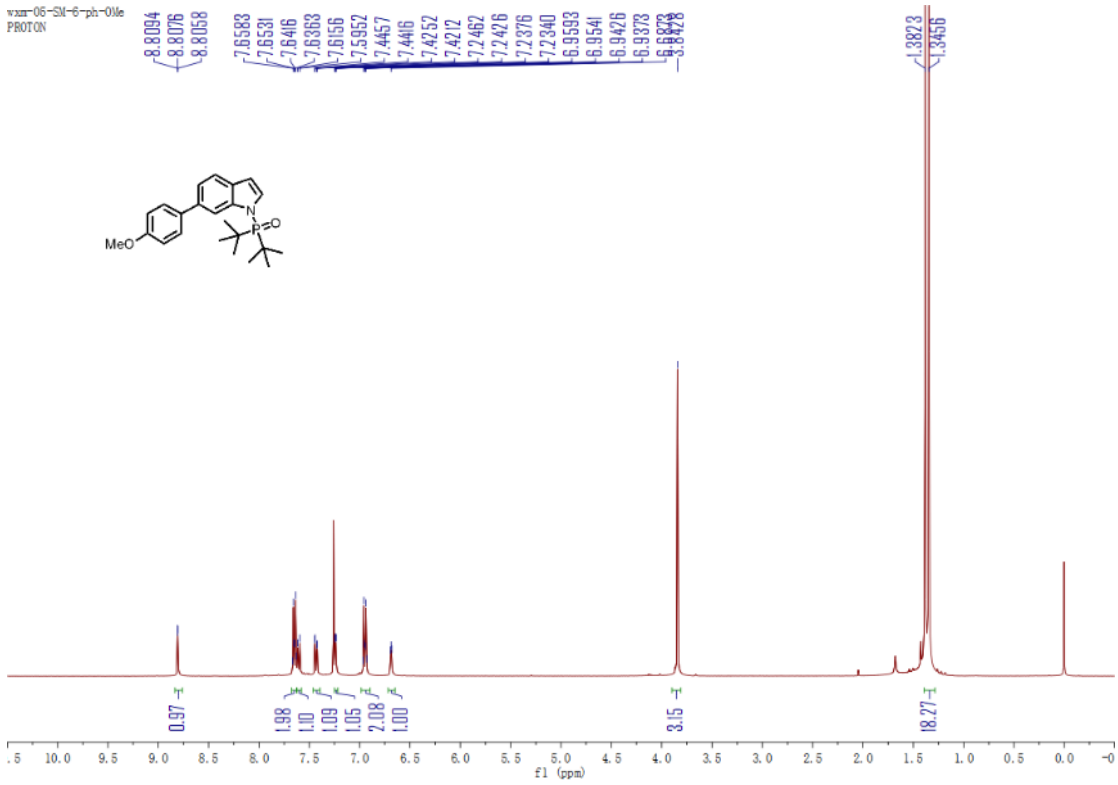
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1j**



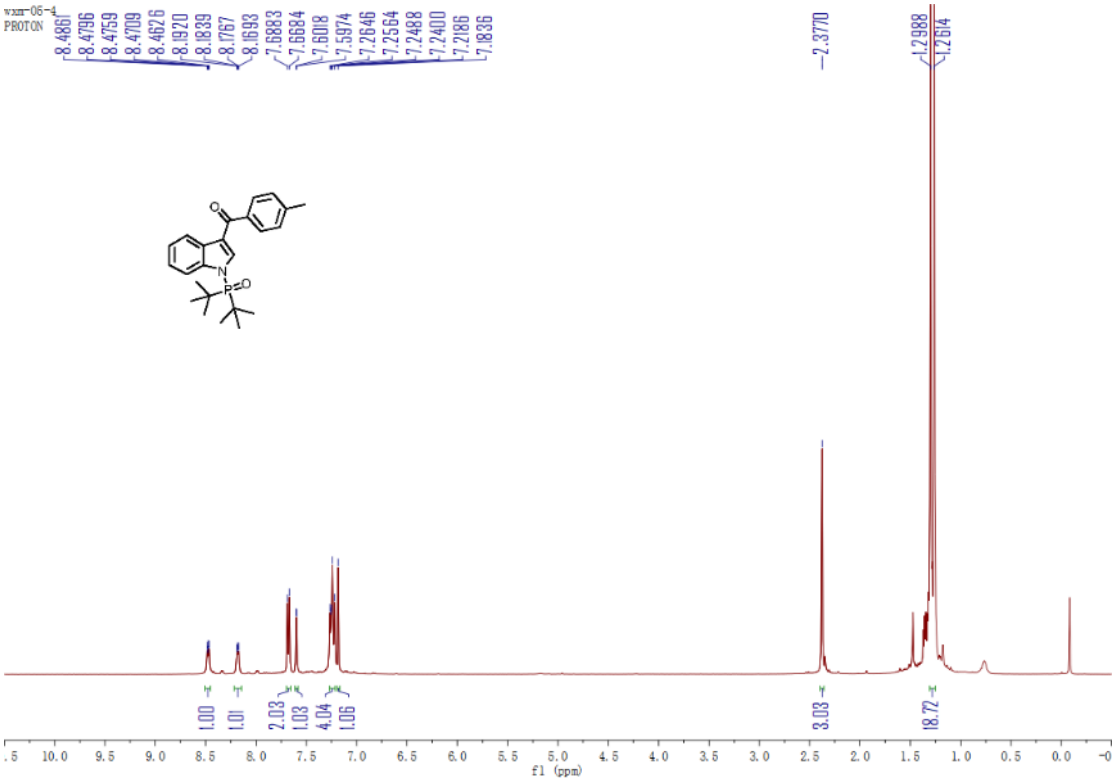
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1k**



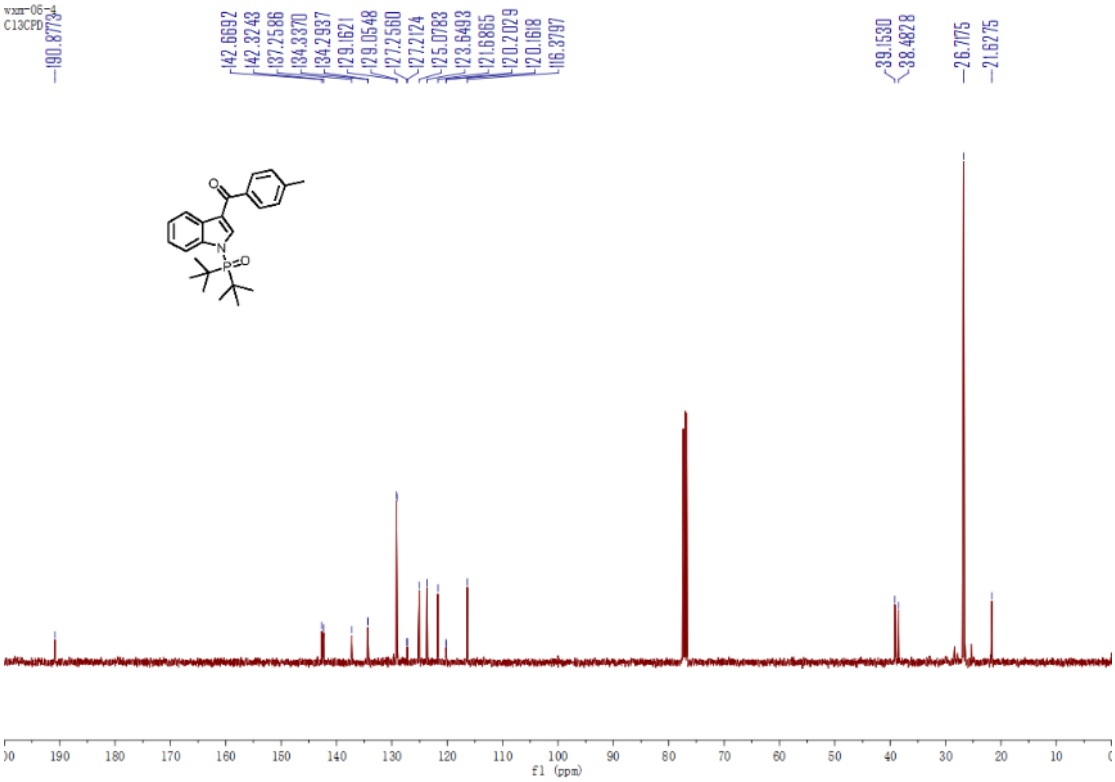
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **1l**



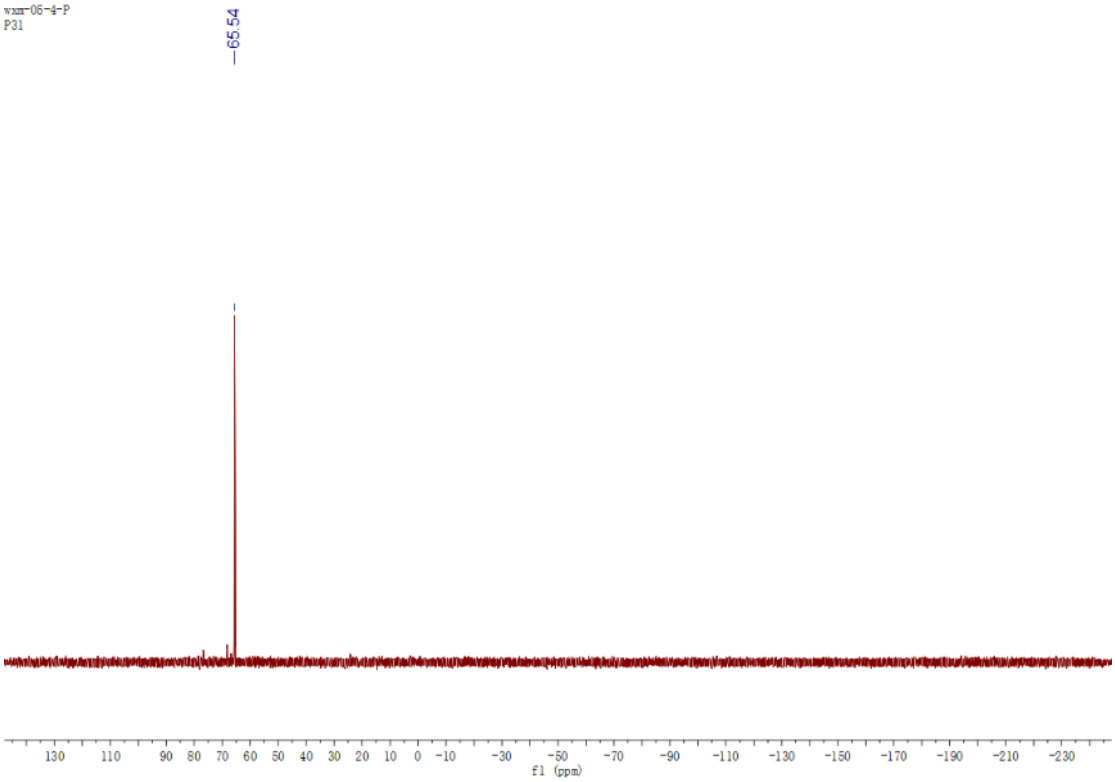
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3a**



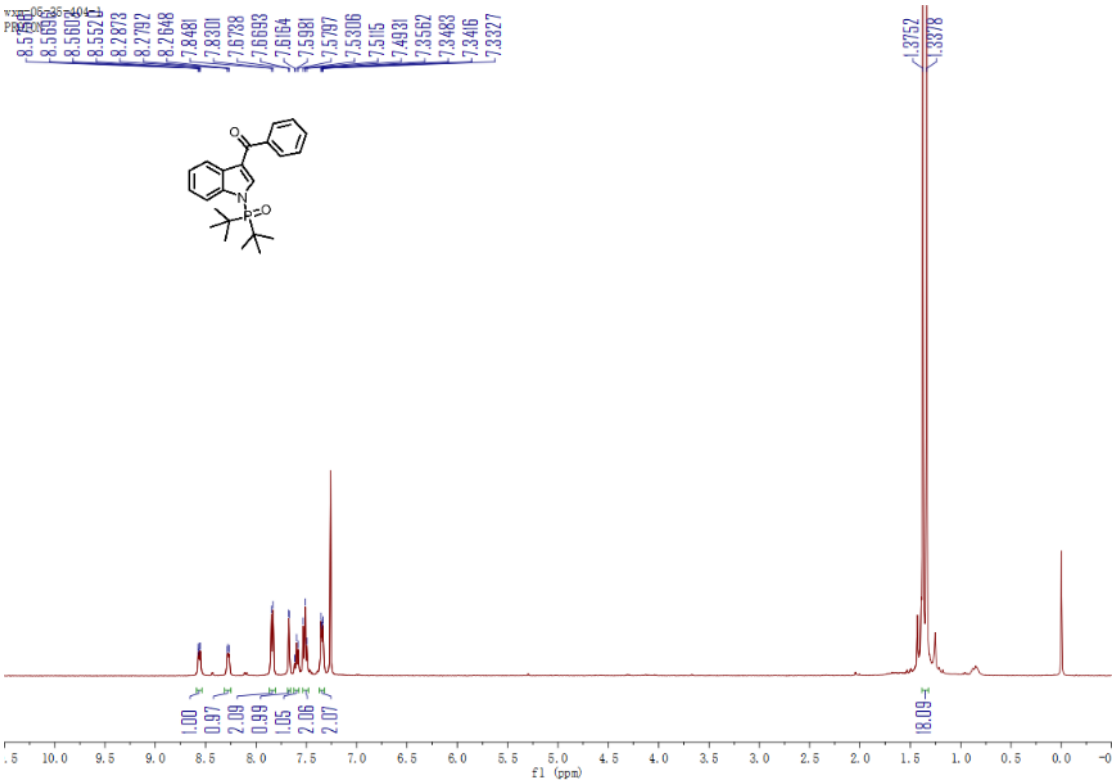
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3a**



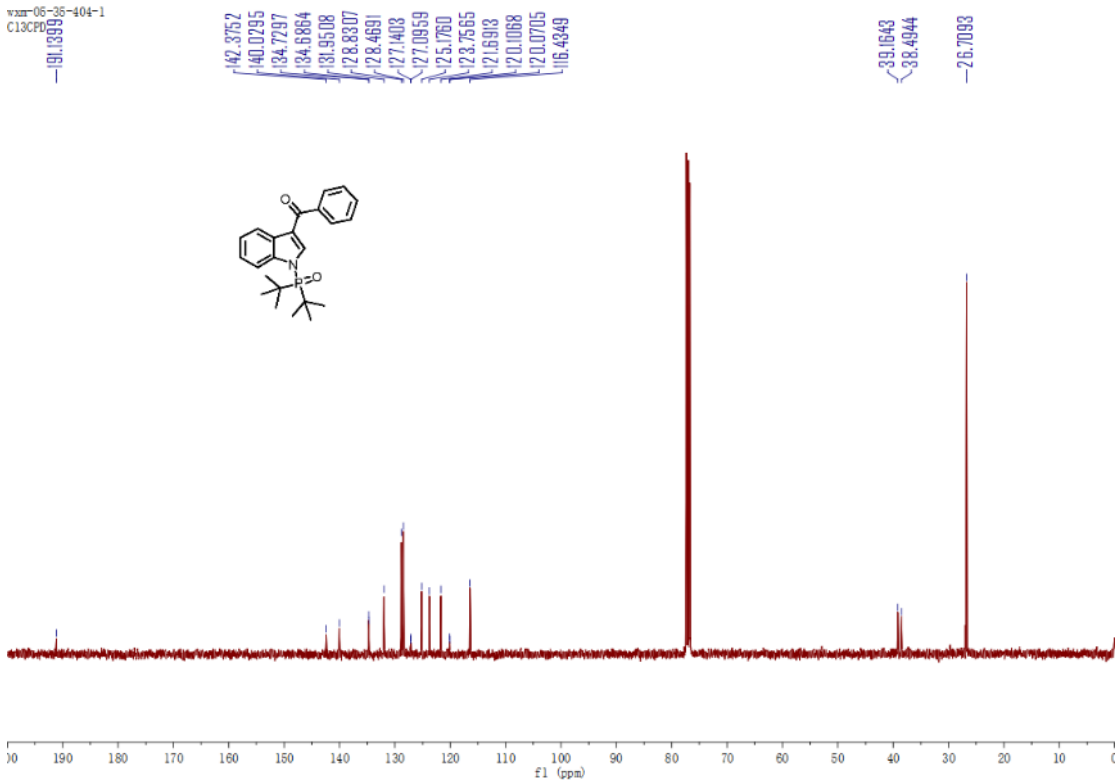
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3a**



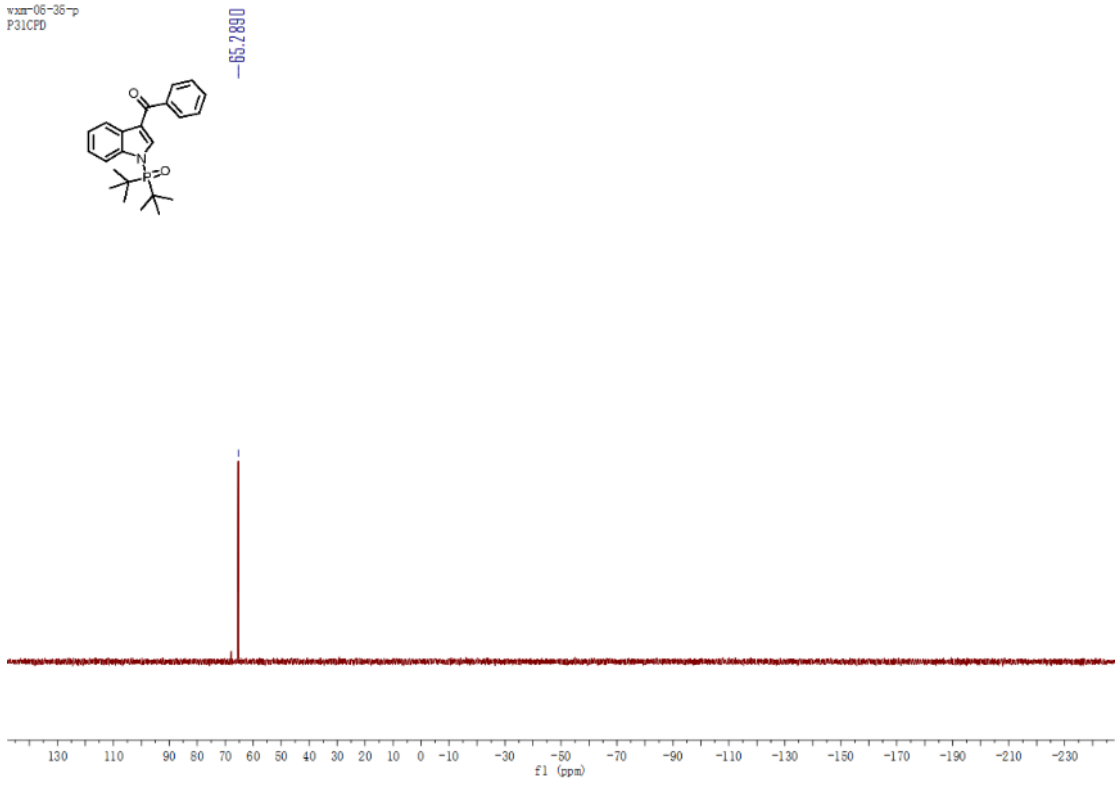
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3b**



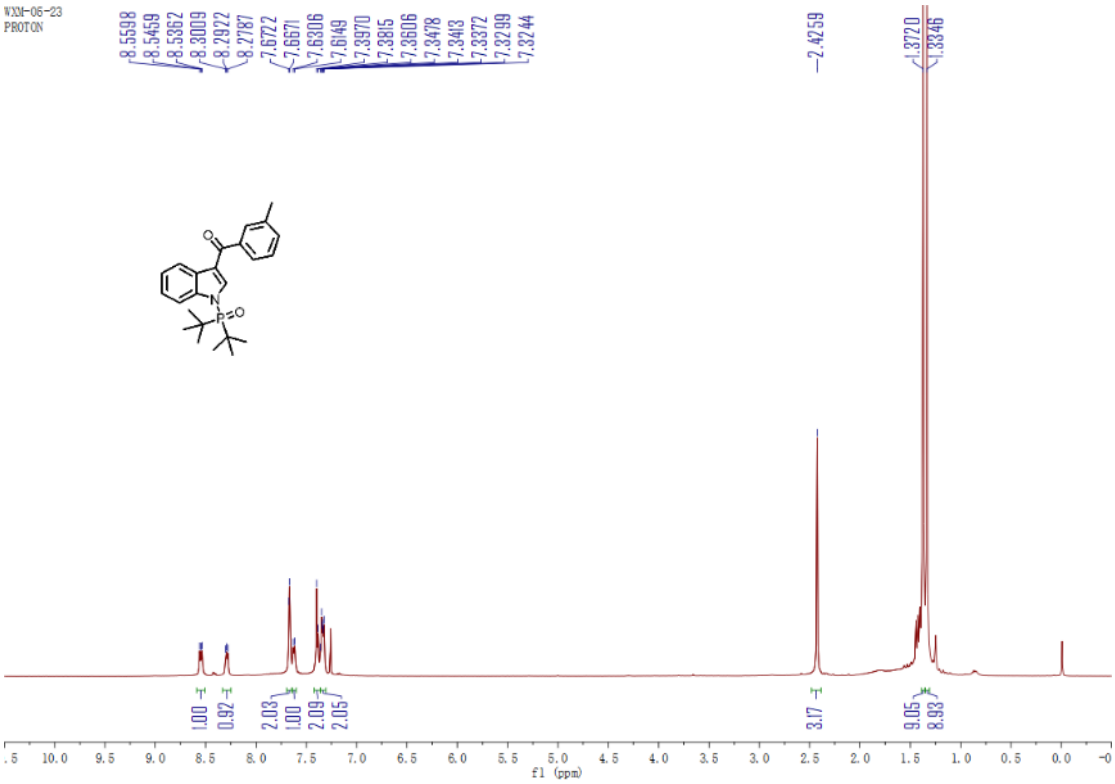
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3b**



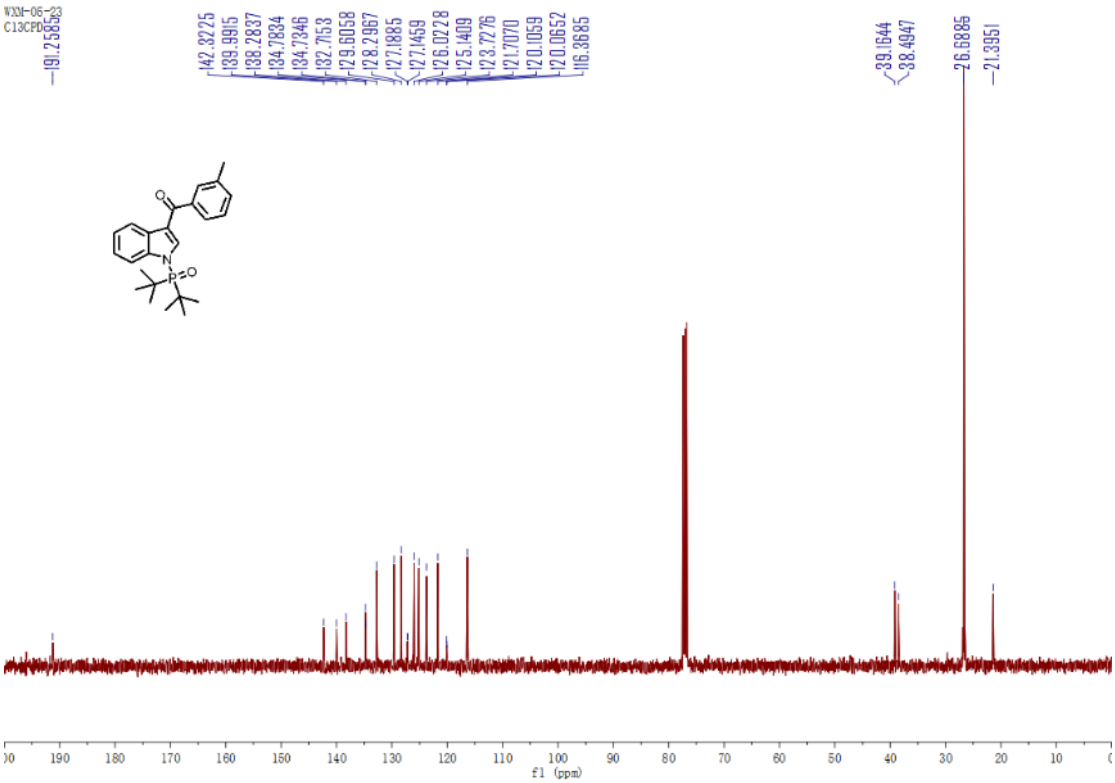
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3b**



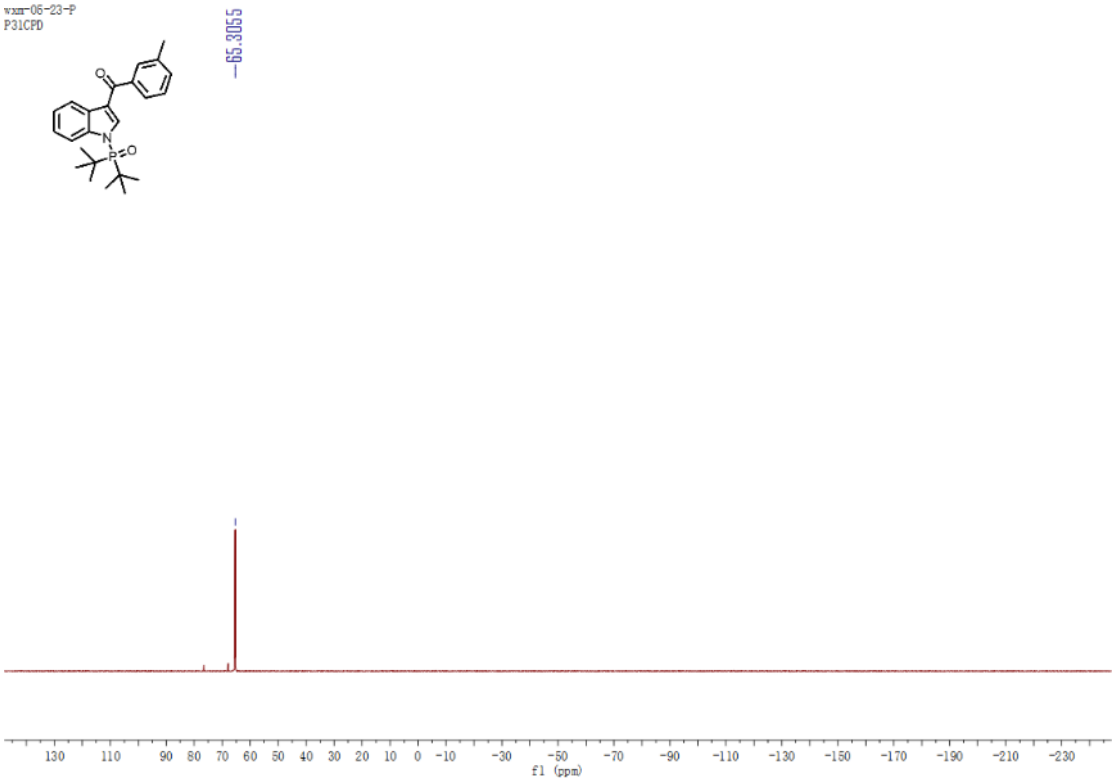
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3c**



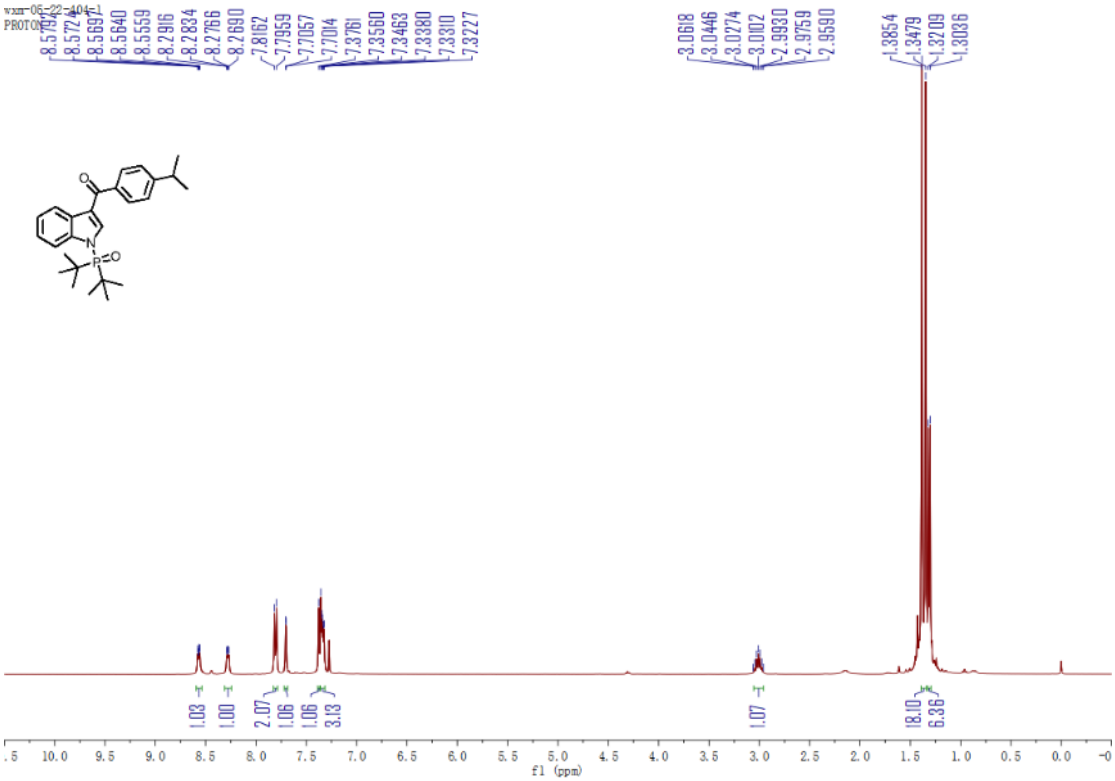
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3c**



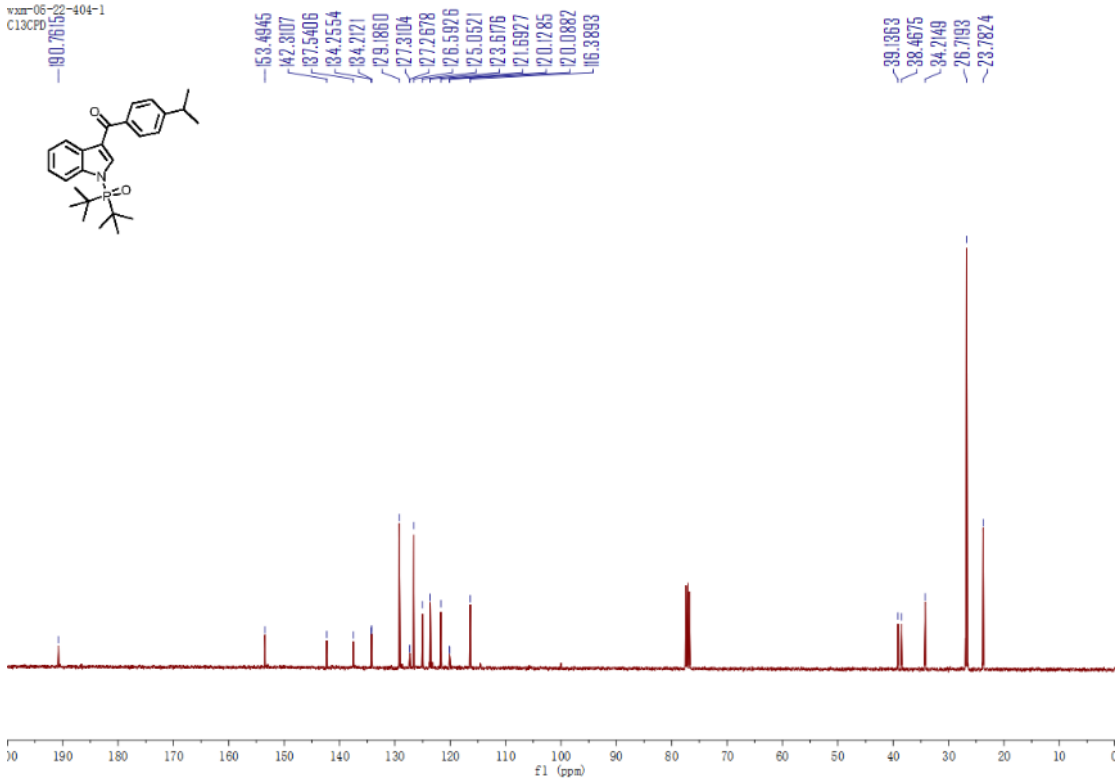
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3c**



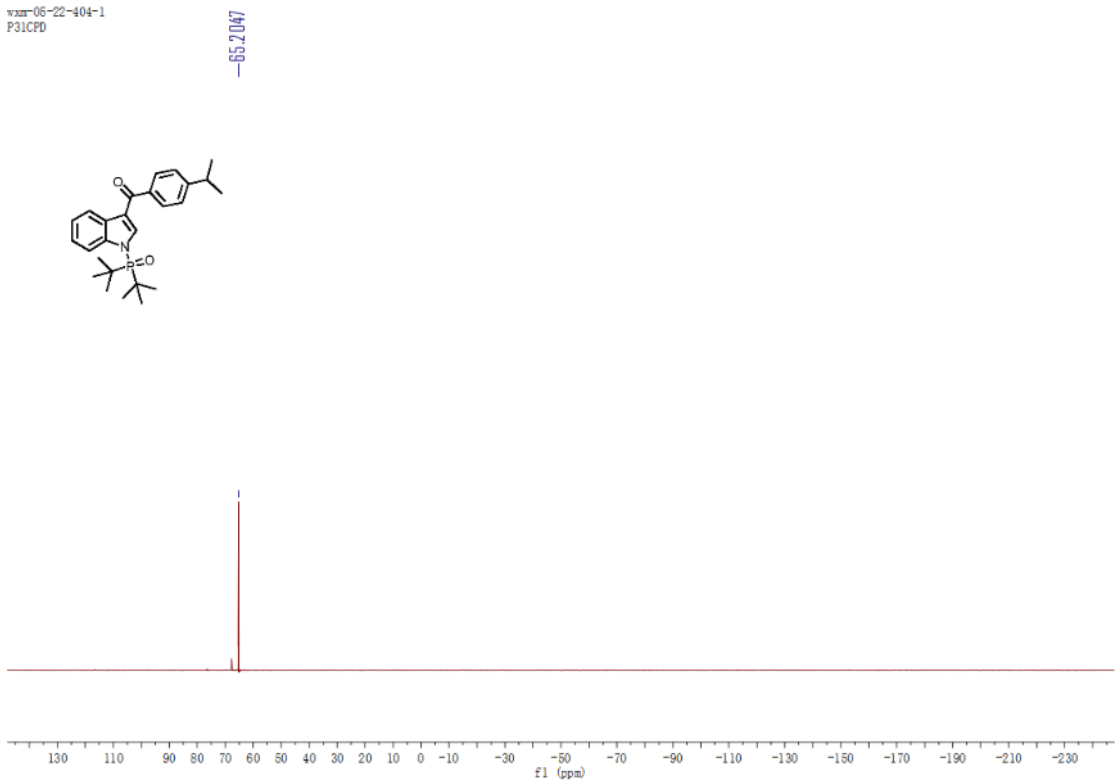
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3d**



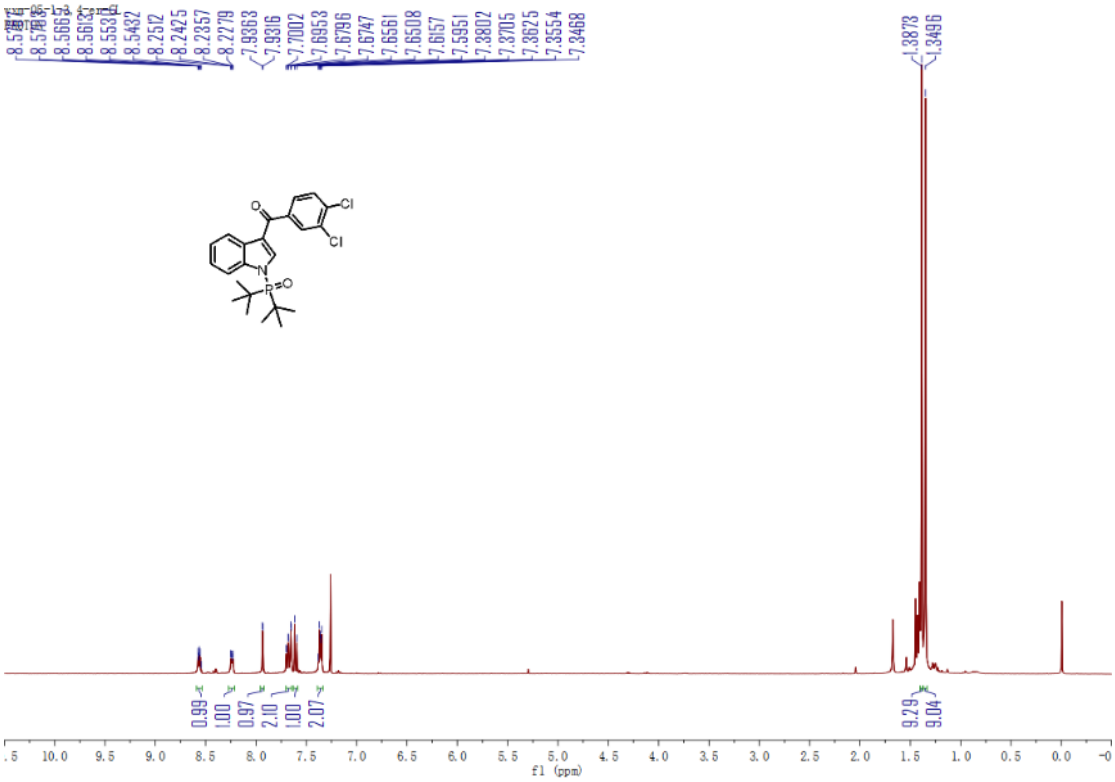
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3d**



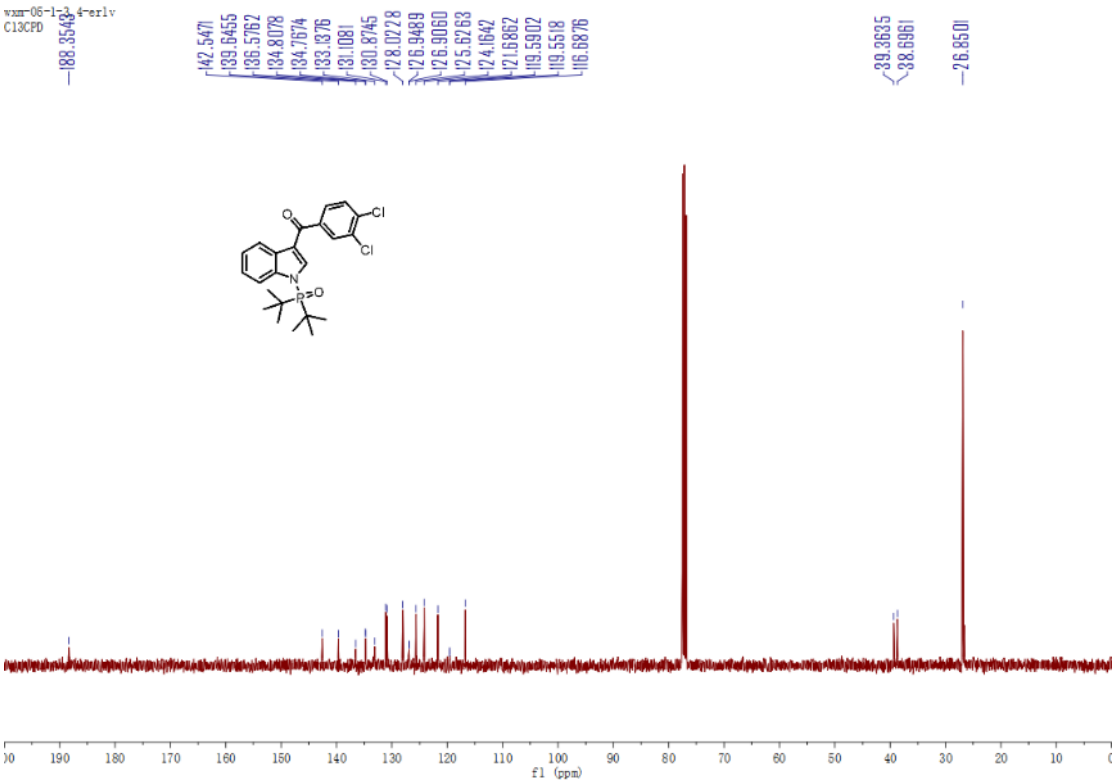
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3d**



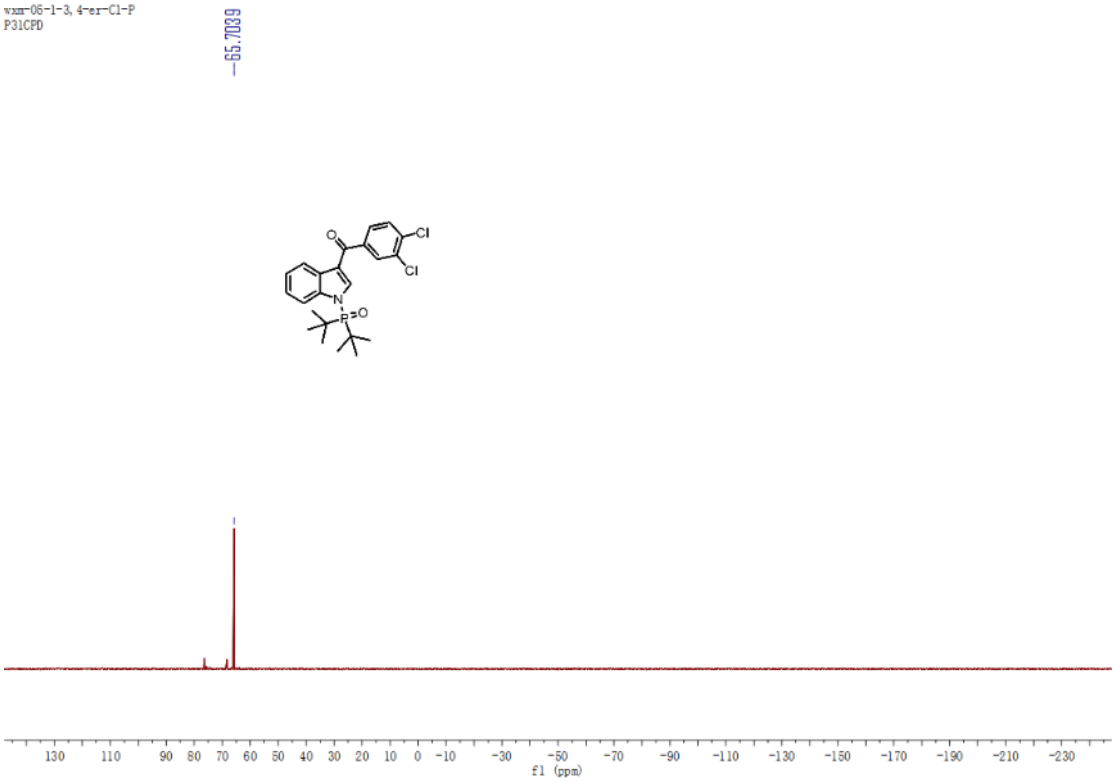
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3e**



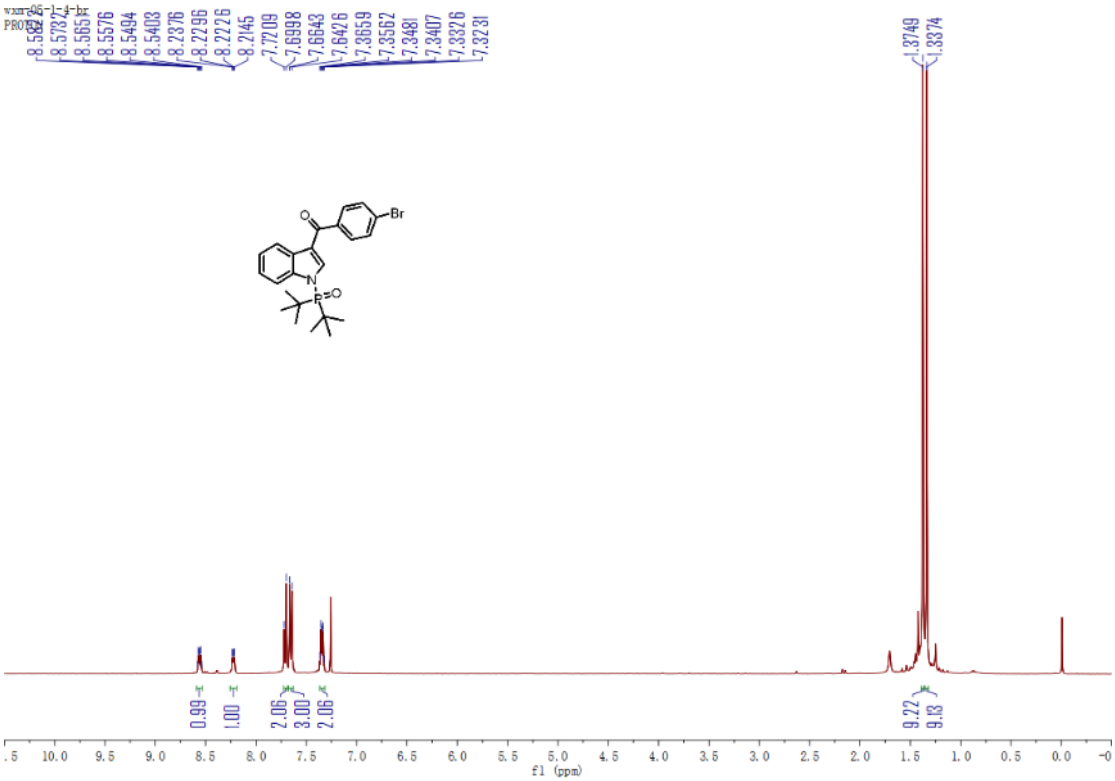
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3e**



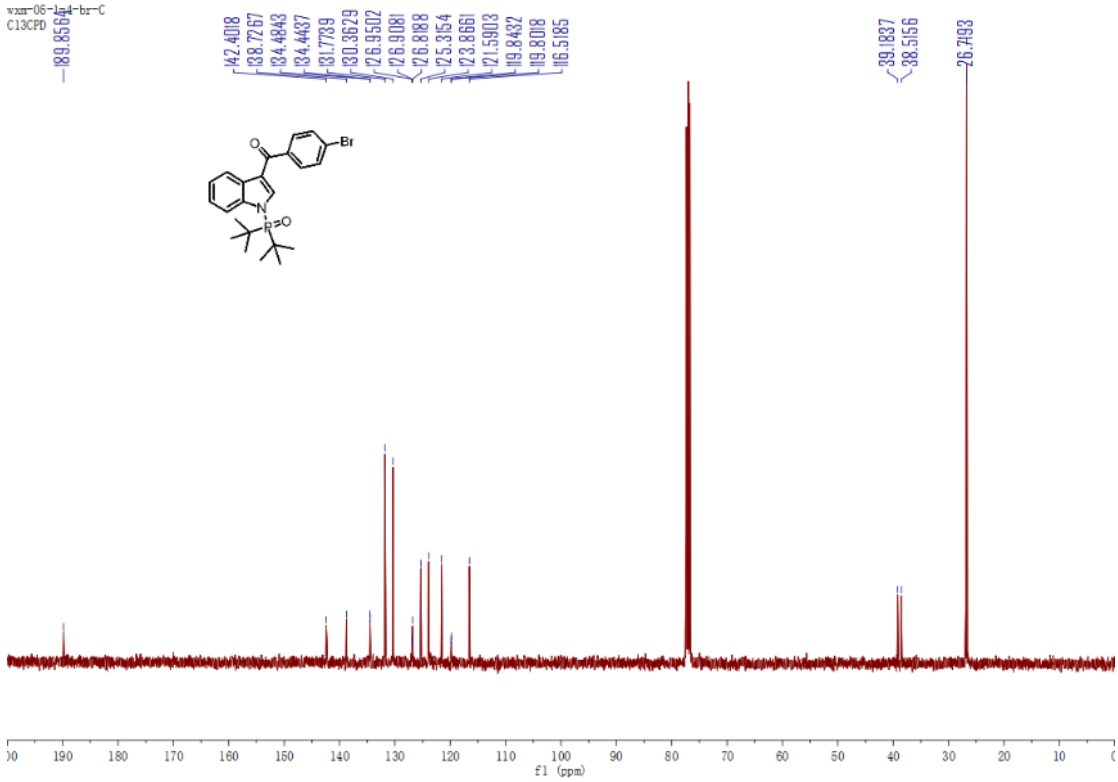
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3e**



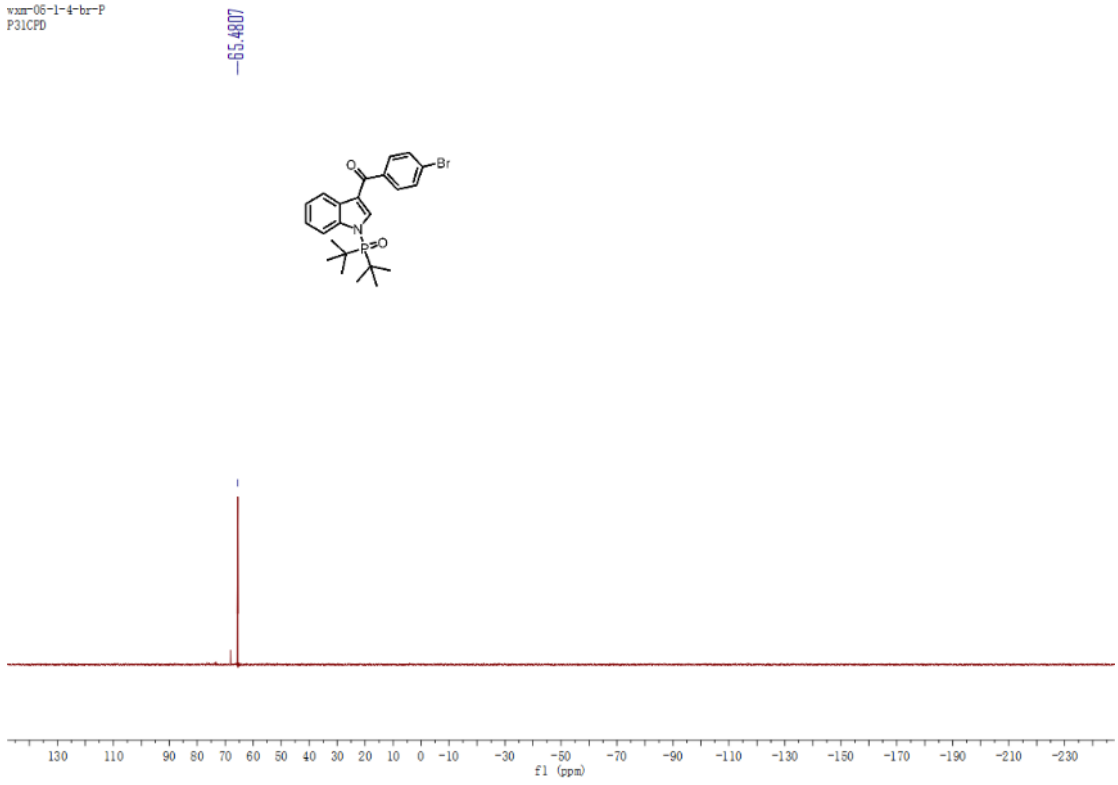
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3f**



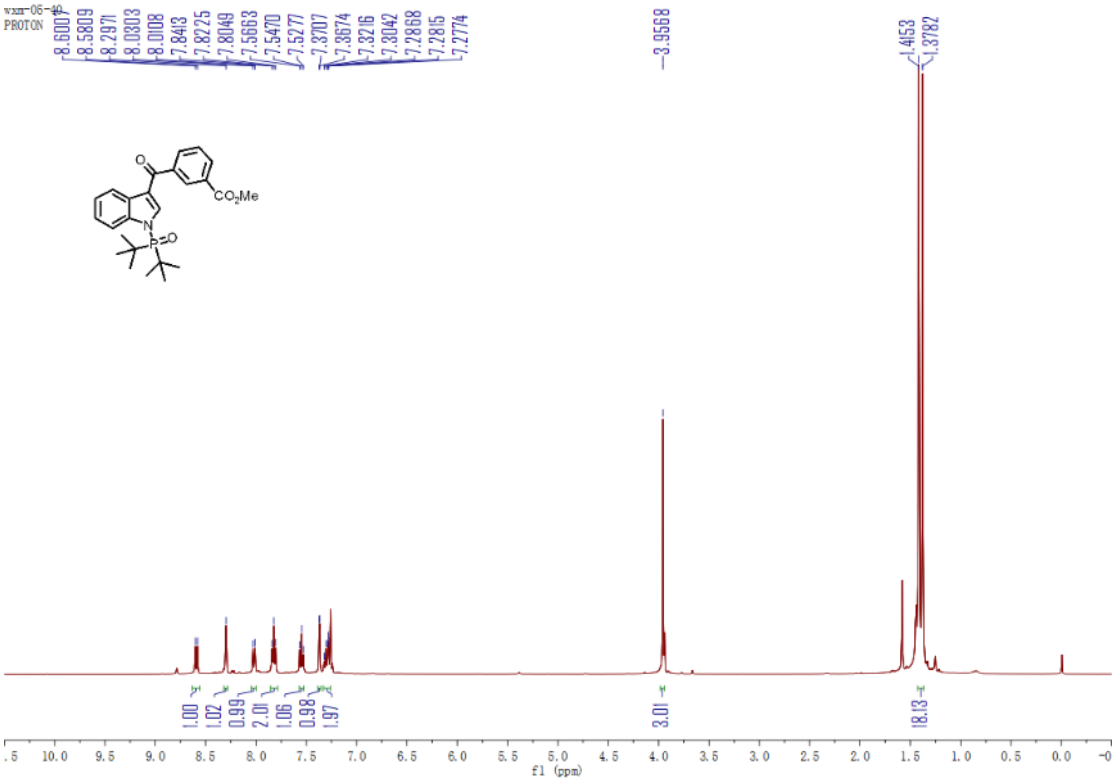
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3f**



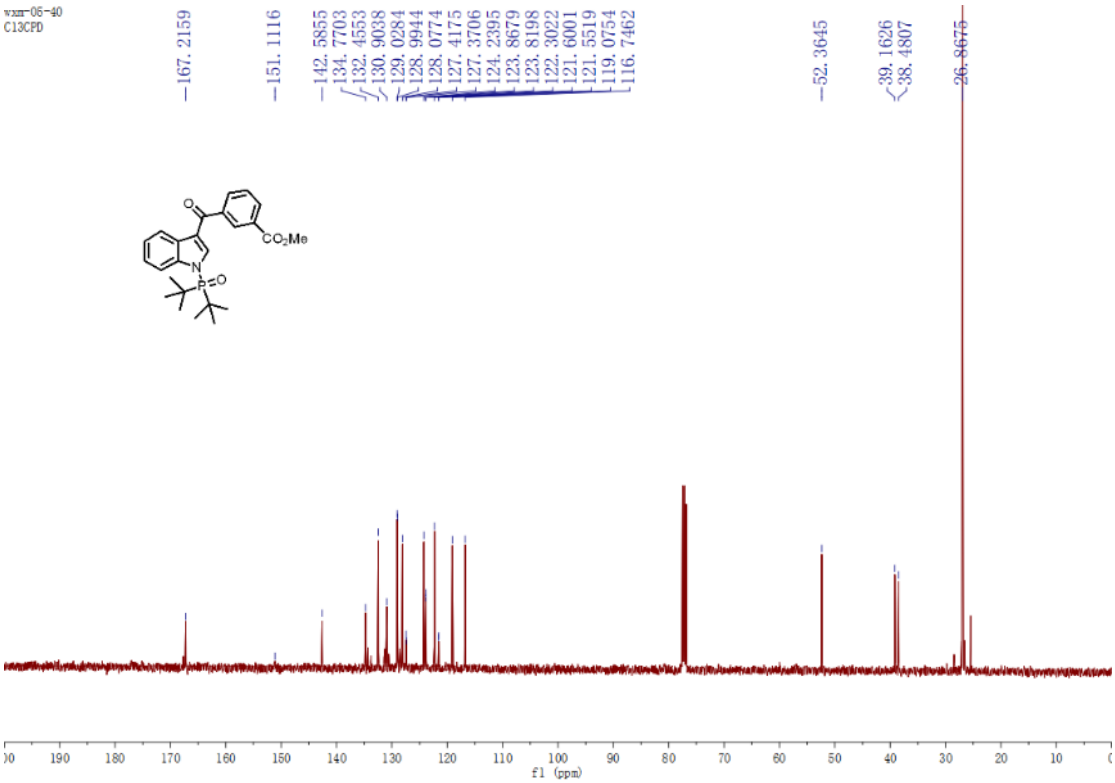
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3f**



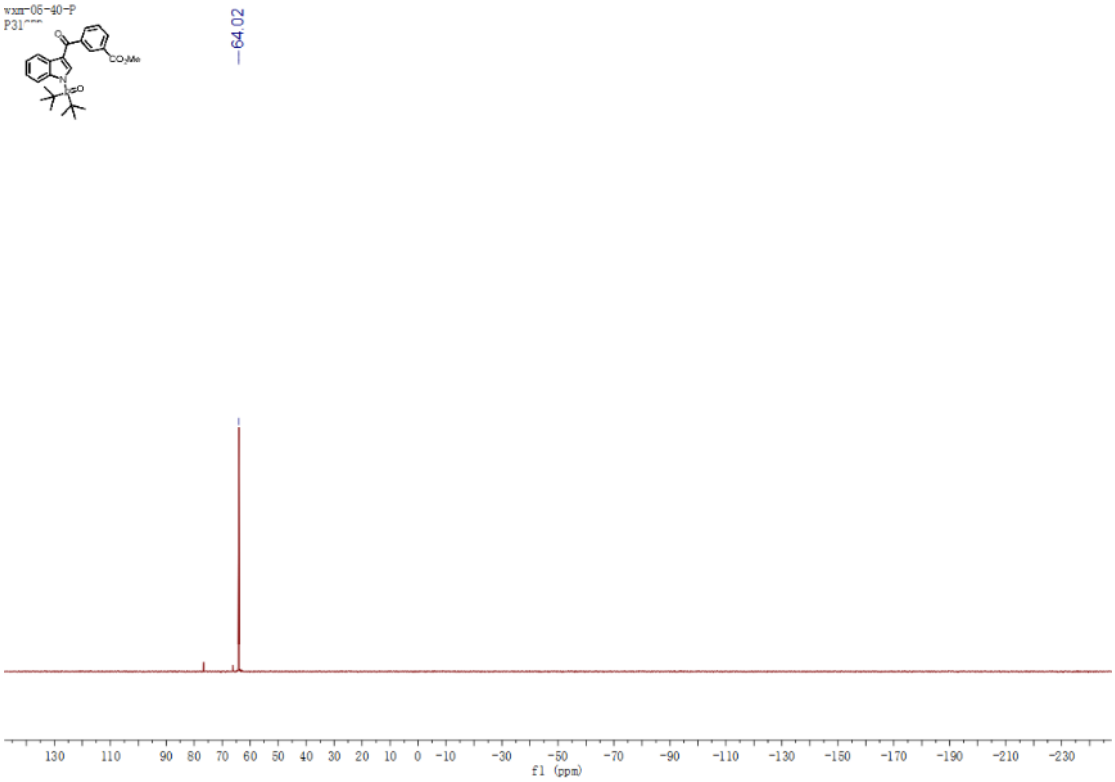
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3g**



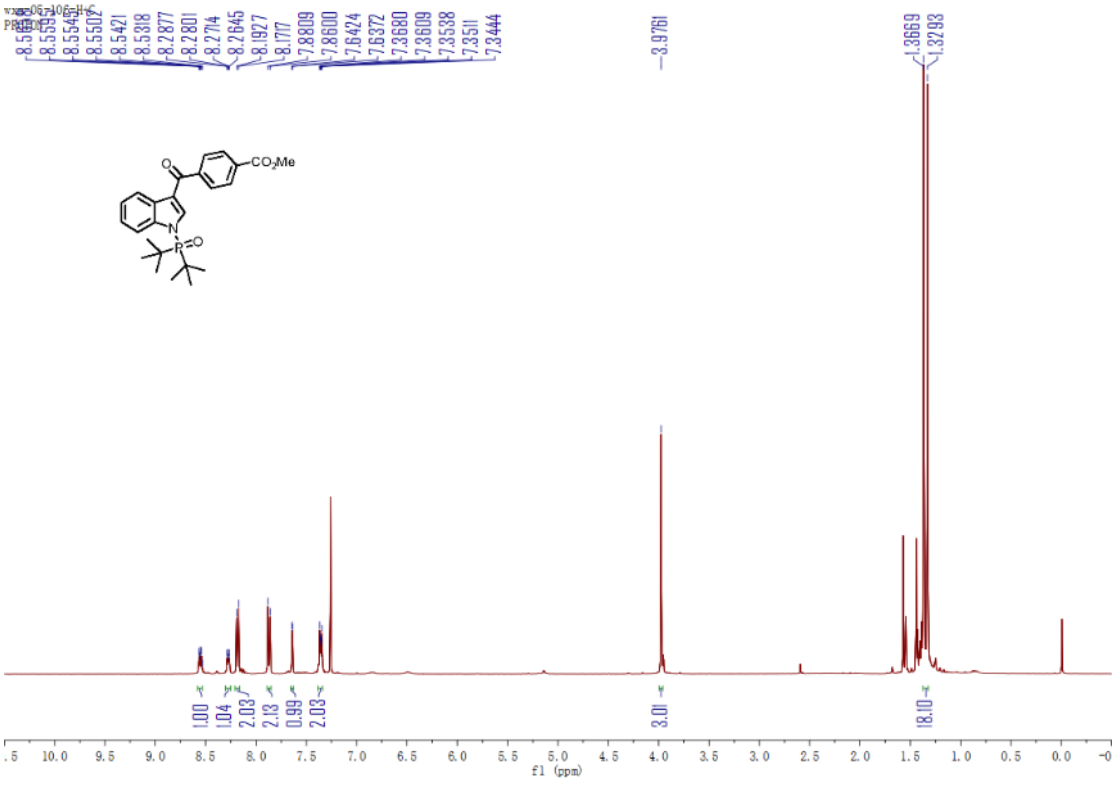
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3g**



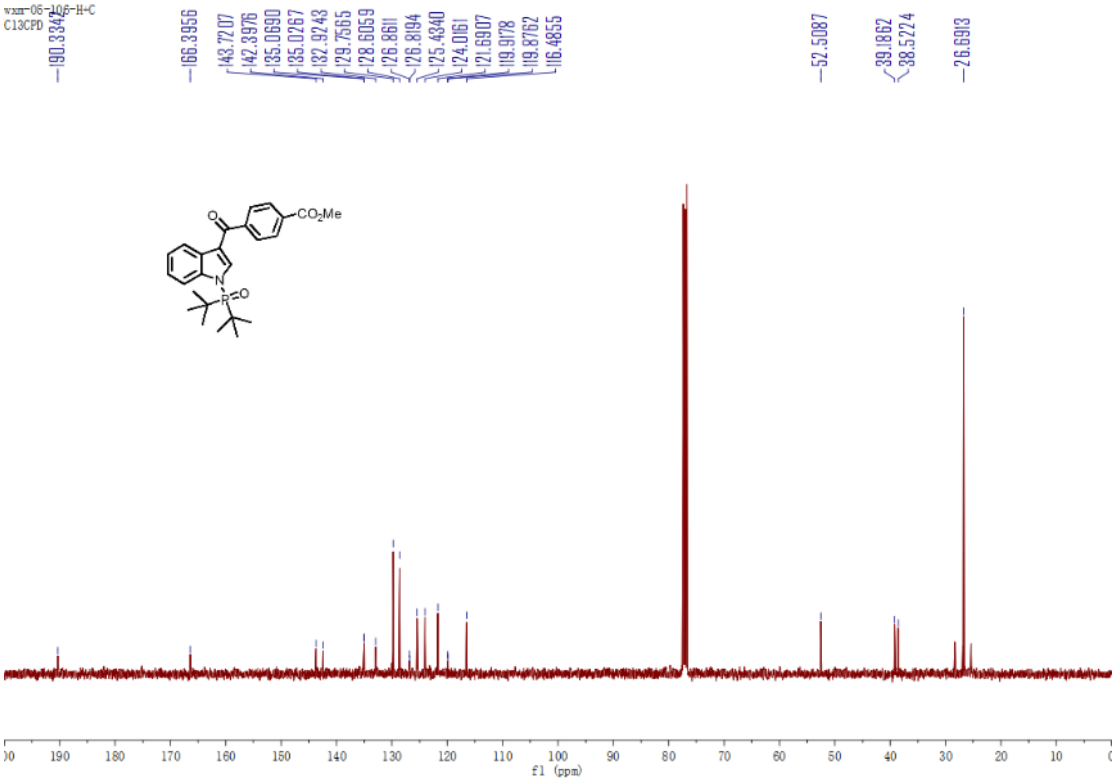
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3g**



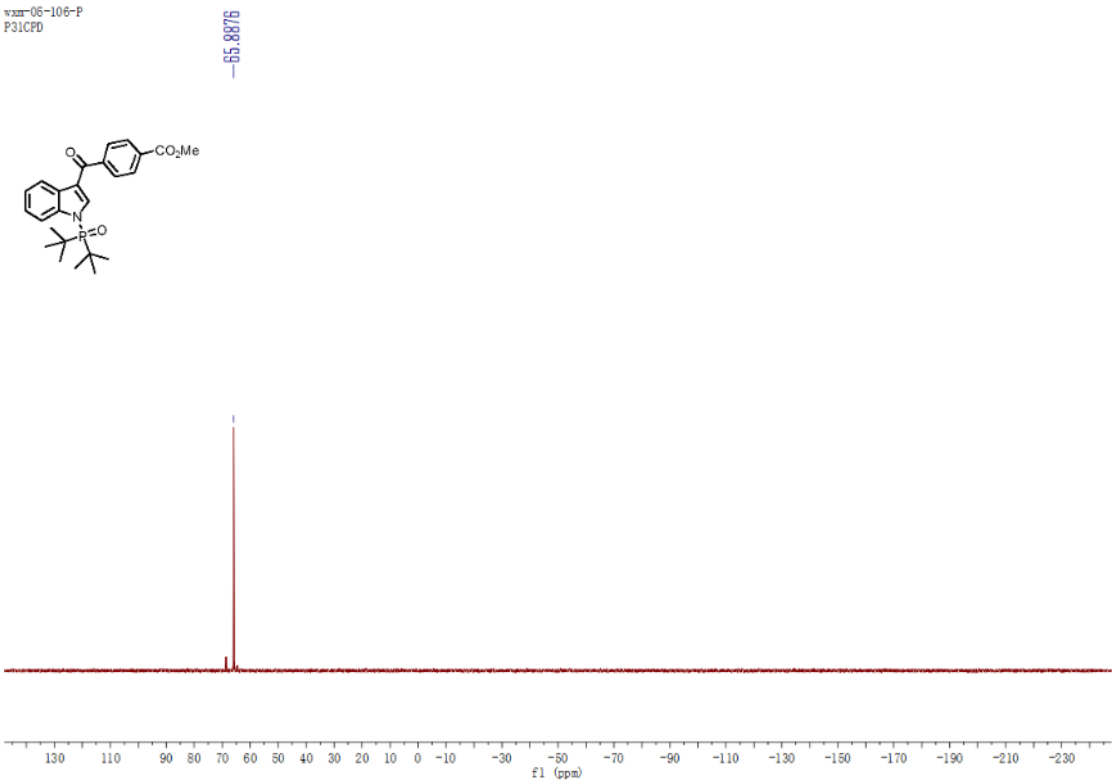
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3h**



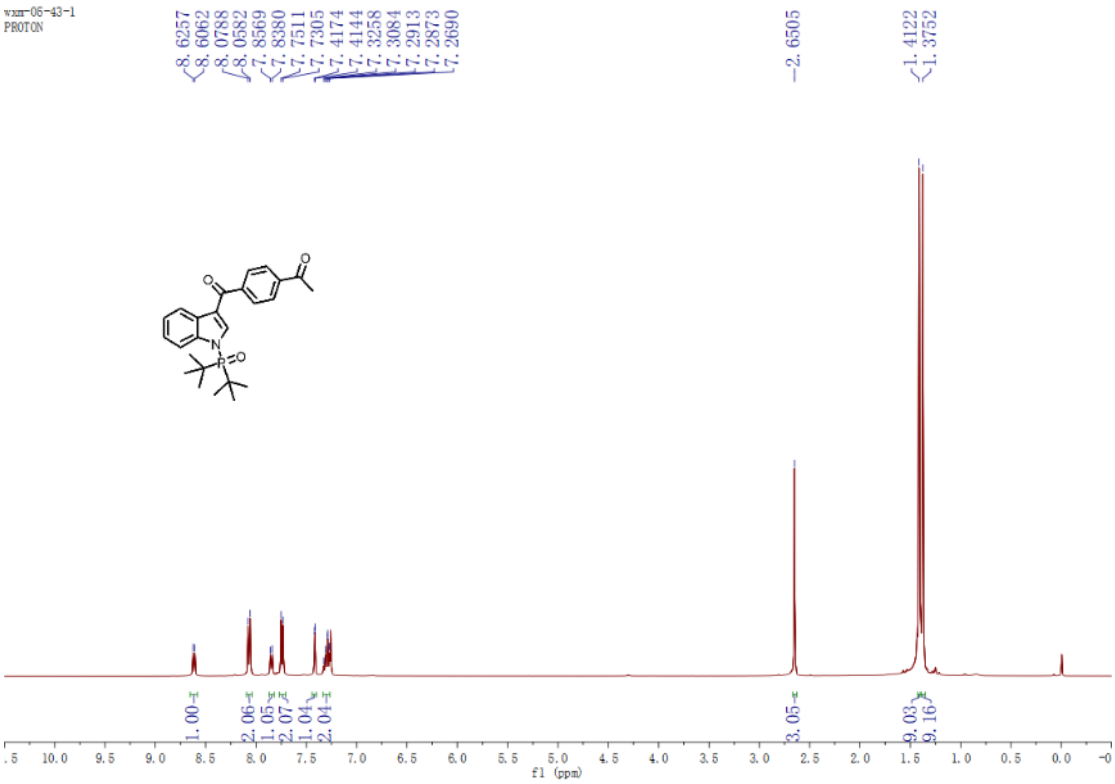
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3h**



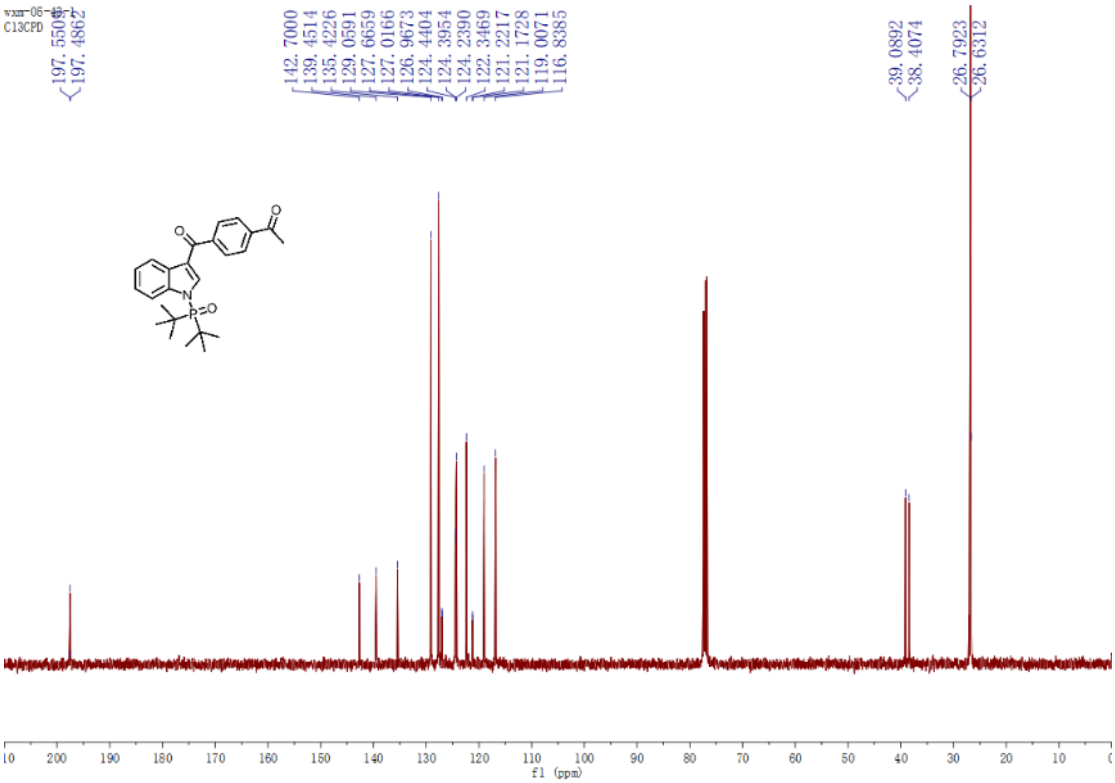
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3h**



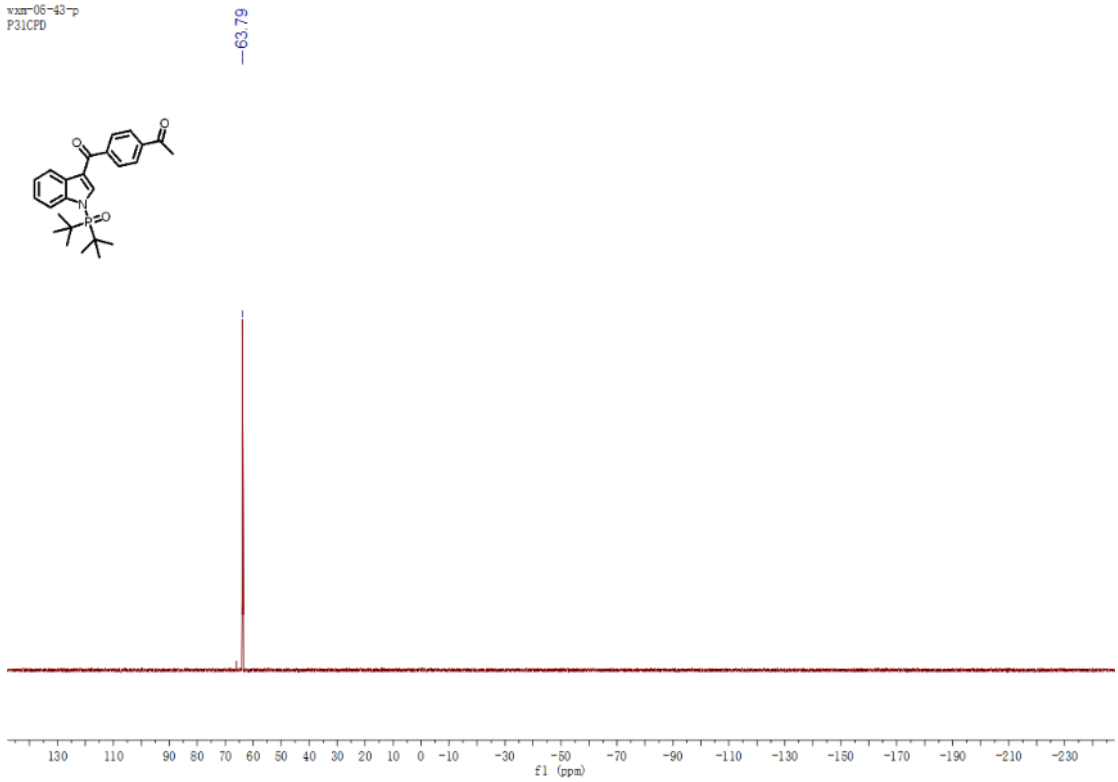
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3i**



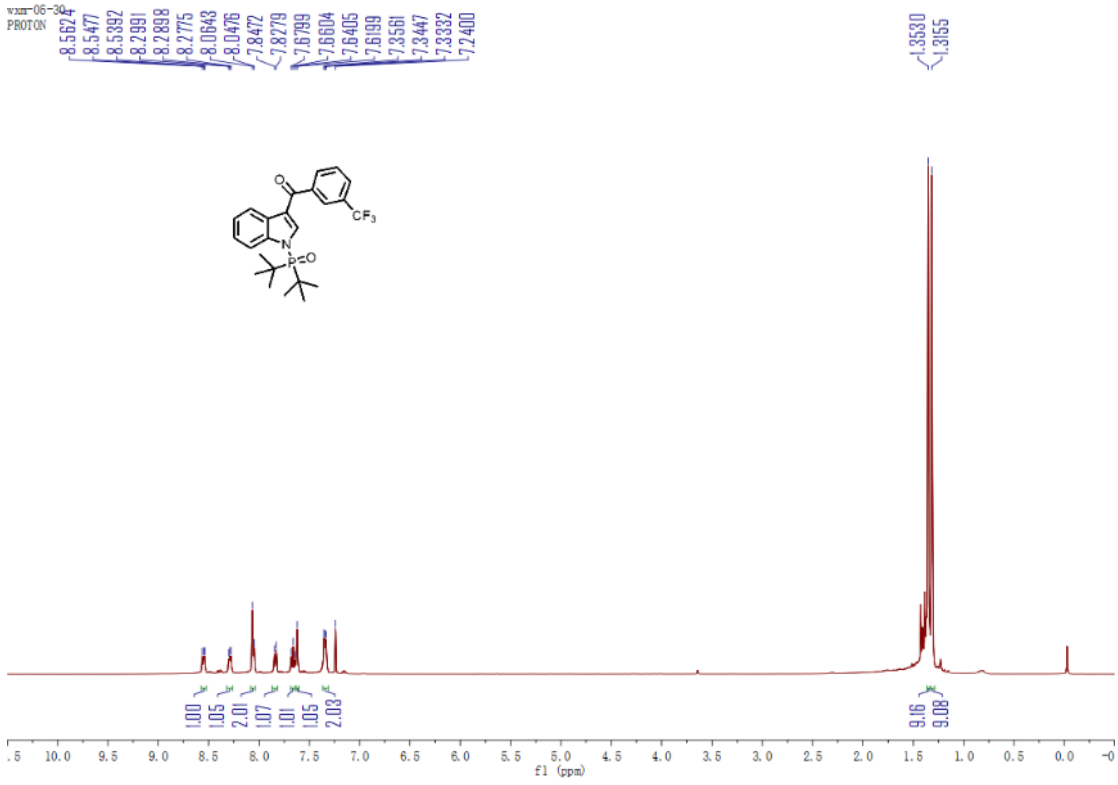
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3i**



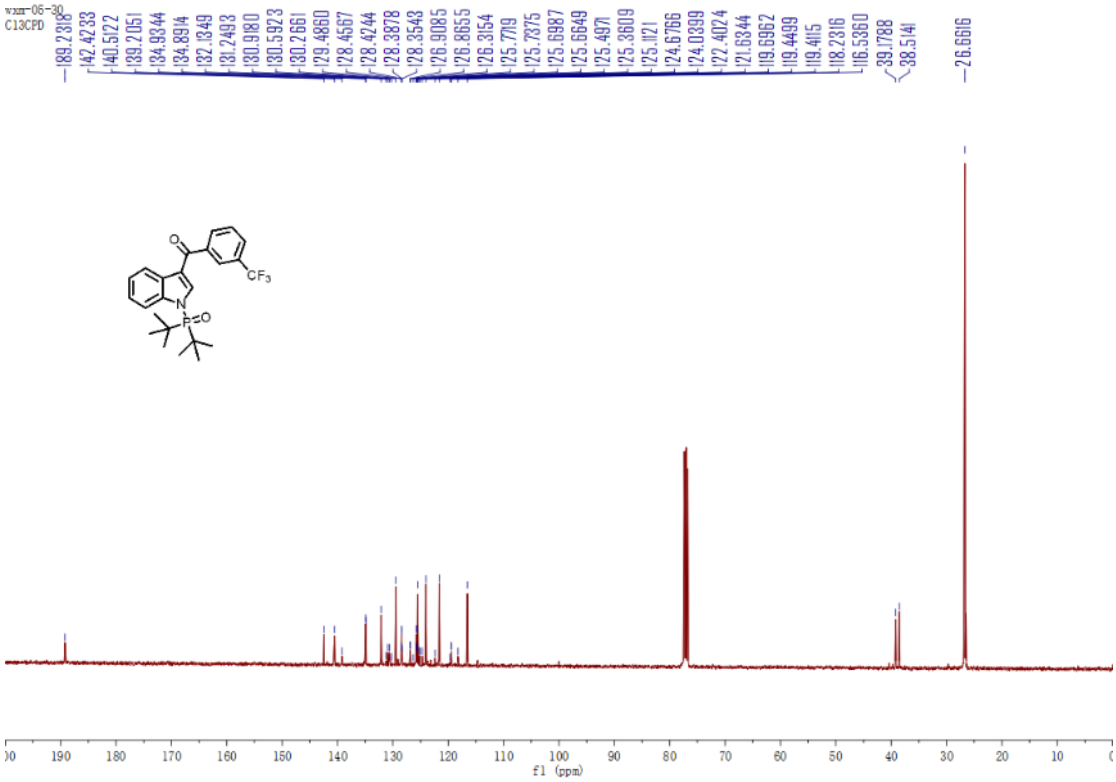
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3i**



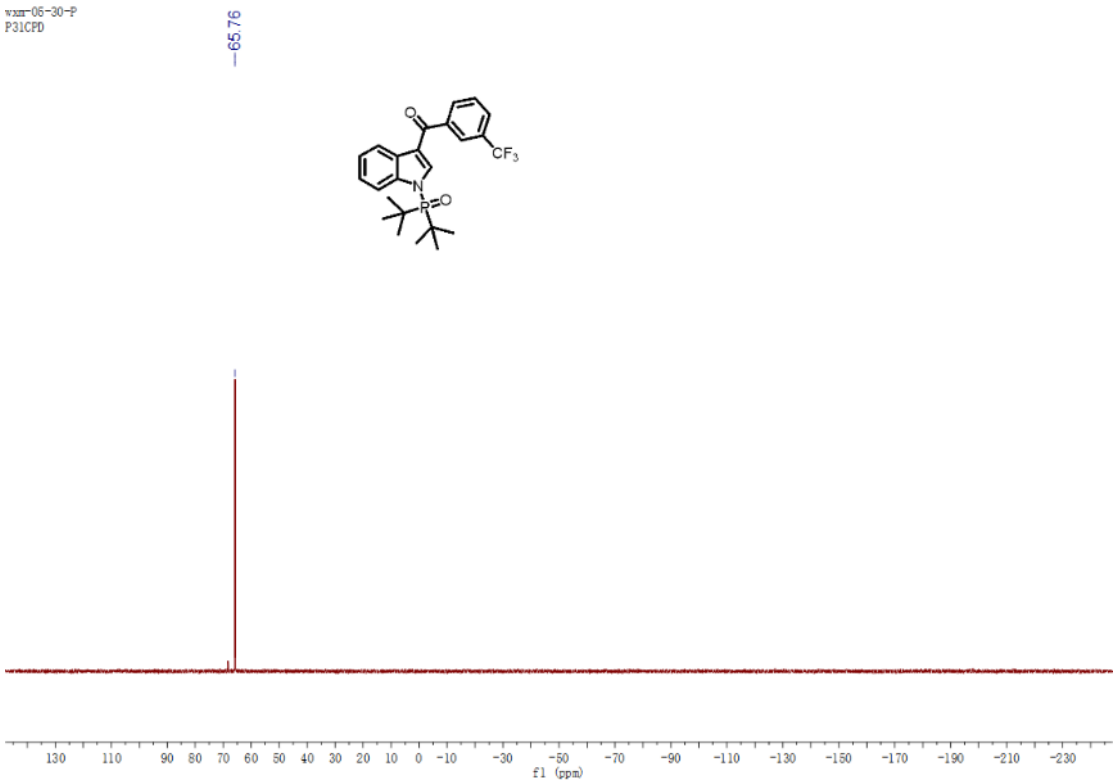
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3j**



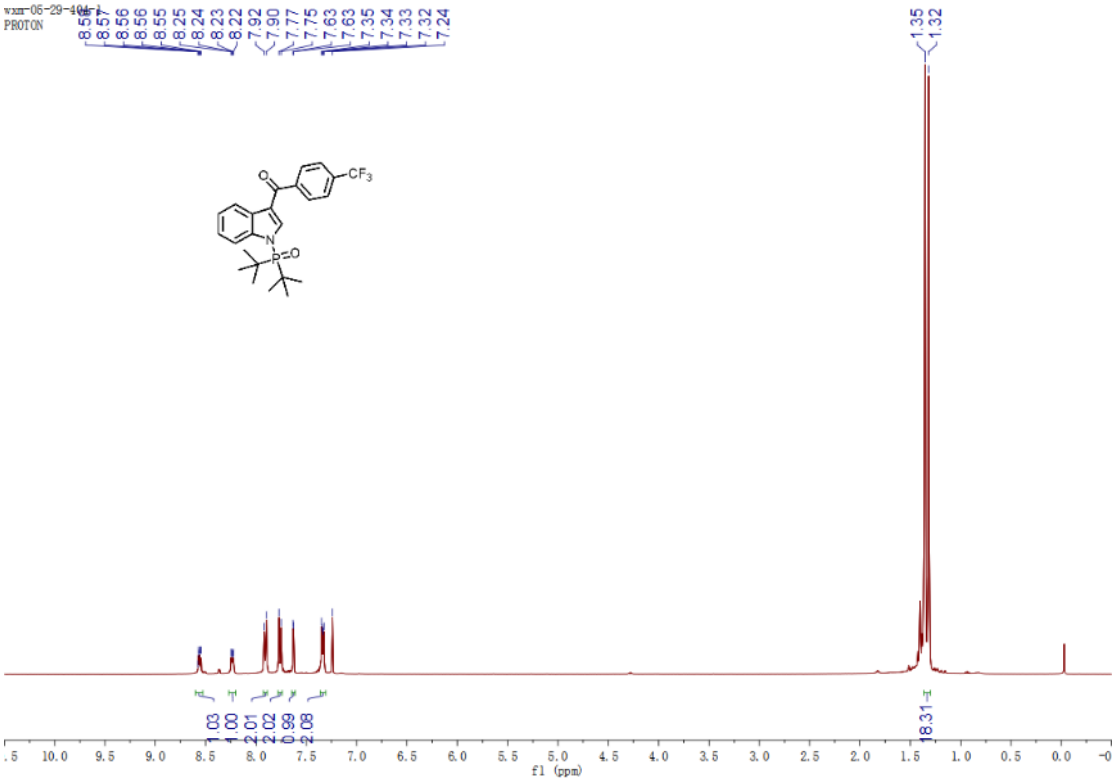
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3j**



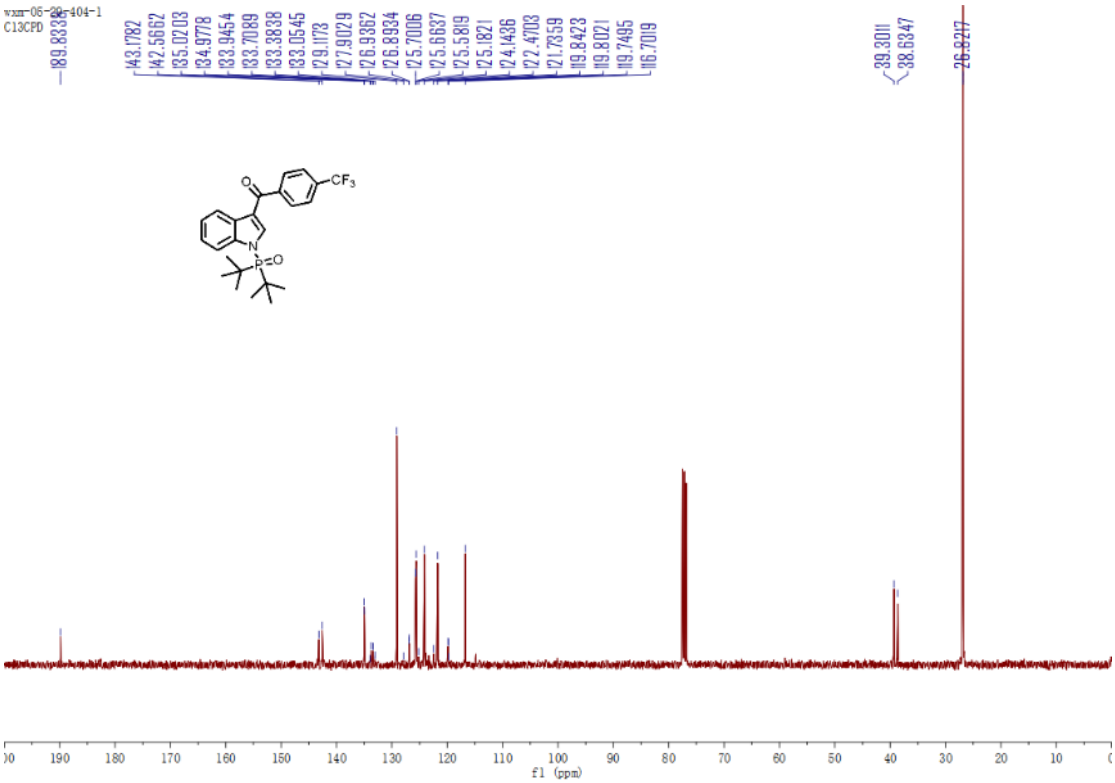
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3j**



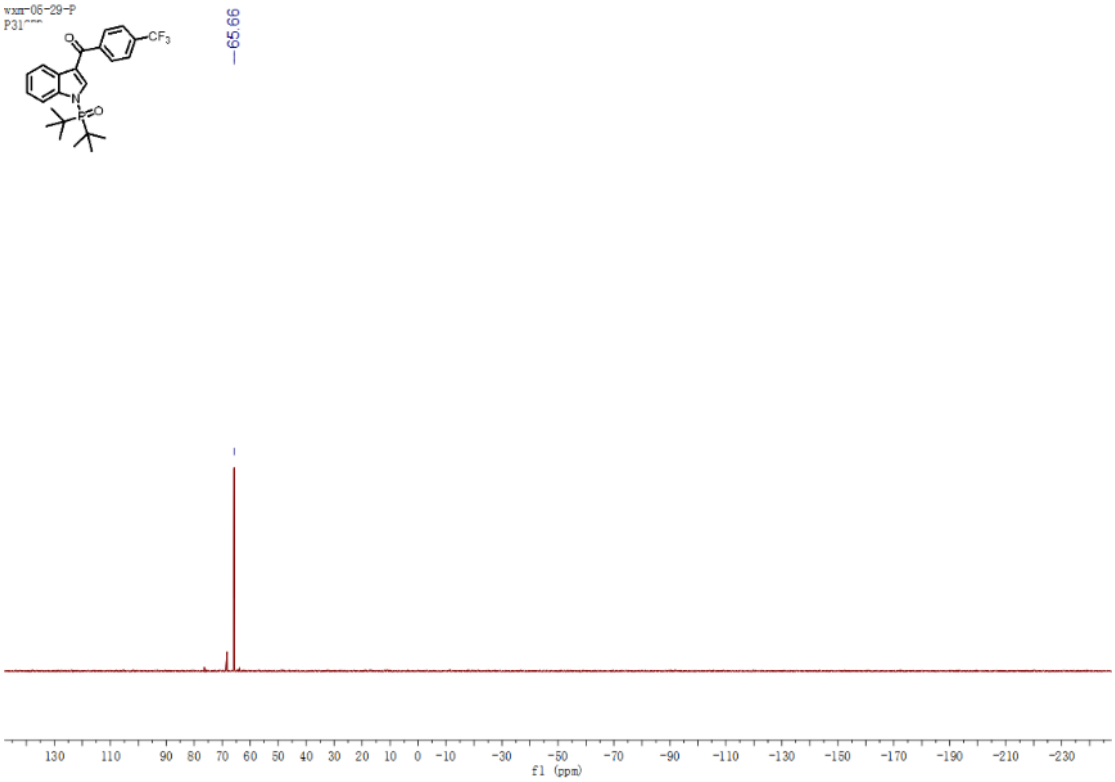
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3k**



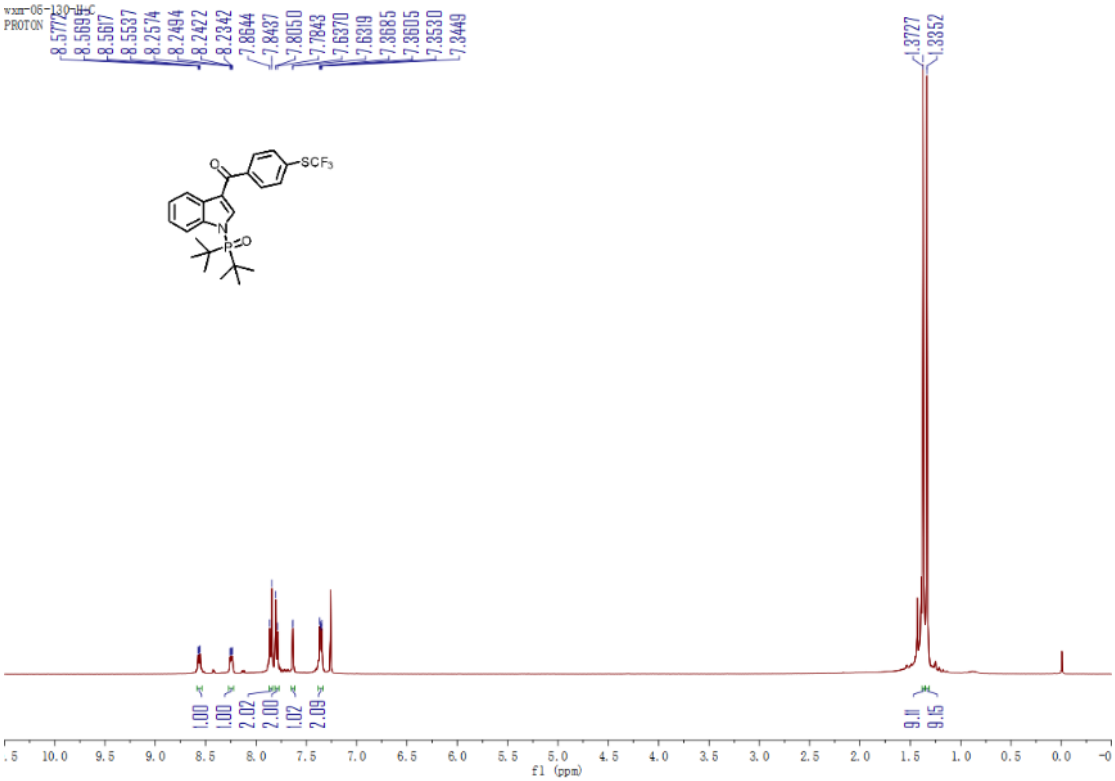
^{13}C NMR spectrum (100 MHz, CDCl3) of compound 3**k**



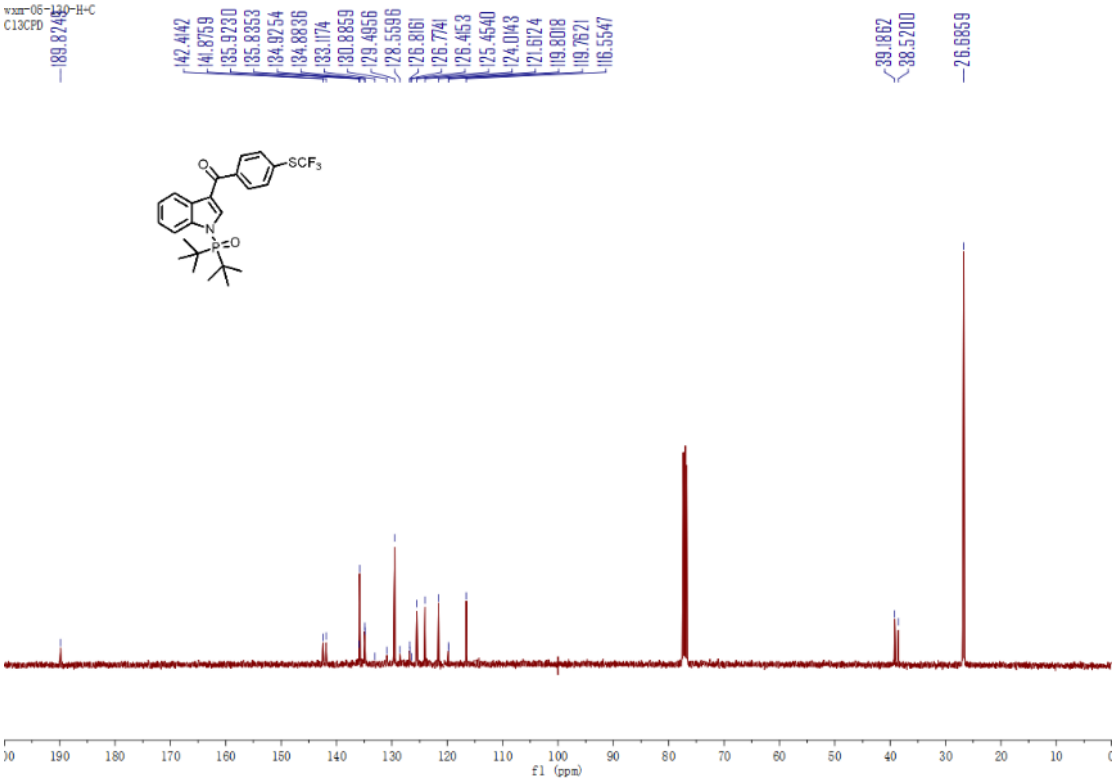
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3k**



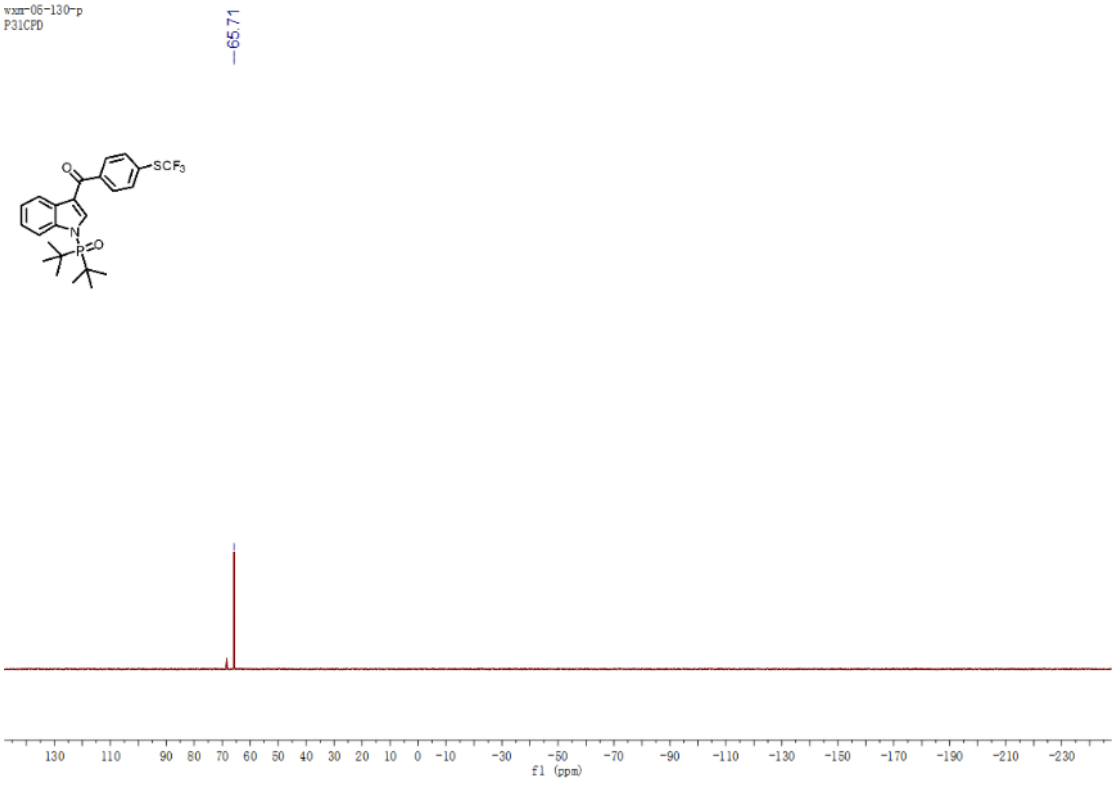
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3l**



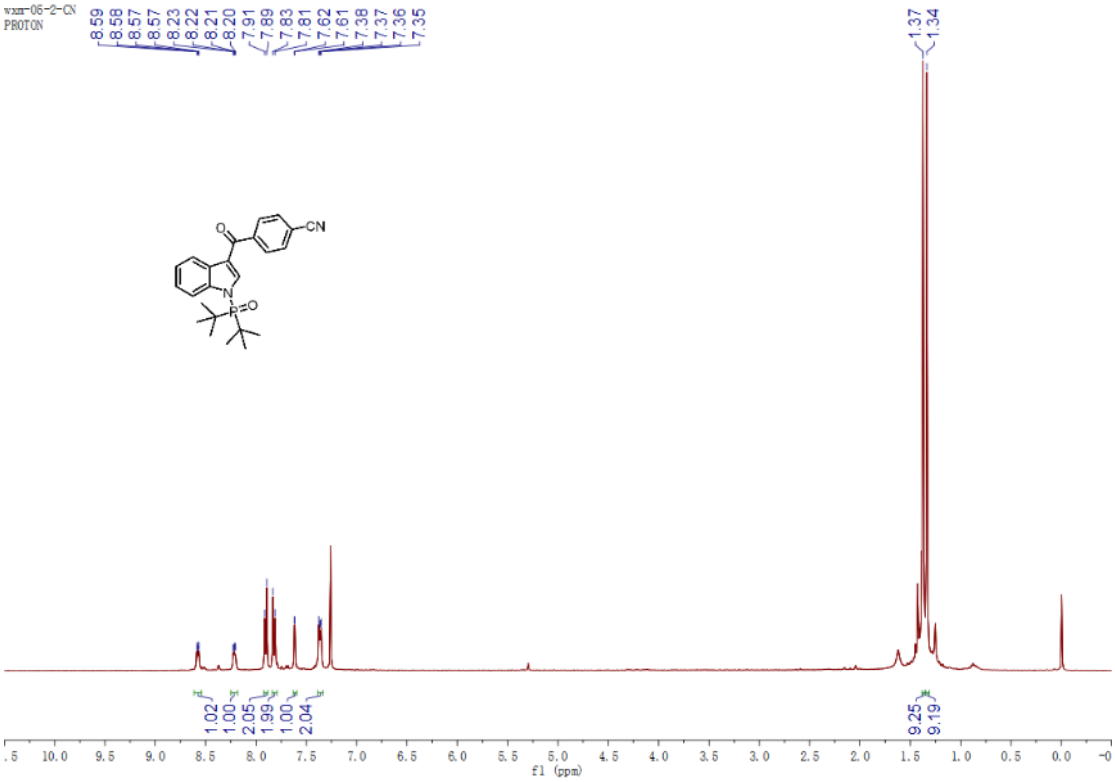
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3l**



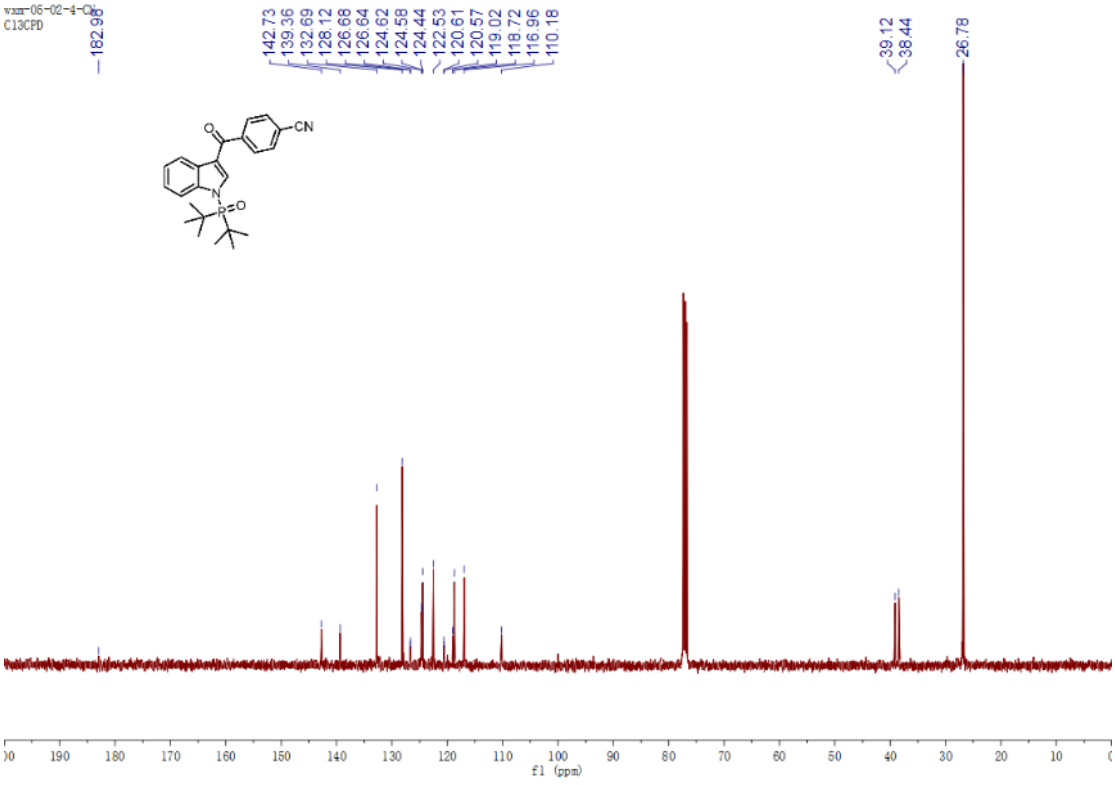
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3l**



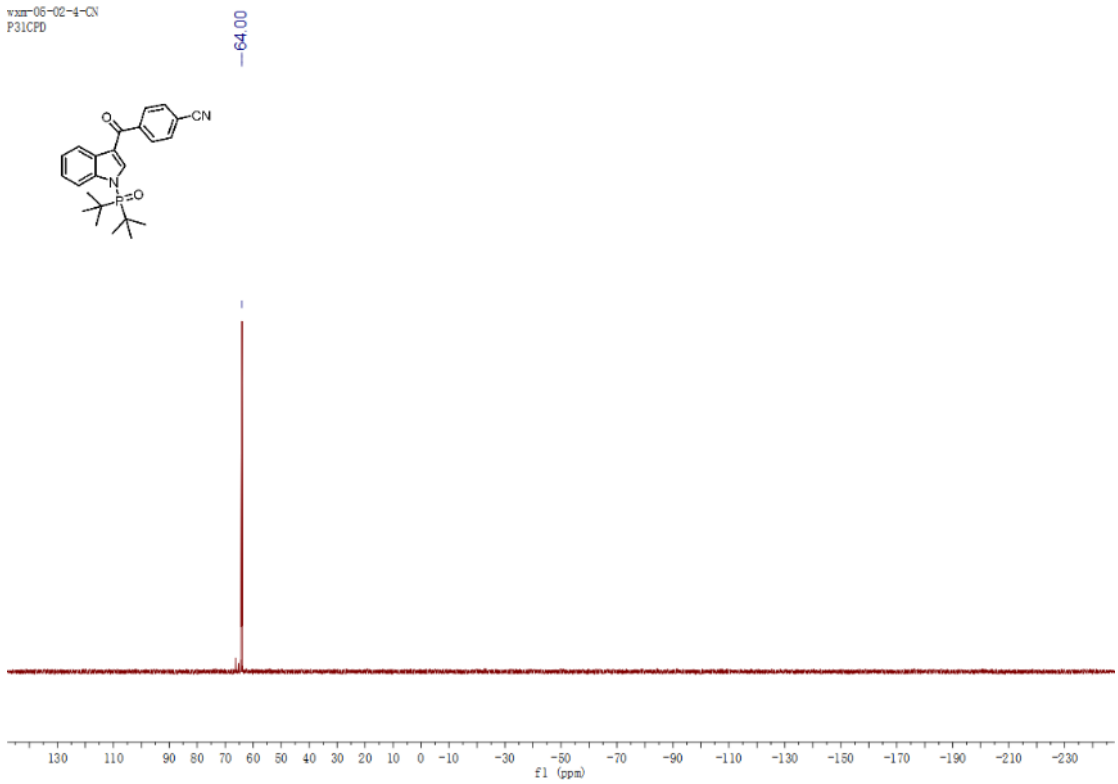
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3m**



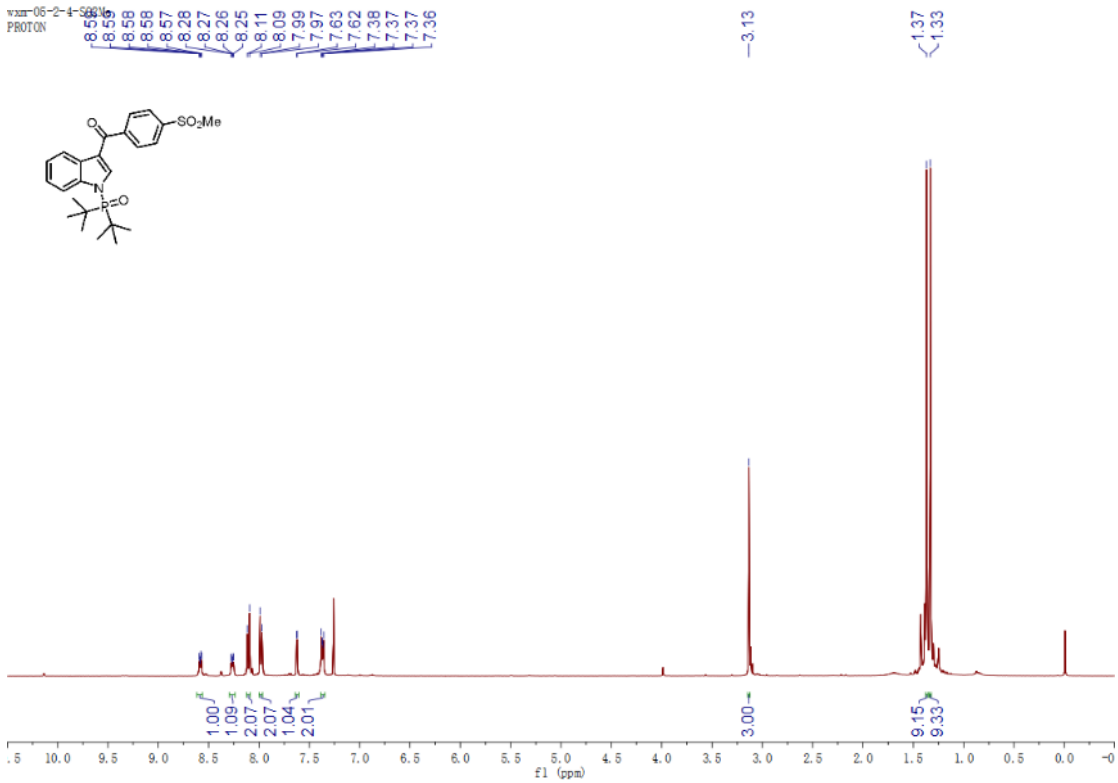
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3m**



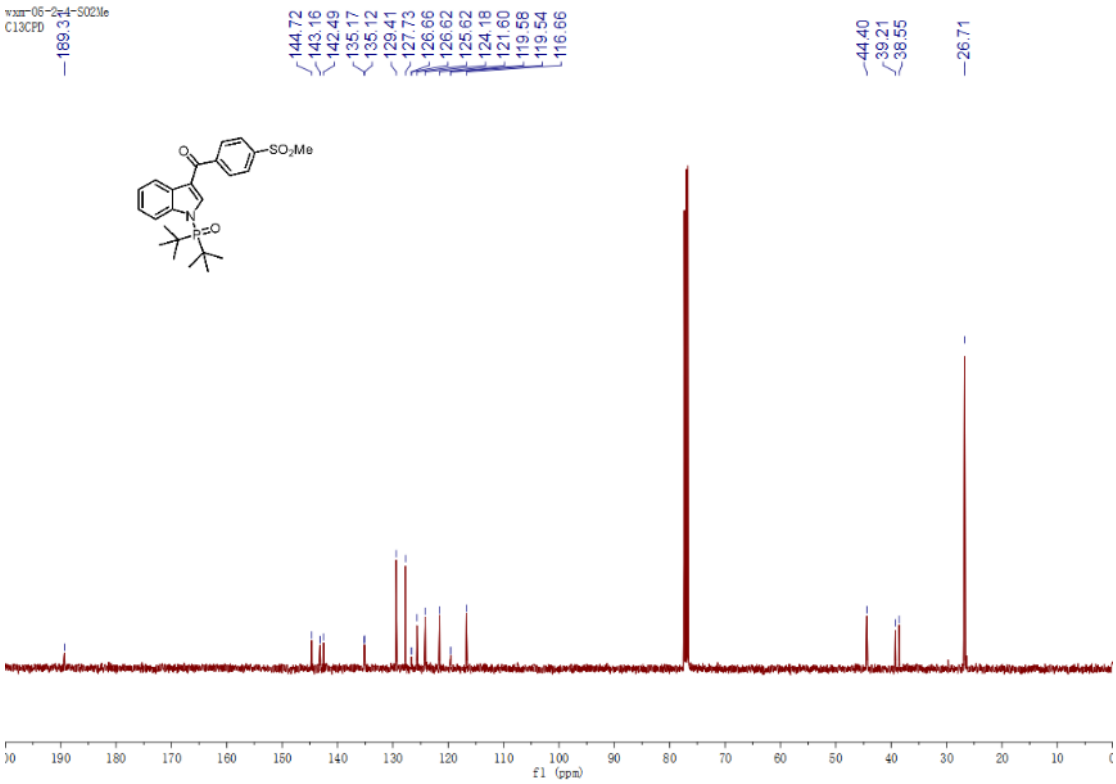
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3m**



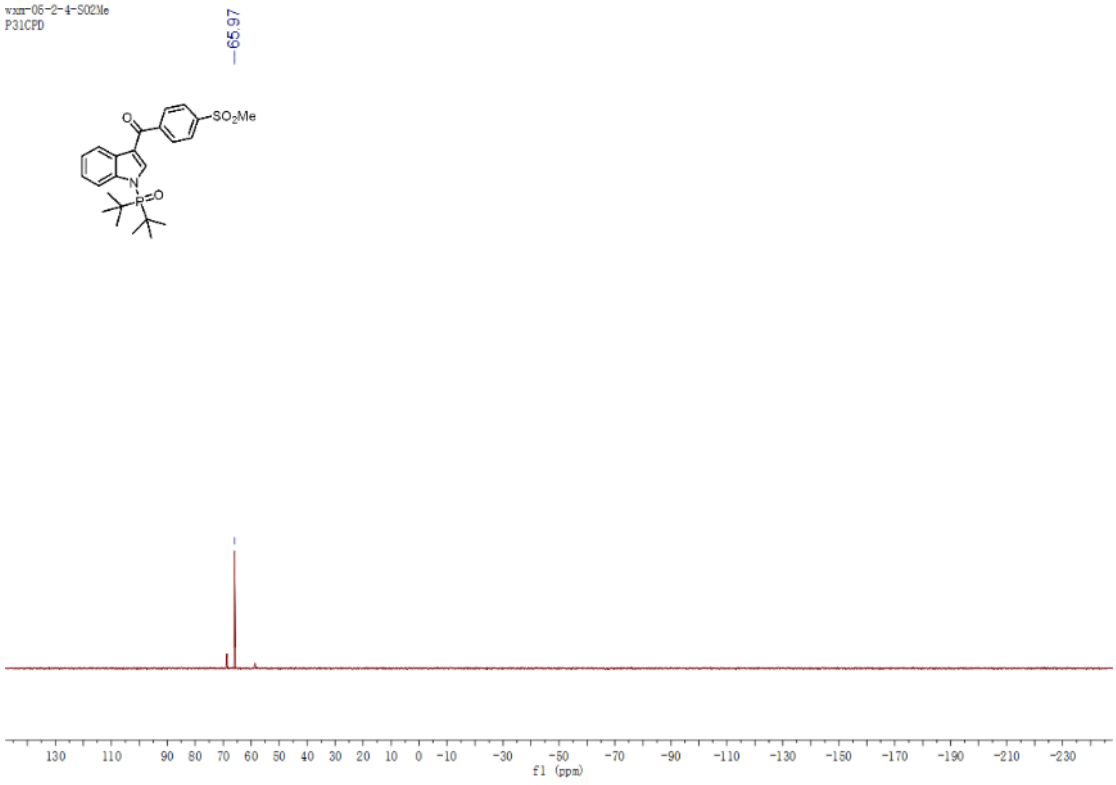
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3n**



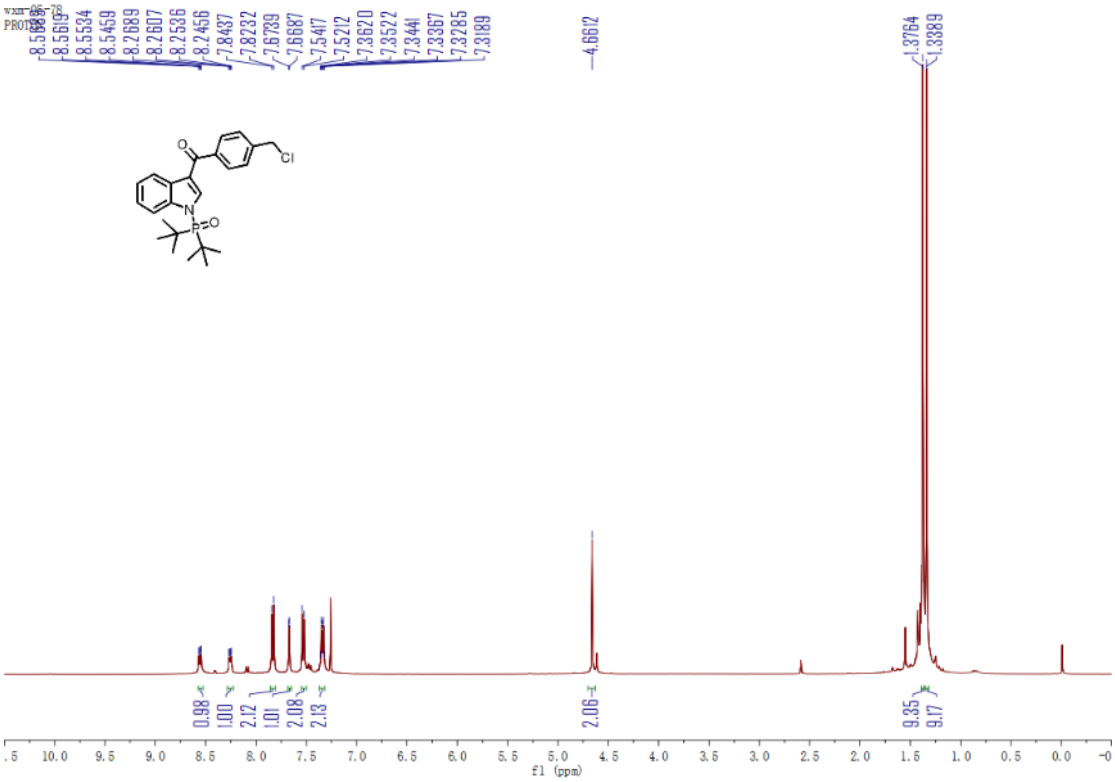
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3n**



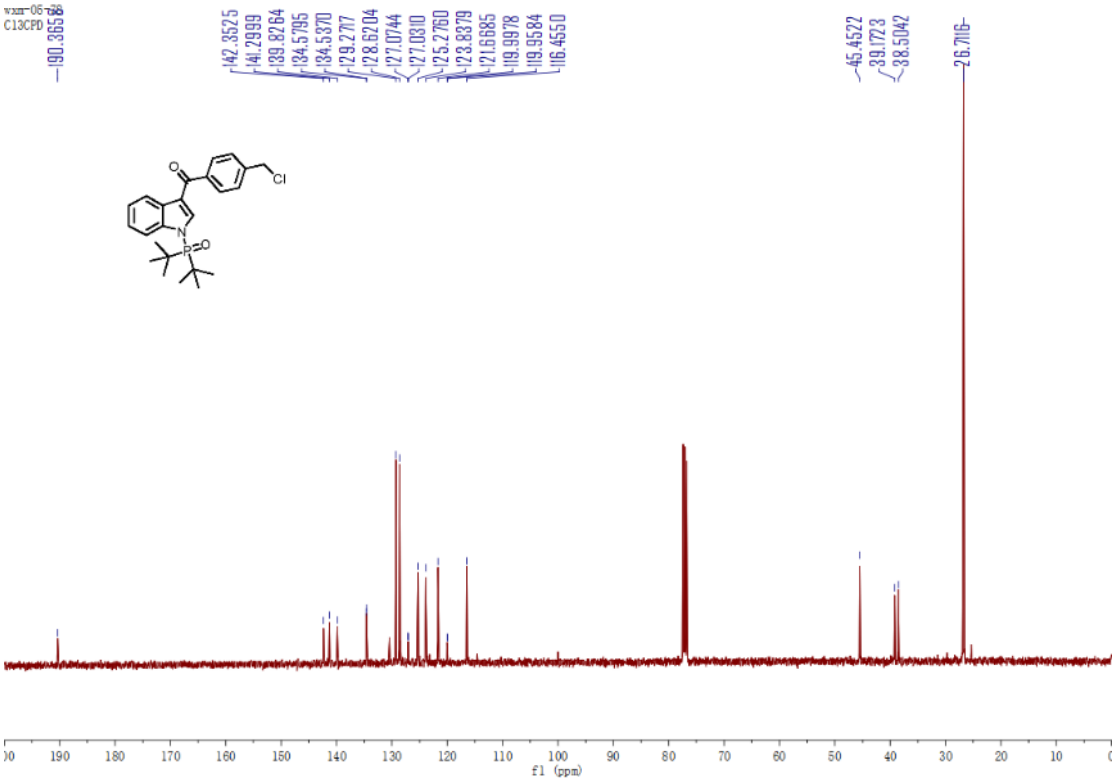
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3n**



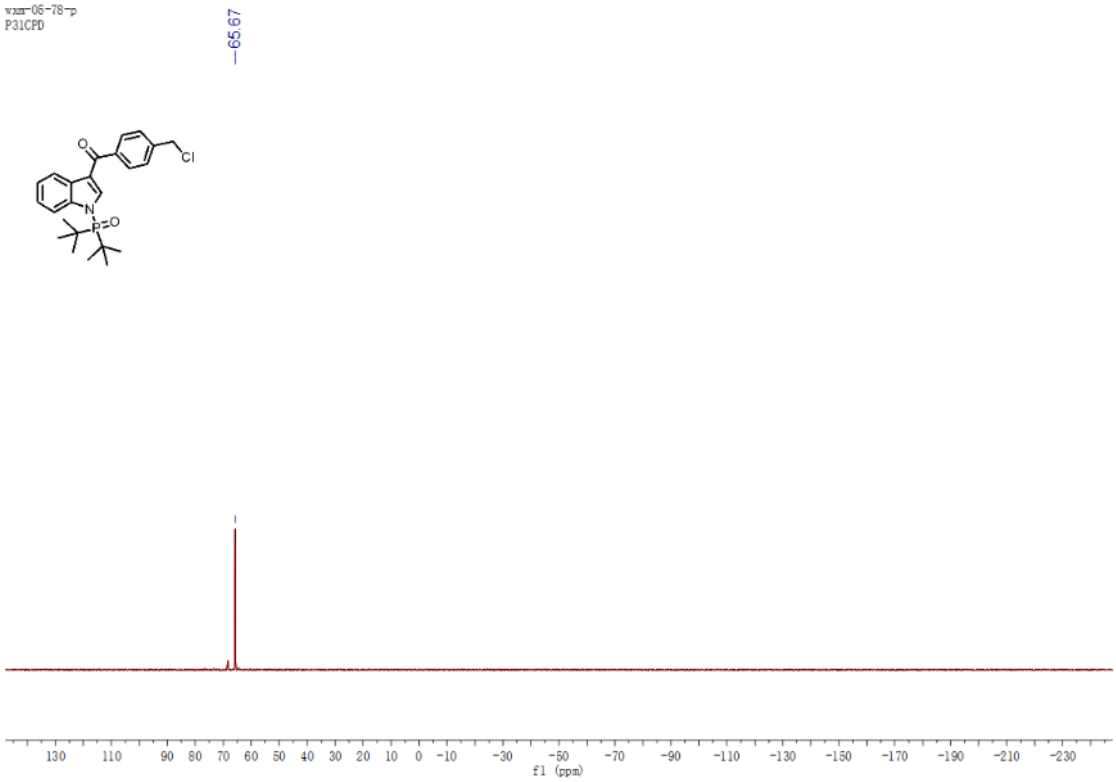
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3o**



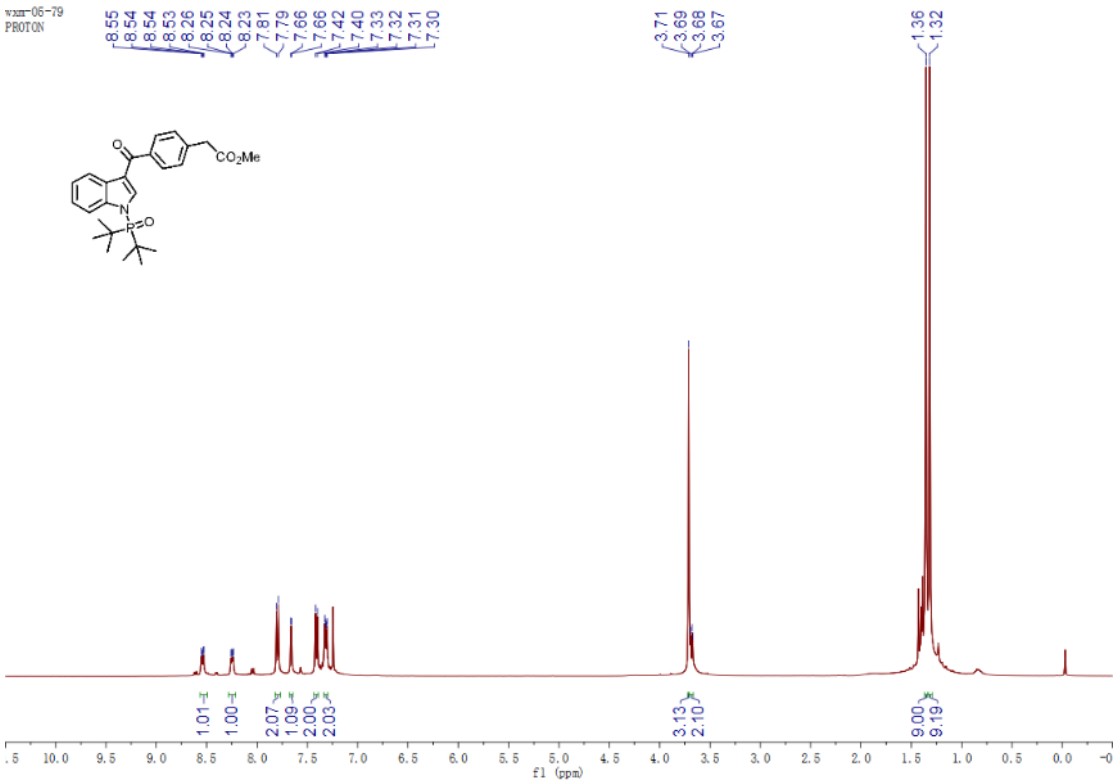
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3o**



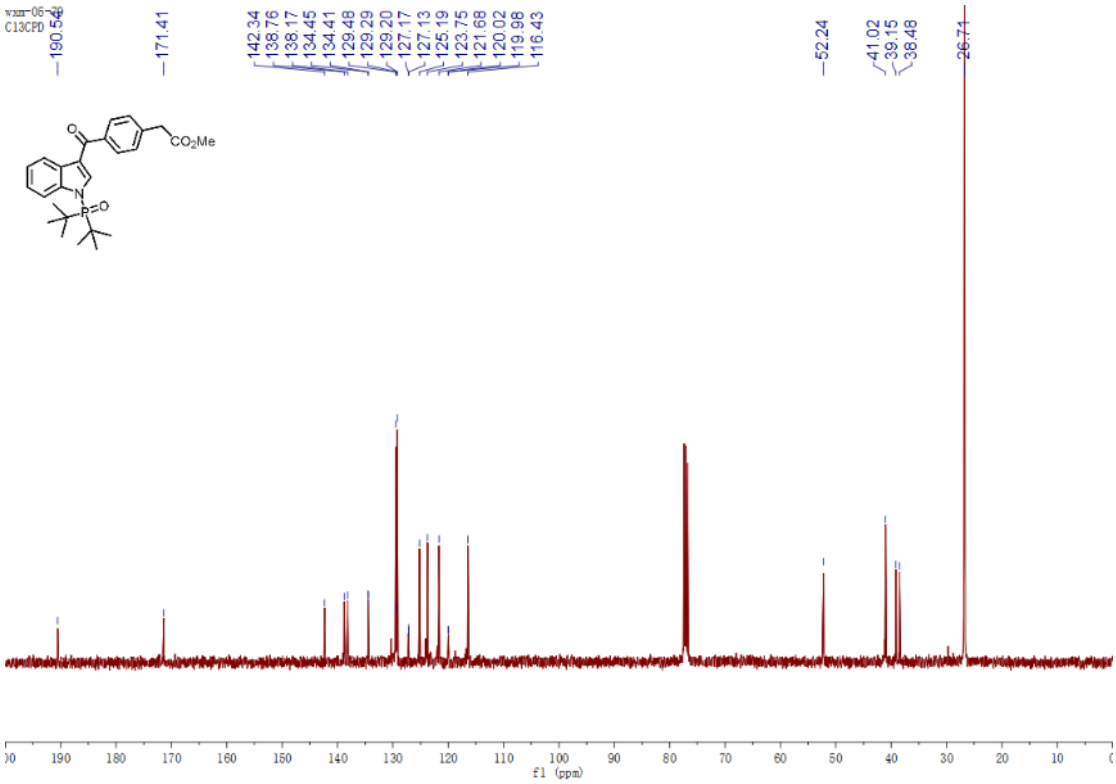
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3o**



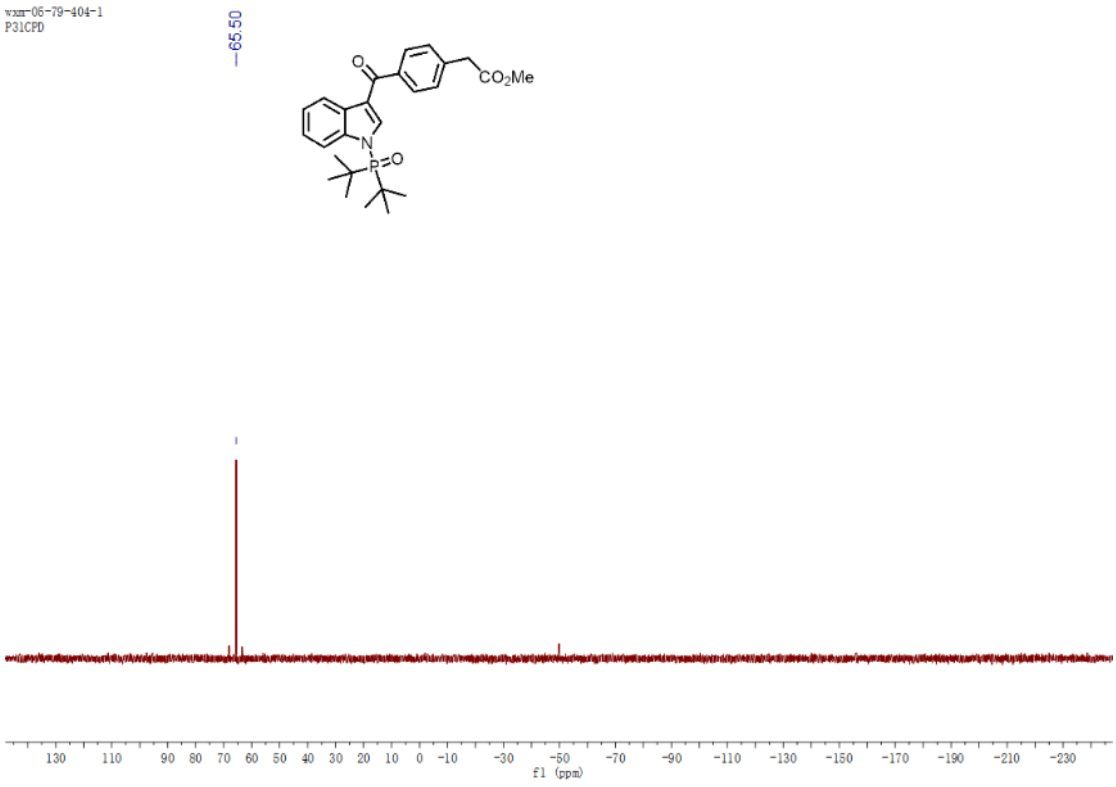
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3p**



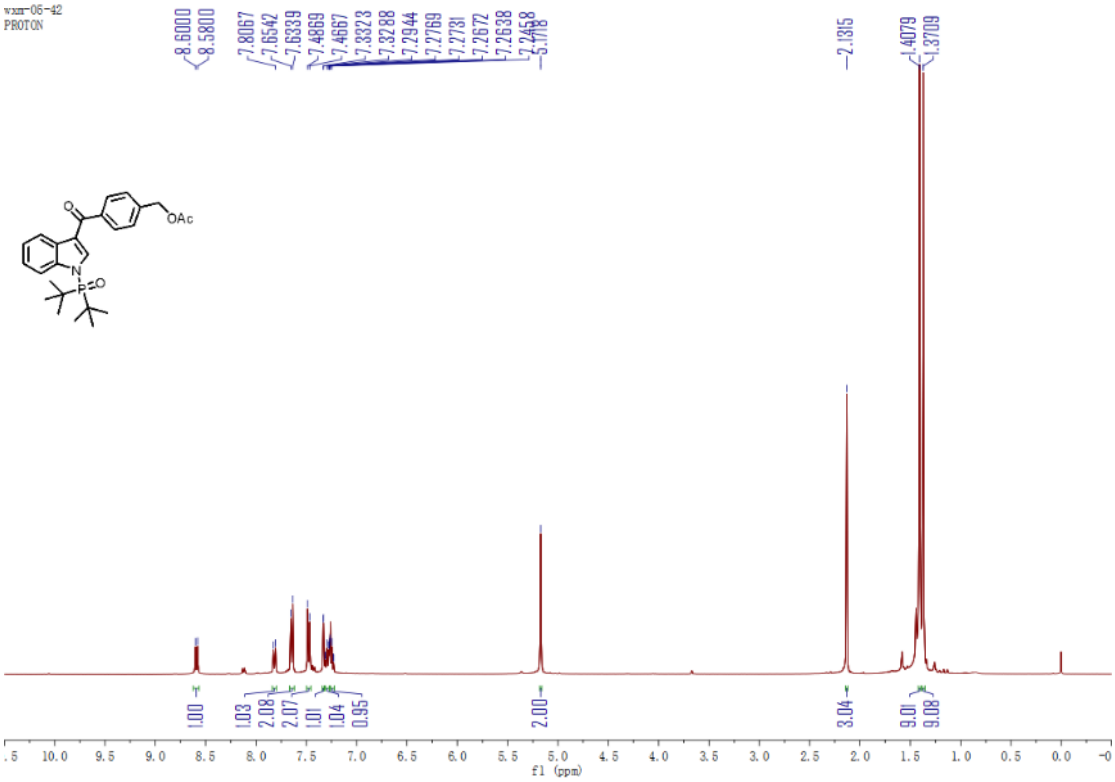
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3p**



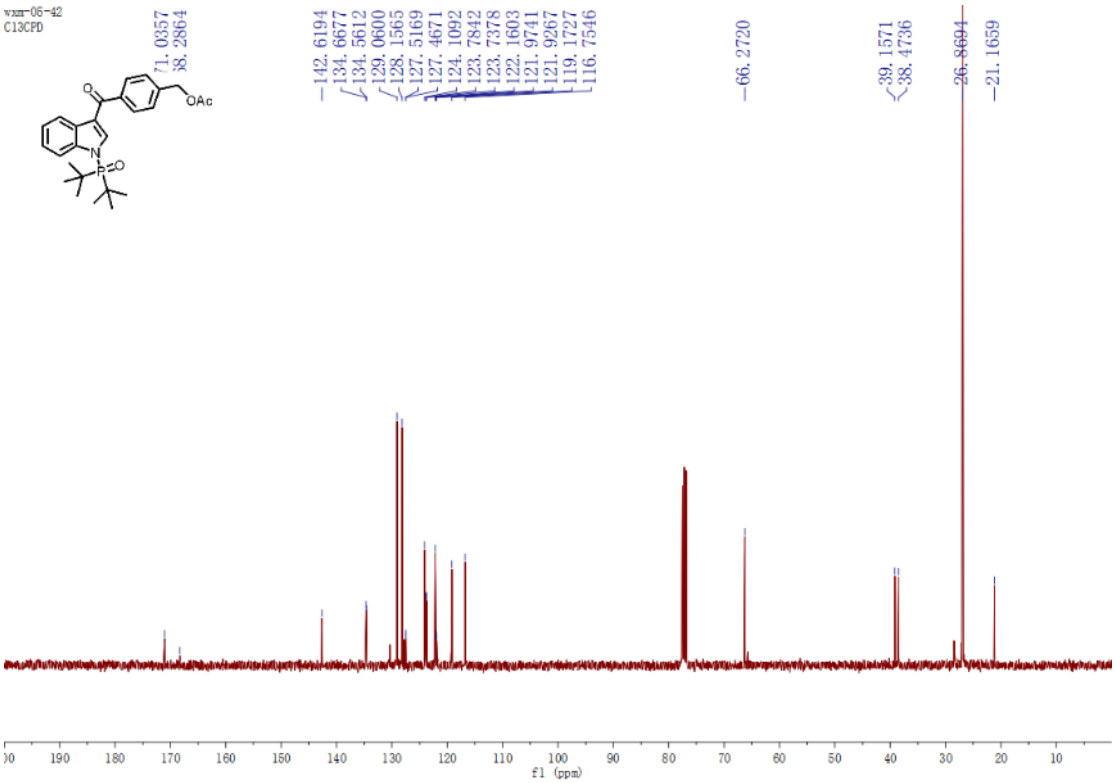
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3p**



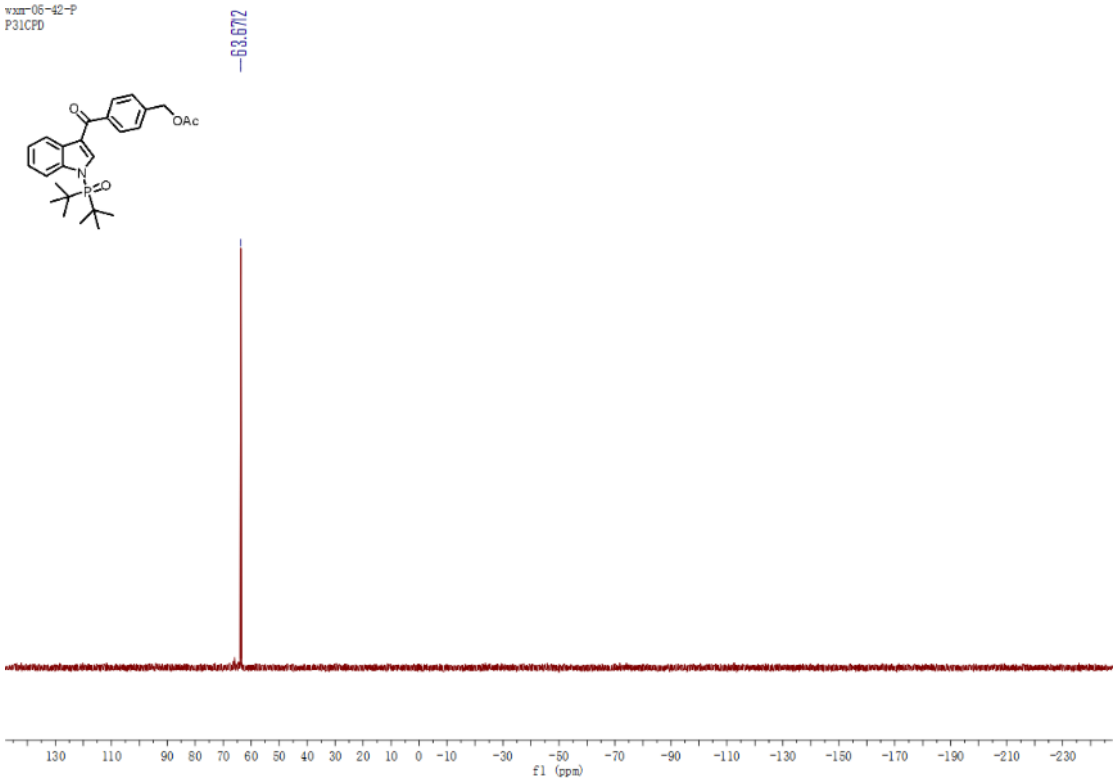
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3q**



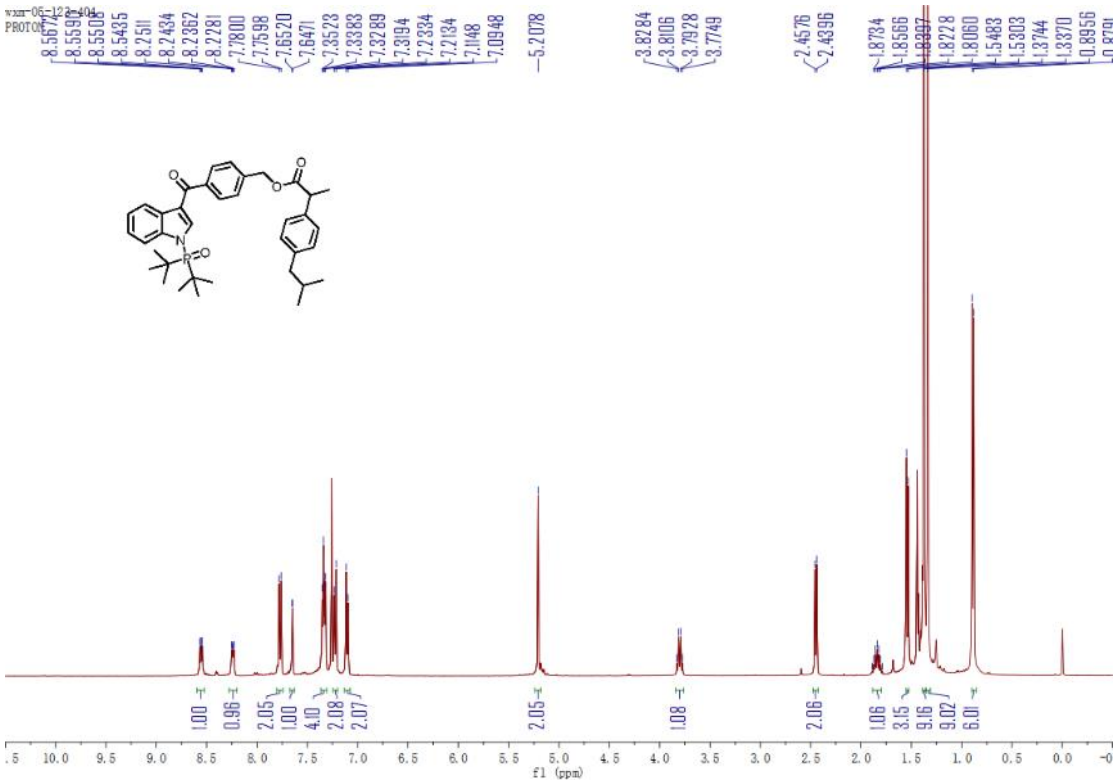
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3q**



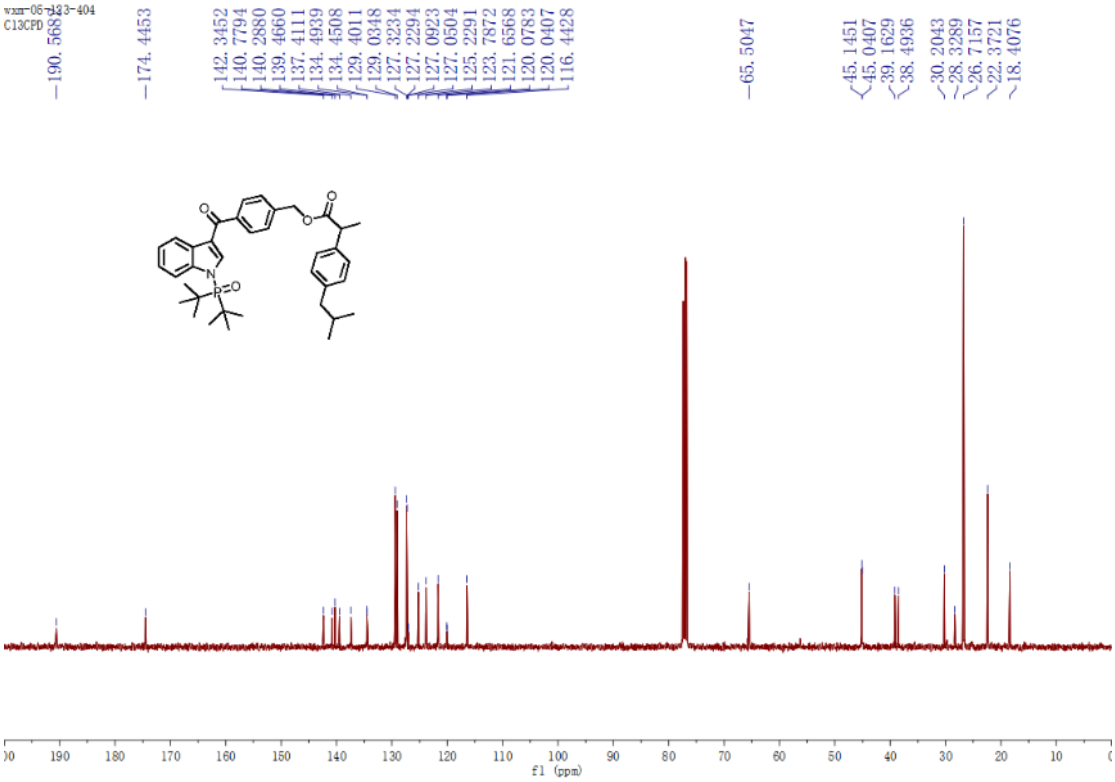
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3q**



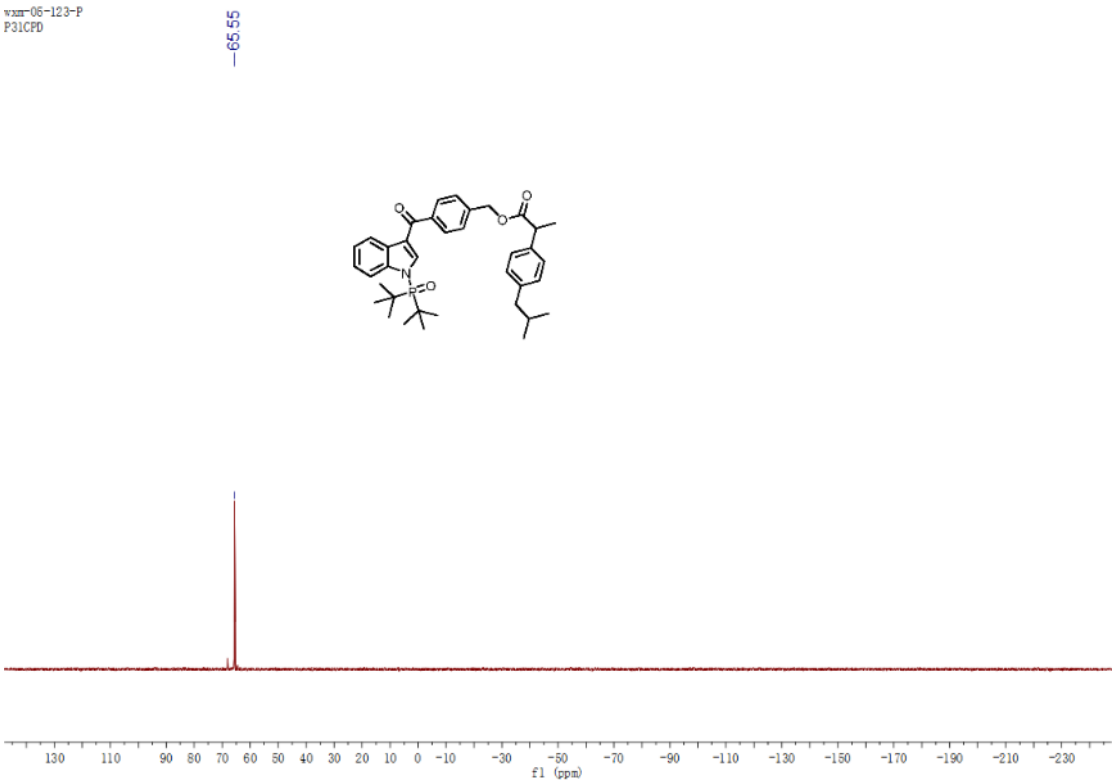
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3r**



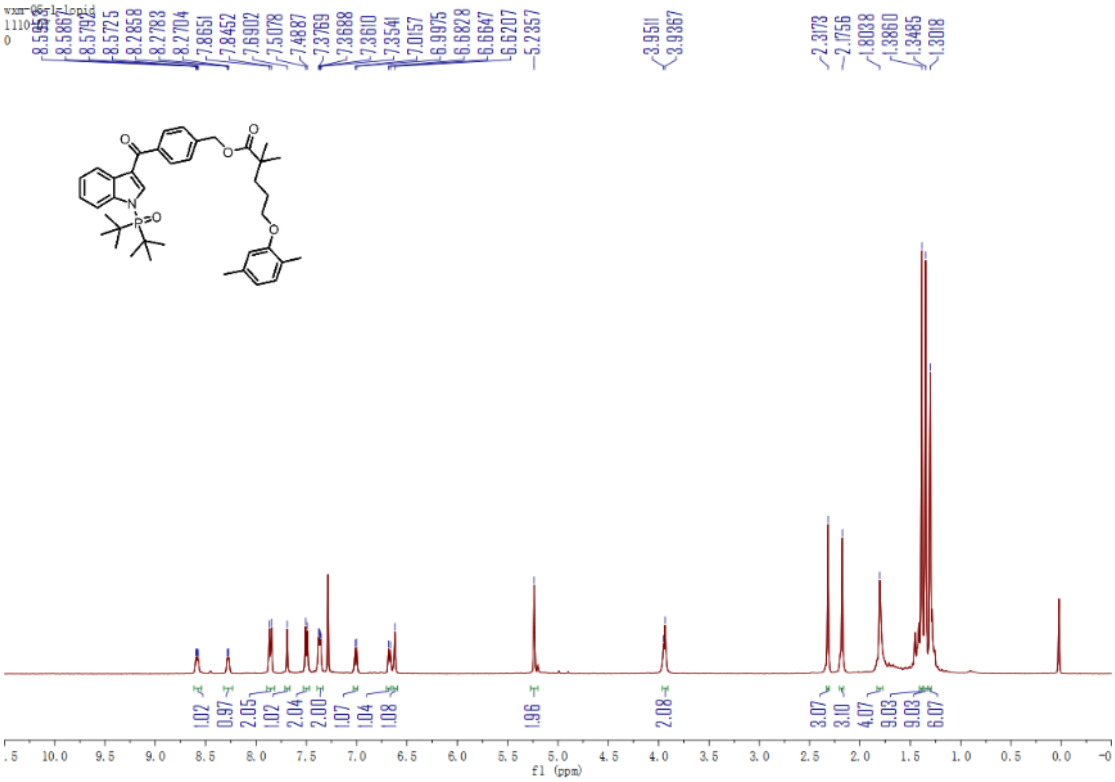
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3r**



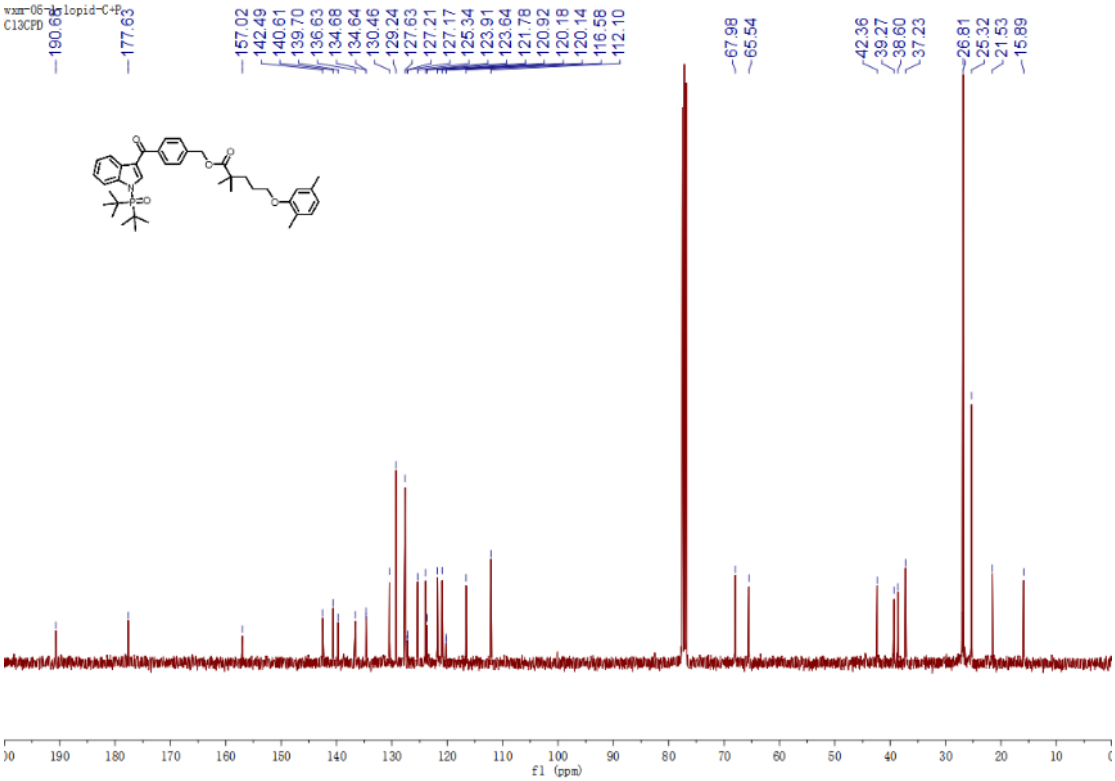
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3r**



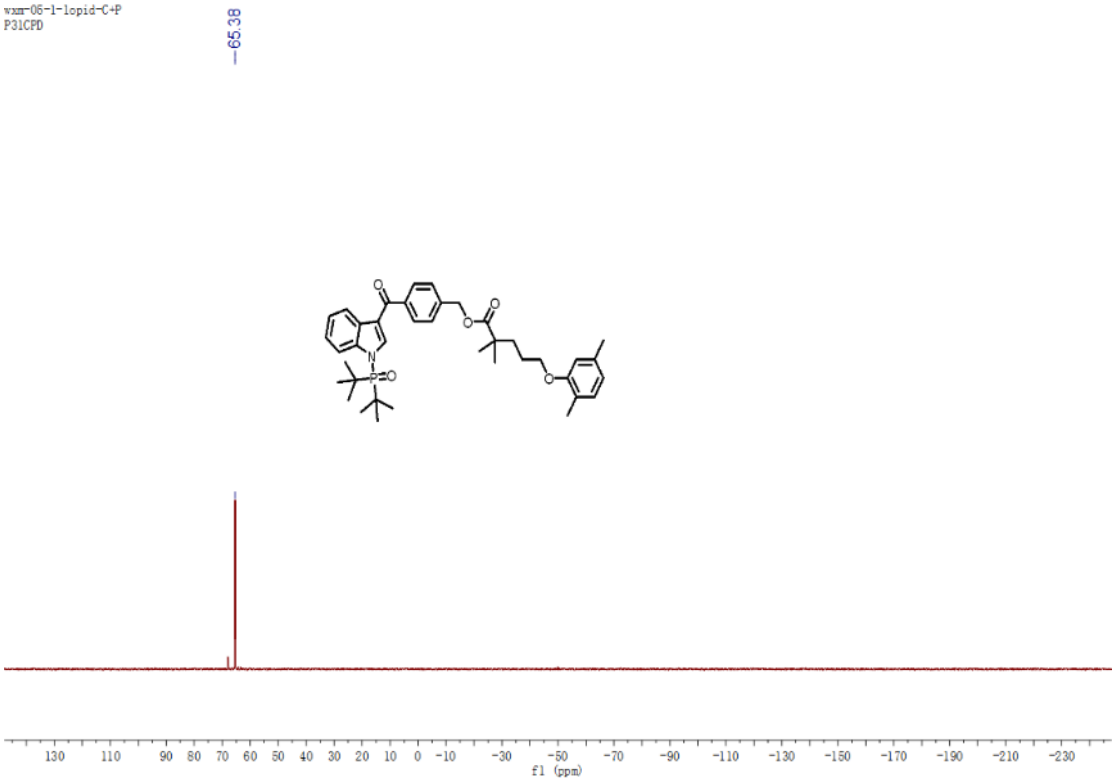
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3s**



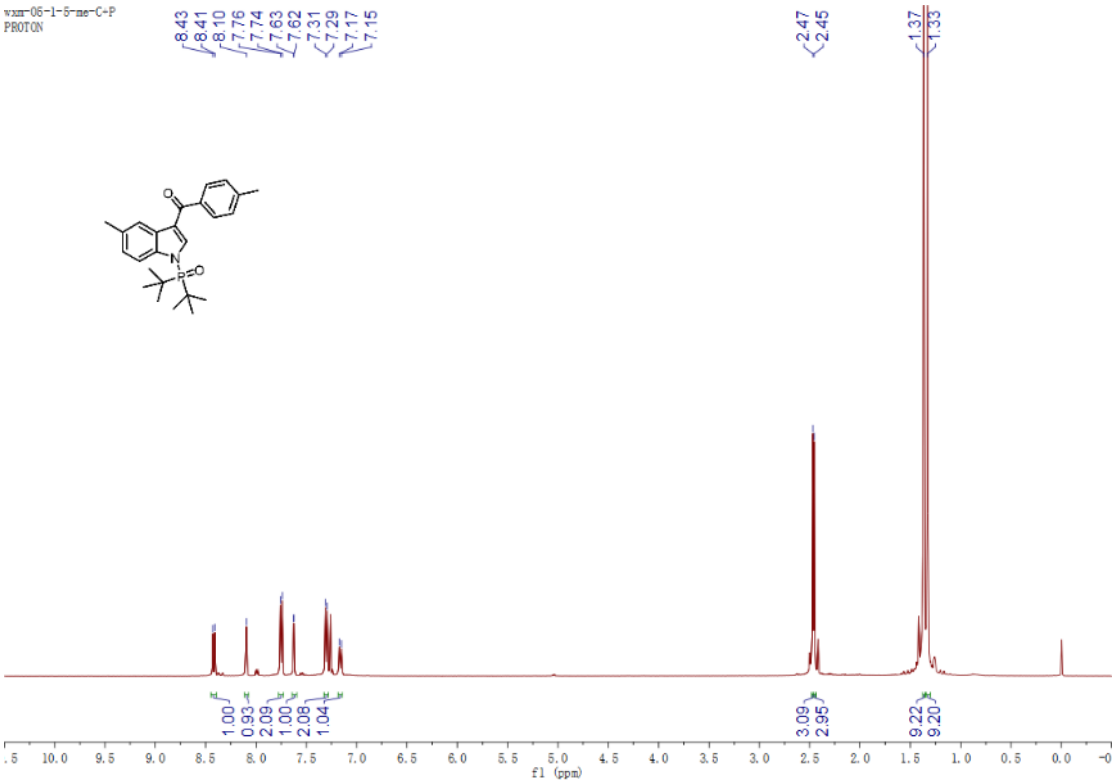
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3s**



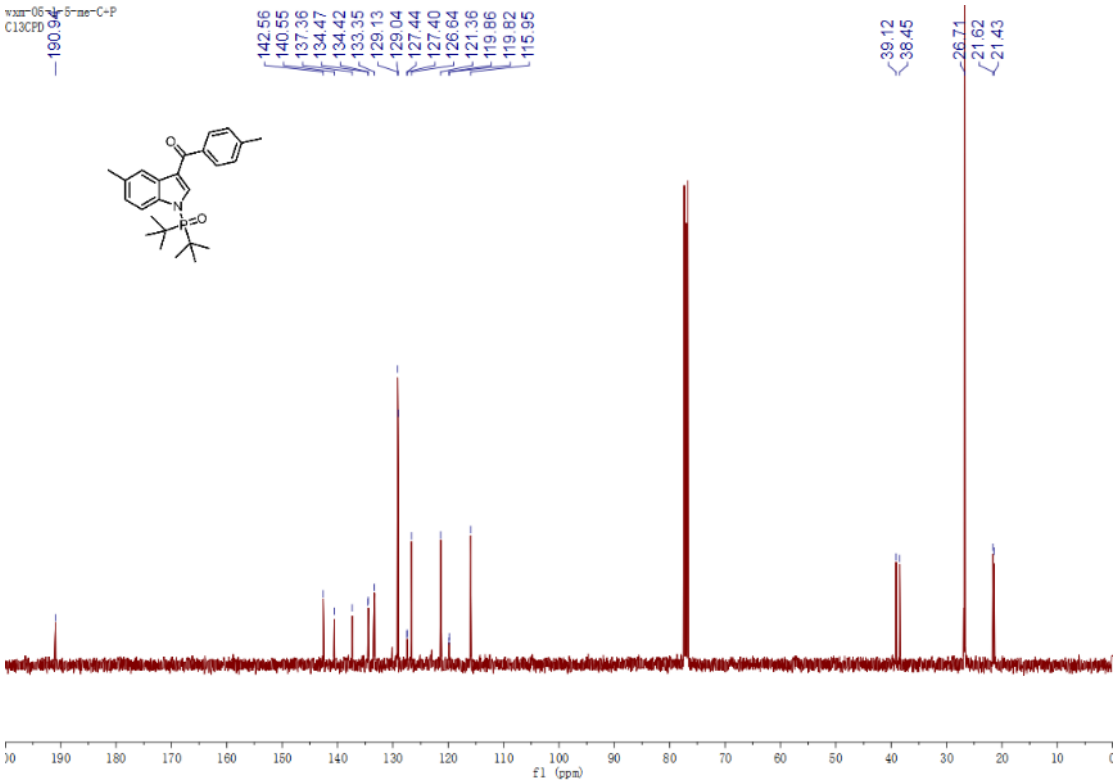
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3s**



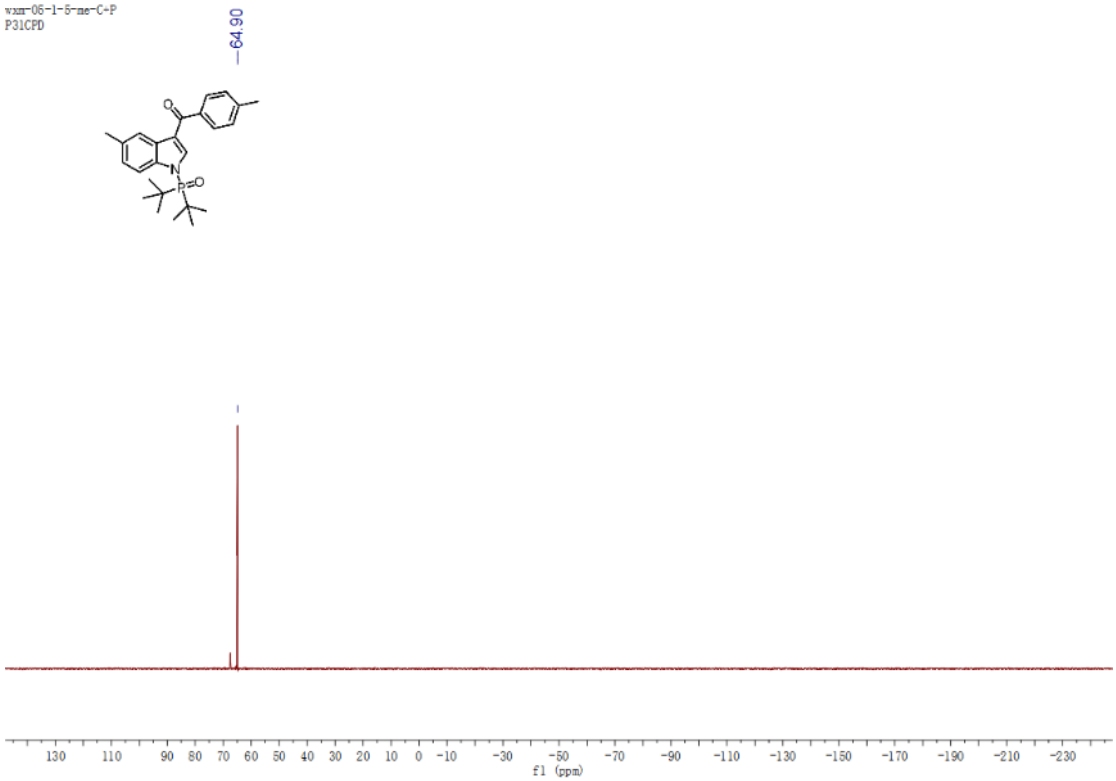
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3t**



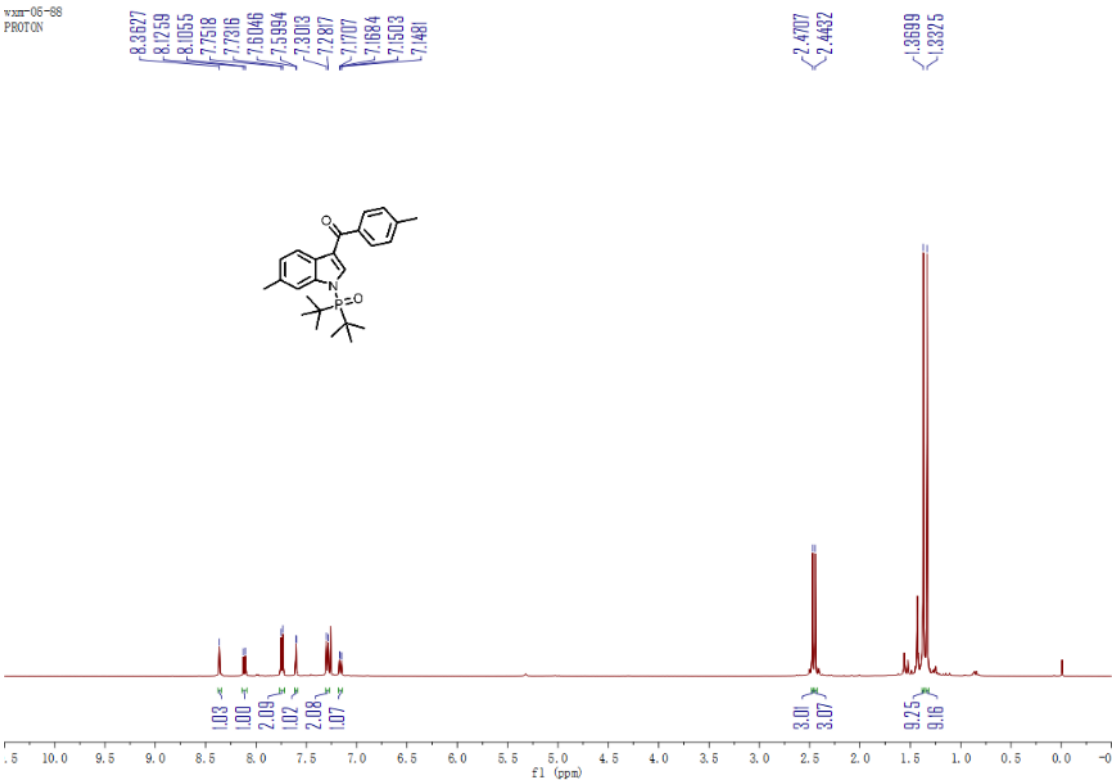
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3t**



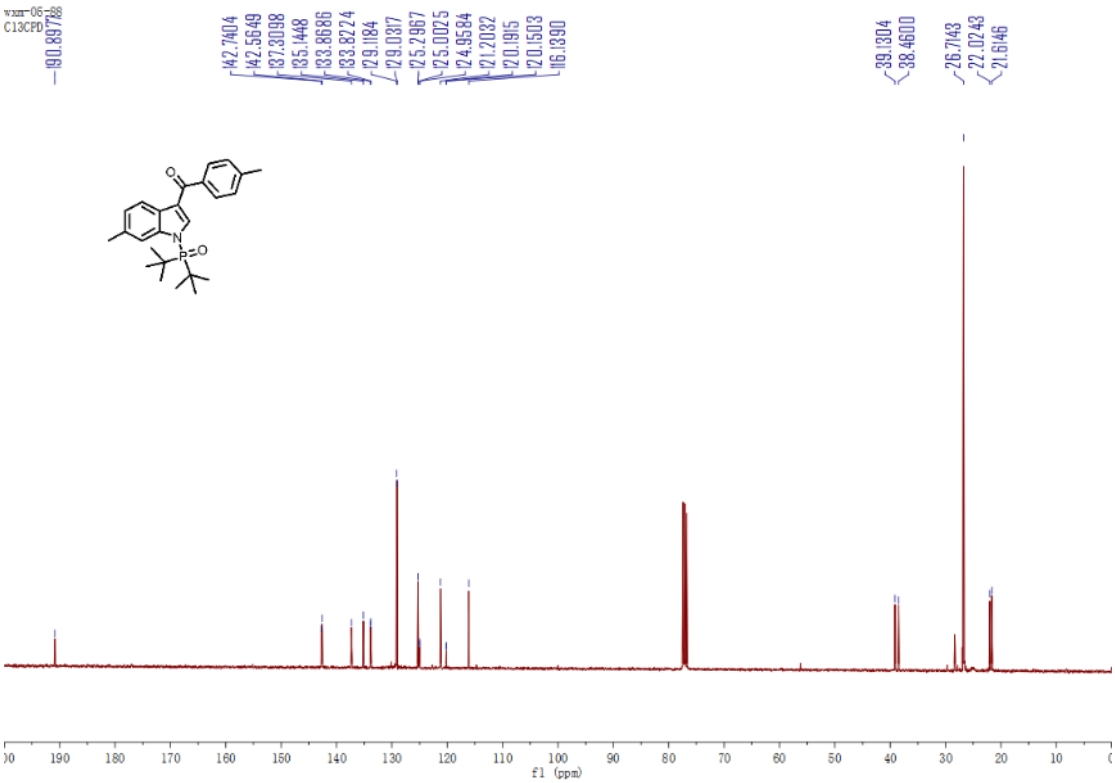
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3t**



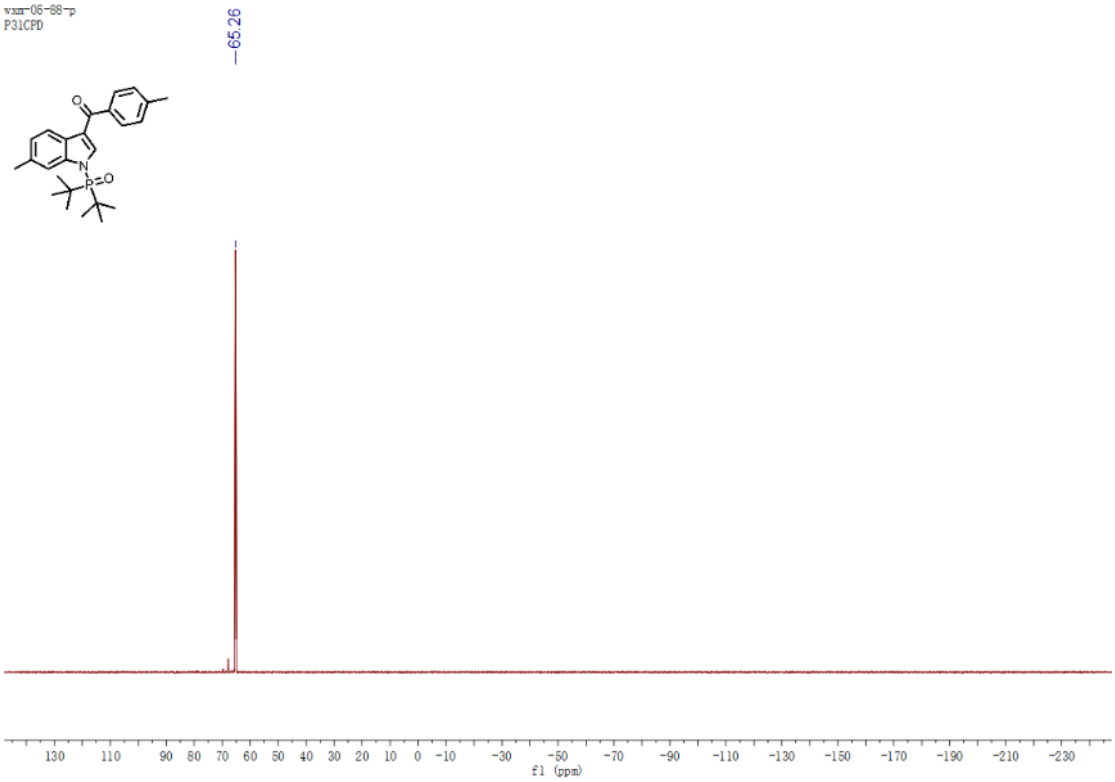
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3u**



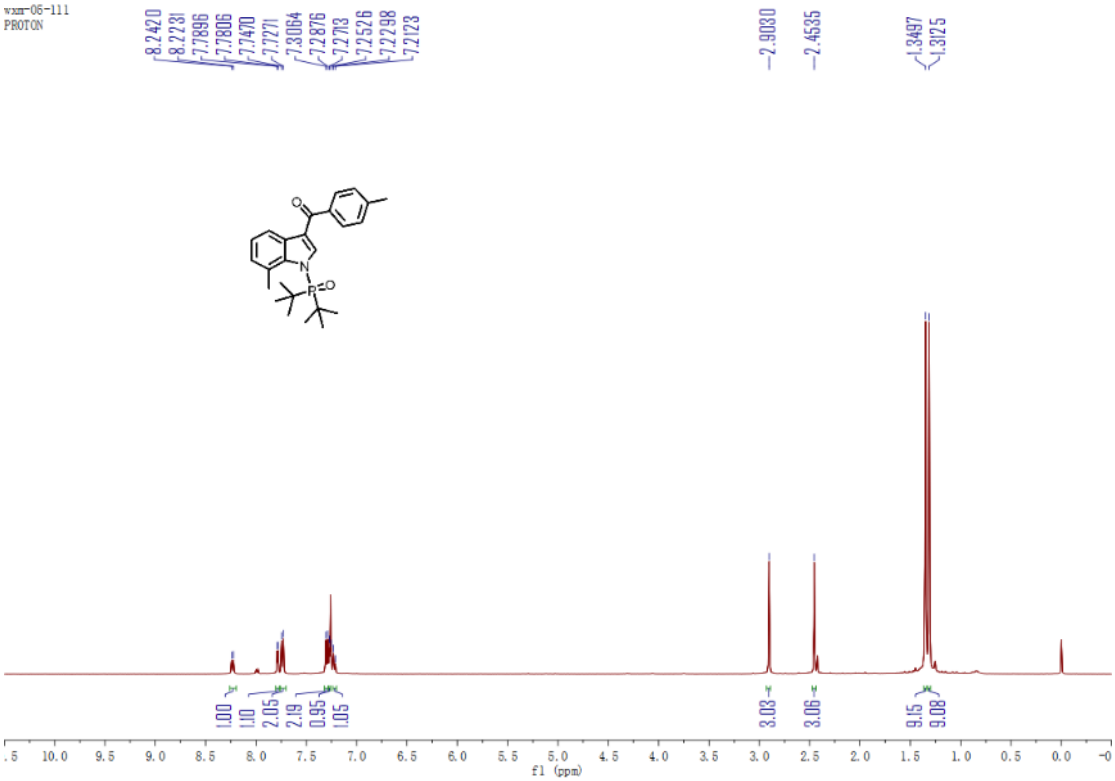
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3u**



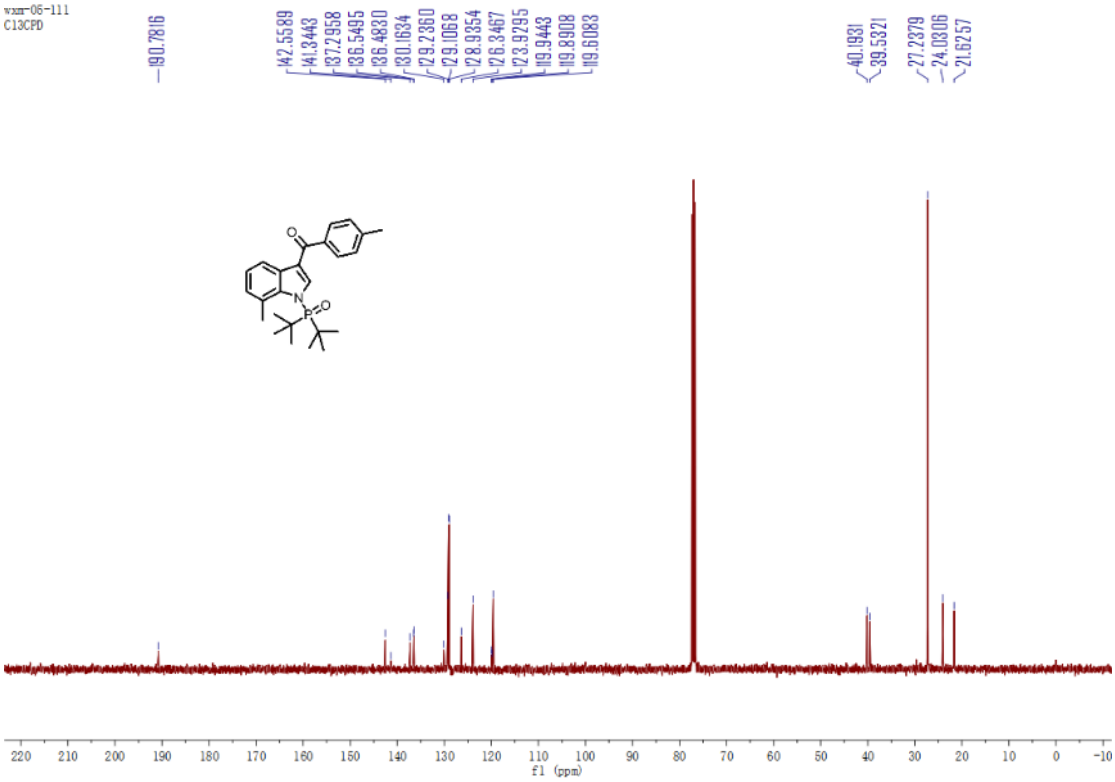
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3u**



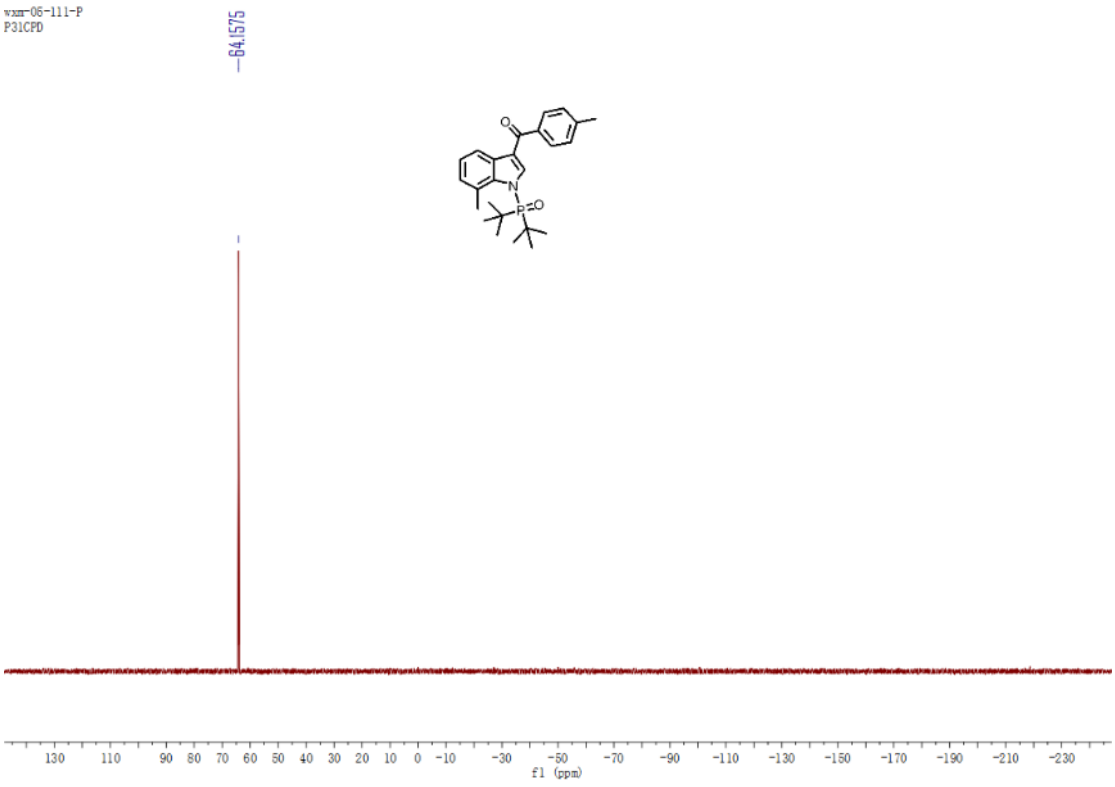
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3v**



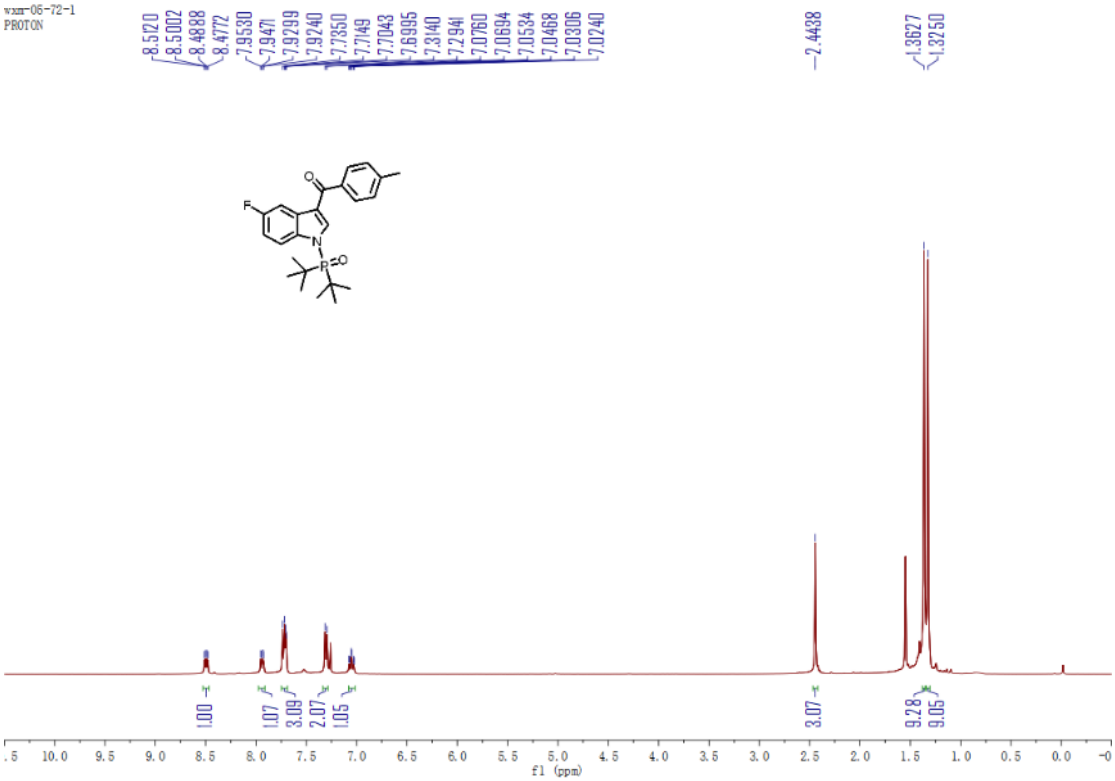
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3v**



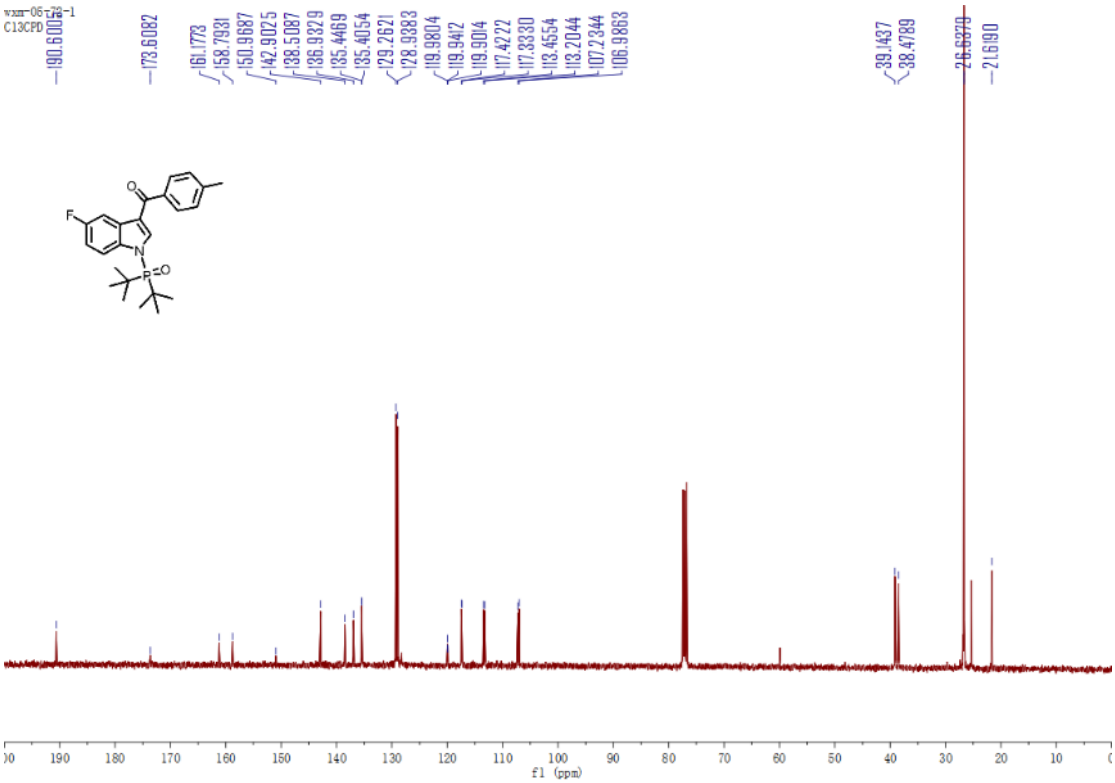
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3v**



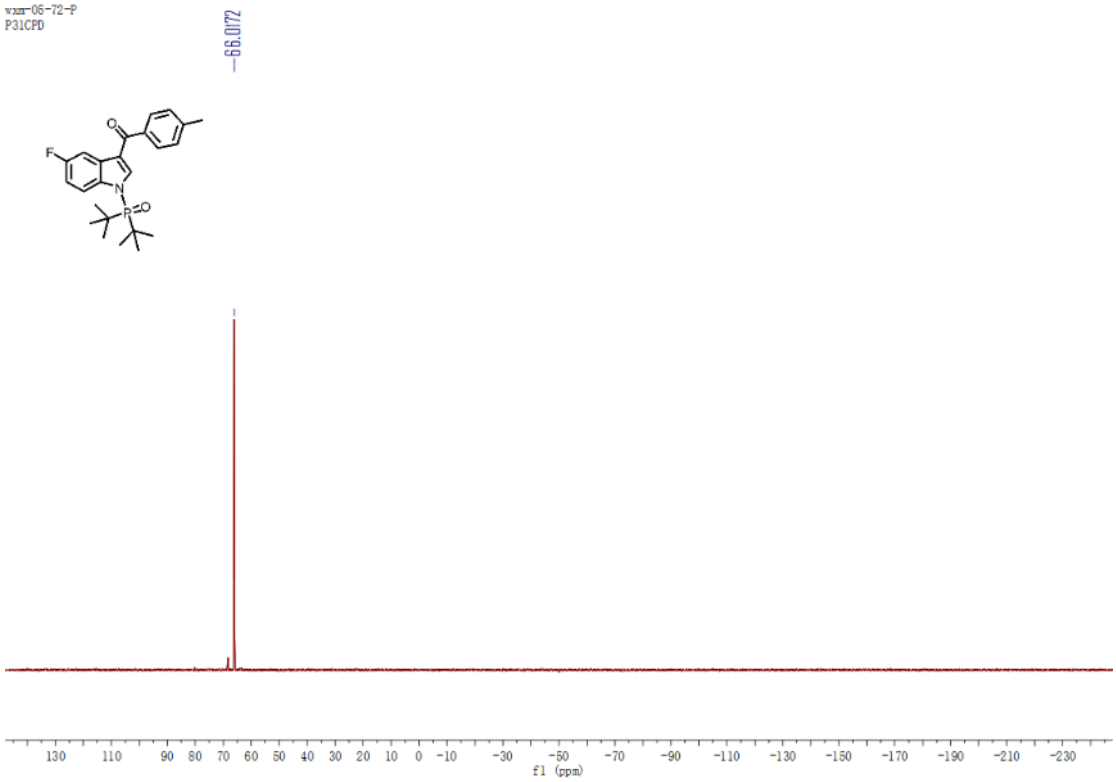
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3w**



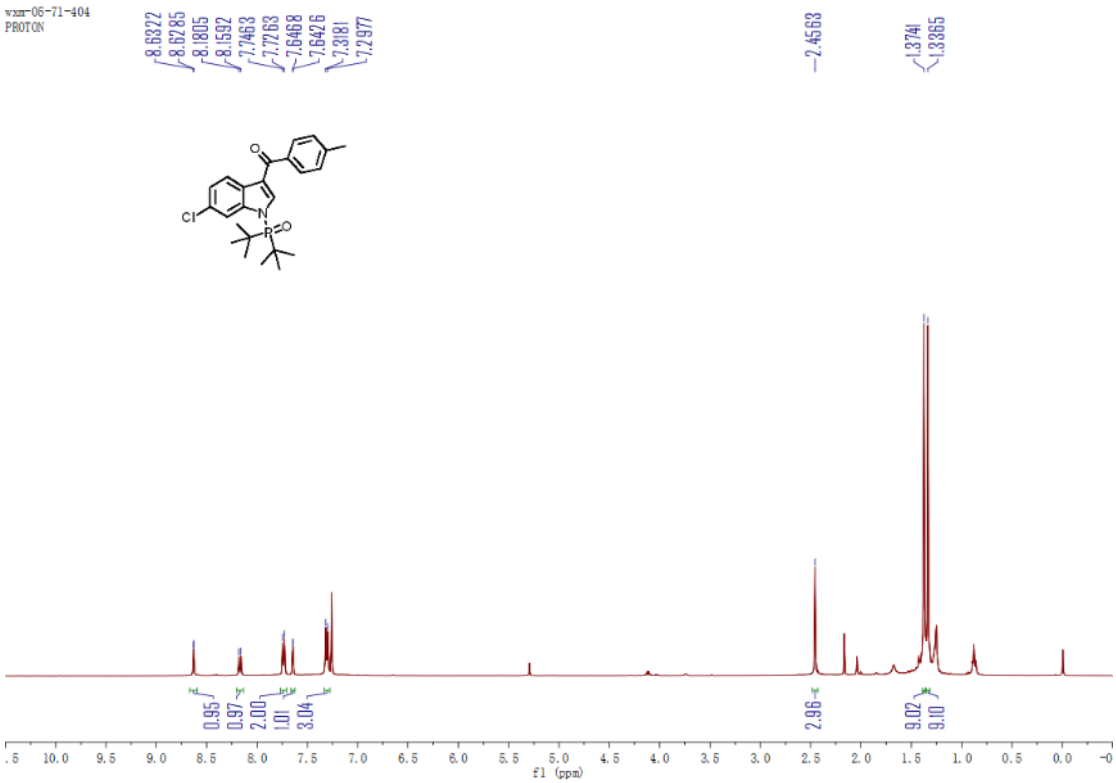
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3w**



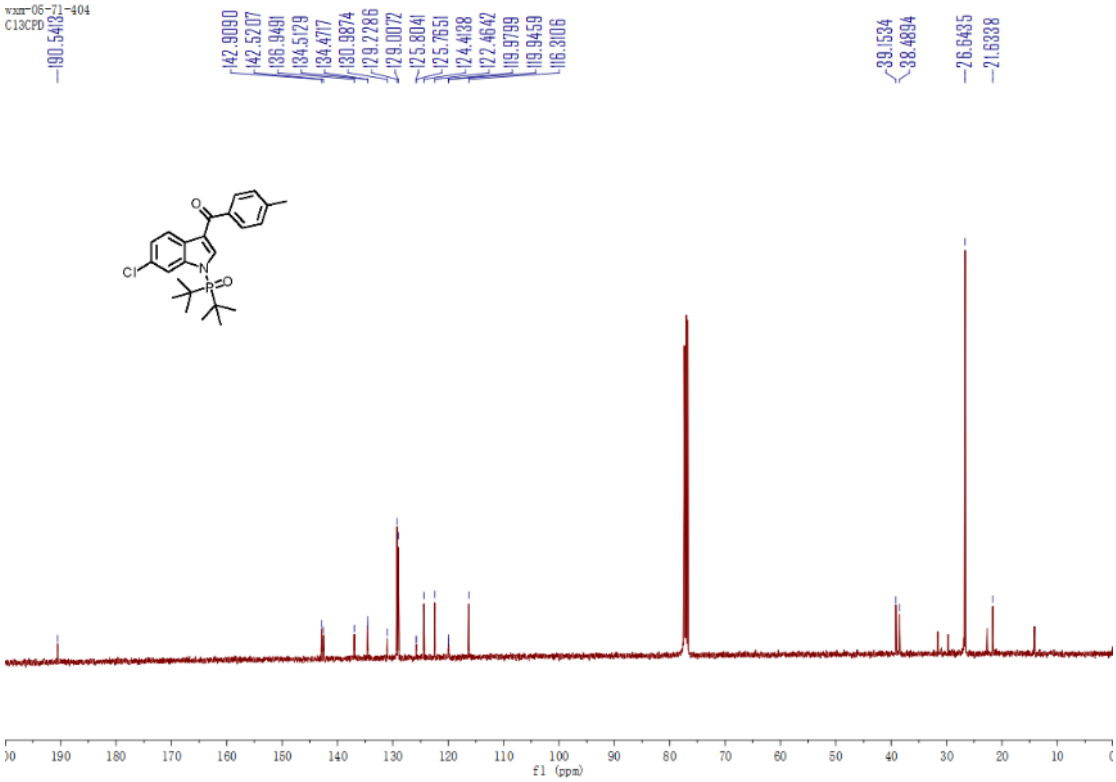
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3w**



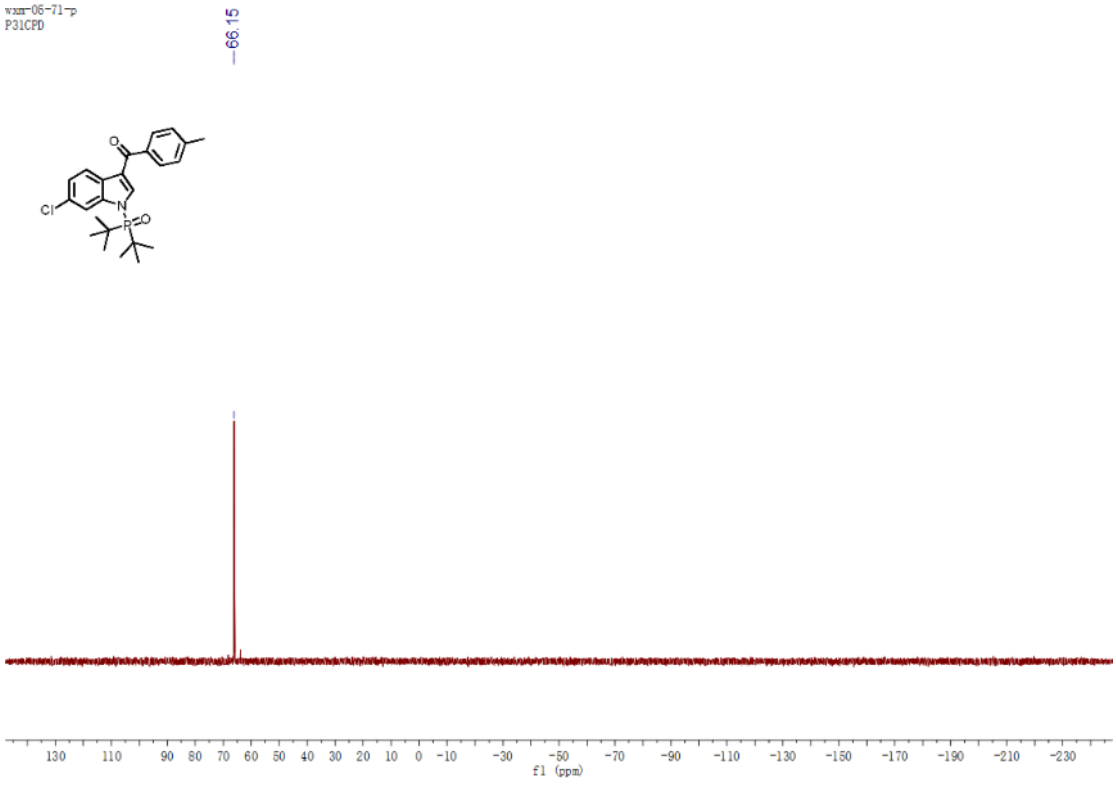
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3x**



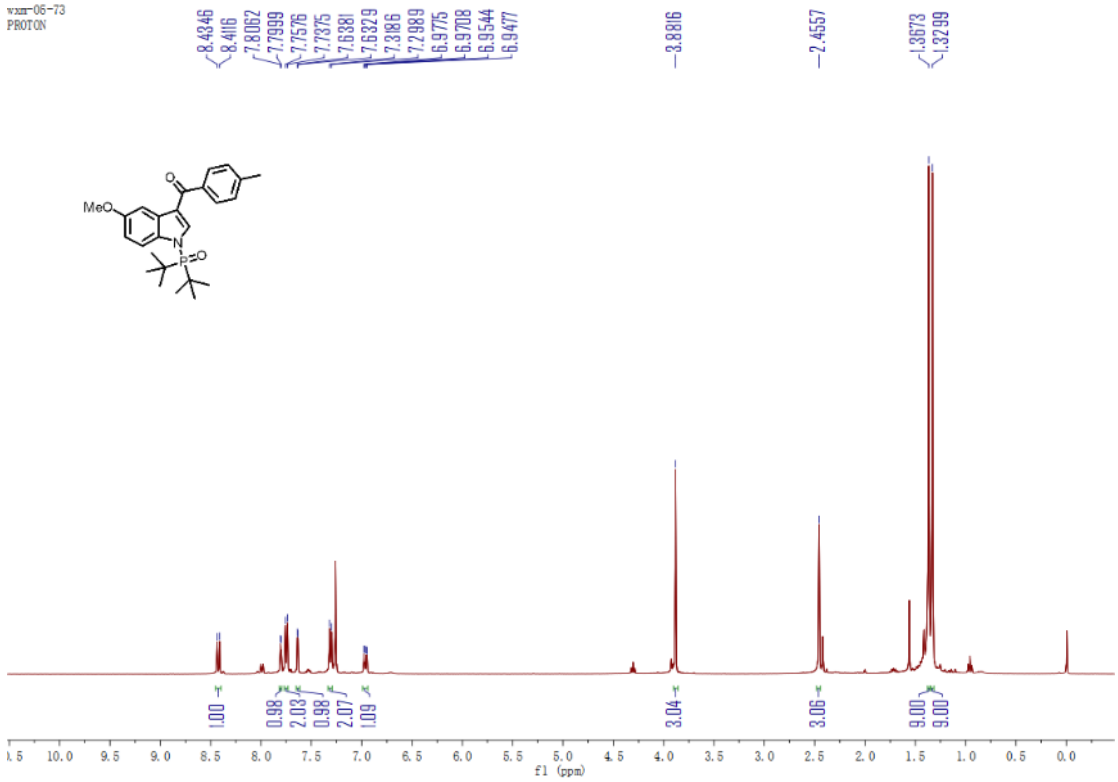
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3x**



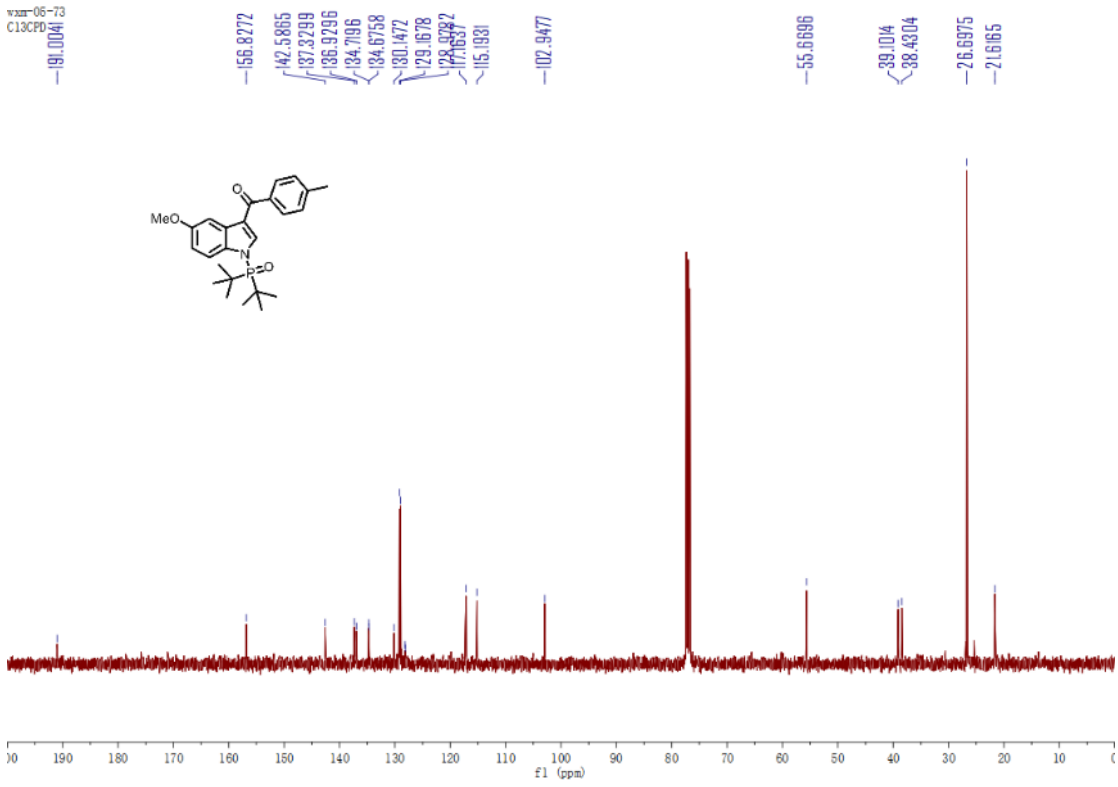
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3x**



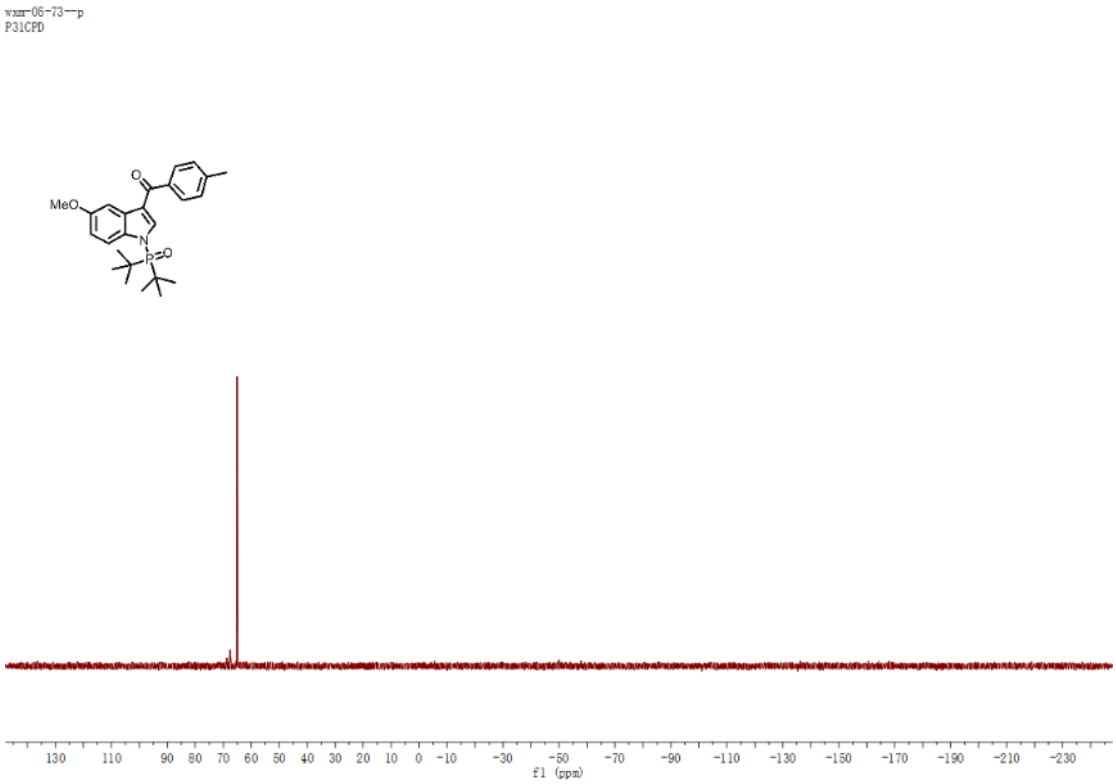
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3y**



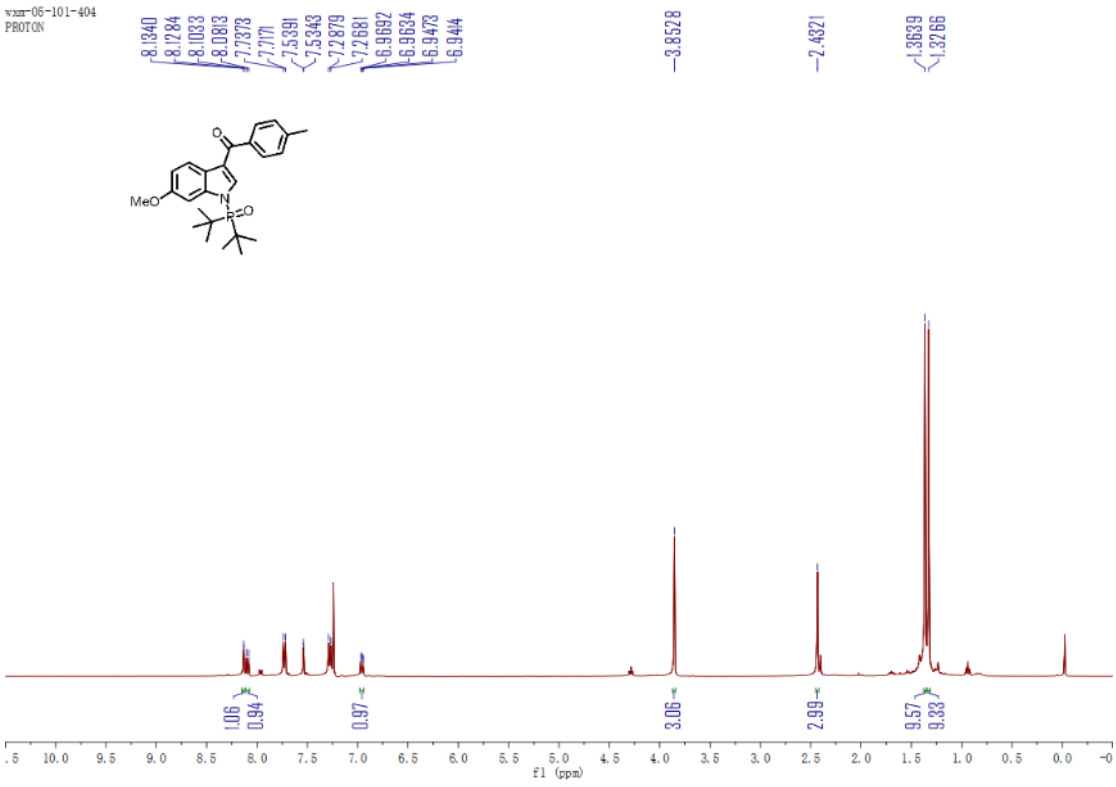
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3y**



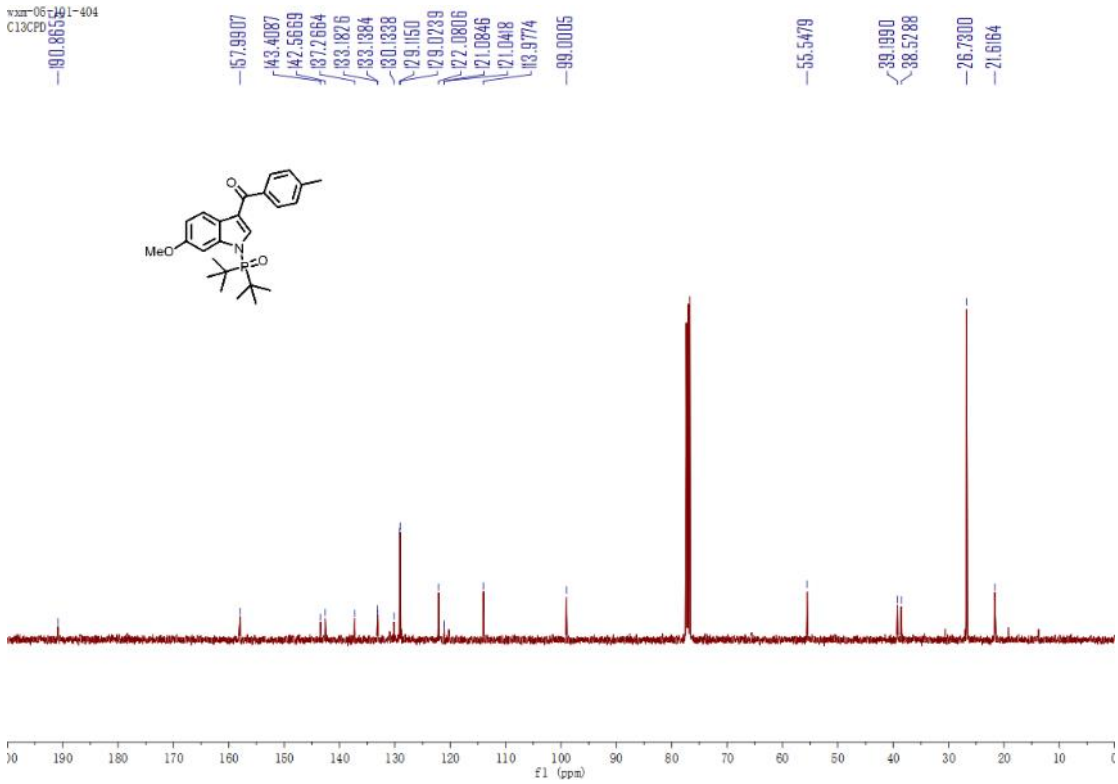
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3y**



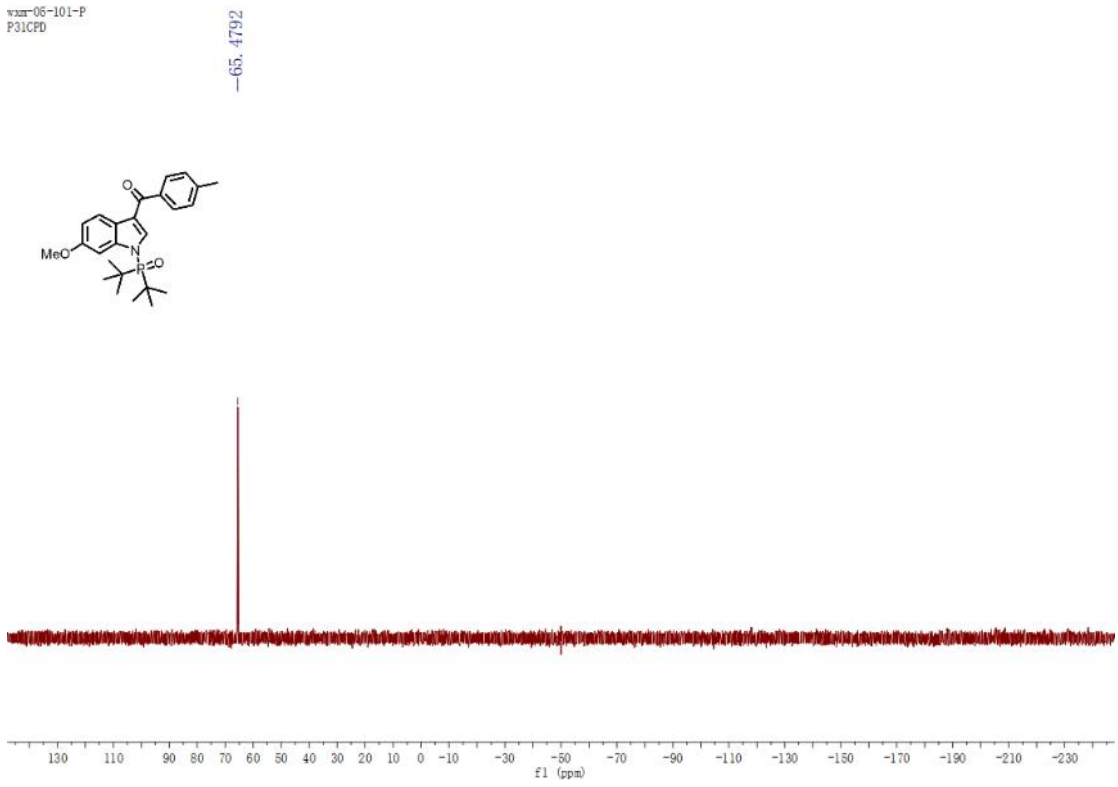
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3z**



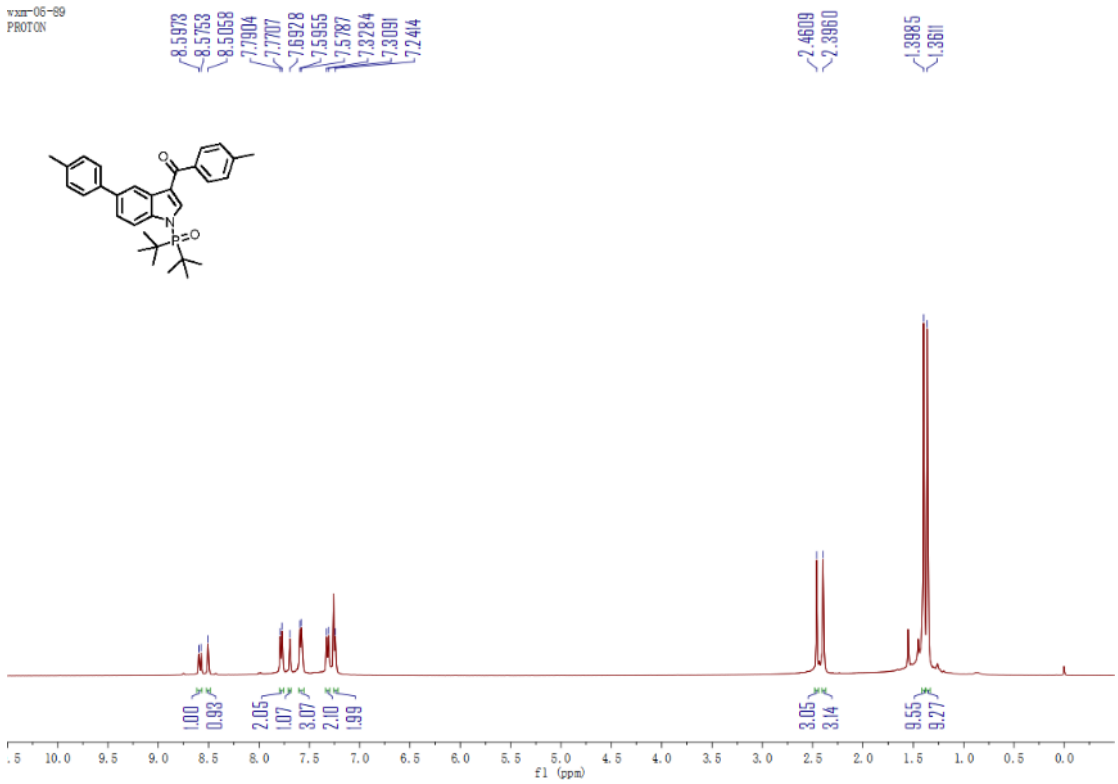
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3z**



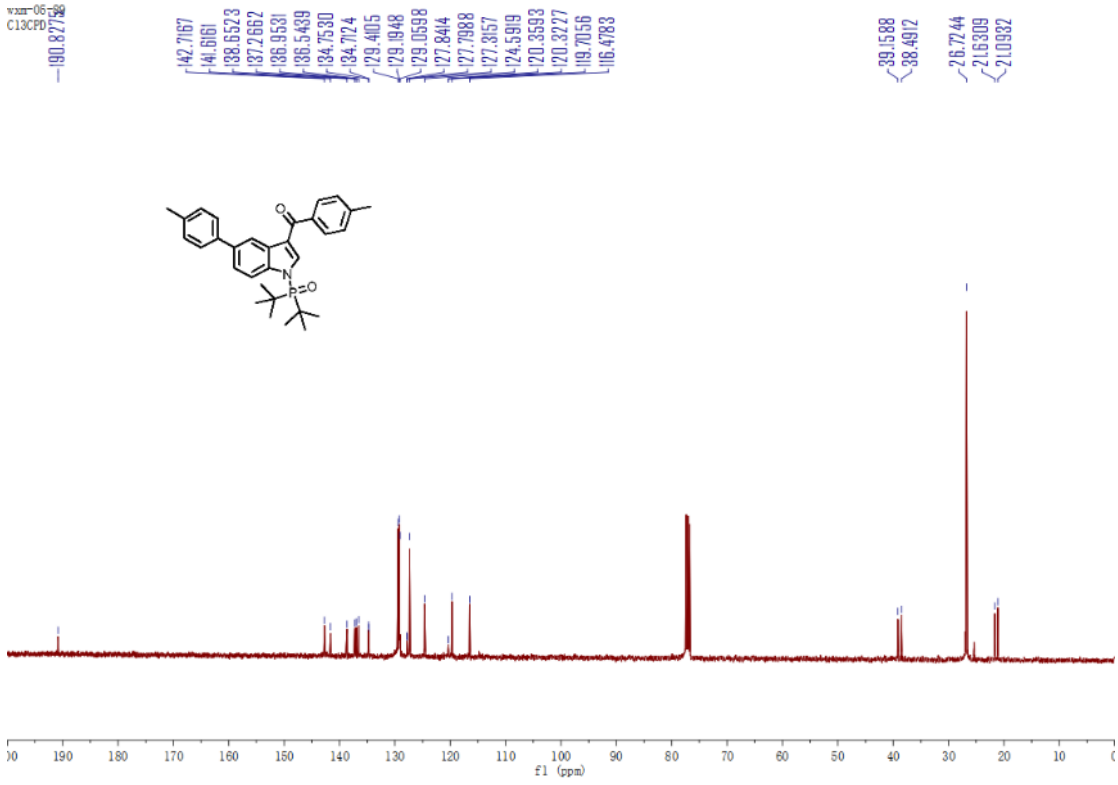
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3z**



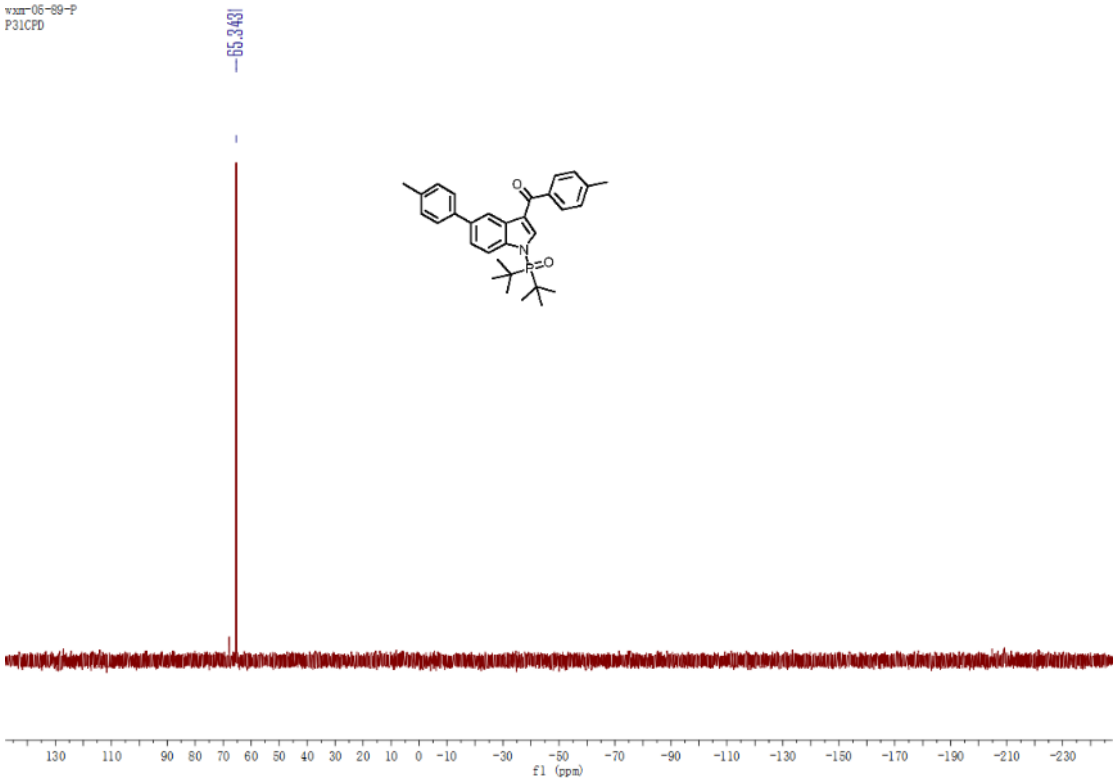
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3aa**



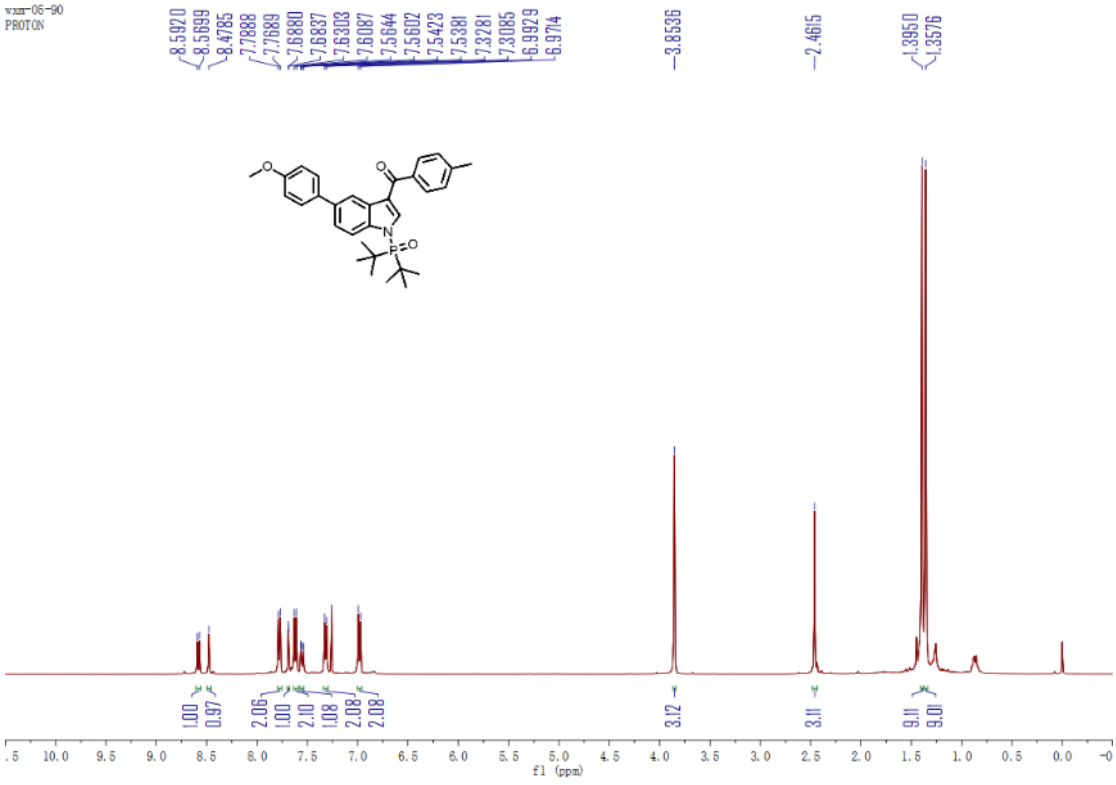
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3aa**



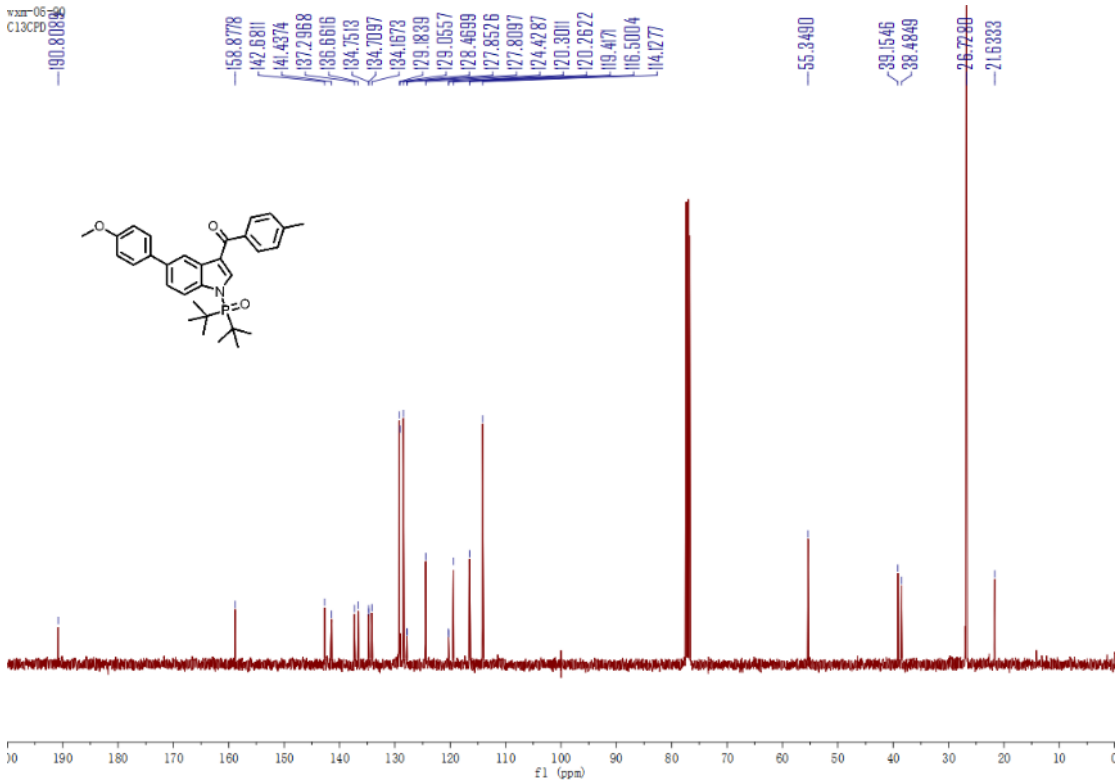
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3aa**



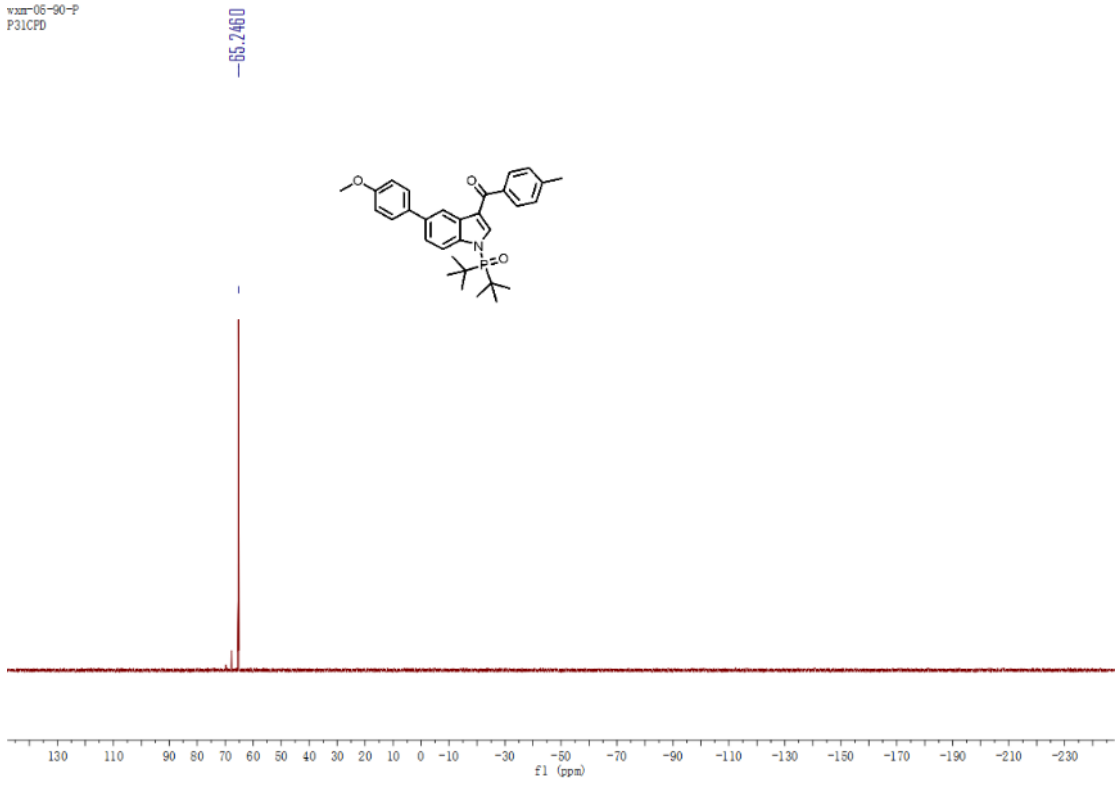
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3bb**



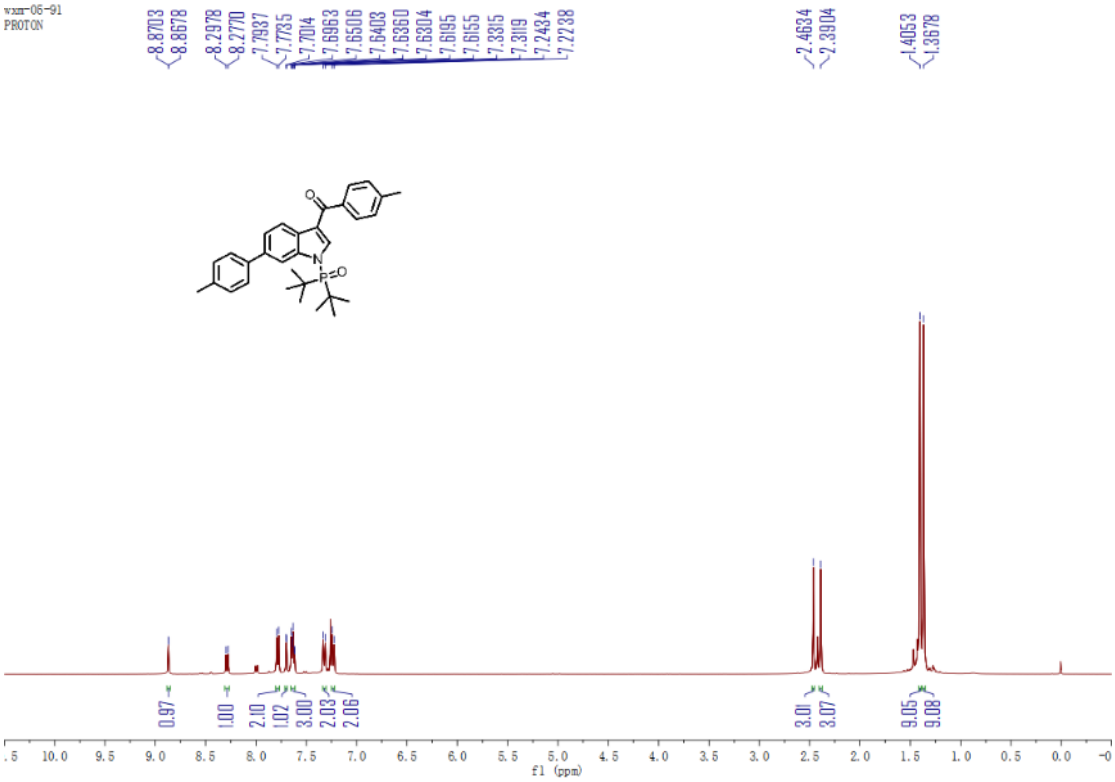
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3bb**



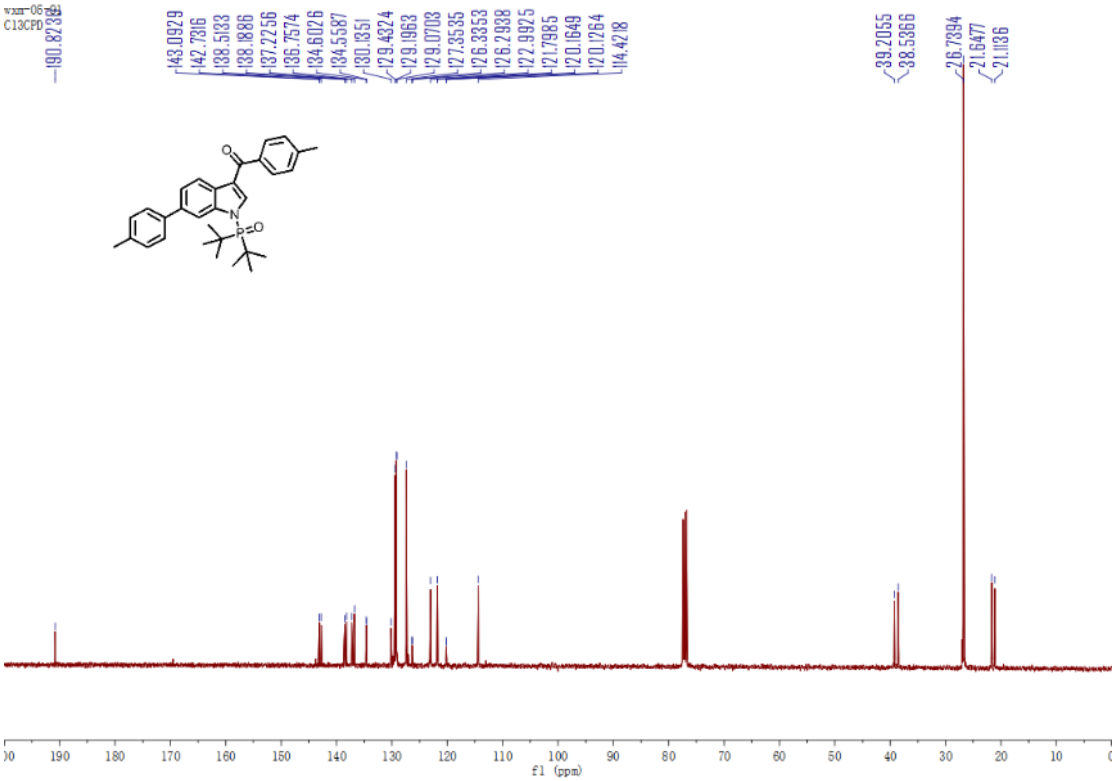
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3bb**



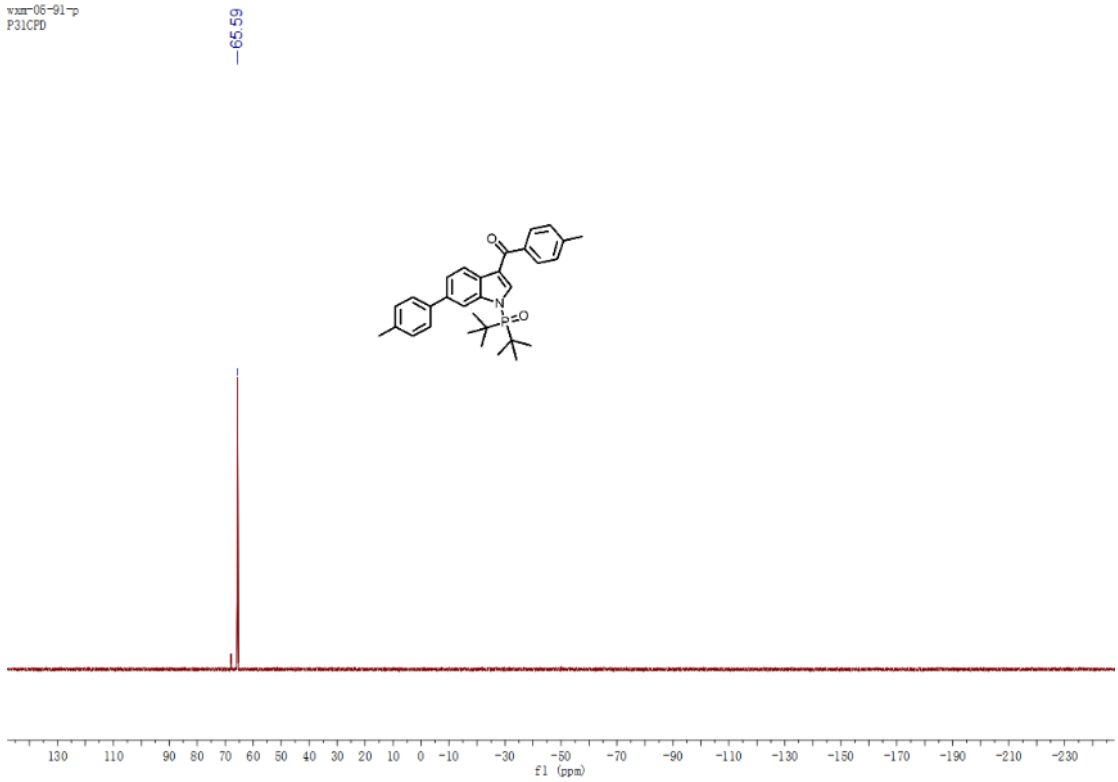
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3cc**



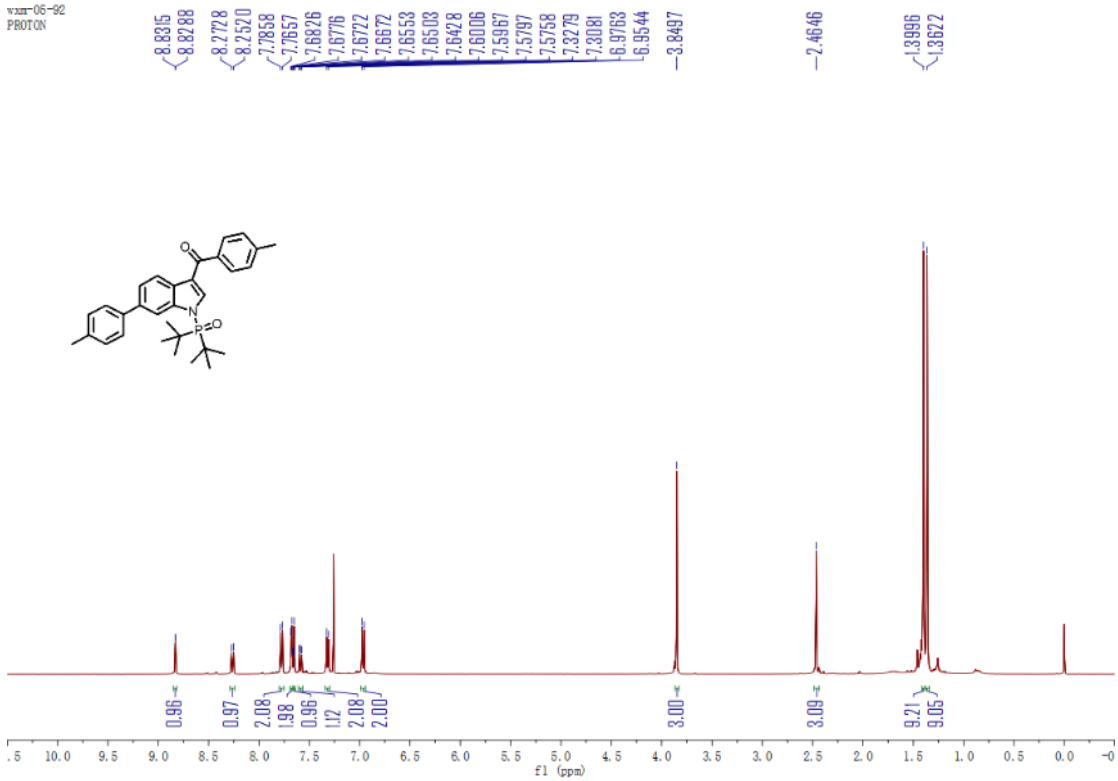
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3cc**



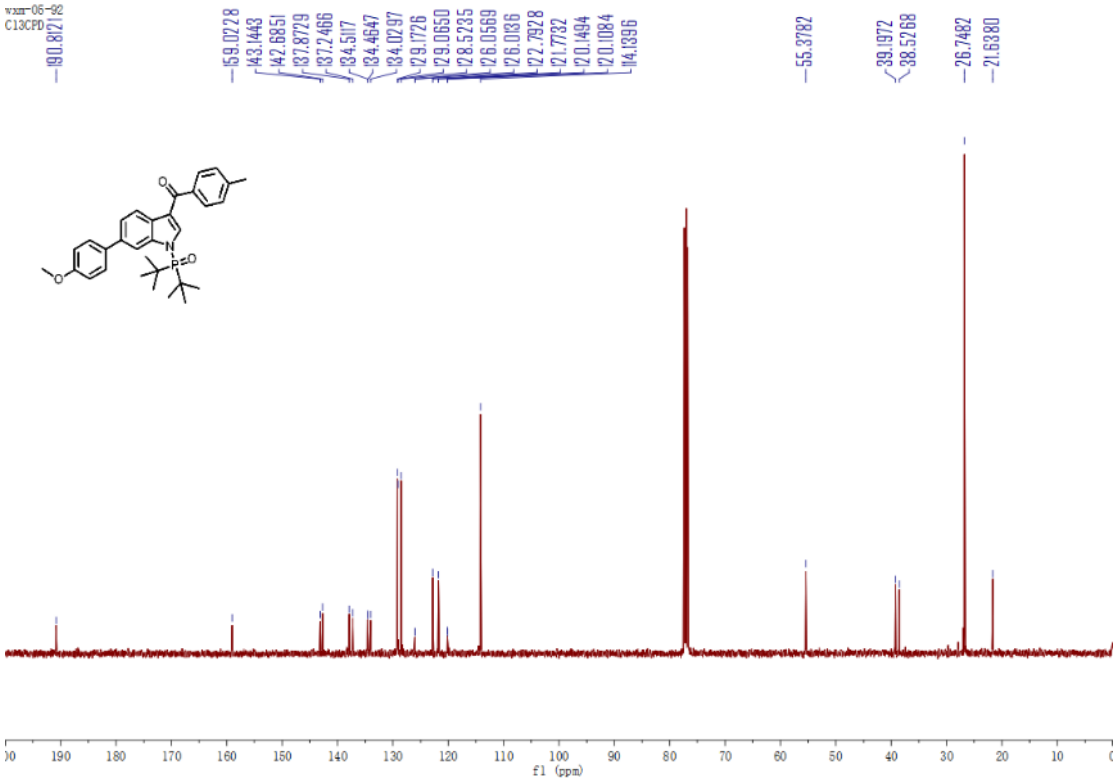
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3cc**



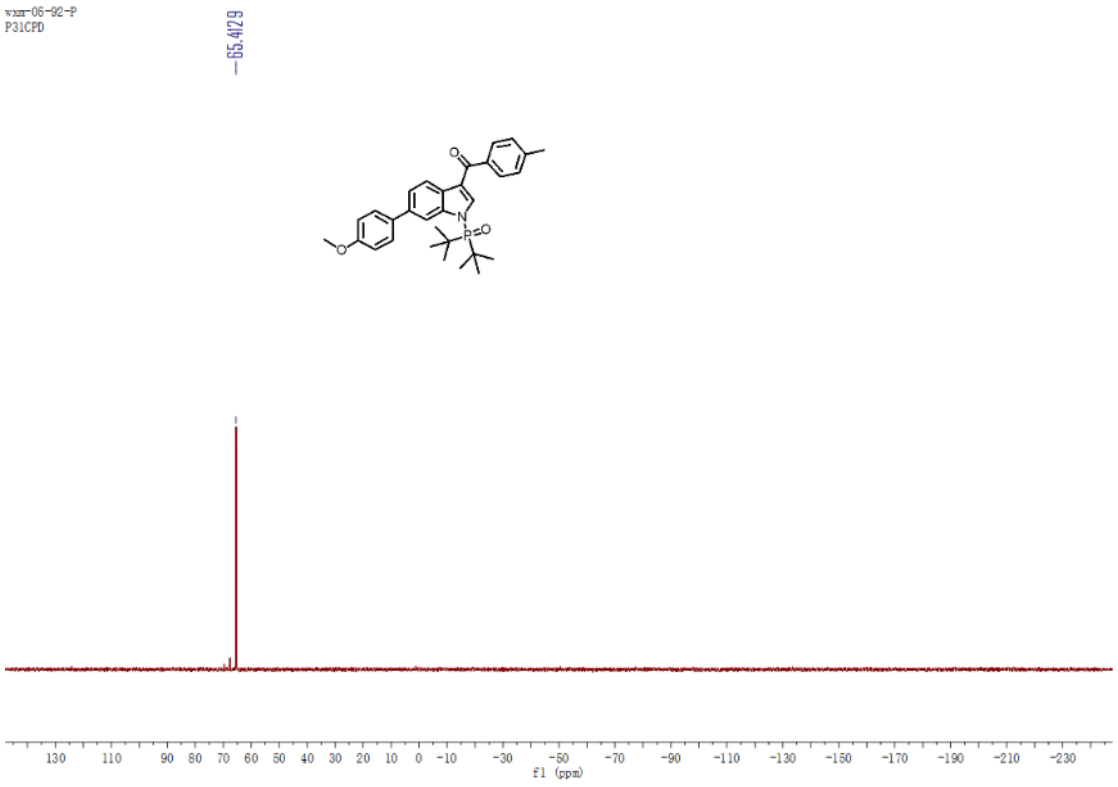
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **3dd**



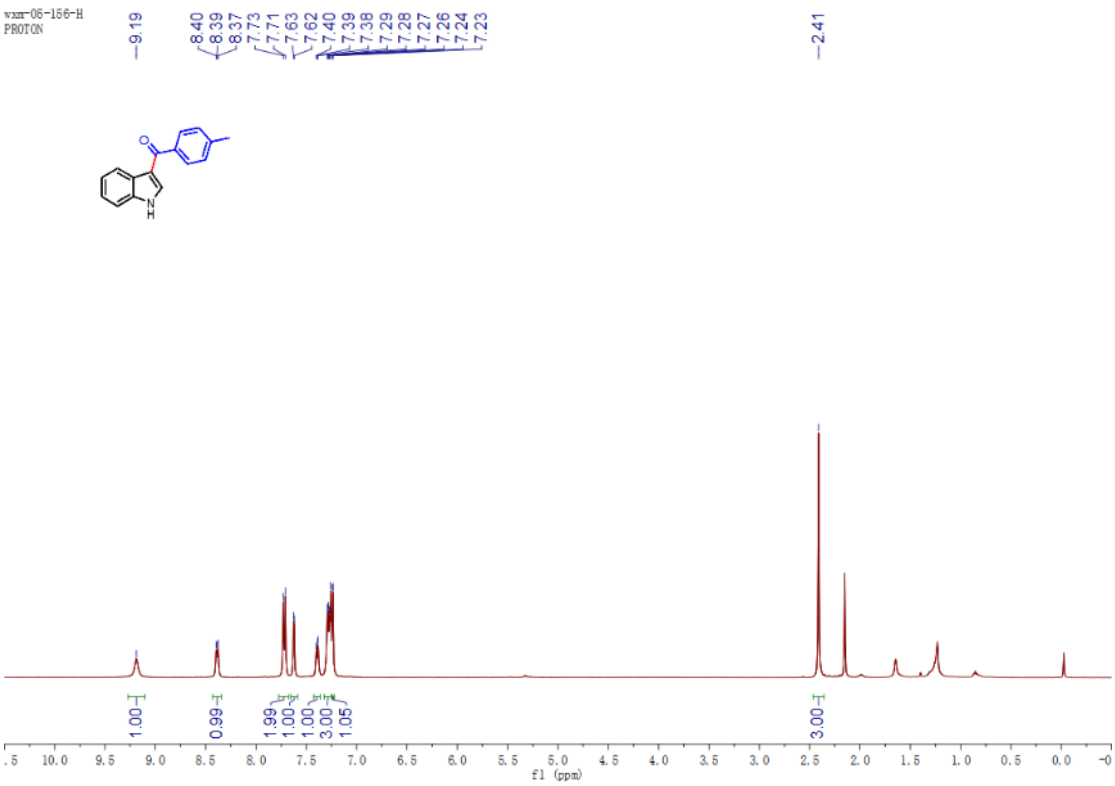
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **3dd**



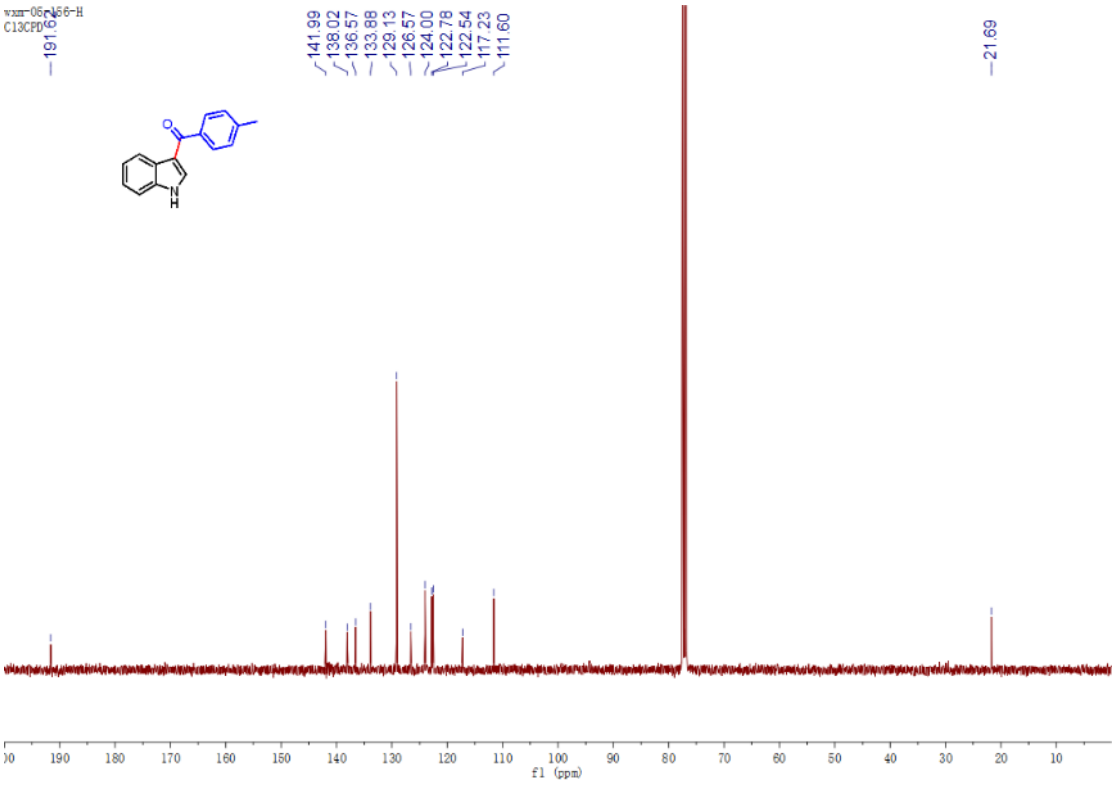
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **3dd**



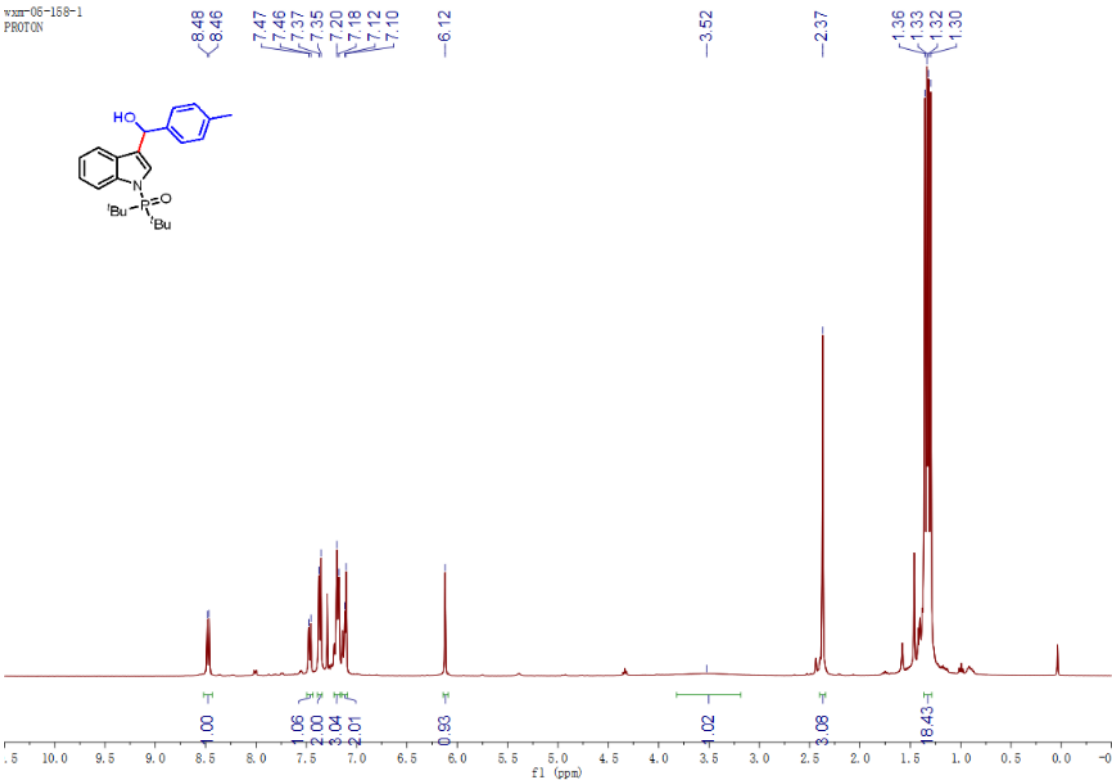
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **4**



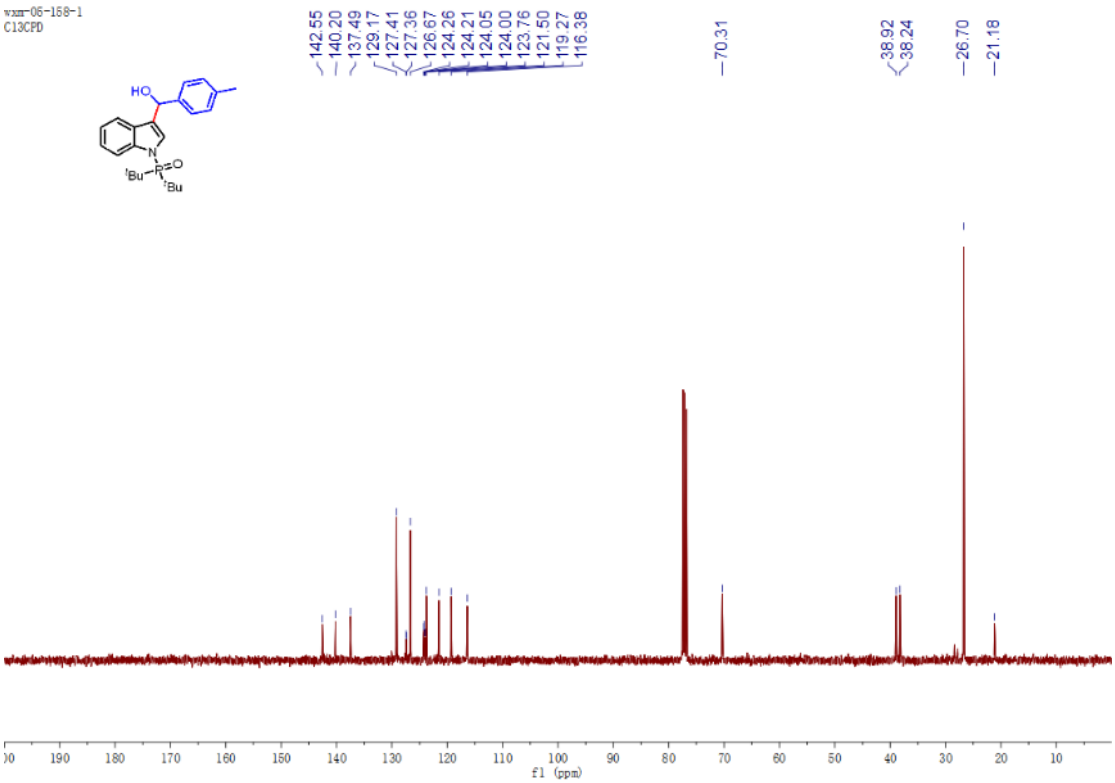
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **4**



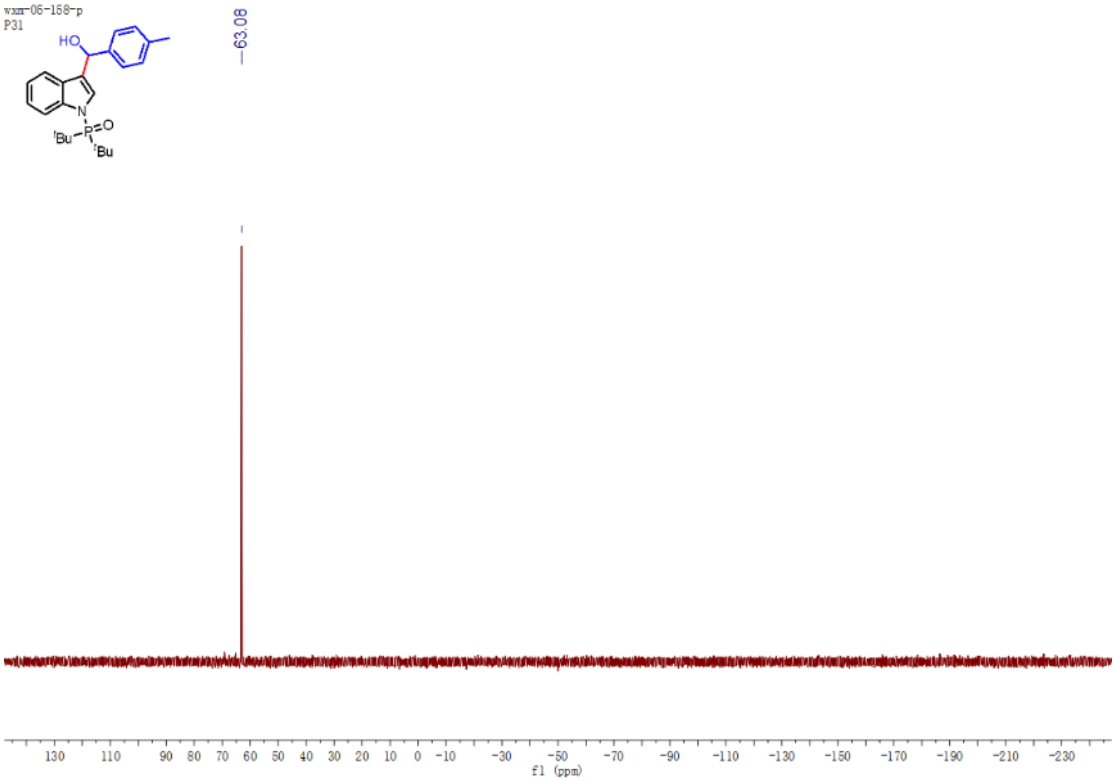
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **5**



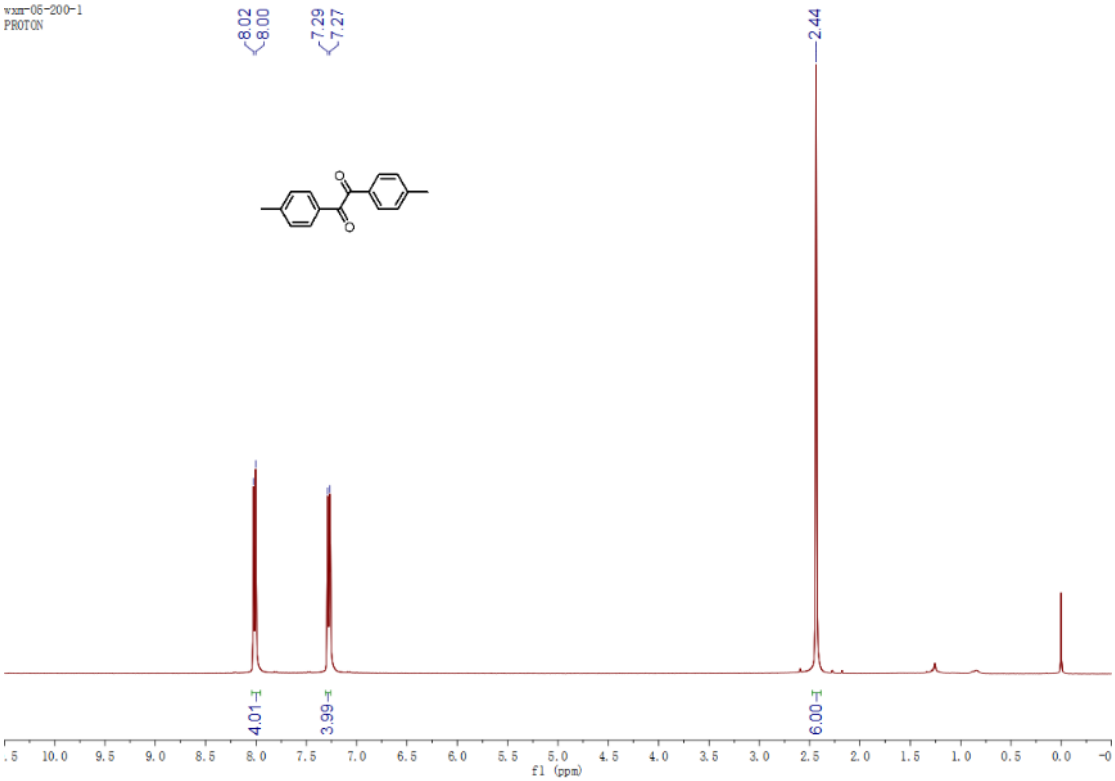
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **5**



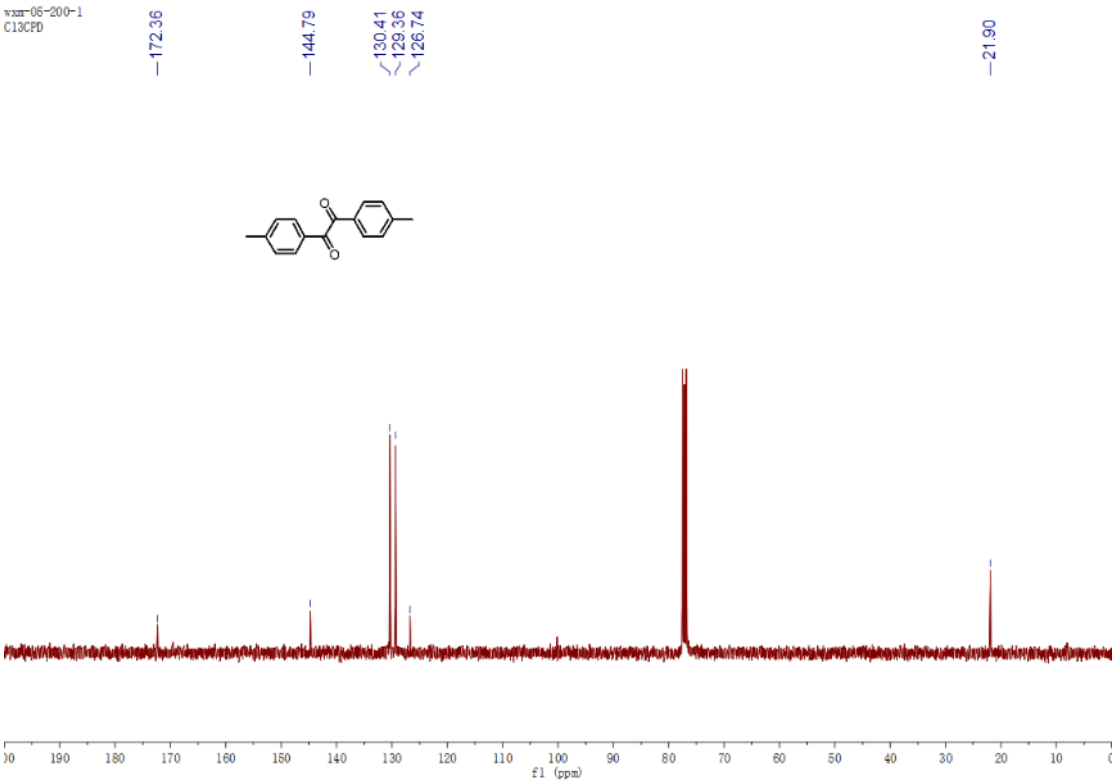
^{31}P NMR spectrum (162 MHz, CDCl3) of compound **5**



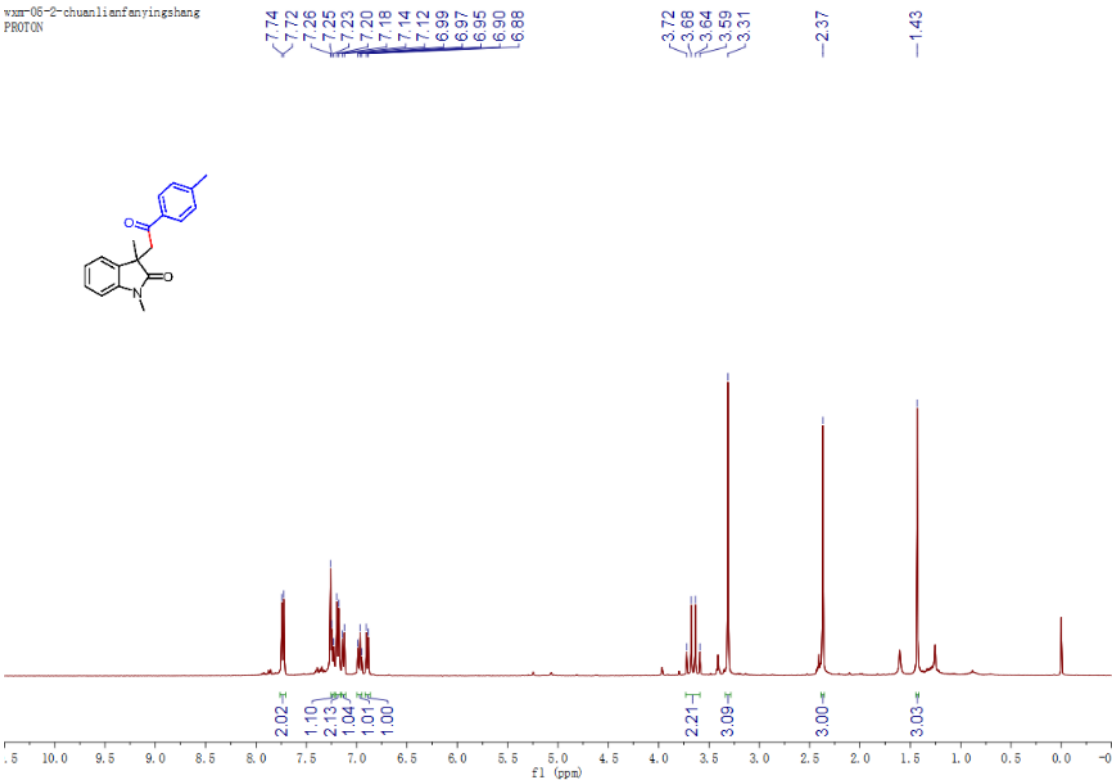
^{1}H NMR spectrum (400 MHz, CDCl3) of compound **6**



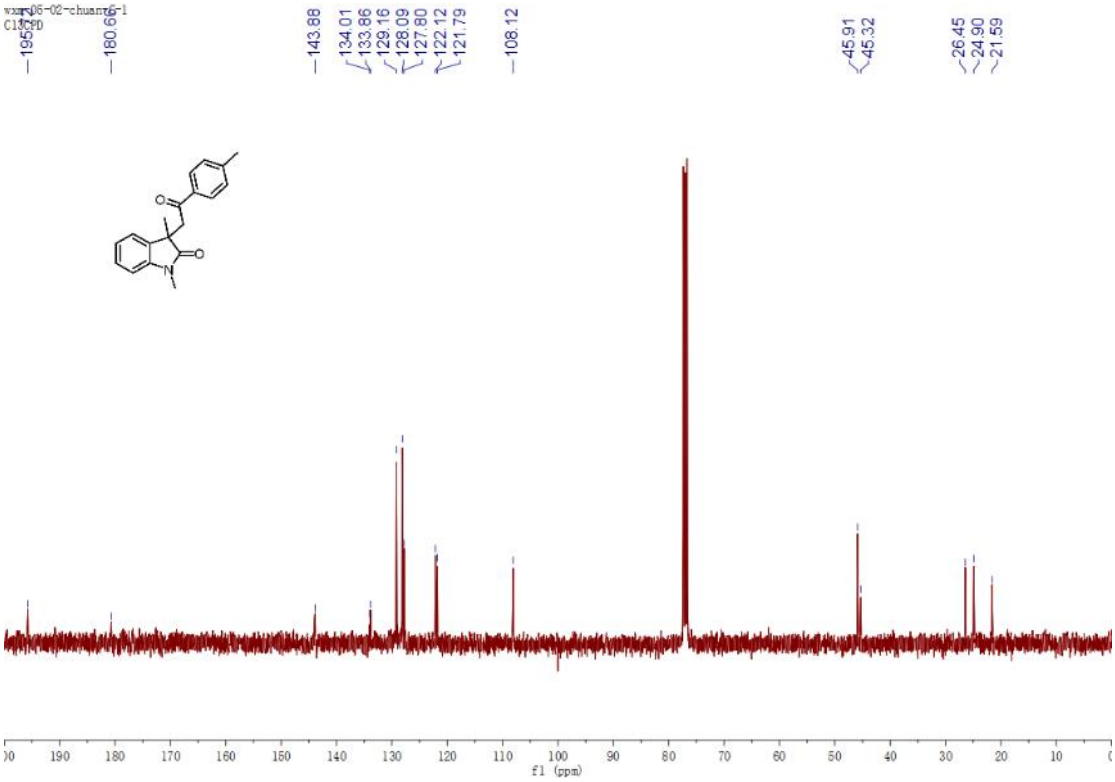
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **6**



^{1}H NMR spectrum (400 MHz, CDCl3) of compound **8**



^{13}C NMR spectrum (100 MHz, CDCl3) of compound **8**



9. References

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