Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Solvent-Controlled Regioselective Arylation of Indoles and Mechanistic Explorations

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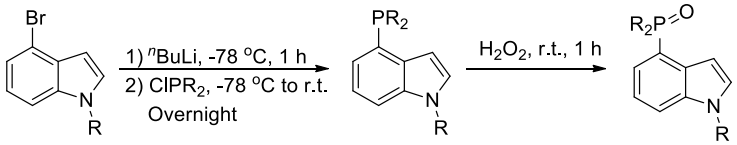
Table of content

1. General information

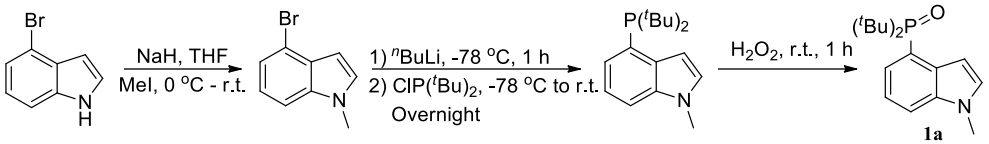
^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H and 101 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal tandard.^{31}P and ^{19}F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants are reported in Hertz (Hz). High resolution mass spectroscopic (HRMS) and general resolution mass spectra (GRMS) were measured using Bruker micro TOF-Q mass spectrometer and Thermo Scientific DS II mass spectrometer. Analytical thin layer chromatography (TLC) was carried out using commercial silica-gel plates, spots were detected with UV light (254 nm) and revealed with phosphomolybdic acid solutions. UV Vis absorption spectrum was obtained by Agilent UV-Cary 5000. Fluorescence spectrum and absolute quantum yields was obtained by Edinburgh Instrument FLS-920. All photophysical properties were tested in the form of solution [CH_2Cl_2 ($1 \times 10{-}5$ mol/L)]. The starting materials were purchased from Aldrich, Across Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from “Purification of Laboratory Chemicals book”. Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. Synthesis of P-sources

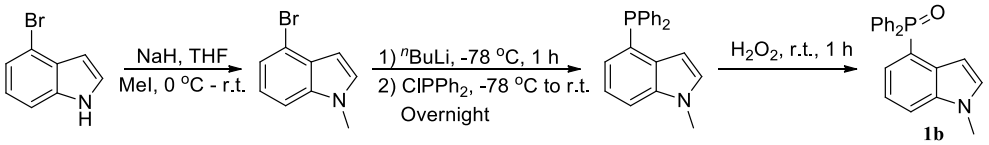


General procedure (GP):

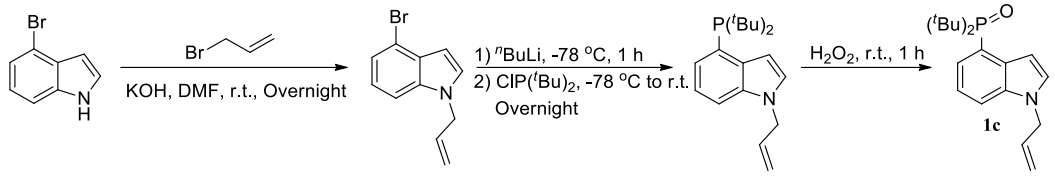
To a distilled THF solution (50 mL) of 4-bromo-1-protective group-1H-indole (10 mmol) was added dropwise ^{n}BuLi (5 mL, 12 mmol, 2.4 M in hexane) at -78 °C under Ar atmosphere. The reaction mixture was stirred for 1 hour, then R_2PCl (11 mmol) was added at -78 °C, then the temperature was slowly raised to room temperature and stirred overnight. H_2O_2 (2.5 mL, 30% aq) was added dropwise under ice bath. Water (30 mL) was added and the organic phase was extracted with ethyl acetate (2 × 40 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed in vacuo, the residue was purified by preparative column chromatography (silica gel) and eluted with petroleum ether/ethyl acetate to afford the desire products.



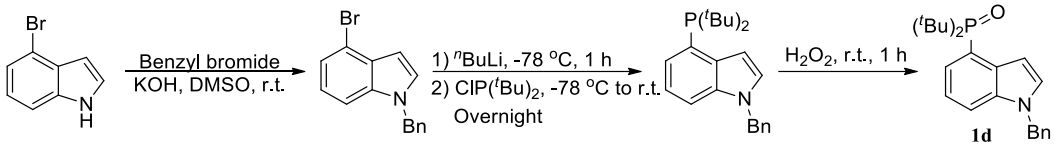
4-bromo-1-methyl-1H-indole was prepared according to the reported literature[1]. Then pass through GP and get **1a** (yield:63%) as a white solid from slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 3.1 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.33 (dd, *J* = 9.8, 7.4 Hz, 1H), 7.20 (td, *J* = 7.7, 2.8 Hz, 1H), 7.10 (d, *J* = 3.1 Hz, 1H), 3.78 (s, 3H), 1.34 (s, 9H), 1.31 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.75 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.01 (d, *J* = 10.6 Hz), 132.96 (d, *J* = 5.7 Hz), 129.88 (s), 122.77 (d, *J* = 10.3 Hz), 122.21 (d, *J* = 81.4 Hz), 119.40 (d, *J* = 11.9 Hz), 111.74 (d, *J* = 2.8 Hz), 103.83 (d, *J* = 1.1 Hz), 36.85 (d, *J* = 59.5 Hz), 32.75 (s), 27.28 (s). GRMS calcd for $C_{17}H_{26}NOP$: $[M+H]^+$ 292.1825, found 292.1451.



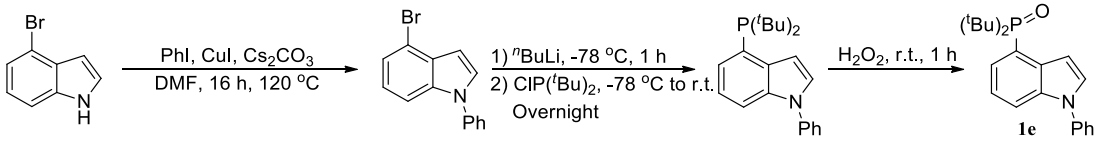
4-bromo-1-methyl-1H-indole was prepared according to the reported literature[1]. Then pass through GP and get **1b** (yield:61%) as a white solid from slica gel chromatography (petroleum ether : ethyl acetate = 2:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 4H), 7.52 – 7.46 (m, 3H), 7.44 – 7.38 (m, 4H), 7.25 – 7.18 (m, 2H), 7.00 (d, *J* = 3.2 Hz, 1H), 6.41 (d, *J* = 3.0 Hz, 1H), 3.75 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.16 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.66 (d, *J* = 12.6 Hz), 133.21 (d, *J* = 103.8 Hz), 132.10 (d, *J* = 10.0 Hz), 131.66 (d, *J* = 2.7 Hz), 130.34 (s), 129.66 (d, *J* = 10.3 Hz), 128.39 (d, *J* = 12.1 Hz), 125.40 (d, *J* = 10.3 Hz), 123.08 (d, *J* = 106.0 Hz), 120.58 (d, *J* = 13.4 Hz), 113.43 (d, *J* = 2.8 Hz), 102.03 (d, *J* = 3.0 Hz), 32.96 (s). GRMS calcd for $C_{21}H_{18}NOP$: $[M+H]^+$ 332.1199, found 332.0801.



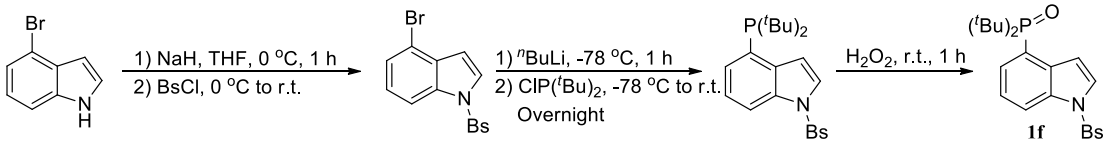
1-allyl-4-bromo-1H-indole was prepared according to the reported literature[2]. Then pass through GP and get **1c** (yield:58%) as a white solid from slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.22 – 7.14 (m, 2H), 5.99 (ddt, *J* = 15.7, 10.4, 5.3 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 5.07 (d, *J* = 17.1 Hz, 1H), 4.74 (d, *J* = 5.0 Hz, 2H), 1.33 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.93 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.41 (d, *J* = 10.7 Hz), 133.31 (s), 133.14 (d, *J* = 5.6 Hz), 128.99 (s), 122.96 (d, *J* = 10.3 Hz), 122.22 (d, *J* = 81.4 Hz), 119.43 (d, *J* = 11.9 Hz), 117.43 (s), 112.12 (d, *J* = 2.7 Hz), 104.19 (s), 48.81 (s), 36.85 (d, *J* = 59.5 Hz), 27.31 (s). GRMS calcd for $C_{19}H_{28}NOP$: $[M+H]^+$ 318.1981, found 318.2456.



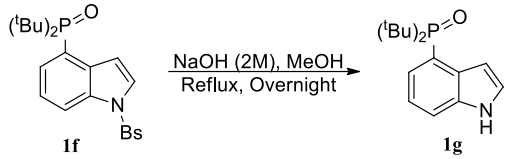
1-benzyl-4-bromo-1H-indole was prepared according to the reported literature[3]. Then pass through GP and get **1d** (yield:55%) as a white solid from slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 3.1 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.24 (m, 4H), 7.19 (d, *J* = 3.2 Hz, 1H), 7.17 – 7.08 (m, 3H), 5.31 (s, 2H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.08 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.24 (s), 136.64 (d, *J* = 10.6 Hz), 133.27 (d, *J* = 5.6 Hz), 129.45 (s), 128.77 (s), 127.68 (s), 126.85 (s), 123.06 (d, *J* = 10.3 Hz), 122.31 (d, *J* = 81.3 Hz), 119.61 (d, *J* = 11.9 Hz), 112.24 (d, *J* = 2.7 Hz), 104.49 (d, *J* = 1.1 Hz), 50.09 (s), 36.88 (d, *J* = 59.5 Hz), 27.33 (s). GRMS calcd for $C_{23}H_{30}NOP$: $[M+H]^+$ 368.2138, found 368.1704.



4-bromo-1-phenyl-1H-indole was prepared according to the reported literature[4]. Then pass through GP and get **1e** (yield:50%) as a pale yellow colloid from slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 3.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.44 (m, 4H), 7.42 – 7.33 (m, 3H), 7.19 (td, *J* = 7.8, 2.8 Hz, 1H), 1.36 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.85 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.45 (s), 136.31 (d, *J* = 10.6 Hz), 133.81 (d, *J* = 5.6 Hz), 129.65 (s), 129.06 (s), 126.67 (s), 124.66 (s), 123.82 (d, *J* = 10.2 Hz), 122.54 (d, *J* = 80.9 Hz), 120.30 (d, *J* = 11.8 Hz), 113.05 (d, *J* = 2.6 Hz), 106.08 (d, *J* = 0.9 Hz), 36.90 (d, *J* = 59.5 Hz), 27.33 (s). GRMS calcd for $C_{22}H_{28}NOP$: $[M+H]^+$ 354.1981, found 354.2474.

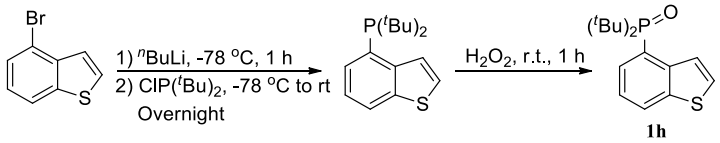


4-bromo-1-(phenylsulfonyl)-1H-indole was prepared according to the reported literature[5]. Then pass through GP and get **1f** (yield:40%) as a pale yellow solid from slica gel chromatography (petroleum ether : ethyl acetate = 2:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.7 Hz, 1H), 8.15 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.39 (m, 4H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 3.7 Hz, 1H), 1.17 (d, *J* = 14.3 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.15 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.32 (s), 139.89 (d, *J* = 3.8 Hz), 133.23 (s), 129.85 (d, *J* = 72.2 Hz), 128.30 (s), 127.96 (s), 127.43 (d, *J* = 10.3 Hz), 126.59 (s), 123.57 (s), 121.50 (s), 119.81 (d, *J* = 12.5 Hz), 116.02 (s), 38.34 (d, *J* = 62.4 Hz), 27.03 (s). GRMS calcd for $C_{22}H_{28}NO_3PS$: $[M+H]^+$ 418.1600, found 418.0972.



1f **1g**

A solution of NaOH (2.0 M, 4 mL) was added to a stirring solution **1f** (2 mmol) in methanol (10 mL) and the resulting mixture refluxed under nitrogen for overnight. The reaction mixture was concentrated under reduced pressure and extracted with ethyl acetate, and the organic layer washed successively with brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude solid was purified by slica gel chromatography (ethyl acetate) and get **1g** (yield:92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.80 (s, 1H), 1.32 (d, *J* = 14.3 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 53.24 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.26 (d, *J* = 7.7 Hz), 128.45 (d, *J* = 10.1 Hz), 126.32 (d, *J* = 92.4 Hz), 123.05 (s), 121.04 (s), 120.02 (s), 112.33 (s), 108.04 (d, *J* = 11.4 Hz), 36.01 (d, *J* = 63.5 Hz), 26.45 (s). GRMS calcd for $C_{16}H_{24}NOP$: $[M+H]^+$ 278.1668, found 278.2118.



1h

4-bromo-benzo[*b*]thiophene was commercial available. Then pass through GP and get **1h** (yield:60%) as a white solid from slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.6 Hz, 1H), 7.94 – 7.85 (m, 2H), 7.46 – 7.37 (m, 2H), 1.34 (d, *J* = 14.3 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.86 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.34 (d, *J* = 3.3 Hz), 138.87 (d, *J* = 11.7 Hz), 134.78 (d, *J* = 5.0 Hz), 131.89 (d, *J* = 73.5 Hz), 125.78 (s), 124.69 (s), 124.65 (s), 122.08 (d, *J* = 1.2 Hz), 36.03 (d, *J* = 63.1 Hz), 26.70 (s). GRMS calcd for $C_{16}H_{23}OPS$: $[M+H]^+$ 295.1280, found 295.1746.

3. Synthesis of diaryliodonium salts

3.1 Synthesis of symmetric diaryliodonium salts

Symmetric diaryliodonium salts were synthesized according to corresponding literature[6]. Aryl boronic acid (10 mmol, 1.0 equiv) and CH_2Cl_2 (40 mL) were combined in a dried round-bottom flask. The mixture was cooled to 0 °C for 5 min, BF_3•OEt_2 (1.36 mL, 1.10 equiv) was added, and the mixture was stirred for 10 min. A solution of 2-(diacetoxyiodo)arene (1.05 equiv) in CH_2Cl_2

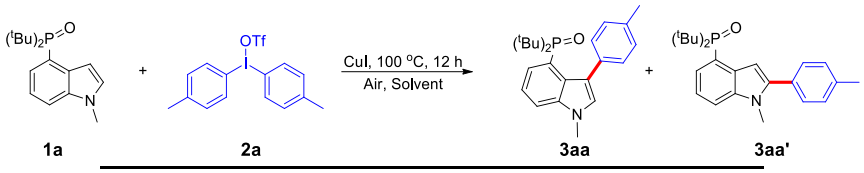
(20 mL) was added slowly for 10-15 min and stirred for additional 10 min. The mixture was warmed to room temperature and stirred for 1 h. The reaction was cooled to 0 °C again and TfOH (1.0 mL, 1.1 equiv) was dropped into the mixture. Then, the mixture was stirred for 10 min at 0 °C and warmed to room temperature for additional 10 min. At this time, the solvent was removed under reduced pressure and the residual ran through a short silica gel column (about 5 cm) with 5% of MeOH in CH_2Cl_2 quickly. The mixture was concentrated under vacuum and Et_2O (100 mL) was added to the residual. Filtrated and obtained the symmetric diaryliodonium salts as solid.

3.2 Synthesis of asymmetric diaryliodonium salts

Asymmetric diaryliodonium salts were synthesized according to corresponding literature[7].

4. Screening of reaction conditions

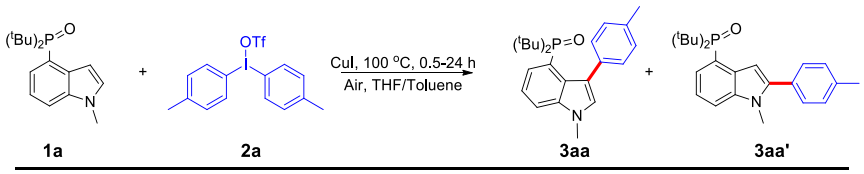
Table S1. Solvent screening[a].



Entry	Solvent	Yield of **3aa**[b]	Yield of **3aa'**[b]
1	THF	88%	Trace
2	Dioxane	43%	31%
3	DCE	13%	65%
4	DME	73%	10%
5	Toluene	Trace	73%
6	CH_3CN	N.R.	N.R.

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), CuI (10 mol%) in solvent for 12 h at 100 °C under air. [b]Isolated yield.

Table S2. Screening of reaction time[a].

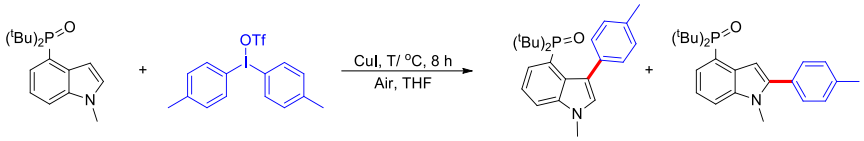


Entry	Solvent	Time	Yield of **3aa**[b]	Yield of **3aa'**[b]
1	THF	0.5 h	23%	N.D.
2	THF	1 h	58%	Trace
3	THF	2 h	71%	Trace
4	THF	4 h	81%	<5%
5	THF	6 h	85%	<5%
6	THF	8 h	88%	<5%
7	THF	12 h	88%	<5%
8	THF	24 h	88%	<5%

9	Toluene	0.5 h	15%	N.D.
10	Toluene	1 h	34%	Trace
11	Toluene	2 h	39%	12%
12	Toluene	4 h	30%	28%
13	Toluene	6 h	23%	45%
14	Toluene	8 h	15%	58%
15	Toluene	12 h	Trace	73%
16	Toluene	16 h	Trace	73%
17	Toluene	24 h	Trace	73%

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), CuI (10 mol%) in THF/toluene for 0.5-24 h at 100 °C under air. [b]Isolated yield.

Table S3. Temperture screening of C_3 arylation[a].

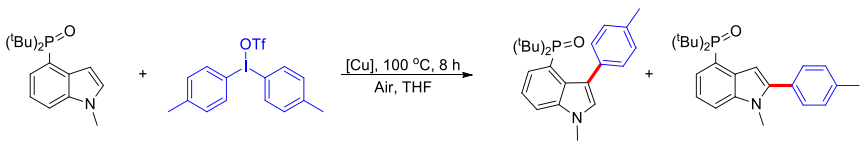


1a **2a** **3aa** **3aa'**

Entry	T/ °C	Yield of **3aa**[b]	Yield of **3aa'**[b]
1	40	36%	Trace
2	60	52%	Trace
3	80	72%	<5%
4	100	88%	<5%
5	120	68%	10%

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), CuI (10 mol%) in THF for 8 h at T/ °C under air. [b]Isolated yield.

Table S4. Catalyst screening of C_3 arylation[a].



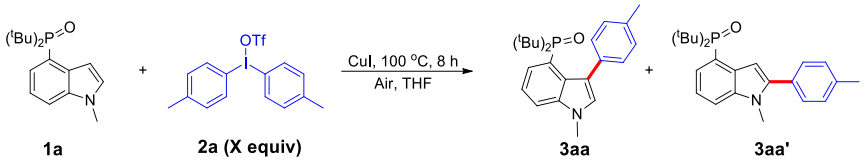
1a **2a** **3aa** **3aa'**

Entry	[Cu]	Yield of **3aa**[b]	Yield of **3aa'**[b]
1	CuI	88%	<5%
2	CuCl	84%	<5%
3	CuOTf	84%	<5%
4	$Cu(CH_3CN)_4PF_6$	42%	5%
5	Cu_2O	71%	5%
6	$Cu(OTf)_2$	47%	Trace
7	$Cu(acac)_2$	71%	5%
8	$Cu(OAc)_2$	79%	5%
9	CuO	62%	Trace

10	$CuCl_2$	81%	7%
11[c]	CuI	78%	5%

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), [Cu] (10 mol%) in THF for 8 h at 100 °C under air. [b]Isolated yield. [c]CuI (5 mol%, 0.005 mmol).

Table S5. Equivalents screening of **2a** for C_3 arylation[a].

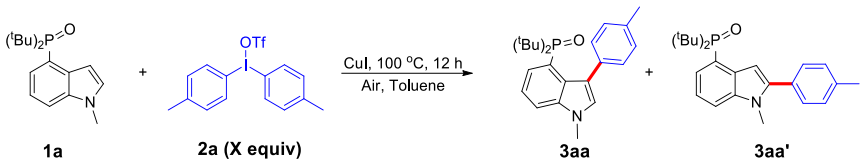


1a **2a (X equiv)** **3aa** **3aa'**

Entry	X/ equiv	Yield of **3aa**[b]	Yield of **3aa'**[b]
1	1.0	76%	Trace
2	1.2	80%	Trace
3	1.5	88%	<5%
4	2.0	92%	<5%
5	3.0	90%	7%

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (X equiv), CuI (10 mol%) in THF for 8 h at 100 °C under air. [b]Isolated yield.

Table S6. Equivalents screening of **2a** for C_2 arylation[a].

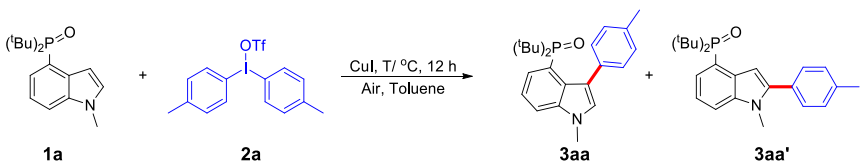


1a **2a (X equiv)** **3aa** **3aa'**

Entry	X/ equiv	Yield of **3aa**[b]	Yield of **3aa'**[b]
1	1.0	60%	13%
2	1.5	Trace	73%
3	2.0	Trace	92%
4	3.0	Trace	92%

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (X equiv), CuI (10 mol%) in toluene for 12 h at 100 °C under air. [b]Isolated yield.

Table S7. Temperture screening of C_2 arylation[a].



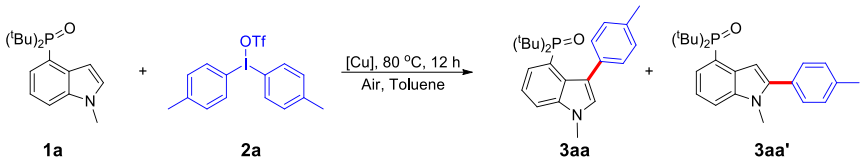
1a **2a** **3aa** **3aa'**

Entry	T/ °C	Yield of **3aa**[b]	Yield of **3aa'**[b]
1	40	35%	Trace
2	60	35%	58%
3	80	Trace	92%
4	100	Trace	92%

5	120	Trace	83%

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), CuI (10 mol%) in toluene for 12 h at T/ °C under air. [b]Isolated yield.

Table S8. Catalyst screening of C_2 arylation[a].

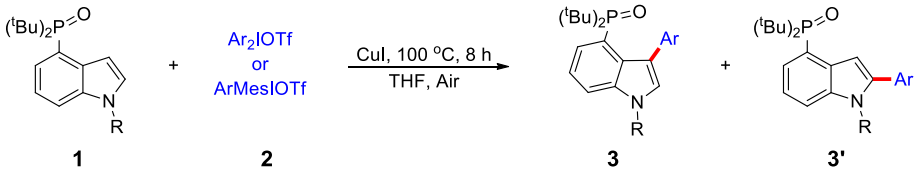


Entry	[Cu]	Yield of **3aa**[b]	Yield of **3aa'**[b]
1	CuI	Trace	92%
2	CuCl	Trace	90%
3	CuOTf	Trace	90%
4	$Cu(CH_3CN)_4PF_6$	Trace	82%
5	Cu_2O	Trace	71%
6	$Cu(OTf)_2$	Trace	77%
7	$Cu(acac)_2$	Trace	74%
8	$Cu(OAc)_2$	Trace	77%
9	CuO	Trace	80%
10	$CuCl_2$	Trace	82%
11[c]	CuI	Trace	81%

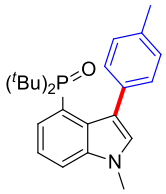
[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), [Cu] (10 mol%) in toluene for 12 h at 80 °C under air. [b]Isolated yield. [c]CuI (5 mol%, 0.005 mmol).

5. General procedure for C2/C3 arylation of indole phosphorus sources

5.1 General procedure for C3 arylation

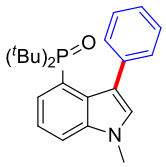


A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **1** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv), CuI (0.01 mmol, 10 mol%) and THF (1 mL) under air. The mixture was stirred at 100 °C for 8 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate.



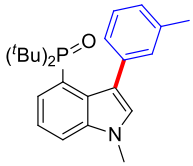
Di-tert-butyl(1-methyl-3-(*p*-tolyl)-1H-indol-4-yl)phosphine oxide **(3aa)**

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 3:1) to afford **3aa** (0.092 mmol) as a white solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 12.1, 7.4 Hz, 1H), 7.27 – 7.19 (m, 3H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.95 (s, 1H), 3.79 (s, 3H), 2.37 (s, 3H), 1.20 (d, *J* = 13.1 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.15 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.83 (d, *J* = 10.8 Hz), 136.31 (s), 134.69 (s), 132.10 (s), 130.53 (s), 129.24 (d, *J* = 5.3 Hz), 127.22 (s), 124.51 (d, *J* = 12.1 Hz), 124.16 (d, *J* = 81.2 Hz), 119.74 (d, *J* = 1.7 Hz), 118.85 (d, *J* = 12.9 Hz), 112.32 (d, *J* = 2.8 Hz), 37.52 (d, *J* = 58.6 Hz), 32.77 (s), 27.83 (s), 21.56 (s). HRMS calcd for $C_{24}H_{32}NOP$: $[M+H]^+$ 382.2294, found 382.2299.



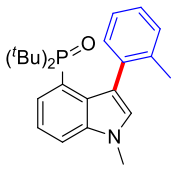
Di-tert-butyl(1-methyl-3-phenyl-1H-indol-4-yl)phosphine oxide (**3ab**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3ab** (0.079 mmol) as a pale yellow solid in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 12.0, 6.8 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.30 – 7.22 (m, 4H), 6.98 (s, 1H), 3.81 (s, 3H), 1.19 (d, *J* = 13.1 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.11 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.33 (s), 137.76 (d, *J* = 10.7 Hz), 131.85 (s), 130.80 (s), 129.26 (d, *J* = 5.1 Hz), 126.27 (s), 125.82 (s), 124.50 (d, *J* = 12.0 Hz), 124.12 (d, *J* = 81.2 Hz), 119.77 (d, *J* = 1.9 Hz), 118.95 (d, *J* = 12.9 Hz), 112.33 (d, *J* = 2.8 Hz), 37.51 (d, *J* = 58.6 Hz), 32.79 (s), 27.76 (s). HRMS calcd for $C_{23}H_{30}NOP$: $[M+H]^+$ 368.2138, found 368.2144.



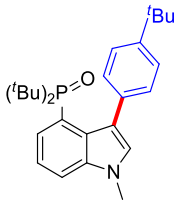
Di-tert-butyl(1-methyl-3-(*m*-tolyl)-1H-indol-4-yl)phosphine oxide (**3ac**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 3:1) to afford **3ac** (0.084 mmol) as a white solid in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.25 (td, *J* = 7.8, 2.2 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.11 (s, 1H), 7.07 (d, *J* = 6.9 Hz, 1H), 6.98 (s, 1H), 3.80 (s, 3H), 2.34 (s, 3H), 1.20 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.20 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.21 (s), 137.82 (d, *J* = 10.8 Hz), 135.27 (s), 131.77 (s), 131.51 (s), 129.24 (d, *J* = 5.2 Hz), 127.58 (s), 126.50 (s), 126.36 (s), 124.50 (d, *J* = 12.2 Hz), 124.04 (d, *J* = 81.5 Hz), 119.89 (d, *J* = 1.8 Hz), 118.95 (d, *J* = 12.9 Hz), 112.35 (d, *J* = 2.8 Hz), 37.57 (d, *J* = 58.6 Hz), 32.79 (s), 27.75 (s), 21.54 (s). HRMS calcd for $C_{24}H_{32}NOP$: $[M+H]^+$ 382.2294, found 382.2300.

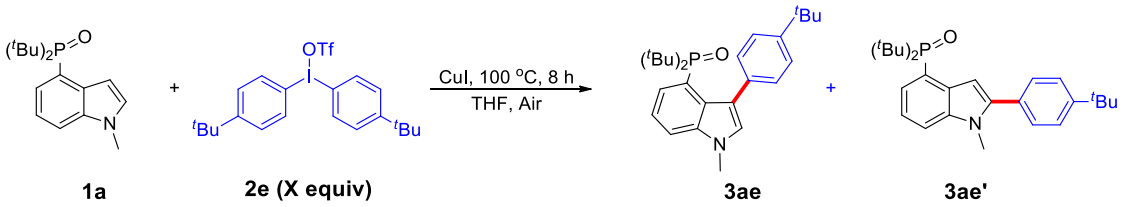


Di-tert-butyl(1-methyl-3-(*o*-tolyl)-1H-indol-4-yl)phosphine oxide (**3ad**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 3:1) to afford **3ad** (0.048 mmol) as a white solid in 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 1H), 7.40 (ddd, *J* = 12.0, 7.4, 0.9 Hz, 1H), 7.25 (td, *J* = 7.9, 2.3 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.12 – 7.03 (m, 2H), 6.91 (s, 1H), 3.82 (s, 3H), 2.16 (s, 3H), 1.26 (d, *J* = 13.0 Hz, 9H), 1.11 (d, *J* = 13.3 Hz, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.76 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.35 (s), 139.20 (s), 137.76 (d, *J* = 10.9 Hz), 131.28 (s), 131.08 (s), 129.96 (d, *J* = 5.4 Hz), 128.39 (s), 126.27 (s), 124.27 (d, *J* = 12.2 Hz), 123.73 (d, *J* = 82.4 Hz), 123.52 (s), 118.78 (d, *J* = 12.9 Hz), 118.20 (d, *J* = 1.8 Hz), 112.40 (d, *J* = 2.8 Hz), 37.78 (d, *J* = 58.3 Hz), 37.04 (d, *J* = 58.5 Hz), 32.80 (s), 28.41 (s), 27.20 (s), 21.17 (s). HRMS calcd for $C_{24}H_{32}NOP$: $[M+H]^+$ 382.2294, found 382.2301.



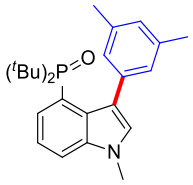
Di-tert-butyl(3-(4-(tert-butyl)phenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3ae**)



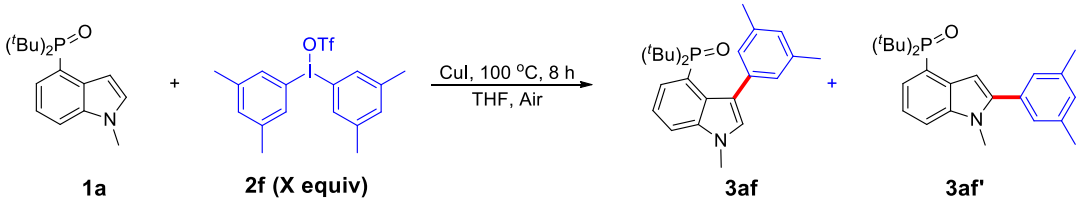
1a **2e (X equiv)** **3ae** **3ae'**

Entry	X/ equiv	Yield of **3ae**	Yield of **3ae'**
1	1.0	64%	8%
2	1.2	72%	12%
3	**1.5**	**83%**	**12%**
4	2.0	78%	19%

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3ae** as a yellow colloid in 64% (0.064 mmol) to 83% (0.083 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 12.1, 7.4 Hz, 1H), 7.29 (s, 4H), 7.24 (td, *J* = 7.5, 2.1 Hz, 1H), 6.95 (s, 1H), 3.77 (s, 3H), 1.36 (s, 9H), 1.20 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.39 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.54 (s), 137.92 (d, *J* = 10.8 Hz), 136.51 (s), 132.58 (s), 130.42 (s), 129.11 (d, *J* = 5.2 Hz), 124.49 (d, *J* = 11.9 Hz), 124.05 (d, *J* = 82.1 Hz), 123.24 (s), 119.75 (d, *J* = 1.7 Hz), 118.88 (d, *J* = 12.9 Hz), 112.43 (d, *J* = 2.8 Hz), 37.54 (d, *J* = 58.5 Hz), 34.43 (s), 32.76 (s), 31.63 (s), 27.80 (s). HRMS calcd for $C_{27}H_{38}NOP$: $[M+H]^+$ 424.2764, found 424.2769.



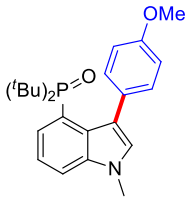
Di-tert-butyl(3-(3,5-dimethylphenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3af**)



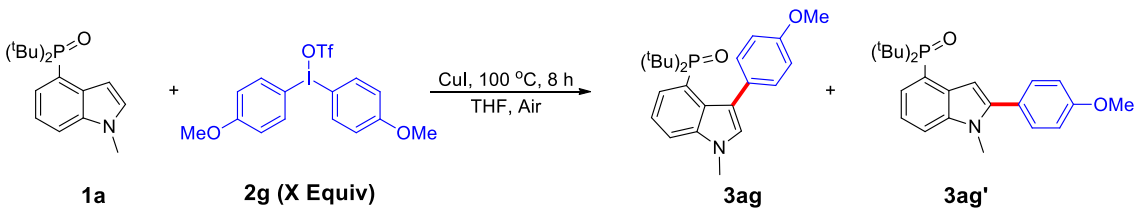
1a **2f (X equiv)** **3af** **3af'**

Entry	X/ equiv	Yield of **3af**	Yield of **3af'**
1	1.0	60%	5%
2	1.2	70%	8%
3	**1.5**	**83%**	**8%**
4	2.0	78%	15%

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 3:1) to afford **3af** as a pale yellow solid in 60% (0.060 mmol) to 83% (0.083 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.42 (dd, *J* = 11.9, 7.2 Hz, 1H), 7.28 – 7.21 (m, 1H), 6.98 (s, 1H), 6.96 (s, 2H), 6.88 (s, 1H), 3.79 (s, 3H), 2.31 (s, 6H), 1.20 (d, *J* = 13.1 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.84 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.11 (s), 137.89 (d, *J* = 10.7 Hz), 135.27 (s), 131.72 (s), 129.19 (d, *J* = 5.2 Hz), 128.31 (s), 127.42 (s), 124.50 (d, *J* = 12.0 Hz), 124.15 (d, *J* = 82.2 Hz), 120.07 (d, *J* = 1.6 Hz), 118.92 (d, *J* = 12.9 Hz), 112.30 (d, *J* = 2.8 Hz), 37.63 (d, *J* = 58.6 Hz), 32.77 (s), 27.77 (s), 21.46 (s). HRMS calcd for $C_{25}H_{34}NOP$: $[M+H]^+$ 396.2451, found 396.2457.



Di-tert-butyl(3-(4-methoxyphenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3ag**)

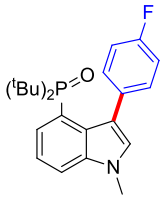


1a **2g (X Equiv)** **3ag** **3ag'**

Entry	X/ Equiv	Yield of **3ag**	Yield of **3ag'**
1	**1.0**	**58%**	**17%**
2	1.2	53%	21%
3	1.5	51%	21%

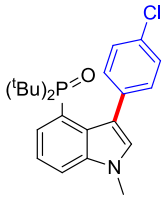
4	2.0	45%	29%

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 1:1) to afford **3ag** as a yellow colloid in 45% (0.045 mmol) to 58% (0.058 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 1H), 7.42 (dd, *J* = 12.0, 7.4 Hz, 1H), 7.27 – 7.21 (m, 3H), 6.95 (s, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.79 (s, 3H), 1.20 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.52 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.62 (s), 137.79 (d, *J* = 10.8 Hz), 132.07 (s), 131.78 (s), 131.68 (s), 129.44 (d, *J* = 5.3 Hz), 124.48 (d, *J* = 12.0 Hz), 124.02 (d, *J* = 81.2 Hz), 119.24 (d, *J* = 1.4 Hz), 118.84 (d, *J* = 12.9 Hz), 112.38 (d, *J* = 2.7 Hz), 111.77 (s), 54.96 (s), 37.52 (d, *J* = 58.5 Hz), 32.75 (s), 27.80 (s). HRMS calcd for $C_{24}H_{32}NO_2P$: $[M+H]^+$ 398.2243, found 398.2248.



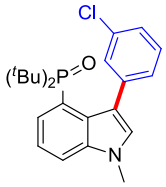
Di-tert-butyl(3-(4-fluorophenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3ah**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3ah** (0.092 mmol) as a white solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.29 – 7.23 (m, 3H), 6.98 – 6.90 (m, 3H), 3.81 (s, 3H), 1.20 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.47 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.38 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.40 (d, *J* = 242.4 Hz), 137.76 (d, *J* = 10.8 Hz), 135.07 (d, *J* = 3.3 Hz), 131.96 (d, *J* = 7.9 Hz), 131.94 (s), 129.28 (d, *J* = 5.2 Hz), 124.61 (d, *J* = 12.0 Hz), 124.03 (d, *J* = 81.1 Hz), 119.05 (d, *J* = 12.8 Hz), 118.62 (d, *J* = 1.8 Hz), 113.15 (d, *J* = 21.0 Hz), 112.41 (d, *J* = 2.8 Hz), 37.46 (d, *J* = 58.6 Hz), 32.79 (s), 27.77 (s). HRMS calcd for $C_{23}H_{29}FNOP$: $[M+H]^+$ 386.2044, found 386.2049.



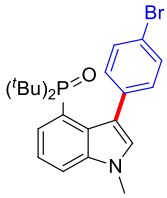
Di-tert-butyl(3-(4-chlorophenyl)-1-methyl-1H-indol-4-yl)phosphine oxide(**3ai**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 3:1) to afford **3ai** (0.092 mmol) as a pale yellow solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 1H), 7.44 (dd, *J* = 12.0, 7.4 Hz, 1H), 7.30 – 7.19 (m, 5H), 6.94 (s, 1H), 3.81 (s, 3H), 1.20 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.57 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.88 (s), 137.79 (s), 132.01 (s), 131.85 (s), 131.38 (s), 129.02 (d, *J* = 5.3 Hz), 126.50 (s), 124.66 (d, *J* = 12.0 Hz), 123.96 (d, *J* = 81.2 Hz), 119.18 (d, *J* = 12.8 Hz), 118.51 (d, *J* = 1.8 Hz), 112.48 (d, *J* = 2.8 Hz), 37.46 (d, *J* = 58.6 Hz), 32.83 (s), 27.75 (s). HRMS calcd for $C_{23}H_{29}ClNOP$: $[M+H]^+$ 402.1748, found 402.1754.



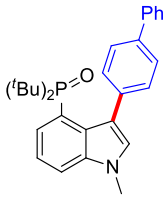
Di-tert-butyl(3-(3-chlorophenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3aj**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 3:1) to afford **3aj** (0.089 mmol) as a yellow colloid in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 1H), 7.44 (dd, *J* = 11.8, 7.4 Hz, 1H), 7.31 – 7.17 (m, 5H), 6.98 (s, 1H), 3.81 (s, 3H), 1.20 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.47 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.18 (s), 137.82 (d, *J* = 10.6 Hz), 131.81 (s), 131.79 (s), 130.57 (s), 129.02 (d, *J* = 5.1 Hz), 128.69 (s), 127.58 (s), 125.84 (s), 124.69 (d, *J* = 12.0 Hz), 123.96 (d, *J* = 80.9 Hz), 119.27 (d, *J* = 12.8 Hz), 118.41 (d, *J* = 1.7 Hz), 112.46 (d, *J* = 2.7 Hz), 37.52 (d, *J* = 58.6 Hz), 32.84 (s), 27.71 (s). HRMS calcd for $C_{23}H_{29}ClNOP$: $[M+H]^+$ 402.1748, found 402.1754.



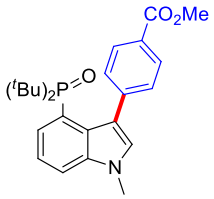
(3-(4-bromophenyl)-1-methyl-1H-indol-4-yl)di-tert-butylphosphine oxide (**3ak**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 3:1) to afford **3ak** (0.091 mmol) as a pale yellow solid in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 1H), 7.44 (dd, *J* = 12.0, 7.3 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.94 (s, 1H), 3.81 (s, 3H), 1.20 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.72 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.45 (s), 137.85 (d, *J* = 10.7 Hz), 132.30 (s), 131.98 (s), 129.38 (s), 128.96 (d, *J* = 5.2 Hz), 124.65 (d, *J* = 12.0 Hz), 123.86 (d, *J* = 81.4 Hz), 119.71 (s), 119.21 (d, *J* = 12.8 Hz), 118.46 (d, *J* = 1.8 Hz), 112.52 (d, *J* = 2.8 Hz), 37.46 (d, *J* = 58.5 Hz), 32.85 (s), 27.73 (s). HRMS calcd for $C_{23}H_{29}BrNOP$: $[M+H]^+$ 446.1243, found 446.1252.



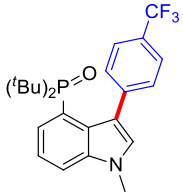
(3-([1,1'-biphenyl]-4-yl)-1-methyl-1H-indol-4-yl)di-tert-butylphosphine oxide (**3al**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3al** (0.088 mmol) as a yellow colloid in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.38 (m, 5H), 7.31 – 7.22 (m, 2H), 7.00 (s, 1H), 3.79 (s, 3H), 1.21 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.76 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.57 (s), 138.86 (s), 137.98 (s), 137.87 (s), 132.23 (s), 131.12 (s), 129.17 (d, *J* = 5.2 Hz), 128.60 (s), 127.07 (s), 126.65 (s), 125.03 (s), 124.57 (d, *J* = 12.1 Hz), 123.90 (d, *J* = 81.9 Hz), 119.33 (d, *J* = 1.5 Hz), 119.09 (d, *J* = 12.9 Hz), 112.53 (d, *J* = 2.7 Hz), 37.55 (d, *J* = 58.5 Hz), 32.83 (s), 27.76 (s). HRMS calcd for $C_{29}H_{34}NOP$: $[M+H]^+$ 444.2451, found 444.2455.



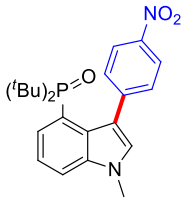
Methyl 4-(4-(di-tert-butylphosphoryl)-1-methyl-1H-indol-3-yl)benzoate (**3am**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3am** (0.085 mmol) as a yellow colloid in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 11.8, 7.3 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.26 (m, 1H), 6.98 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 1.19 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.35 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.75 (s), 144.70 (s), 137.93 (d, *J* = 10.7 Hz), 131.90 (s), 130.29 (s), 128.83 (d, *J* = 5.1 Hz), 127.85 (s), 127.21 (s), 124.74 (d, *J* = 11.9 Hz), 123.97 (d, *J* = 80.9 Hz), 119.36 (d, *J* = 12.7 Hz), 118.92 (d, *J* = 1.7 Hz), 112.51 (d, *J* = 2.7 Hz), 51.74 (s), 37.49 (d, *J* = 58.6 Hz), 32.87 (s), 27.70 (s). HRMS calcd for $C_{25}H_{32}NO_3P$: $[M+H]^+$ 426.2193, found 426.2199.



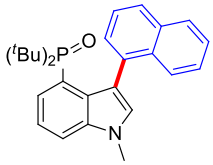
Di-tert-butyl(1-methyl-3-(4-(trifluoromethyl)phenyl)-1H-indol-4-yl)phosphine oxide (**3an**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3an** (0.081 mmol) as a white solid in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 3H), 7.49 – 7.40 (m, 3H), 7.30 (td, *J* = 7.9, 1.8 Hz, 1H), 6.96 (s, 1H), 3.82 (s, 3H), 1.20 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.96 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.60 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.47 (s), 137.92 (d, *J* = 10.7 Hz), 132.19 (s), 130.67 (s), 128.78 (d, *J* = 5.2 Hz), 127.28 (d, *J* = 31.7 Hz), 126.27 (s), 124.73 (d, *J* = 11.9 Hz), 123.75 (d, *J* = 81.5 Hz), 123.23 (q, *J* = 3.7 Hz), 119.42 (d, *J* = 12.8 Hz), 118.50 (s), 112.60 (d, *J* = 2.8 Hz), 37.45 (d, *J* = 58.5 Hz), 32.86 (s), 27.64 (s). HRMS calcd for $C_{24}H_{29}F_3NOP$: $[M+H]^+$ 436.2012, found 436.2018.



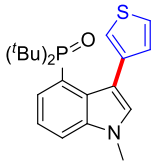
Di-tert-butyl(1-methyl-3-(4-nitrophenyl)-1H-indol-4-yl)phosphine oxide (**3ao**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3ao** (0.043 mmol) as a yellow solid in 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.32 (td, *J* = 7.8, 2.1 Hz, 1H), 7.01 (s, 1H), 3.86 (s, 3H), 1.20 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 56.66 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.01 (s), 145.92 (s), 138.03 (d, *J* = 10.5 Hz), 131.95 (s), 130.58 (s), 128.57 (d, *J* = 5.1 Hz), 125.02 (d, *J* = 11.7 Hz), 123.94 (d, *J* = 80.3 Hz), 121.95 (s), 119.76 (d, *J* = 12.6 Hz), 117.91 (d, *J* = 1.7 Hz), 112.65 (d, *J* = 2.8 Hz), 37.44 (d, *J* = 58.6 Hz), 32.99 (s), 27.66 (s). HRMS calcd for $C_{23}H_{29}N_2O_3P$: $[M+H]^+$ 412.1916, found 412.1919.



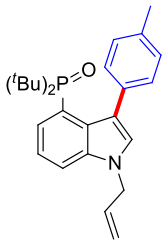
Di-tert-butyl(1-methyl-3-(naphthalen-1-yl)-1H-indol-4-yl)phosphine oxide (**3ap**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3ap** (0.068 mmol) as a white solid in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 8.9 Hz, 2H), 7.55 (dd, *J* = 17.9, 8.3 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.36 – 7.27 (m, 3H), 7.20 – 7.14 (m, 1H), 7.03 (s, 1H), 3.86 (s, 3H), 1.12 – 1.02 (m, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.56 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.72 (d, *J* = 10.7 Hz), 137.51 (s), 135.55 (s), 132.87 (s), 132.17 (s), 130.81 (d, *J* = 5.2 Hz), 127.82 (s), 127.65 (s), 127.49 (s), 126.62 (s), 124.70 (s), 124.49 (s), 124.40 (d, *J* = 12.2 Hz), 124.26 (s), 124.11 (d, *J* = 81.0 Hz), 118.99 (d, *J* = 12.7 Hz), 116.76 (d, *J* = 1.8 Hz), 112.33 (d, *J* = 2.7 Hz), 37.74 (d, *J* = 22.4 Hz), 37.16 (d, *J* = 22.7 Hz), 32.87 (s), 28.02 (s), 27.32 (s). HRMS calcd for $C_{27}H_{32}NOP$: $[M+H]^+$ 418.2294, found 418.2301.



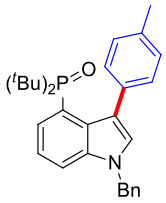
Di-tert-butyl(1-methyl-3-(thiophen-3-yl)-1H-indol-4-yl)phosphine oxide (**3aq**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3aq** (0.033 mmol) as a brown solid in 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 11.7, 7.6 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.21 – 7.14 (m, 2H), 7.05 (s, 1H), 7.00 (d, *J* = 1.4 Hz, 1H), 3.81 (s, 3H), 1.22 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.76 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.87 (s), 137.89 (d, *J* = 10.7 Hz), 132.66 (s), 132.19 (s), 129.60 (d, *J* = 5.1 Hz), 124.57 (d, *J* = 12.1 Hz), 124.01 (d, *J* = 81.9 Hz), 121.58 (s), 121.36 (s), 118.97 (d, *J* = 13.0 Hz), 113.69 (s), 112.46 (d, *J* = 2.7 Hz), 37.50 (d, *J* = 58.6 Hz), 32.77 (s), 27.77 (s). HRMS calcd for $C_{21}H_{28}NOPS$: $[M+H]^+$ 374.1702, found 374.1709.



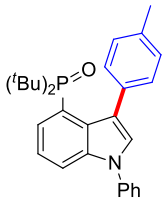
(1-allyl-3-(*p*-tolyl)-1H-indol-4-yl)di-tert-butylphosphine oxide (**3ca**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3ca** (0.087 mmol) as a yellow solid in 87% yield. ^{1}H NMR (400 MHz, CDCl3) δ 7.49 (d, J = 8.1 Hz, 1H), 7.43 (dd, J = 11.9, 7.5 Hz, 1H), 7.24 (d, J = 7.9 Hz, 3H), 7.08 (d, J = 7.7 Hz, 2H), 7.00 (s, 1H), 6.01 (ddt, J = 15.8, 10.7, 5.5 Hz, 1H), 5.23 (d, J = 10.2 Hz, 1H), 5.14 (d, J = 17.1 Hz, 1H), 4.73 (d, J = 5.3 Hz, 2H), 2.37 (s, 3H), 1.21 (d, J = 13.1 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.95 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.24 (d, *J* = 10.8 Hz), 136.32 (s), 134.74 (s), 132.95 (s), 131.02 (s), 130.39 (s), 129.43 (d, *J* = 5.2 Hz), 127.27 (s), 124.66 (d, *J* = 12.1 Hz), 124.16 (d, *J* = 81.3 Hz), 120.05 (d, *J* = 1.6 Hz), 118.86 (d, *J* = 12.9 Hz), 118.02 (s), 112.64 (d, *J* = 2.6 Hz), 48.80 (s), 37.54 (d, *J* = 58.6 Hz), 27.84 (s), 21.61 (s). HRMS calcd for $C_{26}H_{34}NOP$: $[M+H]^+$ 408.2451, found 408.2451.



(1-benzyl-3-(*p*-tolyl)-1H-indol-4-yl)di-tert-butylphosphine oxide (**3da**)

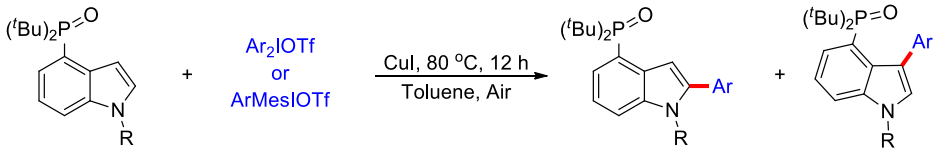
Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3da** (0.076 mmol) as a pale yellow solid in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.34 – 7.26 (m, 3H), 7.26 – 7.23 (m, 2H), 7.21 – 7.15 (m, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.01 (s, 1H), 5.30 (s, 2H), 2.37 (s, 3H), 1.21 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.86 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.47 (d, *J* = 10.8 Hz), 136.71 (s), 136.40 (s), 134.76 (s), 131.40 (s), 130.51 (s), 129.63 (d, *J* = 5.1 Hz), 128.88 (s), 127.86 (s), 127.22 (s), 127.17 (s), 124.71 (d, *J* = 12.2 Hz), 124.05 (d, *J* = 81.8 Hz), 120.21 (d, *J* = 1.8 Hz), 119.05 (d, *J* = 12.8 Hz), 112.82 (d, *J* = 2.8 Hz), 50.08 (s), 37.58 (d, *J* = 58.4 Hz), 27.79 (s), 21.48 (s). HRMS calcd for $C_{30}H_{36}NOP$: $[M+H]^+$ 458.2607, found 458.2612.



Di-tert-butyl(1-phenyl-3-(*p*-tolyl)-1H-indol-4-yl)phosphine oxide (**3ea**)

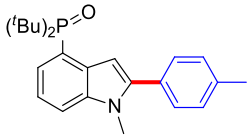
Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3ea** (0.079 mmol) as a pale yellow colloid in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.43 (m, 5H), 7.41 – 7.35 (m, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 1.24 (d, *J* = 13.2 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.17 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.96 (s), 137.28 (d, *J* = 10.7 Hz), 135.90 (s), 135.02 (s), 131.12 (s), 130.39 (s), 130.11 (d, *J* = 5.2 Hz), 129.68 (s), 127.33 (s), 127.00 (s), 125.47 (d, *J* = 11.9 Hz), 125.10 (s), 124.43 (d, *J* = 80.9 Hz), 121.75 (d, *J* = 1.8 Hz), 119.59 (d, *J* = 12.8 Hz), 113.58 (d, *J* = 2.7 Hz), 37.60 (d, *J* = 58.6 Hz), 27.89 (s), 21.65 (s). HRMS calcd for $C_{29}H_{34}NOP$: $[M+H]^+$ 444.2451, found 444.2451.

5.2 General procedure for C2 arylation



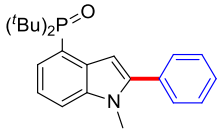
1 **2** **3'** **3**

A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **1** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv), CuI (0.01 mmol, 10 mol%) and toluene (1 mL) under air. The mixture was stirred at 80 °C for 12 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate.



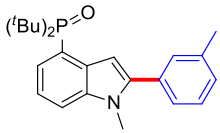
Di-tert-butyl(1-methyl-2-(p-tolyl)-1H-indol-4-yl)phosphine oxide (**3aa'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3aa'** (0.092 mmol) as a pale yellow solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.45 (d, *J* = 7.9 Hz, 3H), 7.38 – 7.32 (m, 1H), 7.27 – 7.17 (m, 3H), 3.76 (s, 3H), 2.39 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.78 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.67 (s), 138.90 (d, *J* = 10.6 Hz), 137.69 (s), 132.66 (d, *J* = 5.7 Hz), 129.65 (s), 129.34 (s), 129.09 (s), 123.21 (d, *J* = 10.4 Hz), 121.69 (d, *J* = 81.7 Hz), 119.34 (d, *J* = 12.0 Hz), 112.07 (d, *J* = 2.7 Hz), 104.28 (s), 36.89 (d, *J* = 59.5 Hz), 31.19 (s), 27.34 (s), 21.26 (s). HRMS calcd for $C_{24}H_{32}NOP$: $[M+H]^+$ 382.2294, found 382.2299.



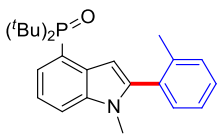
Di-tert-butyl(1-methyl-2-phenyl-1H-indol-4-yl)phosphine oxide (**3ab'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3ab'** (0.085 mmol) as a yellow colloid in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.40 (m, 3H), 7.36 (t, *J* = 8.1 Hz, 2H), 7.22 (td, *J* = 7.8, 2.8 Hz, 1H), 3.78 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.85 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.57 (s), 138.96 (d, *J* = 10.5 Hz), 132.62 (s), 132.56 (s), 129.46 (s), 128.36 (s), 127.83 (s), 123.28 (d, *J* = 10.4 Hz), 121.87 (d, *J* = 81.6 Hz), 119.51 (d, *J* = 11.9 Hz), 112.14 (d, *J* = 2.6 Hz), 104.66 (s), 36.89 (d, *J* = 59.5 Hz), 31.23 (s), 27.33 (s). HRMS calcd for $C_{23}H_{30}NOP$: $[M+H]^+$ 368.2138, found 368.2143.



Di-tert-butyl(1-methyl-2-(*m*-tolyl)-1H-indol-4-yl)phosphine oxide (**3ac'**)

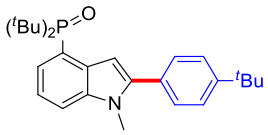
Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3ac'** (0.078 mmol) as a yellow colloid in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.38 – 7.31 (m, 3H), 7.25 – 7.16 (m, 2H), 3.78 (s, 3H), 2.40 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.03 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.75 (s), 138.96 (d, *J* = 10.7 Hz), 138.14 (s), 132.60 (d, *J* = 5.8 Hz), 132.43 (s), 130.28 (s), 128.60 (s), 128.18 (s), 126.36 (s), 123.24 (d, *J* = 10.5 Hz), 121.70 (d, *J* = 81.7 Hz), 119.43 (d, *J* = 12.0 Hz), 112.13 (d, *J* = 2.6 Hz), 104.55 (d, *J* = 0.9 Hz), 36.89 (d, *J* = 59.5 Hz), 31.27 (s), 27.32 (s), 21.42 (s). HRMS calcd for $C_{24}H_{32}NOP$: $[M+H]^+$ 382.2294, found 382.2299.



Di-tert-butyl(1-methyl-2-(*o*-tolyl)-1H-indol-4-yl)phosphine oxide (**3ad'**)

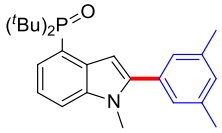
Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3ad'** (0.034 mmol) as a yellow colloid in 34% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 9.6, 7.7 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.26 – 7.19 (m, 2H), 3.54 (s, 3H), 2.20 (s, 3H), 1.35 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.27 (s). ^{13}C NMR (101

MHz, $CDCl_3$) δ 141.66 (s), 137.85 (s), 137.77 (d, *J* = 10.8 Hz), 132.58 (d, *J* = 5.7 Hz), 132.23 (s), 131.18 (s), 130.01 (s), 128.53 (s), 125.42 (s), 123.14 (d, *J* = 10.5 Hz), 121.52 (d, *J* = 81.9 Hz), 119.11 (d, *J* = 11.9 Hz), 111.93 (d, *J* = 2.7 Hz), 104.55 (s), 36.87 (d, *J* = 59.5 Hz), 30.35 (s), 27.36 (s), 20.10 (s). HRMS calcd for $C_{24}H_{32}NOP$: $[M+H]^+$ 382.2294, found 382.2301.



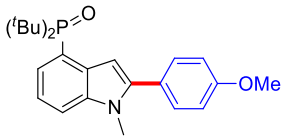
Di-tert-butyl(2-(4-(tert-butyl)phenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3ae'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3ae'** (0.075 mmol) as a brown solid in 75% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.52 – 7.42 (m, 5H), 7.35 (dd, *J* = 9.3, 7.8 Hz, 1H), 7.21 (td, *J* = 7.9, 2.8 Hz, 1H), 3.79 (s, 3H), 1.36 (d, *J* = 3.3 Hz, 18H), 1.32 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.07 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.89 (s), 142.64 (s), 138.93 (d, *J* = 10.6 Hz), 132.63 (d, *J* = 5.4 Hz), 129.59 (s), 129.11 (s), 125.32 (s), 123.23 (d, *J* = 10.4 Hz), 121.57 (d, *J* = 82.0 Hz), 119.31 (d, *J* = 12.0 Hz), 112.10 (d, *J* = 2.5 Hz), 104.33 (s), 36.90 (d, *J* = 59.5 Hz), 34.67 (s), 31.34 (s), 31.29 (s), 27.34 (s). HRMS calcd for $C_{27}H_{38}NOP$: $[M+H]^+$ 424.2764, found 424.2769.



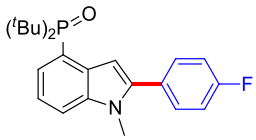
Di-tert-butyl(2-(3,5-dimethylphenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3af'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3af'** (0.087 mmol) as a yellow colloid in 87% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 9.6, 7.5 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.01 (s, 1H), 3.78 (s, 3H), 2.36 (s, 6H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.88 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.87 (s), 138.97 (d, *J* = 10.6 Hz), 137.91 (s), 132.64 (d, *J* = 5.6 Hz), 132.36 (s), 129.51 (s), 127.22 (s), 123.19 (d, *J* = 10.5 Hz), 121.65 (d, *J* = 81.8 Hz), 119.37 (d, *J* = 11.9 Hz), 112.10 (d, *J* = 2.7 Hz), 104.51 (d, *J* = 0.9 Hz), 36.89 (d, *J* = 59.5 Hz), 31.29 (s), 27.33 (s), 21.33 (s). HRMS calcd for $C_{25}H_{34}NOP$: $[M+H]^+$ 396.2451, found 396.2456.



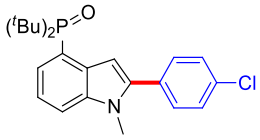
Di-tert-butyl(2-(4-methoxyphenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3ag'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 2:1 to 1:2) to afford **3ag'** as a brown solid in 78% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 10.0 Hz, 1H), 7.35 (dd, *J* = 9.8, 7.4 Hz, 1H), 7.20 (td, *J* = 7.8, 2.9 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.75 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.16 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.44 (s), 142.49 (s), 138.78 (d, *J* = 10.6 Hz), 132.65 (d, *J* = 5.6 Hz), 130.72 (s), 125.01 (s), 123.21 (d, *J* = 10.5 Hz), 121.41 (d, *J* = 81.9 Hz), 119.22 (d, *J* = 12.0 Hz), 113.86 (s), 112.05 (d, *J* = 2.7 Hz), 103.89 (d, *J* = 1.0 Hz), 55.33 (s), 36.89 (d, *J* = 59.4 Hz), 31.15 (s), 27.33 (s). HRMS calcd for $C_{24}H_{32}NO_2P$: $[M+H]^+$ 398.2243, found 398.2248.



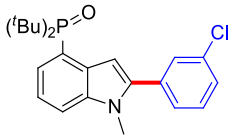
Di-tert-butyl(2-(4-fluorophenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3ah'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3ah'** (0.077 mmol) as a white solid in 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.51 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.23 (td, *J* = 7.8, 2.7 Hz, 1H), 7.13 (t, *J* = 8.6 Hz, 2H), 3.74 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.00 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.87 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.60 (d, *J* = 247.7 Hz), 141.47 (s), 138.86 (d, *J* = 10.6 Hz), 132.47 (d, *J* = 5.5 Hz), 131.15 (d, *J* = 8.1 Hz), 128.66 (d, *J* = 3.3 Hz), 123.37 (d, *J* = 10.4 Hz), 121.85 (d, *J* = 81.5 Hz), 119.67 (d, *J* = 11.9 Hz), 115.42 (d, *J* = 21.6 Hz), 112.19 (d, *J* = 2.7 Hz), 104.63 (s), 36.88 (d, *J* = 59.5 Hz), 31.12 (s), 27.30 (s). HRMS calcd for $C_{23}H_{29}FNOP$: $[M+H]^+$ 386.2044, found 386.2050.

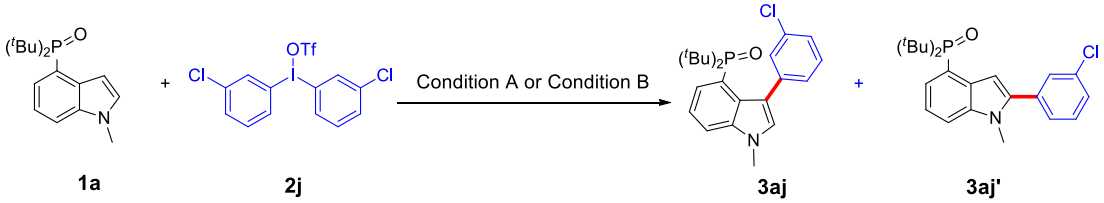


Di-tert-butyl(2-(4-chlorophenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3ai'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3ai'** (0.080 mmol) as a yellow solid in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.52 – 7.45 (m, 3H), 7.43 – 7.40 (m, 2H), 7.37 (dd, *J* = 9.8, 7.4 Hz, 1H), 7.26 – 7.21 (m, 1H), 3.76 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.13 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.25 (s), 139.05 (d, *J* = 10.6 Hz), 133.96 (s), 132.43 (d, *J* = 5.6 Hz), 131.02 (s), 130.62 (s), 128.65 (s), 123.44 (d, *J* = 10.3 Hz), 121.97 (d, *J* = 81.3 Hz), 119.85 (d, *J* = 11.9 Hz), 112.25 (d, *J* = 2.6 Hz), 104.93 (d, *J* = 1.0 Hz), 36.89 (d, *J* = 59.5 Hz), 31.23 (s), 27.29 (s). HRMS calcd for $C_{23}H_{29}ClNOP$: $[M+H]^+$ 402.1748, found 402.1756.



Di-tert-butyl(2-(3-chlorophenyl)-1-methyl-1H-indol-4-yl)phosphine oxide (**3aj'**)

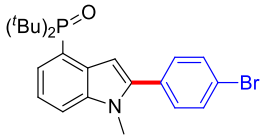


1a **2j** **3aj** **3aj'**

Condition A: **1a** (0.1 mmol, 1.0 equiv), **2j** (0.2 mmol, 2.0 equiv), CuI (0.01 mmol, 10 mol%) in toluene at 80 °C for 12 h under air. Condition B: Adding HOTf (1.0 equiv) directly to the final reaction system of condition A (two steps in one potion).

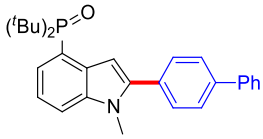
Entry	Condition	Yield of **3aj**	Yield of **3aj'**
1	A	63%	32%
2	B	Trace	92%

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3aj'** as a yellow colloid in 32% (0.032 mmol) or 92% (0.092 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.57 (s, 1H), 7.47 (dd, *J* = 14.3, 7.5 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.28 – 7.22 (m, 1H), 3.78 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.11 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.94 (s), 139.11 (d, *J* = 10.5 Hz), 134.34 (s), 134.33 (s), 132.36 (d, *J* = 5.4 Hz), 129.64 (s), 129.30 (s), 127.89 (s), 127.46 (s), 123.46 (d, *J* = 10.4 Hz), 122.13 (d, *J* = 81.3 Hz), 120.00 (d, *J* = 11.9 Hz), 112.30 (d, *J* = 2.7 Hz), 105.33 (s), 36.89 (d, *J* = 59.5 Hz), 31.29 (s), 27.28 (s). HRMS calcd for $C_{23}H_{29}ClNOP$: $[M+H]^+$ 402.1748, found 402.1756.



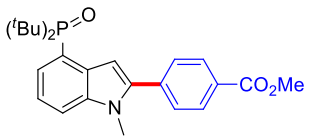
(2-(4-bromophenyl)-1-methyl-1H-indol-4-yl)di-tert-butylphosphine oxide (**3ak'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3ak'** (0.072 mmol) as a pale yellow solid in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.37 (dd, *J* = 9.5, 7.6 Hz, 1H), 7.24 (td, *J* = 7.8, 2.9 Hz, 1H), 3.75 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.00 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.23 (s), 139.08 (d, *J* = 10.6 Hz), 132.43 (d, *J* = 5.6 Hz), 131.59 (s), 131.48 (s), 130.89 (s), 123.45 (d, *J* = 10.3 Hz), 122.17 (s), 122.04 (d, *J* = 81.3 Hz), 119.89 (d, *J* = 11.9 Hz), 112.25 (d, *J* = 2.7 Hz), 104.95 (d, *J* = 1.0 Hz), 36.88 (d, *J* = 59.5 Hz), 31.24 (s), 27.29 (s). HRMS calcd for $C_{23}H_{29}BrNOP$: $[M+H]^+$ 446.1243, found 446.1252.

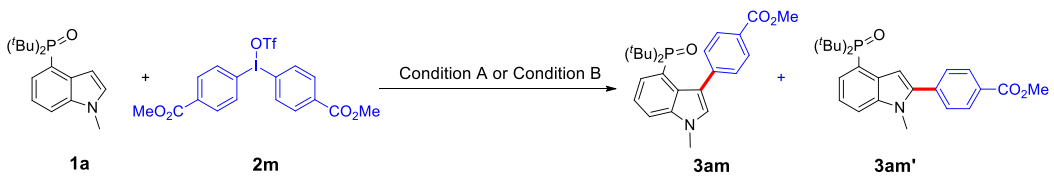


(2-([1,1'-biphenyl]-4-yl)-1-methyl-1H-indol-4-yl)di-tert-butylphosphine oxide (**3al'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3al'** (0.089 mmol) as a white solid in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.68 – 7.62 (m, 6H), 7.49 – 7.42 (m, 3H), 7.40 – 7.32 (m, 2H), 7.24 – 7.19 (m, 1H), 3.80 (s, 3H), 1.35 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.90 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.21 (s), 140.56 (d, *J* = 1.5 Hz), 139.14 (d, *J* = 10.7 Hz), 132.63 (d, *J* = 5.6 Hz), 131.49 (s), 129.79 (s), 128.87 (s), 127.50 (s), 127.09 (s), 123.35 (d, *J* = 10.4 Hz), 121.87 (d, *J* = 81.5 Hz), 119.64 (d, *J* = 11.9 Hz), 112.21 (d, *J* = 2.7 Hz), 104.80 (s), 36.91 (d, *J* = 59.5 Hz), 31.38 (s), 27.35 (s). HRMS calcd for $C_{29}H_{34}NOP$: $[M+H]^+$ 444.2451, found 444.2455.



Methyl 4-(4-(di-tert-butylphosphoryl)-1-methyl-1H-indol-2-yl)benzoate (**3am**')

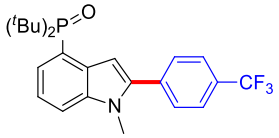


1a **2m** **3am** **3am'**

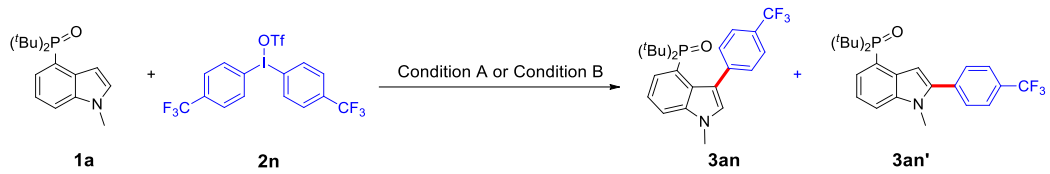
Condition A: **1a** (0.1 mmol, 1.0 equiv), **2m** (0.2 mmol, 2.0 equiv), CuI (0.01 mmol, 10 mol%) in toluene at 80 °C for 12 h under air. Condition B: Adding HOTf (1.0 equiv) directly to the final reaction system of condition A (two steps in one potion).

Entry	Condition	Yield of **3am**	Yield of **3am'**
1	A	56%	10%
2	B	Trace	63%

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3am'** as a pale yellow solid in 10% (0.010 mmol) or 63% (0.063 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.81 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.29 – 7.23 (m, 1H), 3.95 (s, 3H), 3.80 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.10 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87 (s), 141.30 (s), 139.41 (d, *J* = 10.5 Hz), 137.02 (s), 132.36 (d, *J* = 5.5 Hz), 129.68 (s), 129.20 (s), 129.14 (s), 123.54 (d, *J* = 10.3 Hz), 122.26 (d, *J* = 81.1 Hz), 120.21 (d, *J* = 11.9 Hz), 112.36 (d, *J* = 2.7 Hz), 105.81 (s), 52.19 (s), 36.88 (d, *J* = 59.5 Hz), 31.47 (s), 27.27 (s). HRMS calcd for $C_{25}H_{32}NO_3P$: $[M+H]^+$ 426.2193, found 426.2199.



Di-tert-butyl(1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-indol-4-yl)phosphine oxide (**3an'**)

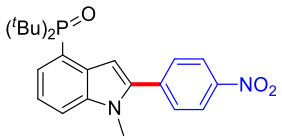


Condition A: **1a** (0.1 mmol, 1.0 equiv), **2n** (0.2 mmol, 2.0 equiv), CuI (0.01 mmol, 10 mol%) in toluene at 80 °C for 12 h under air. Condition B: Adding HOTf (1.0 equiv) directly to the final reaction system of condition A (two steps in one potion).

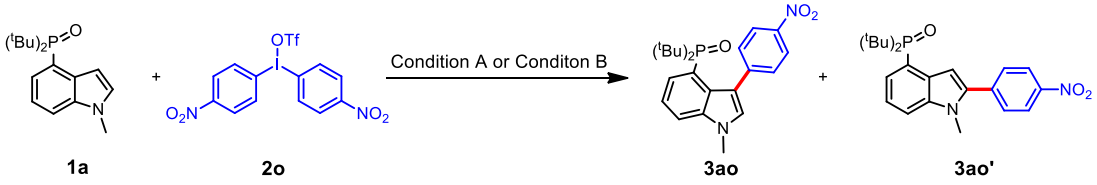
Entry	Condition	Yield of **3an**	Yield of **3an'**
1	A	56%	15%
2	B	Trace	71%

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3an'** as a yellow solid in 15% (0.015 mmol) or 71% (0.071 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.73 – 7.66 (m, 4H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.39 (dd, *J* = 9.7, 7.3 Hz, 1H), 7.30 – 7.24 (m, 1H), 3.79 (s, 3H), 1.34 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.21 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.50 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.83 (s), 139.32 (d, *J* = 10.5 Hz), 136.13 (s), 132.32 (d, *J* = 5.5 Hz), 129.53 (s), 125.37 (q, *J* = 3.7 Hz), 123.59 (d, *J* = 10.3 Hz), 122.32 (d, *J* = 80.9 Hz), 120.26 (d, *J* = 11.9 Hz), 112.39 (d, *J* = 2.7 Hz), 105.79 (s),

36.90 (d, J = 59.5 Hz), 31.37 (s), 27.27 (s). HRMS calcd for $C_{24}H_{29}F_3NOP$: $[M+H]^+$ 436.2012, found 436.2019.

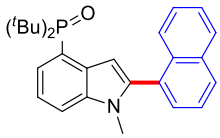


Di-tert-butyl(1-methyl-2-(4-nitrophenyl)-1H-indol-4-yl)phosphine oxide (**3ao'**)

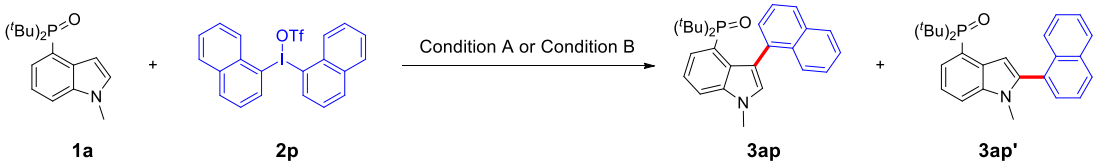


Condition A: **1a** (0.1 mmol, 1.0 equiv), **2o** (0.2 mmol, 2.0 equiv), CuI (0.01 mmol, 10 mol%) in toluene at 80 °C for 12 h under air. Condition B: Adding HOTf (1.0 equiv) directly to the final reaction system of condition A (two steps in one potion).

Entry	Condition	Yield of **3ao**	Yield of **3ao'**
1	A	58%	Trace
2	B	55%	Trace



Di-tert-butyl(1-methyl-2-(naphthalen-1-yl)-1H-indol-4-yl)phosphine oxide (**3ap'**)

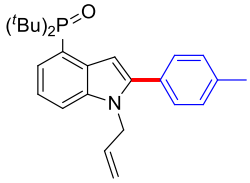


Condition A: **1a** (0.1 mmol, 1.0 equiv), **2n** (0.2 mmol, 2.0 equiv), CuI (0.01 mmol, 10 mol%) in toluene at 80 °C for 12 h under air. Condition B: Adding HOTf (1.0 equiv) directly to the final reaction system of condition A (two steps in one potion).

Entry	Condition	Yield of **3ap**	Yield of **3ap'**
1	A	9%	37%
2	B	Trace	43%

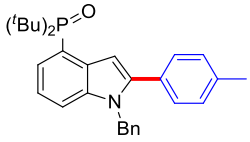
Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3ap'** as a brown colloid in 37% (0.037 mmol) or 43% (0.043 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.72 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 5.8 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.45 – 7.38 (m, 2H), 7.30 – 7.24 (m, 1H), 3.49 (s, 3H), 1.37 (d, J = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.24 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.76 (s), 138.18 (d, J = 10.7 Hz), 133.46 (s), 132.71 (s), 132.65 (d, J = 5.7 Hz), 130.29 (s), 129.28 (s), 128.96 (s), 128.25

(s), 126.56 (s), 126.16 (s), 125.94 (s), 125.17 (s), 123.28 (d, *J* = 10.5 Hz), 121.80 (d, *J* = 81.6 Hz), 119.41 (d, *J* = 12.0 Hz), 112.02 (d, *J* = 2.6 Hz), 105.91 (s), 36.91 (d, *J* = 59.4 Hz), 30.85 (s), 27.38 (s). HRMS calcd for $C_{27}H_{32}NOP$: $[M+H]^+$ 418.2294, found 418.2303.



(1-allyl-2-(p-tolyl)-1H-indol-4-yl)di-tert-butylphosphine oxide (**3ca'**)

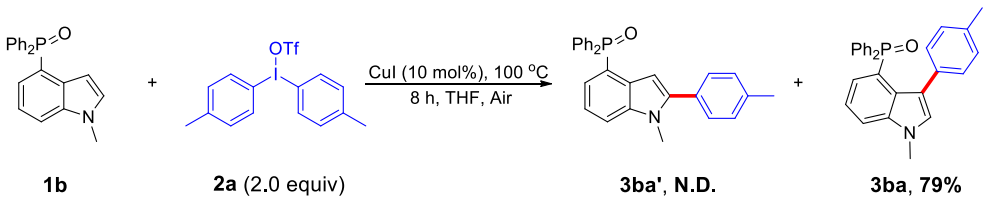
Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3ca'** (0.064 mmol) as a brown colloid in 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.24 – 7.14 (m, 3H), 6.11 – 5.93 (m, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 4.99 (d, *J* = 17.3 Hz, 1H), 4.75 (s, 2H), 2.39 (s, 3H), 1.35 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.97 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.67 (s), 138.44 (d, *J* = 10.7 Hz), 137.84 (s), 133.90 (s), 132.85 (d, *J* = 5.6 Hz), 129.54 (s), 129.12 (s), 129.05 (s), 123.41 (d, *J* = 10.3 Hz), 121.66 (d, *J* = 81.9 Hz), 119.41 (d, *J* = 11.9 Hz), 116.60 (s), 112.82 (d, *J* = 2.6 Hz), 104.49 (s), 46.57 (s), 36.87 (d, *J* = 59.4 Hz), 27.37 (s), 21.32 (s). HRMS calcd for $C_{26}H_{34}NOP$: $[M+H]^+$ 408.2451, found 408.2451.

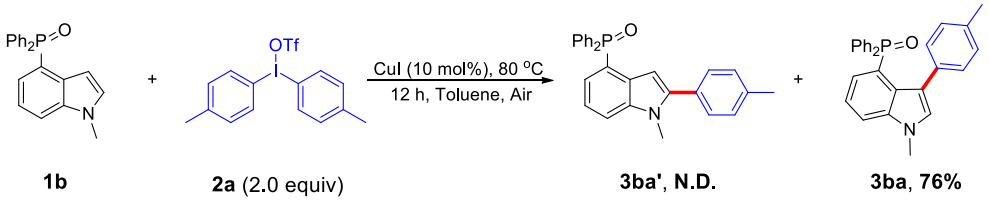


(1-benzyl-2-(*p*-tolyl)-1H-indol-4-yl)di-tert-butylphosphine oxide (**3da'**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 1:1) to afford **3da'** (0.050 mmol) as a brown colloid in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.22 (m, 5H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.09 (td, *J* = 8.0, 2.8 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 2H), 5.38 (s, 2H), 2.35 (s, 3H), 1.36 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.45 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.05 (s), 138.58 (d, *J* = 10.6 Hz), 138.16 (s), 137.91 (s), 133.01 (d, *J* = 5.7 Hz), 129.45 (s), 129.18 (s), 129.12 (s), 128.78 (s), 127.19 (s), 125.93 (s), 123.54 (d, *J* = 10.4 Hz), 121.61 (d, *J* = 82.0 Hz), 119.61 (d, *J* = 11.9 Hz), 113.06 (d, *J* = 2.6 Hz), 104.74 (s), 47.75 (s), 36.91 (d, *J* = 59.4 Hz), 27.38 (s), 21.26 (s). HRMS calcd for $C_{30}H_{36}NOP$: $[M+H]^+$ 458.2607, found 458.2613.

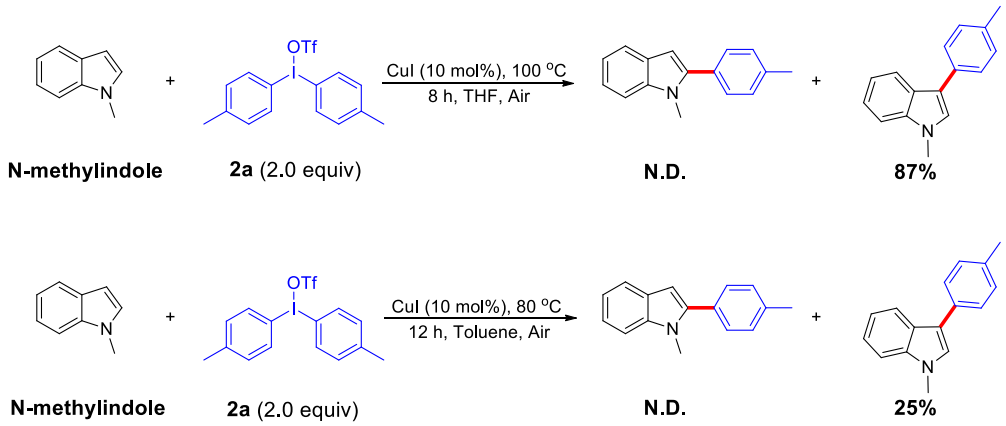
5.3 Reaction results of 1b under different standard conditions.





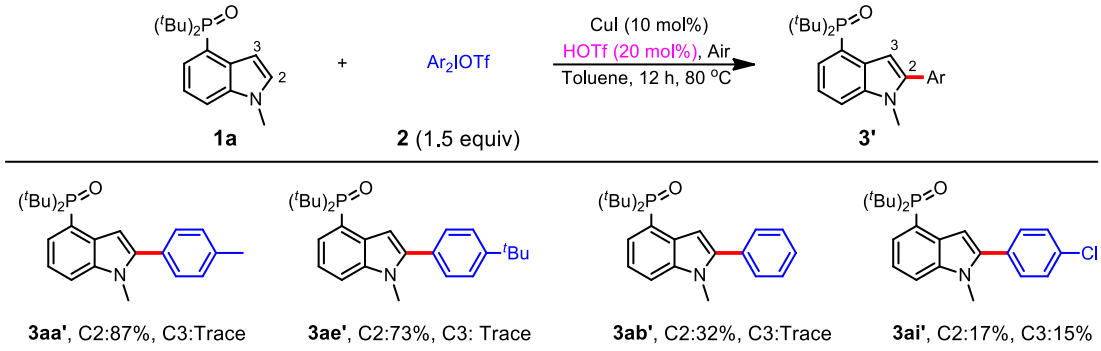
A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **1b** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), CuI (0.01 mmol, 10 mol%) and THF or toluene (1 mL) under air. The mixture was stirred at 100 °C or 80 °C for 8-12 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (3:1 to 2:1). Only **3ba** could be obtained no matter THF or Toluene as solvent. **3ba** is a pale yellow solid in 79% (0.079 mmol) or 76% (0.076 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.33 (m, 6H), 7.29 – 7.22 (m 4H), 7.15 – 7.06 (m, 1H), 6.95 – 6.85 (m, 4H), 6.78 (d, *J* = 7.7 Hz, 2H), 3.83 (s, 3H), 2.29 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.23 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.28 (d, *J* = 12.7 Hz), 135.25 (s), 134.31 (s), 133.27 (s), 132.05 (s), 131.62 (d, *J* = 9.5 Hz), 131.38 (s), 130.79 (d, *J* = 2.7 Hz), 130.56 (s), 127.93 (d, *J* = 12.2 Hz), 127.75 (s), 127.45 (d, *J* = 9.5 Hz), 123.97 (d, *J* = 104.3 Hz), 120.16 (d, *J* = 14.1 Hz), 119.15 (d, *J* = 2.2 Hz), 113.86 (d, *J* = 2.6 Hz), 32.93 (s), 21.16 (s). HRMS calcd for $C_{30}H_{36}NOP$: $[M+H]^+$ 422.1668, found 422.1675.

5.4 Reaction results of N-methylindole under different standard conditions.



A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **N-methylindole** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), CuI (0.01 mmol, 10 mol%) and THF or toluene (1 mL) under air. The mixture was stirred at 100 °C or 80 °C for 8-12 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (20:1 to 10:1). We could only get 3-arylation product under both standard conditions, and the yield in toluene was only 25% (0.025 mmol).

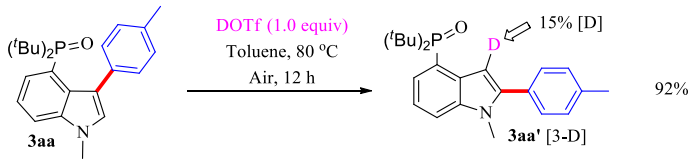
6. Investigated the effect of additional HOTf on the reaction [a]



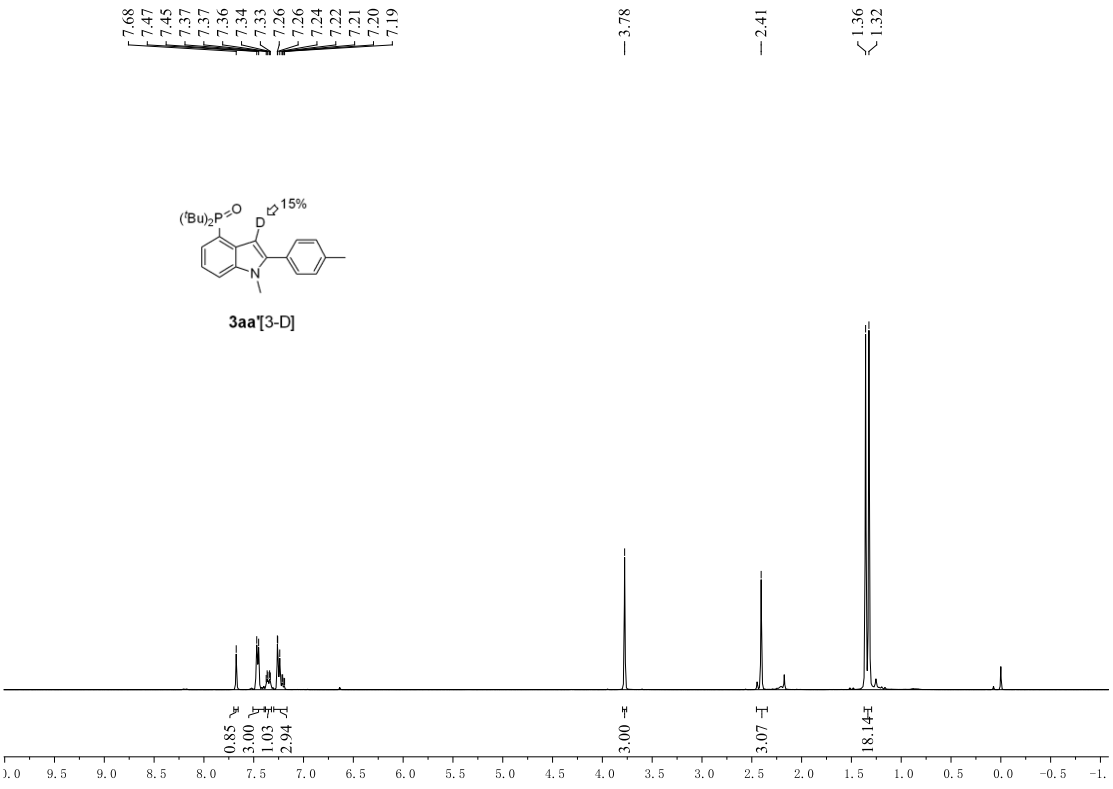
[a] **1a** (0.1 mmol, 1.0 equiv), **2** (0.15 mmol, 1.5 equiv), CuI (0.01 mmol, 10 mol%) and HOTf (0.02 mmol, 20 mol%) in toluene at 80 °C for 12 h under air.

We had previously considered to increase the yield and selectivity of C2-arylation by reducing the proportion of diaryliodonium triflate salts and adding additional HOTf. But the reaction results were worse then before, especially for the diaryliodonium triflate salts containing electron-deficient aromatics (**3ab'**, **3ai'**). The poor reaction results of electron-deficient aromatics were due to the low electrophilicity of Cu (III) formed by its oxidative addition with Cu (I). And the initial acidic atmosphere inhibited the activation of H3 by it to a certain extent, which eventually made the reaction difficult to proceed smoothly.

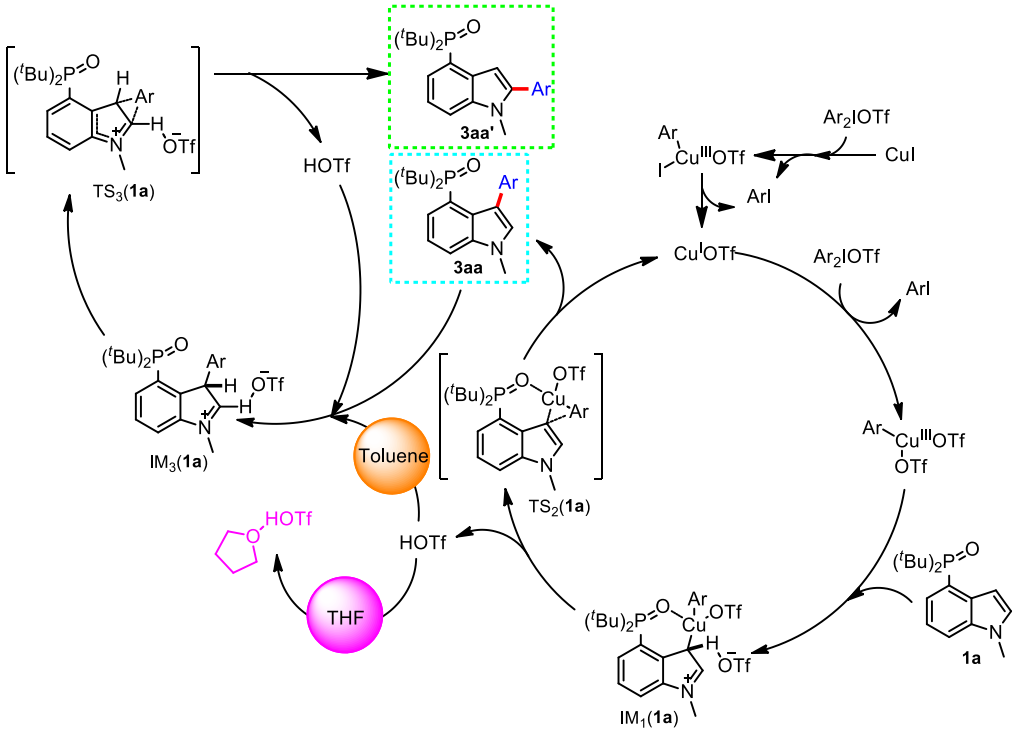
7. Deuterization experiment of indole H3 position



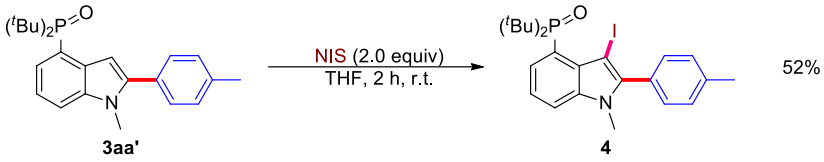
A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **3aa** (0.1 mmol, 1.0 equiv), DOTf (1.0 equiv) (following a reported procedure[8]) and toluene (1 mL) under air. The mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the solvent was removed under vaccum directly and purified by flash silica gel chromatography with petroleum ether/ethyl acetate (2:1 to 1:1) to afford **3aa'**[3-D] (0.092 mmol) as a pale yellow solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 0.85H), 7.46 (d, J = 7.7 Hz, 3H), 7.39 – 7.31 (m, 1H), 7.29 – 7.17 (m, 3H), 3.78 (s, 3H), 2.41 (s, 3H), 1.34 (d, J = 13.4 Hz, 18H).



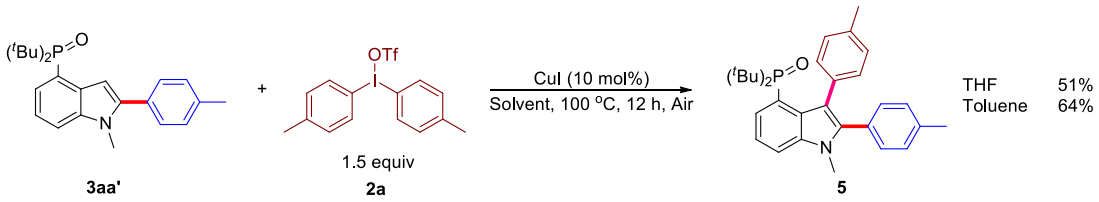
8 Proposed catalytic cycle



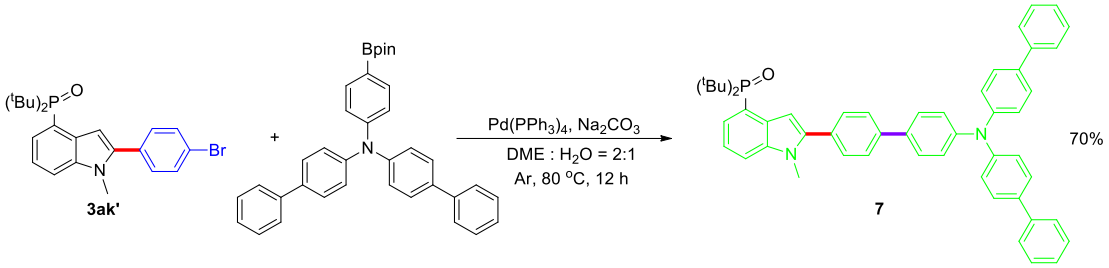
9. Synthesis of 2-aryl indole derivatives and potential fluorescent molecules



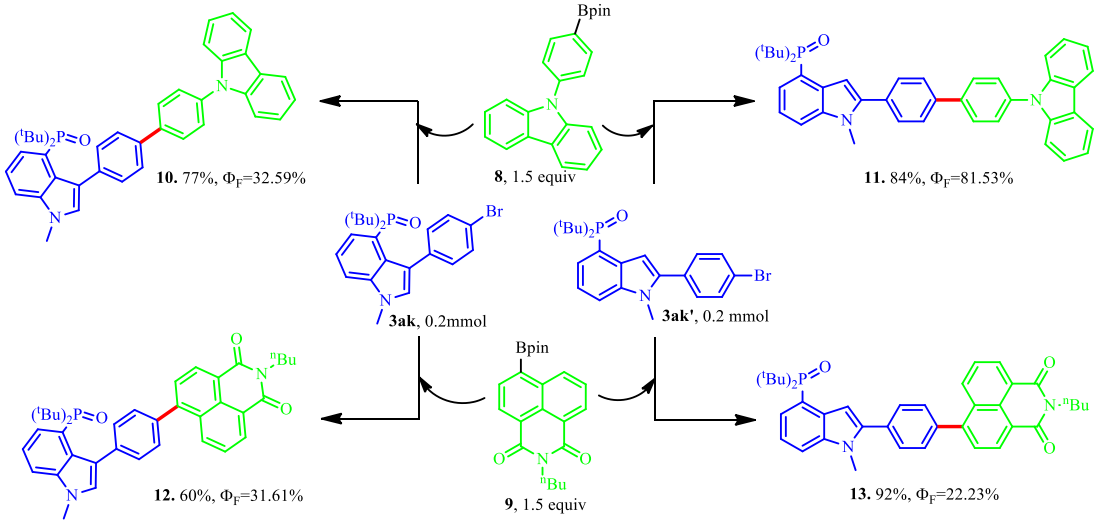
NIS(0.2 mmol, 2.0 equiv) was added in one pot to a solution of **3aa'** (0.1 mmol, 1.0 equiv) in THF (1 mL) at 0 °C. Then the reaction was stirred at room temperature for 2 h and monitored by TLC. After quenching with sodium thiosulfate aqueous solution, the reaction mixture was extracted with ethyl acetate (3×3 mL). The collected organic layers were dried with Na_2SO_4. The solvent was evaporated and purified by flash silica gel chromatography with petroleum ether/ethyl acetate (3:1 to 2:1) to afford **4** (0.052 mmol) as a brown oil in 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 2H), 7.33 – 7.28 (m, 4H), 7.28 – 7.23 (m, 1H), 3.60 (s, 3H), 2.44 (s, 3H), 1.39 (d, *J* = 13.3 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.94 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.79 (s), 138.89 (d, *J* = 10.4 Hz), 138.88 (s), 132.48 (d, *J* = 4.9 Hz), 131.22 (s), 130.95 (s), 129.07 (s), 125.60 (d, *J* = 12.0 Hz), 122.57 (d, *J* = 81.1 Hz), 119.05 (d, *J* = 12.9 Hz), 113.10 (d, *J* = 2.7 Hz), 55.43 (s), 37.96 (d, *J* = 58.3 Hz), 32.37 (s), 28.20 (s), 21.50 (s). HRMS calcd for $C_{24}H_{31}INOP$: $[M+H]^+$ 508.1261, found 508.1262.



A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **3aa'** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), CuI (0.01 mmol, 10 mol%) and solvent (1 mL) under air. The mixture was stirred at 100 °C for 12 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (3:1) to afford **5** as a pale yellow solid in 51% (0.051 mmol) or 64% (0.064 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 12.3, 7.4 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.06 – 6.94 (m, 6H), 6.89 (d, *J* = 7.7 Hz, 2H), 3.62 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 1.21 (d, *J* = 13.1 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.74 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.97 (s), 137.66 (d, *J* = 11.0 Hz), 137.21 (s), 135.71 (s), 134.04 (s), 132.19 (s), 130.86 (s), 129.77 (d, *J* = 5.1 Hz), 129.09 (s), 128.40 (s), 126.81 (s), 124.88 (d, *J* = 12.6 Hz), 123.42 (d, *J* = 82.5 Hz), 118.52 (d, *J* = 13.2 Hz), 117.78 (d, *J* = 1.6 Hz), 112.42 (d, *J* = 2.9 Hz), 37.59 (d, *J* = 58.4 Hz), 31.27 (s), 27.85 (s), 21.45 (s), 21.29 (s). HRMS calcd for $C_{31}H_{38}NOP$: $[M+H]^+$ 472.2764, found 472.2769.



To a solution of substrate **3ak'** (0.2 mmol, 1.0 equiv) in DME (2 mL) was added N-([1,1'-biphenyl]-4-yl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-amine (0.3 mmol 1.5 equiv), (following the general procedure for borylation[9]) $Pd(PPh_3)_4$ (5 mol%) and 0.5 M sodium carbonate aqueous solution (1 mL) at rt. The mixtue was heated to 80 °C for overnight under Ar. After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (2×5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (2:1) to afford **7** (0.14 mmol) as a pale yellow solid with fluorescence in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.64 (q, *J* = 8.6 Hz, 4H), 7.60 – 7.55 (m, 6H), 7.54 – 7.50 (m, 4H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.35 (m, 5H), 7.34 – 7.28 (m, 2H), 7.27 – 7.21 (m, 5.7 Hz, 7H), 3.80 (s, 3H), 1.35 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.02 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.08 (s), 146.81 (s), 142.33 (s), 140.60 (s), 139.94 (s), 139.16 (d, *J* = 10.5 Hz), 135.76 (s), 134.86 (s), 132.66 (d, *J* = 5.7 Hz), 131.07 (s), 129.83 (s), 128.82 (s), 127.97 (s), 127.88 (s), 126.96 (s), 126.74 (s), 126.59 (s), 124.55 (s), 124.40 (s), 123.35 (d, *J* = 10.8 Hz), 121.81 (d, *J* = 81.6 Hz), 119.61 (d, *J* = 12.3 Hz), 112.21 (d, *J* = 2.5 Hz), 104.73 (s), 36.94 (d, *J* = 59.5 Hz), 31.40 (s), 27.37 (s). HRMS calcd for $C_{53}H_{51}N_2OP$: $[M+H]^+$ 763.3812, found 763.3828.



8 and **9** were synthesized according to the general procedure for borylation[9]. And the synthesis method of **10-13** was as follows: to a solution of substrate **3ak**/**3ak'** (0.2 mmol, 1.0 equiv) in DME (2 mL) was added **8**/**9** (0.3 mmol 1.5 equiv), $Pd(PPh_3)_4$ (5 mol%) and 0.5 M sodium carbonate aqueous solution (1 mL) at r.t.. The mixtue was heated to 80 °C for overnight under Ar. After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (2×5 mL). The combined organic layers were dried over Na_2SO_4,

filtered and concentrated in vacuo. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate.

10 (yield: 77%, 0.15 mmol) as a yellow solid with fluorescence from slica gel chromatography (petroleum ether : ethyl acetate = 2:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.35 (m, 8H), 7.31 – 7.24 (m, 3H), 7.01 (s, 1H), 3.77 (s, 3H), 1.23 (d, *J* = 13.1 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.39 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.02 (s), 140.88 (s), 139.19 (s), 137.99 (d, *J* = 10.7 Hz), 136.86 (s), 136.06 (s), 132.35 (s), 131.18 (s), 129.09 (d, *J* = 5.3 Hz), 128.38 (s), 127.13 (s), 126.01 (s), 125.09 (s), 124.73 (d, *J* = 12.0 Hz), 124.12 (d, *J* = 81.3 Hz), 123.39 (s), 120.33 (s), 119.89 (s), 119.33 (d, *J* = 1.6 Hz), 119.17 (d, *J* = 12.8 Hz), 112.57 (d, *J* = 2.6 Hz), 110.05 (s), 37.61 (d, *J* = 58.6 Hz), 32.89 (s), 27.89 (s). HRMS calcd for $C_{41}H_{41}N_2OP$: $[M+H]^+$ 609.3029, found 609.3029.

11 (yield: 84% 0.17 mmol) as a yellow solid with fluorescence from slica gel chromatography (petroleum ether : ethyl acetate = 1.5:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 5.5 Hz, 3H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 3H), 7.45 – 7.34 (m, 3H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.19 (m, 1H), 3.82 (s, 3H), 1.36 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.87 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.06 (s), 140.83 (s), 139.56 (d, *J* = 5.5 Hz), 139.20 (d, *J* = 10.4 Hz), 137.04 (s), 132.62 (d, *J* = 5.5 Hz), 131.89 (s), 129.97 (s), 128.48 (s), 127.40 (s), 127.10 (s), 126.07 (s), 123.47 (s), 123.40 (s), 121.97 (d, *J* = 81.4 Hz), 120.41 (s), 120.08 (s), 119.79 (d, *J* = 11.8 Hz), 112.29 (d, *J* = 2.2 Hz), 109.91 (s), 104.96 (s), 36.94 (d, *J* = 59.5 Hz), 31.48 (s), 27.39 (s). HRMS calcd for $C_{41}H_{41}N_2OP$: $[M+H]^+$ 609.3029, found 609.3029.

12 (yield: 60% 0.12 mmol) as a yellow solid with fluorescence from slica gel chromatography (petroleum ether : ethyl acetate = 2:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 13.5, 7.3 Hz, 2H), 8.57 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.60 – 7.38 (m, 6H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.12 (s, 1H), 4.22 (t, *J* = 7.5 Hz, 2H), 3.87 (s, 3H), 1.82 – 1.68 (m, 2H), 1.54 – 1.42 (m, 2H), 1.24 (d, *J* = 13.1 Hz, 18H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.12 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.62 (s), 164.41 (s), 148.02 (s), 139.92 (s), 137.94 (d, *J* = 10.7 Hz), 135.61 (s), 133.83 (s), 132.00 (s), 131.01 (d, *J* = 8.7 Hz), 130.80 (s), 130.37 (s), 129.16 (d, *J* = 5.2 Hz), 128.79 (s), 128.17 (s), 127.83 (s), 126.49 (s), 124.76 (d, *J* = 11.8 Hz), 124.15 (d, *J* = 81.0 Hz), 122.67 (s), 121.10 (s), 119.30 (d, *J* = 12.8 Hz), 119.06 (d, *J* = 1.4 Hz), 112.54 (d, *J* = 2.4 Hz), 40.25 (s), 37.56 (d, *J* = 58.6 Hz), 32.96 (s), 30.29 (s), 27.78 (s), 20.48 (s), 13.97 (s). HRMS calcd for $C_{39}H_{43}N_2O_3P$: $[M+H]^+$ 619.3084, found 619.3084.

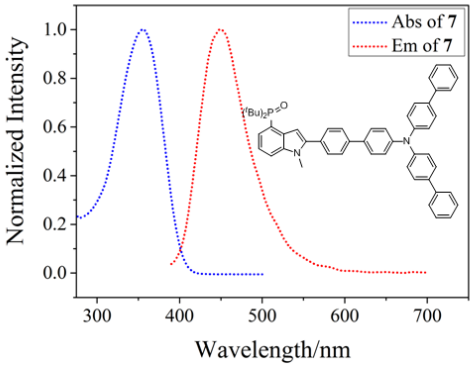
13 (yield: 92% 0.18 mmol) as a yellow solid with fluorescence from slica gel chromatography (petroleum ether : ethyl acetate = 1.5:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 – 8.63 (m, 2H), 8.34 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.86 (s, 1H), 7.80 – 7.73 (m, 3H), 7.70 – 7.66 (m, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.32 – 7.25 (m, 1H), 4.26 – 4.17 (m, 2H), 3.90 (s, 3H), 1.80 – 1.70 (m, 2H), 1.54 – 1.44 (m, 2H), 1.37 (d, *J* = 13.4 Hz, 18H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.93 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.34 (s), 164.14 (s), 146.30 (s), 141.63 (s), 139.22 (d, *J* = 10.5 Hz), 138.16 (s), 132.69 (d, *J* = 25.4 Hz), 132.10 (d, *J* = 9.9 Hz), 131.99 (d, *J* = 2.8 Hz), 131.26 (s), 130.83 (s), 130.02 (s), 129.56 (s), 128.70 (s), 128.54 (d, *J* = 12.1 Hz), 127.90 (s), 127.01 (s), 123.53 (d, *J* = 10.3 Hz), 122.92 (s), 122.07 (d, *J* = 81.2 Hz), 121.86 (s), 119.99 (d, *J* = 11.9 Hz), 112.34 (d, *J* = 2.5 Hz), 105.34 (s),

40.32 (s), 36.89 (d, *J* = 59.5 Hz), 31.53 (s), 30.25 (s), 27.33 (s), 20.45 (s), 13.95 (s). HRMS calcd for $C_{39}H_{43}N_2O_3P$: $[M+H]^+$ 619.3084, found 619.3084.

10. Photophysical properties

10.1 Photophysical data and spectra of 7

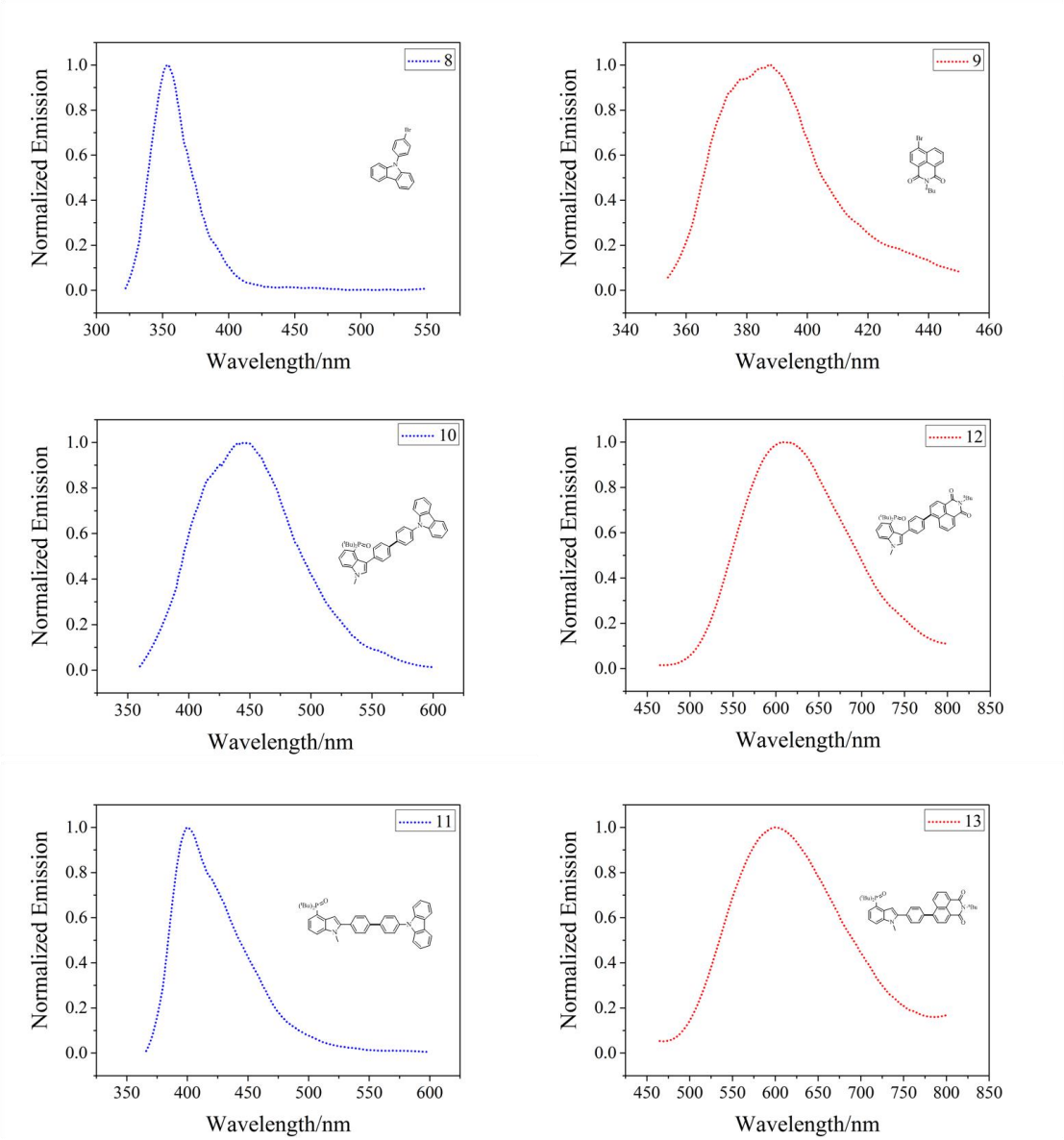
Compounds	λ_{abs} (nm)	λ_{ex} (nm)	λ_{em} (nm)	Φ_F
7	355	363	449	65.99%



Absorption and emission spectra of **7** in CH_2Cl_2 (1.0×10^{-5} mol/L). Absolute quantum yield in CH_2Cl_2 (1.0×10^{-5} mol/L) determined with an integrating sphere system.

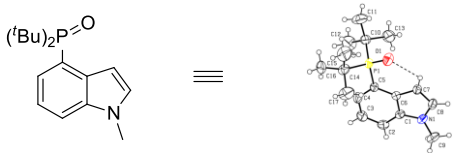
10.2 Photophysical data and spectra of 8, 9, 10, 11, 12 and 13

Compounds	λ_{ex} (nm)	λ_{em} (nm)	Φ_F
8	300	354	8.87%
9	310	388	1.11%
10	310	445	32.59%
11	340	400	81.53%
12	340	611	31.61%
13	340	600	22.23%



Emission spectra of **8, 9, 10, 11, 12** and **13** in CH_2Cl_2 (1.0×10^{-5} mol/L). Absolute quantum yields in CH_2Cl_2 (1.0×10^{-5} mol/L) determined with an integrating sphere system.

11. Crystallographic data



1a ≡ **CCDC: 2042999**

Table S9. Crystal data and structure refinement for **1a**.

Identification code	1a
Empirical formula	$C_{17}H_{26}NOP$
Formula weight	291.18

Temperature/K	292.65(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.9412(2)
b/Å	13.9538(6)
c/Å	16.5476(8)
α/°	112.708(4)
β/°	90.345(3)
γ/°	96.480(3)
Volume/Å^3	1678.23(13)
Z	2
ρcalcg/cm^3	1.153
μ/mm^{-1}	1.407
F(000)	632.0
Crystal size/mm^3	0.14 × 0.09 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.092 to 133.198
Index ranges	-5 ≤ h ≤ 9, -16 ≤ k ≤ 15, -19 ≤ l ≤ 19
Reflections collected	10903
Independent reflections	5924 [R_{int} = 0.0311, R_{sigma} = 0.0337]
Data/restraints/parameters	5924/0/375
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1281
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.1333
Largest diff. peak/hole / e Å^{-3}	0.25/-0.38

Single crystals of $C_{17}H_{26}NOP$ (**1a**) was collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 292.65(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Table S9. CCDC 2042999 contains the supplementary crystallographic data for **1a**. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

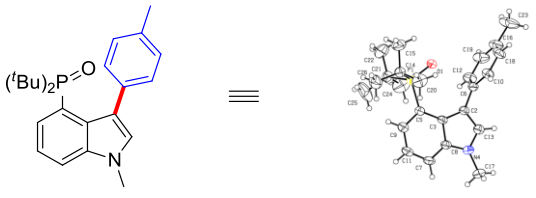
1b ≡ **CCDC: 2043000**

Table S10. Crystal data and structure refinement for **1b**.

Identification code	1b
Empirical formula	$C_{21}H_{18}NOP$
Formula weight	331.33

Temperature/K	292.19(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.7400(3)
b/Å	11.2344(5)
c/Å	17.1171(5)
α/°	90
β/°	94.056(3)
γ/°	90
Volume/Å^3	1676.50(10)
Z	4
ρcalcg/cm^3	1.313
μ/mm^{-1}	1.493
F(000)	696.0
Crystal size/mm^3	0.08 × 0.07 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.424 to 133.162
Index ranges	$-10 \leq h \leq 9$, $-9 \leq k \leq 13$, $-20 \leq l \leq 19$
Reflections collected	6054
Independent reflections	2957 [R_{int} = 0.0199, R_{sigma} = 0.0268]
Data/restraints/parameters	2957/0/219
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0362, wR_2 = 0.0981
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.1018
Largest diff. peak/hole / e Å^{-3}	0.33/-0.29

Single crystals of $C_{21}H_{18}NOP$ (**1b**) was collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 292.19(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Table S10. CCDC 2043000 contains the supplementary crystallographic data for **1b**. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.



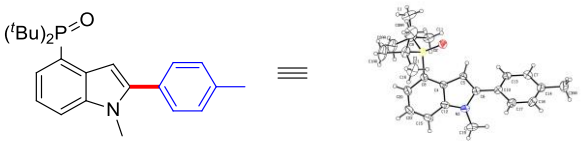
3aa **CCDC: 2042997**

Table S11. Crystal data and structure refinement for **3aa**.

Identification code	3aa
Empirical formula	$C_{24}H_{32}NOP$
Formula weight	381.47

Temperature/K	293.37(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	14.5242(3)
b/Å	15.7499(3)
c/Å	19.4992(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4460.55(14)
Z	8
ρcalcg/cm^3	1.136
μ/mm^{-1}	1.172
F(000)	1648.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.07 to 133.19
Index ranges	-17 ≤ h ≤ 14, -18 ≤ k ≤ 18, -23 ≤ l ≤ 11
Reflections collected	10855
Independent reflections	3922 [R_{int} = 0.0275, R_{sigma} = 0.0316]
Data/restraints/parameters	3922/0/252
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1187
Final R indexes [all data]	R_1 = 0.0569, wR_2 = 0.1287
Largest diff. peak/hole / e Å^{-3}	0.18/-0.32

Single crystals of $C_{24}H_{32}NOP$ (**3aa**) was collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 293.37(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Table S11. CCDC 2042997 contains the supplementary crystallographic data for **3aa**. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.



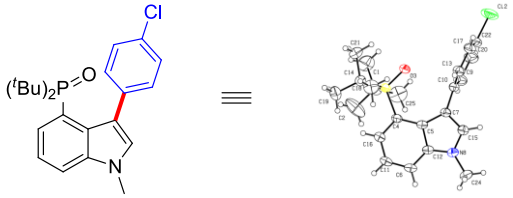
3aa' **CCDC: 2043003**

Table S12. Crystal data and structure refinement for **3aa'**.

Identification code	3aa'
Empirical formula	$C_{24}H_{32}NOP$
Formula weight	381.47
Temperature/K	293.14(10)

Crystal system	monoclinic
Space group	C2/c
a/Å	32.4047(7)
b/Å	7.95437(17)
c/Å	17.7118(3)
α/°	90
β/°	92.0211(19)
γ/°	90
Volume/Å^3	4562.54(16)
Z	8
ρcalcg/cm^3	1.111
μ/mm^{-1}	1.146
F(000)	1648.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.994 to 133.128
Index ranges	-37 ≤ h ≤ 38, -9 ≤ k ≤ 9, -21 ≤ l ≤ 14
Reflections collected	8667
Independent reflections	4041 [R_{int} = 0.0209, R_{sigma} = 0.0259]
Data/restraints/parameters	4041/0/252
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0430, wR_2 = 0.1192
Final R indexes [all data]	R_1 = 0.0509, wR_2 = 0.1273
Largest diff. peak/hole / e Å^{-3}	0.20/-0.25

Single crystals of $C_{24}H_{32}NOP$ (**3aa'**) was collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 293.14(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Table S12. CCDC 2043003 contains the supplementary crystallographic data for **3aa'**. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.



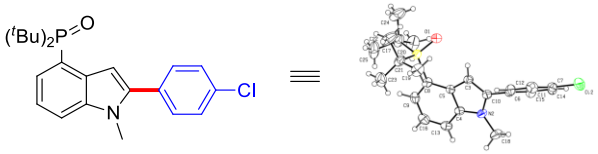
3ai **CCDC: 2043001**

Table S13. Crystal data and structure refinement for **3ah**

Identification code	3ai
Empirical formula	$C_{23}H_{29}ClNOP$
Formula weight	401.89
Temperature/K	230(17)

Crystal system	orthorhombic
Space group	Pbca
a/Å	14.3409(3)
b/Å	15.6455(3)
c/Å	19.8457(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4452.76(17)
Z	8
ρcalcg/cm^3	1.199
μ/mm^{-1}	2.279
F(000)	1712.0
Crystal size/mm^3	0.19 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.912 to 133.172
Index ranges	-13 ≤ h ≤ 17, -17 ≤ k ≤ 18, -23 ≤ l ≤ 22
Reflections collected	9938
Independent reflections	3936 [R_{int} = 0.0314, R_{sigma} = 0.0337]
Data/restraints/parameters	3936/0/251
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0531, wR_2 = 0.1400
Final R indexes [all data]	R_1 = 0.0620, wR_2 = 0.1512
Largest diff. peak/hole / e Å^{-3}	0.35/-0.58

Single crystals of $C_{23}H_{29}ClNOP$ (**3ai**) was collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 230(17) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Table S13. CCDC 2043001 contains the supplementary crystallographic data for **3ai**. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.



3ai' **CCDC: 2043002**

Table S14. Crystal data and structure refinement for **3ah'**

Identification code	3ai'
Empirical formula	$C_{23}H_{29}ClNOP$
Formula weight	401.89
Temperature/K	291.76(10)
Crystal system	monoclinic

Space group	C2/c
a/Å	31.5630(8)
b/Å	7.9513(2)
c/Å	17.9128(5)
α/°	90
β/°	96.877(2)
γ/°	90
Volume/Å^3	4463.2(2)
Z	8
ρcalcg/cm^3	1.196
μ/mm^{-1}	2.273
F(000)	1712.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.948 to 133.154
Index ranges	-37 ≤ h ≤ 36, -9 ≤ k ≤ 8, -21 ≤ l ≤ 19
Reflections collected	7520
Independent reflections	3852 [R_{int} = 0.0216, R_{sigma} = 0.0254]
Data/restraints/parameters	3825/0/251
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0459, wR_2 = 0.1209
Final R indexes [all data]	R_1 = 0.0509, wR_2 = 0.1274
Largest diff. peak/hole / e Å^{-3}	0.28/-0.49

Single crystals of $C_{23}H_{29}ClNOP$ (**3ai'**) was collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 291.76(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Table S14. CCDC 2043002 contains the supplementary crystallographic data for **3ai'**. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif

12. References

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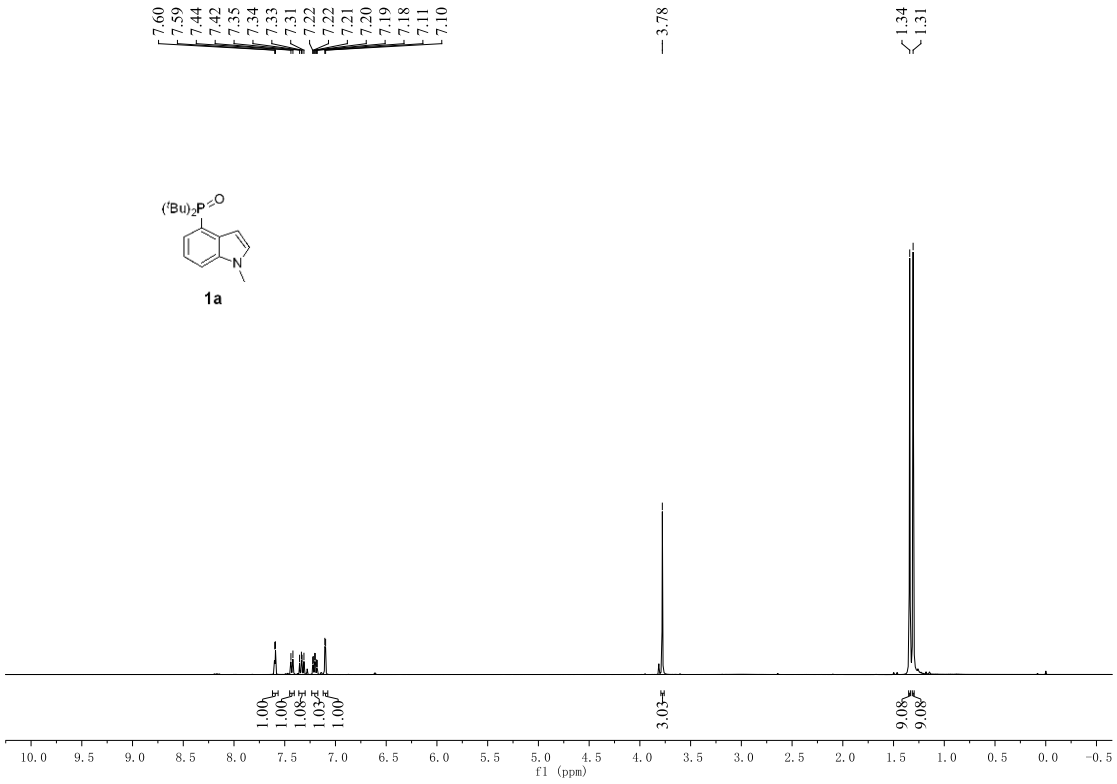
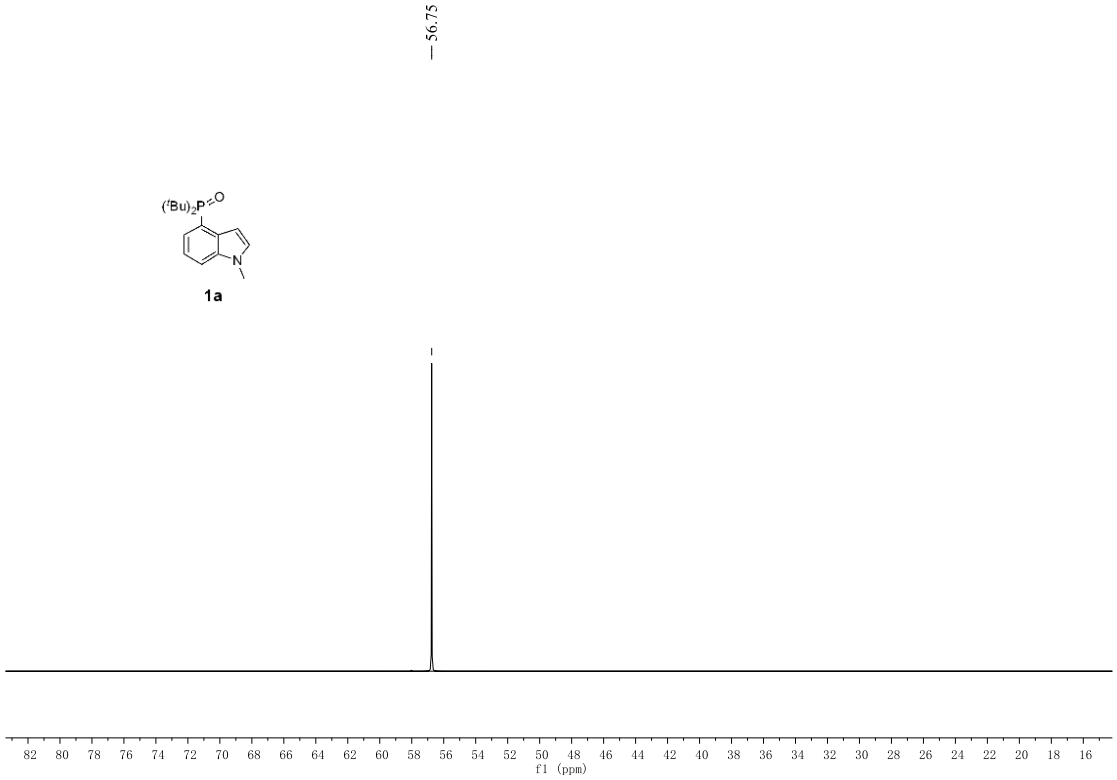
13. Copies of NMR spectra

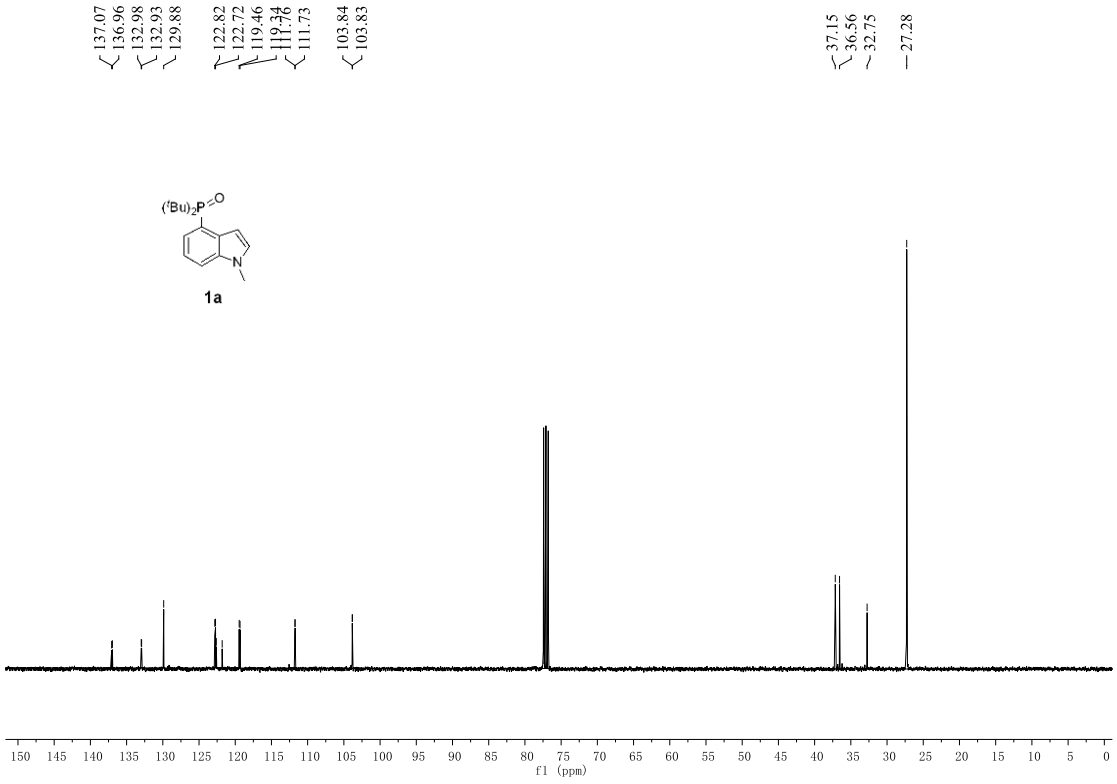
^{1}H NMR spectrum for **1a**



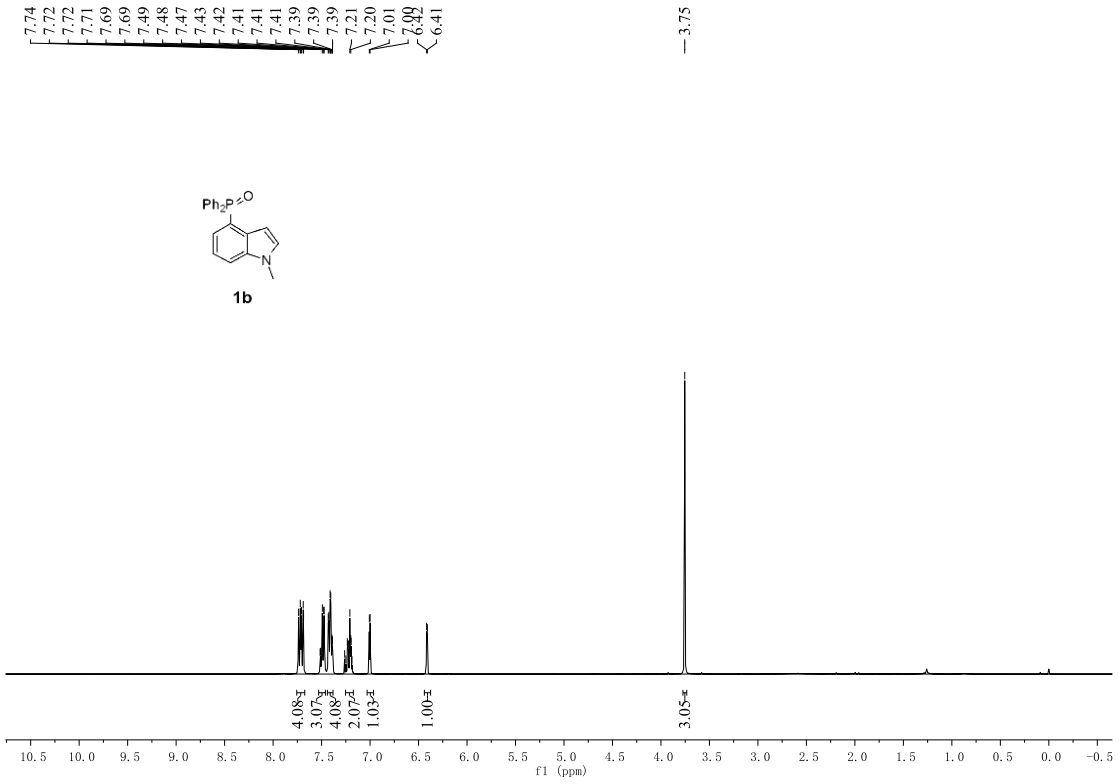
^{31}P NMR spectrum for **1a**



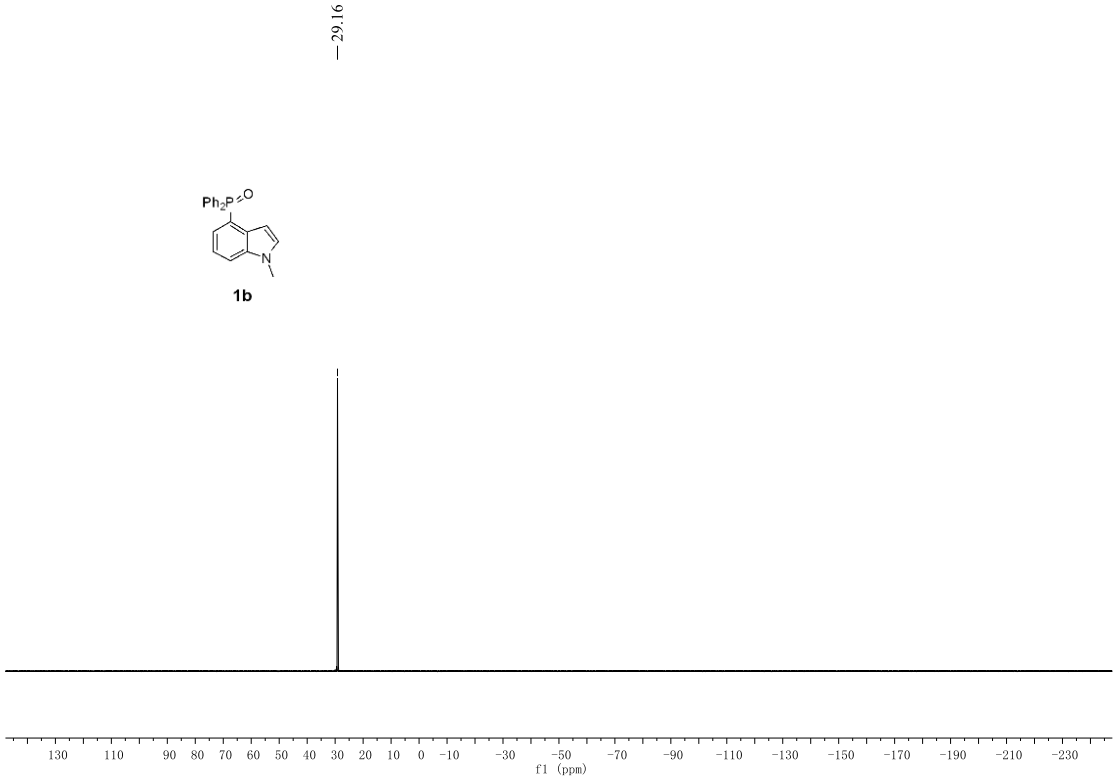
^{13}C NMR spectrum for **1a**



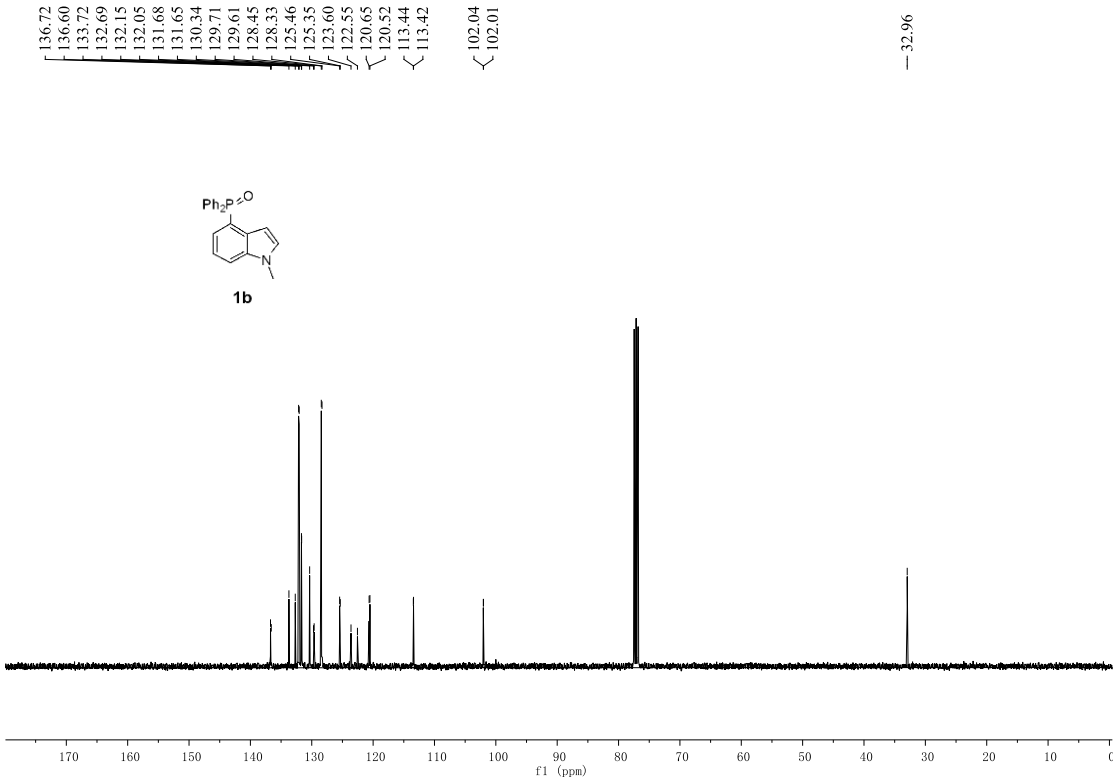
^{1}H NMR spectrum for **1b**



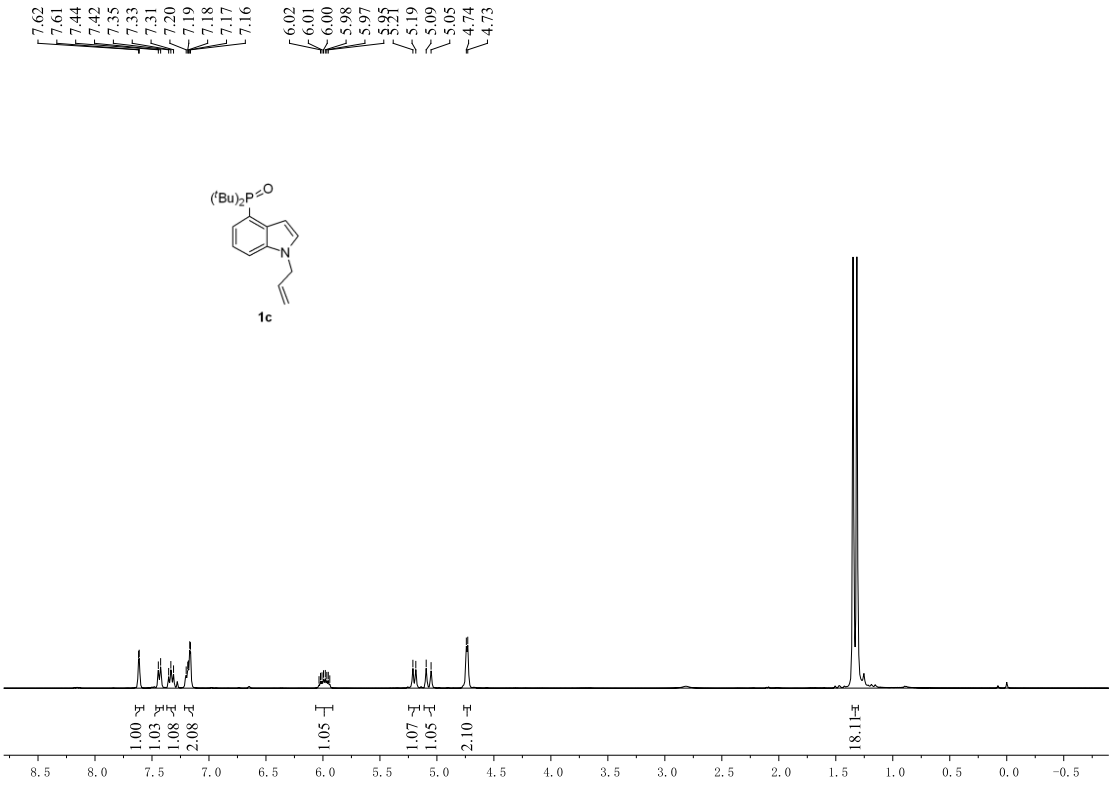
^{31}P NMR spectrum for **1b**



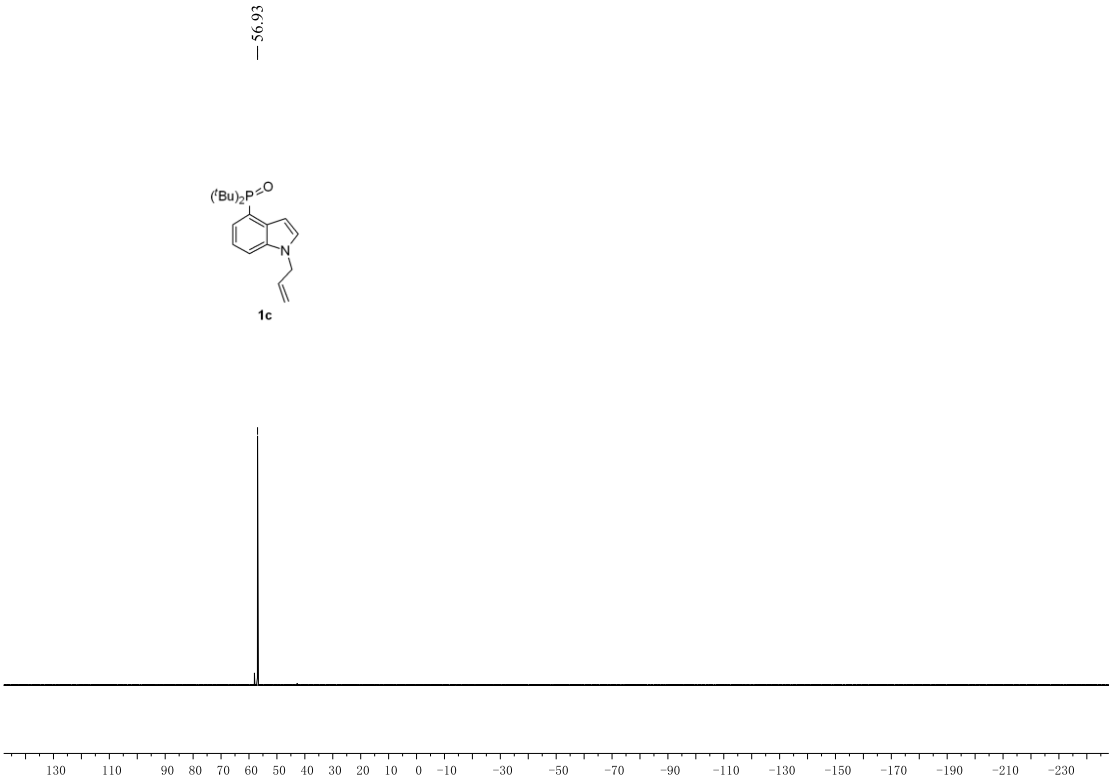
^{13}C NMR spectrum for **1b**



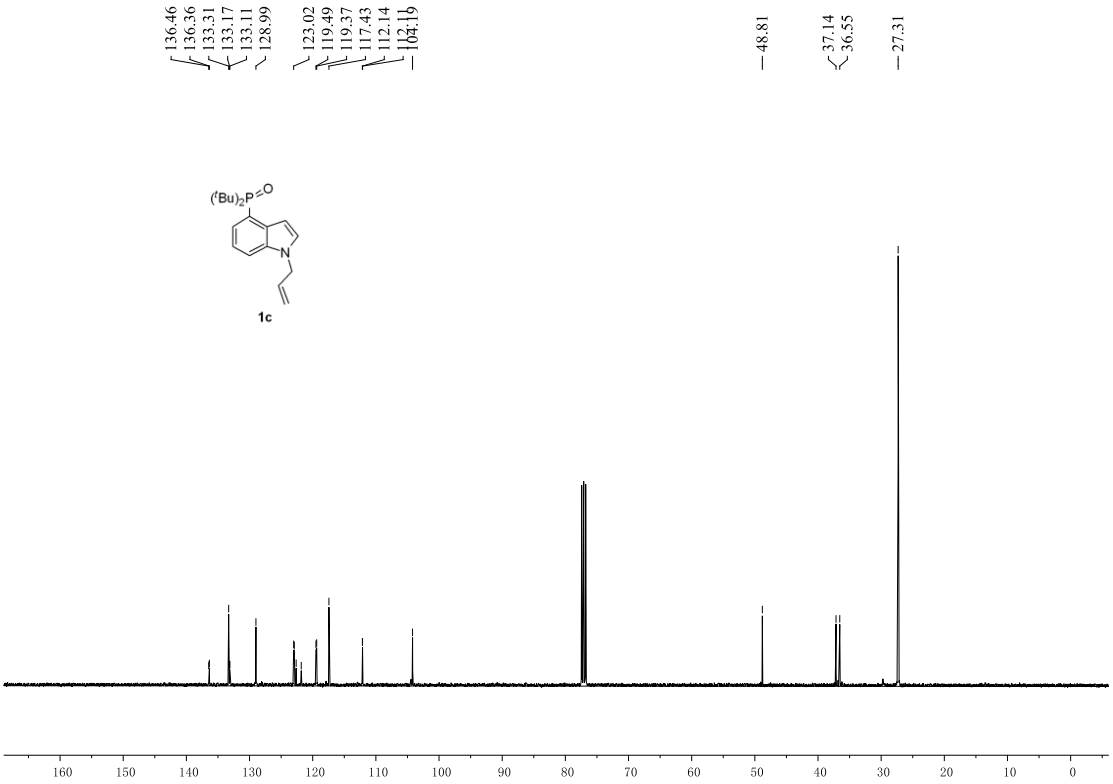
^{1}H NMR spectrum for **1c**



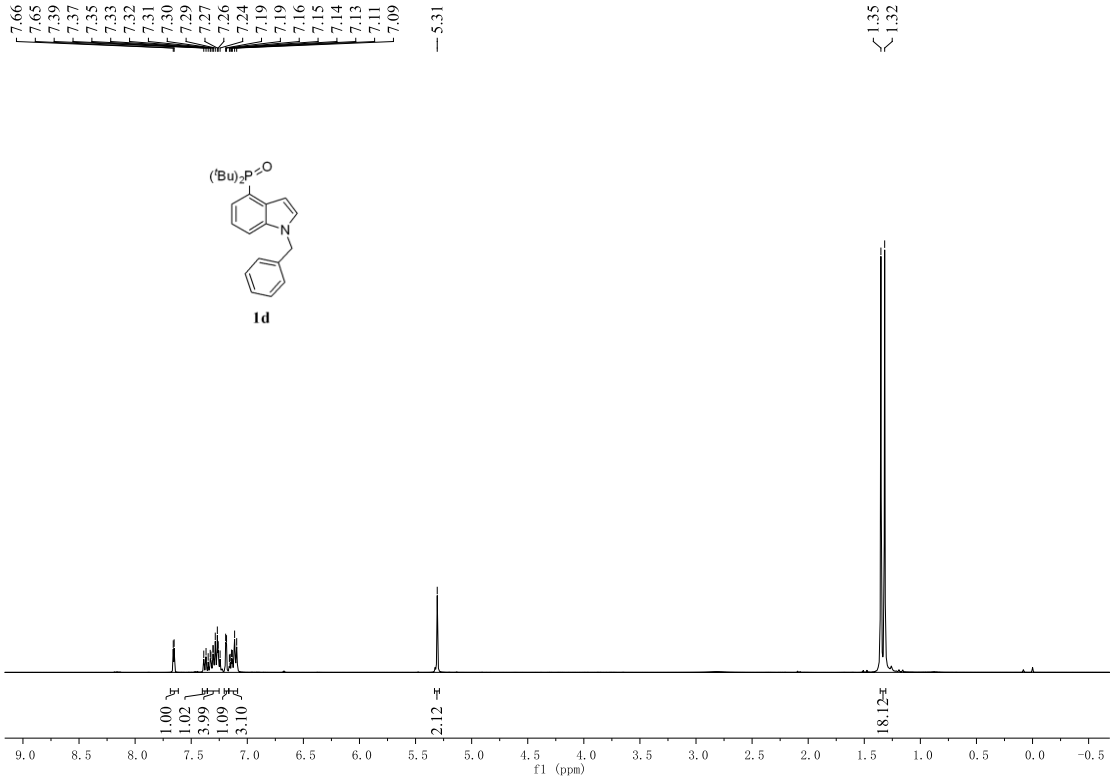
^{31}P NMR spectrum for **1c**



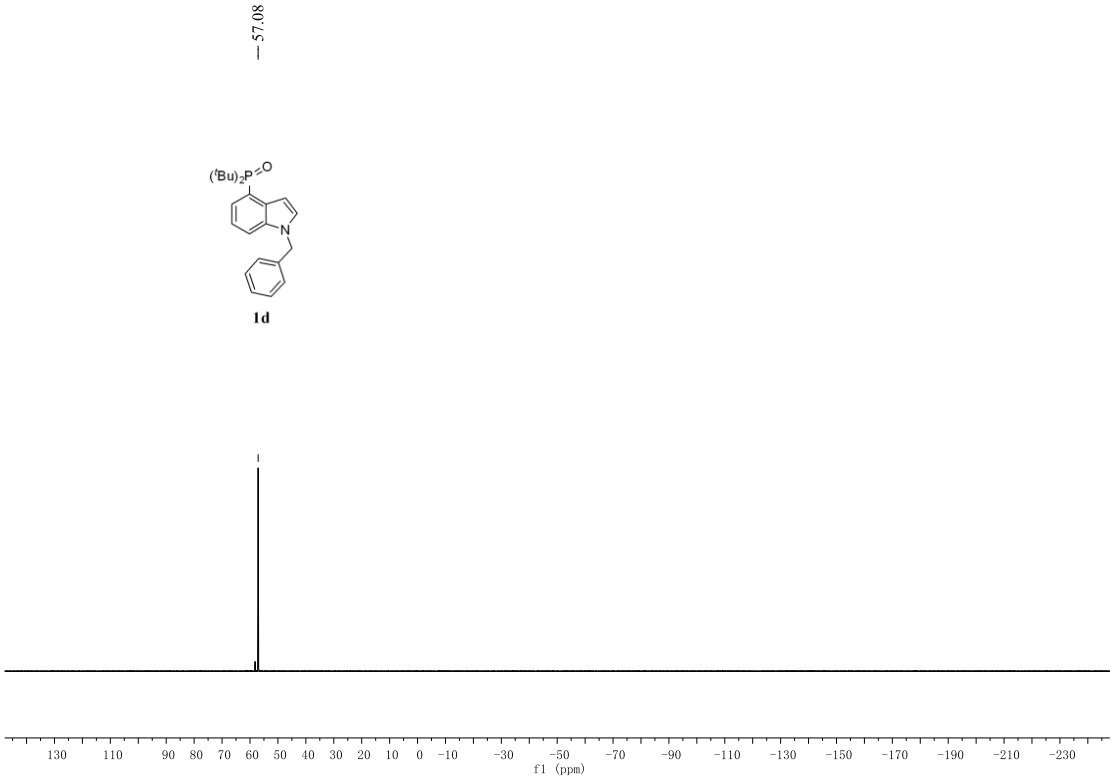
^{13}C NMR spectrum for **1c**



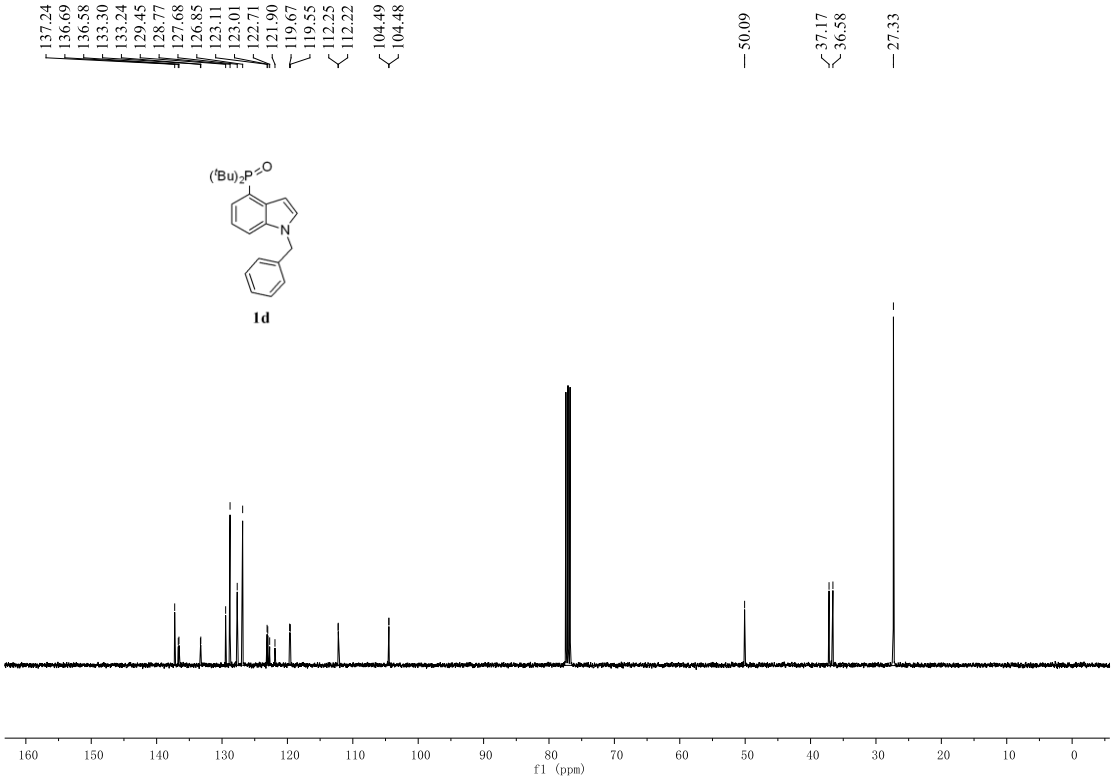
^{1}H NMR spectrum for **1d**



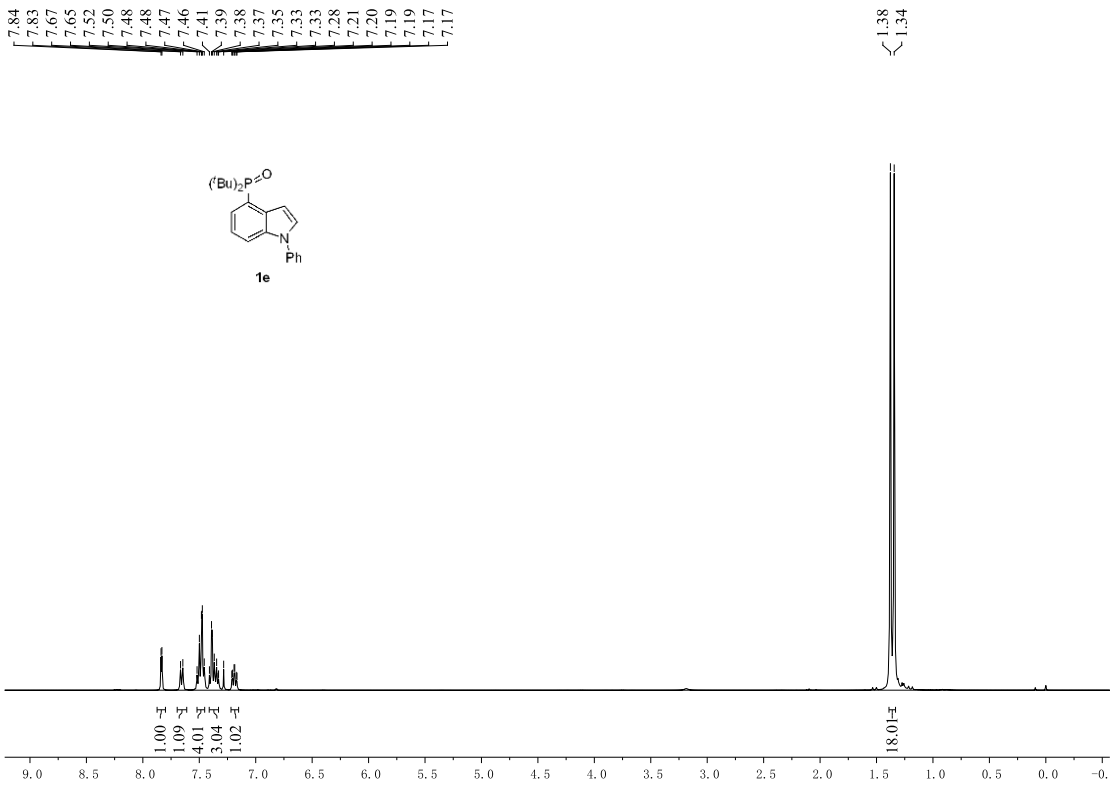
^{31}P NMR spectrum for **1d**



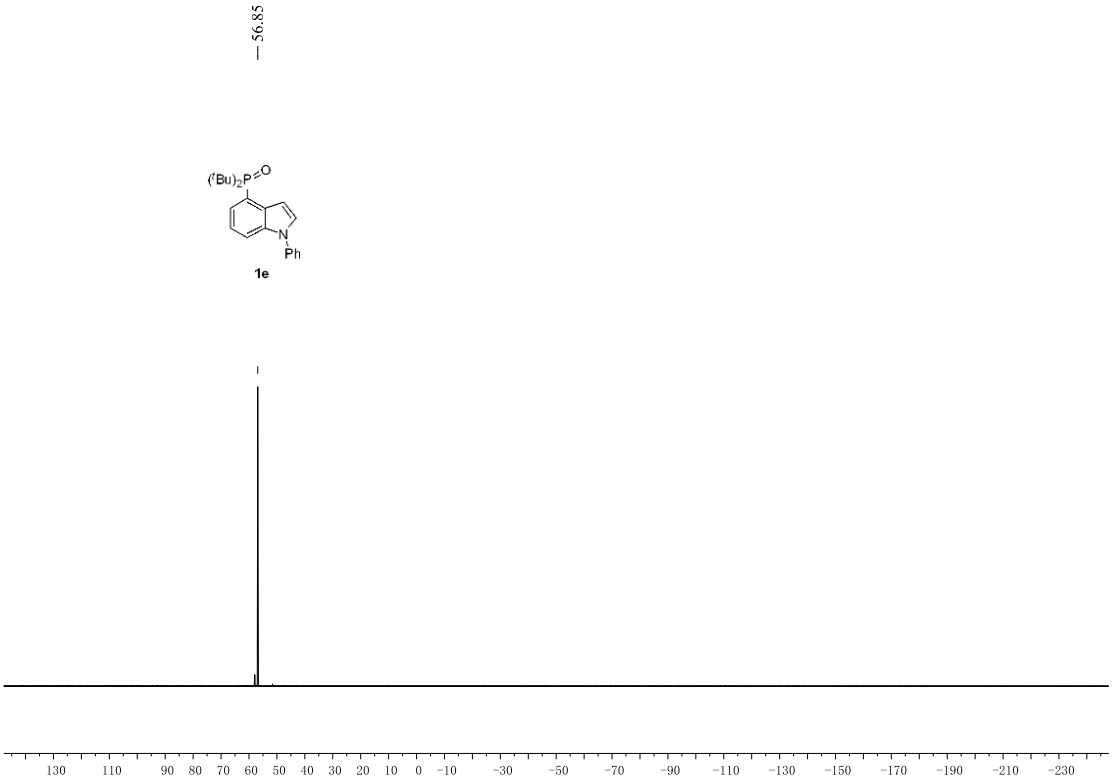
^{13}C NMR spectrum for **1d**



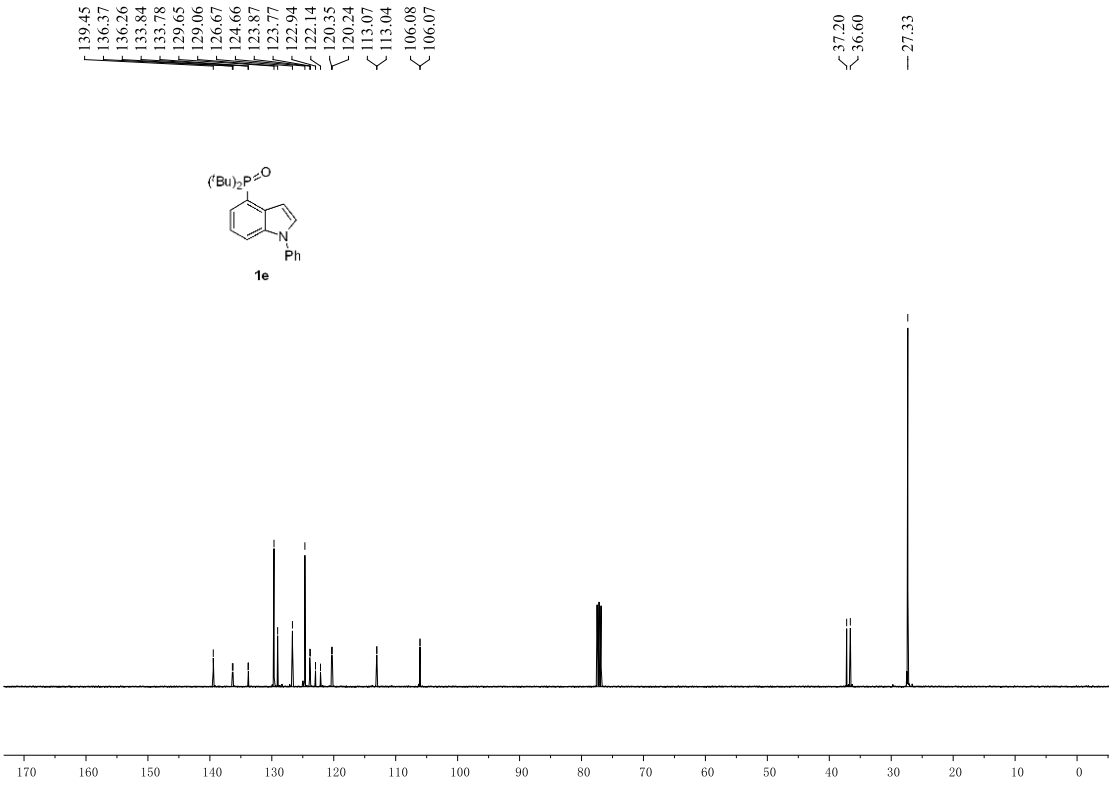
^{1}H NMR spectrum for **1e**



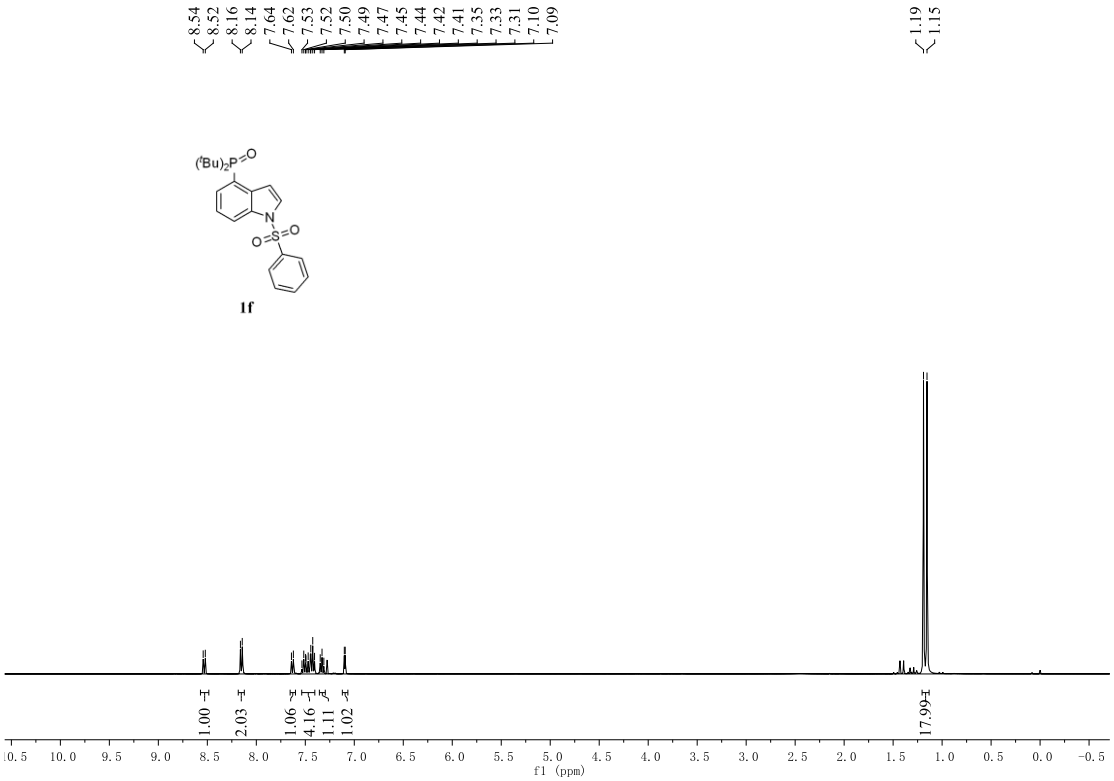
^{31}P NMR spectrum for **1e**



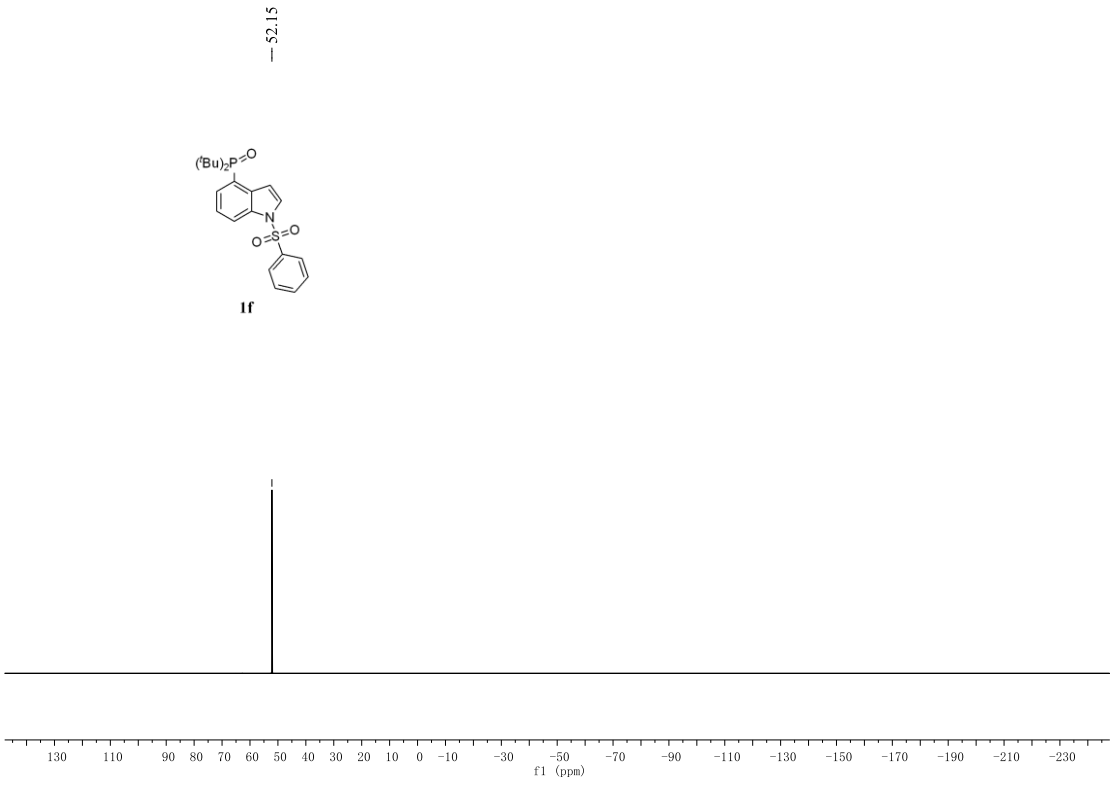
^{13}C NMR spectrum for **1e**



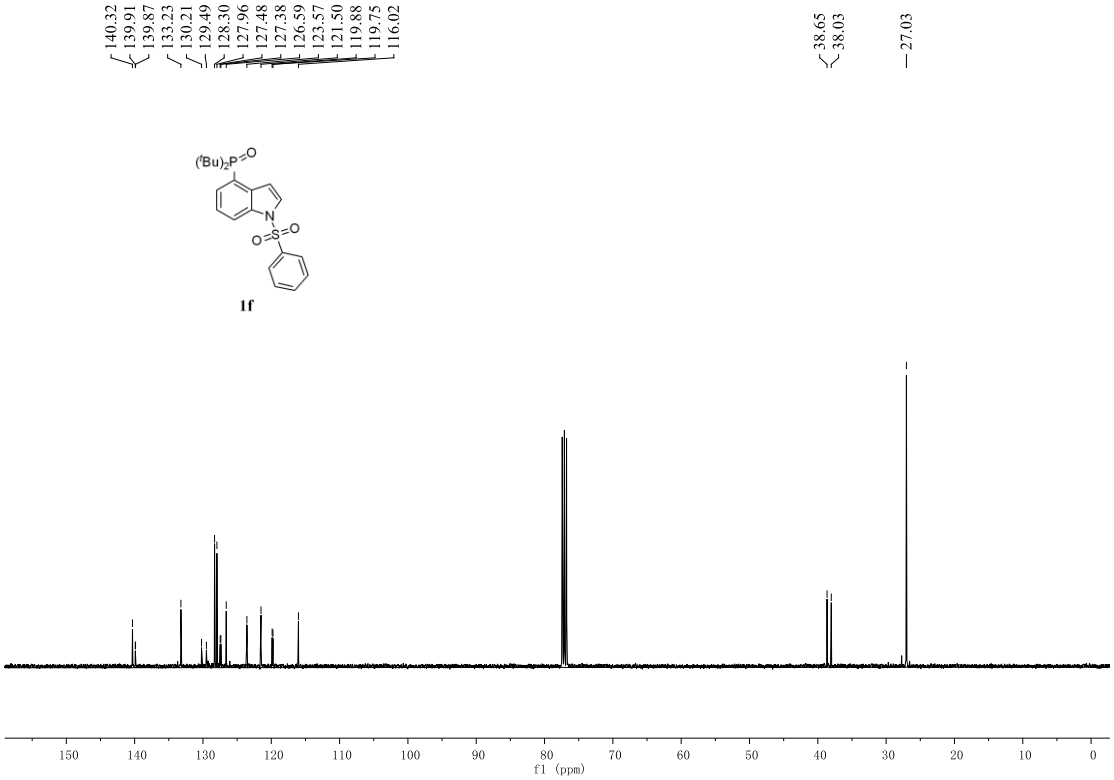
^{1}H NMR spectrum for **1f**



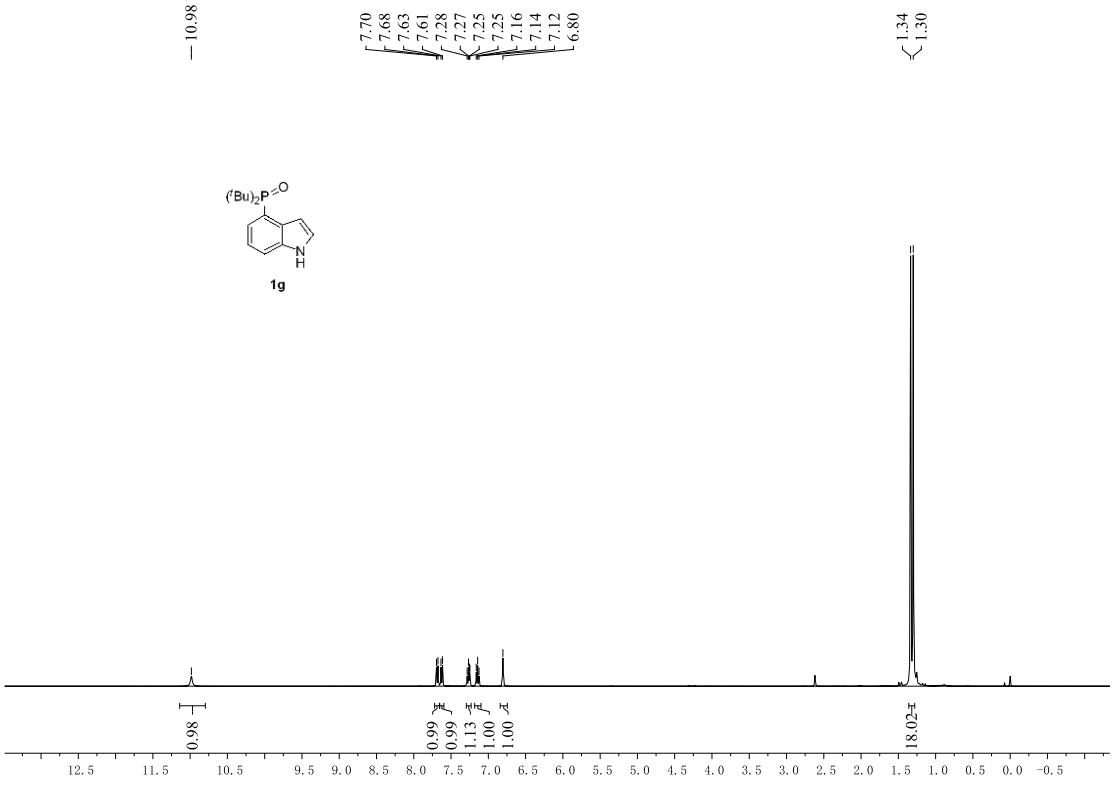
^{31}P NMR spectrum for **1f**



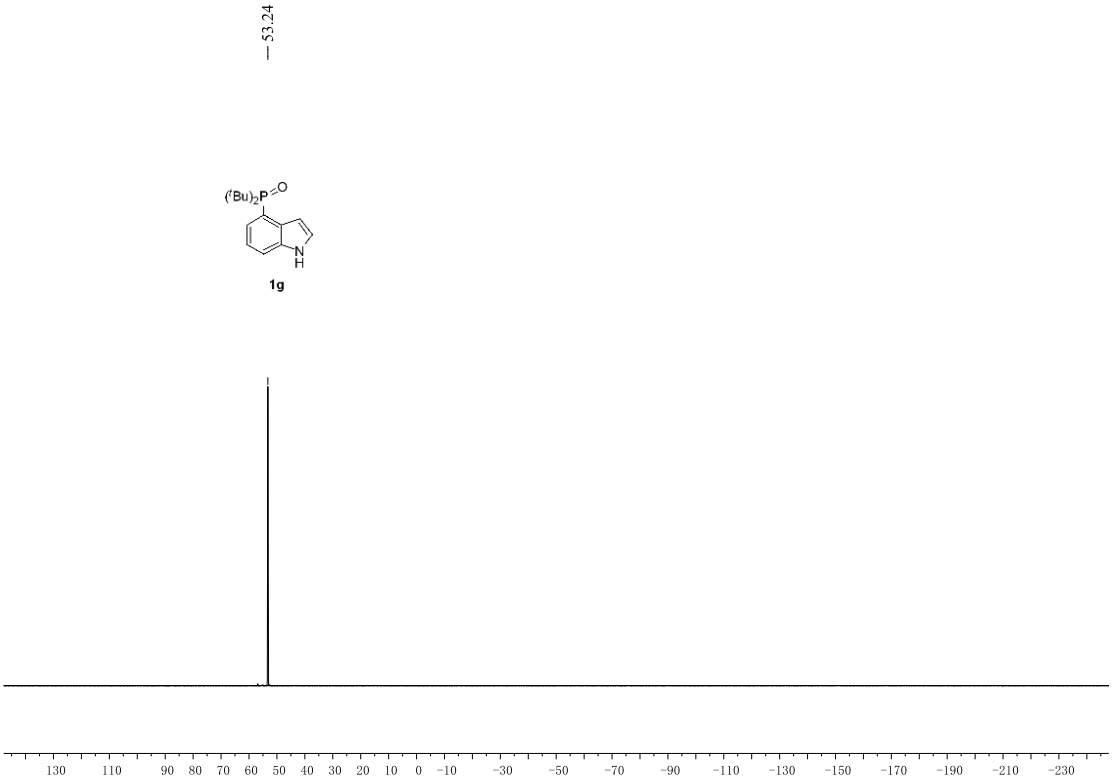
^{13}C NMR spectrum for **1f**



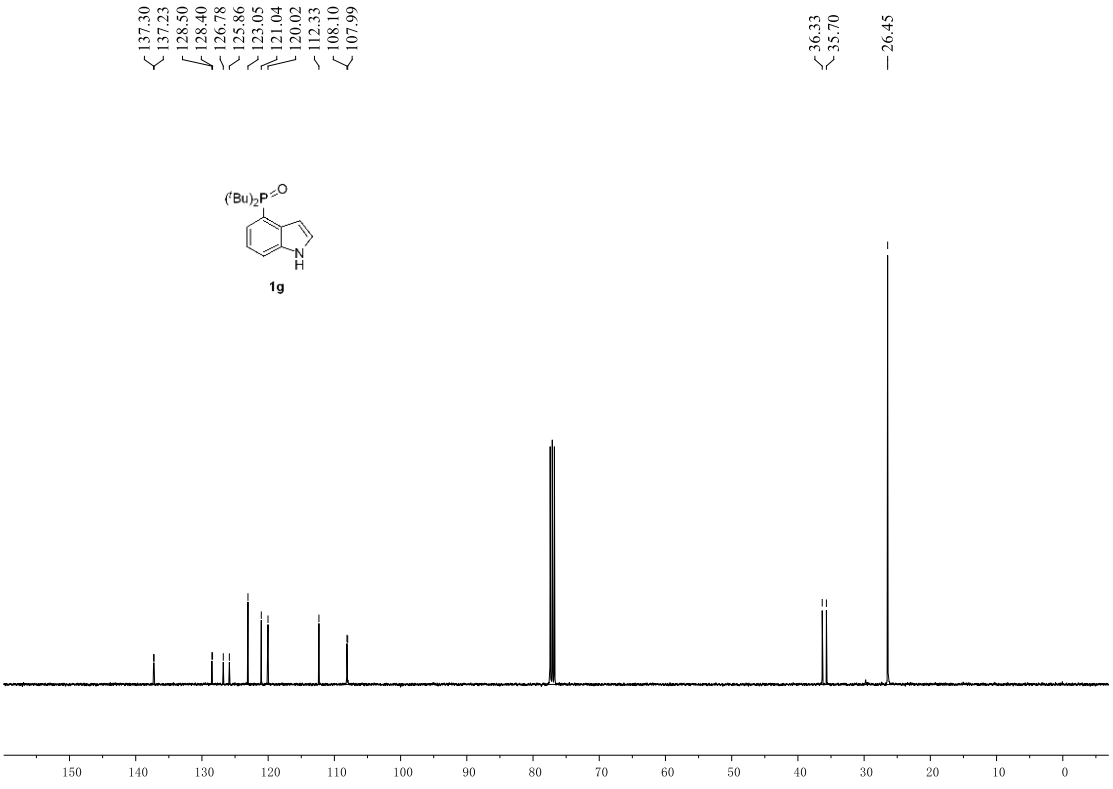
^{1}H NMR spectrum for **1g**



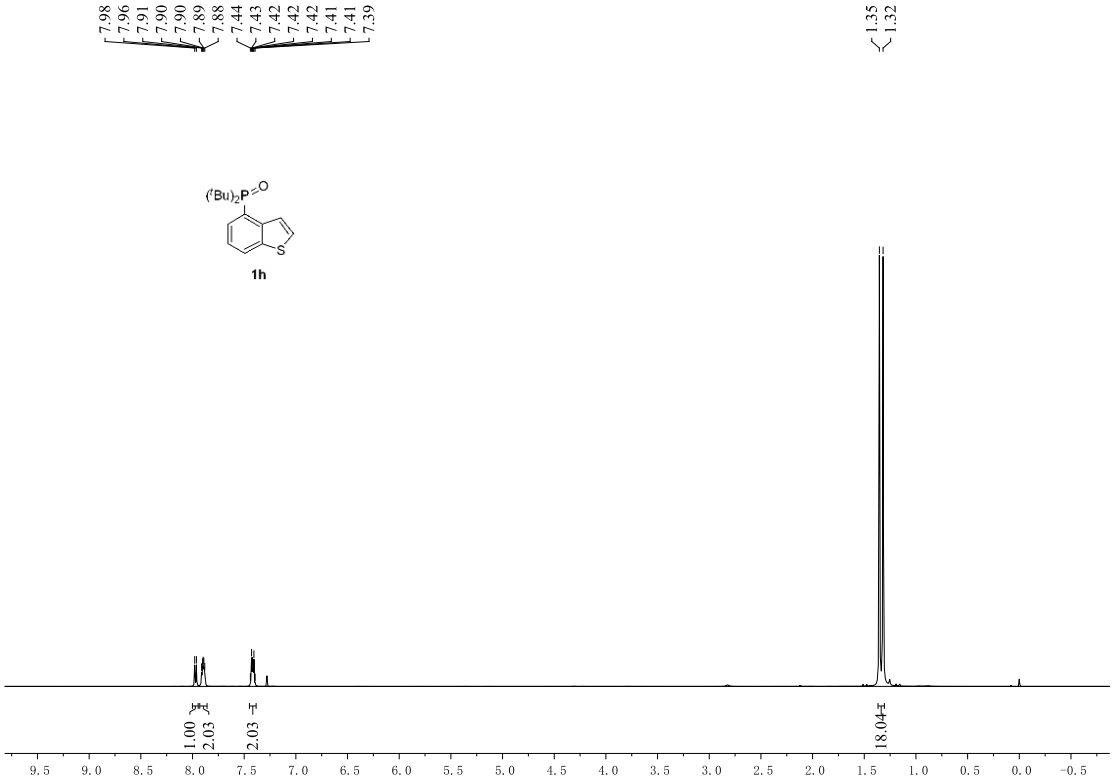
^{31}P NMR spectrum for **1g**



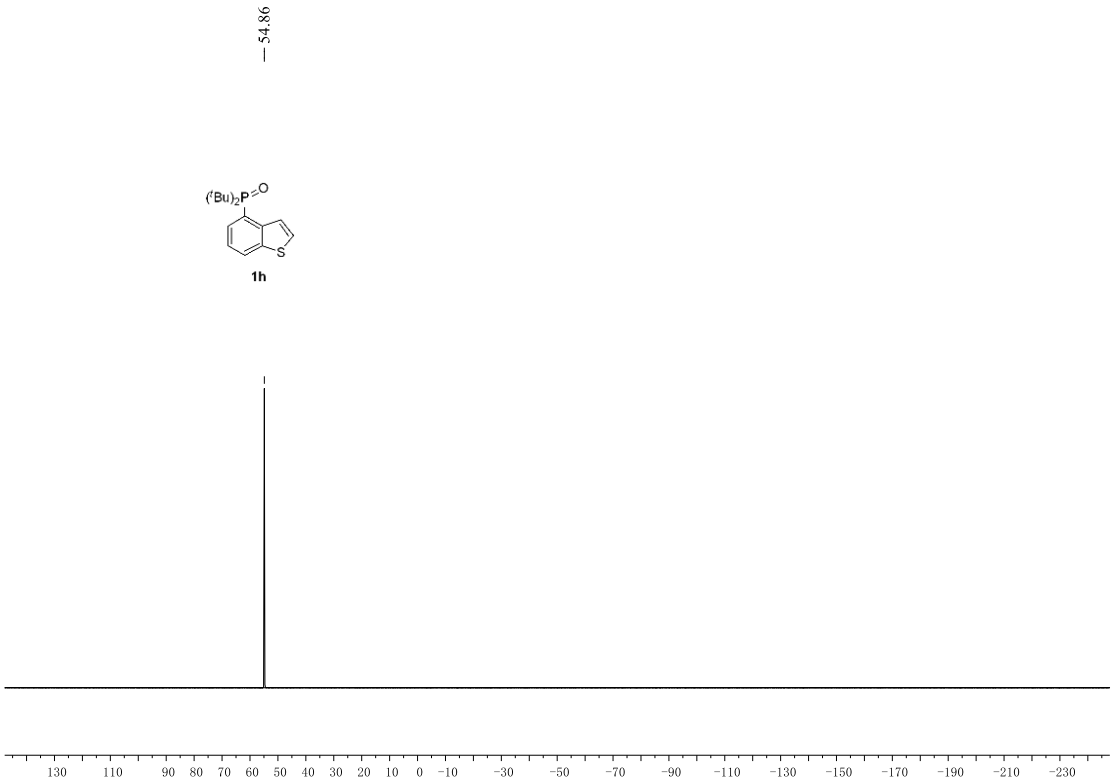
^{13}C NMR spectrum for **1g**



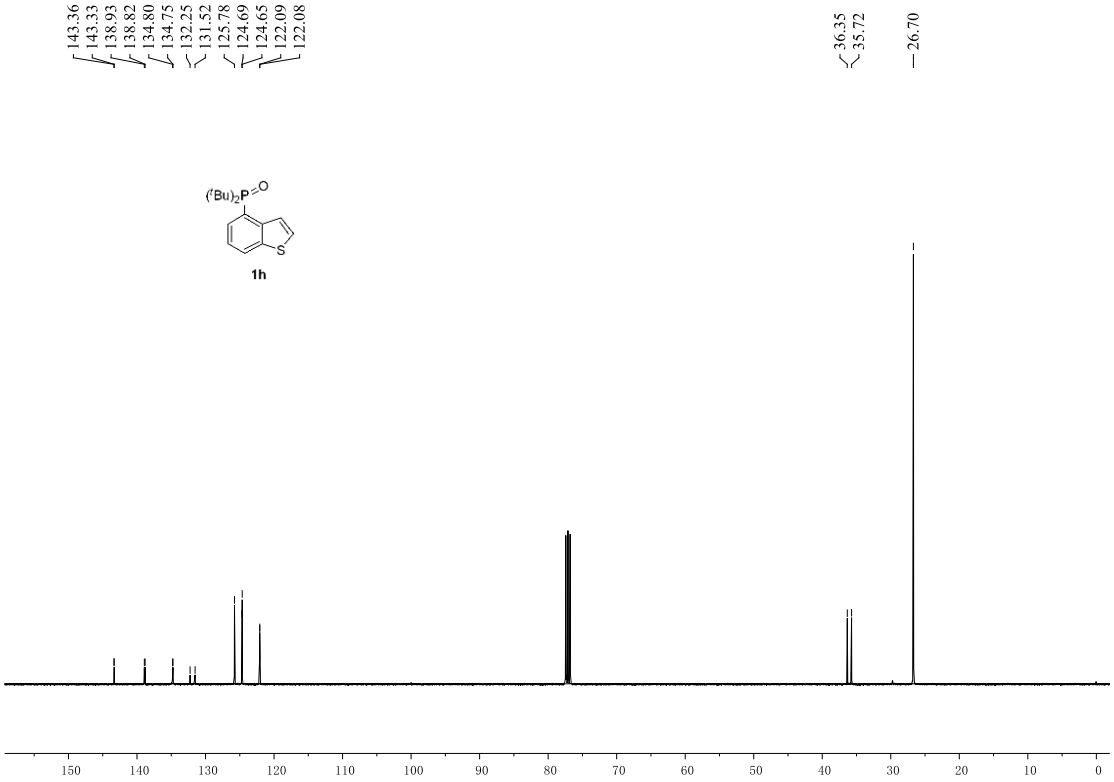
^{1}H NMR spectrum for **1h**



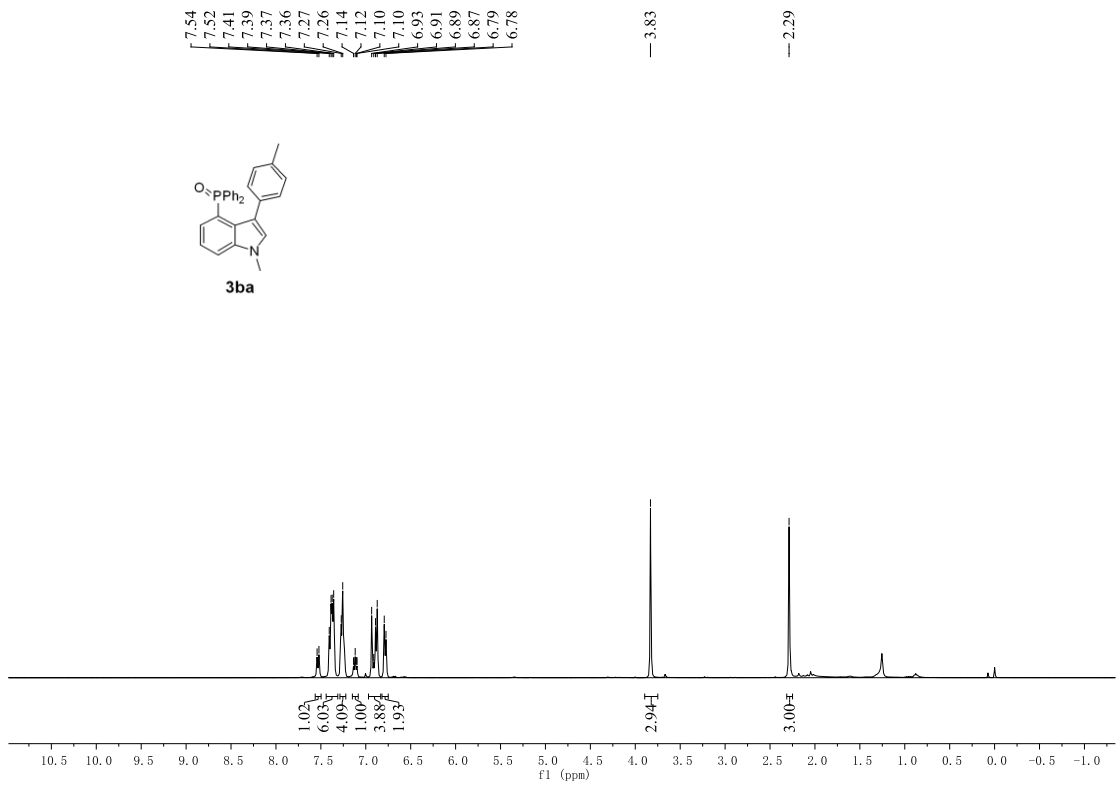
^{31}P NMR spectrum for **1h**



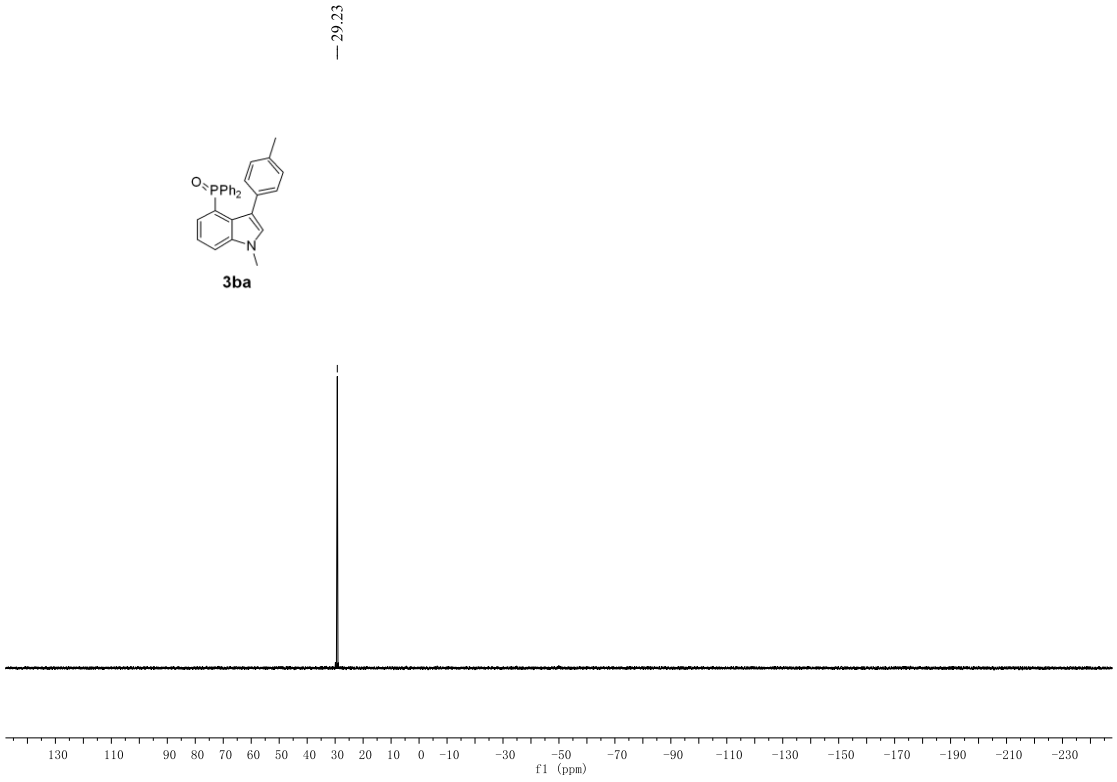
^{13}C NMR spectrum for **1h**



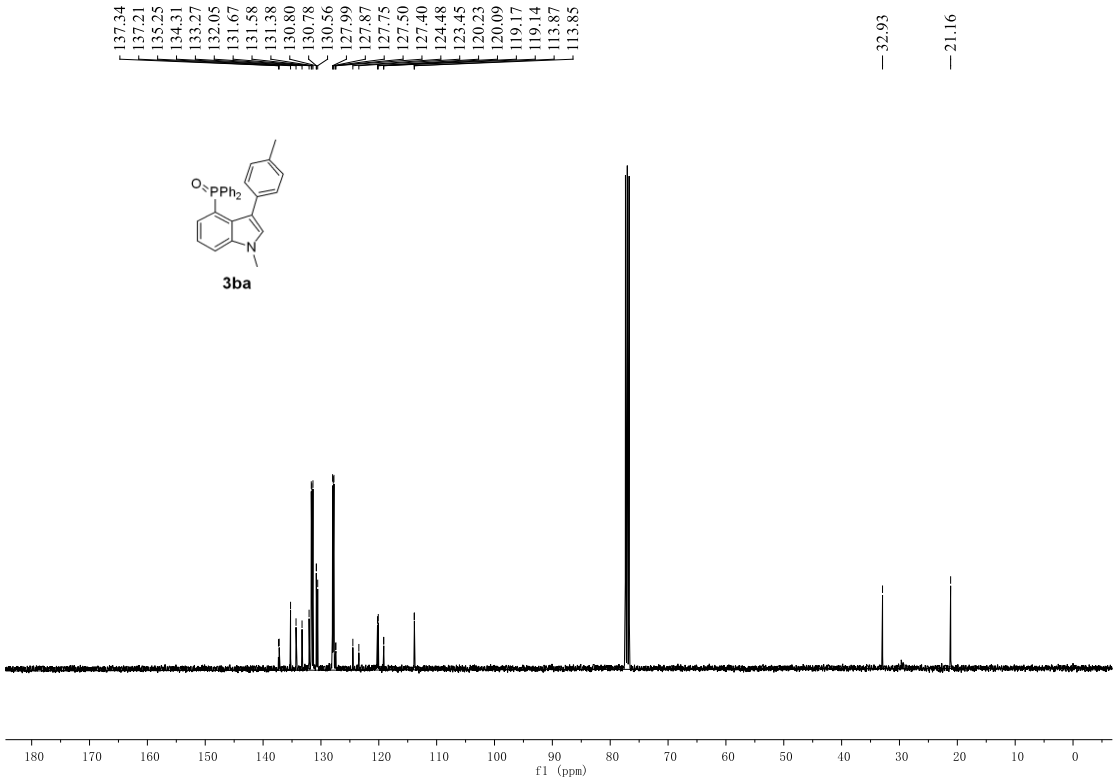
^{1}H NMR spectrum for **3ba**



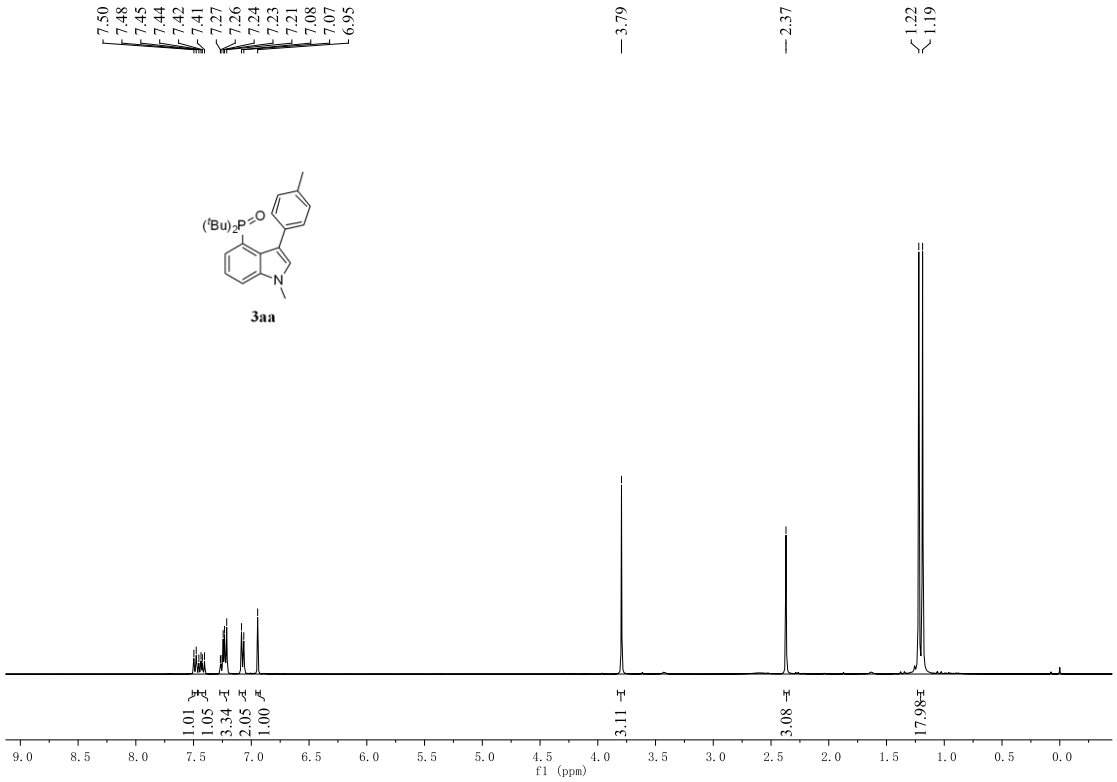
^{31}P NMR spectrum for **3ba**



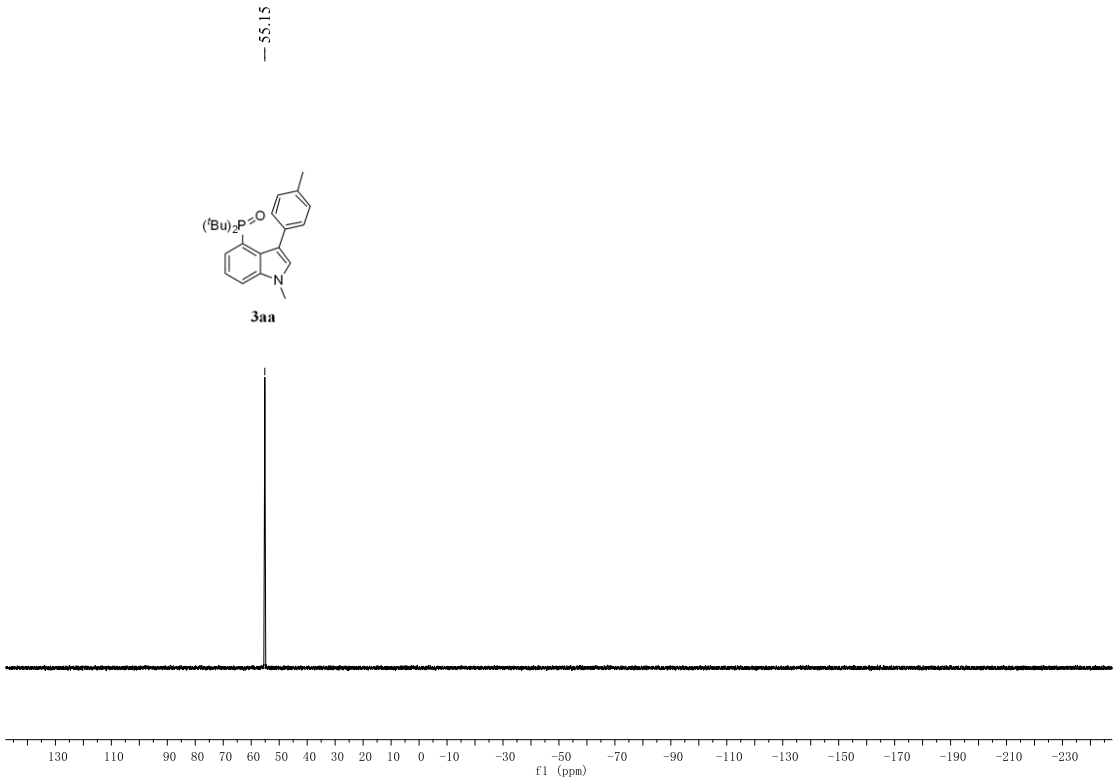
^{13}C NMR spectrum for **3ba**



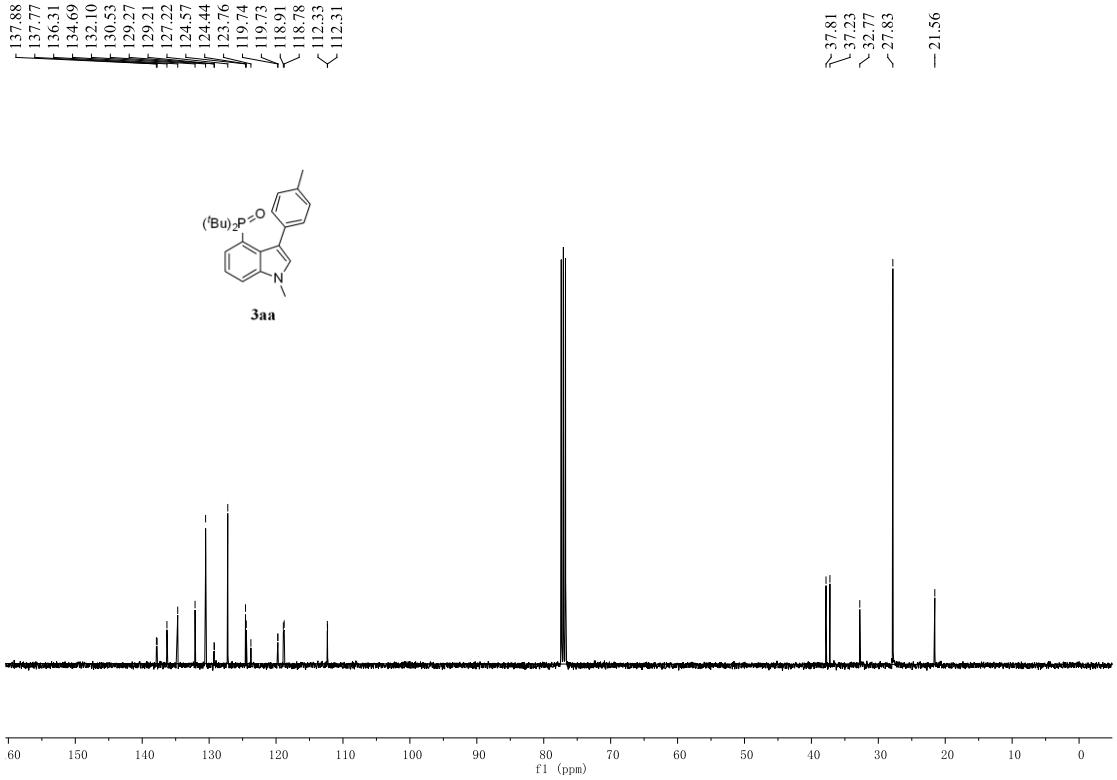
^{1}H NMR spectrum for **3aa**



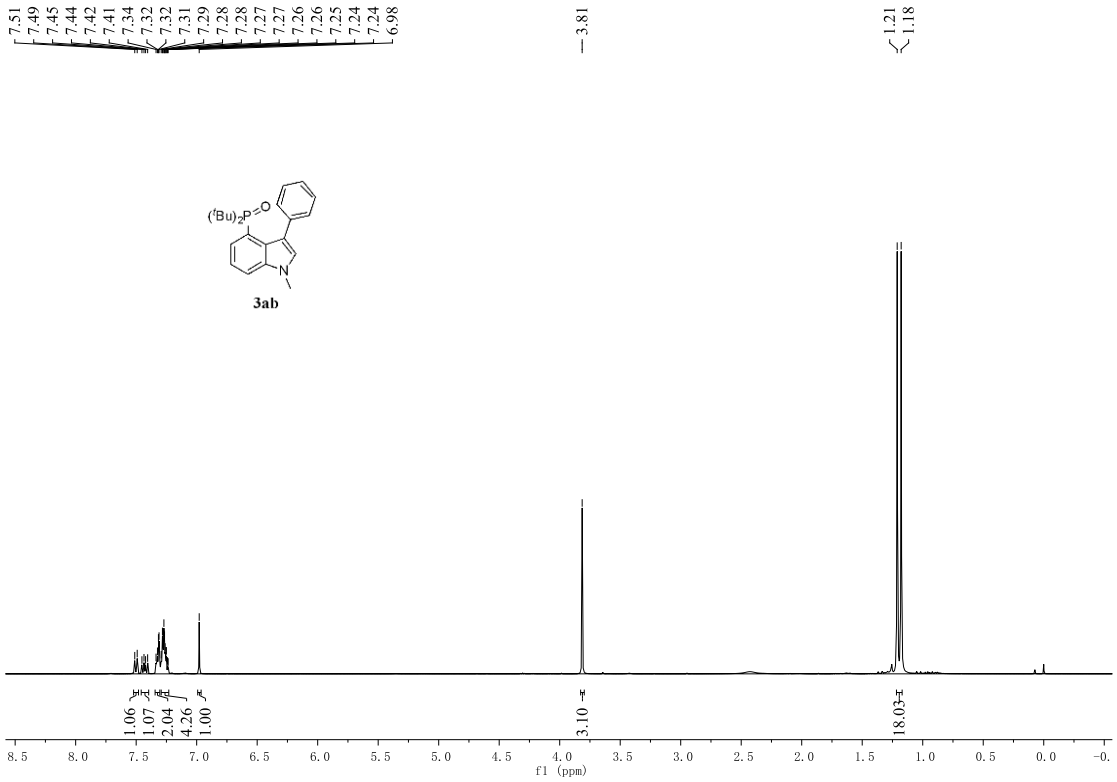
^{31}P NMR spectrum for **3aa**



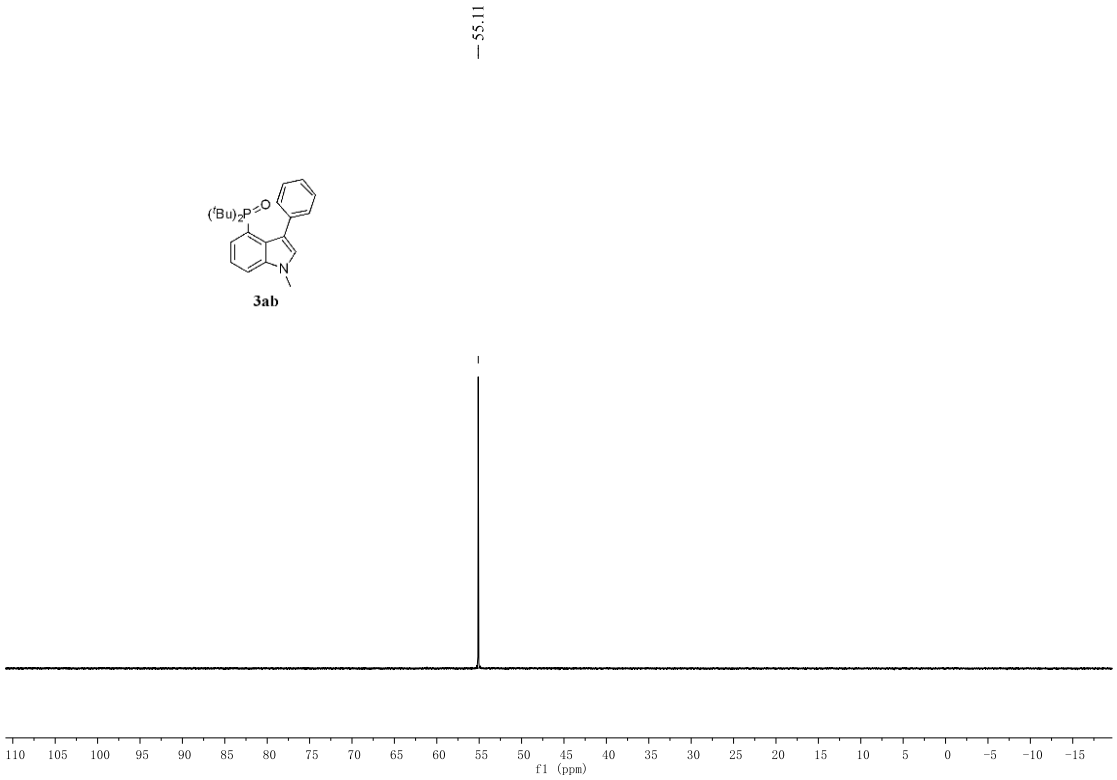
^{13}C NMR spectrum for **3aa**



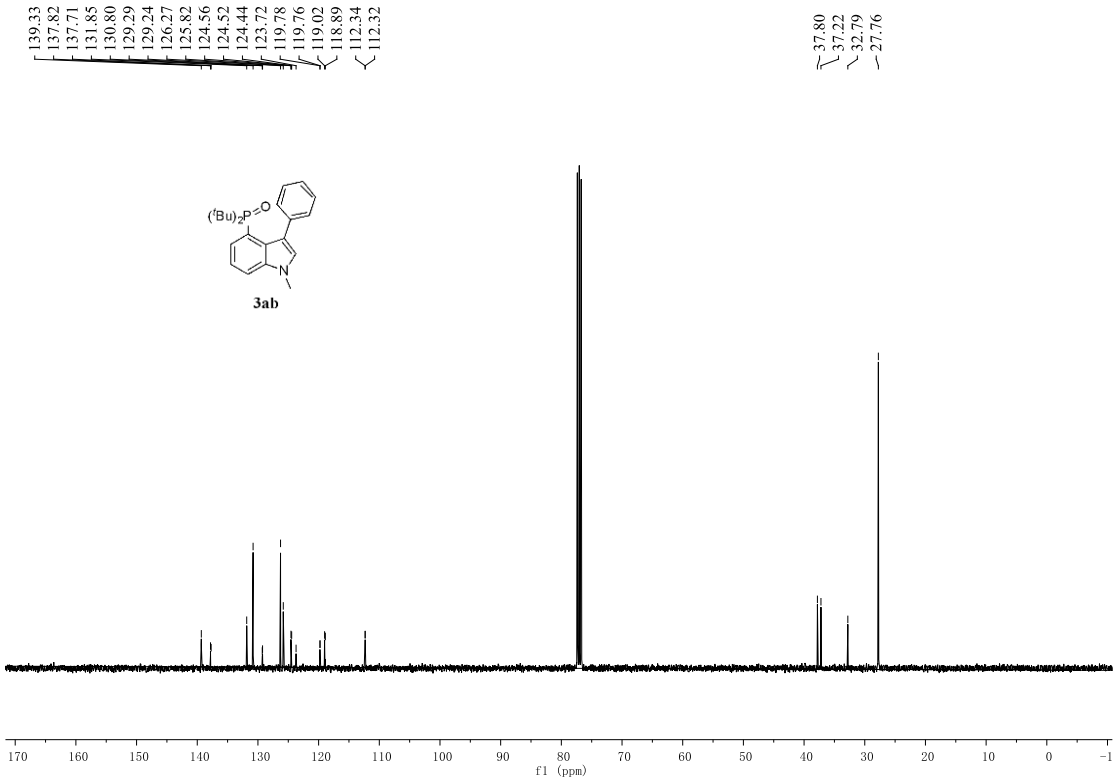
^{1}H NMR spectrum for **3ab**



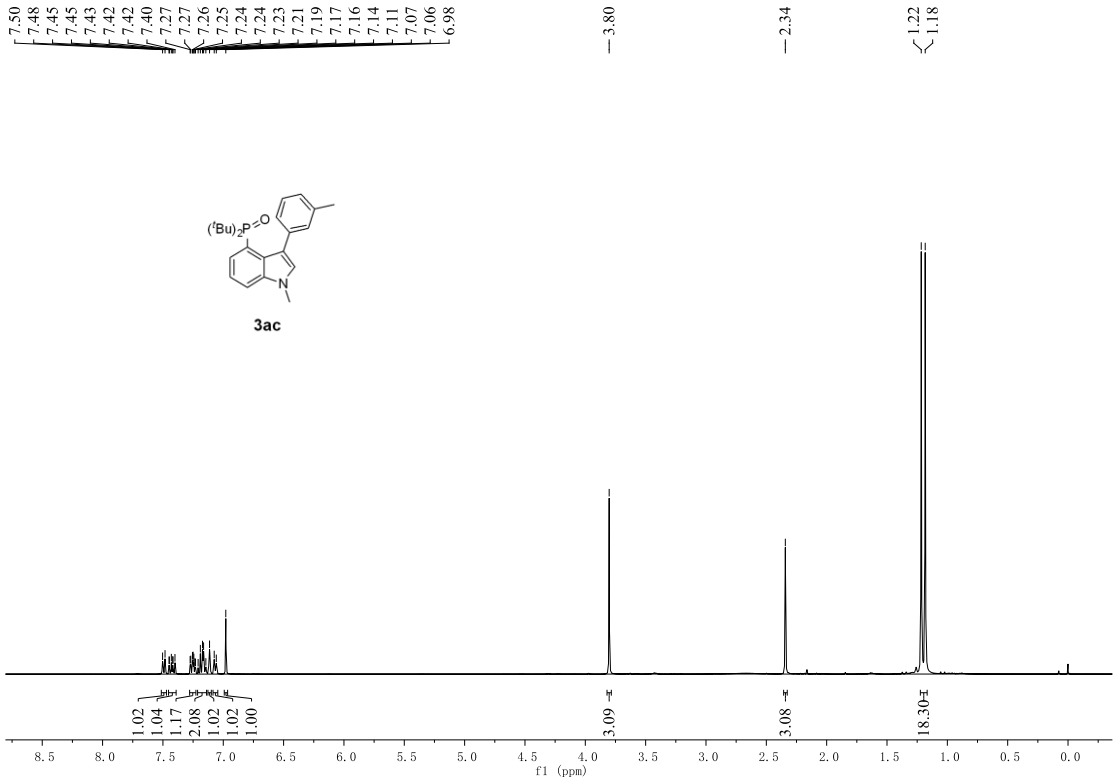
^{31}P NMR spectrum for **3ab**



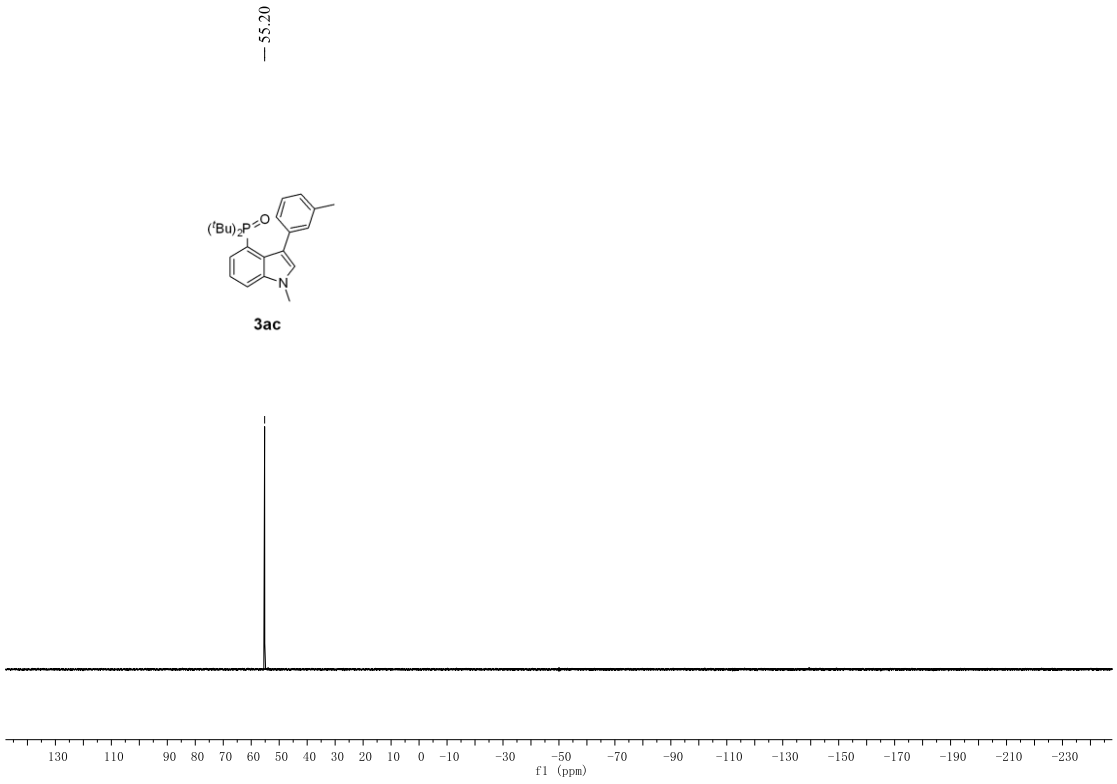
^{13}C NMR spectrum for **3ab**



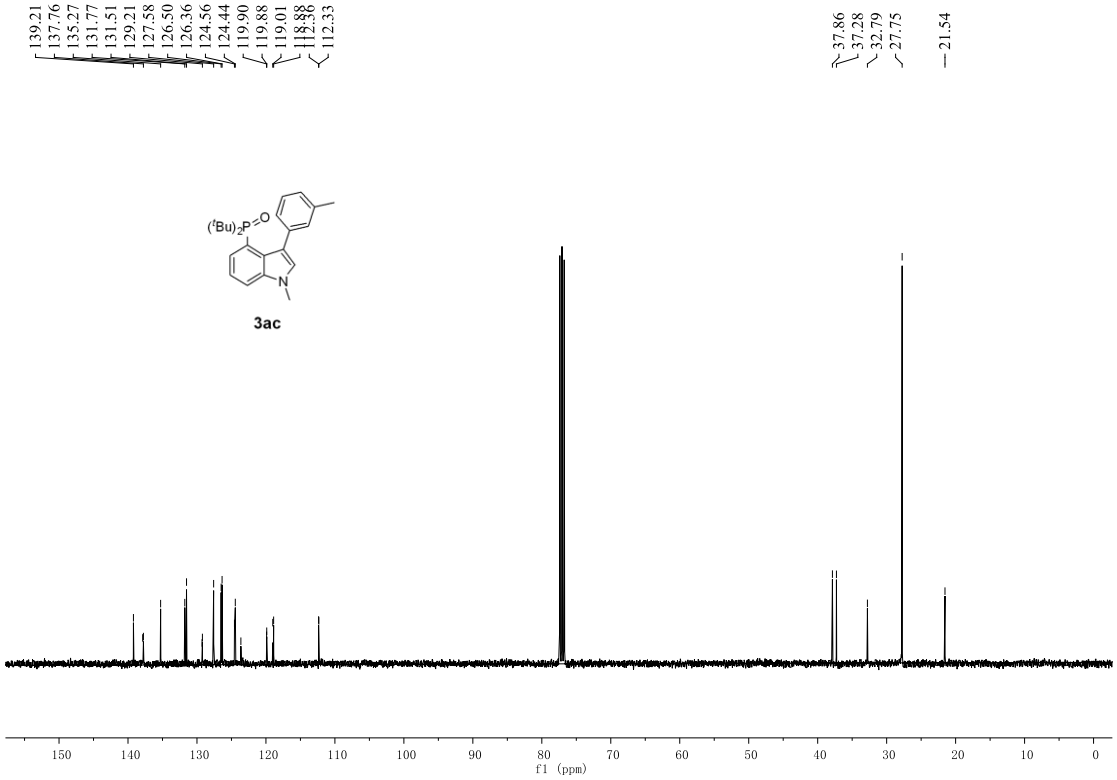
^{1}H NMR spectrum for **3ac**



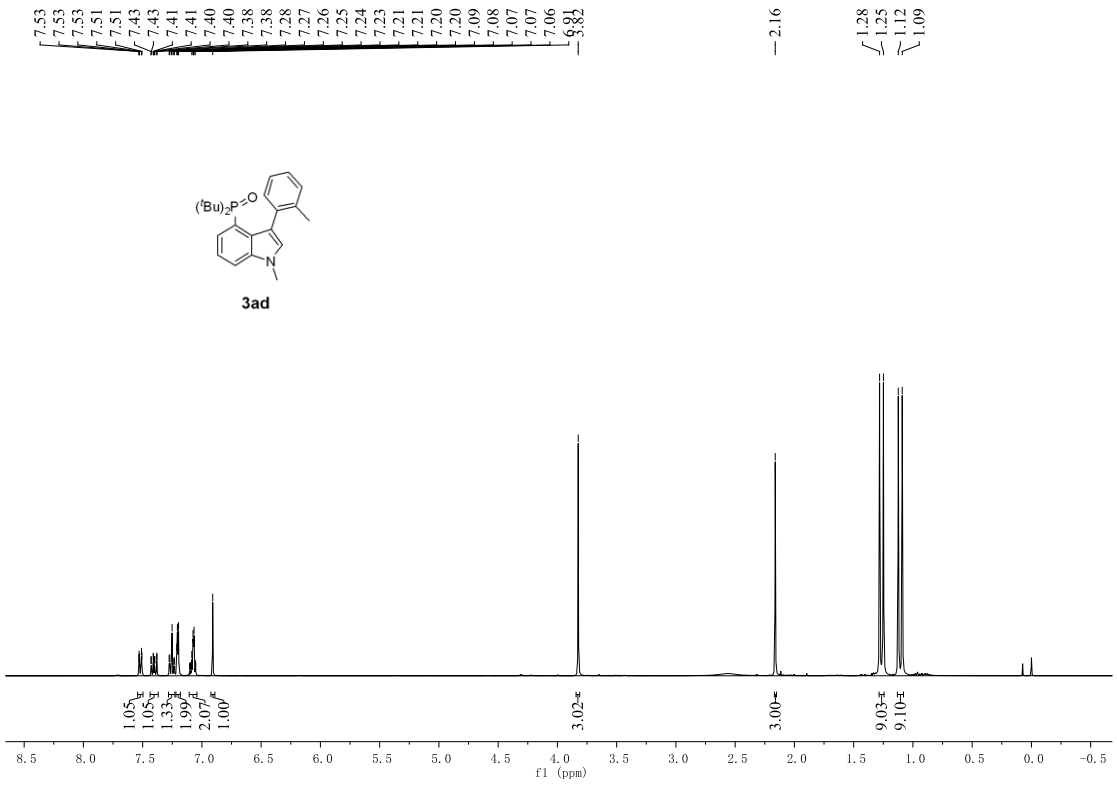
^{31}P NMR spectrum for **3ac**



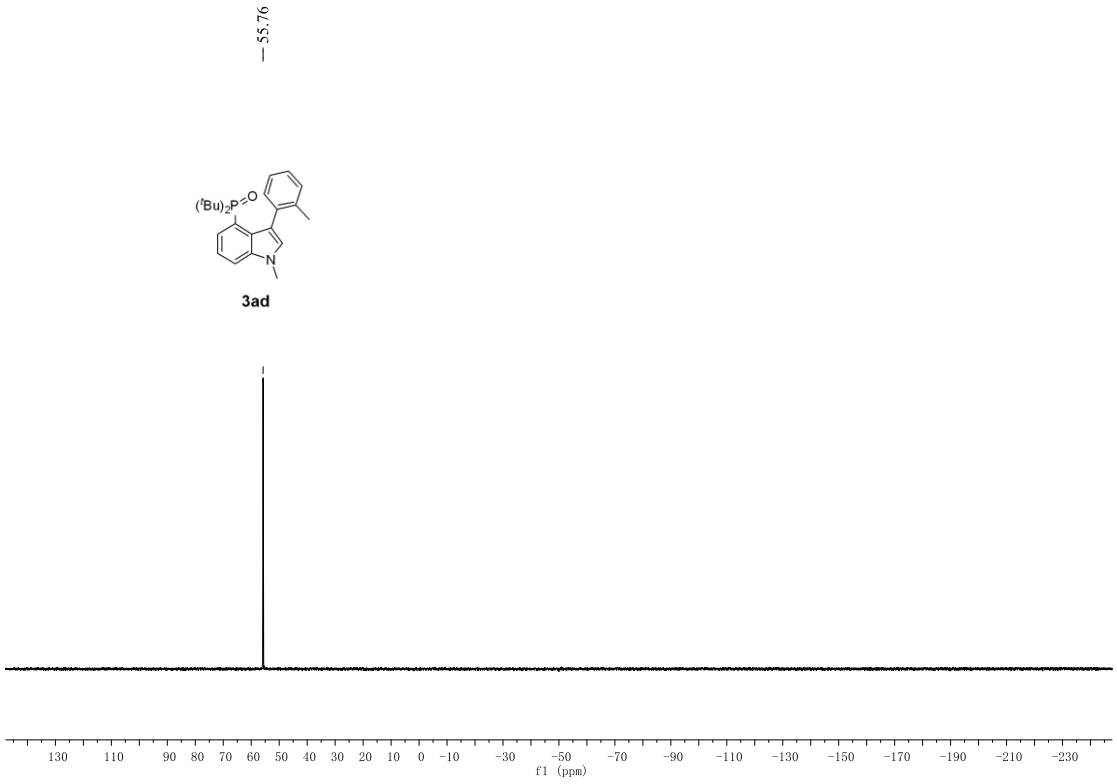
^{13}C NMR spectrum for **3ac**



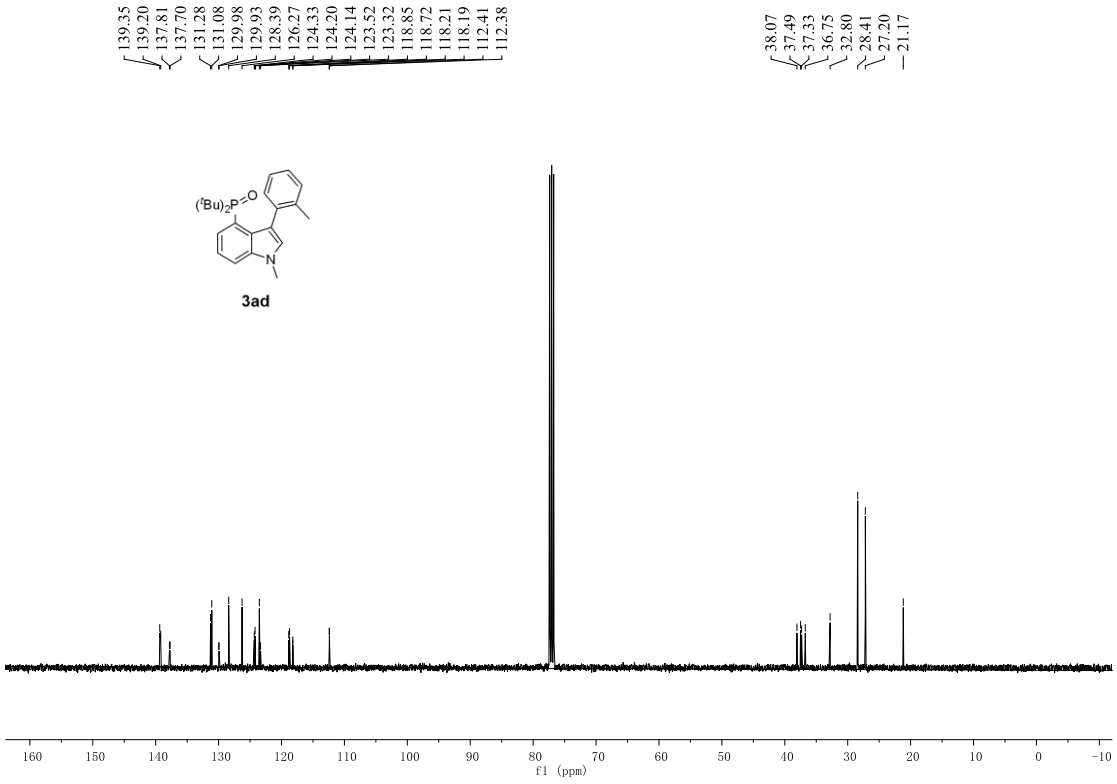
^{1}H NMR spectrum for **3ad**



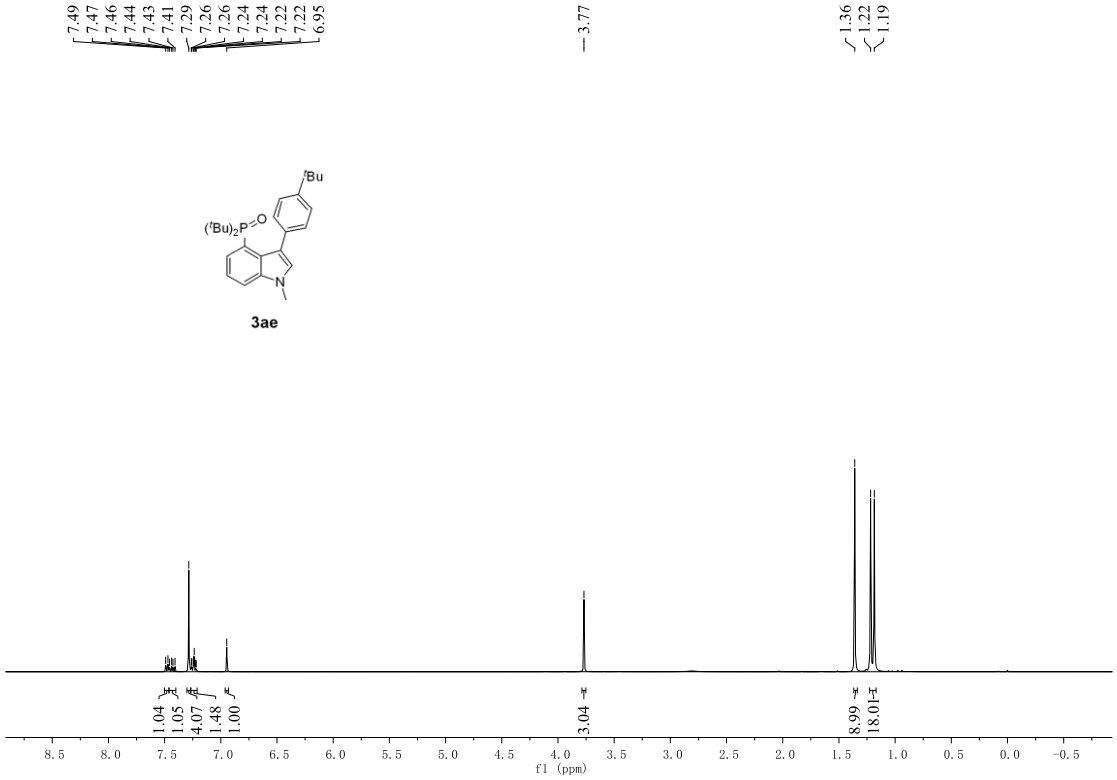
^{31}P NMR spectrum for **3ad**



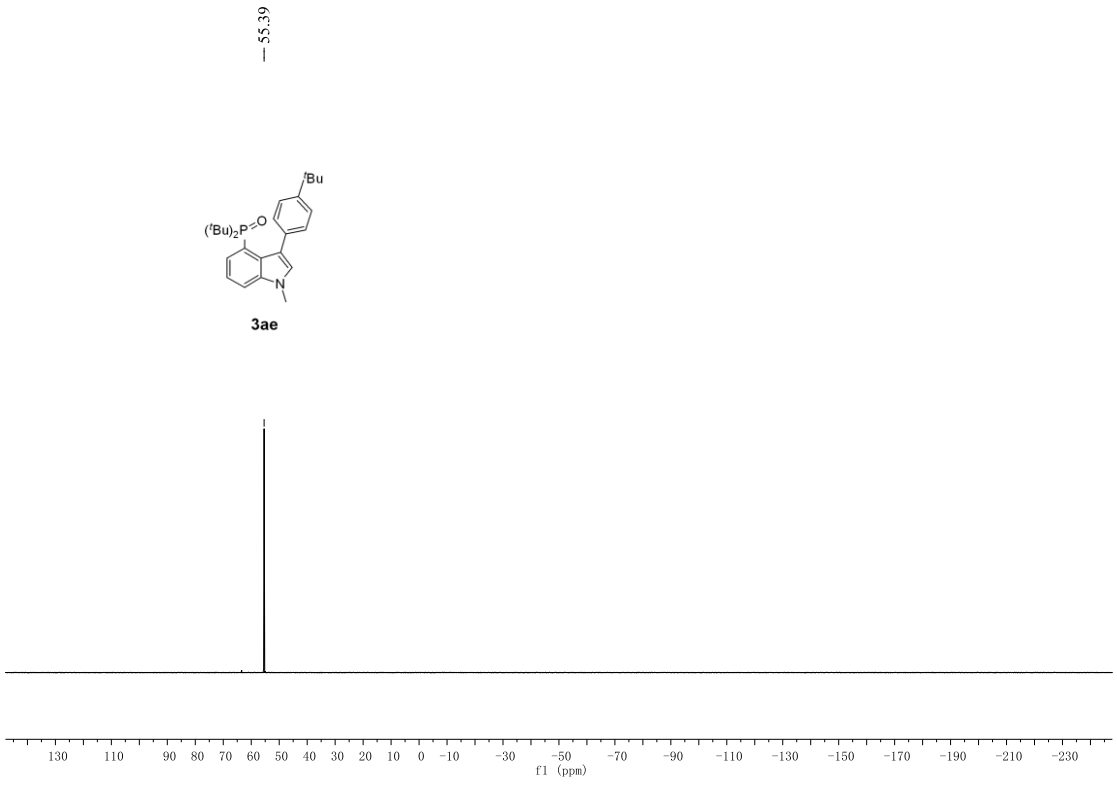
^{13}C NMR spectrum for **3ad**



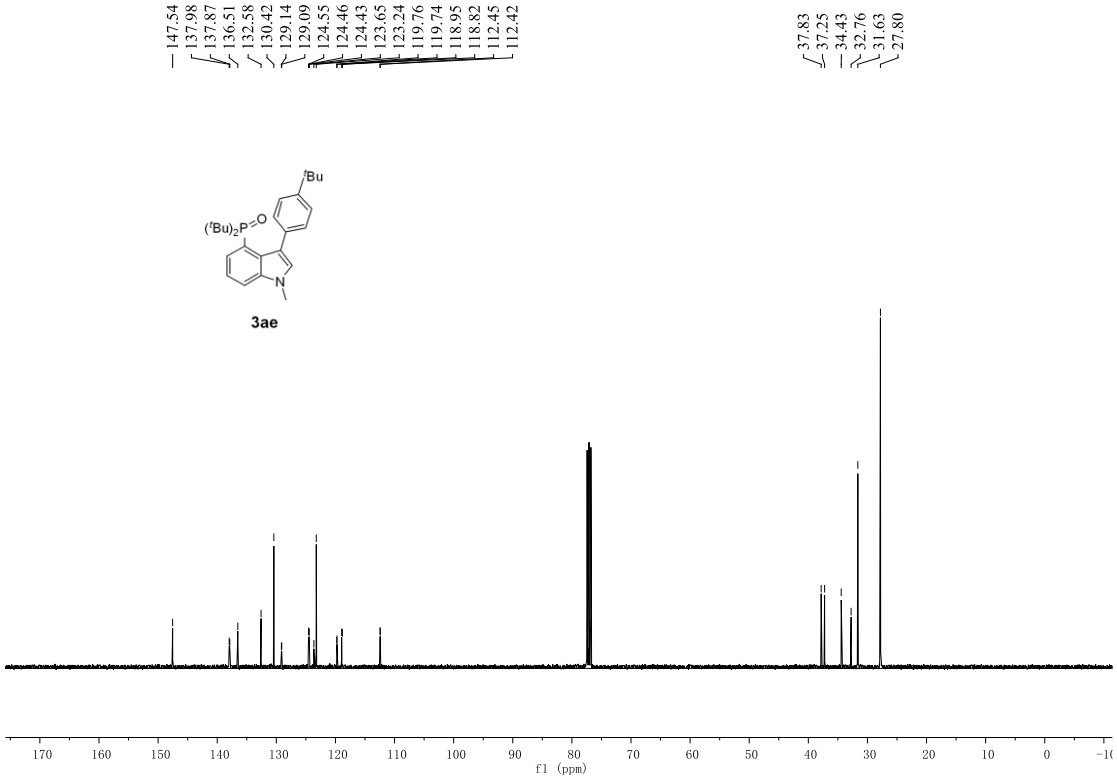
^{1}H NMR spectrum for **3ae**



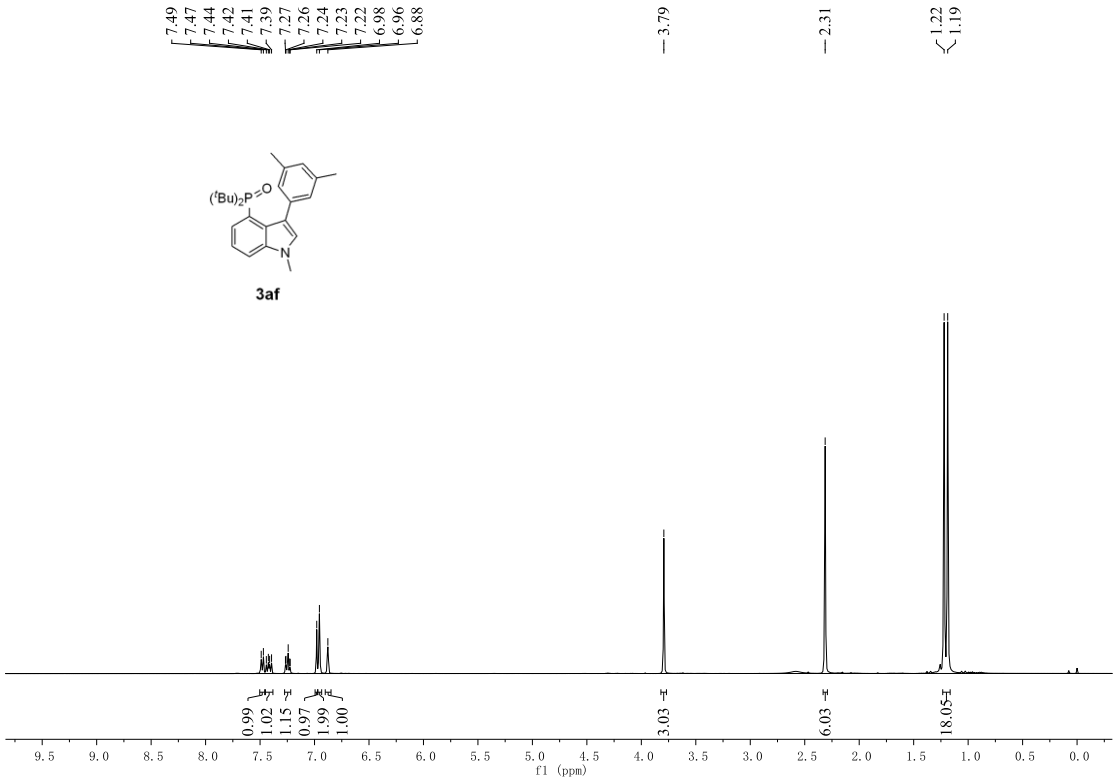
^{31}P NMR spectrum for **3ae**



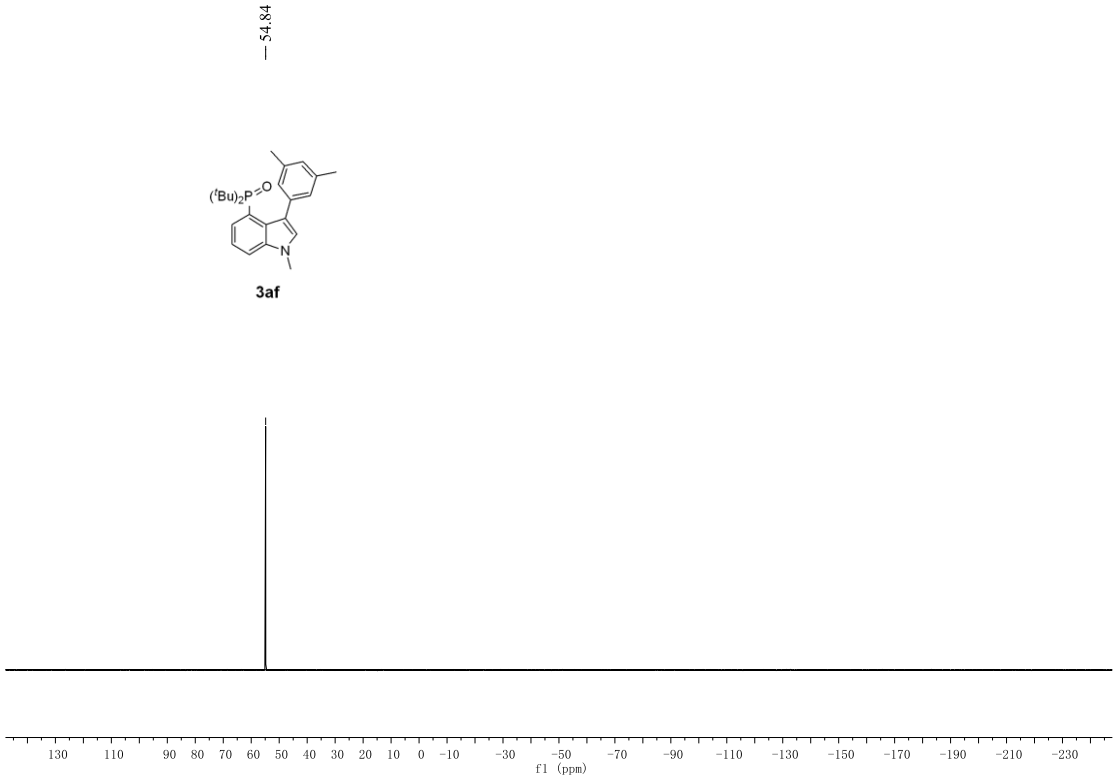
^{13}C NMR spectrum for **3ae**



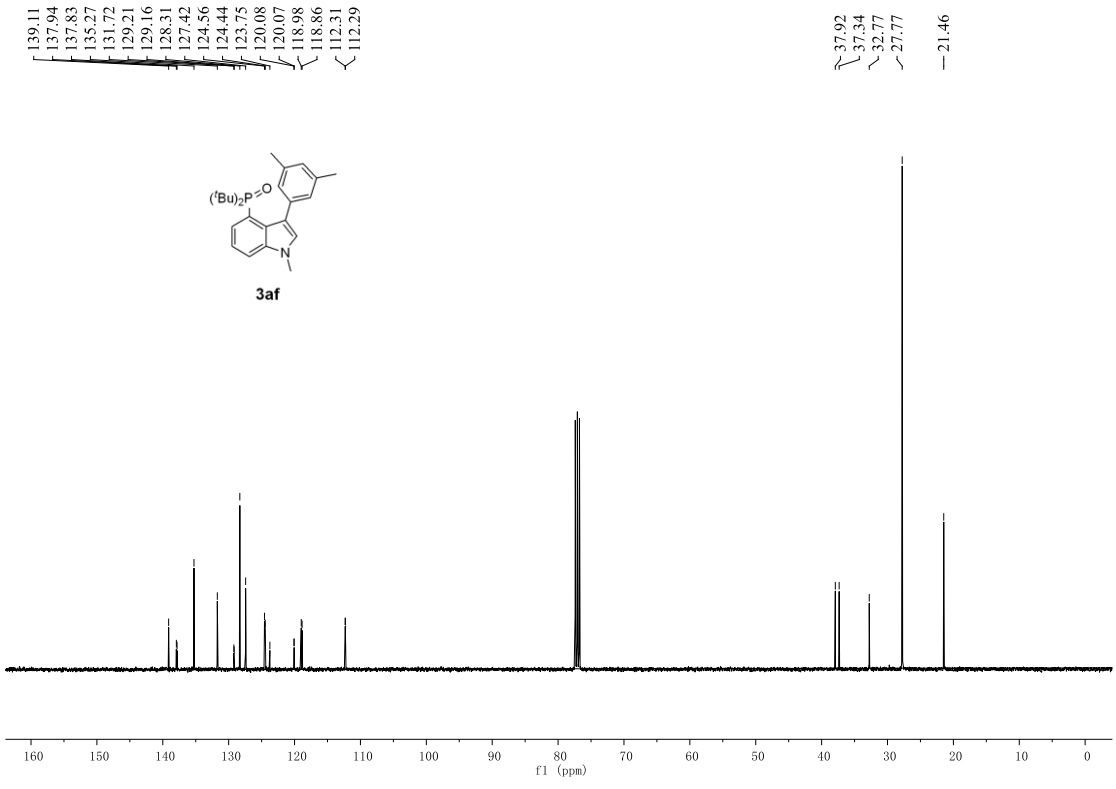
^{1}H NMR spectrum for **3af**



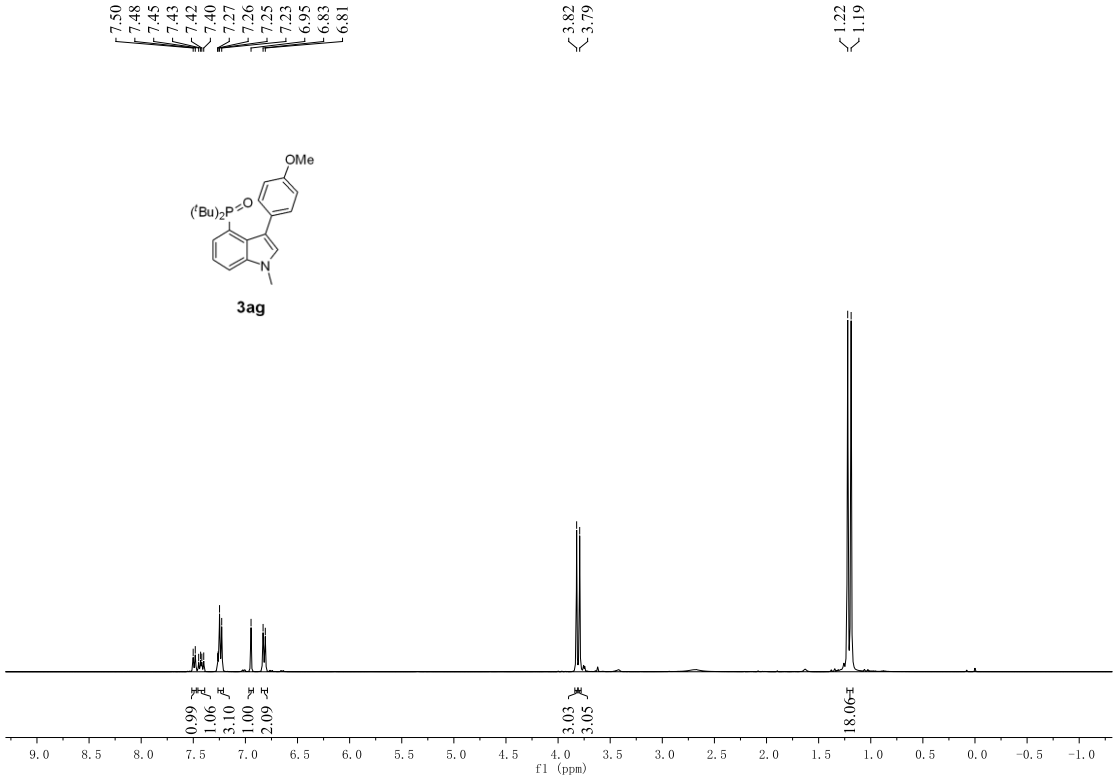
^{31}P NMR spectrum for **3af**



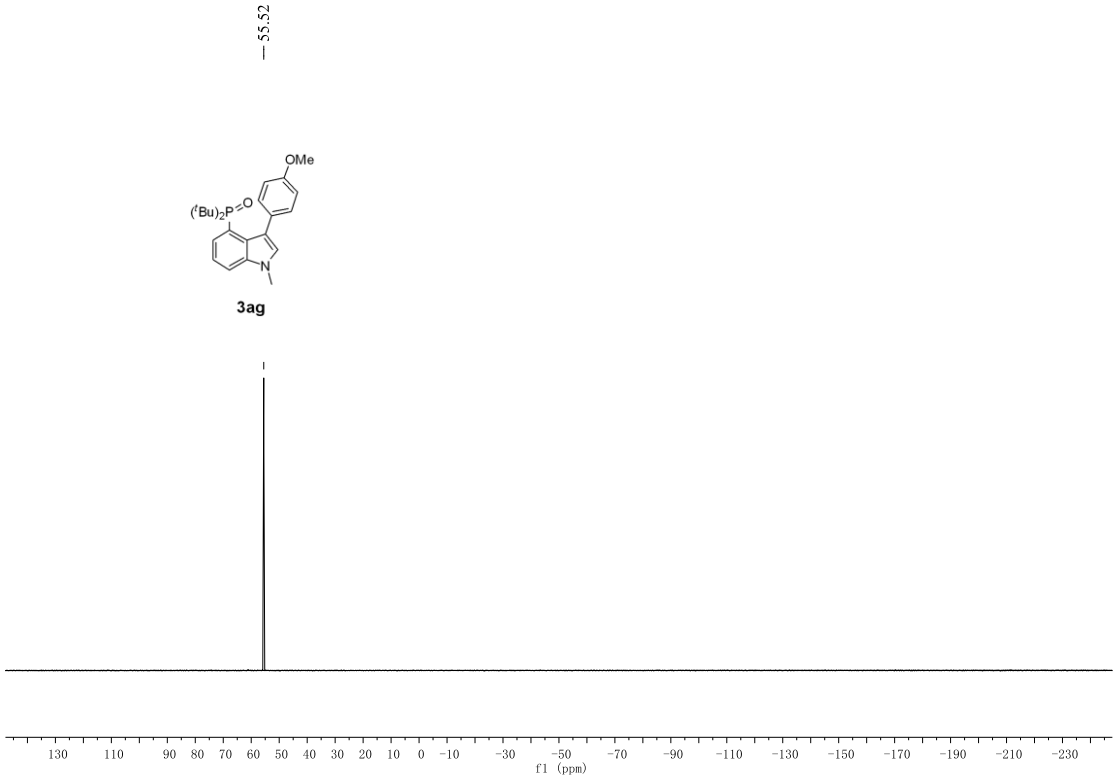
^{13}C NMR spectrum for **3af**



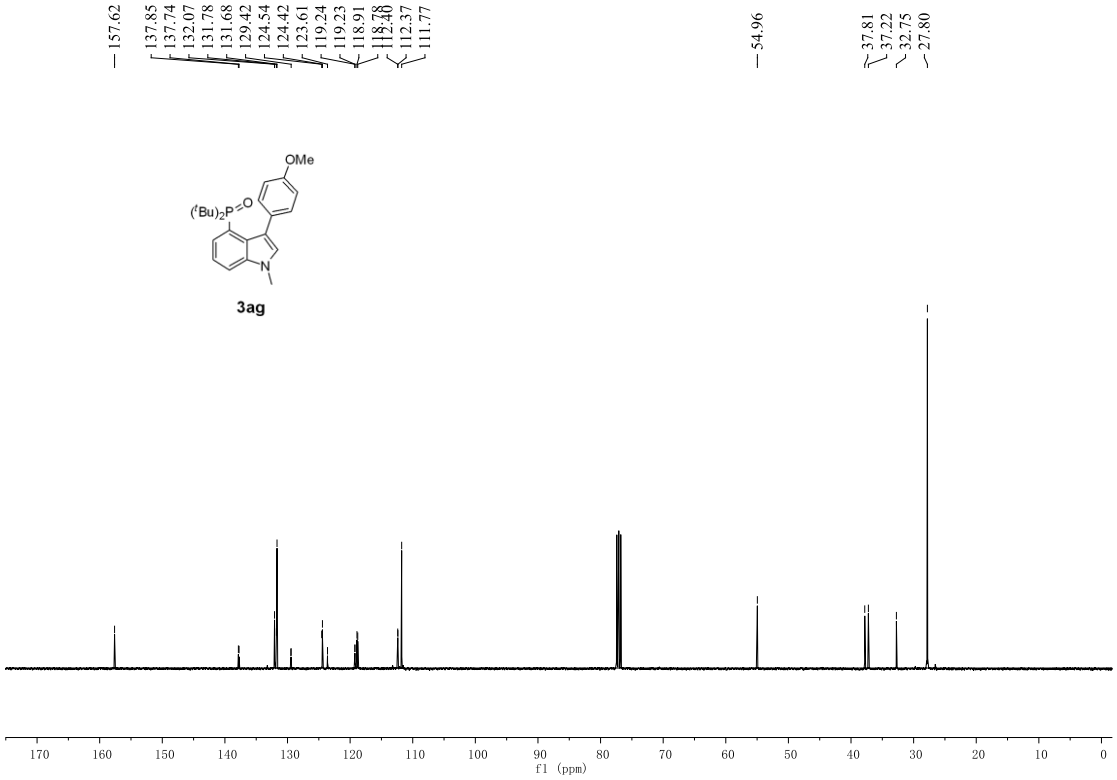
^{1}H NMR spectrum for **3ag**



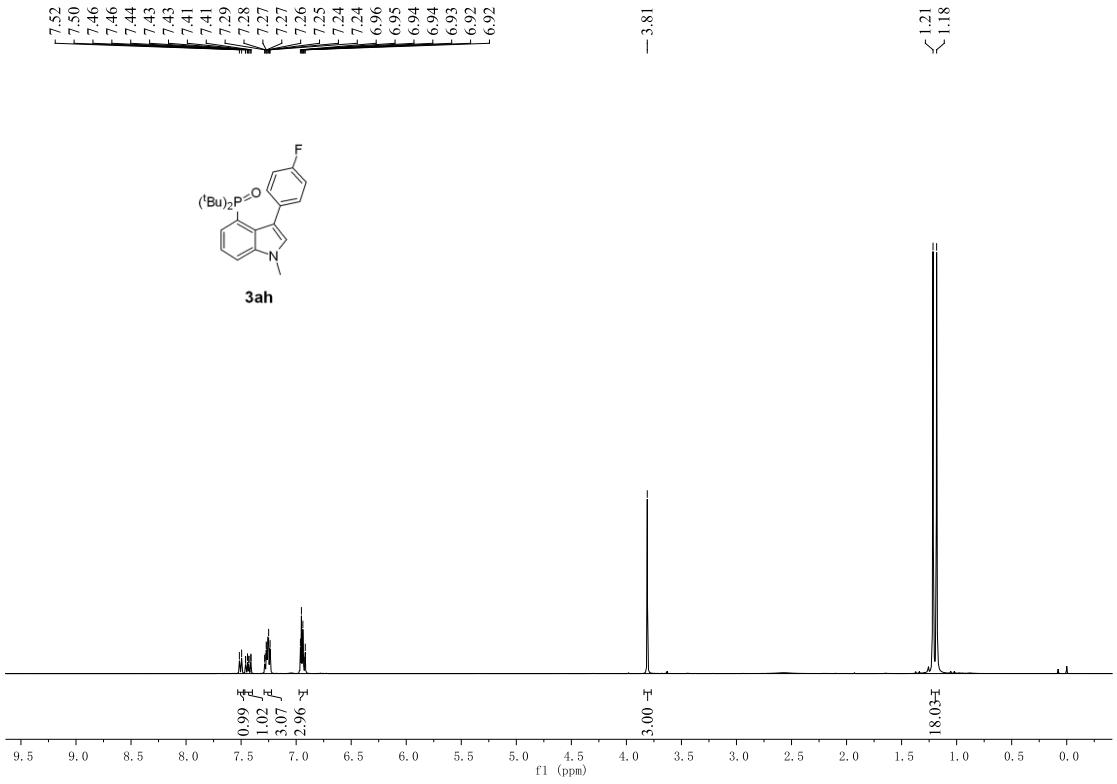
^{31}P NMR spectrum for **3ag**



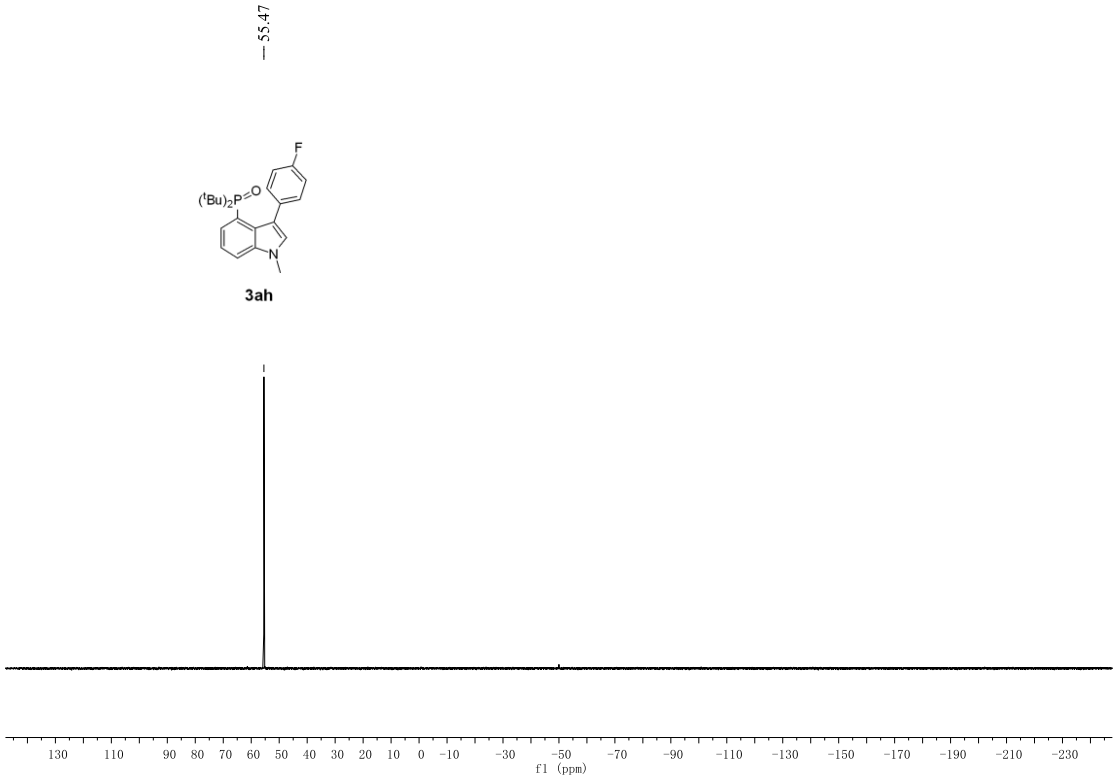
^{13}C NMR spectrum for **3ag**



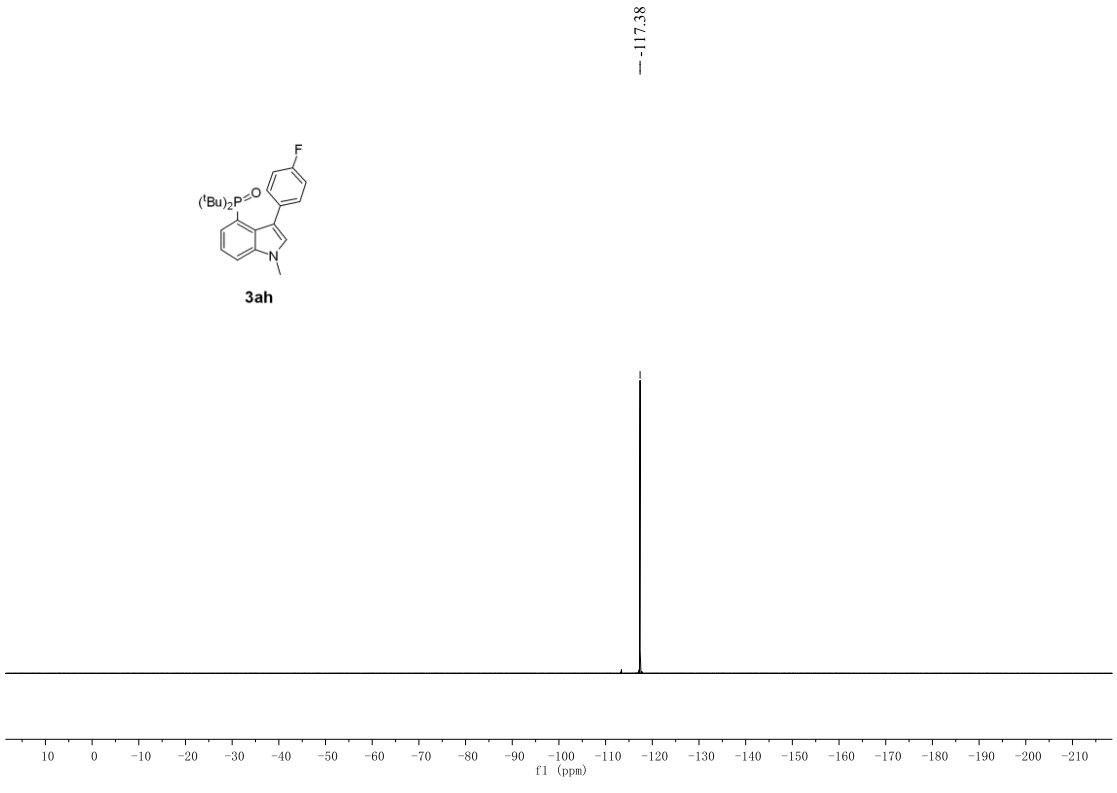
^{1}H NMR spectrum for **3ah**



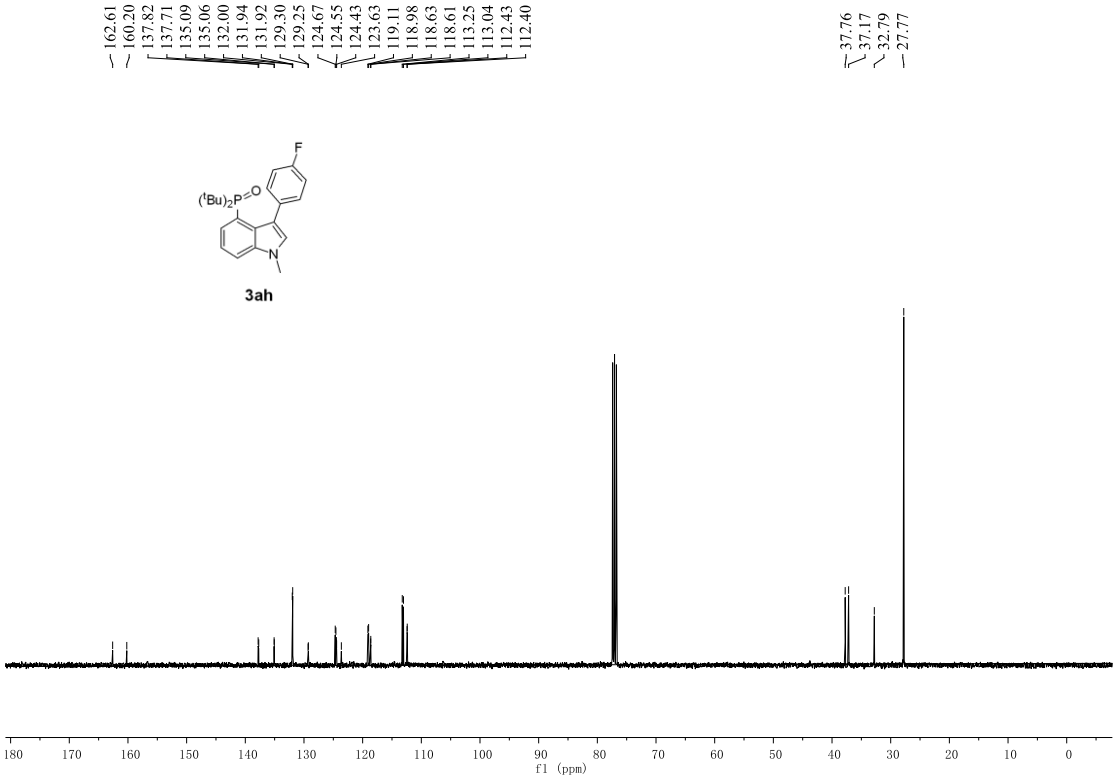
^{31}P NMR spectrum for **3ah**



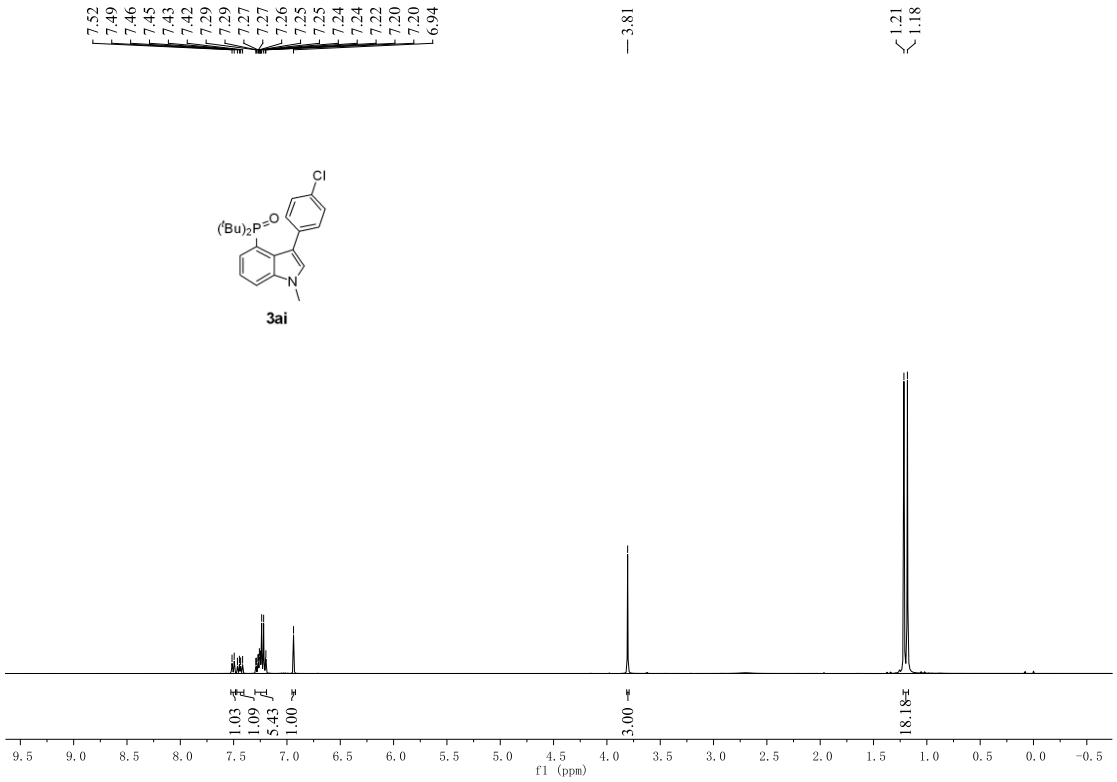
^{19}F NMR spectrum for **3ah**



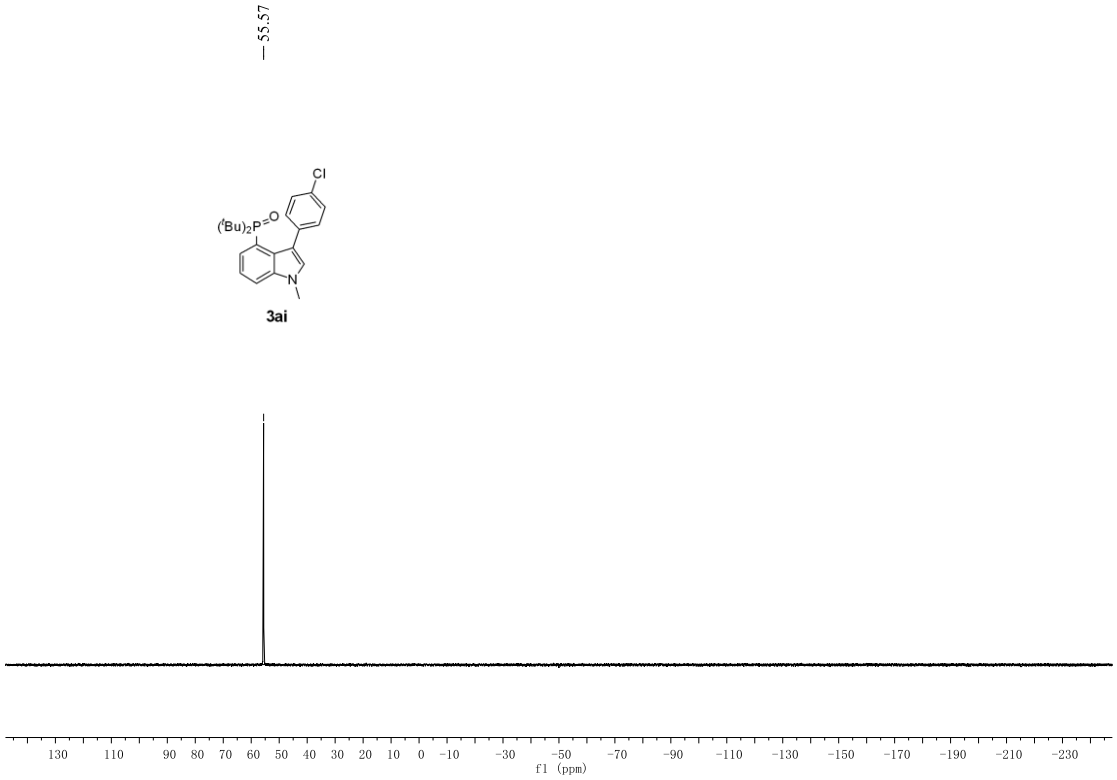
^{13}C NMR spectrum for **3ah**



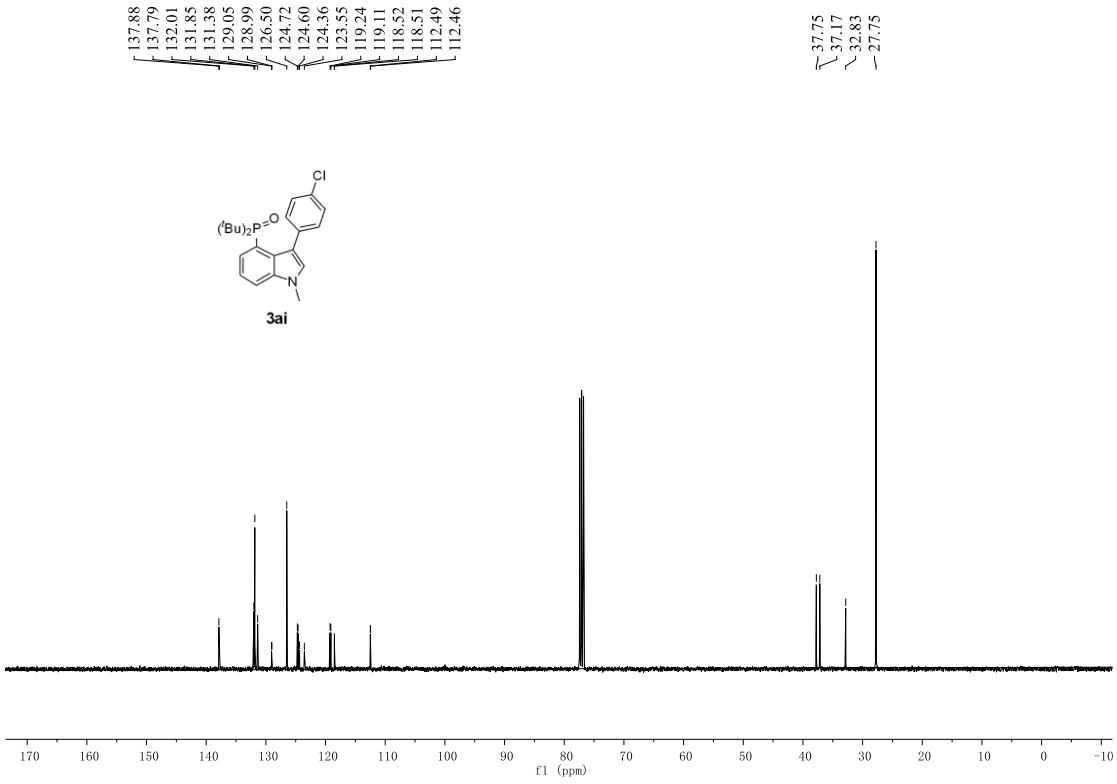
^{1}H NMR spectrum for **3ai**



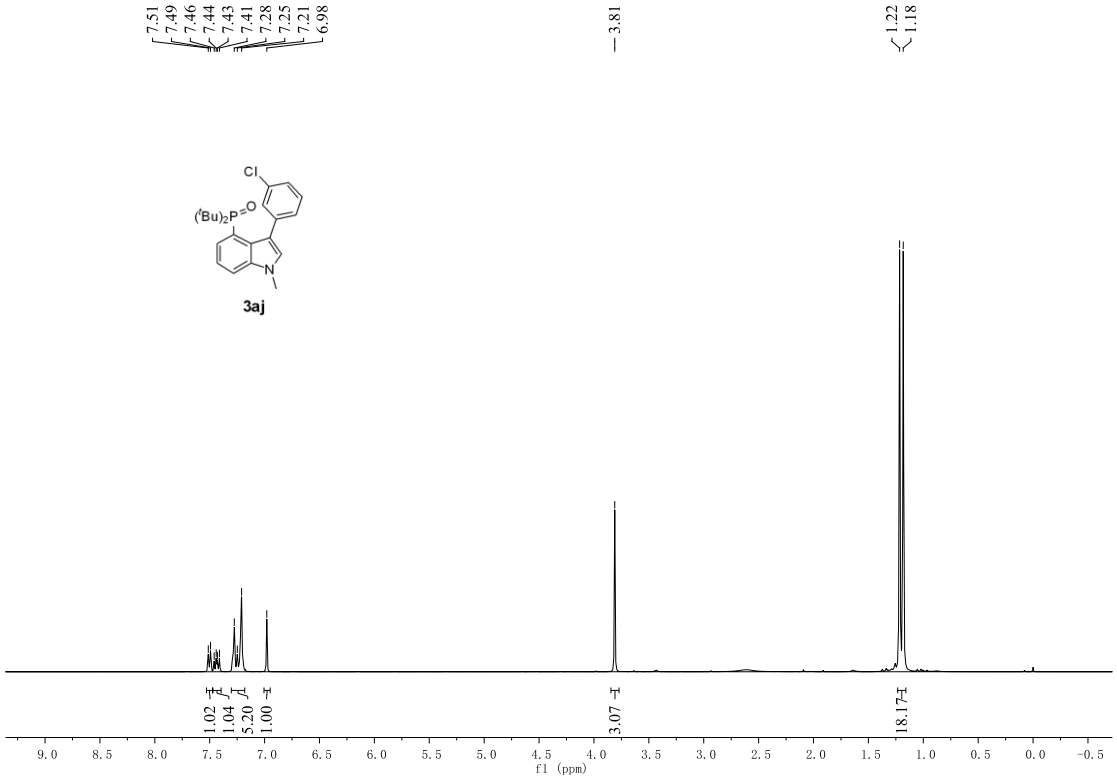
^{31}P NMR spectrum for **3ai**



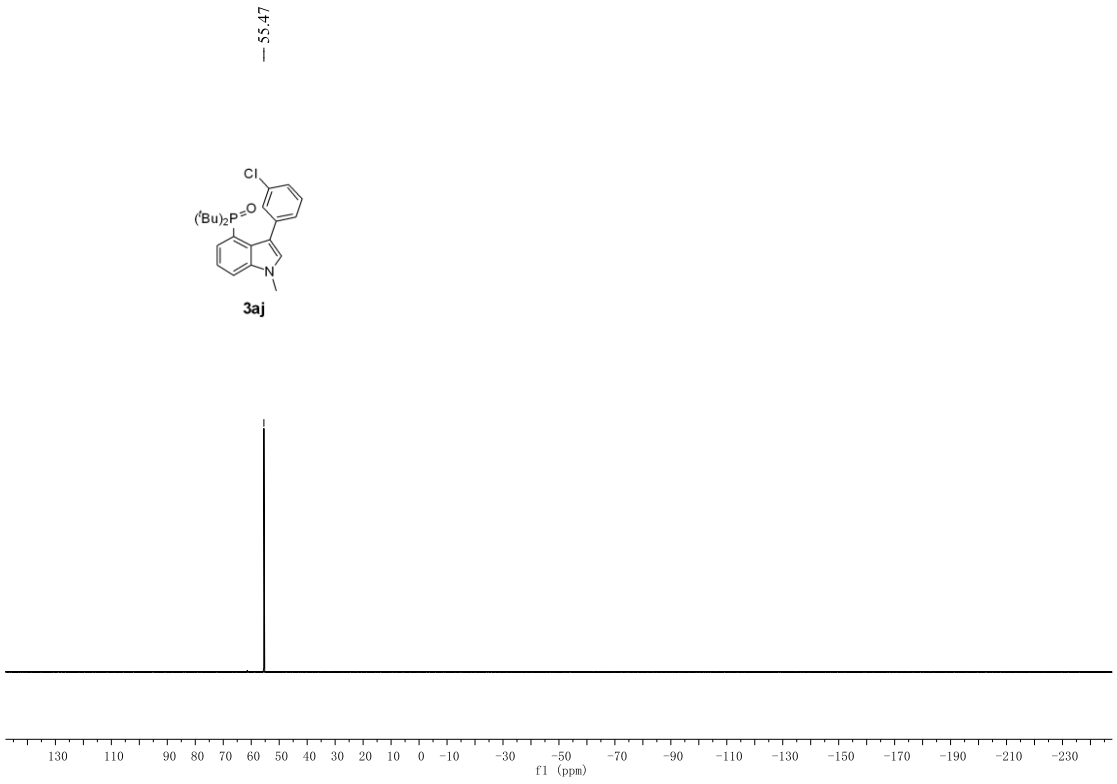
^{13}C NMR spectrum for **3ai**



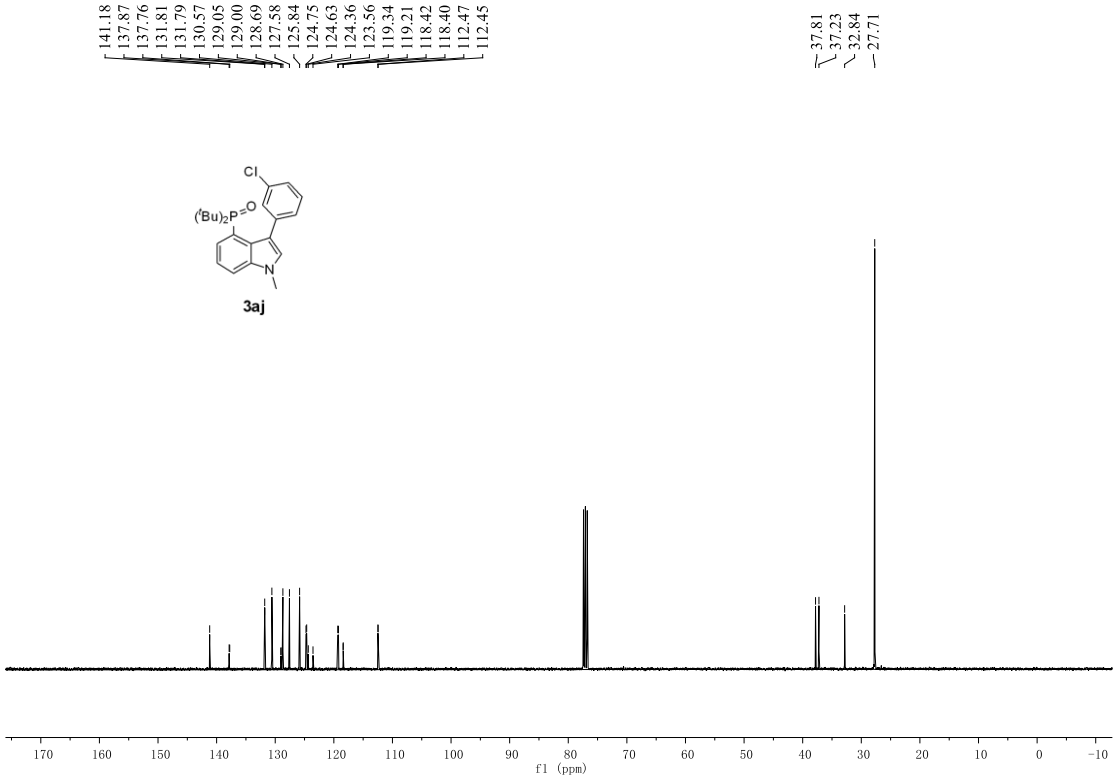
^{1}H NMR spectrum for **3aj**



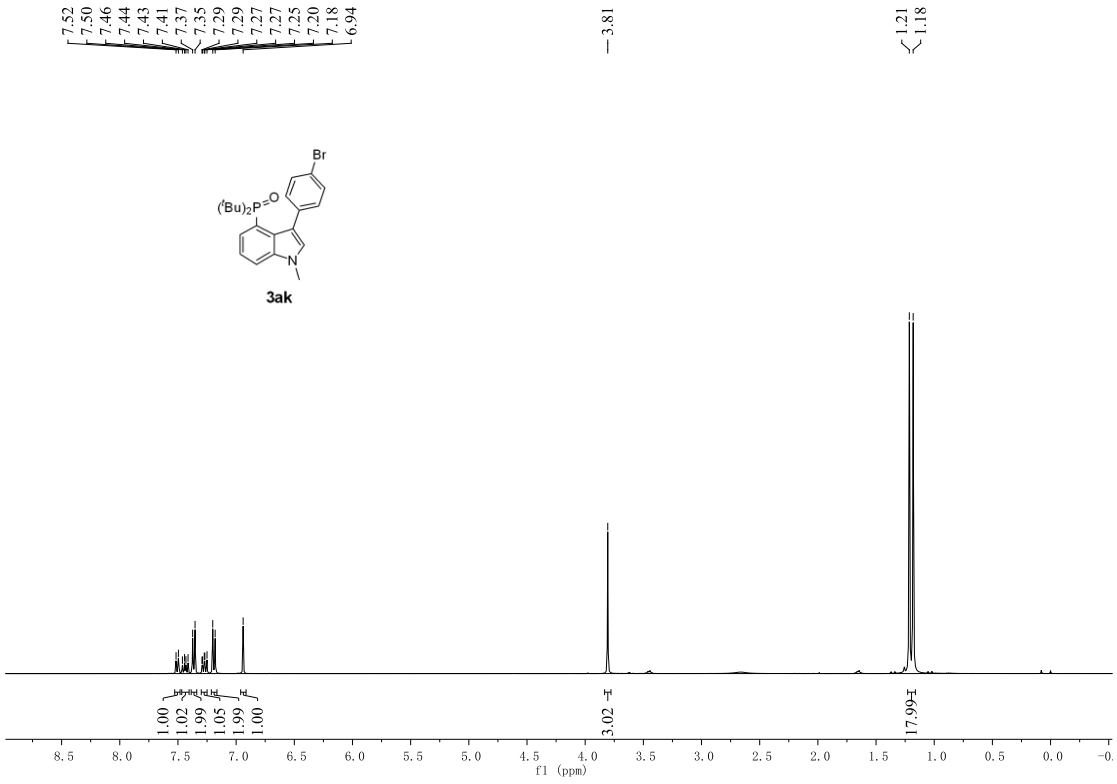
^{31}P NMR spectrum for **3aj**



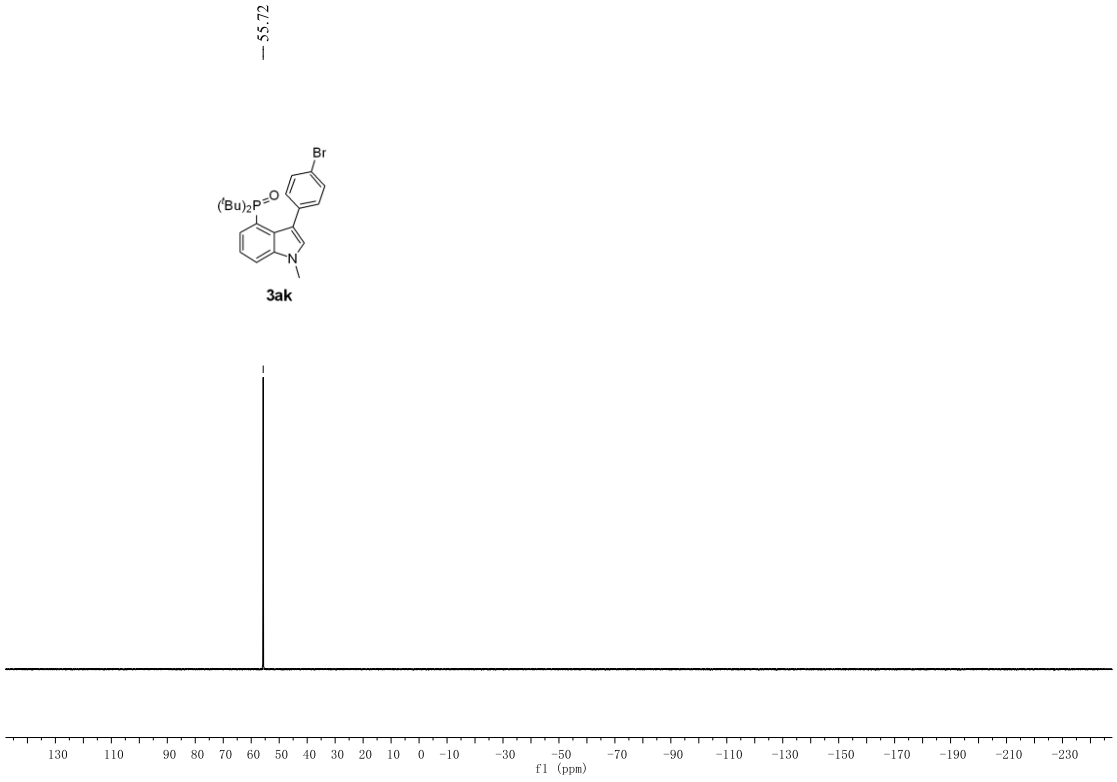
^{13}C NMR spectrum for **3aj**



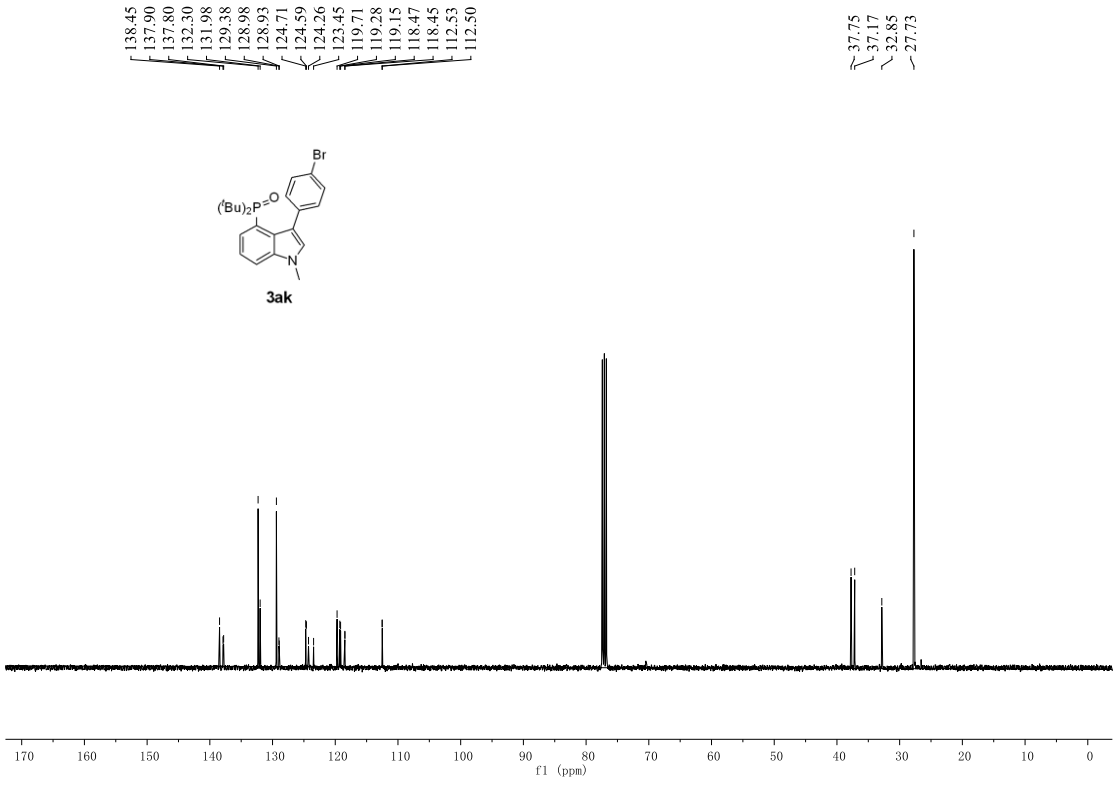
^{1}H NMR spectrum for **3ak**



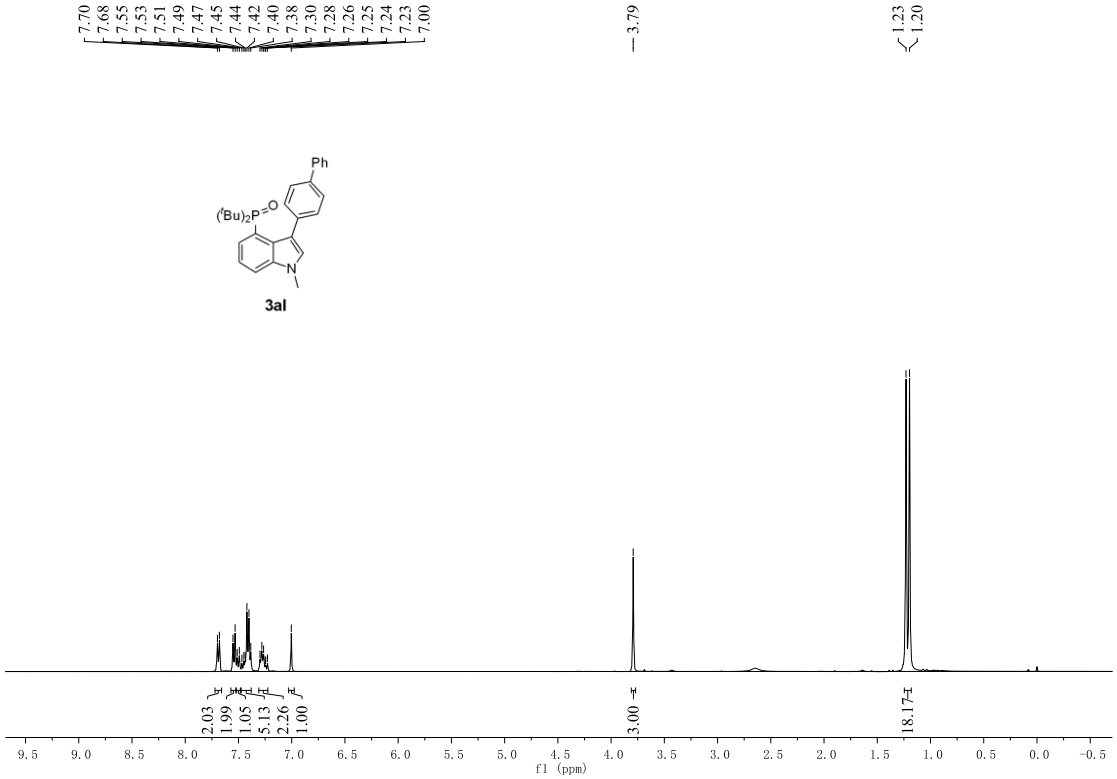
^{31}P NMR spectrum for **3ak**



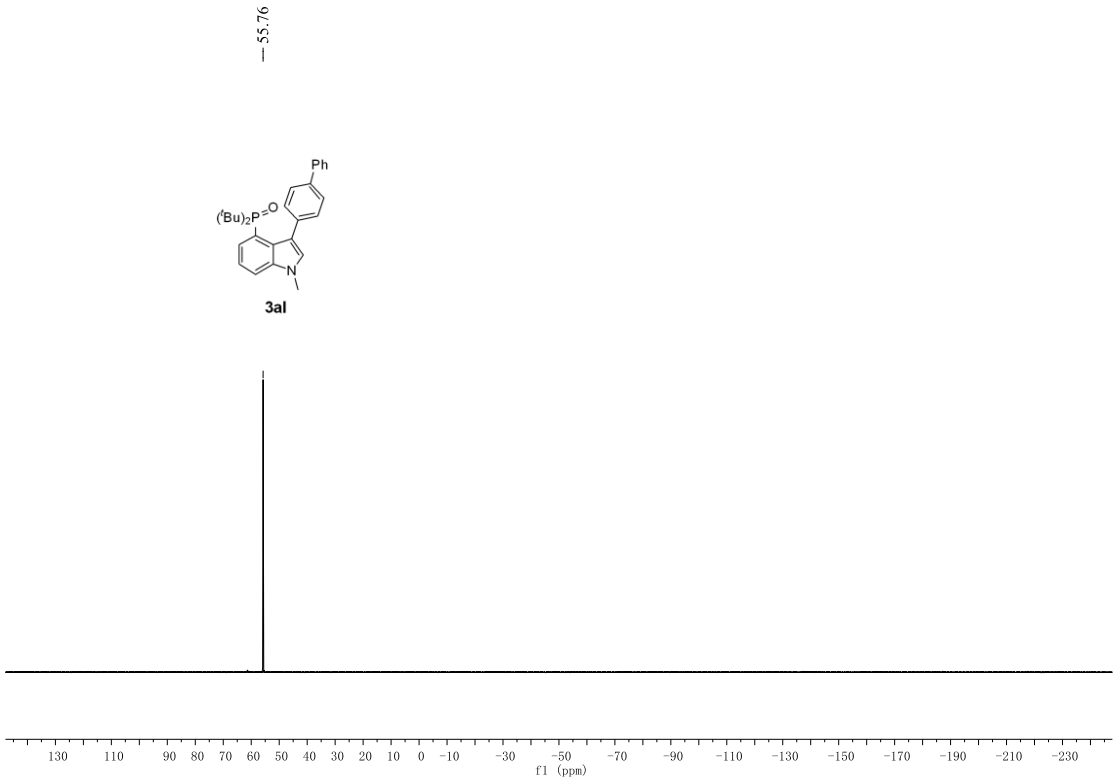
^{13}C NMR spectrum for **3ak**



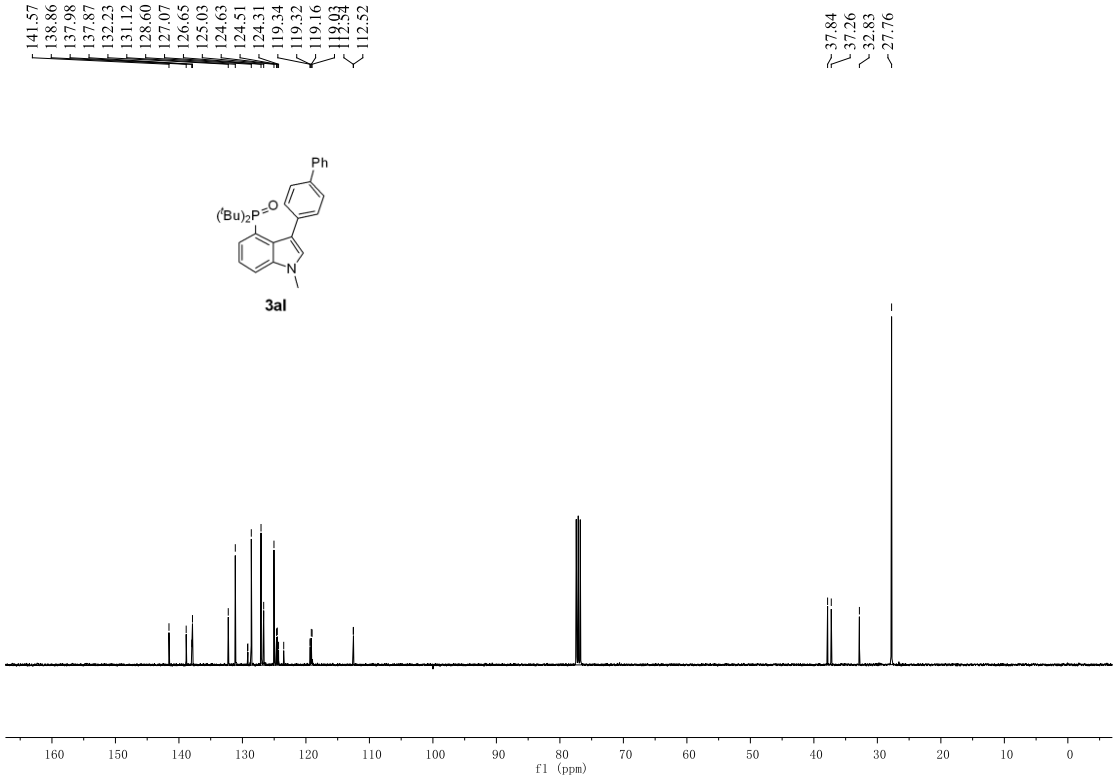
^{1}H NMR spectrum for **3al**



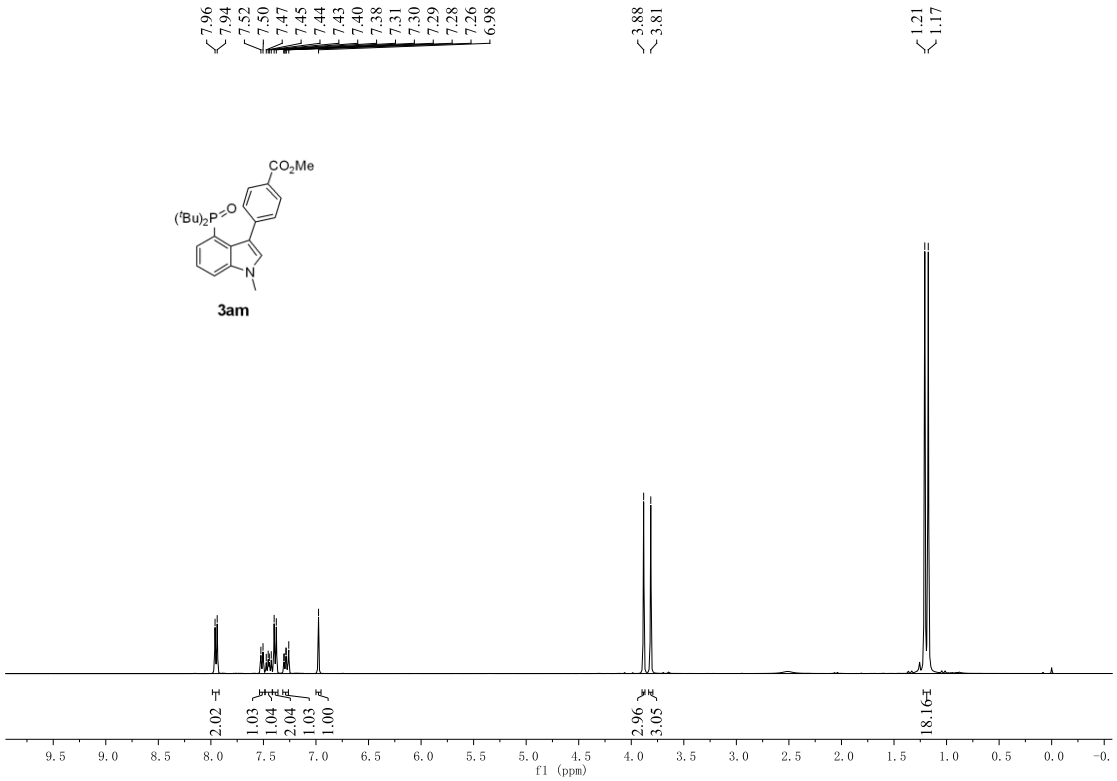
^{31}P NMR spectrum for **3al**



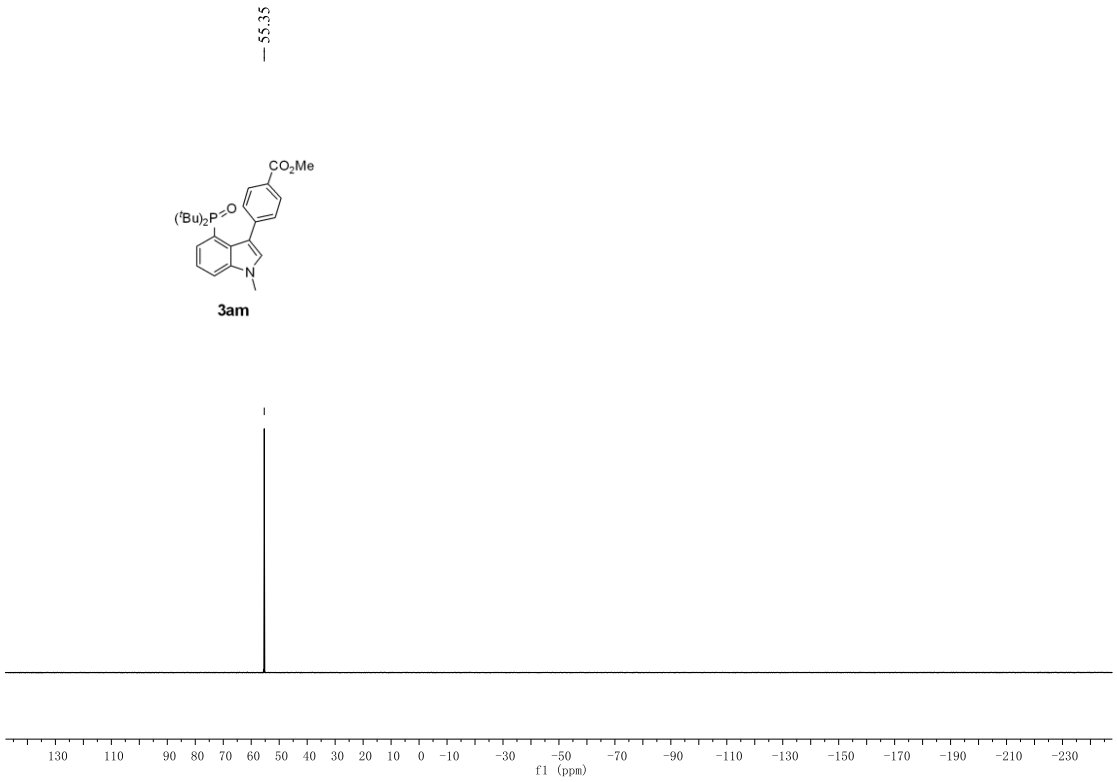
^{13}C NMR spectrum for **3al**



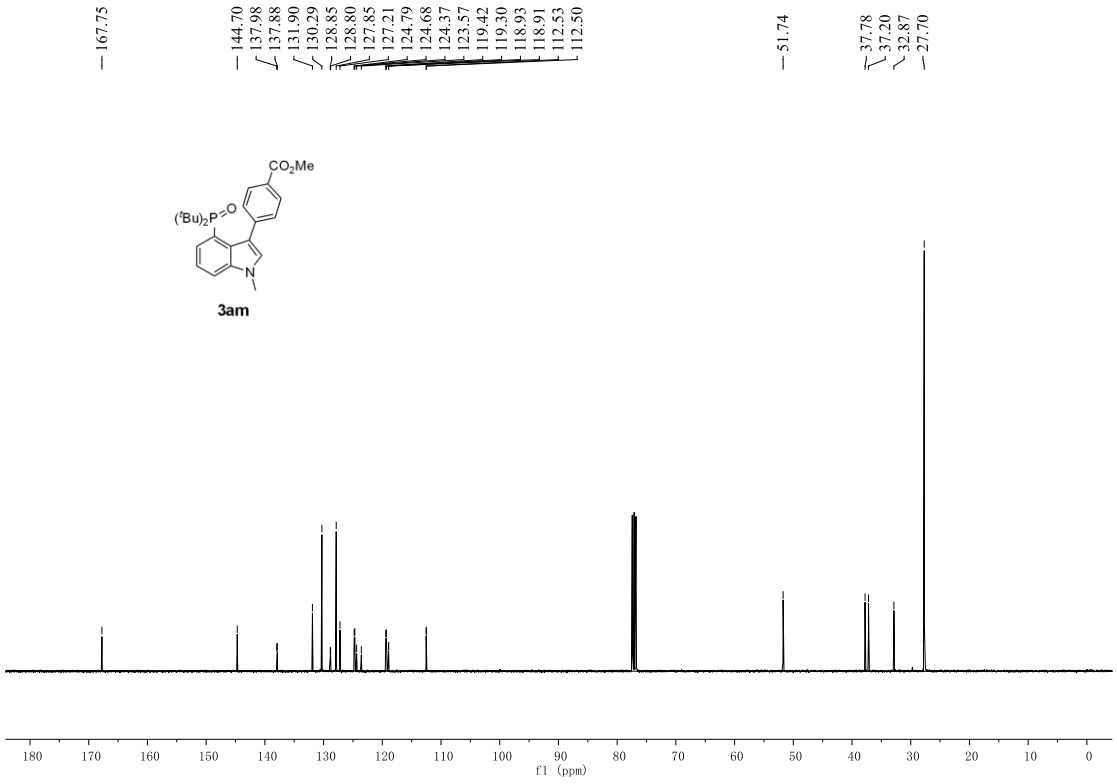
^{1}H NMR spectrum for **3am**



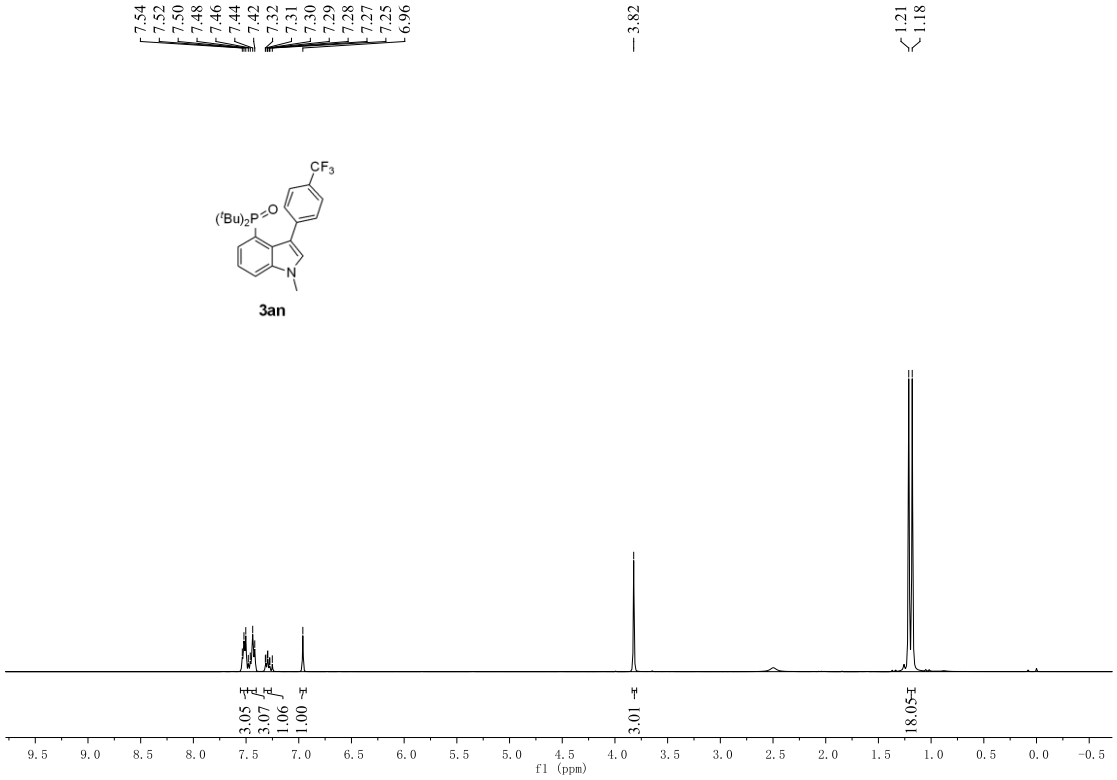
^{31}P NMR spectrum for **3am**



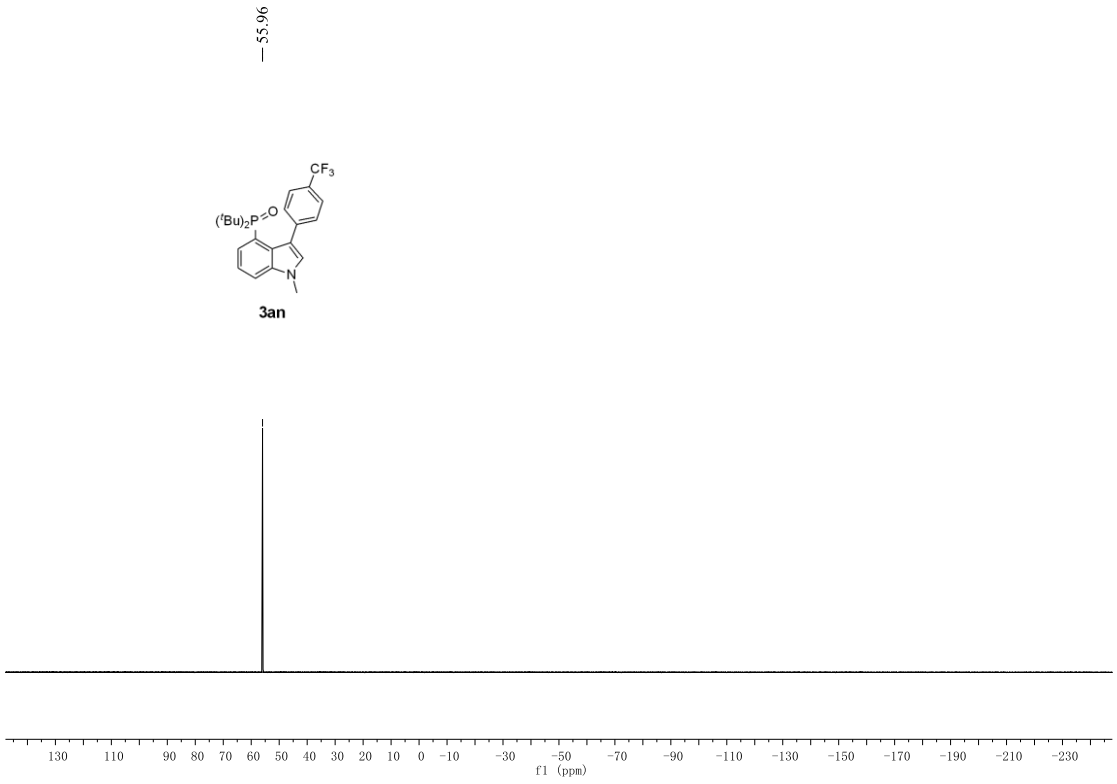
^{13}C NMR spectrum for **3am**



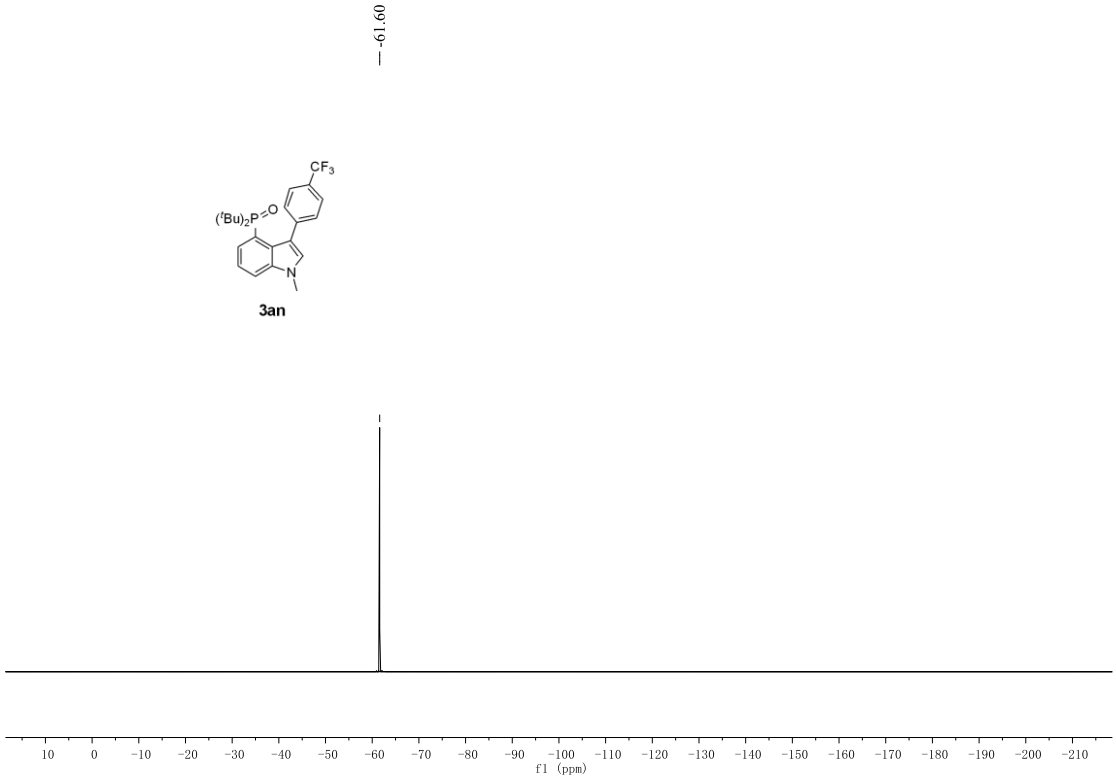
^{1}H NMR spectrum for **3an**



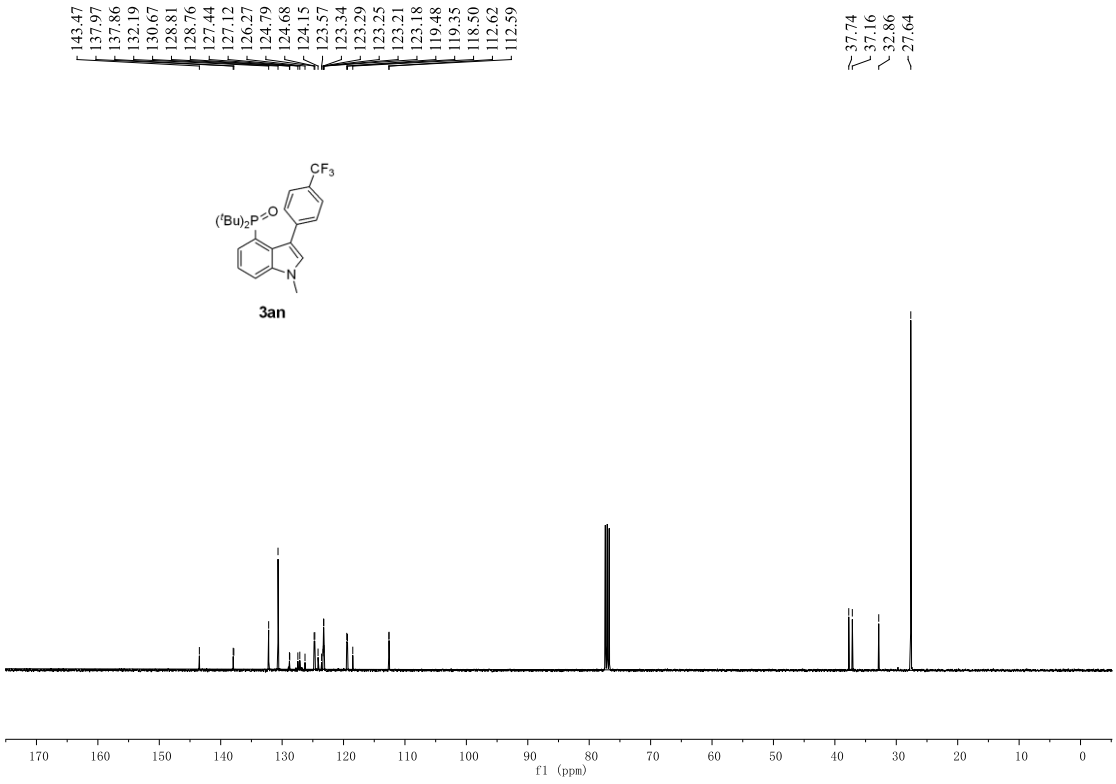
^{31}P NMR spectrum for **3an**



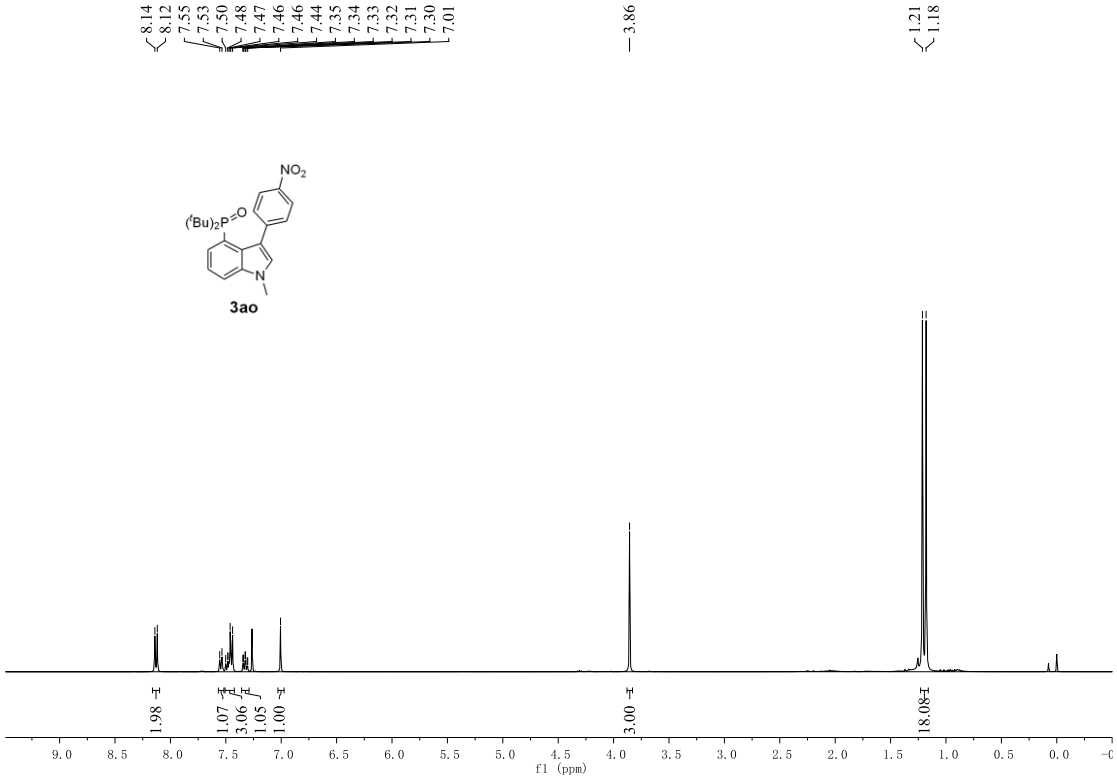
^{19}F NMR spectrum for **3an**



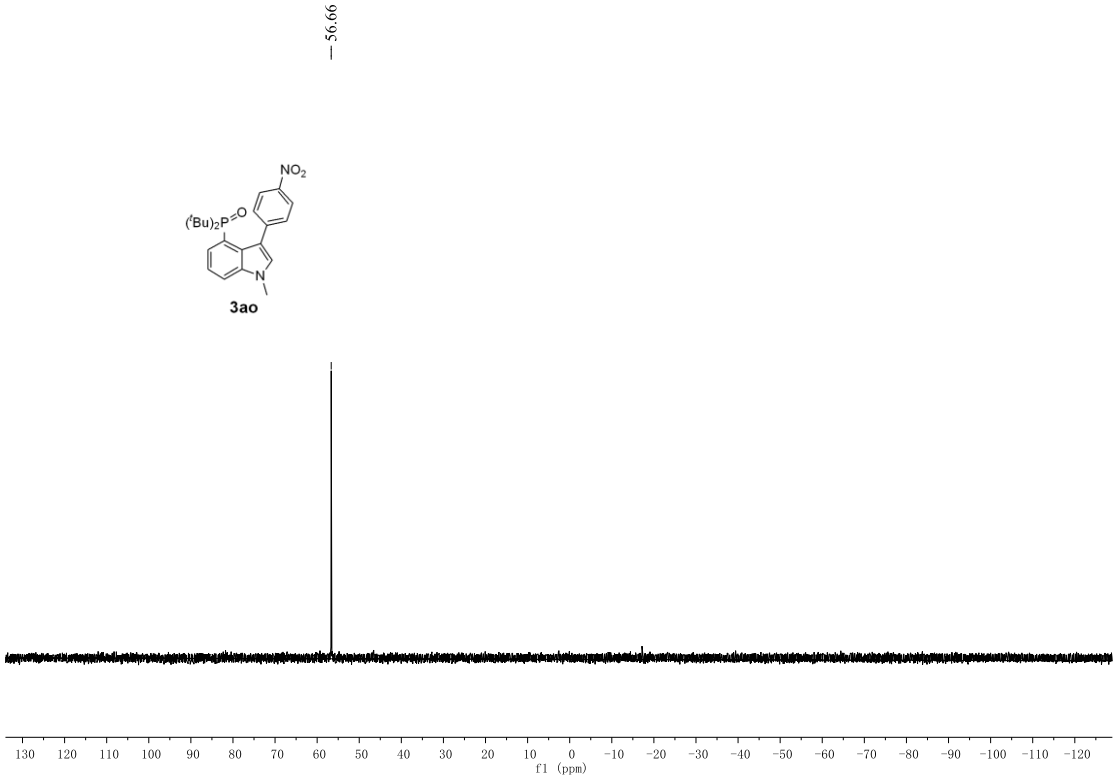
^{13}C NMR spectrum for **3an**



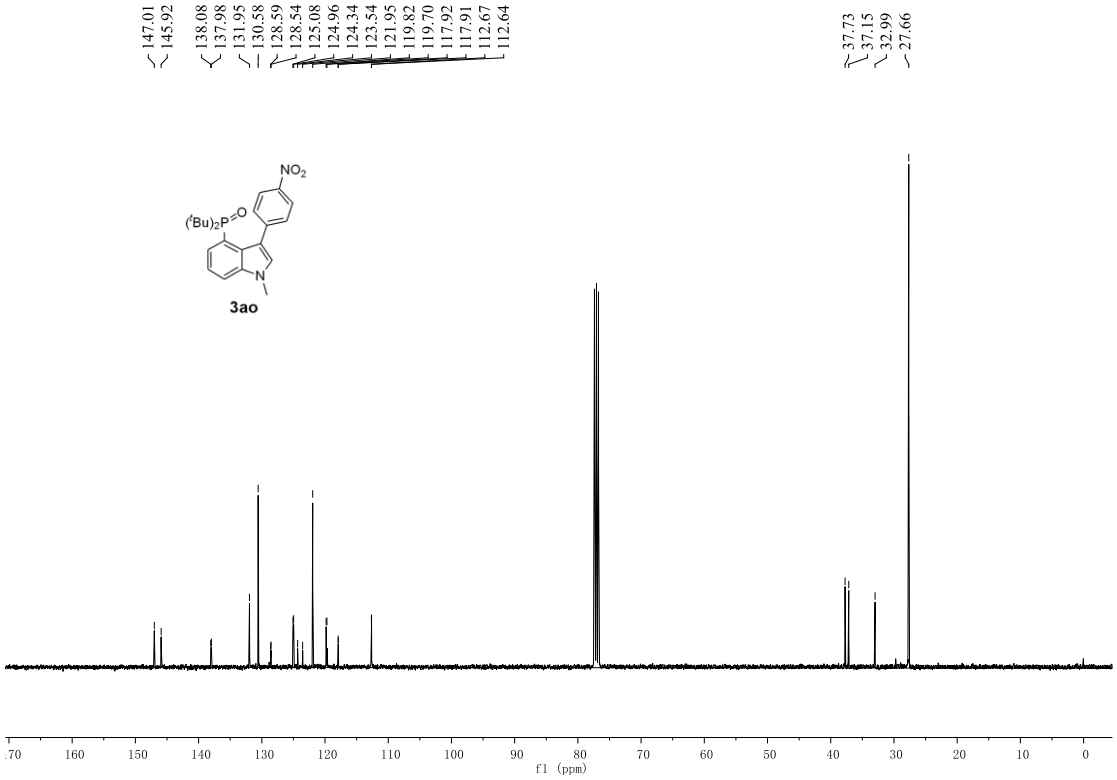
^{1}H NMR spectrum for **3ao**



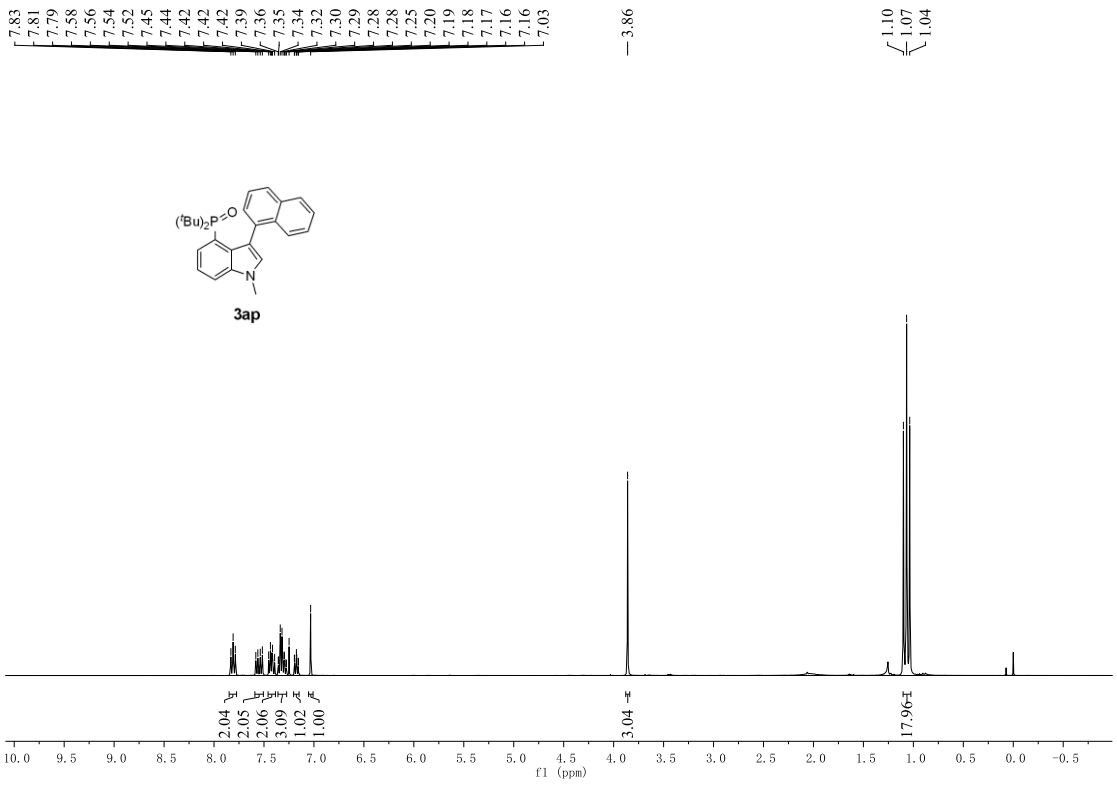
^{31}P NMR spectrum for **3ao**



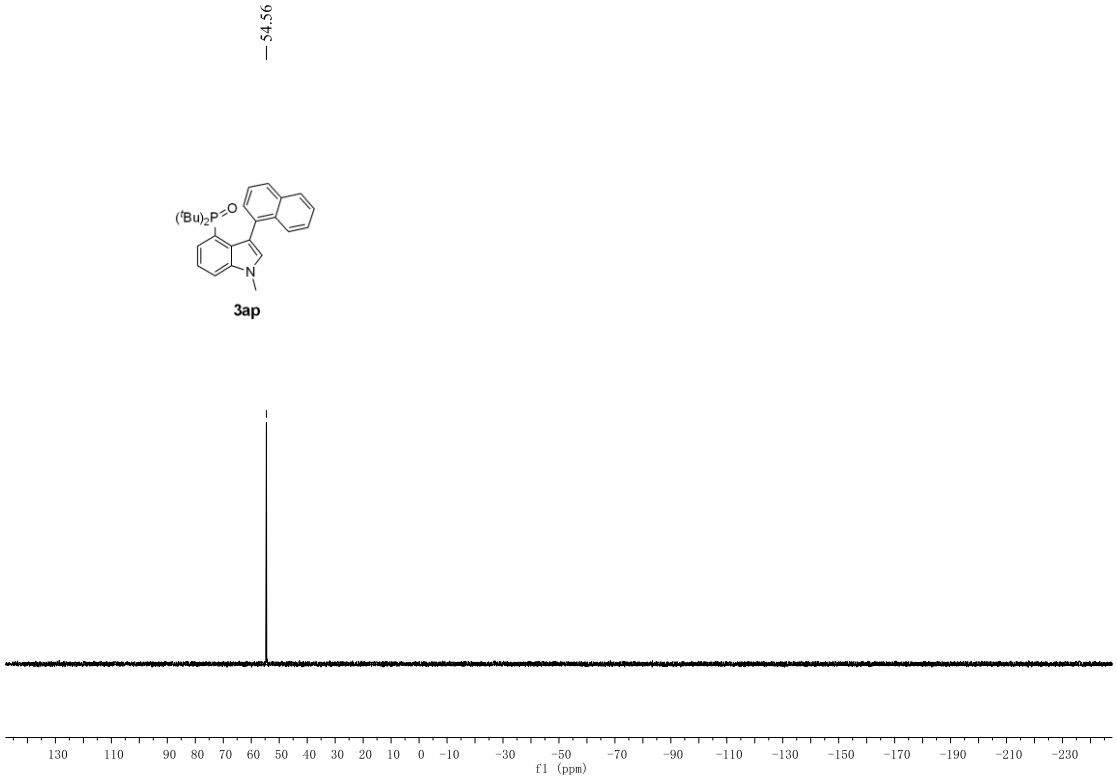
^{13}C NMR spectrum for **3ao**



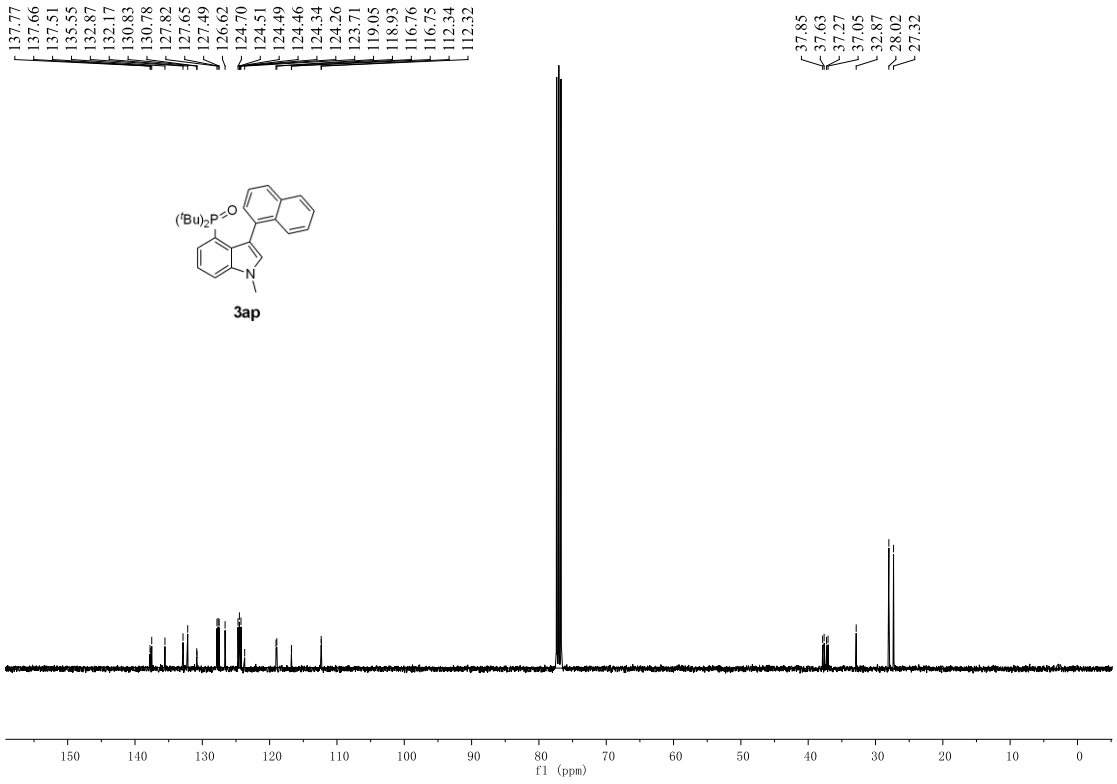
^{1}H NMR spectrum for **3ap**



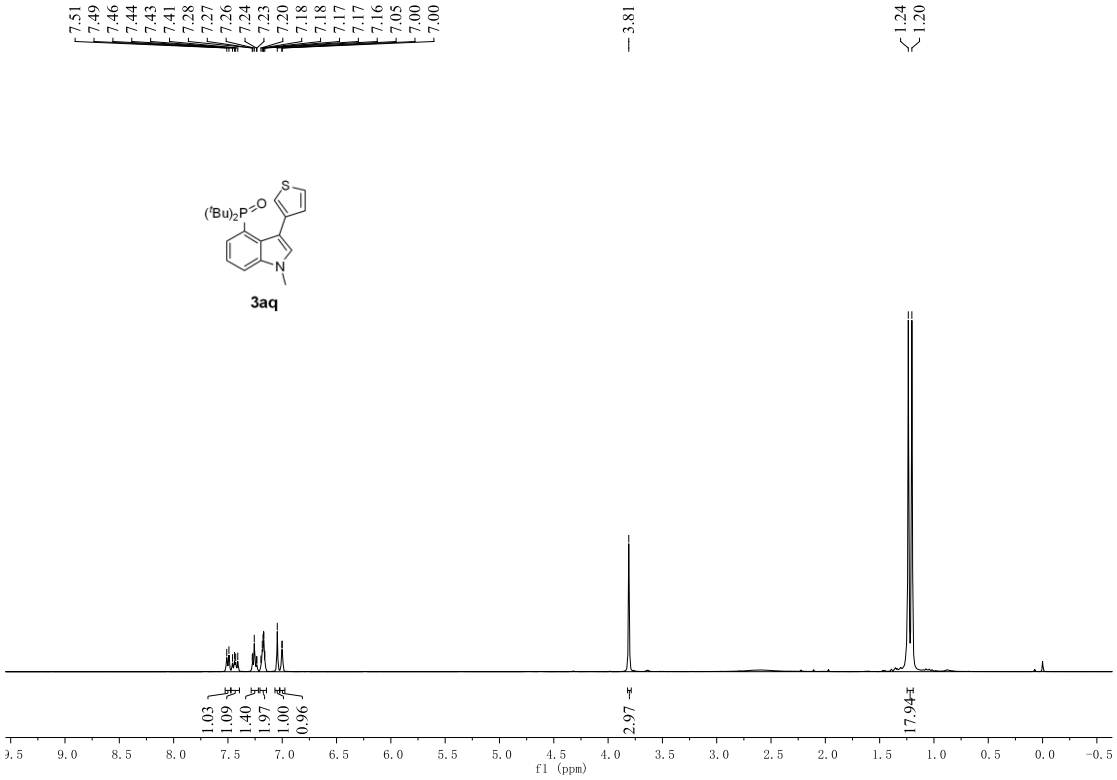
^{31}P NMR spectrum for **3ap**



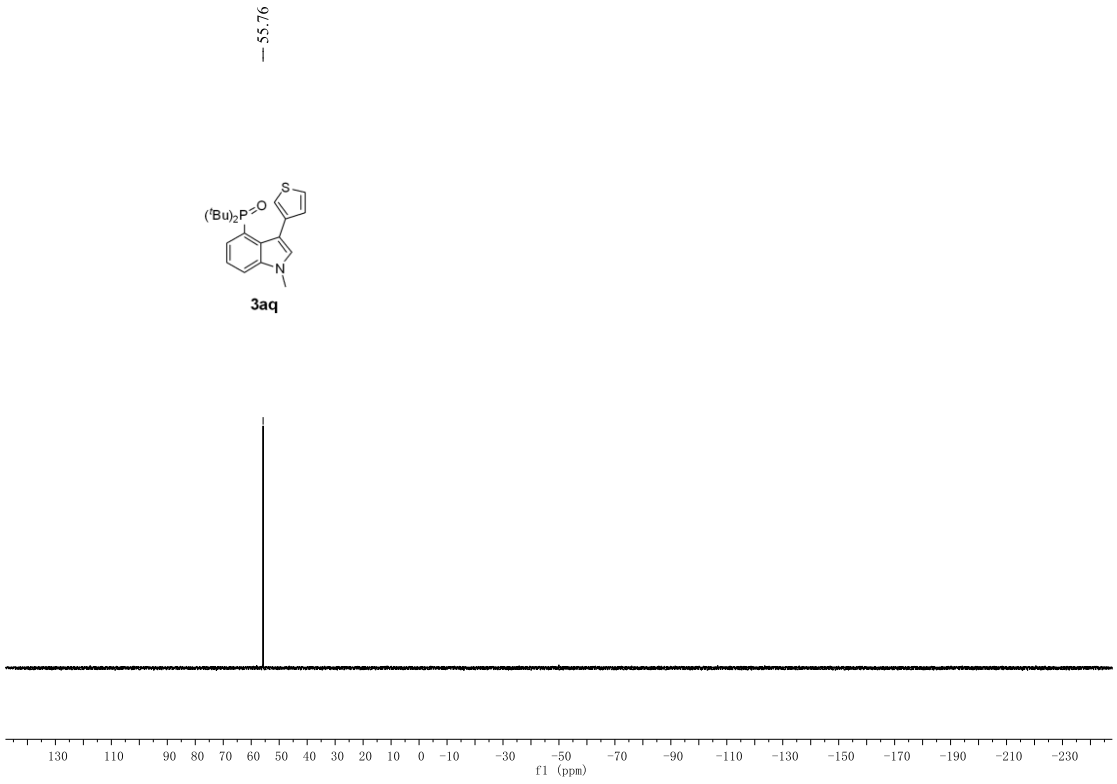
^{13}C NMR spectrum for **3ap**



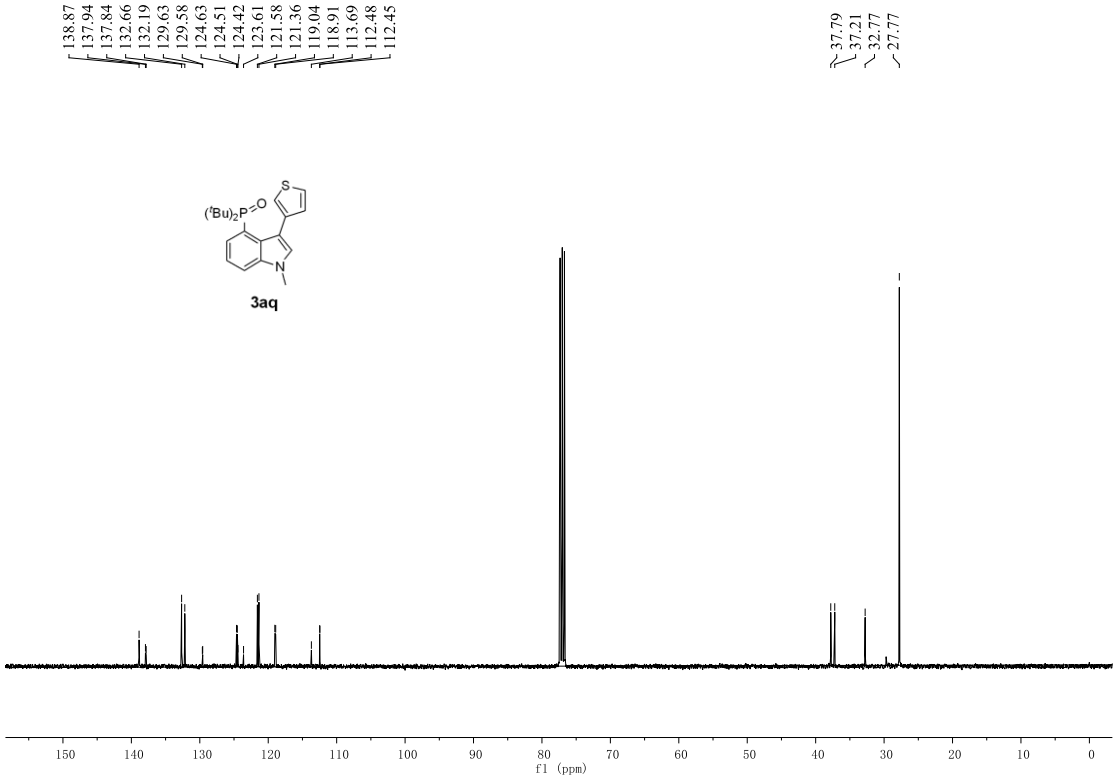
^{1}H NMR spectrum for **3aq**



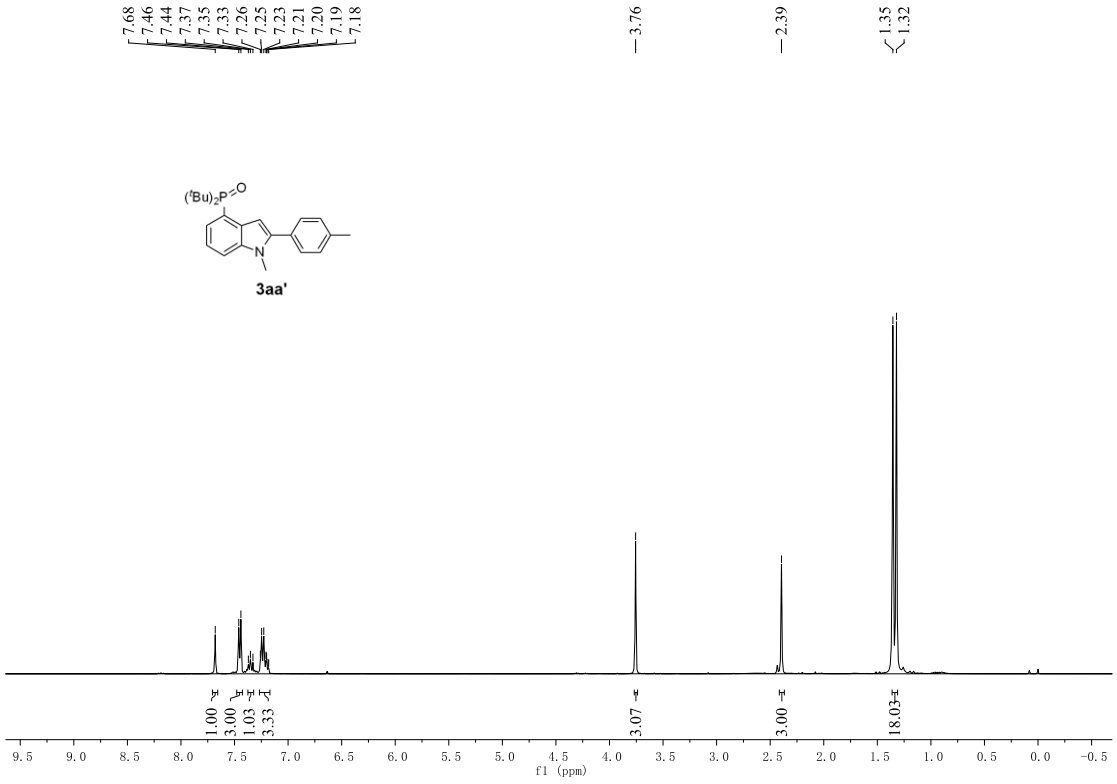
^{31}P NMR spectrum for **3aq**



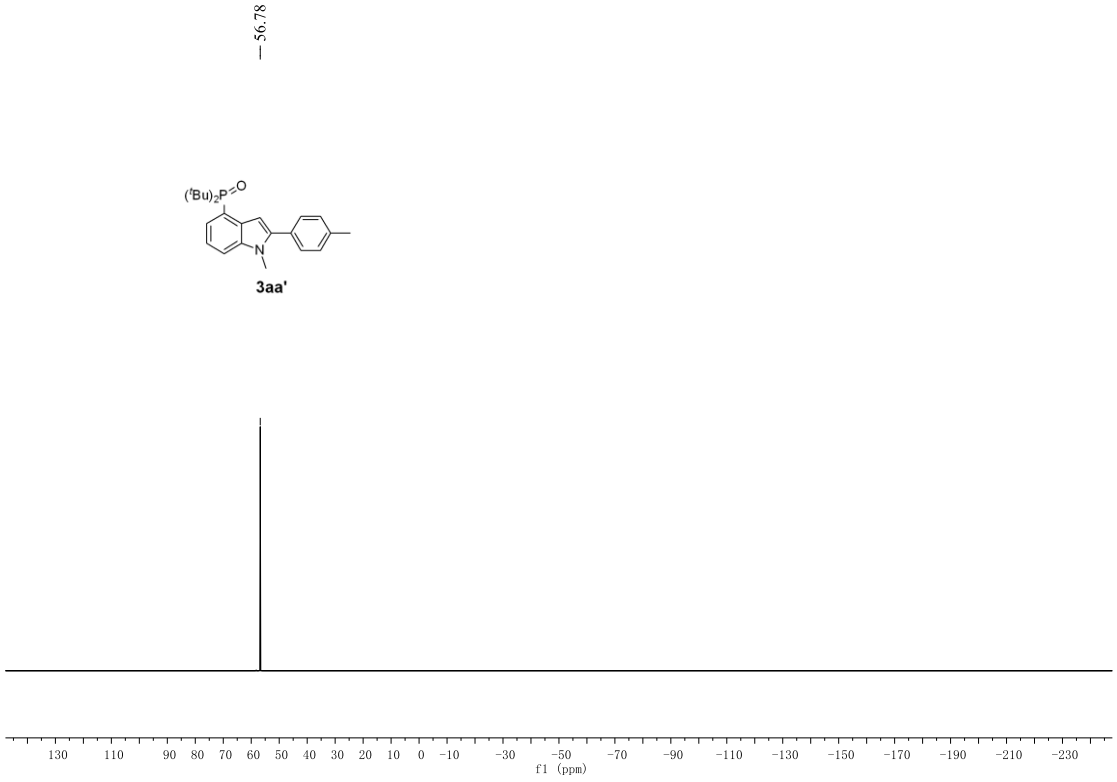
^{13}C NMR spectrum for **3aq**



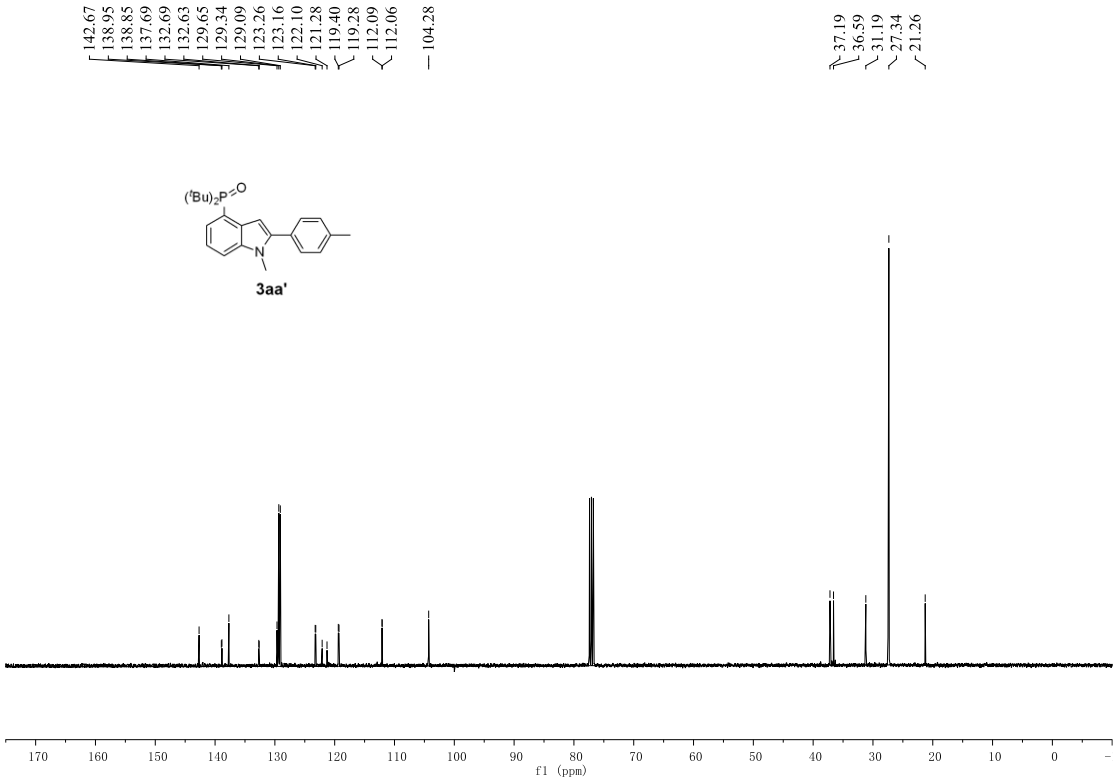
^{1}H NMR spectrum for **3aa'**



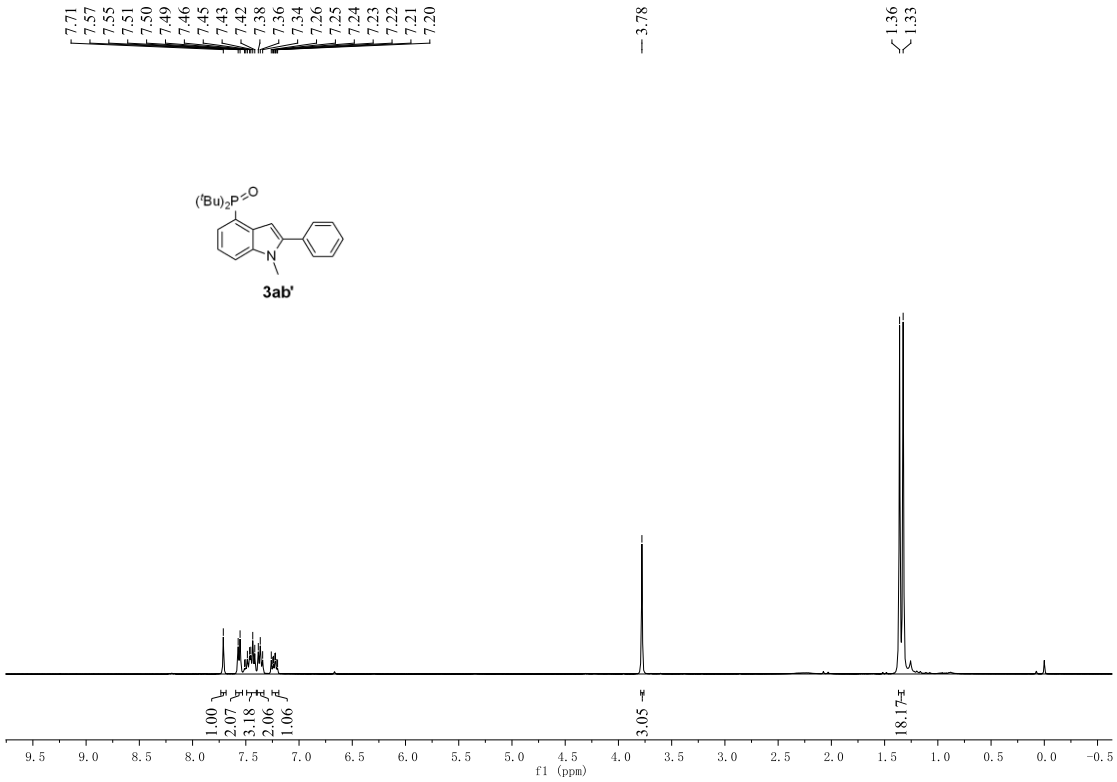
^{31}P NMR spectrum for **3aa'**



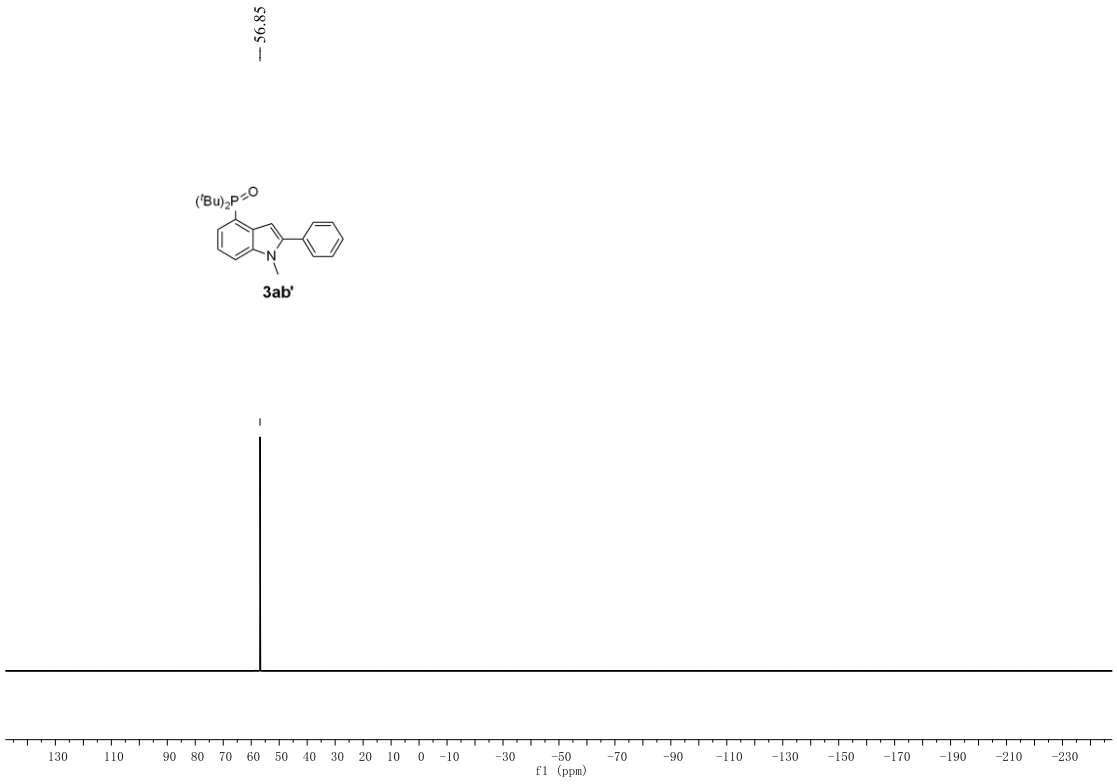
^{13}C NMR spectrum for **3aa'**



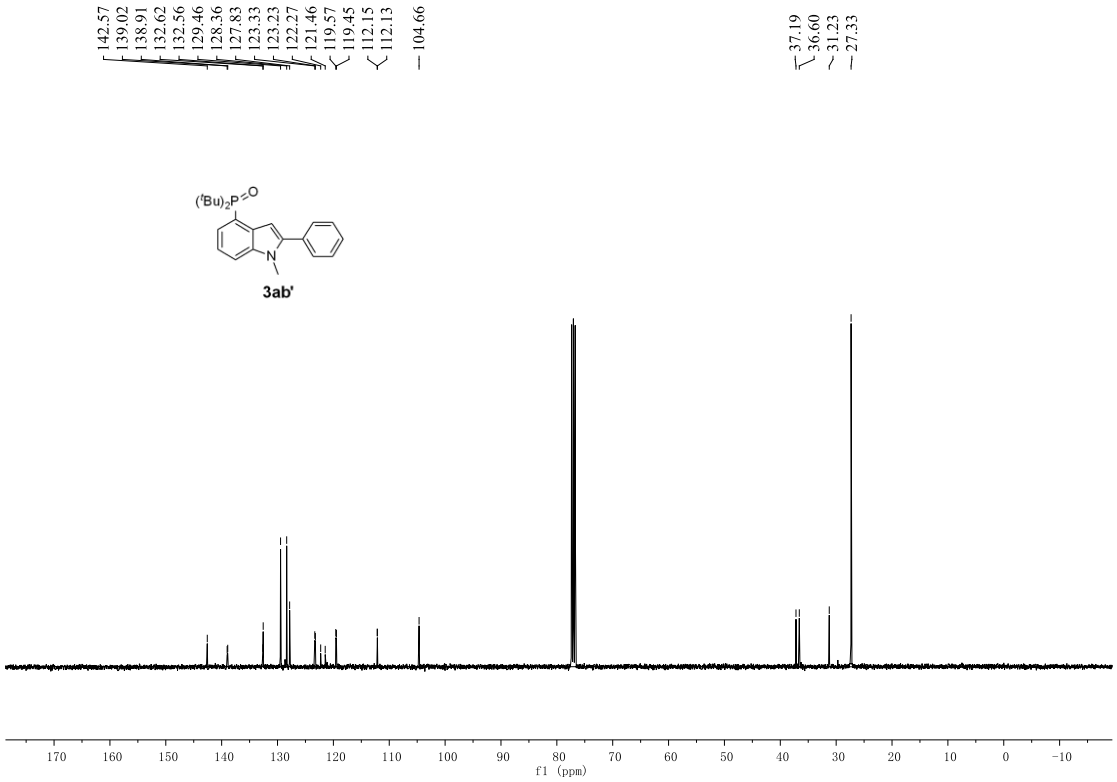
^{1}H NMR spectrum for **3ab'**



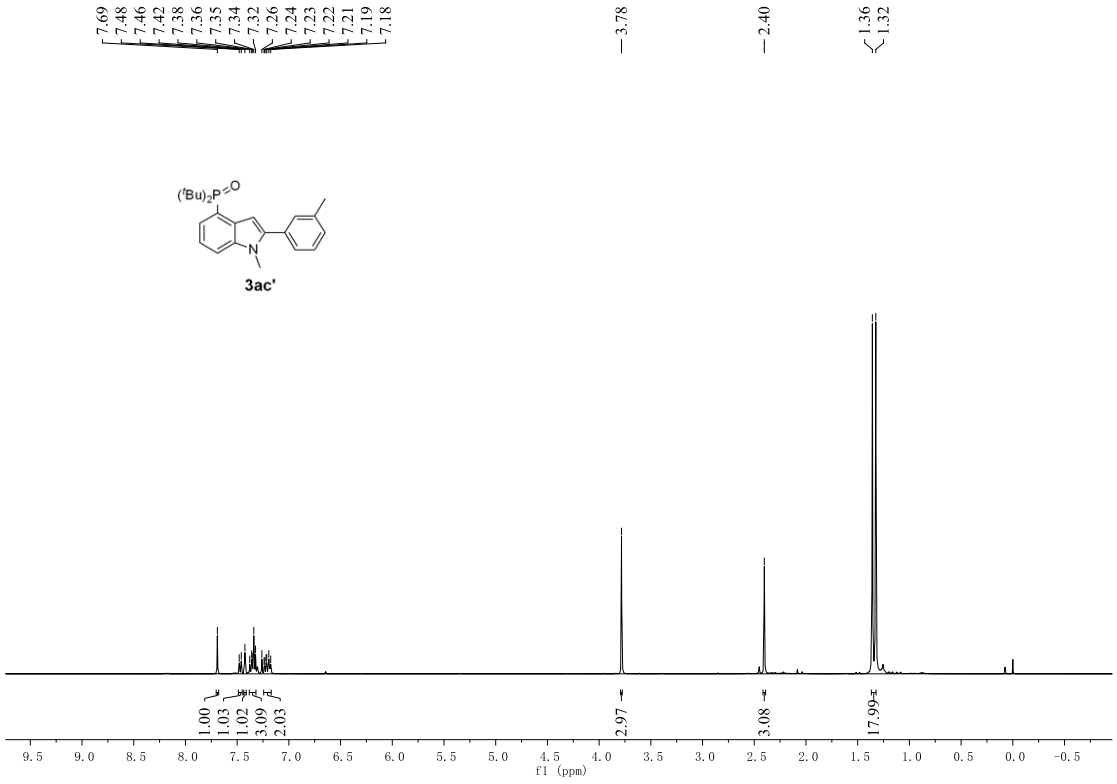
^{31}P NMR spectrum for **3ab'**



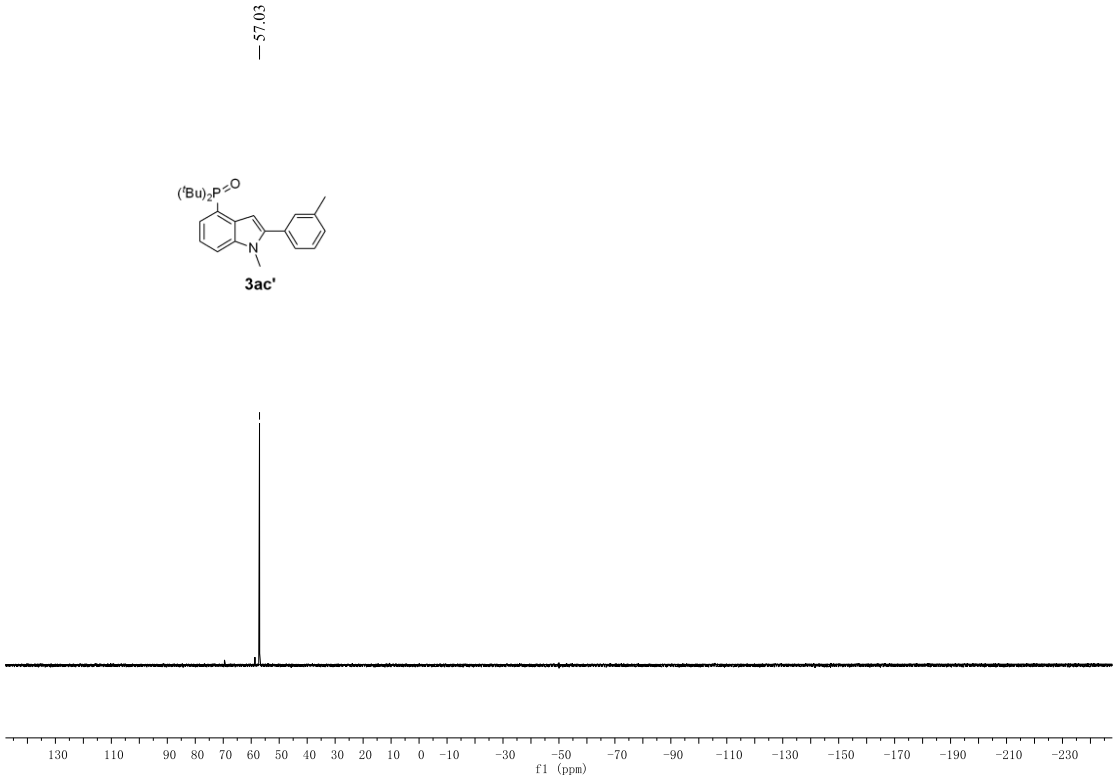
^{13}C NMR spectrum for **3ab'**



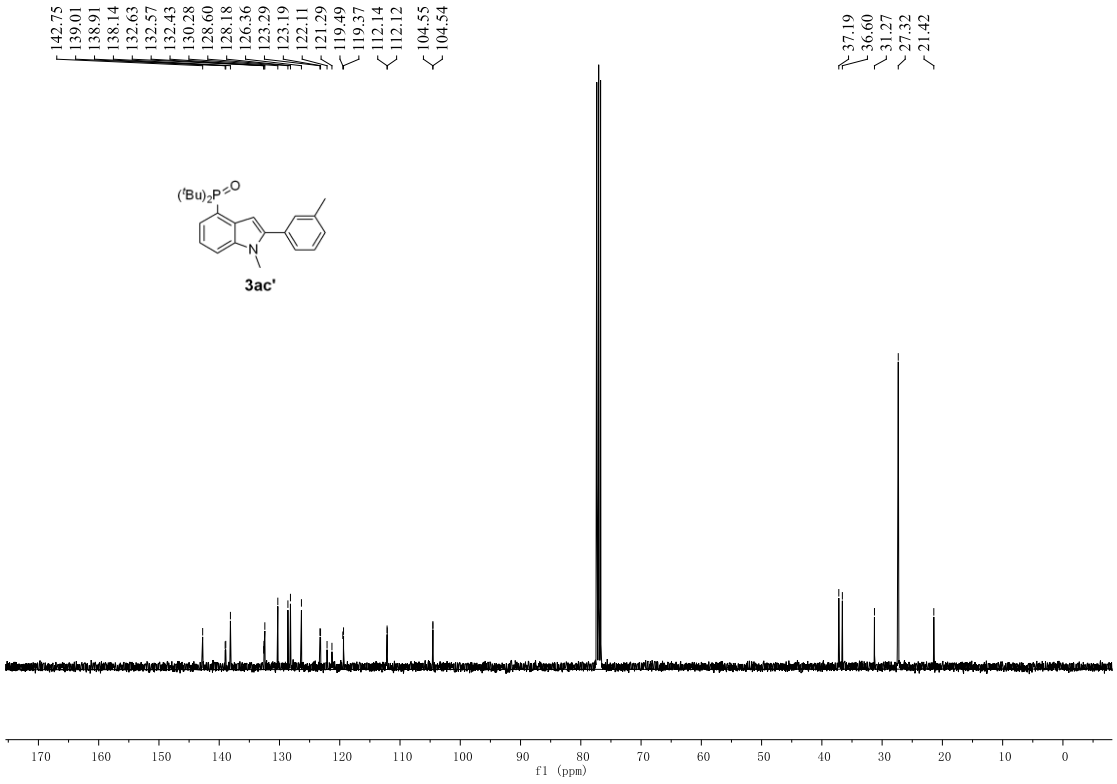
^{1}H NMR spectrum for **3ac'**



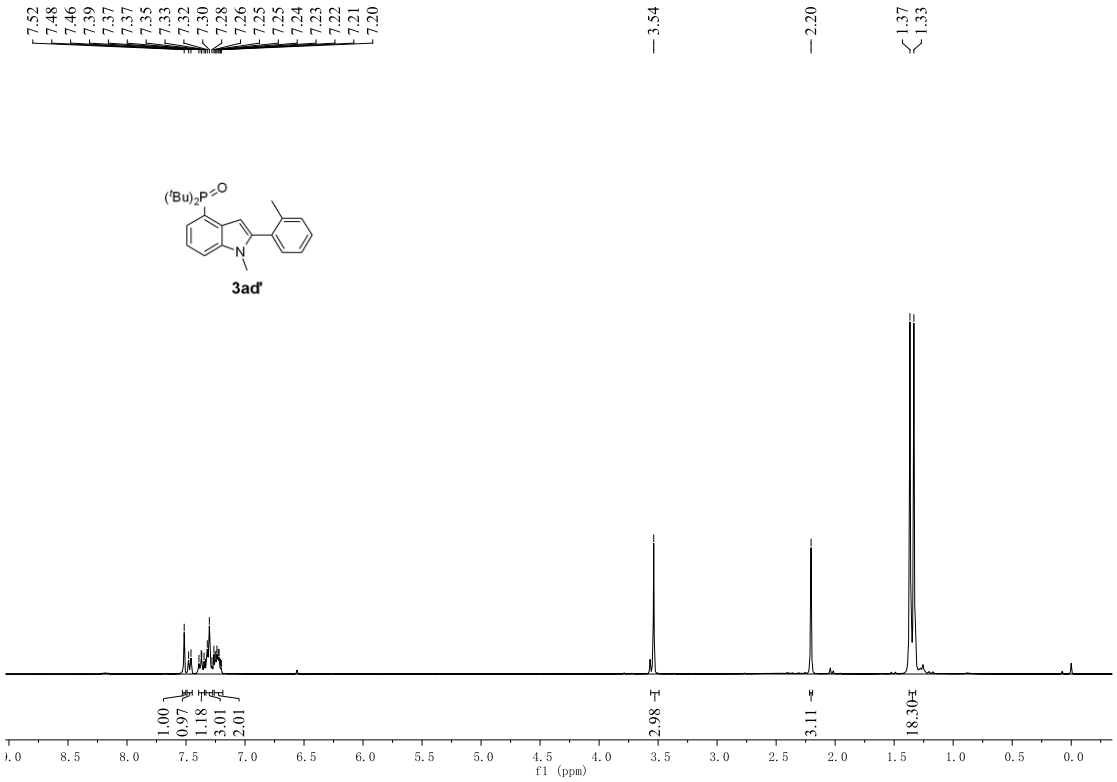
^{31}P NMR spectrum for **3ac'**



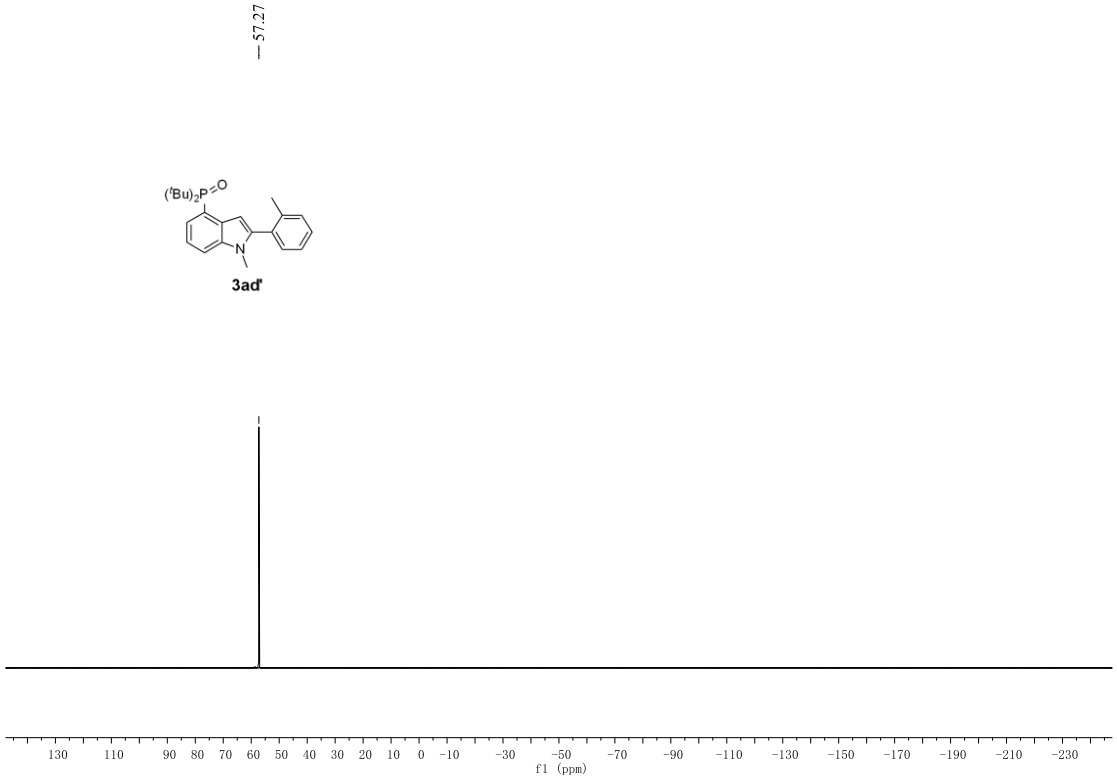
^{13}C NMR spectrum for **3ac'**



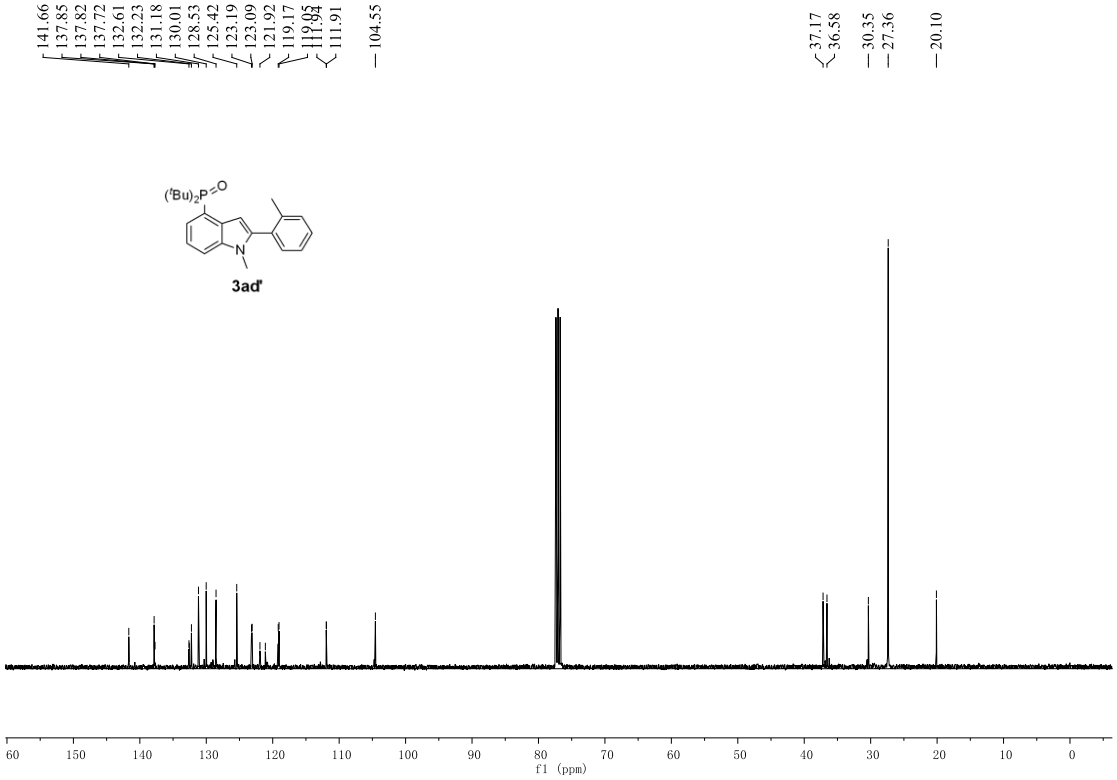
^{1}H NMR spectrum for **3ad'**



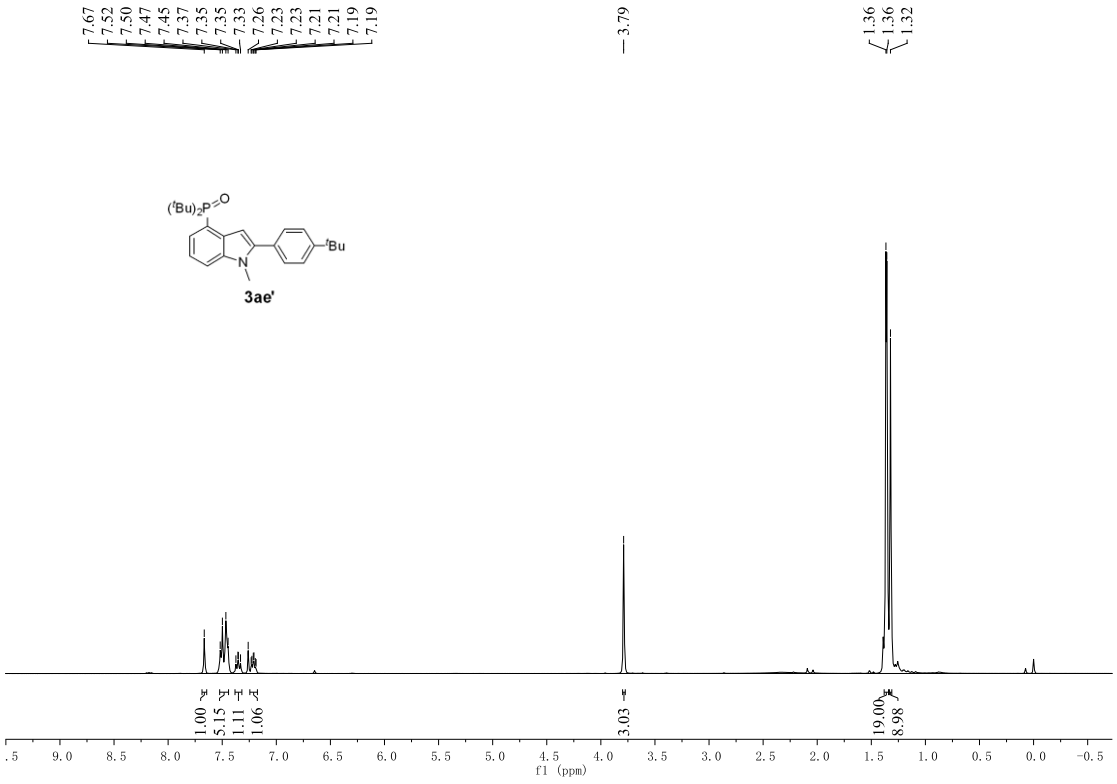
^{31}P NMR spectrum for **3ad'**



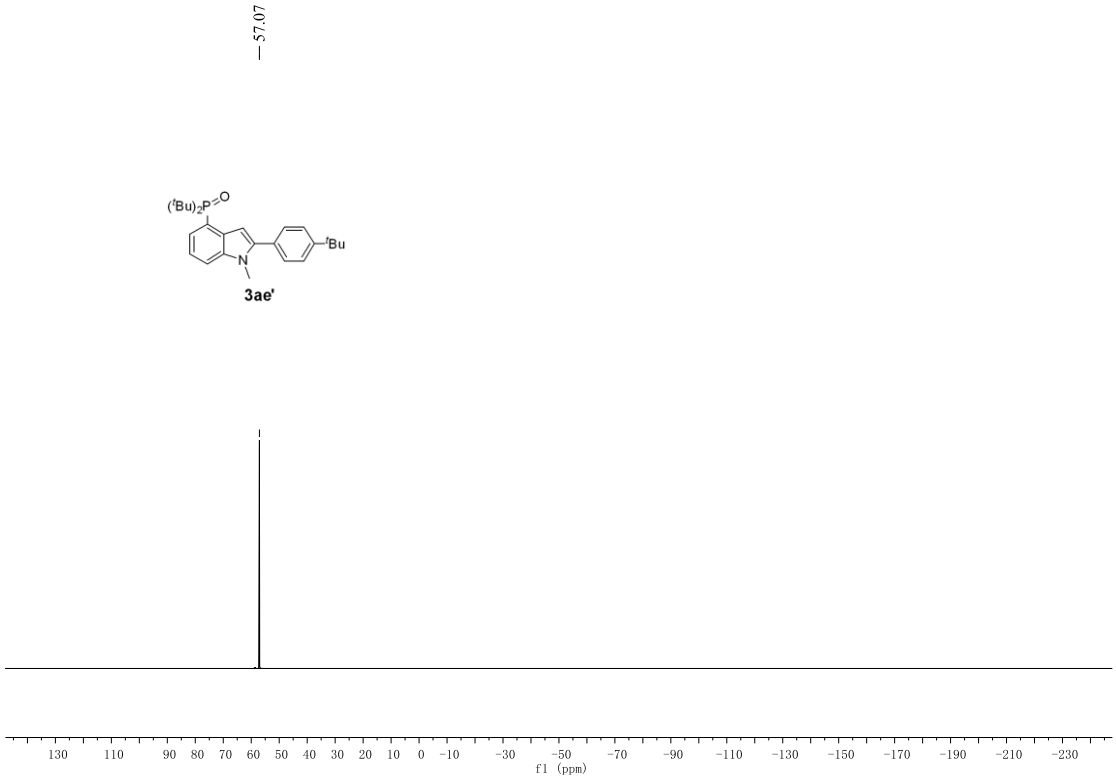
^{13}C NMR spectrum for **3ad'**



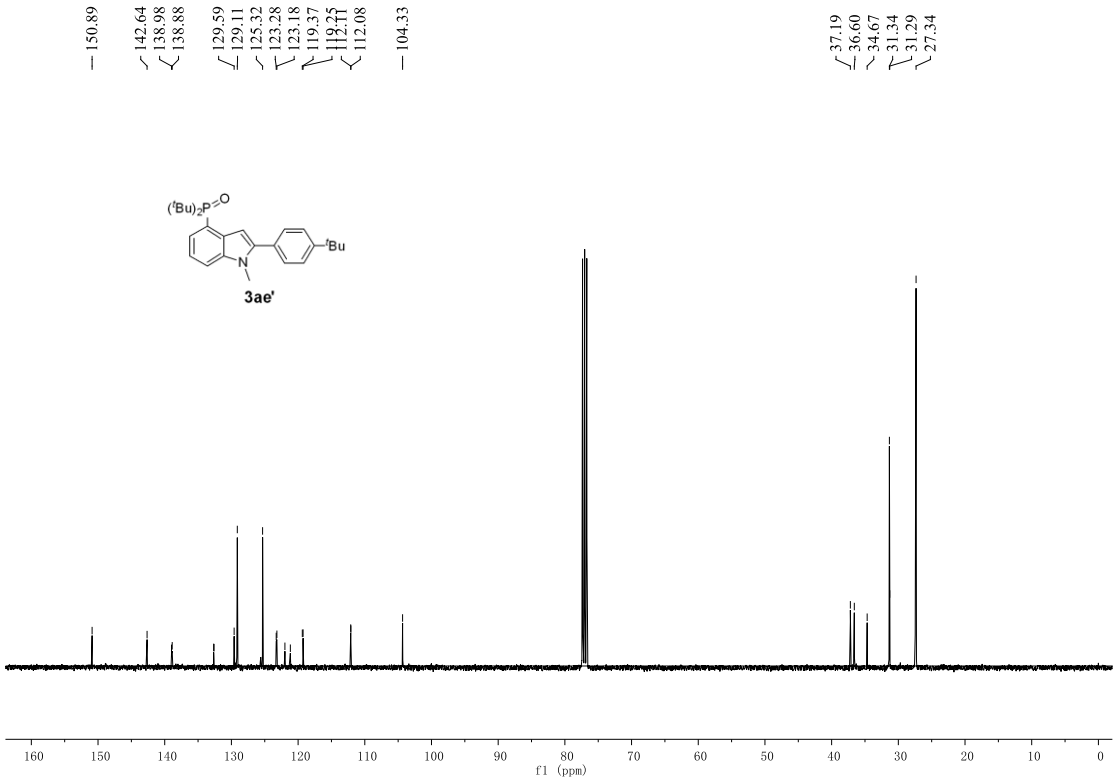
^{1}H NMR spectrum for **3ae'**



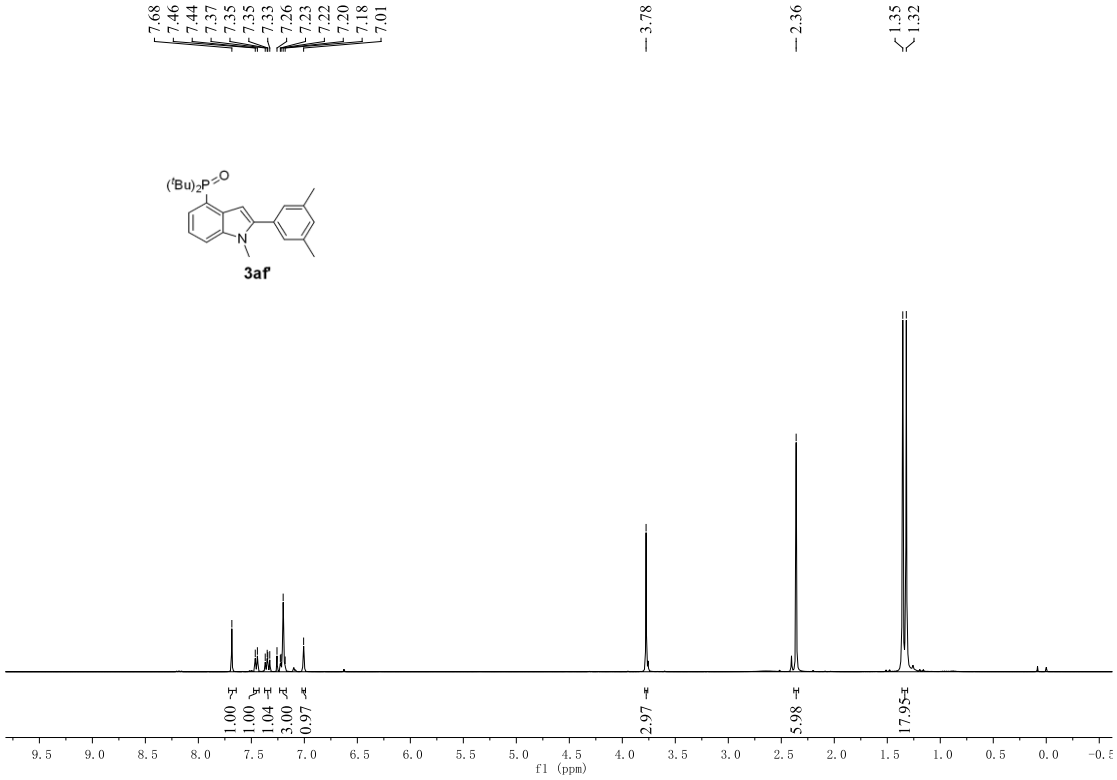
^{31}P NMR spectrum for **3ae'**



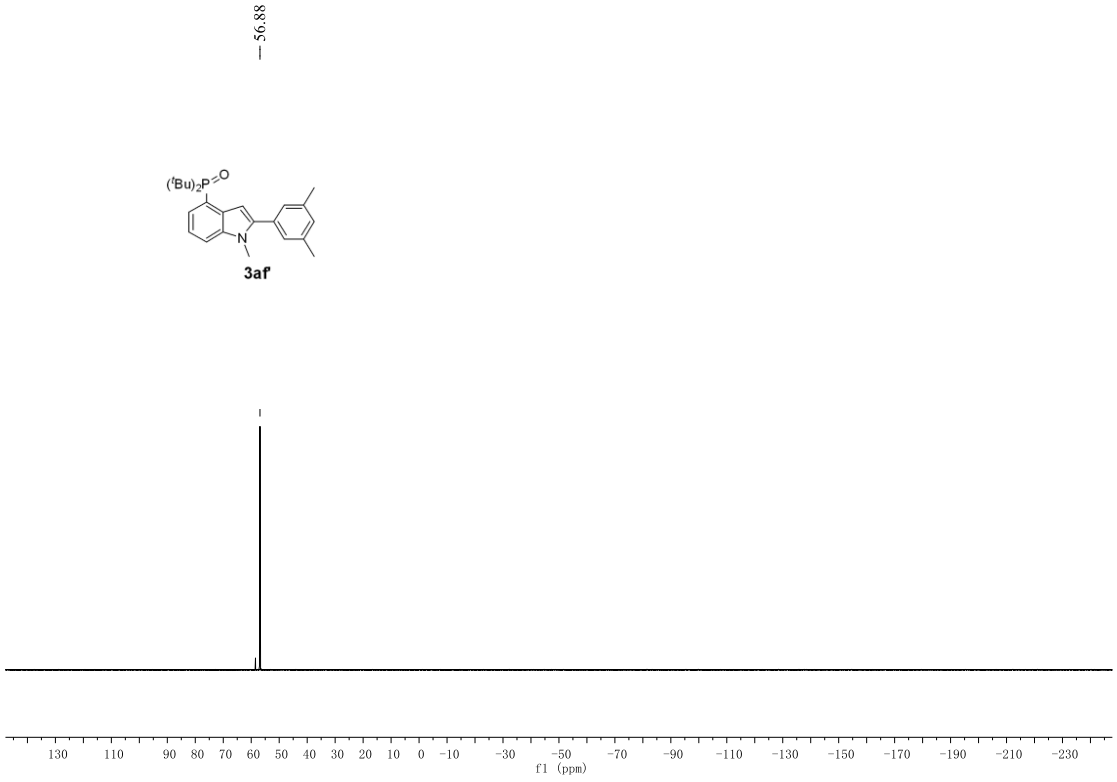
^{13}C NMR spectrum for **3ae'**



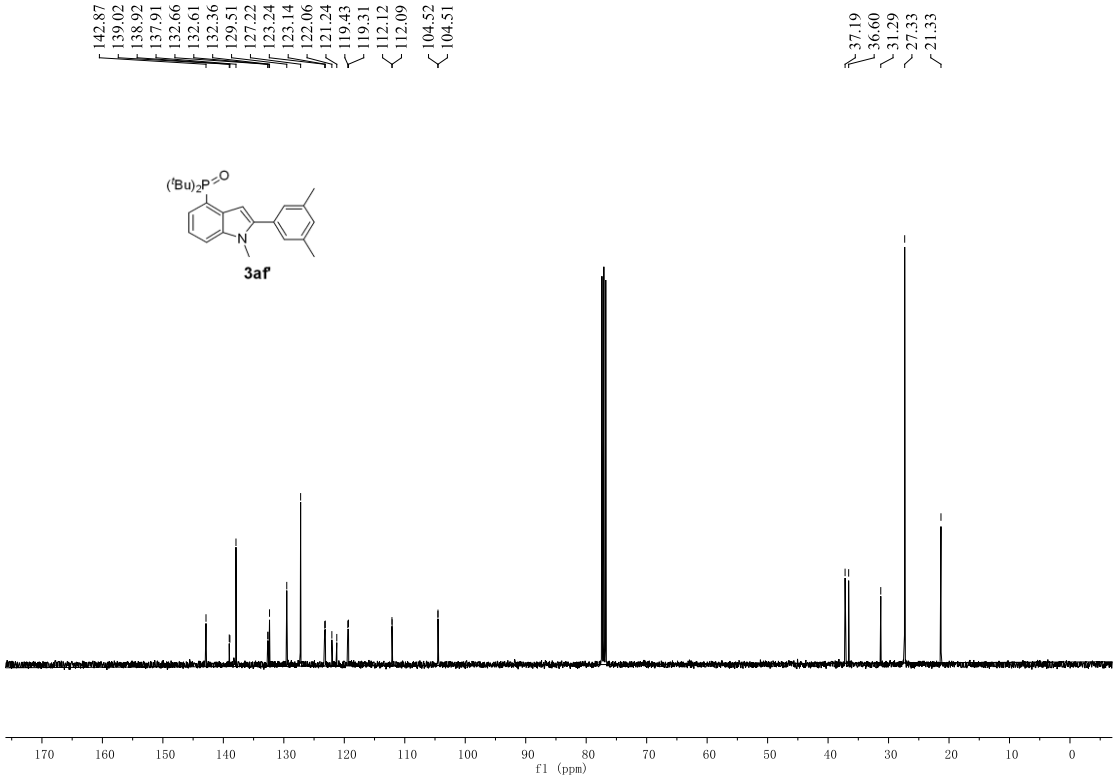
^{1}H NMR spectrum for **3af'**



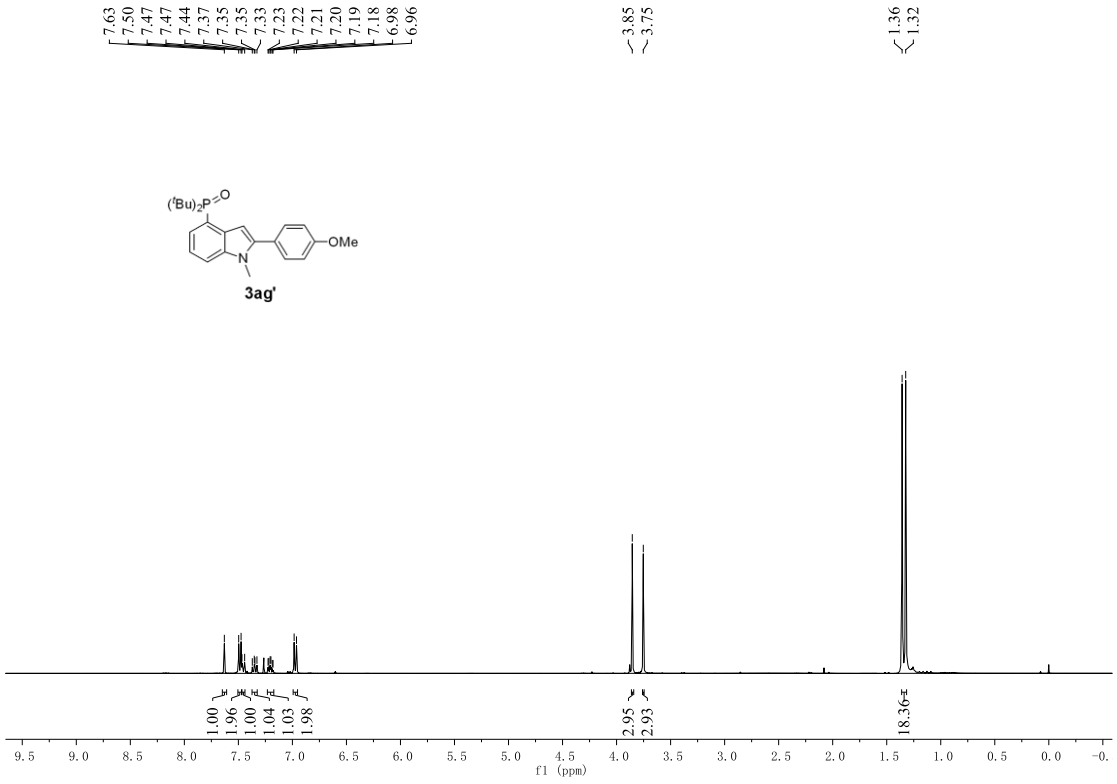
^{31}P NMR spectrum for **3af'**



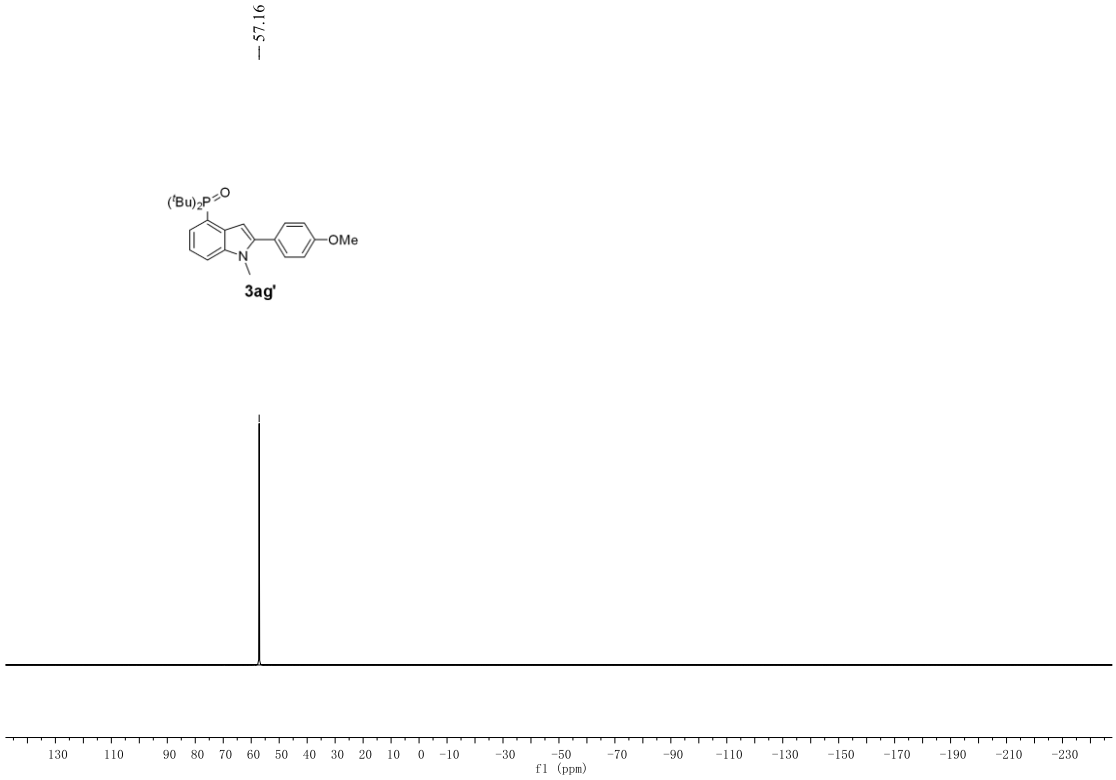
^{13}C NMR spectrum for **3af'**



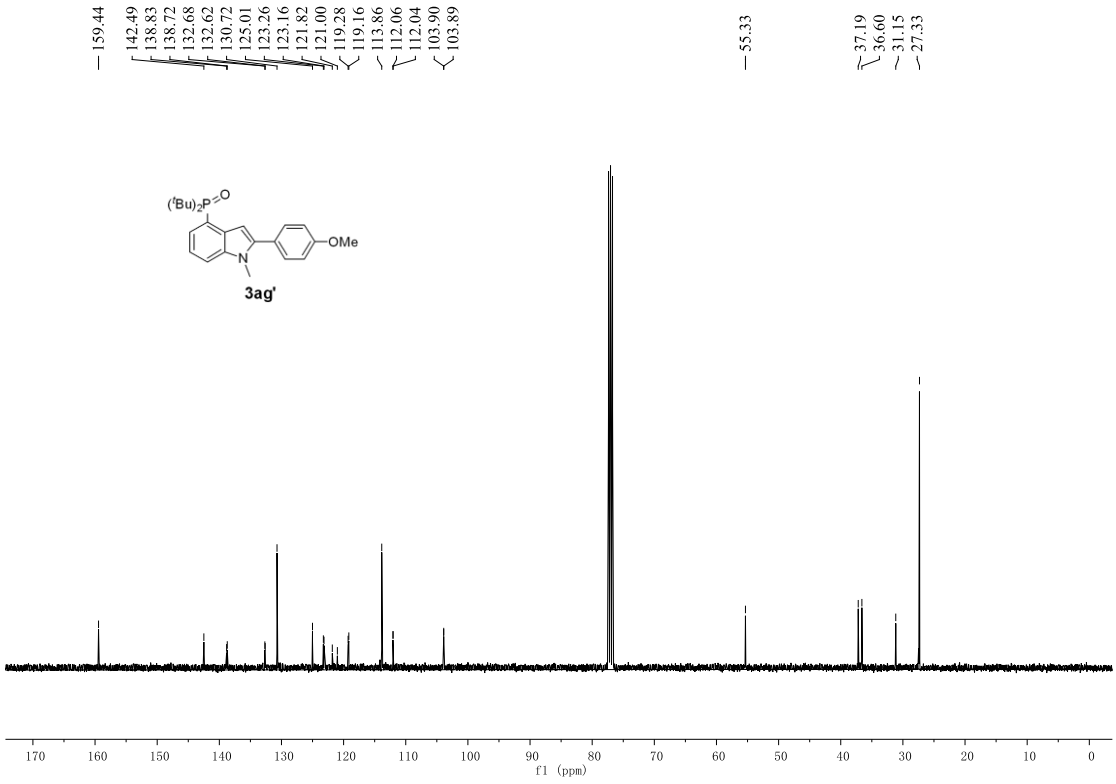
^{1}H NMR spectrum for **3ag'**



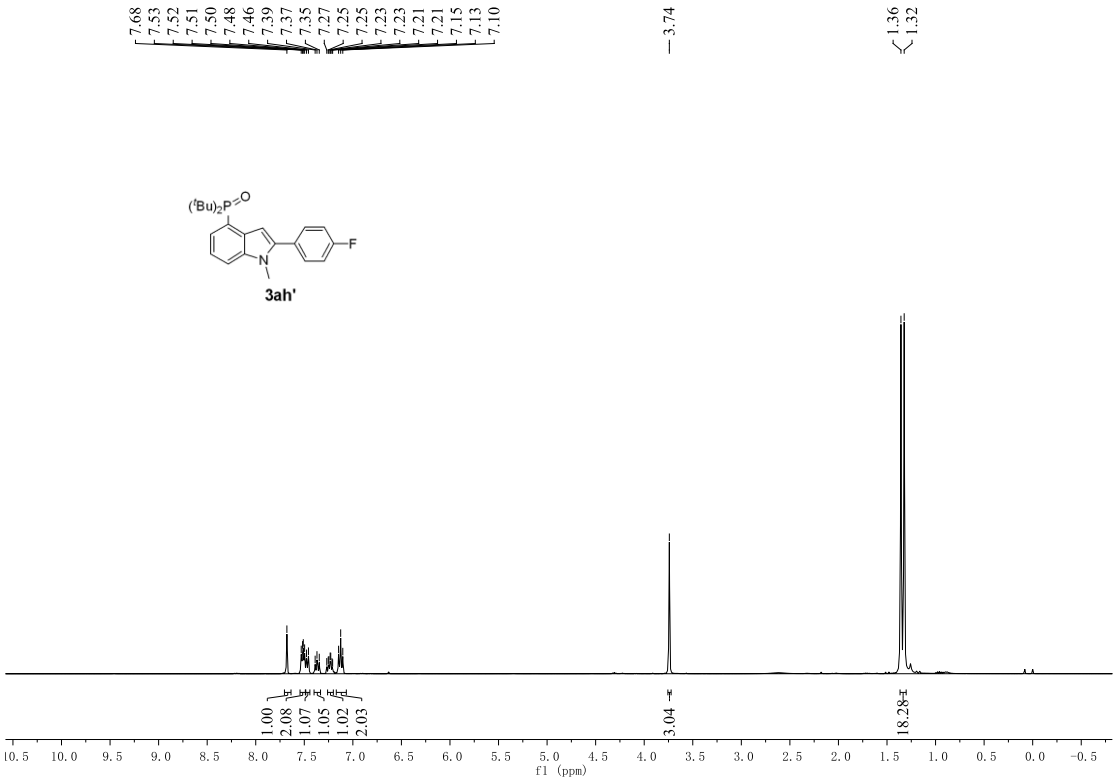
^{31}P NMR spectrum for **3ag'**



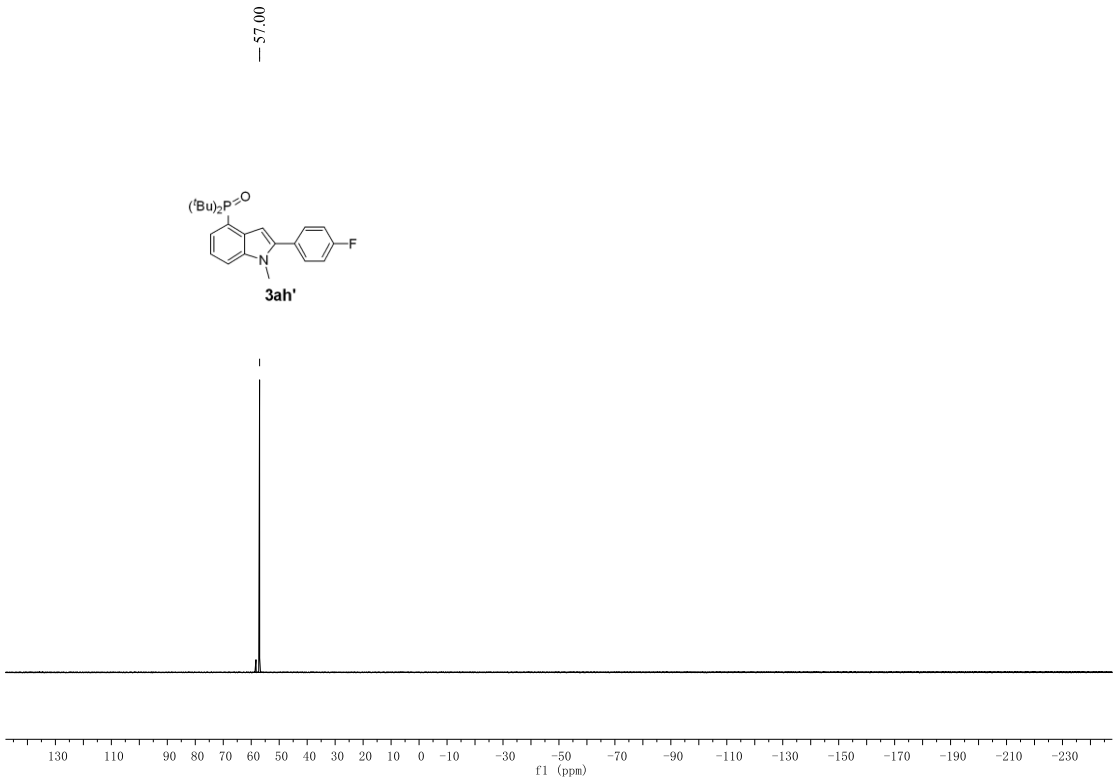
^{31}C NMR spectrum for **3ag'**



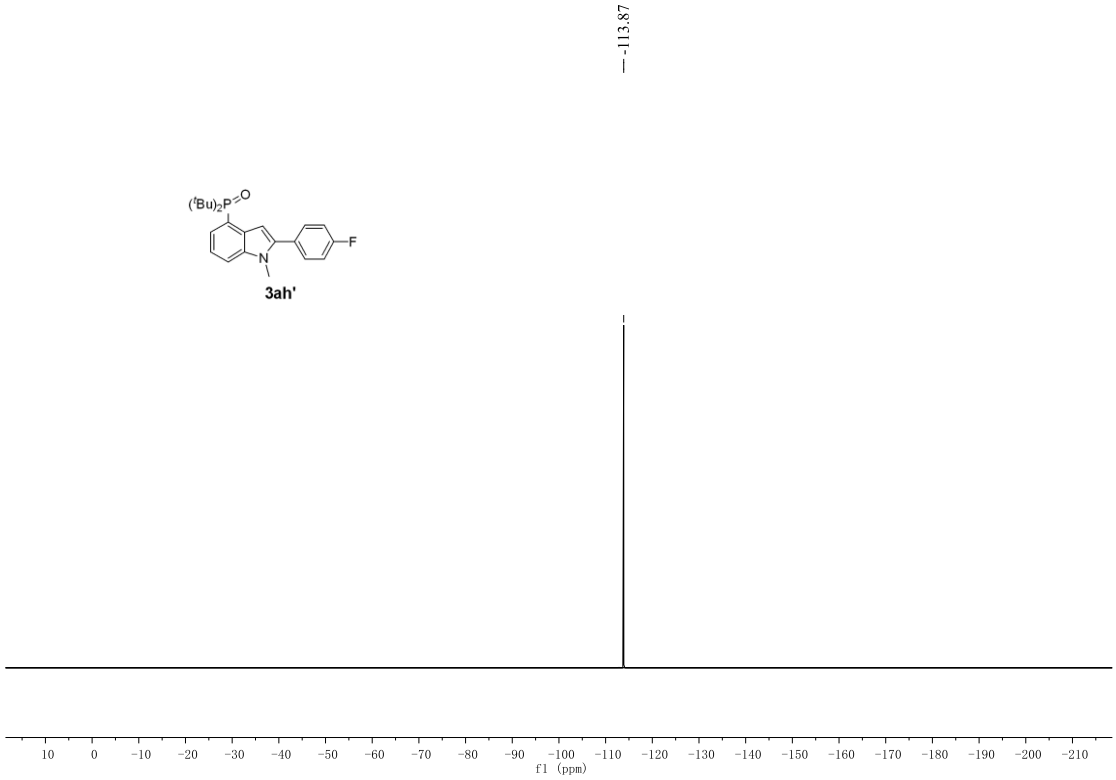
^{1}H NMR spectrum for **3ah'**



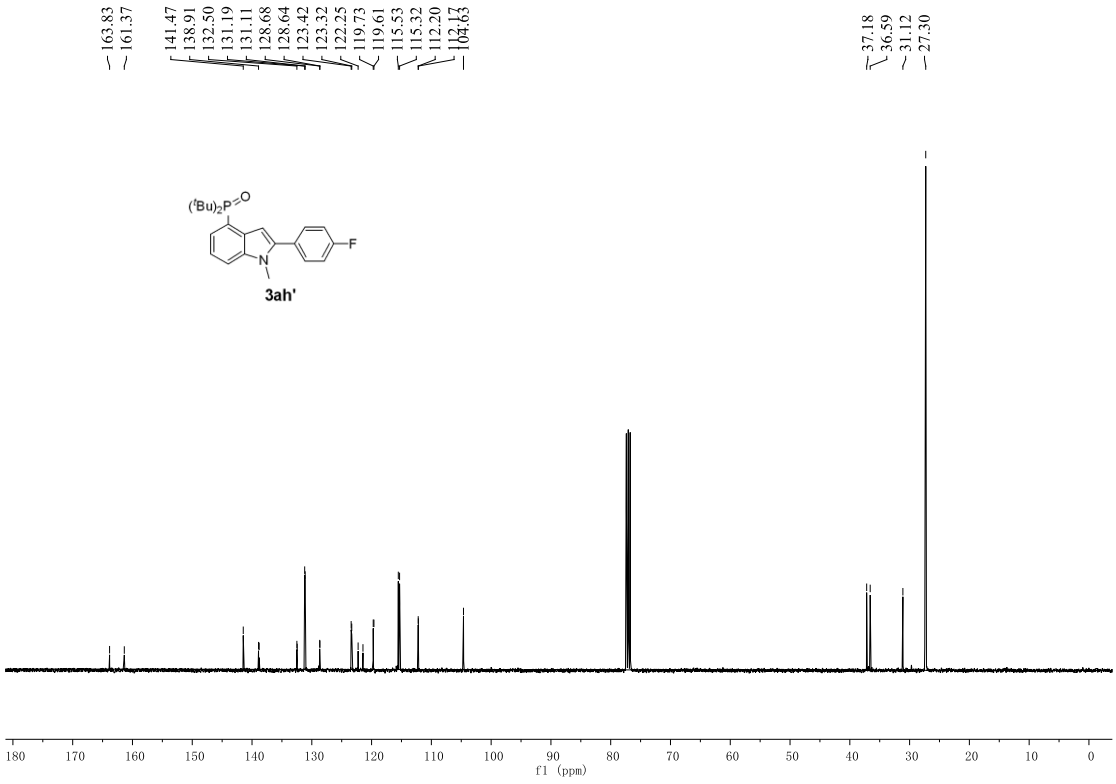
^{31}P NMR spectrum for **3ah'**



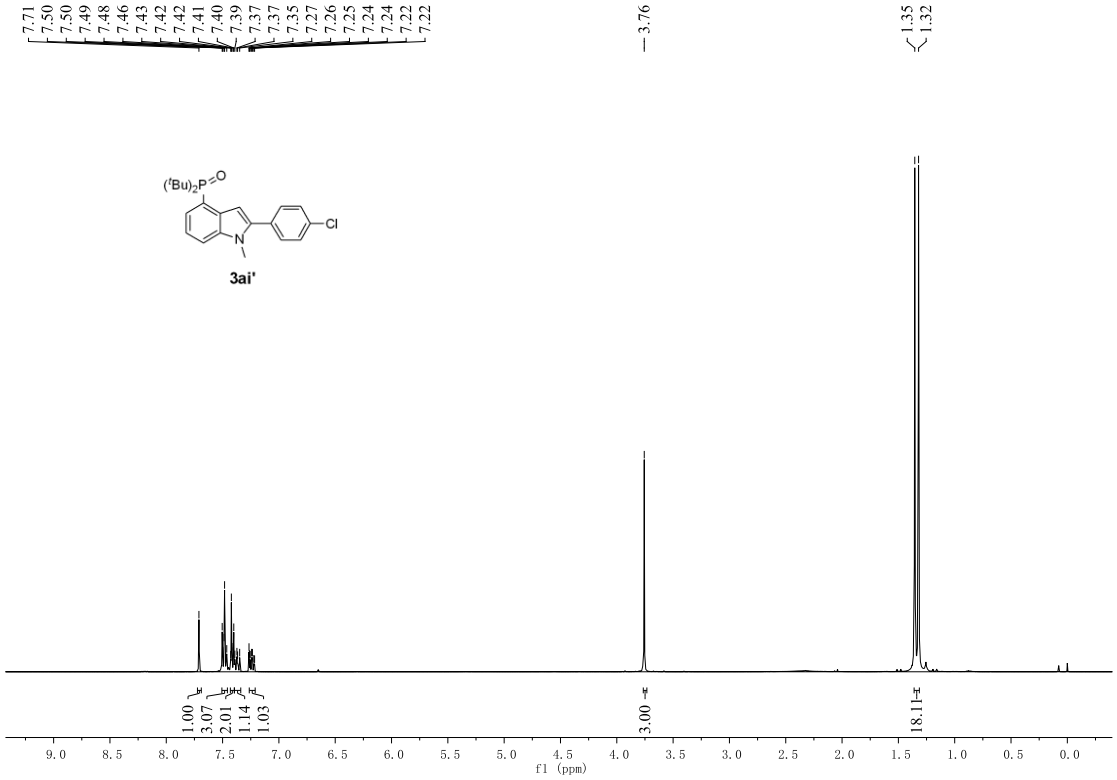
^{19}F NMR spectrum for **3ah'**



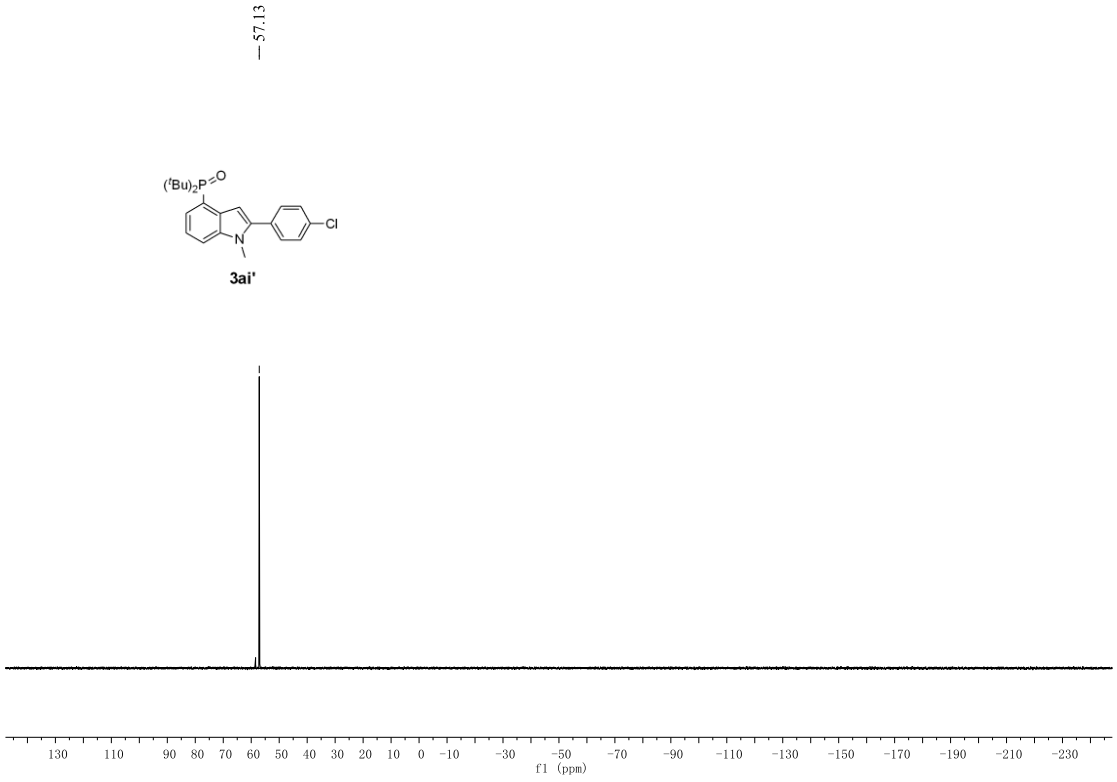
^{13}C NMR spectrum for **3ah'**



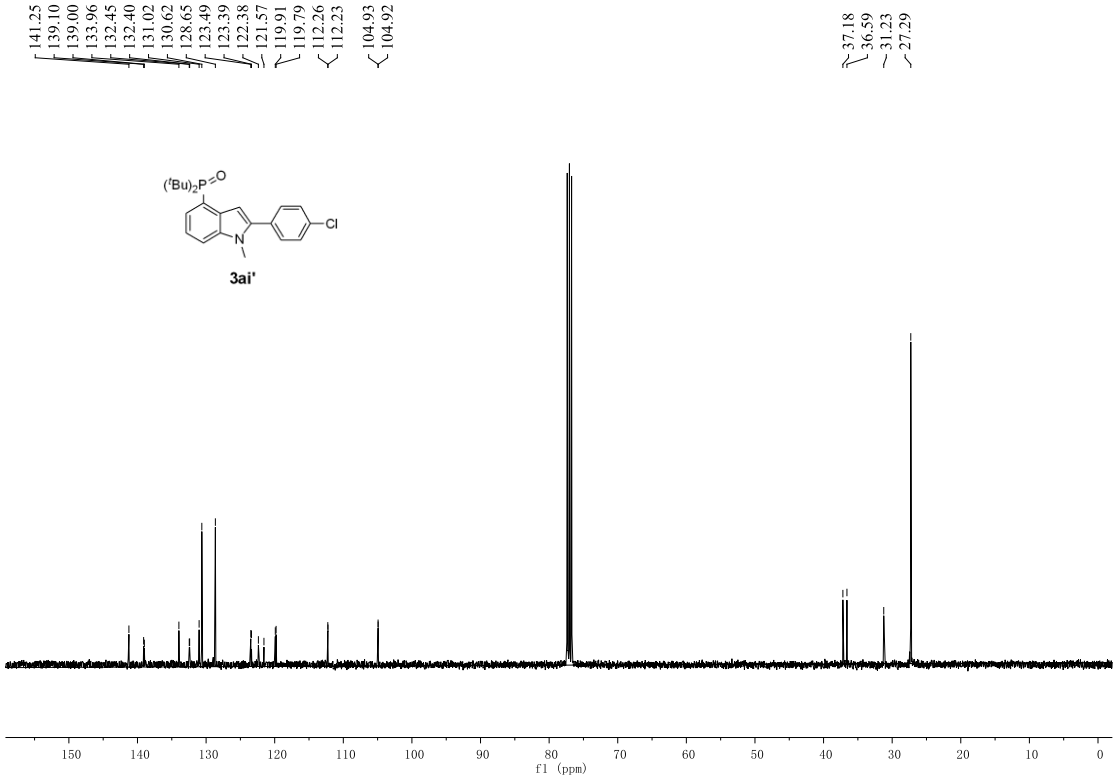
^{1}H NMR spectrum for **3ai'**



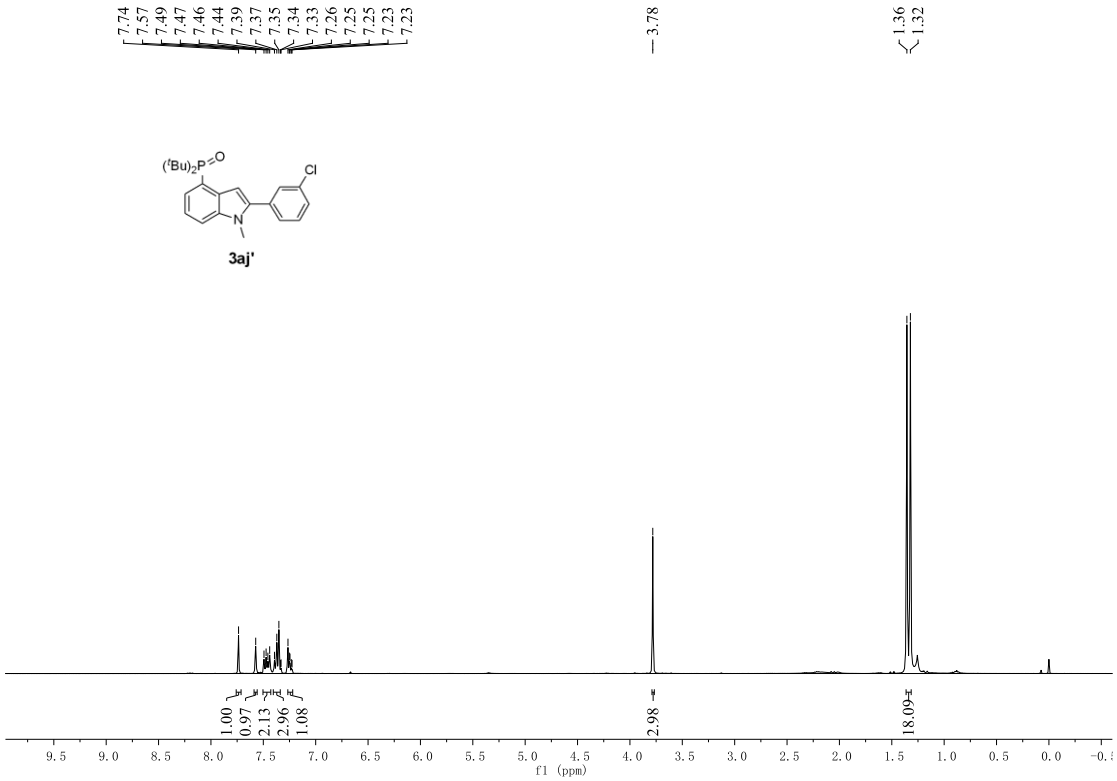
^{31}P NMR spectrum for **3ai'**



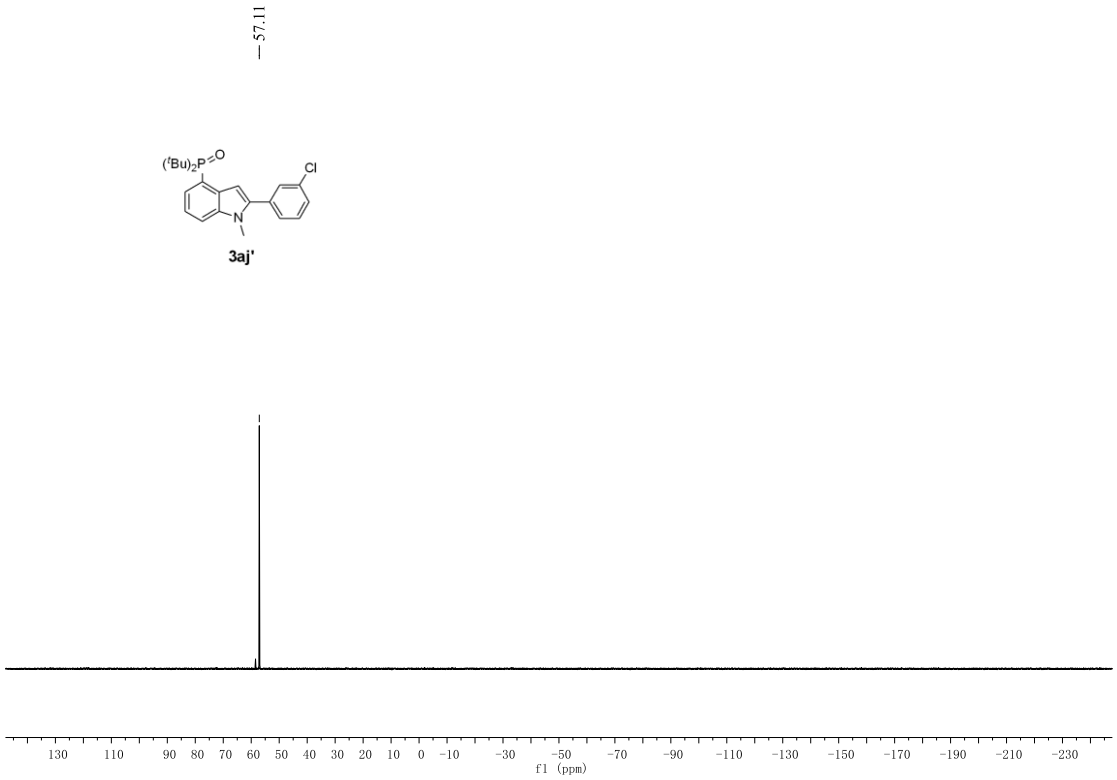
^{13}C NMR spectrum for **3ai'**



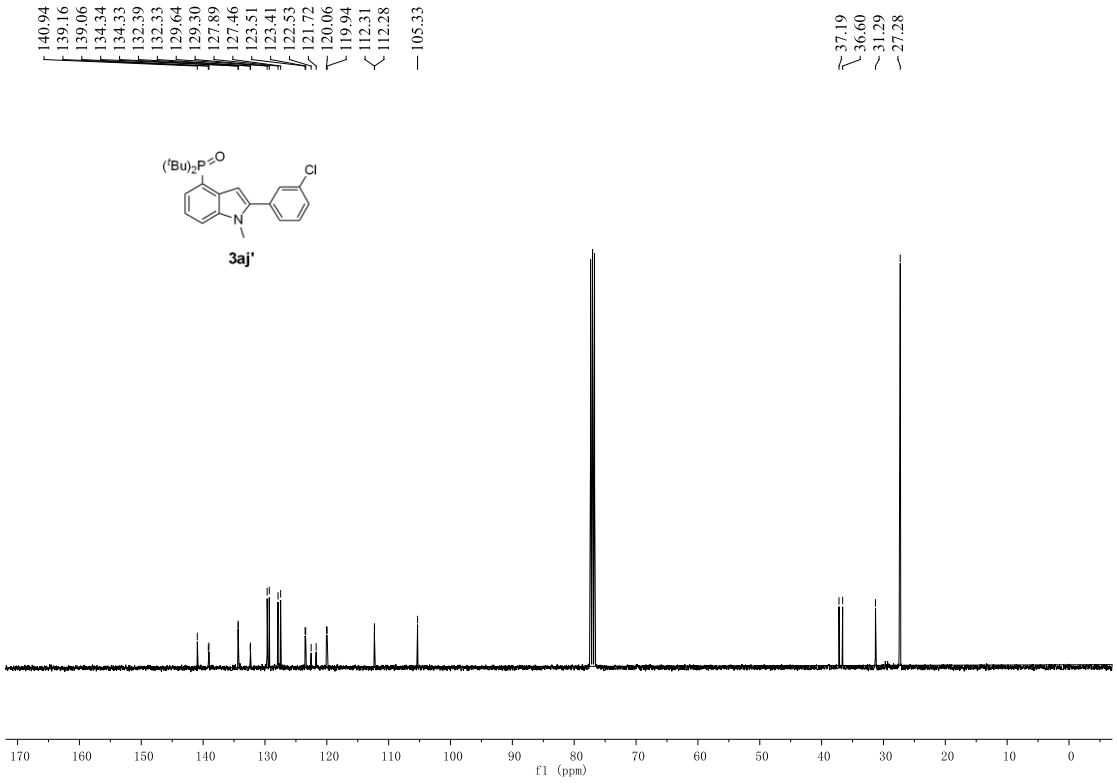
^{1}H NMR spectrum for **3aj'**



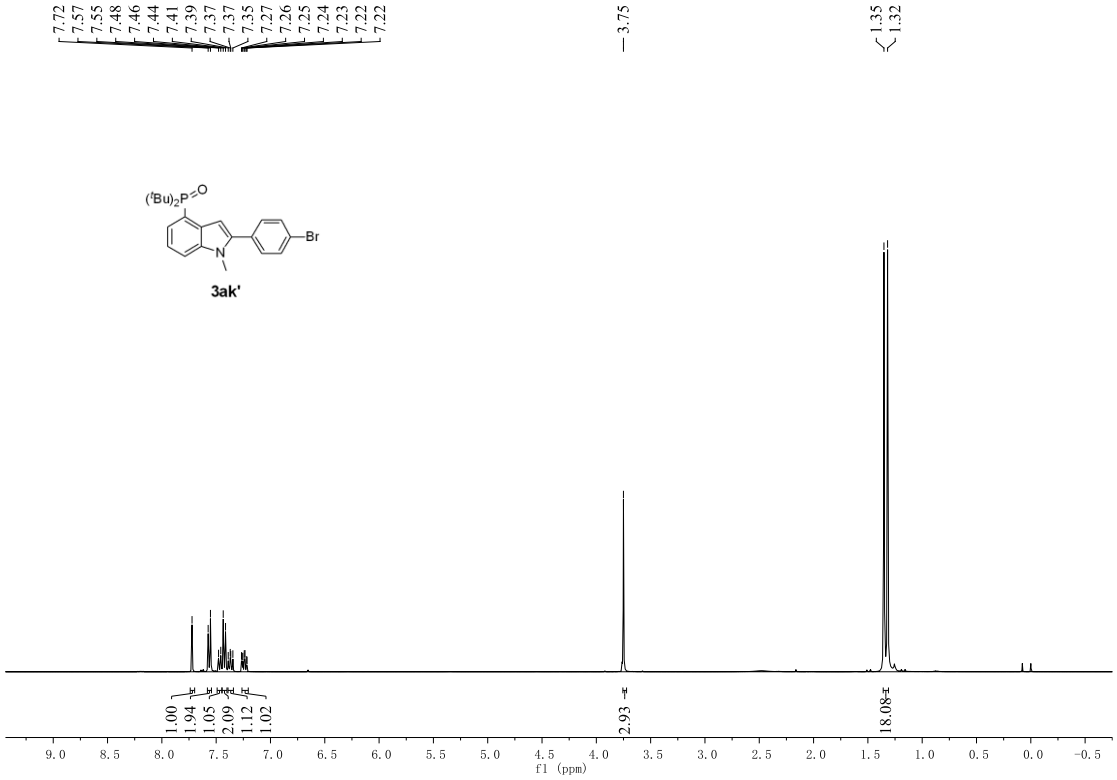
^{31}P NMR spectrum for **3aj'**



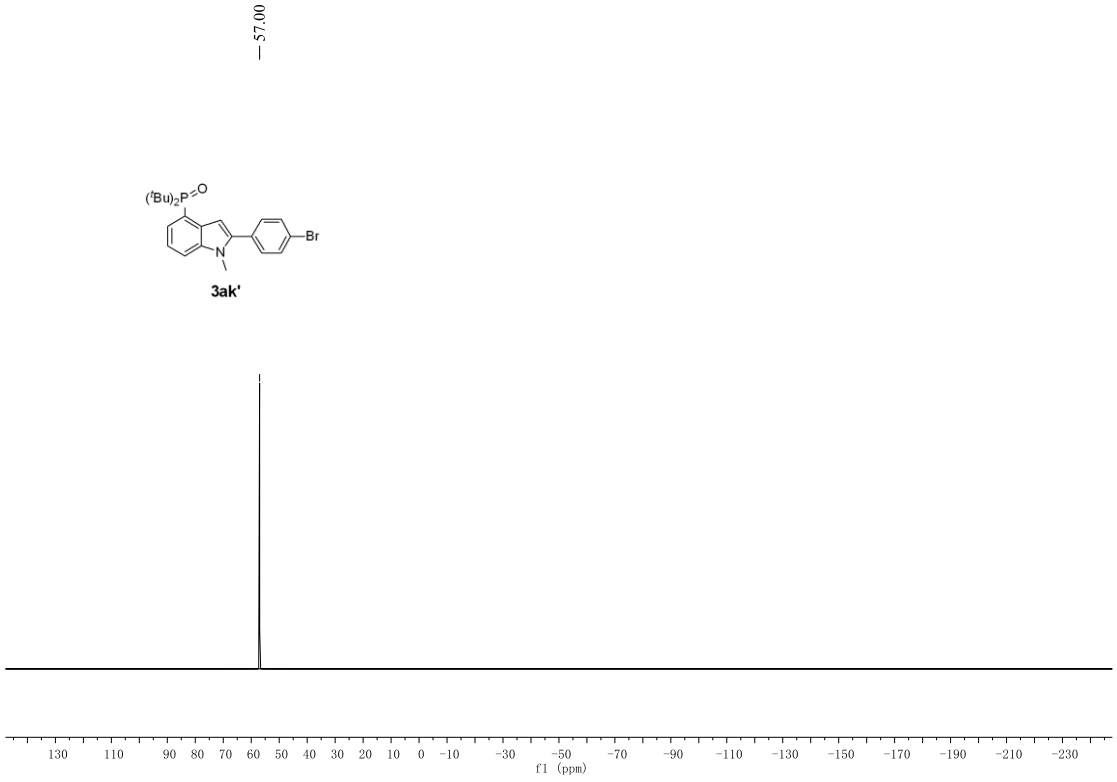
^{13}C NMR spectrum for **3aj'**



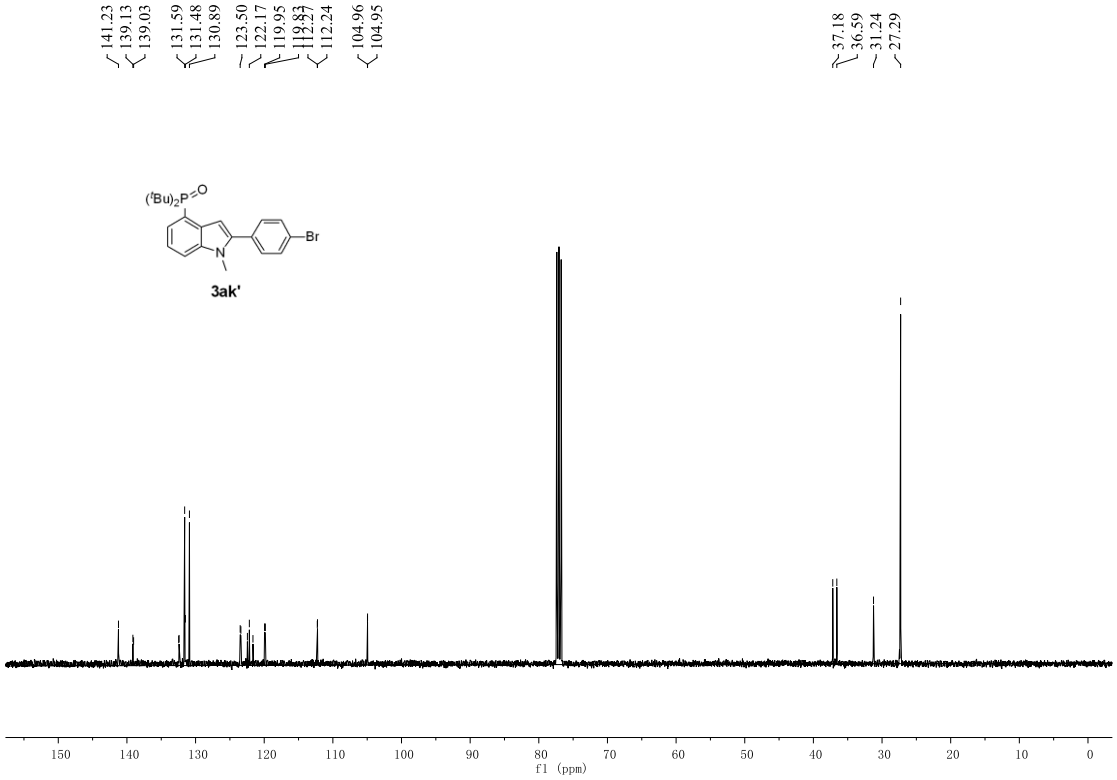
^{1}H NMR spectrum for **3ak'**



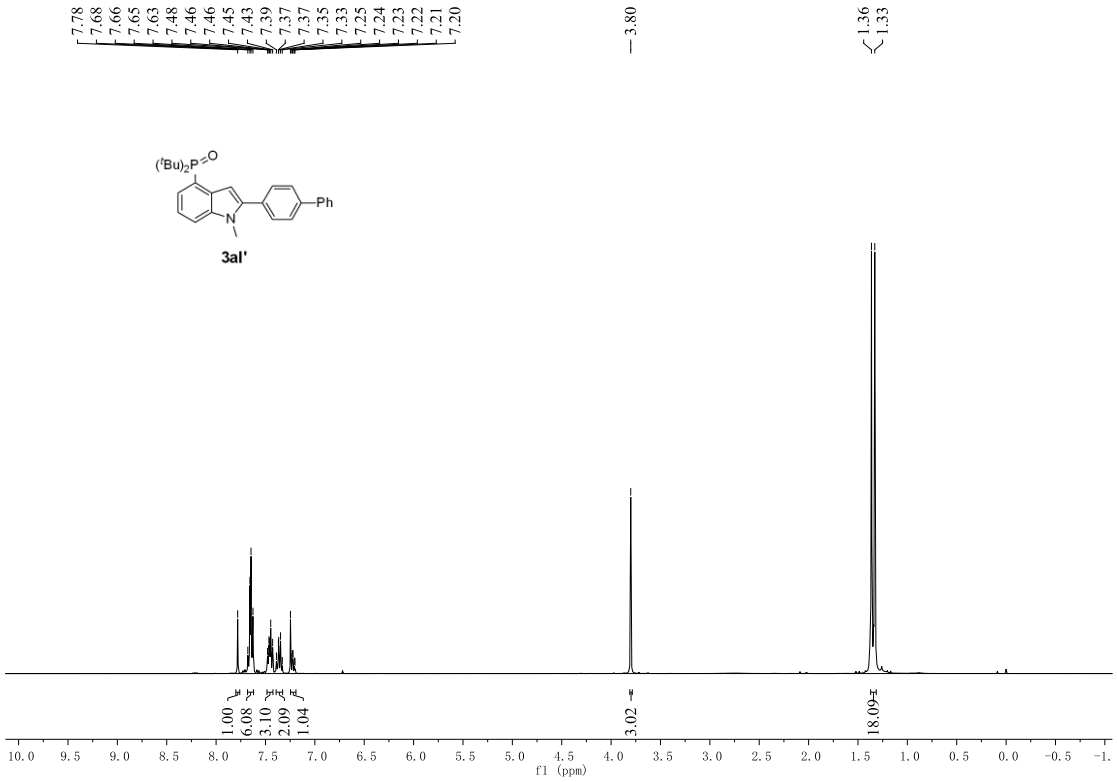
^{31}P NMR spectrum for **3ak'**



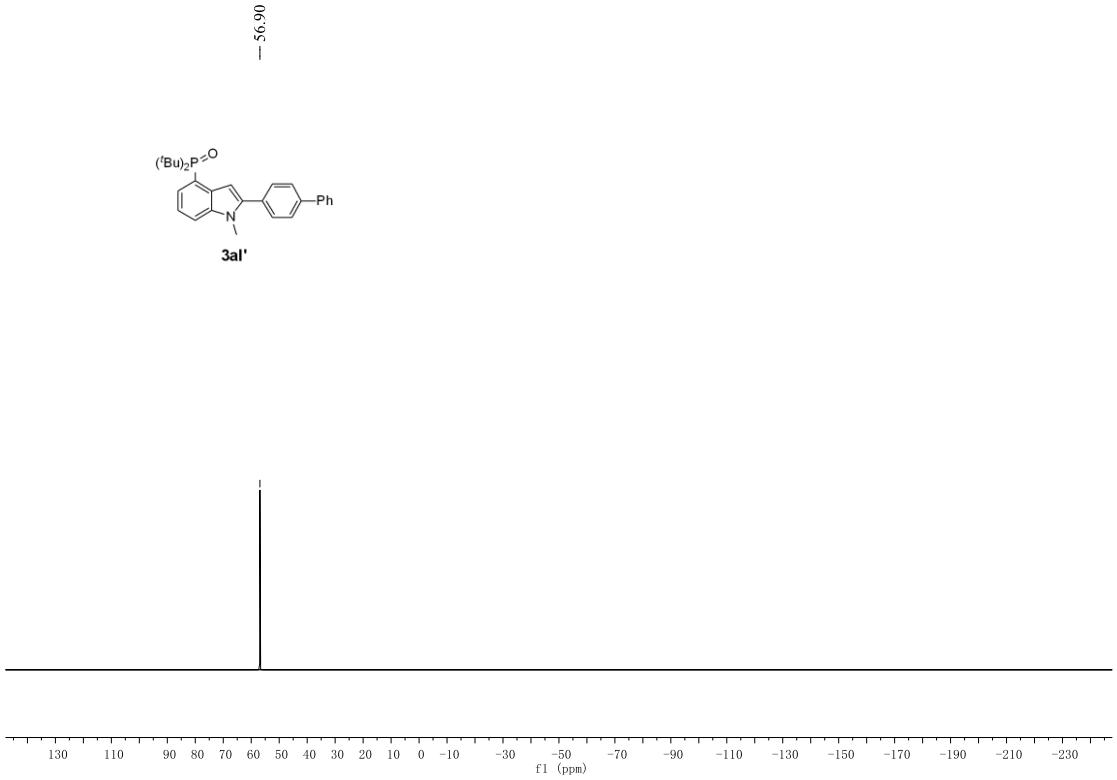
^{13}C NMR spectrum for **3ak'**



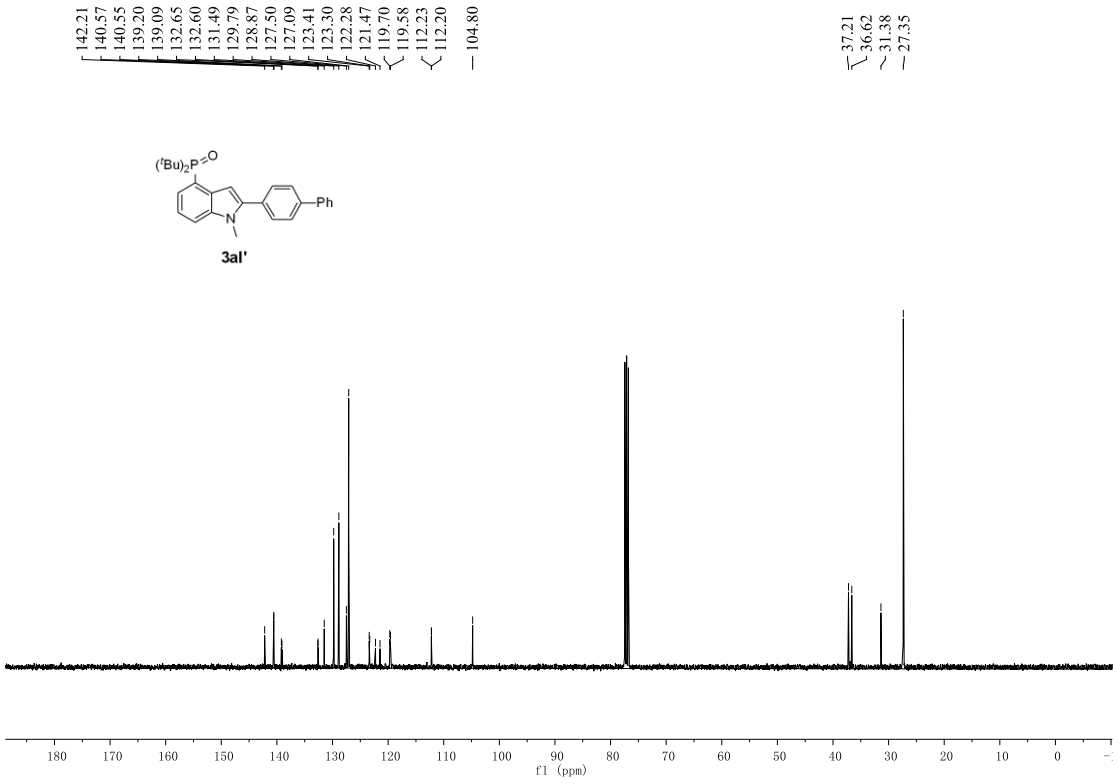
^{1}H NMR spectrum for **3al'**



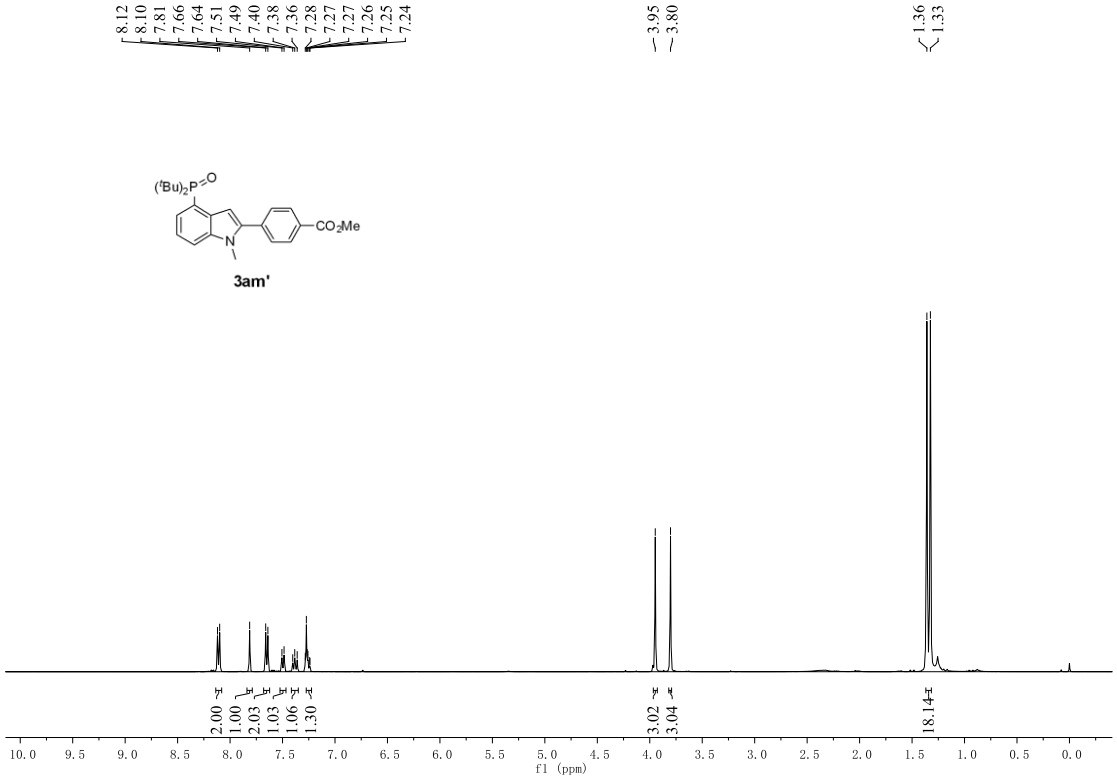
^{31}P NMR spectrum for **3al'**



^{13}C NMR spectrum for **3al'**



^{1}H NMR spectrum for **3am'**



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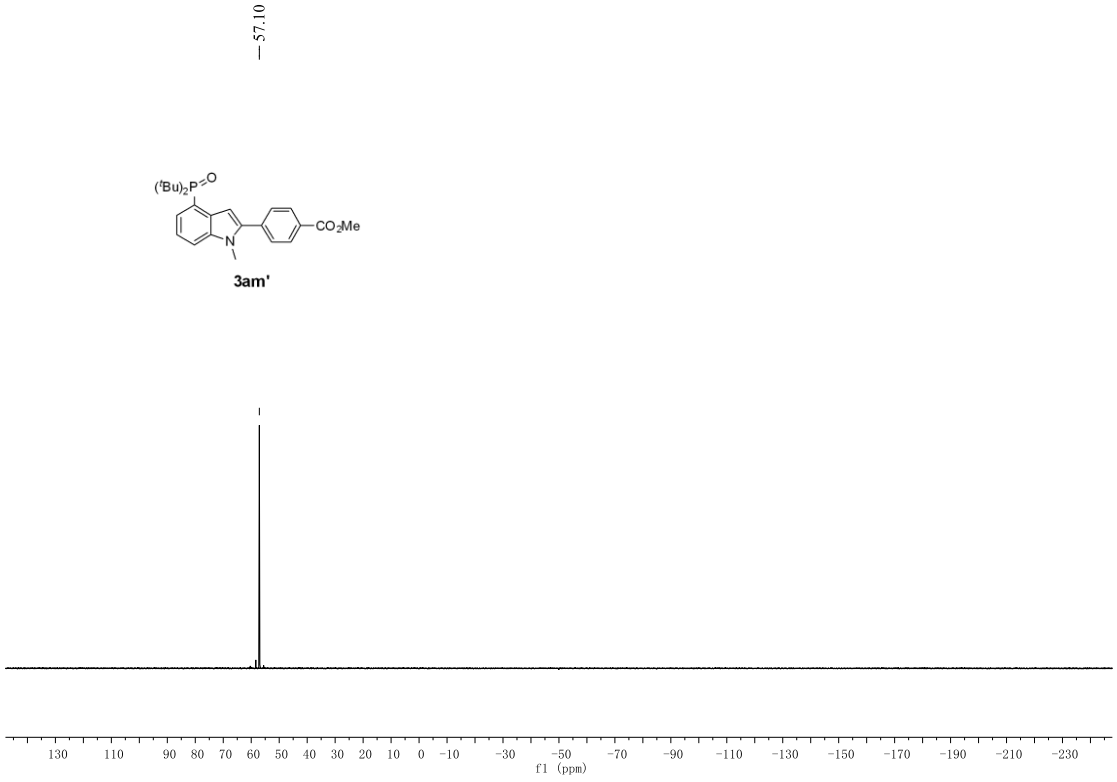
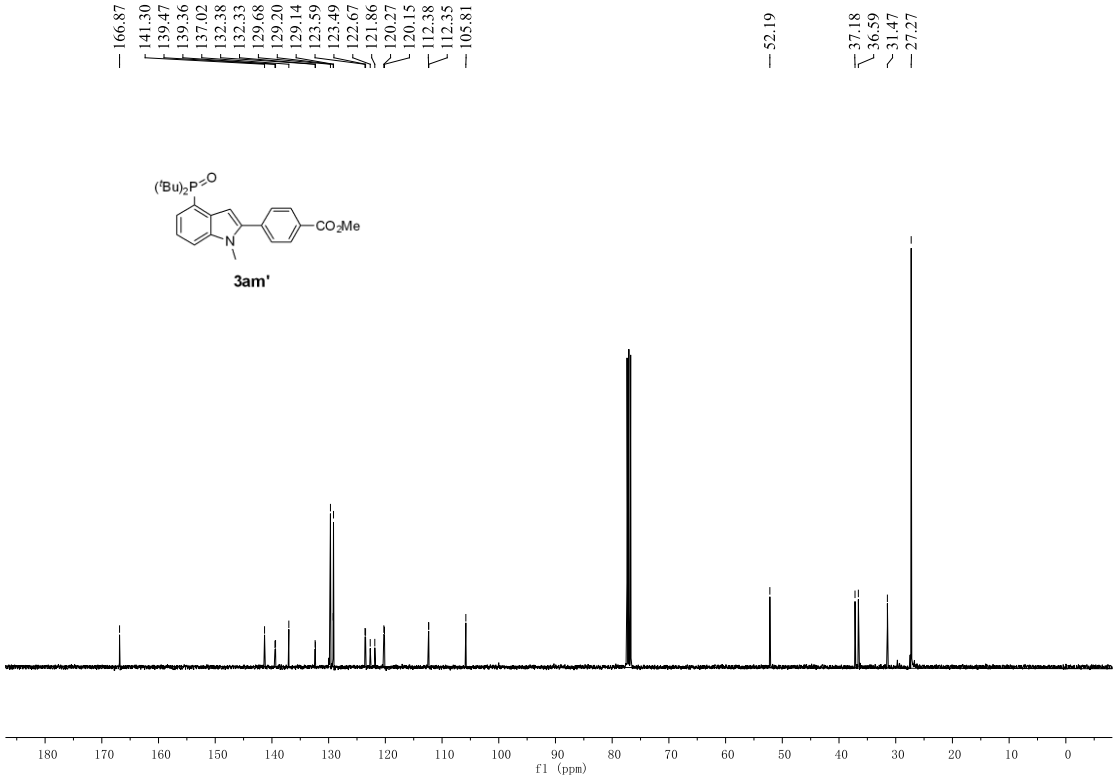
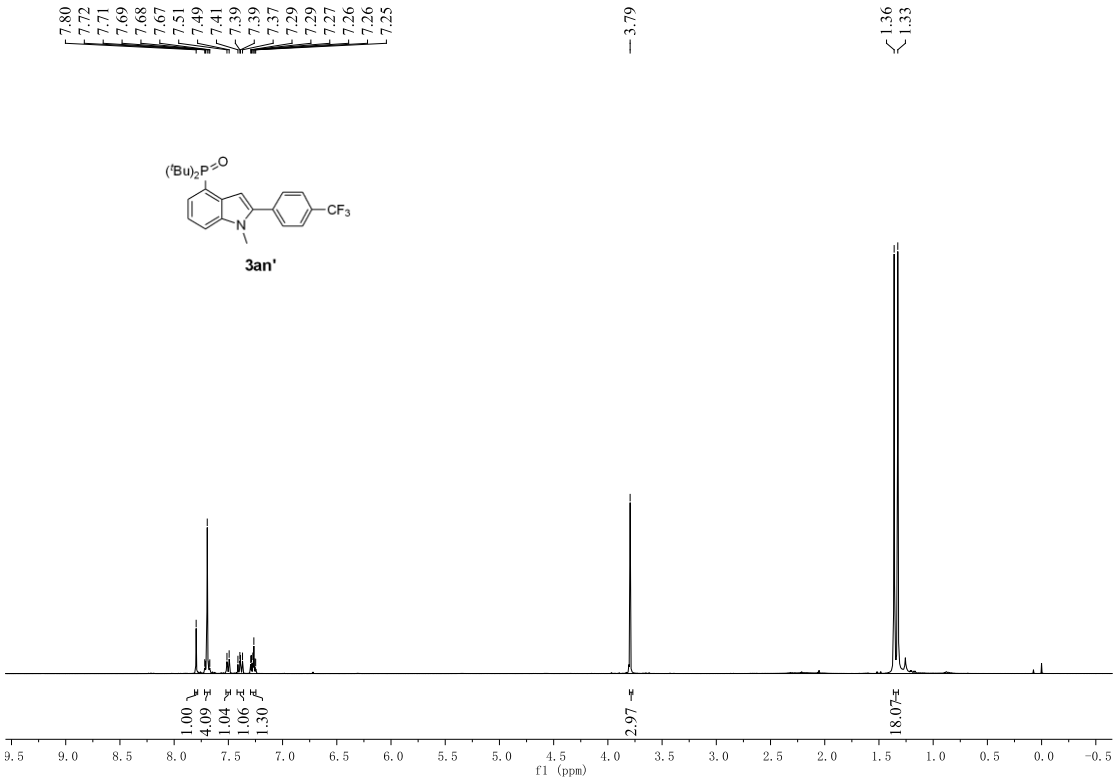


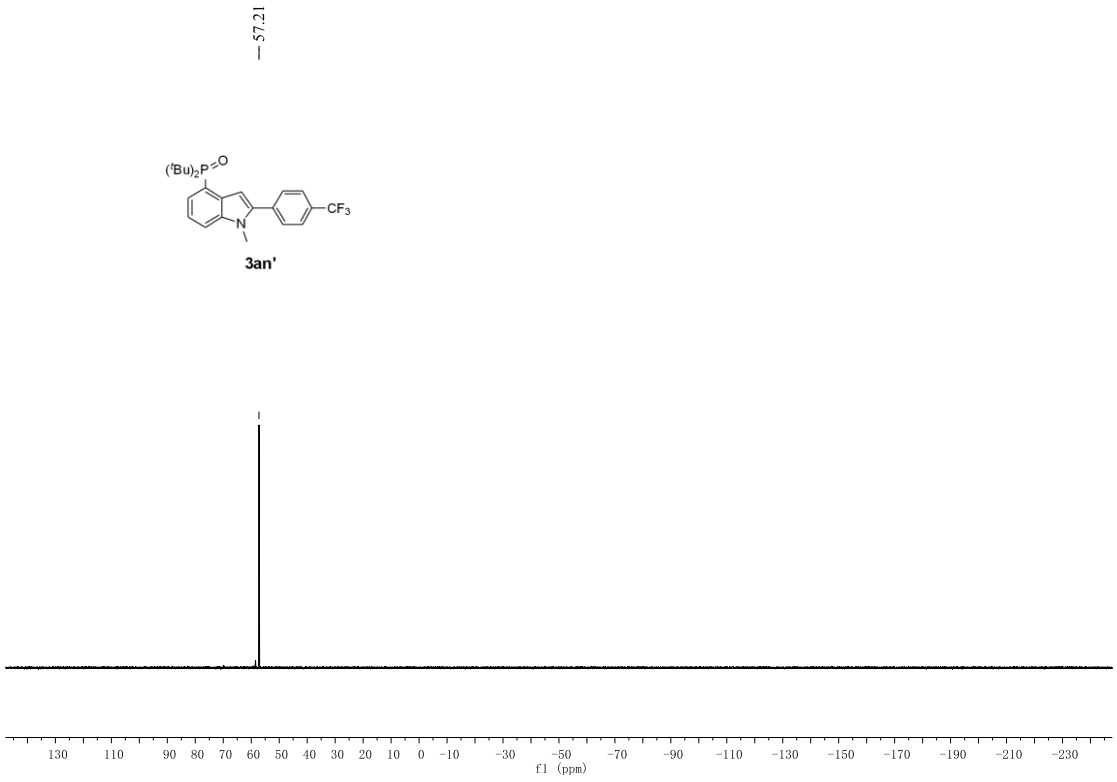
^{13}C NMR spectrum for **3am'**



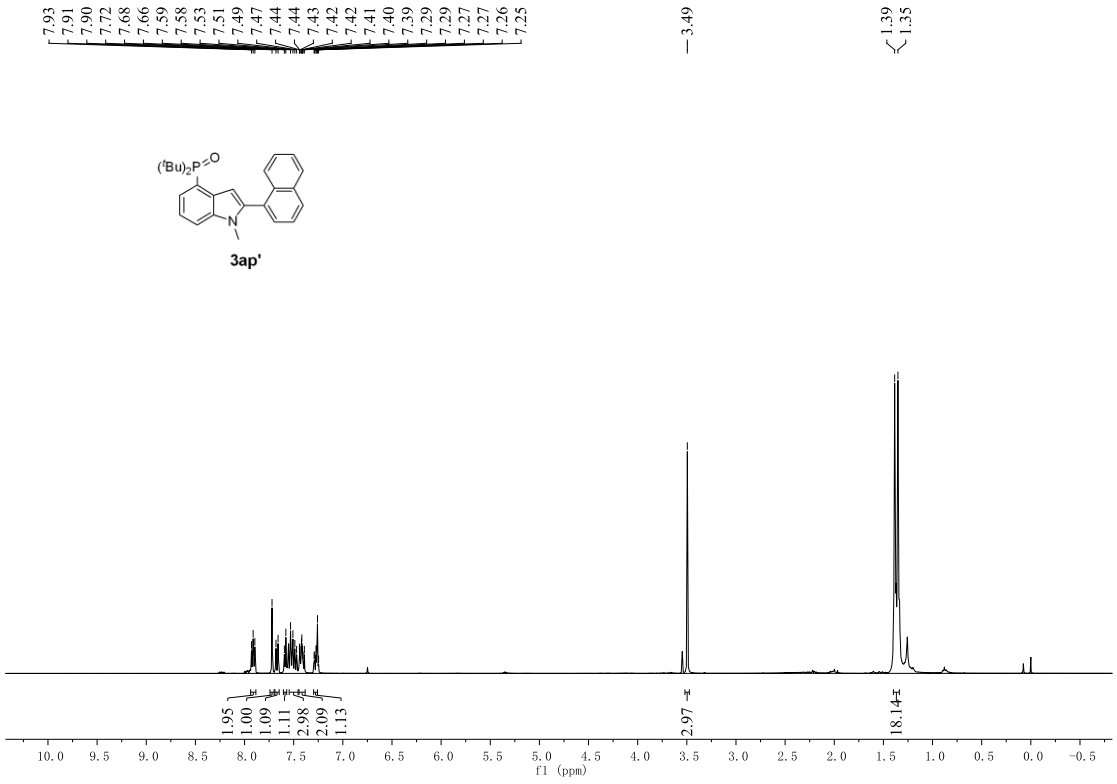
^{1}H NMR spectrum for **3an'**



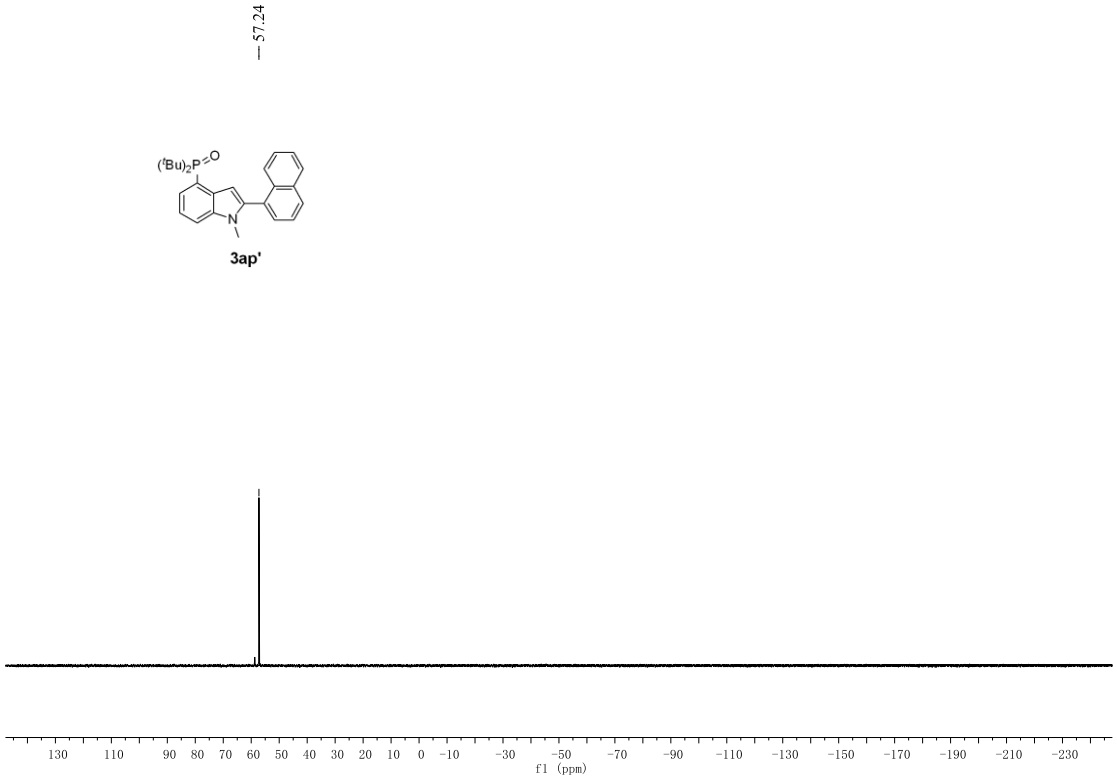
^{31}P NMR spectrum for **3an'**



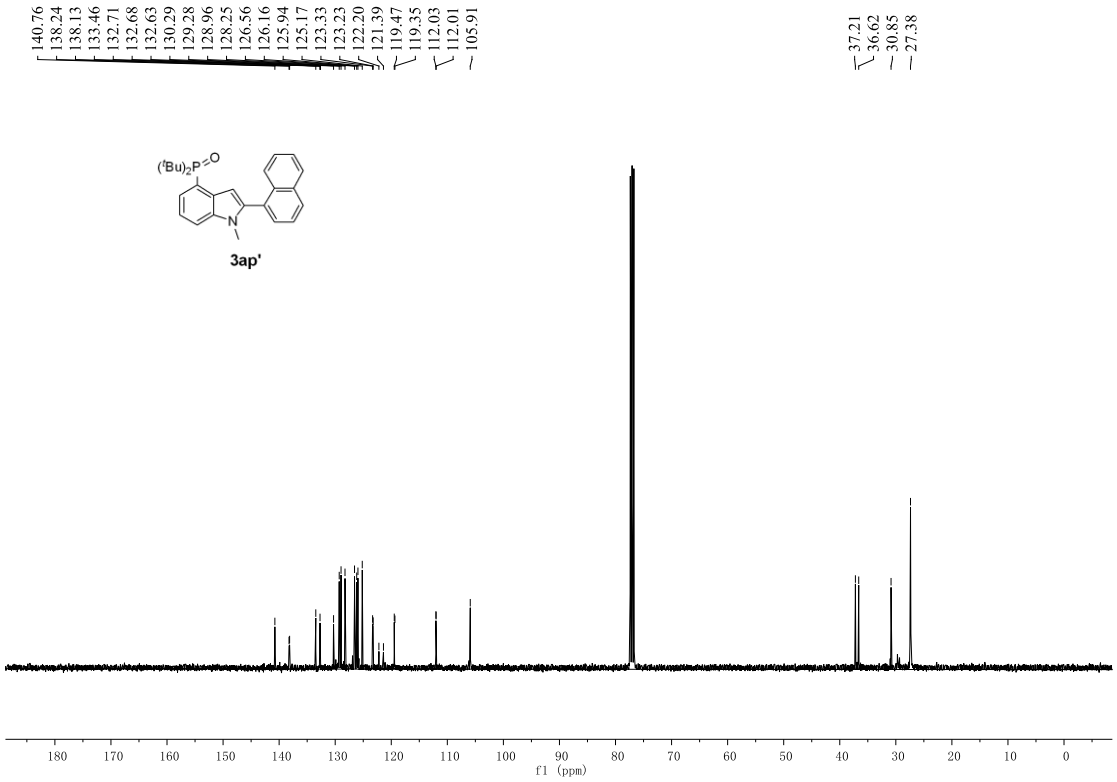
^{1}H NMR spectrum for **3ap'**



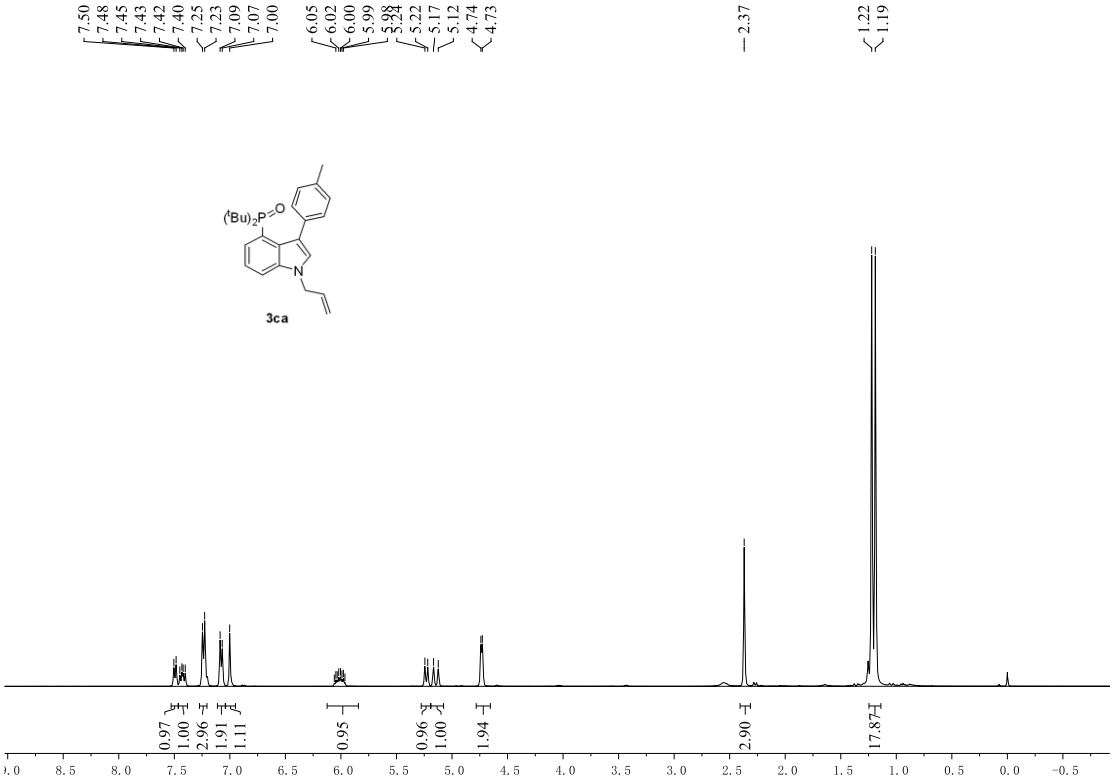
^{31}P NMR spectrum for **3ap'**



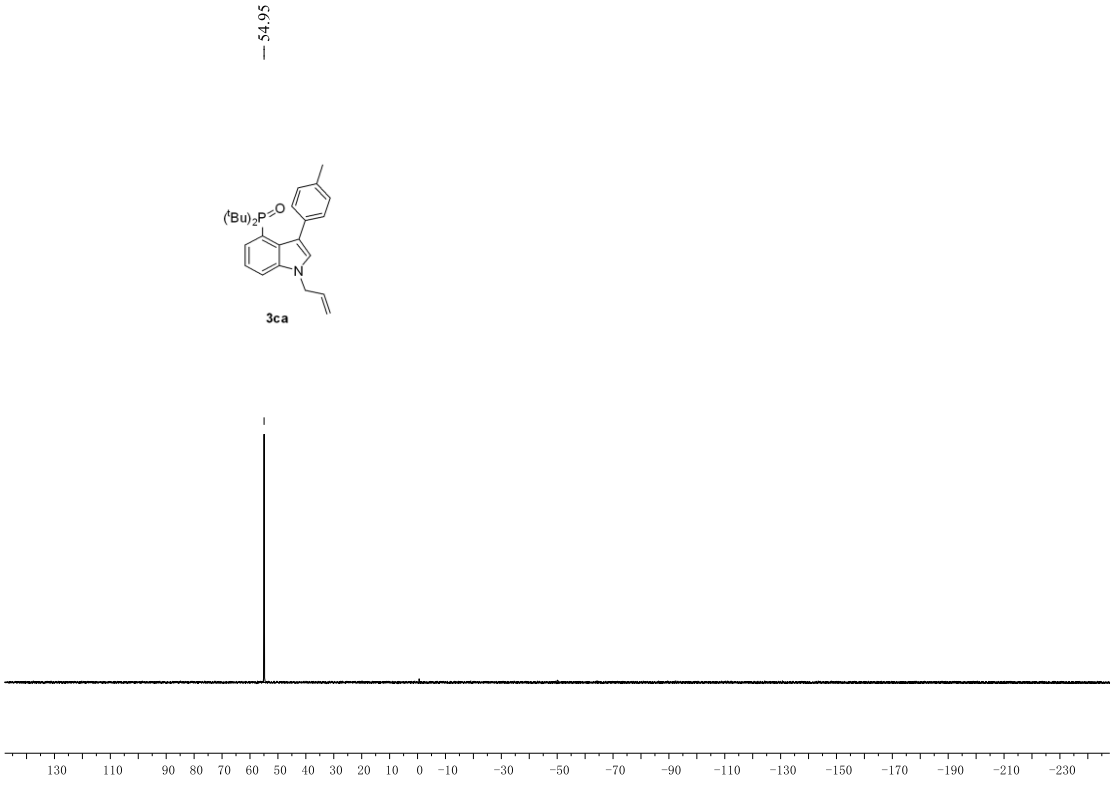
^{13}C NMR spectrum for **3ap'**



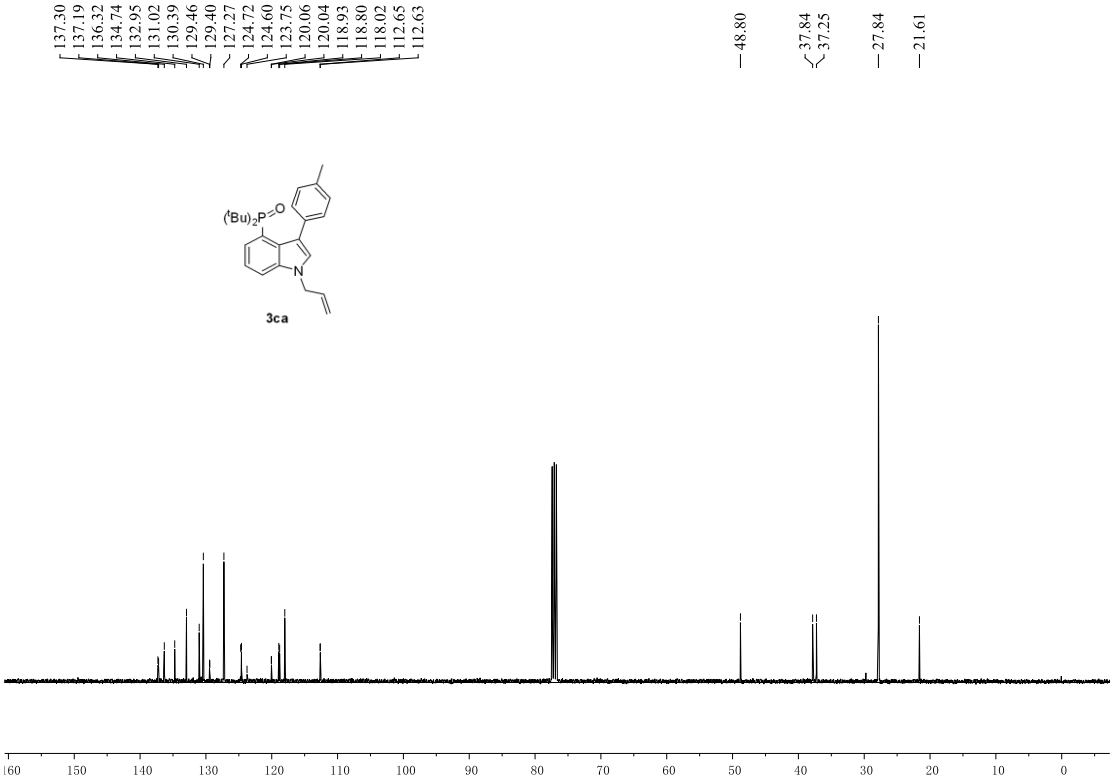
^{1}H NMR spectrum for **3ca**



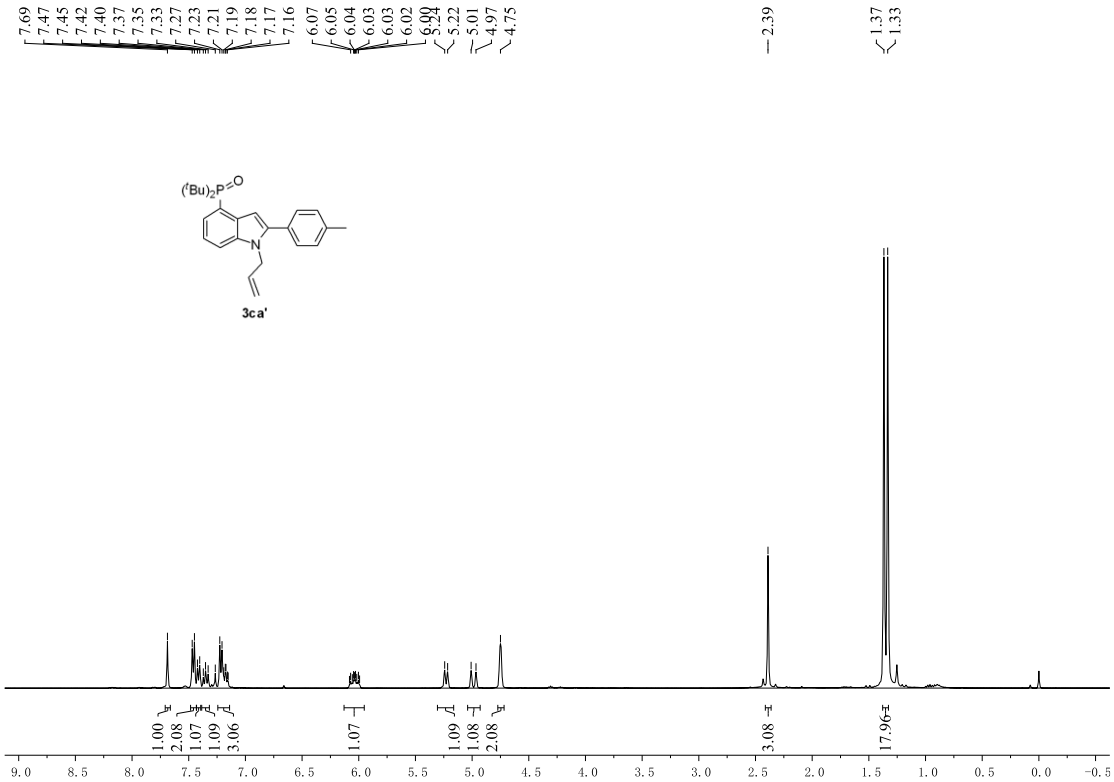
^{31}P NMR spectrum for **3ca**



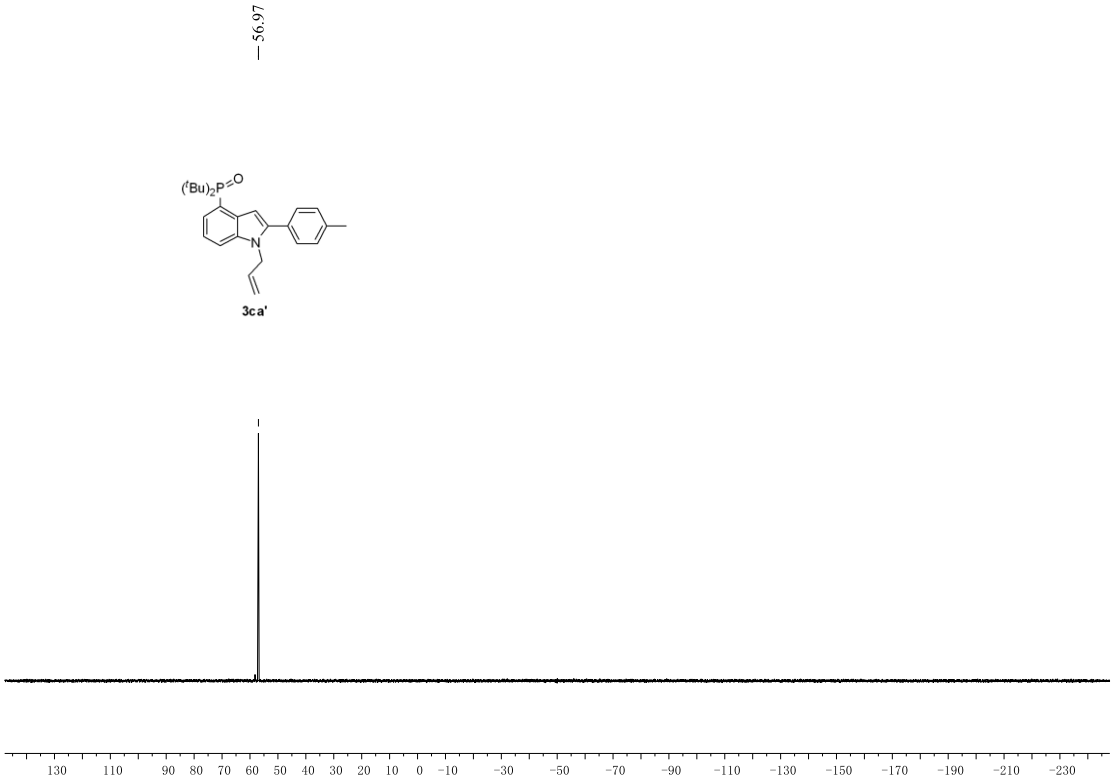
^{13}C NMR spectrum for **3ca**



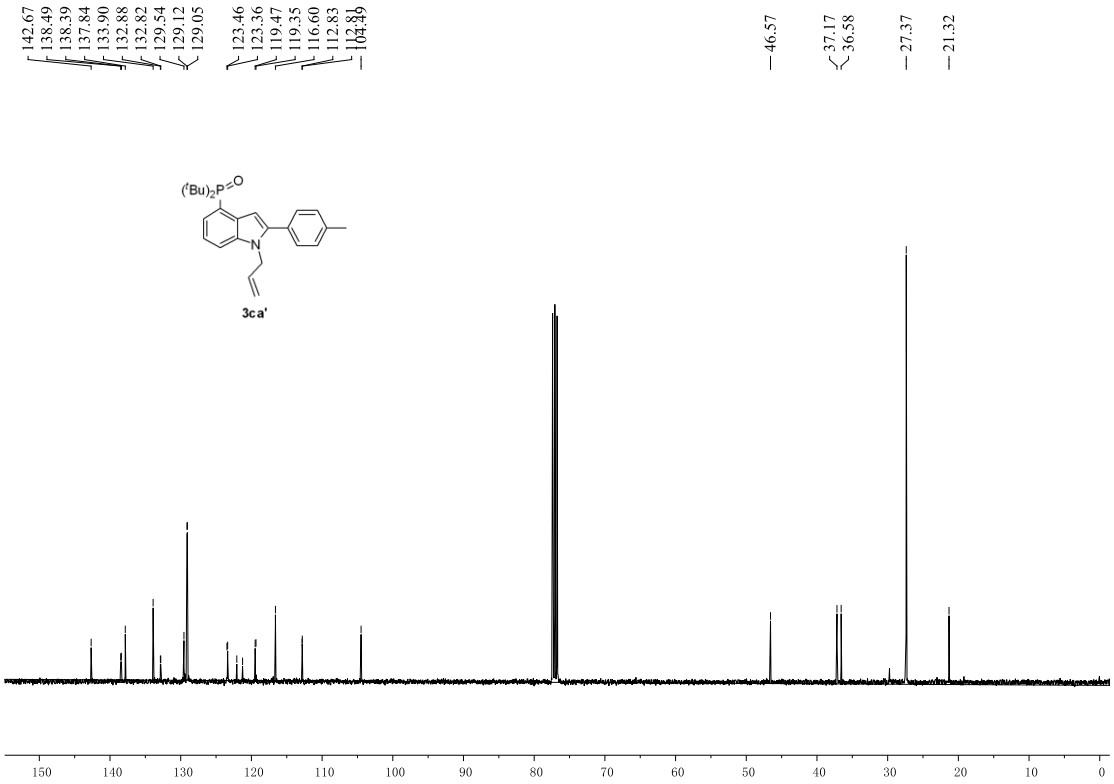
^{1}H NMR spectrum for **3ca'**



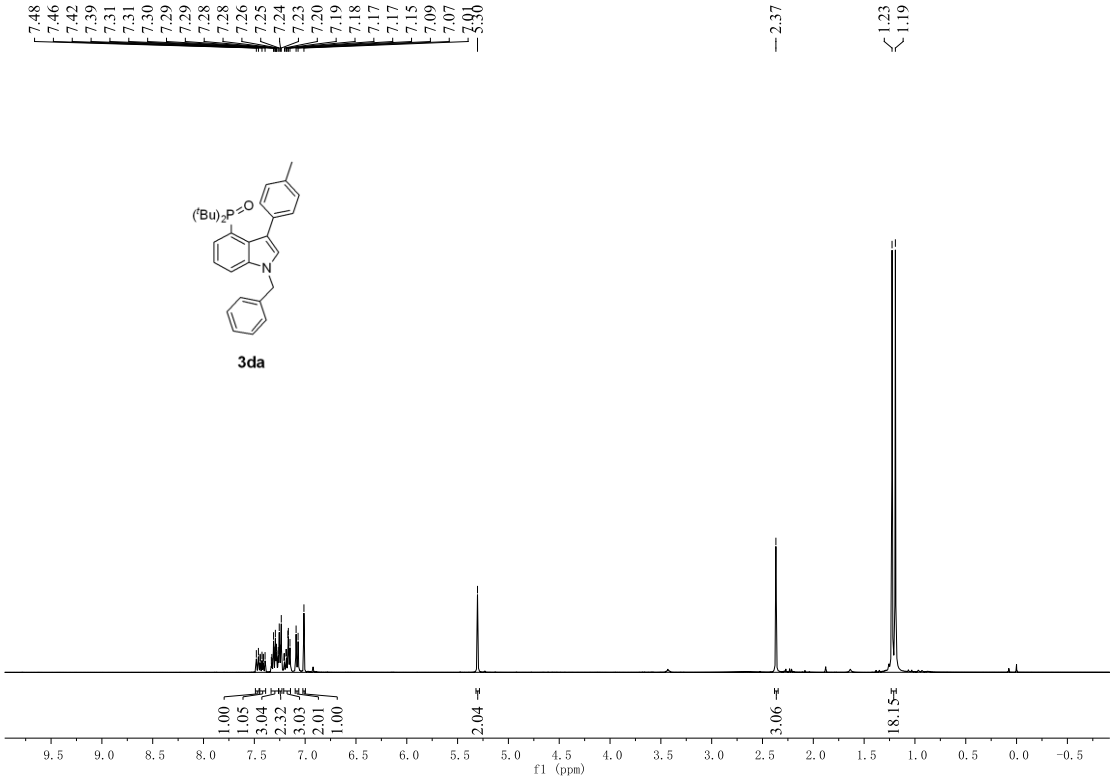
^{31}P NMR spectrum for **3ca'**



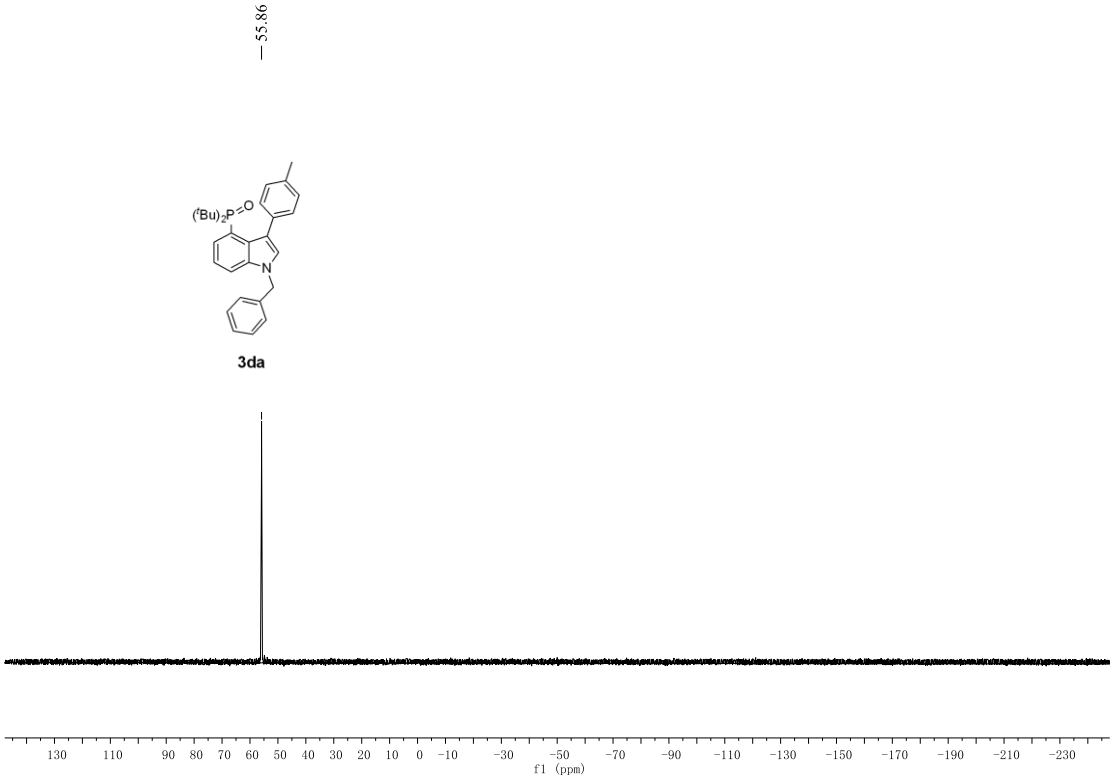
^{13}C NMR spectrum for **3ca'**



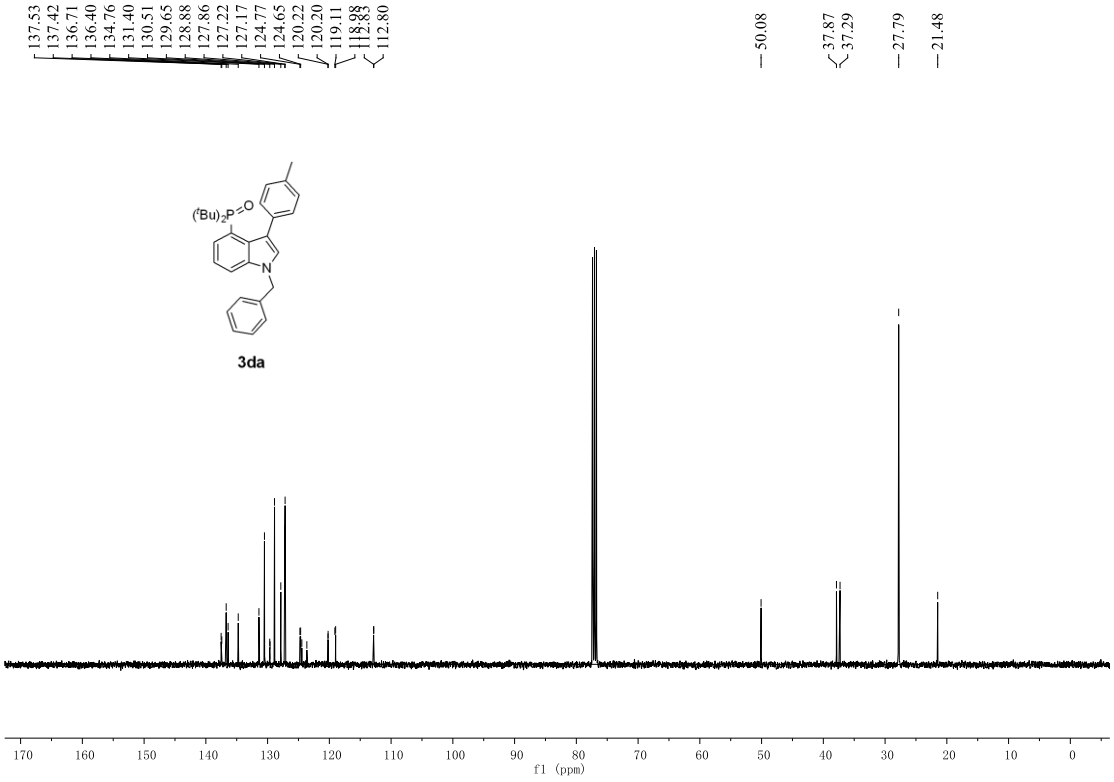
^{1}H NMR spectrum for **3da**



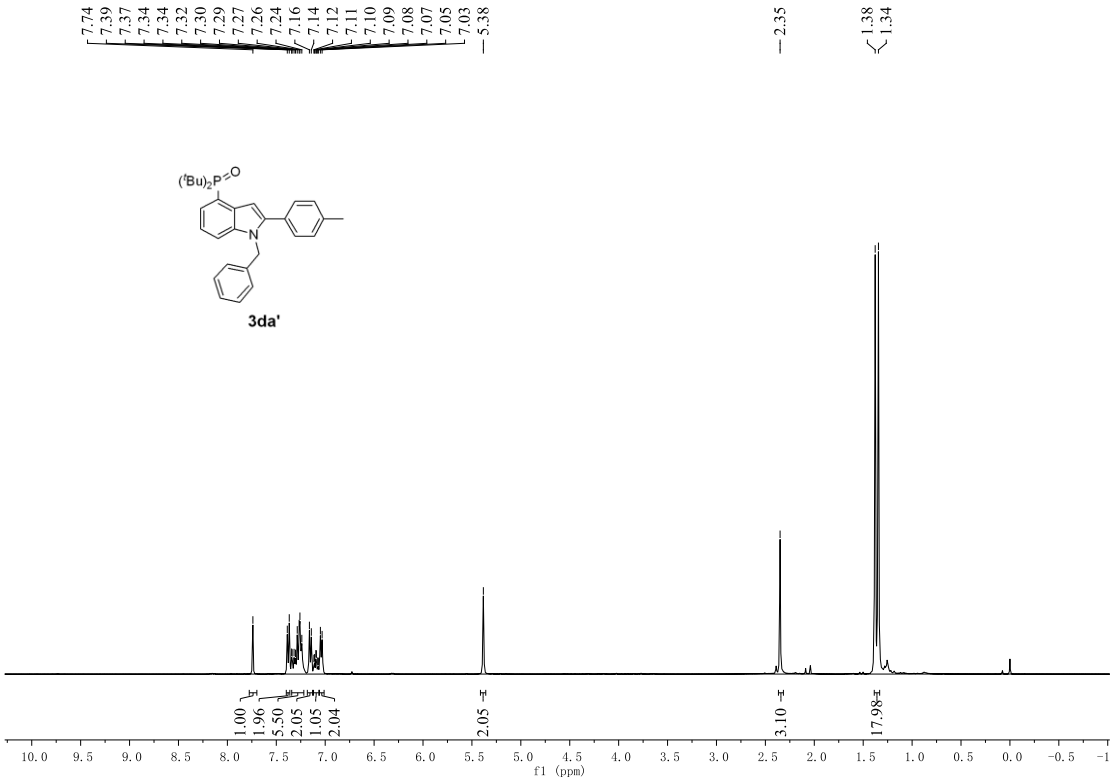
^{31}P NMR spectrum for **3da**



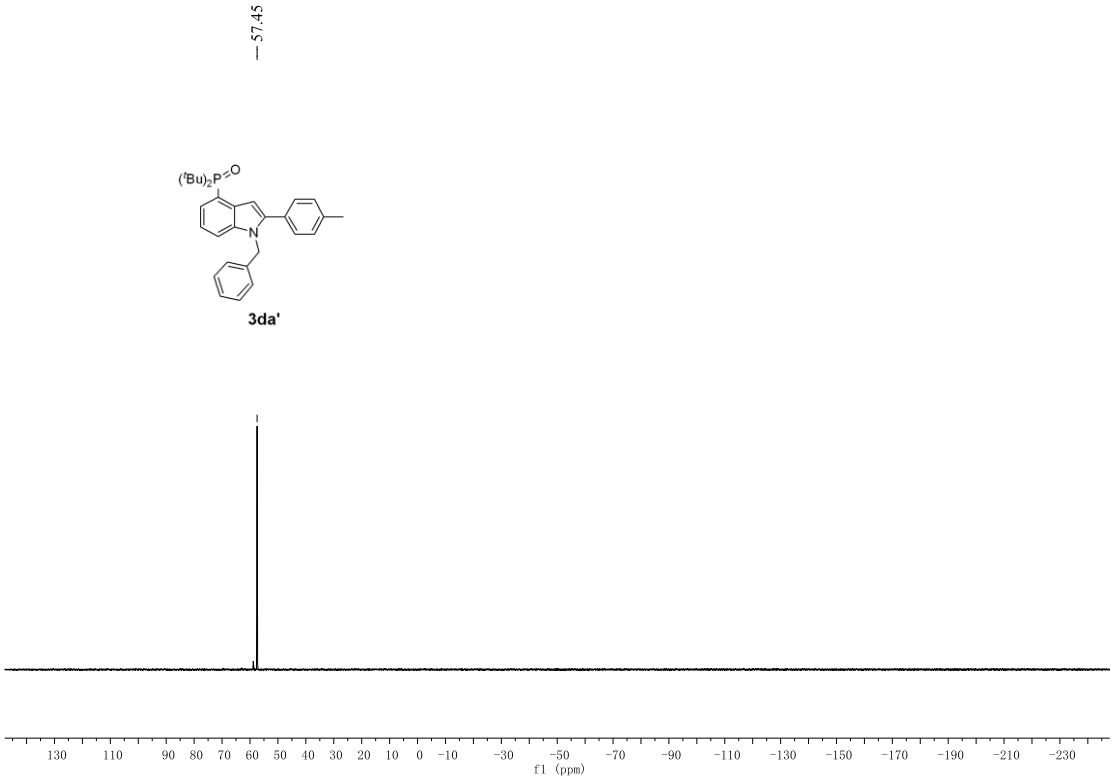
^{13}C NMR spectrum for **3da**



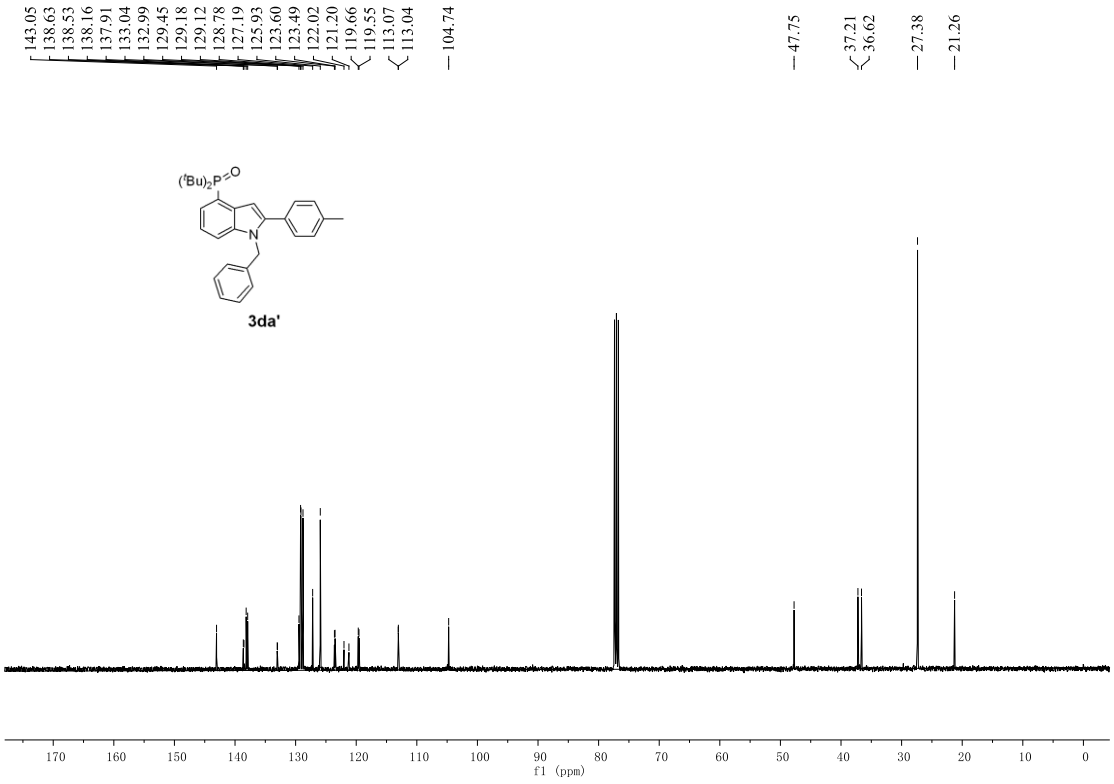
^{1}H NMR spectrum for **3da'**



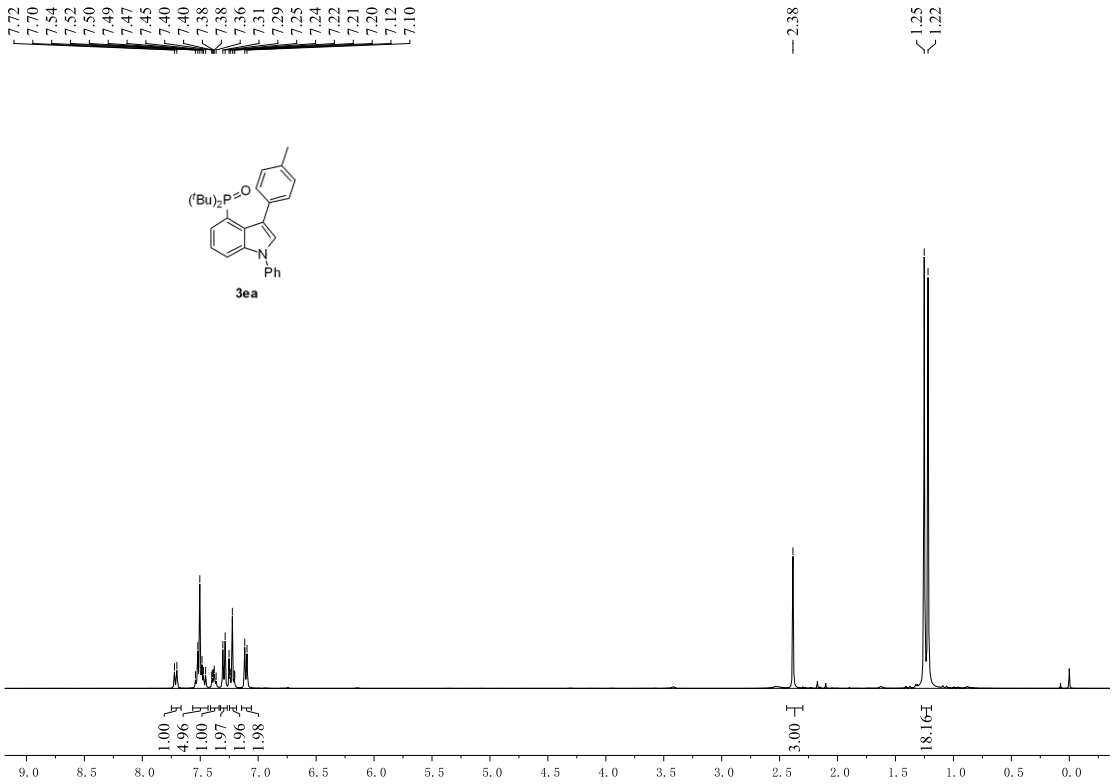
^{31}P NMR spectrum for **3da'**



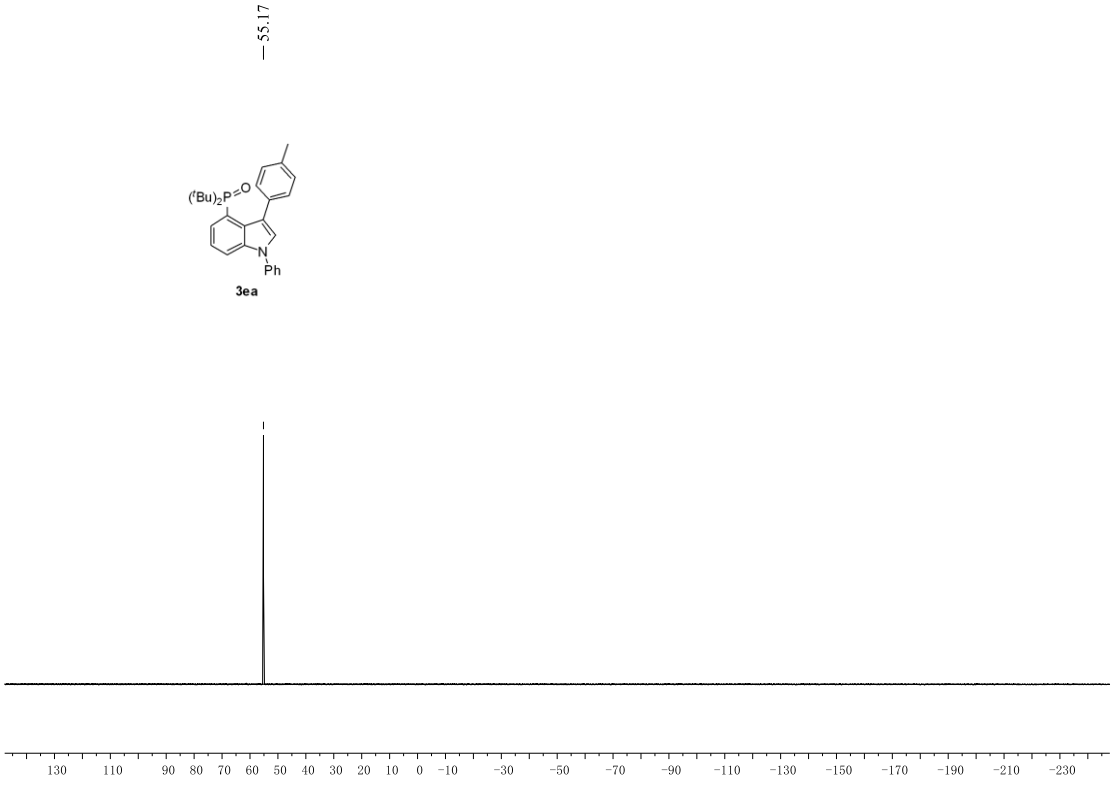
^{13}C NMR spectrum for **3da'**



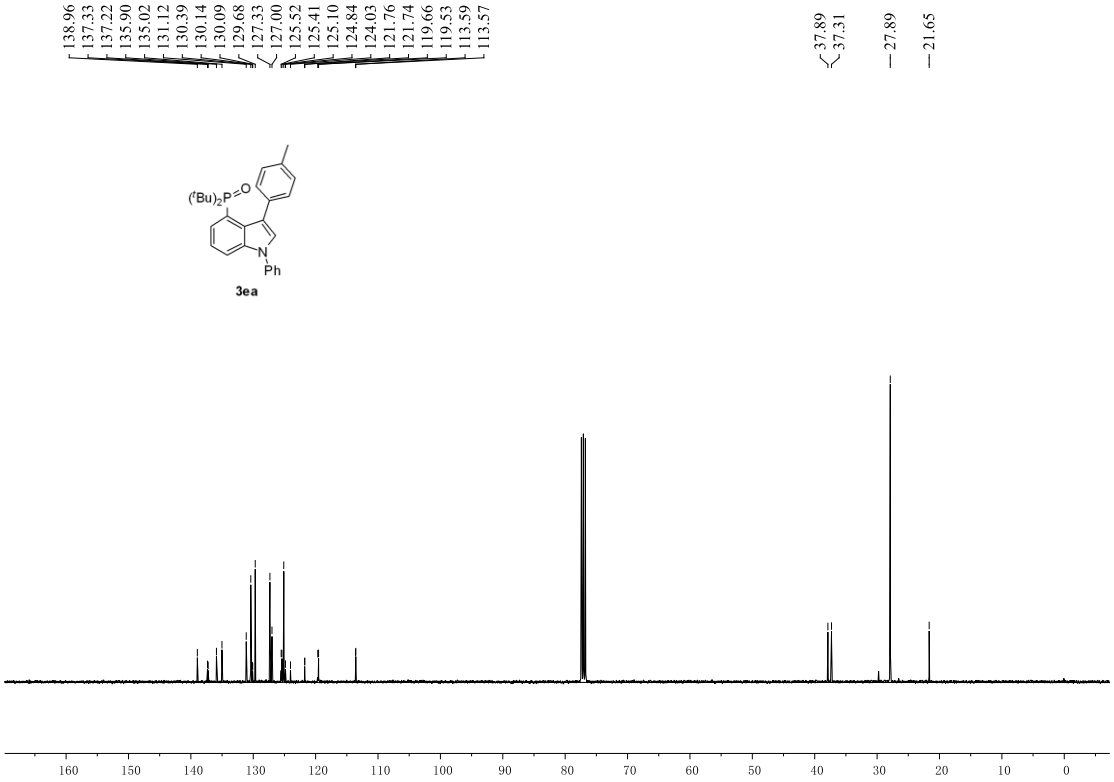
^{1}H NMR spectrum for **3ea**



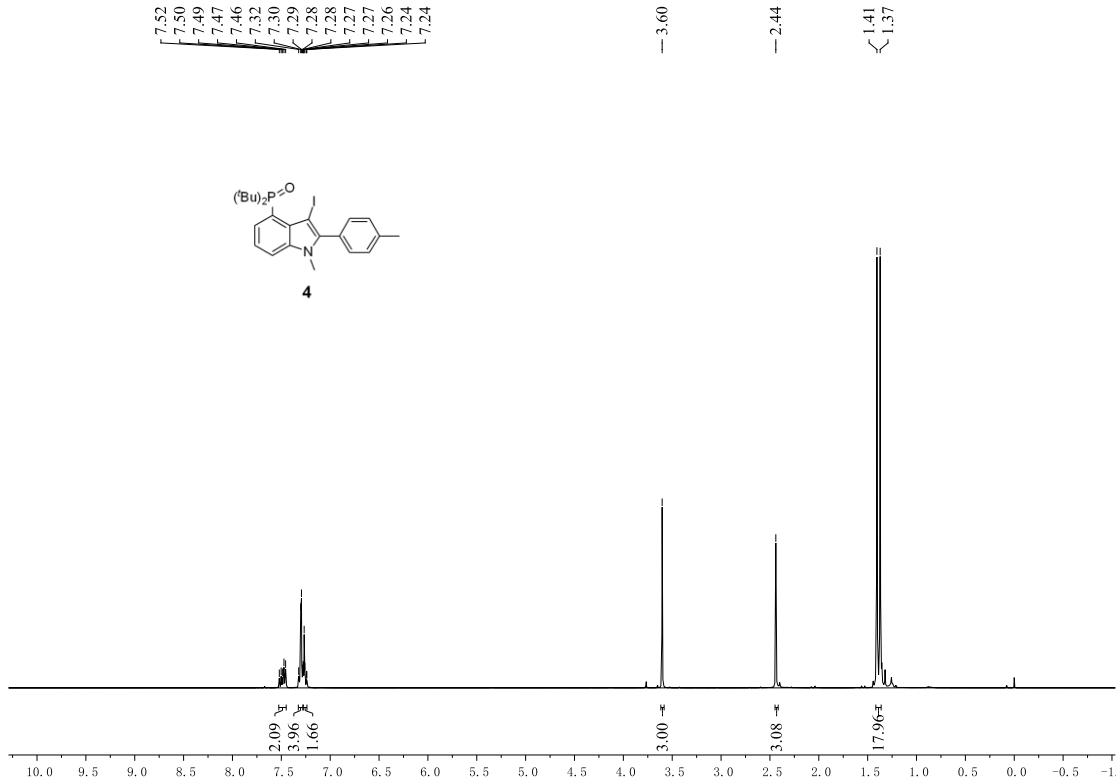
^{31}P NMR spectrum for **3ea**



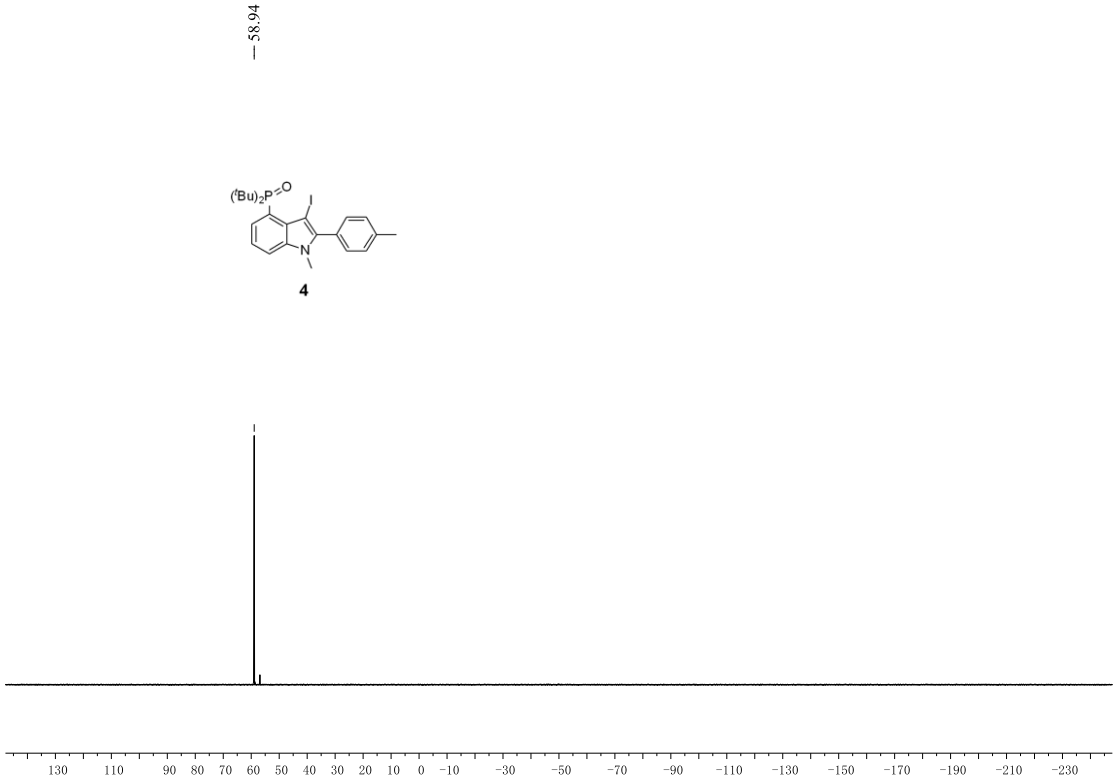
^{13}C NMR spectrum for **3ea**



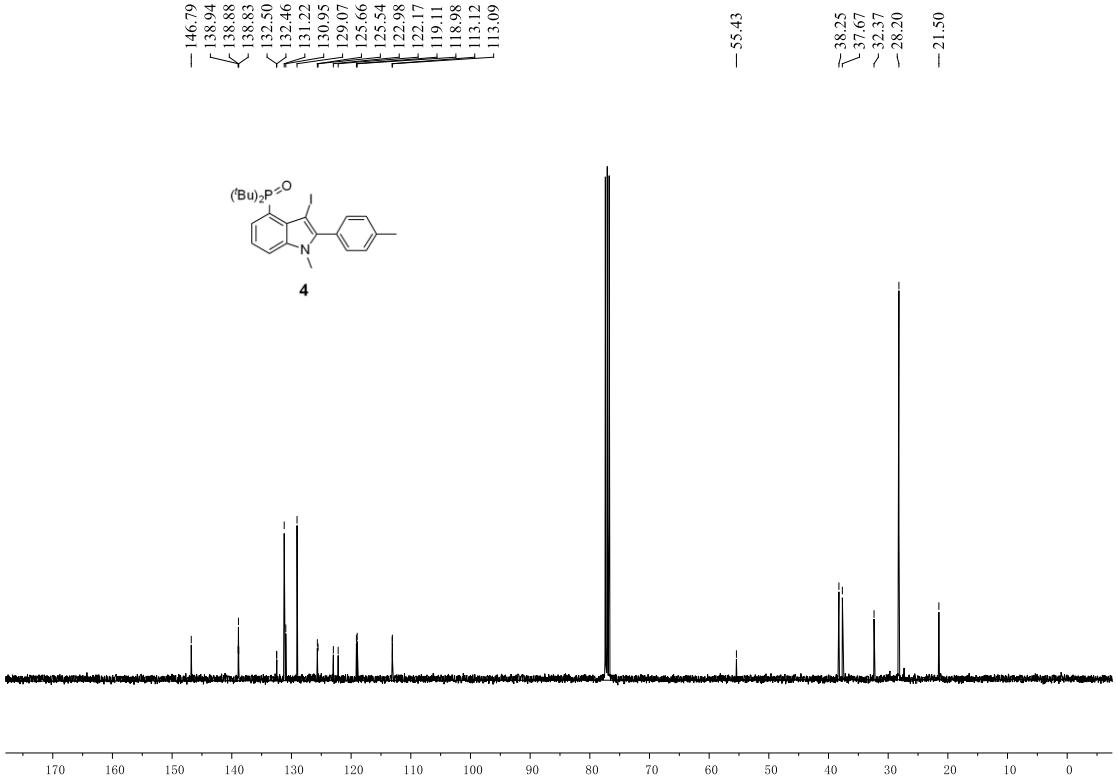
^{1}H NMR spectrum for **4**



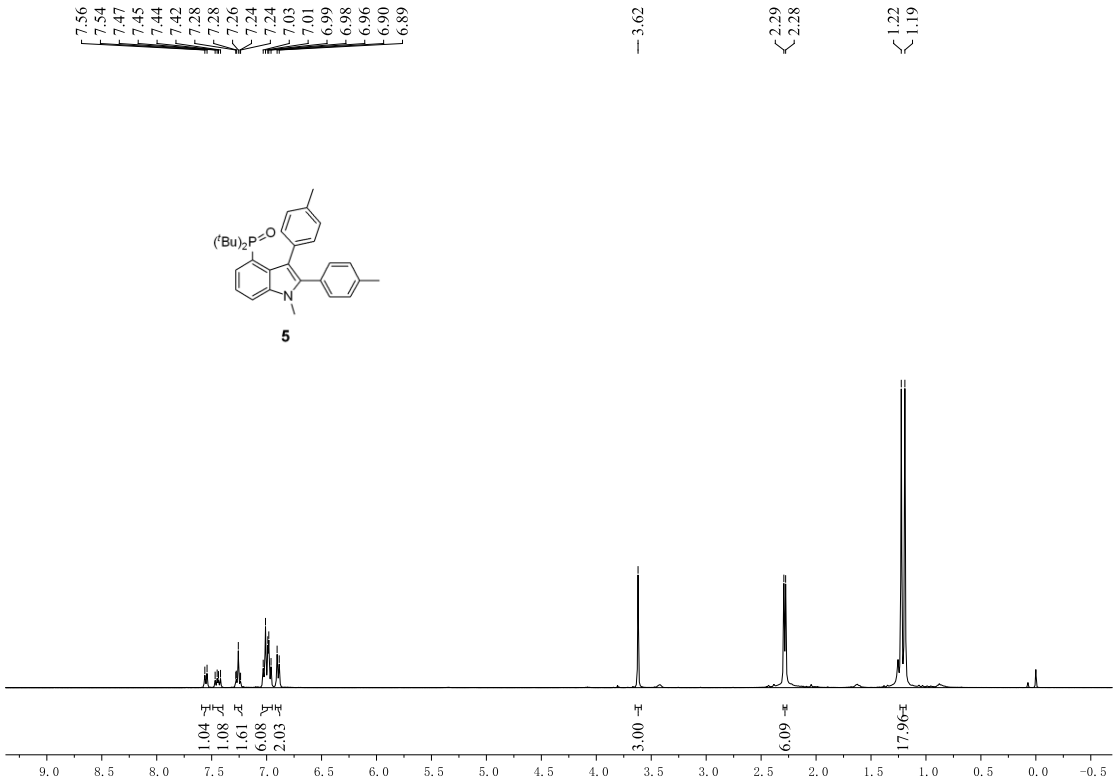
^{31}P NMR spectrum for **4**



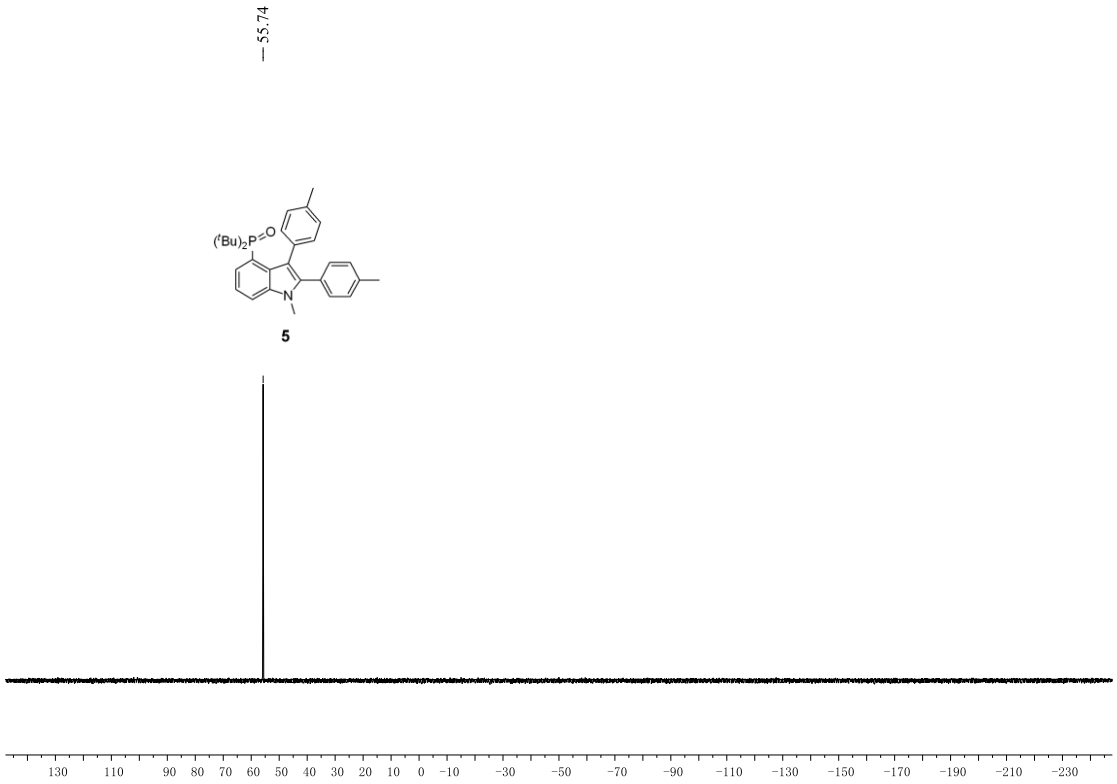
^{13}C NMR spectrum for **4**



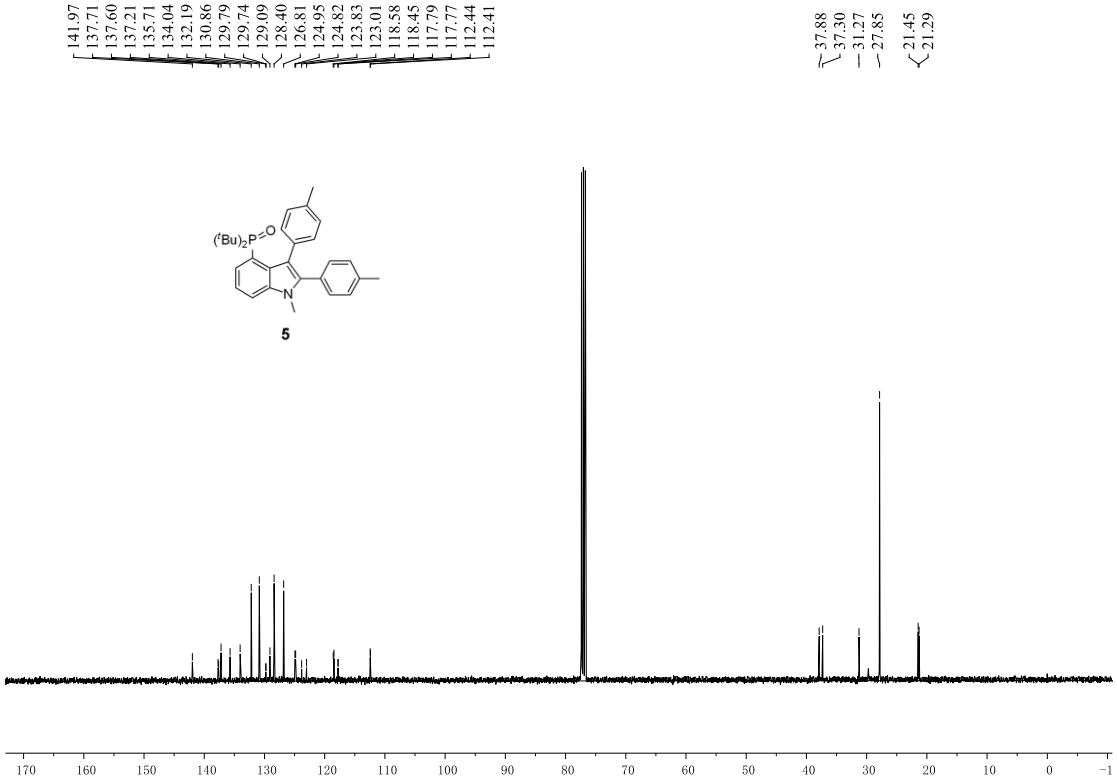
^{1}H NMR spectrum for **5**



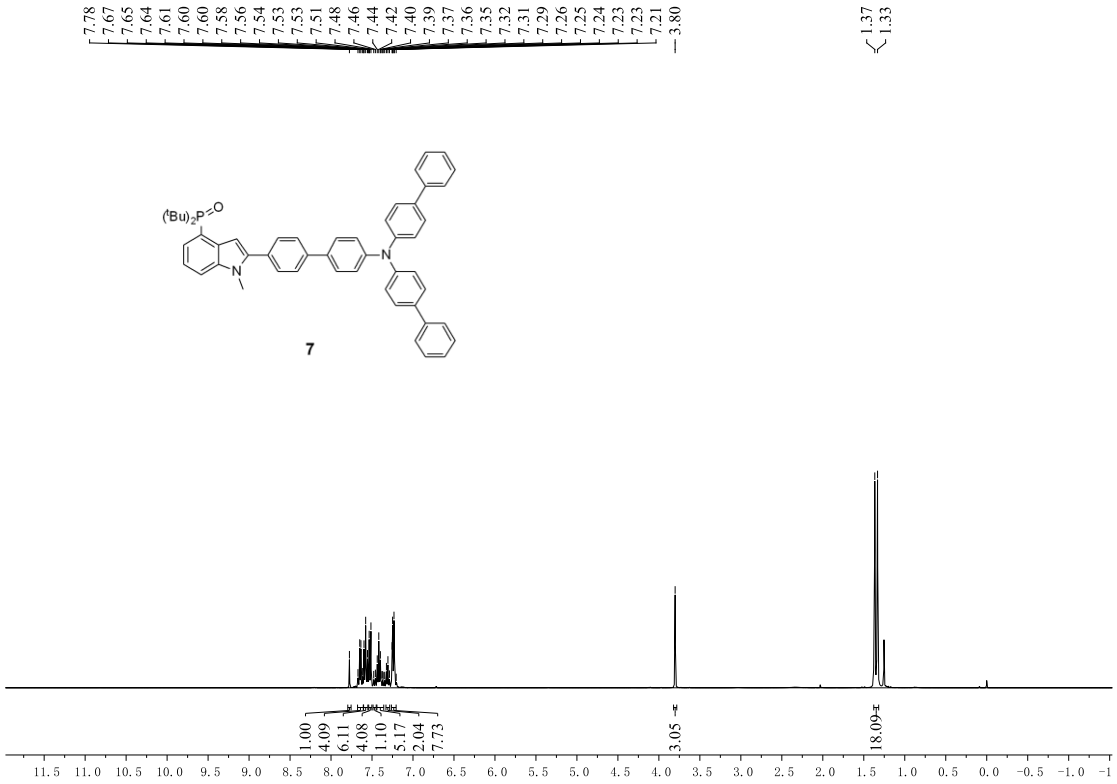
^{31}P NMR spectrum for **5**



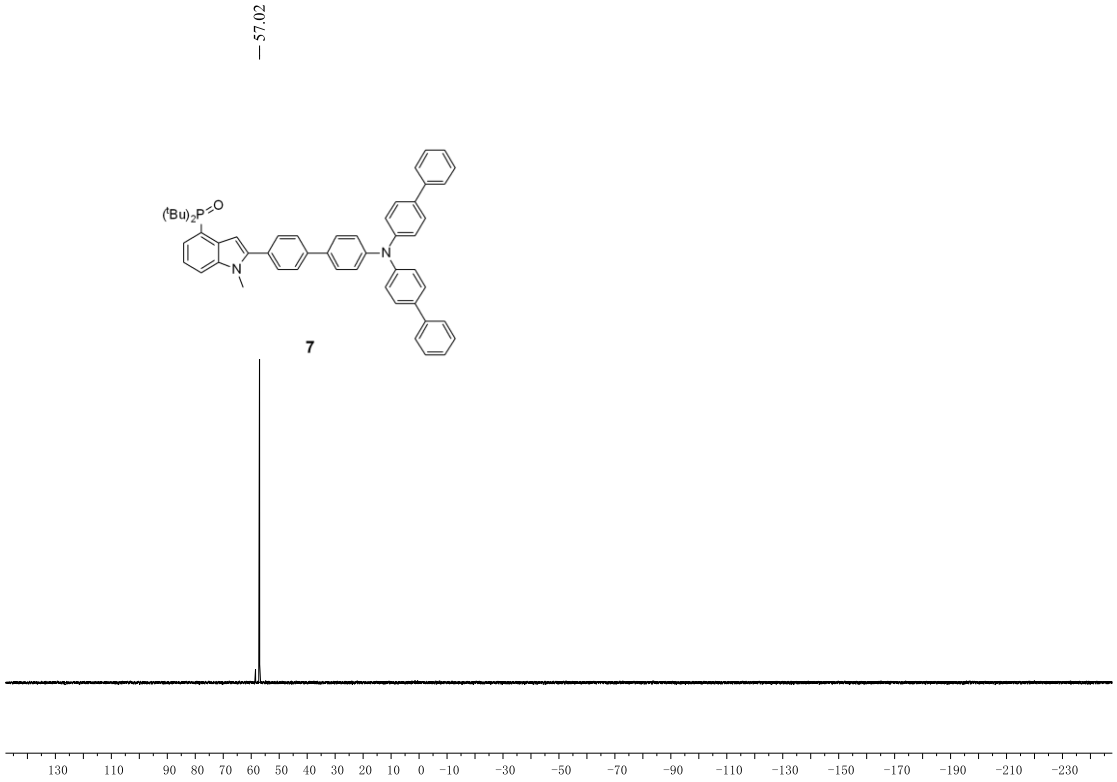
^{13}C NMR spectrum for **5**



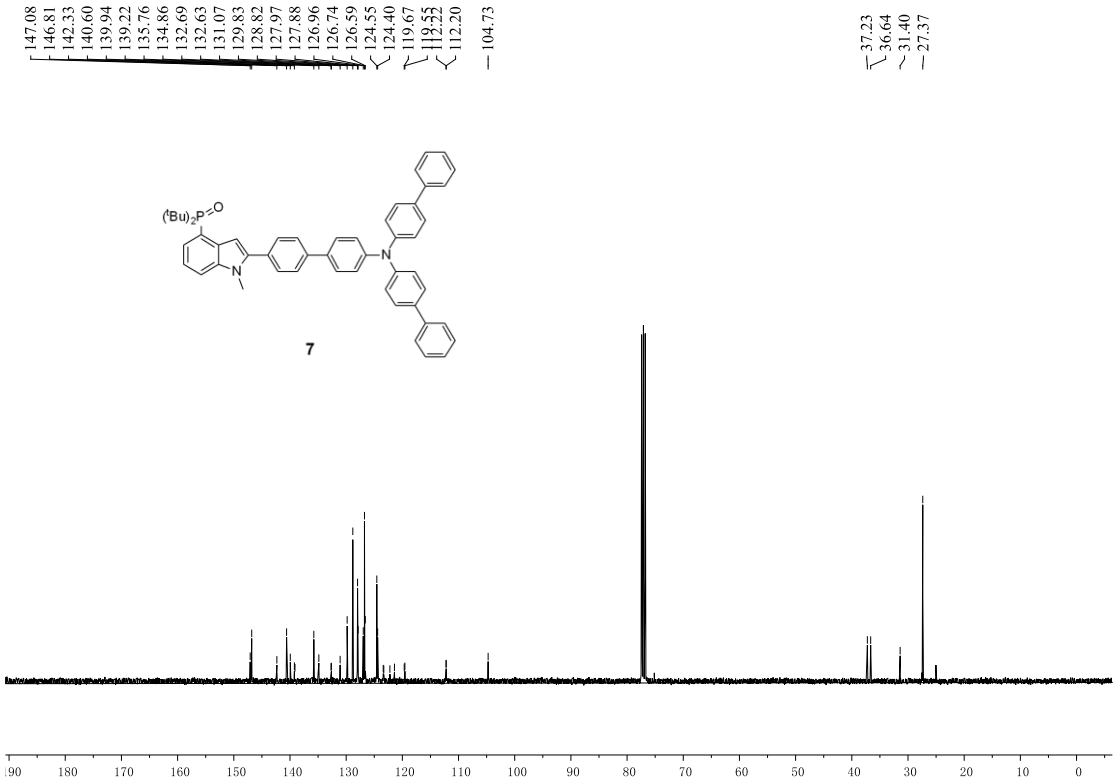
^{1}H NMR spectrum for **7**



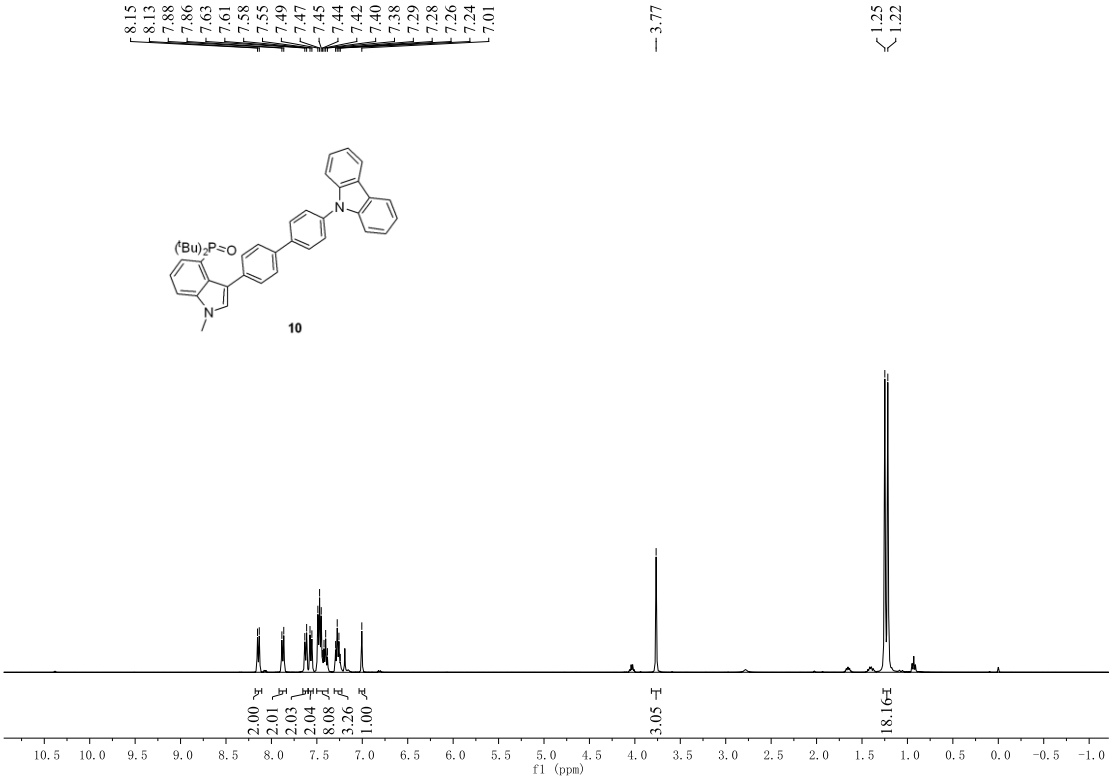
^{31}P NMR spectrum for **7**



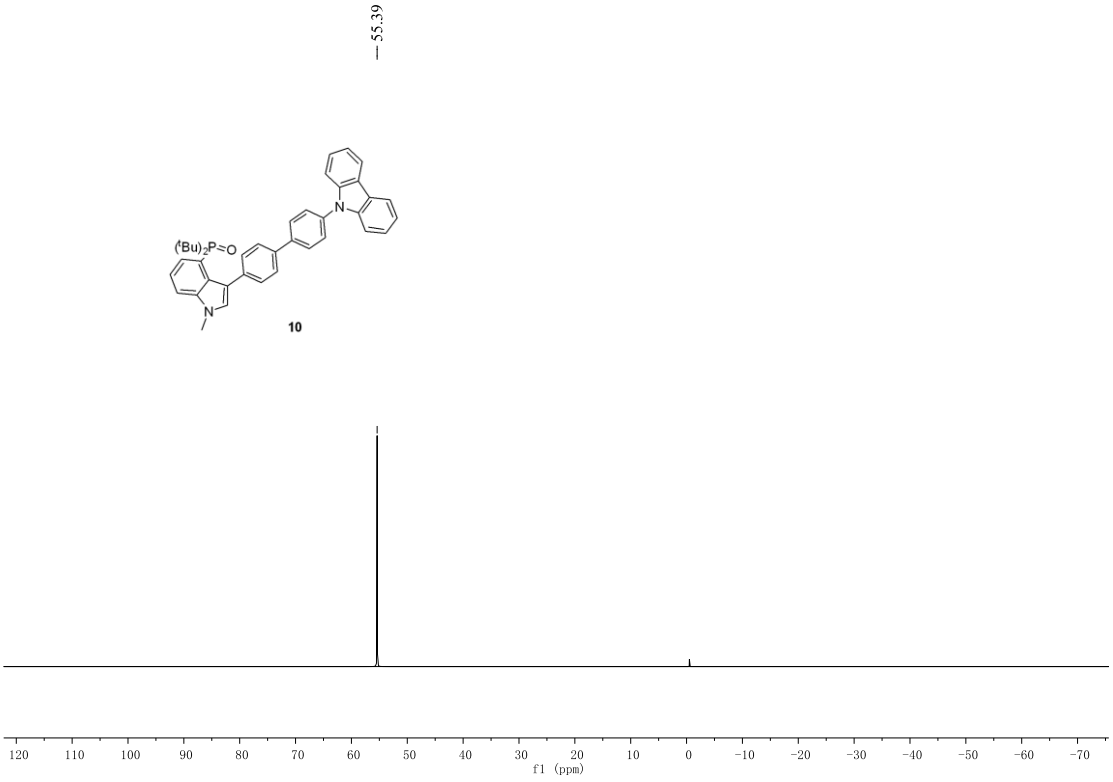
^{13}C NMR spectrum for **7**



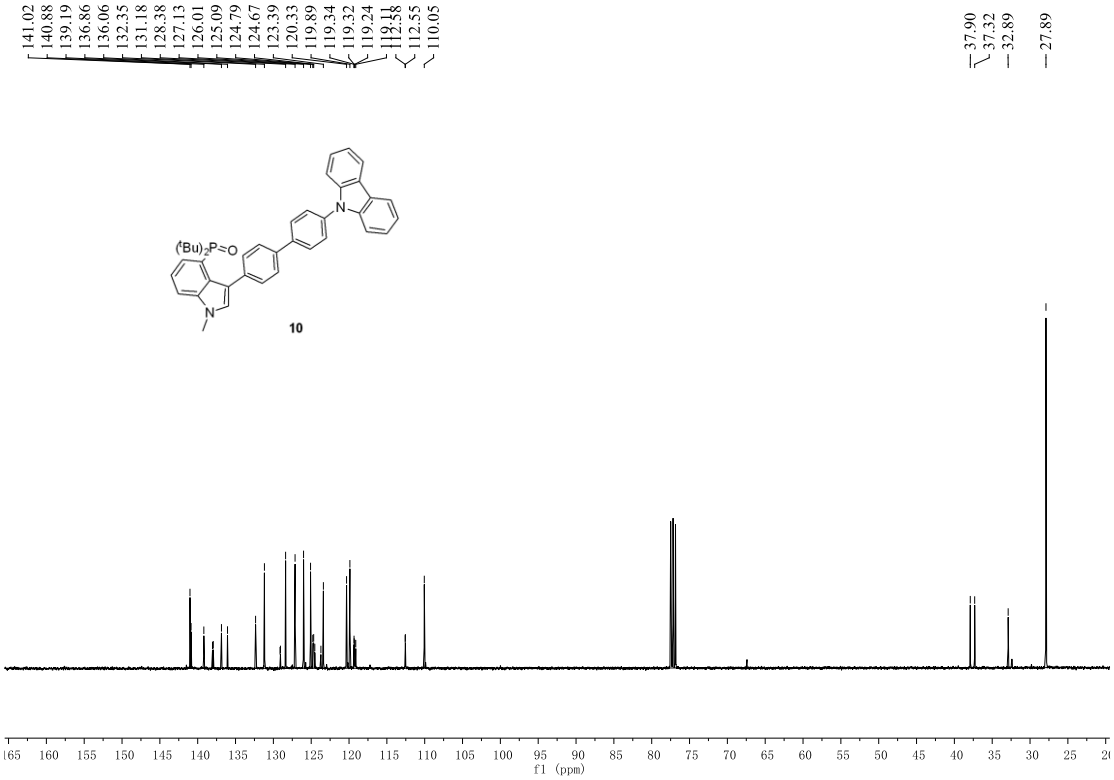
^{1}H NMR spectrum for **10**



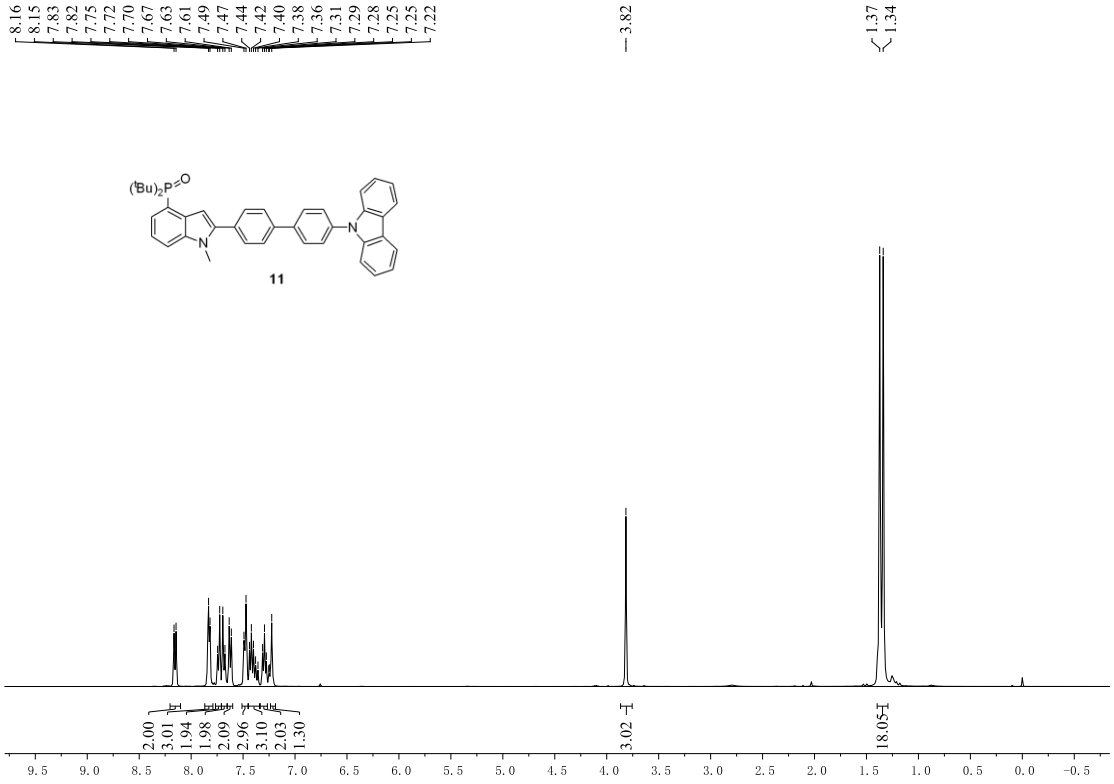
^{31}P NMR spectrum for **10**



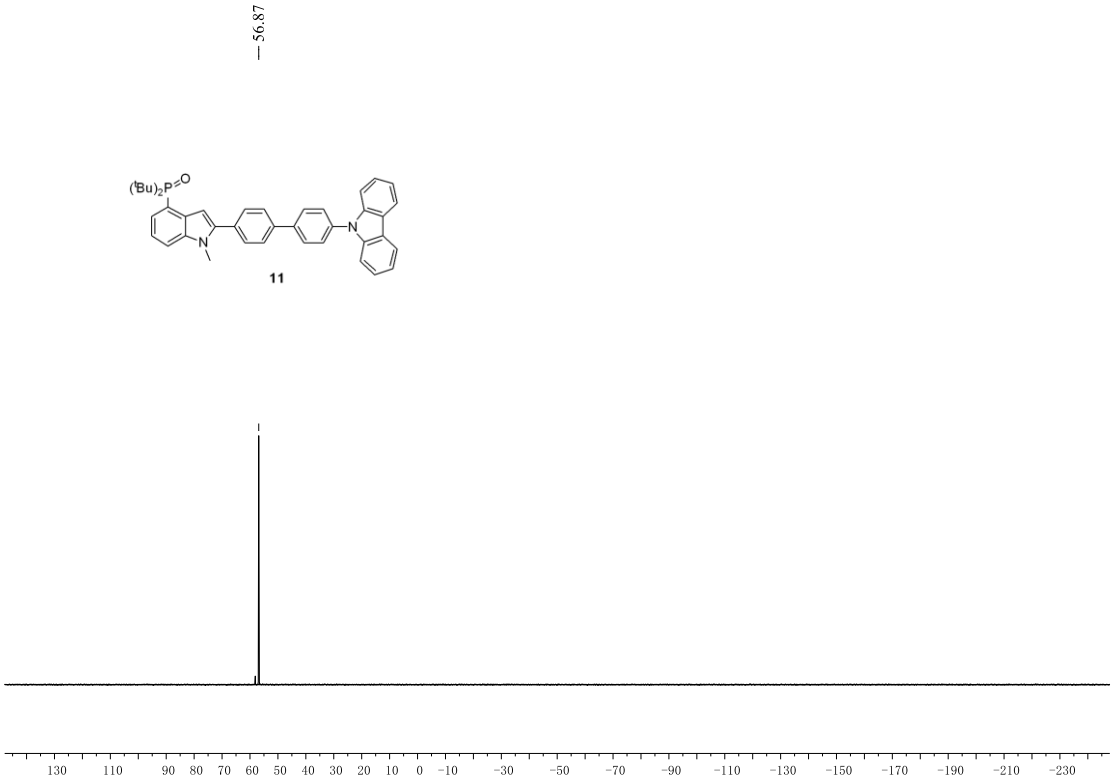
^{13}C NMR spectrum for **10**



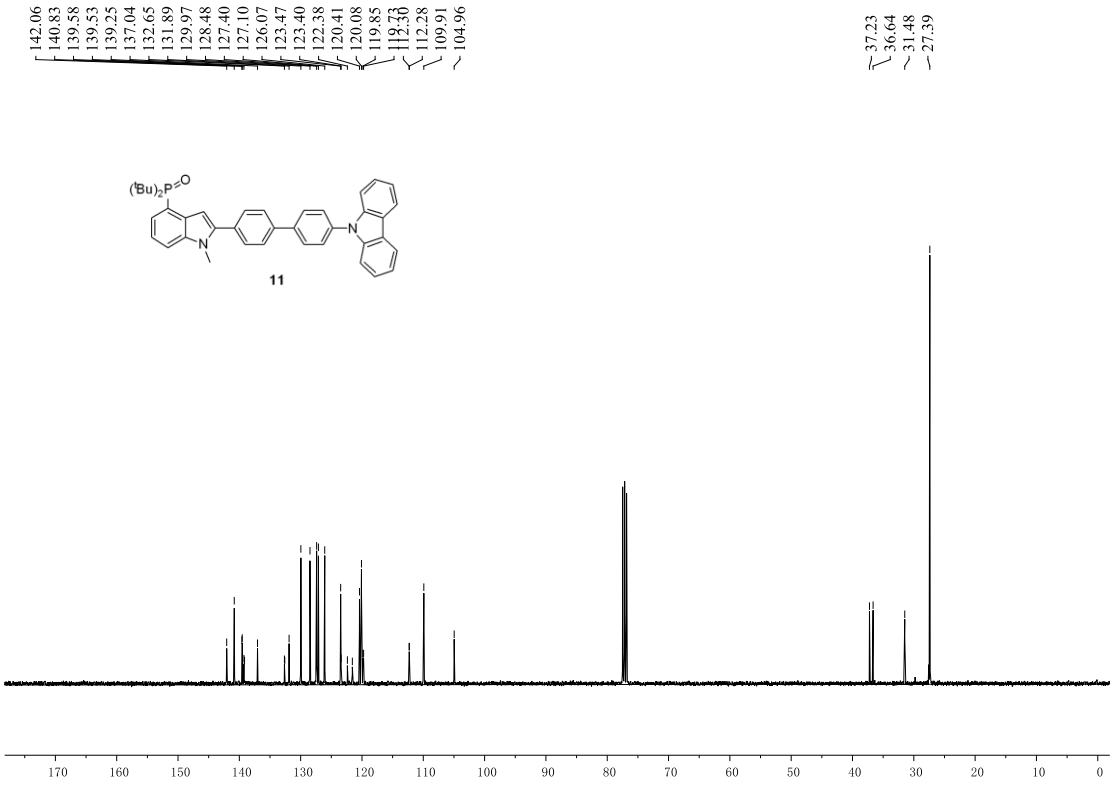
^{1}H NMR spectrum for **11**



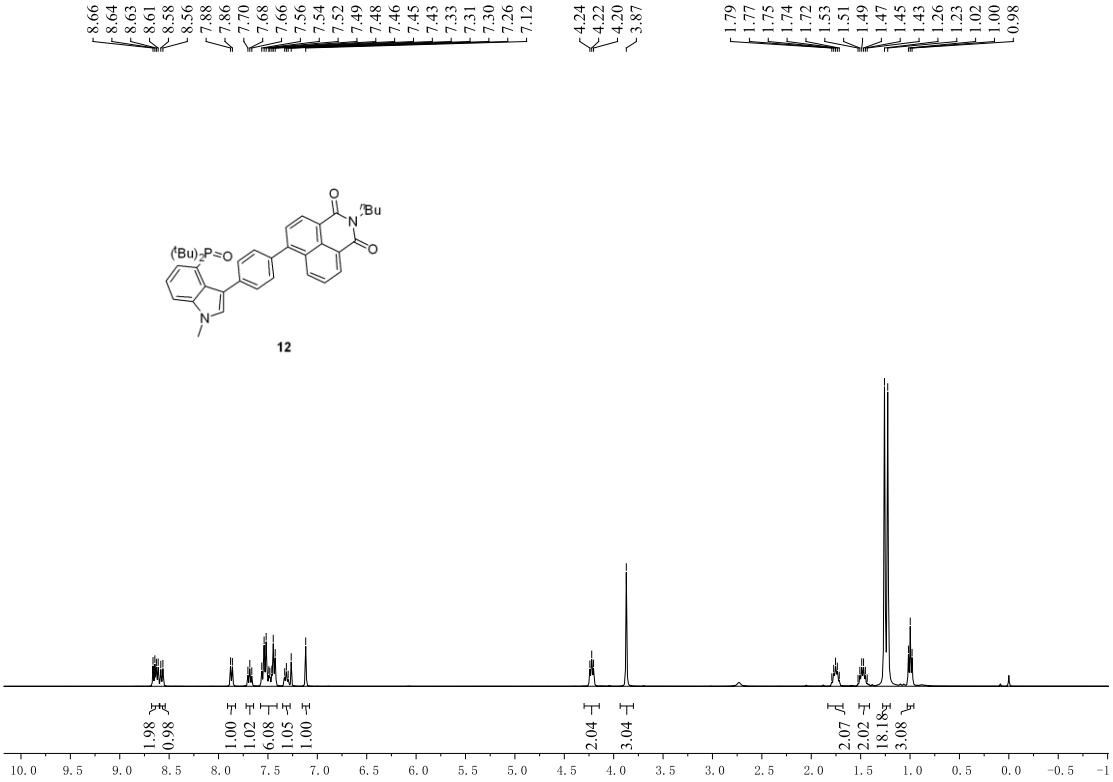
^{31}P NMR spectrum for **11**



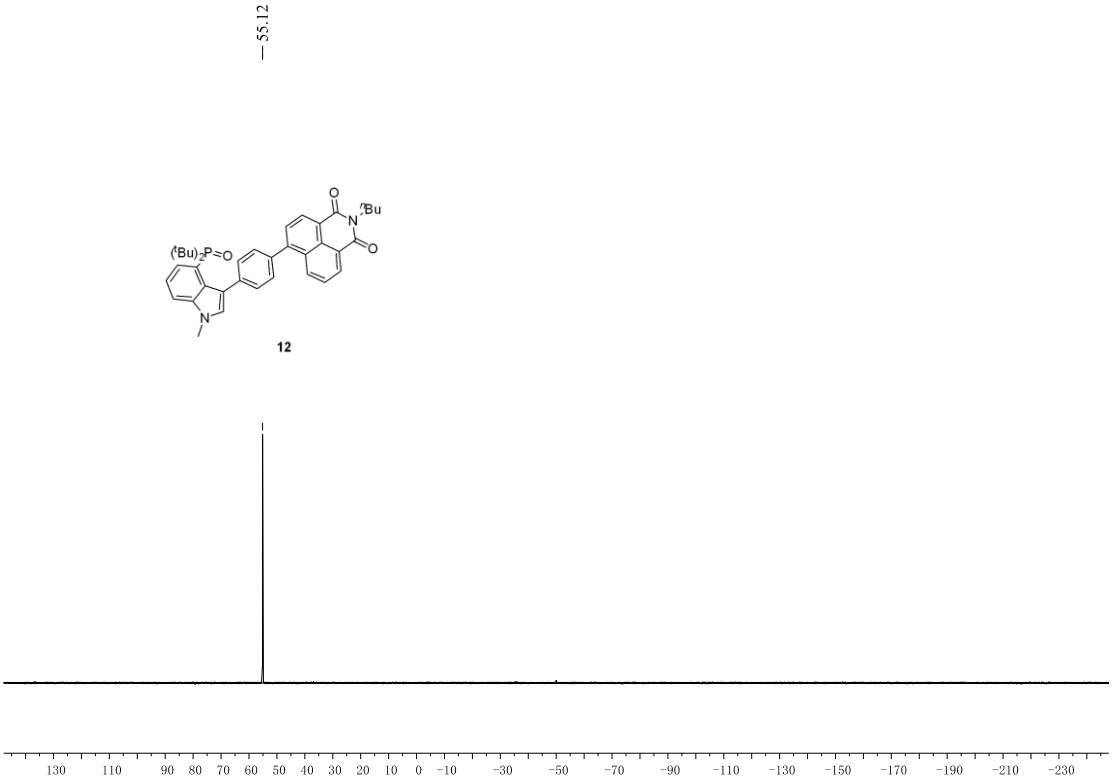
^{13}C NMR spectrum for **11**



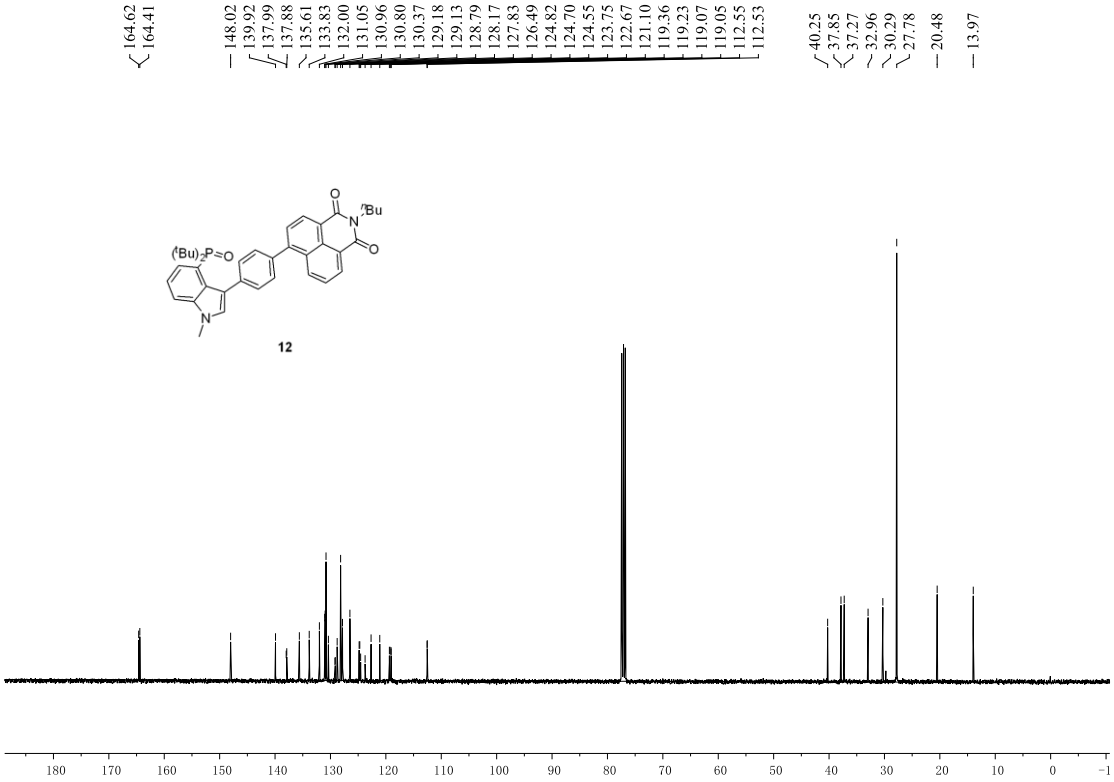
^{1}H NMR spectrum for **12**



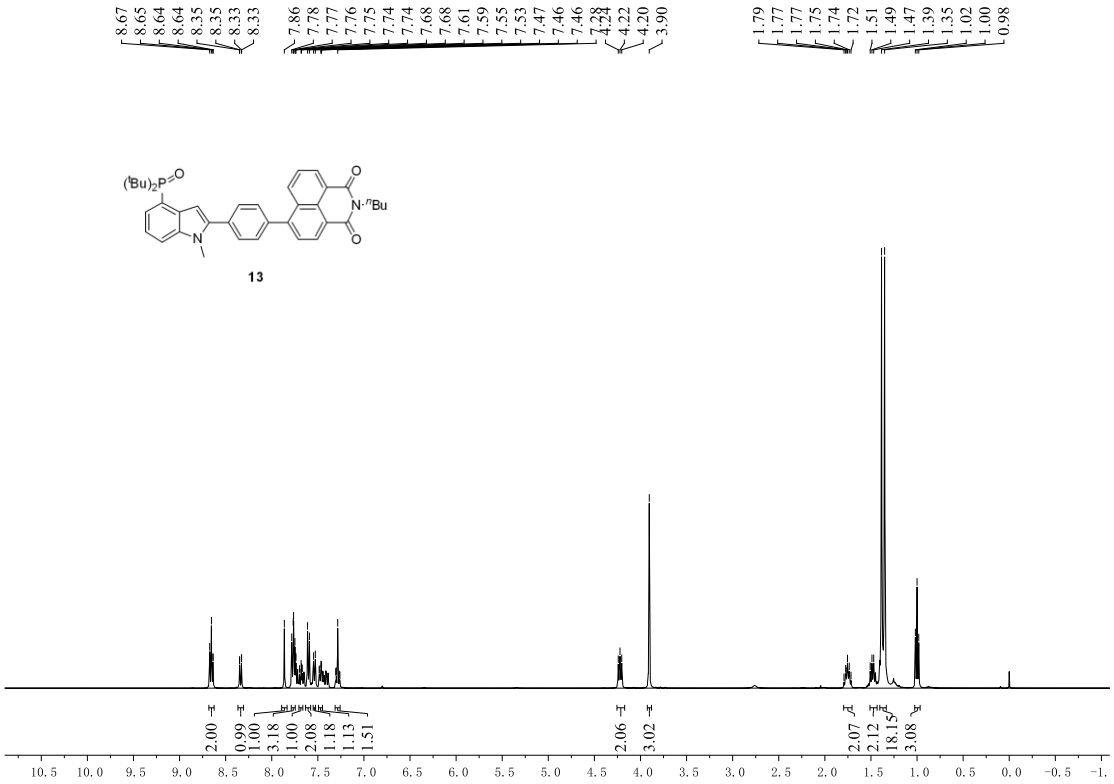
^{31}P NMR spectrum for **12**



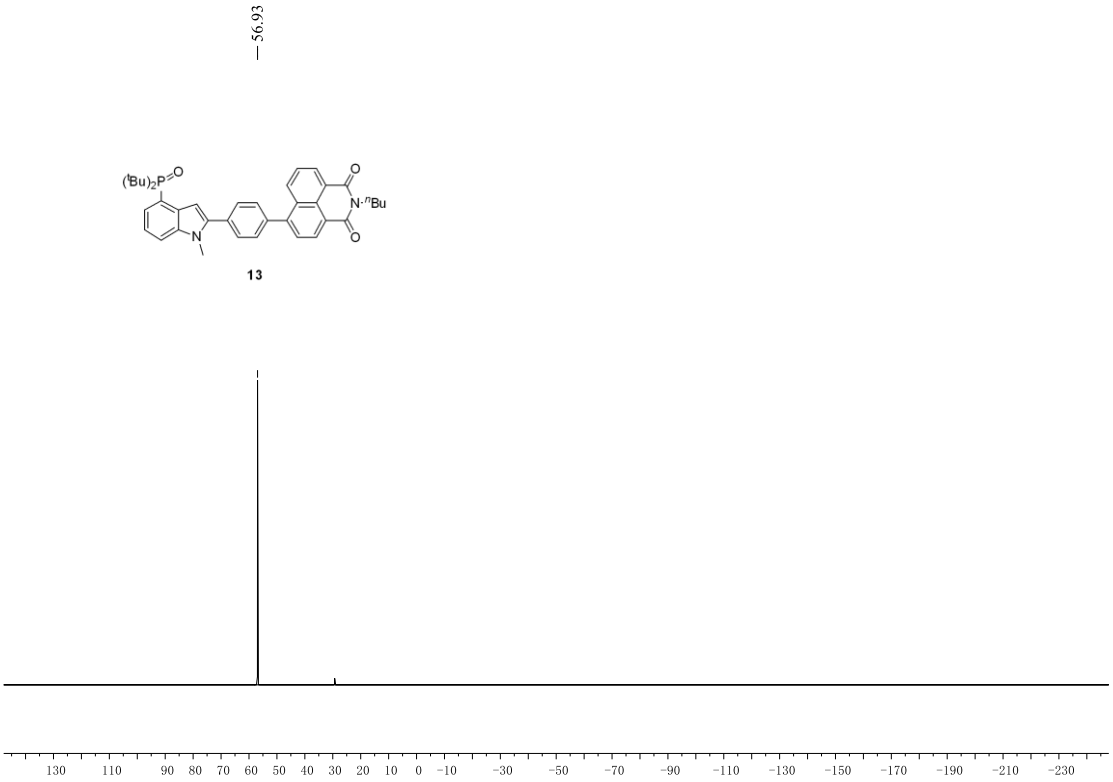
^{13}C NMR spectrum for **12**



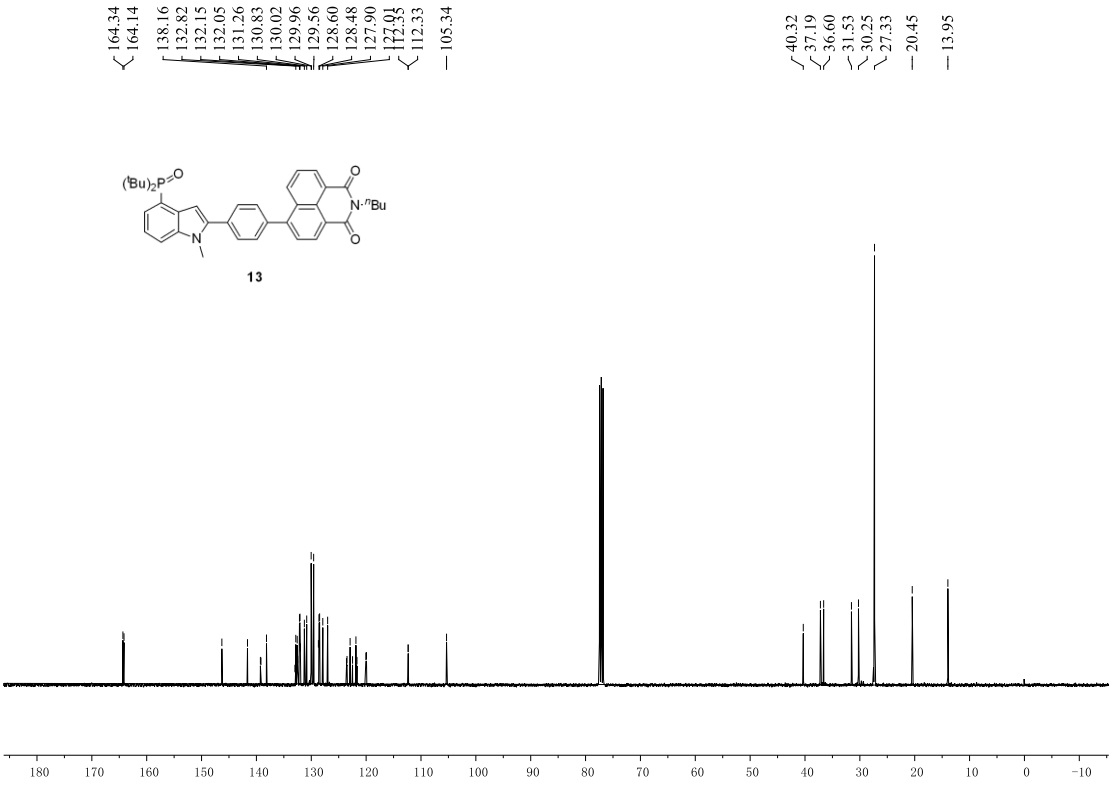
^{1}H NMR spectrum for **13**



^{31}P NMR spectrum for **13**



^{13}C NMR spectrum for **13**

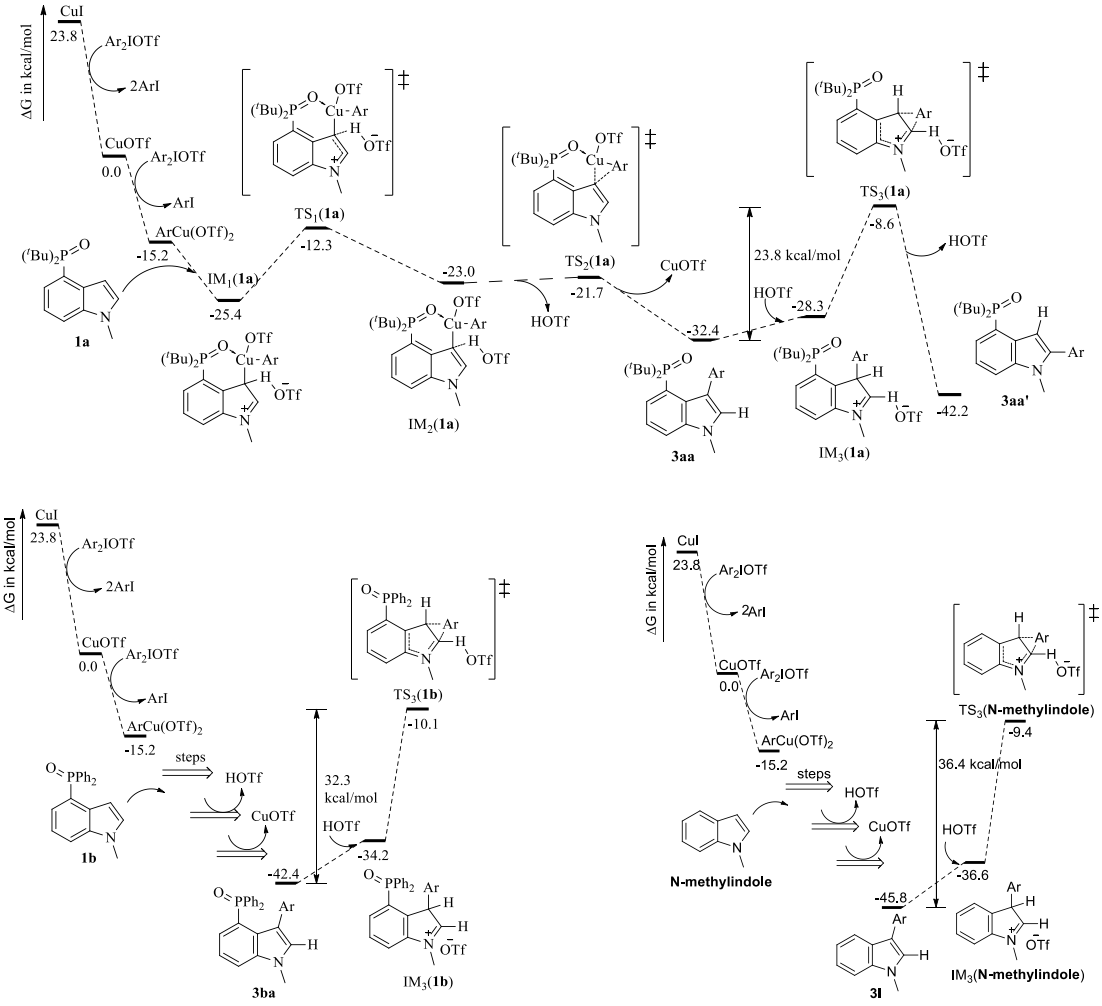


14. Computational details

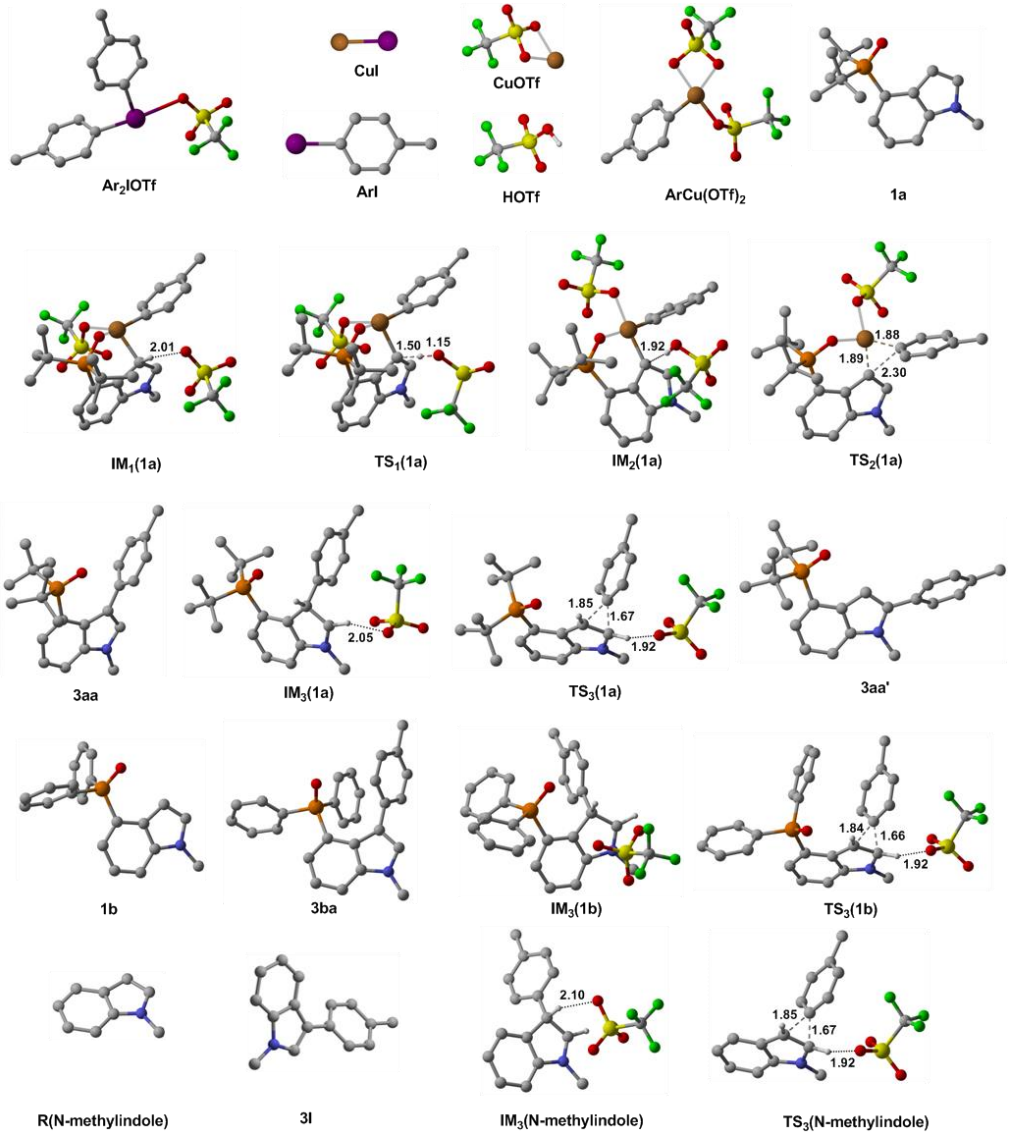
14.1 General information

All geometry opimizations were carried out at B3LYP[1]-D3[2]/BS1 level of theory (BS1: SDD[3] for Cu and I, 6-31G(d) for other atoms). Vibrational frequencies were calculated at the same level of theory to verify that each transition state (**TS**) structure has only one imaginary frequency and other structures have no imaginary frequency, and temperature was set to 353 K to obtain Gibbs free energy correction (GFEC) values. Intrincis reaction coordinate (IRC)[4] calculations were also carried out to verify each **TS** connected corresponding reactant and product. Single-point energies (E) were calculated at B3LYP-D3/BS2/SMD[5] (solvent) level of theory (BS2: SDD for Cu and I, Def2-TZVP[6] for other atoms; solvent=toluene or THF). The Gibbs free energy (G) of each structure was calculated as follows: G=GFEC+E. All calculations were performed using Gaussian 09 D.01 software package,[7] the optimized structures were drawn using CYLview software.[8]

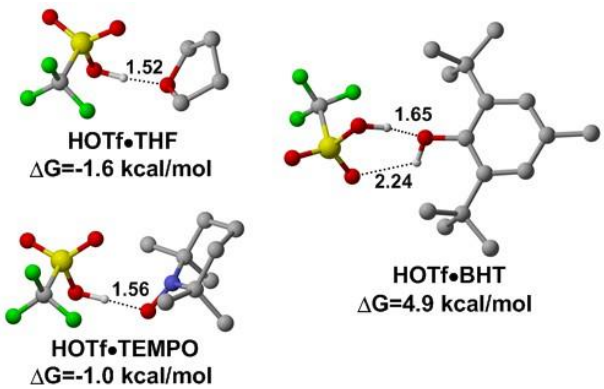
14.2 Proposed reaction pathways of 1a, 1b and N-methylindole under toluene at 80 °C. Some non-critical steps were omitted for clarity. Ar=*p*-MeC_6H_5. The Gibbs free energies of CuOTf, Ar_2IOTf and 1a, 1b or N-methylindole were set to 0.0 kcal/mol as references.



14.3 Optimized structures involved in reaction pathways of 1a, 1b and N-methylindole. Some hydrogen atoms and intermolecular interactions were omitted for clarity. Distances were in Å. Ar = *p*-MeC$_6$H$_5$



14.4 Optimized structures and relative Gibbs free energies of hydrogen bond complexes HOTf·THF, HOTf·TEMPO, and HOTf·BHT. Some hydrogen atoms and intermolecular interactions were omitted for clarity. Distances were in Å.



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14.5 Calculated Gibbs free energy correction (GFEC) values, energies (E), Gibbs free energies (G) of all optimzied structures, and imaginary frequency (ν_i) of each TS structure.

Name	GFEC/a.u.	E/a.u.	G/a.u.	ν_i/cm^{-1}
Ar_2IOTf	0.179009	-1515.288606	-1515.109597	
CuI	-0.032161	-208.833475	-208.865636	
ArI	0.071653	-282.497210	-282.425557	
CuOTf	-0.020396	-1159.141670	-1159.162066	
HOTf	-0.005629	-962.358586	-962.364215	
$ArCu(OTf)_2$	0.096369	-2391.966713	-2391.870344	
1a	0.333387	-1135.245205	-1134.911818	
IM_1(1a)	0.470287	-3527.268754	-3526.798467	
TS_1(1a)	0.466084	-3527.243622	-3526.777538	-824.19
IM_2(1a)	0.470606	-3527.265186	-3526.794580	
TS_2(1a)	0.442821	-2564.871109	-2564.428288	-55.91
3aa	0.437153	-1405.720409	-1405.283256	
IM_3(1a)	0.465769	-2368.106705	-2367.640936	
TS_3(1a)	0.457461	-2368.067017	-2367.609556	-301.68
3aa'	0.435969	-1405.734935	-1405.298966	
1b	0.271459	-1282.892617	-1282.621158	
3ba	0.370496	-1553.379115	-1553.008619	

IM_3(1b)	0.394776	-2515.754527	-2515.359751	
TS_3(1b)	0.392047	-2515.713284	-2515.321237	-289.95
N-methylindole	0.116635	-403.303130	-403.186495	
3I	0.213460	-673.792747	-673.579287	
IM_3(N-methylindole)	0.234464	-1636.163301	-1635.928837	
TS_3(N-methylindole)	0.236414	-1636.121901	-1635.885487	-341.64
THF	0.082335	-232.557046	-232.474711	
HOTf·THF	0.105350	-1194.946828	-1194.841478	
TEMPO	0.218922	-483.944245	-483.725323	
HOTf·TEMPO	0.240710	-1446.331882	-1446.091172	
BHT	0.303658	-661.587914	-661.284256	
HOTf·BHT	0.326573	-1623.967211	-1623.640638	

14.6 Cartesian Coordinates (Ar=*p*-MeC_6H_5)

Ar_2IOTf

S	3.28237200	-0.65664900	-0.75321100
O	4.46555000	-0.30585900	-1.53874800
O	2.27091700	0.46765200	-0.61885200
O	2.62009600	-1.95341100	-1.01288100
C	3.87770900	-0.80618900	1.00105400
F	4.76195700	-1.80339900	1.11957500
F	2.83308700	-1.06759200	1.81602700
F	4.45286900	0.33119000	1.41242500
I	-0.13894400	-0.53389100	-0.34356700
C	-2.18533700	-1.18045600	-0.11418100
C	-3.05835300	-1.11327300	-1.20060300
C	-2.60800600	-1.68098500	1.11775100
C	-4.37271400	-1.55079100	-1.04136000
H	-2.72640300	-0.72232100	-2.15727700
C	-3.92702200	-2.11619500	1.25695600
H	-1.92698800	-1.73019600	1.96185300
C	-4.82653900	-2.06065400	0.18392900
H	-5.05598800	-1.49614900	-1.88520200
H	-4.25919300	-2.50393400	2.21670400
C	-0.66212600	1.58997200	-0.08522500
C	-1.84476000	1.91040400	0.56403600
C	0.21925800	2.54007500	-0.58407100
C	-2.16025300	3.26481200	0.70793900
H	-2.51303800	1.15031600	0.95156100
C	-0.12815500	3.88292800	-0.41981800
H	1.15211300	2.25352500	-1.05338100
C	-1.31490900	4.26743800	0.21894700
H	-3.08181400	3.53560700	1.21711300
H	0.54989900	4.64338300	-0.79907700

C	-1.67460000	5.72765200	0.35703800
H	-0.79947800	6.32911500	0.62591000
H	-2.06367100	6.12543300	-0.58914300
H	-2.44218800	5.88356100	1.12154300
C	-6.24093700	-2.56659600	0.33314300
H	-6.30278900	-3.62798000	0.05951000
H	-6.59426000	-2.47412900	1.36514500
H	-6.93338500	-2.02132800	-0.31641500

CuI

Cu	0.00000000	0.00000000	-1.55303800
I	0.00000000	0.00000000	0.84977600

ArI

C	2.26663500	-1.20027100	-0.01076900
C	0.87050000	-1.21272000	-0.00504900
C	0.18437100	0.00034500	-0.00129800
C	0.87004000	1.21328100	-0.00504100
C	2.26653800	1.20113300	-0.01077800
C	2.98727700	0.00067200	-0.01083300
H	2.80176100	-2.14718600	-0.01704100
H	0.33387000	-2.15525200	-0.00744000
H	0.33335700	2.15578000	-0.00740800
H	2.80131700	2.14819400	-0.01692600
C	4.49781400	-0.00062800	0.01697100
H	4.90883000	0.90386300	-0.44377100
H	4.87242600	-0.04140300	1.04841500
H	4.90815100	-0.86734700	-0.51238800
I	-1.97393900	-0.00014200	0.00221400

CuOTf

O	-0.61554600	0.41724900	-1.21908700
S	0.21836100	0.78676700	0.00013800
O	0.86688300	2.08859900	-0.00009300
O	-0.61540300	0.41725300	1.21912100
C	1.56576000	-0.50393100	-0.00004800
F	2.31988300	-0.36931700	-1.08943800
F	1.00363000	-1.72309500	-0.00035700
F	2.31967500	-0.36986300	1.08964800
Cu	-2.09532800	-0.37203500	-0.00000400

HOTf

O	1.25041800	1.10654600	-0.89152900
S	0.85470400	-0.14869800	0.07573000

O	1.22428700	-1.36532100	-0.61592500
O	1.25712000	0.16557600	1.43939800
C	-1.00820300	0.00607400	-0.00201700
F	-1.42440600	-0.16677500	-1.25190500
F	-1.35710400	1.22191900	0.42639200
F	-1.54357000	-0.92032400	0.78830600
H	1.44506400	1.87494800	-0.32026500

$ArCu(OTf)_2$

S	-0.46220700	2.29610200	0.36025500
O	-1.56498400	3.24444600	0.40637100
O	-0.18420000	1.39237500	1.48393400
O	-0.48323000	1.47073500	-0.98777300
C	1.10586900	3.26978500	0.07490300
F	0.99724700	3.99121100	-1.03925500
F	2.13246200	2.42354900	-0.03685400
F	1.30586100	4.07747900	1.11697300
C	-1.93310500	-0.64752800	-0.30308000
C	-2.12769300	-1.45758000	0.79852300
C	-2.92295200	-0.10739000	-1.09692600
C	-3.45562300	-1.80084400	1.07979900
H	-1.30732000	-1.82753400	1.40116200
C	-4.23674100	-0.48925300	-0.78872600
H	-2.70569500	0.59132500	-1.89505300
C	-4.51825200	-1.33119200	0.29400700
H	-3.65371200	-2.45022600	1.92910000
H	-5.04743500	-0.09373900	-1.39539400
Cu	-0.09338000	-0.30275100	-0.73806400
C	-5.93873600	-1.73955600	0.60755200
H	-6.16911400	-2.71648100	0.16317000
H	-6.10083200	-1.82502300	1.68707300
H	-6.66039500	-1.01869700	0.21112300
O	0.43832000	-2.13430000	-0.52904500
S	1.94531700	-1.88076900	-0.79821400
O	2.63350200	-2.88888000	-1.57912700
O	1.97202800	-0.43895500	-1.23145600
C	2.66639600	-1.88869300	0.92695500
F	2.57068800	-3.11503900	1.43442200
F	1.97534500	-1.03313600	1.68439200
F	3.94020900	-1.51462500	0.86796000

1a

C	-1.60800500	0.11430300	-0.29903300
C	-2.84914600	-0.27494000	0.29471700

C	-2.92339400	-1.05497700	1.45007900
C	-1.72435100	-1.45570200	2.02958300
C	-0.48920600	-1.08377400	1.46911900
C	-0.40068900	-0.30352500	0.31080600
C	-1.93695600	0.89672900	-1.45880200
C	-3.30305100	0.95249300	-1.52280200
H	-3.87964300	-1.33905900	1.88024900
H	-1.73813900	-2.06429800	2.92935400
H	0.41505700	-1.41622400	1.96563000
H	-1.22681100	1.33661500	-2.14019100
H	-3.94383900	1.44127800	-2.24472500
N	-3.86871600	0.25003400	-0.47029900
C	-5.28121700	0.07780900	-0.20768100
H	-5.54841900	0.48045800	0.77682300
H	-5.85409200	0.61151400	-0.96908100
H	-5.56037500	-0.98244500	-0.23918500
P	1.20062500	0.20824600	-0.43022600
O	1.02173300	0.85074000	-1.78608600
C	2.26204600	-1.35048100	-0.62895600
C	2.94236600	-1.88297800	0.64399400
C	1.33381600	-2.43773800	-1.21483500
C	3.34323900	-1.01757900	-1.68174500
H	3.65177500	-1.16475700	1.06590700
H	2.22755600	-2.16110600	1.42407600
H	3.50913600	-2.78877900	0.39100700
H	0.80845600	-2.07128700	-2.10312300
H	1.93718900	-3.30554600	-1.51080700
H	0.58692700	-2.77371300	-0.48980600
H	3.88345100	-1.93740000	-1.94136800
H	2.89239200	-0.60400400	-2.58672100
H	4.07707600	-0.29720700	-1.30873400
C	1.91972700	1.47261200	0.77362800
C	1.00000100	2.70652100	0.62111100
C	1.93928300	1.04848800	2.25245100
C	3.34027400	1.85047700	0.30933800
H	0.97520400	3.05337700	-0.41510700
H	-0.02708900	2.48185200	0.92994400
H	1.37545200	3.51800000	1.25798300
H	2.55457200	0.16273700	2.43429900
H	2.36151400	1.86752200	2.84949100
H	0.93164200	0.85154800	2.62865500
H	3.67891200	2.73748700	0.86027200
H	4.06297300	1.05075400	0.50283300
H	3.35845600	2.08641000	-0.75934100

IM_1(1a)

S	3.28561600	0.39870100	0.74714700
O	2.52898700	1.39770200	1.53389100
O	3.60136100	-0.87133200	1.41074500
O	2.75816700	0.23704200	-0.67014100
C	4.91411400	1.22905200	0.40681800
F	4.70398400	2.39587400	-0.22631000
F	5.68566000	0.45490700	-0.36187000
F	5.54860200	1.47462000	1.55826600
C	0.34351100	2.29553400	-1.08411700
C	1.36533700	3.20184300	-0.80410500
C	-0.85287300	2.67284700	-1.69980100
C	1.22445100	4.50630800	-1.28352900
H	2.24689600	2.90318000	-0.25480500
C	-0.96047700	3.98649900	-2.16614100
H	-1.69137500	1.98992600	-1.79487300
C	0.07061300	4.91598600	-1.97001300
H	2.02711700	5.21890500	-1.10678000
H	-1.87918800	4.29056500	-2.66154200
Cu	0.72420100	0.44983900	-1.04485100
C	-0.05894300	6.32931800	-2.48468800
H	-1.10295800	6.65909300	-2.49144000
H	0.51997300	7.03363500	-1.87822000
H	0.31356400	6.40147400	-3.51525000
O	-3.18189200	1.04295500	1.59682100
S	-4.00378600	1.29186400	0.37136900
O	-4.62275100	2.62065600	0.28457400
O	-3.34951900	0.80368800	-0.87998900
C	-5.41626700	0.10160600	0.58627600
F	-6.11160100	0.38541700	1.69507700
F	-4.95246600	-1.16155600	0.69392600
F	-6.24314400	0.15348900	-0.46596800
C	-0.06660100	-0.77174400	1.16112000
C	0.20980000	-0.25197700	2.43861500
C	0.76764600	-1.00266900	3.46005100
C	1.04609000	-2.34179900	3.17867500
C	0.80848300	-2.88103600	1.90960800
C	0.28723200	-2.10197100	0.86832800
C	-0.66502300	0.32472200	0.36895200
C	-0.73378100	1.43388900	1.30716200
H	0.99160300	-0.57289200	4.42990900
H	1.48539600	-2.96817000	3.94823500
H	1.07739100	-3.91524000	1.73028000

H	-1.53940300	0.18921900	-0.26849900
H	-1.13883800	2.41525700	1.13234600
N	-0.18970900	1.10566100	2.45927300
C	0.06830800	2.00161200	3.57746300
H	1.15033500	2.12149000	3.67773100
H	-0.39853400	2.96528900	3.37187900
H	-0.35995900	1.58069800	4.49078600
P	0.17061800	-2.64722600	-0.87938600
O	0.26371500	-1.37326700	-1.74548200
C	-1.51923900	-3.44259800	-1.05857200
C	-1.75166100	-4.52671300	0.01332900
C	-2.55408200	-2.31460600	-0.85890200
C	-1.68424600	-4.03094600	-2.47378400
H	-1.07446400	-5.37845700	-0.08355800
H	-1.65957900	-4.12173000	1.02621500
H	-2.77478500	-4.90522500	-0.09621100
H	-2.43606200	-1.50180700	-1.57782400
H	-3.55952100	-2.72988600	-0.98873000
H	-2.52101300	-1.88968200	0.14731100
H	-2.72657000	-4.34599700	-2.60230900
H	-1.46280600	-3.28807400	-3.24685500
H	-1.05365900	-4.90992600	-2.63812300
C	1.62550000	-3.75164200	-1.33739100
C	2.90577800	-3.12065000	-0.74799100
C	1.49170100	-5.21495300	-0.87803000
C	1.73911900	-3.70417500	-2.88080500
H	3.01650100	-2.07568900	-1.04469600
H	2.94229100	-3.15193400	0.34181300
H	3.76875000	-3.67902300	-1.13180900
H	0.66090800	-5.73167100	-1.36681100
H	2.41201600	-5.74597600	-1.14935600
H	1.36976000	-5.31674400	0.20462200
H	2.63473600	-4.26538900	-3.17317800
H	0.88326400	-4.15889200	-3.38572300
H	1.84498200	-2.67668700	-3.23683900

TS_1(1a)

S	3.00962700	0.30239800	1.01402200
O	2.30819400	1.41718900	1.68726100
O	3.11578100	-0.95784600	1.76198600
O	2.61795100	0.12823300	-0.43709900
C	4.75029900	0.92389600	0.81943300
F	4.74718500	2.07727600	0.12568300
F	5.49980600	0.03173100	0.15927000

F	5.30303500	1.15077600	2.01739800
C	0.39100200	2.35267200	-1.24964900
C	1.45357400	3.16645300	-0.85179700
C	-0.70382100	2.85678300	-1.95577000
C	1.45285000	4.49852000	-1.27028100
H	2.25846000	2.77558200	-0.24500800
C	-0.67543100	4.19362300	-2.36259500
H	-1.55998500	2.23385100	-2.18555900
C	0.39798900	5.03027800	-2.02834000
H	2.28677600	5.13773700	-0.98861600
H	-1.51325700	4.59042100	-2.93119000
Cu	0.60631200	0.50251000	-1.22718400
C	0.42427100	6.47080100	-2.48052200
H	-0.58699000	6.86955000	-2.61201000
H	0.95280800	7.10746100	-1.76308600
H	0.94219300	6.56613300	-3.44423000
O	-3.27266200	2.43527300	1.00720800
S	-3.93618500	1.52117200	0.07338400
O	-5.10314600	1.94321100	-0.68506800
O	-2.90516300	0.81162000	-0.86345300
C	-4.46055100	0.06819200	1.11283400
F	-5.30491600	0.46541300	2.06536100
F	-3.37324400	-0.47593000	1.69478900
F	-5.04895300	-0.86279900	0.35797300
C	-0.27284100	-0.72310500	1.05235600
C	-0.29524500	-0.38415500	2.42966300
C	-0.14170200	-1.31141200	3.45247300
C	0.07087800	-2.63786800	3.08629700
C	0.12972500	-3.00537500	1.73702100
C	-0.02733100	-2.06971300	0.70594400
C	-0.54762000	0.52563300	0.31214300
C	-0.57219000	1.52543000	1.31300100
H	-0.16901100	-1.01285900	4.49530200
H	0.21425900	-3.39275300	3.85276900
H	0.32547900	-4.04408800	1.49662200
H	-1.87812000	0.66257900	-0.35656600
H	-0.70155500	2.58667600	1.18098700
N	-0.49586700	0.99524800	2.53740000
C	-0.44961700	1.73749400	3.78609900
H	0.56715300	1.69722600	4.18837800
H	-0.72491700	2.77431500	3.58913200
H	-1.15685100	1.31133600	4.50328000
P	0.11638900	-2.56658600	-1.04698300
O	0.31340900	-1.29789600	-1.90776200

C	-1.53510600	-3.33392200	-1.50916900
C	-1.96483500	-4.47269600	-0.56314900
C	-2.56063900	-2.18801900	-1.39092300
C	-1.49175800	-3.82546700	-2.96952200
H	-1.30216400	-5.34025200	-0.59967800
H	-2.03389000	-4.13078900	0.47391900
H	-2.96350000	-4.81142400	-0.86481700
H	-2.31332900	-1.34640200	-2.03973700
H	-3.55041300	-2.56253600	-1.67779100
H	-2.63644100	-1.81844800	-0.36629300
H	-2.50665700	-4.10415800	-3.27829300
H	-1.13918500	-3.04052700	-3.64607200
H	-0.85740800	-4.70828300	-3.09547600
C	1.60360900	-3.69214000	-1.32568800
C	2.77975600	-3.16454900	-0.47821400
C	1.34685300	-5.17539300	-0.99972800
C	1.98482600	-3.55524600	-2.81962500
H	3.00891900	-2.12386900	-0.71139600
H	2.59414800	-3.22011800	0.59566700
H	3.66398600	-3.77329800	-0.70592500
H	0.57659500	-5.61925200	-1.63635100
H	2.27645600	-5.72956300	-1.17691200
H	1.07188000	-5.34199900	0.04619200
H	2.89206700	-4.14630400	-2.99370300
H	1.21009400	-3.92894600	-3.49450500
H	2.19671600	-2.51560700	-3.07885400

IM_2(1a)

S	-3.55433700	1.23132300	-0.42780200
O	-3.42280600	1.14507700	1.04264500
O	-3.62532100	2.56222000	-1.03675100
O	-2.58340600	0.27865900	-1.13365600
C	-5.17009500	0.39315100	-0.82244200
F	-5.18917300	-0.83542900	-0.28951700
F	-5.33195600	0.29622800	-2.14509000
F	-6.18105600	1.10302900	-0.30700600
C	-1.75838600	-1.88218300	0.27944000
C	-2.71128900	-2.01818800	1.28144300
C	-1.43205700	-2.92431700	-0.57969800
C	-3.36564000	-3.24643900	1.41052400
H	-2.96818400	-1.17898200	1.91799200
C	-2.10328900	-4.14408200	-0.43205600
H	-0.67793300	-2.80468700	-1.35109800
C	-3.07365200	-4.32371400	0.56178300

H	-4.12225300	-3.36204100	2.18385900
H	-1.86125500	-4.96471500	-1.10397500
Cu	-1.03139500	-0.16456100	-0.01981900
C	-3.81421000	-5.63439100	0.69706600
H	-3.23548900	-6.46825900	0.28573100
H	-4.04020800	-5.86198000	1.74480800
H	-4.77051500	-5.60238300	0.15845200
O	2.99065700	-3.16407400	-0.09910800
S	2.91363900	-2.54541500	-1.41858300
O	2.99587000	-3.31186600	-2.64595600
O	1.63412100	-1.58231600	-1.51264600
C	4.26470000	-1.26138700	-1.47897500
F	5.44471200	-1.87872000	-1.43114800
F	4.14874200	-0.44341600	-0.42723400
F	4.17245900	-0.55459100	-2.60428800
C	1.55376700	0.15603800	1.39937800
C	2.43645600	-0.60314400	2.22671700
C	3.63674200	-0.09586700	2.72677200
C	3.96415500	1.21814300	2.41350400
C	3.10700900	2.00223700	1.62421400
C	1.90755700	1.49524500	1.11387400
C	0.46180600	-0.73656700	1.02122600
C	0.73529300	-1.93364200	1.66780100
H	4.29623300	-0.70954300	3.33260300
H	4.89148700	1.64614800	2.78173200
H	3.39476900	3.02627500	1.41304900
H	1.26891600	-1.37489700	-0.59476400
H	0.18001500	-2.85831600	1.64277100
N	1.89634900	-1.86321000	2.38710000
C	2.57397400	-2.98735100	3.00964800
H	2.92748700	-2.70672500	4.00638900
H	1.86765900	-3.81377900	3.10753800
H	3.41572700	-3.31136200	2.39032200
P	0.76585800	2.49705300	0.11897000
O	-0.33147700	1.57776100	-0.44495800
C	1.65832300	3.17885000	-1.38701200
C	2.51629000	4.42382400	-1.10429500
C	2.54719000	2.03404700	-1.92139500
C	0.58559100	3.51138500	-2.44994400
H	1.90912800	5.27986500	-0.79556500
H	3.28377600	4.24614700	-0.34407000
H	3.03568300	4.70729400	-2.02796400
H	1.97075600	1.11859400	-2.08718800
H	2.97346500	2.33848500	-2.88481400

H	3.37224400	1.80123300	-1.24443200
H	1.09668500	3.81016200	-3.37348400
H	-0.04625500	2.64636600	-2.66347700
H	-0.06393400	4.33624500	-2.14688100
C	-0.03384100	3.74286100	1.26099400
C	-0.82873100	2.89612300	2.28364500
C	0.97787700	4.62399000	2.01880900
C	-1.01499400	4.61456600	0.44909400
H	-1.60687800	2.29728000	1.80577700
H	-0.17183300	2.23473500	2.86009700
H	-1.31725300	3.57962800	2.98884300
H	1.60100200	5.23228600	1.35761500
H	0.41671100	5.31211100	2.66263400
H	1.63039800	4.03035300	2.66607900
H	-1.61236500	5.20998100	1.15009900
H	-0.48871000	5.31496200	-0.20864700
H	-1.70769500	4.01124000	-0.14607600

TS_2(1a)

S	-2.33308100	-2.00226900	-1.22804100
O	-2.51803600	-0.79583400	-2.05834100
O	-2.03987600	-3.27063400	-1.89735500
O	-1.42276700	-1.75211100	-0.02496700
C	-3.96757400	-2.23555400	-0.37051200
F	-4.28713200	-1.12535800	0.31772200
F	-3.91177100	-3.26460300	0.48178100
F	-4.93087300	-2.46805000	-1.27124000
C	-1.62060100	1.48123000	0.67258800
C	-2.86506400	1.63146000	0.06377300
C	-1.32650900	2.05827900	1.90609200
C	-3.85431600	2.33941800	0.74923500
H	-3.06566800	1.15926600	-0.89226900
C	-2.33565000	2.75874400	2.57320100
H	-0.33725100	1.95389700	2.33938700
C	-3.60882400	2.90984600	2.00738800
H	-4.84052200	2.43631000	0.30019900
H	-2.12244000	3.20308600	3.54310100
Cu	-0.55565900	0.01719000	0.15306700
C	-4.70333300	3.64528200	2.74508300
H	-4.29374400	4.37498200	3.45169500
H	-5.36663200	4.17668300	2.05376100
H	-5.32607300	2.94668500	3.31961500
C	1.69936200	1.51317500	-0.80339600
C	2.00256900	2.53866400	-1.75818300

C	3.29380500	2.80421700	-2.21672500
C	4.32751700	2.01365000	-1.73204300
C	4.06522600	0.97680900	-0.82157700
C	2.77762300	0.71438200	-0.33816200
C	0.24840900	1.51404500	-0.66421000
C	-0.21415100	2.50958600	-1.49531900
H	3.47803600	3.58838400	-2.94522100
H	5.34466300	2.18146200	-2.07290600
H	4.89556900	0.35563700	-0.50937300
H	-1.22923700	2.83324400	-1.66762300
N	0.82236100	3.13183400	-2.14998800
C	0.70393100	4.18677800	-3.13776600
H	1.04877100	3.84260200	-4.11969100
H	-0.34406100	4.48200100	-3.21695000
H	1.29411200	5.06056300	-2.83999000
P	2.45559000	-0.74935400	0.70440400
O	1.01111500	-0.73210400	1.21068100
C	3.53934500	-0.67127700	2.24009200
C	5.04875800	-0.47909600	2.00551100
C	2.99914000	0.54139100	3.03531500
C	3.29805500	-1.95899400	3.05588200
H	5.48412300	-1.24851700	1.36188900
H	5.27193700	0.50278400	1.58026000
H	5.55940400	-0.53638900	2.97497100
H	1.94160700	0.41536500	3.28093500
H	3.56777400	0.63585900	3.96871600
H	3.11652600	1.47450100	2.47236500
H	3.73739700	-1.83471800	4.05354000
H	2.23062300	-2.16507000	3.17777000
H	3.77399600	-2.83028800	2.59453700
C	2.66137800	-2.26432500	-0.39666500
C	2.00218100	-1.92075700	-1.75368600
C	4.12801600	-2.66836100	-0.61912700
C	1.86287400	-3.42414300	0.23977100
H	0.95367800	-1.63007200	-1.63292900
H	2.53130700	-1.12365000	-2.28403500
H	2.01308900	-2.81837400	-2.38304600
H	4.61255000	-2.99103300	0.30813100
H	4.16084600	-3.51472800	-1.31604000
H	4.71959100	-1.85990100	-1.06250300
H	1.90517500	-4.28482300	-0.43889000
H	2.27564500	-3.73935300	1.20171300
H	0.81369000	-3.15026000	0.37858500

3aa

C	-0.11909600	1.69277000	-0.13014700
C	-0.38476800	3.10460200	-0.08684500
C	-1.66413100	3.66029600	-0.04607900
C	-2.73987700	2.78628400	-0.03092500
C	-2.52146400	1.40016900	-0.05675800
C	-1.24749800	0.82221600	-0.11444400
C	1.33098800	1.56636800	-0.13797800
C	1.82647400	2.84856200	-0.09595100
H	-1.80669200	4.73669200	-0.01851600
H	-3.75556000	3.16926700	0.00641100
H	-3.39153500	0.75734800	-0.02281000
H	2.86154100	3.16293600	-0.09198900
N	0.81454800	3.77995100	-0.07182300
C	0.96615400	5.21866500	-0.02748400
H	0.51057400	5.63325900	0.87979700
H	2.03021400	5.46401000	-0.02763100
H	0.49805200	5.68870100	-0.90045600
P	-1.13111700	-1.01725800	-0.07722200
O	0.19638700	-1.54853300	-0.54788800
C	-2.48025200	-1.72607600	-1.22747300
C	-3.91497900	-1.82204100	-0.67755100
C	-2.46524200	-0.87847500	-2.51865500
C	-2.00363200	-3.15298400	-1.59108800
H	-3.97622200	-2.46934600	0.20209900
H	-4.34917900	-0.85290900	-0.41702300
H	-4.55957900	-2.26296100	-1.44952400
H	-1.44758000	-0.77940200	-2.91161000
H	-3.07551700	-1.37589200	-3.28361400
H	-2.86961500	0.12533600	-2.36423000
H	-2.67095300	-3.56325300	-2.36031200
H	-0.98187200	-3.14002900	-1.97525000
H	-2.03115300	-3.83059800	-0.73284400
C	-1.39371300	-1.45969400	1.74074700
C	-0.11939600	-0.94595300	2.44855300
C	-2.62771400	-0.82324700	2.40256200
C	-1.44414900	-2.99458200	1.87207000
H	0.78150500	-1.38173100	2.00949700
H	-0.03353500	0.14430000	2.38081200
H	-0.16358900	-1.21579800	3.51197900
H	-3.56762900	-1.14144800	1.94319100
H	-2.66022300	-1.12495400	3.45773600
H	-2.58494700	0.26927500	2.37092900
H	-1.37920900	-3.27150500	2.93243300

H	-2.37790800	-3.41331400	1.48270200
H	-0.60584200	-3.46181300	1.34602900
C	2.26725500	0.41331700	-0.16484300
C	2.54962700	-0.27347900	-1.35341500
C	2.98448100	0.06739600	0.98478000
C	3.50222000	-1.28422500	-1.38122300
H	2.00020300	-0.01889900	-2.25407600
C	3.93604100	-0.95487000	0.95662900
H	2.78846600	0.60052200	1.91156600
C	4.20696200	-1.65024200	-0.22479800
H	3.70056900	-1.80779000	-2.31432200
H	4.47558500	-1.21094600	1.86630700
C	5.20954200	-2.77997600	-0.25960000
H	4.70576500	-3.75584700	-0.26696600
H	5.83484200	-2.73511600	-1.15932400
H	5.87183800	-2.75940700	0.61269200

IM_3(1a)

C	0.98847300	-1.32004200	0.03227500
C	0.33373700	-2.46369200	0.50574600
C	0.88343500	-3.34872900	1.41927000
C	2.17557600	-3.05642100	1.86485500
C	2.86858100	-1.94755500	1.37340300
C	2.30091000	-1.05881800	0.43757800
C	0.01984500	-0.58583600	-0.87796200
C	-1.14598300	-1.52417600	-0.90329700
H	0.34299900	-4.21971700	1.77359900
H	2.65315000	-3.70886500	2.58927500
H	3.87845500	-1.78043100	1.72826000
H	-2.10008700	-1.40156000	-1.41652800
N	-0.95007200	-2.54403800	-0.11911100
C	-1.92211600	-3.59988700	0.18092400
H	-2.25589200	-3.46770900	1.21146900
H	-2.77928900	-3.47703200	-0.47978100
H	-1.43491700	-4.56837200	0.04095400
P	3.24678800	0.30280800	-0.38727400
O	2.43224200	0.87826700	-1.52116100
C	-0.48926700	0.76777700	-0.36672200
C	-0.43167400	1.89564500	-1.18564600
C	-1.08725200	0.85839700	0.89376200
C	-0.98541300	3.09811900	-0.74972000
H	0.07024500	1.83909500	-2.14515800
C	-1.63880500	2.06201100	1.31818500
H	-1.17540300	-0.01803700	1.52540700

C	-1.61470000	3.19613500	0.49727300
H	-0.94103100	3.97021200	-1.39778900
H	-2.13488300	2.10675500	2.28385900
C	-2.31025200	4.46276200	0.93023700
H	-2.01932400	5.31940300	0.31377700
H	-3.39750200	4.33910900	0.84260600
H	-2.09529600	4.70485900	1.97740700
H	0.43979200	-0.43709700	-1.87831500
C	4.80004300	-0.51039900	-1.11142000
C	5.93775800	-0.81495300	-0.12287900
C	4.33915700	-1.81975300	-1.79124900
C	5.31684100	0.44506200	-2.21207400
H	6.33916800	0.09040300	0.34111200
H	5.63679600	-1.50673400	0.66915100
H	6.76133100	-1.29267800	-0.66879500
H	3.49370500	-1.64134100	-2.46399000
H	5.16576600	-2.22272800	-2.38926500
H	4.04920700	-2.58443400	-1.06443200
H	6.12851500	-0.05174200	-2.75824400
H	4.52194200	0.69791100	-2.91746400
H	5.71677000	1.37605900	-1.80172600
C	3.60059200	1.58743100	0.94156800
C	2.24459500	2.27130800	1.22159200
C	4.14967200	1.01053400	2.25927500
C	4.57721200	2.63476300	0.36919700
H	1.81740700	2.70814500	0.31670200
H	1.50830300	1.57285500	1.62995900
H	2.39613800	3.06847400	1.96018900
H	5.09330300	0.47197400	2.13470400
H	4.33761800	1.83983000	2.95242000
H	3.42820600	0.34384000	2.74073400
H	4.62919700	3.48766900	1.05715200
H	5.59239200	2.24061500	0.26036100
H	4.23970700	3.00758400	-0.60306500
O	-4.10191700	-1.79907200	-1.25427500
S	-4.45311000	-1.11556200	0.03140100
O	-5.78151200	-1.41193600	0.57934100
O	-3.32113400	-1.12955000	1.00133800
C	-4.53689900	0.67298500	-0.49735000
F	-5.60682800	0.89884400	-1.27035400
F	-3.43441200	0.99679900	-1.20755700
F	-4.60030000	1.49670900	0.56380800

TS_3(1a)

C	1.34469400	-1.14430000	0.43603100
C	0.71772600	-1.99394900	1.39193100
C	1.45230200	-2.61095900	2.41491500
C	2.82131100	-2.38082400	2.43570100
C	3.45494900	-1.55344600	1.48660500
C	2.73439300	-0.91199200	0.47598200
C	0.29096900	-0.65820300	-0.42583100
C	-0.94322400	-1.20673400	0.07151600
H	0.97040700	-3.24489800	3.15144400
H	3.42604900	-2.85131900	3.20596000
H	4.52717500	-1.41839900	1.56231400
H	-1.84010700	-1.40183900	-0.52177000
N	-0.63148100	-2.05132000	1.14698900
C	-1.63084500	-2.64296200	2.02873500
H	-1.50409200	-2.25906700	3.04828000
H	-2.62034000	-2.35418300	1.66758700
H	-1.52893800	-3.73289800	2.03792300
P	3.48398500	0.20824300	-0.79048200
O	2.48373800	0.51639200	-1.87993600
C	-0.93900500	0.41942800	0.43553900
C	-1.72062300	1.20759100	-0.42705400
C	-0.59360400	0.90078300	1.71094700
C	-2.16215900	2.45211100	-0.00160900
H	-2.04587200	0.80353800	-1.37968400
C	-1.04188900	2.14621300	2.11569500
H	0.01750800	0.30141400	2.37789100
C	-1.82838200	2.94649800	1.26638500
H	-2.80661000	3.03252100	-0.65362300
H	-0.78379000	2.51076000	3.10644200
C	-2.29206300	4.31129000	1.70399300
H	-3.28455200	4.53948200	1.30258100
H	-2.33333600	4.39374800	2.79457400
H	-1.60609500	5.08788200	1.33939600
H	0.45660900	-0.18522100	-1.38195100
C	4.96760600	-0.69716900	-1.53369900
C	6.24976400	-0.69902400	-0.68412000
C	4.51270800	-2.14938600	-1.80210600
C	5.25421800	-0.01866500	-2.89288700
H	6.64320400	0.30950100	-0.52814800
H	6.11510800	-1.17186300	0.29333700
H	7.02224600	-1.27100100	-1.21340000
H	3.57655900	-2.17423700	-2.36980500
H	5.28018400	-2.66027900	-2.39632500
H	4.37030400	-2.71646400	-0.87740600

H	6.02522800	-0.59531900	-3.41901000
H	4.35591200	0.01591500	-3.51344600
H	5.62646100	1.00302000	-2.77659900
C	3.91827900	1.77932000	0.15540100
C	2.55190300	2.41518900	0.50167100
C	4.71243200	1.56610300	1.45609400
C	4.68402800	2.72348800	-0.79265200
H	1.94643800	2.57740600	-0.39382900
H	1.97610100	1.78901000	1.19102400
H	2.72021400	3.38176000	0.99279000
H	5.69237300	1.11146100	1.28933900
H	4.88209000	2.54224400	1.92794700
H	4.16209600	0.94829700	2.17175800
H	4.75939700	3.71570100	-0.33049700
H	5.70351400	2.37485500	-0.98597800
H	4.16434900	2.83387000	-1.74952700
O	-3.39902300	-1.22140900	-1.62139800
S	-4.46414000	-1.18900500	-0.56936800
O	-5.42061000	-2.30355700	-0.59672400
O	-3.92977500	-0.81292600	0.76909300
C	-5.47434600	0.29936000	-1.06384900
F	-6.07885100	0.09769900	-2.24212000
F	-4.68812400	1.39616500	-1.18882000
F	-6.41085500	0.57254700	-0.14457800

3aa'

C	-0.09061000	0.91540900	-0.07074500
C	0.57857100	2.17565800	-0.00123700
C	-0.11006500	3.38834300	0.06178700
C	-1.50064900	3.33789900	0.06970900
C	-2.18227300	2.10927500	0.01888100
C	-1.50622500	0.88668100	-0.05443300
C	0.93299300	-0.08132600	-0.13640000
C	2.15030100	0.56250700	-0.09939300
H	0.41524900	4.33749600	0.11445100
H	-2.07126400	4.26078100	0.12307300
H	-3.26587400	2.12692400	0.03980700
H	0.77325600	-1.14710700	-0.17125600
N	1.93954100	1.94454000	-0.01809700
C	2.92559100	2.99983200	-0.16542900
H	3.12708700	3.50217000	0.78903700
H	3.85754500	2.57972800	-0.54420200
H	2.56363500	3.74408000	-0.88263100
P	-2.36467500	-0.73723700	-0.09408700

O	-1.43395600	-1.86363700	-0.47956900
C	-3.75700900	-0.62814200	-1.37790500
C	-5.04335800	0.09066500	-0.93533200
C	-3.16107700	0.08114300	-2.61449700
C	-4.10245400	-2.08148800	-1.77485600
H	-5.53436500	-0.41889000	-0.10085500
H	-4.87421600	1.13266700	-0.64934000
H	-5.75189900	0.09812600	-1.77417300
H	-2.22445600	-0.39304500	-2.92641200
H	-3.87177400	0.01049000	-3.44808300
H	-2.96118700	1.13986200	-2.42681500
H	-4.80018200	-2.06264600	-2.62221000
H	-3.20475100	-2.63125000	-2.06622900
H	-4.58582200	-2.62970000	-0.96091700
C	-2.98203200	-0.99893900	1.67122400
C	-1.69385500	-1.22664800	2.49585800
C	-3.75845400	0.18203300	2.27929300
C	-3.83446600	-2.28163500	1.71717900
H	-1.11879700	-2.06888000	2.10242300
H	-1.04903200	-0.34097000	2.48846400
H	-1.96530100	-1.43950400	3.53795500
H	-4.68986100	0.39841000	1.74880900
H	-4.02347800	-0.06436800	3.31593600
H	-3.15484900	1.09383400	2.30048700
H	-4.02008400	-2.55890300	2.76297800
H	-4.80966900	-2.14616400	1.23777200
H	-3.31918900	-3.11571500	1.23054200
C	3.48077500	-0.05705900	-0.10057400
C	3.73015900	-1.16063000	-0.93578700
C	4.51530800	0.37659500	0.74527100
C	4.96657700	-1.79752100	-0.92497000
H	2.94429600	-1.50407500	-1.60204900
C	5.75449900	-0.26170600	0.74302400
H	4.34041800	1.20166500	1.42990400
C	6.00400800	-1.35930400	-0.08894100
H	5.13521800	-2.64601900	-1.58458100
H	6.53771200	0.09270800	1.40950300
C	7.33566700	-2.07150700	-0.07165500
H	8.11873600	-1.45172700	0.37742600
H	7.27901000	-3.00190100	0.50893800
H	7.65734800	-2.34301400	-1.08363800

1b

C	-2.02851100	-0.32574700	-0.37372600

C	-3.15850000	-0.78003100	0.36751000
C	-3.03534000	-1.56339900	1.51837800
C	-1.75133900	-1.90371600	1.93114400
C	-0.61688900	-1.46561800	1.22080100
C	-0.73405900	-0.67243800	0.07715200
C	-2.53506800	0.43076500	-1.48198000
C	-3.90085200	0.41477700	-1.37598400
H	-3.90946800	-1.89997000	2.06884200
H	-1.61832900	-2.52058700	2.81540200
H	0.36629300	-1.76233700	1.57266400
H	-1.94567000	0.88966600	-2.26120700
H	-4.65178200	0.86031600	-2.01475600
N	-4.29220300	-0.31076200	-0.26234600
C	-5.65059000	-0.56439500	0.16818200
H	-5.81970600	-0.17400600	1.17883700
H	-6.34162800	-0.06858800	-0.51689700
H	-5.86738300	-1.63938100	0.16720100
P	0.69805200	0.00845200	-0.82009200
C	2.14320100	-1.00478200	-0.33867800
C	2.82615500	-0.85869700	0.87706700
C	2.56961400	-1.97099900	-1.26045400
C	3.90962700	-1.68580900	1.17558700
H	2.52285900	-0.09166200	1.58411200
C	3.65558600	-2.79377000	-0.96049400
H	2.05259600	-2.05496900	-2.21190000
C	4.32283200	-2.65541600	0.25869200
H	4.43622500	-1.56773700	2.11894700
H	3.98381700	-3.53963500	-1.67952400
H	5.16945900	-3.29617000	0.49112300
C	0.97561300	1.65724000	-0.07766100
C	1.49756800	2.65410600	-0.91298800
C	0.70012400	1.95149200	1.26527900
C	1.75870300	3.92685900	-0.40491600
H	1.67817800	2.42305900	-1.95886800
C	0.96608800	3.22457300	1.77115700
H	0.26268300	1.19263700	1.90886300
C	1.49807400	4.21142200	0.93767300
H	2.16115000	4.69778700	-1.05673000
H	0.74943600	3.44893400	2.81233400
H	1.70095200	5.20358500	1.33249200
O	0.52159200	0.07363800	-2.31294600

3ba

C	0.29639800	2.00873600	-0.21839900

C	0.27485800	3.41182900	0.05929900
C	-0.89842600	4.16683200	0.12598200
C	-2.09935900	3.50367300	-0.07821000
C	-2.12095000	2.11815400	-0.31532700
C	-0.95449500	1.34806300	-0.37700700
C	1.69311600	1.61808200	-0.21175300
C	2.40739200	2.75844100	0.07848400
H	-0.86844500	5.23317300	0.33099100
H	-3.03564300	4.05292800	-0.04177400
H	-3.08336500	1.63578800	-0.44419400
H	3.47999400	2.87672200	0.15288100
N	1.57194000	3.84022200	0.24409900
C	1.97201200	5.20545500	0.51265700
H	1.49791900	5.57575100	1.42907100
H	3.05569700	5.24004500	0.64246500
H	1.69582700	5.86680500	-0.31727300
P	-1.11570900	-0.45149900	-0.68391100
O	-0.72868100	-0.92381100	-2.06015100
C	2.34582600	0.31585800	-0.46652400
C	2.19288600	-0.35799200	-1.68547500
C	3.18867100	-0.24826400	0.50392800
C	2.83994000	-1.57160800	-1.90930100
H	1.53850800	0.04924600	-2.44645300
C	3.83979500	-1.45586500	0.26990100
H	3.30508600	0.25562800	1.45954400
C	3.66783300	-2.14496400	-0.93763300
H	2.68843900	-2.08481100	-2.85615700
H	4.47463400	-1.88142800	1.04435600
C	4.31568600	-3.49138800	-1.15730100
H	4.43009800	-3.71533700	-2.22326000
H	5.30576700	-3.54487200	-0.69027400
H	3.70772500	-4.29499500	-0.71863600
C	-2.87065200	-0.85977600	-0.34035900
C	-3.43497600	-0.83847300	0.94321500
C	-3.66167600	-1.22521700	-1.43702300
C	-4.77751100	-1.16796400	1.12378100
H	-2.82598900	-0.57317600	1.80260300
C	-5.00612700	-1.55447200	-1.25359600
H	-3.20648700	-1.25759300	-2.42241600
C	-5.56515100	-1.52393100	0.02502000
H	-5.20893500	-1.15201900	2.12124100
H	-5.61480600	-1.83819400	-2.10812100
H	-6.61113500	-1.78250200	0.16846600
C	-0.19400600	-1.26396500	0.66767100

C	0.35984200	-2.52319900	0.40684200
C	-0.06341500	-0.69887500	1.94382400
C	1.02922000	-3.21435400	1.41586500
H	0.28649100	-2.93442700	-0.59494700
C	0.60301200	-1.39517800	2.95225200
H	-0.45929600	0.29351500	2.14217600
C	1.14740600	-2.65435000	2.68964900
H	1.46750500	-4.18634000	1.20514700
H	0.70635400	-0.95102900	3.93894100
H	1.67267900	-3.19319000	3.47402800

IM_3(1b)

C	0.15162600	-0.63750300	0.89907900
C	0.90272100	-1.13487200	1.96514300
C	1.09444300	-0.44978700	3.15277600
C	0.47795200	0.80141900	3.25544900
C	-0.26601600	1.32590500	2.19604100
C	-0.44099900	0.61606500	0.99512400
C	0.21237100	-1.63500800	-0.23844500
C	1.20212900	-2.62075900	0.30672900
H	1.72286500	-0.83723600	3.94664600
H	0.60869700	1.38692800	4.16020400
H	-0.68341900	2.32356500	2.29234900
H	1.53208400	-3.52432200	-0.18359200
N	1.47503000	-2.38530700	1.56329200
C	2.48364700	-3.08313600	2.35477600
H	2.09978300	-3.24981400	3.36400300
H	2.70823000	-4.03889400	1.88036800
H	3.37595900	-2.44894300	2.36750800
P	-1.35265600	1.29983300	-0.44547400
O	-1.07508100	0.53535600	-1.71010100
C	-1.11097100	-2.32673300	-0.56470800
C	-1.52939600	-2.45816000	-1.89144900
C	-1.92858400	-2.82220500	0.45648600
C	-2.74987000	-3.06380600	-2.18523200
H	-0.92004300	-2.04241700	-2.68657500
C	-3.15089200	-3.42068400	0.15679000
H	-1.62335600	-2.71337700	1.49460400
C	-3.58535200	-3.54637900	-1.16852800
H	-3.06681900	-3.14627400	-3.22227700
H	-3.78094100	-3.78570200	0.96457900
C	-4.93582700	-4.14242800	-1.48813700
H	-4.94907200	-4.60057500	-2.48263700
H	-5.22223000	-4.90612200	-0.75705100

H	-5.71803900	-3.37108200	-1.47457700
H	0.61968600	-1.16451200	-1.13641500
O	2.61875800	0.66593900	-0.40548700
S	3.53655200	-0.45699400	-0.12577300
O	3.98545300	-0.59005000	1.28068800
O	3.11240500	-1.76275700	-0.74168400
C	5.08377800	-0.05519200	-1.07993900
F	5.61548800	1.09023400	-0.62938600
F	4.80915800	0.08424100	-2.38336400
F	5.99070000	-1.03248400	-0.93541900
C	-0.87265600	3.05326700	-0.46534200
C	-1.80718900	4.08109900	-0.65451200
C	0.49922200	3.35711100	-0.39376700
C	-1.37890800	5.40581800	-0.75000000
H	-2.86573700	3.84964000	-0.72667300
C	0.91762100	4.68309600	-0.49338700
H	1.23434700	2.56462300	-0.27259600
C	-0.01817800	5.70677500	-0.66611300
H	-2.10673600	6.20007700	-0.89253500
H	1.97745100	4.91523600	-0.43825300
H	0.31414900	6.73893800	-0.74092200
C	-3.10692700	1.17503300	0.05016900
C	-3.87167100	0.20576300	-0.61283900
C	-3.67853200	1.91457500	1.09651500
C	-5.19538000	-0.01931900	-0.23345800
H	-3.41668500	-0.37027600	-1.41193600
C	-5.00429000	1.69206900	1.46704600
H	-3.09450400	2.66979300	1.61546000
C	-5.76296400	0.72315100	0.80326000
H	-5.78116700	-0.77599800	-0.74874100
H	-5.44569400	2.27255600	2.27272300
H	-6.79486500	0.54887100	1.09677600

TS_3(1b)

C	1.02807800	-1.55728400	0.27930100
C	0.40016400	-2.31464600	1.30301100
C	1.15958300	-2.92252000	2.31746000
C	2.53814000	-2.76137400	2.26493700
C	3.17012500	-1.98508800	1.26741500
C	2.42018700	-1.35540700	0.27735900
C	-0.02020300	-1.06806900	-0.58013700
C	-1.26751900	-1.48739300	0.01017800
H	0.68645000	-3.49749600	3.10627300
H	3.15276400	-3.23617300	3.02475300

H	4.24986100	-1.87445100	1.28523600
H	-2.19936800	-1.66804500	-0.53126600
N	-0.95921100	-2.28636100	1.12576200
C	-1.95555000	-2.79614200	2.06106700
H	-1.72709500	-2.44641600	3.07455200
H	-2.93243100	-2.40652300	1.76502800
H	-1.96234000	-3.89107900	2.04975200
P	3.07087800	-0.13781400	-0.92579800
O	2.42505100	-0.25714900	-2.27899500
C	-1.13570700	0.15011900	0.24012500
C	-1.89365900	0.92495400	-0.65508300
C	-0.64695800	0.72381600	1.42990700
C	-2.16607200	2.25157900	-0.34943600
H	-2.32396900	0.46235500	-1.53685800
C	-0.93030700	2.04489800	1.71554600
H	-0.03856500	0.14010500	2.11210500
C	-1.68274200	2.83671900	0.82657700
H	-2.78545600	2.83121900	-1.02604800
H	-0.54671500	2.48741700	2.63019600
C	-1.93466100	4.28690200	1.14276100
H	-2.62821500	4.74348300	0.43130500
H	-2.34990100	4.40559700	2.15035900
H	-0.99360700	4.85186900	1.11204300
H	0.12984800	-0.69022000	-1.58099300
O	-3.81543000	-1.43658200	-1.54794300
S	-4.81043000	-1.26582600	-0.44194600
O	-5.84411200	-2.30529900	-0.34990500
O	-4.17146400	-0.85685700	0.83998400
C	-5.73711900	0.26545500	-0.96677200
F	-6.40809600	0.05190200	-2.10653200
F	-4.88252300	1.29486800	-1.18050500
F	-6.60886700	0.64835200	-0.02332400
C	4.87697400	-0.35599500	-0.96758300
C	5.74910900	0.15865500	0.00267800
C	5.38964800	-1.09903900	-2.04145100
C	7.11940800	-0.08562800	-0.09183400
H	5.36749800	0.76414500	0.81902200
C	6.76072100	-1.33806800	-2.13212800
H	4.70955700	-1.46776200	-2.80360900
C	7.62466900	-0.83638700	-1.15607300
H	7.79278400	0.31747300	0.65951300
H	7.15482300	-1.91102300	-2.96672400
H	8.69276700	-1.02221400	-1.22891700
C	2.68869000	1.45158000	-0.10675500

C	2.15294100	2.46672900	-0.90996500
C	2.85871400	1.67072800	1.26919300
C	1.81051200	3.69629100	-0.34523000
H	1.99516100	2.27524900	-1.96719900
C	2.53015600	2.90589500	1.82648000
H	3.22453700	0.87170100	1.90883500
C	2.00752900	3.91959300	1.01879000
H	1.38878100	4.47830300	-0.97036500
H	2.66876900	3.07339400	2.89117500
H	1.74616700	4.87982000	1.45570000

N-methylindole

C	-0.38815300	0.98686400	0.00015100
C	0.15226200	-0.33071400	-0.00071600
C	-0.65677700	-1.47246300	-0.00060000
C	-2.03440400	-1.28178400	-0.00016000
C	-2.59238300	0.01385600	0.00034400
C	-1.78432500	1.14443000	0.00047800
C	0.72761700	1.89005000	0.00043100
C	1.86198900	1.12174900	-0.00057000
H	-0.22667000	-2.47016200	-0.00064100
H	-2.69256900	-2.14646600	-0.00012000
H	-3.67327000	0.12586000	0.00075000
H	0.69073300	2.97068300	0.00071200
H	2.90299100	1.41669000	-0.00104800
N	1.52953500	-0.22256200	-0.00167200
C	2.45106900	-1.33781500	0.00153100
H	2.30101500	-1.97079600	-0.88136400
H	3.47507900	-0.95794600	-0.01194900
H	2.31773400	-1.95402400	0.89901500
H	-2.22315000	2.13905500	0.00101500

3I

C	1.28831100	0.49965500	-0.04985600
C	2.52367100	-0.20199000	0.02061200
C	3.76159400	0.44619500	-0.04511600
C	3.75403800	1.82854500	-0.19723500
C	2.54262900	2.54353800	-0.29162200
C	1.31569300	1.89373900	-0.22377200
C	0.23525000	-0.48829300	0.04013000
C	0.86875100	-1.70649300	0.15341600
H	4.69357500	-0.10872100	0.01597900
H	4.69745900	2.36500100	-0.25076500
H	2.57130100	3.62162800	-0.42462000

H	0.43645500	-2.69094300	0.27234500
N	2.24043500	-1.54882300	0.14320000
C	3.22802700	-2.59753200	0.28015800
H	3.81902400	-2.46409500	1.19447600
H	2.72125300	-3.56377600	0.32832000
H	3.90983900	-2.60203800	-0.57849100
C	-1.21668000	-0.26948000	0.02127300
C	-2.08043500	-1.18213700	-0.60860500
C	-1.79599200	0.84591700	0.65087200
C	-3.45962600	-0.99024000	-0.60218200
H	-1.65819100	-2.04231700	-1.12222100
C	-3.17567400	1.03857600	0.64338400
H	-1.15887500	1.54980200	1.17795000
C	-4.03506100	0.12727100	0.01673700
H	-4.10183400	-1.71551300	-1.09795800
H	-3.59446300	1.90868800	1.14509500
C	-5.52766900	0.35731600	-0.01722300
H	-6.07909100	-0.58818700	-0.06569600
H	-5.87007500	0.90295500	0.86908300
H	-5.81997300	0.94915800	-0.89536900
H	0.38958600	2.45259400	-0.31636300

IM_3(N-methylindole)

C	1.11371400	-1.75387300	-0.44710900
C	0.26124300	-2.42828000	0.43184300
C	-0.05555300	-3.77330600	0.31264500
C	0.54828800	-4.46300200	-0.74265800
C	1.42072000	-3.81313800	-1.62562200
C	1.70683500	-2.44938000	-1.49191200
C	1.11812300	-0.29915400	-0.06073500
C	0.32736800	-0.32128400	1.20258000
H	-0.74104300	-4.26570400	0.99372400
H	0.33448800	-5.51855500	-0.87896800
H	1.87686700	-4.37720700	-2.43369400
H	0.05581500	0.53326900	1.80773500
N	-0.18537700	-1.49669000	1.41768800
C	-1.24369300	-1.80444400	2.38147300
H	-0.92991600	-2.64429800	3.00589500
H	-1.45126100	-0.91441000	2.97157200
H	-2.13496400	-2.04410600	1.79701400
C	2.39629300	0.51261700	-0.04058400
C	2.32429500	1.89377600	-0.26000100
C	3.63600400	-0.07386300	0.22749500
C	3.47973900	2.66997500	-0.20887500

H	1.35891100	2.35085600	-0.46625300
C	4.78850900	0.71110900	0.26884200
H	3.70251200	-1.14527400	0.39808000
C	4.73115700	2.09325400	0.05092500
H	3.40986600	3.74161900	-0.37992800
H	5.74738900	0.24156500	0.47607100
C	5.98348800	2.93761200	0.06411300
H	5.79155700	3.93114700	0.48356000
H	6.77950800	2.46846500	0.65172800
H	6.36960800	3.08431400	-0.95324300
H	0.38827000	0.21713600	-0.72665400
O	-2.46472600	-0.72385000	-0.27664300
S	-2.33108400	0.71963900	0.04357100
O	-2.24024300	1.00849200	1.50235700
O	-1.31520900	1.43881500	-0.77453300
C	-3.95094500	1.47223200	-0.47514600
F	-4.96285900	0.90459700	0.19907600
F	-4.15468200	1.28363700	-1.78620700
F	-3.95894800	2.78901300	-0.22589100
H	2.37368600	-1.94420100	-2.18347100

TS_3(N-methylindole)

C	-3.25039400	-0.33911900	0.98561900
C	-3.17465200	-1.03367100	-0.25416400
C	-4.32668700	-1.30401200	-1.00714800
C	-5.54403100	-0.89801300	-0.47351600
C	-5.63382600	-0.22593900	0.76517800
C	-4.49026800	0.06789900	1.49570100
C	-1.89700300	-0.19207000	1.45563600
C	-1.04171000	-0.79055000	0.46137300
H	-4.26764300	-1.81653200	-1.96133700
H	-6.45588700	-1.10409000	-1.02701500
H	-6.60830700	0.06819500	1.14186200
H	-0.06281800	-1.23585600	0.65174000
N	-1.86156700	-1.32856000	-0.53550600
C	-1.35597800	-1.83764000	-1.80498200
H	-1.68183400	-1.18705700	-2.62573700
H	-0.26455200	-1.83281700	-1.76663900
H	-1.72920100	-2.85194800	-1.97729300
C	-0.82353900	0.86696800	0.38263500
C	0.38143200	1.30019000	0.96394900
C	-1.48463200	1.67553600	-0.56041100
C	0.92928600	2.51367700	0.57215500
H	0.92256300	0.64562200	1.63924200

C	-0.92209100	2.88308200	-0.93486200
H	-2.42959700	1.35925700	-0.98982200
C	0.29503100	3.32283200	-0.37977900
H	1.88525200	2.81658400	0.98646400
H	-1.42969300	3.50359100	-1.66867500
C	0.92159700	4.61514500	-0.83296300
H	1.53403800	5.06385000	-0.04469700
H	1.57886000	4.43462100	-1.69397700
H	0.16621500	5.34402000	-1.14455200
H	-1.59227400	0.04614300	2.46475400
O	1.73814400	-1.57382600	1.22286300
S	2.42212300	-1.51316000	-0.10887700
O	3.06667400	-2.75615800	-0.55120400
O	1.61141900	-0.78978600	-1.12740600
C	3.84140400	-0.34692000	0.22050600
F	4.72504000	-0.89434500	1.06470300
F	3.39801400	0.80526700	0.78235800
F	4.47556400	-0.02743100	-0.91576300
H	-4.54923500	0.59927300	2.44101800

THF

C	-1.16678000	0.42639400	0.12987600
O	-0.00283700	1.25217400	0.00696700
C	1.16213300	0.43271300	-0.13872200
C	0.73590500	-0.99258100	0.23381300
C	-0.72803800	-0.99941700	-0.22980000
H	-1.54074700	0.47417900	1.16465900
H	-1.94944100	0.81675800	-0.53165100
H	1.51611000	0.47671200	-1.18108800
H	1.95481800	0.83070500	0.50572000
H	1.35198900	-1.76054000	-0.24417700
H	0.79121800	-1.13629300	1.31971500
H	-0.78150300	-1.15407800	-1.31429700
H	-1.33907100	-1.76748800	0.25438400

HOTf•THF

C	2.76526300	1.04251400	-0.36202400
O	2.00765200	0.03185600	-1.08965200
C	2.15574700	-1.26248300	-0.43986100
C	3.35076300	-1.10369400	0.49750600
C	3.22135000	0.36593900	0.92976600
H	3.60553000	1.34521200	-0.99744800
H	2.10906600	1.90045100	-0.19526700
H	1.23812700	-1.48088000	0.11407800

H	2.29524900	-2.00879600	-1.22656400
H	3.31214000	-1.80429700	1.33641200
H	4.28892100	-1.26723700	-0.04551900
H	2.44535600	0.46993600	1.69304000
H	4.15547800	0.78760400	1.31167700
O	-0.39443400	0.87600600	-1.29581300
S	-1.05813100	0.86885100	0.14549800
O	-0.03549800	0.65810800	1.17116100
O	-2.03065800	1.94177300	0.23719100
C	-2.01420800	-0.73086200	0.04652700
F	-1.17080100	-1.73247500	-0.25154200
F	-2.95038100	-0.65463400	-0.89546500
F	-2.58263700	-0.97537000	1.22677600
H	0.56461900	0.48825600	-1.25086200

TEMPO

C	-1.32685400	-0.06911400	-0.03040400
C	-1.24638000	1.40089700	-0.48733300
C	-0.00009600	2.12908400	0.01963800
C	1.24602300	1.40089500	-0.48767300
C	1.32686300	-0.06895900	-0.03043000
H	-0.00014600	3.16499600	-0.34009300
H	-1.24398800	1.42963900	-1.58566000
H	-2.16218900	1.90866700	-0.16102300
H	1.24299200	1.42921000	-1.58601700
H	2.16197600	1.90889800	-0.16210800
H	-0.00000300	2.18264800	1.11530000
N	0.00003700	-0.74384900	-0.22101500
O	0.00008100	-2.01975100	-0.06384000
C	-2.34558300	-0.82464800	-0.89810500
H	-2.43273500	-1.86332200	-0.57443500
H	-3.32504300	-0.33989400	-0.81980800
H	-2.03604900	-0.81687000	-1.94855900
C	-1.73739100	-0.18213100	1.45222500
H	-2.77634400	0.14219400	1.57944800
H	-1.65122200	-1.22418000	1.77233700
H	-1.11063200	0.43280600	2.10388300
C	1.73764100	-0.18182000	1.45213700
H	1.65178100	-1.22389300	1.77225700
H	2.77659400	0.14263900	1.57907400
H	1.11106600	0.43310000	2.10399800
C	2.34562000	-0.82451900	-0.89807100
H	3.32494800	-0.33942600	-0.82021900
H	2.43320400	-1.86303600	-0.57400000

H	2.03582700	-0.81733200	-1.94845300

HOTf•TEMPO

O	1.55224000	-1.17675500	-1.10118900
S	2.14592200	-0.85641600	0.33786700
O	1.08456000	-0.43479400	1.25265000
O	3.09551000	-1.89507000	0.69418300
C	3.13821100	0.67647800	-0.05356500
F	2.33968300	1.59948300	-0.60344100
F	4.11927900	0.38151600	-0.90332300
F	3.65454200	1.15902300	1.07786600
H	0.63738600	-0.73183800	-1.23080600
C	-1.93012500	1.42431000	-0.04302200
C	-2.61634500	1.36705500	1.33560700
C	-3.65766300	0.25391600	1.45598600
C	-2.97745100	-1.09341100	1.21067600
C	-2.31911100	-1.20899700	-0.17796000
H	-4.10277800	0.26802500	2.45749700
H	-1.84517100	1.21104300	2.10100900
H	-3.06148900	2.35055600	1.52713500
H	-2.20312100	-1.24120200	1.97448200
H	-3.68858900	-1.92166700	1.31222700
H	-4.48160300	0.41043800	0.74902900
N	-1.53426300	0.03923700	-0.46920500
O	-0.72297800	-0.01263400	-1.47262700
C	-0.64734900	2.26282800	0.05672000
H	-0.16704600	2.36581700	-0.91737000
H	-0.90520200	3.25889500	0.43201900
H	0.06147800	1.79684900	0.74450700
C	-2.85456400	2.02171500	-1.12417800
H	-3.01142000	3.08603900	-0.91923400
H	-2.38558600	1.91978600	-2.10670500
H	-3.83337400	1.53604700	-1.15265000
C	-3.36314300	-1.39030700	-1.30008500
H	-2.86870700	-1.33829900	-2.27409300
H	-3.83835600	-2.37179000	-1.19914000
H	-4.14724500	-0.63001300	-1.26619100
C	-1.35232700	-2.40214000	-0.18384900
H	-1.90904200	-3.30491300	0.08780000
H	-0.90848400	-2.55619600	-1.16935400
H	-0.55354400	-2.25443900	0.54635700

BHT

C	-1.23132700	0.16866900	-0.00013200

C	-1.18781800	1.56985600	-0.00863000
C	0.00737500	2.28402500	-0.00959700
C	1.20415100	1.56411000	-0.00796900
C	1.24780900	0.16766400	0.00015800
C	0.00718400	-0.51402500	0.00583400
H	-2.11331700	2.13335200	-0.01530900
H	2.13081600	2.12628200	-0.01457400
C	2.59342400	-0.59106000	-0.00115600
C	2.71807900	-1.46330300	1.27193000
C	2.70984000	-1.47384500	-1.26774300
C	3.79704100	0.37465000	-0.00897000
H	2.66913400	-0.83738500	2.17097500
H	1.92548000	-2.21026400	1.32918000
H	3.68406600	-1.98377200	1.27508200
H	2.65547400	-0.85525300	-2.17153300
H	3.67557300	-1.99477800	-1.27271500
H	1.91659200	-2.22089700	-1.31380200
H	4.72529200	-0.20755700	-0.00917300
H	3.80801100	1.01151800	-0.90088800
H	3.81320000	1.01940600	0.87717700
C	-2.58639000	-0.57912900	-0.00117300
C	-2.73181800	-1.44899600	-1.27862600
C	-2.74082400	-1.43508300	1.28456500
C	-3.78587300	0.39309900	-0.01045600
H	-2.70605800	-0.81123900	-2.16856400
H	-1.94113700	-2.19493800	-1.40967400
H	-3.68858100	-1.98437700	-1.26735200
H	-2.72207700	-0.78770900	2.16770800
H	-3.69716500	-1.97117300	1.27194600
H	-1.95085300	-2.17914600	1.42992500
H	-4.71885800	-0.18167900	-0.01046700
H	-3.79484700	1.03820200	0.87438000
H	-3.78888200	1.02849300	-0.90233400
C	0.01694500	3.79553400	0.01175000
H	-0.94869200	4.20823700	-0.30007200
H	0.22816200	4.18243200	1.01794600
H	0.78580200	4.20187600	-0.65600000
O	0.07942900	-1.89227300	0.01304300
H	-0.80935600	-2.26444400	0.01508200

HOTf•BHT

O	-1.92236400	-0.37179400	1.44999200
S	-2.97767900	-0.94582700	0.39190700
O	-2.26621000	-1.55340700	-0.73500600

O	-4.02717000	-1.64005400	1.10999500
C	-3.69119400	0.65754500	-0.25291300
F	-2.69904800	1.40957400	-0.74420900
F	-4.29865700	1.31321700	0.73141700
F	-4.56273400	0.38327500	-1.22148900
H	-1.05541100	-0.18954000	0.96258000
C	1.98679600	1.35538800	0.02037800
C	3.36809400	1.46662300	0.21529200
C	4.21183100	0.35642100	0.26369800
C	3.65293800	-0.90975800	0.09992600
C	2.27707100	-1.11169300	-0.07631800
C	1.47303600	0.04708900	-0.09774500
H	3.81723700	2.44672300	0.32115600
H	4.32101900	-1.76161900	0.11987800
C	1.70345100	-2.54153400	-0.24392400
C	0.72399200	-2.87806900	0.90619300
C	1.00125800	-2.70612200	-1.61919700
C	2.81921200	-3.60810000	-0.20342900
H	1.23065200	-2.79954300	1.87415200
H	-0.14776800	-2.22544100	0.93052600
H	0.35567300	-3.90457800	0.79574800
H	1.65787400	-2.37933500	-2.43223400
H	0.75129000	-3.76035800	-1.78252100
H	0.04816600	-2.17316600	-1.71585300
H	2.37130800	-4.60127400	-0.31363800
H	3.54272600	-3.47953000	-1.01610200
H	3.36024700	-3.59710100	0.74861700
C	1.09499100	2.61379700	-0.09603600
C	0.38661700	2.63813000	-1.47265200
C	0.04703800	2.66195600	1.04157000
C	1.92681500	3.90995100	0.00862400
H	1.12412300	2.64382800	-2.28366100
H	-0.27103000	1.77923400	-1.60806100
H	-0.22072500	3.54716000	-1.56235100
H	0.52934400	2.57005600	2.02135700
H	-0.48466000	3.62085300	1.01632000
H	-0.70398500	1.87908100	0.94991200
H	1.26192500	4.77277100	-0.10605100
H	2.42235400	4.00477700	0.98144200
H	2.68742700	3.97503500	-0.77721500
C	5.69396000	0.52670300	0.50599200
H	6.08099700	1.42433200	0.01071400
H	5.91162400	0.62928000	1.57752000
H	6.26372000	-0.33330200	0.13835900

O	0.08340500	-0.05806600	-0.22495700
H	-0.16403500	-0.79310400	-0.80951600