Supporting Information

Electrochemical Oxidative N-H/P-H Cross-Coupling with H_2 Evolution towards the Synthesis of Tertiary Phosphines

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Contents

1. General information

1.1. Reagents and experimental conditions

All reactions were carried out under an atmosphere of argon in oven-dried glassware, unless otherwise noted. Except where stated, all starting materials were commercially available and used without further purification.

1.2. Analytical techniques

Chronoamperometry and cyclic voltammograms were obtained on a CorrTest® CS2350H bipotentiostat. Hydrogen gas content was analyzed by gas chromatography (GC9790 Plus, Fuli, China, TCD, N_2 as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector).

GC yields were recorded by SHIMADZU™ GC-2014 gas chromatography. Molecular weights of products were determined by SHIMADZU™ GCMS-QP2010 SE gas chromatgraphy mass spectrometrometry. All new compounds were characterized by High resolution mass spectra (HRMS). All undivided cells were purchased from Jiehengda® limited liability company (https://www.whjiehengda.com).

^1H and ^{13}C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform, 39.60 ppm, dimethylsulfoxide), respectively.

1.3. Compound purification

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm). Flash chromatography columns were packed with 200-300 silica gel in petroleum (b.p. 60-90 °C).

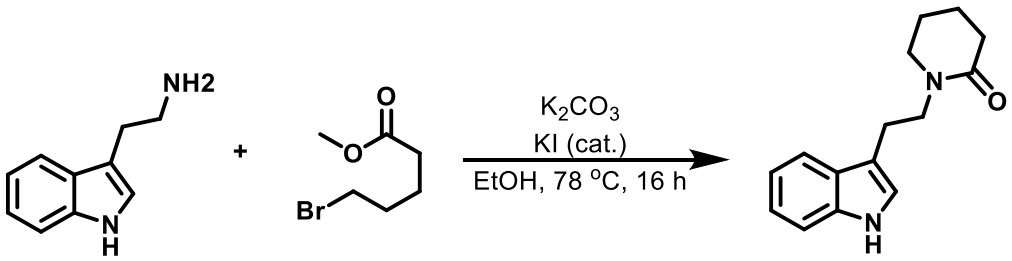
1.4. Electrochemical set-up

The instrument for electrolysis was Current (HSPY-120-01) (made in China).

2. Experimental procedures and characterization data

2.1. Synthesis of substrates

Synthesis of 1-(2-(1H-indol-3-yl)ethyl)piperidin-2-one (8s)[3]



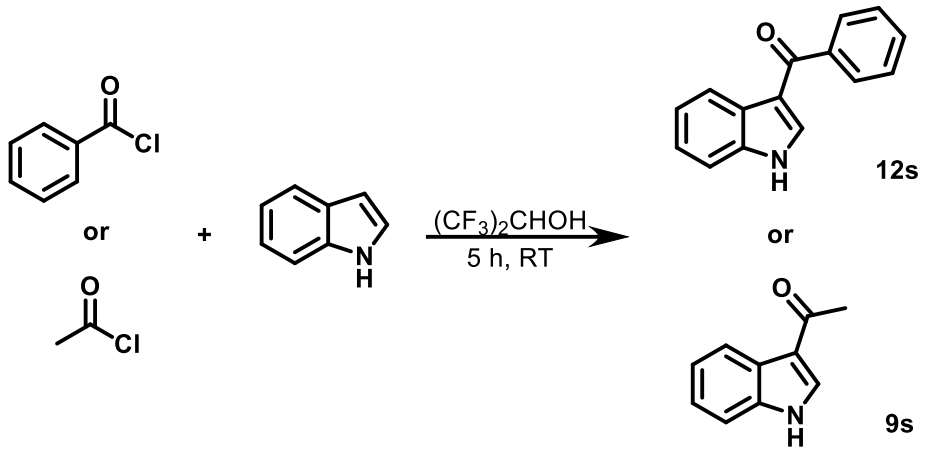
8s

A suspension of tryptamine (1 equiv.), methyl bromovalerate (1 equiv.), K_2CO_3 (22 equiv.) and KI (0.01 equiv.) in EtOH (2 mL/ mmol tryptamine) was refluxed for 16 h before being allowed to reach rt. The resulting suspension was concentrated in vacuo until most of the ethanol was evaporated, and then partitioned between H_2O (4 mL/ mmol tryptamine) and CH_2Cl_2 (4 mL/ mmol tryptamine). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 2 mL/ mmol tryptamine). The combined organic layers were washed with brine, dried with Na_2SO_4 and

concentrated in vacuo. Trituration afforded the indole-tethered lactam.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.89 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.19 (s, 1H), 7.16 – 6.97 (m, 2H), 3.60 – 3.43 (m, 3H), 3.19 (d, *J* = 6.5 Hz, 2H), 3.03 – 2.80 (m, 2H), 2.25 (s, 2H), 1.64 (s, 3H).

Synthesis of (1H-indol-3-yl)(phenyl)methanone (12s) and 1-(1H-indol-3-yl)ethan-1-one (9s) [1]

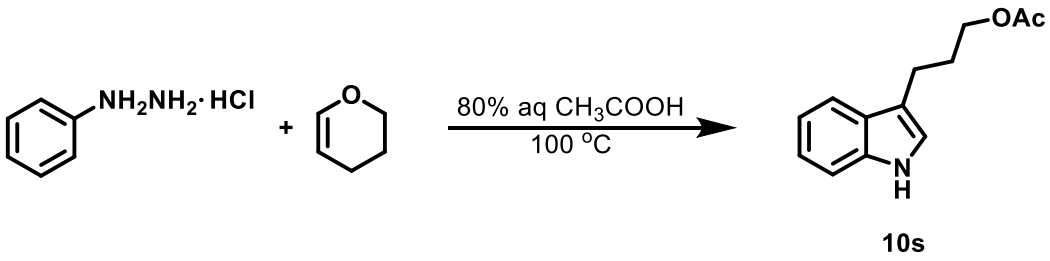


To a solution of indole (22. 5 mmol, 3.0 equiv.) in HFIP (10 mL) in an oven-dried N_2-flushed 2-dram vial, benzoyl chloride or acetyl chloride (7.50 mmol, 1.0 equiv.) was added. The resultant mixture was stirred at room temperature for 5 h. The reaction mixture was concentrated and the crude was purified using a normal phase silica flash column to afford ketone products.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.10 (s, 1H), 8.30 – 8.26 (m, 1H), 7.96 (d, *J* = 2.7 Hz, 1H), 7.84 – 7.75 (m, 2H), 7.65 – 7.59 (m, 1H), 7.59 – 7.52 (m, 3H), 7.32 – 7.22 (m, 2H).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.99 (s, 1H), 8.33 (d, *J* = 3.1 Hz, 1H), 8.27 (d, *J* = 6.4 Hz, 1H), 7.53 (d, *J* = 6.9 Hz, 1H), 7.23 (tt, *J* = 7.5, 5.7 Hz, 2H), 2.50 (s, 3H).

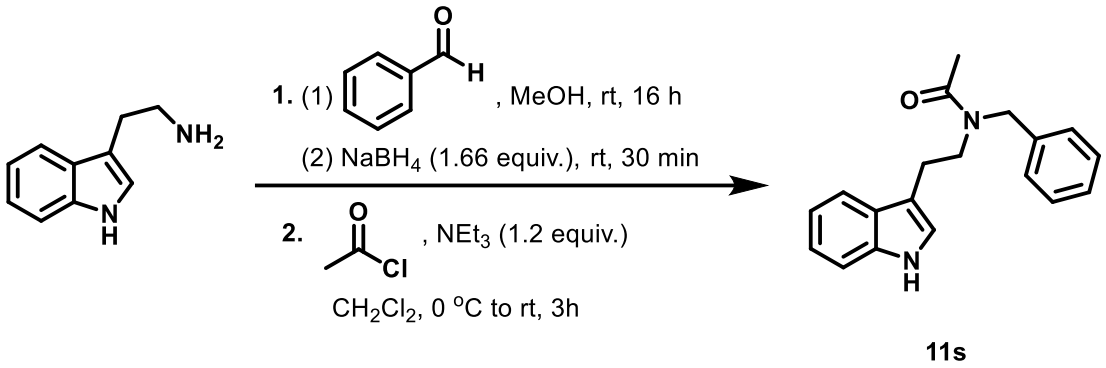
Synthesis of 3-(1H-indol-3-yl)propyl acetate (10s)[2]



Dihydropyran (0.92 g,11 mmol) was added dropwise to a solution of Phenylhydrazine Hydrochloride (1.44 g, 10 mmol) in 80% aqueous acetic acid over 2 min at room temperature. The reaction was refluxed for 140 min. The reaction mixture was quenched with 100 mL saturated aqueous $NaHCO_3$ solution and extracted with 2 x 50 mL ethyl acetate. The combined organic layers were dried over $NaSO_4$ and concentrated. Purify the crude product by column chromatography on silica gel.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.83 (s, 1H), 7.53 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 7.13 – 7.07 (m, 1H), 7.04 – 6.96 (m, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 2.82 – 2.74 (m, 2H), 2.04 (s, 3H), 2.02 – 1.92 (m, 2H).

Synthesis of N-(2-(1H-indol-3-yl)ethyl)-N-benzylacetamide (11s)[3]

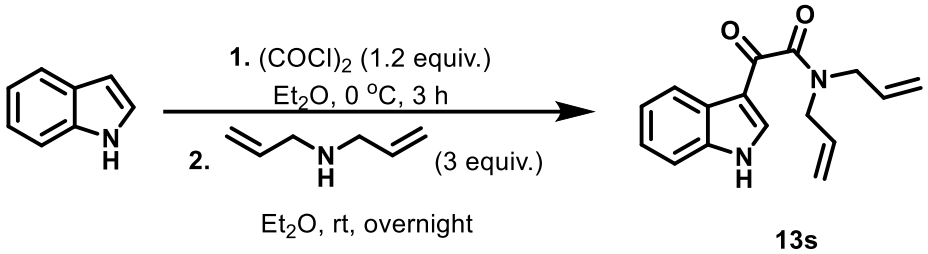


The Benzaldehyde was added to a solution of the tryptamine in MeOH (4 mL/mmol tryptamine) and stirred for 16 h. $NaBH_4$ (1.66 equiv.) was then added portionwise at rt and the resulting solution was stirred for 30 minutes before being concentrated in vacuo to about a third of its original volume. It was then quenched with saturated $NaHCO_3$ (3 mL /mmol tryptamine) and partitioned between EtOAc (5 ml/mmol tryptamine) and H_2O (5 mL/mmol tryptamine). The layers were separated and the organic layer was washed with brine, dried with Na_2SO_4 and concentrated in vacuo. The crude amine was used in the next step without further purification

A solution of the tryptamine (1 equiv.) and NEt_3 (1.2 equiv.) in CH_2Cl_2 (7 mL/mmol tryptamine) was added dropwise at 0 °C to a solution of the Acetyl Chloride (1.05 equiv.) in CH_2Cl_2 (3 mL/mmol tryptamine). The resulting solution was left to reach rt over 3 hours. H_2O (5 mL/ mmol tryptamine) was then added, the layers separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 2 mL/mmol tryptamine). The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated in vacuo. Trituration afforded the indole-tethered amide.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.03 – 10.89 (m, 1H), 7.60 (dd, *J* = 19.5, 7.5 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.41 – 7.27 (m, 4H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.22 – 7.11 (m, 1H), 7.06 (ddd, *J* = 11.3, 8.7, 5.8 Hz, 1H), 4.65 (s, 1H), 4.17 (d, *J* = 298.7 Hz, 1H), 3.60 (dd, *J* = 9.2, 6.5 Hz, 1H), 3.56 – 3.46 (m, 1H), 2.98 (dq, *J* = 12.1, 5.8 Hz, 2H), 2.93 – 1.87 (m, 3H).

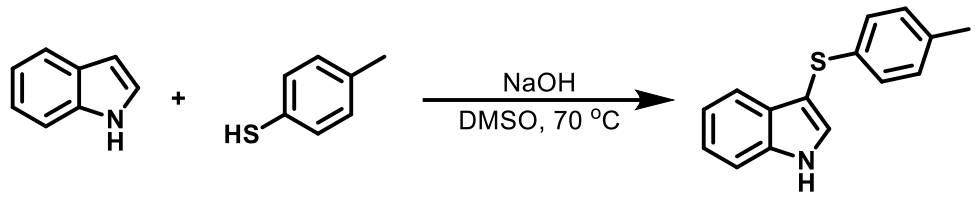
Synthesis of N,N-diallyl-2-(1H-indol-3-yl)-2-oxoacetamide (13s) [4]



Oxalyl chloride (12 mmol) was added dropwise at 0 °C to the solution of indole (10 mmol) in anhydrous diethyl ether (20 mL). The reaction mixture was stirred at 0 °C for 3 h. Next, the solution of diallylamine (30 mmol) in dry diethyl ether (20 mL) was added dropwise and the reaction mixture was stirred at ambient temperature overnight. Saturated aqueous solution of $NaHCO_3$ (30 mL) was added and phases were separated. Organic phase was dried with anhydrous $MgSO_4$, filtered and volatiles were removed in vacuo. The crude was purified product by column chromatography on silica gel.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 12.36 (s, 1H), 8.40 – 8.04 (m, 2H), 7.66 – 7.43 (m, 1H), 7.47 – 7.18 (m, 2H), 5.98 – 5.81 (m, 1H), 5.83 – 5.65 (m, 1H), 5.31 – 5.08 (m, 4H), 4.05 (d, *J* = 5.7 Hz, 2H), 3.87 (d, *J* = 5.8 Hz, 2H).

Synthesis of 3-(p-tolylthio)-1H-indole (14s)[5]

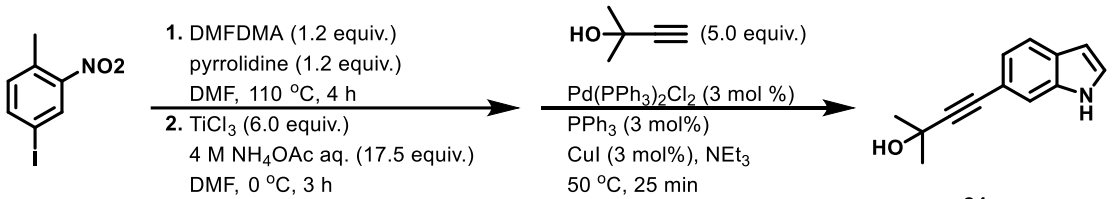


14s

The indole (10 mmol), thiol (20 mmol), NaOH (20 mmol) and DMSO (20 mL) were added in a 25 mL round bottom flask. The mixture was stirred for 6 h at 70 °C (TLC) in open air atmosphere. The reaction was allowed to cool down to room temperature, upon completion and 100 mL water was added. The heterogeneous mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic phase was dried overnight with anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.76 (s, 1H), 7.79 (d, *J* = 2.6 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.19 – 7.05 (m, 1H), 6.99 (s, 3H), 2.18 (s, 3H).

Synthesis of 4-(1H-indol-6-yl)-2-methylbut-3-yn-2-ol (24s)[6]



24s

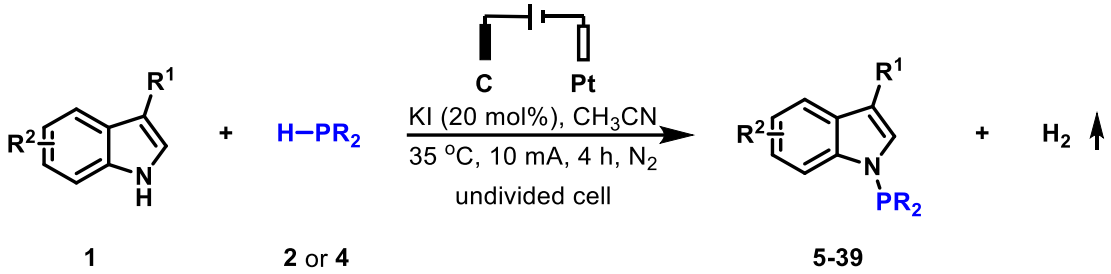
4-iodo-1-methyl-2-nitrobenzene (10.0 mmol, 1.0 equiv.) was dissolved in DMF (50 mL). DMFDMA (12.0 mmol, 1.2 equiv.) was added, followed by pyrrolidine (12.0 mmol, 1.2 equiv.). The mixture was heated to 110 °C for 4 h until complete consumption of starting material as monitored by TLC, and allowed to cool to rt. DMF (50 mL) and 4 M aqueous NH_4OAc buffer (17.5 equiv.) were added and the solution was cooled with an ice bath. An aqueous solution of 20% $TiCl_3$ in 3% HCl (60.0 mmol, 6.0 equiv.) was added via a dropping funnel. The reaction mixture was stirred for 3 h followed by extraction with TBME (3 × 50 mL). The organic phase was washed with 2 M NaOH (50 mL), H_2O (50 mL) and dried with $MgSO_4$. Purify the 6-iodo-1H-indole by column chromatography on silica gel

6-iodo-1H-indole (2.0 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (0.06 mmol, 3 mol %) and PPh_3 0.06 mmol, 3 mol %) were dissolved in NEt_3 (8 mL) under inert conditions und degassed for 15 min. Separately, NEt_3 (4 mL) was degassed followed by addition of CuI (0.06 mmol, 3 mol %) and degassed again for 5 min. The CuI solution was added to the reaction mixture. 2-Methylbut-3-yn-2-ol (10.0 mmol, 5.0 equiv.) was dissolved in NEt_3 (4 mL), degassed for 15 min and subsequently added to the reaction mixture followed by heating to 50 °C for 25 min. After completion of the reaction as monitored by TLC, the reaction mixture was filtered over Celite 545. The Celite had to be

thoroughly washed with EA (100 mL). Purify the crude product by column chromatography on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.63 – 7.56 (m, 1H), 7.55 – 7.50 (m, 1H), 7.27 (dd, *J* = 3.2, 2.4 Hz, 1H), 7.21 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.60 – 6.54 (m, 1H), 2.25 (s, 1H), 1.68 (s, 6H).

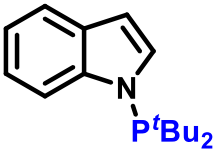
2.2. Synthesis of compound



1 **2 or 4** **5-39**

General procedure (GP1) for the electrochemical oxidative N-H/P-H Cross-Coupling reaction (5-39): In an oven-dried undivided three-necked flask (25.0 mL) equipped with a stir bar. The bottle was equipped with a carbon plate (1.5 × 2.0 × 0.10 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Indole (**1**, 0.5 mmol), and KI (16.7 mg, 20 mol%) were added. This was followed by the addition of Di-tert-butyl phosphine (73 mg, 0.5 mmol) and super dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixture was stirred at a constant current of 10.0 mA at 35 °C for 4 h (*J* = 4.4 mA/cm^2, 3.0 F/mol). At the end of the reaction, the desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 silica gel (petroleum: EtOAc = 100:1).

1-(Di-tert-butylphosphanyl)-1H-indole (3)



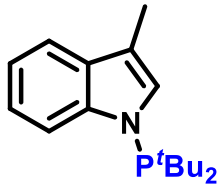
Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 1*H*-indole (59 mg, 0.5 mmol) and was obtained as white solid (124.0 mg, yield 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 3.4 Hz, 1H), 7.28 – 7.15 (m, 1H), 7.16 – 7.02 (m, 1H), 6.64 (s, 1H), 2.17 – 0.41 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.65 (d, *J* = 21.0 Hz), 130.51 (d, *J* = 8.7 Hz), 128.71 (d, *J* = 3.1 Hz), 121.78, 120.13, 120.03, 112.92 (d, *J* = 20.2 Hz), 105.37, 35.08 (d, *J* = 24.9 Hz), 29.07 (d, *J* = 16.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 71.27.

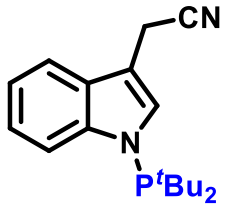
1-(Di-tert-butylphosphanyl)-3-methyl-1H-indole (5)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 3-methyl-1*H*-indole (63 mg, 0.5 mmol) and was obtained as white solid (134.8 mg, yield 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.19 (t, 2H), 7.12 (d, *J* = 7.1 Hz, 1H), 2.33 (m, *J* = 5.1 Hz, 3H), 1.19 (dd, *J* = 12.7, 4.6 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.17 (dd, *J* = 21.4, 1.8 Hz), 129.29 (d, *J* = 3.5 Hz), 127.70 (d, *J* = 9.1 Hz), 121.74, 119.47, 118.17, 114.17 (d, *J* = 1.9 Hz), 112.84 (d, *J* = 20.5 Hz), 35.01 (d, *J* = 24.9 Hz), 29.15 (d, *J* = 16.4 Hz), 9.91.
^{31}P NMR (162 MHz, $CDCl_3$) δ 70.05.

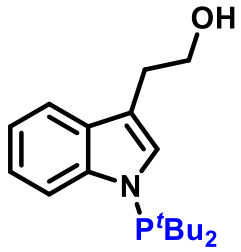
2-(1-(Di-tert-butylphosphanyl)-1H-indol-3-yl)acetonitrile (6)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 2-(1H-indol-3-yl)acetonitrile (78 mg, 0.5 mmol) and was obtained as white solid (141.0 mg, yield 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.45 (s, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 3.78 (s, 2H), 1.19 (d, *J* = 12.9 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.34 (d, *J* = 21.2 Hz), 128.97 (d, *J* = 9.2 Hz), 126.95 (d, *J* = 3.2 Hz), 122.92 (d, *J* = 1.9 Hz), 120.63 (d, *J* = 1.4 Hz), 118.15, 117.73, 113.54 (d, *J* = 20.2 Hz), 107.55 (d, *J* = 2.7 Hz), 35.21 (d, *J* = 25.6 Hz), 29.20 (d, *J* = 16.3 Hz), 14.62.
^{31}P NMR (162 MHz, $CDCl_3$) δ 72.88.

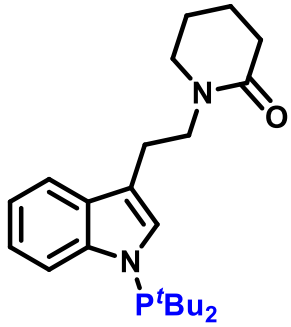
2-(1-(Di-tert-butylphosphaneyl)-1H-indol-3-yl)ethan-1-ol (7)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 2-(1H-indol-3-yl)ethan-1-ol (81 mg, 0.5 mmol) and was obtained as white solid (128.1 mg, yield 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.39 (s, 1H), 7.33 – 7.27 (m, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 3.97 (t, *J* = 6.5 Hz, 2H), 3.11 (t, *J* = 6.5 Hz, 2H), 1.87 (s, 1H), 1.28 (d, *J* = 12.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.26 (d, *J* = 21.2 Hz), 128.76 (d, *J* = 9.0 Hz), 128.28 (d, *J* = 3.3 Hz), 122.00 (d, *J* = 1.8 Hz), 119.74 (d, *J* = 1.5 Hz), 118.18, 114.72 (d, *J* = 2.2 Hz), 113.11 (d, *J* = 20.2 Hz), 62.43, 35.04 (d, *J* = 25.1 Hz), 29.09 (d, *J* = 16.3 Hz), 28.83.
^{31}P NMR (162 MHz, $CDCl_3$) δ 70.92.
HRMS (ESI): m/z calcd for $C_{18}H_{28}NOP$ $[M+H]^+$: 306.1981, found: 306.1972.

1-(2-(1-(Di-tert-butylphosphaneyl)-1H-indol-3-yl)ethyl)piperidin-2-one (8)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 1-(2-(1H-indol-3-yl)ethyl)piperidin-2-one (121 mg, 0.5 mmol) and was obtained as white solid (164.1 mg, yield 85%).

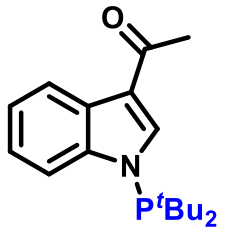
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 3.73 (t, *J* = 7.2 Hz, 2H), 3.14 (t, *J* = 5.9 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 1H), 2.39 (t, *J* = 6.5 Hz, 2H), 1.74 – 1.59 (m, 4H), 1.22 (d, *J* = 12.7 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.43, 143.99 (d, *J* = 21.3 Hz), 128.31 (d, *J* = 3.3 Hz), 127.91 (d, *J* = 9.2 Hz), 121.72 (d, *J* = 1.8 Hz), 119.49, 117.99, 115.71 (d, *J* = 2.1 Hz), 112.86 (d, *J* = 20.5 Hz), 48.35, 47.67, 34.95, 34.70, 32.22, 28.95 (d, *J* = 16.4 Hz), 22.94, 21.02.

^{31}P NMR (162 MHz, $CDCl_3$) δ 70.64.

HRMS (ESI): m/z calcd for $C_{23}H_{35}N_2OP$ $[M+H]^+$: 387.2560, found: 387.2550.

1-(1-(Di-tert-butylphosphanyl)-1H-indol-3-yl)ethan-1-one (9)



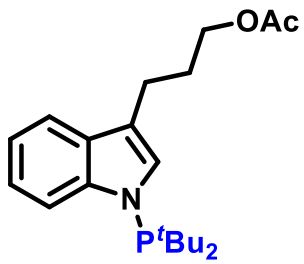
Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 1-(1H-indol-3-yl)ethan-1-one (80 mg, 0.5 mmol) and was obtained as white solid (128.8 mg, yield 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.31 (m, 1H), 8.10 (s, 1H), 7.92 – 7.82 (m, 1H), 7.32 – 7.21 (m, 2H), 2.57 (s, 3H), 1.22 (d, *J* = 12.9 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.86, 144.09 (d, *J* = 20.0 Hz), 137.56 (d, *J* = 9.0 Hz), 125.71 (d, *J* = 2.6 Hz), 123.21 (d, *J* = 1.9 Hz), 122.36 (d, *J* = 1.4 Hz), 121.53, 120.24 (d, *J* = 2.6 Hz), 112.94 (d, *J* = 20.2 Hz), 34.83 (d, *J* = 27.1 Hz), 28.72 (d, *J* = 16.4 Hz), 27.56.

^{31}P NMR (162 MHz, $CDCl_3$) δ 76.71.

3-(1-(Di-tert-butylphosphanyl)-1H-indol-3-yl)propyl acetate (10)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 3-(1H-indol-3-yl)propyl acetate (108 mg, 0.5 mmol) and was obtained as white solid (122.7 mg, yield 68%).

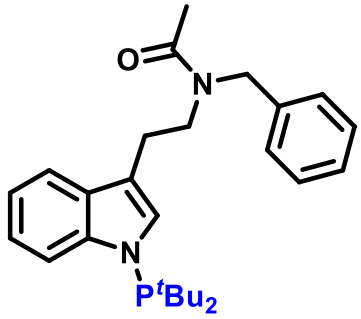
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.15 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.05 (m, *J* = 7.4 Hz, 5H), 1.24 – 1.15 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.89, 144.21 (d, *J* = 21.2 Hz), 128.21 (d, *J* = 3.4 Hz), 127.51 (d, *J* =

9.1 Hz), 121.80 (d, *J* = 1.8 Hz), 119.49, 118.06, 117.66 (d, *J* = 2.2 Hz), 112.95 (d, *J* = 20.3 Hz), 63.84, 34.96 (d, *J* = 25.3 Hz), 29.05 (d, *J* = 16.3 Hz), 28.62, 21.47, 20.85.

^{31}P NMR (162 MHz, $CDCl_3$) δ 70.48.

N-benzyl-N-(2-(1-(di-tert-butylphosphaneyl)-1H-indol-3-yl)ethyl)acetamide (11)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and N-(2-(1H-indol-3-yl)ethyl)-N-benzylacetamide (146 mg, 0.5 mmol) and was obtained as white solid (163.5 mg, yield 72%).

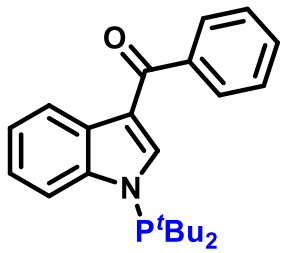
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (m, *J* = 8.1, 5.1, 2.6 Hz, 1H), 7.54 (dd, *J* = 25.2, 7.8 Hz, 1H), 7.41 – 7.10 (m, 8H), 4.69 (s, 0.9H), 4.36 (s, 1.1H), 3.75 (t, *J* = 7.3 Hz, 1.1H), 3.60 (t, *J* = 7.2 Hz, 0.9H), 3.13 (t, *J* = 7.2 Hz, 1.1H), 3.04 (t, *J* = 7.2 Hz, 0.9H), 2.18 (s, 1,65H), 2.08 (s, 1.35H), 1.28 (d, *J* = 2.4 Hz, 8H), 1.25 (d, *J* = 2.5 Hz, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.80, 170.46, 144.18 (d, *J* = 3.2 Hz), 143.97 (d, *J* = 3.1 Hz), 137.69, 136.70, 128.70, 128.40, 128.31, 128.25 (d, *J* = 6.1 Hz), 128.15 (d, *J* = 9.9 Hz), 128.07, 127.81 (d, *J* = 3.3 Hz), 127.39, 127.17, 126.15, 122.11, 121.84 (d, *J* = 1.8 Hz), 119.87, 119.63, 118.05, 117.58, 115.76 (d, *J* = 2.1 Hz), 114.74 (d, *J* = 2.5 Hz), 113.22 (d, *J* = 20.6 Hz), 112.96 (d, *J* = 20.5 Hz), 52.71, 48.18 (d, *J* = 6.2 Hz), 46.83, 35.04, 34.79, 29.01 (dd, *J* = 16.3, 2.7 Hz), 24.58, 23.44, 21.77, 21.32.

^{31}P NMR (162 MHz, $CDCl_3$) δ 71.24, 70.65.

HRMS (ESI): m/z calcd for $C_{27}H_{37}N_2OP$ $[M+H]^+$: 437.2716, found: 437.2715.

(1-(Di-tert-butylphosphaneyl)-1H-indol-3-yl)(phenyl)methanone (12)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and (1H-indol-3-yl)(phenyl)methanone (111 mg, 0.5 mmol) and was obtained as white solid (98.6 mg, yield 54%).

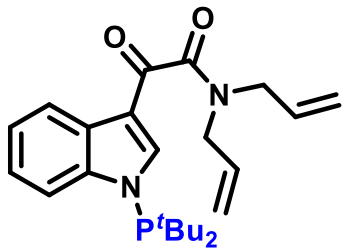
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.39 (m, 1H), 7.97 (d, *J* = 3.6 Hz, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.65 – 7.58 (m, 1H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.43 – 7.34 (m, 2H), 1.26 (d, *J* = 12.9 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.06, 144.21 (d, *J* = 19.9 Hz), 140.44, 140.00 (d, *J* = 9.1 Hz), 131.44, 128.74, 128.24, 126.87 (d, *J* = 2.4 Hz), 123.72 (d, *J* = 1.8 Hz), 122.70 (d, *J* = 1.4 Hz), 121.79, 118.97 (d, *J* = 2.6 Hz), 113.14 (d, *J* = 19.8 Hz), 35.07 (d, *J* = 27.0 Hz), 28.89 (d, *J* = 16.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 76.78.

HRMS (ESI): m/z calcd for $C_{23}H_{28}NOP$ $[M+H]^+$: 366.1981, found: 366.1970.

N,N-diallyl-2-(1-(di-tert-butylphosphaneyl)-1H-indol-3-yl)-2-oxoacetamide (13)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and N, N-diallyl-2-(1H-indol-3-yl)-2-oxoacetamide (134 mg, 0.5 mmol) and was obtained as white solid (127.7 mg, yield 62%).

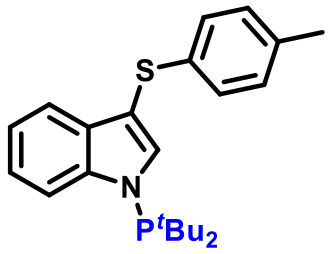
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.30 (m, 1H), 8.24 (s, 1H), 7.90 (dt, *J* = 6.6, 2.4 Hz, 1H), 7.41 – 7.31 (m, 2H), 5.95 – 5.75 (m, 2H), 5.32 – 5.22 (m, 2H), 5.22 – 5.14 (m, 2H), 4.15 (d, *J* = 5.7 Hz, 2H), 3.98 (d, *J* = 5.9 Hz, 2H), 1.25 (d, *J* = 12.9 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.60, 167.25, 144.21 (d, *J* = 19.6 Hz), 142.04 (d, *J* = 8.9 Hz), 132.87, 131.91, 125.67 (d, *J* = 2.2 Hz), 124.00 (d, *J* = 1.9 Hz), 123.13, 121.56, 118.42, 117.69, 116.76 (d, *J* = 2.5 Hz), 113.33 (d, *J* = 19.5 Hz), 49.66, 46.06, 35.11 (d, *J* = 27.2 Hz), 28.80 (d, *J* = 16.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 78.71.

HRMS (ESI): m/z calcd for $C_{24}H_{33}N_2O_2P_1$ $[M+H]^+$: 413.2352, found: 413.2343.

1-(Di-tert-butylphosphanyl)-3-(p-tolylthio)-1H-indole (14)



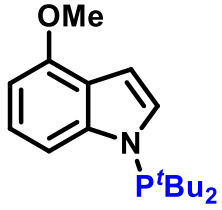
Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 3-(p-tolylthio)-1H-indole (120 mg, 0.5 mmol) and was obtained as white solid (132.1 mg, yield 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 1H), 7.75 – 7.68 (m, 1H), 7.55 (dd, *J* = 8.1, 3.4 Hz, 1H), 7.30 – 7.20 (m, 1H), 7.12 (td, *J* = 7.2, 6.7, 3.1 Hz, 1H), 7.05 – 6.92 (m, 4H), 2.21 (m, *J* = 2.6 Hz, 3H), 1.22 (m, *J* = 12.9, 2.7 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.32 (d, *J* = 20.7 Hz), 136.48 (d, *J* = 9.3 Hz), 135.16, 134.39, 129.44, 125.99, 122.78, 120.94, 119.13, 113.31 (d, *J* = 20.0 Hz), 106.04, 35.04 (d, *J* = 26.0 Hz), 29.01 (d, *J* = 16.3 Hz), 20.77 (d, *J* = 3.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 73.94.

1-(Di-tert-butylphosphanyl)-4-methoxy-1H-indole (15)



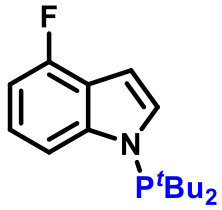
Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 4-methoxy-1H-indole (74 mg, 0.5 mmol) and was obtained as white solid (144.0 mg, yield 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.33 (d, *J* = 3.4 Hz, 1H), 7.12 (t, *J* = 8.1 Hz, 1H), 6.77 (dd, *J* = 3.1, 1.3 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 3.90 (s, 3H), 1.18 (d, *J* = 12.7 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.08 (d, *J* = 21.7 Hz), 129.07 (d, *J* = 8.8 Hz), 119.15 (d, *J* = 3.5 Hz), 106.36 (d, *J* = 20.5 Hz), 99.84, 55.07, 34.99 (d, *J* = 25.4 Hz), 29.03 (d, *J* = 16.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 72.78.

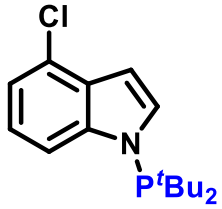
1-(Di-tert-butylphosphanyl)-4-fluoro-1H-indole (16)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 4-fluoro-1H-indole (68 mg, 0.5 mmol) and was obtained as white solid (128.3 mg, yield 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.40 (d, *J* = 3.4 Hz, 1H), 7.10 (td, *J* = 8.1, 5.3 Hz, 1H), 6.84 – 6.70 (m, 2H), 1.18 (d, *J* = 12.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.11 (dd, *J* = 246.3, 1.7 Hz), 146.34 (dd, *J* = 21.7, 10.4 Hz), 130.54 (d, *J* = 8.9 Hz), 122.06 (dd, *J* = 7.7, 1.5 Hz), 117.77 (dd, *J* = 21.9, 3.3 Hz), 109.08 (dd, *J* = 20.6, 3.5 Hz), 104.83 (d, *J* = 18.7 Hz), 101.14 (d, *J* = 2.1 Hz), 35.10 (d, *J* = 25.6 Hz), 29.01 (d, *J* = 16.3 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 74.26.
^{19}F NMR (376 MHz, $CDCl_3$) δ -122.83.

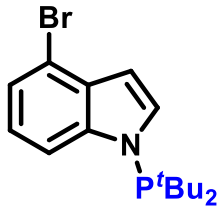
4-Chloro-1-(di-tert-butylphosphanyl)-1H-indole (17)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 4-chloro-1H-indole (76 mg, 0.5 mmol) and was obtained as white solid (132.8 mg, yield 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 1H), 7.46 (d, *J* = 3.3 Hz, 1H), 7.11 (q, *J* = 4.1, 3.5 Hz, 2H), 6.76 – 6.74 (m, 1H), 1.17 (d, *J* = 12.9 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.56 (d, *J* = 21.5 Hz), 131.40 (d, *J* = 8.6 Hz), 127.71 (d, *J* = 3.1 Hz), 125.60 (d, *J* = 1.4 Hz), 122.48 (d, *J* = 1.7 Hz), 119.95, 111.77 (d, *J* = 20.7 Hz), 103.94 (d, *J* = 2.2 Hz), 35.25 (d, *J* = 25.6 Hz), 29.16 (d, *J* = 16.3 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 74.34.

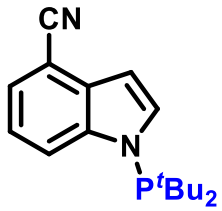
4-Bromo-1-(di-tert-butylphosphanyl)-1H-indole (18)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 4-bromo-1H-indole (97 mg, 0.5 mmol) and was obtained as white solid (159.3 mg, yield 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.47 (d, *J* = 3.3 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.73 – 6.68 (m, 1H), 1.17 (d, *J* = 12.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.96 (d, *J* = 21.5 Hz), 131.22 (d, *J* = 8.6 Hz), 129.41 (d, *J* = 2.9 Hz), 122.92, 122.65 (d, *J* = 1.6 Hz), 114.13 (d, *J* = 1.3 Hz), 112.12 (d, *J* = 20.8 Hz), 105.47 (d, *J* = 2.2 Hz), 35.07 (d, *J* = 25.7 Hz), 29.00 (d, *J* = 16.3 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 74.43.

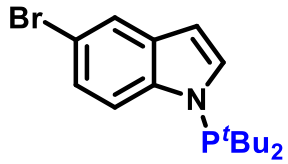
1-(Di-tert-butylphosphanyl)-1H-indole-4-carbonitrile (19)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 1H-indole-4-carbonitrile (71 mg, 0.5 mmol) and was obtained as white solid (128.7 mg, yield 90%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.63 (d, *J* = 3.3 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.28 – 7.19 (m, 1H), 1.19 (d, *J* = 12.9 Hz, 18H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 143.38 (d, *J* = 21.5 Hz), 133.52 (d, *J* = 8.8 Hz), 130.30 (d, *J* = 2.9 Hz), 121.64 (d, *J* = 1.9 Hz), 118.74, 117.76 (d, *J* = 20.9 Hz), 104.16 (d, *J* = 2.3 Hz), 102.74 (d, *J* = 1.4 Hz), 35.17 (d, *J* = 25.8 Hz), 29.00 (d, *J* = 16.3 Hz).
^{31}P NMR (162 MHz, CDCl$_3$) δ 74.74.

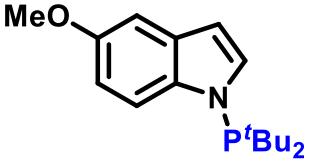
5-Bromo-1-(di-tert-butylphosphanyl)-1H-indole (20)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 5-bromo-1H-indole (97 mg, 0.5 mmol) and was obtained as white solid (161.0 mg, yield 95%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 – 7.58 (m, 2H), 7.32 (d, *J* = 3.3 Hz, 1H), 7.18 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.46 (d, *J* = 3.0 Hz, 1H), 1.06 (d, *J* = 12.9 Hz, 18H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 142.34 (d, *J* = 21.6 Hz), 131.74 (d, *J* = 8.8 Hz), 130.38 (d, *J* = 2.9 Hz), 124.61 (d, *J* = 1.9 Hz), 122.62, 114.37 (d, *J* = 21.0 Hz), 113.32 (d, *J* = 2.2 Hz), 104.75 (d, *J* = 2.0 Hz), 35.05 (d, *J* = 25.6 Hz), 28.97 (d, *J* = 16.1 Hz).
^{31}P NMR (162 MHz, CDCl$_3$) δ 72.99.

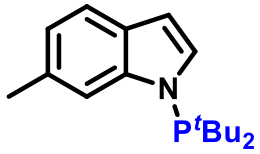
1-(Di-tert-butylphosphanyl)-5-methoxy-1H-indole (21)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 5-methoxy-1H-indole (63 mg, 0.5 mmol) and was obtained as white solid (114.9 mg, yield 79%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.41 (d, *J* = 3.2 Hz, 1H), 7.13 – 7.02 (m, 1H), 6.86 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.57 (d, *J* = 1.5 Hz, 1H), 3.82 (s, 3H), 1.19 (d, *J* = 12.7 Hz, 18H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 154.29 (d, *J* = 1.5 Hz), 138.71 (d, *J* = 21.6 Hz), 131.21 (d, *J* = 8.8 Hz), 128.99 (d, *J* = 3.1 Hz), 113.53 (d, *J* = 20.0 Hz), 111.65 (d, *J* = 1.7 Hz), 105.08 (d, *J* = 1.8 Hz), 101.95, 55.63, 35.09 (d, *J* = 25.2 Hz), 29.03 (d, *J* = 16.3 Hz).
^{31}P NMR (162 MHz, CDCl$_3$) δ 71.88.

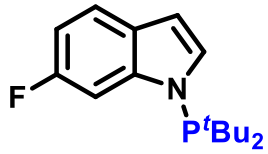
1-(Di-tert-butylphosphanyl)-6-methyl-1H-indole (22)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 6-methyl-1H-indole (63 mg, 0.5 mmol) and was obtained as white solid (114.1 mg, yield 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 0H), 7.37 (dd, *J* = 8.2, 2.8 Hz, 1H), 7.26 (t, *J* = 2.7 Hz, 1H), 6.86 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.49 (s, 1H), 2.38 (m, *J* = 2.5 Hz, 3H), 1.31 – 0.80 (m, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.08 (d, *J* = 20.8 Hz), 131.47 (d, *J* = 1.7 Hz), 129.94 (d, *J* = 8.7 Hz), 126.53 (d, *J* = 3.3 Hz), 121.80, 119.73, 112.89 (d, *J* = 20.0 Hz), 107.45 – 103.55 (m), 35.08 (d, *J* = 25.0 Hz), 29.12 (d, *J* = 16.4 Hz), 21.87.
^{31}P NMR (162 MHz, $CDCl_3$) δ 70.61.

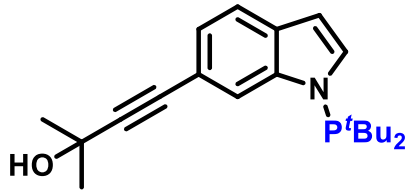
1-(Di-tert-butylphosphanyl)-6-fluoro-1H-indole (23)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 6-fluoro-1H-indole (68 mg, 0.5 mmol) and was obtained as white solid (133.9 mg, yield 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 10.7, 2.7 Hz, 1H), 7.46 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.39 (d, *J* = 2.9 Hz, 1H), 6.93 – 6.82 (m, 1H), 6.60 (d, *J* = 2.2 Hz, 1H), 1.18 (d, *J* = 12.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.84 (d, *J* = 236.9 Hz), 144.06 (dd, *J* = 22.3, 12.0 Hz), 131.00 (dd, *J* = 8.7, 3.8 Hz), 125.11 (d, *J* = 3.0 Hz), 120.62 (d, *J* = 10.0 Hz), 108.68 (d, *J* = 24.6 Hz), 105.28 (d, *J* = 1.9 Hz), 99.48 (dd, *J* = 26.9, 20.8 Hz), 35.07 (d, *J* = 25.3 Hz), 29.00 (d, *J* = 16.3 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) 73.12.
^{19}F NMR (376 MHz, $CDCl_3$) δ -107.15 – -128.72 (m).

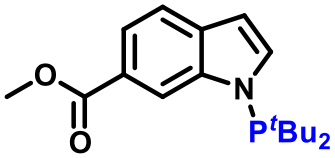
1-(Di-tert-butylphosphanyl)-3-methyl-1H-indole (24)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 4-(1H-indol-6-yl)-2-methylbut-3-yn-2-ol (100 mg, 0.5 mmol) and was obtained as white solid (154.4 mg, yield 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 1H), 7.57 – 7.48 (m, 2H), 7.22 (dd, 1H), 6.69 – 6.63 (m, 1H), 2.37 (s, 1H), 1.69 (s, 6H), 1.23 (d, *J* = 12.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.14 (d, *J* = 21.2 Hz), 131.97 (d, *J* = 8.7 Hz), 128.79 (d, *J* = 3.0 Hz), 123.73 (d, *J* = 1.3 Hz), 119.97, 116.48 (d, *J* = 20.7 Hz), 115.56 (d, *J* = 1.8 Hz), 105.49 (d, *J* = 2.0 Hz), 91.95, 83.71, 65.61, 35.03 (d, *J* = 25.3 Hz), 31.57, 28.99 (d, *J* = 16.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$)δ 71.92.
HRMS (ESI): m/z calcd for $C_{21}H_{31}NOP$ $[M+H]^+$: 344.2138, found: 344.2129.

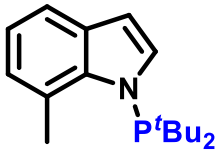
Methyl 1-(di-tert-butylphosphaneyl)-1H-indole-6-carboxylate (25)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and methyl 1H-indole-6-carboxylate (88 mg, 0.5 mmol) and was obtained as white solid (132.4 mg, yield 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.88 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.73 – 7.59 (m, 2H), 6.82 – 6.64 (m, 1H), 3.97 (s, 3H), 1.24 (d, *J* = 12.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.16, 143.00 (d, *J* = 21.3 Hz), 133.92 (d, *J* = 8.8 Hz), 132.42 (d, *J* = 2.9 Hz), 123.60 (d, *J* = 1.7 Hz), 121.22, 119.76, 115.04 (d, *J* = 20.5 Hz), 105.51 (d, *J* = 2.1 Hz), 51.76, 35.05 (d, *J* = 25.7 Hz), 28.96 (d, *J* = 16.4 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 72.71.
HRMS (ESI): m/z calcd for $C_{18}H_{26}NO_2P$ $[M+H]^+$: 320.1774, found: 320.1767

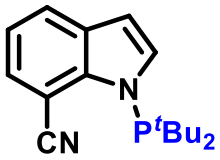
1-(Di-tert-butylphosphanyl)-7-methyl-1H-indole (26)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 7-methyl-1H-indole (76 mg, 0.5 mmol) and was obtained as white solid (134.8 mg, yield 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 2H), 6.94 (td, *J* = 7.4, 1.4 Hz, 1H), 6.54 (dt, *J* = 3.2, 1.5 Hz, 1H), 2.79 (d, *J* = 4.4 Hz, 3H), 1.12 (dd, *J* = 12.6, 1.4 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.03 (d, *J* = 15.2 Hz), 132.10 (d, *J* = 6.1 Hz), 129.81 (d, *J* = 2.9 Hz), 125.91, 123.67, 120.33, 118.50, 105.65 (d, *J* = 2.4 Hz), 35.76 (d, *J* = 29.7 Hz), 29.35 (d, *J* = 17.3 Hz), 24.56 (d, *J* = 28.3 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 78.97.

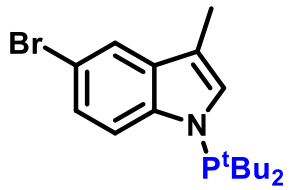
1-(Di-tert-butylphosphanyl)-1H-indole-7-carbonitrile (27)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 1H-indole-7-carbonitrile (71 mg, 0.5 mmol) and was obtained as white solid (114.4 mg, yield 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 1H), 7.58 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.53 (d, *J* = 3.4 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.72 (dd, *J* = 3.4, 1.5 Hz, 1H), 1.24 (d, *J* = 12.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.81 (d, *J* = 18.2 Hz), 132.87 (d, *J* = 6.3 Hz), 130.59 (d, *J* = 2.2 Hz), 130.33, 125.46, 119.86, 118.90 (d, *J* = 3.3 Hz), 105.87 (d, *J* = 2.6 Hz), 96.96 (d, *J* = 13.0 Hz), 35.26 (d, *J* = 29.4 Hz), 28.93 (d, *J* = 16.9 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 74.06.

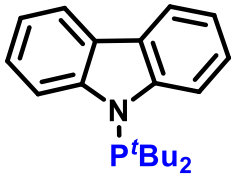
5-Bromo-1-(di-tert-butylphosphaneyl)-3-methyl-1H-indole (28)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 5-bromo-3-methyl-1H-indole (104 mg, 0.5 mmol) and was obtained as white solid (158.9 mg, yield 90%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.73 (t, *J* = 1.6 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.29 (s, 1H), 2.38 (d, *J* = 1.2 Hz, 3H), 1.27 (d, *J* = 12.8 Hz, 18H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 142.80 (d, *J* = 21.7 Hz), 130.99 (d, *J* = 3.2 Hz), 128.95 (d, *J* = 9.1 Hz), 124.52 (d, *J* = 1.9 Hz), 120.88, 114.34 (d, *J* = 21.0 Hz), 113.71 (d, *J* = 2.2 Hz), 112.83 (d, *J* = 2.2 Hz), 35.01 (d, *J* = 25.2 Hz), 29.03 (d, *J* = 16.4 Hz), 9.79.
^{31}P NMR (162 MHz, CDCl$_3$) δ 71.63.
HRMS (ESI): m/z calcd for $C_{17}H_{25}BrNP$ $[M+H]^+$: 354.0981, found: 354.0976.

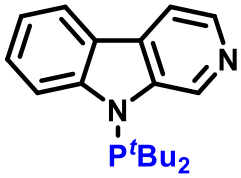
9-(Di-tert-butylphosphanyl)-9H-carbazole (29)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 9H-carbazole (84 mg, 0.5 mmol) and was obtained as white solid (138.4 mg, yield 89%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.16 (dd, *J* = 8.5, 3.7 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.38 (dt, *J* = 18.8, 7.8 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 1.29 (d, *J* = 13.4 Hz, 18H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 147.98 (d, *J* = 26.4 Hz), 143.13 (d, *J* = 13.4 Hz), 126.21 (d, *J* = 1.9 Hz), 125.50 (d, *J* = 2.7 Hz), 124.77, 124.62 (d, *J* = 3.4 Hz), 120.07, 120.04, 119.95, 119.24, 115.42, 114.12 (d, *J* = 30.1 Hz).
^{31}P NMR (162 MHz, CDCl$_3$) δ 78.71.

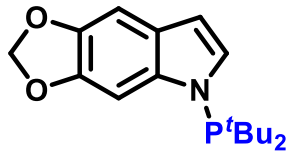
9-(Di-tert-butylphosphaneyl)-9H-pyrido[3,4-b]indole (30)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 9H-pyrido[3,4-b]indole (84 mg, 0.5 mmol) and was obtained as white solid (101.4 mg, yield 65%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.55 (d, *J* = 3.5 Hz, 0.6H), 9.34 (s, 0.4H), 8.49 (t, *J* = 5.5 Hz, 1H), 8.24 (dd, *J* = 8.5, 3.8 Hz, 0.4H), δ 8.12 (dd, *J* = 18.6, 7.7 Hz, 1H), 7.97 (dd, *J* = 6.9, 4.2 Hz, 1H), 7.91 (d, *J* = 5.2 Hz, 0.6H), 7.63 – 7.53 (m, 1H), 7.40 – 7.26 (m, 1H), 1.36 (d, *J* = 13.6 Hz, 18H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 148.72 (d, *J* = 25.9 Hz), 143.86 (dd, *J* = 18.3, 4.7 Hz), 140.28 – 139.37 (m), 137.82, 137.16 (d, *J* = 33.4 Hz), 131.92 (d, *J* = 2.4 Hz), 130.15 (d, *J* = 3.8 Hz), 128.10 (d, *J* = 2.8 Hz), 127.44, 124.33 (d, *J* = 2.2 Hz), 122.64 (d, *J* = 2.9 Hz), 121.48, 120.65 (d, *J* = 3.1 Hz), 115.97, 114.69 (d, *J* = 29.7 Hz), 114.32, 113.47, 36.09 (dd, *J* = 31.2, 9.1 Hz), 30.15 (dd, *J* = 17.9, 4.9 Hz).
^{31}P NMR (162 MHz, CDCl$_3$) δ 82.53, 81.90.
HRMS (ESI): m/z calcd for $C_{19}H_{25}N_2P$ $[M+H]^+$: 313.1828, found: 313.1818.

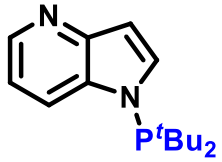
5-(Di-tert-butylphosphaneyl)-5H-[1,3]dioxolo[4,5-f]indole (31)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 5H-[1,3]dioxolo[4,5-f]indole (81 mg, 0.5 mmol) and was obtained as white solid (137.3 mg, yield 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.6 Hz, 1H), 7.38 (d, *J* = 3.3 Hz, 1H), 7.03 (s, 1H), 6.61 – 6.55 (m, 1H), 5.98 (s, 2H), 1.26 (d, *J* = 12.8 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.61 (d, *J* = 1.7 Hz), 142.93 (d, *J* = 1.4 Hz), 138.90 (d, *J* = 22.7 Hz), 129.35 (d, *J* = 8.6 Hz), 122.33 (d, *J* = 3.3 Hz), 105.39 (d, *J* = 2.2 Hz), 100.49, 98.53, 94.13 (d, *J* = 21.8 Hz), 35.08 (d, *J* = 25.1 Hz), 29.02 (d, *J* = 16.4 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 72.70.
HRMS (ESI): m/z calcd for $C_{17}H_{24}NO_2P$ $[M+H]^+$: 306.1617, found: 306.1608.

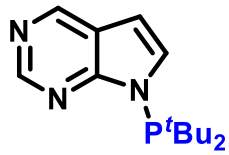
1-(Di-tert-butylphosphaneyl)-1H-pyrrolo[3,2-b]pyridine (32)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 1H-pyrrolo[3,2-b]pyridine (59 mg, 0.5 mmol) and was obtained as white solid (98.3 mg, yield 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.10 (ddt, *J* = 8.4, 2.3, 1.1 Hz, 1H), 7.68 (dd, *J* = 3.4, 0.8 Hz, 1H), 7.12 (dd, *J* = 8.3, 4.6 Hz, 1H), 6.89 – 6.84 (m, 1H), 1.20 (d, *J* = 12.9 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.17 (d, *J* = 3.0 Hz), 143.47 (d, *J* = 1.8 Hz), 136.44 (d, *J* = 21.3 Hz), 134.07 (d, *J* = 8.7 Hz), 119.77 (d, *J* = 19.4 Hz), 116.74 (d, *J* = 2.2 Hz), 106.36 (d, *J* = 2.6 Hz), 35.03 (d, *J* = 25.4 Hz), 28.88 (d, *J* = 16.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 73.58.
HRMS (ESI): m/z calcd for $C_{15}H_{23}N_2P$ $[M+H]^+$: 263.1672, found: 263.1663.

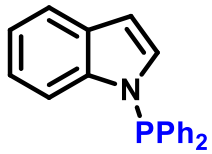
7-(Di-tert-butylphosphaneyl)-7H-pyrrolo[2,3-d]pyrimidine (33)



Synthesized following GP1 using Di-tert-butylphosphine (73 mg, 0.5 mmol), and 7H-pyrrolo[2,3-d]pyrimidine (60 mg, 0.5 mmol) and was obtained as white solid (110.5 mg, yield 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.91 (s, 1H), 7.93 (dd, *J* = 3.8, 2.4 Hz, 1H), 6.69 (d, *J* = 3.8 Hz, 1H), 1.39 (d, *J* = 15.7 Hz, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.09, 151.23, 149.75, 132.20 (d, *J* = 3.0 Hz), 102.20 (d, *J* = 3.8 Hz), 38.48 (d, *J* = 66.4 Hz), 26.37.
^{31}P NMR (162 MHz, $CDCl_3$) δ 69.93.
HRMS (ESI): m/z calcd for $C_{14}H_{22}N_3P$ $[M+H]^+$: 264.1624, found: 264.1614.

1-(Diphenylphosphaneyl)-1H-indole (34)



Synthesized following GP1 using diphenylphosphane (94 mg, 0.5 mmol), and 9H-carbazole (84 mg, 0.5 mmol) and was obtained as white solid (69.2 mg, yield 46%).

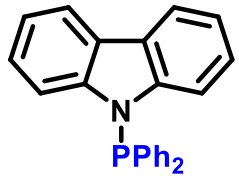
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.40 (m, 9H), 7.34 – 7.21 (m, 2H), 7.07 (t, *J* = 2.8 Hz, 1H), 6.73 (d, *J* = 3.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.12 (d, *J* = 18.1 Hz), 136.18 (d, *J* = 12.5 Hz), 131.98 (d, *J* = 20.9 Hz), 130.37 (d, *J* = 2.7 Hz), 130.13 (d, *J* = 2.8 Hz), 129.67, 128.67 (d, *J* = 6.5 Hz), 122.14, 120.79, 120.70, 112.19 (d, *J* = 15.1 Hz), 106.50.

^{31}P NMR (162 MHz, $CDCl_3$) δ 35.20.

HRMS (ESI): m/z calcd for $C_{20}H_{16}NP$ $[M+H]^+$: 302.1093, found: 302.1088.

9-(Diphenylphosphaneyl)-9H-carbazole (35)



Synthesized following GP1 using diphenylphosphane (94 mg, 0.5 mmol), and 9H-carbazole (84 mg, 0.5 mmol) and was obtained as white solid (80.7 mg, yield 46%).

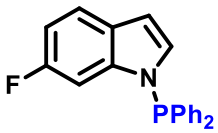
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.22 – 8.15 (m, 2H), 7.48 – 7.42 (m, 2H), 7.40 (d, *J* = 5.0 Hz, 10H), 7.34 – 7.21 (m, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 143.13 (d, *J* = 7.4 Hz), 133.46 (d, *J* = 12.9 Hz), 130.91 (d, *J* = 19.8 Hz), 129.70, 129.07 (d, *J* = 6.1 Hz), 125.97, 125.47, 120.98, 120.59, 113.26 (d, *J* = 12.0 Hz).

^{31}P NMR (162 MHz, DMSO-d_6) δ 31.57.

HRMS (ESI): m/z calcd for $C_{24}H_{18}NP$ $[M+H]^+$: 352.1250, found: 352.1251.

1-(Diphenylphosphaneyl)-6-fluoro-1H-indole (36)



Synthesized following GP1 using diphenylphosphane (94 mg, 0.5 mmol), and 6-fluoro-1H-indole (78 mg, 0.5 mmol) and was obtained as white solid (81.3 mg, yield 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.52 (m, 2H), 7.51 – 7.35 (m, 10H), 7.05 – 6.95 (m, 2H), 6.67 (d, *J* = 3.4 Hz, 1H).

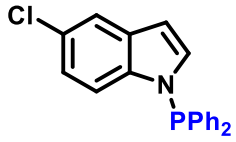
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.86 (d, *J* = 238.1 Hz), 141.39 (dd, *J* = 19.2, 12.1 Hz), 135.75 (d, *J* = 12.2 Hz), 131.98 (d, *J* = 20.9 Hz), 130.46 (t, *J* = 3.5 Hz), 129.84, 128.75 (d, *J* = 6.6 Hz), 126.68, 121.31 (d, *J* = 10.0 Hz), 109.36 (d, *J* = 24.6 Hz), 106.41, 98.90 (dd, *J* = 26.8, 15.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 36.39.

^{19}F NMR (377 MHz, $CDCl_3$) δ -119.92.

HRMS (ESI): m/z calcd for $C_{20}H_{15}FNP$ $[M+H]^+$: 320.0999, found: 320.0996.

5-Chloro-1-(diphenylphosphaneyl)-1H-indole (37)



Synthesized following GP1 using diphenylphosphane (94 mg, 0.5 mmol), and 5-chloro-1H-indole (76 mg, 0.5 mmol) and was obtained as white solid (83.7 mg, yield 49%).

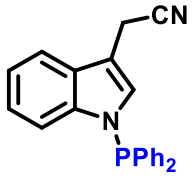
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.71 – 7.63 (m, 2H), 7.51 – 7.43 (m, 6H), 7.35 – 7.29 (m, 3H), 7.22 – 7.16 (m, 2H), 6.70 (dt, *J* = 3.3, 1.0 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 139.11 (d, *J* = 17.3 Hz), 135.16 (d, *J* = 12.1 Hz), 132.26, 131.79 (d, *J* = 20.9 Hz), 131.45 (d, *J* = 2.2 Hz), 130.34, 129.19 (d, *J* = 6.6 Hz), 125.42, 122.29, 120.26, 113.33 (d, *J* = 15.0 Hz), 106.44.

^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 36.77.

HRMS (ESI): m/z calcd for $C_{20}H_{15}ClNP$ $[M+H]^+$: 336.0703, found: 336.0707.

2-(1-(Diphenylphosphaneyl)-1H-indol-3-yl)acetonitrile (38)



Synthesized following GP1 using diphenylphosphane (94 mg, 0.5 mmol), and 2-(1H-indol-3-yl)acetonitrile (78 mg, 0.5 mmol) and was obtained as white solid (78.2 mg, yield 46%).

.

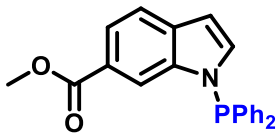
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.75 – 7.67 (m, 2H), 7.52 – 7.46 (m, 6H), 7.37 – 7.31 (m, 4H), 7.30 – 7.20 (m, 2H), 7.15 (d, *J* = 2.3 Hz, 1H), 4.09 (d, *J* = 1.0 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 141.02 (d, *J* = 17.6 Hz), 135.26 (d, *J* = 12.2 Hz), 131.92, 131.71, 130.35, 129.22 (d, *J* = 6.7 Hz), 128.67 (d, *J* = 2.6 Hz), 128.57 (d, *J* = 2.6 Hz), 123.14, 121.04, 119.07, 112.16 (d, *J* = 15.0 Hz), 109.57, 13.36.

^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 35.71.

HRMS (ESI): m/z calcd for $C_{22}H_{17}N_2P$ $[M+H]^+$: 341.1202, found: 341.1204.

Methyl 1-(diphenylphosphaneyl)-1H-indole-6-carboxylate (39)



Synthesized following GP1 using diphenylphosphane (94 mg, 0.5 mmol), and methyl 1H-indole-6-carboxylate (88 mg, 0.5 mmol) and was obtained as white solid (80.8 mg, yield 45%).

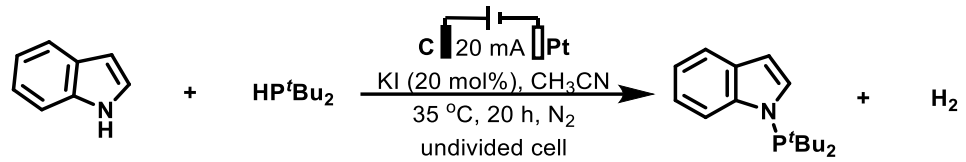
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.46 (s, 1H), 7.79 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.71 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.48 – 7.37 (m, 6H), 7.37 – 7.27 (m, 5H), 6.79 (dt, *J* = 3.3, 1.1 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 166.91, 140.14 (d, *J* = 18.7 Hz), 135.12, 135.01, 133.93 (dd, *J* = 5.0, 3.0 Hz), 131.83 (d, *J* = 21.2 Hz), 130.32, 129.12 (d, *J* = 6.6 Hz), 123.52, 121.51, 120.94, 113.31 (d, *J* = 16.1 Hz), 107.13, 51.96.

^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 35.62.

HRMS (ESI): m/z calcd for $C_{22}H_{18}NO_2P$ $[M+H]^+$: 360.1148, found: 360.1142.

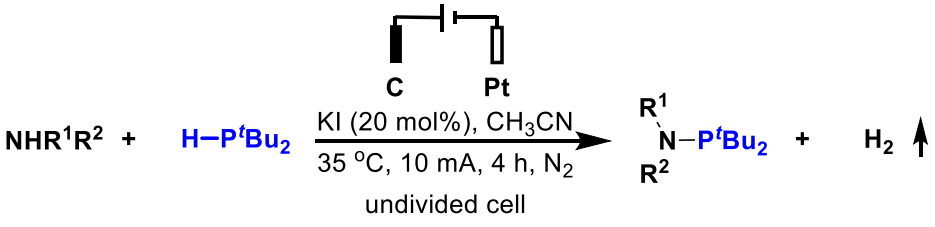
2.3. Gram-scale reaction

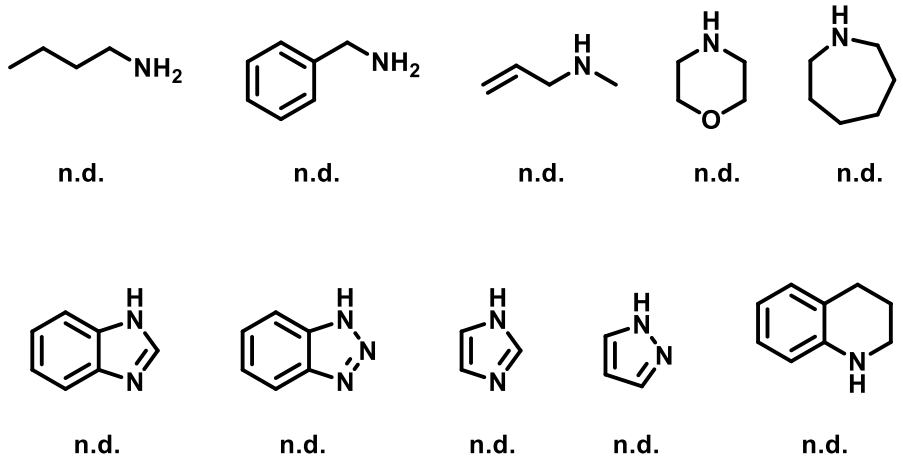


1 **2**
5 mmol **5 mmol**

In an oven-dried three-necked flask equipped with a stir bar. The flask was equipped with a carbon plate (1.5 × 2.0 × 0.10 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. Indole (591 mg, 5 mmol), and KI (167 mg, 20 mol%) were added. This was followed by the addition of diphenylphosphane (730 μL, 5 mmol) and super dry acetonitrile (40 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixtures were stirred at a constant current of 20.0 mA at 35 °C for 20 h. At the end of the reaction, the desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 silica gel (petroleum: EtOAc = 100:1). The white solid (1.08 g) was obtained with 83% isolated yield.

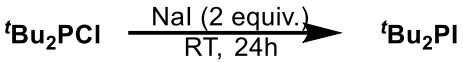
2.4. Unsuccessful examples



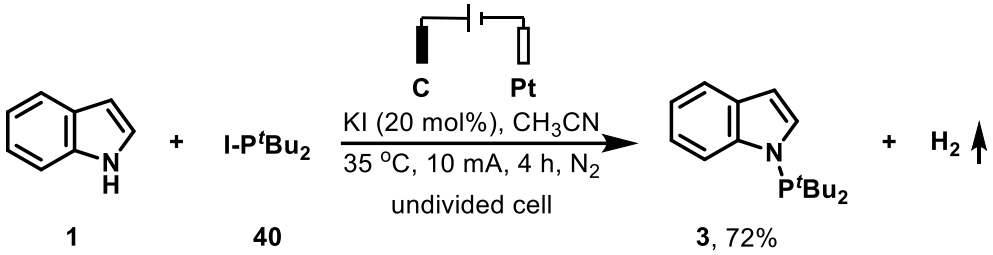


In an oven-dried undivided three-necked flask (25.0 mL) equipped with a stir bar. The bottle was equipped with a carbon plate (1.5 × 2.0 × 0.10 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Amine (0.5 mmol), and KI (16.7 mg, 20 mol%) were added. This was followed by the addition of Di-tert-butyl phosphine (73 mg, 0.5 mmol) and super dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixture was stirred at a constant current of 10.0 mA at 35 °C for 4 h (J = 4.4 mA/cm^2, 3.0 F/mol). At the end of the reaction, no desired products were detected by TLC or GC-MS.

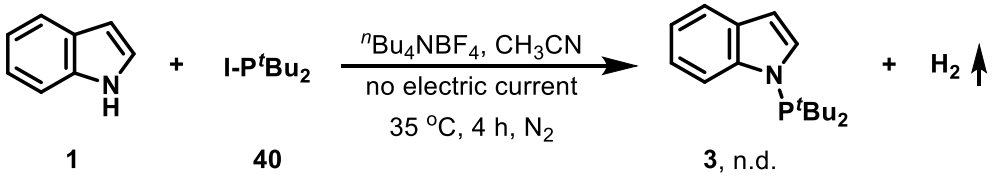
3. Control experiments



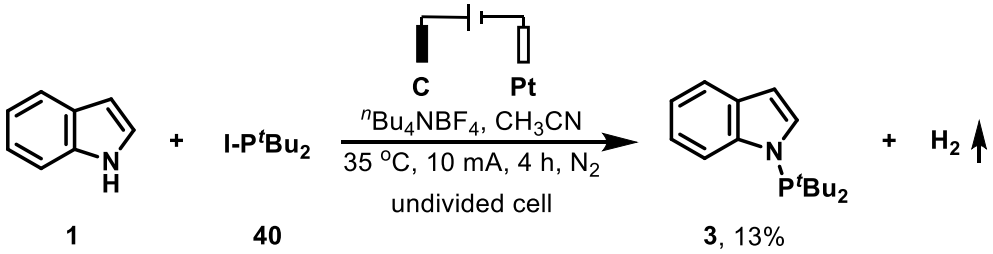
In a100mL round bottom flask, to the toluene solution (10 mL) of di-tert- butylchlorophosphine (1.80 g, 10.0 mmol) was added sodium iodide (3.00 g, 20.0 mmol), and the reaction mixture was s tirred at room temperature for 24 h. No need to deal with for use.



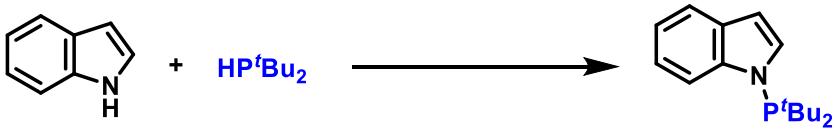
In an oven-dried undivided three-necked flask (25.0 mL) equipped with a stir bar. The bottle was equipped with a carbon plate (1.5 × 2.0 × 0.10 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. Indole (59.1m g, 0.5 mmol), KI (16.7 mg, 20 mol%) and $^tBu_2PI$ in toluene (1 mL, 1 mmol/ 1 mL) were added. This was followed by the addition of super dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixtures were stirred at a constant current of 10.0 mA at 35 °C for 4 h. The target product (yield 72%) is obtained after the reaction.



In an oven-dried undivided three-necked flask (25.0 mL) equipped with a stir bar. The bottle was equipped with a carbon plate (1.5 × 2.0 × 0.10 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. Indole (59.1m g, 0.5 mmol), KI (16.7 mg, 20 mol%) and $^tBu_2PI$ in toluene (1 mL, 1 mmol/ 1 mL) were added. This was followed by the addition of super dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixtures were stirred at 35 °C for 4 h. There is no target product detected by TLC.



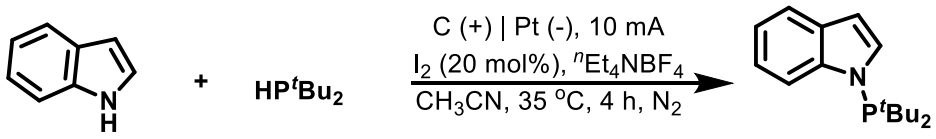
In an oven-dried undivided three-necked flask (25.0 mL) equipped with a stir bar. The bottle was equipped with a carbon plate (1.5 × 2.0 × 0.10 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. Indole (59.1m g, 0.5 mmol), and $^tBu_2PI$ in toluene (1 mL, 1 mmol/ 1 mL) were added. This was followed by the addition of super dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixtures were stirred at a constant current of 10.0 mA at 35 °C for 4 h. The target product (yield 13%) is obtained after the reaction.



1 **2** **3**

entry	conditions	yield (%)
1	standard conditions	95
2	no electric current, KI (20 mol%), CH_3CN, 35 °C, DDQ (1.0 equiv.), 4 h, N_2	0 (**1** revovered)
3	no electric current, KI (20 mol%), CH_3CN, 35 °C, *m*-CPBA (1.0 equiv.), 4 h, N_2	0 (**1** revovered)
4	no electric current, KI (20 mol%), CH_3CN, 35 °C, CAN (1.0 equiv.), 4 h, N_2	0 (**1** revovered)
5	no electric current, KI (20 mol%), CH_3CN, 35 °C, $K_2S_2O_8$ (1.0 equiv.), 4 h, N_2	0 (**1** revovered)
6	no electric current, KI (20 mol%), CH_3CN, 35 °C, TBHP (1.0 equiv.), 4 h, N_2	0 (**1** revovered)
7	no electric current, KI (20 mol%), CH_3CN, 35 °C, DTBP (1.0 equiv.), 4 h, N_2	0 (**1** revovered)
8	no electric current, I_2 (1.0 equiv.), CH_3CN, 35 °C, 4 h, N_2	0 (**1** revovered
9	no electric current, NIS (1.0 equiv.), CH_3CN, 35 °C, 4 h, N_2	0 (**1** revovered

In an oven-dried undivided three-necked flask (25.0 mL) equipped with a stir bar. The bottle was equipped with a carbon plate (1.5 × 2.0 × 0.10 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. Indole (59.1m g, 0.5 mmol), KI (16.7 mg, 20 mol%) were added. This was followed by the addition of 1.0 equiv. DDQ, *m*-CPBA, CAN, $K_2S_2O_8$, TBHP, DTBP, I_2, NIS and added super dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixtures were stirred at 35 °C for 4 h. There are no target product detected by TLC.

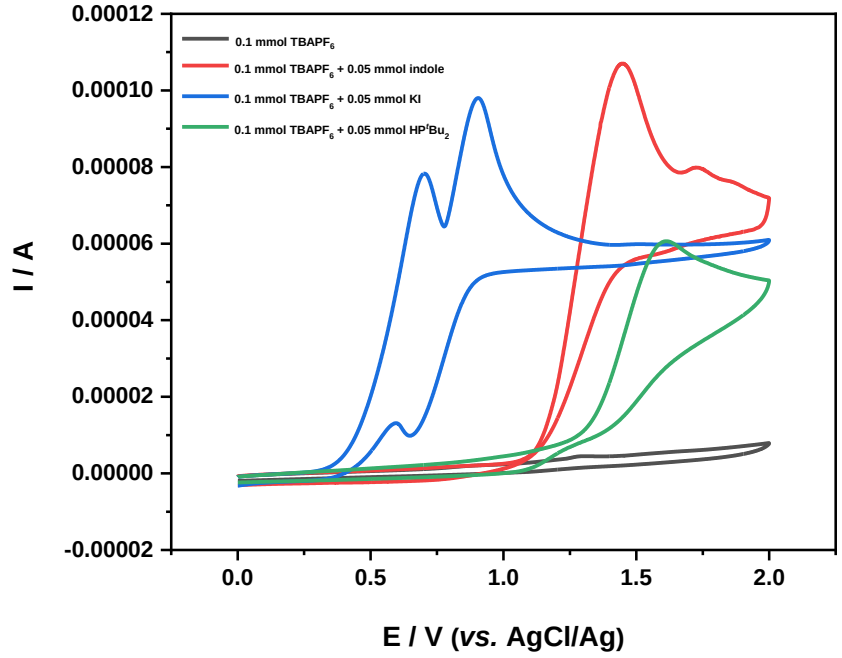


40%

In an oven-dried undivided three-necked flask (25.0 mL) equipped with a stir bar. The bottle was equipped with a carbon plate (1.5 × 2.0 × 0.10 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. Indole (59.1m g, 0.5 mmol), $^nEt_4NBF_4$ (21.7 mg, 0.1 mmol) and I_2 (25 mg, 20 mol%) were added. This was followed by the addition of Di-tert-butyl phosphine (73 mg, 0.5 mmol) and super dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixtures were stirred at a constant current of 10.0 mA at 35 °C for 4 h. The target product (yield 40%) is obtained after the reaction.

4. Electrochemical procedures for cyclic voltammetry

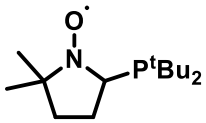
Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 10.0 mL of CH_3CN and 0.1 mmol of $^{n}Bu_4NPF_6$ were added to the electrochemical cell in all experiments. The scan rate was 0.05 V/s, from 0 V to 2.0 V

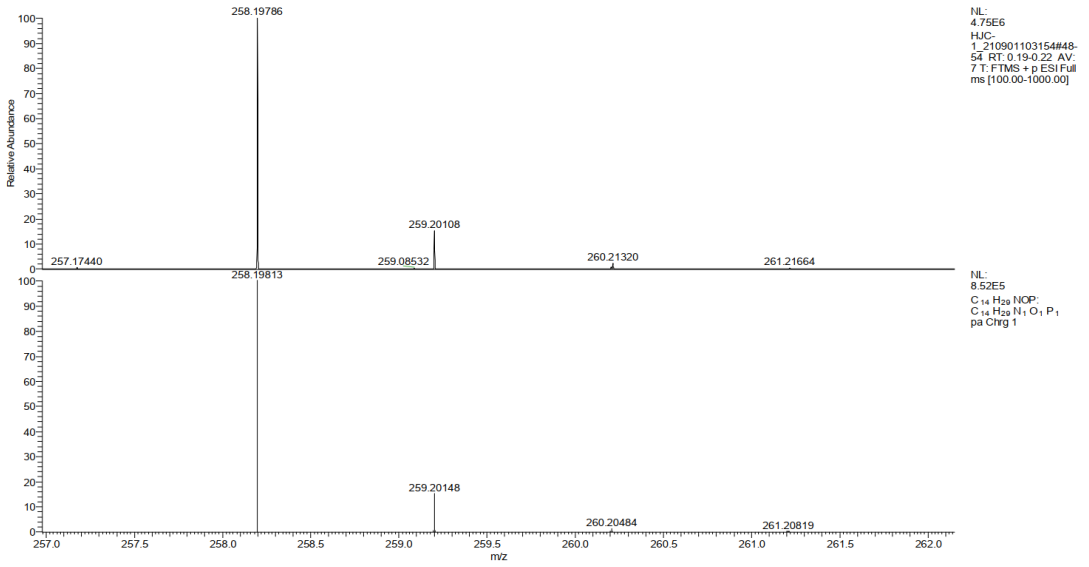


5. Procedure for electron paramagnetic resonance (EPR) experiment

In an oven-dried undivided three-necked bottle equipped with a stir bar, KI (0.1 mmol) and substrates (0.5 mmol) were combined and added. The bottle was equipped with carbon cloth (15 mm * 15 mm * 0.33 mm) as the anode and nickel plate (15 mm * 15 mm * 1.0 mm) as the cathode and then charged with N_2. Under the protection of Ar, CH_3COOH (0.5 mL) and CH_3CN (10 mL) were injected respectively into the bottle via syringes. The reaction mixture was stirred and electrolyzed with a constant current of 10 mA at 35 °C for 15 min. When the reaction was finished, the solution sample was taken out into a small tube and analyzed by EPR. After fitting, we proposed that this radical signal belongs to the carbon radical (g = 2.0066, AN = 14.55 G, AH = 20.54 G).

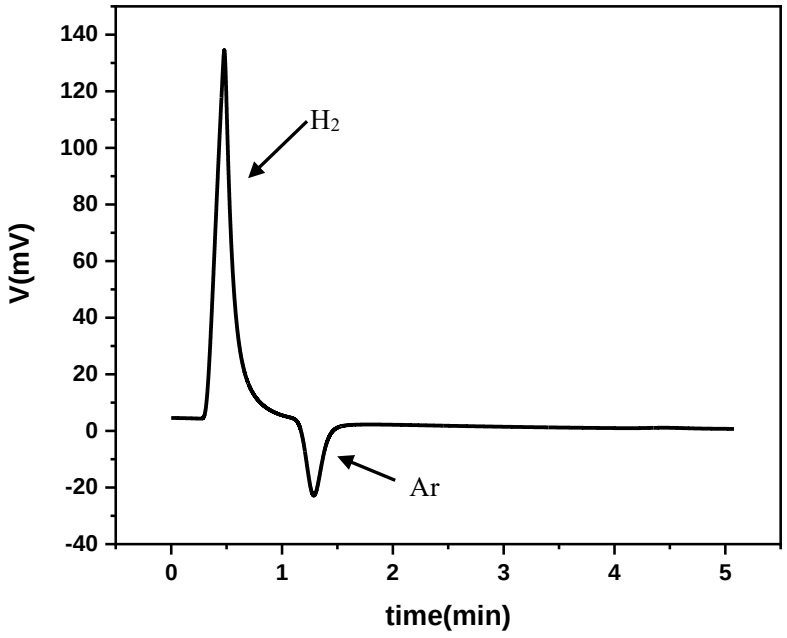
the adduct of phosphorus radical to DMPO：





HRMS (ESI): m/z calcd for $C_{14}H_{29}NOP•$: 258.1987, found: 366.1970.

6. Chromatography of the reaction atmosphere



Monitoring the atmosphere by GC.

7. References

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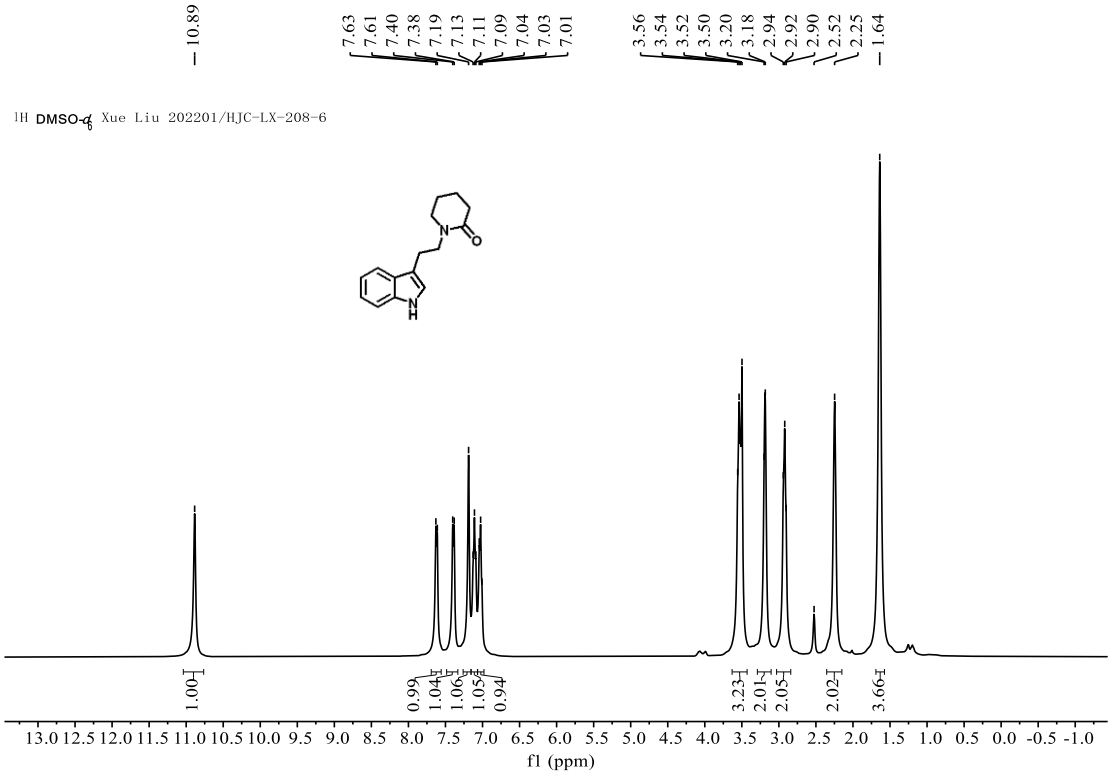
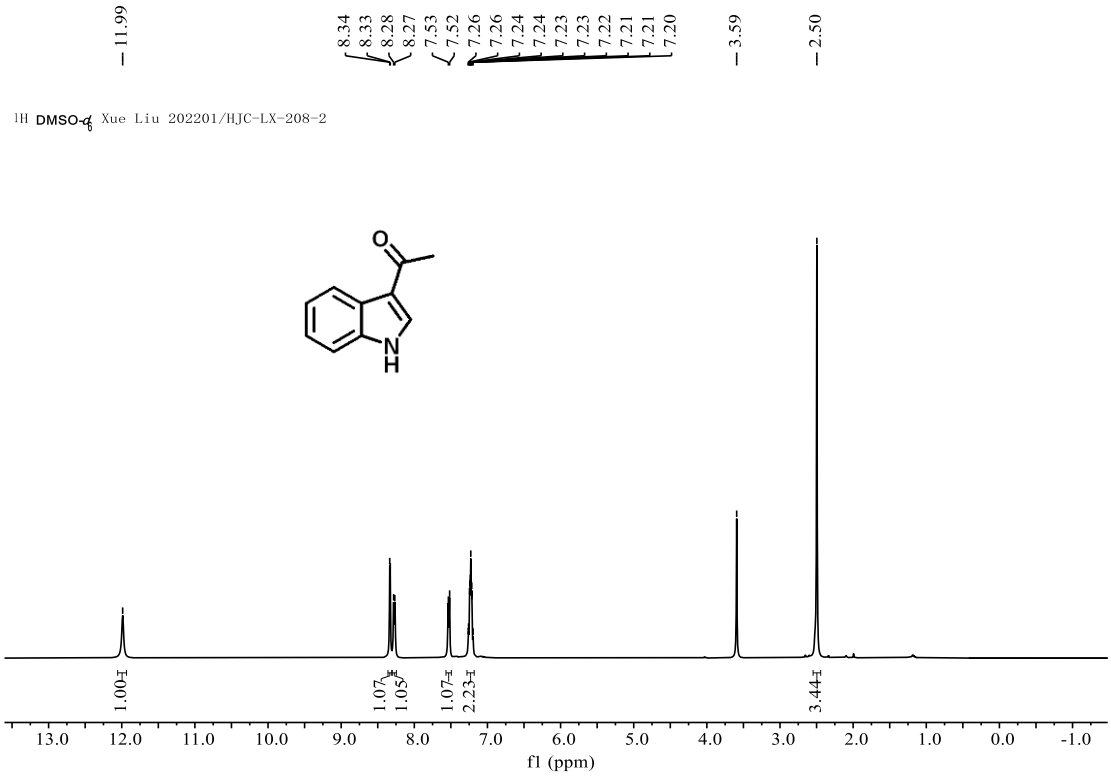
8. Spectral data

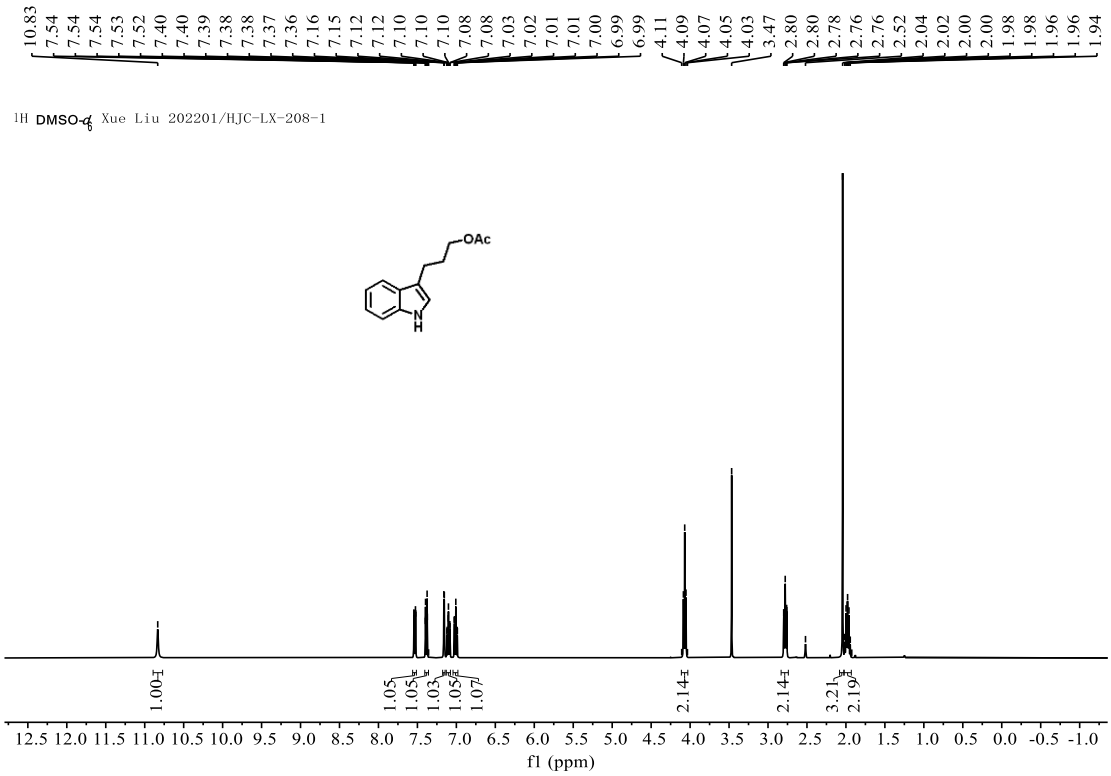
1-(2-(1H-indol-3-yl)ethyl)piperidin-2-one (8s)



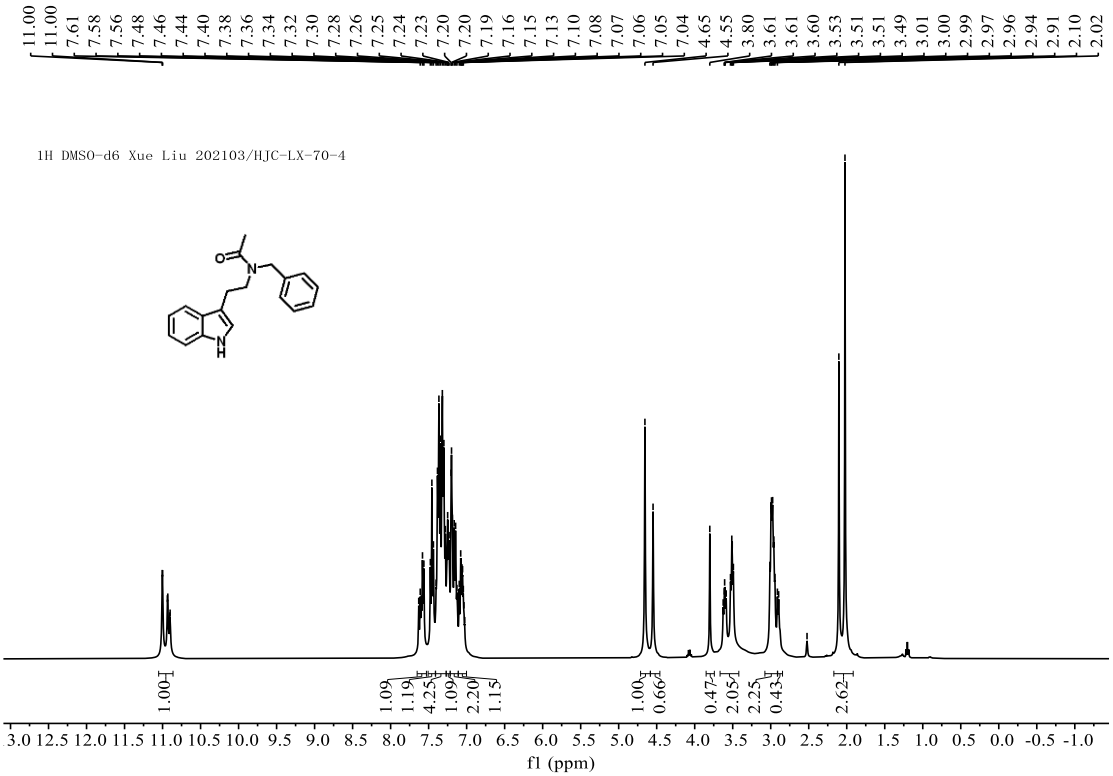
1-(1H-indol-3-yl)ethan-1-one (9s)



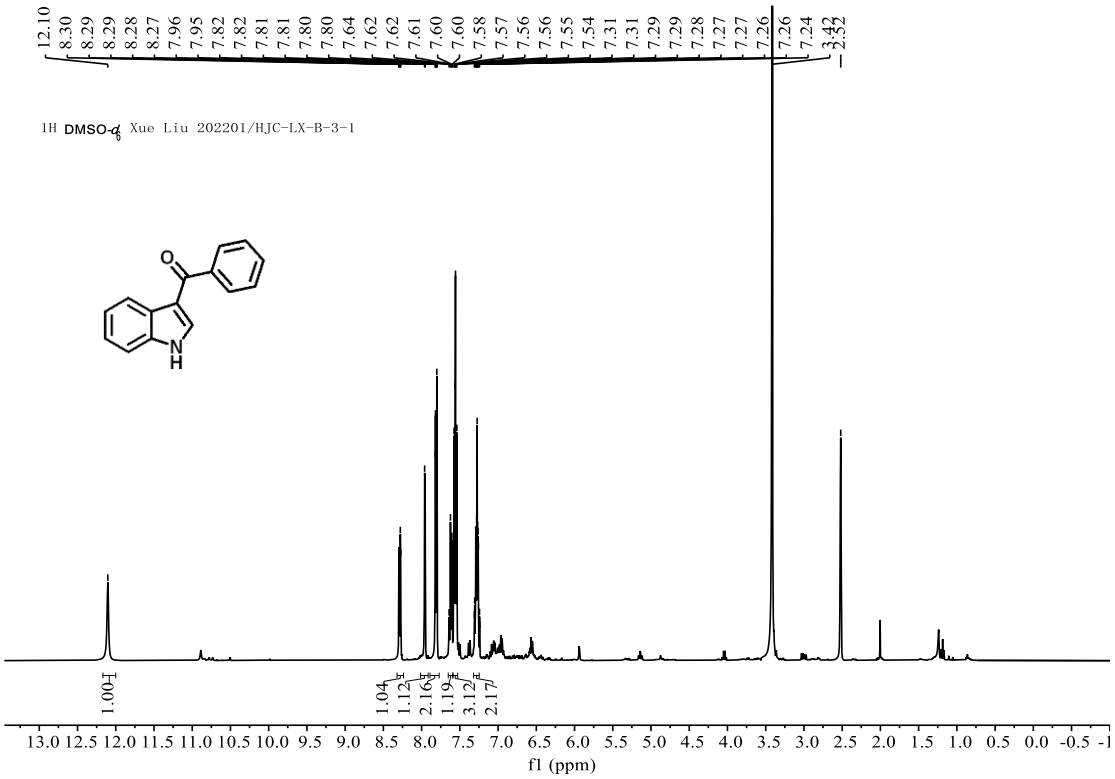
3-(1H-indol-3-yl)propyl acetate (10s)



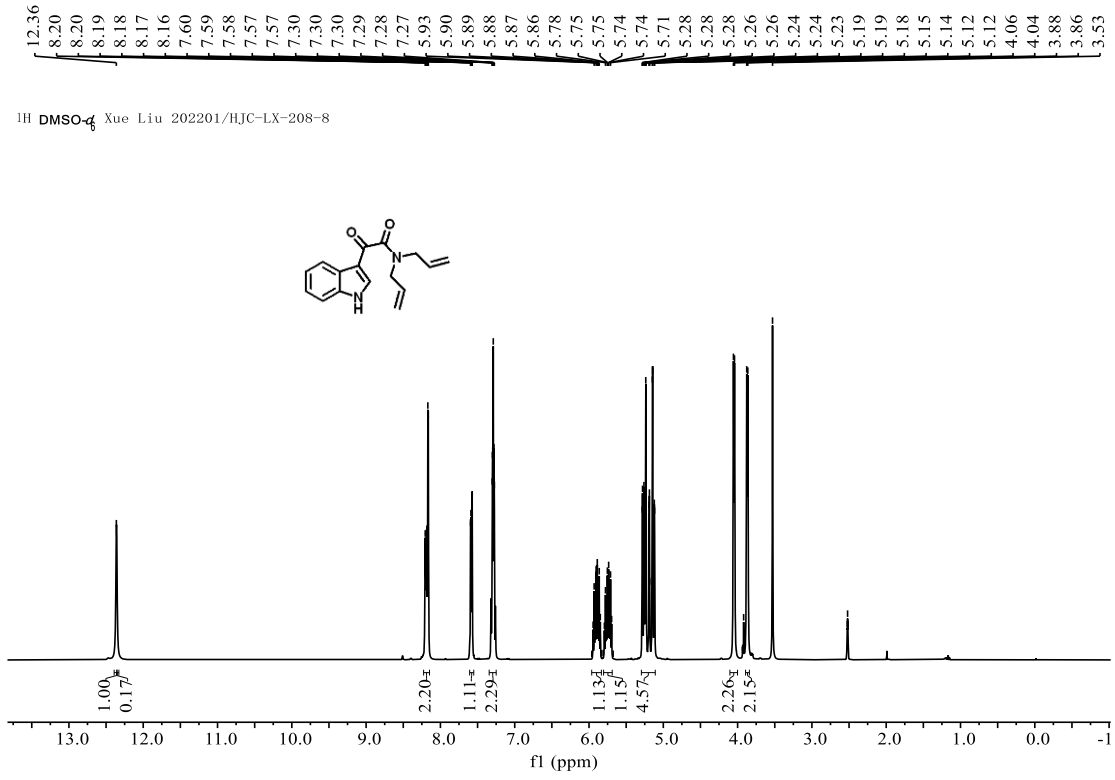
N-(2-(1H-indol-3-yl)ethyl)-N-benzylacetamide (11s)



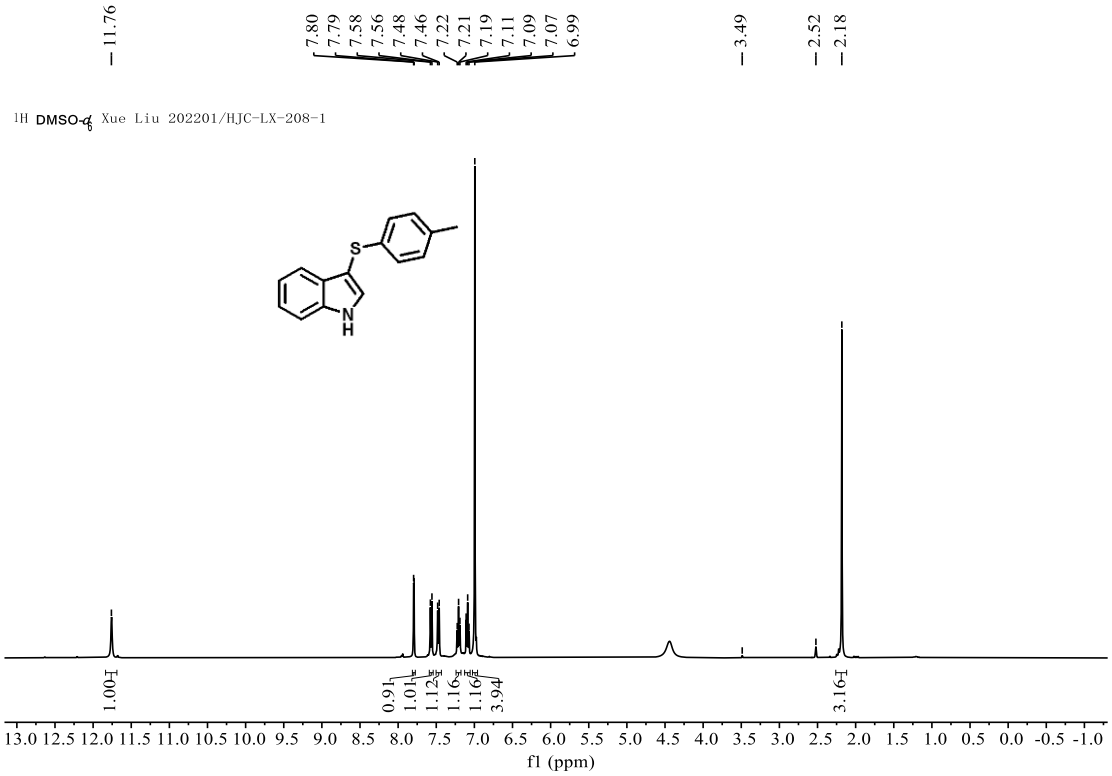
(1H-indol-3-yl)(phenyl)methanone (12s)



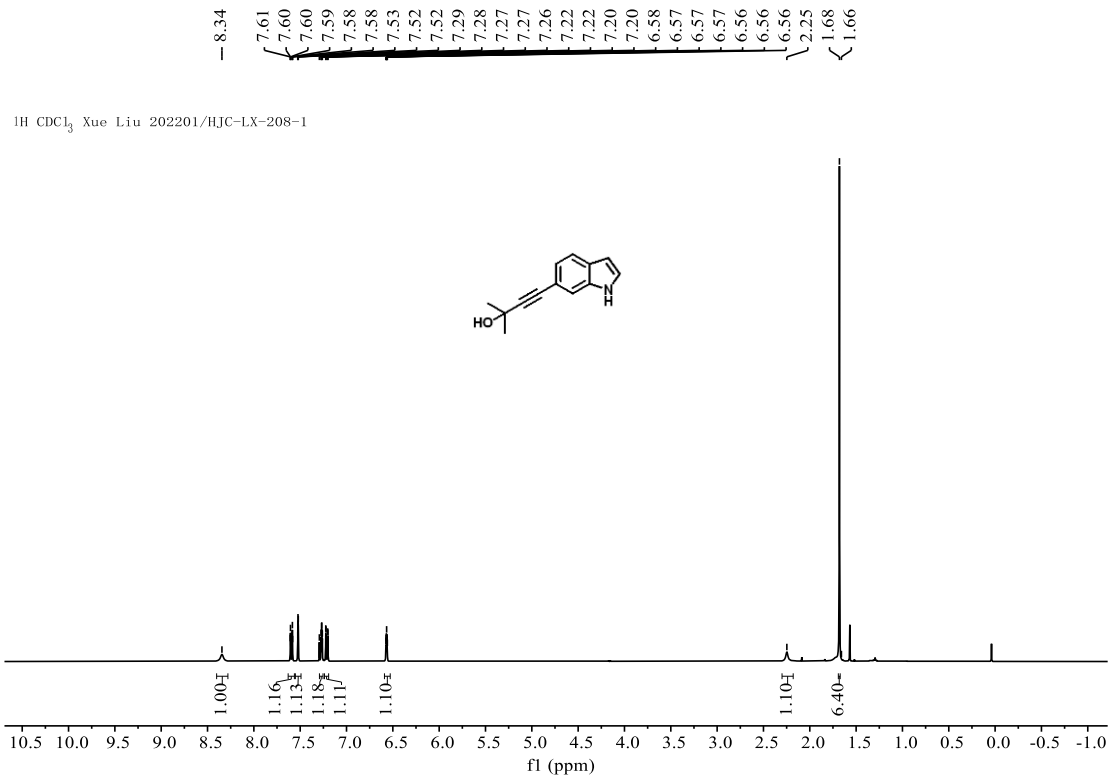
N,N-diallyl-2-(1H-indol-3-yl)-2-oxoacetamide (13s)



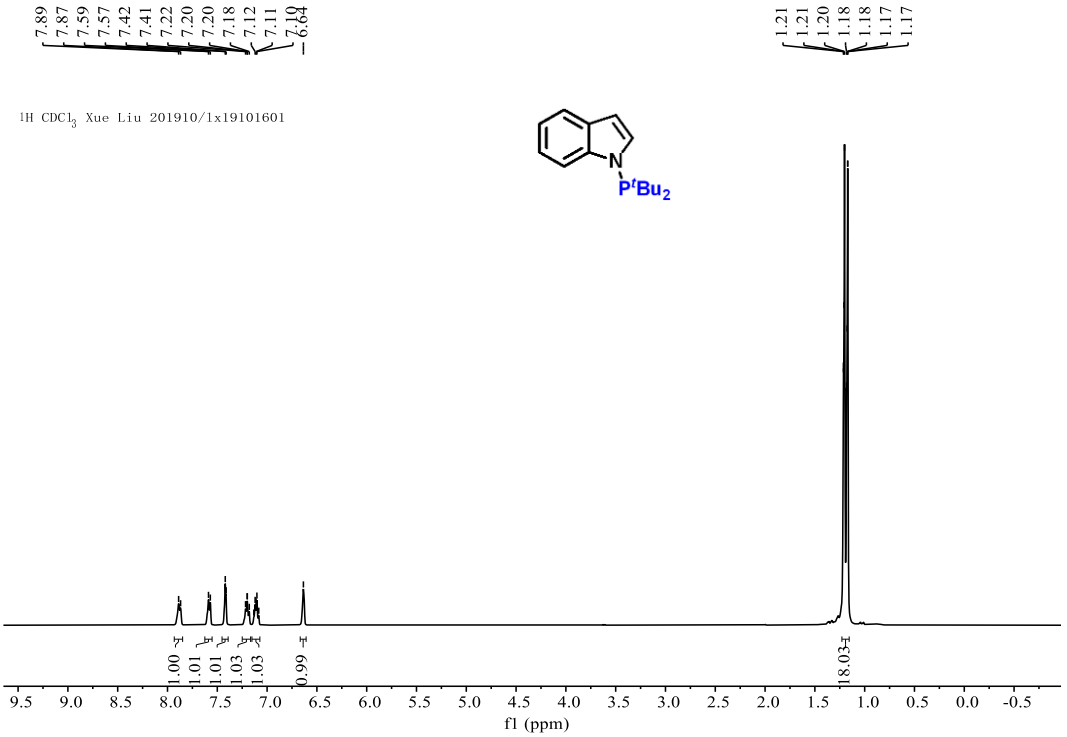
3-(p-tolylthio)-1H-indole (14s)

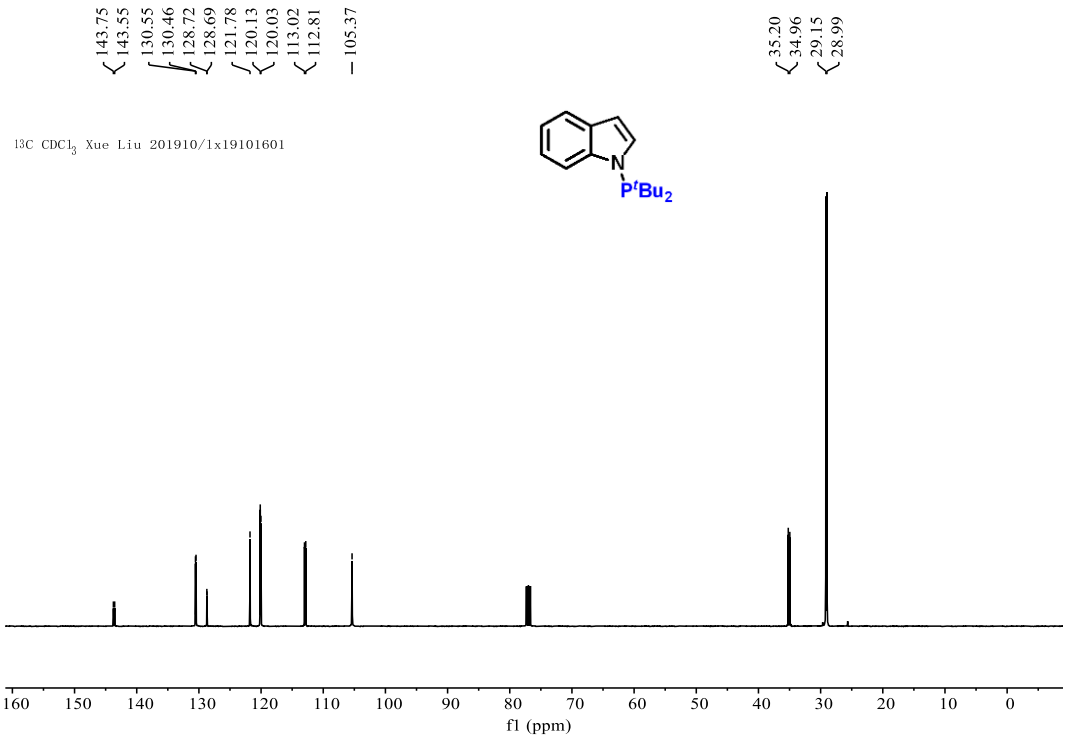


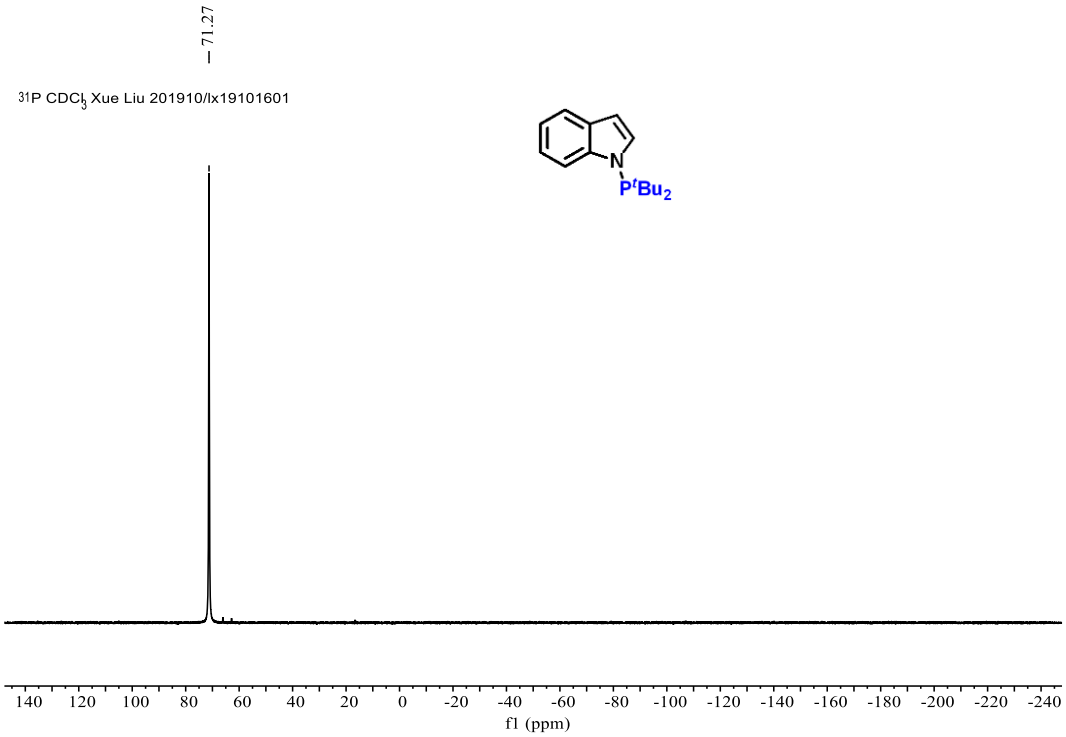
4-(1H-indol-6-yl)-2-methylbut-3-yn-2-ol (24s)



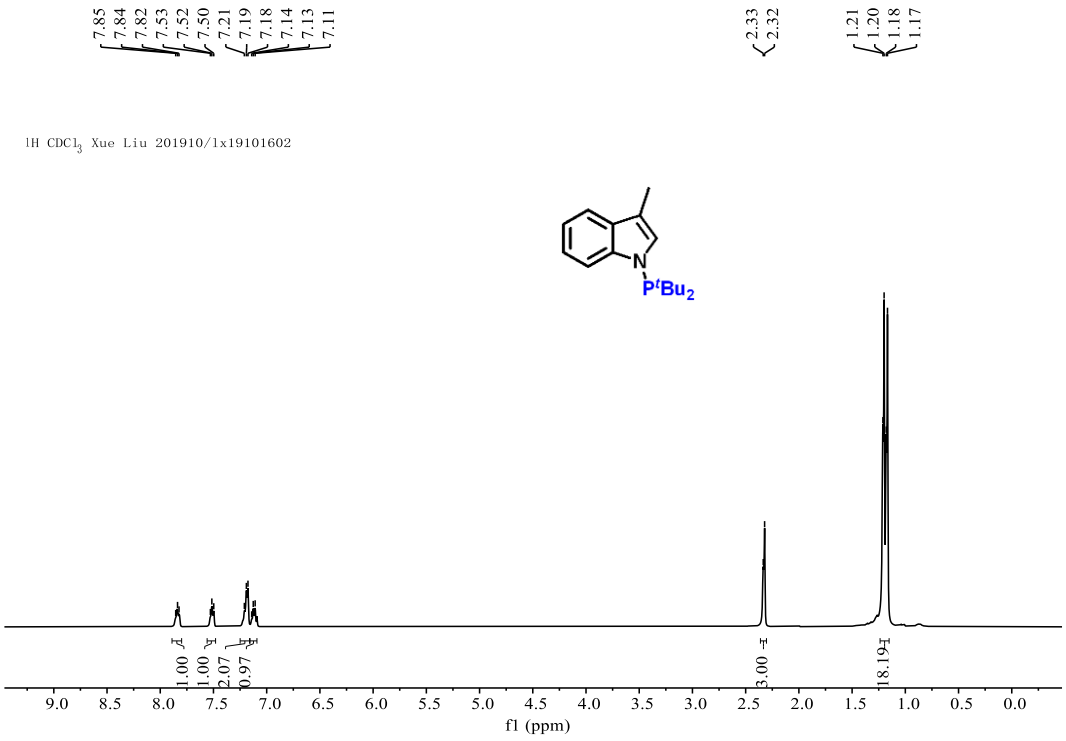
1-(Di-tert-butylphosphanyl)-1H-indole (3)







1-(Di-tert-butylphosphanyl)-3-methyl-1H-indole (5)



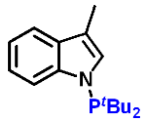
144.29
144.27
144.08
144.06
129.30
129.27
127.75
127.66
121.74
119.47
118.17
114.18
114.16
112.94
112.74

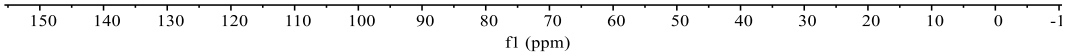
77.32
77.00
76.69

35.13
34.89
29.23
29.07

9.91

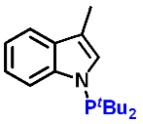
^{13}C $CDCl_3$ Xue Liu 201910/1x19101602

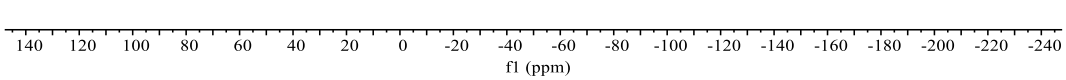




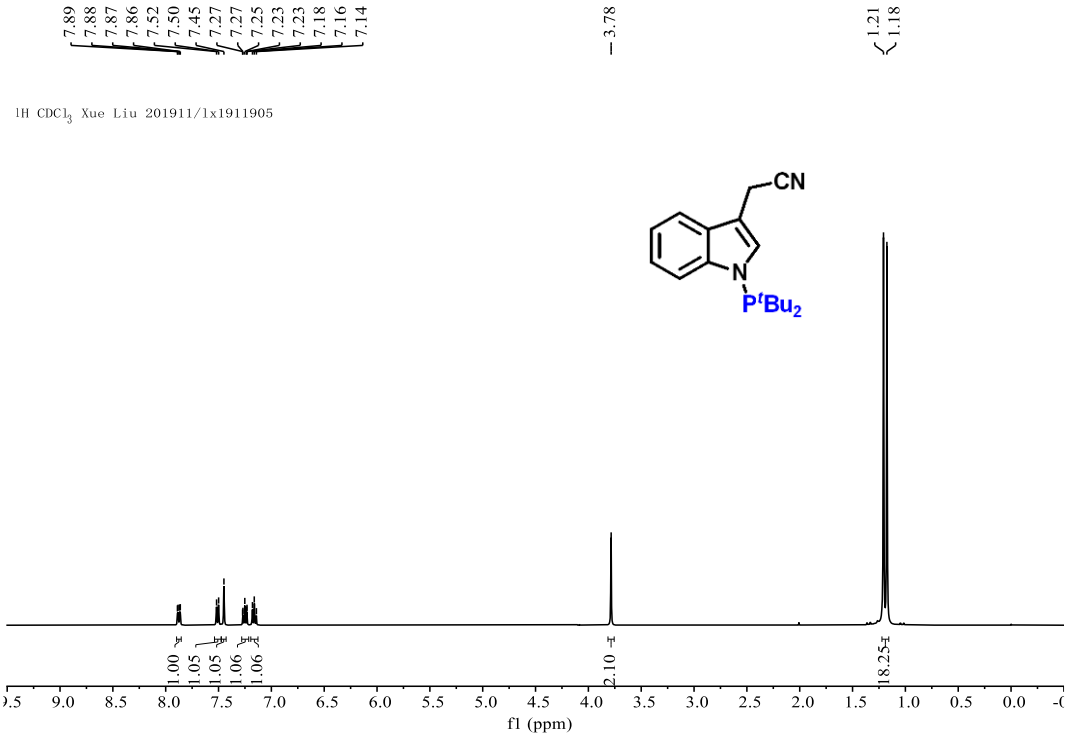
70.05

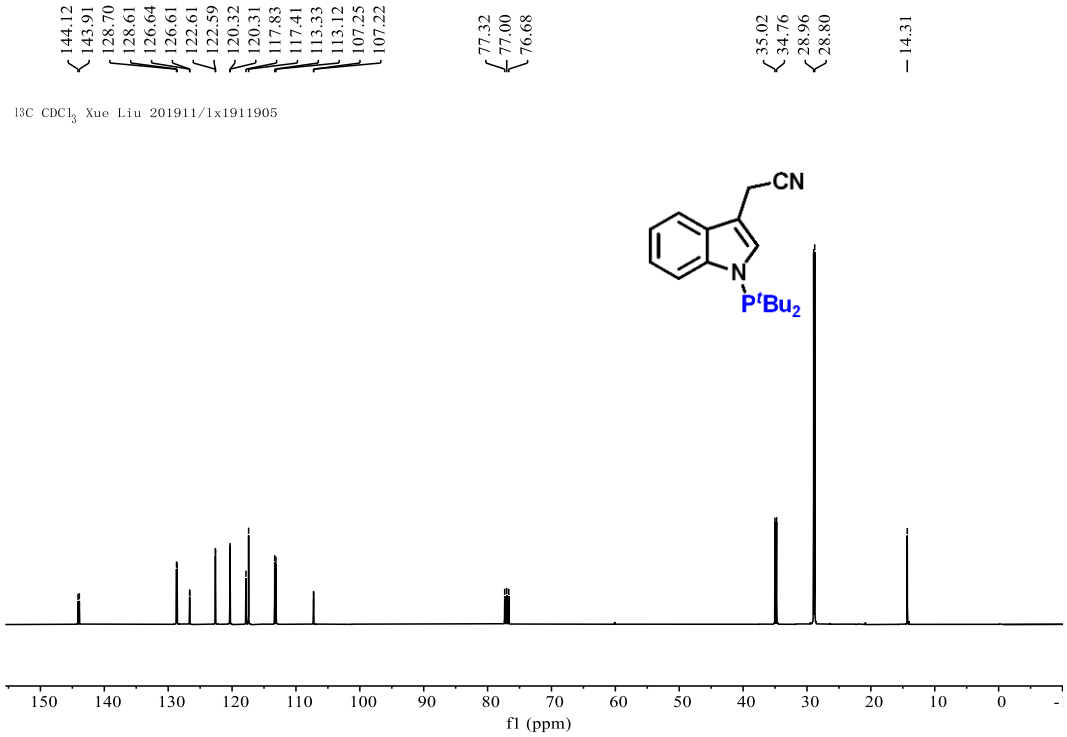
^{31}P $CDCl_3$ Xue Liu 201910/1x19101602

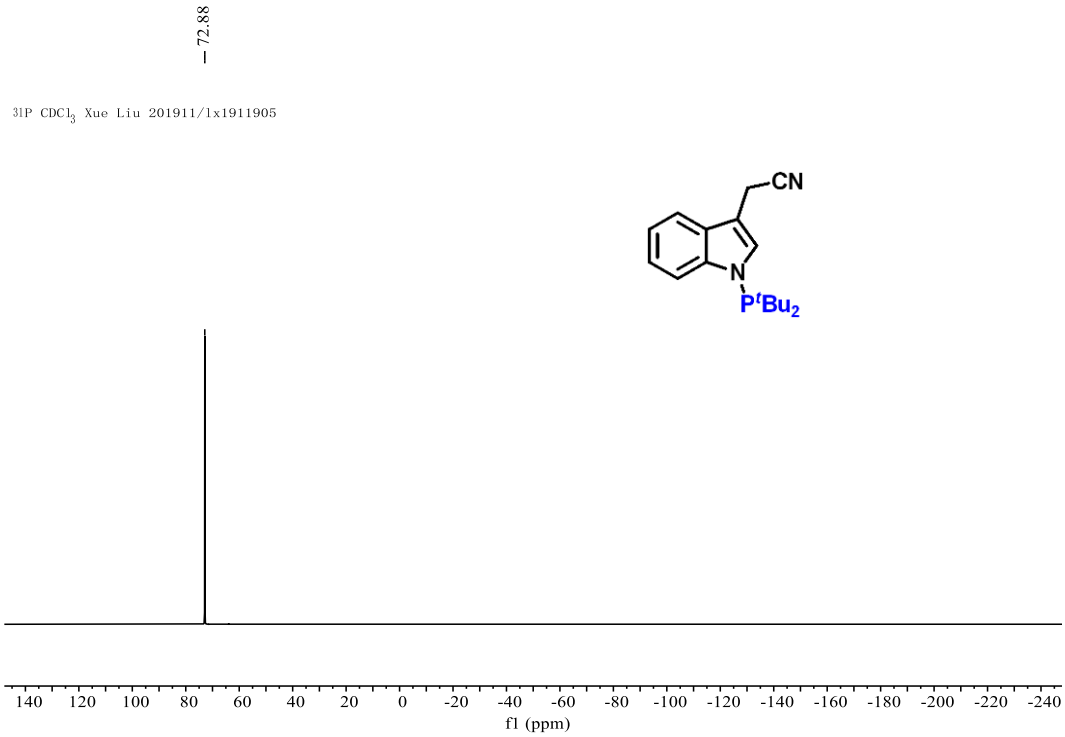




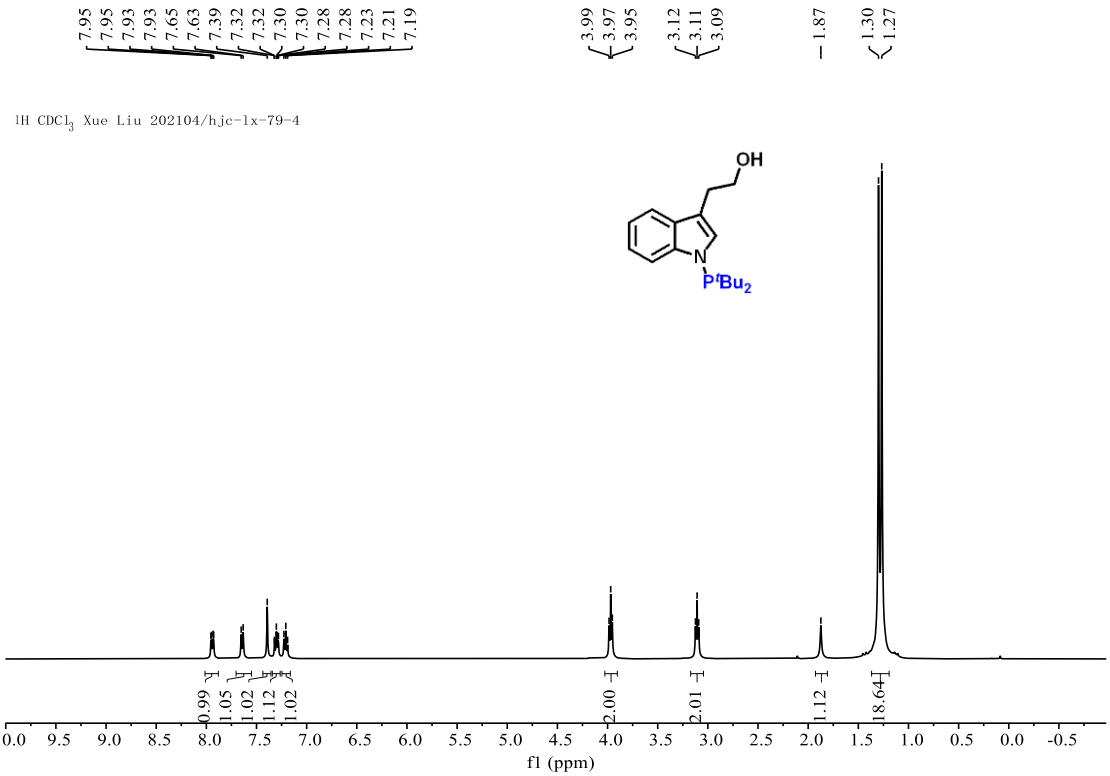
2-(1-(Di-tert-butylphosphanyl)-1H-indol-3-yl)acetonitrile (6)





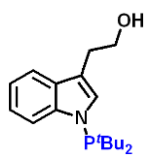


2-(1-(Di-tert-butylphosphaneyl)-1H-indol-3-yl)ethan-1-ol (7)



144.36
144.15
128.81
128.72
128.29
128.26
122.01
121.99
119.75
119.73
118.18
114.73
114.71
113.21
113.01
77.32
77.00
76.68
62.43
35.16
34.91
29.17
29.01
28.83

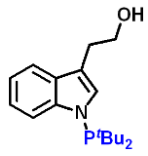
^{13}C $CDCl_3$ Xue Liu 202104/hjc-lx-79-4



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

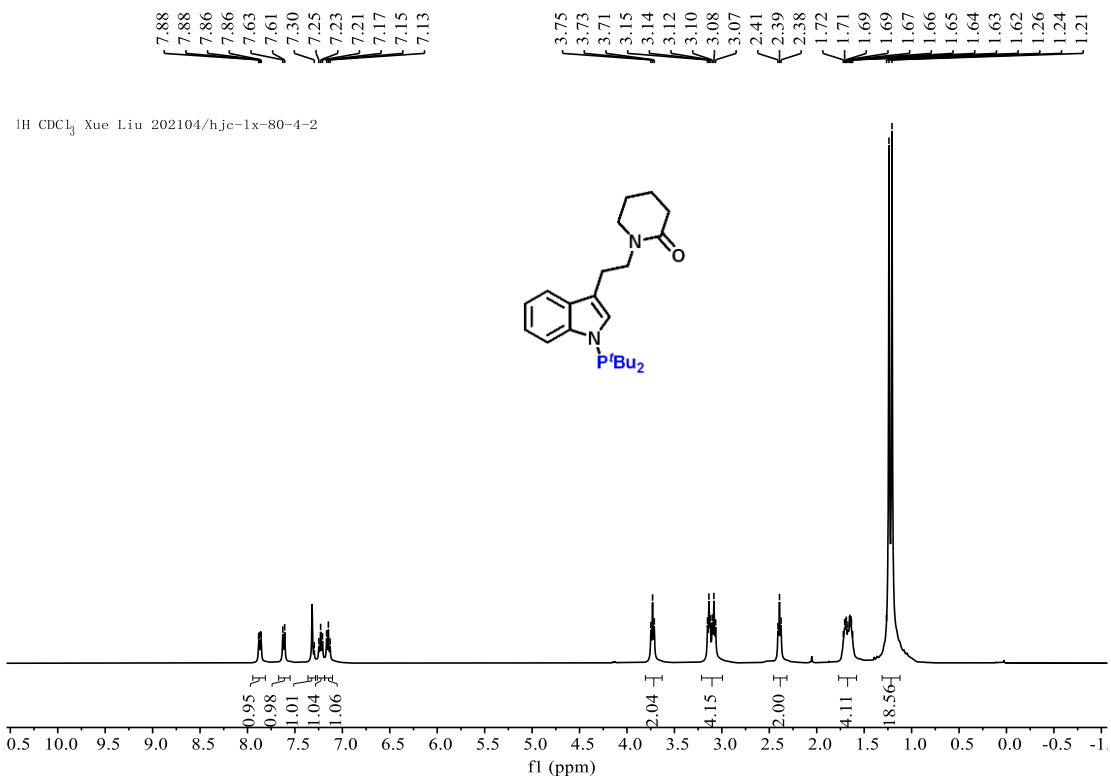
70.92

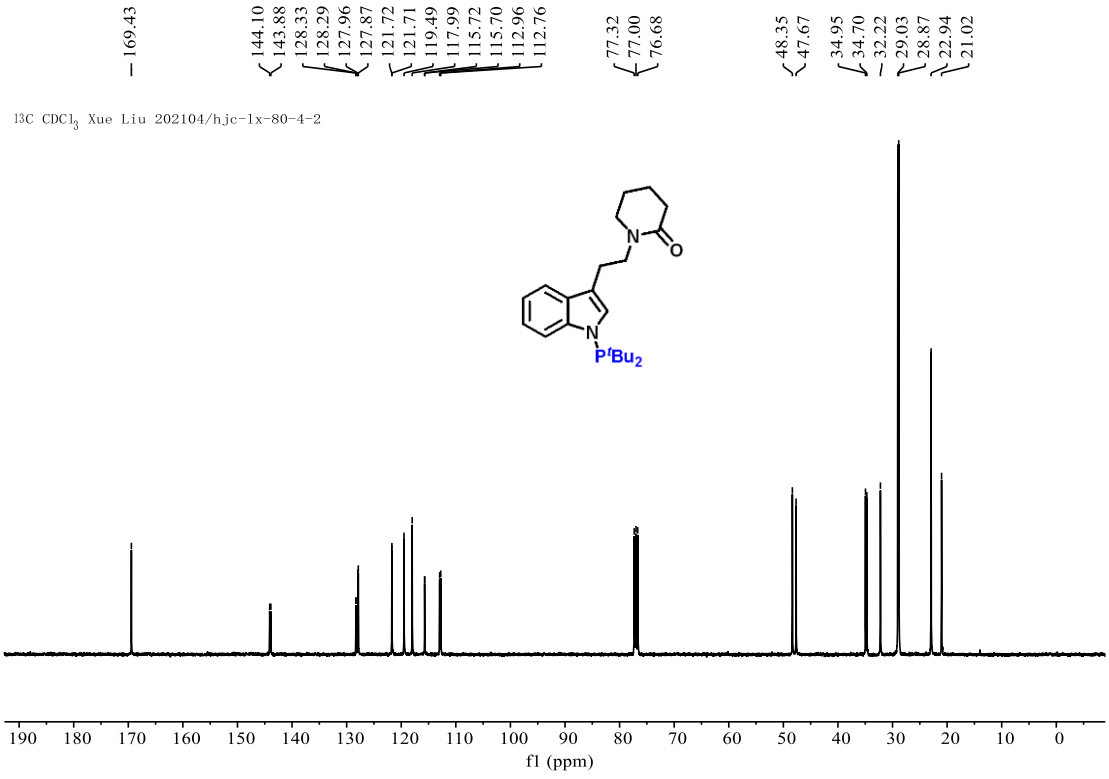
^{31}P $CDCl_3$ Xue Liu 202104/hjc-lx-79-4

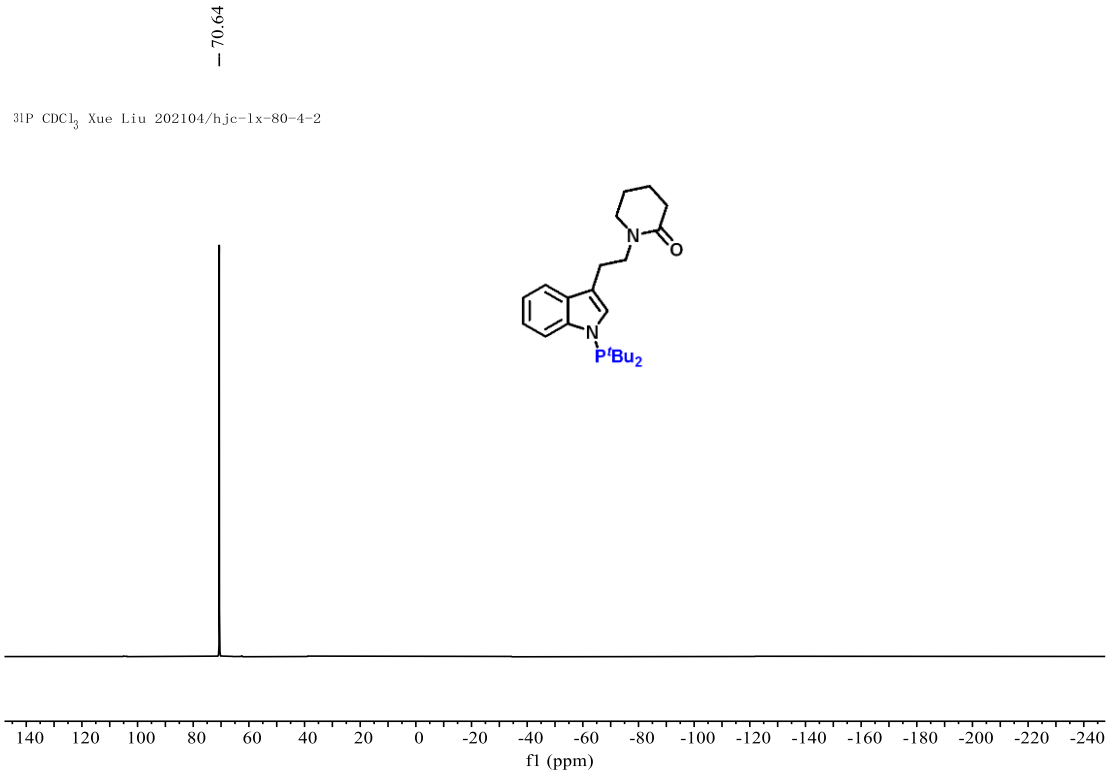


140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

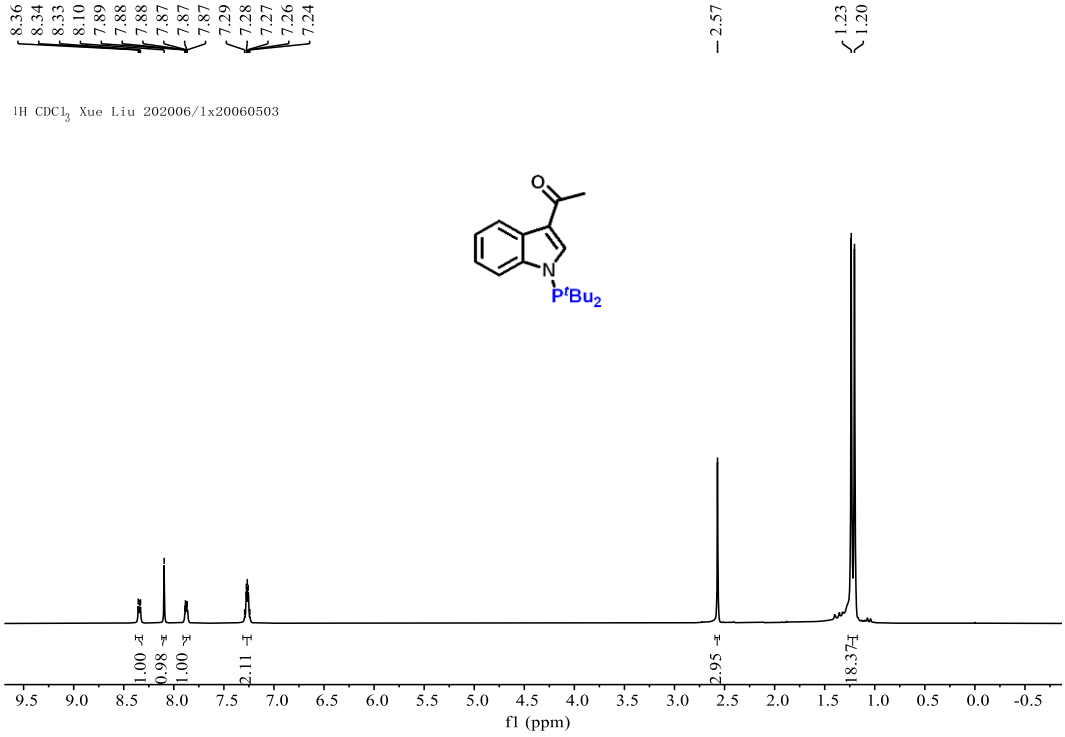
1-(2-(1-(Di-tert-butylphosphaneyl)-1H-indol-3-yl)ethyl)piperidin-2-one (8)

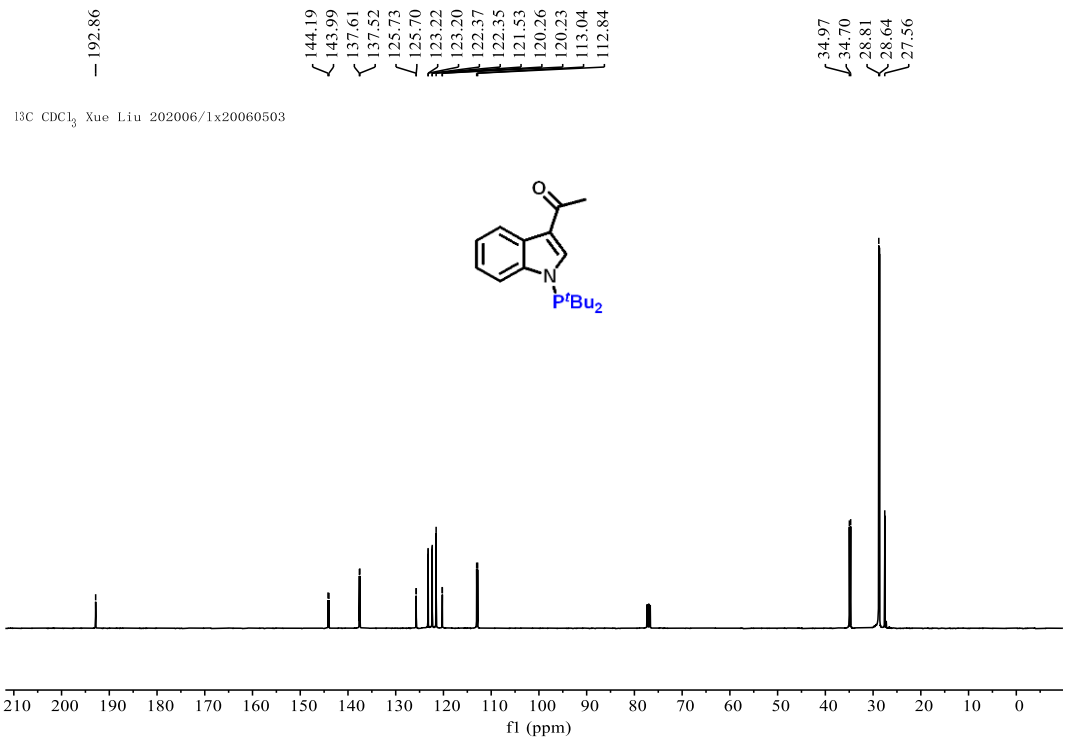


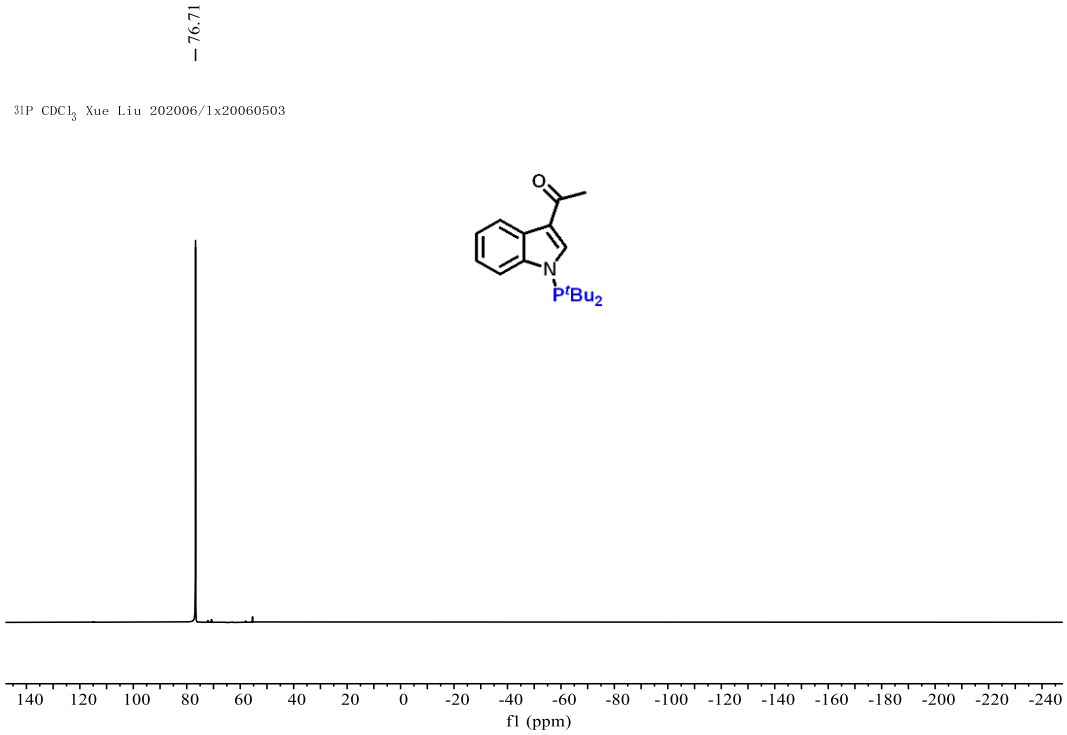




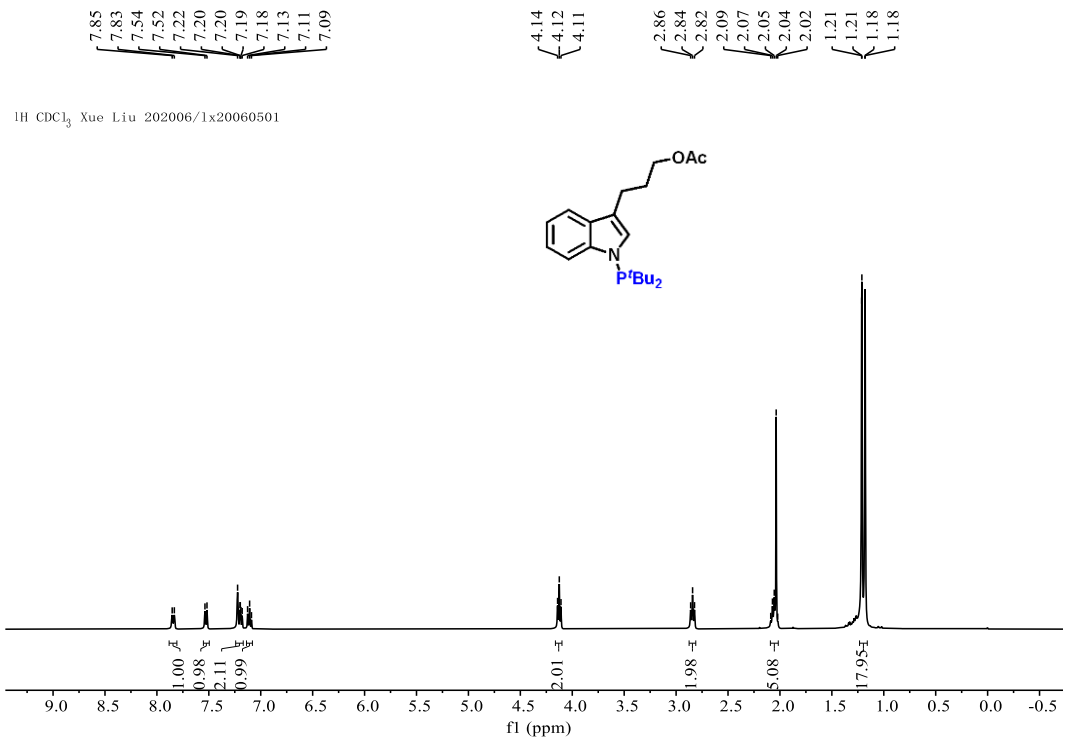
1-(1-(Di-tert-butylphosphanyl)-1H-indol-3-yl)ethan-1-one (9)

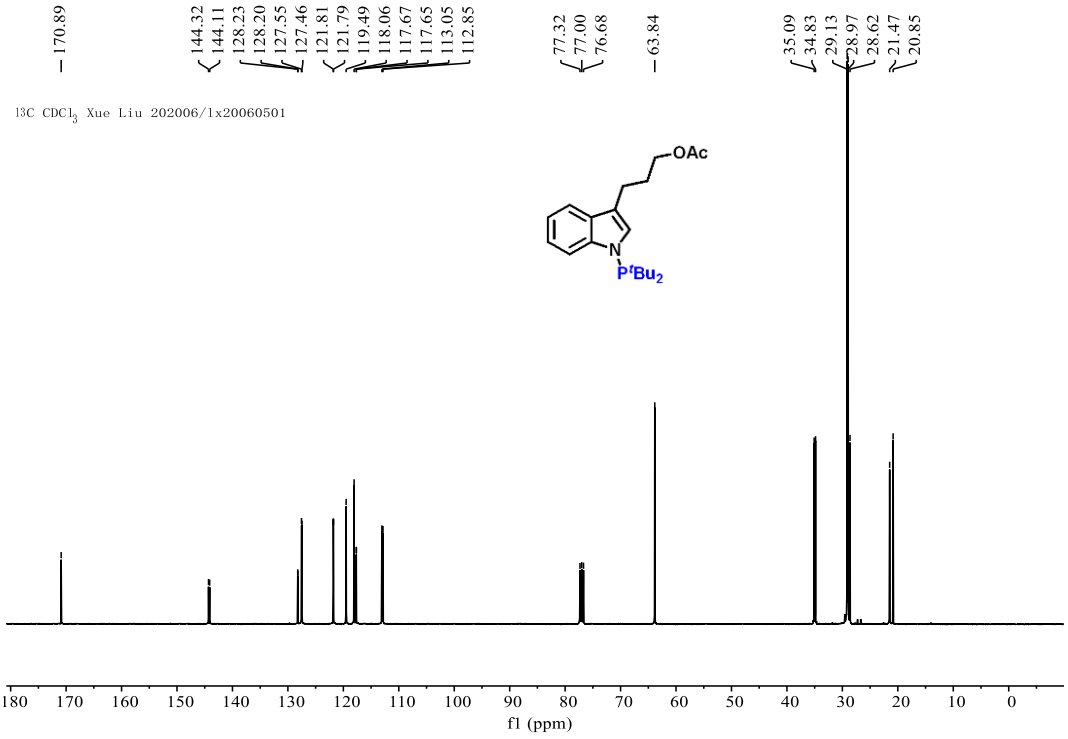


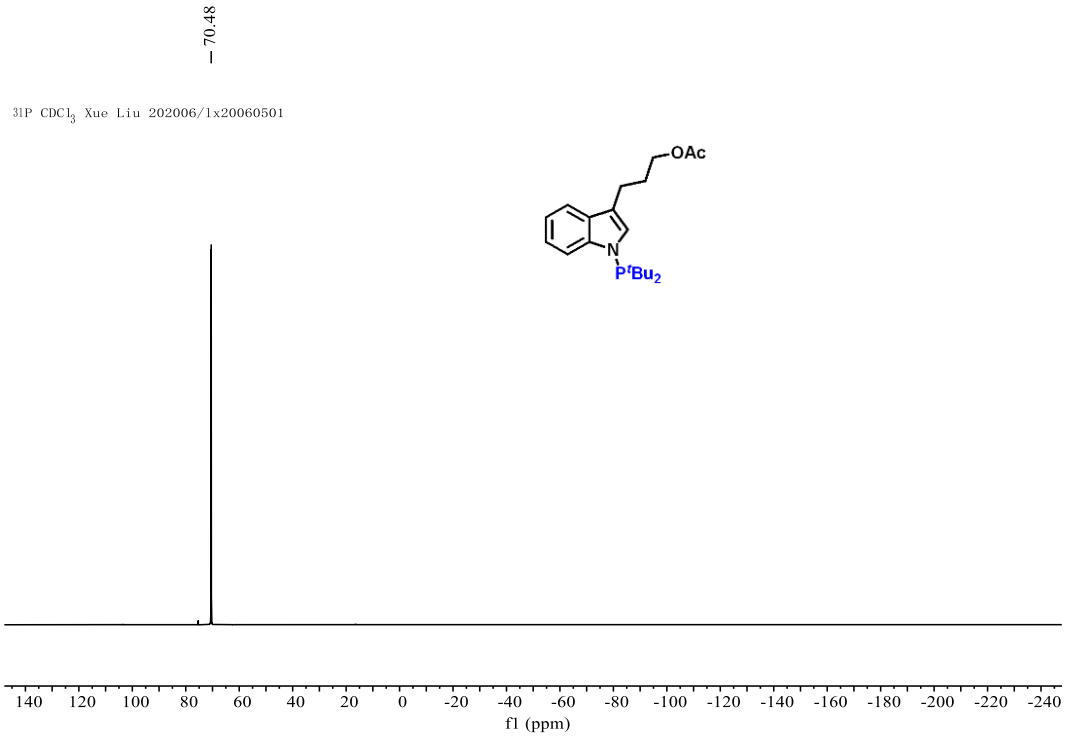

192.86
144.19
143.99
137.61
137.52
125.73
125.70
123.22
123.20
122.37
122.35
121.53
120.26
120.23
113.04
112.84
34.97
34.70
28.81
28.64
27.56
13C CDCl3 Xue Liu 202006/1x20060503
O
N
PtBu2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


76.71
31P CDCl3 Xue Liu 202006/1x20060503
O
N
PtBu2
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

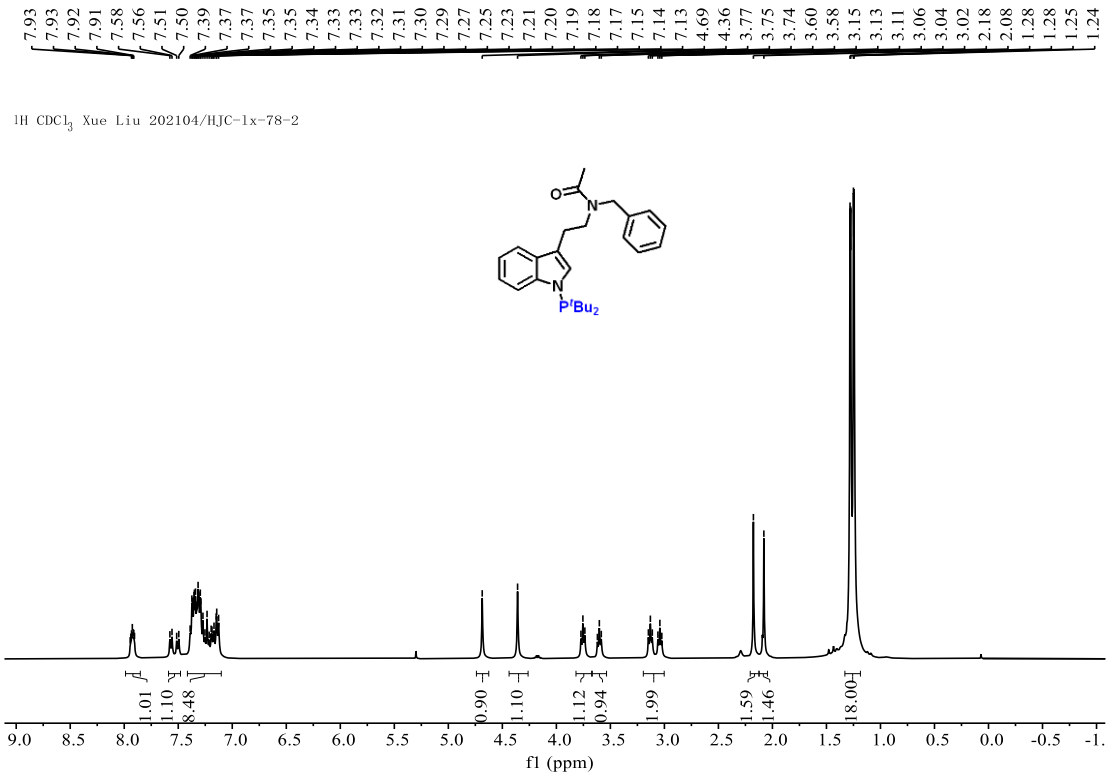
3-(1-(Di-tert-butylphosphanyl)-1H-indol-3-yl)propyl acetate (10)





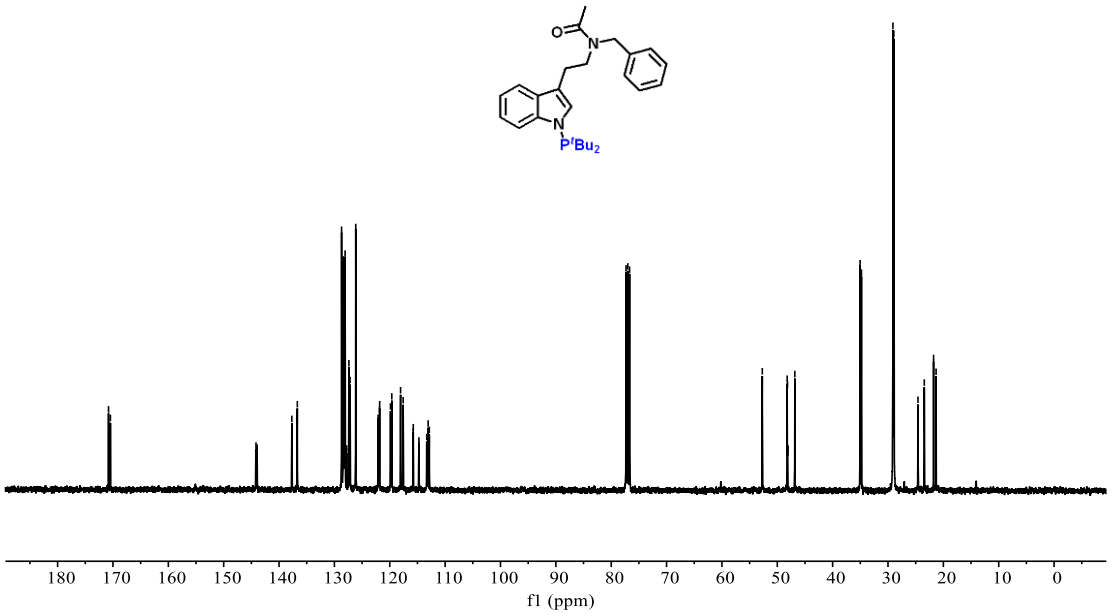


N-benzyl-N-(2-(1-(di-tert-butylphosphaneyl)-1H-indol-3-yl)ethyl)acetamide (11)



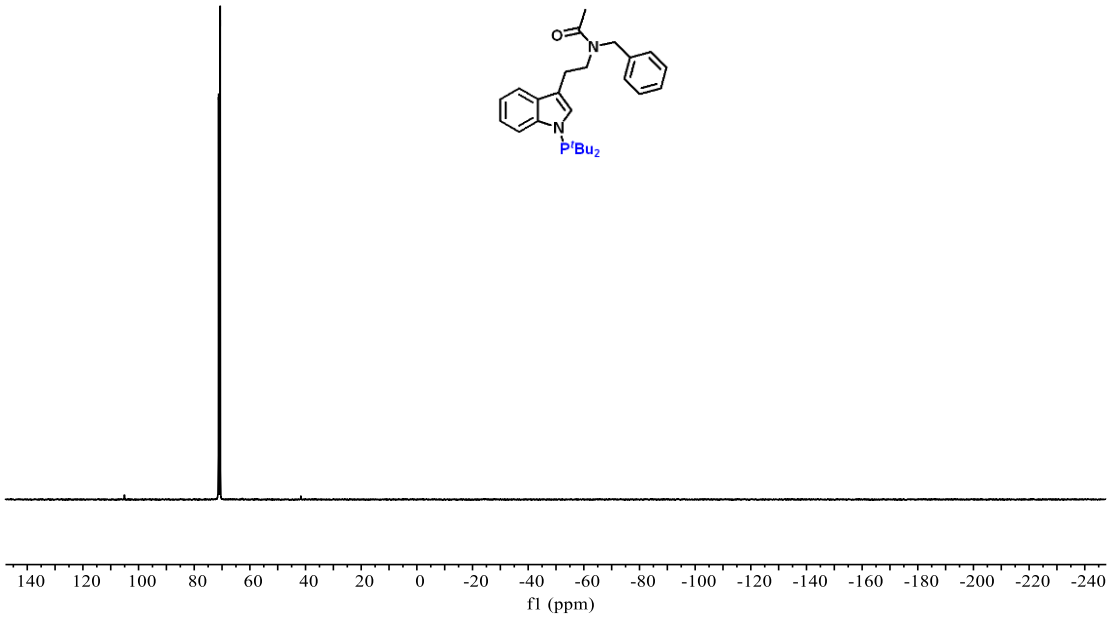
170.80
170.46
144.17
143.96
137.69
136.70
128.70
128.40
128.31
128.28
128.22
128.19
128.10
128.07
127.79
127.39
127.17
126.15
122.11
121.85
121.83
119.87
119.63
118.05
117.58
115.77
115.75
114.75
114.73
113.32
113.12
113.06
112.85
77.32
77.00
76.68
52.71
48.21
48.15
46.83
35.04
34.79
29.11
29.08
28.95
28.92
24.58
23.44
21.77
21.32

^{13}C $CDCl_3$ Xue Liu 202104/HJC-lx-78-2

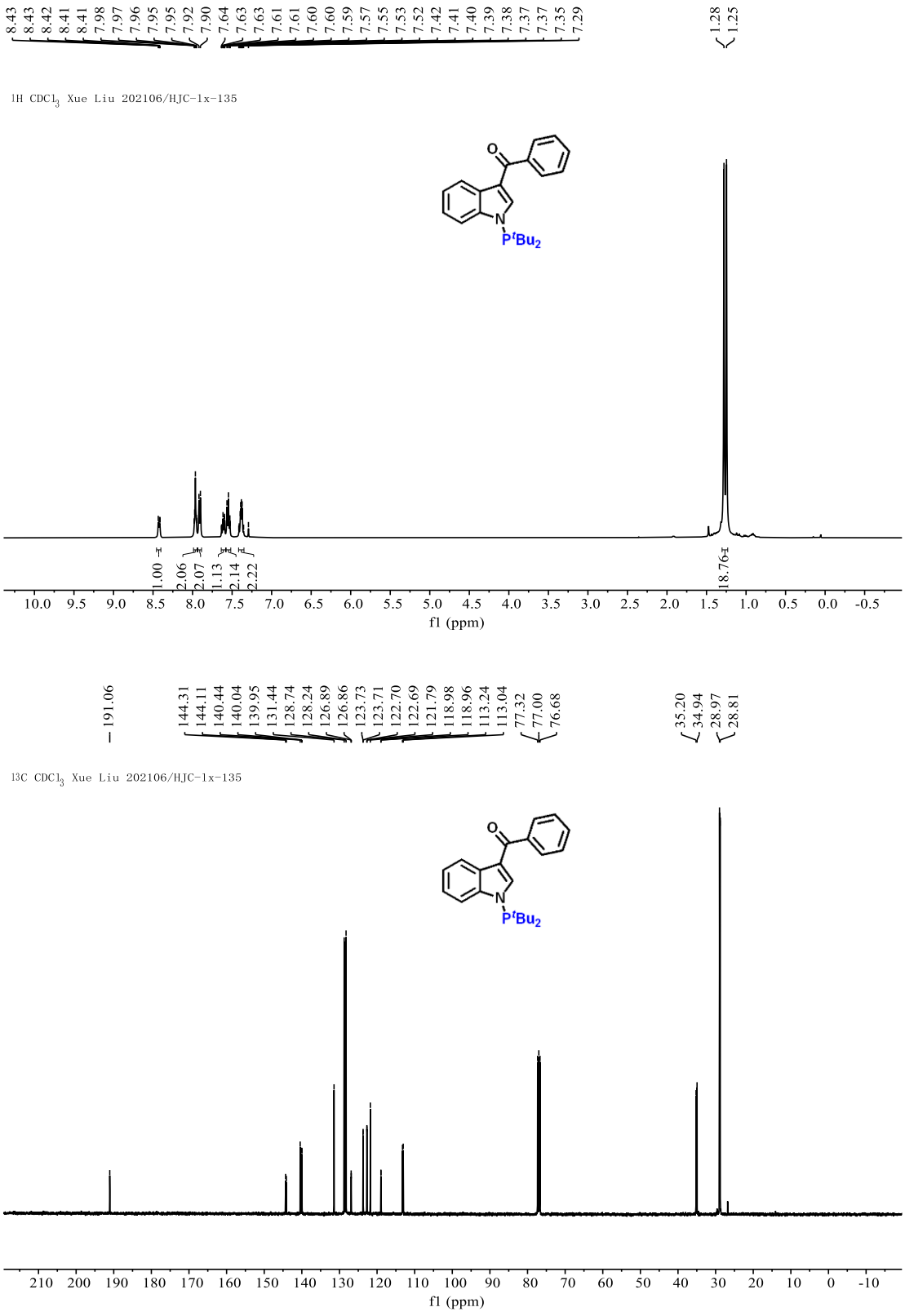


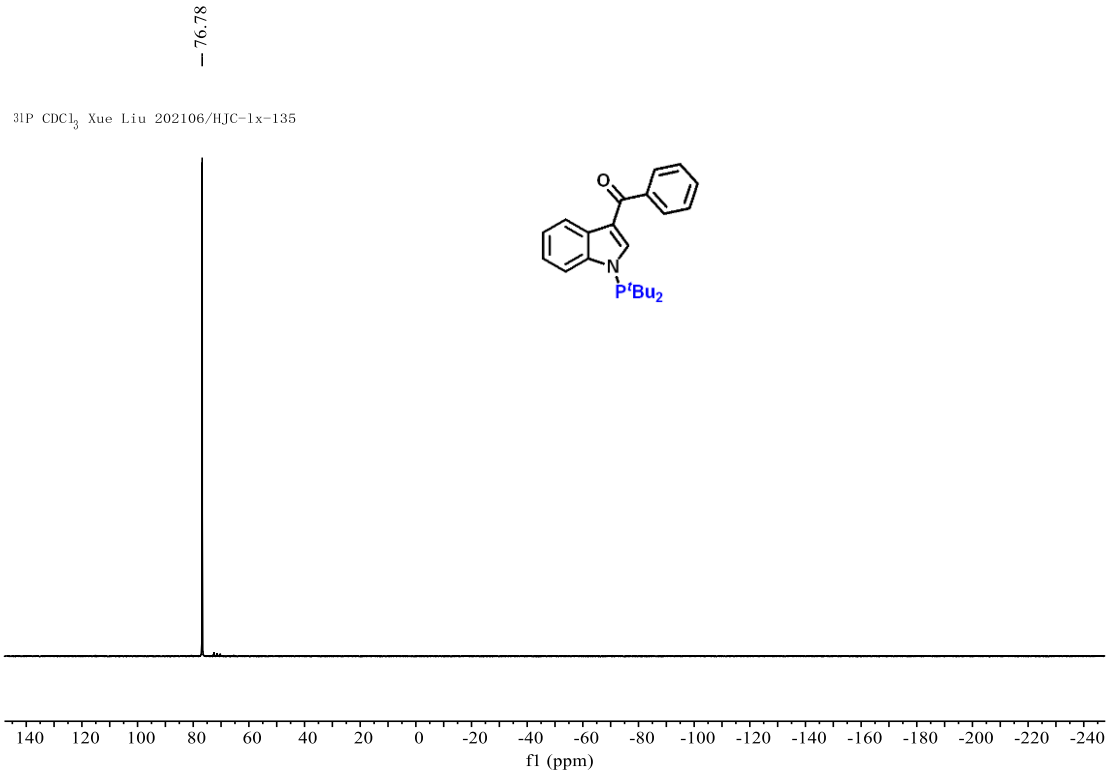
71.24
70.65

^{31}P $CDCl_3$ Xue Liu 202104/HJC-lx-78-2

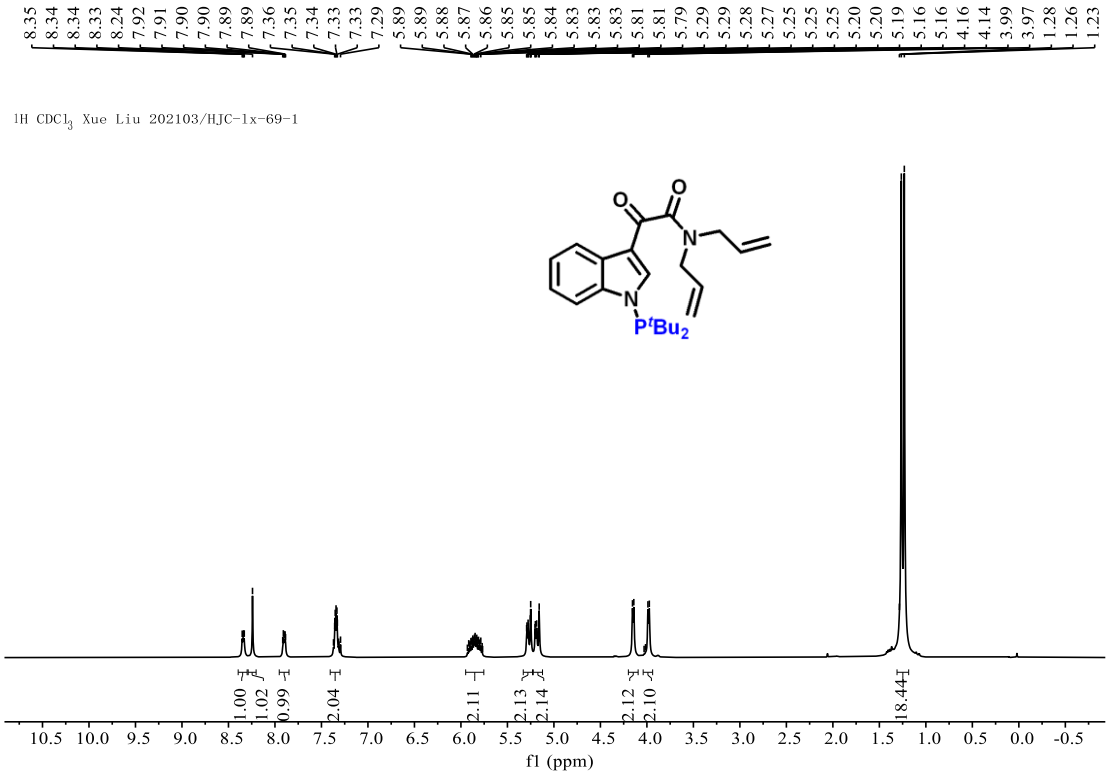


(1-(Di-tert-butylphosphaneyl)-1H-indol-3-yl)(phenyl)methanone (12)



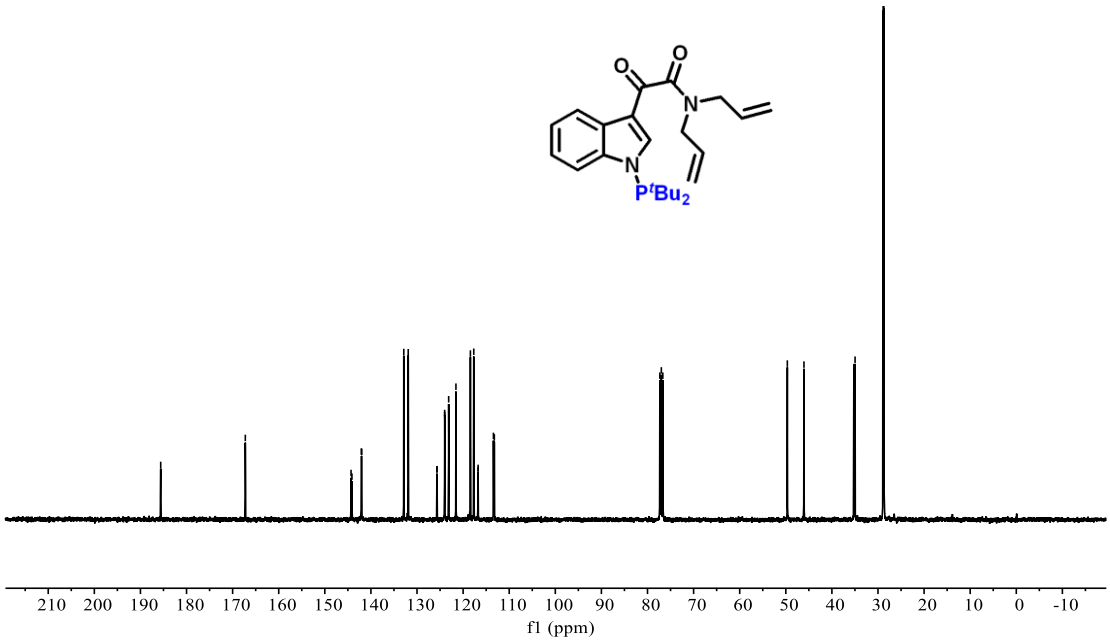


N,N-diallyl-2-(1-(di-tert-butylphosphaneyl)-1H-indol-3-yl)-2-oxoacetamide (13)



185.60
167.25
144.31
144.12
142.08
141.99
132.87
131.91
125.68
125.66
124.01
123.99
123.13
121.56
118.42
117.69
116.77
116.74
113.42
113.23
77.32
77.00
76.68
49.66
46.06
35.24
34.97
28.89
28.72

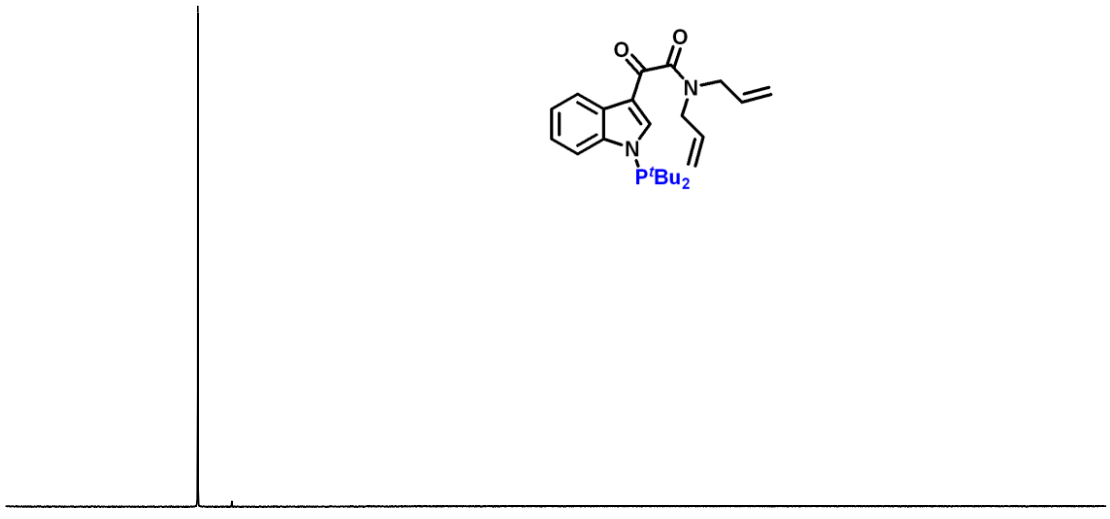
^{13}C $CDCl_3$ Xue Liu 202103/HJC-1x-69-1



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

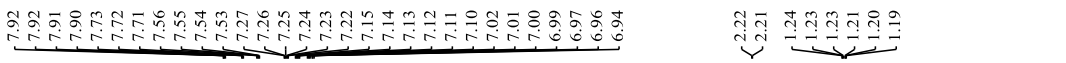
78.71

^{31}P $CDCl_3$ Xue Liu 202103/HJC-1x-69-1

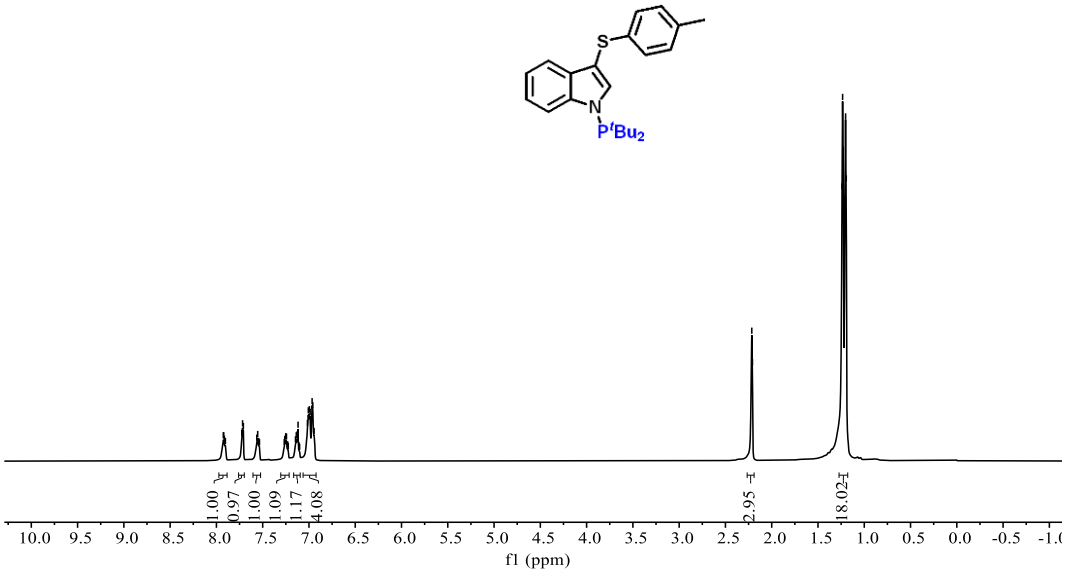


140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

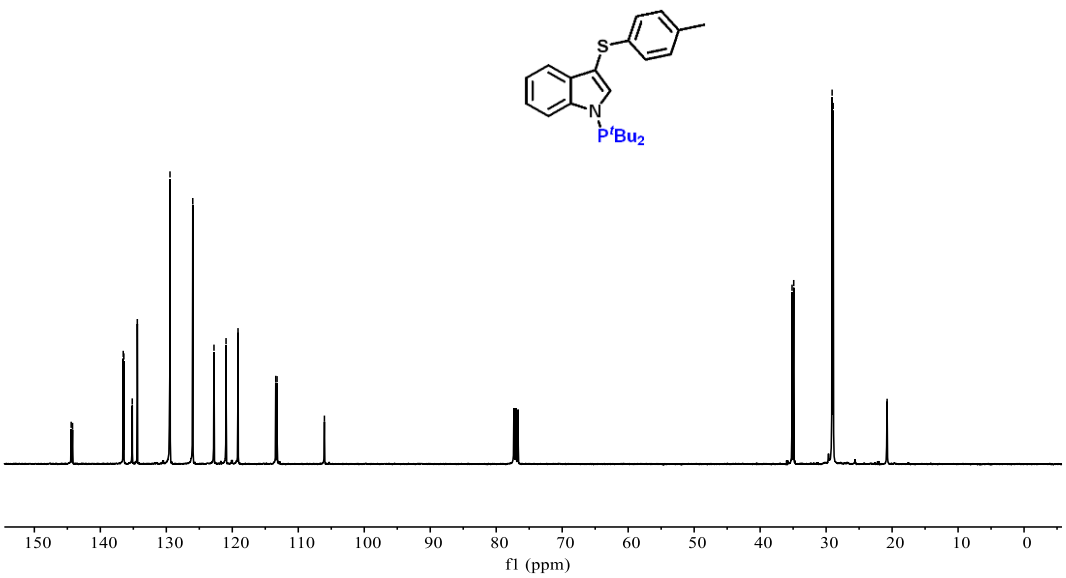
1-(Di-tert-butylphosphanyl)-3-(p-tolylthio)-1H-indole (14)

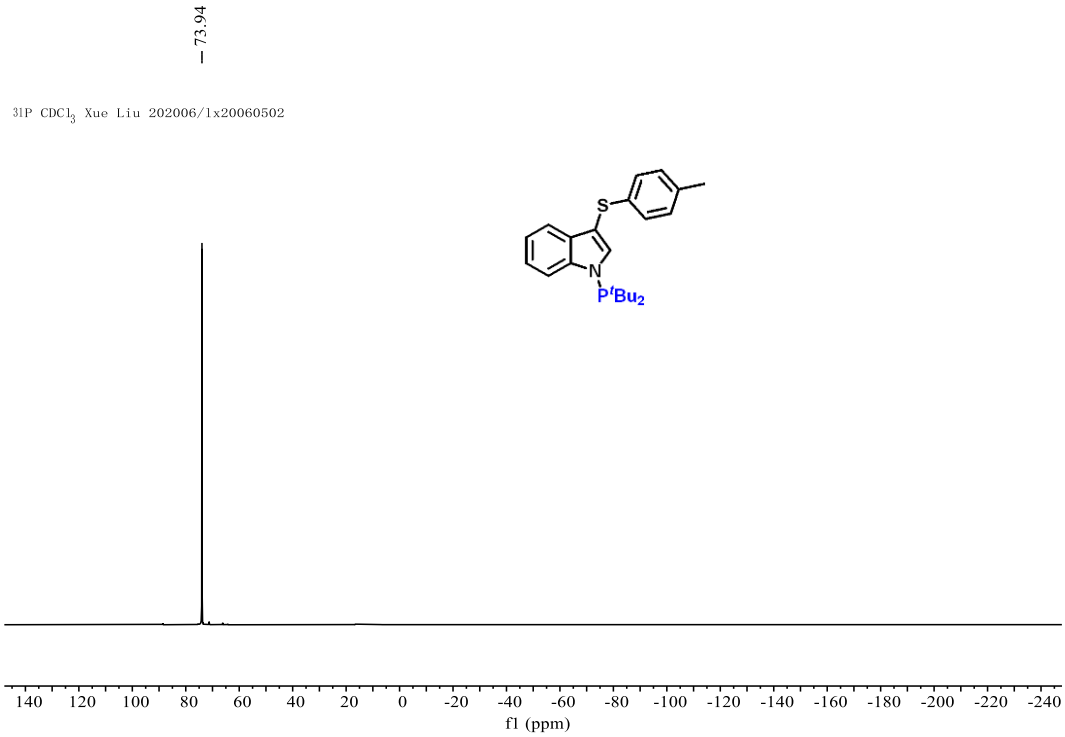


^{1}H $CDCl_3$ Xue Liu 202006/lx20060502

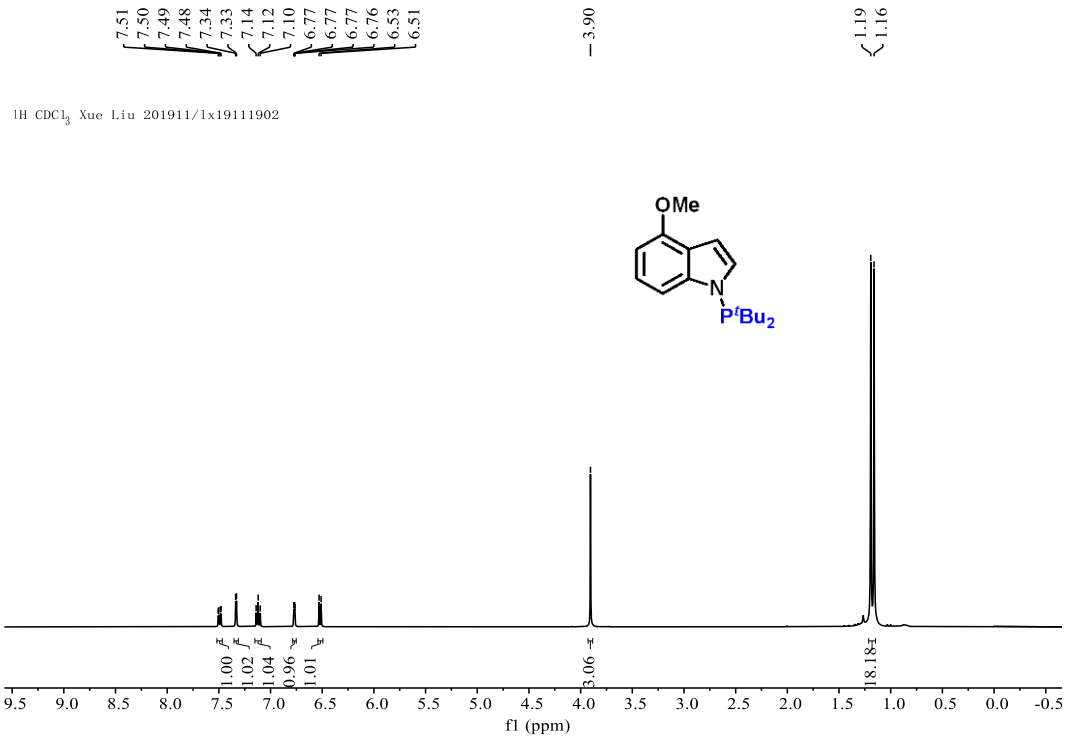


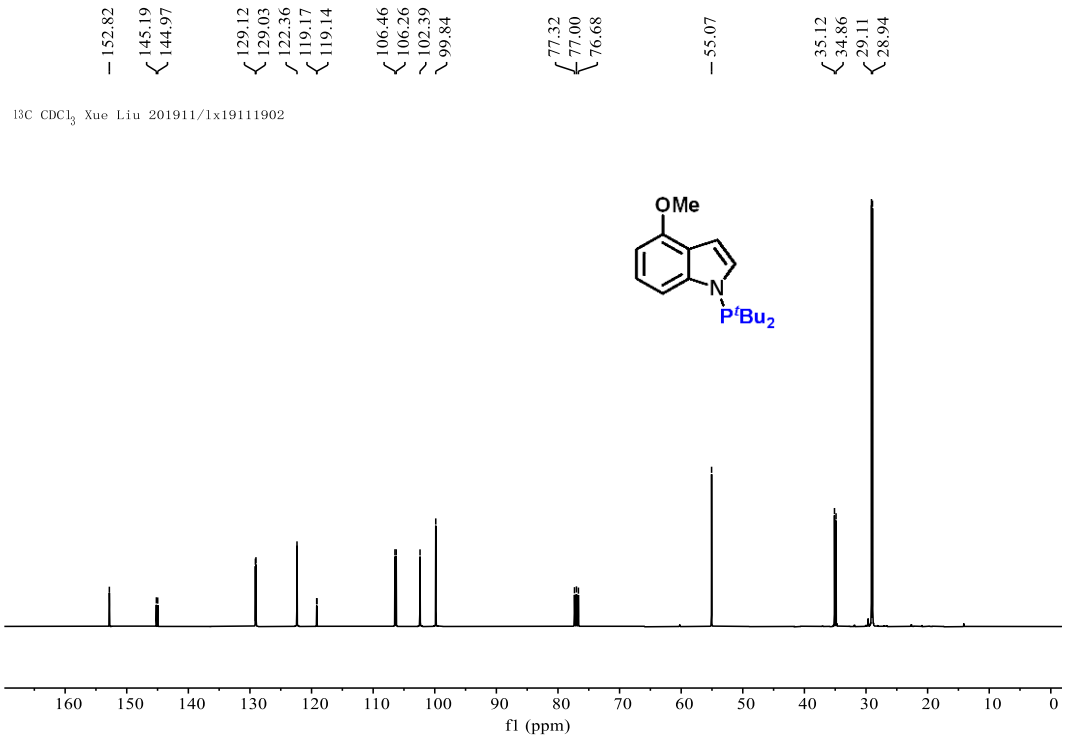
^{13}C $CDCl_3$ Xue Liu 202006/lx20060502

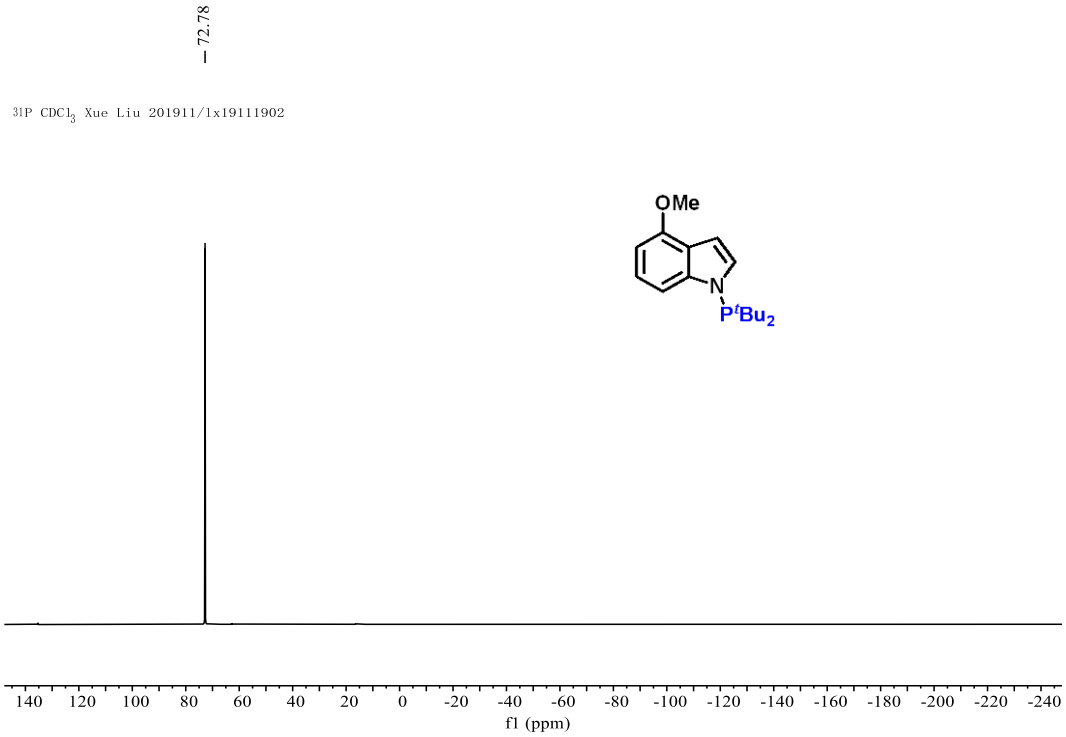




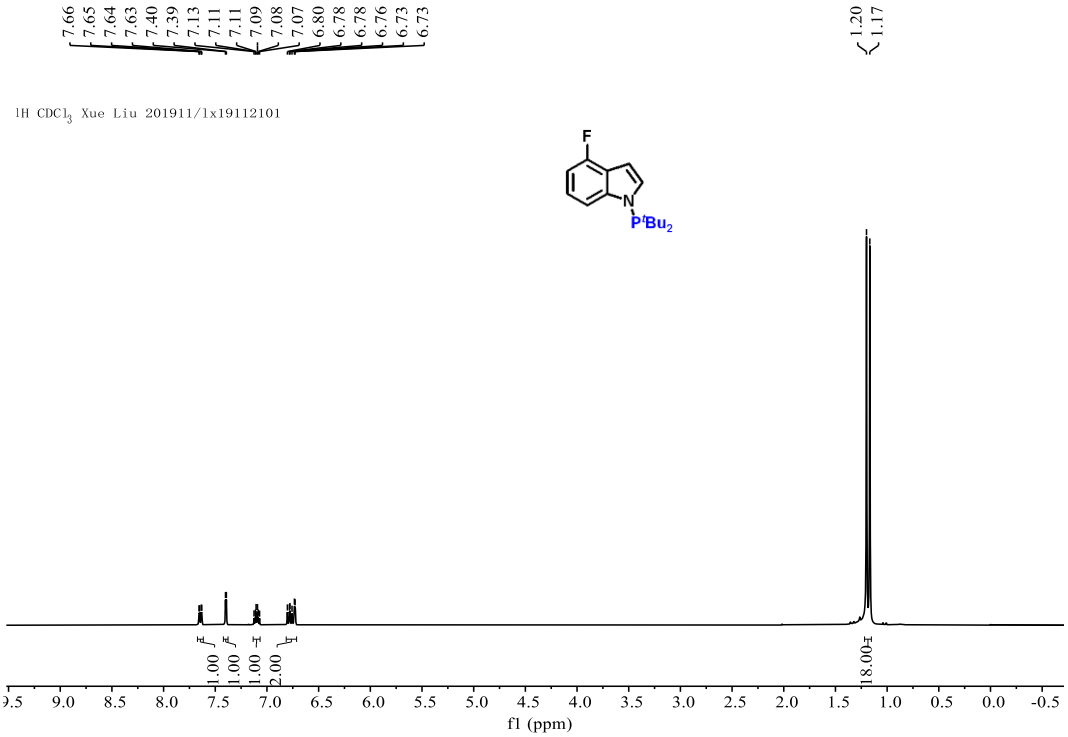
1-(Di-tert-butylphosphanyl)-4-methoxy-1H-indole (15)

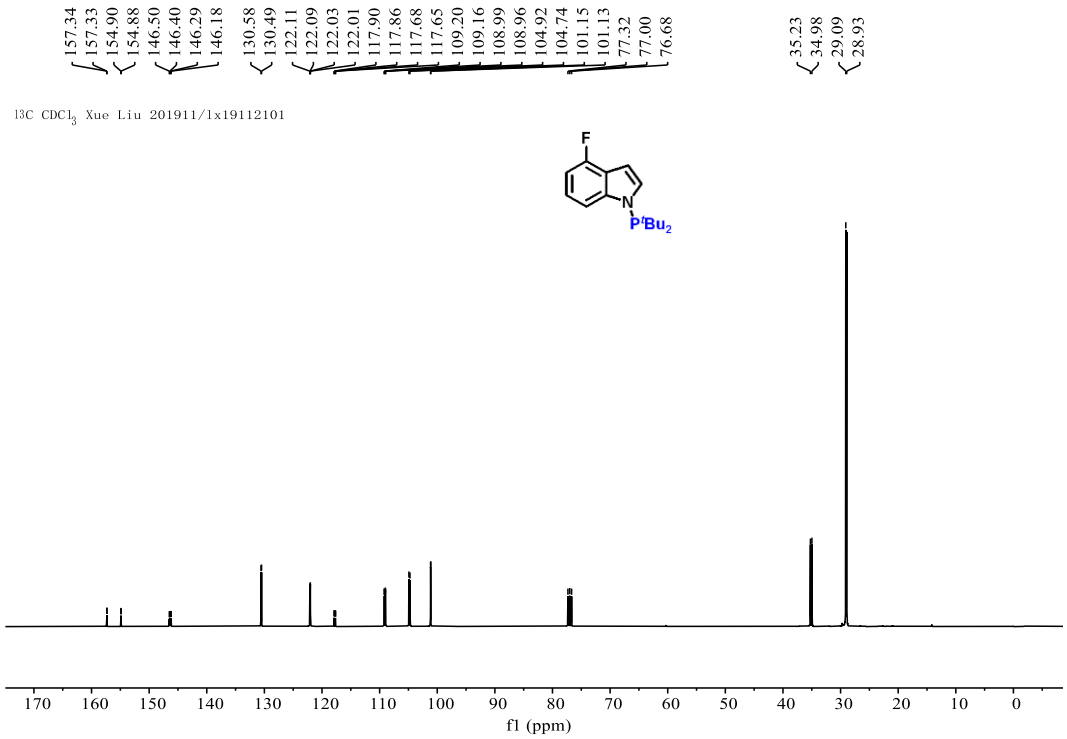



152.82
145.19
144.97
129.12
129.03
122.36
119.17
119.14
106.46
106.26
102.39
99.84
77.32
77.00
76.68
55.07
35.12
34.86
29.11
28.94
13C CDCl3 Xue Liu 201911/1x19111902
OMe
N
P^{t}Bu$_2$
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


72.78
31P CDCl3 Xue Liu 201911/1x19111902
OMe
N
P^{t}Bu$_2$
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

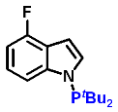
1-(Di-tert-butylphosphanyl)-4-fluoro-1H-indole (16)

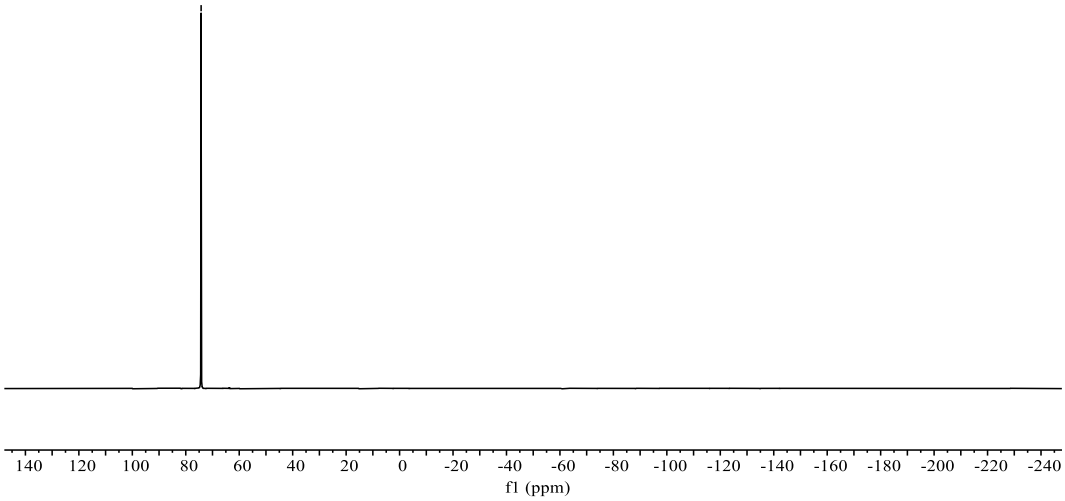




74.26

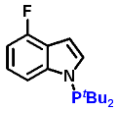
31P $CDCl_3$ Xue Liu 201911/1x19112101

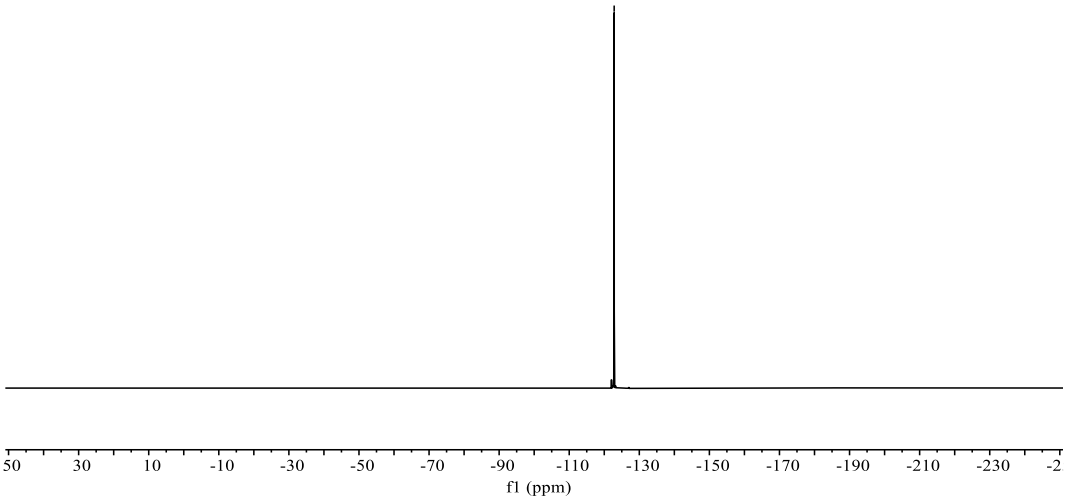




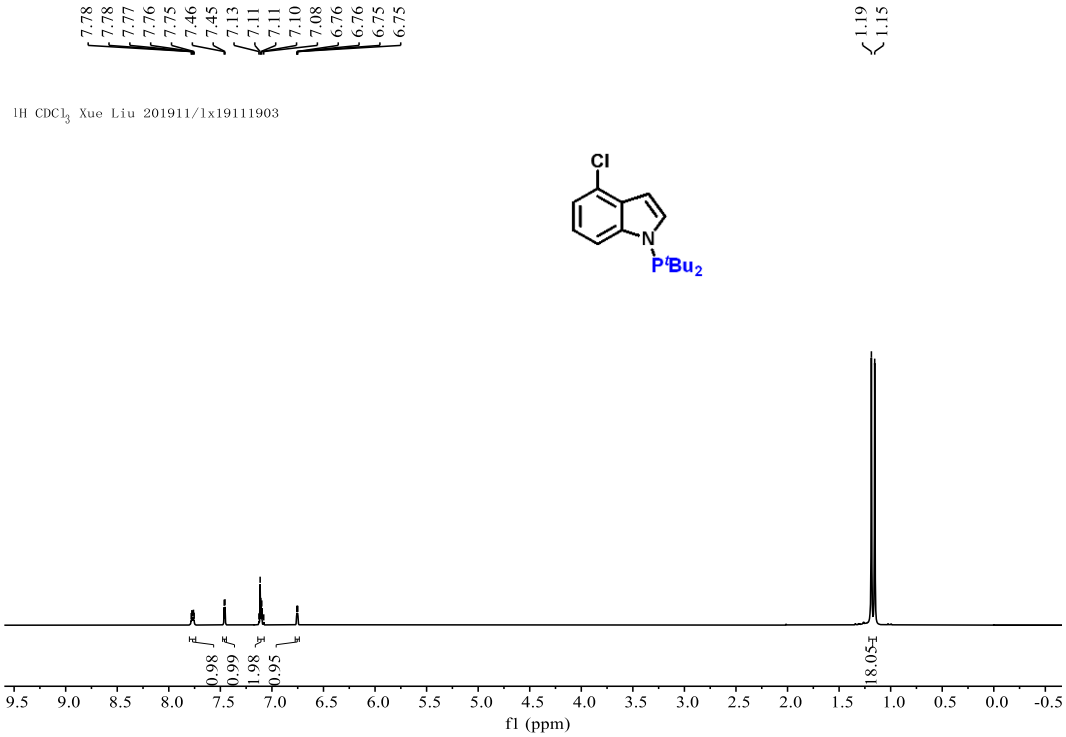
-122.83

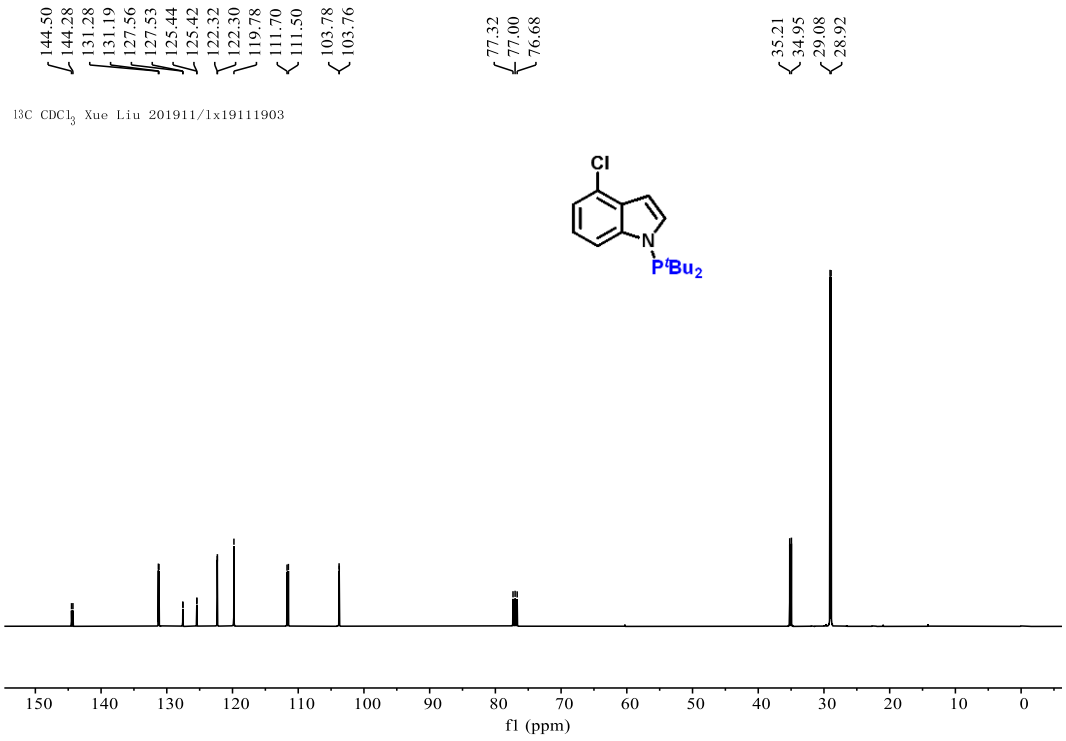
19F $CDCl_3$ Xue Liu 202006/1x20062303

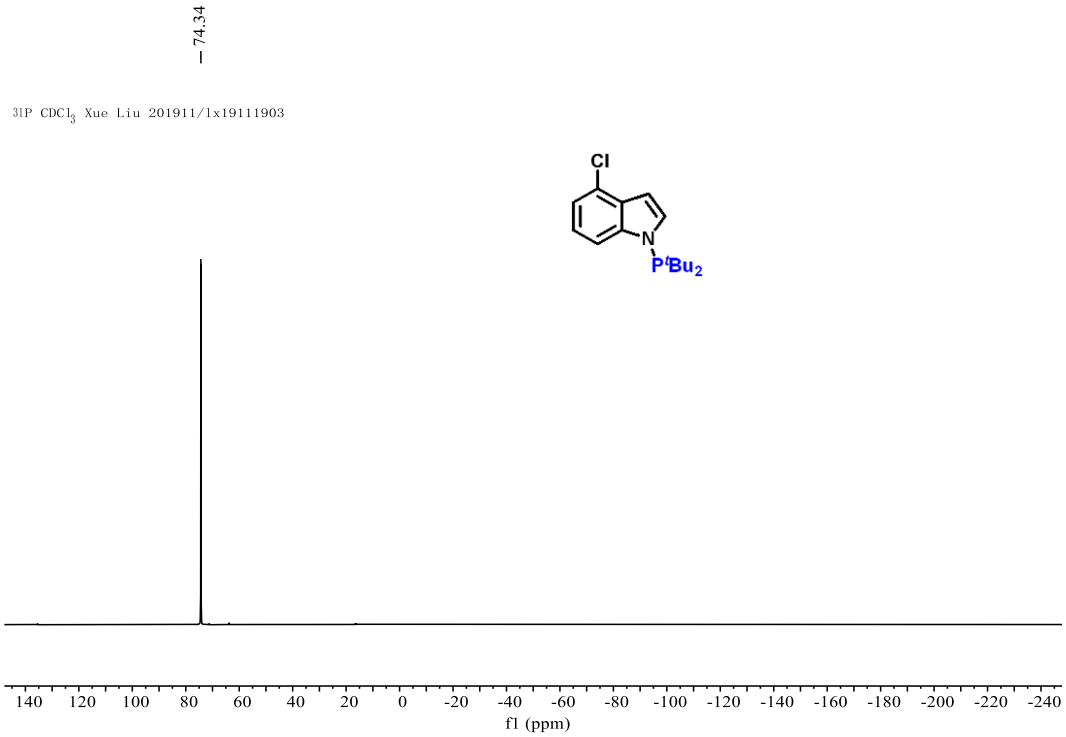




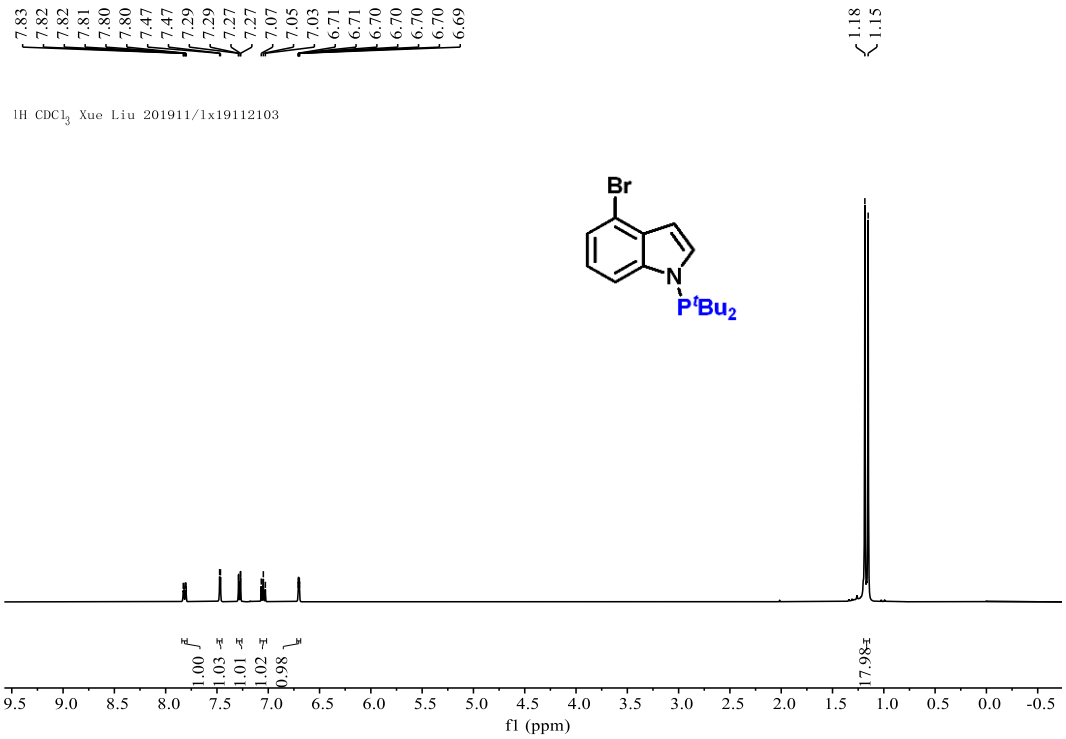
4-Chloro-1-(di-tert-butylphosphanyl)-1H-indole (17)





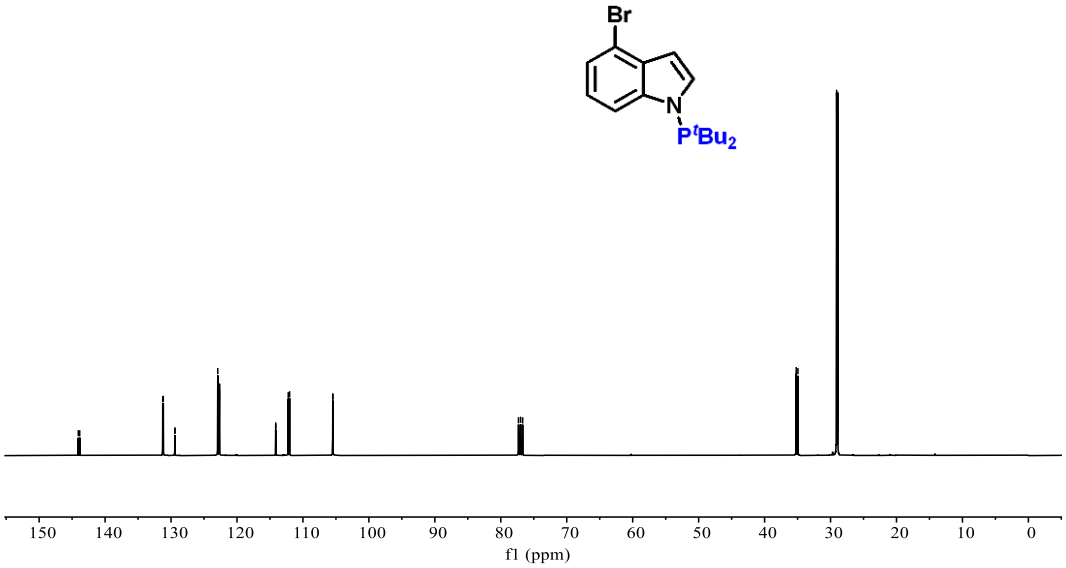


4-Bromo-1-(di-tert-butylphosphanyl)-1H-indole (18)



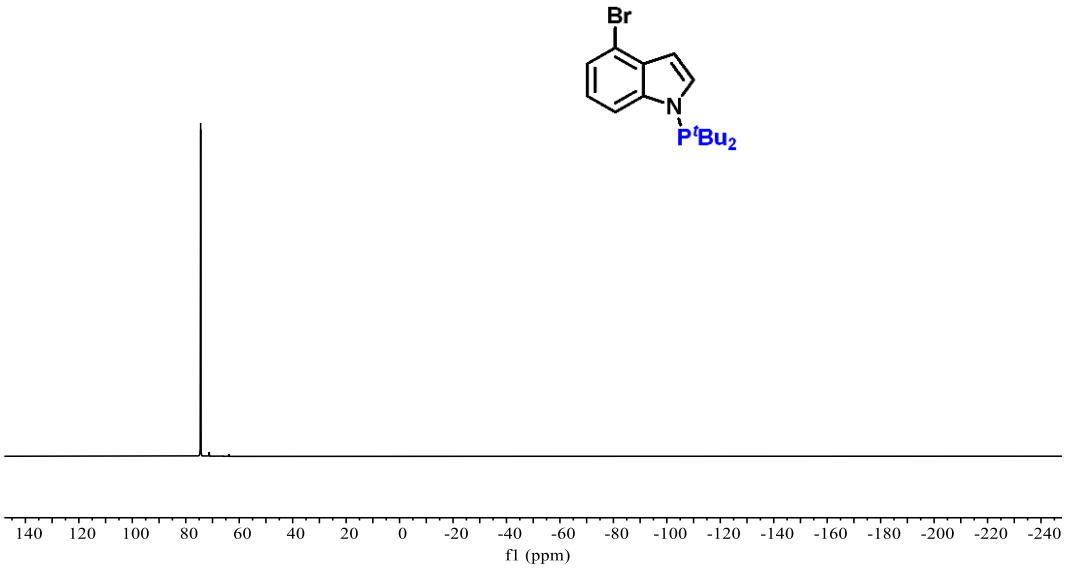
144.06
143.85
131.26
131.17
129.43
129.40
122.92
122.66
122.64
114.13
114.12
112.23
112.02
105.48
105.46
77.32
77.00
76.68
35.20
34.95
29.08
28.92

^{13}C $CDCl_3$ Xue Liu 201911/lx19112103



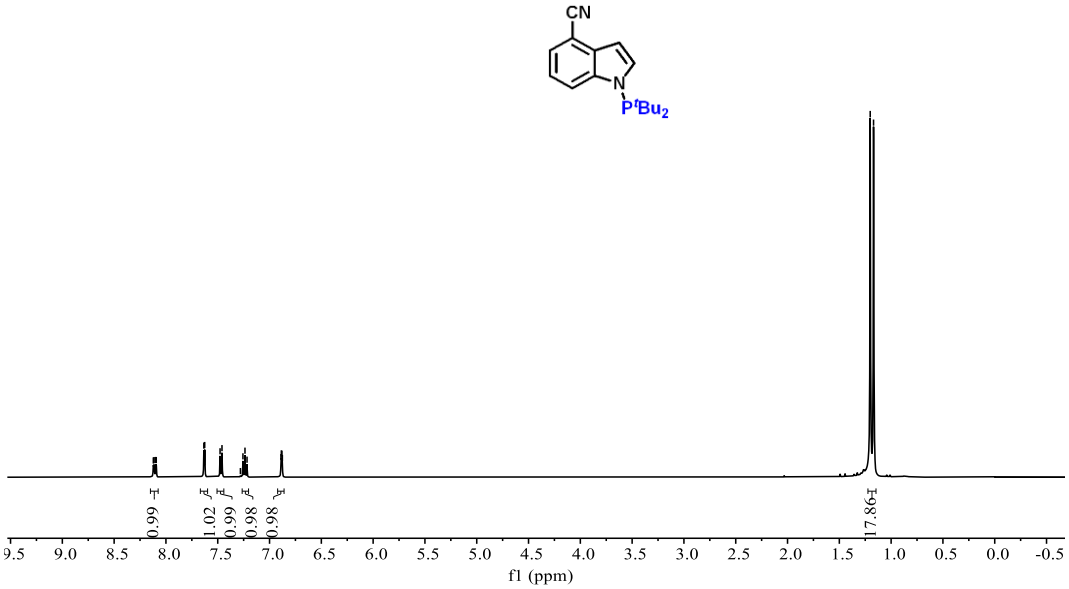
74.43

^{31}P $CDCl_3$ Xue Liu 201911/lx19112103

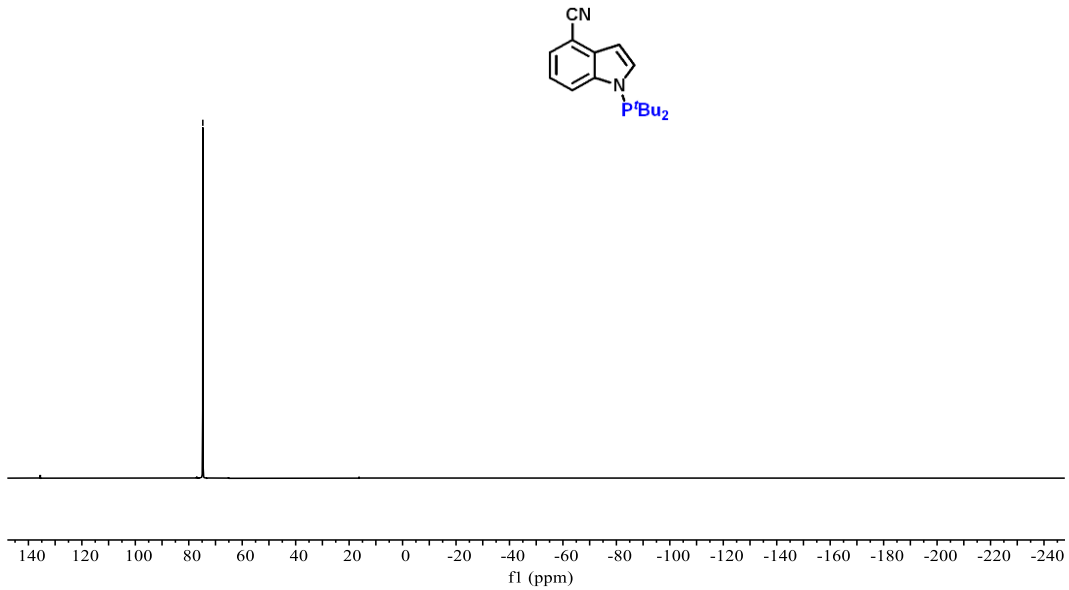


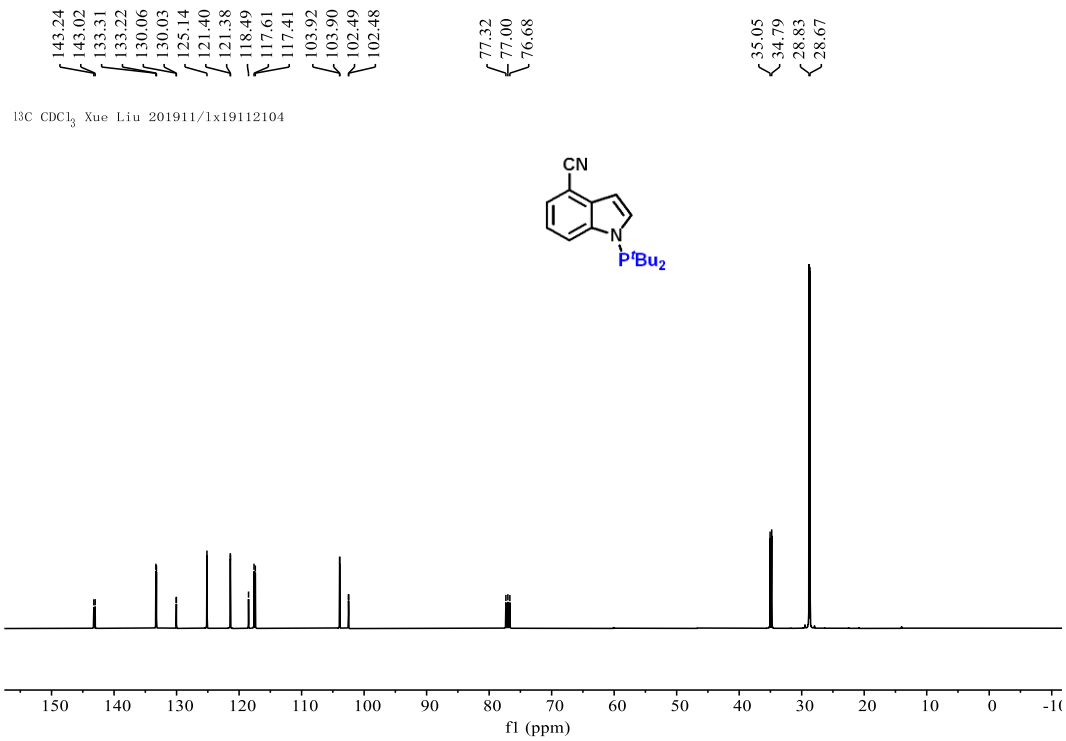
1-(Di-tert-butylphosphanyl)-1H-indole-4-carbonitrile (19)

1H $CDCl_3$ Xue Liu 201911/lx19112104

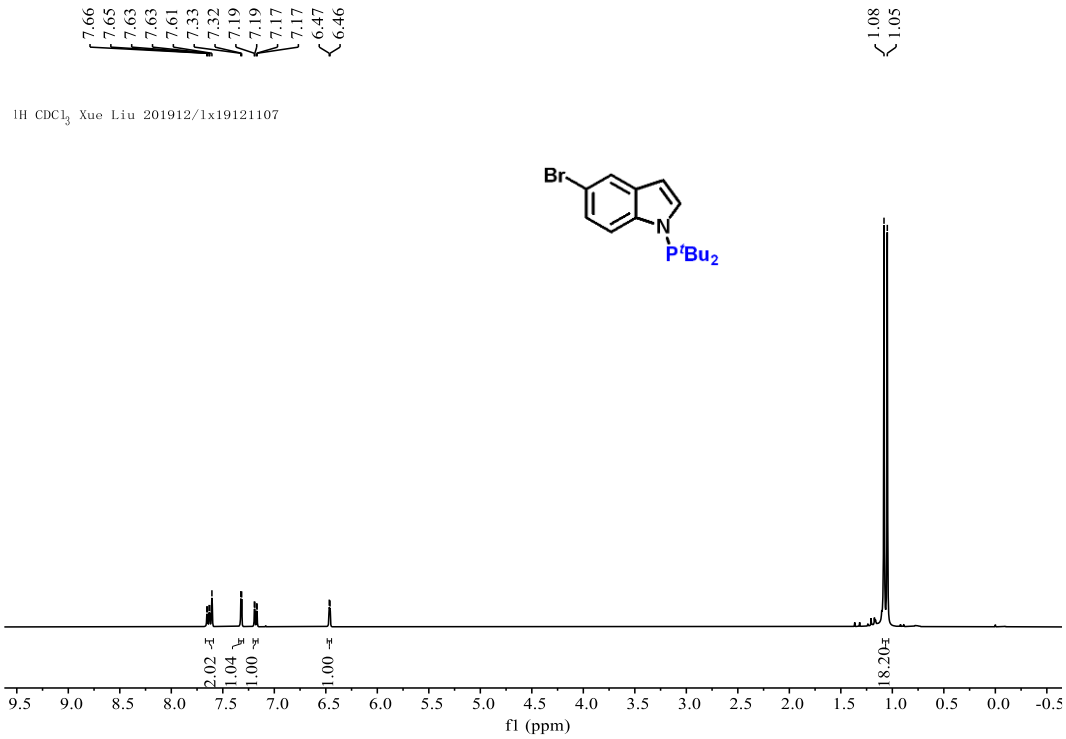


31P $CDCl_3$ Xue Liu 201911/lx19112104



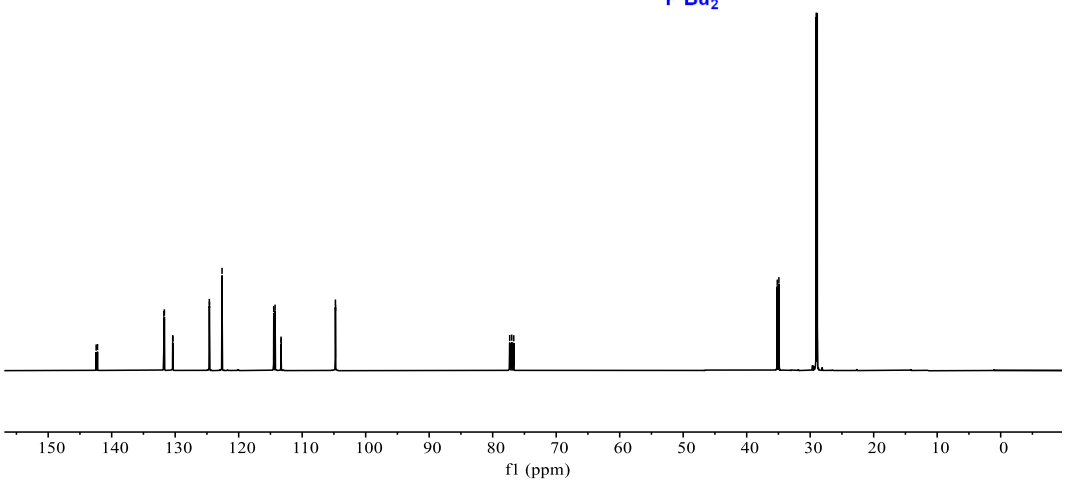


5-Bromo-1-(di-tert-butylphosphanyl)-1H-indole (20)



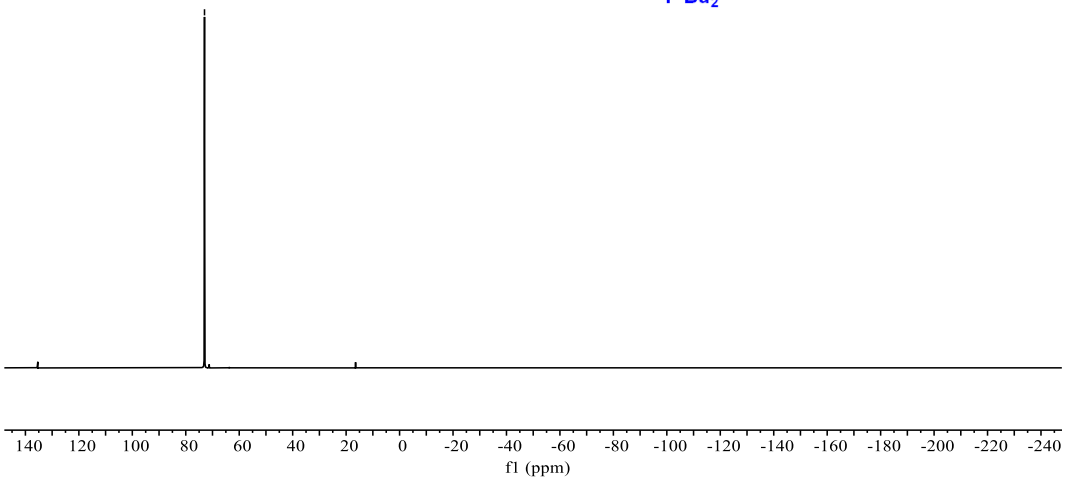
142.45
142.23
131.79
131.70
130.39
130.36
124.62
124.60
122.62
114.48
114.27
113.33
113.30
104.76
104.74
77.32
77.00
76.68
35.18
34.93
29.05
28.89

^{13}C $CDCl_3$ Xue Liu 201912/lx19121107

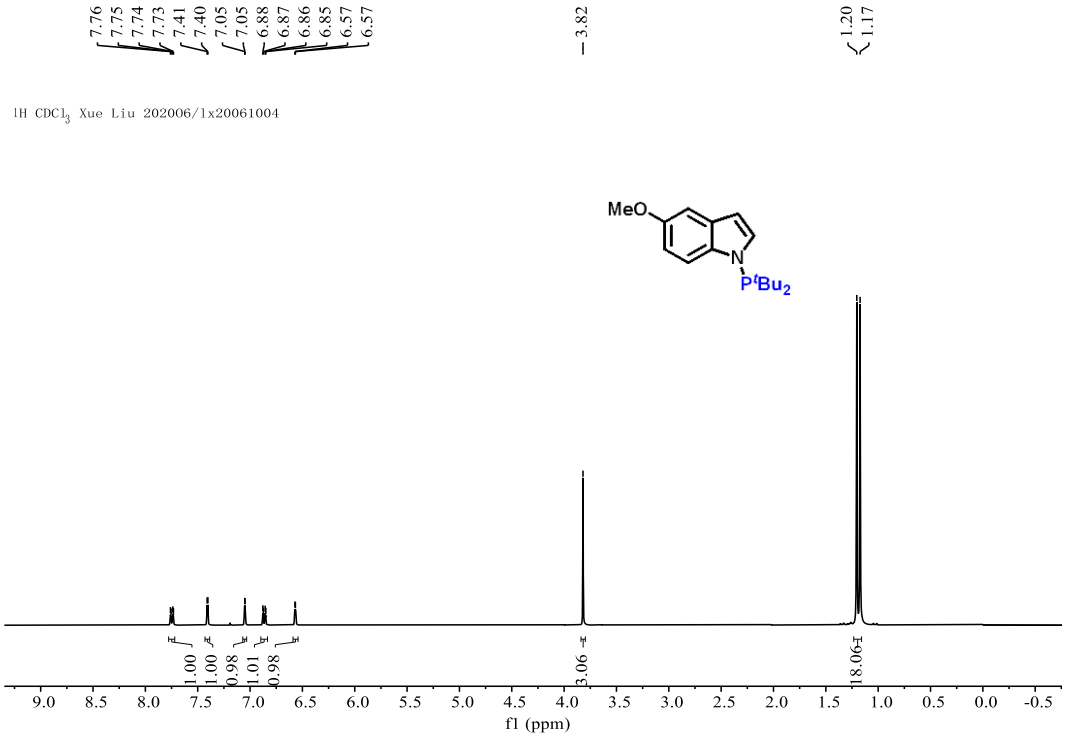


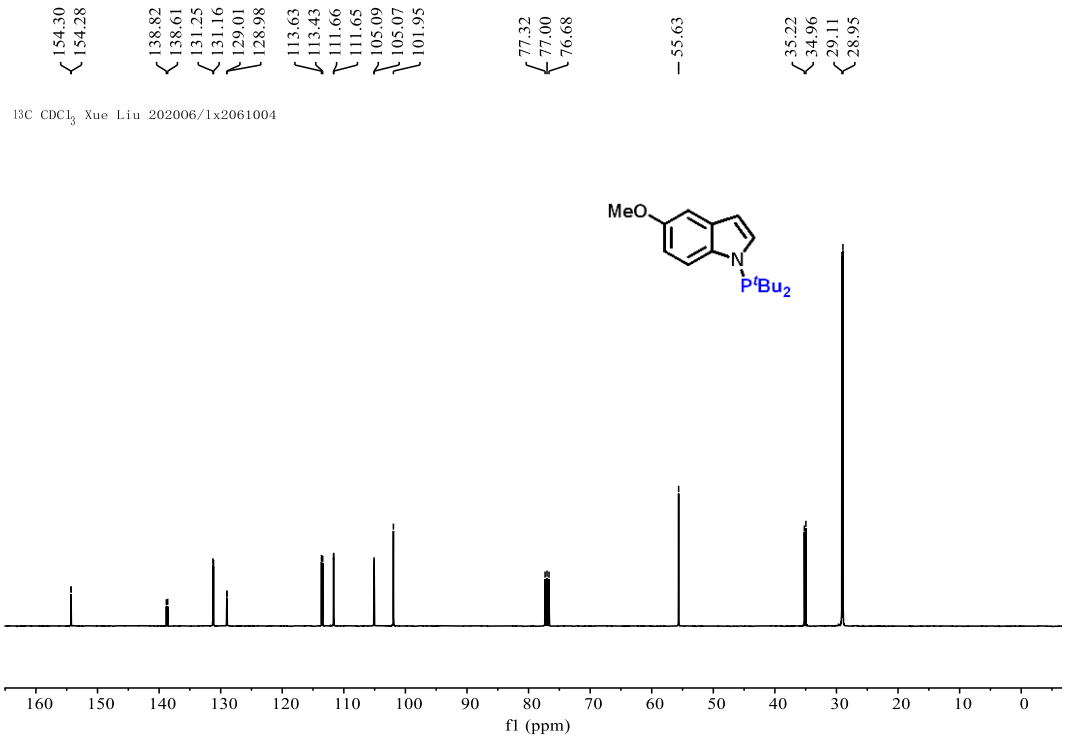
72.99

^{31}P $CDCl_3$ Xue Liu 201912/lx19121107



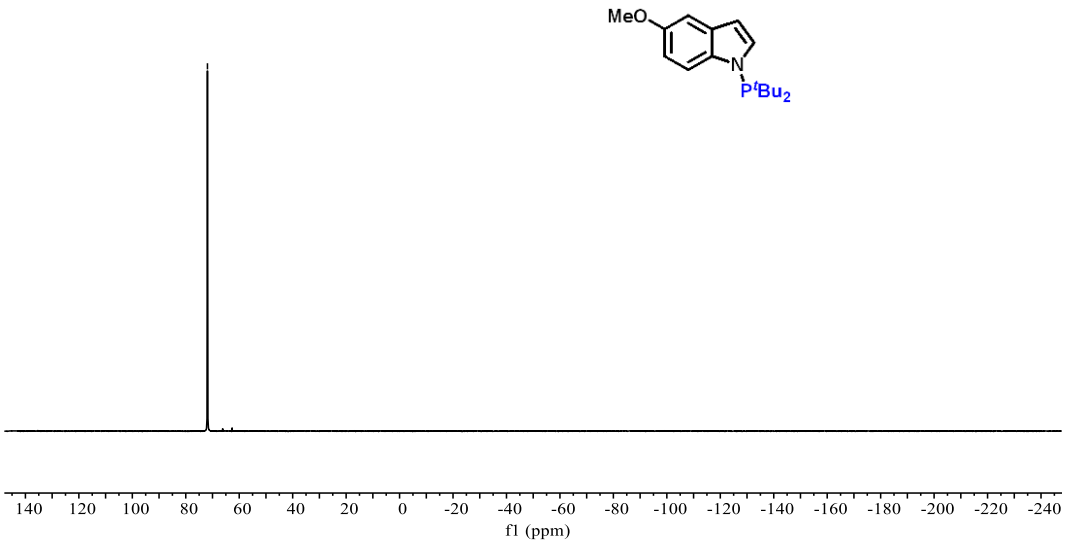
1-(Di-tert-butylphosphanyl)-5-methoxy-1H-indole (21)





71.88

31P $CDCl_3$ Xue Liu 202006/1x20061004



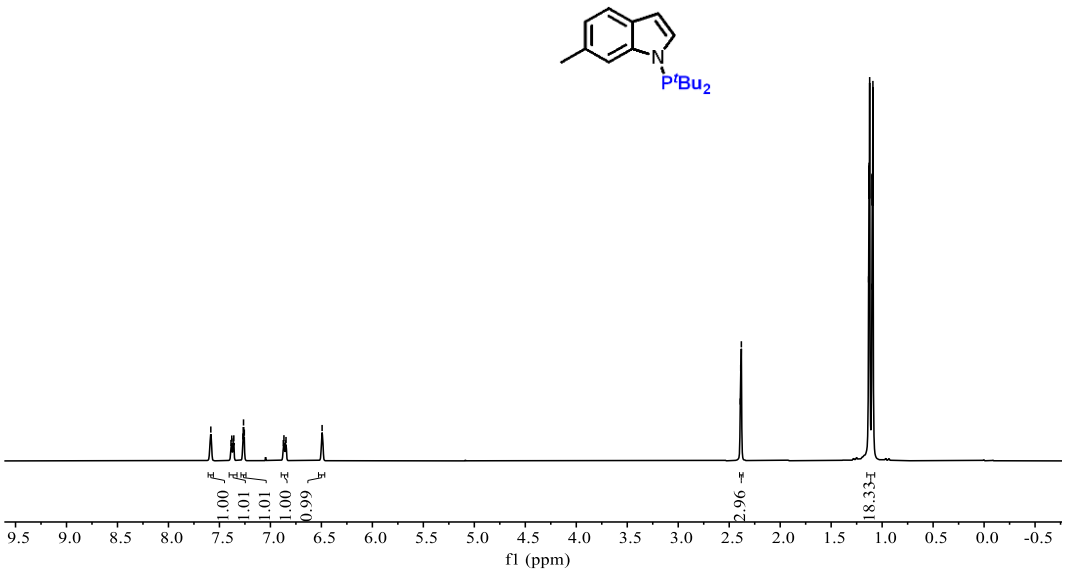
1-(Di-tert-butylphosphanyl)-6-methyl-1H-indole (22)

7.58 7.39 7.38 7.37 7.36 7.27 7.26 7.26 6.87 6.87 6.85 6.85 6.49

2.39 2.39 2.38

1.13 1.13 1.12 1.10 1.10 1.09

1H $CDCl_3$ Xue Liu 202006/1x20061002



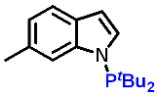
144.18
143.98
131.47
131.46
129.98
129.89
126.55
126.52
121.80
119.73
112.99
112.79
105.16
105.16

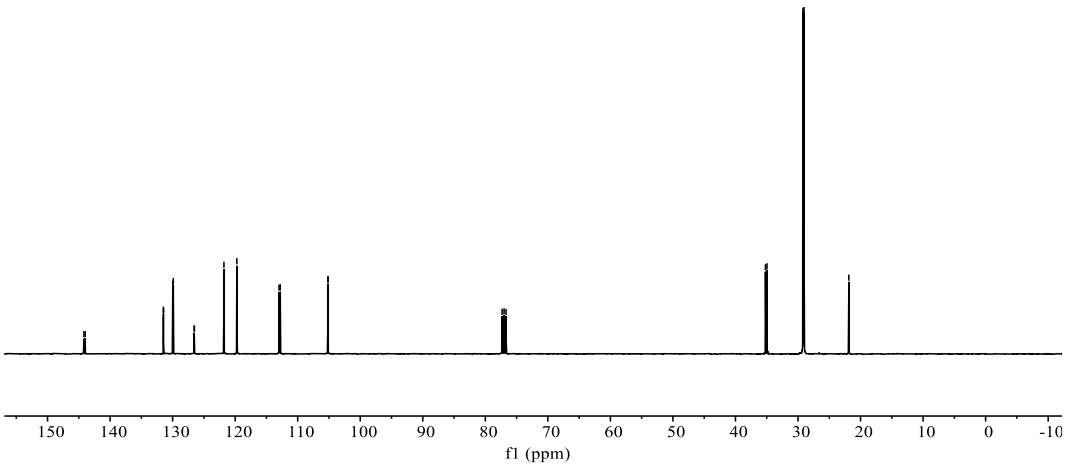
77.32
77.00
76.68

35.21
34.96
29.20
29.04

21.87

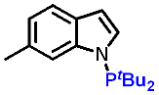
^{13}C $CDCl_3$ Xue Liu 202006/1x20061002

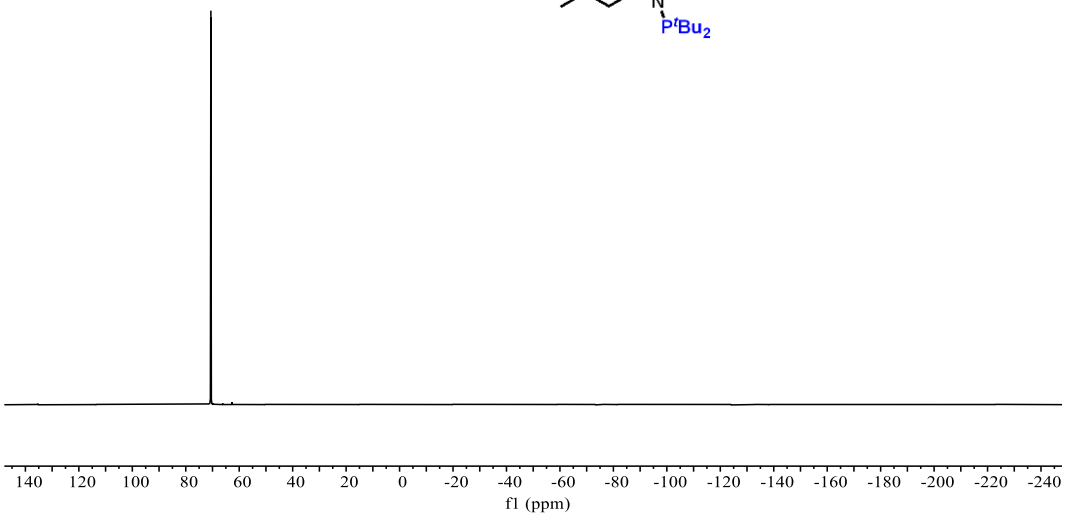




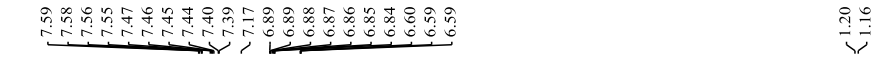
70.61

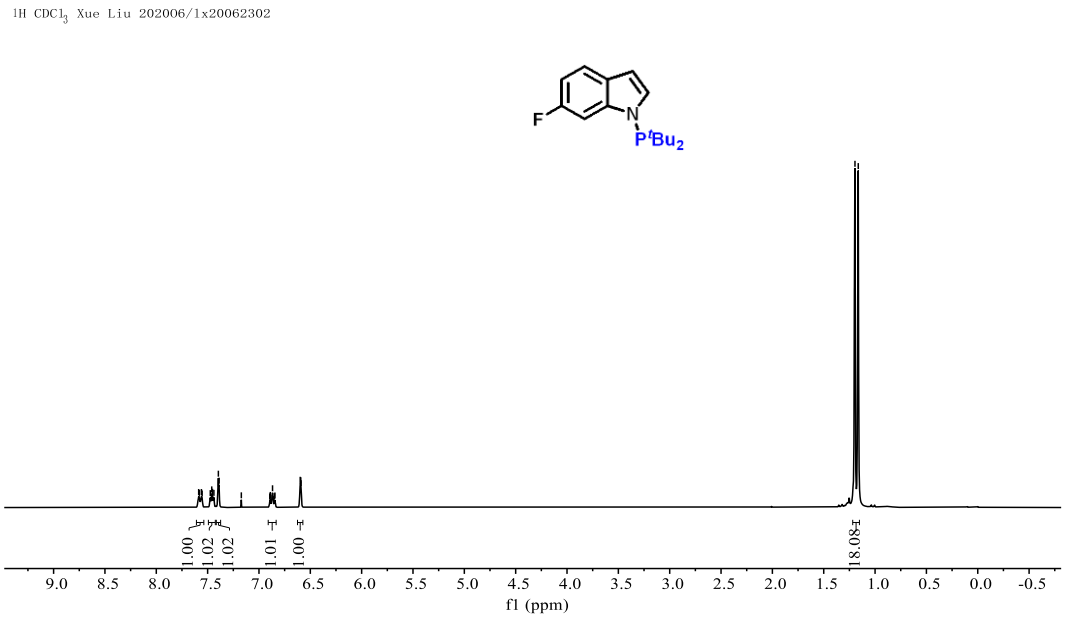
^{31}P $CDCl_3$ Xue Liu 202006/1x20061002

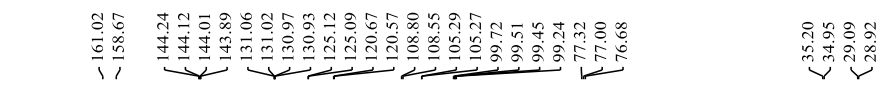


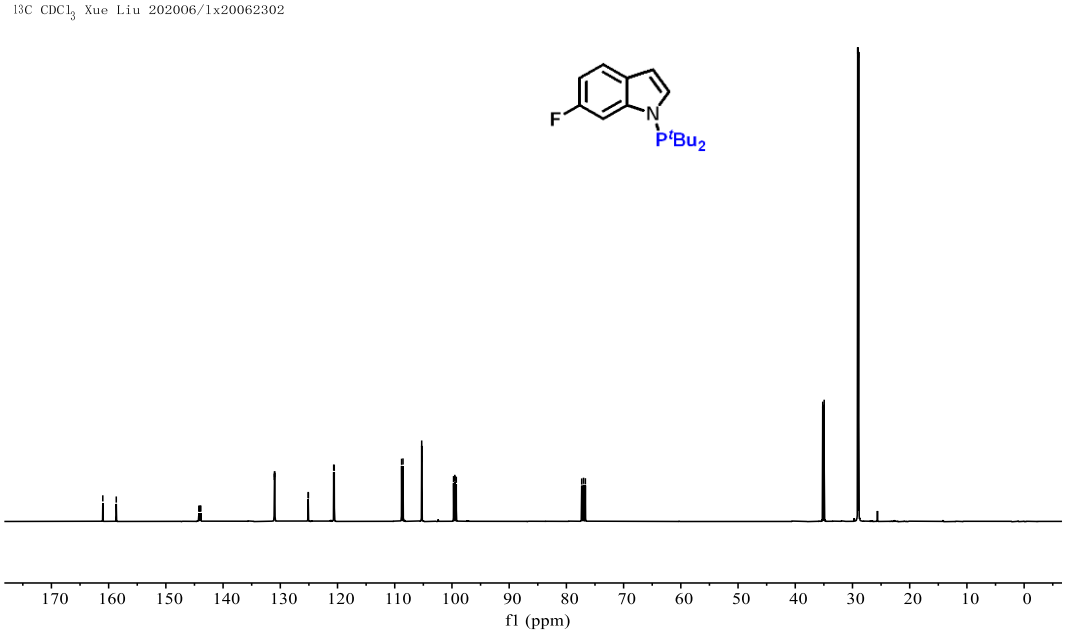


1-(Di-tert-butylphosphanyl)-6-fluoro-1H-indole (23)



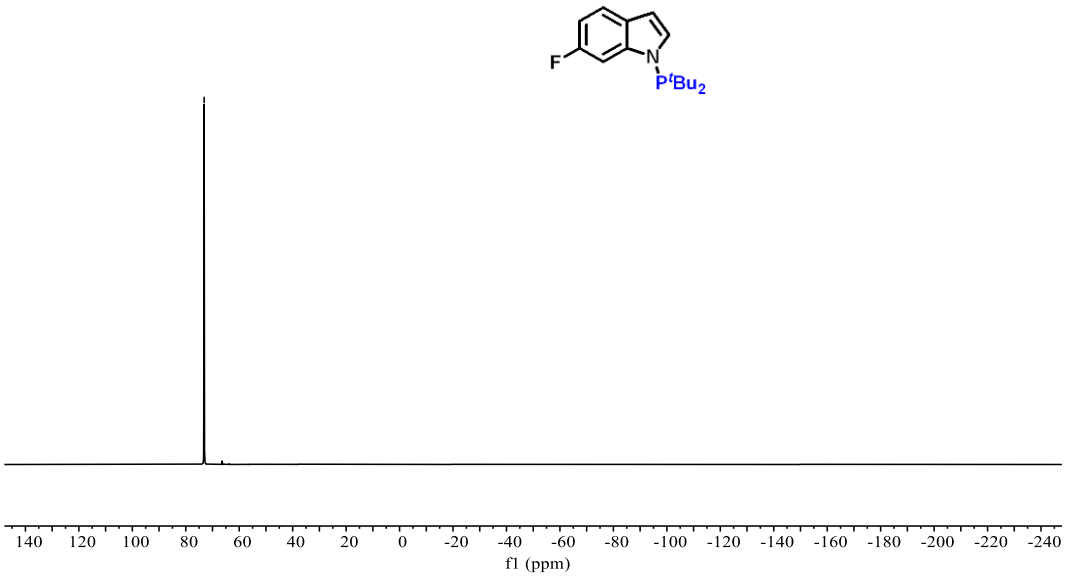






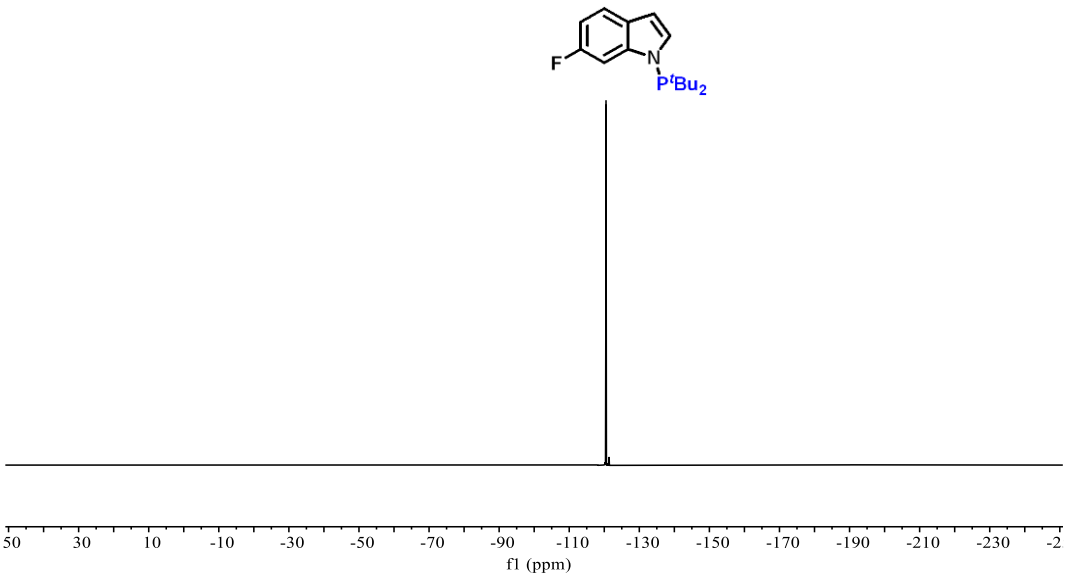
73.12

31P $CDCl_3$ Xue Liu 202006/1x20062302

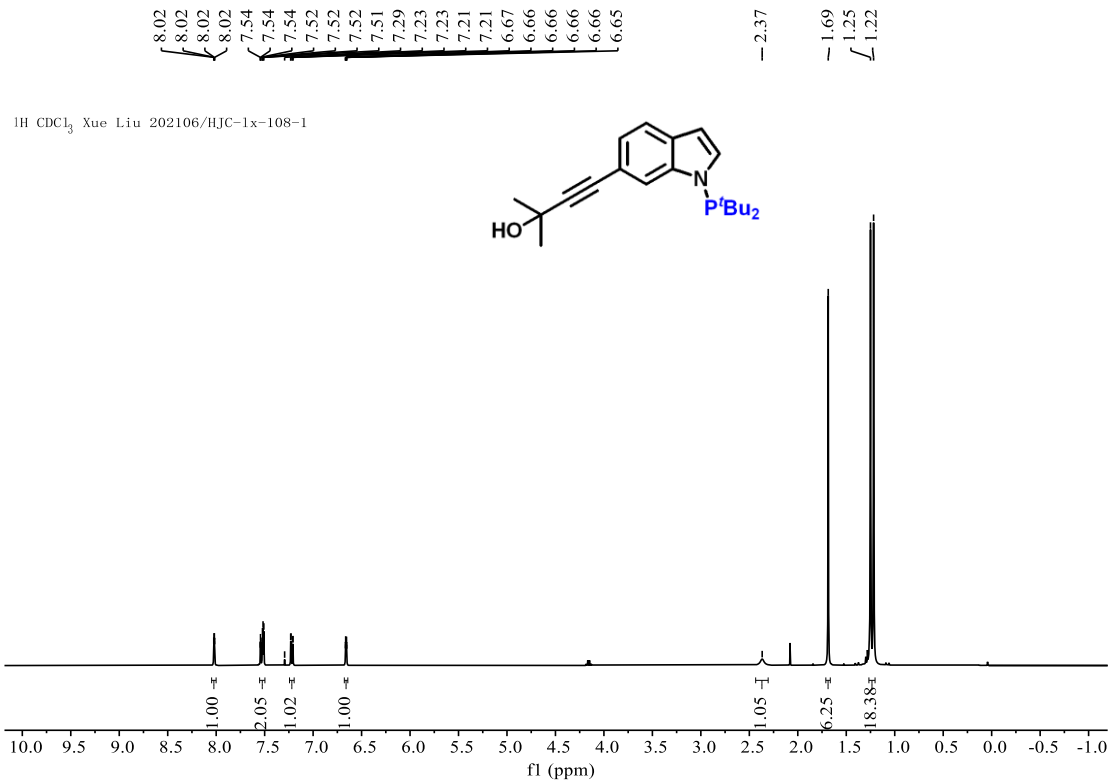


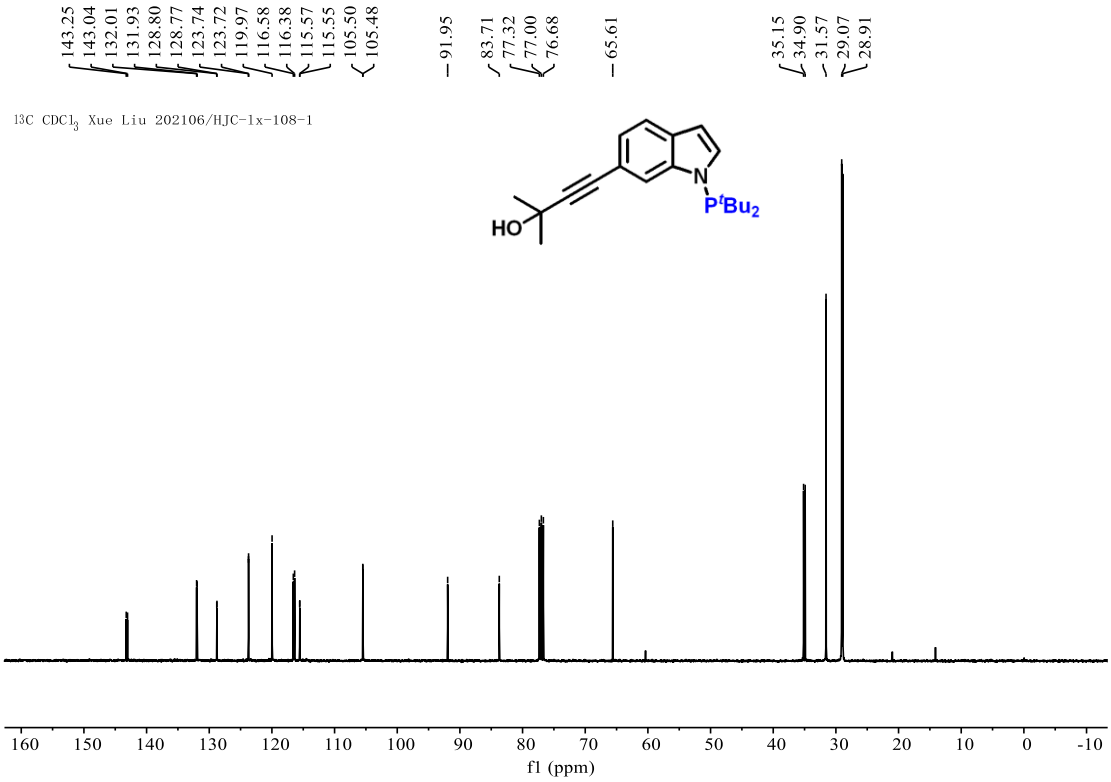
-120.45
-120.47
-120.49
-120.50

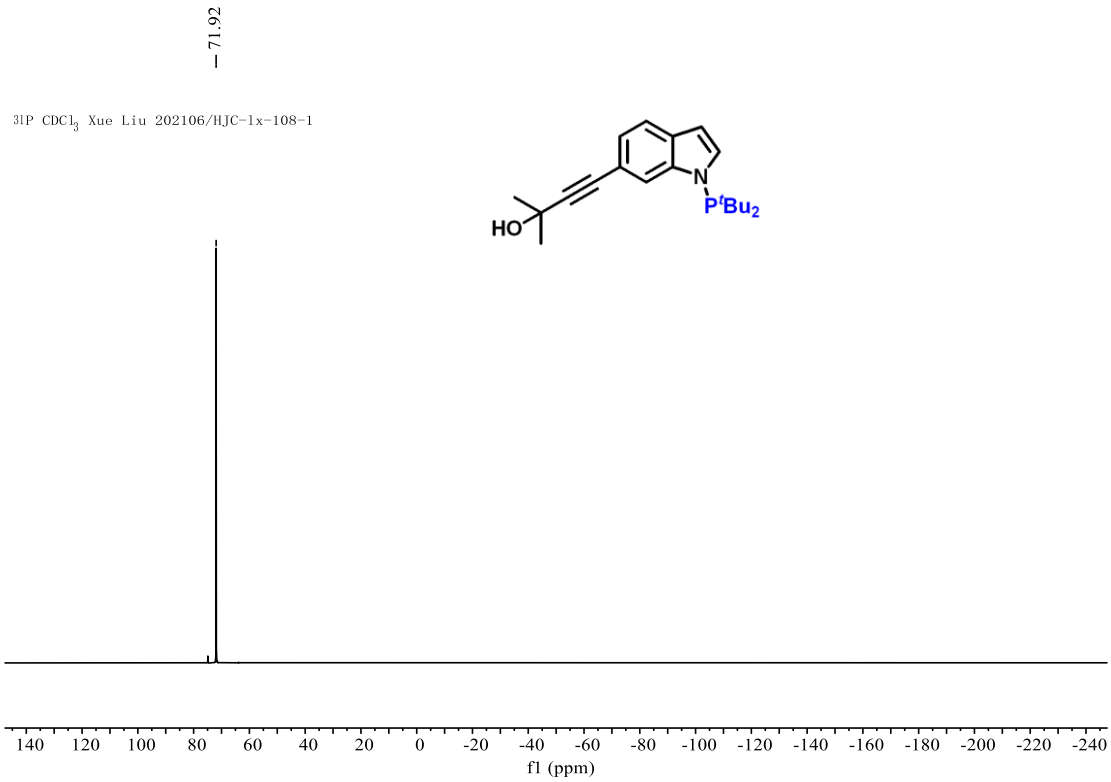
19F $CDCl_3$ Xue Liu 202006/1x20062302



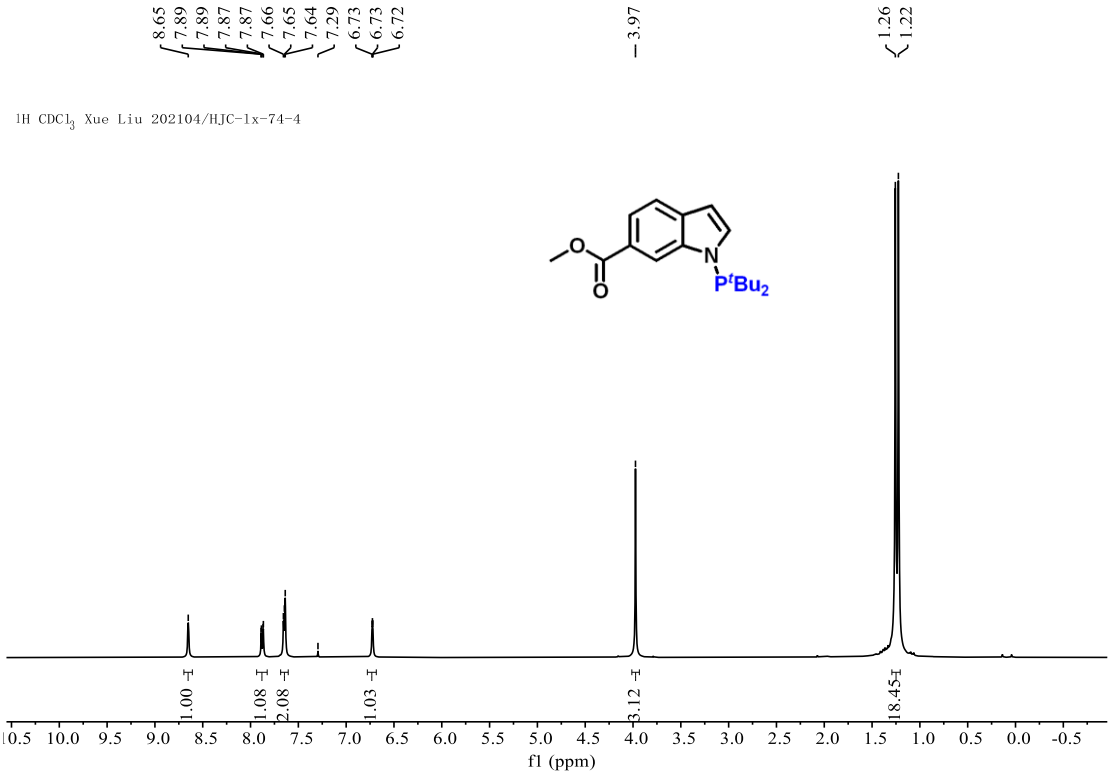
4-(1-(Di-tert-butylphosphaneyl)-1H-indol-6-yl)-2-methylbut-3-yn-2-ol (24)

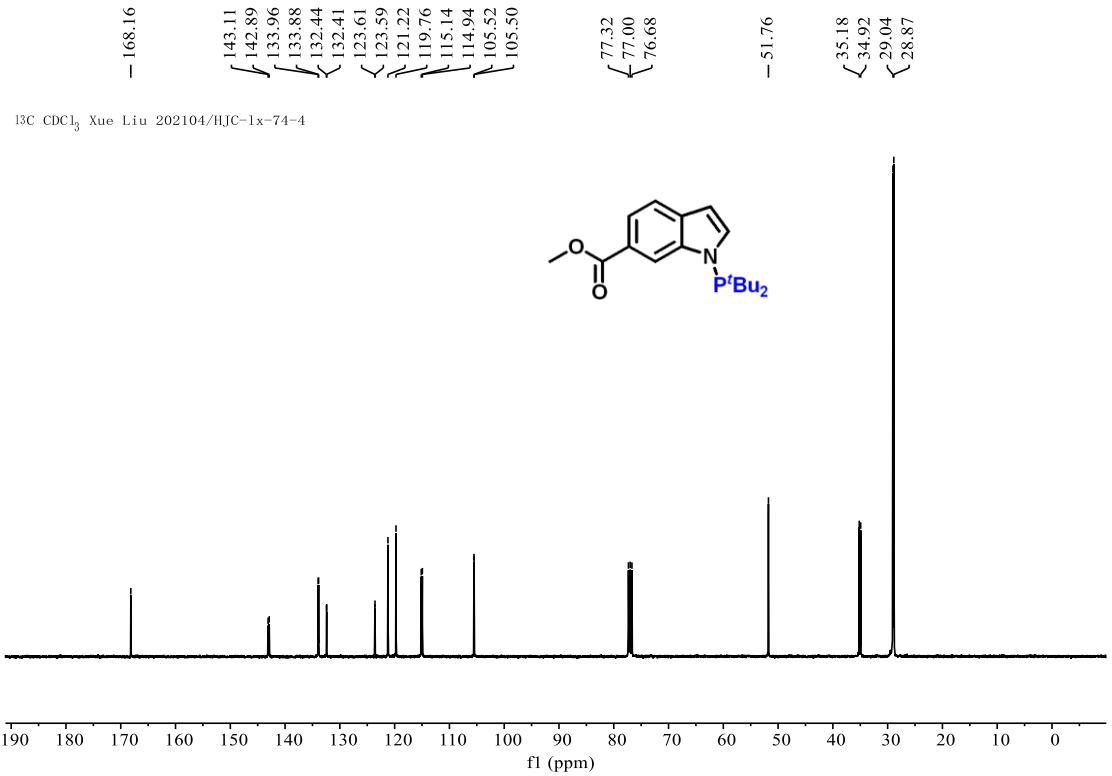


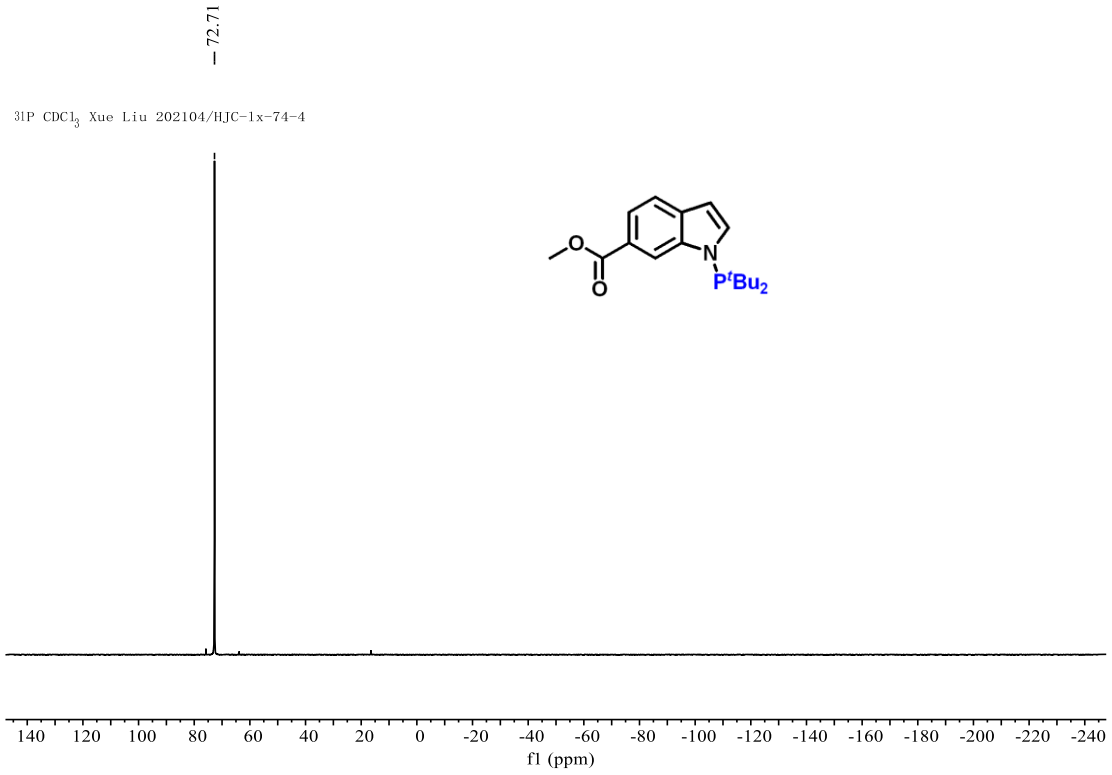




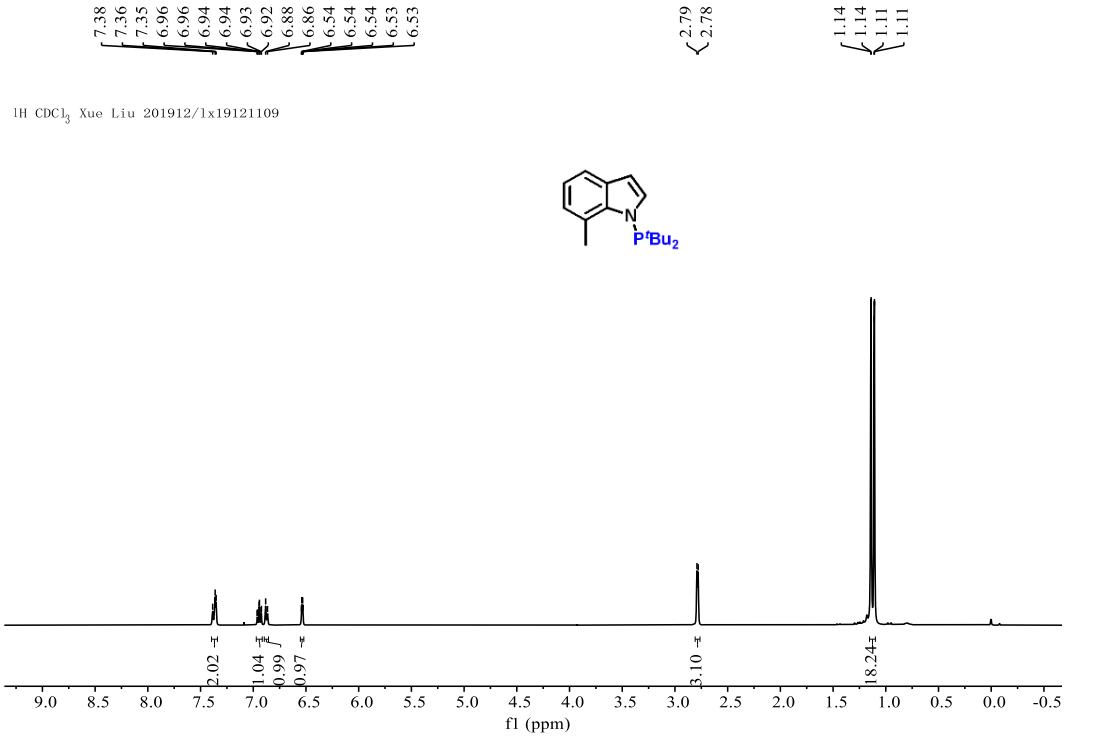
Methyl 1-(di-tert-butylphosphaneyl)-1H-indole-6-carboxylate (25)

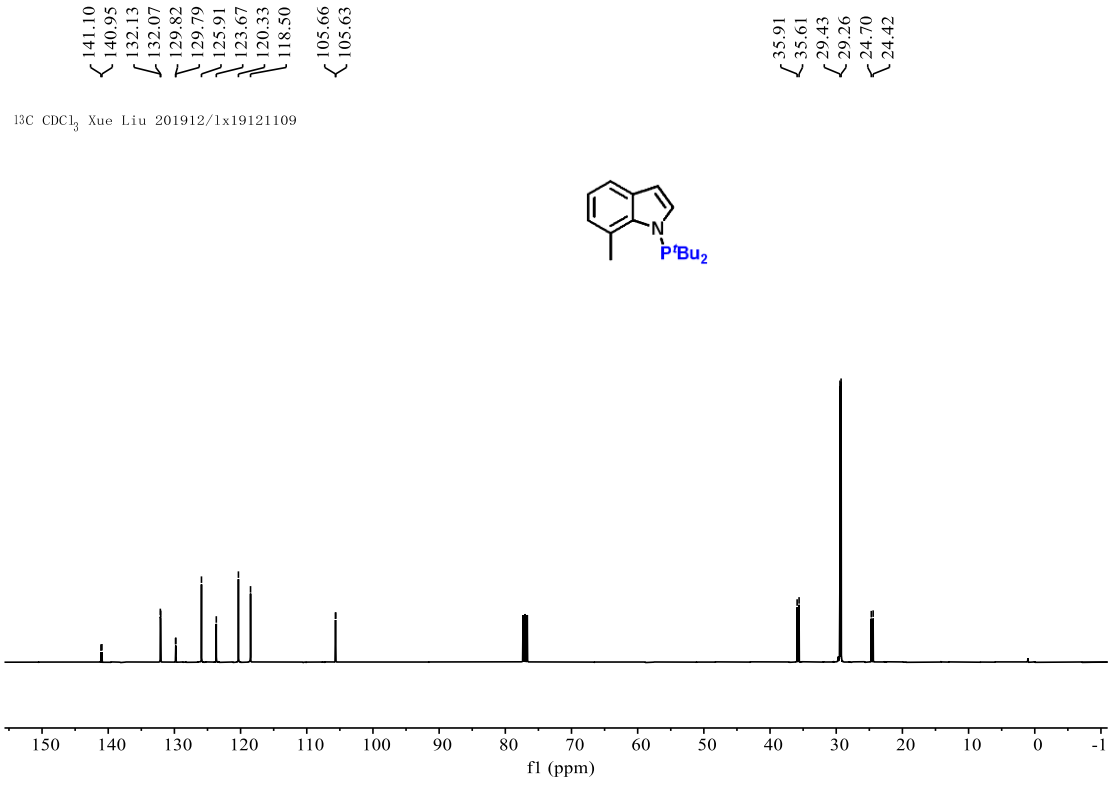


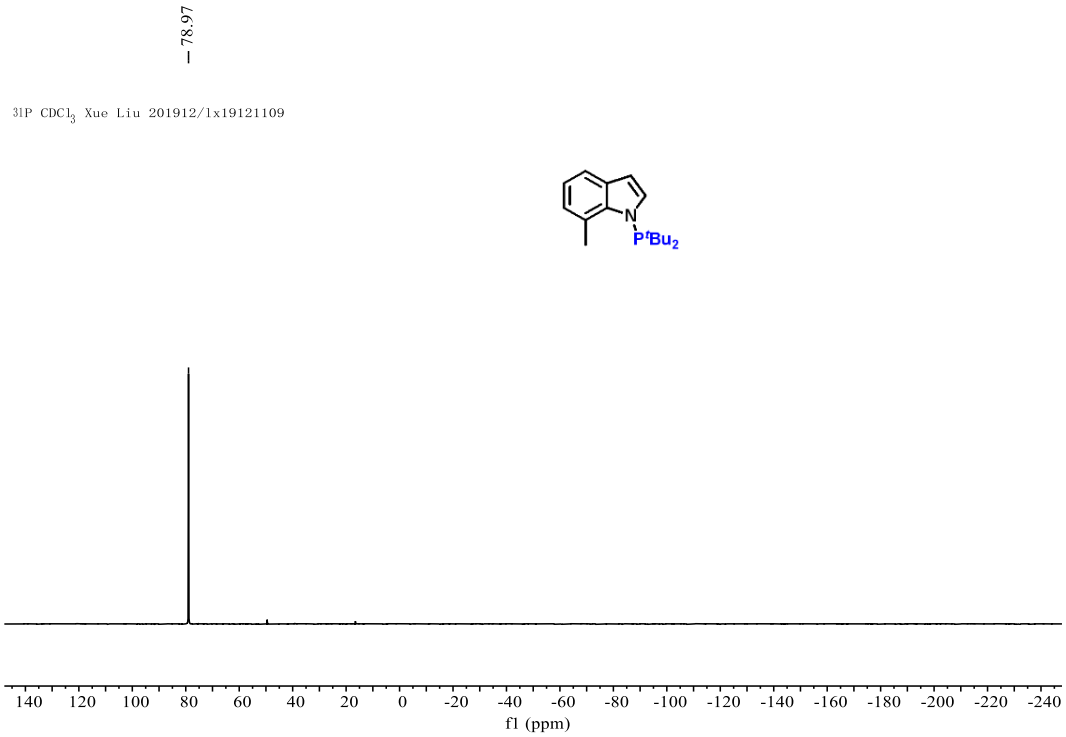

168.16
143.11
142.89
133.96
133.88
132.44
132.41
123.61
123.59
121.22
119.76
115.14
114.94
105.52
105.50
77.32
77.00
76.68
51.76
35.18
34.92
29.04
28.87
13C CDCl3 Xue Liu 202104/HJC-lx-74-4
O
O
N
PtBu2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


72.71
31P CDCl3 Xue Liu 202104/HJC-lx-74-4
O
O
N
PtBu2
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

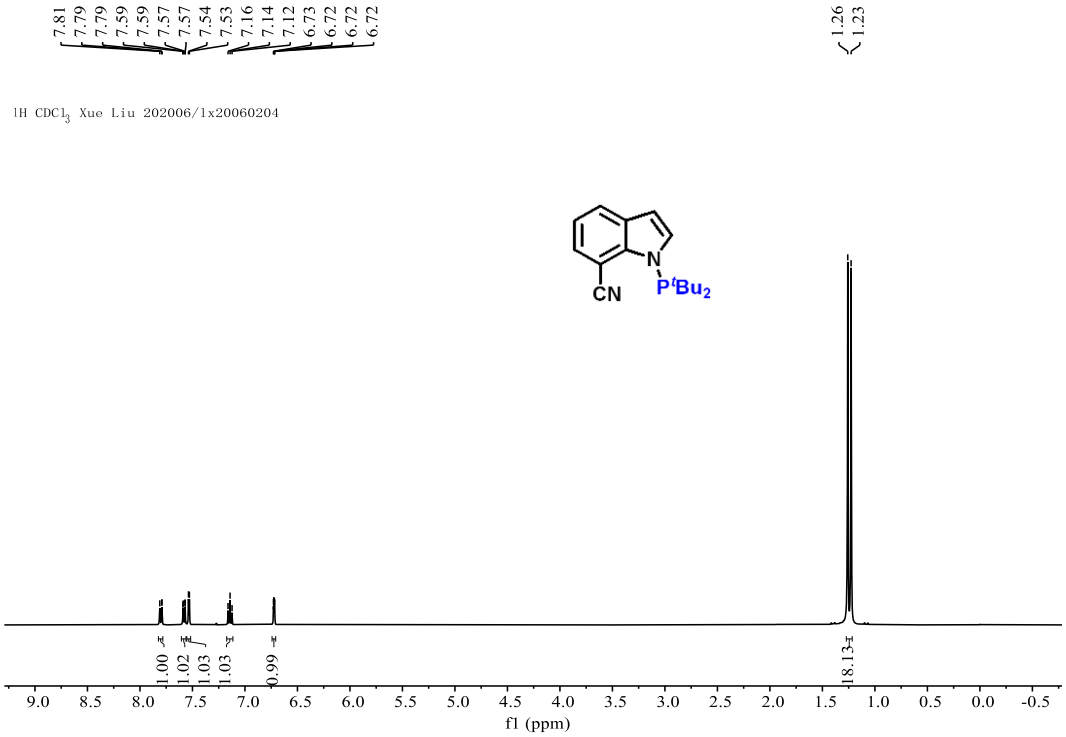
1-(Di-tert-butylphosphanyl)-7-methyl-1H-indole (26)





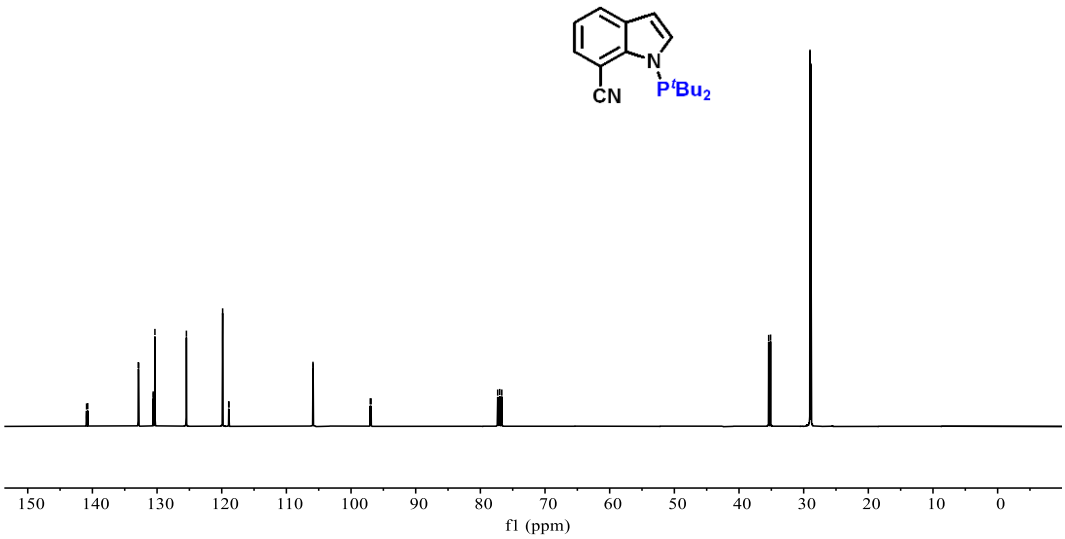


1-(Di-tert-butylphosphanyl)-1H-indole-7-carbonitrile (27)



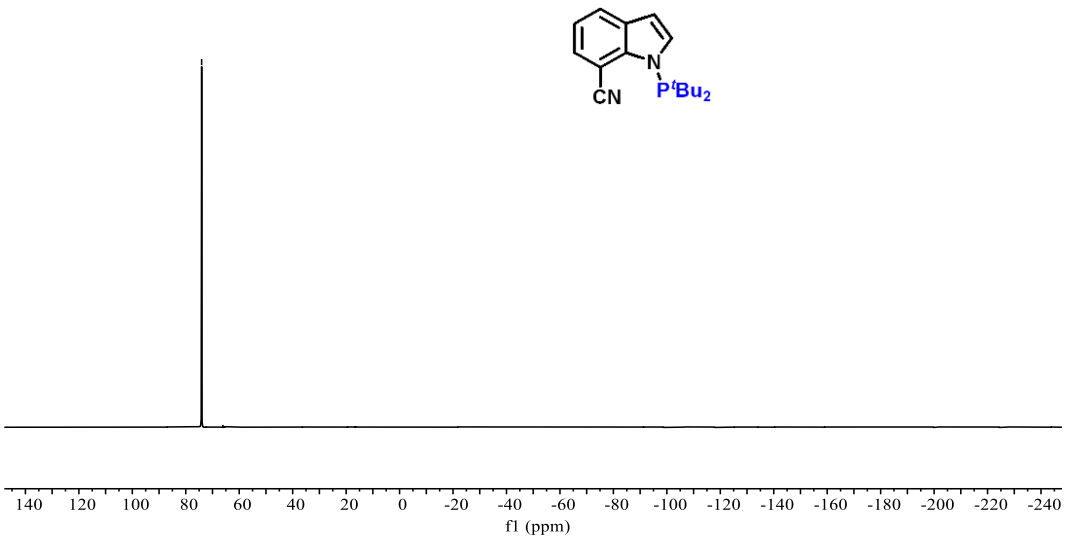
140.90
140.72
132.90
132.84
130.60
130.58
130.33
125.46
119.86
118.92
118.88
105.89
105.86
97.03
96.90
77.32
77.00
76.68
35.41
35.12
29.02
28.85

^{13}C $CDCl_3$ Xue Liu 202006/1x20060204

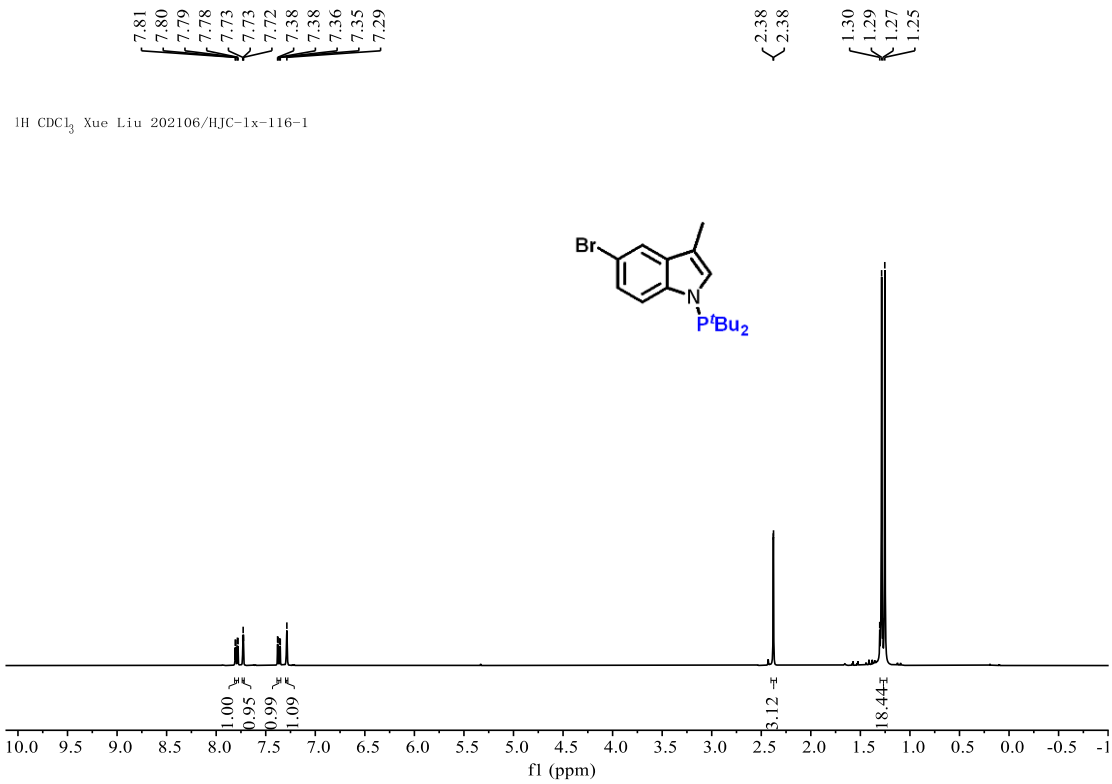


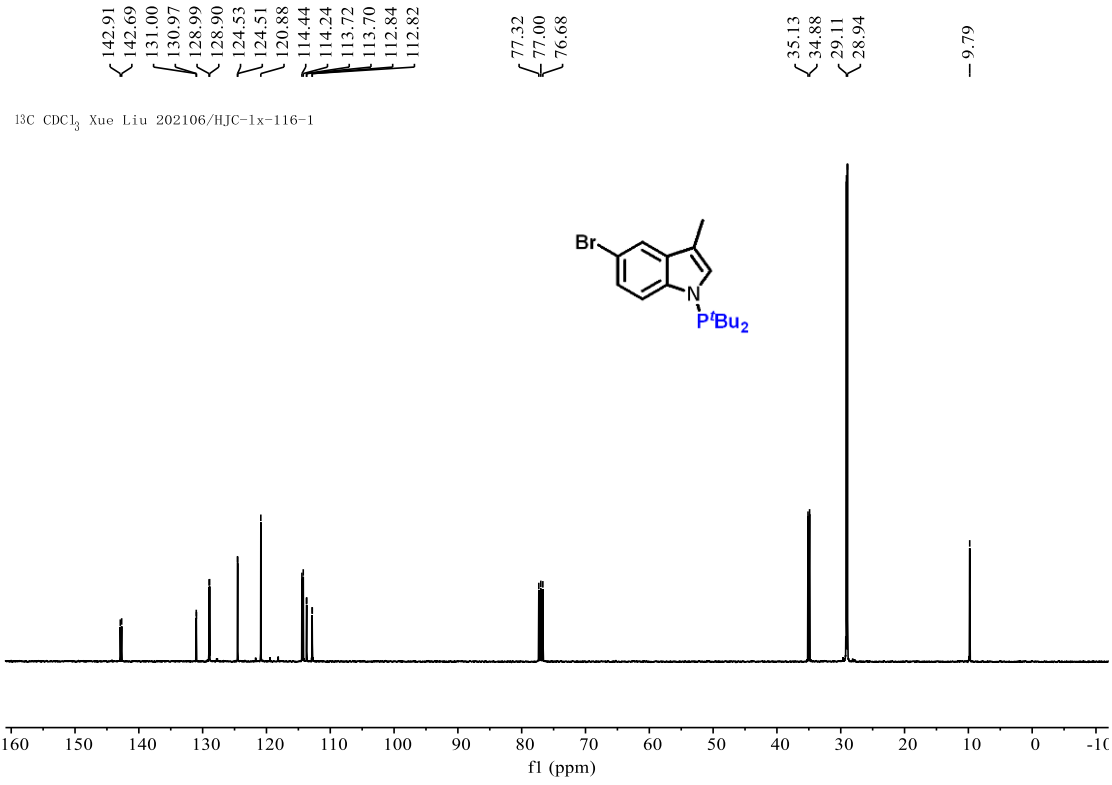
74.06

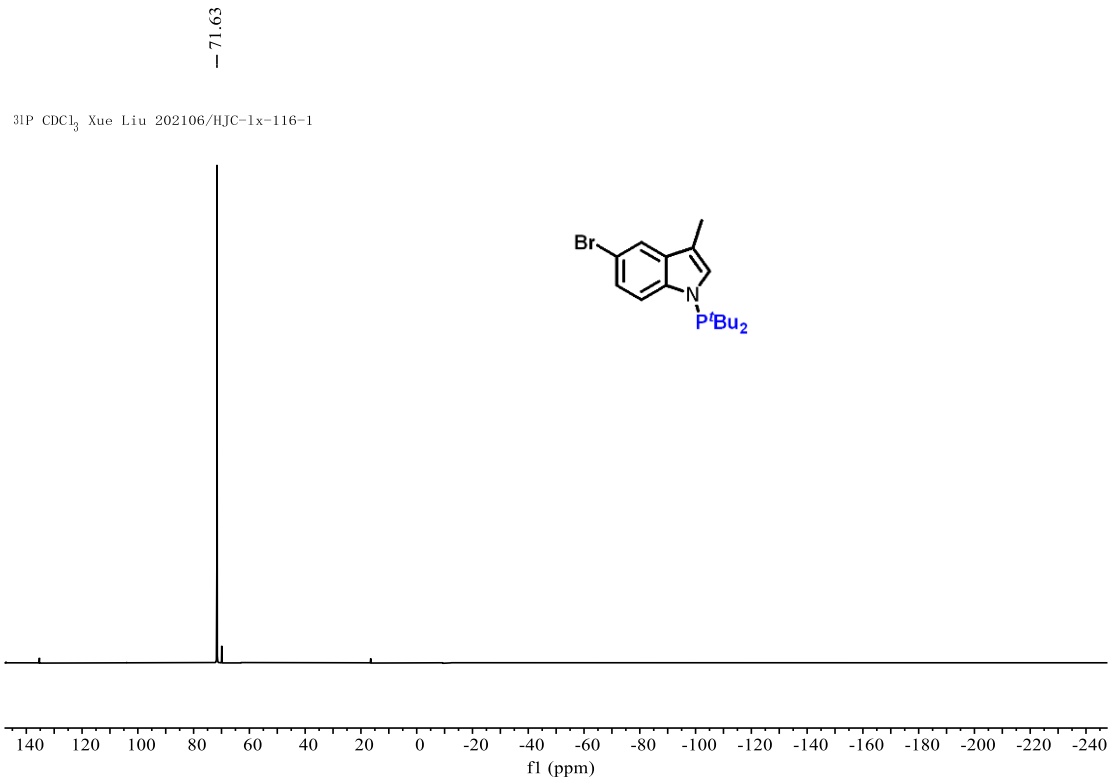
^{31}P $CDCl_3$ Xue Liu 202006/1x20060204



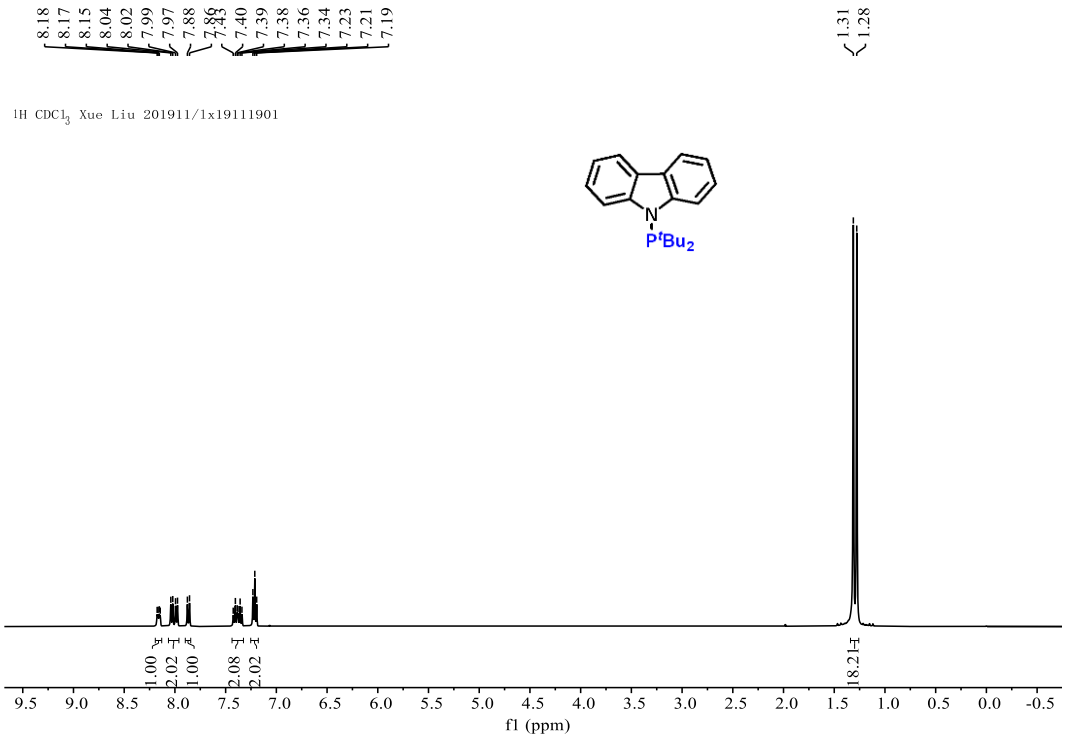
5-Bromo-3-methyl-1-(2,2,4,4-tetramethylpentan-3-yl)-1H-indole (28)







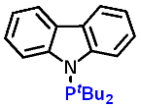
9-(Di-tert-butylphosphanyl)-9H-carbazole (29)

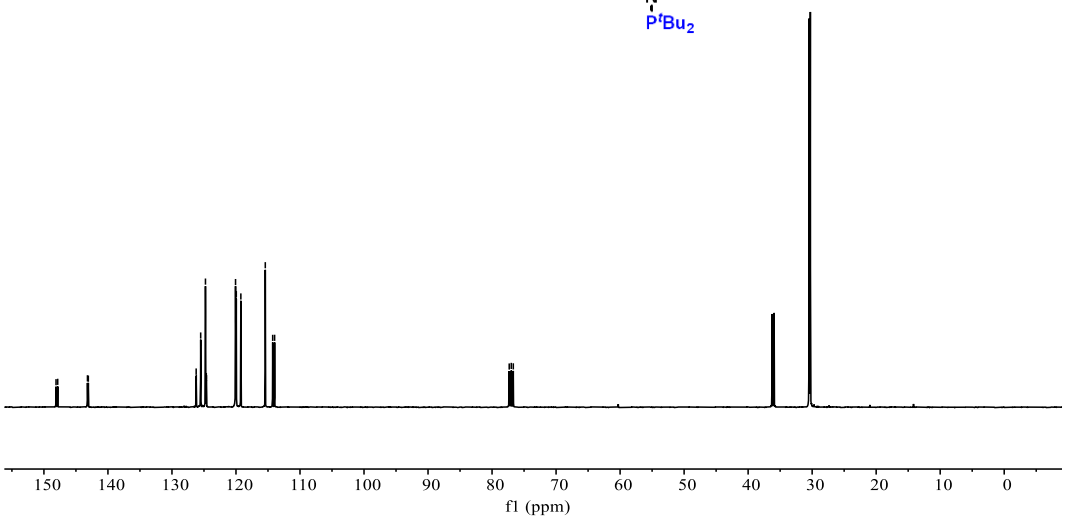


148.11
147.85
143.20
143.06
126.22
126.20
125.51
125.49
124.77
124.64
124.61
120.07
120.04
119.95
119.24
115.42
114.26
113.97

77.32
77.00
76.68

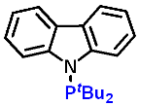
^{13}C $CDCl_3$ Xue Liu 201911/1x19111901

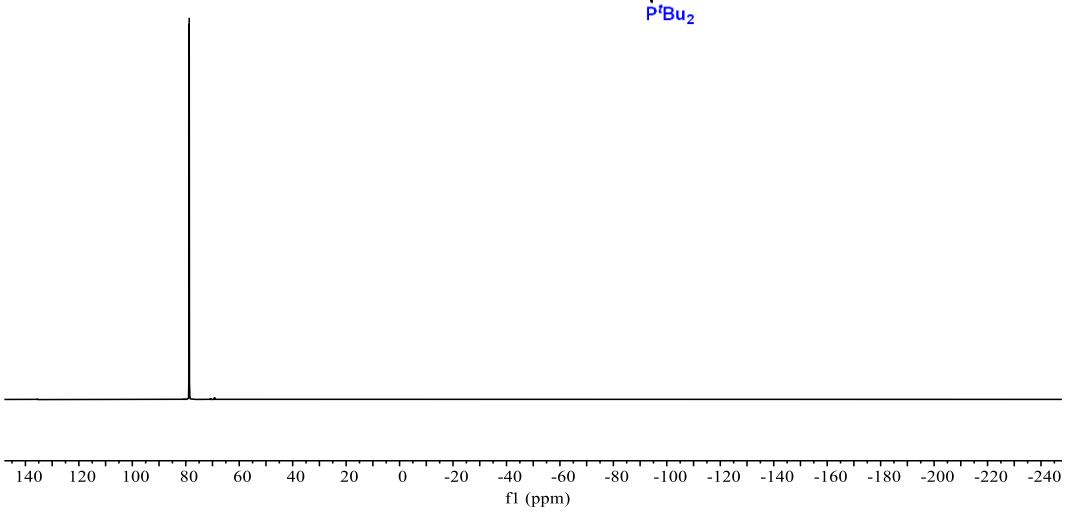




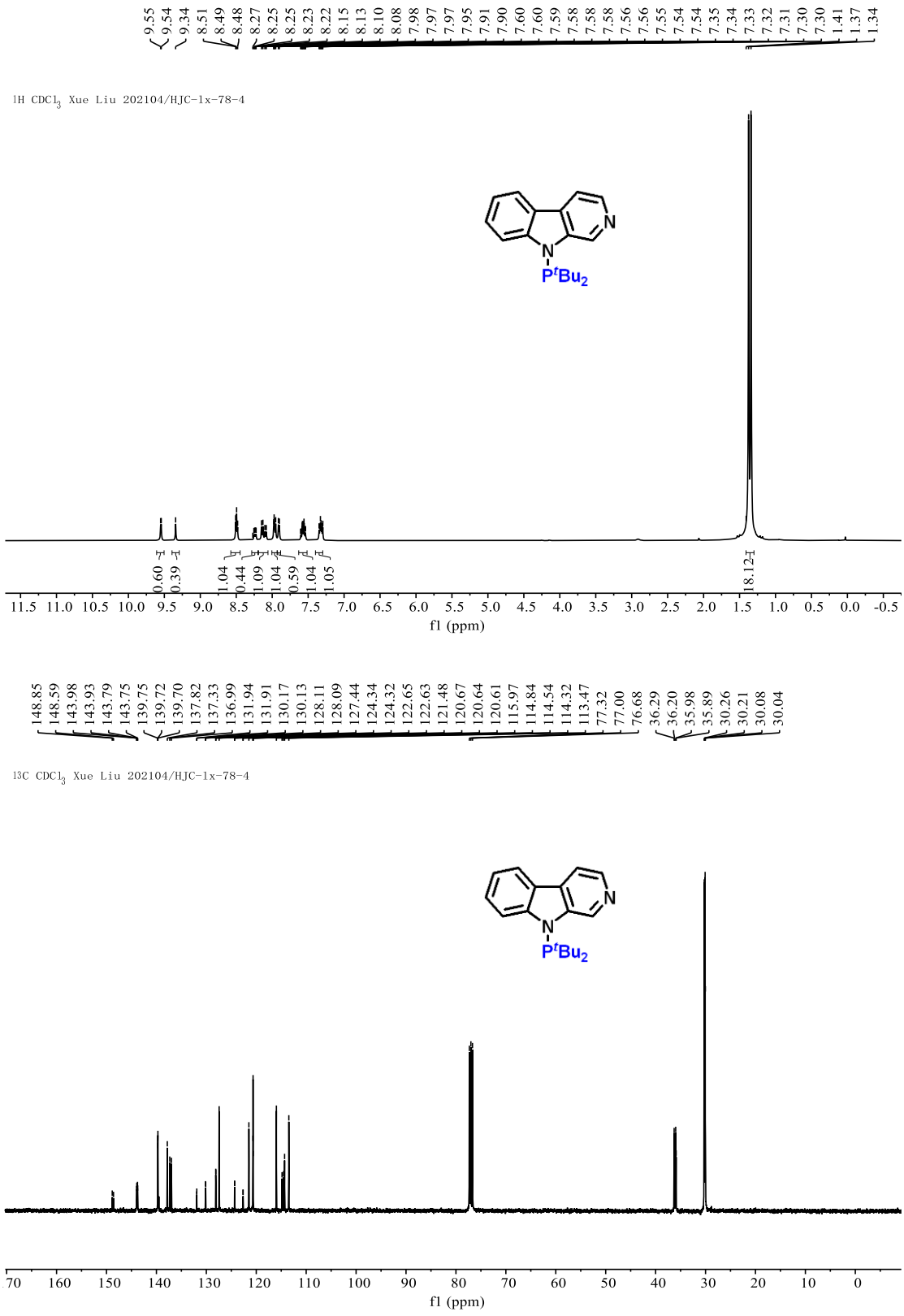
78.71

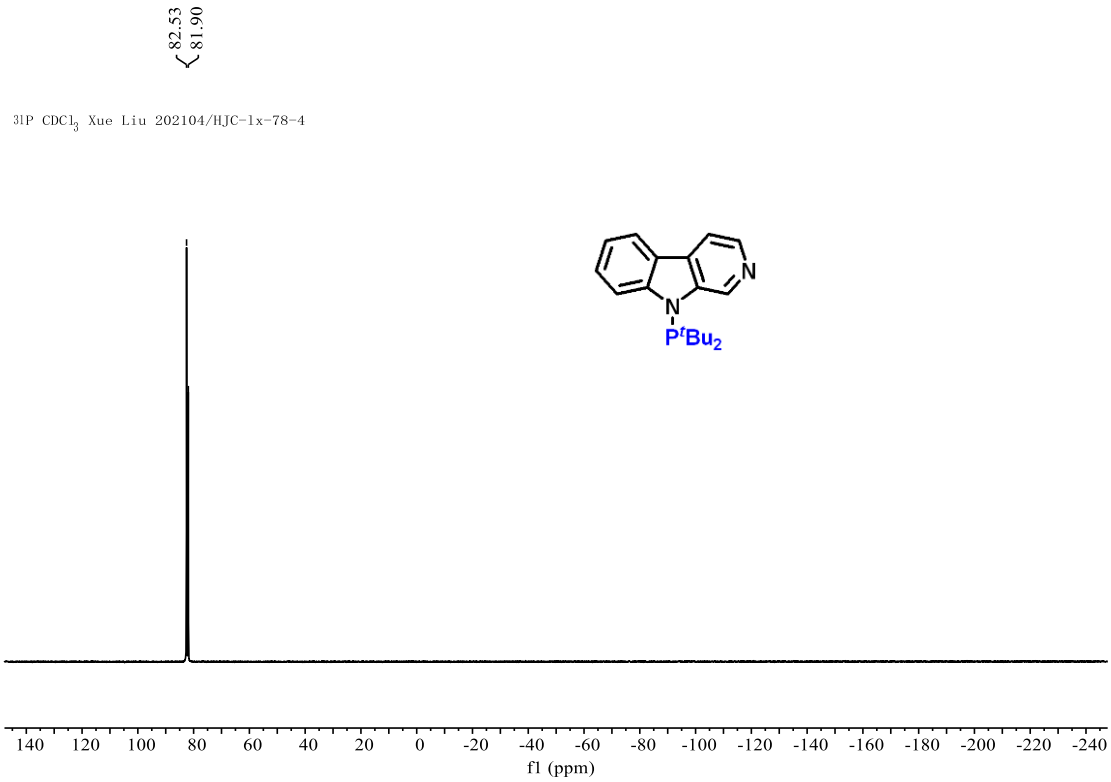
^{31}P $CDCl_3$ Xue Liu 201911/1x19111901



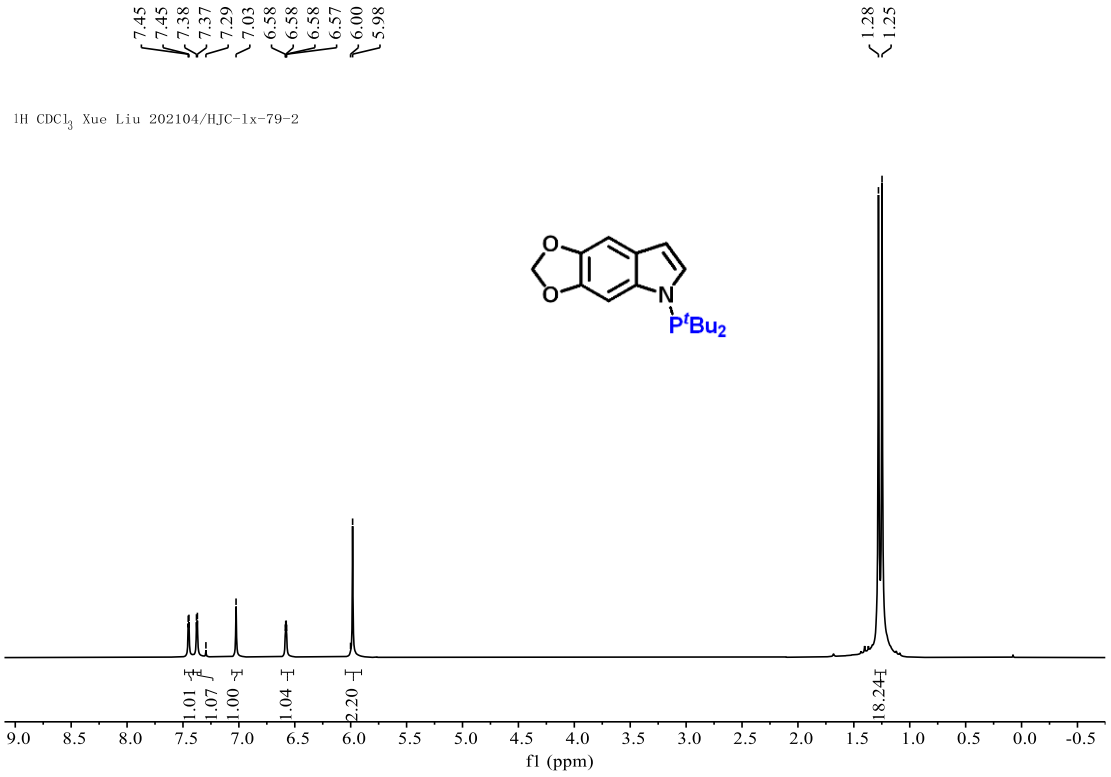


9-(Di-tert-butylphosphaneyl)-9H-pyrido[3,4-b]indole (30)



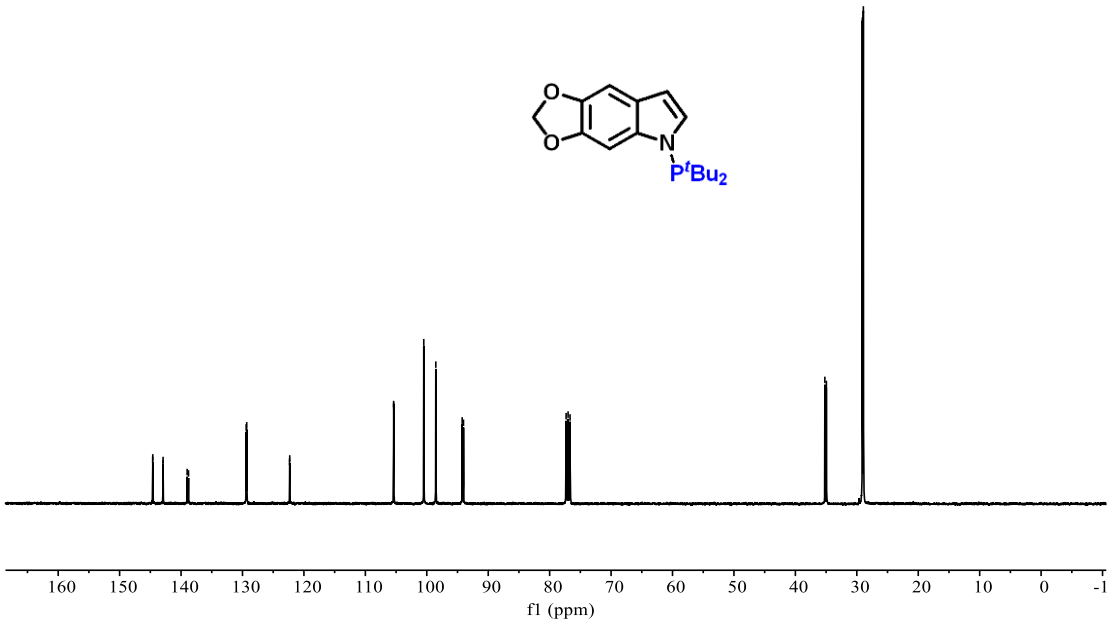


5-(Di-tert-butylphosphaneyl)-5H-[1,3]dioxolo[4,5-f]indole (31)



144.62
144.60
142.94
142.93
139.01
138.78
129.40
129.31
122.34
122.31
105.40
105.38
100.49
98.53
94.24
94.02
77.32
77.00
76.68
35.20
34.95
29.10
28.94

^{13}C $CDCl_3$ Xue Liu 202104/HJC-lx-79-2

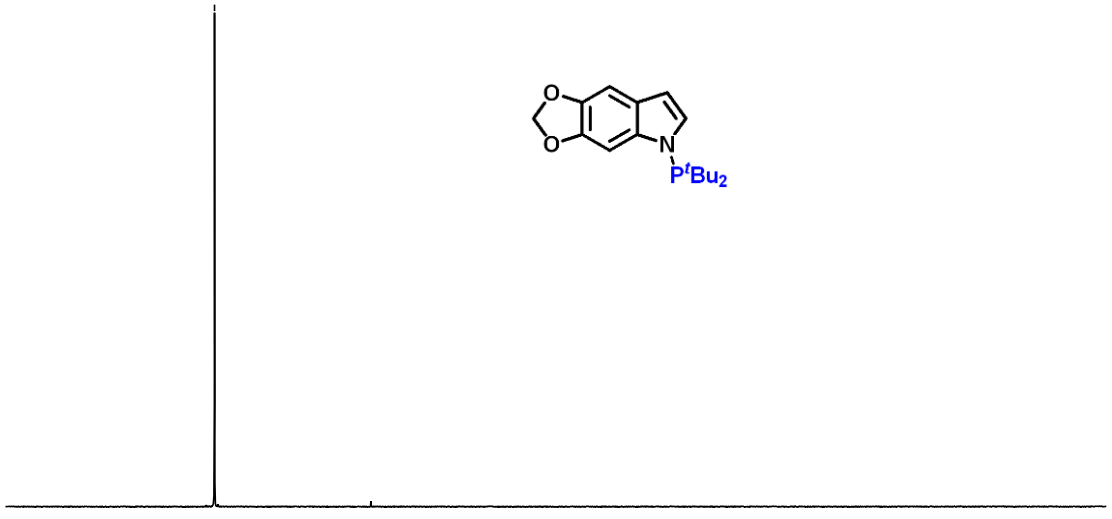


160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

72.70

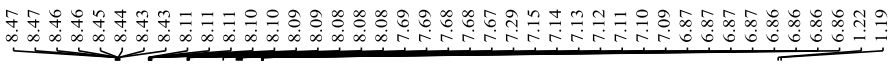
^{31}P $CDCl_3$ Xue Liu 202104/HJC-lx-79-2



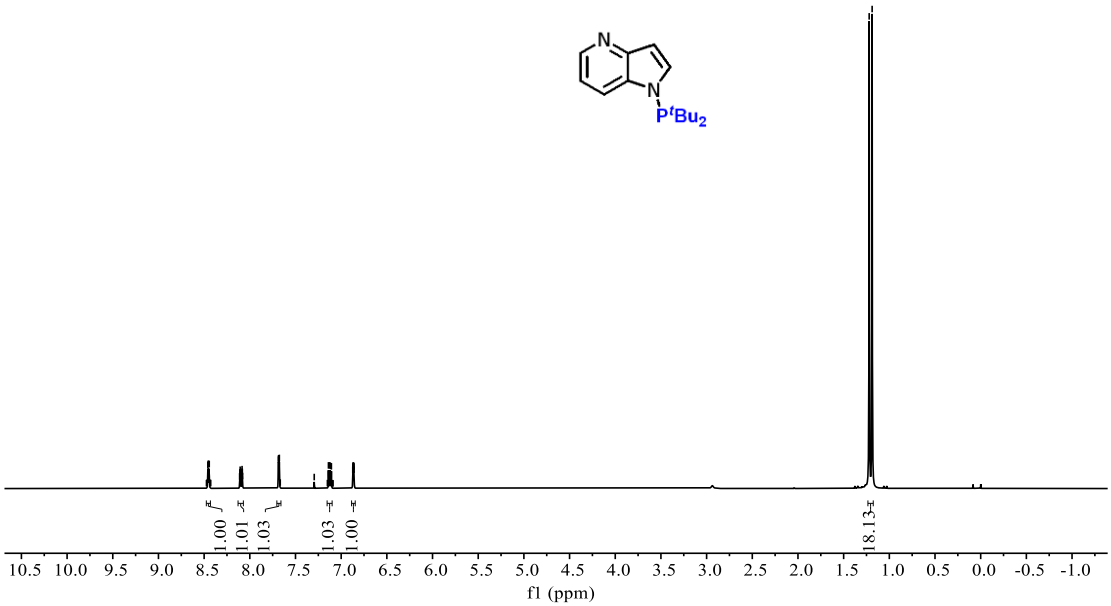
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240

f1 (ppm)

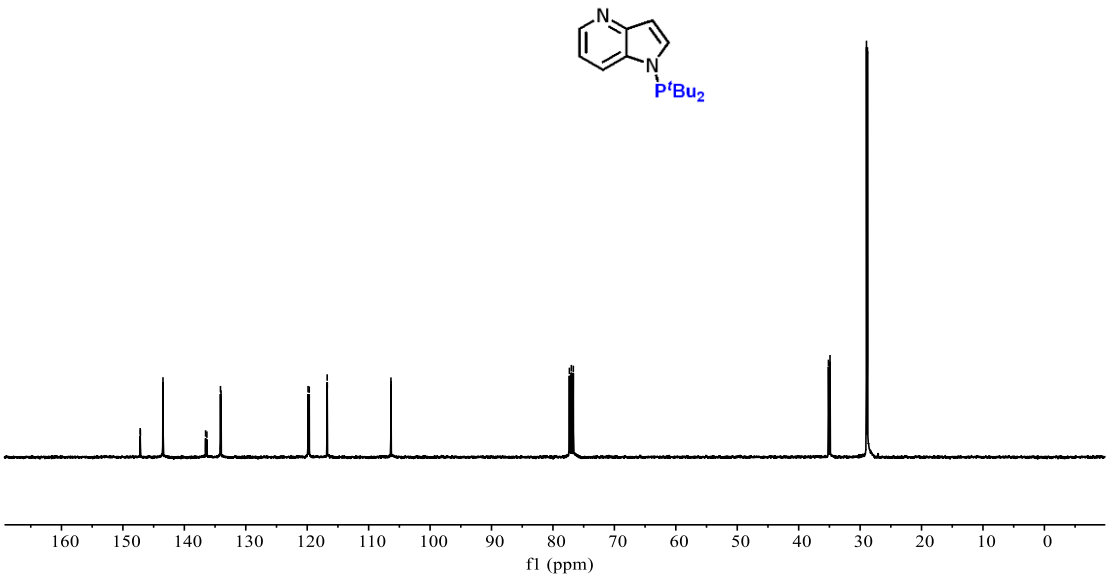
1-(Di-tert-butylphosphaneyl)-1H-pyrrolo[3,2-b]pyridine (32)

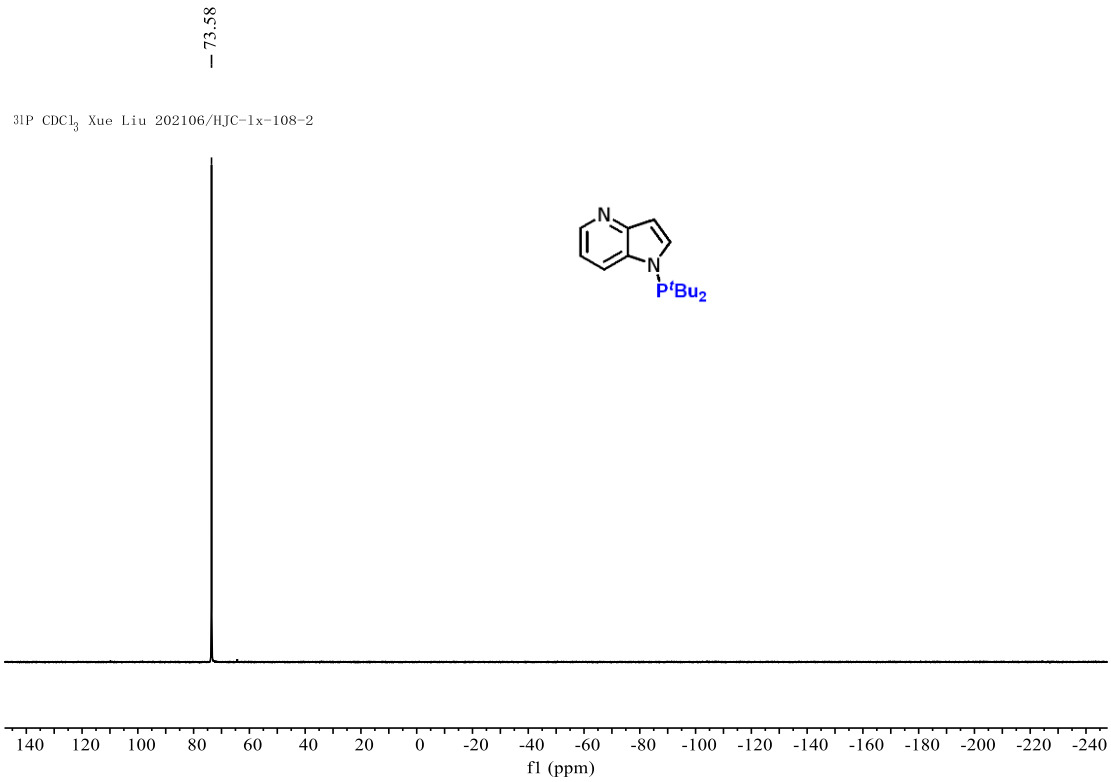


^{1}H $CDCl_3$ Xue Liu 202106/HJC-1x-108-2

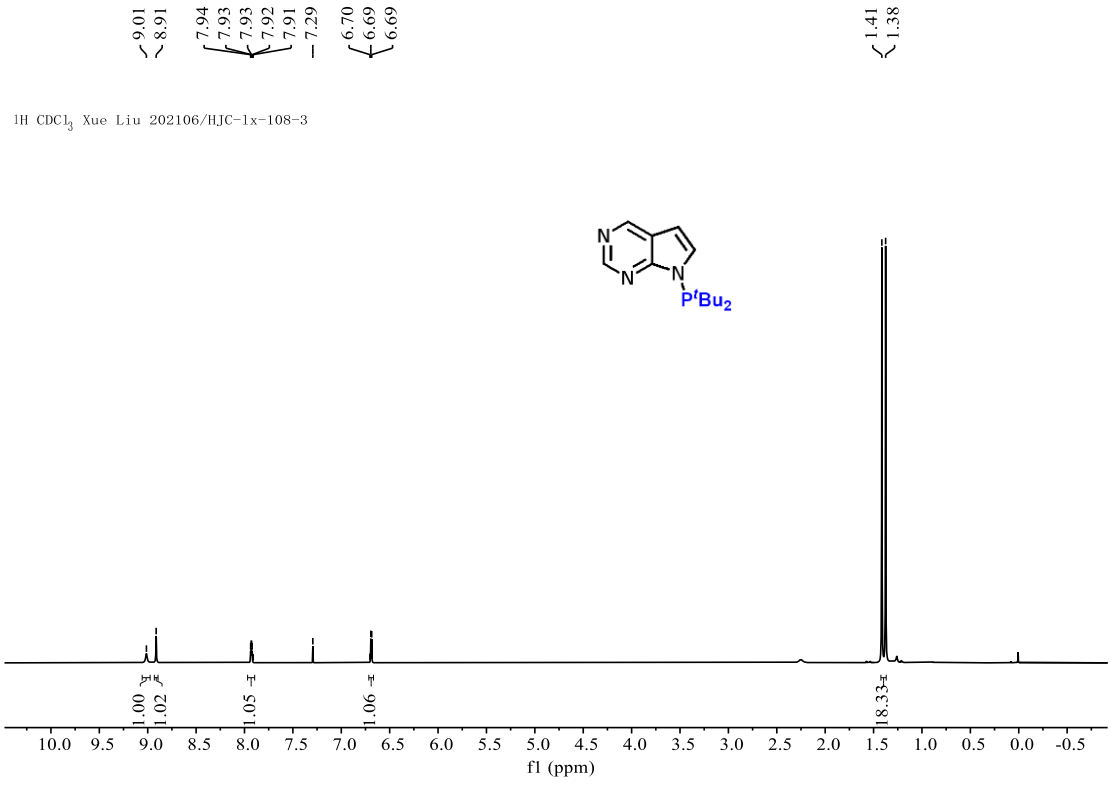


^{13}C $CDCl_3$ Xue Liu 202106/HJC-1x-108-2



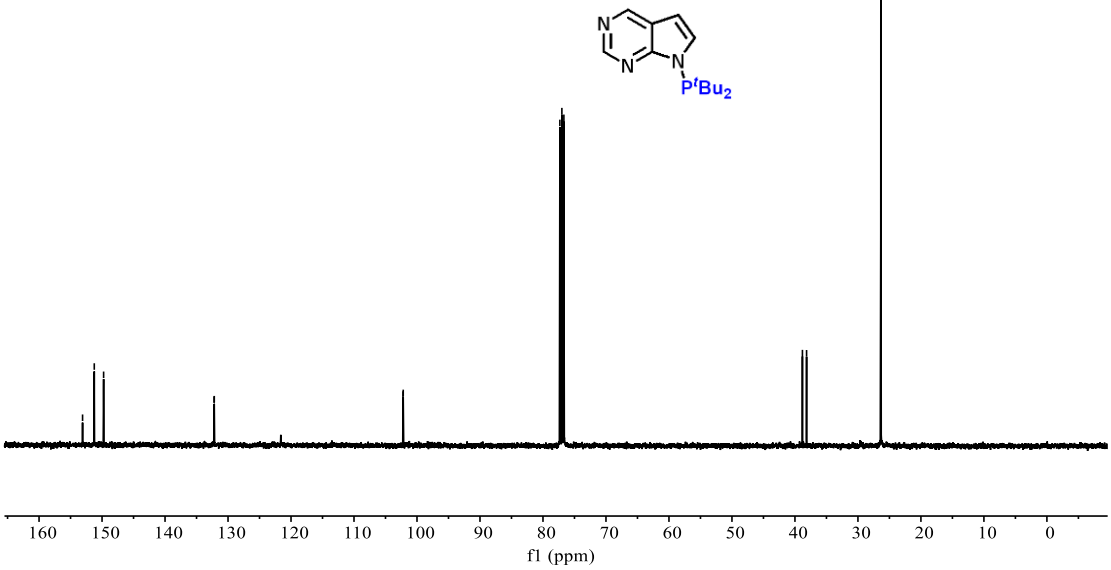


7-(Di-tert-butylphosphaneyl)-7H-pyrrolo[2,3-d]pyrimidine (33)



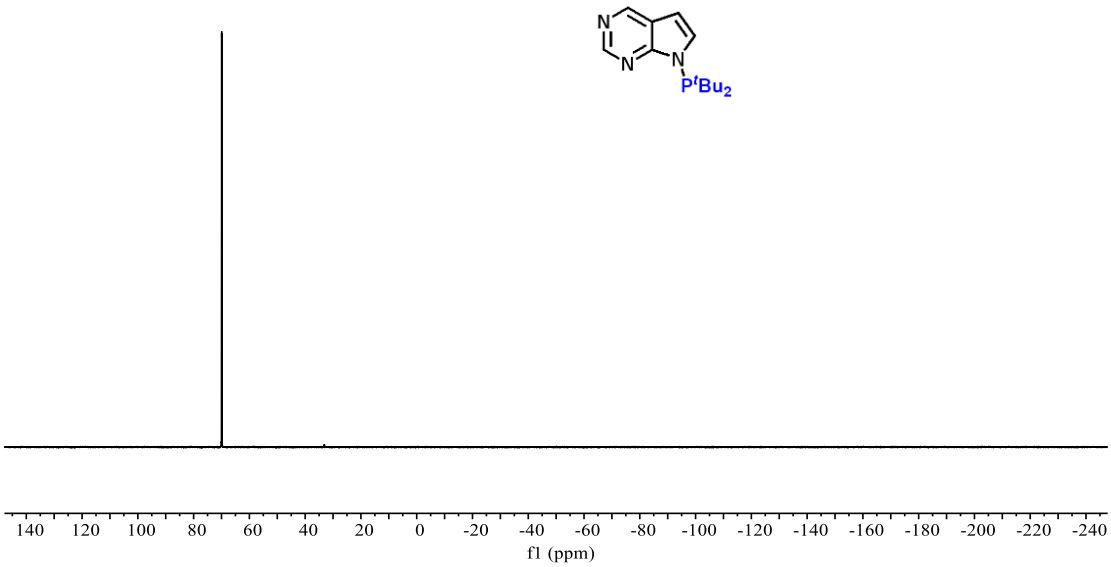
153.09
151.23
149.75
132.21
132.18
102.22
102.19
77.32
77.00
76.68
38.81
38.15
26.37

^{13}C $CDCl_3$ Xue Liu 202106/HJC-1x-108-3

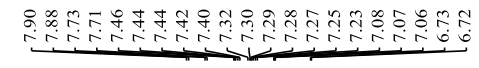


69.93

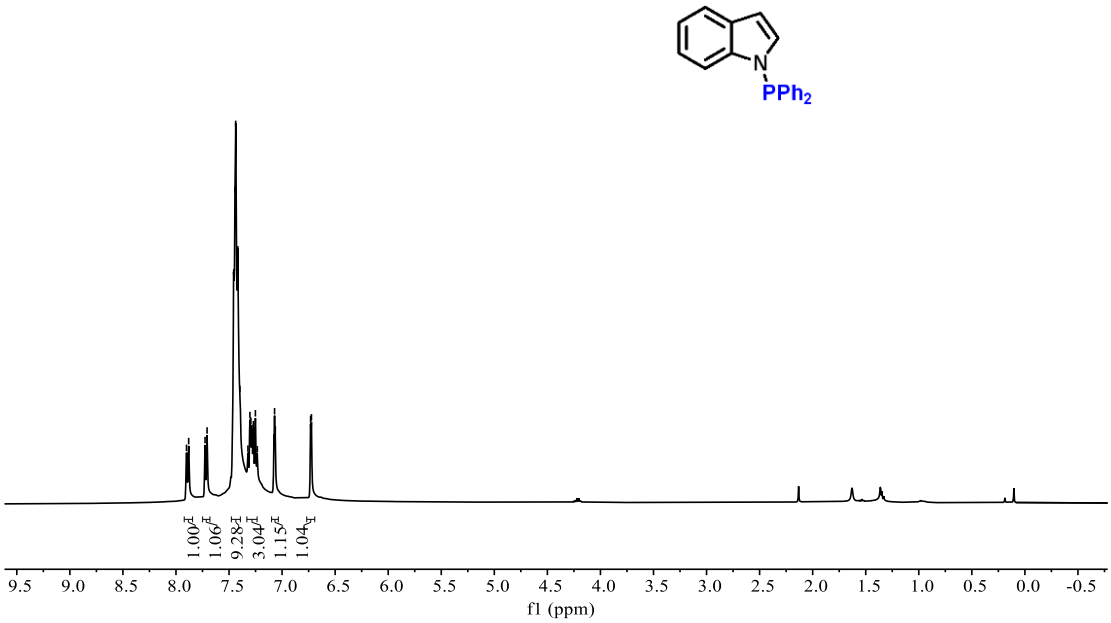
^{31}P $CDCl_3$ Xue Liu 202106/HJC-1x-108-3

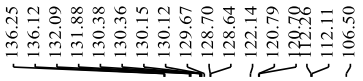


1-(Diphenylphosphaneyl)-1H-indole (34)

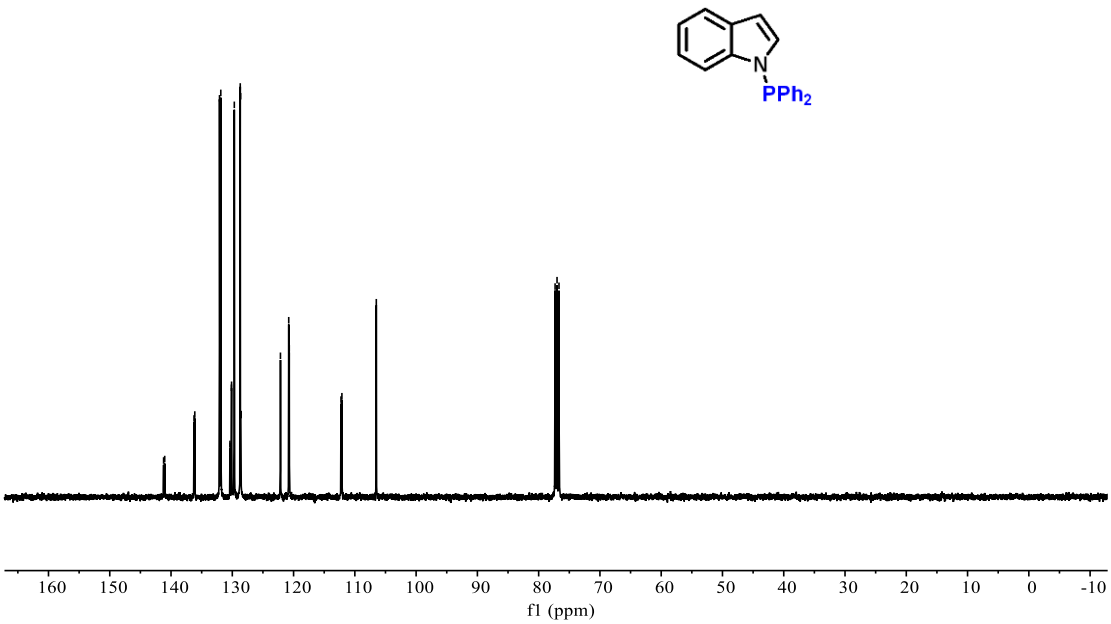


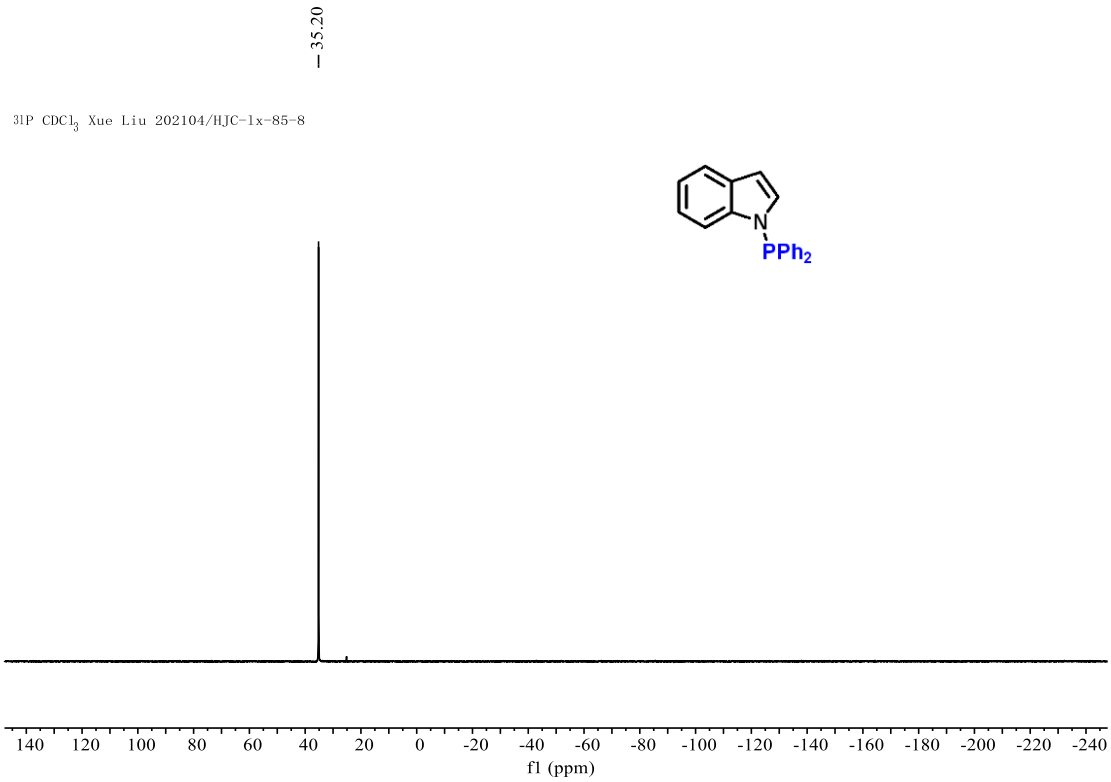
^{1}H $CDCl_3$ Xue Liu 202104/HJC-1x-85-8



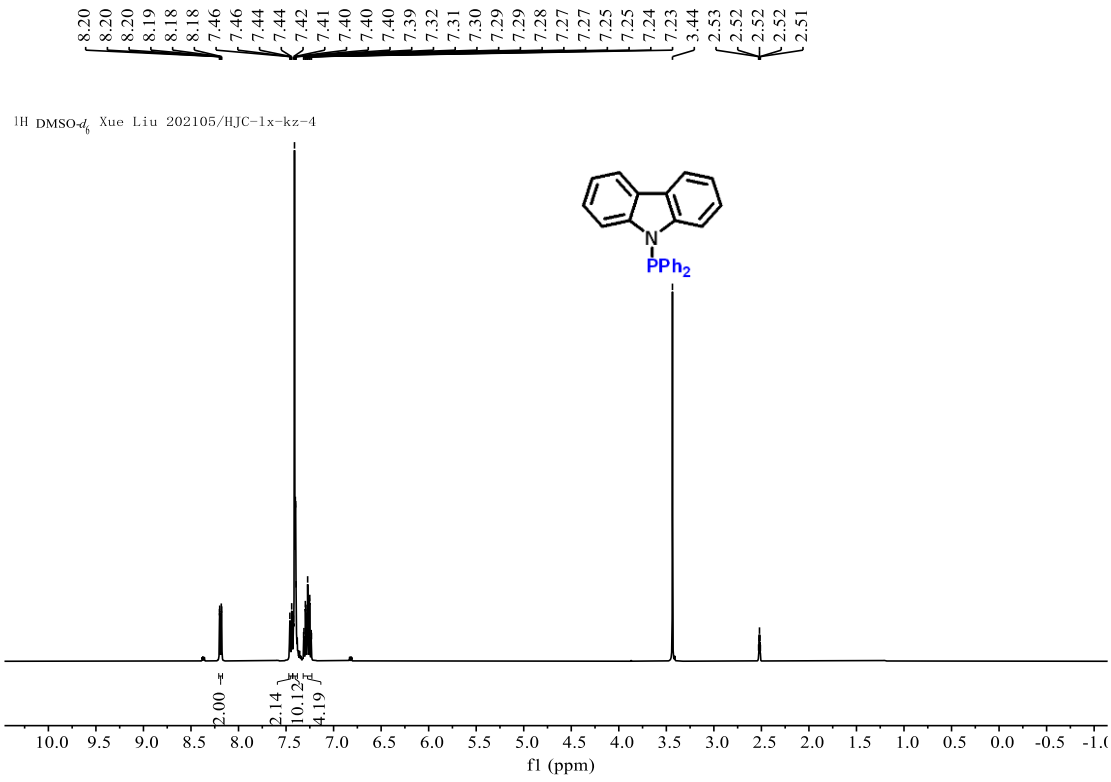


^{13}C $CDCl_3$ Xue Liu 202104/HJC-1x-85-8





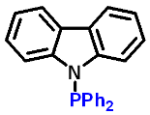
9-(Diphenylphosphaneyl)-9H-carbazole (35)

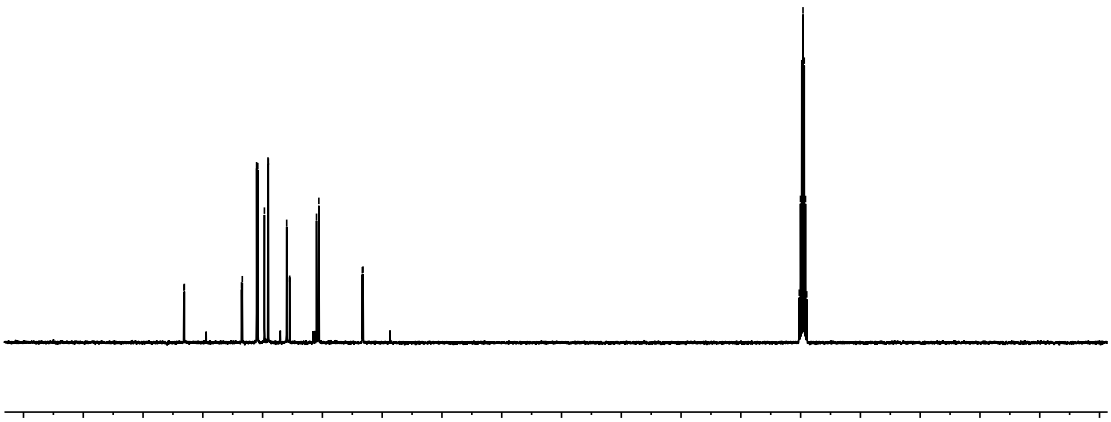


143.16
143.09
133.53
133.40
131.01
130.81
129.70
129.10
129.04
125.97
125.47
120.98
120.59
113.32
113.20

40.23
40.02
39.81
39.60
39.39
39.18
38.98

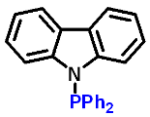
^{13}C DMSO-d_6 Xue Liu 202105/HJC-1x-kz-4



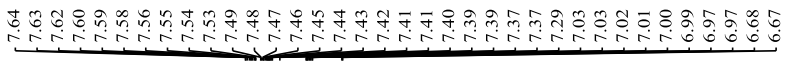


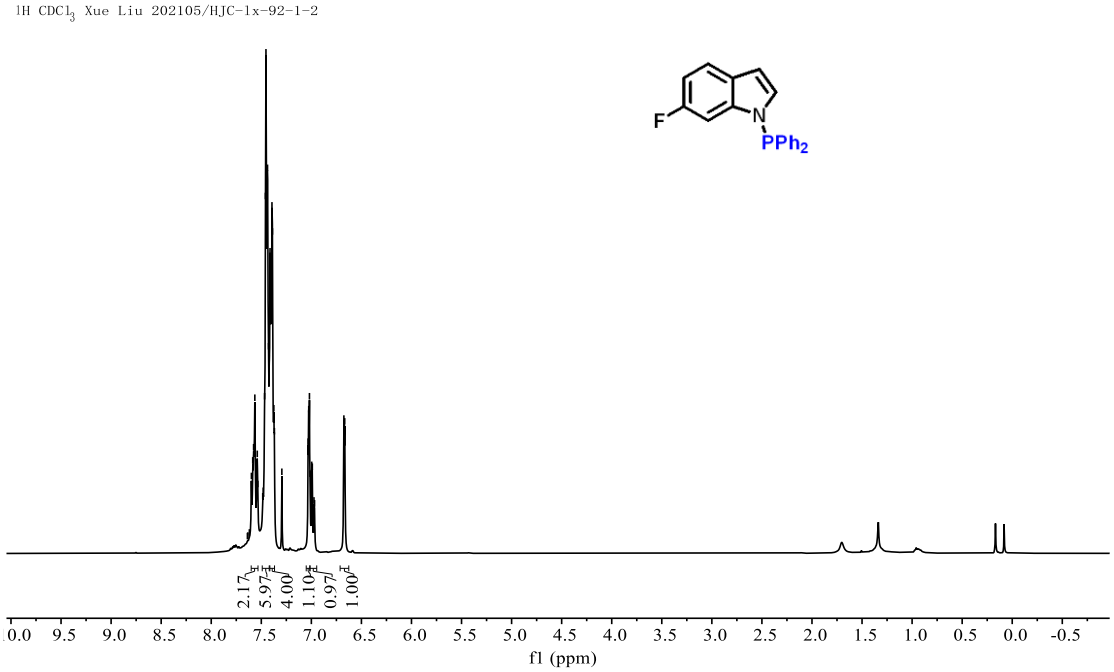
31.57

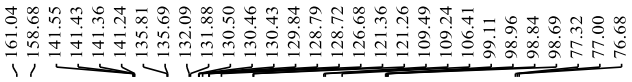
^{31}P DMSO-d_6 Xue Liu 202105/HJC-1x-kz-4

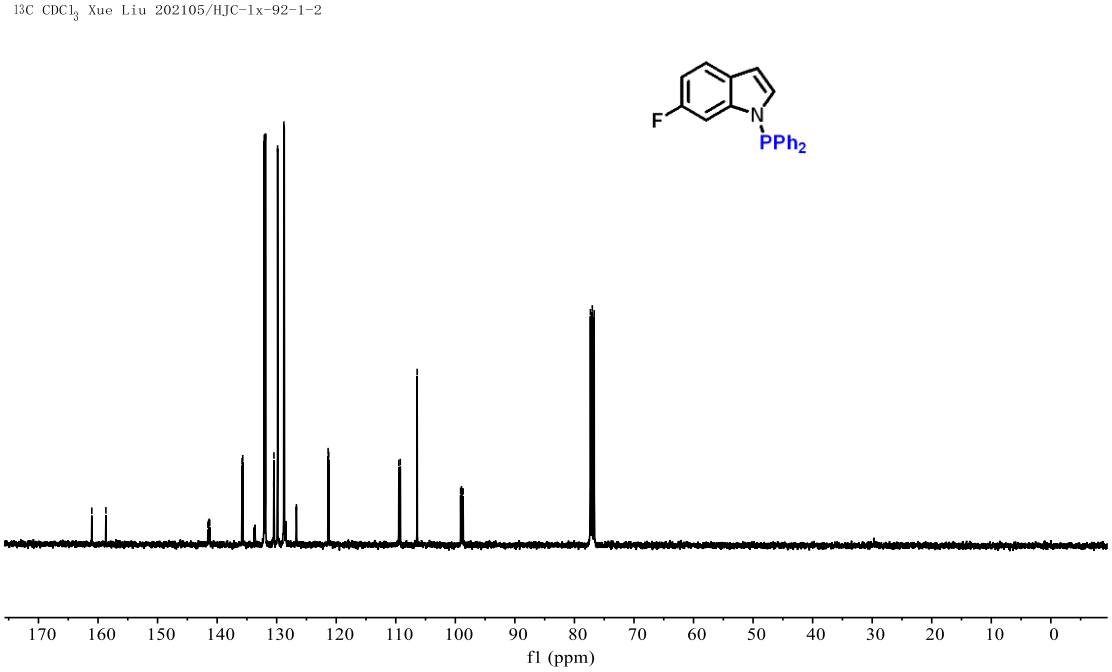


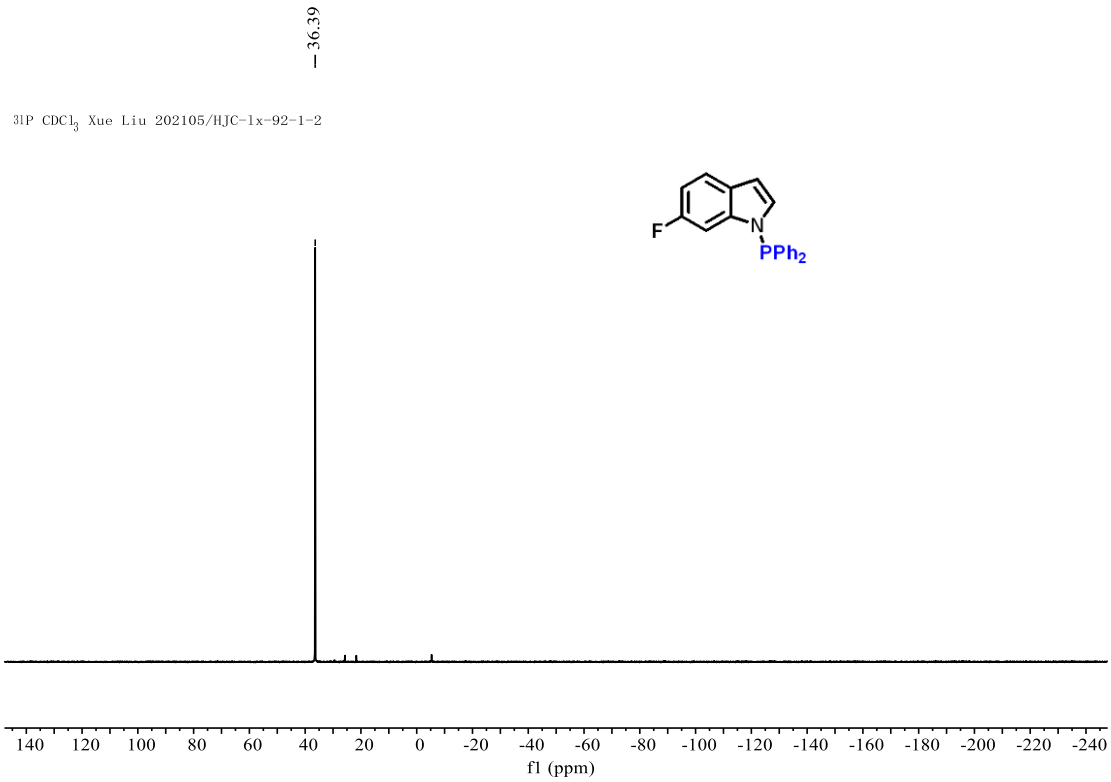
1-(Diphenylphosphaneyl)-6-fluoro-1H-indole (36)

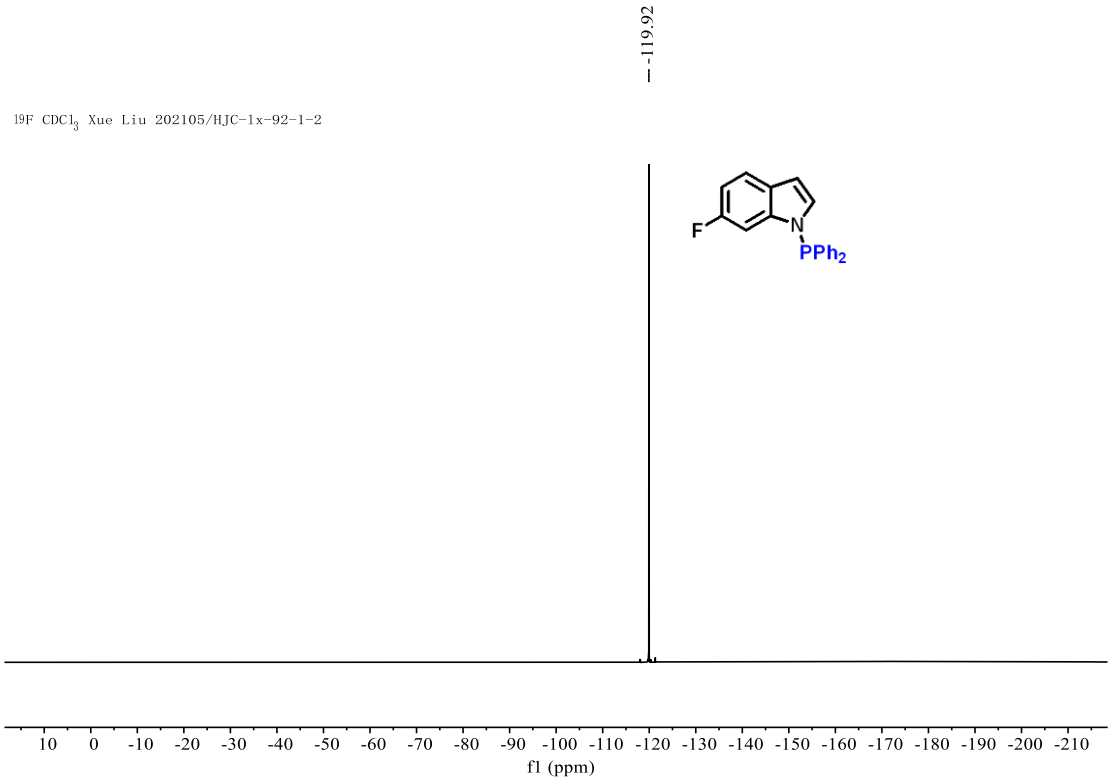




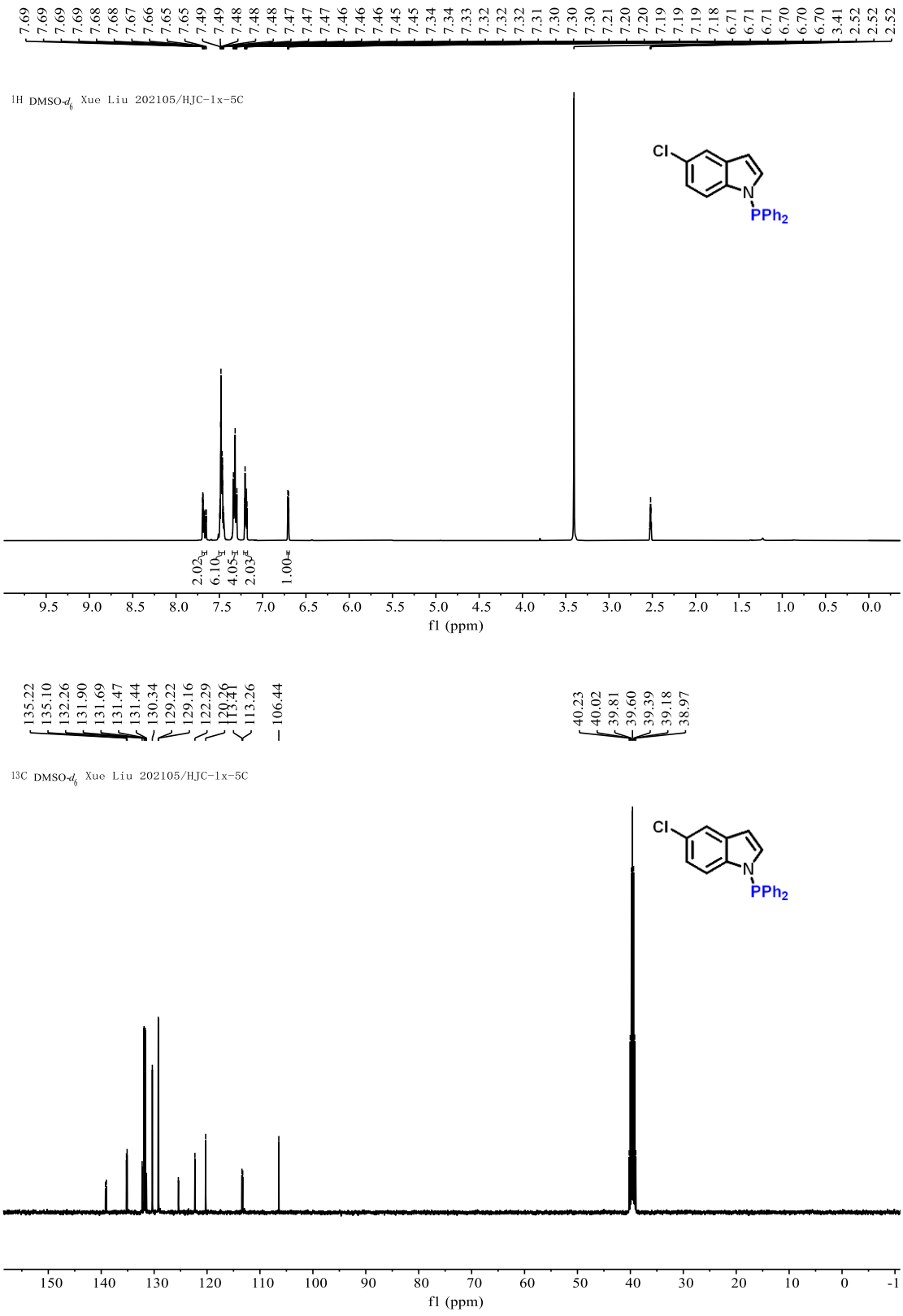


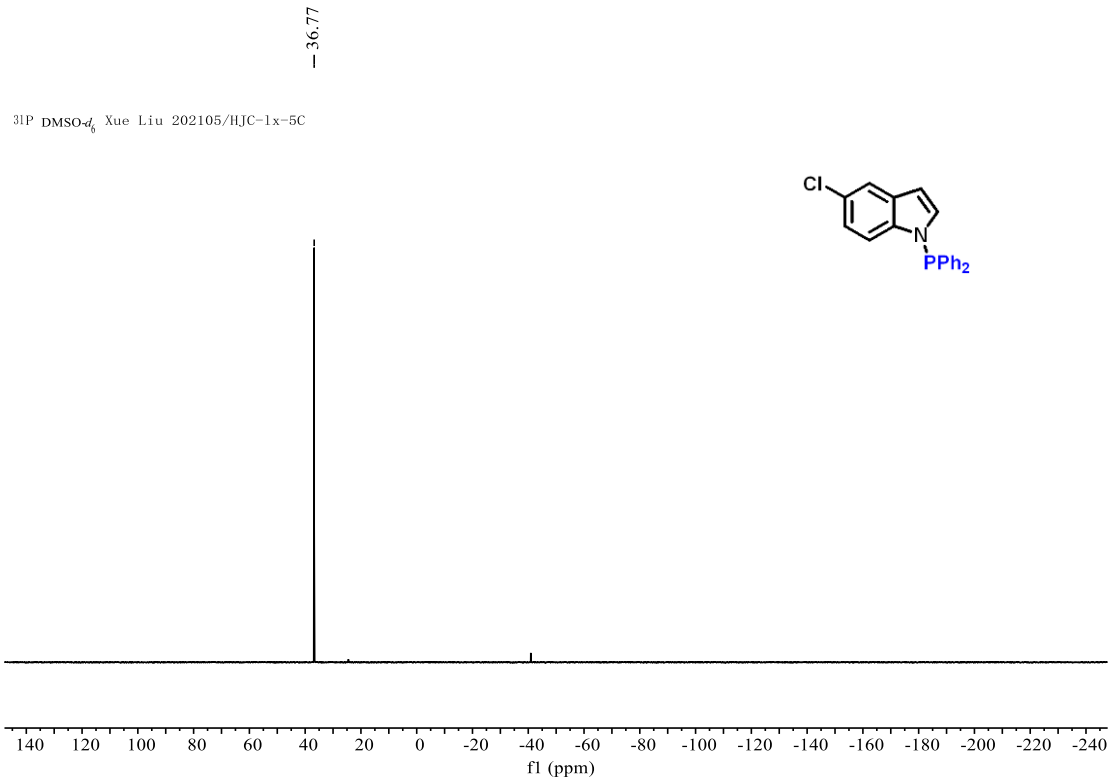



36.39
31P CDCl3 Xue Liu 202105/HJC-1x-92-1-2
F
N
PPh2
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

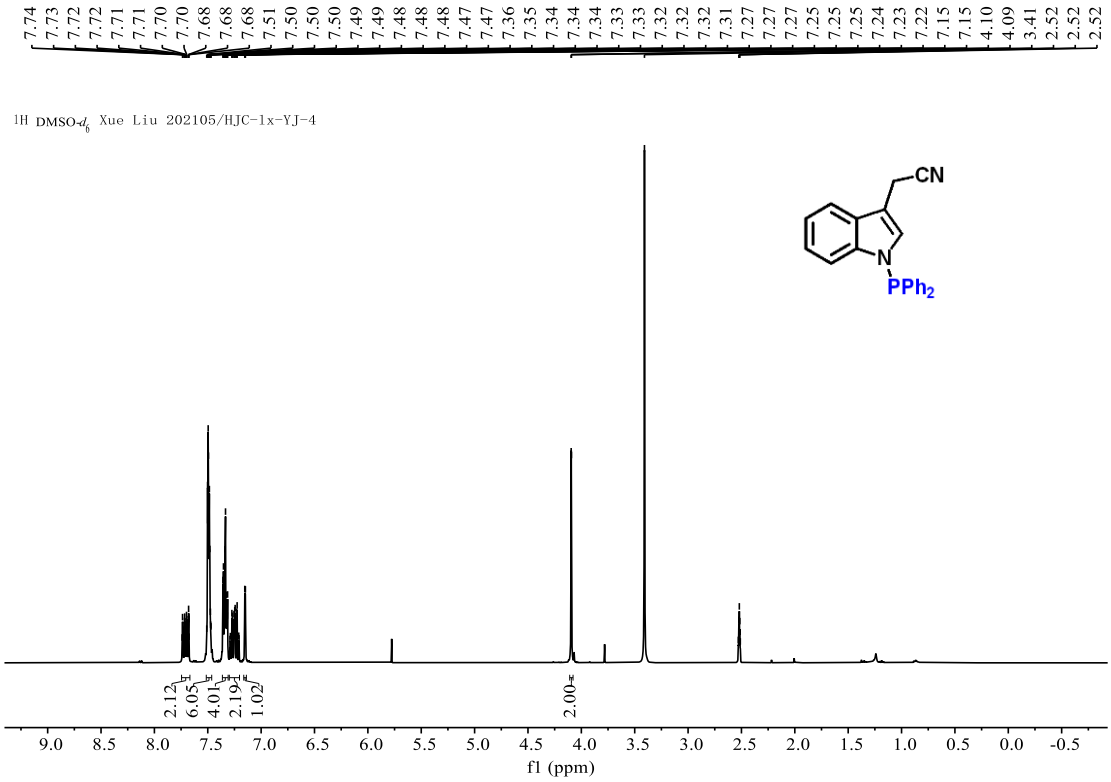

-119.92
19F CDCl3 Xue Liu 202105/HJC-1x-92-1-2
F
N
PPh2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

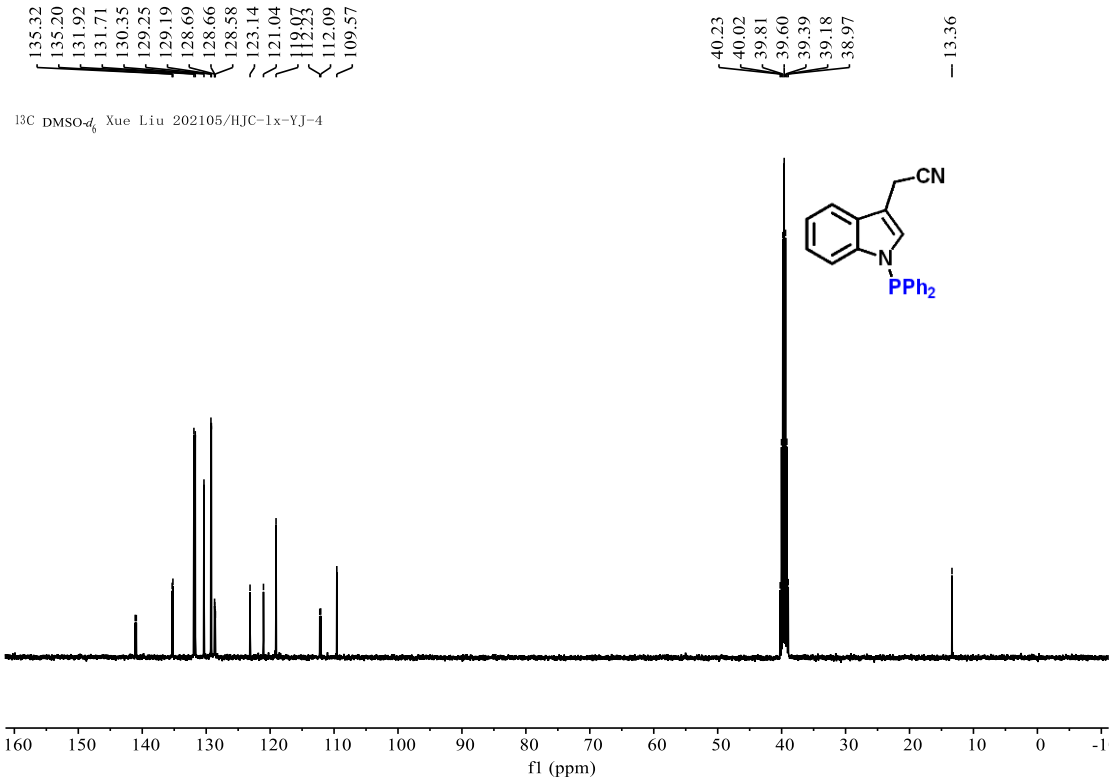
5-Chloro-1-(diphenylphosphaneyl)-1H-indole (37)

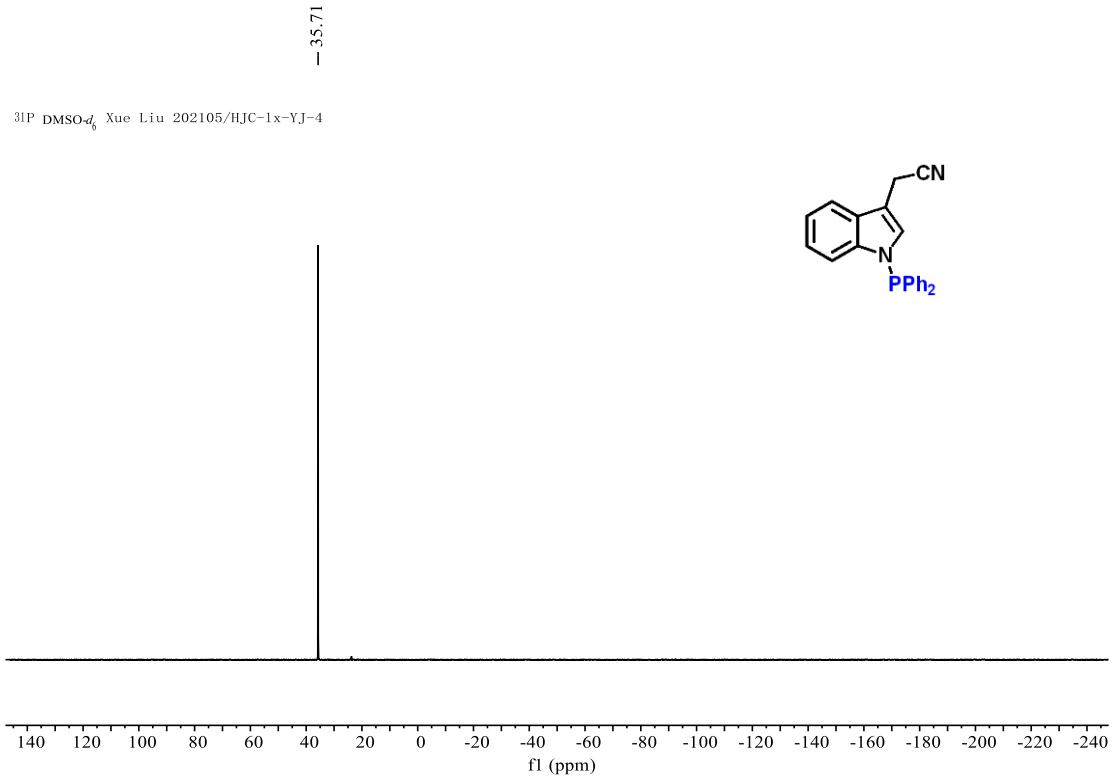




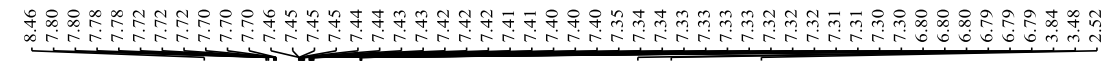
2-(1-(Diphenylphosphaneyl)-1H-indol-3-yl)acetonitrile (38)

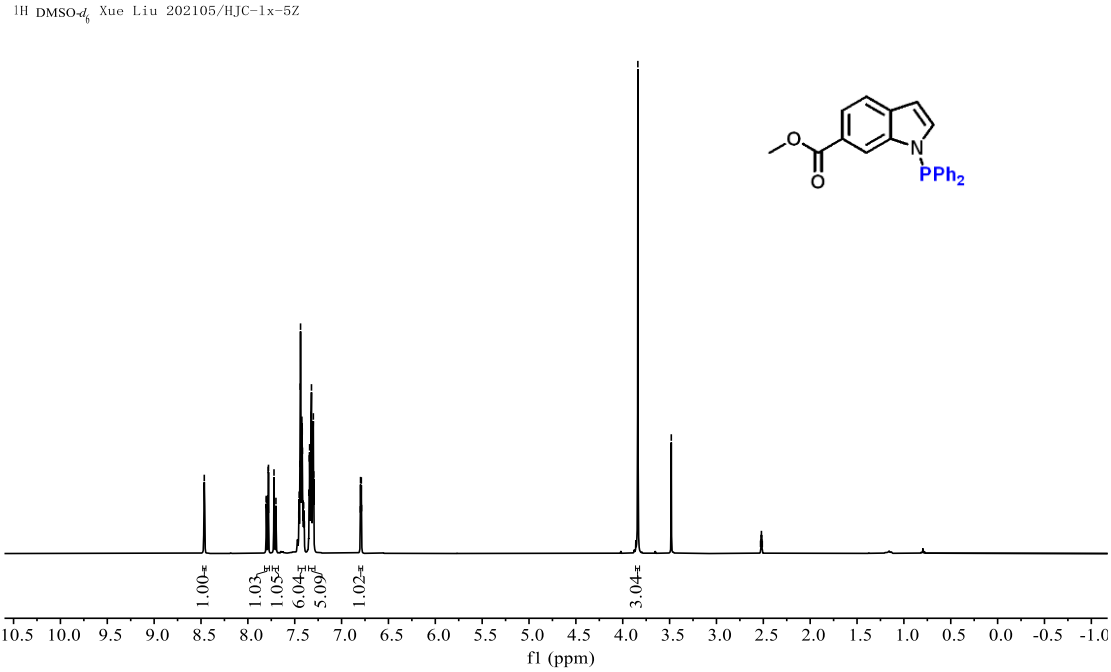


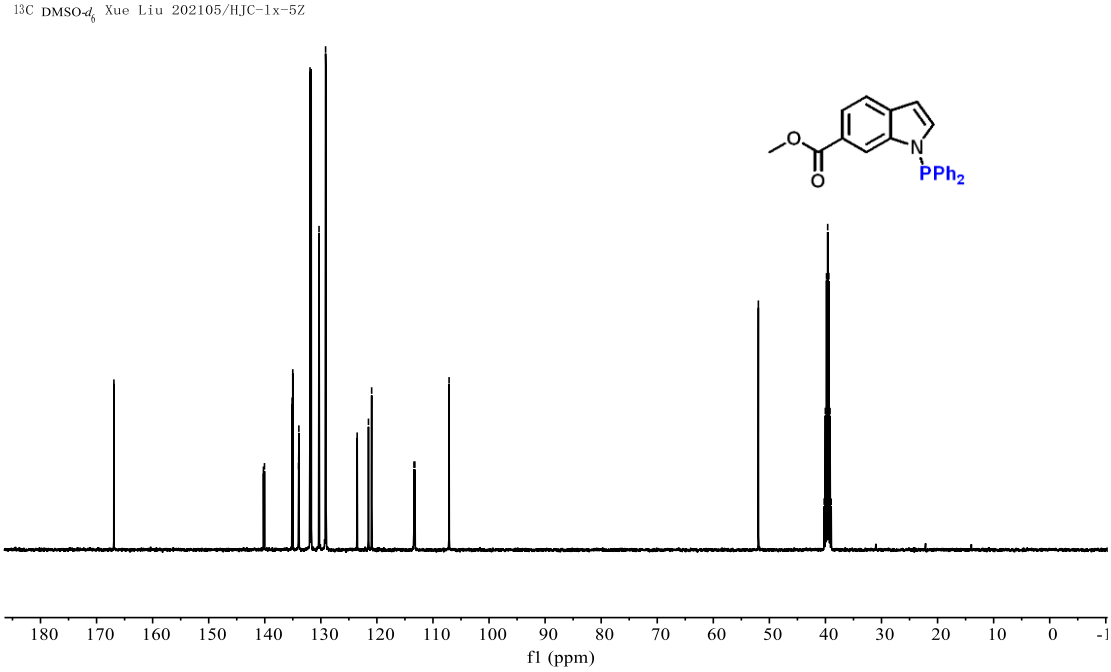

135.32
135.20
131.92
131.71
130.35
129.25
129.19
128.69
128.66
128.58
123.14
121.04
112.09
109.57
40.23
40.02
39.81
39.60
39.39
39.18
38.97
13.36
13C DMSO-d_6 Xue Liu 202105/HJC-1x-YJ-4
CN
N
PPh2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

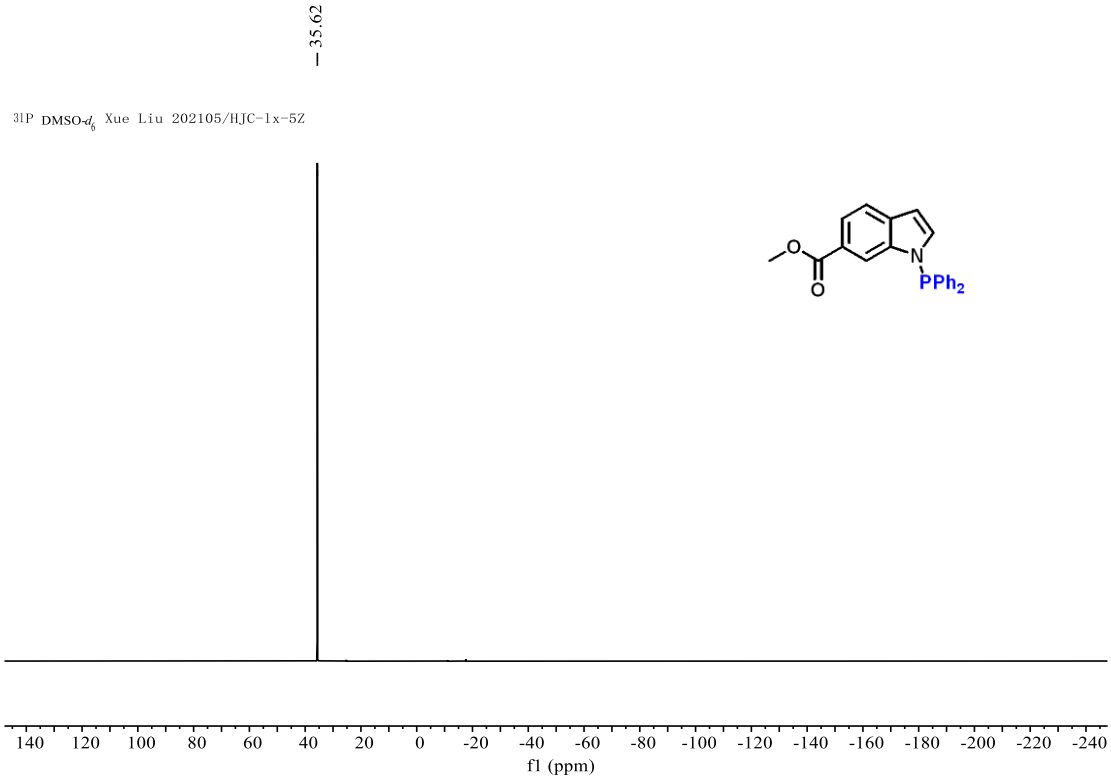

35.71
31P DMSO-d_6 Xue Liu 202105/HJC-1x-YJ-4
CN
N
PPh2
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

Methyl 1-(diphenylphosphaneyl)-1H-indole-6-carboxylate (39)








35.62
31P DMSO-d_6 Xue Liu 202105/HJC-1x-5Z
O
O
N
PPh2
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)