Supporting Information

Iridium-Catalyzed P(III)-Directed ortho-C–H Silylation of Arylphosphines with Hydrosilanes

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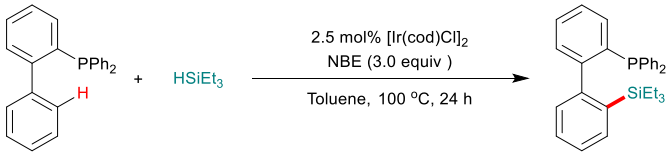
1. General Experimental Details

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade and freshly distilled prior to use. DMF used in reactions was acquired from SPS. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel (Macherey Nagel, particle size 0.040-0.063 mm). 1H-NMR and 13C-NMR were recorded on a Varian AV300, AV400 or AV600 spectrometer in $CDCl_3$ and are reported relative to the solvent residual peaks. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra (EIMS, 70 eV) were conducted on a Finnigan SSQ 7000 spectrometer. HRMS were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer. Gas chromatography (GC) was performed on a Shimadzu GC-2010 chromatograph. UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Emission spectra were recorded on a JASCO FP-8200 spectrofluorometer.

2. Optimization of the Reaction Condition

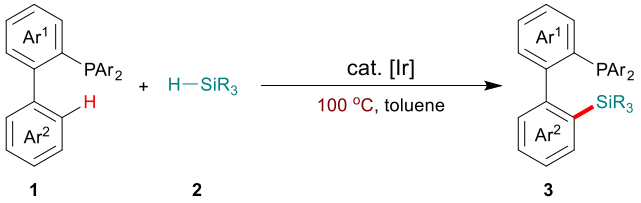


1a **2a** **3aa**

Entry	Deviation from Standard Conditions	**3aa** [%]
1	none	82
2	Using $[Ir(coe)_2Cl]_2$ instead of $[Ir(cod)Cl]_2$	78
3	Using $[Ir(coe)_2OMe]_2$ instead of $[Ir(cod)Cl]_2$	80
4	Using $IrCl_3$ instead of $[Ir(cod)Cl]_2$	37
5	Using $[Cp^*IrCl_2]_2$ instead of $[Ir(cod)Cl]_2$	35
6	Using COE instead of NBE	72
7	Using NBD instead of NBE	77
8	Using cyclohexene instead of NBE	75
9	Using xylene instead of toluene	78
10	Using benzene instead of toluene	71
11	Using THF instead of toluene	56
12	at 80 °C	70
13	w/o [Ir] or NBE	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $[Ir(cod)Cl]_2$ (2.5 mol%), and NBE (0.6 mmol) in 1.0 mL of toluene at 100 °C under argon, 24 h, isolated yields.

3. General Procedures

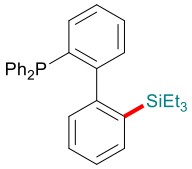


1 2 3

In a Schlenk tube, monophosphine ligands **1** (1.0 equiv, 0.20 mmol), hydrosilanes **2** (3.0 equiv, 0.60 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), norbornene (3.0 equiv, 56.4 mg, 0.6 mmol) were dissolved in toluene (1.0 mL). The mixture was stirred at 100 °C under argon for 24 hours. Upon the completion of the reaction, the solvent was removed. The crude mixture was directly subjected to column Chromatography on silica gel using PE/EA as eluent to give the desired products **3**.

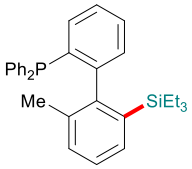
4. Spectroscopic Data of the Products

Diphenyl(2'-(triethylsilyl)-[1,1'-biphenyl]-2-yl)phosphine (3aa)



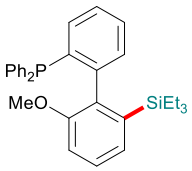
A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1a** (67.6 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3aa** (74 mg, 82%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.60 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.35 – 7.14 (m, 15H), 6.96 (td, *J* = 7.5, 1.4 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 1H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.62 – 0.48 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.67 (d, *J* = 31.9 Hz), 148.11 (d, *J* = 6.9 Hz), 138.51 (d, *J* = 14.1 Hz), 137.79 (d, *J* = 11.7 Hz), 136.78 (d, *J* = 12.9 Hz), 135.47, 134.32 (d, *J* = 20.3 Hz), 133.77 (d, *J* = 1.8 Hz), 133.74, 133.55, 131.04 (d, *J* = 4.2 Hz), 130.70 (d, *J* = 5.2 Hz), 128.60, 128.36, 128.30, 128.12, 127.96, 127.51, 127.07, 126.21, 7.74, 4.15. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -15.45.

(2'-methyl-6'-(triethylsilyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ba)



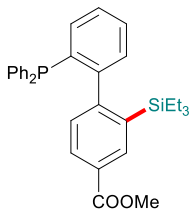
A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1b** (70.4 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ba** (65.2 mg, 70%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.45 (dd, J = 7.5, 1.4 Hz, 1H), 7.42-7.18 (m, 14H), 7.16-7.10 (m, 1H), 7.06 -6.99 (m, 1H), 1.38 (s, 3H), 0.78 (t, *J* = 7.9 Hz, 9H), 0.48-0.26 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.12 (d, *J* = 33.1 Hz), 147.21 (d, *J* = 6.9 Hz), 137.92 (d, *J* = 14.6 Hz), 137.56 (d, *J* = 13.6 Hz), 137.14 (d, *J* = 13.1 Hz), 136.63, 136.24, 134.72 (d, *J* = 21.2 Hz), 133.75, 133.62, 133.54, 132.70, 130.44 (d, *J* = 5.9 Hz), 130.12, 128.63 (d, *J* = 3.6 Hz), 128.22 (d, *J* = 3.0 Hz), 128.10, 128.04, 127.33, 126.57, 20.63, 7.78, 4.02. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -16.10.

(2'-methoxy-6'-(triethylsilyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ca)



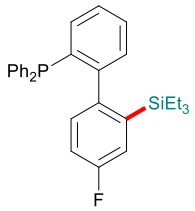
A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1c** (73.6 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ca** (63.6 mg, 66%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.41-7.39 (m, 1H), 7.38- 7.21 (m, 15H), 6.71 (dd, *J* = 8.1, 1.1 Hz, 1H), 2.95 (s, 3H), 0.82 (t, *J* = 7.9 Hz, 9H), 0.53 -0.34 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 156.63 (d, *J* = 2.1 Hz), 146.31 (d, *J* = 34.6 Hz), 138.92 (d, *J* = 14.0 Hz), 138.14 (d, *J* = 12.2 Hz), 137.80, 137.51 (d, *J* = 11.4 Hz), 136.84 (d, *J* = 6.9 Hz), 134.42 (d, *J* = 2.5 Hz), 133.90 (d, *J* = 12.2 Hz), 133.73 (d, *J* = 11.8 Hz), 131.04 (d, *J* = 6.3 Hz), 128.60, 128.14, 128.08, 128.04, 127.94, 127.870, 127.85, 127.83, 127.34 (d, *J* = 10.8 Hz), 110.04, 53.80, 7.75, 4.01. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -16.01.

Methyl 2'-(diphenylphosphanyl)-2-(triethylsilyl)-[1,1'-biphenyl]-4-carboxylate (3da)



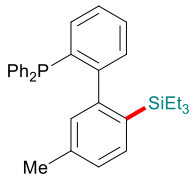
A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1d** (79.2 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3da** (45.9 mg, 45%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.28 (d, *J* = 1.9 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.37-7.28 (m, 8H), 7.23-7.13 (m, 6H), 6.59 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 0.88 (t, *J* = 7.8 Hz, 9H), 0.66-0.49 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 167.43, 136.1, 133.9, 133.7, 133.3, 133.2, 133.0, 130.6, 130.6, 129.7, 129.6, 128.3, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.4, 51.5, 7.1, 3.5. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -15.70.

(4'-fluoro-2'-(triethylsilyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ea)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1e** (71.2 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ea** (59.2 mg, 63%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.40 – 7.25 (m, 10H), 7.22 – 7.10 (m, 5H), 6.64 (td, *J* = 8.4, 2.8 Hz, 1H), 6.45 (ddd, *J* = 8.4, 5.5, 0.8 Hz, 1H), 0.89 (t, *J* = 7.8 Hz, 9H), 0.65 – 0.45 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 161.5 (d, J = 247.5 Hz), 148.5 (d, J = 31.4 Hz), 143.8, 138.8 (d, *J* = 3.7 Hz), 138.1 (d, *J* = 13.6 Hz), 137.3 (d, *J* = 11.6 Hz), 137.1, 134.4 (d, *J* = 20.6 Hz), 133.62, 133.58 (d, *J* = 19.0 Hz), 132.7 (d, *J* = 4.0 Hz), 132.6, 130.8 (d, *J* = 5.1 Hz), 128.7, 128.4 (d, *J* = 2.2 Hz), 128.3, 128.2, 128.0, 127.7, 121.6 (d, *J* = 18.9 Hz), 113.8 (d, *J* = 21.0 Hz), 7.6, 3.9. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -15.90. **^{19}F NMR (376 MHz, $CDCl_3$) δ** -114.5.

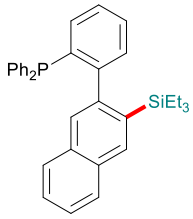
(5'-methyl-2'-(triethylsilyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3fa)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged

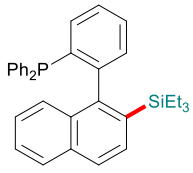
with **1e** (70.4 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3fa** (57.8 mg, 62%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.48 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.06 (m, 15H), 6.23 (s, 1H), 1.90 (d, *J* = 1.9 Hz, 3H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.63 – 0.45 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.55 (d, *J* = 31.6 Hz), 147.92 (d, *J* = 7.1 Hz), 138.53 (d, *J* = 14.0 Hz), 137.83 (d, *J* = 11.5 Hz), 137.15 (d, *J* = 13.0 Hz), 136.74, 135.57, 134.62 (d, *J* = 21.0 Hz), 133.62, 133.52, 133.43, 132.52 (d, *J* = 4.3 Hz), 131.55, 130.48 (d, *J* = 5.1 Hz), 128.68, 128.36, 128.30, 127.94 (d, *J* = 13.6 Hz), 127.20 (d, *J* = 35.4 Hz), 20.89, 7.77, 4.18. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -14.81.

Diphenyl(2-(3-(triethylsilyl)naphthalen-2-yl)phenyl)phosphane (3ga)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1f** (77.6 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ga** (74 mg, 74%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.02 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.01 (m, 17H), 6.73 (s, 1H), 0.86 (t, *J* = 7.8 Hz, 9H), 0.66 – 0.50 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.02 (d, *J* = 31.4 Hz), 144.03 (d, *J* = 7.3 Hz), 138.42 (d, *J* = 13.6 Hz), 137.63 (d, *J* = 7.5 Hz), 137.51 (d, *J* = 9.2 Hz), 136.52, 134.77 (d, *J* = 20.9 Hz), 133.77, 133.52, 133.42, 133.33, 131.82 (d, *J* = 36.8 Hz), 130.77 (d, *J* = 5.1 Hz), 130.08 (d, *J* = 4.4 Hz), 128.74, 128.39, 128.32, 128.27, 127.96, 127.80 (d, *J* = 3.3 Hz), 127.49 (d, *J* = 2.1 Hz), 126.35, 125.66, 7.74 (d, *J* = 1.6 Hz), 4.19. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -14.71.

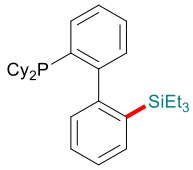
Diphenyl(2-(2-(triethylsilyl)naphthalen-1-yl)phenyl)phosphane (3ha)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged

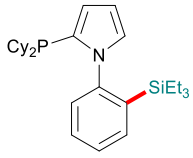
with **1g** (77.6 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ha** (54 mg, 54%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.83 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.44 (dt, *J* = 9.4, 4.3 Hz, 3H), 7.32 – 7.13 (m, 8H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 2H), 6.77 – 6.64 (m, 2H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.53 (ddt, *J* = 30.8, 14.9, 7.7 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 147.83 (d, *J* = 33.2 Hz), 146.61 (d, *J* = 6.7 Hz), 138.79 (d, *J* = 14.1 Hz), 137.98 (d, *J* = 14.2 Hz), 136.91 (d, *J* = 12.7 Hz), 134.31 (d, *J* = 21.7 Hz), 133.94 (d, *J* = 2.0 Hz), 133.84 (d, *J* = 2.1 Hz), 133.34 (d, *J* = 18.7 Hz), 132.87, 132.79 (d, *J* = 2.7 Hz), 131.39 (d, *J* = 5.8 Hz), 130.98, 128.36 (d, *J* = 5.0 Hz), 128.18, 128.13, 127.98, 127.88, 127.68, 127.12, 127.07, 126.29, 125.50, 124.65, 7.74, 3.94. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -16.60.

Dicyclohexyl(2'-(triethylsilyl)-[1,1'-biphenyl]-2-yl)phosphane (3ia)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1h** (70.0 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ia** (61.2 mg, 66%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.65 – 7.52 (m, 2H), 7.42 – 7.25 (m, 4H), 7.21 – 7.17 (m, 2H), 1.98 – 1.61 (m, 12H), 1.32 – 1.02 (m, 10H), 0.84 (td, *J* = 7.9, 1.8 Hz, 9H), 0.62 – 0.37 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 151.04 (d, *J* = 29.7 Hz), 148.83 (d, *J* = 6.1 Hz), 135.90, 135.53, 135.29, 132.22 (d, *J* = 2.9 Hz), 131.82 (d, *J* = 5.0 Hz), 131.17 (d, *J* = 5.3 Hz), 127.16, 126.77, 126.45, 125.80, 36.10 (d, *J* = 15.6 Hz), 33.80 (d, *J* = 15.3 Hz), 31.15 (d, *J* = 14.4 Hz), 30.59 (d, *J* = 13.0 Hz), 30.00 (d, *J* = 16.4 Hz), 29.51 (d, *J* = 11.1 Hz), 27.89 (d, *J* = 10.6 Hz), 27.57 (d, *J* = 8.9 Hz), 27.41 (d, *J* = 9.6 Hz), 27.21, 27.10, 26.42, 7.70, 4.27. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -11.80.

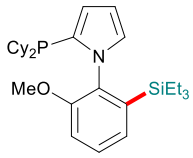
2-(dicyclohexylphosphanyl)-1-(2-(triethylsilyl)phenyl)-1H-pyrrole (3ka)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged

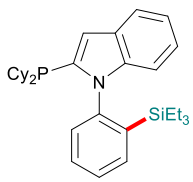
with **1j** (67.8 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ka** (68.8 mg, 76%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.59 – 7.53 (m, 1H), 7.38 – 7.32 (m, 2H), 7.14 (dt, *J* = 5.7, 2.0 Hz, 1H), 6.84 (ddd, *J* = 3.4, 2.6, 1.6 Hz, 1H), 6.48 (dd, *J* = 3.6, 1.6 Hz, 1H), 6.29 (dd, *J* = 3.6, 2.6 Hz, 1H), 1.82 – 1.64 (m, 11H), 1.16 (dt, *J* = 30.6, 8.4 Hz, 11H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.63 – 0.46 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** δ 146.27, 135.92, 134.97, 130.63, 130.57, 128.40, 127.35, 126.94, 116.60 (d, *J* = 4.5 Hz), 108.11, 35.36 (d, *J* = 9.4 Hz), 34.42 (d, *J* = 8.8 Hz), 30.44, 30.40, 30.33, 30.20 (d, *J* = 12.2 Hz), 29.79 (d, *J* = 13.7 Hz), 27.57, 27.48, 27.39, 27.31 (d, *J* = 6.5 Hz), 26.45 (d, *J* = 6.3 Hz), 7.62, 3.37. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -26.42.

2-(dicyclohexylphosphanyl)-1-(2-methoxy-6-(triethylsilyl)phenyl)-1H-pyrrole (3la)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1k** (73.8 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3la** (42.5 mg, 44%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.59 – 7.53 (m, 1H), 7.38 – 7.32 (m, 2H), 7.14 (dt, *J* = 5.7, 2.0 Hz, 1H), 6.84 (ddd, *J* = 3.4, 2.6, 1.6 Hz, 1H), 6.48 (dd, *J* = 3.6, 1.6 Hz, 1H), 6.29 (dd, *J* = 3.6, 2.6 Hz, 1H), 1.82 – 1.64 (m, 11H), 1.16 (dt, *J* = 30.6, 8.4 Hz, 11H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.63 – 0.46 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 137.78, 128.59, 126.86, 126.47, 115.60, 115.56, 111.24, 108.74, 108.25, 95.97, 54.95, 34.53 (d, *J* = 8.8 Hz), 34.03 (d, *J* = 9.6 Hz), 30.91 (d, *J* = 15.8 Hz), 30.56 (d, *J* = 11.8 Hz), 29.43 (d, *J* = 12.3 Hz), 29.17 (d, *J* = 11.3 Hz), 27.74 (d, *J* = 9.1 Hz), 27.63 (d, *J* = 7.3 Hz), 27.47 (d, *J* = 3.0 Hz), 27.38 (d, *J* = 4.0 Hz), 26.58, 26.44, 7.69, 3.22. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -23.17.

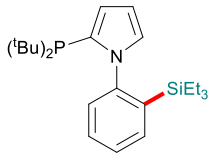
2-(dicyclohexylphosphanyl)-1-(2-(triethylsilyl)phenyl)-1H-indole (3ma)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged

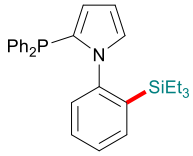
with **1l** (77.8 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ma** (57.2 mg, 56%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.73 – 7.59 (m, 2H), 7.48 – 7.39 (m, 2H), 7.13 – 7.03 (m, 3H), 6.84 – 6.75 (m, 2H), 2.01 – 1.65 (m, 11H), 1.31 – 1.04 (m, 11H), 0.74 (t, *J* = 7.9 Hz, 9H), 0.45 – 0.23 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 143.77, 141.41, 138.52, 138.33 (d, *J* = 9.9 Hz), 136.15, 131.56, 129.06, 127.68, 127.49, 121.76, 120.02, 119.66, 111.28, 109.23, 35.49 (d, *J* = 12.1 Hz), 33.94 (d, *J* = 9.4 Hz), 31.05 (d, *J* = 13.6 Hz), 30.15 (d, *J* = 10.6 Hz), 29.99, 29.88, 29.76, 27.68, 27.58, 27.46, 27.23 (d, *J* = 10.1 Hz), 26.42 (d, *J* = 7.4 Hz), 7.53, 3.14. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -24.12.

2-(di-*tert*-butylphosphanyl)-1-(2-(triethylsilyl)phenyl)-1H-pyrrole (3na)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1m** (57.4 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3na** (32.2 mg, 39%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.55 (dd, *J* = 6.9, 2.3 Hz, 1H), 7.40 – 7.27 (m, 3H), 6.88 (ddd, *J* = 4.1, 2.6, 1.6 Hz, 1H), 6.73 (dd, *J* = 3.7, 1.6 Hz, 1H), 6.30 (dd, *J* = 3.7, 2.6 Hz, 1H), 1.24 (d, *J* = 11.8 Hz, 9H), 1.09 (d, *J* = 12.2 Hz, 9H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.53 (dq, *J* = 9.6, 8.2, 7.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 146.33, 135.85, 134.98, 131.23 (d, *J* = 7.1 Hz), 128.14, 127.39 (d, *J* = 1.9 Hz), 126.65, 118.96 (d, *J* = 4.9 Hz), 107.76, 33.40 (d, *J* = 18.2 Hz), 32.28 (d, *J* = 16.8 Hz), 30.78 (d, *J* = 14.3 Hz), 30.60 (d, *J* = 14.9 Hz), 7.74, 3.71. **^{31}P NMR (162 MHz, $CDCl_3$) δ** 2.71.

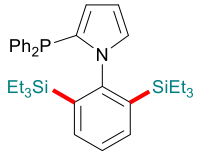
2-(diphenylphosphanyl)-1-(2-(triethylsilyl)phenyl)-1H-pyrrole (3oa)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1n** (65.4 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction

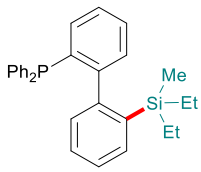
mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3oa** (64.3 mg, 73%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.59 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.42 – 7.25 (m, 11H), 7.10 (td, *J* = 7.6, 1.6 Hz, 1H), 6.91 (td, *J* = 2.9, 1.6 Hz, 1H), 6.68 (dt, *J* = 7.8, 1.4 Hz, 1H), 6.30 (dd, *J* = 3.6, 2.6 Hz, 1H), 6.18 (dd, *J* = 3.7, 1.7 Hz, 1H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.70 – 0.52 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 145.83 (d, *J* = 2.7 Hz), 138.21 (d, *J* = 5.4 Hz), 137.82 (d, *J* = 9.4 Hz), 136.20, 135.06, 133.74 (d, *J* = 20.5 Hz), 133.17 (d, *J* = 18.8 Hz), 130.20 (d, *J* = 2.1 Hz), 129.34 (d, *J* = 3.9 Hz), 128.69, 128.56, 128.35, 128.28, 128.08, 128.02 (d, *J* = 1.5 Hz), 127.87 (d, *J* = 2.4 Hz), 127.37, 118.79 (d, *J* = 2.4 Hz), 108.88, 7.65, 3.29. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -31.68.

1-(2,6-bis(triethylsilyl)phenyl)-2-(diphenylphosphanyl)-1H-pyrrole (3oa')



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1n** (65.4 mg, 0.2 mmol), **2a** (92.8 mg, 0.8 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (75.2 mg, 0.8 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 120 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3oa'** (64.6 mg, 57%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.55 (d, *J* = 7.3 Hz, 2H), 7.40 (dddd, *J* = 7.7, 4.3, 3.2, 2.0 Hz, 5H), 7.25 – 7.17 (m, 6H), 6.86 (ddd, *J* = 4.1, 2.5, 1.6 Hz, 1H), 6.62 (dd, *J* = 3.7, 1.6 Hz, 1H), 6.32 (dd, *J* = 3.7, 2.6 Hz, 1H), 0.69 (t, *J* = 7.9 Hz, 18H), 0.25 (q, *J* = 8.1 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 137.34, 136.38, 134.00, 133.79, 130.57, 128.27, 128.25, 127.98, 127.87, 127.80, 126.53, 117.98, 117.95, 108.81, 7.64, 2.83. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -32.8.

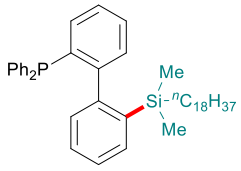
(2'-(diethyl(methyl)silyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ab)



A 25 mL schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1a** (67.6 mg, 0.2 mmol), **2b** (61.2 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ab** (73.6 mg, 84%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.60 (dd, *J* =

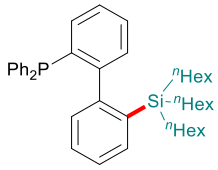
7.6, 1.4 Hz, 1H), 7.36 – 7.13 (m, 15H), 6.97 (td, *J* = 7.5, 1.4 Hz, 1H), 6.53 (dd, *J* = 7.6, 1.4 Hz, 1H), 0.89 (dt, *J* = 15.6, 7.9 Hz, 6H), 0.69 – 0.46 (m, 4H), -0.11 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.49 (d, *J* = 31.8 Hz), 147.84 (d, *J* = 6.7 Hz), 138.33 (d, *J* = 13.6 Hz), 137.57 (d, *J* = 11.8 Hz), 136.77 (d, *J* = 12.5 Hz), 136.31, 135.07, 134.26 (d, *J* = 20.2 Hz), 133.70, 133.58 (d, *J* = 14.2 Hz), 130.80 (d, *J* = 4.3 Hz), 130.66 (d, *J* = 5.4 Hz), 128.56, 128.32, 128.25, 128.11, 127.94, 127.49, 127.10, 126.26, 7.73 (d, *J* = 9.2 Hz), 6.46 (d, *J* = 22.0 Hz), -4.81. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -15.36.

(2'-(dimethyl(nonadecyl)silyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ac)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1a** (67.6 mg, 0.2 mmol), **2c** (195 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ac** (106.0 mg, 80%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.62 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.34 – 7.11 (m, 15H), 6.97 (td, *J* = 7.5, 1.4 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 1.23 (d, *J* = 15.0 Hz, 32H), 0.90 – 0.86 (m, 3H), 0.65 – 0.47 (m, 2H), 0.04 (s, 3H), -0.07 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.42 (d, *J* = 31.7 Hz), 147.57 (d, *J* = 7.3 Hz), 138.26 (d, *J* = 13.2 Hz), 137.60, 137.47 (d, *J* = 11.0 Hz), 136.83 (d, *J* = 12.2 Hz), 134.72, 134.27 (d, *J* = 20.1 Hz), 133.65 (d, *J* = 19.2 Hz), 133.63 (d, *J* = 1.7 Hz), 130.68 (d, *J* = 10.0 Hz), 130.67, 128.57, 128.31 (d, *J* = 2.3 Hz), 128.25, 128.04 (d, *J* = 18.1 Hz), 127.33 (d, *J* = 37.0 Hz), 126.40, 33.65, 31.93, 29.71, 29.66, 29.64, 29.37, 29.30, 23.97, 22.70, 16.73, 14.13, -1.58, -1.60. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -15.21.

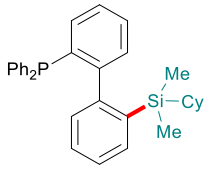
(2'-(dimethyl(nonadecyl)silyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ad)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1a** (67.6 mg, 0.2 mmol), **2d** (170.4 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the

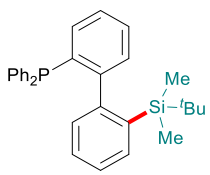
product as a white solid **3ad** (95.4 mg, 77%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.60 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.27 (m, 8H), 7.27 – 7.17 (m, 6H), 7.13 (ddd, *J* = 7.6, 3.6, 1.3 Hz, 1H), 6.99 (td, *J* = 7.5, 1.3 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 1.28 – 1.17 (m, 24H), 0.87 (t, *J* = 7.0 Hz, 9H), 0.64 – 0.54 (m, 3H), 0.52 – 0.38 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.84 (d, *J* = 32.0 Hz), 147.98 (d, *J* = 7.2 Hz), 138.48 (d, *J* = 14.0 Hz), 137.79 (d, *J* = 11.8 Hz), 136.80 (d, *J* = 12.5 Hz), 136.20, 135.23, 134.36, 134.16, 133.82, 133.76 (d, *J* = 1.7 Hz), 133.63, 130.89 (d, *J* = 4.2 Hz), 130.57 (d, *J* = 5.3 Hz), 128.42 (d, *J* = 20.5 Hz), 128.23 (d, *J* = 1.8 Hz), 128.14 (d, *J* = 5.5 Hz), 127.45, 126.93, 126.15, 33.50, 31.44, 23.86, 22.67, 14.17, 13.24. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -15.54.

(2'-(dimethyl(nonadecyl)silyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ae)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1a** (67.6 mg, 0.2 mmol), **2e** (84.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ae** (62.1 mg, 65%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.59 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.37 – 7.28 (m, 8H), 7.26 – 7.15 (m, 6H), 7.11 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.98 (td, *J* = 7.5, 1.4 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 1.65 (dd, *J* = 27.9, 9.0 Hz, 5H), 1.20 – 1.04 (m, 5H), 0.81 – 0.74 (m, 1H), 0.05 (s, 3H), -0.23 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.51 (d, *J* = 31.8 Hz), 147.59 (d, *J* = 7.2 Hz), 138.21 (d, *J* = 13.6 Hz), 137.55 (d, *J* = 11.3 Hz), 136.83 (d, *J* = 12.3 Hz), 136.69, 135.08, 134.27 (d, *J* = 20.3 Hz), 133.70 (d, *J* = 19.1 Hz), 133.52 (d, *J* = 1.7 Hz), 130.71 (d, *J* = 4.0 Hz), 130.60 (d, *J* = 5.3 Hz), 128.54, 128.30 (d, *J* = 3.2 Hz), 128.24 (d, *J* = 4.4 Hz), 128.14, 127.96, 127.46, 127.02, 126.17, 28.17, 27.64, 27.61, 26.97, 26.38, -3.77, -3.79, -3.87. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -15.27.

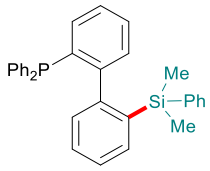
(2'-(tert-butyldimethylsilyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3af)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1a** (67.6 mg, 0.2 mmol), **2f** (69.0 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg,

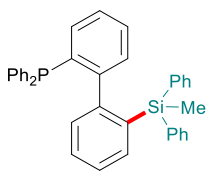
0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3af** (47.9 mg, 53%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.61 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.34 – 7.22 (m, 10H), 7.21 – 7.11 (m, 4H), 7.09 – 7.02 (m, 1H), 6.93 (td, *J* = 7.5, 1.4 Hz, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 0.87 (s, 9H), 0.19 (s, 3H), -0.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.76 (d, *J* = 31.3 Hz), 147.49 (d, *J* = 7.2 Hz), 138.00 (d, *J* = 13.9 Hz), 137.39 (d, *J* = 7.3 Hz), 137.28 (d, *J* = 8.2 Hz), 135.88, 134.28 (d, *J* = 20.3 Hz), 133.82 (d, *J* = 19.7 Hz), 133.09, 130.90 (d, *J* = 3.4 Hz), 130.49 (d, *J* = 5.1 Hz), 128.41 (d, *J* = 7.5 Hz), 128.31, 128.25, 128.12 (d, *J* = 7.2 Hz), 127.79, 127.35, 127.00, 125.64, 27.49, 17.94, -3.17, -4.82. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -15.24.

(2'-(dimethyl(phenyl)silyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ag)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1a** (67.6 mg, 0.2 mmol), **2g** (81.0 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ag** (62.3 mg, 66%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.63 – 7.59 (m, 1H), 7.42 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.33 – 7.23 (m, 13H), 7.17 – 7.06 (m, 4H), 7.00 (td, *J* = 7.5, 1.4 Hz, 1H), 6.93 (ddd, *J* = 7.6, 4.4, 1.4 Hz, 1H), 6.58 – 6.53 (m, 1H), 0.32 (s, 3H), 0.15 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 148.95 (d, *J* = 31.6 Hz), 147.83 (d, *J* = 7.3 Hz), 140.00, 138.24, 138.11, 137.44 (d, *J* = 10.9 Hz), 136.69 (d, *J* = 12.2 Hz), 136.17, 136.07, 135.64, 134.35, 134.15, 134.13, 133.77, 133.58, 130.84 (d, *J* = 9.7 Hz), 130.84, 128.62 (d, *J* = 6.7 Hz), 128.33 (d, *J* = 1.7 Hz), 128.27, 128.16, 127.58, 127.56 (d, *J* = 9.2 Hz), 126.46, -0.52, -1.87. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -15.97.

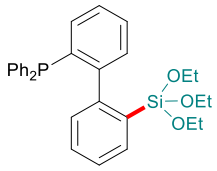
(2'-(methyldiphenylsilyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ah)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1a** (67.6 mg, 0.2 mmol), **2h** (118.8 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg,

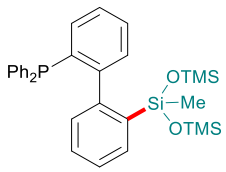
0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ah** (59.8 mg, 56%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.48 – 7.44 (m, 3H), 7.41 – 7.22 (m, 18H), 7.13 – 6.98 (m, 5H), 6.79 (dd, *J* = 6.6, 5.5 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 0.15 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 148.85 (d, *J* = 31.6 Hz), 148.34 (d, *J* = 7.2 Hz), 138.22 (d, *J* = 13.3 Hz), 137.92, 137.57 (d, *J* = 11.3 Hz), 137.49, 137.36, 136.62 (d, *J* = 12.4 Hz), 135.24 (d, *J* = 42.7 Hz), 134.21 (d, *J* = 20.0 Hz), 133.72 (d, *J* = 19.1 Hz), 131.02 (d, *J* = 4.6 Hz), 130.81 (d, *J* = 5.2 Hz), 128.97 (d, *J* = 4.6 Hz), 128.56, 128.34 (d, *J* = 3.5 Hz), 128.28 (d, *J* = 2.3 Hz), 128.18, 127.98, 127.89, 127.70, 127.64, 127.53, 126.28, -3.14. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -15.31.

Diphenyl(2'-(triethoxysilyl)-[1,1'-biphenyl]-2-yl)phosphane (3ai)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **1a** (67.6 mg, 0.2 mmol), **2i** (98.4 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3ai** (49.0 mg, 49%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.87 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.36 – 7.29 (m, 6H), 7.28 – 7.18 (m, 8H), 7.12 (td, *J* = 8.8, 8.1, 2.1 Hz, 2H), 6.75 (dd, *J* = 7.7, 1.3 Hz, 1H), 3.63 (qd, *J* = 7.0, 4.2 Hz, 6H), 1.09 (t, *J* = 7.0 Hz, 9H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.65 (d, *J* = 32.2 Hz), 148.15 (d, *J* = 7.5 Hz), 138.95 (d, *J* = 14.0 Hz), 137.79 (d, *J* = 12.3 Hz), 136.15, 134.09, 133.96 (d, *J* = 2.1 Hz), 133.90, 133.67, 133.48, 130.90 (d, *J* = 4.9 Hz), 130.27 (d, *J* = 5.5 Hz), 128.68, 128.35, 128.26 (d, *J* = 6.9 Hz), 128.01 (d, *J* = 6.2 Hz), 127.89, 127.86, 127.16, 126.31, 58.30, 18.06. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -16.02.

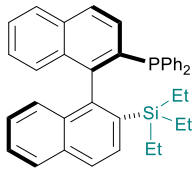
(2'-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3aj)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged

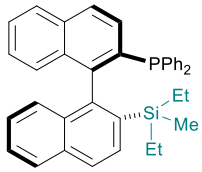
with **1a** (67.6 mg, 0.2 mmol), **2j** (133.2 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 100 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid **3aj** (51.3 mg, 46%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.84 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.29 (m, 12H), 7.20 – 7.14 (m, 3H), 7.09 (td, *J* = 7.5, 1.4 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 0.21 (s, 9H), 0.10 (s, 9H), -0.26 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.33 (d, *J* = 31.6 Hz), 146.75 (d, *J* = 7.2 Hz), 138.53 (d, *J* = 13.4 Hz), 137.69 (d, *J* = 11.3 Hz), 136.75, 136.27 (d, *J* = 12.6 Hz), 134.32 (d, *J* = 17.3 Hz), 134.03, 133.94 (d, *J* = 1.8 Hz), 133.70, 133.51, 131.29 (d, *J* = 5.4 Hz), 130.69 (d, *J* = 5.0 Hz), 128.53, 128.35 (d, *J* = 7.2 Hz), 128.23 (d, *J* = 6.2 Hz), 128.05 (d, *J* = 5.3 Hz), 127.80, 127.42, 126.32, 2.08, 1.97, 0.80 (d, *J* = 2.0 Hz). **^{31}P NMR (162 MHz, $CDCl_3$) δ** -15.48.

(*R*)-diphenyl(2'-(triethylsilyl)-[1,1'-binaphthalen]-2-yl)phosphane (*R*-L1)



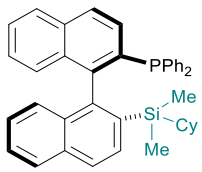
A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with ***R*-L** (87.6 mg, 0.2 mmol), **2a** (69.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 120 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid ***R*-L1** (73.9 mg, 67%, > 99% ee). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.92 – 7.72 (m, 5H), 7.53 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.42 (ddd, *J* = 8.1, 5.7, 2.3 Hz, 1H), 7.29 – 7.16 (m, 8H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.99 (td, *J* = 7.5, 1.5 Hz, 2H), 6.91 (td, *J* = 8.0, 1.4 Hz, 2H), 6.63 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 6.49 (dd, *J* = 8.5, 1.0 Hz, 1H), 0.69 (t, *J* = 7.9 Hz, 9H), 0.42 – 0.29 (m, 3H), 0.19 – 0.07 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 146.78 (d, *J* = 33.7 Hz), 144.29 (d, *J* = 8.1 Hz), 138.30 (d, *J* = 14.5 Hz), 137.23 (d, *J* = 13.9 Hz), 135.94 (d, *J* = 2.7 Hz), 135.61 (d, *J* = 13.1 Hz), 134.30 (d, *J* = 21.8 Hz), 134.13, 133.28, 133.19 (d, *J* = 3.1 Hz), 133.09, 133.03, 131.29, 130.04 (d, *J* = 2.0 Hz), 128.27 (d, *J* = 4.5 Hz), 128.19, 127.92 (d, *J* = 7.6 Hz), 127.82, 127.69, 127.68, 127.65, 127.26, 127.13, 126.66, 126.41, 125.99, 125.62, 124.96, 7.71, 3.67. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -16.00.

(*R*)-(2'-(diethyl(methyl)silyl)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (*R*-L2)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with ***R*-L** (87.6 mg, 0.2 mmol), **2a** (60.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 120 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid ***R*-L2** (61.3 mg, 57%, > 99% ee). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.92 (q, *J* = 8.3, 7.8 Hz, 3H), 7.83 – 7.76 (m, 2H), 7.56 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.36 – 7.23 (m, 8H), 7.18 – 7.12 (m, 1H), 7.05 (tt, *J* = 7.1, 1.5 Hz, 2H), 6.98 – 6.88 (m, 2H), 6.72 (ddd, *J* = 8.3, 6.7, 1.4 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 0.78 (td, *J* = 7.9, 2.1 Hz, 3H), 0.71 (td, *J* = 7.9, 2.0 Hz, 3H), 0.61 – 0.51 (m, 1H), 0.48 – 0.36 (m, 2H), 0.25 (dd, *J* = 15.1, 7.6 Hz, 1H), -0.58 – -0.66 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.72 (d, *J* = 33.6 Hz), 143.90 (d, *J* = 8.3 Hz), 138.12 (d, *J* = 14.2 Hz), 137.32 (d, *J* = 13.5 Hz), 136.52 (d, *J* = 2.7 Hz), 135.62 (d, *J* = 12.8 Hz), 134.25, 134.17 (d, *J* = 7.0 Hz), 134.04, 133.42, 133.31, 133.23, 133.12, 133.07, 130.96, 130.07 (d, *J* = 1.9 Hz), 128.29, 128.24, 127.97, 127.92 (d, *J* = 4.4 Hz), 127.68 (d, *J* = 3.5 Hz), 127.59 (d, *J* = 2.9 Hz), 127.33, 127.07, 126.63 (d, *J* = 11.2 Hz), 126.07, 125.67, 125.09, 7.70, 7.60, 6.15, 5.98, -5.58. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -16.10.

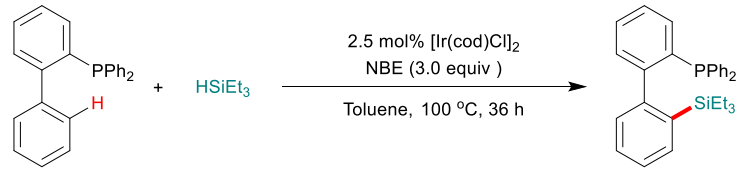
(*R*)-(2'-(cyclohexyldimethylsilyl)-[1,1'-binaphthalen]-2-yl)diphenylphosphane (*R*-L3)



A 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with ***R*-L** (87.6 mg, 0.2 mmol), **2e** (84.6 mg, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.005 mmol), NBE (56.4 mg, 0.6 mmol), and toluene (1.0 mL) solvent. The reaction mixture was stirred at 120 °C under argon for 24 h. Then the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford the product as a white solid ***R*-L$_{si}$** (70.5 mg, 61%, > 99% ee). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.92 – 7.82 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.52 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.44 (dt, *J* = 8.1, 4.0 Hz, 1H), 7.28 – 7.17 (m, 8H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 8.1 Hz, 2H), 6.90 (t, *J* = 8.0 Hz, 2H), 6.72 – 6.64 (m, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 1.61 – 1.44 (m, 5H), 1.05 – 0.81 (m, 5H), 0.74 – 0.61 (m, 1H), -0.33 (s, 3H), -0.63 (s, 3H). **^{13}C NMR (101 MHz,**

$CDCl_3$) δ 146.73 (d, *J* = 33.6 Hz), 143.88 (d, *J* = 8.5 Hz), 138.13 (d, *J* = 14.1 Hz), 137.41 (d, *J* = 13.5 Hz), 136.63 (d, *J* = 2.5 Hz), 135.60 (d, *J* = 12.7 Hz), 134.26, 134.17 (d, *J* = 7.1 Hz), 134.04, 133.41, 133.31, 133.22, 133.10 (d, *J* = 2.8 Hz), 133.03, 131.06, 130.11 (d, *J* = 1.9 Hz), 128.26 (d, *J* = 3.9 Hz), 128.22, 127.95, 127.90 (d, *J* = 4.5 Hz), 127.67 (d, *J* = 3.2 Hz), 127.35, 127.11, 126.69, 126.48, 126.05, 125.67, 125.11, 28.00 (d, *J* = 4.6 Hz), 27.57, 26.87, 25.80, -4.09, -4.61. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -16.40.

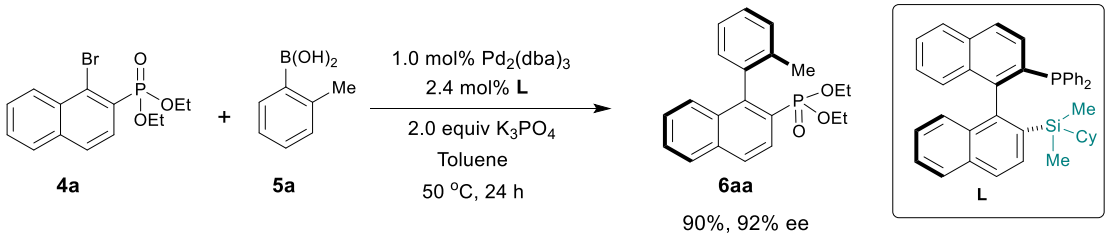
5. Gram-scale reaction



1a 5.0 mmol | **2a** 3.0 equiv | **3aa** 72%, 1.62 g

In a Schlenk tube, monophosphine ligands **1a** (1.69g, 1.0 equiv, 5.0 mmol), hydrosilanes **2** (1.74g, 3.0 equiv, 15.0 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 85 mg, 0.125 mmol), norbornene (1.41 g, 3.0 equiv, 15.0 mmol) were dissolved in toluene (25 mL). The mixture was stirred at 100 °C under argon for 36 hours. Upon the completion of the reaction, the solvent was removed. The crude mixture was directly subjected to column Chromatography on silica gel using PE/EA as eluent to give the desired products **3aa** (72%, 1.62g).

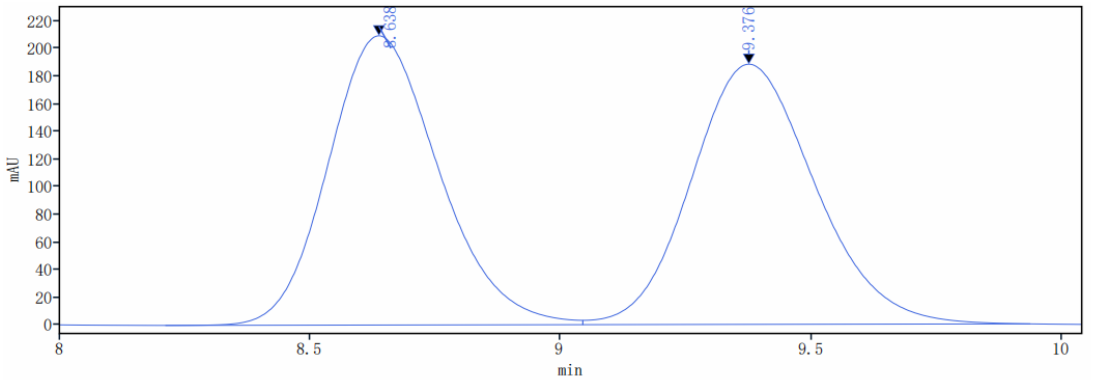
6. Synthetic Applications



4a | **5a** | **6aa** 90%, 92% ee | **L**

A flame-dried resealable Schlenk tube was charged with the aryl halide **4a** (34.2 mg, 0.1mmol, 1.0 equiv), arylboronic acid **5a** (27.0 mg, 0.2mmol, 2.0 equiv), and K_3PO_4 (42.4 mg, 0.2mmol, 2 equiv). The Schlenk tube was capped with a rubber septum, and twice evacuated and backfilled with argon. A solution of $Pd_2(dba)_3$ (1.0 mg, 1.0 mol%) and phosphine ***R*-L_{si}** (1.38 mg, 0.024 mmol, 2.4 mol%) in 1/2 of the total amount of toluene (0.4 mL total per mmol aryl bromide) was sonicated for about 30 seconds and injected into the Schlenk tube followed by addition of the rest of toluene. The septum was replaced with a teflon screw cap. The Schlenk tube was sealed, and the mixture was stirred at the room temperature for 24h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, filtered, and

concentrated. The crude material was purified by column chromatography on silica gel affording 32.2 mg (90%) of **6aa** in 92% ee (Chiralpak AD-H column, hexane/iPrOH, 95:5 v/v, flow rate 1 mL/min, λ = 214 nm, 25 °C), t_R (major) = 8.668 min, t_R (minor) = 9.423 min) as colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.09 (dd, *J* = 12.1, 8.6 Hz, 1H), 8.00 – 7.71 (m, 2H), 7.60 – 7.50 (m, 1H), 7.42 – 7.18 (m, 6H), 4.24 – 3.65 (m, 4H), 1.92 (s, 3H), 1.18 (dt, *J* = 11.4, 7.1 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 130.66, 129.29, 128.27, 128.16, 127.98, 127.96, 127.76, 127.29, 127.14, 127.03, 126.72, 126.70, 124.87, 61.82, 61.76, 61.72, 61.66, 19.96, 16.25, 16.19, 16.12, 16.05.**^{31}P NMR (162 MHz, $CDCl_3$) δ** 17.88. Column: OD-H; Eluent: i-PrOH/Hexane: 10%; Flow rate (mL/min): 0.8.



Signal VWD1A, Wavelength=214 nm

	Ret. Time	Area	Height	Area%
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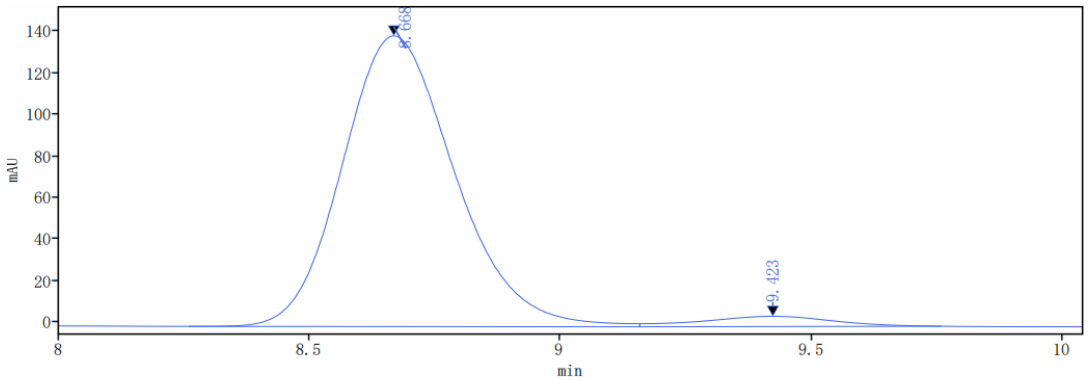
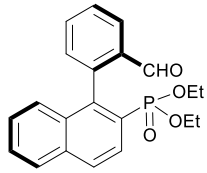
	9.376	3230.709	188.172	50.113
Total	18.013	6446.91	397.372	100.000



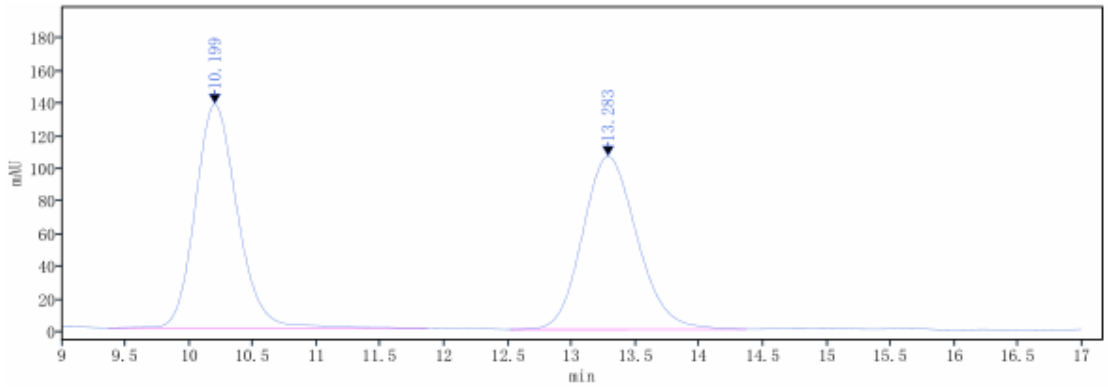
Signal VWD1A, Wavelength=214 nm

	Ret. Time	Area	Height	Area%
	8.668	2173.673	139.673	96.090
	9.423	88.452	4.928	3.910
Total	18.092	2262.12	144.601	100.000

Diethyl (R)-(1-(2-formylphenyl)naphthalen-2-yl)phosphonate (6ab)

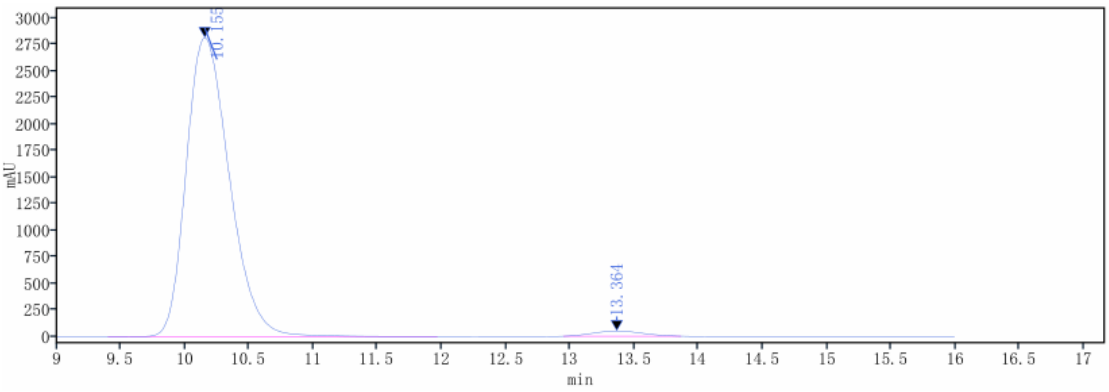


A flame-dried resealable Schlenk tube was charged with the aryl halide **4a** (34.2 mg, 0.1 mmol, 1.0 equiv), arylboronic acid **5b** (30.0 mg, 0.2 mmol, 2.0 equiv), and K_3PO_4 (42.4 mg, 0.2mmol, 2.0 equiv). The Schlenk tube was capped with a rubber septum, and twice evacuated and backfilled with argon. A solution of $Pd_2(dba)_3$ (1.0 mg, 1.0 mol%) and phosphine ***R*-L3** (1.38 mg, 0.024 mmol, 2.4 mol%) in 1/2 of the total amount of toluene (0.4 mL total per mmol aryl bromide) was sonicated for about 30 seconds and injected into the Schlenk tube followed by addition of the rest of toluene. The Schlenk tube was sealed, and the mixture was stirred at the room temperature for 24h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, filtered, and concentrated. The crude material was purified by column chromatography on silica gel affording 32.3 mg (88%) of **6ab** in 96% ee (determined by HPLC analysis (Chiralpak OD-H column, hexane/iPrOH, 90:10 v/v, flow rate 1 mL/min, λ = 224 nm, 25 °C), t_R (major) = 10.155 min, t_R (minor) = 13.364 min) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 9.43 (s, 1H), 8.16 – 8.10 (m, 2H), 8.02 (dd, *J* = 8.6, 3.7 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.70 (td, *J* = 7.5, 1.5 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.43 – 7.36 (m, 2H), 7.26 – 7.22 (m, 1H), 3.94 – 3.77 (m, 4H), 1.14 (dt, *J* = 17.1, 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 191.37, 141.87, 135.17, 134.78, 132.80, 132.13, 128.65, 128.28, 128.18, 128.15, 128.11, 127.92, 127.86, 127.25, 127.13, 126.64, 62.19, 62.15, 61.84, 61.80, 16.08, 16.04, 16.02, 15.98. **^{31}P NMR (162 MHz, $CDCl_3$) δ** 18.28.



Signal VWD1A, Wavelength=224 nm

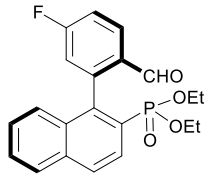
	Ret. Time	Area	Height	Area%
	10.199	3143.723	136.681	50.071
	13.283	3134.748	105.670	49.929
Total	23.482	6278.47	242.351	100.000



Signal VWD1A, Wavelength=224 nm

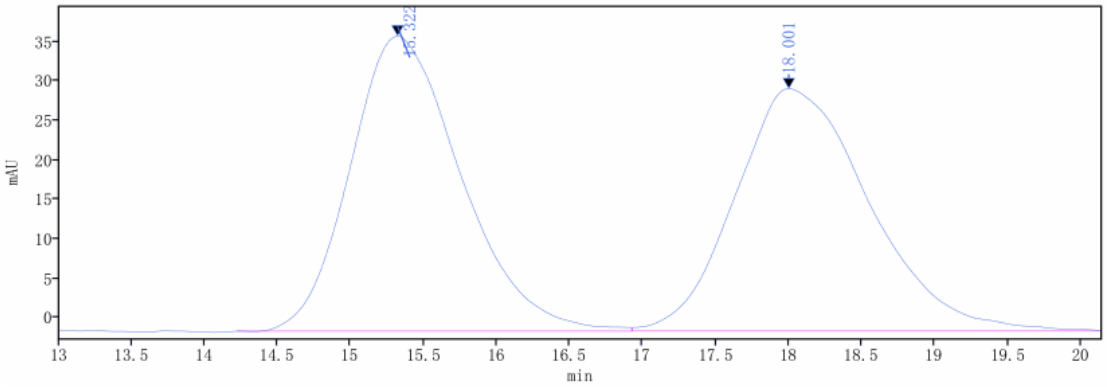
	Ret. Time	Area	Height	Area%
	10.155	65789.429	2812.236	98.054
	13.364	1305.660	49.346	1.946
Total	23.519	67095.09	2861.582	100.000

Diethyl (R)-(1-(5-fluoro-2-formylphenyl)naphthalen-2-yl)phosphonate (6ac)



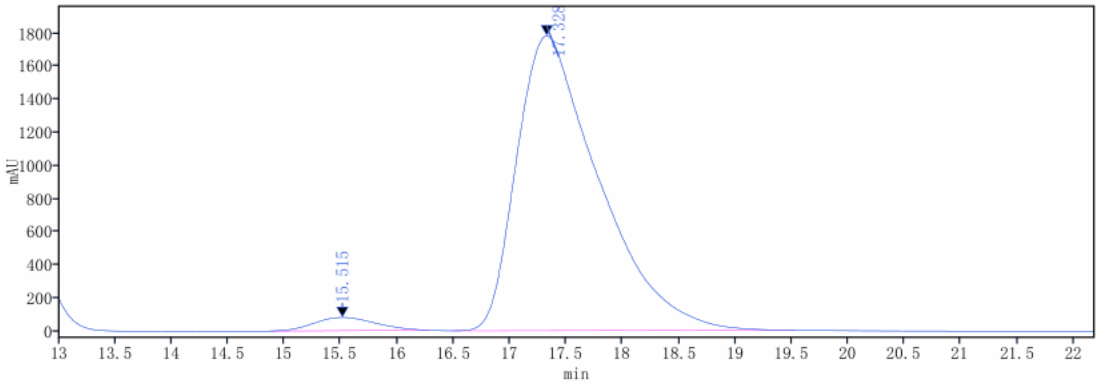
A flame-dried resealable Schlenk tube was charged with the aryl halide **4a** (34.2 mg, 0.1 mmol, 1.0 equiv), arylboronic acid **5c** (33.6 mg, 0.2 mmol, 2.0 equiv), and K_3PO_4 (42.4 mg, 0.2mmol, 2.0 equiv). The Schlenk tube was capped with a rubber septum, and twice evacuated and backfilled with argon. A solution of $Pd_2(dba)_3$ (1.0 mg, 1.0 mol%) and phosphine ***R*-L3** (1.38 mg, 0.024 mmol, 2.4 mol%) in 1/2 of the total amount of toluene (0.4 mL total per mmol aryl bromide) was sonicated for about 30 seconds and injected into the Schlenk tube followed by addition of the rest of toluene. The Schlenk tube was sealed, and the mixture was stirred at the room temperature for 24h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, filtered, and concentrated. The crude material was purified by column chromatography on silica gel affording 26.2 mg (68%) of **6ac** in 94% ee (determined by HPLC analysis (Chiralpak OD-H column, hexane/iPrOH, 98:2 v/v, flow rate 1 mL/min, λ = 224 nm, 25 °C), t_R (minor) = 15.515 min, t_R (major) = 17.328 min) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 9.35 (s, 1H), 8.19 – 8.10 (m, 2H), 8.04 (dd, *J* = 8.5, 3.7 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.10 (dd, *J* = 8.9, 2.6 Hz, 1H), 4.00 – 3.83 (m, 4H), 1.17 (dt, *J* = 16.8, 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 189.75, 164.25, 139.17, 139.11, 134.81, 131.98, 131.96, 129.50, 129.44, 128.72, 128.63, 128.35, 128.26, 127.98,

127.92, 127.58, 126.81, 126.68, 125.44, 119.29, 119.15, 116.22, 116.08, 62.27, 62.23, 62.03, 61.99, 16.09, 16.05, 16.02, 15.97. **^{19}F NMR (376 MHz, Chloroform-*d*) δ** -104.63. **^{31}P NMR (162 MHz, $CDCl_3$) δ** 18.12.



Signal VWD1A, Wavelength=224 nm

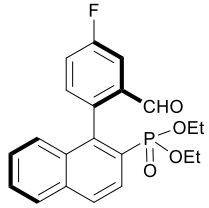
	Ret. Time	Area	Height	Area%
	15.322	1974.682	37.457	50.118
	18.001	1965.395	30.752	49.882
Total	33.323	3940.08	68.209	100.000



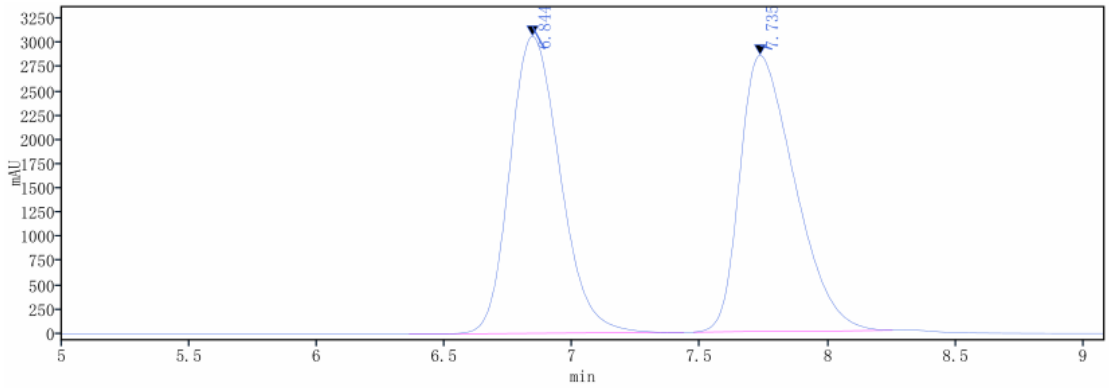
Signal VWD1A, Wavelength=224 nm

	Ret. Time	Area	Height	Area%
	15.515	3039.709	80.182	3.251
	17.328	90470.050	1782.503	96.749
Total	32.843	93509.76	1862.685	100.000

Diethyl (R)-(1-(4-fluoro-2-formylphenyl)naphthalen-2-yl)phosphonate (6ad)

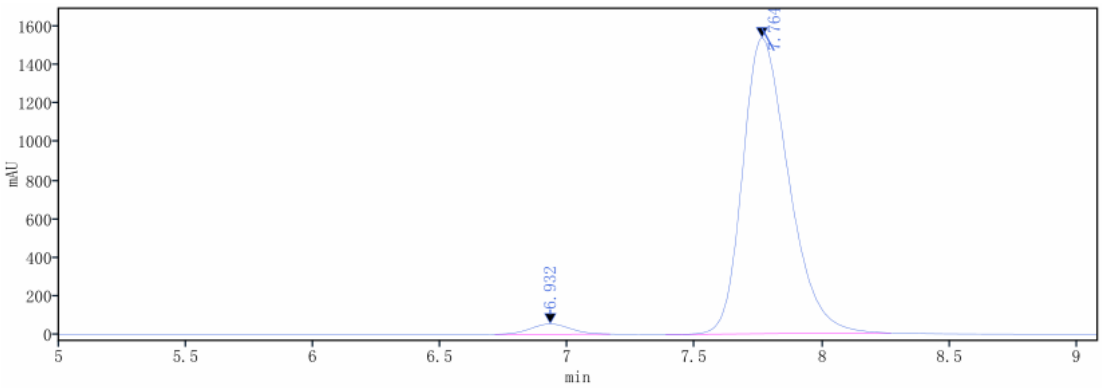


A flame-dried resealable Schlenk tube was charged with the aryl halide **4a** (34.2 mg, 0.1 mmol, 1.0 equiv), arylboronic acid **5d** (33.6 mg, 0.2 mmol, 2.0 equiv), and K_3PO_4 (42.4 mg, 0.2mmol, 2.0 equiv). The Schlenk tube was capped with a rubber septum, and twice evacuated and backfilled with argon. A solution of $Pd_2(dba)_3$ (1.0 mg, 1.0 mol%) and phosphine ***R*-L3** (1.38 mg, 0.024 mmol, 2.4 mol%) in 1/2 of the total amount of toluene (0.4 mL total per mmol aryl bromide) was sonicated for about 30 seconds and injected into the Schlenk tube followed by addition of the rest of toluene. The Schlenk tube was sealed, and the mixture was stirred at the room temperature for 24h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, filtered, and concentrated. The crude material was purified by column chromatography on silica gel affording 24.1 mg (60%) of **6ad** in 94% ee (determined by HPLC analysis (Chiralpak OD-H column, hexane/iPrOH, 99:1 v/v, flow rate 0.4 mL/min, λ = 254 nm, 25 °C), t_R (minor) = 6.932 min, t_R (major) = 7.764 min) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 9.35 (d, *J* = 3.2 Hz, 1H), 8.12 (dd, *J* = 12.2, 8.5 Hz, 1H), 8.04 (dd, *J* = 8.6, 3.7 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.80 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.61 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.27 – 7.20 (m, 1H), 3.98 – 3.82 (m, 4H), 1.17 (dt, *J* = 11.8, 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 190.14, 162.80 (d, *J* = 249.9 Hz), 137.03, 136.99, 134.84, 134.13, 134.08, 128.62, 128.53, 128.31, 128.25, 127.84, 127.78, 127.50, 127.16, 126.91, 125.91, 120.16, 120.02, 112.91, 112.77, 62.35, 62.31, 62.01, 61.97, 16.15, 16.11, 16.08, 16.04. **^{19}F NMR (376 MHz, Chloroform-*d*) δ** -111.7. **^{31}P NMR (162 MHz, $CDCl_3$) δ** 18.95.



Signal VWD1B, Wavelength=254 nm

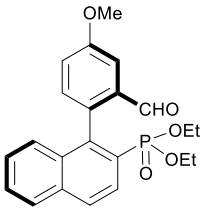
	Ret. Time	Area	Height	Area%
	6.844	41936.946	3067.014	49.597
	7.735	42618.851	2854.403	50.403
Total	14.579	84555.80	5921.417	100.000



Signal VWD1B, Wavelength=254 nm

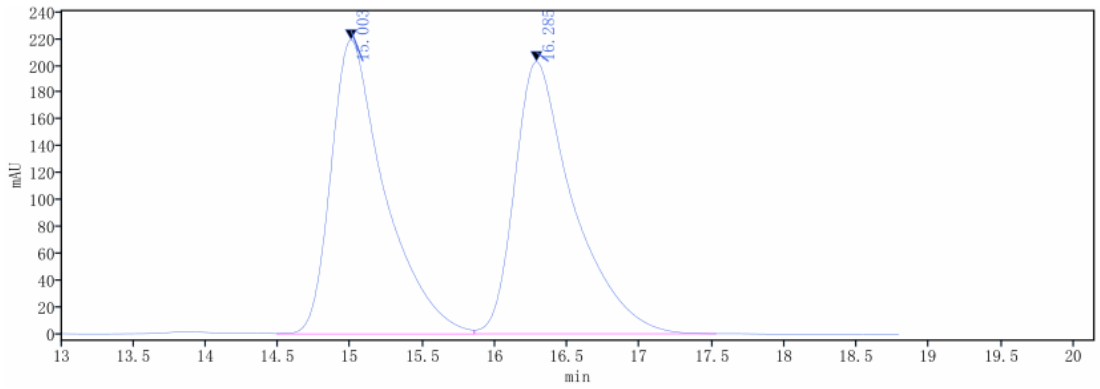
	Ret. Time	Area	Height	Area%
	6.932	571.179	53.348	2.859
	7.764	19408.551	1541.387	97.141
Total	14.695	19979.73	1594.735	100.000

Diethyl (R)-(1-(4-methoxy-2-methylphenyl)naphthalen-2-yl)phosphonate (6ae)



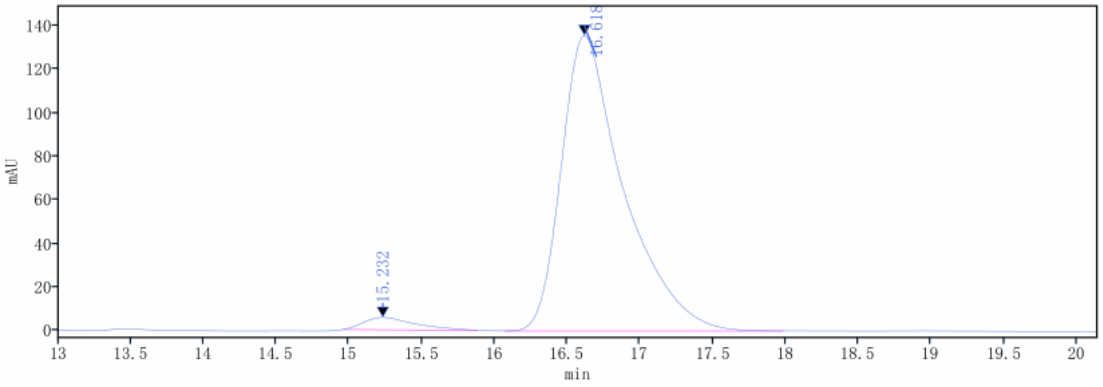
A flame-dried resealable Schlenk tube was charged with the aryl halide **4a** (34.2 mg, 0.1 mmol, 1.0 equiv), arylboronic acid **5e** (36.0 mg, 0.2 mmol, 2.0 equiv), and K_3PO_4 (42.4 mg, 0.2mmol, 2.0 equiv). The Schlenk tube was capped with a rubber septum, and twice evacuated and backfilled with argon. A solution of $Pd_2(dba)_3$ (1.0 mg, 1.0 mol%) and phosphine ***R*-L3** (1.38 mg, 0.024 mmol, 2.4 mol%) in 1/2 of the total amount of toluene (0.4 mL total per mmol aryl bromide) was sonicated for about 30 seconds and injected into the Schlenk tube followed by addition of the rest of toluene. The Schlenk tube was sealed, and the mixture was stirred at the room temperature for 24h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, filtered, and concentrated. The crude material was purified by column chromatography on silica gel affording 34.5 mg (91%) of **6ae** in 94% ee (determined by HPLC analysis (Chiralpak AD-H column, hexane/iPrOH, 95:5 v/v, flow rate 0.9 mL/min, λ = 254 nm, 25 °C), t_R (minor) = 15.232 min, t_R (major) = 16.618 min) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 9.35 (s, 1H), 8.19 – 8.10 (m, 2H), 8.04 (dd, *J* = 8.5, 3.7 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.10 (dd, *J* = 8.9, 2.6 Hz, 1H), 4.00 – 3.83 (m, 4H), 1.17 (dt, *J* = 16.8, 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 191.25, 159.78,

136.19, 134.85, 134.50, 133.33, 128.23, 128.14, 128.11, 127.92, 127.86, 127.23, 120.41, 109.12, 62.20, 62.16, 61.89, 61.85, 55.61, 16.16, 16.11, 16.09, 16.05. **^{31}P NMR (162 MHz, $CDCl_3$) δ** 18.40.



Signal VWD1B, Wavelength=254 nm

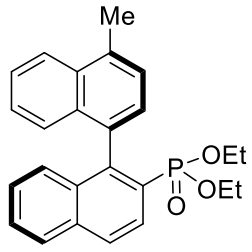
	Ret. Time	Area	Height	Area%
	15.003	5693.852	219.330	49.825
	16.285	5733.912	203.035	50.175
Total	31.288	11427.76	422.364	100.000



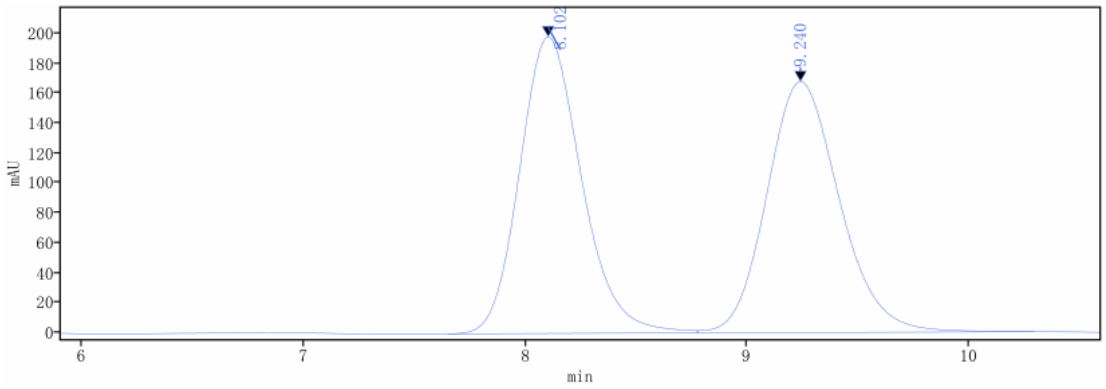
Signal VWD1B, Wavelength=254 nm

	Ret. Time	Area	Height	Area%
	15.232	137.497	5.647	3.293
	16.618	4038.262	135.795	96.707
Total	31.850	4175.76	141.442	100.000

Diethyl (R)-(4'-methyl-[1,1'-binaphthalen]-2-yl)phosphonate (6af)

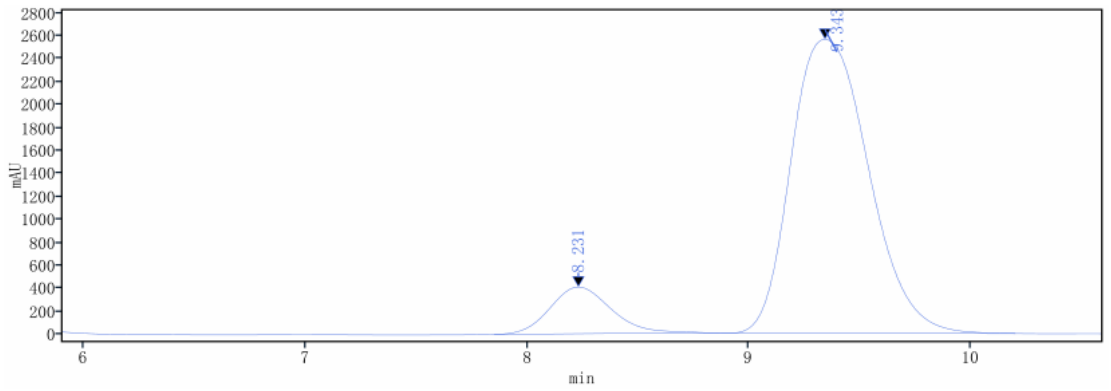


A flame-dried resealable Schlenk tube was charged with the aryl halide **4a** (34.2 mg, 0.1 mmol, 1.0 equiv), arylboronic acid **5f** (37.2 mg, 0.2 mmol, 2.0 equiv), and K_3PO_4 (42.4 mg, 0.2mmol, 2.0 equiv). The Schlenk tube was capped with a rubber septum, and twice evacuated and backfilled with argon. A solution of $Pd_2(dba)_3$ (1.0 mg, 1.0 mol%) and phosphine ***R*-L3** (1.38 mg, 0.024 mmol, 2.4 mol%) in 1/2 of the total amount of toluene (0.4 mL total per mmol aryl bromide) was sonicated for about 30 seconds and injected into the Schlenk tube followed by addition of the rest of toluene. The Schlenk tube was sealed, and the mixture was stirred at the room temperature for 24h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, filtered, and concentrated. The crude material was purified by column chromatography on silica gel affording 33.4 mg (82%) of **6af** in 78% ee (determined by HPLC analysis (Chiralpak AD-H column, hexane/iPrOH, 93:7 v/v, flow rate 1 mL/min, λ = 224 nm, 25 °C), t_R (minor) = 8.231 min, t_R (major) = 9.343 min) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.20 (dd, *J* = 12.1, 8.6 Hz, 1H), 8.08 (dt, *J* = 8.5, 0.9 Hz, 1H), 8.02 (dd, *J* = 3.8, 0.8 Hz, 1H), 7.93 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.55 – 7.42 (m, 3H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.27 – 7.17 (m, 3H), 7.09 (dd, *J* = 8.5, 1.1 Hz, 1H), 3.82 – 3.56 (m, 4H), 2.81 (d, *J* = 1.0 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.78 – 0.64 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 134.91, 134.50, 134.06, 133.37, 133.35, 132.27, 128.72, 128.65, 128.36, 127.94, 127.87, 127.78, 127.61, 127.51, 127.32, 126.61, 125.74, 125.47, 125.39, 124.14, 61.78, 61.74, 61.59, 61.55, 19.69, 15.95, 15.91, 15.48, 15.44. **^{31}P NMR (162 MHz, $CDCl_3$) δ** 18.98.



Signal VWD1A, Wavelength=224 nm

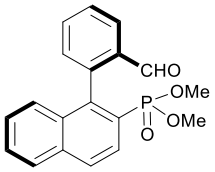
	Ret. Time	Area	Height	Area%
	8.102	3839.726	198.130	50.176
	9.240	3812.730	167.684	49.824
Total	17.342	7652.46	365.814	100.000



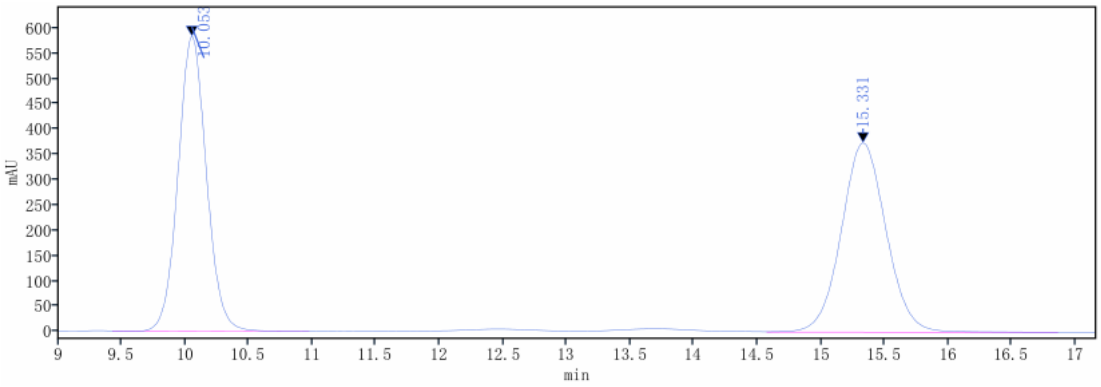
Signal VWD1A, Wavelength=224 nm

	Ret. Time	Area	Height	Area%
	8.231	7734.368	406.283	11.083
	9.343	62050.123	2553.882	88.917
Total	17.573	69784.49	2960.164	100.000

Dimethyl (R)-(1-(2-formylphenyl)naphthalen-2-yl)phosphonate (6ba)

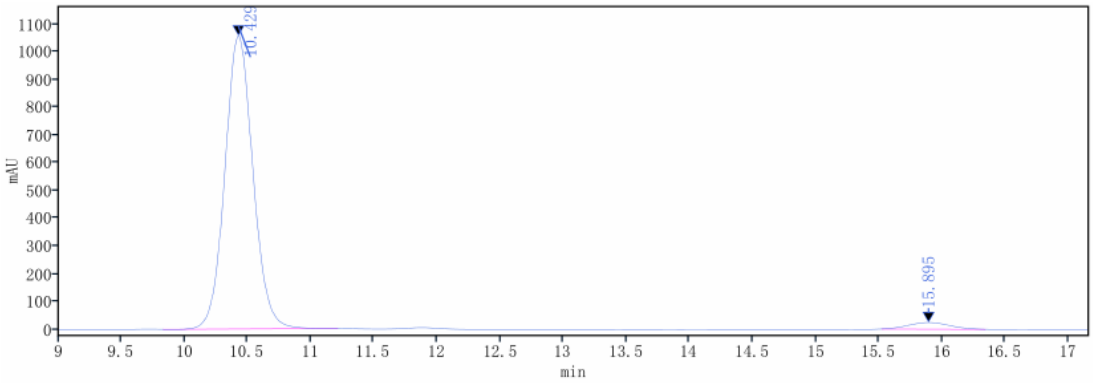


A flame-dried resealable Schlenk tube was charged with the aryl halide **4b** (31.3 mg, 0.1 mmol, 1.0 equiv), arylboronic acid **5a** (27.0 mg, 0.2mmol, 2.0 equiv), and K_3PO_4 (42.4 mg, 0.2mmol, 2.0 equiv). The Schlenk tube was capped with a rubber septum, and twice evacuated and backfilled with argon. A solution of $Pd_2(dba)_3$ (1.0 mg, 1.0 mol%) and phosphine ***R*-L3** (1.38 mg, 0.024 mmol, 2.4 mol%) in 1/2 of the total amount of toluene (0.4 mL total per mmol aryl bromide) was sonicated for about 30 seconds and injected into the Schlenk tube followed by addition of the rest of toluene. The Schlenk tube was sealed, and the mixture was stirred at the room temperature for 24h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, filtered, and concentrated. The crude material was purified by column chromatography on silica gel affording 27.8 mg (82%) of **6ba** in 94% ee (Chiralpak AD-H column, hexane/iPrOH, 95:5 v/v, flow rate 1 mL/min, λ = 224 nm, 25 °C), t_R (major) = 10.429 min, t_R (minor) = 15.895 min) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 9.44 (s, 1H), 8.18 – 8.06 (m, 2H), 8.02 (dd, *J* = 8.6, 3.8 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.71 (td, *J* = 7.5, 1.3 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.45 – 7.35 (m, 2H), 7.29 – 7.26 (m, 1H), 3.50 (dd, *J* = 48.3, 11.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 191.17, 141.69, 135.09, 134.96, 132.91, 131.94, 128.82, 128.41, 128.36, 128.31, 128.20, 128.05, 127.99, 127.39, 127.21, 126.90, 125.70, 52.65, 52.61, 52.37, 52.33. **^{31}P NMR (162 MHz, $CDCl_3$) δ** 20.7.



Signal VWD1A, Wavelength=224 nm

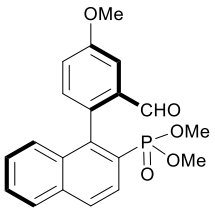
	Ret. Time	Area	Height	Area%
	10.053	9051.799	582.894	49.750
	15.331	9142.749	374.150	50.250
Total	25.385	18194.55	957.045	100.000



Signal VWD1A, Wavelength=224 nm

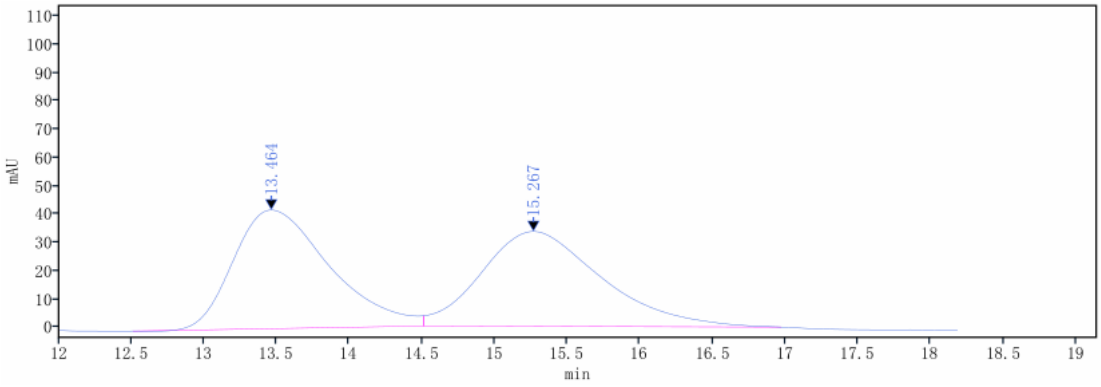
	Ret. Time	Area	Height	Area%
	10.429	16397.926	1057.313	96.834
	15.895	536.185	23.895	3.166
Total	26.323	16934.11	1081.208	100.000

Dimethyl (R)-(1-(2-formyl-4-methoxyphenyl)naphthalen-2-yl)phosphonate (6be)



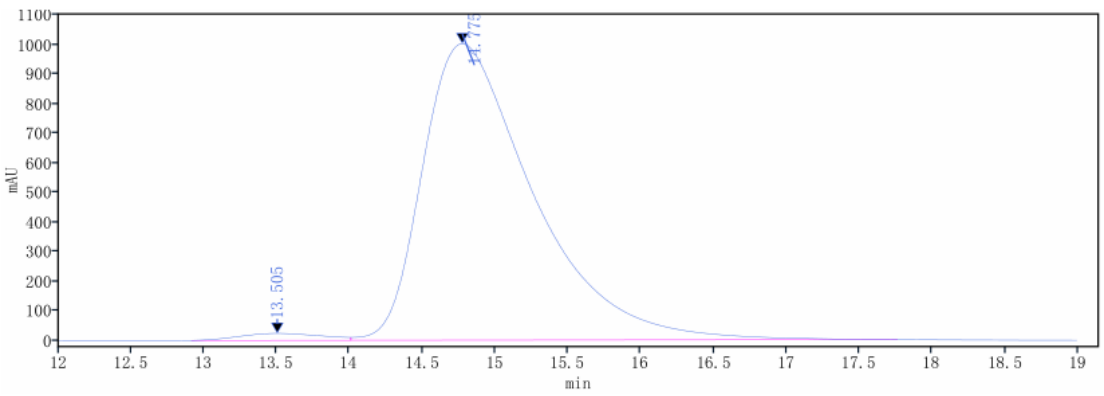
A flame-dried resealable Schlenk tube was charged with the aryl halide **4b** (31.3 mg, 0.1 mmol, 1.0 equiv), arylboronic acid **5e** (36.0 mg, 0.2 mmol, 2.0 equiv), and K_3PO_4 (42.4 mg, 0.2mmol, 2.0 equiv). The Schlenk tube was capped with a rubber

septum, and twice evacuated and backfilled with argon. A solution of $Pd_2(dba)_3$ (1.0 mg, 1.0 mol%) and phosphine ***R*-L3** (1.38 mg, 0.024 mmol, 2.4 mol%) in 1/2 of the total amount of toluene (0.4 mL total per mmol aryl bromide) was sonicated for about 30 seconds and injected into the Schlenk tube followed by addition of the rest of toluene. The Schlenk tube was sealed, and the mixture was stirred at the room temperature for 24h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, filtered, and concentrated. The crude material was purified by column chromatography on silica gel affording 29.7 mg (84%) of **6be** in 96% ee (determined by HPLC analysis (Chiralpak OD-H column, hexane/iPrOH, 90:10 v/v, flow rate 1 mL/min, λ = 224 nm, 25 °C), t_R (minor) = 13.505 min, t_R (major) = 14.775 min) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 9.38 (s, 1H), 8.09 (dd, *J* = 12.1, 8.5 Hz, 1H), 8.04 – 7.99 (m, 1H), 7.97 – 7.92 (m, 1H), 7.65 – 7.57 (m, 2H), 7.43 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.32 – 7.26 (m, 3H), 3.97 (s, 3H), 3.54 (dd, *J* = 34.5, 11.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 190.98, 159.80, 141.02, 136.07, 134.97, 134.23, 134.19, 133.74, 133.63, 133.08, 128.30, 128.21, 128.14, 128.02, 127.96, 127.30, 127.25, 126.12, 124.87, 120.45, 109.30, 55.59, 52.64, 52.60, 52.38, 52.34. **^{31}P NMR (162 MHz, $CDCl_3$) δ** 20.59.



Signal VWD1A, Wavelength=224 nm

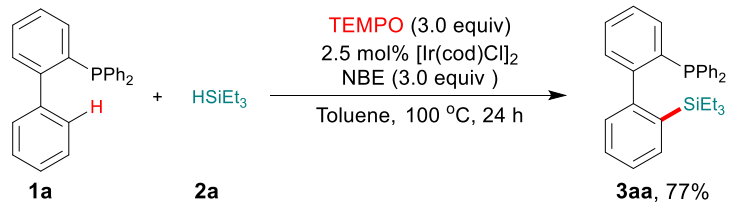
	Ret. Time	Area	Height	Area%
	13.464	1926.785	41.938	50.056
	15.267	1922.502	33.522	49.944
Total	28.731	3849.29	75.460	100.000



Signal VWD1A, Wavelength=224 nm

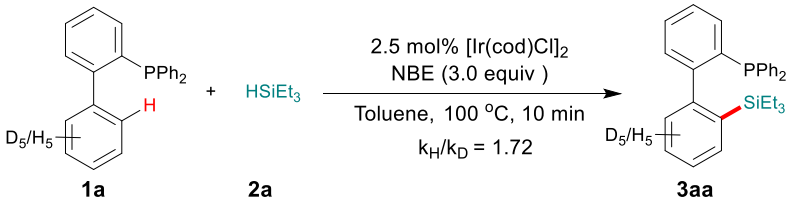
	Ret. Time	Area	Height	Area%
	13.505	909.133	23.315	1.684
	14.775	53090.709	1001.547	98.316
Total	28.279	53999.84	1024.862	100.000

7. Mechanistic experiments.



1a **2a** **3aa**, 77%

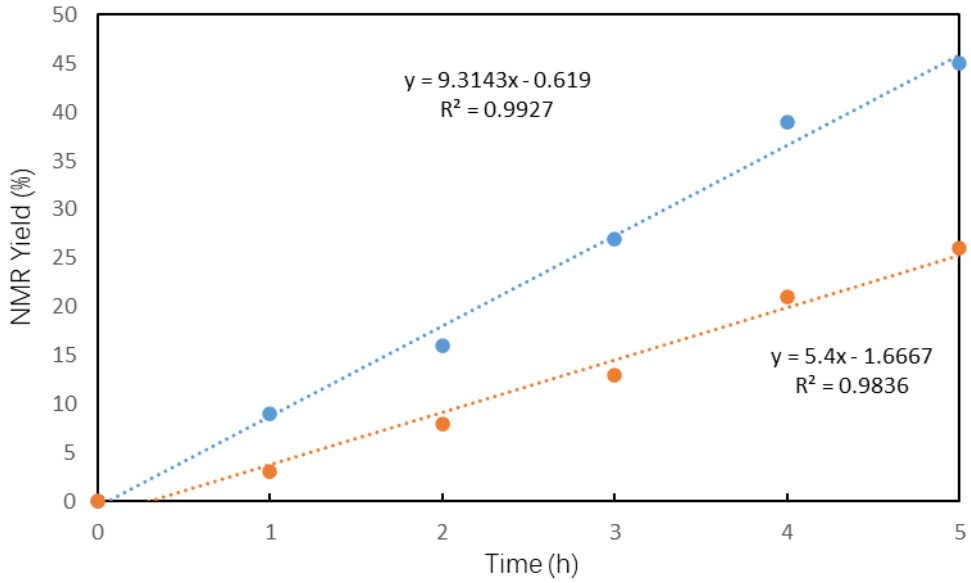
In a Schlenk tube, monophosphine ligands **1a** (67.6 mg, 1.0 equiv, 0.2 mmol), hydrosilanes **2a** (69.6 mg, 3.0 equiv, 0.6 mmol), $[Ir(COD)Cl]_2$ (2.5 mol%, 3.4 mg, 0.05 mmol), norbornene (56.4 mg, 3.0 equiv, 0.6 mmol), and TEMPO (93.6 mg, 3.0 equiv, 0.6 mmol) were dissolved in toluene (1.0 mL). The mixture was stirred at 100 °C under argon for 24 hours. Upon the completion of the reaction, the solvent was removed. The crude mixture was directly subjected to column Chromatography on silica gel using PE/EA as the eluent to yield the desired product **3aa** (77%, 69.6 mg).



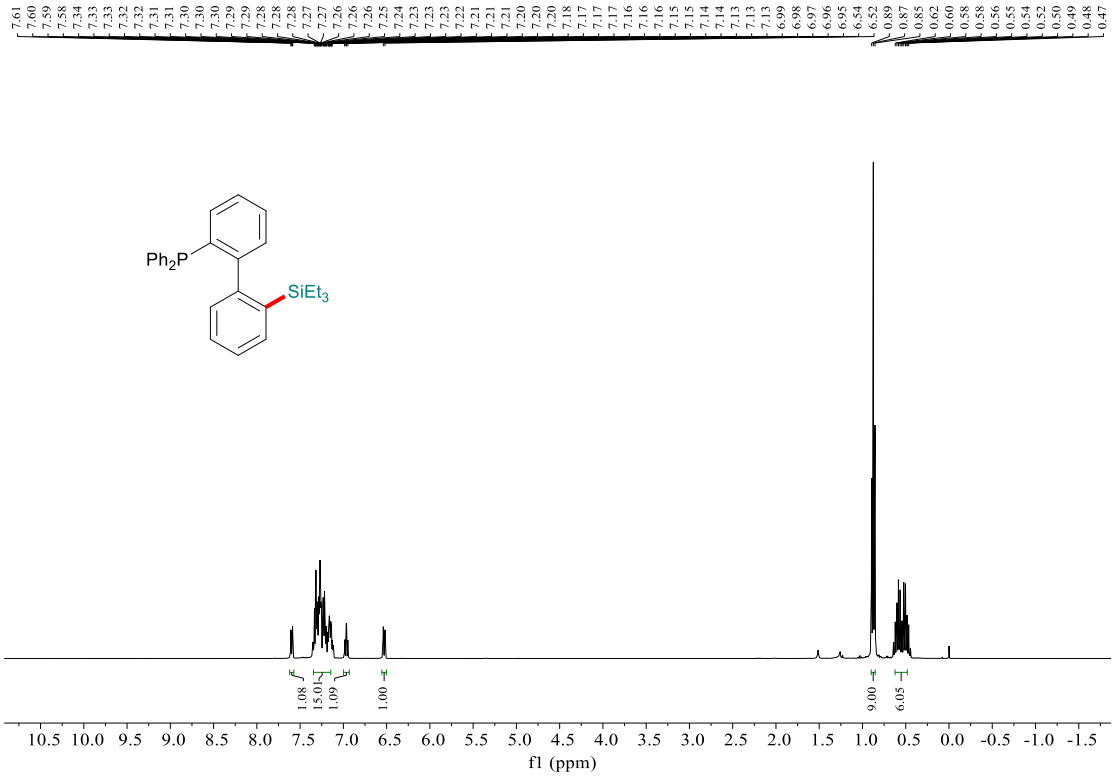
1a **2a** **3aa**

The reaction of **D-1a** (0.20 mmol), **2a** (0.60 mmol) and $[Ir(COD)Cl]_2$ (0.005 mmol) in toluene (1.0 mL) at 100 ºC under Ar for the indicated time (five parallel runs). And Parallel experiment was conducted using **1a** to replace **D-1a** under the above standard condition. The result was analyzed by ^1H NMR spectrum. For **1a**, y = 9.3143x-0.619, R^2

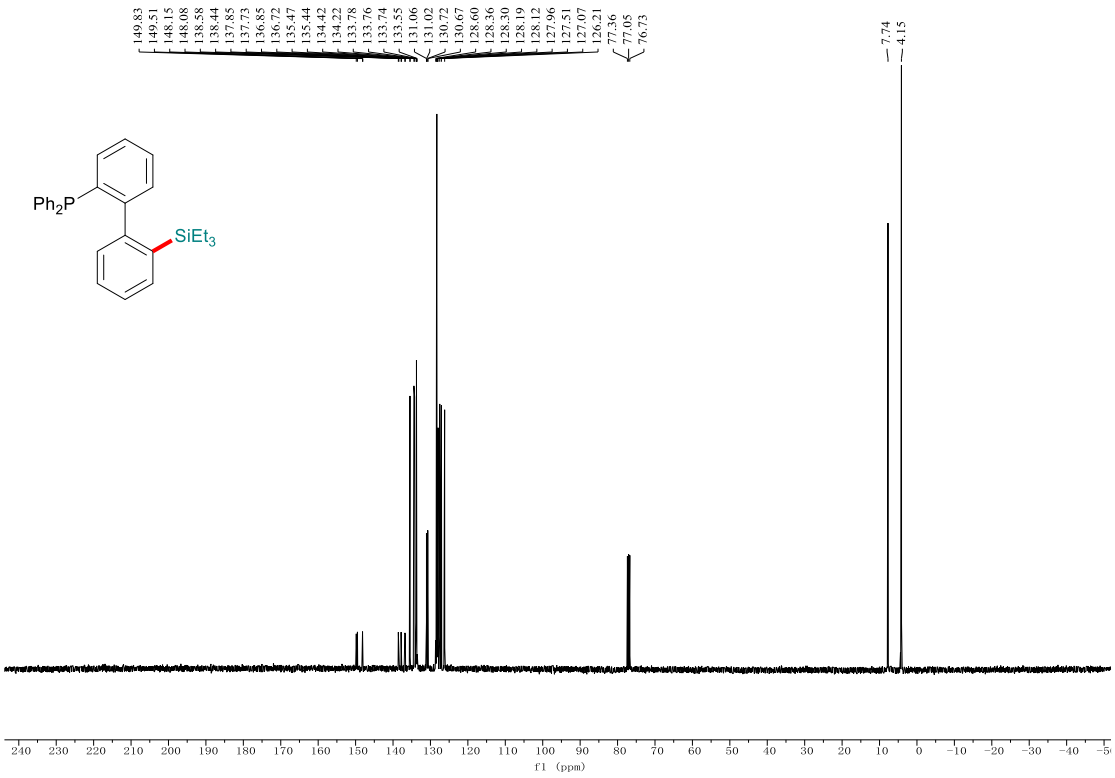
= 0.9927; for **D-1a**, y = 5.4x-1.6667, R2 = 0.9836. KIE value (1.72) was determined by comparing the relative initial rates.



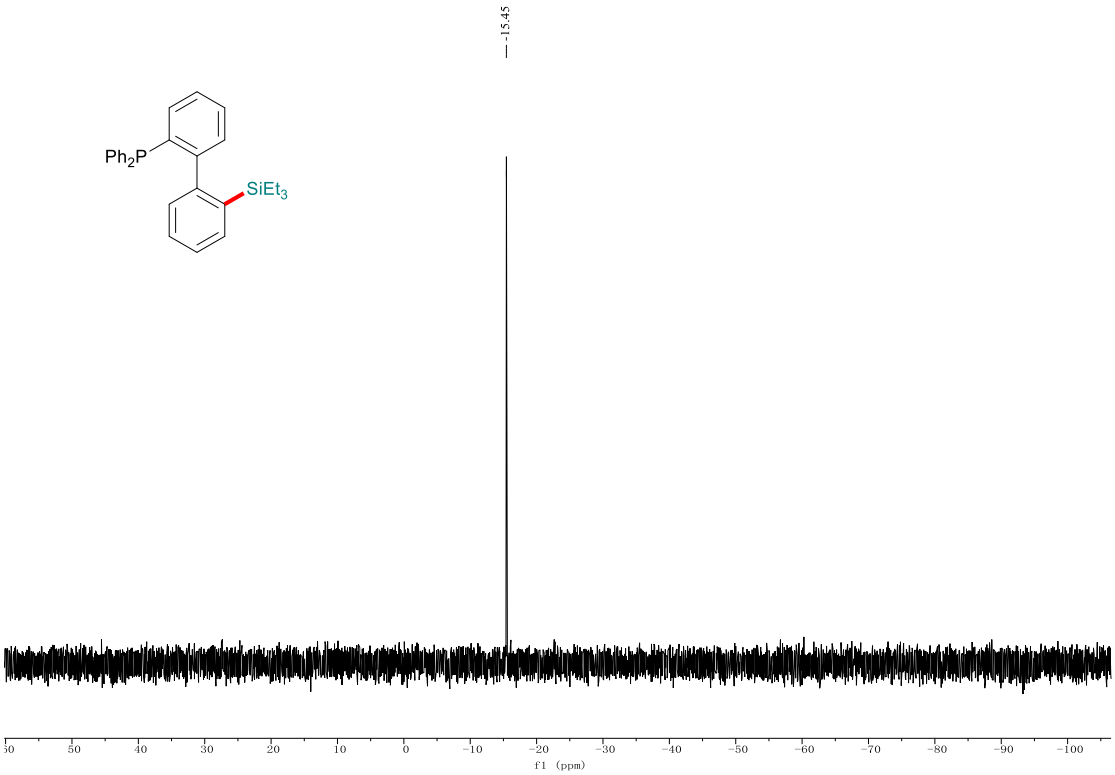
8. NMR Spectra



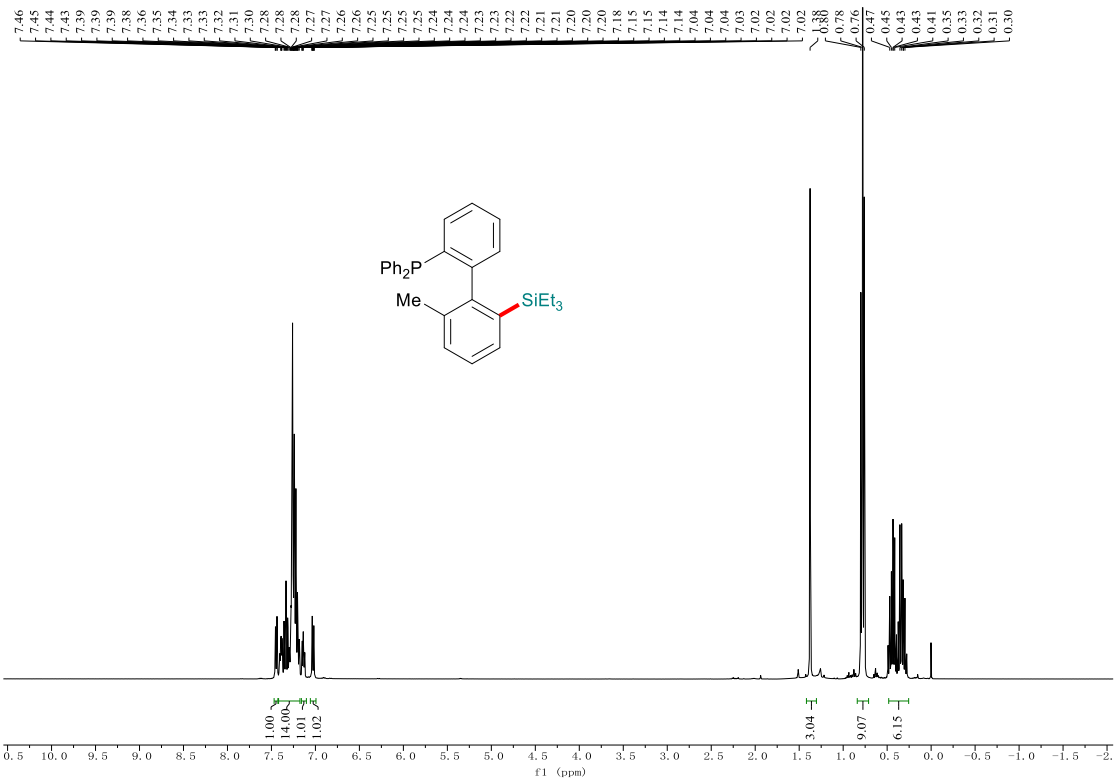
^{1}H NMR Spectrum of Compound **3aa**



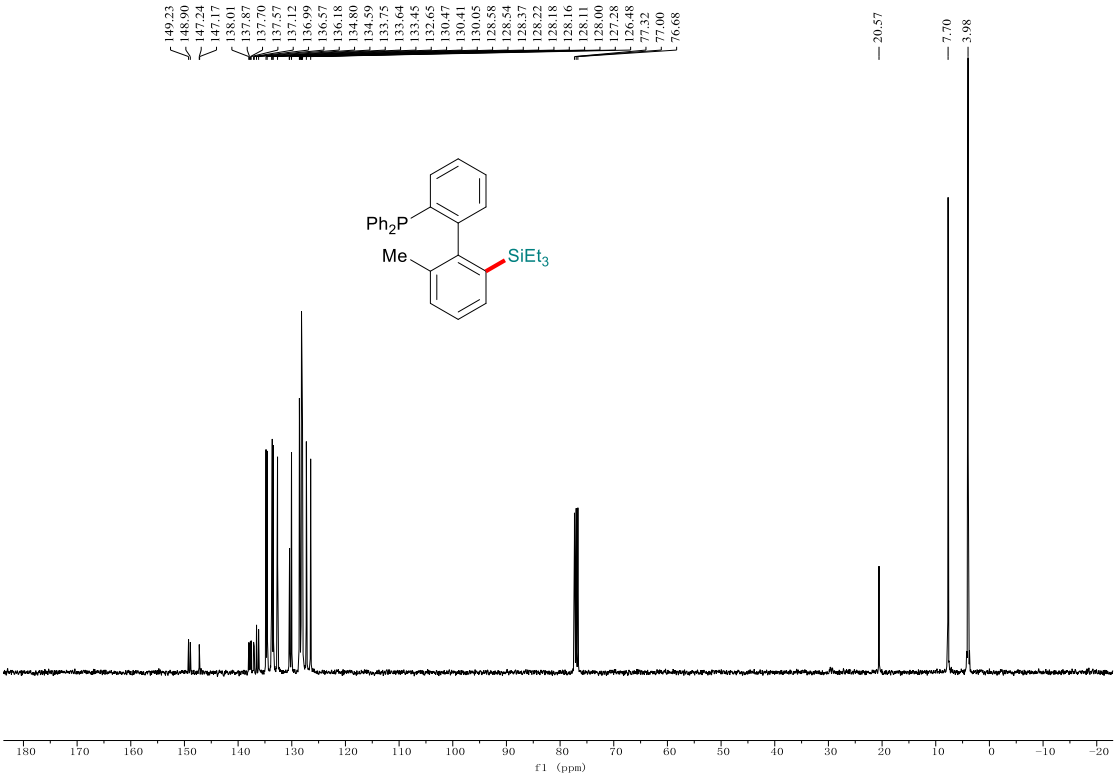
^{13}C NMR Spectrum of Compound **3aa**



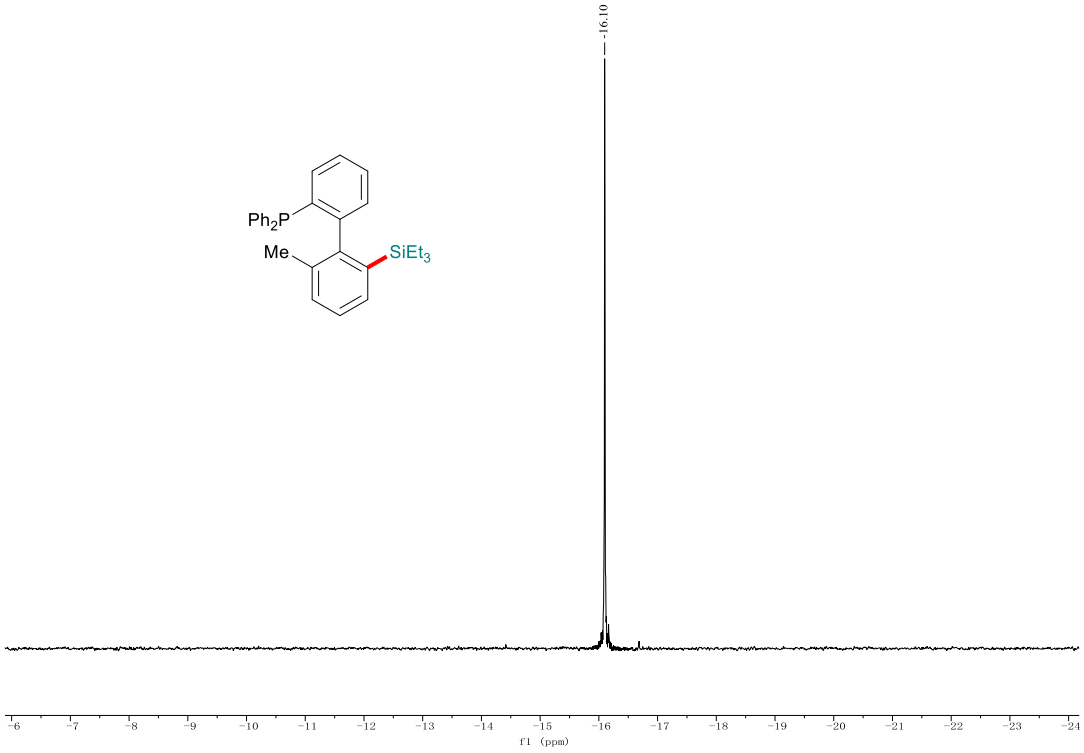
^{31}P NMR Spectrum of Compound **3aa**



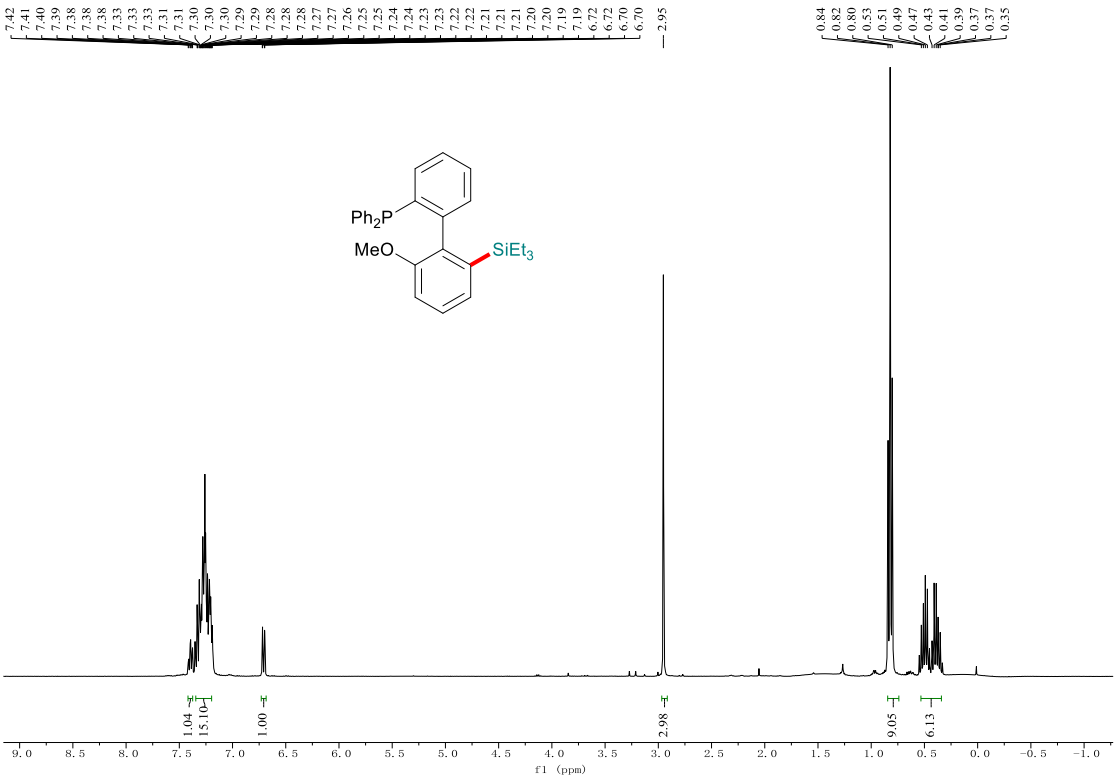
^{1}H NMR Spectrum of Compound **3ba**



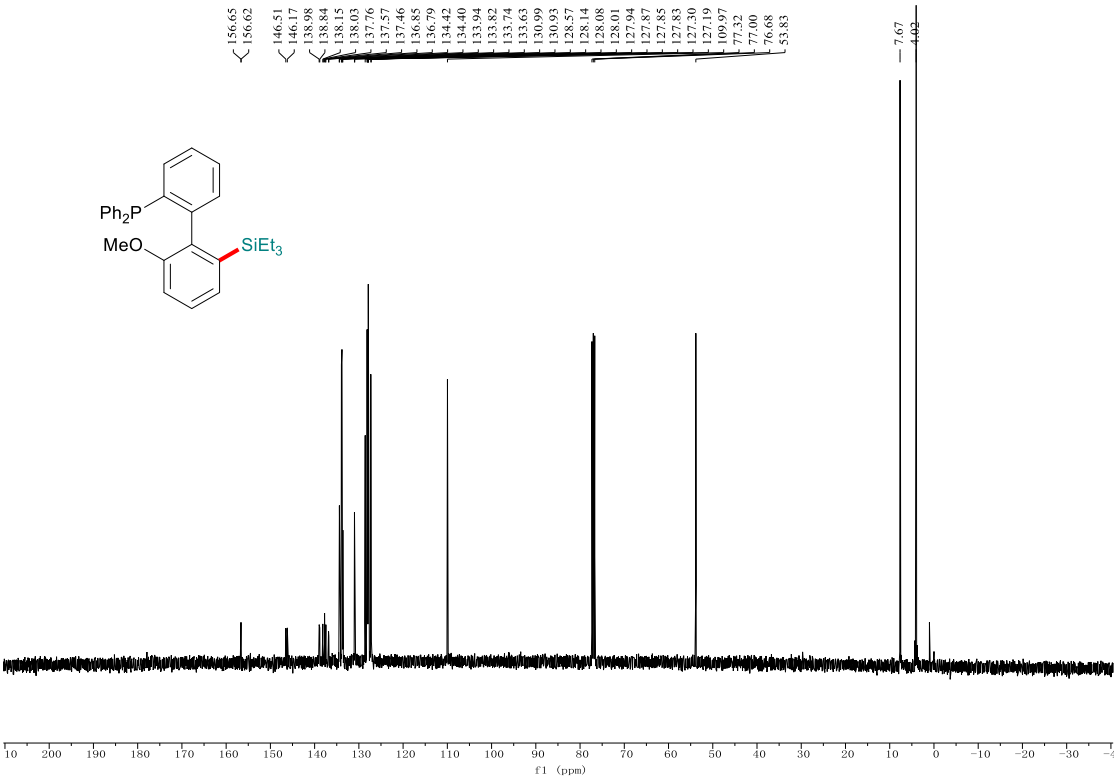
^{13}C NMR Spectrum of Compound **3ba**



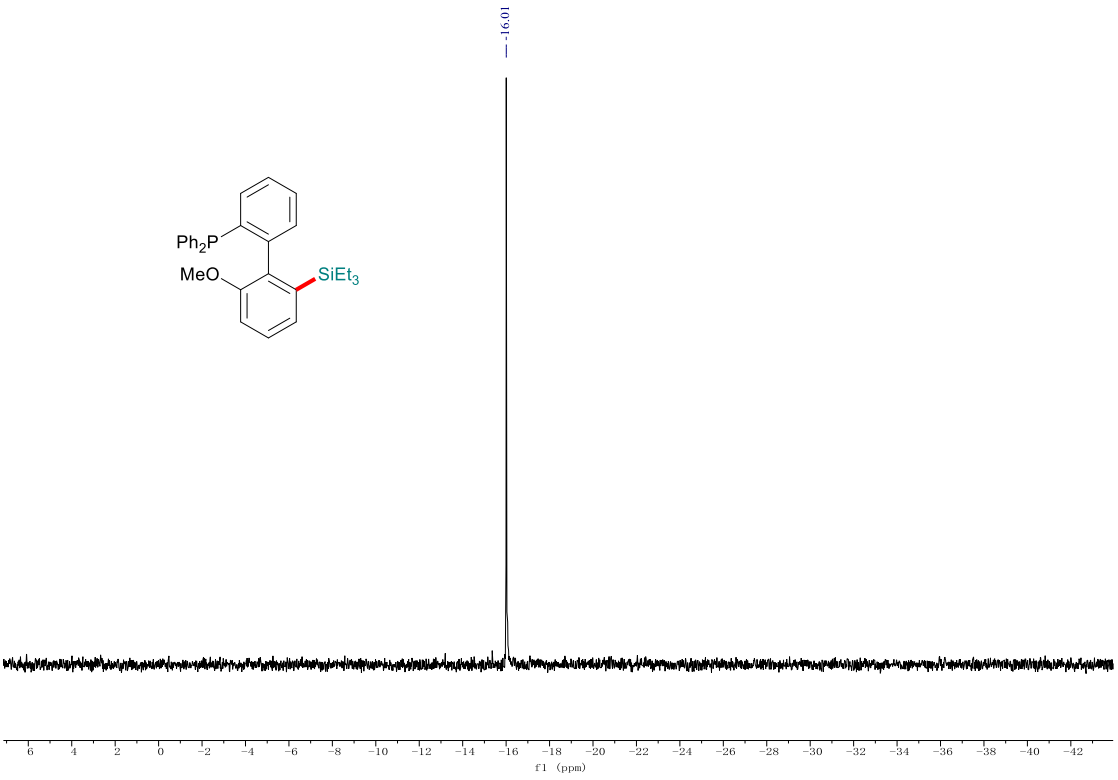
^{31}P NMR Spectrum of Compound **3ba**



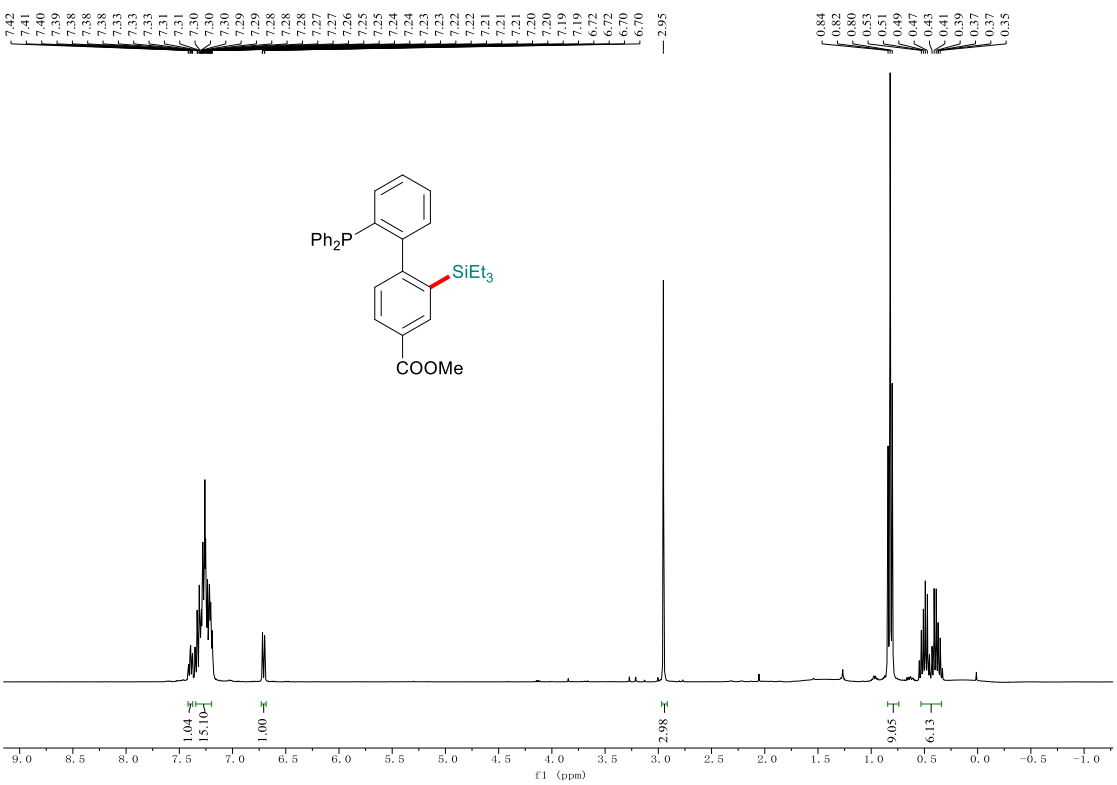
^{1}H NMR Spectrum of Compound **3ca**



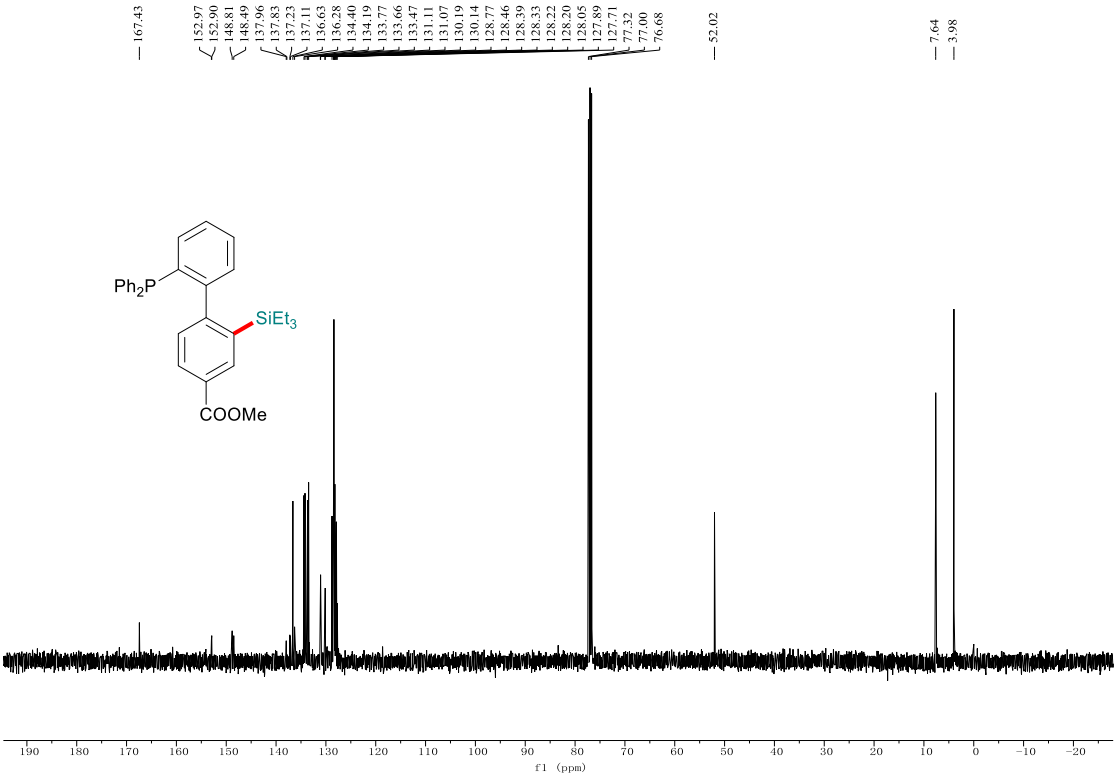
^{13}C NMR Spectrum of Compound **3ca**



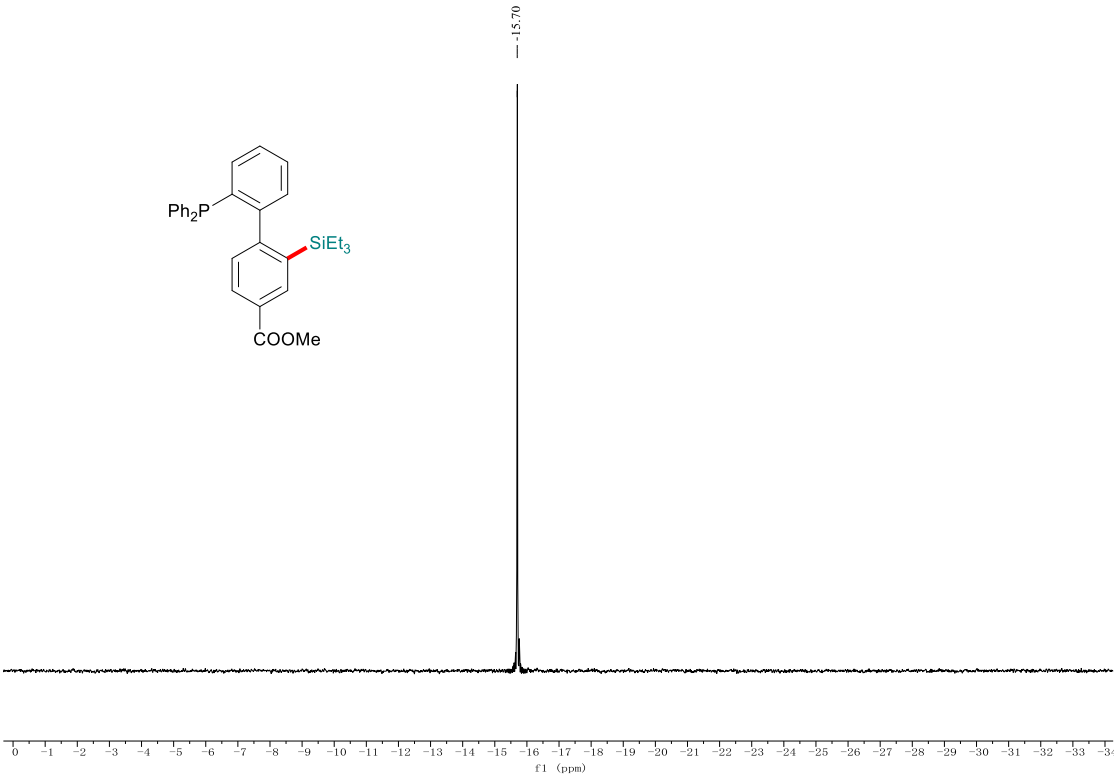
^{31}P NMR Spectrum of Compound **3ca**



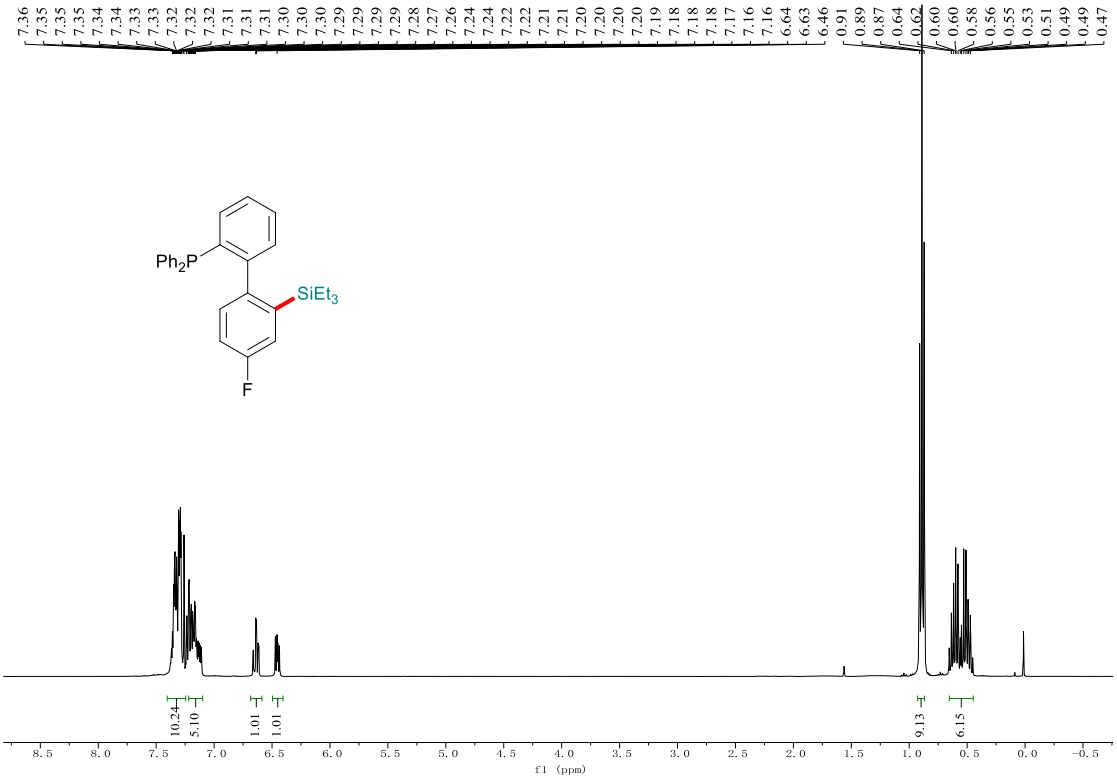
^{1}H NMR Spectrum of Compound **3da**



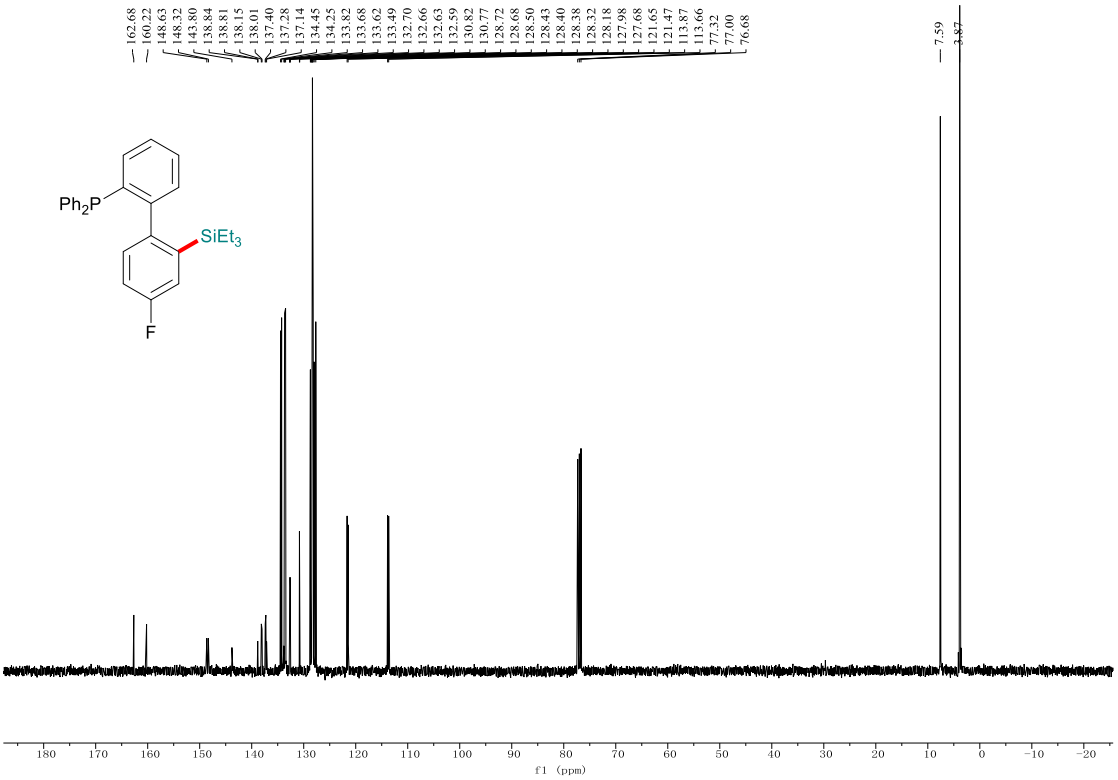
^{13}C NMR Spectrum of Compound **3da**



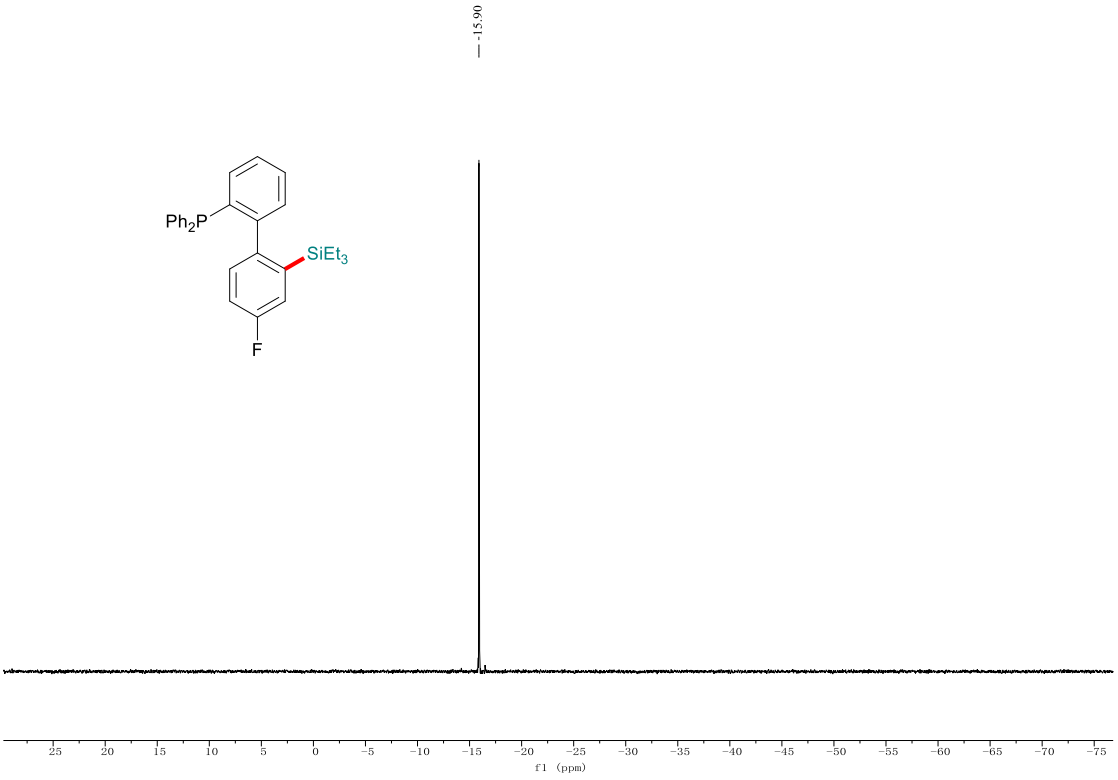
^{31}P NMR Spectrum of Compound **3da**



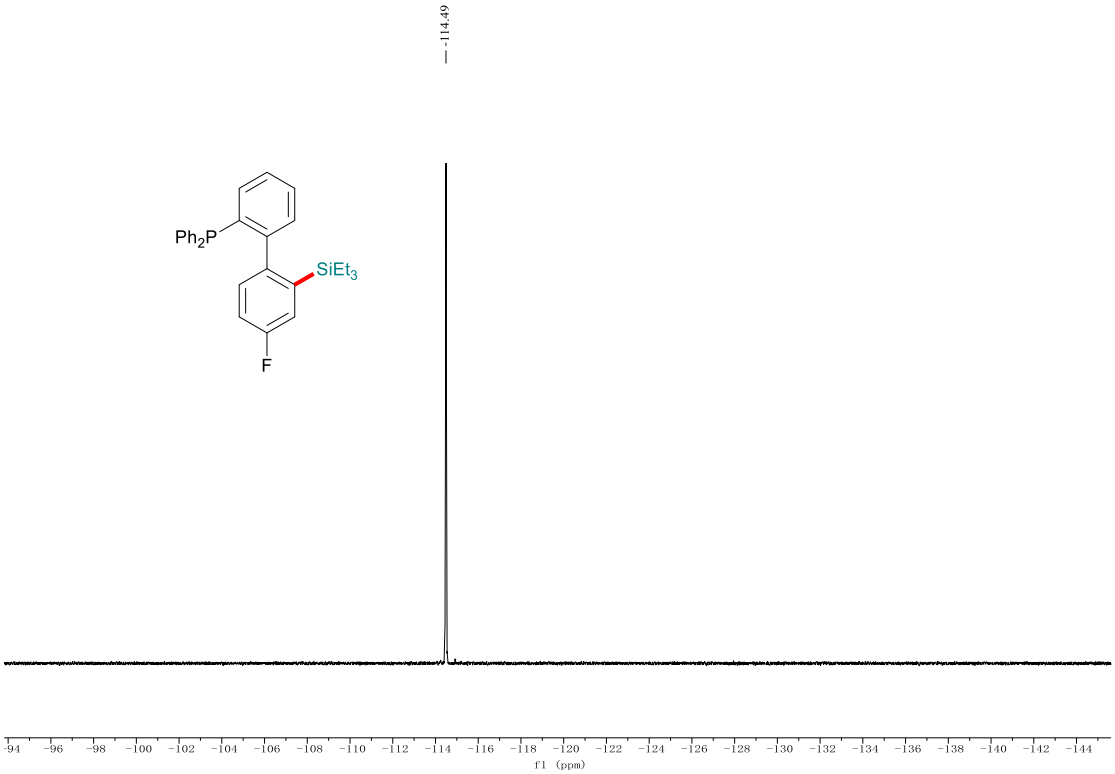
^{1}H NMR Spectrum of Compound **3ea**



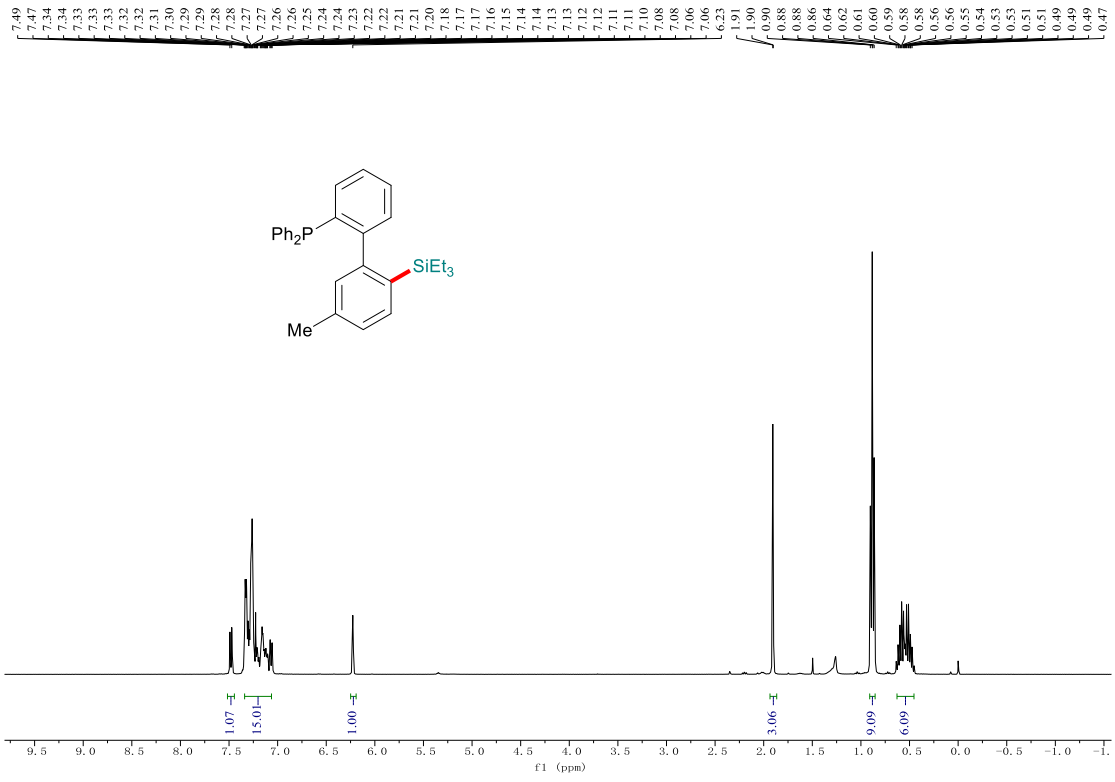
^{13}C NMR Spectrum of Compound **3ea**



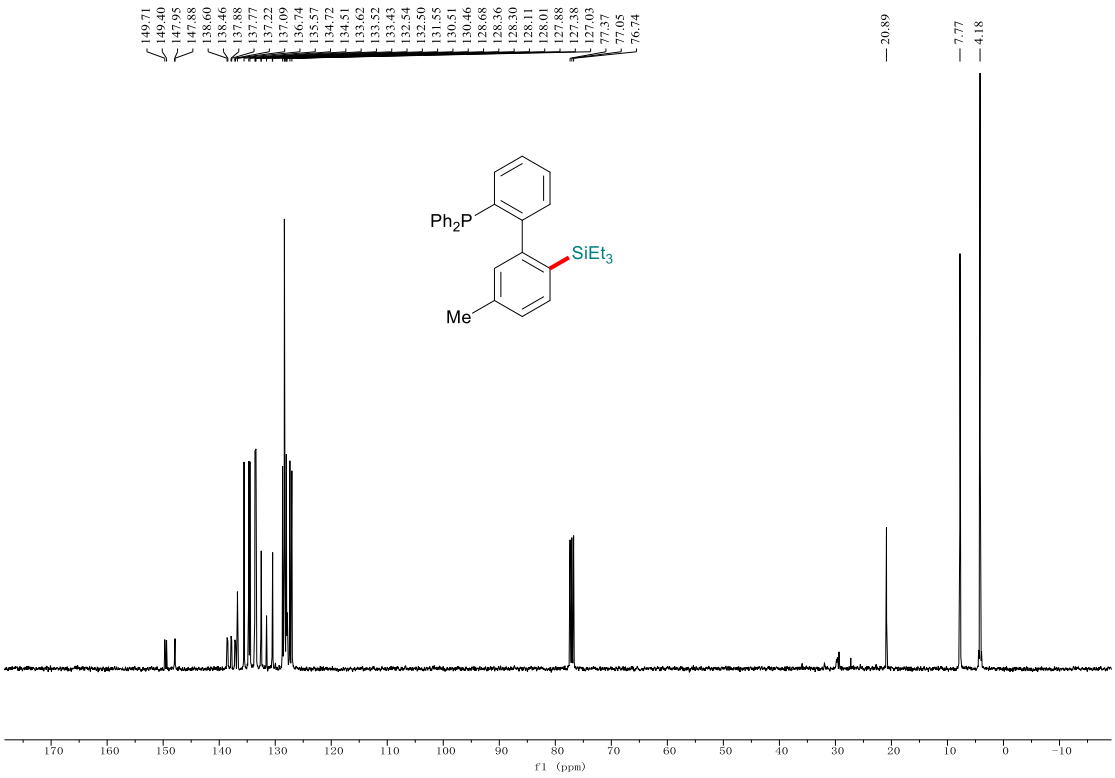
^{31}P NMR Spectrum of Compound **3ea**



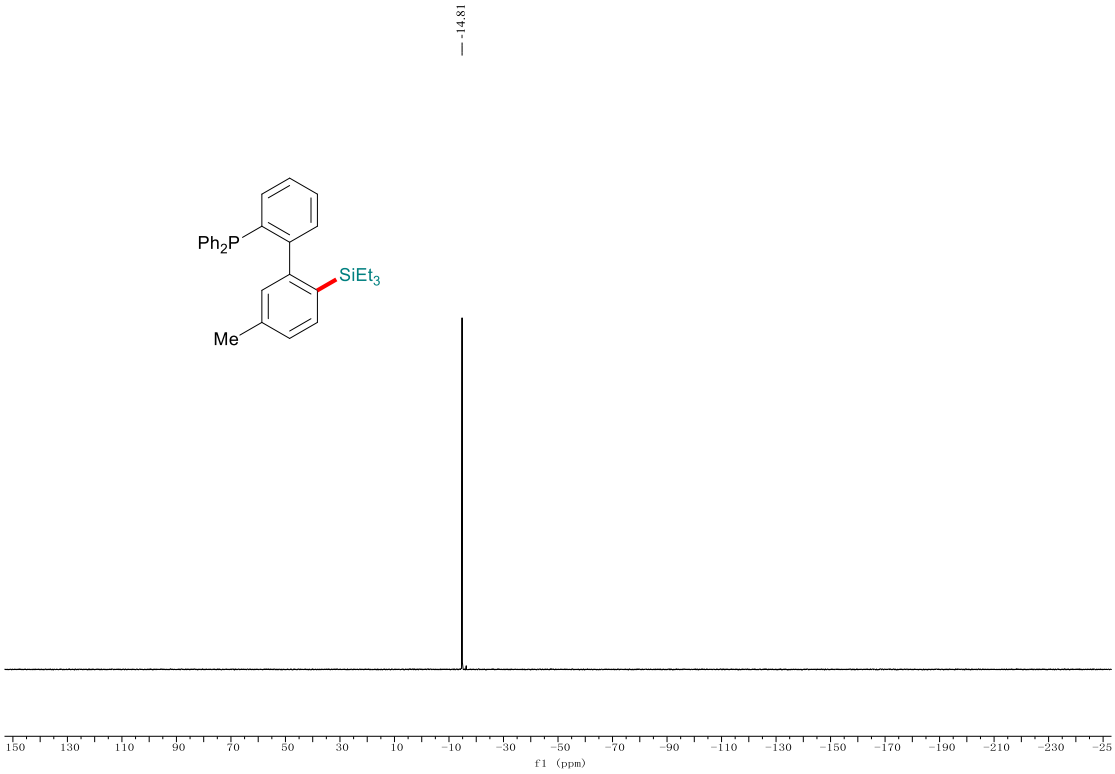
^{19}F NMR Spectrum of Compound **3ea**



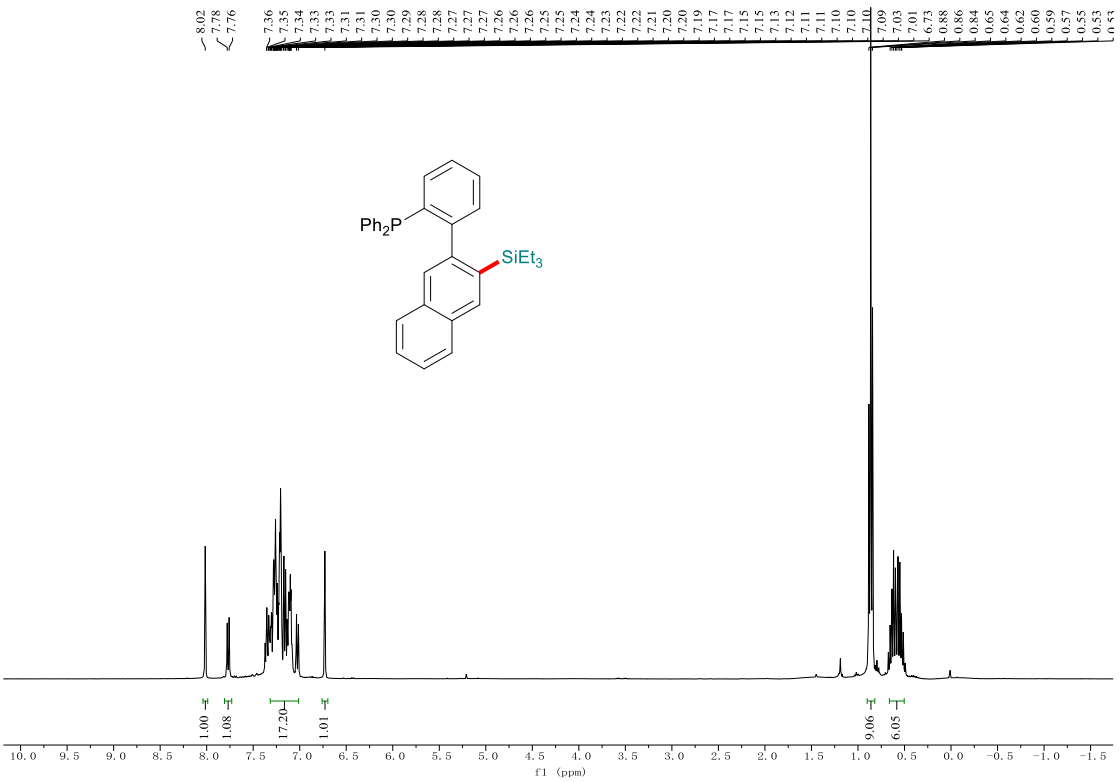
^{1}H NMR Spectrum of Compound **3fa**



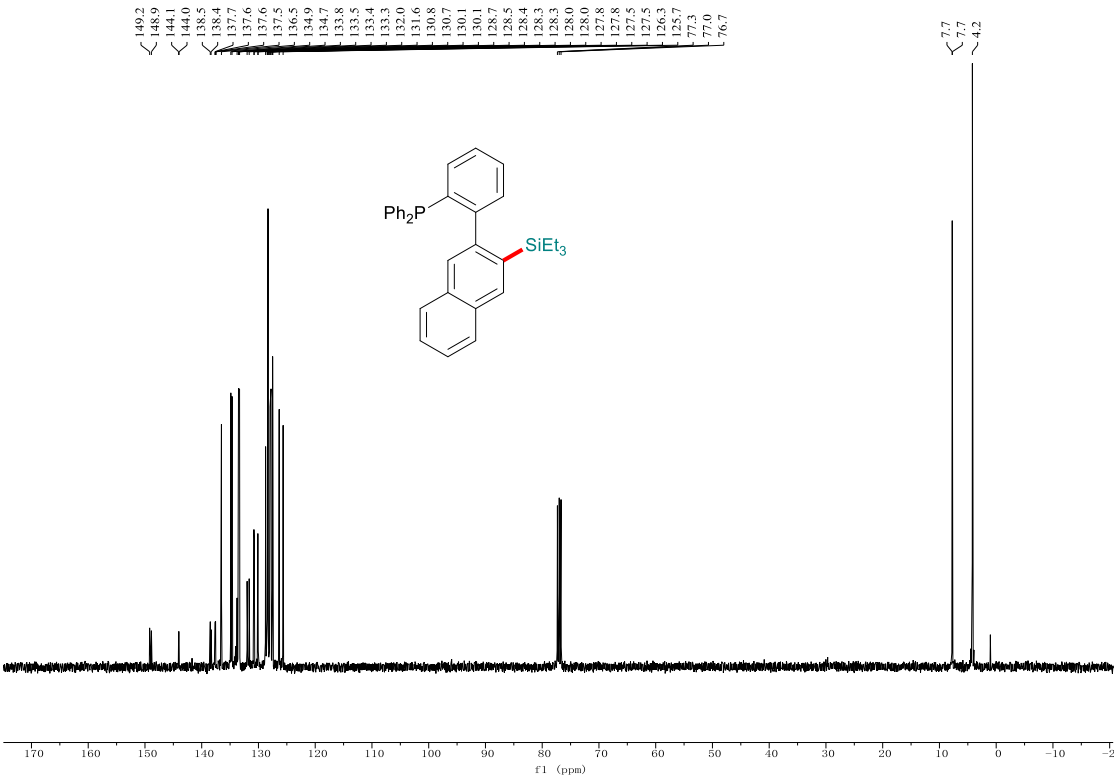
^{13}C NMR Spectrum of Compound **3fa**



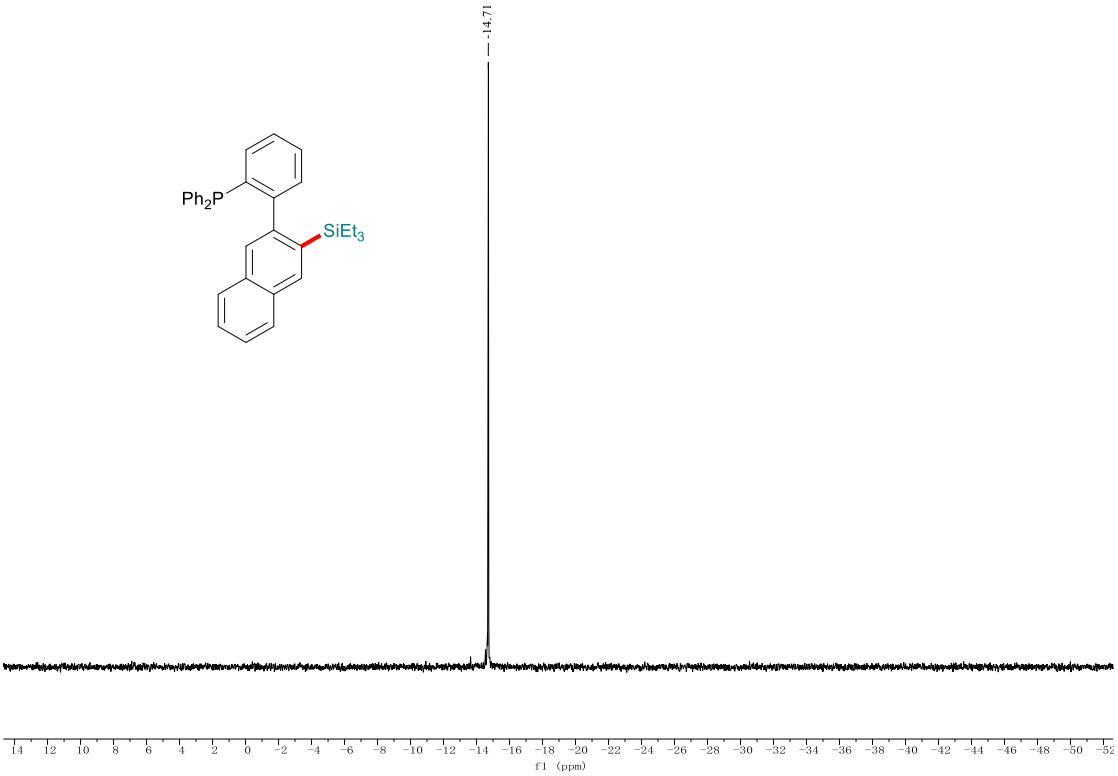
^{31}P NMR Spectrum of Compound **3fa**



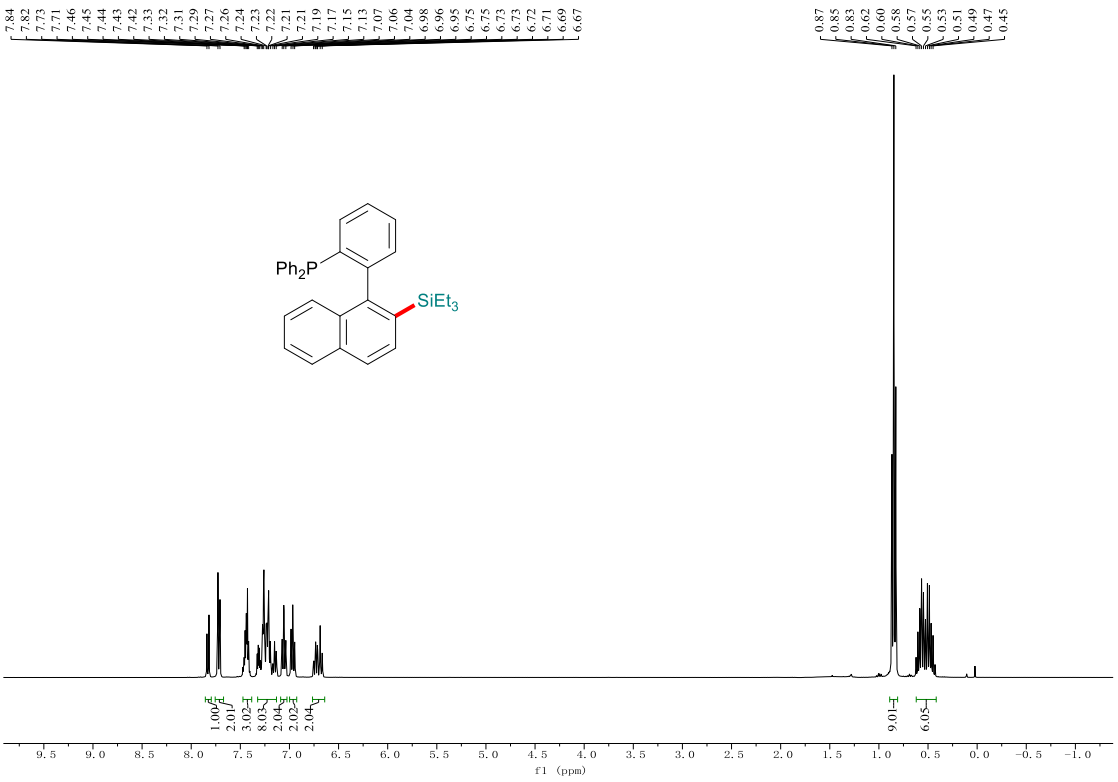
^{1}H NMR Spectrum of Compound **3ga**



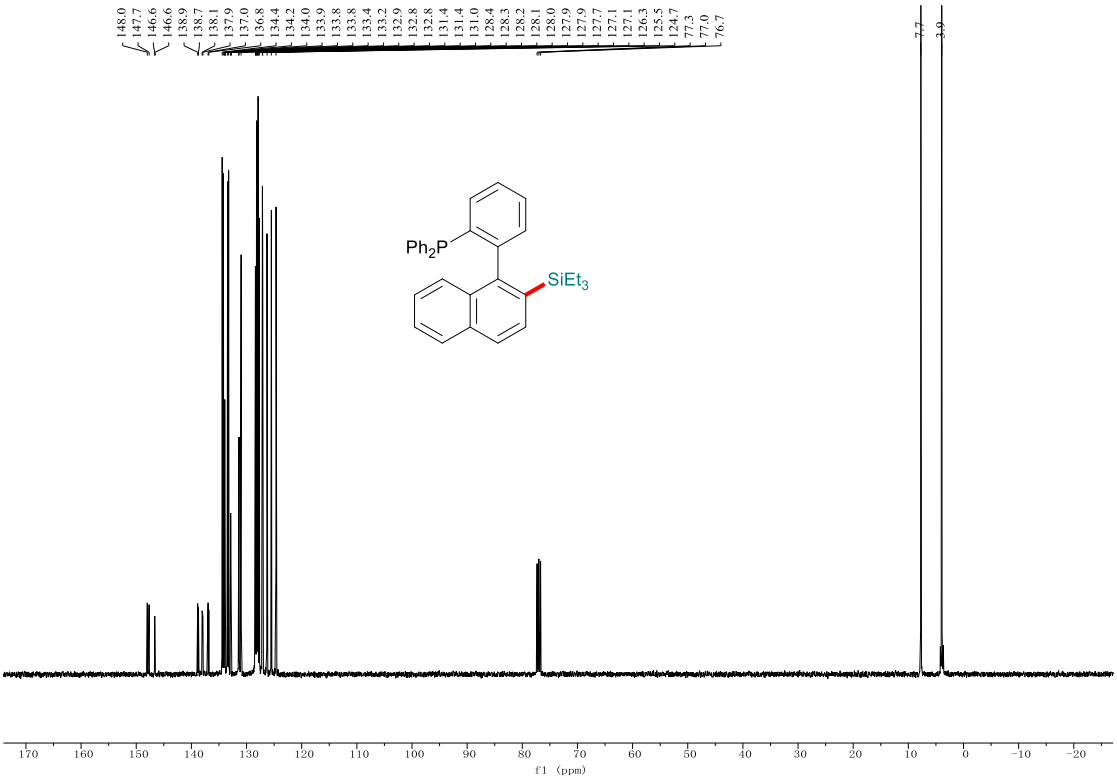
^{13}C NMR Spectrum of Compound **3ga**



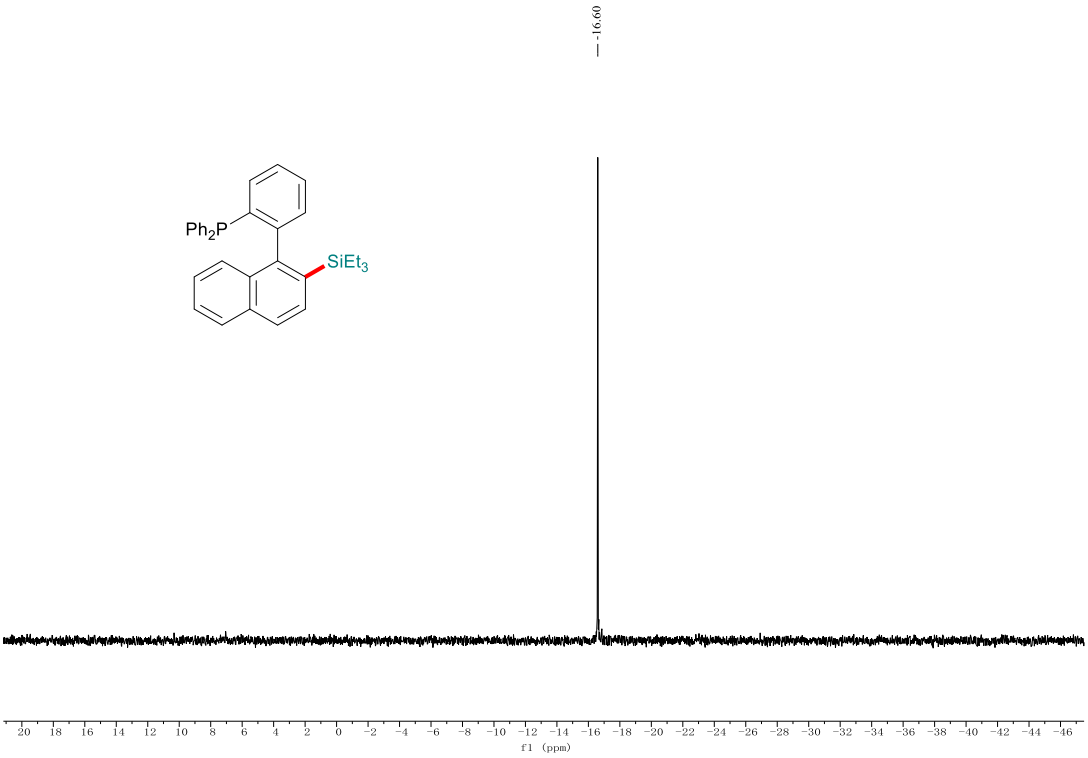
^{31}P NMR Spectrum of Compound **3ga**



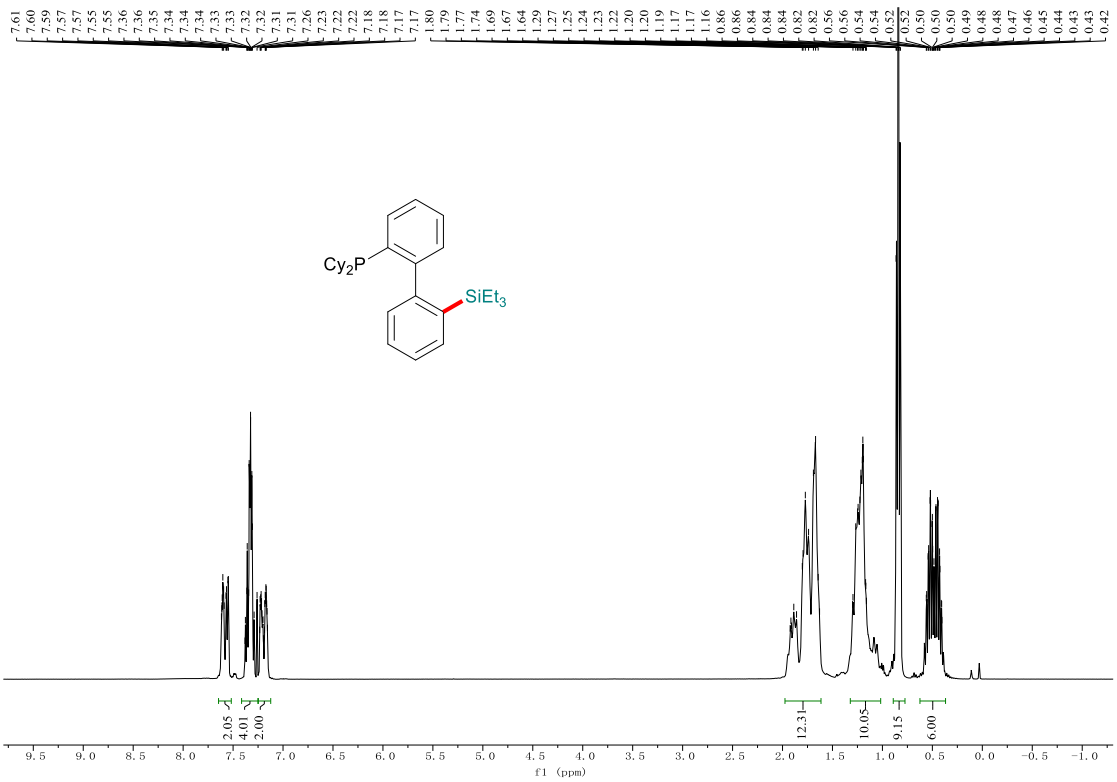
^{1}H NMR Spectrum of Compound **3ha**



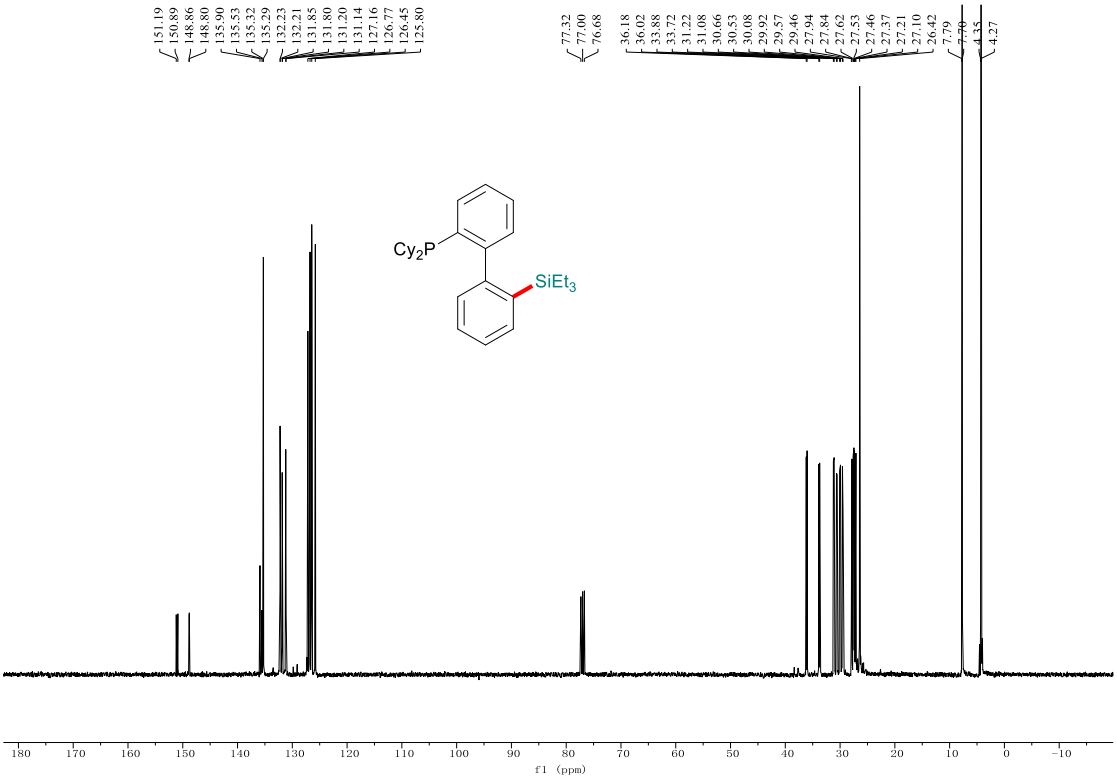
^{13}C NMR Spectrum of Compound **3ha**



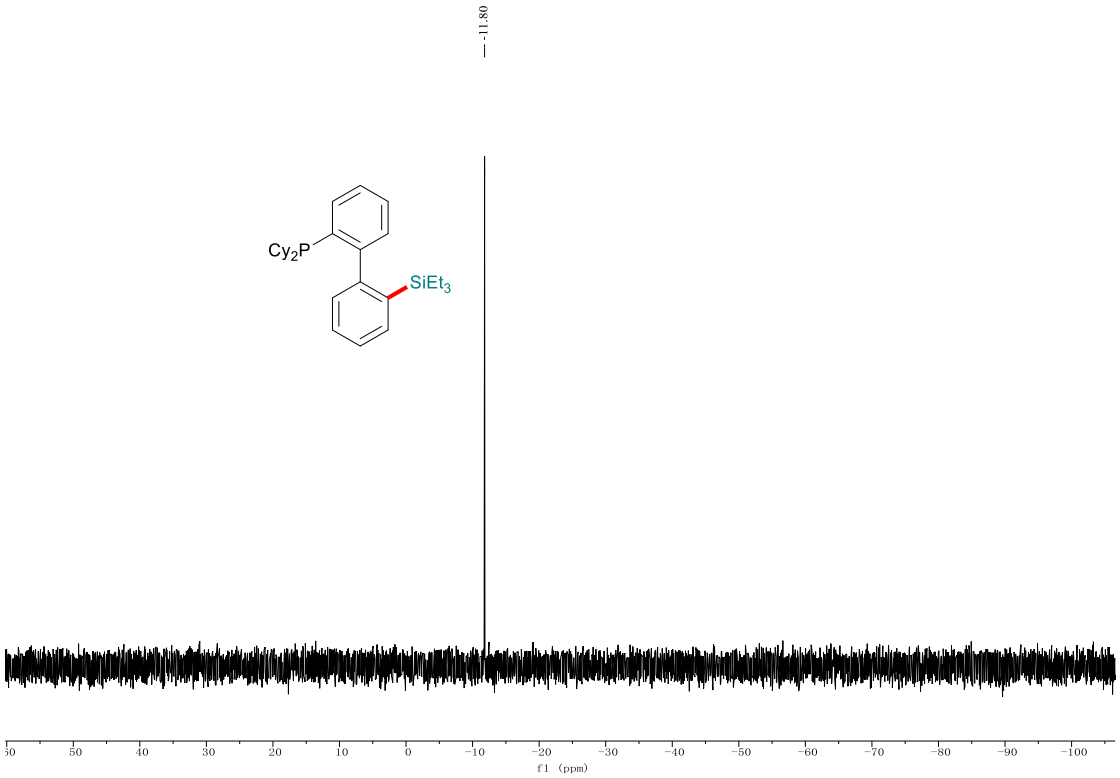
^{31}P NMR Spectrum of Compound **3ha**



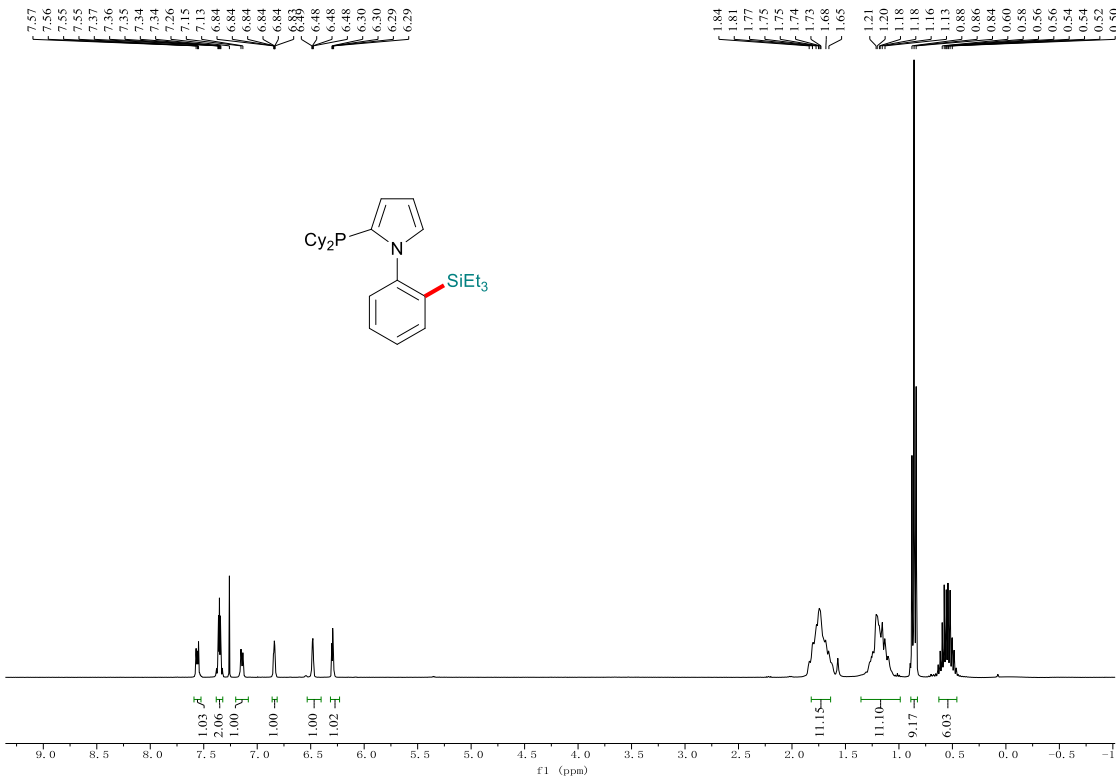
^{1}H NMR Spectrum of Compound **3ia**



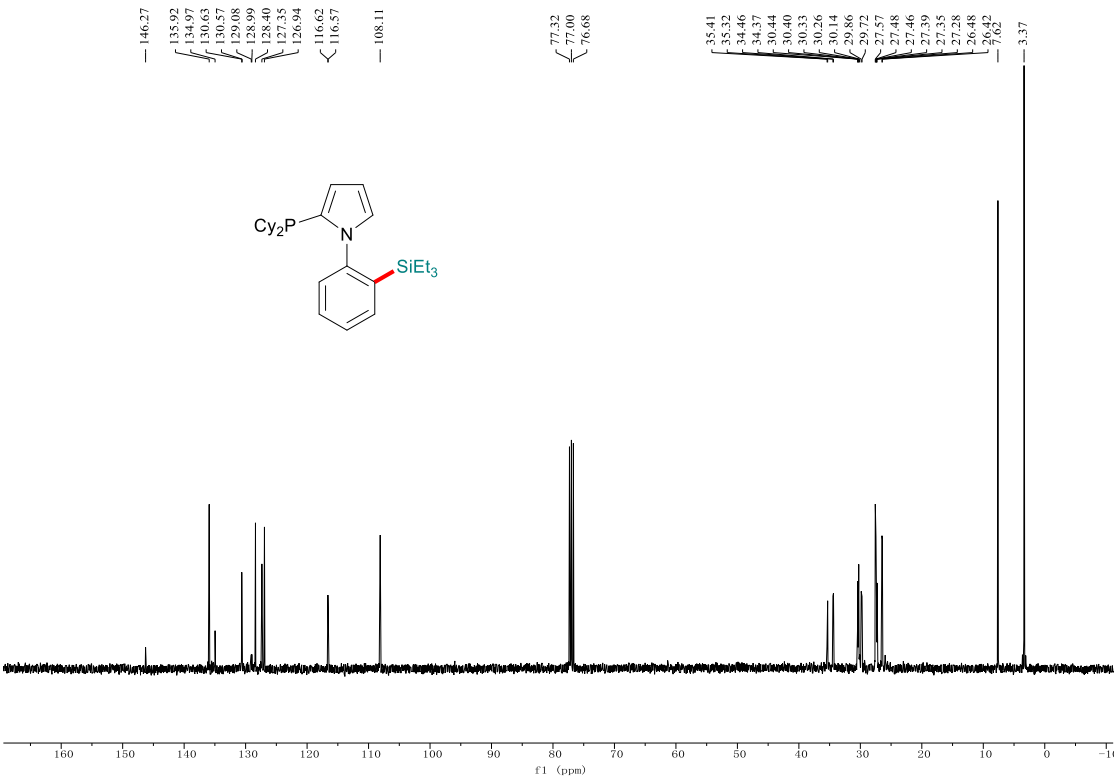
^{13}C NMR Spectrum of Compound **3ia**



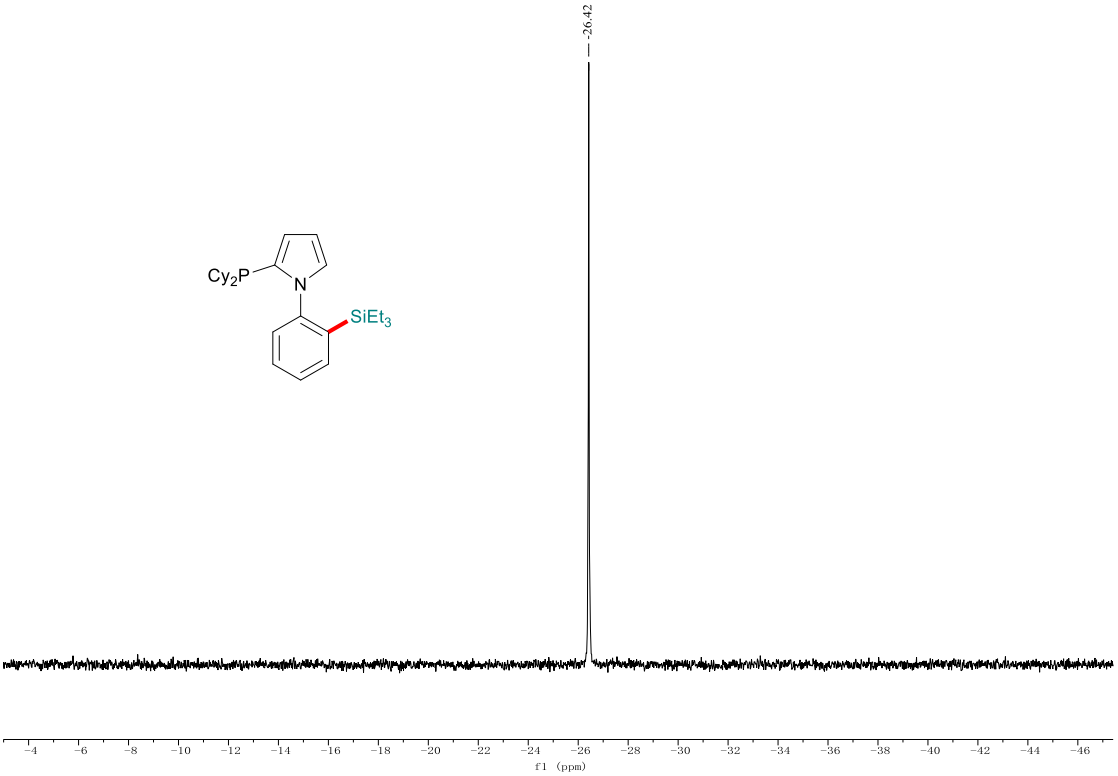
^{31}P NMR Spectrum of Compound **3ia**



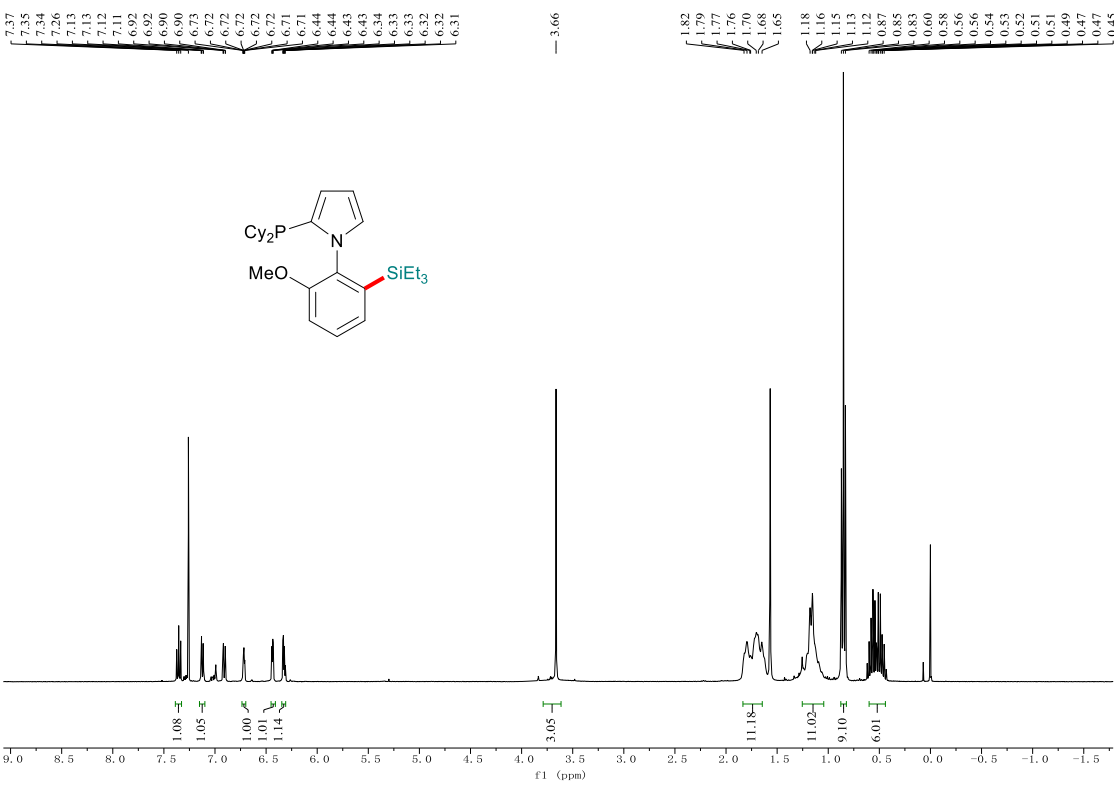
^{1}H NMR Spectrum of Compound **3ka**



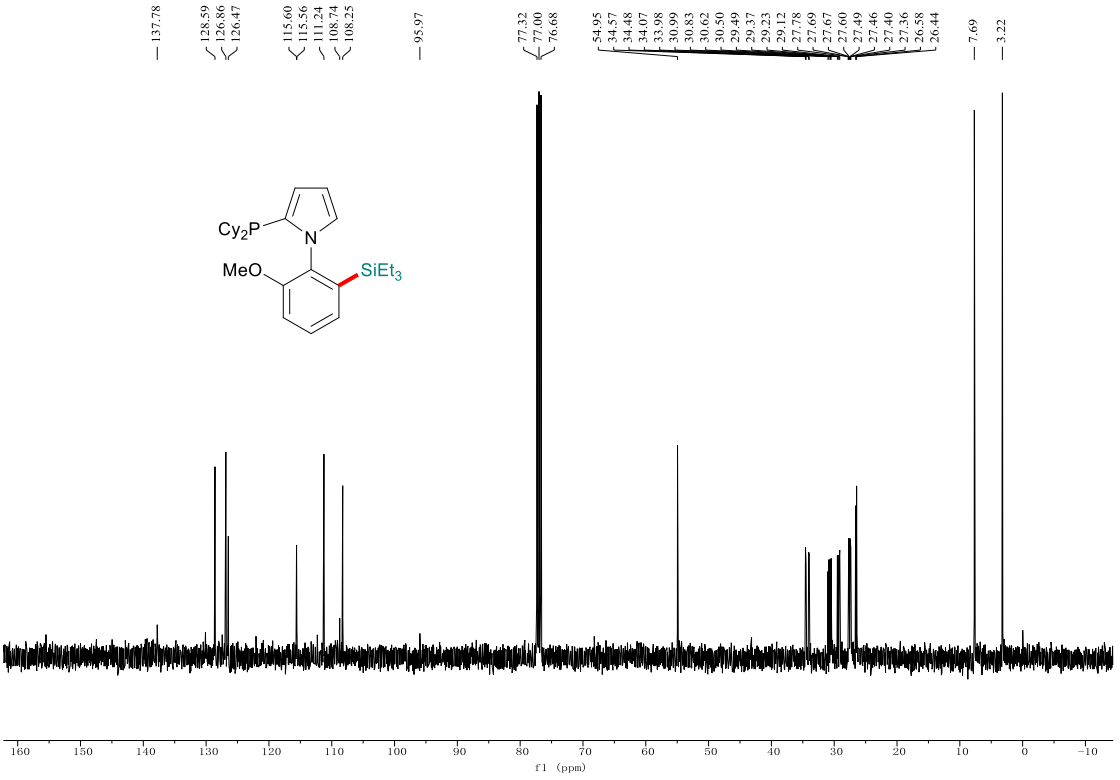
^{13}C NMR Spectrum of Compound **3ka**



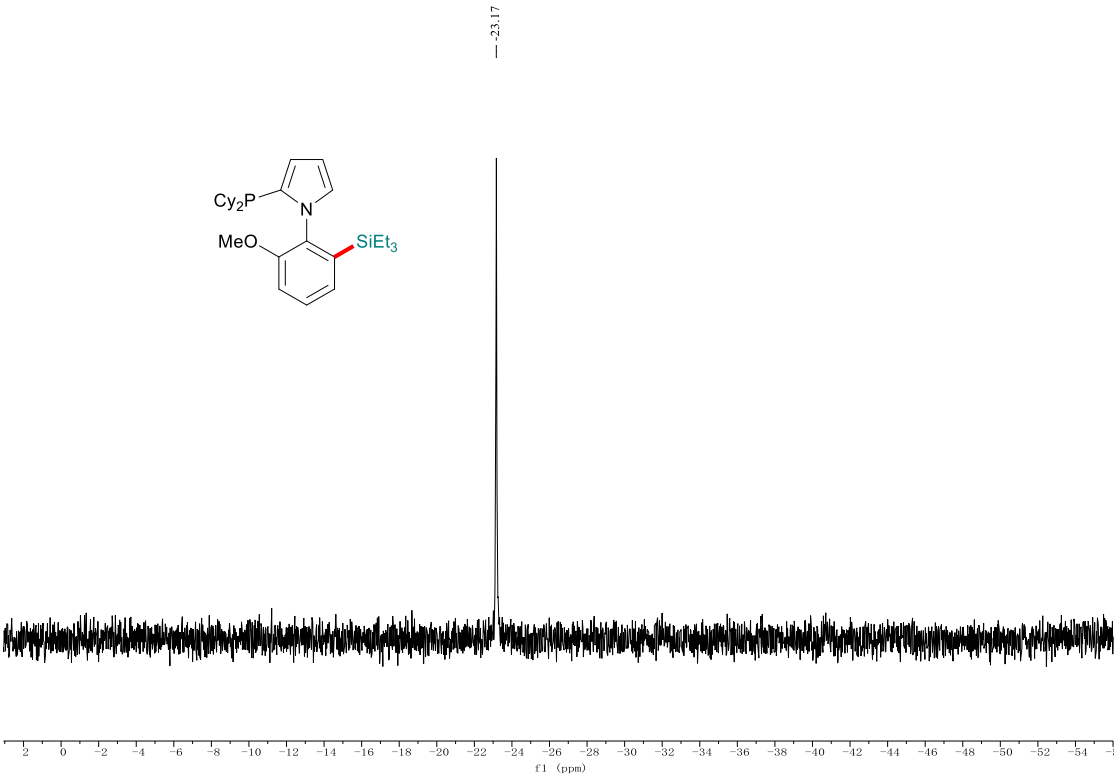
^{31}P NMR Spectrum of Compound **3ka**



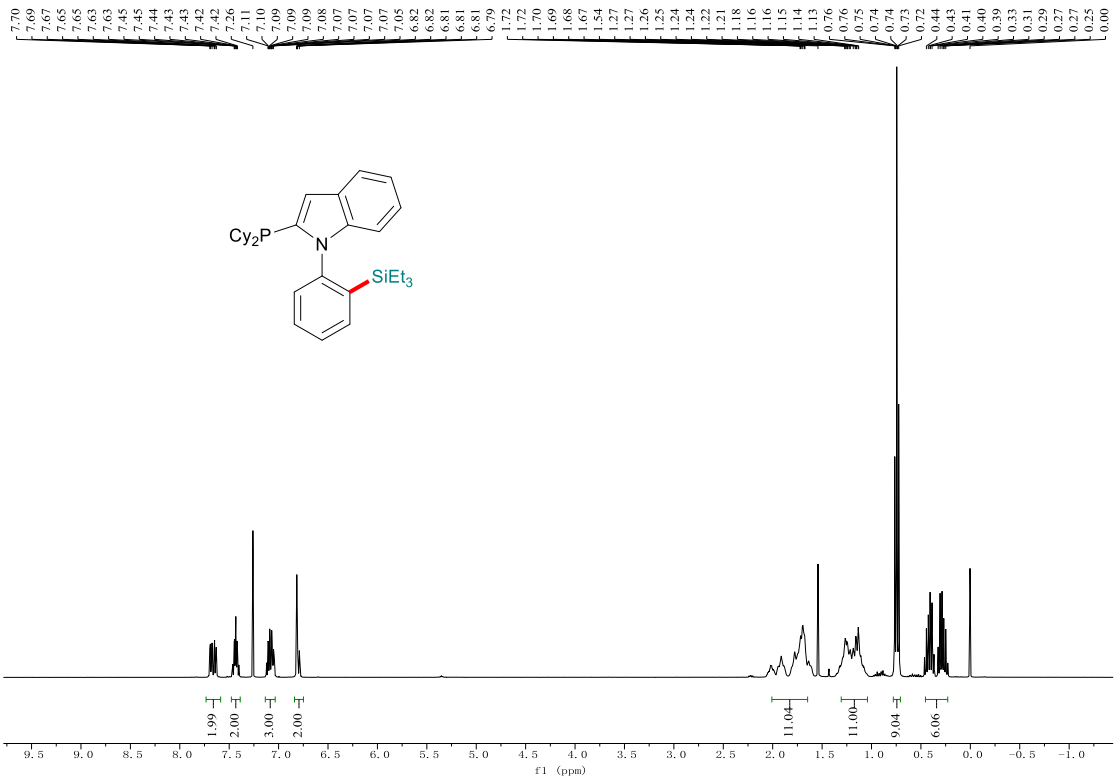
^{1}H NMR Spectrum of Compound **3la**



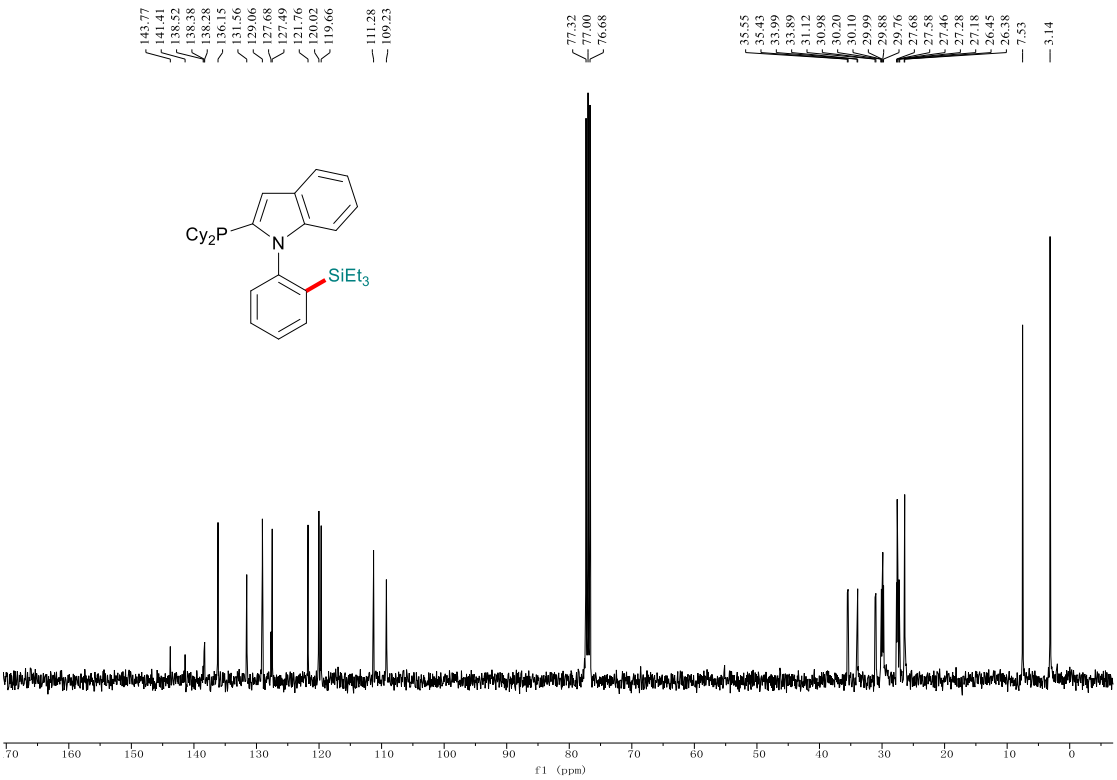
^{13}C NMR Spectrum of Compound **3la**



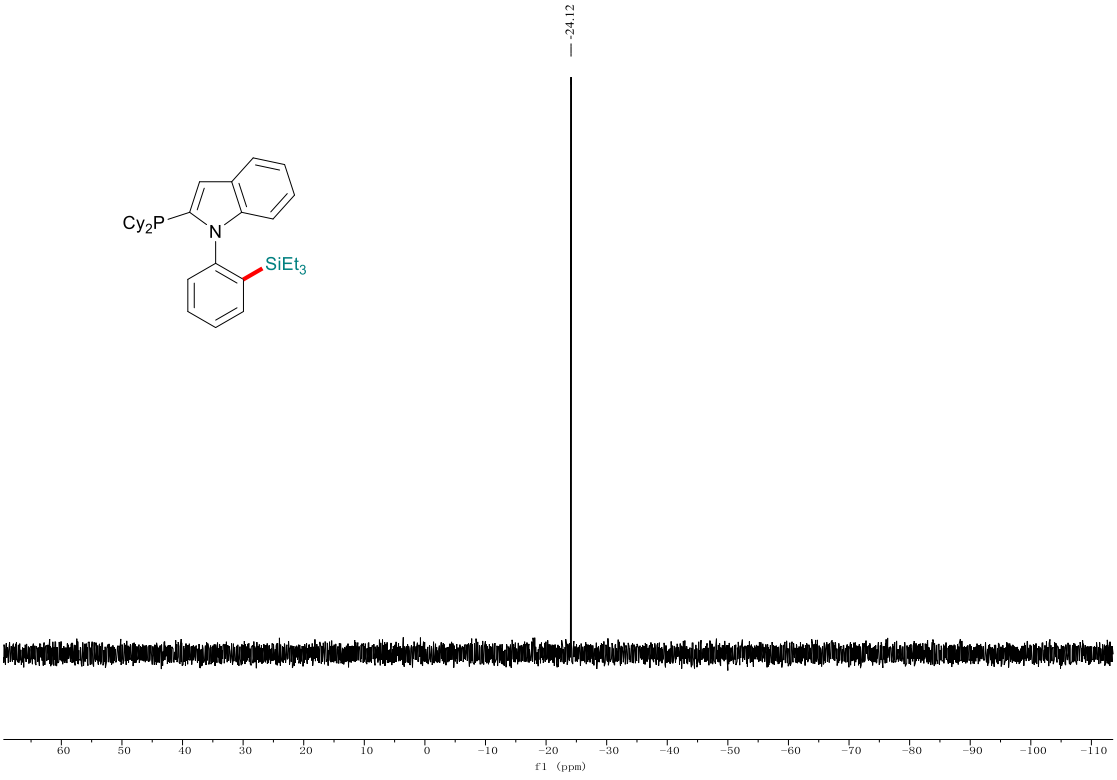
^{31}P NMR Spectrum of Compound **3la**



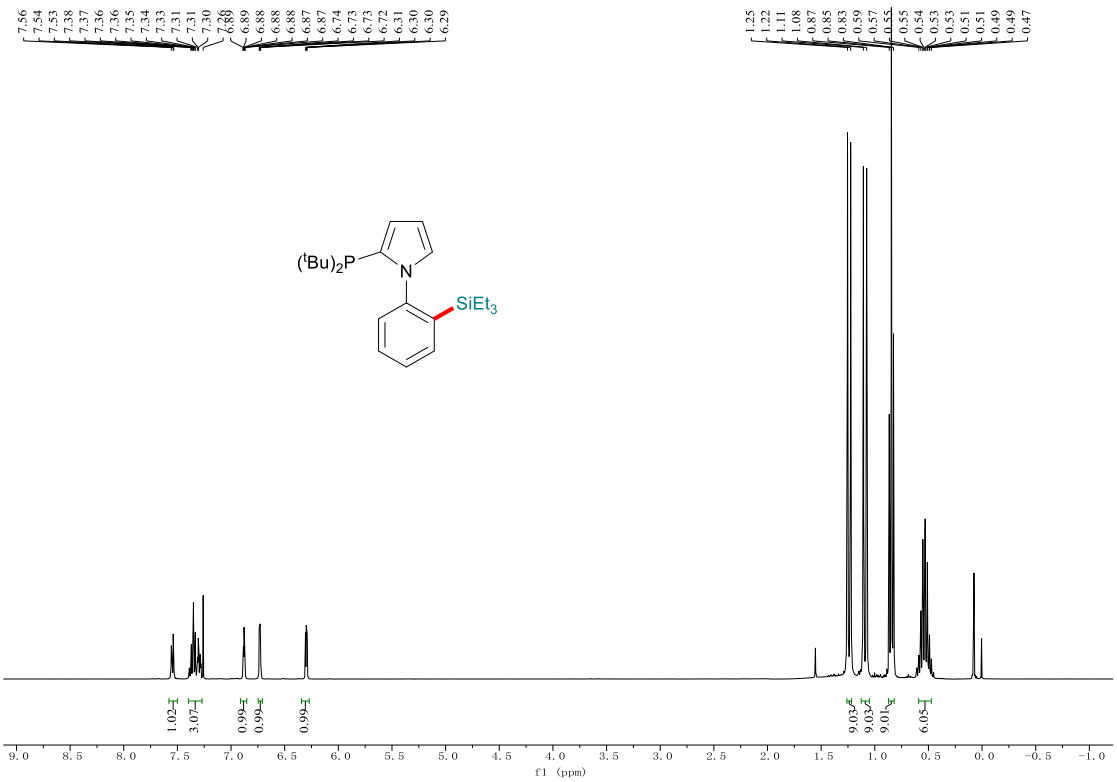
^{1}H NMR Spectrum of Compound **3ma**



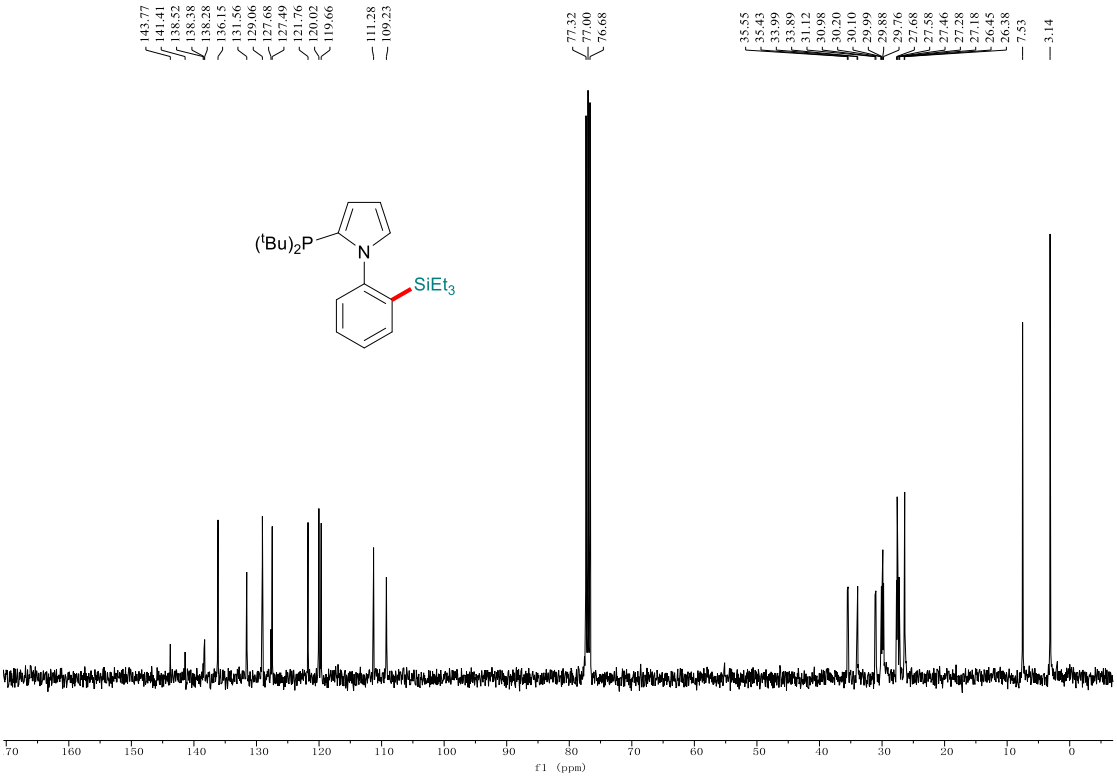
^{13}C NMR Spectrum of Compound **3ma**



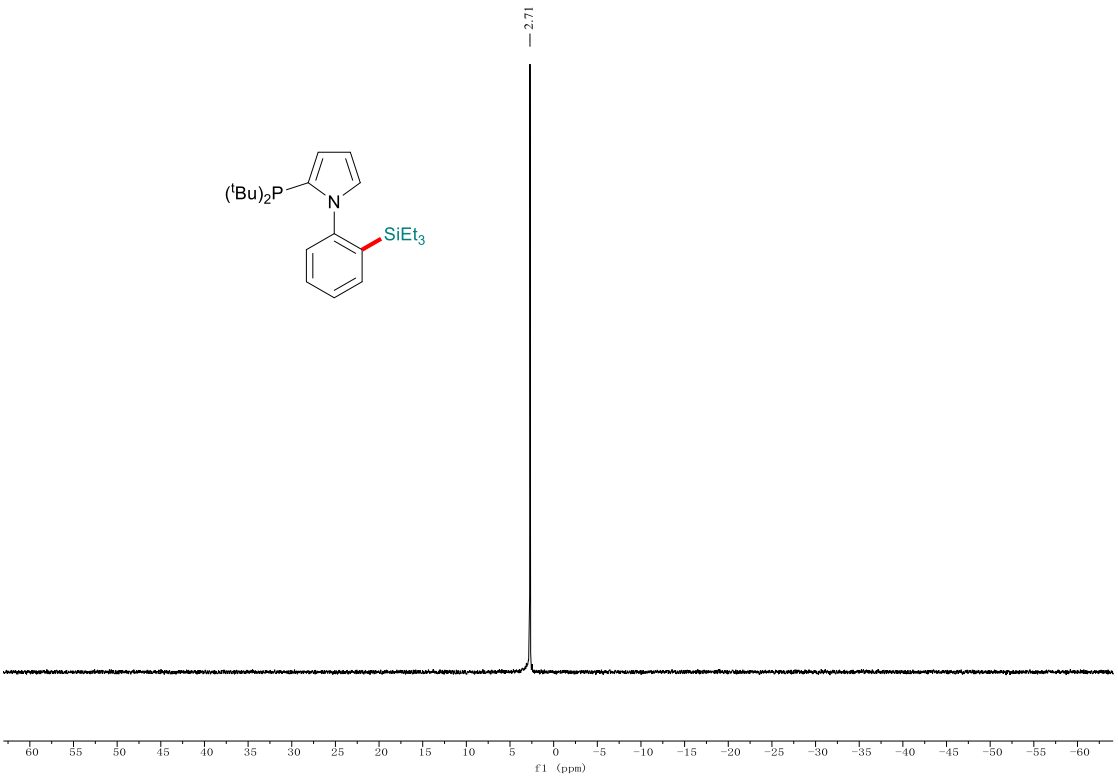
^{31}P NMR Spectrum of Compound **3ma**



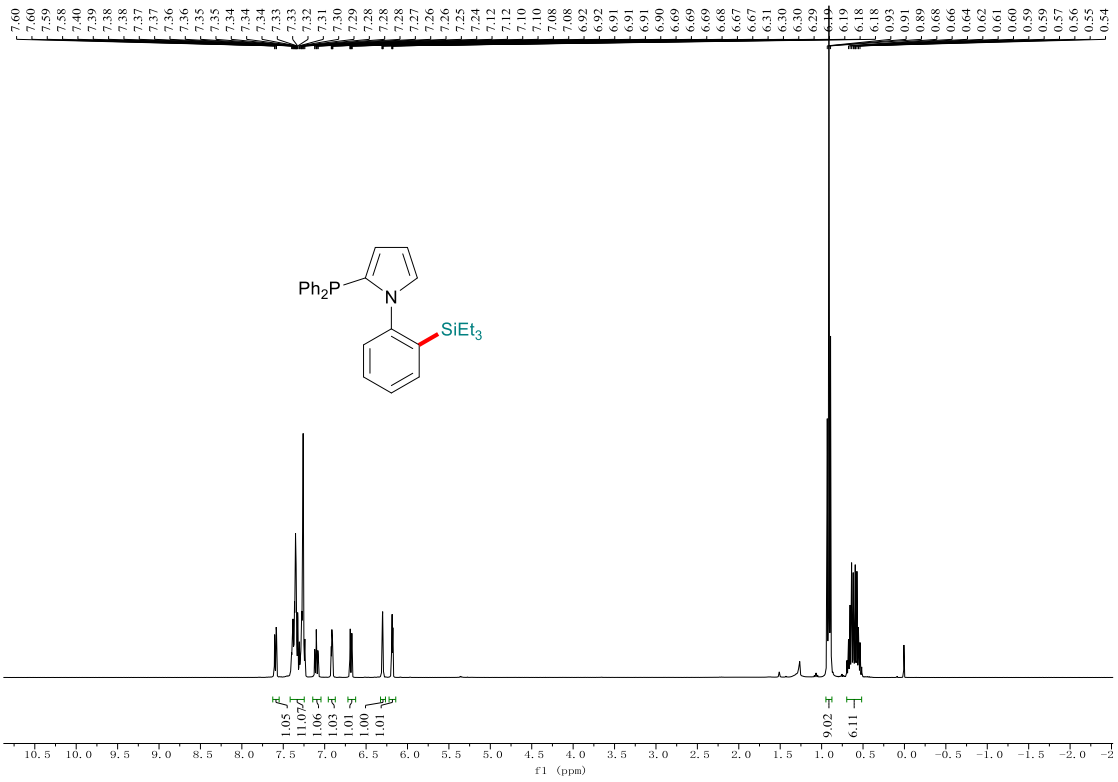
^{1}H NMR Spectrum of Compound **3na**



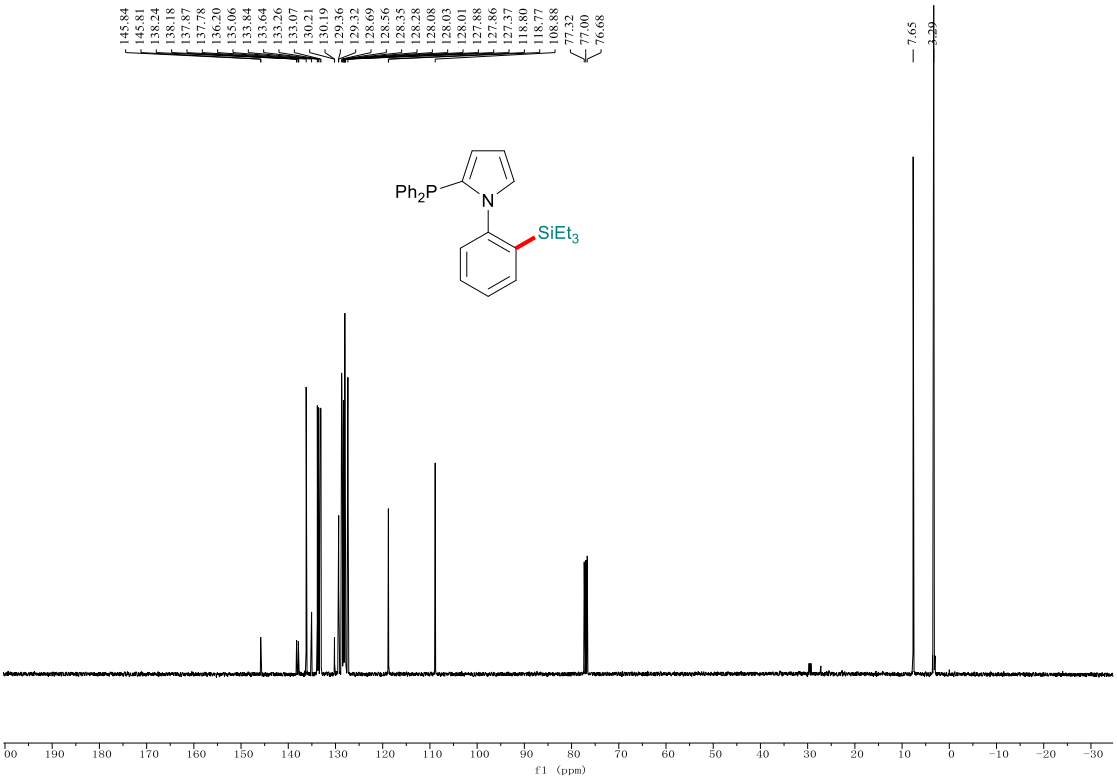
^{13}C NMR Spectrum of Compound **3na**



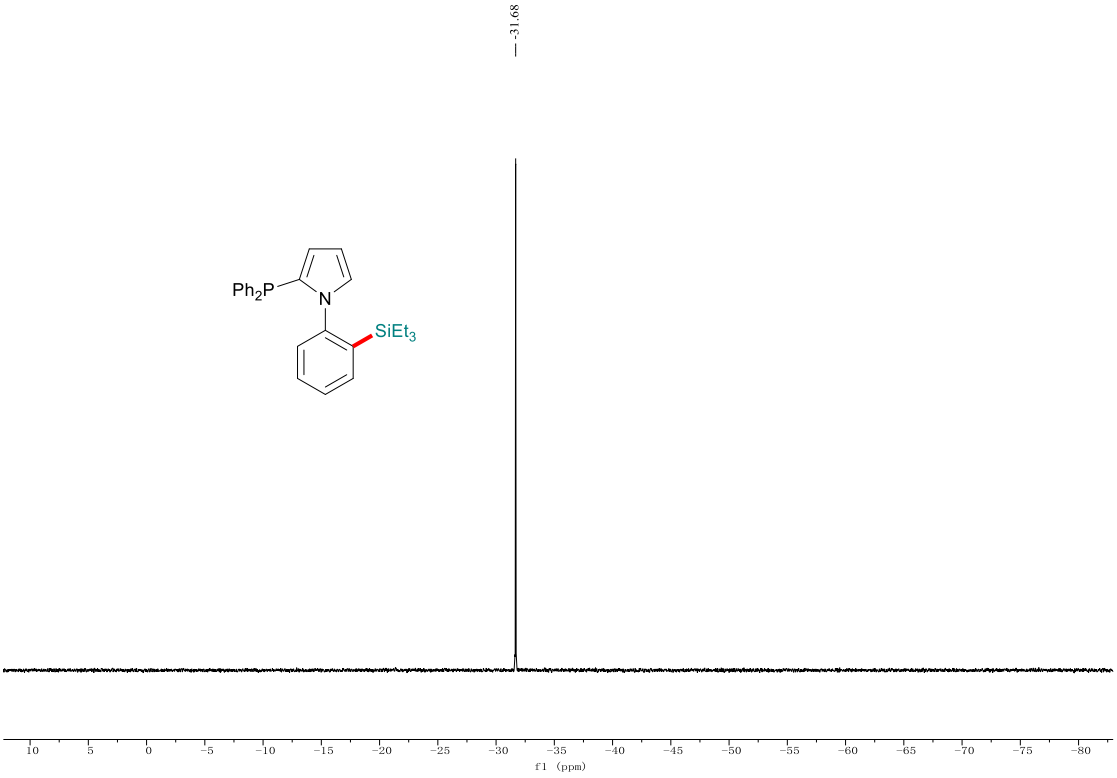
^{31}P NMR Spectrum of Compound **3na**



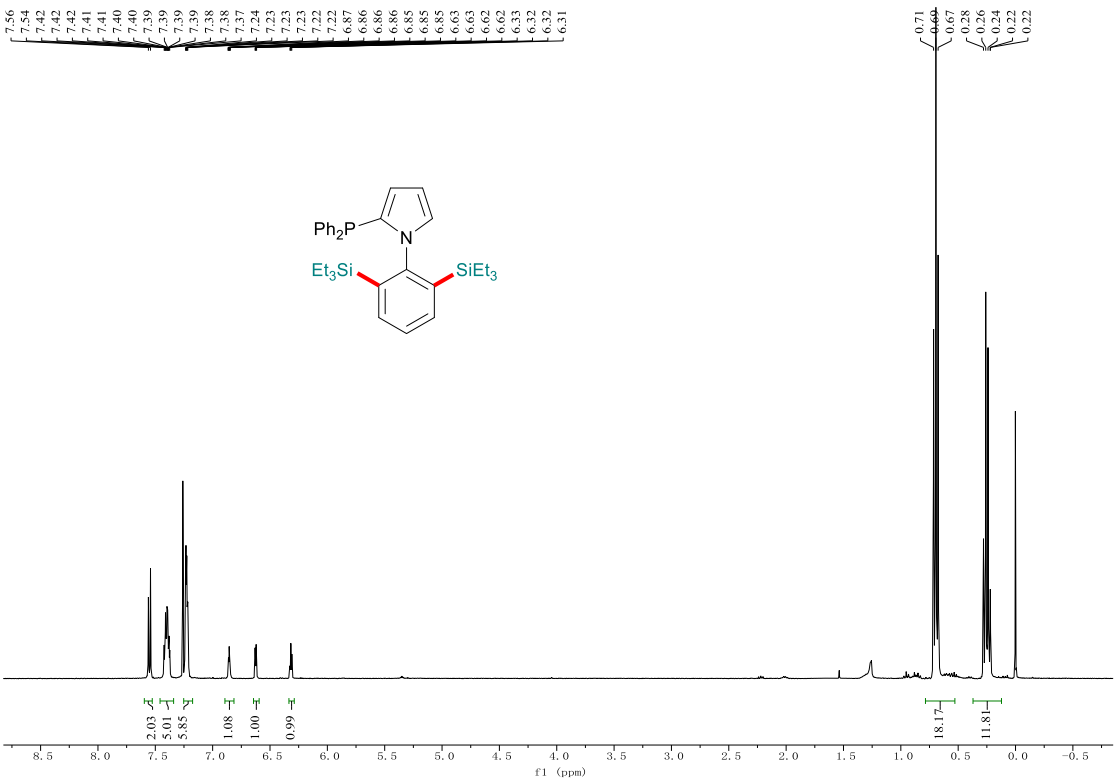
^{1}H NMR Spectrum of Compound **3oa**



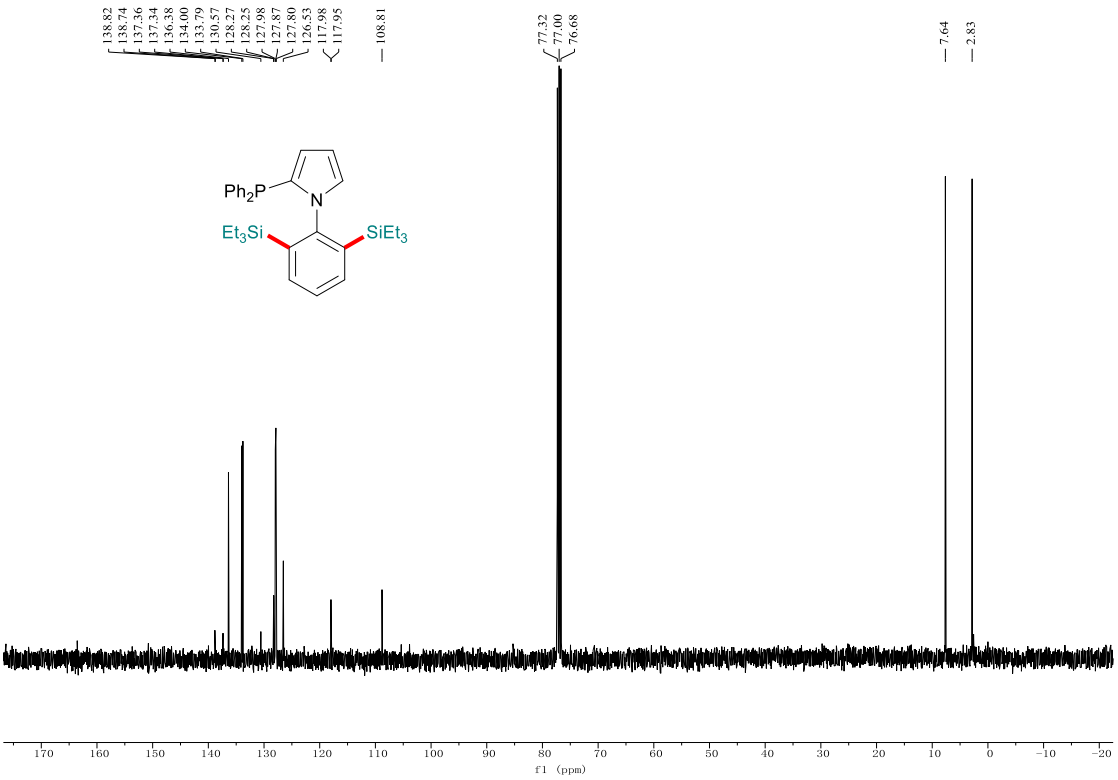
^{13}C NMR Spectrum of Compound **3oa**



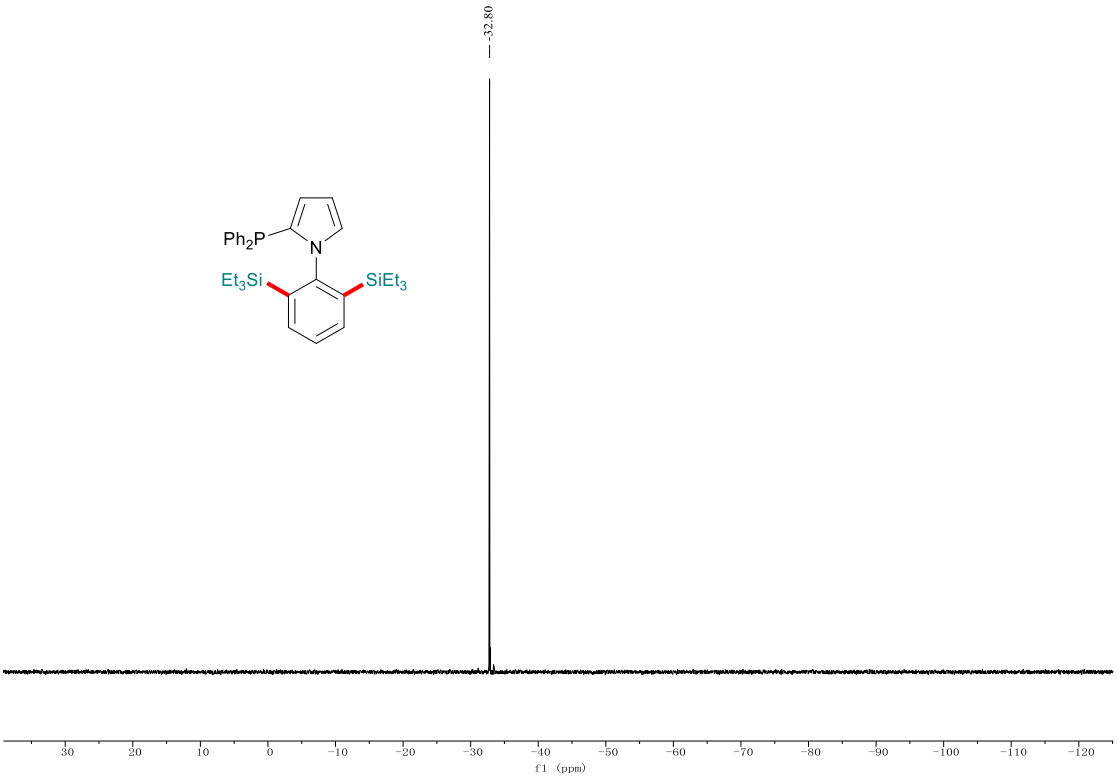
^{31}P NMR Spectrum of Compound **3oa**



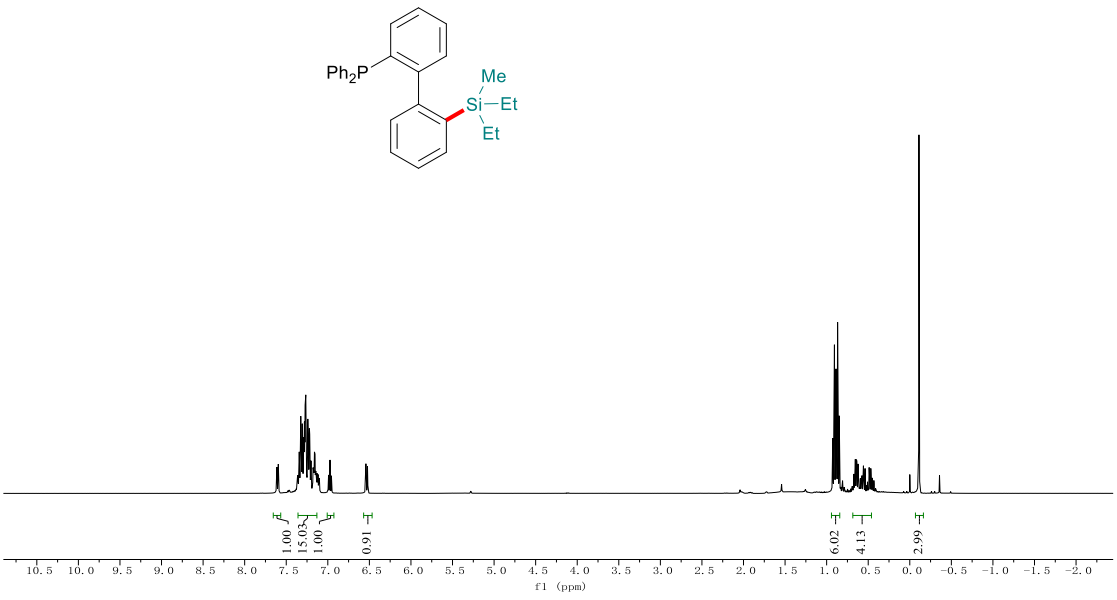
^{1}H NMR Spectrum of Compound **3oa'**



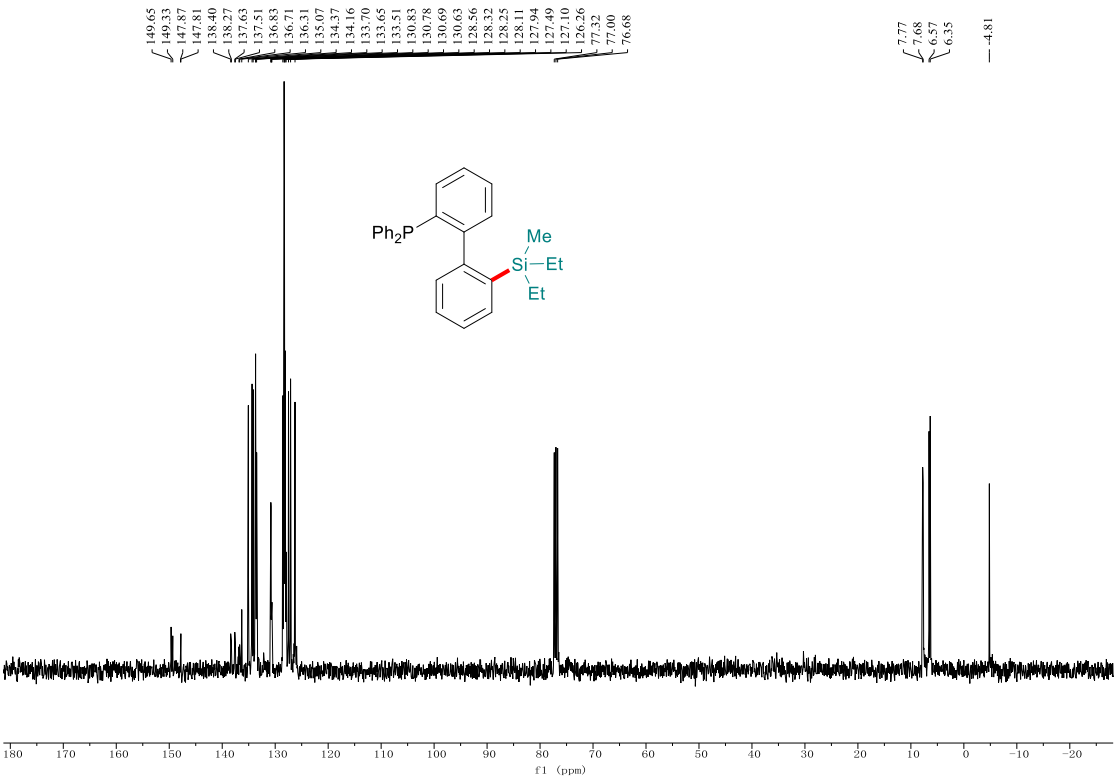
^{13}C NMR Spectrum of Compound **3oa'**



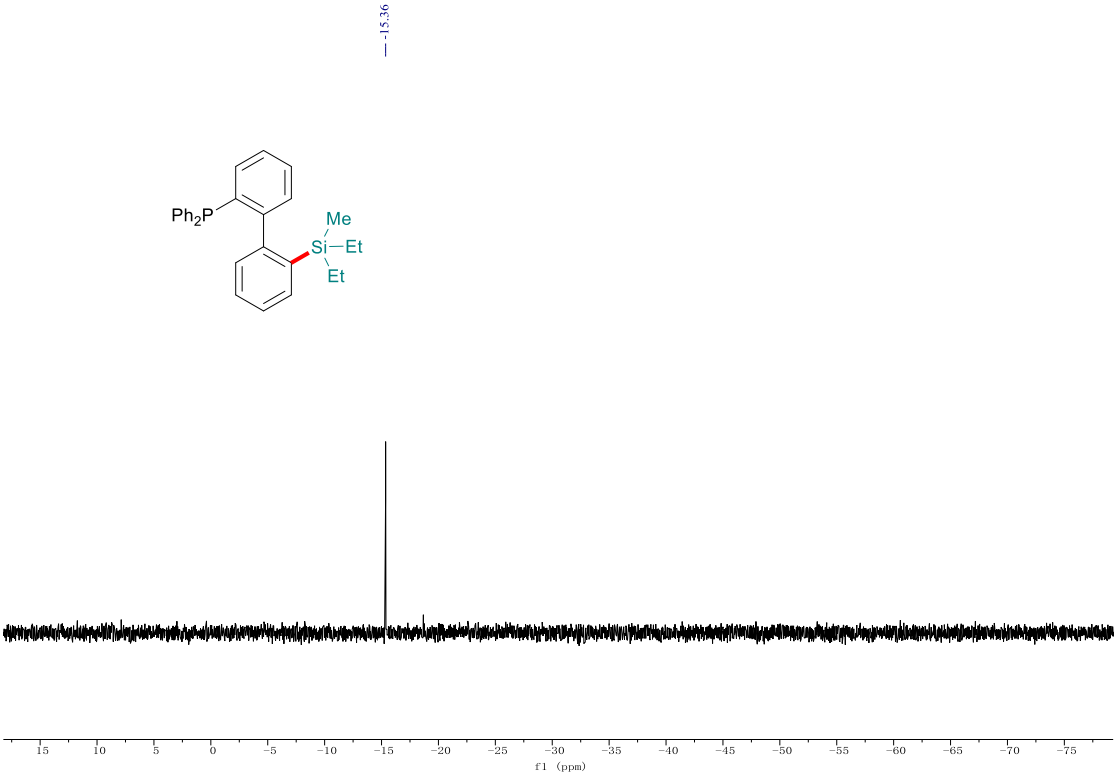
^{31}P NMR Spectrum of Compound **3oa'**



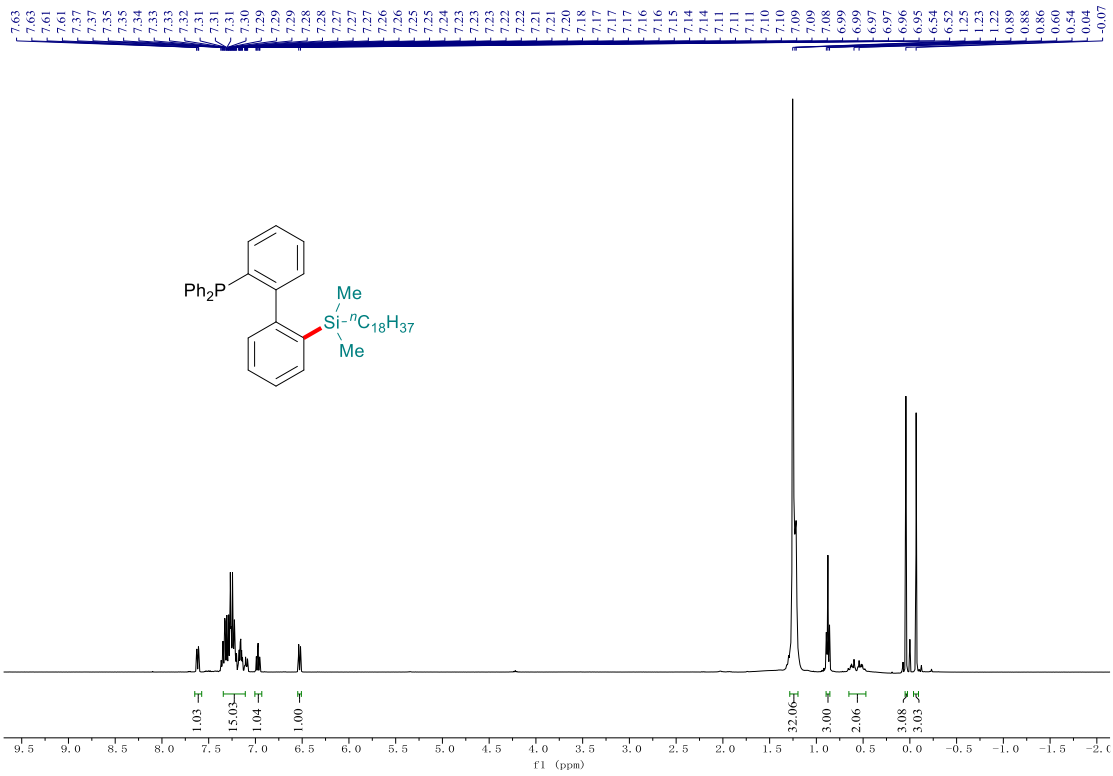
^{1}H NMR Spectrum of Compound **3ab**



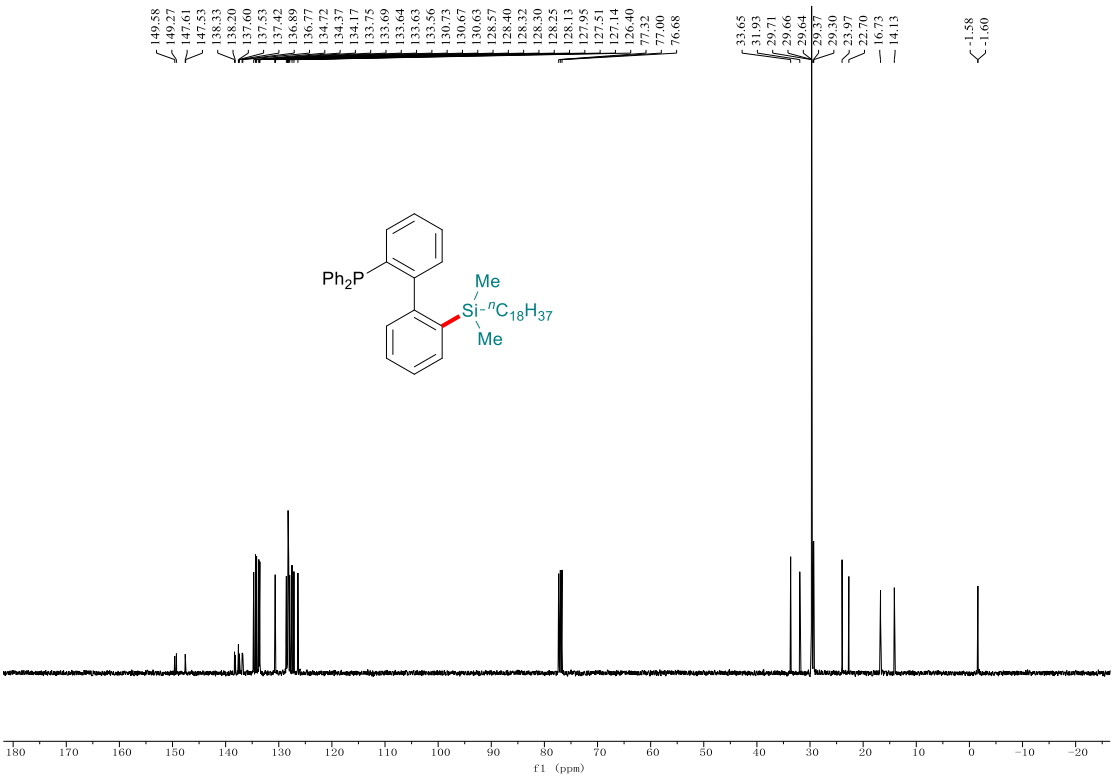
^{13}C NMR Spectrum of Compound **3ab**



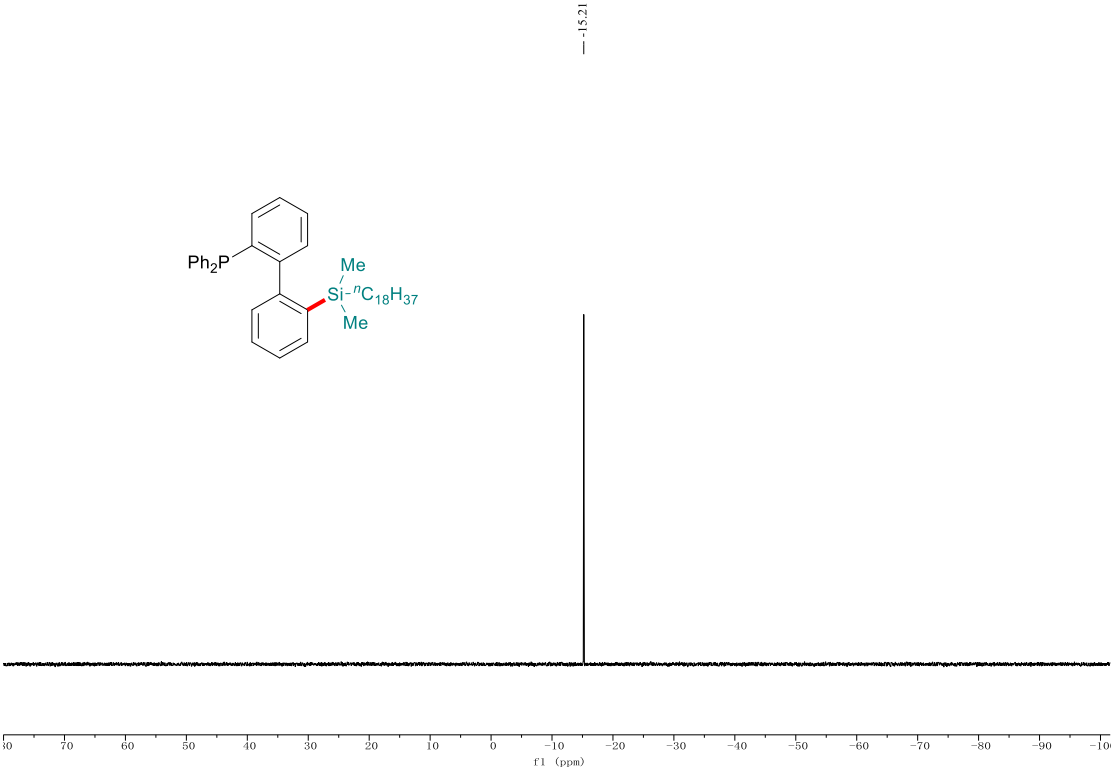
^{31}P NMR Spectrum of Compound **3ab**



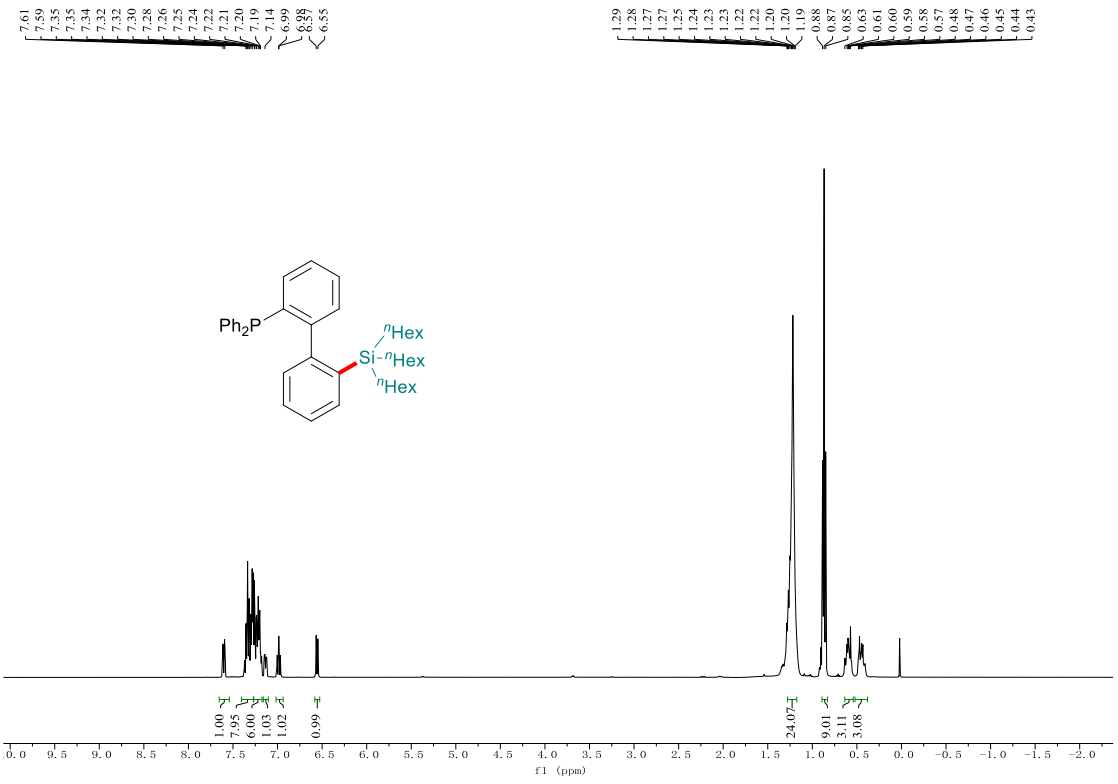
^{1}H NMR Spectrum of Compound **3ac**



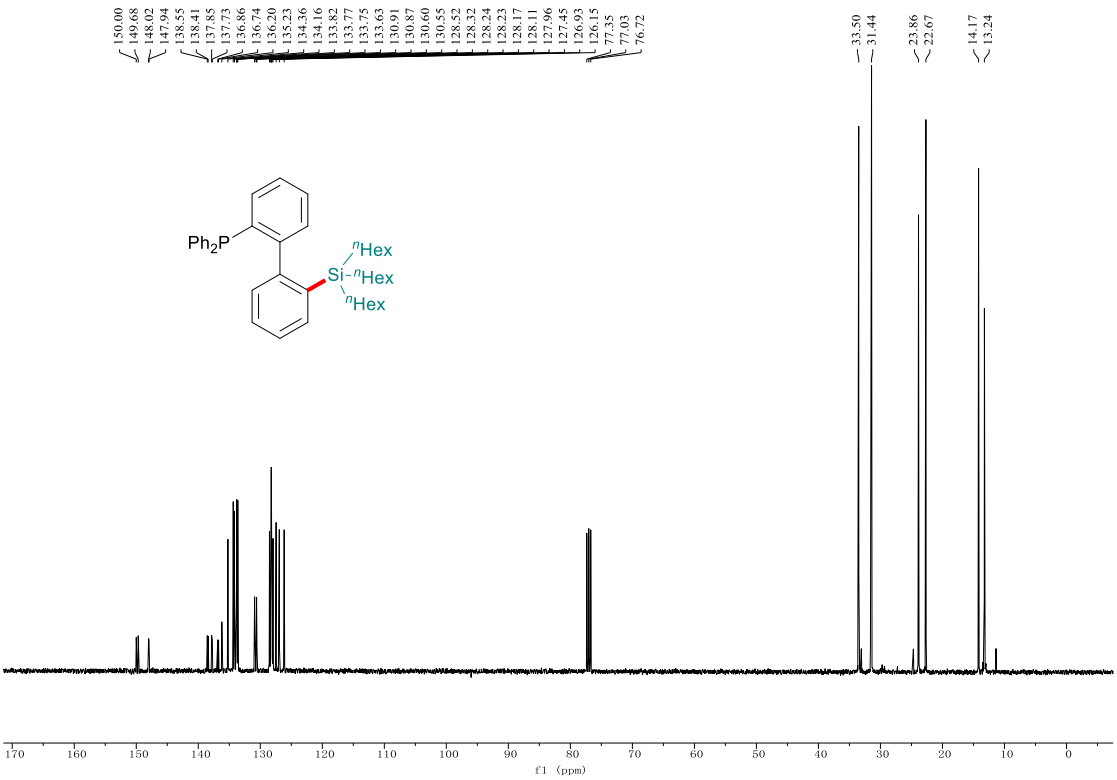
^{13}C NMR Spectrum of Compound **3ac**



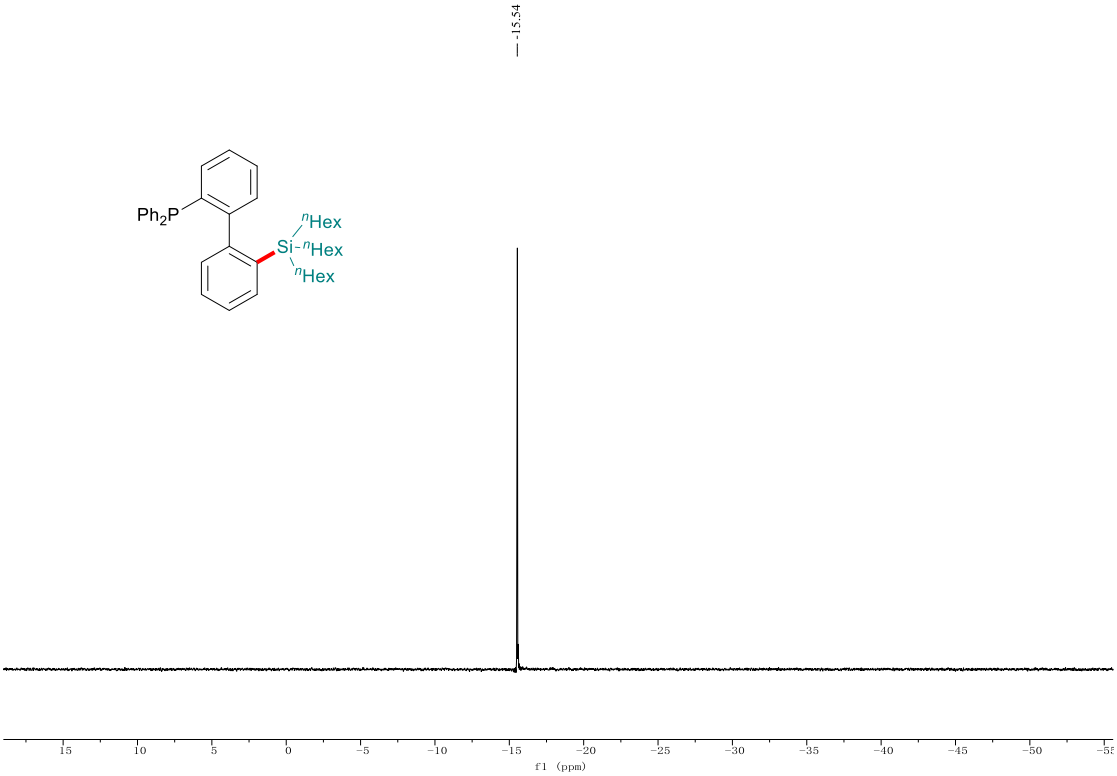
^{31}P NMR Spectrum of Compound **3ac**



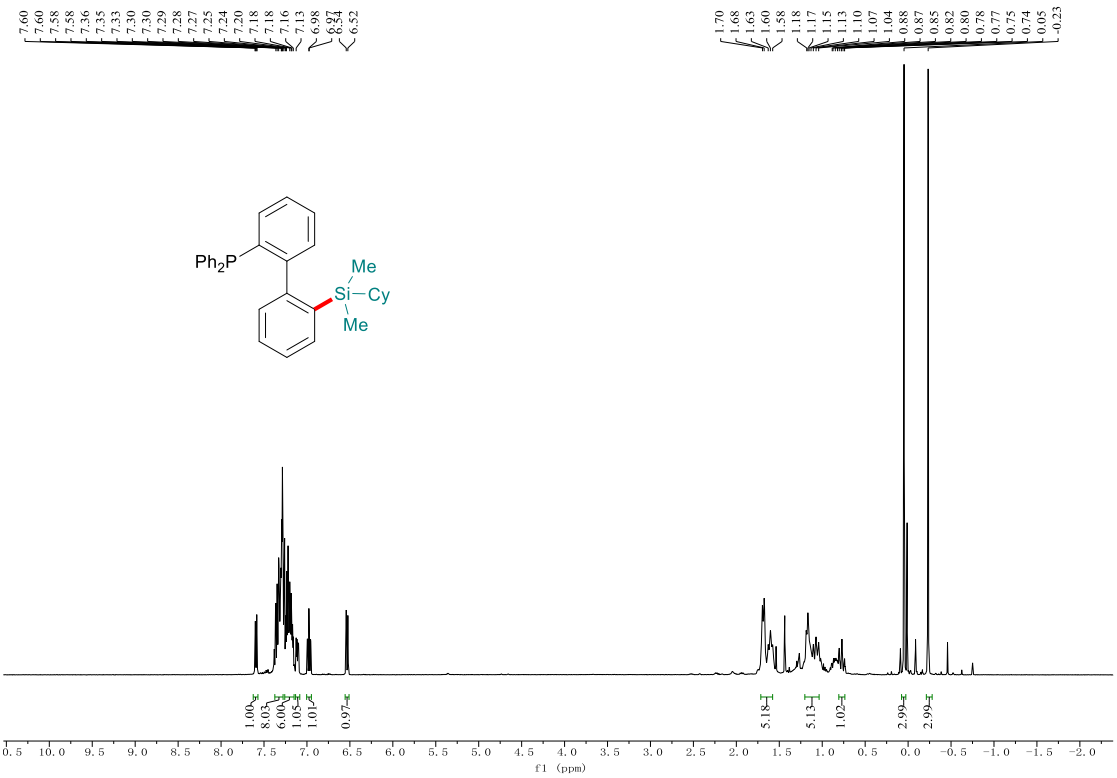
^{1}H NMR Spectrum of Compound **3ad**



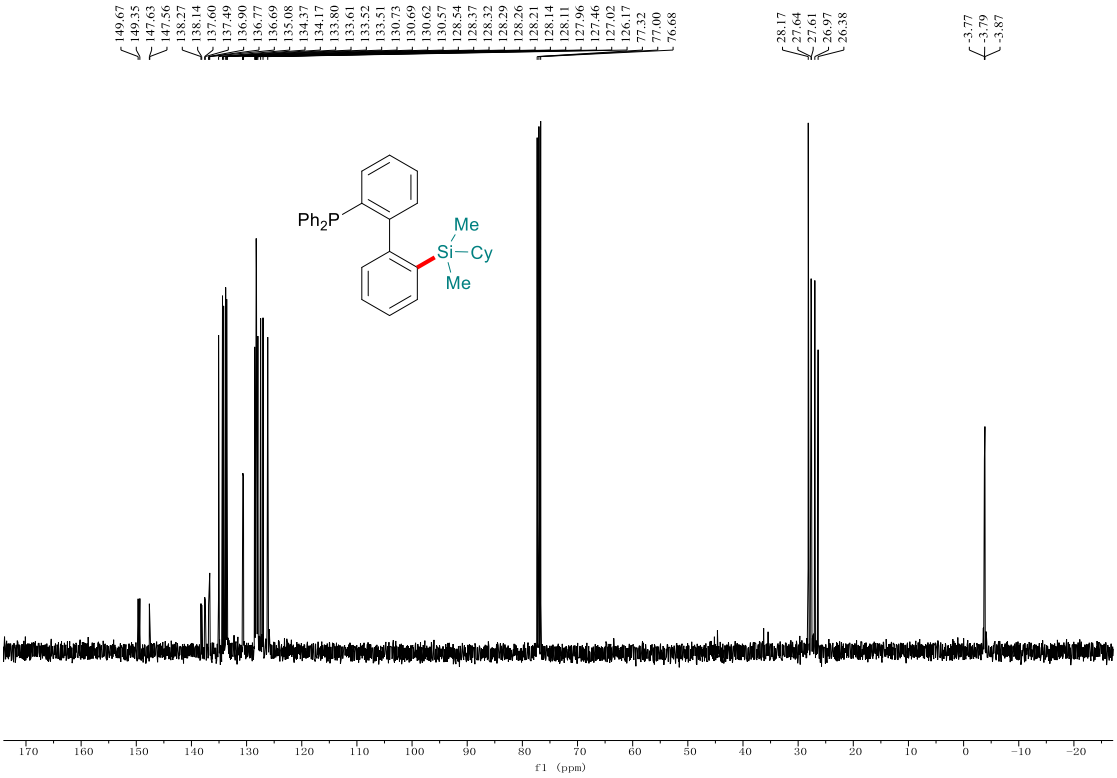
^{13}C NMR Spectrum of Compound **3ad**



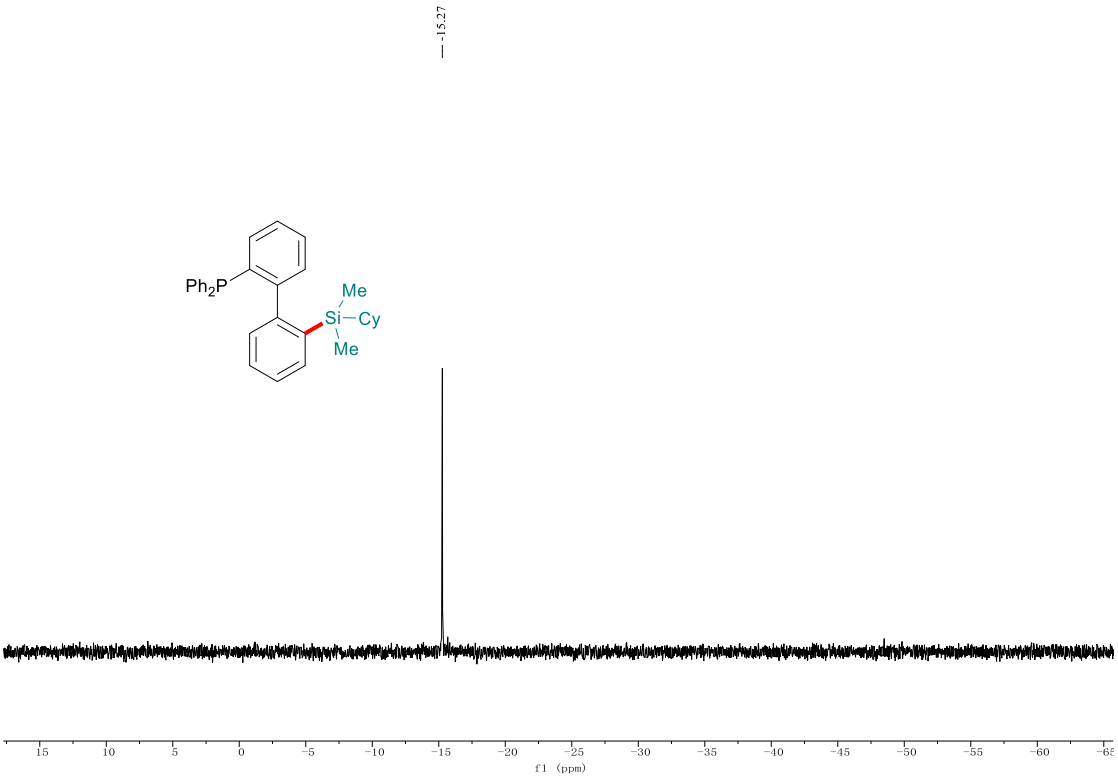
^{31}P NMR Spectrum of Compound **3ad**



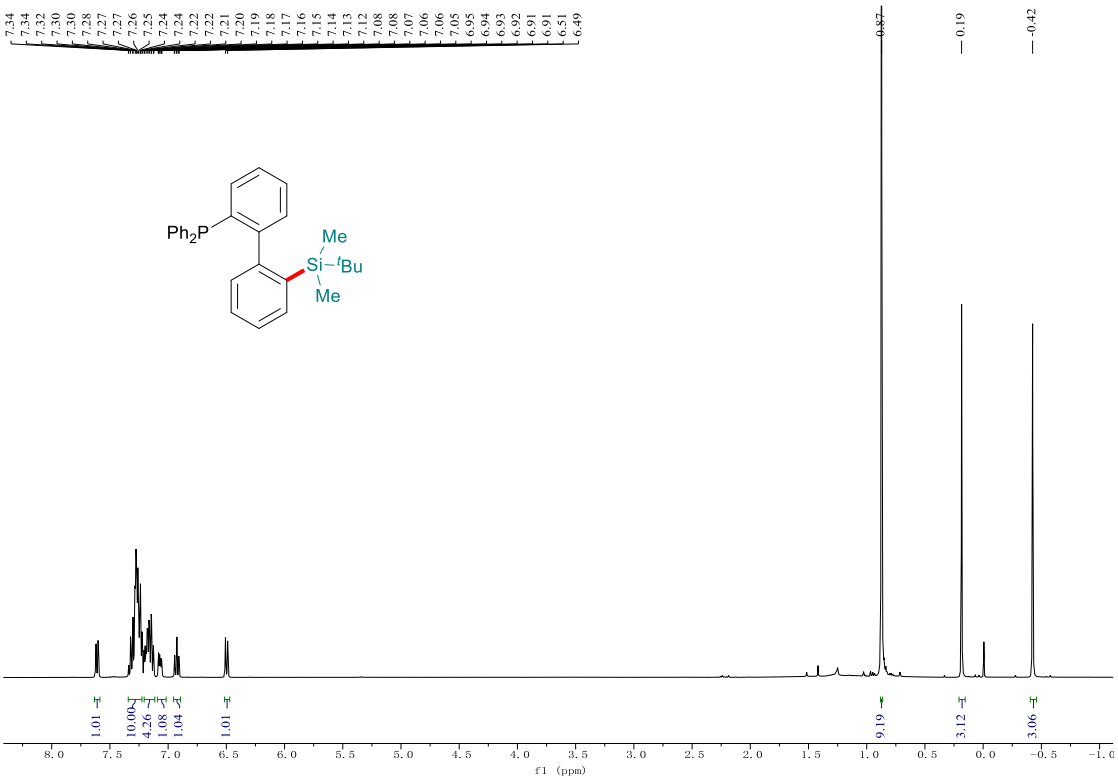
^{1}H NMR Spectrum of Compound **3ae**



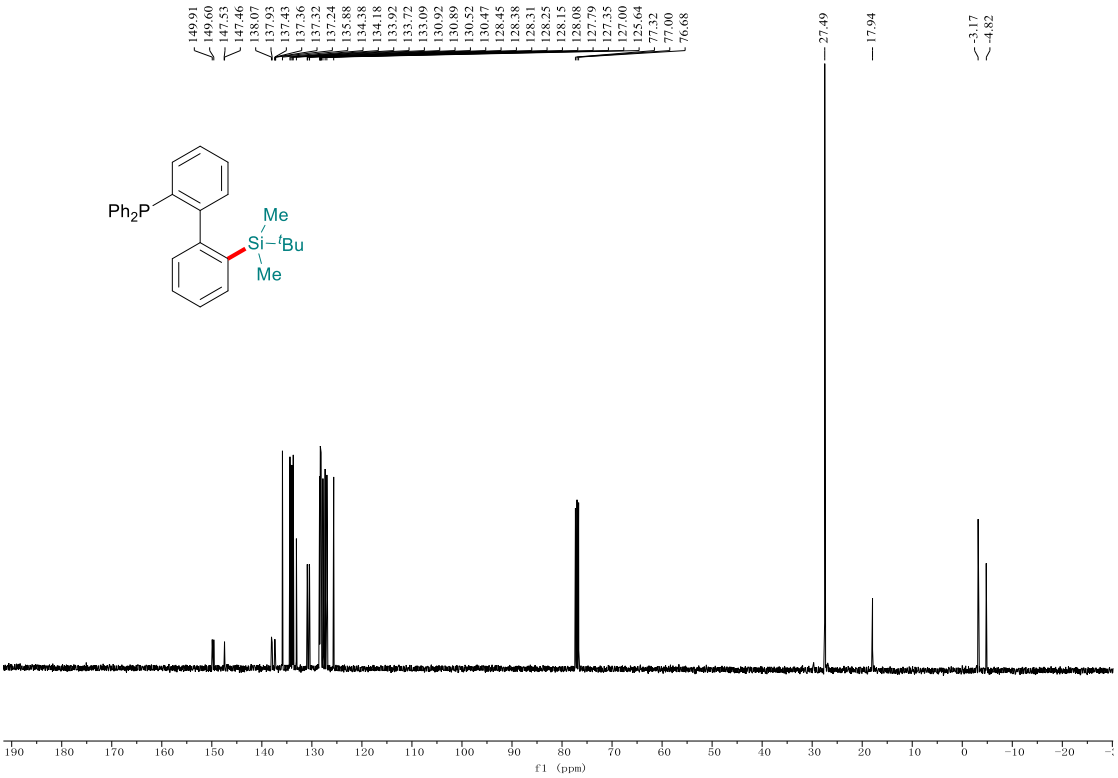
^{13}C NMR Spectrum of Compound **3ae**



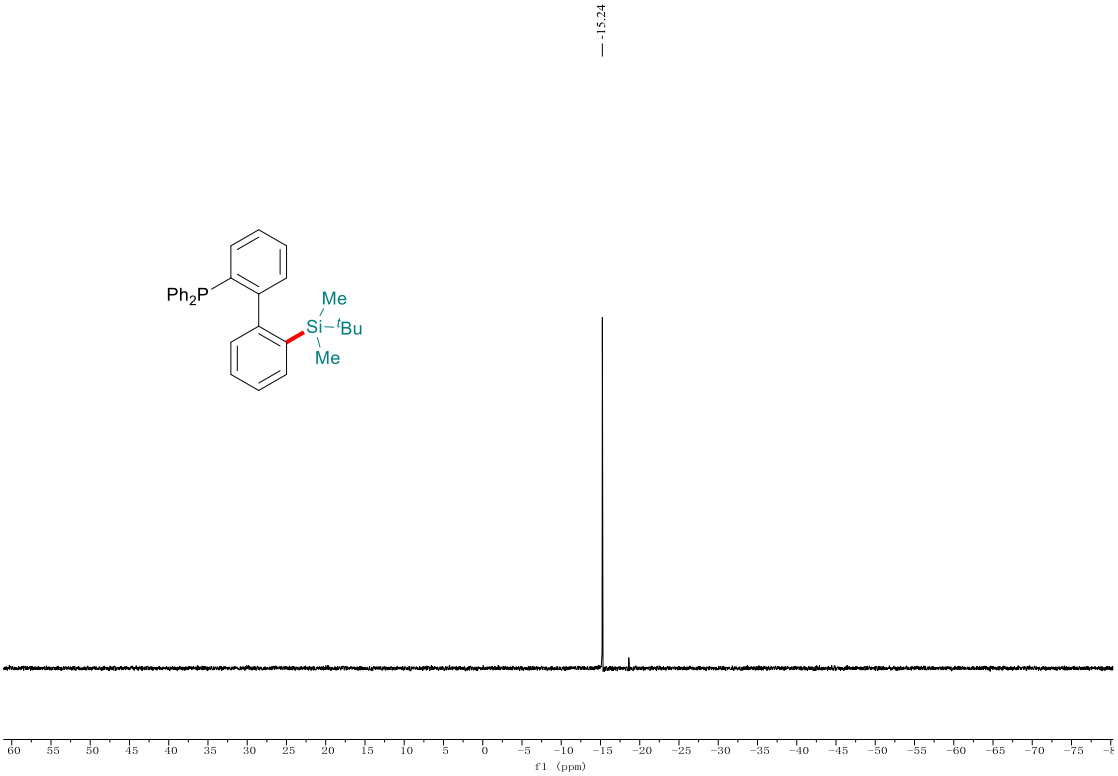
^{31}P NMR Spectrum of Compound **3ae**



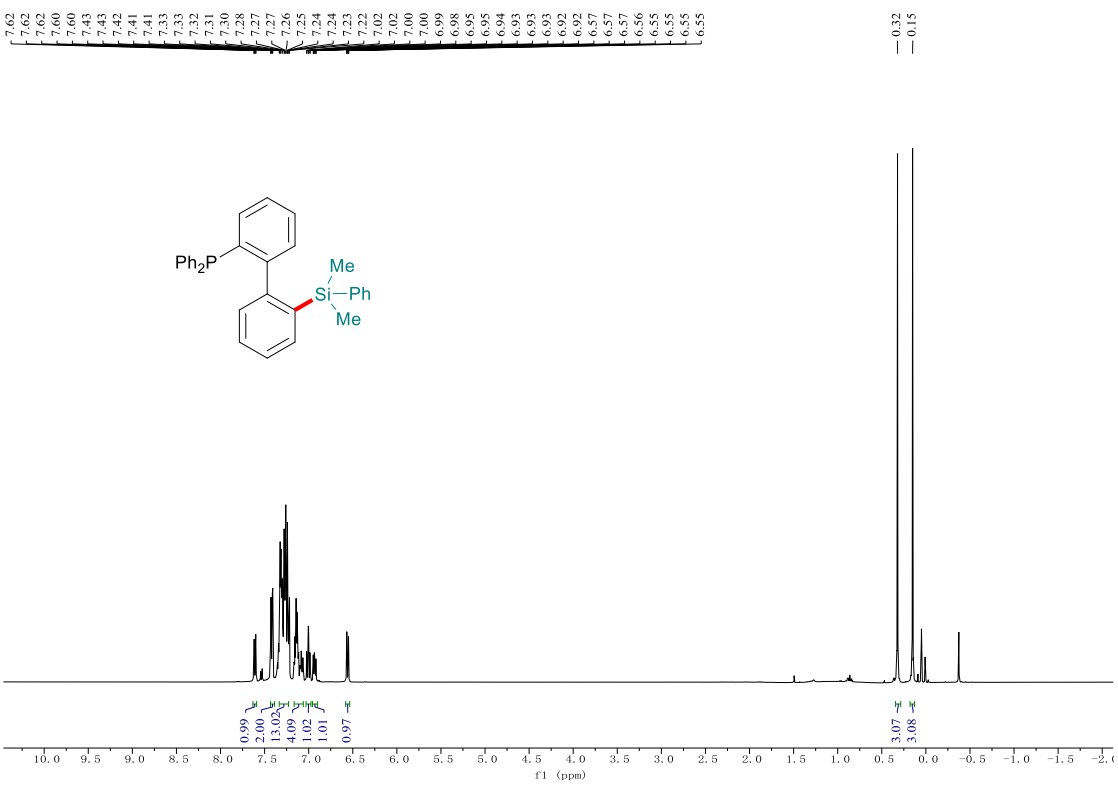
^{1}H NMR Spectrum of Compound **3af**



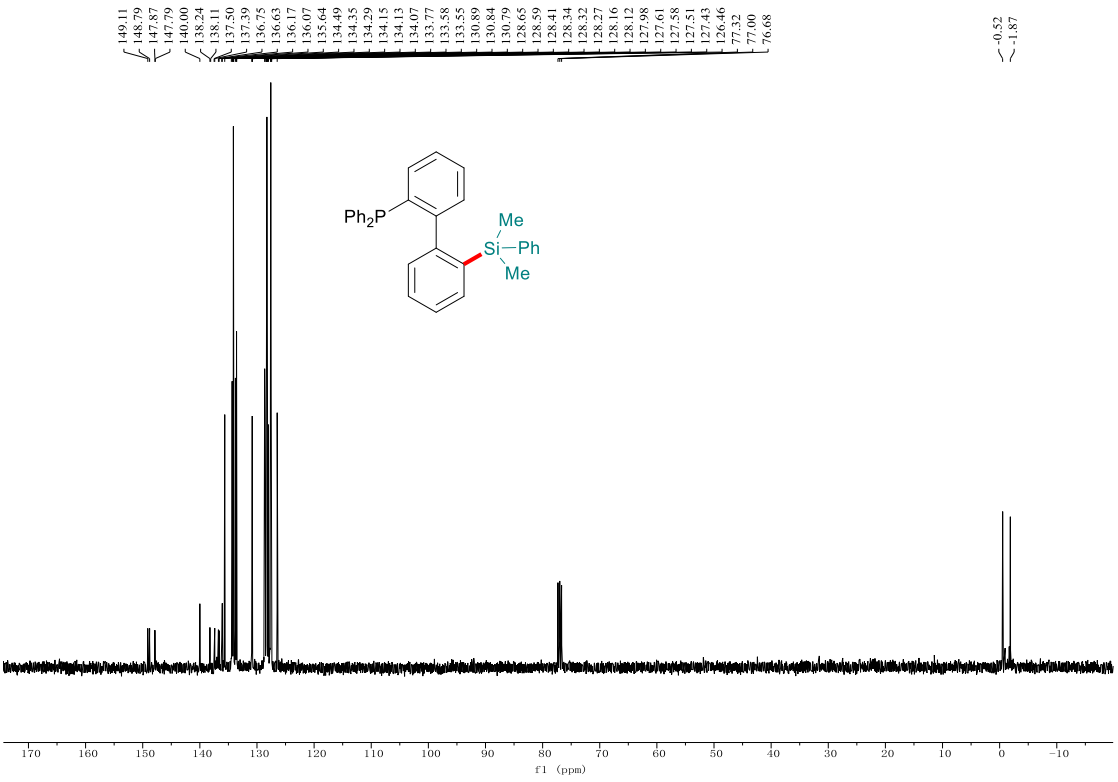
^{13}C NMR Spectrum of Compound **3af**



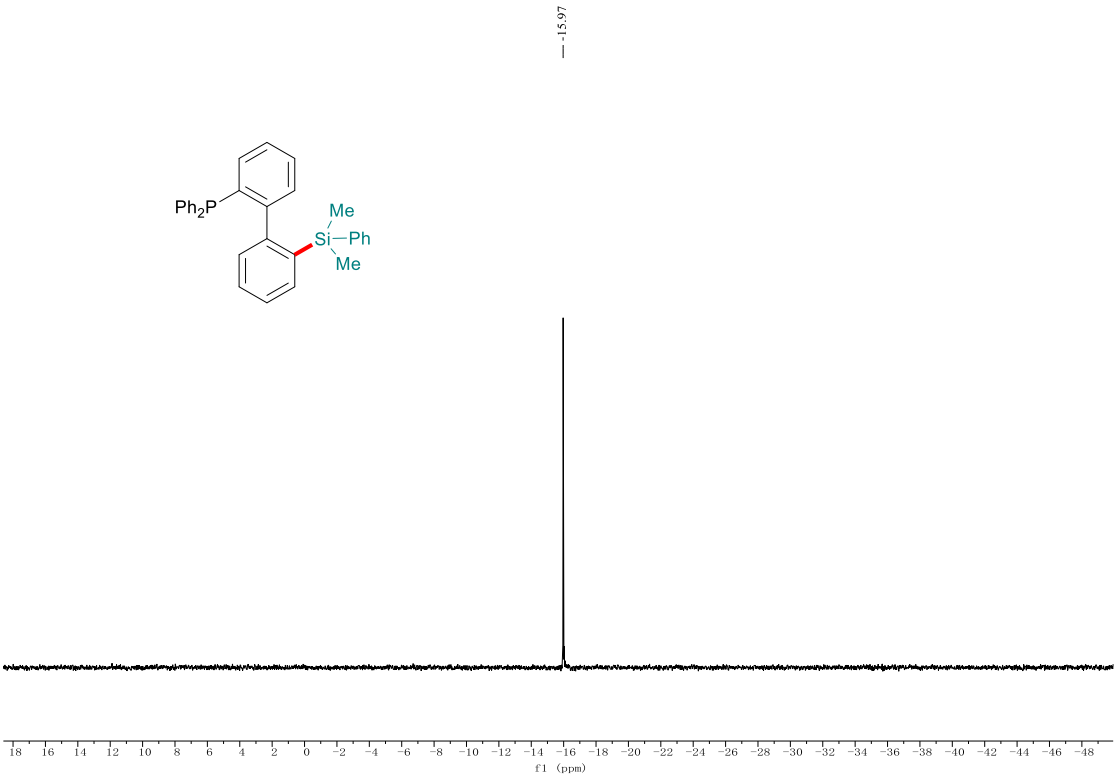
^{31}P NMR Spectrum of Compound **3af**



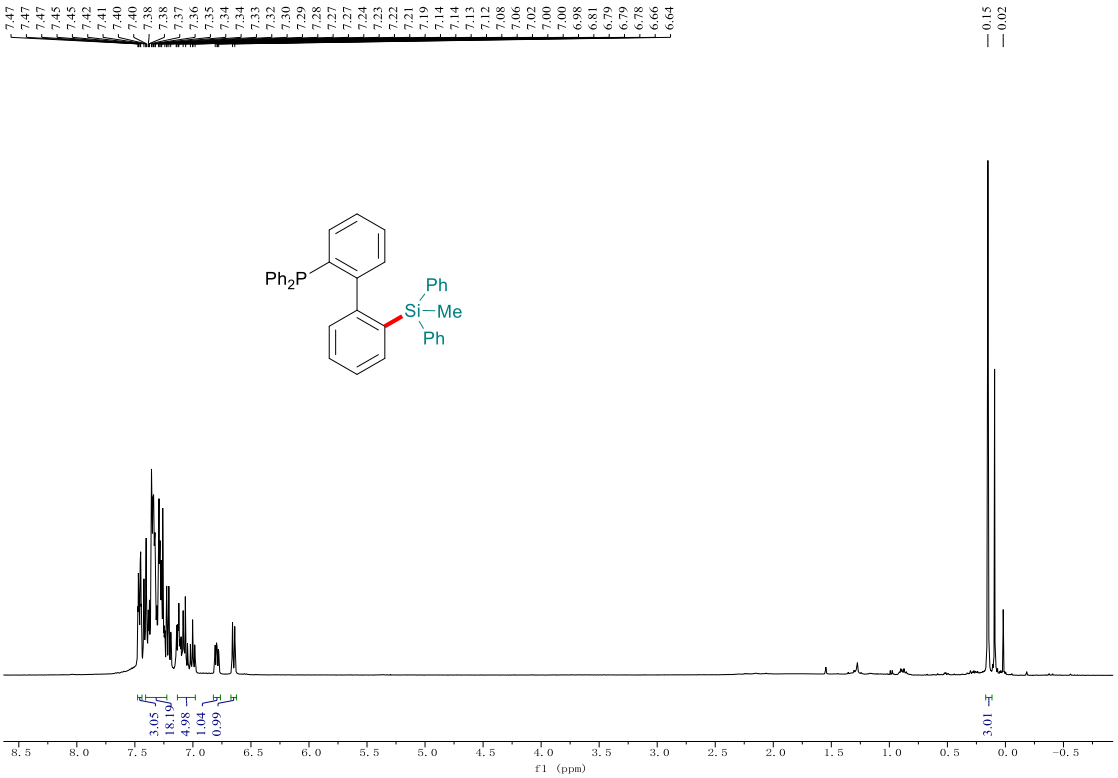
^{1}H NMR Spectrum of Compound **3ag**



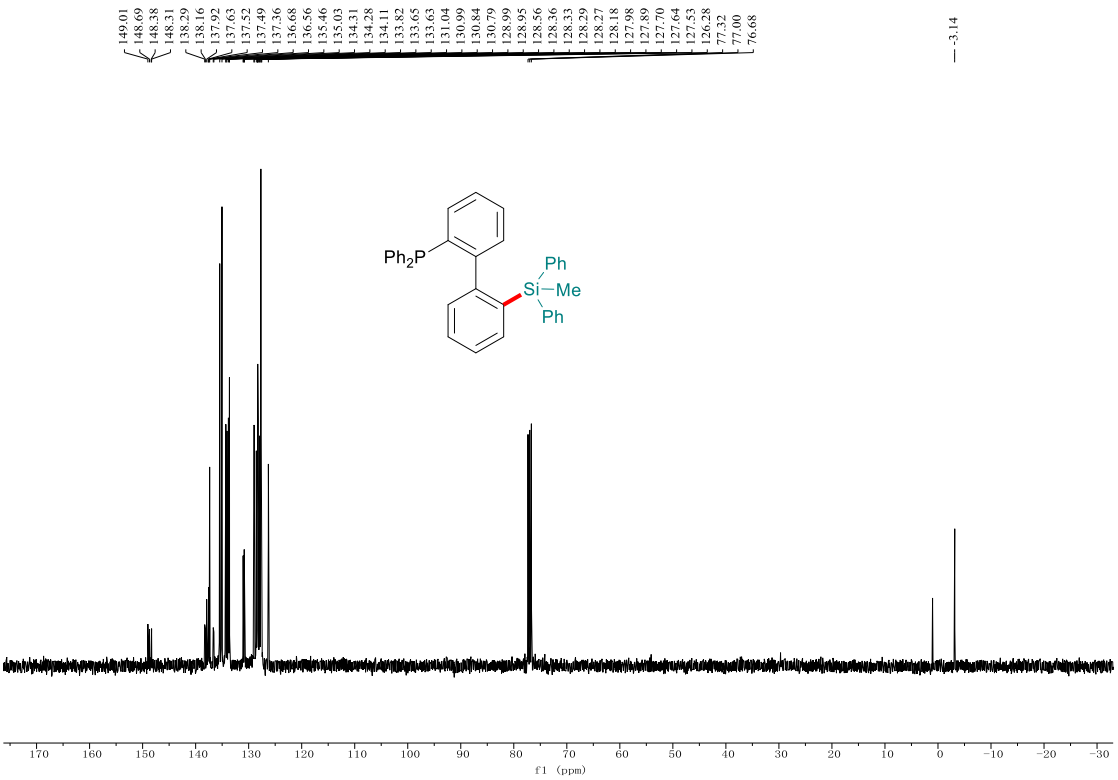
^{13}C NMR Spectrum of Compound **3ag**



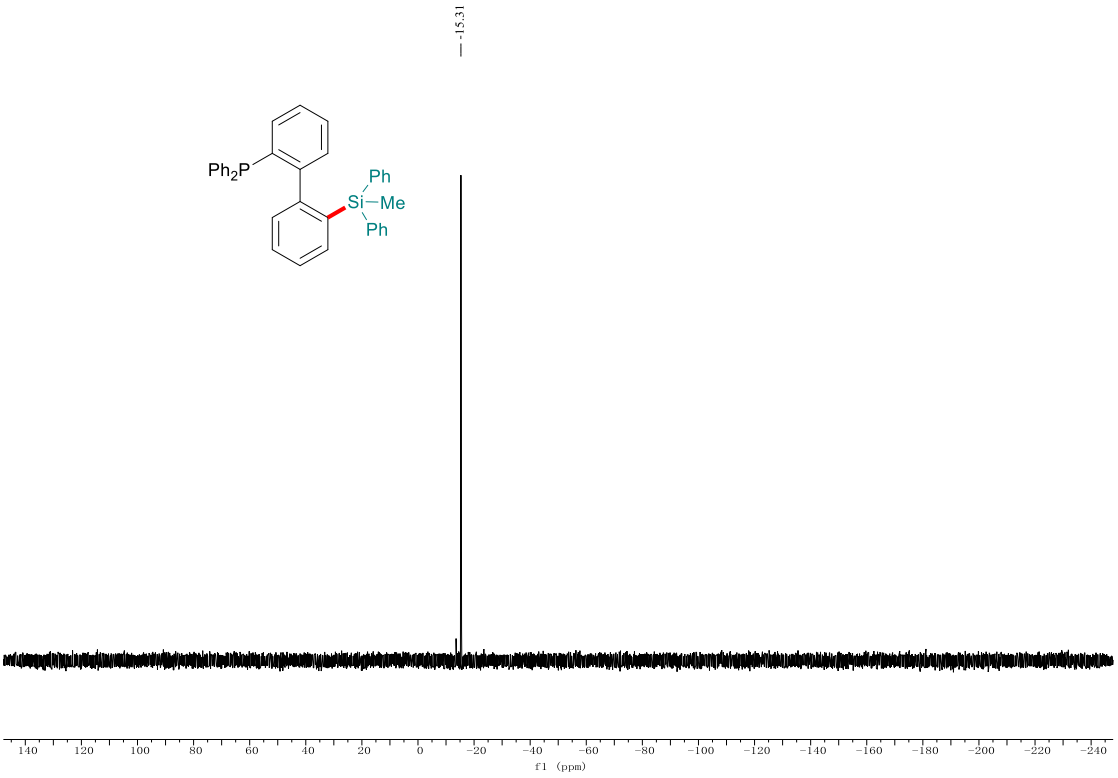
^{31}P NMR Spectrum of Compound **3ag**



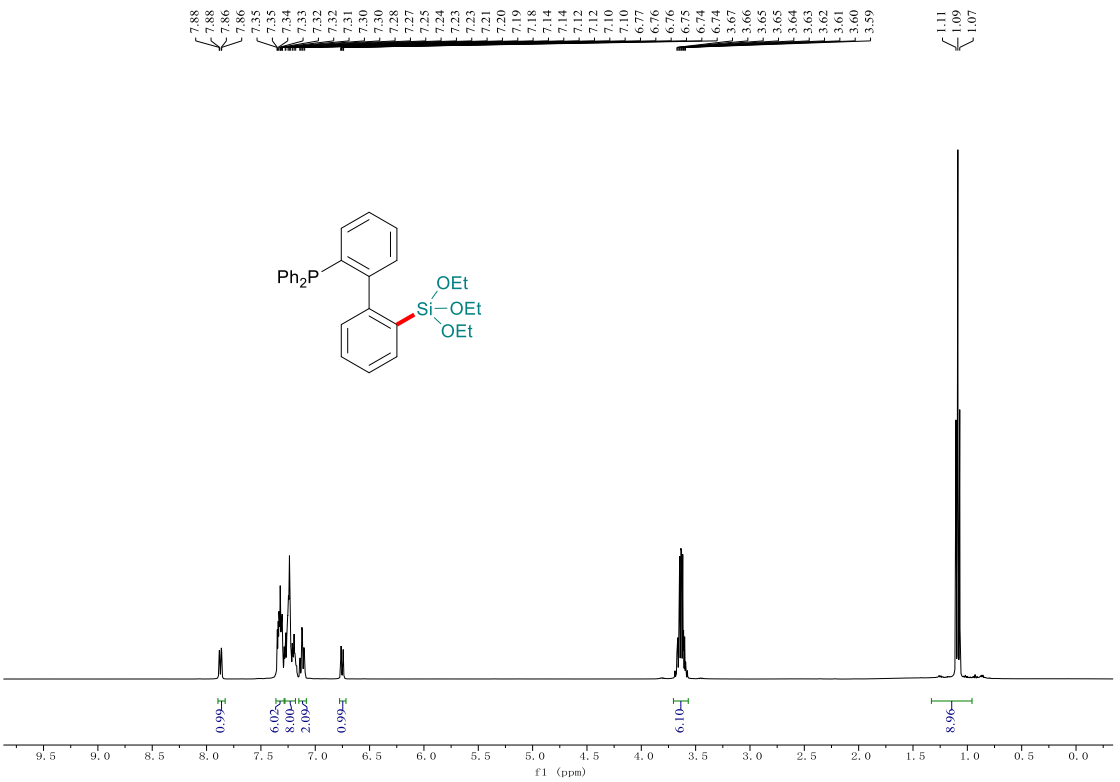
^{1}H NMR Spectrum of Compound **3ah**



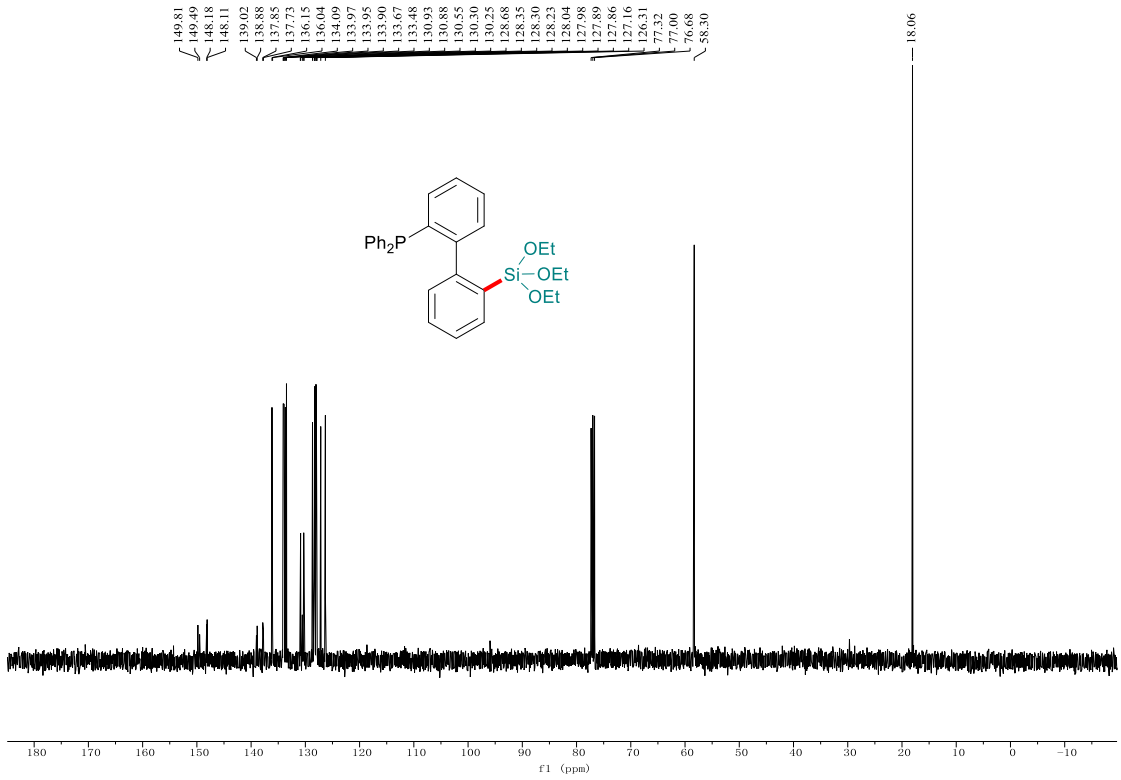
^{13}C NMR Spectrum of Compound **3ah**



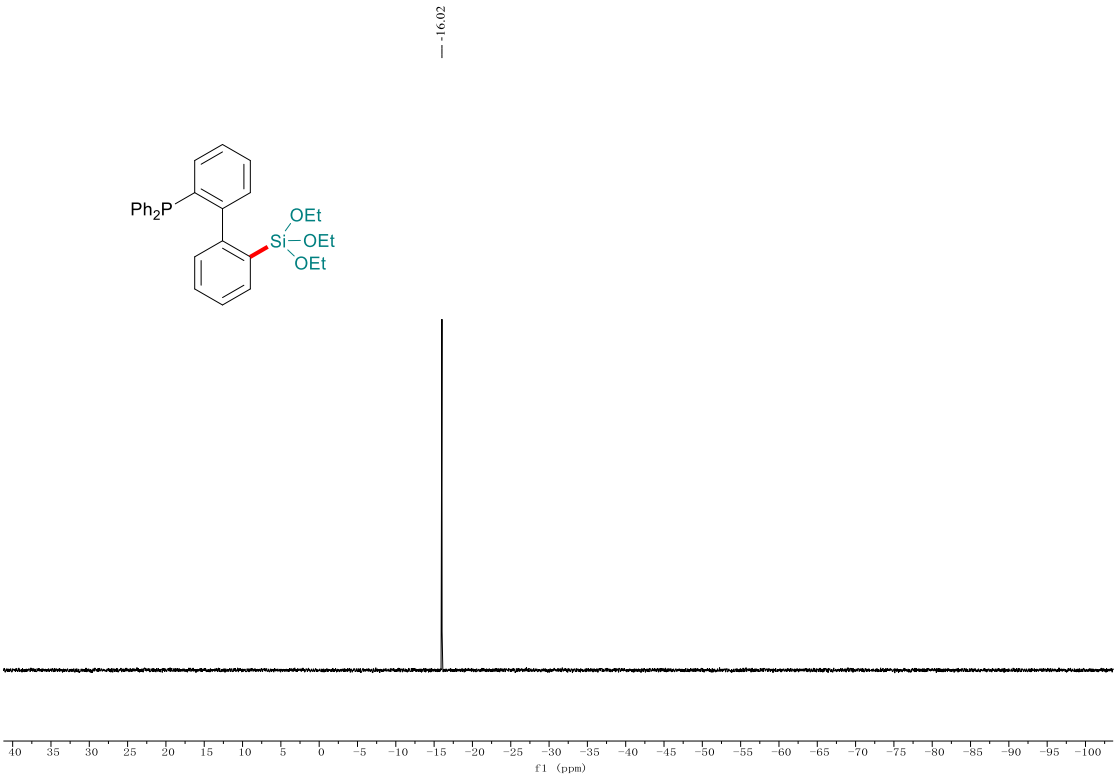
^{31}P NMR Spectrum of Compound **3ah**



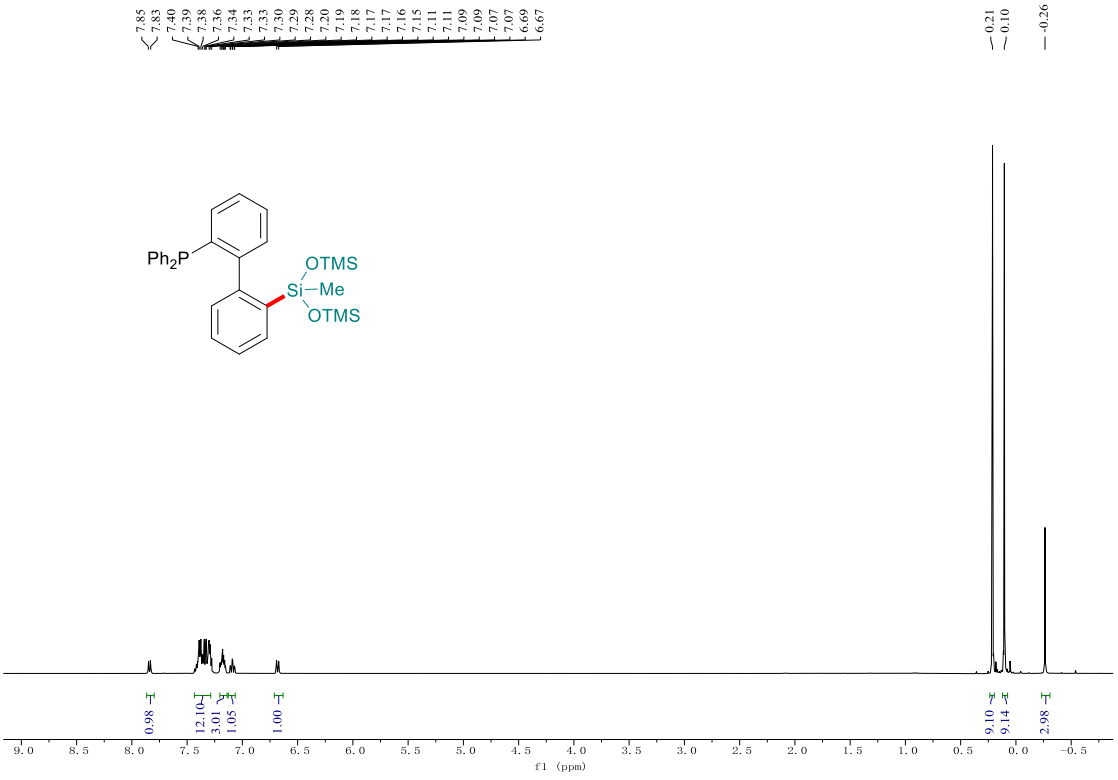
^{1}H NMR Spectrum of Compound **3ai**



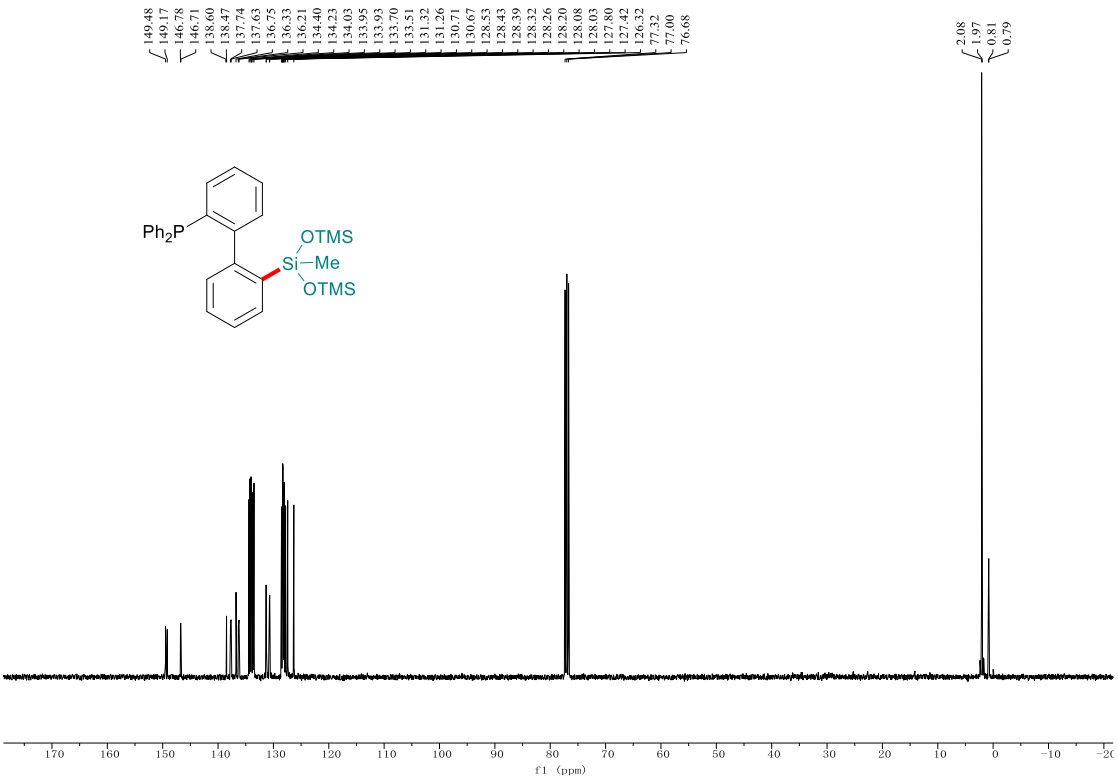
^{13}C NMR Spectrum of Compound **3ai**



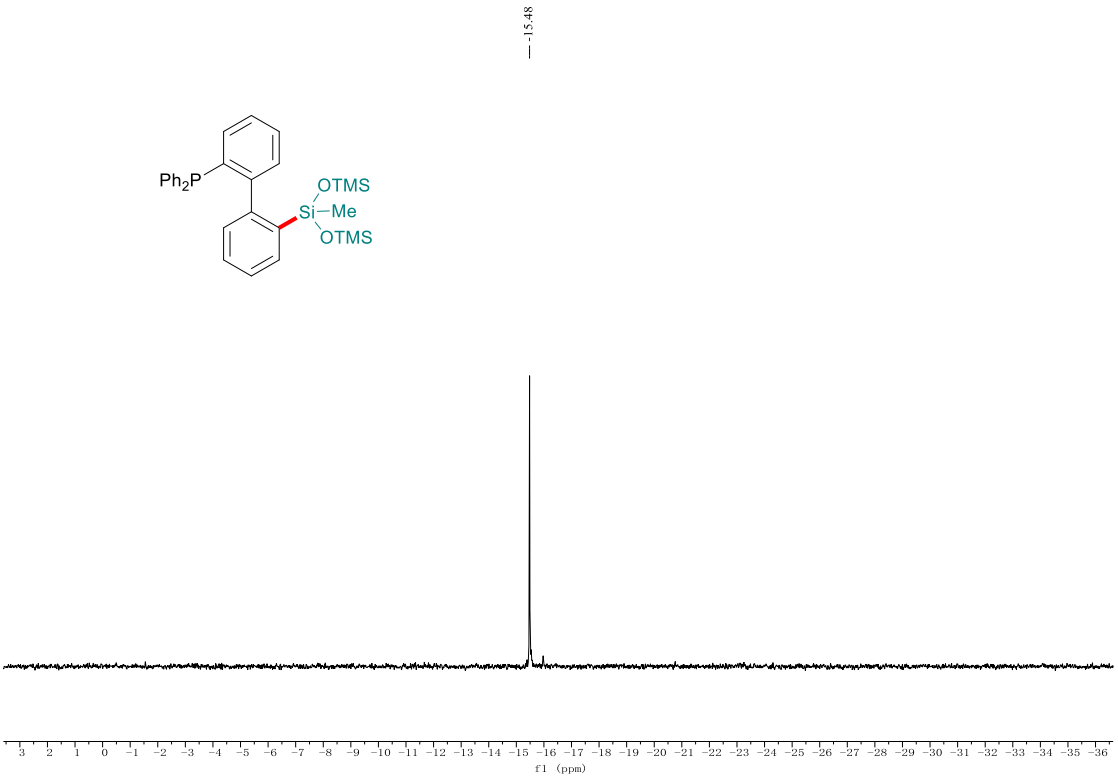
^{31}P NMR Spectrum of Compound **3ai**



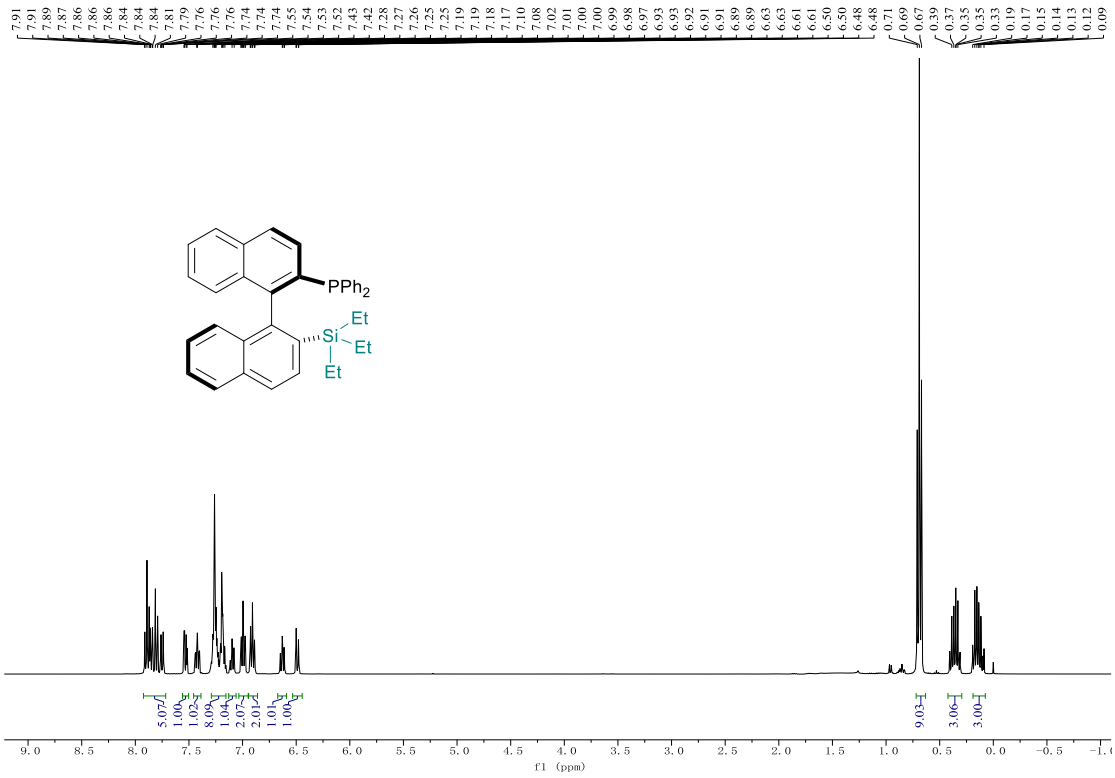
^{1}H NMR Spectrum of Compound **3aj**



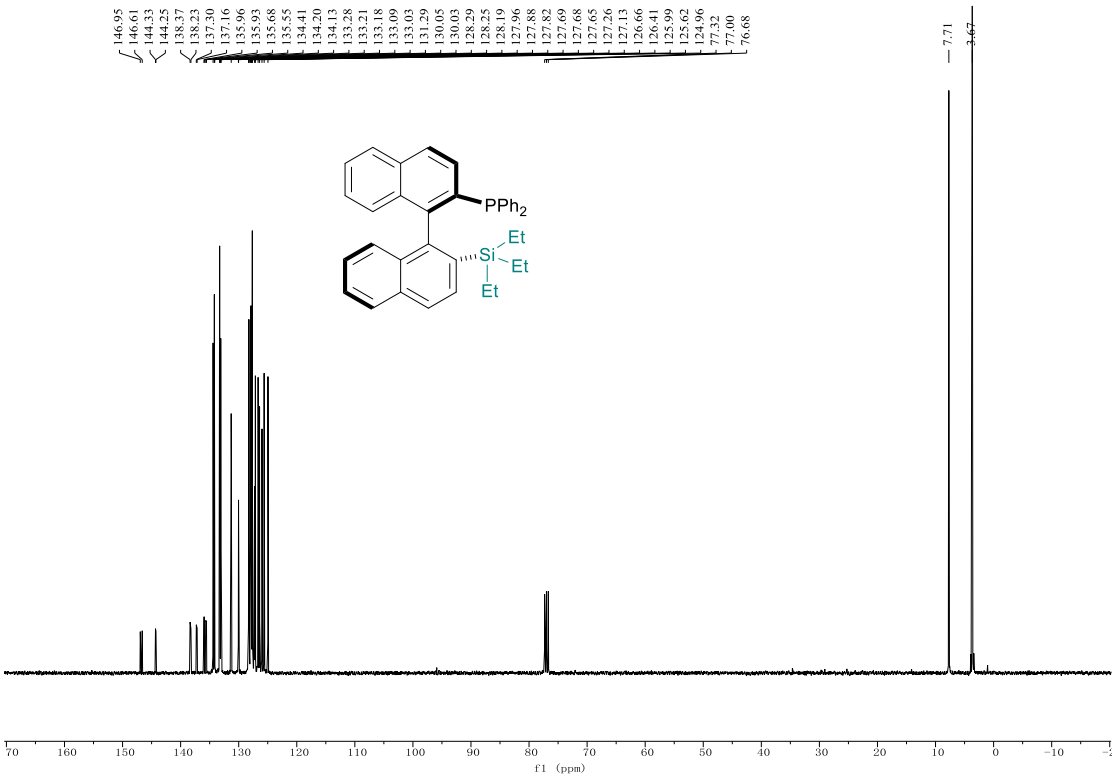
^{13}C NMR Spectrum of Compound **3aj**



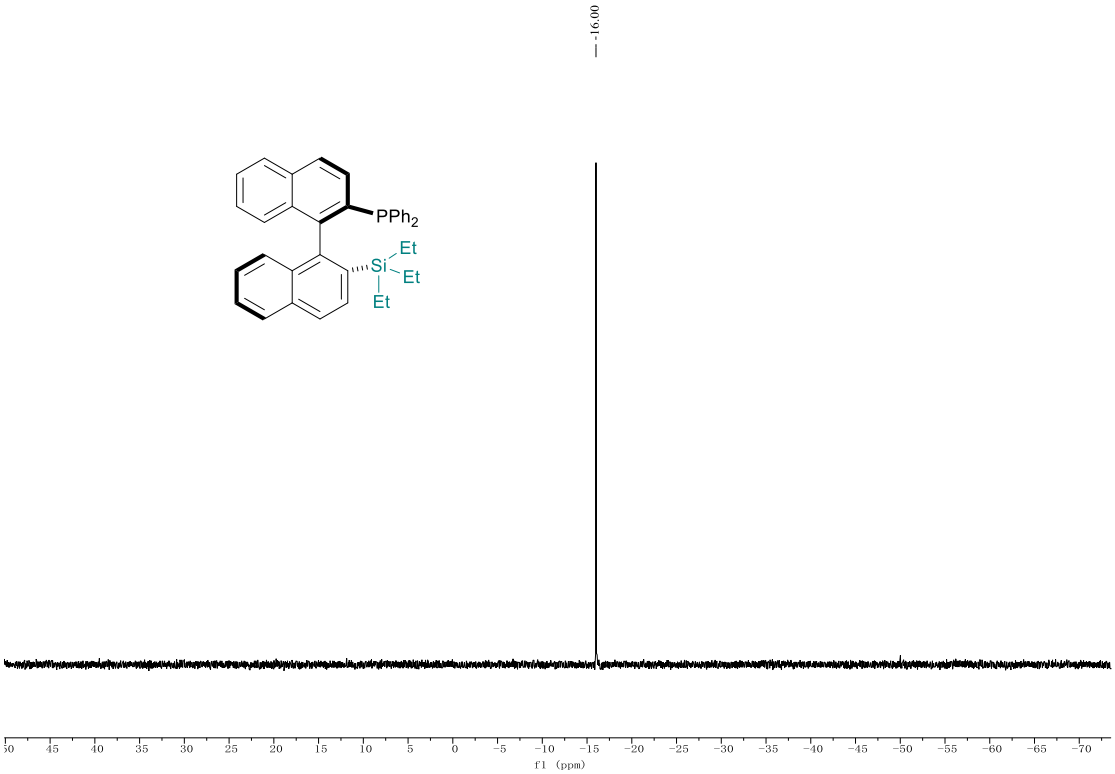
^{31}P NMR Spectrum of Compound **3aj**



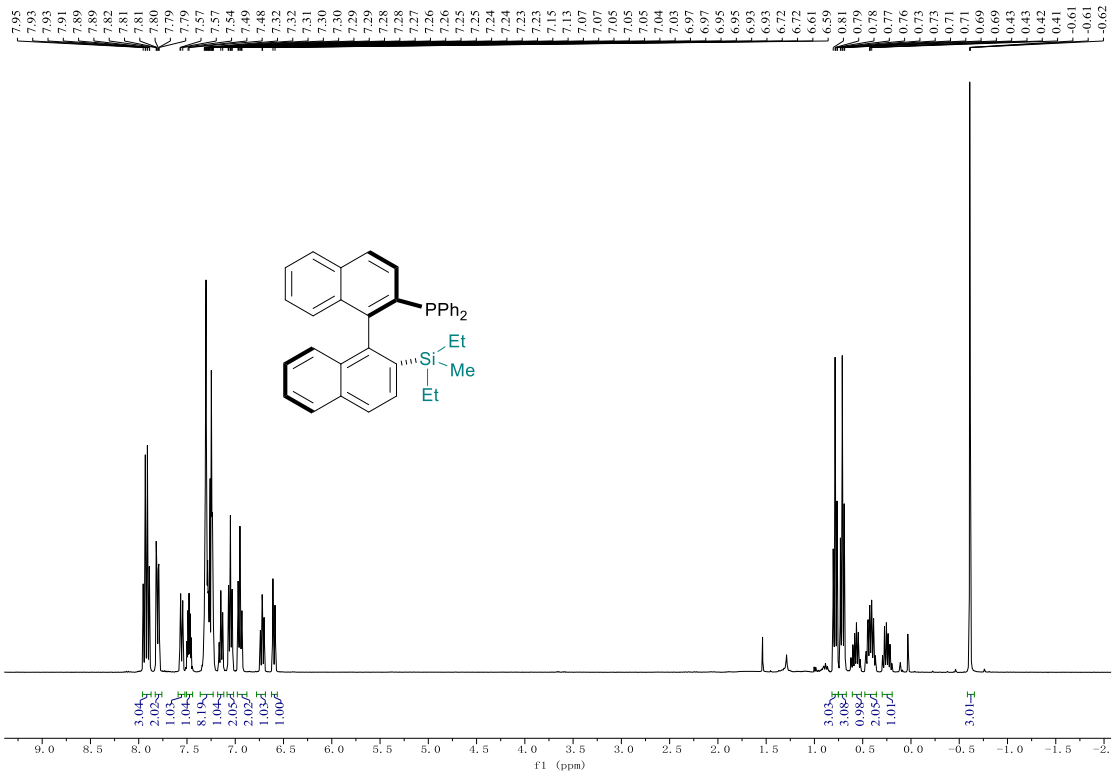
^{1}H NMR Spectrum of Compound **(*R*)-L1**



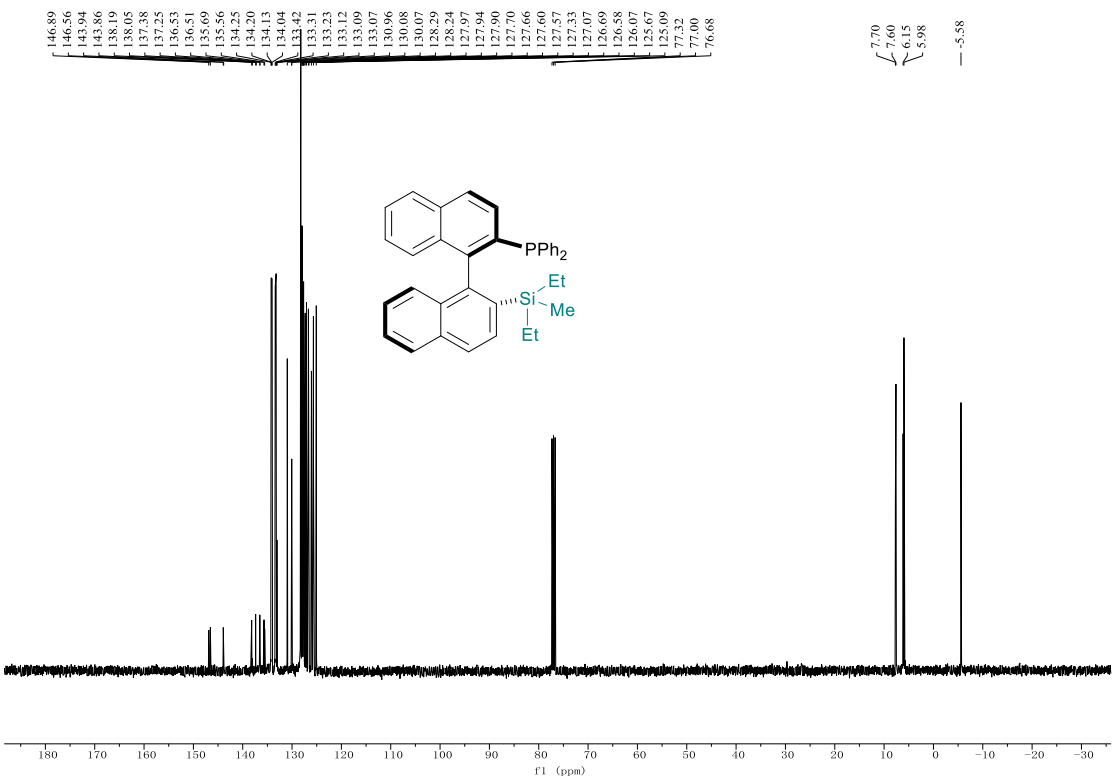
^{13}C NMR Spectrum of Compound **(*R*)-L1**



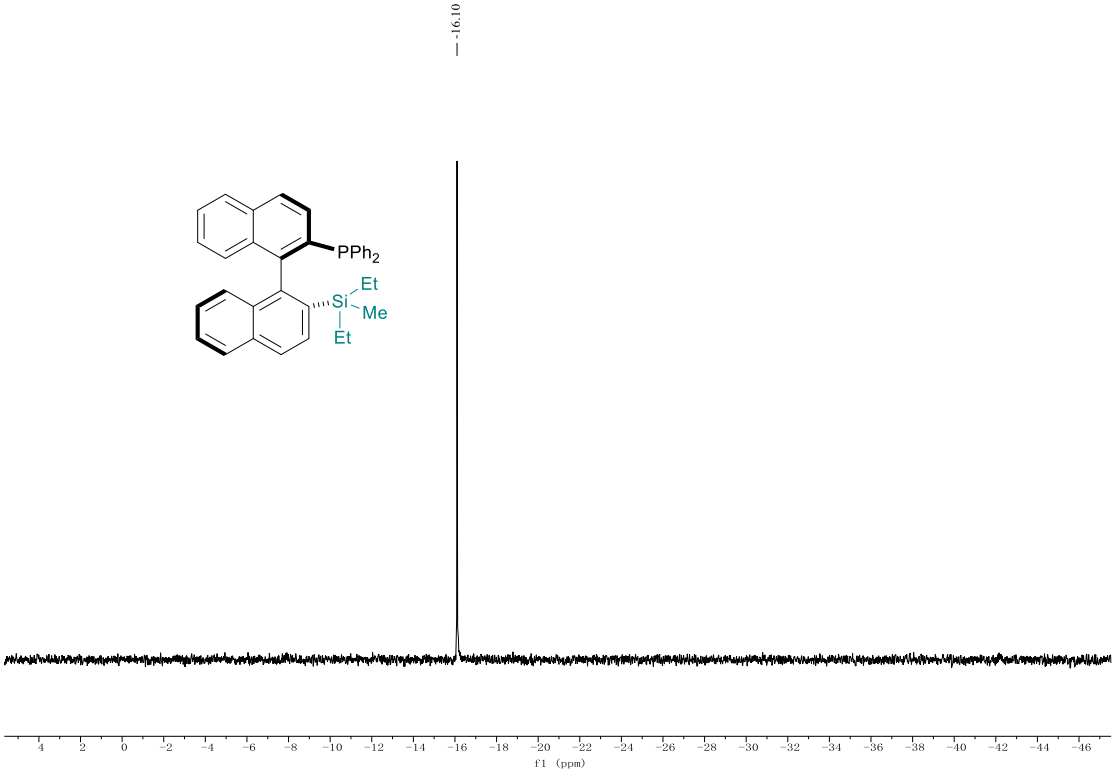
^{31}P NMR Spectrum of Compound **(*R*)-L1**



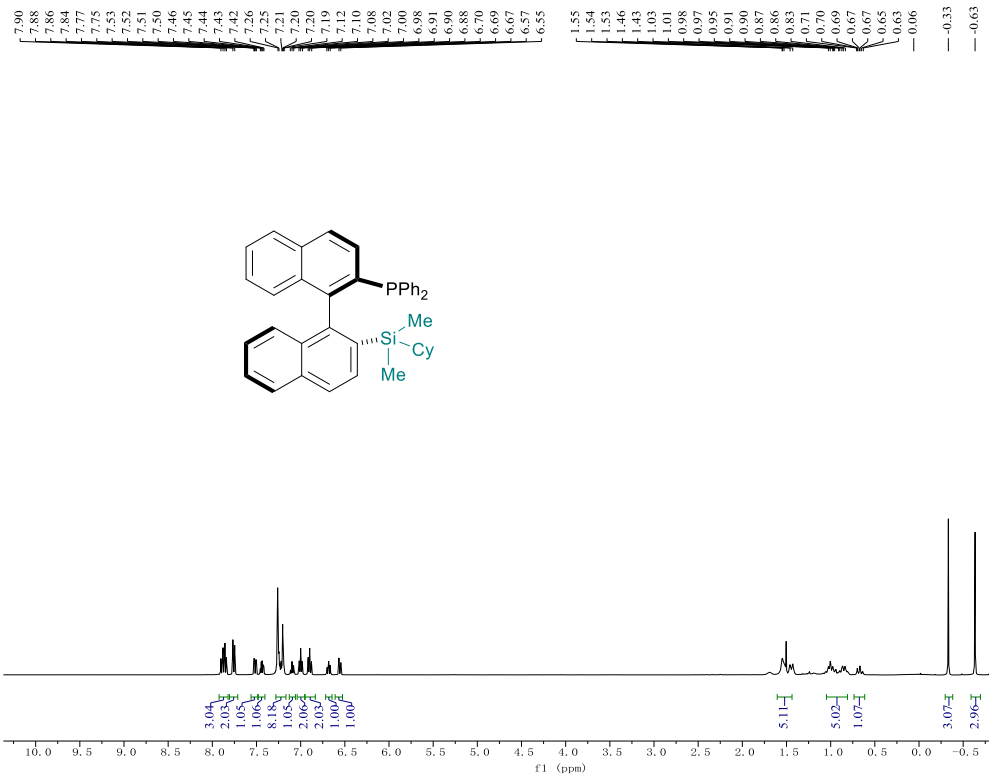
^{1}H NMR Spectrum of Compound **(*R*)-L2**



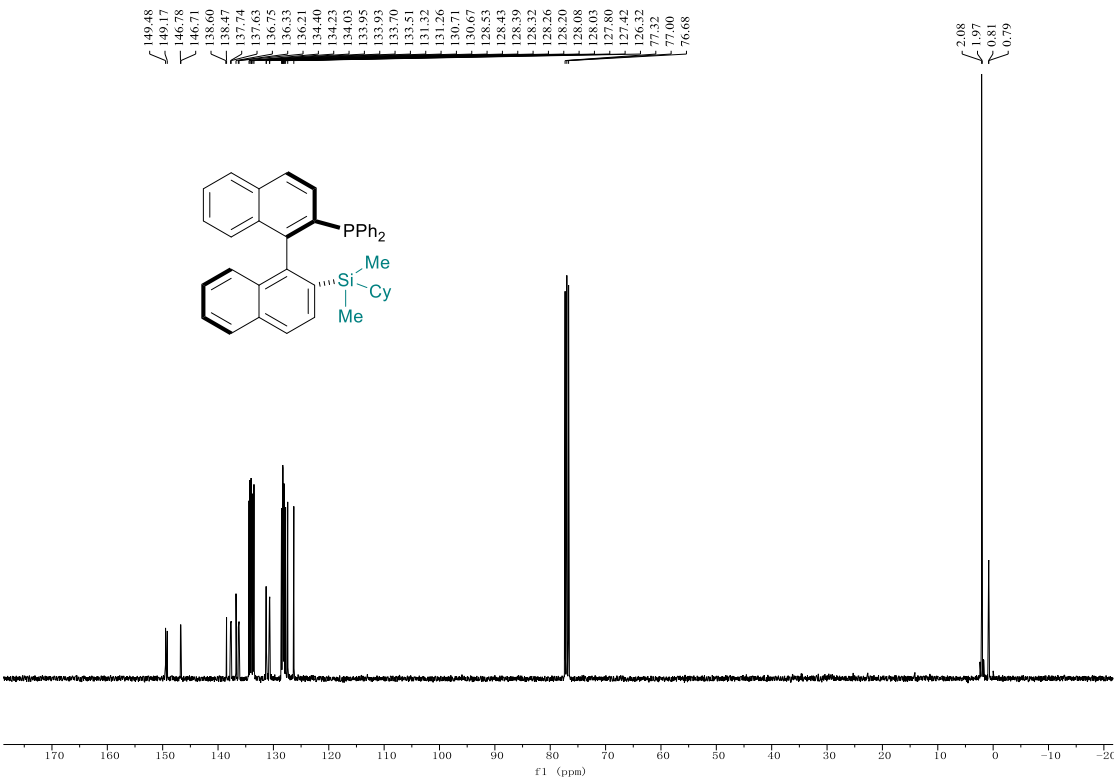
^{13}C NMR Spectrum of Compound **(*R*)-L2**



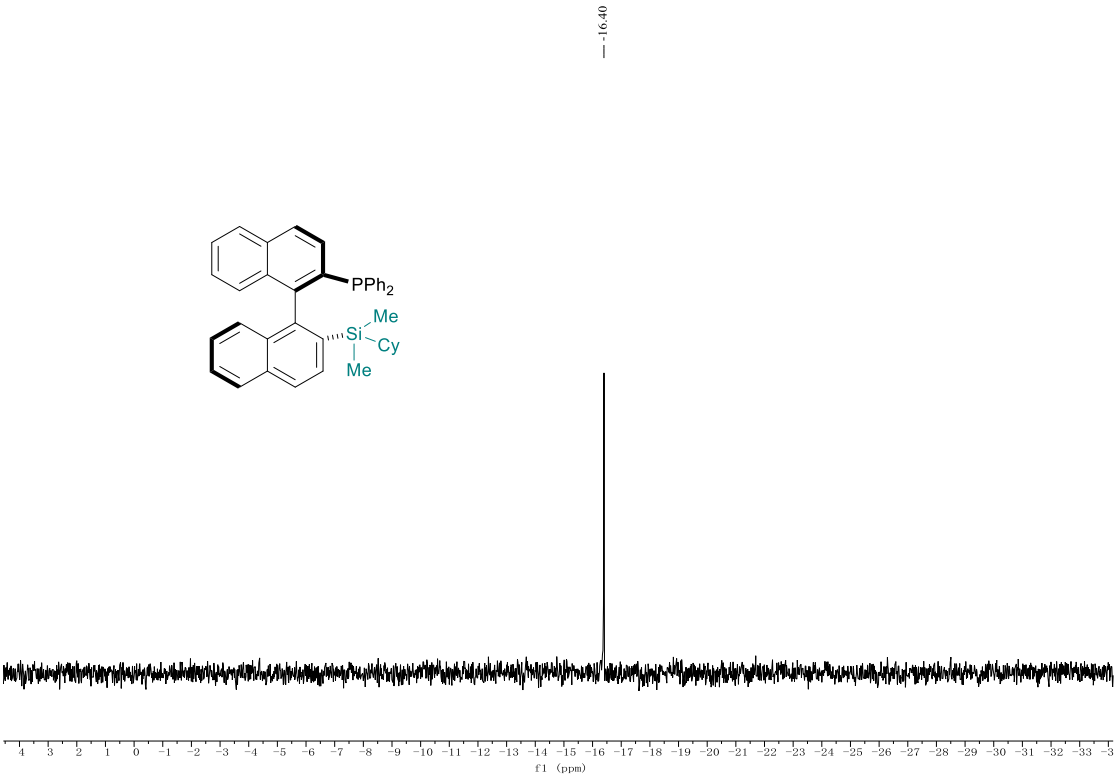
^{31}P NMR Spectrum of Compound **(*R*)-L2**



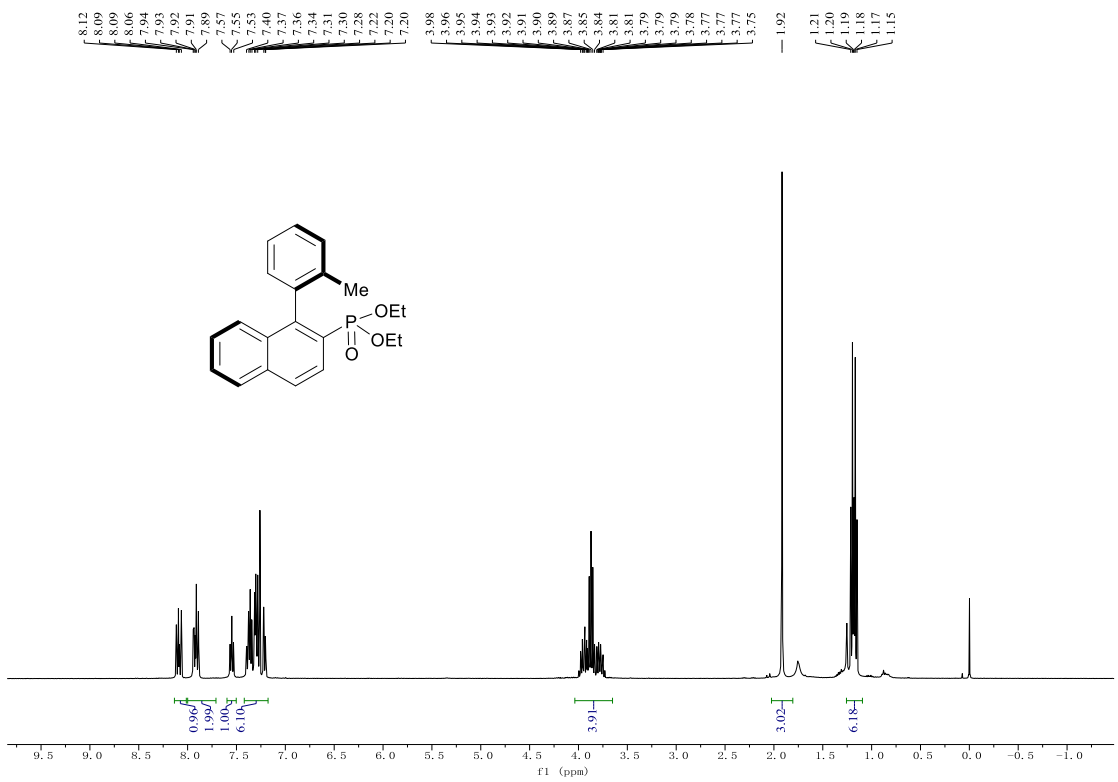
^{1}H NMR Spectrum of Compound **(*R*)-L3**



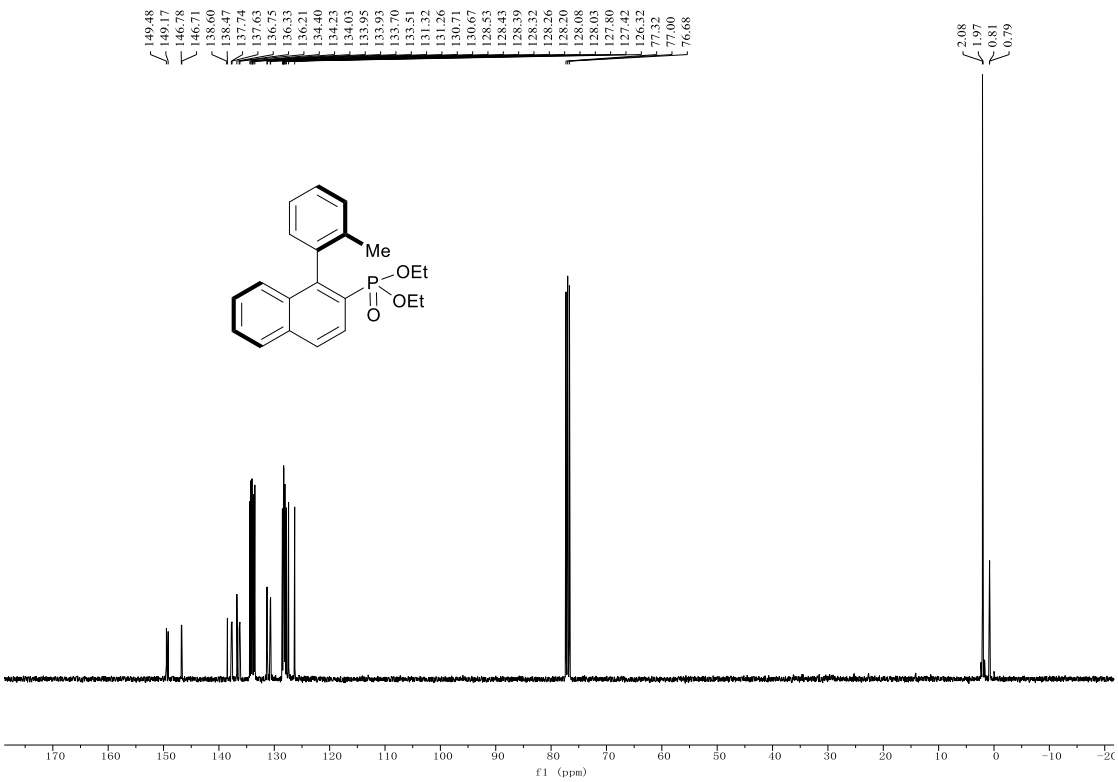
^{13}C NMR Spectrum of Compound **(*R*)-L3**



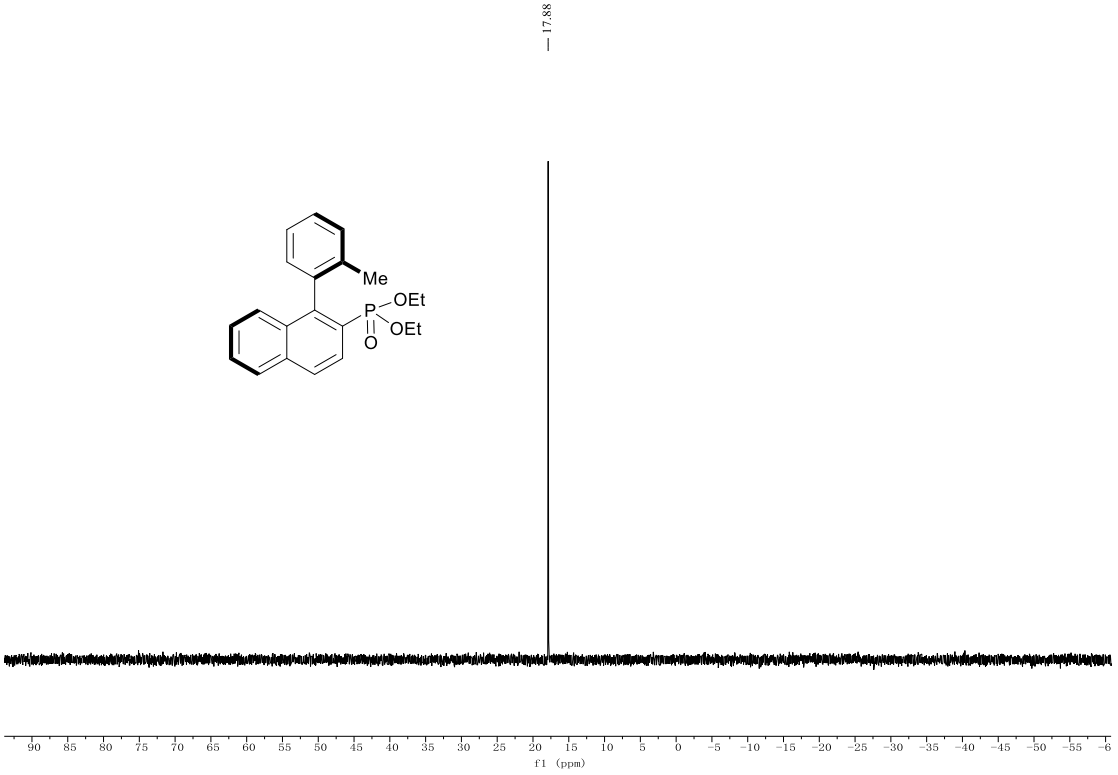
^{31}P NMR Spectrum of Compound **(*R*)-L3**



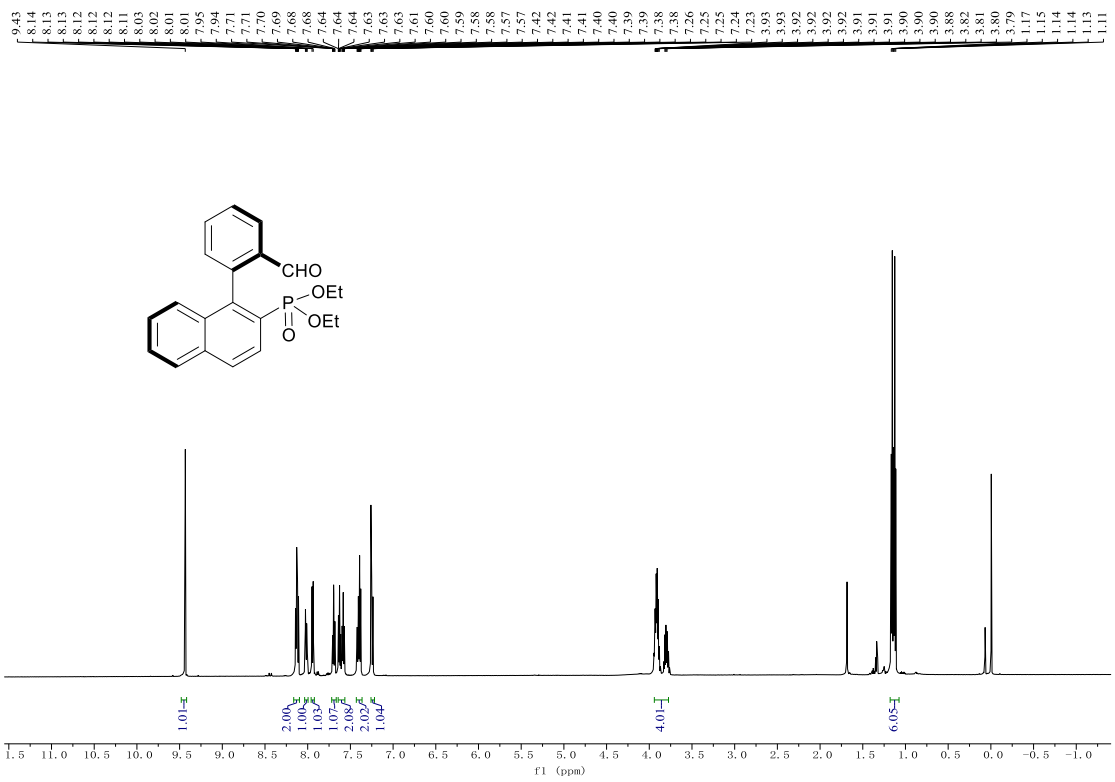
^{1}H NMR Spectrum of Compound **6aa**



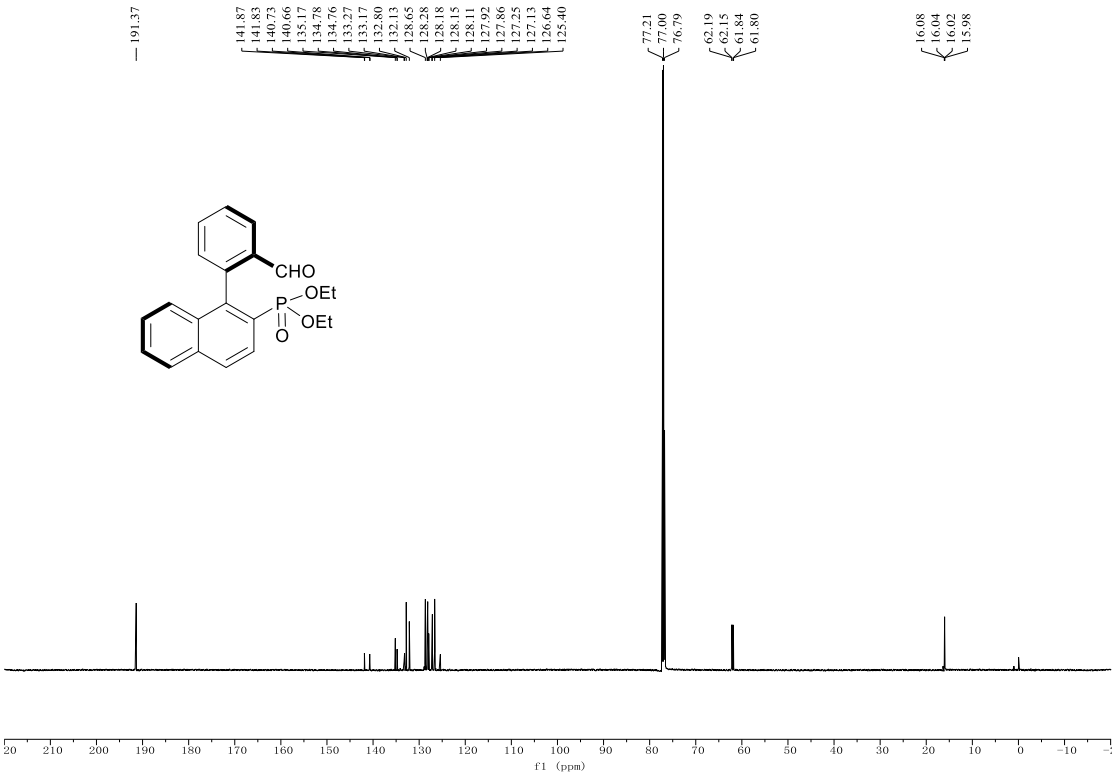
^{13}C NMR Spectrum of Compound **6aa**



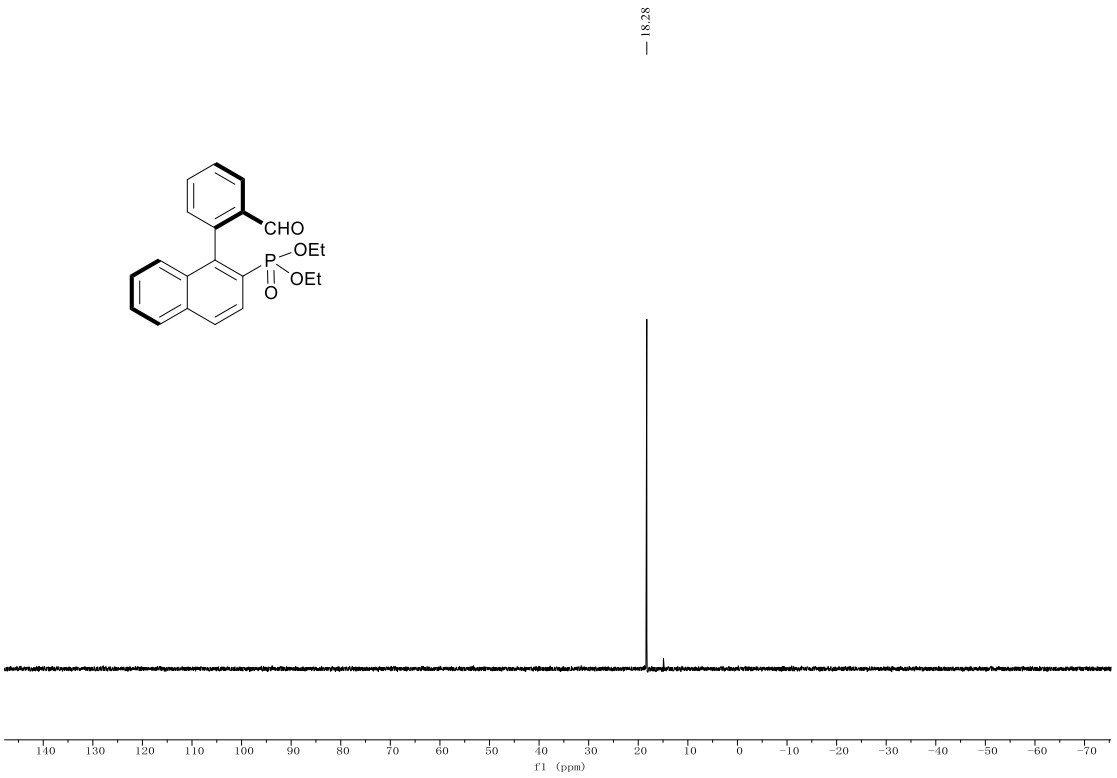
^{31}P NMR Spectrum of Compound **6aa**



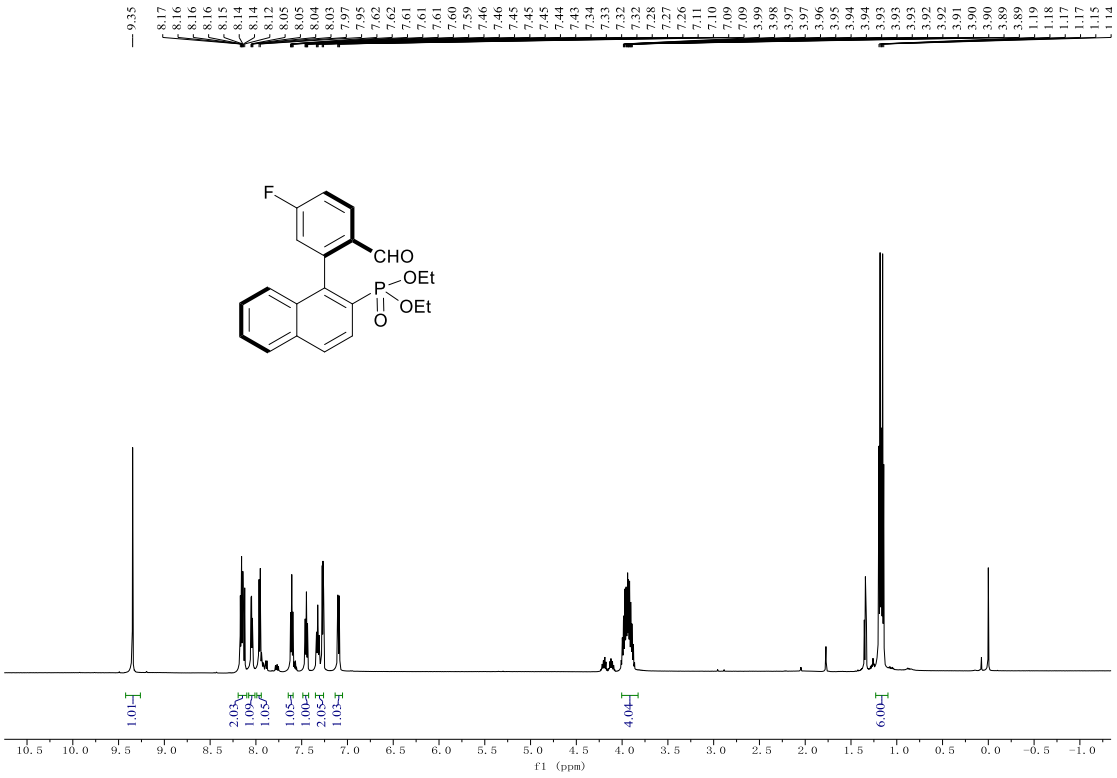
^{1}H NMR Spectrum of Compound **6ab**



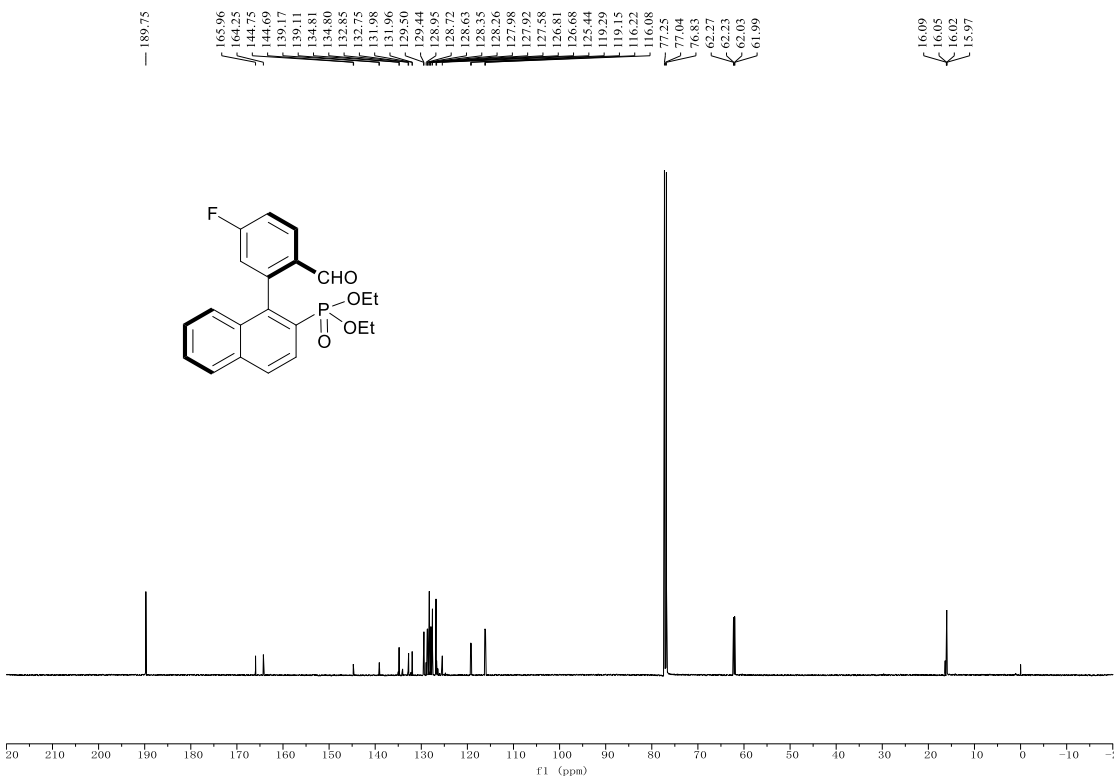
^{13}C NMR Spectrum of Compound **6ab**



^{31}P NMR Spectrum of Compound **6ab**

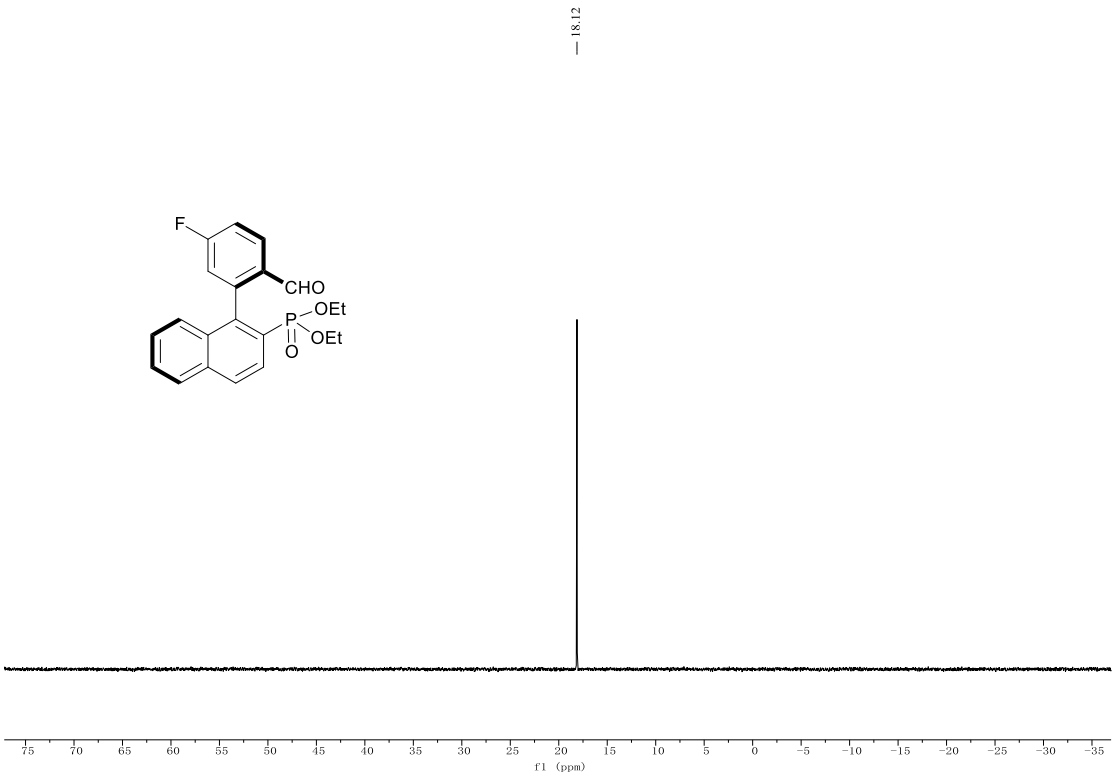


^{1}H NMR Spectrum of Compound **6ac**

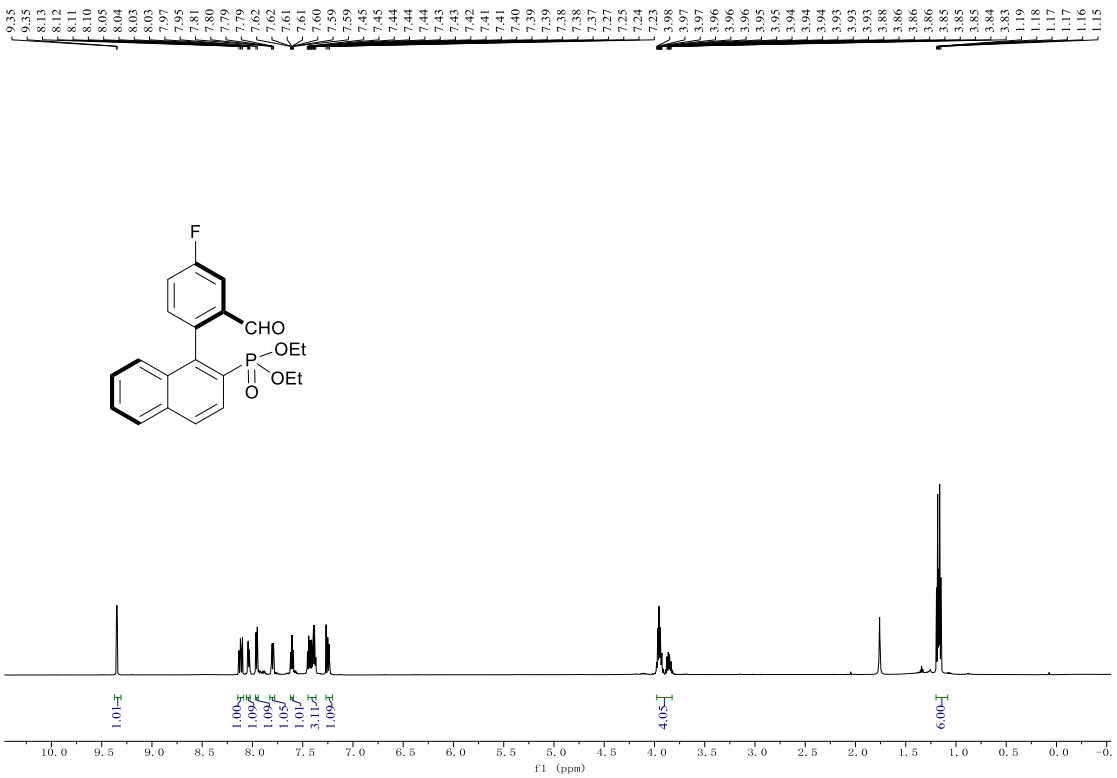


^{13}C NMR Spectrum of Compound **6ac**

^{19}F NMR Spectrum of Compound **6ac**

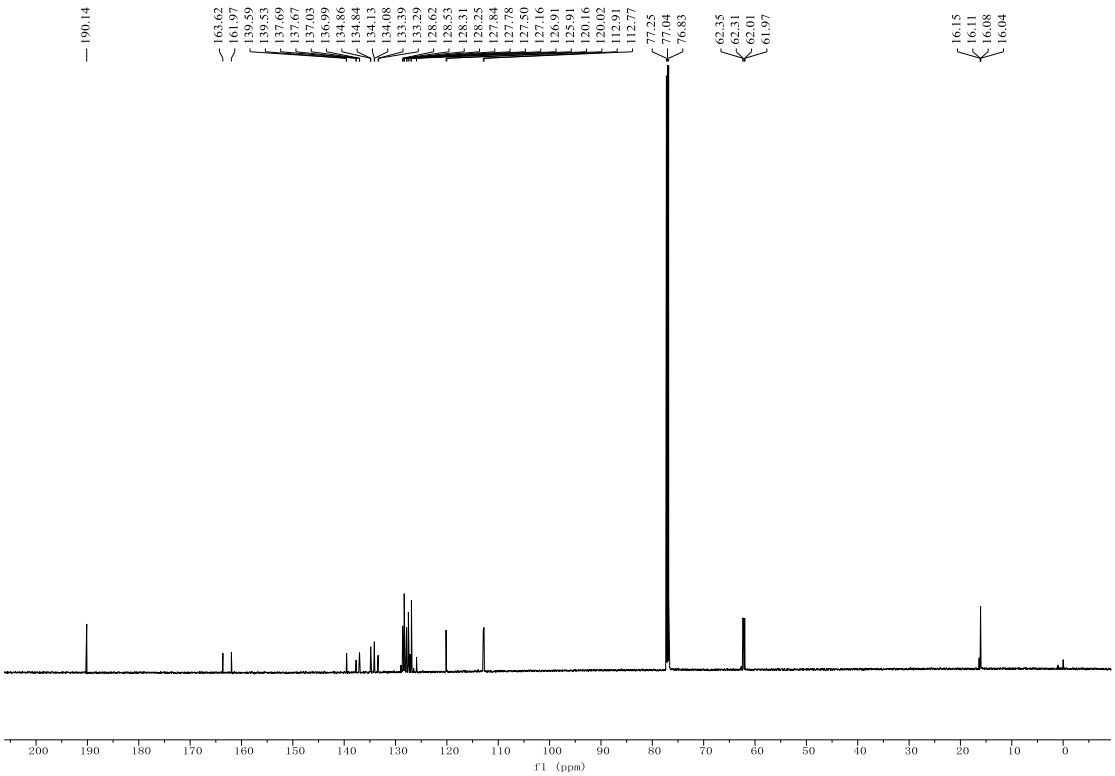


^{31}P NMR Spectrum of Compound **6ac**

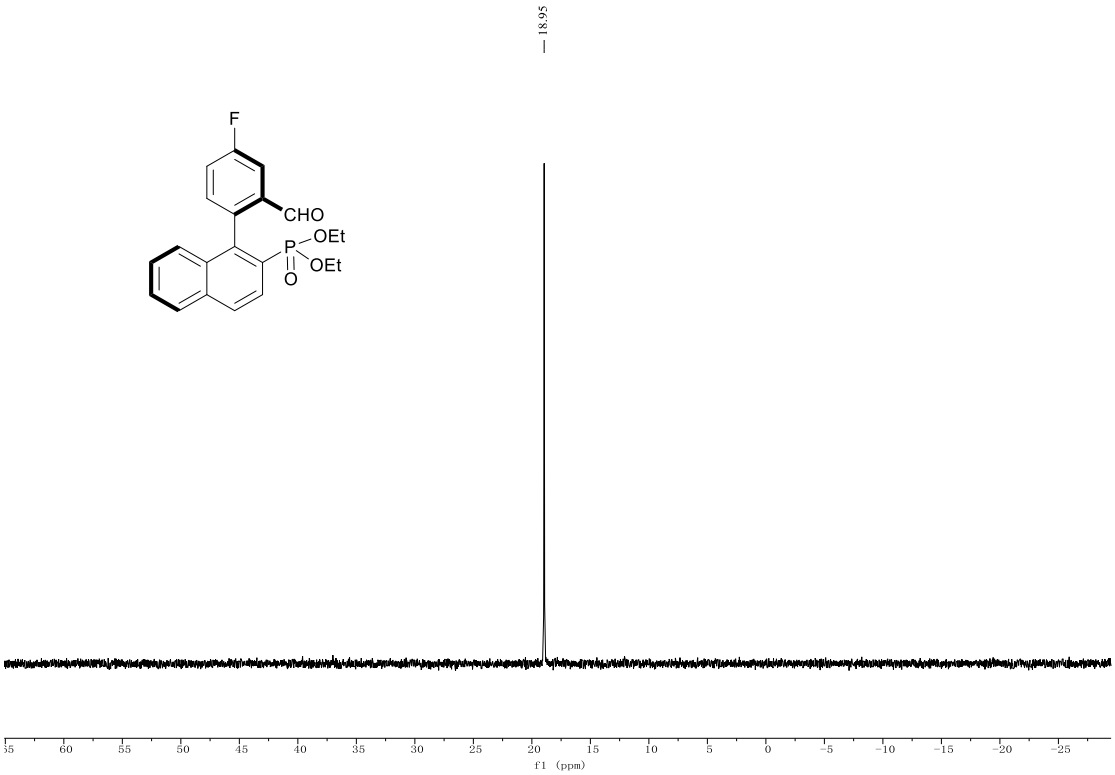


^{1}H NMR Spectrum of Compound **6ad**

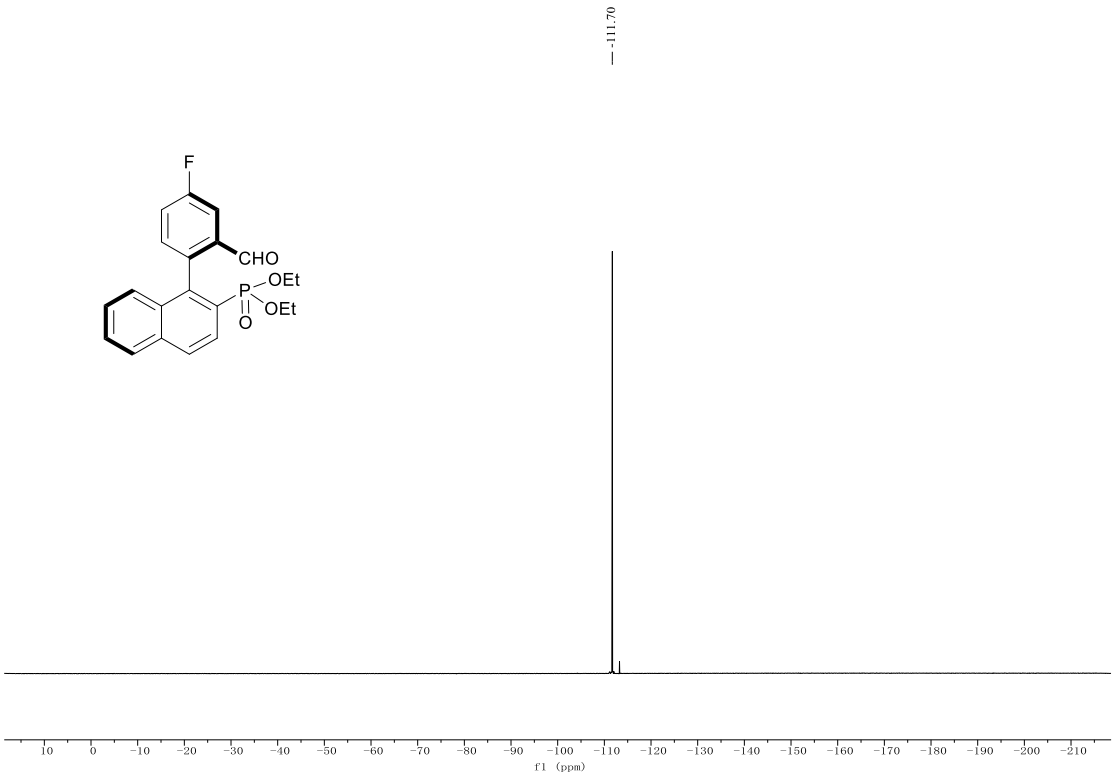
F



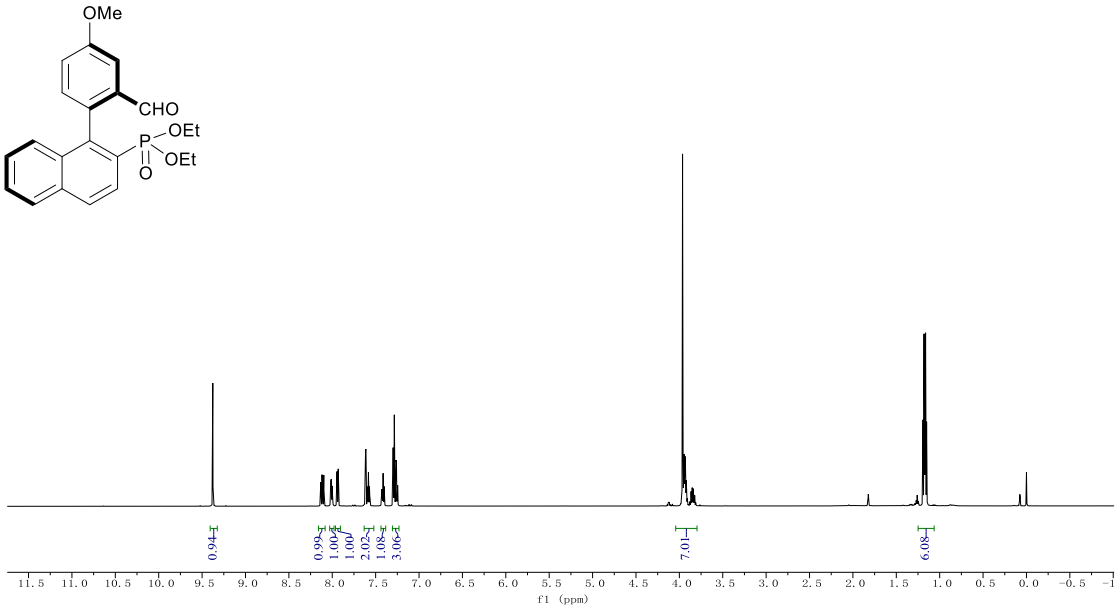
^{13}C NMR Spectrum of Compound **6ad**



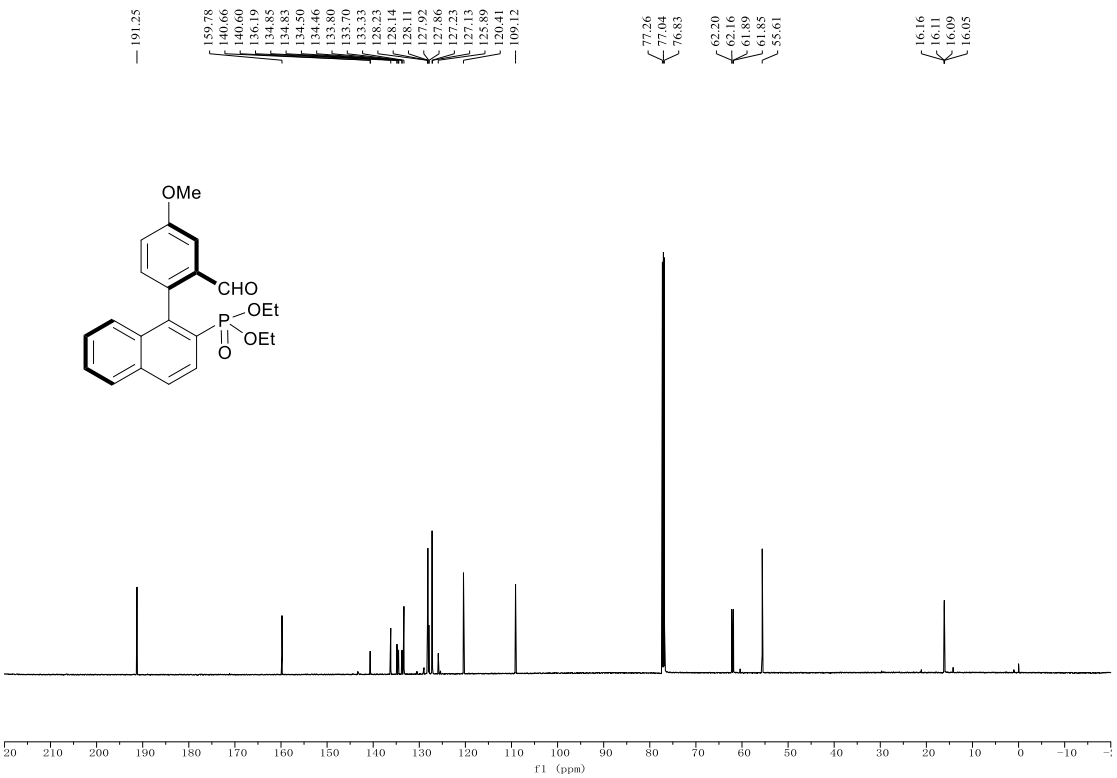
^{31}P NMR Spectrum of Compound **6ad**



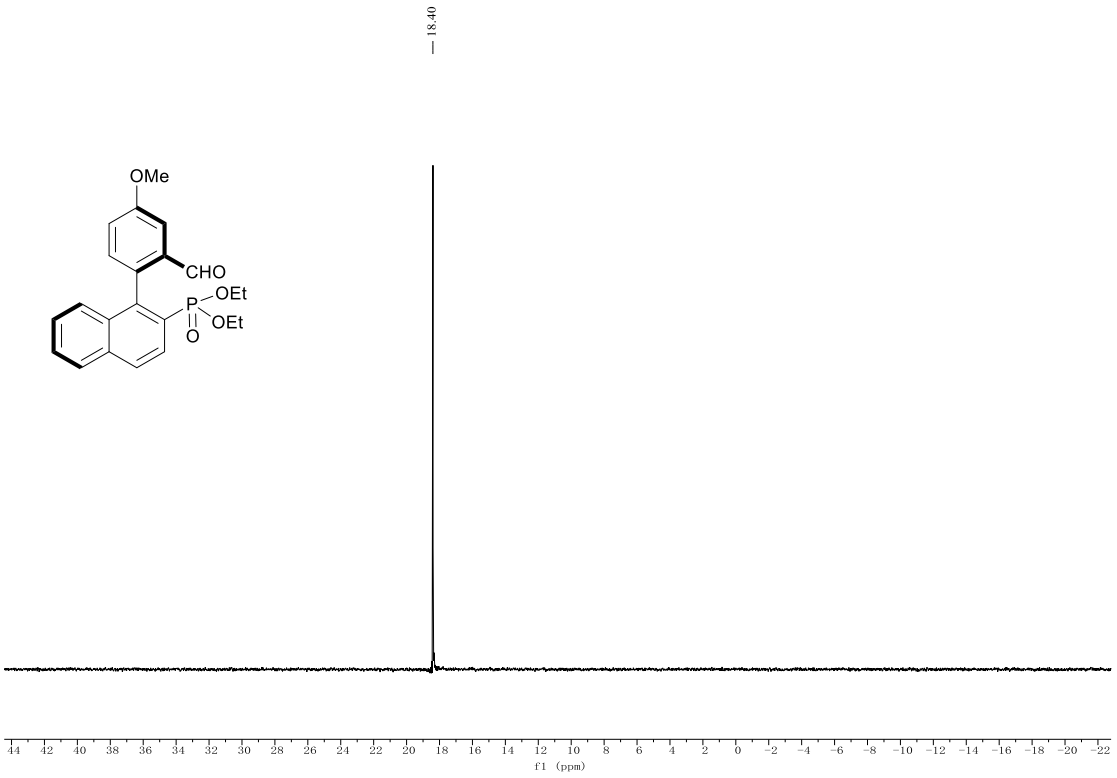
^{19}F NMR Spectrum of Compound **6ad**



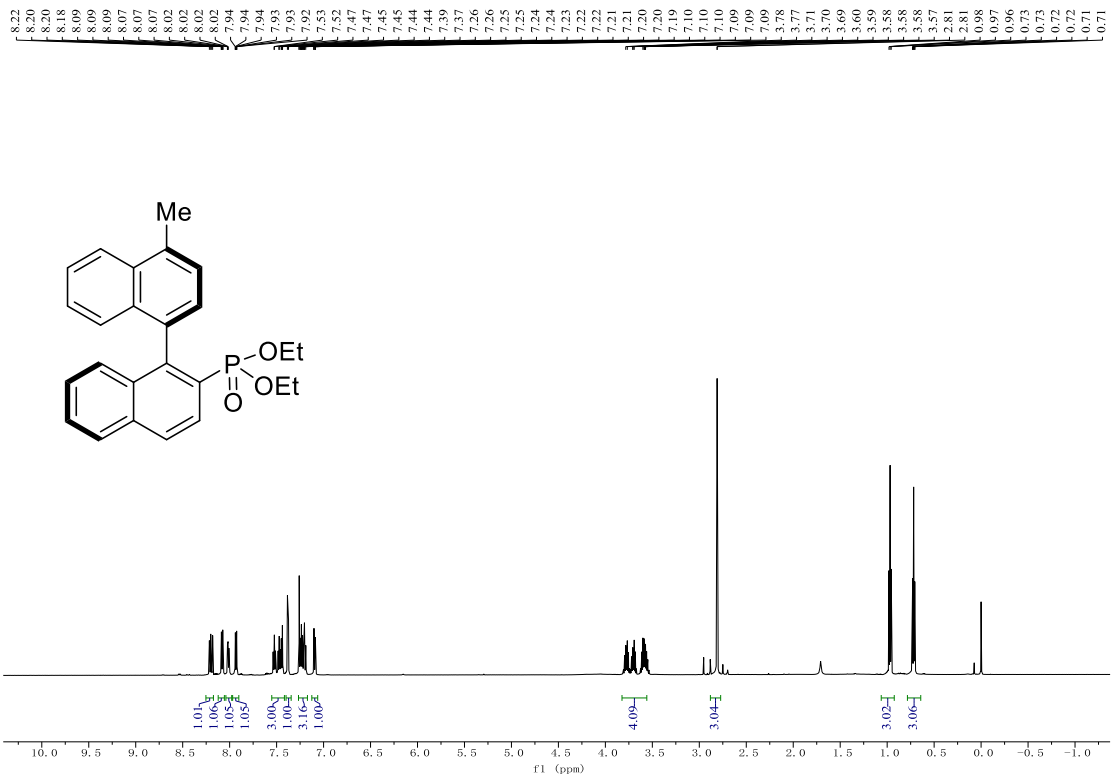
^{1}H NMR Spectrum of Compound **6ae**



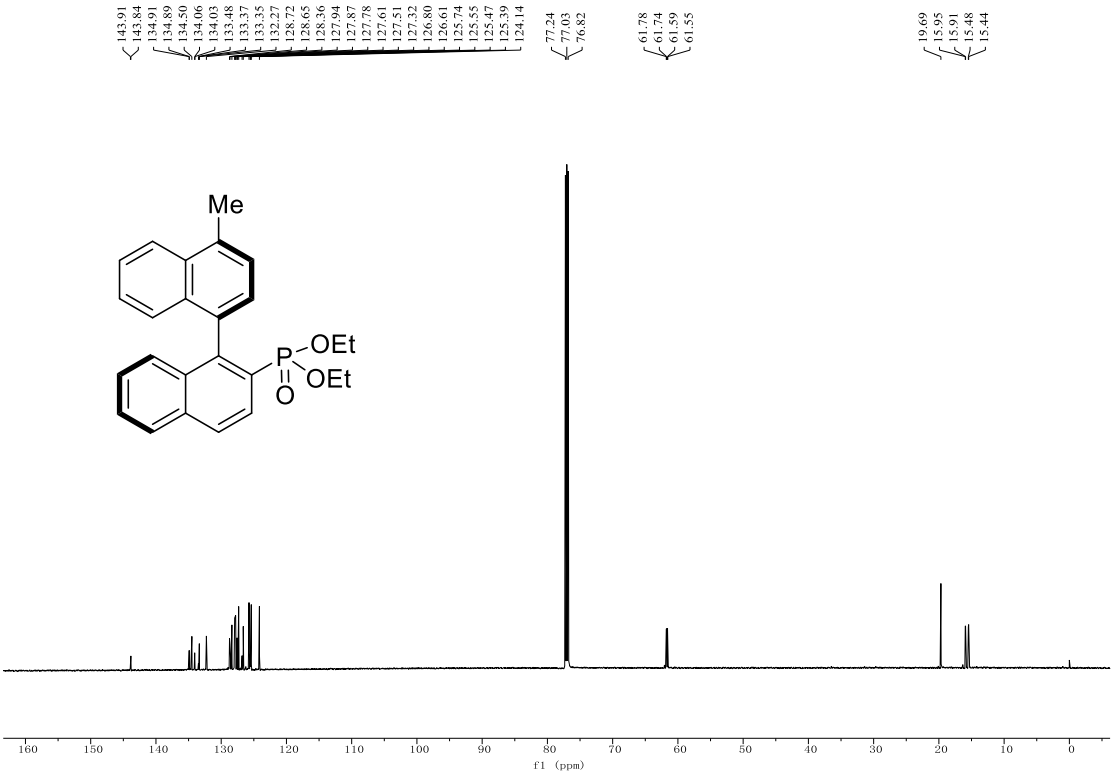
^{13}C NMR Spectrum of Compound **6ae**



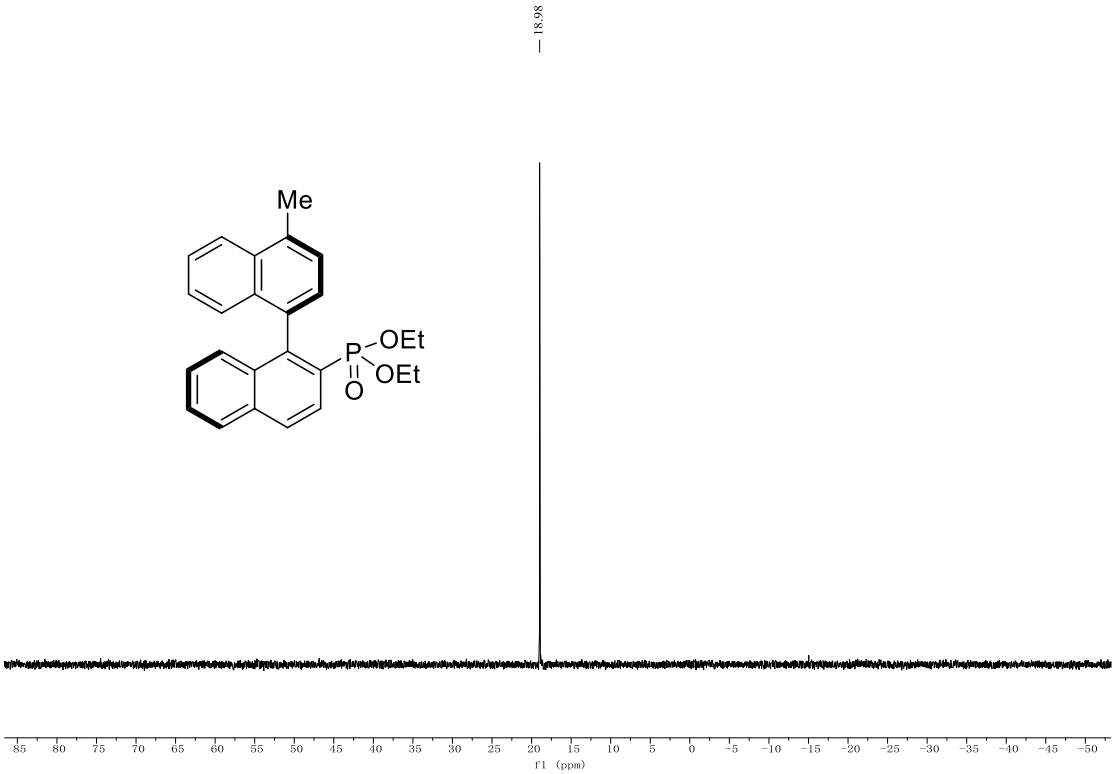
^{31}P NMR Spectrum of Compound **6ae**



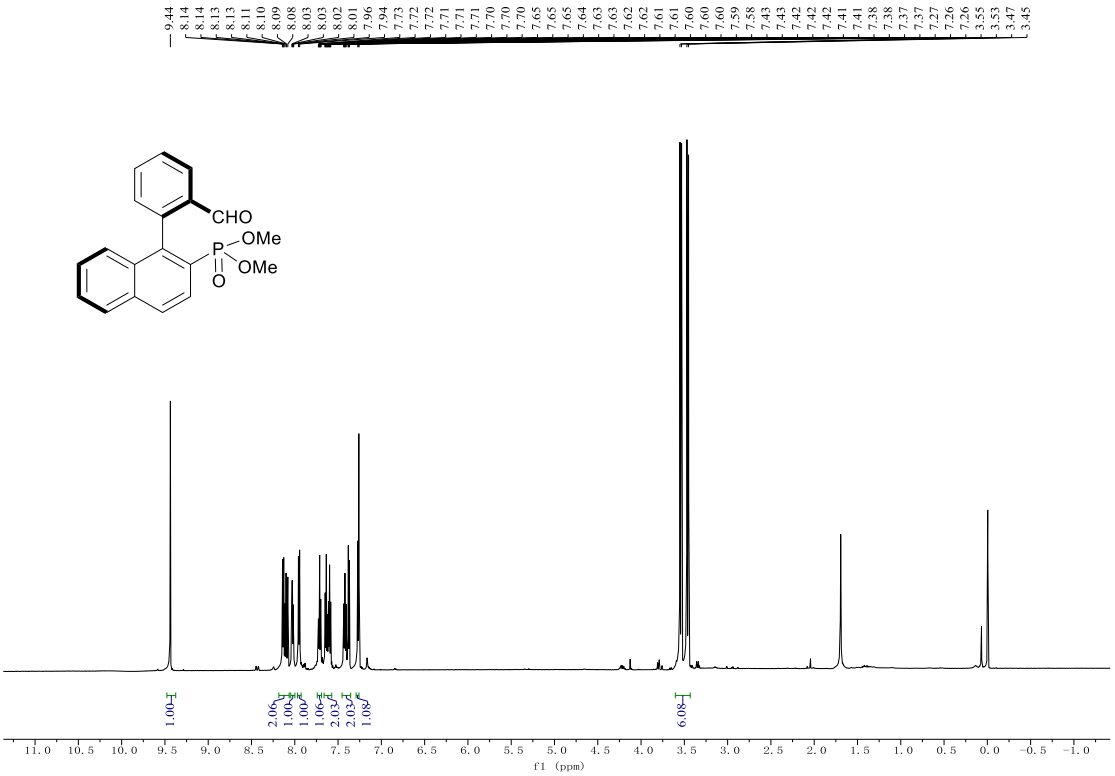
^{1}H NMR Spectrum of Compound **6af**



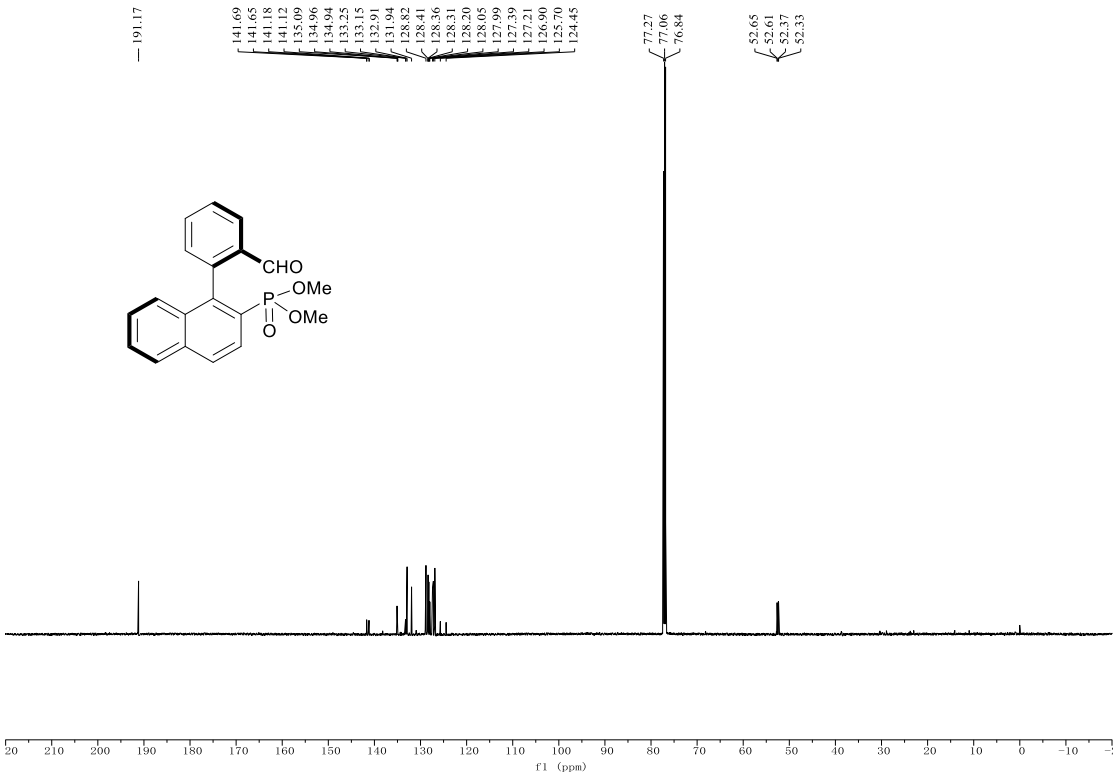
^{13}C NMR Spectrum of Compound **6af**



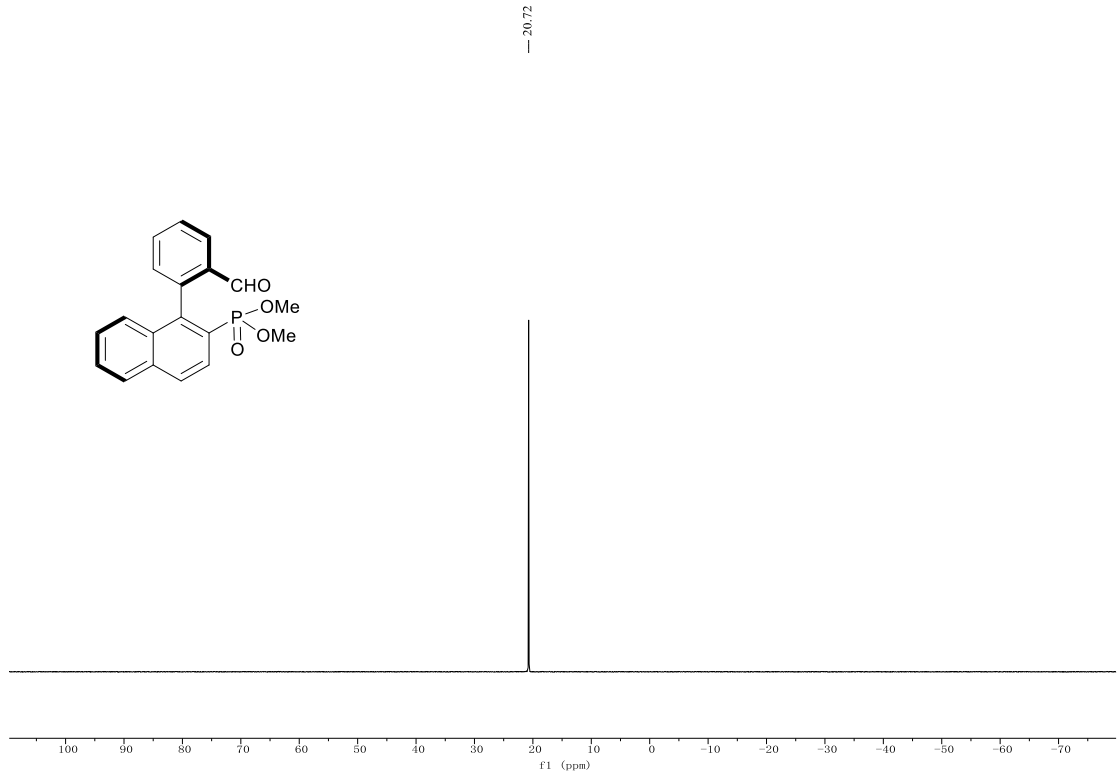
^{31}P NMR Spectrum of Compound **6af**



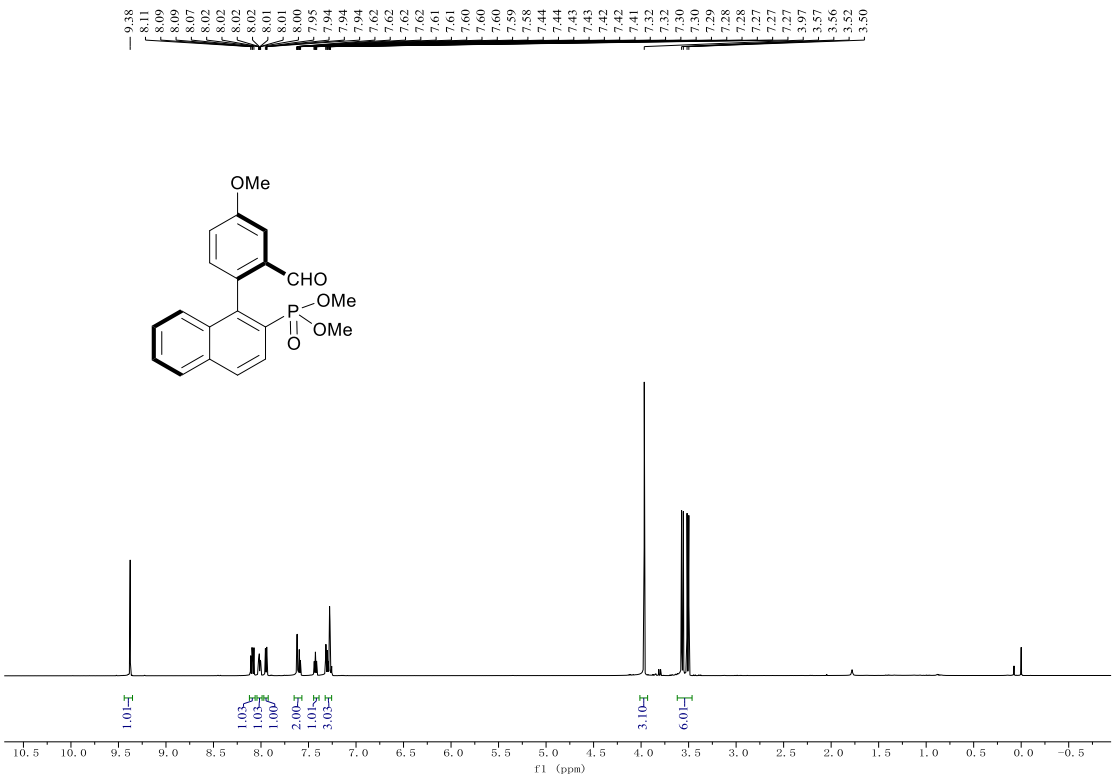
^{1}H NMR Spectrum of Compound **6ba**



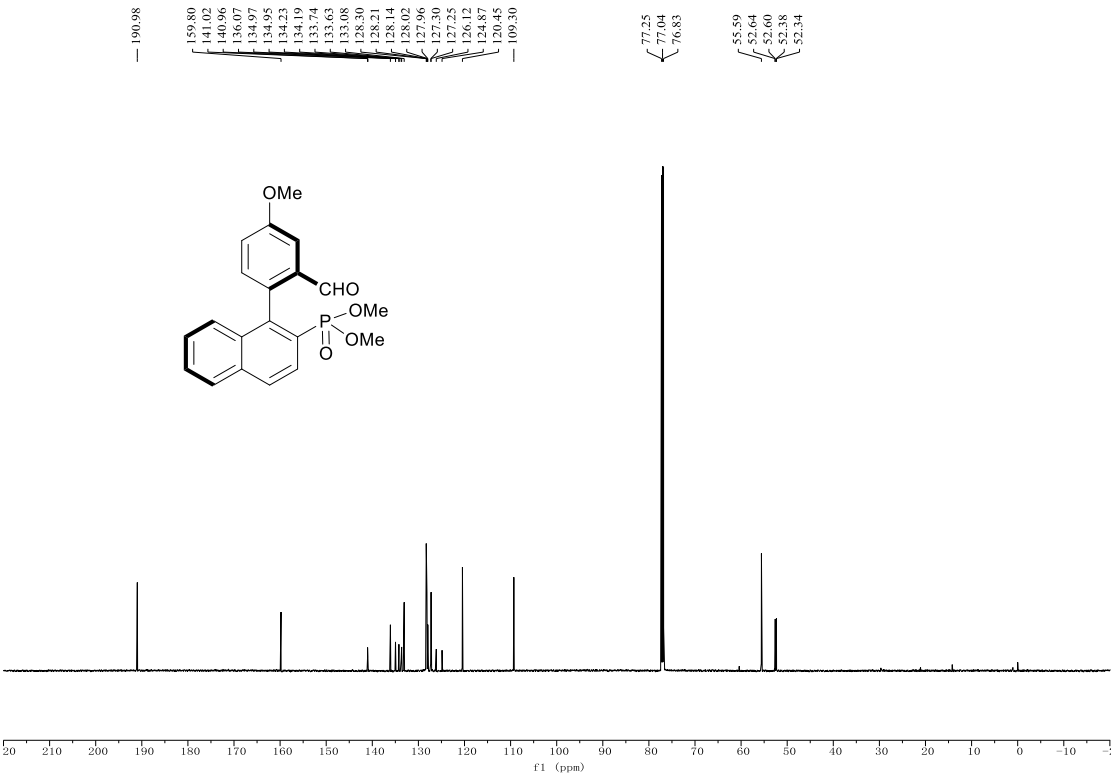
^{13}C NMR Spectrum of Compound **6ba**



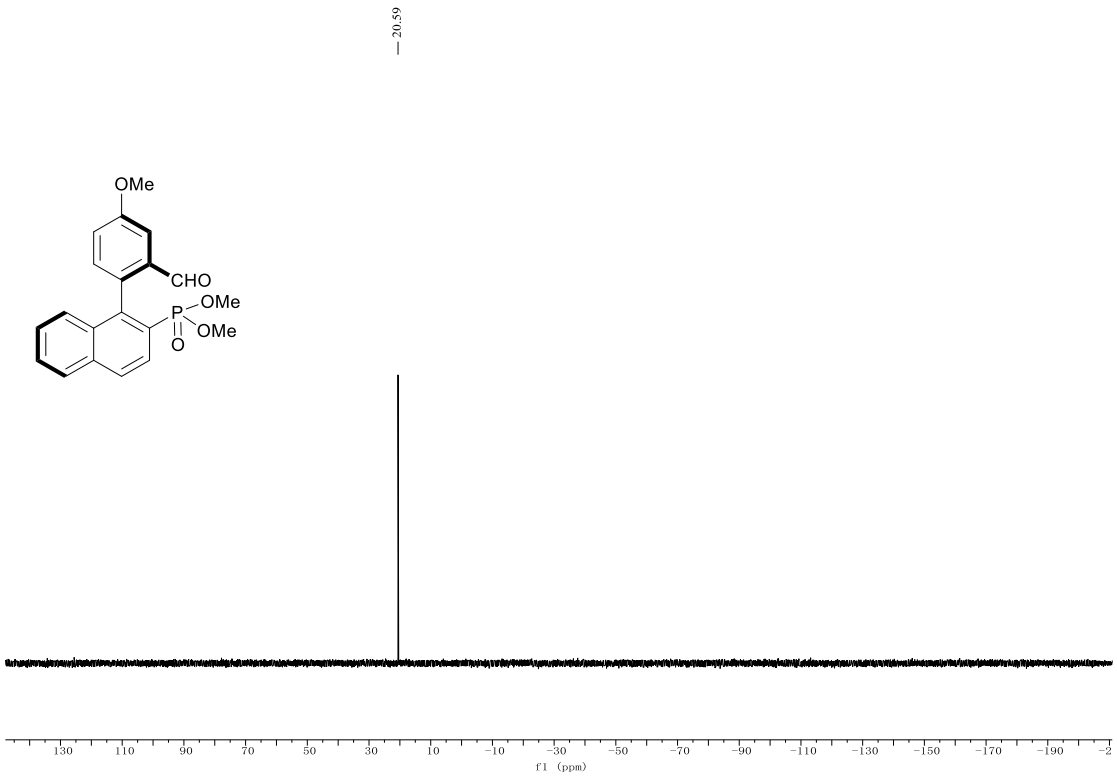
^{31}P NMR Spectrum of Compound **6ba**



^{1}H NMR Spectrum of Compound **6be**



^{13}C NMR Spectrum of Compound **6be**



^{31}P NMR Spectrum of Compound **6be**